Supporting Information

Sequential Regioselective Arylation of Pyrazolones with Diaryliodonium Salts

Wenbo Liao[a#], Hairui Du[a#], Mingxiu Chen[a], Yan Xiong [a], Heye Zhou[a], Tao Qin[*a], and Bin Liu[*a]

[a.] *College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang, Hubei 443002, PR China China*
E-mail: qintao@ctgu.edu.cn; liubin1@ctgu.edu.cn.

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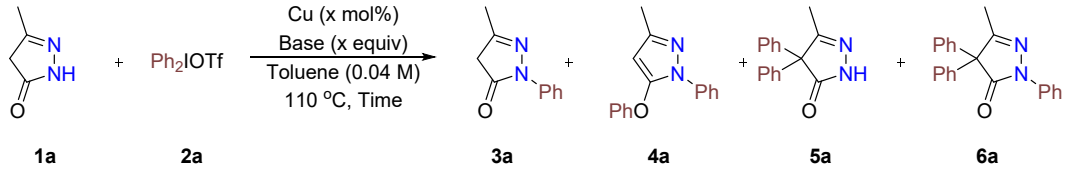
1. General Information

All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). ^{1}H, ^{13}C spectra were recorded with, Bruker 400 MHz (Avance-400) instrument. All ^{1}H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 7.26 ppm ($CDCl_3$). All ^{13}C NMR spectra are decoupled and reported in ppm relative to the solvent signal at 77.16 ppm ($CDCl_3$). High-resolution mass spectra HRMS (ESI-TOF) were recorded on Brucker microtof. Compounds were visualized by irradiation with UV light, or stained with iodine/silica gel, or potassium permanganate. Preparatory thin-layer chromatography (Prep-TLC) was performed on silica gel GF with UV 254 (20 × 20 cm, 1000 microns, from Yantai Jiang you Silica Gel Development Co., Ltd.) and visualized with UV light.

Materials. Reaction solvents THF and toluene were distilled over sodium and stored under nitrogen atmosphere. While DCM, DCE and CH_3CN was distilled over CaH_2 and stored under nitrogen atmosphere. Compounds **2a-2l** were known and prepared according to the previously reported procedures[1-3]. All other commercial reagents and solvents were purchased from Energy-Chemical Ltd, and used as received unless otherwise noted.

2. Detailed Optimization Studies

Table S1. Screening Reaction Conditions of 3a.[a]



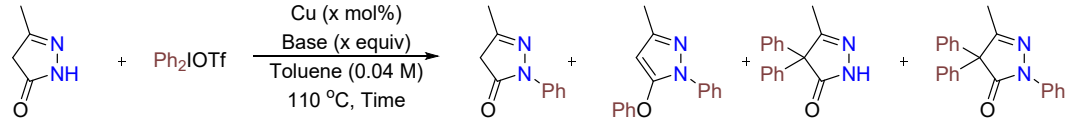
1a 2a 3a 4a 5a 6a

Entry	2a (equiv)	Cu (mol%)	Base (equiv)	Time (h)	3a/%[b]	4a/%[b]	5a/%[b]	6a/%[b]
1	5.0	--	K_2CO_3 (4.0)	12	12	7	5	26
2	5.0	--	Cs_2CO_3 (4.0)	12	trace	trace	6	17
3	5.0	--	Na_2CO_3 (4.0)	12	0	trace	10	trace
4	5.0	--	NaH (4.0)	12	0	6	9	5
5	5.0	--	NaOH (4.0)	12	trace	trace	11	6
6	5.0	--	DMAP (4.0)	12	0	4	9	trace
7	5.0	--	^{t}BuOK (4.0)	12	0	5	13	4
8	5.0	--	Et_3N (4.0)	12	0	trace	trace	trace
9	5.0	CuI (10)	K_2CO_3 (4.0)	12	21	49	0	5
10	1.05	CuI (10)	K_2CO_3 (4.0)	3	83	5	0	trace
11	1.05	CuI (10)	Na_2CO_3 (4.0)	3	74	10	0	0
12	1.05	CuI (10)	Cs_2CO_3 (4.0)	3	0	trace	trace	9
13	1.05	CuI (10)	^{t}BuOK (4.0)	3	0	0	0	trace
14	1.05	CuI (10)	DMAP (4.0)	3	0	trace	0	trace
15	**1.05**	**CuI (10)**	**K_2CO_3 (2.0)**	**3**	**85**	**5**	**0**	**trace**
16	1.05	$Cu(OTf)_2$ (10)	K_2CO_3 (2.0)	3	43	14	trace	trace
17	1.05	$CuBr_2$ (10)	K_2CO_3 (2.0)	3	71	trace	6	trace
18	1.05	Cu_2O (10)	K_2CO_3 (2.0)	3	73	6	0	0
19	1.05	CuO (10)	K_2CO_3 (2.0)	3	21	trace	trace	3
20	1.05	CuI (10)	--	3	29	23	0	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (x equiv), CuI (x mol%), base (x equiv) in 5 mL of Toluene at 110 °C.

[b]Yield determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

Table S2. Screening Reaction Conditions of 4a.[a]

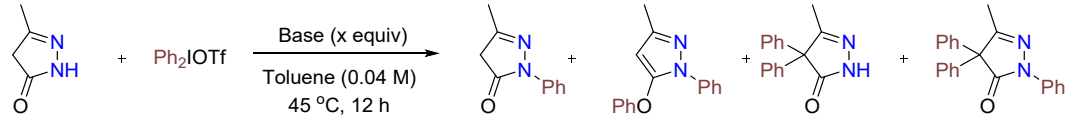


1a **2a** **3a** **4a** **5a** **6a**

Entry	2a (equiv)	Cu (mol%)	Base (equiv)	Tim (h)	3a/%[b]	4a/%[b]	5a/%[b]	6a/%[b]
1	2.5	CuI (10)	Na_2CO_3 (4.0)	3	trace	81	0	3
2	2.5	CuI (10)	K_2CO_3 (4.0)	3	3	78	0	7
3	**2.5**	**CuI (10)**	**Na_2CO_3 (2.0)**	**3**	**trace**	**83**	**0**	**trace**
7	2.5	$Cu(OTf)_2$ (10)	Na_2CO_3 (2.0)	3	26	37	trace	trace
8	2.5	$CuBr_2$ (10)	Na_2CO_3 (2.0)	3	trace	82	0	0
9	2.5	CuO (10)	Na_2CO_3 (2.0)	3	23	6	trace	9
10	2.5	Cu_2O (10)	Na_2CO_3 (2.0)	3	trace	81	0	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (2.5 equiv), CuI (x mol%), base (x equiv) in 5 mL of Toluene at 110 °C. [b]Yield determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

Table S3. Screening Reaction Conditions of 5a.[a]

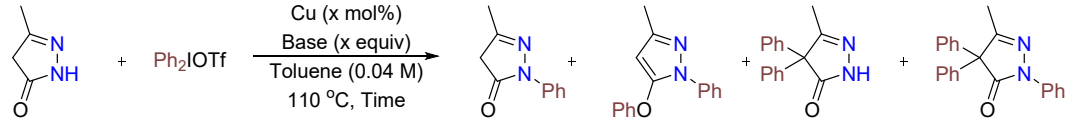


1a **2a** **3a** **4a** **5a** **6a**

Entry	2a (equiv)	Base (equiv)	3a/%[b]	4a/%[b]	5a/%[b]	6a/%[b]
1	2.2	Et_3N (4.0)	0	0	trace	trace
2	2.2	NaOH (4.0)	trace	0	trace	9
3	2.2	Na_2CO_3 (4.0)	0	0	6	0
4	2.2	DMAP (4.0)	0	0	11	trace
5	2.2	^{t}BuOK (4.0)	0	6	tracre	8
6	2.2	K_2CO_3 (4.0)	0	0	57	4
7[c]	**2.2**	**K_2CO_3 (2.0)**	**trace**	**0**	**62**	**trace**
8	2.2	Cs_2CO_3 (4.0)	tarce	0	43	6

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (2.2 equiv), base (x equiv) in 5 mL of Toluene at 45 °C for 12 h. [b]Yield determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard. [c]18 h

Table S4. Screening Reaction Conditions of 6a.[a]



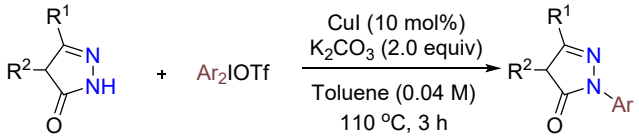
Entry	2a (equiv)	Cu (mol%)	Base (equiv)	Time (h)	3a/%[b]	4a/%[b]	5a/%[b]	6a/%[b]
1	4.0	CuI (10)	Cs_2CO_3 (4.0)	6	trace	21	trace	56
2	4.0	CuI (10)	DMAP (4.0)	6	8	19	0	44
3	4.0	CuI (10)	^{t}BuOK (4.0)	6	trace	16	0	31
4	4.0	$Cu(OTf)_2$ (10)	Cs_2CO_3 (4.0)	6	trace	61	trace	16
5	4.0	$CuBr_2$ (10)	Cs_2CO_3 (4.0)	6	trace	33	trace	37
6	4.0	CuO (10)	Cs_2CO_3 (4.0)	6	0	11	0	47
7	4.0	Cu_2O (10)	Cs_2CO_3 (4.0)	6	0	14	0	50
8	4.0	CuI (10)	Cs_2CO_3 (2.0)	6	trace	27	0	34
9	**4.0**	**CuI (1)**	**Cs_2CO_3 (4.0)**	**6**	**trace**	**10**	**0**	**68**

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (4 equiv), CuI (x mol%), base (x equiv) in 5 mL of Toluene at 110 °C.

[b]Yield determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

3. Experimental Procedures

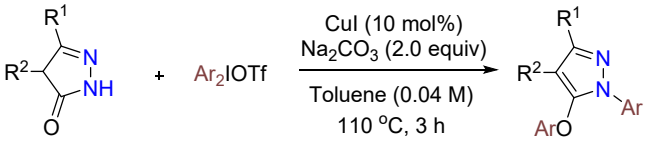
a) General Procedure for 3



1a **2** **3**

Added pyrazolones **1** (19.6 mg 0.2 mmol, 1.0 equiv), **2a** (1.05 equiv), CuI (3.8 mg, 0.1 equiv) and K_2CO_3 (55.2 mg, 2 equiv) in 5.0 mL of toluene. The solution was submitted to a 110 °C oil bath and stirred for 3 hours, until the product was not increasing as indicated by TLC. The reaction mixture was then quenched with H_2O, extracted with CH_2Cl_2 (3×10 mL) and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

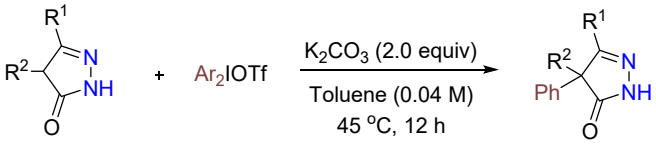
b) General Procedure for 4



1a **2** **4**

Added pyrazolones **1** (19.6 mg 0.2 mmol, 1.0 equiv), **2a** (2.5 equiv), CuI (3.8 mg, 0.1 equiv) and Na_2CO_3 (42.4 mg, 2 equiv) in 5.0 mL of toluene. The solution was submitted to a 110 °C oil bath and stirred for 3 hours, until the product was not increasing as indicated by TLC. The reaction mixture was then quenched with H_2O, extracted with CH_2Cl_2 (3×10 mL) and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

c) General Procedure for 5

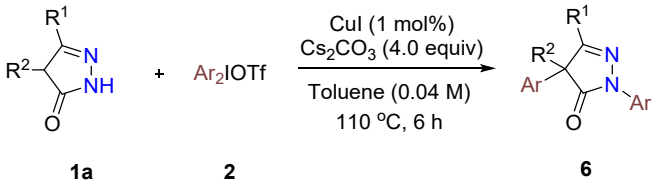


1a **2** **5**

Added 5-methyl-2,4-dihydro-3H-pyrazol-3-one 1a (19.6 mg 0.2 mmol, 1.0 equiv), **2** (2.2 equiv) and K_2CO_3 (55.2 mg, 2 equiv) in 5.0 mL of toluene. The solution was warmed up to 45 °C and it was stirred for 12 hours, until the product was not increasing as indicated by TLC. The reaction

mixture was then quenched with H_2O, extracted with CH_2Cl_2 (3×10 mL) and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

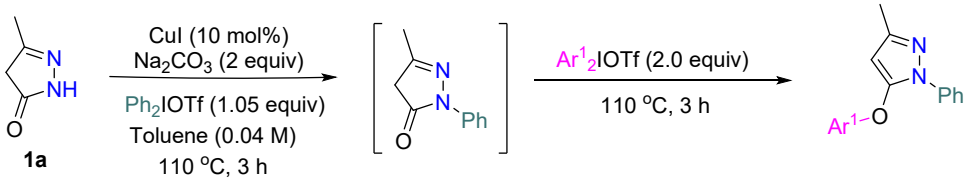
d) General Procedure for 6



1a **2** **6**

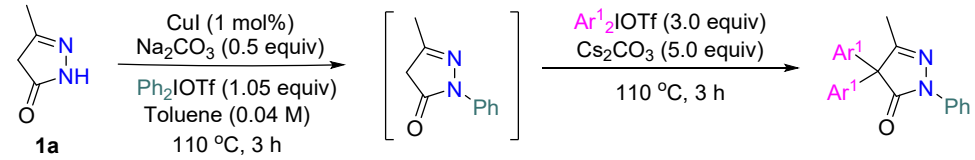
Added pyrazolones **1** (19.6 mg 0.2 mmol, 1.0 equiv), **2** (4.0 equiv), CuI (0.4 mg, 0.01 equiv.) and Cs_2CO_3 (260.7 mg, 4.0 equiv.) in 5.0 mL of toluene. The solution was submitted to a 110 °C oil bath and stirred for 3 hours, until the product was not increasing as indicated by TLC. The reaction mixture was then quenched with H_2O, extracted with CH_2Cl_2 (3×10 mL) and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

e) General Procedure for 7, 8, 9



Added pyrazolones **1** (19.6 mg 0.2 mmol,), diphenyliodonium trifluoromethanesulfonate **2a** (90.2 mg, 1.05 equiv), CuI (3.8 mg, 0.1 equiv.) and Na_2CO_3 (42.4 mg, 2 equiv.) in 5.0 mL of toluene. The solution was submitted to a 110 °C oil bath and stirred for 3 hours, until the product was not increasing as indicated by TLC. Next another diaryliodonium salts (2.0 equiv.) are added. Then the solution continues stirred at 110 °C for 3 hours, until the product was not increasing as indicated by TLC. The reaction mixture was then quenched with H_2O, extracted with CH_2Cl_2 (3×10 mL) and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain products.

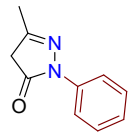
f) General Procedure for 10, 11, 12



Added 5-methyl-2,4-dihydro-3H-pyrazol-3-one **1a** (19.6 mg 0.2 mmol, 1.0 equiv), diphenyliodonium trifluoromethanesulfonate **2a** (90.2 mg, 1.05 equiv), CuI (0.4 mg, 0.01 equiv.) and Na_2CO_3 (10.6 mg, 0.5 equiv.) in 5.0 mL of toluene. The solution was submitted to a 110 °C oil bath and it was stirred for 3 hours, until the product was not increasing as indicated by TLC. Next another diaryliodonium salts (3.0 equiv.) and Cs_2CO_3 (325.8 mg, 5.0 equiv.) were added. Then the solution continues stirred at 110 °C for 3 hours, until the product was not increasing as indicated by TLC. The reaction mixture was then quenched with H_2O, extracted with CH_2Cl_2 (3×10 mL) and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

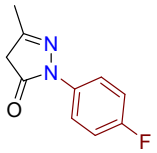
4. Analytical data of New Compounds

5-Methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3a)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 2:1 to afford **3a** as white solid (29.6 mg, 85% yield), TLC: R_f = 0.38 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 3.43 (s, 2H), 2.19 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.7, 156.5, 138.1, 129.0, 125.2, 119.0, 43.2, 17.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{10}H_{11}N_2O$ ([M + H]$^+$), 175.0866, found, 175.0868.

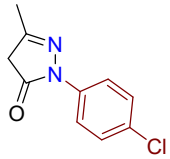
2-(4-Fluorophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (3b)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 2:1 to afford **3b** as white solid (24.2 mg, 63% yield), TLC: R_f = 0.35 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 9.2, 4.8 Hz, 2H), 7.07 (t, *J* = 8.8 Hz, 2H), 3.42 (s, 2H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.4, 160.0 (d, *J* = 242.9 Hz), 156.6, 134.3 (d, *J* = 2.8 Hz), 120.4 (d, *J* = 8.0 Hz), 115.6 (t, *J* = 22.4 Hz), 43.1, 17.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{10}H_{10}FN_2O$ ([M + H]$^+$), 193.0772, found, 193.0778.

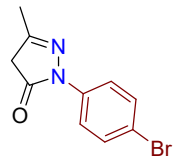
2-(4-Chlorophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (3c)

The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 2:1 to afford



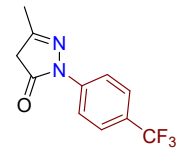
3c as white solid (30.0 mg, 72% yield), TLC: R_f = 0.41 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 3.42 (s, 2H), 2.19 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.5, 156.7, 136.8, 130.0, 129.0, 120.0, 43.2, 17.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{10}H_{10}ClN_2O$ ([M + H]$^+$), 209.0476, found, 209.0484.

2-(4-Bromophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (3d)



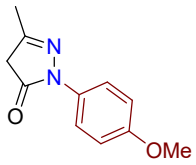
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 2:1 to afford **3d** as white solid (44.0 mg, 87% yield), TLC: R_f = 0.43 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 9.2 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 3.42 (s, 2H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.6, 156.7, 137.3, 131.9, 120.2, 117.9, 43.2, 17.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{10}H_{10}BrN_2O$ ([M + H]$^+$), 252.9971, found, 252.9966.

5-Methyl-2-(4-(trifluoromethyl)phenyl)-2,4-dihydro-3*H*-pyrazol-3-one (3e)



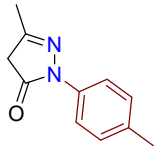
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 2:1 to afford **3e** as white solid (23.2 mg, 48% yield), TLC: R_f = 0.38 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 3.47 (s, 2H), 2.22 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.9, 157.0, 141.0, 126.6 (d, *J* = 32.5 Hz), 126.2 (dd, *J* = 7.6, 3.9 Hz), 124.3 (d, *J* = 269.8 Hz), 118.2, 43.3, 17.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_{10}F_3N_2O$ ([M + H]$^+$), 243.0740, found, 243.0741.

2-(4-Methoxyphenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (3f)



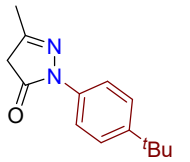
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 1:1 to afford **3f** as white solid (13.5 mg, 33% yield), TLC: R_f = 0.38 (Petroleum ether : Ethyl acetate = 1:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 9.2 Hz, 2H), 6.91 (d, *J* = 9.2 Hz, 2H), 3.81 (s, 3H), 3.41 (s, 2H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.4, 157.2, 156.3, 131.5, 121.0, 114.1, 55.6, 43.1, 17.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_{13}N_2O_2$ ([M + H]$^+$), 205.0972, found, 205.0980.

5-Methyl-2-(*p*-tolyl)-2,4-dihydro-3*H*-pyrazol-3-one (3g)



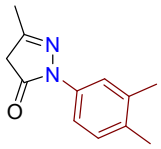
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 2:1 to afford **3g** as white solid (27.5 mg, 73% yield), TLC: R_f = 0.35 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 3.40 (s, 2H), 2.33 (s, 3H), 2.17 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.5, 156.3, 135.7, 134.9, 129.5, 119.1, 43.2, 21.1, 17.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_{13}N_2O$ ([M + H]$^+$), 189.1023, found, 189.1030.

2-(4-(Tert-butyl)phenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (3h)



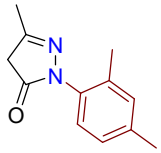
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 2:1 to afford **3h** as white solid (42.3 mg, 92% yield), TLC: R_f = 0.45 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 3.40 (s, 2H), 2.17 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.6, 156.3, 148.2, 135.6, 125.8, 119.0, 43.1, 34.5, 31.5, 17.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{19}N_2O$ ([M + H]$^+$), 231.1492, found, 231.1489.

2-(3,4-Dimethylphenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (3i)



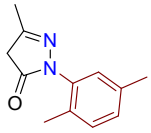
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 2:1 to afford **3i** as white solid (17.8 mg, 44% yield), TLC: R_f = 0.37 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 3.40 (s, 2H), 2.28 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.6, 156.2, 137.2, 135.9, 133.7, 129.9, 120.4, 116.8, 43.1, 20.1, 19.4, 17.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{15}N_2O$ ([M + H]$^+$), 203.1179, found, 203.1176.

2-(2,4-Dimethylphenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (3j)



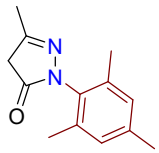
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 1:1 to afford **3j** as white solid (24.7 mg, 61% yield), TLC: R_f = 0.27 (Petroleum ether : Ethyl acetate = 1:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 8.0 Hz, 1H), 7.09 – 7.02 (m, 2H), 3.37 (s, 2H), 2.32 (s, 3H), 2.22 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.5, 156.2, 138.6, 134.9, 133.2, 131.8, 127.4, 126.5, 41.7, 21.1, 18.3, 17.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{15}N_2O$ ([M + H]$^+$), 203.1179, found, 203.1184.

2-(2,5-Dimethylphenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (3k)



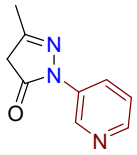
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 1:1 to afford **3k** as white solid (21.0 mg, 52% yield), TLC: R_f = 0.32 (Petroleum ether : Ethyl acetate = 1:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 8.0 Hz, 1H), 7.08 (s, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 3.37 (s, 2H), 2.32 (s, 3H), 2.22 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.4, 156.3, 136.5, 135.5, 132.0, 131.1, 129.5, 127.1, 41.8, 20.9, 18.0, 17.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{15}N_2O$ ($[M + H]^+$), 203.1179, found, 203.1186.

2-Mesityl-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (3l)



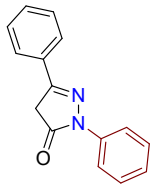
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 1:1 to afford **3l** as white solid (15.6 mg, 36% yield), TLC: R_f = 0.25 (Petroleum ether : Ethyl acetate = 1:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.92 (s, 2H), 3.39 (s, 2H), 2.28 (s, 3H), 2.16 (d, *J* = 3.6 Hz, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.6, 156.3, 148.2, 135.6, 125.8, 119.0, 43.1, 34.6, 31.5, 17.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{17}N_2O$ ($[M + H]^+$), 217.1335, found, 217.1333.

5-methyl-2-(pyridin-3-yl)-2,4-dihydro-3*H*-pyrazol-3-one (3m)



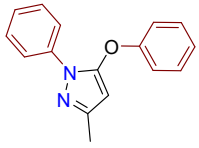
The crude was purified by flash chromatography using Ethyl acetate/ Methanol 30:1 to afford **3m** as white solid (15.1 mg, 43% yield), TLC: R_f = 0.40 (Ethyl acetate/ Methanol 30:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.15 (d, *J* = 2.8 Hz, 1H), 8.39 (d, *J* = 4.8 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.30 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.49 (s, 2H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.8, 155.7, 145.7, 140.5, 135.1, 125.7, 123.4, 45.6, 9.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_9H_{10}N_3O$ ($[M + H]^+$), 176.0818, found, 176.0813.

2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (3n)



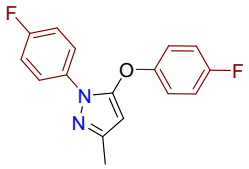
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **3n** as colorless oil (40.6 mg, 86% yield), TLC: R_f = 0.46 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.81 – 7.72 (m, 2H), 7.50 – 7.38 (m, 5H), 7.22 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.4, 154.8, 138.2, 131.0, 130.8, 129.0, 129.0, 126.1, 125.4, 119.2, 39.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{15}H_{13}N_2O$ ($[M + H]^+$), 237.1022, found, 237.1031.

3-Methyl-5-phenoxy-1-phenyl-1*H*-pyrazole (4a)



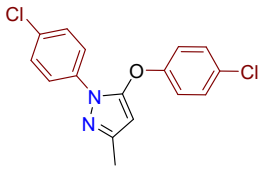
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **4a** as colorless oil (41.5 mg, 83% yield), TLC: R_f = 0.24 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.45 – 7.35 (m, 4H), 7.29 (d, *J* = 6.0 Hz, 1H), 7.18 (dd, *J* = 11.2, 7.2 Hz, 3H), 5.58 (s, 1H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.4, 151.7, 149.0, 138.4, 130.0, 129.1, 126.6, 124.7, 122.3, 118.2, 91.8, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{15}N_2O$ ($[M + H]^+$), 251.1179, found, 251.1181.

5-(4-Fluorophenoxy)-1-(4-fluorophenyl)-3-methyl-1*H*-pyrazole (4b)



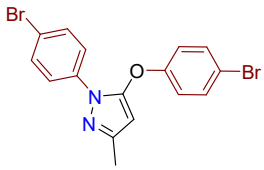
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **4b** as colorless oil (41.8 mg, 73% yield), TLC: R_f = 0.21 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 9.2, 4.8 Hz, 2H), 7.13 – 7.01 (m, 6H), 5.48 (s, 1H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 162.4, 160.8, 159.2 (d, *J* = 158.4 Hz), 152.1 (t, *J* = 3.1 Hz), 149.1, 134.6 (d, *J* = 3.0 Hz), 124.2 (d, *J* = 8.4 Hz), 119.8 (d, *J* = 8.3 Hz), 116.6 (d, *J* = 22.3 Hz), 115.9 (d, *J* = 22.7 Hz), 91.1, 14.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}F_2N_2O$ ([M + H]$^+$), 287.0991, found, 287.0990.

5-(4-Chlorophenoxy)-1-(4-chlorophenyl)-3-methyl-1*H*-pyrazole (4c)



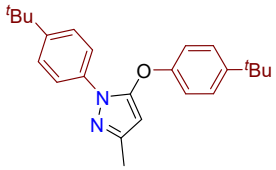
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **4c** as colorless oil (44.5 mg, 70% yield), TLC: R_f = 0.25 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.33 (dd, *J* = 21.2, 8.8 Hz, 4H), 7.06 (d, *J* = 8.8 Hz, 2H), 5.56 (s, 1H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.7, 151.3, 149.4, 136.9, 132.2, 130.1, 130.0, 129.2, 123.3, 119.4, 92.2, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}Cl_2N_2O$ ([M + H]$^+$), 319.0400, found, 319.0394.

5-(4-Bromophenoxy)-1-(4-bromophenyl)-3-methyl-1*H*-pyrazole (4d)



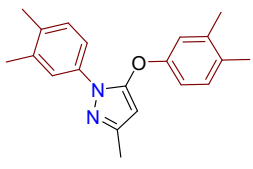
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **4d** as colorless oil (61.7 mg, 76% yield), TLC: R_f = 0.30 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-d) δ **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 – 7.49 (m, 4H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 5.56 (s, 1H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.3, 151.2, 149.5, 137.4, 133.1, 132.2, 123.6, 120.1, 119.8, 117.5, 92.4, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}Br_2N_2O$ ([M + H]$^+$), 406.9389, found, 406.9392.

5-(4-(Tert-butyl)phenoxy)-1-(4-(tert-butyl)phenyl)-3-methyl-1*H*-pyrazole (4e)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **4e** as colorless oil (49.3 mg, 68% yield), TLC: R_f = 0.31 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 5.53 (s, 1H), 2.28 (s, 3H), 1.33 (d, *J* = 1.6 Hz, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.2, 152.0, 149.4, 148.6, 147.5, 136.1, 126.7, 125.9, 121.9, 117.7, 91.2, 34.6, 34.5, 31.6, 31.4, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{31}N_2O$ ([M + H]$^+$), 363.2431, found, 363.2435.

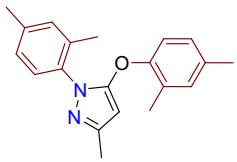
5-(3,4-Dimethylphenoxy)-1-(3,4-dimethylphenyl)-3-methyl-1*H*-pyrazole (4f)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **4f** as colorless oil (42.3 mg, 69% yield), TLC: R_f = 0.26 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 2.8 Hz, 1H), 7.40 (dd, *J* = 8.0, 2.4 Hz,

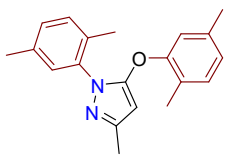
1H), 7.12 (dd, *J* = 21.2, 8.4 Hz, 2H), 6.94 (d, *J* = 2.8 Hz, 1H), 6.88 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.49 (s, 1H), 2.29 – 2.23 (m, 15H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.5, 152.2, 148.5, 138.4, 137.4, 136.3, 135.0, 132.8, 130.7, 130.0, 123.6, 119.7, 119.5, 115.5, 91.1, 20.0, 20.0, 19.4, 19.1, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{23}N_2O$ ([M + H]$^+$), 307.1805, found, 307.1797.

5-(2,4-Dimethylphenoxy)-1-(2,4-dimethylphenyl)-3-methyl-1*H*-pyrazole (4g)



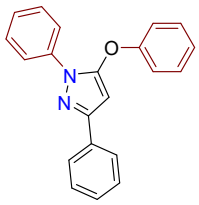
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **4g** as colorless oil (22.0 mg, 36% yield), TLC: R_f = 0.15 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 10.0 Hz, 3H), 5.28 (s, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 2.24 (d, *J* = 5.2 Hz, 6H), 2.13 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.5, 152.3, 148.4, 138.7, 135.7, 134.5, 134.4, 132.1, 131.4, 128.7, 127.7, 127.6, 127.1, 118.6, 88.3, 21.2, 20.8, 17.7, 15.9, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{23}N_2O$ ([M + H]$^+$), 307.1805, found, 307.1801.

5-(2,5-Dimethylphenoxy)-1-(2,5-dimethylphenyl)-3-methyl-1*H*-pyrazole (4h)



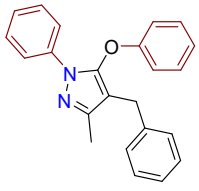
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **4h** as colorless oil (14.7 mg, 24% yield), TLC: R_f = 0.17 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 9.2 Hz, 2H), 5.33 (s, 1H), 2.27 (dd, *J* = 27.2, 14.8 Hz, 12H), 2.11 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.3, 153.1, 148.6, 137.2, 136.8, 136.2, 132.7, 131.2, 130.6, 129.7, 128.4, 125.8, 125.6, 119.1, 88.8, 21.1, 20.9, 17.4, 15.6, 14.8. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{23}N_2O$ ([M + H]$^+$), 307.1805, found, 307.1811.

5-Phenoxy-1,3-diphenyl-1*H*-pyrazole (4i)



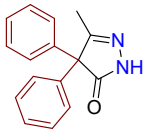
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **4i** as colorless oil (48.7 mg, 78% yield), TLC: R_f = 0.44 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 – 7.80 (m, 4H), 7.49 – 7.29 (m, 8H), 7.22 (d, *J* = 8.0 Hz, 3H), 6.09 (s, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.3, 152.4, 150.8, 138.5, 133.3, 130.1, 129.1, 128.7, 128.3, 126.9, 125.6, 124.8, 122.6, 118.3, 89.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}N_2O$ ([M + H]$^+$), 313.1335, found, 313.1331.

4-Benzyl-3-methyl-5-phenoxy-1-phenyl-1*H*-pyrazole (4j)



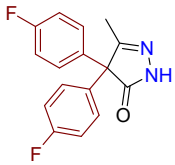
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **4j** as colorless oil (30.6 mg, 45% yield), TLC: R_f = 0.19 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.25 – 7.12 (m, 6H), 7.08 (d, *J* = 6.8 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 2H), 3.59 (s, 2H), 2.22 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.8, 148.8, 146.4, 139.7, 138.5, 129.9, 129.1, 128.4, 128.4, 126.5, 126.1, 123.3, 121.9, 115.7, 106.7, 28.6, 13.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{21}N_2O$ ([M + H]$^+$), 341.1649, found, 341.1644.

5-Methyl-4,4-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (5a)



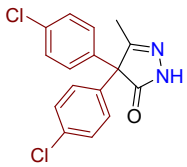
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **5a** as white solid (31.0 mg, 62% yield), TLC: R_f = 0.34 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.41 (s, 1H), 7.44 – 7.36 (m, 6H), 7.09 (d, J = 6.8 Hz, 4H), 1.94 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 177.2, 160.5, 137.3, 129.0, 128.0, 127.8, 65.8, 15.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{15}N_2O$ ([M + H]$^+$), 251.1179, found, 251.1182.

4,4-Bis(4-fluorophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (5b)



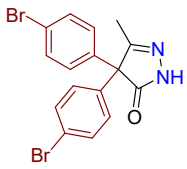
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **5b** as white solid (26.9 mg, 47% yield), TLC: R_f = 0.33 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.50 (s, 1H), 7.25 (t, J = 8.8 Hz, 4H), 7.12 (dd, J = 9.2, 5.2 Hz, 4H), 1.95 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 177.0, 162.9, 160.4 (d, J = 15.6 Hz), 133.4 (d, J = 2.2 Hz), 130.2 (d, J = 8.4 Hz), 116.0 (d, J = 21.5 Hz), 64.4, 15.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}F_2N_2O$ ([M + H]$^+$), 287.0991, found, 287.0987.

4,4-Bis(4-chlorophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (5c)



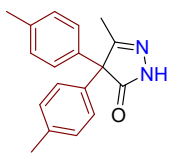
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **5c** as white solid (36.9 mg, 58% yield), TLC: R_f = 0.38 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.56 (s, 1H), 7.49 (d, J = 8.8 Hz, 4H), 7.10 (d, J = 8.8 Hz, 4H), 1.95 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 176.5, 159.9, 135.9, 132.9, 130.0, 129.1, 64.7, 15.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}Cl_2N_2O$ ([M + H]$^+$), 319.0400, found, 319.0402.

4,4-Bis(4-bromophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (5d)



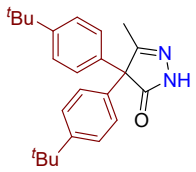
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **5d** as white solid (49.5 mg, 61% yield), TLC: R_f = 0.40 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.55 (s, 1H), 7.62 (d, J = 8.4 Hz, 4H), 7.03 (d, J = 8.4 Hz, 4H), 1.95 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 176.4, 159.8, 136.3, 132.1, 130.3, 121.5, 64.9, 15.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}Br_2N_2O$ ([M + H]$^+$), 406.9389, found, 406.9386.

5-Methyl-4,4-di-p-tolyl-2,4-dihydro-3*H*-pyrazol-3-one (5e)



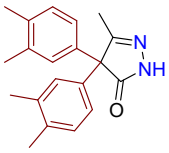
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **5e** as white solid (22.8 mg, 41% yield), TLC: R_f = 0.38 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.33 (s, 1H), 7.20 (d, J = 8.4 Hz, 4H), 6.96 (d, J = 8.4 Hz, 4H), 2.30 (s, 6H), 1.91 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 177.4, 160.8, 137.1, 134.4, 129.5, 128.0, 65.1, 20.6, 15.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{18}H_{19}N_2O$ ([M + H]$^+$), 279.1492, found, 279.1498.

4,4-Bis(4-(tert-butyl)phenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (5f)



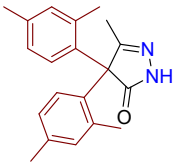
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **5f** as white solid (58.0 mg, 80% yield), TLC: R_f = 0.56 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.35 (s, 1H), 7.42 (d, J = 8.8 Hz, 4H), 7.01 (d, J = 8.4 Hz, 4H), 1.92 (s, 3H), 1.27 (s, 18H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 177.4, 160.8, 150.1, 134.3, 127.8, 125.7, 65.1, 34.3, 31.1, 15.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{31}N_2O$ ([M + H]$^+$), 363.2431, found, 363.2430.

4,4-Bis(3,4-dimethylphenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (5g)



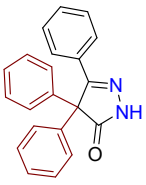
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **5g** as white solid (31.8 mg, 52% yield), TLC: R_f = 0.39 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.28 (s, 1H), 7.14 (d, J = 8.0 Hz, 2H), 6.82 (s, 2H), 6.78 (d, J = 7.6 Hz, 2H), 2.19 (d, J = 10.0 Hz, 12H), 1.91 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 177.5, 160.9, 136.7, 135.8, 134.8, 129.9, 128.9, 125.5, 65.1, 19.6, 19.0, 15.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{23}N_2O$ ([M + H]$^+$), 307.1805, found, 307.1807.

4,4-Bis(2,4-dimethylphenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (5h)



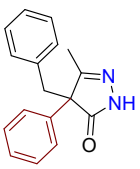
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **5h** as white solid (16.5 mg, 27% yield), TLC: R_f = 0.36 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.14 (s, 1H), 7.03 (s, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.83 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 2.24 (s, 3H), 2.15 (d, J = 10.4 Hz, 6H), 2.06 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 178.1, 157.7, 152.9, 136.8, 136.1, 131.3, 130.8, 130.5, 128.0, 127.0, 126.7, 126.2, 116.6, 105.8, 62.9, 20.7, 20.1, 19.7, 15.8, 10.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{23}N_2O$ ([M + H]$^+$), 307.1805, found, 307.1799.

4,4,5-triphenyl-2,4-dihydro-3*H*-pyrazol-3-one (5i)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **5i** as colorless oil (33.1 mg, 53% yield), TLC: R_f = 0.44 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.83 (s, 1H), 7.63 (d, J = 7.2 Hz, 2H), 7.42 (dd, J = 7.6, 2.0 Hz, 4H), 7.37 – 7.32 (m, 6H), 7.29 (d, J = 7.2 Hz, 1H), 7.24 (t, J = 7.2 Hz, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 179.4, 161.7, 136.4, 131.5, 130.0, 129.0, 129.0, 128.5, 128.3, 127.4, 65.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}N_2O$ ([M + H]$^+$), 313.1335, found, 313.1339.

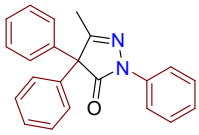
4-benzyl-5-methyl-4-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (5j)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 3:1 to afford **5j** as white solid (24.8 mg, 47% yield), TLC: R_f = 0.34 (Petroleum ether : Ethyl acetate = 3:1) [UV]. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.36 (d, J = 7.2 Hz, 1H), 7.30 – 7.18 (m, 7H), 3.44 (q, J = 13.2 Hz, 2H), 1.90 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 178.1,

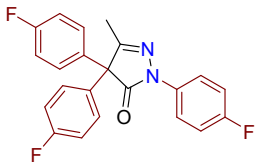
161.2, 136.3, 135.4, 129.4, 129.1, 128.1, 127.8, 127.0, 126.5, 61.9, 37.3, 14.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{17}N_2O$ ([M + H]$^+$), 265.1336, found, 265.1327.

5-Methyl-2,4,4-triphenyl-2,4-dihydro-3*H*-pyrazol-3-one (6a)



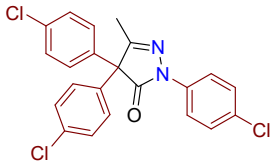
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **6a** as colorless oil (44.4 mg, 68% yield), TLC: R_f = 0.27 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) 7.99 (d, *J* = 7.6 Hz, 2H), 7.44 – 7.34 (m, 8H), 7.25 – 7.19 (m, 5H), 2.17 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.76, 161.97, 138.19, 137.33, 129.20, 129.00, 128.60, 128.34, 125.29, 119.03, 69.14, 15.64. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{22}H_{19}N_2O$ ([M + H]$^+$), 327.1492, found, 327.1500.

2,4,4-Tris(4-fluorophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (6b)



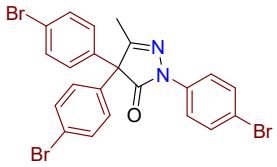
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **6b** as colorless oil (38.8 mg, 51% yield), TLC: R_f = 0.29 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 9.2, 4.8 Hz, 2H), 7.19 (dd, *J* = 8.8, 5.2 Hz, 4H), 7.09 (td, *J* = 8.8, 4.4 Hz, 6H), 2.15 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.3, 164.0, 161.5 (t, *J* = 12.3 Hz), 159.0, 134.2 (d, *J* = 2.9 Hz), 132.9 (d, *J* = 3.5 Hz), 130.3 (d, *J* = 8.4 Hz), 120.8 (d, *J* = 7.9 Hz), 116.4 (d, *J* = 21.7 Hz), 115.8 (d, *J* = 22.5 Hz), 67.5, 15.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{22}H_{16}F_3N_2O$ ([M + H]$^+$), 381.1209, found, 381.1215.

2,4,4-Tris(4-chlorophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (6c)



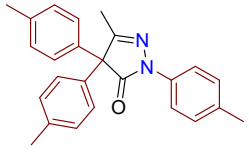
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **6c** as colorless oil (33.4 mg, 39% yield), TLC: R_f = 0.35 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 6H), 7.13 (d, *J* = 8.4 Hz, 4H), 2.15 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.9, 161.3, 136.5, 135.3, 134.9, 130.7, 129.8, 129.6, 129.1, 120.1, 67.9, 15.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{22}H_{16}Cl_3N_2O$ ([M + H]$^+$), 429.0323, found, 429.0328.

2,4,4-Tris(4-bromophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (6d)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **6d** as colorless oil (53.7 mg, 48% yield), TLC: R_f = 0.38 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.52 (dd, *J* = 8.8, 2.8 Hz, 6H), 7.07 (d, *J* = 8.8 Hz, 4H), 2.14 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.8, 161.2, 137.0, 135.7, 132.6, 132.1, 130.1, 123.1, 120.4, 118.4, 68.1, 15.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{22}H_{16}Br_3N_2O$ ([M + H]$^+$), 560.8808, found, 560.8804.

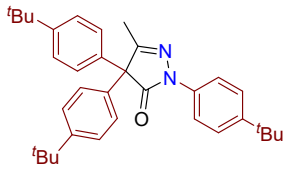
5-Methyl-2,4,4-tri-p-tolyl-2,4-dihydro-3*H*-pyrazol-3-one (6e)



The crude was purified by flash chromatography using Petroleum ether/

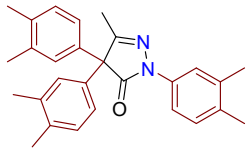
Ethyl acetate 40:1 to afford **6e** as colorless oil (38.3 mg, 52% yield), TLC: R_f = 0.25 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.17 (m, 6H), 7.12 (d, *J* = 8.4 Hz, 4H), 2.36 (s, 9H), 2.15 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.9, 162.1, 138.1, 135.9, 134.8, 134.5, 129.8, 129.4, 128.4, 119.1, 68.5, 21.2, 21.1, 15.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{25}H_{25}N_2O$ ([M + H]$^+$), 369.1962, found, 369.1953.

2,4,4-Tris(4-(tert-butyl)phenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (6f)



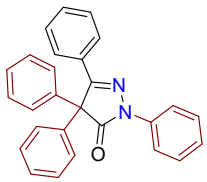
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **6f** as colorless oil (54.4 mg, 55% yield), TLC: R_f = 0.41 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.40 (dd, *J* = 18.8, 8.8 Hz, 6H), 7.15 (d, *J* = 8.8 Hz, 4H), 2.15 (s, 3H), 1.32 (d, *J* = 5.2 Hz, 27H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 174.1, 162.3, 151.1, 148.1, 135.8, 134.3, 128.2, 126.1, 125.8, 118.9, 68.5, 34.7, 34.6, 31.5, 31.4, 15.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{34}H_{43}N_2O$ ([M + H]$^+$), 495.3370, found, 495.3364.

2,4,4-Tris(3,4-dimethylphenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (6g)



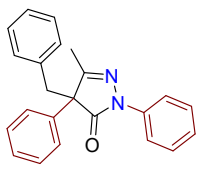
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **6g** as colorless oil (26.3 mg, 32% yield), TLC: R_f = 0.20 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.70 (d, *J* = 10.8 Hz, 1H), 7.14 (dd, *J* = 12.4, 8.0 Hz, 3H), 7.01 – 6.91 (m, 4H), 2.29 (s, 3H), 2.26 (s, 9H), 2.23 (s, 6H), 2.14 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 174.0, 162.3, 137.4, 137.2, 136.7, 136.2, 134.9, 133.5, 130.3, 129.9, 129.5, 126.0, 120.2, 116.6, 68.6, 20.1, 20.1, 19.6, 19.4, 15.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{28}H_{31}N_2O$ ([M + H]$^+$), 411.2431, found, 411.2432.

2,4,4,5-tetraphenyl-2,4-dihydro-3*H*-pyrazol-3-one (6h)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **6h** as colorless oil (44.2 mg, 57% yield), TLC: R_f = 0.24 (Petroleum ether/ Ethyl acetate 40:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.41 (m, 6H), 7.39 – 7.31 (m, 7H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 175.0, 160.3, 138.3, 136.8, 131.1, 130.3, 129.1, 129.0, 129.0, 128.6, 128.4, 127.8, 125.5, 119.3, 67.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{27}H_{21}N_2O$ ([M + H]$^+$), 389.1647, found, 389.1650.

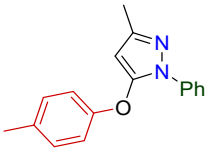
4-benzyl-5-methyl-2,4-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (6i)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 20:1 to afford **6i** as colorless oil (40.8 mg, 60% yield), TLC: R_f = 0.21 (Petroleum ether/ Ethyl acetate 20:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.39 – 7.29 (m, 5H), 7.20 (s, 6H), 3.81 (d, *J* = 13.2 Hz, 1H), 3.40 (d, *J* = 13.2 Hz, 1H), 2.10 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 174.6, 162.2, 137.7, 135.8, 134.6, 129.5, 129.3, 128.8, 128.6, 128.4, 127.6, 126.6, 125.4, 119.6, 64.9, 39.0, 15.1. **HRMS** (ESI-TOF) (m/z): Calcd for

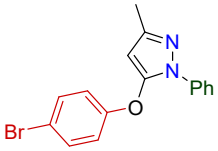
$C_{23}H_{21}N_2O$ ([M + H]$^+$), 341.1647, found, 341.1644.

3-Methyl-1-phenyl-5-(*p*-tolyloxy)-1*H*-pyrazole (7)



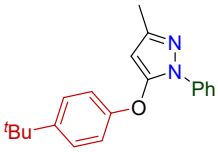
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **7** as colorless oil (32.2 mg, 61% yield), TLC: R_f = 0.23 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 5.49 (s, 1H), 2.33 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.2, 152.3, 149.0, 138.5, 134.4, 130.4, 129.1, 126.5, 122.3, 118.2, 91.3, 20.9, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{17}N_2O$ ([M + H]$^+$), 265.1335, found, 265.1329.

5-(4-Bromophenoxy)-3-methyl-1-phenyl-1*H*-pyrazole (8)



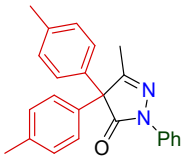
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **8** as colorless oil (34.8 mg, 53% yield), TLC: R_f = 0.19 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.48 – 7.39 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 5.60 (s, 1H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.5, 150.9, 149.1, 138.2, 133.0, 129.1, 126.8, 122.4, 119.7, 117.2, 92.2, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}BrN_2O$ ([M + H]$^+$), 329.0284, found, 329.0285.

5-(4-(Tert-butyl)phenoxy)-3-methyl-1-phenyl-1*H*-pyrazole (9)



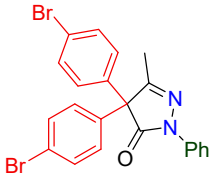
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 25:1 to afford **9** as colorless oil (33.7 mg, 55% yield), TLC: R_f = 0.31 (Petroleum ether : Ethyl acetate = 25:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.10 – 7.05 (m, 2H), 5.53 (s, 1H), 2.28 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.0, 152.2, 149.0, 147.7, 138.5, 129.0, 126.8, 126.5, 122.3, 117.8, 91.4, 34.5, 31.6, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{23}N_2O$ ([M + H]$^+$), 307.1805, found, 387.1804.

5-Methyl-2-phenyl-4,4-di-p-tolyl-2,4-dihydro-3*H*-pyrazol-3-one (10)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **10** as colorless oil (27.6 mg, 39% yield), TLC: R_f = 0.26 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 5H), 7.13 (d, *J* = 8.4 Hz, 4H), 2.37 (s, 6H), 2.17 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 174.1, 162.2, 138.3, 138.1, 134.4, 129.8, 128.9, 128.4, 125.1, 119.0, 68.5, 21.2, 15.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{23}N_2O$ ([M + H]$^+$), 355.1805, found, 355.1808.

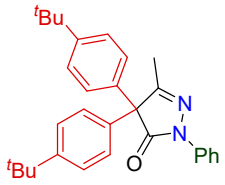
4,4-Bis(4-bromophenyl)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (11)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **11** as colorless oil (35.7 mg, 37% yield), TLC: R_f = 0.35 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **^{1}H NMR** (400 MHz,

Chloroform-*d*) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 4H), 7.45 – 7.38 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 4H), 2.15 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.8, 160.8, 137.9, 135.9, 132.5, 130.2, 129.1, 125.6, 123.0, 119.0, 68.1, 15.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{22}H_{17}Br_2N_2O$ ($[M + H]^+$), 482.9702, found, 482.9698.

4,4-bis(4-(tert-butyl)phenyl)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (12)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 40:1 to afford **12** as colorless oil (37.7 mg, 43% yield), TLC: R_f = 0.38 (Petroleum ether : Ethyl acetate = 40:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.36 (m, 6H), 7.22 – 7.14 (m, 5H), 2.17 (s, 3H), 1.32 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 174.2, 162.4, 151.2, 138.3, 134.3, 129.0, 128.2, 126.1, 125.1, 119.1, 68.6, 34.7, 31.4, 15.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{30}H_{35}N_2O$ ($[M + H]^+$), 439.2744, found, 439.2743.

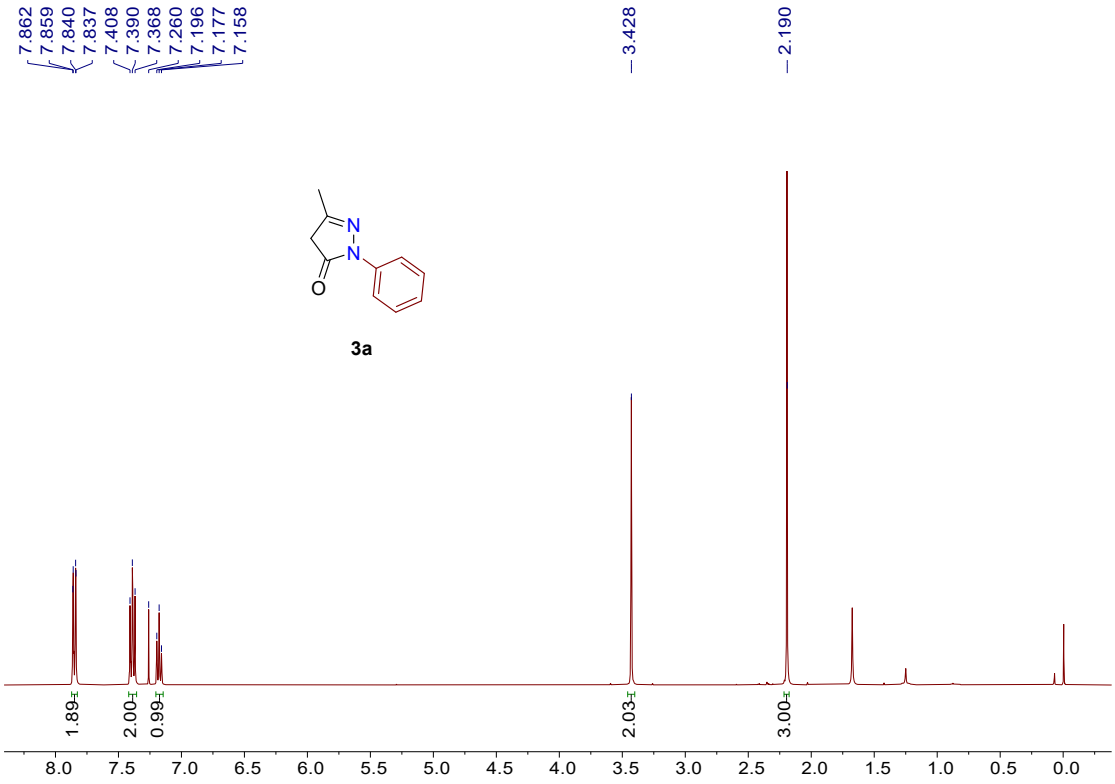
5. References

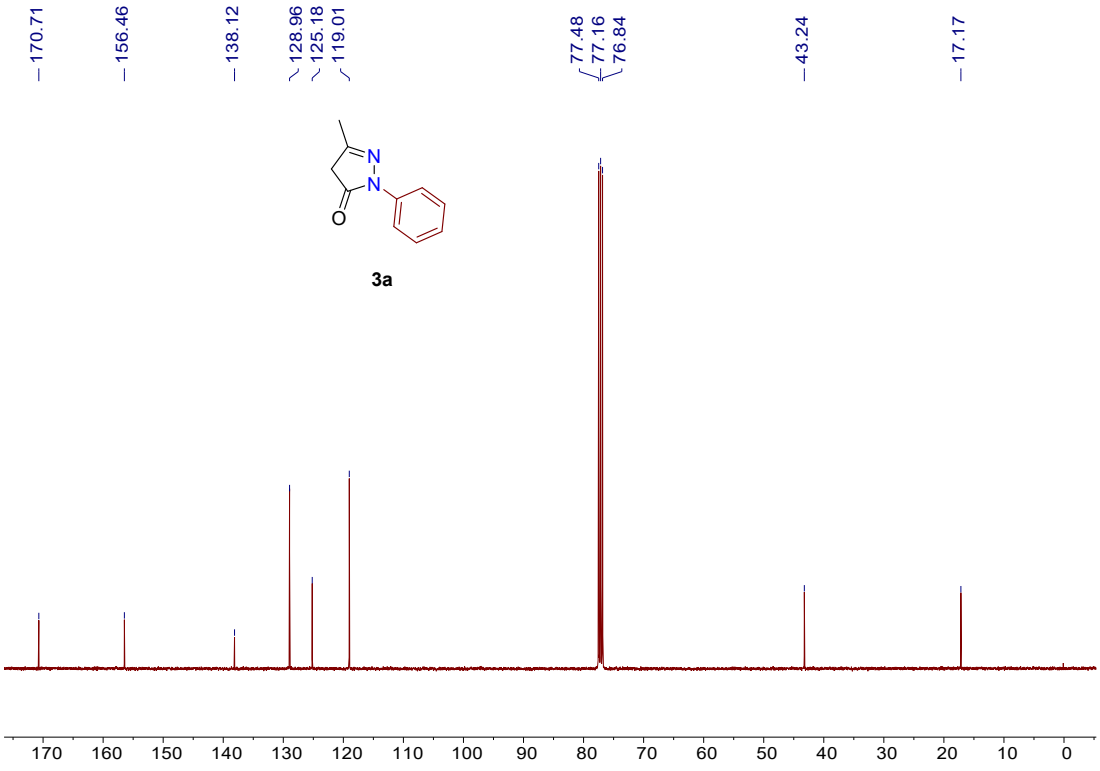
[1] M. Bielawski, M. Zhu, B. Olofsson, *Adv. Synth. Catal*. 2006, **349**, 2610.

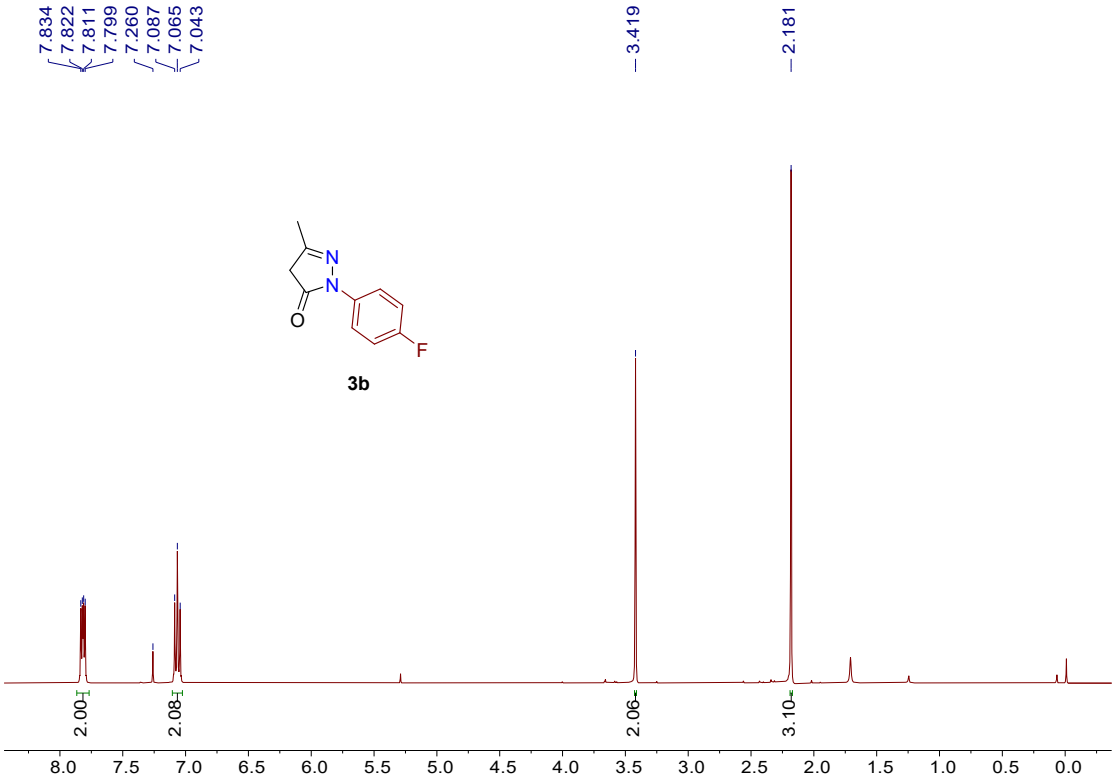
[2] M. Bielawski, D. Aili, B. Olofsson, *J. Org. Chem.* 2008, **73**, 4602.

[3] H. Kaneko, T. Ikawa, Y. Yamamoto, S. Arulmozhiraja, H. Tokiwa, S. Akai, *Synlett*. 2018, **29,** 943.

6. ^{1}H and ^{13}C Spectra of New Compounds



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7.065
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2.181
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2.08
2.06
3.10
8.0
7.5
7.0
6.5
6.0
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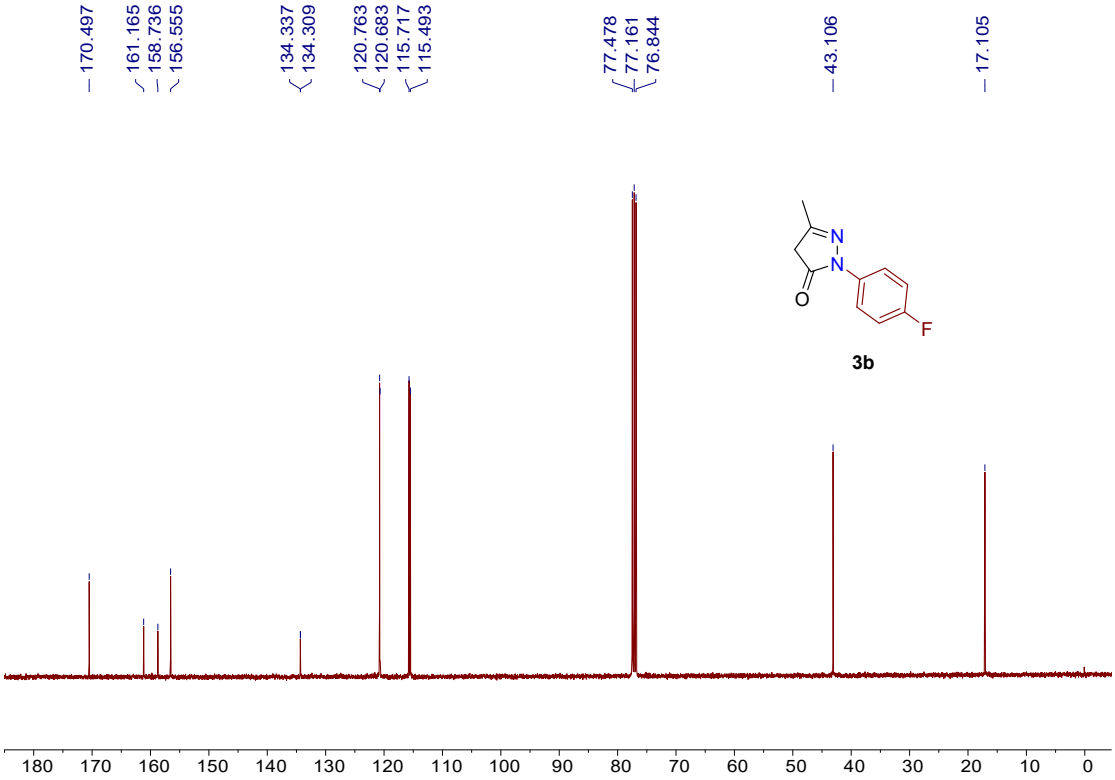
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43.106
17.105
3b
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150
140
130
120
110
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90
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70
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50
40
30
20
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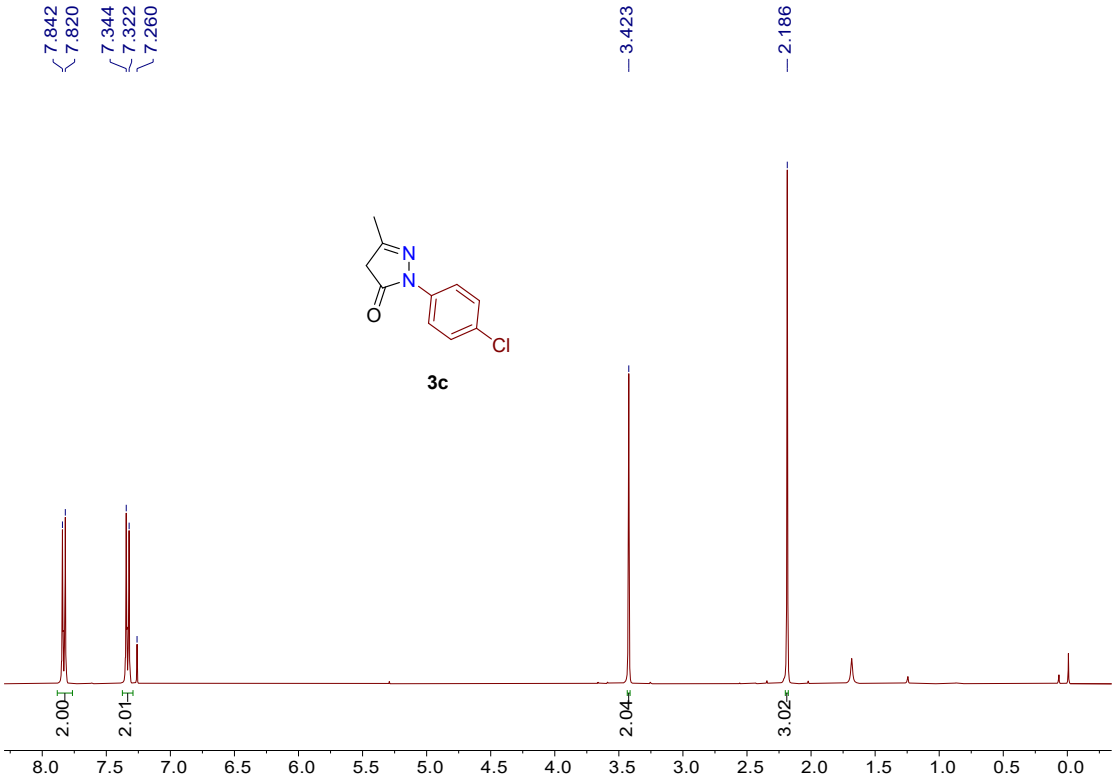
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Cl
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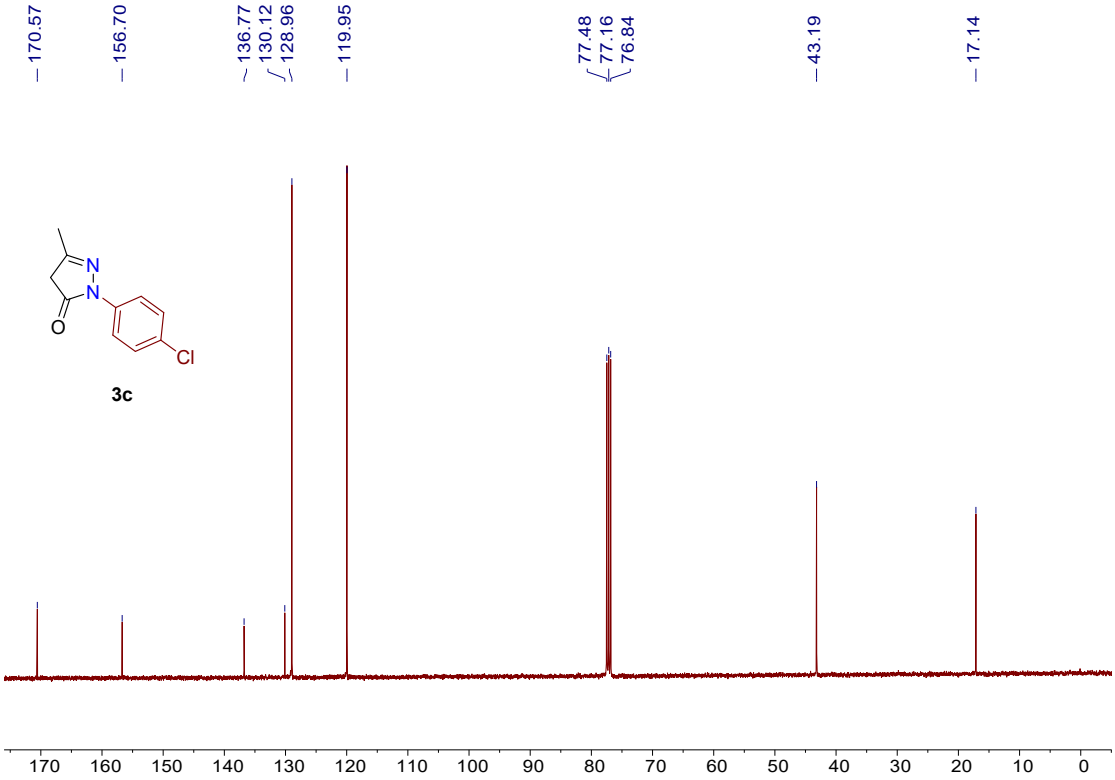
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O
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10
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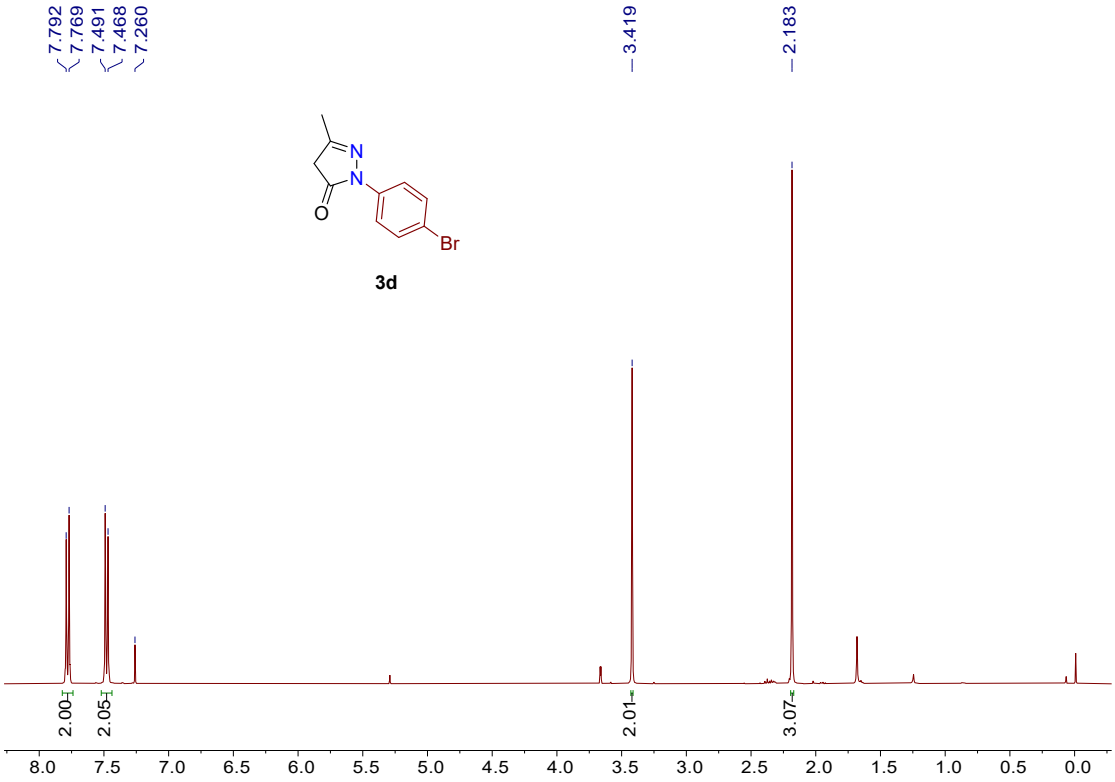
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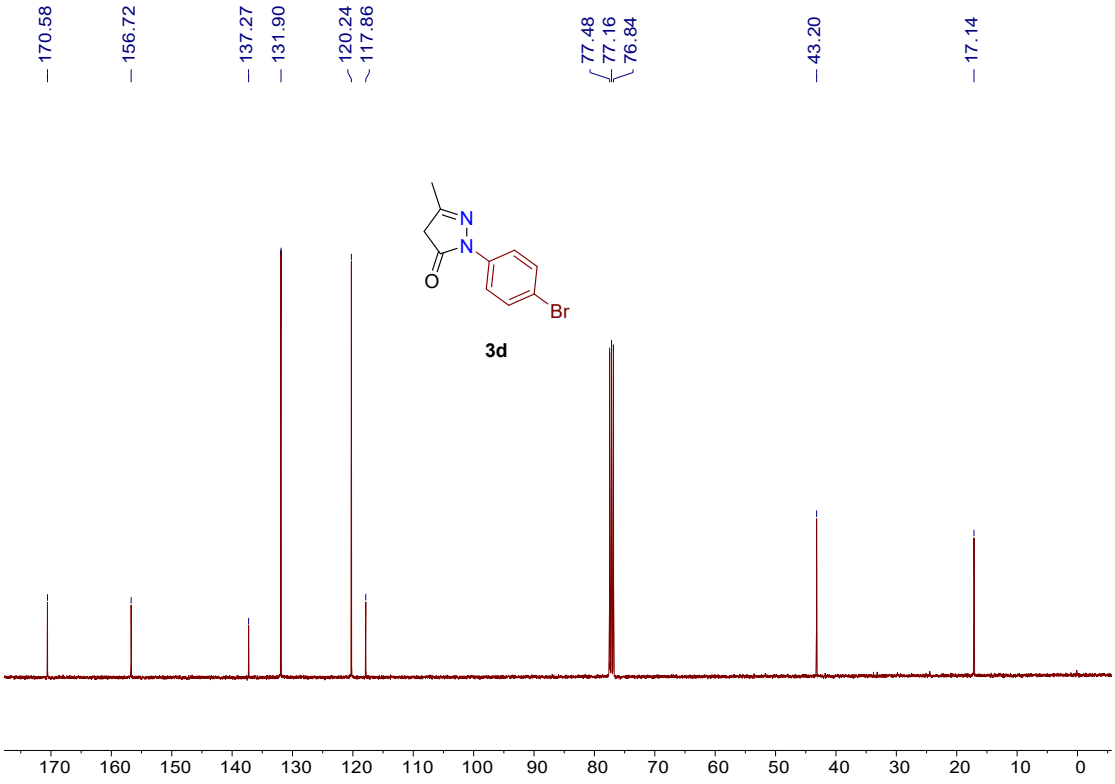
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150
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30
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10
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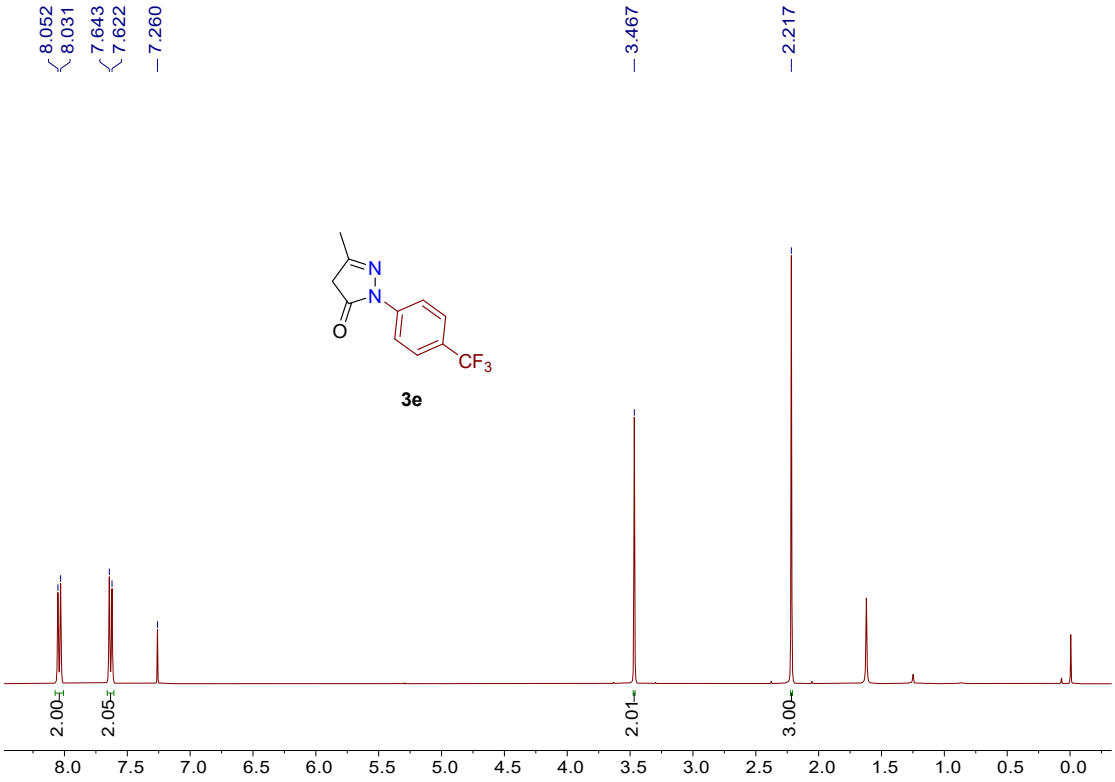
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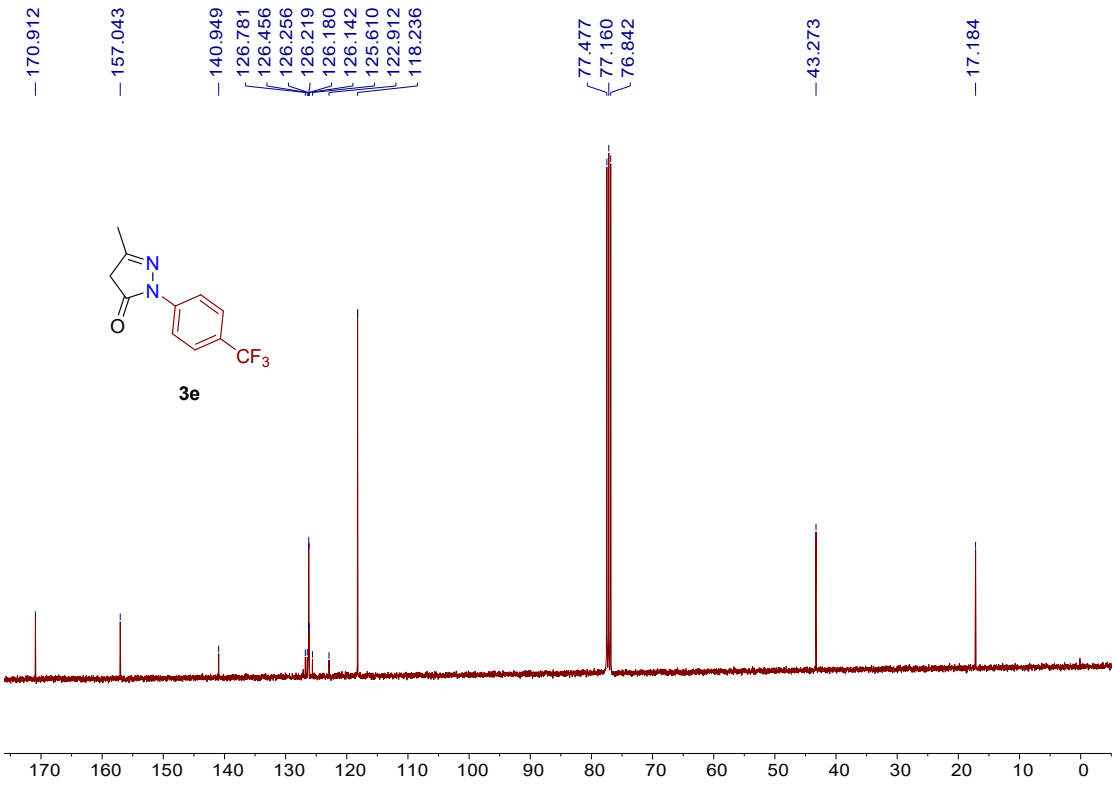
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43.273
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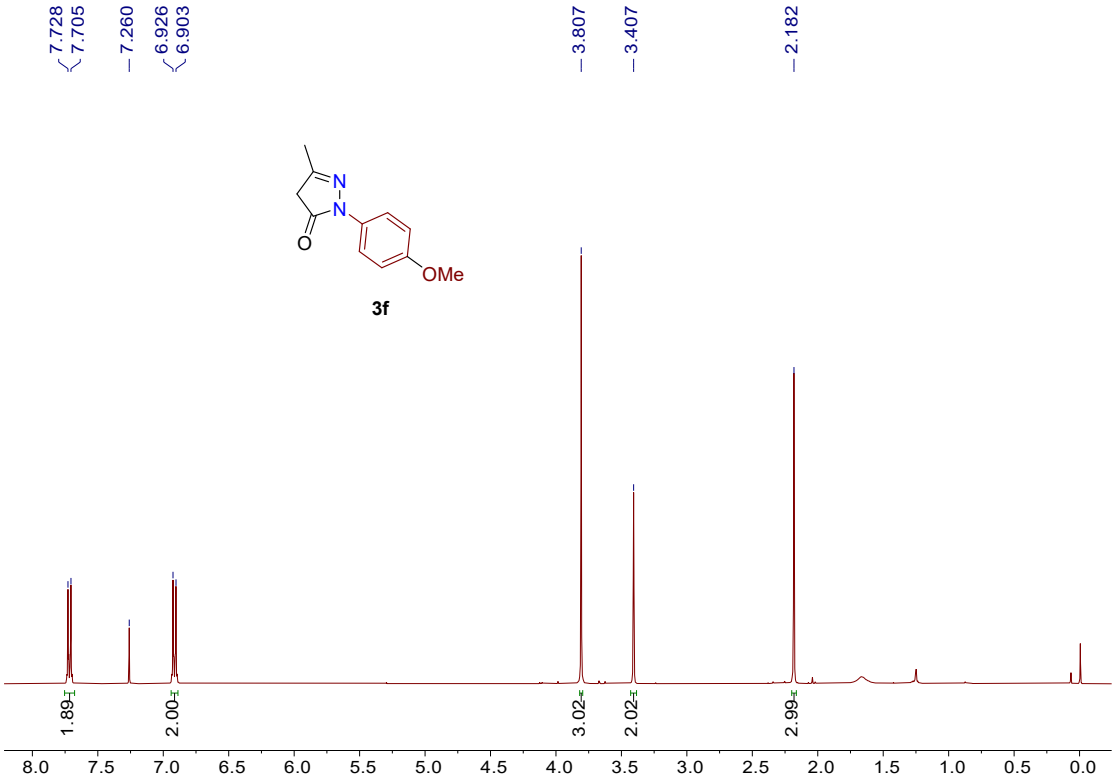
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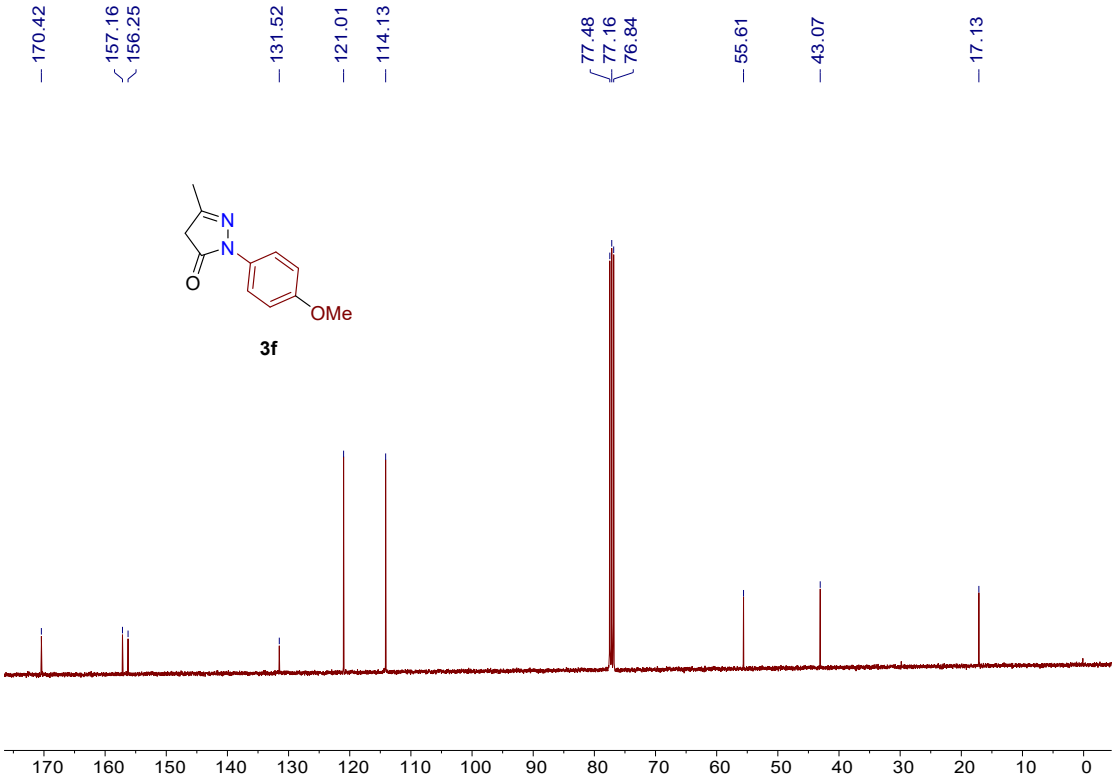
3f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O
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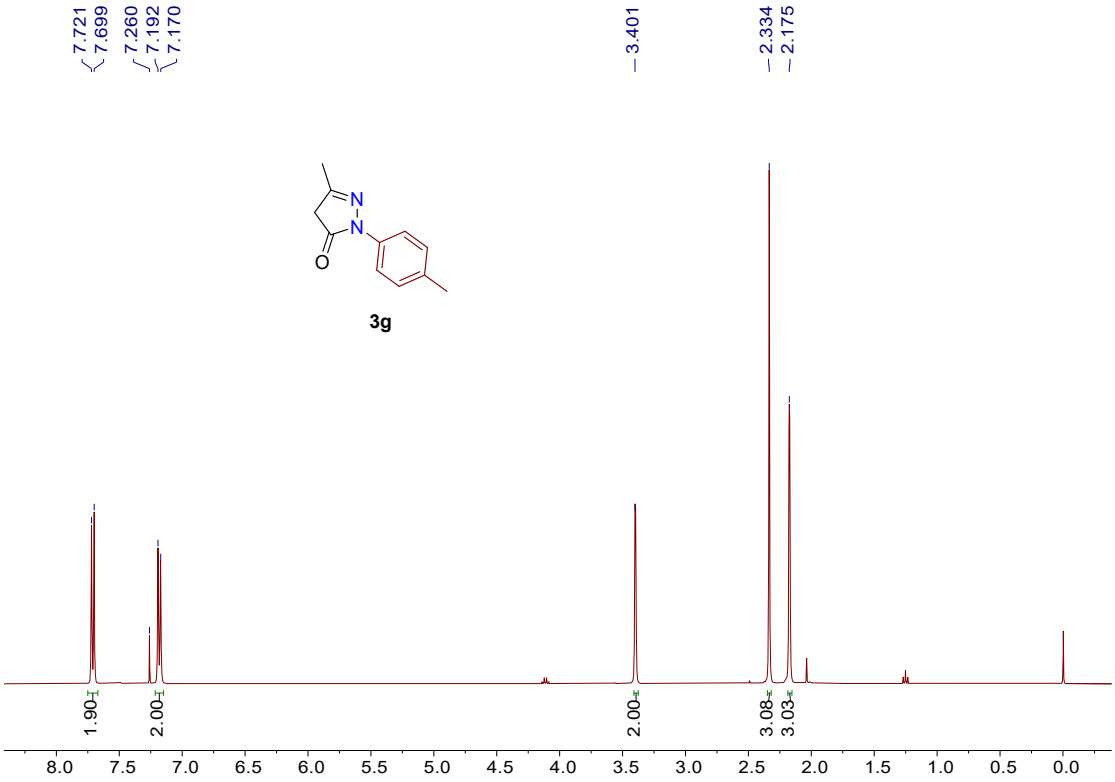
3f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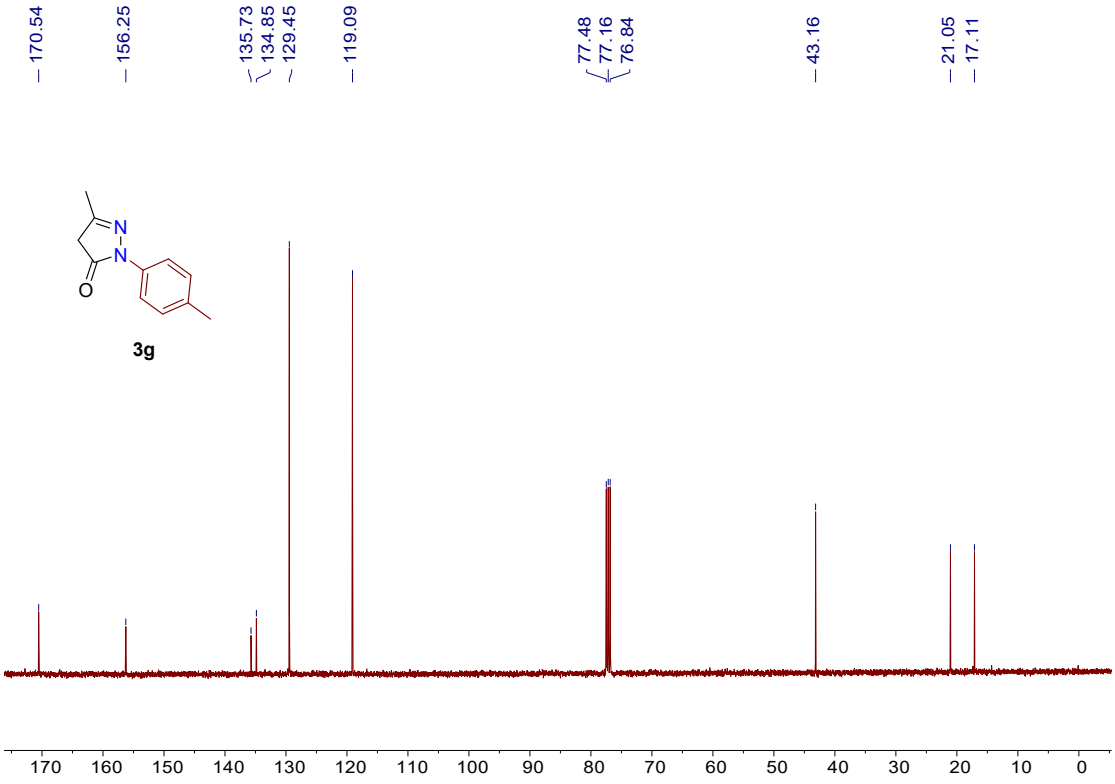
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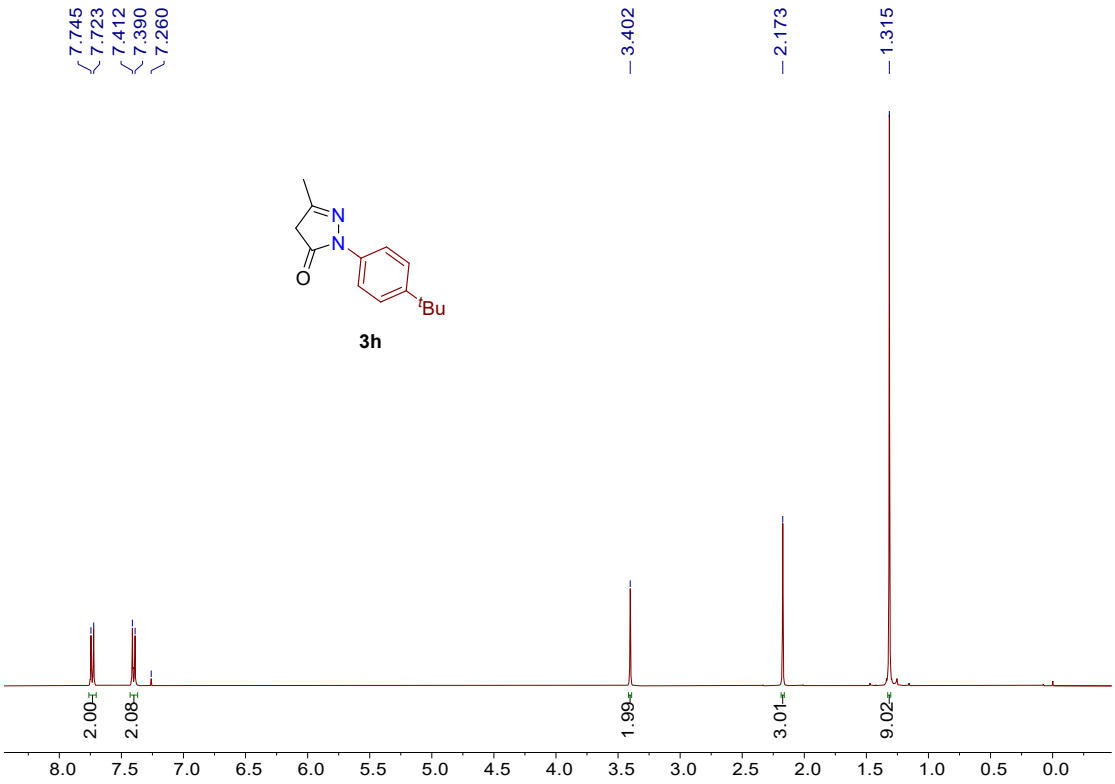
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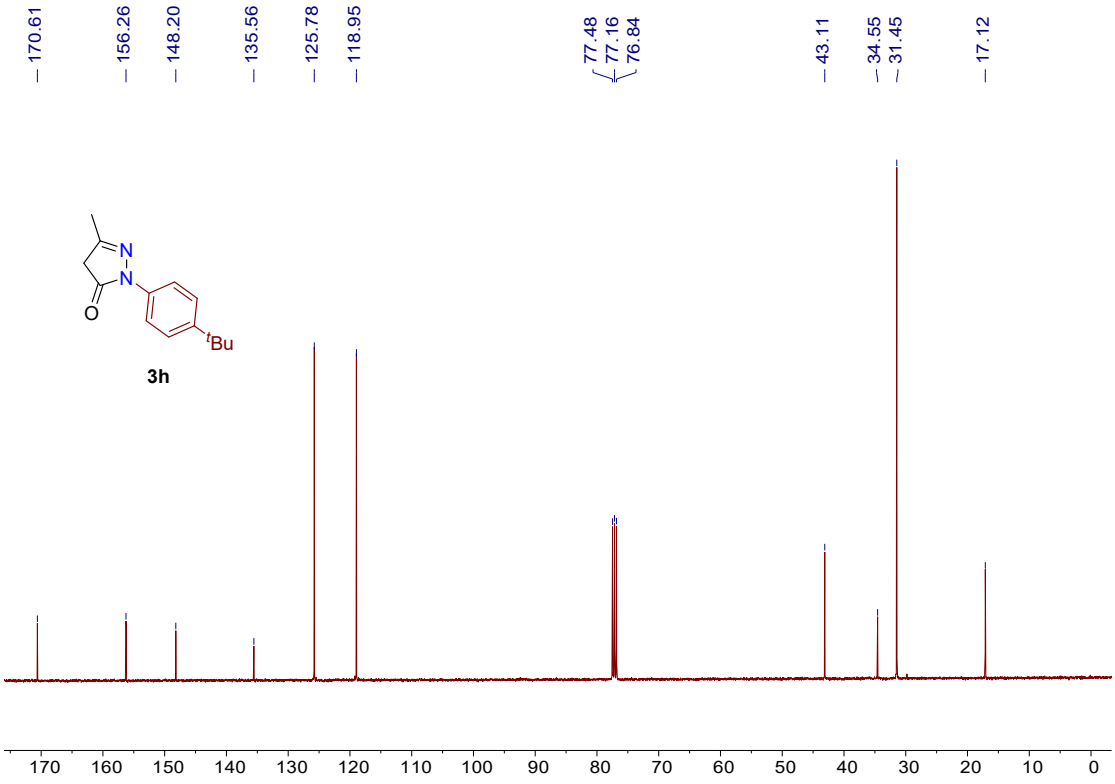
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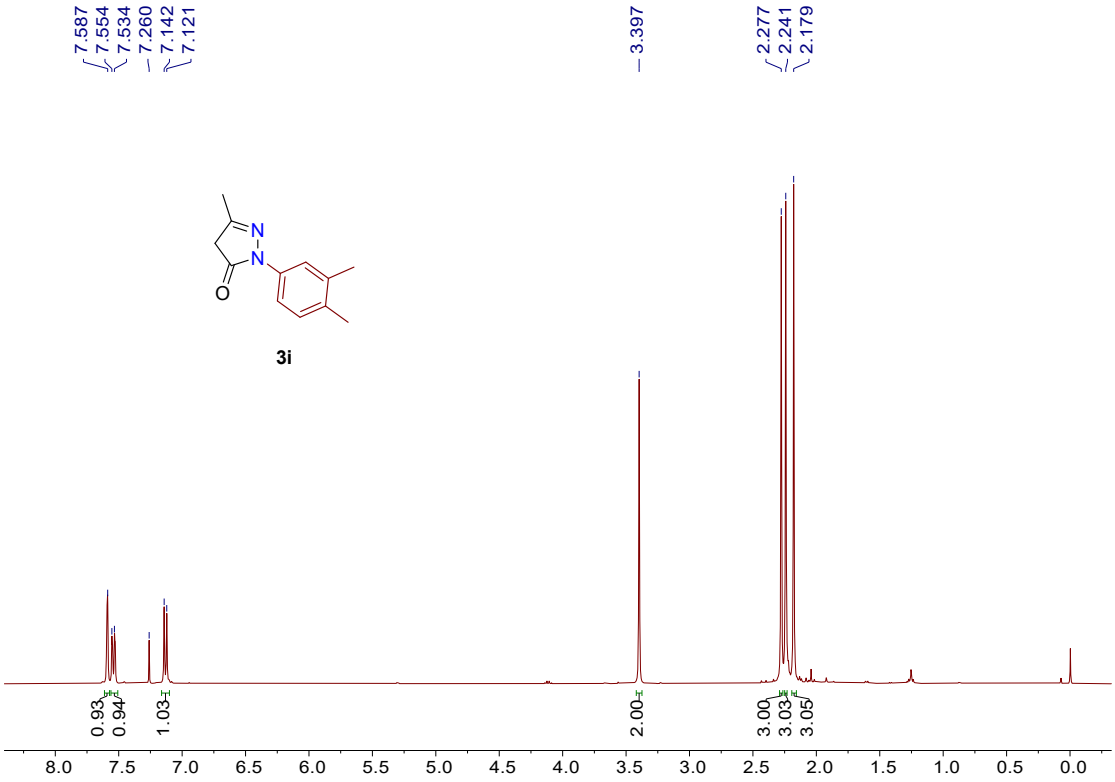
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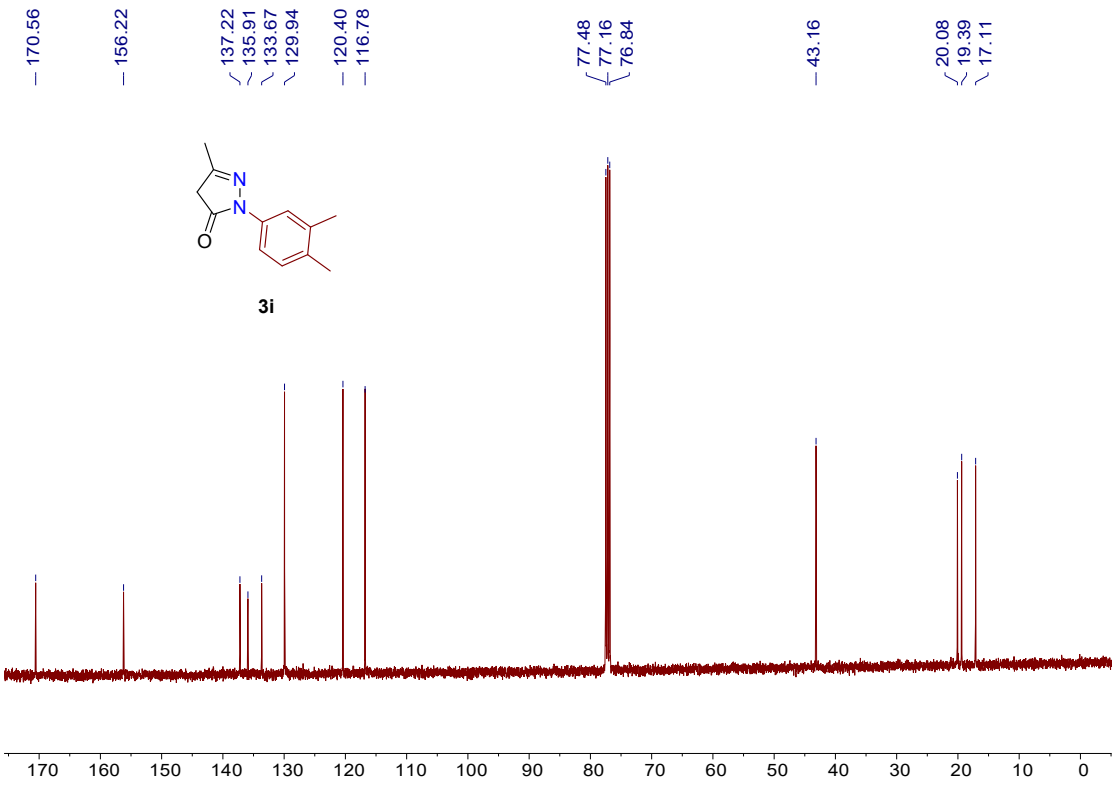
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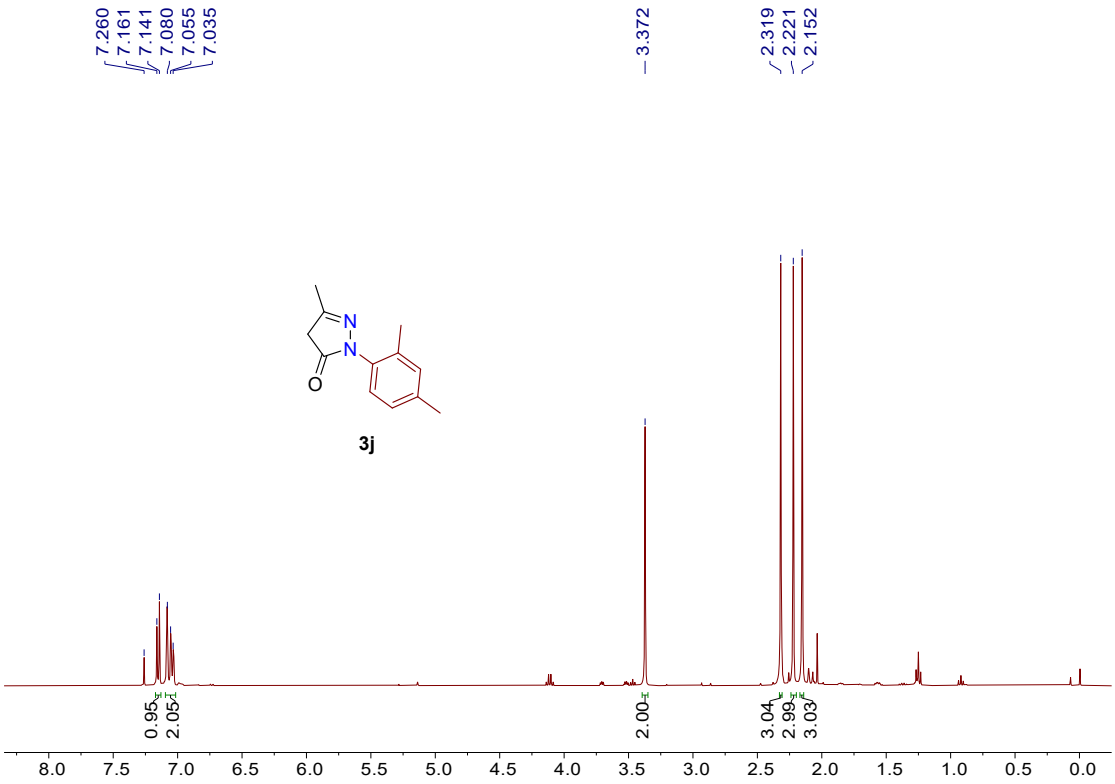
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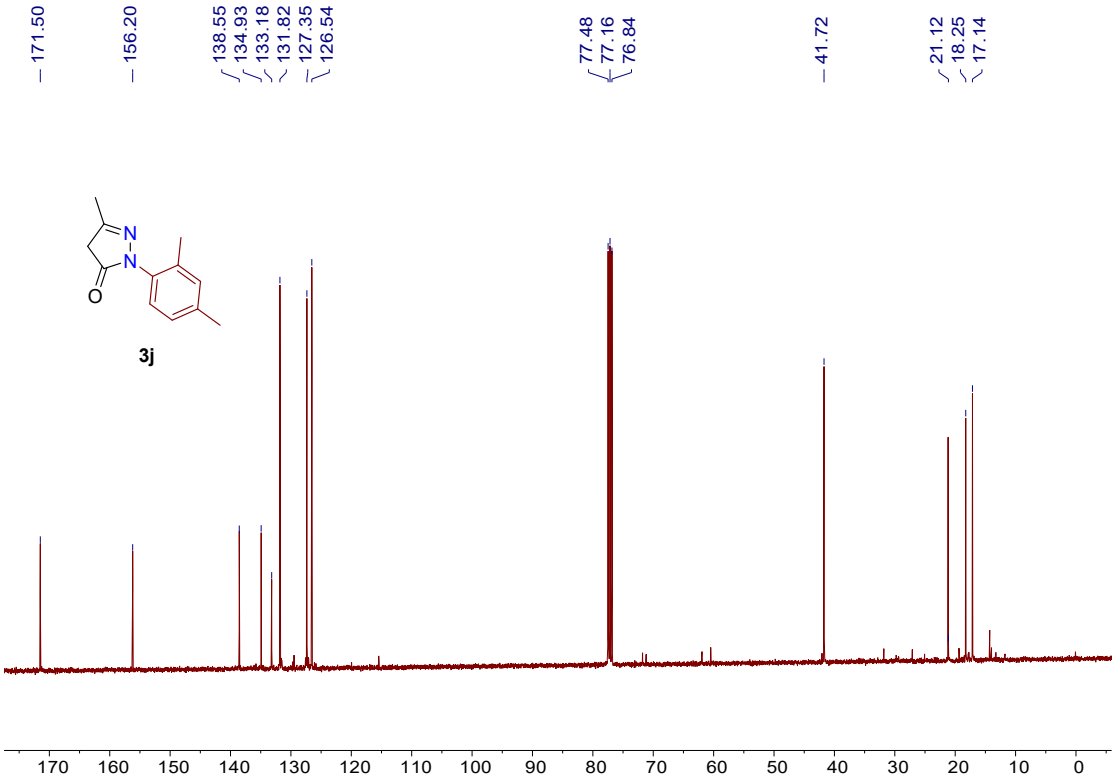
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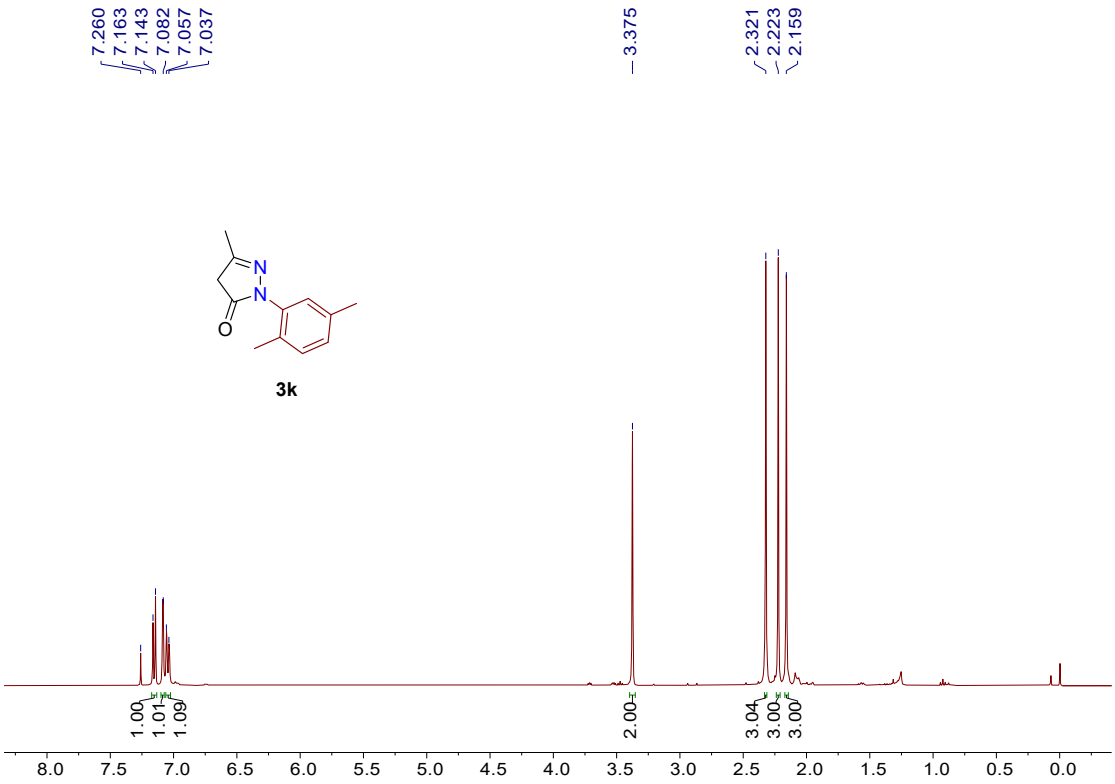
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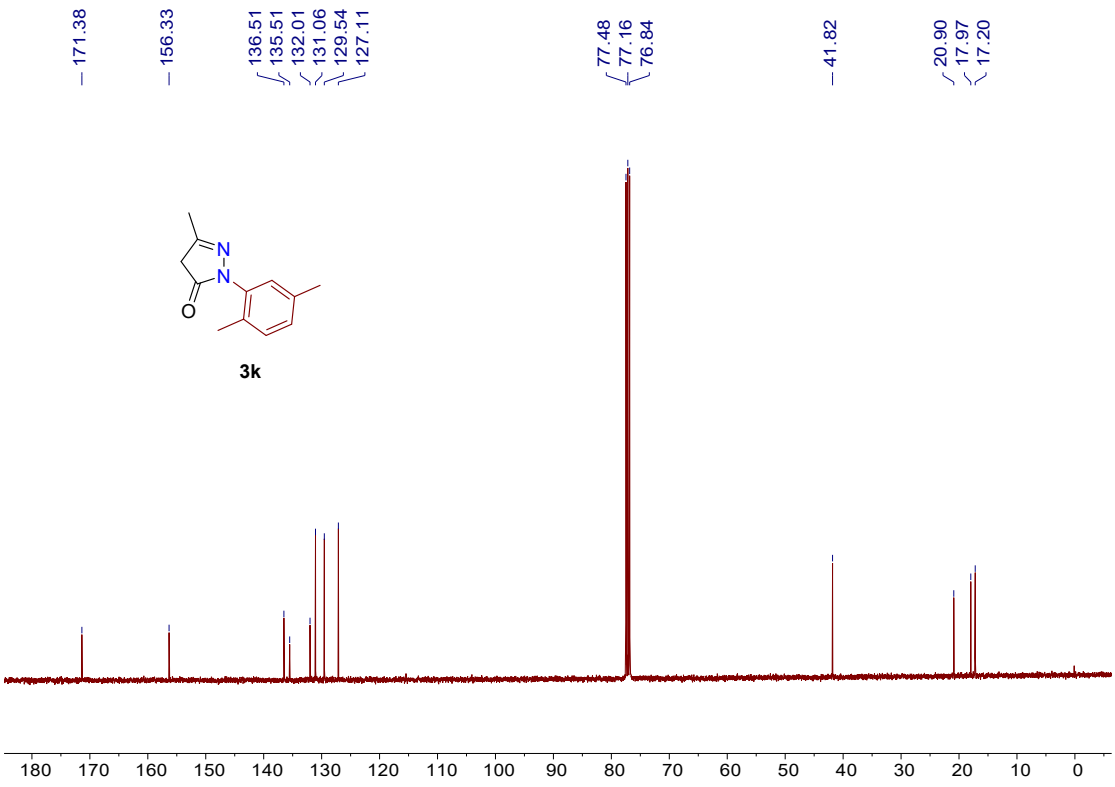
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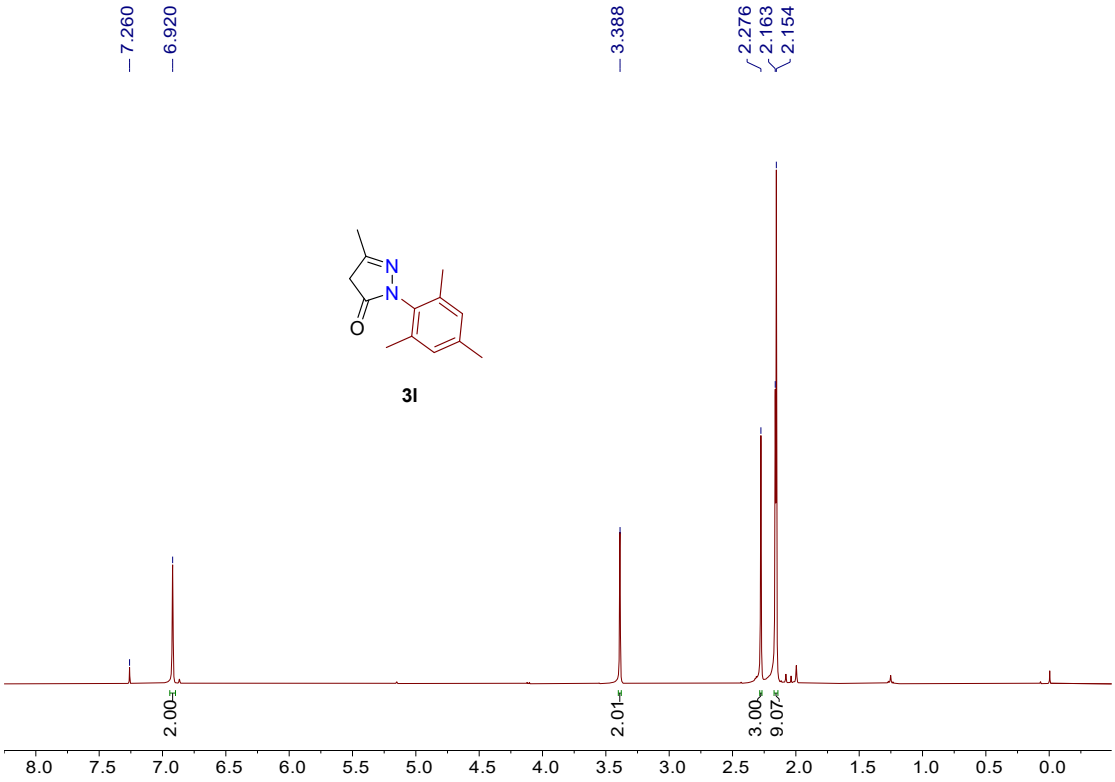
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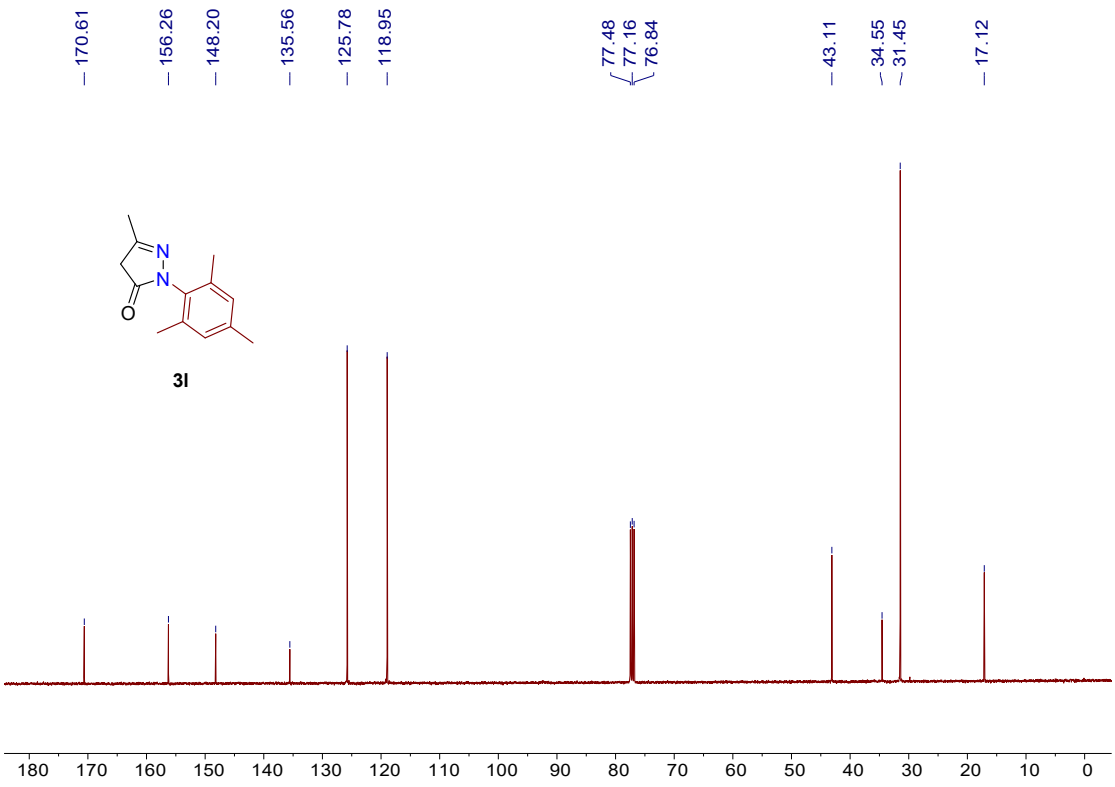
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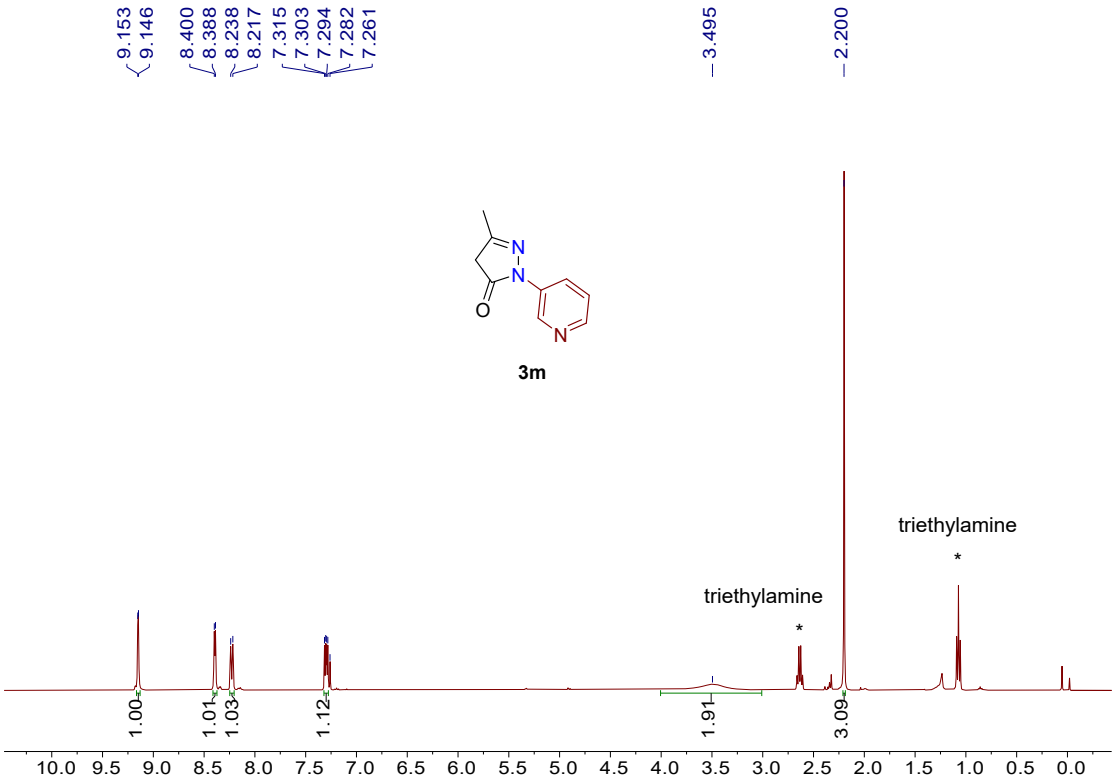
3l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2.200
3m
triethylamine
*
triethylamine
*
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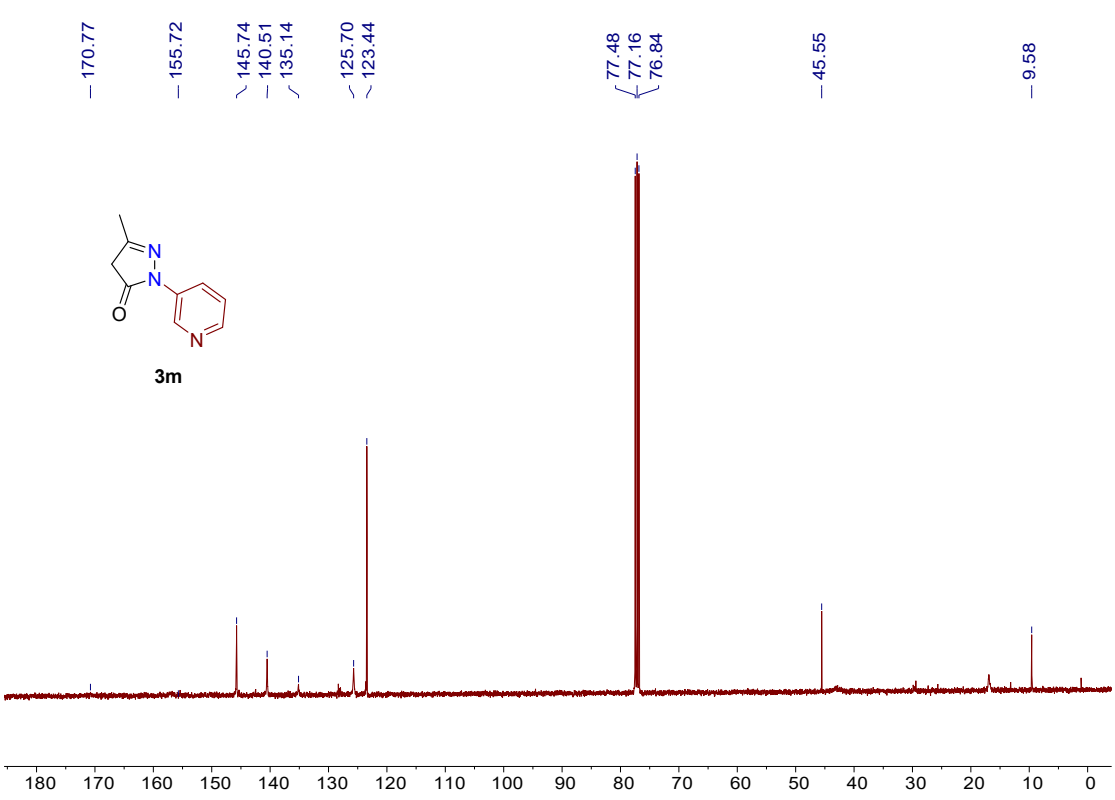
1.01
1.03
1.12
1.91
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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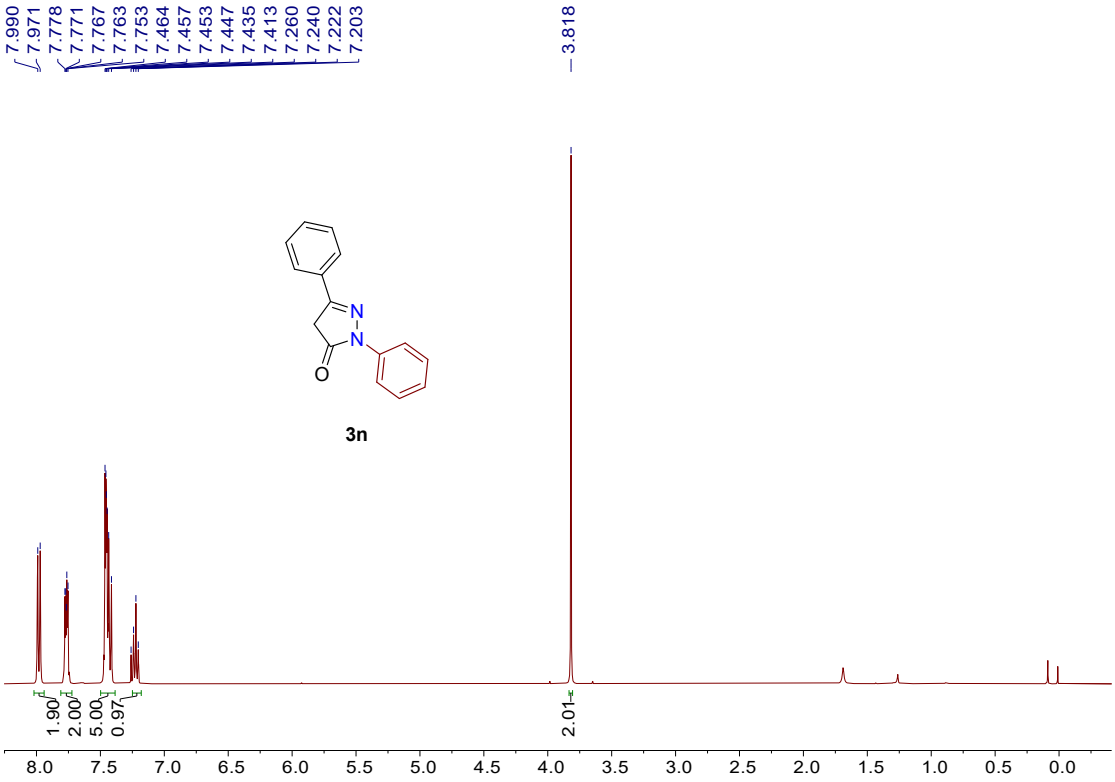
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5.00
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6.5
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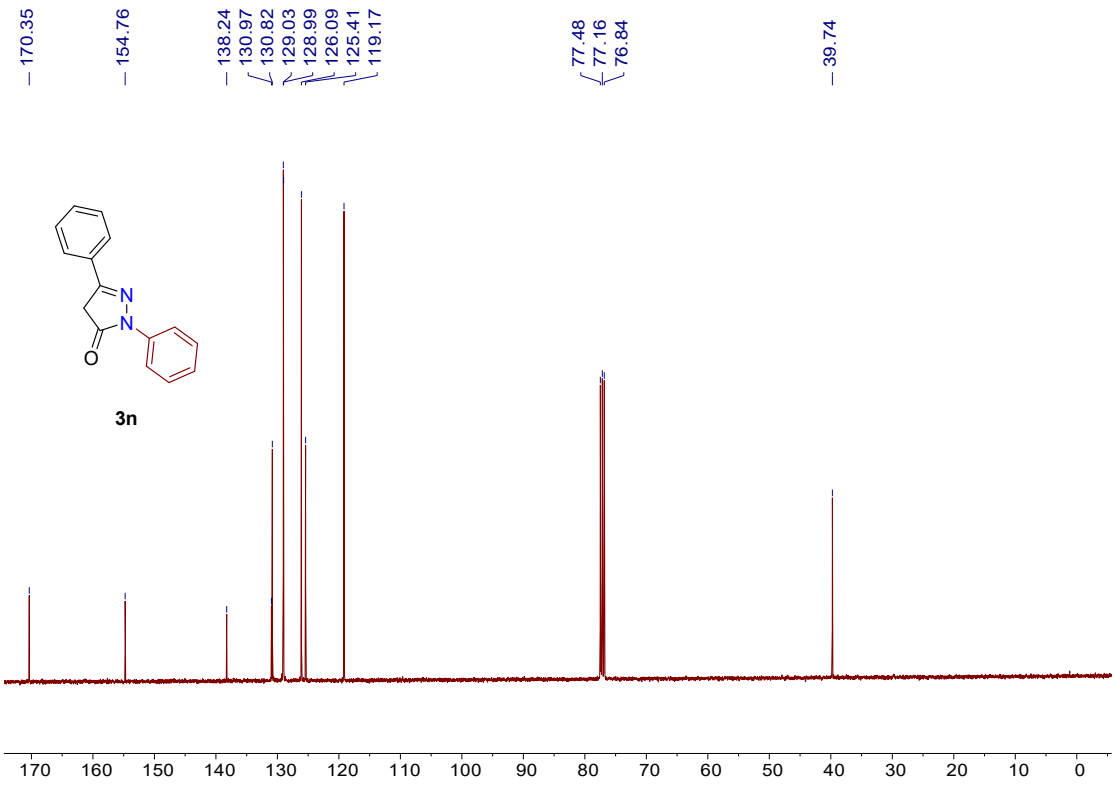
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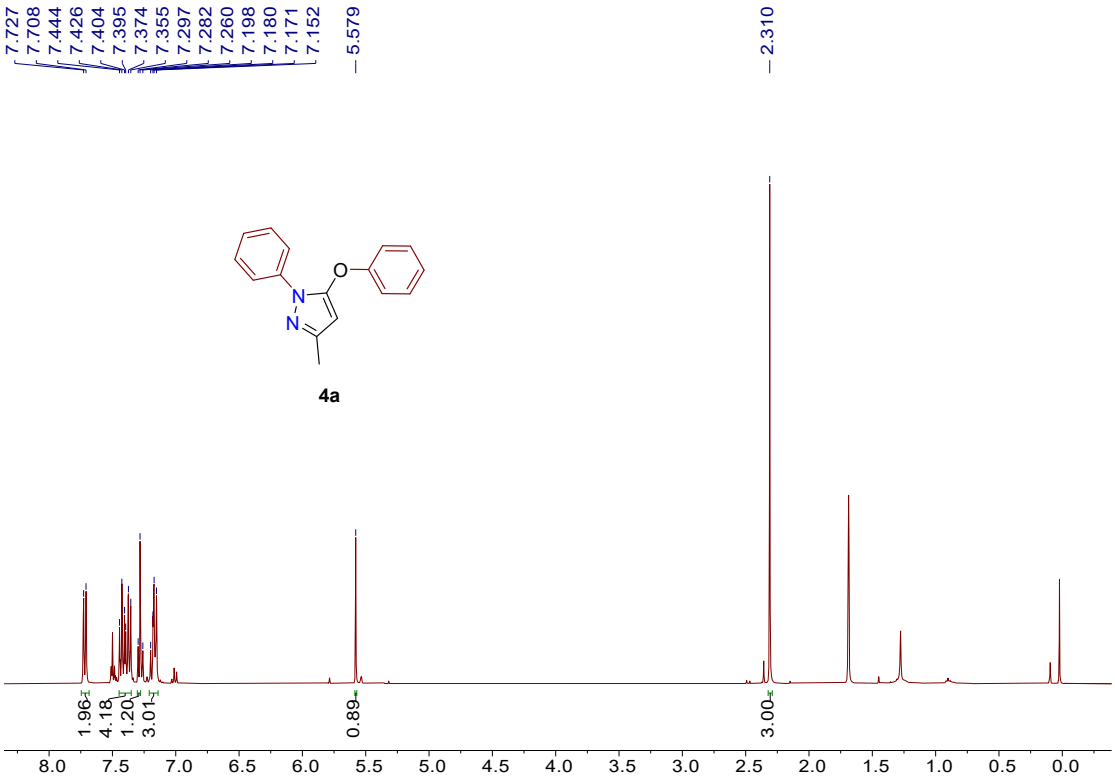
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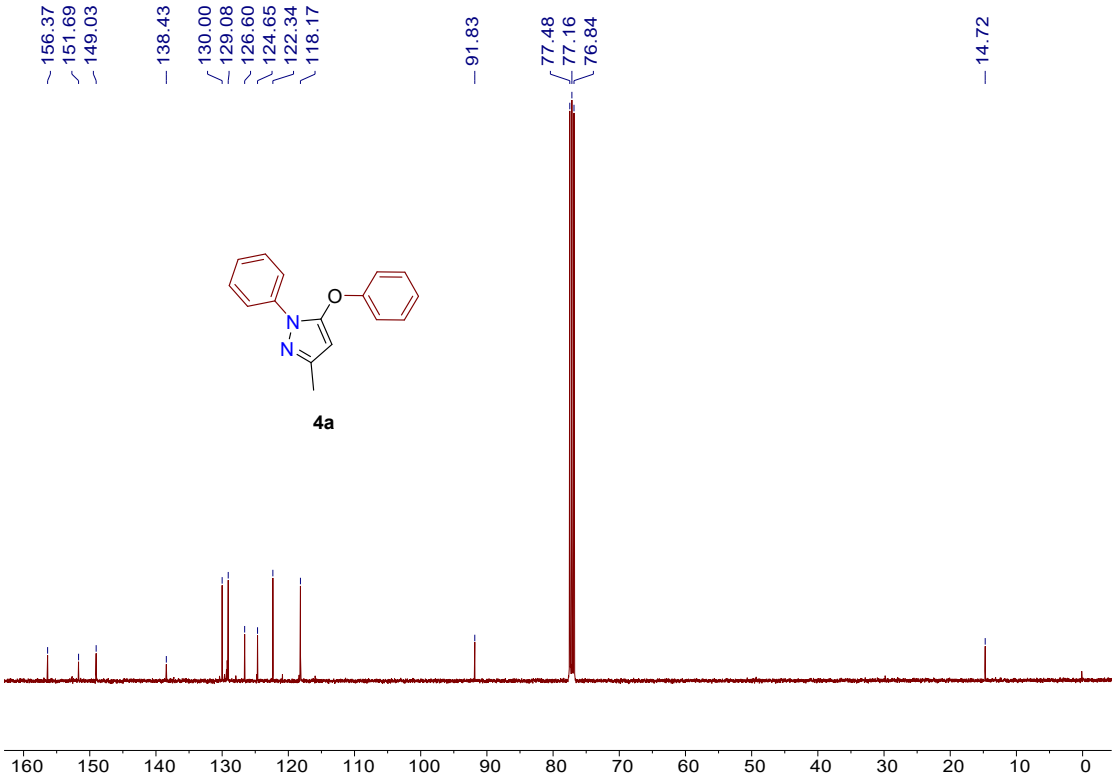
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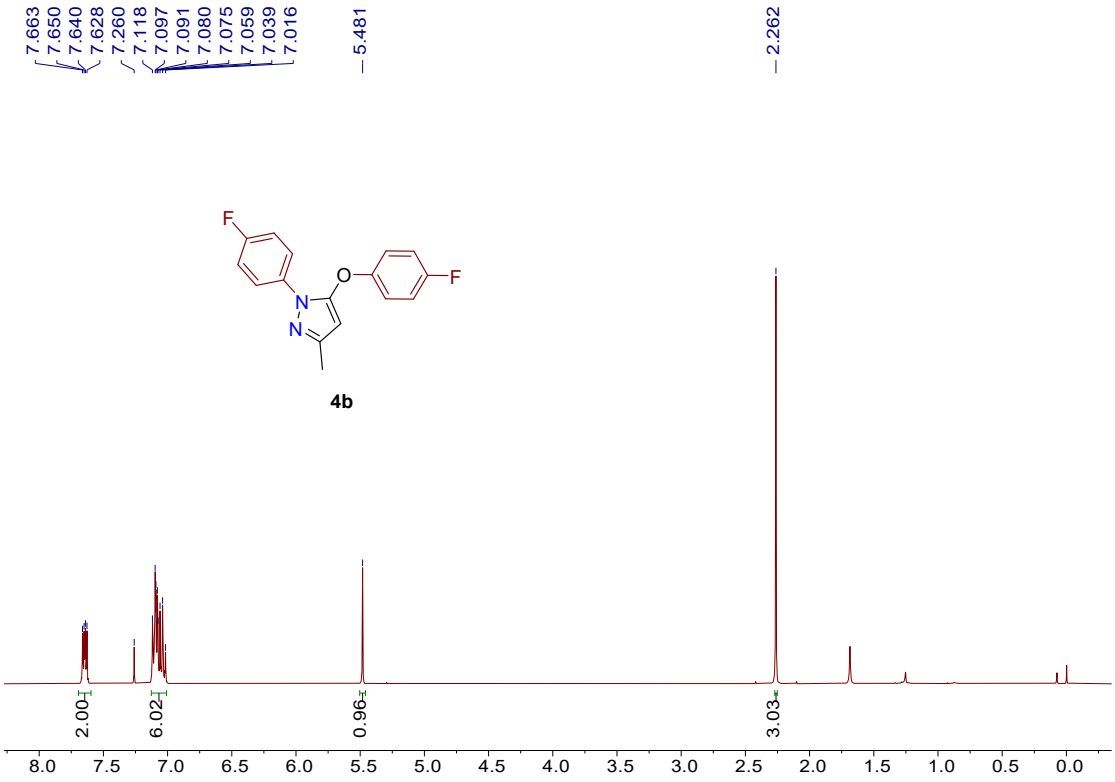
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F
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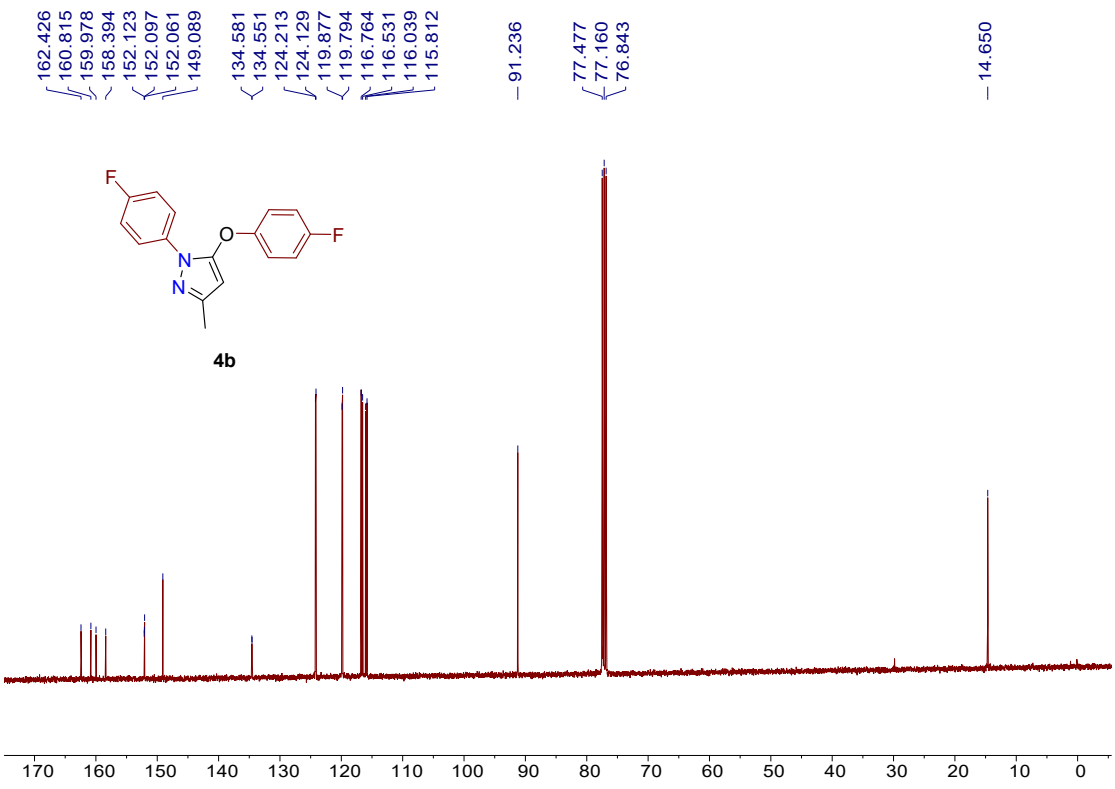
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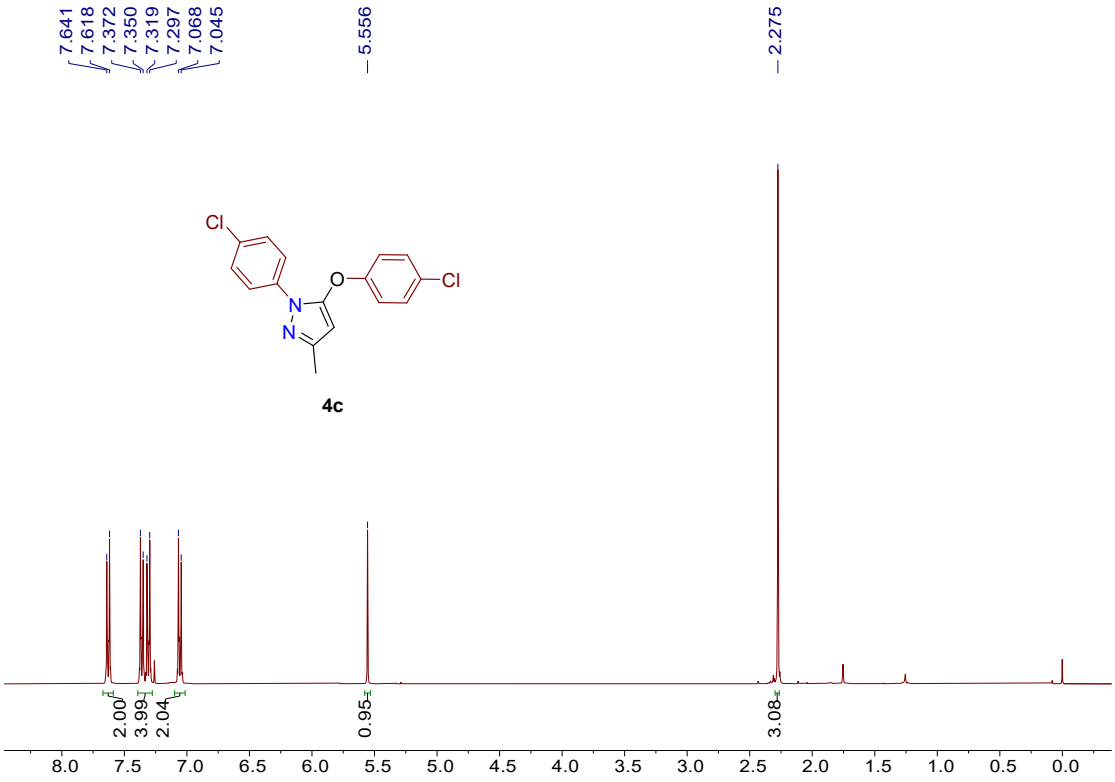
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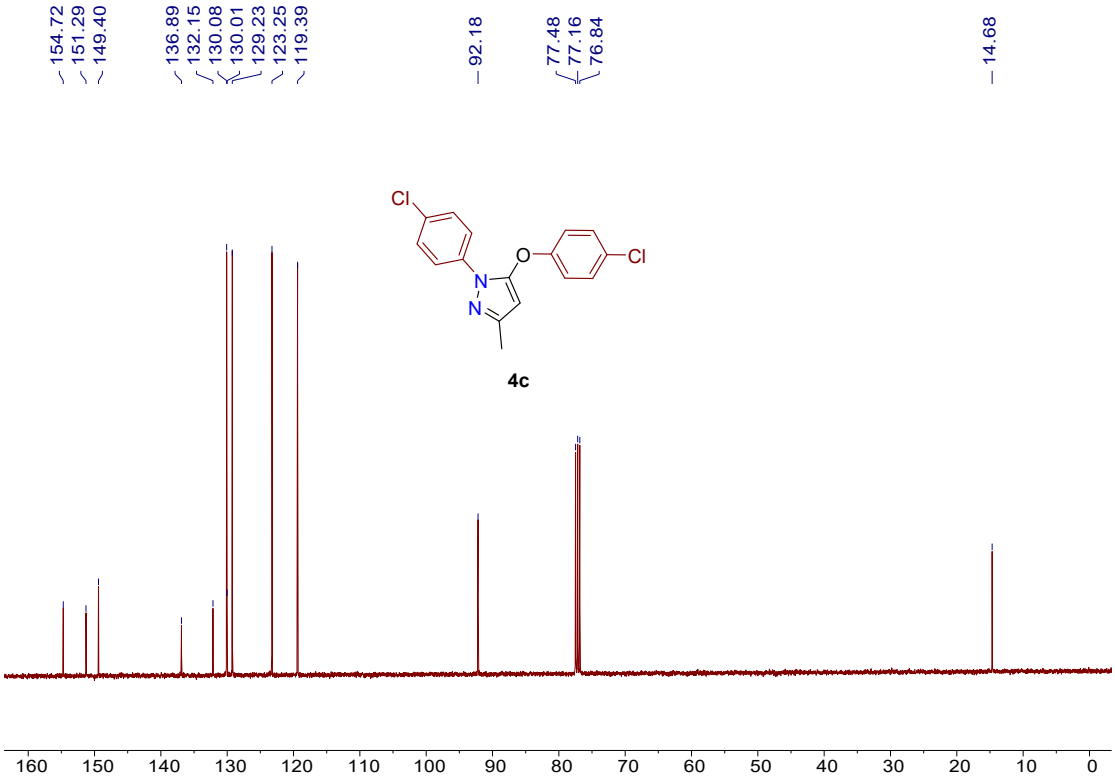
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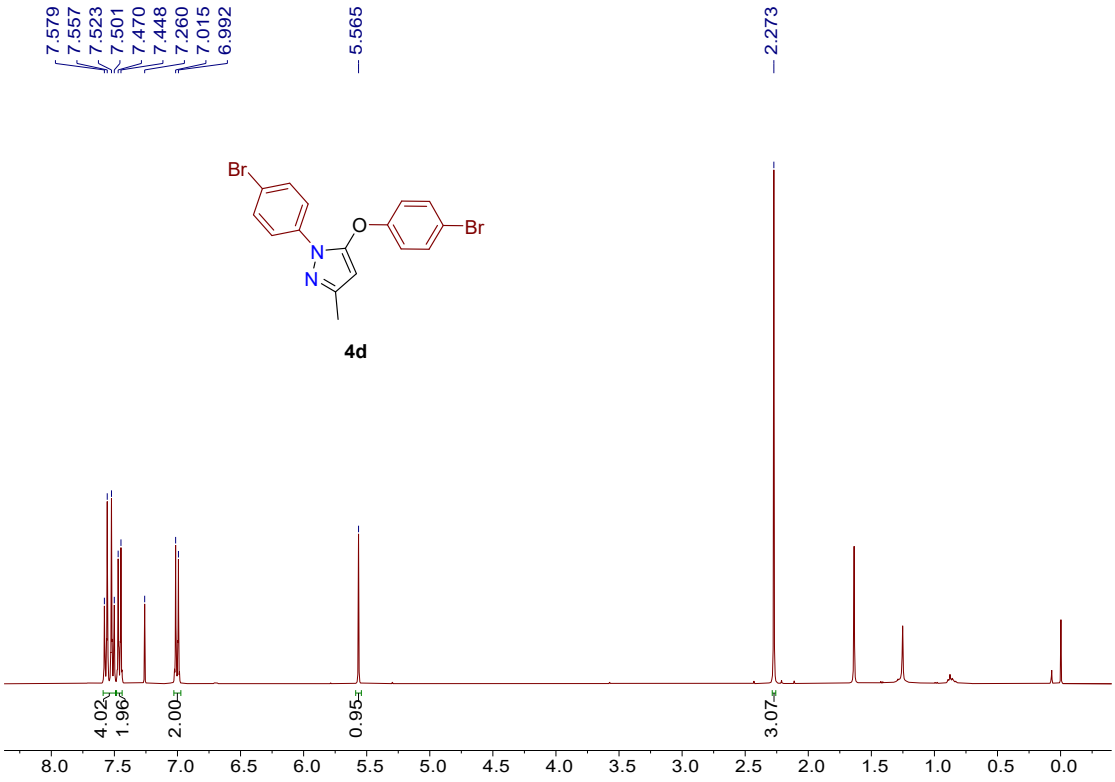
4c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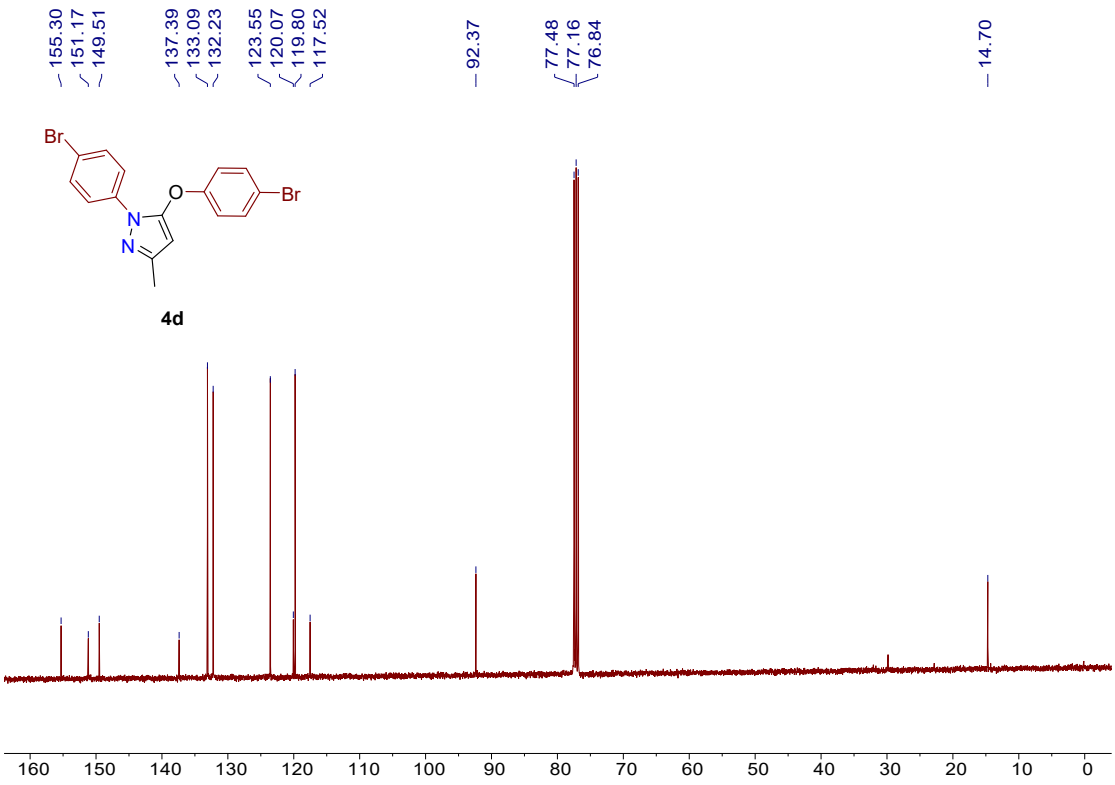
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Br
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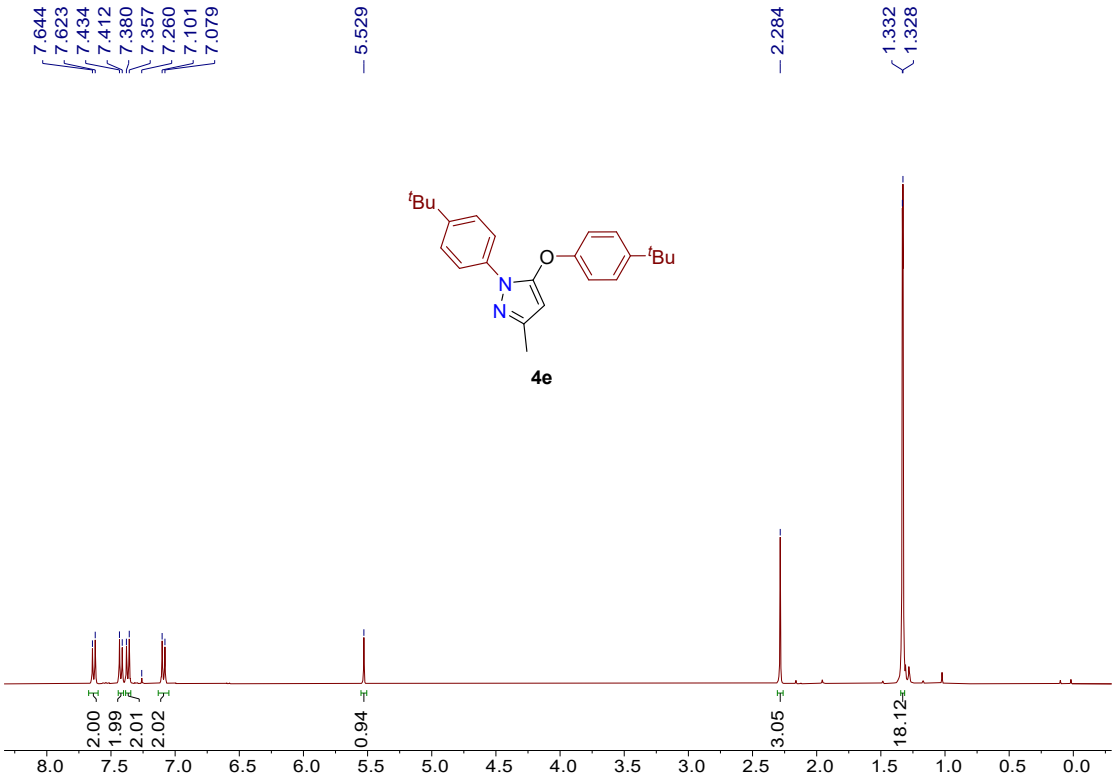
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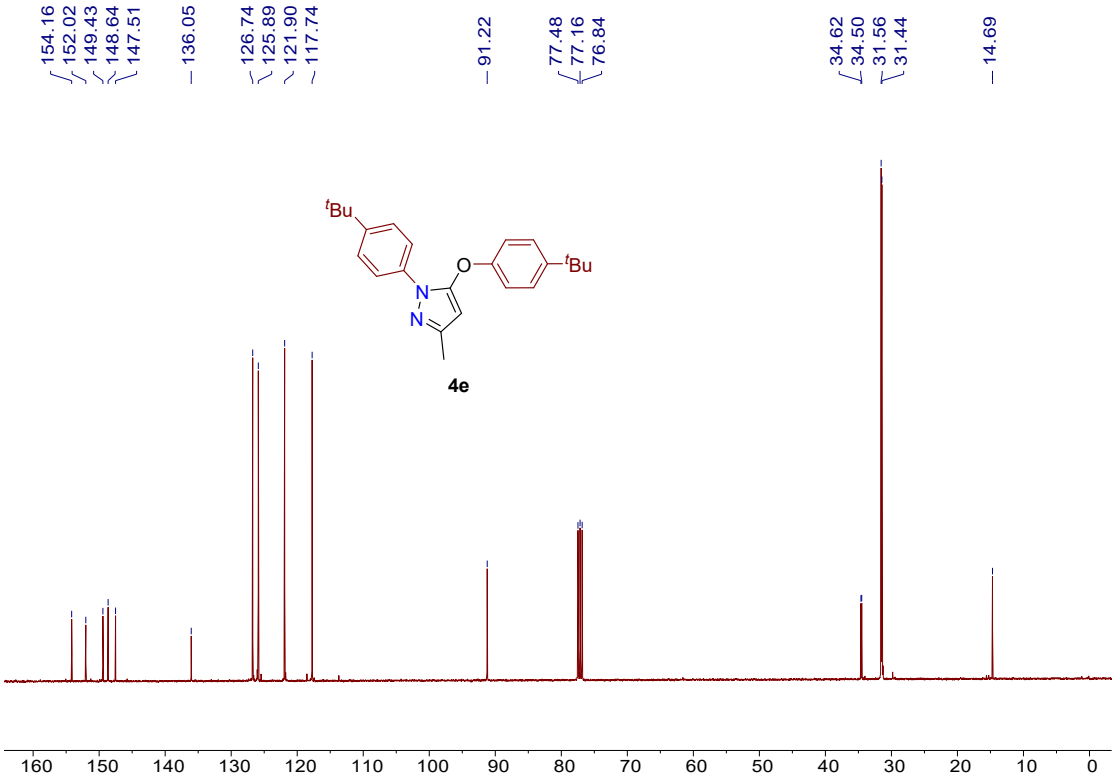
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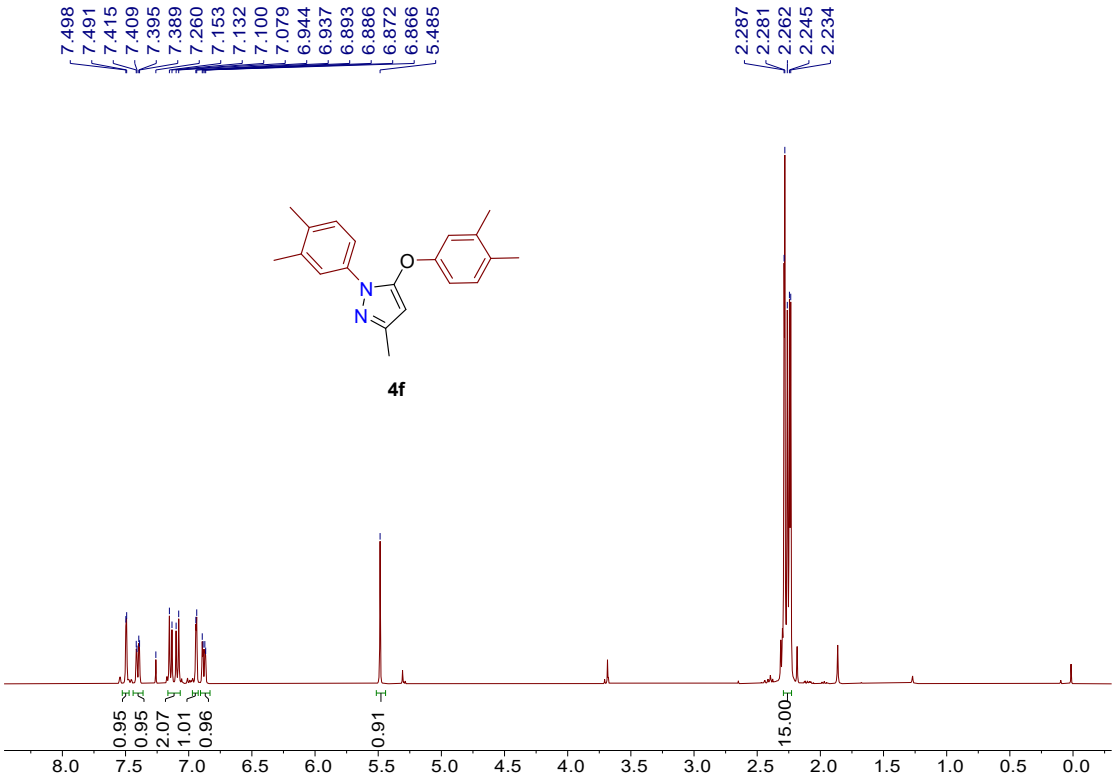
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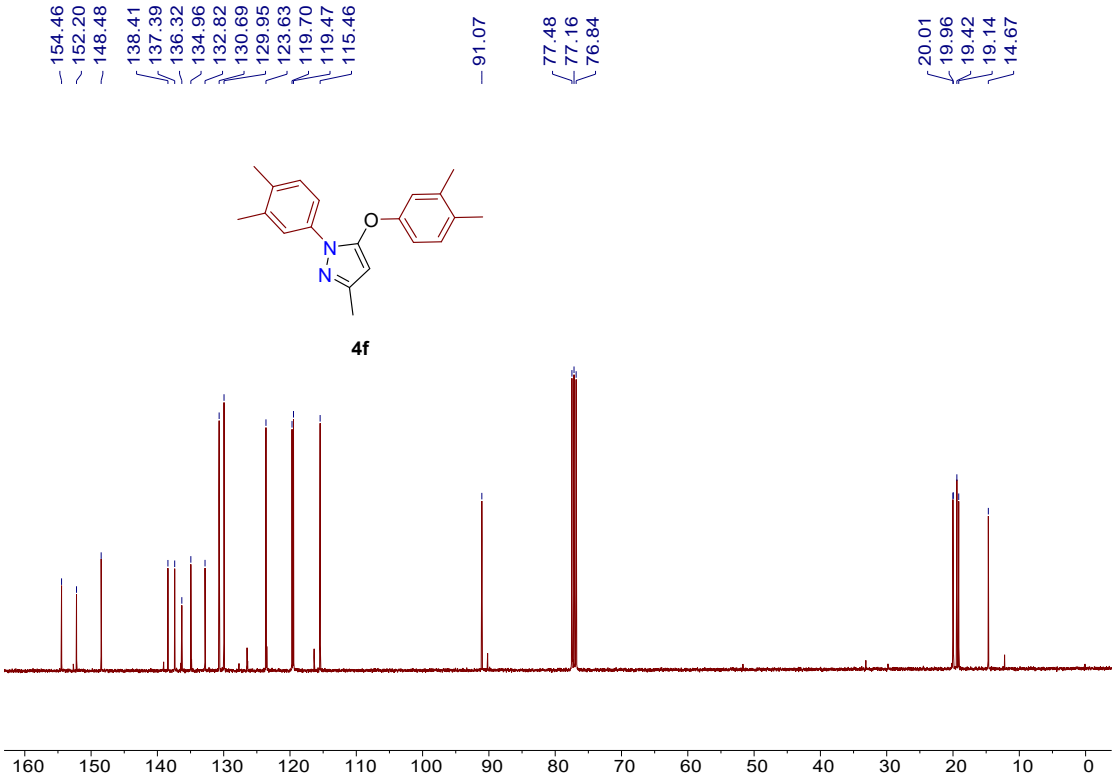
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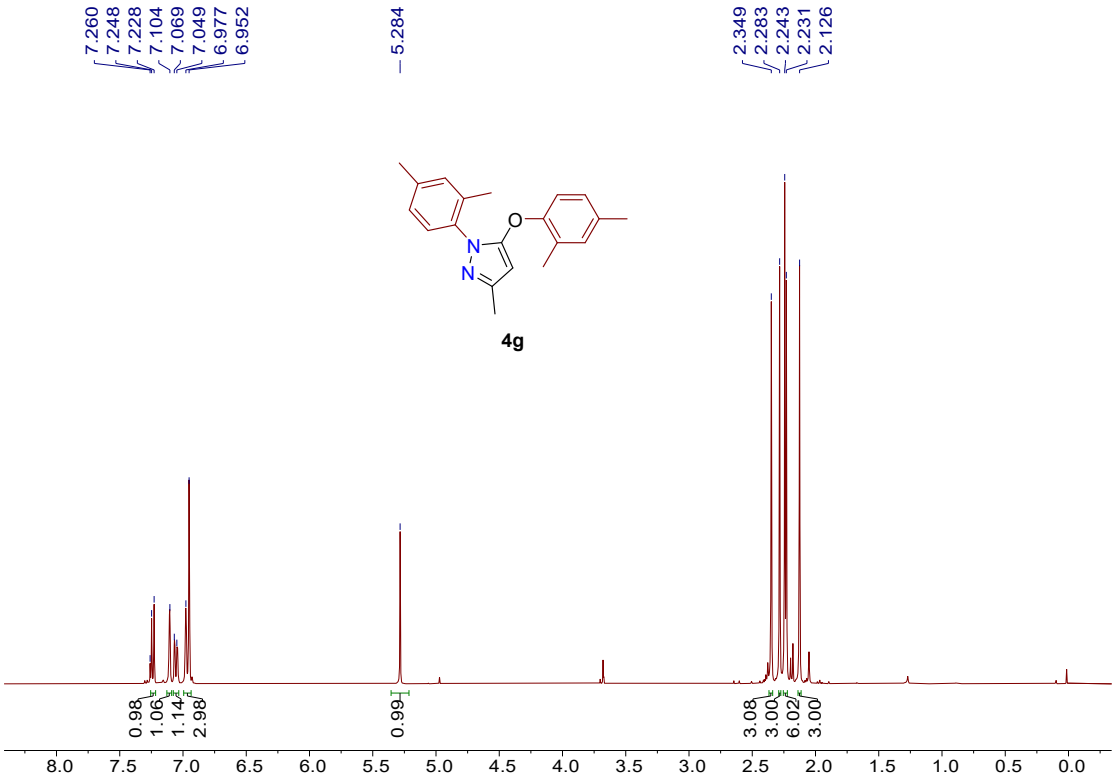
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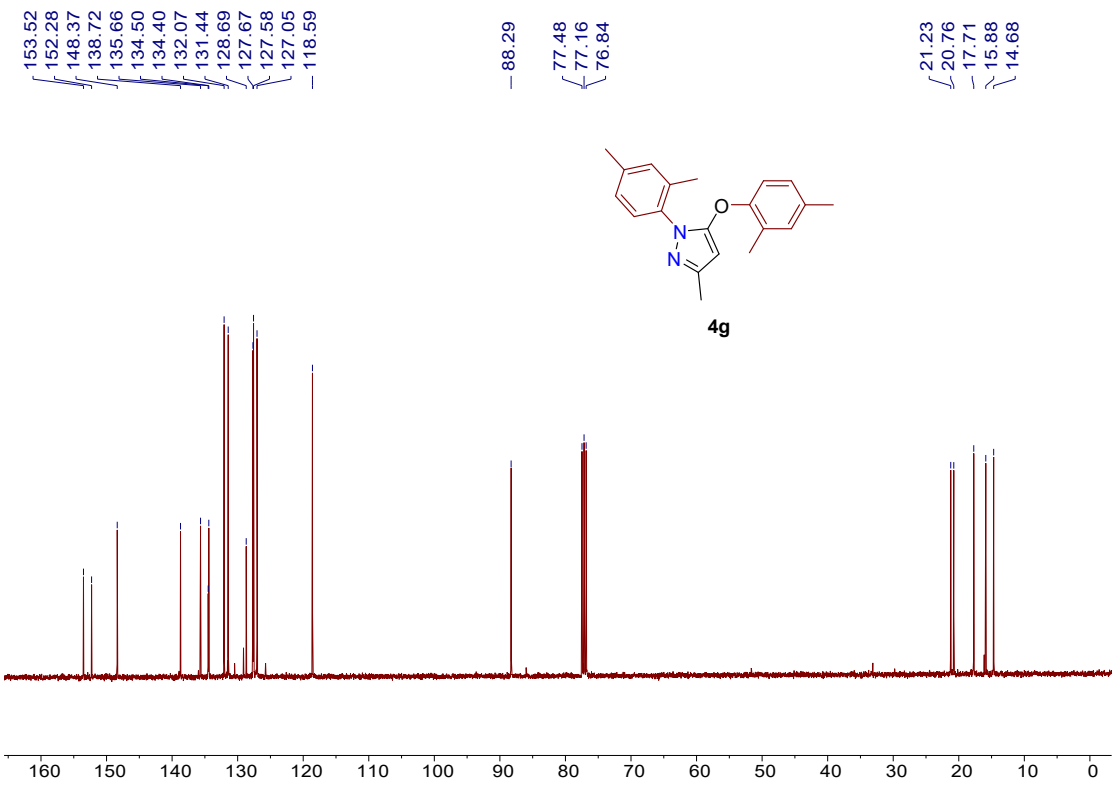
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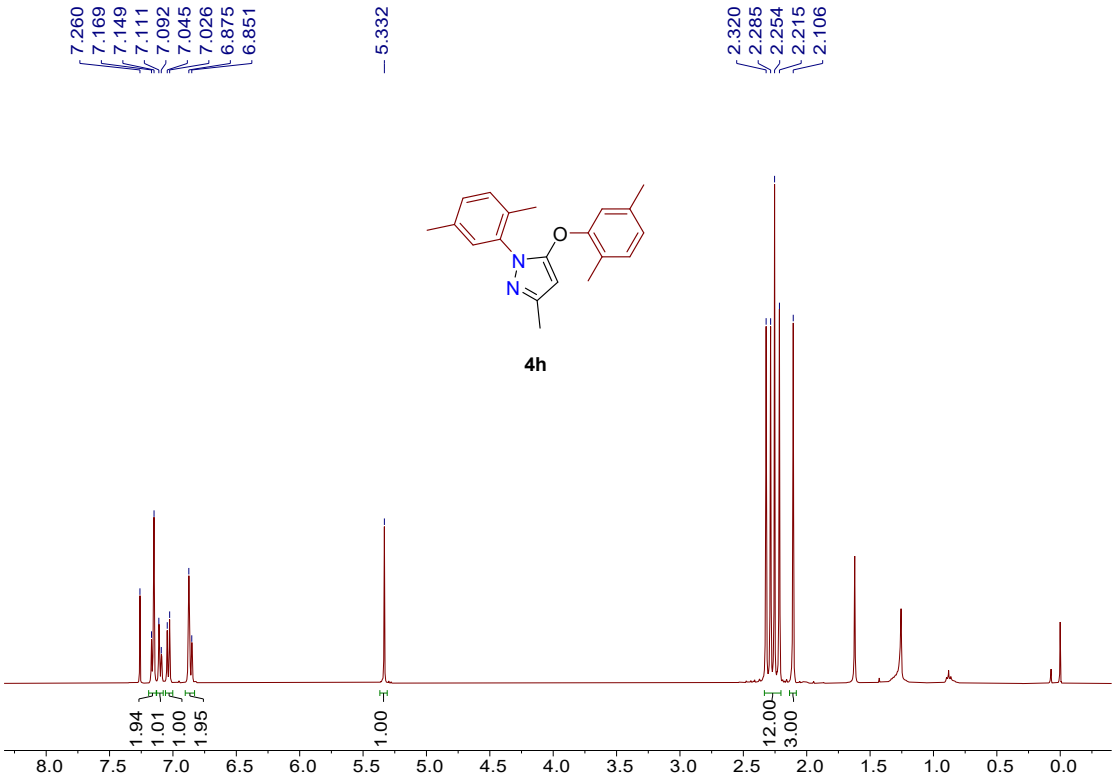
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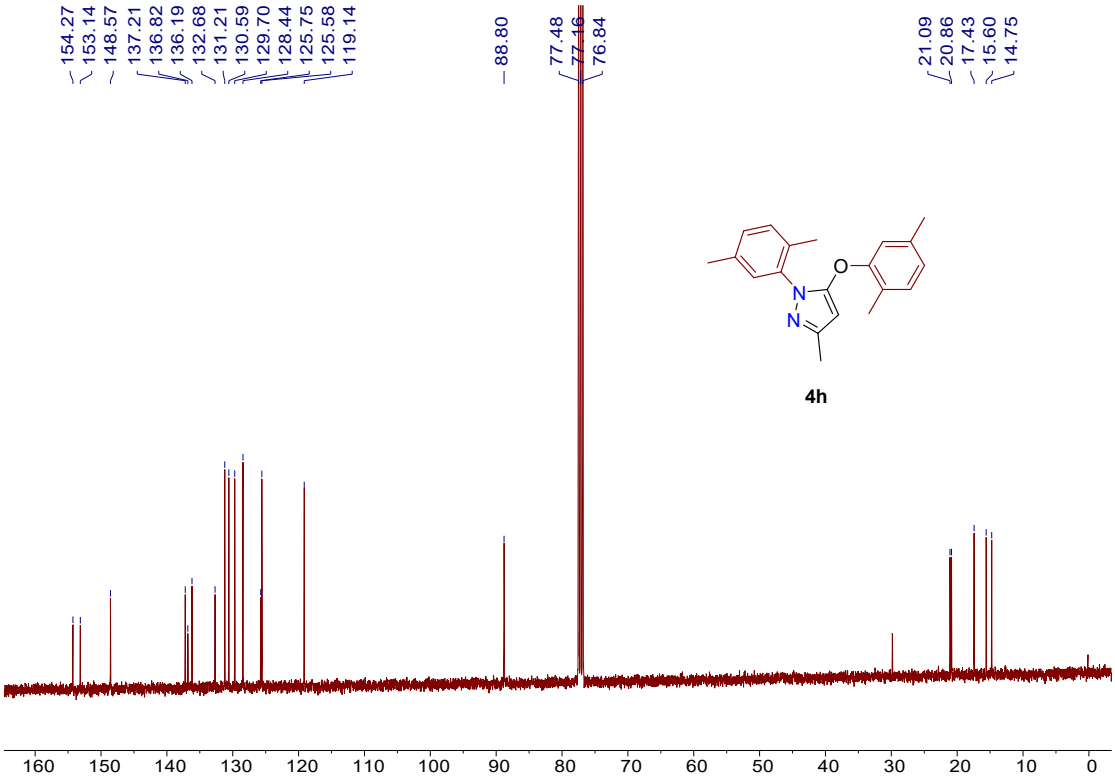
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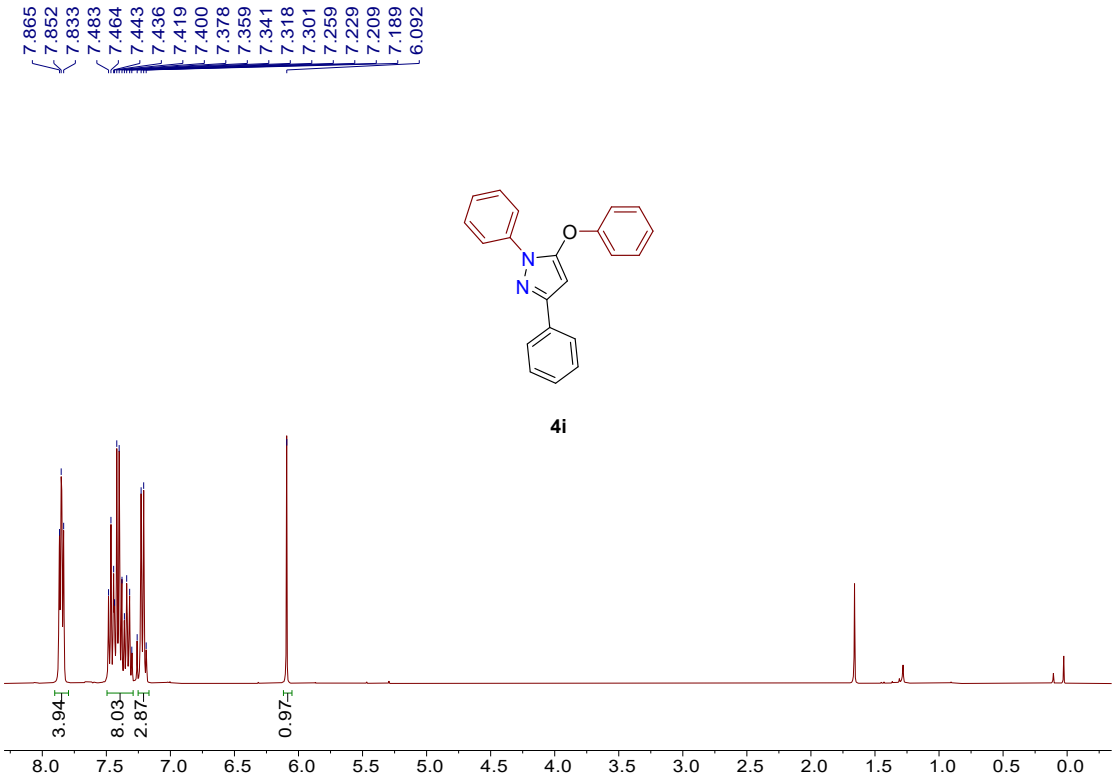
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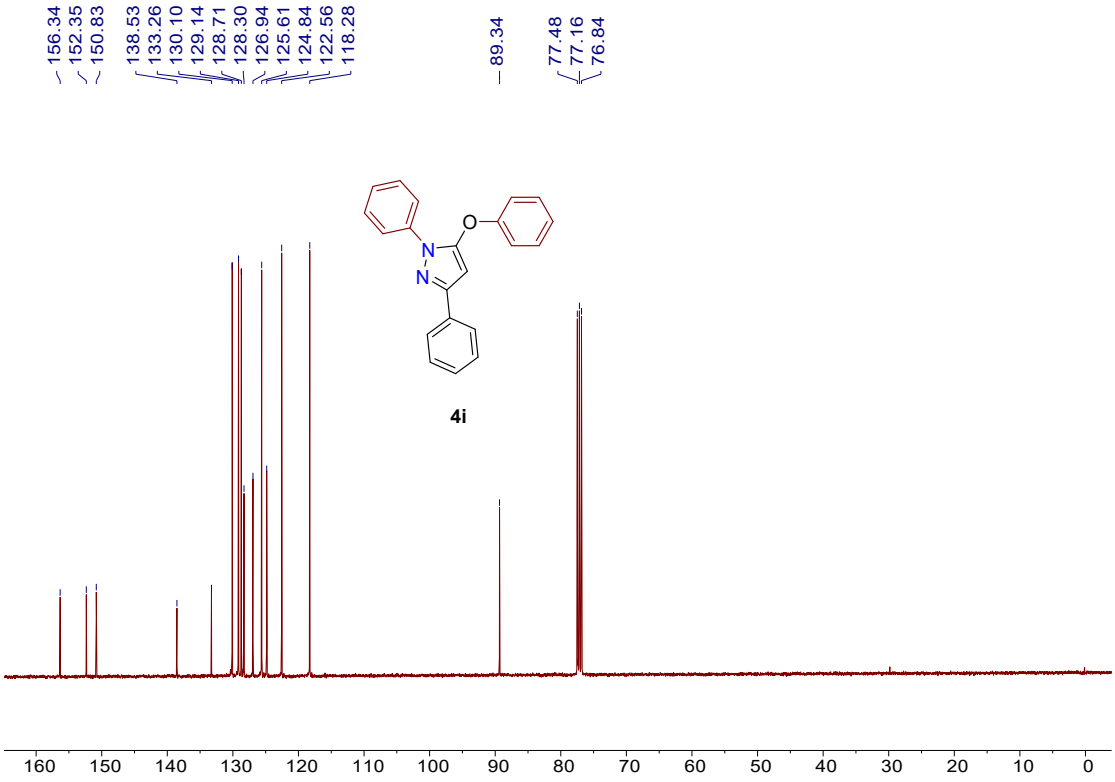
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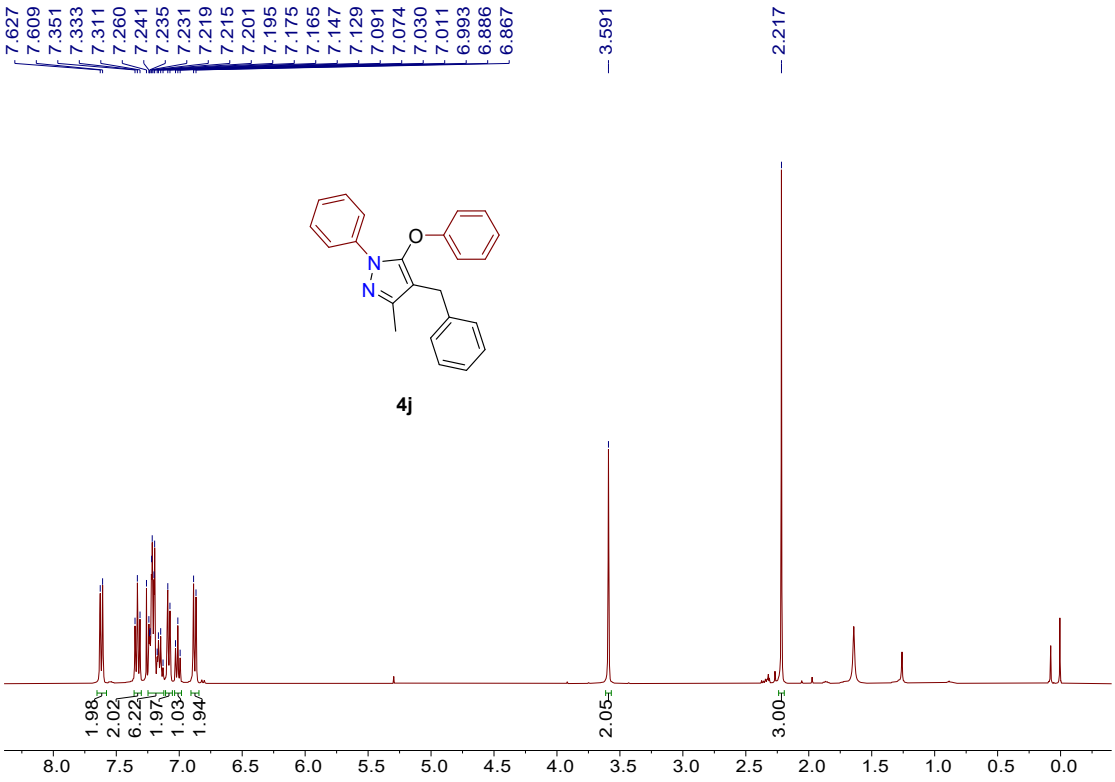
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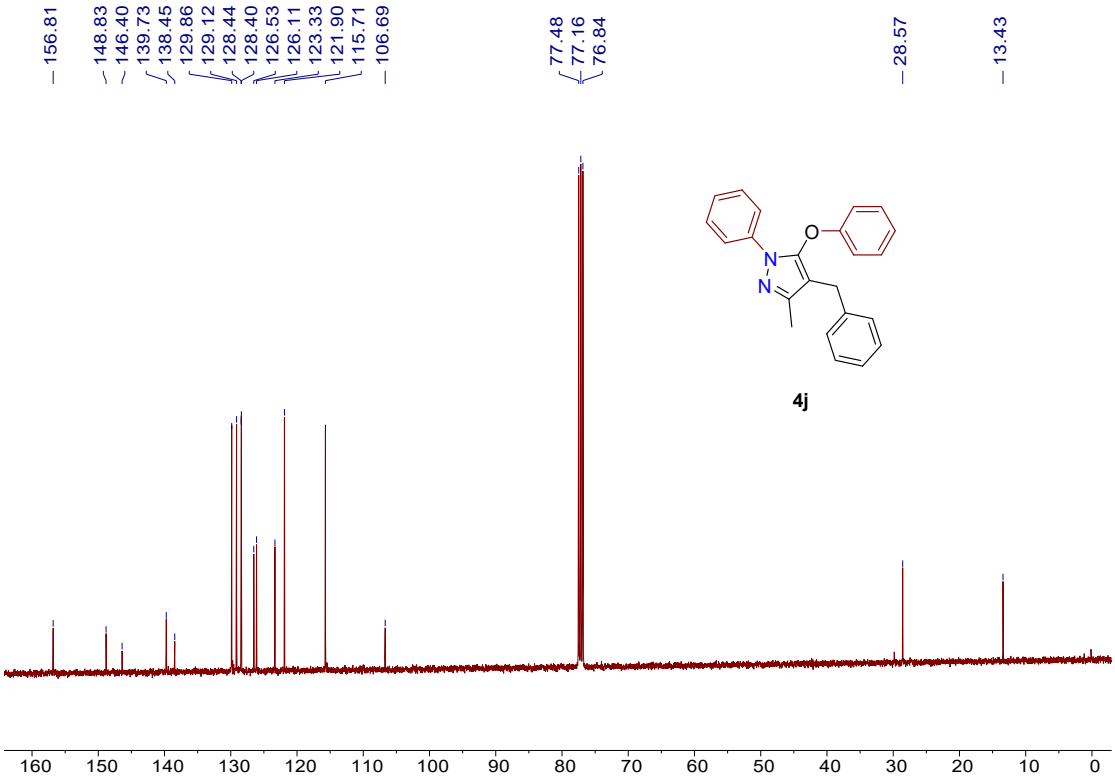
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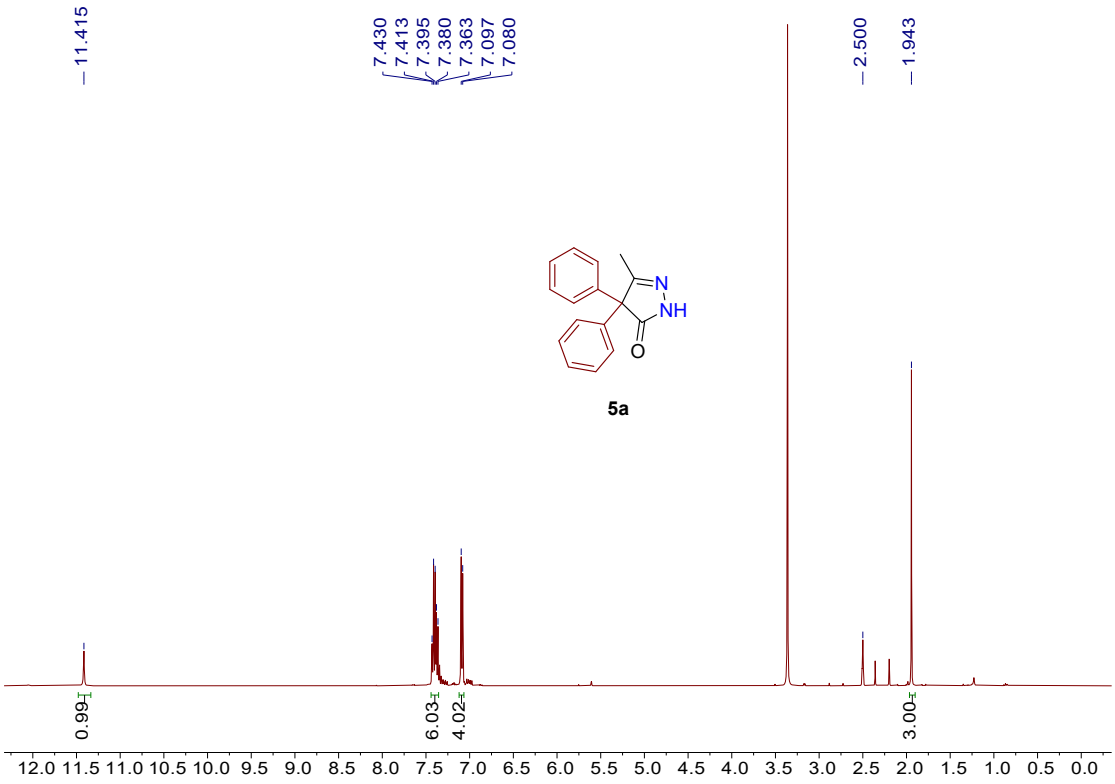
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4.02
3.00
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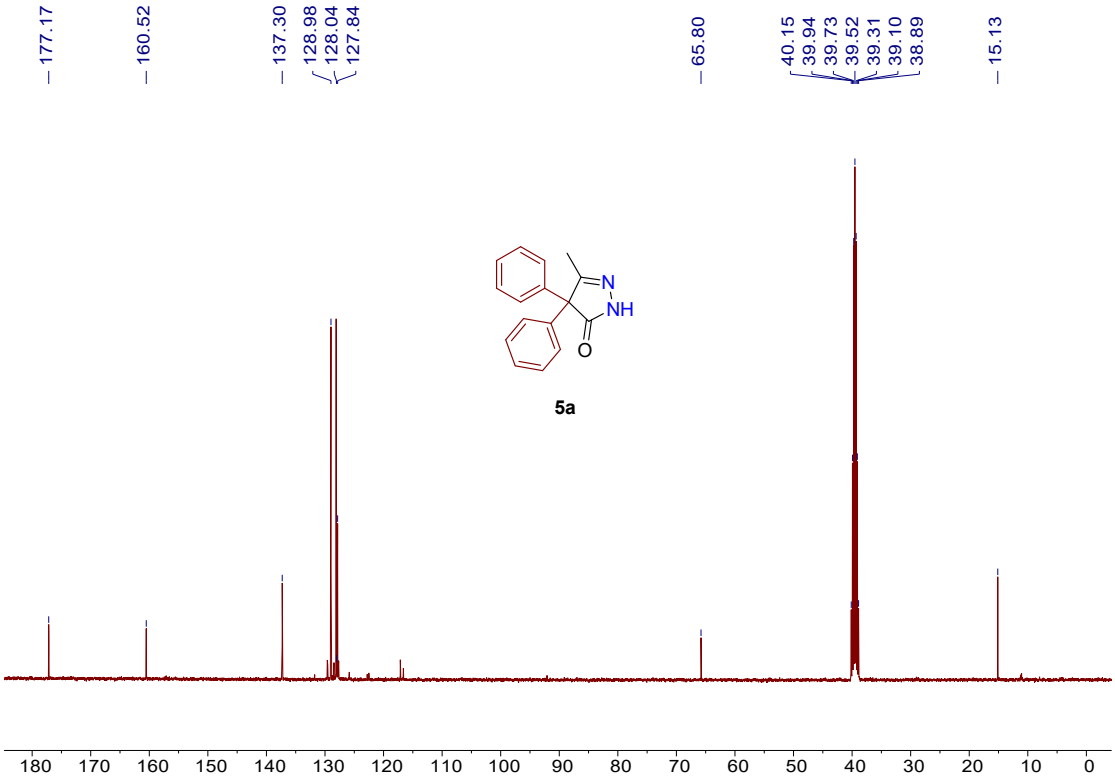
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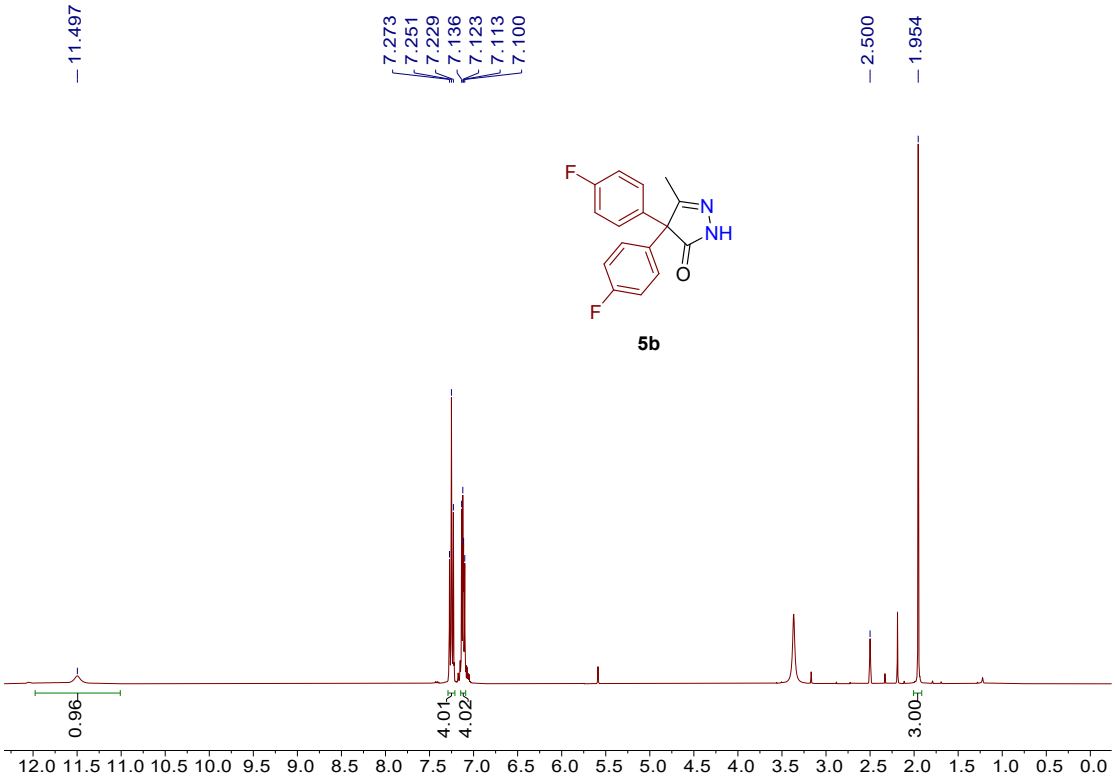
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4.02
3.00
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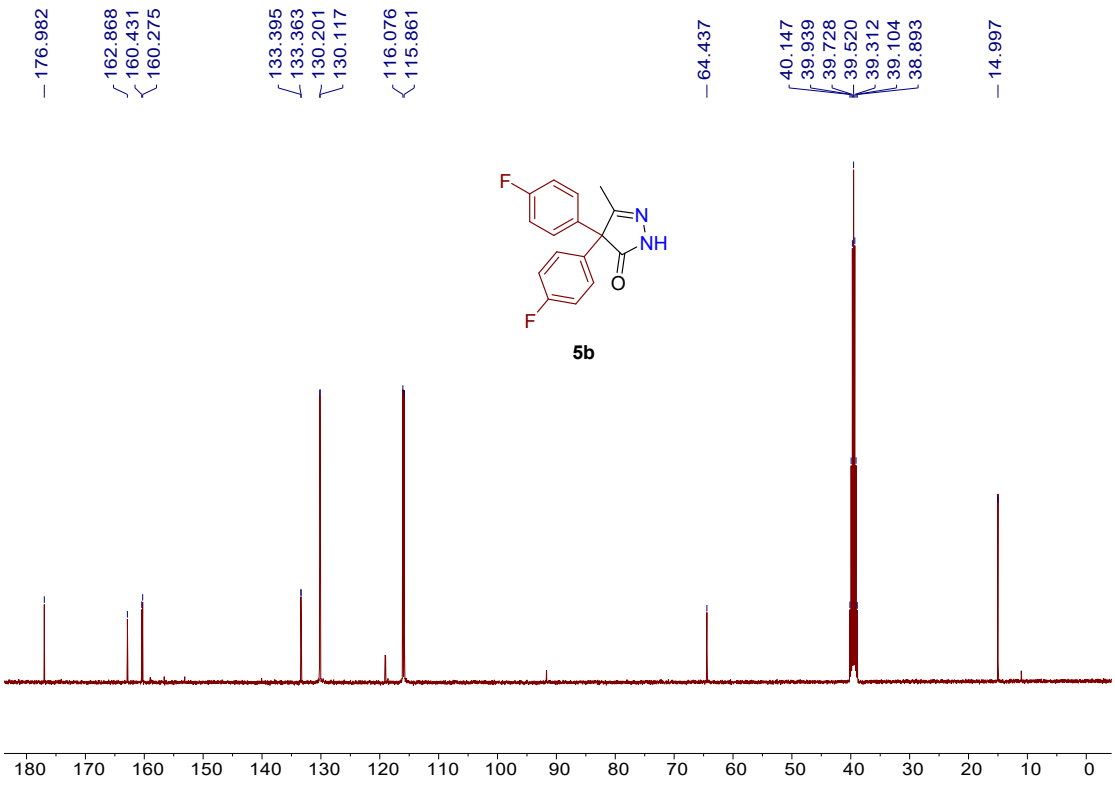
5b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39.728
39.520
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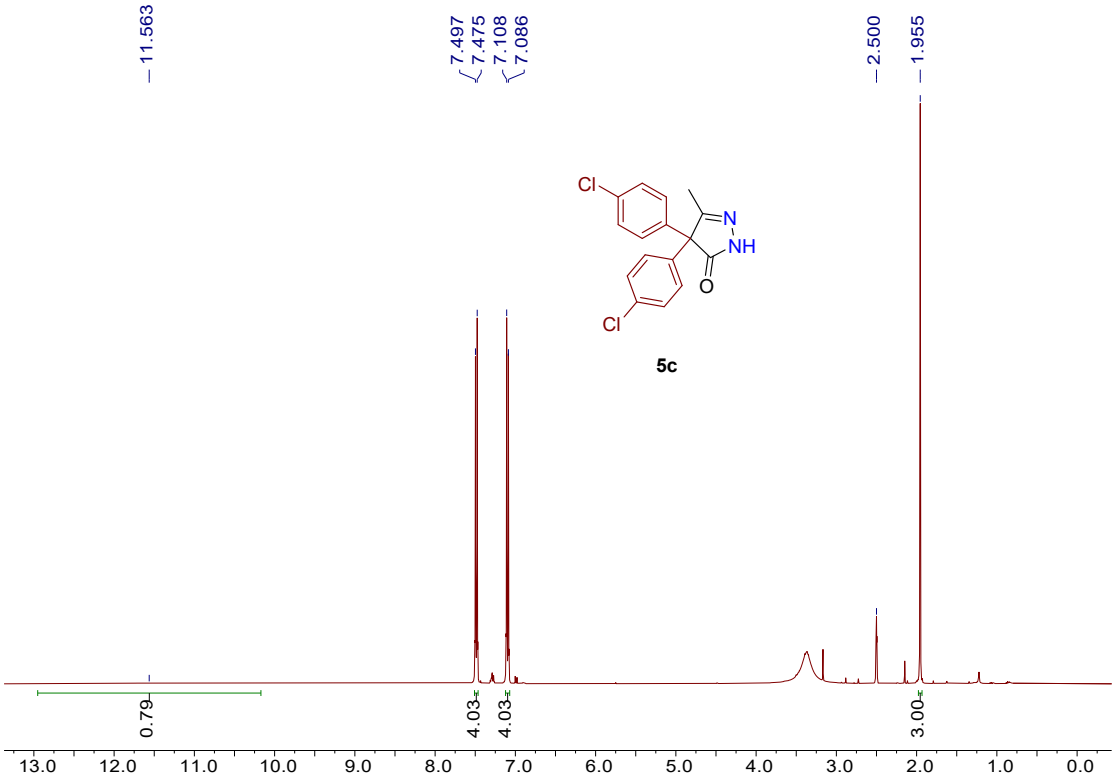
5b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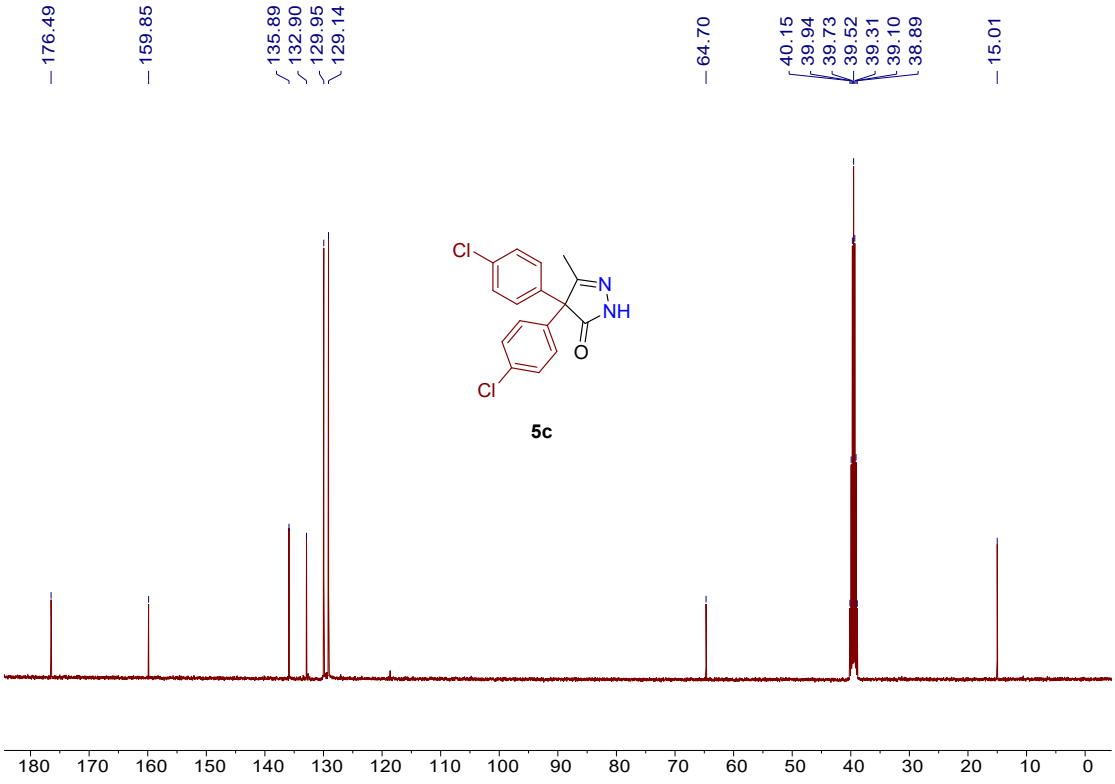
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O
Cl
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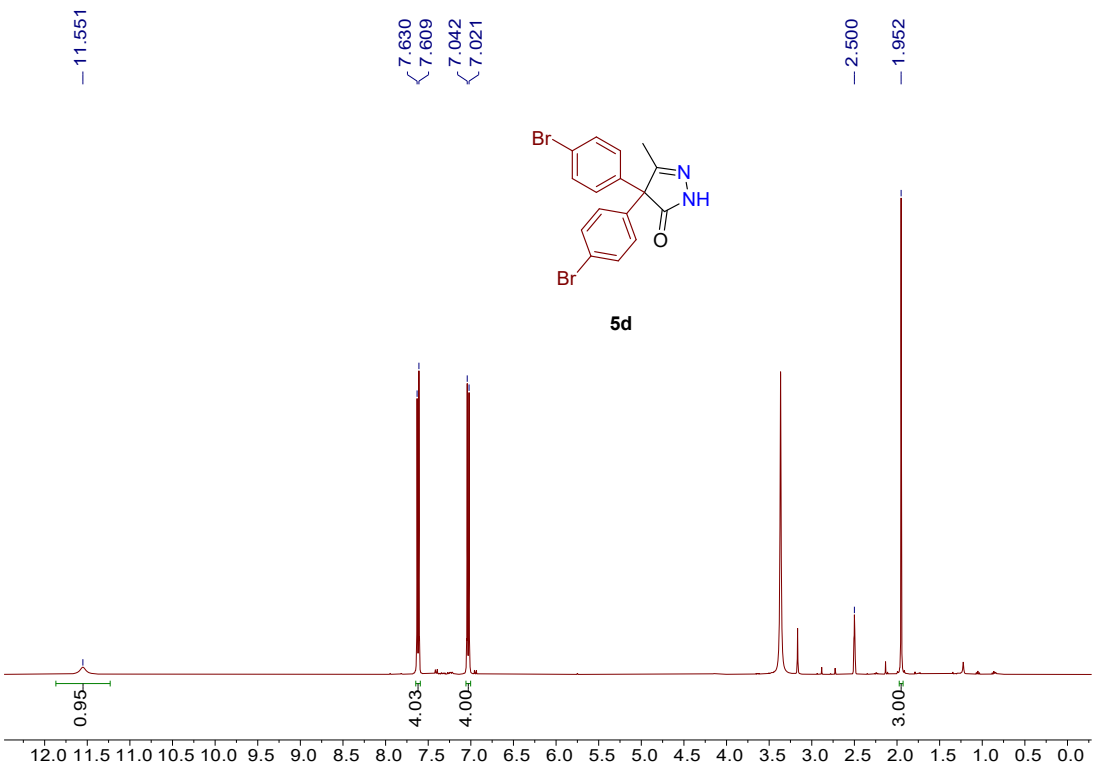
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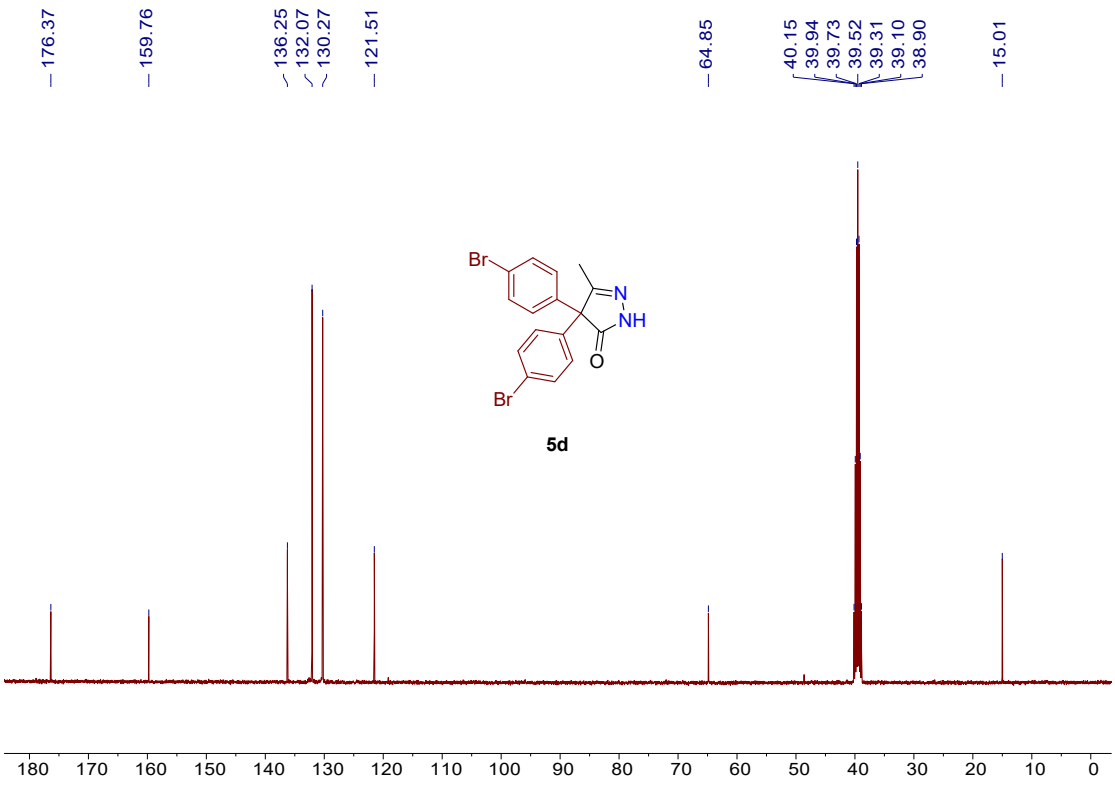
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15.01
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NH
O
Br
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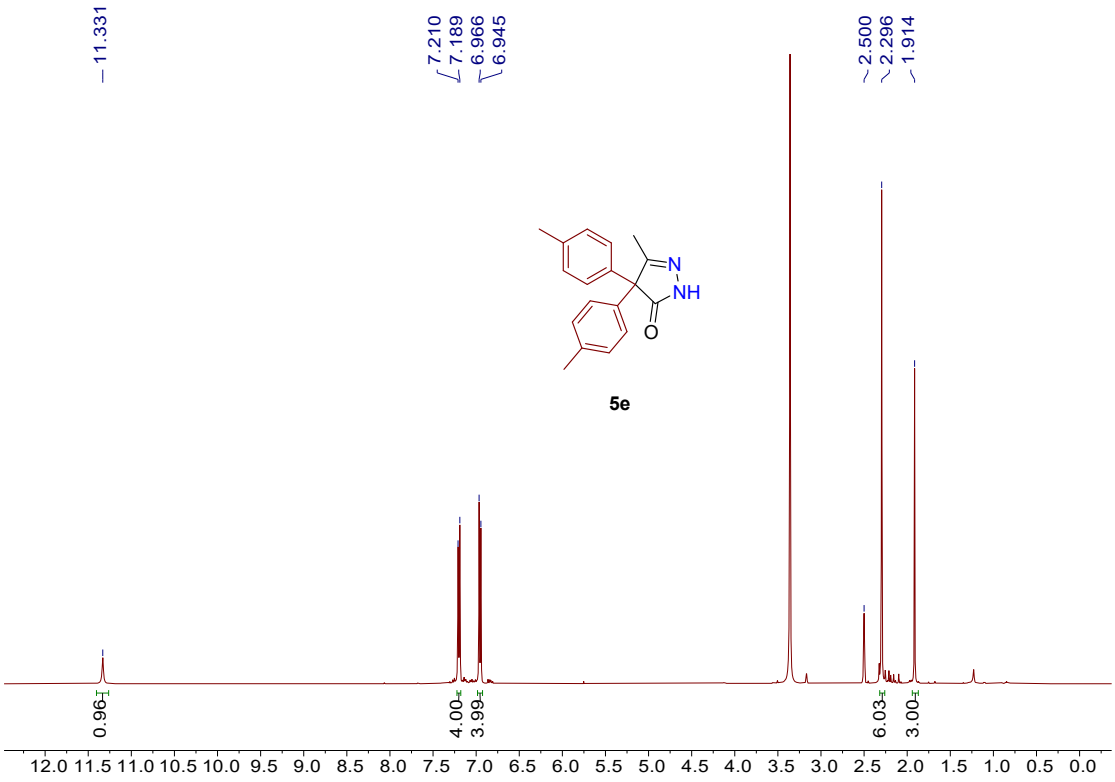
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3.00
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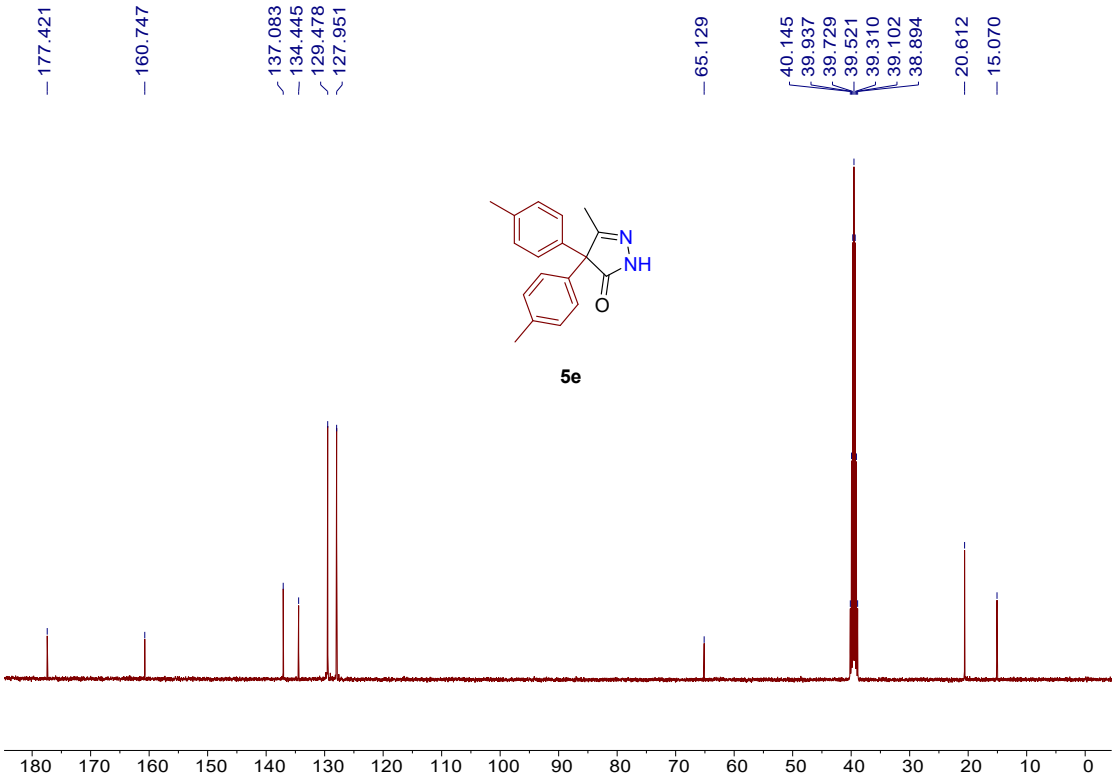
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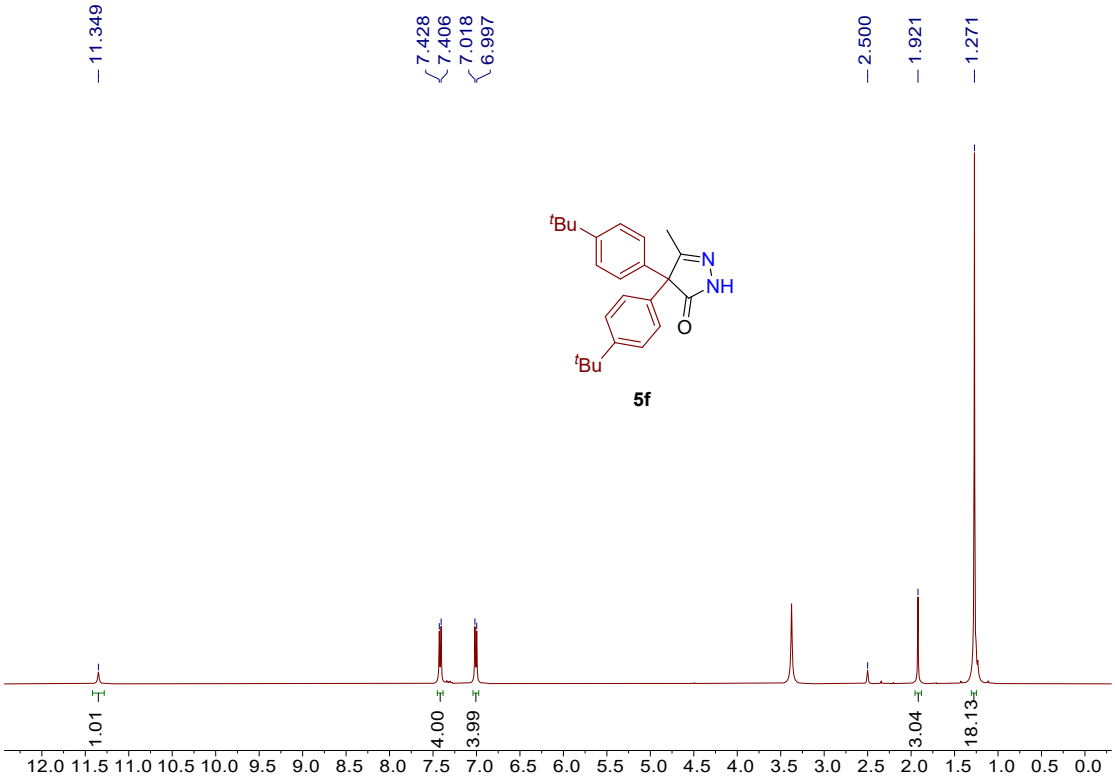
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4.00
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3.04
18.13
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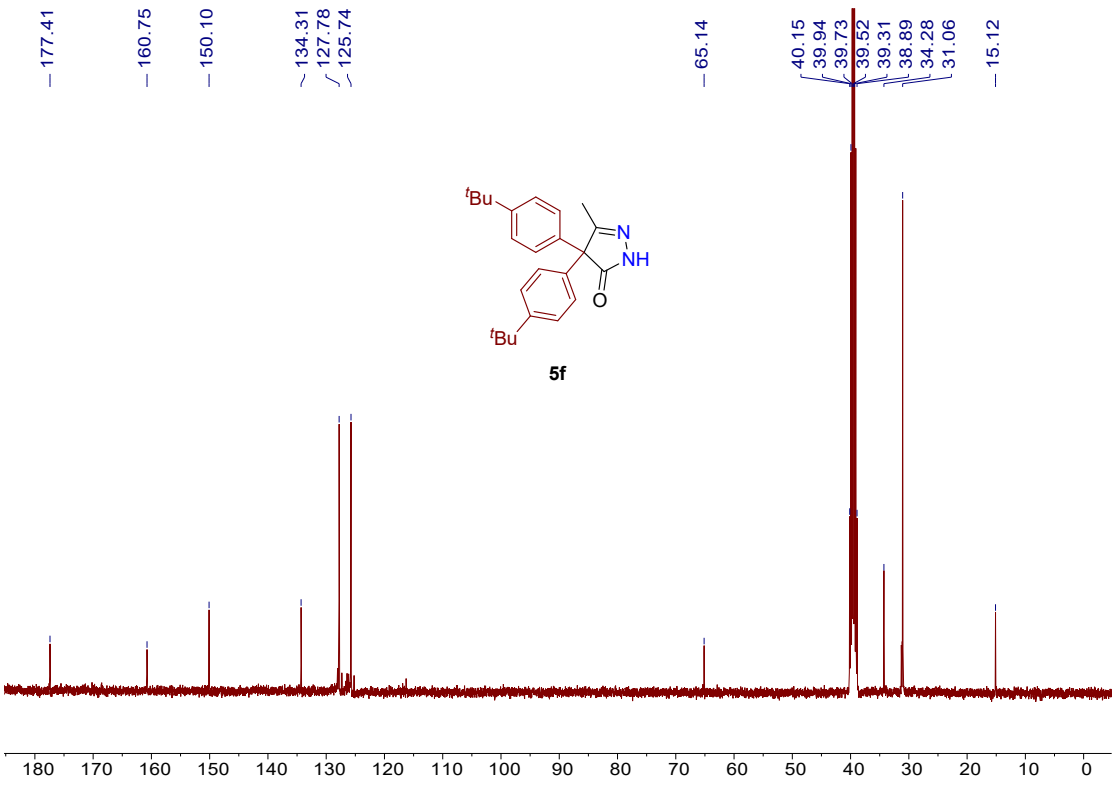
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tBu
5f
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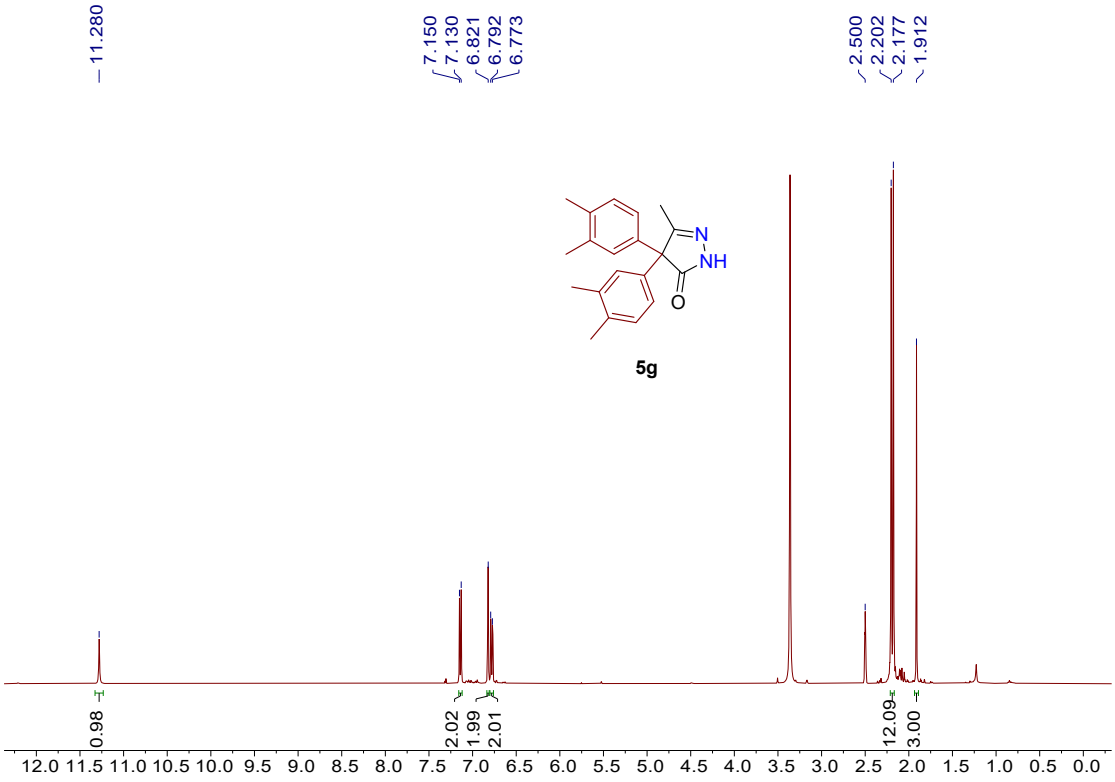
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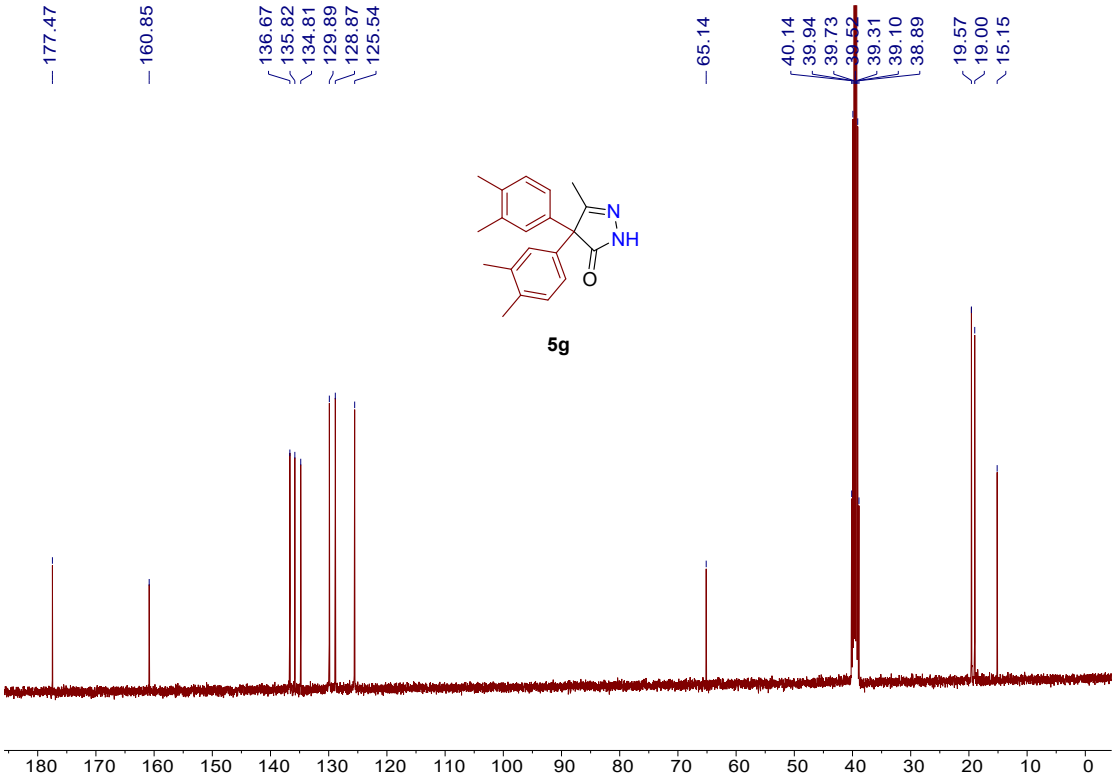
1.99
2.01
12.09
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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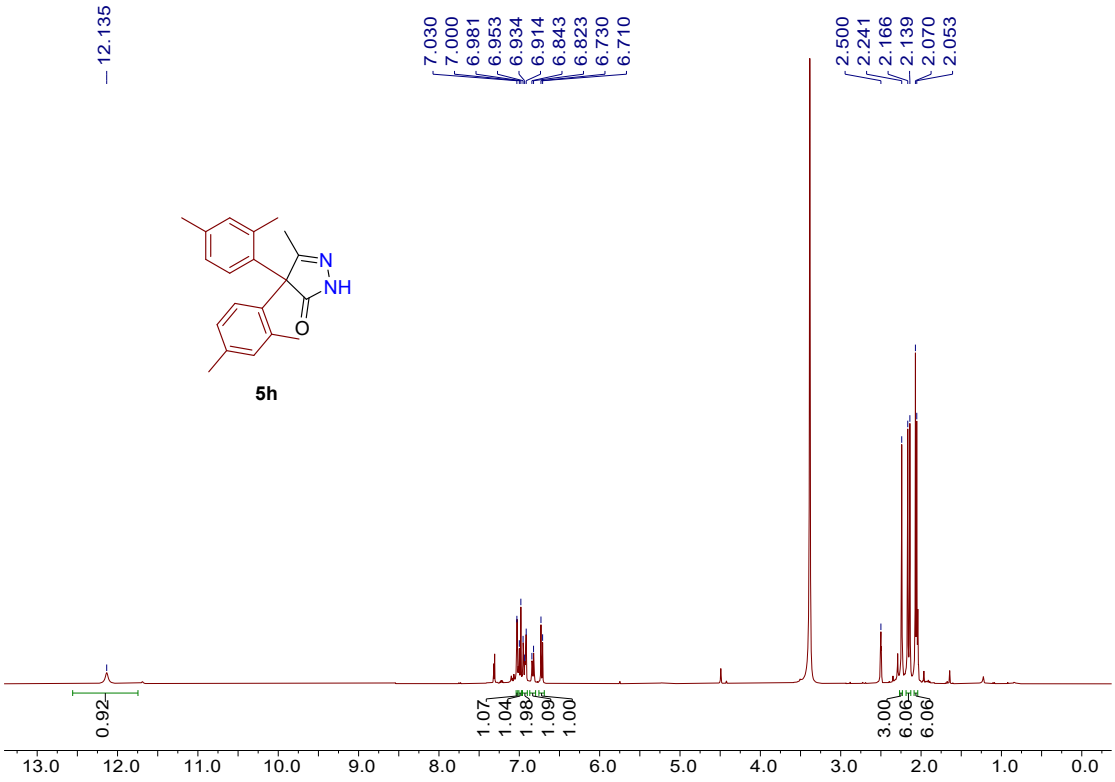
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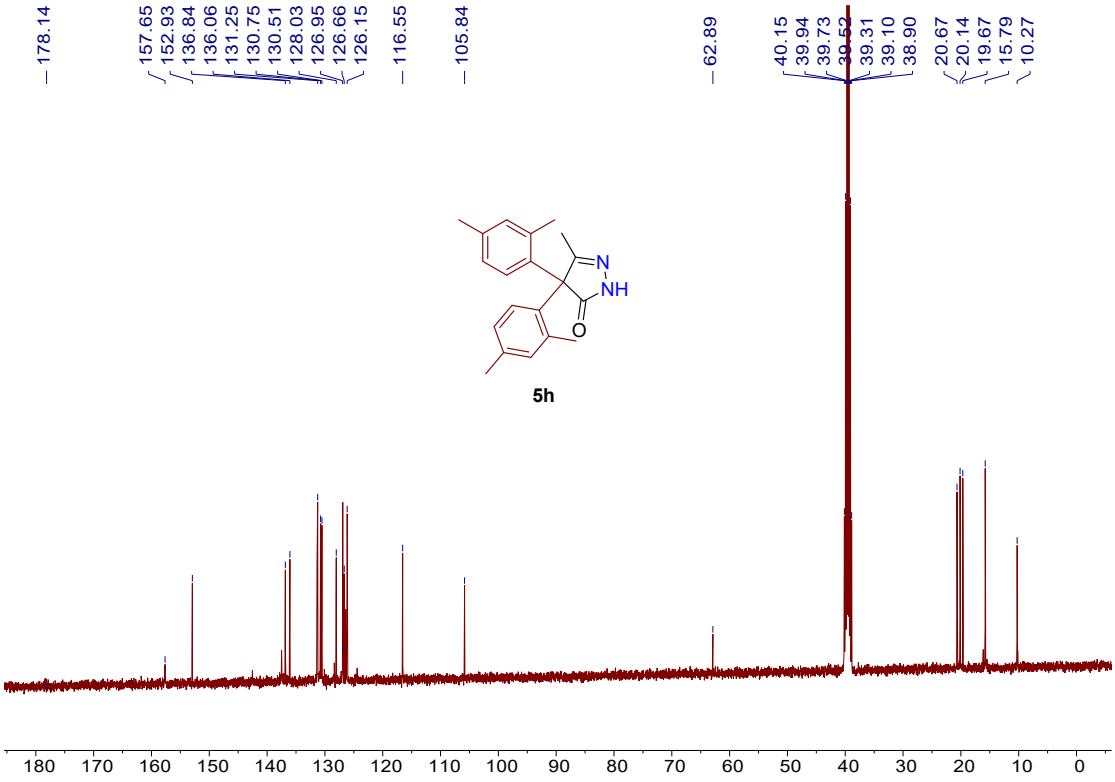
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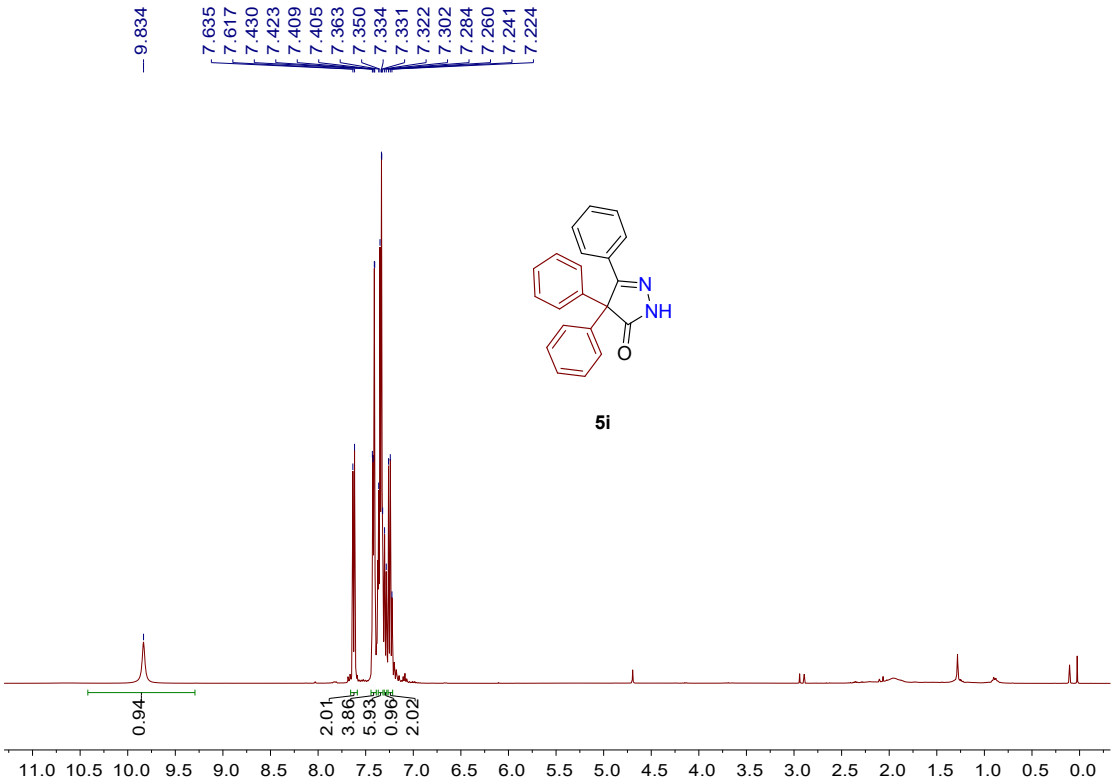
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3.86
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2.02
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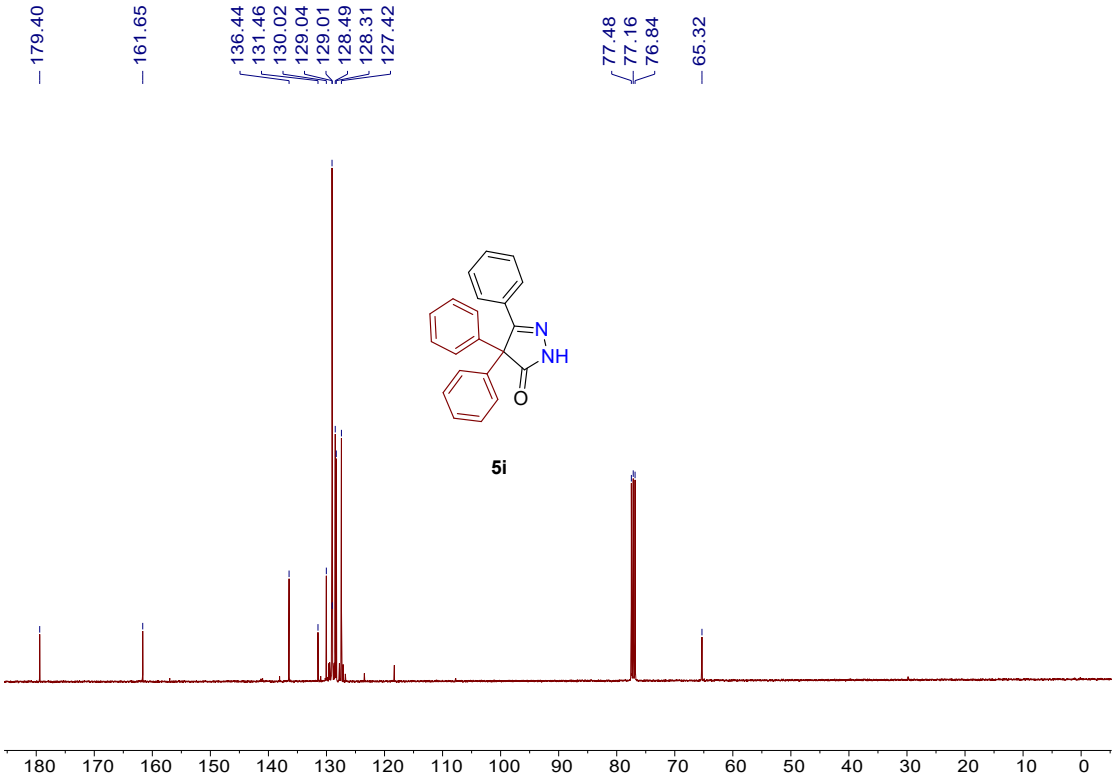
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NH
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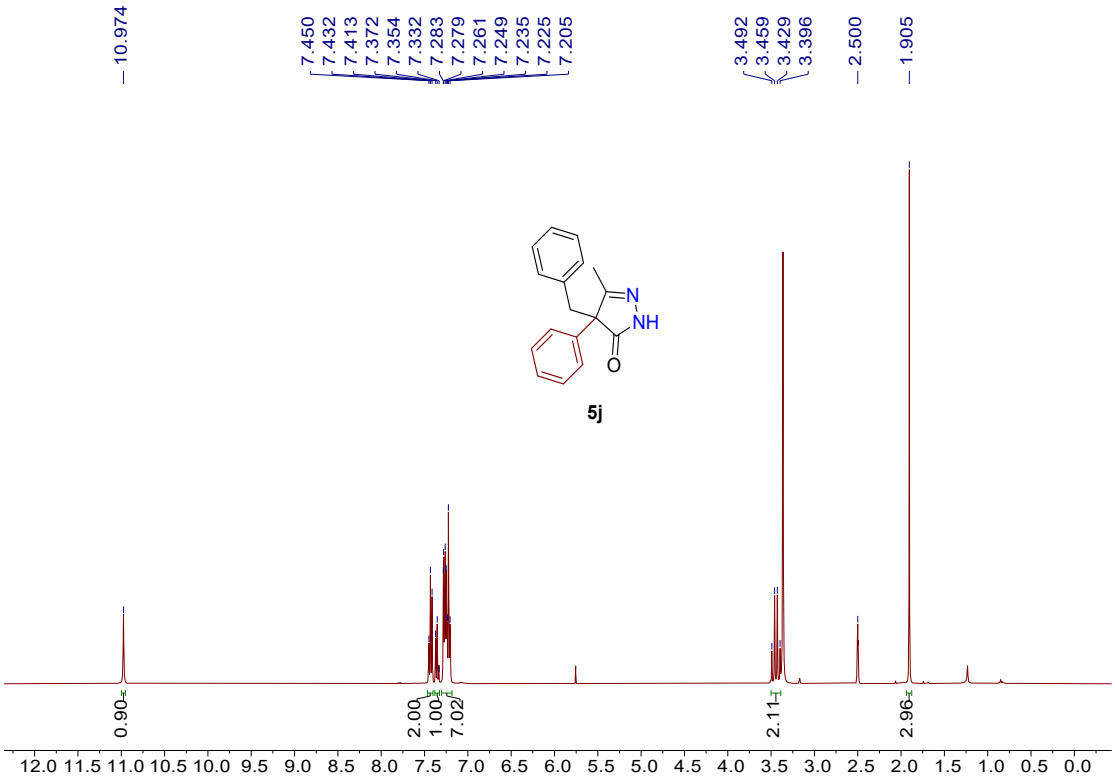
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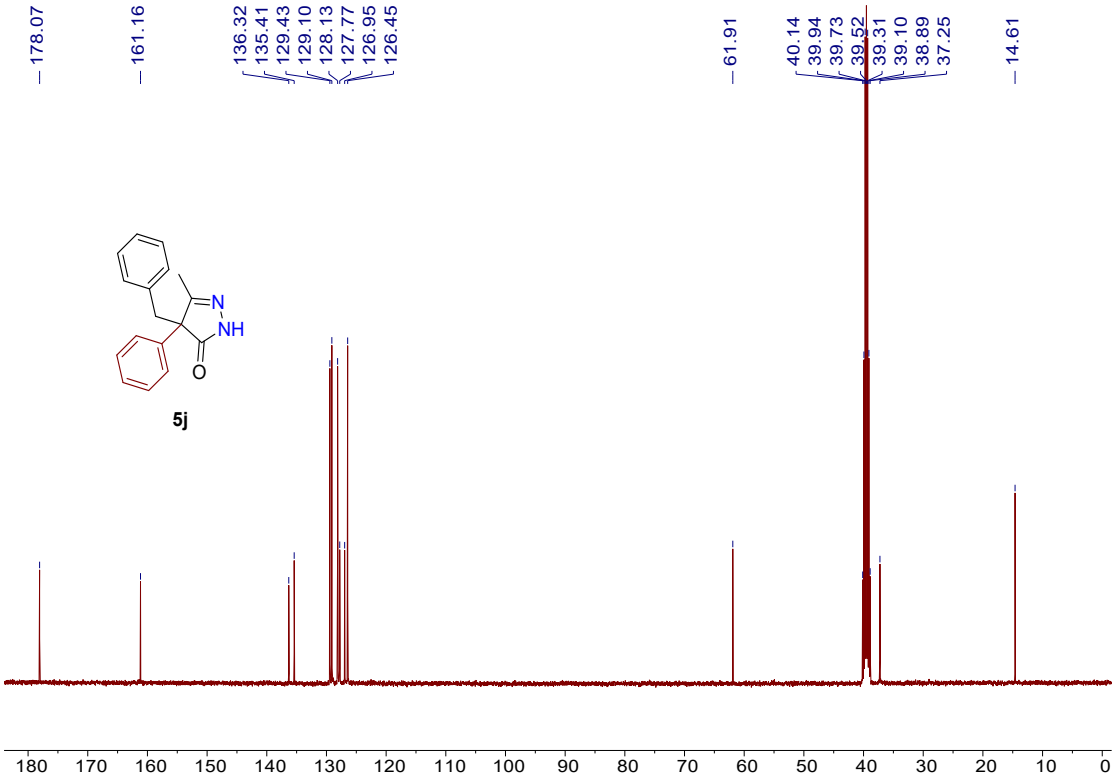
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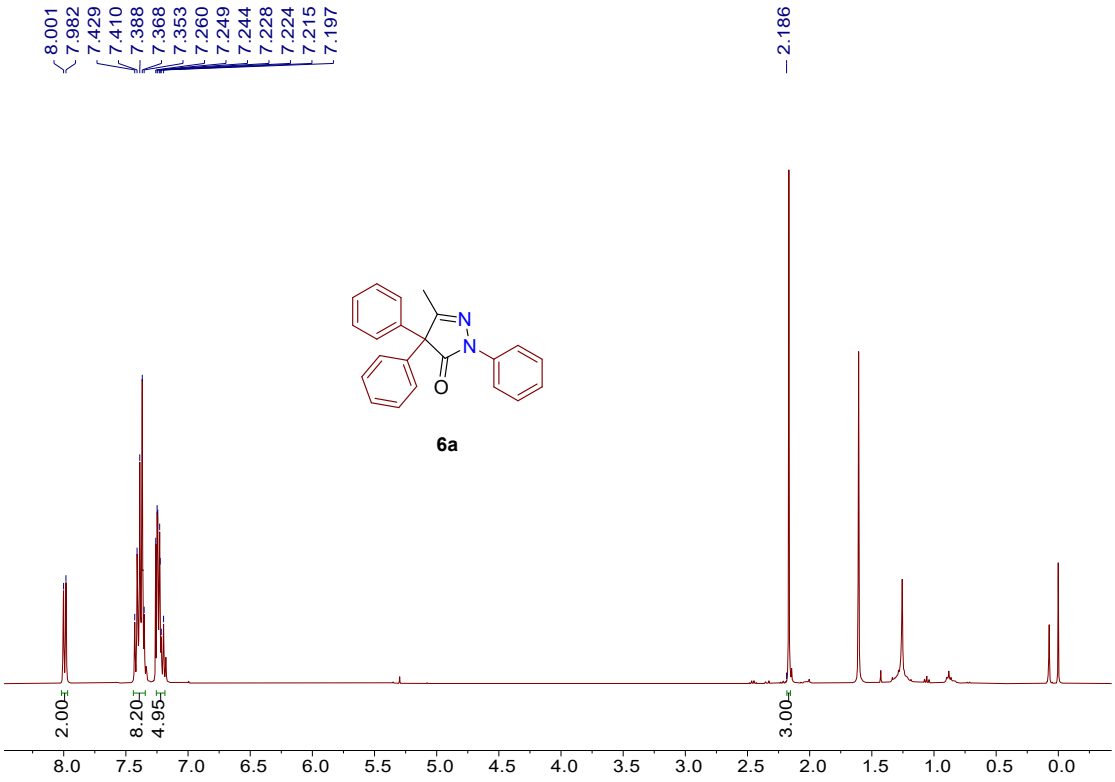
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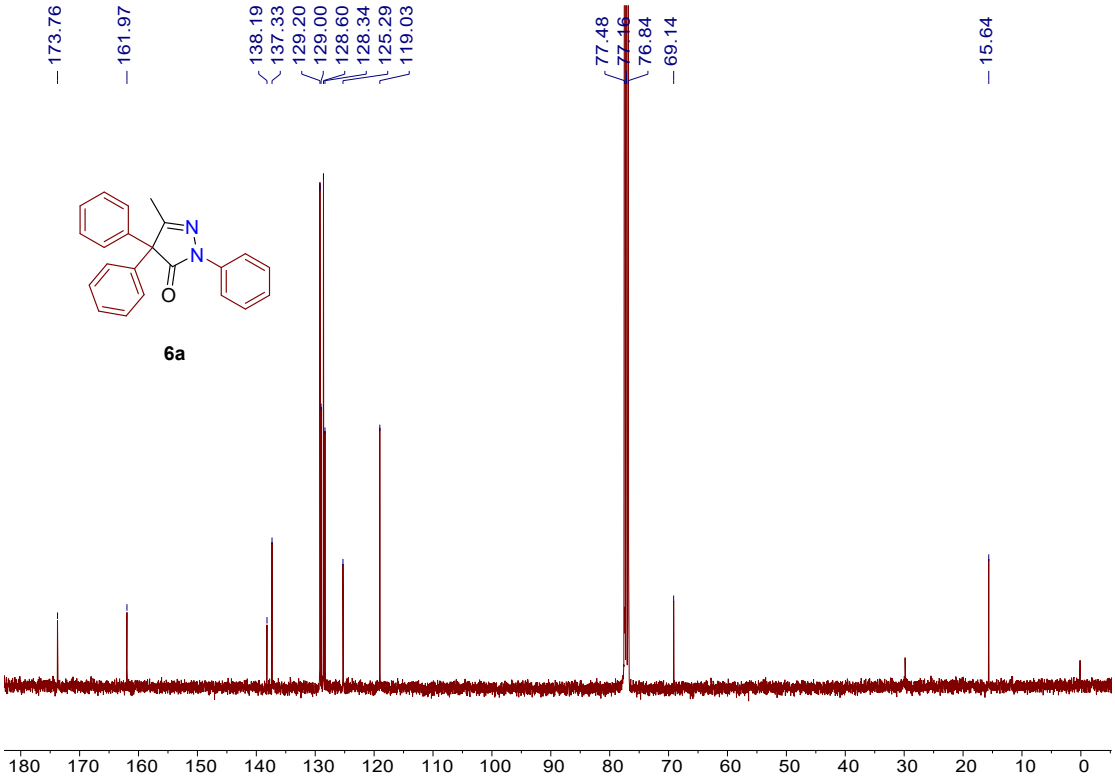
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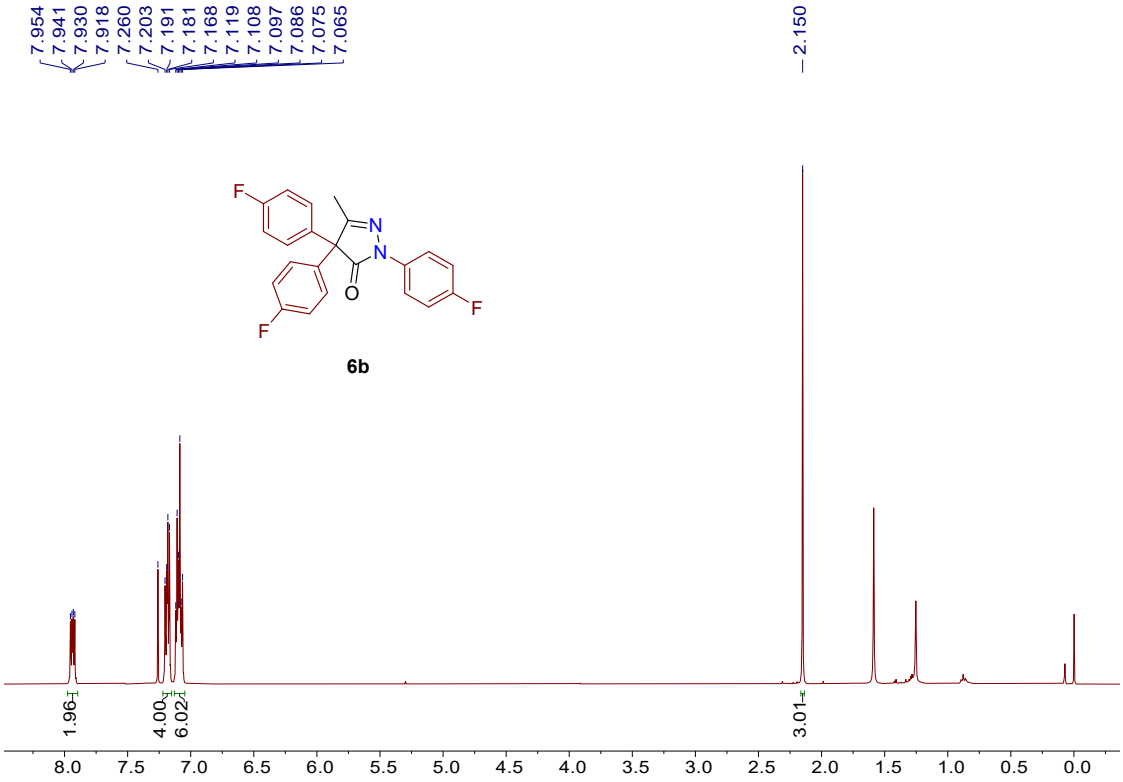
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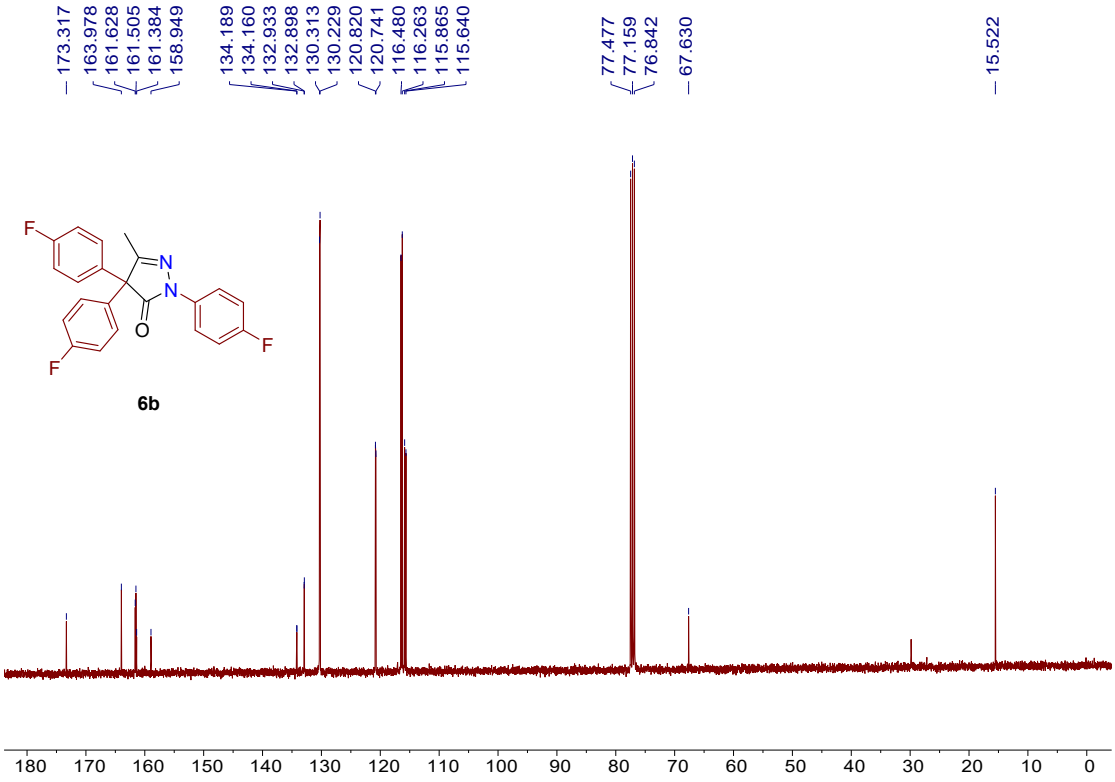
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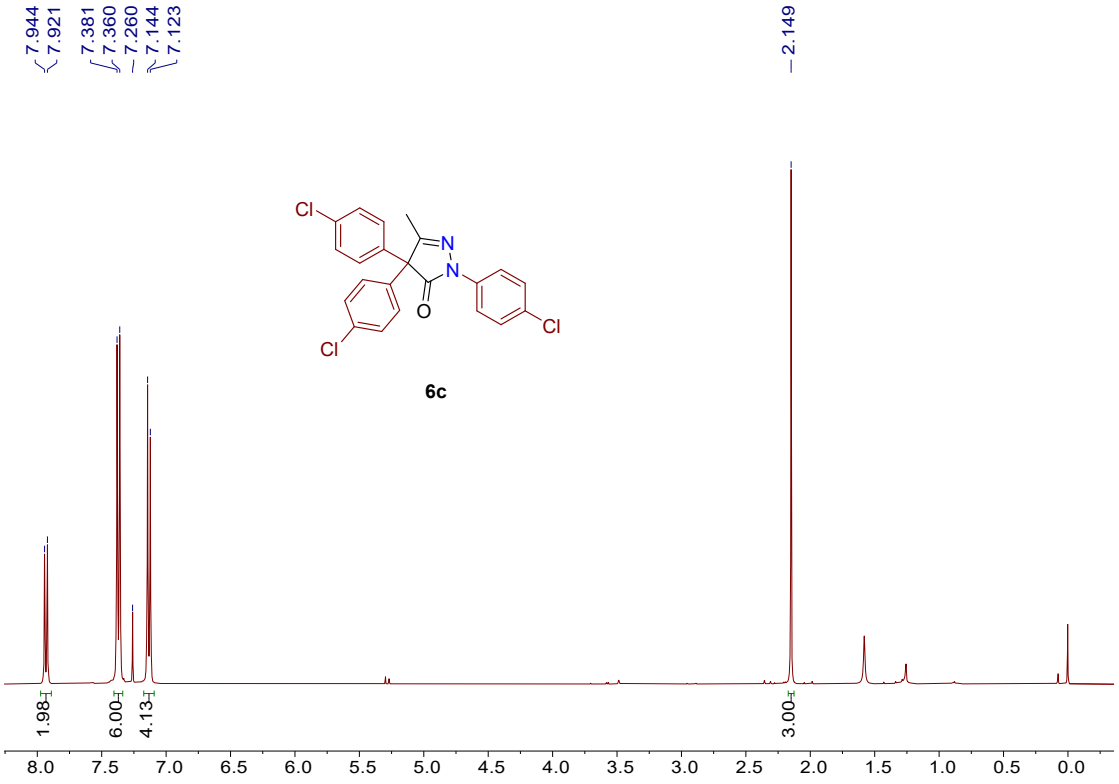
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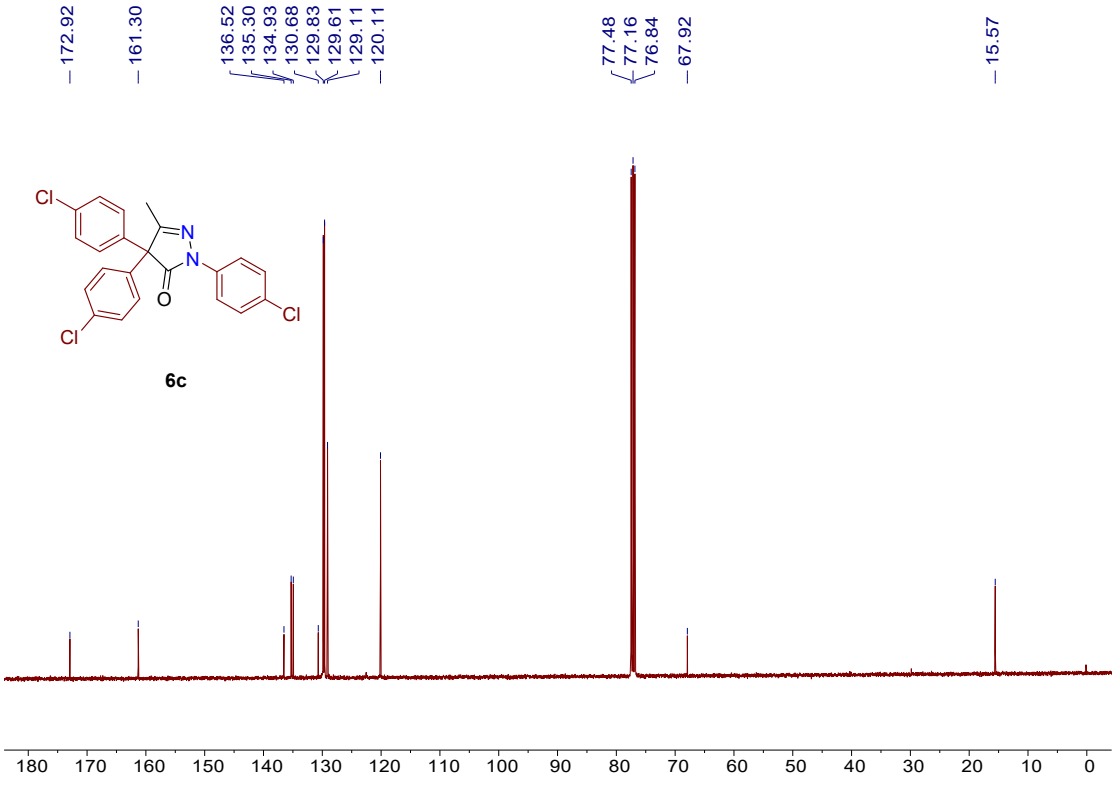
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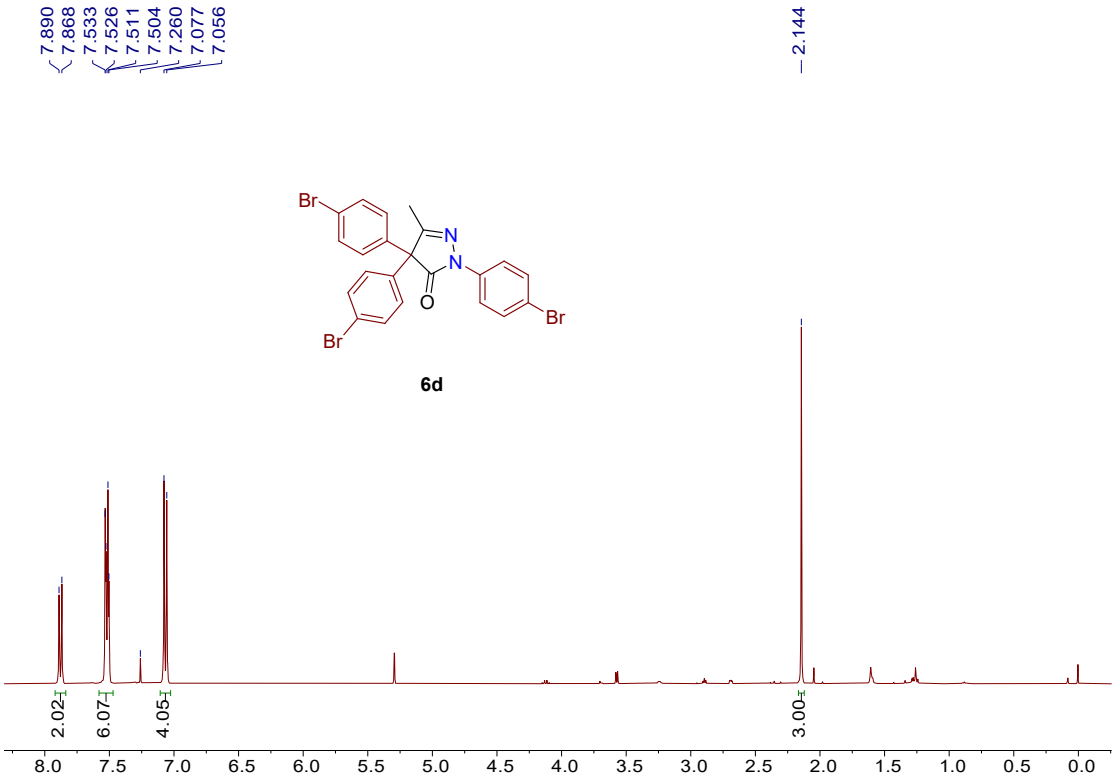
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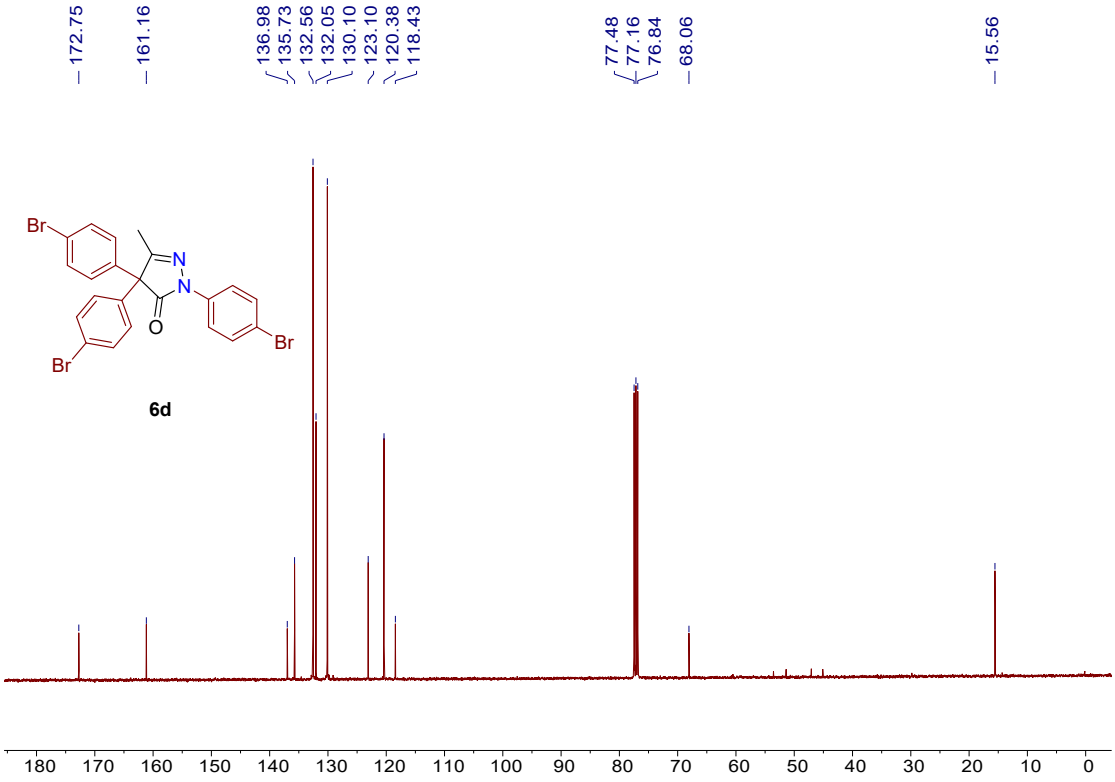
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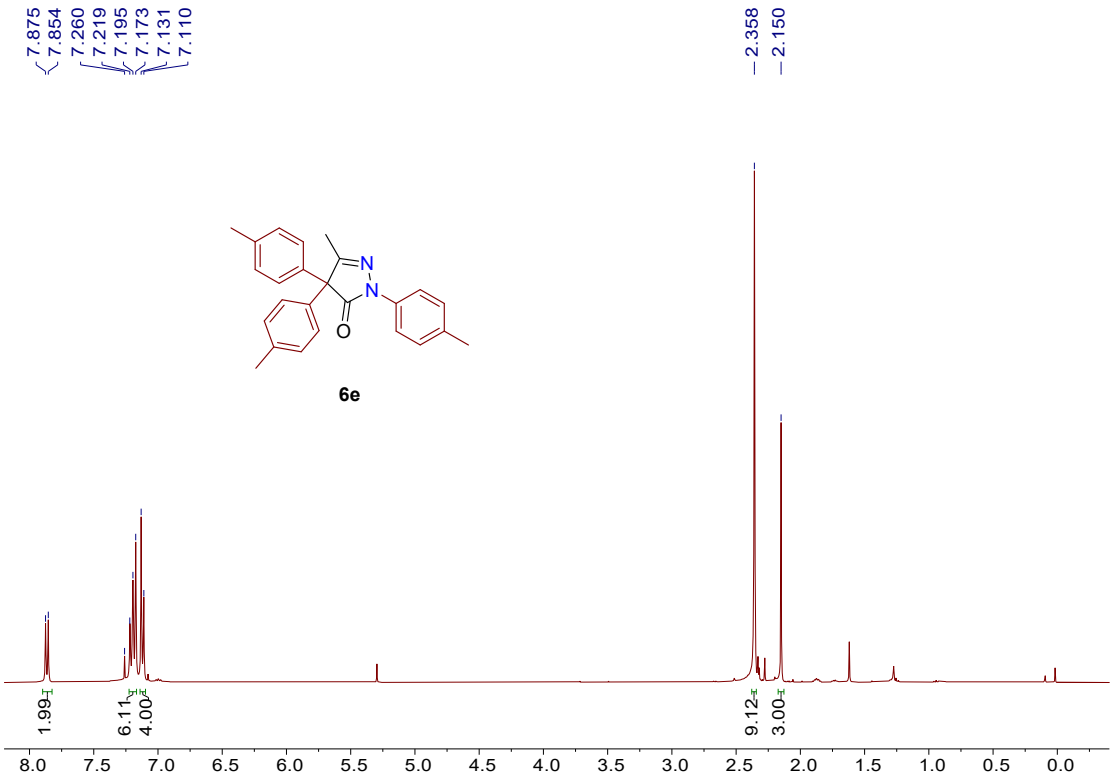
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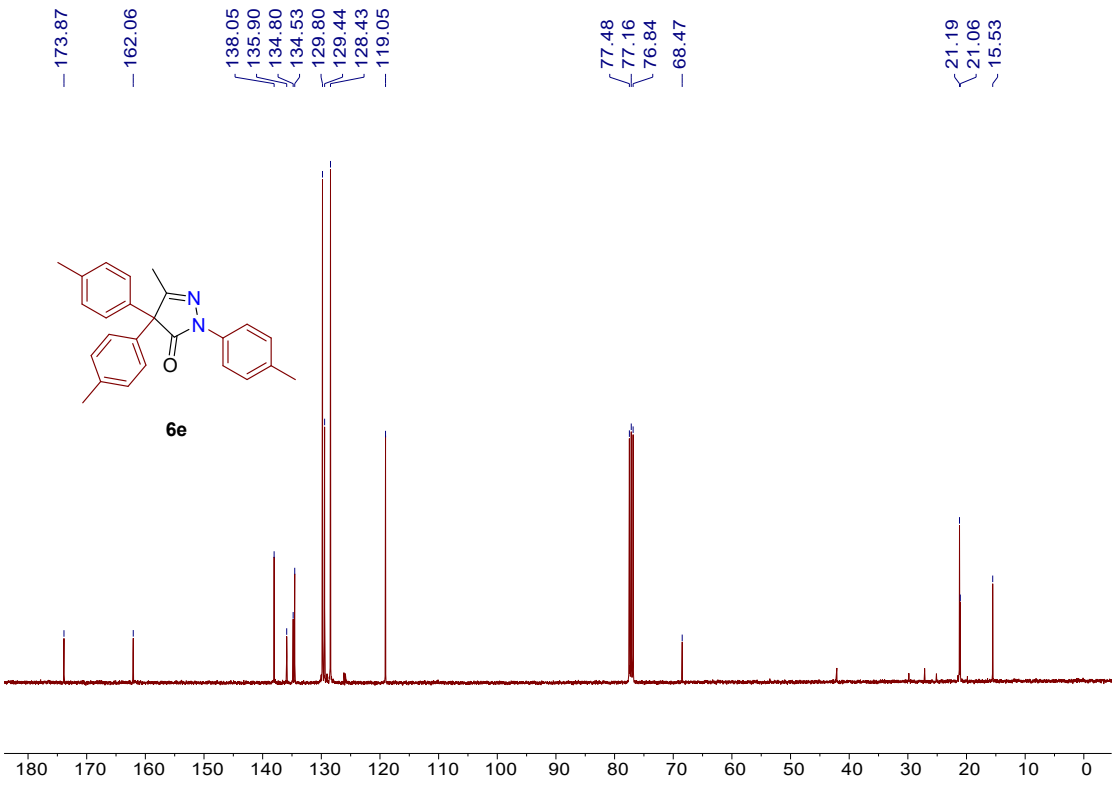
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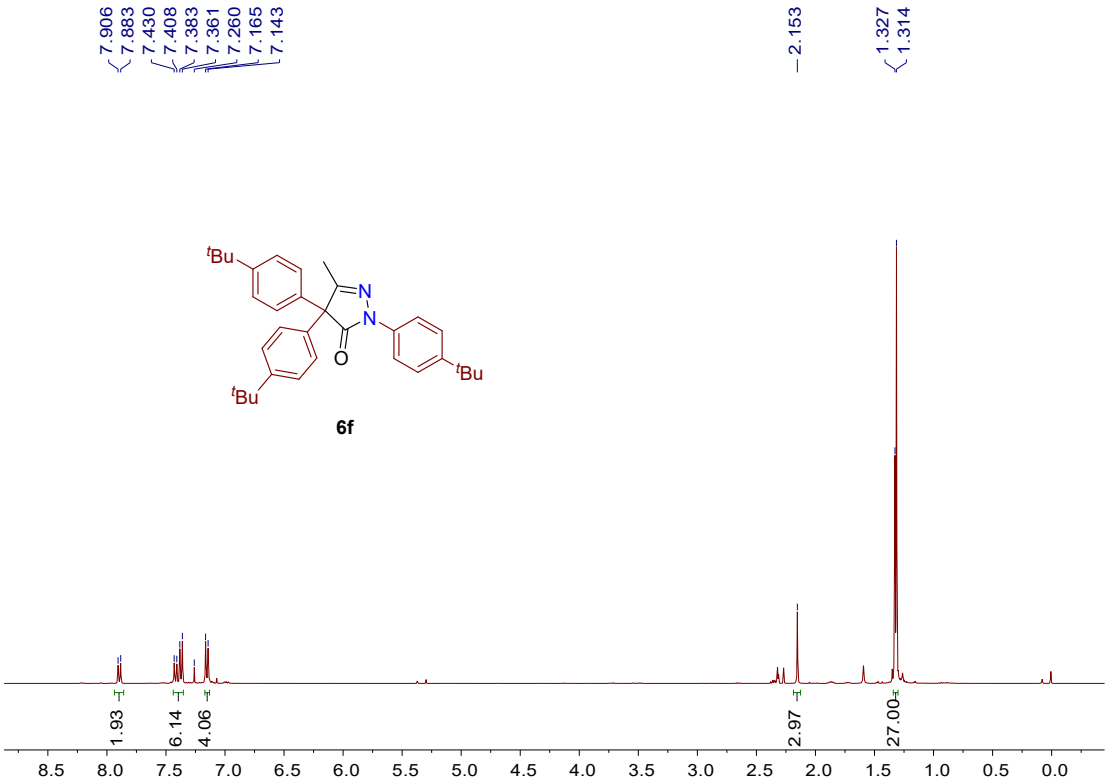
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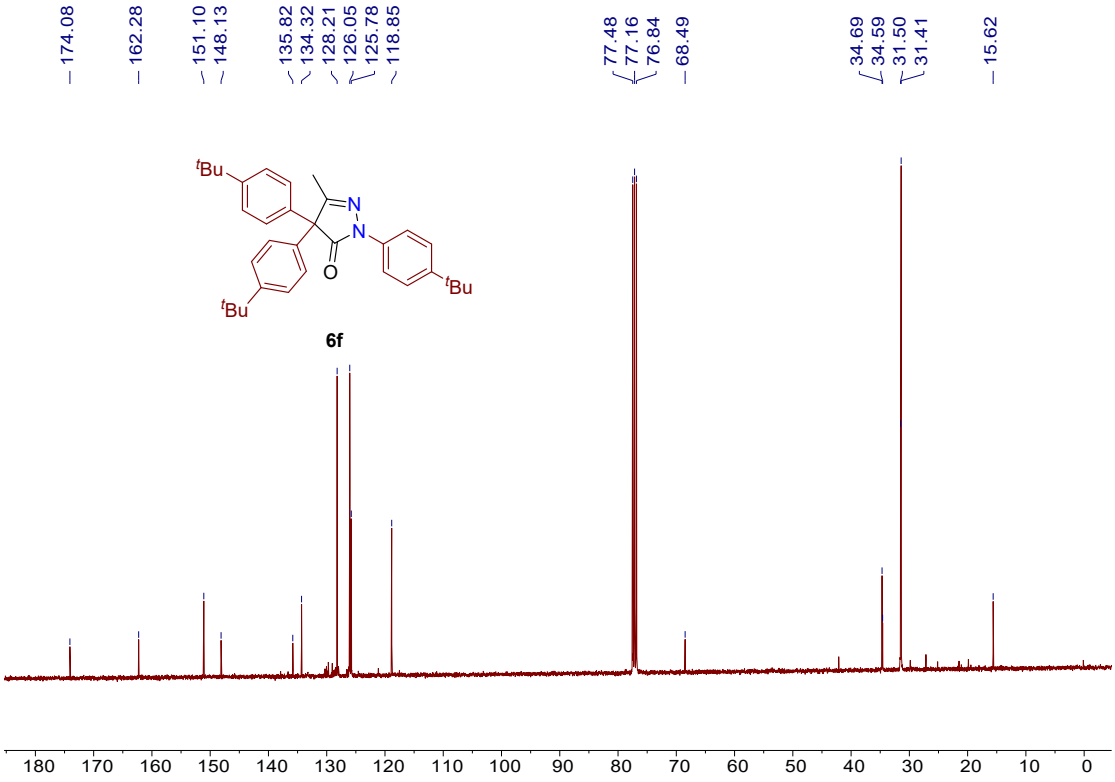
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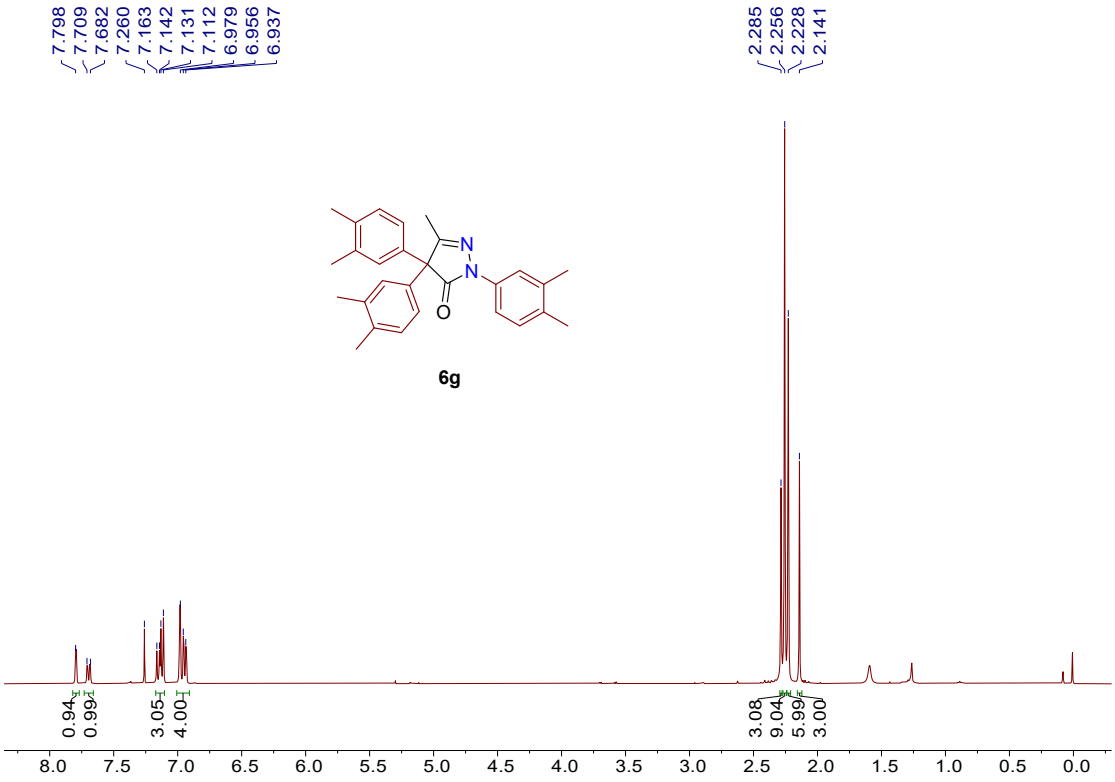
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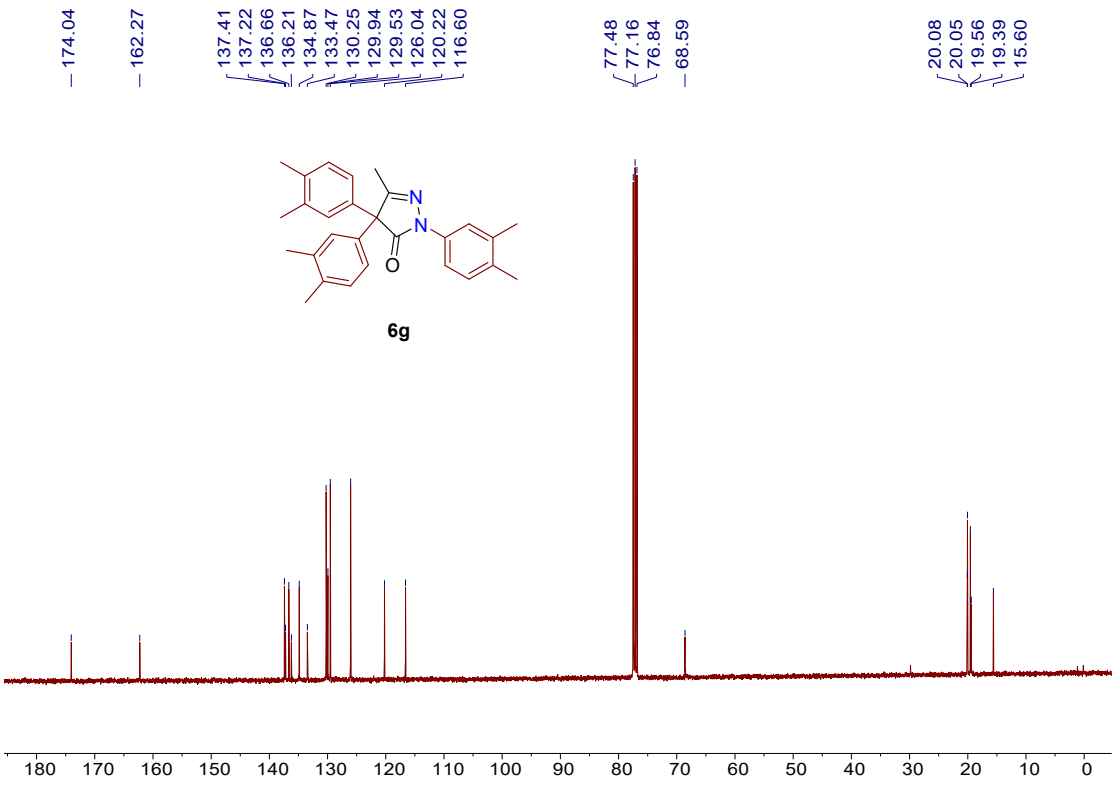
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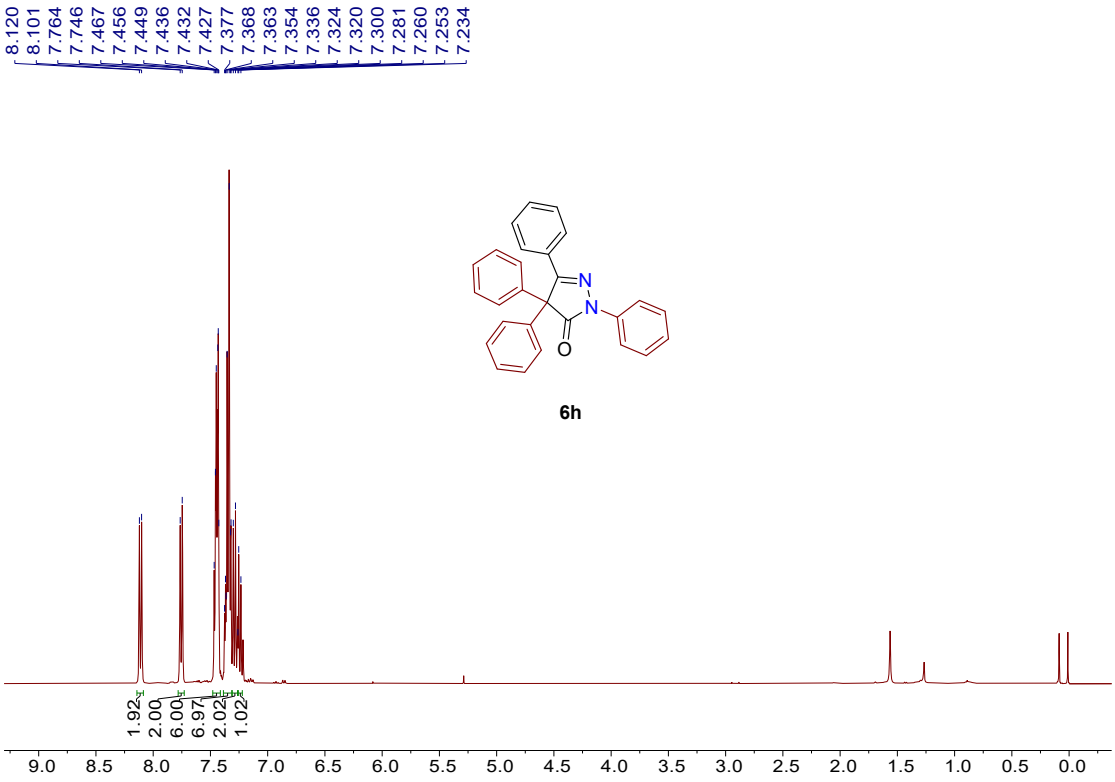
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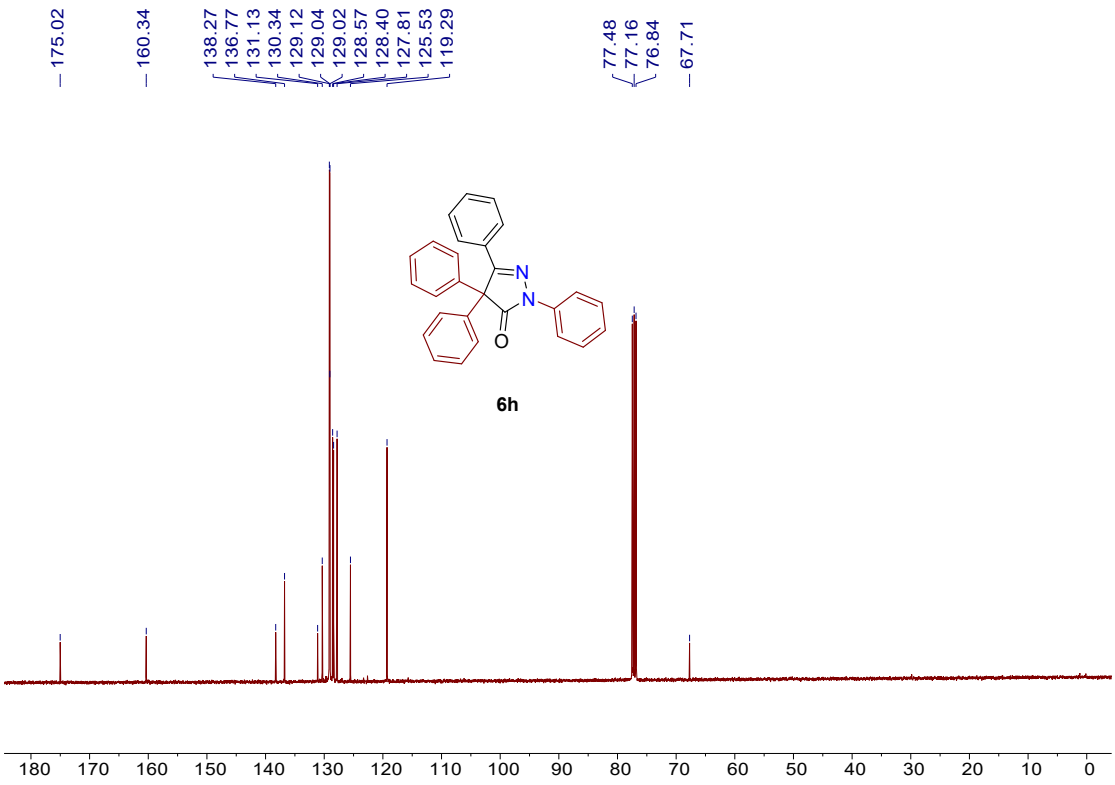
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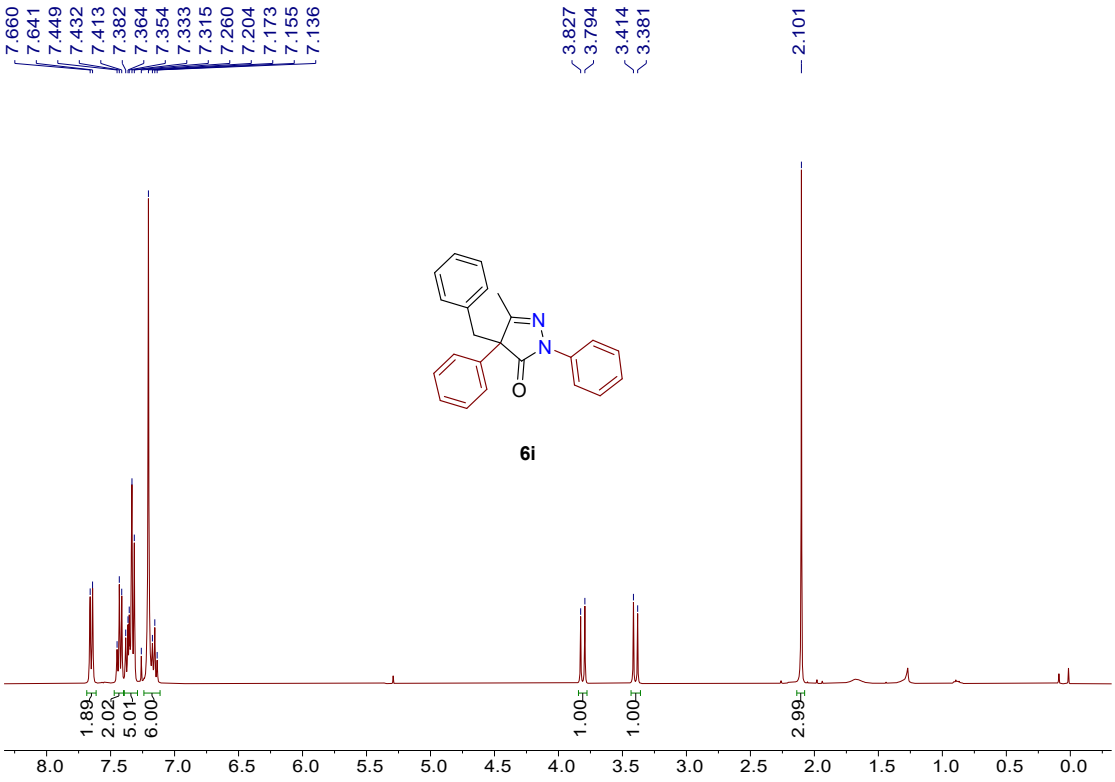
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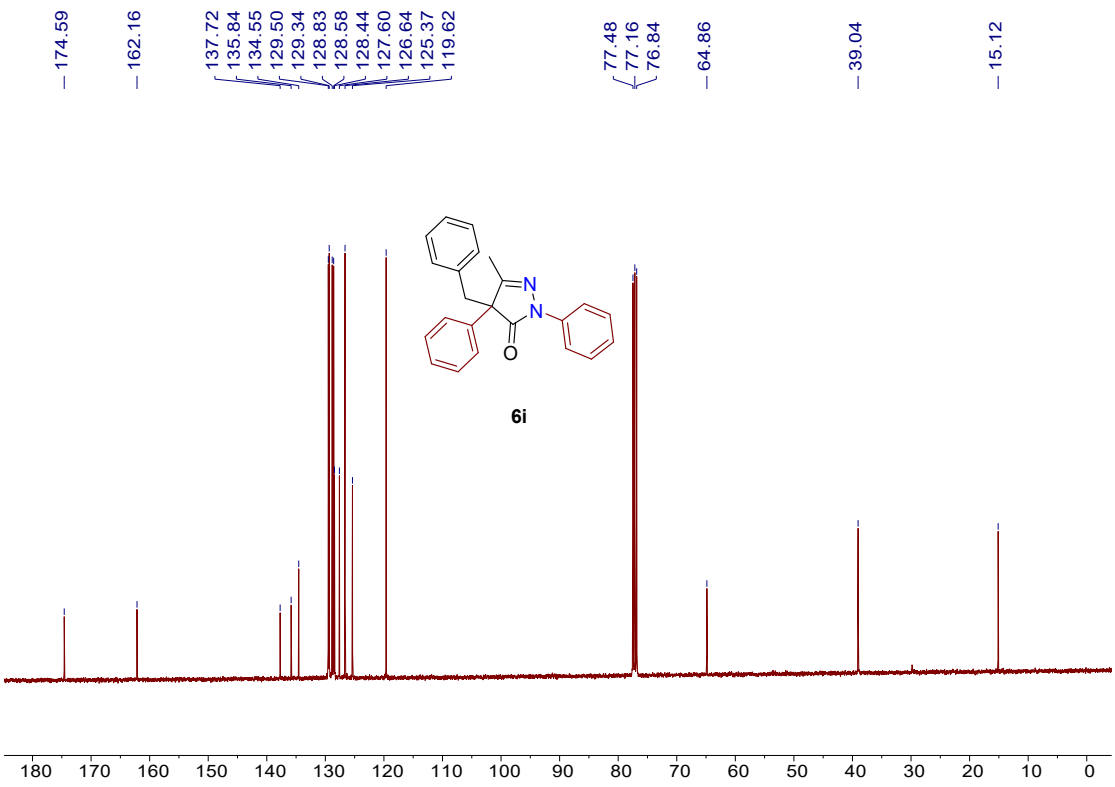
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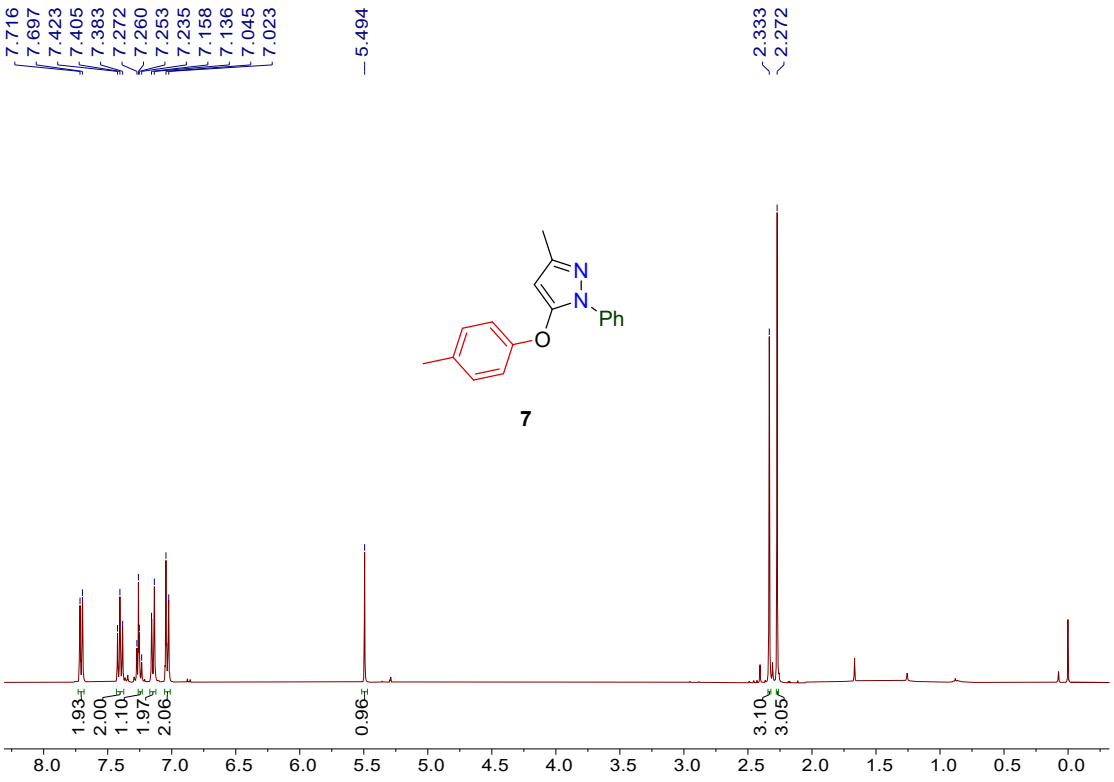
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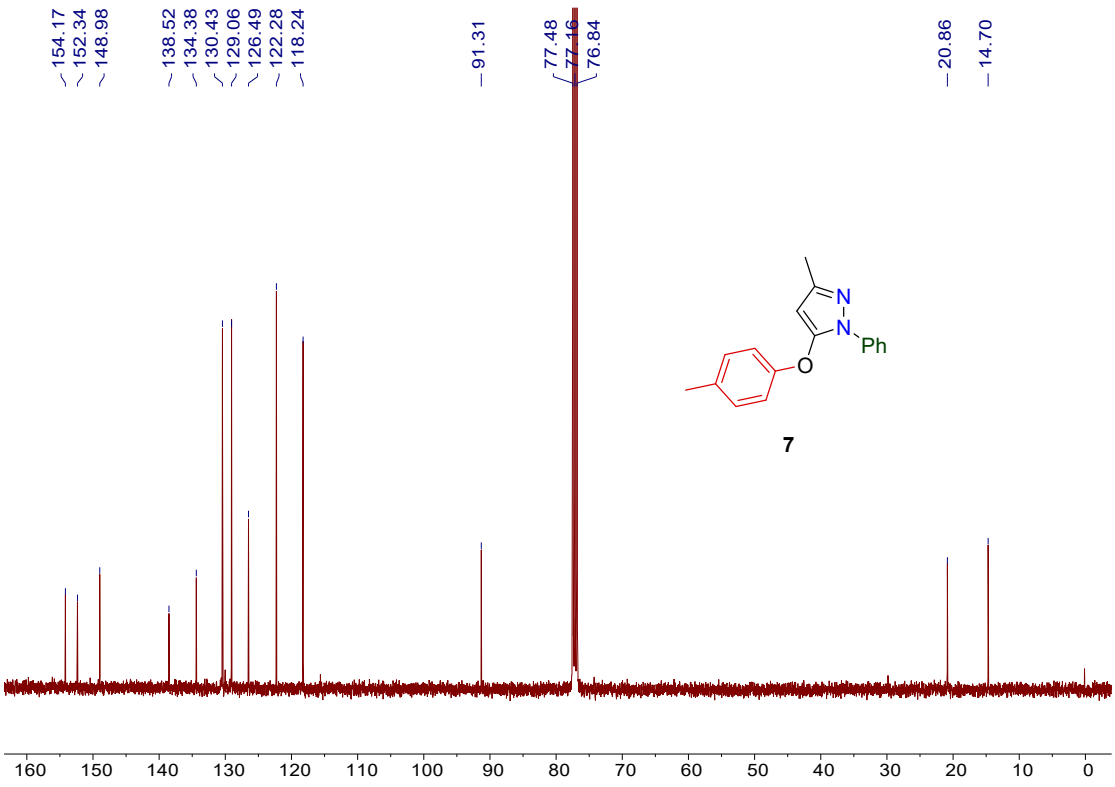
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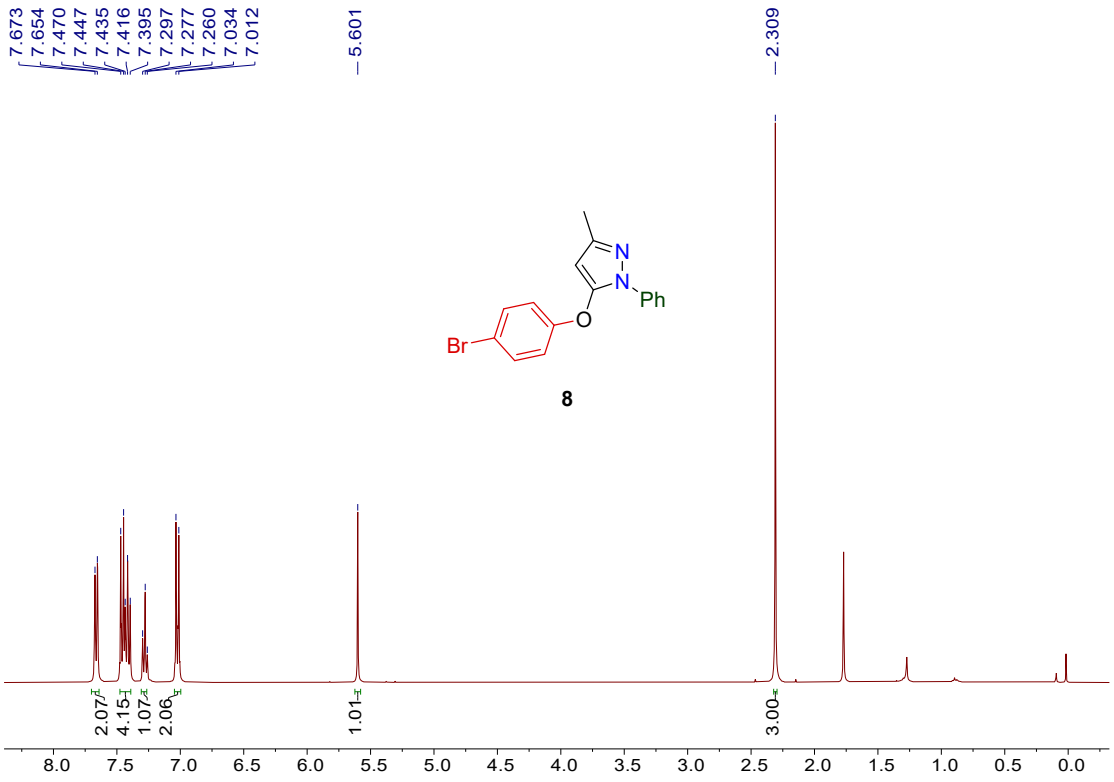
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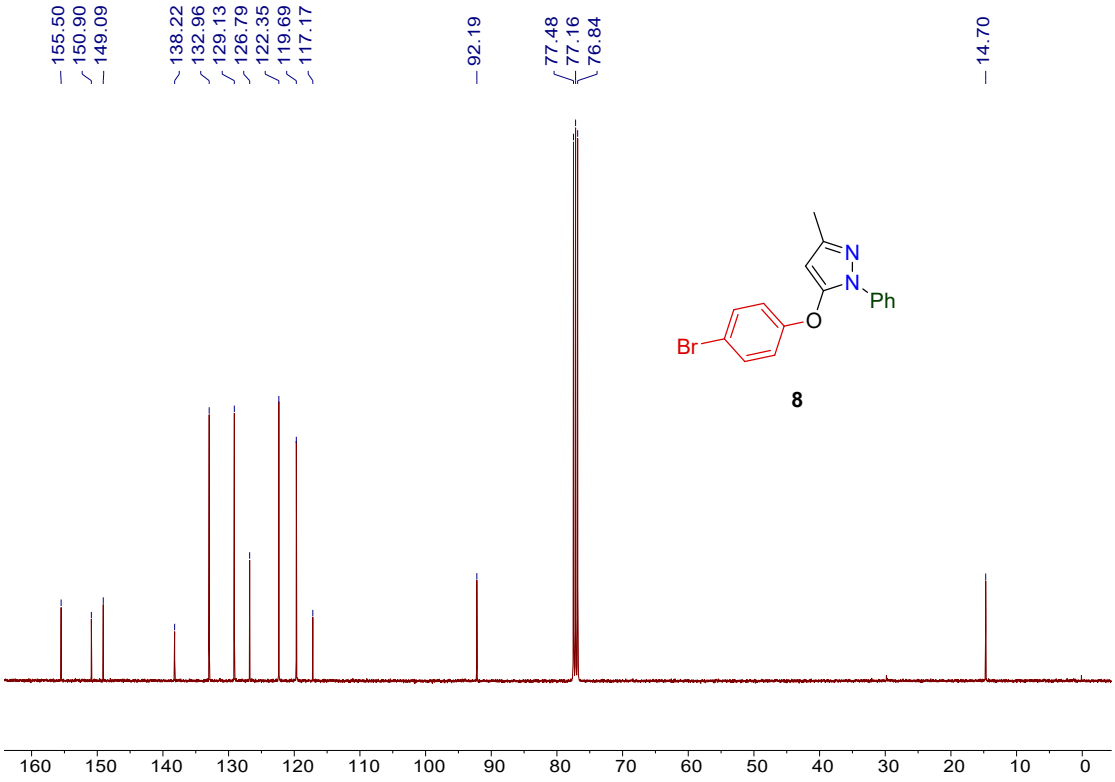
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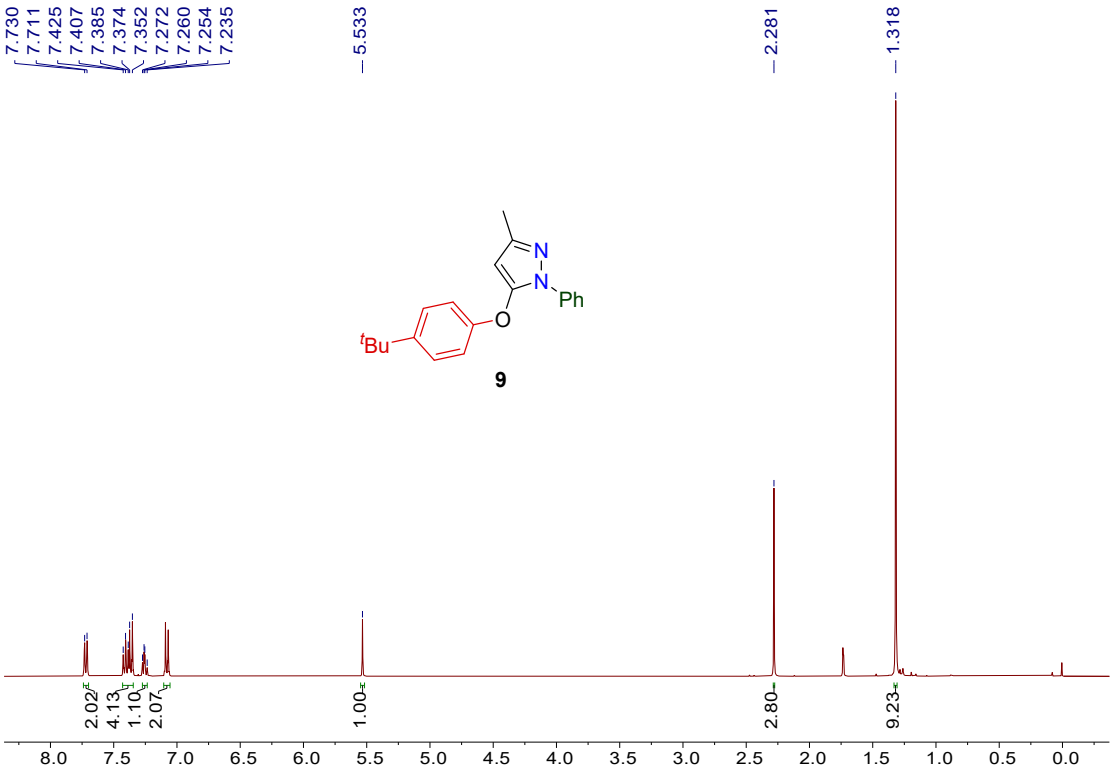
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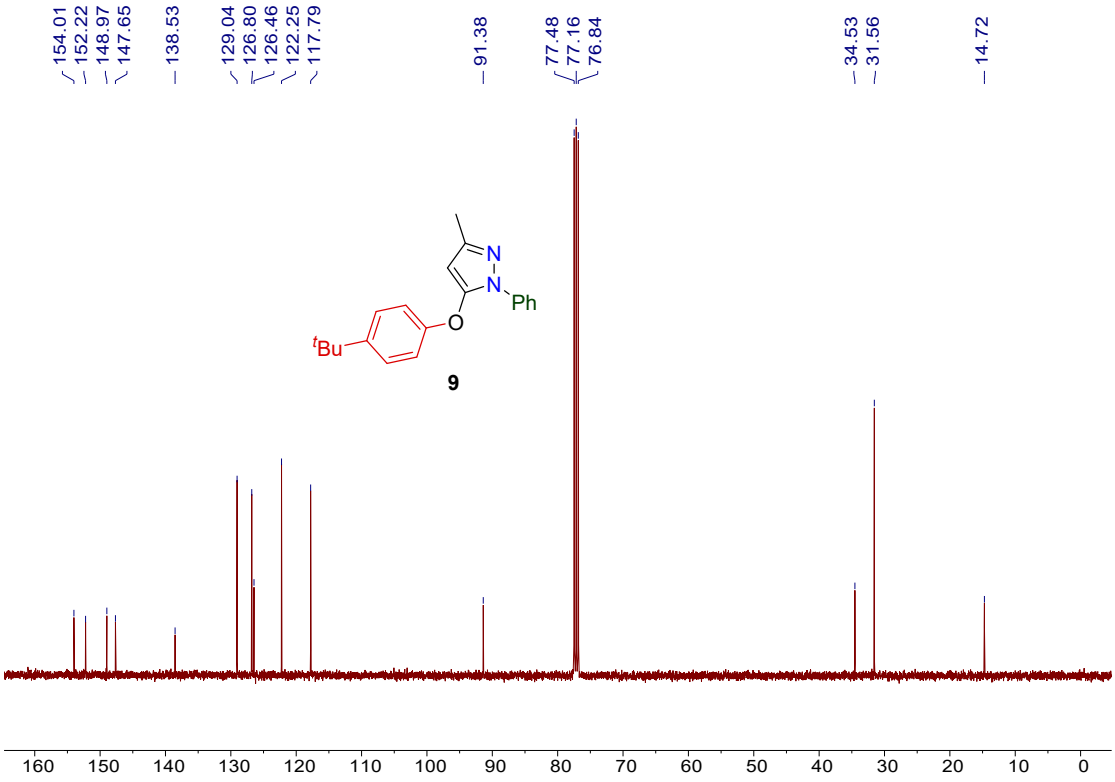
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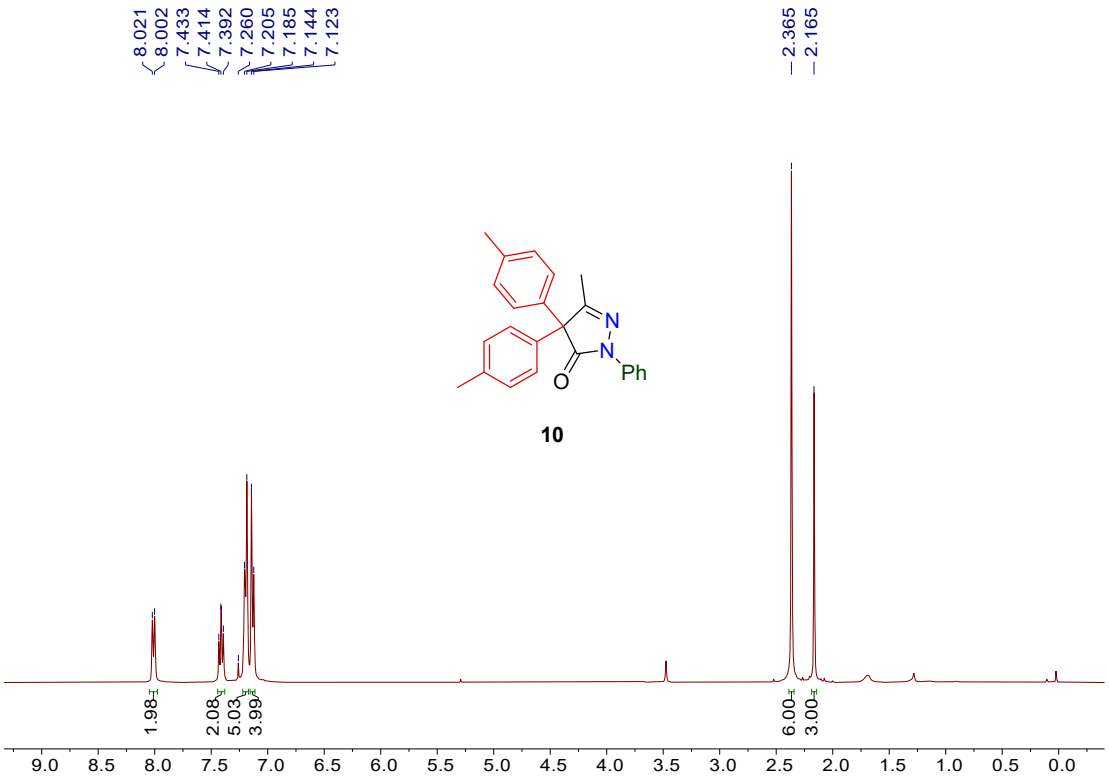
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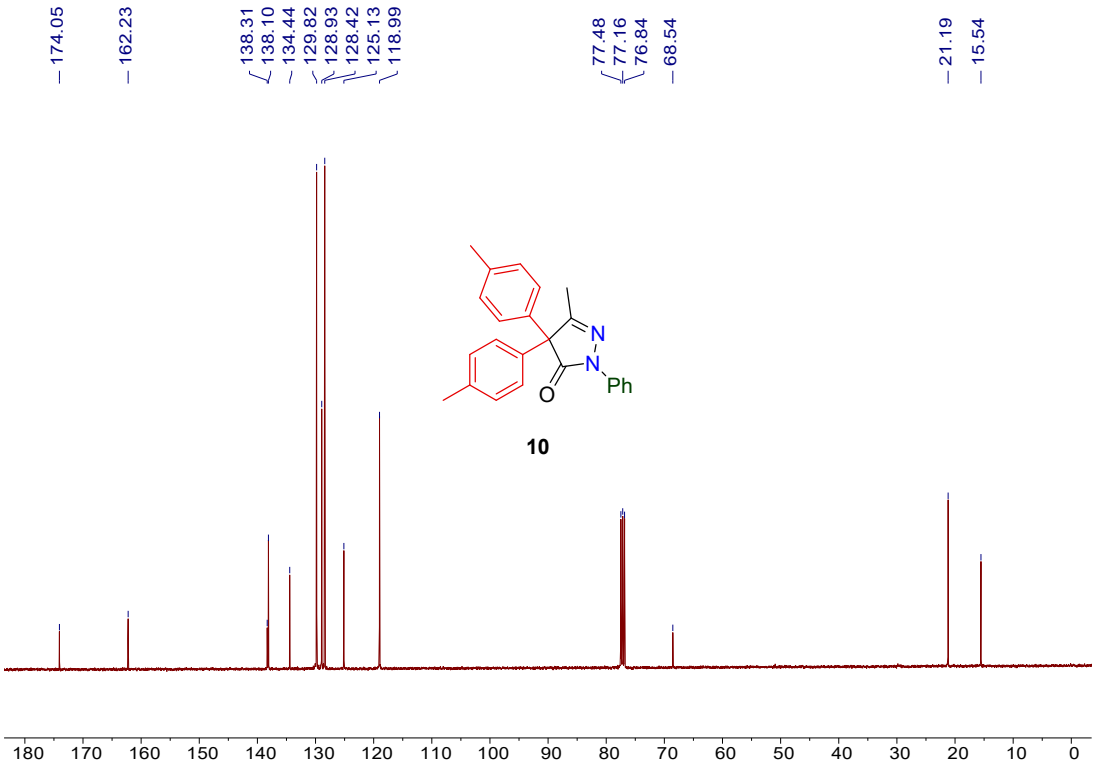
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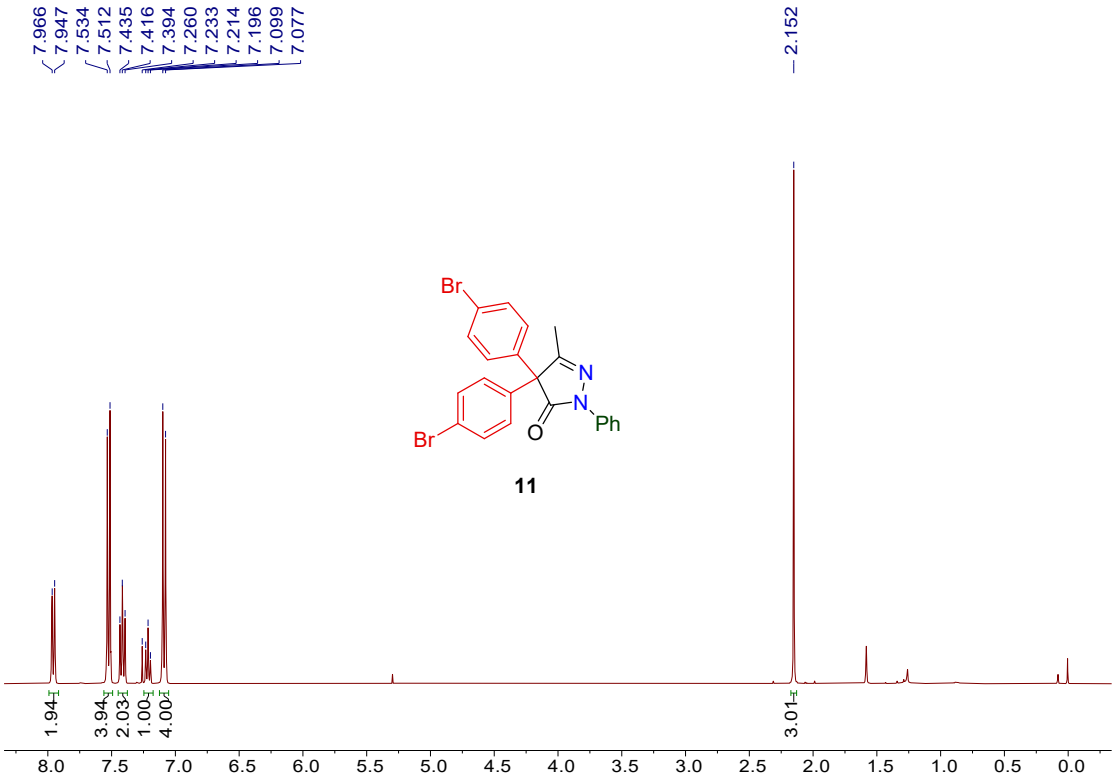
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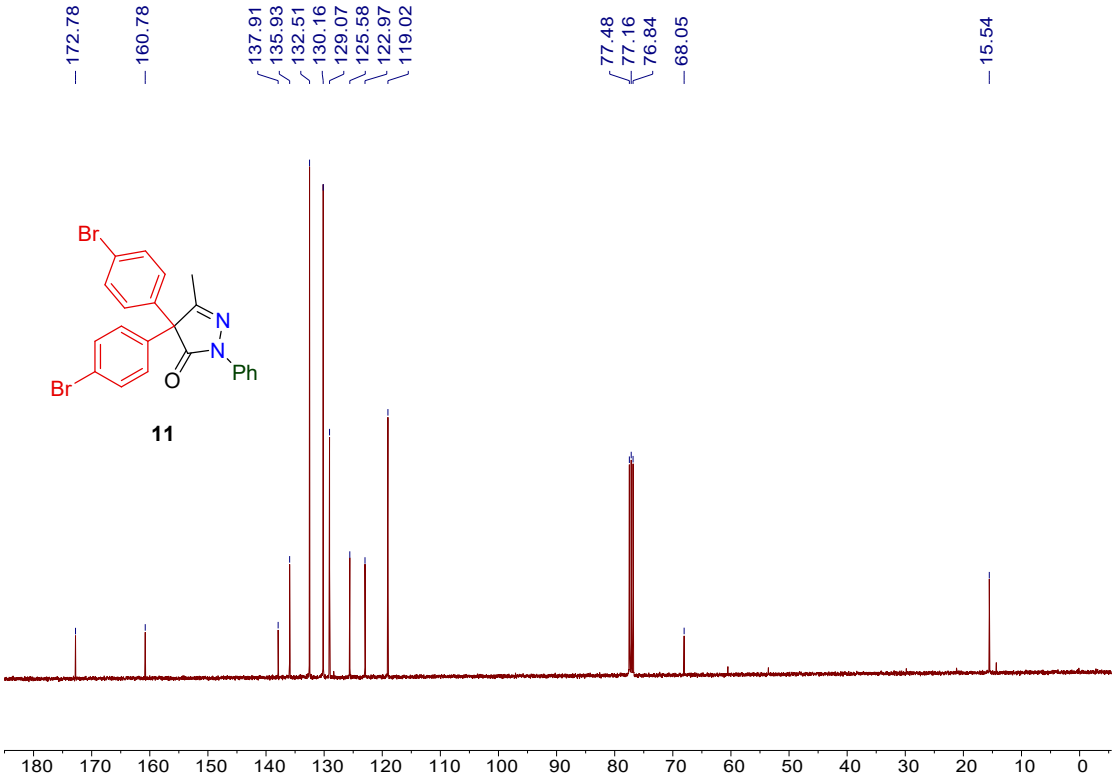
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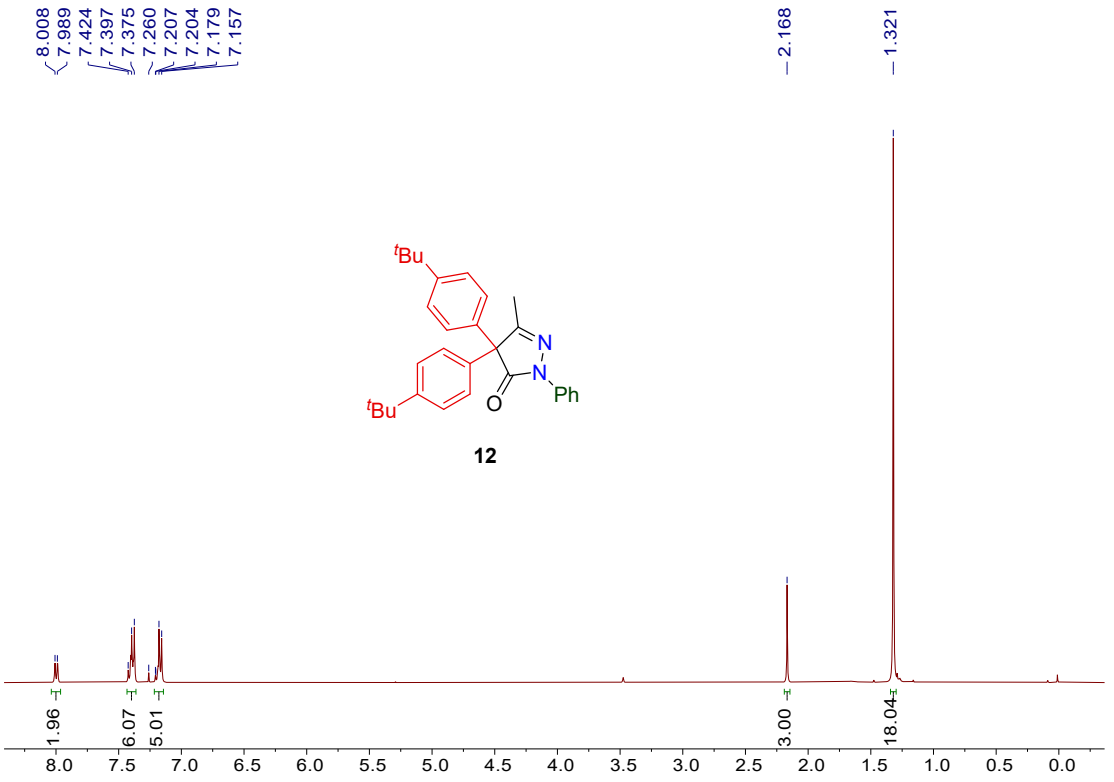
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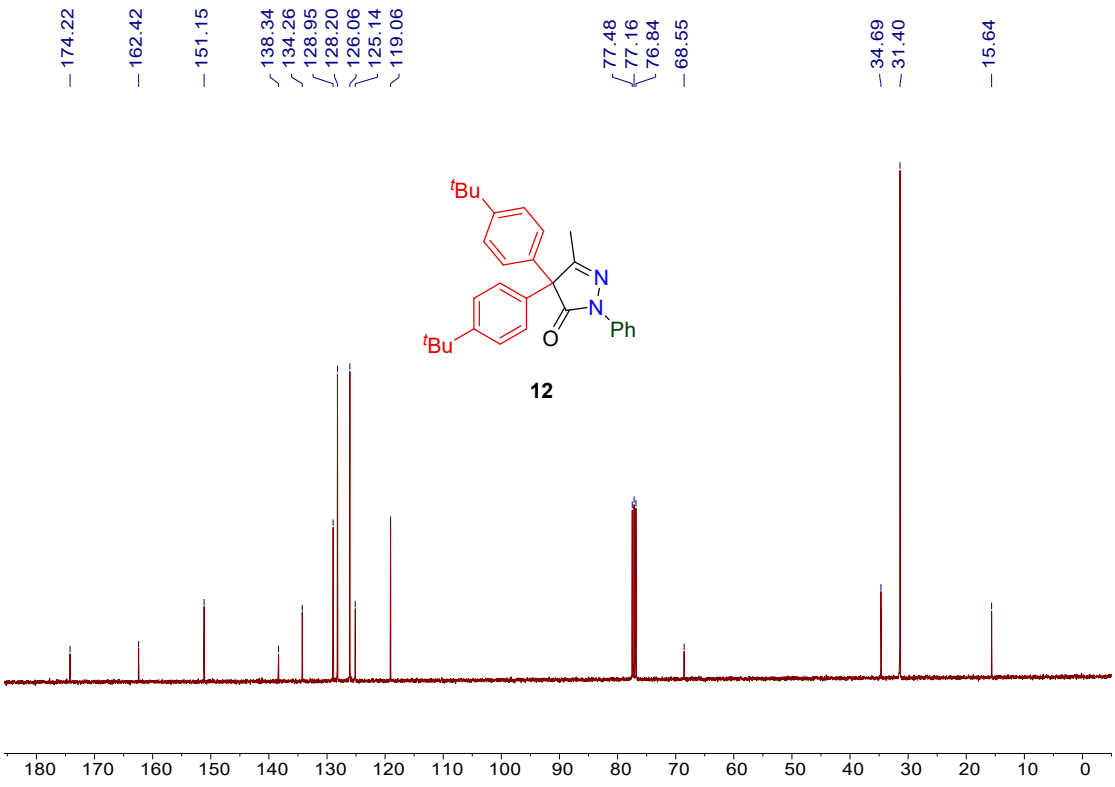
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12