

Supporting Information

Temperature-controlled divergent synthesis of pyrazoles and 1-tosyl-1*H*-pyrazoles under transition-metal-catalyst and oxidant-free conditions

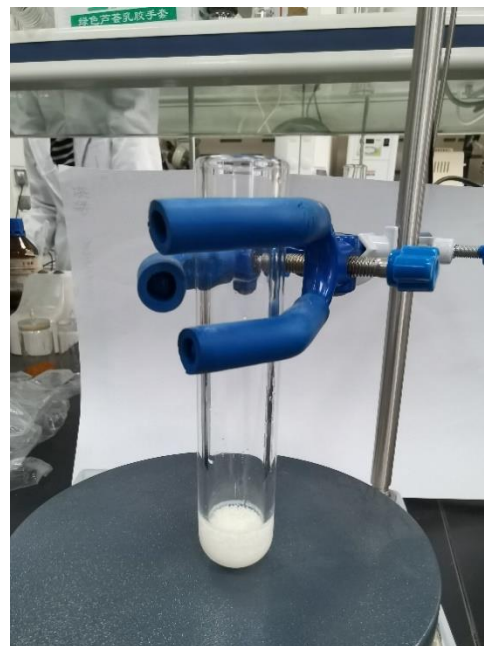
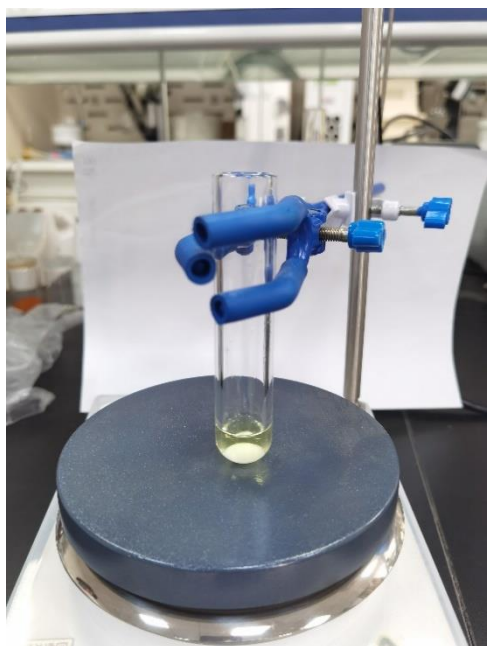
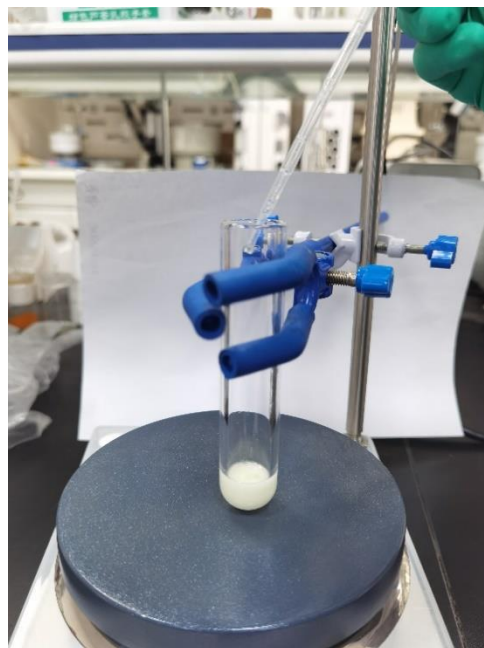
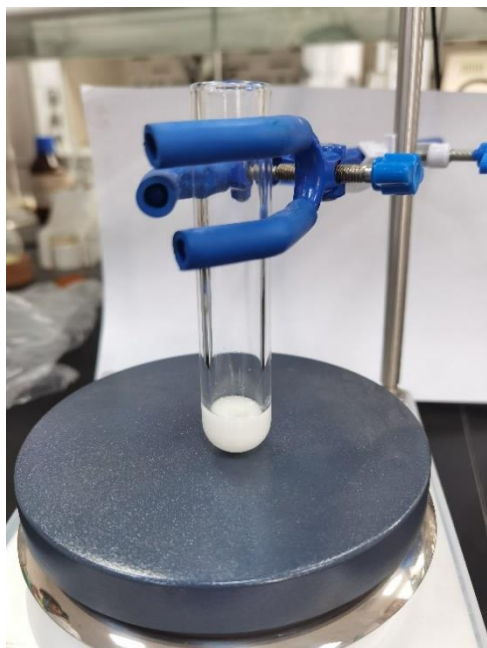
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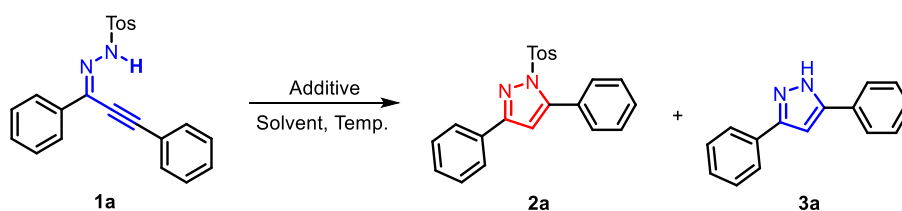
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1. Reaction progress diagram of 2a.



2. Optimization of Reaction Conditions ^{a,b}



Entry	Solvent	Yield of 2a [%] ^b	Yield of 3a [%] ^b
1	CH ₃ CN	N.R.	N.R.
2	DMSO	N.R.	N.R.
3	THF	N.R.	N.R.
4	AcOH	N.R.	N.R.
5	EtOH	N.R. (95) ^d	N.R. (65) ^e
6	EtOH	73 ^f	38 ^g
7	EtOH	47 ^h (97) ⁱ	28 ^h (68) ⁱ
8	[HDBU][OAc]	98	85 ^c (13) ^j
9	[HDBU][NHS]	95	78 ^c
10	[HTMG][NHS]	78	63 ^c
11	[HDBU][OAc][NHS]	86	68 ^c
12	[HTMG][HDBU][OAc][NHS]	80	58 ^c

^[a] Reaction conditions: **1a** (0.2 mmol), solvent (2.0 mL), rt., 0.5 h; ^[b] Isolated yields; ^[c] 95 °C, 12 h. ^[d] DBU (1.0 equiv.) additive, rt., 0.5 h. ^[e] DBU (1.0 equiv.) additive, 95 °C, 12 h. ^[f] DBU (1.0 equiv.) additive, 50 °C., 0.5 h. ^[g] DBU (1.0 equiv.) additive, 50 °C., 12 h. ^[h] DBU (0.5 equiv.) additive, rt., 0.5 h. ^[i] DBU (2.0 equiv.) additive, 95 °C, 12 h. ^[j] 40 °C, 12 h. [HDBU] = 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepin-1-ium, [NHS] = 2,5-dioxopyrrolidin-1-olate, [HTMG] = bis(dimethylamino)-methaniminium.

3. Yields of recyclability test.

Run Yield (%)	1	2	3	4	5
2a	95	93	92	88	84
3a	85	82	77	71	72

4. ^1H and ^{13}C NMR spectra of the products.

Figure S1 ^1H NMR Spectra of Compound of 2a

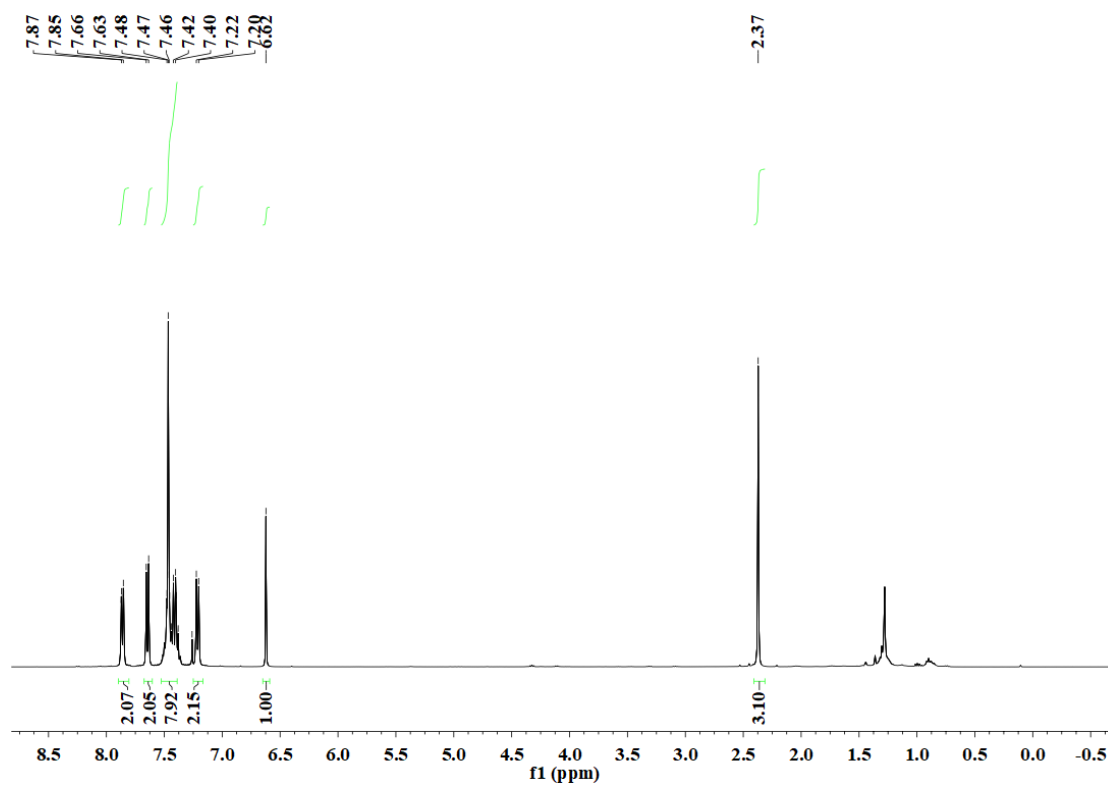


Figure S2 ^{13}C NMR Spectra of Compound of 2a

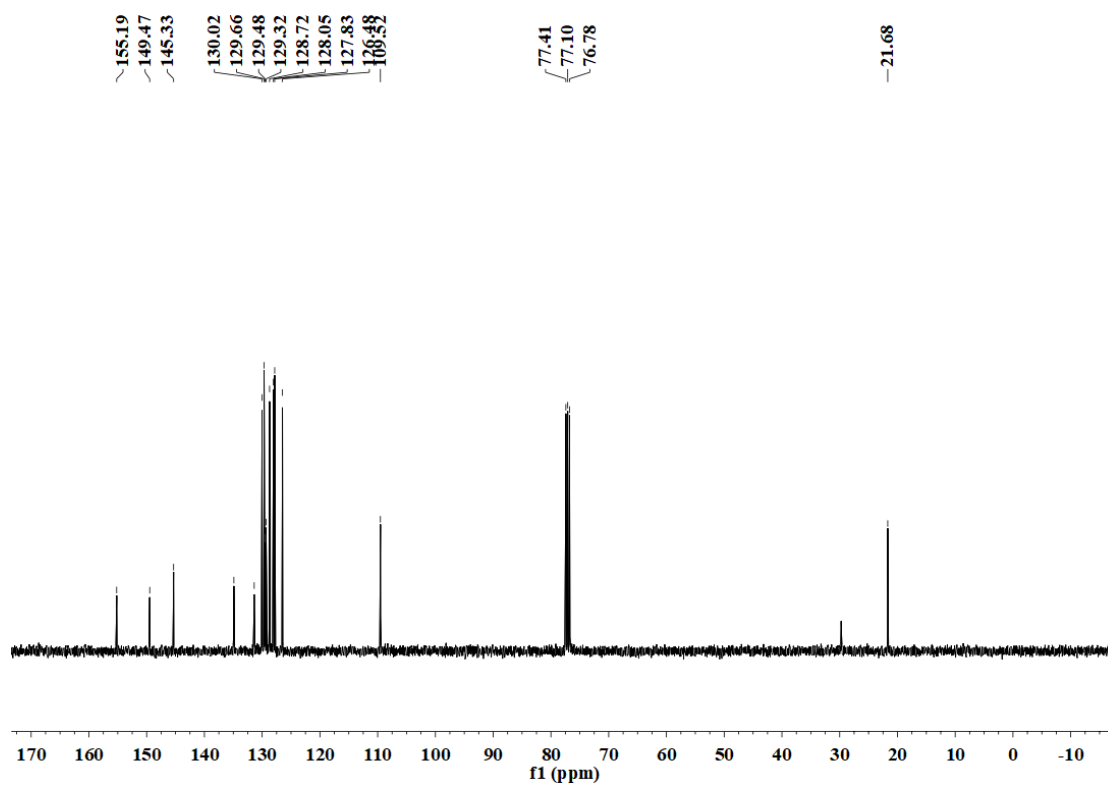


Figure S3 ^1H NMR Spectra of Compound of 2b

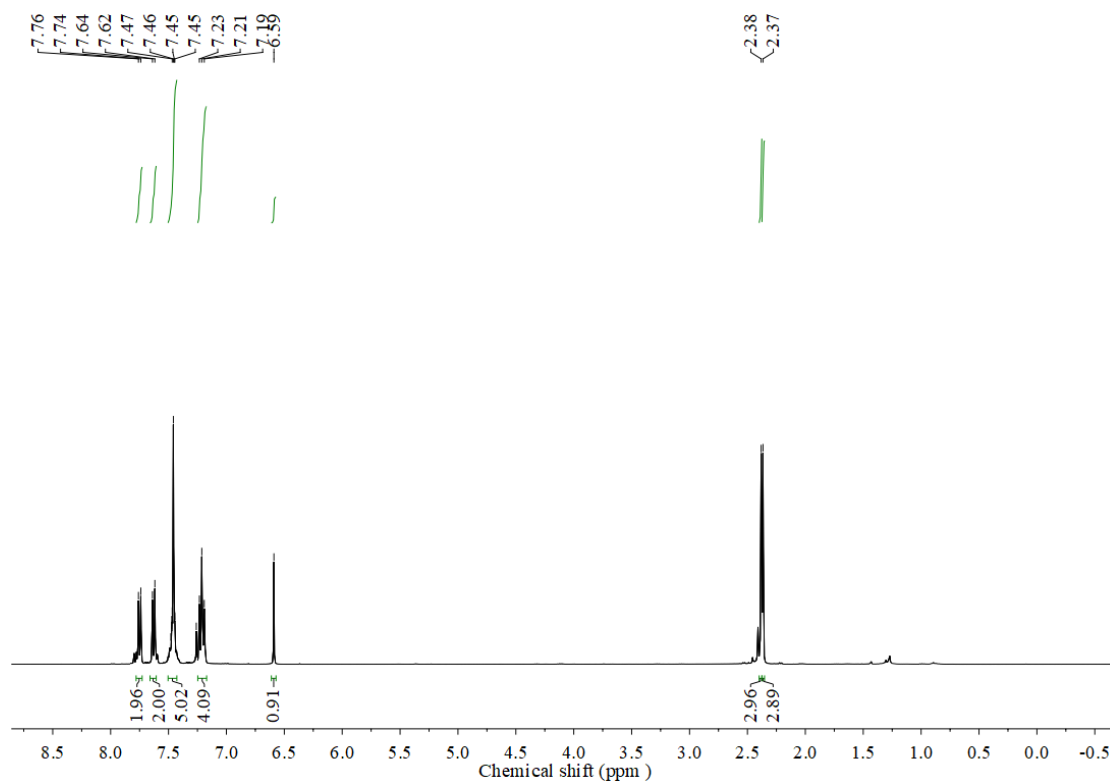


Figure S4 ^{13}C NMR Spectra of Compound of 2b

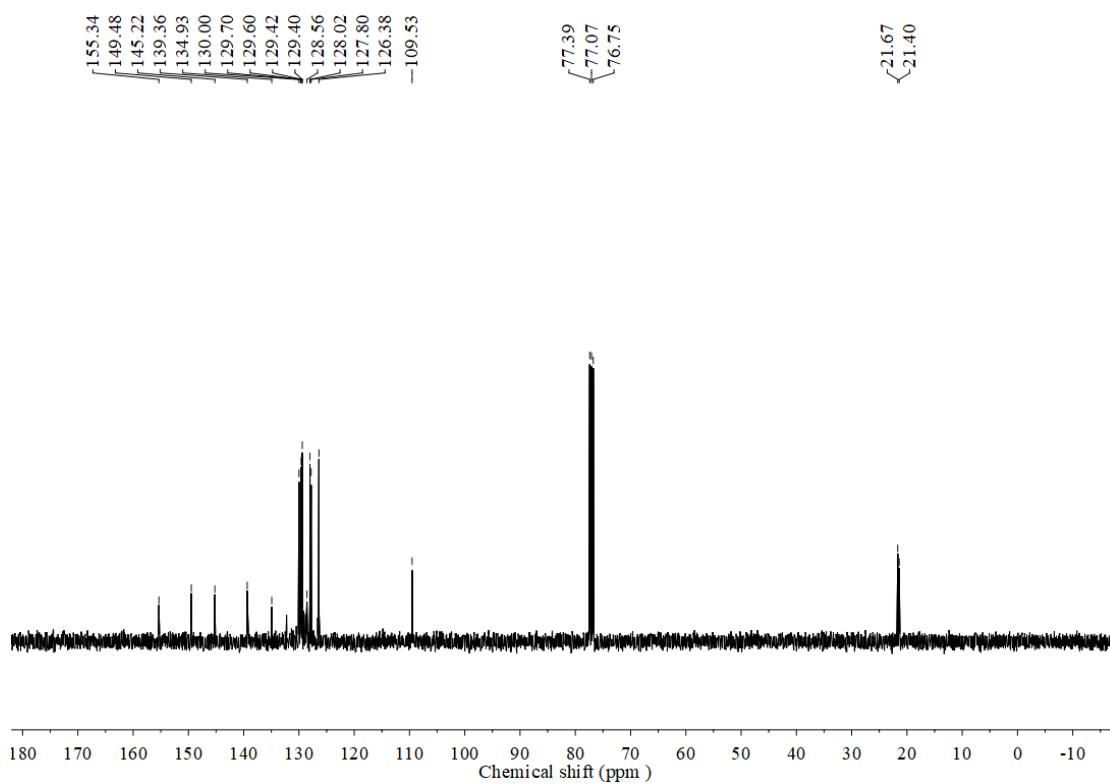


Figure S5 ^1H NMR Spectra of Compound of 2c

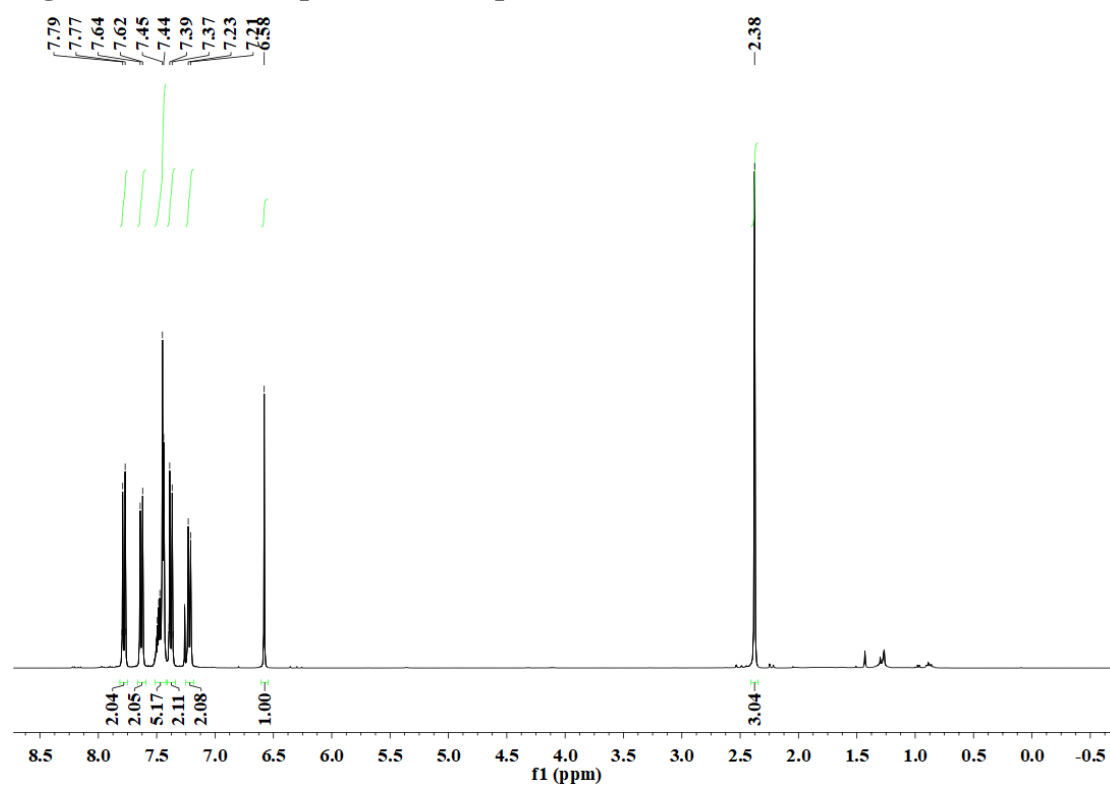


Figure S6 ^{13}C NMR Spectra of Compound of 2c

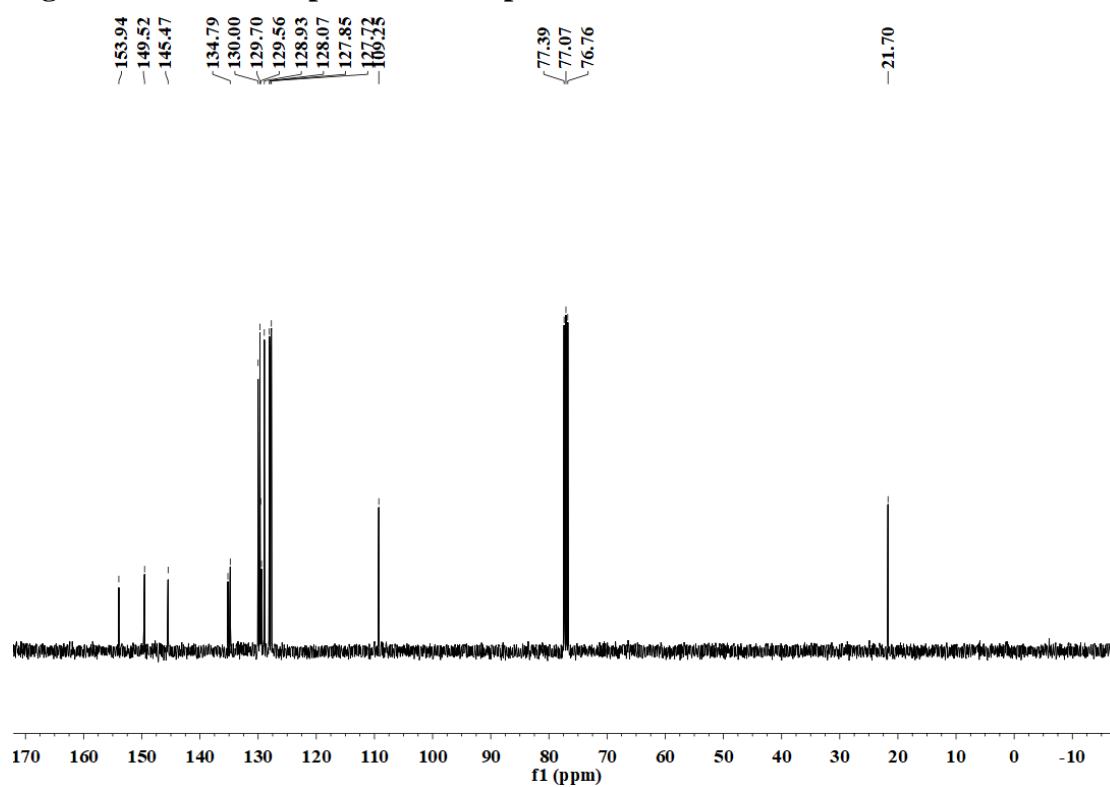


Figure S7 ^1H NMR Spectra of Compound of 2d

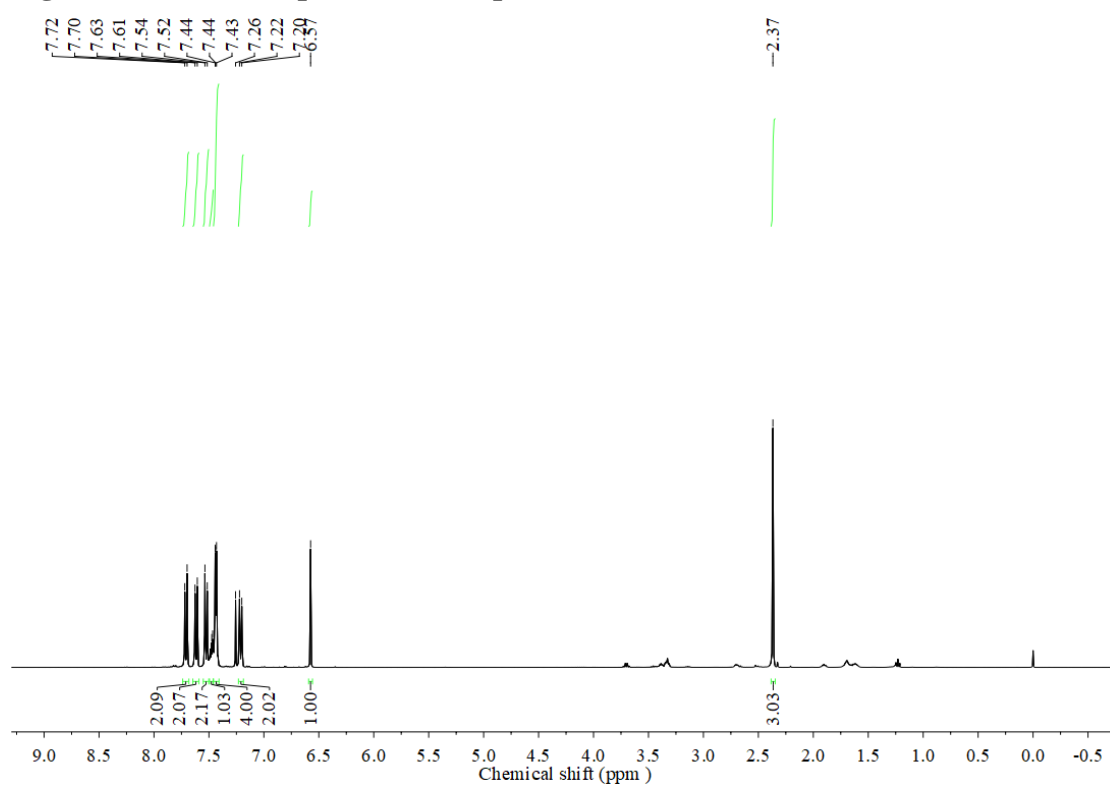


Figure S8 ^{13}C NMR Spectra of Compound of 2d

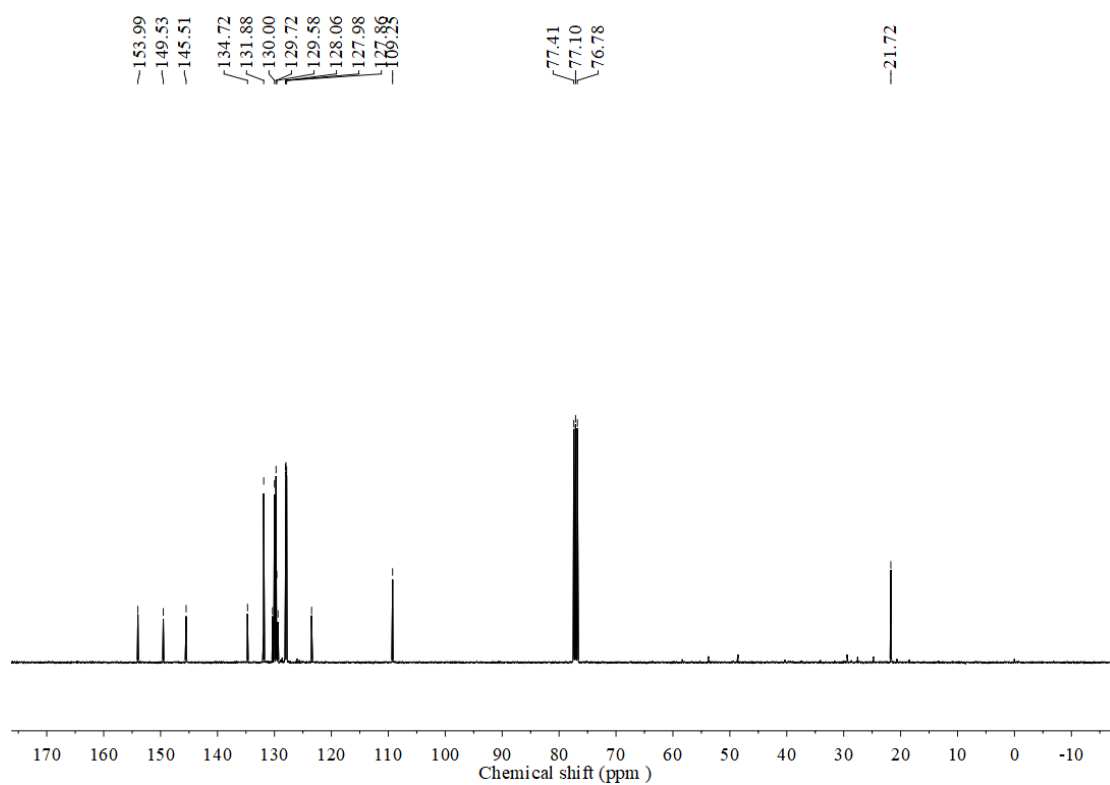


Figure S9 ^1H NMR Spectra of Compound of 2e

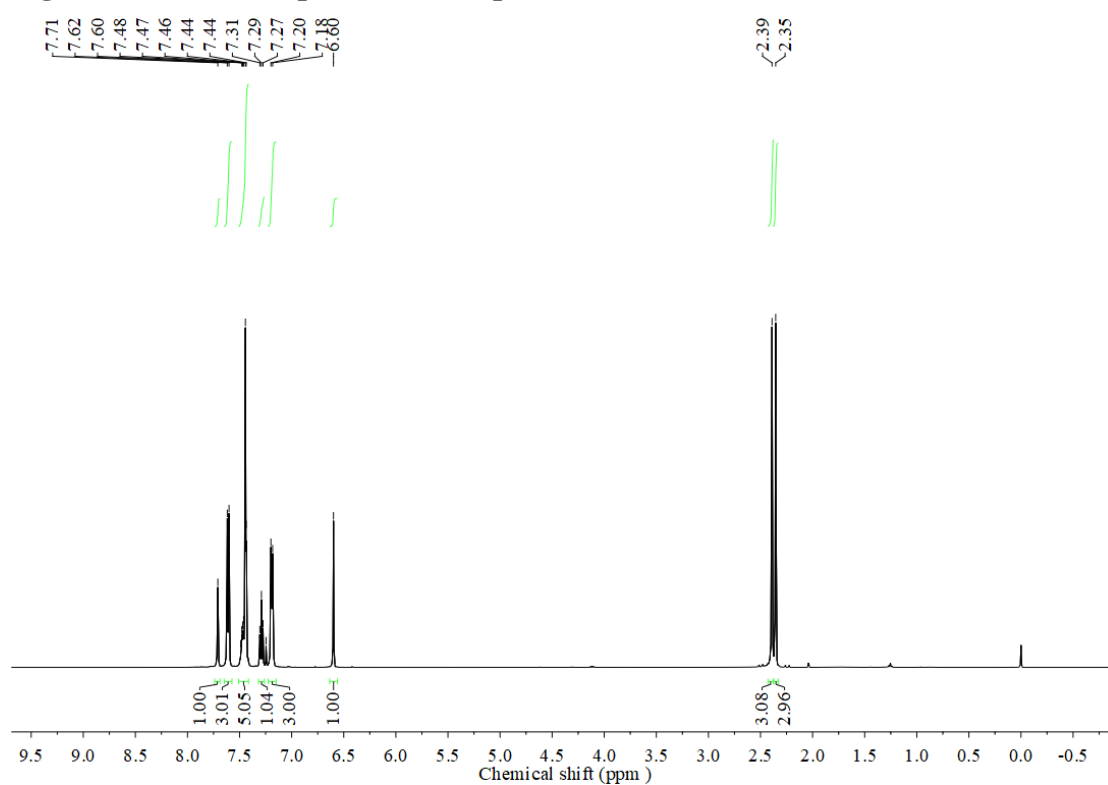


Figure S10 ^{13}C NMR Spectra of Compound of 2e

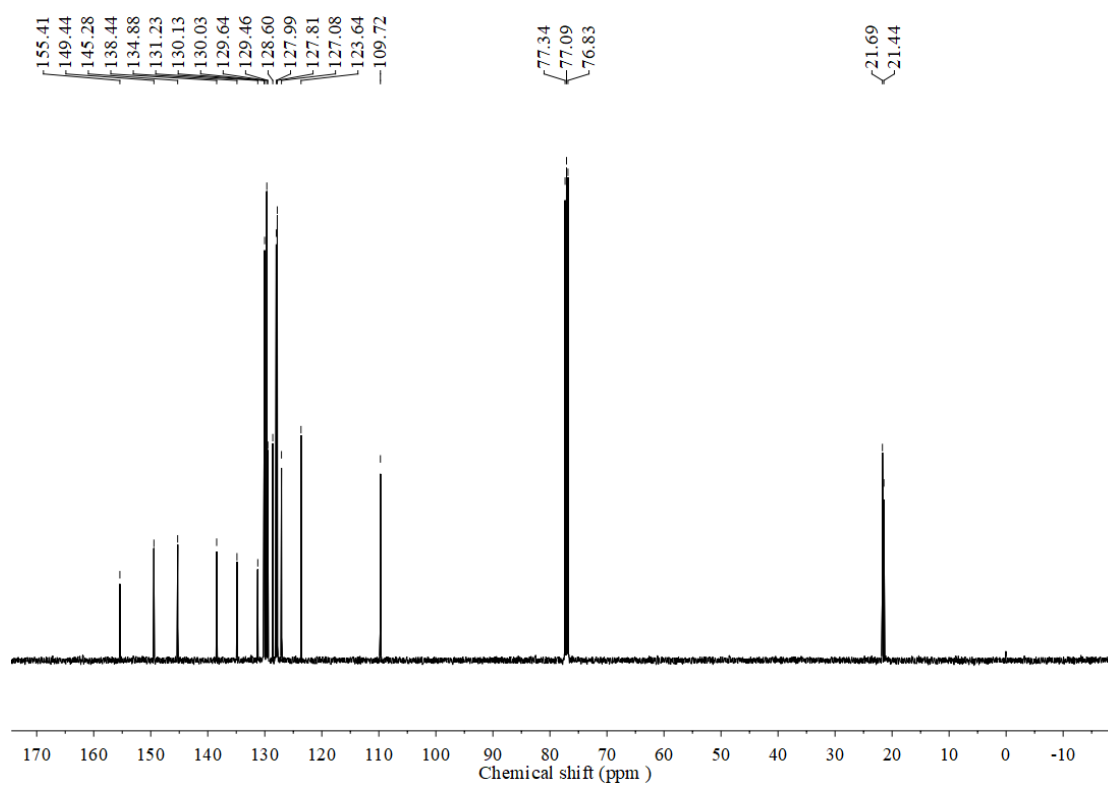


Figure S11 ^1H NMR Spectra of Compound of 2f

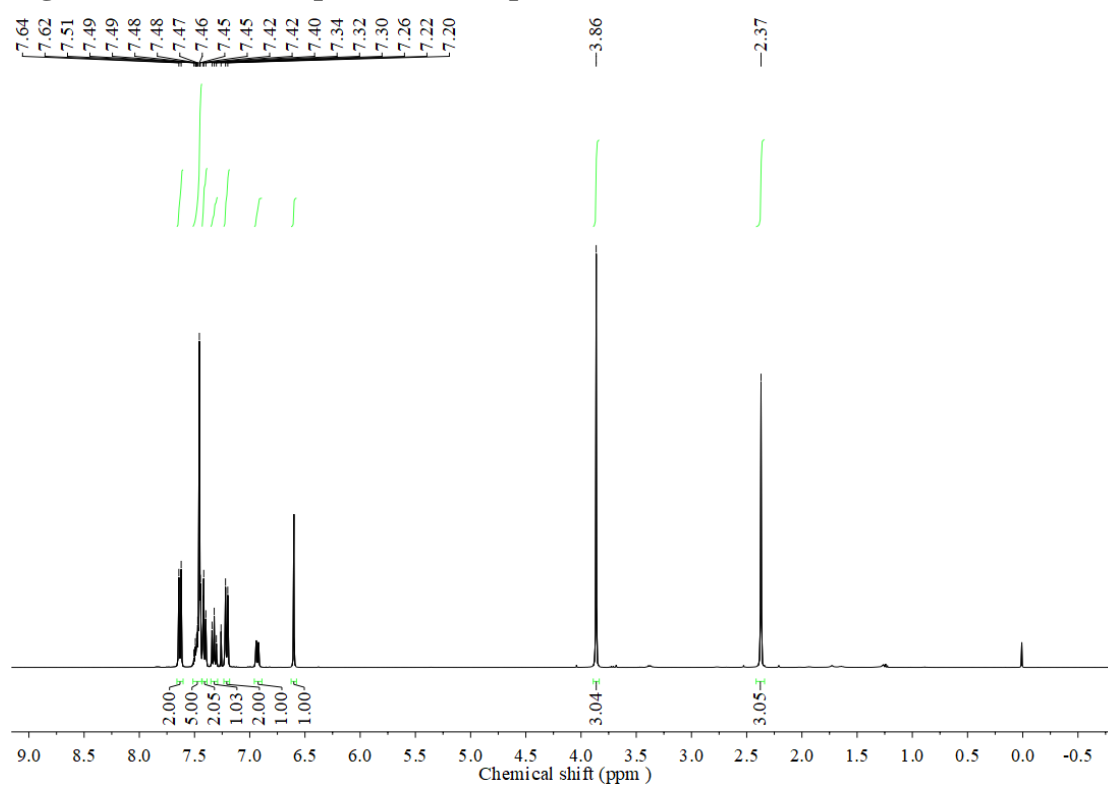


Figure S12 ^{13}C NMR Spectra of Compound of 2f

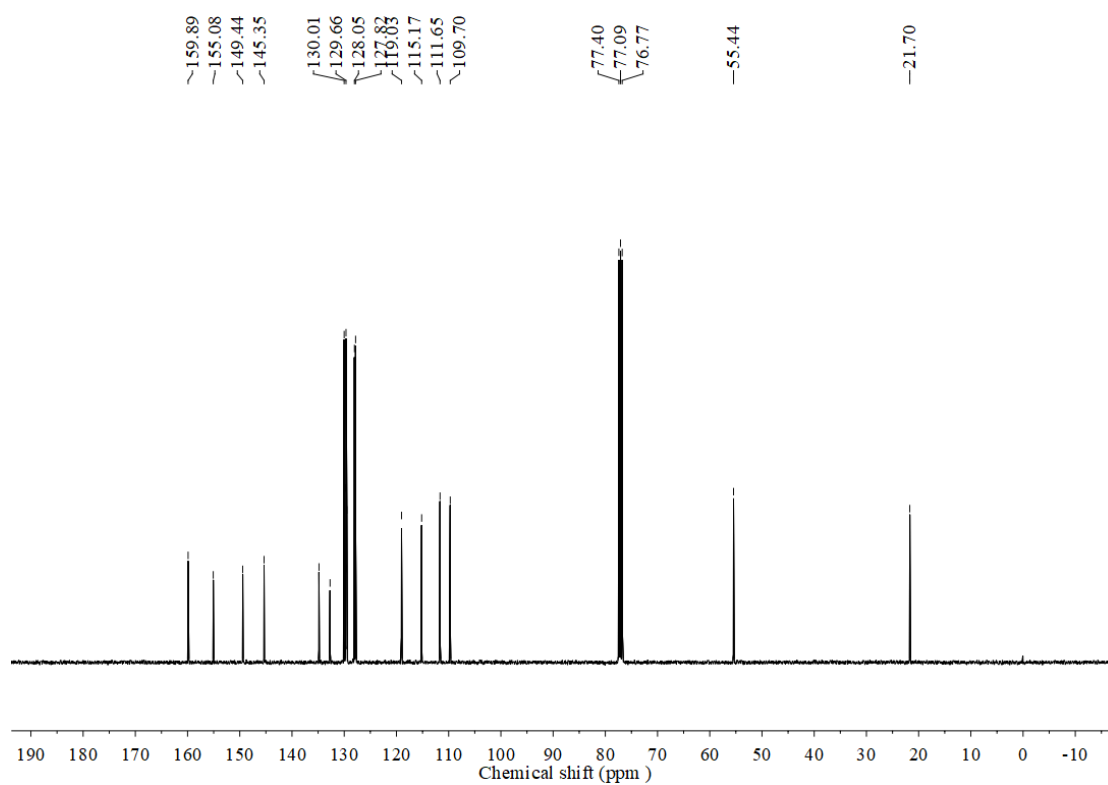


Figure S13 ^1H NMR Spectra of Compound of 2g

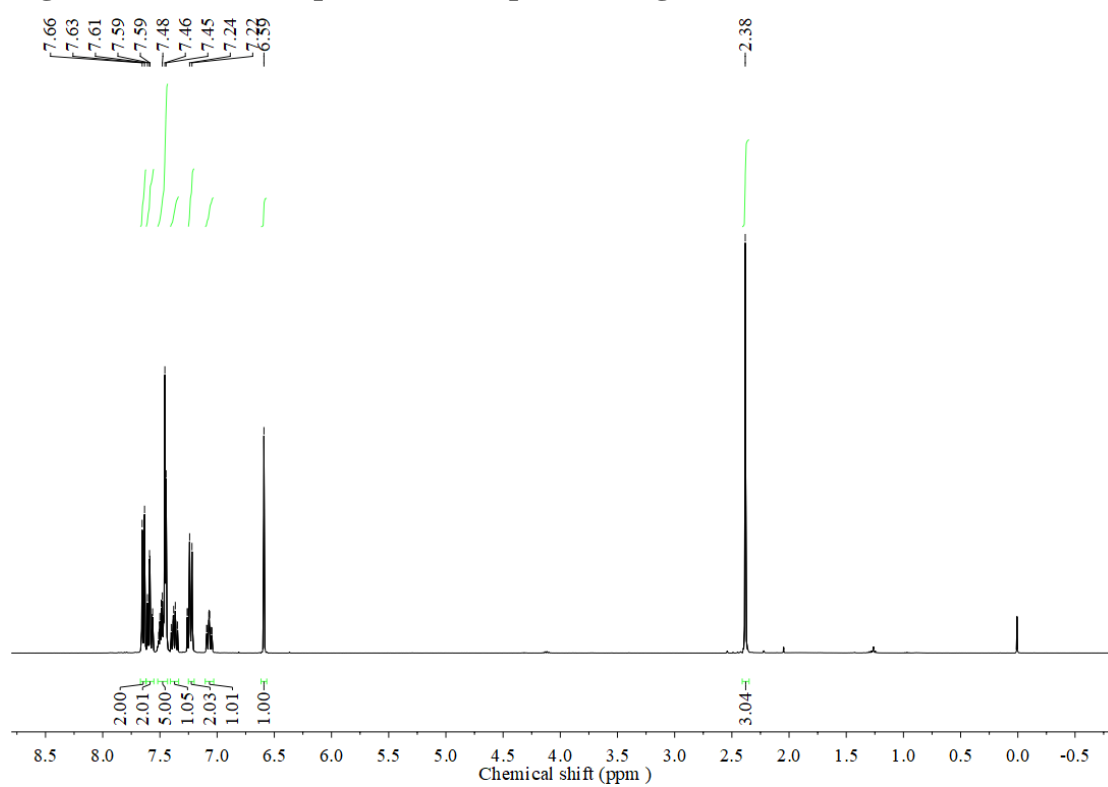


Figure S14 ^{13}C NMR Spectra of Compound of 2g

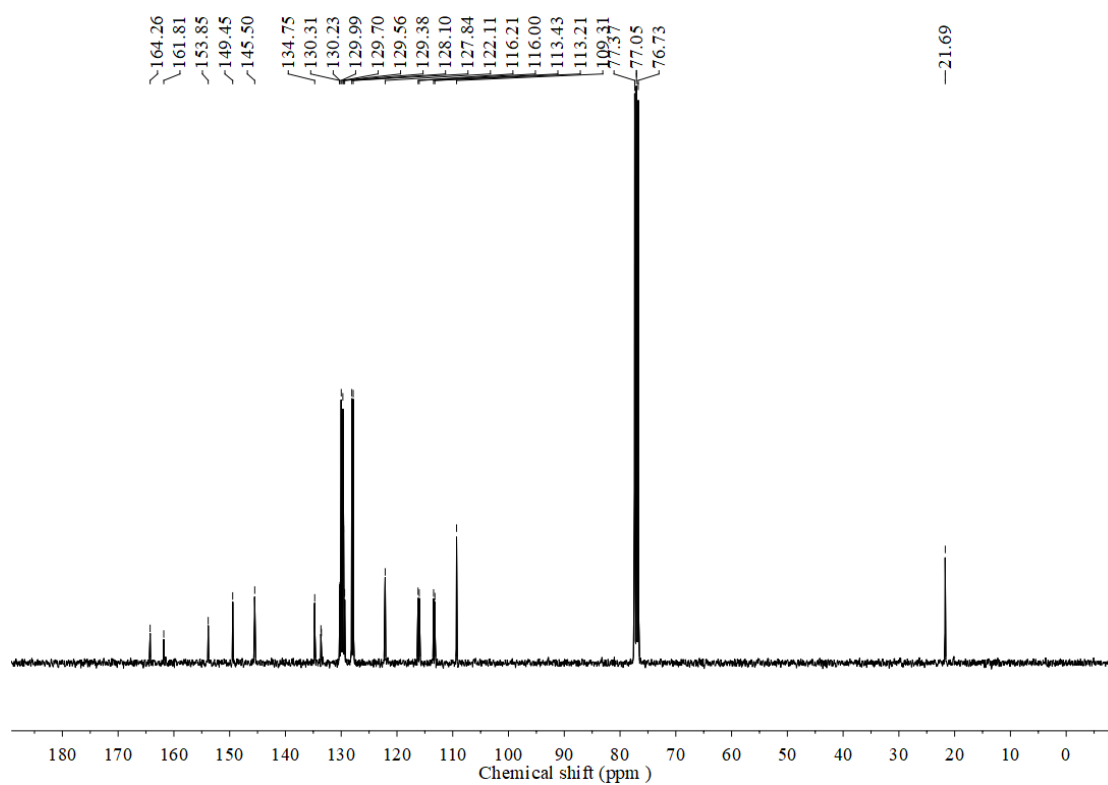


Figure S15 ^1H NMR Spectra of Compound of 2h

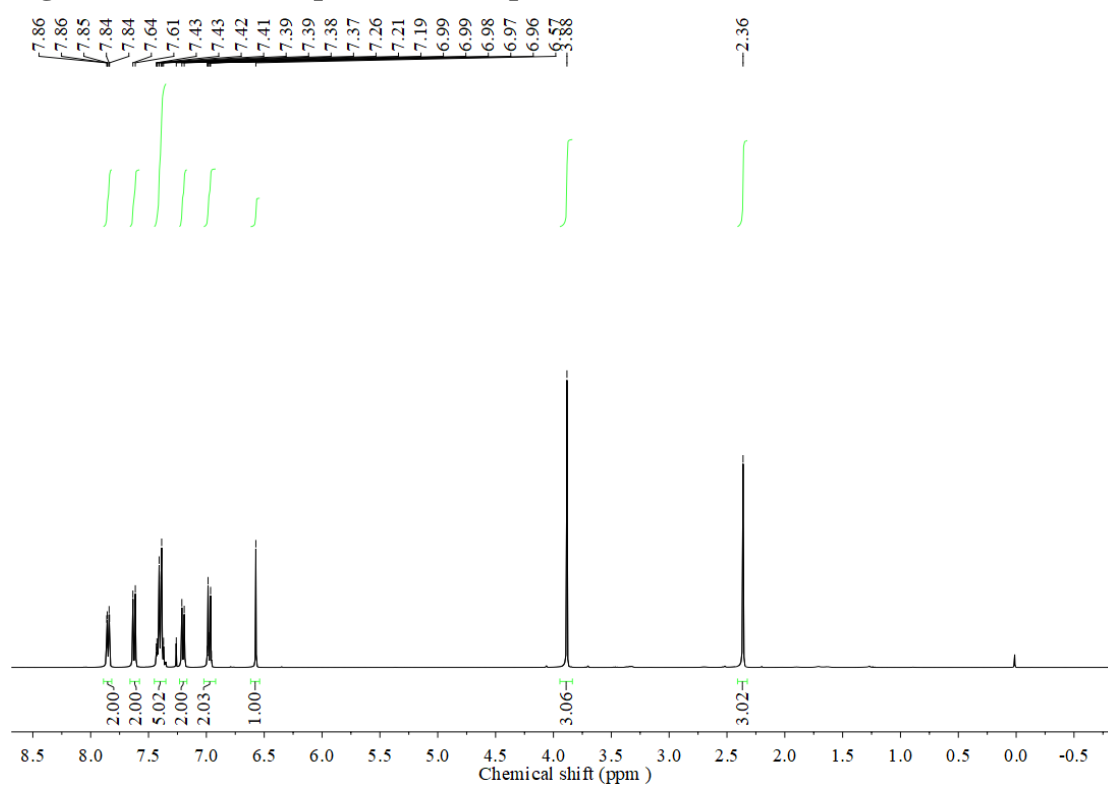


Figure S16 ^{13}C NMR Spectra of Compound of 2h

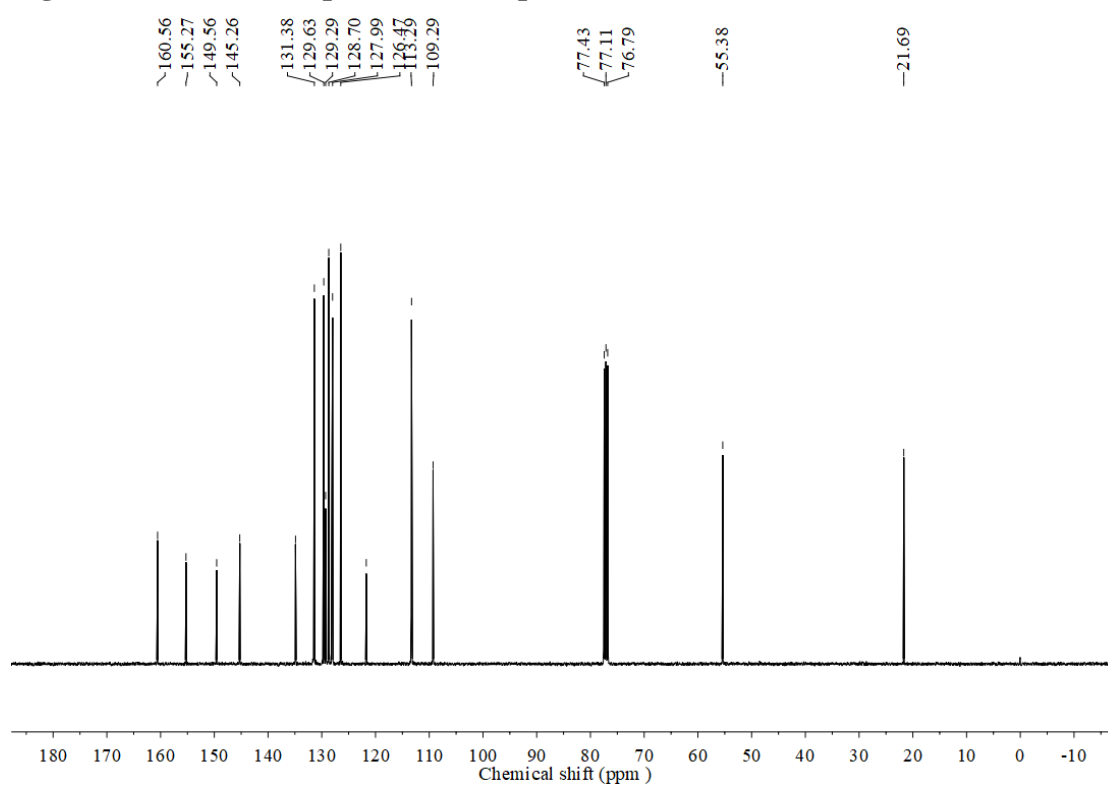


Figure S17 ^1H NMR Spectra of Compound of 2i

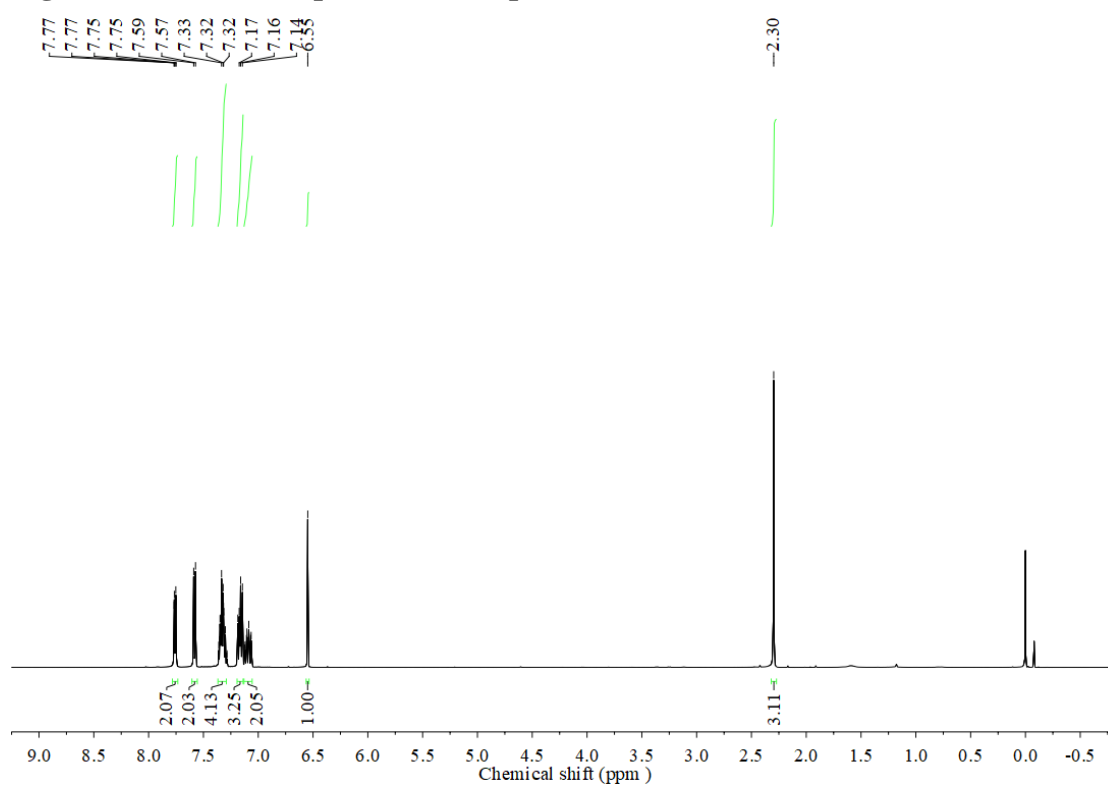


Figure S18 ^{13}C NMR Spectra of Compound of 2i

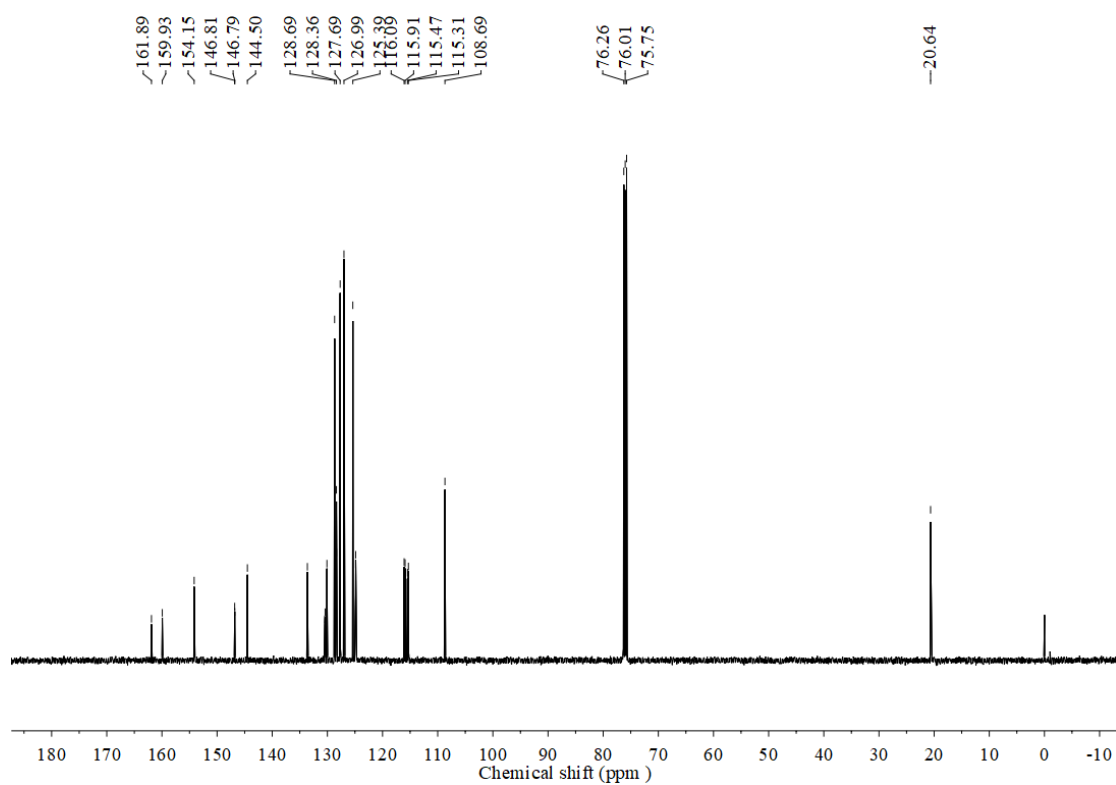


Figure S19 ^1H NMR Spectra of Compound of 2j

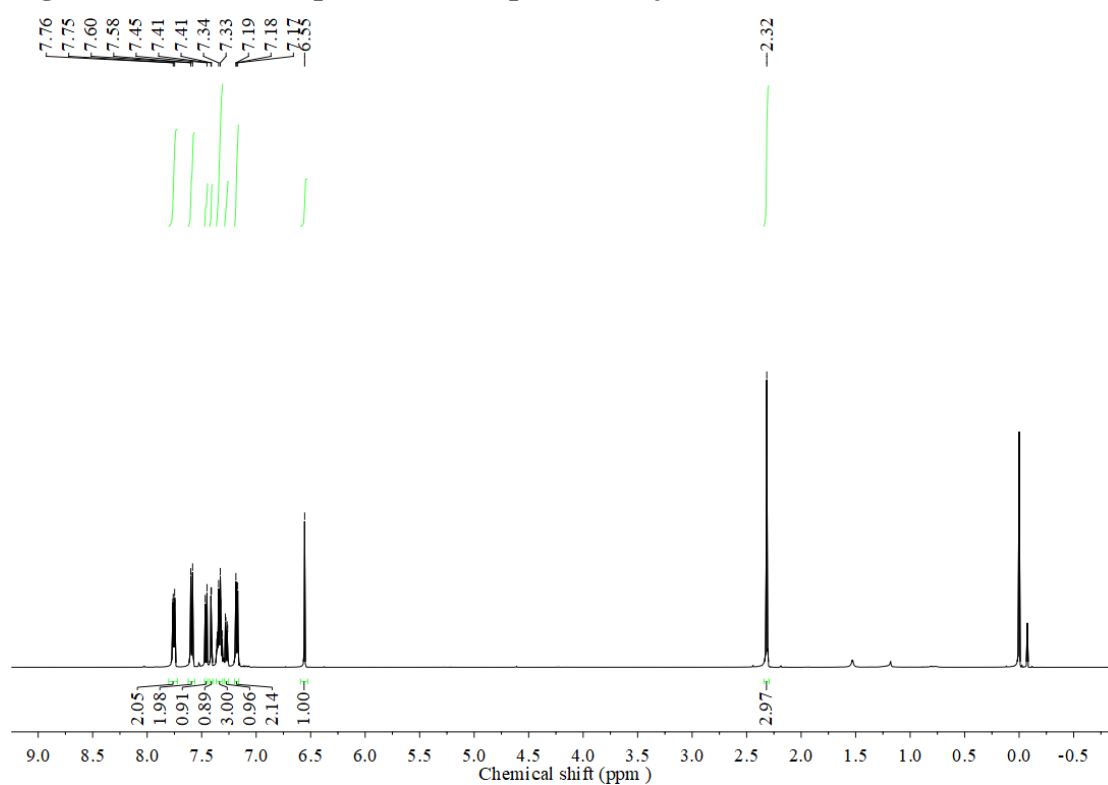


Figure S20 ^{13}C NMR Spectra of Compound of 2j

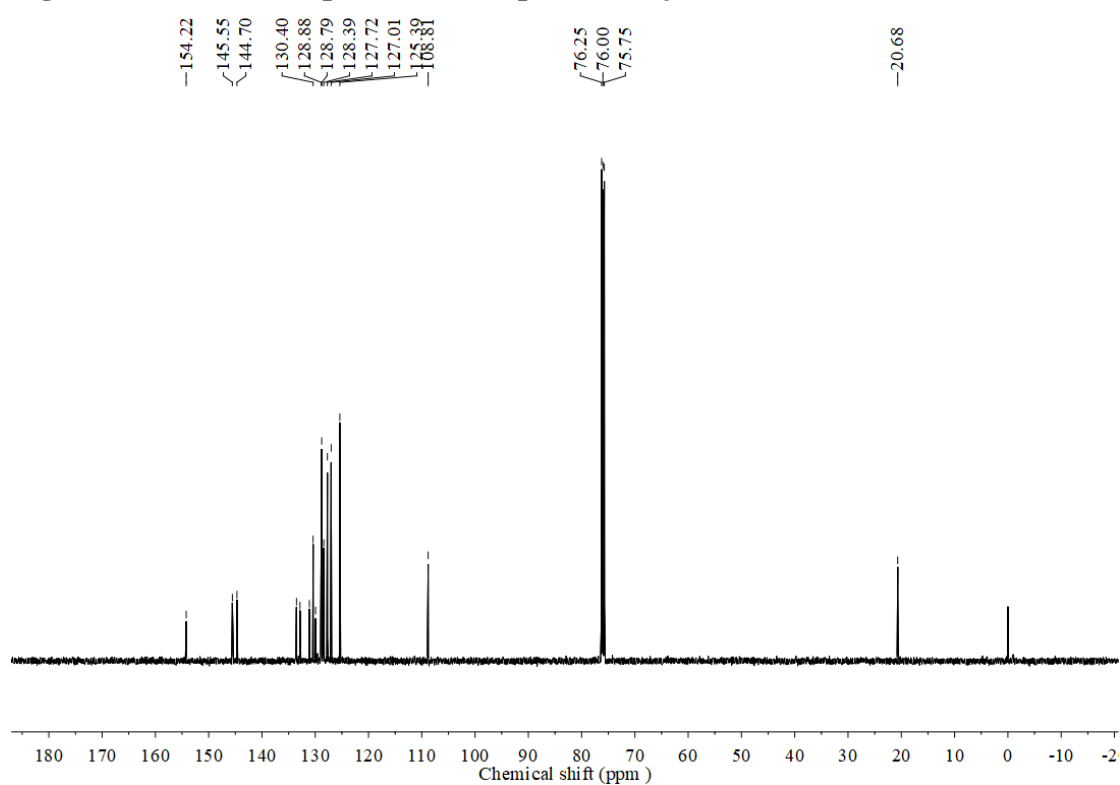


Figure S21 ^1H NMR Spectra of Compound of 2k

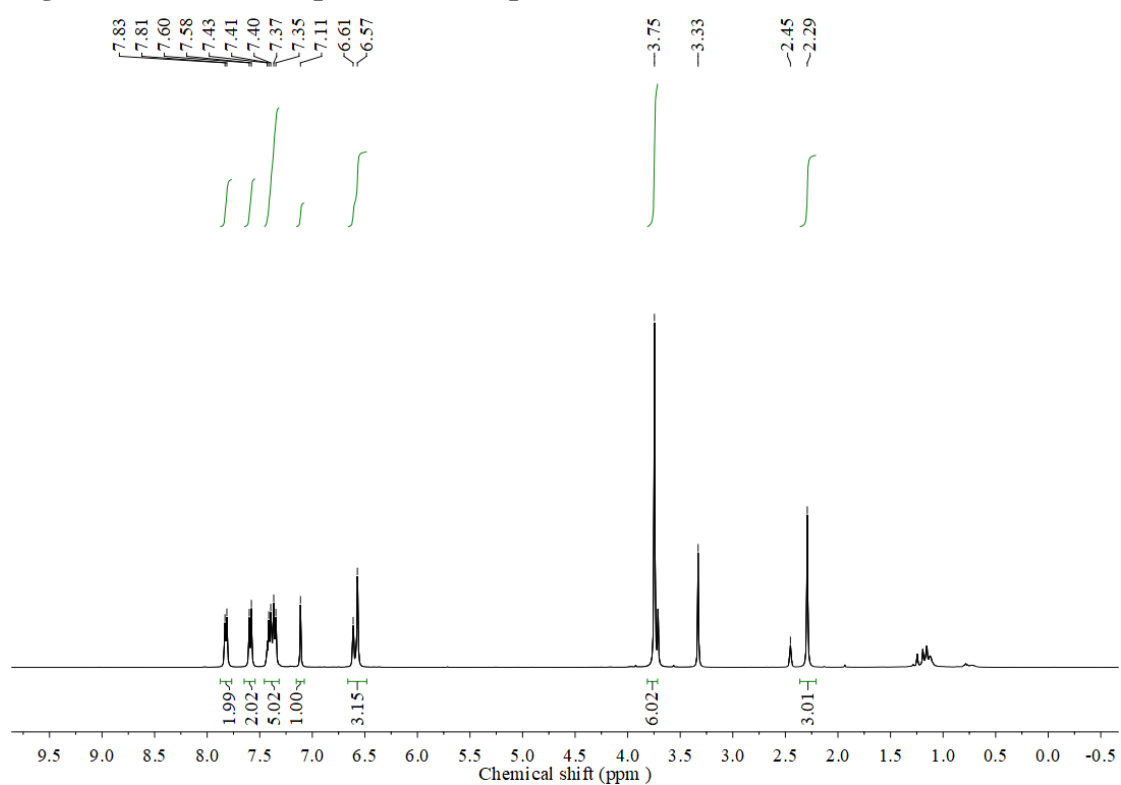


Figure S22 ^{13}C NMR Spectra of Compound of 2k

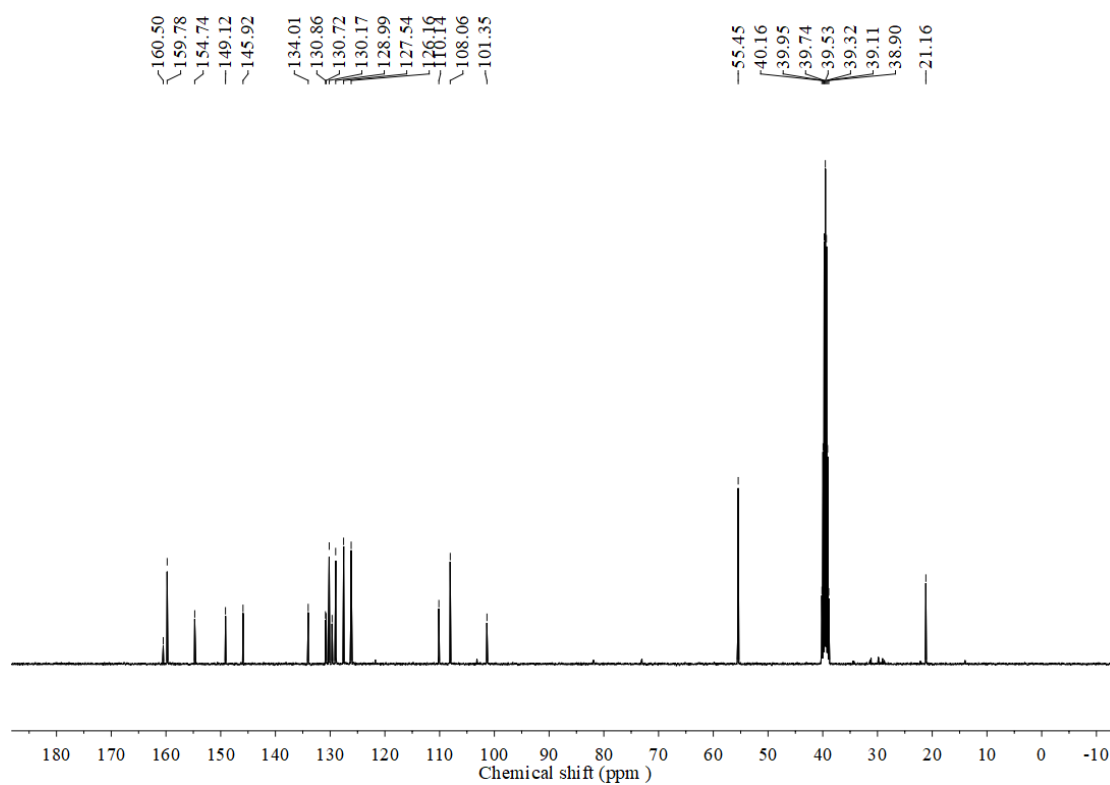


Figure S23 ^1H NMR Spectra of Compound of 2l

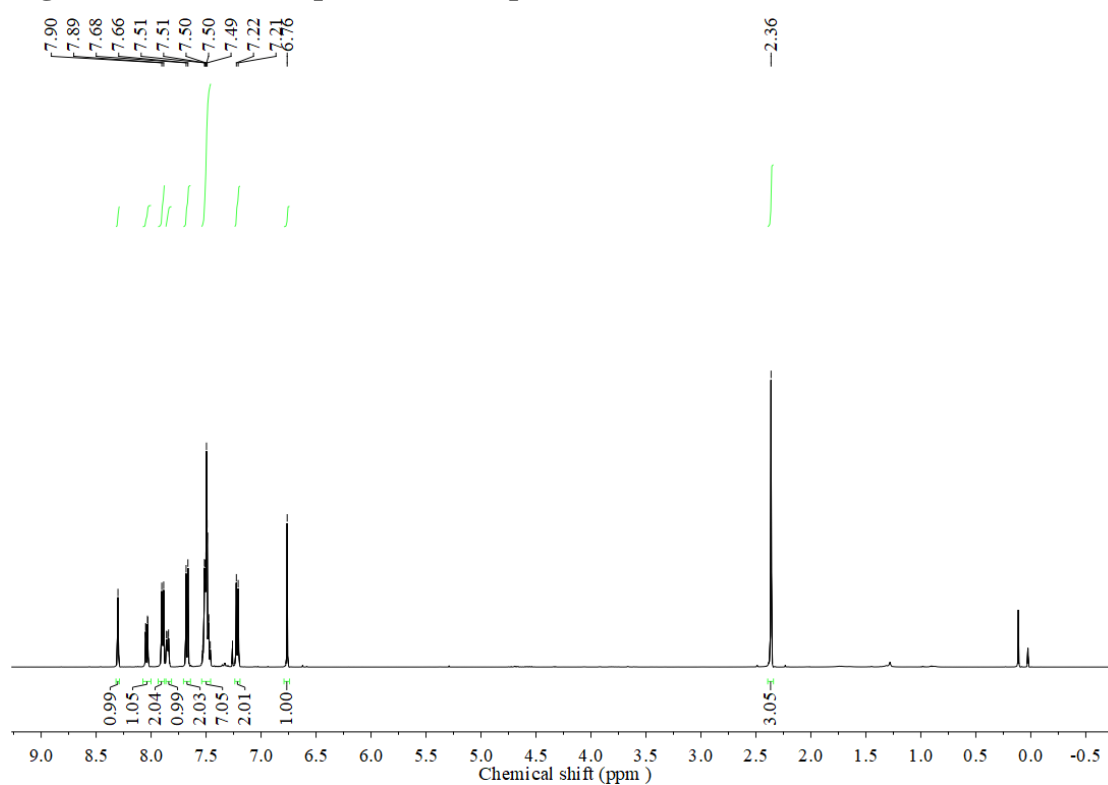


Figure S24 ^{13}C NMR Spectra of Compound of 2l

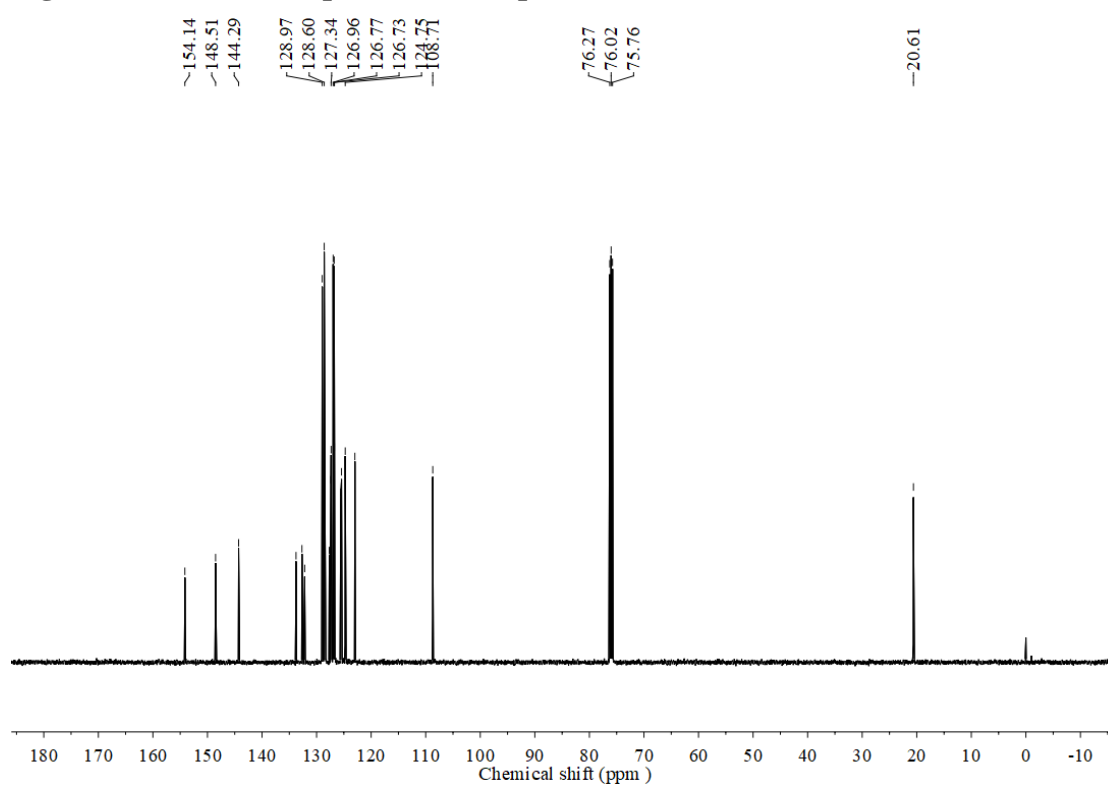


Figure S25 ^1H NMR Spectra of Compound of 2m

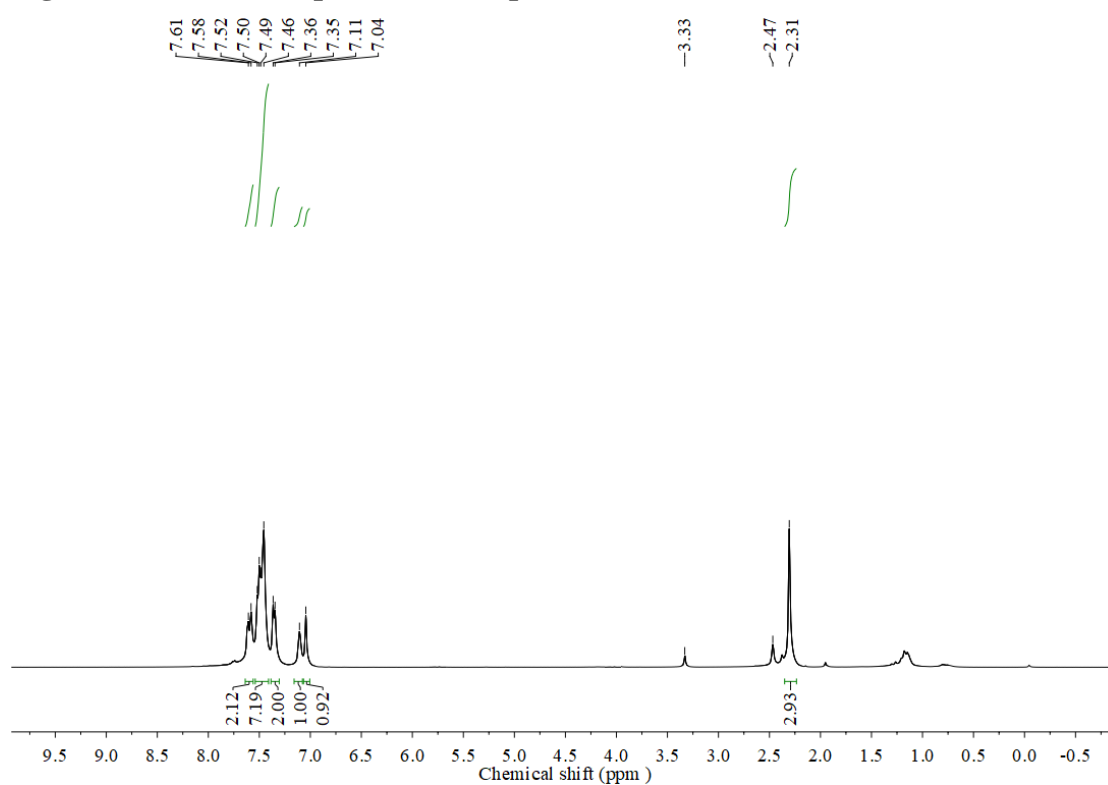


Figure S26 ^{13}C NMR Spectra of Compound of 2m

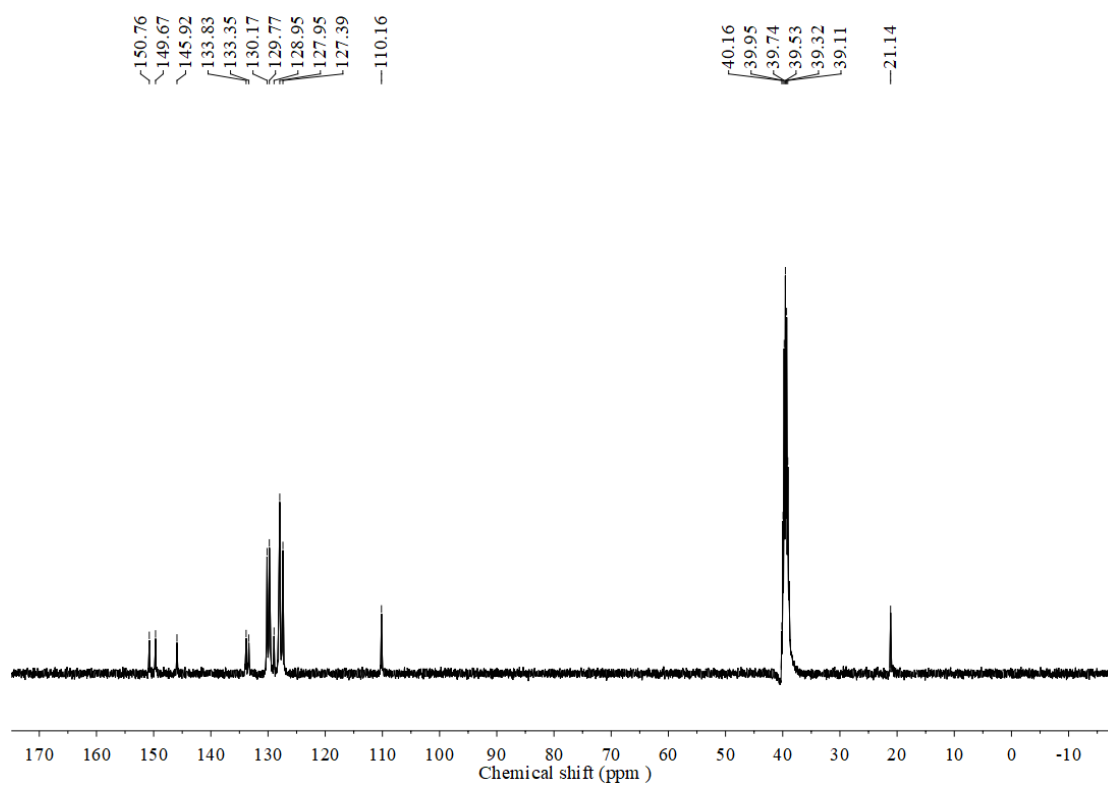


Figure S27 ^1H NMR Spectra of Compound of 2n

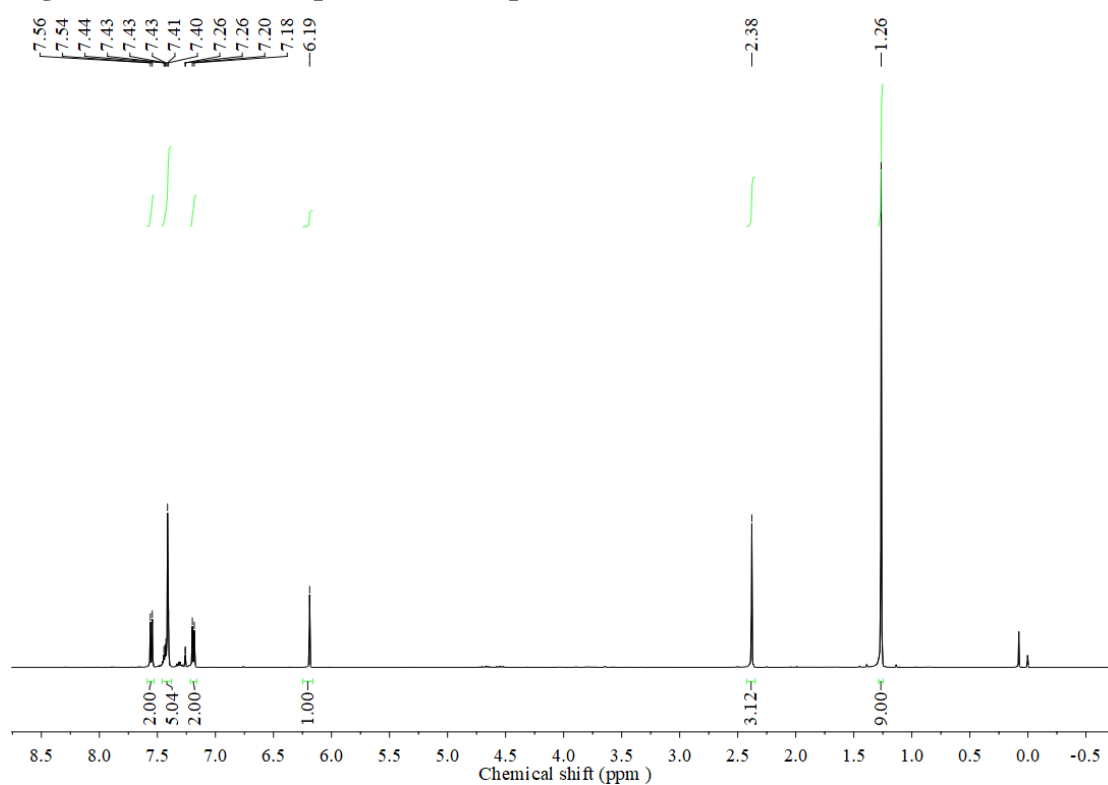


Figure S28 ^{13}C NMR Spectra of Compound of 2n

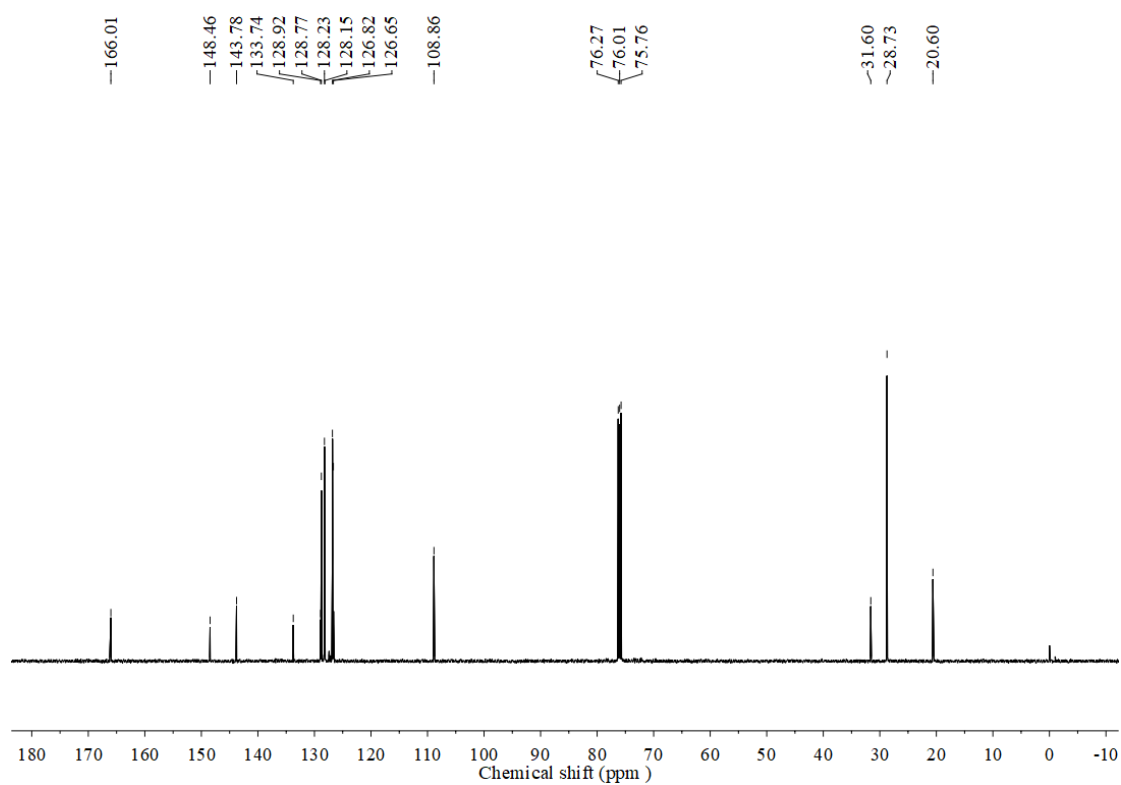


Figure S29 ^1H NMR Spectra of Compound of 2o

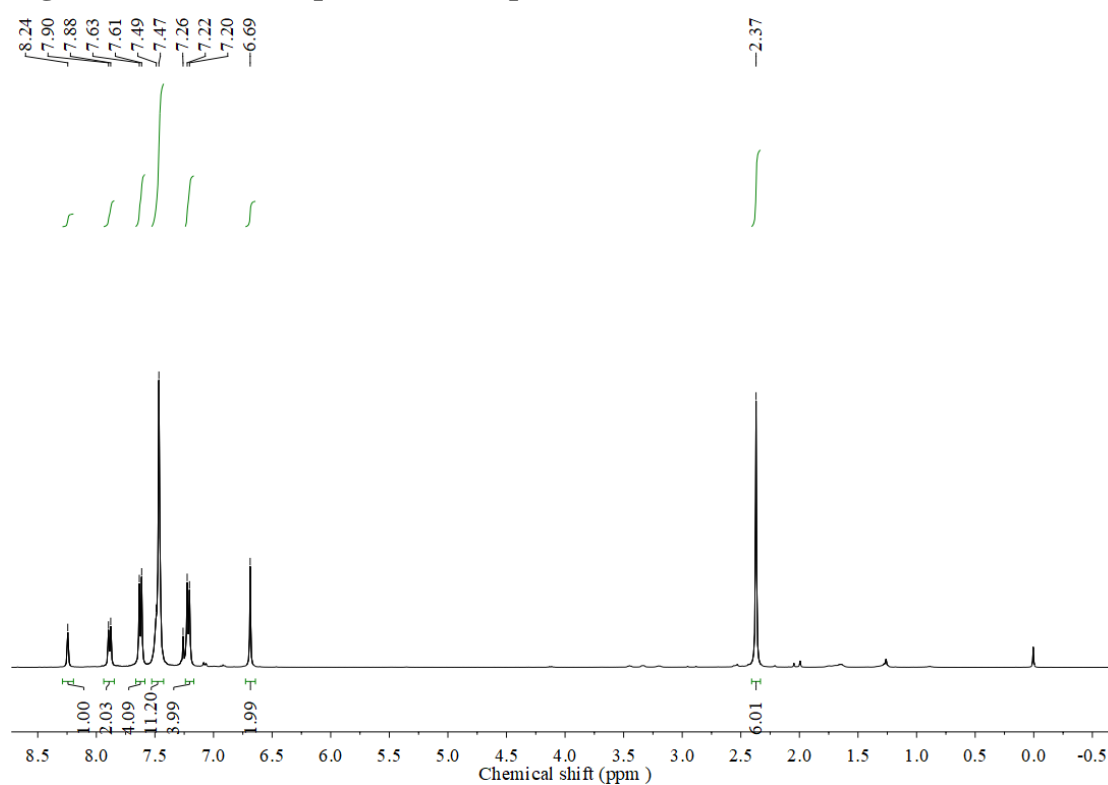


Figure S30 ^{13}C NMR Spectra of Compound of 2o

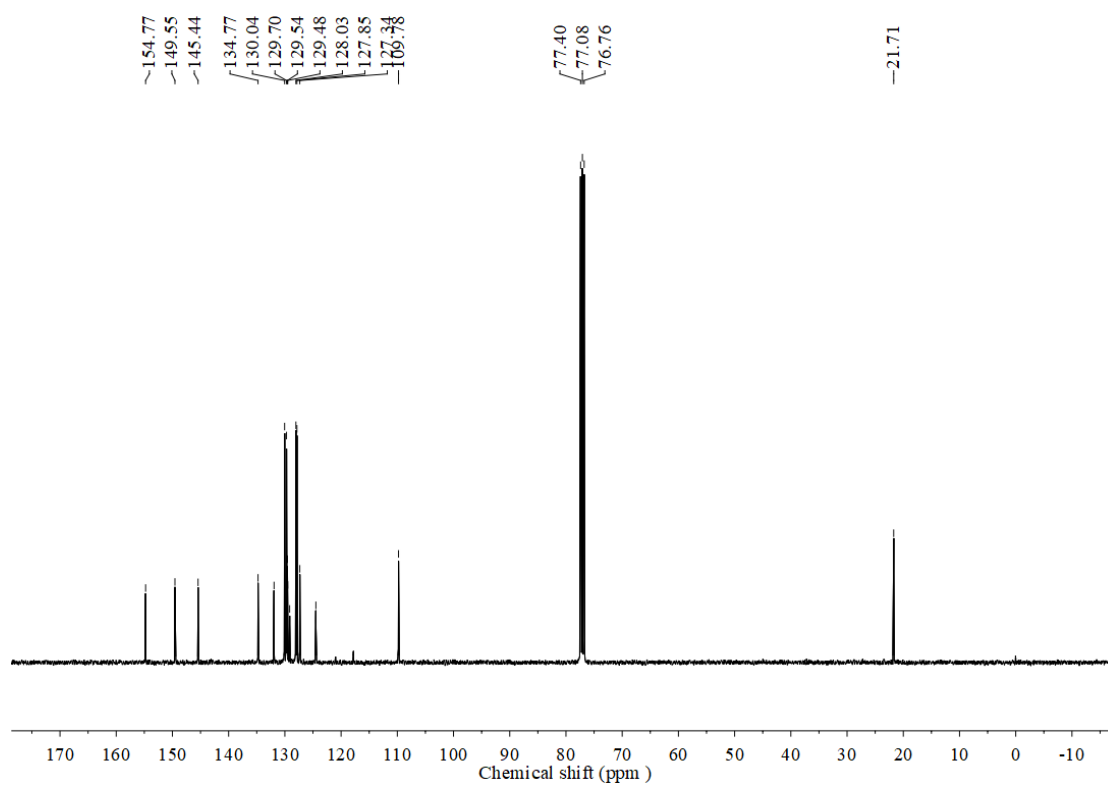


Figure S31 ^1H NMR Spectra of Compound of 2p

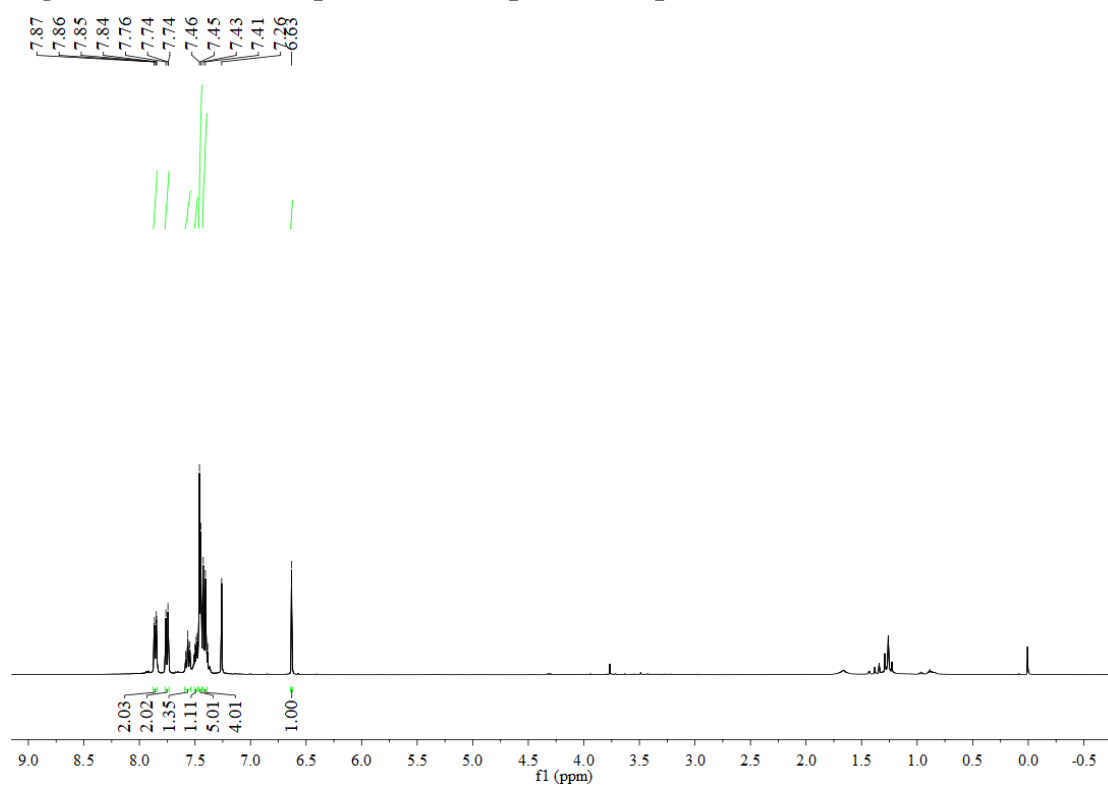


Figure S32 ^{13}C NMR Spectra of Compound of 2p

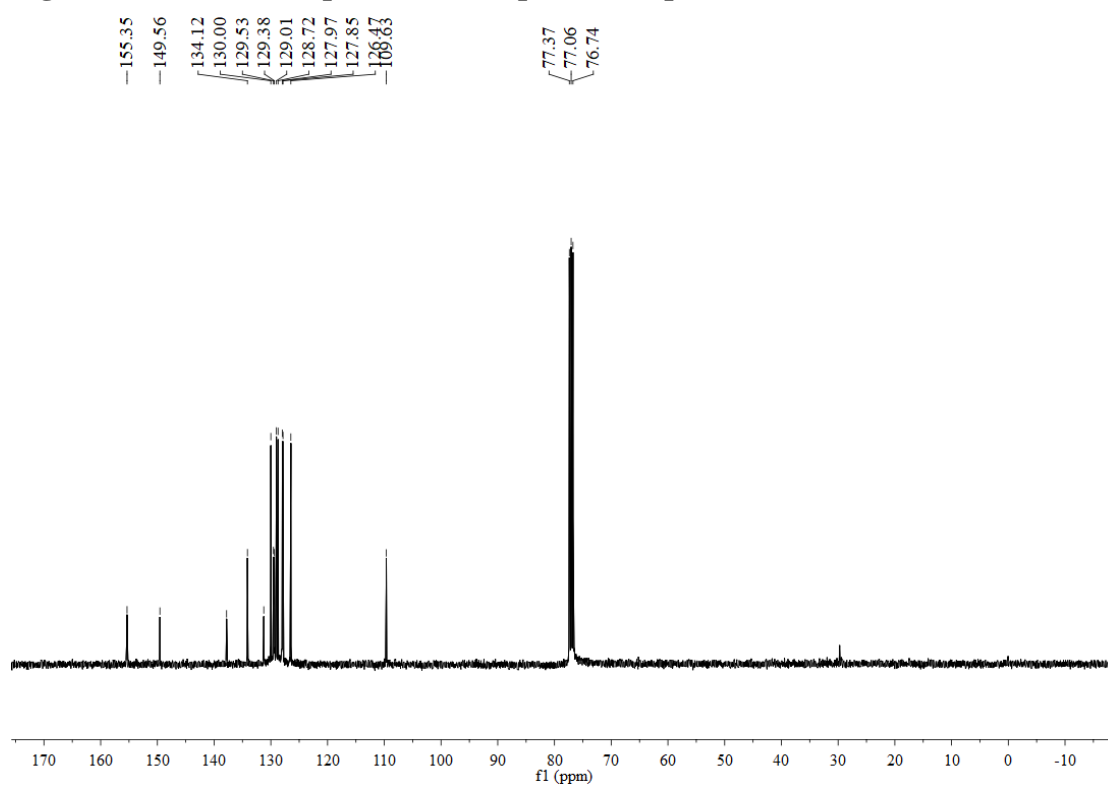


Figure S33 ^1H NMR Spectra of Compound of 3a

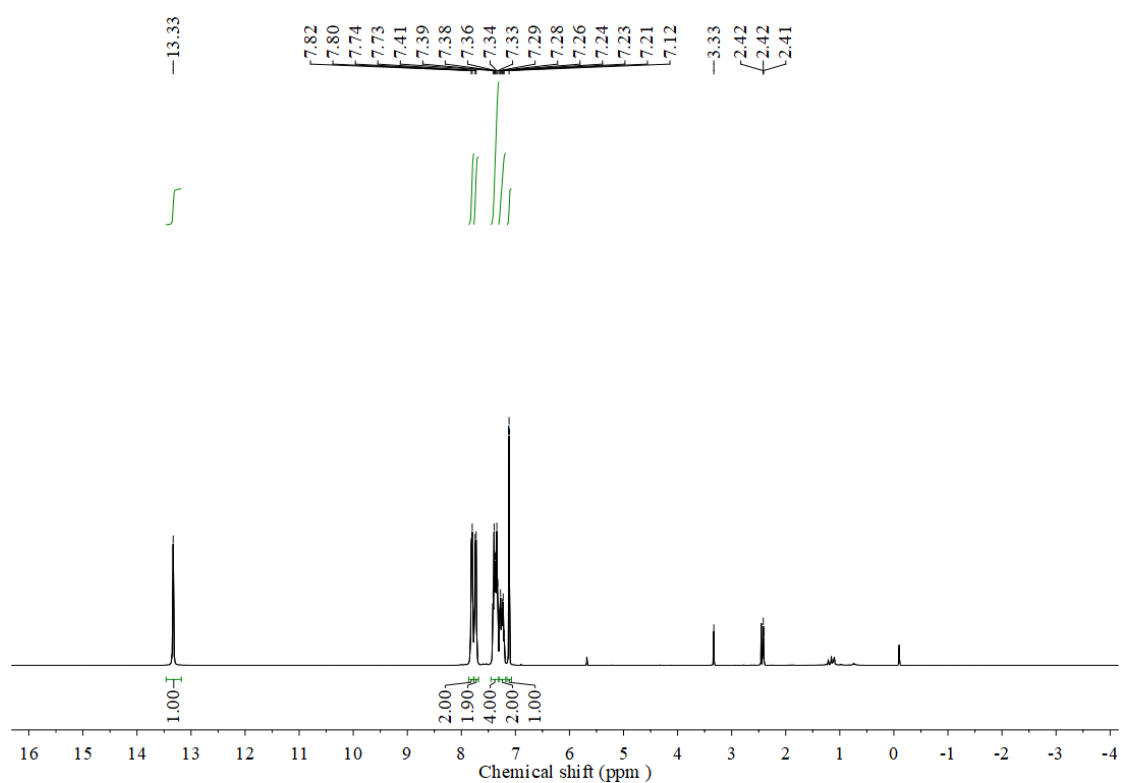


Figure S34 ^{13}C NMR Spectra of Compound of 3a

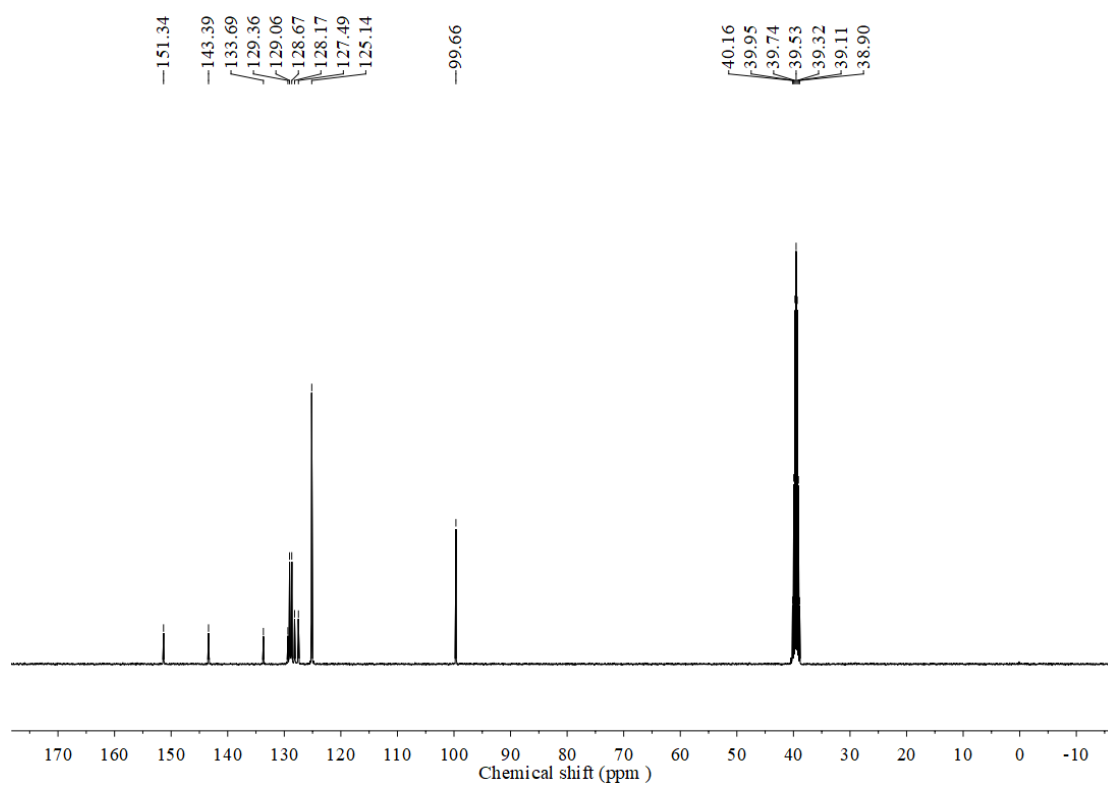


Figure S35 ^1H NMR Spectra of Compound of 3b

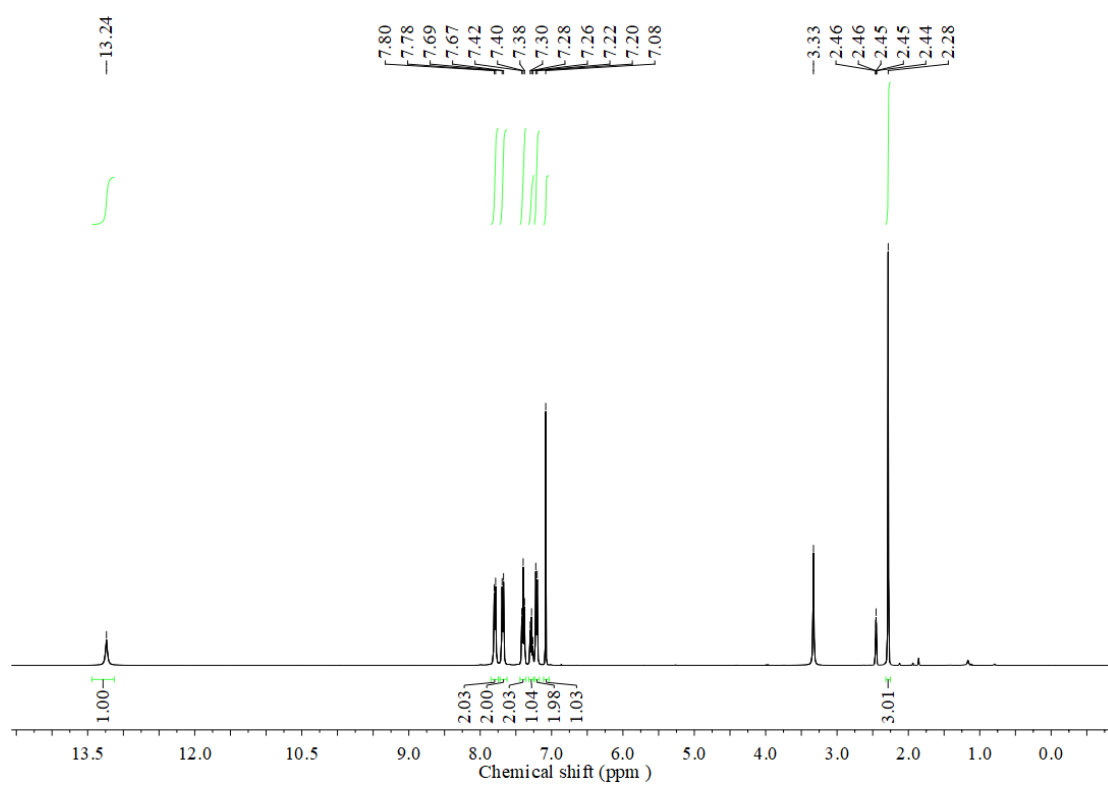


Figure S36 ^{13}C NMR Spectra of Compound of 3b

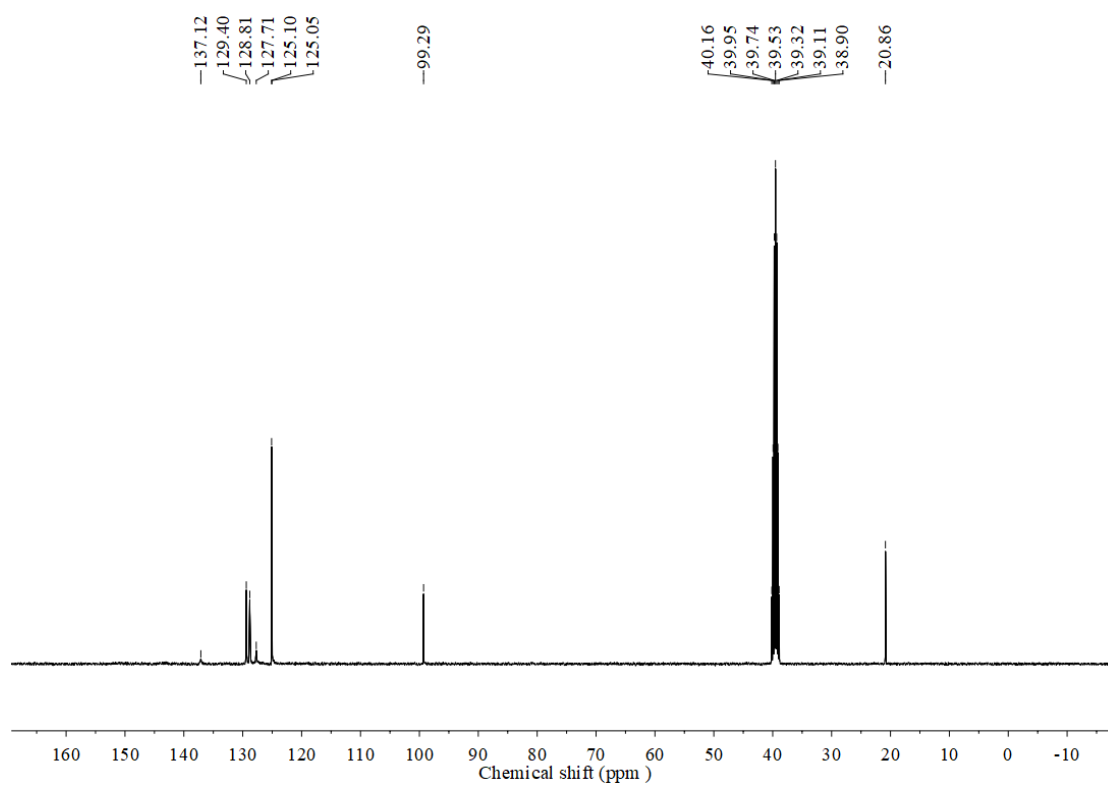


Figure S37 ^1H NMR Spectra of Compound of 3c

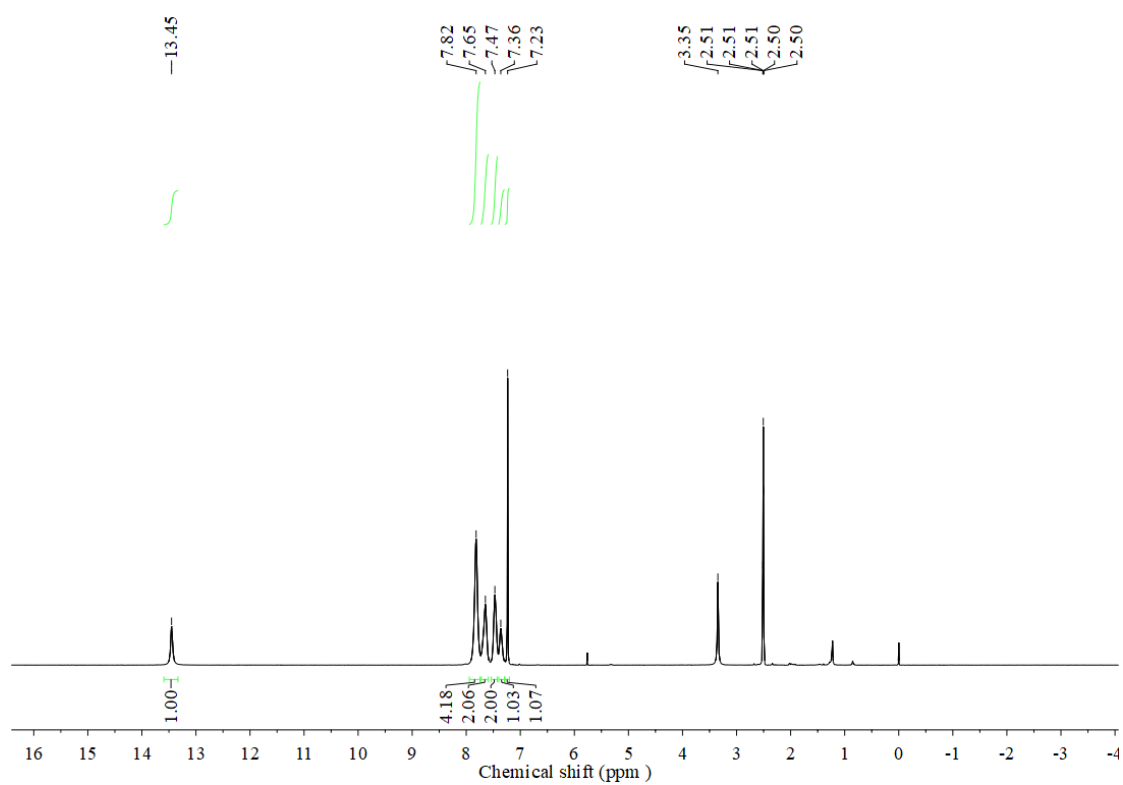


Figure S38 ^{13}C NMR Spectra of Compound of 3c

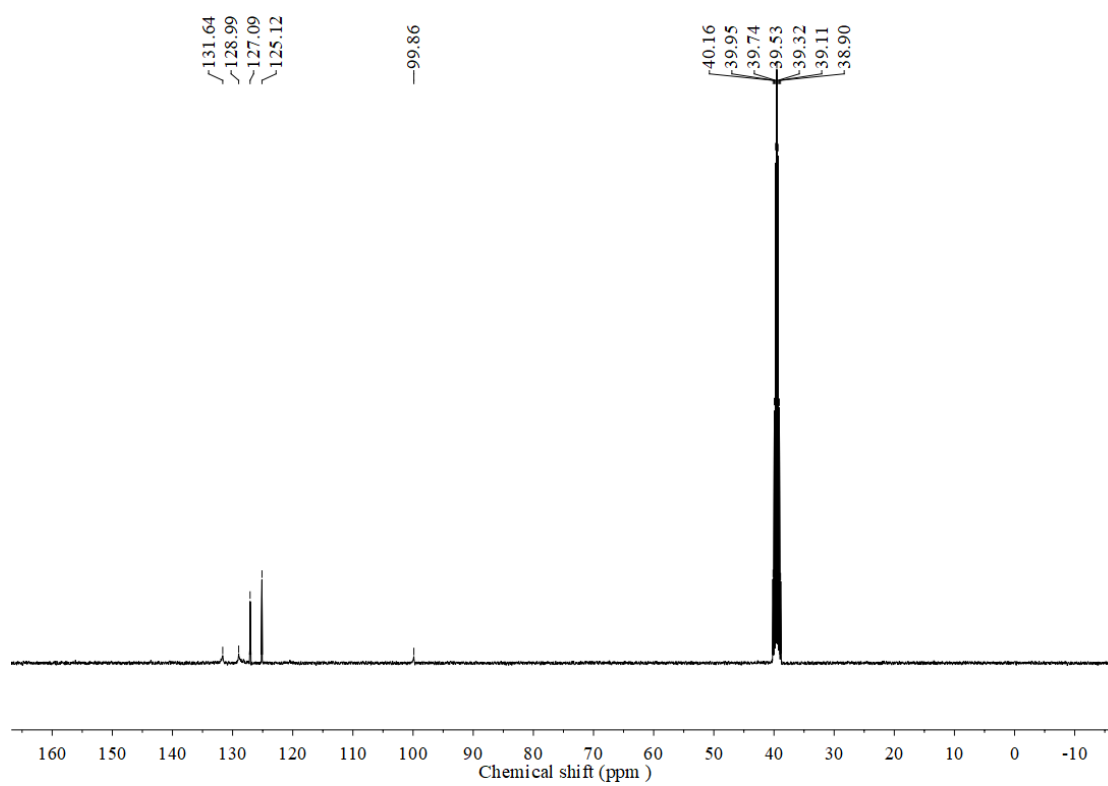


Figure S39 ^1H NMR Spectra of Compound of 3d

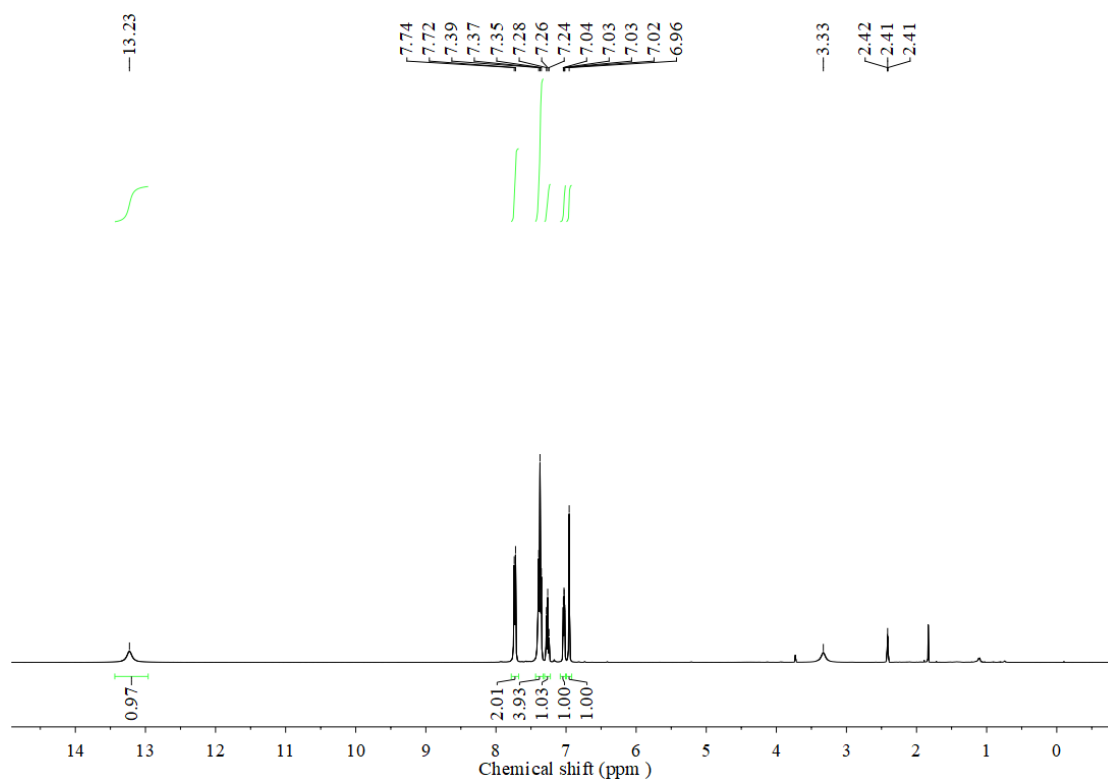


Figure S40 ^{13}C NMR Spectra of Compound of 3d

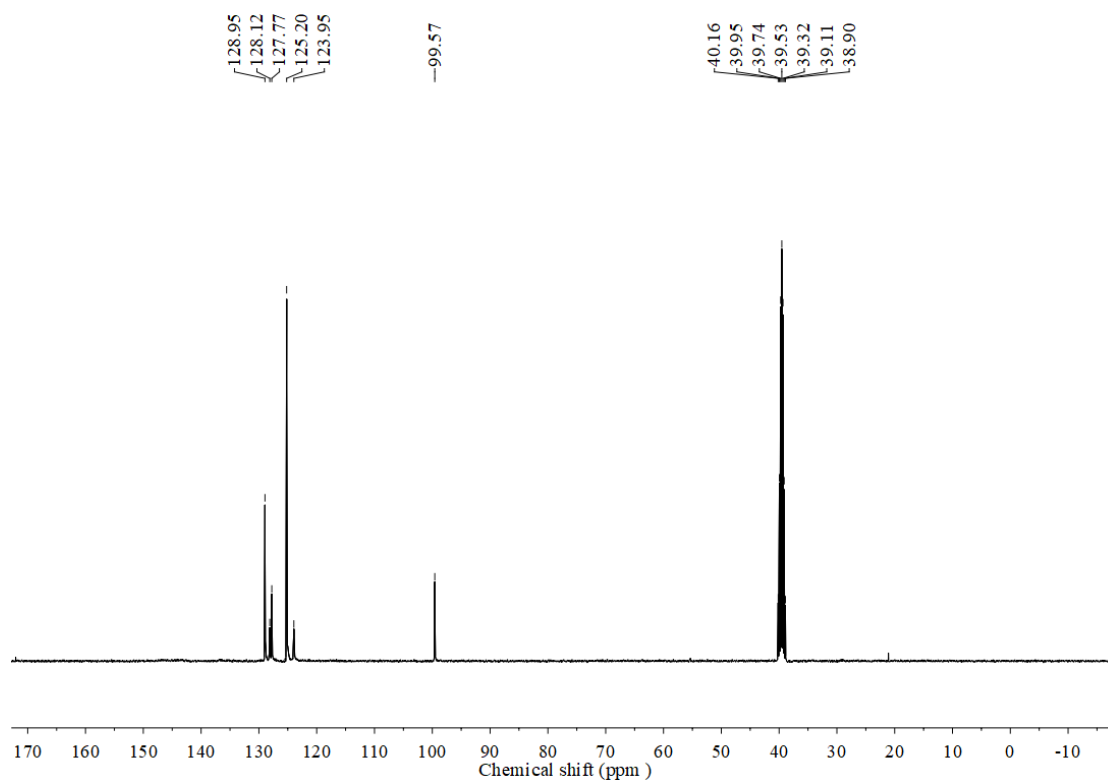


Figure S41 ^1H NMR Spectra of Compound of 3e

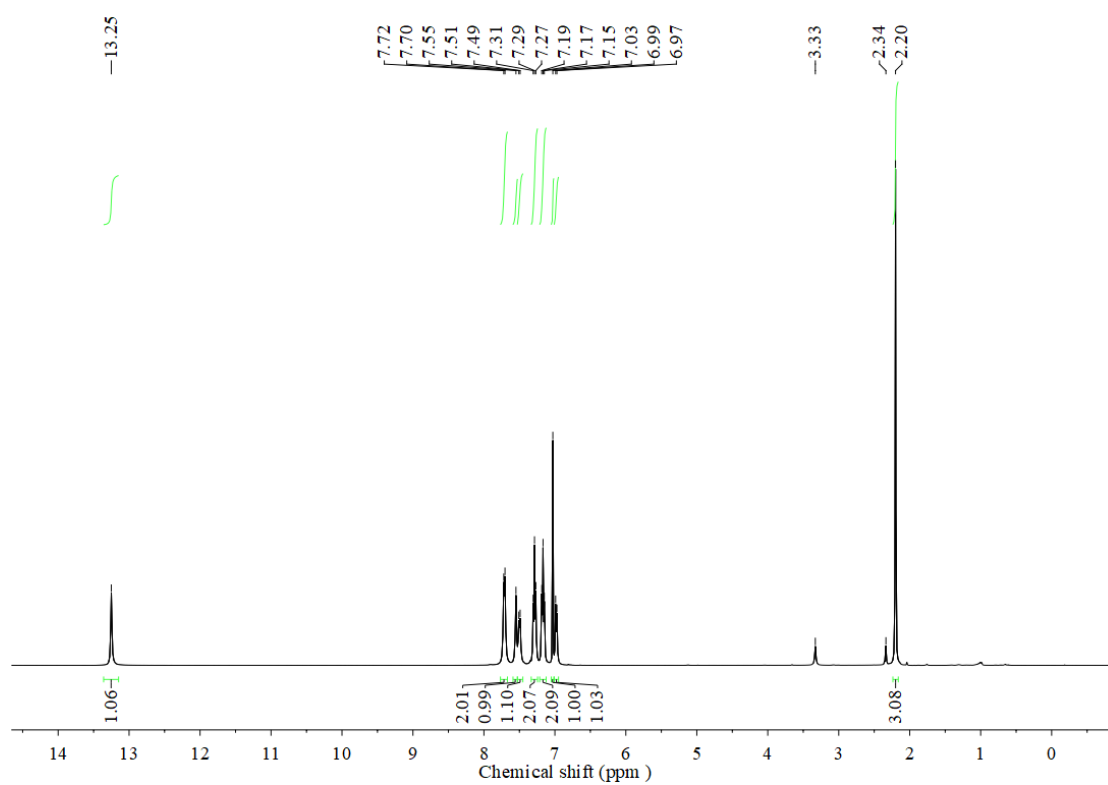


Figure S42 ^{13}C NMR Spectra of Compound of 3e

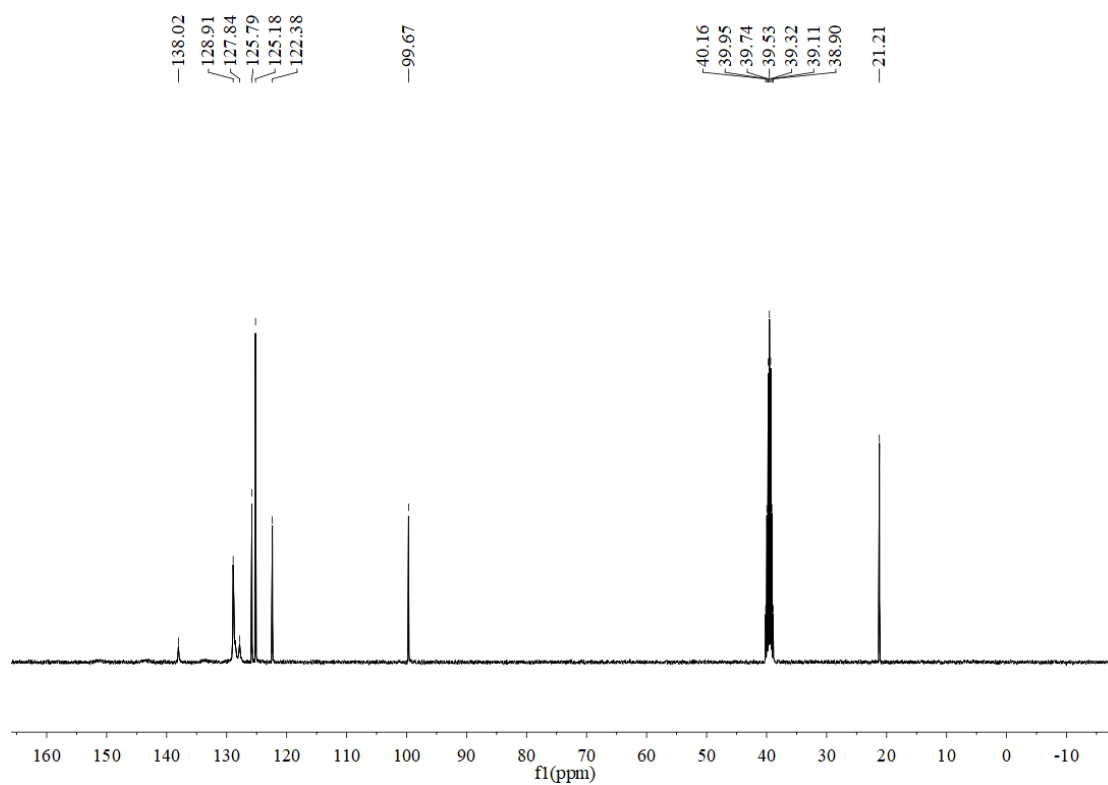


Figure S43 ^1H NMR Spectra of Compound of 3f

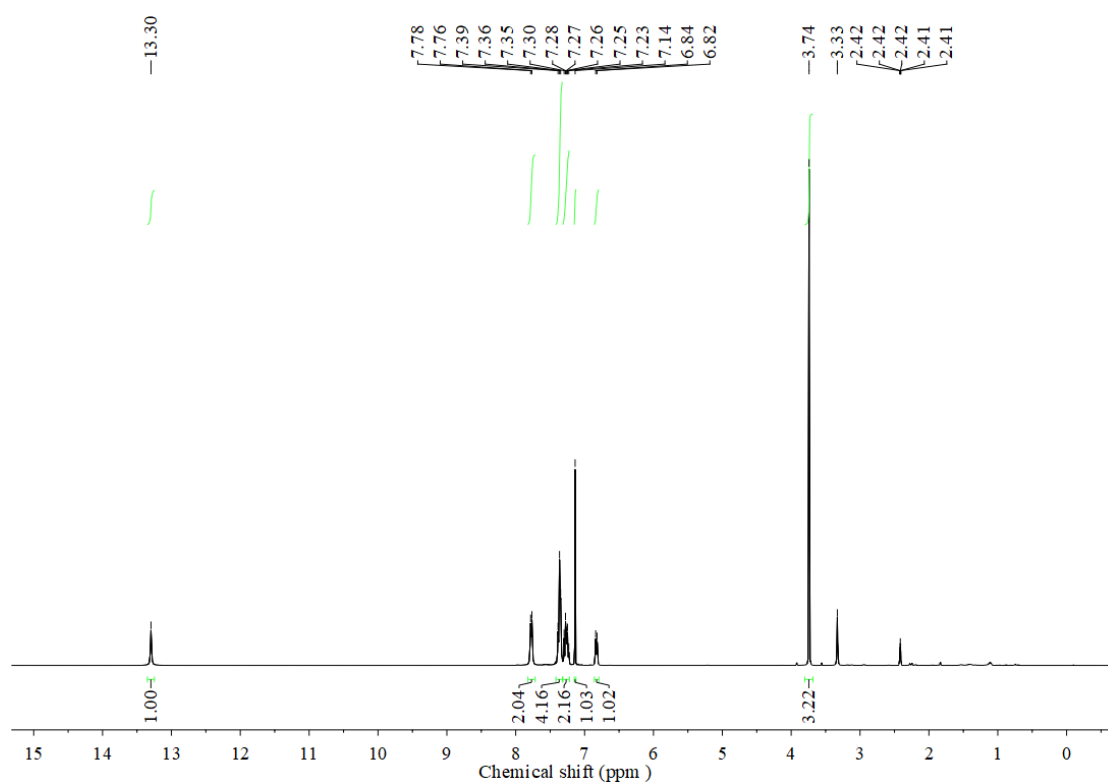


Figure S44 ^{13}C NMR Spectra of Compound of 3f

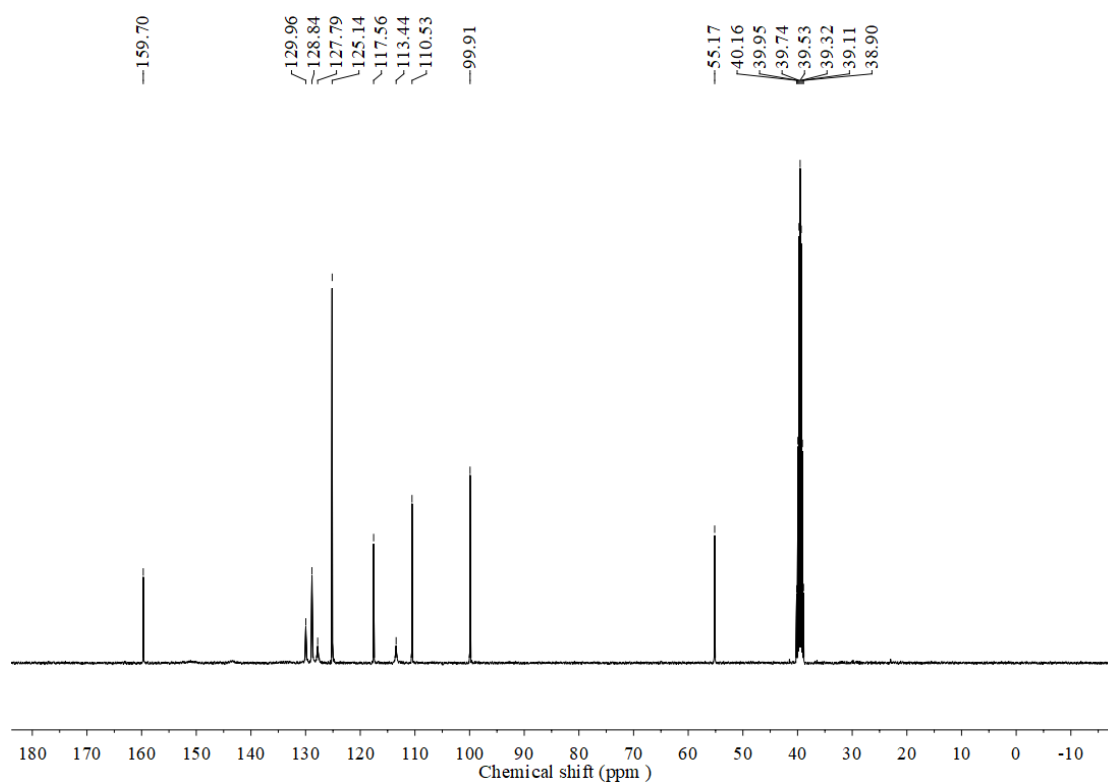


Figure S45 ^1H NMR Spectra of Compound of 3g

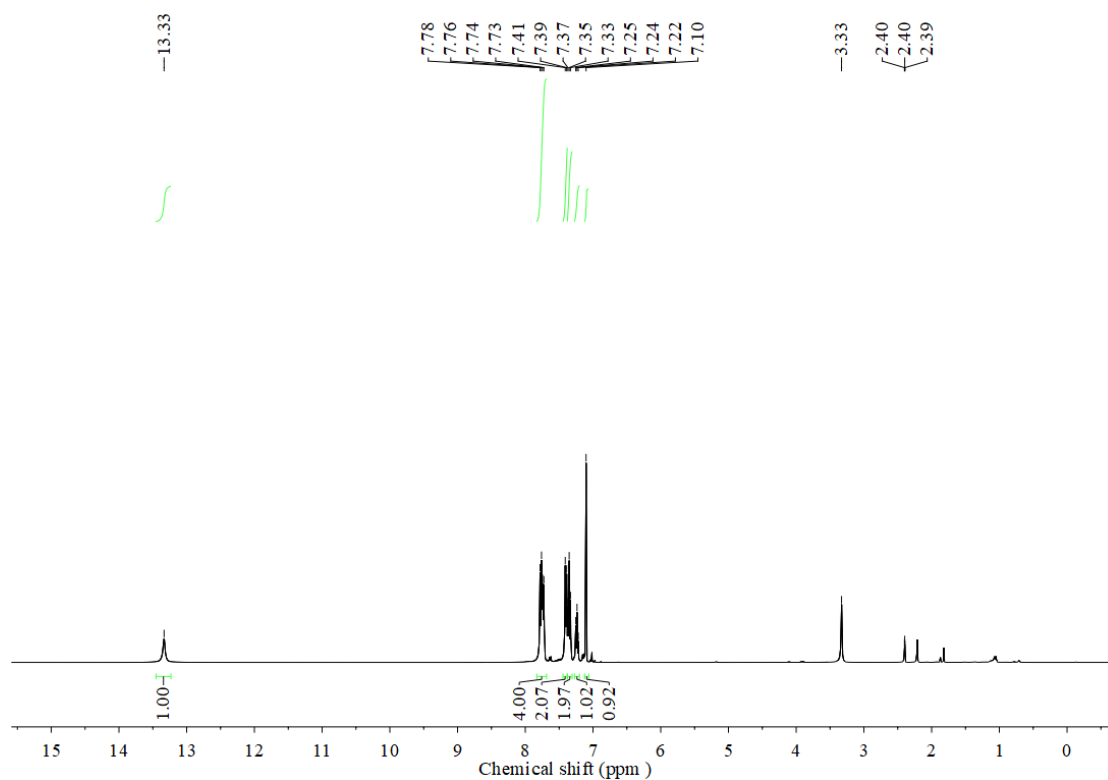


Figure S46 ^{13}C NMR Spectra of Compound of 3g

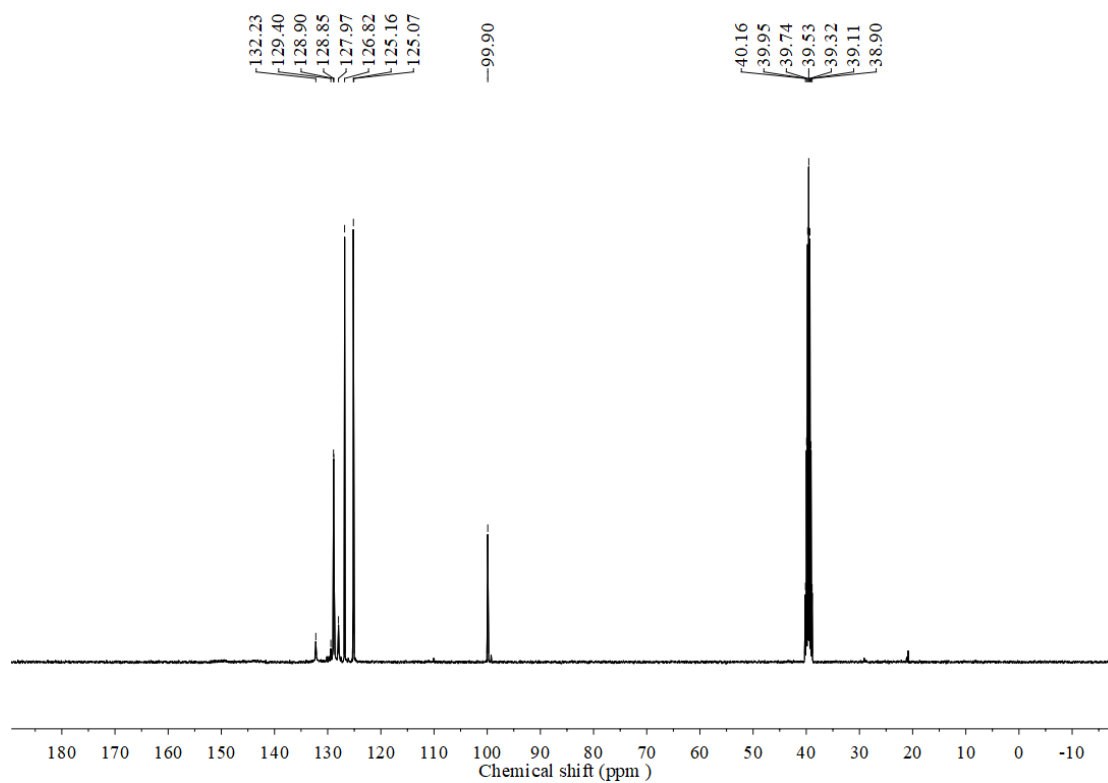


Figure S47 ^1H NMR Spectra of Compound of 3h

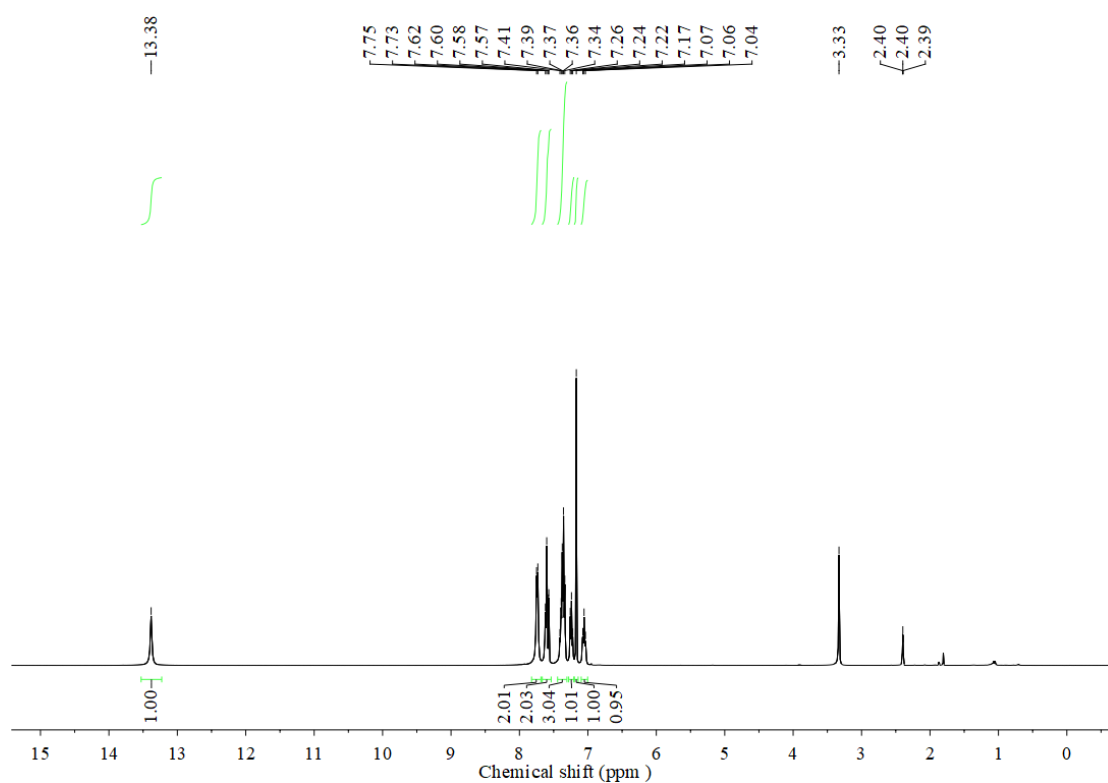


Figure S48 ^{13}C NMR Spectra of Compound of 3h

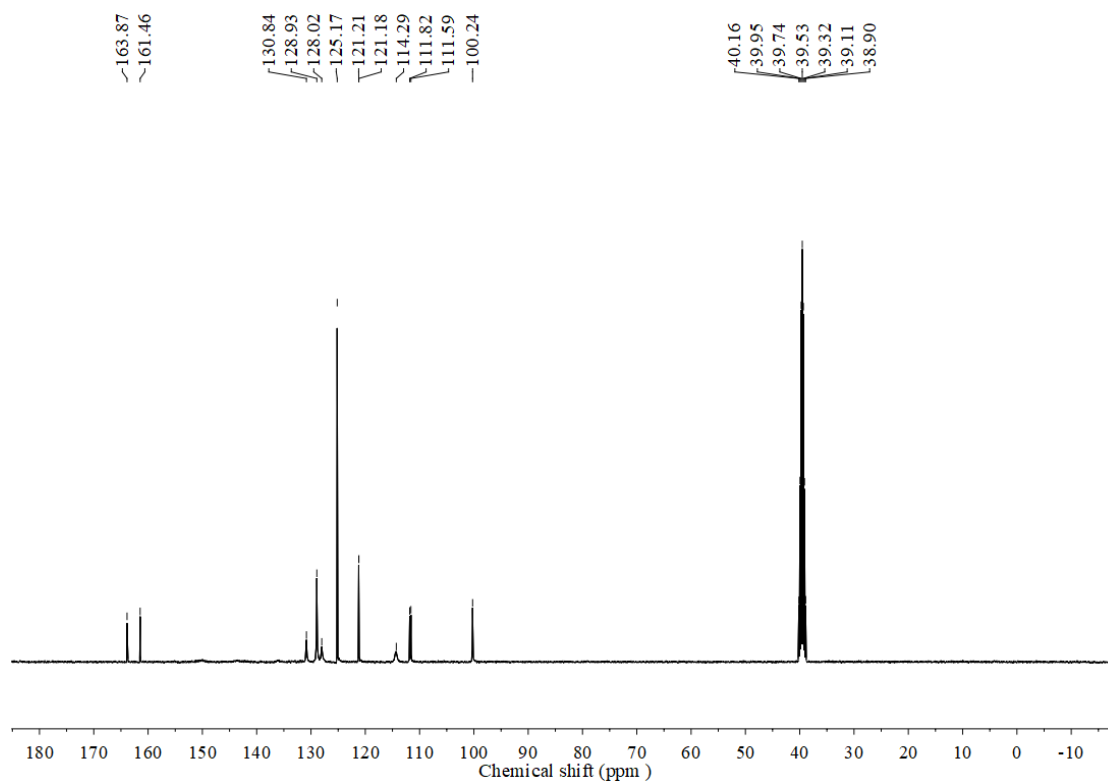


Figure S49 ^1H NMR Spectra of Compound of 3i

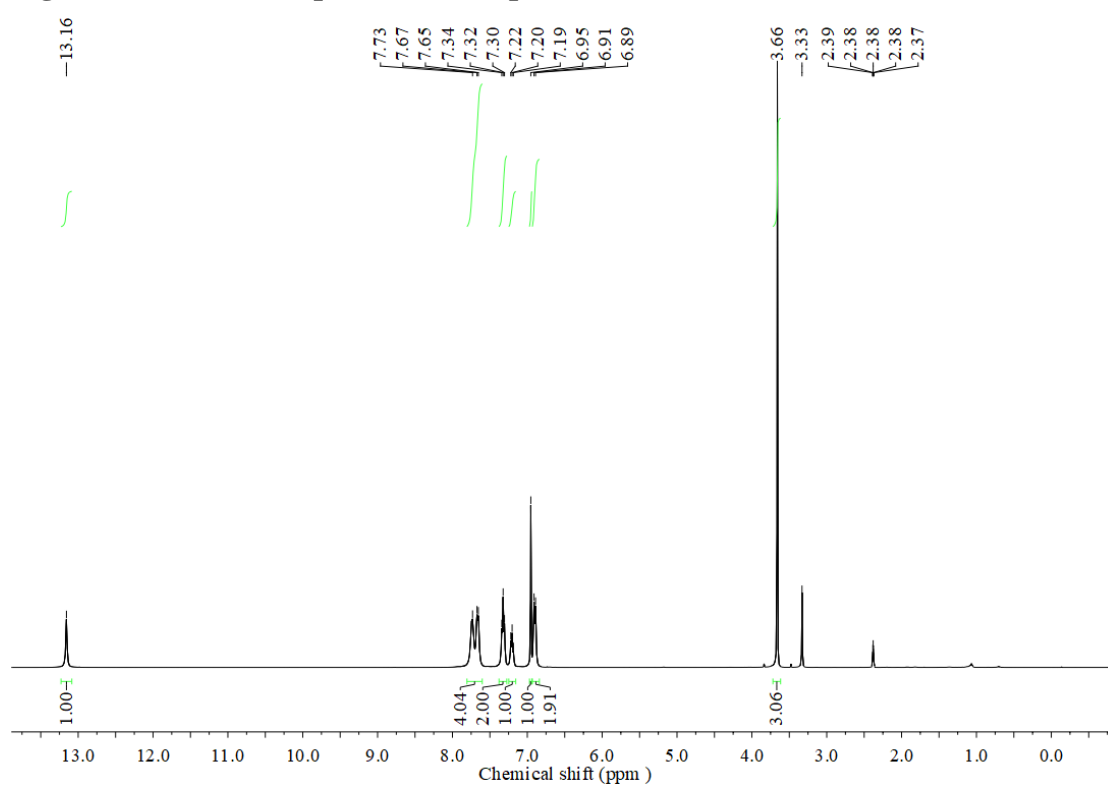


Figure S50 ^{13}C NMR Spectra of Compound of 3i

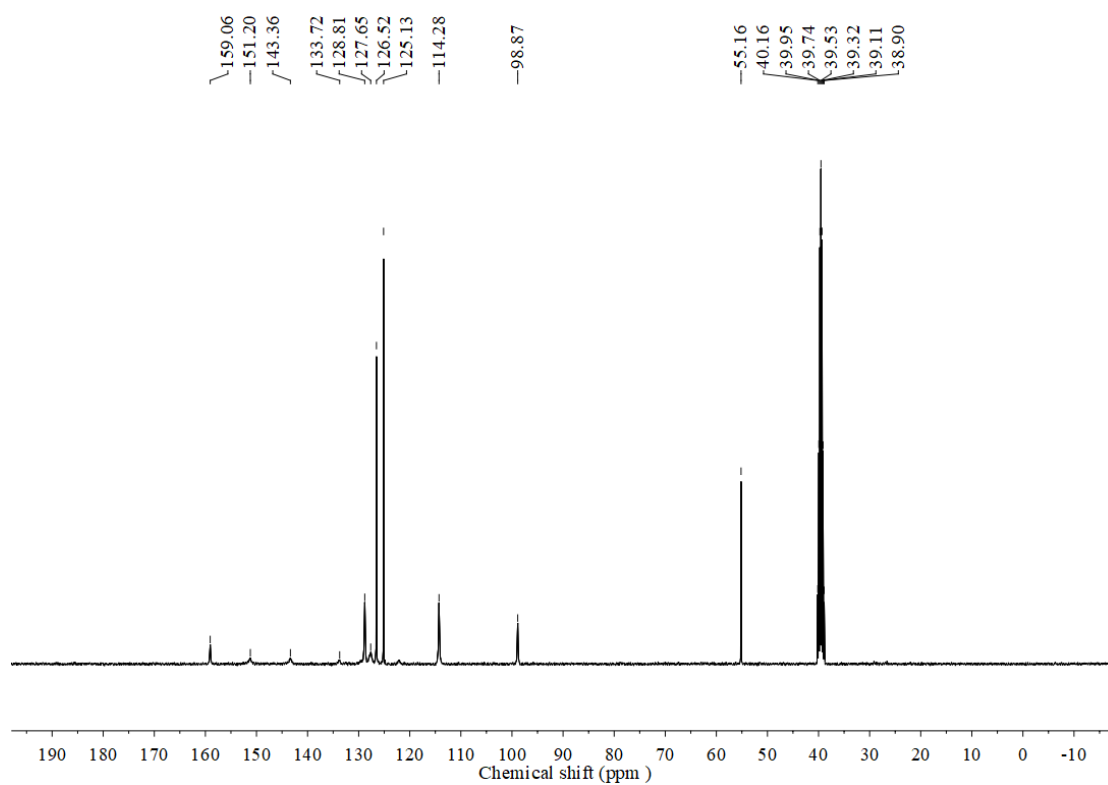


Figure S51 ^1H NMR Spectra of Compound of 3j

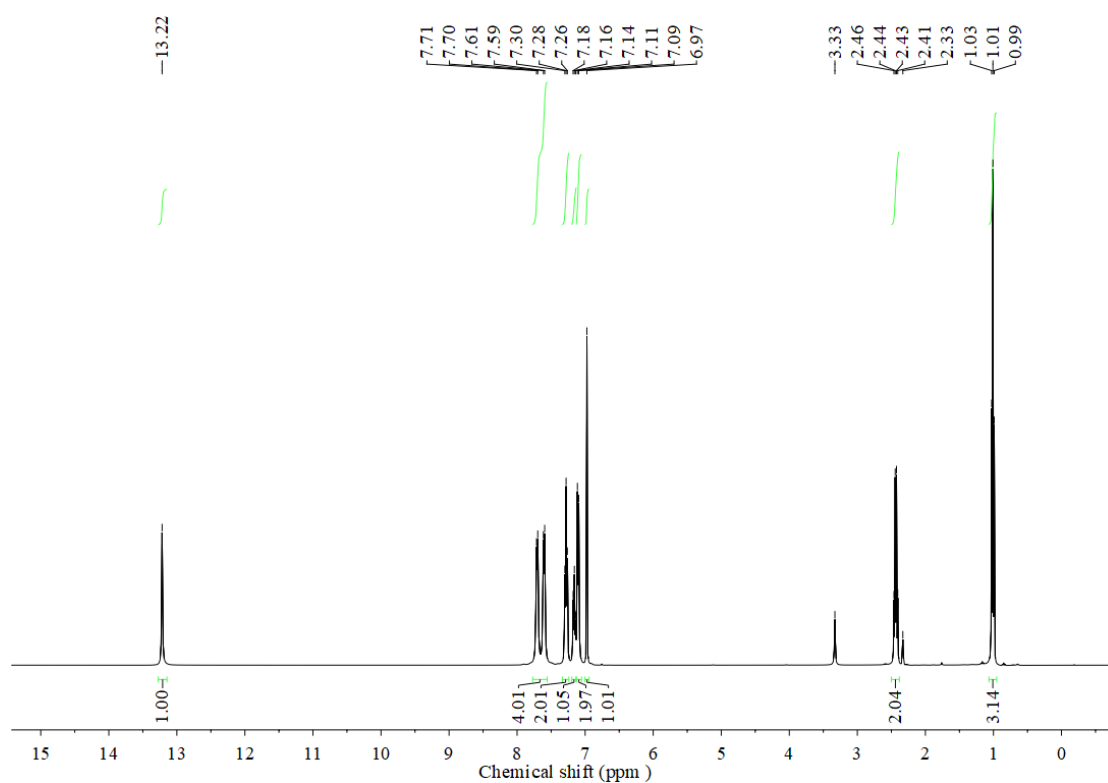


Figure S52 ^{13}C NMR Spectra of Compound of 3j

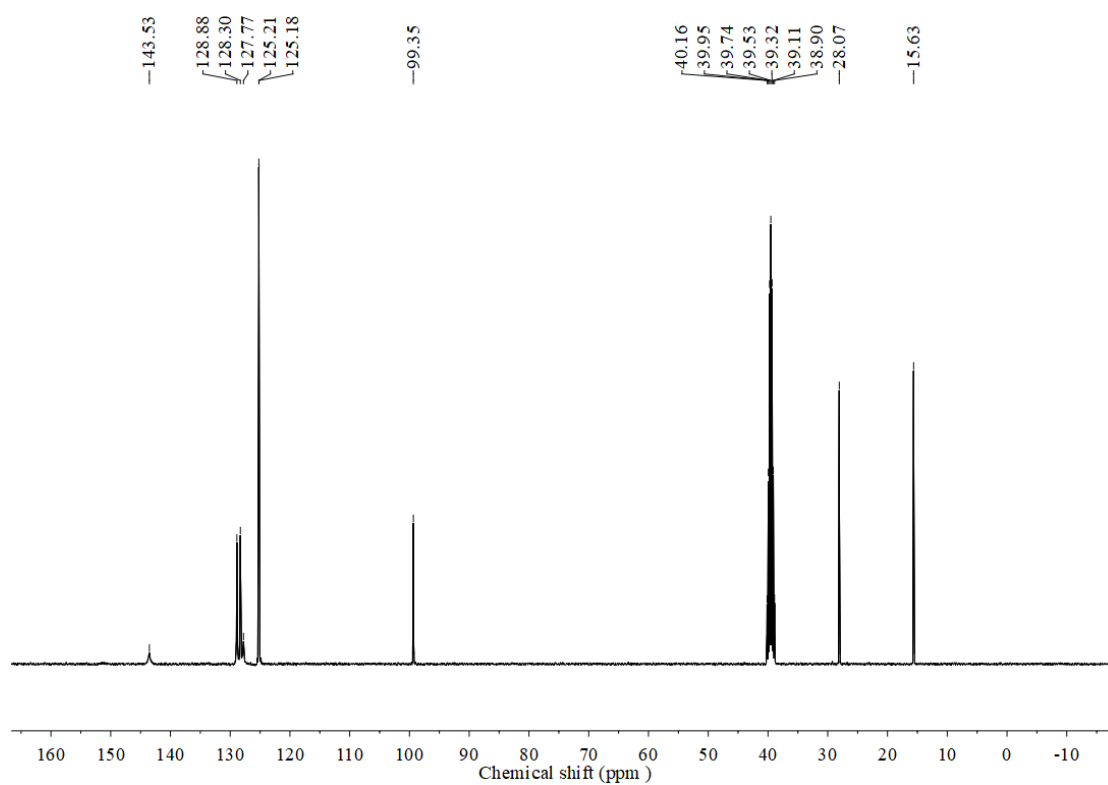


Figure S53 ^1H NMR Spectra of Compound of 3k

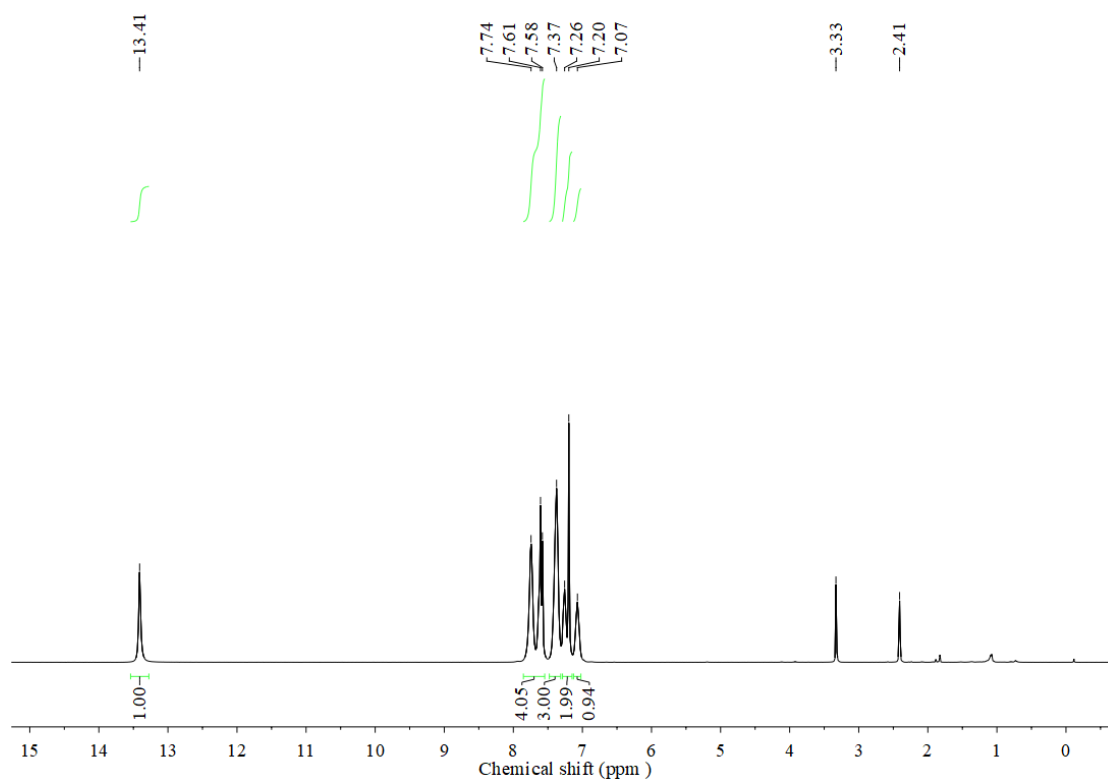


Figure S54 ^{13}C NMR Spectra of Compound of 3k

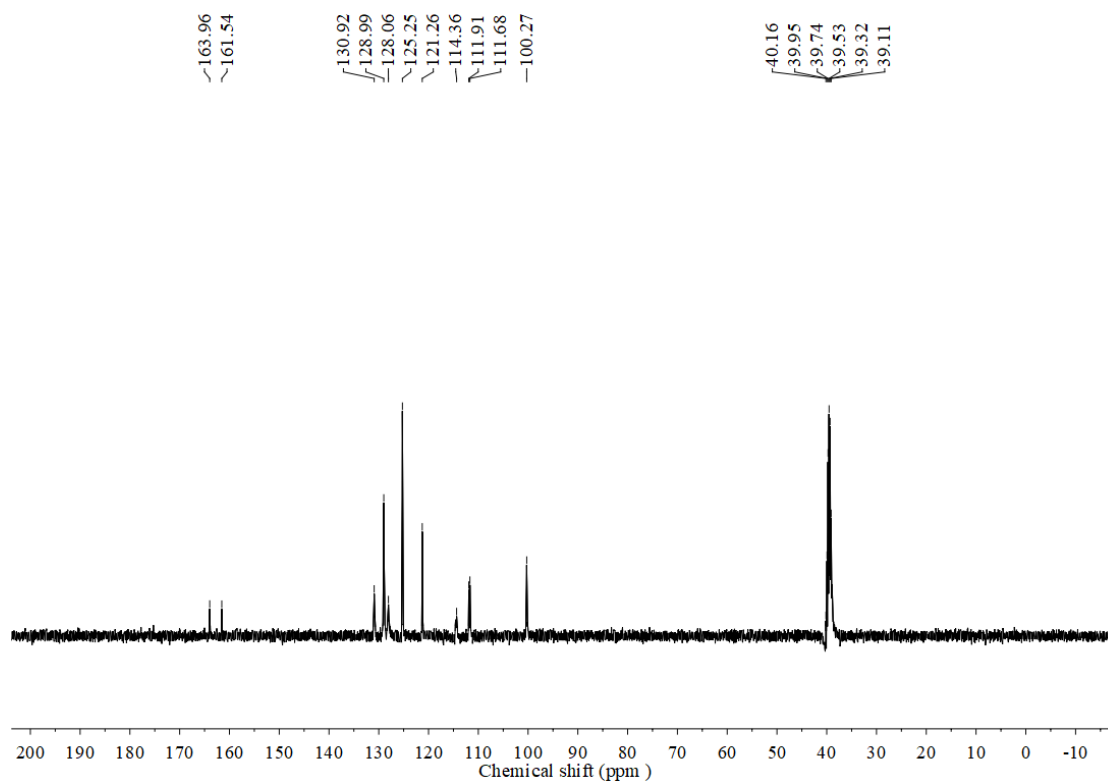


Figure S55 ^1H NMR Spectra of Compound of 3l

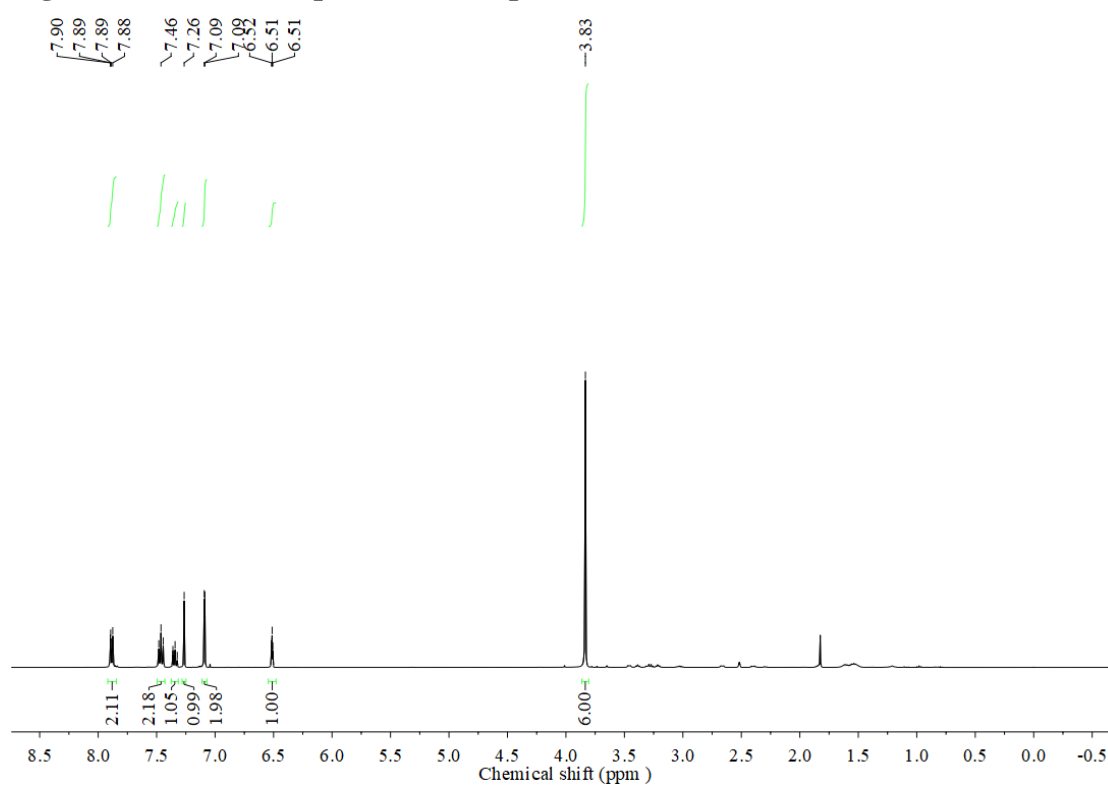


Figure S56 ^{13}C NMR Spectra of Compound of 3l

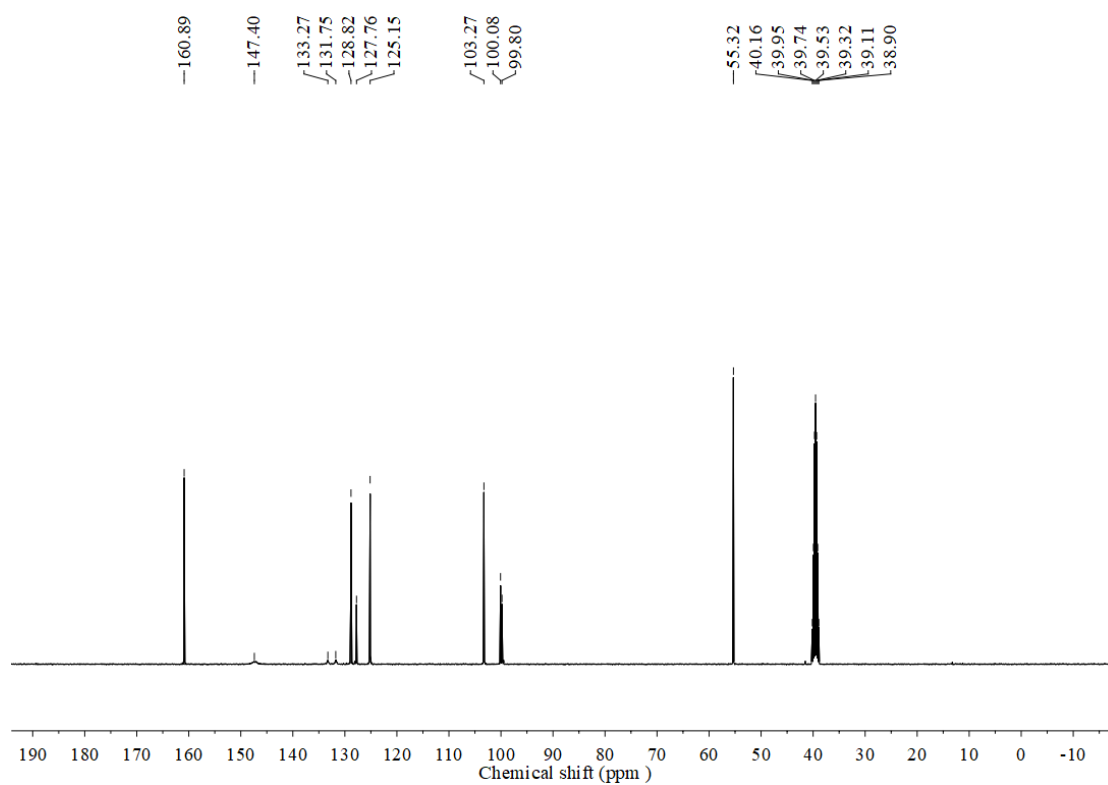


Figure S57 ^1H NMR Spectra of Compound of 3m

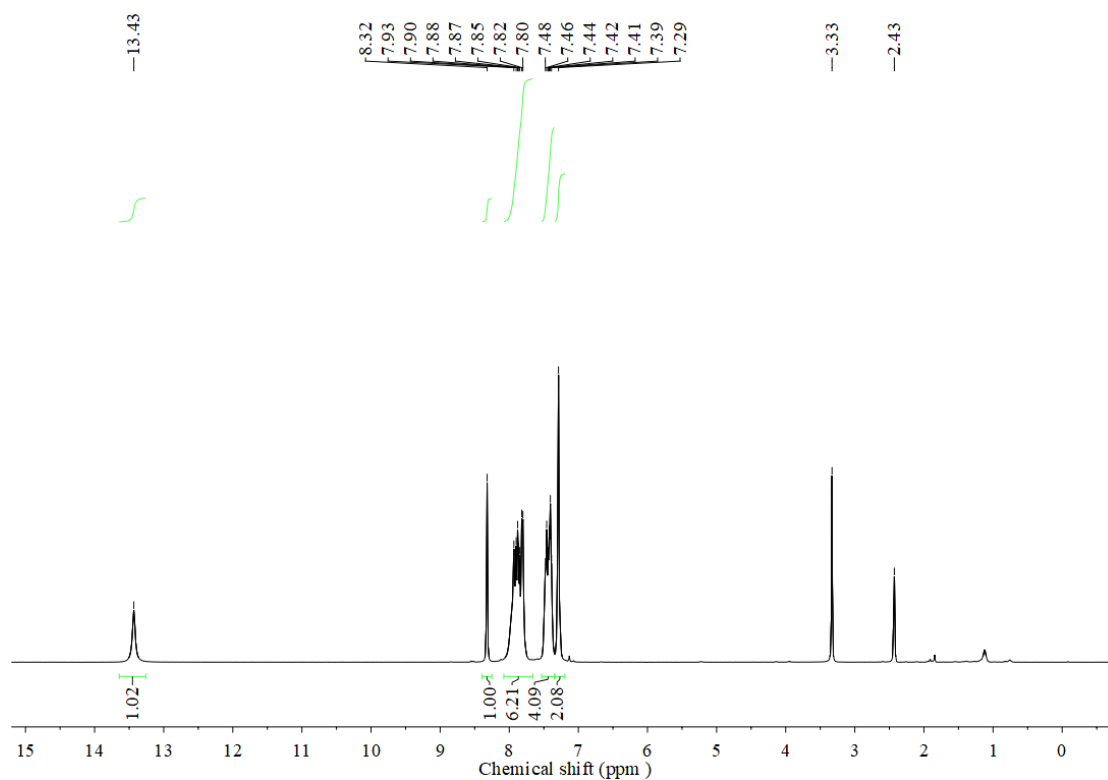


Figure S58 ^{13}C NMR Spectra of Compound of 3m

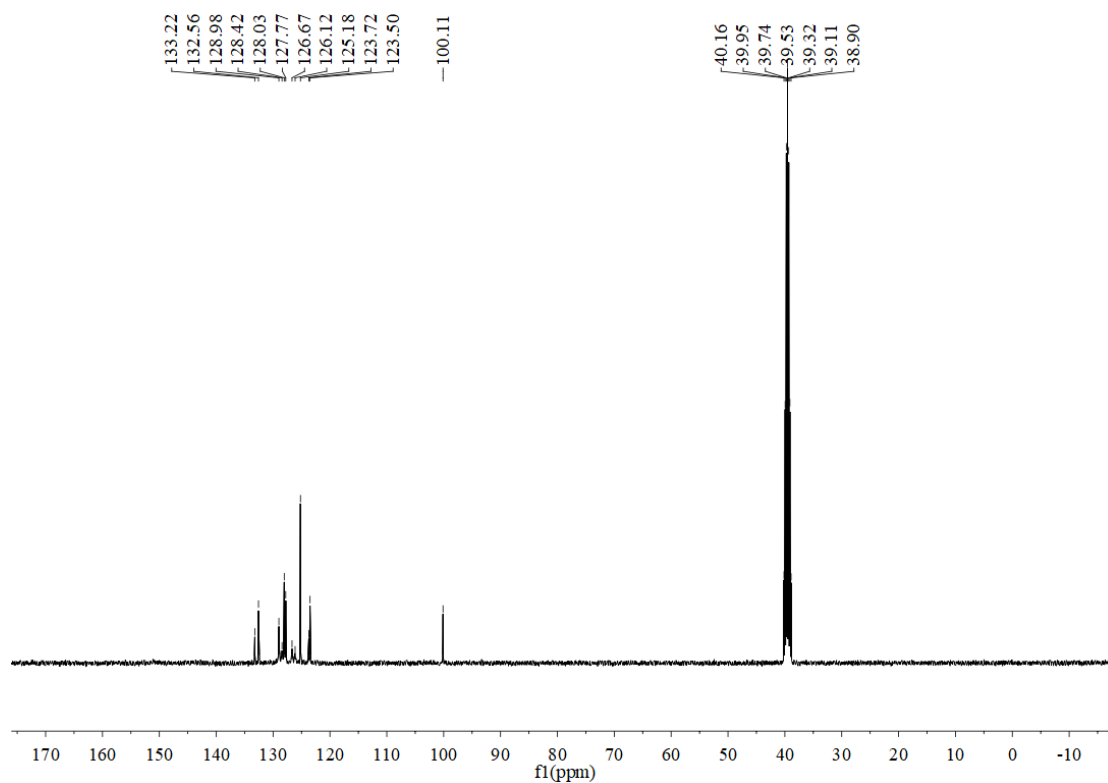


Figure S59 ^1H NMR Spectra of Compound of 3n

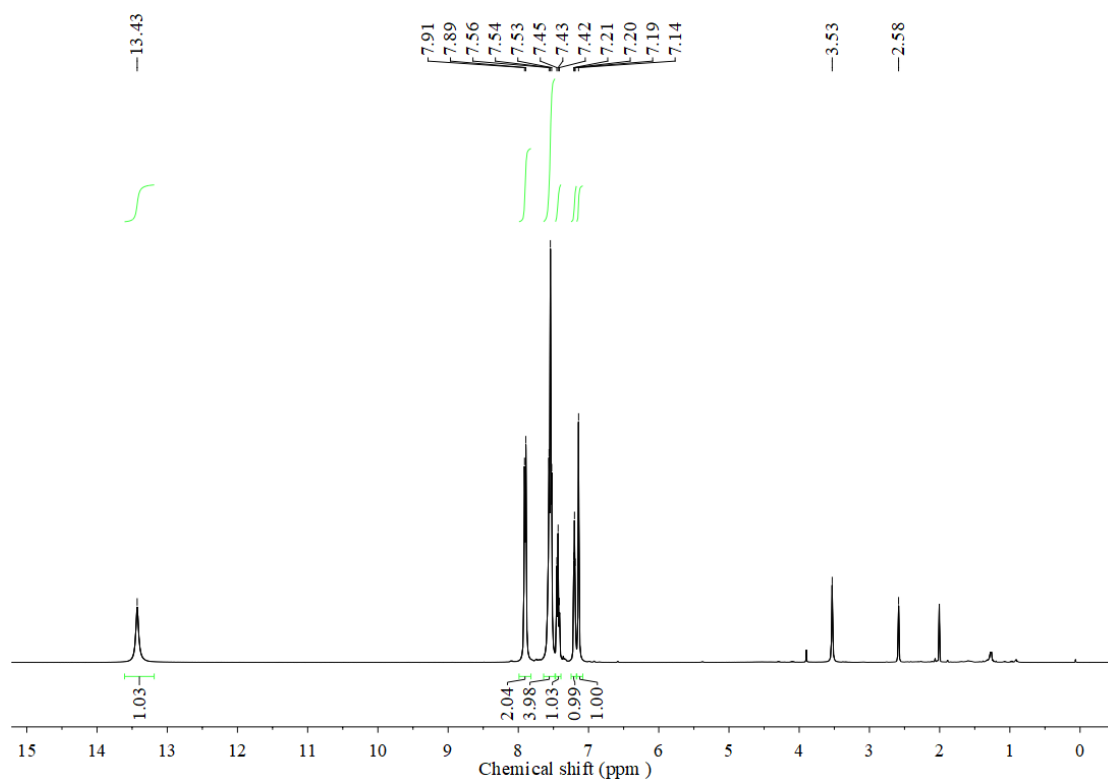


Figure S60 ^{13}C NMR Spectra of Compound of 3n

