

Supporting information

I₂-catalyzed Oxidative Coupling Reactions of Hydrazones and Amines and the Application in the Synthesis of 1,3,5-Trisubstituted 1,2,4-Triazoles

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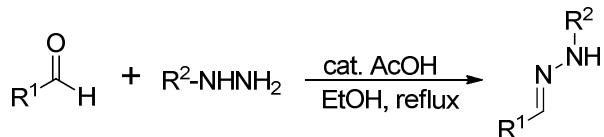
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General Unless otherwise stated, all reactions were performed under air in a flame-dried reaction flask. Toluene, CH₃CN, 1,4-Dioxane, DCE and DMF were dried by calcium hydride and freshly distilled. DMSO was used without purification. The other materials and solvents were purchased from Adamas-beta and other commercial suppliers, and used without additional purification. For chromatography, 300-400 mesh silica gel (Qingdao, China) was employed. ¹H NMR spectra were recorded on a Bruke Avance operating at for ¹H NMR at 400 MHz, and ¹³C NMR at 100 MHz using TMS as internal standard. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or Waters TOFMS GCT Premier using EI or ESI ionization. Fluorescence excitation and emission spectra were recorded by SENS-9000 luminescope with C₈ = 2.8 × 10⁻⁶ mol/L. Melting points were measured with WRR digital point apparatus and not corrected.

Synthesis of Substrates 1 ^[1]



To a solution of hydrazine (10 mmol) and the aldehyde (10 mmol) in ethanol (10 mL) was added a few drops of AcOH. The mixture was stirred and heated to reflux for 3-6 h. The precipitated hydrazone was filtered, washed and dried. The pure hydrazone was obtained after recrystallization from ethanol. For some hydrazones derived from aliphatic hydrazine hydrochlorides or aliphatic aldehydes, the desired hydrazone products were obtained by fast column chromatography on silica gel and kept in low temperature for their instability.

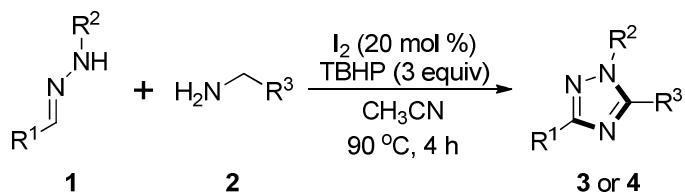
Optimization of the Reaction Conditions^a (Table S1)

		catalyst (x equiv) oxidant (3 equiv) solvent 90 °C, 4 h		3b
entry	cat. (equiv)	oxidant	solvent	yield (%) ^b
1	I ₂ /0.1	TBHP	dioxane	40
2	I ₂ /0.2	TBHP	dioxane	45
3	I ₂ /0.5	TBHP	dioxane	23
4	I ₂ /1.0	TBHP	dioxane	14
5	--	TBHP	dioxane	7
6	I ₂ /0.2	TBHP	toluene	30
7	I ₂ /0.2	TBHP	DMF	39
8	I₂/0.2	TBHP	CH₃CN	77
9	I ₂ /0.2	TBHP	DMSO	26
10	I ₂ /0.2	TBHP	H ₂ O	16

11	I ₂ /0.2	TBHP	DCE	28
12	KI/0.2	TBHP	CH ₃ CN	70
13	TBAI/0.2	TBHP	CH ₃ CN	74
14	NIS/0.2	TBHP	CH ₃ CN	65
15	I ₂ /0.2	TBPB	CH ₃ CN	38
16	I ₂ /0.2	DTBP	CH ₃ CN	trace
17	I ₂ /0.2	H ₂ O ₂	CH ₃ CN	26
18	I ₂ /0.2	BPO	CH ₃ CN	20
19	I ₂ /0.2	TBHP	CH ₃ CN	65 ^c
20	I ₂ /0.2	TBHP	CH ₃ CN	58, ^d 65, ^e 70 ^f

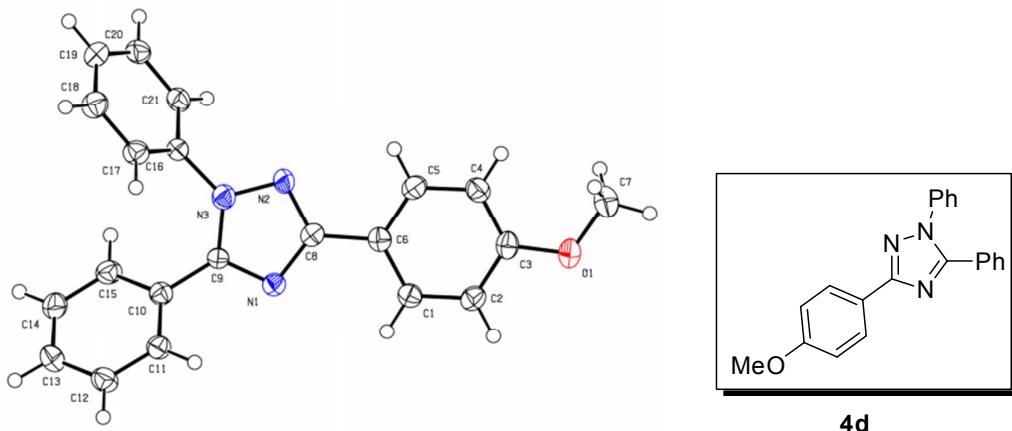
^a Reaction conditions: **1a** (0.3 mmol), **2b** (0.9 mmol), catalyst (x equiv), oxidant (0.9 mmol) in solvent (1 mL) under air at 90 °C for 4 h. ^b Isolated yields. ^c Under N₂ atmosphere. ^d At room temperature. ^e At 60 °C. ^f At 120 °C. TBAI = Tertabutyl ammonium iodine, NIS = *N*-Iodosuccinimide, TBHP = 70% *t*-BuOOH in water, DTBP = 2-(*t*-Butylperoxy)-2-methylpropane, TBPB = *t*-Buytl peroxybenzoate, BPO = benzoyl peroxide, H₂O₂ = 30% in water.

Typical Procedure for the Product



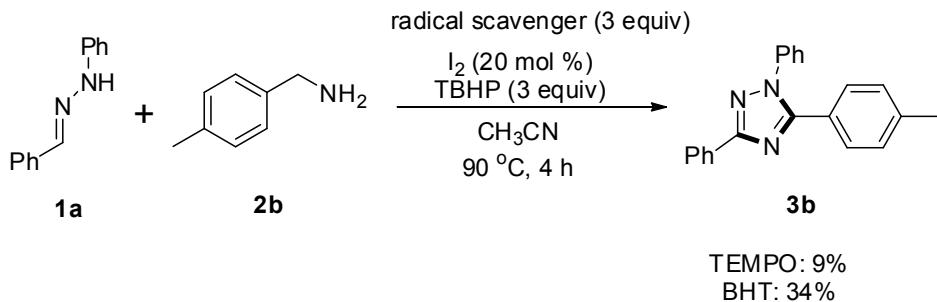
Molecular iodine (I₂) (20 mol %) and TBHP (70% aq. 0.9 mmol) was added to a mixture of hydrazone **1** (0.3 mmol), aliphatic amine **2** (0.9 mmol) in CH₃CN (1 mL). The mixture was stirred at 90 °C under air for 4 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to ambient temperature and 15 mL water was added to the mixture, then extracted by EtOAc for 3 times (3 × 30 mL). The extract was washed with 10% Na₂S₂O₃ solution (w/w), dried over anhydrous Na₂SO₄ and the solvent was removed in vacuo to provide a crude product, which was purified by fast column chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA= 10/1) as eluent to afford pure products **3** or **4**.

The Crystal Structure of the Triazole **4d**



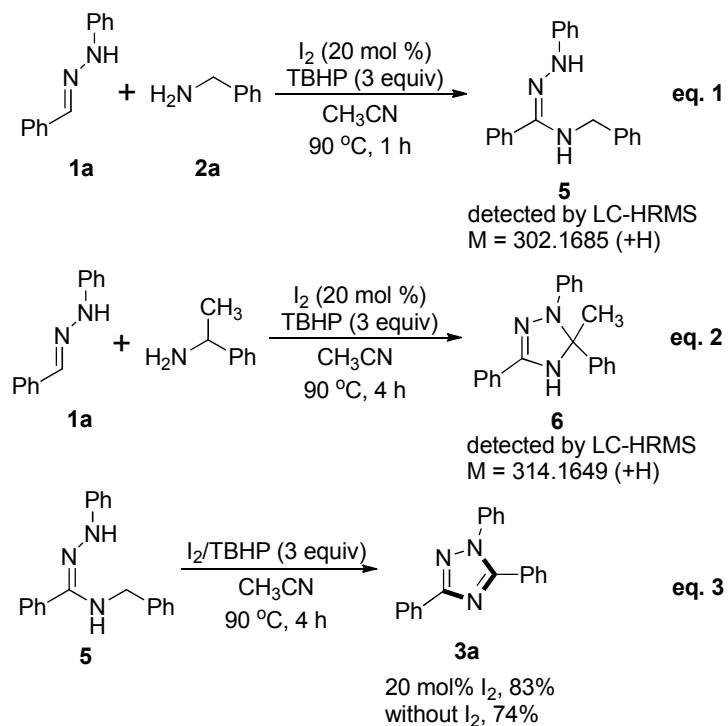
CCDC **1436037**. Selected bond lengths (\AA): N1-C8, 1.361; N2-N3, 1.356; N1-C9, 1.344; N2-C8, 1.336; N3-C9, 1.350; C9-C10, 1.459; C6-C8, 1.469.

The Radical Trapping Experiments

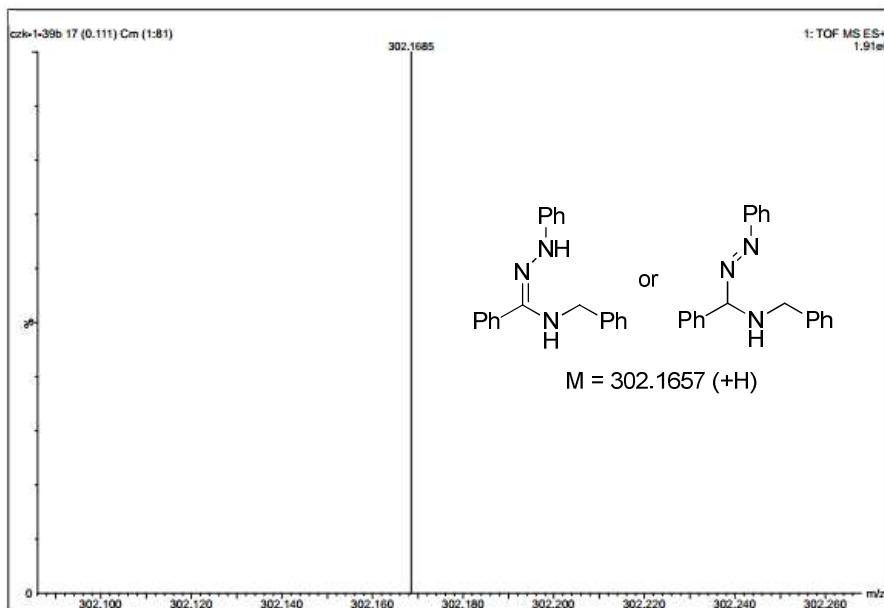


Molecular iodine (I_2) (20 mol %) and TBHP (70% aq. 0.9 mmol) was added to a mixture of hydrazone **1a** (0.3 mmol), *p*-tolylmethanamine **2b** (0.9 mmol) in CH_3CN (1 mL). Radical scavenger TEMPO or BHT (0.9 mmol) was added to the mixture respectively. The mixture was stirred at 90 °C under air for 4 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to ambient temperature and 15 mL water was added to the mixture, then extracted by EtOAc for 3 times (3×30 mL). The extract was washed with 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution (w/w), dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA= 10/1) as eluent to afford product **3b** in 9% or 34% yields respectively.

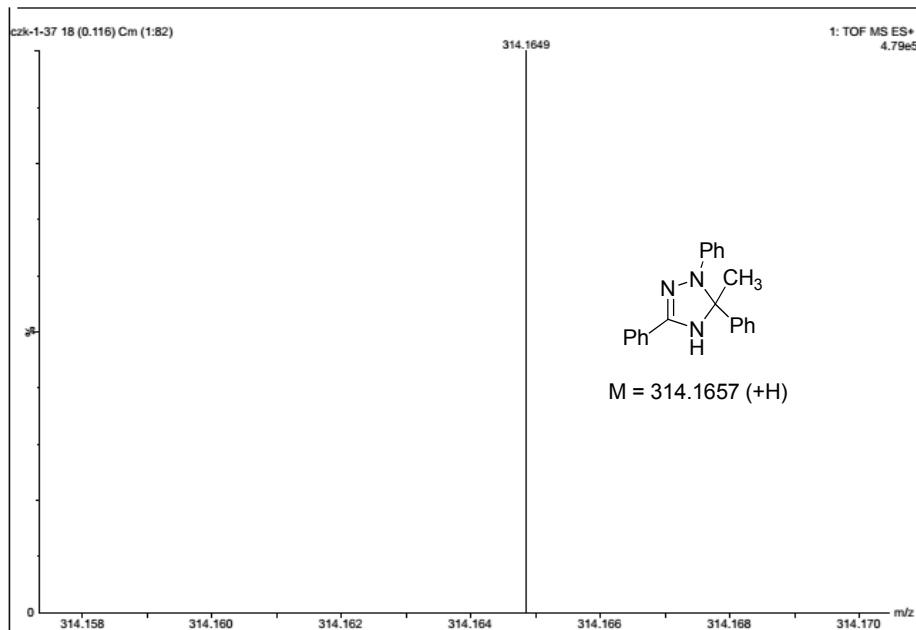
The Control Experiments



Eq.1: Molecular iodine (I_2) (20 mol %) and TBHP (70% aq. 0.9 mmol) was added to a mixture of hydrazone **1a** (0.3 mmol), benzylamine **2a** (0.9 mmol) in CH_3CN (1 mL). The mixture was stirred at 90°C under air for 1 h. The mixture was tested by Waters TOFMS GCT Premier and the molecular mass of intermediate **5** was detected successfully.

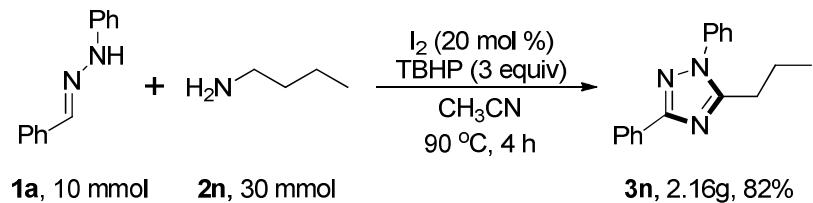


Eq.2: Molecular iodine (I_2) (20 mol %) and TBHP (70% aq. 0.3 mmol) was added to a mixture of hydrazone **1a** (0.3 mmol), 1-phenylethanamine (0.9 mmol) in CH_3CN (1 mL). The mixture was stirred at 90 °C under air for 4 h. The mixture was tested by Waters TOFMS GCT Premier and the molecular mass of intermediate **6** was detected successfully.



Eq.3: Molecular iodine (I_2) (20 mol %) or without I_2 and TBHP (70% aq. 0.3 mmol) was added to a mixture of prepared intermediate **5** (0.1 mmol) in CH_3CN (0.5 mL). The mixture was stirred at 90 °C under air for 1 h. The solvent was removed in vacuo and the crude mixture was purified by column chromatography on silica gel to afford product **3a** in 83% or 74% yields respectively.

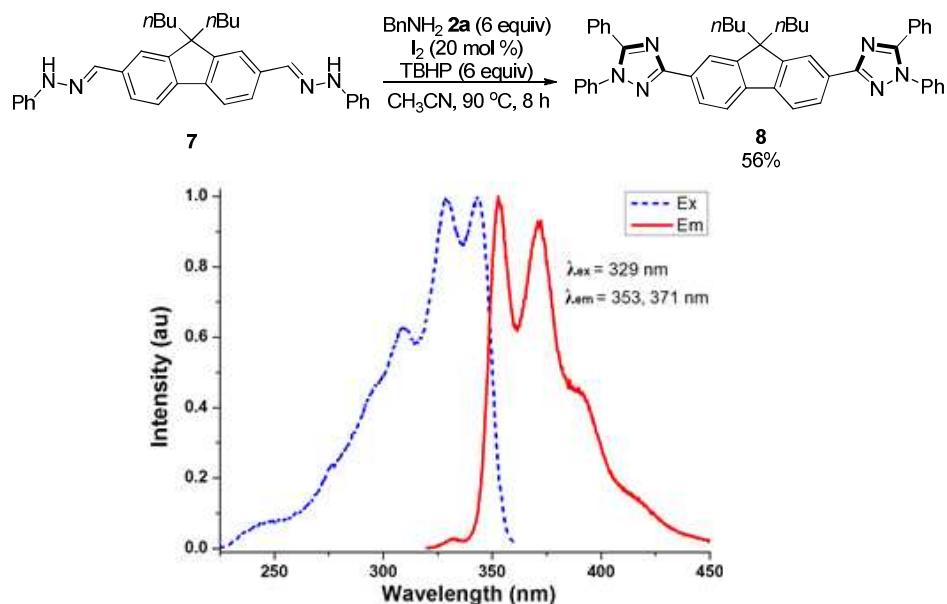
The Scale-up Reaction



Molecular iodine (I_2) (20 mol %) and TBHP (70% aq. 30 mmol) was added to a mixture of hydrazone **1a** (10 mmol), butan-1-amine **2n** (30 mmol) in CH_3CN (30 mL). The mixture was stirred at 90 °C under air for 4 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to ambient temperature and 50 mL water was added to the mixture, then extracted by EtOAc for 3 times (3×50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography

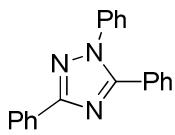
on silica gel using petroleum ether and ethyl acetate (PE/EA= 10/1) as eluent to afford pure product **3n** as light yellow solid 2.16g (82%).

Synthetic Application



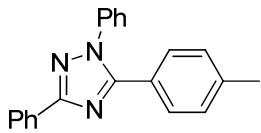
Molecular iodine (**I₂**) (20 mol %) and TBHP (70% aq. 1.8 mmol) was added to a mixture of hydrazone **7** (0.3 mmol), benzylamine **2a** (1.8 mmol) in **CH₃CN** (1 mL). The mixture was stirred at **90 °C** under air for 8 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to ambient temperature and 15 mL water was added to the mixture, then extracted by EtOAc for 3 times (3 × 30 mL). The extract was washed with 10% **Na₂S₂O₃** solution (w/w), dried over anhydrous **Na₂SO₄** and the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA= 5/1) as eluent to afford pure product **8**. The fluorescence excitation and emission spectra of compound **8** were recorded by SENS-9000 luminoscope with **C₈ = 2.8 × 10⁻⁶ mol/L**.

Characterization Data of the Corresponding Products



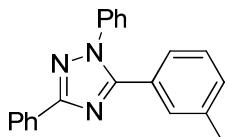
1,3,5-triphenyl-1H-1,2,4-triazole (3a) ^[2]

Yield: 71%; 63.5 mg, light yellow solid; m.p = 94-96 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.26 (d, 2H, *J* = 6.8 Hz), 7.58 (d, 2H, *J* = 7.2 Hz), 7.36-7.48 (m, 11H). ¹³C NMR (CDCl₃, 100 MHz) δ 161.9, 154.7, 138.2, 130.6, 130.0, 129.4, 129.4, 129.0, 128.8, 128.6, 127.9, 126.6, 125.4. HRMS (EI-TOF) calcd for C₂₀H₁₆N₃ (M+H⁺): 298.1344, found: 298.1349.



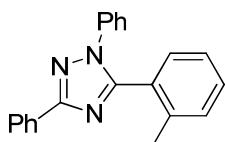
1,3-diphenyl-5-(*p*-tolyl)-1H-1,2,4-triazole (3b) ^[3]

Yield: 77%; 71.8 mg, light yellow solid; m.p = 81-82 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.24 (dd, 2H, *J* = 8.0 Hz, 1.6 Hz), 7.43-7.47 (m, 10H), 7.16 (d, 2H, *J* = 8.0 Hz), 2.37 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 161.8, 154.8, 140.3, 138.4, 130.7, 129.4, 129.3, 129.0, 128.9, 128.8, 128.5, 126.6, 125.5, 125.0, 21.4. HRMS (EI-TOF) calcd for C₂₁H₁₈N₃ (M+H⁺): 312.1501, found: 312.1518.



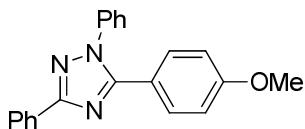
1,3-diphenyl-5-(*m*-tolyl)-1H-1,2,4-triazole (3c) ^[4]

Yield: 66%; 61.6 mg, light brown yellow solid; m.p = 61-63 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.28 (d, 2H, *J* = 7.2 Hz), 7.46-7.54 (m, 9H), 7.23-7.26 (m, 3H), 2.37 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 161.8, 154.9, 138.5, 138.3, 130.7, 130.7, 129.6, 129.3, 129.3, 128.7, 128.5, 128.3, 127.8, 126.5, 125.9, 125.3, 21.3. HRMS (EI-TOF) calcd for C₂₁H₁₈N₃ (M+H⁺): 312.1501, found: 312.1515.



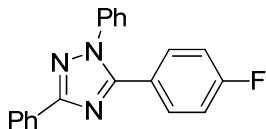
1,3-diphenyl-5-(o-tolyl)-1H-1,2,4-triazole (3d) [5]

Yield: 74%; 69.0 mg, light brown yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 8.30 (d, 2H, $J = 7.6$ Hz), 7.46-7.52 (m, 3H), 7.34-7.40 (m, 7H), 7.27 (d, 2H, $J = 7.2$ Hz), 2.16 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.7, 154.6, 137.8, 137.4, 130.7, 130.6, 130.2, 129.4, 129.1, 128.6, 128.5, 128.0, 126.5, 126.0, 123.5, 19.7. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3$ ($\text{M}+\text{H}^+$): 312.1501, found: 312.1516.



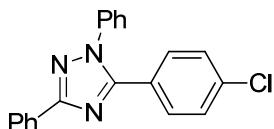
5-(4-methoxyphenyl)-1,3-diphenyl-1H-1,2,4-triazole (3e) [3]

Yield: 77%; 75.5 mg, light yellow solid; m.p = 101-103 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.24 (dd, 2H, $J = 8.4$ Hz, 1.4Hz), 7.42-7.51 (m, 10H), 6.87 (d, 2H, $J = 8.78$ Hz), 3.81 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.7, 160.9, 154.6, 138.4, 130.8, 130.5, 129.4, 129.3, 128.7, 128.5, 126.6, 125.5, 120.2, 114.0, 55.3. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3\text{O}$ ($\text{M}+\text{H}^+$): 328.1450, found: 328.1454.



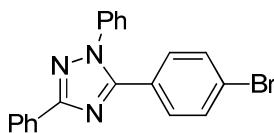
5-(4-fluorophenyl)-1,3-diphenyl-1H-1,2,4-triazole (3f) [new compound]

Yield: 65%; 61.6 mg, light yellow solid; m.p = 99-101 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.23 (d, 2H, $J = 7.6$ Hz), 7.55-7.58 (m, 2H), 7.41-7.49 (m, 8H), 7.06 (t, 2H, $J = 8.6$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 163.6 (d, $J_{\text{C}-\text{F}} = 250.1$ Hz), 161.9, 153.8, 138.1, 131.1 (d, $J_{\text{C}-\text{F}} = 8.2$ Hz), 130.5, 129.5, 129.5, 129.0, 128.6, 126.5, 125.4, 124.1 (d, $J_{\text{C}-\text{F}} = 2.8$ Hz), 115.8 (d, $J_{\text{C}-\text{F}} = 21.7$ Hz). HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{15}\text{FN}_3$ ($\text{M}+\text{H}^+$): 316.1250, found: 316.1259.



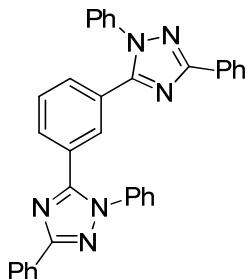
5-(4-chlorophenyl)-1,3-diphenyl-1H-1,2,4-triazole (3g) [3]

Yield: 71%; 70.5 mg, light yellow solid; m.p = 131-133 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.24 (d, 2H, J = 6.8 Hz), 7.40-7.52 (m, 10H), 7.34 (d, 2H, J = 8.4 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.0, 153.7, 138.1, 136.2, 130.5, 130.2, 129.5, 129.5, 129.1, 128.9, 128.6, 126.6, 126.4, 125.5. HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{15}\text{ClN}_3$ ($\text{M}+\text{H}^+$): 332.0955, found: 332.0958.



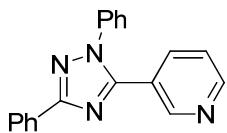
5-(4-bromophenyl)-1,3-diphenyl-1H-1,2,4-triazole (3h) [new compound]

Yield: 75%; 84.4 mg, light yellow solid; m.p = 118-120 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.23 (d, 2H, J = 7.2 Hz), 7.41-7.52 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.0, 153.7, 138.0, 131.8, 130.4, 129.6, 129.5, 129.1, 128.6, 126.8, 126.5, 125.4, 124.6. HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{15}\text{BrN}_3$ ($\text{M}+\text{H}^+$): 376.0499, found: 376.0457.



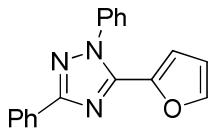
1,3-bis(1,3-diphenyl-1H-1,2,4-triazol-5-yl)benzene (3i) [new compound]

Yield: 55%; 85.1 mg, light orange solid; m.p = 162-164 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.21 (d, 4H, J = 7.6 Hz), 7.94 (s, 1H), 7.56 (dd, 2H, J = 7.8 Hz, 0.8 Hz), 7.37-7.50 (m, 16H), 7.33 (t, 1H, J = 8.0 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.0, 153.7, 138.0, 130.5, 130.2, 129.6, 129.5, 128.8, 128.6, 126.5, 125.5. HRMS (EI-TOF) calcd for $\text{C}_{34}\text{H}_{25}\text{N}_6$ ($\text{M}+\text{H}^+$): 517.2141, found: 517.2148.



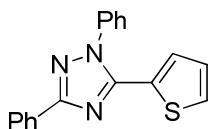
3-(1,3-diphenyl-1H-1,2,4-triazol-5-yl)pyridine (3j) [6]

Yield: 56%; 50.1 mg, light yellow solid; m.p = 113-115 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.82 (s, 1H), 8.68 (d, 1H, J = 5.2 Hz), 8.27 (d, 2H, J = 7.6 Hz), 7.93 (d, 1H, J = 7.6 Hz), 7.43-7.50 (m, 8H), 7.31-7.36 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.4, 152.1, 150.7, 149.5, 137.8, 136.1, 130.3, 129.7, 129.6, 129.4, 128.6, 126.5, 125.5, 124.3, 123.3. HRMS (EI-TOF) calcd for $\text{C}_{19}\text{H}_{15}\text{N}_4$ ($\text{M}+\text{H}^+$): 299.1297, found: 299.1305.



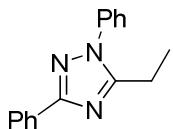
5-(furan-2-yl)-1,3-diphenyl-1H-1,2,4-triazole (3k) [new compound]

Yield: 71%; 61.1 mg, yellow solid; m.p = 93-95 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.24 (d, 2H, J = 7.6 Hz), 7.44-7.53 (m, 9H), 6.49 (d, 1H, J = 3.6 Hz), 6.43 (d, 1H, J = 1.2 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.1, 144.3, 138.0, 130.3, 129.6, 129.5, 129.4, 128.5, 126.6, 126.1, 112.8, 111.6. HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{O}$ ($\text{M}+\text{H}^+$): 288.1137, found: 288.1149.



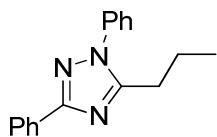
1,3-diphenyl-5-(thiophen-2-yl)-1H-1,2,4-triazole (3l) [new compound]

Yield: 66%; 60.0 mg, white solid; m.p = 142-144 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.22 (d, 2H, J = 7.6 Hz), 7.39-7.56 (m, 9H), 7.08 (d, 1H, J = 7.6 Hz), 6.97 (t, 1H, J = 4.4 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.9, 150.1, 137.9, 130.4, 129.9, 129.6, 129.4, 129.3, 128.9, 128.8, 128.5, 127.6, 126.7, 126.6. HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{S}$ ($\text{M}+\text{H}^+$): 304.0908, found: 304.0926.



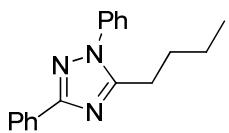
5-ethyl-1,3-diphenyl-1H-1,2,4-triazole (3m) ^[4]

Yield: 83%; 62.0 mg, light yellow solid; m.p = 66-67 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.16 (d, 2H, *J* = 7.6 Hz), 7.39-7.53 (m, 8H), 2.87 (q, 2H, *J* = 7.6 Hz), 1.36 (t, 3H, *J* = 7.6 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 161.4, 157.9, 137.5, 130.9, 129.4, 129.2, 128.9, 128.5, 126.4, 125.1, 20.2, 12.4. HRMS (EI-TOF) calcd for C₁₆H₁₆N₃ (M+H⁺): 250.1344, found: 250.1364.



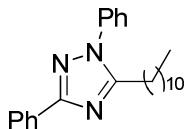
1,3-diphenyl-5-propyl-1H-1,2,4-triazole (3n) ^[4]

Yield: 85%; 67.1 mg, light yellow solid; m.p = 54-56 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.16 (dd, 2H, *J* = 8.0 Hz, 1.2 Hz), 7.39-7.53 (m, 8H), 2.81 (t, 2H, *J* = 7.8 Hz), 1.79-1.85 (m, 2H), 0.97 (t, 3H, *J* = 7.4 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 161.4, 156.9, 137.5, 130.9, 129.4, 129.1, 128.9, 128.5, 126.4, 125.2, 28.4, 21.4, 13.7. HRMS (EI-TOF) calcd for C₁₇H₁₈N₃ (M+H⁺): 264.1501, found: 264.1513.



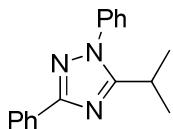
5-butyl-1,3-diphenyl-1H-1,2,4-triazole (3o) ^[7]

Yield: 92%; 76.5 mg, light yellow oil; ¹H NMR (CDCl₃, 400 MHz) δ 8.11 (d, 2H, *J* = 8.0 Hz), 7.31-7.46 (m, 8H), 2.75 (t, 2H, *J* = 8.0 Hz), 1.66-1.72 (m, 2H), 1.26-1.32 (m, 2H), 0.81 (t, 3H, *J* = 7.4 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 161.3, 157.0, 137.5, 130.9, 129.3, 129.1, 128.8, 128.4, 126.3, 125.1, 30.0, 26.2, 22.2, 13.5. HRMS (EI-TOF) calcd for C₁₈H₂₀N₃ (M+H⁺): 278.1657, found: 278.1660.



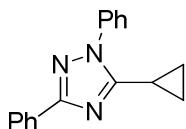
1,3-diphenyl-5-undecyl-1H-1,2,4-triazole (3p) [new compound]

Yield: 73%; 82.1 mg, light yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 8.20 (d, 2H, $J = 7.2$ Hz), 7.41-7.55 (m, 8H), 2.85 (t, 2H, $J = 7.8$ Hz), 1.77-1.84 (m, 2H), 1.26-1.36 (m, 16H), 0.91 (t, 3H, $J = 6.8$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.4, 157.0, 137.6, 130.9, 129.4, 129.1, 128.8, 128.4, 126.4, 125.2, 31.8, 29.5, 29.3, 29.2, 29.1, 29.1, 27.9, 26.5, 22.6, 14.0. HRMS (EI-TOF) calcd for $\text{C}_{25}\text{H}_{34}\text{N}_3$ ($\text{M}+\text{H}^+$): 376.2753, found: 376.2742.



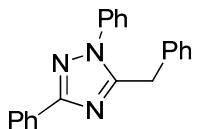
5-isopropyl-1,3-diphenyl-1H-1,2,4-triazole (3q) ^[8]

Yield: 82%; 64.7 mg, light brown yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 8.19 (d, 2H, $J = 7.6$ Hz), 7.39-7.55 (m, 8H), 3.12-3.18 (m, 1H), 1.38 (d, 6H, $J = 6.8$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.8, 161.4, 137.5, 131.0, 129.4, 129.0, 129.0, 128.4, 126.5, 125.6, 25.8, 21.6. HRMS (EI-TOF) calcd for $\text{C}_{17}\text{H}_{18}\text{N}_3$ ($\text{M}+\text{H}^+$): 264.1501, found: 264.1491.



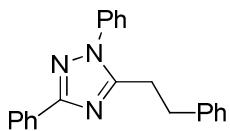
5-cyclopropyl-1,3-diphenyl-1H-1,2,4-triazole (3r) [new compound]

Yield: 79%; 61.9 mg, light brown yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 8.14 (d, 2H, $J = 6.8$ Hz), 7.66 (d, 2H, $J = 7.6$ Hz), 7.54 (t, 2H, $J = 7.6$ Hz), 7.36-7.47 (m, 4H), 1.96-2.01 (m, 1H), 1.30-1.34 (m, 2H), 1.07-1.12 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.1, 158.2, 137.6, 130.9, 129.3, 129.0, 128.4, 128.4, 126.4, 124.8, 9.3, 7.6. HRMS (EI-TOF) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_3$ ($\text{M}+\text{H}^+$): 262.1344, found: 262.1339.



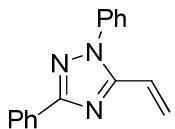
5-benzyl-1,3-diphenyl-1H-1,2,4-triazole (3s) [8]

Yield: 60%; 56.0 mg, light yellow solid; m.p = 71-73 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.22 (d, 2H, J = 7.6 Hz), 7.39-7.50 (m, 8H), 7.25-7.32 (m, 3H), 7.20 (d, 2H, J = 7.2 Hz), 4.26 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.7, 155.0, 137.3, 135.9, 130.8, 129.3, 129.3, 129.1, 128.7, 128.5, 128.4, 126.9, 126.5, 125.3, 32.5. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3$ ($\text{M}+\text{H}^+$): 312.1501, found: 312.1514.



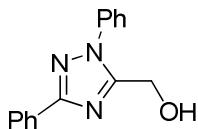
5-phenethyl-1,3-diphenyl-1H-1,2,4-triazole (3t) [new compound]

Yield: 89%; 86.8 mg, light brown yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 8.24 (d, 2H, J = 8.0 Hz), 7.45-7.52 (m, 6H), 7.23-7.31 (m, 5H), 7.14 (d, 2H, J = 7.6 Hz), 3.13-3.21 (m, 4H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.4, 156.0, 140.2, 137.2, 130.9, 129.3, 129.2, 128.9, 128.5, 128.4, 126.4, 126.4, 125.3, 34.1, 28.6. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{20}\text{N}_3$ ($\text{M}+\text{H}^+$): 326.1657, found: 326.1664.



1,3-diphenyl-5-vinyl-1H-1,2,4-triazole (3u) [8]

Yield: 50%; 37.1 mg, light yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 8.21 (d, 2H, J = 6.8 Hz), 7.41-7.54 (m, 8H), 6.50-6.63 (m, 2H), 5.69 (dd, 1H, J = 10.4 Hz, 1.4Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.8, 152.9, 137.1, 130.7, 129.4, 129.4, 129.0, 128.5, 126.5, 125.3, 123.7, 121.6. HRMS (EI-TOF) calcd for $\text{C}_{16}\text{H}_{14}\text{N}_3$ ($\text{M}+\text{H}^+$): 248.1188, found: 248.1193.



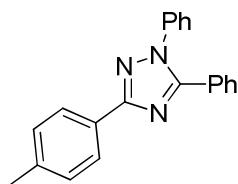
(1,3-diphenyl-1H-1,2,4-triazol-5-yl)methanol (3v) [9]

Yield: 70%; 52.7 mg, white solid; m.p = 168-170 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.13 (d, 2H, J = 6.8 Hz), 7.70 (d, 2H, J = 7.6 Hz), 7.55 (t, 2H, J = 7.6 Hz), 7.41-7.50 (m, 4H), 5.84 (t, 1H, J = 6.2 Hz), 4.86 (d, 2H, J = 6.4 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.2, 155.5, 136.9, 130.1, 129.6, 129.5, 129.0, 128.7, 126.5, 124.2, 54.9. HRMS (EI-TOF) calcd for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O} (\text{M}+\text{H}^+)$: 252.1137, found: 252.1155.



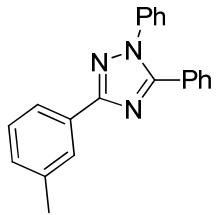
ethyl 1,3-diphenyl-1H-1,2,4-triazole-5-carboxylate (3w) [10]

Yield: 40%; 35.2 mg, light brown red solid; m.p = 83-85 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.21 (dd, 2H, J = 7.6 Hz, 1.6Hz), 7.45-7.52 (m, 8H), 4.40 (q, 2H, J = 7.2 Hz), 1.33 (t, 3H, J = 7.2 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.1, 157.5, 145.6, 138.0, 129.9, 129.7, 128.9, 128.6, 126.7, 125.8, 62.7, 13.9. HRMS (EI-TOF) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}_2 (\text{M}+\text{H}^+)$: 294.1243, found: 294.1260.



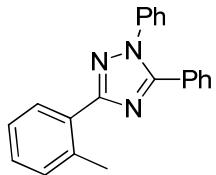
1,5-diphenyl-3-(p-tolyl)-1H-1,2,4-triazole (4a) [11]

Yield: 65%; 60.1 mg, light white solid; m.p = 139-141 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.16 (d, 2H, J = 8.0 Hz), 7.59 (d, 2H, J = 6.8 Hz), 7.37-7.45 (m, 8H), 7.30 (d, 2H, J = 8.0 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.0, 154.6, 139.3, 138.3, 129.9, 129.3, 129.3, 129.0, 128.7, 128.5, 128.0, 127.9, 126.5, 125.4, 21.1. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3 (\text{M}+\text{H}^+)$: 312.1501, found: 312.1518.



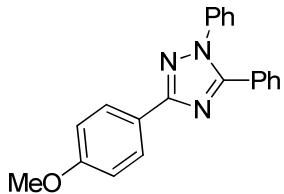
1,5-diphenyl-3-(m-tolyl)-1H-1,2,4-triazole (4b) [new compound]

Yield: 60%; 56.0 mg, light white solid; m.p = 98-100 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.12 (s, 1H), 8.08 (d, 1H, J = 8.0 Hz), 7.59 (d, 2H, J = 7.2 Hz), 7.37-7.46 (m, 9H), 7.28 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.0, 154.7, 138.2, 138.2, 130.5, 130.2, 129.9, 129.3, 128.9, 128.8, 128.5, 128.5, 127.9, 127.1, 125.4, 123.7, 21.3. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3$ ($\text{M}+\text{H}^+$): 312.1501, found: 312.1518.



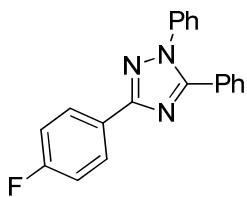
1,5-diphenyl-3-(o-tolyl)-1H-1,2,4-triazole (4c) [new compound]

Yield: 34%; 31.7 mg, brown red solid; m.p = 57-59 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.08-8.10 (m, 1H), 7.57-7.59 (m, 2H), 7.40-7.45 (m, 6H), 7.30-7.37 (m, 5H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.6, 153.8, 138.3, 137.3, 131.1, 129.9, 129.6, 129.3, 129.0, 128.9, 128.6, 128.5, 128.1, 125.7, 125.3, 123.3, 21.8. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3$ ($\text{M}+\text{H}^+$): 312.1501, found: 312.1507.



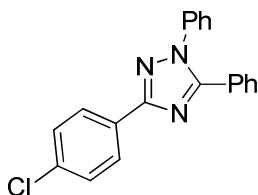
3-(4-methoxyphenyl)-1,5-diphenyl-1H-1,2,4-triazole (4d)^[12]

Yield: 74%; 72.6 mg, light yellow solid; m.p = 120-122 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.19 (d, 2H, J = 8.0 Hz), 7.56 (d, 2H, J = 8.0 Hz), 7.33-7.42 (m, 8H), 7.00 (d, 2H, J = 8.78 Hz), 3.86 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.7, 160.6, 154.5, 138.2, 129.9, 129.3, 128.9, 128.7, 128.5, 128.0, 128.0, 125.3, 123.4, 113.9, 55.2. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3\text{O}$ ($\text{M}+\text{H}^+$): 328.1450 found: 328.1455.



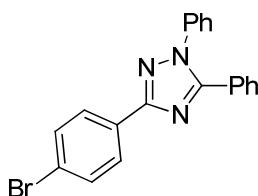
3-(4-fluorophenyl)-1,5-diphenyl-1H-1,2,4-triazole (4e) [new compound]

Yield: 53%; 50.1 mg, light yellow solid; m.p = 122-124 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.21-8.25 (m, 2H), 7.55 (d, 2H, J = 6.8 Hz), 7.34-7.43 (m, 8H), 7.15 (t, 3H, J = 8.8 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 163.6 (d, $J_{\text{C}-\text{F}}$ = 246.5 Hz), 161.1, 154.8, 138.2, 130.0, 129.4, 128.9, 128.9, 128.6, 128.5 (d, $J_{\text{C}-\text{F}}$ = 8.1 Hz), 127.8, 126.9 (d, $J_{\text{C}-\text{F}}$ = 2.8 Hz), 125.4, 115.5 (d, $J_{\text{C}-\text{F}}$ = 21.7 Hz). HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{15}\text{FN}_3$ ($\text{M}+\text{H}^+$): 316.1250, found: 316.1261.



3-(4-chlorophenyl)-1,5-diphenyl-1H-1,2,4-triazole (4f) ^[13]

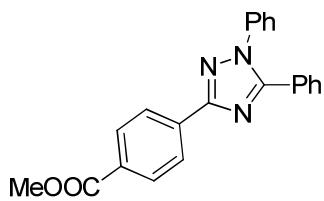
Yield: 60%; 59.6 mg, light brown yellow solid; m.p = 104-106 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.19 (d, 2H, J = 8.4 Hz), 7.55 (d, 2H, J = 6.8 Hz), 7.34-7.45 (m, 10H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.0, 154.9, 138.1, 135.3, 130.1, 129.4, 129.3, 128.9, 128.8, 128.6, 128.2, 127.9, 127.8, 125.4. HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{15}\text{ClN}_3$ ($\text{M}+\text{H}^+$): 332.0955, found: 332.0956.



3-(4-bromophenyl)-1,5-diphenyl-1H-1,2,4-triazole (4g) [new compound]

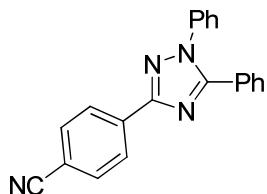
Yield: 59%; 66.4 mg, light yellow solid; m.p = 141-143 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.11 (d, 2H, J = 8.4 Hz), 7.60 (d, 2H, J = 8.0 Hz), 7.55 (d, 2H, J = 7.6 Hz), 7.41-7.44 (m, 6H), 7.36 (t, 2H, J = 7.4 Hz). ^{13}C

NMR (CDCl_3 , 100 MHz) δ 161.1, 154.9, 138.2, 131.8, 130.1, 129.7, 129.4, 128.9, 128.6, 128.1, 127.8, 125.4, 123.6. HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{15}\text{BrN}_3$ ($\text{M}+\text{H}^+$): 376.0449 found: 376.0447.



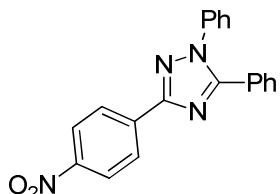
methyl 4-(1,5-diphenyl-1H-1,2,4-triazol-3-yl)benzoate (4h) [new compound]

Yield: 73%; 77.7 mg, light yellow solid; m.p = 164-165 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.32 (d, 2H, J = 8.4 Hz), 8.14 (d, 2H, J = 8.4 Hz), 7.56 (dd, 2H, J = 8.4 Hz, 1.2 Hz), 7.35-7.45 (m, 8H), 3.94 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.9, 161.0, 155.0, 138.1, 134.9, 130.7, 130.2, 129.9, 129.4, 129.0, 128.9, 128.6, 127.7, 126.4, 125.4, 52.1. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2$ ($\text{M}+\text{H}^+$): 356.1399, found: 356.1404.



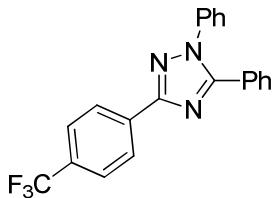
4-(1,5-diphenyl-1H-1,2,4-triazol-3-yl)benzonitrile (4i) [new compound]

Yield: 55%; 53.1 mg, light white solid; m.p = 176-177 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.35 (d, 2H, J = 8.4 Hz), 7.75 (d, 2H, J = 8.4 Hz), 7.55 (d, 2H, J = 7.2 Hz), 7.36-7.54 (m, 8H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.2, 155.2, 138.0, 135.0, 132.4, 130.3, 129.5, 129.2, 128.9, 128.7, 127.5, 127.0, 125.3, 118.8, 112.6. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{15}\text{N}_4$ ($\text{M}+\text{H}^+$): 323.1297, found: 323.1308.



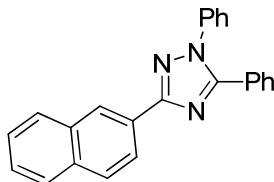
3-(4-nitrophenyl)-1,5-diphenyl-1H-1,2,4-triazole (4j) [new compound]

Yield: 58%; 59.5 mg, orange yellow solid; m.p = 179-181 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.37 (q, 4H, J = 9.2 Hz), 7.55-7.57 (m, 2H), 7.36-7.48 (m, 8H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.0, 148.3, 138.0, 136.8, 130.4, 129.5, 129.2, 129.0, 128.7, 127.4, 127.2, 125.3, 123.9. HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{15}\text{N}_4\text{O}_2$ ($\text{M}+\text{H}^+$): 343.1195, found: 343.1190.



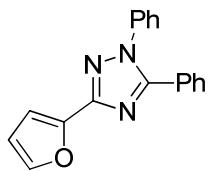
1,5-diphenyl-3-(4-(trifluoromethyl)phenyl)-1H-1,2,4-triazole (4k) [new compound]

Yield: 55%; 60.2 mg, light yellow solid; m.p = 125-127 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.37 (d, 2H, J = 8.4 Hz), 7.73 (d, 2H, J = 8.0 Hz), 7.57 (d, 2H, J = 7.2 Hz), 7.42-7.45 (m, 6H), 7.38 (t, 2H, J = 7.2 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.7, 155.1, 138.1, 134.1, 131.1 (q, $J_{\text{C-CF}_3}$ = 32.5 Hz), 130.2, 129.5, 129.1, 129.0, 128.7, 127.7, 126.8, 125.5 (q, $J_{\text{C-CF}_3}$ = 3.6 Hz), 125.4. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{15}\text{N}_3\text{F}_3$ ($\text{M}+\text{H}^+$): 366.1218, found: 366.1219.



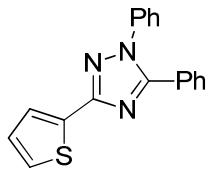
3-(naphthalen-2-yl)-1,5-diphenyl-1H-1,2,4-triazole (4l) [new compound]

Yield: 72%; 75.0 mg, white solid; m.p = 165-167 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.80 (s, 1H), 8.37 (dd, 1H, J = 8.4 Hz, 1.2Hz), 7.94-7.99 (m, 2H), 7.87-7.90 (m, 1H), 7.61 (d, 2H, J = 6.8 Hz), 7.37-7.53 (m, 10H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.9, 154.9, 138.2, 133.9, 133.4, 130.0, 129.4, 129.0, 128.8, 128.6, 128.3, 128.1, 128.0, 127.7, 126.5, 126.3, 126.0, 125.4, 124.1. HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{18}\text{N}_3$ ($\text{M}+\text{H}^+$): 348.1501, found: 348.1511.



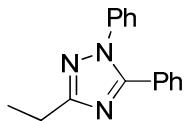
3-(furan-2-yl)-1,5-diphenyl-1H-1,2,4-triazole (4m) [new compound]

Yield: 43%; 37.0 mg, brown red oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.55 (d, 3H, $J = 8.4$ Hz), 7.33-7.42 (m, 8H), 7.10 (d, 1H, $J = 2.4$ Hz), 6.54 (d, 1H, $J = 1.2$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 155.2, 154.7, 146.1, 143.4, 138.0, 130.2, 129.3, 129.0, 129.0, 128.5, 127.5, 125.4, 111.5, 109.8. HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{O} (\text{M}+\text{H}^+)$: 288.1137, found: 288.1159.



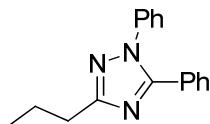
1,5-diphenyl-3-(thiophen-2-yl)-1H-1,2,4-triazole (4n) [new compound]

Yield: 60%; 54.5 mg, light yellow solid; m.p = 95-97 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.82 (d, 1H, $J = 3.6$ Hz), 7.54 (d, 2H, $J = 7.2$ Hz), 7.33-7.42 (m, 9H), 7.13 (t, 1H, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.1, 154.6, 138.0, 133.5, 130.1, 129.4, 129.0, 128.9, 128.5, 127.7, 127.6, 126.6, 126.6, 125.4. HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{S} (\text{M}+\text{H}^+)$: 304.0908, found: 304.0910.



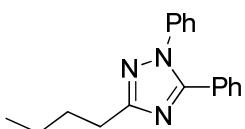
3-ethyl-1,5-diphenyl-1H-1,2,4-triazole (4o) ^[14]

Yield: 54%; 40.5 mg, light yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.48 (d, 2H, $J = 7.6$ Hz), 7.30-7.41 (m, 8H), 2.87 (q, 2H, $J = 7.6$ Hz), 1.42 (t, 3H, $J = 7.6$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.6, 154.0, 138.2, 129.8, 129.3, 128.9, 128.6, 128.5, 128.0, 125.3, 21.8, 12.7. HRMS (EI-TOF) calcd for $\text{C}_{16}\text{H}_{16}\text{N}_3 (\text{M}+\text{H}^+)$: 250.1344, found: 250.1356.



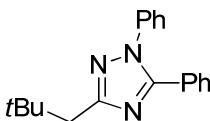
1,5-diphenyl-3-propyl-1H-1,2,4-triazole (4p) [new compound]

Yield: 60%; 47.3 mg, light yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.47 (d, 2H, $J = 7.6$ Hz), 7.29-7.39 (m, 8H), 2.80 (t, 2H, $J = 7.6$ Hz), 1.83-1.92 (m, 2H), 1.04 (t, 3H, $J = 7.4$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 164.5, 153.9, 138.2, 129.8, 129.3, 128.8, 128.5, 128.5, 128.0, 125.2, 30.3, 21.8, 14.0. HRMS (EI-TOF) calcd for $\text{C}_{17}\text{H}_{18}\text{N}_3$ ($\text{M}+\text{H}^+$): 264.1501, found: 264.1515.



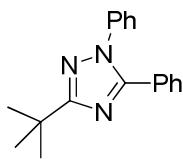
3-butyl-1,5-diphenyl-1H-1,2,4-triazole (4q) [new compound]

Yield: 58%; 48.2 mg, light yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.48 (d, 2H, $J = 7.2$ Hz), 7.30-7.40 (m, 8H), 2.83 (t, 2H, $J = 7.8$ Hz), 1.80-1.86 (m, 2H), 1.45-1.51 (m, 2H), 0.97 (t, 3H, $J = 7.4$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 164.7, 154.0, 138.2, 129.8, 129.3, 128.9, 128.5, 128.5, 128.0, 125.3, 30.6, 28.1, 22.6, 13.8. HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{20}\text{N}_3$ ($\text{M}+\text{H}^+$): 278.1657, found: 278.1673.



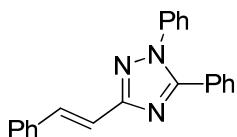
3-neopentyl-1,5-diphenyl-1H-1,2,4-triazole (4r) [new compound]

Yield: 41%; 35.8 mg, light yellow solid; m.p = 116-118 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.48 (d, 2H, $J = 7.2$ Hz), 7.32-7.40 (m, 8H), 2.74 (s, 2H), 1.09 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.9, 154.6, 138.3, 129.7, 129.3, 128.9, 128.5, 128.5, 128.1, 125.3, 41.9, 31.4, 29.6. HRMS (EI-TOF) calcd for $\text{C}_{19}\text{H}_{22}\text{N}_3$ ($\text{M}+\text{H}^+$): 292.1814, found: 292.1833.



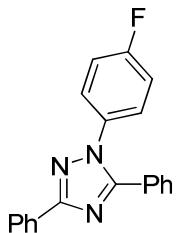
3-(tert-butyl)-1,5-diphenyl-1H-1,2,4-triazole (4s) [new compound]

Yield: 83%; 69.0 mg, white solid; m.p = 169-171 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.47 (d, 2H, J = 7.2 Hz), 7.30-7.39 (m, 8H), 1.48 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.7, 153.8, 138.3, 130.0, 129.2, 129.0, 128.4, 128.4, 128.3, 125.4, 32.9, 29.6. HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{20}\text{N}_3$ ($\text{M}+\text{H}^+$): 278.1657, found: 278.1666.



(E)-1,5-diphenyl-3-styryl-1H-1,2,4-triazole (4t) [new compound]

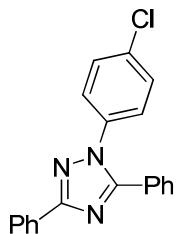
Yield: 49%; 47.5 mg, brown yellow solid; m.p = 113-115 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.77 (d, 1H, J = 16.0 Hz), 7.59 (d, 2H, J = 7.6 Hz), 7.54 (d, 2H, J = 7.2 Hz), 7.31-7.43 (m, 11H), 7.19 (d, 1H, J = 16.4 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.4, 154.5, 138.1, 136.4, 134.5, 130.1, 129.4, 128.9, 128.8, 128.7, 128.6, 128.4, 127.8, 127.0, 125.2, 117.3. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3$ ($\text{M}+\text{H}^+$): 324.1501, found: 324.1513.



1-(4-fluorophenyl)-3,5-diphenyl-1H-1,2,4-triazole (4u)^[2]

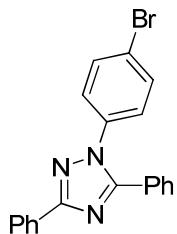
Yield: 61%; 57.6 mg, light white solid; m.p = 110-112 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.23 (d, 2H, J = 7.2 Hz), 7.56 (d, 2H, J = 7.2 Hz), 7.36-7.49 (m, 8H), 7.14 (t, 2H, J = 8.4 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.4 (d, $J_{\text{C}-\text{F}} = 248.3$ Hz), 161.9, 154.8, 134.3 (d, $J_{\text{C}-\text{F}} = 2.7$ Hz), 130.5, 130.2, 129.5, 128.9, 128.7, 128.6,

127.7, 127.3 (d, $J_{C-F} = 8.1$ Hz), 126.6, 116.4 (d, $J_{C-F} = 22.6$ Hz). HRMS (EI-TOF) calcd for C₂₀H₁₅FN₃ (M+H⁺): 316.1250, found: 316.1252.



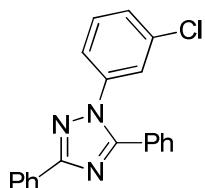
1-(4-chlorophenyl)-3,5-diphenyl-1H-1,2,4-triazole (4v) [2]

Yield: 50%; 49.7 mg, light yellow solid; m.p = 102-104 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.24 (d, 2H, $J = 7.2$ Hz), 7.56 (d, 2H, $J = 7.2$ Hz), 7.38-7.50 (m, 10H). ¹³C NMR (CDCl₃, 100 MHz) δ 162.1, 154.8, 136.7, 134.5, 130.5, 130.2, 129.5, 129.0, 128.7, 128.6, 127.7, 126.6, 126.5. HRMS (EI-TOF) calcd for C₂₀H₁₅ClN₃ (M+H⁺): 332.0955, found: 332.0949.



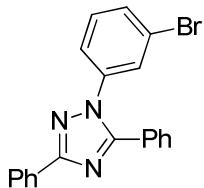
1-(4-bromophenyl)-3,5-diphenyl-1H-1,2,4-triazole (4w) [15]

Yield: 57%; 64.1 mg, brown yellow oil; m.p = 110-112 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.23 (d, 2H, $J = 7.2$ Hz), 7.55-7.57 (m, 4H), 7.38-7.49 (m, 6H), 7.31 (d, 2H, $J = 8.4$ Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 162.1, 154.8, 137.2, 132.5, 130.4, 130.2, 129.5, 129.0, 128.7, 128.6, 127.7, 126.7, 126.6, 122.5. HRMS (EI-TOF) calcd for C₂₀H₁₅BrN₃ (M+H⁺): 376.0499, found: 376.0453.



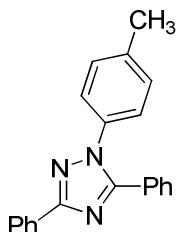
1-(3-chlorophenyl)-3,5-diphenyl-1H-1,2,4-triazole (4x) [new compound]

Yield: 55%; 54.6 mg, brown yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 8.23 (d, 2H, $J = 7.2$ Hz), 7.57 (d, 3H, $J = 6.8$ Hz), 7.38-7.50 (m, 7H), 7.34 (t, 1H, $J = 8.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.2, 154.9, 139.2, 135.1, 130.4, 130.3, 130.2, 129.6, 129.0, 128.9, 128.7, 128.6, 127.6, 126.6, 125.5, 123.4. HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{15}\text{ClN}_3$ ($\text{M}+\text{H}^+$): 332.0955, found: 332.0955.



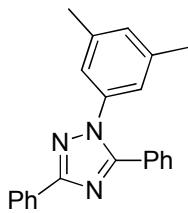
1-(3-bromophenyl)-3,5-diphenyl-1H-1,2,4-triazole (4y) [new compound]

Yield: 43%; 48.4 mg, brown yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 8.23 (d, 2H, $J = 6.8$ Hz), 7.71 (s, 1H), 7.40-7.57 (m, 10H), 7.27 (br s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.2, 154.9, 139.3, 131.8, 130.4, 130.3, 129.6, 129.0, 128.7, 128.6, 128.3, 127.6, 126.6, 123.8, 122.8. HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{15}\text{BrN}_3$ ($\text{M}+\text{H}^+$): 376.0449, found: 376.0444.



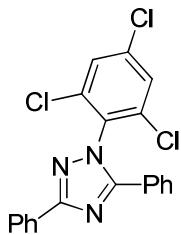
3,5-diphenyl-1-(p-tolyl)-1H-1,2,4-triazole (4z)^[16]

Yield: 84%; 78.4 mg, light brown yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 8.18 (d, 2H, $J = 6.8$ Hz), 7.51 (d, 2H, $J = 7.6$ Hz), 7.28-7.41 (m, 6H), 7.23 (d, 2H, $J = 8.0$ Hz), 7.16 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.7, 154.6, 138.9, 135.8, 130.7, 129.9, 129.9, 129.3, 128.9, 128.5, 128.5, 128.0, 126.5, 125.2, 21.1. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3$ ($\text{M}+\text{H}^+$): 312.1501, found: 312.1503.



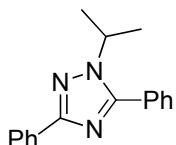
1-(3,5-dimethylphenyl)-3,5-diphenyl-1H-1,2,4-triazole (4aa) [new compound]

Yield: 67%; 65.3 mg, brown yellow solid; m.p = 73-75 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.26 (dd, 2H, J = 8.6 Hz, 1.4Hz), 7.60 (dd, 2H, J = 8.8 Hz, 2.0Hz), 7.36-7.49 (m, 6H), 7.06 (s, 1H), 7.04 (s, 2H), 2.32 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.7, 154.5, 139.3, 138.1, 130.8, 130.5, 129.9, 129.3, 128.9, 128.5, 128.4, 128.0, 126.5, 123.2, 21.1. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{20}\text{N}_3$ ($\text{M}+\text{H}^+$): 326.1657, found: 326.1671.



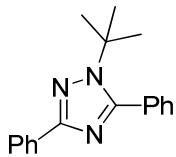
3,5-diphenyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazole (4ab) ^[17]

Yield: 35%; 41.9 mg, light yellow solid; m.p = 117-119 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.25 (d, 2H, J = 6.8 Hz), 7.59 (d, 2H, J = 6.8 Hz), 7.43-7.50 (m, 6H), 7.38 (t, 2H, J = 7.2 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 163.2, 156.9, 136.9, 135.4, 133.3, 130.6, 130.3, 129.7, 129.0, 128.8, 128.6, 127.7, 127.1, 126.7. HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{13}\text{Cl}_3\text{N}_3$ ($\text{M}+\text{H}^+$): 400.0175, found: 400.0165.



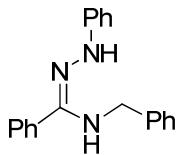
1-isopropyl-3,5-diphenyl-1H-1,2,4-triazole (4ac) ^[18]

Yield: 38%; 30.0 mg, light yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ 8.18 (d, 2H, J = 7.2 Hz), 7.62-7.65 (m, 2H), 7.51-7.53 (m, 3H), 7.38-7.46 (m, 3H), 4.65-4.71 (m, 1H), 1.56 (d, 6H, J = 6.4 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.2, 154.6, 131.4, 129.9, 129.0, 128.9, 128.6, 128.5, 126.4, 50.6, 22.8. HRMS (EI-TOF) calcd for $\text{C}_{17}\text{H}_{18}\text{N}_3$ ($\text{M}+\text{H}^+$): 264.1501, found: 264.1528.



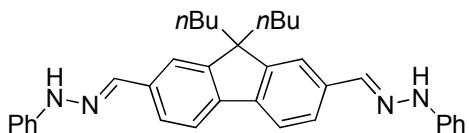
1-(tert-butyl)-3,5-diphenyl-1H-1,2,4-triazole (4ad) [new compound]

Yield: 46%; 38.2 mg, light white solid; m.p = 122-124 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.16 (d, 2H, J = 7.2 Hz), 7.38-7.48 (m, 8H), 1.53 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.9, 154.6, 132.3, 131.3, 129.8, 129.6, 128.8, 128.4, 128.2, 126.3, 61.0, 30.8. HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{20}\text{N}_3$ ($\text{M}+\text{H}^+$): 278.1657, found: 278.1664.



N-benzyl-N'-phenylbenzohydrazoneamide (5)^[8]

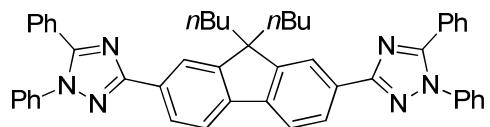
Yield: 75% (mixture of Z/E isomer); 67.7 mg, light yellow solid; m.p = 77-79 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.62 (t, 2H, J = 3.6 Hz), 7.43-7.52 (m, 6H), 7.31-7.37 (m, 4H), 7.25-7.28 (m, 4H), 7.20 (t, 1H, J = 7.8 Hz), 7.02 (d, 2H, J = 8.4 Hz), 6.91 (t, 2H, J = 8.4 Hz), 6.01 (br s, 1H), 5.47 (br s, 1H), 4.59 (s, 1H), 4.34 (s, 2H). HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{20}\text{N}_3$ ($\text{M}+\text{H}^+$): 302.1657 found: 302.1652.



(2E,2'E)-2,2'-(9,9-dibutyl-9H-fluorene-2,7-diyl)bis(methanlylidene))bis(1-phenylhydrazine) (7) [new compound]

Yield: 85%; 436.9 mg (1 mmol scale), brown yellow solid; m.p = 210-211 °C; ^1H NMR ($d_6\text{-DMSO}$, 400 MHz) δ 10.36 (s, 2H), 7.94 (s, 2H), 7.79 (d, 2H, J = 8.0 Hz), 7.69 (s, 2H), 7.62 (d, 2H, J = 7.6 Hz), 7.23 (t, 4H, J = 7.8 Hz), 7.12 (d, 4H, J = 8.4 Hz), 6.75 (t, 2H, J = 7.2 Hz), 2.03 (t, 4H, J = 7.6 Hz), 0.98-1.07 (m, 4H), 0.59 (t, 6H, J = 7.4 Hz), 0.47-0.55 (m, 4H). ^{13}C NMR ($d_6\text{-DMSO}$, 100 MHz) δ 150.9, 145.3, 140.3,

137.1, 134.9, 129.1, 125.0, 120.1, 119.6, 118.7, 112.0, 54.4, 25.8, 22.4, 13.7. HRMS (EI-TOF) calcd for C₃₅H₃₉N₄ (M+H⁺): 515.3175, found: 515.3192.



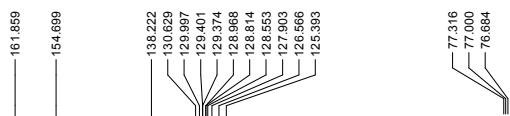
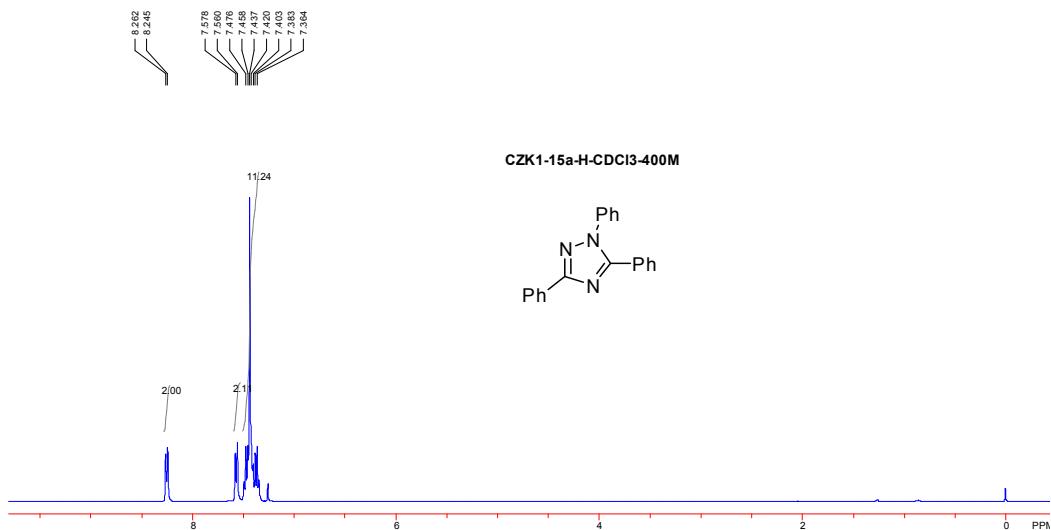
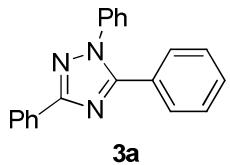
3,3'-(9,9-dibutyl-9H-fluorene-2,7-diyl)bis(1,5-diphenyl-1H-1,2,4-triazole) (8) [new compound]

Yield: 56%; 120.3 mg, light yellow solid; m.p = 281-283 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.31 (d, 2H, *J* = 8.0 Hz), 8.24 (s, 2H), 7.84 (d, 2H, *J* = 7.6 Hz), 7.59 (d, 4H, *J* = 7.2 Hz), 7.43-7.48 (m, 10H), 7.36-7.42 (m, 6H), 2.14 (t, 4H, *J* = 7.6 Hz), 1.03-1.12 (m, 4H), 0.63 (t, 10H, *J* = 6.8 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 162.4, 154.8, 151.6, 142.1, 138.2, 130.0, 129.6, 129.5, 129.0, 128.8, 128.6, 128.0, 125.7, 125.5, 120.8, 120.1, 55.6, 40.4, 25.9, 23.1, 13.9. HRMS (EI-TOF) calcd for C₄₉H₄₅N₆ (M+H⁺): 717.3706, found: 717.3818.

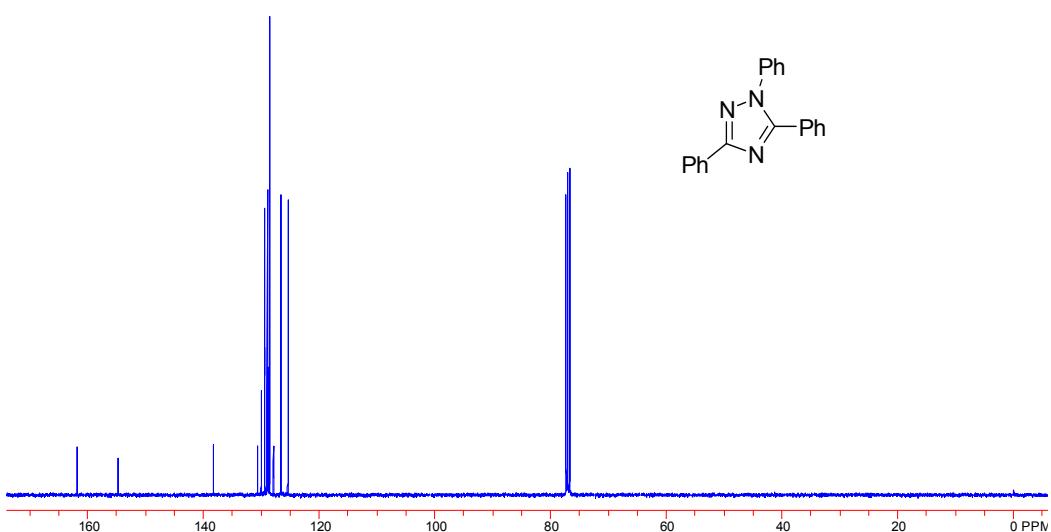
References

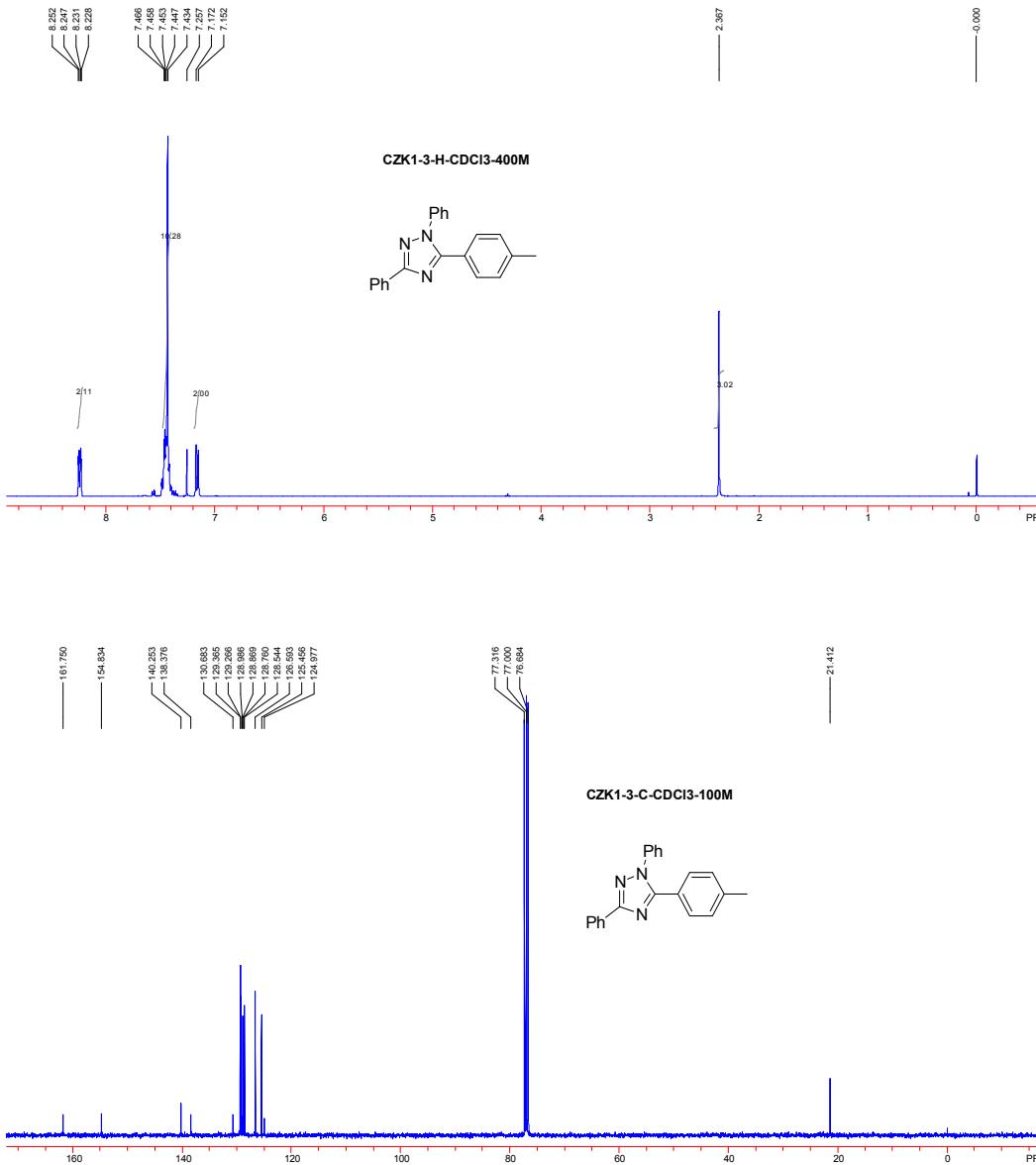
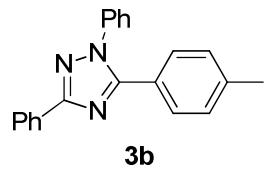
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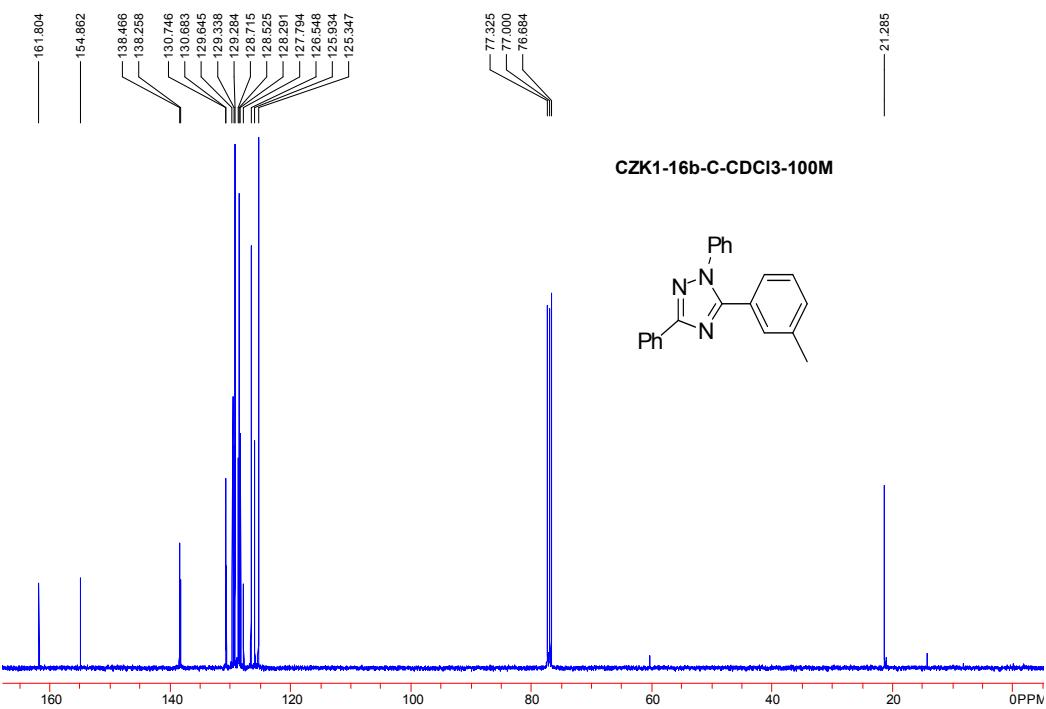
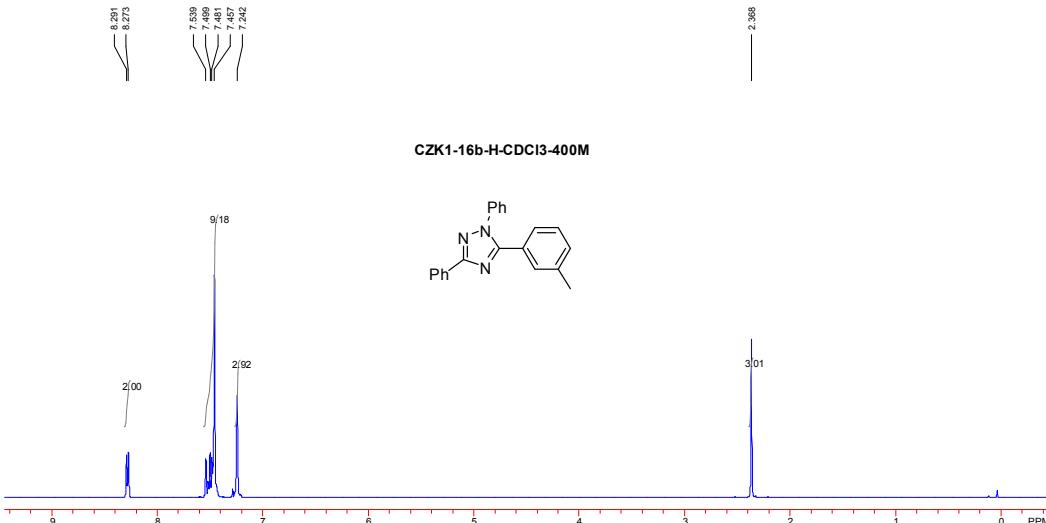
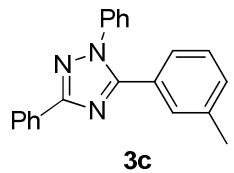
¹H and ¹³C NMR Spectra of Products

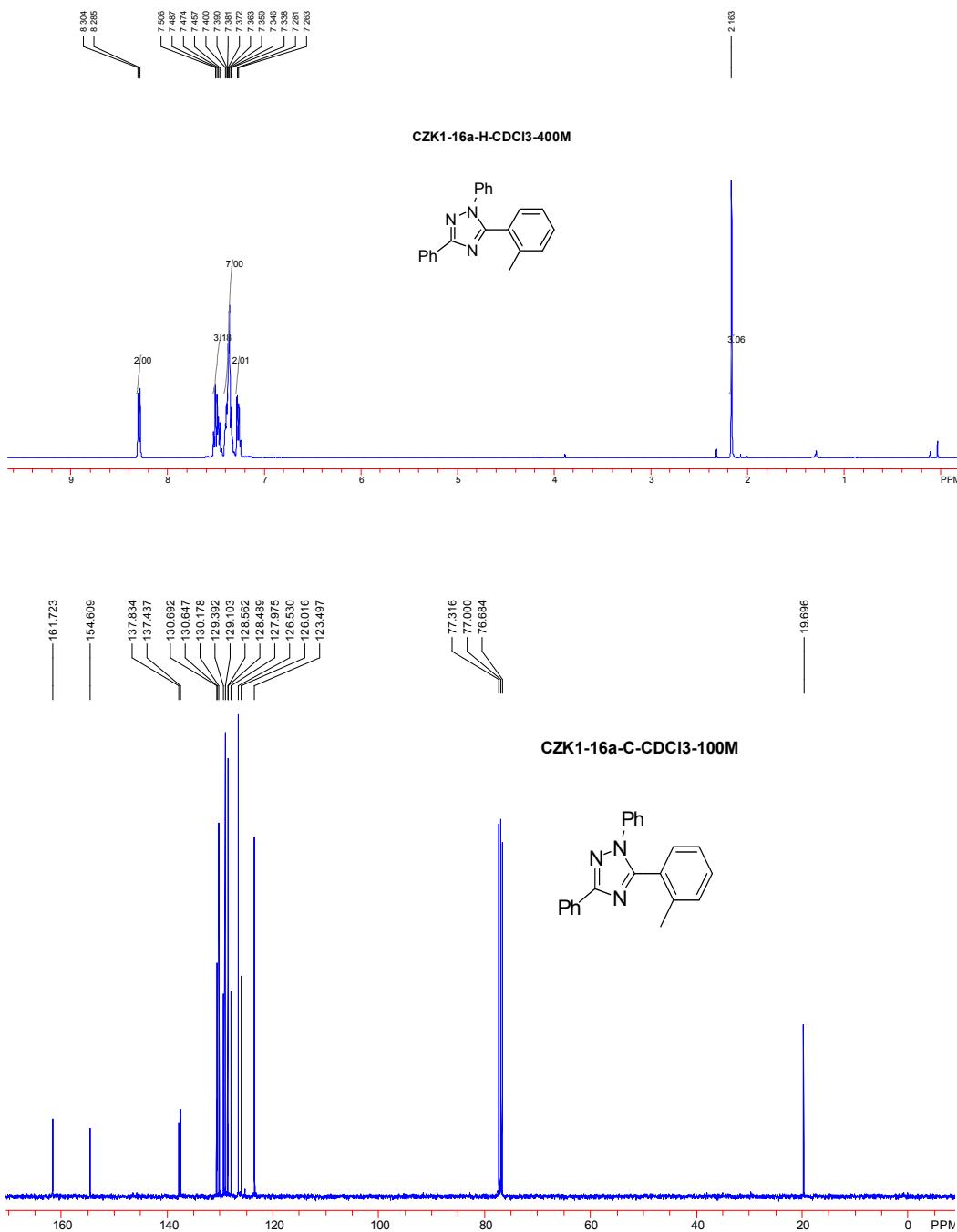
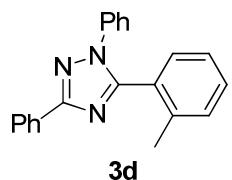


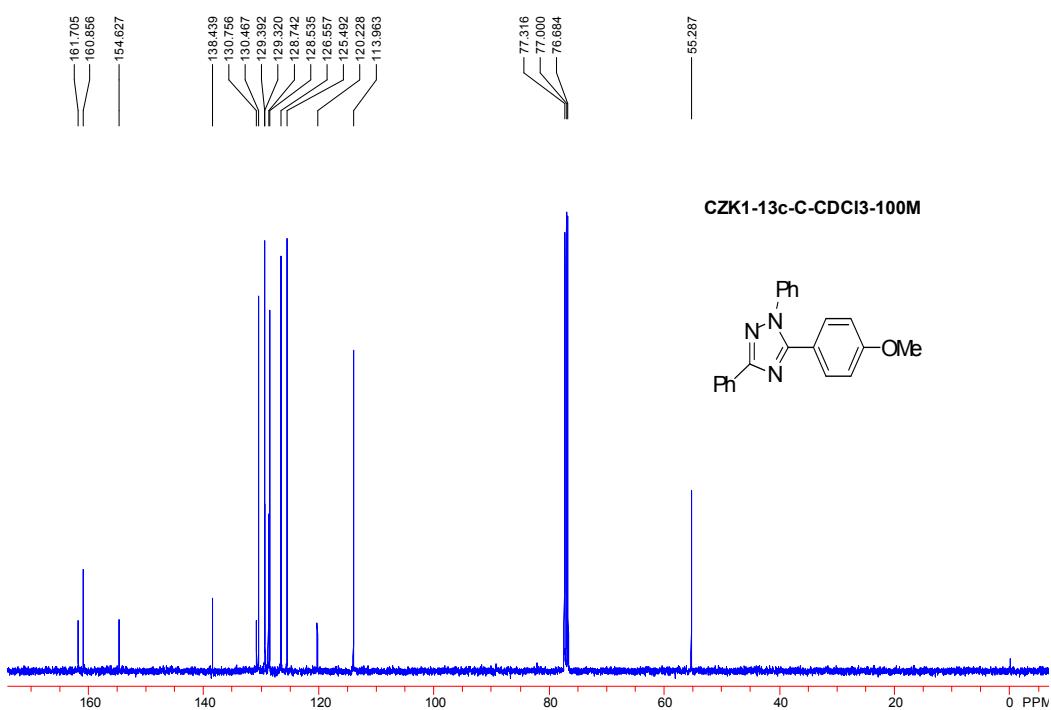
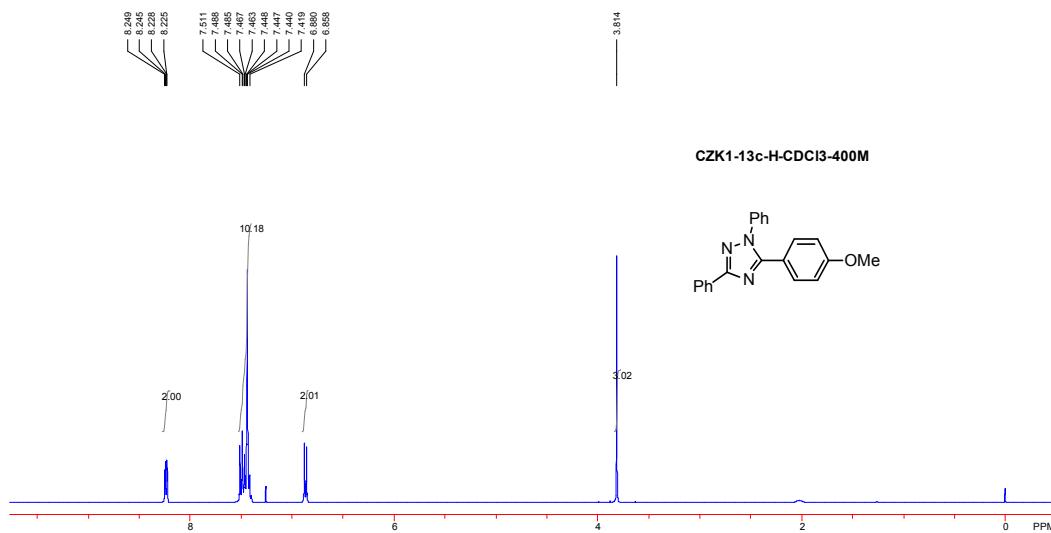
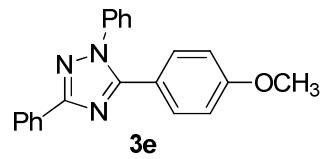
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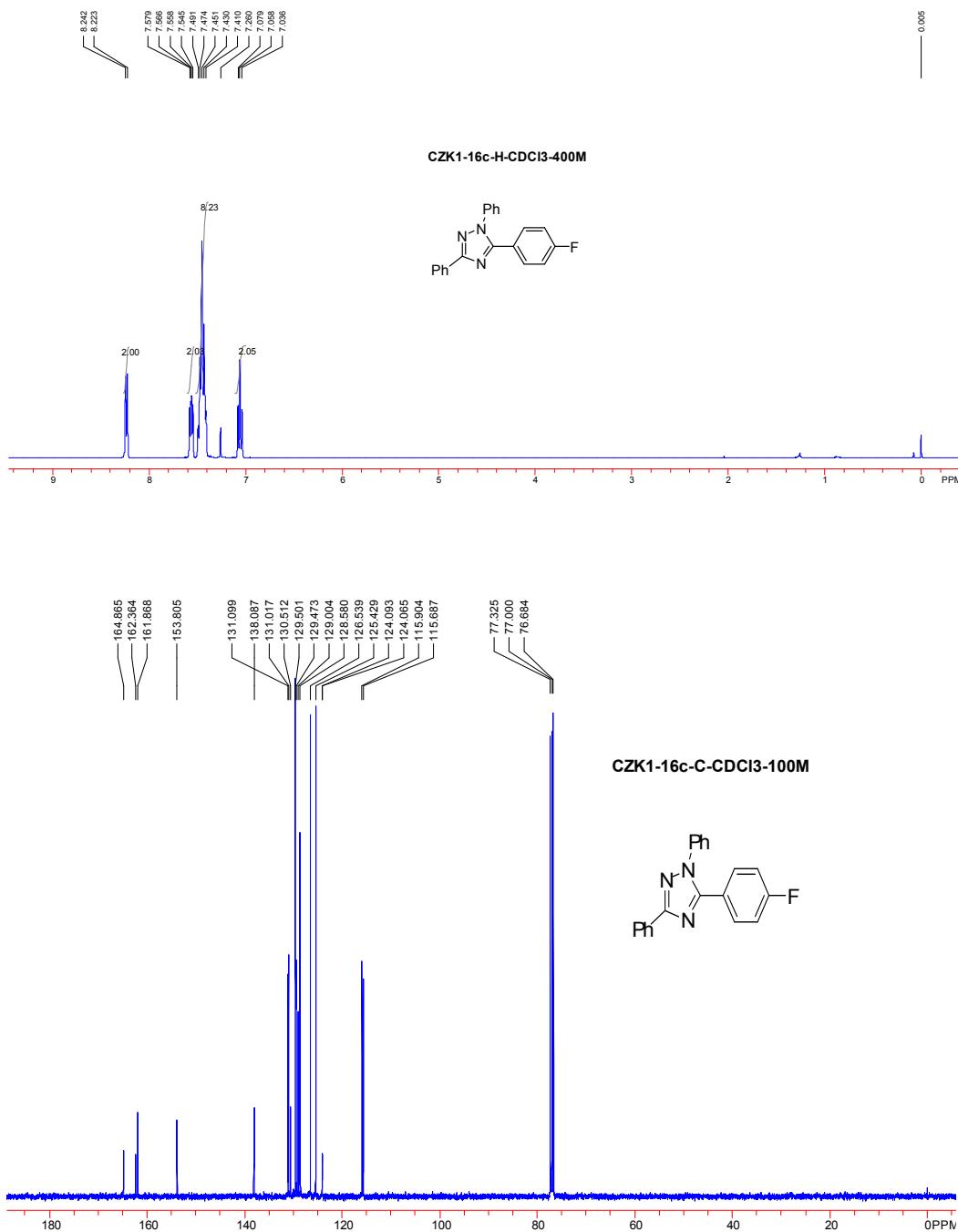
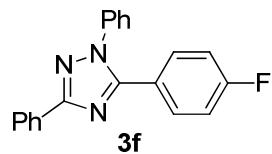


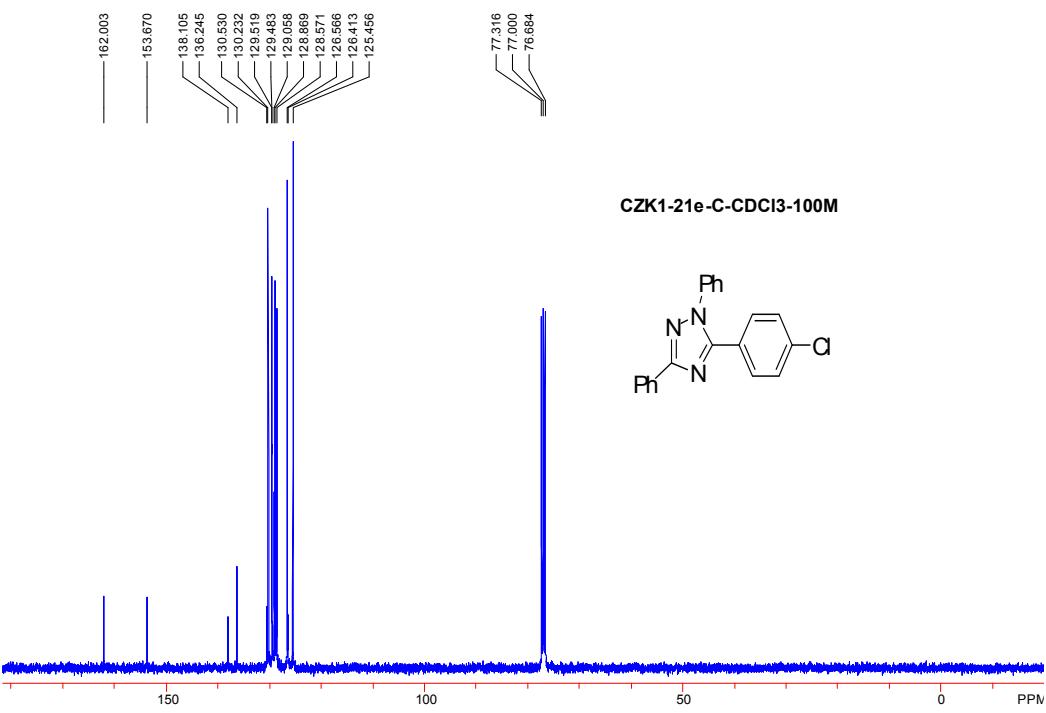
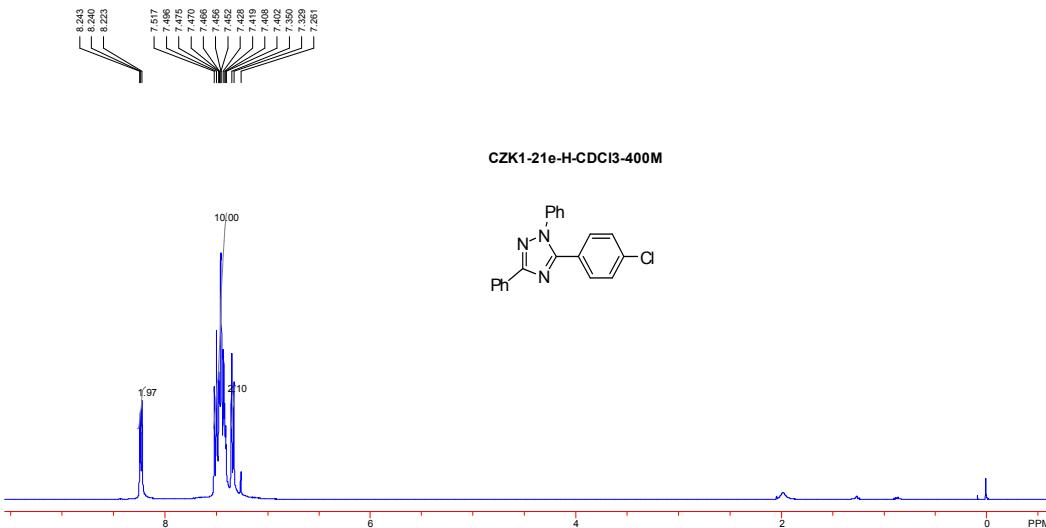
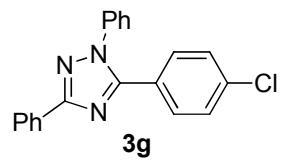


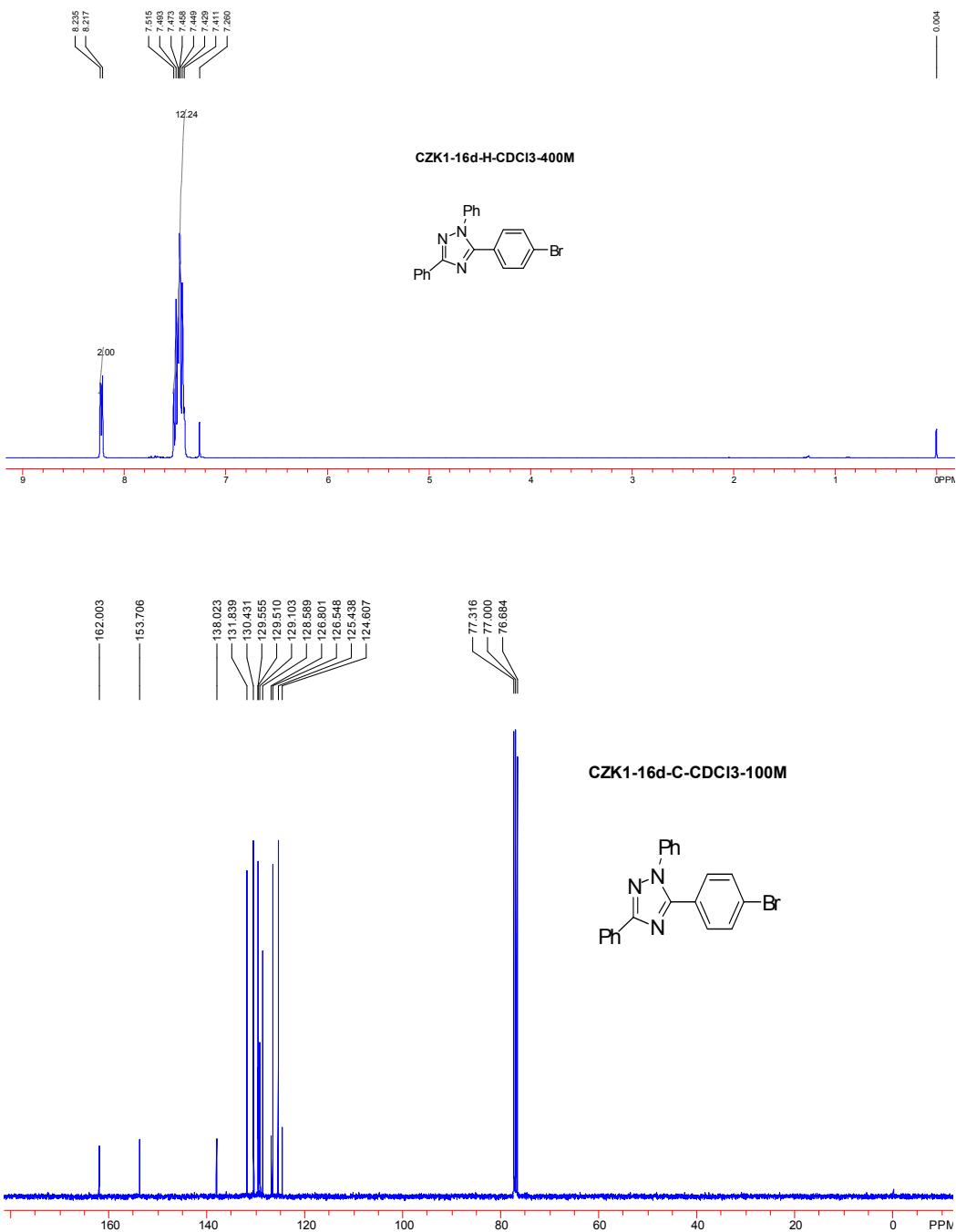
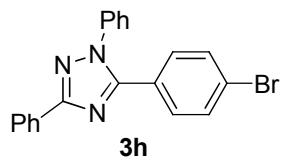


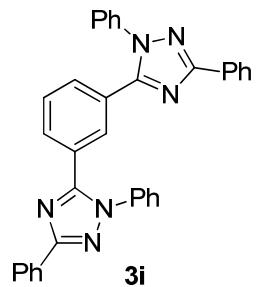




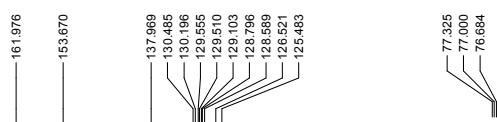
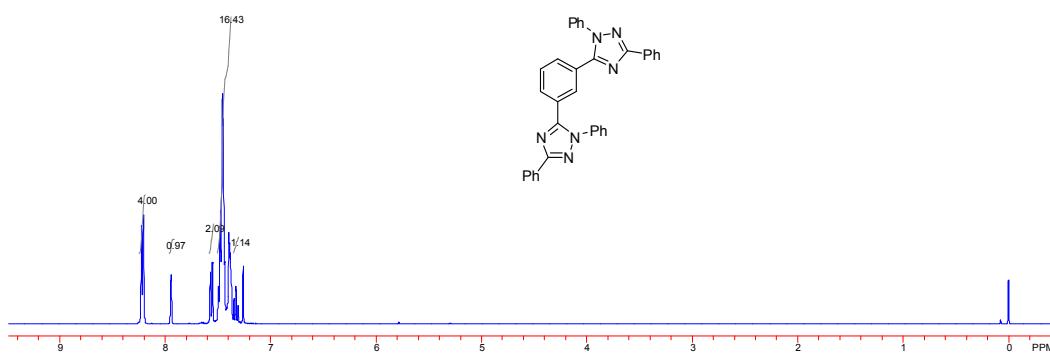




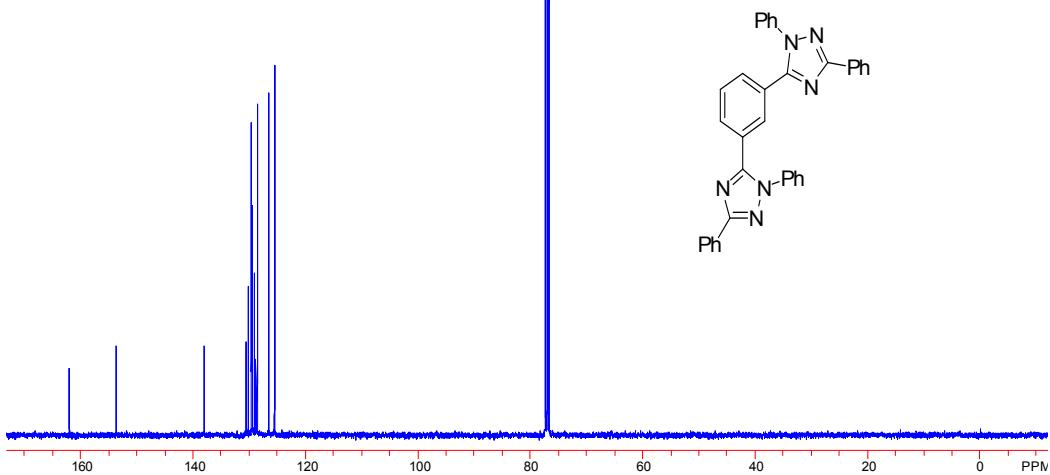


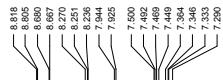
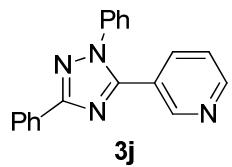


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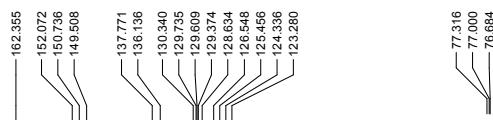
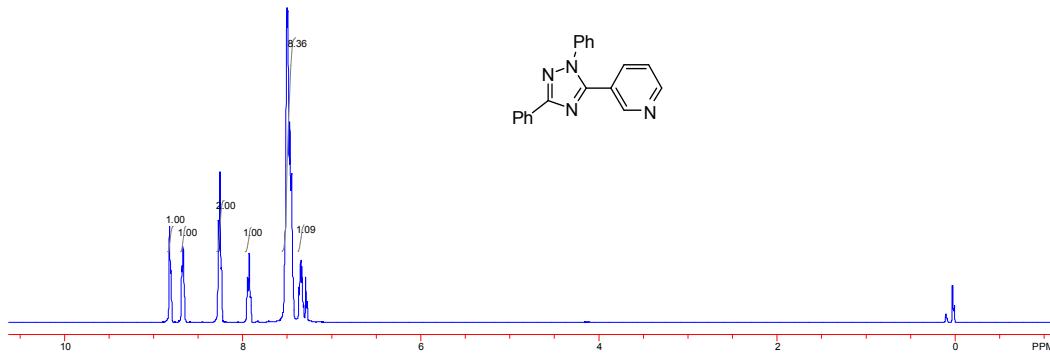


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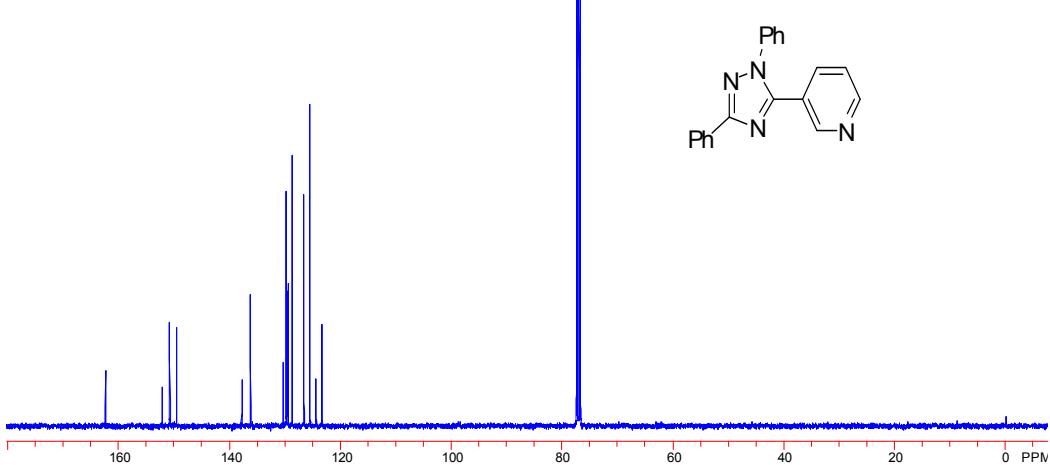


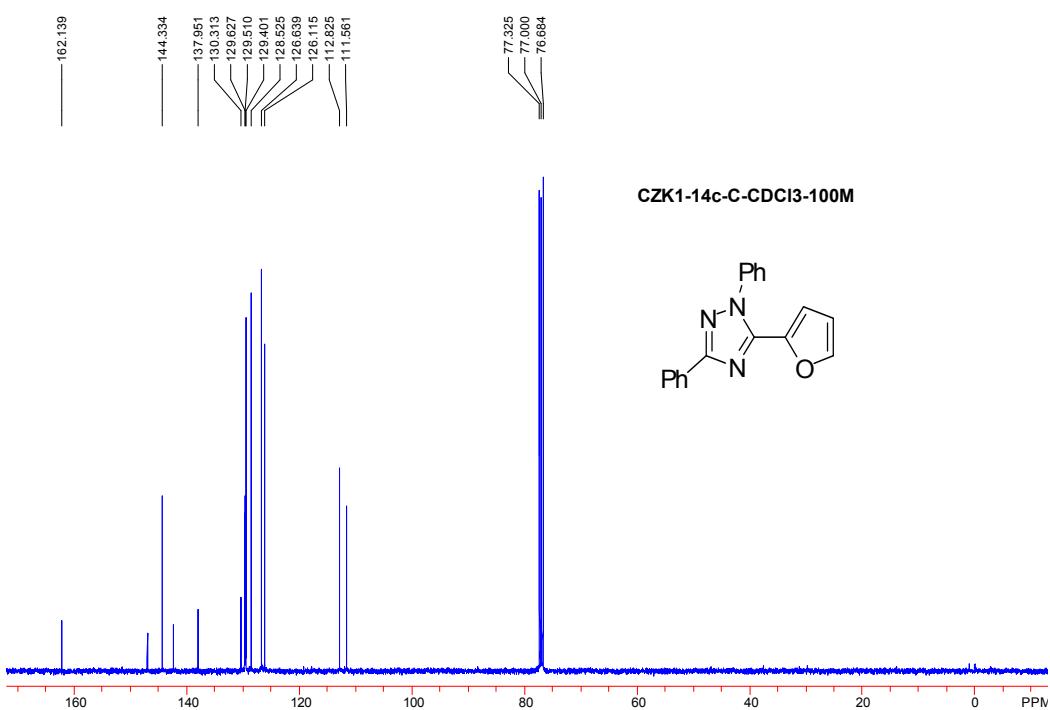
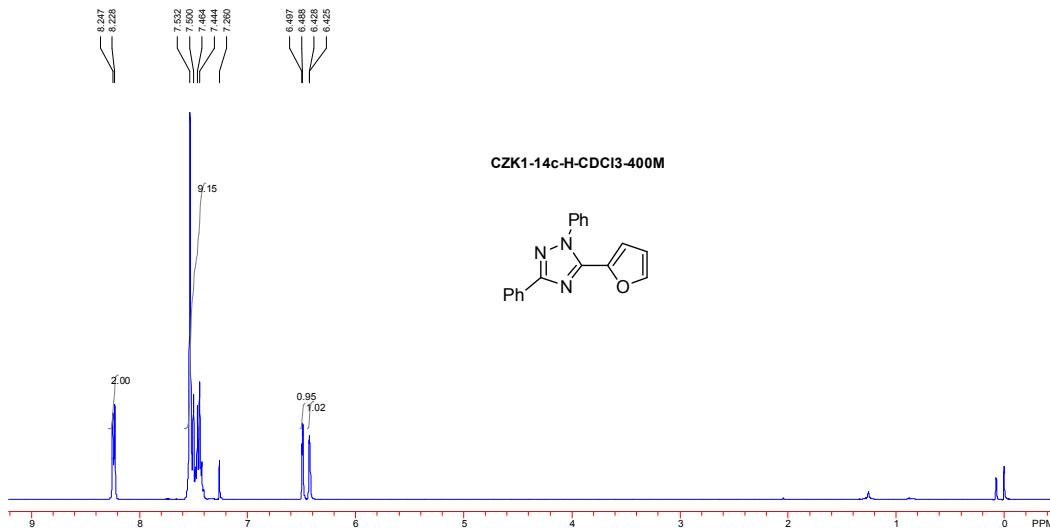
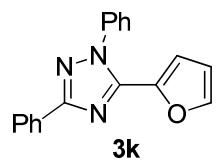


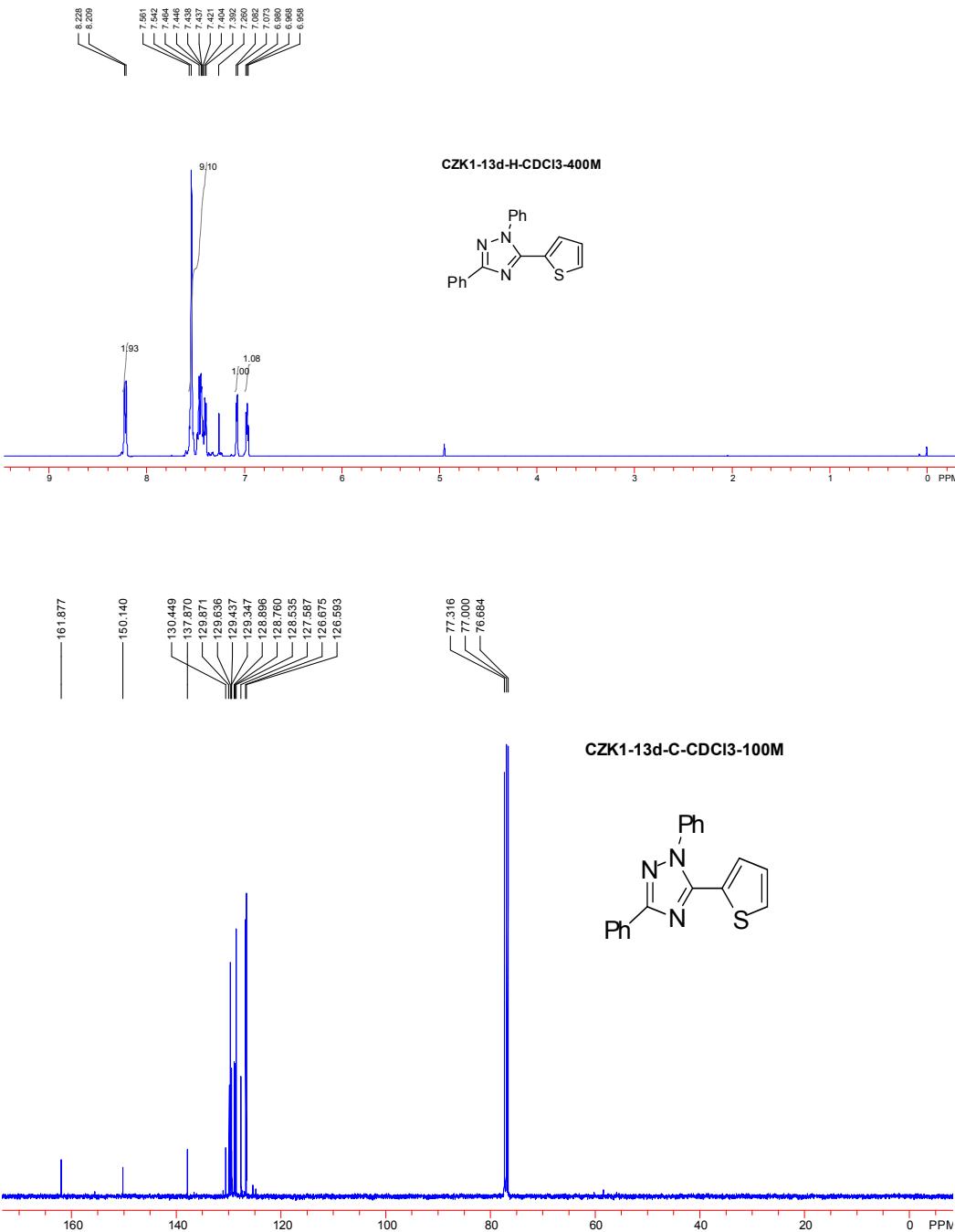
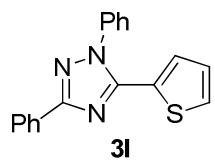
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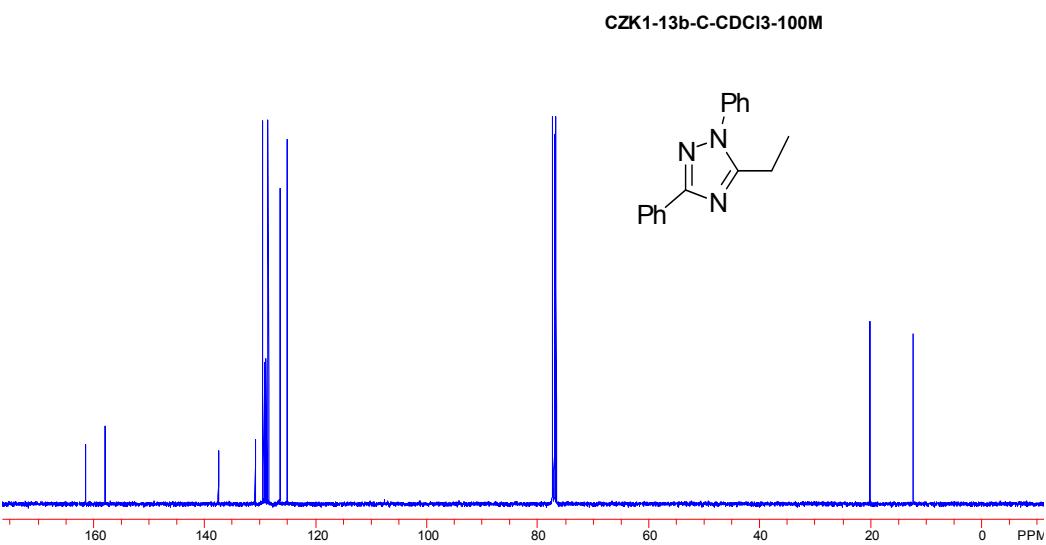
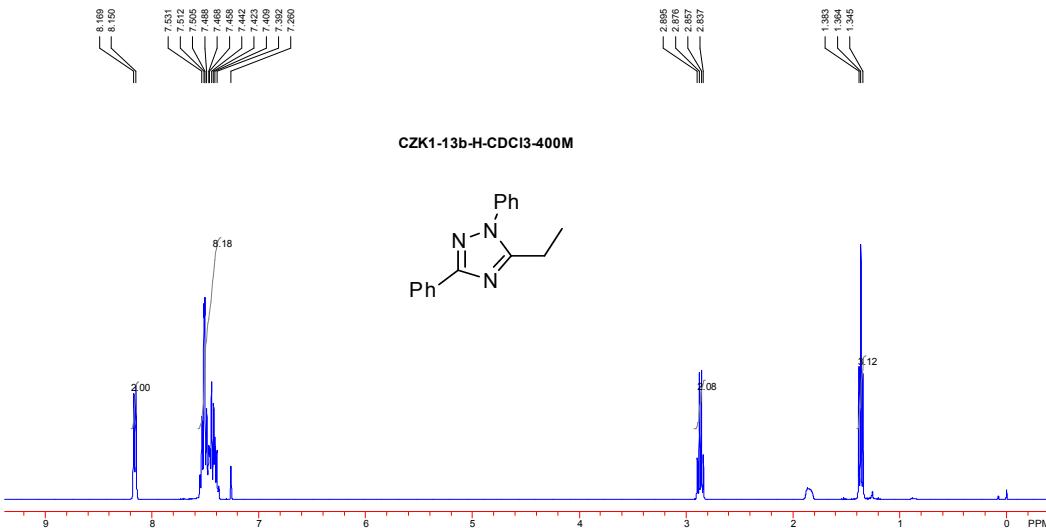
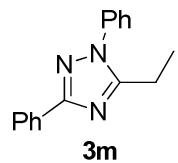


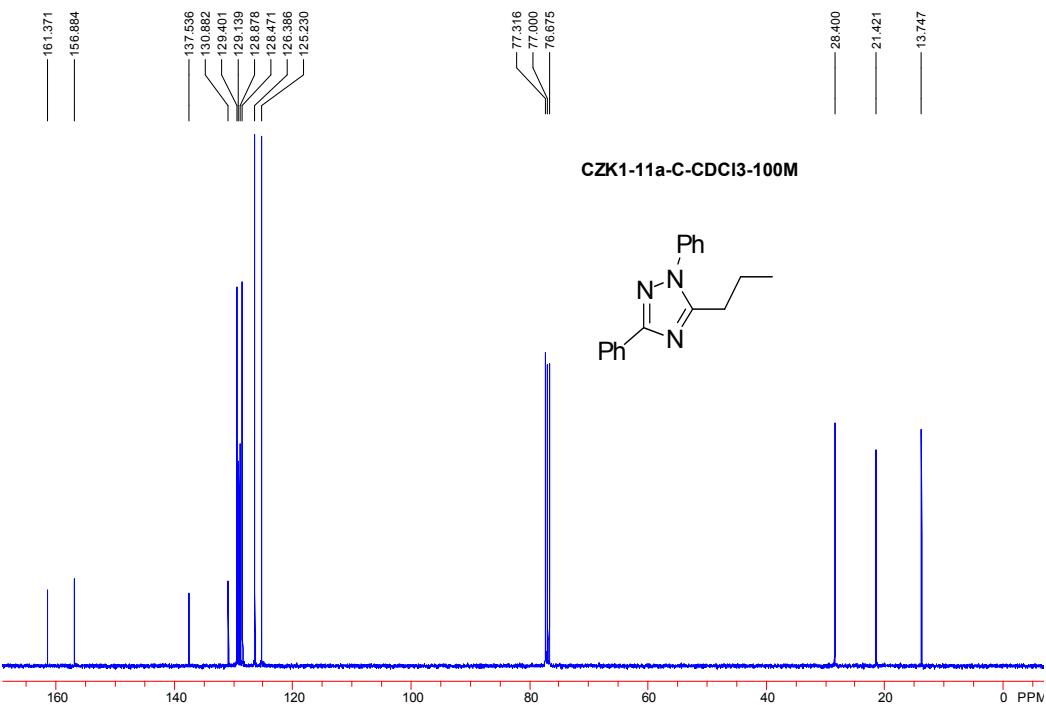
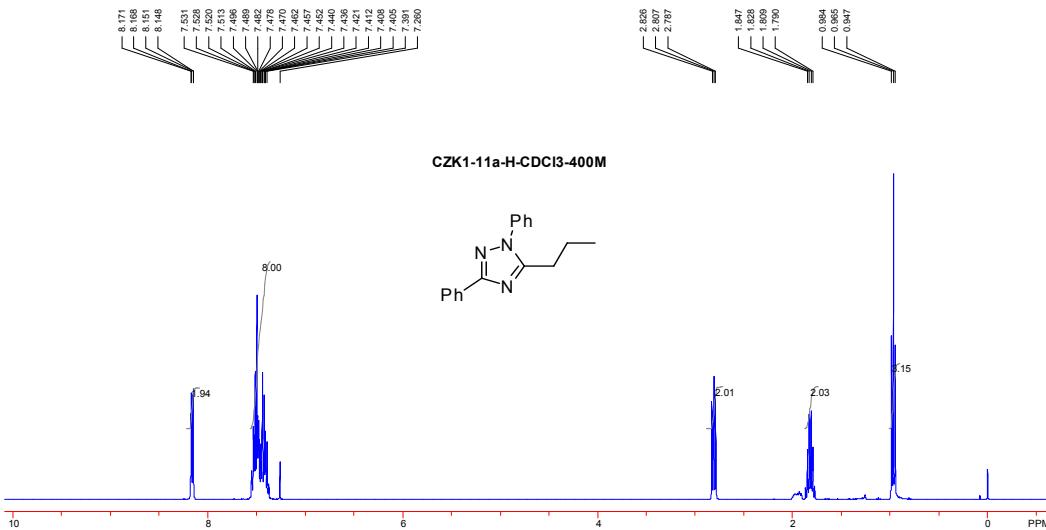
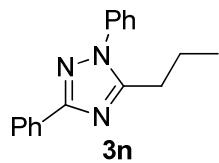
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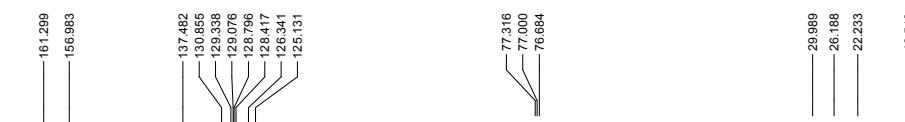
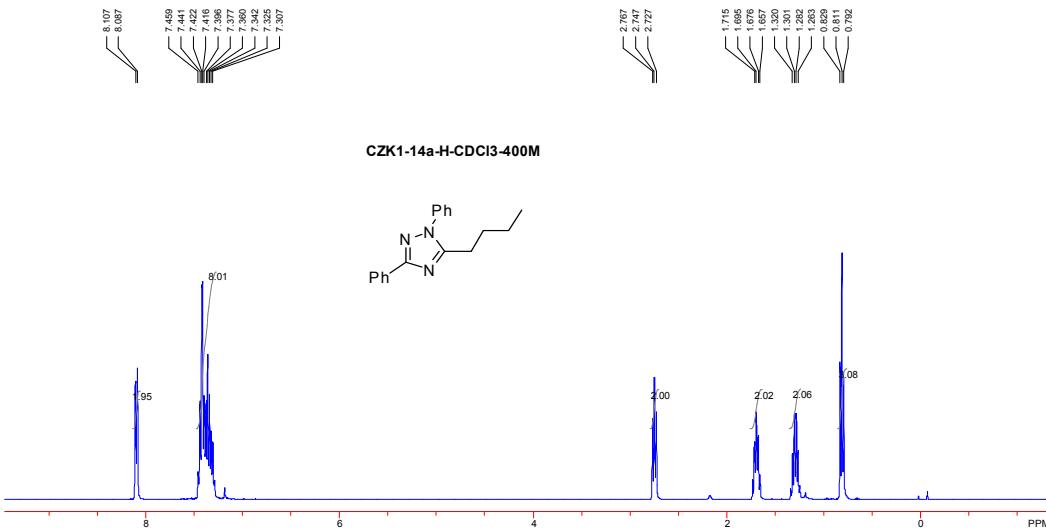
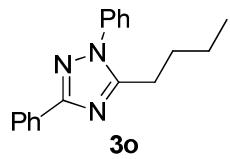




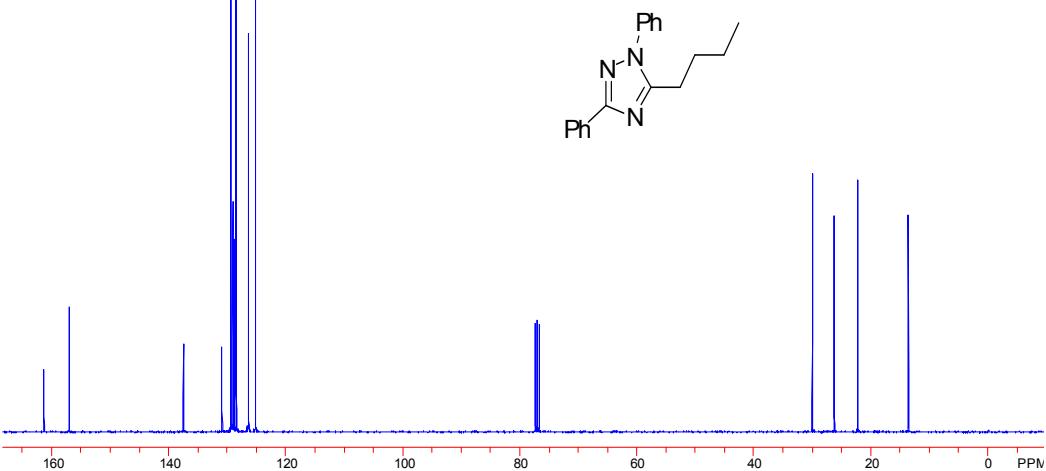


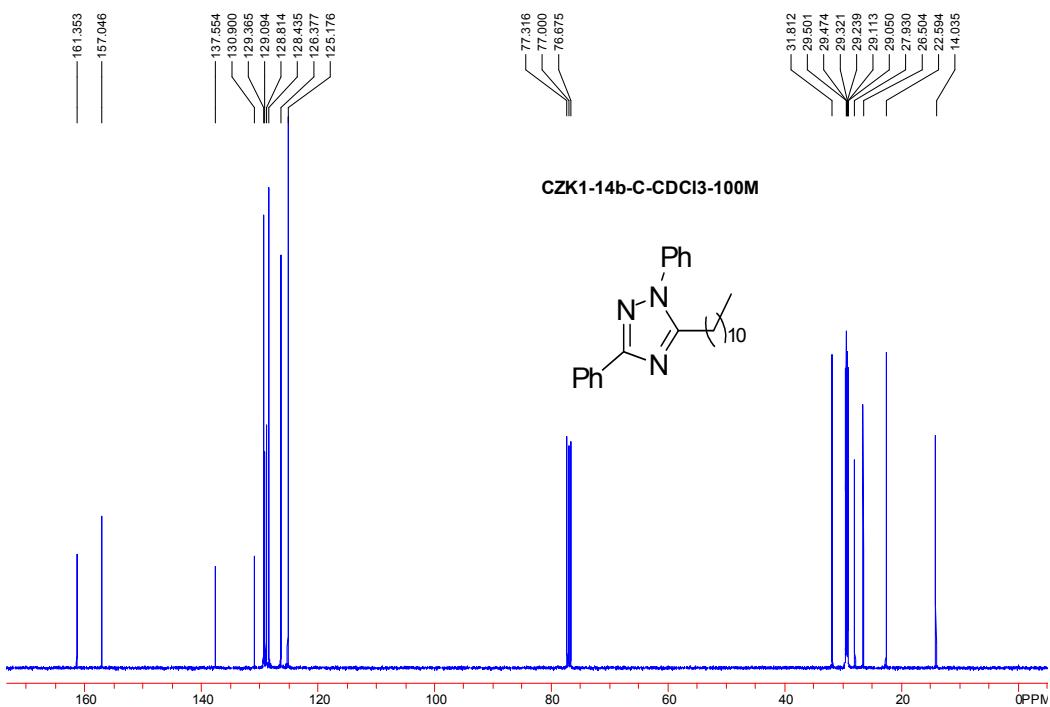
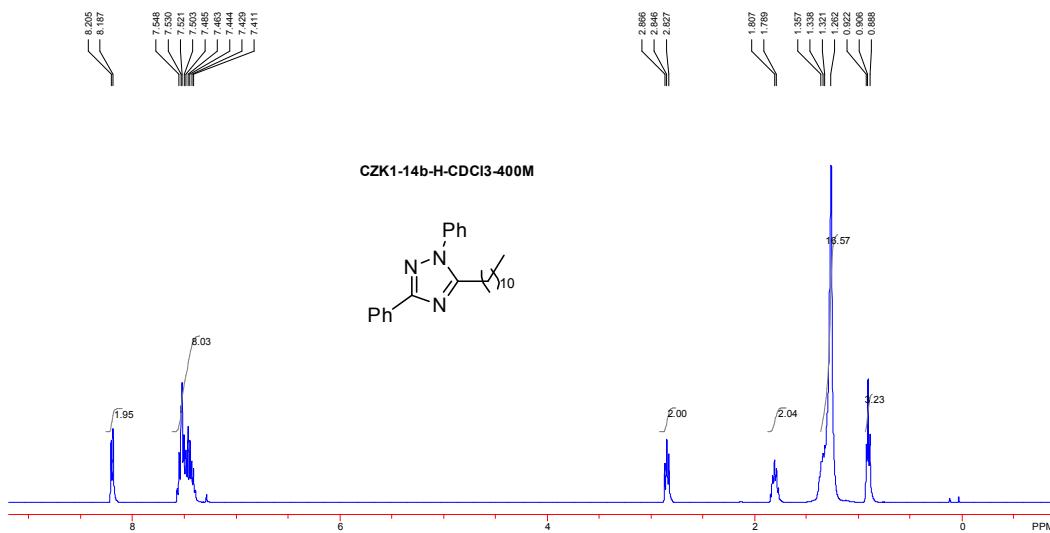
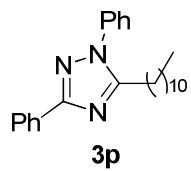


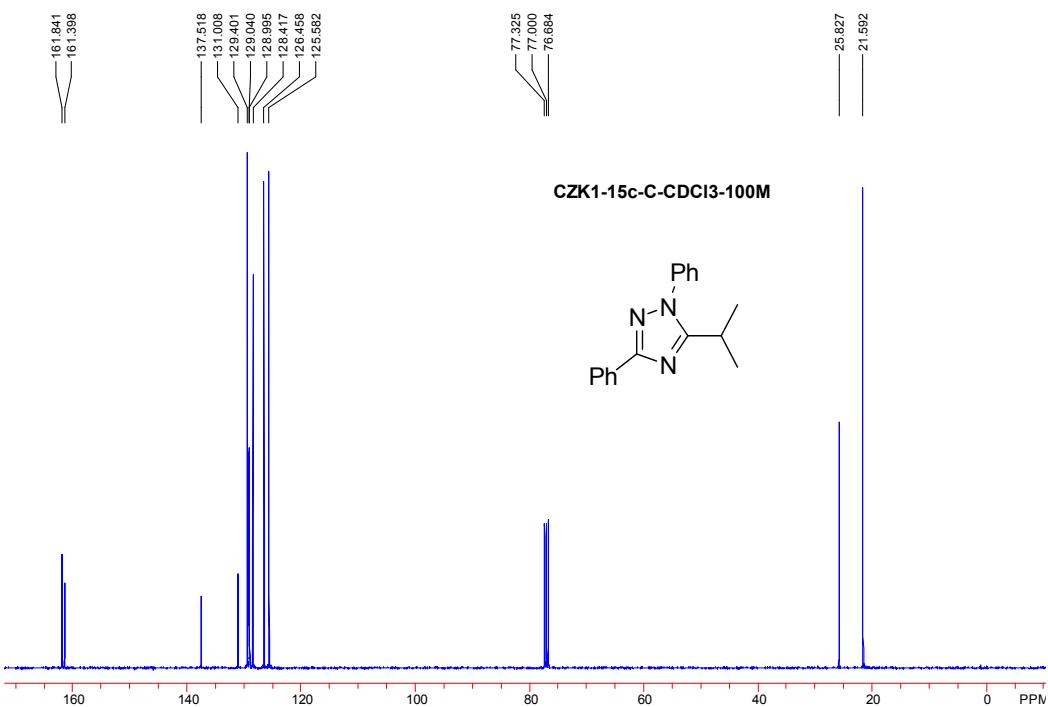
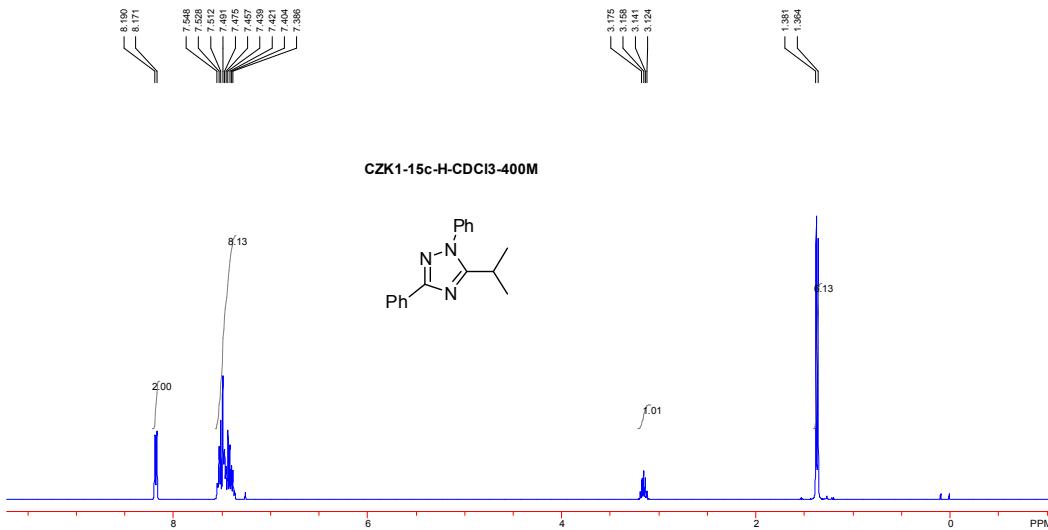
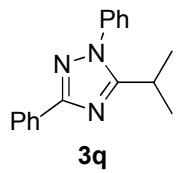


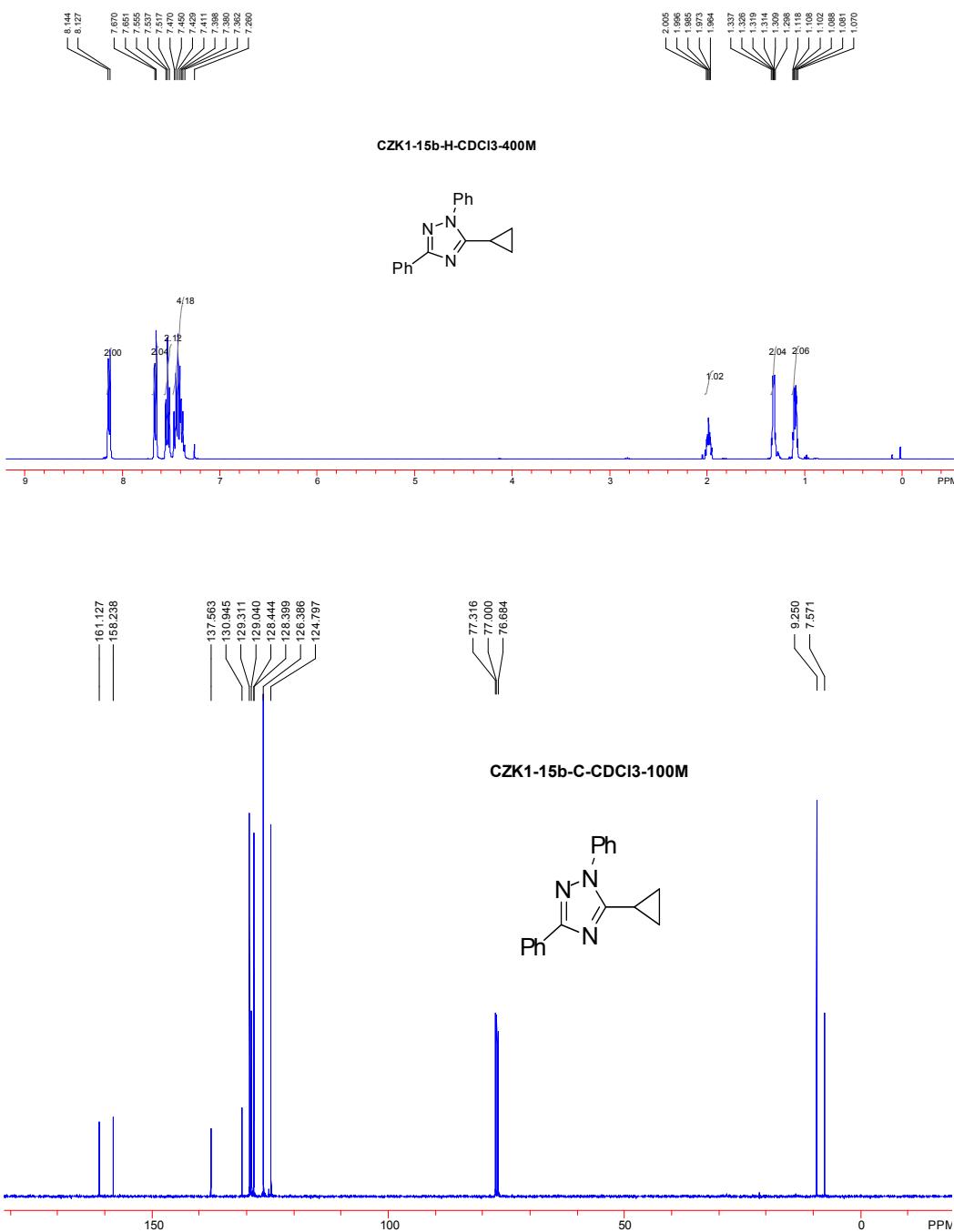
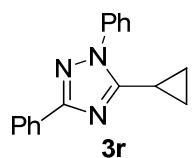


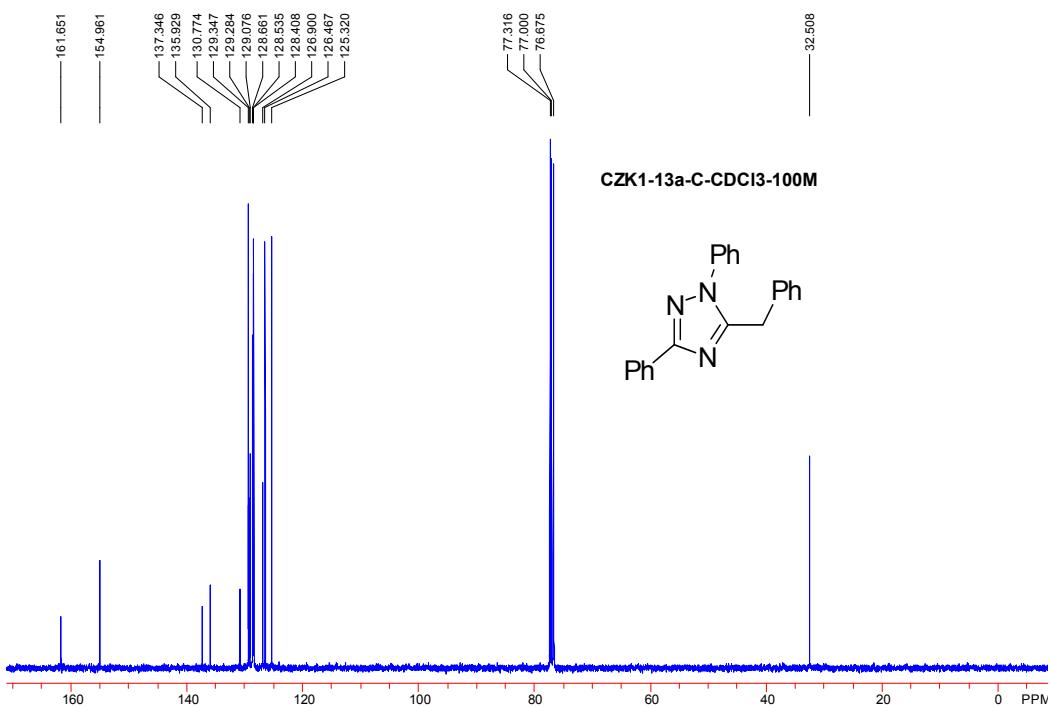
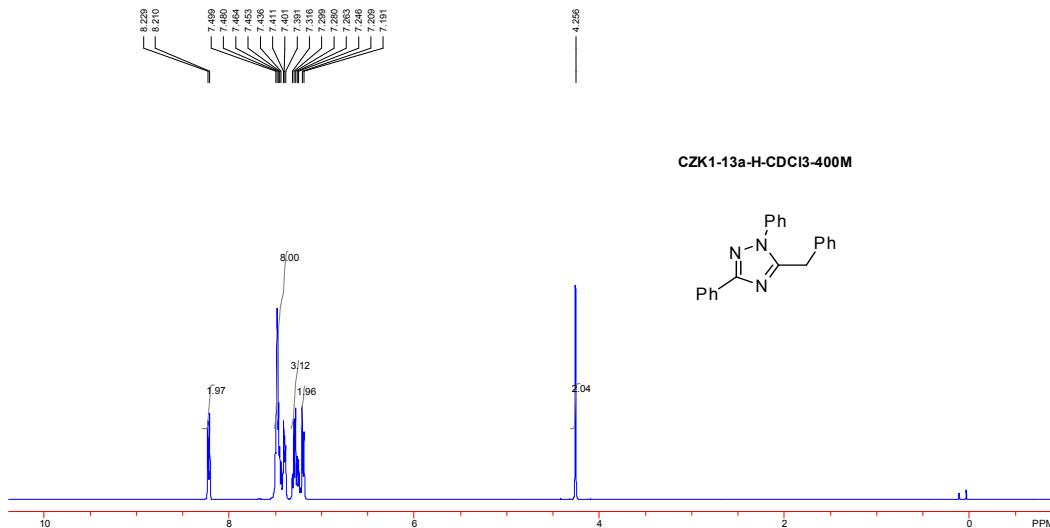
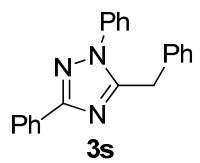
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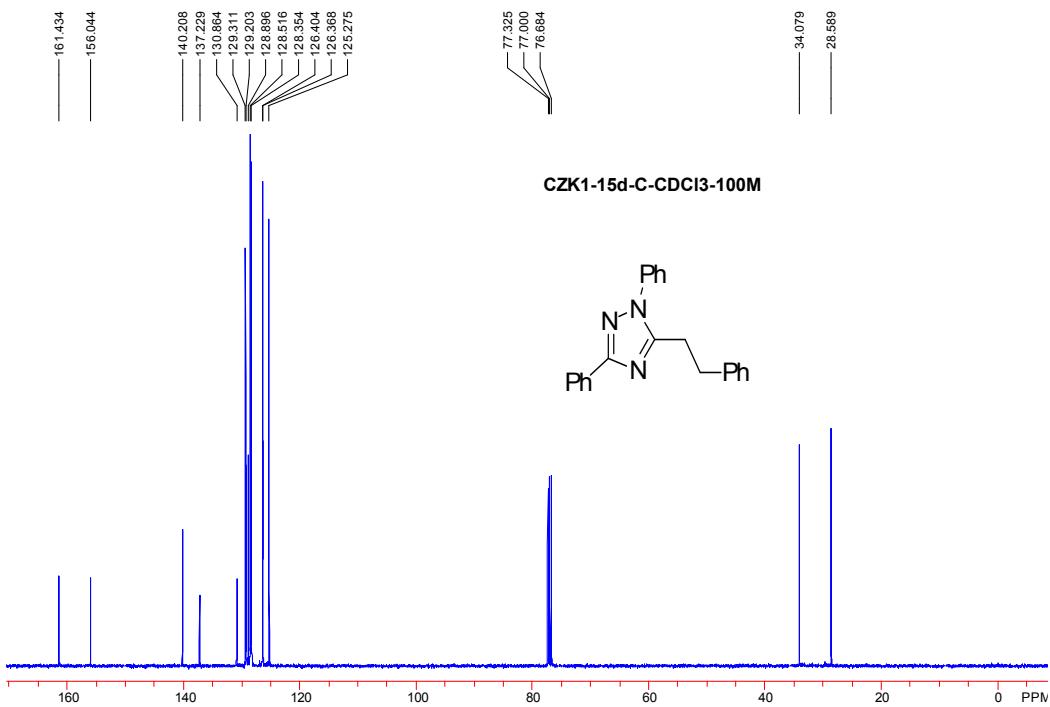
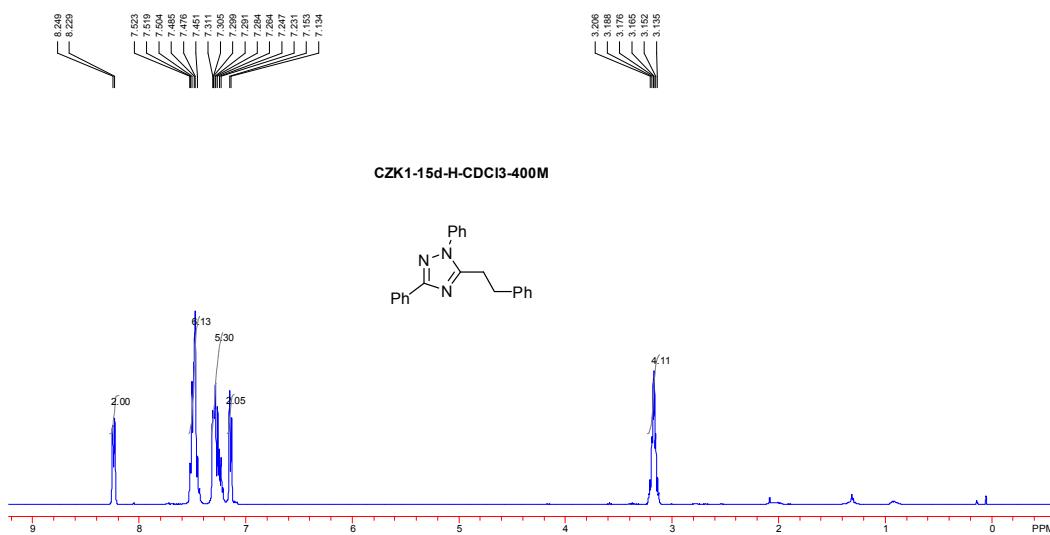
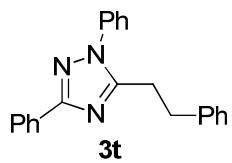


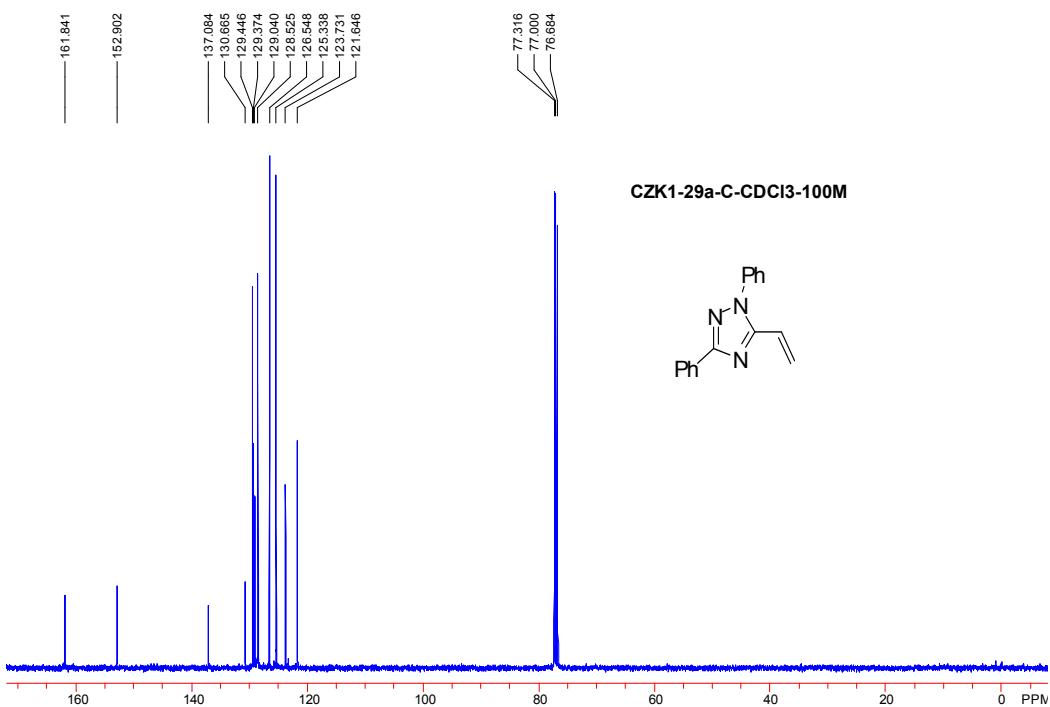
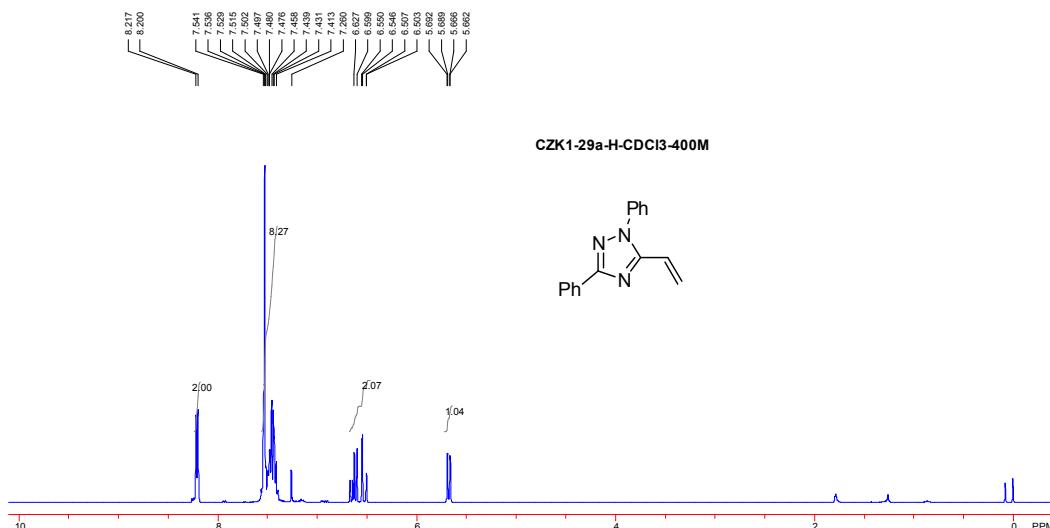
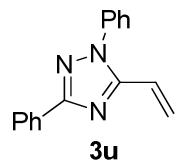


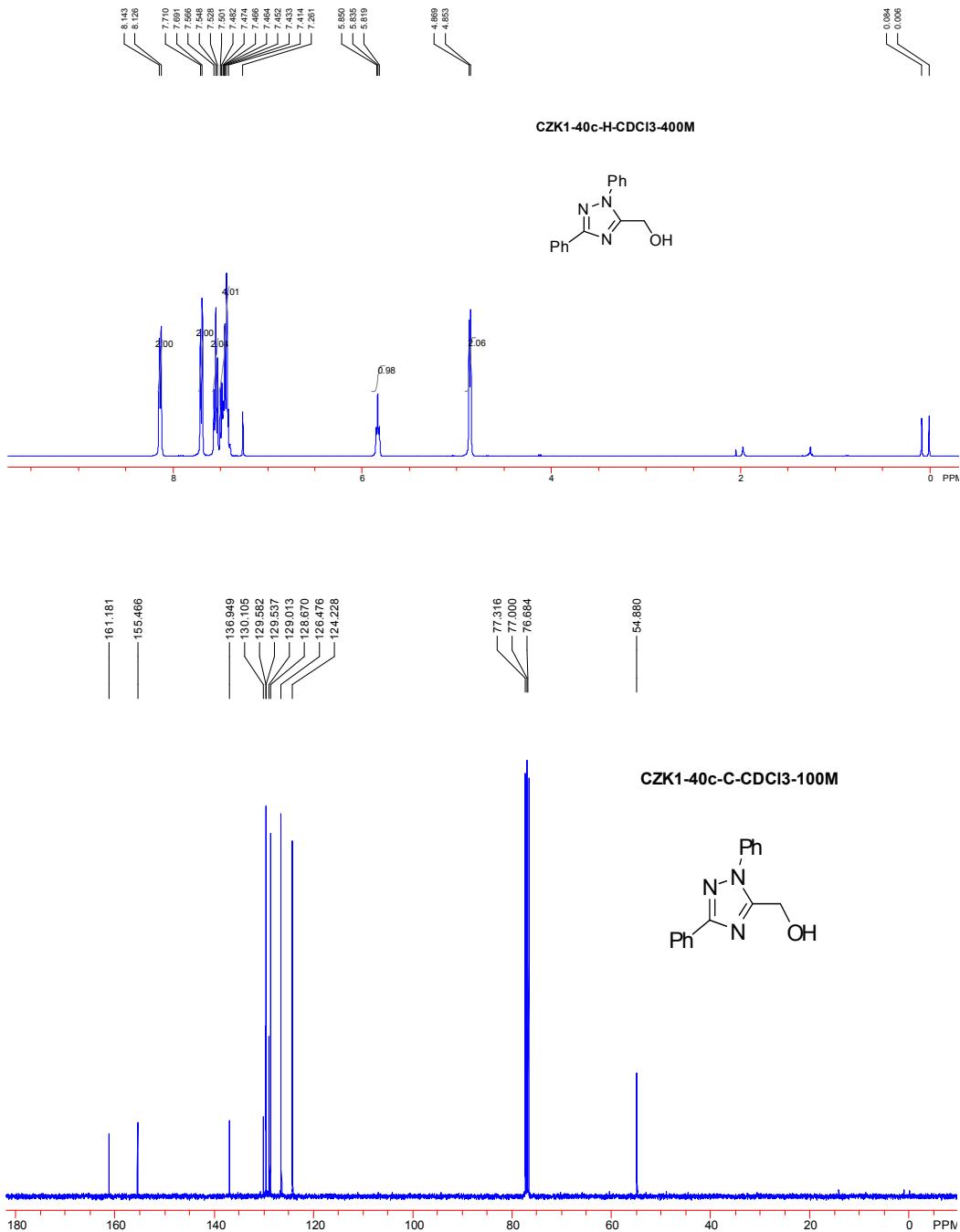
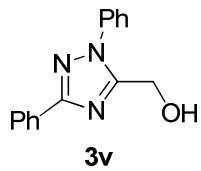


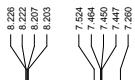
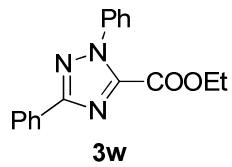




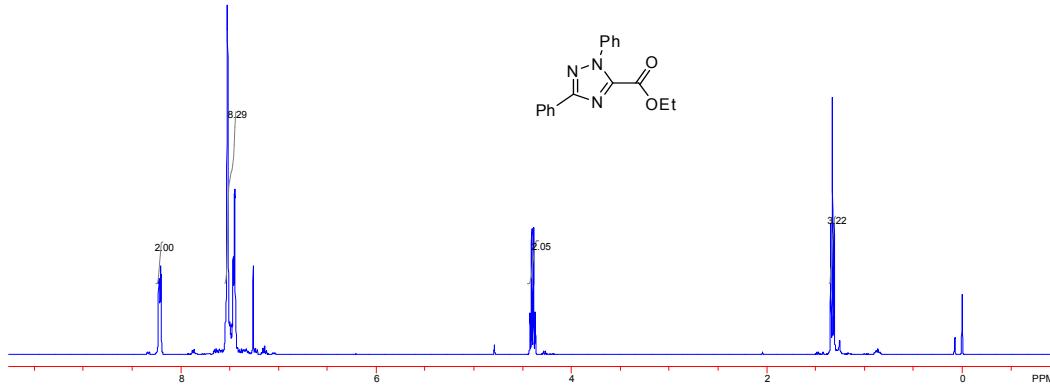




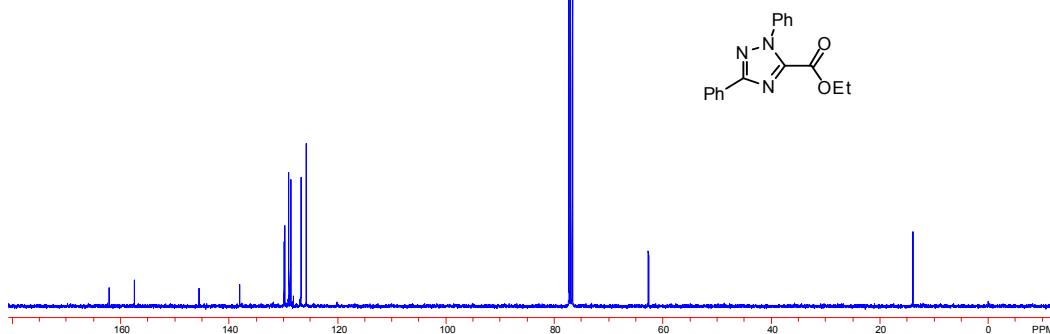


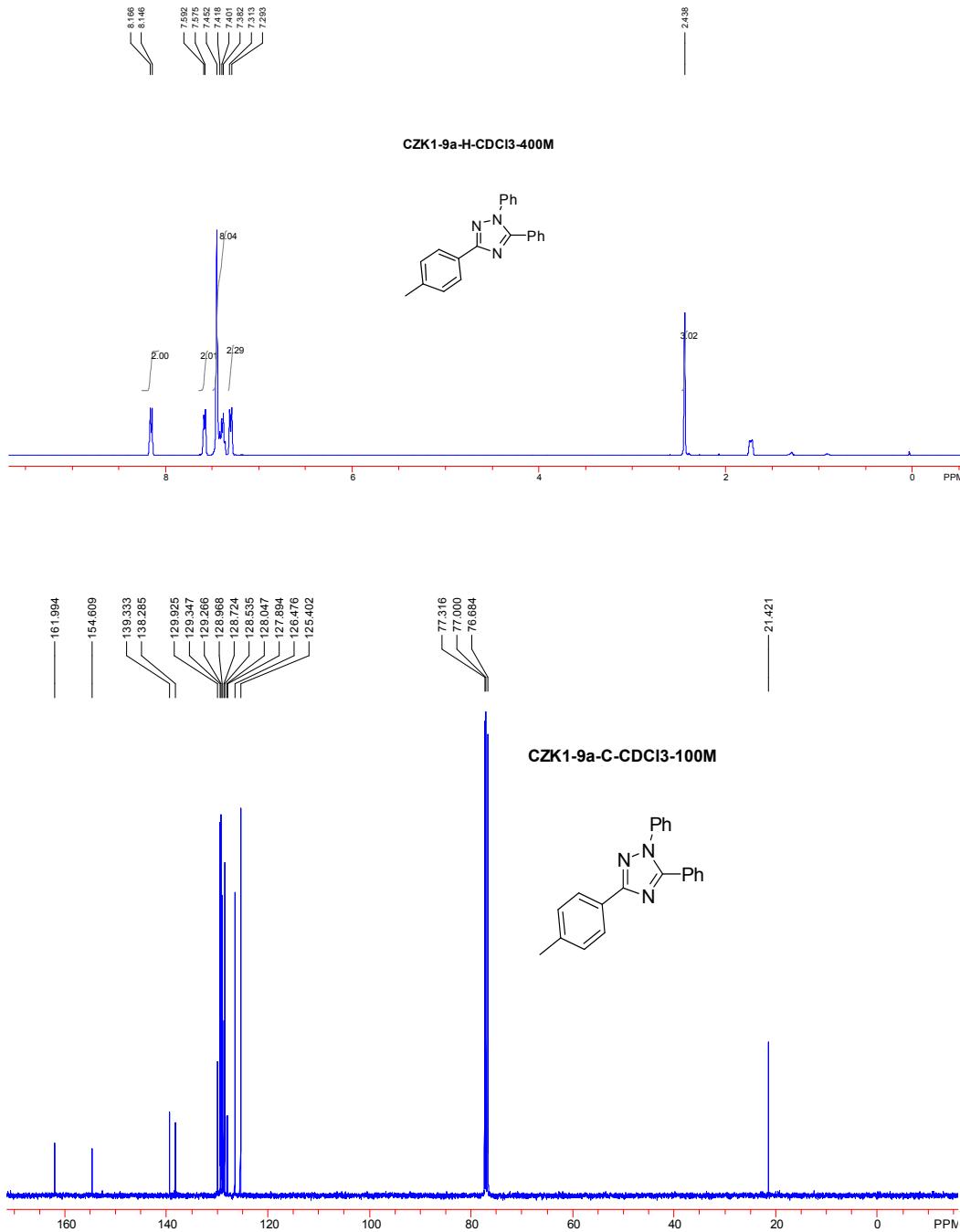
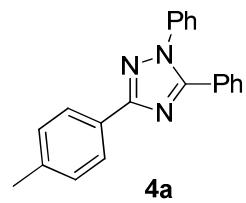


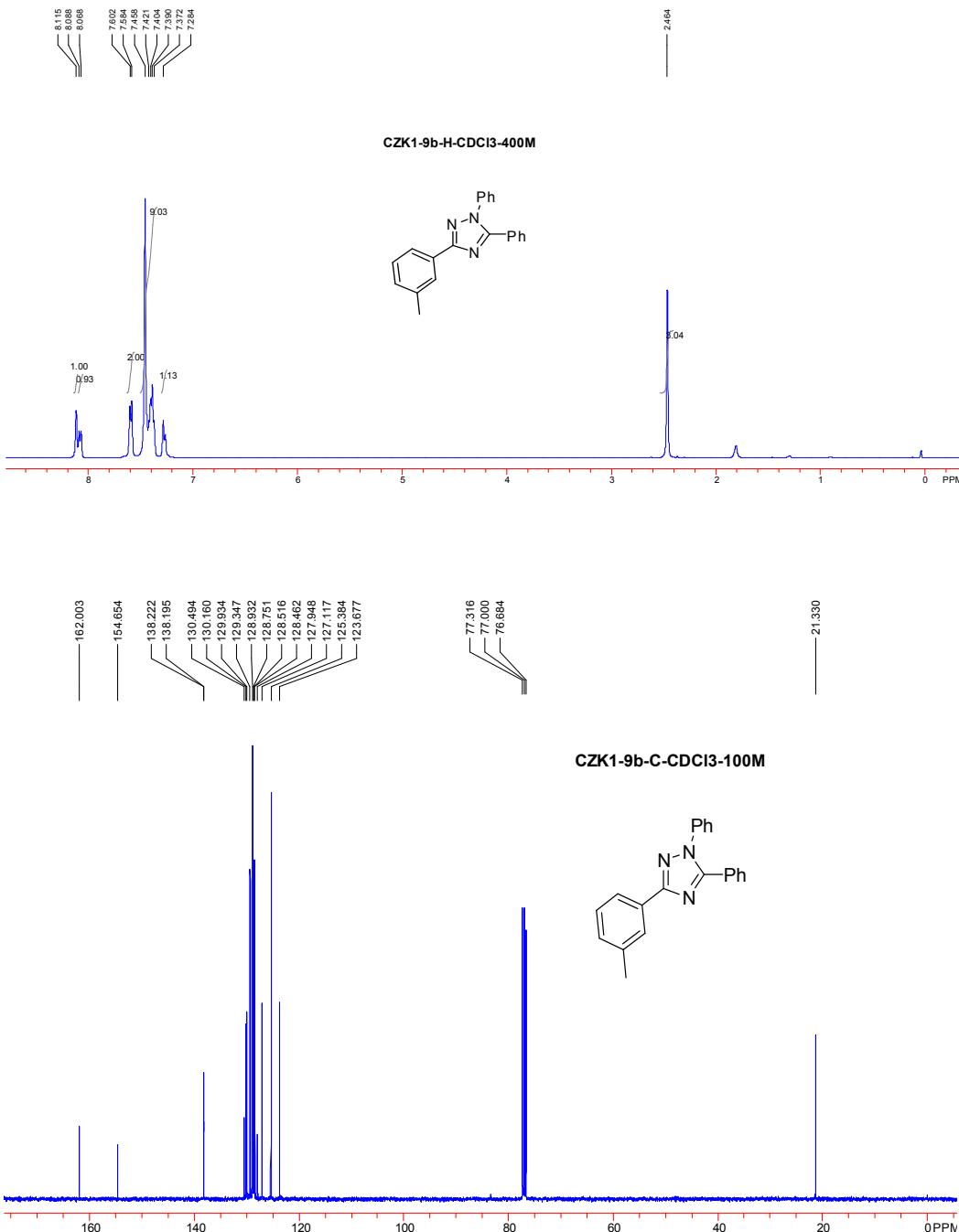
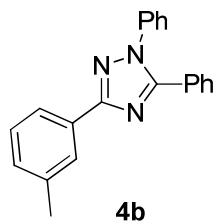
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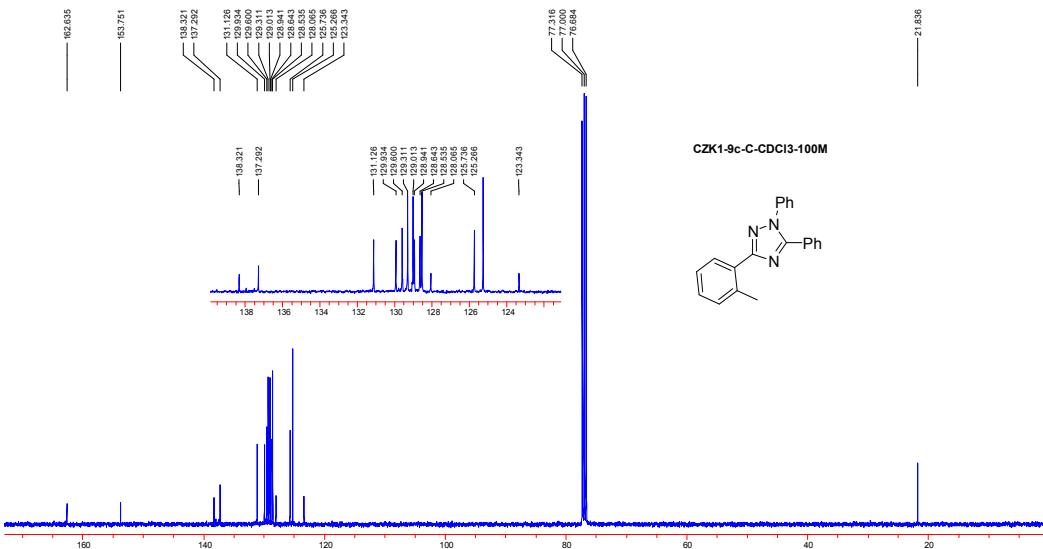
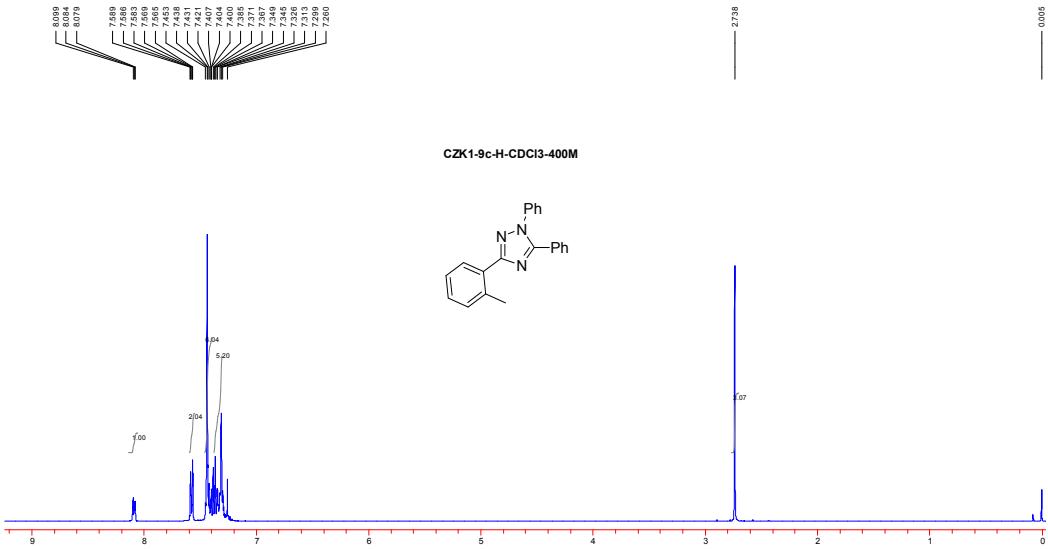
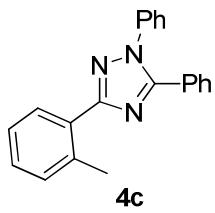


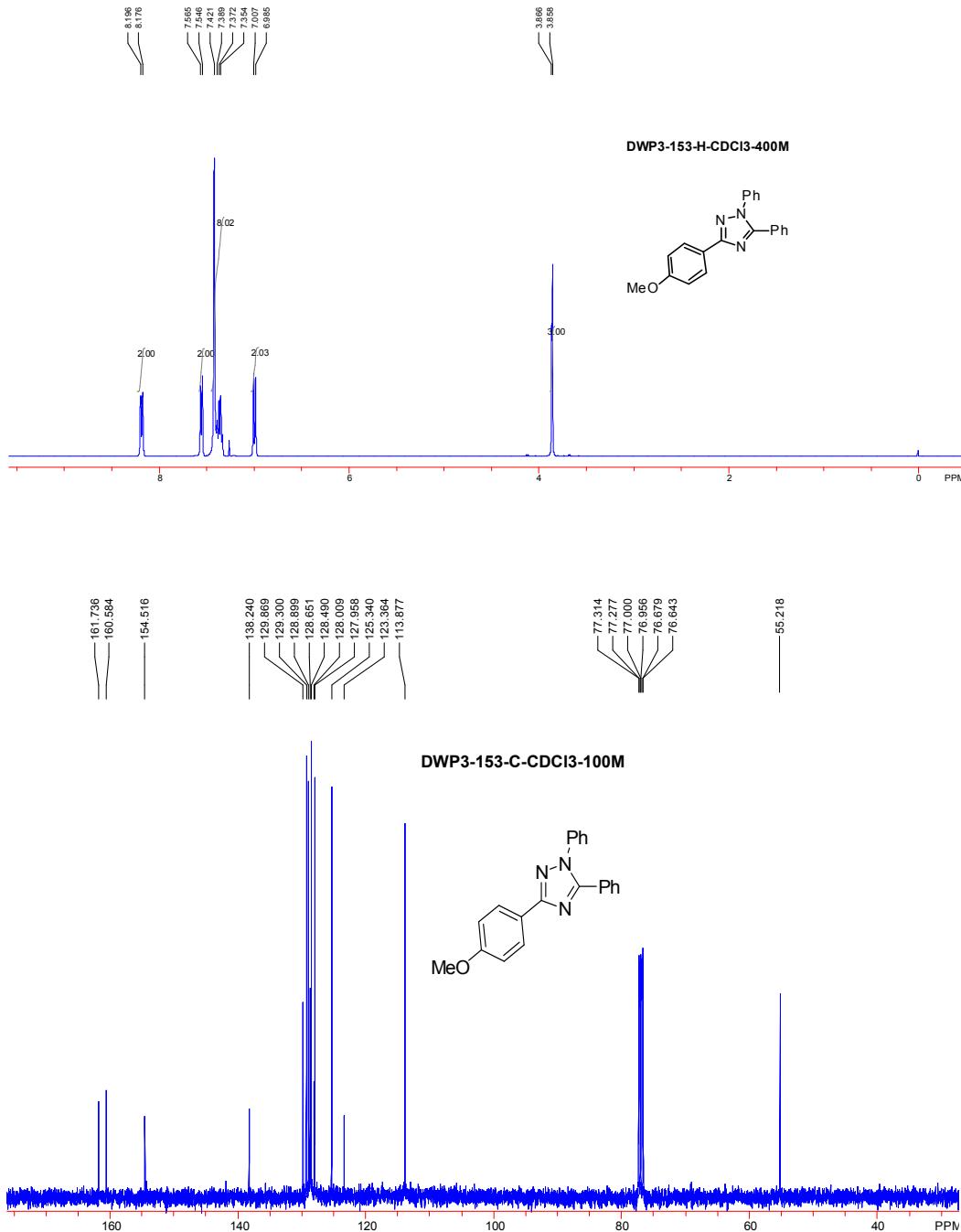
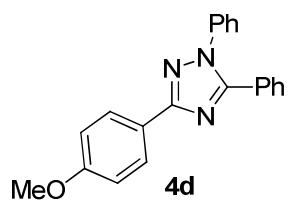
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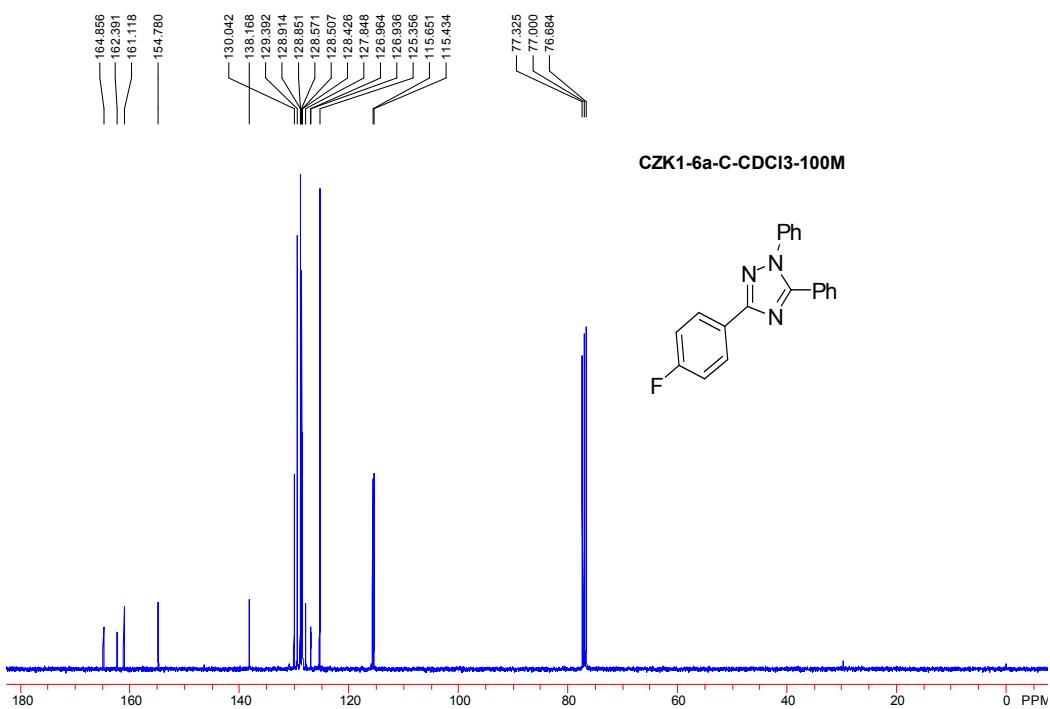
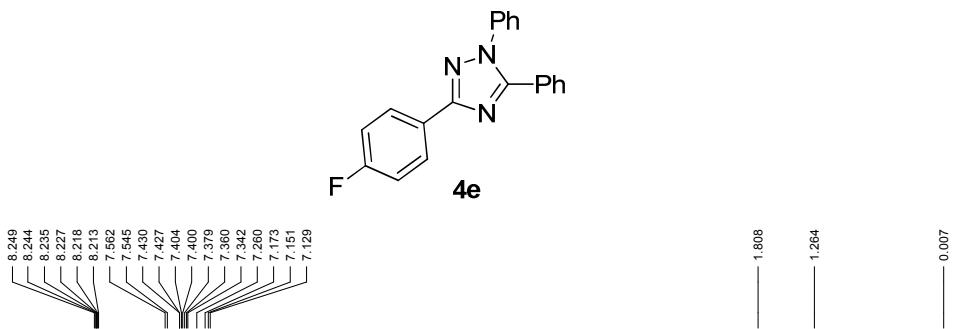


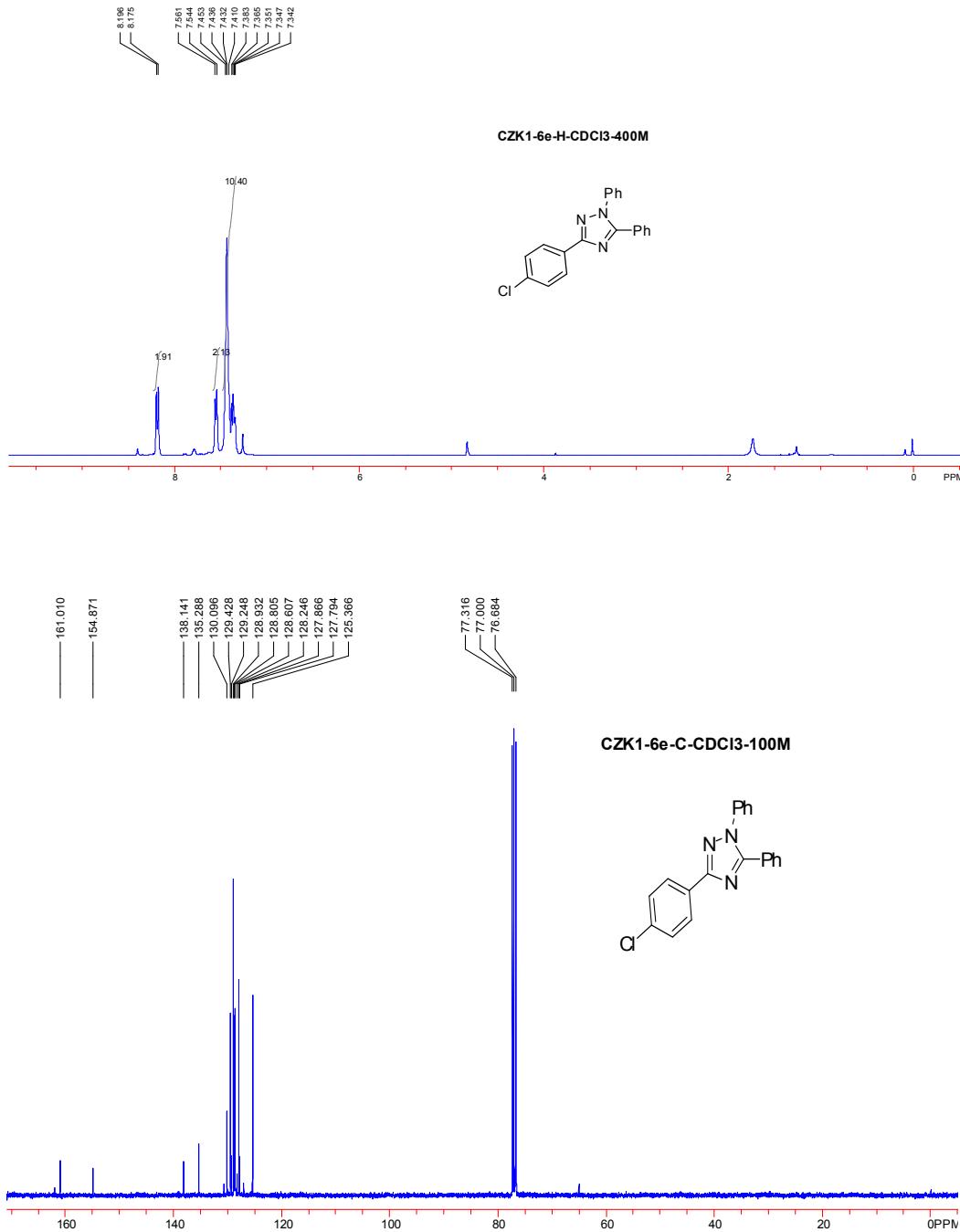
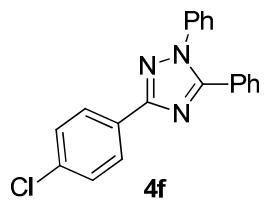


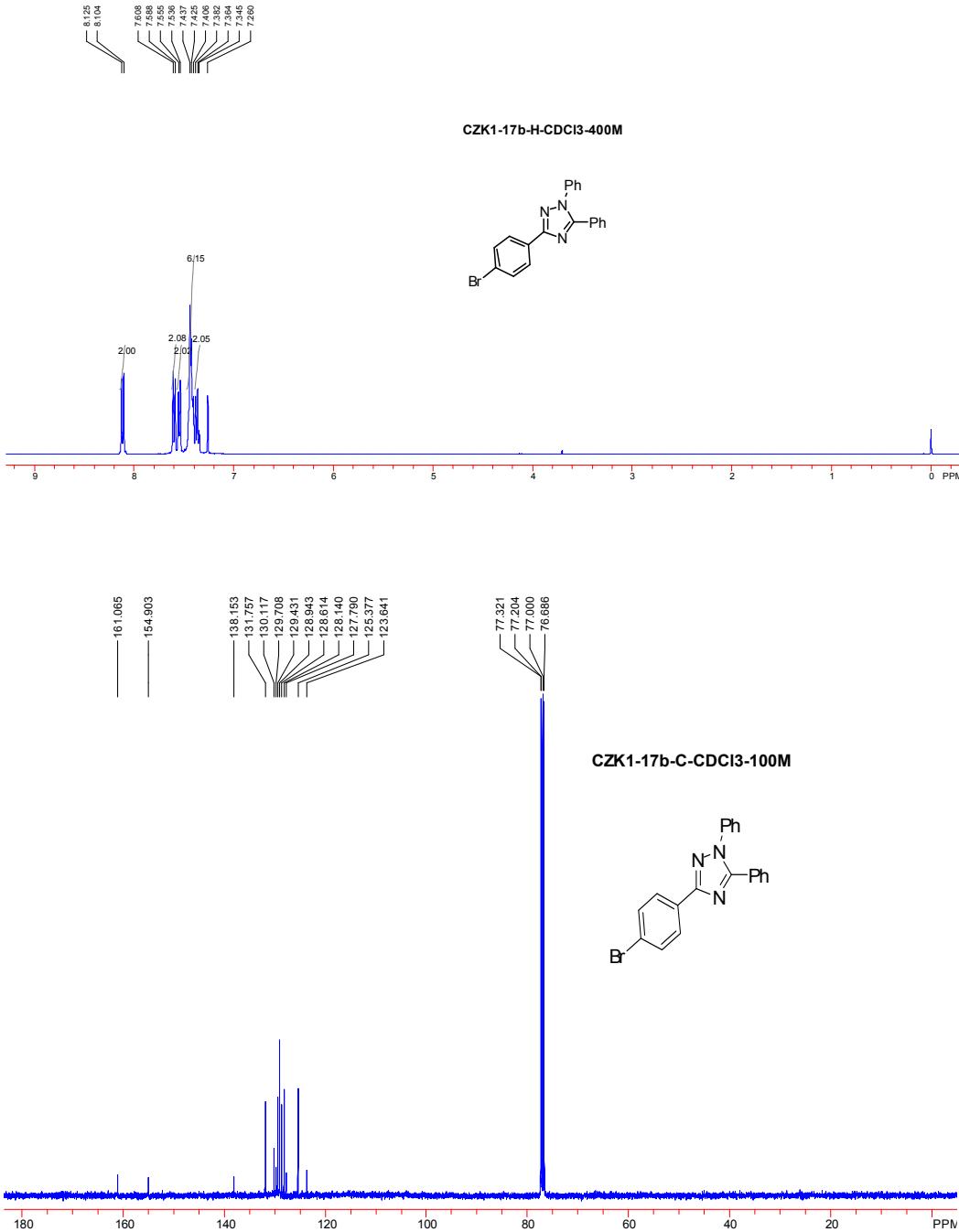
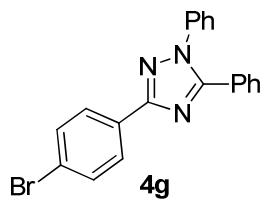


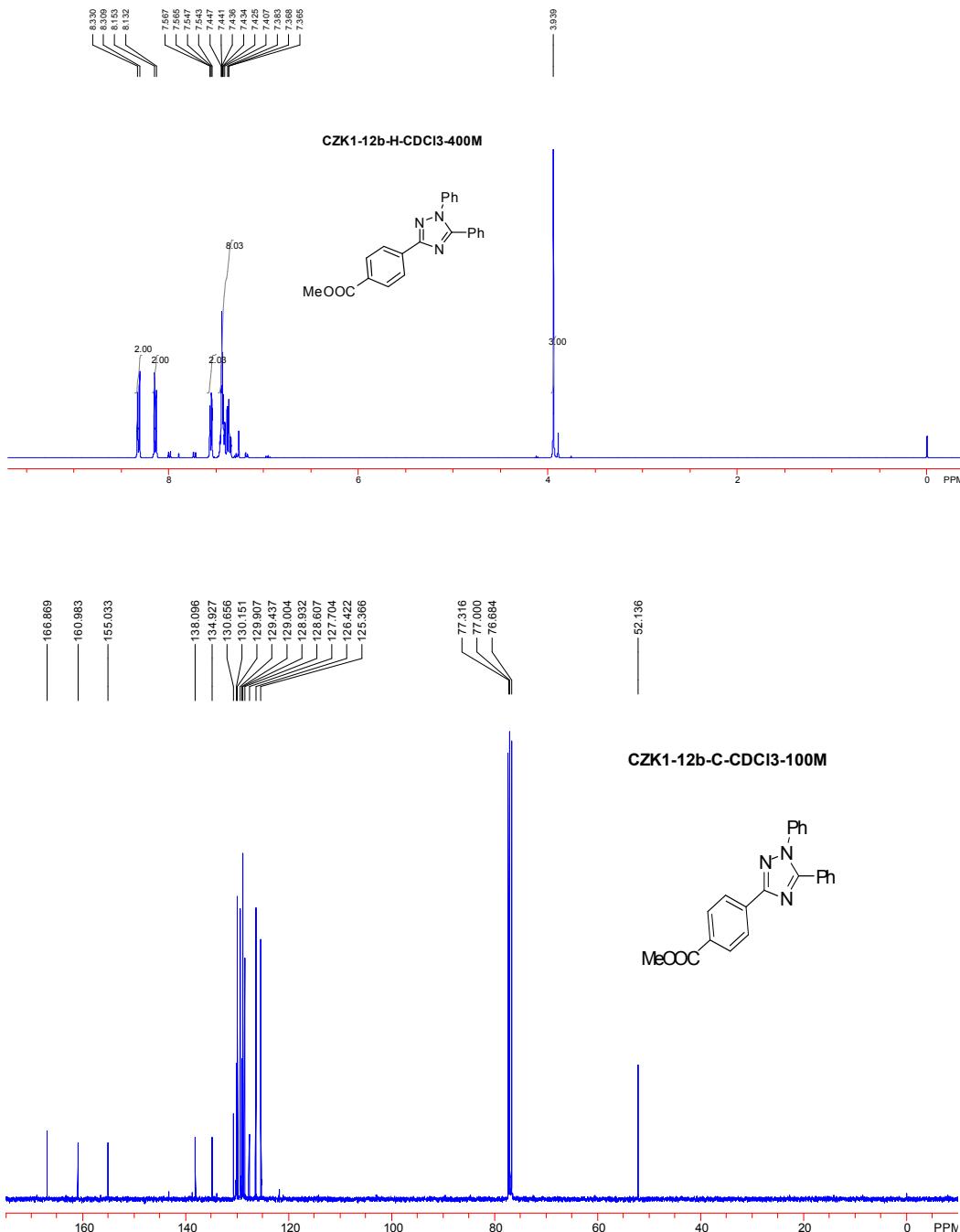
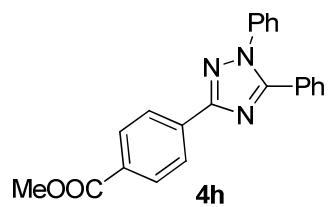


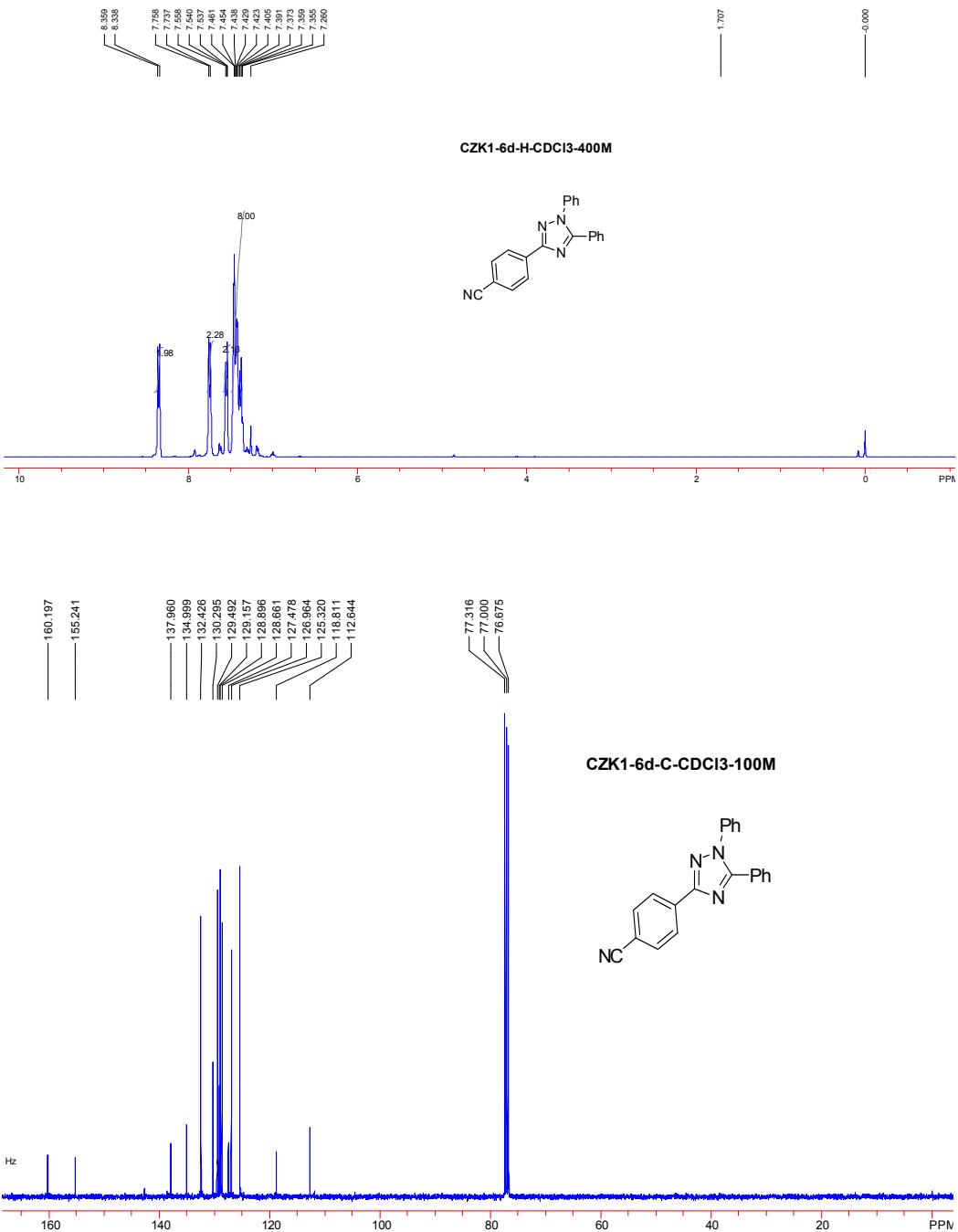
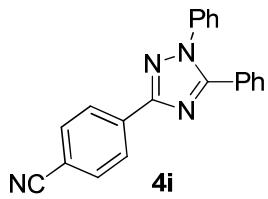


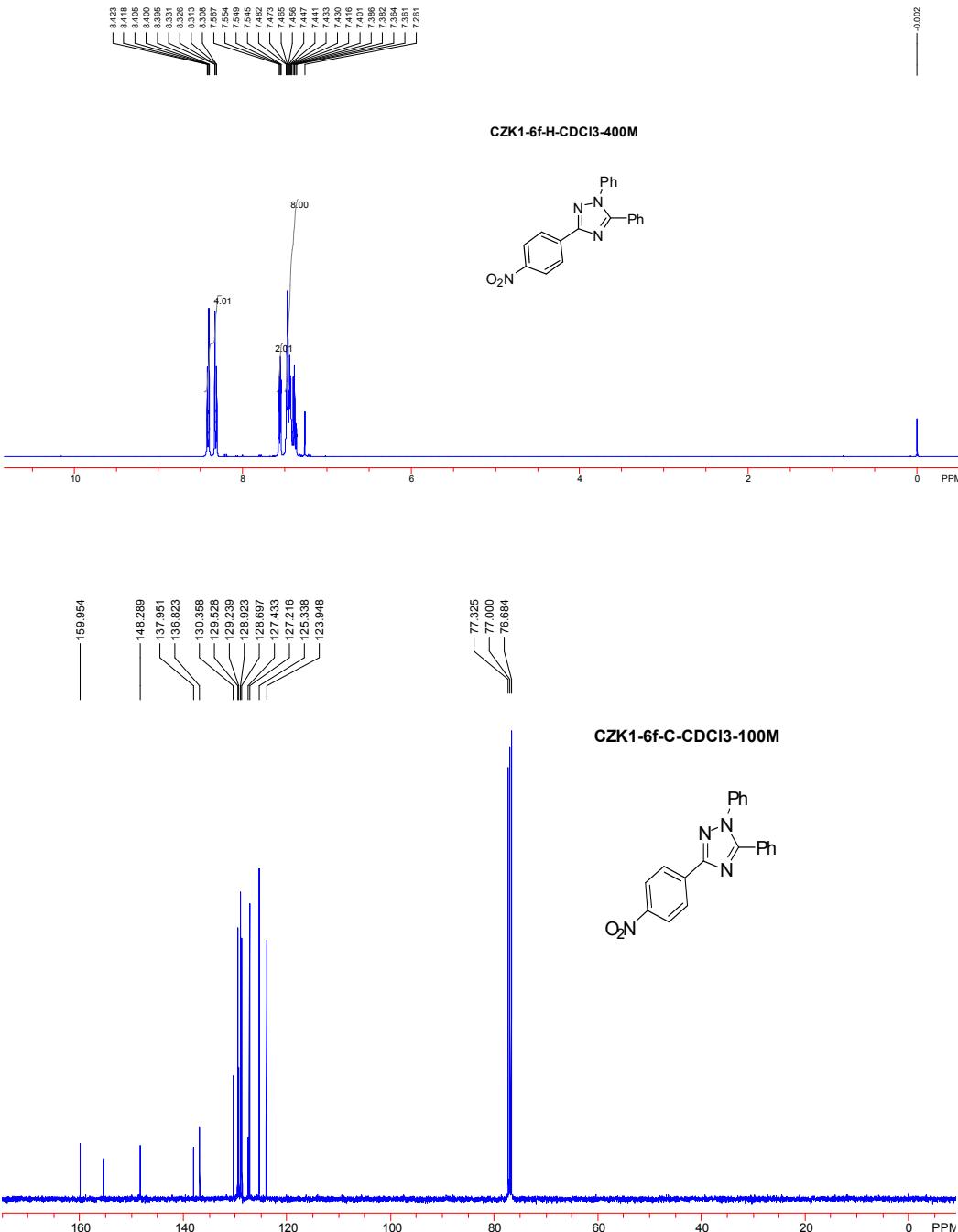
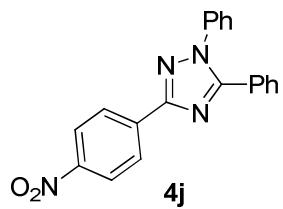


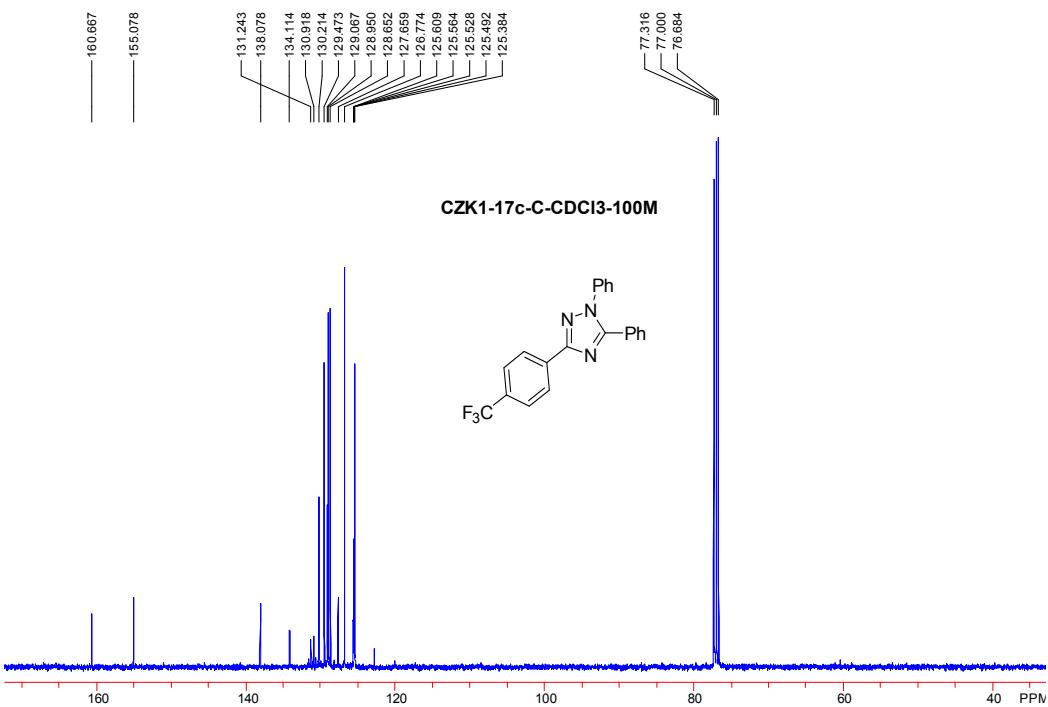
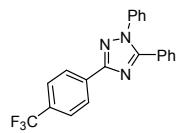
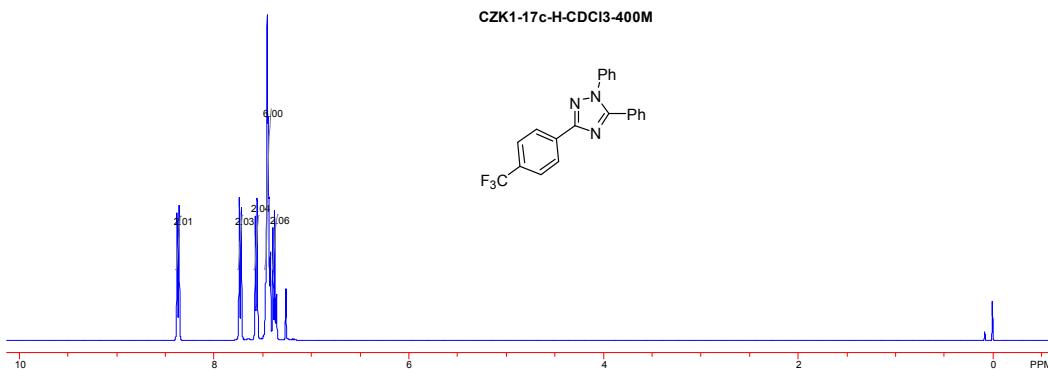
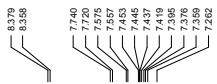
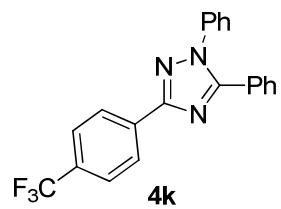


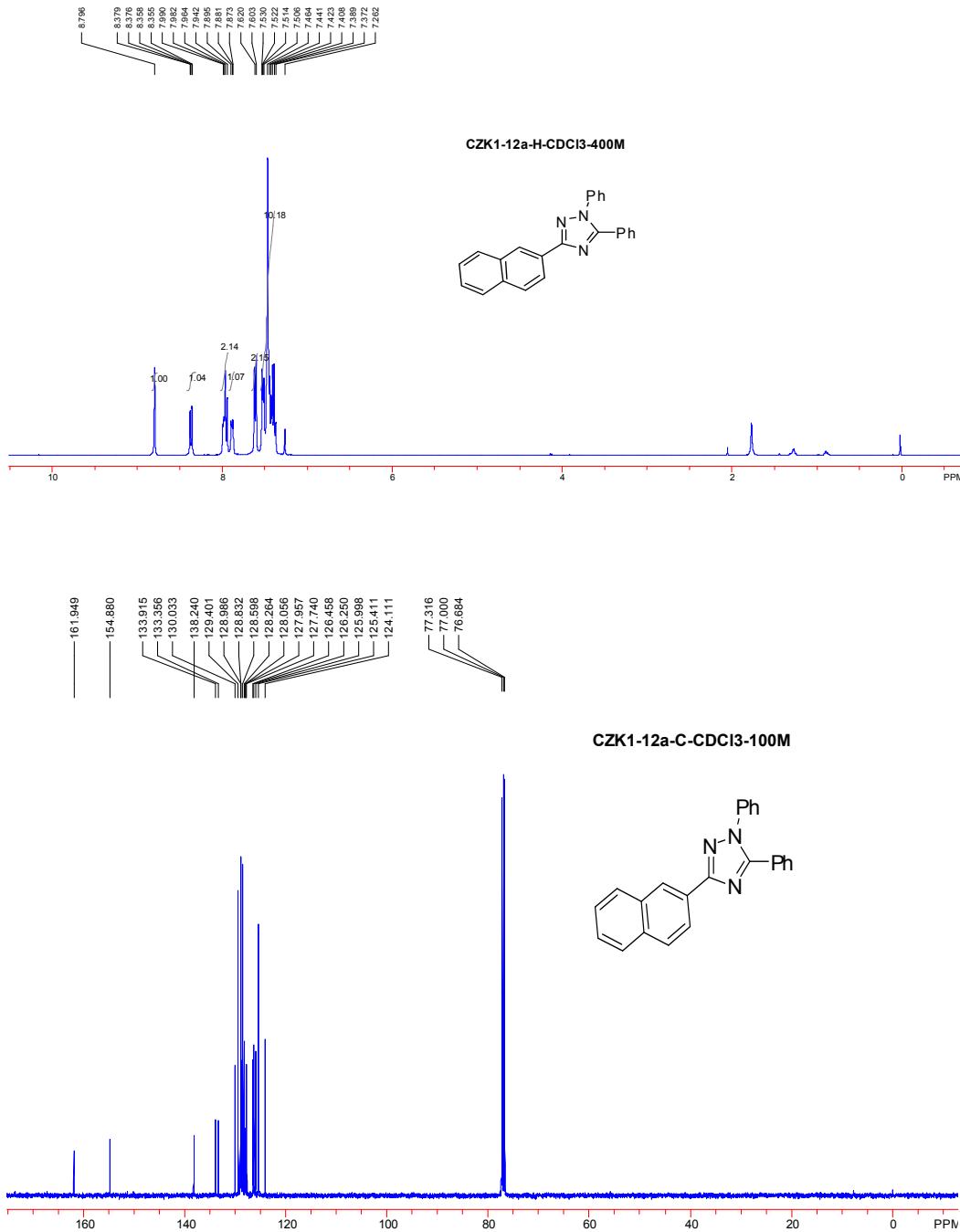
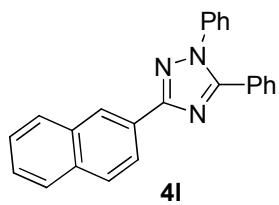


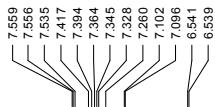
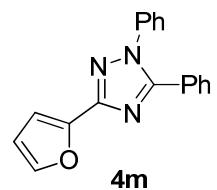




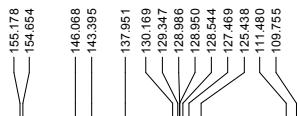
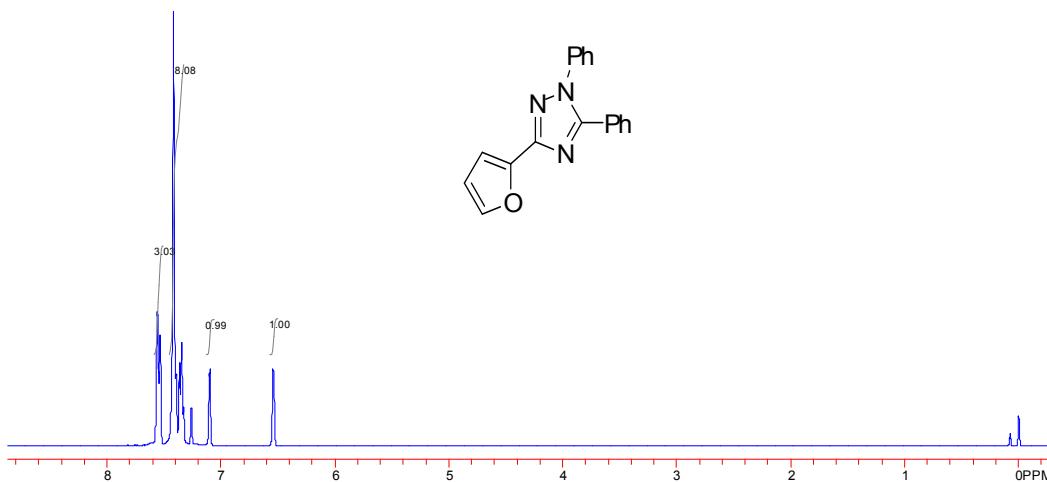




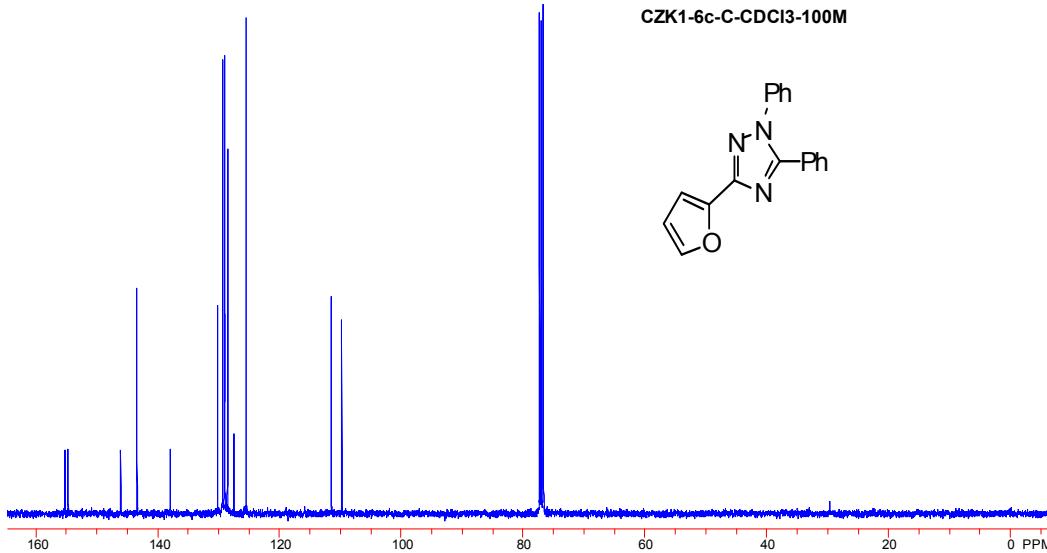


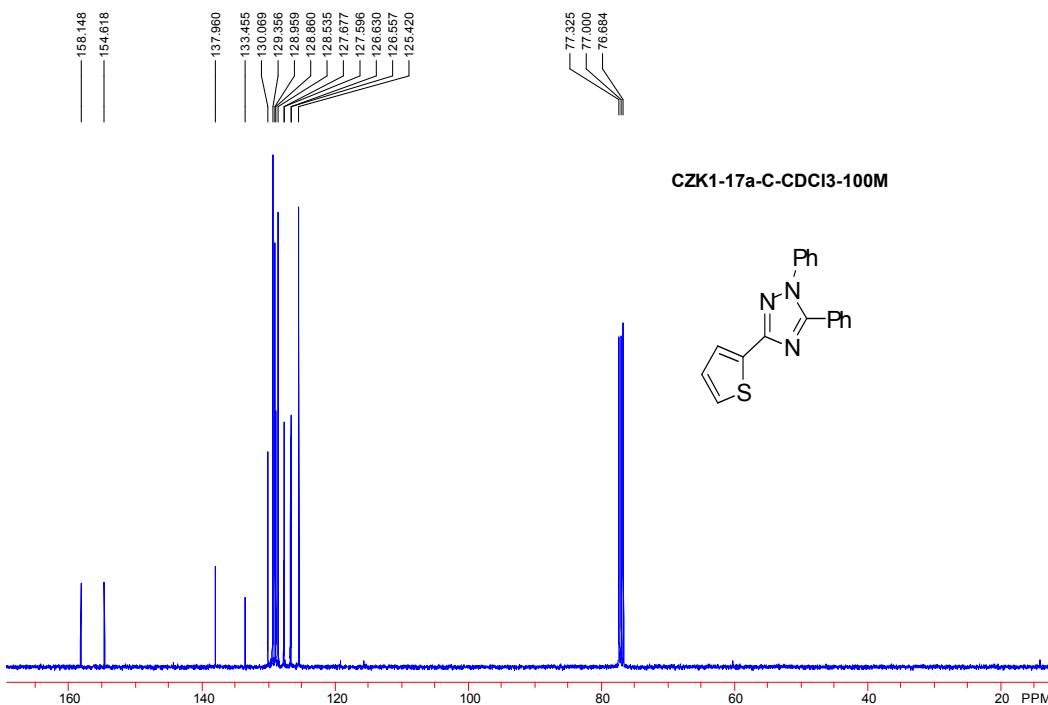
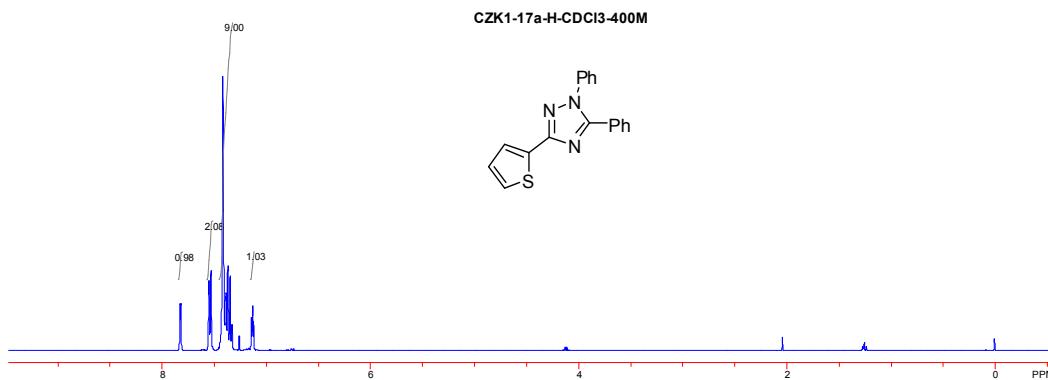
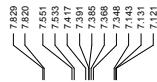
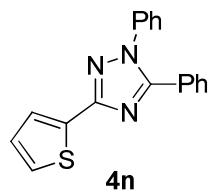


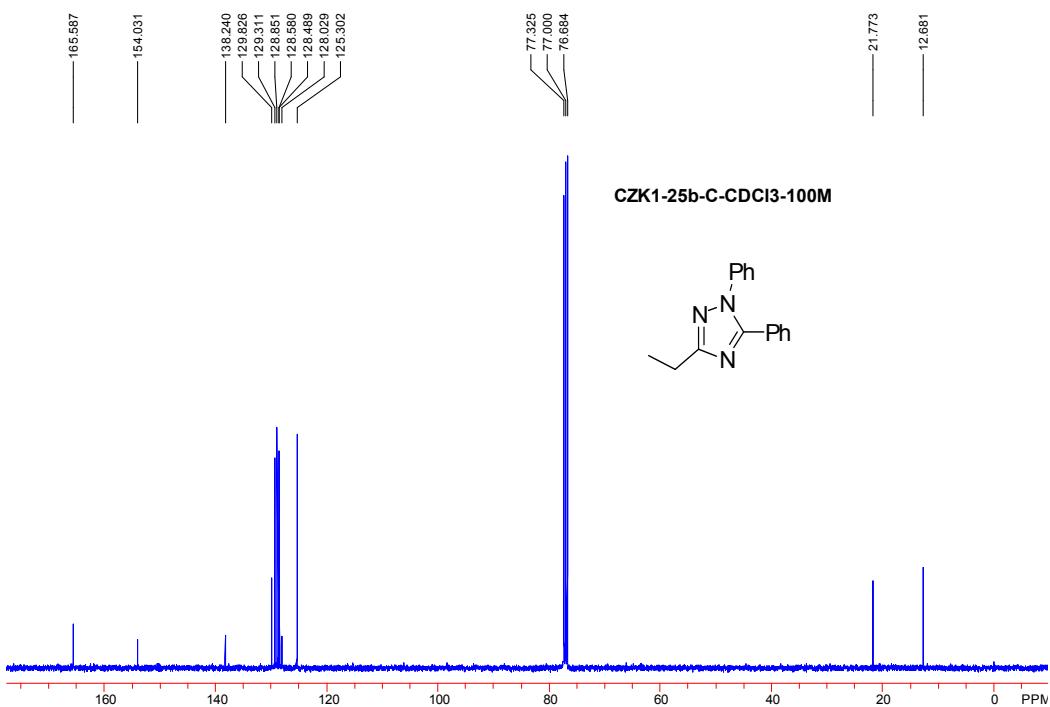
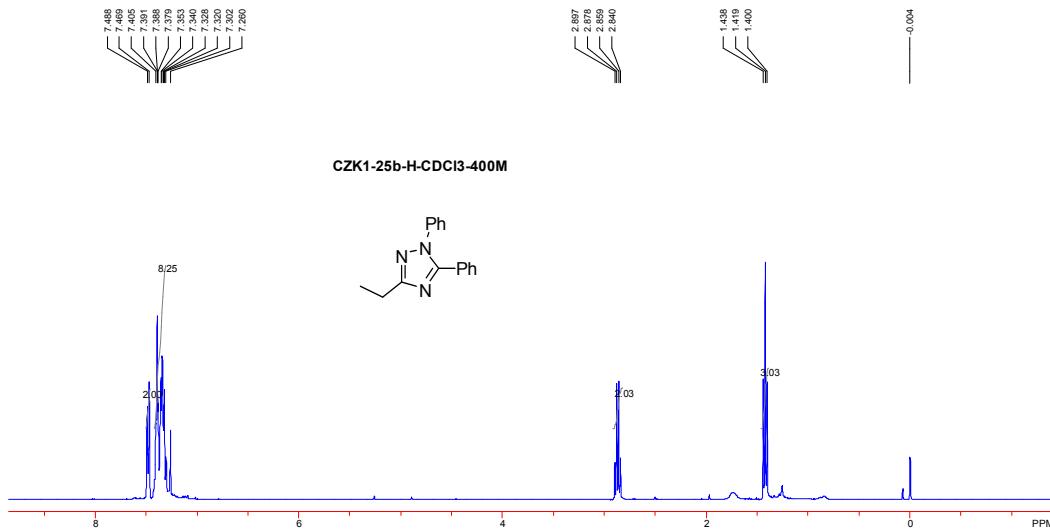
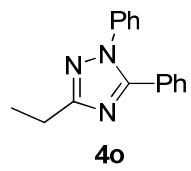
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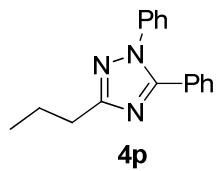


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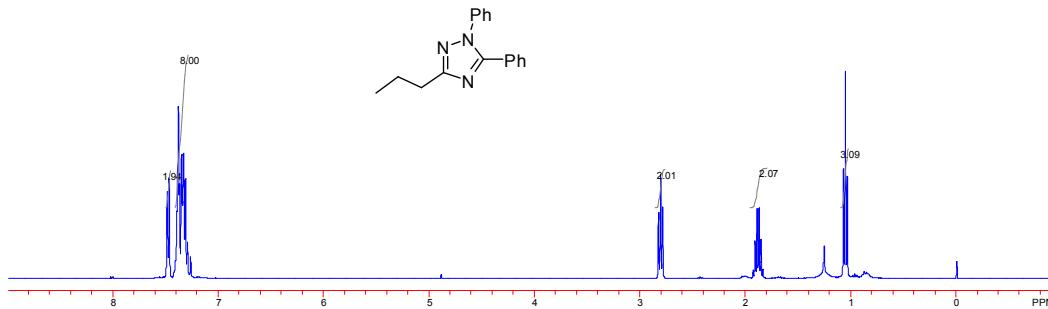


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 7.327
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 7.291
 7.200

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 2.802
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 1.049
 1.030

CZK1-25d-H-CDCl₃-400M

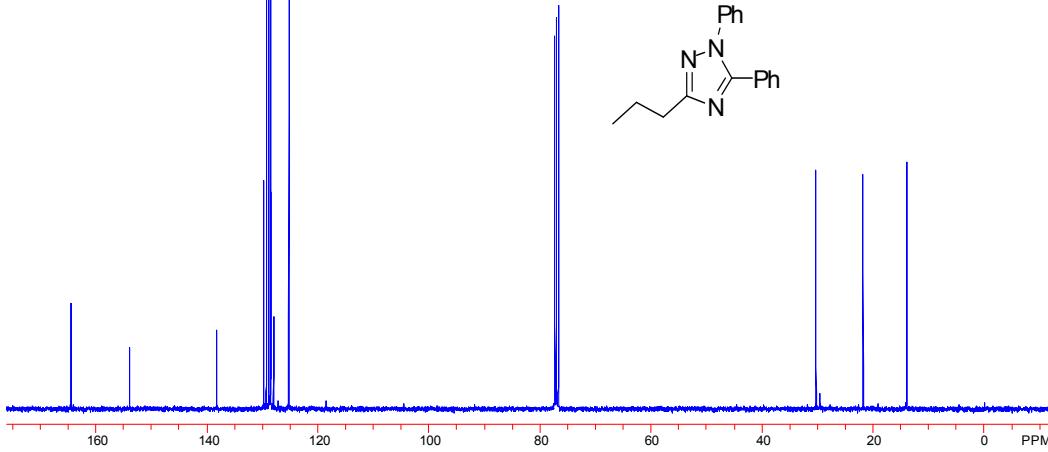


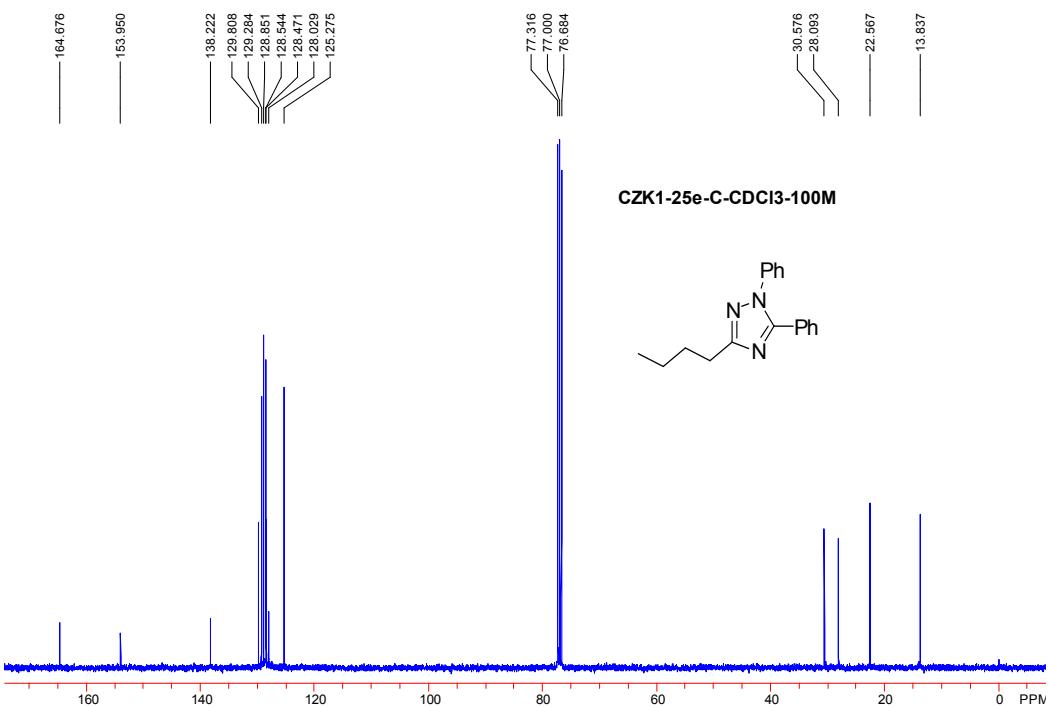
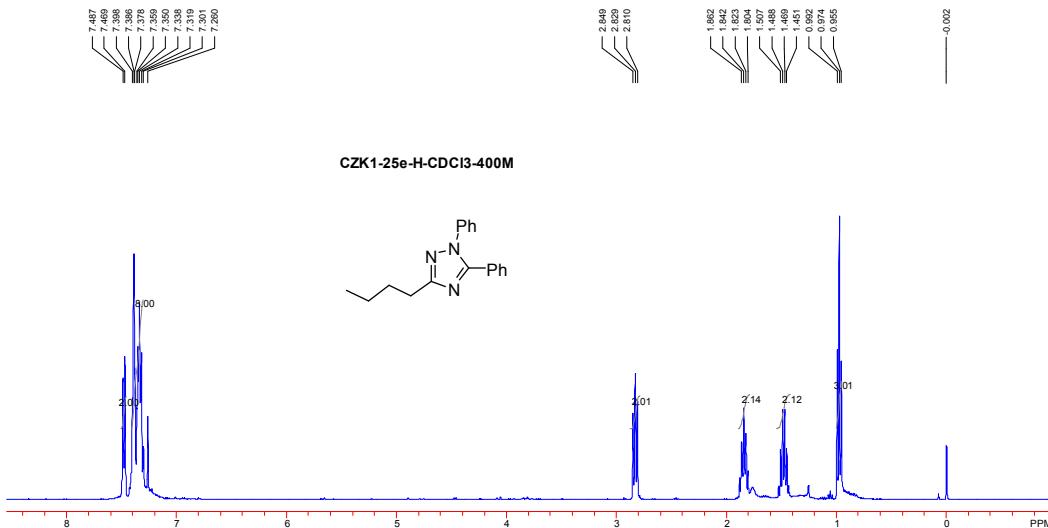
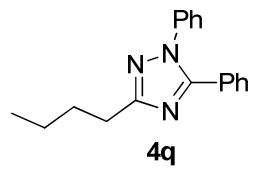
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 128.002
 125.239

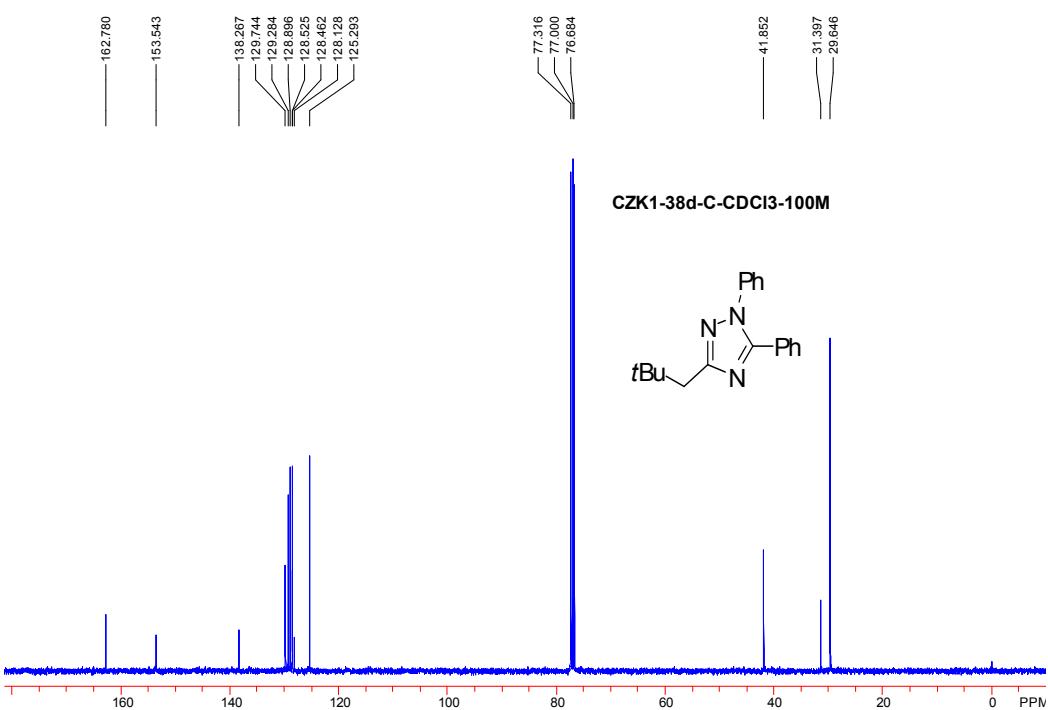
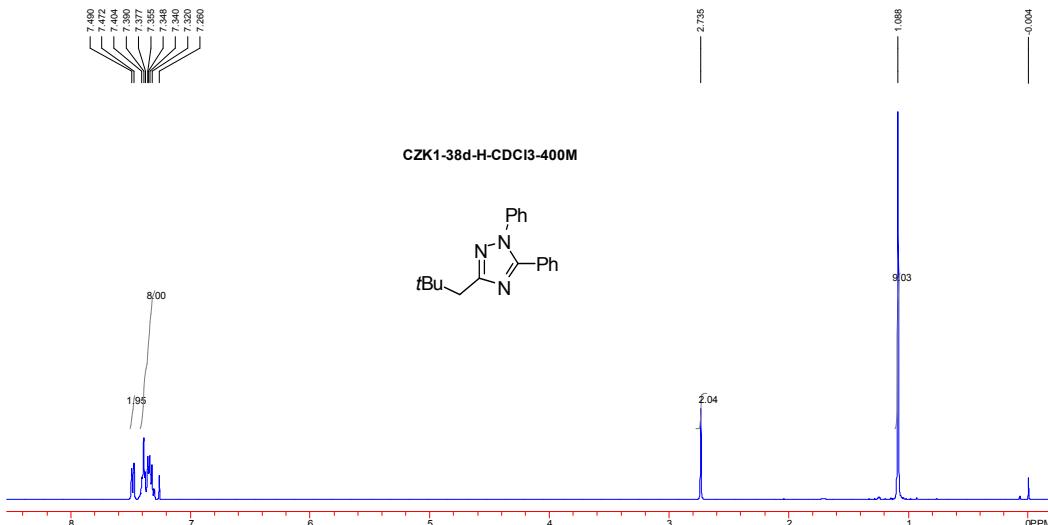
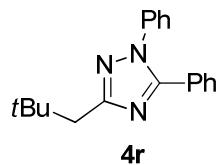
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 76.584

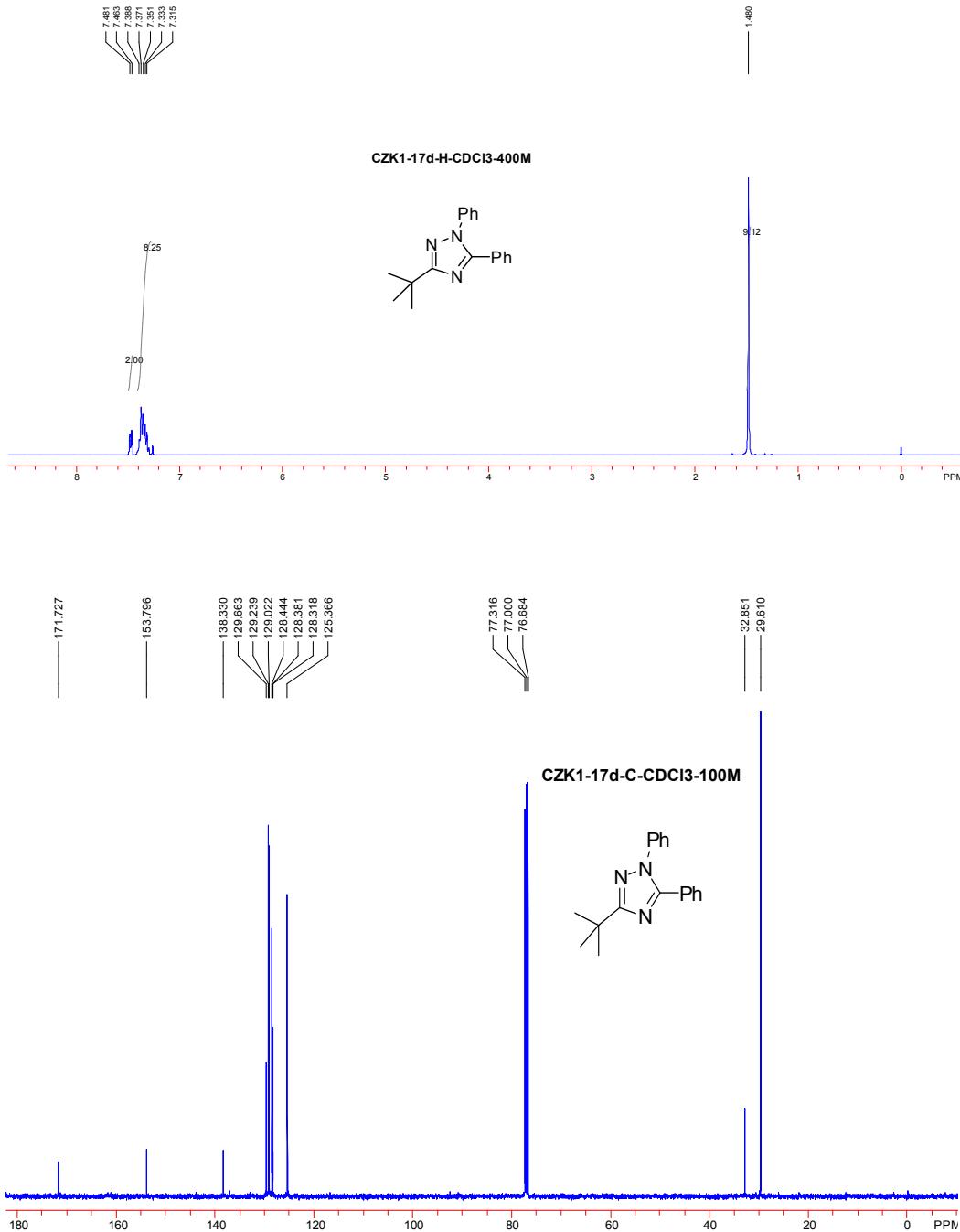
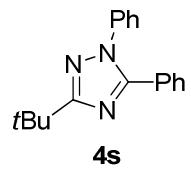
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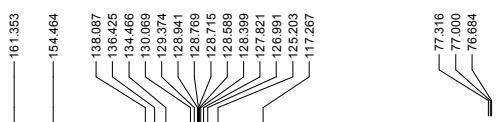
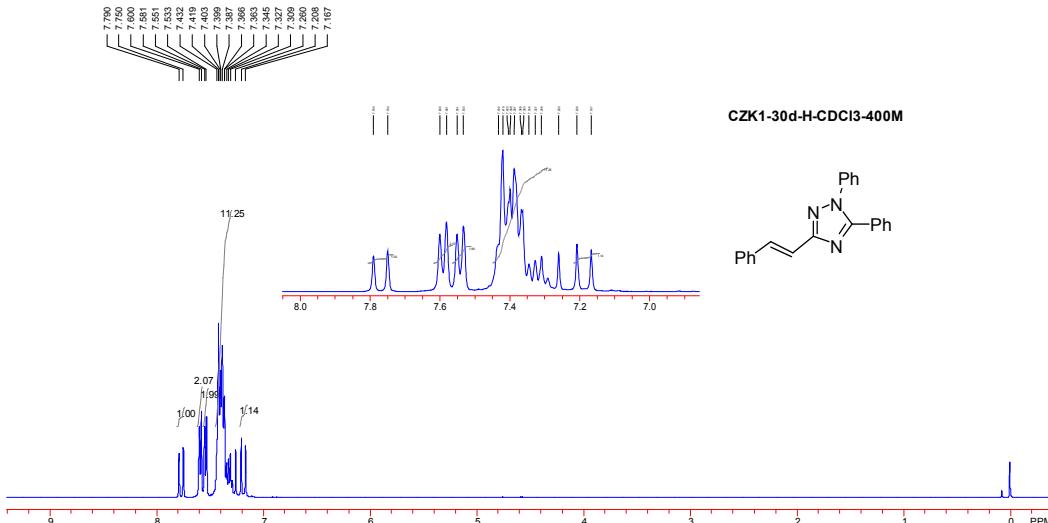
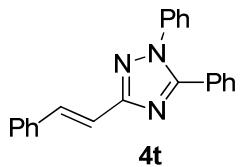
CZK1-25d-C-CDCl₃-100M











CZK1-30d-C-CDCL3-100M

