Supporting Information

Multicomponent Coupling Reactions of Two N-Tosyl

Hydrazones and Elemental Sulfur: Selective Denitrogenation Pathway toward Unsymmetric

2,5-Disubstituted 1,3,4-Thiadiazoles

Zhen Zhou, Yang Liu, Jiangfei Chen, En Yao, and Jiang Cheng*

School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, Jiangsu Province Key Laboratory of Fine Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China. jiangcheng@cczu.edu.cn

Table of Contents

1. General Considerations	S2
2. Synthesis and Reaction	S2
3. Mechanism Study	S 3
4. Characterization Data for the Products	S6
5. Reference	S11
6. Copies of the ¹ H NMR, ¹³ C NMR Spectra	S12

1. General Considerations

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ¹³C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl₃ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants *J* are given in Hz. High-resolution mass spectra (HRMS) were obtained using a Bruker micro-TOF II focus spectrometer (ESI). IR spectra were recorded on a spectrometer using KBr discs. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

2. Synthesis and Reaction

2.1 General procedure for the preparation of *N*-tosylhydrazones

Substrates 2a-2j, 1b-1e and 1i, were synthesized according to Method A: Method A:

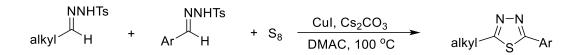
A solution of pure 4-methyl-benzenesulfonohydrazide (5 mmol) in methanol (5 mL) was stirred and heated to 60 °C until the 4-methyl-benzenesulfonohydrazide was completely dissolved. Then carbonyl compounds (5 mmol) were dropped to the mixture slowly. After approximately 5-30 min., the crude products were obtained as precipitates. The precipitates were washed by petroleum ether then were dried *in vacuo* to afford the pure product.

Substrates 1a, 1f, 1g and 1h were synthesized according to Method B:²

Method B:

A solution of pure 4-methyl-benzenesulfonohydrazide (25 mmol) in methanol (10 mL) was stirred and heated to 60 °C until the 4-methyl-benzenesulfonohydrazide was completely dissolved. Then the reaction mixture was cooled to 0 °C. Subsequently, carbonyl compounds (25 mmol) were dropped to the mixture slowly. After approximately 30 min, 10 mL of water was added. The crude products were obtained as precipitates. The precipitates were washed by petroleum ether then were dried *in vacuo* to afford the pure products.

2.2 General procedure for the preparation of thiadiazoles

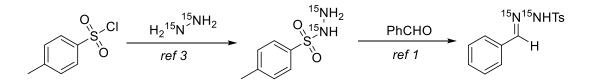


Scheme S1. Standard procedure of the synthesis of thiadiazoles

A 20 mL of Schlenk tube equipped with a stir bar was charged with alkyl aldehyde *N*-tosyl hydrazones (0.12 mmol), aryl aldehyde *N*-tosyl hydrazones (0.1 mmol), S_8 (0.0625 mmol), Cs_2CO_3 (0.2 mmol), CuI (3.8 mg, 20 mol %). The tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at 100 °C for 12 h in oil bath. Then the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product.

3. Mechanism Study

3.1 General procedure for the preparation of ¹⁵N-benzaldehyde *N*-tosyl hydrazone (Scheme S2)



Scheme S2. Synthesis of ¹⁵N-benzaldehyde *N*-tosyl hydrazine

Preparation of ¹⁵N-4-methyl-benzenesulfonohydrazide:³

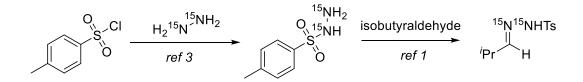
A water (0.9 mL) solution of ¹⁵N-hydrazine hydrate (37.5 mg; 0.75 mmol) was cooled in ice-water bath to ~ 5 °C. The temperature was then maintained below 8 °C, while the tetrahydrofuran (0.75 mL) solution of 4-methyl-benzenesulfonyl chloride (71.25 mg, 0.375 mmol) was slowly added with stirring under nitrogen atmosphere.

After the addition was completed the reaction mixture was stirred at room temperature for thirty minutes and tetrahydrofuran was evaporated at reduced pressure. Then the reaction mixture was extracted with EtOAc (8 mL). The combined extract was dried over Na₂SO₄. Then the solvent was removed under reduced pressure to get the crude product.

Preparation of ¹⁵N- benzaldehyde N-tosyl hydrazone¹

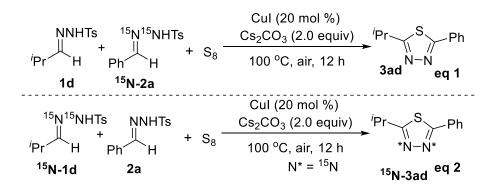
A solution of pure ¹⁵N-4-methyl-benzenesulfonohydrazide (0.15 mmol) in methanol (0.15 mL) was stirred and heated to °C 60 until the ¹⁵N-4-methyl-benzenesulfonohydrazide was completely dissolved. Then benzaldehyde (0.15 mmol) was dropped to the mixture slowly. After the addition was completed the reaction mixture was stirred for thirty min. Then the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product.

3.2 General procedure for the preparation of ¹⁵N-isobutyraldehyde *N*-tosylhydrazone (Scheme S3)



Scheme S3. Synthesis of ¹⁵N-isobutyraldehyde *N*-tosylhydrazone

3.3 ¹⁵N Labelling Experiments



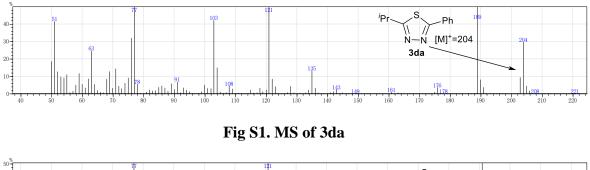
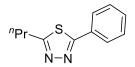




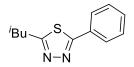
Fig S2. MS of ¹⁵N-3da

4. Characterization Data for the Products **2**-(*n*-propyl)-**5**-phenyl-**1**,**3**,**4**-thiadiazole (**3**aa):⁴



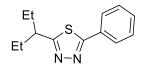
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3aa** (12.6 mg, 62% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.95-7.92 (m, 2H), 7.47-7.46 (m, 2H), 3.12 (t, J = 7.6 Hz, 2H), 1.92-1.83 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 170.1, 168.4, 130.8, 130.3, 129.1, 127.8, 32.1, 23.4, 13.6.

2-isobutyl-5-phenyl-1,3,4-thiadiazole (3ba)⁵



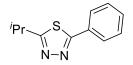
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ba** (11.1 mg, 51% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.96-7.93 (m, 2H), 7.49-7.43 (m, 3H), 3.01 (d, J = 7.2 Hz, 2H), 2.19-2.08 (m, 1H), 1.04 (d, J = 6.6 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 169.0, 168.4, 130.8, 130.3, 129.1, 127.8, 127.8, 38.9, 29.8, 22.2.

2-(pentan-3-yl)-5-phenyl-1,3,4-thiadiazole (3ca)



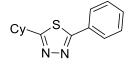
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ca** (12.1 mg, 52% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.96-7.93 (m, 2H), 7.49-7.45 (m, 3H), 3.15-3.08 (m, 1H), 1.90-1.83 (m, 2H), 1.78-1.70 (m, 2H), 0.93 (t, J = 7.4 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 174.9, 168.0, 130.8, 130.4, 129.0, 127.8, 45.0, 29.2, 11.7; HRMS (ESI) m/z calcd for C₁₃H₁₇N₂S(M+H)⁺ 233.1107, found 233.1103; IR (KBr) 3065, 2963, 2928, 2874, 2856, 1637, 1458, 1383, 1331 cm⁻¹.

2-isopropyl-5-phenyl-1,3,4-thiadiazole (3da)⁶



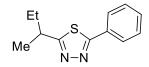
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3da** (12.2 mg, 60% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.94-7.92 (m, 2H), 7.47-7.45 (m, 3H), 3.55-3.45 (m, 1H), 1.48 (d, *J* = 6.9 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 176.8, 168.0, 130.8, 130.4, 129.0, 127.8, 30.9, 23.4.

2-cyclohexyl-5-phenyl-1,3,4-thiadiazole (3ea)



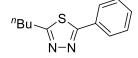
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ea** (12.7 mg, 52% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.94-7.92 (m, 2H), 7.47-7.44 (m, 3H), 3.22-3.15 (m, 1H), 2.14-2.17 (m, 2H), 1.90-1.85 (m, 2H), 1.79-1.74 (m, 1H), 1.64-1.54 (m, 2H), 1.50-1.39 (m, 2H), 1.36-1.28 (m, 1H), ¹³C NMR (CDCl₃, 100 MHz) δ 175.9, 167.7, 130.7, 130.4, 129.0, 127.8, 40.0, 33.9, 25.9, 25.6; HRMS (ESI) m/z calcd for C₁₄H₁₇N₂S(M+H)⁺ 245.1107, found 245.1103; IR (KBr) 3063, 2927, 2852, 1684, 1453, 1428, 1382, 1314 cm⁻¹.

2-(sec-butyl)-5-phenyl-1,3,4-thiadiazole (3fa)⁵



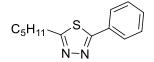
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3fa** (10.2 mg, 47% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.95-7.93 (m, 2H), 7.47-7.45 (m, 3H), 3.35-3.26 (m, 1H), 1.89-1.72 (m, 2H), 1.44 (d, J = 6.9 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 176.0, 168.0, 130.8, 130.4, 129.0, 127.8, 37.7, 31.0, 21.1, 11.6.

2-(*n*-butyl)-5-phenyl-1,3,4-thiadiazole (3ga)⁴



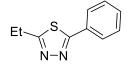
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ga** (11.8 mg, 54% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.94-7.92 (m, 2H), 7.50-7.43 (m, 3H), 3.13 (t, J = 7.7 Hz, 2H), 1.86-1.78 (m, 2H), 1.51-1.42(m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 170.4, 168.3, 130.8, 130.3, 129.0, 127.8, 32.1, 29.9, 22.1, 13.6.

2-pentyl-5-phenyl-1,3,4-thiadiazole (3ha)⁷



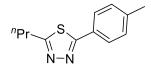
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ha** (9.5 mg, 41% yield) as a yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.94-7.91 (m, 2H), 7.47-7.44 (m, 3H), 3.12 (t, J = 7.7 Hz, 2H), 1.88-1.78 (m, 2H), 1.44-1.34 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.4, 168.3, 130.8, 130.3, 129.0, 127.8, 31.1, 30.0, 29.7, 22.2, 13.9.

2-ethyl-5-phenyl-1,3,4-thiadiazole (3ia)⁸



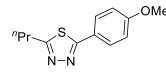
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ia** (10.8 mg, 57% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.95-7.92 (m, 2H), 7.48-7.45 (m, 3H), 3.20-3.14 (m, 2H), 1.46 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 171.7, 168.4, 130.8, 130.3, 129.1, 127.8, 23.9, 14.4.

2-(*n*-propyl)-5-(*p*-tolyl)-1,3,4-thiadiazole (3ab)



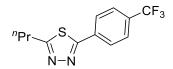
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ab** (11.1 mg, 51% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.82 (d, J = 8.1 Hz, 2H), 7.26 (t, J = 4.0 Hz, 2H), 3.10 (t, J = 7.6 Hz, 2H), 2.40 (s, 3H), 1.91-1.82 (m, 2H), 1.06 (t, J = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 169.7, 168.5, 141.2, 129.7, 127.7, 127.6 (weak) , 32.1, 23.5, 21.5, 13.6; HRMS (ESI) m/z calcd for C₁₂H₁₅N₂S(M+H)⁺ 219.0950, found 219.0949; IR (KBr) 3021, 2962, 2926, 2872, 1612, 1463, 1382, 1312 cm⁻¹.

2-(*n*-propyl)-5-(*p*-methoxyphenyl)-1,3,4-thiadiazole (3ac)⁴



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ac** (12.4 mg, 53% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.86 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.08 (t, J = 7.6 Hz, 2H), 1.90-1.81 (m, 2H), 1.05 (t, J = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 169.3, 168.1, 161.7, 129.3, 123.0, 114.4, 55.4, 32.6, 23.4, 13.6;

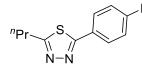
2-(*n*-propyl)-5-(*p*-(trifluoromethyl)phenyl)-1,3,4-thiadiazole (3ad)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ad** (12.2 mg, 45% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 8.06 (d, J = 8.17 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 3.14 (t, J = 7.6 Hz, 2H), 1.94-1.84 (m, 2H), 1.07 (t, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 171.1, 166.8, 133.6, 132.49 (q, $J_{C-F} = 35.0$ Hz), 128.1, 126.1 (q, $J_{C-F} = 3.0$ Hz), 123.7 (q, $J_{C-F} = 271.0$ Hz), 32.1,

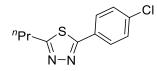
23.4, 13.6; HRMS (ESI) m/z calcd for $C_{12}H_{12}F_3N_2S(M+H)^+$ 273.0668, found 273.0664; IR (KBr) 3075, 2963, 2926, 2881, 2854, 1639, 1615, 1464, 1384, 1335 cm⁻¹.

2-(*n*-propyl)-5-(*p*-fluorophenyl)-1,3,4-thiadiazole (3ae)



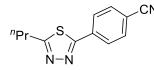
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ae** (10.0 mg, 45% yield) as a yellow oil.¹H NMR (CDCl₃, 400 MHz) δ 7.94-7.91 (m, 2H), 7.17-7.13 (m, 2H), 3.10 (t, J = 6.0 Hz, 2H), 1.91-1.82 (m, 2H), 1.07-1.04 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 170.2, 167.2, 164.2 (d, $J_{C-F} = 250.0$ Hz), 129.8 (d, $J_{C-F} = 9.0$ Hz), 126.3 (d, $J_{C-F} = 4.0$ Hz), 116.2 (d, $J_{C-F} = 22.0$ Hz), 32.1, 23.4, 13.6; HRMS (ESI) m/z calcd for C₁₁H₁₂FN₂S(M+H)⁺ 223.0700, found 223.0692; IR (KBr) 3076, 2960, 2929, 2901, 2872, 2855, 1637, 1463 1376 1301cm⁻¹.

2-(*n*-propyl)-5-(*p*-chlorophenyl)-1,3,4-thiadiazole (3af)



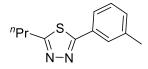
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3af** (11.4 mg, 48% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.87 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 3.11 (t, J = 7.6 Hz, 2H), 1.91-1.82 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 170.4, 167.1, 136.9, 129.3, 128.9, 128.8, 32.1, 23.4, 13.6; HRMS (ESI) m/z calcd for C₁₁H₁₂ClN₂S(M+H)⁺ 239.0404, found 239.0399; IR (KBr) 3083, 3069, 2957, 2929, 2872, 1642, 1463, 1438, 1384, 1338 cm⁻¹.

4-(5-propyl-1,3,4-thiadiazol-2-yl)benzonitrile (3ag)



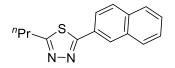
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ag** (9.8 mg, 43% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 3.13 (t, *J* = 7.5 Hz, 2H), 1.92-1.83 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 171.5, 166.3, 134.2, 132.8, 128.2, 118.0, 114.2, 32.1, 23.4, 13.5; HRMS (ESI) m/z calcd for C₁₂H₁₂N₃S(M+H)⁺ 230.0746, found 230.0746; IR (KBr) 3073, 3054 2965, 2926, 2874, 1651, 1462, 1384, 1317 cm⁻¹.

2-(*n*-propyl)-5-(*m*-tolyl)-1,3,4-thiadiazole (3ah)



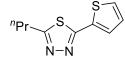
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ah** (10.9 mg, 50% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.77 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 3.10 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.91-1.82 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 170.0, 168.6, 138.9, 131.6, 130.2, 129.0, 128.3, 125.1, 32.1, 23.4, 21.3, 13.6; HRMS (ESI) m/z calcd for C₁₂H₁₅N₂S(M+H)⁺ 219.0950, found 219.0948; IR (KBr) 3031, 2968, 2932, 2858, 1632, 1451, 1373, 1342 cm⁻¹.

2-(*n*-propyl)-5-(naphthalen-2-yl)-1,3,4-thiadiazole (3ai)



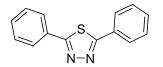
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ai** (13.2 mg, 52% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 8.37 (s, 1H), 8.10-8.07 (m, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.87 (t, *J* = 4.0 Hz, 1H), 7.57-7.52 (m, 2H), 3.14 (t, *J* = 6.0 Hz, 2H), 1.89 (t, *J* = 8.0 Hz, 2H), 1.08 (t, *J* = 6.0 Hz, 3H); HRMS (ESI) m/z calcd for C₁₅H₁₅N₂S (M+H)⁺ 255.0950, found 255.0947; IR (KBr) 3083, 2959, 2923, 2852, 1637, 1617, 1457, 1425, 1384, 1339 cm⁻¹.

2-(*n*-propyl)-5-(thiophen-2-yl)-1,3,4-thiadiazole (3aj)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3aj** (11.6 mg, 55% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.50-7.49 (m, 1H), 7.46-7.44 (m, 1H), 7.11-7.09 (m, 1H), 3.08 (t, J = 7.6 Hz, 2H), 1.90-1.80 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 170.2, 168.5, 134.4, 133.1, 128.9, 128.6, 127.9, 127.8, 127.7, 127.4, 126.9, 124.5, 32.1, 23.5, 21.5, 13.6; HRMS (ESI) m/z calcd for C₉H₁₁N₂S₂ (M+H)⁺ 211.0358, found 211.0359; IR (KBr) 3104, 3083, 2959, 2926, 2870, 2859, 1639, 1452, 1411, 1384, 1338 cm⁻¹.

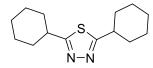
2,5-diphenyl-1,3,4-thiadiazole (4)⁹



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **4** (8.0 mg, 67% yield) as a white solid. m.p. 141-142 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.05-7.99 (m, 4H), 7.54-7.46 (m, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.1,

131.1, 130.1, 129.2, 127.9.

2,5-dicyclohexyl-1,3,4-thiadiazole (5)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **5** (5.5 mg, 44% yield) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 3.14-3.07 (m, 1H), 2.45-2.26 (m, 1H), 2.22-1.95 (m, 3H), 1.86-1.56 (m, 7H), 1.54-1.28 (m, 9H), 0.89-0.34 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 175.2, 39.9, 33.9, 25.9, 25.7; HRMS (ESI) m/z calcd for C₁₄H₂₃N₂S (M+H)⁺ 251.1576, found 251.1572.

5. Reference

1 Ye, F.; Ma, X.; Xiao, Q.; Li, H.; Zhang, Y.; Wang, J. J. Am. Chem. Soc. 2012, 134, 5742.

2 Pieper, M.; Teichert, W.; Meier, H. Liebigs Ann. Chem. 1986, 1334.

3 Backes, G. L.; Neumann, D. M.; Jursic. B. S. Bioorg. Med. Chem. 2014, 22, 4629.

4 Demchuk, D. V.; Lutsenko, A. I.; Troyanskii, E. I.; Nikishin, G. I. Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya **1989**, 8, 1843.

5 Pakal'nis, V. V.; Zerova, I. V.; Alekseev, V. V.; Yakimovich, S. I. Vestnik Sankt-Peterburgskogo Universiteta, Seriya 4: Fizika, Khimiya **2013**, 4, 125.

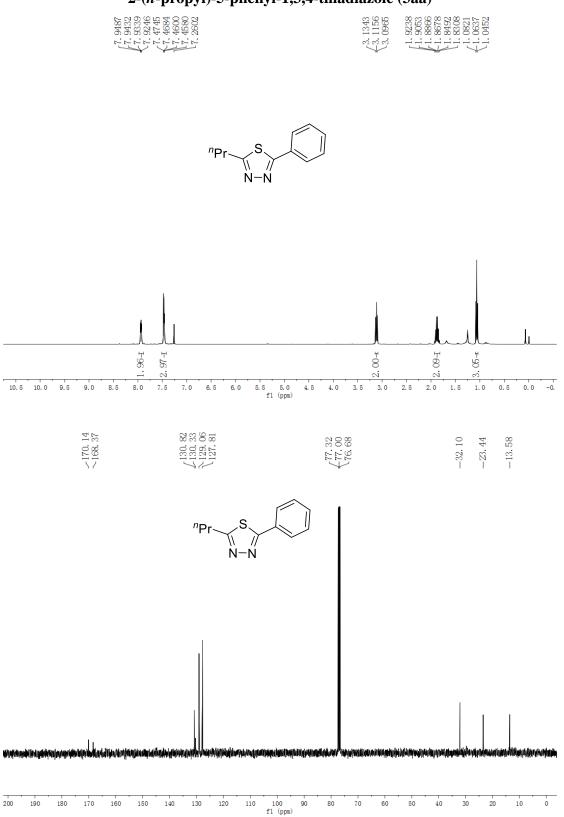
6 Knaus, G.; Meyers, A. I. J. Org. Chem. 1974, 39, 1189.

7 Gierczyk, B.; Zalas, M. Org. Prep. Proced. Int. 2005, 37, 213.

8 Meyers, A. I.; Knaus, G. N. J. Am. Chem. Soc. 1973, 95, 3408.

9 Fan, X.; Jiang, X.; Zhang, Y.; Chen, Z.; Zhu, Y. Org. Biomol. Chem. 2015, 13, 10402.

6. Copies of the ¹H NMR, ¹³C NMR Spectra



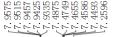
2-(*n*-propyl)-5-phenyl-1,3,4-thiadiazole (3aa)

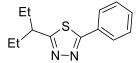
2-isobutyl-5-phenyl-1,3,4-thiadiazole (3ba)

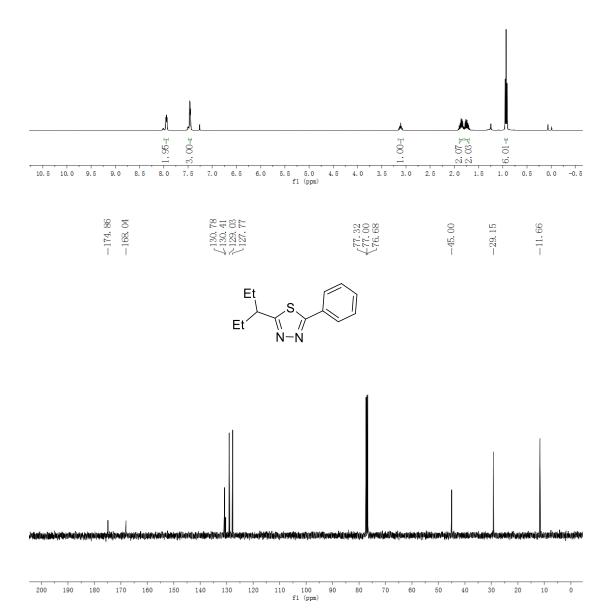
257 257 257 257 257 257 257 250 250 250 250 250 250 250 250 250 250	2. 1020 2. 1020 2. 1178 2. 1178 2. 1178 2. 1178 2. 1178 2. 10308 2.
ⁱ Bu N-N	
$\swarrow^{169, 04}_{168, 43}$	$ \begin{array}{c} 77.32 \\ 77.00 \\ -38.91 \\ -29.77 \\ -22.20 \end{array} $
⁶⁹¹ ¹⁰ ¹⁰ ¹⁰ ¹⁰ ¹⁰ ¹⁰ ¹⁰ ¹	
	diselectronic ministration in the providence of the state of the stat
200 190 180 170 160 150 140 130 120 110 100 f1 (pp	

2-(pentan-3-yl)-5-phenyl-1,3,4-thiadiazole (3ca)

9575 94257 94257 94257 94255 94255 94255 2596 2596 2596 2596	1473 1336 1255 1255 11200 1118 1036 0982 0982 0982 0982	8622 8477 8434 7574 7574 7574 9310 9310 9124
	ઌ૽ઌ૽ઌ૽ઌ૽ઌ૽ઌ૽ઌ	

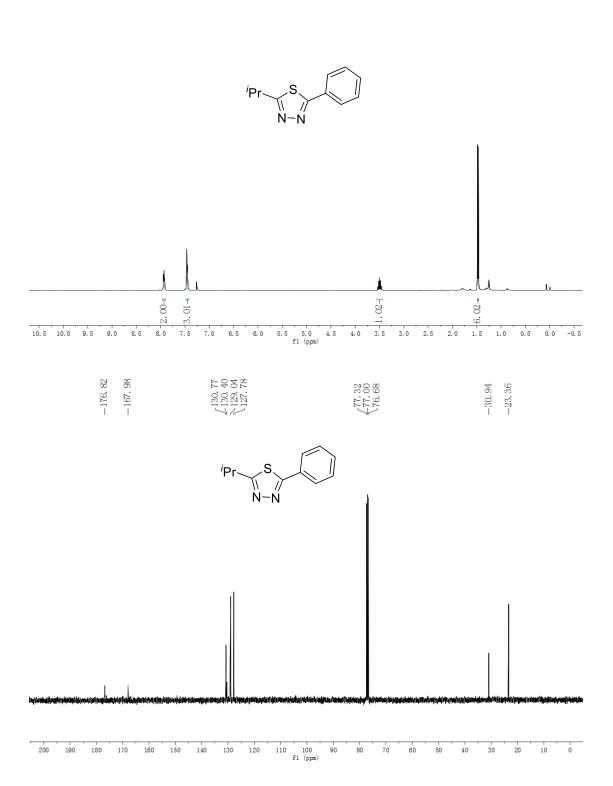






2-isopropyl-5-phenyl-1,3,4-thiadiazole (3da)

9444 9296 9296 9203 9203 9203 9203 2602 2602 2602	5497 5524 55324 4979 4807 4634 4634	4844 4672



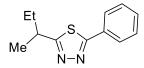
2-cyclohexyl-5-phenyl-1,3,4-thiadiazole(3ea) Су // N-N H00. . 854 0.99₁ 1.022 e i 5.5 5.0 f1 (ppm) 4.5 0.5 0.0 -0.5 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 4.0 3. 5 3. 0 2.5 1. 0 2.0 1.5 $\begin{smallmatrix} \mathcal{I}_{130.73} \\ \mathcal{I}_{130.40} \\ \mathring{\chi}_{129.02} \\ \mathring{\chi}_{127.76} \end{split}$ -175.85-167.71 $\underbrace{ \begin{array}{c} 77.32\\ 77.00\\ 76.68 \end{array} }$ --39.96 --33.93 <25.62 ∠25.62 Су ∬ // N−N Asayon MANA Interspectrum Participation and

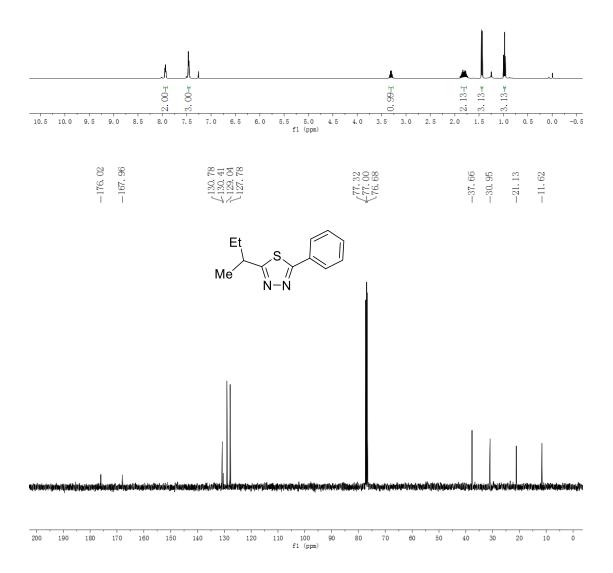
200 70 20 0 150 130 120 110 100 f1 (ppm) 80 60 50 40 30 10 190 180 170 160 140 90

2-(sec-butyl)-5-phenyl-1,3,4-thiadiazole(3fa)

$\begin{array}{c} 9509\\9451\\9359\\9268\\4674\\4526\\4509\\4510\\2596\end{array}$
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

510 337 163 988 814 640	510 326 913 522 349 522 504 504
0000000	88385733888
ന്ന്ന്ന്ന്	

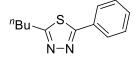


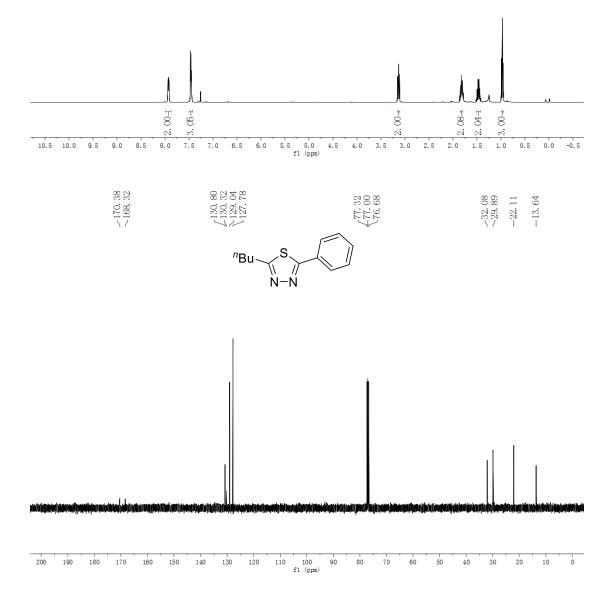


## 2-(*n*-butyl)-5-phenyl-1,3,4-thiadiazole(3ga)

9402 9348 9256 9163 9163 4991 4854 4677 4677	

1530 1340 1146	88399 88207 88207 8819 8819 44578 44578 94388 94388 94388 94388 94388 94388 94388 94388 9518
nini ni	

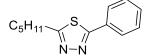


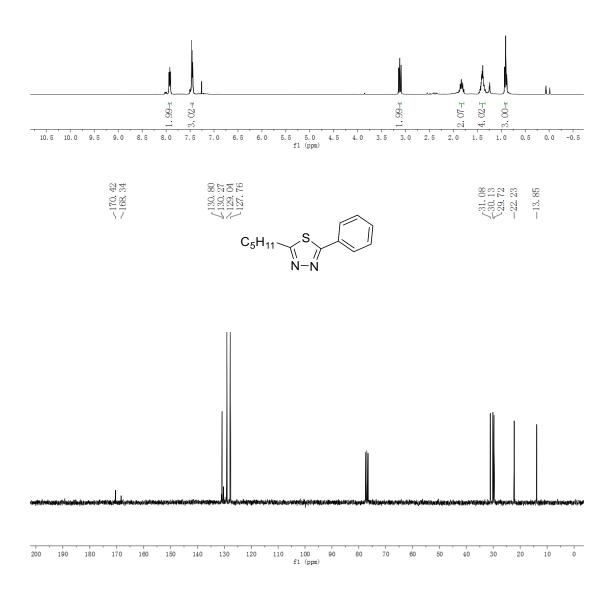


## 2-pentyl-5-phenyl-1,3,4-thiadiazole (3ha)

1444 1193 0934	8329 8076 8076 3369 3361 33793 3793 3793 3793 3793 3793 3793 8841 8841
minini Minini	

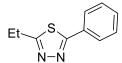


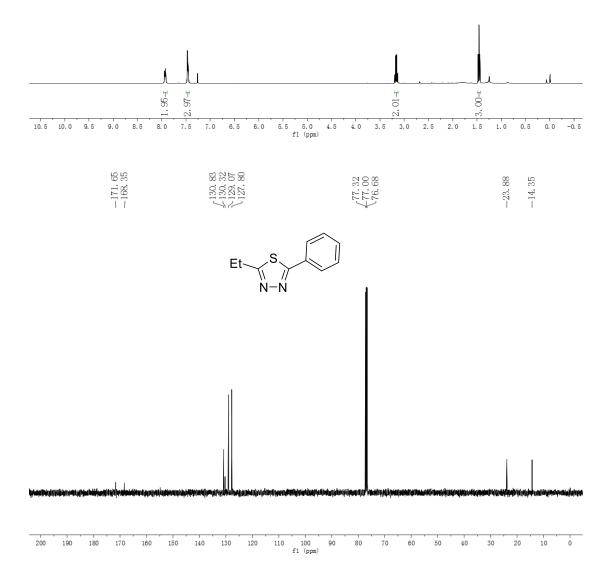




## 2-ethyl-5-phenyl-1,3,4-thiadiazole (3ia)

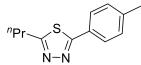
9512 9420 9365 9271 9178 4514 4573 4573 2597 2597 2597	1950 1760 1571 1382	4778 4589 4399
	ri ri ri ri	$\checkmark^1_1$

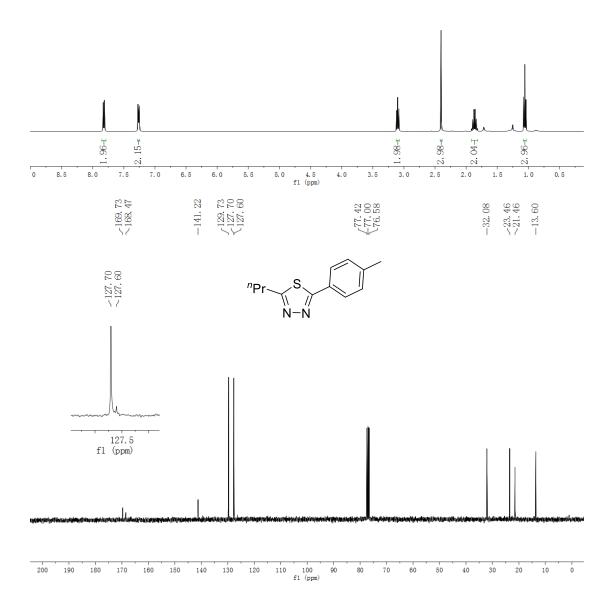




108	$\int_{-2.5}^{-2.5} \frac{1000}{1000}$	$\underbrace{\bigwedge^{1.\ 0755}_{1.\ 0571}}_{1.\ 0387}$
-----	----------------------------------------	-----------------------------------------------------------

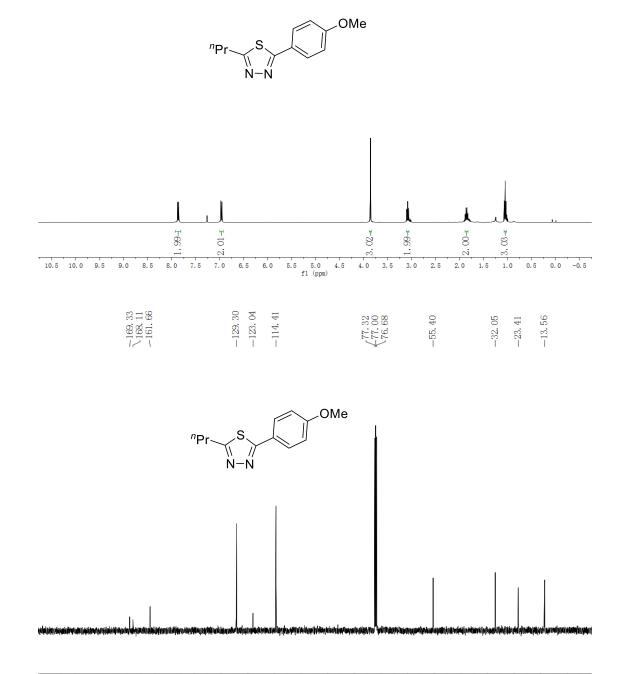






## 2-(*n*-propyl)-5-(*p*-methoxyphenyl)-1,3,4-thiadiazole (3ac)

8730 8510	2595 9712 9492	8539	0994 0806 0806 8892 8832 8832 88132 88132 88132 88132 8064 8064 0658 00474 0058
∼ <u>∼</u>	20.7 6.0	°.	

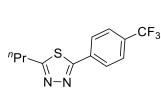


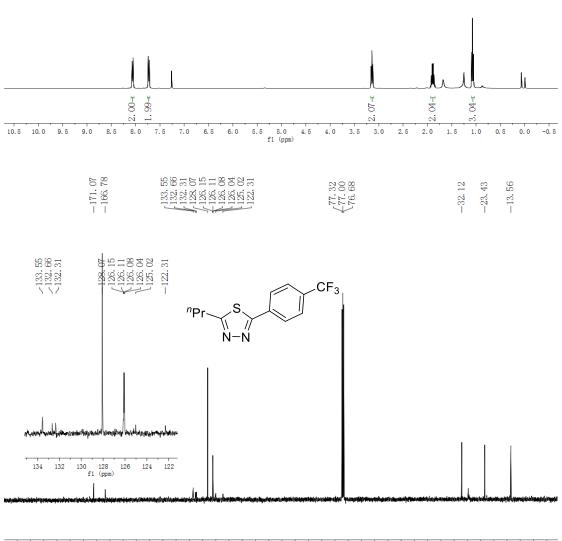
f1 (ppm) 

 $\label{eq:constraint} 2 \text{-} (\textit{n-propyl}) \text{-} 5 \text{-} (\textit{p-(trifluoromethyl)phenyl}) \text{-} 1, 3, 4 \text{-} thiadiazole(3ad)$ 

0719 0515 7398 7193 7193	2600	
8.8.1-1-	2.	

1596 1409 1218	9372 9187 9001 8814 8628 8444 0902 0718 0534
en en en	



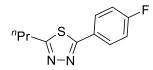


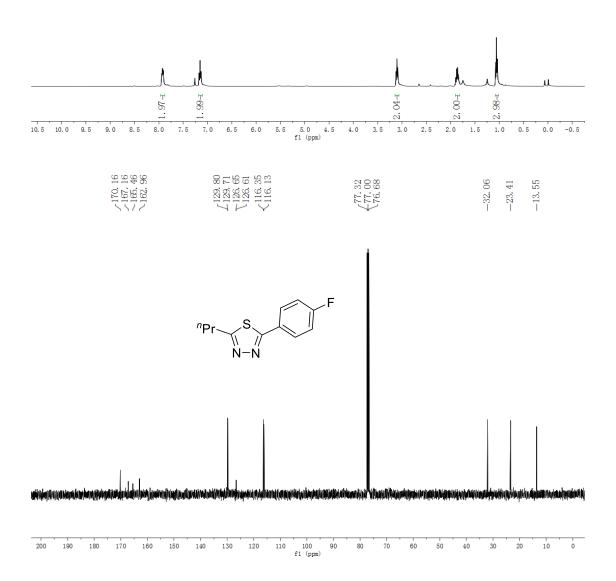
f1 (ppm) 

## 2-(*n*-propyl)-5-(*p*-fluorophenyl)-1,3,4-thiadiazole(3ae)

9420 9364 9287 9287 9125 9125 9125 11735 11523 11523 11523 11523 11308	

1229 1042 0851	9132 8947 8575 8575 8575 8575 0149 0749 0565 0382 0382
n'n'n'	

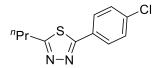


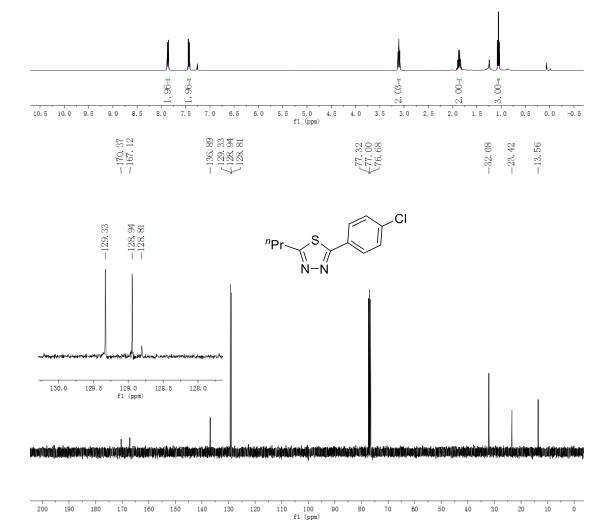


2-(*n*-propyl)-5-(*p*-chlorophenyl)-1,3,4-thiadiazole (3af)

8778 8566 4431 4219 2602	

1259 1072 0881	9125 8940 8567 8567 8195 0734 0734 0550
n'n'n'	

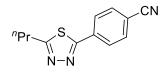


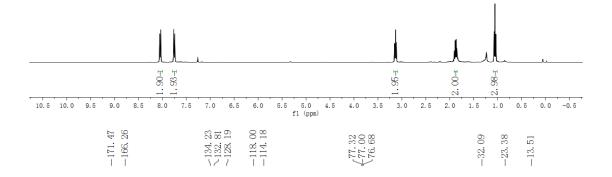


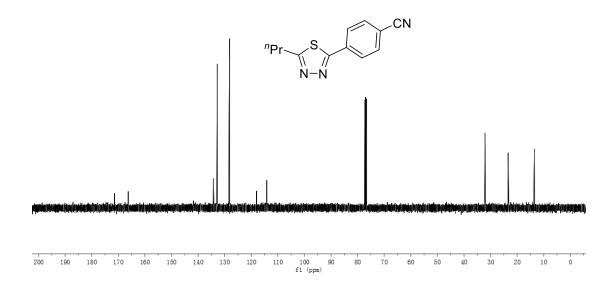
## 4-(5-propyl-1,3,4-thiadiazol-2-yl)benzonitrile (3ag)

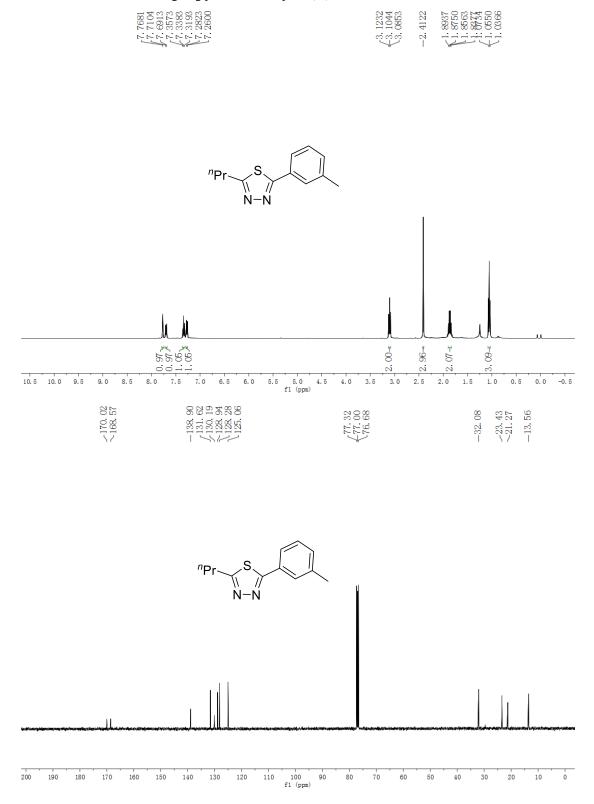
0551 0345 7615 7408	2598
8, 6, 1, 2, 8, 8, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1,	-2.

1512 1325 1135	9218 9033 8661 8661 8475 8291 0729 0546 0546
mini mi	





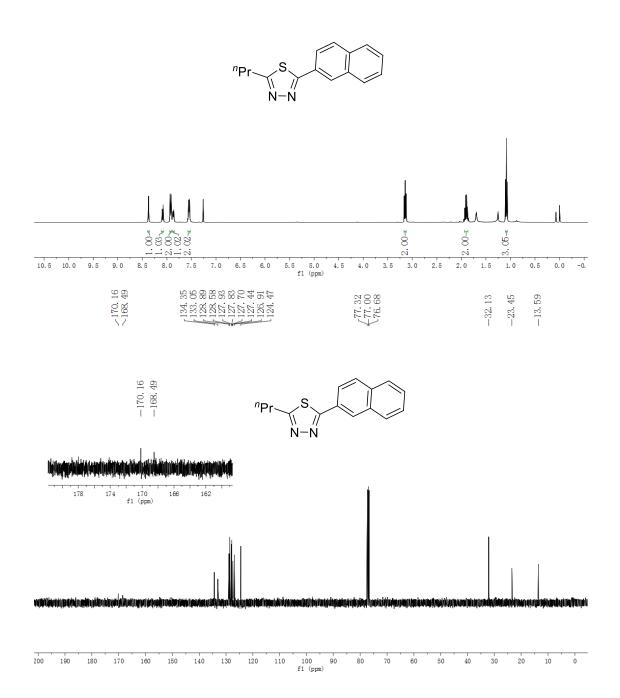




### 2-(*n*-propyl)-5-(*m*-tolyl)-1,3,4-thiadiazole (3ah)

## 2-(*n*-propyl)-5-(naphthalen-2-yl)-1,3,4-thiadiazole (3ai)

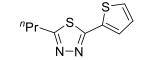
2598 2528 2528 2538 2538 2538 2538 2538 253	1637 1449 1258	9494 9308 9308 8748 8748 8564 1031 0848 0663
8 8 8 8 8 8 1 1 1 1 1 1 1 1 1 1 1 1 1 1	က်ယ်သို	

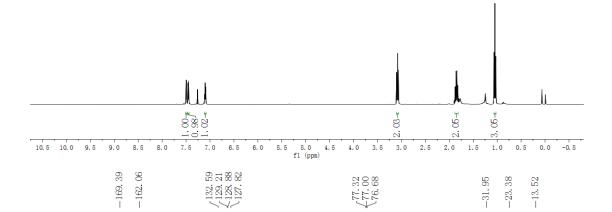


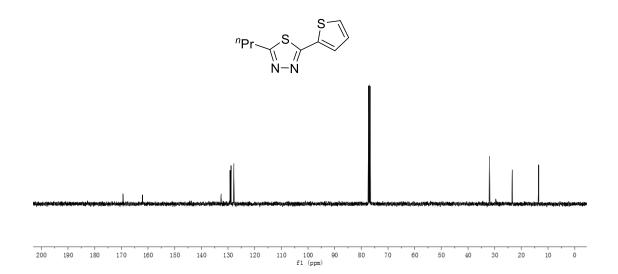
## 2-(*n*-propyl)-5-(thiophen-2-yl)-1,3,4-thiadiazole (3aj)

55013 44923 44502 44573 44573 122599 0010 00170 0010 0010 0010 0010 0010 0	1008 0821 0630	8954 8768 8582 8582 8394 8208 8024 0648 0648 0648 0648
	e e e e e e e e e e e e e e e e e e e	









## 2,5-diphenyl-1,3,4-thiadiazole (4)

$\begin{array}{c} 0476\\ 0433\\ 0281\\ 0281\\ 0195\\ 0195\\ 0195\\ 0195\\ 0099\\ 00066\\ 00099\\ 00083\\ 0000\\ 00066\\ 0003\\ 00099\\ 00023\\ 00099\\ 00005\\ 00099\\ 00099\\ 00003\\ 00099\\ 00003\\ 00099\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00009\\ 00000\\ 00009\\ 00000\\ 00000\\ 00000\\ 00000\\ 00000\\ 00000\\ 00000\\ 00000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 0000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ 000\\ $	$\begin{array}{c} 498 \\ 492 \\ 478 \\ 458 \\ 458 \\ 458 \\ 458 \\ 458 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\ 259 \\$
$\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\alpha}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}\overset{\sigma}{\sim}$	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

