Supporting Information

For

Controlled mono-olefination versus diolefination of arenes *via* C-H activation in water: A key role of Catalysts

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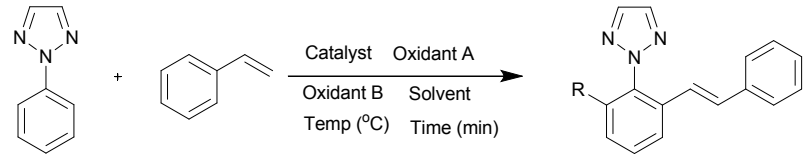
Conditions Screening

To find out the optimal conditions to synthesize the *mono*-/diolefination of 2-aryl-1,2,3-triazole, various conditions were probed. (S table 1) Finally, the reaction conditions of mono-olefination were optimized as follows: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), $AgNTf_2$ (0.04 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.2 mmol) in H_2O (0.5 ml) at 120 °C under Ar for 60 min; The reaction conditions of diolefination were optimized as follows: **1a** (0.2 mmol), **2a** (0.8 mmol), $[Cp^*RhCl_2]_2$ (1 mol %), $AgNTf_2$ (0.04 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.8 mmol) in H_2O (0.5 ml) at 120 °C under Ar for 30 min.

S Table 1. Conditions Screening of the Reaction Condition[a,b]



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

3a, R = H,
3aa, R = styryl

entry	Catalyst	Catalyst (mol %)	**2a** (equiv)	Oxidant A (0.2 equiv)	Oxidant B (equiv)	solvent	Time (min)	Yield of **3a**/**3aa** (%)	Conversion[c] of **1a** (%)
1	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	10	1	$AgSbF_6$	1	*t*-AmOH	900	51/34	89
2	$[Cp^*Co(MeCN)_3][SbF_6]_2$	10	1	$AgSbF_6$	1	*t*-AmOH	900	-	-
3	$[Cp^*IrCl_2]_2$	10	1	$AgSbF_6$	1	*t*-AmOH	900	41/-	46
4	$[Cp^*RhCl_2]_2$	10	1	$AgSbF_6$	1	*t*-AmOH	900	22/68	96
5	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	$AgSbF_6$	1	*t*-AmOH	900	65/11	98
6	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	Ag_2SO_4	1	*t*-AmOH	900	52/28	94
7	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	$AgNTf_2$	1	*t*-AmOH	900	74/21	99
8	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	AgOAc	1	*t*-AmOH	900	61/24	97
9	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	AgOTf	1	*t*-AmOH	900	67/16	93
10	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	$AgNTf_2$	0.5	*t*-AmOH	900	31/8	43
11	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	$AgNTf_2$	0.75	*t*-AmOH	900	57/11	64
12	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	$AgNTf_2$	1.5	*t*-AmOH	900	56/27	96
13	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	$AgNTf_2$	1	HFIP	900	81/18	99
14	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	$AgNTf_2$	1	H_2O	900	81/18	99
15	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	$AgNTf_2$	1	DMF	900	-	-
16	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	$AgNTf_2$	1	Tolene	900	-	-
17	$[Ru(p\text{-cymene})Cl_2]_2$	10	1	$AgNTf_2$	1	DCE	900	41/46	87
18	$[Ru(p\text{-cymene})Cl_2]_2$	10	2	$AgNTf_2$	1	H_2O	900	87/9	99
19	$[Ru(p\text{-cymene})Cl_2]_2$	10	3	$AgNTf_2$	1	H_2O	900	84/11	98
20	$[Ru(p\text{-cymene})Cl_2]_2$	10	2	$AgNTf_2$	1	H_2O	450	85/10	97
21	$[Ru(p\text{-cymene})Cl_2]_2$	10	2	$AgNTf_2$	1	H_2O	120	88/6	98

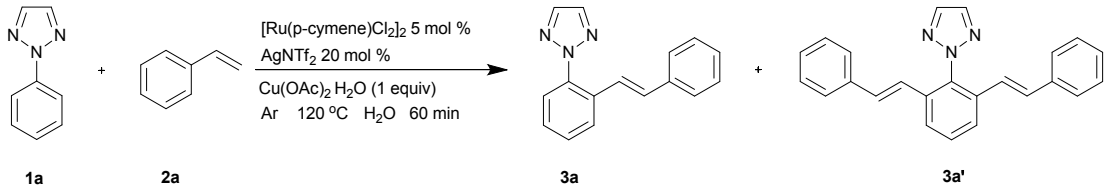
22	$[Ru(p\text{-cymene})Cl_2]_2$	10	2	$AgNTf_2$	1	H_2O	60	86/9	99
23	$[Ru(p\text{-cymene})Cl_2]_2$	10	2	$AgNTf_2$	1	H_2O	30	56/14	79
24	**$[Ru(p\text{-cymene})Cl_2]_2$**	**5**	**2**	**$AgNTf_2$**	**1**	**H_2O**	**60**	**85/8**	**98**
25	$[Ru(p\text{-cymene})Cl_2]_2$	1	2	$AgNTf_2$	1	H_2O	60	61/7	71
26	$[Cp^*RhCl_2]_2$	10	1	$AgNTf_2$	1	H_2O	30	16/75	97
27	$[Cp^*RhCl_2]_2$	10	2	$AgNTf_2$	1	H_2O	30	14/78	98
28	$[Cp^*RhCl_2]_2$	10	3	$AgNTf_2$	1	H_2O	30	13/84	98
29	$[Cp^*RhCl_2]_2$	10	4	$AgNTf_2$	1	H_2O	30	13/85	98
30	$[Cp^*RhCl_2]_2$	10	4	$AgNTf_2$	2	H_2O	30	7/91	98
31	$[Cp^*RhCl_2]_2$	10	4	$AgNTf_2$	3	H_2O	30	9/88	98
32	$[Cp^*RhCl_2]_2$	10	4	$AgNTf_2$	4	H_2O	30	7/91	98
33	$[Cp^*RhCl_2]_2$	10	4	$AgNTf_2$	4	H_2O	10	6/92	99
34	$[Cp^*RhCl_2]_2$	5	4	$AgNTf_2$	4	H_2O	10	9/81	98
35	$[Cp^*RhCl_2]_2$	1	4	$AgNTf_2$	4	H_2O	10	36/57	98
36	$[Cp^*RhCl_2]_2$	1	4	$AgNTf_2$	4	H_2O	20	19/77	99
37	**$[Cp^*RhCl_2]_2$**	1	**4**	**$AgNTf_2$**	**4**	**H_2O**	30	**4/93**	**99**

[a] the reaction conditions of mono-olefination: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), $AgNTf_2$ (0.04 mmol),$Cu(OAc)_2 \cdot H_2O$ (0.2 mmol) in H_2O (0.5 ml) were stirred at 120 °C for 60 min; The reaction conditions of diolefination: **1a** (0.2 mmol), **2a** (0.8 mmol), $[Cp^*RhCl_2]_2$ (1 mol %), $AgNTf_2$ (0.04 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.8 mmol) in H_2O (0.5 ml) were stirred at 120 °C for 30 min. [b] Yield of product isolated after column chromatography. [c] Conversion based on the yield of the recovered **1a**.

General Information

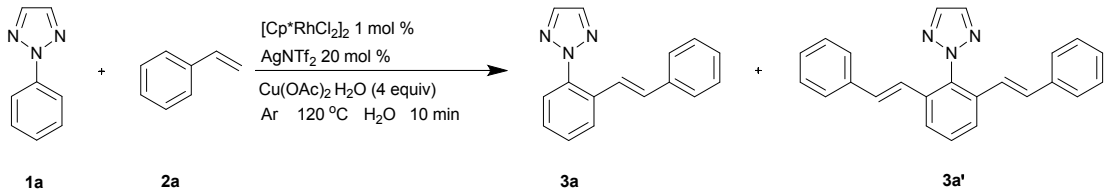
The reactions were carried out in Schlenk tubes under an argon atmosphere. The 2-aryl-1,2,3-triazoles were synthesized according to previously described methods. Other materials were purchased from commercial suppliers and used without further purification. All the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light. The product purification was done using silica gel column chromatography. ^1H and ^{19}F and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS, $\delta = 0.00$ ppm) as the internal standard. ^1H NMR spectra was recorded at 600 MHz (Varian), ^{19}F NMR was recorded at 376 MHz (Varian) and ^{13}C NMR spectra was recorded at 150 MHz (Varian). Melting points were measured with YRT-3 melting point apparatus (Shantou Keyi Instrument & Equipment Co., Ltd., Shantou, China). High resolution mass spectroscopy data was collected on a Waters Micromass GCT or a Bruker Apex IV FTMS instrument.

General Procedure for the Synthesis of 3a



A 15ml sealed tube was charged with 2-phenyl-2*H*-1,2,3-triazole **1a** (14.5 mg, 0.1 mmol), styrene **2a** (20.8mg, 0.2 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (3mg, 0.005 mmol), $AgNTf_2$ (7.7mg, 0.02mol), $Cu(OAc)_2{\cdot}H_2O$ (21.8mg, 0.1 mmol), and H_2O 0.5ml. The mixture was stirred at 120 °C for 60 min and monitored by TLC. Then cooled down to ambient temperature. The mixture was extracted with diethyl ether (3 × 5 mL) and then the combined organic extracts were washed with brine (2 × 10 mL), dried with sodium sulfate. The solvent was evaporated in vacuo and the residue was further purified by flash chromatography of silica gel (silica gel, acetone / petroleum ether = 1:200), affording the product **3a**.

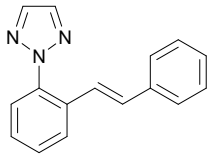
General Procedure for the Synthesis of 3a'



A 15ml sealed tube was charged with 2-phenyl-2*H*-1,2,3-triazole **1a** (14.5 mg, 0.1 mmol), styrene **2a** (41.6mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (0.6mg, 0.001 mmol), $AgNTf_2$ (7.8mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (87.2mg, 0.4 mmol), and H_2O 0.5ml. The mixture was stirred at 120 °C for 10 min and monitored by TLC. Then cooled down to ambient temperature. The mixture was extracted with diethyl ether (3×5 mL) and then the combined organic extracts were washed with brine (2×10 mL), dried with sodium sulfate.The solvent was evaporated in vacuo and the residue was further purified by flash chromatography of silica gel (silica gel, acetone / petroleum ether = 1:150), affording the product **3aa**.

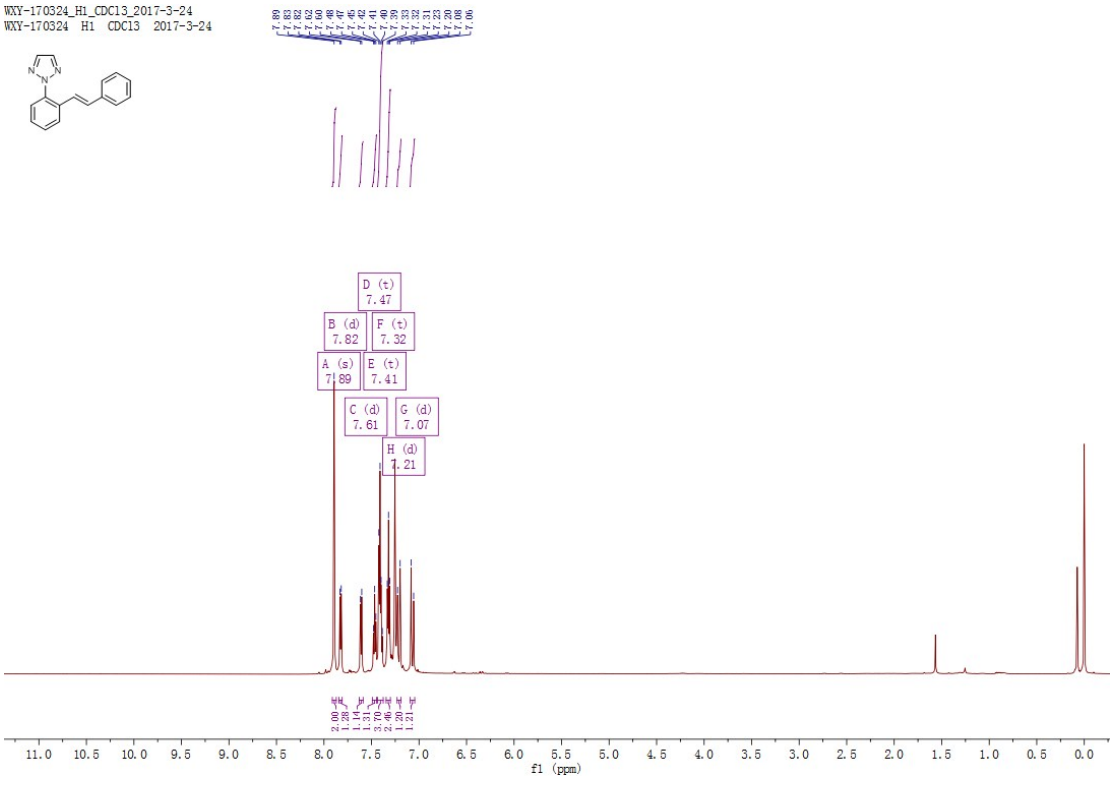
Characterization Data and NMR Spectra of Products 3a-4g

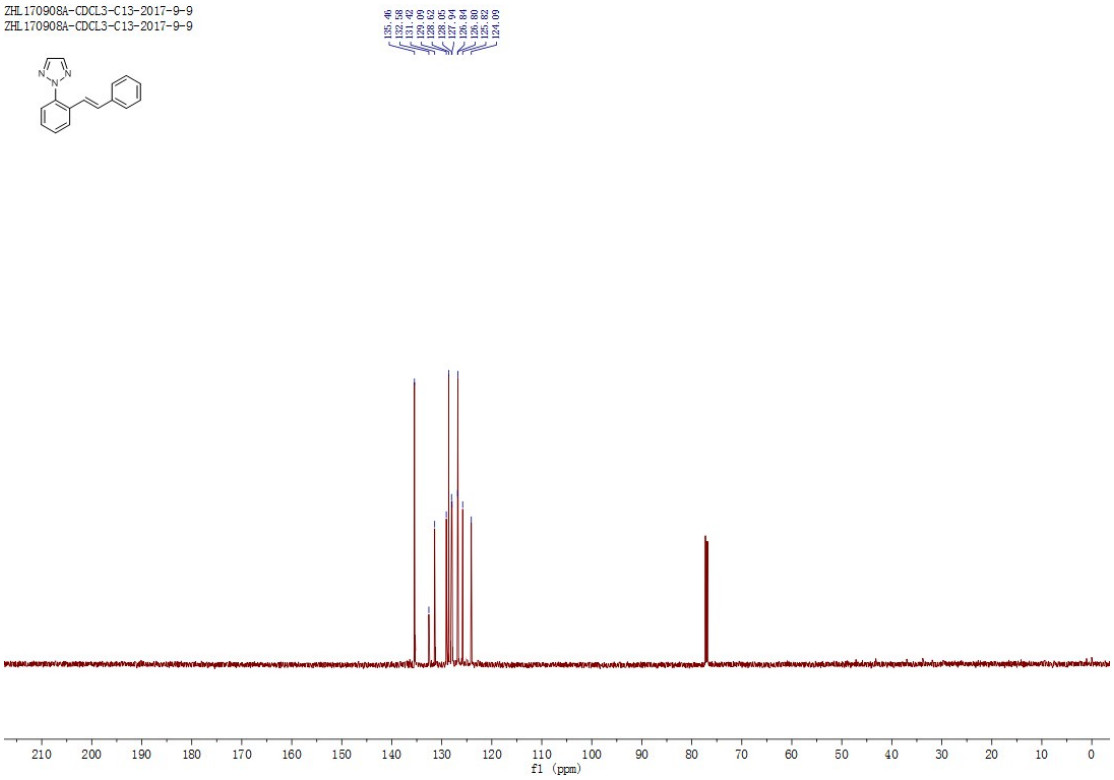
(*E*)-2-(2-styrylphenyl)-2*H*-1,2,3-triazole



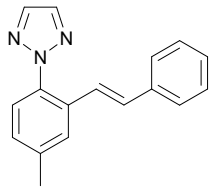
3a

White solid, yield 81 %, mp 158-160 ^{o}C, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.89 (s, 2H), 7.82 (d, *J*=8.4Hz, 1H), 7.61 (d, *J*=8.4Hz, 1H), 7.47 (t, *J*=8.4Hz, 1H), 7.41 (t, *J*=8.4Hz, 3H), 7.32 (t, *J*=8.4Hz, 2H), 7.25 (d, *J*=8.4Hz, 1H), 7.21 (d, *J*=16.2Hz, 1H), 7.07 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 135.5, 131.4, 129.1, 128.6, 128.1, 128.0, 127.9, 126.8, 126.8, 125.8, 124.1; HRMS (ESI) Calcd. For $C_{16}H_{13}N_3Na$:270.1007, Found: m/z 270.1005.



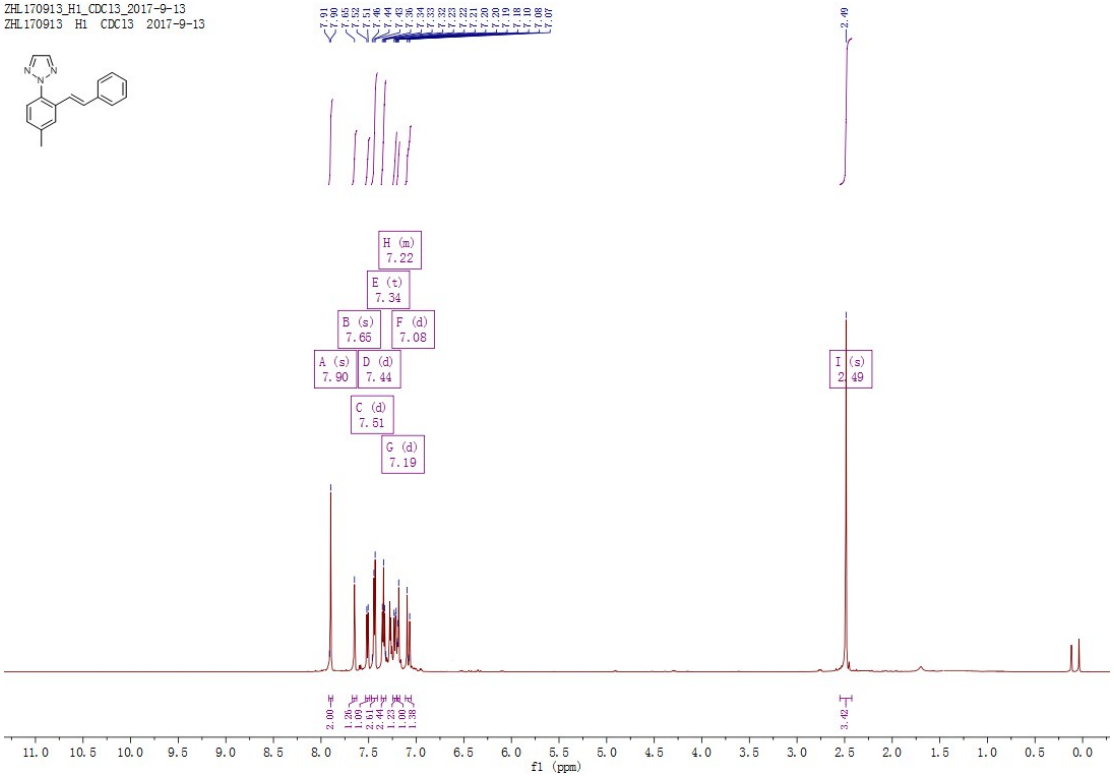


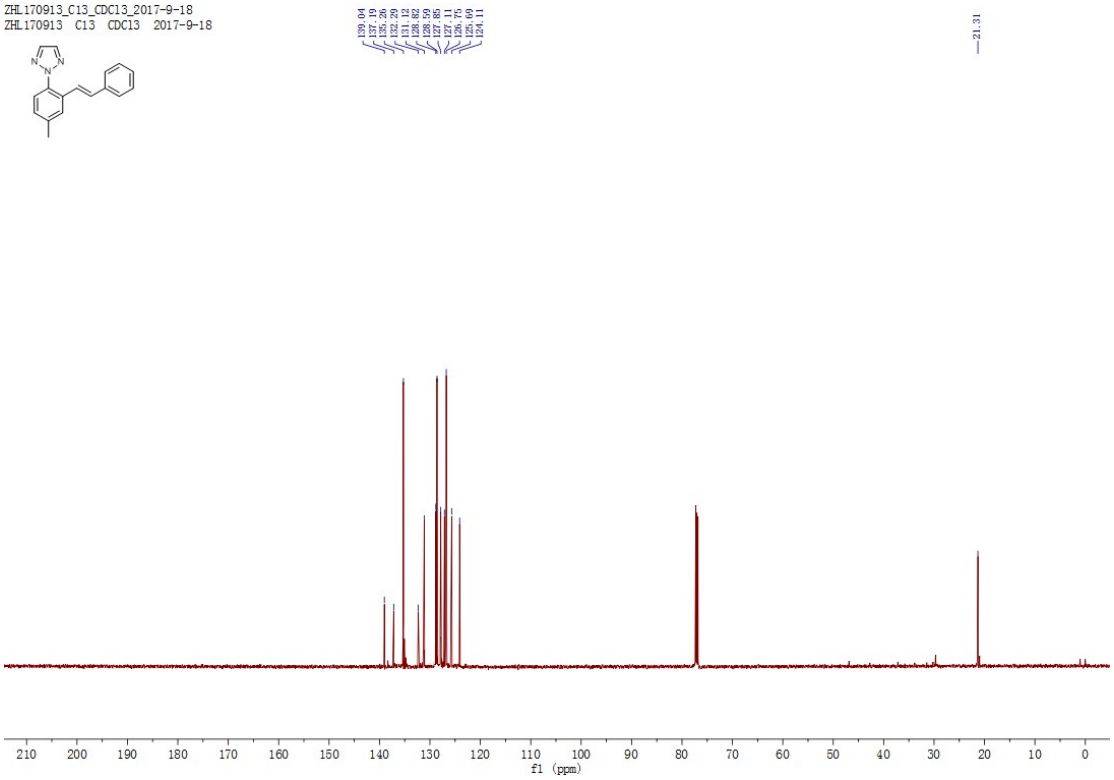
(*E*)-2-(4-methyl-2-styrylphenyl)-2*H*-1,2,3-triazole



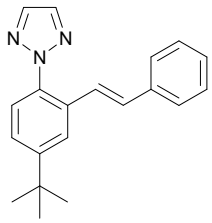
3b

Light yellow liquid, yield 86 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.90 (s, 2H), 7.45 (s, 1H), 7.51 (d, *J*=8.4Hz, 1H), 7.44 (d, *J*=8.4Hz, 2H), 7.34 (t, *J*=8.4Hz, 3H), 7.27 (d, *J*=8.4Hz, 1H), 7.23-7.18 (m, 1H), 7.08 (d, *J*=16.2Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (150MHz, $CDCl_3$): δ 139.1, 135.4, 132.3, 131.2, 128.9, 128.5, 127.9, 127.1, 126.7, 125.6, 124.1, 21.3; HRMS (ESI) Calcd. For $C_{17}H_{15}N_3Na$:284.1164, Found: m/z 284.1163.



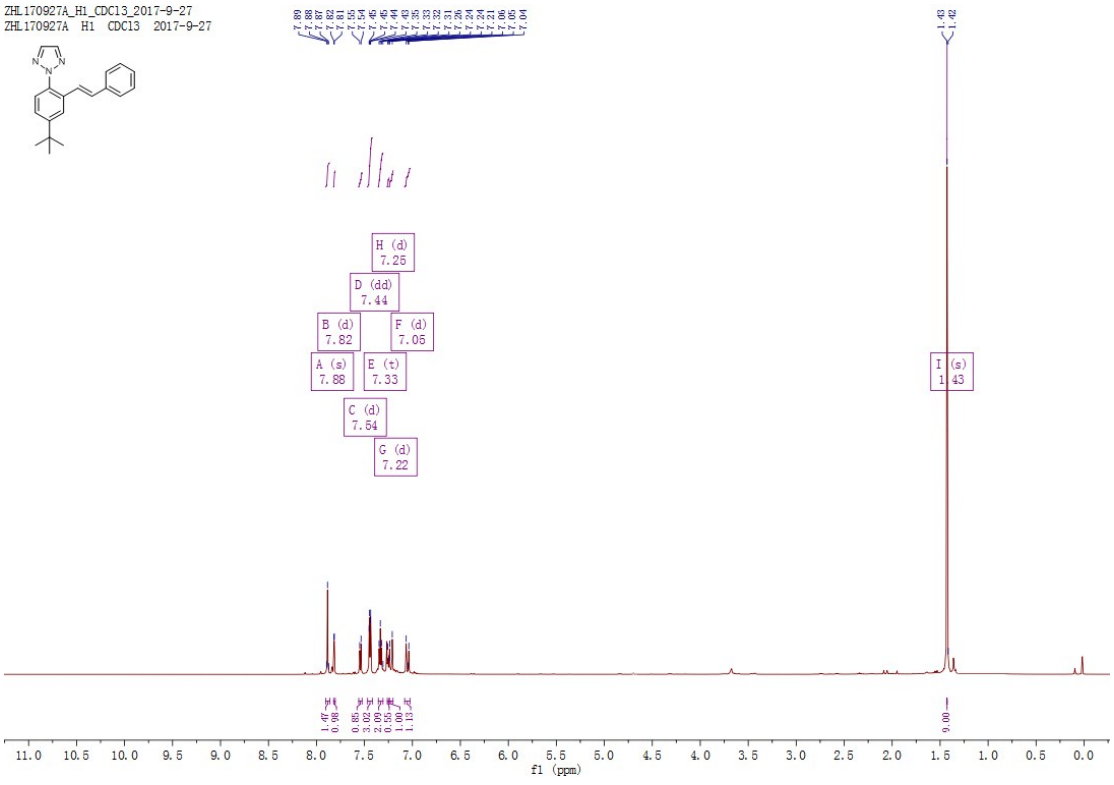


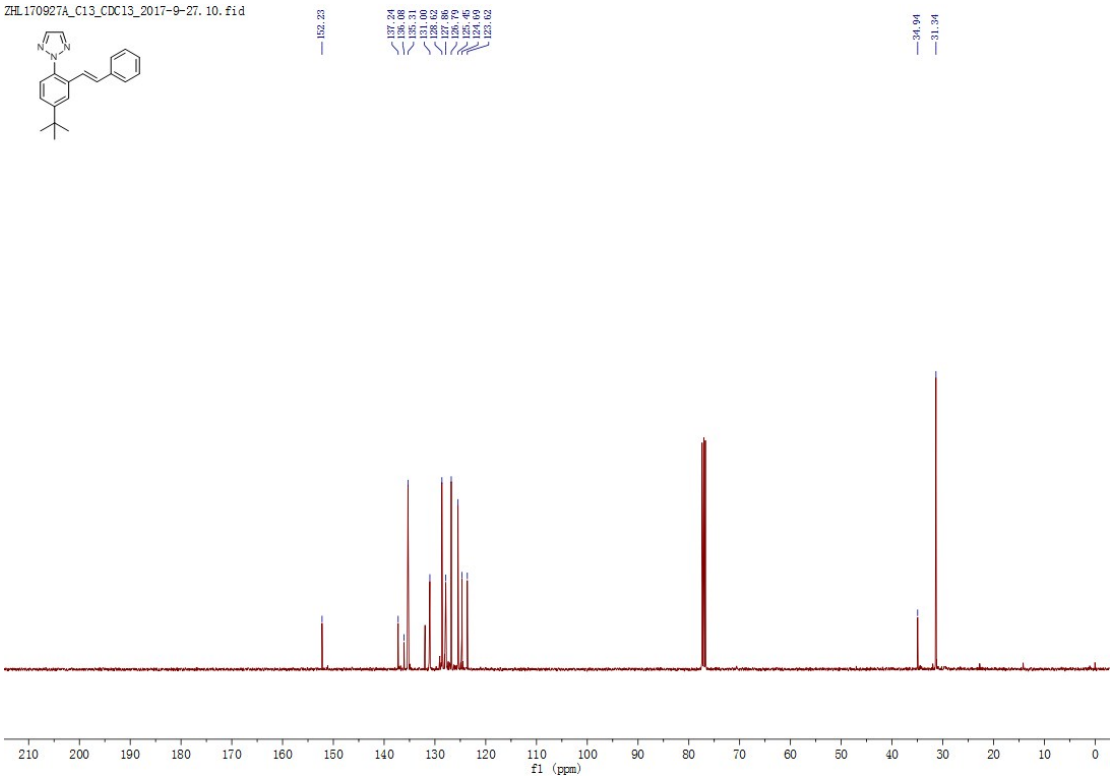
(*E*)-2-(4-(tert-butyl)-2-styrylphenyl)-2*H*-1,2,3-triazole



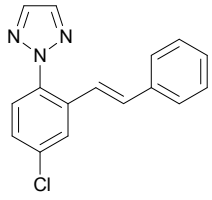
3c

Yellow oil, yield 86 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.89 (s, 2H), 7.82 (s, 1H), 7.54 (d, *J*=8.4Hz, 1H), 7.44 (d, *J*=8.4Hz, 3H), 7.33 (t, *J*=8.4Hz, 3H), 7.22 (d, *J*=16.2Hz, 1H), 7.05 (d, *J*=16.2Hz, 1H), 1.44 (s, 9H); ^{13}C NMR (150MHz, $CDCl_3$): δ 152.3, 137.4, 135.3, 131.9, 131.1, 128.5, 127.8, 126.8, 125.6, 124.8, 123.8, 34.9, 31.3; HRMS (ESI) Calcd. For $C_{20}H_{21}N_3Na$:326.1633, Found: m/z 326.1631.



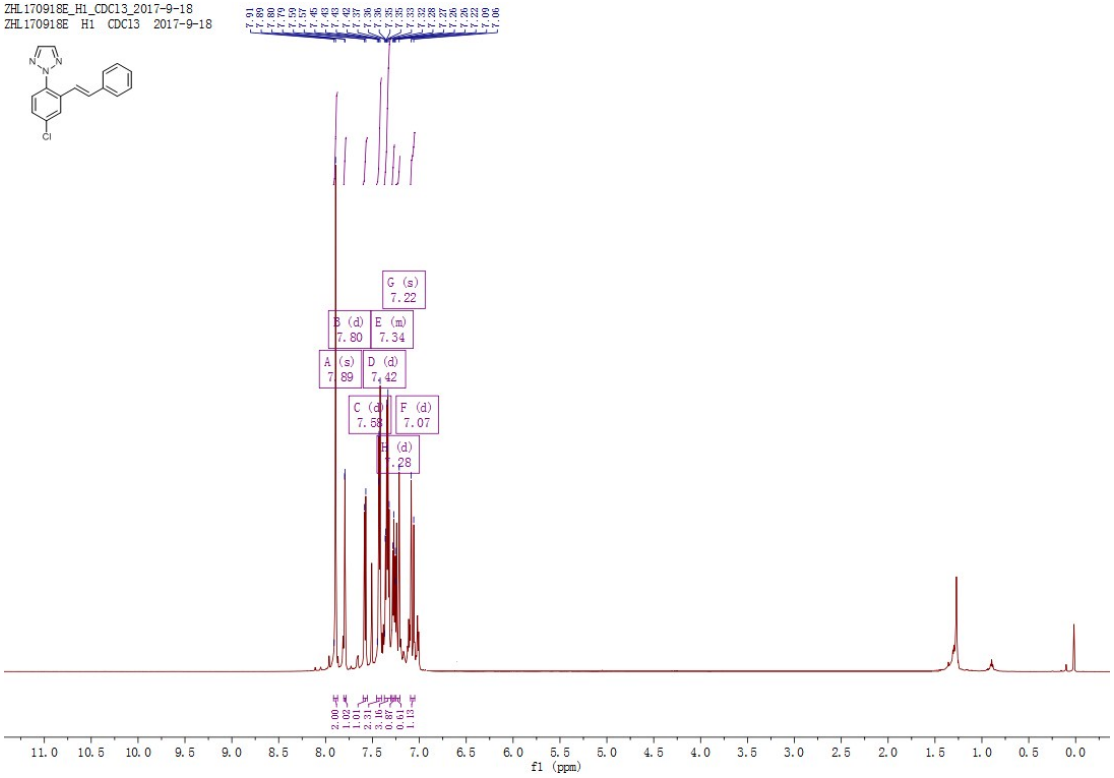


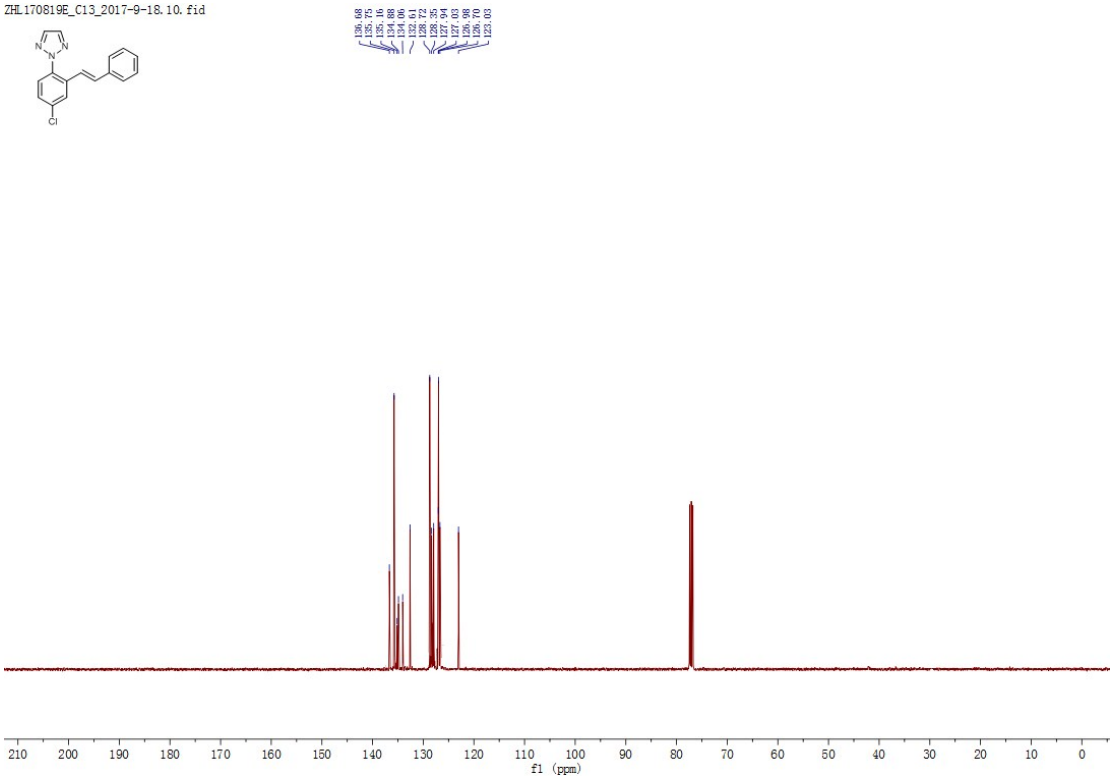
(*E*)-2-(4-chloro-2-styrylphenyl)-2*H*-1,2,3-triazole



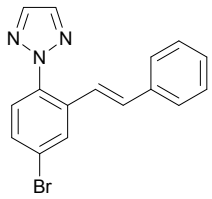
3d

White solid, yield 83 %, mp 52-54 ^{o}C, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.89 (s, 2H), 7.80 (s, 1H), 7.58 (d, *J*=8.4Hz, 1H), 7.42 (d, *J*=8.4Hz, 2H), 7.34 (m, 3H), 7.27 (t, *J*=8.4Hz, 1H), 7.23 (d, *J*=16.2Hz, 1H), 7.07 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 136.7, 135.7, 132.7, 128.7, 128.3, 127.9, 127.1, 127.0, 126.7, 123.0; HRMS (ESI) Calcd. For $C_{16}H_{12}N_3ClNa$:304.0167, Found: m/z 304.0167.



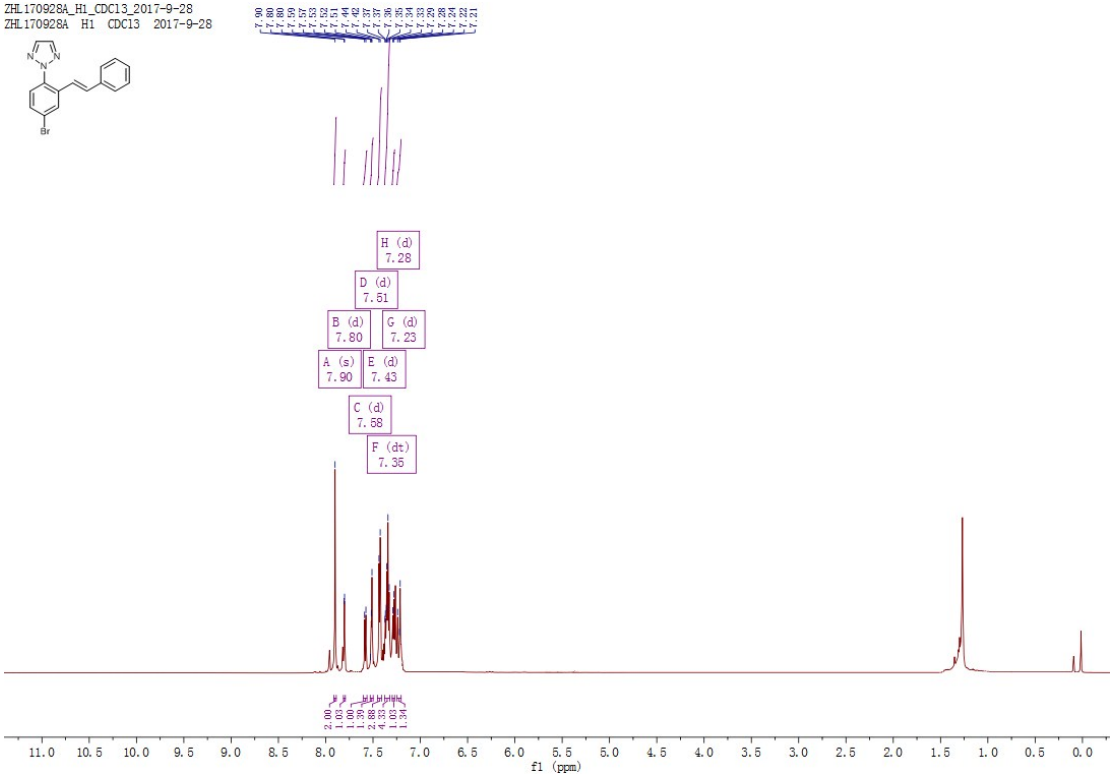


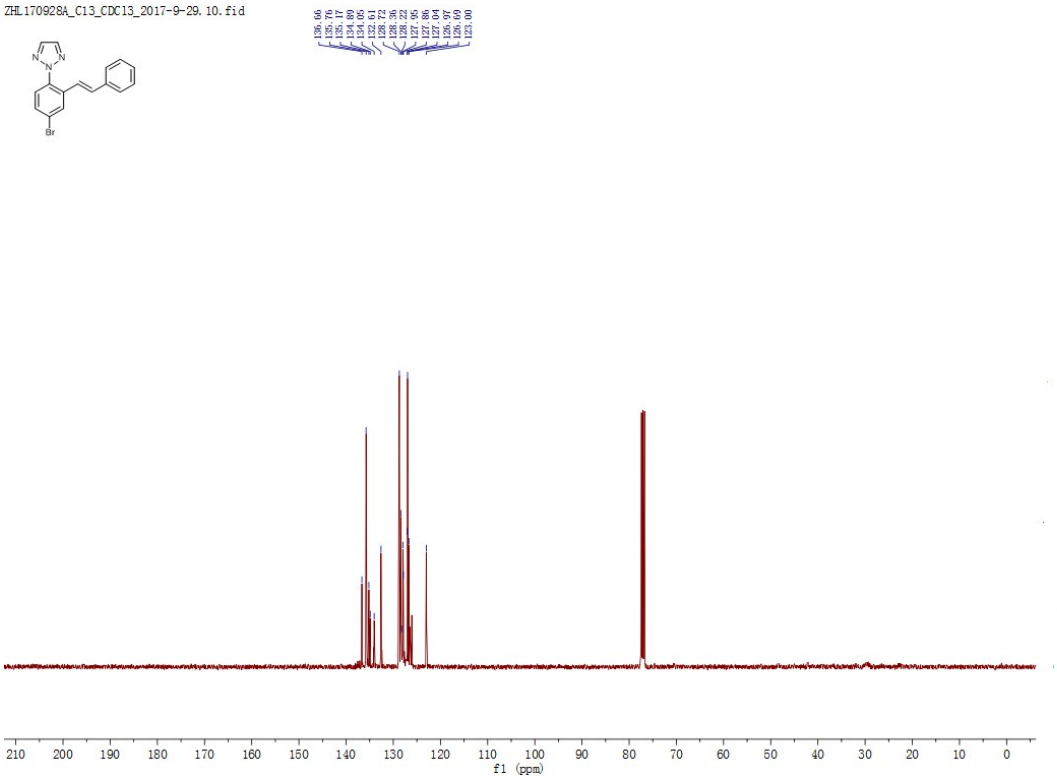
(*E*)-2-(4-bromo-2-styrylphenyl)-2*H*-1,2,3-triazole



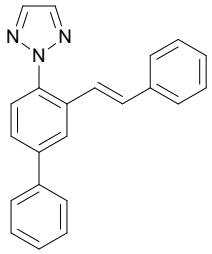
3e

Light yellow liquid, yield 81 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.90 (s, 2H), 7.80 (s, 1H), 7.58 (d, *J*=8.4Hz, 1H), 7.51 (d, *J*=8.4Hz, 3H), 7.43 (d, *J*=8.4Hz, 2H), 7.34 (t, *J*=8.4Hz, 3H), 7.28 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, $CDCl_3$): δ 136.7, 135.8, 132.7, 128.7, 128.4, 127.0, 127.0, 126.7, 123.0; HRMS (ESI) Calcd. For $C_{16}H_{12}N_3BrNa$:348.0112, Found: m/z 348.0111.



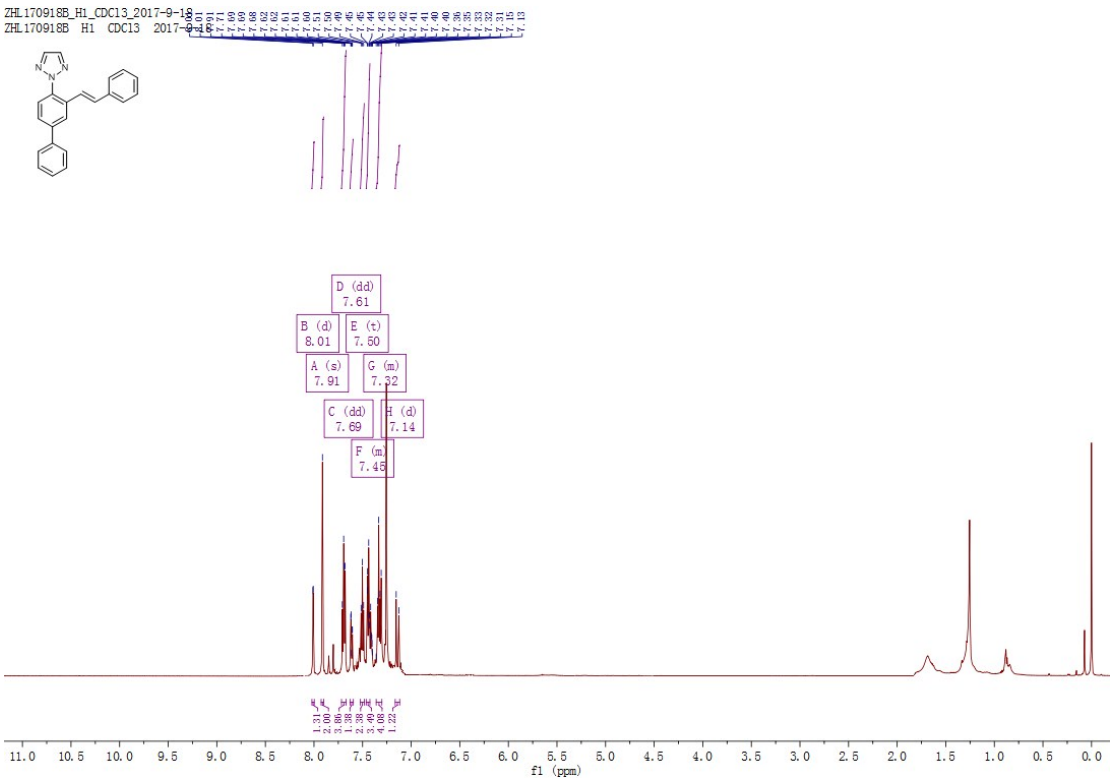


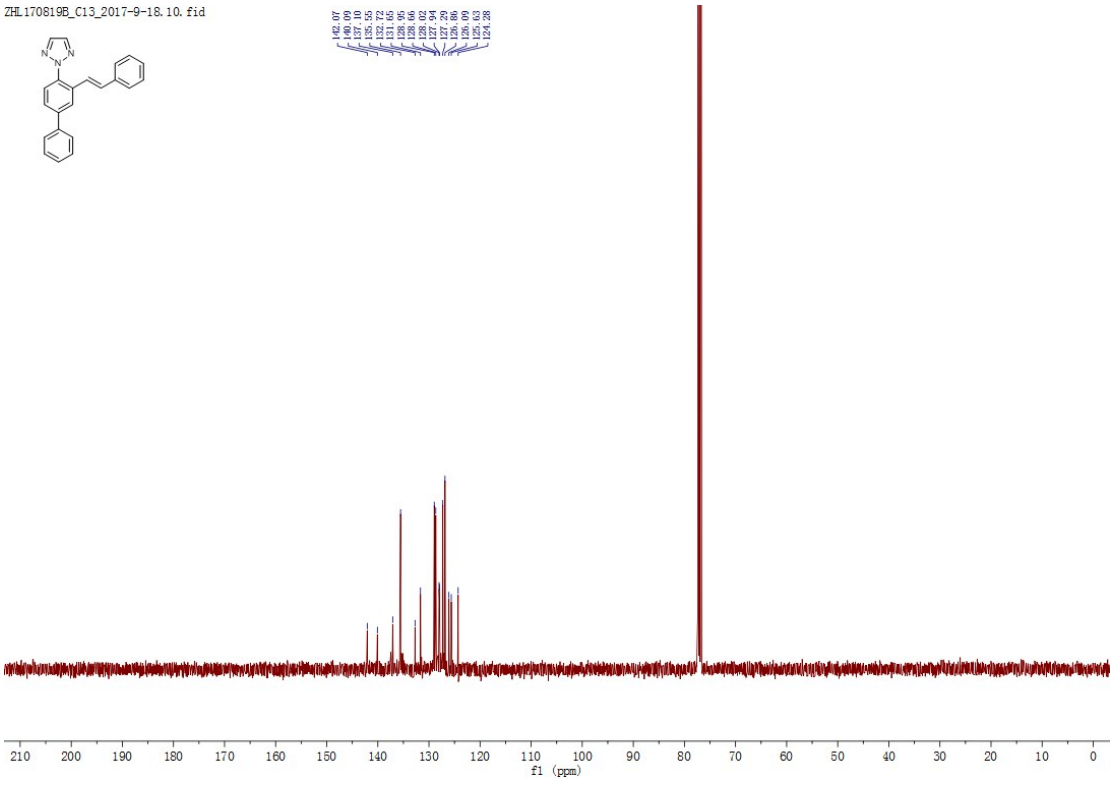
(E) -2-(3-styryl-[1,1'-biphenyl]-4-yl)-2*H*-1,2,3-triazole



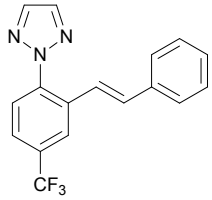
3f

Yellow liquid, yield 75 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.91 (s, 2H), 7.69 (d, *J*=8.4Hz, 2H), 7.61 (d, *J*=8.4Hz, 1H), 7.50 (t, *J*=8.4Hz, 2H), 7.43 (m, 4H), 7.32 (m, 4H), 7.14 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 142.1, 137.1, 135.6, 132.7, 131.6, 129.0, 128.7, 128.0, 127.9, 127.3, 126.9, 126.1, 125.7, 124.3; HRMS (ESI) Calcd. For $C_{22}H_{13}N_3Na$:346.1320, Found: m/z 346.1317.



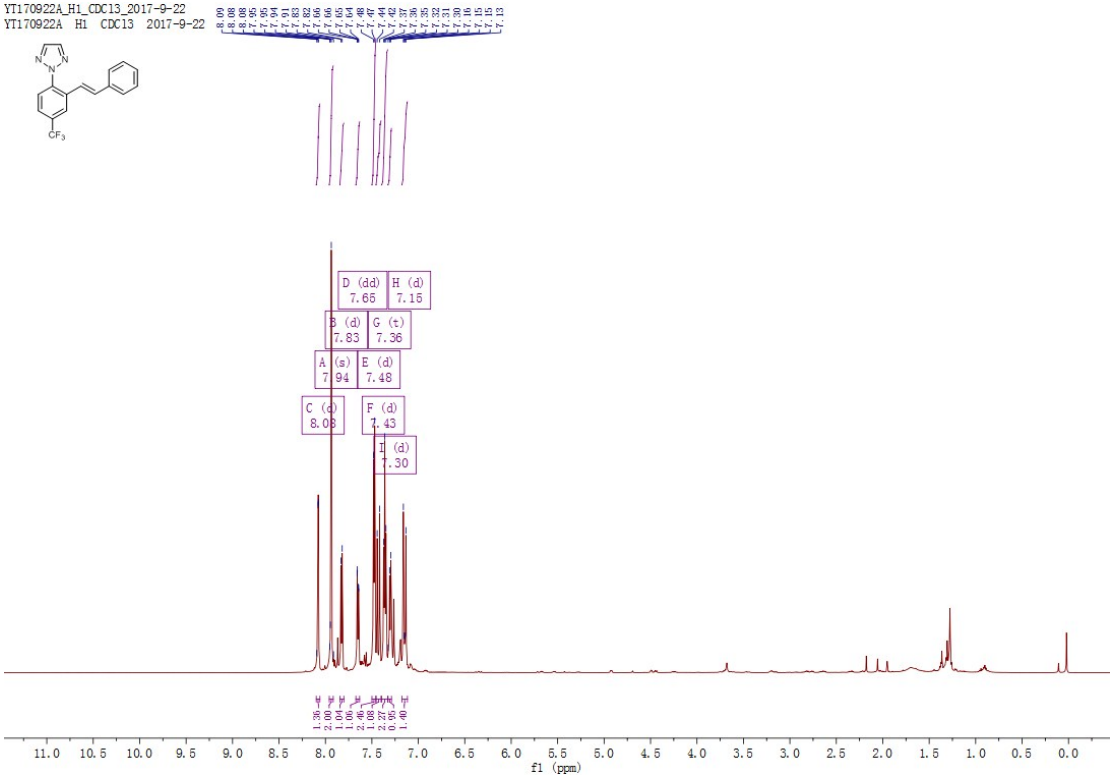


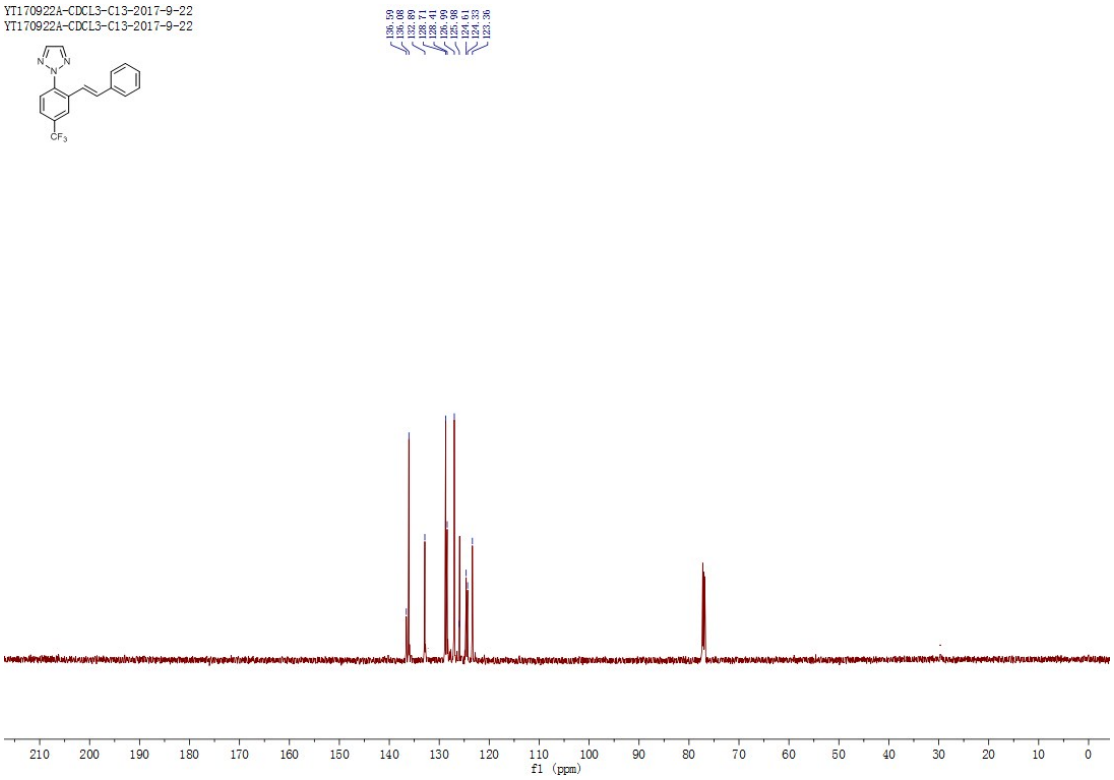
(*E*)-2-(2-styryl-4-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole

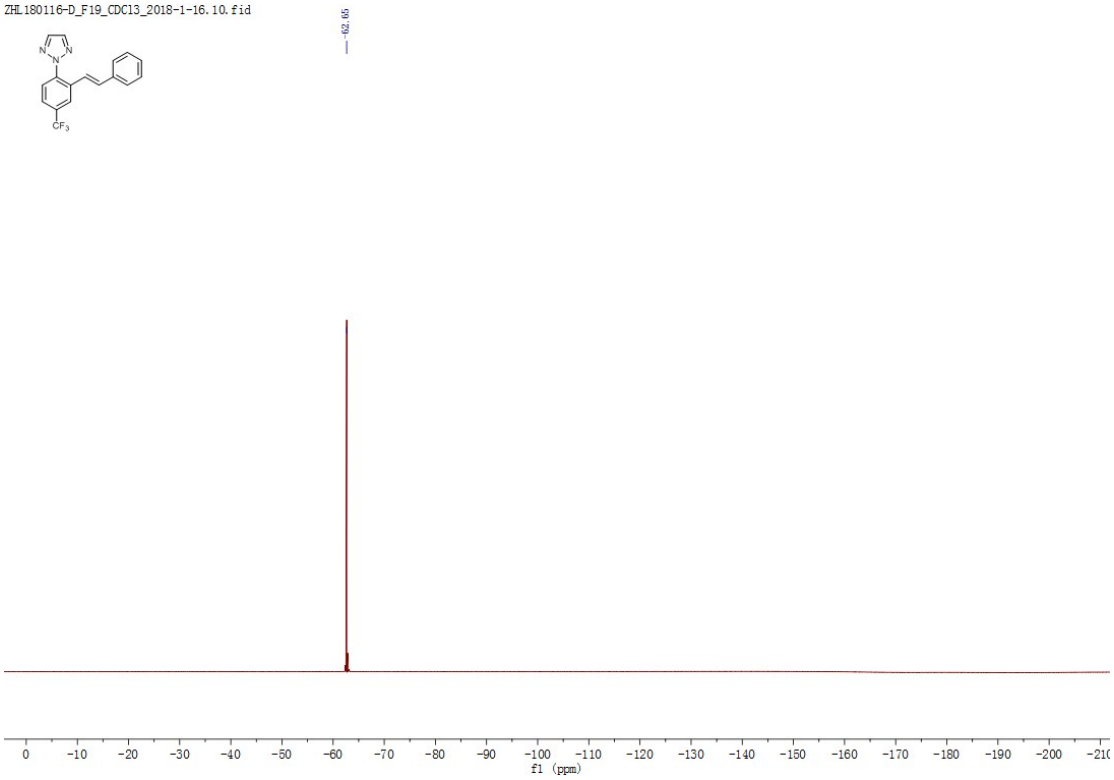


3g

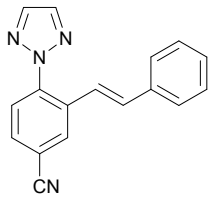
White solid, yield 78 %, mp 110-112 °C, ^{1}HNMR (600MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.94 (s, 2H), 7.83 (d, *J*=8.4Hz, 1H), 7.65 (d, *J*=8.4Hz, 2H), 7.47 (m, *J*=8.4Hz, 2H), 7.43 (d, *J*=16.2Hz, 1H), 7.36 (d, *J*=16.2Hz, 2H), 7.30 (d, *J*=8.4Hz, 1H), 7.15(d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 136.6, 136.3, 133.0, 128.9, 128.5, 127.1, 126.0, 124.6, 124.4, 123.4; ^{19}F NMR (376MHz, DMSO): -62.65; HRMS (ESI) Calcd. For $C_{17}H_{12}F_3N_3Na$:338.0881, Found: m/z 338.0880.





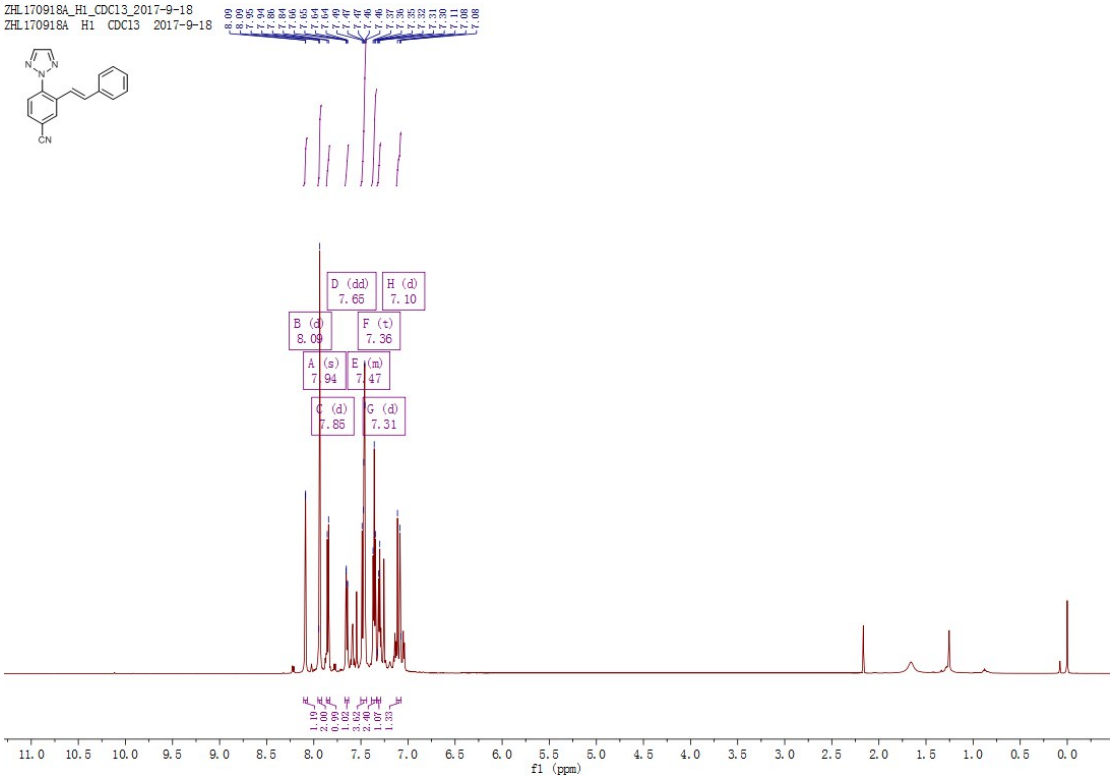


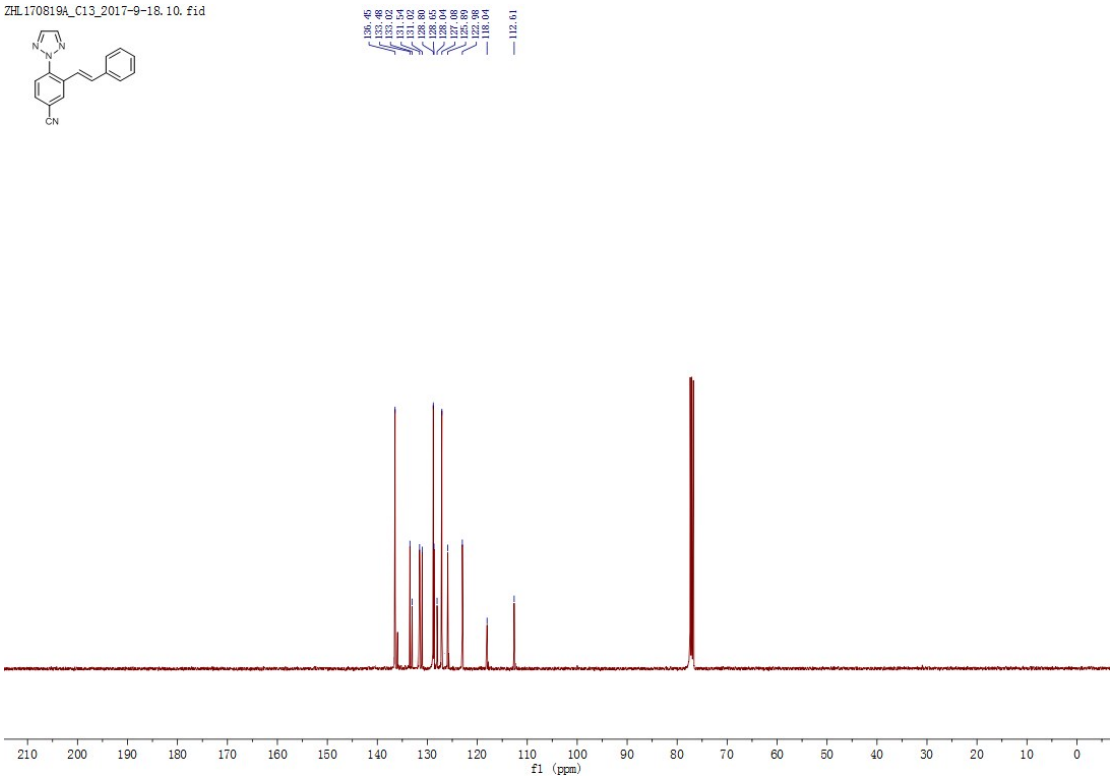
(*E*)-3-styryl-4-(2*H*-1,2,3-triazol-2-yl)benzonitrile



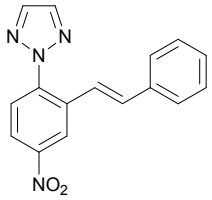
3h

Light white solid, yield 81 %, mp 126-128 °C, ^{1}HNMR (600MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.94 (s, 2H), 7.85 (d, *J*=8.4Hz, 1H), 7.65 (d, *J*=8.4Hz, 2H), 7.46 (d, *J*=8.4Hz, 2H), 7.36 (t, *J*=16.2Hz, 2H), 7.30 (d, *J*=8.4Hz, 2H), 7.09 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 136.6, 136.3, 133.0, 128.9, 128.5, 127.1, 126.0, 124.6, 124.4, 123.4; HRMS (ESI) Calcd. For $C_{17}H_{12}N_4Na$:295.0960, Found: m/z 295.0961.



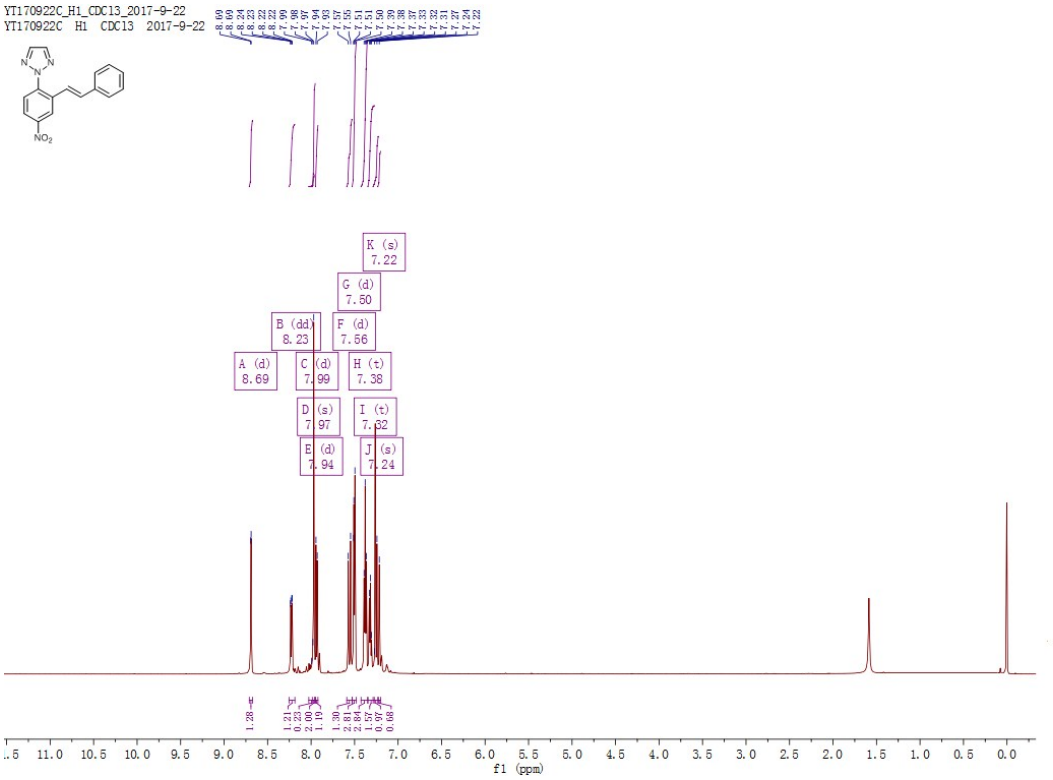


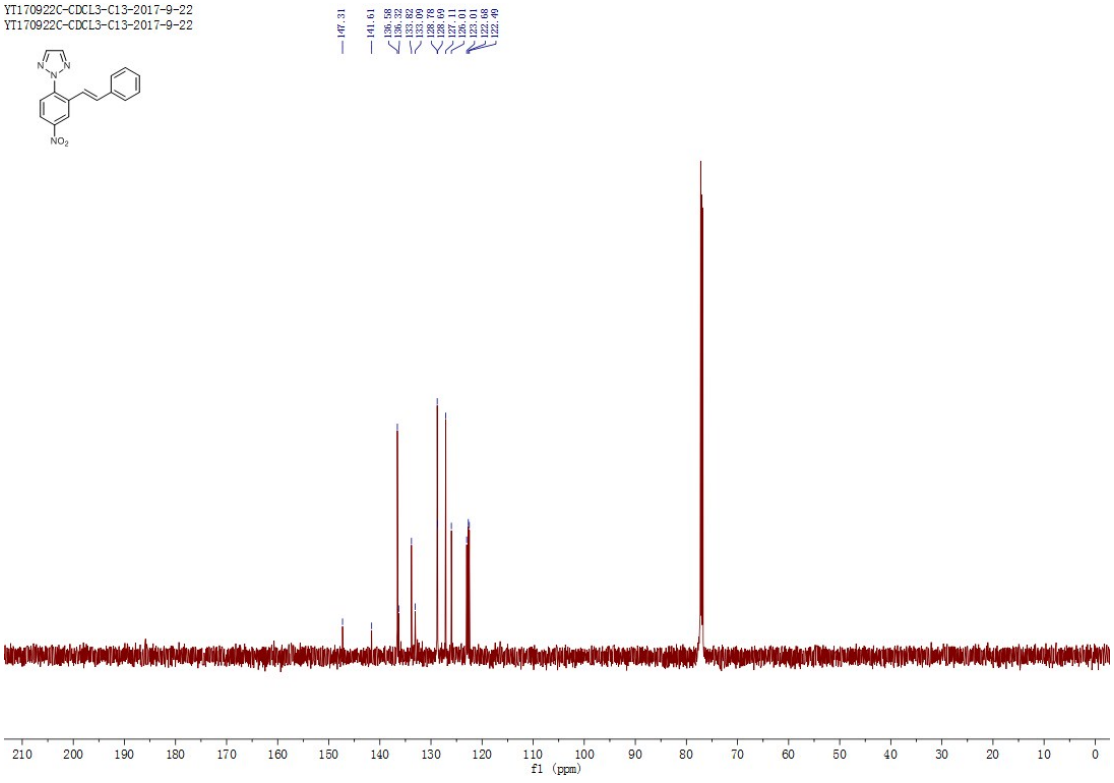
(*E*)-2-(4-nitro-2-styrylphenyl)-2*H*-1,2,3-triazole



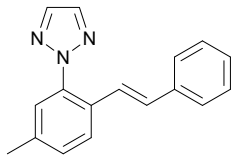
3i

Yellow solid, yield 83 %, mp 168-170 ^{o}C, ^{1}HNMR (600MHz, $CDCl_3$): δ 8.69 (d, *J*=8.4Hz, 1H), 8.23 (d, *J*=8.4Hz, 1H), 7.97 (s, 2H), 7.94 (d, *J*=8.4Hz, 1H), 7.56 (d, *J*=16.2Hz, 1H), 7.50 (d, *J*=8.4Hz, 2H), 7.38 (d, *J*=8.4Hz, 2H), 7.32 (d, *J*=8.4Hz, 1H), 7.23 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 136.6, 133.8, 128.8, 128.7, 127.1, 126.0, 123.0, 122.7, 122.5; HRMS (ESI) Calcd. For $C_{16}H_{12}N_4O_2Na$:315.0858, Found: m/z 315.0857.



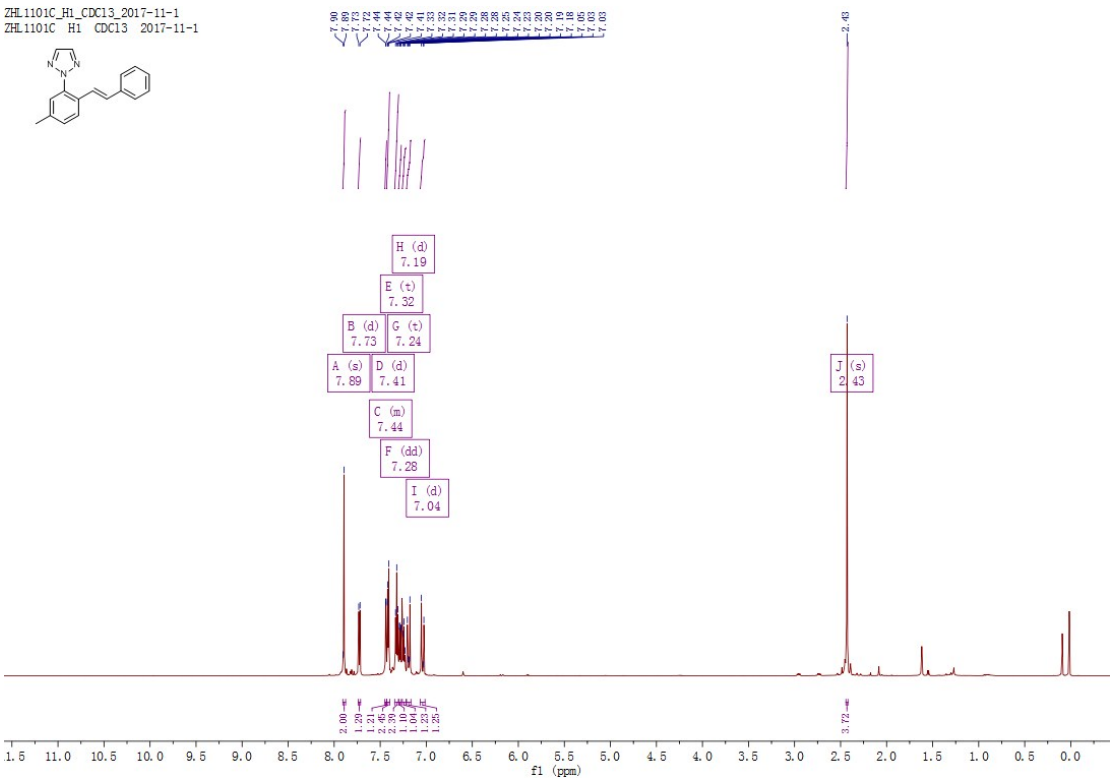


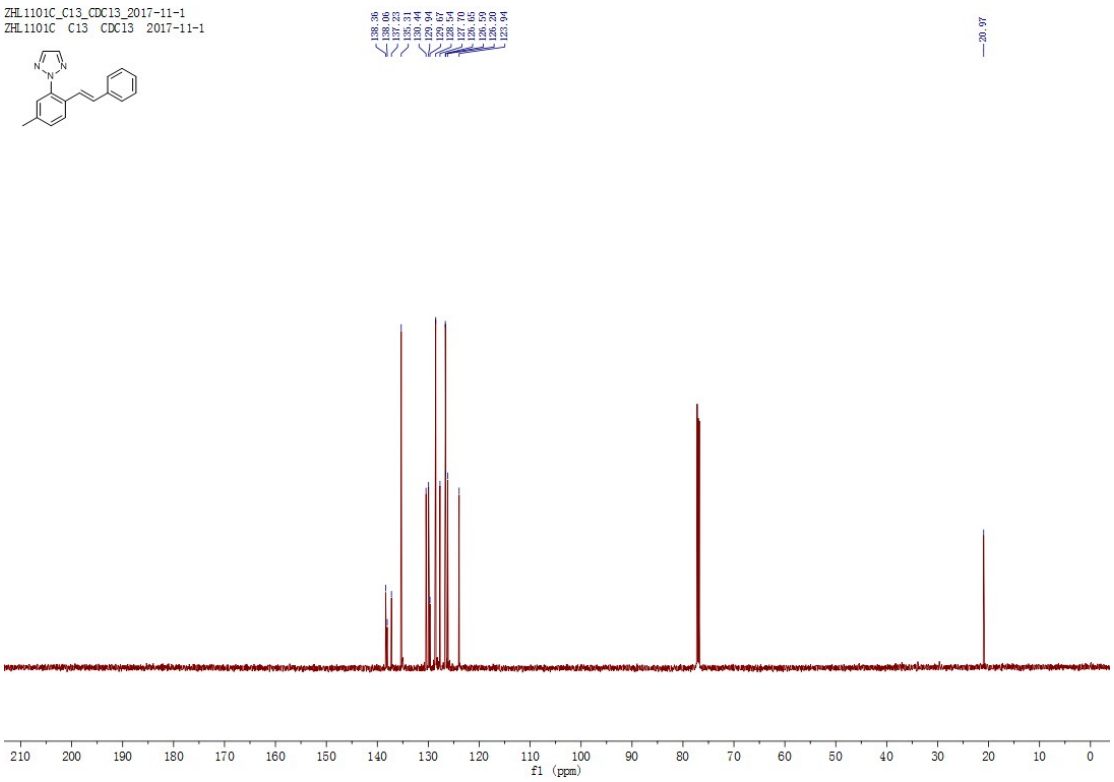
(*E*)-2-(5-methyl-2-styrylphenyl)-2*H*-1,2,3-triazole



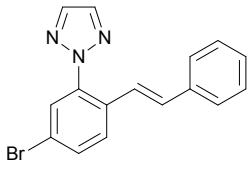
3j

White solid, yield 84 %, mp 58-60 °C, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.89 (s, 2H), 7.73 (d, *J*=8.4Hz, 1H), 7.44 (s, 1H), 7.41 (d, *J*=8.4Hz, 2H), 7.32 (t, *J*=8.4Hz, 2H), 7.29 (d, *J*=8.4Hz, 1H), 7.25 (d, *J*=8.4Hz, 1H), 7.19 (d, *J*=16.2Hz, 1H), 7.04 (d, *J*=16.2Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (150MHz, $CDCl_3$): δ 138.4, 138.1, 137.2, 135.3, 130.5, 130.0, 129.7, 128.5, 127.7, 126.7, 126.6, 126.2, 123.9, 21.0; HRMS (ESI) Calcd. For $C_{17}H_{15}N_3Na$: 284.1164, Found: m/z 284.1163.



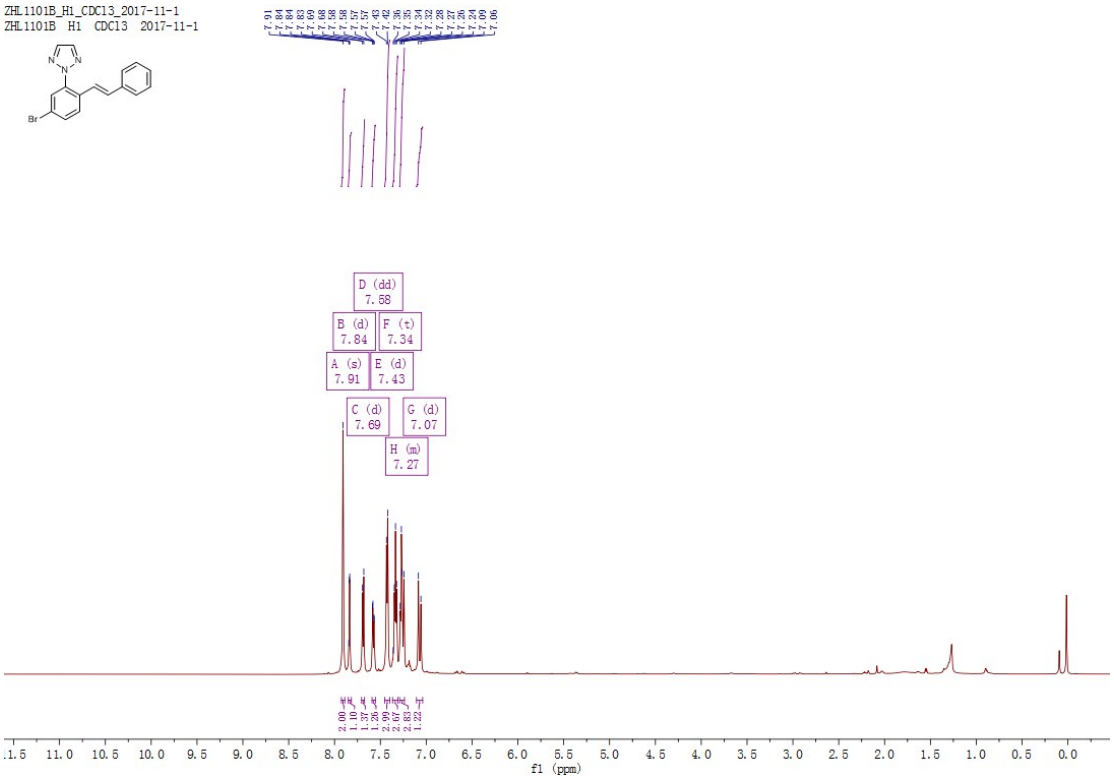


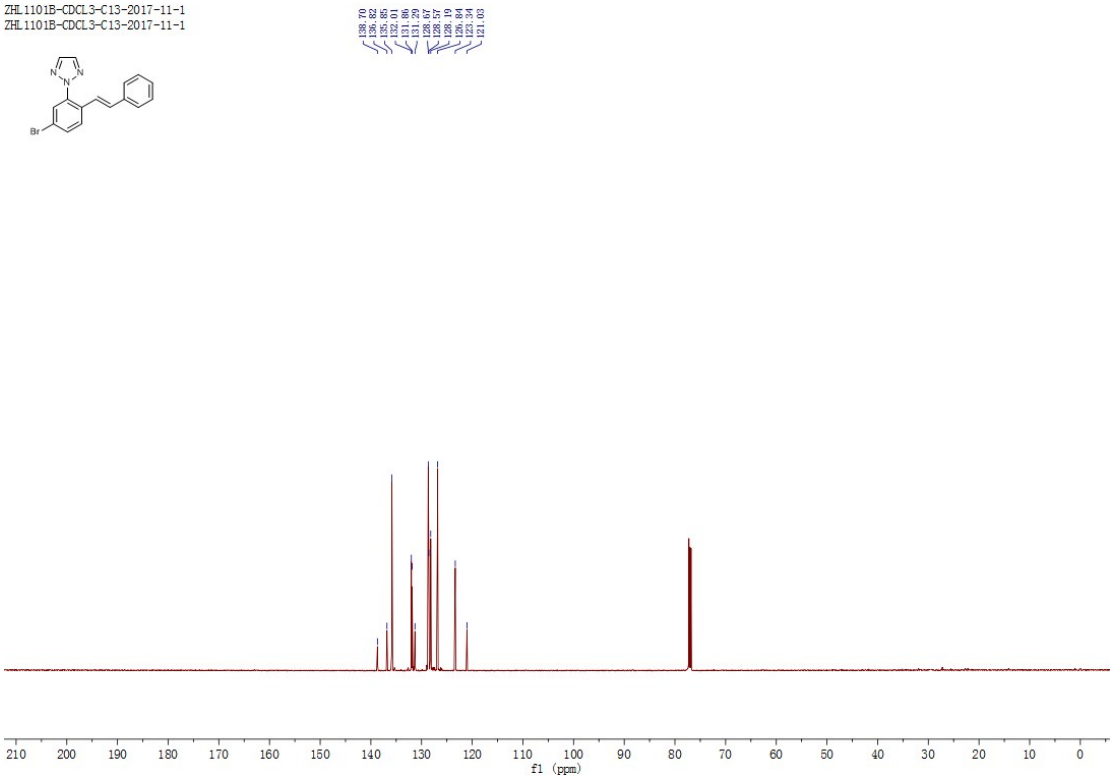
(*E*)-2-(5-bromo-2-styrylphenyl)-2*H*-1,2,3-triazole



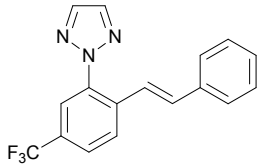
3k

Light yellow solid, yield 79 %, mp 76-78 ^{o}C, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.91 (s, 2H), 7.84 (s, 1H), 7.69 (d, *J*=8.4Hz, 1H), 7.58 (d, *J*=8.4Hz, 1H), 7.43 (d, *J*=8.4Hz, 2H), 7.34 (t, *J*=8.4Hz, 2H), 7.27 (m, 1H), 7.07 (d, *J*=16.2Hz, 1H), 7.04 (d, *J*=16.2Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (150MHz, $CDCl_3$): δ 138.7, 136.8, 135.8, 132.0, 131.9, 131.3, 128.7, 128.6, 128.2, 126.8, 123.4, 121.1; HRMS (ESI) Calcd. For $C_{16}H_{12}BrN_3Na$: 348.0112, Found: m/z 348.0111.



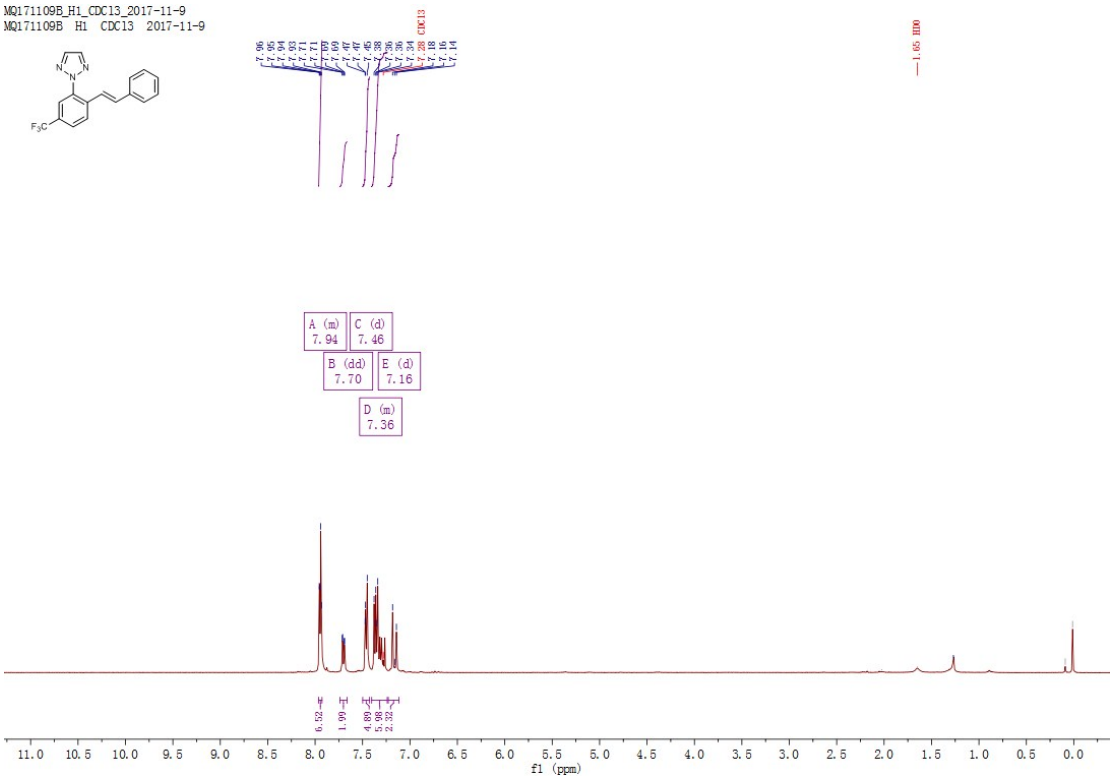


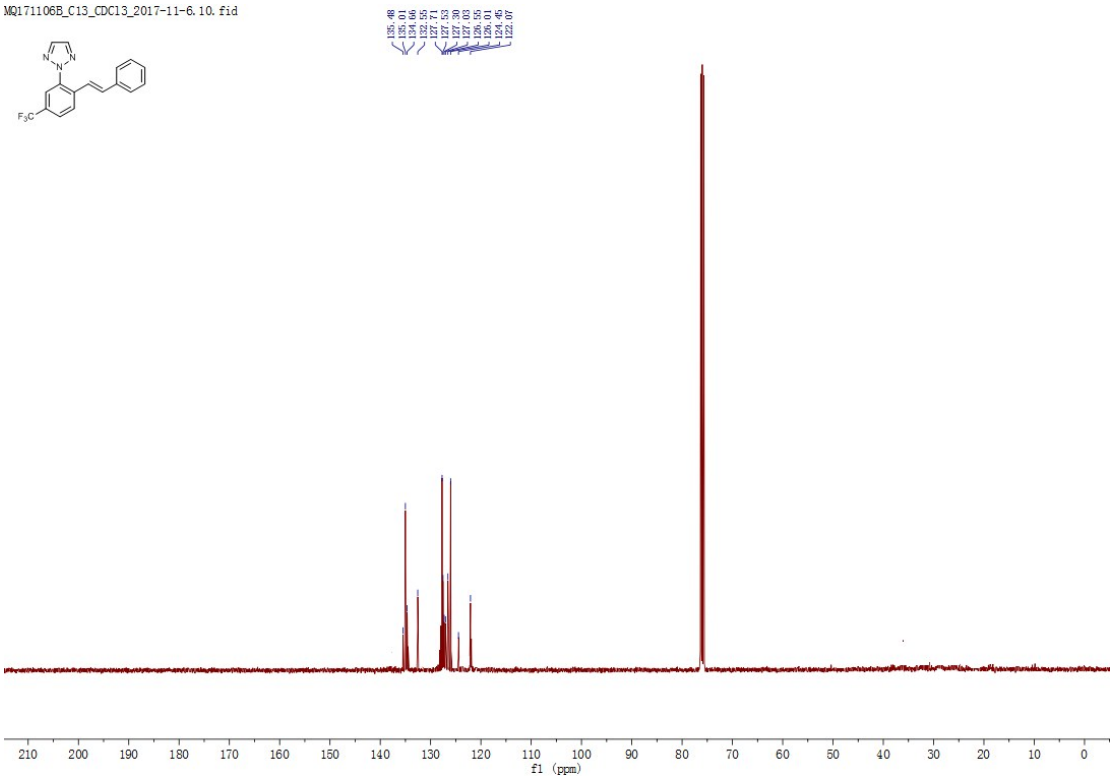
(*E*)-2-(2-styryl-5-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole

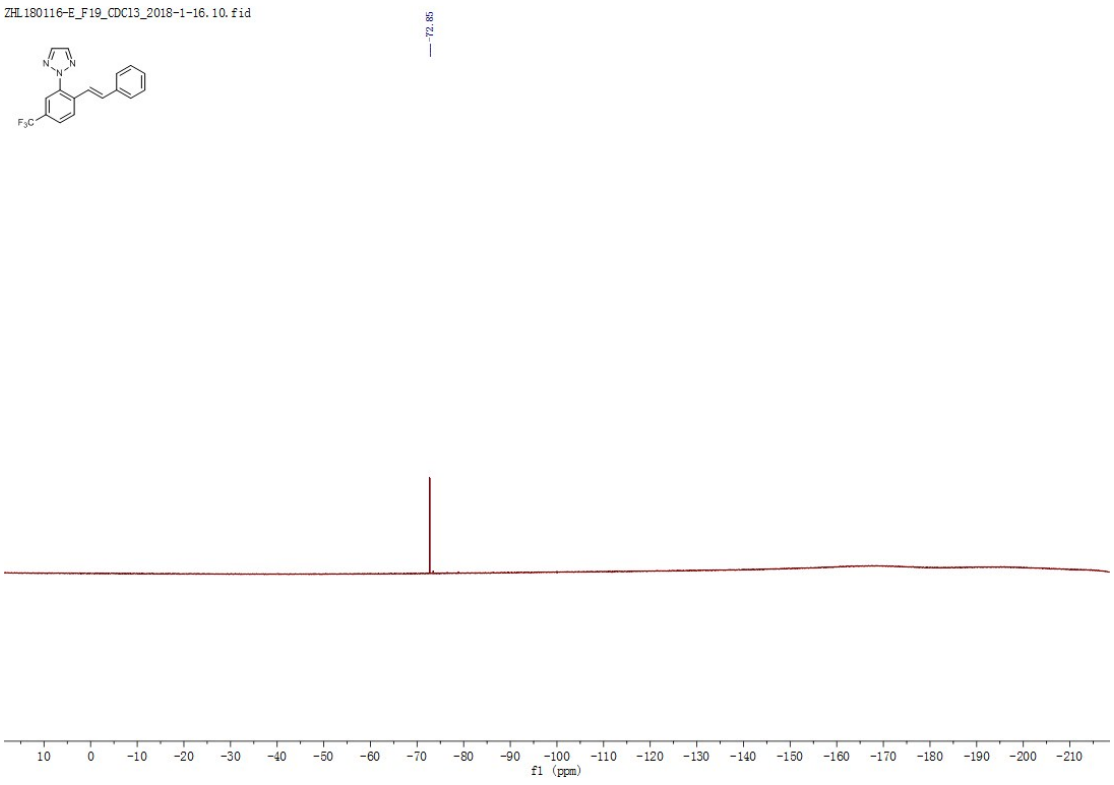


3l

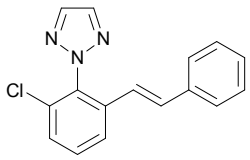
Yellow liquid, yield 75 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.94 (m, 3H), 7.70 (d, *J*=8.4Hz, 1H), 7.46 (d, *J*=8.4Hz, 3H), 7.34 (m, 4H), 7.16 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 135.5, 135.0, 134.7, 132.6, 128.0, 127.7, 127.5, 126.6, 126.0, 122.1; ^{19}F NMR (376MHz, DMSO): -72.77; HRMS (ESI) Calcd. For $C_{17}H_{12}F_3N_3Na$: 338.0881, Found: m/z 338.0880.





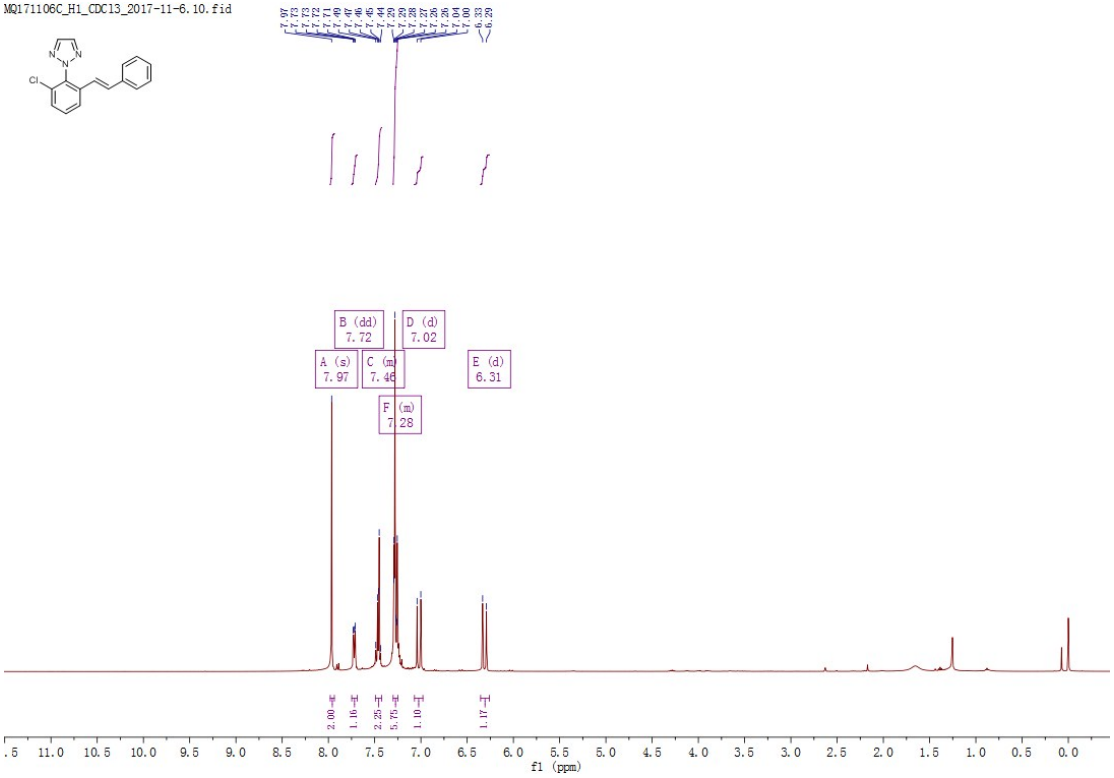


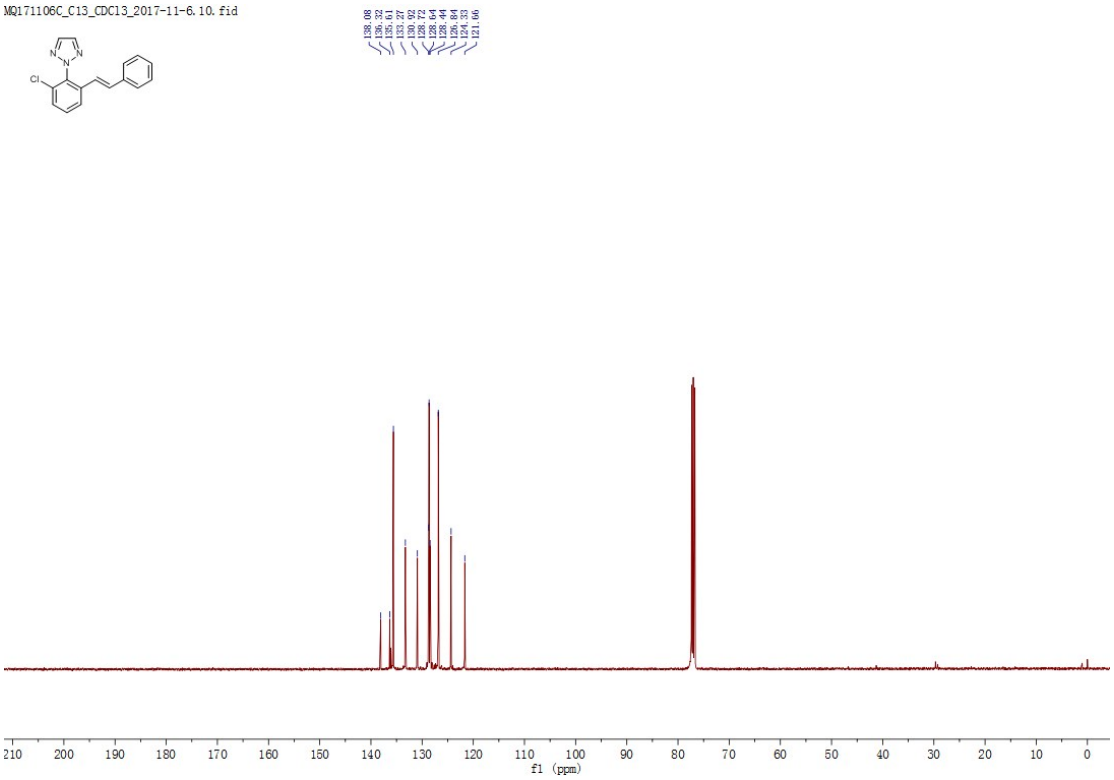
(*E*)-2-(2-chloro-6-styrylphenyl)-2*H*-1,2,3-triazole



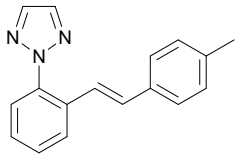
3m

Yellow liquid, yield 56 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.97 (s, 2H), 7.72 (dd, *J*=8.4Hz, 1H), 7.46 (d, *J*=8.4Hz, 2H), 7.27 (m, 5H), 7.02 (d, *J*=16.2Hz, 1H), 6.31 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 138.1, 136.3, 135.6, 133.3, 130.9, 128.7, 128.6, 128.4, 128.2, 126.8, 124.3, 121.7; HRMS (ESI) Calcd. For $C_{16}H_{12}ClN_3Na$: 304.0617, Found: m/z 304.0617.



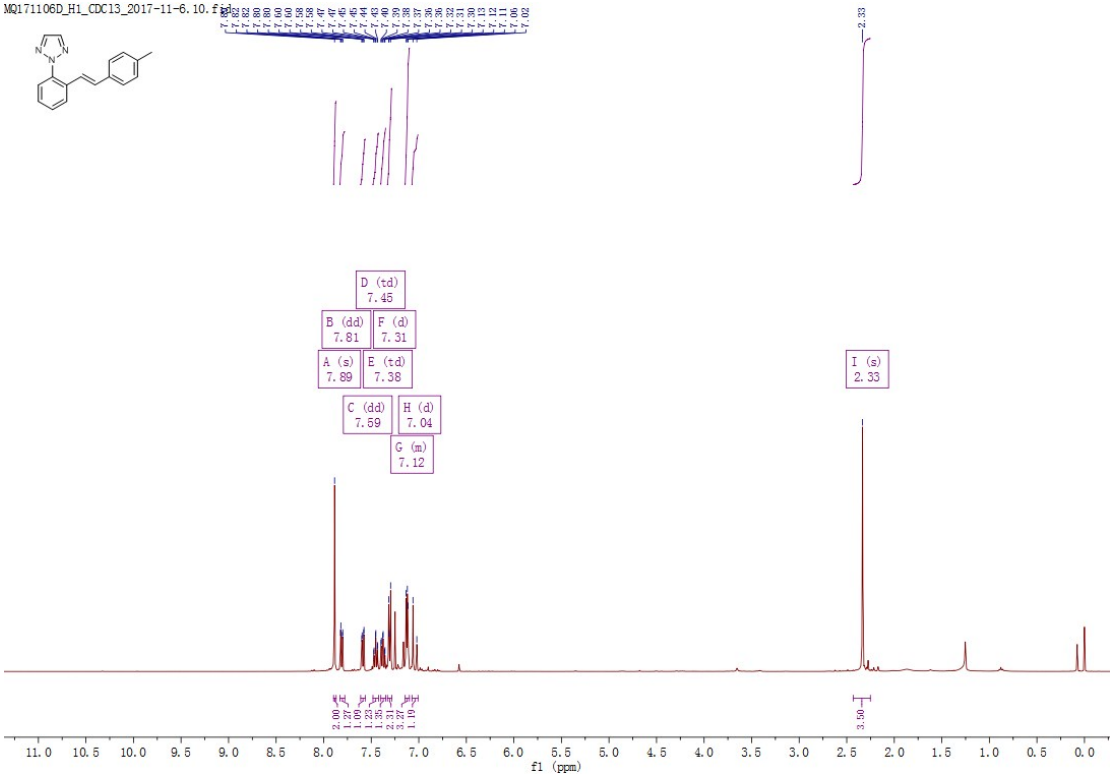


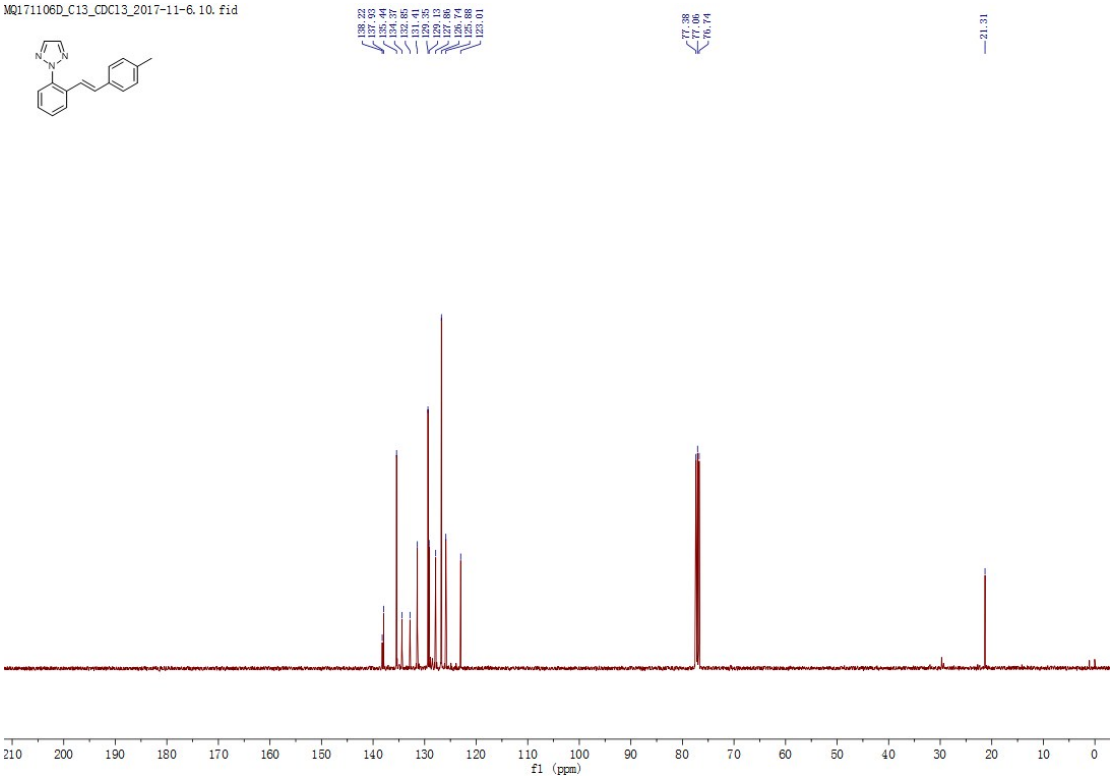
(*E*)-2-(2-(4-methylstyryl)phenyl)-2*H*-1,2,3-triazole



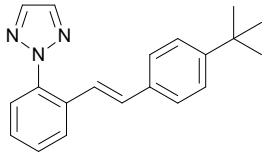
3n

White solid, yield 71 %, mp >200 ^{o}C, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.89 (s, 2H), 7.81 (d, *J*=8.4Hz, 1H), 7.59 (d, *J*=8.4Hz, 1H), 7.45 (t, *J*=8.4Hz, 1H), 7.38 (t, *J*=8.4Hz, 1H), 7.31 (d, *J*=8.4Hz, 2H), 7.13 (m, 3H), 7.04 (d, *J*=16.2Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (150MHz, $CDCl_3$): δ 138.2, 137.9, 135.5, 134.4, 132.8, 131.5, 129.4, 129.1, 127.9, 126.7, 125.9, 123.0, 21.4; HRMS (ESI) Calcd. For $C_{17}H_{15}N_3Na$: 284.1164, Found: m/z 284.1163.



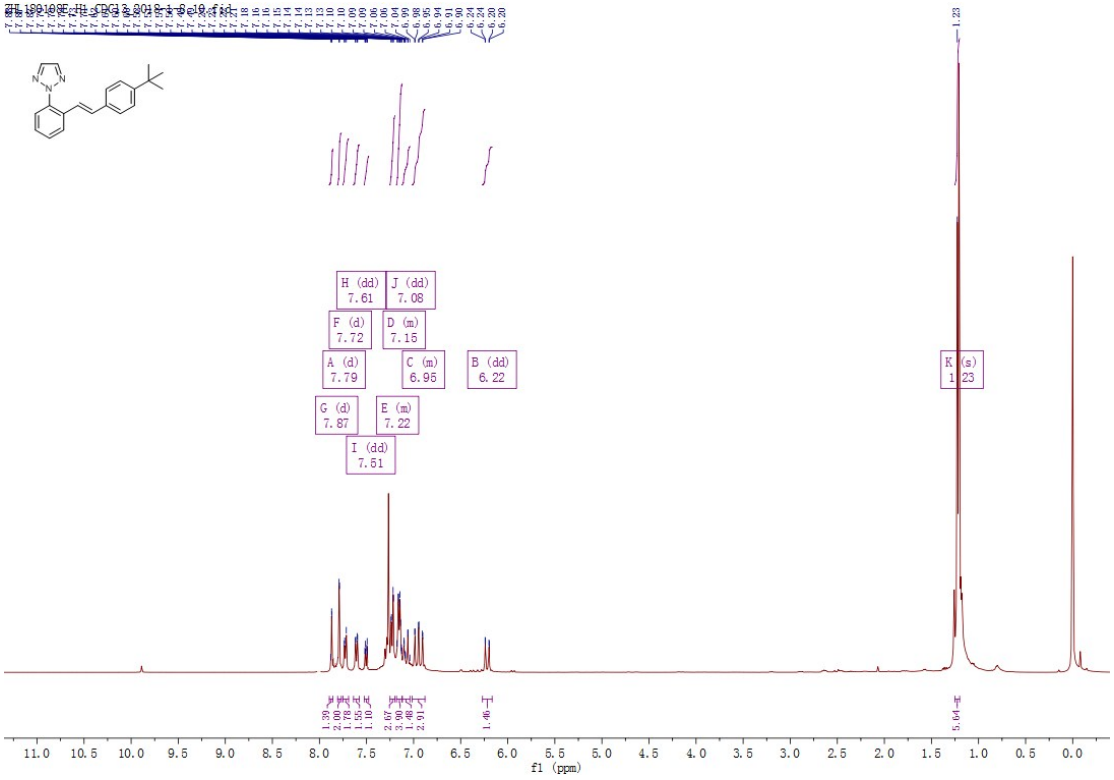


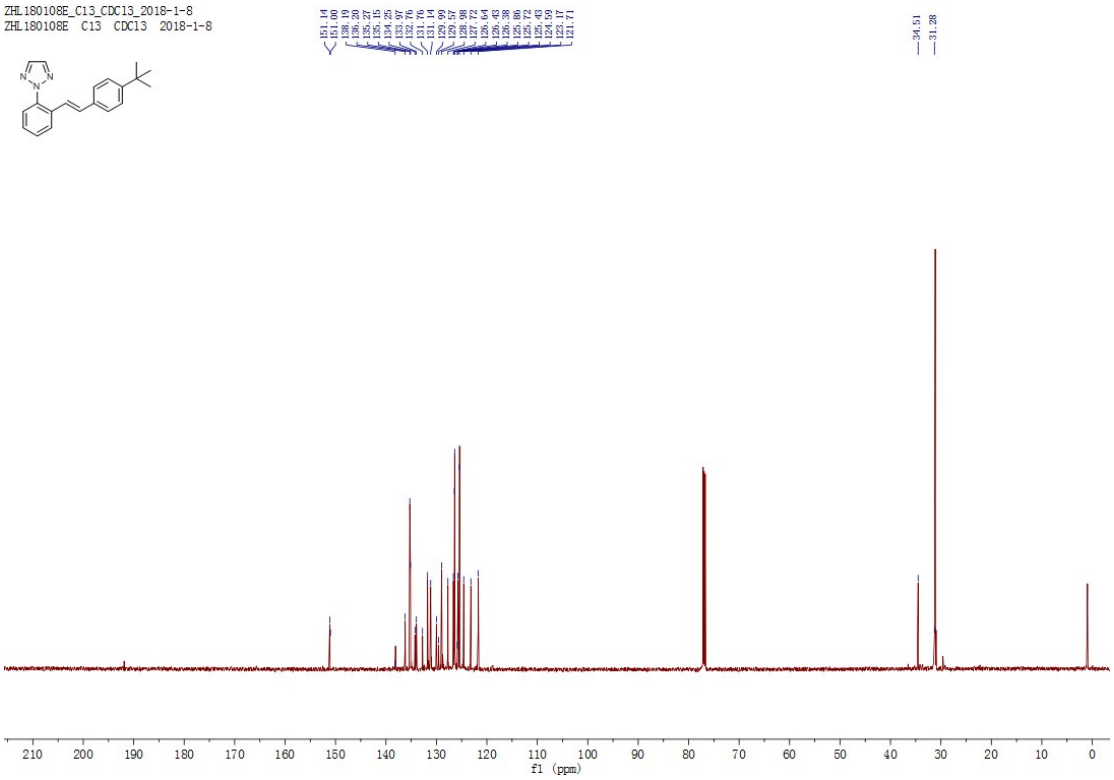
(E) -2-(2-(4-(*tert*-butyl)styryl)phenyl)-2*H*-1,2,3-triazole



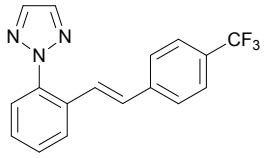
3o

Yellow liquid, yield 73 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.79 (s, 2H), 7.72 (d, *J*=8.4Hz, 1H),7.61 (d, *J*=8.4Hz, 1H), 7.50 (d, *J*=8.4Hz, 1H), 7.22 (d, *J*=8.4Hz, 1H), 7.15 (d, *J*=8.4Hz, 1H), 7.08 (d, *J*=16.2Hz, 1H), 6.22 (d, *J*=16.2Hz, 1H), 1.23 (s, 9H); ^{13}C NMR (150MHz, $CDCl_3$): δ 151.3, 138.2, 136.3, 135.2, 131.8, 131.1, 129.0, 127.7, 126.7, 126.5, 125.8, 125.5, 124.6, 123.2, 121.8, 34.5, 31.2; HRMS (ESI) Calcd. For $C_{20}H_{21}N_3Na$: 326.1633, Found: m/z 326.1633.





(E)-2-(2-(4-(trifluoromethyl)styryl)phenyl)-2*H*-1,2,3-triazole



3p

Yellow liquid, yield 64 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.84 (s, 2H), 7.75 (d, *J*=8.4Hz, 1H), 7.59 (d, *J*=8.4Hz, 1H), 7.50 (d, *J*=8.4Hz, 2H), 7.41 (m, 1H), 7.27 (d, *J*=16.2Hz, 1H), 7.01 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 139.5, 137.4, 134.6, 130.7, 128.7, 128.4, 128.1, 127.7, 126.0, 126.5, 125.9, 125.8, 124.7, 124.6, 124.6, 124.5, 124.5; ^{19}F NMR (376MHz, DMSO): -62.51; HRMS (ESI) Calcd. For $C_{17}H_{12}F_3N_3Na$: 338.0881, Found: m/z338.0880.

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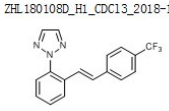

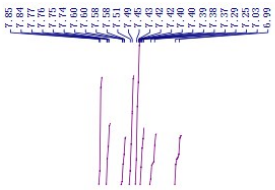

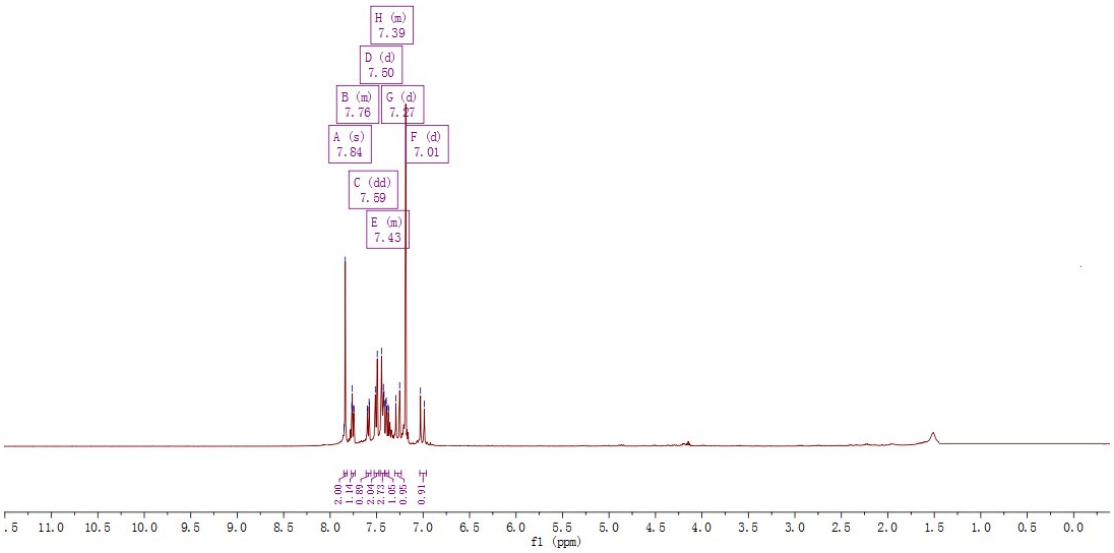

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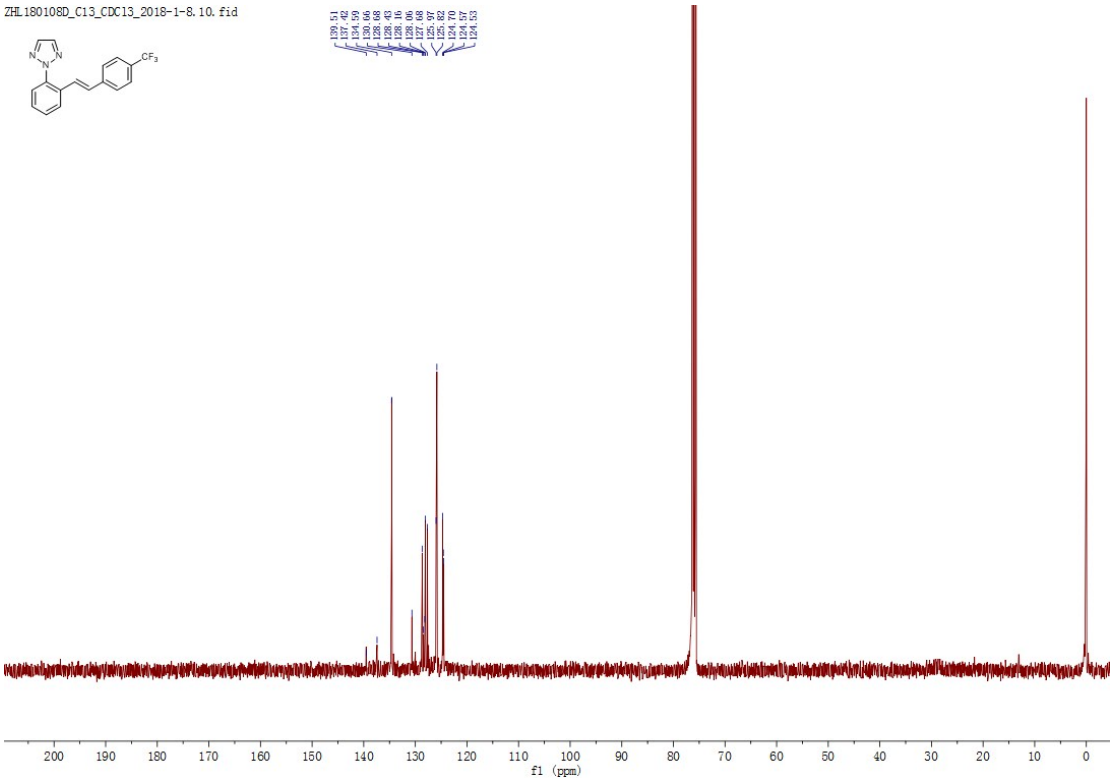
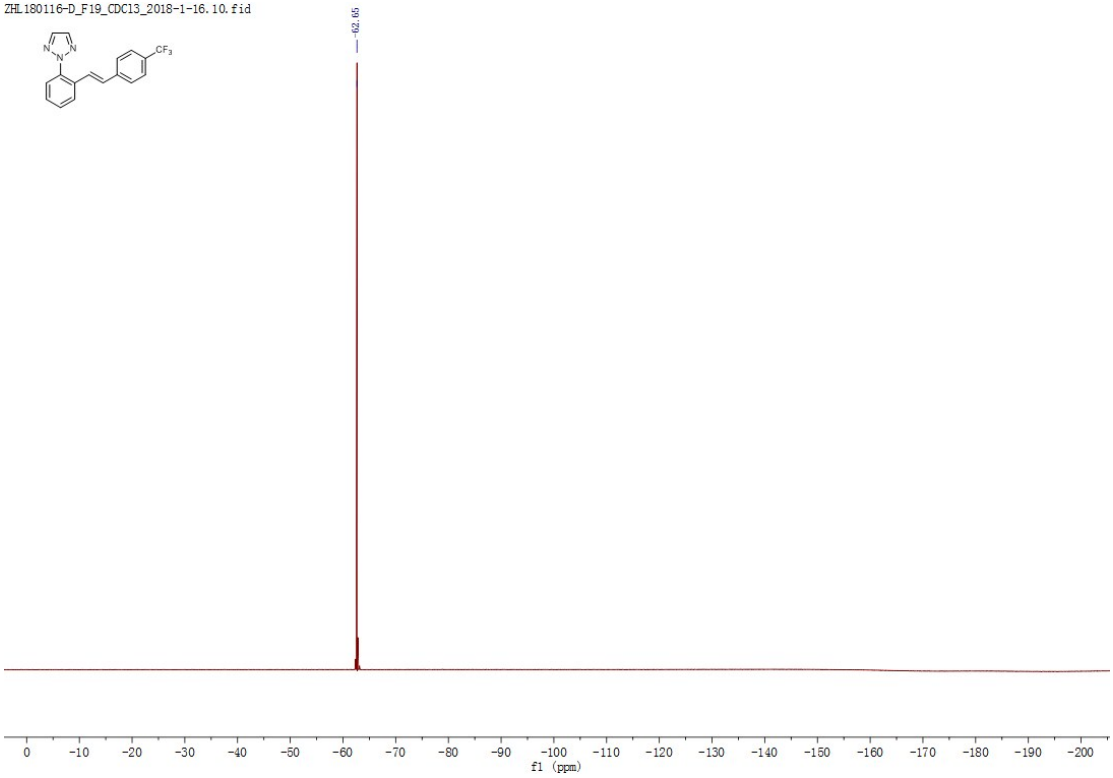
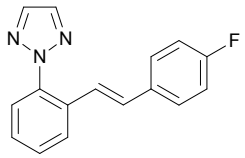




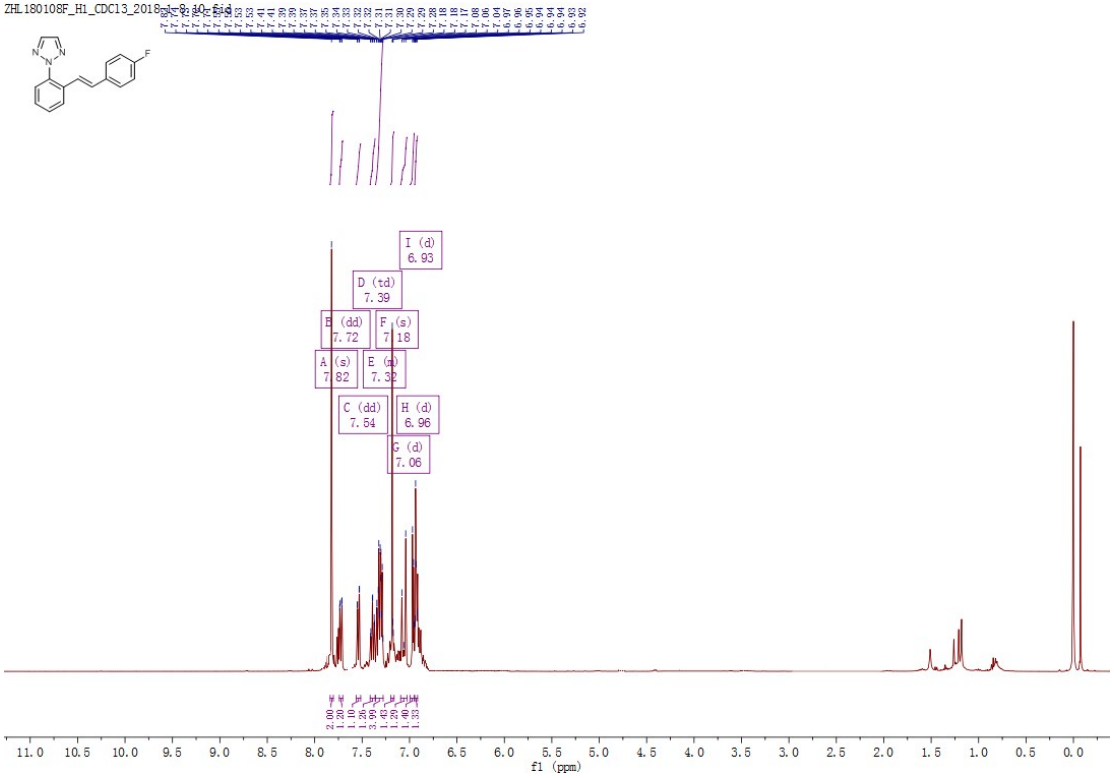
(E)-2-(2-(4-fluorostyryl)phenyl)-2*H*-1,2,3-triazole



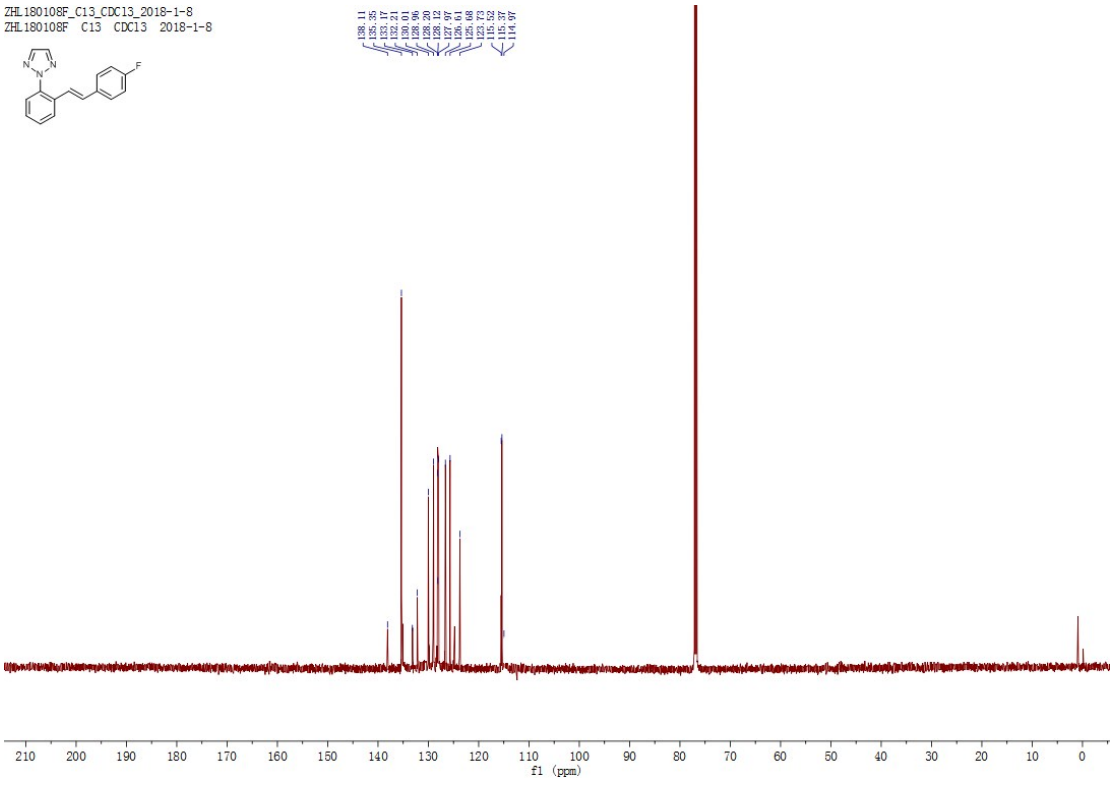
3q

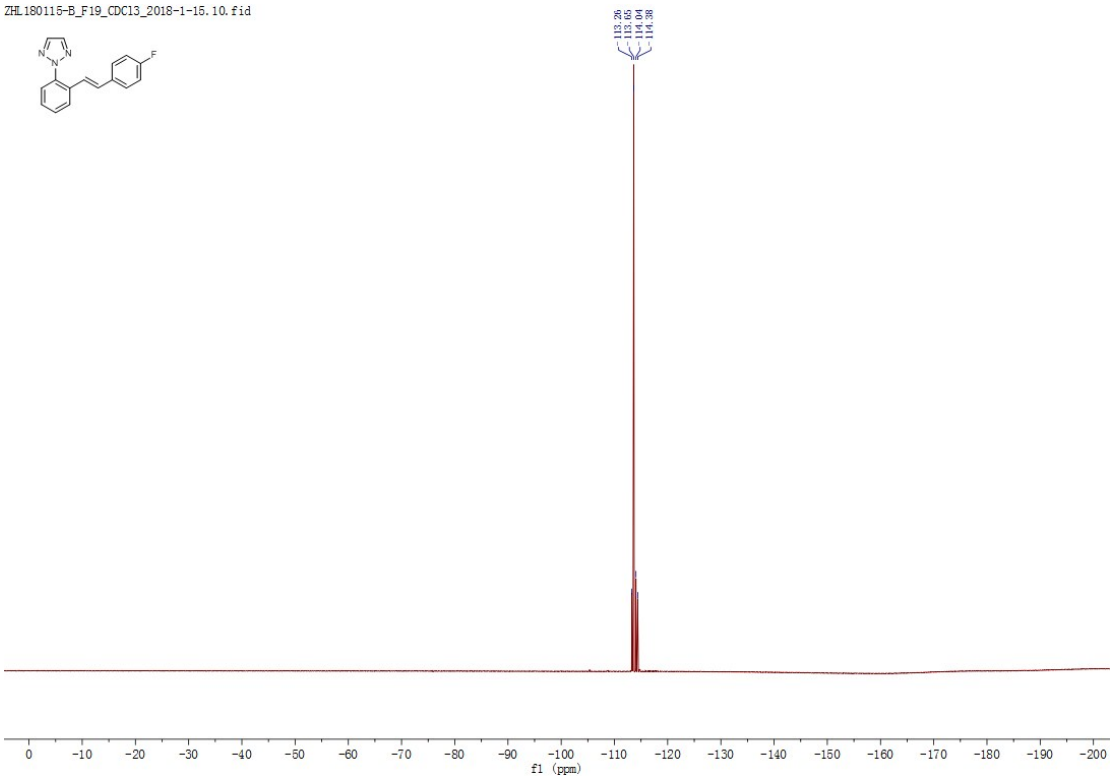
Liquid, yield 67 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.82 (s, 2H), 7.73 (d, *J*=8.4Hz, 1H), 7.54 (d, *J*=8.4Hz, 1H), 7.31 (m, 3H), 7.06 (d, *J*=16.2Hz, 1H), 6.94 (m, 4H); ^{13}C NMR (150MHz, $CDCl_3$): δ 135.4, 132.3, 129.9, 129.0, 128.1, 127.9, 126.6, 125.6, 123.8, 115.3; ^{19}F NMR (376MHz, DMSO): -113.65; HRMS (ESI) Calcd. For $C_{17}H_{12}F_3N_3Na$: 338.0881, Found: m/z338.0880.

ZHL180108F_H1_CDC13_2018-1-8.10.fid

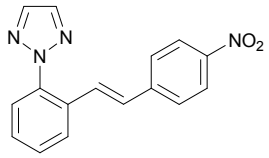


ZHL180108F_C13_CDC13_2018-1-8
ZHL180108F C13 CDC13 2018-1-8



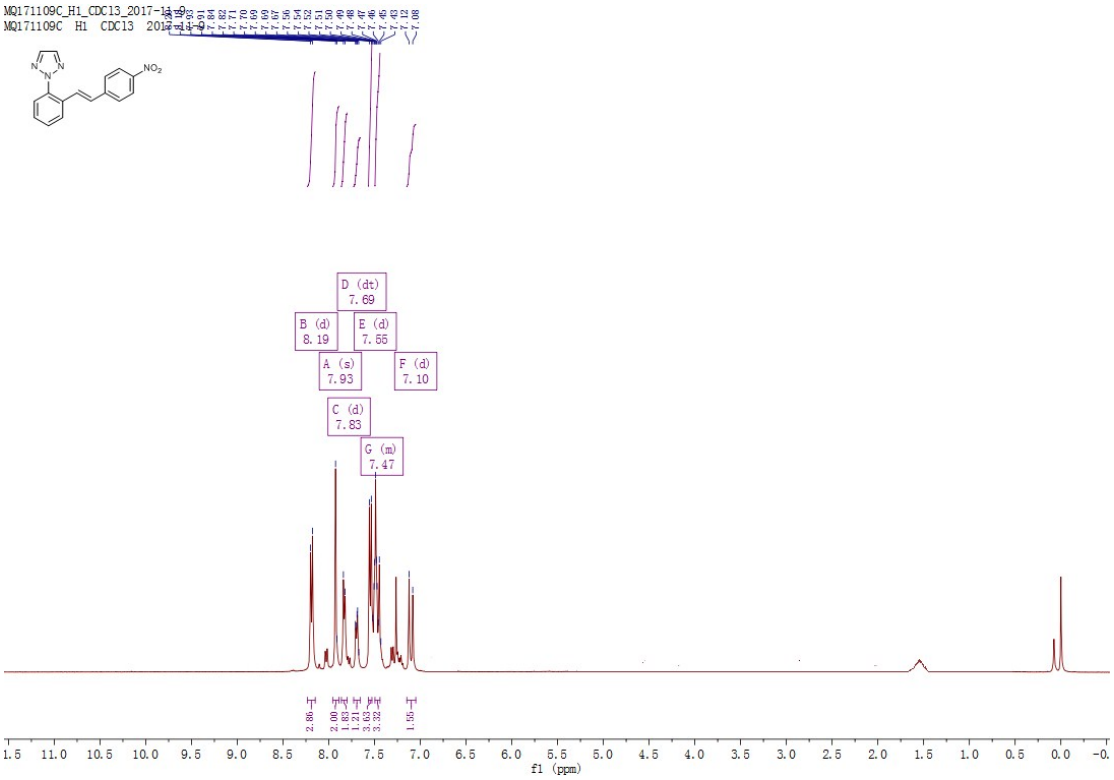


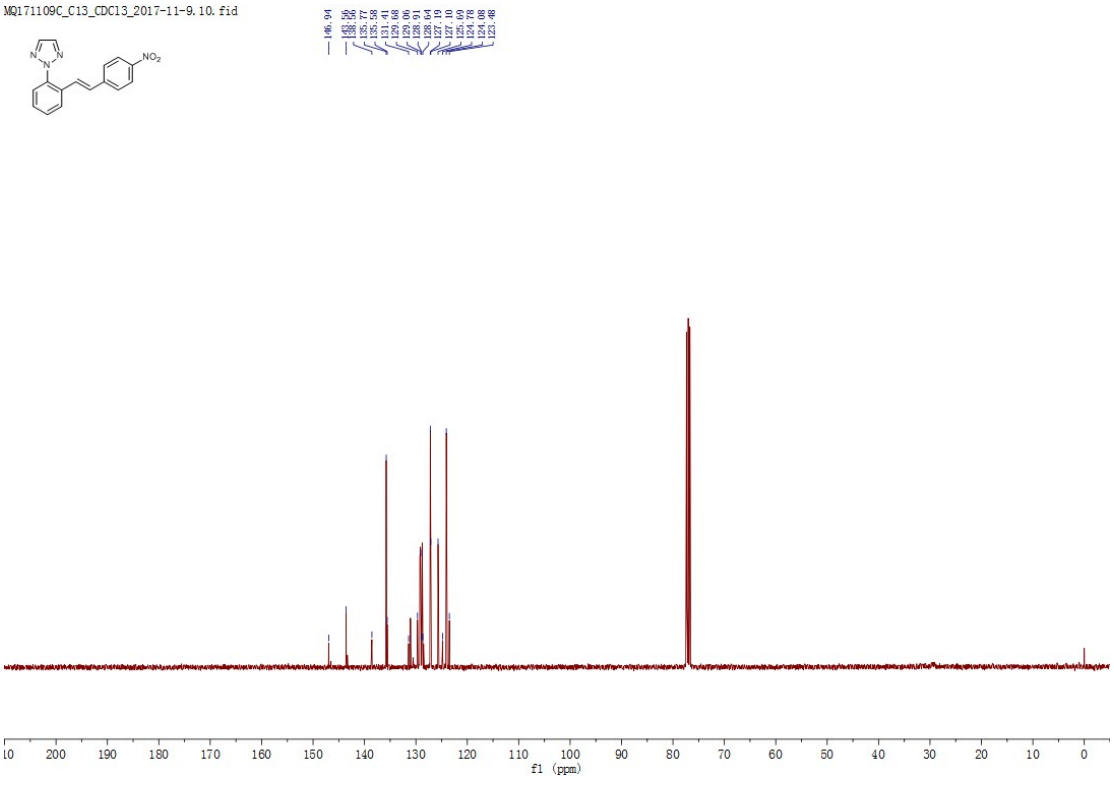
(*E*)-2-(2-(4-nitrostyryl)phenyl)-2*H*-1,2,3-triazole



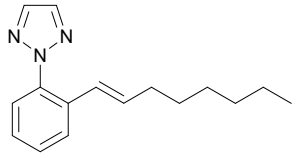
3r

Yellow solid, yield 57 %, mp 134-136 ^{o}C, ^{1}HNMR (600MHz, $CDCl_3$): δ 8.19 (d, *J*=8.4Hz, 2H), 7.10 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 147.0, 143.6, 138.6, 135.8, 135.6, 131.1, 129.7, 129.2, 129.1, 129.0, 128.8, 127.2, 127.1, 125.7, 124.1; HRMS (ESI) Calcd. For $C_{16}H_{12}N_4Na$: 315.0858, Found: m/z 315.0857.



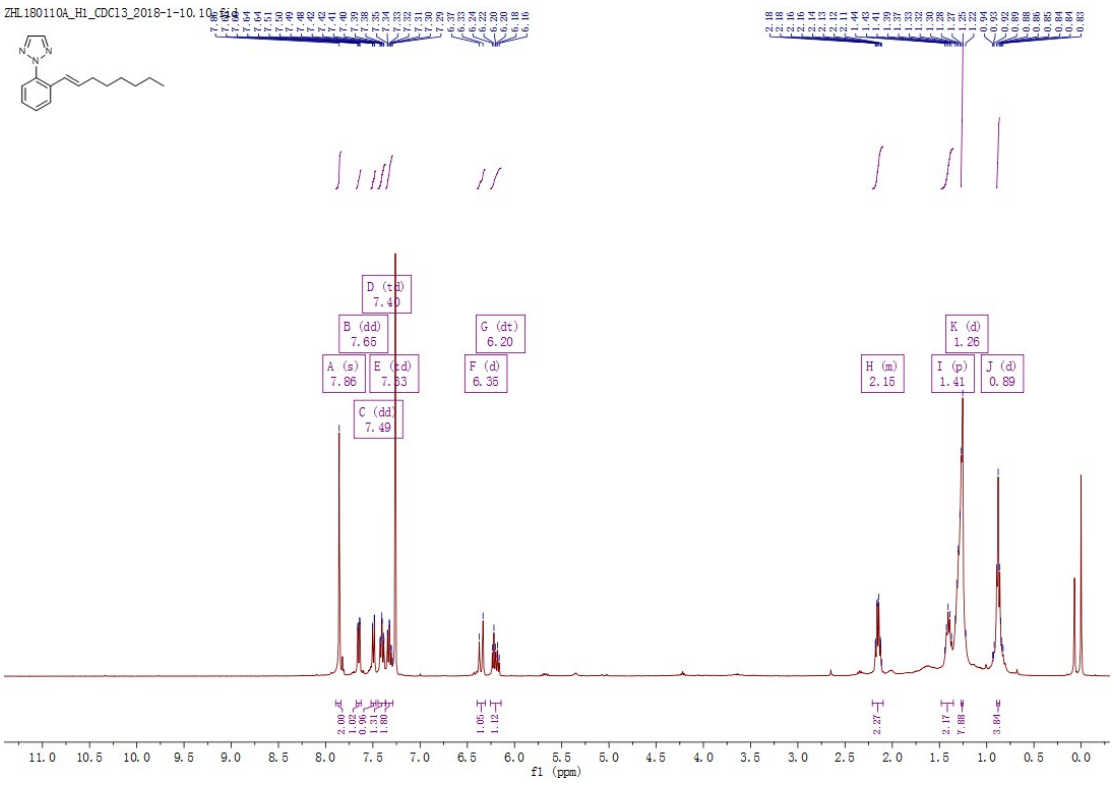


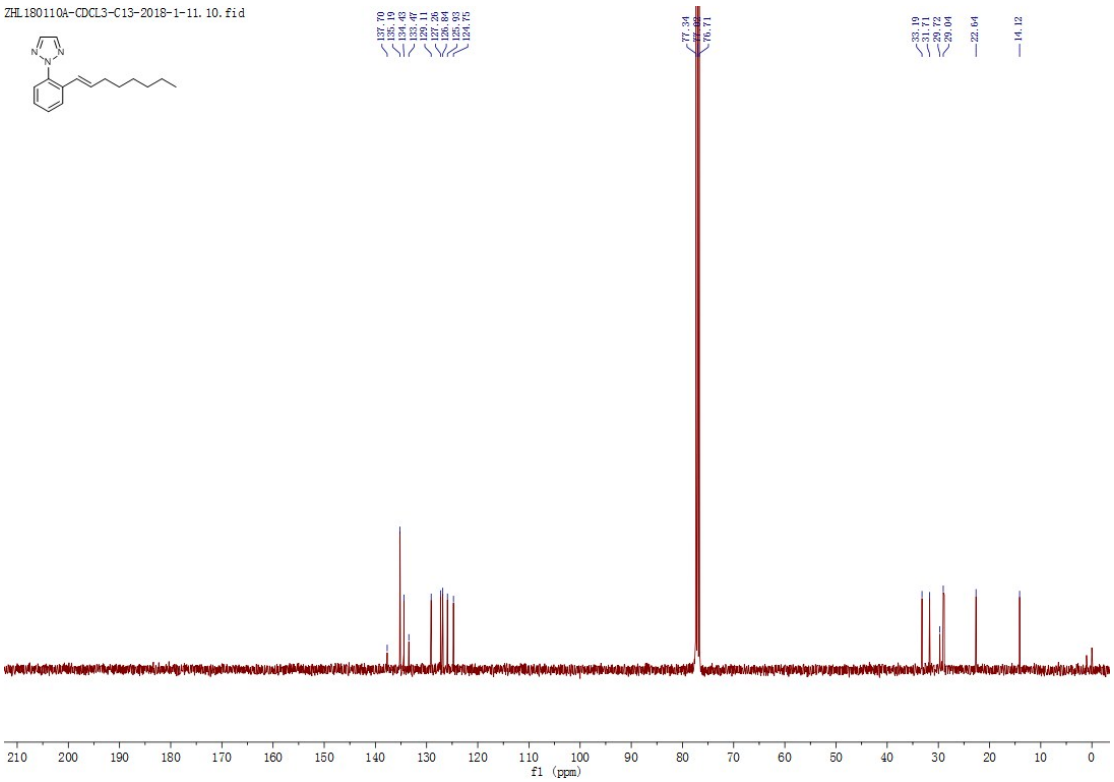
(E)-2-(2-(oct-1-en-1-yl)phenyl)-2*H*-1,2,3-triazole



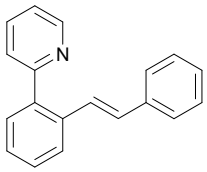
3s

Light yellow liquid, yield 67 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.86 (s, 2H), 7.65 (d, *J*=8.4Hz, 1H), 7.49 (d, *J*=8.4Hz, 1H), 7.41 (t, *J*=8.4Hz, 1H), 7.32 (t, *J*=8.4Hz, 1H), 6.35 (d, *J*=16.2Hz, 1H), 6.20 (m, 1H), 2.15 (q, *J*=4.8Hz, 2H), 1.28 (m, 8H), 0.88 (t, *J*=4.8Hz, 3H); ^{13}C NMR (150MHz, $CDCl_3$): δ 135.2, 134.4, 129.1, 127.3, 126.8, 125.9, 124.8, 33.2, 31.7, 29.7, 29.0, 28.9, 22.6, 14.1; HRMS (ESI) Calcd. For $C_{16}H_{21}N_3Na$: 278.1633, Found: m/z 278.1631.



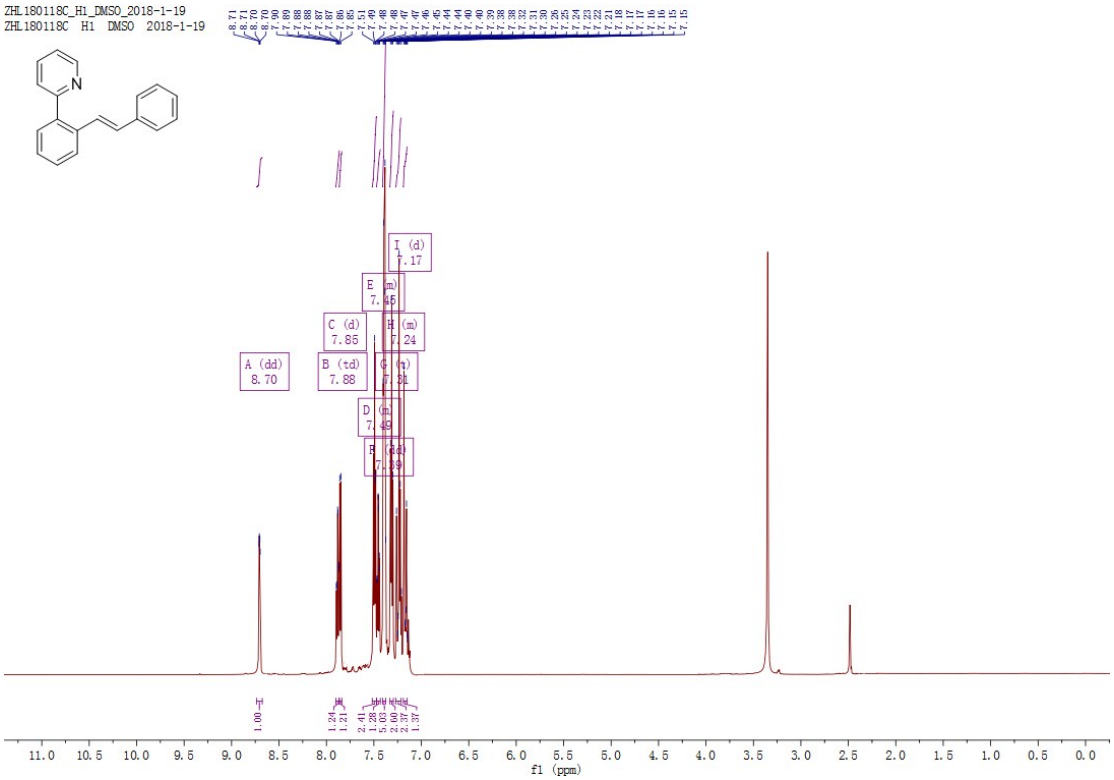


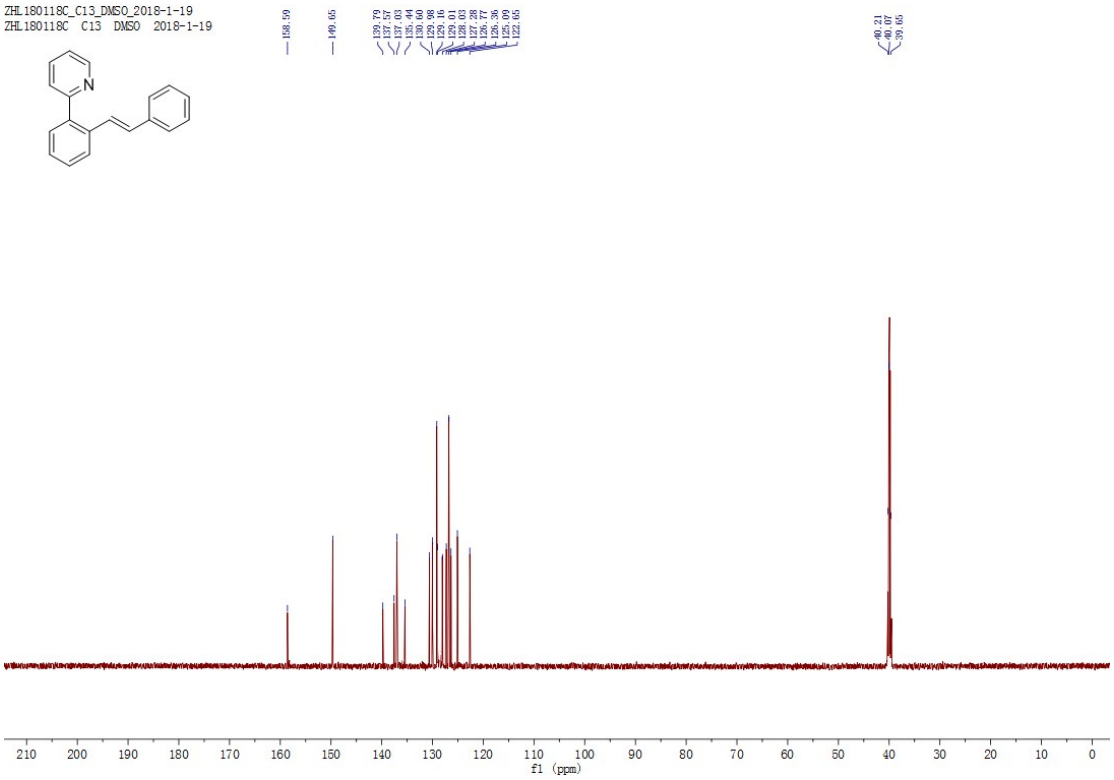
(E)-2-(2-styrylphenyl)pyridine



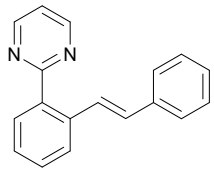
4a

Little yellow oil, yield 81%, ^{1}HNMR (600MHz, DMSO): δ 8.71 (s, 1H), 7.88 (t, *J*=8.4Hz, 1H), 7.85 (d, *J*=8.4Hz, 1H), 7.49 (t, *J*=8.4Hz, 2H), 7.45 (t, *J*=8.4Hz, 1H), 7.39 (m, 4H), 7.24 (m, 2H), 7.17 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, DMSO): δ 158.6, 149.7, 139.8, 137.6, 137.0, 135.4, 130.6, 130.0, 129.2, 129.0, 128.0, 127.3, 126.8, 126.4, 125.1, 122.7; HRMS (ESI) Calcd. For $C_{19}H_{15}NNa$: 280.1102, Found: m/z 280.1101.



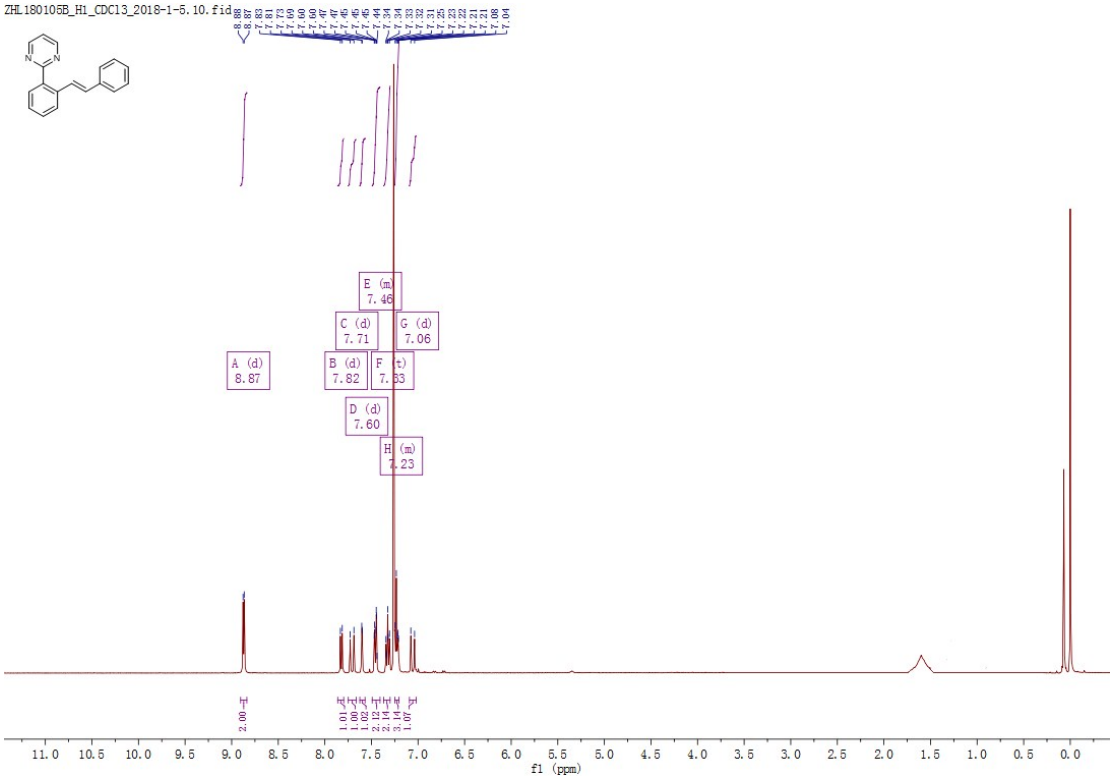


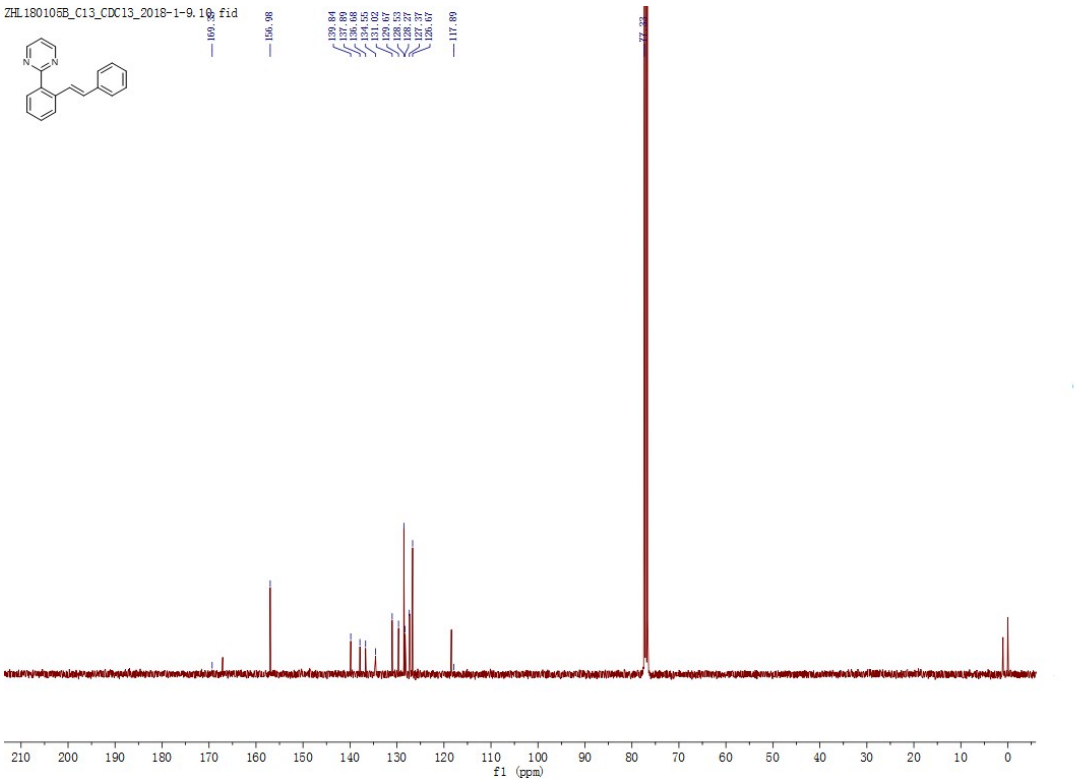
(E)-2-(2-styrylphenyl)pyrimidine



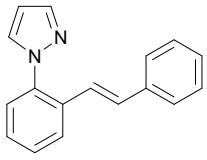
4b

Yellow oil, yield 73 %, ^{1}HNMR (600MHz, $CDCl_3$): δ 8.88 (d, *J*=8.4Hz, 2H), 7.83 (d, *J*=8.4Hz, 1H), 7.71 (d, *J*=16.2Hz, 1H), 7.60 (s, 1H), 7.46 (d, *J*=8.4Hz, 2H), 7.33 (t, *J*=8.4Hz, 2H), 7.23 (m, 4H), 7.06 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$): δ 167.2, 157.0, 139.8, 137.8, 136.7, 134.7, 131.1, 129.8, 128.7, 128.3, 127.4, 126.9, 118.6; HRMS (ESI) Calcd. For $C_{18}H_{14}N_2Na$: 281.1055, Found: m/z 281.1055.



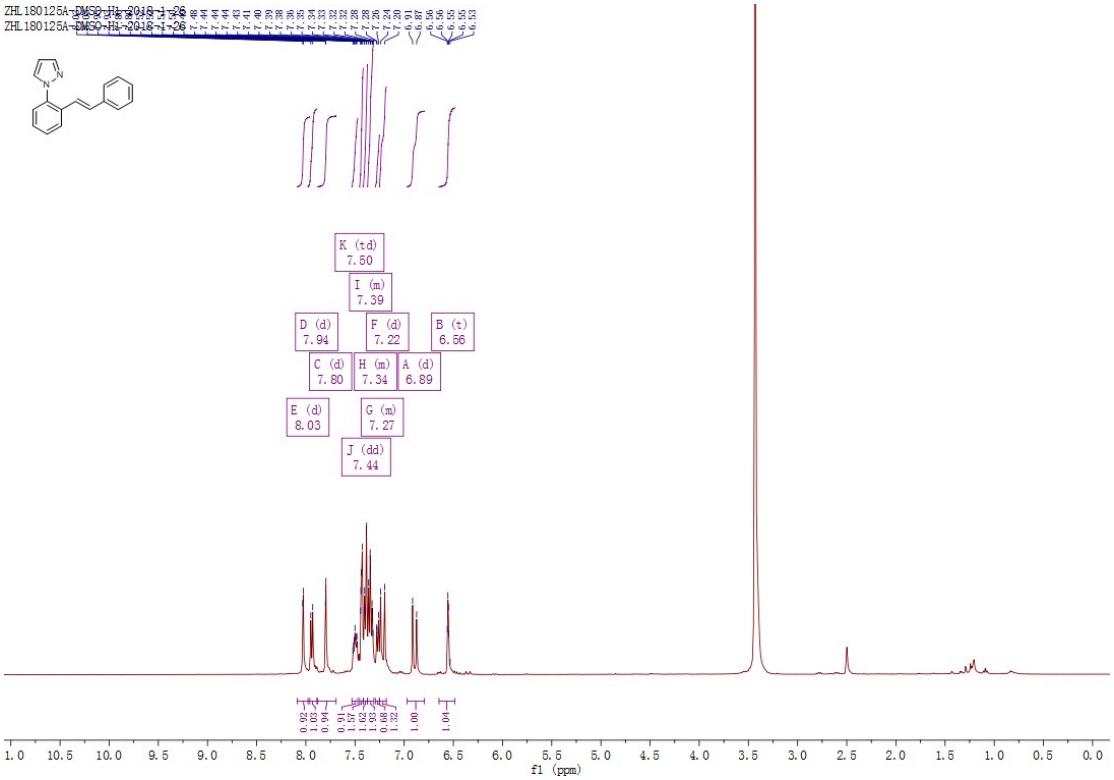


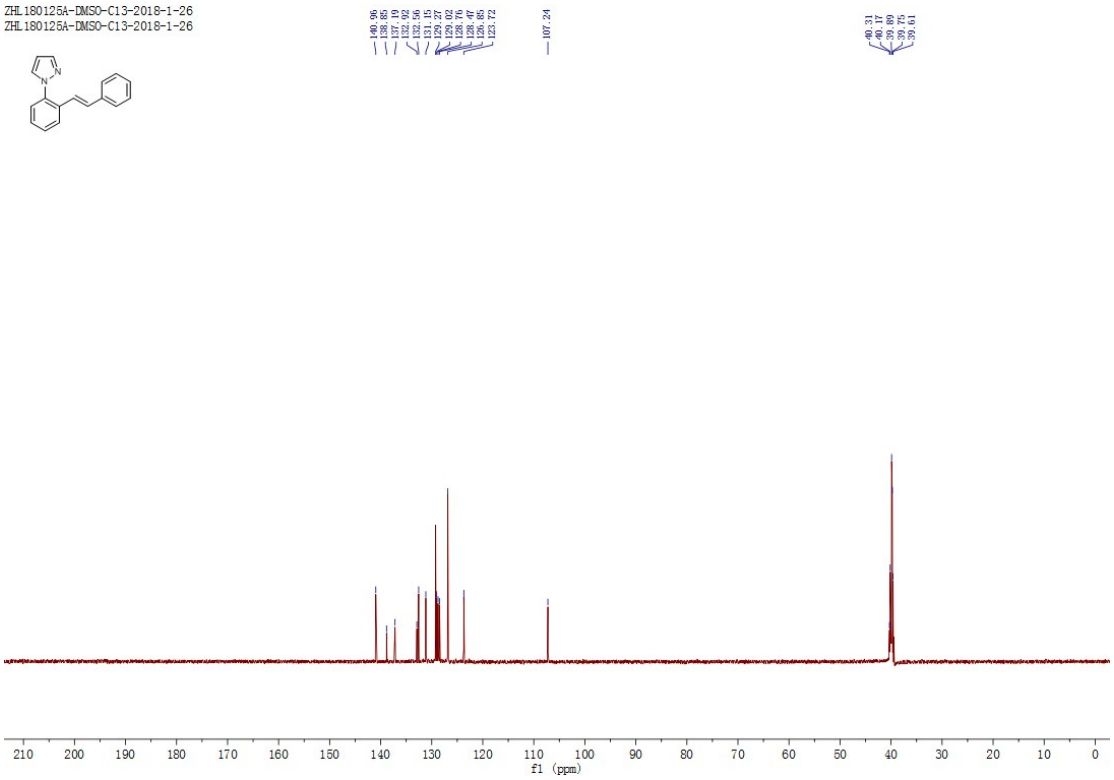
(E)-1-(2-styrylphenyl)-1H-pyrazole



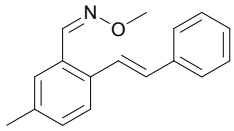
4c

Yellow oil, yield 80 %, ^{1}HNMR (600MHz, DMSO): δ 8.03 (s, 1H), 7.94 (d, *J*=8.4Hz, 1H), 7.80 (s, 1H), 7.50 (m, 1H), 7.43 (m, 2H), 7.38 (t, *J*=8.4Hz, 2H), 7.35 (t, *J*=8.4Hz, 2H), 7.26 (t, *J*=8.4Hz, 1H), 7.22 (d, *J*=16.4Hz, 1H), 6.89 (d, *J*=16.4Hz, 1H), 6.55 (s, 1H); ^{13}C NMR (150MHz, DMSO): δ 141.0, 139.9, 137.2, 132.9, 132.7, 131.1, 129.3, 129.0, 128.8, 128.5, 126.9, 126.8, 123.7; HRMS (ESI) Calcd. For $C_{17}H_{14}N_2Na$: 269.1055, Found: m/z 269.1054.



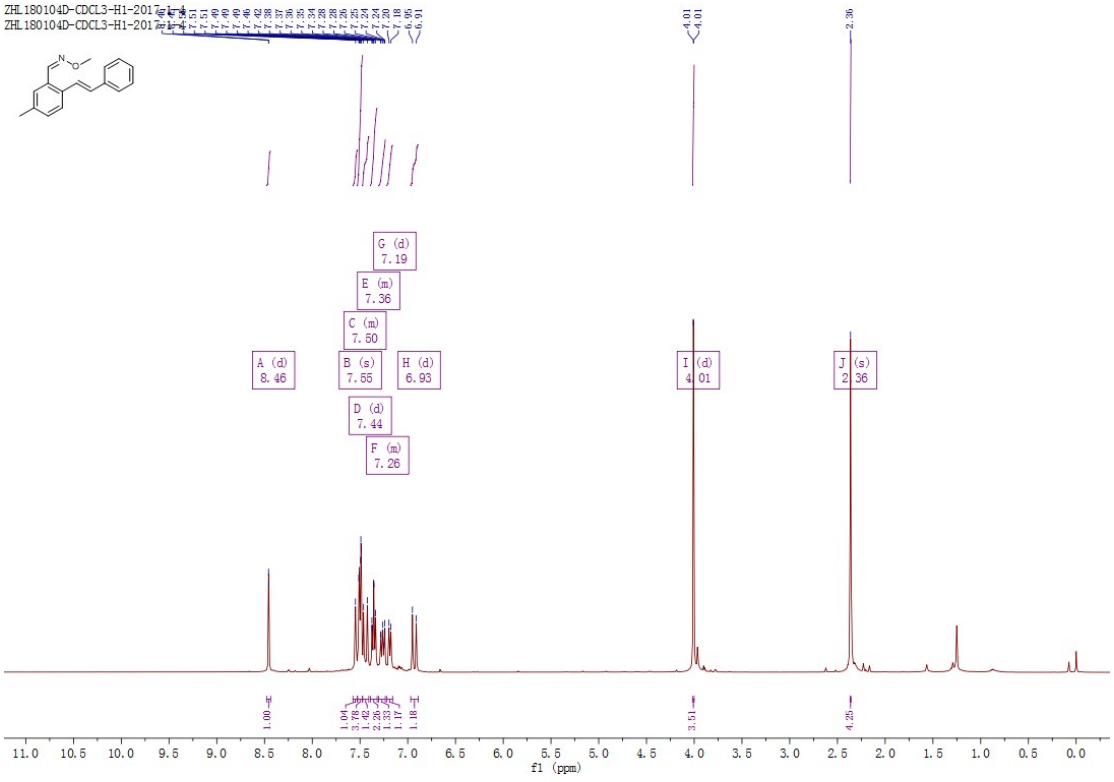


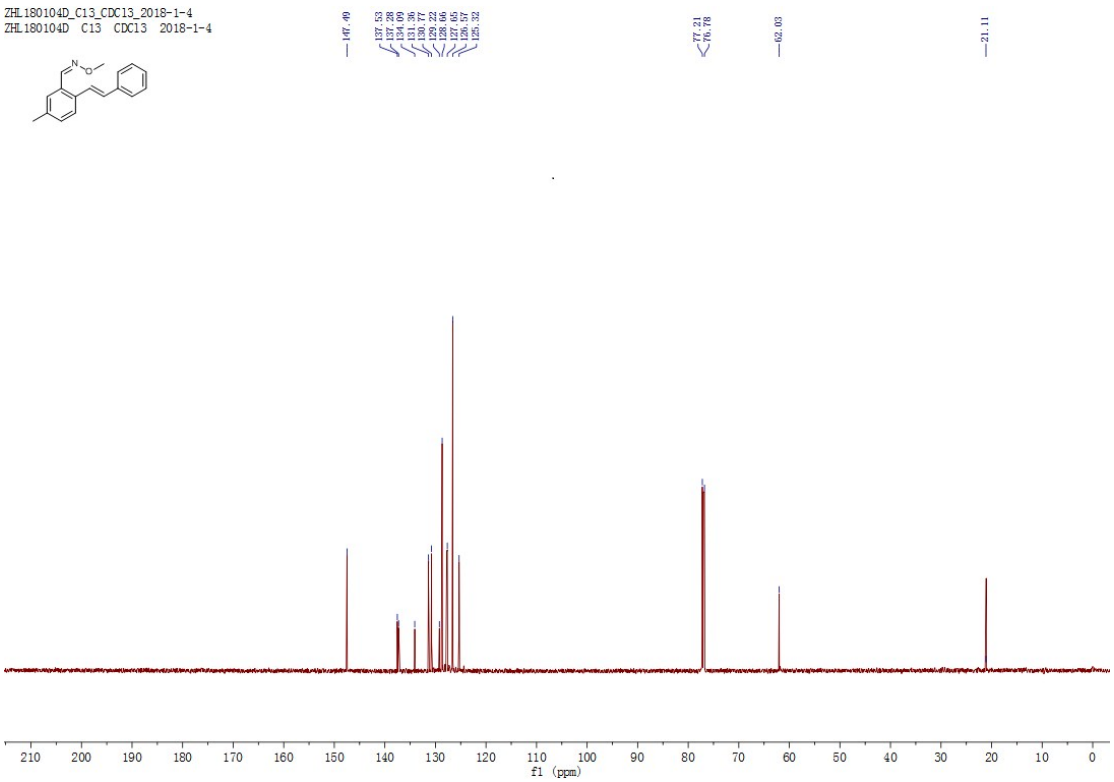
(E)-5-methyl-2-((E)-styryl)benzaldehyde O-methyl oxime



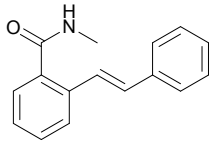
4d

White solid, yield 78 %, mp > 230 °C, ^{1}HNMR (600MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.55 (s,1H), 7.50 (d, *J*=16.2Hz, 3H), 7.44 (d, *J*=16.2Hz, 1H), 7.36 (t, *J*=8.4Hz, 2H), 7.26 (t, *J*=8.4Hz, 1H), 7.19 (d, *J*=8.4Hz, 1H), 6.93 (d, *J*=16.2Hz, 1H), 4.02 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (150MHz, $CDCl_3$): δ 147.5, 137.5, 137.3, 134.1, 131.4, 130.8, 129.2, 129.7, 127.8, 127.7, 125.6, 125.3, 62.0, 21.1; HRMS (ESI) Calcd. For $C_{17}H_{17}NONa$: 274.1208, Found: m/z 274.1207.



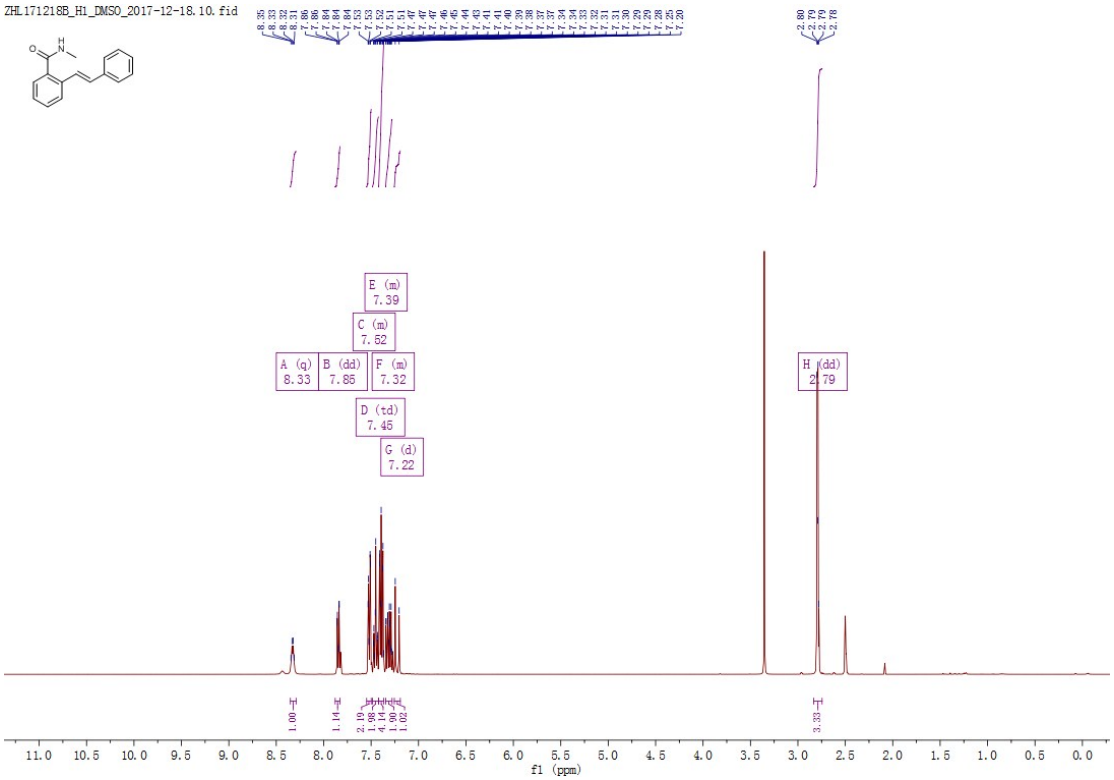


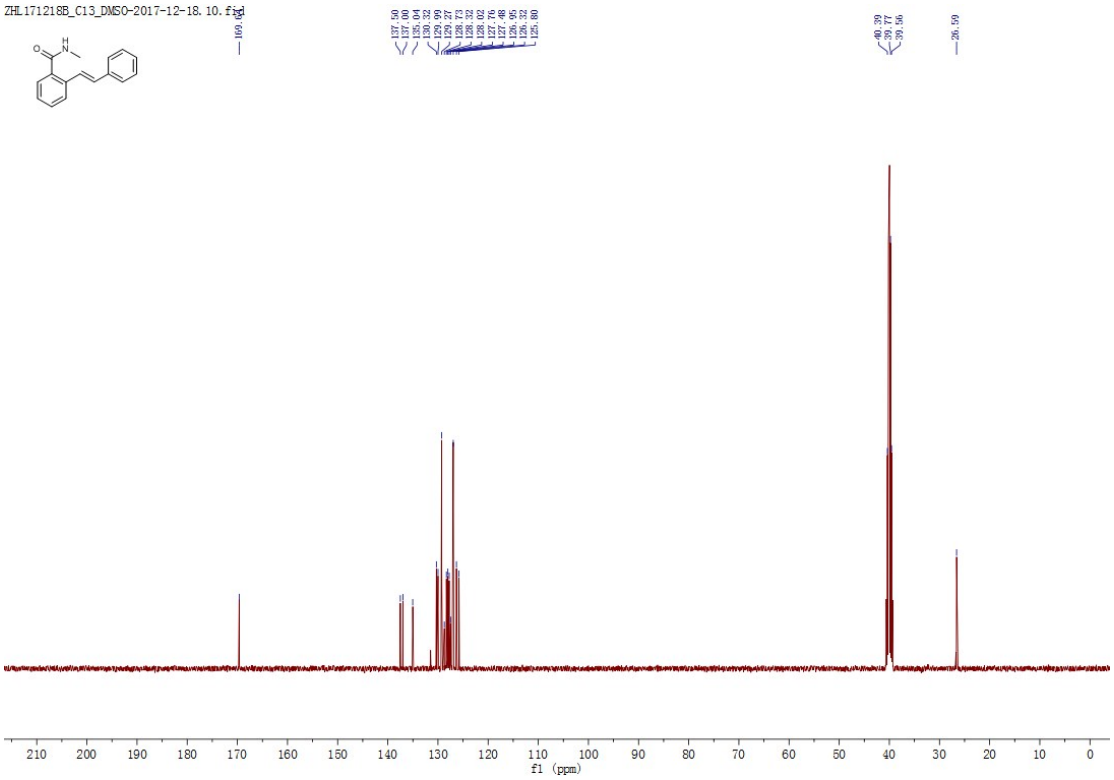
(E)-N-methyl-2-styrylbenzamide



4e

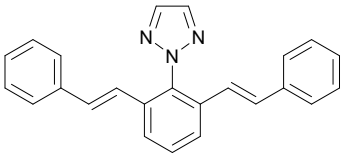
White solid, yield 57 %, mp > 230 °C, ^{1}HNMR (600MHz, $CDCl_3$): 8.33 (d, *J*=8.4Hz, 1H), 7.85 (d, *J*=8.4Hz, 1H), 7.52 (d, *J*=8.4Hz, 2H), 7.45 (t, *J*=8.4Hz, 2H), 7.39 (t, *J*=8.4Hz, 3H), 7.31 (m, 3H), 7.23 (d, *J*=16.2Hz, 1H), 2.80 (s, 3H); ^{13}C NMR (150MHz, $CDCl_3$): δ 169.7, 137.6, 136.9, 134.9, 130.2, 129.2, 128.0, 127.5, 126.9, 126.5, 125.8, 26.6; HRMS (ESI) Calcd. For $C_{16}H_{15}NONa$: 260.1051, Found: m/z 260.1050.





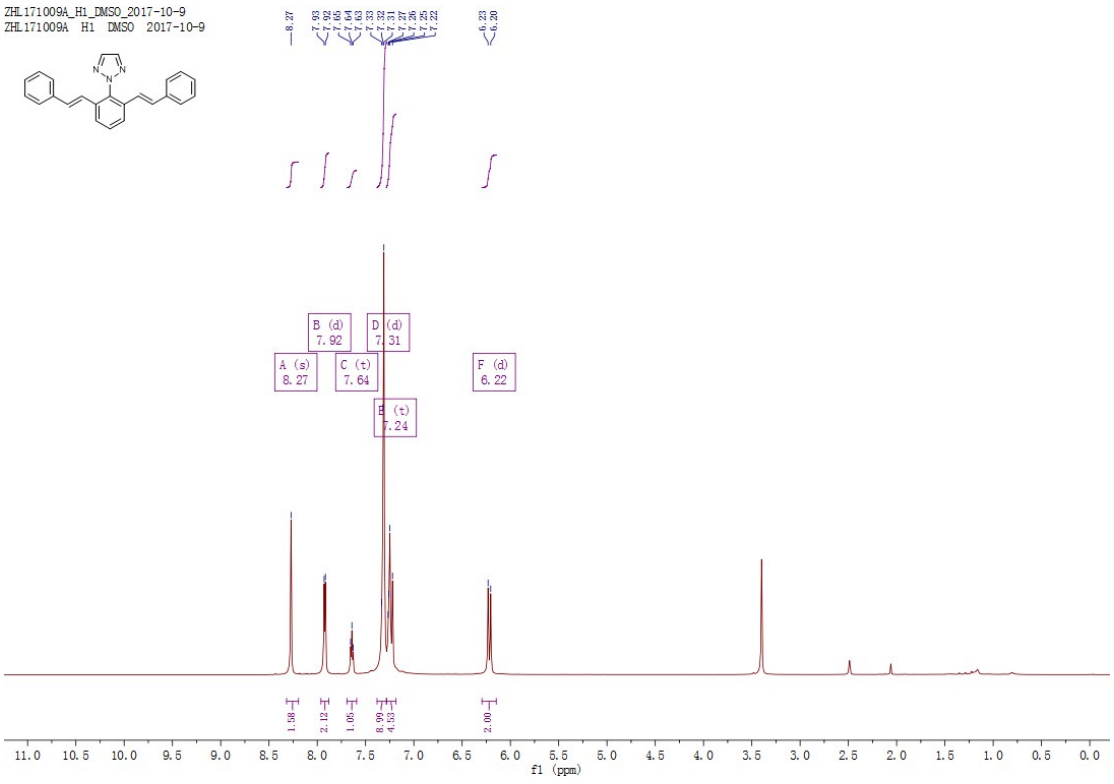
Characterization Data and NMR Spectra of Products 3a'-4c'

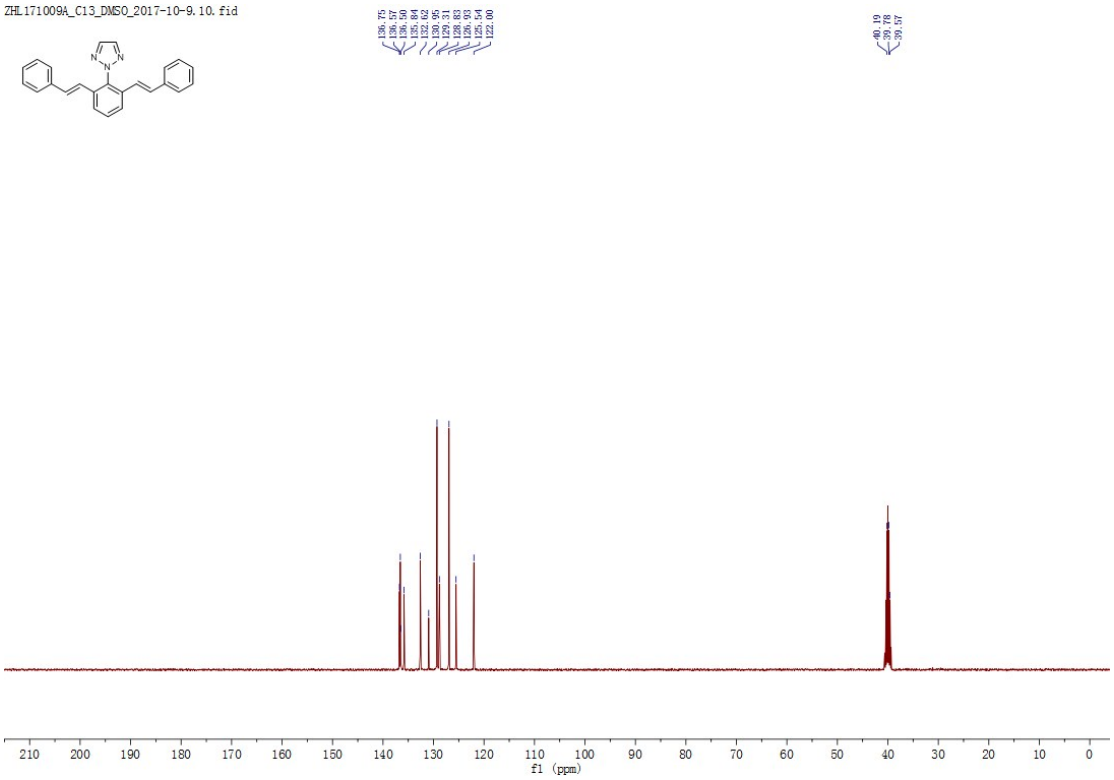
2-(2,6-di((*E*)-styryl)phenyl)-2*H*-1,2,3-triazole



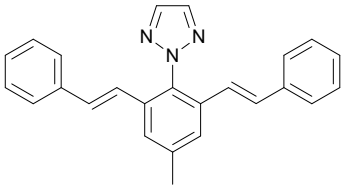
3a'

White solid, yield 93 %, mp 166-168 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.27 (s, 2H), 7.92 (d, *J*=8.4Hz, 2H), 7.64 (t, *J*=8.4Hz, 1H), 7.28 (m, 12H), 6.22 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, DMSO): δ 136.8, 136.6, 136.5, 135.8, 132.6, 131.0, 129.3, 128.9, 126.9, 125.6, 122.0; HRMS (ESI) Calcd. For $C_{24}H_{19}N_3Na$:372.1477, Found: m/z 372.1476.



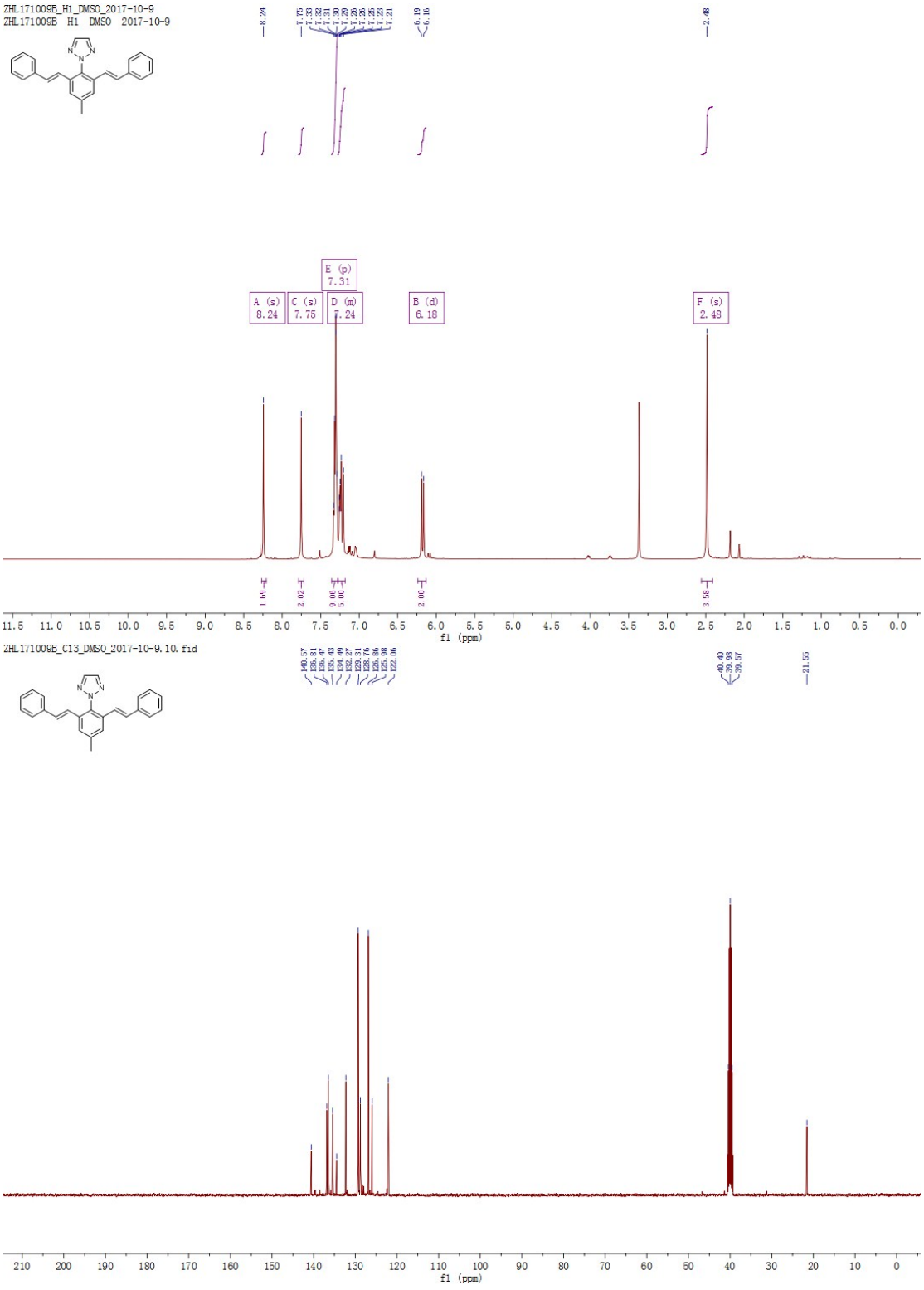


2-(4-methyl-2,6-di((*E*)-styryl)phenyl)-2*H*-1,2,3-triazole

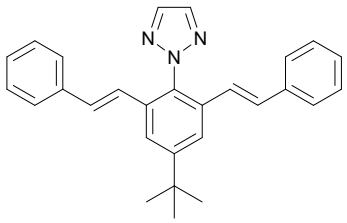


3b'

White solid, yield 87 %, mp 168-170 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.24 (s, 2H), 7.75 (s, 2H), 7.28 (m, 12H), 6.17 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, DMSO): δ 140.6, 136.8, 136.5, 135.5, 134.5, 132.3, 129.3, 128.8, 126.9, 126.0, 122.1, 21.5; HRMS (ESI) Calcd. For $C_{25}H_{21}N_3Na$:386.1633, Found: m/z 386.1633.

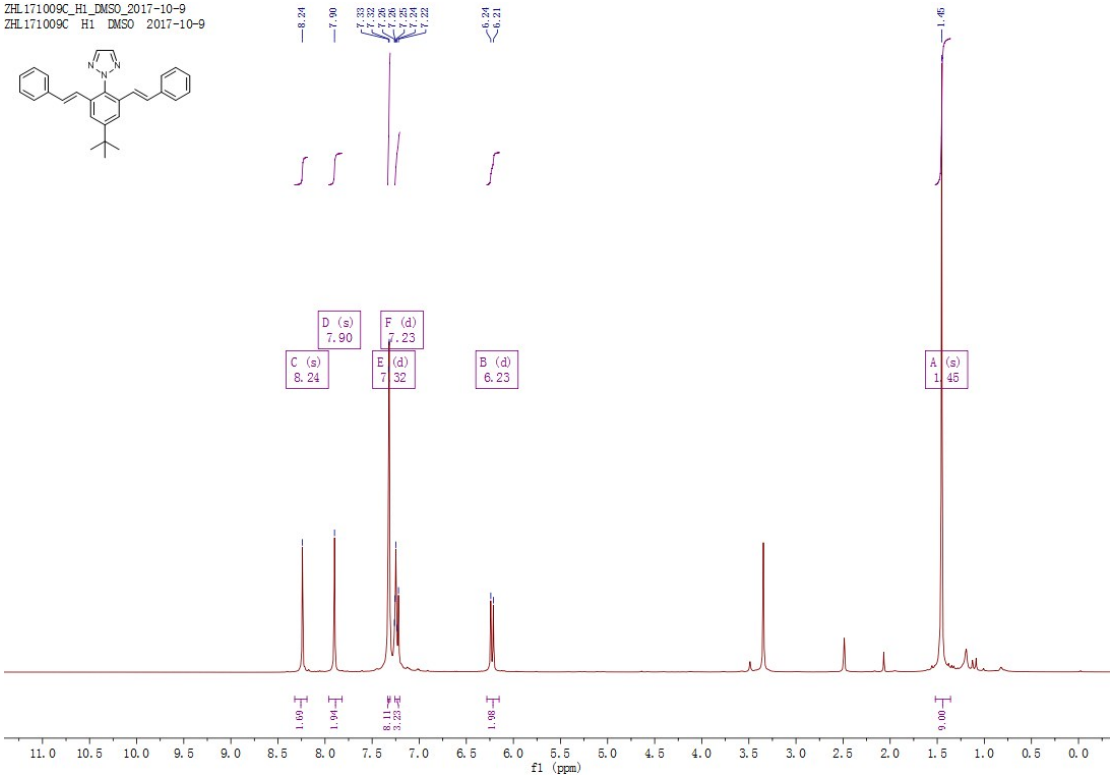


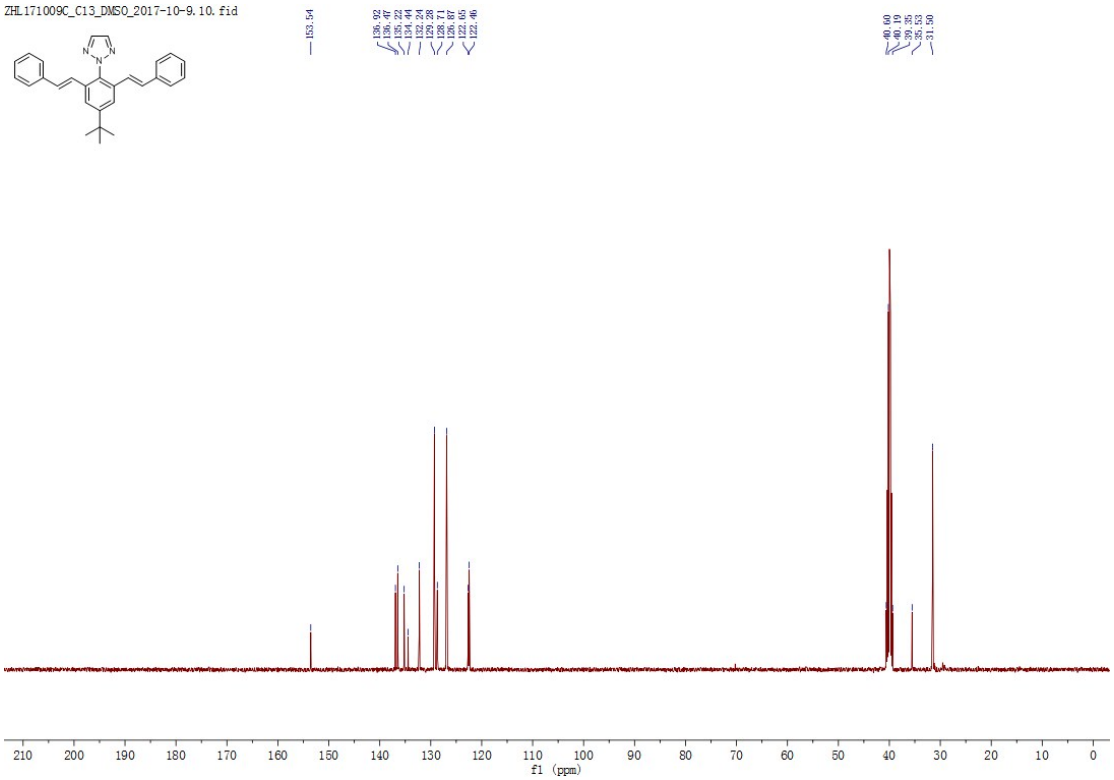
2-(4-(tert-butyl)-2,6-di((*E*)-styryl)phenyl)-2*H*-1,2,3-triazole



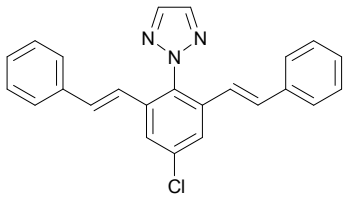
3c'

White solid, yield 91 %, mp 178-180 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.24 (s, 2H), 7.89 (s, 2H), 7.28 (m, 12H), 6.22 (d, *J*=16.2Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (150MHz, DMSO): δ 153.5, 137.0, 136.5, 135.3, 134.4, 132.2, 129.3, 128.7, 126.8, 122.6, 122.5, 35.3, 31.5; HRMS (ESI) Calcd. For $C_{28}H_{27}N_3Na$:428.2103, Found: m/z 428.2101.



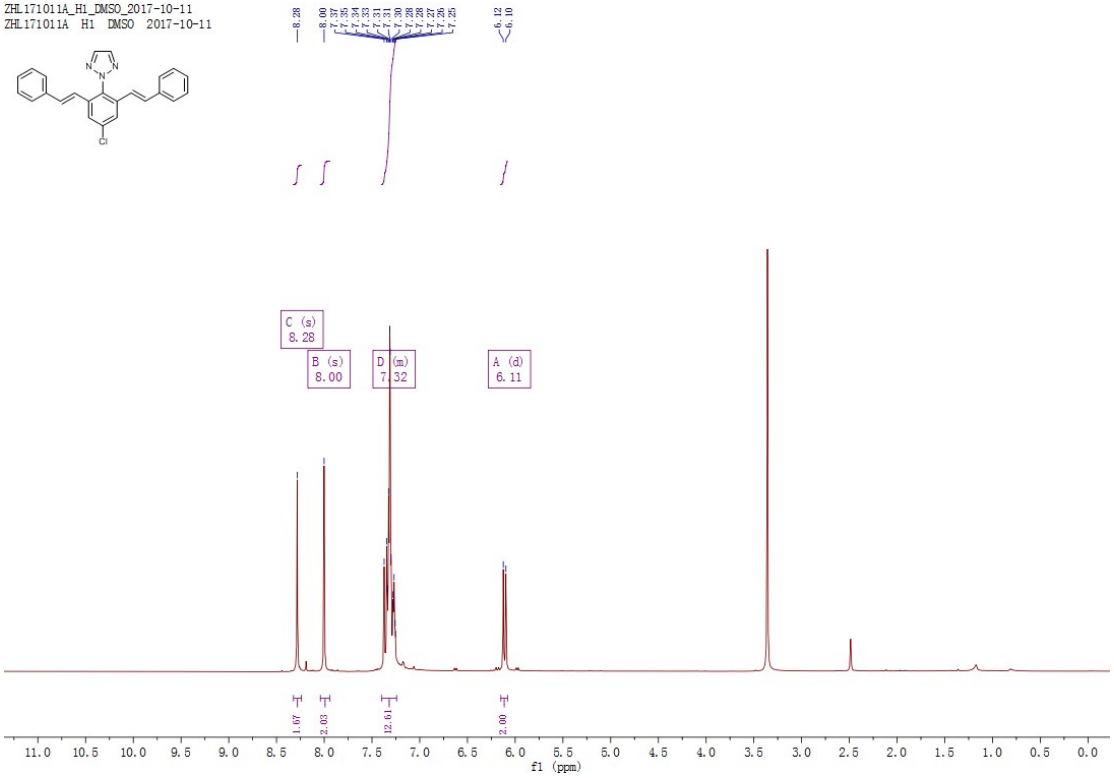


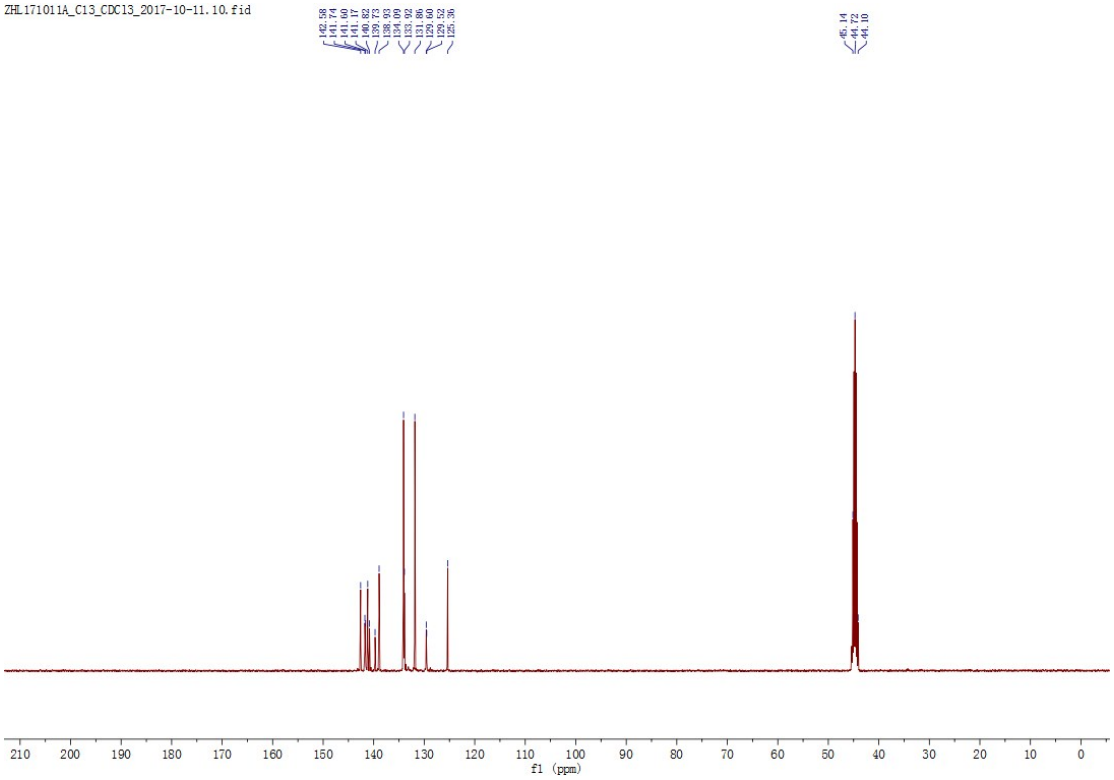
2-(4-chloro-2,6-di((*E*)-styryl)phenyl)-2*H*-1,2,3-triazole



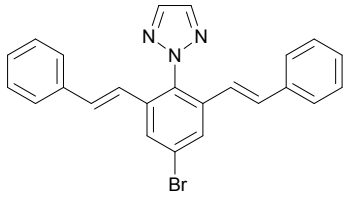
3d'

White solid, yield 79 %, mp 132-134 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.30 (s, 2H), 8.00 (s, 2H), 7.31 (m, 12H), 6.11 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, DMSO): δ 142.6, 141.8, 141.6, 141.2, 140.3, 139.7, 138.9, 134.1, 131.9, 129.5, 125.4; HRMS (ESI) Calcd. For $C_{24}H_{18}N_3ClNa$:406.1087, Found: m/z 406.1086.



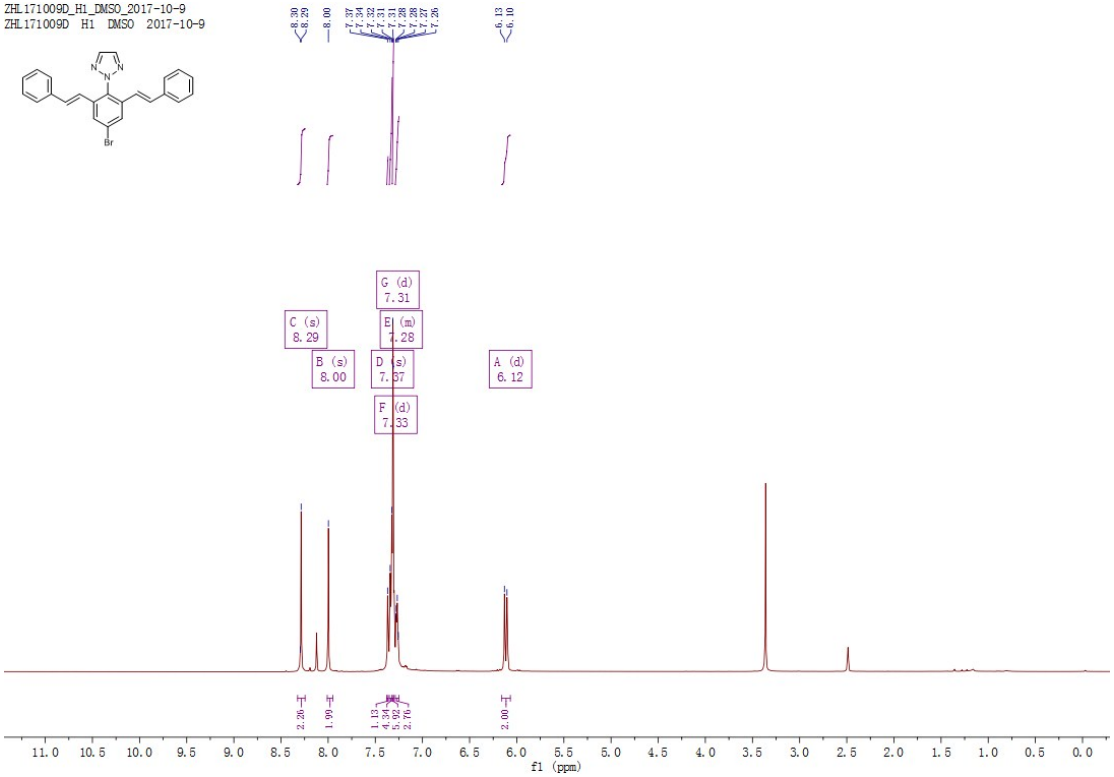


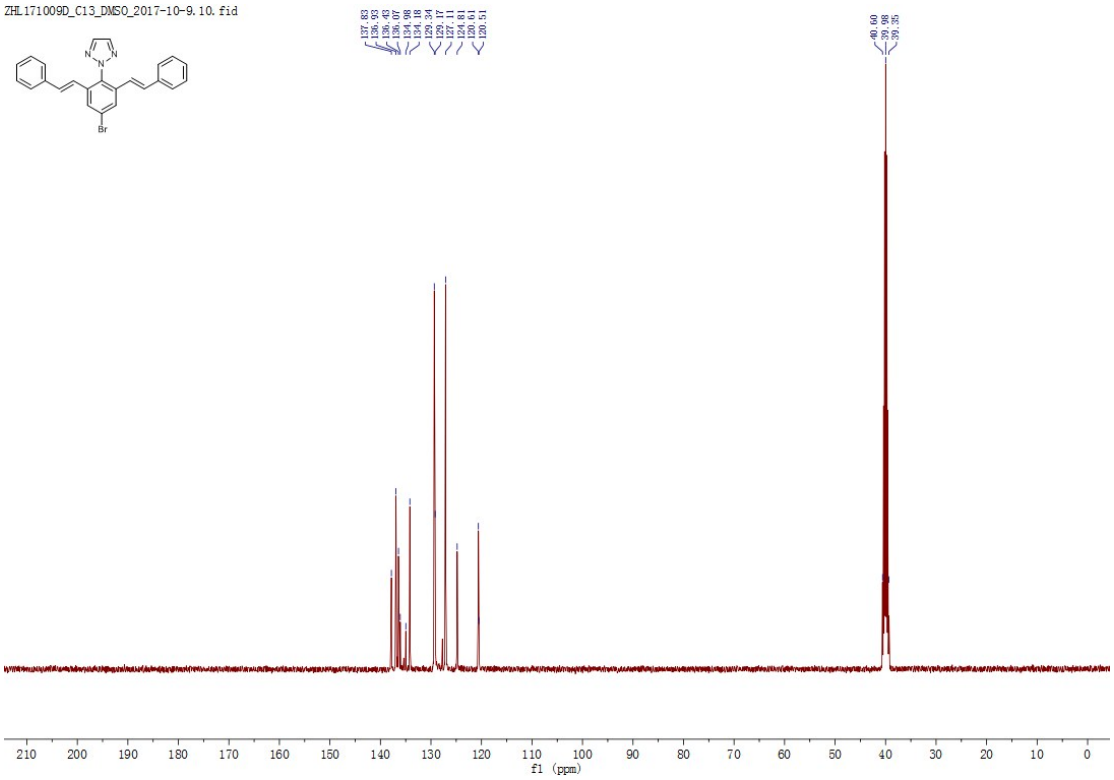
2-(4-bromo-2,6-di((*E*)-styryl)phenyl)-2*H*-1,2,3-triazole



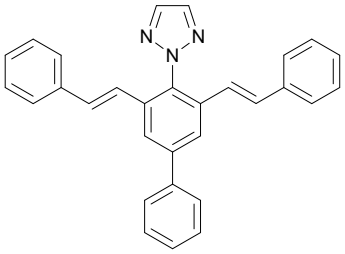
3e'

White solid, yield 72 %, mp 164-166 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.29 (s, 2H), 8.00 (s, 2H), 7.32 (m, 12H), 6.11 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, DMSO): δ 137.8, 136.9, 136.4, 136.1, 135.0, 134.2, 129.3, 129.3, 127.1, 124.8, 120.6, 122.6; HRMS (ESI) Calcd. For $C_{24}H_{18}N_3BrNa$:450.0582, Found: m/z 450.0582.



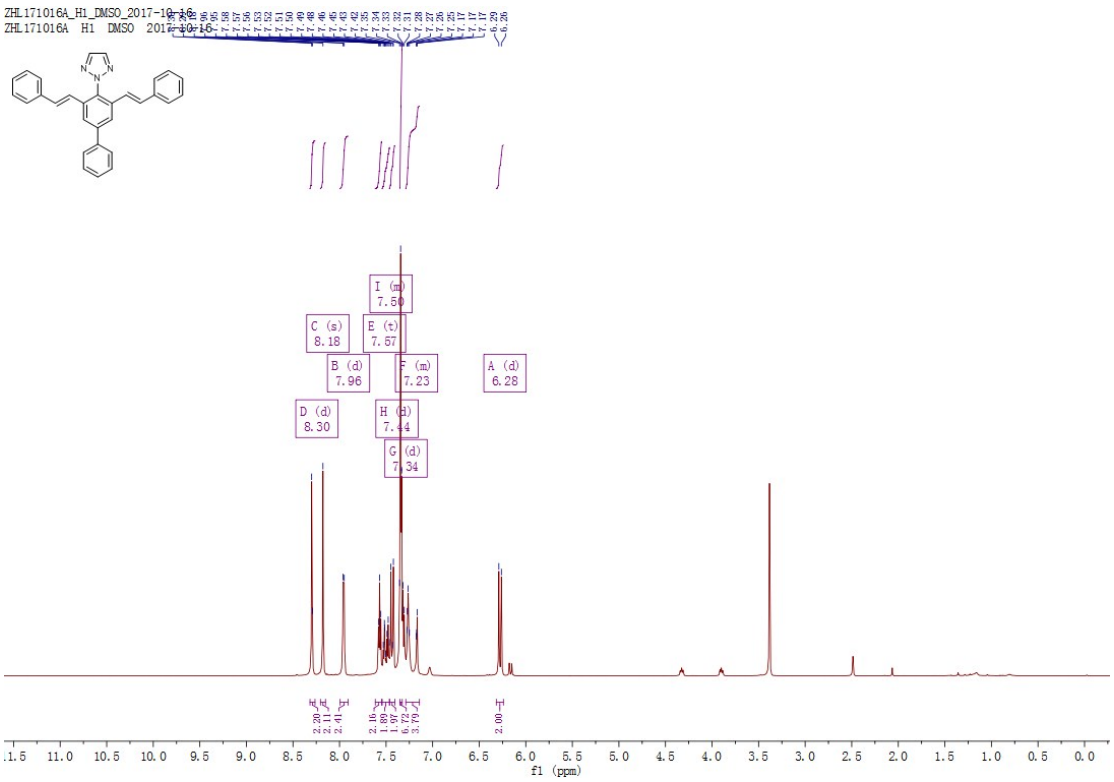


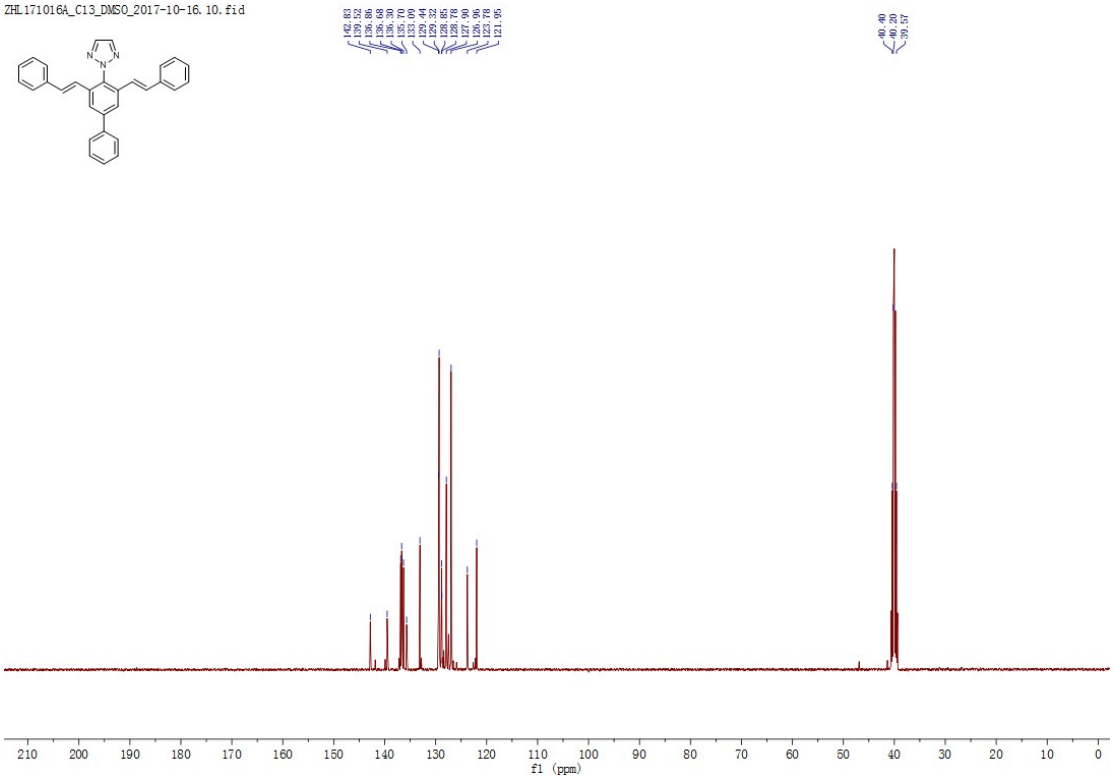
2-(3,5-di((*E*)-styryl)-[1,1'-biphenyl]-4-yl)-2*H*-1,2,3-triazole



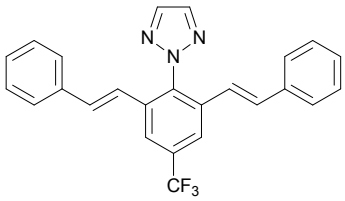
3f'

Light yellow solid, yield 76 %, mp 166-168 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.30 (s, 2H), 8.18 (s, 2H), 7.95 (d, *J*=8.4Hz, 2H), 7.57 (t, *J*=8.4Hz, 2H), 7.43 (d, *J*=16.2Hz, 2H), 7.35 (m, 9H), 7.26 (m, 2H), 6.27 (s, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, DMSO): δ 142.9, 139.5, 136.9, 136.7, 136.3, 135.7, 133.1, 129.4, 128.9, 128.8, 127.9, 126.9, 123.8, 122.0; HRMS (ESI) Calcd. For $C_{30}H_{23}N_3Na$:448.1790, Found: m/z 448.1788.



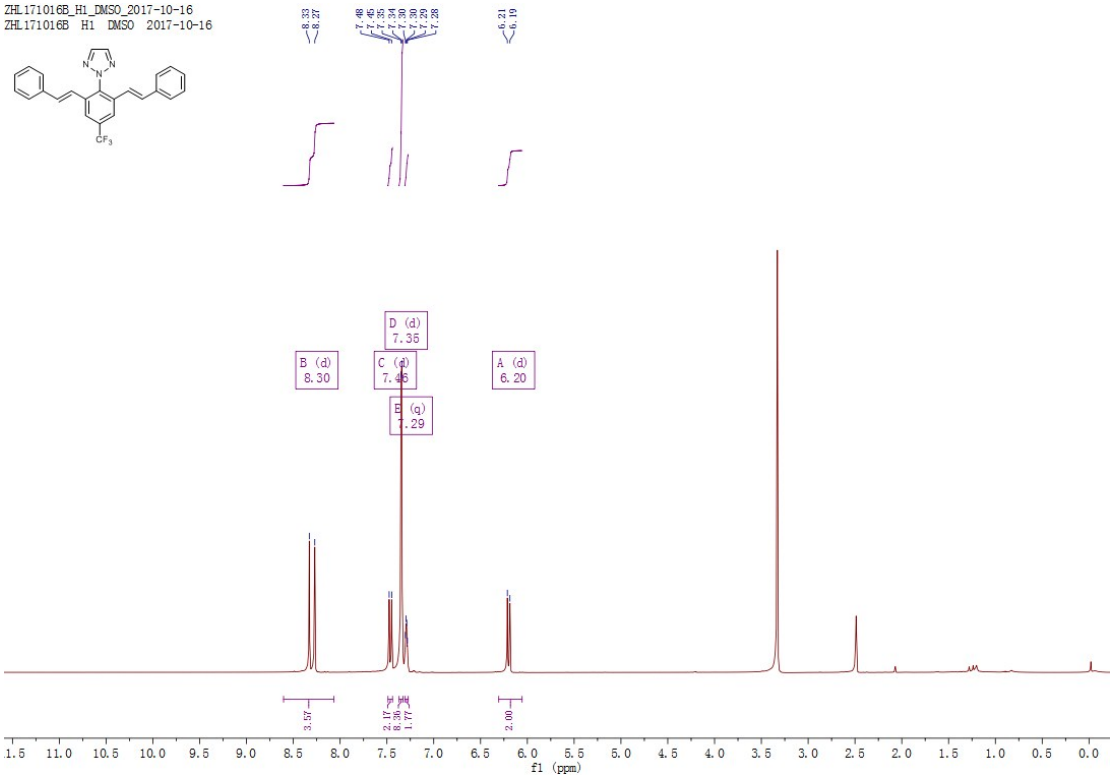


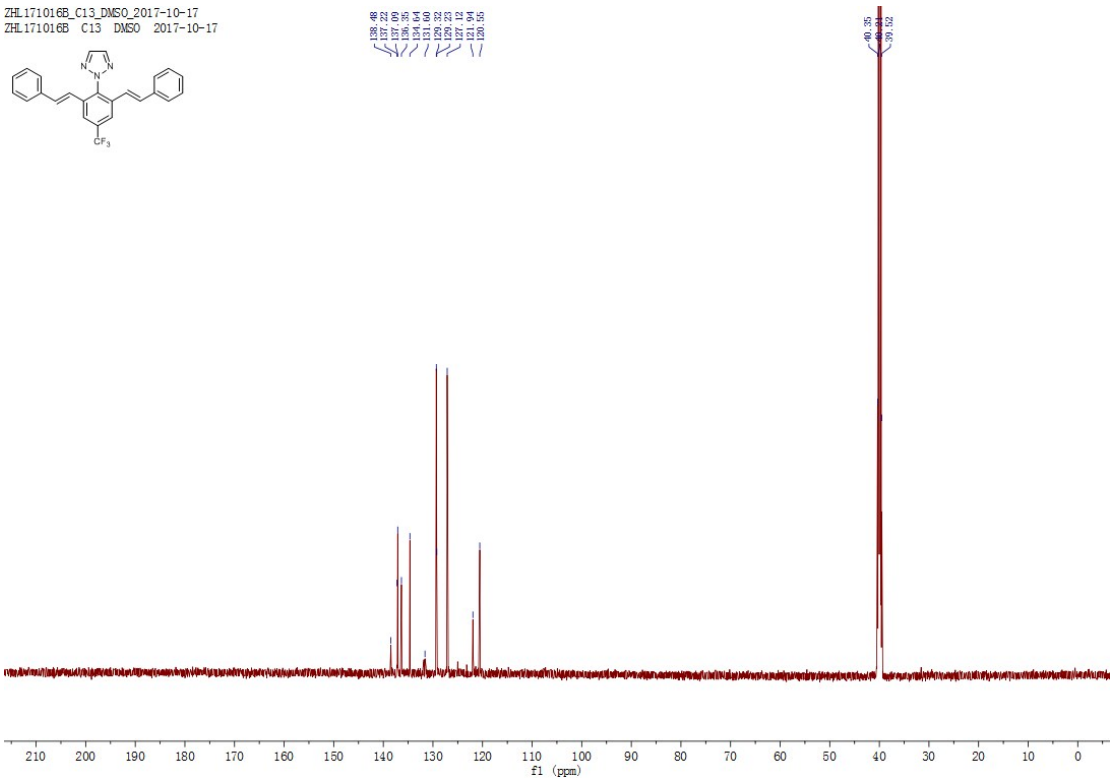
2-(2,6-di((*E*)-styryl)-4-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole

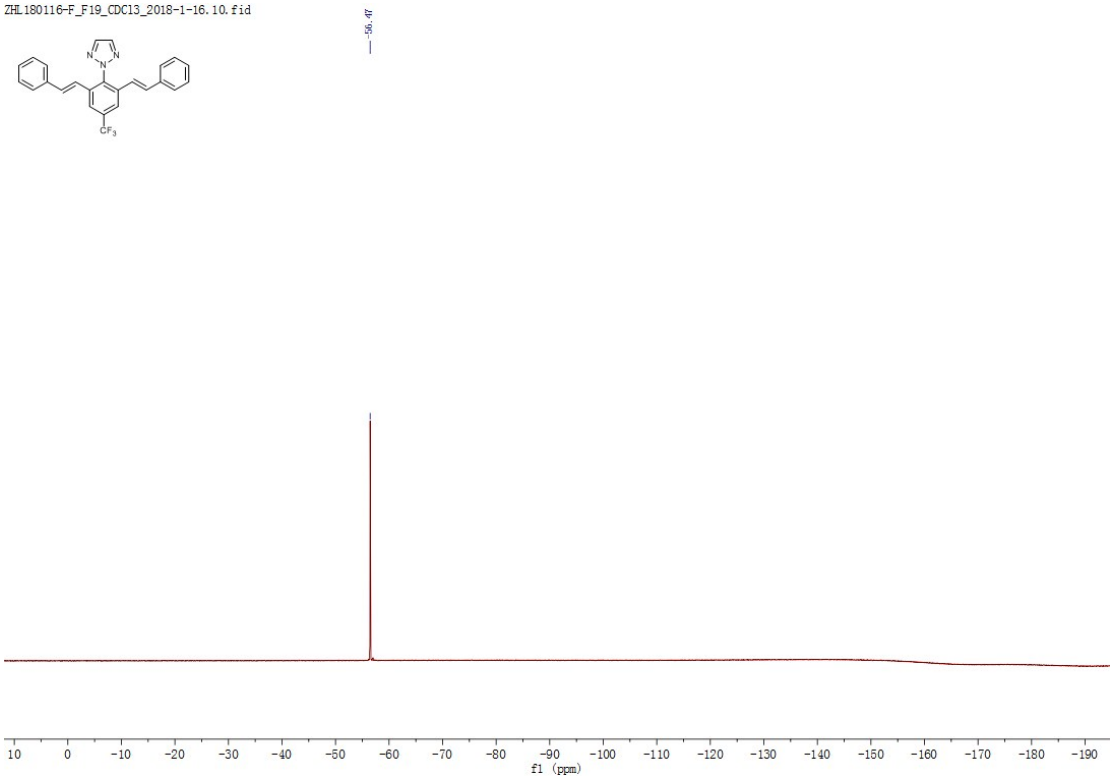


3g'

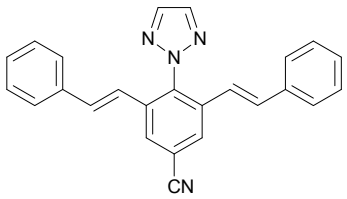
Light yellow solid, yield 59 %, mp 186-190 °C, ^{1}HNMR (600MHz, DMSO): δ 8.30 (d, *J*=8.4Hz, 4H), 7.47 (d, *J*=16.2Hz, 2H), 7.33 (m, 10H), 6.20 (d, *J* =16.2Hz, 2H); ^{13}C NMR (150MHz, DMSO): δ 138.5, 137.3, 137.1, 136.3, 134.6, 129.3, 129.2, 127.1, 121.9, 120.5; ^{19}F NMR (376MHz, DMSO): -56.39; HRMS (ESI) Calcd. For $C_{25}H_{18}N_3F_3Na$:417.1453, Found: m/z 417.1452.





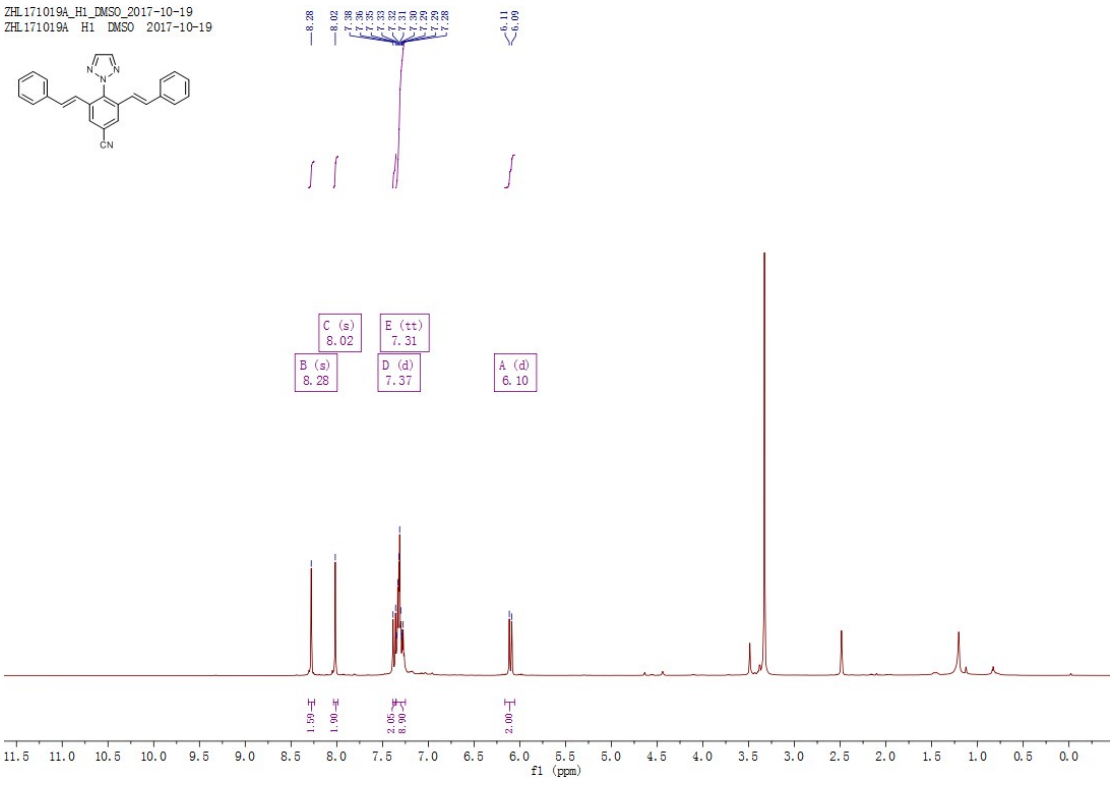


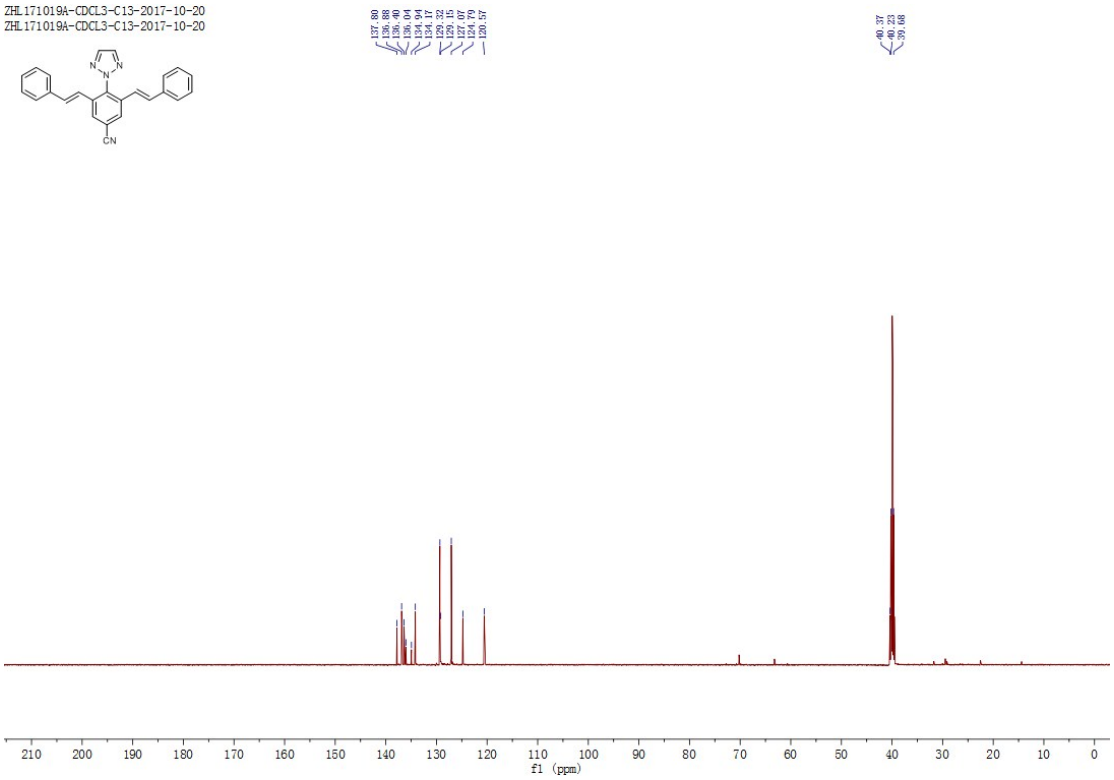
3,5-di((*E*)-styryl)-4-(2*H*-1,2,3-triazol-2-yl)benzonitrile



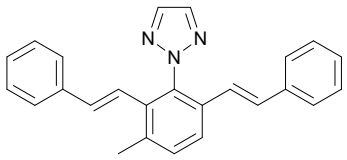
3h'

Light yellow solid, yield 83 %, mp 168-170 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.28 (s, 4H), 8.03 (s, 2H), 7.32 (m, 12H), 6.10 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, DMSO): δ 137.8, 136.9, 136.4, 136.1, 134.2, 129.3, 129.2, 127.1, 124.8, 120.6; HRMS (ESI) Calcd. For $C_{25}H_{18}N_4Na$:397.1429, Found: m/z 397.1429.



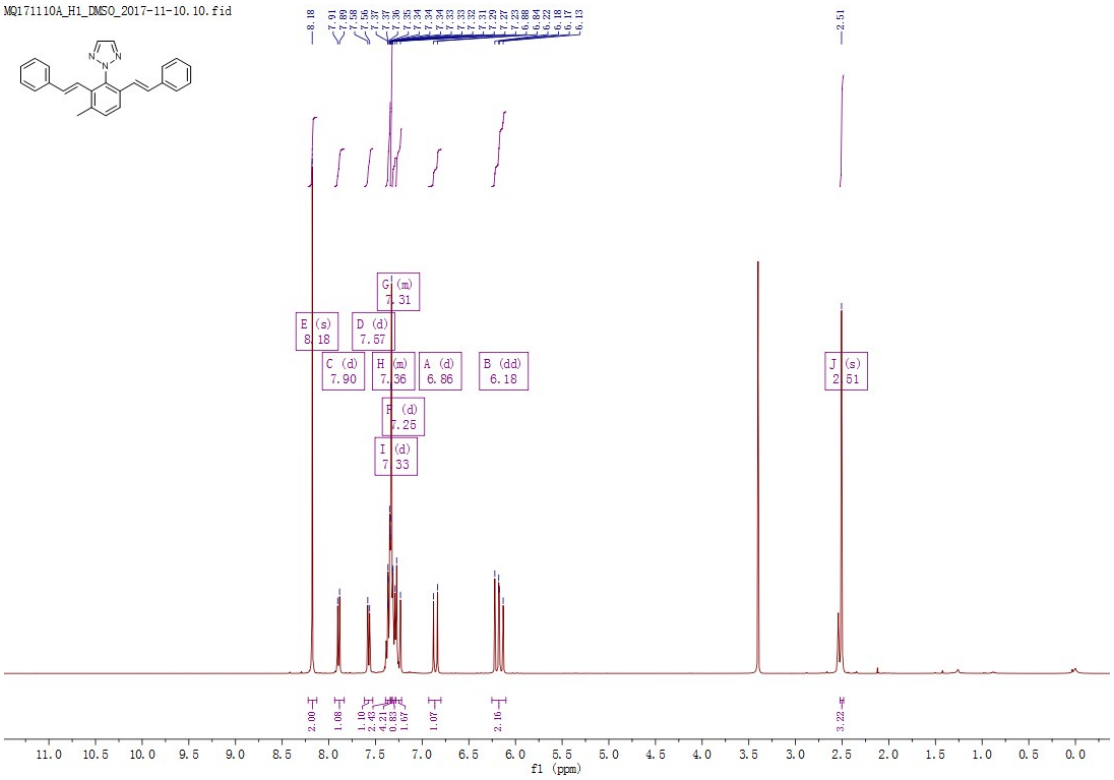


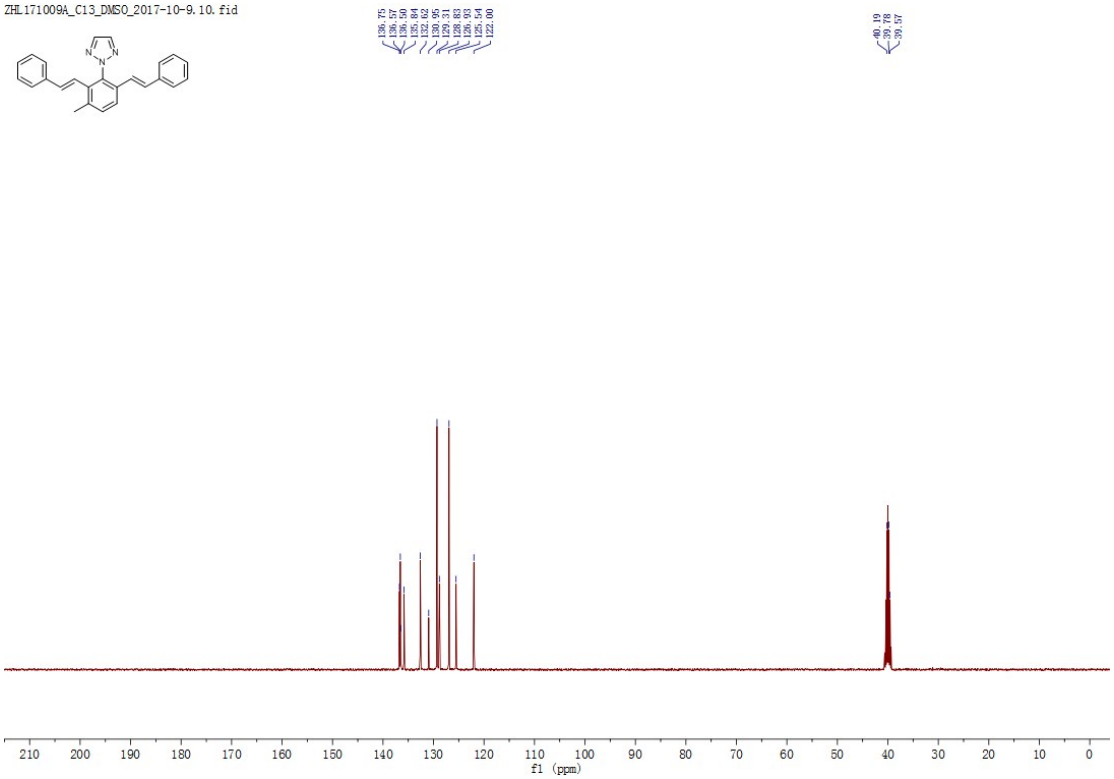
(*E*)-2-(5-methyl-2-styrylphenyl)-2*H*-1,2,3-triazole



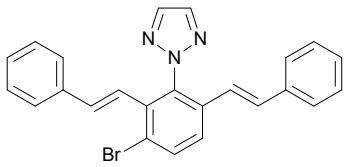
3j'

Light yellow solid, yield 82 %, mp 136-138 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.18 (s, 2H), 7.90 (d, *J*=8.4Hz, 1H), 7.57 (d, *J*=12.0Hz, 1H), 7.33 (m, 11H), 6.85 (d, *J*=16.2Hz, 1H), 6.18 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, DMSO): δ 137.5, 137.0, 136.9, 136.0, 135.8, 134.0, 133.5, 132.6, 131.5, 129.3, 129.1, 128.7, 128.5, 126.8, 126.7, 124.6, 122.9, 122.1, 21.0; HRMS (ESI) Calcd. For $C_{25}H_{21}N_3Na$: 386.1633, Found: m/z 386.1631.



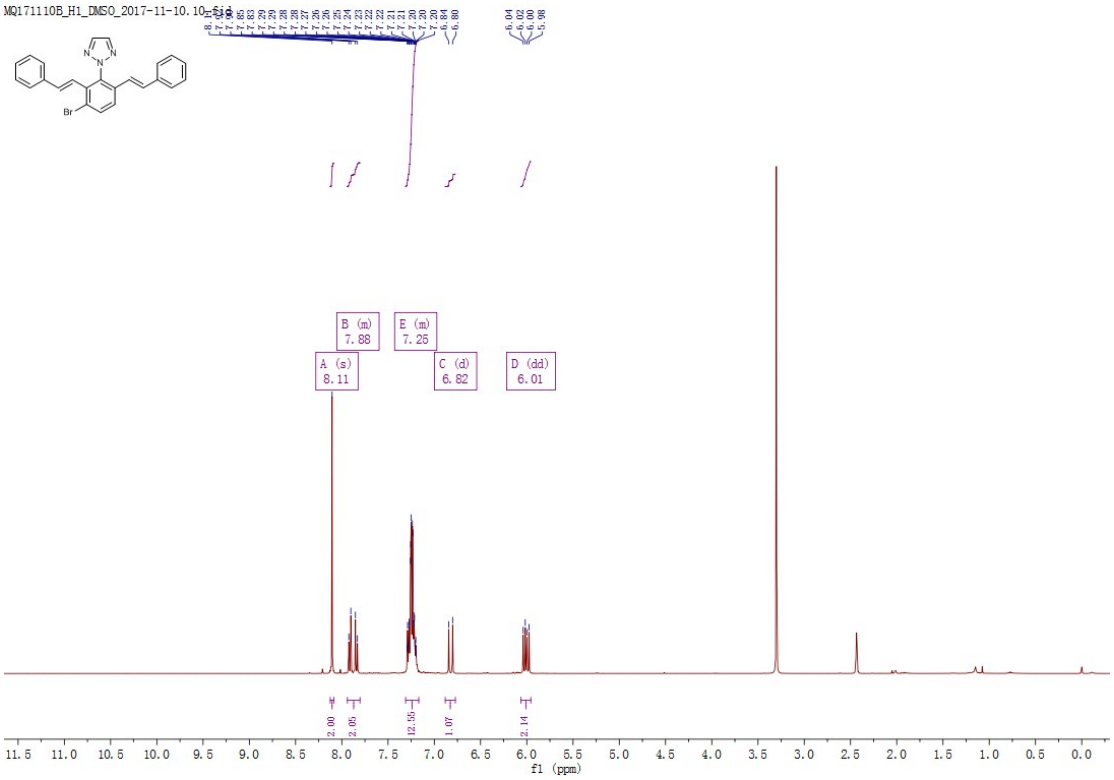


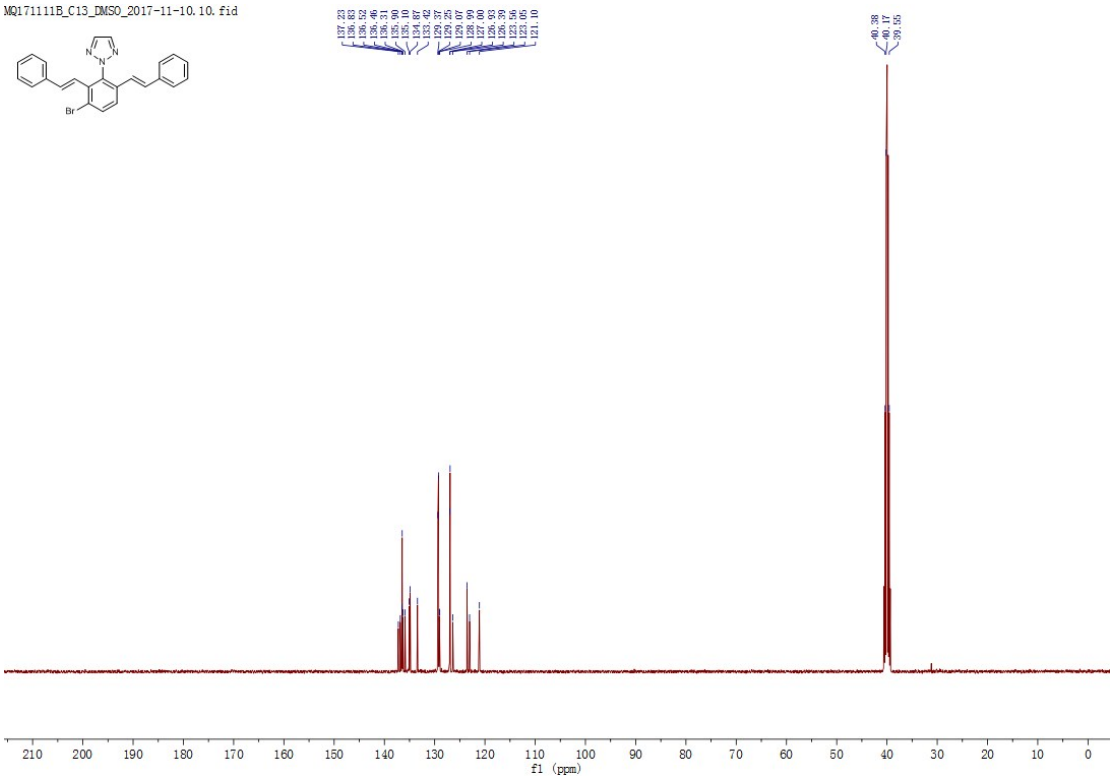
2-(3-bromo-2,6-di((*E*)-styryl)phenyl)-2*H*-1,2,3-triazole



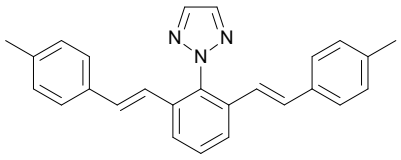
3k'

White solid, yield 71 %, mp 132-134 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.11 (s, 2H), 7.91 (d, *J*=8.4Hz, 1H), 7.84 (d, *J*=8.4Hz, 1H), 7.24 (m, 11H), 6.82 (d, *J*=16.2Hz, 1H), 6.01 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, DMSO): δ 137.2, 136.8, 136.5, 136.4, 136.3, 135.9, 135.1, 134.9, 133.4, 129.4, 129.3, 129.1, 129.0, 127.0, 126.9, 126.4, 123.6, 123.0, 121.1; HRMS (ESI) Calcd. For $C_{24}H_{18}BrN_3Na$: 450.0582, Found: m/z 450.0582.



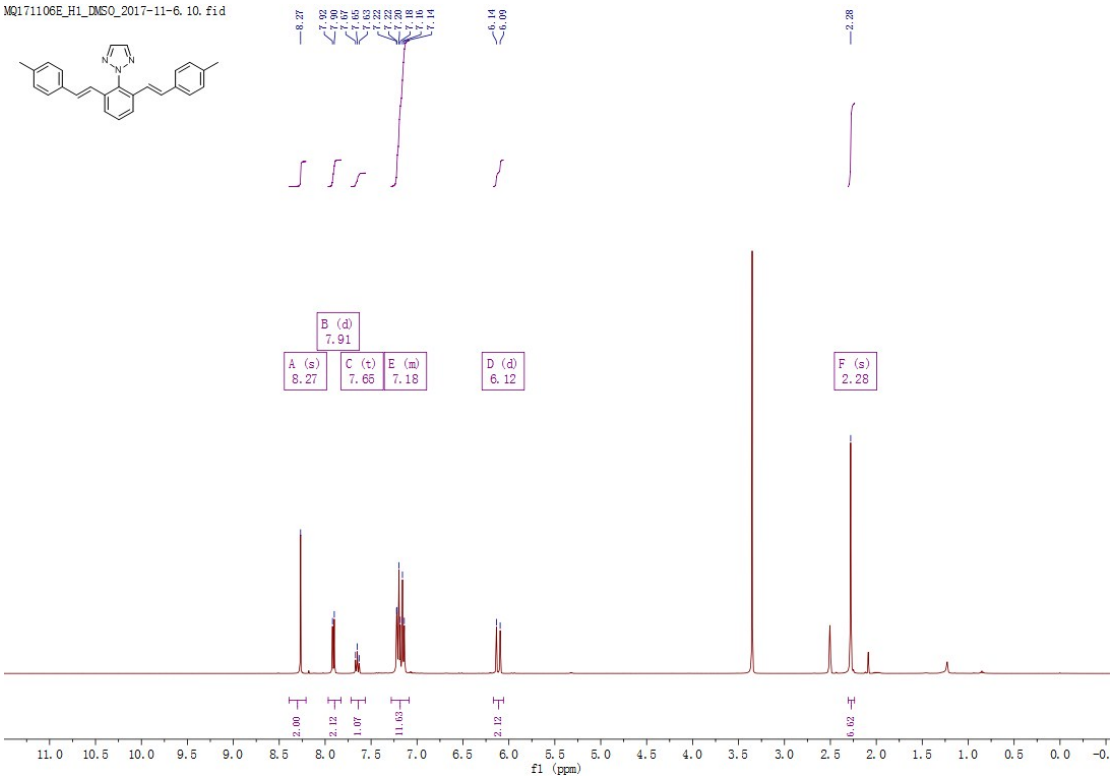


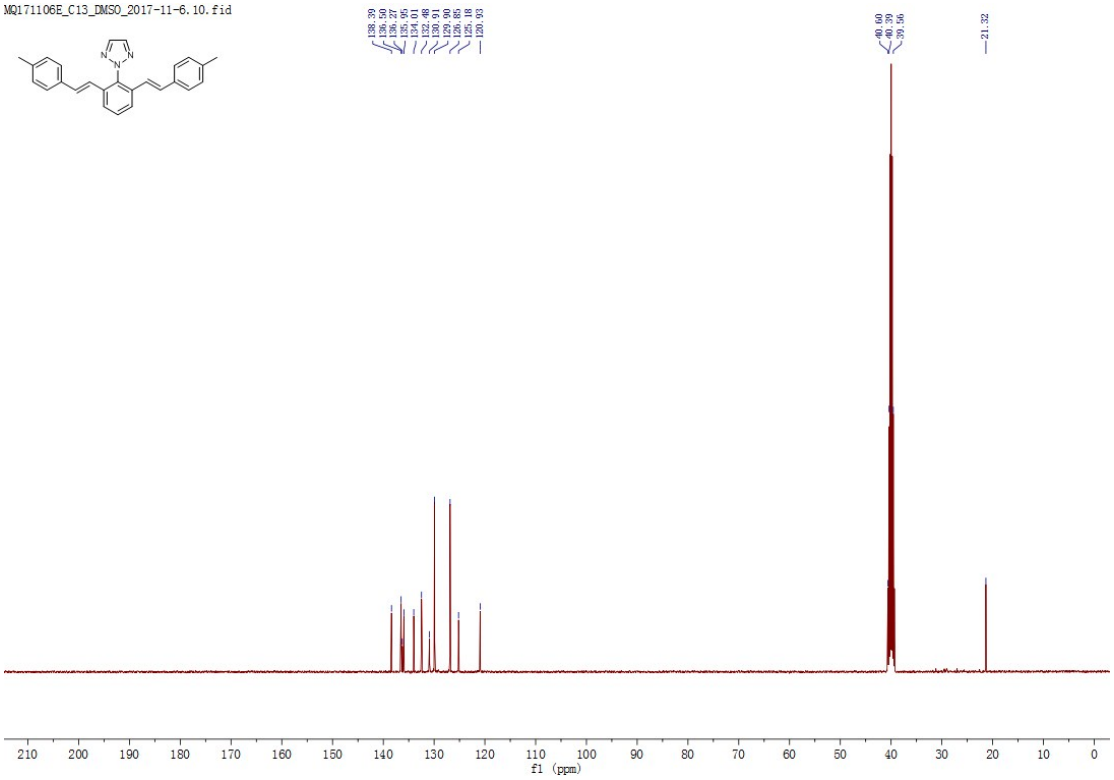
2-(2,6-bis((*E*)-4-methylstyryl)phenyl)-2*H*-1,2,3-triazole



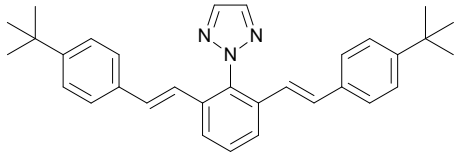
3n'

White solid, yield 82 %, mp >200 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.26 (s, 2H), 7.91 (d, *J*=8.4Hz, 2H), 7.65 (t, *J*=8.4Hz, 1H), 7.18 (m, 10H), 6.12 (d, *J*=16.2Hz, 2H), 2.28 (s, 6H); ^{13}C NMR (150MHz, DMSO): δ 138.4, 136.5, 136.3, 136.0, 134.0, 132.5, 130.9, 129.9, 126.9, 125.2, 120.9, 21.2; HRMS (ESI) Calcd. For $C_{26}H_{23}N_3Na$: 400.1790, Found: m/z 400.1788.



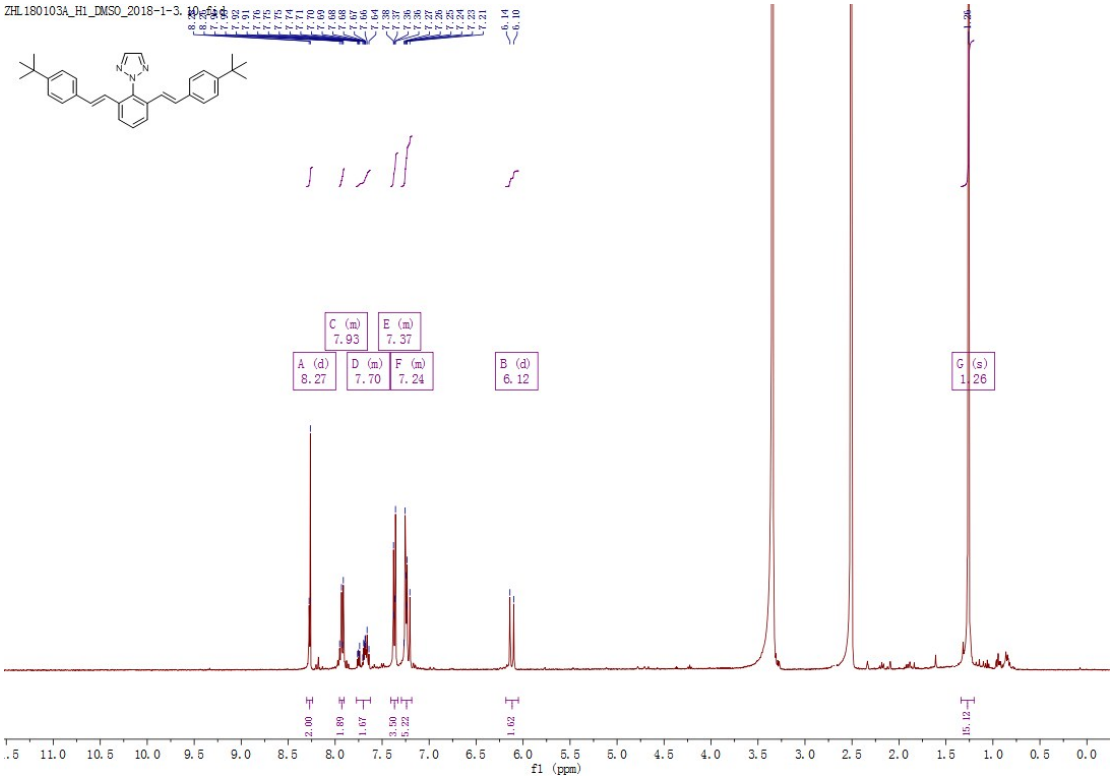


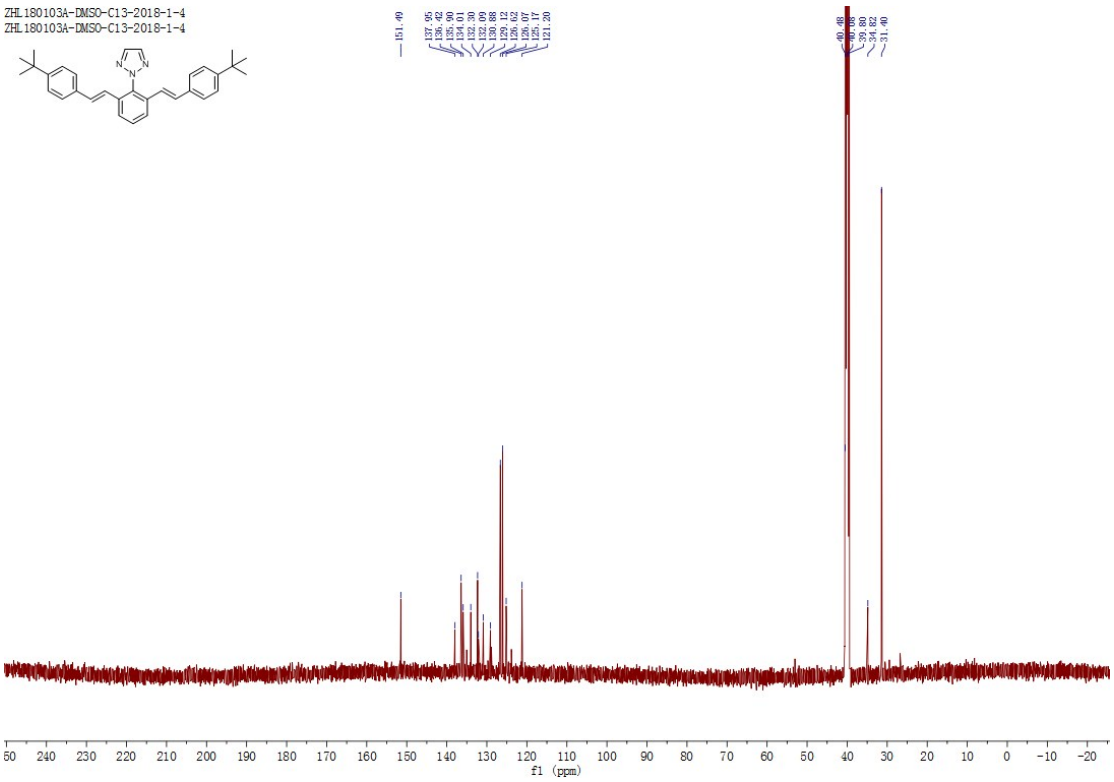
2-(2,6-bis((E)-4-(tert-butyl)styryl)phenyl)-2*H*-1,2,3-triazole



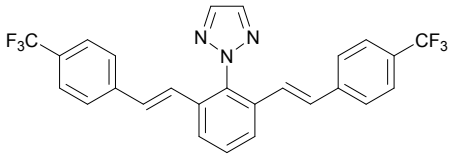
3o'

White solid, yield 79 %, mp 138-140 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.27 (s, 2H), 7.92 (d, *J*=8.4Hz, 2H), 7.69 (m, 2H), 7.39 (d, *J*=8.4Hz, 4H), 7.25 (d, *J*=8.4Hz, 3H) 7.22 (d, *J*=16.2Hz, 2H), 6.12 (d, *J*=16.2Hz, 2H), 1.28 (s, 18H); ^{13}C NMR (150MHz, DMSO): δ 151.5, 138.0, 136.4, 136.3, 135.9, 134.0, 132.3, 132.1, 130.9, 129.1, 128.9,126.6, 126.1, 125.2, 123.9, 121.2, 34.8, 31.4; HRMS (ESI) Calcd. For $C_{32}H_{35}N_3Na$: 484.2729, Found: m/z 484.2728.





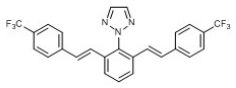
2-(2,6-bis((E)-4-(trifluoromethyl)styryl)phenyl)-2*H*-1,2,3-triazole

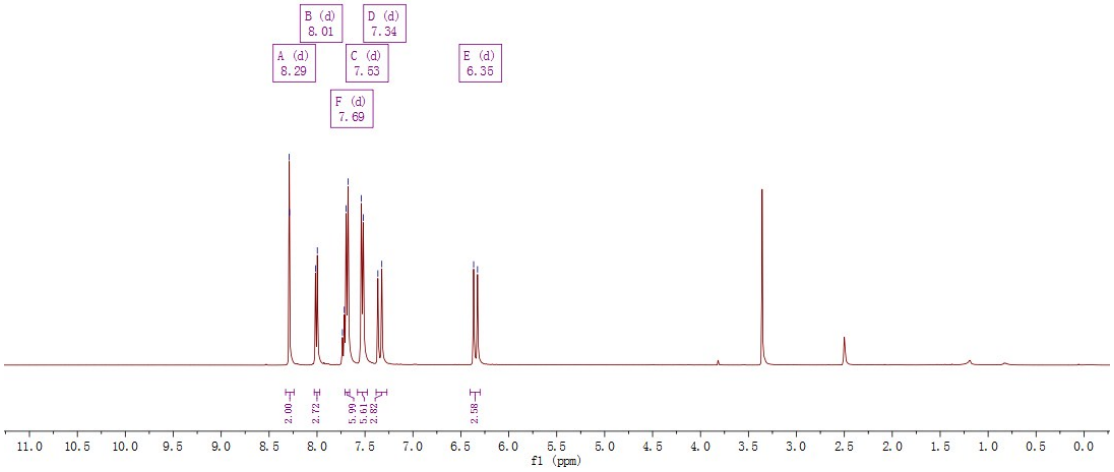


3p'

White solid, yield 61 %, mp 178-180 °C, ^{1}HNMR (600MHz, DMSO): δ 8.28 (s, 2H), 7.99 (d, *J*=8.4Hz, 2H), 7.68 (m, 5H), 7.54d, (*J*=8.4Hz, 4H), 7.35 (d, *J*=16.2Hz, 2H), 6.34 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, DMSO): δ 140.8, 136.9, 136.8, 135.4, 131.3, 129.1, 128.8, 128.7, 128.5, 128.2, 127.5,,126.5, 126.3, 126.2, 126.1, 126.0, 124.8, 123.3; ^{19}F NMR (376MHz, DMSO): -61.00; HRMS (ESI) Calcd. For $C_{26}H_{17}F_6N_3Na$: 508.1224, Found: m/z 508.1224.

ZHL180104E-DMSO-H1-2017-1-4





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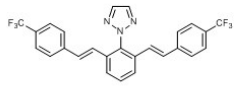
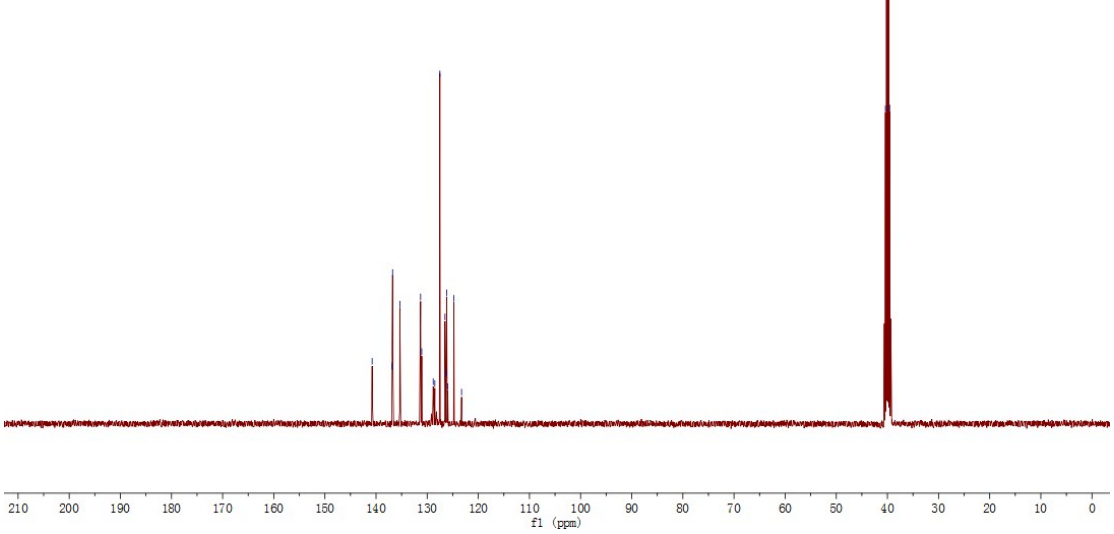
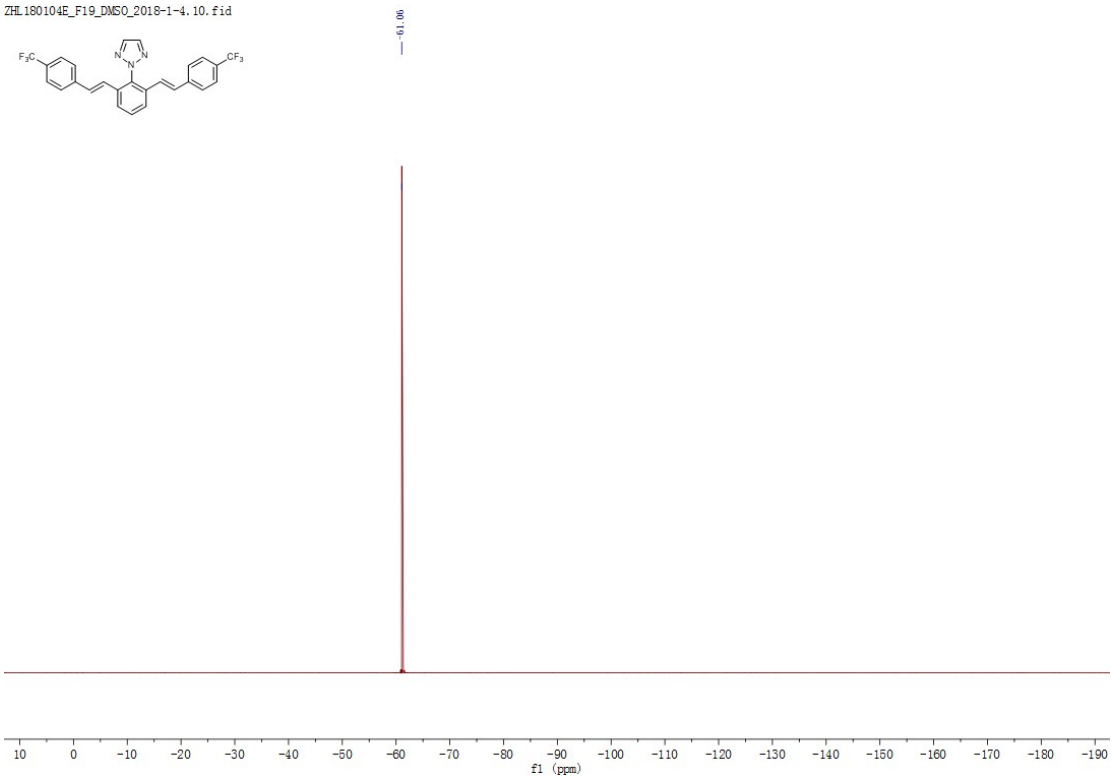
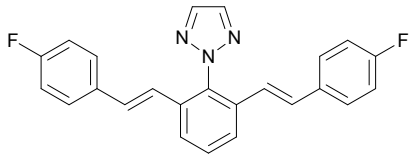






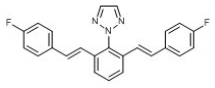
2-(2,6-bis((E)-4-fluorostyryl)phenyl)-2*H*-1,2,3-triazole

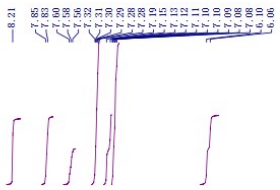


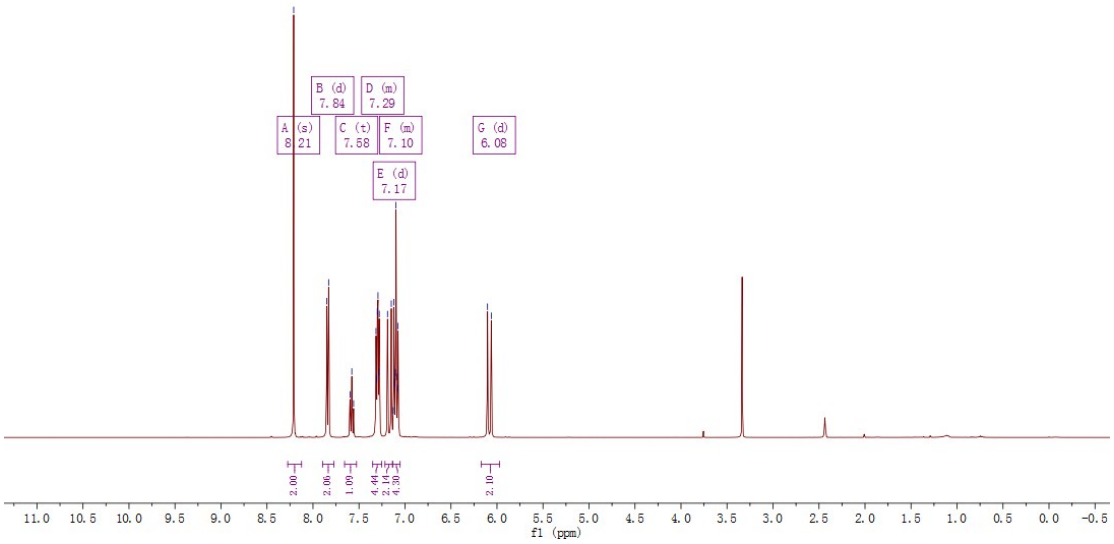
3q'

White solid, yield 80 %, mp150-152 ^{o}C, ^{1}HNMR (600MHz, DMSO): δ 8.21 (s, 2H), 7.84 (d, *J*=8.4Hz, 2H), 7.58 (t, *J*=8.4Hz, 1H), 7.30 (m, 4H), 7.17 (d, *J*=16.2Hz, 2H), 7.10.28 (t, *J*=8.4Hz, 4H), 6.08 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, DMSO): δ 163.8, 161.4, 136.6, 135.8, 133.3, 131.4, 130.9, 128.9, 125.4, 122.0, 116.4, 116.0; ^{19}F NMR (376MHz, DMSO): -113.08; HRMS (ESI) Calcd. For $C_{24}H_{17}F_2N_3Na$: 408.1228, Found: m/z 408.1228.

ZHL180103B_H1_DMSO_2018-1-3.10.fid







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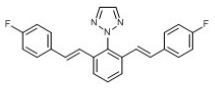
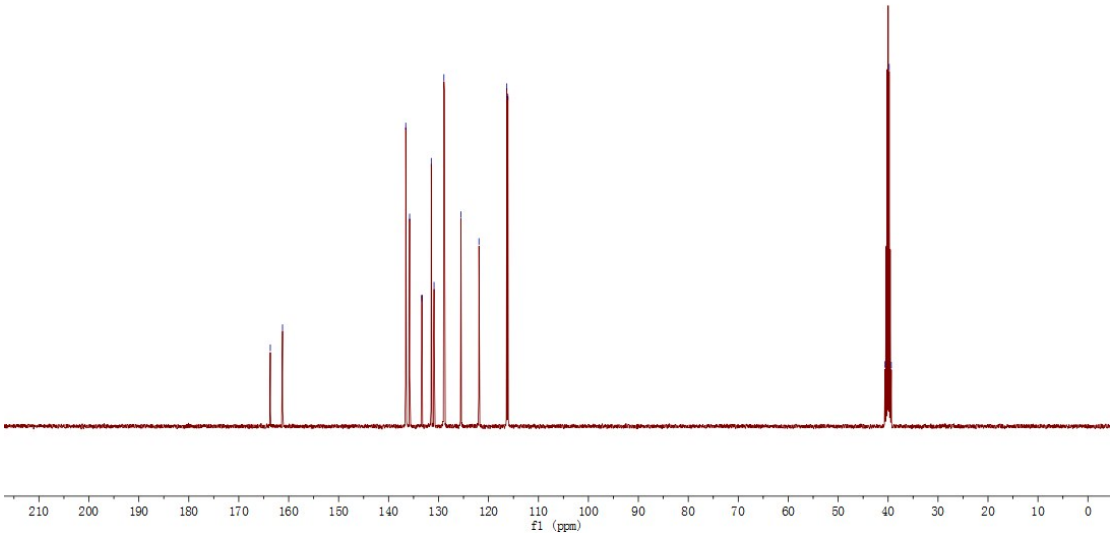
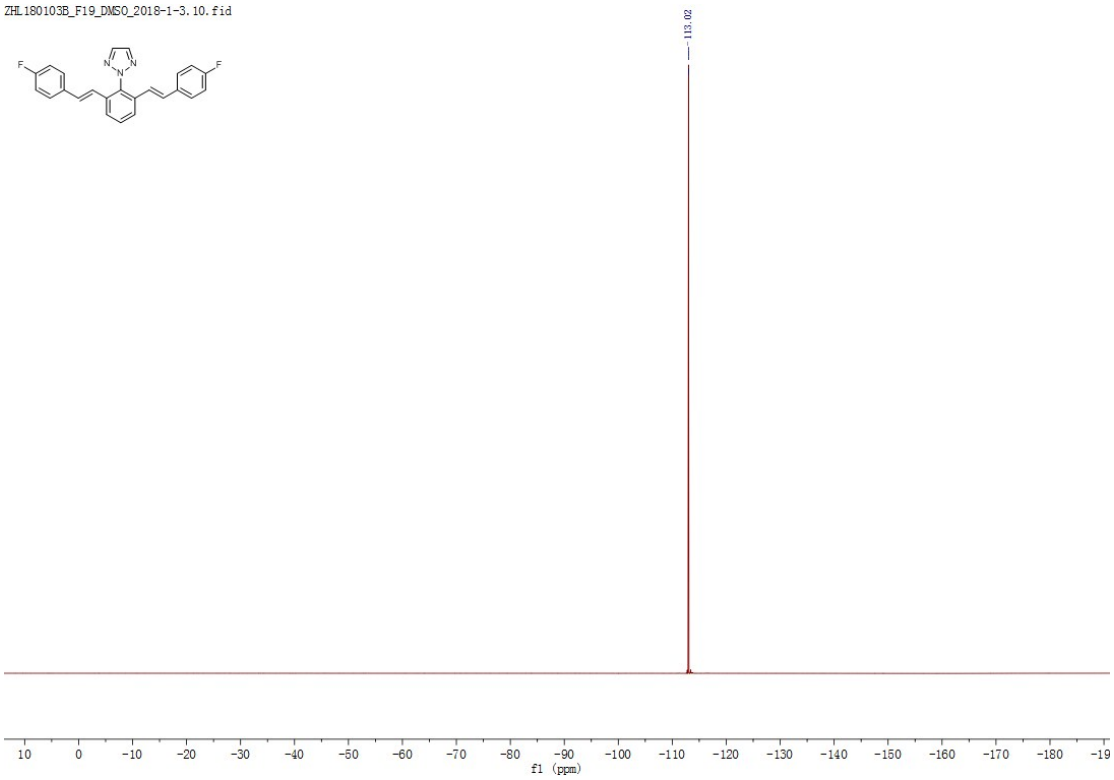
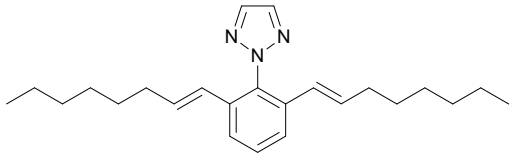




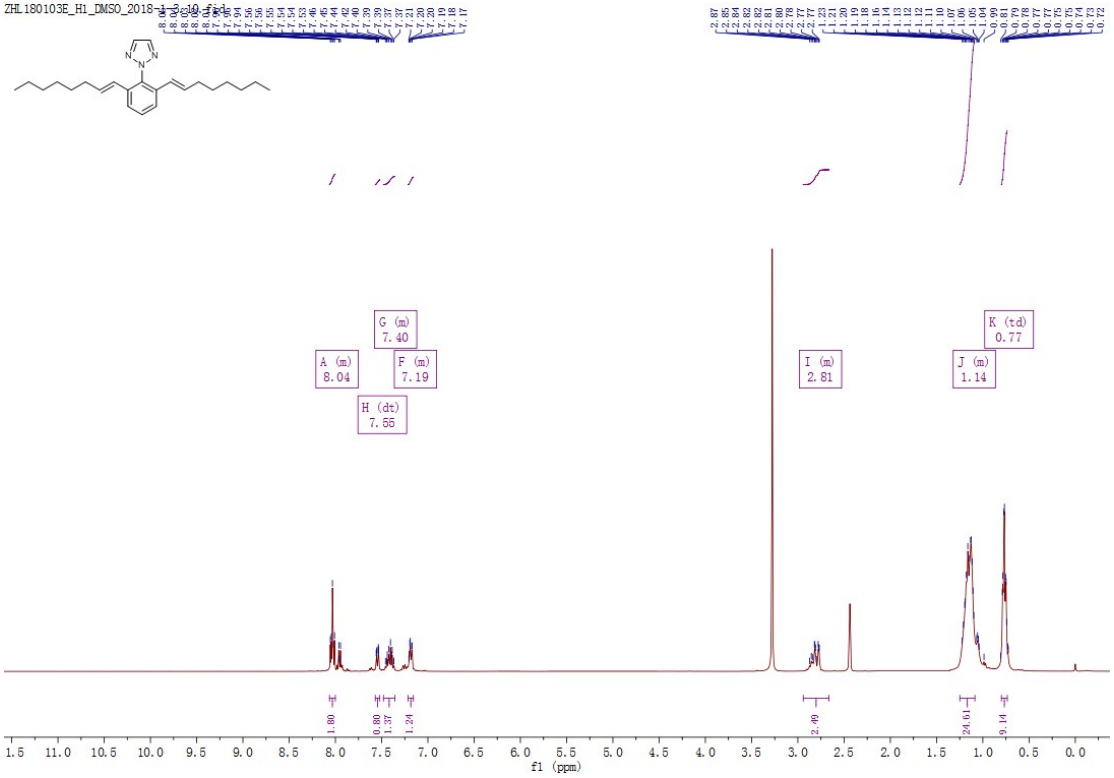


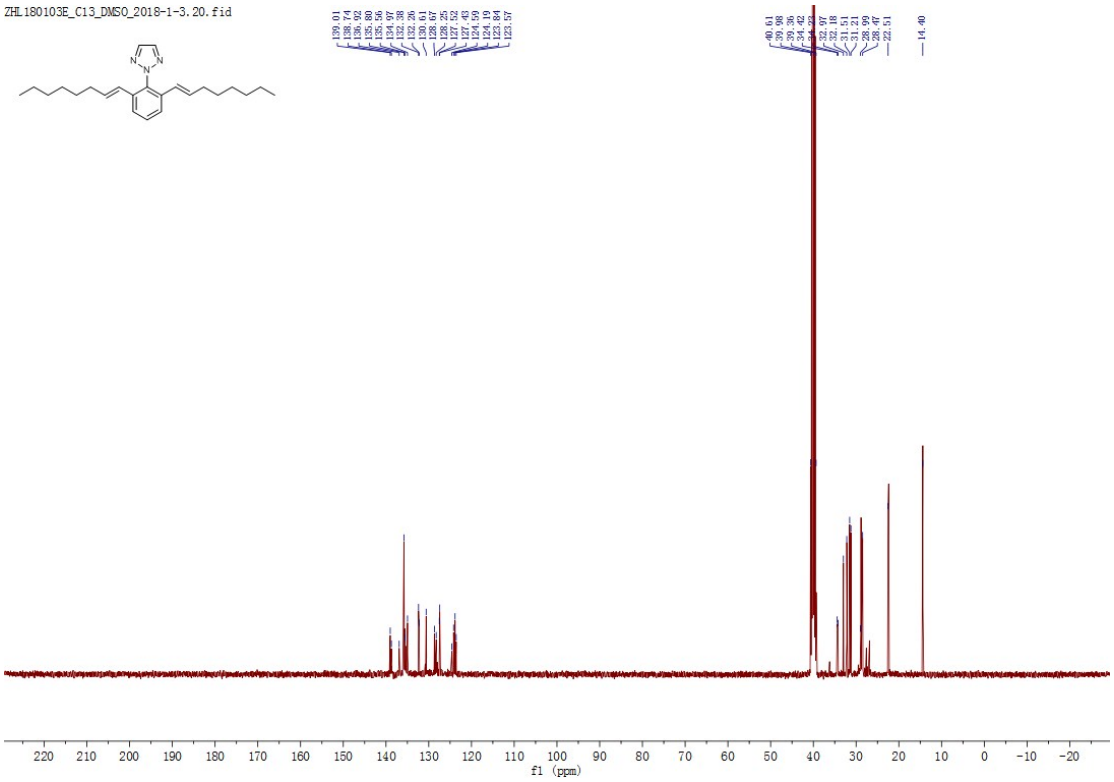
2-(2,6-di((*E*)-oct-1-en-1-yl)phenyl)-2*H*-1,2,3-triazole



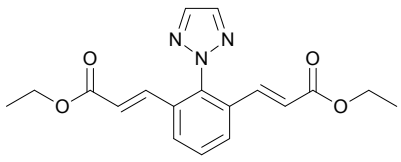
3s'

White solid, yield 58 %, mp >230 ^{o}C, ^{1}HNMR (600MHz, $CDCl_3$): δ 8.04 (s, 2H), 7.96 (t, *J*=8.4Hz, 1H), 7.42 (m, 2H), 7.18 (d, *J*=8.4Hz, 2H), 6.15 (m, 2H), 1.84 (m, 4H), 1.13 (m, 16H), 0.77 (m, 6H); ^{13}C NMR (150MHz, $CDCl_3$): δ 136.0, 135.7, 135.6, 135.4, 135.3, 135.2, 135.0, 132.4, 132.3, 131.3, 130.8, 130.6, 130.5, 129.3, 128.7, 29.5, 28.9, 28.7, 28.6, 28.5, 27.6, 22.5, 21.4; HRMS (ESI) Calcd. For $C_{22}H_{27}N_3O_4Na$: 420.1899, Found: m/z420.1898.



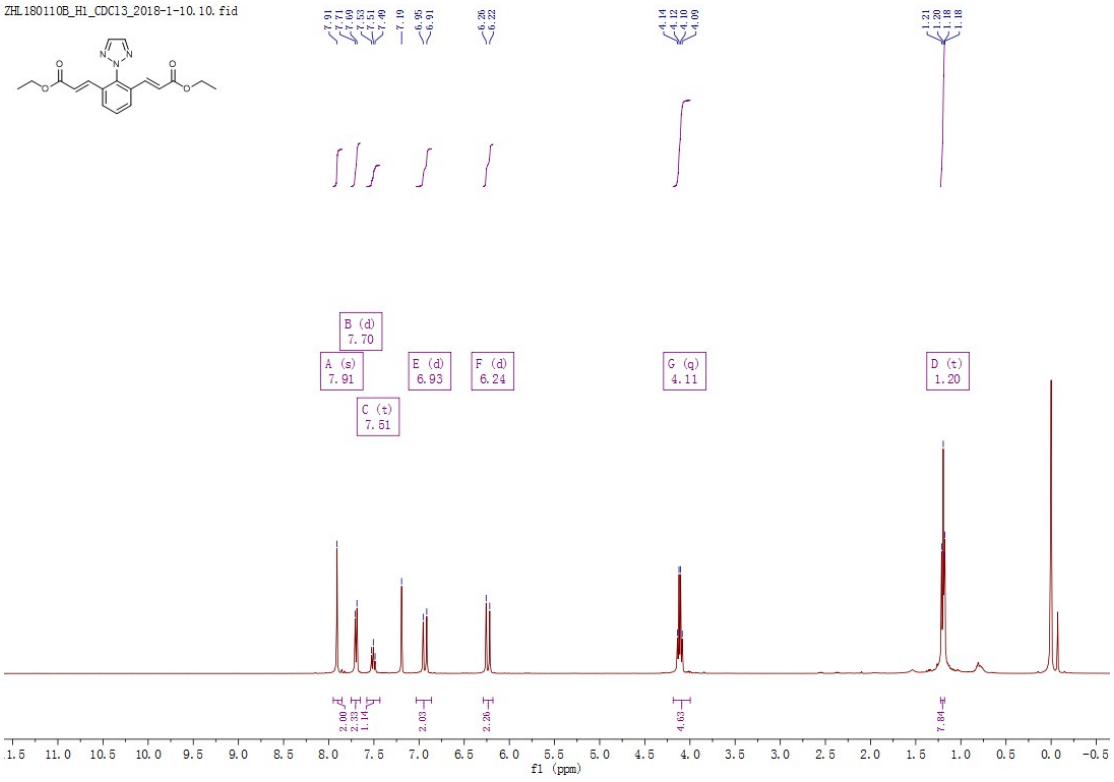


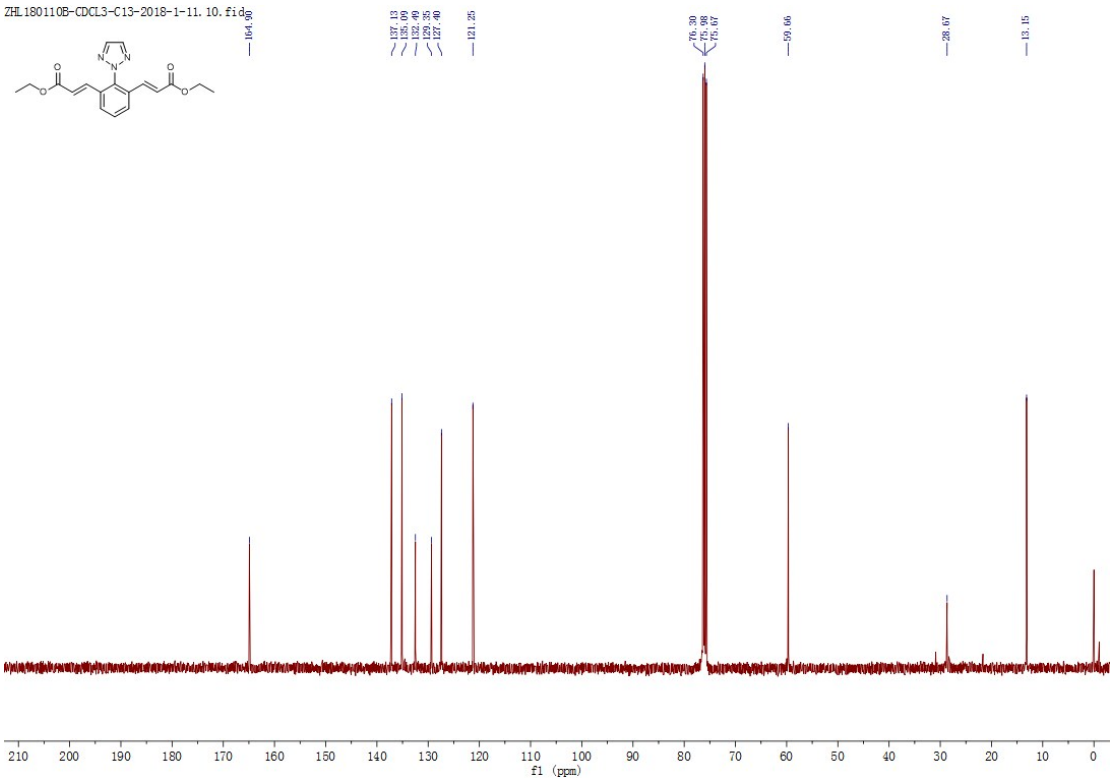
(2E,2'E)-diethyl 3,3'-(2-(2*H*-1,2,3-triazol-2-yl)-1,3-phenylene)diacrylate



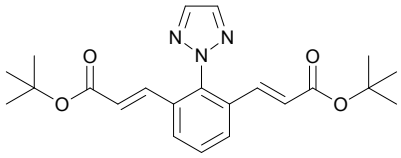
3t'

White solid, yield 73 %, mp 125-127 °C, ^{1}HNMR (600MHz, $CDCl_3$): δ 7.91 (s, 2H), 7.69 (d, *J*=8.4Hz, 2H), 7.51 (t, *J*=8.4Hz, 1H), 6.94 (d, *J*=16.2Hz, 2H), 6.24 (d, *J*=16.2Hz, 2H), 4.11 (q, *J*=4.8Hz, 4H), 1.19 (t, *J*=4.8Hz, 6H); ^{13}C NMR (150MHz, $CDCl_3$): δ 154.9, 137.3, 137.1, 135.1, 132.5, 129.4, 127.4, 121.3, 59.7, 13.2; HRMS (ESI) Calcd. For $C_{18}H_{19}N_3O_4Na$: 364.1273, Found: m/z 364.1271.



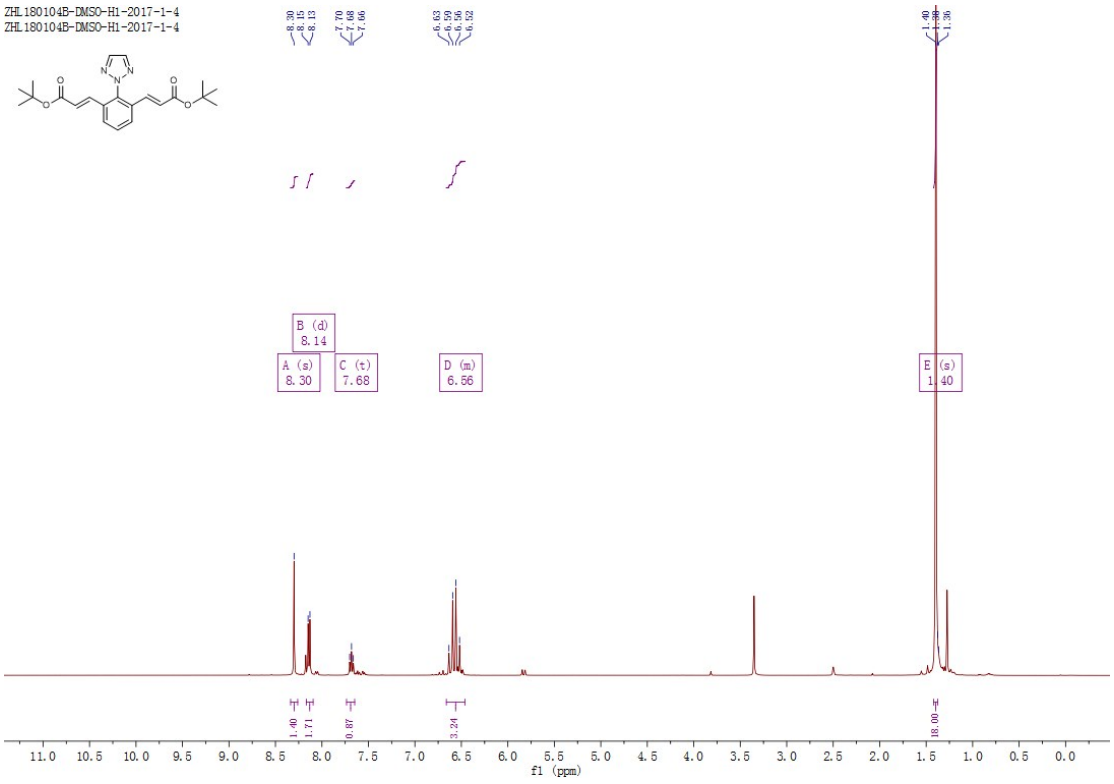


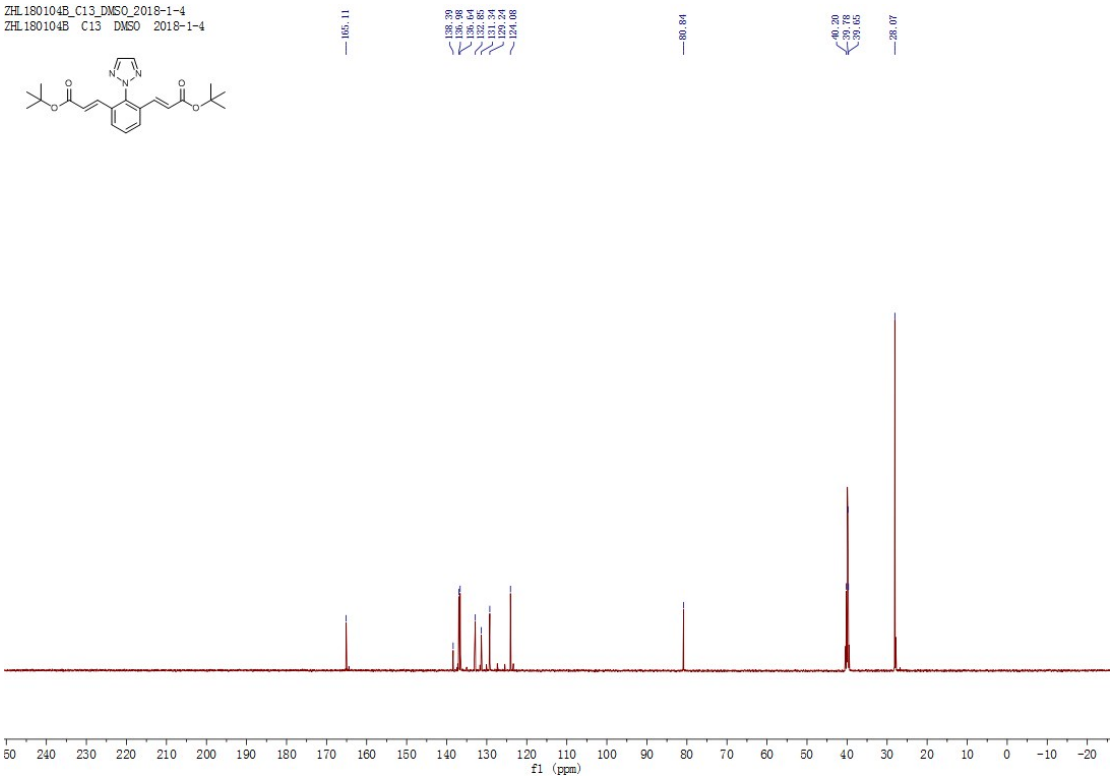
(2E,2'E)-di-tert-butyl 3,3'-(2-(2*H*-1,2,3-triazol-2-yl)-1,3-phenylene)diacrylate



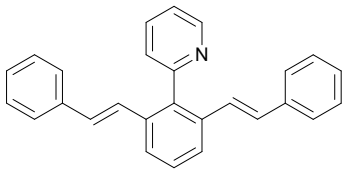
3u'

White solid, yield 75 %, mp 135-137 °C, ^{1}HNMR (600MHz, $CDCl_3$): δ 8.30 (s, 2H), 8.14 (d, *J*=8.4Hz, 2H), 7.68 (t, *J*=8.4Hz, 1H), 6.57 (m, 4H), 1.41 (s, 18H); ^{13}C NMR (150MHz, $CDCl_3$): δ 155.1, 138.4, 137.0, 136.8, 136.6, 136.6, 132.9, 131.3, 129.2, 127.4, 124.1, 80.8, 28.1; HRMS (ESI) Calcd. For $C_{22}H_{27}N_3O_4Na$: 420.1899, Found: m/z420.1898.



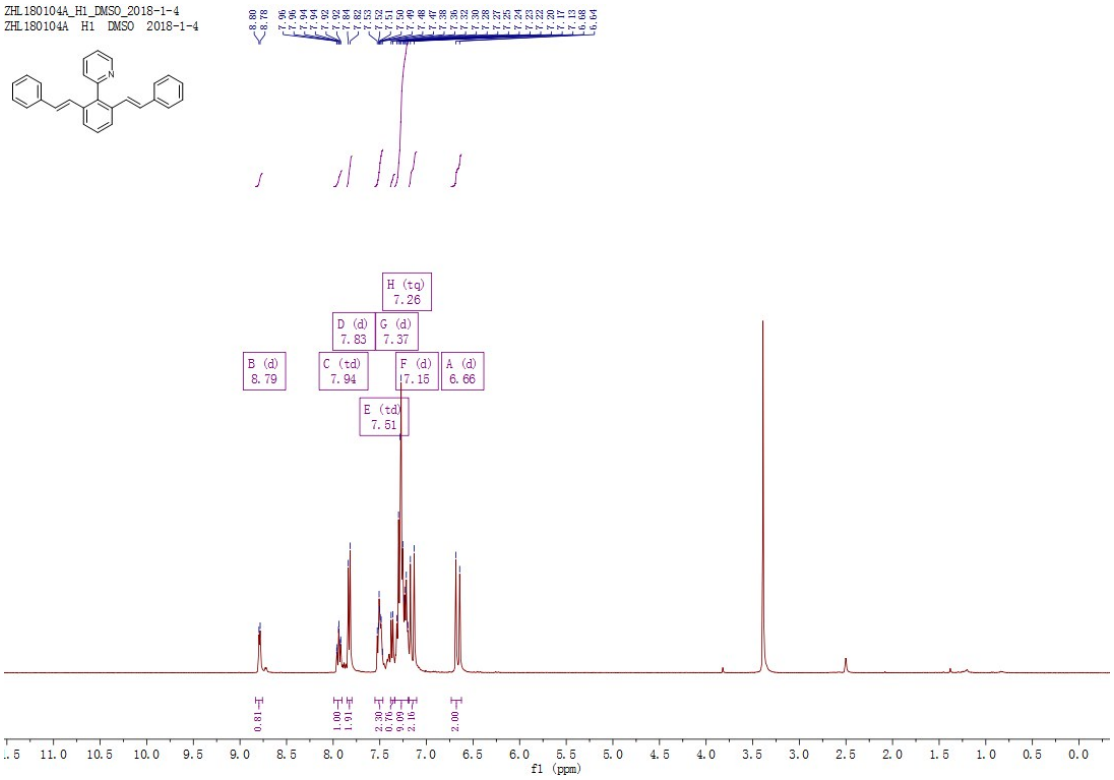


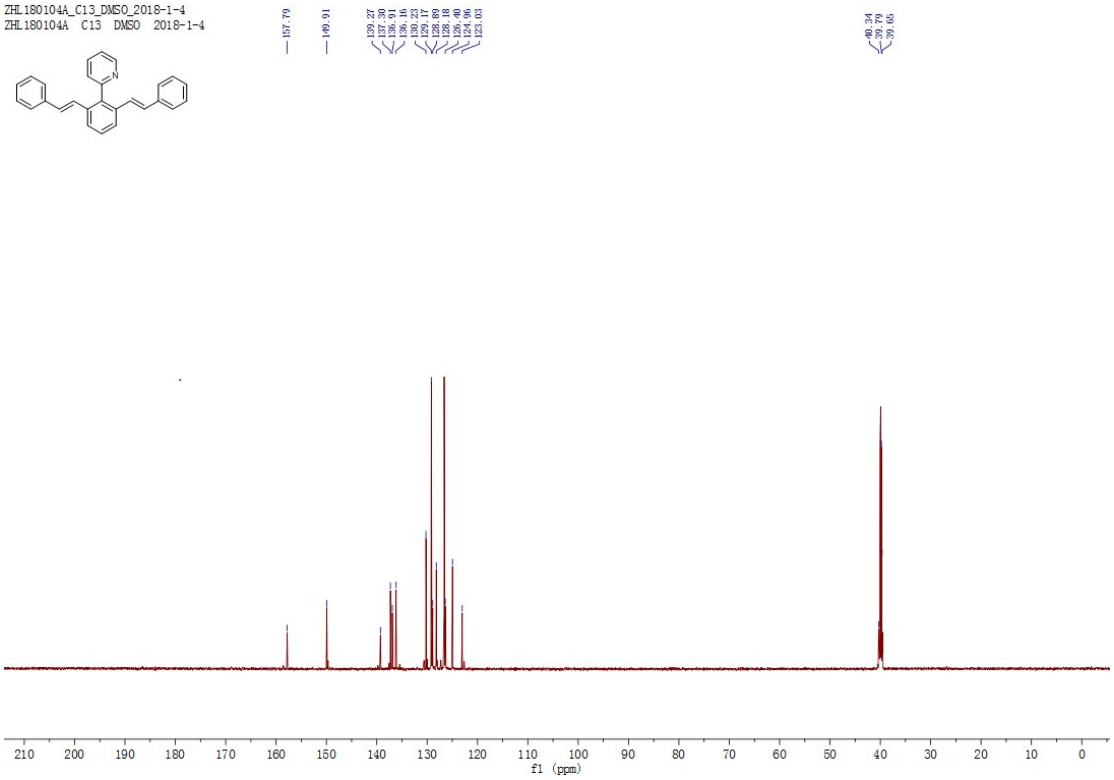
2-(2,6-di((E)-styryl)phenyl)pyridine



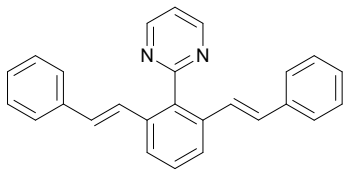
4a'

White solid, yield 76 %, mp 142-144 °C, ^{1}HNMR (600MHz, $CDCl_3$): δ 8.79 (d, *J*=8.4Hz, 1H), 7.94 (t, *J*=8.4Hz, 1H), 7.83 (d, *J*=8.4Hz, 2H), 7.50 (m, 2H), 7.28 (m, 11H), 7.15 (d, *J*=16.2Hz, 2H), 6.66 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, $CDCl_3$): δ 157.8, 149.9, 139.3, 137.3, 136.9, 136.2, 130.2, 129.2, 128.9, 128.2, 126.8, 126.6, 126.6, 126.4, 125.0, 123.0; HRMS (ESI) Calcd. For $C_{27}H_{21}NNa$: 382.1572, Found: m/z 382.1571.



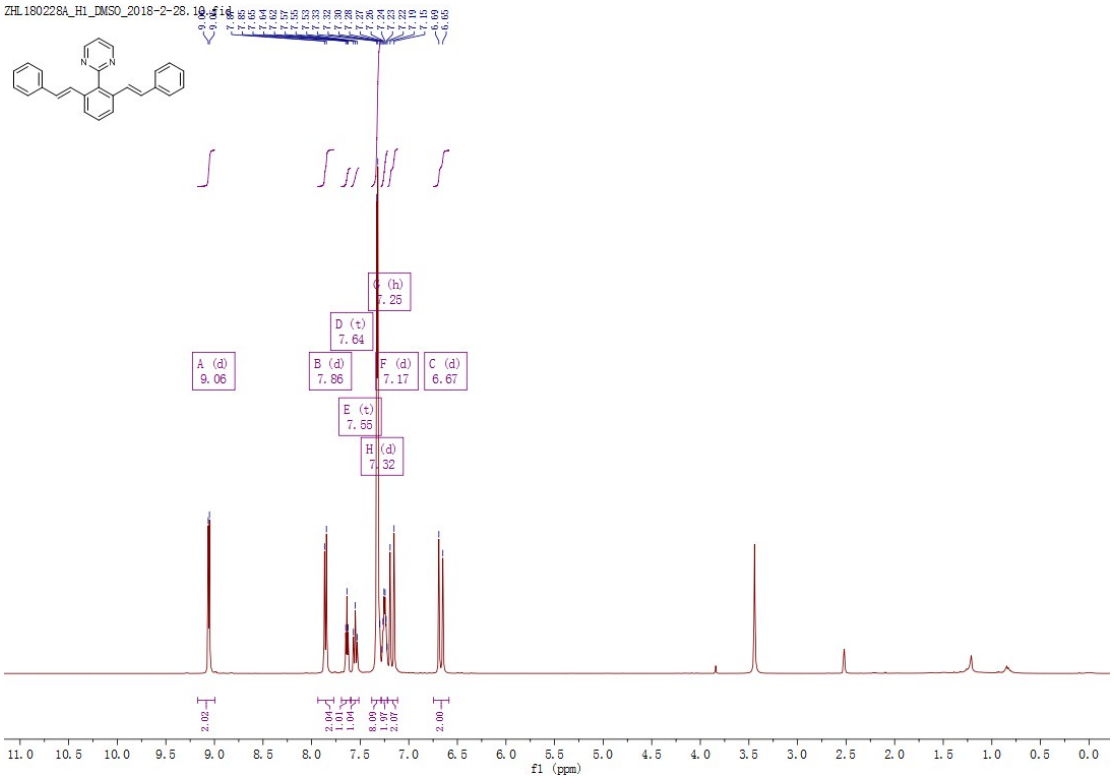


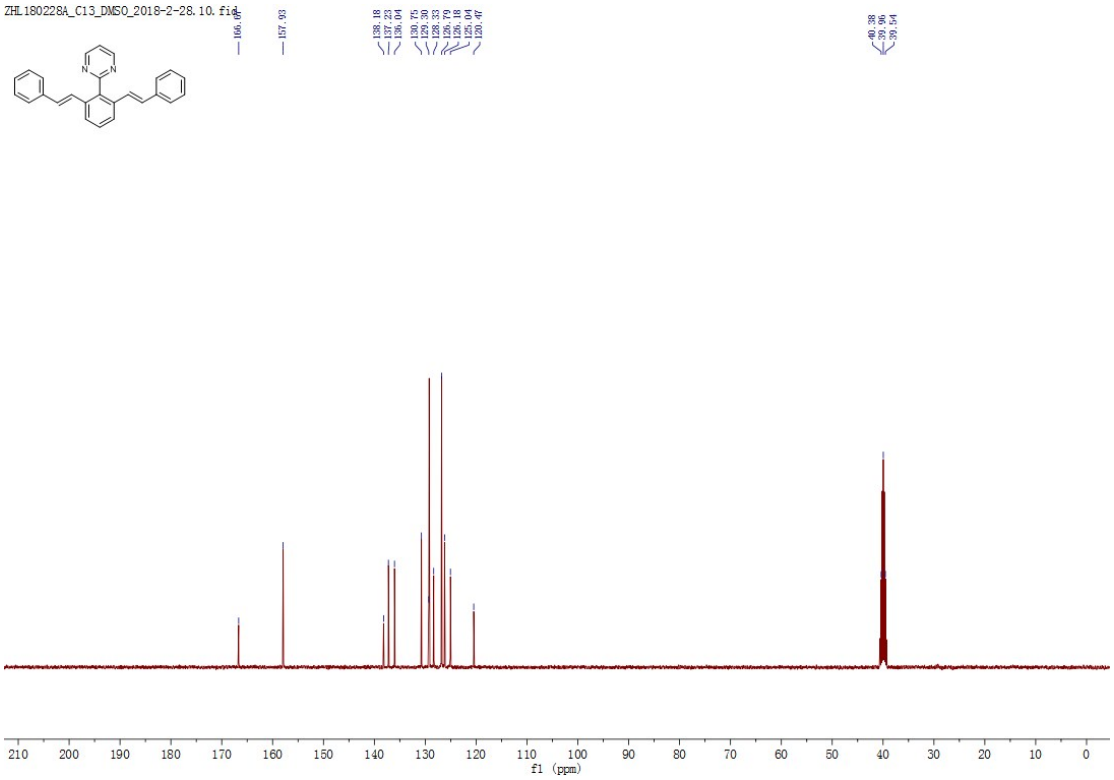
2-(2,6-di((E)-styryl)phenyl)pyrimidine



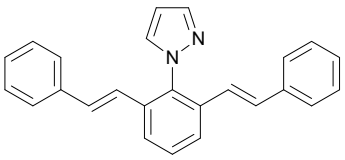
4b'

Yellow solid, yield 78 %, ^{1}HNMR (600MHz, DMSO): δ 9.05 (s, 2H), 7.85 (d, *J*=8.4Hz, 2H), 7.64 (t, *J*=8.4Hz, 1H), 7.55 (t, *J*=8.4Hz, 1H), 7.32 (m, 10H), 7.25 (m, 2H), 7.17 (d, *J*=16.2Hz, 2H), 6.67 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, $CDCl_3$): δ 166.5, 157.9, 138.2, 137.2, 136.0, 130.8, 129.3, 128.3, 126.8, 126.2, 125.0, 120.5; HRMS (ESI) Calcd. For $C_{26}H_{20}N_2Na$: 383.1524, Found: m/z 383.1523.



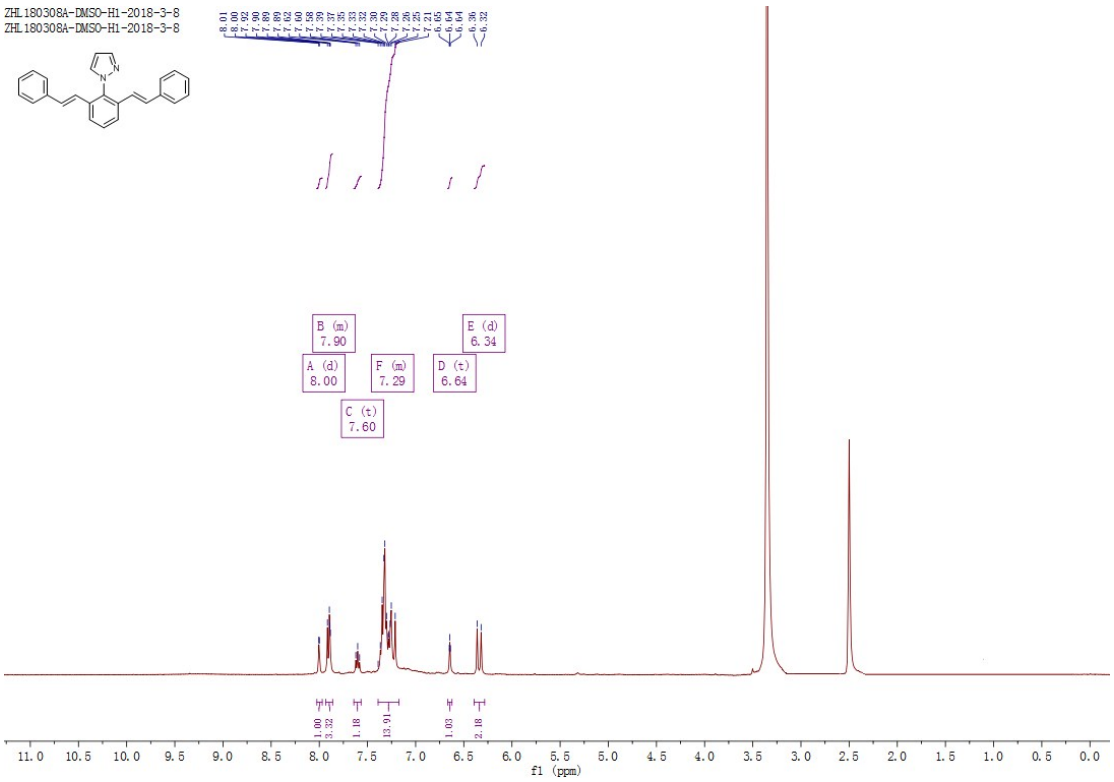


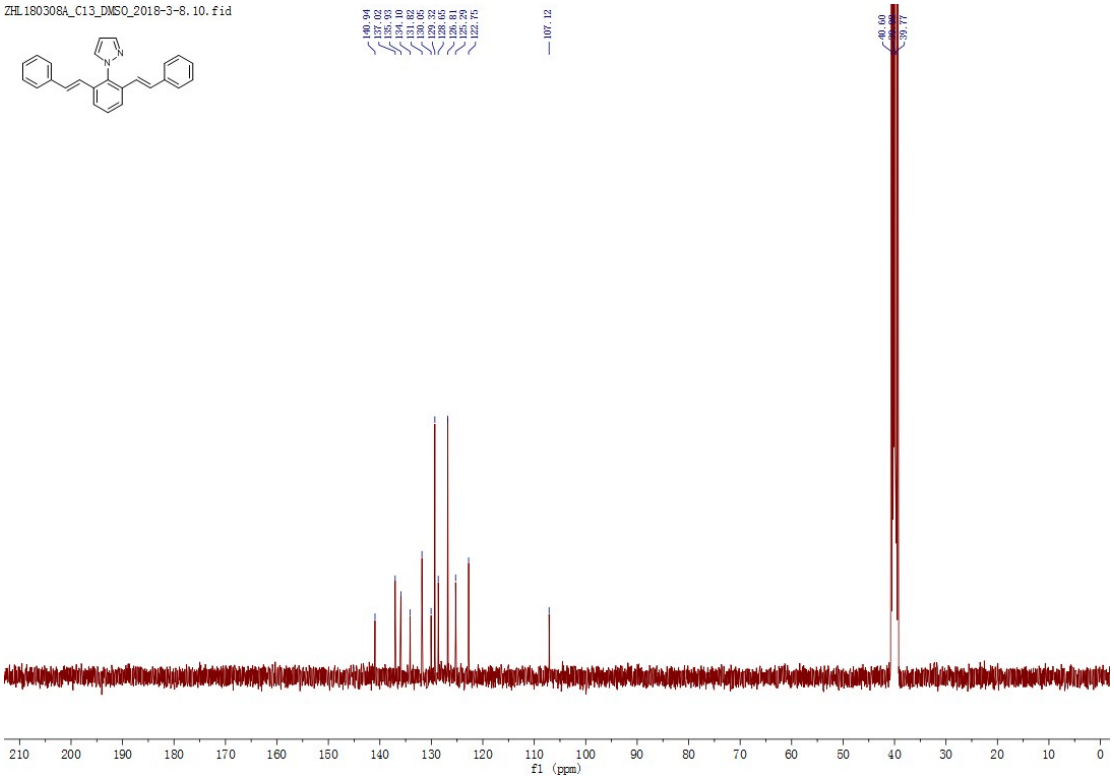
1-(2,6-di((E)-styryl)phenyl)-1*H*-pyrazole



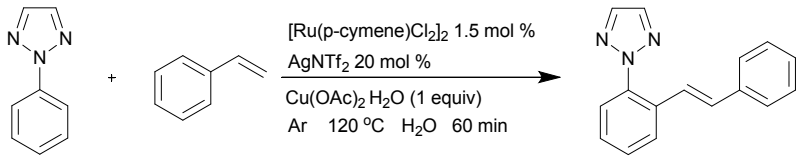
4c'

White solid, yield 76 %, ^{1}HNMR (600MHz, DMSO): δ 8.00 (s, 1H), 7.90 (m, 3H), 7.60 (t, *J*=8.4Hz, 1H), 7.29 (m, 14H), 6.64 (s, 1H), 6.34 (d, *J*=16.2Hz, 2H); ^{13}C NMR (150MHz, $CDCl_3$): δ 141.0, 137.0, 136.9, 134.1, 131.8, 130.1, 128.7, 126.8, 125.3, 122.8, 107.1; HRMS (ESI) Calcd. For $C_{25}H_{20}N_2Na$: 371.1524, Found: m/z 371.1523.


ZHL180308A-DMSO-H1-2018-3-8
ZHL180308A-DMSO-H1-2018-3-8
B (m)
7.90
E (d)
6.34
A (d)
8.00
F (m)
7.29
D (t)
6.64
C (t)
7.60
f1 (ppm)


ZHL180308A_C13_DMSO_2018-3-8.10.fid
f1 (ppm)

Gram-scale Mono-olefination of 1,2,3-triazole



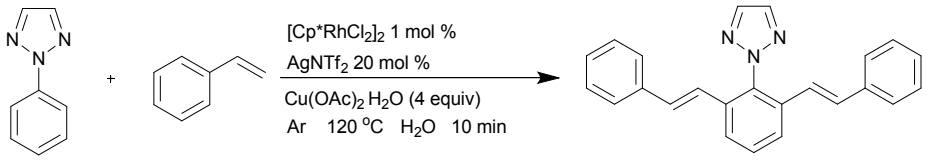
1a 1g

2a 1.43g

3a 1.32g (yield = 78%)

A 15ml sealed tube was charged with 2-phenyl-1,2,3-triazole **1a** (1g, 6.89 mmol), styrene **2a** (1.43g, 13.79 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (63 mg, 0.1033 mmol), $AgNTf_2$ (535.1mg, 1.379 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.5g, 6.89 mmol) and H2O (3ml). The mixture was stirred at 120℃for 60 min. Then cooled down to ambient temperature. The solvent was evaporated in vacuo and the residue was further purified by flash chromatography of silica gel (silica gel, acetone / petroleum ether = 1:150), affording the product **3a** in 78%. (white solid)

Gram-scale Diolefination of 1,2,3-triazole



1a 1g

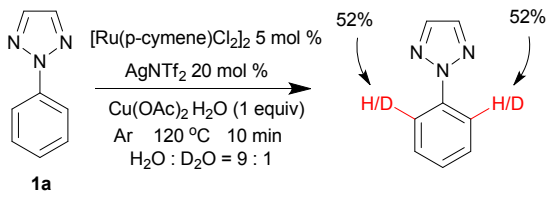
2a 2.86g

3a' 1.92g (yield = 80%)

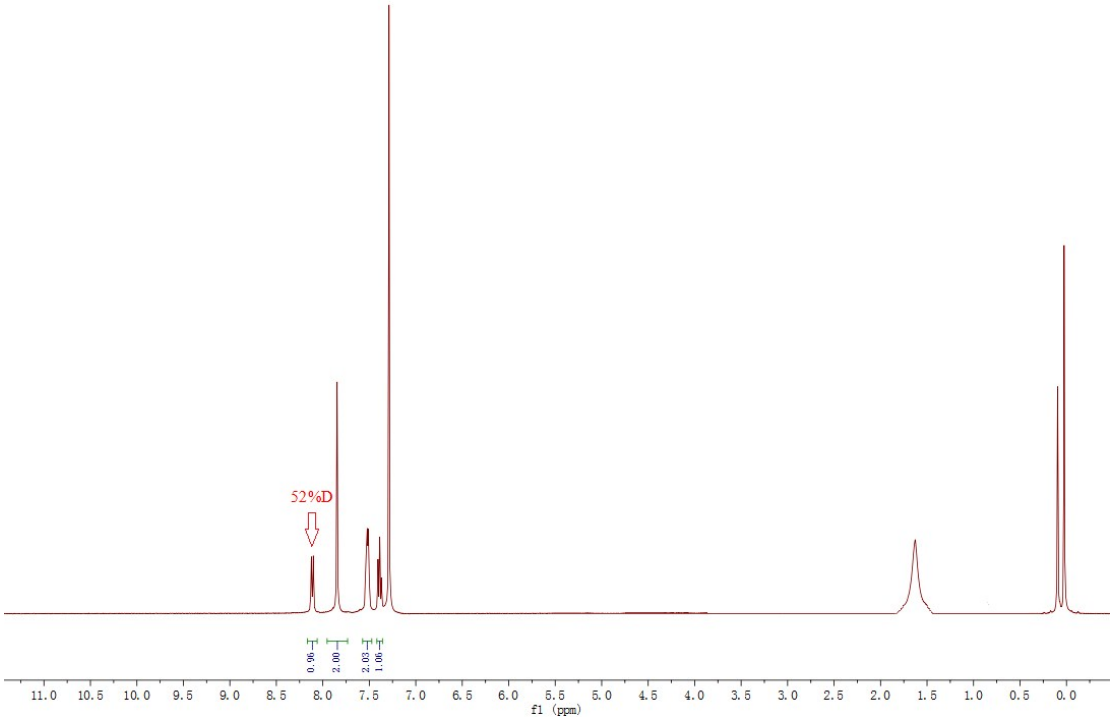
A 15ml sealed tube was charged with 2-phenyl-1,2,3-triazole **1a** (1g, 6.89 mmol), styrene **2a** (2.86g, 27.56 mmol), $[Cp^*RhCl_2]_2$ (42.6mg, 0.0689 mmol), $AgNTf_2$ (535.1mg, 1.379 mmol), $Cu(OAc)_2 \cdot H_2O$ (6.0g, 27.56 mmol) and H_2O (3ml). The mixture was stirred at 120℃for 10min. Then cooled down to ambient temperature. The solvent was evaporated in vacuo and the residue was further purified by flash chromatography of silica gel (silica gel, acetone / petroleum ether = 1:100), affording the product **3a'** in 80%. (yellow solid)

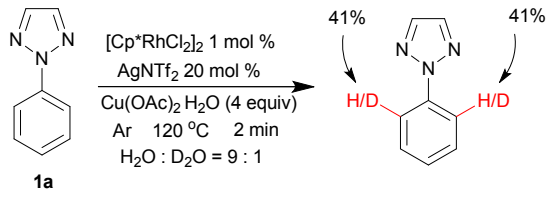
Mechanistic studies

The H/D exchange experiment



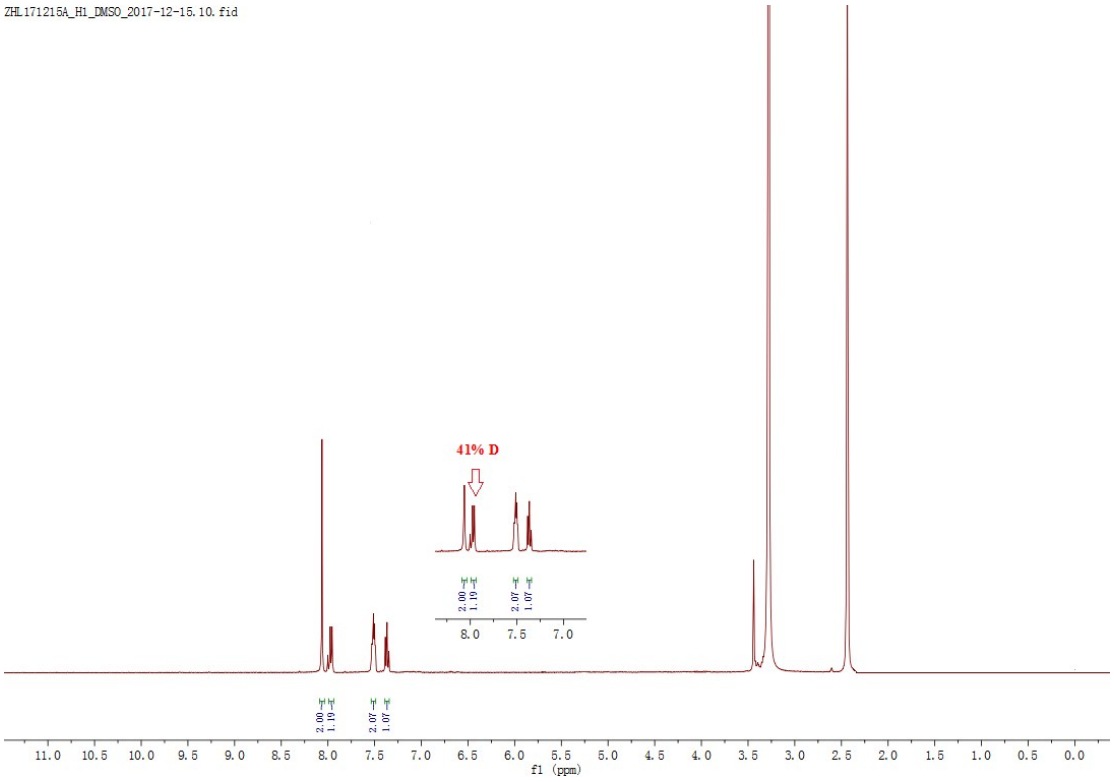
A 15ml sealed tube was charged with 2-phenyl-2*H*-1,2,3-triazole **1a** (14.5 mg, 0.1 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (3mg, 0.005 mmol), $AgNTf_2$ (7.8mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (21.8mg, 0.1 mmol), H_2O (0.45ml) and D_2O (0.05ml). The mixture was stirred at 120 °C for 10 min. Then cooled down to ambient temperature. The solvent was evaporated in vacuo and the residue was further purified by flash chromatography of silica gel (silica gel, acetone / petroleum ether = 1:200), affording the deuterated product. ^{1}H-NMR analyzed 52% of the *ortho*-C-H within **1a** was deuterated. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 0.96H), 7.84 (s, 2H), 7.51 (m, , 2H), 7.40 (t, J = 8.4Hz, 1H).



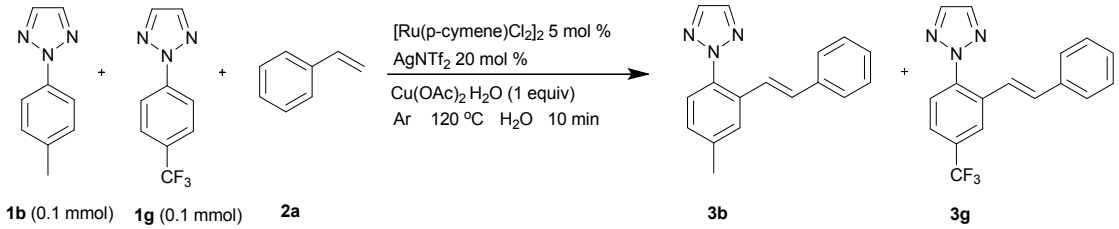


A 15ml sealed tube was charged with 2-phenyl-2*H*-1,2,3-triazole **1a** (14.5 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (0.6mg, 0.001 mmol), $AgNTf_2$ (7.8mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (87.2mg, 0.4 mmol), H_2O (0.45ml) and D_2O (0.05ml). The mixture was stirred at 120 °C for 2 min. Then cooled down to ambient temperature. The solvent was evaporated in vacuo and the residue was further purified by flash chromatography of silica gel (silica gel, acetone / petroleum ether = 1:150), affording

the deuterated product. ^{1}H-NMR analyzed 41% of the *ortho*-C-H within **1a** was deuterated. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.07(s, 2H), 7.97 (d, J = 8.4 Hz, 1.19H), 7.51 (m, 2H), 7.37 (t, J = 8.4Hz, 1H).



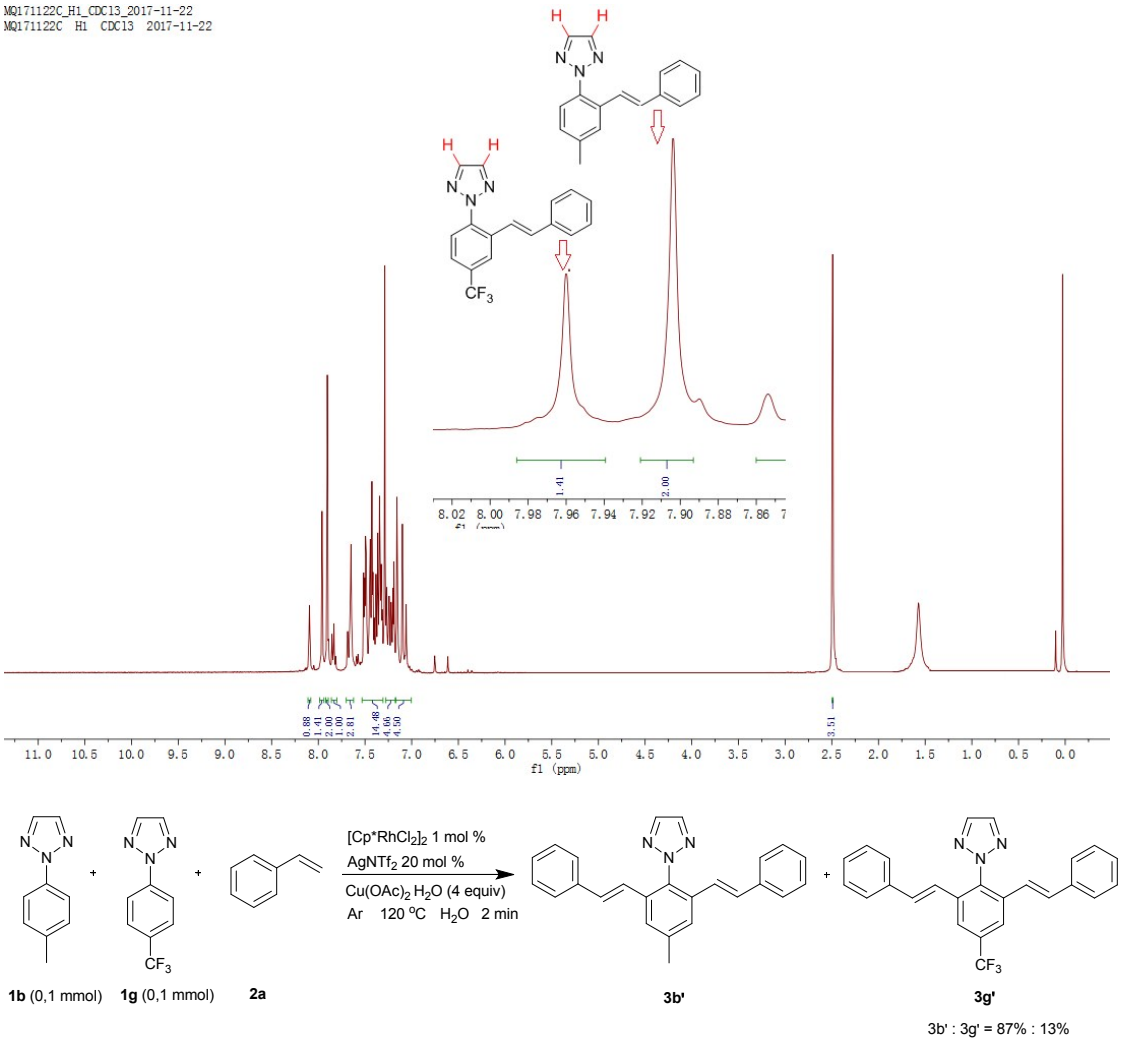
The competition experiment



1b (0.1 mmol) **1g** (0.1 mmol) **2a** **3b** **3g**

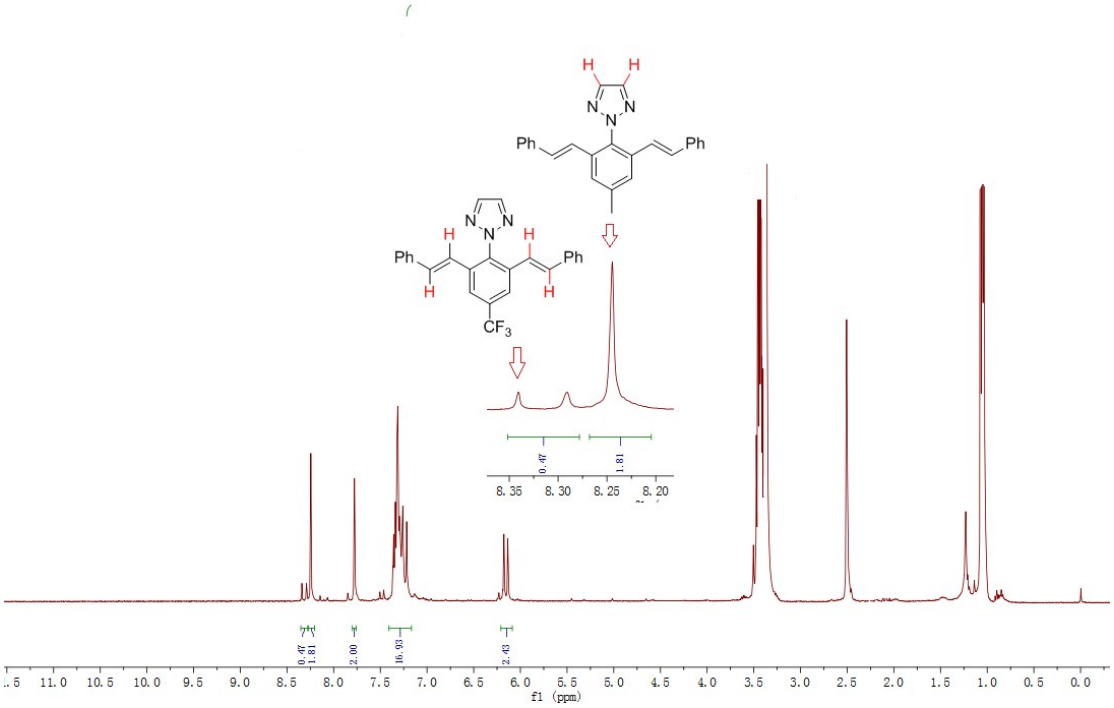
3b : 3g = 58% : 42%

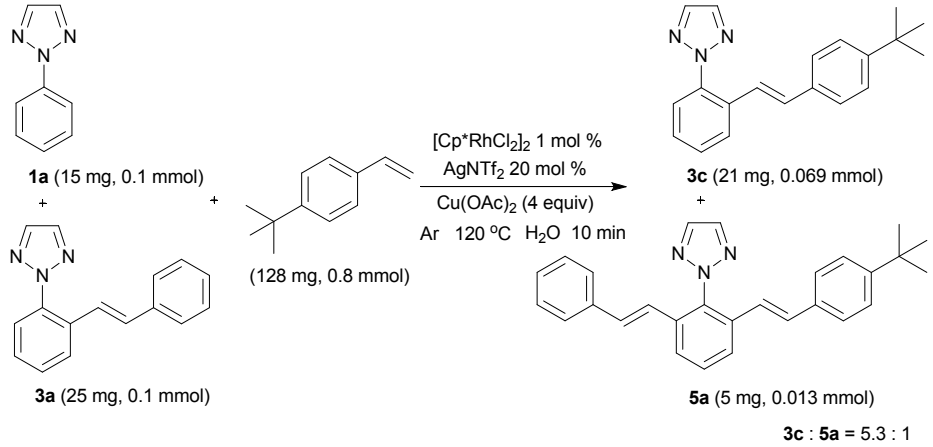
A15ml sealed tube was charged with 2-(4-methyl-phenyl)-2*H*-1,2,3-triazole **1b** (14.5 mg, 0.1 mmol), 2-(4-trifluoromethyl-phenyl)-2*H*-1,2,3-triazole **1g** (21.4mg, 0.1mmol), styrene **2a** (58.1mg, 0.4 mmol) $[Ru(p\text{-cymene})Cl_2]_2$ (6.1mg, 0.01 mmol), $AgNTf_2$ (15.6mg, 0.04 mmol), $Cu(OAc)_2{\cdot}H_2O$ (87.2mg, 0.4 mmol) and H_2O (0.5ml). The mixture was stirred at 120 °C for 10 min. Then cooled down to ambient temperature. The solvent was evaporated in vacuo and the residue was further purified by flash chromatography of silica gel (silica gel, acetone / petroleum ether = 1:200), affording the products at the rate of 0.58:0.42. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.09 (s, 0.88H), 7.96 (s, 1.43H), 7.91 (s, , 2H), 7.65 (m, 3H), 7.41 (m, 14H), 7.16 (m, 9H), 2.47 (s, 3H).



A 15ml sealed tube was charged with 2-(4-methyl-phenyl)-2*H*-1,2,3-triazole **1b** (14.5 mg, 0.1 mmol), 2-(4-trifluoromethyl-phenyl)-2*H*-1,2,3-triazole **1g** (21.4mg, 0.1 mmol), styrene **2a** (116.1mg, 0.8 mmol), $[Cp^*RhCl_2]_2$ (1.2mg, 0.002 mmol), $AgNTf_2$ (15.6mg, 0.04 mmol), $Cu(OAc)_2 \cdot H_2O$ (174mg, 0.8 mmol) and H_2O (0.5ml). The mixture was stirred at 120 °C for 2 min. Then cooled down to ambient temperature. The solvent was evaporated in vacuo and the residue was further purified by flash chromatography of silica gel (silica gel, acetone / petroleum ether = 1:150), affording the products at the rate of 0.87 : 0.13. ^{1}H-NMR (600 MHz, DMSO) δ 8.32 (d, J = 16.2Hz, 0.47H), 8.24 (s, 1.81H), 7.78 (s, 2H), 7.30 (s, 17H), 6.15 (d, J = 16.2Hz, 2.43H), 3.47 (s, 3H).

MQ171122D_H1_DMSO_2017-11-22
MQ171122D H1 DMSO 2017-11-22





A 15ml sealed tube was charged with 2--phenyl-1,2,3-triazole **1a** (15 mg, 0.1 mmol), 2-(2-styrylphenyl)-2*H*-1,2,3-triazole **3a** (25mg, 0.1 mmol), 1-(*tert*-butyl)-4-vinylbenzene (128mg, 0.8 mmol), $[Cp^*RhCl_2]_2$ (1.2mg, 0.002 mmol), $AgNTf_2$ (15.6mg, 0.04 mmol), $Cu(OAc)_2 \cdot H_2O$ (174mg, 0.8 mmol) and H_2O (0.5ml). The mixture was stirred at 120 °C for 10 min. Then cooled down to ambient temperature. The solvent was evaporated in vacuo and the residue was further purified by flash chromatography of silica gel (silica gel, acetone / petroleum ether = 1:150), affording the products at the rate of 0.069 : 0.013. ^{1}H-NMR (**5a**, 600 MHz, DMSO) δ 8.27 (s, 2H), 7.93 (d, J = 8.4Hz, 2H), 7.67 (t, J = 8.4Hz, 1H), 7.34 (m, 7H), 7.25 (m, 4H), 6.15 (m, 2H), 1.25 (s, 9H).

ZHL180502A_H1_DMSO_2018-5-2.10.fid