Supplmentary Materials for Heterocycles manuscript entitiled:

BIFURANS VIA PALLADIUM-CATALYZED SUZUKI COUPLING

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Preparation of 1-3 [S1-S2]

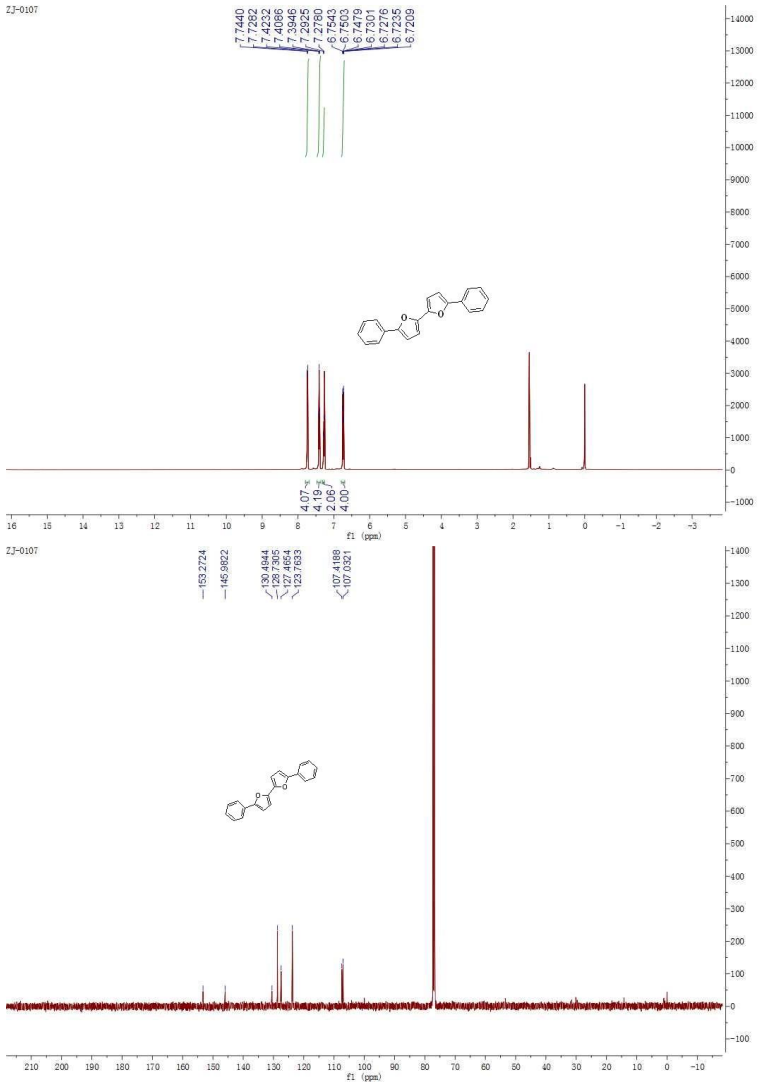
A Schlenk flask was charged with furan (2 mL, 0.028 mol) and THF (30 mL) (freshly distilled over Na and benzophenone diketal). After it was cooled to -78 °C, a solution of n-BuLi (17.3 mL, 1.6 M, 0.028 mmol) was added dropwise. After addition, the mixture was warmed slowly to room temperature and then heated at 50 °C for 3h. Again the mixture was cooled to -78 °C and anhydrous CuCl (4.76 g, 0.028 mol) was added portion-wise, then it was warmed to room temperature and stirred overnight before diluted aq. HCl (10%, 20 mL) was added to quench the reaction at 0-5v °C, and it was subsequently extracted with CH_2Cl_2 (3 x 100 mL). The organic phase was washed twice with water and the solvent was carefully removed to obtained crude 2,2'-bifuran, which was purified by column separation (Petro-ether, PE) to afford a yellow liquid (0.85 g, 45%). R_f 0.80 (PE). ^{1}H NMR δ: 7.43 (d, J = 1.6 Hz, 2H), 6.58 (d, J = 3.3 Hz, 2H), 6.47 (dd, J = 3.3, 1.8 Hz, 2H).

5,5'-dibromo-2,2'-bifuran (**2)** and 3,3',5,5'-tetrabromo-2,2'-bifuran (**3**) [S2]

A three-necked round flask was charged with 2,2'-bifuran (0.85 g, 6.34 mmol) and benzene (30 mL), then NBS (2.25 g, 12.68 mmol for **2**; 4.5 g, 25.36 mmol for **3**) was added with exclusion of light. The stirring was continued for 5h before the solvents were evaporated. The residue was dissolved in CH_2Cl_2 and washed with water (3 x 50 mL). After column separation with petro-ether (PE), a white solid of **2** was obtained (1.3 g，72%), mp 75.1- 76.4°C. R_f 0.56 (PE). ^{1}H NMR δ: 6.51 (d, J = 3.4 Hz, 2H), 6.36 (d, J = 3.4 Hz, 2H). This materials has to be used immediately before it became dark; 3,3',5,5'-tetrabromo-2,2'- bifuran (**3**), white solid (1.8 g, 64%), mp 111-112 °C. R_f 0.66 (PE) ^{1}H NMR δ: 6.48 (s, 2H).

S1 T. Kauffmann, H. Lexy, *Chem. Ber.* 1981,**114**, 3667;

S2 H. Ishida, K. Yui, Y. Aso, T. Otsubo, F. Ogura, *Bull. Chem. Soc. Jpn.* 1990, **63**, 2828.



Mass Spectrum List Report

Analysis Info

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Sample Name	ZJ-17	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

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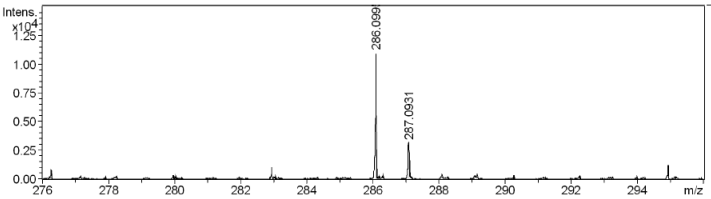

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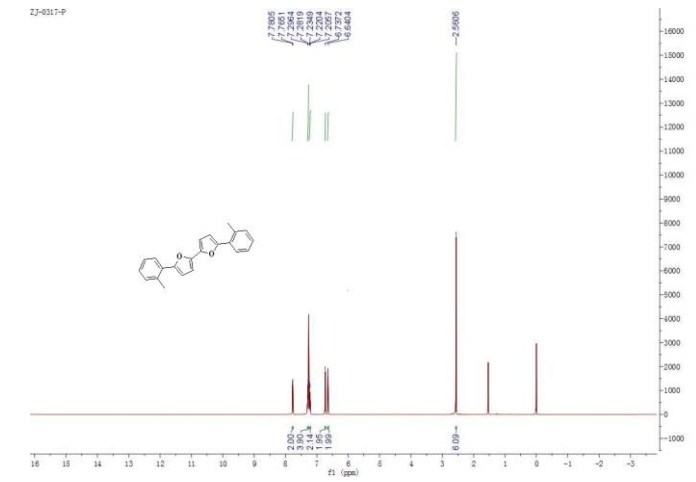
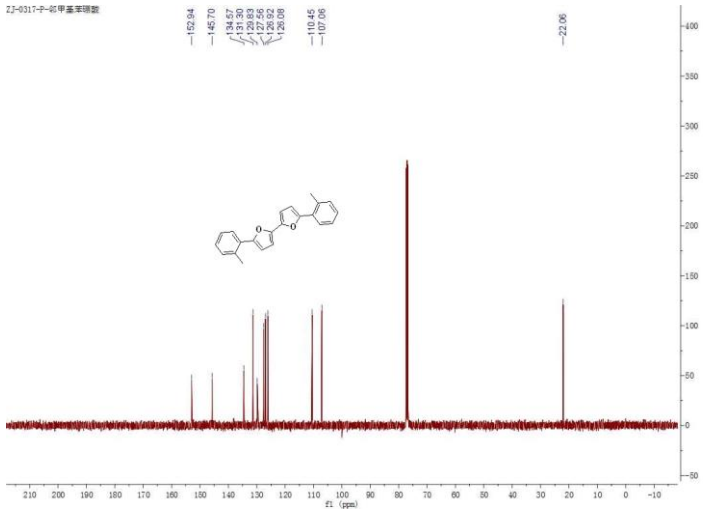
1	286.0995	15646	447.1	10876	100.0	0.0183
2	287.0931	7917	127.6	3112	28.6	0.0363

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e⁻ Conf	N-Rule
286.0995	1	C20H14O2	286.0988	-2.2	40.1	1	100.00	14.0	odd	ok

Fig.1 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **4a**





Mass Spectrum List Report

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Sample Name	ZJ-16	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

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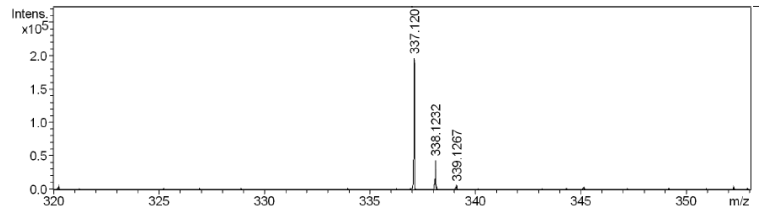
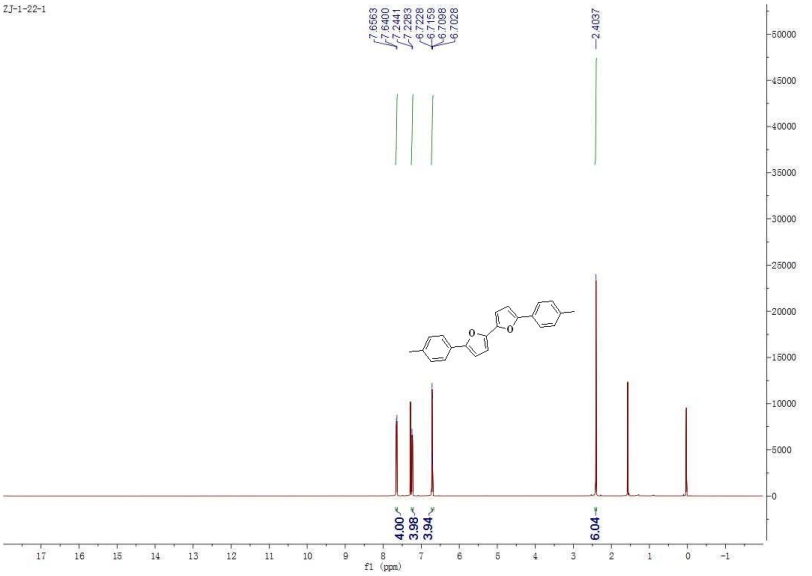
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

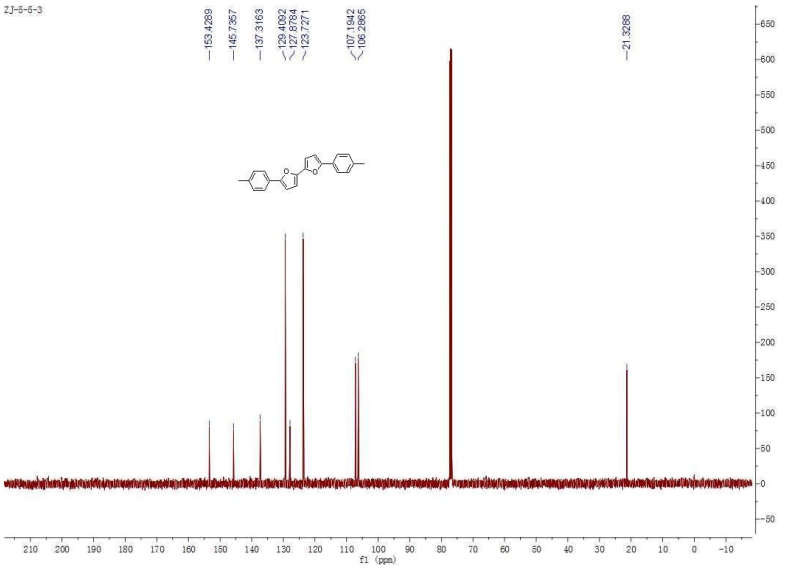


#	m/z	Res.	S/N	I	I %	FWHM
1	337.1201	22482	2431.8	196231	100.0	0.0150
2	338.1232	16345	545.4	44131	22.5	0.0207
3	339.1267	12603	81.2	6606	3.4	0.0269

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
337.1201	1	C22H18NaO2	337.1199	-0.7	9.2	1	100.00	13.5	even	ok

Fig.2 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **4b**





Mass Spectrum List Report

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Sample Name	ZJ-11	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

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Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
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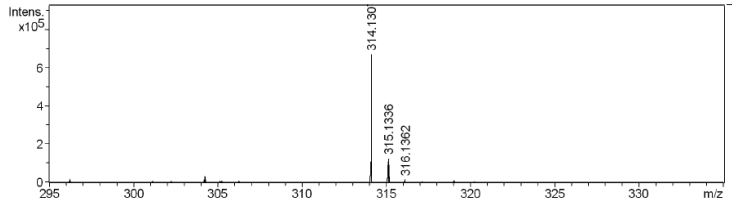
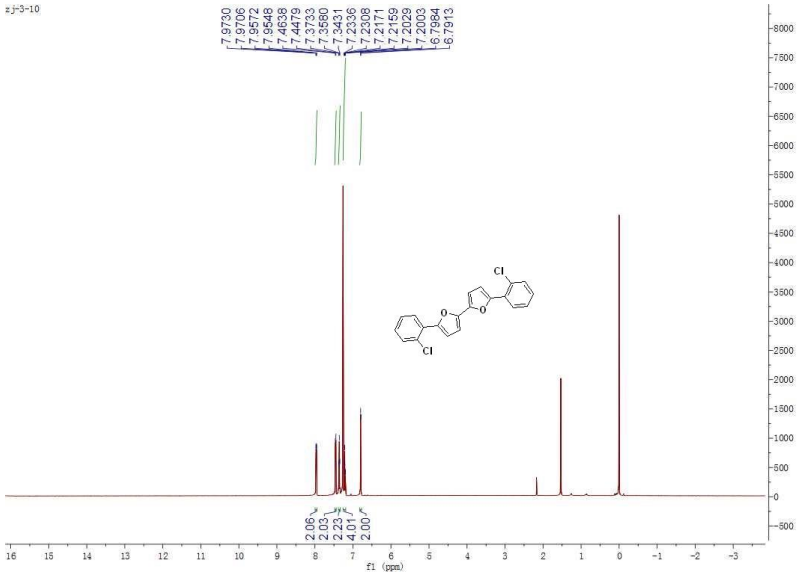
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source

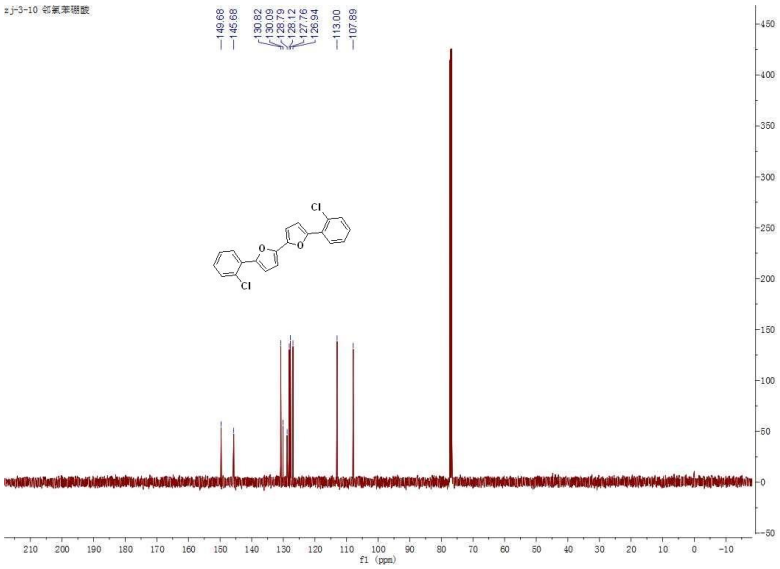


#	m/z	Res.	S/N	I	I %	FWHM
1	314.1307	29065	7708.7	668543	100.0	0.0108
2	315.1336	21176	1463.0	126836	19.0	0.0149
3	316.1362	14243	170.7	14816	2.2	0.0222

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
314.1307	1	C22H18O2	314.1301	-1.9	30.0	1	100.00	14.0	odd	ok

Fig.3 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **4c**





Mass Spectrum List Report

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Sample Name	ZJ-13	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
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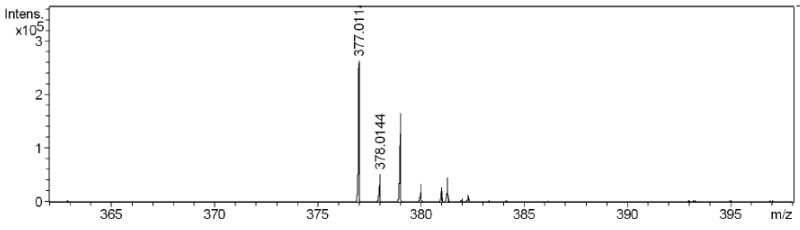
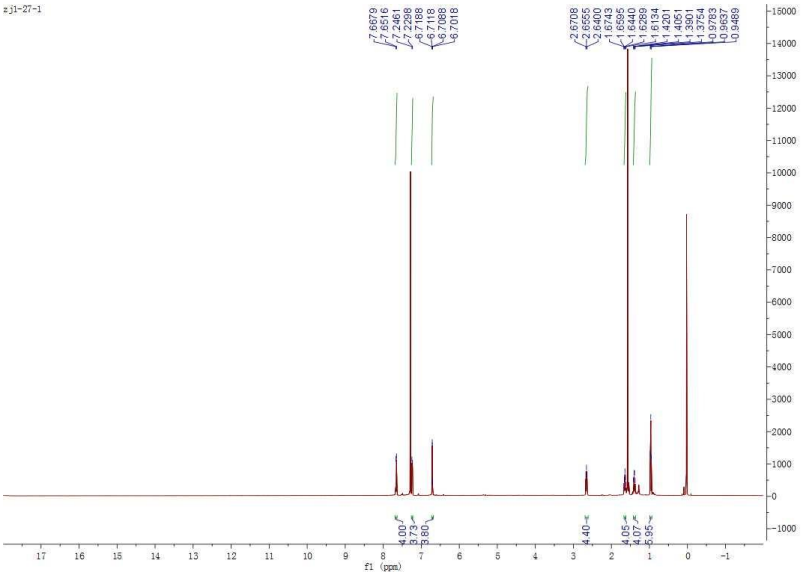
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

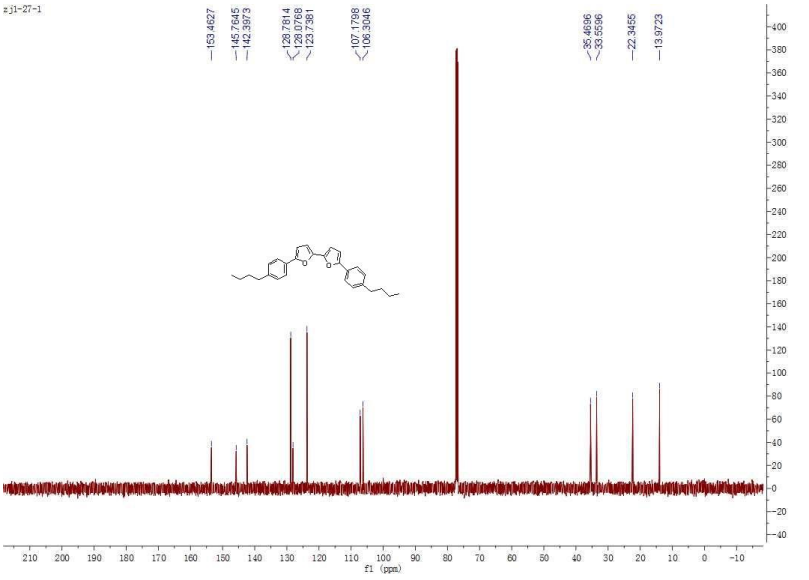


#	m/z	Res.	S/N	I	I %	FWHM
1	377.0114	23746	2745.4	262355	100.0	0.0159
2	378.0144	17039	548.6	52592	20.0	0.0222

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
377.0114	1	C20H12Cl2NaO2	377.0107	-1.9	18.0	1	100.00	13.5	even	ok

Fig.4 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **4d**





Mass Spectrum List Report

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Sample Name	ZJ-15	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

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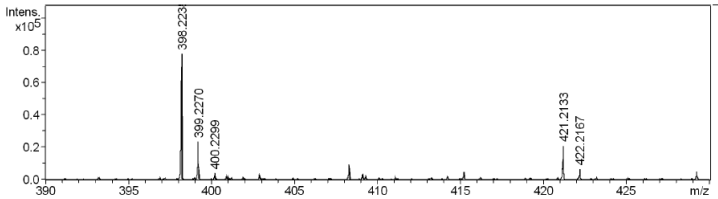
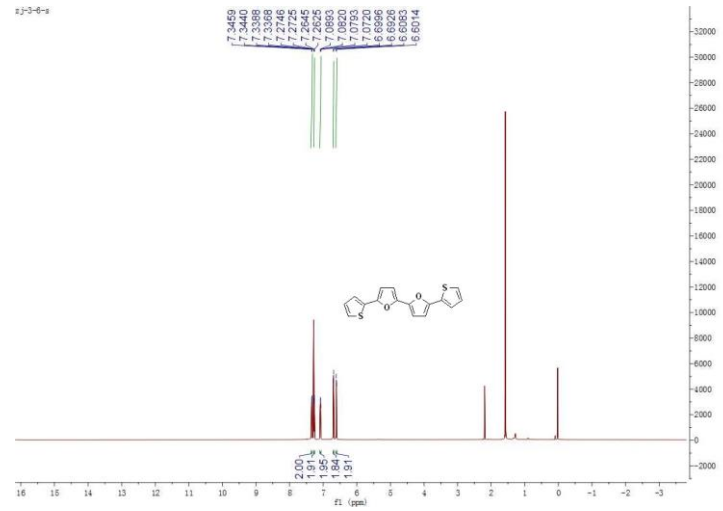
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

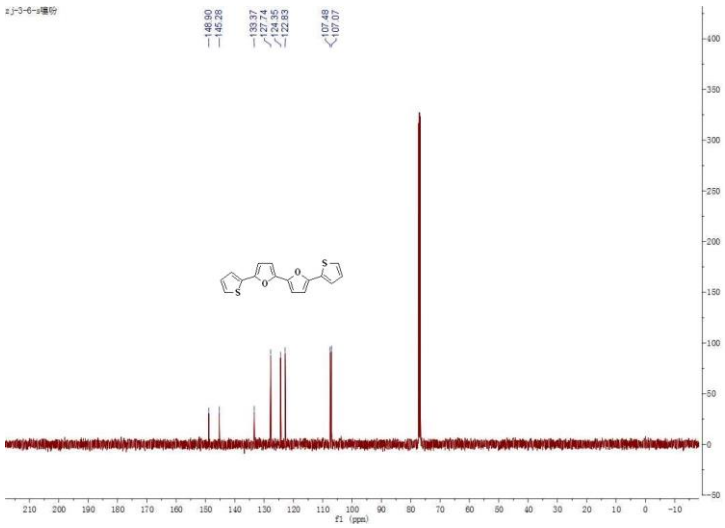


#	m/z	Res.	S/N	I	I %	FWHM
1	398.2238	19858	727.9	77710	100.0	0.0201
2	399.2270	15644	218.4	23452	30.2	0.0255
3	400.2299	13215	37.4	4047	5.2	0.0303
4	421.2133	14052	177.8	21101	27.2	0.0300
5	422.2167	12903	55.4	6593	8.5	0.0327

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
398.2238	1	C28H30O2	398.2240	0.5	3.8	1	100.00	14.0	odd	ok
421.2133	1	C28H30NaO2	421.2138	1.2	9.7	1	100.00	13.5	even	ok

Fig.5 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **4e**





Mass Spectrum List Report

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Sample Name	ZJ-12	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

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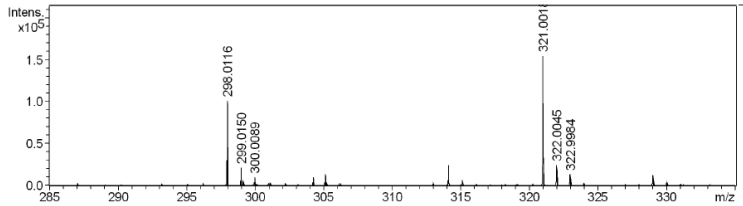
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste



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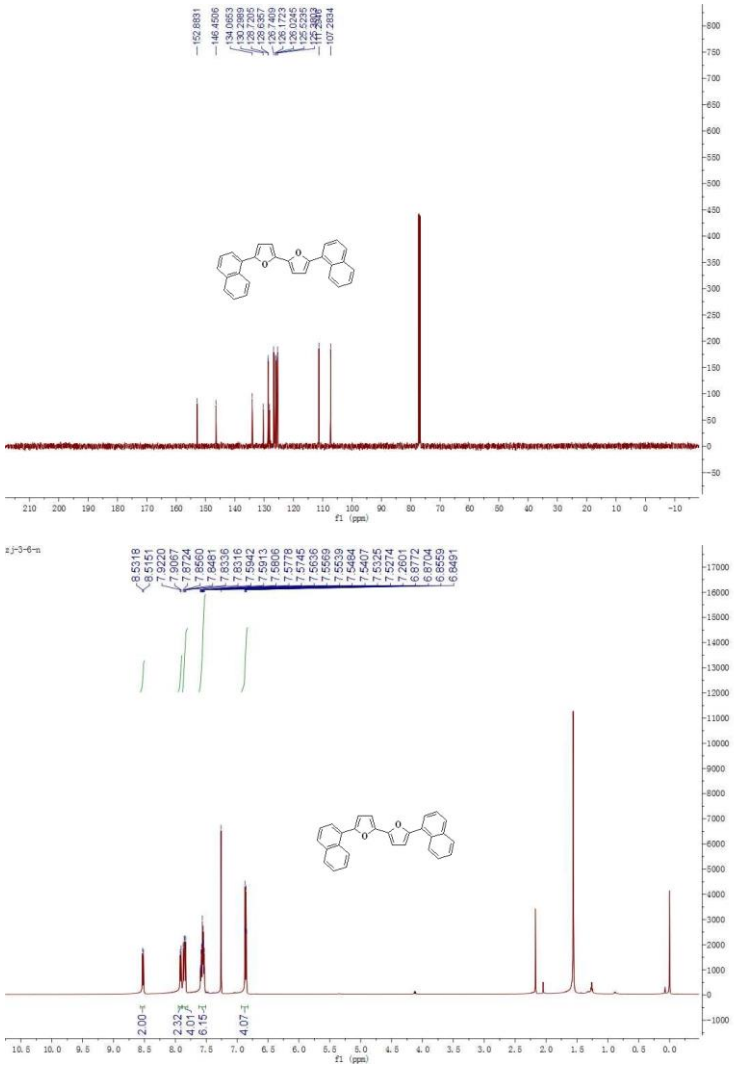
1	298.0116	16979	2070.1	100850	65.4	0.0176
2	299.0150	13757	441.7	21585	14.0	0.0217
3	300.0089	11547	213.7	10467	6.8	0.0260
4	321.0018	25569	2822.5	154120	100.0	0.0126
5	322.0045	16529	454.4	24923	16.2	0.0195
6	322.9984	13705	245.3	13515	8.8	0.0236

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
298.0116	1	C16H10O2S2	298.0117	0.2	11.1	1	100.00	12.0	odd	ok
321.0018	1	C16H10NaO2S2	321.0014	-1.2	16.6	1	100.00	11.5	even	ok

Fig.6 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **4f**



Mass Spectrum List Report

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Sample Name	ZJ-14	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

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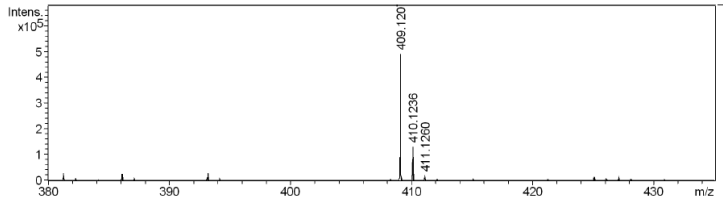
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste



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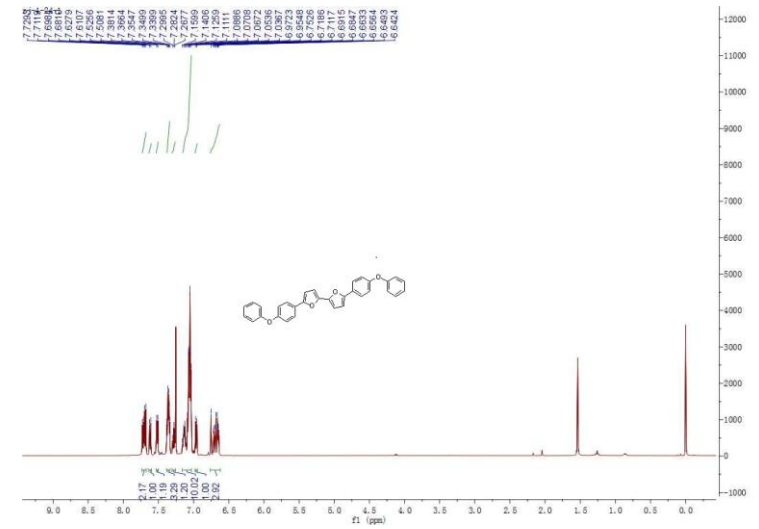
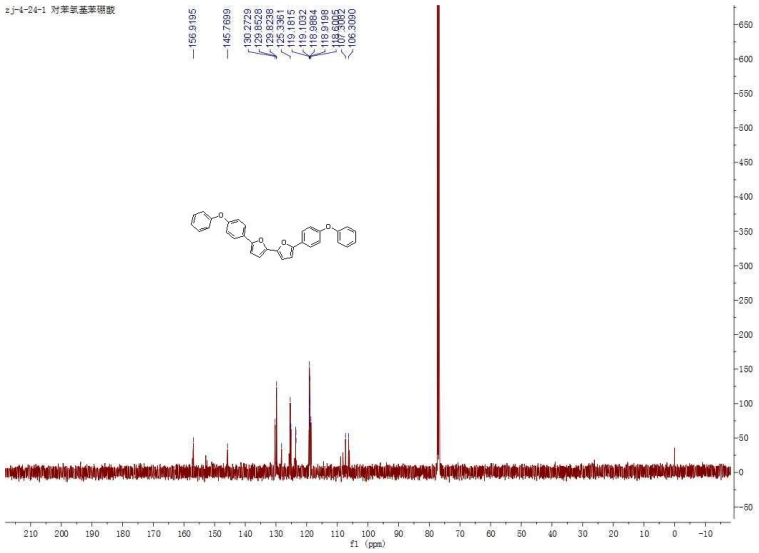
1	409.1207	27671	3569.3	490373	100.0	0.0148
2	410.1236	20365	947.4	130559	26.6	0.0201
3	411.1260	12269	147.0	20294	4.1	0.0335

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
409.1207	1	C28H18NaO2	409.1199	-1.8	20.1	1	100.00	19.5	even	ok

Fig.7 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **4g**





Mass Spectrum List Report

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Sample Name	ZJ-18	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
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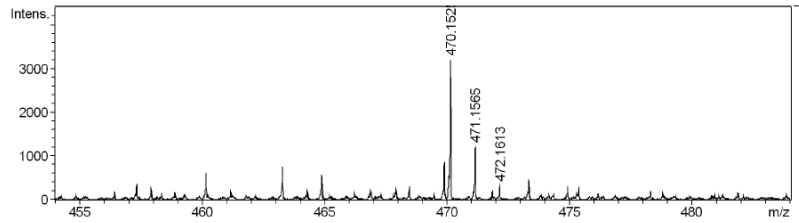
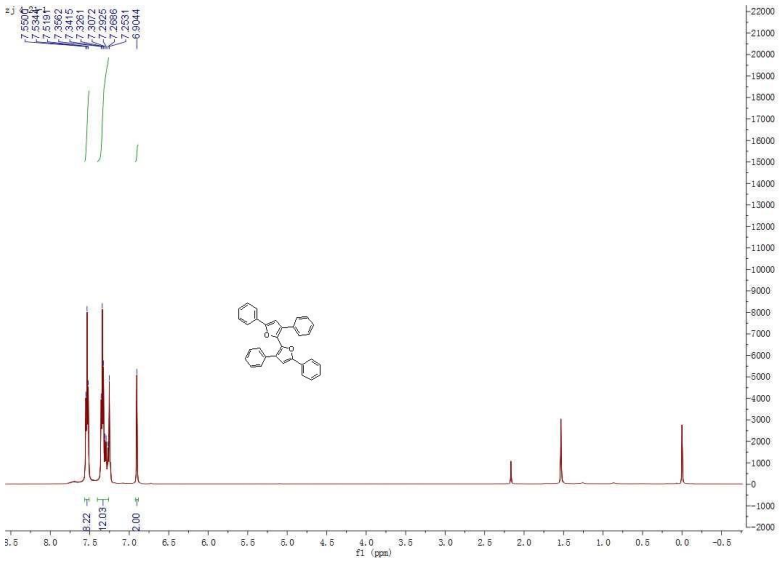
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

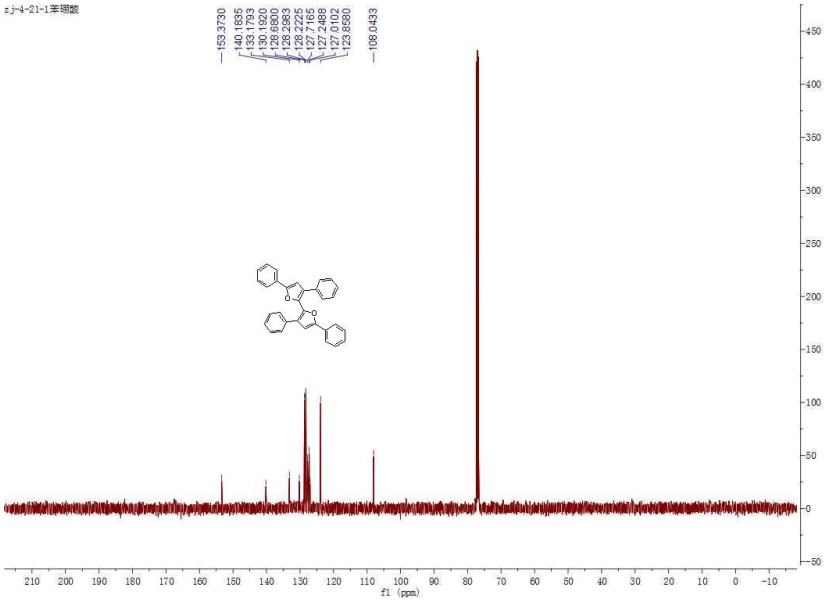


#	m/z	Res.	S/N	I	I %	FWHM
1	470.1525	16311	127.8	3184	100.0	0.0288
2	471.1565	16061	48.4	1208	38.0	0.0293
3	472.1613	14480	12.9	323	10.1	0.0326

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
470.1525	1	C32H22O4	470.1513	-2.7	22.8	1	100.00	22.0	odd	ok

Fig.8 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **4h**





Mass Spectrum List Report

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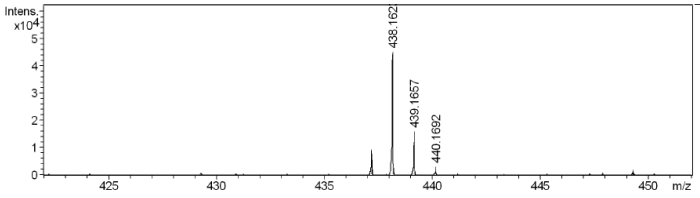
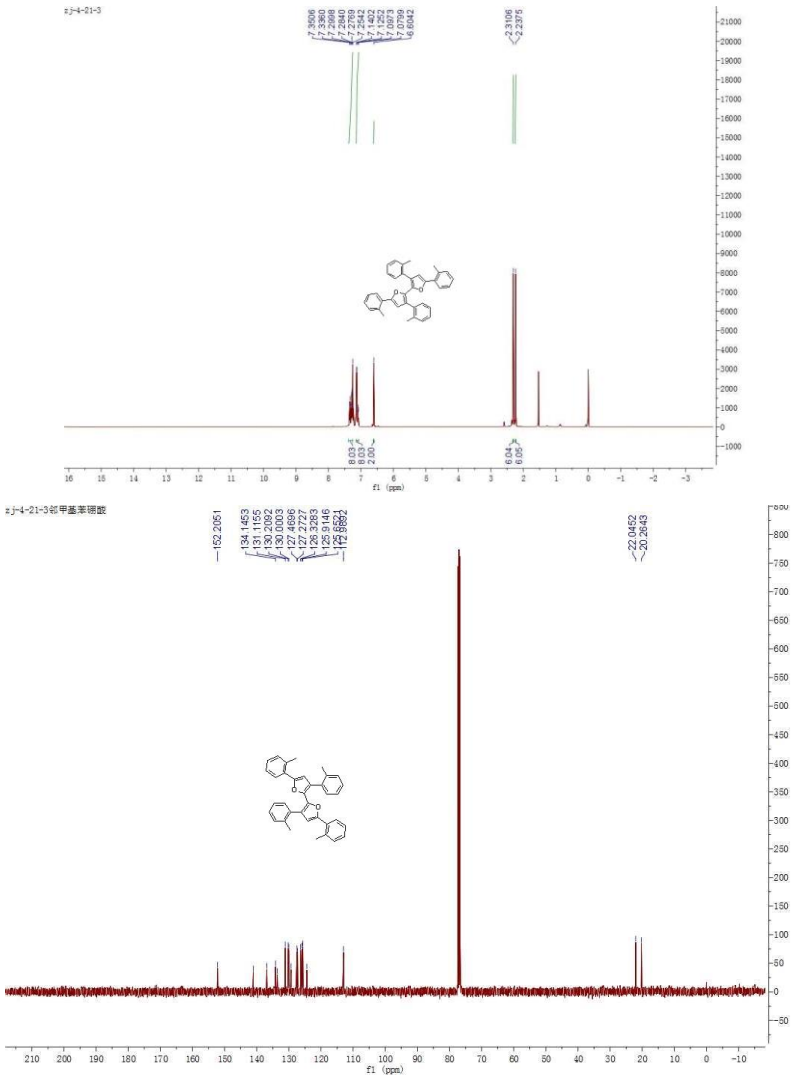
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	438.1623	18078	1197.2	44918	100.0	0.0242
2	439.1657	17663	424.7	15950	35.5	0.0249
3	440.1692	18126	83.5	3138	7.0	0.0243

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
438.1623	1	C32H22O2	438.1614	-2.1	4.4	1	100.00	22.0	odd	ok

Fig. 9 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **5a**



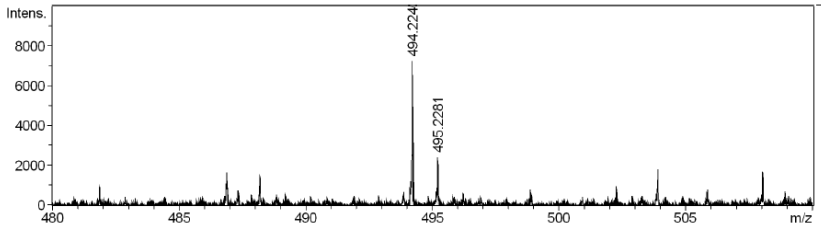
Mass Spectrum List Report

Analysis Info

Analysis Name	D:\Data\chem. dep\liuqiancai\ZHANGJUN\20150427\ZJ-26_P1-B-8_01_1482.d	Acquisition Date	4/27/2015 2:36:24 PM
Method	Tune_pos_low_LC with calibration_2min.m	Operator	ECNU-Chem
Sample Name	ZJ-26	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

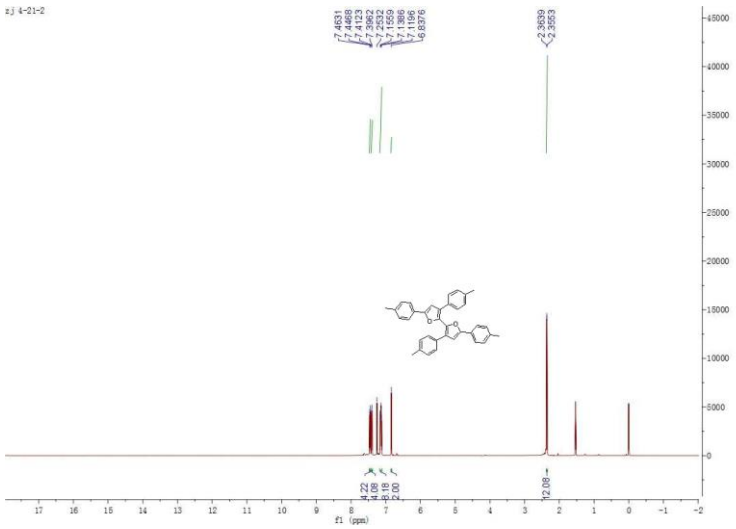
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

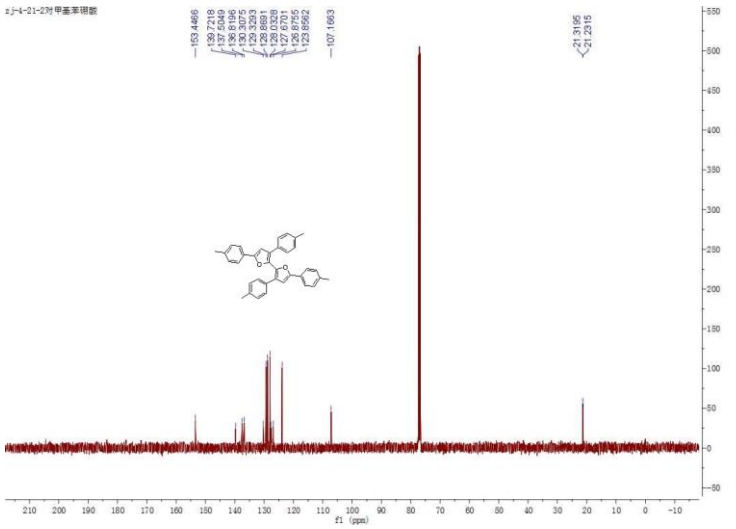


#	m/z	Res.	S/N	I	I %	FWHM
1	494.2240	16998	26.2	7224	100.0	0.0291
2	495.2281	15183	8.7	2404	33.3	0.0326

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
494.2240	1	C36H30O2	494.2240	0.1	34.7	1	100.00	22.0	odd	ok

Fig. 10 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **5b**





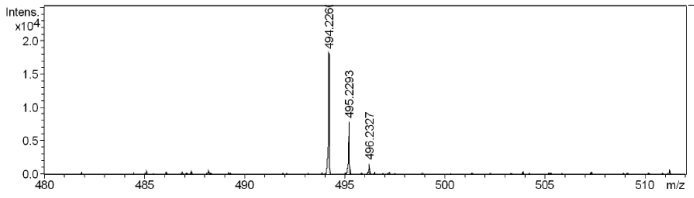
Mass Spectrum List Report

Analysis Info

Analysis Name	D:\Data\chem. dep\liuqiancai\ZHANGJUN\20150427\ZJ-21_P1-B-3_01_1477.d	Acquisition Date	4/27/2015 2:20:46 PM
Method	Tune_pos_low_LC with calibration_2min.m	Operator	ECNU-Chem
Sample Name	ZJ-21	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	494.2260	17646	854.0	18187	100.0	0.0280
2	495.2293	17184	367.4	7839	43.1	0.0288
3	496.2327	15445	76.3	1630	9.0	0.0321

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
494.2260	1	C36H30O2	494.2240	-3.9	19.5	1	100.00	22.0	odd	ok

Fig. 11 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **5c**

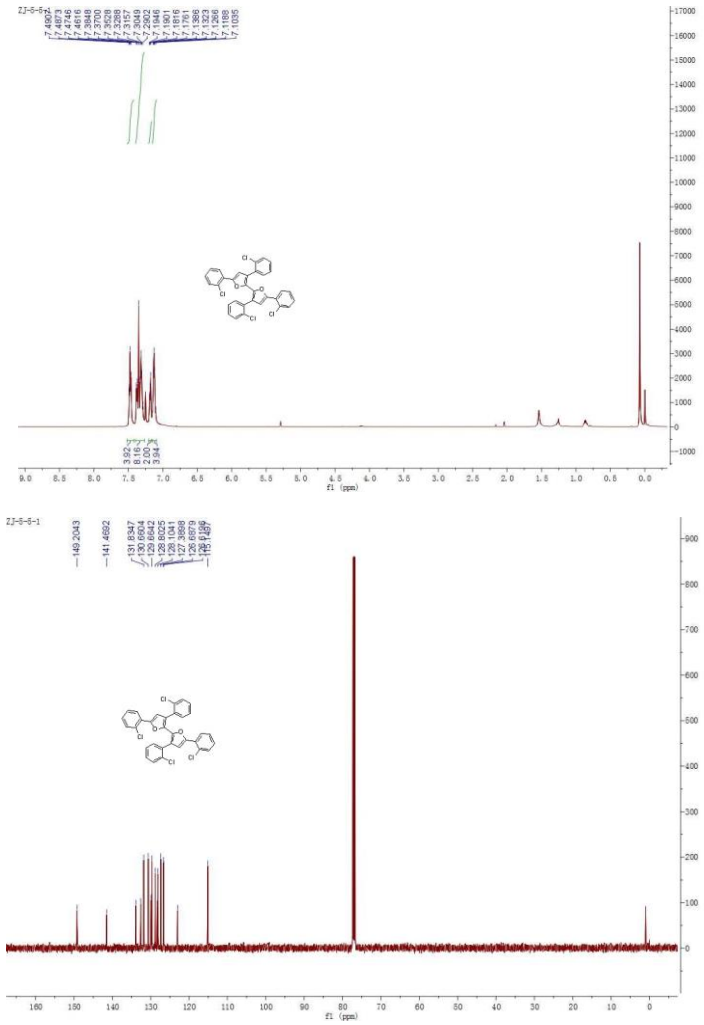
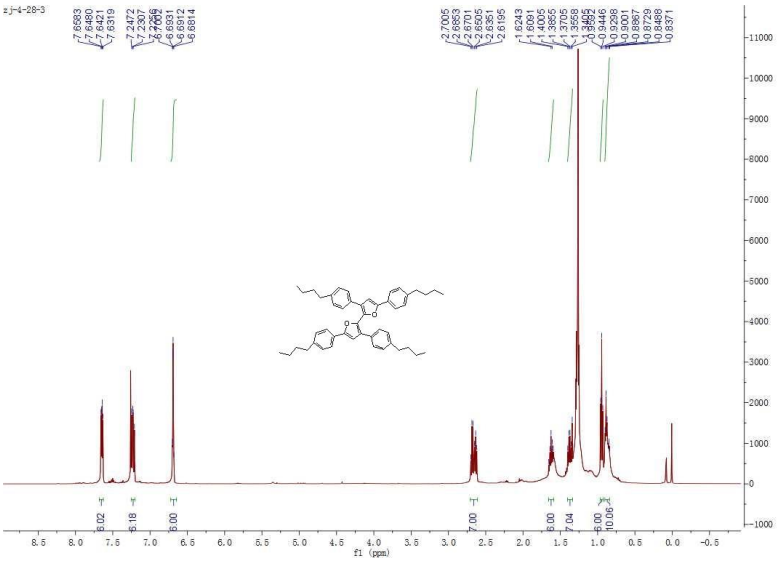


Fig. 12 ^{1}H NMR and ^{13} NMR for 5**d**



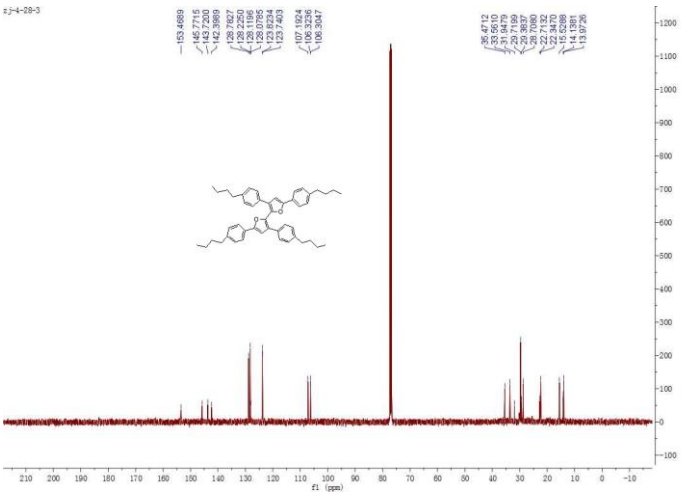
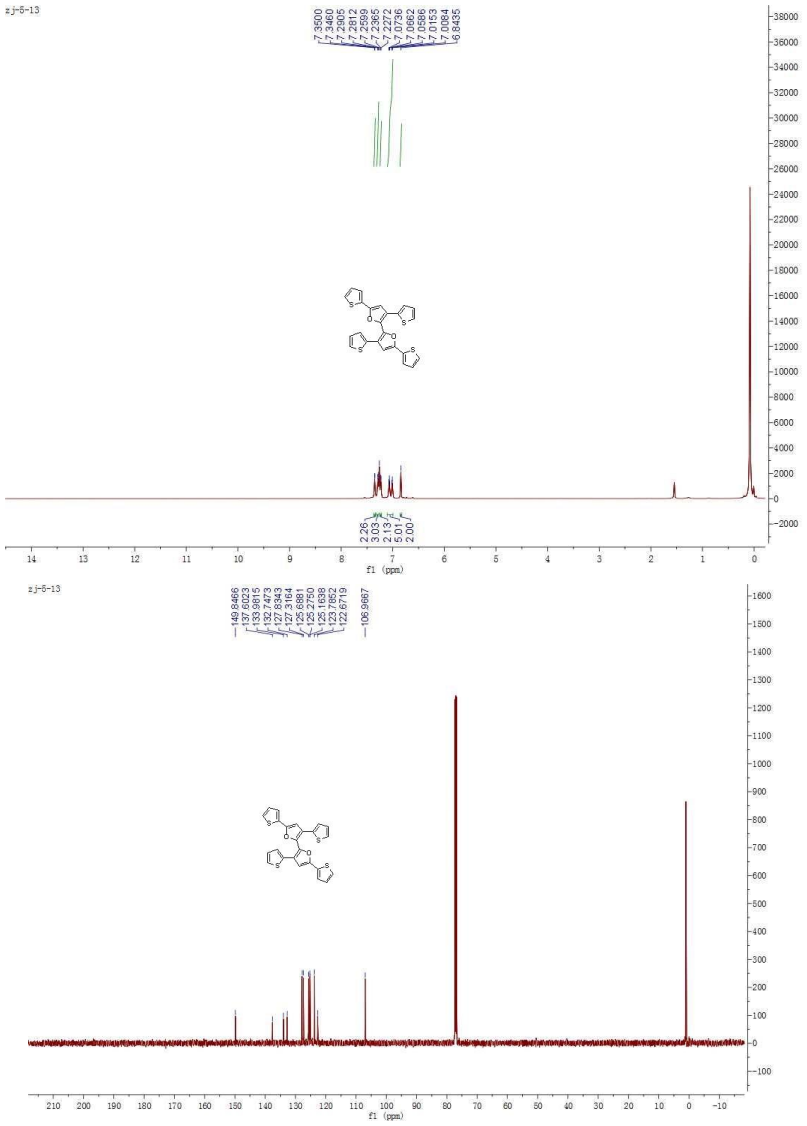


Fig. 13 ^{1}H NMR and ^{13} NMR for **5e**



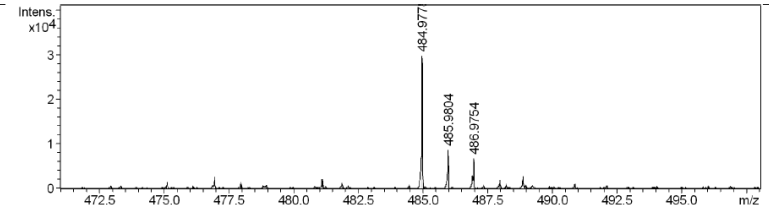
Mass Spectrum List Report

Analysis Info

Analysis Name	D:\Data\chem. dep\liuqiancai\ZHANGJUN\ZJ-22_P1-F-1_01_1599.d	Acquisition Date	5/13/2015 2:32:09 PM
Method	Tune_pos_low_LC with calibration_2min.m	Operator	ECNU-Chem
Sample Name	ZJ-22	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

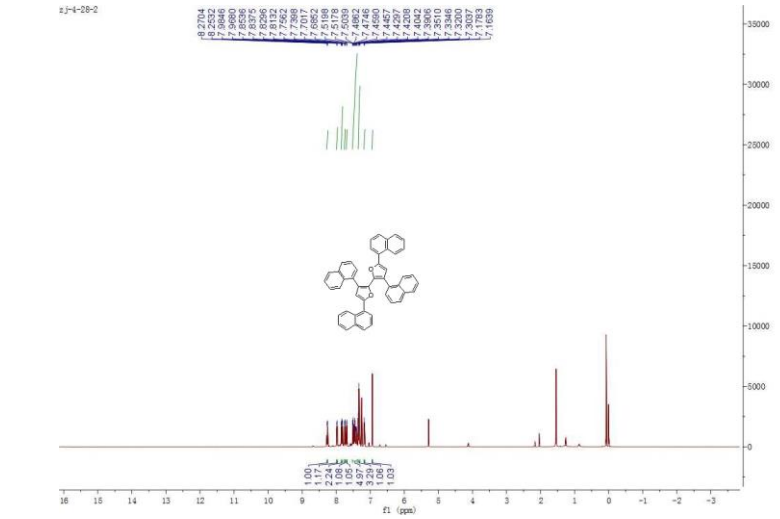
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source

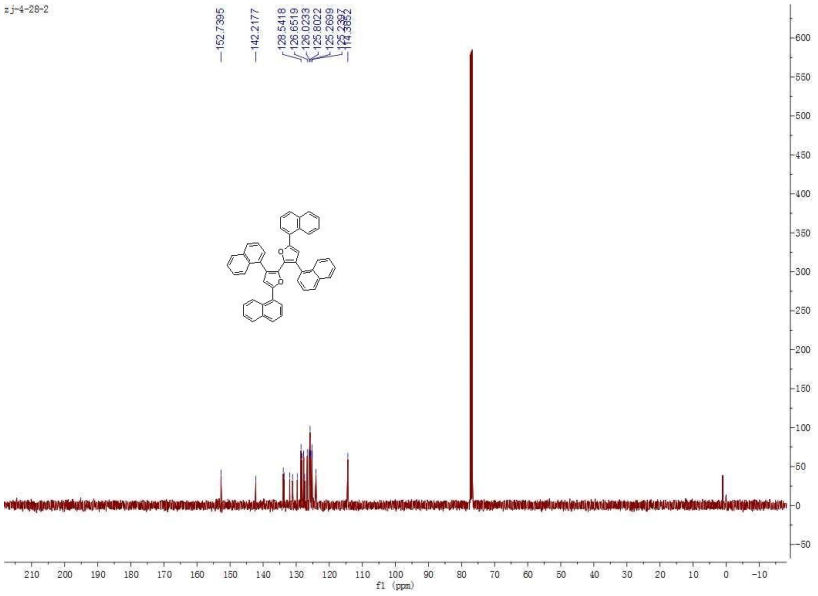


#	m/z	Res.	S/N	I	I %	FWHM
1	484.9778	18429	590.1	29685	100.0	0.0263
2	485.9804	16908	172.1	8663	29.2	0.0287
3	486.9754	15830	133.6	6730	22.7	0.0308

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
484.9778	1	C24H14NaO2S4	484.9769	-1.8	3.7	1	100.00	17.5	even	ok

Fig. 14 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **5f**





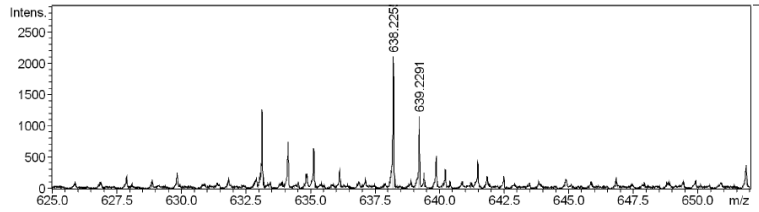
Mass Spectrum List Report

Analysis Info

Analysis Name	D:\Data\chem. dep\liuqiancai\ZHANGJUN\20150427\ZJ-24_P1-B-6_01_1480.d	Acquisition Date	4/27/2015 2:30:09 PM
Method	Tune_pos_low_LC with calibration_2min.m	Operator	ECNU-Chem
Sample Name	ZJ-24	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	638.2255	17369	67.2	2106	100.0	0.0367
2	639.2291	17735	36.8	1154	54.8	0.0360

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
638.2255	1	C48H30O2	638.2240	-2.3	17.9	1	100.00	34.0	odd	ok

Fig. 15 ^{1}H NMR, ^{13} NMR and HR-MS(ESI) for **5g**

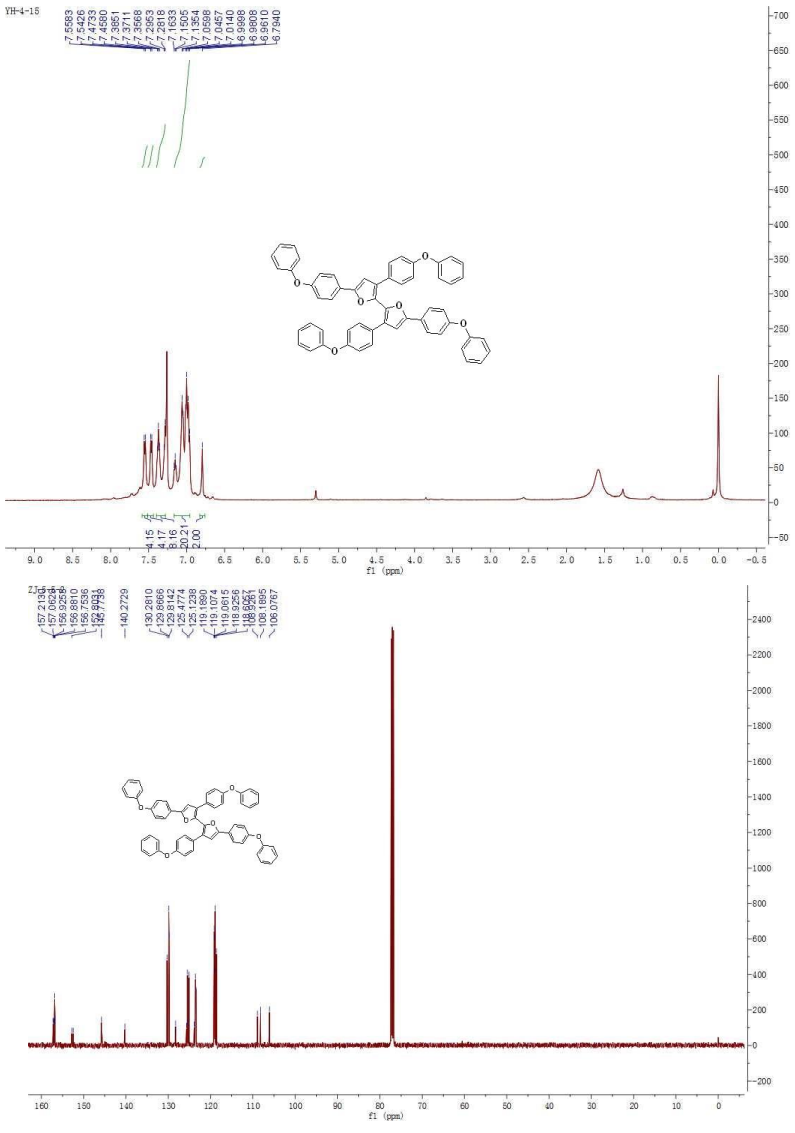


Fig. 16 ^{1}H NMR and ^{13} NMR for **5h**