Asymmetric Chlorination of 4-Substituted Pyrazolones Catalyzed by Natural Cinchona Alkaloid

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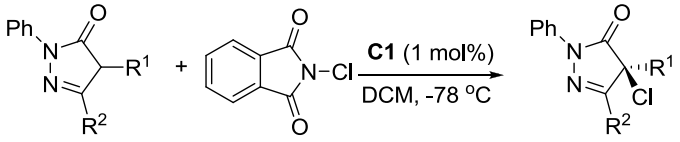
1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (100~200 mesh). Enantiomeric excesses (*ee*) were determined by HPLC using corresponding commercial chiral columns as stated at 30 ℃ with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]^{T}_{D}$ (*c* g/100 mL, solvent). All ^{1}H NMR and ^{19}F NMR spectra were recorded on a Bruker Avance Ⅱ 400 MHz and Bruker Avance Ⅲ 471 MHz respectively, ^{13}C NMR spectra were recorded on a Bruker Avance Ⅱ 101 MHz or Bruker Avance Ⅲ 126 MHz with chemical shifts reported as ppm (in $CDCl_3$, TMS as internal standard). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet, dd = doublet doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XL TM). The absolute configuration of **3p** was assigned by the X-ray analysis.

4-sustitued pyrazolones **1a-r** were prepared from β-keto esters according to the literature.[1] The chlorinating reagents **2a-d** were commercially available and used directly. The racemic product was synthesized using corresponding pyrazolones and NCS without catalyst.

2. Experimental procedures and characterization of products 3a-r, 4-6

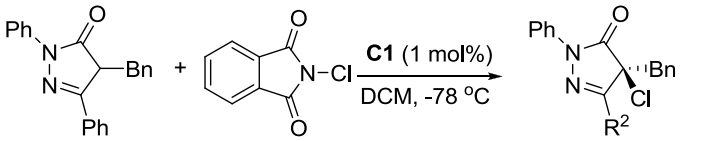
General procedure: synthesis of compound 3a-r



1 **2d** **3**

To a Schlenk tube equipped with a magnetic stir bar was charged with 4-substituted pyrazolone **1** (0.2 mmol, 1.0 eq.) and 1 mL of a fresh solution of the catalyst **C1** (0.002 M in DCM, 0.01 eq.), followed with DCM (3 mL). After cooled to -78 ℃ for 15 min, the chlorinating reagent **2d** (0.22 mmol, 1.1 eq.) was added in one portion. The reaction was detected by TLC. After the consumption of **1**, the reaction mixture was warmed to rt, and purified by column chromatography on silica gel directly to give the product **3**.

Gram synthesis of compound 3a



1a
1.01 g

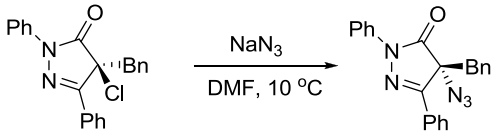
2d

3a
94% yield, 92% ee

To a Schlenk tube equipped with a magnetic stir bar was charged with 4-substituted pyrazolone **1a** (1.01 g, 4.3 mmol, 1.0 eq.) and **C1** (14 mg, 0.043 mmol, 0.01 eq.), followed with DCM (86 mL). After cooled to -78 ℃ for 15 min, the chlorinating reagent **2d** (0.86 g, 4.7 mmol, 1.1 eq.) was added in one portion. The reaction was detected by TLC. After the consumption of **1a**, the reaction mixture was warmed to rt. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel directly to give the product **3a** as light

yellow oil (1.45 g, 94% yield, 92% ee).

Synthesis of (*R*)-4-azido-4-benzyl-1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-one (4)

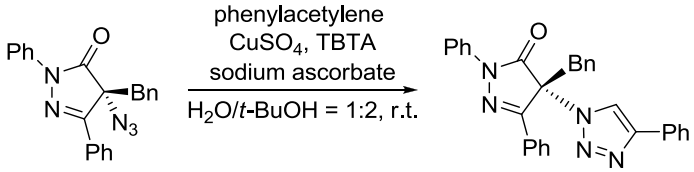


3a
92% ee

4
90% yield, 86% ee

To a solution of **4** (72 mg, 0.2 mmol, 1.0 eq.) in DMF (3.0 mL) was added NaN_3 (39 mg, 0.6 mmol, 3.0 eq.), and the resulting mixture was stirred at 10 °C for 3 h (detected by TLC). The mixture was diluted by H_2O (15 mL), then extracted with Et_2O (10 mL×3). The combined organic layer was washed with water and brine, dried over Na_2SO_4, concentrated. The crude mixture was purified by column chromatography (EtOAc/petroleum ether = 1/20) to give 90% yield of **4** as an oil (66.1 mg, 90% yield, 86% ee).

Synthesis of (*R*)-4-benzyl-1,3-diphenyl-4-(4-phenyl-1H-1,2,3-triazol-1-yl)-4,5-dihydro-1*H*-pyrazol-5-one (5)

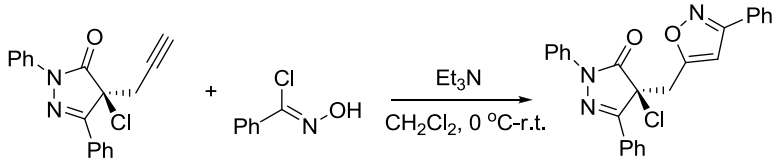


4

5
80% yield, 86% ee

Azide **4** (0.16 mmol, 1.0 eq.) was dissolved in a 2:1 mixture of *t*BuOH and water (900 μL). Benzyne (19.3 mg, 0.19 mmol, 1.2 equiv.), $CuSO_4$ (5.1 mg, 0.03 mmol, 0.2 equiv.), sodium ascorbate (12.6 mg, 0.06 mmol, 0.4 equiv.) and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA) (0.8 mg, 1 mol%) were added and the solution was stirred at room temperature for 12 h. The reaction mixture was diluted with water (15 mL) and extracted with CH_2Cl_2 (3×15 mL). The combined organic phases were washed with brine, dried over $NaSO_4$ and the solvent was evaporated. The crude mixture was purified by silica gel column chromatography (EtOAc/petroleum ether = 1/6) to give **5** as white foam (60.2 mg, 80% yield, 86% ee).

Synthesis of (*S*)-4-chloro-1,3-diphenyl-4-((3-phenylisoxazol-5-yl)methyl)-1*H*-pyrazol-5(4*H*)-one (6)



3l
92% ee

6
96% yield, 91% ee

Triethylamine (0.30 mmol, 2.0 eq.) was added to a solution of chlorobenzaldoxime (0.30 mmol, 2.0 eq.) in dry CH_2Cl_2 (2.0 mL) at 0 ℃. After stirring for 10 min a solution of (*S*)-**3l** (0.15 mmol, 92 % ee, 1.0 eq.) in dry CH_2Cl_2 (1.0 mL) was added dropwise. The mixture was stirred at

room temperature for 36 h. Then the reaction was quenched with water (5 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Chromatography on silica gel (EtOAc/petroleum ether = 1/10) afforded the product **6** (61.1 mg, yield 96 %, 91% ee) as oil.

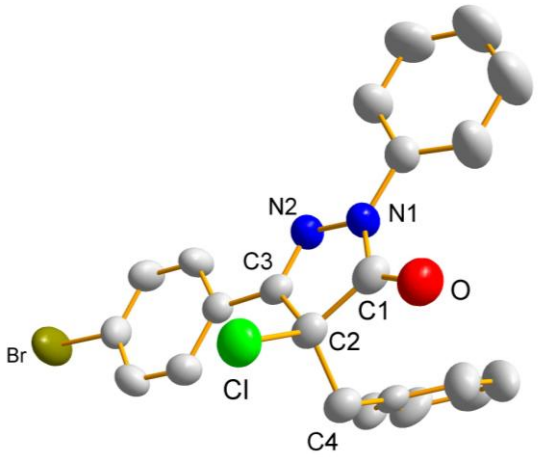


Figure S-1 X-ray crystal structure of the product **3p**.

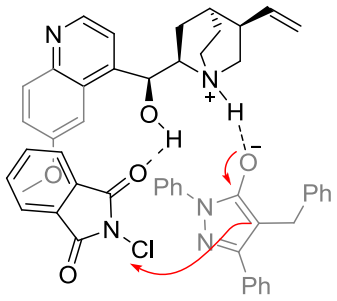
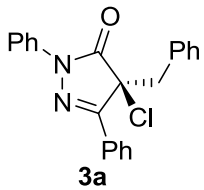


Figure S-2 The stereochemical working model.

The quinuclidine moiety serves as a Lewis base to enhance the nucleophilicity of the pyraolone, while the carbonyl group of the chlorinating reagent was activated and locked through hydrogen bonding with the hydroxyl group at 9-position of the quinidine simultaneously. Thus the nucleophilic attack of the pyrazolone to the chlorine affords the (*S*)-chlorinated product.

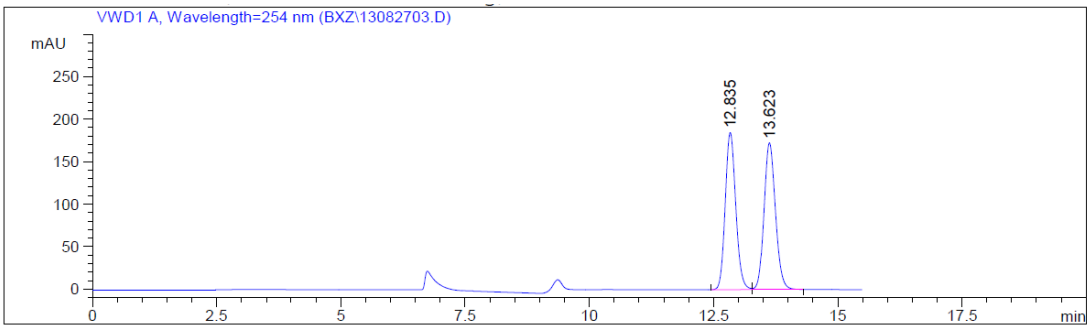
(*S*)-4-benzyl-4-chloro-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (3a)



3a

Prepared according to the general procedure with a reaction time of 20 min as yellow oil (68.4 mg, 95% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{21}$ = -91.3 (*c* 0.66, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) 8.08-8.16 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.54-7.50 (m, 3H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.13-7.04 (m, 3H), 6.85 (d, *J* = 7.3 Hz, 2H), 3.76 (d, *J* = 13.2 Hz, 1H), 3.69 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 155.1, 137.1, 131.9, 131.1, 129.8, 129.6, 129.0, 128.9, 128.4, 128.0, 126.8, 126.0, 119.5, 64.4, 44.0; IR (KBr): 3062, 3025, 2920, 1727, 1597, 1497, 1391, 1327, 1132, 758, 725, 689 cm^{-1}; HRMS (EI) m/z Calcd. for $C_{22}H_{17}ClN_2NaO$ ($[M+Na]^+$) 383.0922, Found 383.0923; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral OD-H column,

hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 13.9 min, t_{minor} = 12.7 min).



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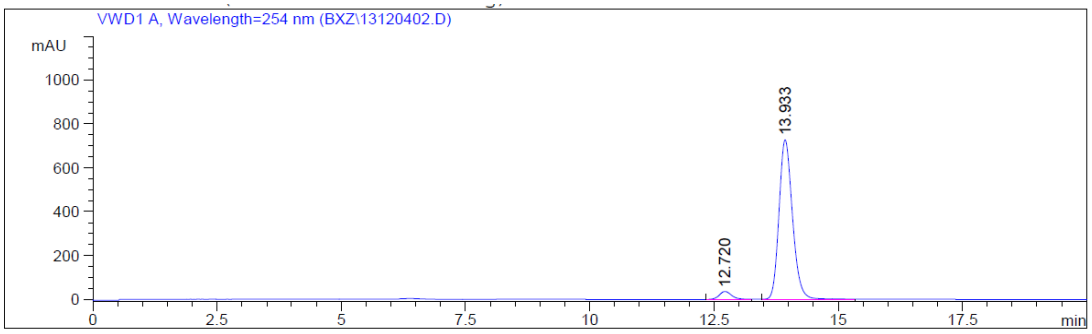
1	12.835	BV	0.2282	2740.88086	185.00984	49.8318
2	13.623	VB	0.2446	2759.38110	172.73917	50.1682



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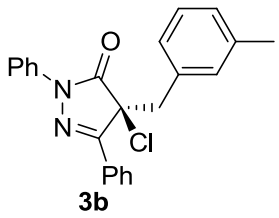
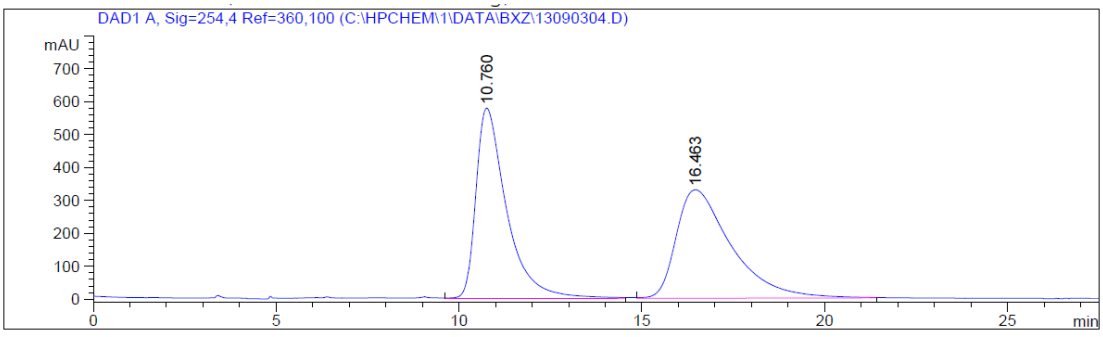
1	12.720	PB	0.2589	600.05554	35.93446	4.1969
2	13.933	PB	0.2897	1.36976e4	727.03949	95.8031

(*S*)-4-chloro-4-(3-methylbenzyl)-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (3b)

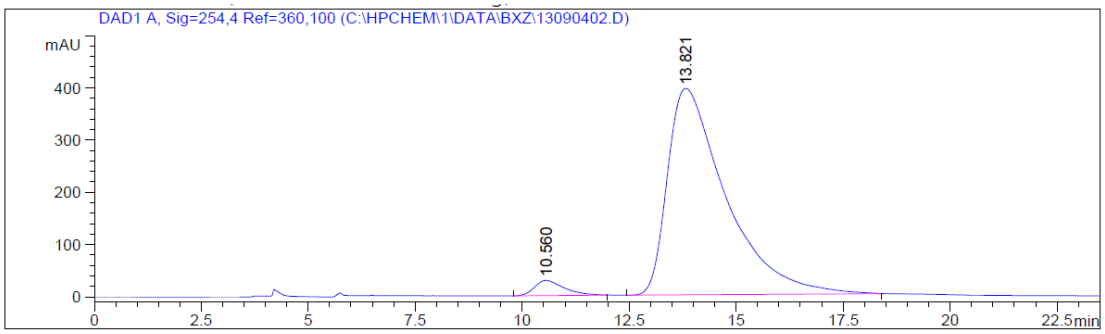


3b

Prepared according to the general procedure with a reaction time of 30 min as yellow oil (70.3 mg, 94% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{21}$ = -99.3 (*c* 0.64, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.52-7.47 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.98-6.86 (m, 2H), 6.63 (d, *J* = 9.4 Hz, 2H), 3.72 (d, *J* = 13.1 Hz, 1H), 3.62 (d, *J* = 13.1 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 155.3, 138.0, 137.2, 131.8, 131.0, 130.6, 129.8, 129.0, 128.9, 128.7, 128.3, 126.9, 126.7, 126.0, 119.6, 64.5, 44.0, 21.1; IR (KBr): 3032, 2920, 2845, 1727, 1597, 1497, 1391, 1327, 1132, 766, 750, 690 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{23}H_{20}ClN_2O$ ($[M+H]^+$) 375.1259, Found 375.1247; Enantiomeric excess was determined to be 93% (determined by HPLC using chiral OJ-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 13.8 min, t_{minor} = 10.6 min).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.760	VB	0.8712	3.38423e4	577.88141	49.6380
2	16.463	BB	1.5219	3.43359e4	328.91537	50.3620



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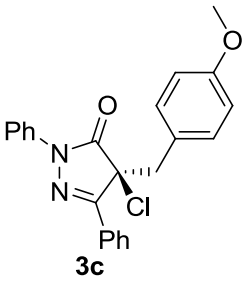
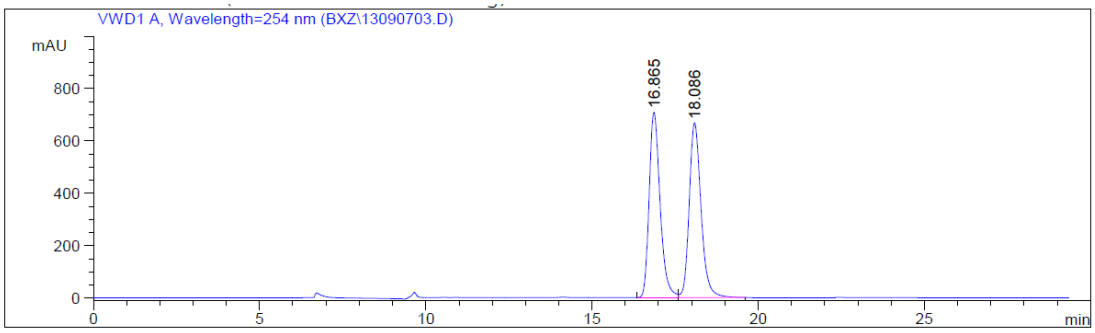
1	10.560	BB	0.6684	1396.34888	29.17399	3.5908
2	13.821	PB	1.3396	3.74907e4	394.88492	96.4092

(*S*)-4-chloro-4-(4-methoxybenzyl)-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (3c)



3c

Prepared according to the general procedure with a reaction time of 35 min as yellow oil (71.0 mg, 91% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{21}$ = -76.5 (*c* 0.68, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-7.99 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.60-7.43 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 8.7 Hz, 2H), 3.70 (d, *J* = 13.4 Hz, 1H), 3.63 (d, *J* = 13.2 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 159.2, 155.2, 137.2, 131.1, 130.9, 129.7, 129.0, 128.9, 126.8, 125.9, 123.8, 119.5, 113.8, 64.4, 55.1, 43.2; IR (KBr): 3032, 2957, 2927, 2830, 1727, 1610, 1596, 1391, 1253, 1180, 1133, 1033, 756, 690 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{23}H_{19}ClN_2NaO_2$ ($[M+Na]^+$) 413.1027, Found 413.1012; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 18.1 min, t_{minor} = 16.9 min).



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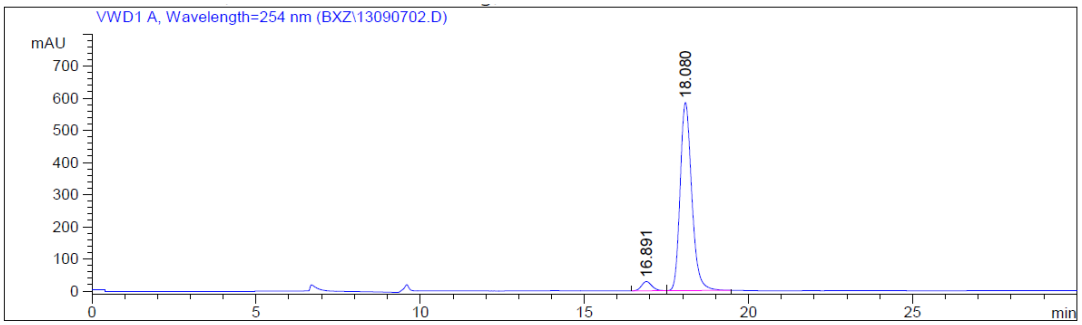
1	16.865	BV	0.3533	1.62215e4	707.85663	49.6471
2	18.086	VB	0.3796	1.64521e4	666.68188	50.3529



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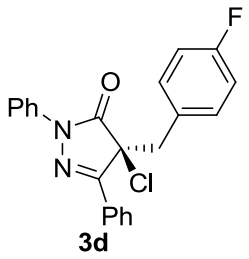
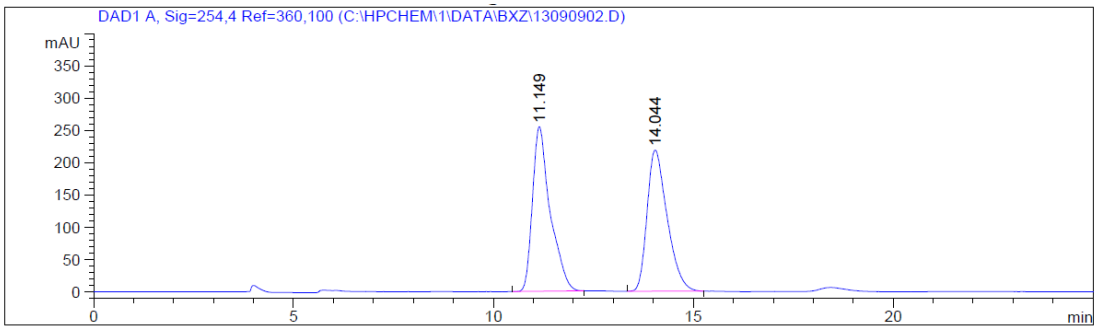
1	16.891	BB	0.3439	635.18634	28.72272	4.2349
2	18.080	BB	0.3753	1.43638e4	585.02826	95.7651

(*S*)-4-chloro-4-(4-methoxybenzyl)-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (3d)



3d

Prepared according to the general procedure with a reaction time of 30 min as yellow oil (68.9 mg, 91% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{21}$ = -87.8 (*c* 0.58, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.00 (m, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.57-7.46 (m, 3H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.88-6.65 (m, 4H), 3.72 (d, *J* = 13.3 Hz, 1H), 3.65 (d, *J* = 13.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 162.4 (d, *J* = 248.5), 155.0, 137.0, 131.52 (d, *J* = 8.1 Hz), 131.2, 129.5, 129.0 (d, *J* = 15.4 Hz), 127.7 (d, *J* = 3.3 Hz), 126.8, 126.1, 119.4, 115.6, 115.4, 64.2 (d, *J* = 1.8 Hz), 43.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.52 (1F, s); IR (KBr): 3039, 2920, 1728, 1597, 1509, 1391, 1225, 1160, 1132, 838, 756, 690 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{22}H_{16}ClFN_2NaO$ ($[M+Na]^+$) 401.0827, Found 401.0813; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 11.5 min, t_{minor} = 14.4 min).



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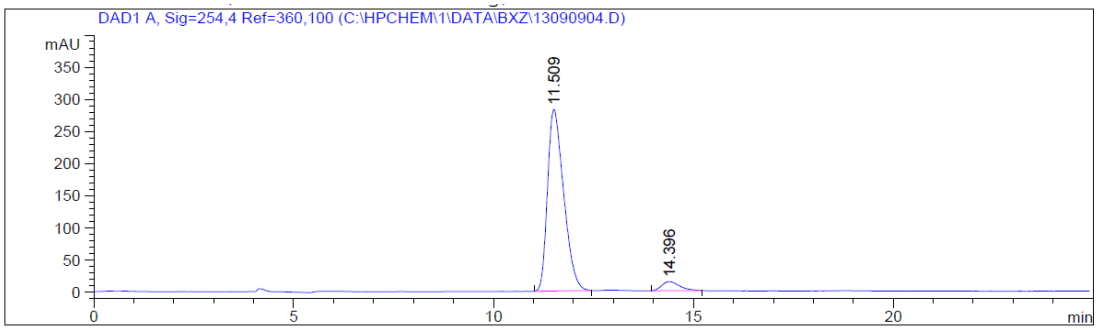
1	11.149	BB	0.4499	7852.77930	254.58397	50.7367
2	14.044	BB	0.5231	7624.72656	218.49043	49.2633



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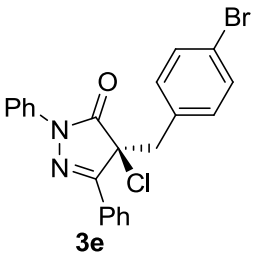
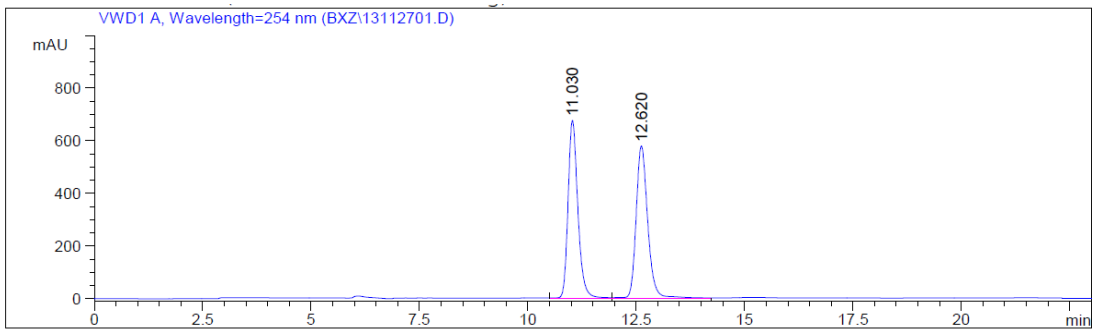
2	14.396	BB	0.4313	431.13818	14.07929	5.1598

(*S*)-4-(4-bromobenzyl)-4-chloro-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (3e)



3e

Prepared according to the general procedure with a reaction time of 20 min as yellow oil (82.3 mg, 94% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{20}$ = -57.4 (*c* 0.66, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.04 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.56-7.49 (m, 3H), 7.41-7.37 (m, 2H), 7.25-7.17 (m, 3H), 6.71 (d, *J* = 8.4 Hz, 2H), 3.70 (d, *J* = 13.2 Hz, 1H), 3.63 (d, *J* = 13.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 154.9, 137.0, 131.7, 131.5, 131.3, 131.0, 129.4, 129.1, 129.0, 126.8, 126.1, 122.4, 119.4, 64.0, 43.3; IR (KBr): 3047, 2912, 1727, 1591, 1489, 1391, 1325, 1135, 1015, 828, 757, 690 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{22}H_{17}BrClN_2O$ ($[M+H]^+$) 439.0207, Found 439.0195; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 13.2 min, t_{minor} = 11.3 min).



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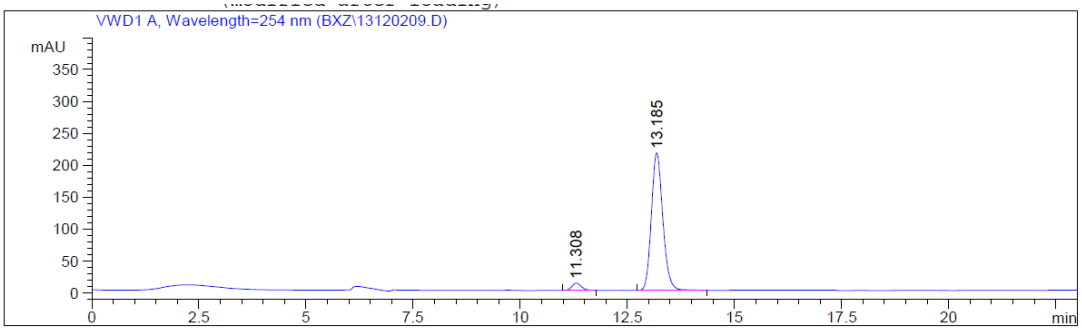
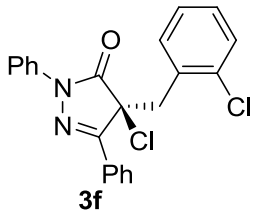
1	11.030	BB	0.2377	1.05451e4	674.62195	49.5988
2	12.620	BB	0.2817	1.07157e4	578.31128	50.4012



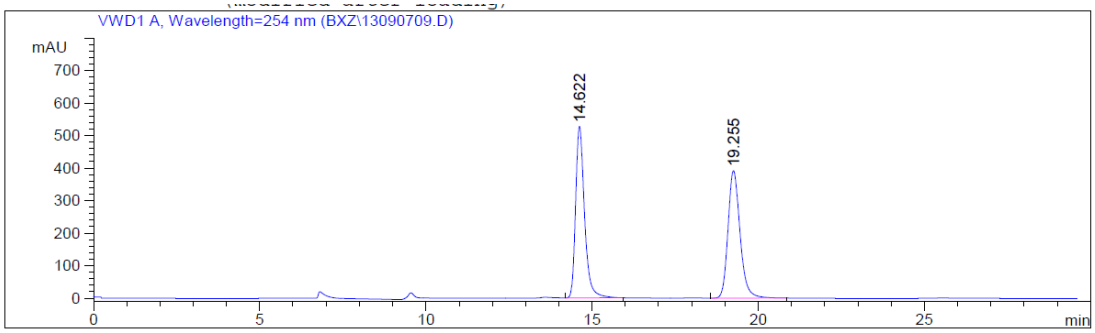
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.308	BB	0.2379	181.17502	11.57755	4.3335
2	13.185	BB	0.2866	3999.63477	215.28976	95.6665

(*S*)-4-chloro-4-(2-chlorobenzyl)-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (3f)

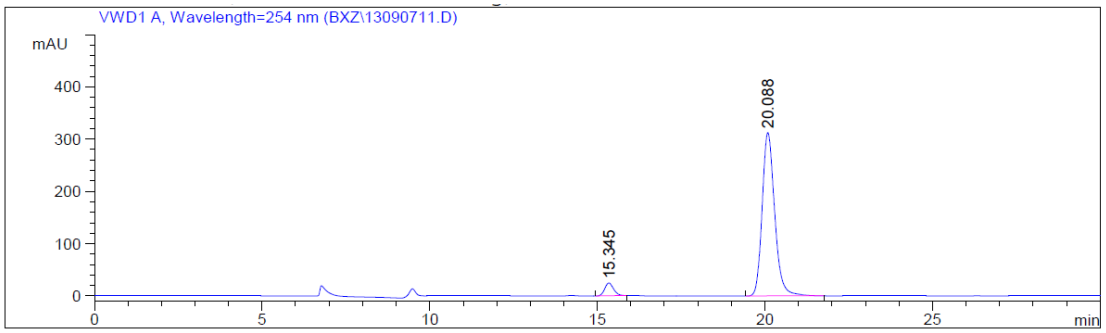


3f

Prepared according to the general procedure with a reaction time of 20 min as red oil (74.9 mg, 95% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{21}$ = -83.6 (*c* 0.58, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.49-7.35 (m, 5H), 7.24-7.20 (m, 2H), 7.16-7.05 (m, 3H), 3.91 (d, *J* = 14.2 Hz, 1H), 3.86 (d, *J* = 14.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 155.6, 137.3, 135.0, 131.6, 131.1, 130.4, 129.8, 129.4, 129.0, 128.7, 127.2, 126.8, 126.0, 119.4, 64.6, 40.1; IR (KBr): 3062, 2920, 1728, 1596, 1497, 1390, 1328, 1129, 756, 689 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{22}H_{17}Cl_2N_2O$ ($[M+H]^+$) 395.0712, Found 395.0697; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 ^{o}C, 0.5 mL/min, t_{major} = 20.1 min, t_{minor} = 15.4 min).

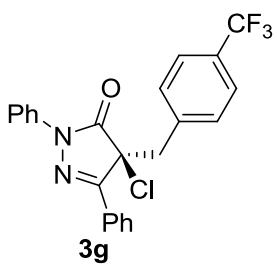


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.622	VB	0.2866	9862.20117	527.39868	50.0266
2	19.255	VB	0.3866	9851.70117	391.72577	49.9734



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.345	PB	0.2781	444.45517	24.38876	5.1913
2	20.088	BB	0.3961	8117.08740	312.62854	94.8087

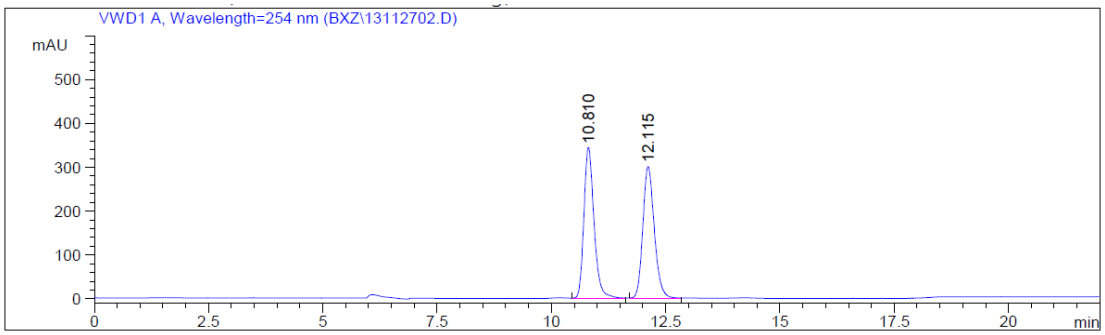
(*S*)-4-chloro-1,3-diphenyl-4-(4-(trifluoromethyl)benzyl)-1*H*-pyrazol-5(4*H*)-one (3g)



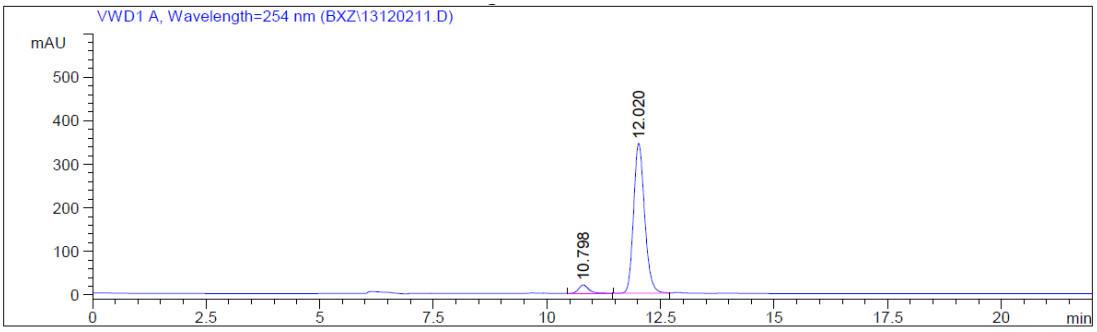
3g

Prepared according to the general procedure with a reaction time of 20 min as colorless oil (79.6 mg, 93% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{19}$ = -68.3 (*c* 0.67, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.51-7.56 (m, 3H), 7.41-7.37 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.25-7.21 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 3.80 (d, *J* = 13.1 Hz, 1H), 3.74 (d, *J* =

13.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 154.8, 136.9, 136.0, 131.3, 130.3 (q, J = 32.3 Hz), 130.2, 129.4, 129.2, 129.0, 126.8, 126.2, 125.41 (q, J = 4.0 Hz), 123.8 (q, J = 272.7 Hz), 119.5, 64.0, 43.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.70 (3F, s); IR (KBr): 3054, 2912, 1728, 1598, 1497, 1392, 1168, 1127, 1069, 844, 754, 689 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{23}H_{17}ClF_3N_2O$ ([M+H]$^+$) 429.0976, Found 429.0966; Enantiomeric excess was determined to be 90% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 12.0 min, t_{minor} = 10.8 min).

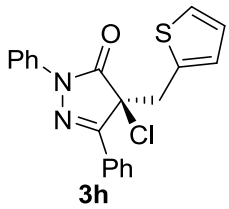


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.810	VB	0.2354	5304.68311	343.73264	50.2787
2	12.115	BB	0.2693	5245.88281	300.26733	49.7213



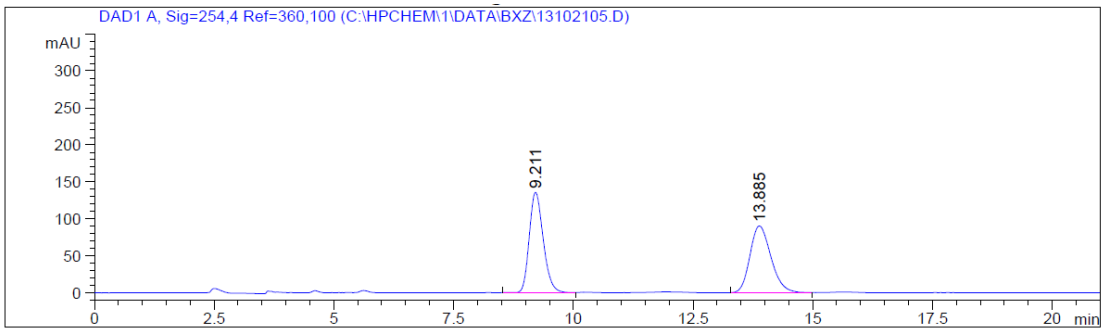
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.798	BB	0.2369	298.77847	19.20210	4.8782
2	12.020	BB	0.2585	5826.05225	344.39304	95.1218

(*S*)-4-chloro-1,3-diphenyl-4-(thiophen-2-ylmethyl)-1*H*-pyrazol-5(4*H*)-one (3h)

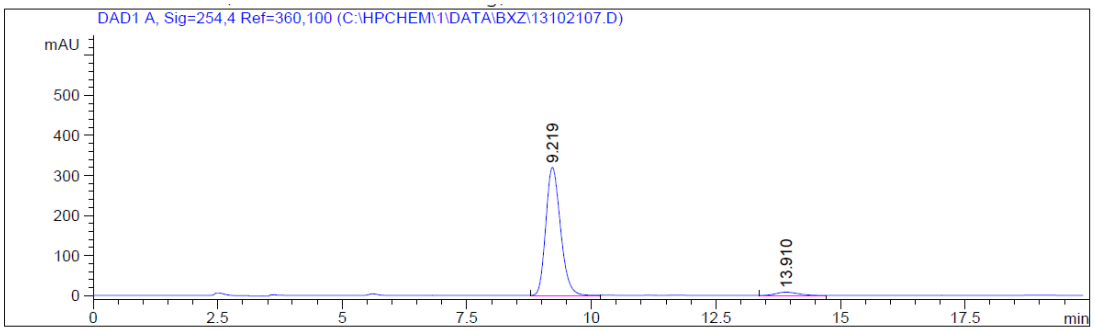


3h

Prepared according to the general procedure with a reaction time of 20 min as yellow oil (69.5 mg, 95% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{18}$ = -142.1 (*c* 0.56, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.07 (m, 2H), 7.87-7.85 (m, 2H), 7.55-7.51 (m, 3H), 7.44-7.40 (m, 2H), 7.26-7.22 (m, 1H), 7.03-7.01 (m, 1H), 6.75-6.73 (m, 1H), 6.60 (d, J = 2.9 Hz, 1H), 4.01 (d, J = 14.4 Hz, 1H), 3.93 (d, J = 14.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 155.2, 137.3, 133.0, 131.2, 129.3, 129.0, 128.2, 127.0, 126.8, 126.0, 125.9, 119.4, 63.4, 37.9; IR (KBr): 2912, 1727, 1597, 1498, 1393, 1327, 1131, 756, 689 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{20}H_{16}ClN_2OS$ ([M+H]$^+$) 367.0666, Found 367.0675; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.2 min, t_{minor} = 13.9 min).

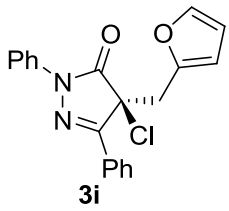


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.211	BB	0.3129	2746.23413	135.24884	49.9331
2	13.885	BB	0.4727	2753.59521	90.07276	50.0669



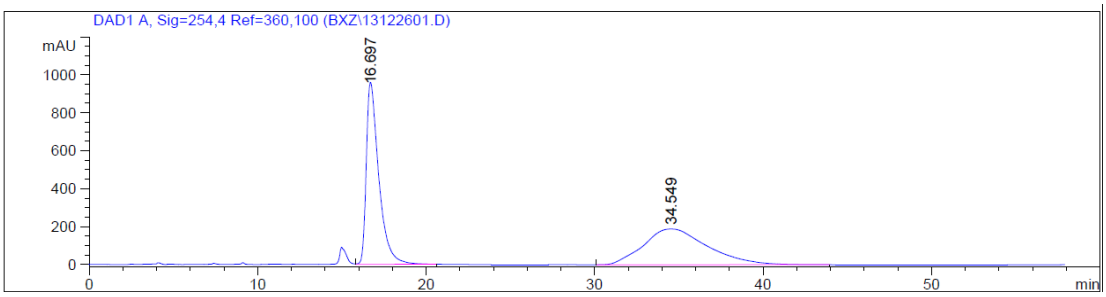
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.219	BB	0.3192	6555.52295	319.72479	96.2056
2	13.910	BB	0.4516	258.55515	8.48260	3.7944

(*S*)-4-chloro-4-(furan-2-ylmethyl)-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (3i)

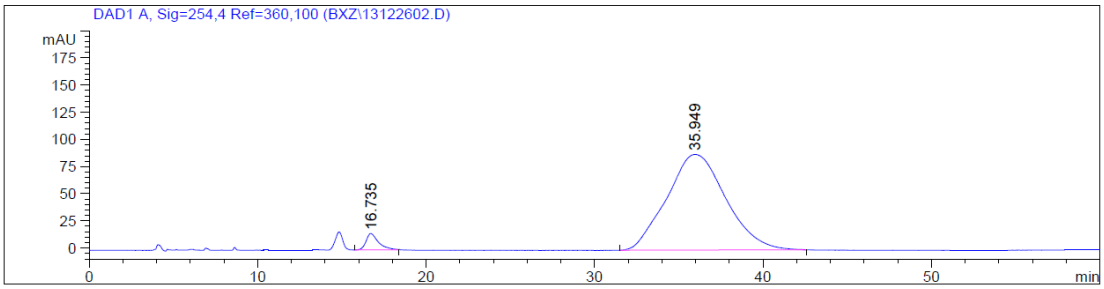


3i

Prepared according to the general procedure with a reaction time of 30 min as yellow oil (63.7 mg, 91% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{21}$ = -98.3 (*c* 0.43, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2H), 7.88-7.85 (m, 2H), 7.51-7.40 (m, 5H), 7.25-7.21 (m, 1H), 7.07 (m, 1H), 6.09-6.08 (m, 1H), 5.89 (d, *J* = 3.2 Hz, 1H), 3.83 (d, *J* = 14.7 Hz, 1H), 3.75 (d, *J* = 14.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 155.6, 146.6, 142.7, 137.4, 131.0, 129.3, 129.0, 128.9, 126.8, 126.0, 119.4, 110.5, 109.3, 62.5, 36.9; IR (KBr): 2912, 1728, 1597, 1500, 1394, 1328, 1131, 753, 688 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{20}H_{16}ClN_2O_2$ ($[M+H]^+$) 351.0895, Found 351.0900; Enantiomeric excess was determined to be 93% (determined by HPLC using chiral OJ-H column, hexane/2-propanol = 95/5, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 35.9 min, t_{minor} = 16.7 min).

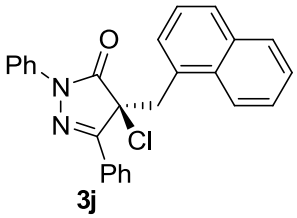


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	16.697	VV	0.7424	4.94981e4	49.7953	?
2	34.549	BV	3.0985	4.99050e4	50.2047	?



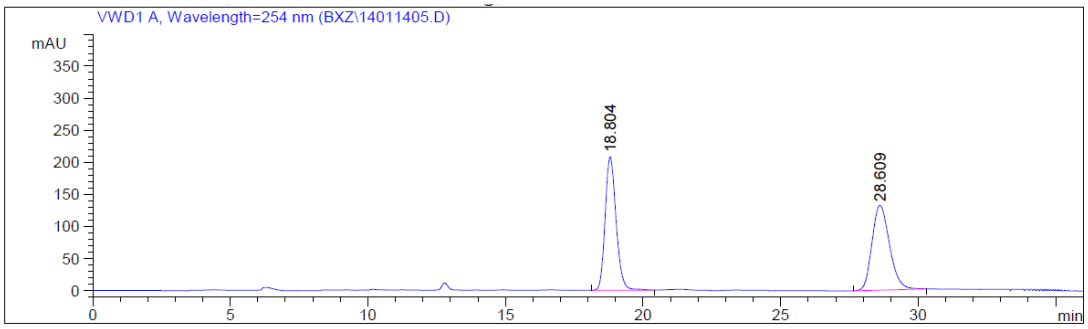
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	16.735	PV	0.6154	758.92603	3.4110	?
2	35.949	BV	2.8658	2.14905e4	96.5890	?

(*S*)-4-chloro-4-(naphthalen-1-ylmethyl)-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (3j)

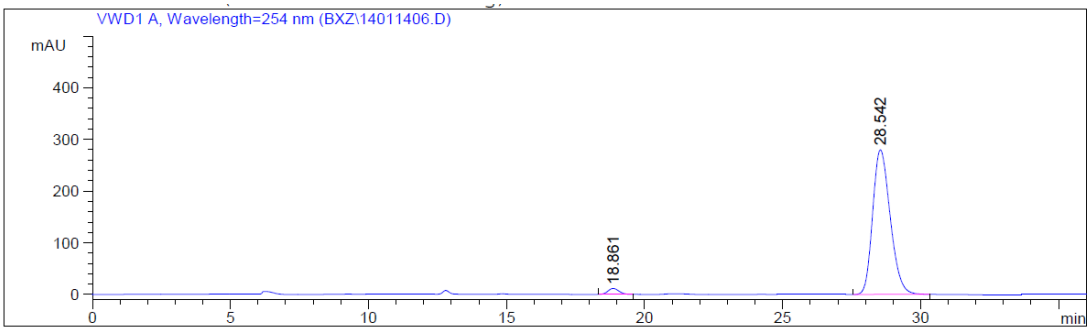


3j

Prepared according to the general procedure with a reaction time of 20 min as orange oil (75.4 mg, 92% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{17}$ = -61.1 (*c* 0.62, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.67-7.62 (m, 4H), 7.50-7.39 (m, 3H), 7.34-7.27 (m, 3H), 7.22-7.11 (m, 4H), 4.26 (d, *J* = 14.1 Hz, 1H), 4.13 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 155.6, 137.1, 133.8, 131.6, 131.1, 129.1, 129.0, 128.7, 128.6, 128.5, 127.1, 126.1, 125.9, 125.7, 124.9, 123.8, 119.6, 65.2, 39.8; IR (KBr): 3062, 2920, 1726, 1596, 1493, 1391, 1327, 1067, 780, 756, 689 cm^{-1}; HRMS m/z (ESI) Calcd. for $C_{26}H_{20}ClN_2O$ ($[M+H]^+$) 411.1259, Found 411.1252; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 28.5 min, t_{minor} = 18.9 min).

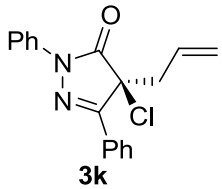


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.804	BB	0.4278	5761.00391	208.07991	49.5464
2	28.609	PB	0.6905	5866.49561	132.31770	50.4536



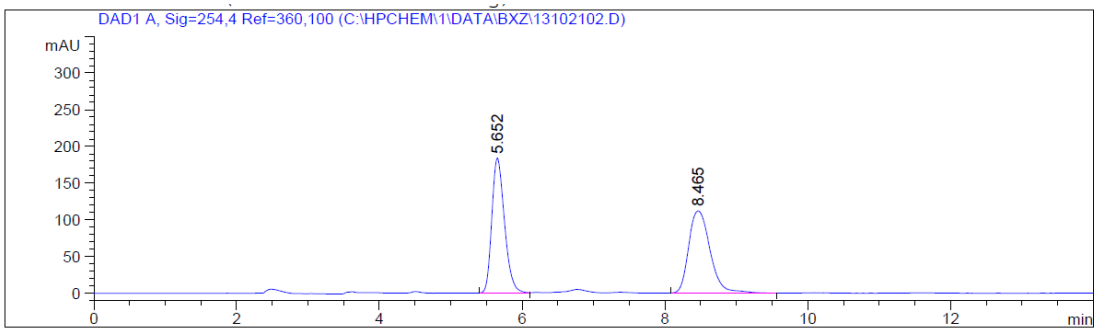
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.861	BB	0.4097	314.06659	11.52359	2.4785
2	28.542	BB	0.6841	1.23577e4	279.82321	97.5215

(*S*)-4-allyl-4-chloro-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (3k)

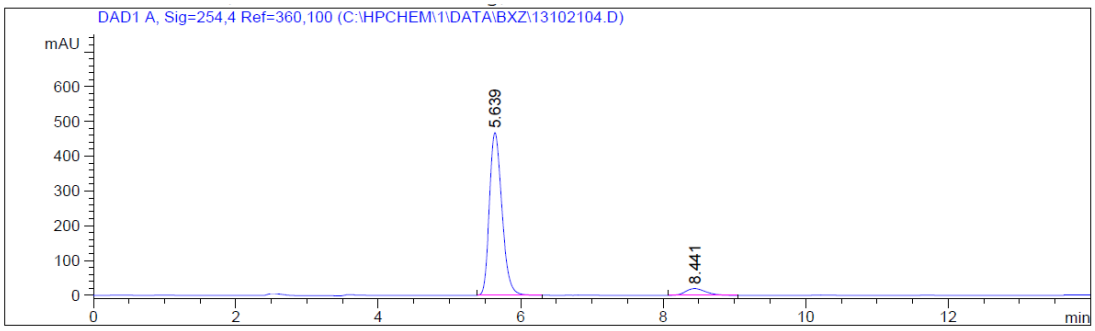


3k

Prepared according to the general procedure with a reaction time of 20 min as yellow oil (57.0 mg, 92% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{17}$ = -83.1 (*c* 0.53, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.50-7.43 (m, 5H), 7.25 (t, *J* = 7.4 Hz, 1H), 5.44-5.34 (m, 1H), 5.09-5.04 (m, 2H), 3.21-3.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 155.4, 137.5, 131.2, 129.2, 129.1, 128.3, 126.8, 126.0, 122.7, 119.2, 63.5, 42.2; IR (KBr): 2920, 2852, 1729, 1597, 1498, 1390, 1325, 1127, 755, 690, 646 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{18}H_{16}ClN_2O$ ($[M+H]^+$) 311.0946, Found 311.0953; Enantiomeric excess was determined to be 88% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 5.6 min, t_{minor} = 8.4 min).

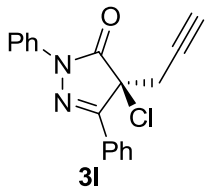


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.652	BV	0.1927	2279.29883	183.71118	49.4040
2	8.465	BB	0.3274	2334.28857	111.86646	50.5960



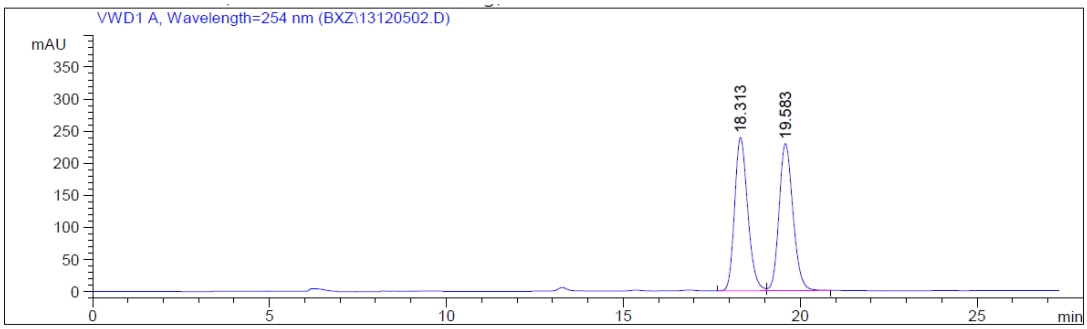
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.639	BB	0.1862	5690.99316	466.82718	93.9020
2	8.441	BB	0.3061	369.57425	19.07324	6.0980

(*S*)-4-chloro-1,3-diphenyl-4-(prop-2-ynyl)-1*H*-pyrazol-5(4*H*)-one (3l)

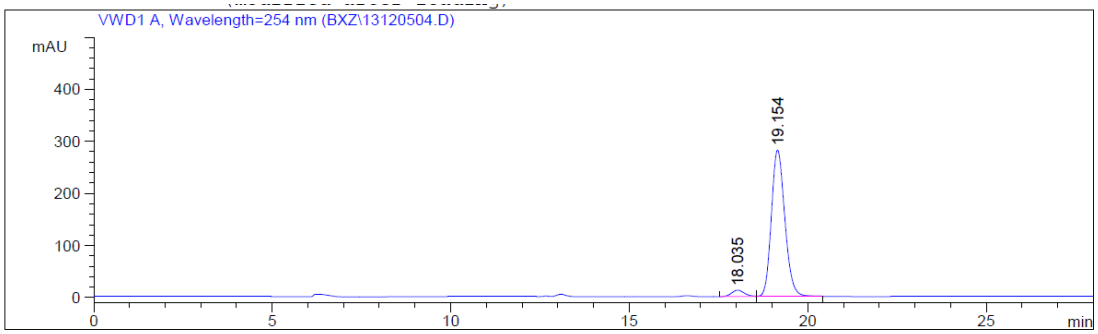


3l

Prepared according to the general procedure with a reaction time of 20 min as yellow oil (54.8 mg, 89% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{20}$ = -98.9 (*c* 0.31, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.00 (m, 4H), 7.53-7.44 (m, 5H), 7.26 (dd, *J* = 12.1, 4.6 Hz, 1H), 3.34 (dd, *J* = 16.4, 2.6 Hz, 1H), 3.22 (dd, *J* = 16.4, 2.6 Hz, 1H), 1.94 (t, *J* = 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 154.8, 137.4, 131.2, 129.1, 129.0, 128.8, 126.8, 126.0, 119.2, 75.0, 72.9, 62.1, 28.2; IR (KBr): 3295, 2912, 1728, 1597, 1493, 1392, 1326, 1135, 756, 689, 644 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{18}H_{14}ClN_2O$ ($[M+H]^+$) 309.0789, Found 309.0779; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 19.2 min, t_{minor} = 18.0 min).

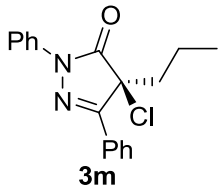


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.313	BV	0.3968	6158.51367	238.96628	49.5592
2	19.583	VB	0.4223	6268.07373	229.31981	50.4408



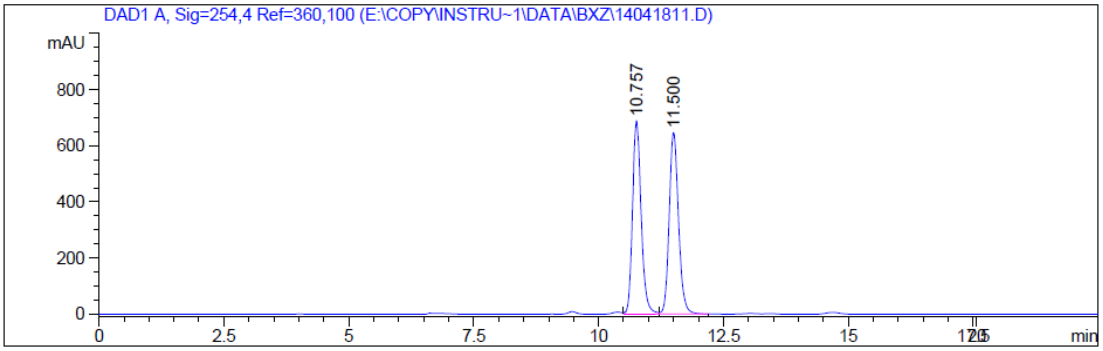
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.035	BV	0.3868	297.71979	12.07114	3.8901
2	19.154	VB	0.4041	7355.51904	281.23947	96.1099

(*S*)-4-chloro-1,3-diphenyl-4-propyl-1*H*-pyrazol-5(4*H*)-one (3m)

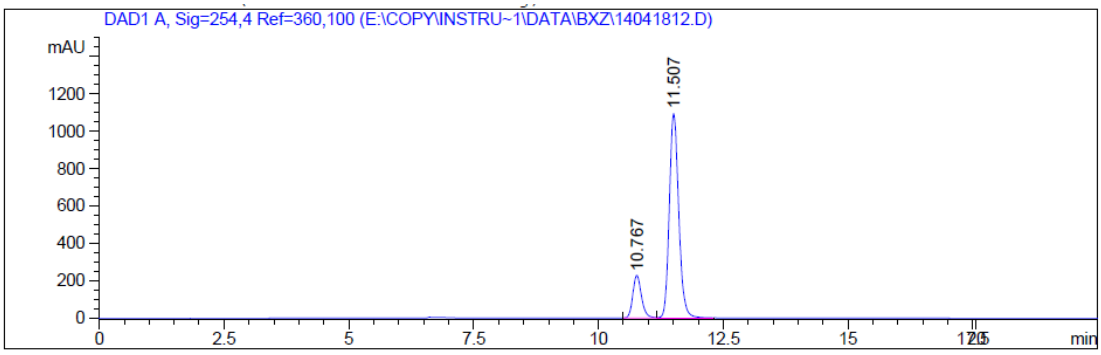


3m

Prepared according to the general procedure with a reaction time of 20 min as yellow oil (58.0 mg, 93% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{25}$ = -56.6 (*c* 0.44, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.01 (m, 4H), 7.50-7.43 (m, 5H), 7.27-7.23 (m, 1H), 2.47-2.32 (m, 2H), 1.18-1.10 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 155.9, 137.5, 131.2, 129.1, 129.0, 126.7, 125.8, 119.0, 64.3, 40.2, 17.8, 13.7; IR (KBr): 2957, 2927, 2867, 1730, 1597, 1498, 1390, 1323, 1130, 756, 689, 644 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{18}H_{18}ClN_2O$ ($[M+H]^+$) 313.1102, Found 313.1109; Enantiomeric excess was determined to be 68% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 11.5 min, t_{minor} = 10.7 min).

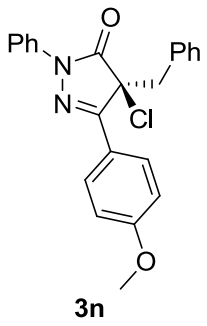


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.757	VV	0.1849	8334.56152	689.89709	49.7901
2	11.500	VB	0.1996	8404.83008	646.67889	50.2099



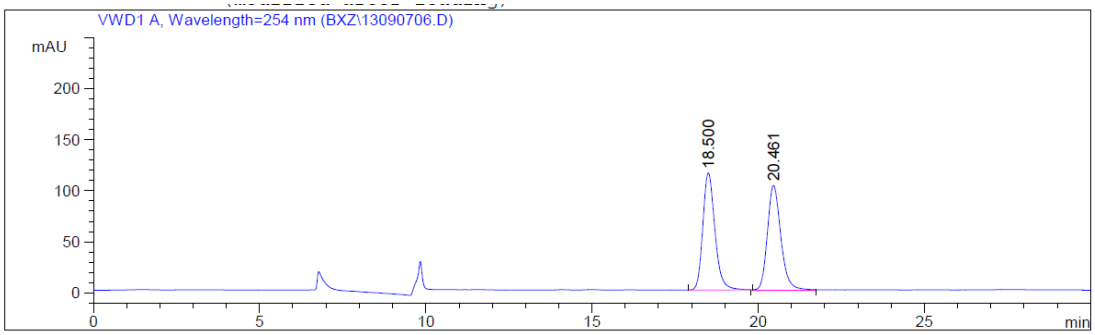
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.767	BV	0.1849	2757.83521	228.30801	16.1244
2	11.507	VB	0.2029	1.43457e4	1094.76465	83.8756

(*S*)-4-benzyl-4-chloro-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-5(4*H*)-one (3n)

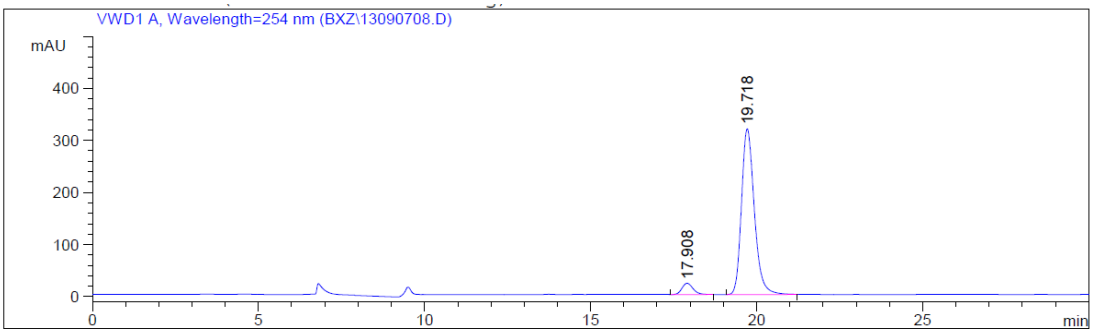


3n

Prepared according to the general procedure with a reaction time of 20 min as yellow oil (69.4 mg, 89% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/15). $[\alpha]_D^{21}$ = -44.7 (*c* 0.65, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.10-7.01 (m, 5H), 6.87 (d, *J* = 7.0 Hz, 2H), 3.90 (s, 3H), 3.74 (d, *J* = 13.1 Hz, 1H), 3.66 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 161.8, 154.9, 137.2, 132.0, 129.8, 128.9, 128.5, 128.4, 128.0, 125.8, 122.2, 119.5, 114.4, 64.6, 55.5, 44.2; IR (KBr): 2935, 1724, 1606, 1516, 1499, 1393, 1326, 1259, 1177, 1132, 1027, 837, 753, 700, 601, 582, 556 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{23}H_{20}ClN_2O_2$ ($[M+H]^+$) 391.1208, Found 391.1193; Enantiomeric excess was determined to be 89% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 19.7 min, t_{minor} = 17.9 min).

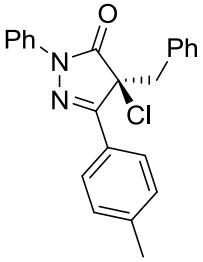


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.500	BB	0.3904	2886.37427	114.42172	50.4117
2	20.461	BB	0.4314	2839.22681	101.87477	49.5883



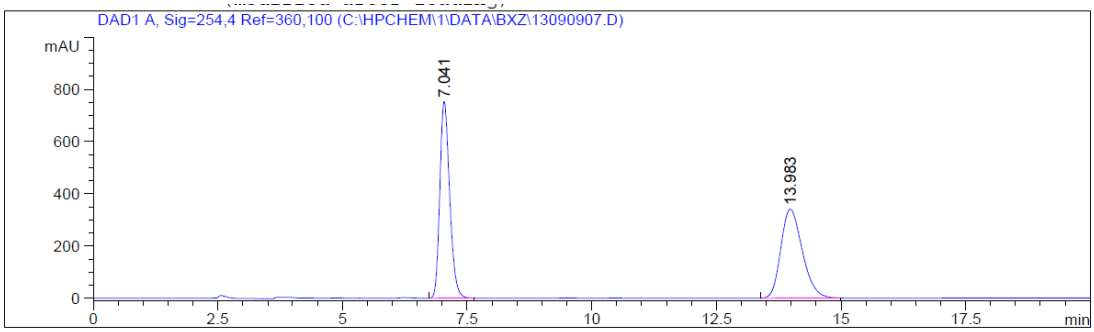
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.908	BB	0.3604	512.56934	21.90541	5.6564
2	19.718	BB	0.4107	8549.11035	318.47806	94.3436

(S)-4-benzyl-4-chloro-1-phenyl-3-p-tolyl-1*H*-pyrazol-5(4*H*)-one (3o)

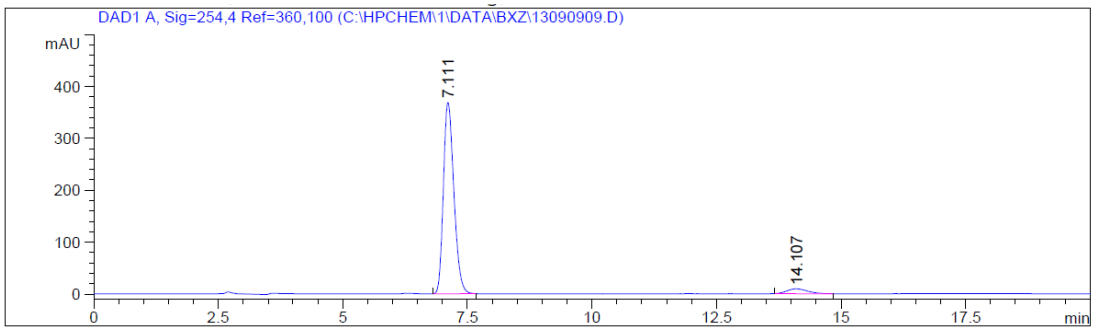


3o

Prepared according to the general procedure with a reaction time of 20 min as yellow oil (68.0 mg, 91% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{21}$ = -59.5 (*c* 0.58, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.71-7.72 (m, 2H), 7.37-7.30 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.10-7.02 (m, 3H), 6.87-6.85 (m, 2H), 3.74 (d, *J* = 13.2 Hz, 1H), 3.68 (d, *J* = 13.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 155.2, 141.5, 137.2, 132.0, 129.8, 128.9, 128.4, 128.0, 126.9, 126.8, 125.9, 119.6, 64.6, 44.2, 21.7; IR (KBr): 3032, 2920, 1726, 1597, 1499, 1391, 1352, 1183, 1131, 820, 755, 727, 700 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{23}H_{20}ClN_2O$ ($[M+H]^+$) 375.1259, Found 375.1245; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 7.1 min, t_{minor} = 14.1 min).

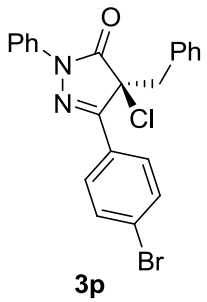


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.041	BB	0.2120	1.03190e4	752.33301	50.3774
2	13.983	BB	0.4645	1.01644e4	340.25671	49.6226



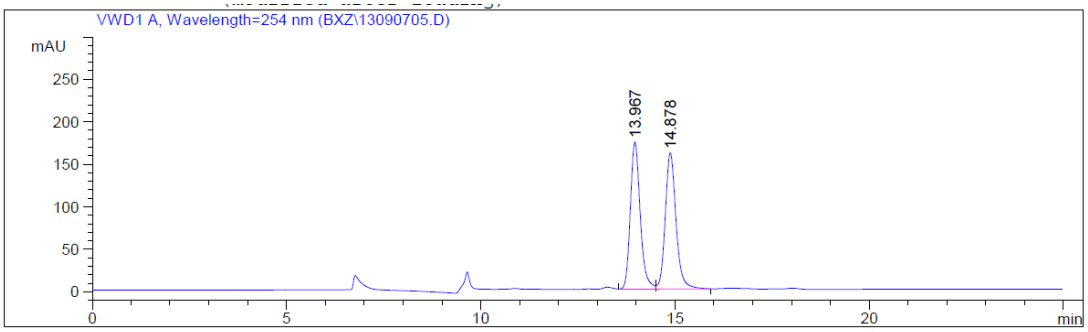
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.111	BB	0.2250	5398.69531	368.35184	95.3403
2	14.107	BB	0.4120	263.85892	9.27254	4.6597

(*S*)-4-benzyl-3-(4-bromophenyl)-4-chloro-1-phenyl-1*H*-pyrazol-5(4*H*)-one (3p)

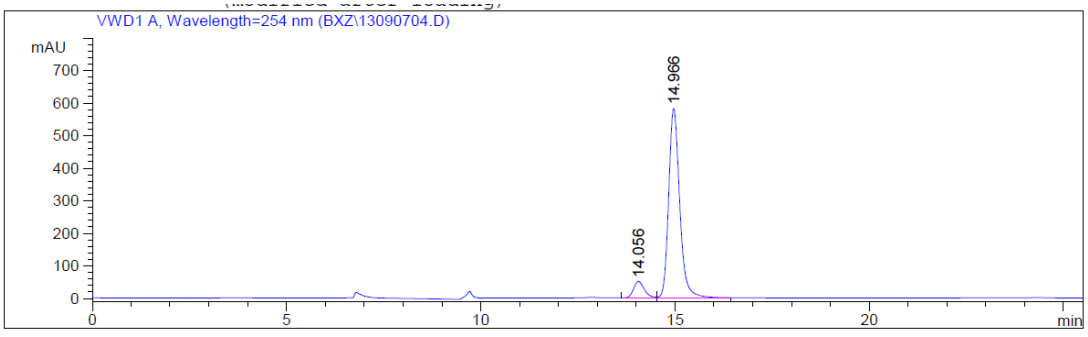


3p

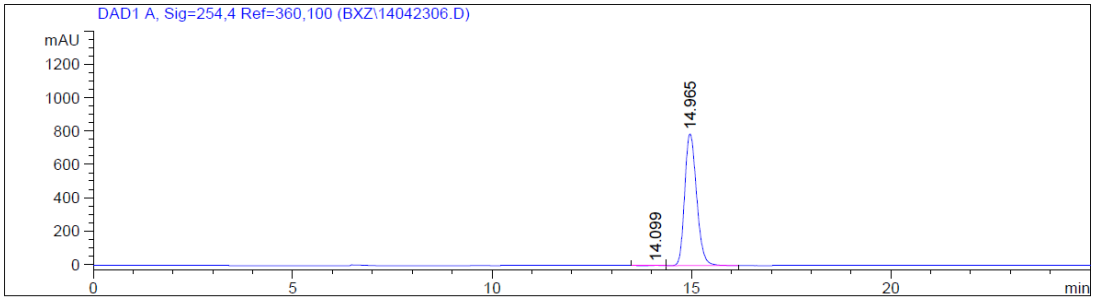
Prepared according to the general procedure with a reaction time of 30 min as yellow solid (83.2 mg, 95% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). Mp: 114.7-116.2 ^{o}C; $[\alpha]_D^{21}$ = -19.8 (*c* 0.64, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.90 (m, 2H), 7.70-7.62 (m, 4H), 7.36 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.11-7.03 (m, 3H), 6.84 (d, *J* = 7.1 Hz, 2H), 3.75 (d, *J* = 13.2 Hz, 1H), 3.62 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 154.2, 137.0, 132.3, 131.7, 129.7, 128.9, 128.6, 128.5, 128.2, 126.2, 125.6, 119.6, 64.2, 44.1; IR (KBr): 3035, 2920, 1728, 1597, 1499, 1385, 1323, 1131, 1073, 1010, 829, 755, 727, 700 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{22}H_{16}BrClN_2NaO$ ([M+Na]$^+$) 461.0027, Found 461.0006; Enantiomeric excess was determined to be 84%, 99% after recrystallization by ester/hexane (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 ^{o}C, 0.5 mL/min, t_{major} = 15.0 min, t_{minor} = 14.0 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.967	VV	0.2699	3054.46045	173.09416	49.7904
2	14.878	VB	0.2928	3080.17236	160.13545	50.2096



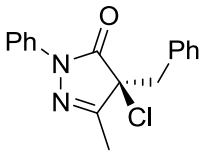
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.056	VV	0.2947	966.49579	50.47221	7.8139
2	14.966	VB	0.3017	1.14024e4	581.12915	92.1861



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	14.099	BV	0.2353	34.36007	0.2094	?
2	14.965	VV	0.3244	1.63760e4	99.7906	?

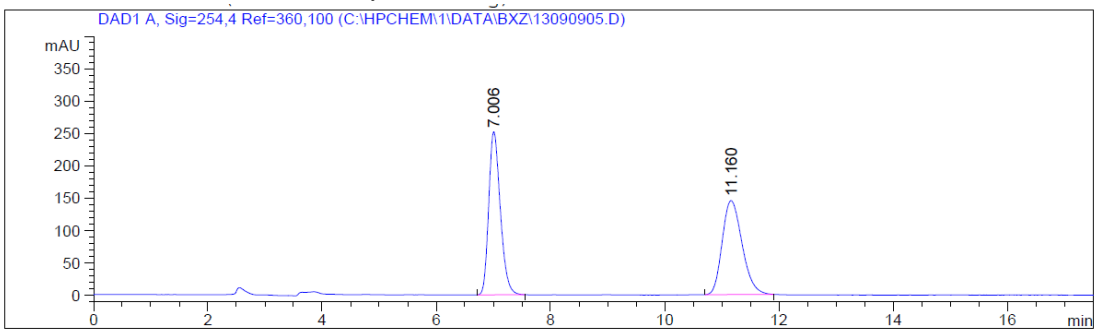
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.660	VB	0.3335	1.01070e4	462.68948	81.5969
2	17.293	BB	0.3629	2279.49219	95.49428	18.4031

(*S*)-4-benzyl-4-chloro-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (3q)

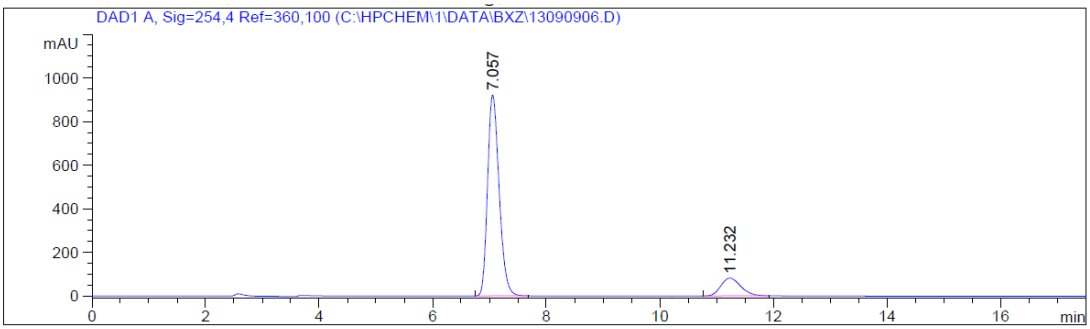


3q

Prepared according to the general procedure with a reaction time of 30 min as colorless oil (54.4 mg, 91% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{21}$ = -117.6 (*c* 0.48, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H), 7.35-7.31 (m, 2H), 7.25-7.13 (m, 6H), 3.62 (d, *J* = 13.6 Hz, 1H), 3.28 (d, *J* = 13.6 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 157.8, 137.1, 132.3, 129.4, 128.9, 128.8, 128.2, 125.7, 119.2, 65.7, 42.6, 13.7; IR (KBr): 3032, 2920, 1723, 1596, 1500, 1400, 1367, 1321, 1116, 756, 724, 699 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{17}H_{16}ClN_2O$ ($[M+H]^+$) 299.0946, Found 299.0936; Enantiomeric excess was determined to be 74% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 ^{o}C, 0.5 mL/min, t_{major} = 7.1 min, t_{minor} = 11.2 min).

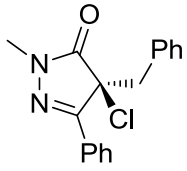


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.006	BB	0.2162	3546.35498	251.93922	50.2483
2	11.160	BB	0.3802	3511.30078	145.18736	49.7517



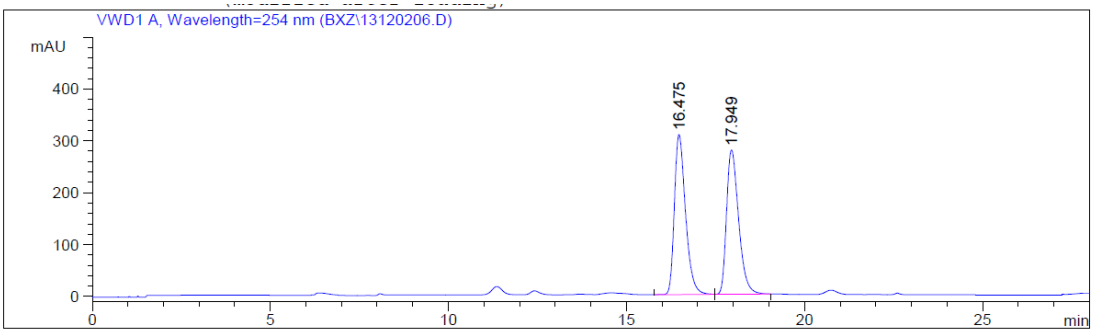
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.057	BB	0.2188	1.30150e4	921.39929	86.8512
2	11.232	BB	0.3810	1970.40698	81.22446	13.1488

(*S*)-4-benzyl-4-chloro-1-methyl-3-phenyl-1*H*-pyrazol-5(4*H*)-one (3r)

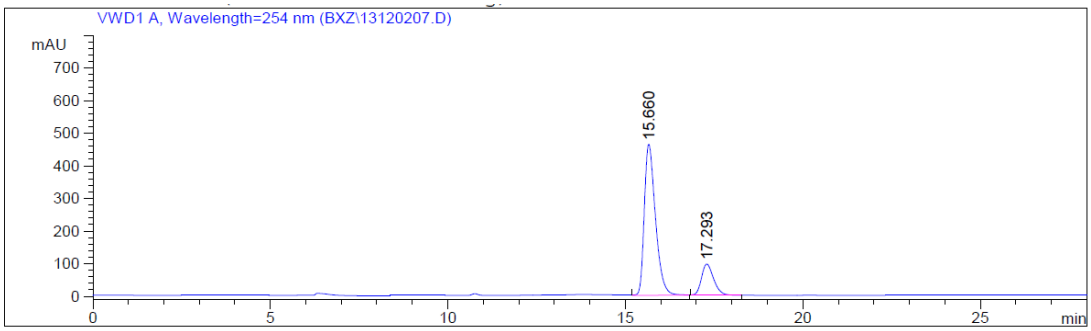


3r

Prepared according to the general procedure with a reaction time of 50 min as colorless oil (54.1 mg, 91% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{20}$ = 11.0 (*c* 0.41, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.49-7.46 (m, 3H), 7.18-7.01 (m, 3H), 6.81 (d, *J* = 7.5 Hz, 2H), 3.62 (s, 2H), 3.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 154.6, 132.1, 130.7, 129.8, 129.0, 128.3, 127.9, 126.4, 63.3, 43.7, 31.6; IR (KBr): 3032, 2920, 1726, 1598, 1392, 1239, 1017, 760, 728, 698 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{17}H_{16}ClN_2O$ ($[M+H]^+$) 299.0946, Found 299.0935; Enantiomeric excess was determined to be 63% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 15.7 min, t_{minor} = 17.3 min).

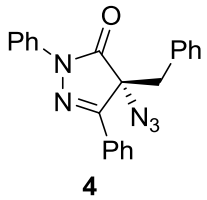


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.475	BV	0.3327	6714.25439	308.32950	50.6239
2	17.949	VB	0.3635	6548.75830	278.12384	49.3761



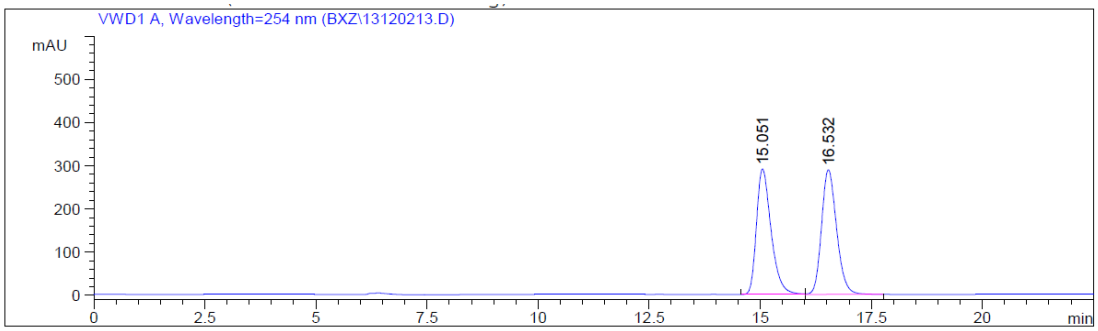
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.660	VB	0.3335	1.01070e4	462.68948	81.5969
2	17.293	BB	0.3629	2279.49219	95.49428	18.4031

(*R*)-4-azido-4-benzyl-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (4)

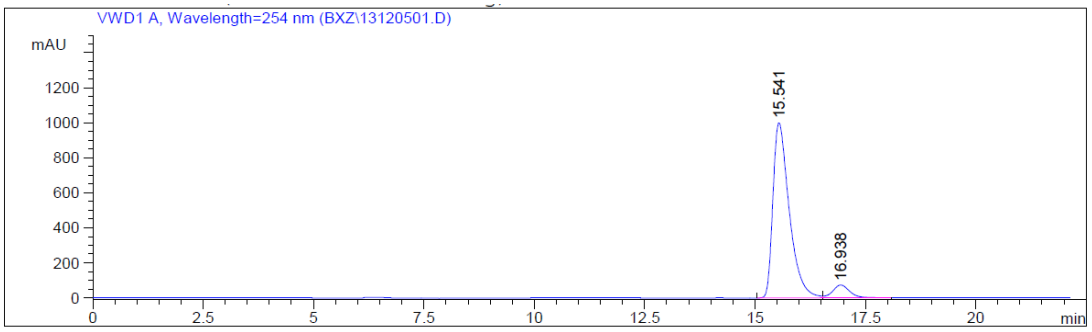


4

Prepared according to the procedure as oil (66.1 mg, 90% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{17}$ = 232.2 (*c* 0.24, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 2H), 7.68-7.65 (m, 2H), 7.53-7.48 (m, 3H), 7.38-7.34 (m, 2H), 7.22-7.18 (m, 1H), 7.14-7.04 (m, 3H), 6.86-6.84 (m, 2H), 3.57 (d, *J* = 12.8 Hz, 1H), 3.46 (d, *J* = 12.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 154.9, 136.9, 131.3, 131.1, 129.8, 129.7, 129.0, 128.9, 128.4, 128.0, 126.8, 126.0, 119.5, 69.9, 41.4; IR (KBr): 3068, 2913, 2108, 1716, 1597, 1495, 1392, 1250, 1131, 756, 723, 690 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{22}H_{17}N_5NaO$ ([M+Na]$^+$) 390.1325, Found 390.1312; Enantiomeric excess was determined to be 86% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 98/2, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 15.5 min, t_{minor} = 16.9 min).

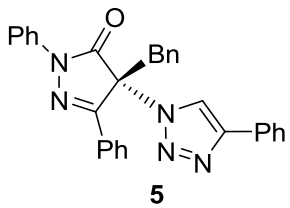


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.051	BV	0.3489	6656.18945	290.48590	49.4519
2	16.532	VB	0.3626	6803.74268	288.39896	50.5481



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.541	PV	0.3868	2.56648e4	999.93011	92.9016
2	16.938	VB	0.4063	1961.00342	73.40585	7.0984

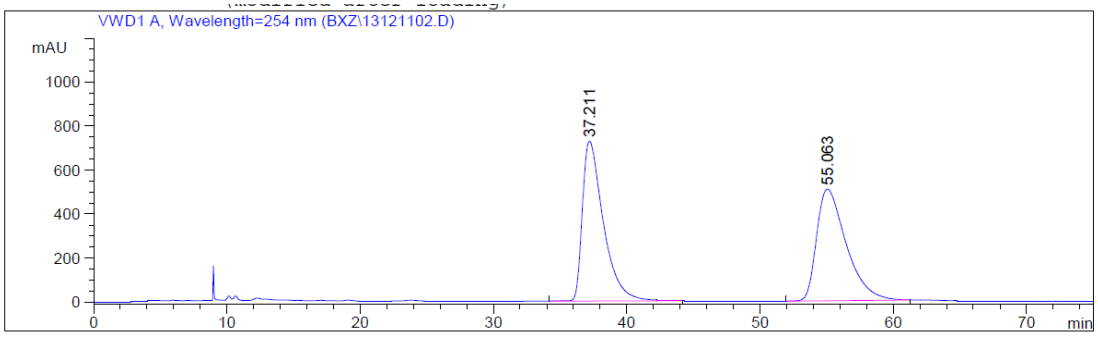
(*R*)-4-benzyl-1,3-diphenyl-4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-1*H*-pyrazol-5(4*H*)-one (5)



5

Prepared according to the procedure as white foam (60.2 mg, 80% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{19}$ = 48.2 (*c* 0.40, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.68-7.46 (m, 4H), 7.48-7.32 (m, 8H), 7.24-7.14 (m, 2H), 7.10 (t, *J* = 7.3 Hz, 2H), 6.96 (d, *J* = 7.1 Hz, 2H), 4.26 (d, *J* = 12.7 Hz,

1H), 4.18 (d, J = 12.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 154.3, 148.7, 136.8, 131.3, 130.4, 130.1, 129.9, 129.3, 128.9, 128.7, 128.4, 128.3, 126.4, 126.3, 126.0, 119.7, 118.5, 73.0, 40.4; IR (KBr): 3062, 2920, 1726, 1597, 1496, 1392, 1120, 1026, 760, 725, 690 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{30}H_{24}N_5O$ ($[M+H]^+$) 470.1975, Found 470.1984; Enantiomeric excess was determined to be 86% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.5 mL/min, t_{major} = 36.9 min, t_{minor} = 56.9 min).



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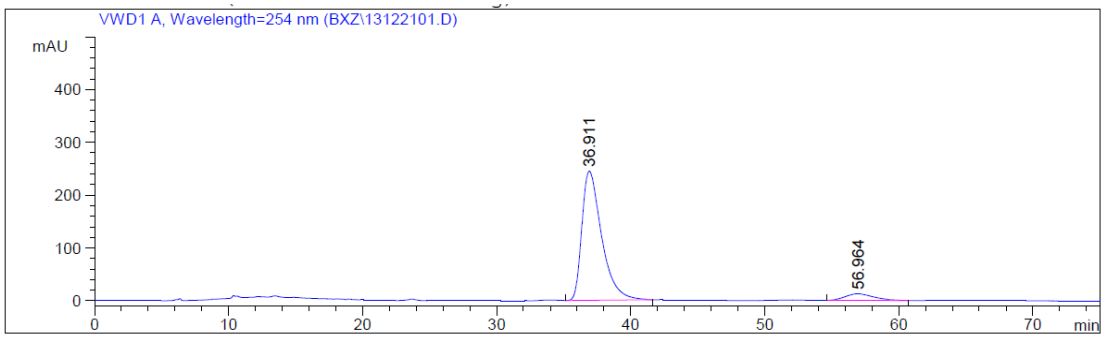
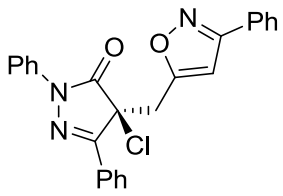
2	55.063	BB	2.3125	7.82087e4	507.32474	49.5956



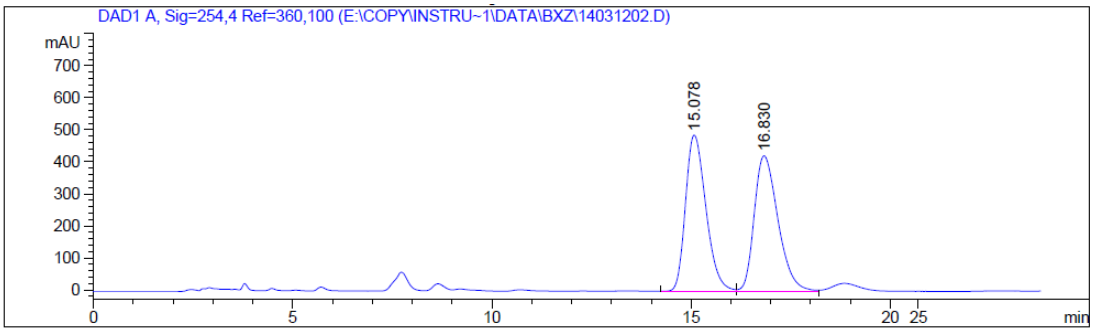
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.911	VB	1.5427	2.50162e4	244.58824	93.3038
2	56.964	BB	1.7138	1795.35583	12.30536	6.6962

(*S*)-4-chloro-1,3-diphenyl-4-((3-phenylisoxazol-5-yl)methyl)-1*H*-pyrazol-5(4*H*)-one (6)

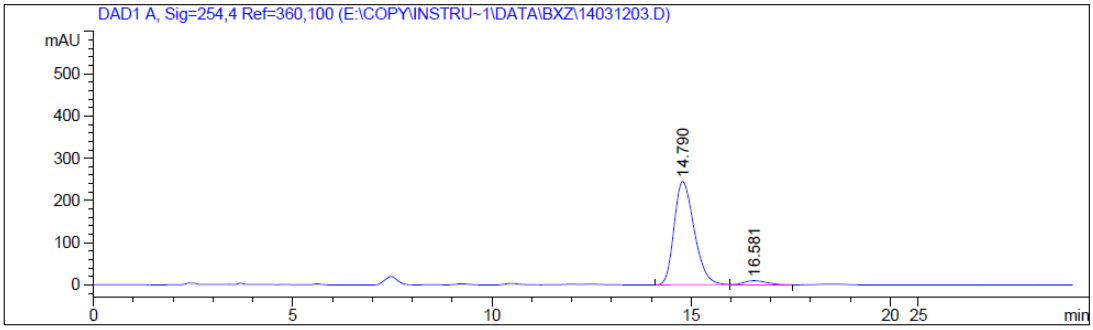


6

Prepared according to the procedure as oil (61.1 mg, 96% yield) after silica gel chromatography (EtOAc/petroleum ether = 1/10). $[\alpha]_D^{20}$ = -20.4 (c 0.46, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 6.3 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.59-7.49 (m, 5H), 7.44-7.35 (m, 5H), 7.26-7.21 (m, 1H), 6.21 (s, 1H), 3.99 (d, J = 14.7 Hz, 1H), 3.92 (d, J = 14.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 164.7, 162.6, 155.1, 137.2, 131.5, 130.3, 129.2, 129.2, 129.0, 128.9, 128.5, 126.9, 126.4, 119.6, 102.1, 61.8, 35.2; IR (KBr): 2950, 2912, 2867, 1721, 1594, 1407, 1389, 1132, 1076, 767, 754, 690 cm^{-1}; HRMS (ESI) m/z Calcd. for $C_{25}H_{19}ClN_3O_2$ ($[M+H]^+$) 428.1160, Found 428.1174; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 9/1, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 14.8 min, t_{minor} = 16.6 min).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.078	PV	0.5552	1.73674e4	487.95114	49.7855
2	16.830	VB	0.6389	1.75170e4	423.16782	50.2145

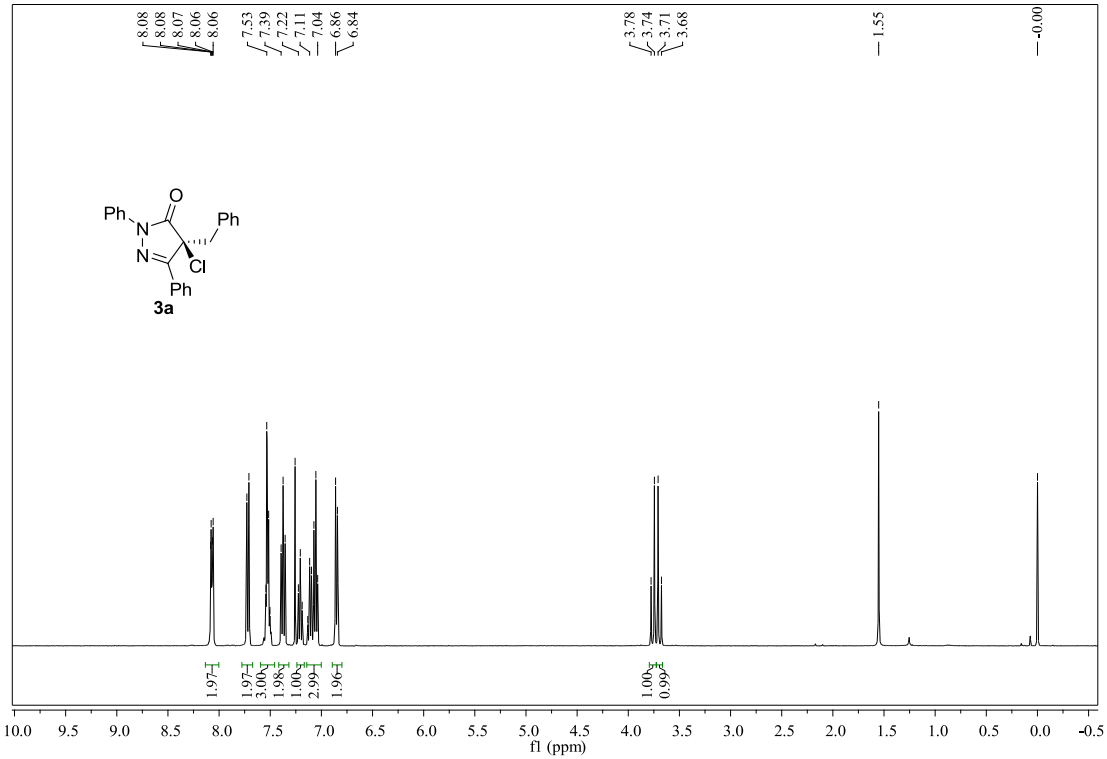


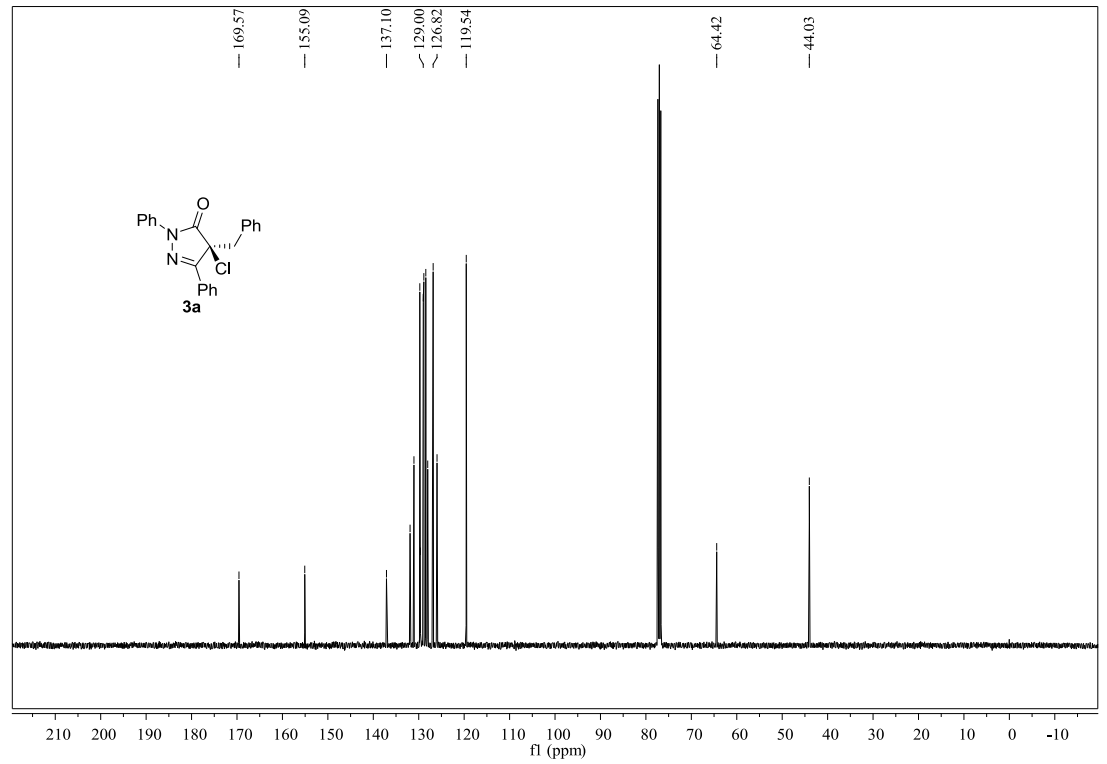
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.790	BB	0.5437	8607.43066	245.13284	95.5849
2	16.581	BB	0.4847	397.58063	9.93860	4.4151

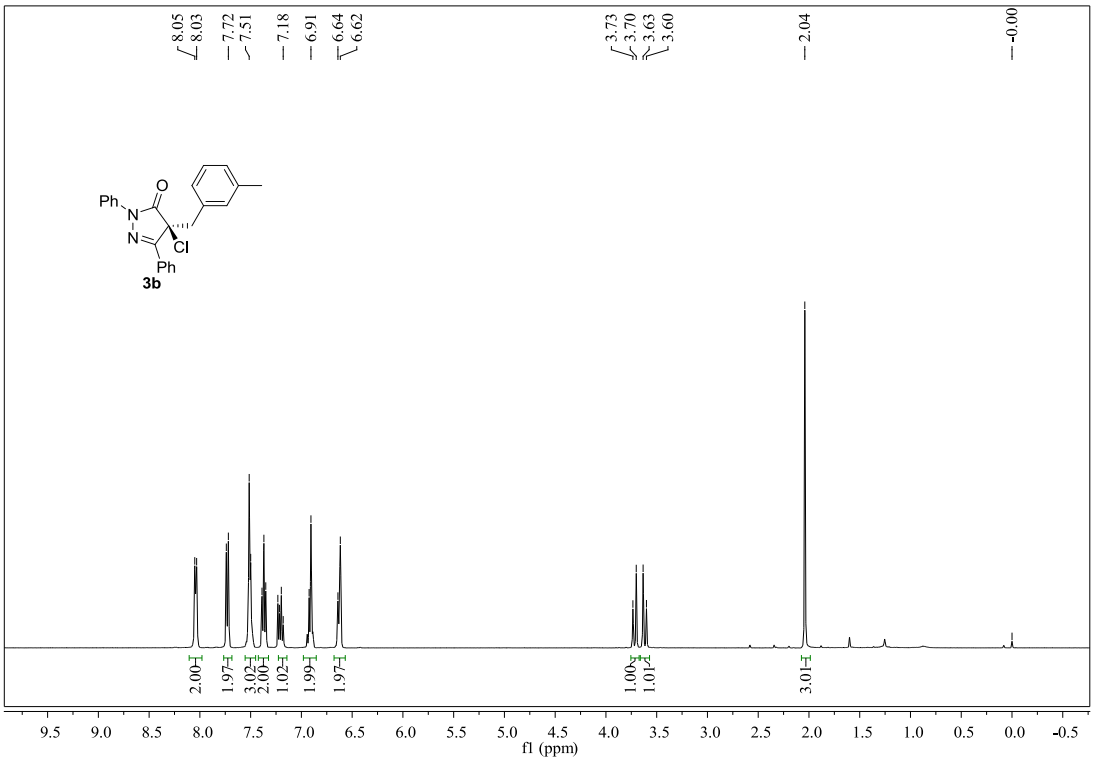
4. Reference

[1] (a) P. E. Gagnon, J. L. Boivin and R. J. Paquin, *Can. J. Chem.* **1953**, *31*,1025; (b) Y.-H. Liao, W.-B. Chen, Z.-J. Wu, X.-L. Du, L.-F. Cun, X.-M. Zhang and W.-C. Yuan, *Adv. Synth. Catal.*, 2010, **352**, 827; (c) Z. Wang, Z. Yang, D. Chen, X. Liu, L. Lin and X. Feng, *Angew. Chem., Int. Ed.*, 2011, **50**, 4928.

5. NMR spectra for compounds



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N
O
Cl
Ph
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2.00
1.02
1.99
1.97
1.00
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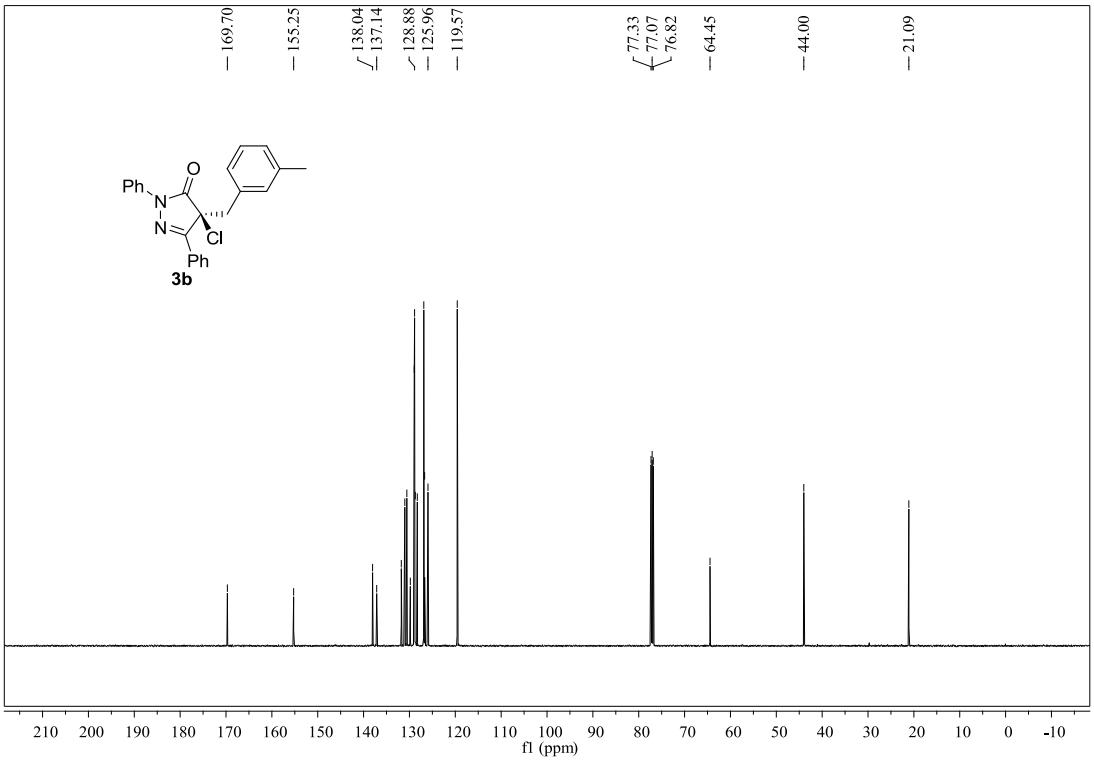
3.01
f1 (ppm)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Ph
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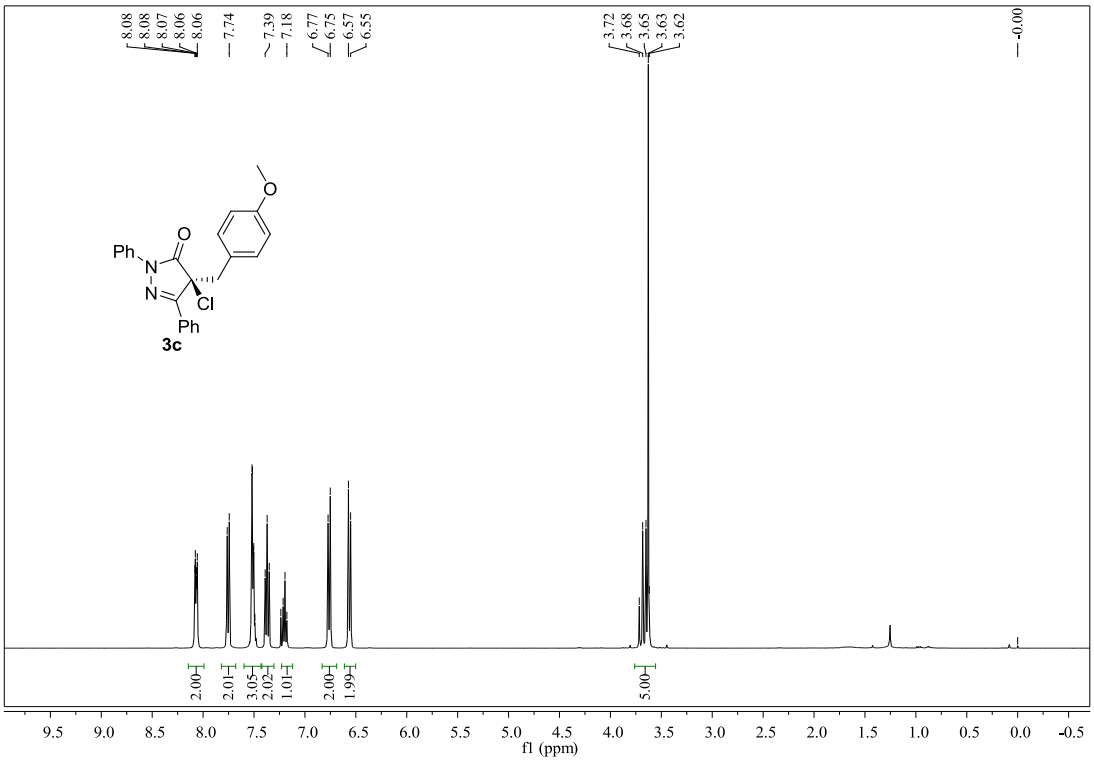
f1 (ppm)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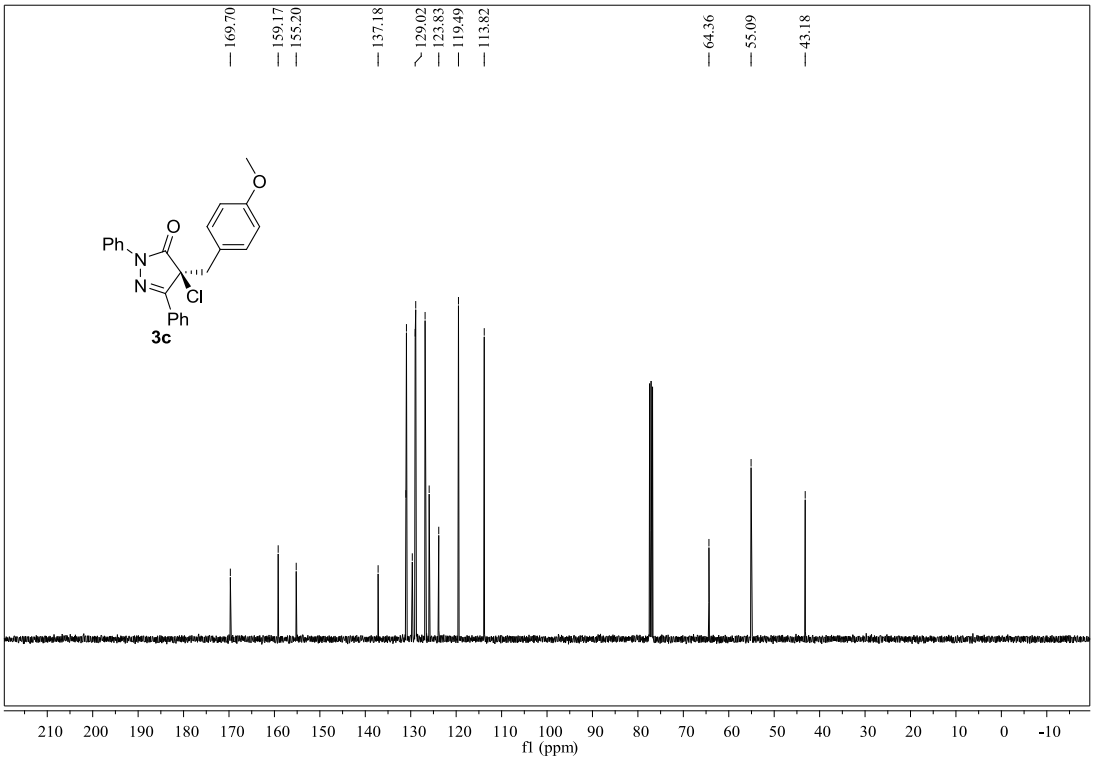
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Cl
Ph
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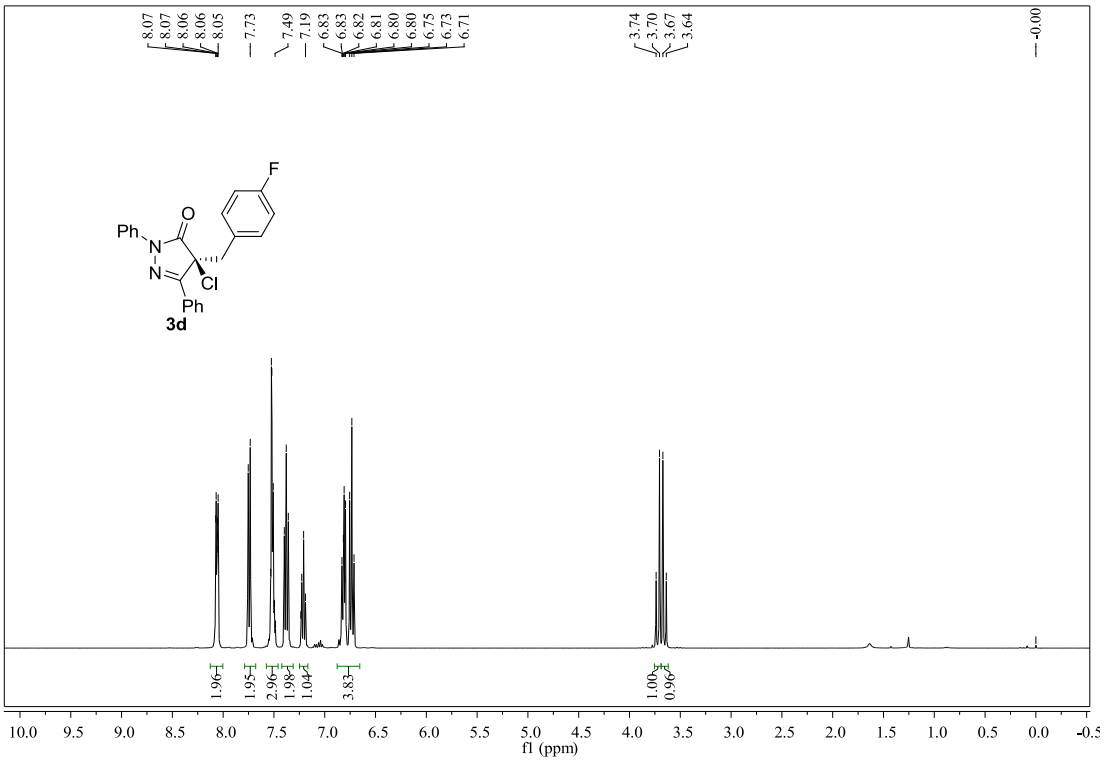
f1 (ppm)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N
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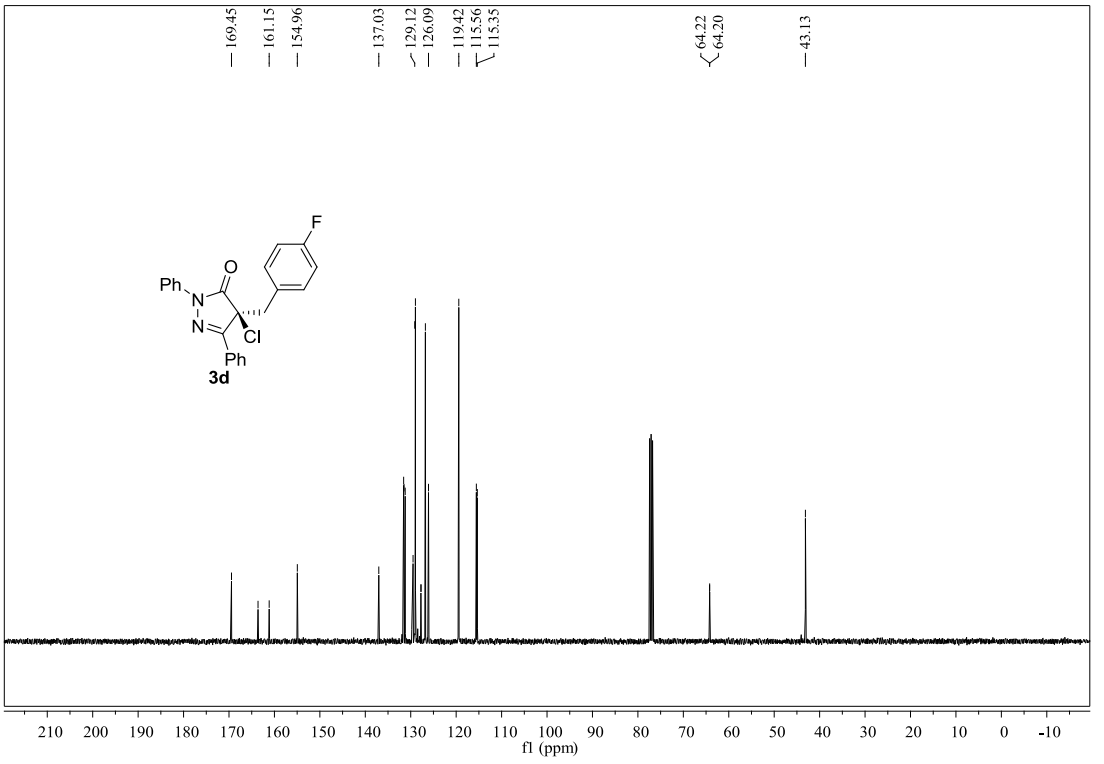
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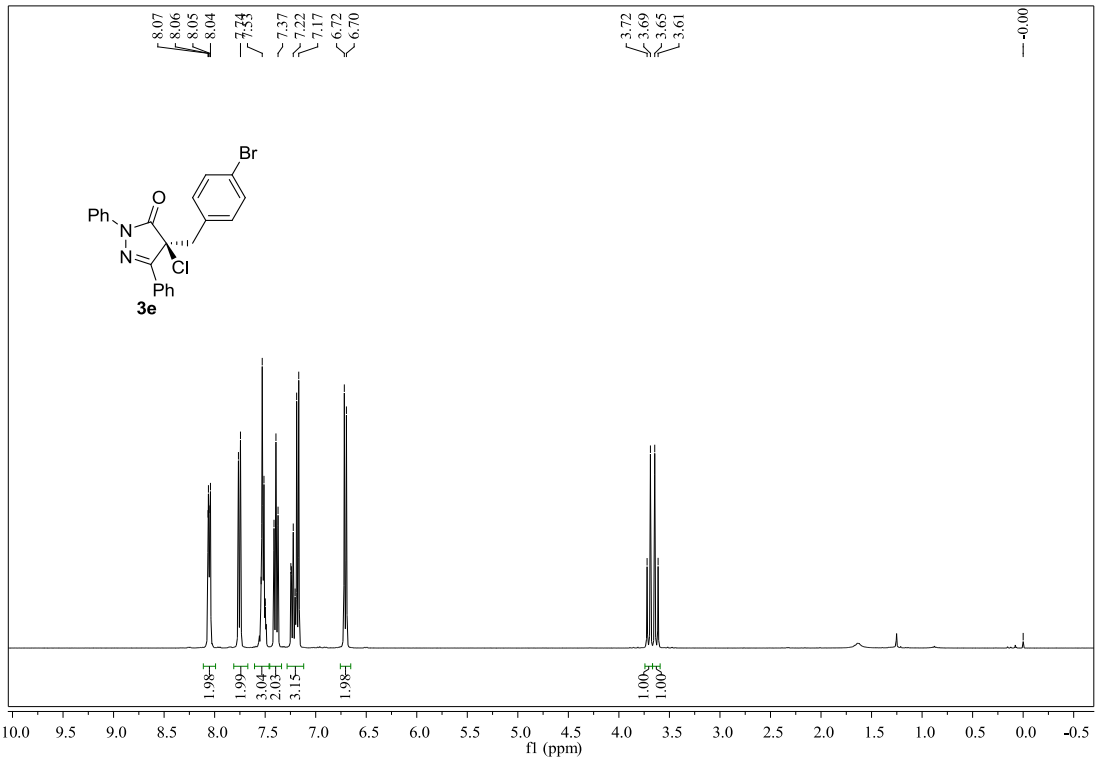
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3.15
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1.00
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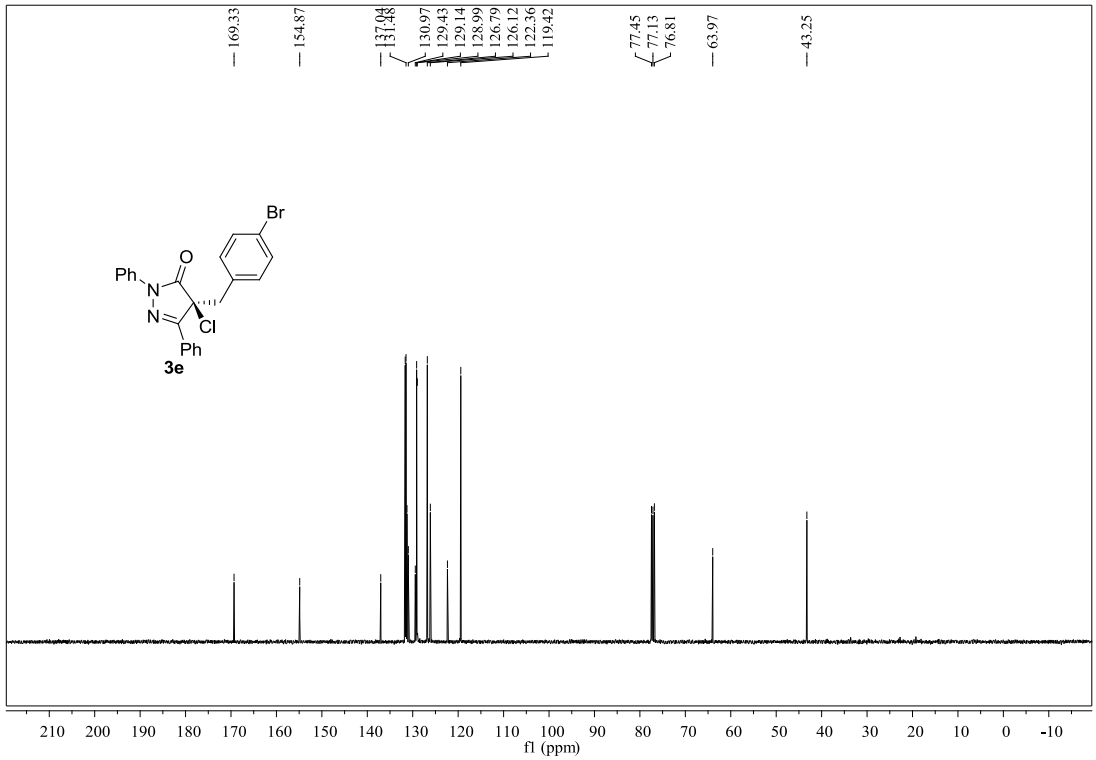
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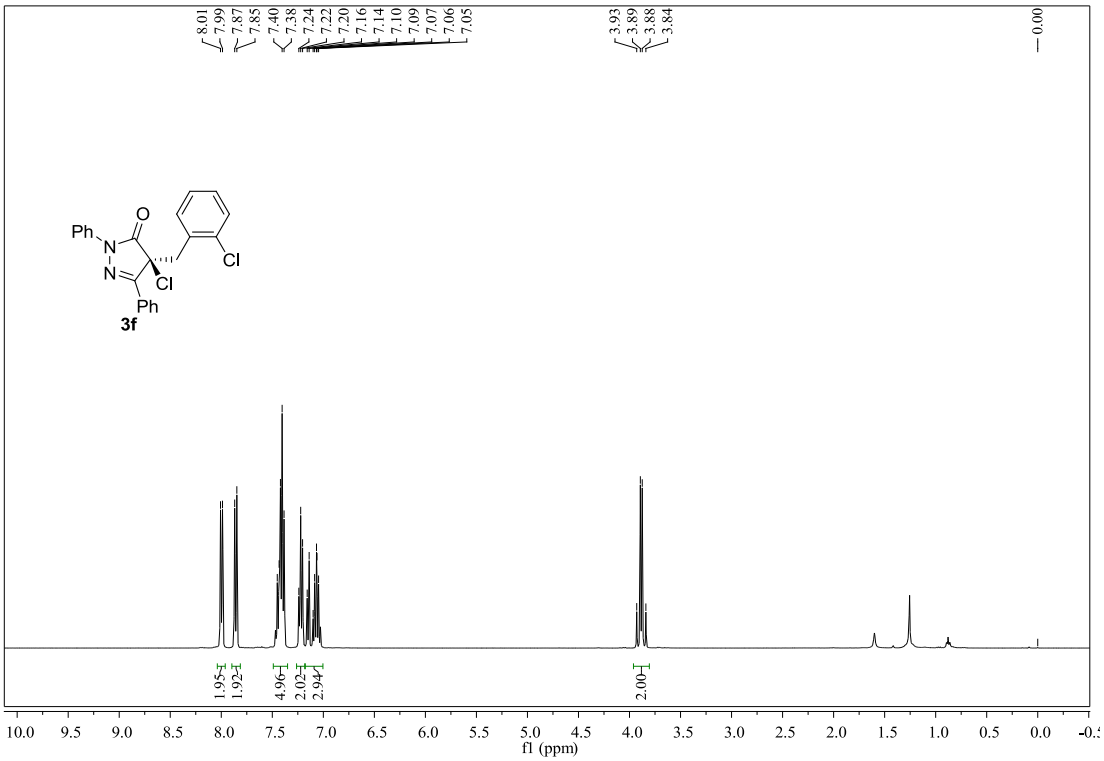
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Cl
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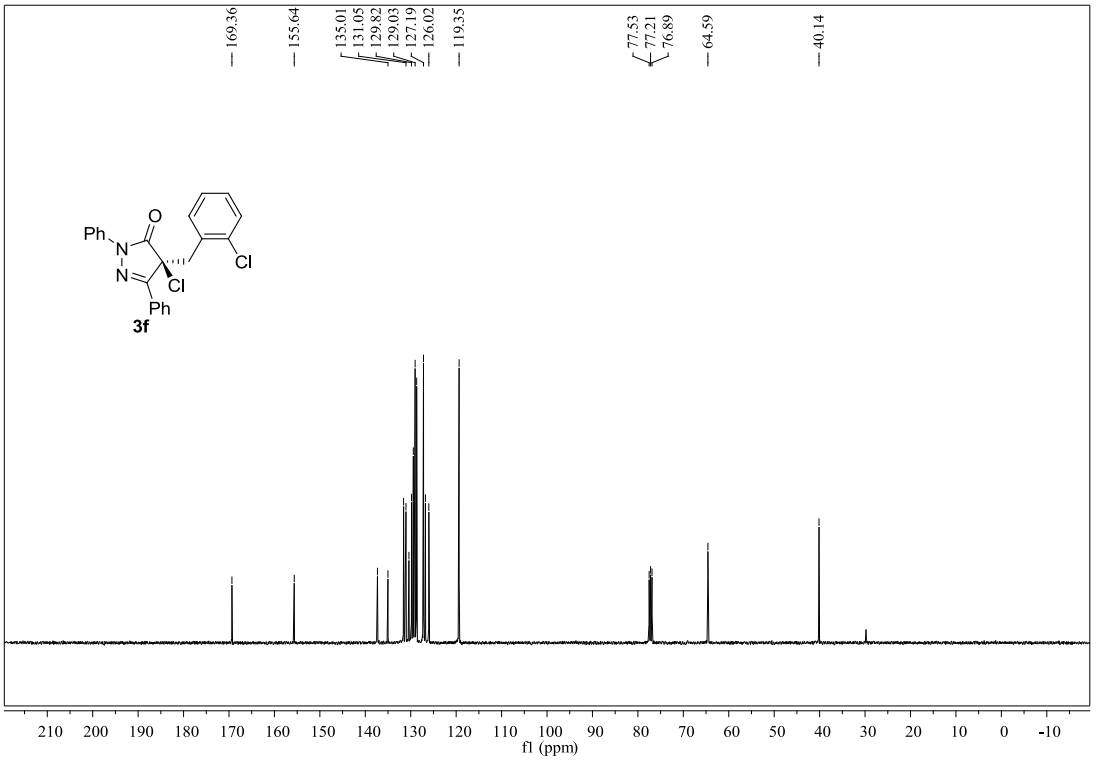
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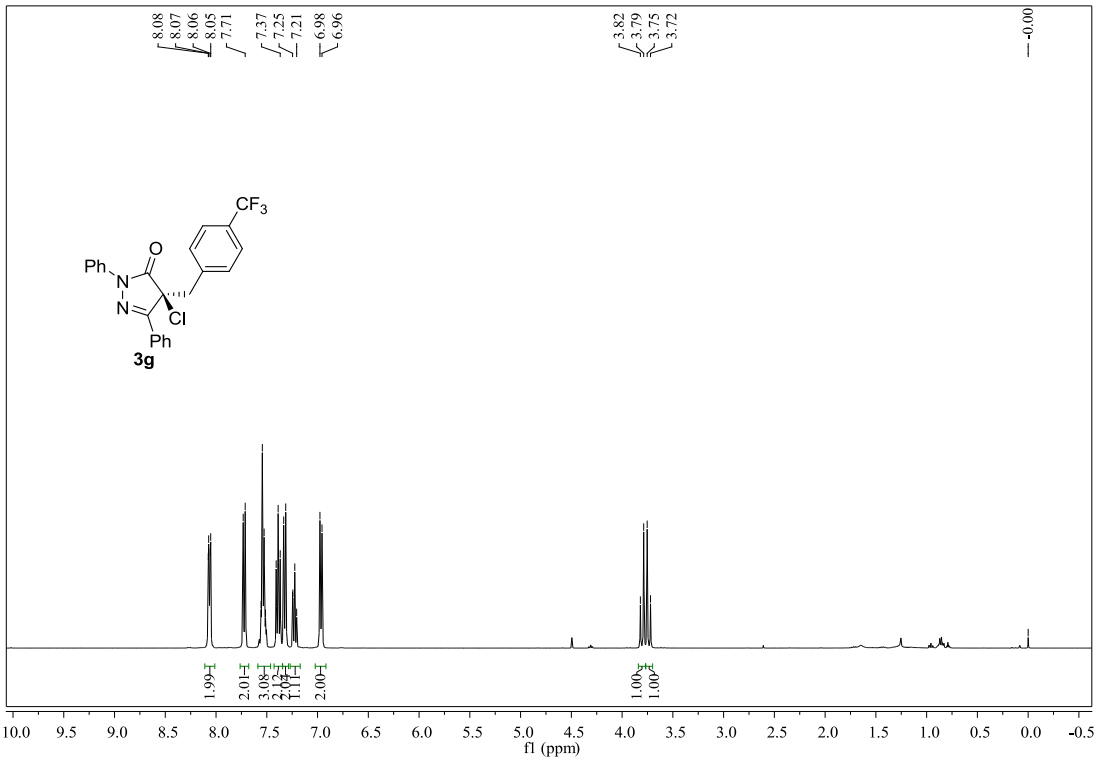
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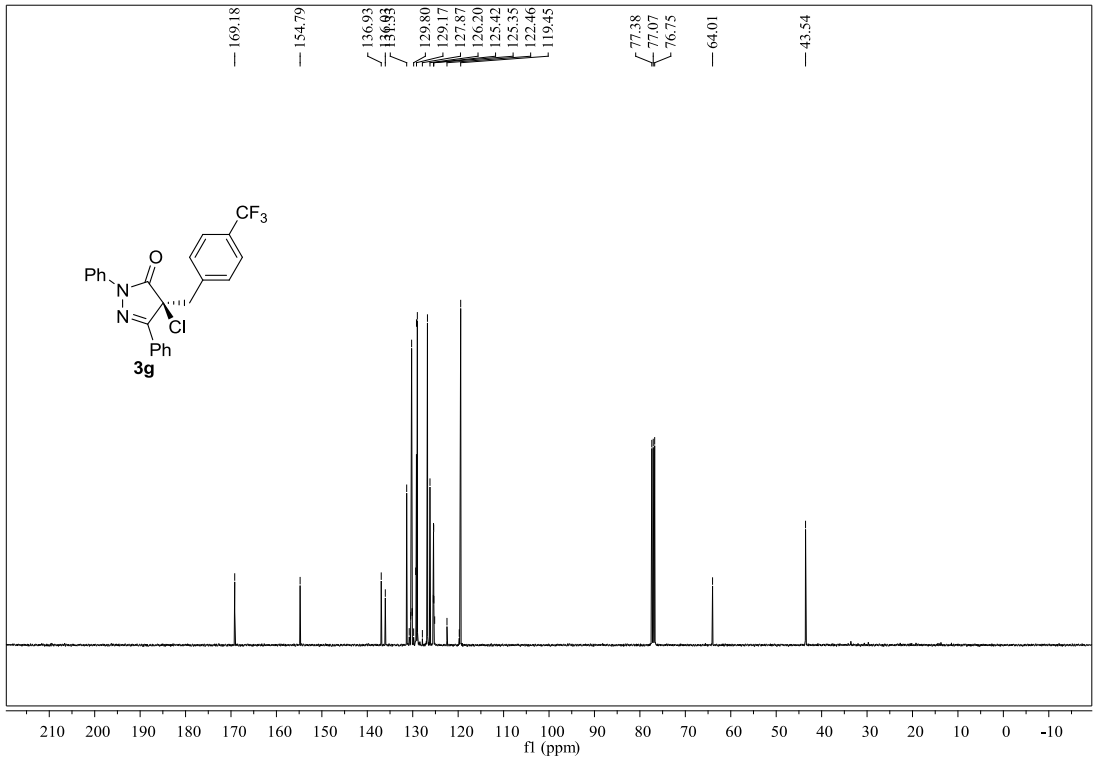
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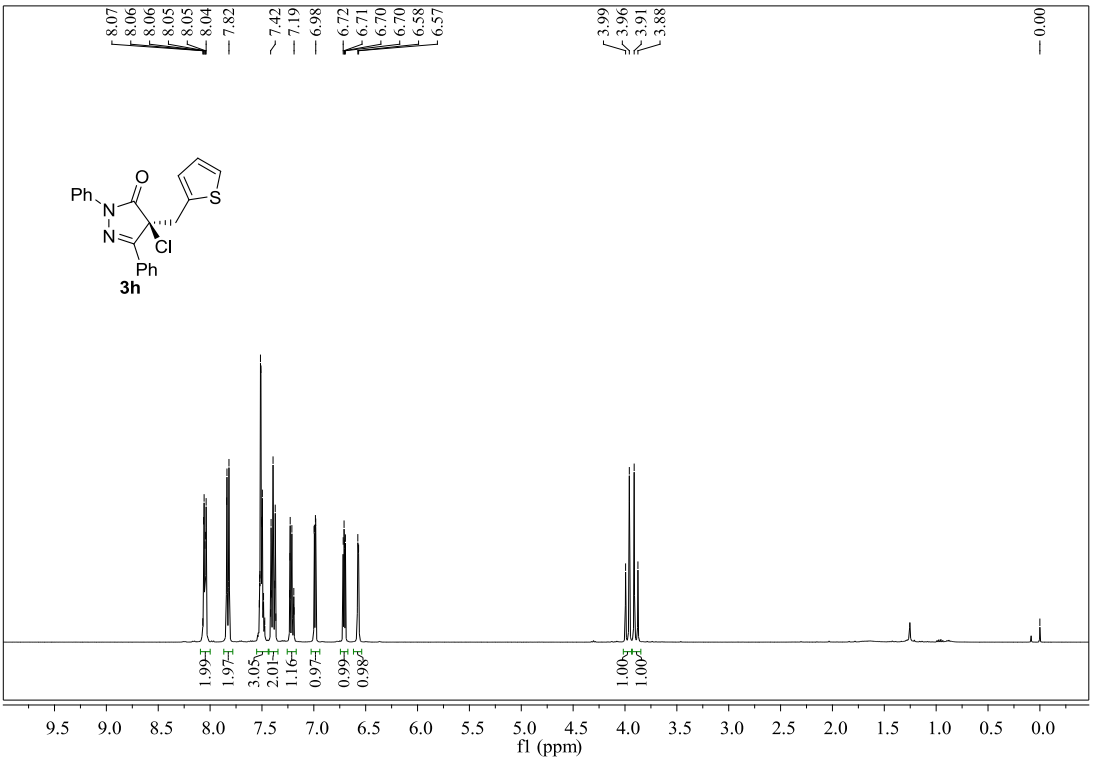
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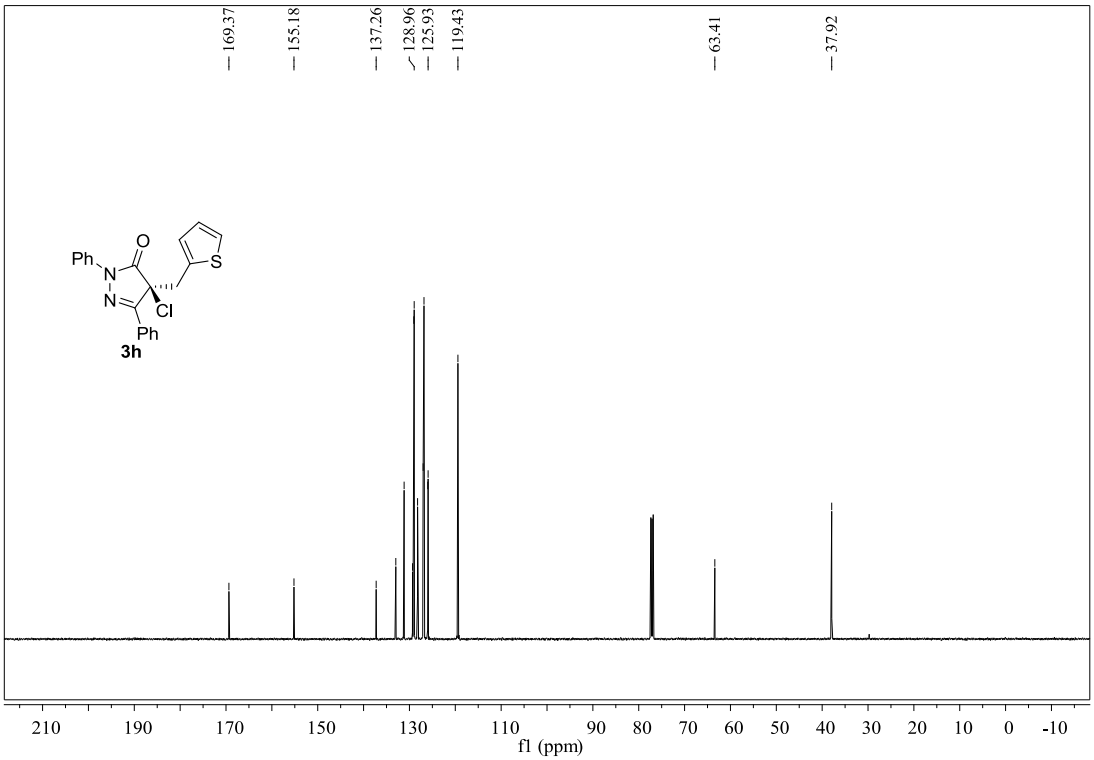
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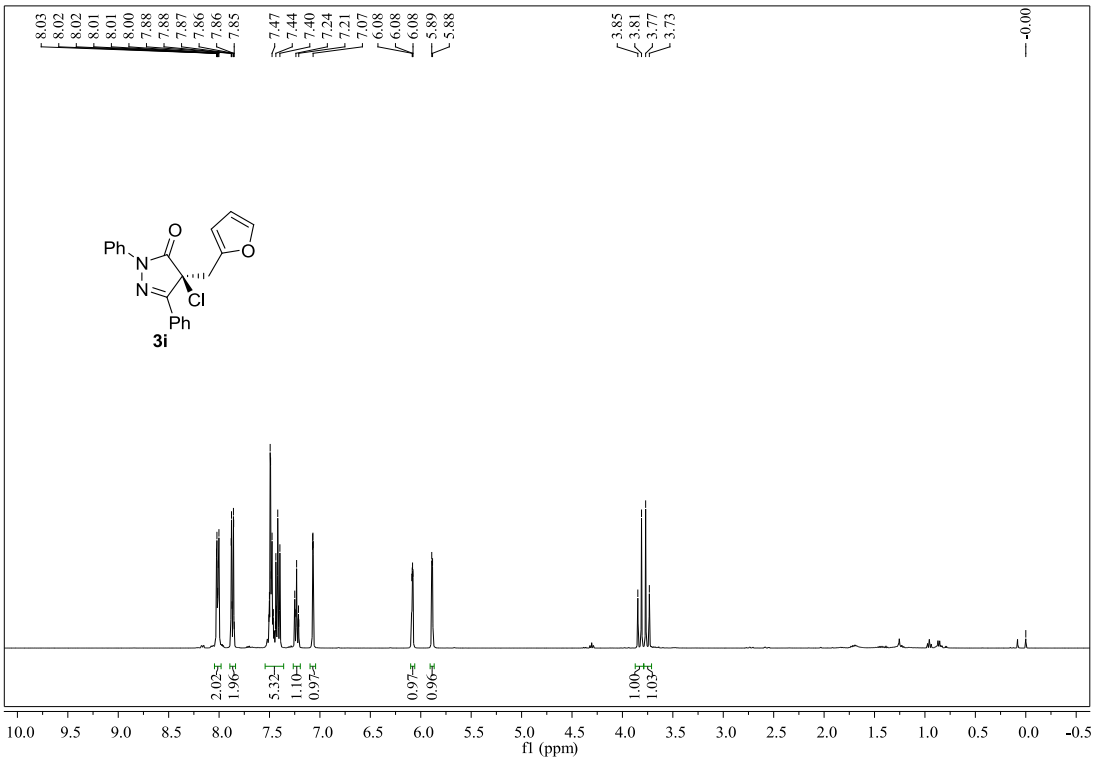
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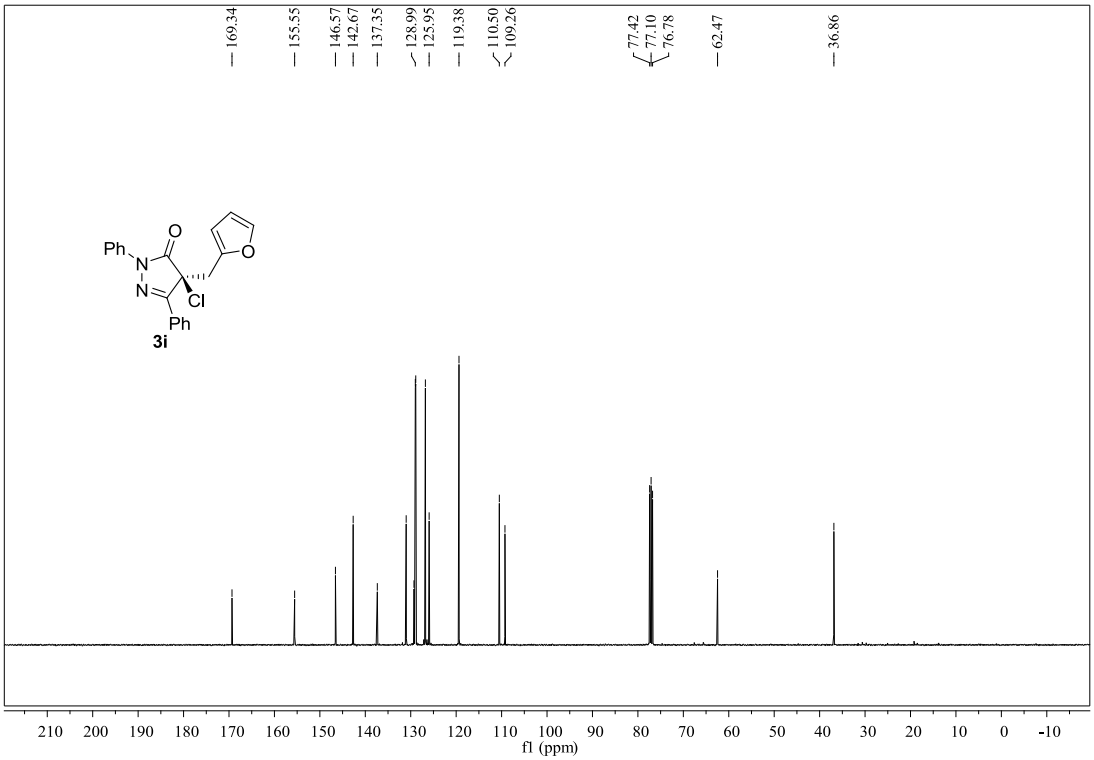
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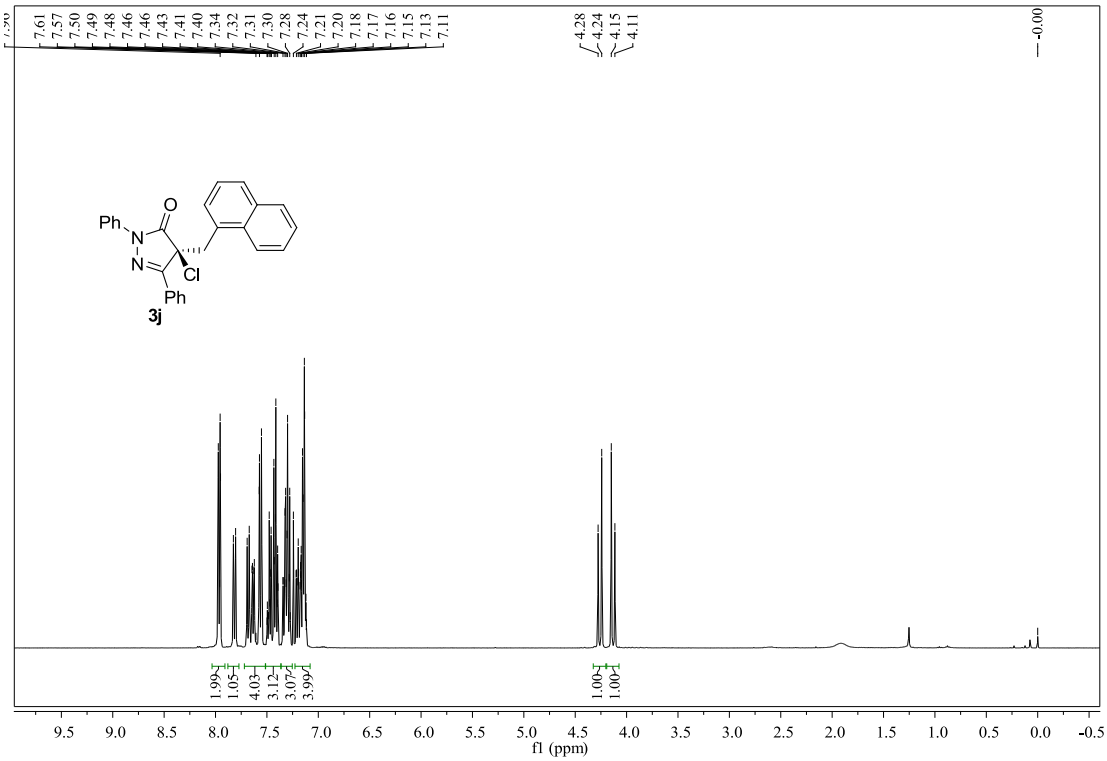
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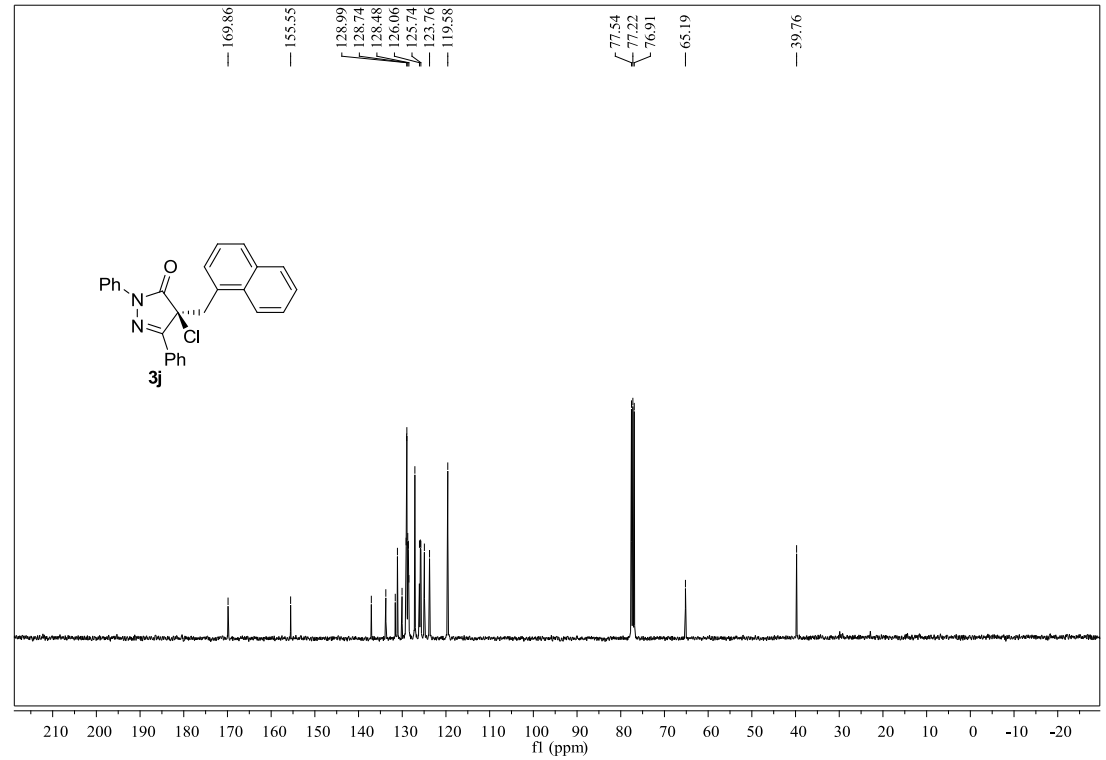
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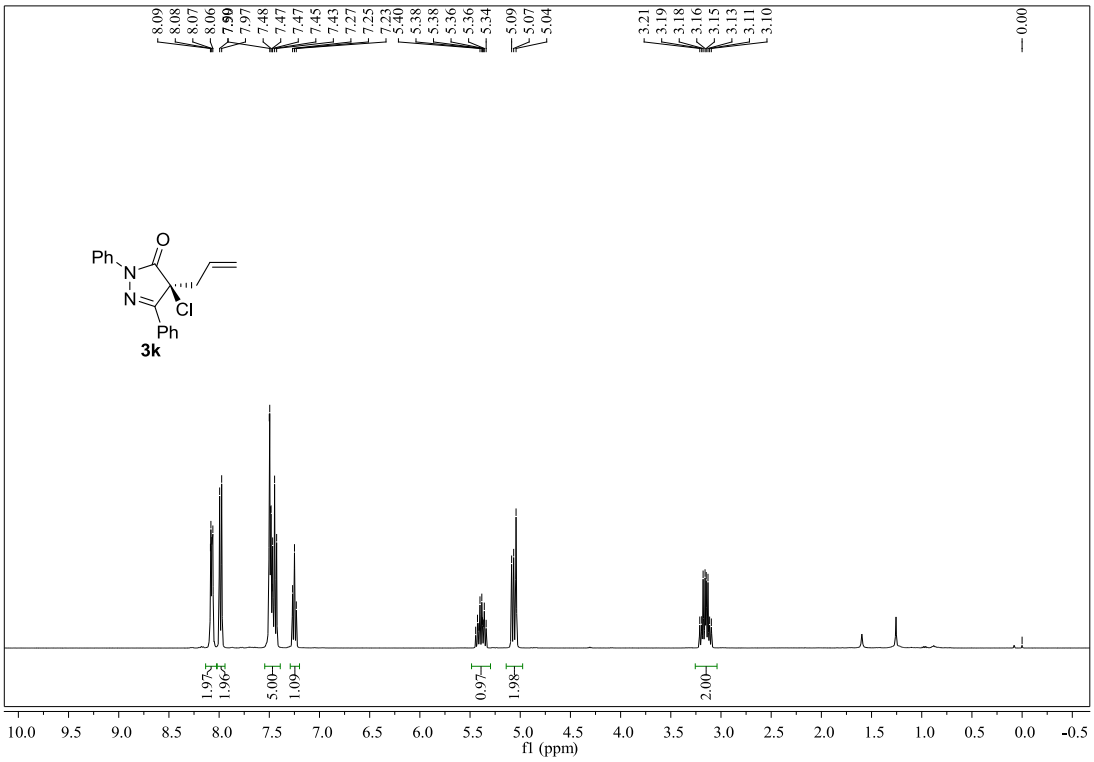
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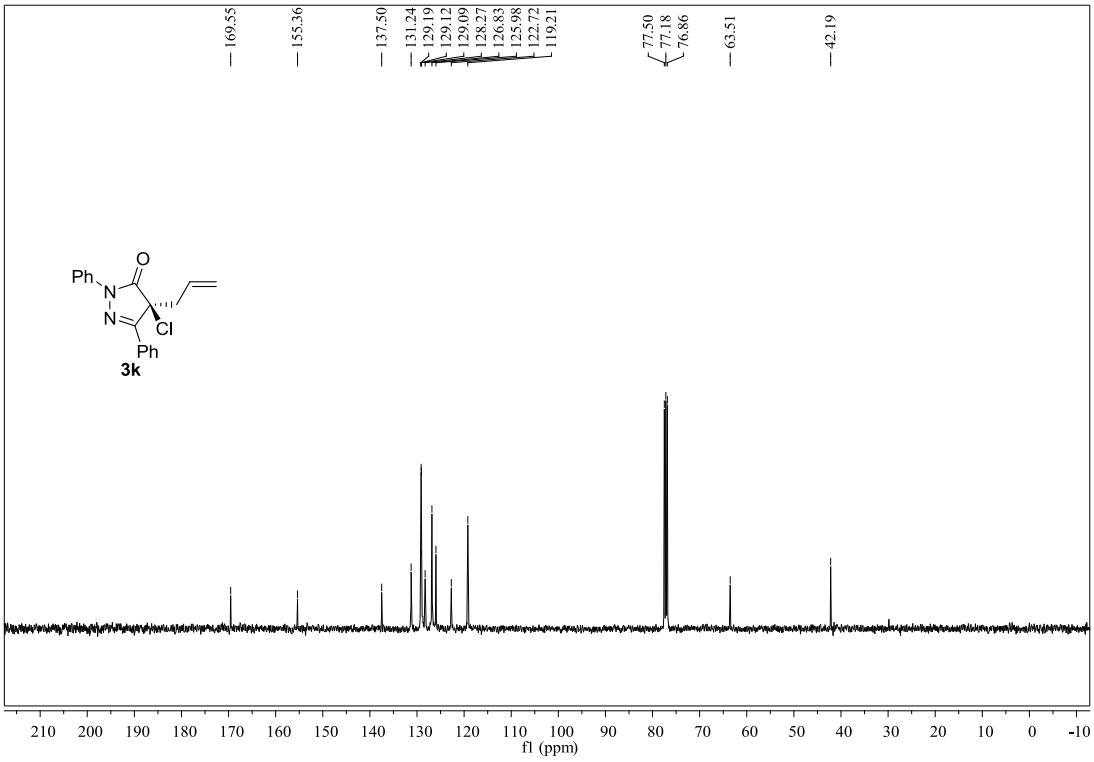
7.97
7.48
7.47
7.47
7.45
7.43
7.27
7.25
7.23
5.40
5.38
5.38
5.36
5.36
5.34
5.09
5.07
5.04
3.21
3.19
3.18
3.16
3.15
3.13
3.11
3.10
0.00
Ph
N
N
O
Cl
Ph
3k
1.97
1.96
5.00
1.09
0.97
1.98
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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155.36
137.50
131.24
129.19
129.12
129.09
128.27
126.83
125.98
122.72
119.21
77.50
77.18
76.86
63.51
42.19
Ph
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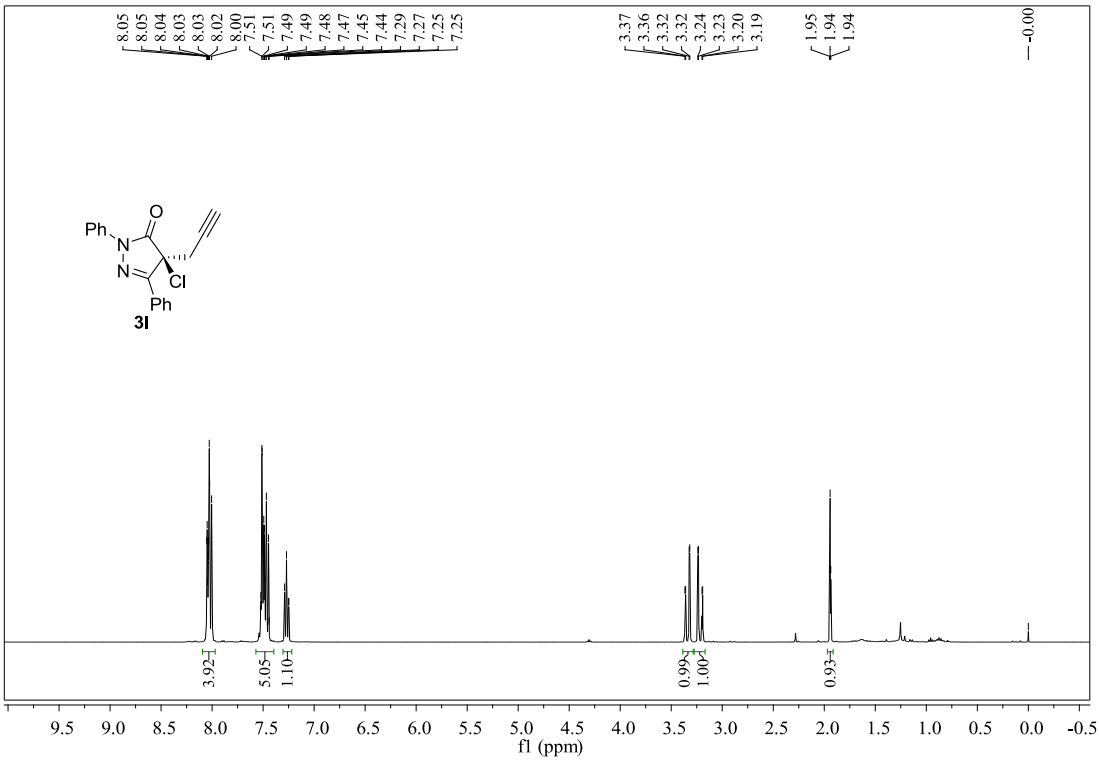
N
O
Cl
Ph
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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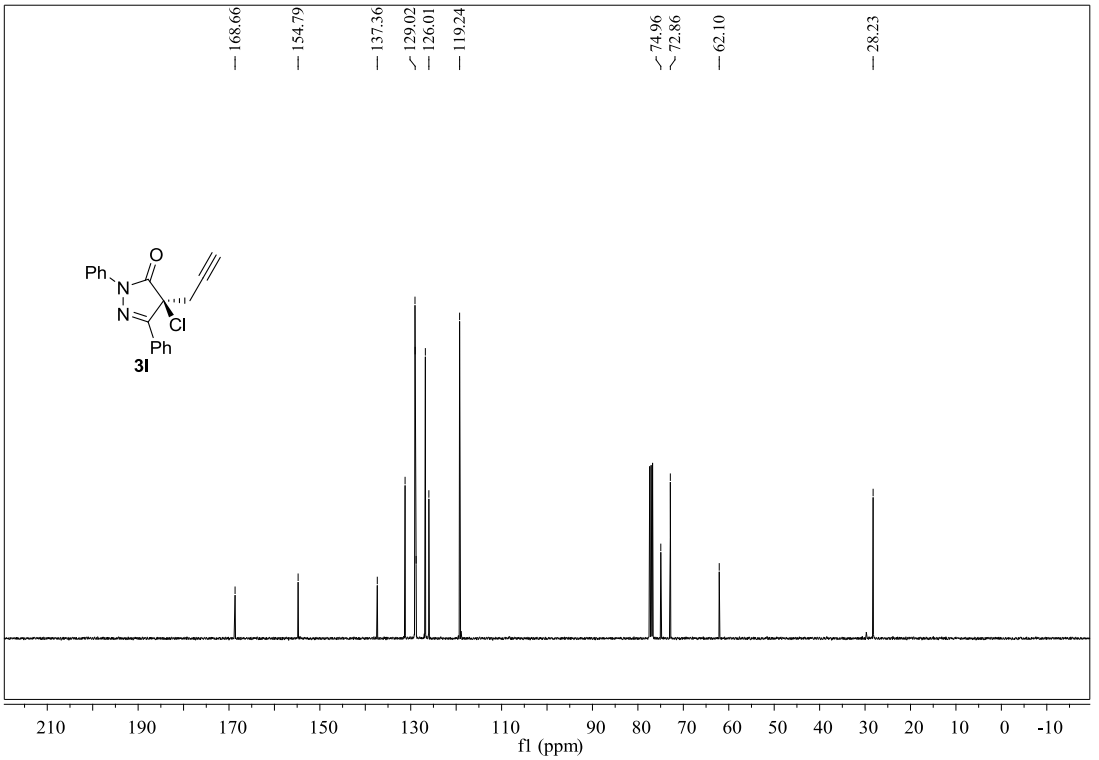
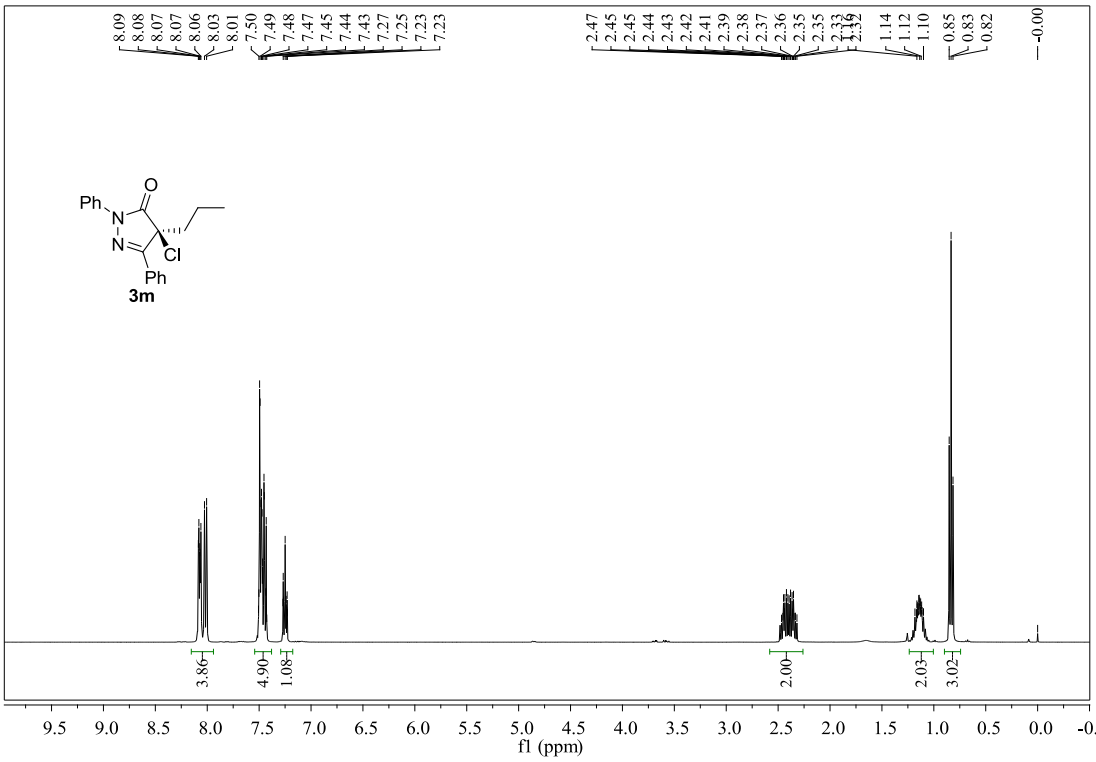
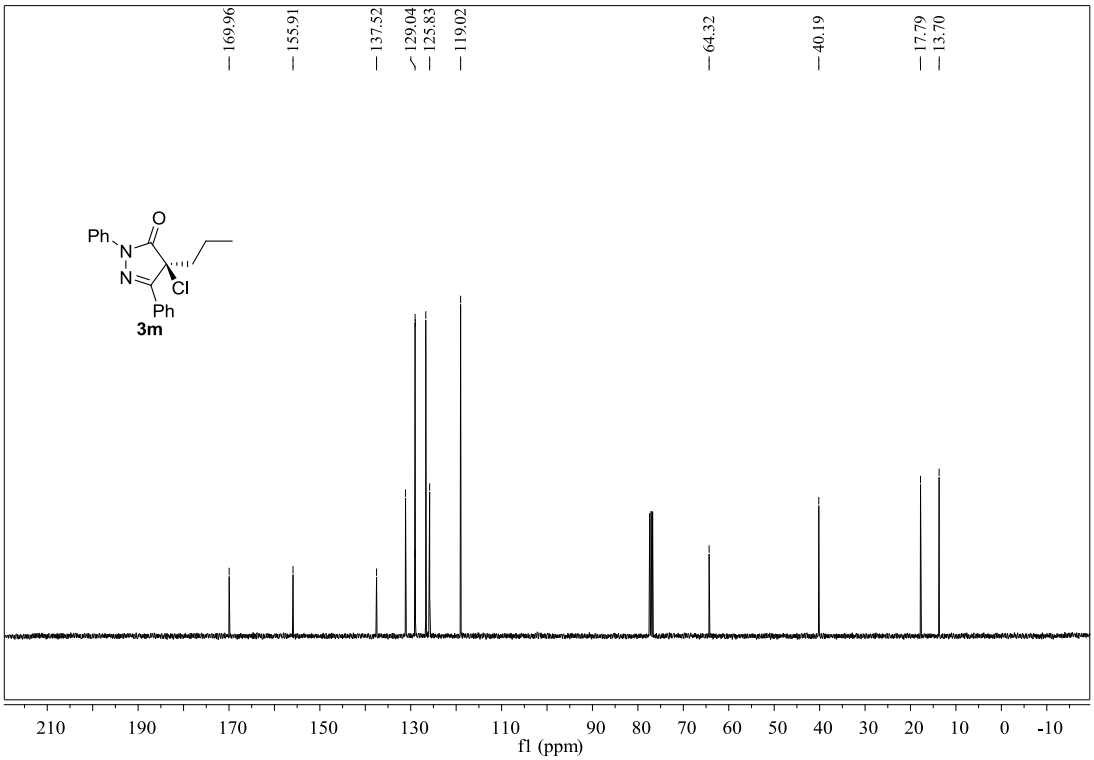
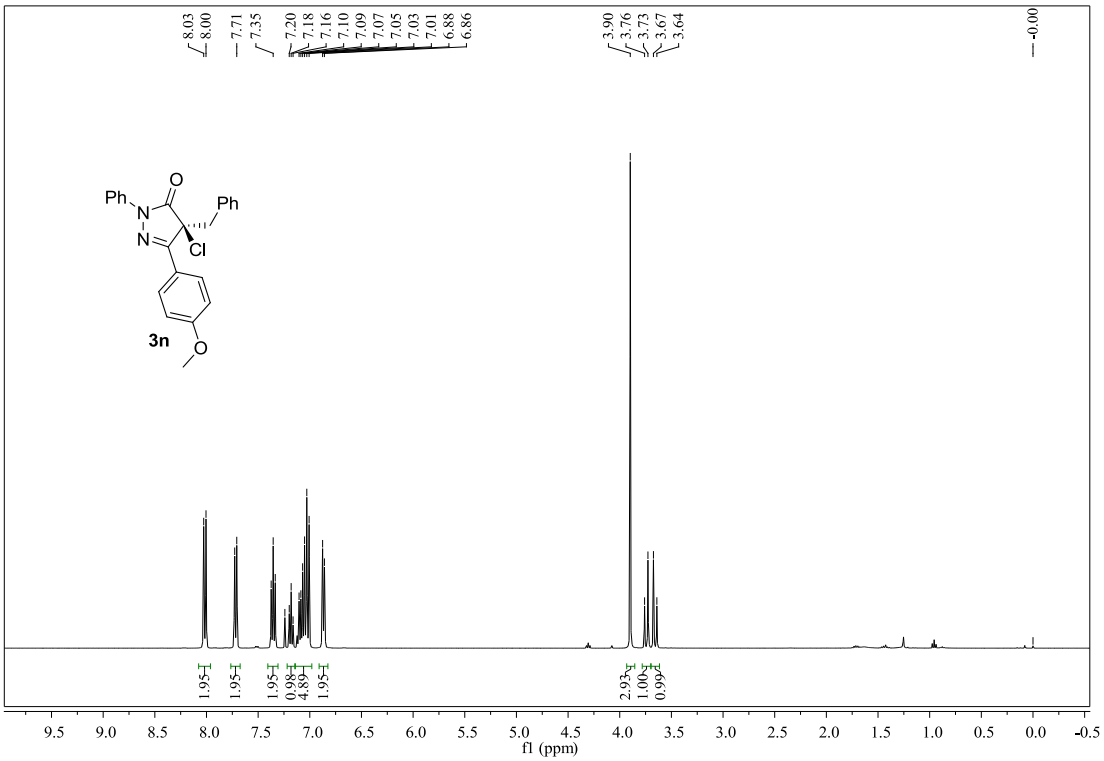
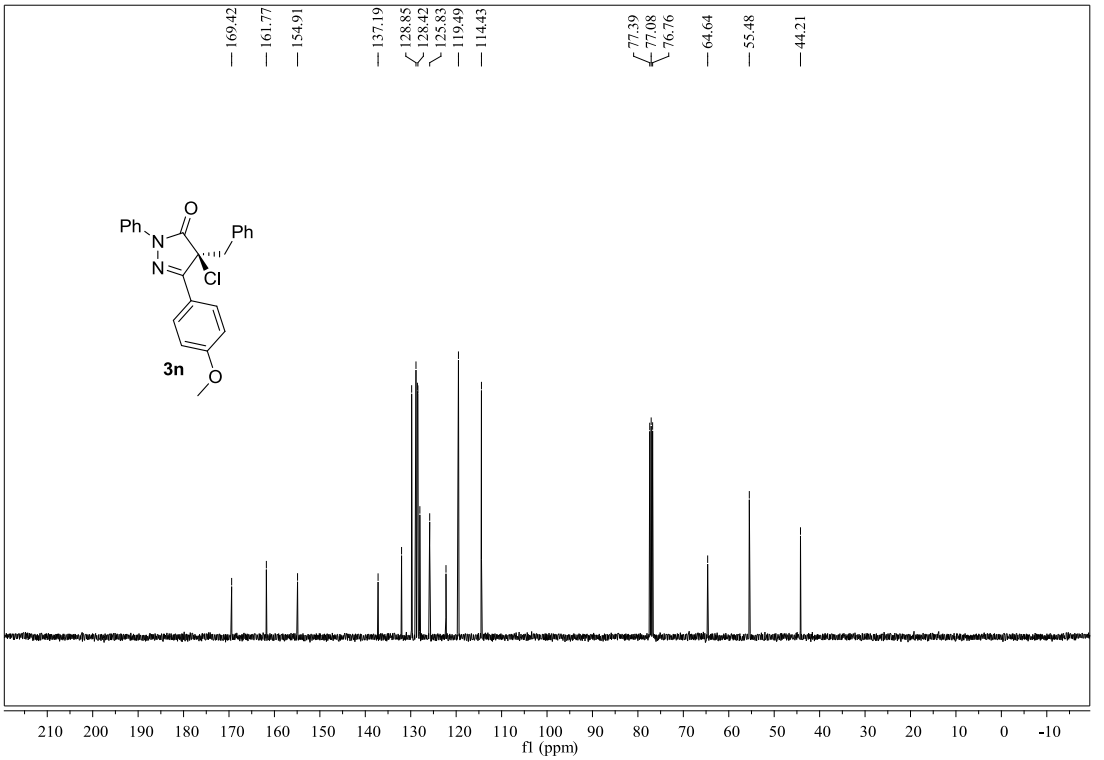
8.05
8.04
8.03
8.03
8.02
8.00
7.51
7.51
7.49
7.49
7.48
7.47
7.45
7.44
7.29
7.27
7.25
7.25
3.37
3.36
3.32
3.32
3.24
3.23
3.20
3.19
1.95
1.94
1.94
-0.00
Ph
N
N
O
Cl
Ph
3l
3.92
5.05
1.10
0.99
1.00
0.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


168.66
154.79
137.36
129.02
126.01
119.24
74.96
72.86
62.10
28.23
Ph
N
N
O
Cl
Ph
3l
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.09
8.08
8.07
8.07
8.06
8.03
8.01
7.50
7.49
7.48
7.47
7.45
7.44
7.43
7.27
7.25
7.23
7.23
2.47
2.45
2.45
2.44
2.43
2.42
2.41
2.39
2.38
2.37
2.36
2.35
2.35
1.14
1.12
1.10
0.85
0.83
0.82
-0.00
Ph
N
N
O
Cl
Ph
3m
3.86
4.90
1.08
2.00
2.03
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.96
155.91
137.52
129.04
125.83
119.02
64.32
40.19
17.79
13.70
Ph
N
N
O
Cl
Ph
3m
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.03
8.00
7.71
7.35
7.20
7.18
7.16
7.10
7.09
7.07
7.05
7.03
7.01
6.88
6.86
3.90
3.76
3.73
3.67
3.64
0.00
Ph
N
N
O
Cl
Ph
O
3n
1.95
1.95
1.95
0.98
4.89
1.95
2.93
1.00
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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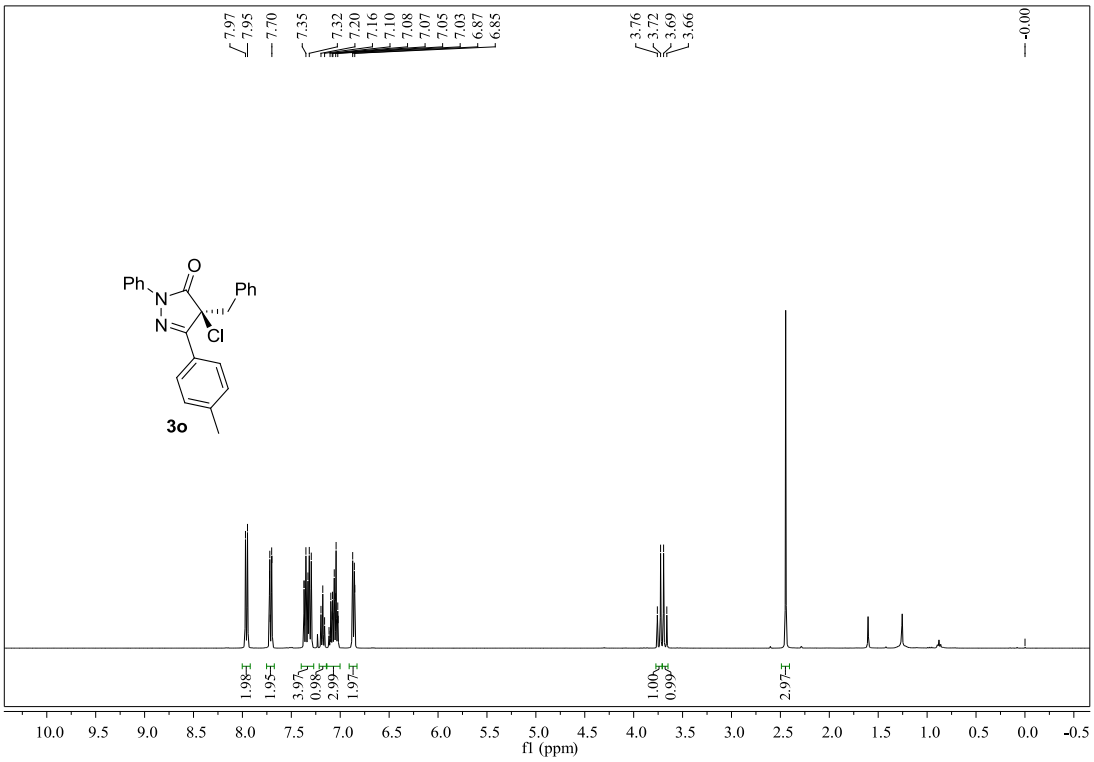
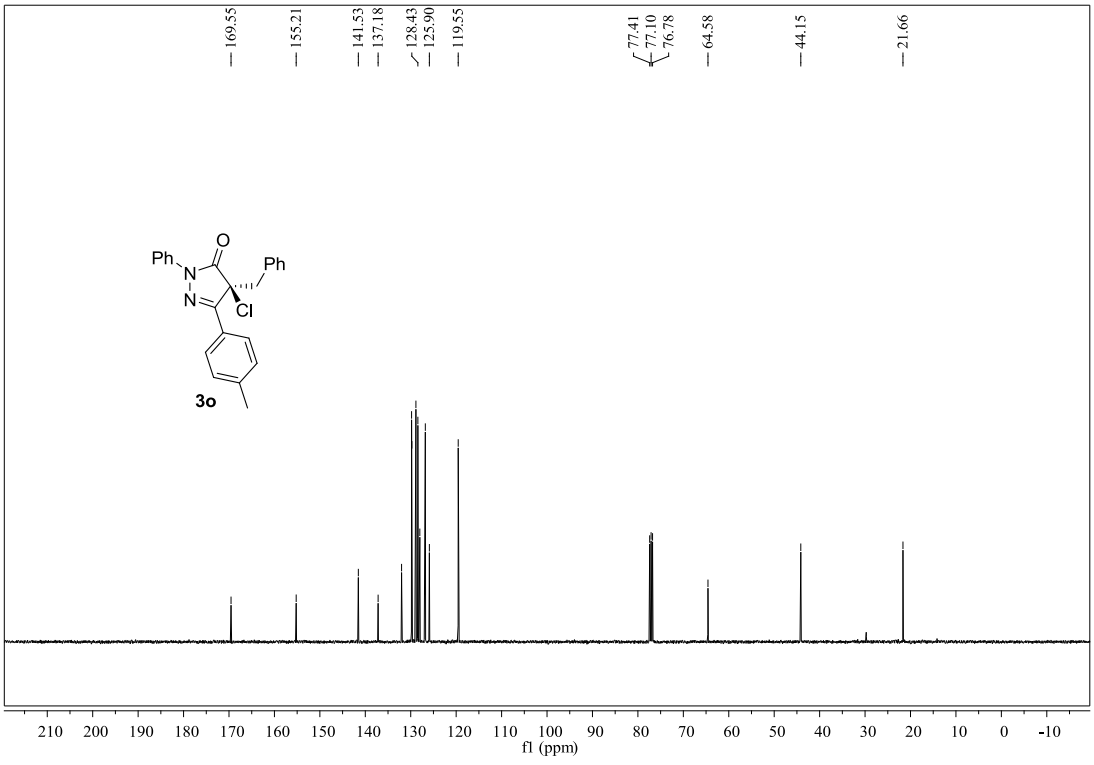
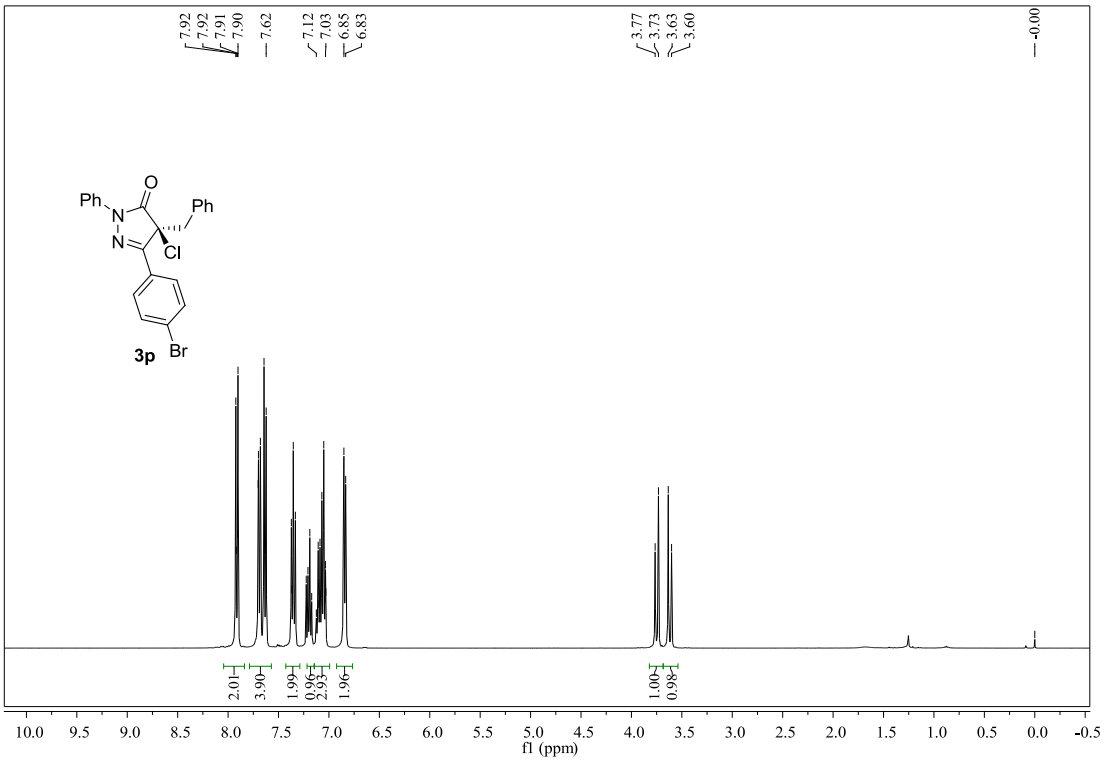
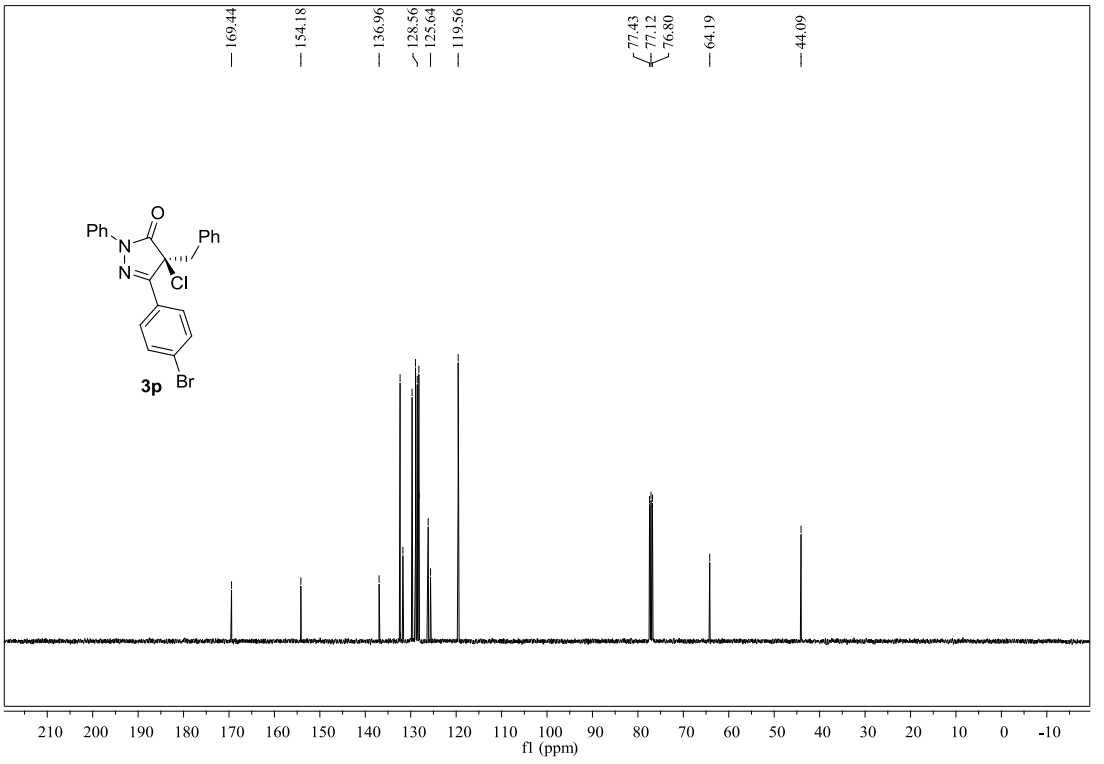
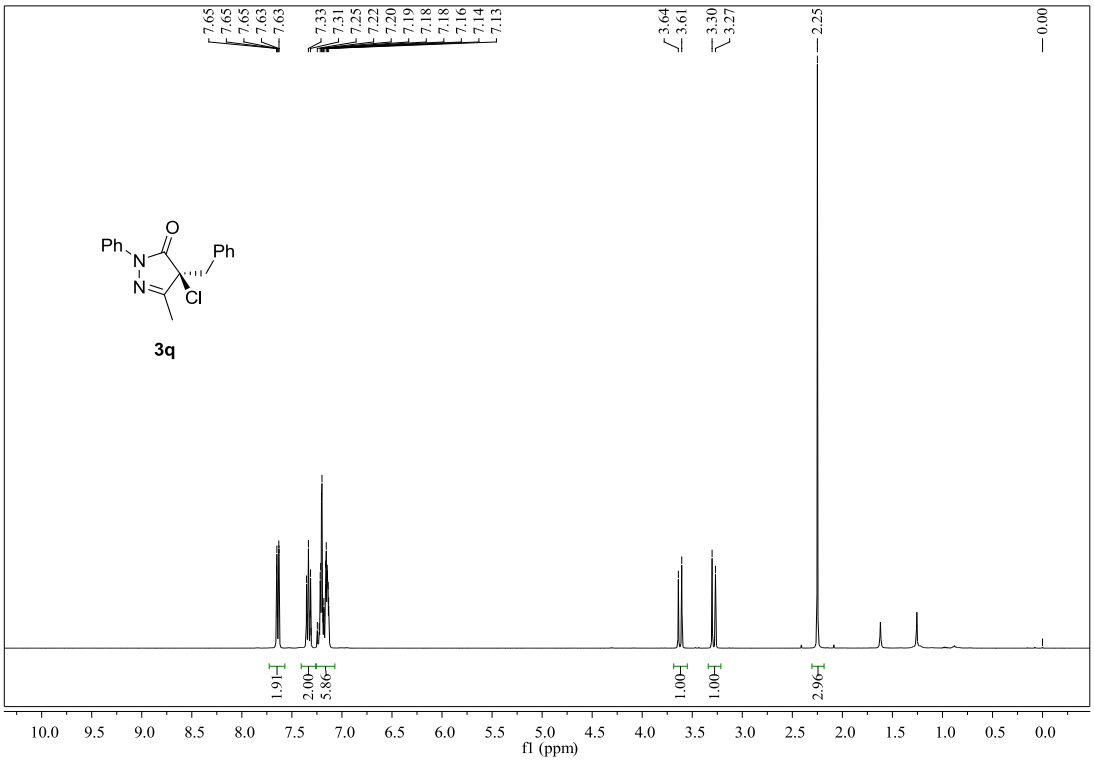
161.77
154.91
137.19
128.85
128.42
125.83
119.49
114.43
77.39
77.08
76.76
64.64
55.48
44.21
Ph
N
N
O
Cl
Ph
O
3n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

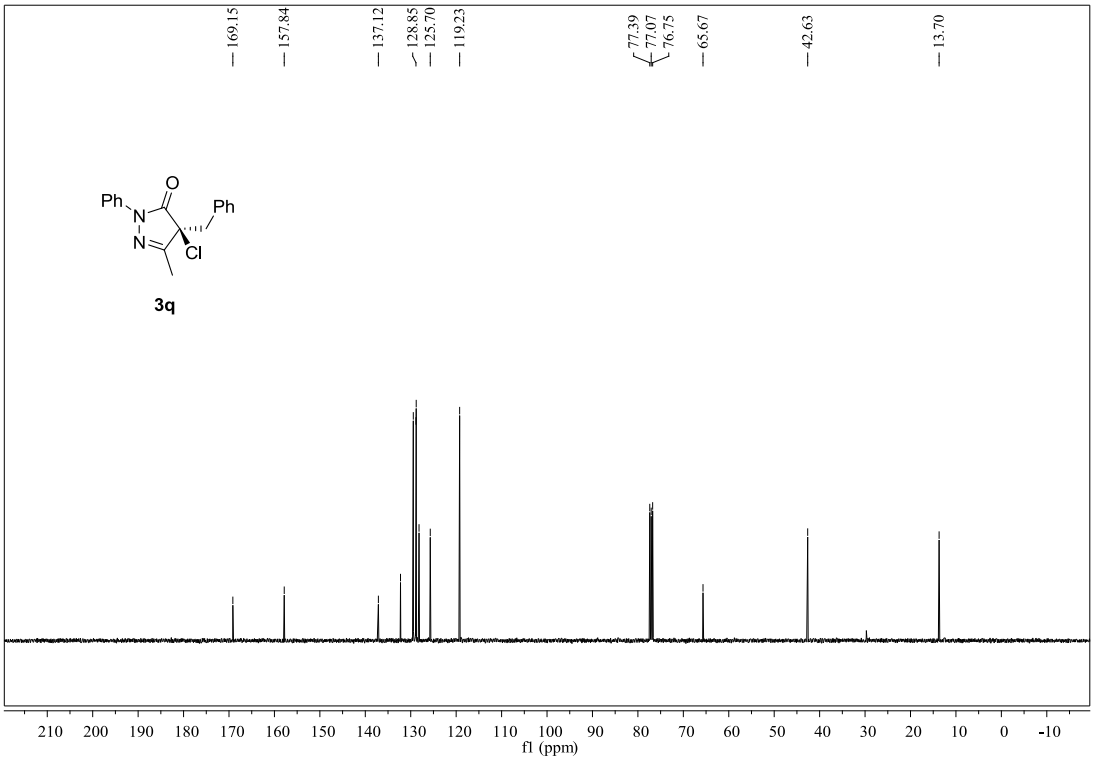

7.97
7.95
7.70
7.35
7.32
7.20
7.16
7.10
7.08
7.07
7.05
7.03
6.87
6.85
3.76
3.72
3.69
3.66
-0.00
Ph
N
N
O
Ph
Cl
3o
1.98
1.95
3.97
0.98
2.99
1.97
1.00
0.99
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

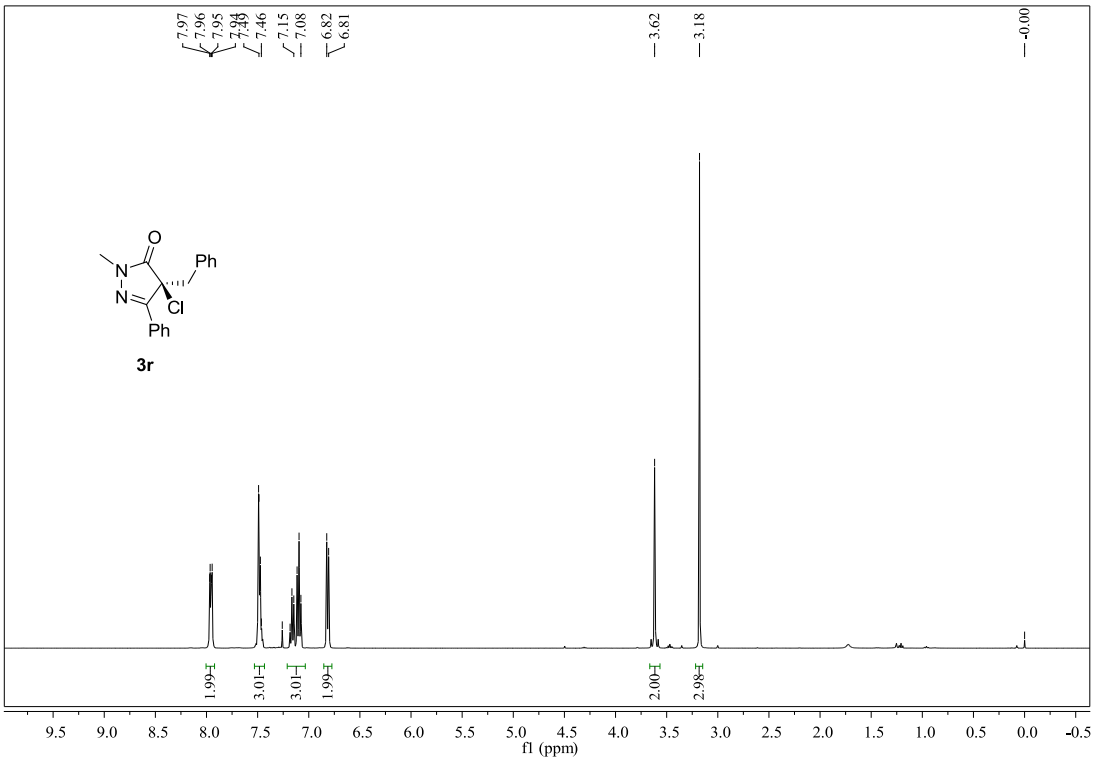

169.55
155.21
141.53
137.18
128.43
125.90
119.55
77.41
77.10
76.78
64.58
44.15
21.66
Ph
N
N
O
Ph
Cl
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

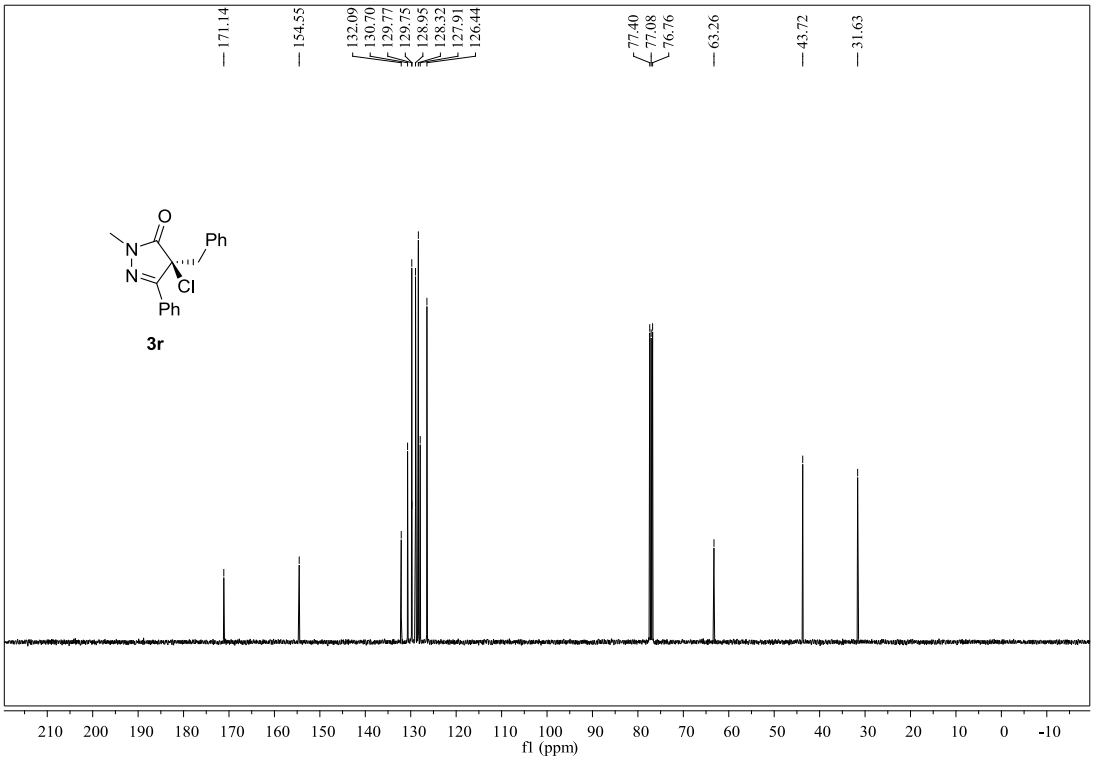

7.92
7.92
7.91
7.90
7.62
7.12
7.03
6.85
6.83
3.77
3.73
3.63
3.60
0.00
Ph
N
N
O
Ph
Cl
Br
3p
2.01
3.90
1.99
0.96
2.93
1.96
1.00
0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


169.44
154.18
136.96
128.56
125.64
119.56
77.43
77.12
76.80
64.19
44.09
Ph
N
N
O
Ph
Cl
Br
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.65
7.65
7.65
7.63
7.63
7.33
7.31
7.25
7.22
7.20
7.19
7.18
7.18
7.16
7.14
7.13
3.64
3.61
3.30
3.27
2.25
0.00
Ph
N
N
O
Cl
Ph
3q
1.91
2.00
5.86
1.00
1.00
2.96
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
f1 (ppm)


169.15
157.84
137.12
128.85
125.70
119.23
77.39
77.07
76.75
65.67
42.63
13.70
Ph
N
N
O
Cl
Ph
3q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.97
7.96
7.95
7.94
7.49
7.46
7.15
7.08
6.82
6.81
3.62
3.18
-0.00
1.99
3.01
3.01
1.99
2.00
2.98
f1 (ppm)
3r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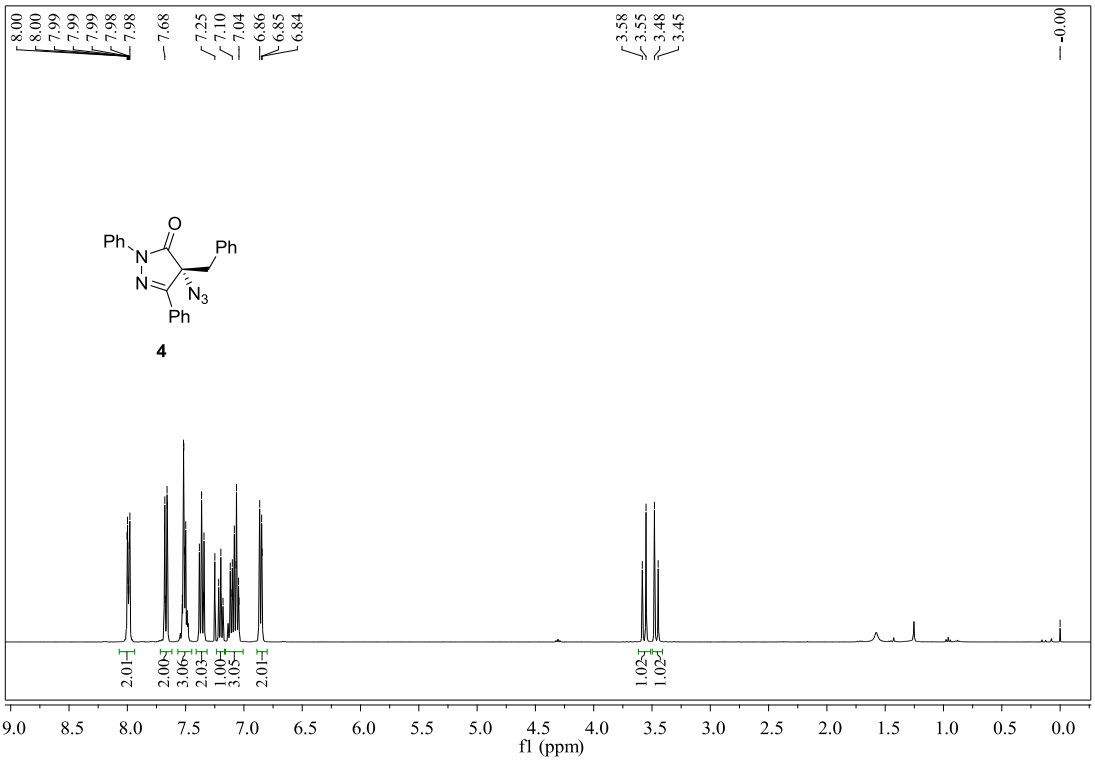
154.55
132.09
130.70
129.77
129.75
128.95
128.32
127.91
126.44
77.40
77.08
76.76
63.26
43.72
31.63
f1 (ppm)
3r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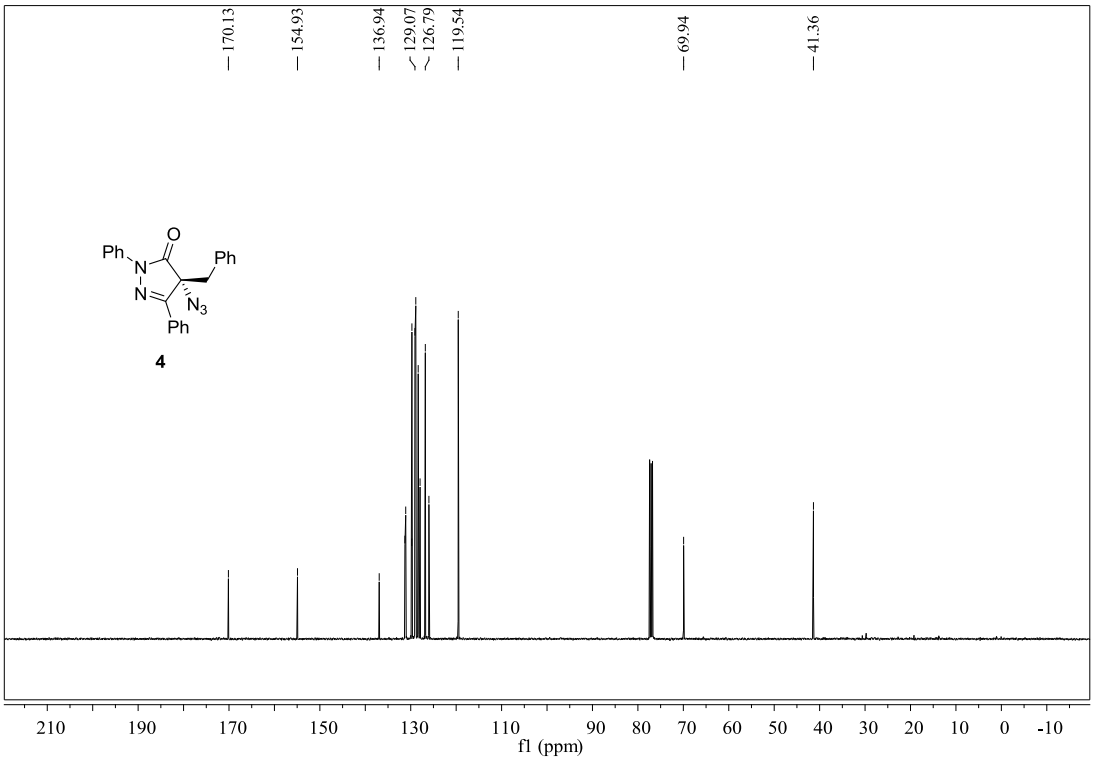
8.00
7.99
7.99
7.99
7.98
7.98
7.68
7.25
7.10
7.04
6.86
6.85
6.84
3.58
3.55
3.48
3.45
0.00
Ph
O
N
N
Ph
N3
Ph
4
2.01
2.00
3.06
2.03
1.00
3.05
2.01
1.02
1.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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154.93
136.94
129.07
126.79
119.54
69.94
41.36
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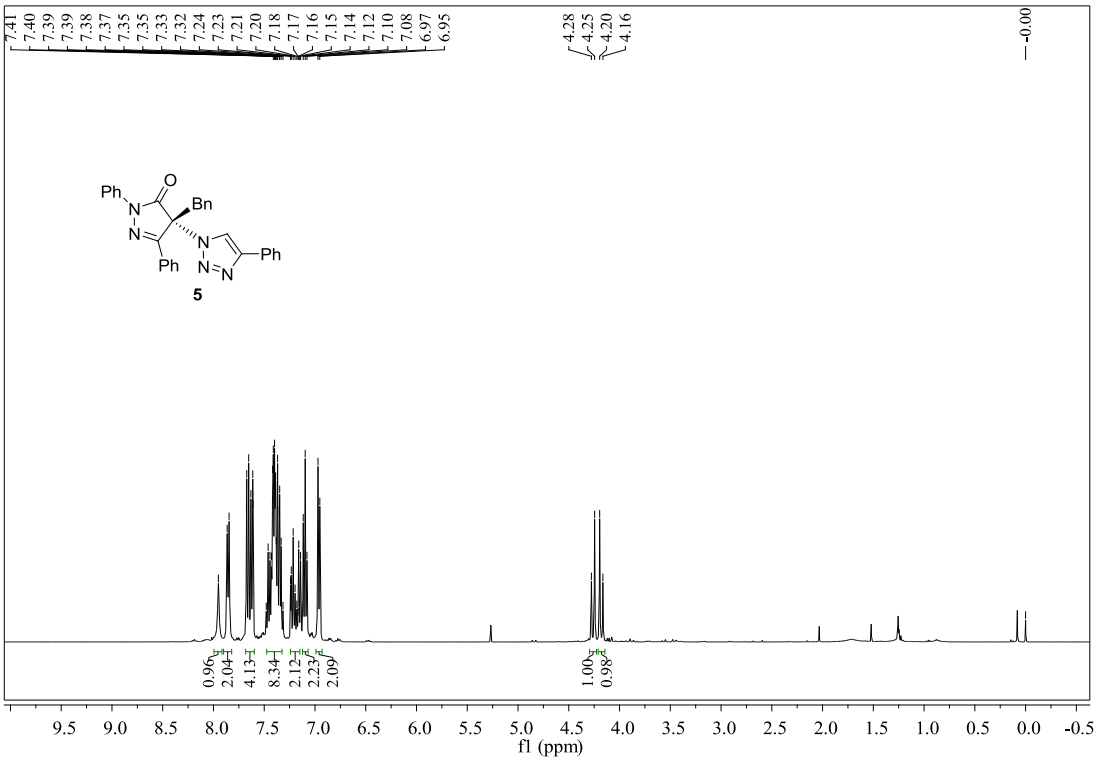
O
N
N
Ph
N3
Ph
4
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.38
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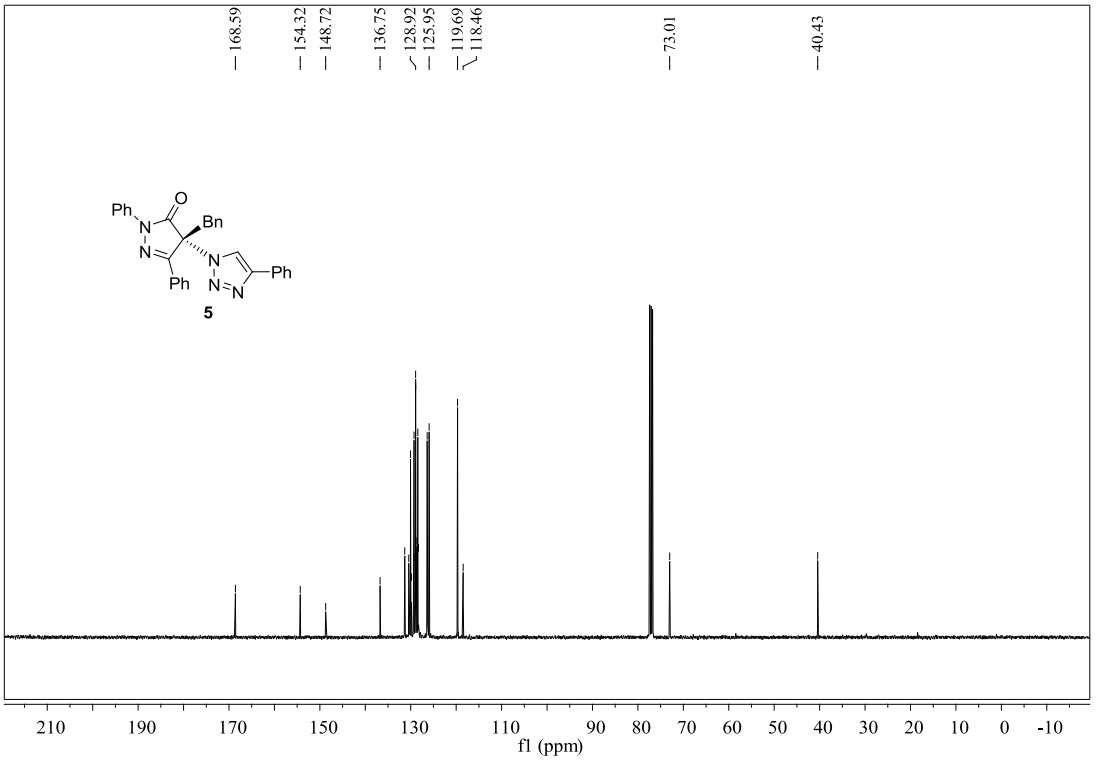
7.35
7.35
7.33
7.32
7.24
7.23
7.21
7.20
7.18
7.17
7.16
7.15
7.14
7.12
7.10
7.08
6.97
6.95
4.28
4.25
4.20
4.16
0.00
Ph
O
Bn
N
N
Ph
N
N
N
Ph
5
0.96
2.04
4.13
8.34
2.12
2.23
2.09
1.00
0.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


168.59
154.32
148.72
136.75
128.92
125.95
119.69
118.46
73.01
40.43
Ph
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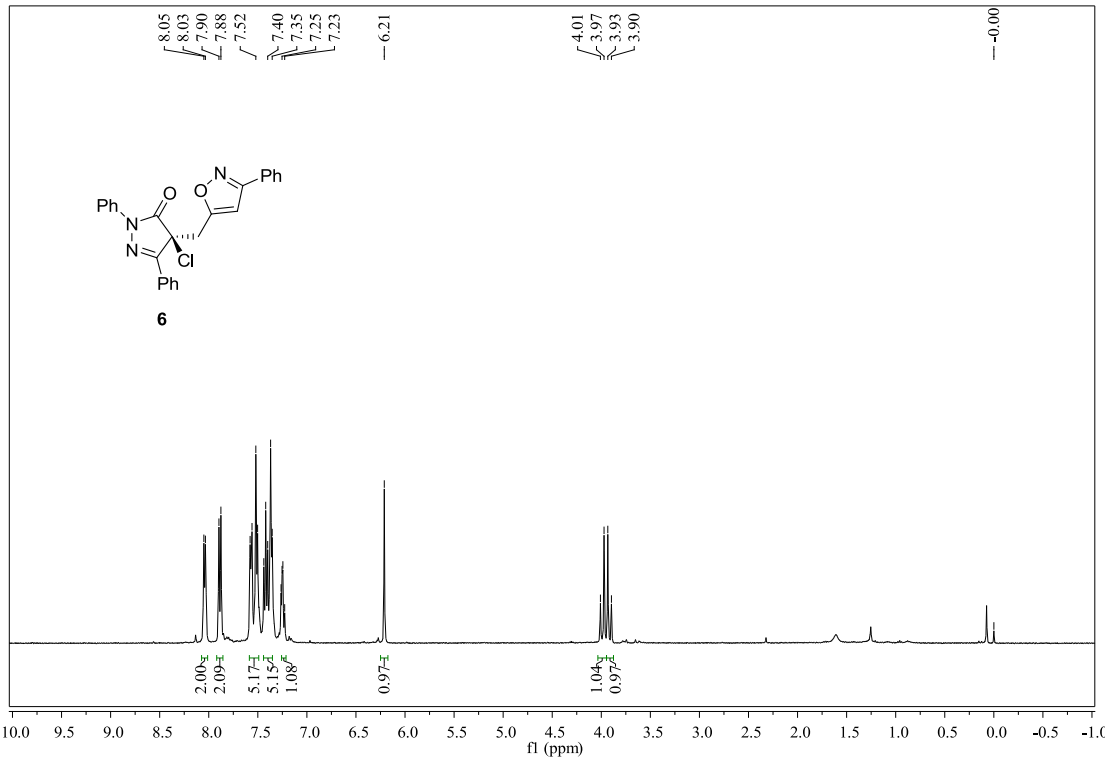
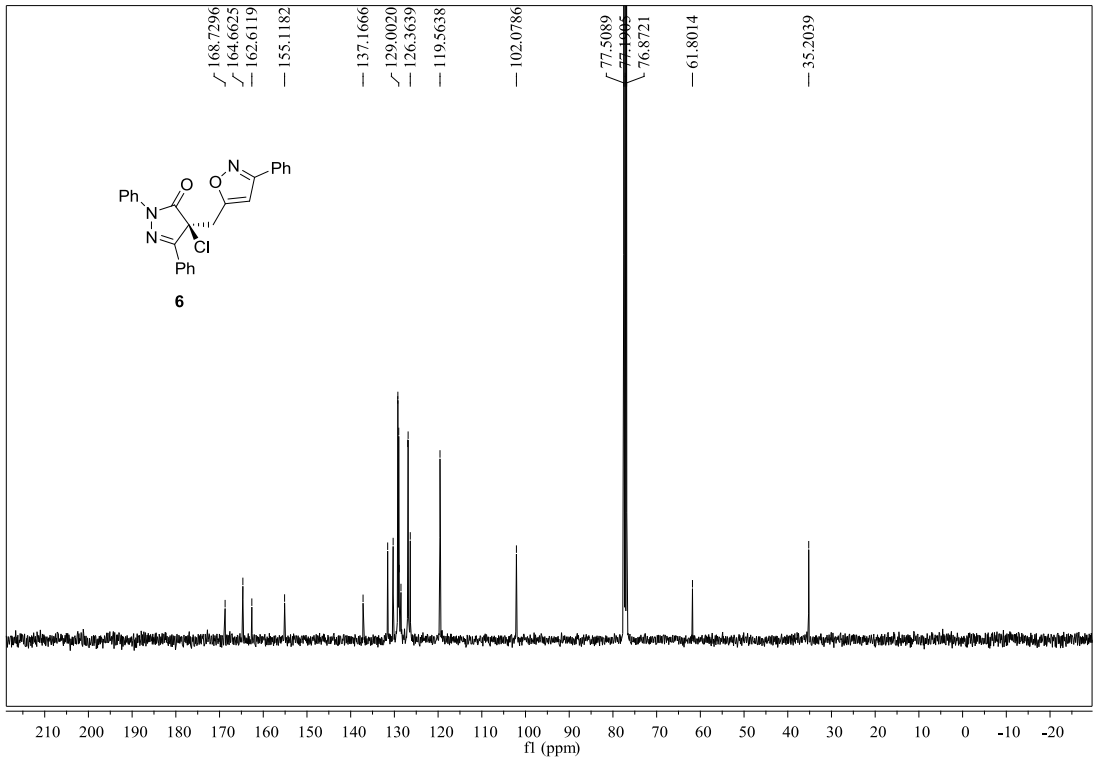
Bn
N
N
Ph
N
N
N
Ph
5
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.05
8.03
7.90
7.88
7.52
7.40
7.35
7.25
7.23
6.21
4.01
3.97
3.93
3.90
0.00
Ph
O
N
O
Ph
N
N
Cl
Ph
6
2.00
2.09
5.17
5.15
1.08
0.97
1.04
0.97
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 -0.5 -1.0
f1 (ppm)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77.5089
77.1905
76.8721
61.8014
35.2039
Ph
O
N
O
Ph
N
N
Cl
Ph
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)