

Supporting Information for

Copper-Catalyzed Synthesis of (*Z*)-2*H*-naphtho[1,8-*bc*]thiophenes with solid emissions

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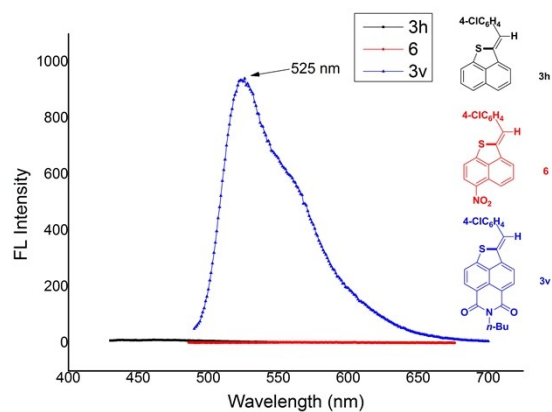
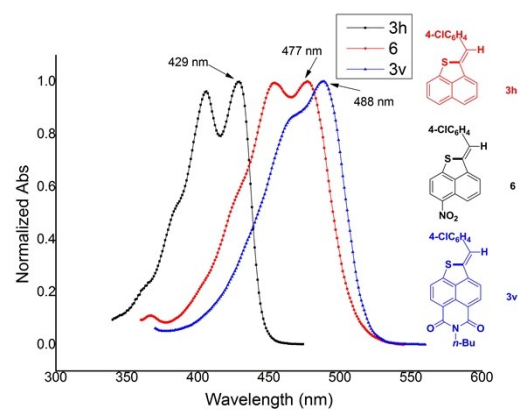
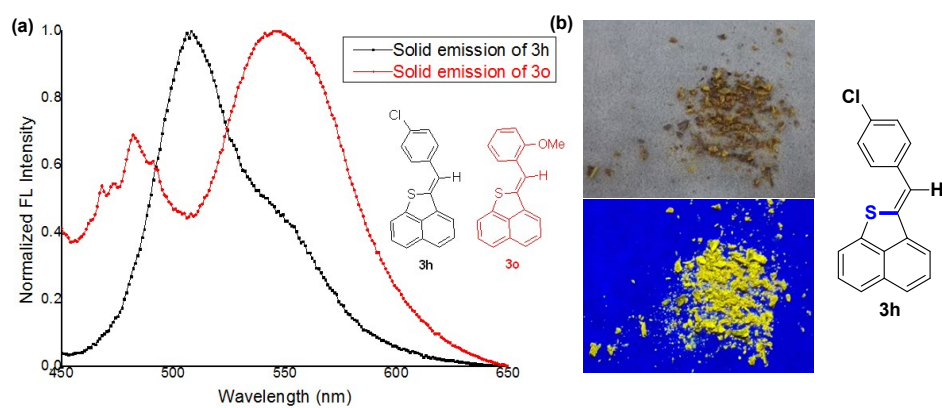
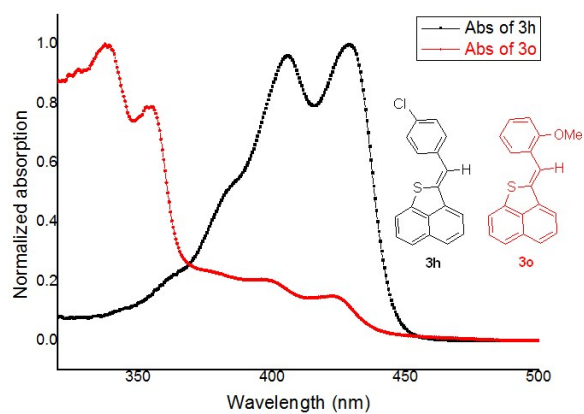
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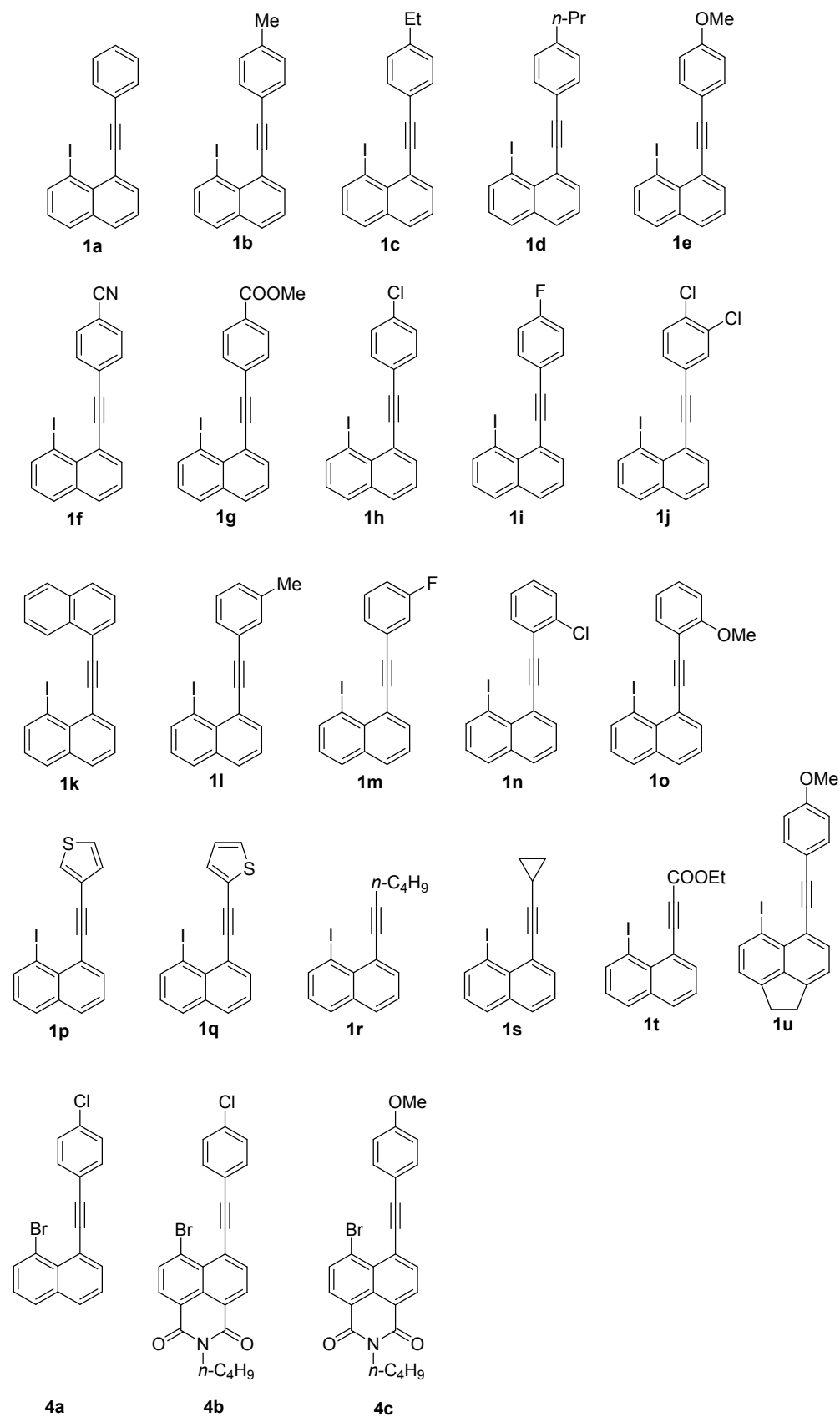
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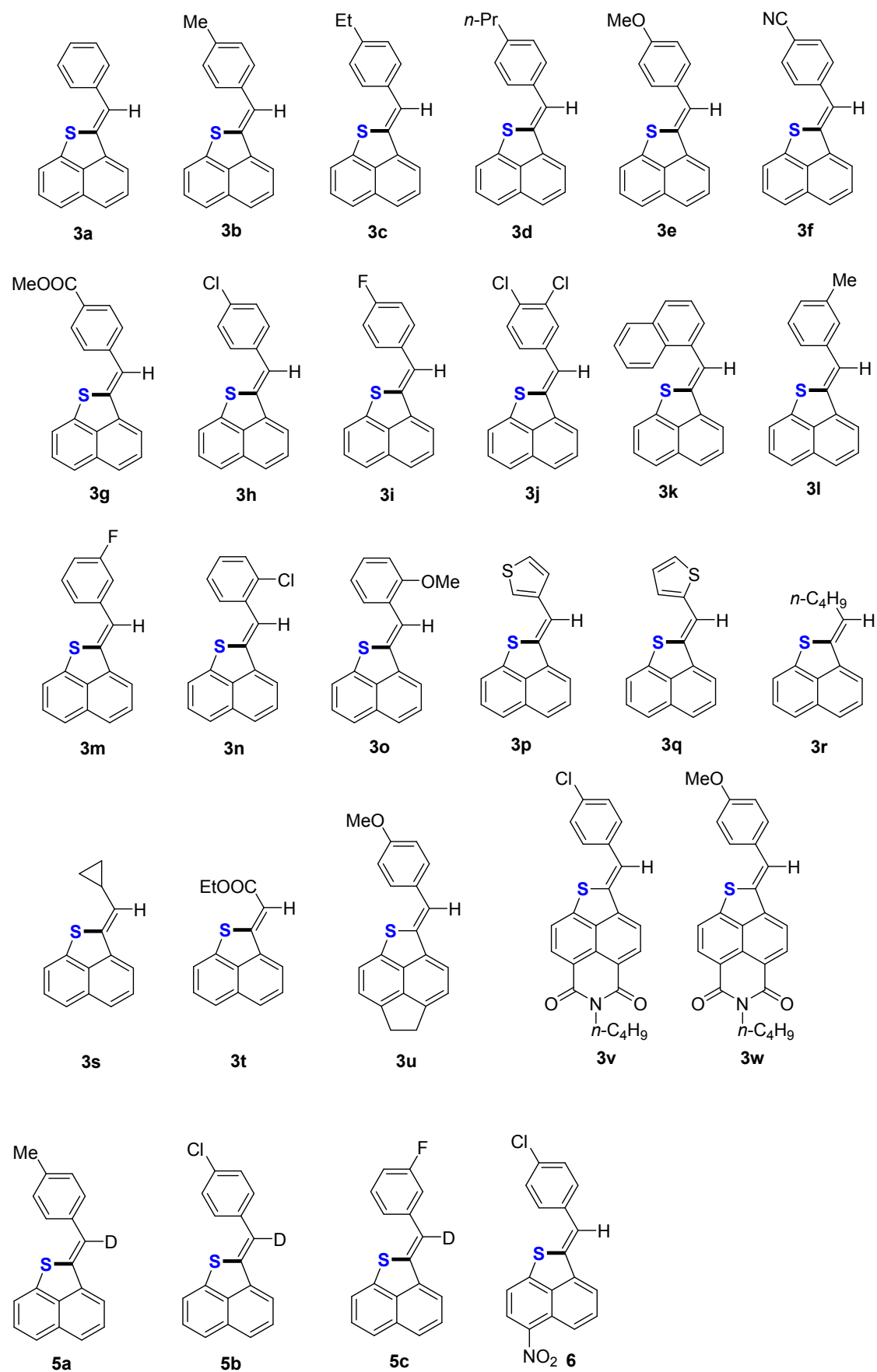
1. The photophysical properties of products



2. Structures of 1a-1u and 4a-4c

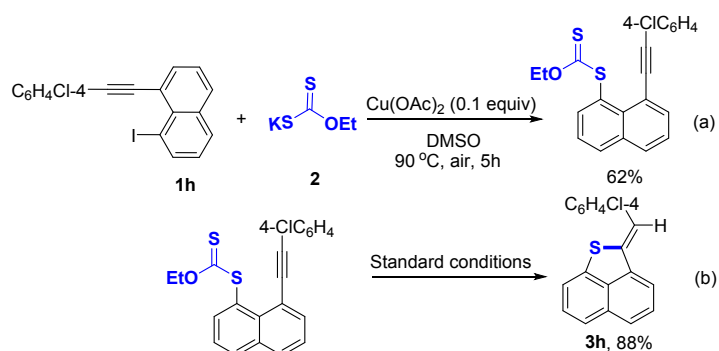


3. Structures of 3a-3w, 5a-5c and 6



4. Control experiments

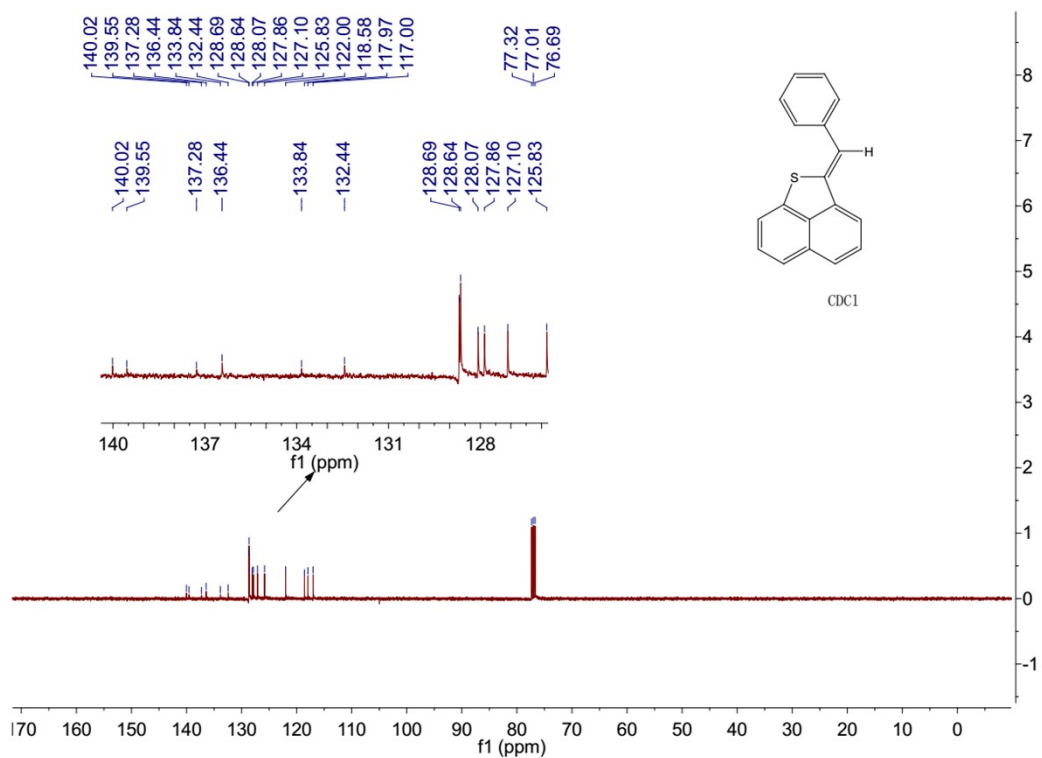
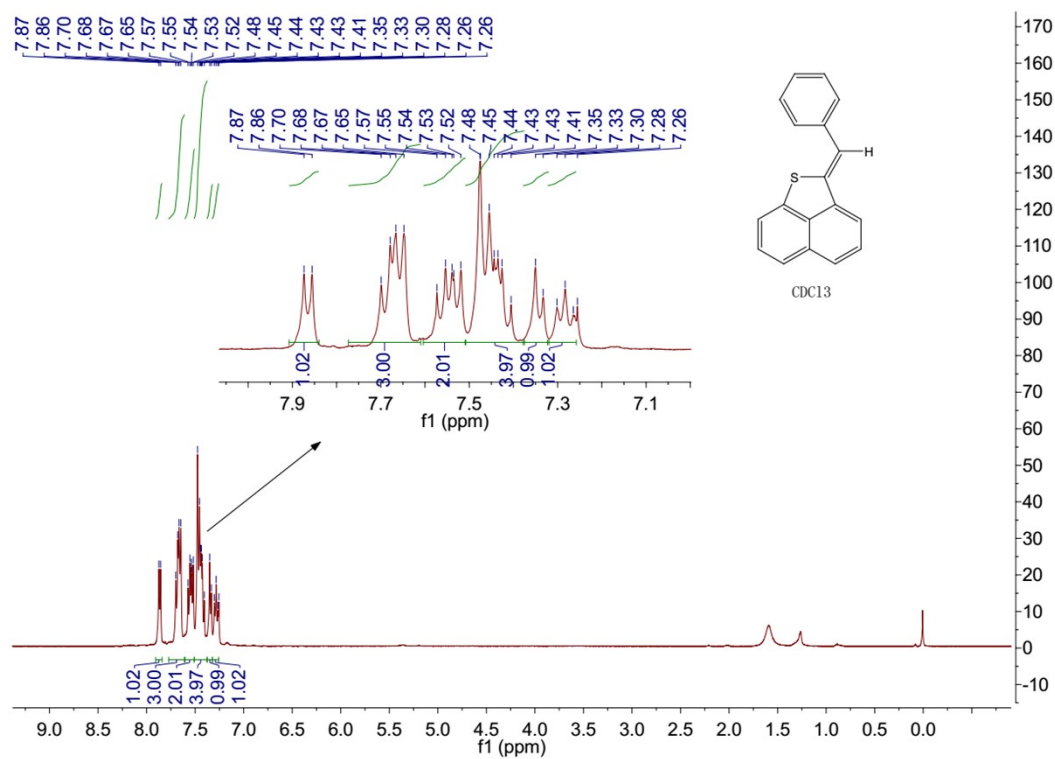
Table S1. Using 1-((4-chlorophenyl)ethynyl)-8-iodonaphthalene as the substrate^a



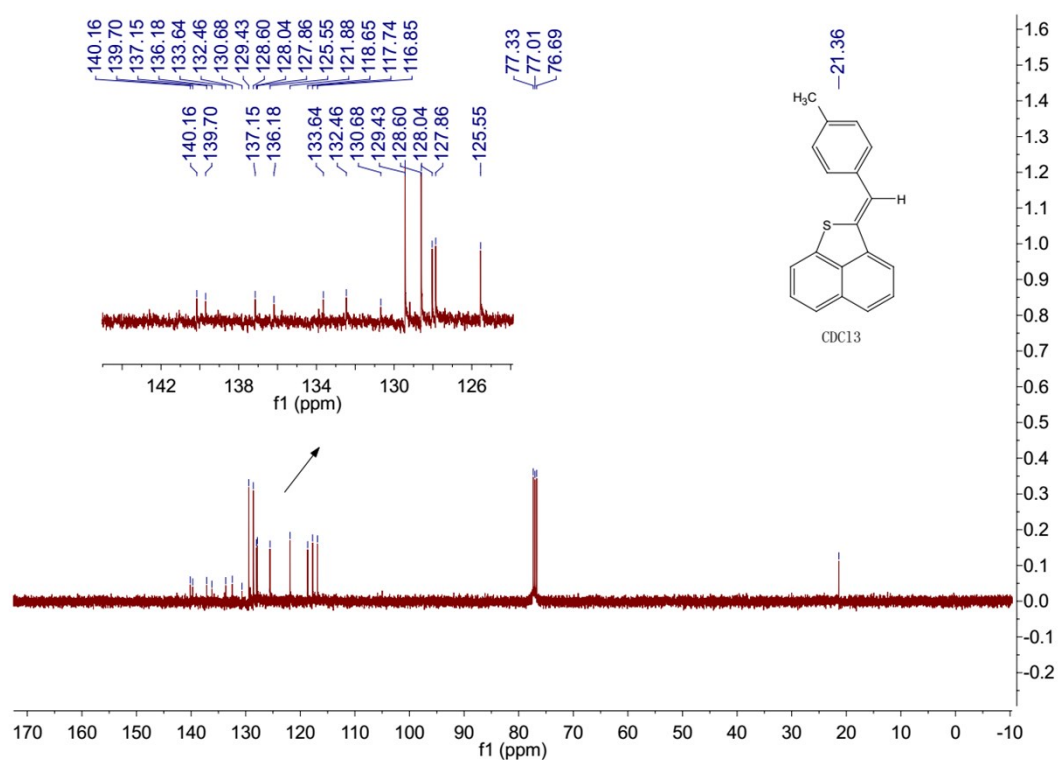
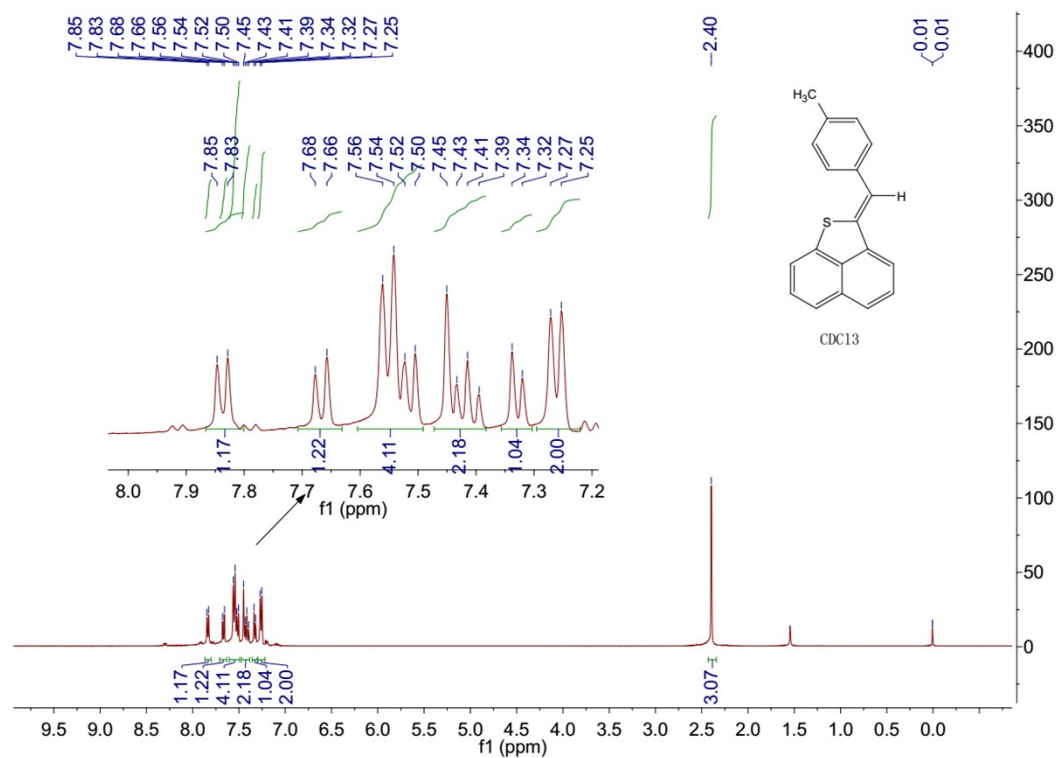
^a Reaction conditions: **1h** (0.2 mmol) and $\text{KSC}(\text{S})\text{OEt}$ (2.0 equiv, 64.1 mg) in 2 ml of DMSO was stirred under air.

5. Copies of the Products ^1H NMR, ^{13}C NMR

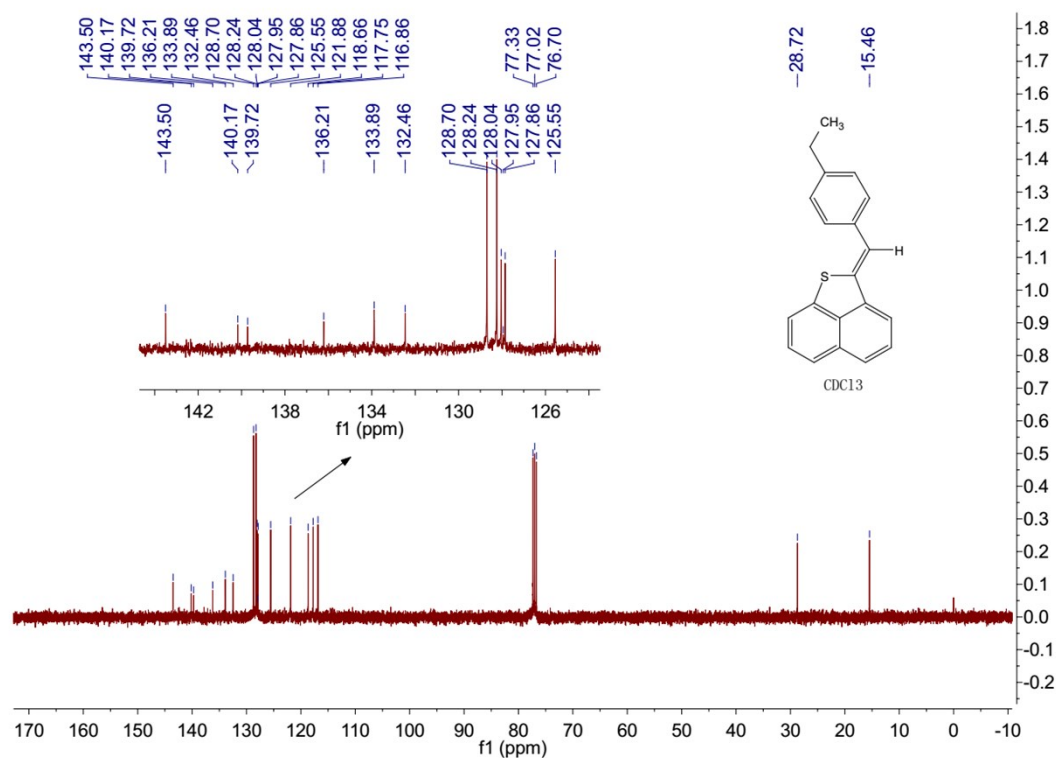
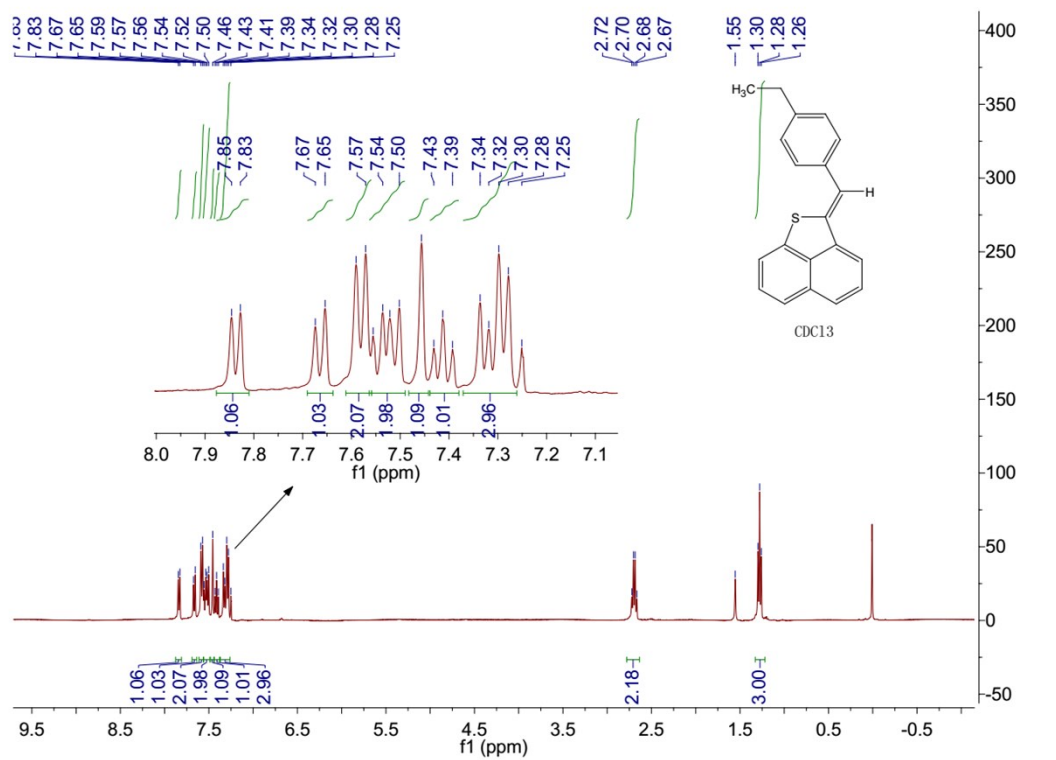
(*Z*)-2-benzylidene-2*H*-naphtho[1,8-*bc*]thiophene (3a)



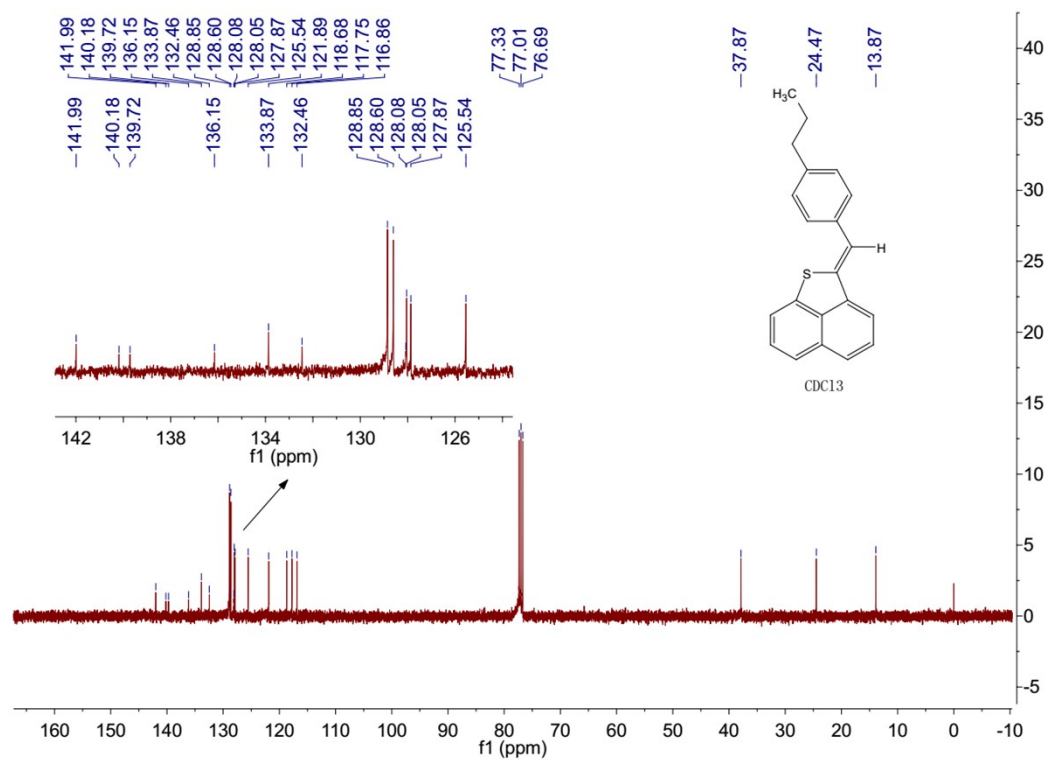
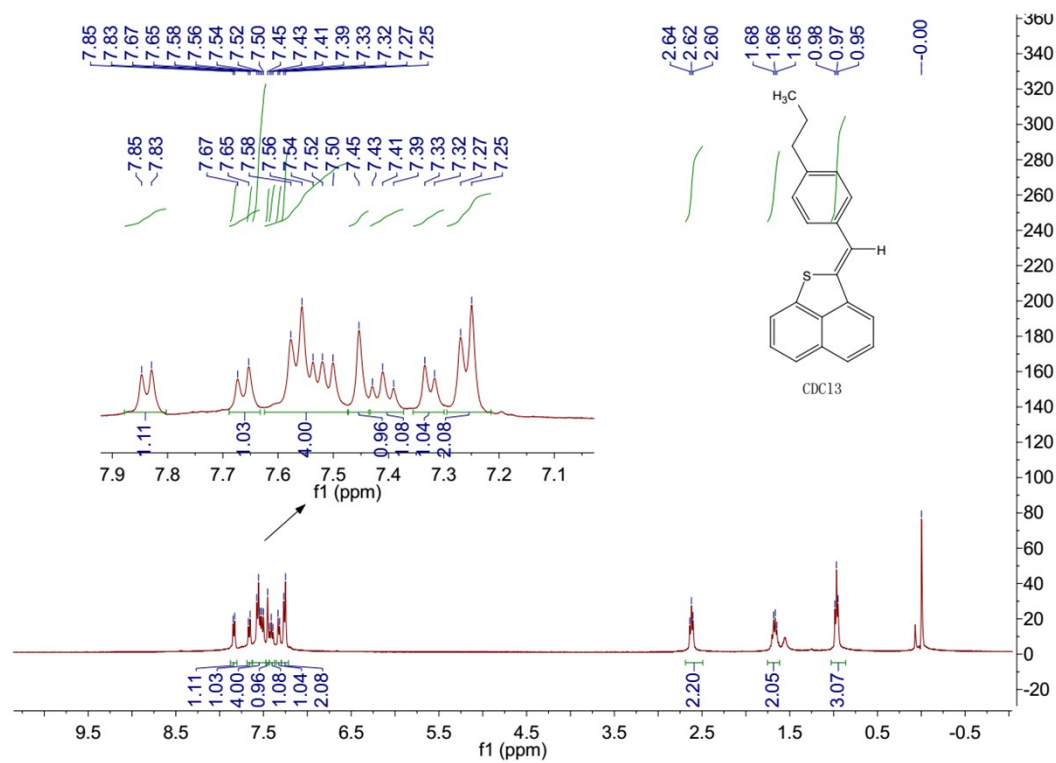
(Z)-2-(4-methylbenzylidene)-2H-naphtho[1,8-bc]thiophene (3b)



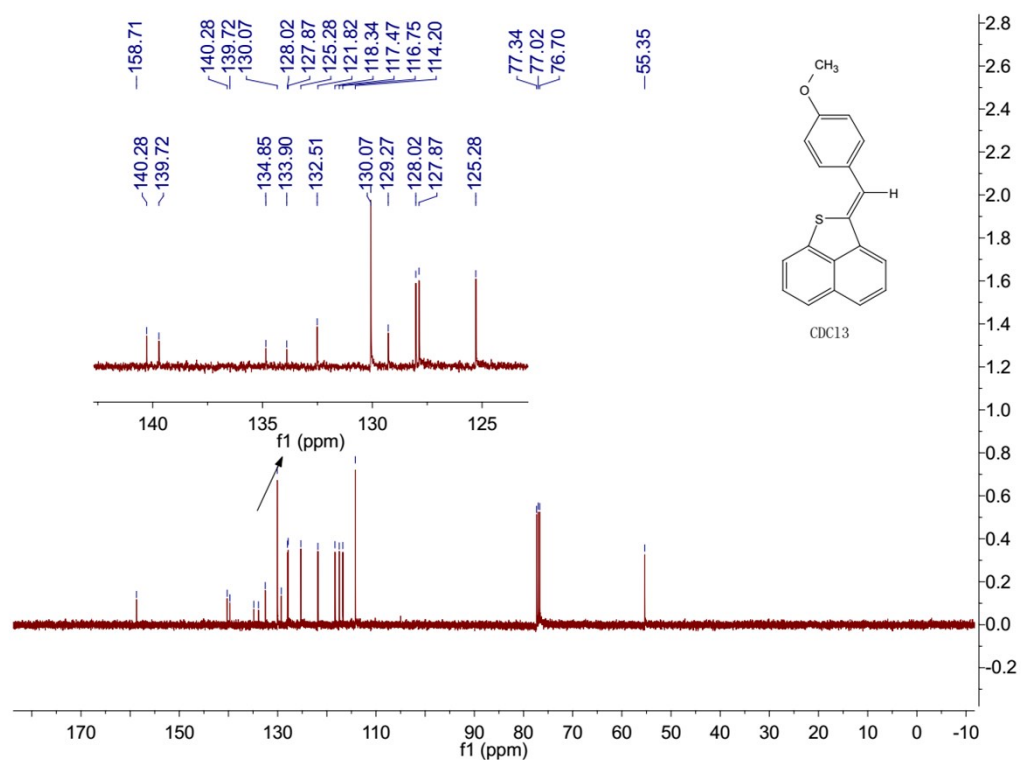
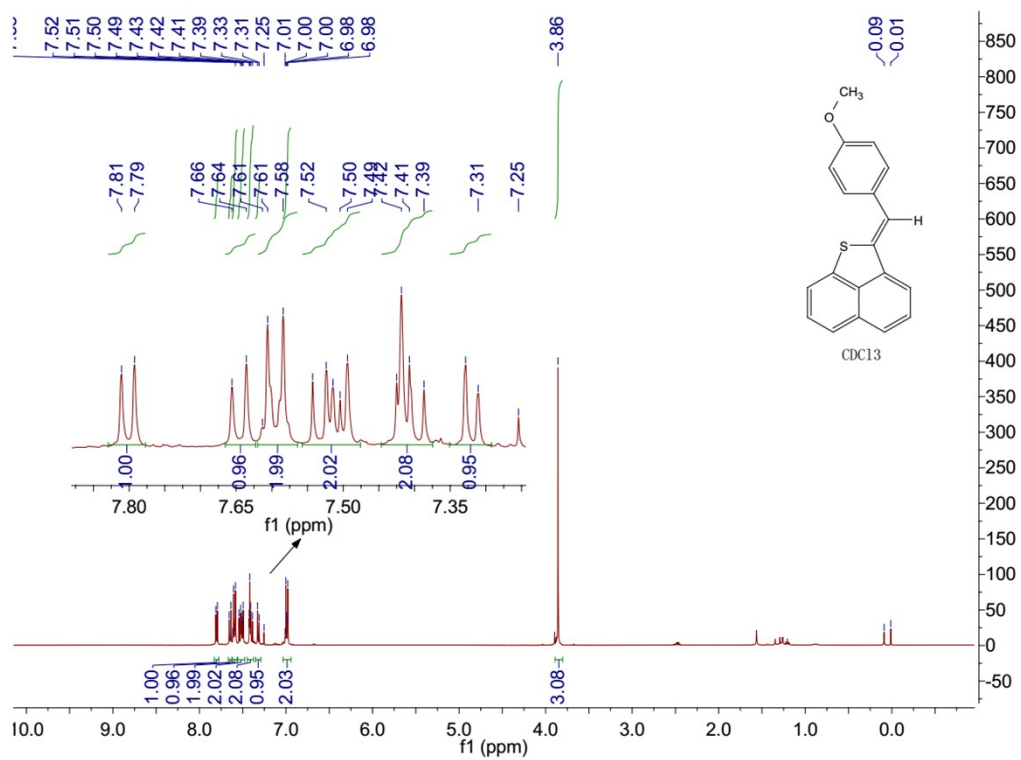
(Z)-2-(4-ethylbenzylidene)-2H-naphtho[1,8-bc]thiophene (3c)



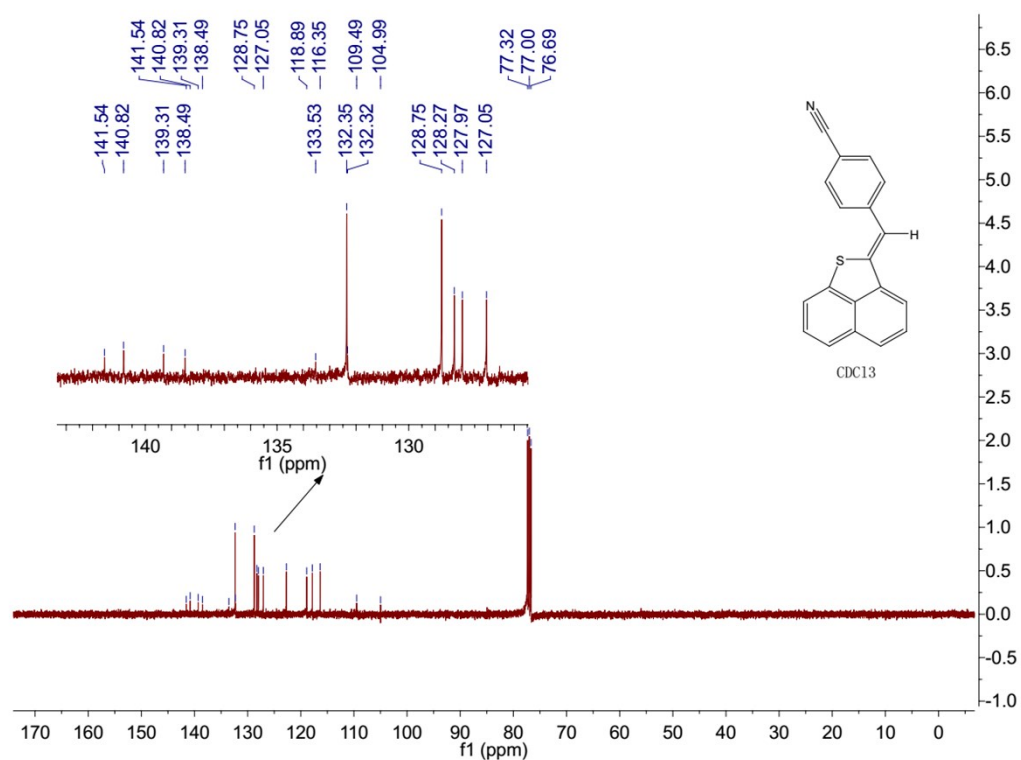
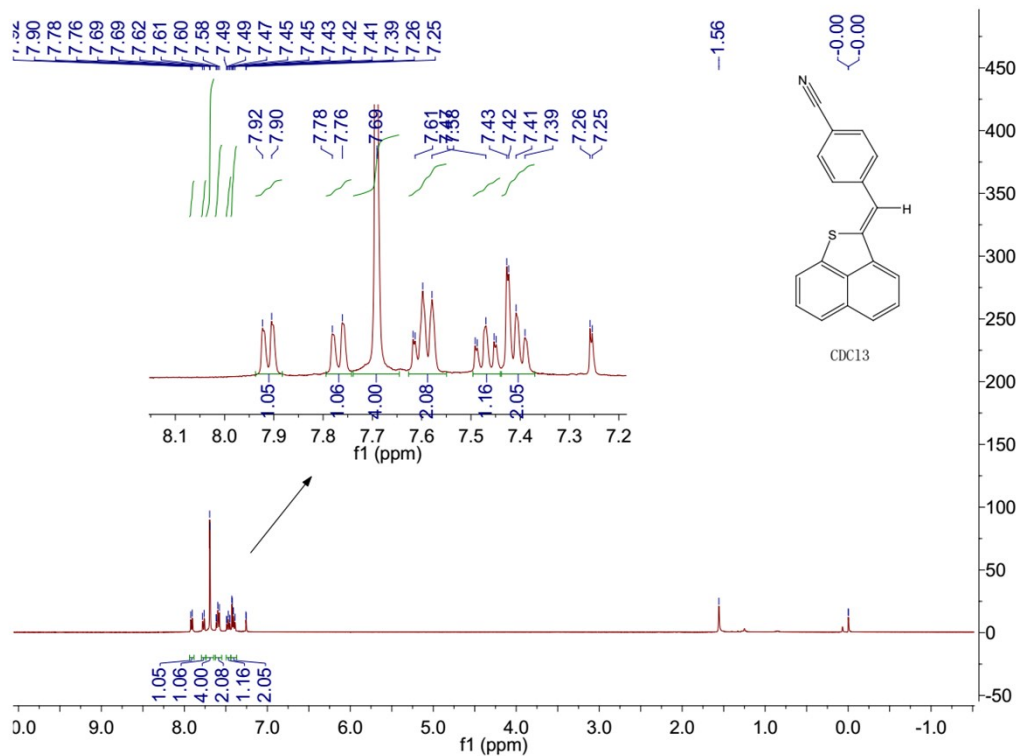
(Z)-2-(4-propylbenzylidene)-2H-naphtho[1,8-bc]thiophene (3d)



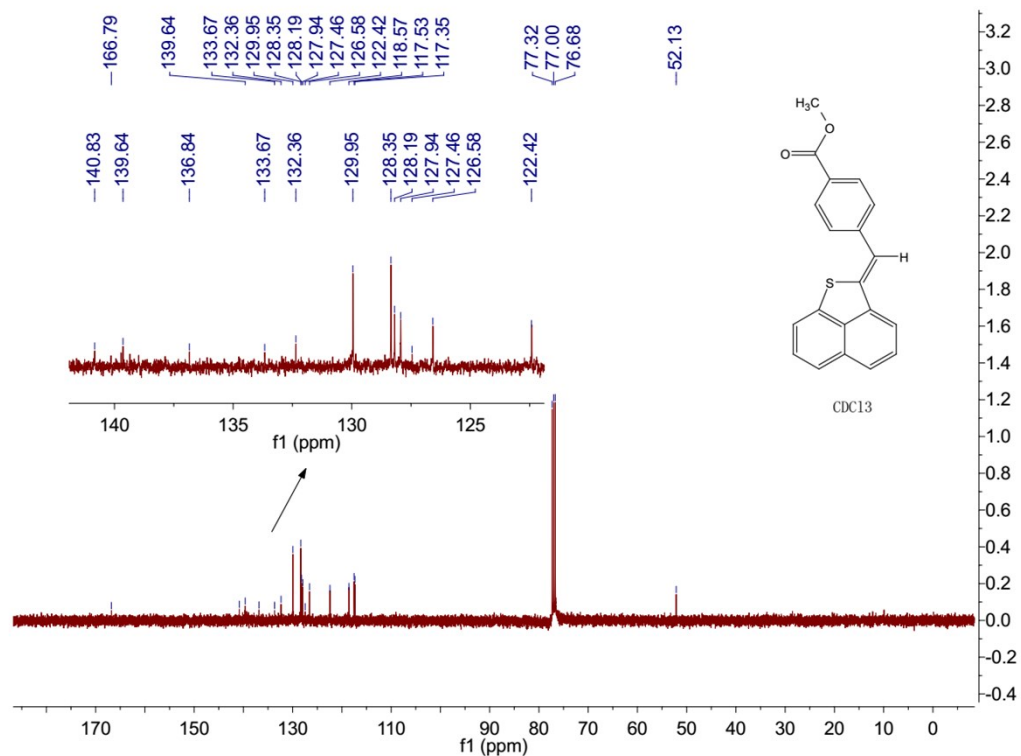
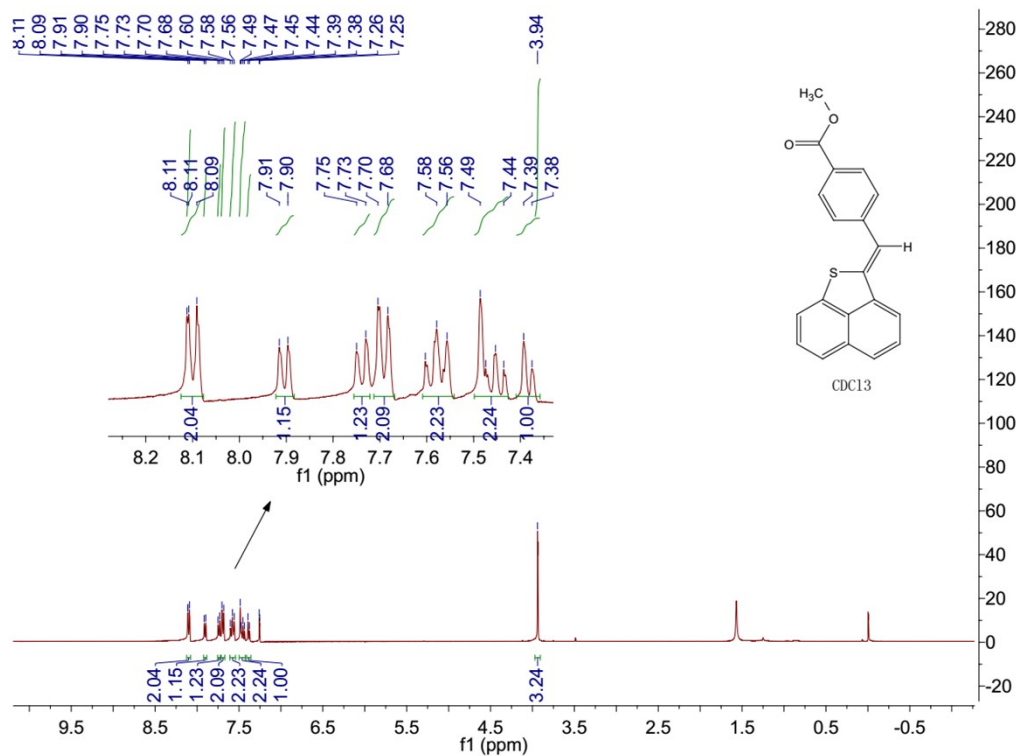
(Z)-2-(4-methoxybenzylidene)-2H-naphtho[1,8-*bc*]thiophene (3e)



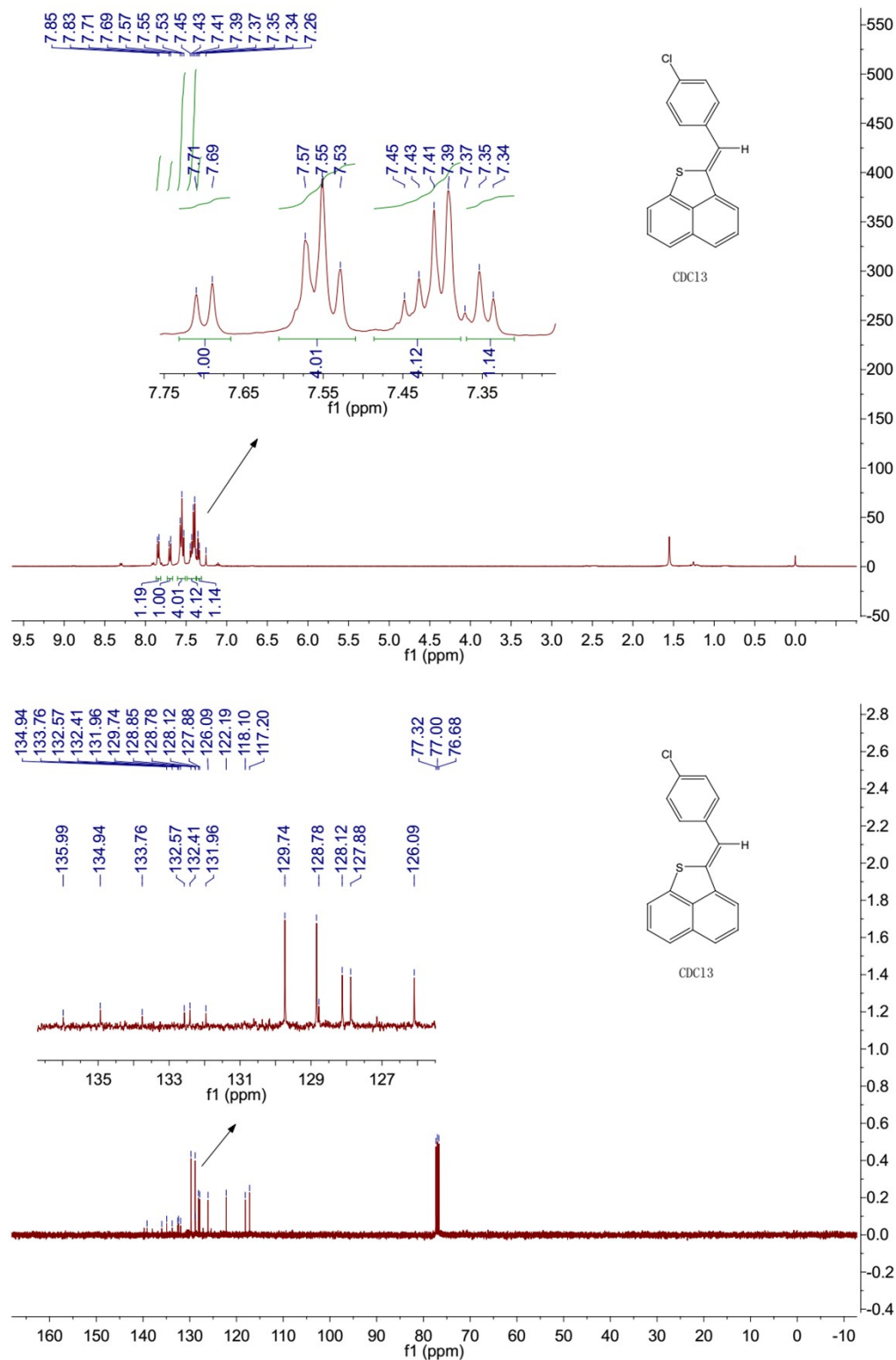
(Z)-4-((2H-naphtho[1,8-bc]thiophen-2-ylidene)methyl)benzonitrile (3f)



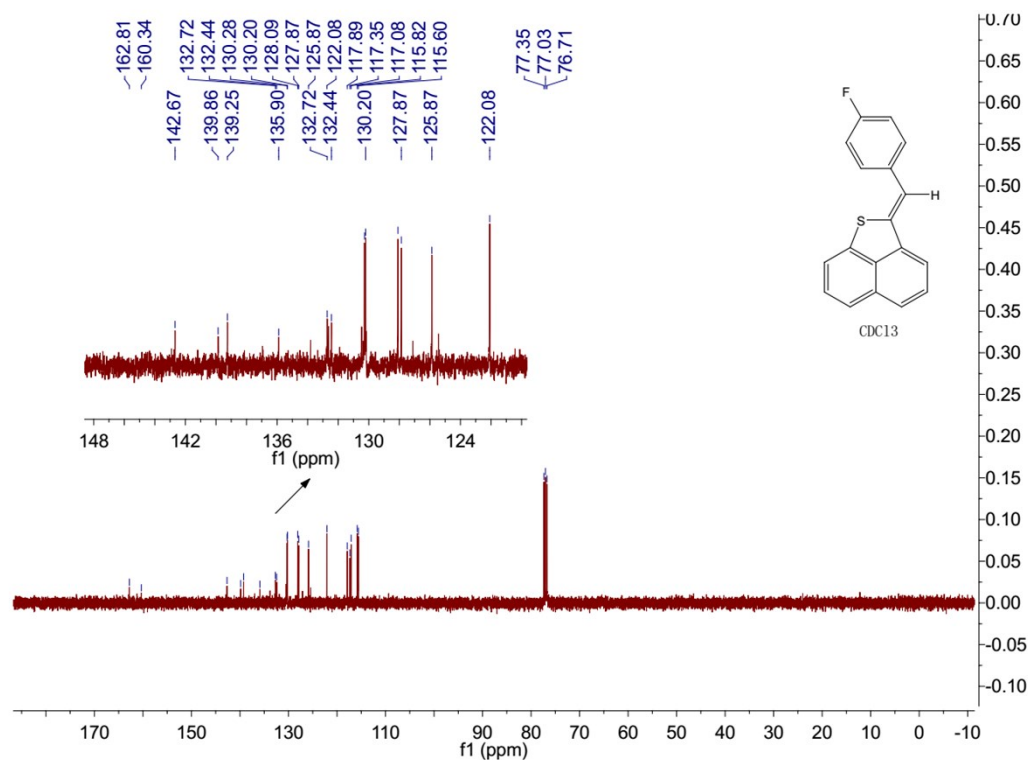
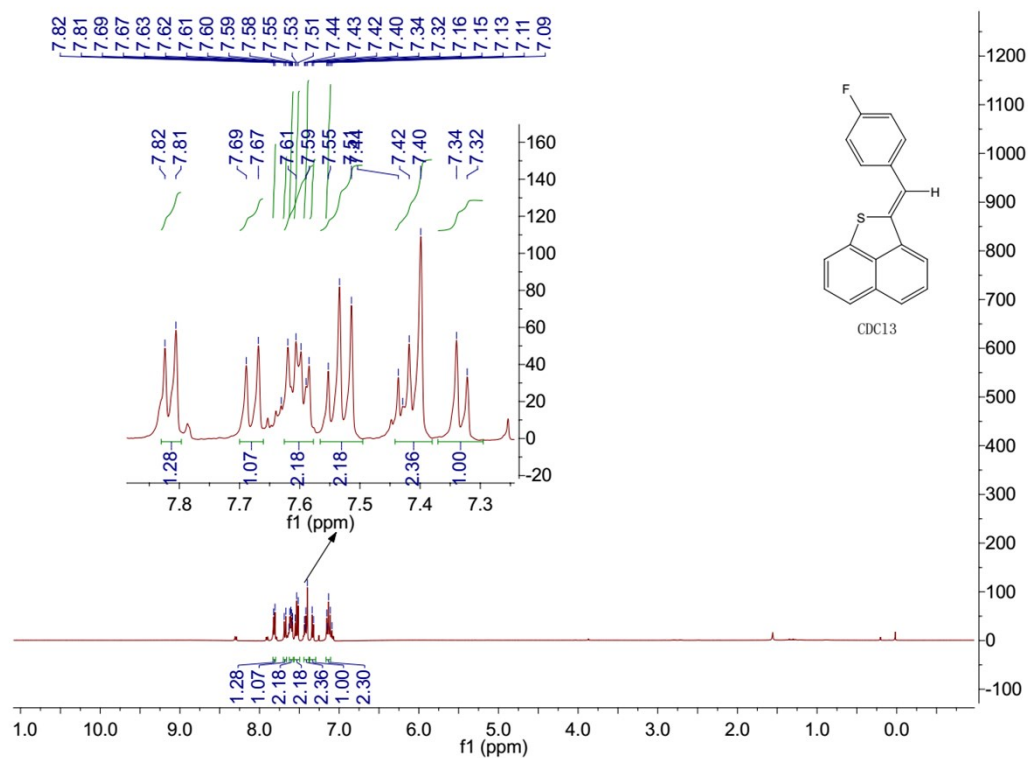
Methyl (Z)-4-((2H-naphtho[1,8-bc]thiophen-2-ylidene)methyl)benzoate (3g)

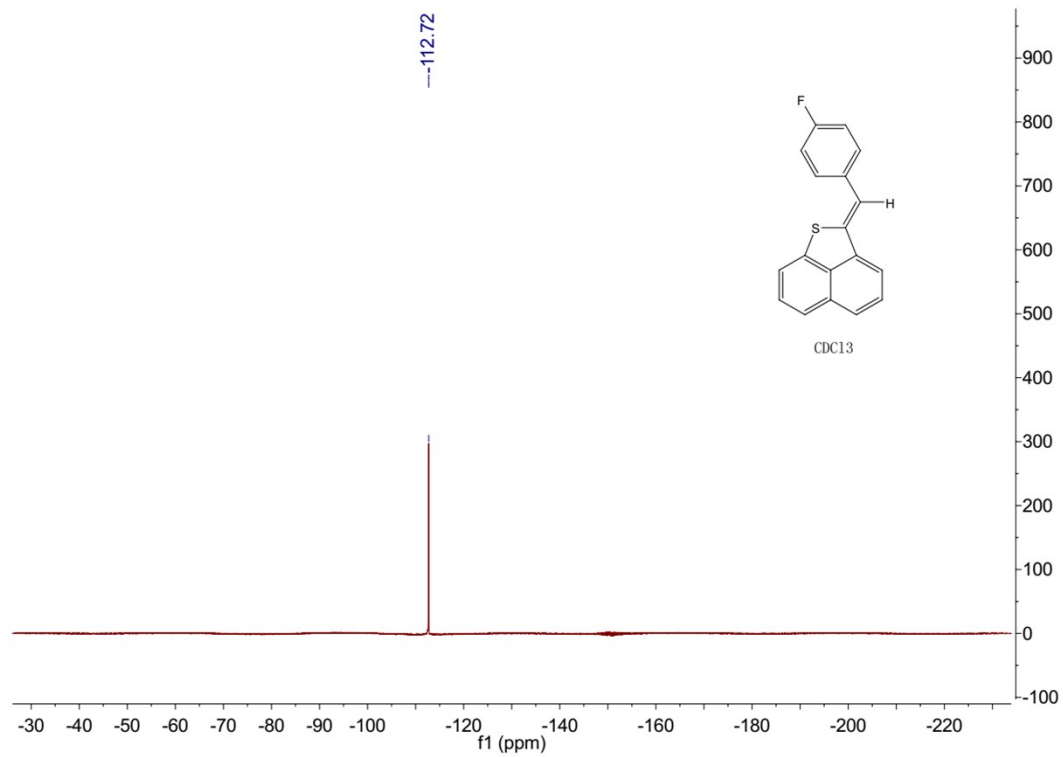


(Z)-2-(4-chlorobenzylidene)-2H-naphtho[1,8-bc]thiophene (3h)

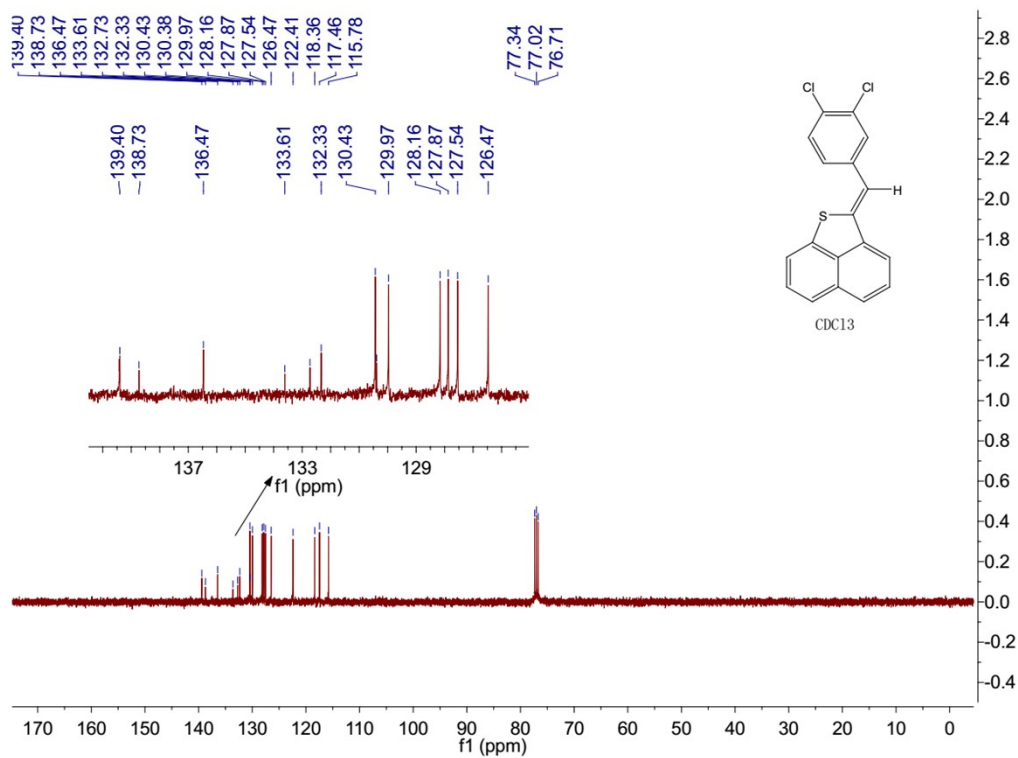
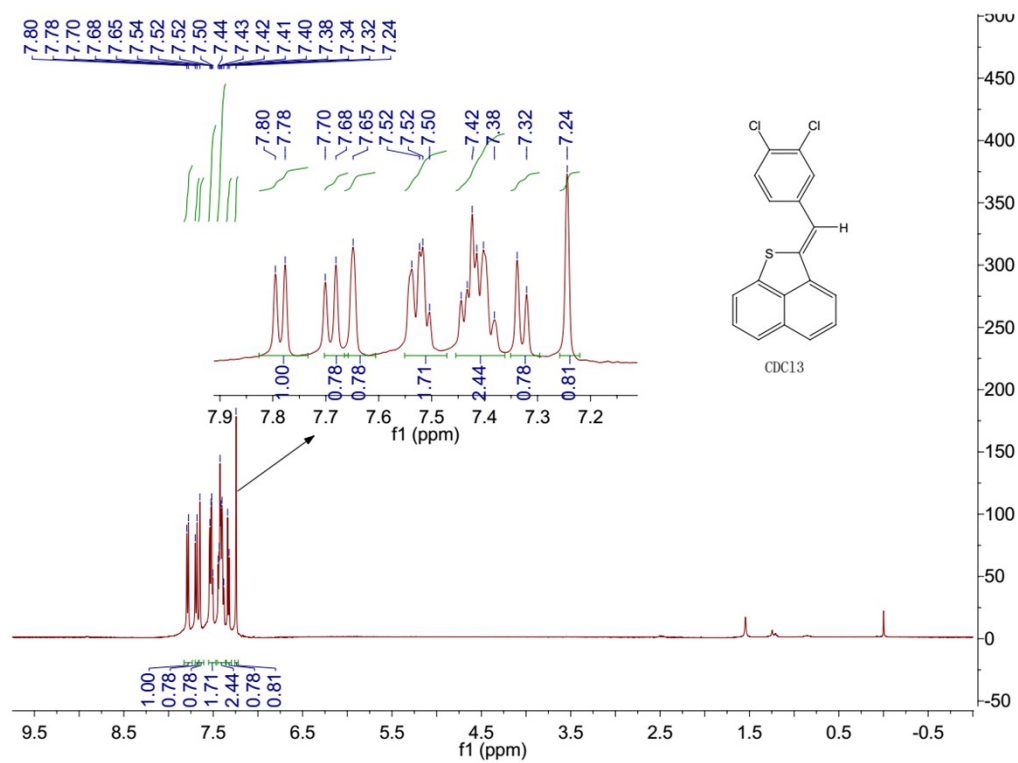


(Z)-2-(4-fluorobenzylidene)-2H-naphtho[1,8-bc]thiophene (3i)

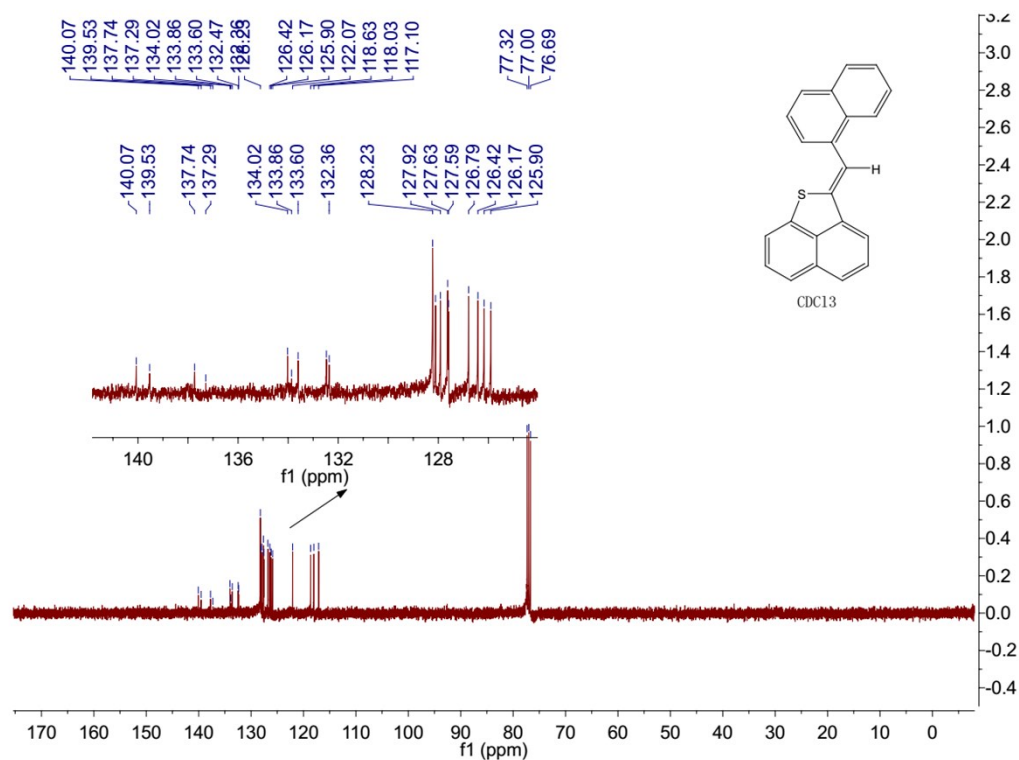
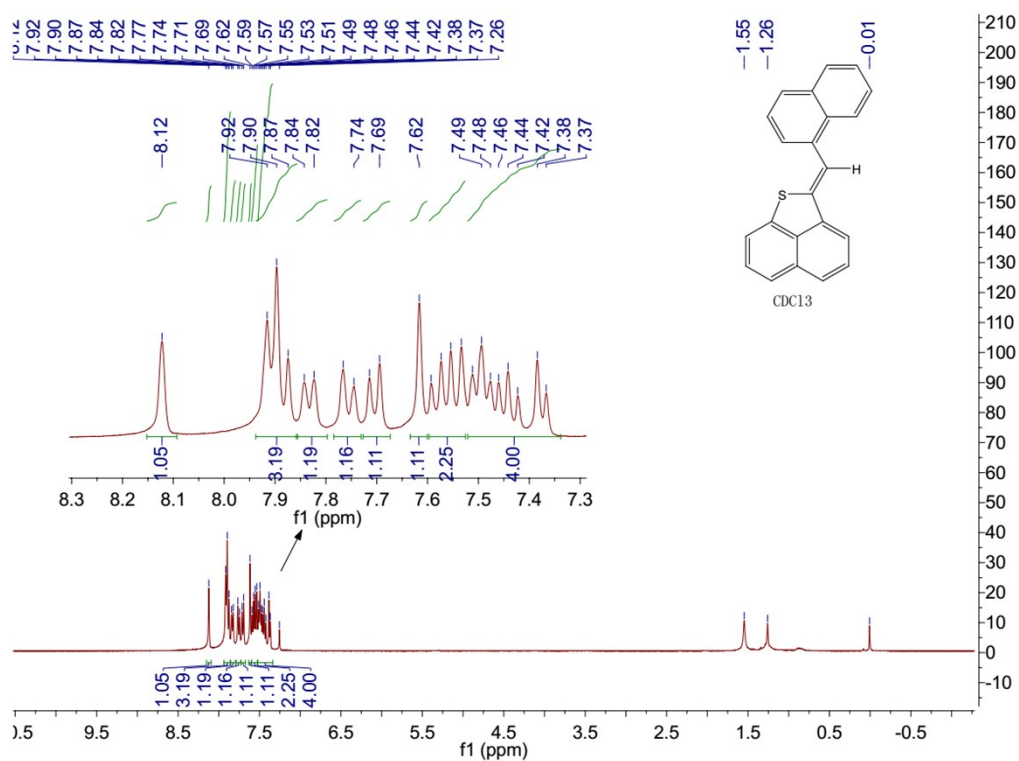




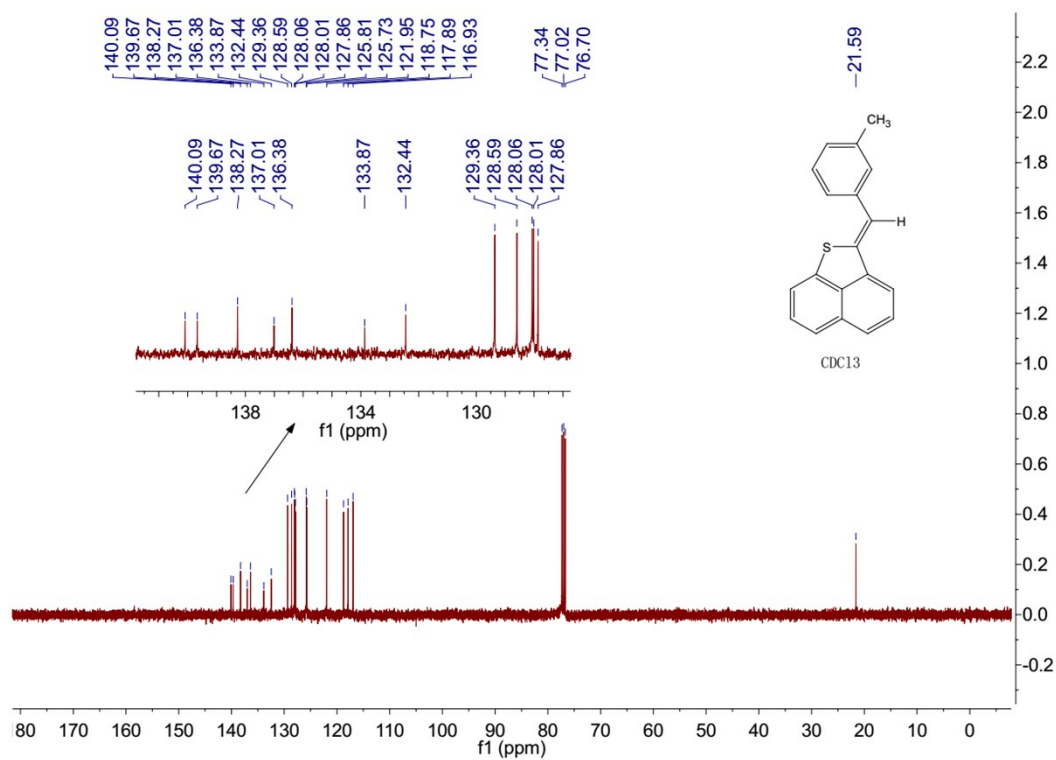
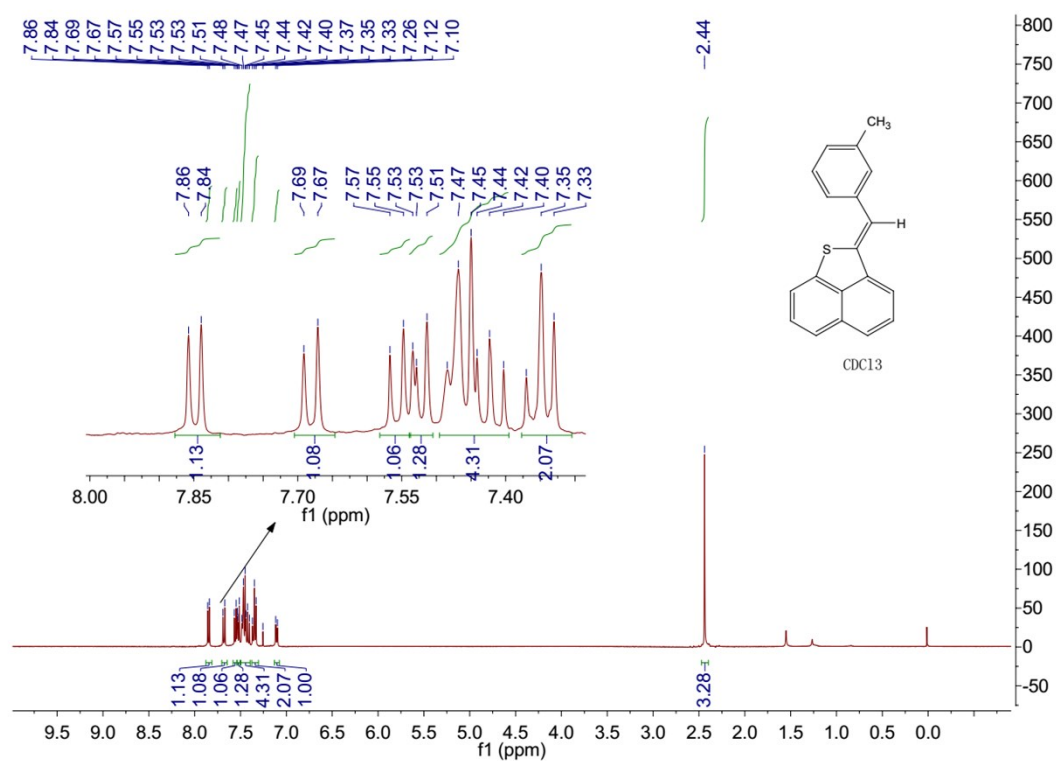
(Z)-2-(3,4-dichlorobenzylidene)-2H-naphtho[1,8-bc]thiophene (3j)



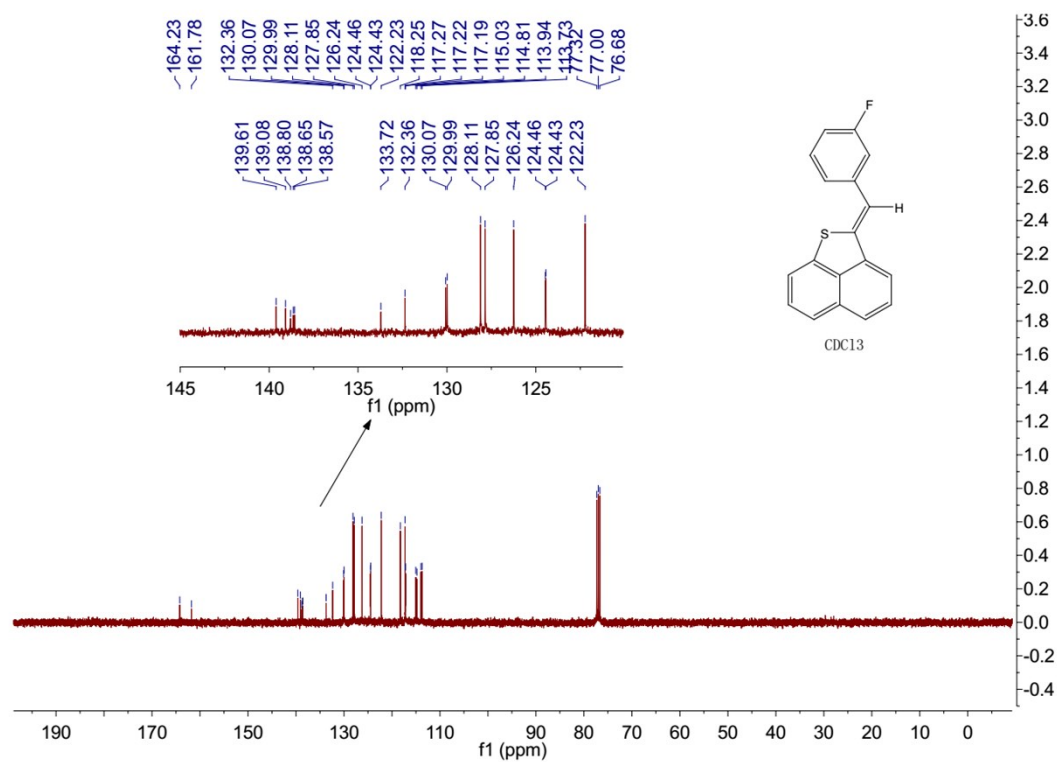
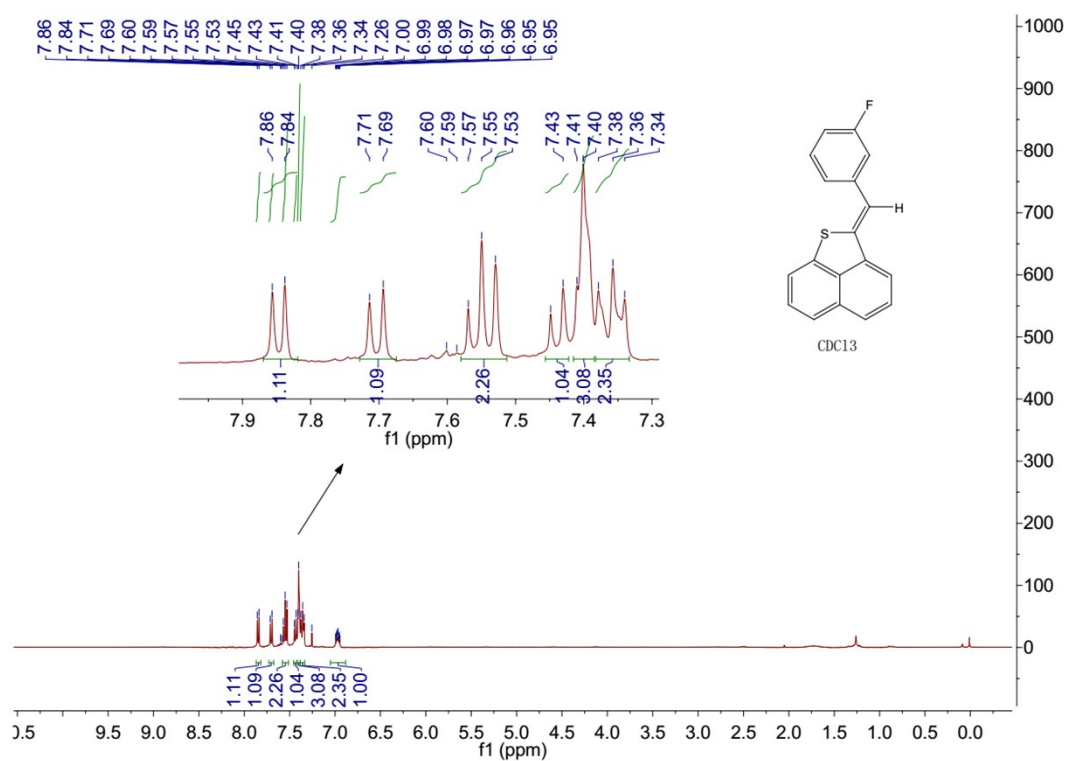
(Z)-2-(naphthalen-1-ylmethylene)-2H-naphtho[1,8-bc]thiophene (3k)

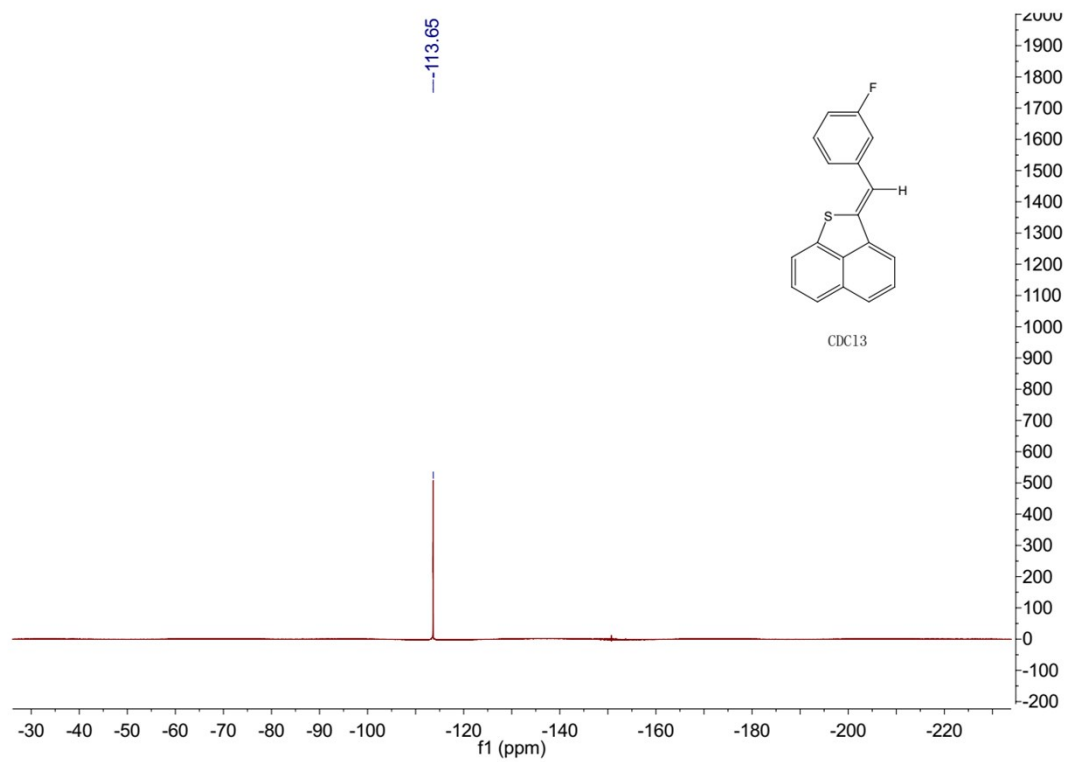


(Z)-2-(3-methylbenzylidene)-2H-naphtho[1,8-bc]thiophene (3l)

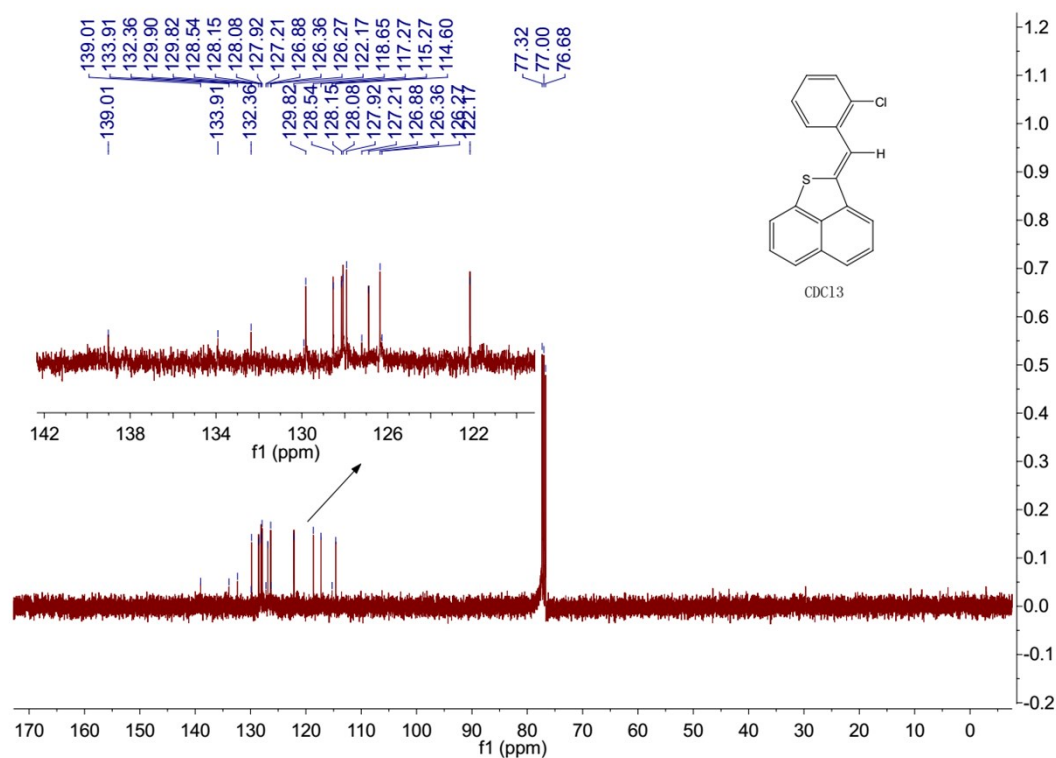
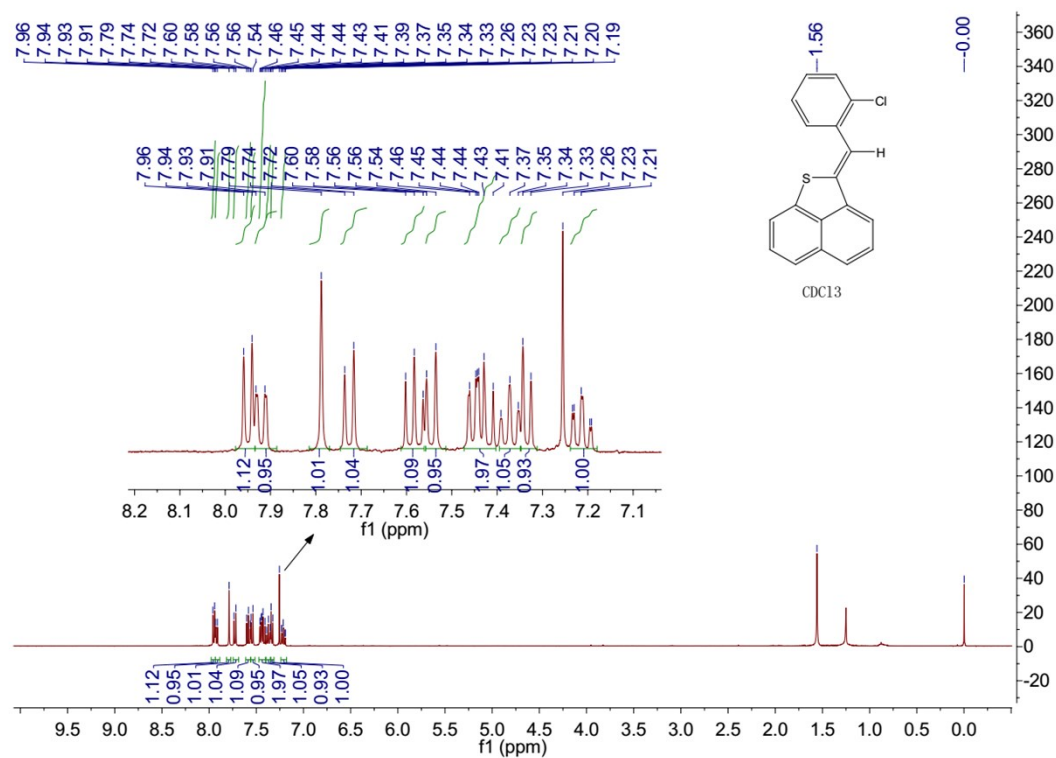


(Z)-2-(3-fluorobenzylidene)-2H-naphtho[1,8-bc]thiophene (3m)

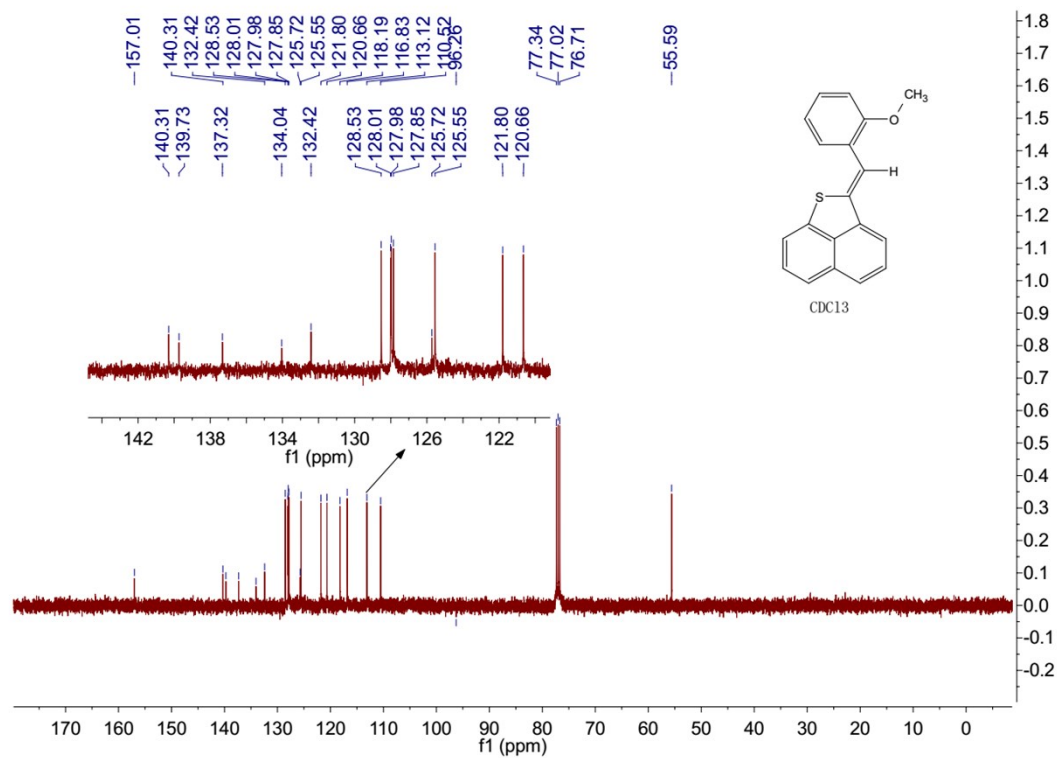
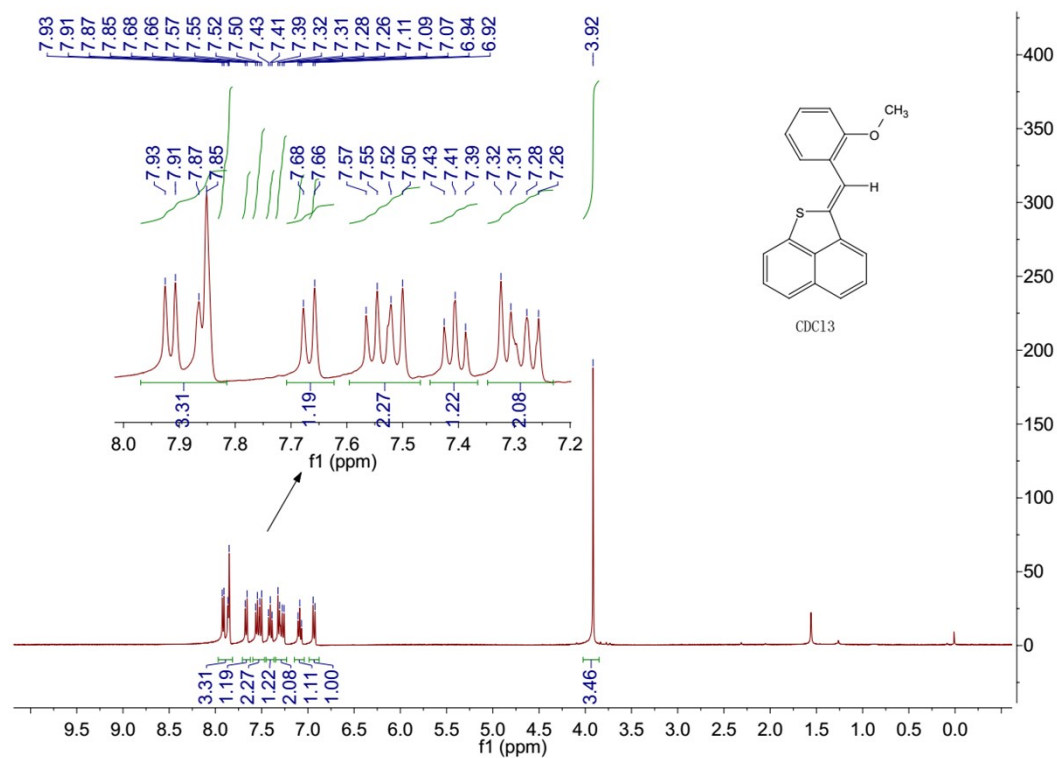




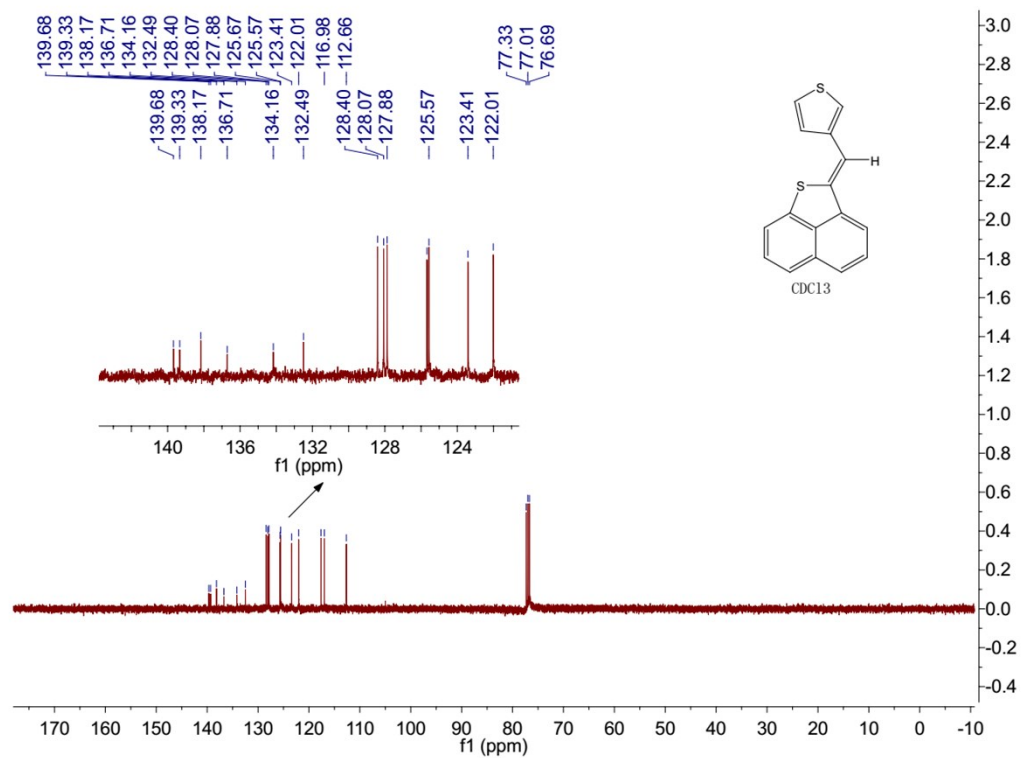
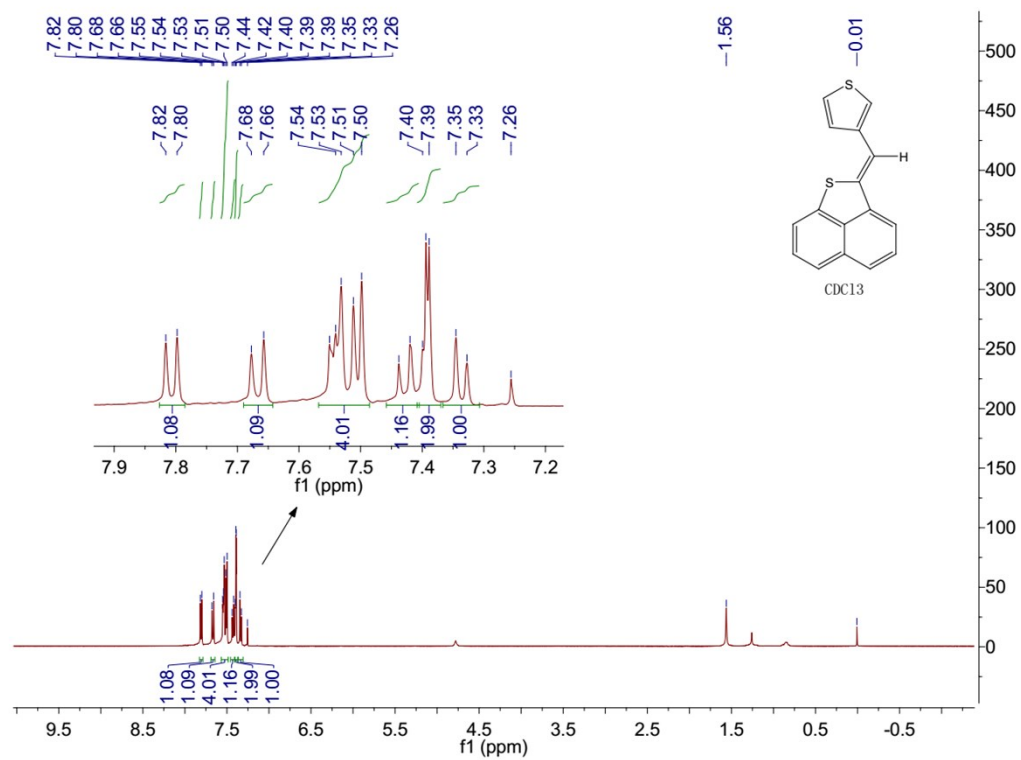
(Z)-2-(2-chlorobenzylidene)-2H-naphtho[1,8-bc]thiophene (3n)



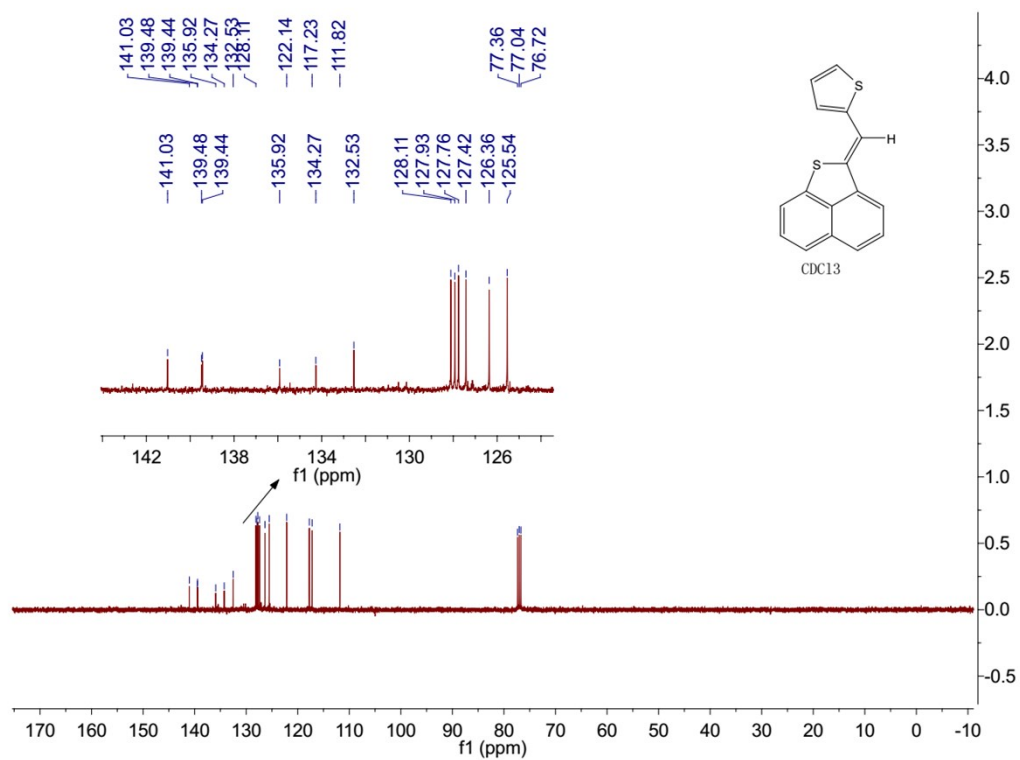
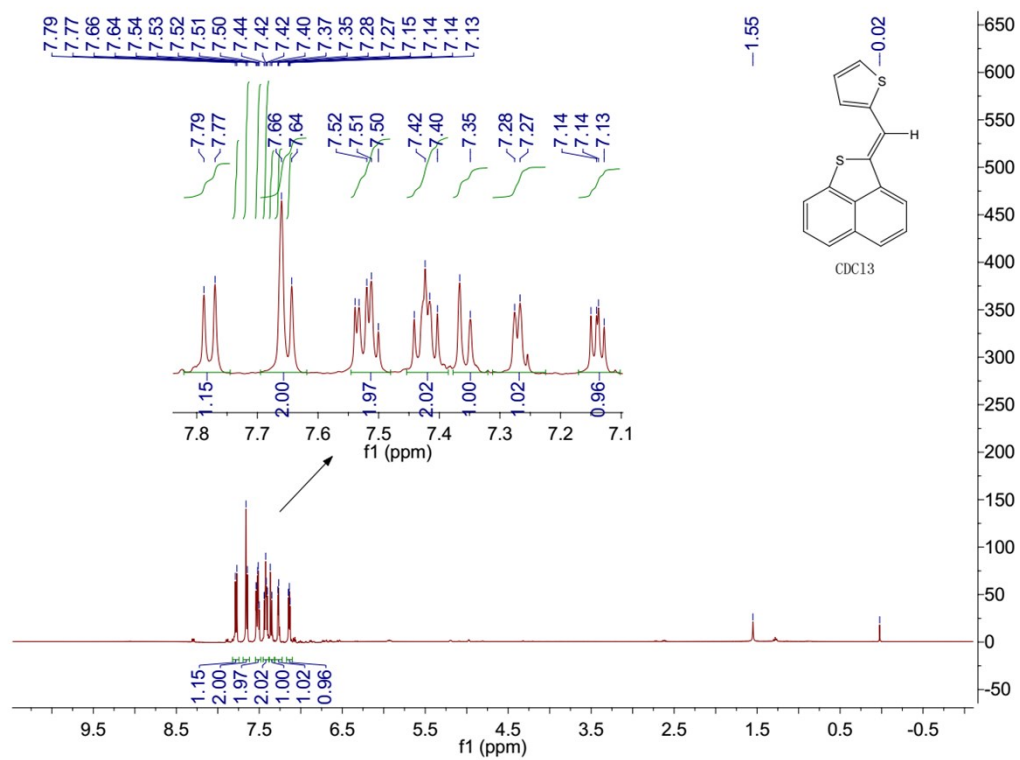
(Z)-2-(2-methoxybenzylidene)-2H-naphtho[1,8-bc]thiophene (3o)



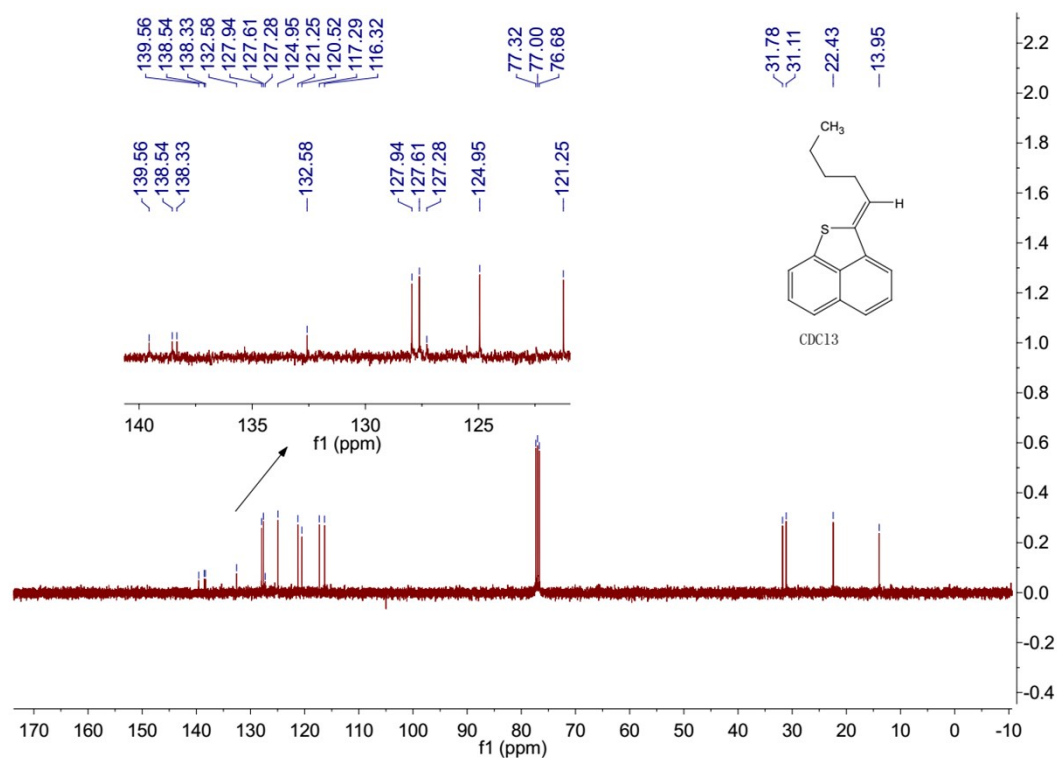
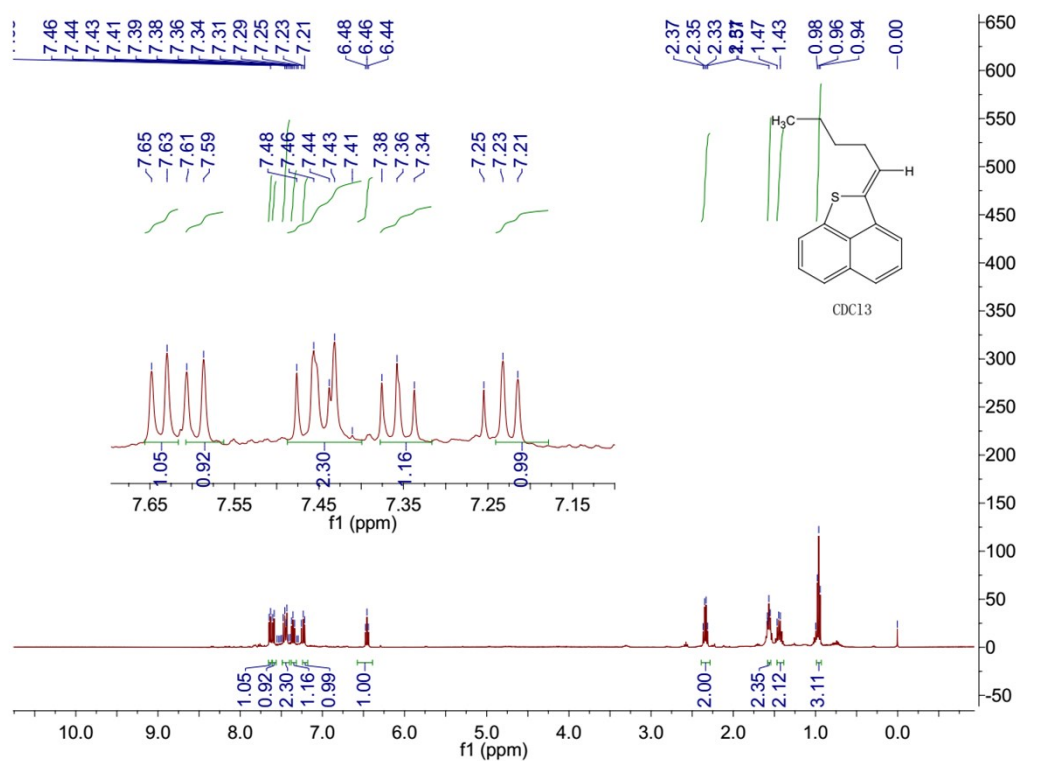
(Z)-2-(thiophen-3-ylmethylene)-2H-naphtho[1,8-*bc*]thiophene (3p)



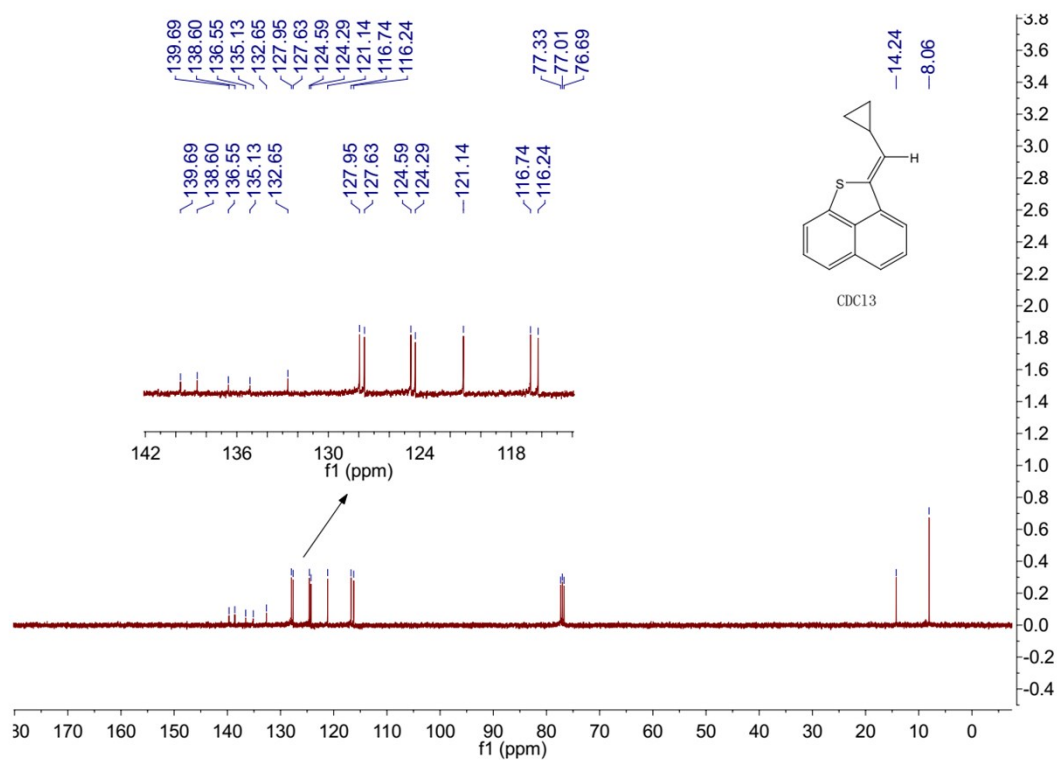
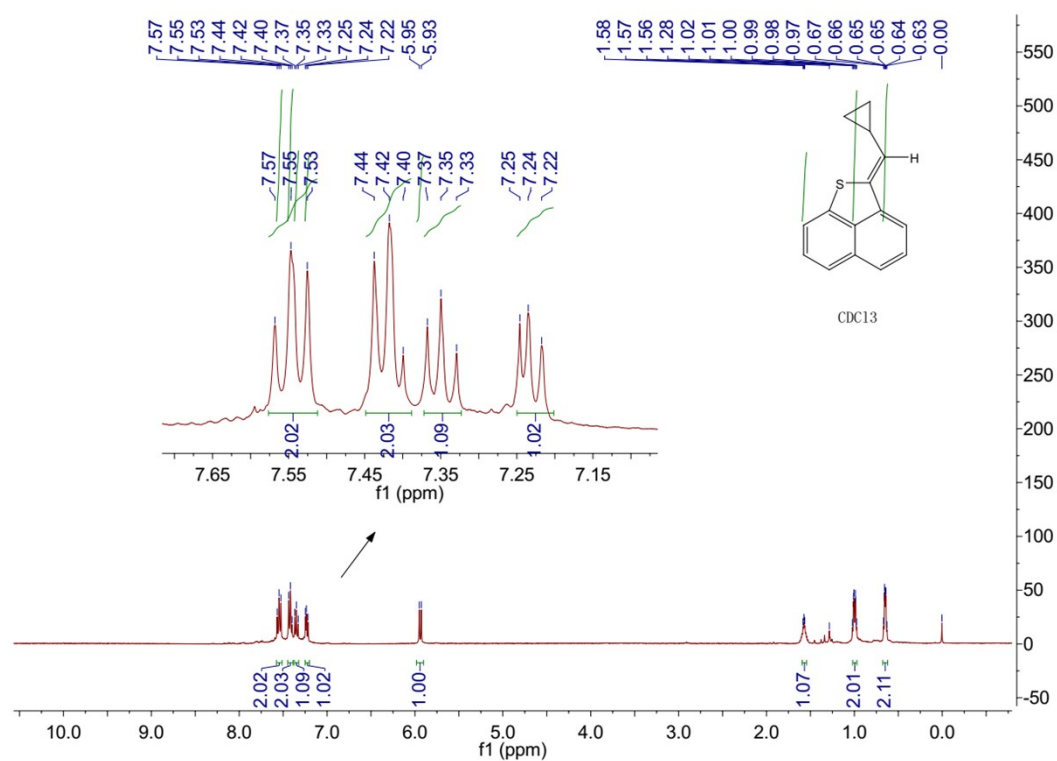
(Z)-2-(thiophen-2-ylmethylene)-2H-naphtho[1,8-*bc*]thiophene (3q)



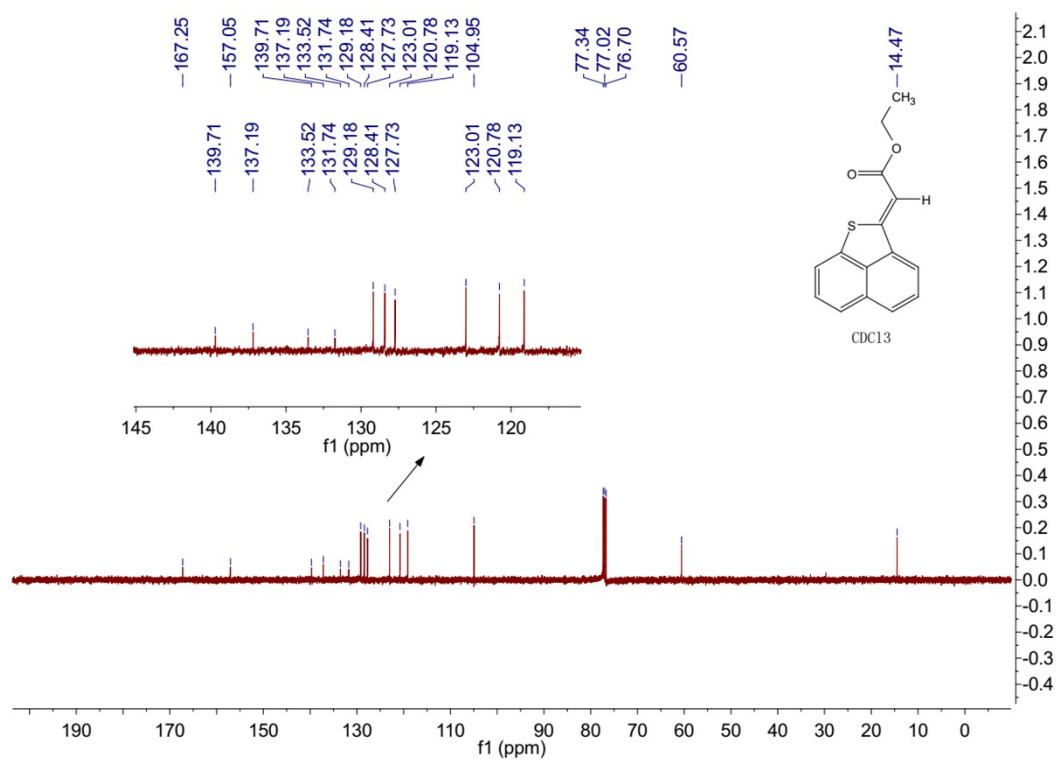
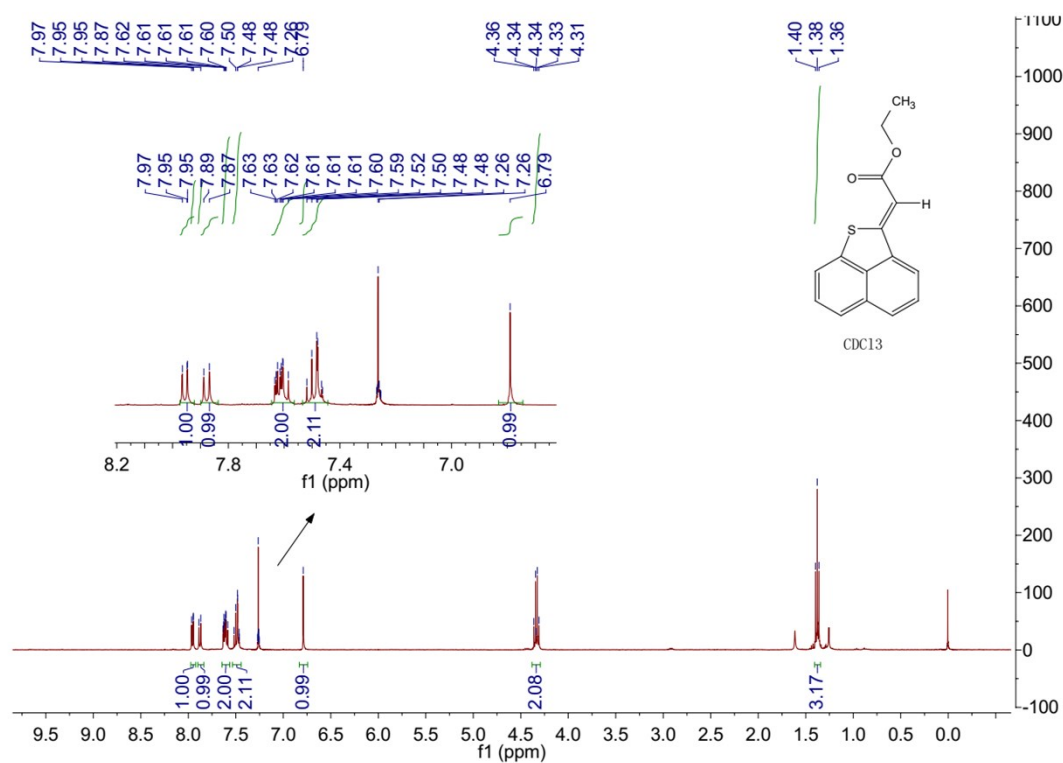
(Z)-2-pentylidene-2H-naphtho[1,8-bc]thiophene (3r)



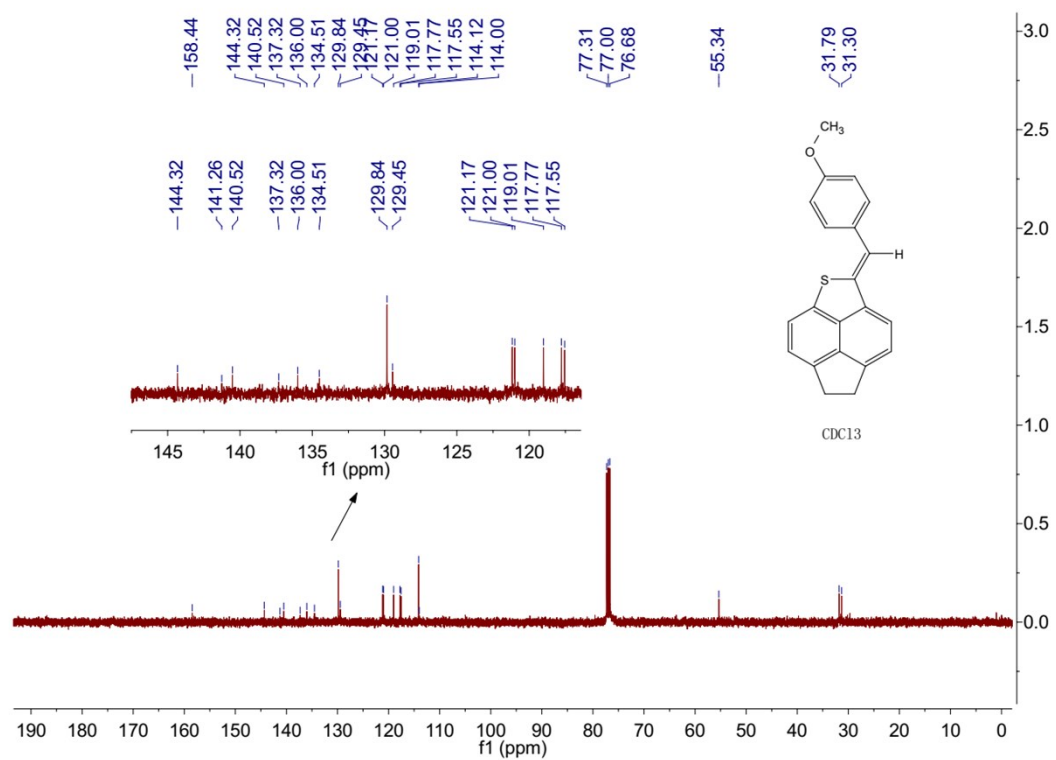
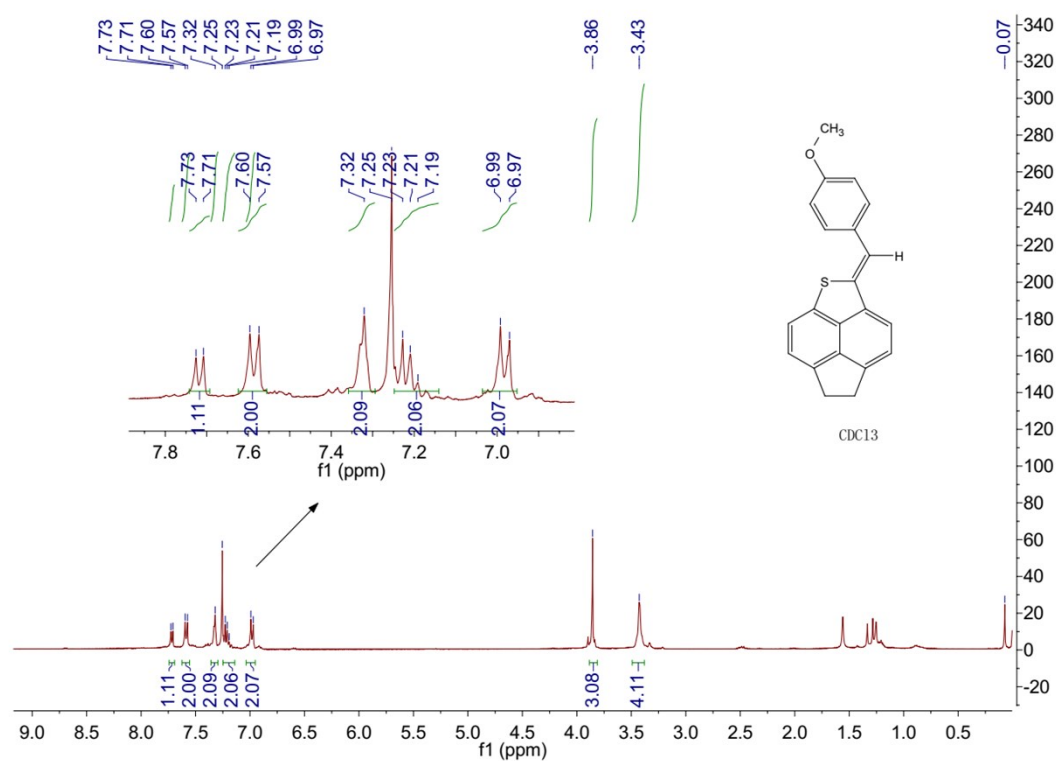
(Z)-2-(cyclopropylmethylene)-2H-naphtho[1,8-bc]thiophene (3s)



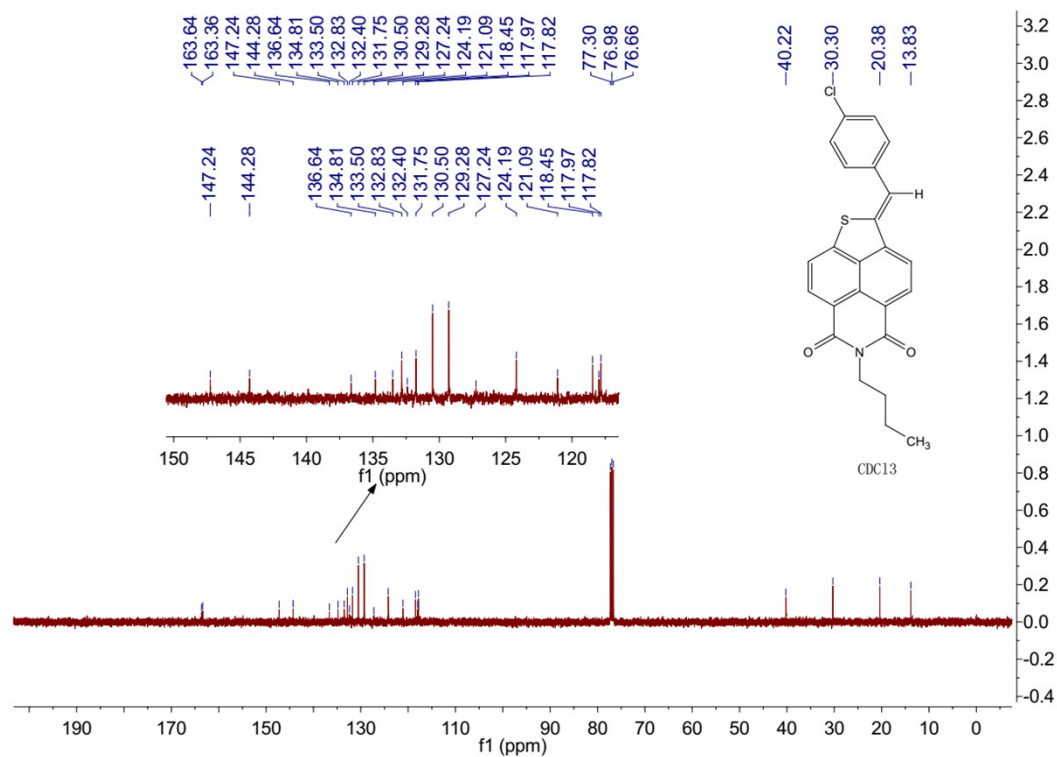
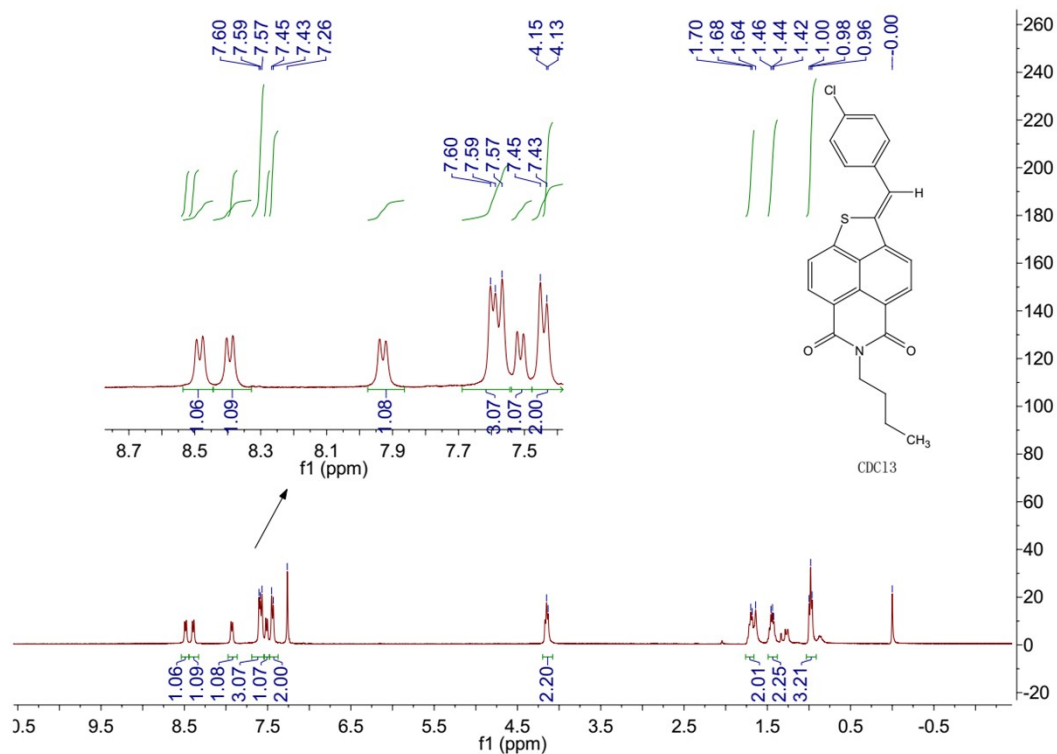
Ethyl (Z)-2-(2H-naphtho[1,8-bc]thiophen-2-ylidene)acetate (3t)



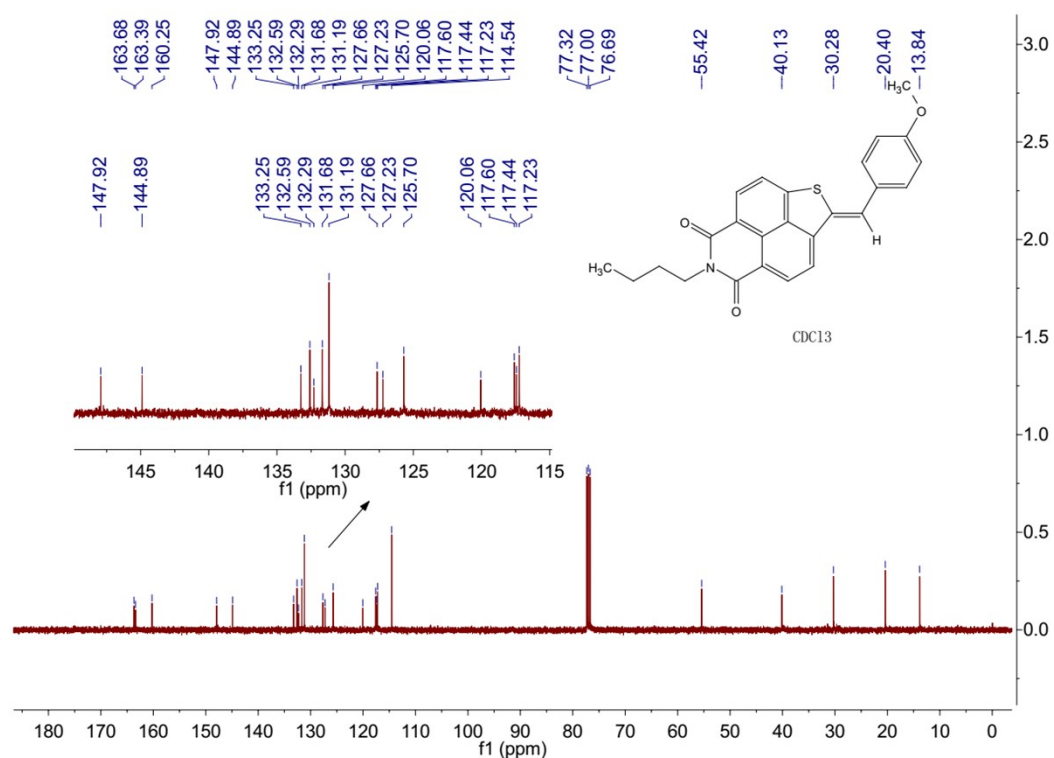
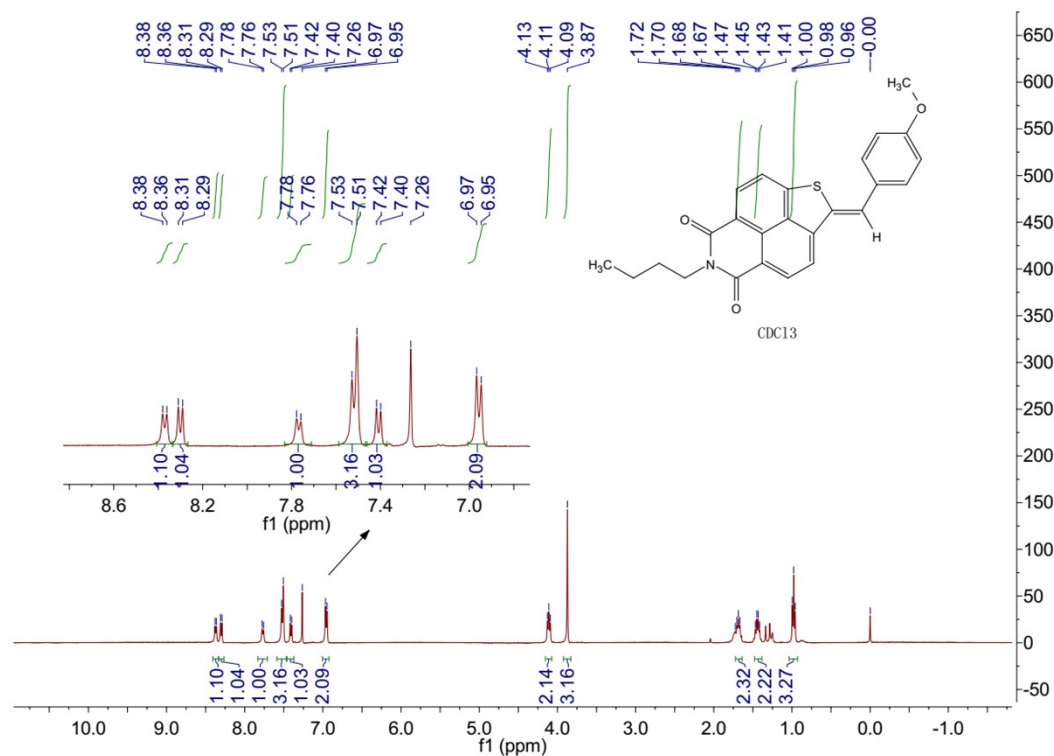
(Z)-2-(4-methoxybenzylidene)-5,6-dihydro-2H-acenaphtho[5,6-*bc*]thiophene (3u)



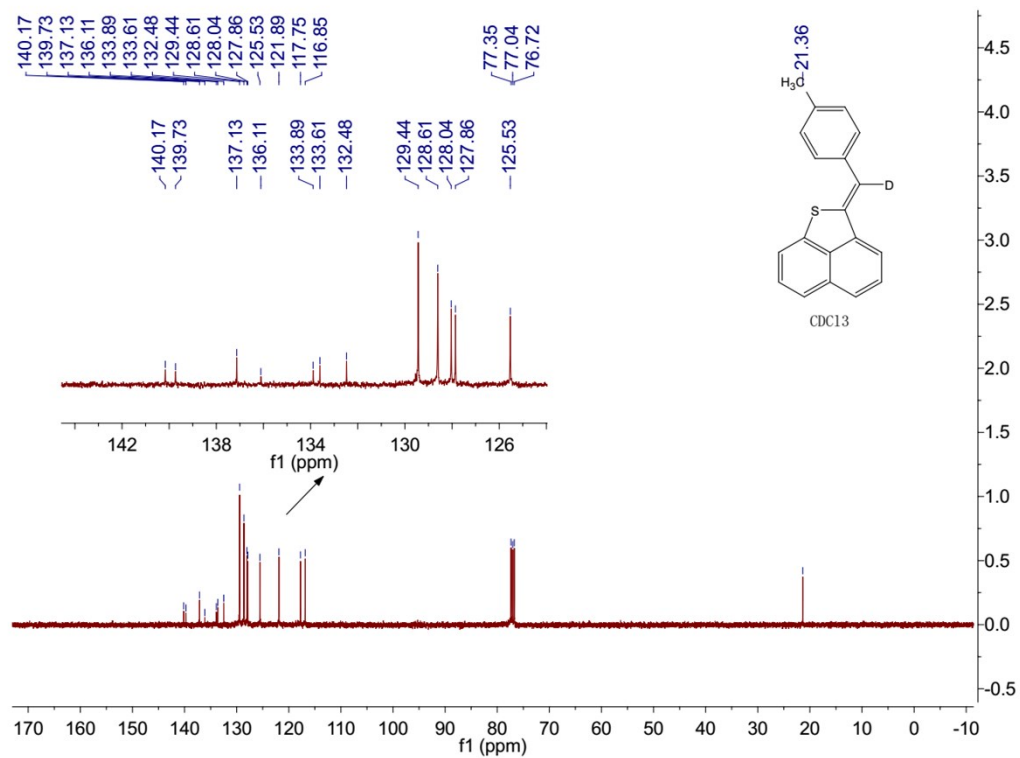
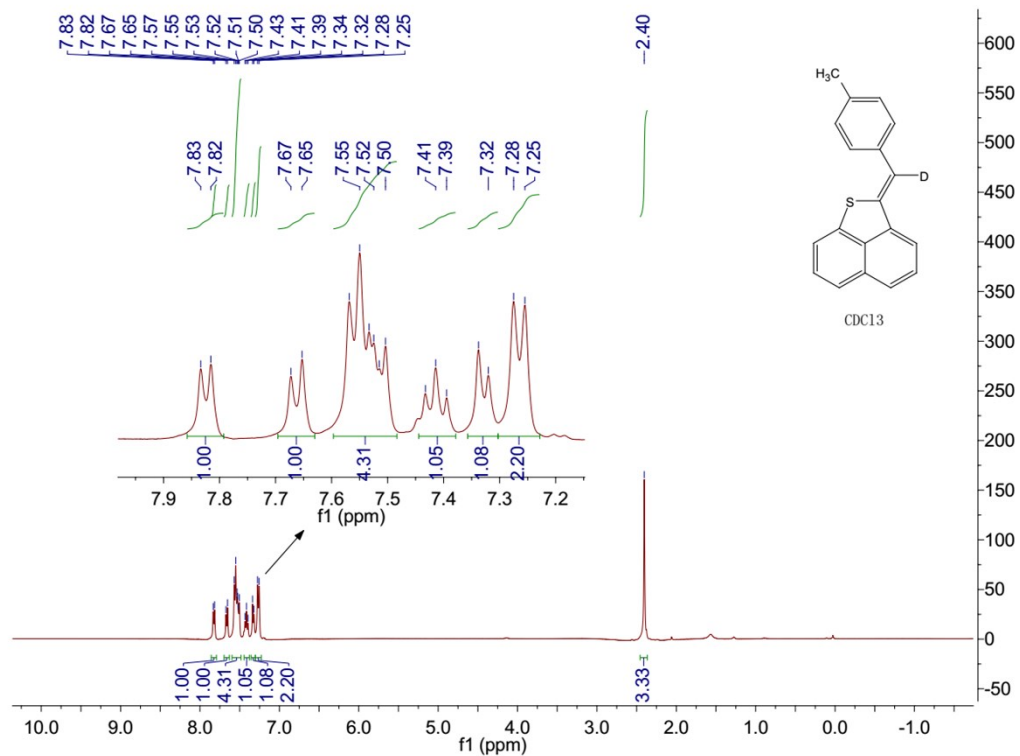
(Z)-6-butyl-2-(4-chlorobenzylidene)thieno[2',3',4':4,5]naphtho[1,8-cd]pyridine-5,7(2H,6H)-dione (3v)



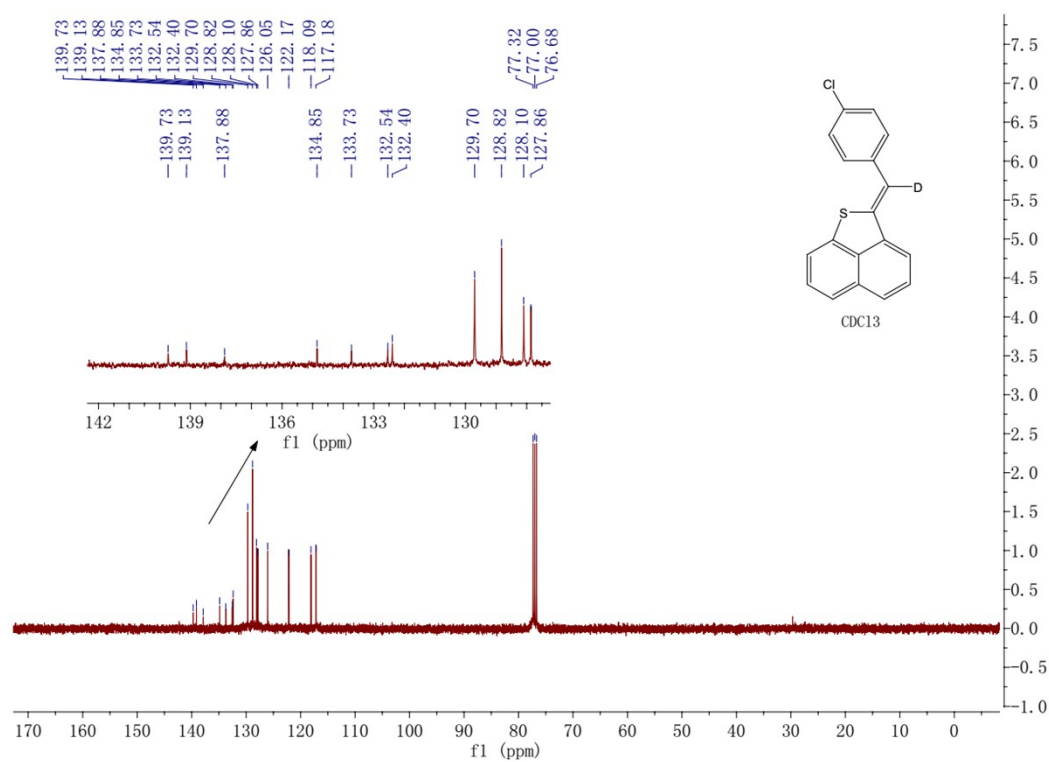
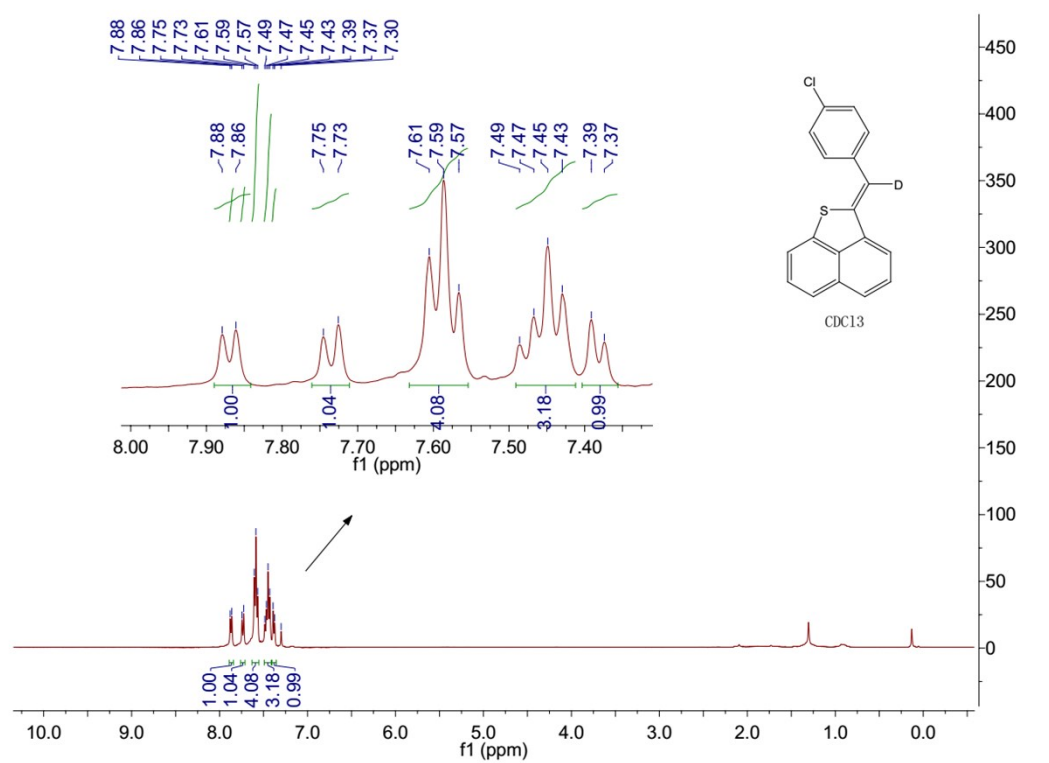
(Z)-6-butyl-2-(4-methoxybenzylidene)thieno[2',3',4':4,5]naphtho[1,8-cd]pyridine-5,7(2H,6H)-dione (3w)



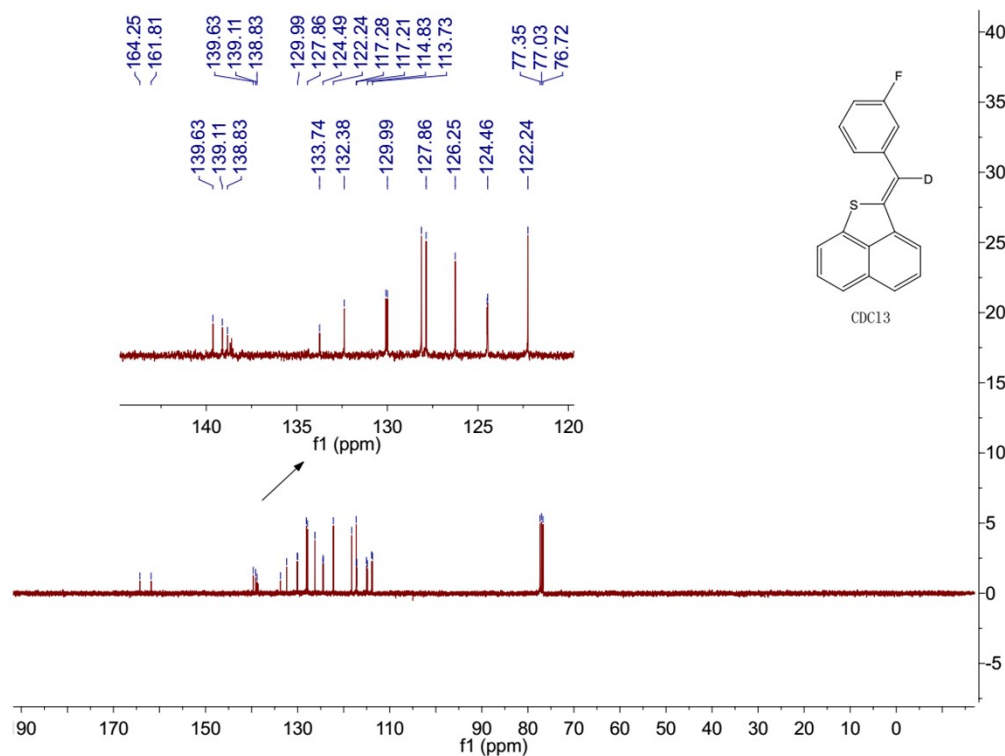
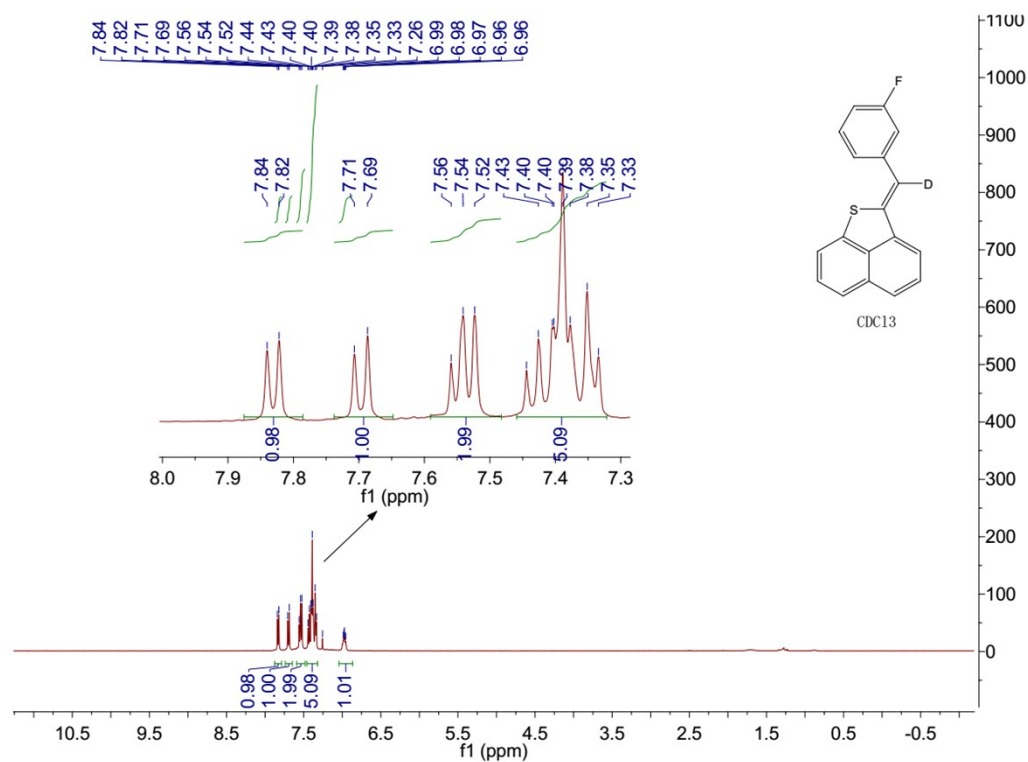
(Z)-2-((4-methylphenyl)methylene-*d*)-2H-naphtho[1,8-*bc*]thiophene (5a)

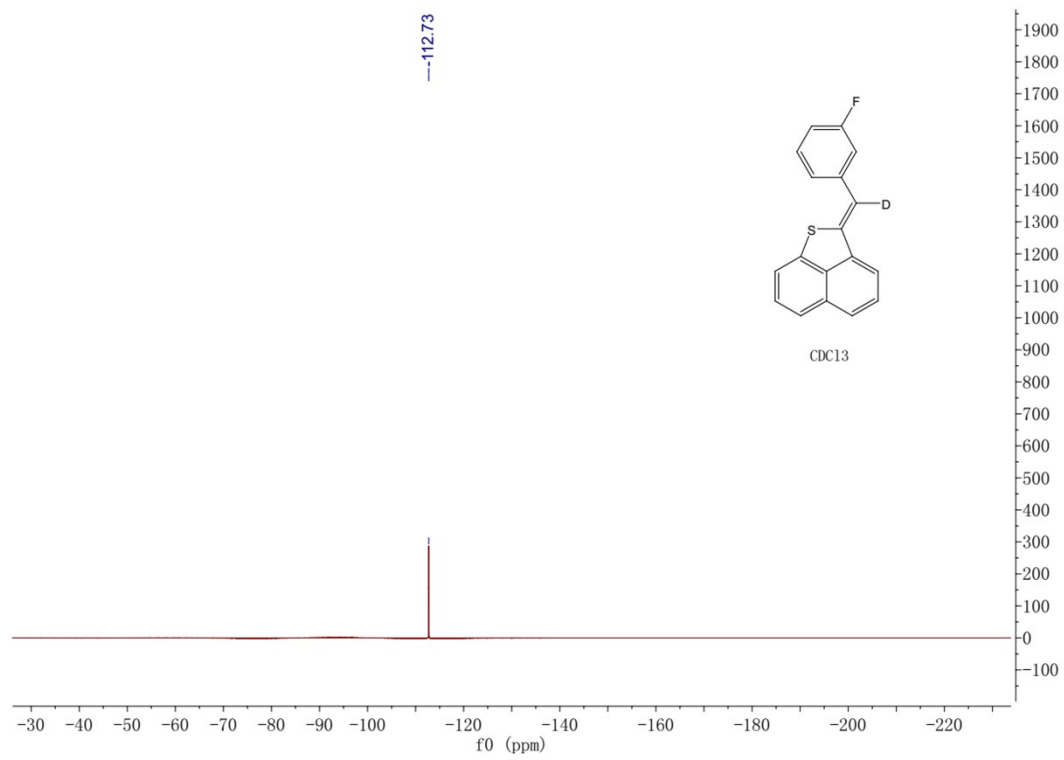


(Z)-2-((4-chlorophenyl)methylene-*d*)-2*H*-naphtho[1,8-*bc*]thiophene (5b)

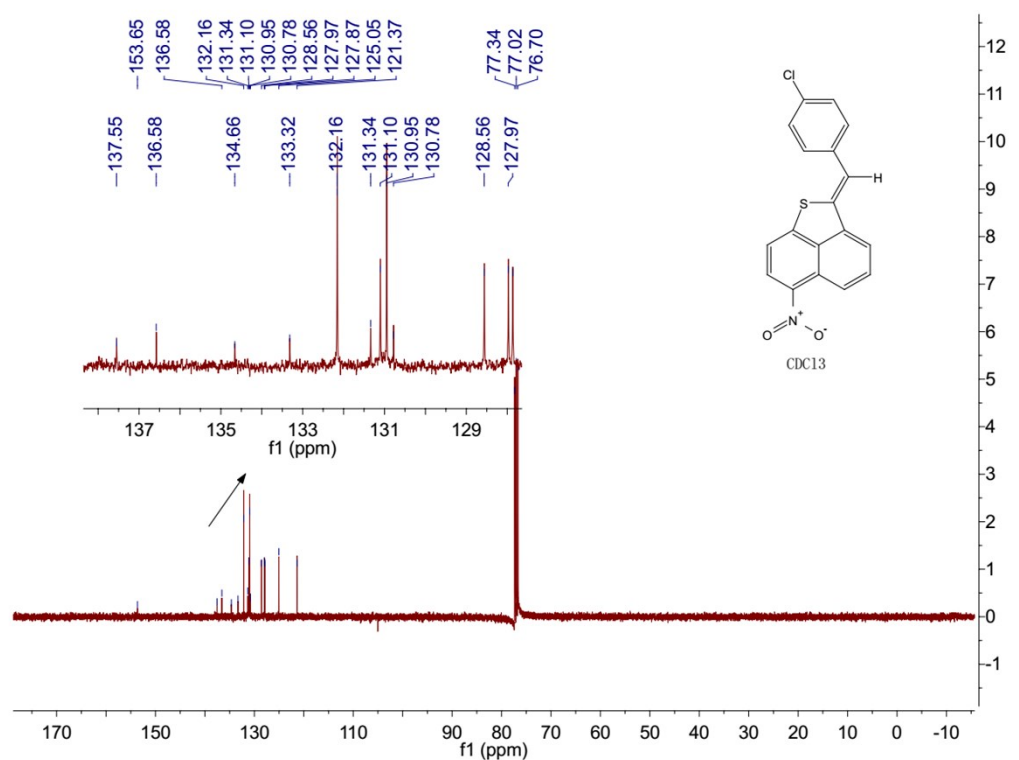
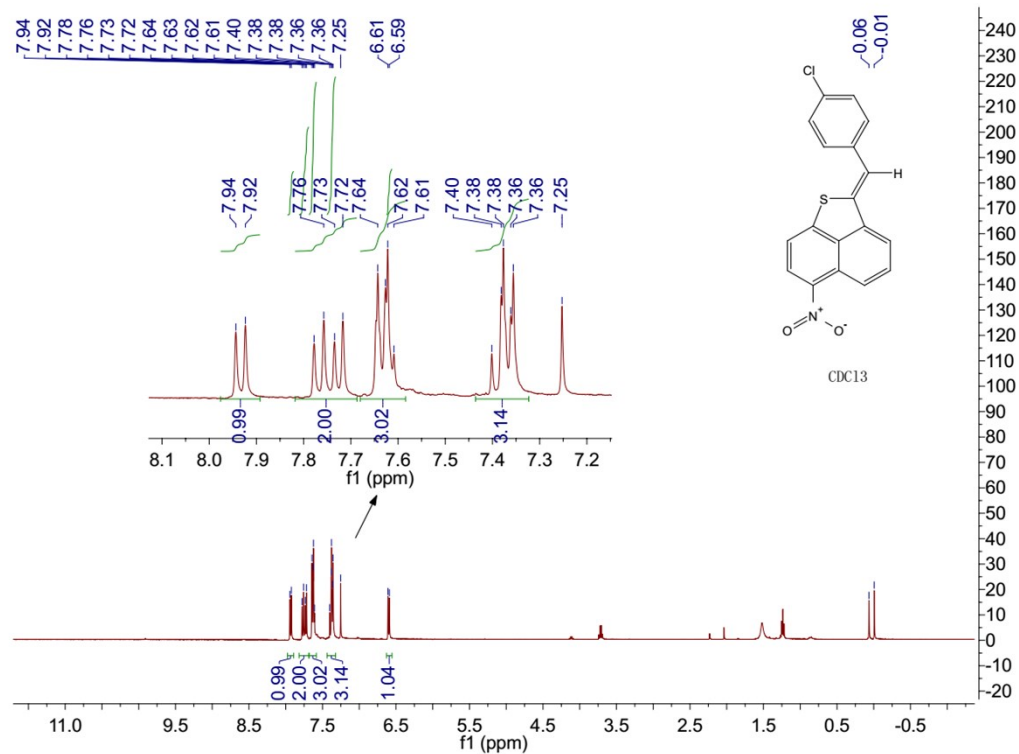


(Z)-2-((3-fluorophenyl)methylene-d)-2H-naphtho[1,8-bc]thiophene (5c)





1-(Naphthalen-2-ylsulfonyl)benzo[*cd*]indol-2(1*H*)-one (6)



S-(8-((4-chlorophenyl)ethynyl)naphthalen-1-yl) O-ethyl carbonodithioate

