Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Group 9 [Cp*M^{III}] Complexes-Catalyzed C-H Olefination of Arenes in Water at Room Temperature: A study on the catalytic activity

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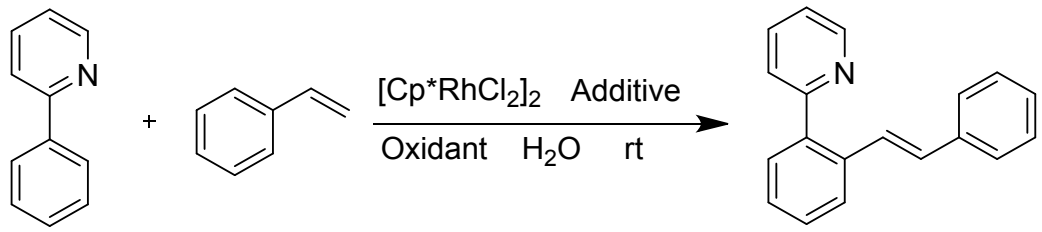
General Remarks

All the reactions were carried out in Schlenk tubes (approx. 15 mL volume) under an oxygen atmosphere. If not noted otherwise, all the starting 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 at 254 nm. The product purification was done using silica gel column chromatography. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR. ^{1}H-NMR, ^{19}F-NMR and ^{13}C-NMR spectra were recorded with tetramethylsilane (TMS, δ= 0.00 ppm) as the internal standard. ^{1}H 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). Chemical shifts (δ) are provided in ppm and are referenced to the residual solvent signal. 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.

Table SI-1: Optimization studies for the rhodium-catalyzed olefination.[a]

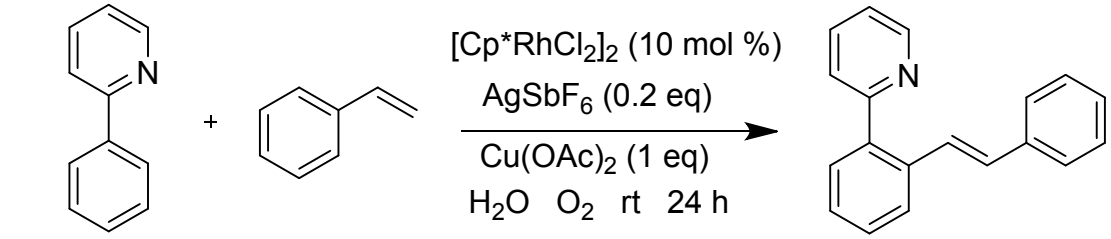


1a **2a** **3a**

Entry	2a (equiv)	$[Cp^*RhCl_2]_2$ (mol %)	Additive	Oxidant	Time (h)	Yield [b] (%)
1	1	10	$AgNTf_2$	$Cu(OAc)_2$	24	63
2	2	10	$AgNTf_2$	$Cu(OAc)_2$	24	78
3	3	10	$AgNTf_2$	$Cu(OAc)_2$	24	76
4	4	10	$AgNTf_2$	$Cu(OAc)_2$	24	79
5	2	5	$AgNTf_2$	$Cu(OAc)_2$	24	57
6	2	15	$AgNTf_2$	$Cu(OAc)_2$	24	79
7	2	10	$AgPF_6$	$Cu(OAc)_2$	24	12
8	2	10	$AgSbF_6$	$Cu(OAc)_2$	24	81
9	2	10	AgOTf	$Cu(OAc)_2$	24	64
10[c]	**2**	**10**	**$AgSbF_6$**	**$Cu(OAc)_2$**	**24**	**83**
11	2	10	$AgSbF_6$	$Cu(TFA)_2$	24	65
12	2	10	$AgSbF_6$	$Cr(OAc)_2$	24	48
13	2	10	$AgSbF_6$	AgOAc	24	19
14[d]	2	10	$AgSbF_6$	$Cu(OAc)_2$	24	35
15[e]	2	10	$AgSbF_6$	$Cu(OAc)_2$	24	81
16	2	10	$AgSbF_6$	$Cu(OAc)_2$	12	47
17	2	10	$AgSbF_6$	$Cu(OAc)_2$	48	84

[a] Reaction conditions: **1a** (0.2 mmol), **2a** catalyst (10 mol %), additive (0.2 eq) and oxidant (1 eq) were stirred in H_2O (0.5 mL) under N_2; [b] Yield of products isolated after column chromatography; [c] O_2; [d] $Cu(OAc)_2$ (2 eq); [e] $Cu(OAc)_2$ (4 eq);

General Procedure for the Synthesis of 3a

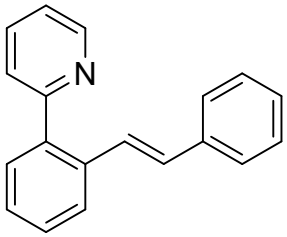


1a (0.1 mmol) **2a** (0.2 mmol) **3a**

A 15ml sealed tube was charged with 2-phenylpyridine **1a** (15.2 mg, 0.1 mmol), styrene **2a** (20.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $AgSbF_6$ (6.9 mg, 0.02 mol), $Cu(OAc)_2$ (20 mg, 0.1 mmol), and H_2O 0.5 mL. The mixture was stirred at room temperature for 24 h and monitored by TLC. 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**.

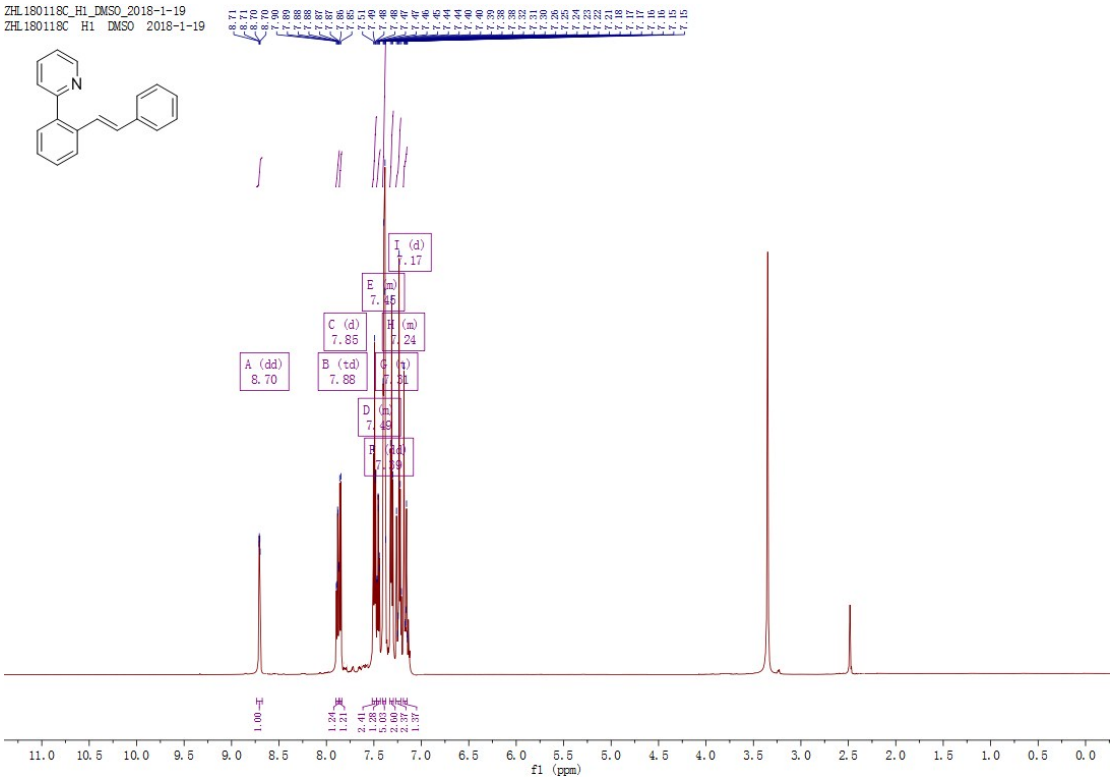
Characterization of products

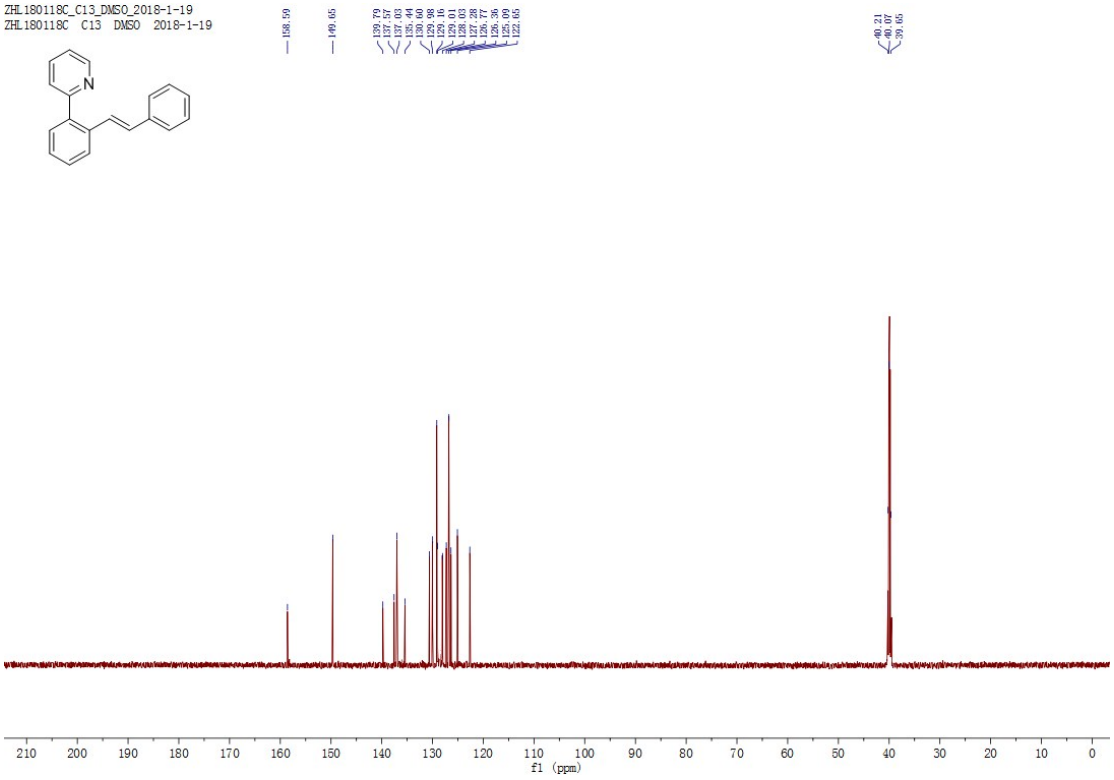
(E)-2-(2-styrylphenyl)pyridine



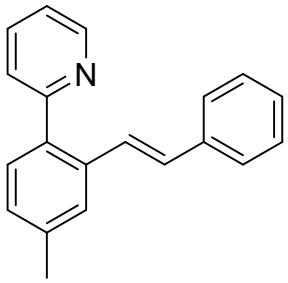
3a

Little yellow oil, yield 83 %, ^{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):δ158.6, 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.



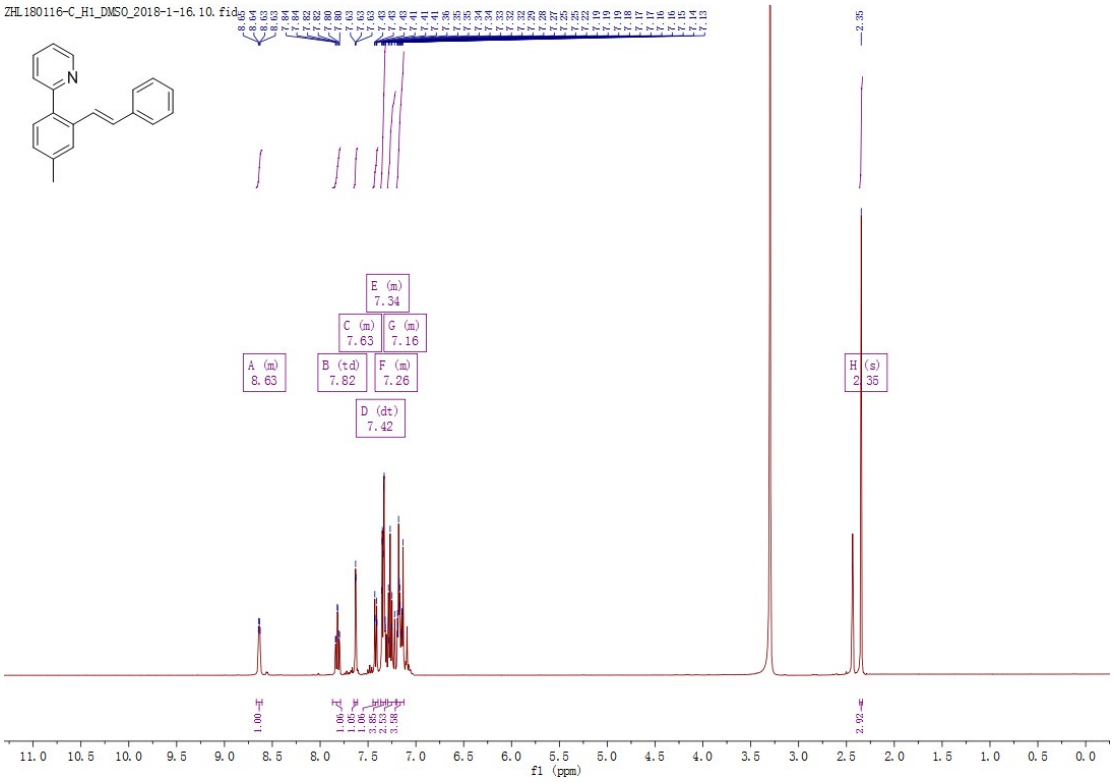


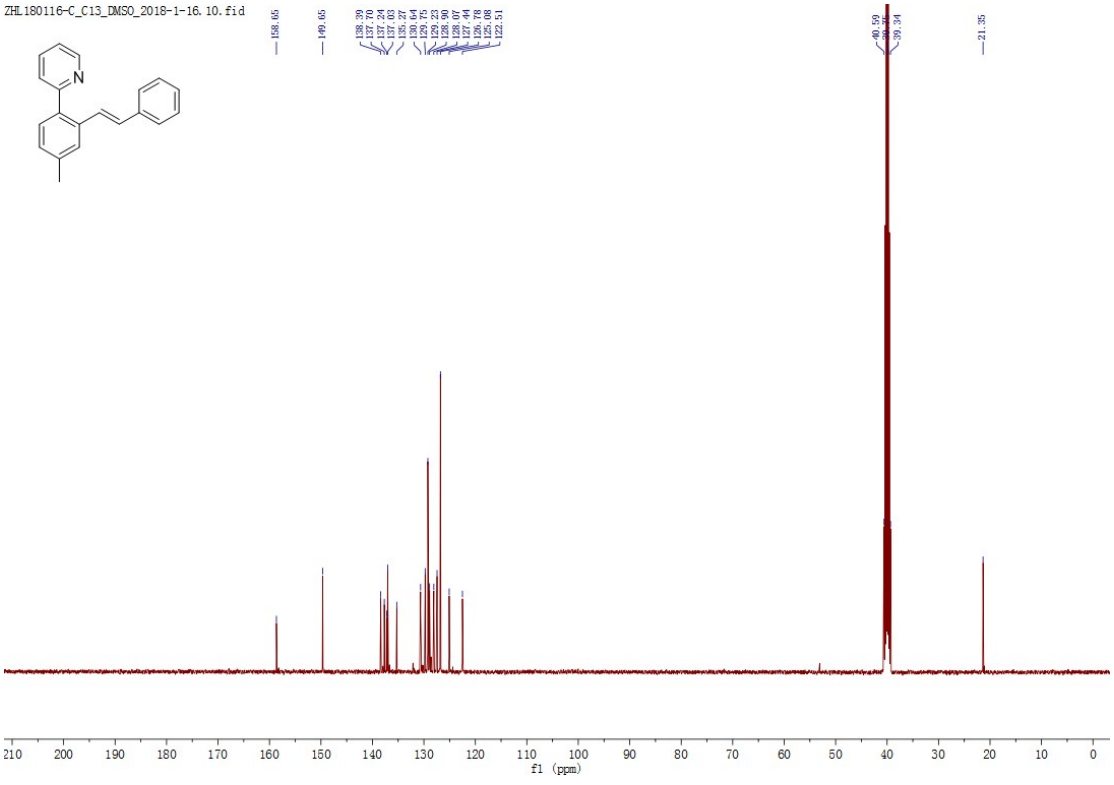
(E)-2-(4-methyl-2-styrylphenyl)pyridine



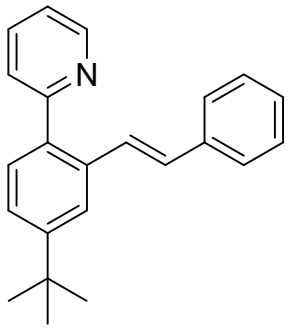
3b

Yellow liquid, yield 87 %, ^{1}HNMR (600MHz, DMSO):δ 8.63 (d, *J*=8.4Hz, 1H), 7.82 (t, *J*=8.4Hz, 1H), 7.63 (s, 1H), 7.42 (d, *J*=16.2Hz, 1H), 7.34 (m, 4H), 7.26 (m, 3H), 7.16 (m, 3H), 2.35 (s, 3H); ^{13}C NMR (150MHz, DMSO):δ158.7, 149.7, 138.4, 137.7, 137.2, 137.0, 135.3, 130.6, 129.8, 129.2, 128.9, 128.1, 127.4, 126.8, 125.2, 122.5, 21.4; HRMS (ESI) Calcd. For $C_{20}H_{17}NNa$: 294.1259, Found: m/z 294.1258.



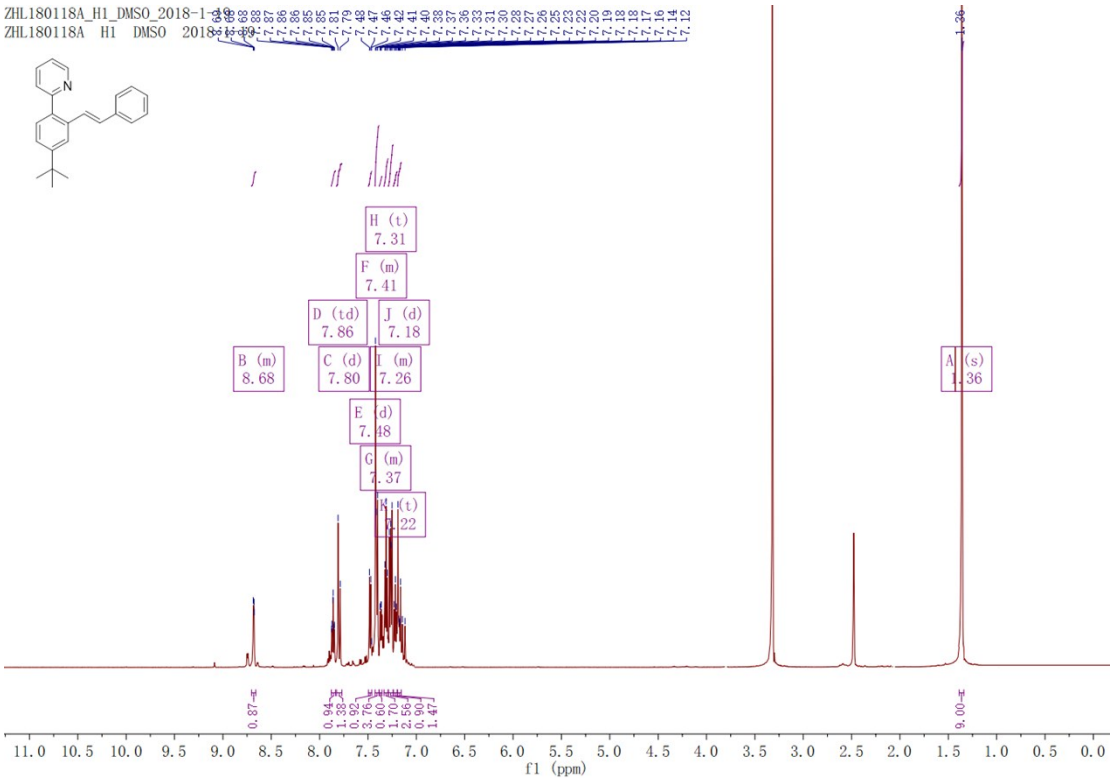


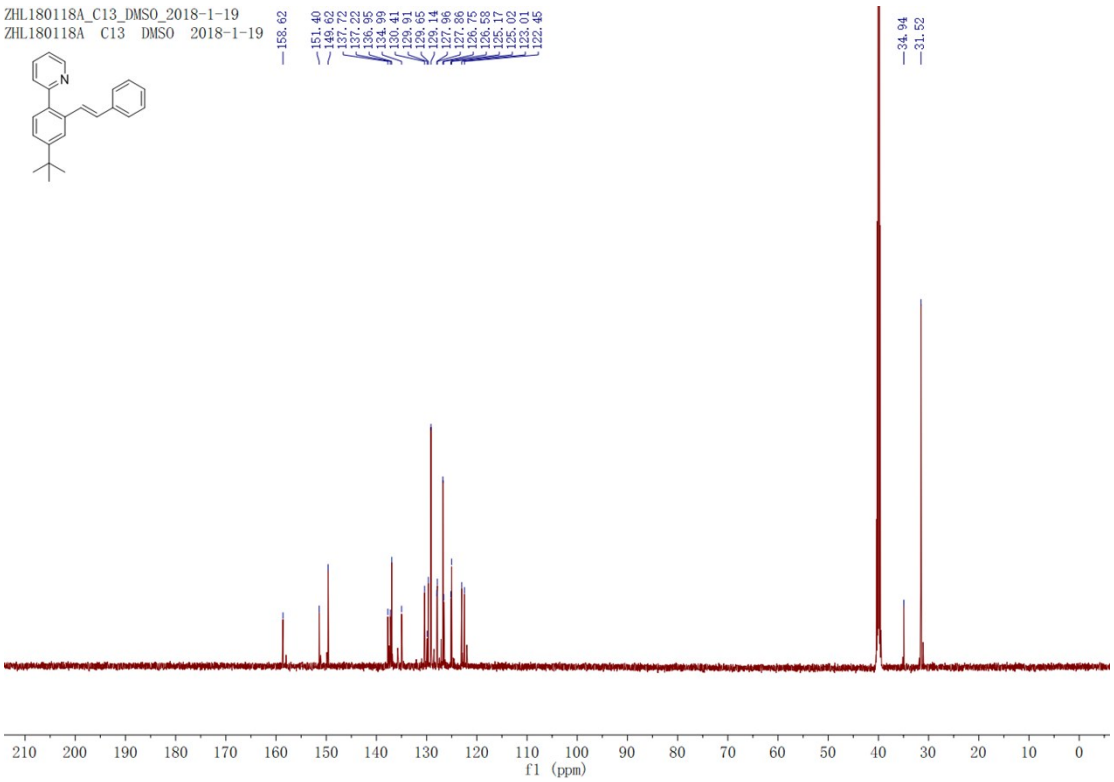
(E)-2-(4-(tert-butyl)-2-styrylphenyl)pyridine



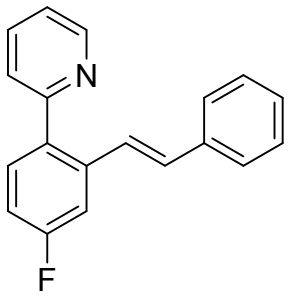
3c

Yellow liquid, yield 88 %, ^{1}HNMR (600MHz, DMSO):δ 8.68 (s, 1H), 7.86 (t, J=8.4Hz, 1H), 7.80 (d, J=8.4Hz, 1H), 7.48 (d, J=8.4Hz, 2H), 7.41 (m, 4H), 7.37(t, J=8.4Hz, 1H), 7.31 (t, J=8.4Hz, 2H), 7.26 (t, J=8.4Hz, 2H), 7.22 (t, J=8.4Hz, 1H), 7.18 (m, 1H), 1.36 (s, 9H); ^{13}C NMR (150MHz, DMSO):δ158.6, 151.4, 149.6, 137.7, 137.2, 137.0, 135.0, 130.4, 129.9, 129.7, 129.1, 128.0, 127.9, 126.8, 126.6, 125.2, 125.0, 123.0, 122.5, 34.9, 31.5; HRMS (ESI) Calcd. For $C_{23}H_{23}NNa$: 336.1728, Found: m/z 336.1727.



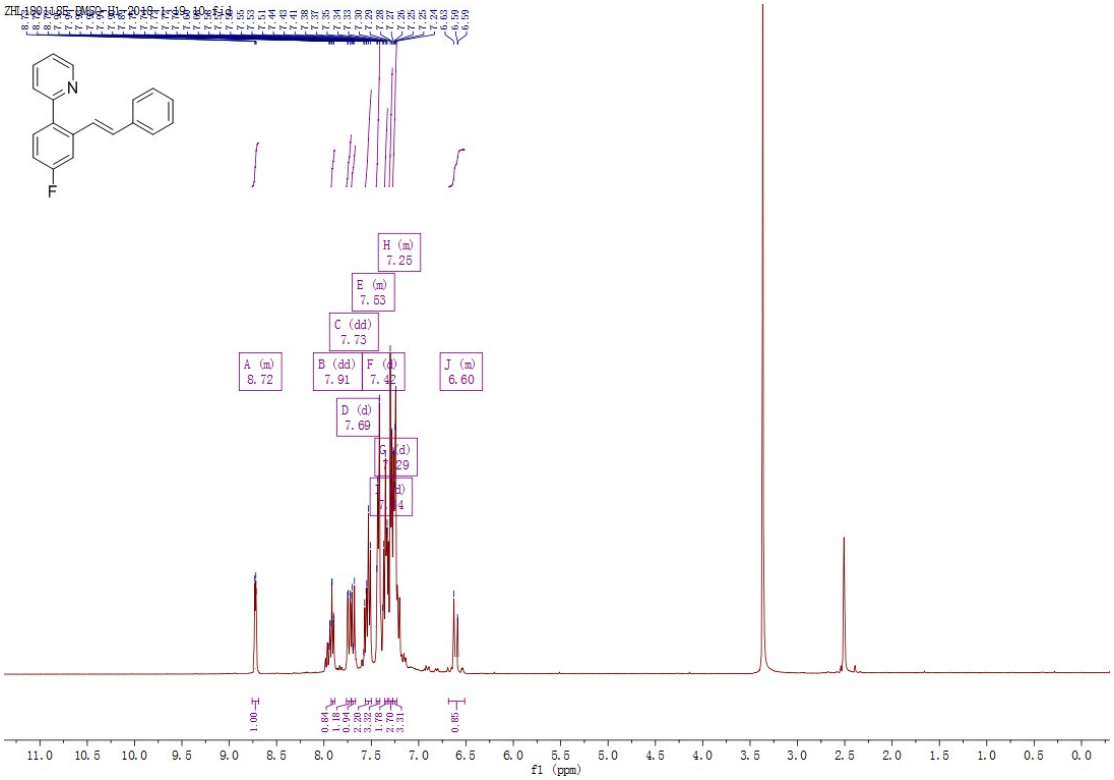


(E)-2-(4-fluoro-2-styrylphenyl)pyridine



3d

Yellow liquid, yield 86 %, ^{1}HNMR (600MHz, DMSO):δ 8.72 (d, *J*=8.4Hz, 1H), 7.91 (t, *J*=8.4Hz, 1H), 7.73 (d, *J*=8.4Hz, 1H), 7.69 (d, *J*=16.2Hz, 1H), 7.53 (m, 2H), 7.39 (m, 4H), 7.27 (m, 5H), 6.60 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, DMSO):δ164.0, 161.5, 157.7, 149.8, 138.8, 138.0, 137.3, 137.1, 136.3, 132.7, 131.3, 129.5, 128.5, 126.8, 125.8, 125.1, 123.0, 115.3, 112.4; ^{19}F NMR (376MHz, DMSO): -113.53; HRMS (ESI) Calcd. For $C_{19}H_{14}FNNa$: 298.1008, Found: m/z 298.1008.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E (m)
7.53
C (dd)
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A (m)
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B (dd)
7.91
F (d)
7.42
J (m)
6.60
D (d)
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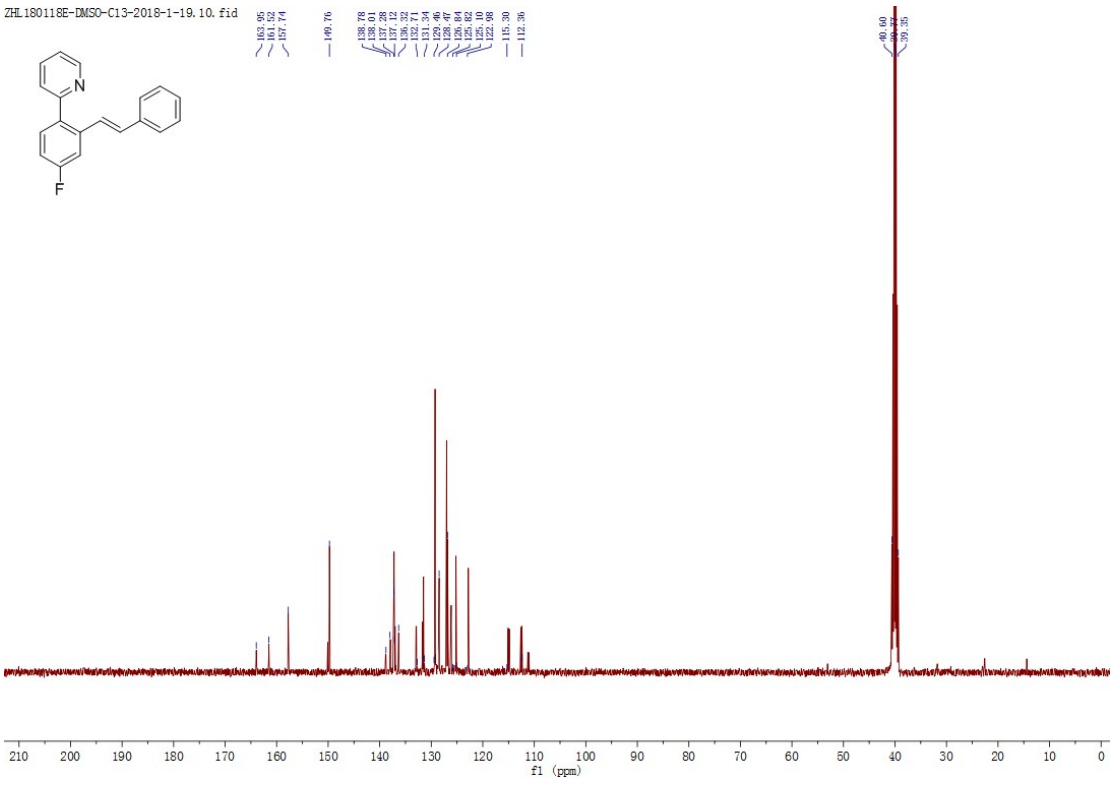
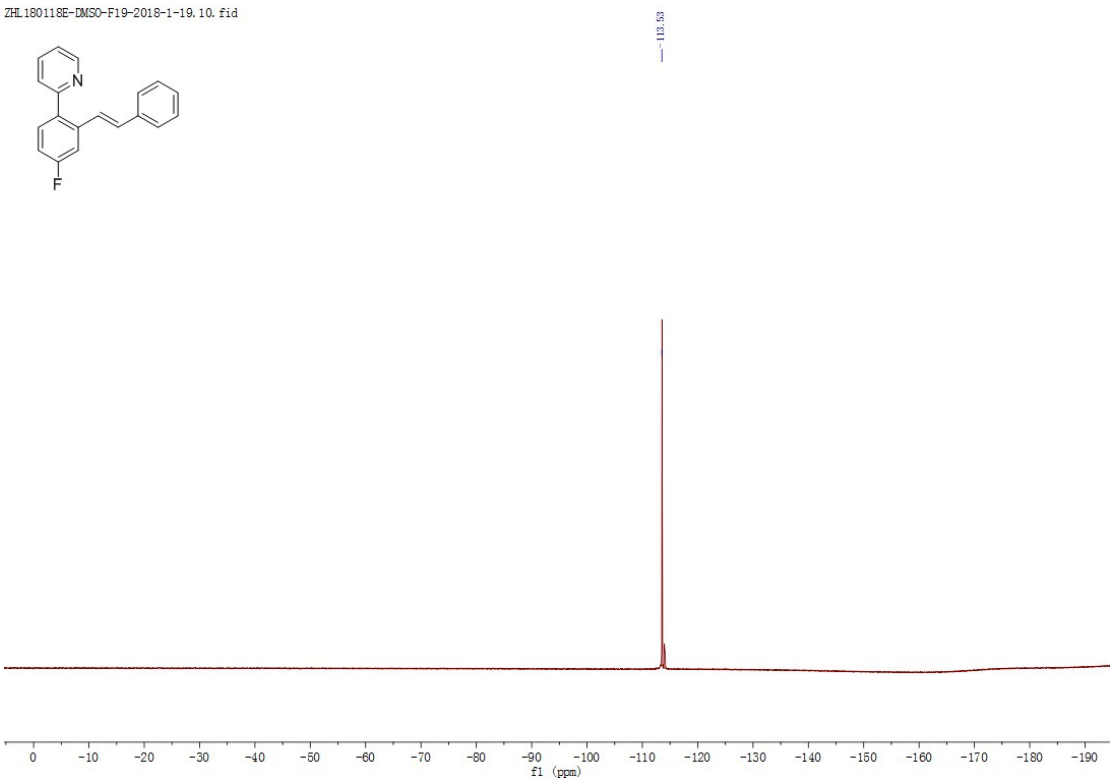
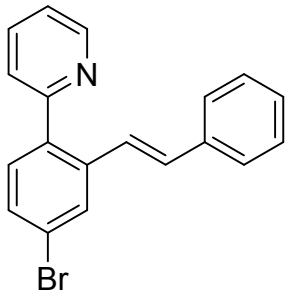
f1 (ppm)


f1 (ppm)

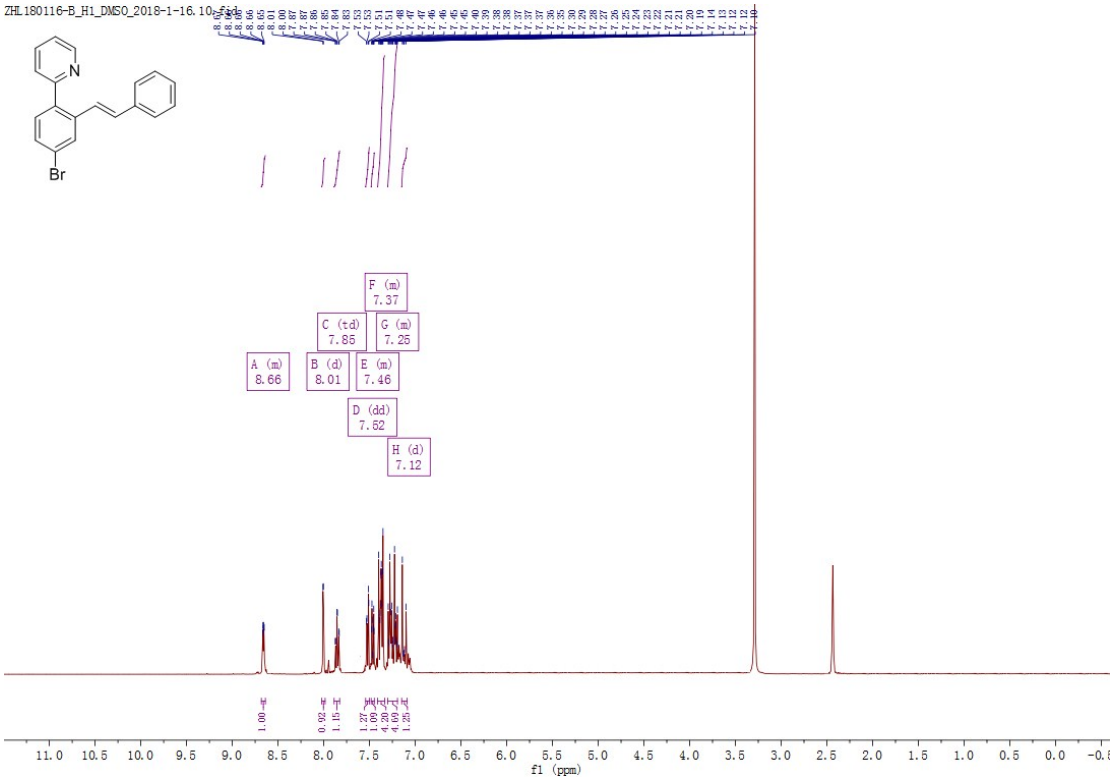


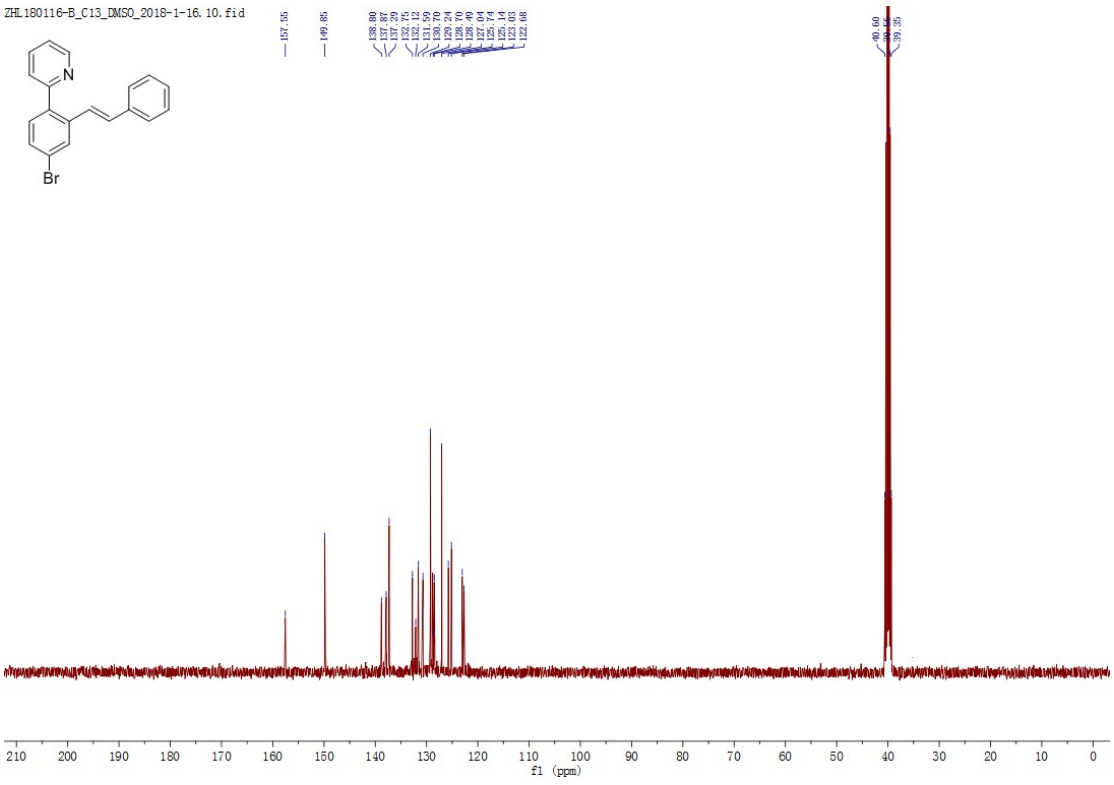
(E)-2-(4-bromo-2-styrylphenyl)pyridine



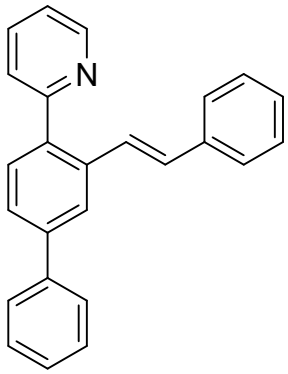
3e

White solid, Mp = 88-90 °C, yield 82 %, ^{1}HNMR (600MHz, DMSO):δ 8.66 (d, *J*=8.4Hz, 1H), 8.01 (s, 1H), 7.85 (t, *J*=8.4Hz, 1H), 7.52 (d, *J*=8.4Hz, 1H), 7.46 (d, *J*=16.2Hz, 1H), 7.37 (m, 4H), 7.25 (m, 5H), 7,12 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, DMSO):δ157.6, 149.9, 138.8, 137.9, 137.3, 132.8, 132.1, 130.7, 129.2, 128.7, 128.5, 127.0, 125.7, 125.1, 123.0, 122.7; HRMS (ESI) Calcd. For $C_{19}H_{14}BrNNa$: 358.0207, Found: m/z 358.0207.



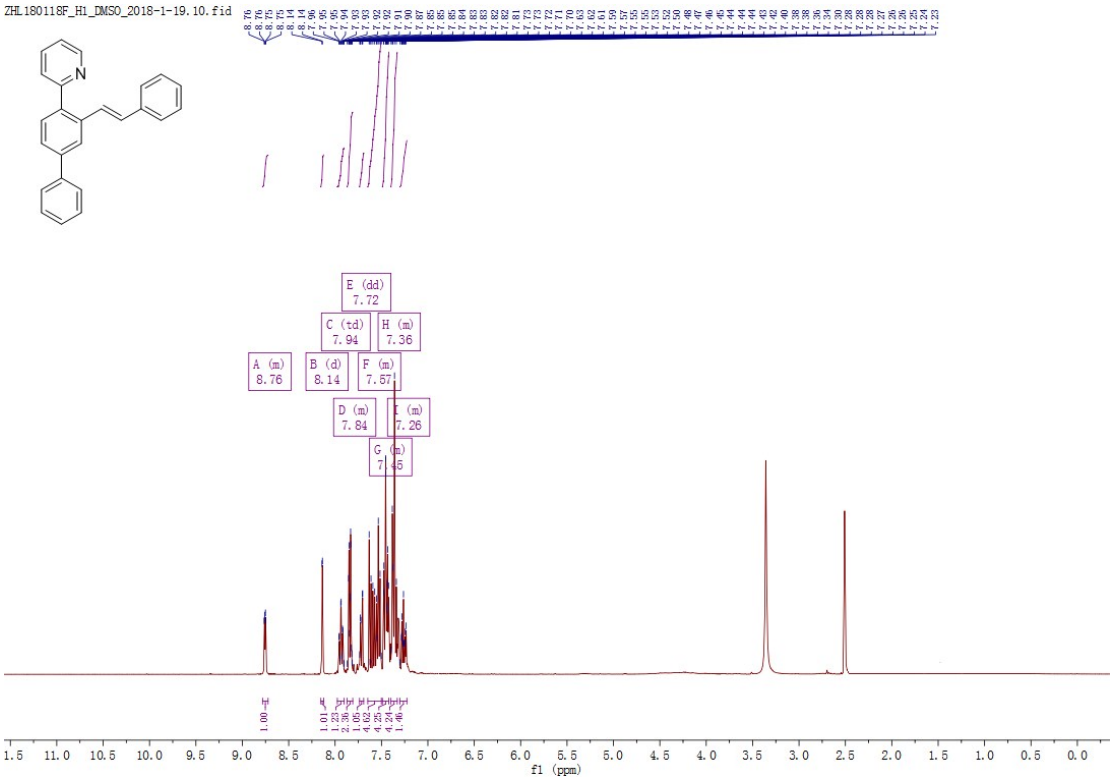


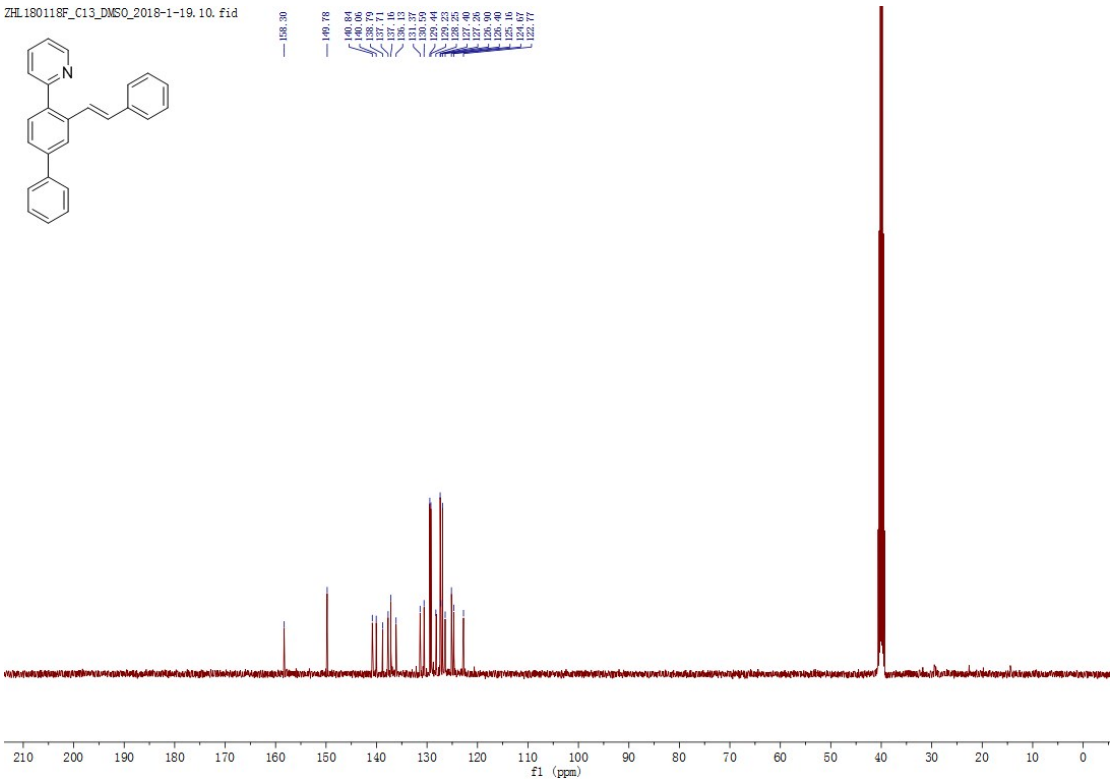
(E)-2-(3-styryl-[1,1'-biphenyl]-4-yl)pyridine



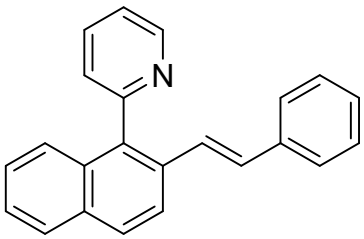
3f

Yellow liquid, yield 56 %, ^{1}HNMR (600MHz, DMSO):δ 8.66 (d, *J*=8.4Hz, 1H), 8.01 (s, 1H), 7.85 (t, *J*=8.4Hz, 1H), 7.52 (d, *J*=8.4Hz, 1H), 7.46 (d, *J*=16.2Hz, 1H), 7.37 (m, 4H), 7.25 (m, 5H), 7,12 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, DMSO):δ158.3, 149.8, 140.8, 140.1, 138.8, 137.7, 137.2, 136.1, 131.4, 130.6, 129.4, 129.2, 128.3, 127.4, 127.3, 126.9, 126.4, 125.2, 124.7, 122.8; HRMS (ESI) Calcd. For $C_{25}H_{19}NNa$: 356.1415, Found: m/z 356.1414.



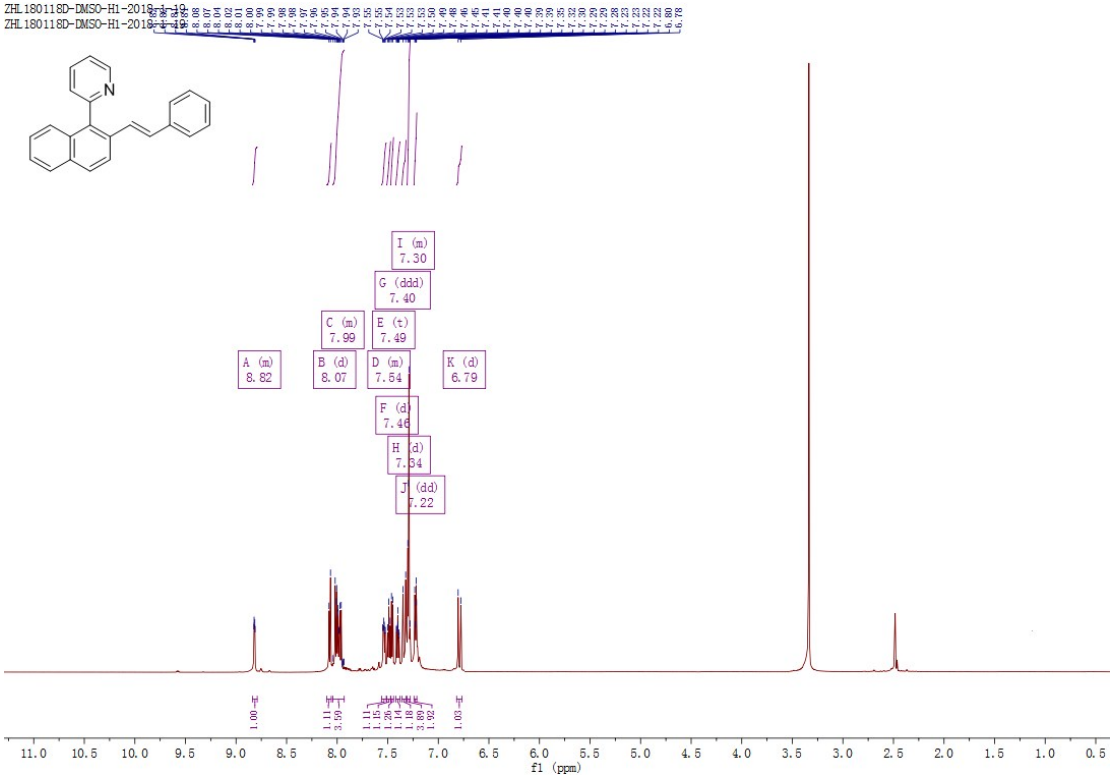


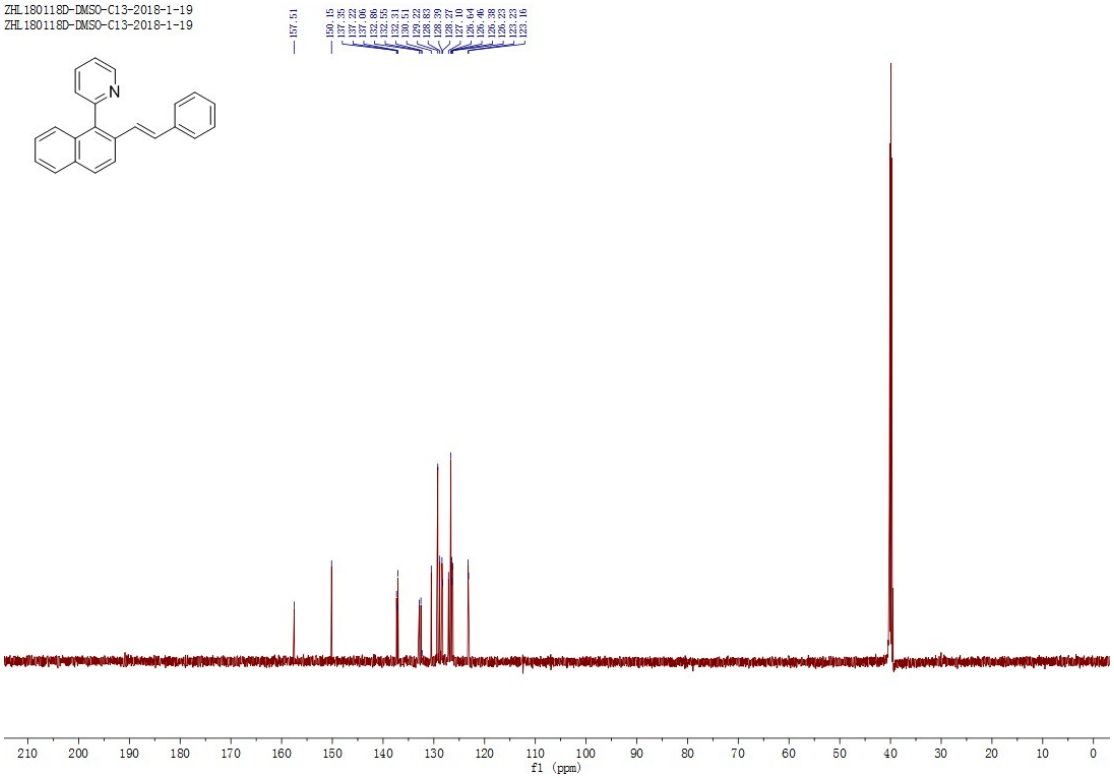
(E)-2-(2-styrylnaphthalen-1-yl)pyridine



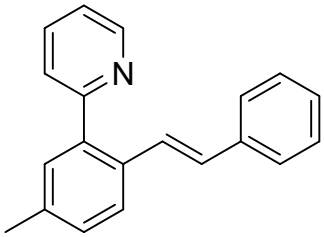
3g

White solid, Mp = 148-150 ^{o}C, yield 81%, ^{1}HNMR (600MHz, DMSO):δ 8.82 (d, *J*=8.4Hz, 1H), 8.07 (d, *J*=8.4Hz, 1H), 7.99 (m, 3H), 7.54 (t, *J*=8.4Hz, 1H), 7.49 (d, *J*=8.4Hz, 1H), 7.46 (t, *J*=8.4Hz, 1H), 7.40 (d, *J*=16.2Hz, 1H), 7,34 (m, 3H), 7.22 (d, *J*=8.4Hz, 1H), 6.79 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, DMSO):δ157.5, 150.2, 137.4, 137.2, 137.1, 132.9, 132.6, 132.3, 130.5, 129.2, 128.8, 128.4, 128.3, 127.1, 126.6, 126.5, 126.4, 126.2, 123.2, 123.1; HRMS (ESI) Calcd. For $C_{23}H_{17}NNa$: 330.1259, Found: m/z 330.1258.



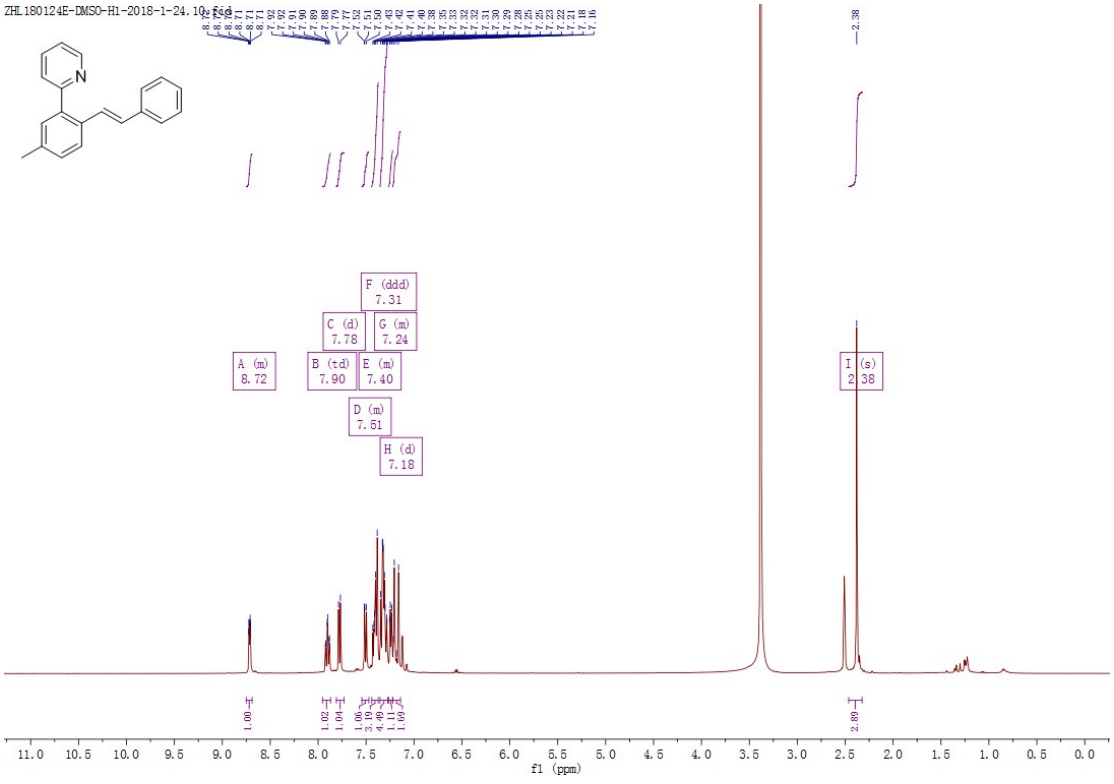


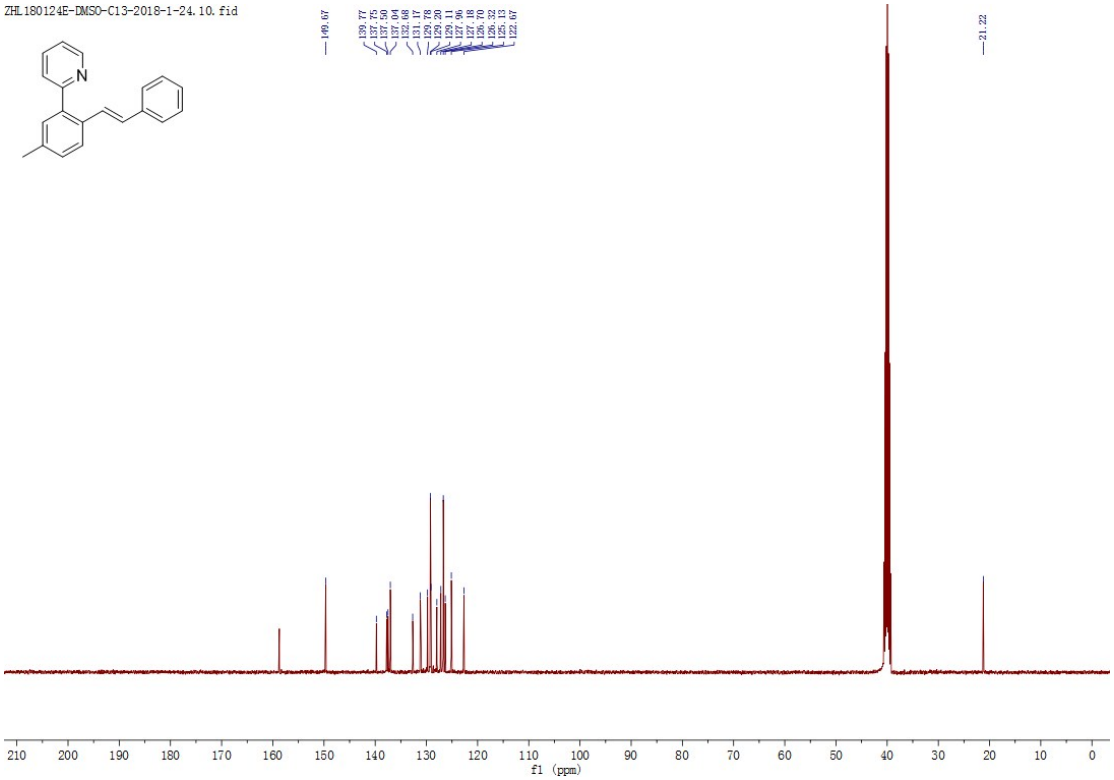
(E)-2-(5-methyl-2-styrylphenyl)pyridine



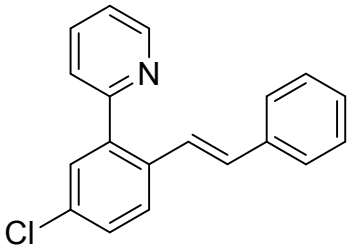
3h

Colourless liquid, yield 86 %, ^{1}HNMR (600MHz, DMSO):δ8.72 (d, *J*=8.4Hz, 1H), 7.90 (t, *J*=8.4Hz, 1H), 7.78 (d, *J*=8.4Hz, 1H), 7.51 (d, *J*=8.4Hz, 1H), 7.40 (m, 3H), 7.31 (m, 5H), 7.24 (d, *J*=8.4Hz, 1H), 7,18 (d, *J*=16.2Hz, 1H), 2.38 (s, 1H); ^{13}C NMR (150MHz, DMSO):δ158.7, 149.7, 139.8, 137.8, 137.5, 137.0, 132.7, 131.2, 129.8, 129.2, 129.1, 128.0, 127.2, 126.7, 126.3, 125.1, 122.8, 21.2; HRMS (ESI) Calcd. For $C_{20}H_{17}NNa$: 294.1259, Found: m/z 294.1258.



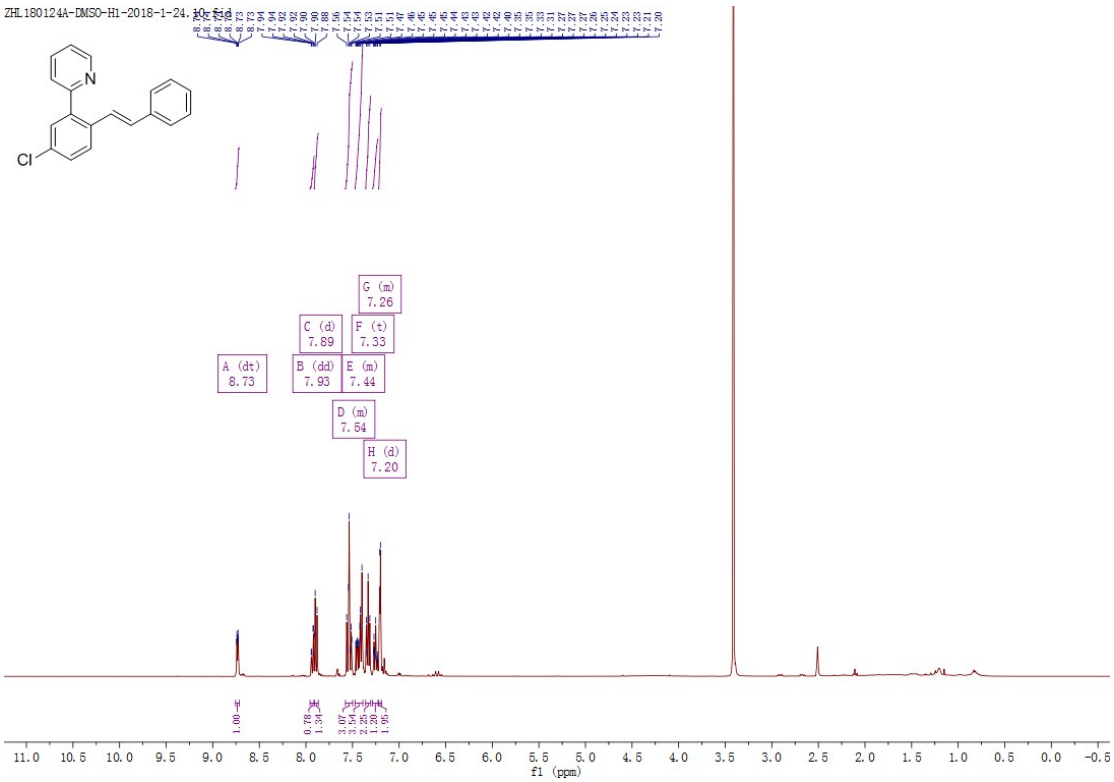


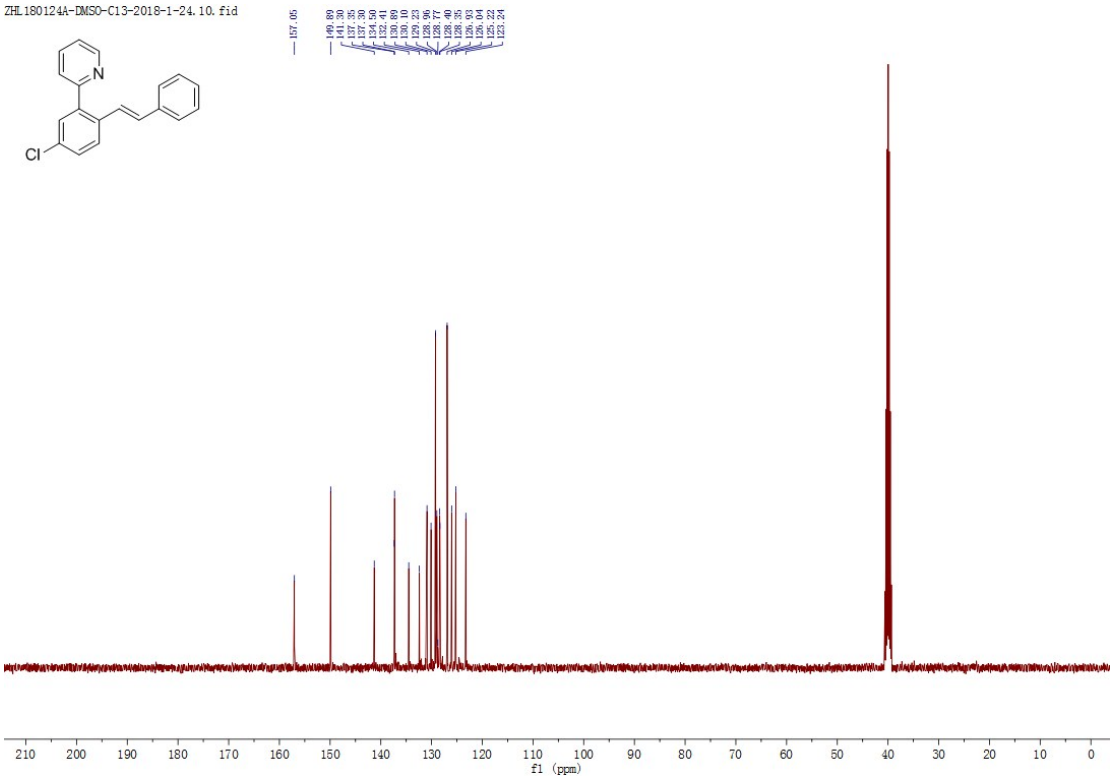
(E)-2-(5-chloro-2-styrylphenyl)pyridine



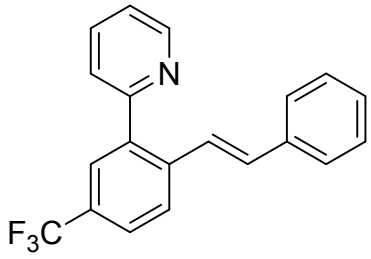
3i

Colourless liquid, yield 84 %, ^{1}HNMR (600MHz, DMSO):δ 8.73 (d, *J*=8.4Hz, 1H), 7.93 (d, *J*=8.4Hz, 1H), 7.89 (d, *J*=8.4Hz, 1H), 7.54 (m, 3H), 7.44 (m, 3H), 7.33 (t, *J*=8.4Hz, 2H), 7.26 (t, *J*=8.4Hz, 1H), 7,20 (d, *J*=8.4Hz, 1H); ^{13}C NMR (150MHz, DMSO):δ157.1, 149.9, 141.3, 137.4, 137.3, 134.5, 132.4, 130.9, 130.1, 129.2, 129.0, 128.8, 128.4, 128.3, 126.9, 126.0, 125.2, 123.2; HRMS (ESI) Calcd. For $C_{19}H_{14}ClNNa$: 314.0712, Found: m/z 314.0710.



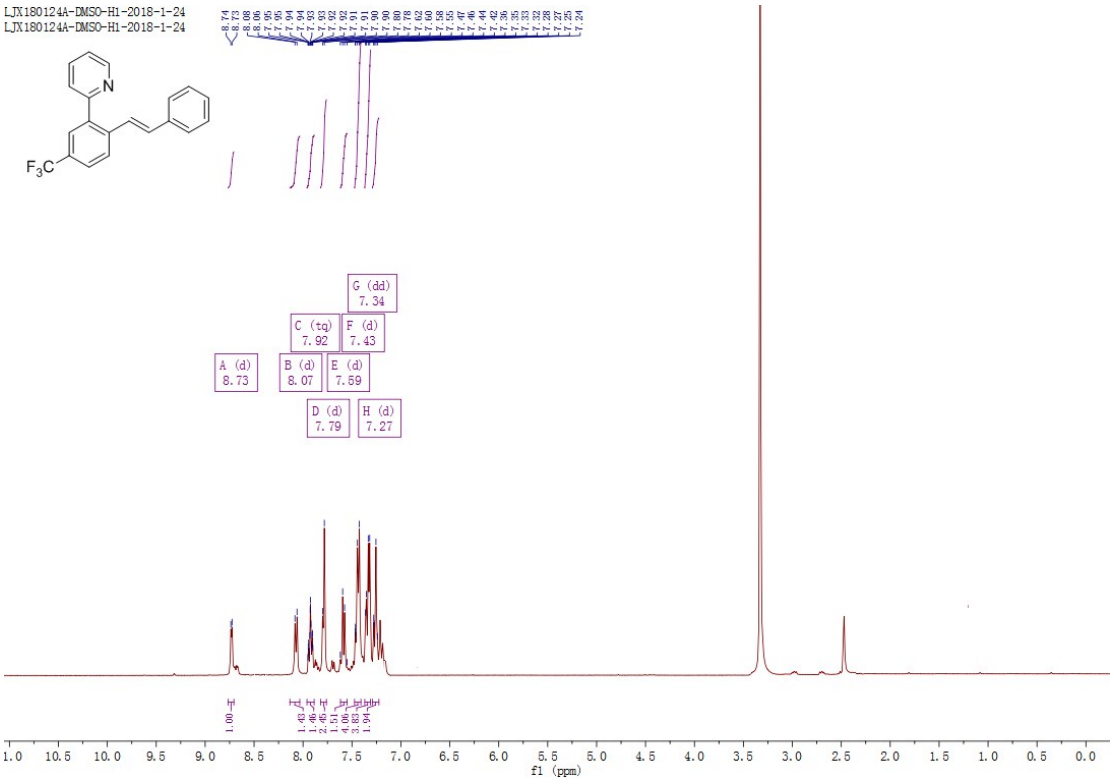


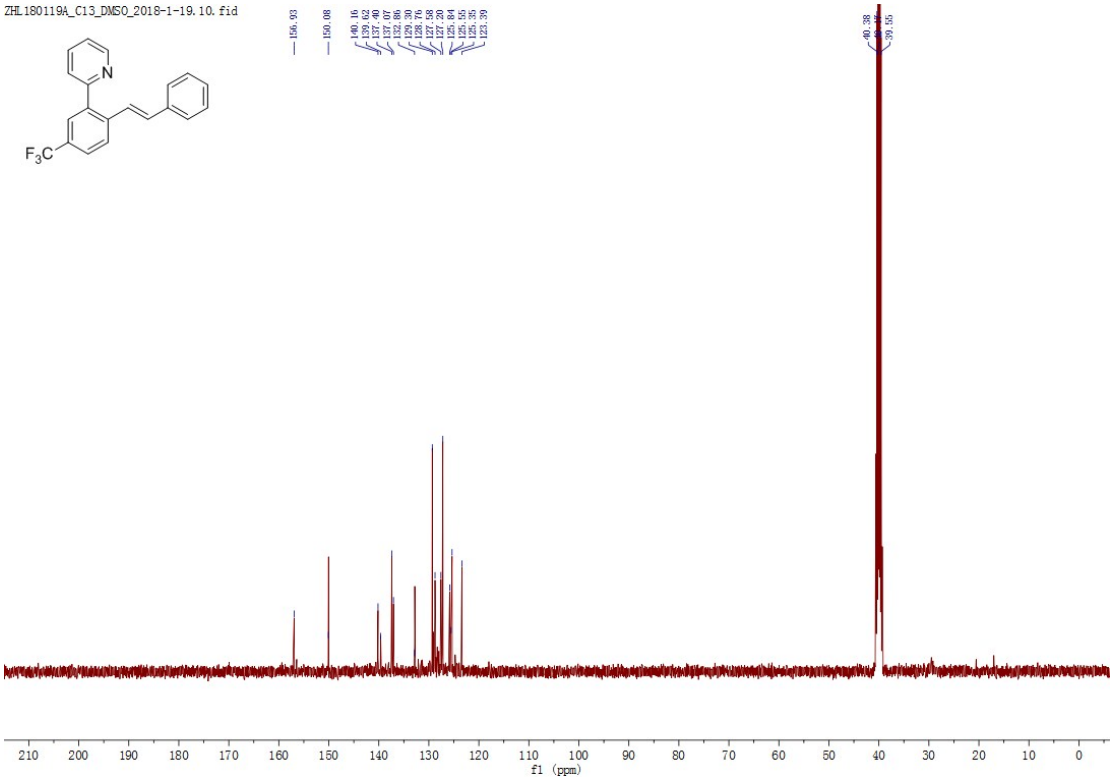
(E)-2-(2-styryl-5-(trifluoromethyl)phenyl)pyridine

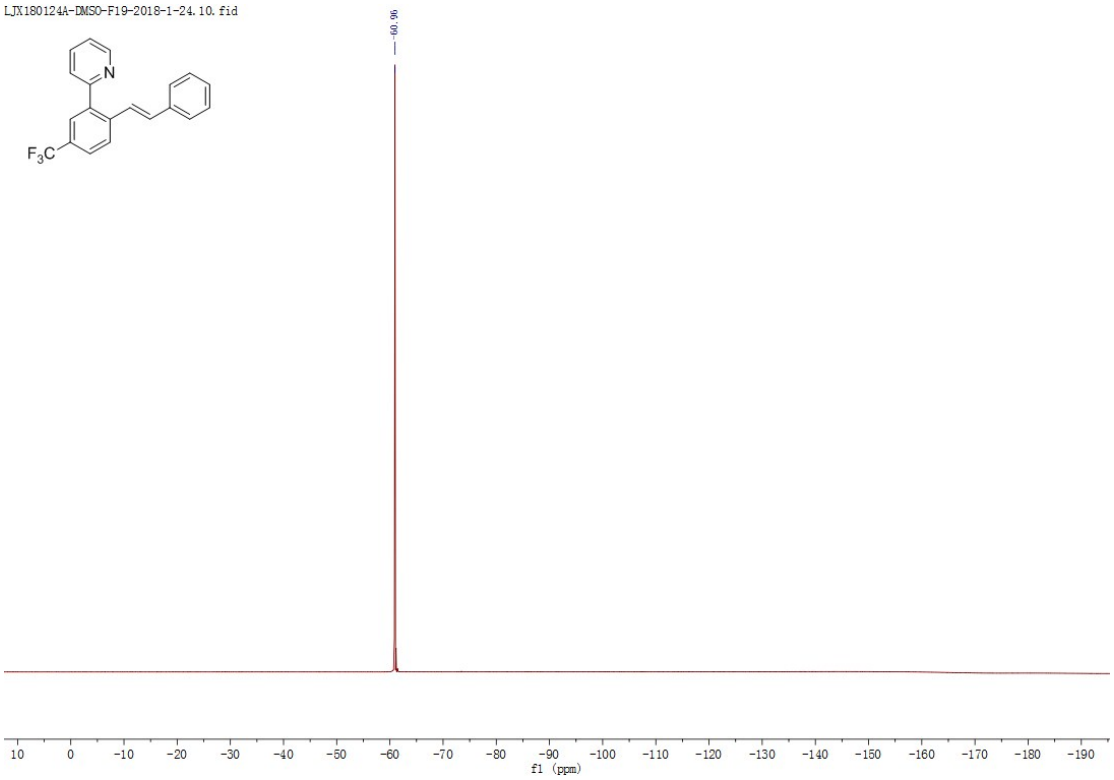


3j

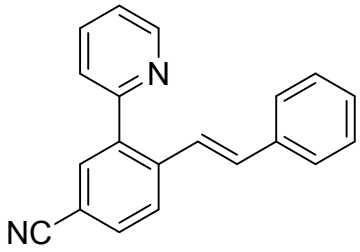
Colourless Liquid, yield 78 %, ^{1}HNMR (600MHz, DMSO):δ 8.73 (d, *J*=8.4Hz, 1H), 8.07 (d, *J*=8.4Hz, 1H), 7.92 (t, *J*=8.4Hz, 1H), 7.79 (m, 2H), 7.59 (d, *J*=8.4Hz, 1H), 7.43 (d, *J*=8.4Hz, 4H), 7.34 (m, 4H), 7,27 (m, 2H); ^{13}C NMR (150MHz, DMSO):δ156.9, 150.1, 140.2, 139.6, 137.4, 137.1, 132.9, 129.3, 128.8, 127.6, 127.2, 125.8, 125.6, 125.4, 123.4; ^{19}F NMR (376MHz, DMSO): -60.96; HRMS (ESI) Calcd. For $C_{20}H_{14}F_3NNa$: 348.0976, Found: m/z 348.0975.





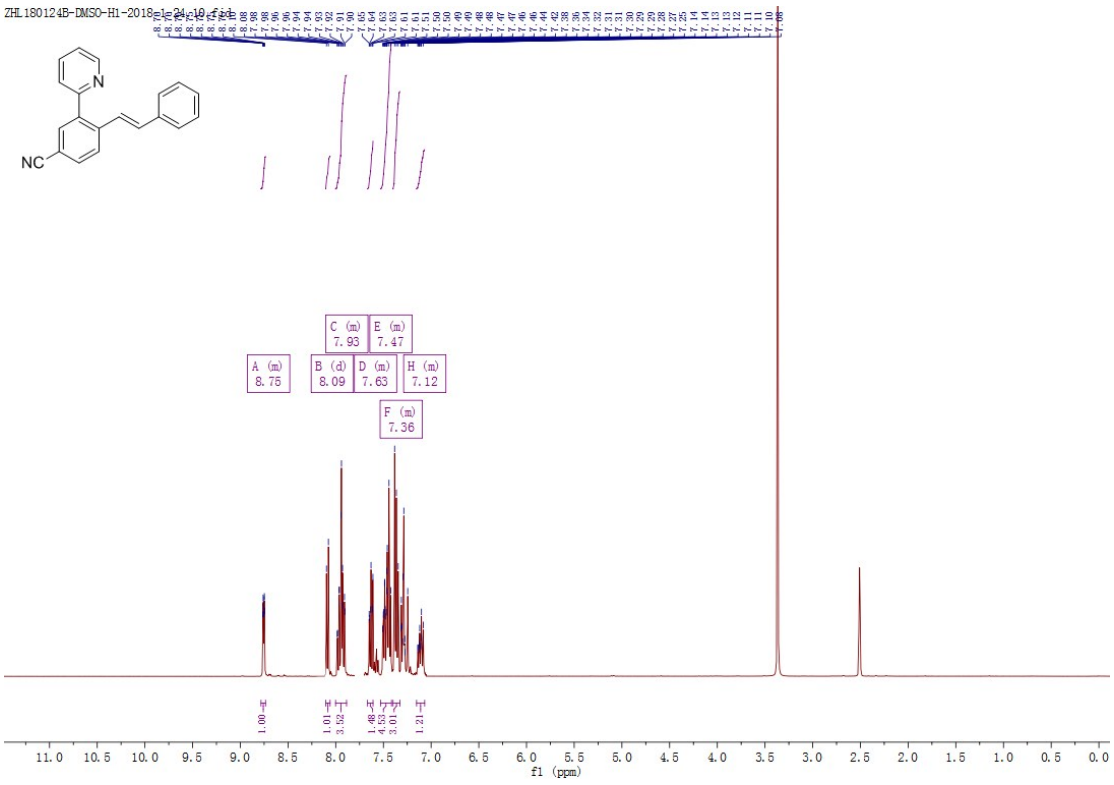


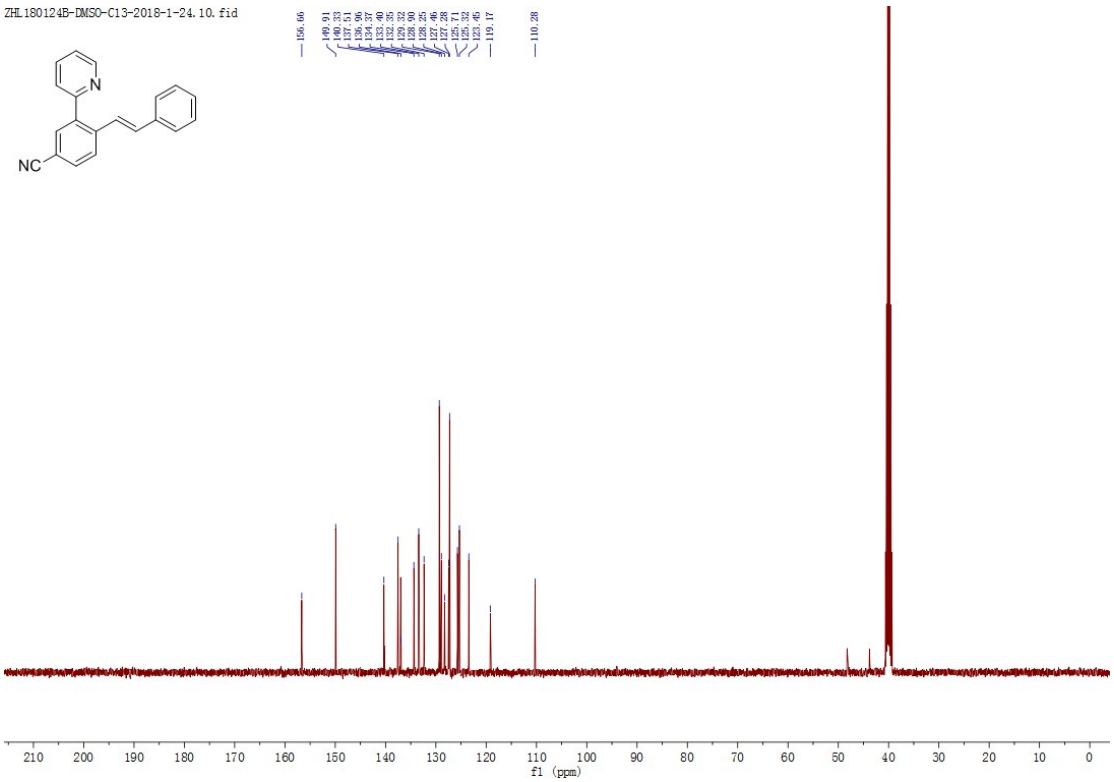
(E)-3-(pyridin-2-yl)-4-styrylbenzonitrile



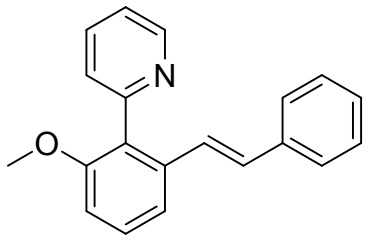
3k

White solid, Mp = 126-128 ℃, yield 79 %, ^{1}HNMR (600MHz, DMSO):δ 8.75 (d, *J*=8.4Hz, 1H), 8.09 (d, *J*=8.4Hz, 1H), 7.93 (m, 3H), 7.63 (m, 1H), 7.47 (m, 4H), 7.36 (t, *J*=8.4Hz, 3H), 7.12 (m, 1H); ^{13}C NMR (150MHz, DMSO):δ156.7, 149.9, 140.3, 137.5, 137.0, 134.4, 133.4, 132.4, 129.3, 128.9, 128.3, 127.5, 127.3, 125.4, 125.3, 123.5, 119.2, 110.3; HRMS (ESI) Calcd. For $C_{20}H_{14}N_2Na$: 305.1055, Found: m/z 305.1055.



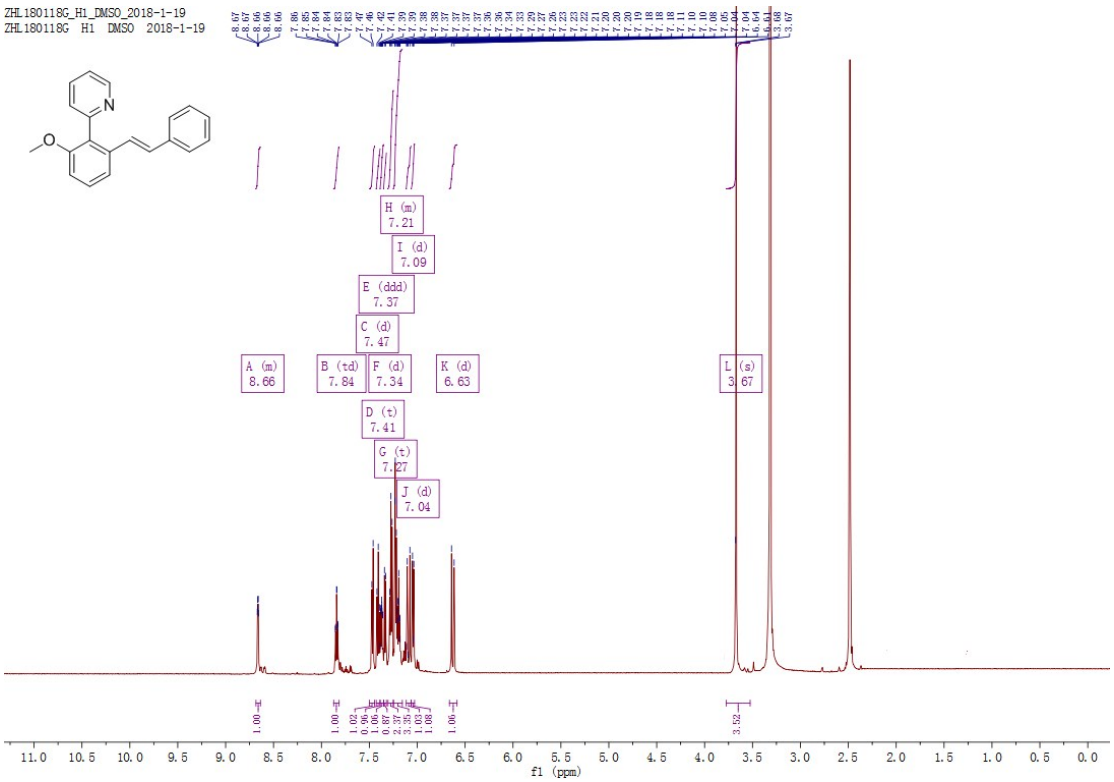


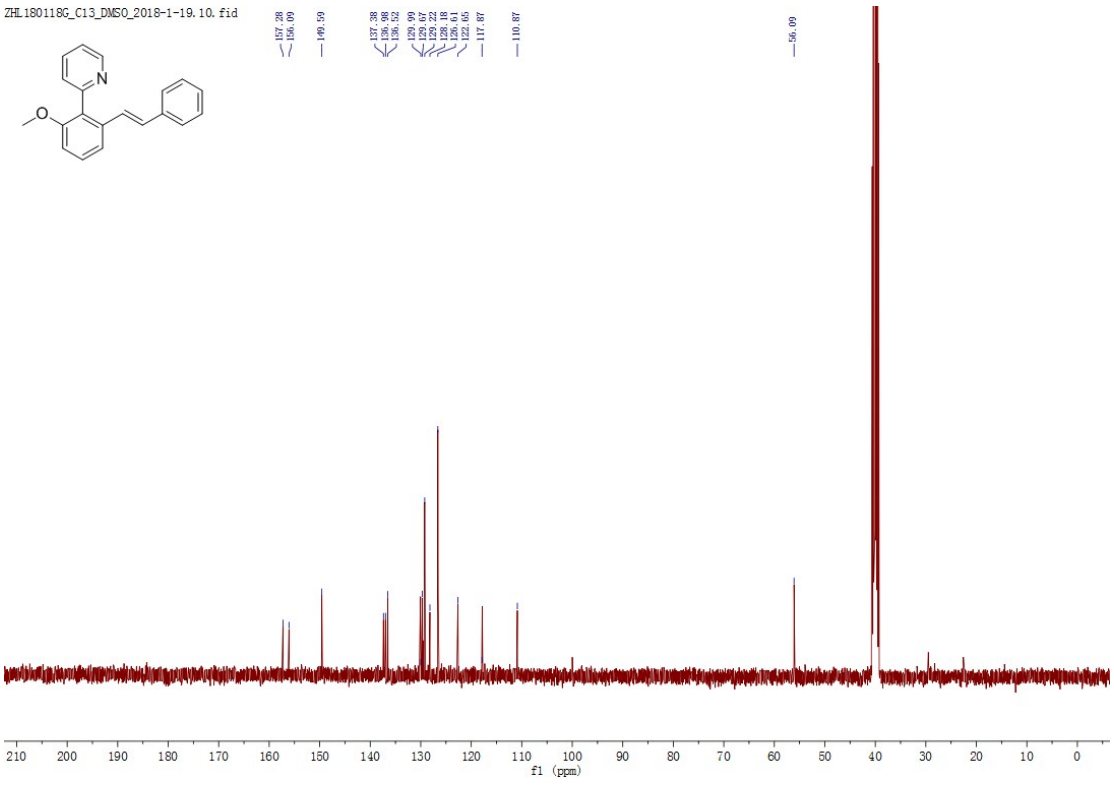
(E)-2-(2-methoxy-6-styrylphenyl)pyridine



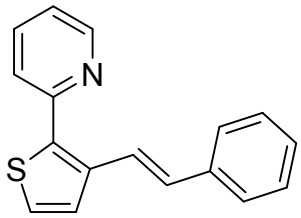
3l

Grey solid, Mp = 100-102 °C, yield 51%, ^{1}HNMR (600MHz, DMSO):δ 8.66 (d, *J*=8.4Hz, 1H), 7.84 (t, *J*=8.4Hz, 1H), 7.47 (d, *J*=8.4Hz, 1H), 7.41 (d, *J*=8.4Hz, 1H), 7.37 (t, *J*=8.4Hz, 1H), 7.34 (d, *J*=8.4Hz, 1H), 7.27 (m, 2H), 7.21 (m, 3H), 7.09 (d, J=16.2Hz, 1H), 7.04 (d, *J*=8.4Hz, 1H), 6.63 (d, J=16.2Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (150MHz, DMSO):δ157.3, 156.1, 149.6, 137.4, 137.0, 136.5, 130.0, 129.7, 129.2, 128.2, 126.6, 122.7, 117.9, 110.9, 56.1; HRMS (ESI) Calcd. For $C_{20}H_{17}NONa$: 310.1208, Found: m/z 310.1208.



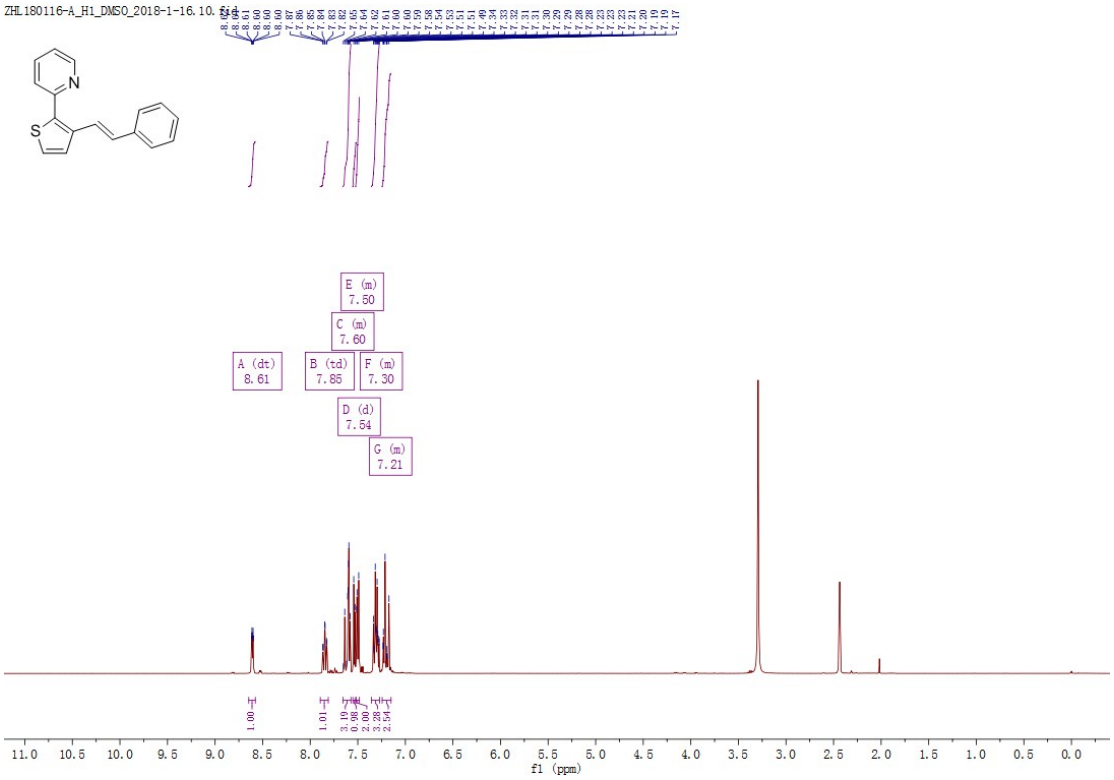


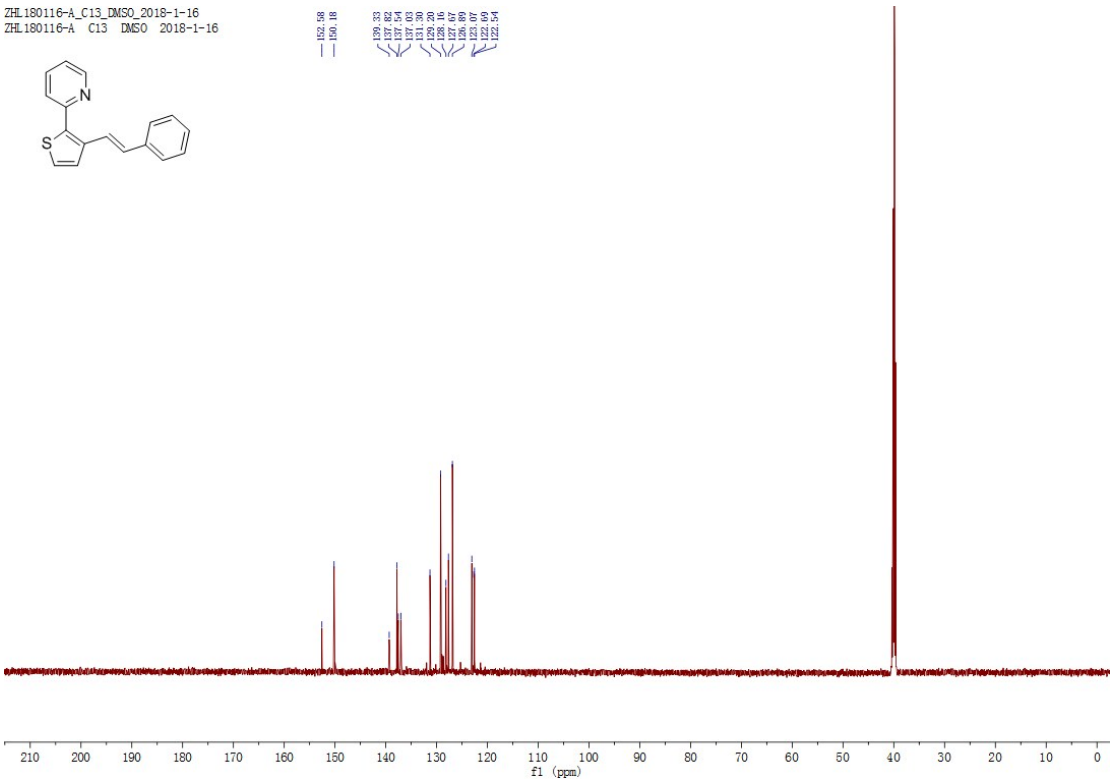
(E)-2-(3-styrylthiophen-2-yl)pyridine



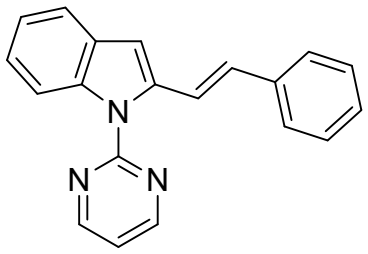
3m

Colourless liquid, yield 85 %, ^{1}HNMR (600MHz, DMSO):δ 8.61 (d, *J*=8.4Hz, 1H), 7.85 (t, *J*=8.4Hz, 1H), 7.60 (m, 3H), 7.54 (d, *J*=8.4Hz, 1H), 7.50 (m, 2H), 7.30 (m, 3H), 7.21 (m, 2H); ^{13}C NMR (150MHz, DMSO):δ152.6, 150.2, 139.3, 137.8, 137.5, 137.0, 131.3, 129.2, 128.2, 127.7, 126.9, 123.1, 122.7, 122.5; HRMS (ESI) Calcd. For $C_{17}H_{13}NSNa$: 286.0666, Found: m/z 286.0665.



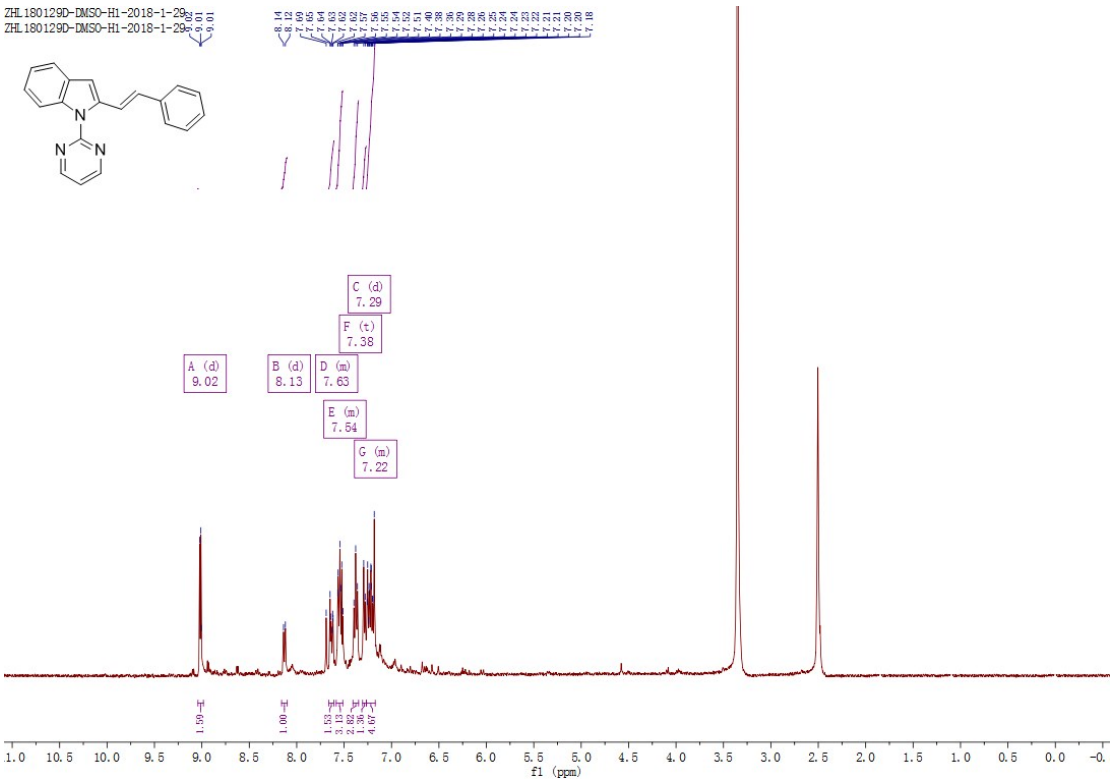


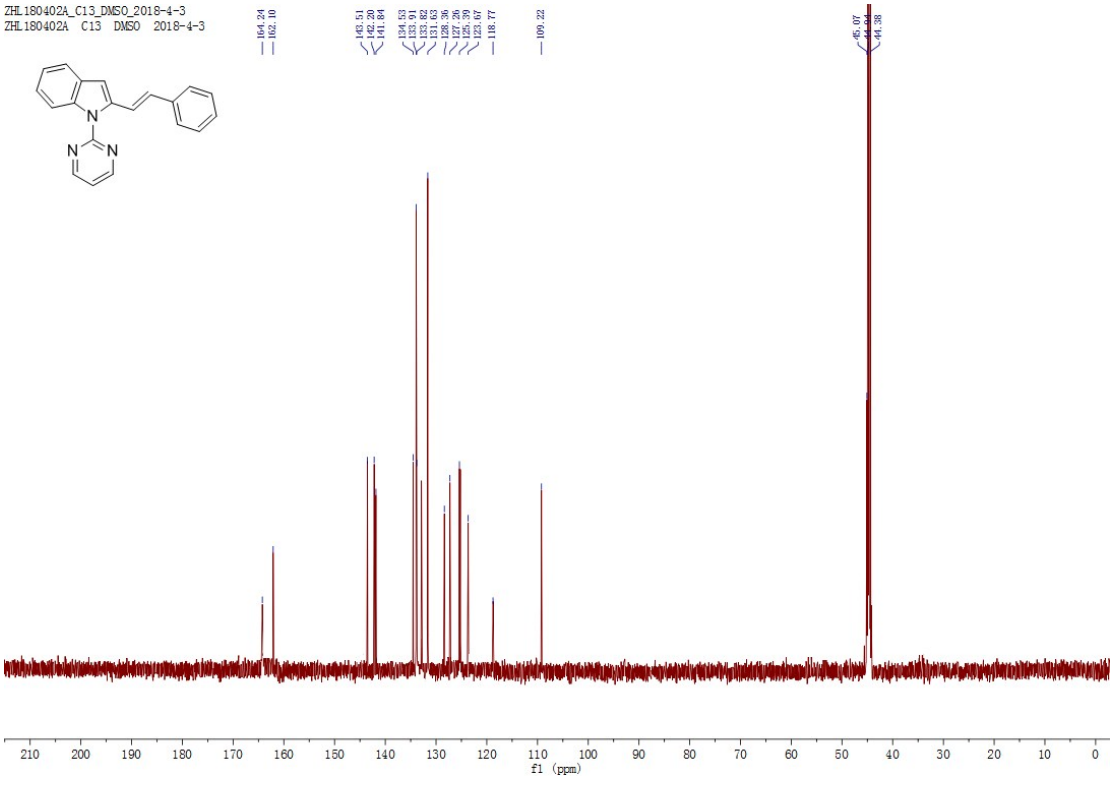
(E)-1-(pyrimidin-2-yl)-2-styryl-1H-indole



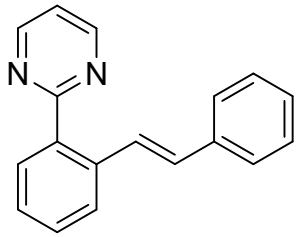
3n

Yellow liquid, yield 62 %, ^{1}HNMR (600MHz, DMSO):δ 9.02 (d, *J*=8.4Hz, 2H), 8.13 (d, *J*=8.4Hz, 1H), 7.63 (m, 1H), 7.54 (m, 3H), 7.38 (t, *J*=8.4Hz, 3H), 7.29 (d, *J*=8.4Hz, 1H), 7.22 (m, 4H); ^{13}C NMR (150MHz, DMSO):δ164.2, 162.1, 143.5, 142.0, 133.9, 133.8, 131.6, 128.4, 127.3, 125.4, 123.7, 118.8, 109.2; HRMS (ESI) Calcd. For $C_{20}H_{15}N_3Na$: 320.1164, Found: m/z 320.1164.



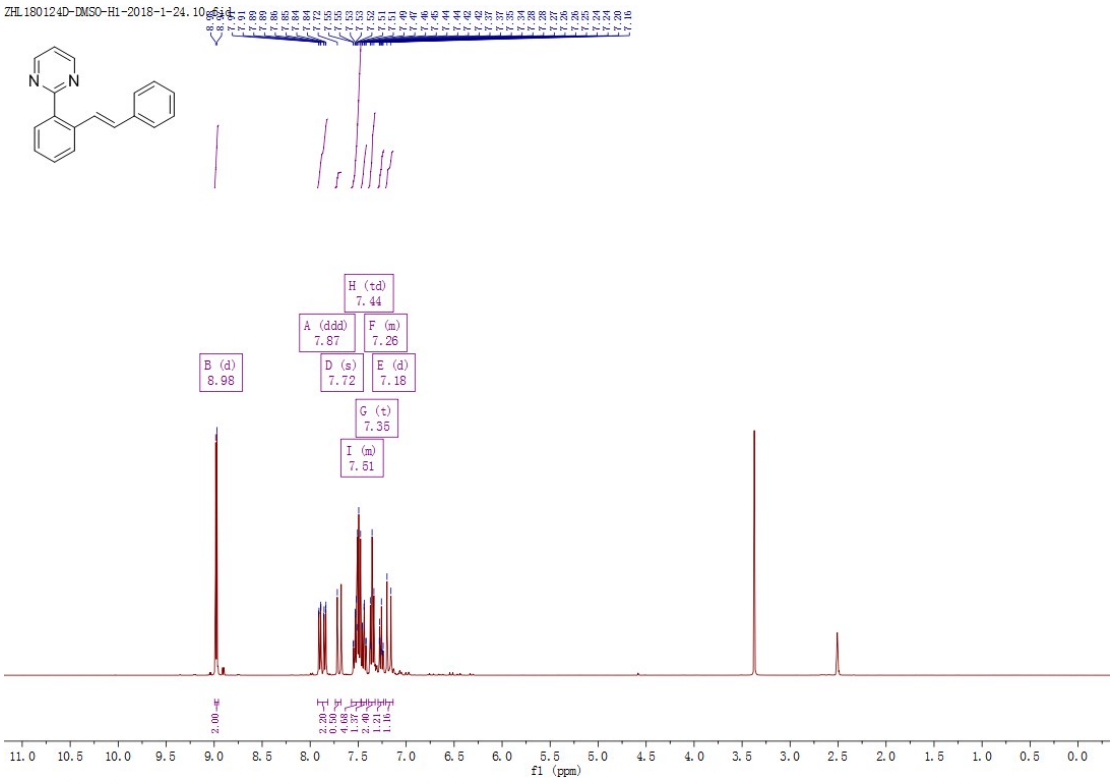


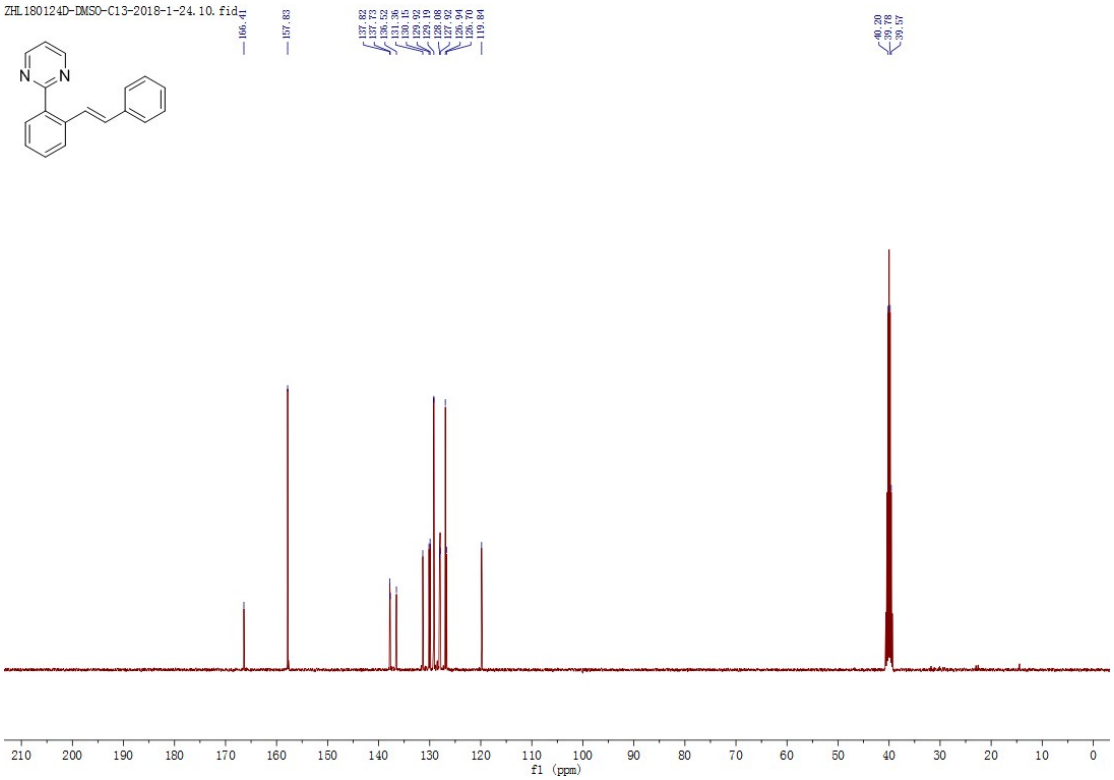
(E)-2-(2-styrylphenyl)pyrimidine



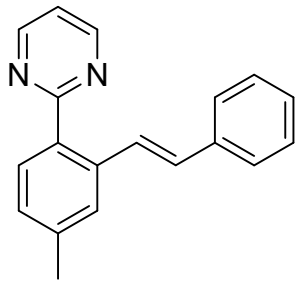
3o

Yellow liquid, yield 82 %, ^{1}HNMR (600MHz, DMSO):δ 8.98 (d, *J*=8.4Hz, 1H), 7.87 (m, 2H), 7.72 (d, *J*=16.2Hz, 1H), 7.51 (m, 4H), 7.44 (t, *J*=8.4Hz, 1H), 7.35 (t, *J*=8.4Hz, 2H), 7.26 (t, *J*=8.4Hz, 1H), 7.18 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, DMSO):δ166.4, 157.8, 137.8, 137.7, 136.5, 131.4, 130.2, 129.9, 129.2, 128.1, 127.9, 126.9, 126.7, 119.8; HRMS (ESI) Calcd. For $C_{18}H_{14}N_2Na$: 281.1055, Found: m/z 281.1055.



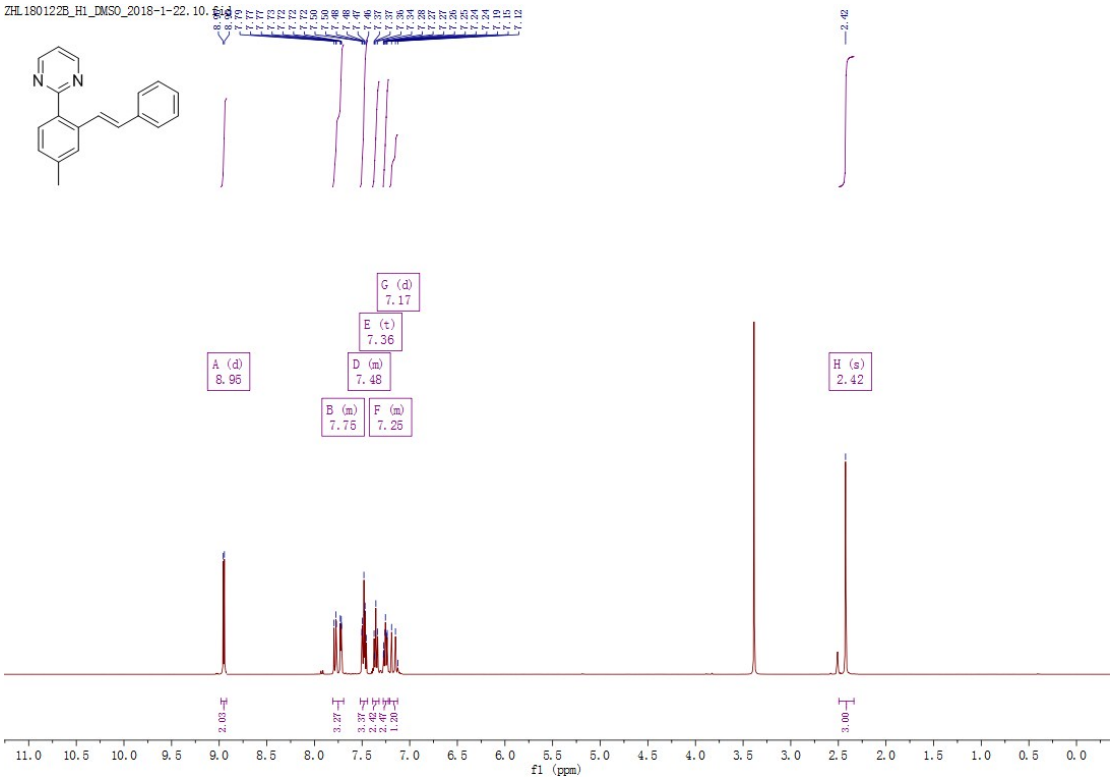


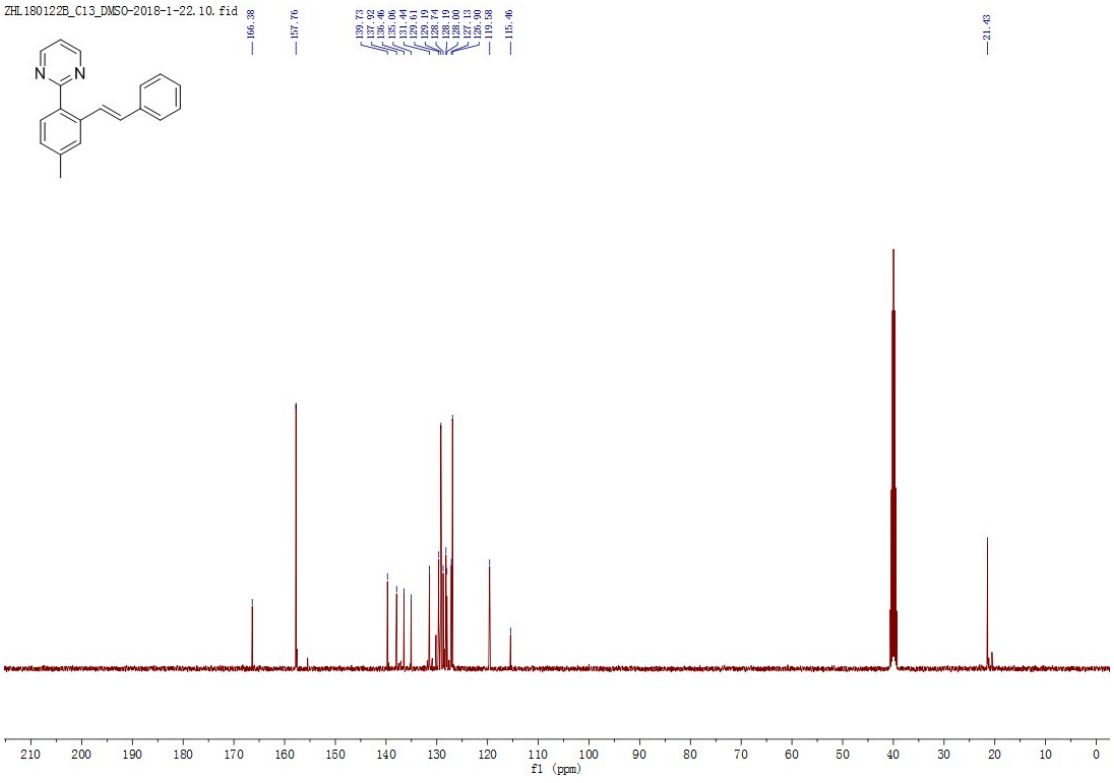
(E)-2-(4-methyl-2-styrylphenyl)pyrimidine



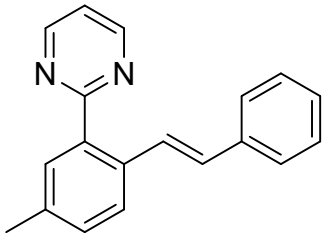
3p

Yellow liquid, yield 89 %, ^{1}HNMR (600MHz, DMSO):δ 8.95 (d, *J*=8.4Hz, 1H), 7.75 (m, 3H), 7.48 (m, 3H), 7.36 (t, *J*=8.4Hz, 2H), 7.25 (t, *J*=8.4Hz, 2H), 7.17 (d, *J*=16.2Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (150MHz, DMSO):δ166.4, 157.8, 139.7, 137.9, 136.5, 136.1, 131.4, 129.6, 129.2, 128.7, 128.2, 128.0, 127.1, 126.9, 119.6, 115.5, 21.4; HRMS (ESI) Calcd. For $C_{19}H_{16}N_2Na$: 295.1211, Found: m/z 295.1210.



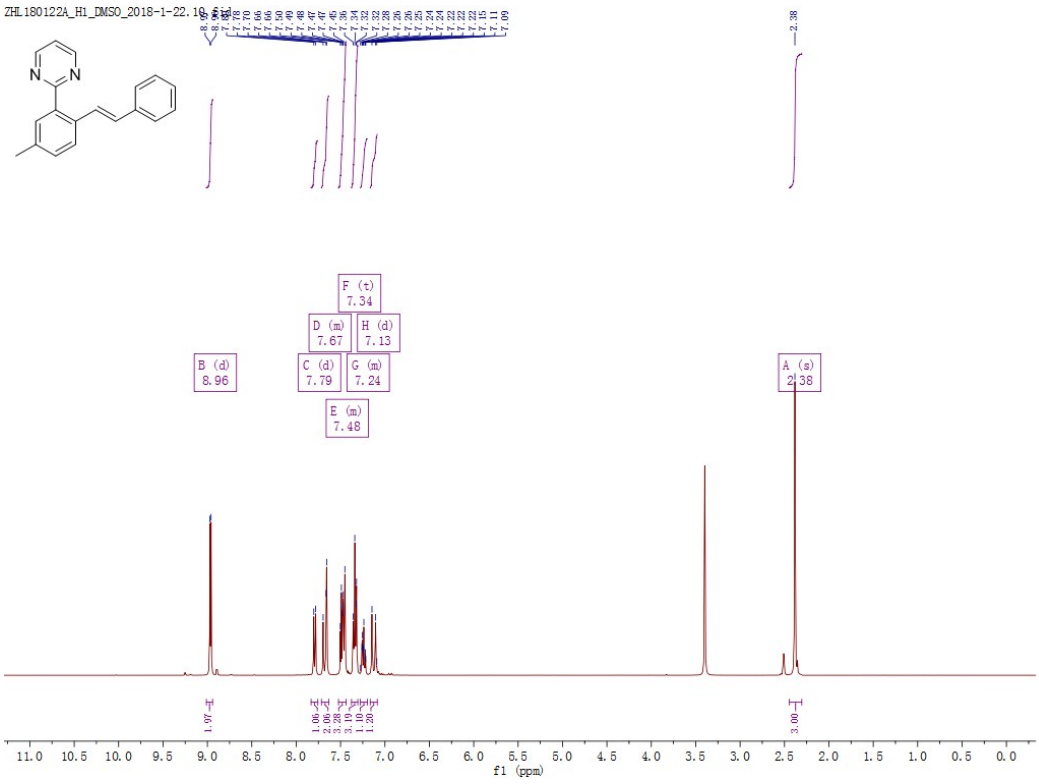


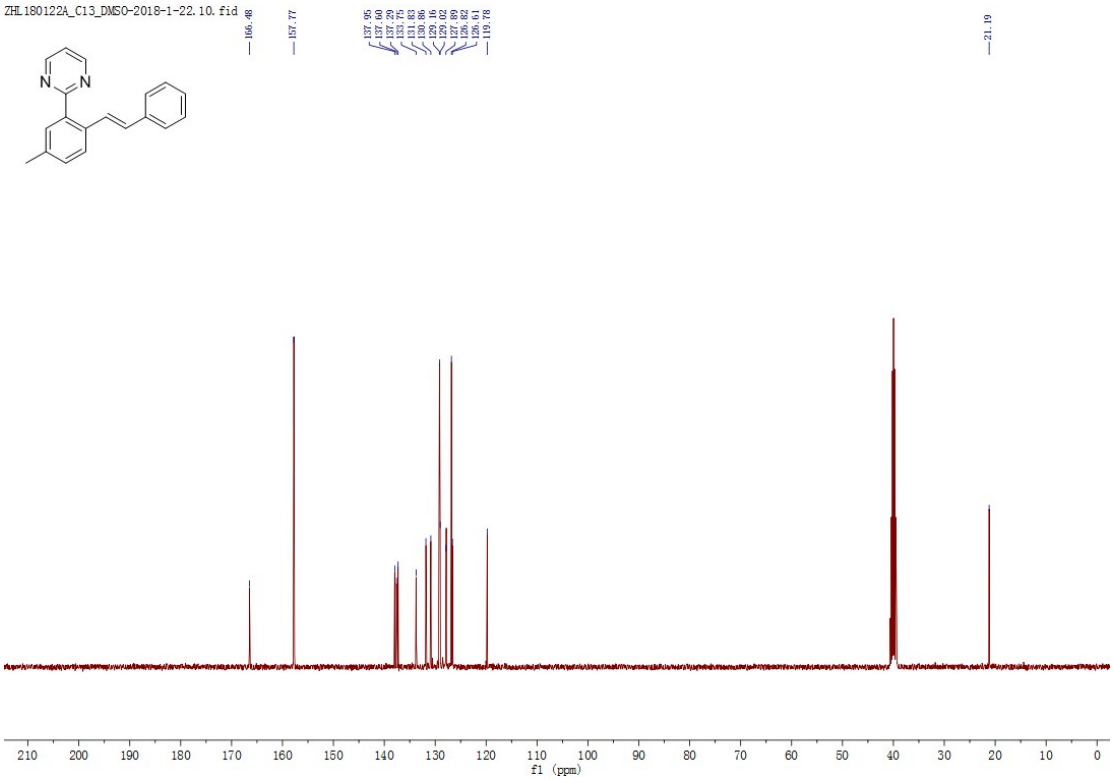
(E)-2-(5-methyl-2-styrylphenyl)pyrimidine



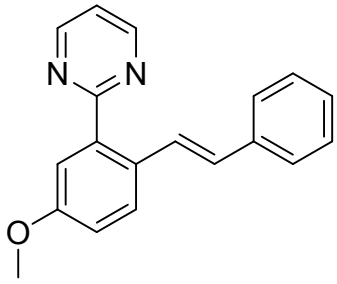
3q

Brown liquid, yield 87 %, ^{1}HNMR (600MHz, DMSO):δ 8.96 (d, *J*=8.4Hz, 2H), 7.79 (d, *J*=8.4Hz, 1H), 7.76 (d, *J*=8.4Hz, 2H), 7.48 (m, 3H), 7.34 (t, *J*=8.4Hz, 3H), 7.24 (t, *J*=8.4Hz, 1H), 7.13 (d, *J*=16.2Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (150MHz, DMSO):δ166.5, 157.8, 138.0, 137.6, 137.3, 133.8, 131.8, 130.9, 129.2, 129.0, 127.9, 126.8, 126.6, 119.8, 21.2; HRMS (ESI) Calcd. For $C_{19}H_{16}N_2Na$: 295.1211, Found: m/z 295.1211.



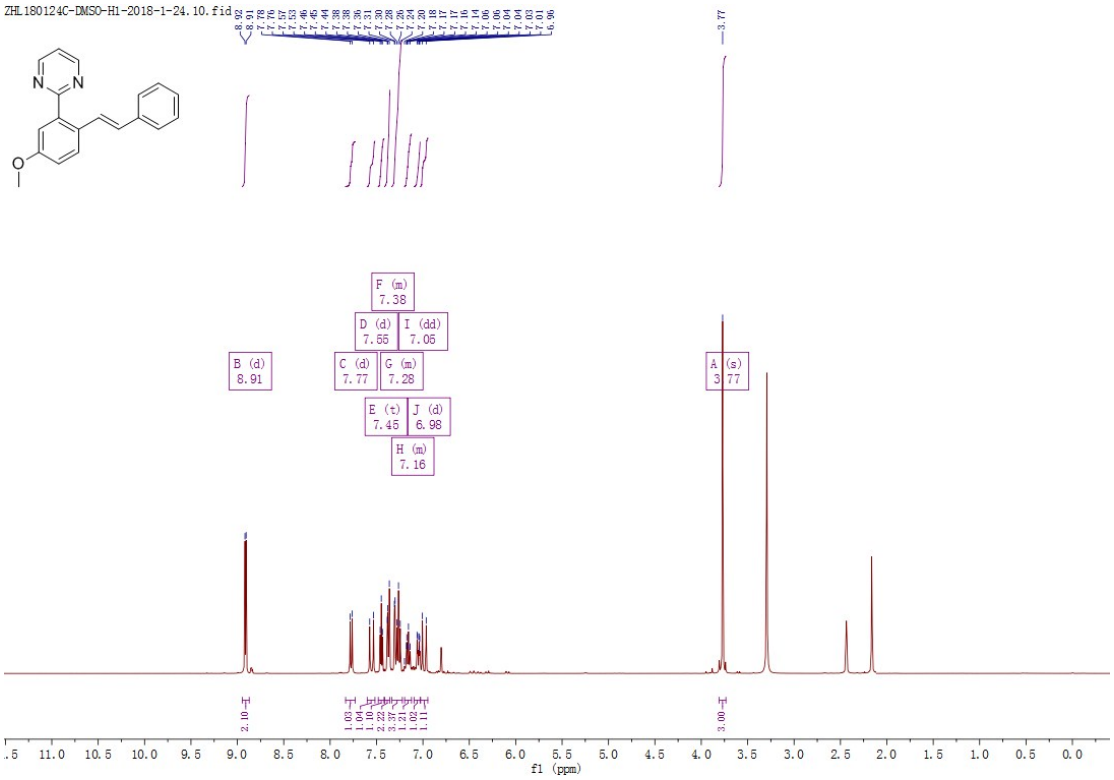


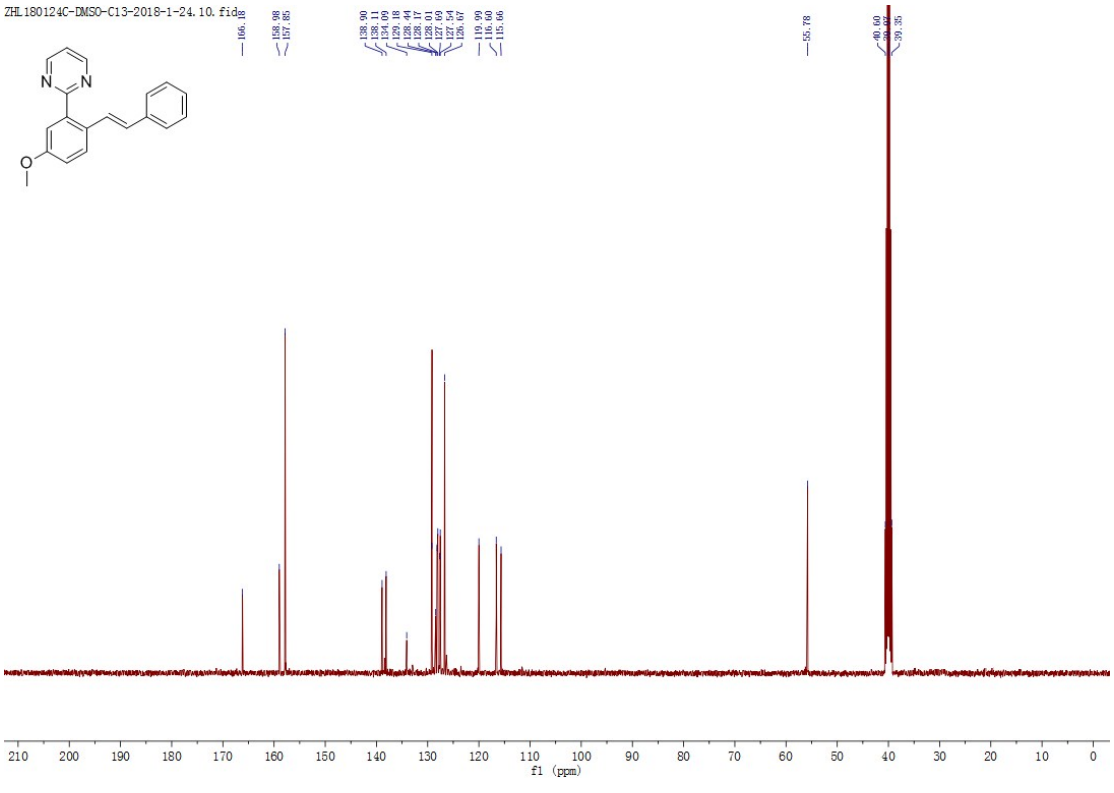
(E) -2-(5-methoxy-2-styrylphenyl)pyrimidine



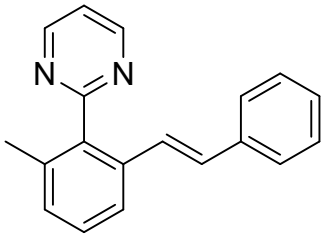
3r

Light yellow liquid, yield 67%, ^{1}HNMR (600MHz, DMSO):δ8.91 (d, *J*=8.4Hz, 2H), 7.77 (d, *J*=8.4Hz, 1H), 7.55 (d, *J*=16.2Hz, 1H), 7.45 (t, *J*=8.4Hz, 1H), 7.38 (d, *J*=8.4Hz, 2H), 7.28 (m, 3H), 7.16 (t, *J*=16.2Hz, 1H), 7.05 (d, *J*=8.4Hz, 1H), 6.98 (t, *J*=16.2Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (150MHz, DMSO):δ166.2, 160.0, 157.9, 138.9, 138.1, 134.1, 129.2, 128.4, 128.2, 128.0, 127.7, 127.5, 126.7, 120.0, 116.6, 115.6, 55.8; HRMS (ESI) Calcd. For $C_{18}H_{15}N_2ONa$: 298.1082, Found: m/z 298.1081.



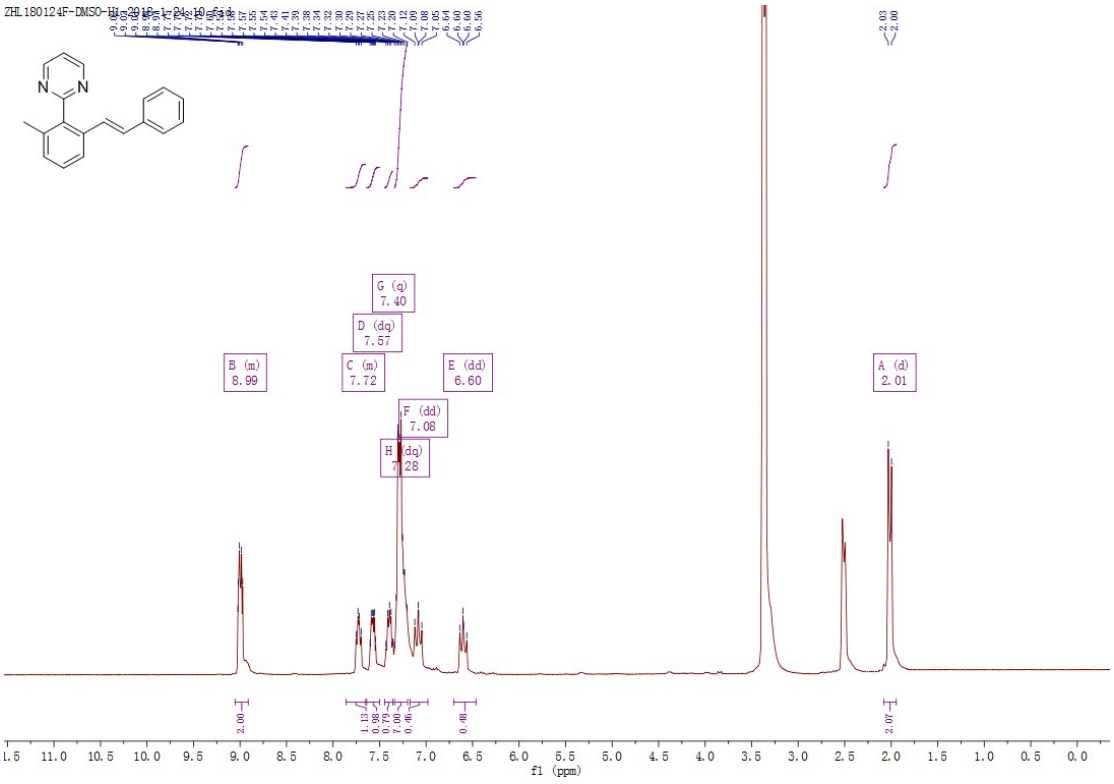


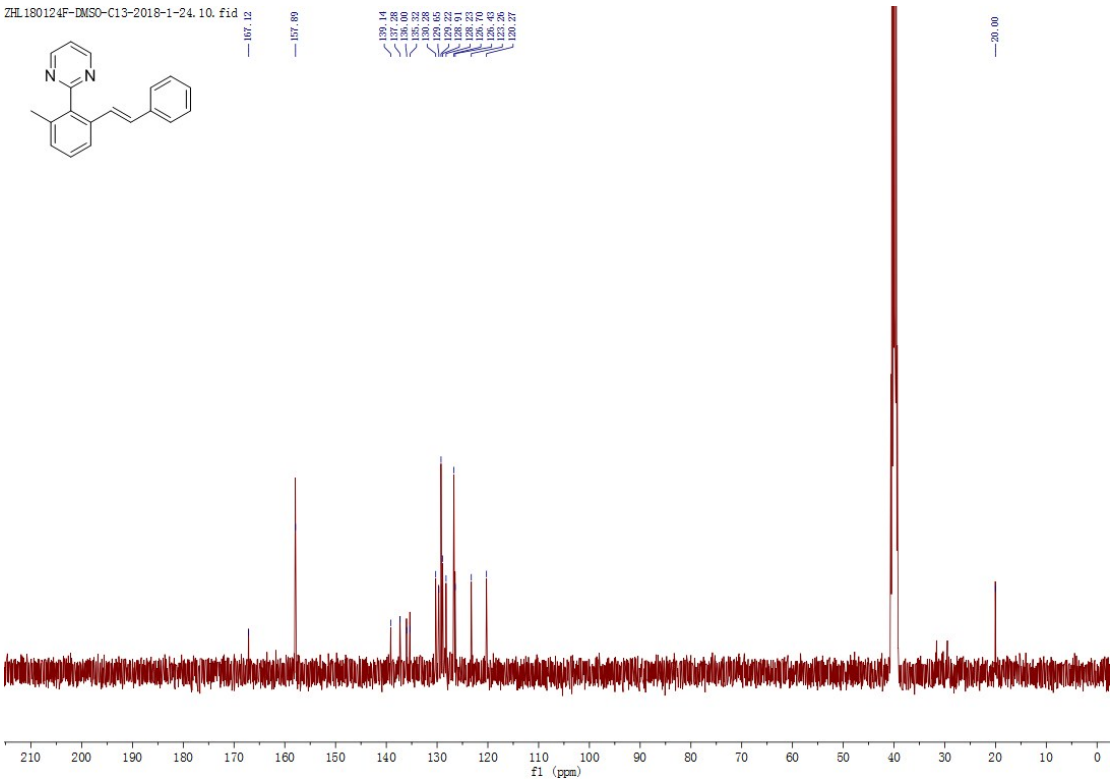
(E)-2-(2-methyl-6-styrylphenyl)pyrimidine



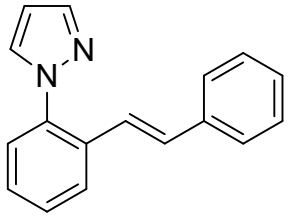
3s

Light yellow liquid, yield 47%, ^{1}HNMR (600MHz, DMSO):δ 8.99 (d, *J*=8.4Hz, 2H), 7.72 (d, *J*=8.4Hz, 1H), 7.57 (d, *J*=8.4Hz, 1H), 7.40 (d, *J*=8.4Hz, 1H), 7.28 (m, 7H), 7.08 (d, *J*=8.4Hz, 1H), 6.60 (d, *J*=16.2Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (150MHz, DMSO):δ167.1, 157.9, 139.1, 137.3, 136.0, 135.3, 130.3, 129.7, 129.2, 126.7, 126.4, 123.3, 120.3, 20.0; HRMS (ESI) Calcd. For $C_{19}H_{16}N_2Na$: 295.1211, Found: m/z 295.1211.



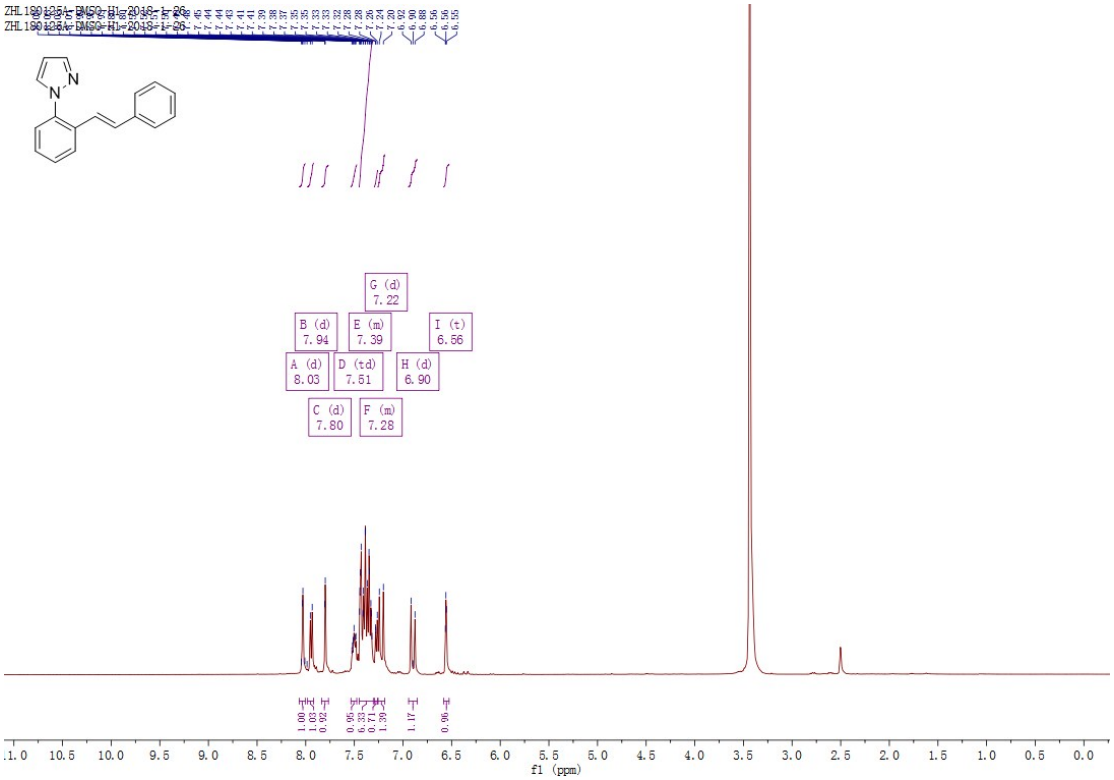


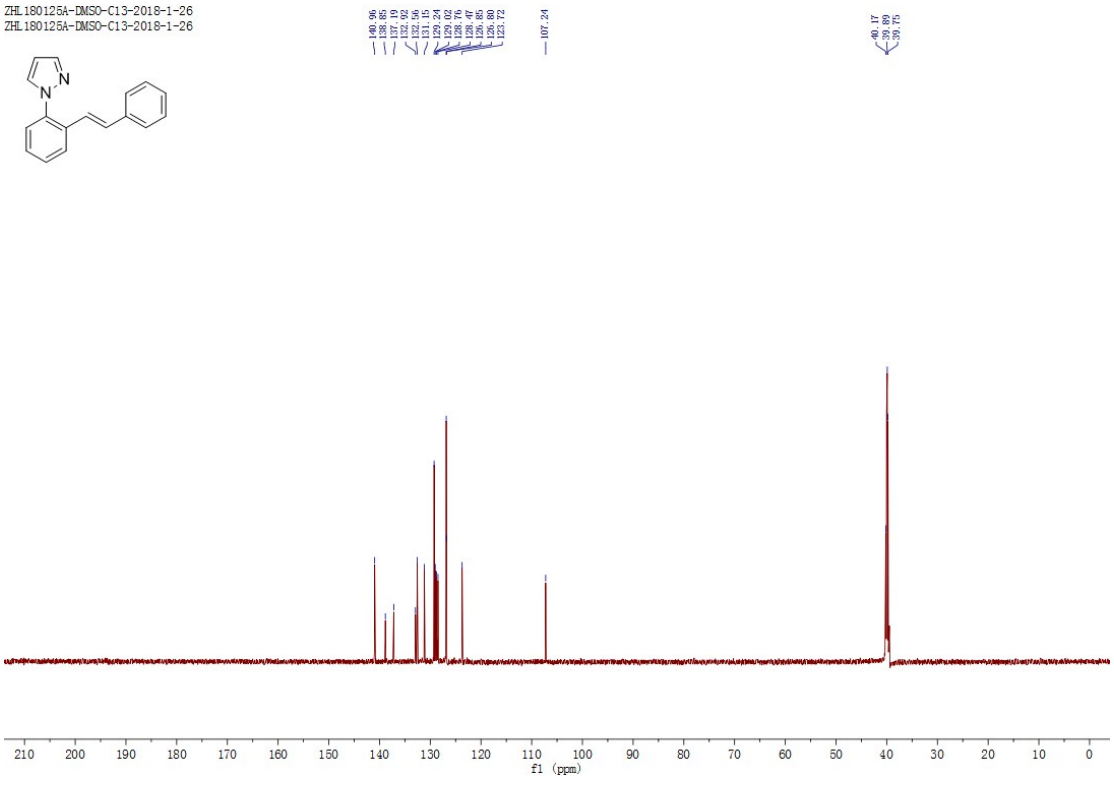
(E)-1-(2-styrylphenyl)-1H-pyrazole



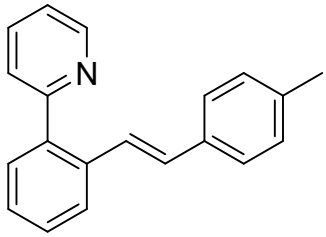
3t

Yellow liquid, yield 83 %, ^{1}HNMR (600MHz, DMSO):δ 8.03 (s, 1H), 7.94 (d, *J*=8.4Hz, 1H), 7.80 (s, 1H), 7.51 (m, 1H), 7.39 (m, 6H), 7.28 (d, *J*=8.4Hz, 1H), 7.22 (d, *J*=16.2Hz, 1H), 6.90 (d, *J*=16.2Hz, 1H), 6.56 (s, 1H); ^{13}C NMR (150MHz, DMSO):δ141.0, 138.9, 137.2, 132.9, 132.6, 131.2, 129.2, 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.



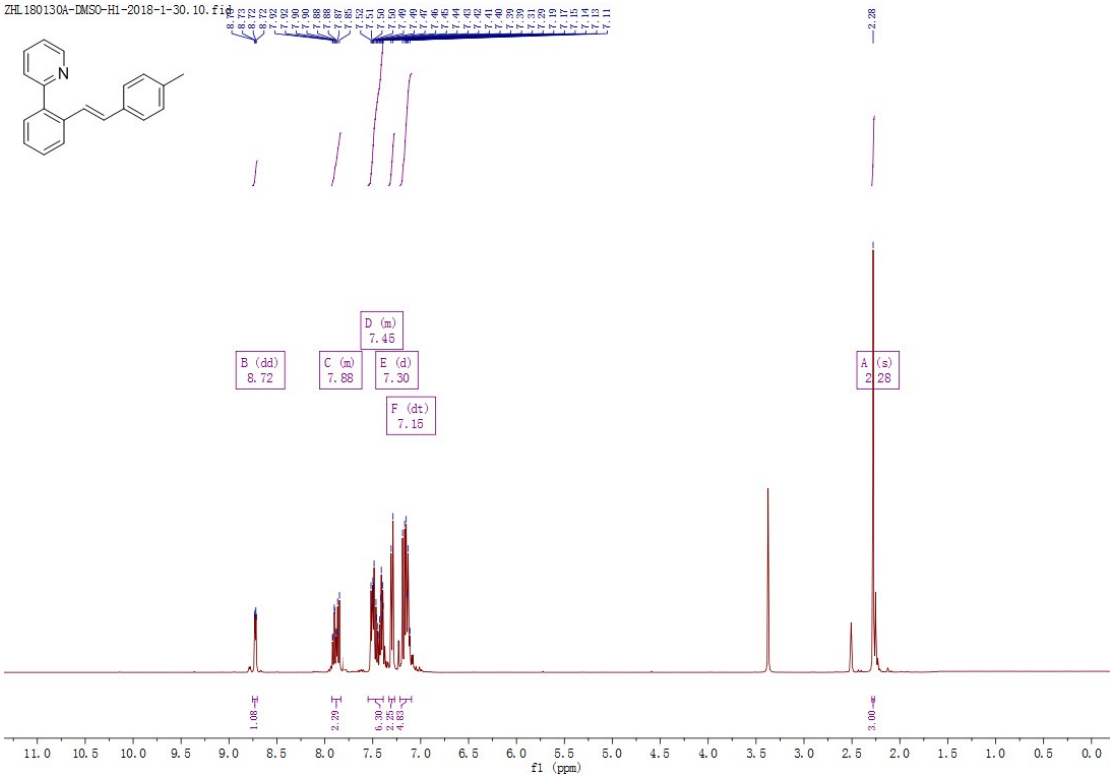


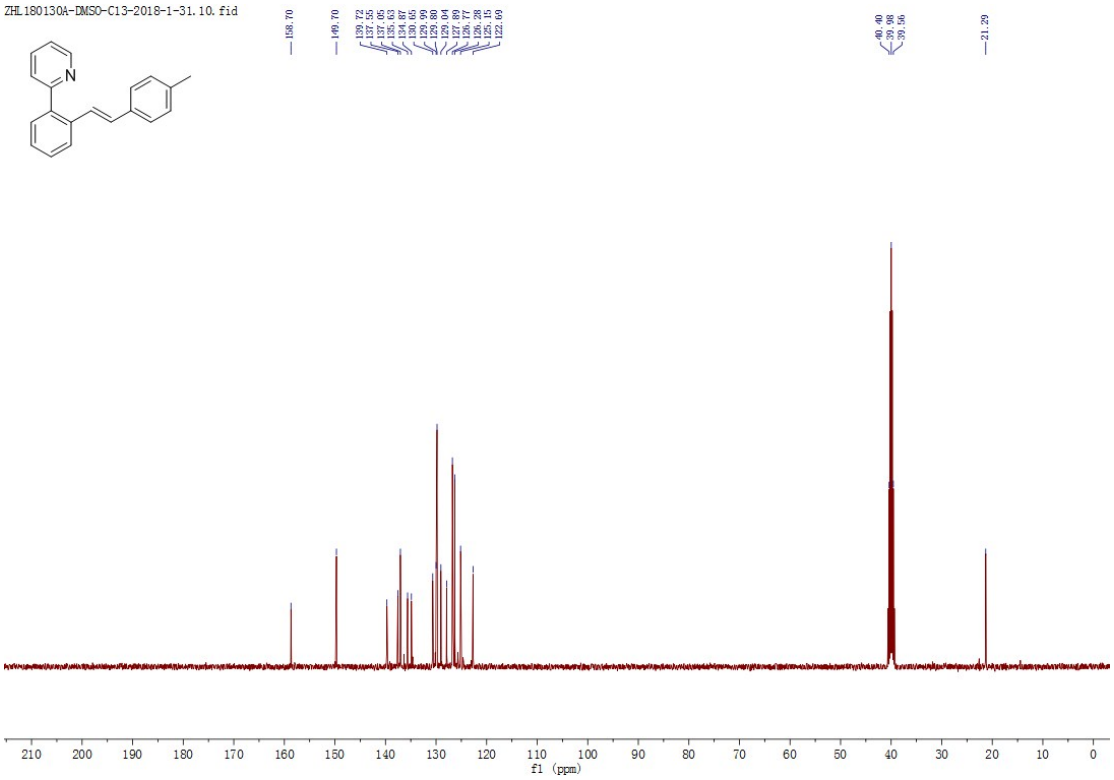
(E)-2-(2-(4-methylstyryl)phenyl)pyridine



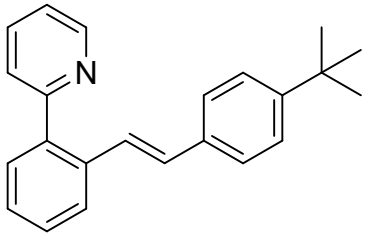
4b

Yellow liquid, yield 84%, ^{1}HNMR (600MHz, DMSO):δ8.72 (d, *J*=8.4Hz, 1H), 7.88 (m, 2H), 7.45 (m, 6H), 7.30 (d, *J*=8.4Hz, 2H), 7.15 (m, 4H), 2.28 (s, 3H); ^{13}C NMR (150MHz, DMSO):δ158.7, 149.7, 139.7, 137.6, 137.1, 135.6, 134.9, 130.7, 130.0, 129.0, 127.9, 126.8, 126.3, 125.2, 122.7, 21.3; HRMS (ESI) Calcd. For $C_{20}H_{17}NNa$: 294.1259, Found: m/z 294.1259.



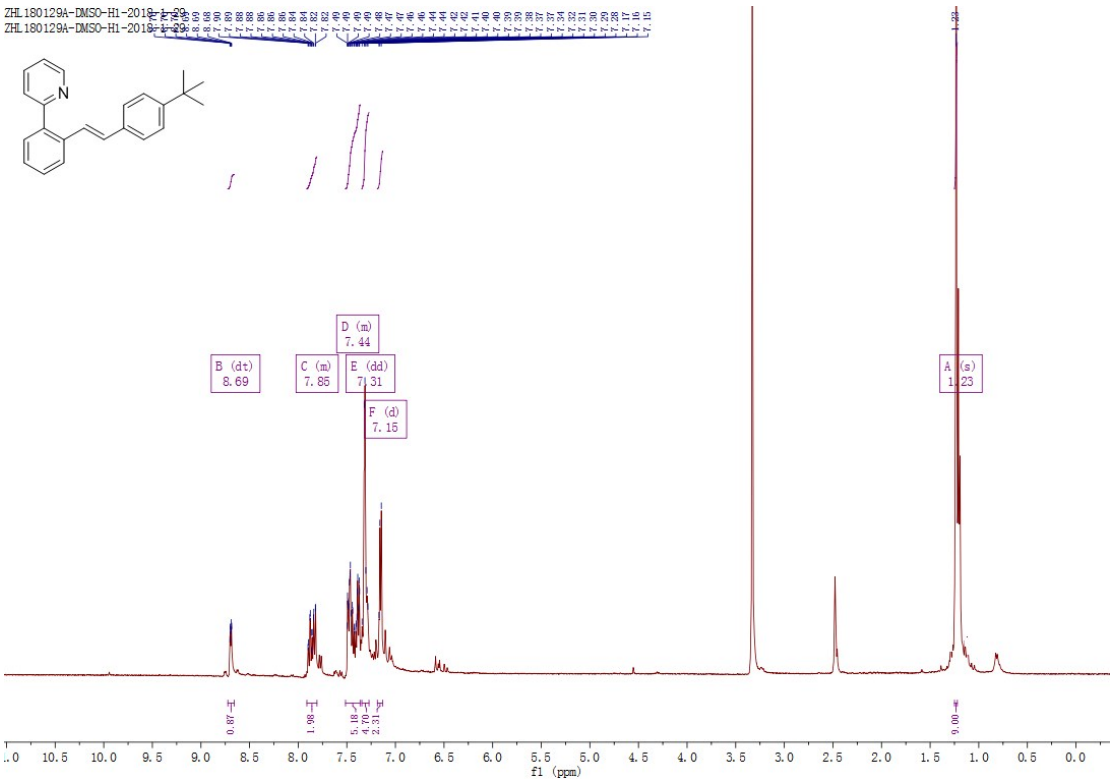


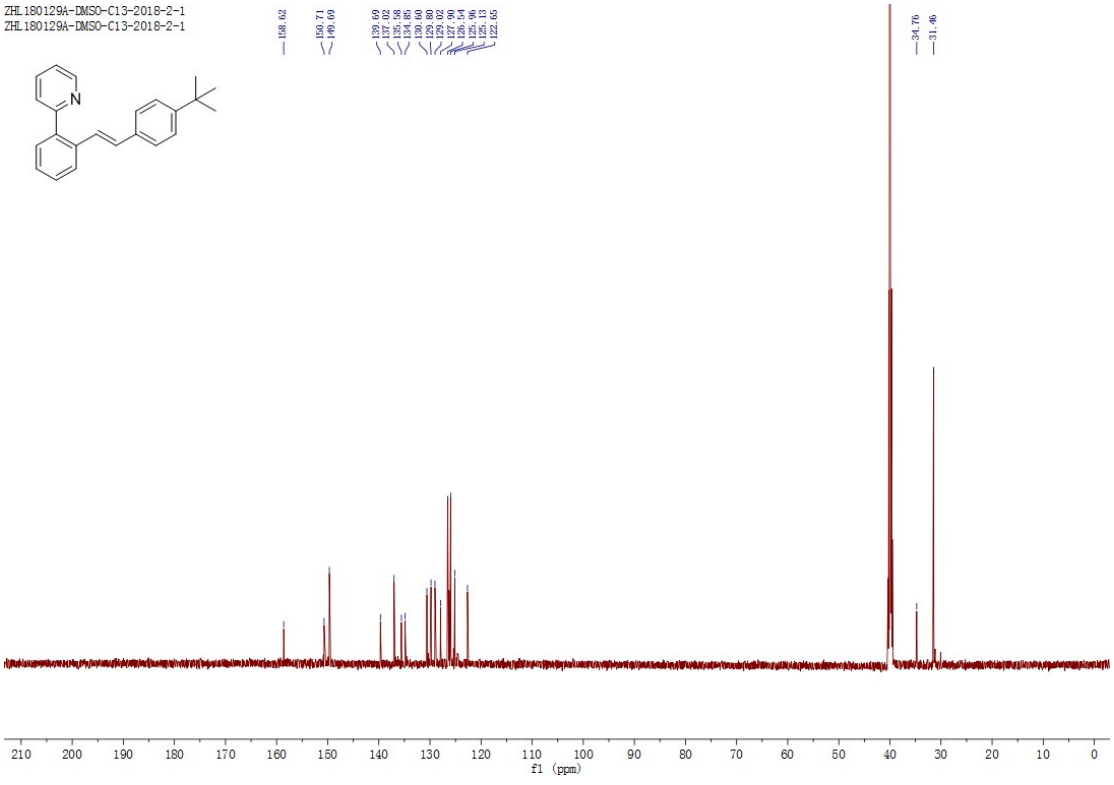
(E)-2-(2-(4-(tert-butyl)styryl)phenyl)pyridine



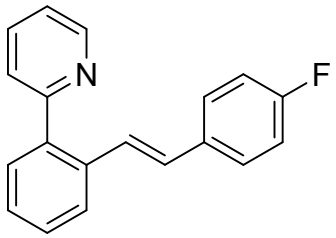
4c

Colourless liquid, yield 81%, ^{1}HNMR (600MHz, DMSO):δ 8.69 (d, *J*=8.4Hz, 1H), 7.85 (m, 2H), 7.44 (m, 5H), 7.31 (m, 4H), 7.15 (d, *J*=8.4Hz, 2H), 1.23 (s, 9H); ^{13}C NMR (150MHz, DMSO):δ158.6, 150.7, 149.7, 139.7, 137.0, 135.6, 134.9, 130.6, 129.8, 129.0, 127.9, 126.5, 126.0, 125.1, 122.7, 34.8, 31.5; HRMS (ESI) Calcd. For $C_{23}H_{23}NNa$: 336.1728, Found: m/z 336.1728.



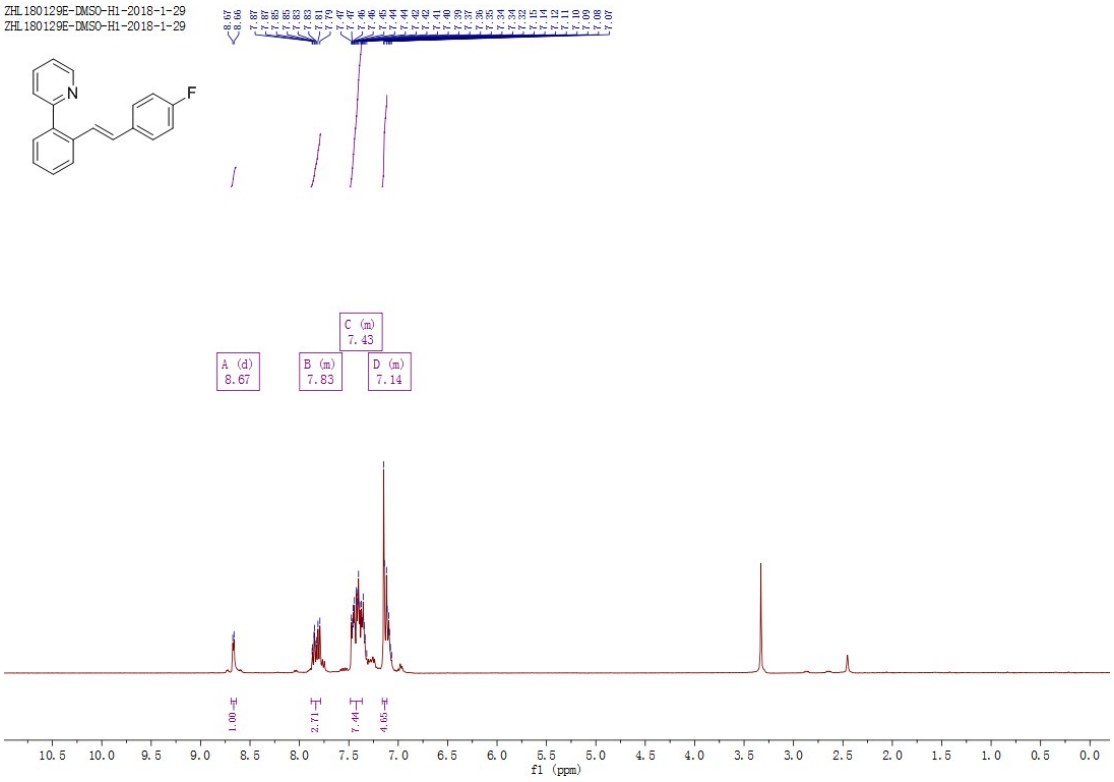


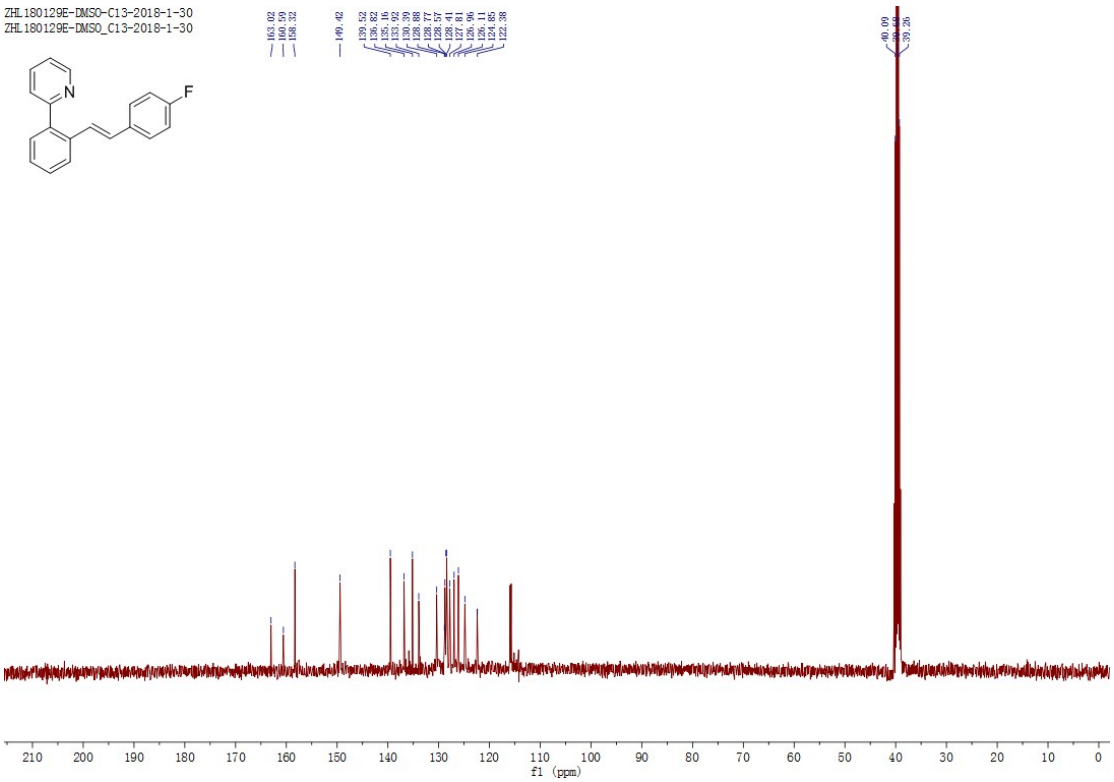
(E)-2-(2-(4-fluorostyryl)phenyl)pyridine

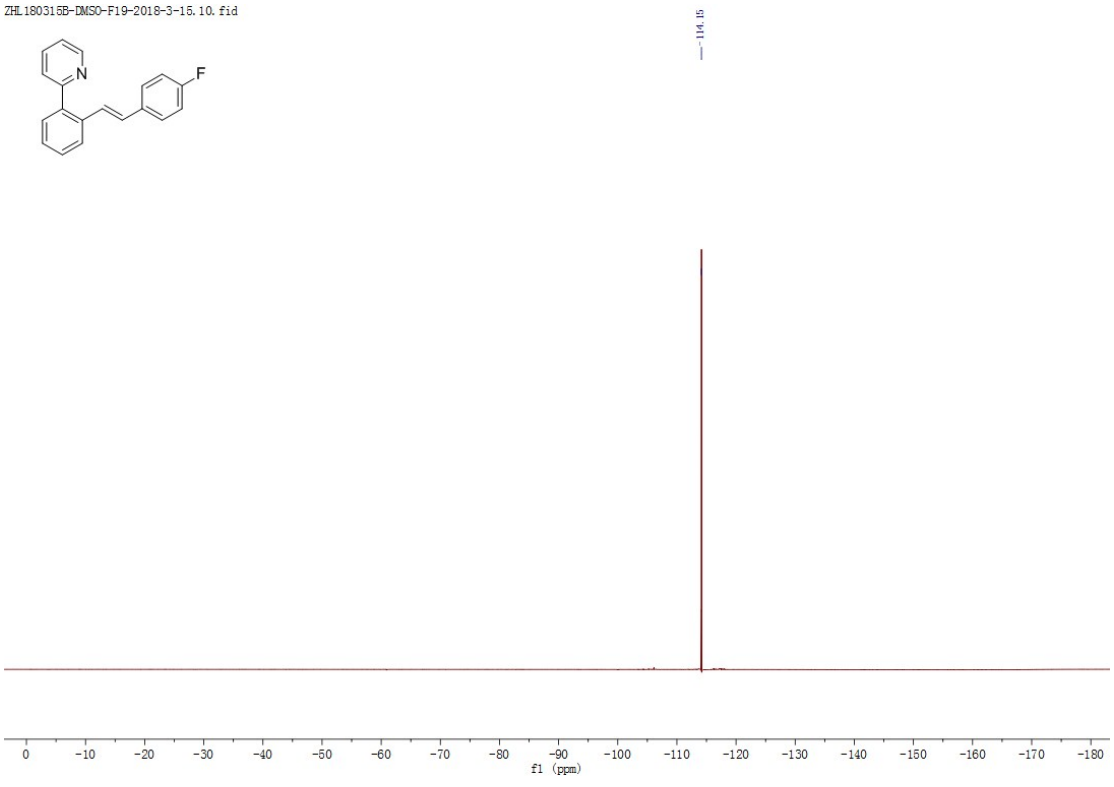


4d

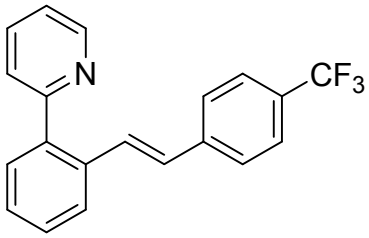
Yellow liquid, yield 85 %, ^{1}HNMR (600MHz, DMSO):δ 8.76 (d, *J*=8.4Hz, 1H), 7.83 (m, 2H), 7.43 (m, 7H), 7.14 (m, 4H); ^{13}C NMR (150MHz, DMSO):δ163.0, 160.6, 158.3, 149.4, 139.5, 136.8, 135.2, 133.9, 130.4, 128.9, 128.8, 128.6, 128.4, 127.8, 127.0, 126.1, 124.9, 122.4; ^{19}F NMR (376MHz, DMSO): -114.15; HRMS (ESI) Calcd. For $C_{19}H_{14}FNNa$: 298.1008, Found: m/z 298.1007.





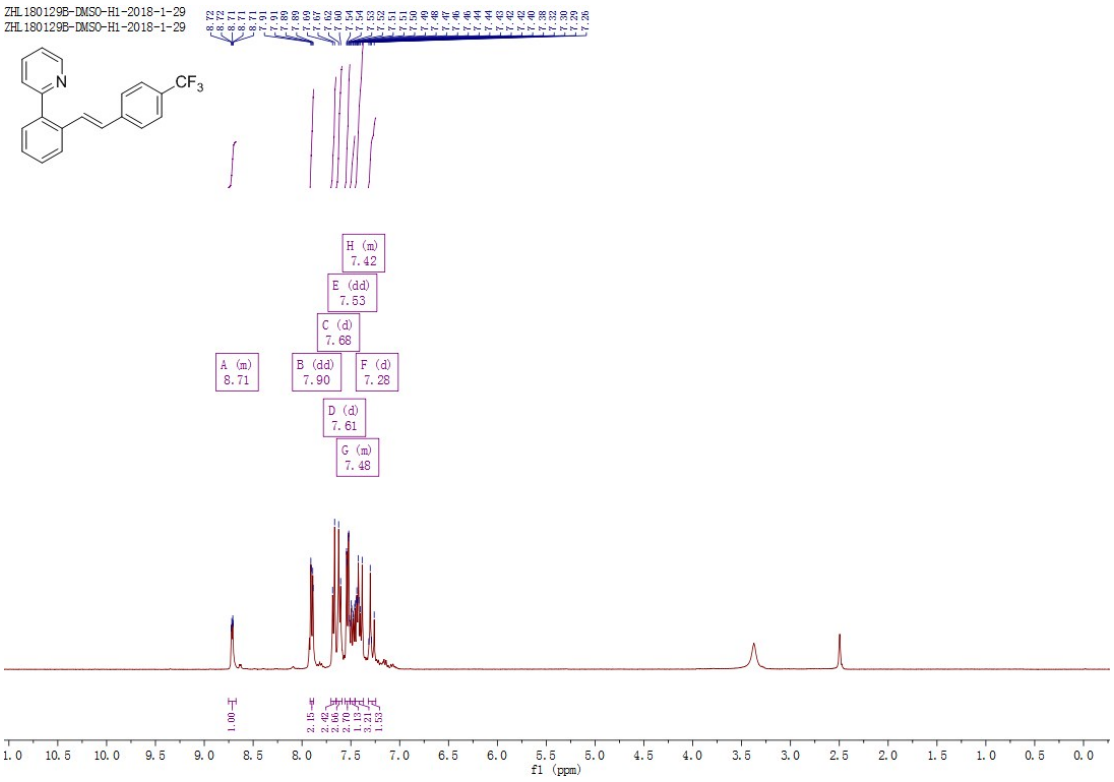


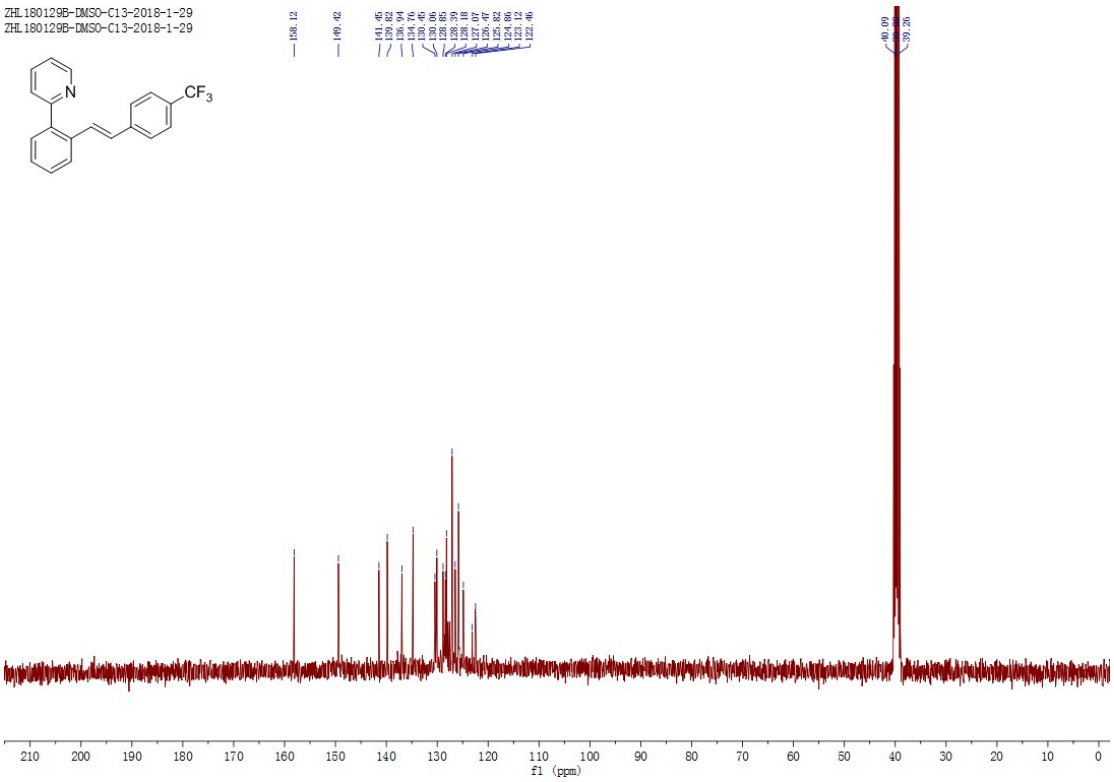
(E)-2-(2-(4-(trifluoromethyl)styryl)phenyl)pyridine

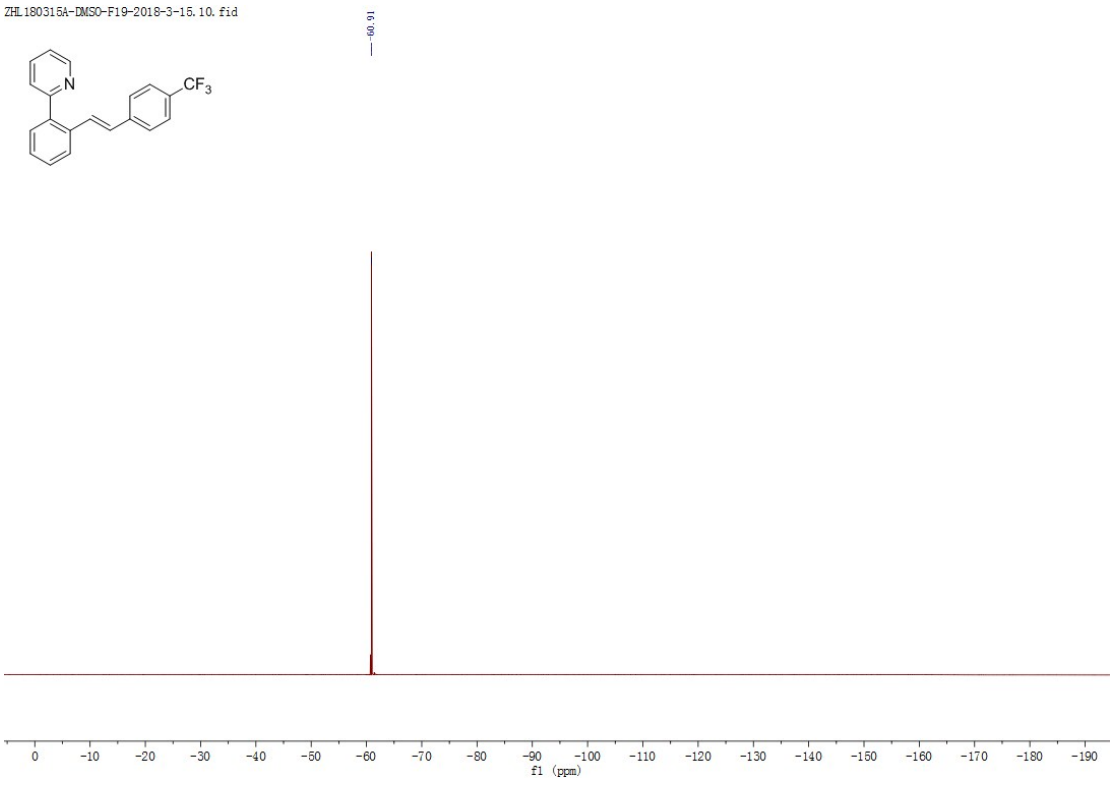


4e

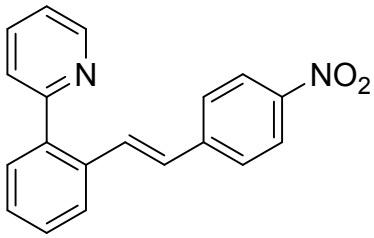
Light yellow liquid, yield 72 %, ^{1}HNMR (600MHz, DMSO):δ 8.71 (d, *J*=8.4Hz, 1H), 7.90 (d, *J*=8.4Hz, 2H), 7.68 (d, *J*=8.4Hz, 2H), 7.61 (d, *J*=8.4Hz, 2H), 7.53 (d, *J*=8.4Hz, 2H), 7.48 (t, *J*=8.4Hz, 1H), 7.42 (m, 2H), 7.28 (m, 1H); ^{13}C NMR (150MHz, DMSO):δ158.1, 149.4, 141.5, 139.8, 136.9, 134.8, 130.5, 130.1, 128.9, 128.4, 128.2, 127.1, 126.5, 125.8, 124.9, 123.1, 122.5; ^{19}F NMR (376MHz, DMSO): -60.91; HRMS (ESI) Calcd. For $C_{20}H_{14}F_3NNa$: 348.0976, Found: m/z 348.0976.





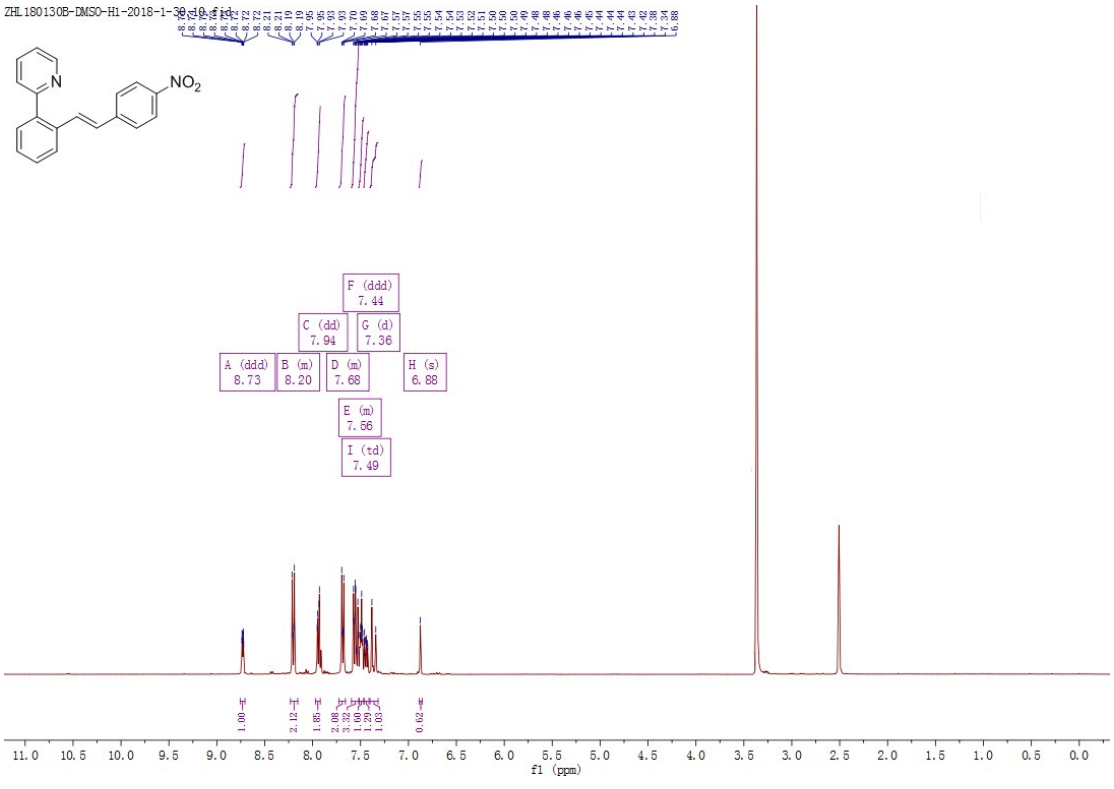


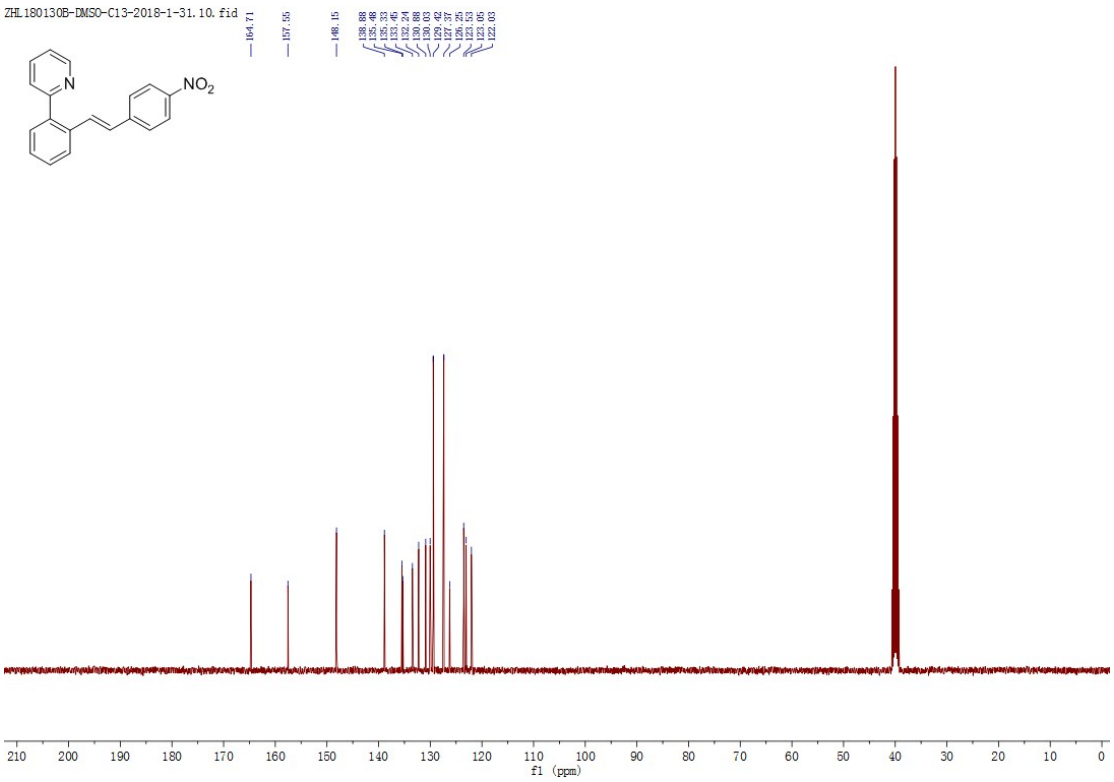
(E)-2-(2-(4-nitrostyryl)phenyl)pyridine



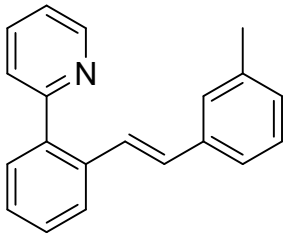
4f

Yellow solid, yield 83 %, ^{1}HNMR (600MHz, DMSO):δ 8.73 (d, *J*=8.4Hz, 1H), 8.20 (d, *J*=8.4Hz, 2H), 7.94 (d, *J*=8.4Hz, 2H), 7.68 (d, *J*=8.4Hz, 2H), 7.56 (m, 3H), 7.49 (m, 1H), 7.44 (t, *J*=8.4Hz, 1H),7.36 (d, *J*=16.2Hz, 1H), 6.88 (s, 1H); ^{13}C NMR (150MHz, DMSO):δ164.7, 157.6, 148.2, 138.9, 135.5, 135.3, 133.5, 132.4, 130.9, 130.0, 129.4, 127.4, 126.3, 123.5, 123.1, 122.0; HRMS (ESI) Calcd. For $C_{19}H_{14}N_2O_2Na$: 325.0953, Found: m/z 325.0953.



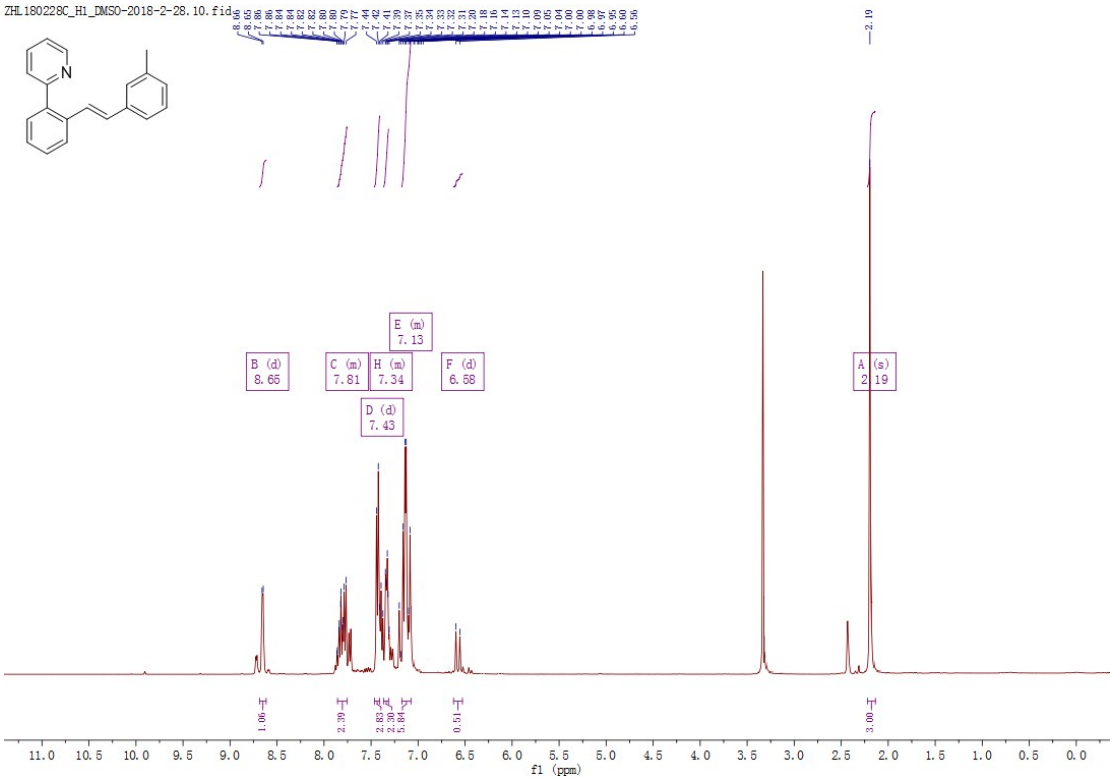


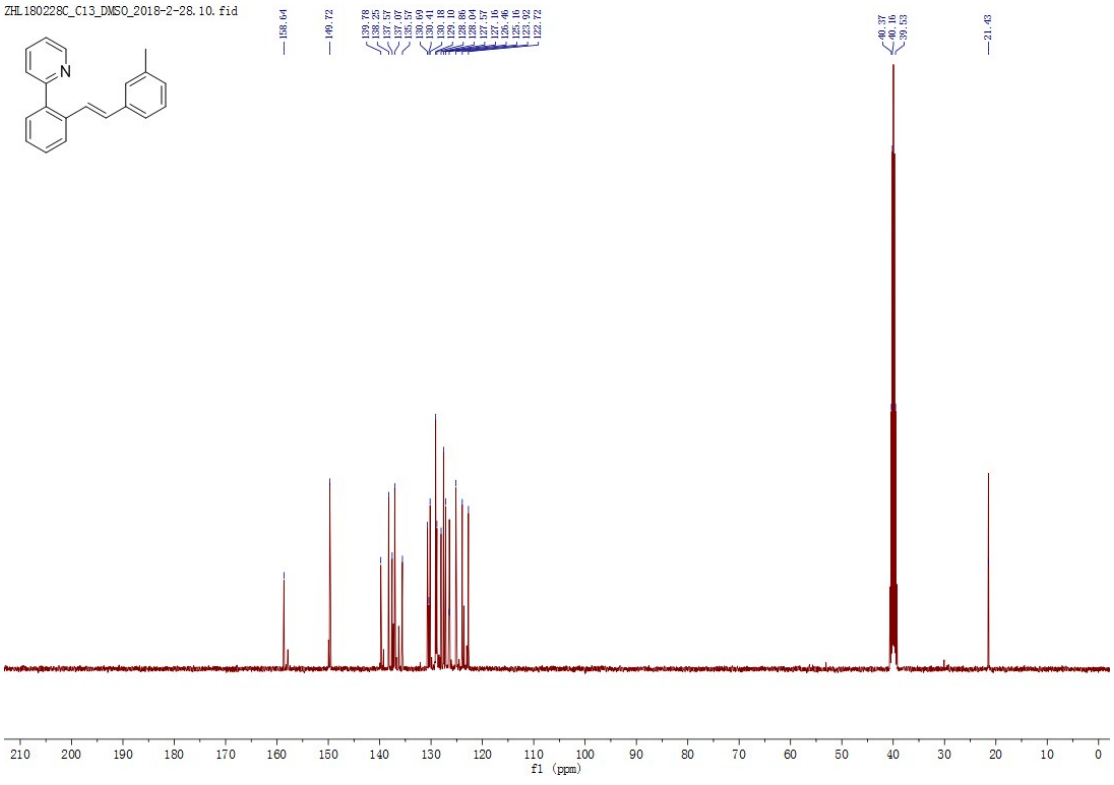
(E)-2-(2-(3-methylstyryl)phenyl)pyridine



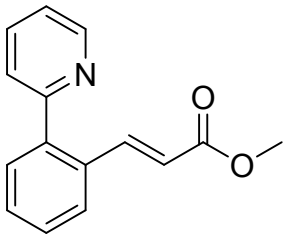
4g

Light green liquid, yield 82 %, ^{1}HNMR (600MHz, DMSO):δ 8.65 (d, *J*=8.4Hz, 1H), 7.81 (m, 2H), 7.43 (m, 2H), 7.34 (m, 2H), 7.13 (m, 6H), 6.58 (d, *J*=16.2Hz, 1H); ^{13}C NMR (150MHz, DMSO):δ158.6, 149.7, 139.8, 138.3, 137.6, 137.1, 136.6, 130.7, 130.4, 130.2, 129.1, 128.9, 128.0, 127.6, 127.2, 126.5, 125.2, 123.9, 122.7, 21.4; HRMS (ESI) Calcd. For $C_{20}H_{17}NNa$: 294.1259, Found: m/z 294.1259.



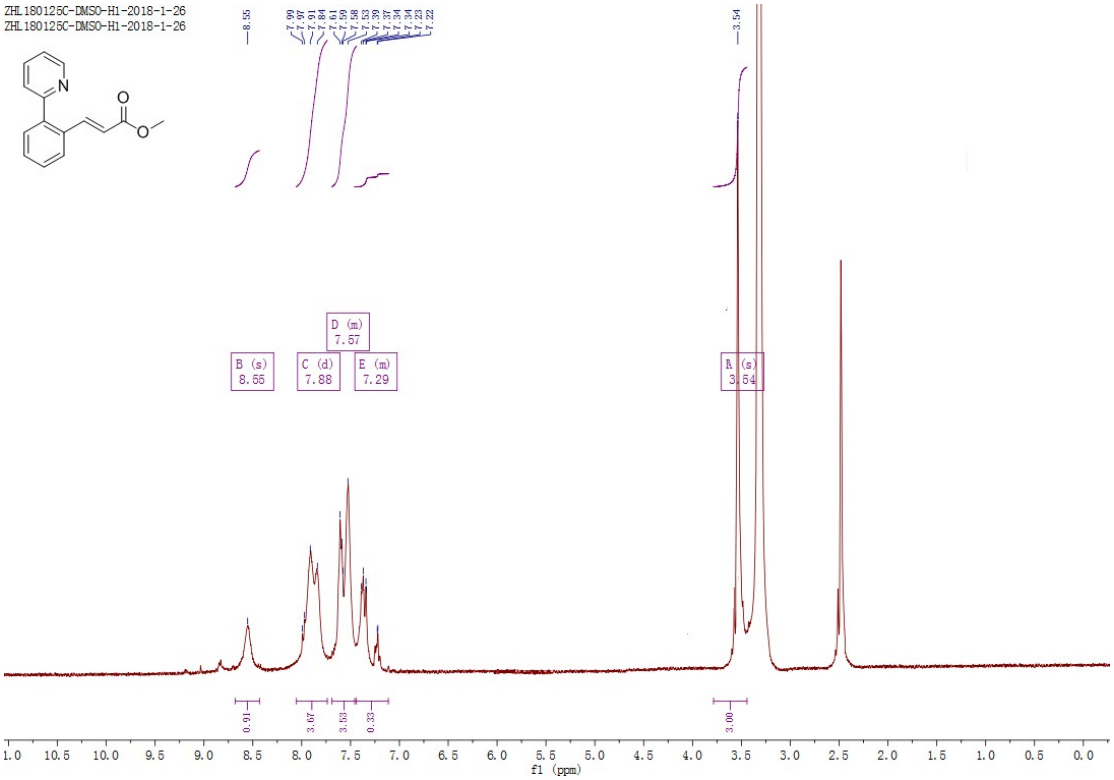


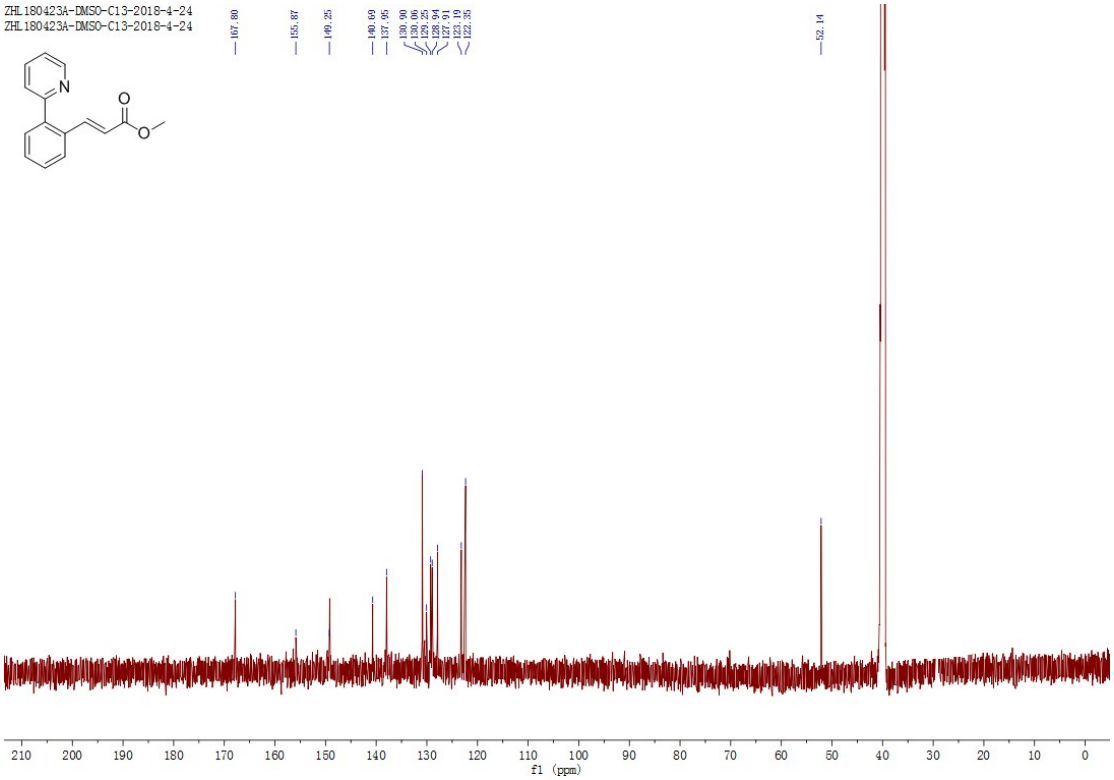
(E)-methyl 3-(2-(pyridin-2-yl)phenyl)acrylate



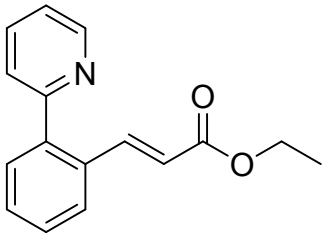
4h

Light yellow liquid, yield 53 %, ^{1}HNMR (600MHz, DMSO):δ 8.55 (s, 1H), 7.88 (m, 4H), 7.57 (m, 4H), 7.29 (m, 1H), 3.54 (s, 3H); ^{13}C NMR (600MHz, DMSO):δ157.8, 156.9, 149.3, 140.7, 138.0, 130.9, 130.1, 129.3, 128.9, 127.9, 123.2, 122.4; HRMS (ESI) Calcd. For $C_{15}H_{13}NO_2Na$: 262.0844, Found: m/z 262.0843.



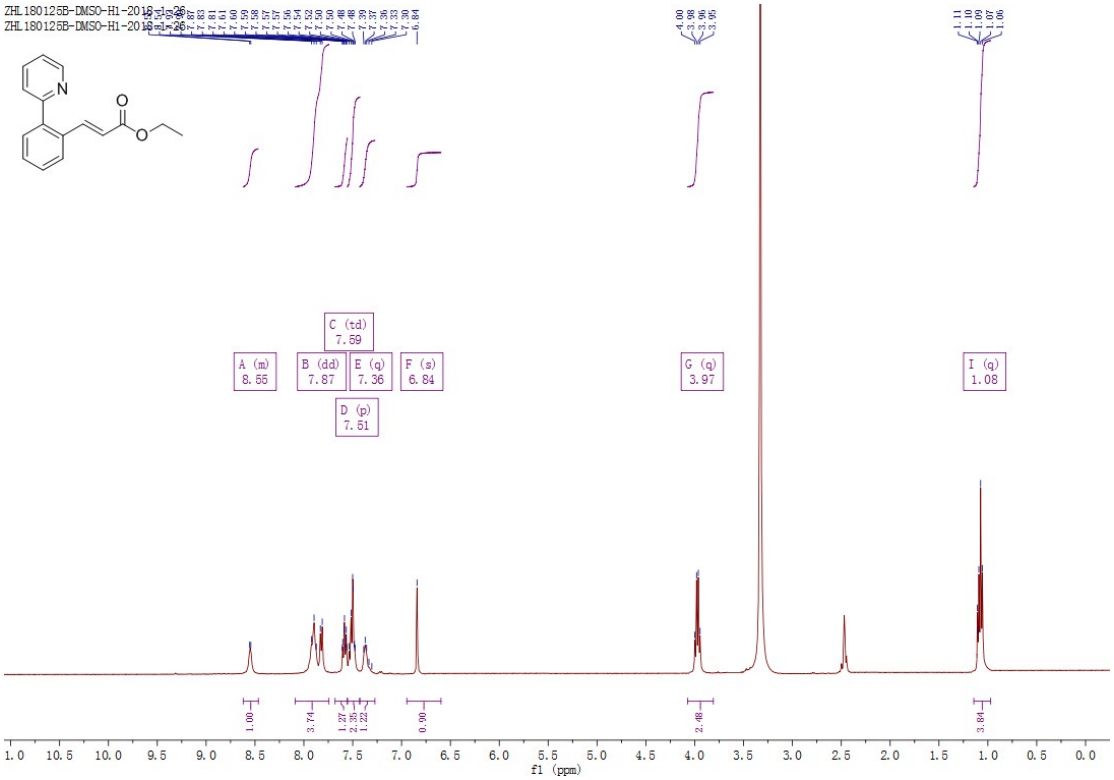


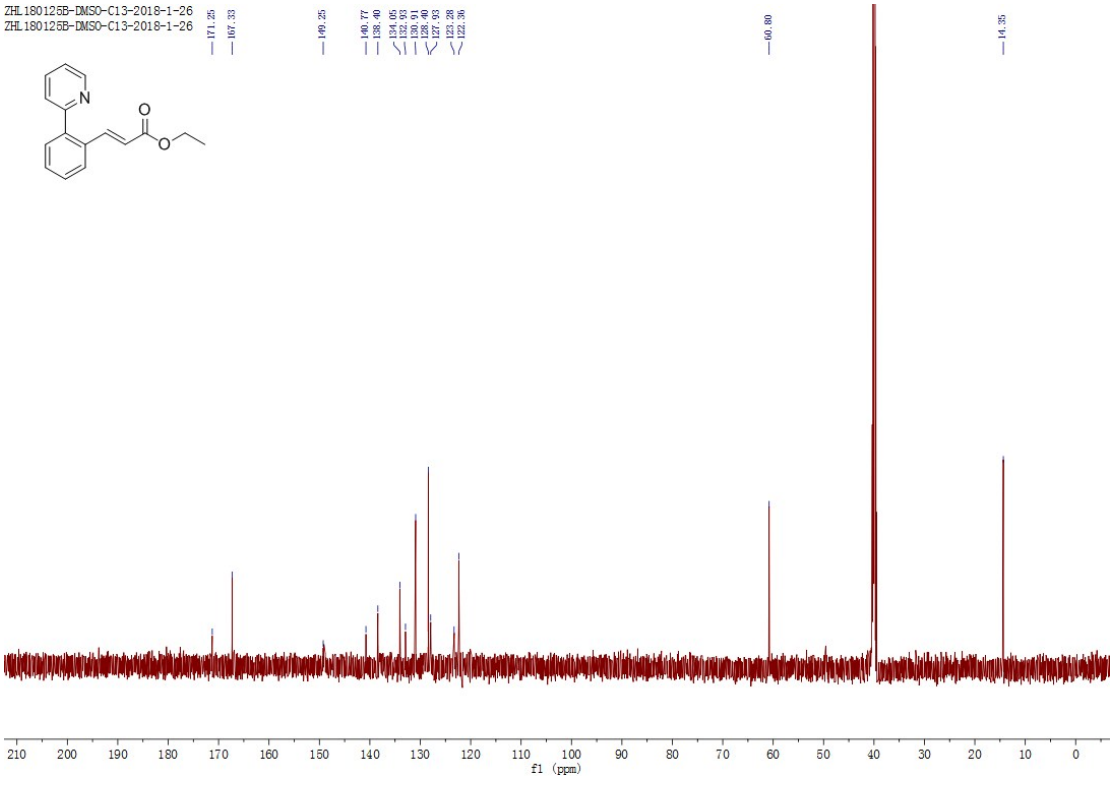
(E)-ethyl 3-(2-(pyridin-2-yl)phenyl)acrylate



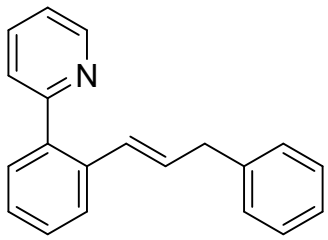
4i

Yellow liquid, yield 59 %, ^{1}HNMR (600MHz, DMSO):δ8.55 (m, 1H), 7.87 (m, 4H), 7.59 (m, 1H), 7.29 (m, 1H), 3.51 (m, 2H), 7.36 (m, 1H), 6.84 (s, 1H), 3.97 (q, *J*=7.2Hz, 2H,), 1.08 (t, *J*=7.2Hz, 3H); ^{13}C NMR (150MHz, DMSO):δ171.3, 167.3, 149.3, 138.4, 134.1, 132.9, 130.9, 128.4, 127.9, 123.3, 122.4, 60.8, 14.4; HRMS (ESI) Calcd. For $C_{16}H_{15}NO_2Na$: 276.1000, Found: m/z 276.0999.



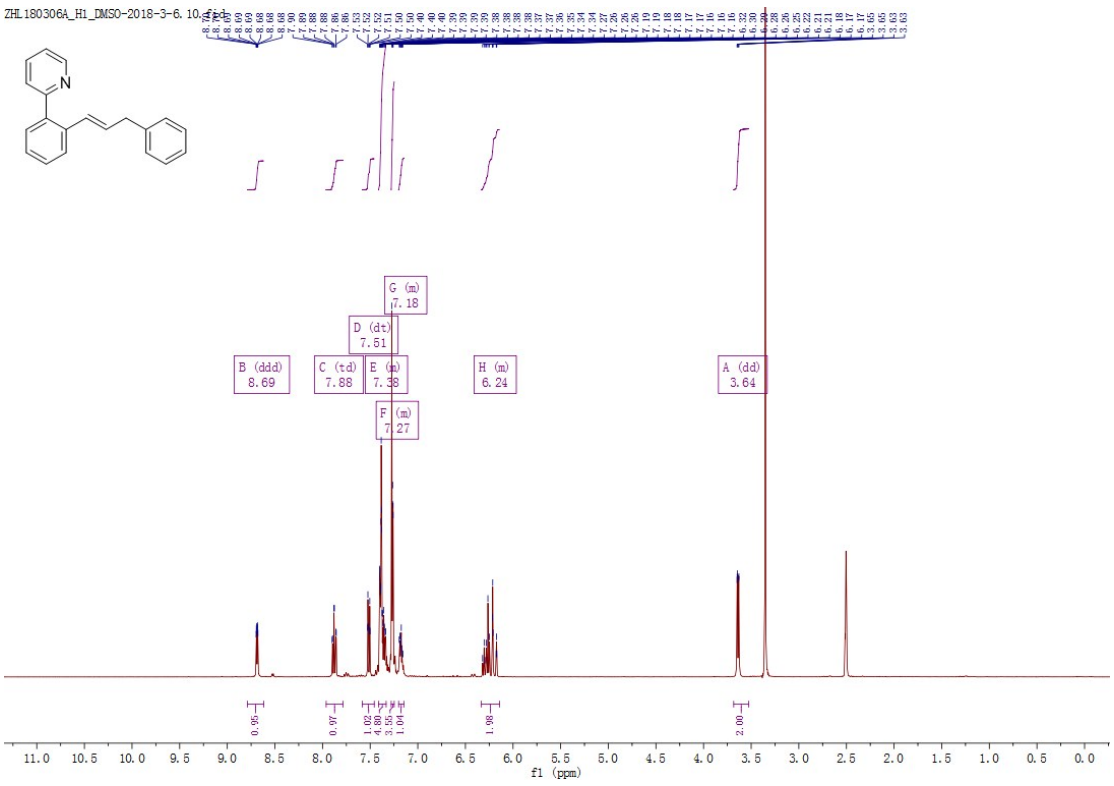


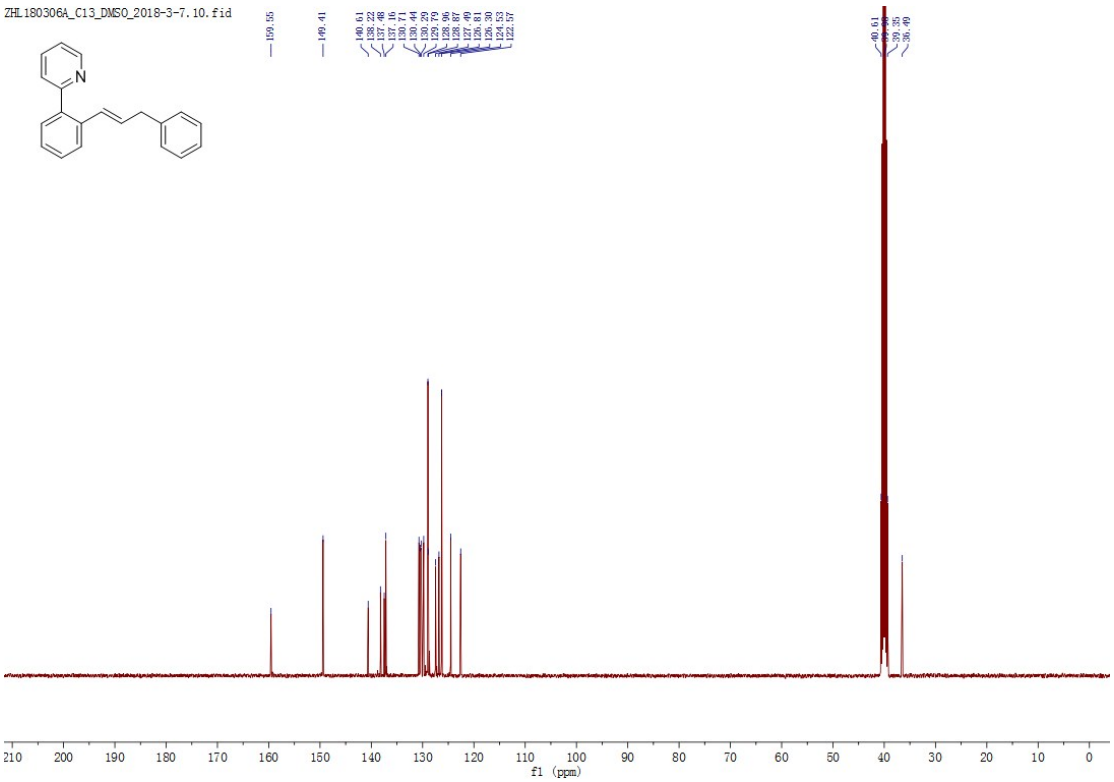
(E)-2-(2-(3-phenylprop-1-en-1-yl)phenyl)pyridine



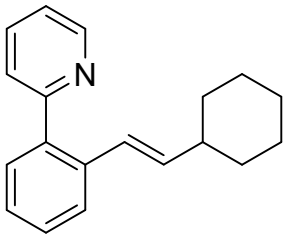
4j

Light yellow liquid, yield 67 %, ^{1}HNMR (600MHz, DMSO):δ 8.69 (m, 1H), 7.88 (t, *J*=8.4Hz, 1H), 7.51 (d, *J*=8.4Hz, 1H), 7.38 (m, 5H), 7.27 (m, 4H), 7.18 (m, 1H), 6.24 (m, 2H), 3.64 (d, *J*=8Hz, 2H); ^{13}C NMR (150MHz, DMSO):δ159.6, 149.4, 140.6, 138.2, 137.5, 130.7, 130.4, 130.3, 129.8, 129.0, 128.9, 127.5, 126.8, 126.3, 124.5, 122.6, 36.5; HRMS (ESI) Calcd. For $C_{20}H_{17}NNa$: 294.1259, Found: m/z 294.1258.



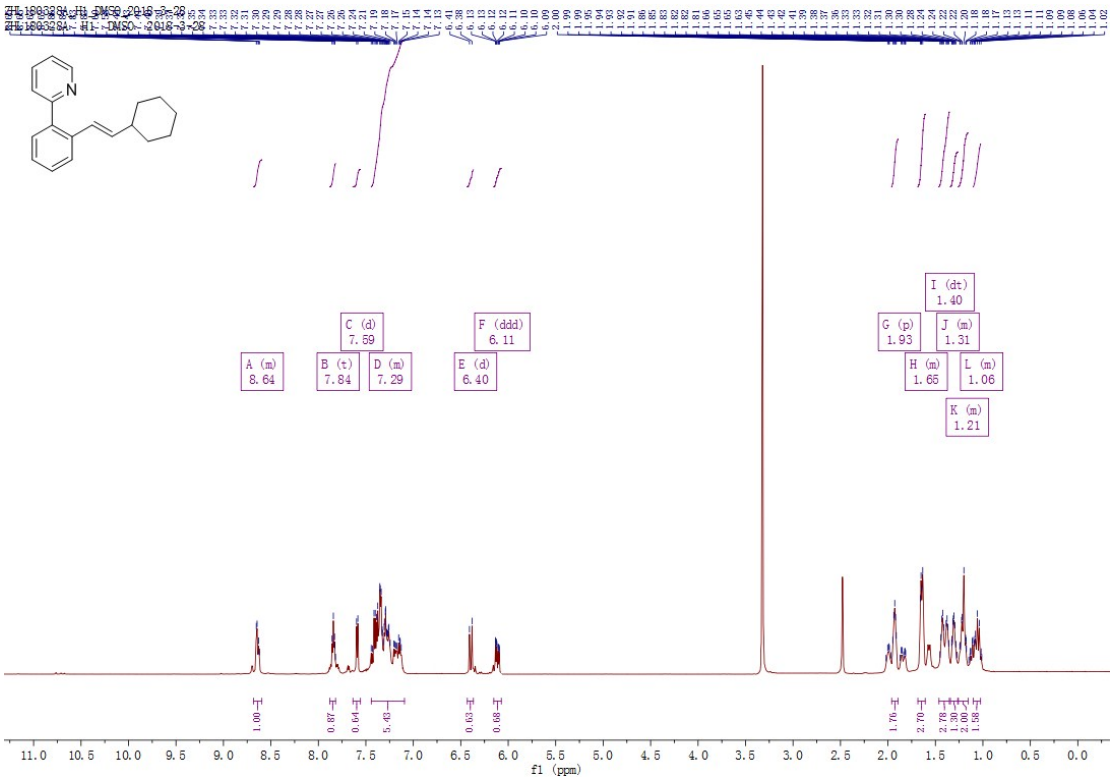


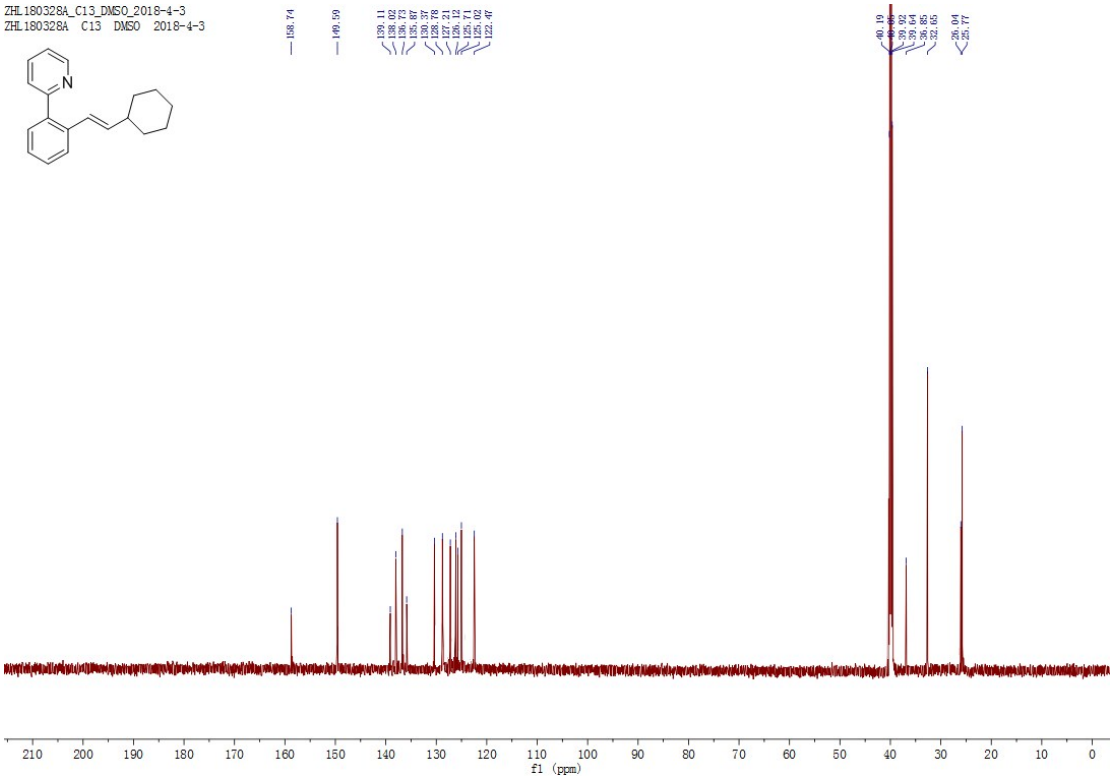
(E)-2-(2-cyclohexylvinyl)-1,1'-biphenyl



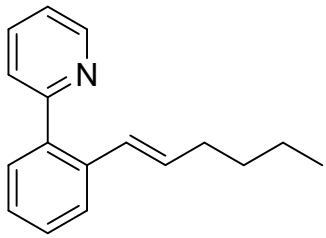
4k

Light yellow liquid, yield 43 %, ^{1}HNMR (600MHz, DMSO):δ 8.64 (d, *J*=8.4Hz, 1H), 7.84 (t, *J*=8.4Hz, 1H), 7.59 (d, *J*=8.4Hz, 1H), 7.29 (m, 5H), 6.40 (d, *J*=16.2Hz, 1H), 6.11 (m, 1H), 1.93 (t, *J*=7.2Hz, 1H), 1.65 (d, *J*=7.2Hz, 3H), 1.40 (d, *J*=7.2Hz, 3H), 1.31 (m, 1H), 1.21 (m, 2H), 1.06 (m, 1H); ^{13}C NMR (150MHz, DMSO):δ158.7, 149.6, 139.1, 138.0, 136.7, 136.9, 130.4, 128.8, 127.2, 126.1, 125.7, 125.0, 122.5, 36.8, 32.7, 26.0, 25.8; HRMS (ESI) Calcd. For $C_{19}H_{21}NNa$: 286.1572, Found: m/z 286.1571.



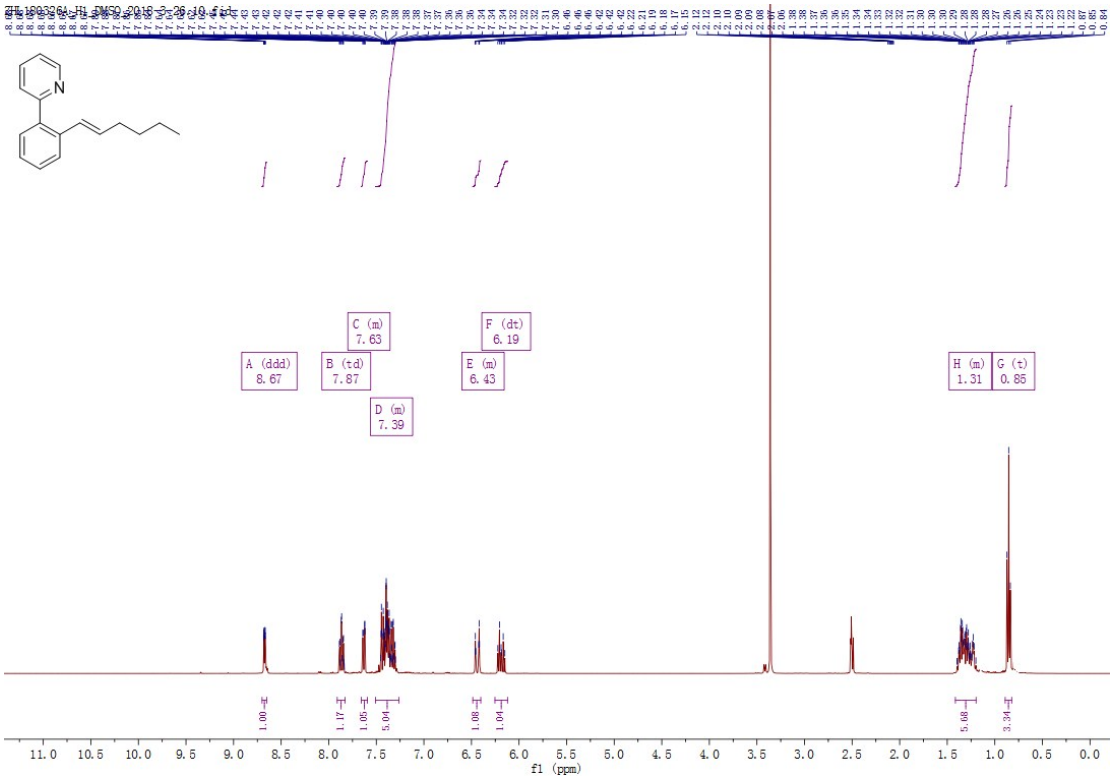


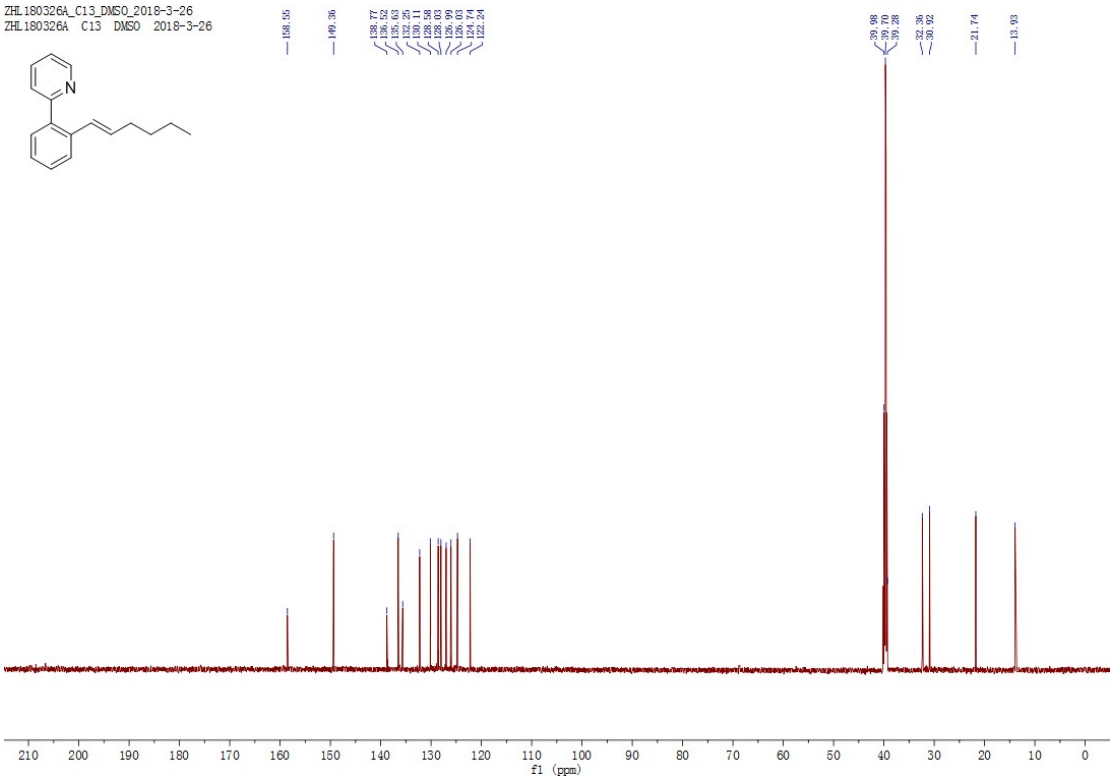
(E)-2-(hex-1-en-1-yl)-1,1'-biphenyl



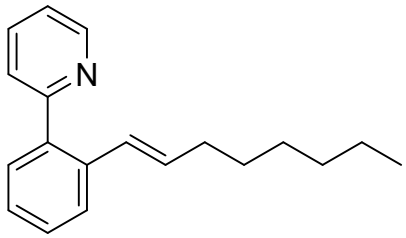
4l

Yellow liquid, yield 38 %, ^{1}HNMR (600MHz, DMSO):δ 8.67 (d, *J*=8.4Hz, 1H), 7.87 (t, *J*=8.4Hz, 1H), 7.63 (d, *J*=8.4Hz, 1H), 7.39 (m, 5H), 6.43 (d, *J*=16.2Hz, 1H), 6.19 (m, 1H), 1.31 (m, 6H), 0.85 (t, *J*=7.2Hz, 3H); ^{13}C NMR (150MHz, DMSO):δ1586, 149.4, 138.8, 136.5, 135.6, 132.3, 130.1, 128.6, 128.0, 127.0, 126.0, 124.7, 122.2, 32.4, 30.9, 21.7, 13.9; HRMS (ESI) Calcd. For $C_{17}H_{19}NNa$: 260.1415, Found: m/z 260.1414.



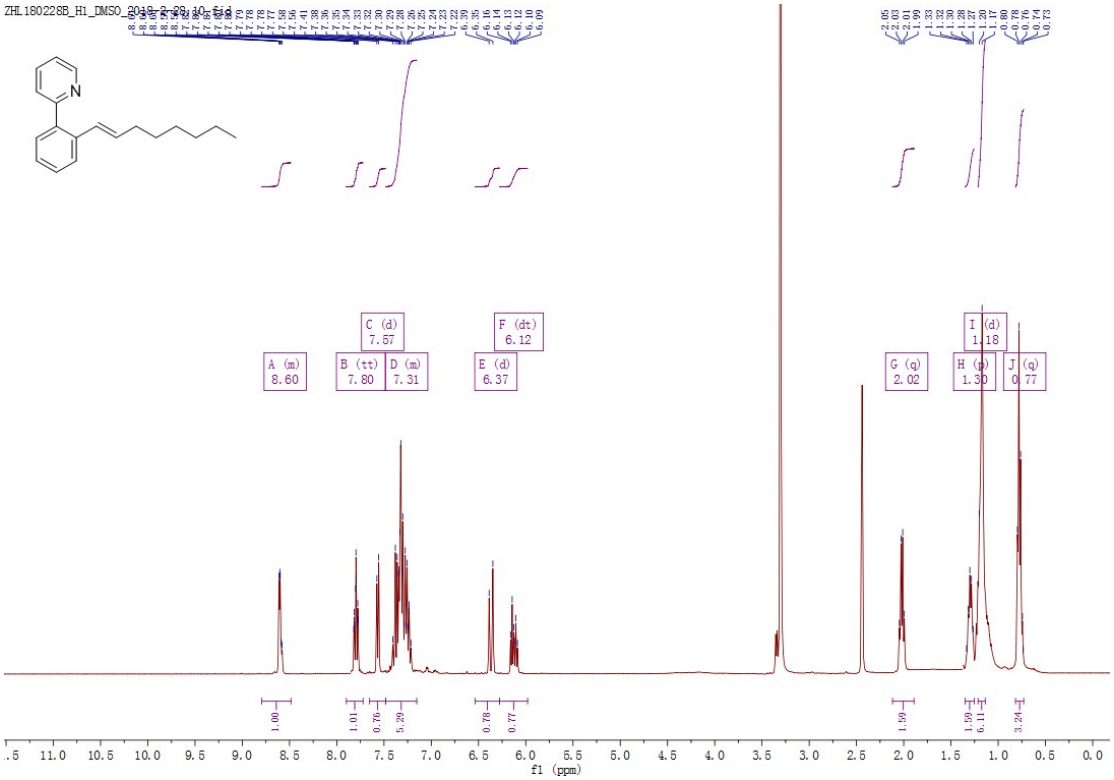


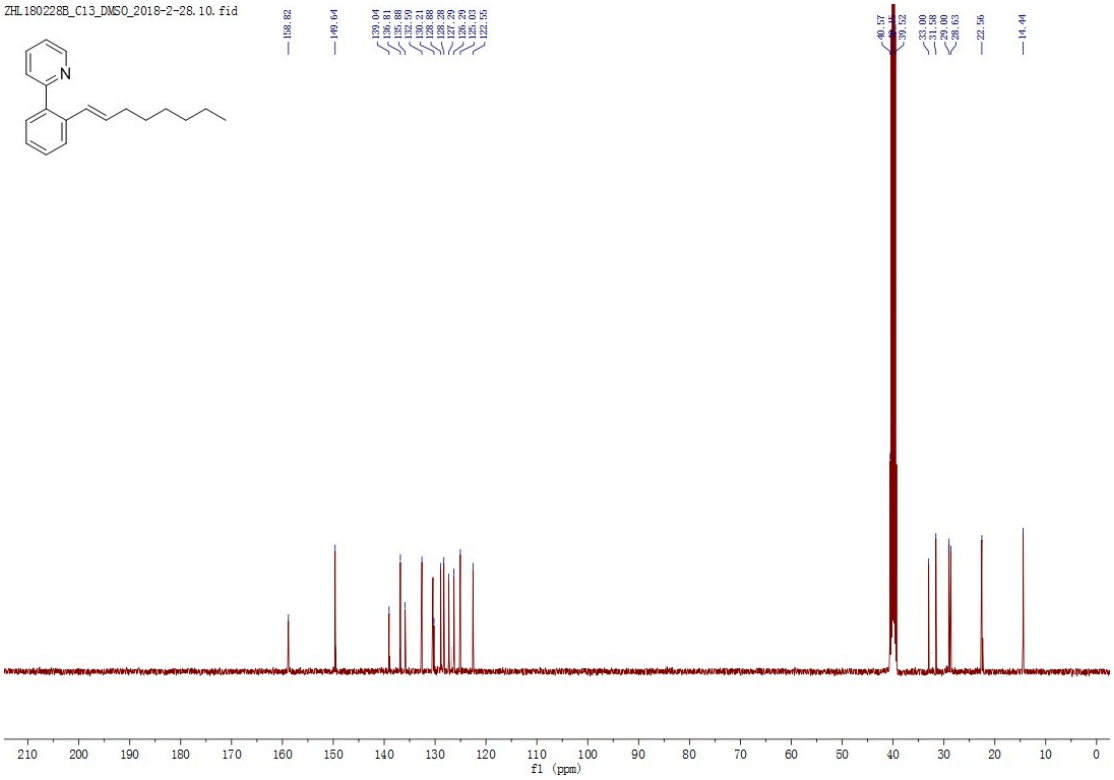
(E)-2-(2-(oct-1-en-1-yl)phenyl)pyridine



4m

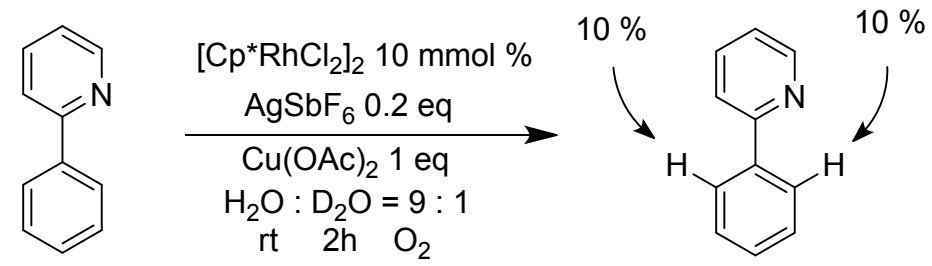
Light yellow liquid, yield 47 %, ^{1}HNMR (600MHz, DMSO):δ 8.60 (d, *J*=8.4Hz, 1H), 7.80 (t, *J*=8.4Hz, 1H), 7.57 (d, *J*=8.4Hz, 1H), 7.31 (m, 5H), 6.37 (d, *J*=16.2Hz, 1H), 6.12 (d, *J*=8.4Hz, 1H), 2.02 (m, 2H), 1.30 (m, 2H), 1.18 (m, 6H), 0.77 (m, 3H); ^{13}C NMR (150MHz, DMSO):δ158.8, 149.6, 139.0, 136.8, 135.9, 132.6, 130.2, 128.9, 128.3, 127.3, 126.3, 125.0, 122.6, 40.6, 40.2, 39.5, 33.0, 31.6, 29.0, 28.6, 22.6, 14.4; HRMS (ESI) Calcd. For $C_{19}H_{23}NNa$: 288.1728, Found: m/z 288.1727.


ZHL180228B_H1_DMSO_2018-2-28.10.fid
A (m) 8.60
B (tt) 7.80
C (d) 7.57
D (m) 7.31
E (d) 6.37
F (dt) 6.12
G (q) 2.02
H (q) 1.30
I (d) 1.18
J (q) 0.77
f1 (ppm)


ZHL180228B_C13_DMSO_2018-2-28.10.fid
f1 (ppm)

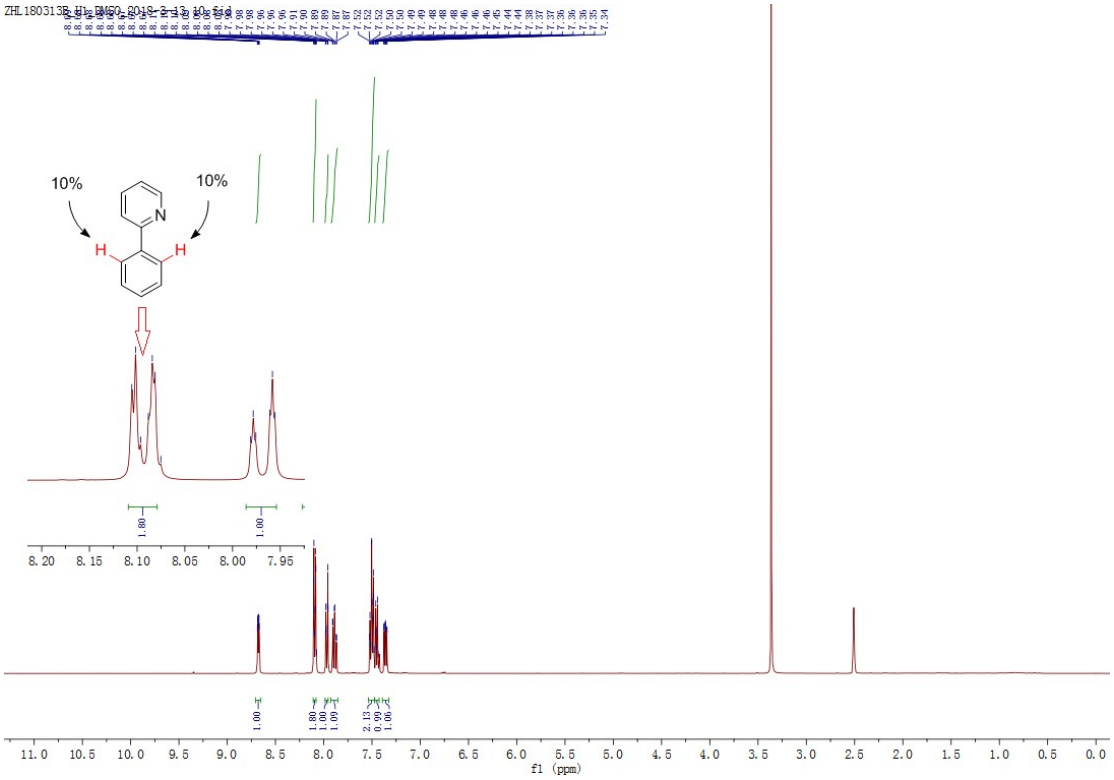
Mechanistic studies

The H/D exchange experiment



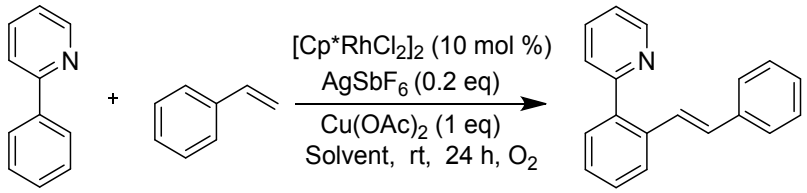
1a (0.1 mmol)

A 15ml sealed tube was charged with 2-phenylpyridine **1a** (15.2 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $AgSbF_6$ (7.2 mg, 0.02 mmol), $Cu(OAc)_2$ (20 mg, 0.1 mmol), H_2O (0.9 ml) and D_2O (0.1 ml). The mixture was stirred at room temperature for 2 hours. The mixture was extracted with diethyl ether (3 × 5 mL) and then the combined organic extracts was washed with brine (2 × 10 mL), dried with sodium sulfate. Then 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 10 % of the *ortho*-C-H within **1a** was deuterated. ^{1}H-NMR (600 MHz, DMSO) δ 8.68 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1.74H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 8.4Hz, 1H), 7.50 (t, *J* = 8.4Hz, 2H), 7.46 (d, *J* = 8.4Hz, 1H), 7.36 (t, *J* = 8.4Hz, 1H).



The effects of solvents

A 15ml sealed tube was charged with 2-phenylpyridine **1a** (15.2 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $AgSbF_6$ (7.2 mg, 0.02 mmol), $Cu(OAc)_2$ (20 mg, 0.1 mmol), and solvent (1 mL). The mixture was stirred at room temperature for 24 hours and monitored by TLC. Then the mixture was extracted with diethyl ether (3 × 5 mL) and the combined organic extracts was washed with brine (2 × 10 mL), dried with sodium sulfate. Then 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 desired product (**3a**).

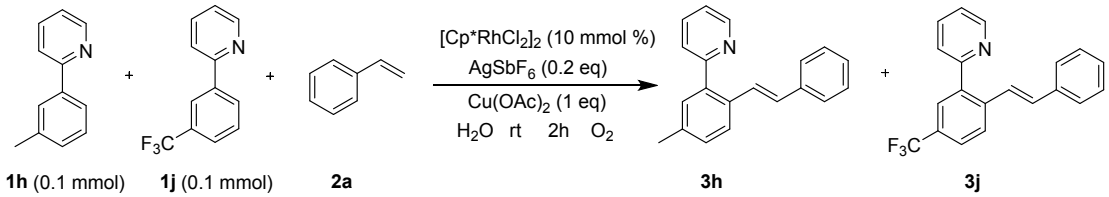


1a **2a** **3a**

Entry	Solvents	Yield (%)	Conversion (%)
1	H_2O	83	87
2	EtOH	84	89
3	*t*-AmOH	86	92
4	THF	76	81
5	n-heptane	0	0
6	cyclohexane	0	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (10 mol %), $AgSbF_6$ (0.04 mmol), $Cu(OAC)_2$ (0.2 mmol), H_2O 0.5 ml at room temperature for 24 h.

The competition experiment



1h (0.1 mmol) **1j** (0.1 mmol) **2a** **3h** **3j**

3h : **3j** = 0.99 : 1.00

A 15ml sealed tube was charged with 2-(m-tolyl)pyridine **1h** (22 mg, 0.1 mmol), 2-(3-(trifluoromethyl)phenyl)pyridine **1j** (17 mg, 0.1 mmol), styrene **2a** (42 mg, 0.4 mmol) $[Cp^*RhCl_2]_2$ (1.2 mg, 0.02 mmol), $AgSbF_6$ (14 mg, 0.04 mmol), $Cu(OAc)_2$ (40 mg, 0.2 mmol) and H_2O (1 ml). The mixture was stirred at room temperature for 2 hours. The mixture was extracted with diethyl ether (3 × 5 mL) and then the combined organic extracts was washed with brine (2 × 10 mL), dried with sodium sulfate. Then 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 0.99 : 1.00. ^{1}H-NMR (600 MHz, DMSO) δ 8.72 (m, 1H), 8.71 (m, 0.99H), 7.90 (m, 2H), 7.79 (s, 0.96H), 7.77 (s, 1.05H), 7.52 (t, *J* = 8.4Hz, 1.09H), 7.50 (t, *J* = 8.4Hz, 0.98H), 7.41 (m, 7H), 7.31 (m, 9H), 7.24 (m, 2H),

7.18 (m, 4H), 7.09 (d, *J* = 16.2Hz, 1H), 2.38 (s, 3H).