

Copper-Catalyzed Tandem Sulfuration/Annulation of Propargylamines with Sulfur via C–N Bond Cleavage

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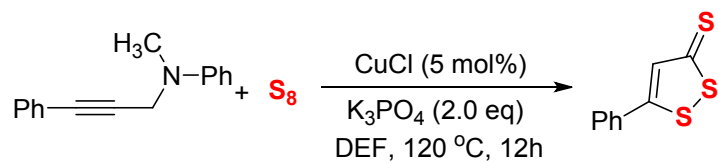
Supporting Information

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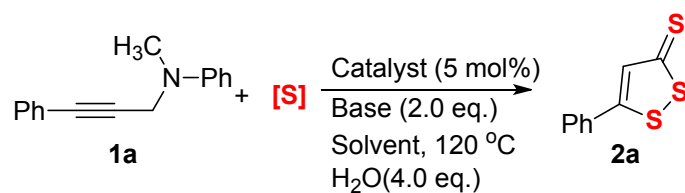
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1. Table S1 The optimization of H₂O equivalent ^a



Entry	H ₂ O (eq.)	Yield (%)
1	0	51
2	2	59
3	4	88
4	6	81
5	8	69
6	10	66
^a Reaction conditions: 1a (0.2 mmol), S₈ (0.3 mmol), CuCl (5 mol%), K ₃ PO ₄ (0.4 mmol), and DEF (2.0 mL), 120 °C, 12 h; isolated yield.		

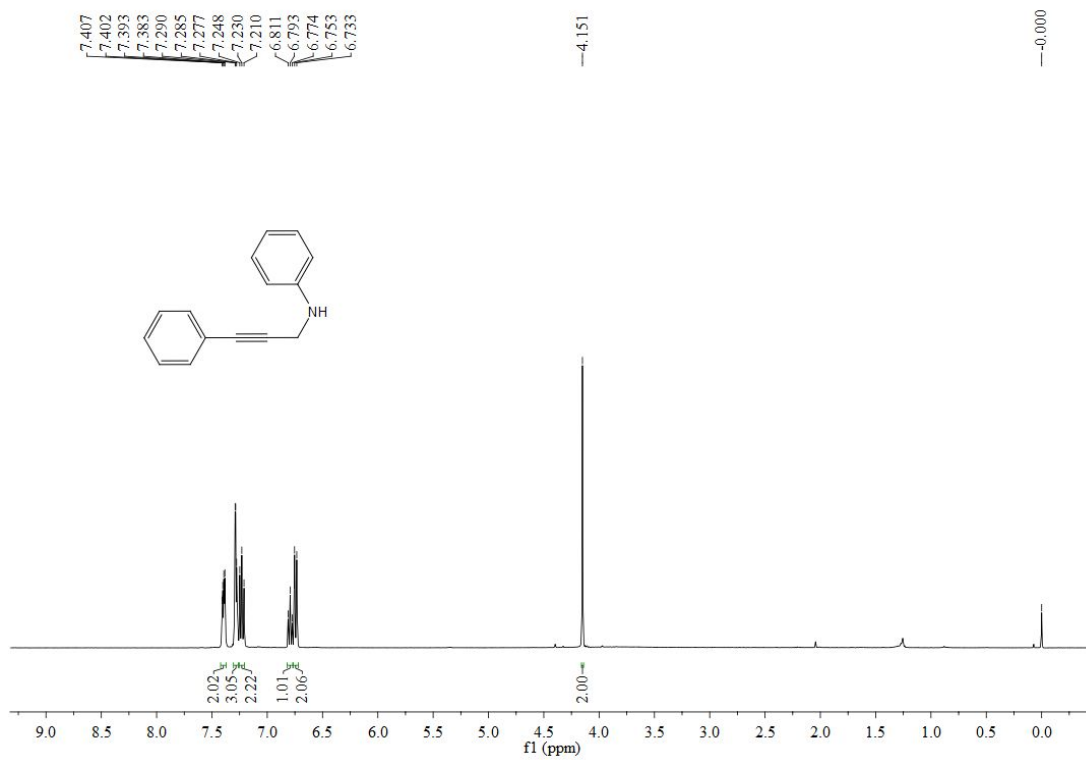
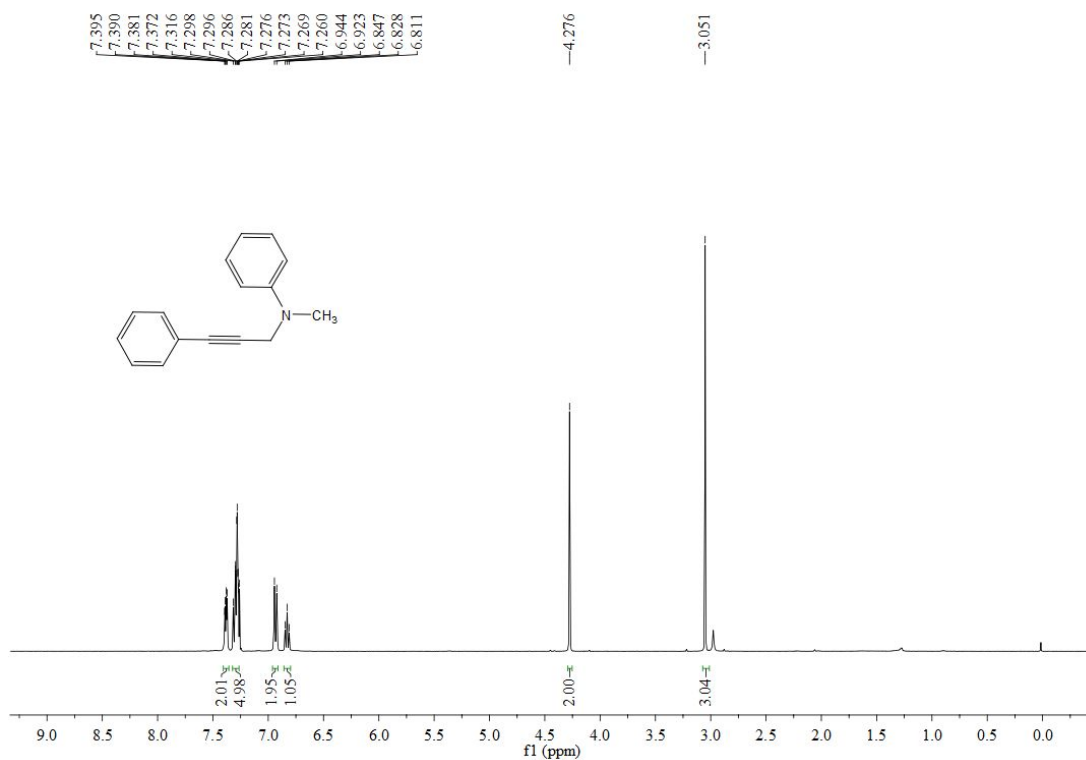
2. Table S2 Optimization of the Reaction Conditions ^a

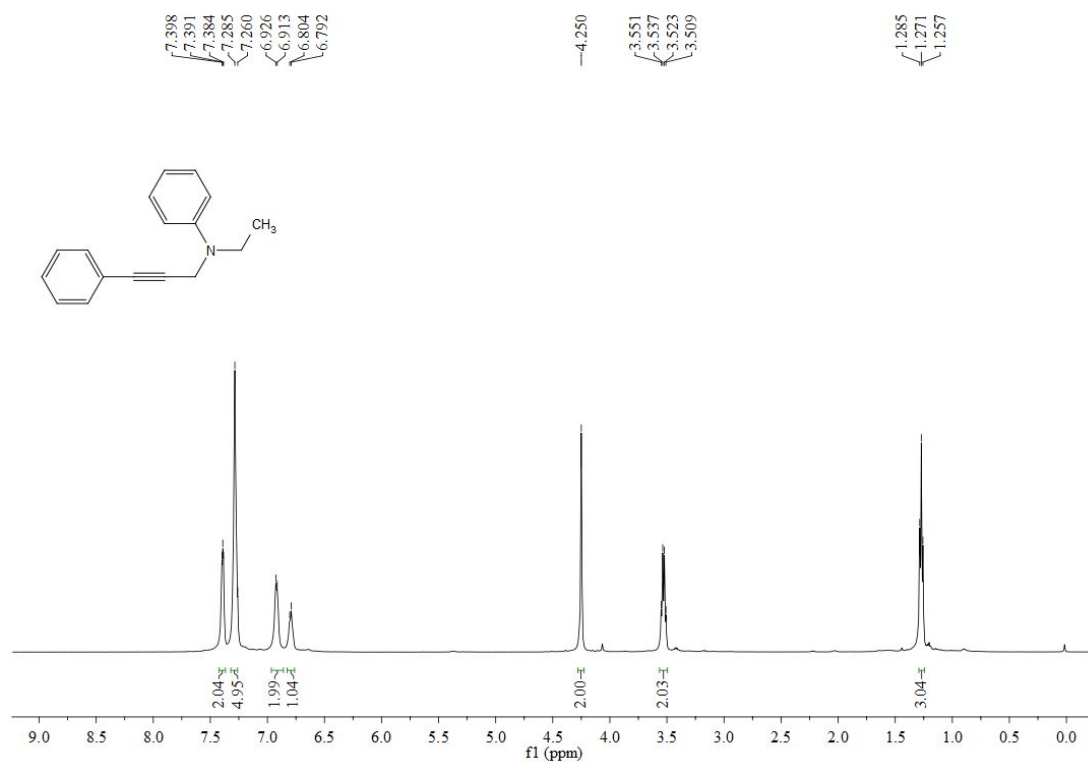


Entry	Catalyst	[S]	Base	Solvent	Yield (%)
1	CuCl	S ₈	NaOAc	NMP	62
2	CuBr	S ₈	NaOAc	NMP	58
3	CuI	S ₈	NaOAc	NMP	55
4	CuOAc	S ₈	NaOAc	NMP	42
5	Cu ₂ O	S ₈	NaOAc	NMP	35
6	Cu(OAc) ₂	S ₈	NaOAc	NMP	32
7	CuCl	S ₈	NaHCO ₃	NMP	63
8	CuCl	S ₈	KOAc	NMP	65
9	CuCl	S ₈	K ₃ PO ₄	NMP	75
10	CuCl	S ₈	KF	NMP	66
11	CuCl	S ₈	t-BuONa	NMP	33
12	CuCl	S ₈	Na ₂ CO ₃	NMP	23
13	CuCl	S ₈	Cs ₂ CO ₃	NMP	27
14	CuCl	S ₈	NEt ₃	NMP	56
15	CuCl	S ₈	DBU	NMP	55
16	CuCl	S ₈	K ₃ PO ₄	DMSO	61
17	CuCl	S ₈	K ₃ PO ₄	DMF	ND
18	CuCl	S ₈	K ₃ PO ₄	DEF	88
19	CuCl	S ₈	K ₃ PO ₄	DMAc	58
20	CuCl	S ₈	K ₃ PO ₄	Toluene	trace
21	CuCl	S ₈	K ₃ PO ₄	DEF	NR ^b
22	-	S ₈	K ₃ PO ₄	DEF	35
23	-	S ₈	K ₃ PO ₄	DEF	trace ^c
24	CuCl	Na ₂ S	K ₃ PO ₄	DEF	NR
25	CuCl	NaHS	K ₃ PO ₄	DEF	NR
26	CuCl	K ₂ S	K ₃ PO ₄	DEF	NR
27	CuCl	Tetramethylthiuram disulfide	K ₃ PO ₄	DEF	NR
28	CuCl	S ₈	K ₃ PO ₄	DEF	68 ^d , 89 ^e
29	CuCl	S ₈	K ₃ PO ₄	DEF	53 ^f , 87 ^g

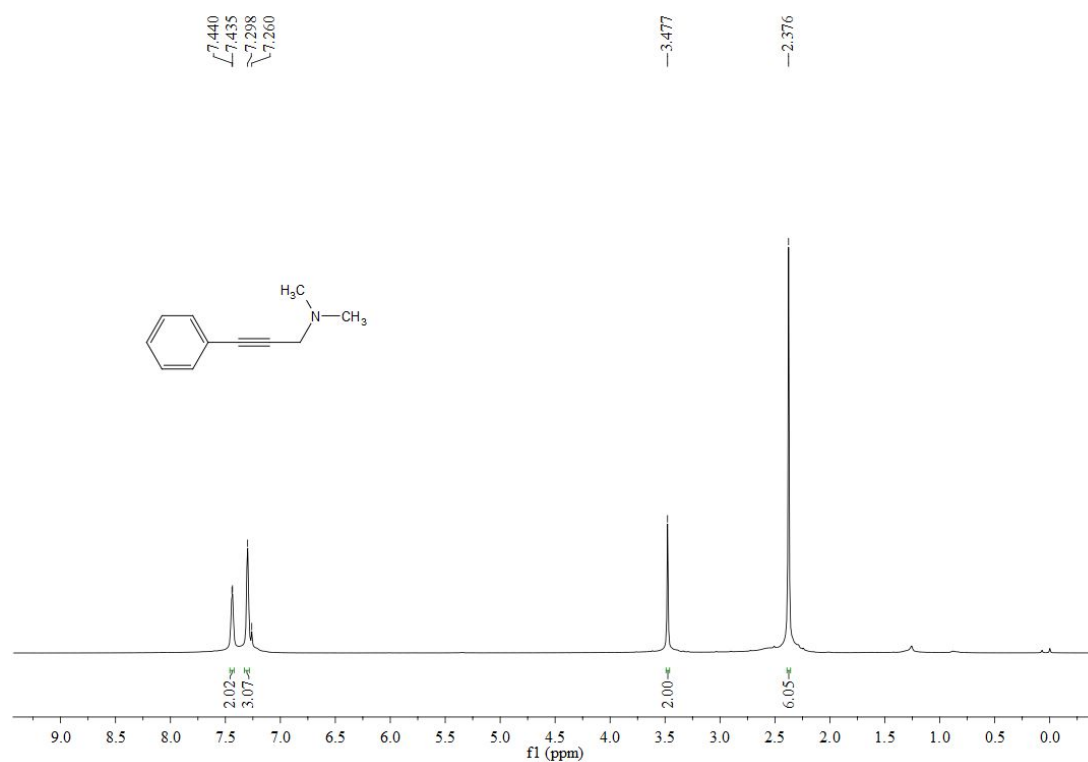
^a Reaction conditions: **1a** (0.2 mmol), [S] (0.3 mmol), catalyst (5 mol%), base (0.4 mmol), H₂O (4.0 eq.) and anhydrous solvent (2.0 mL), 120 °C, 12 h; The isolated yield. ^b under N₂. ^c under O₂. ^d at 110 °C. ^e at 130 °C. ^f for 6 h. ^g for 16 h.

3. NMR Spectra for Starting Reagents 1a-1q.

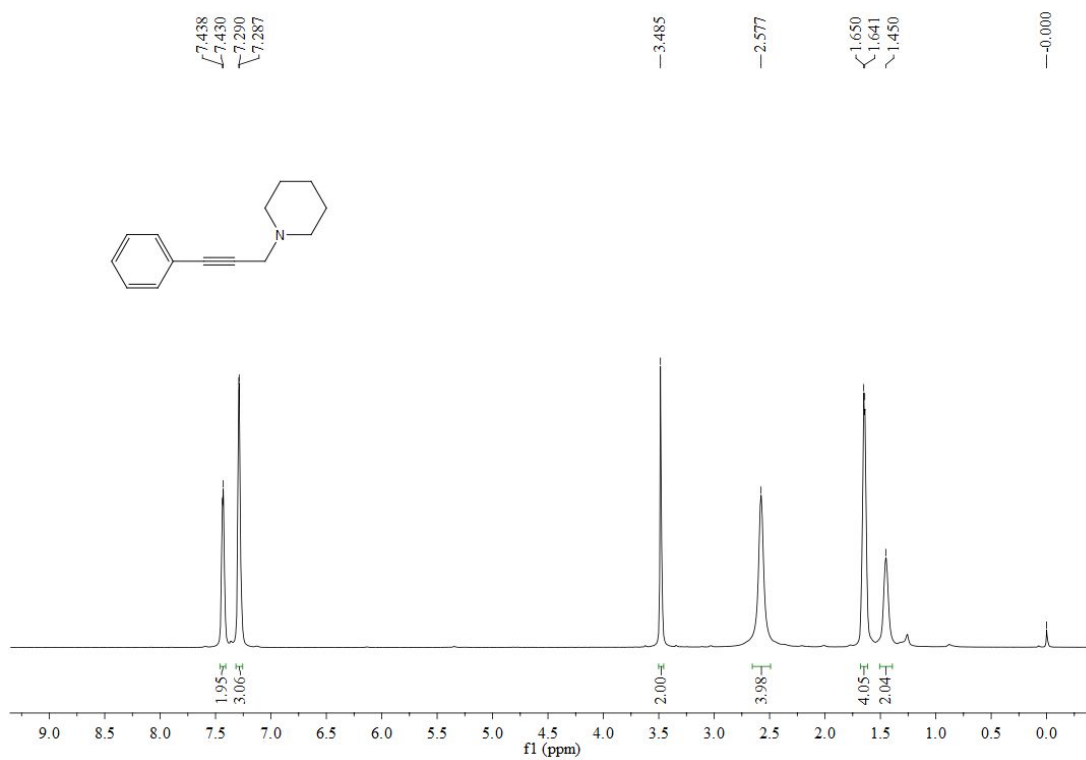
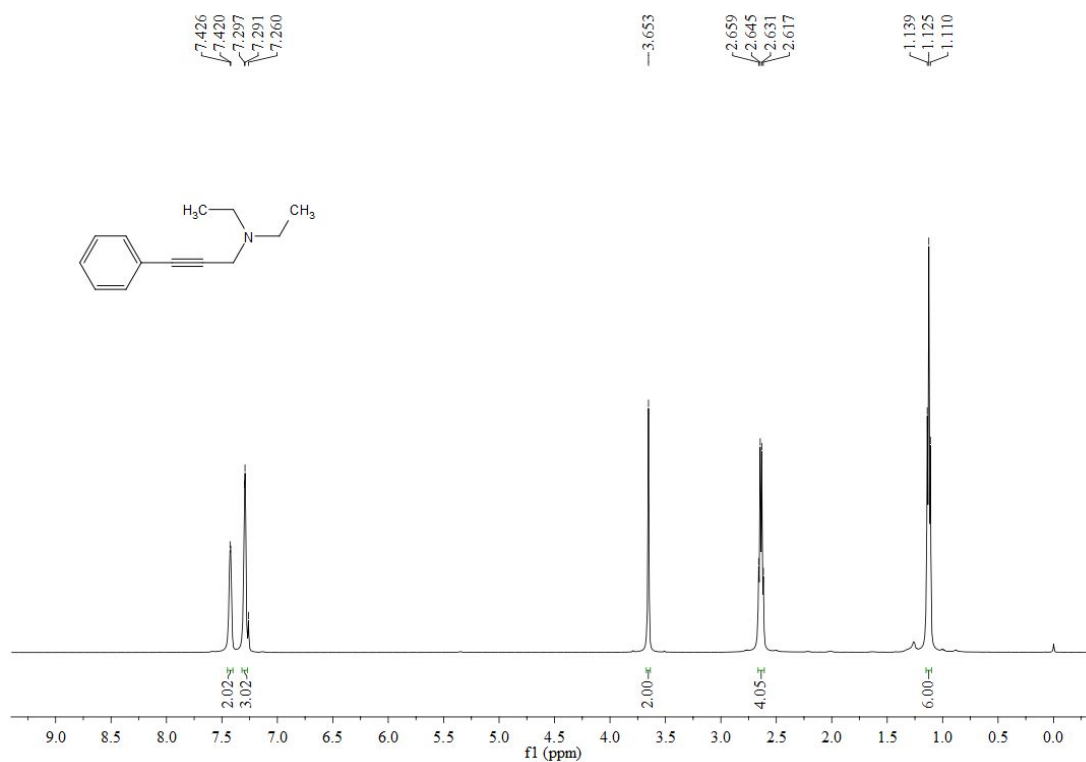


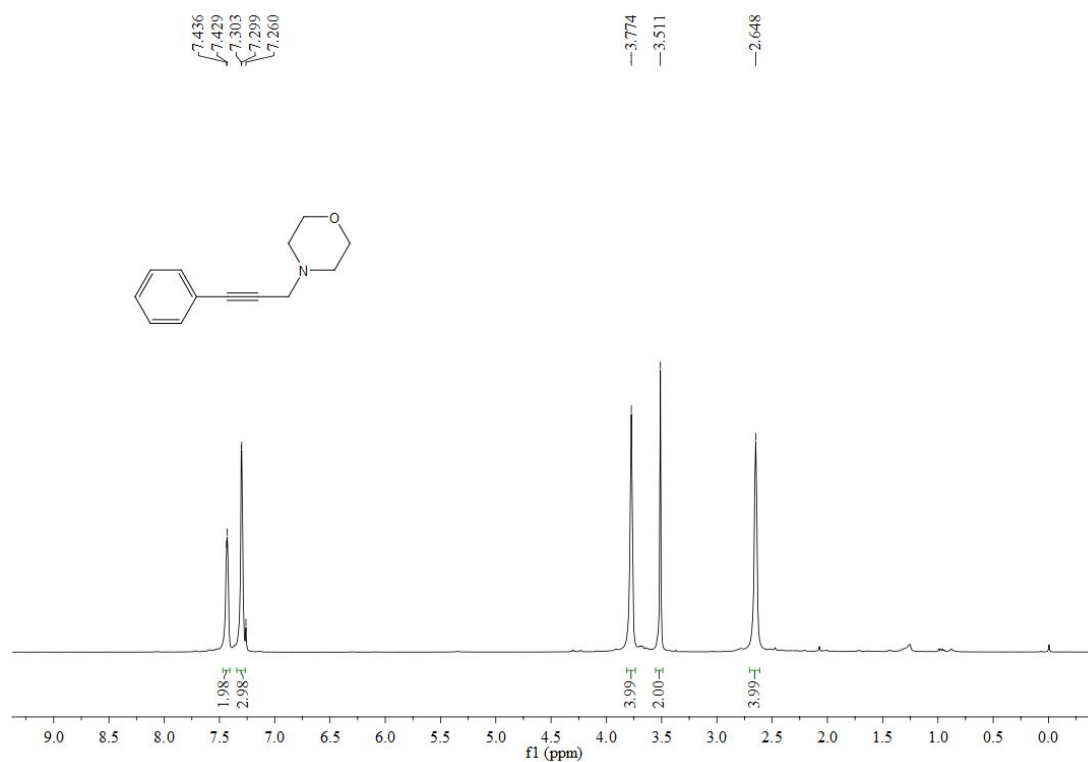


¹H NMR: N-ethyl-N-(3-phenylprop-2-yn-1-yl)aniline (1a-2)

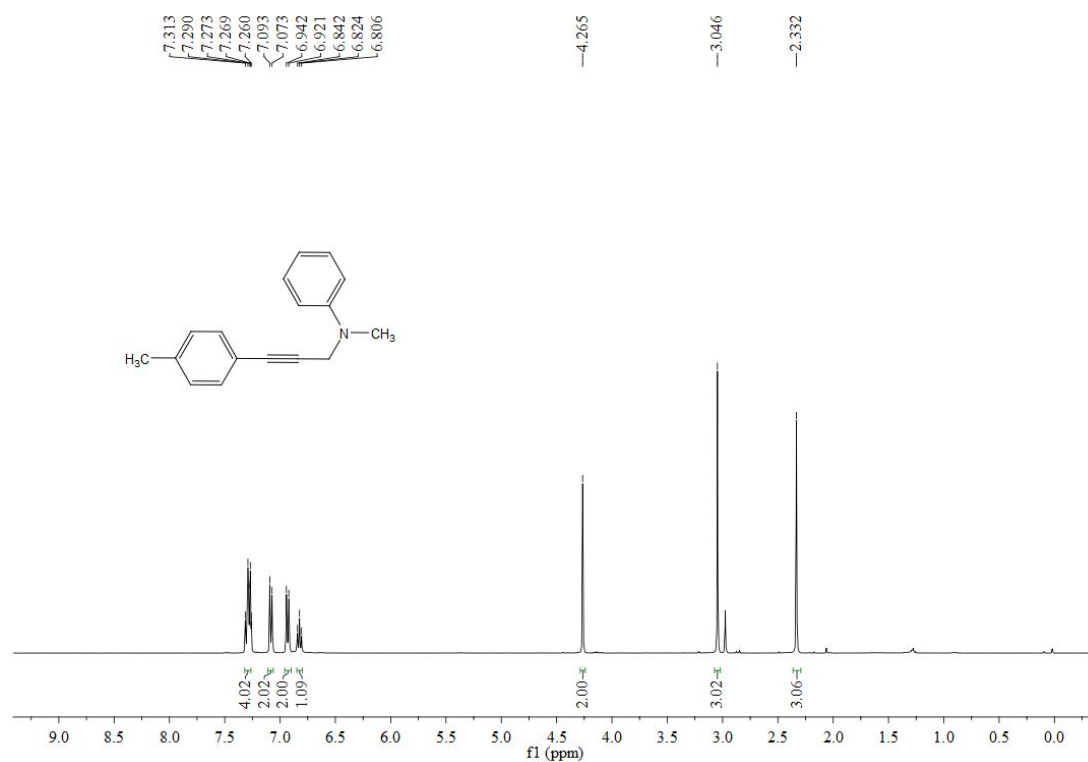


¹H NMR: N,N-dimethyl-3-phenylprop-2-yn-1-amine (1a-3)

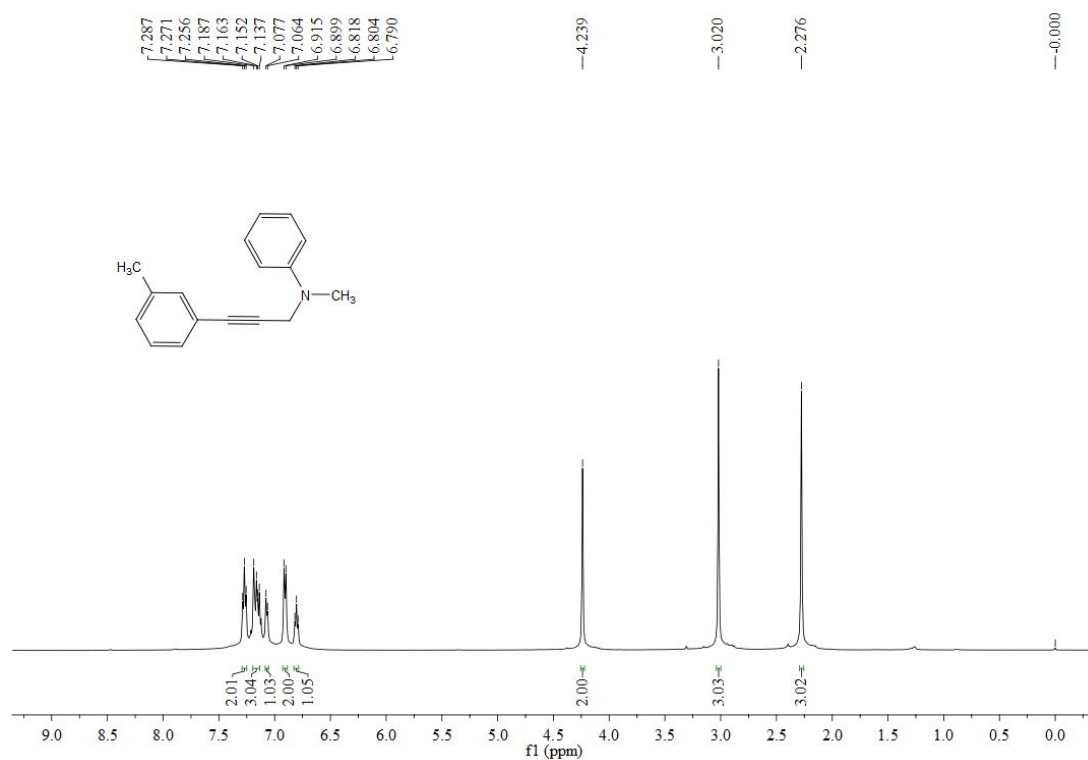




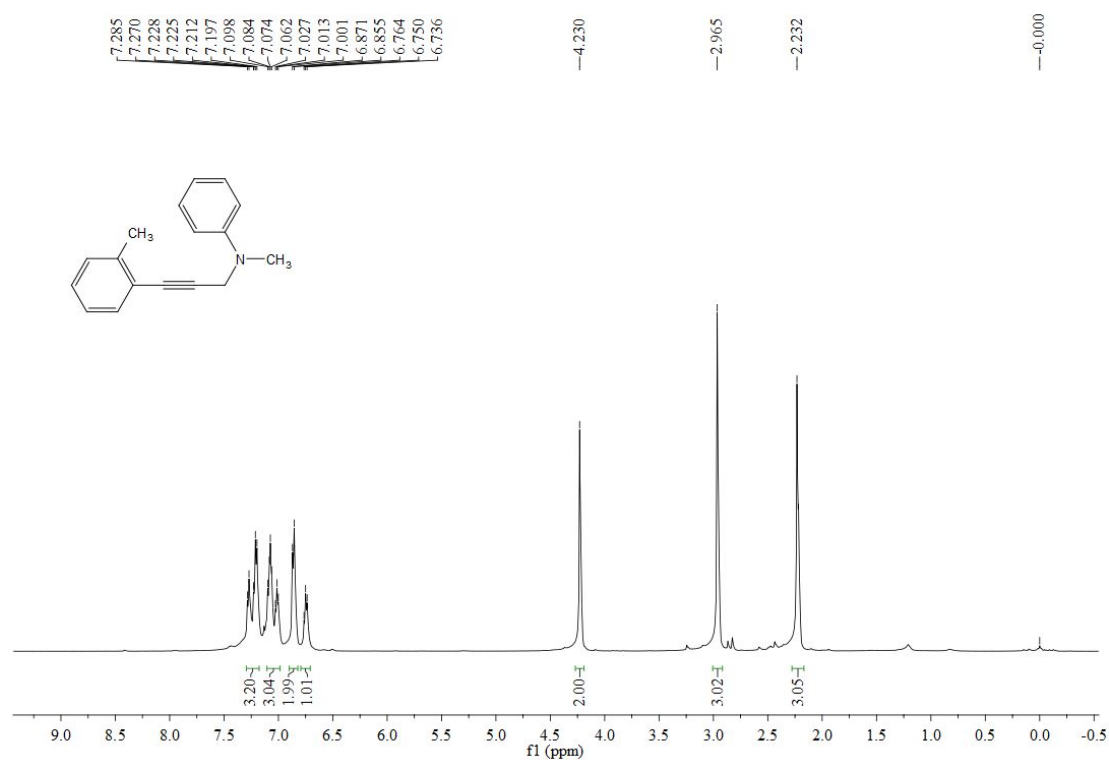
¹H NMR: 4-(3-phenylprop-2-yn-1-yl)morpholine (1a-6)



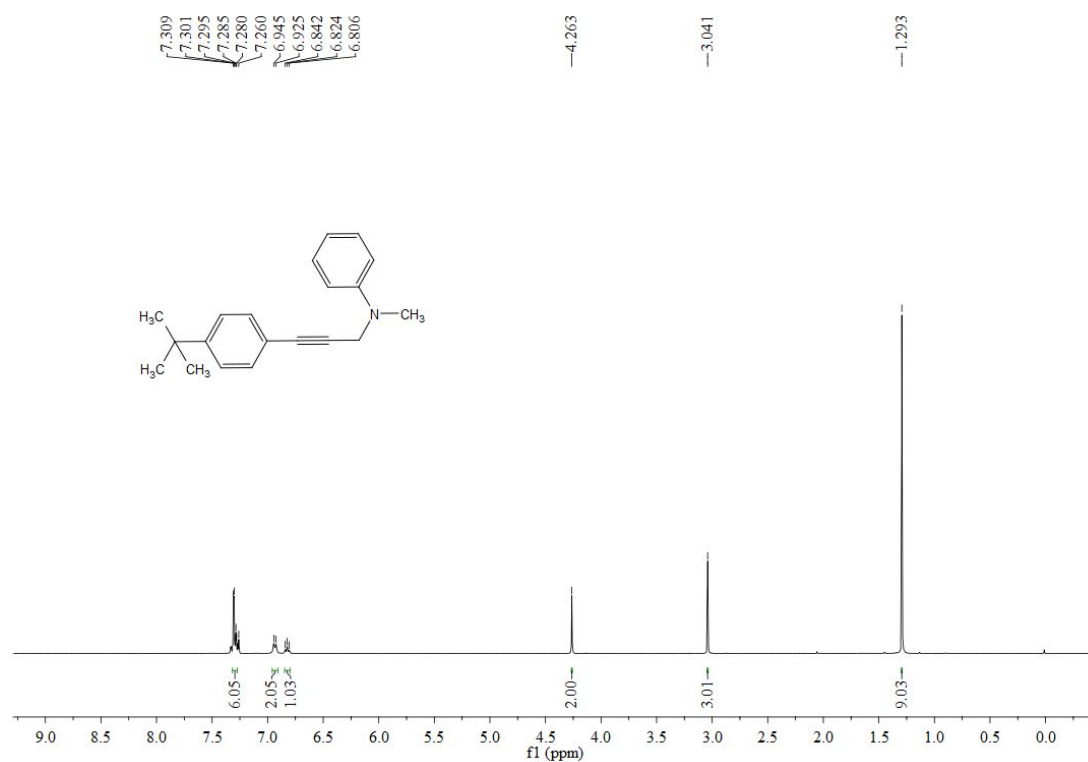
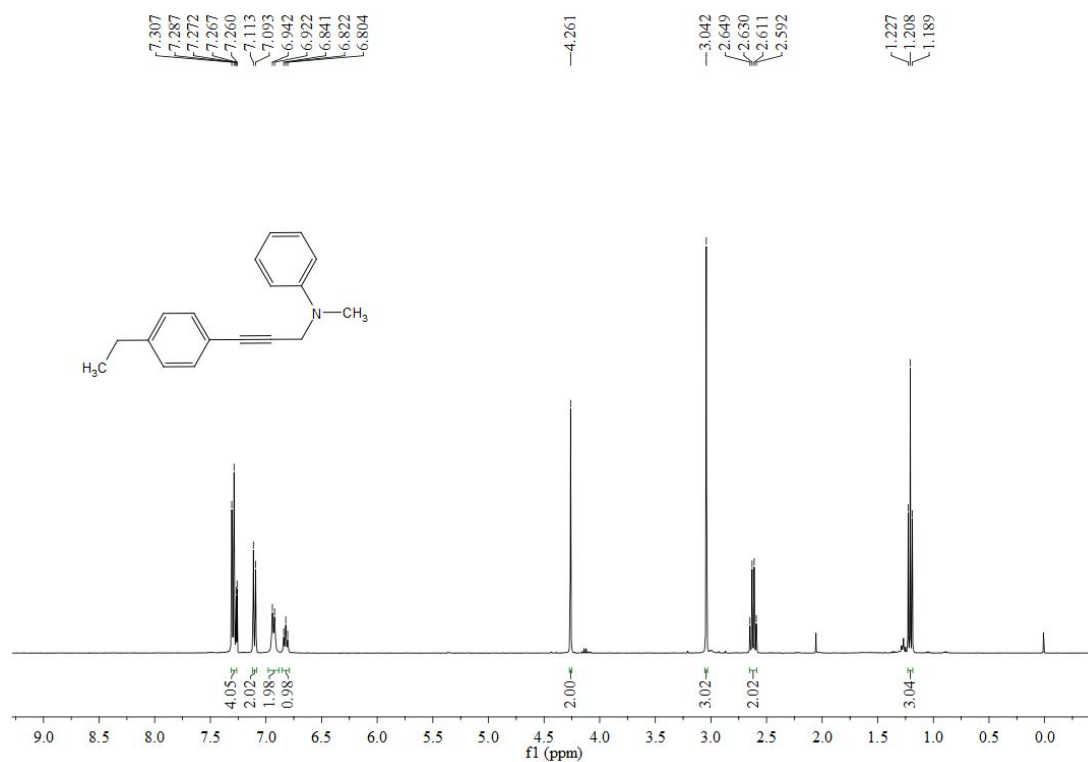
¹H NMR: N-methyl-N-(3-(p-tolyl)prop-2-yn-1-yl)aniline (1b)

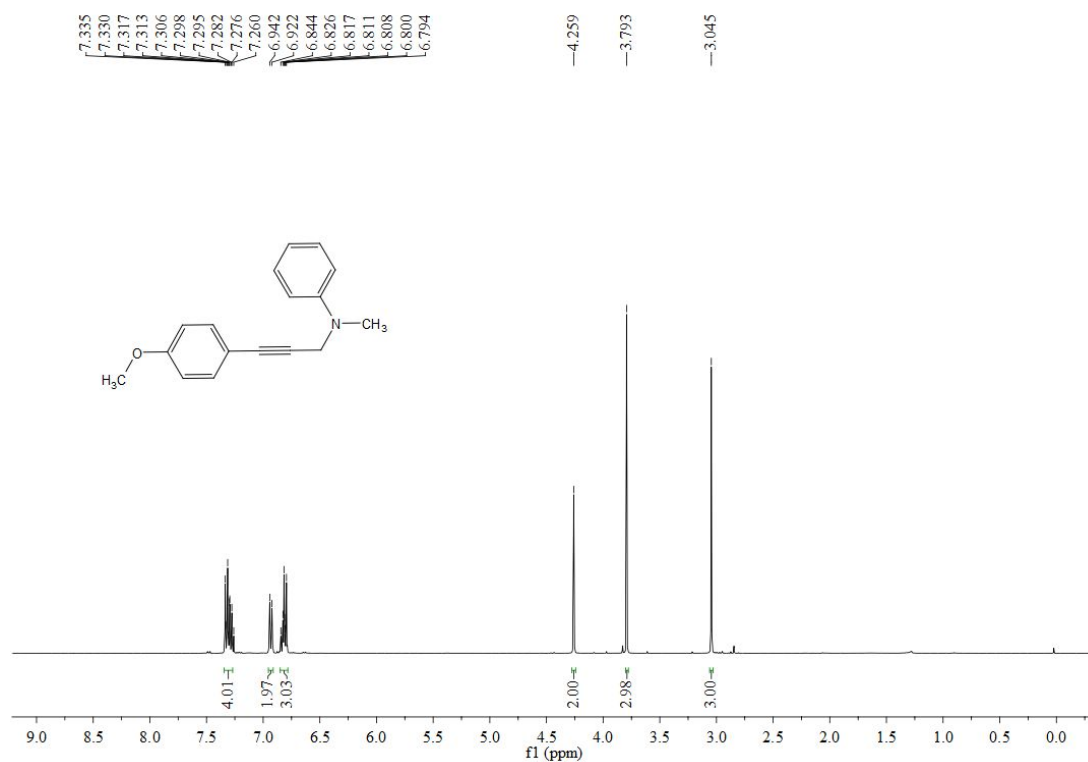


¹H NMR: N-methyl-N-(3-(m-tolyl)prop-2-yn-1-yl)aniline (1c)

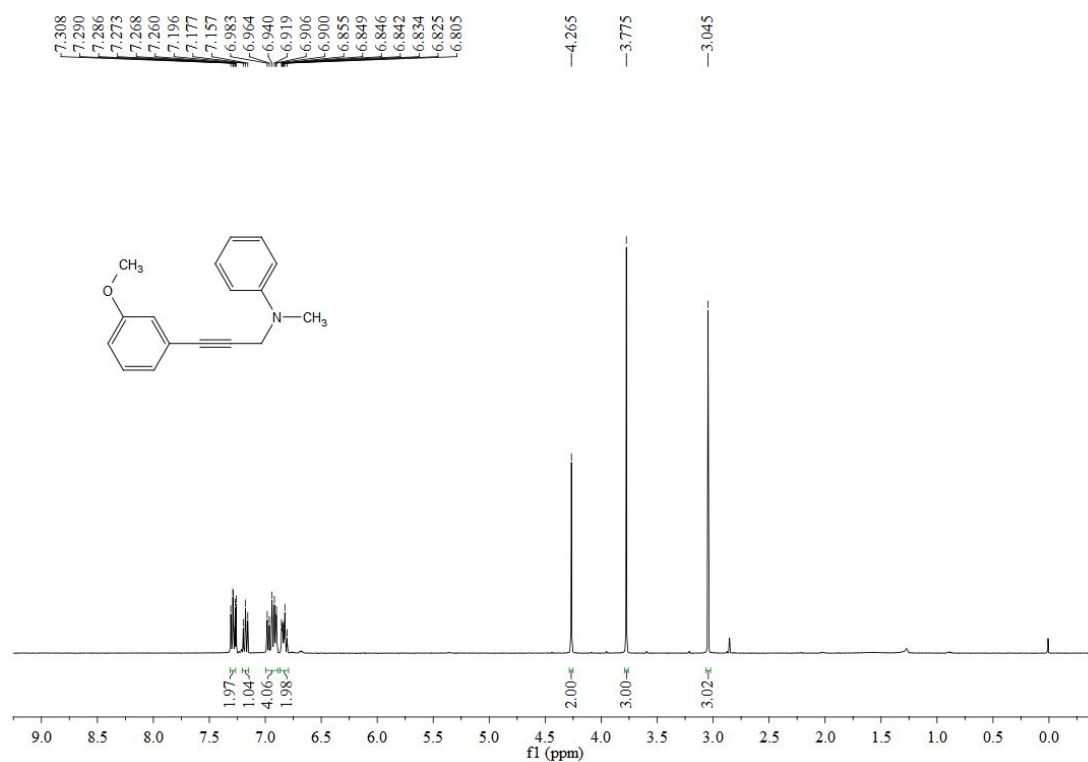


¹H NMR: N-methyl-N-(3-(o-tolyl)prop-2-yn-1-yl)aniline (1d)

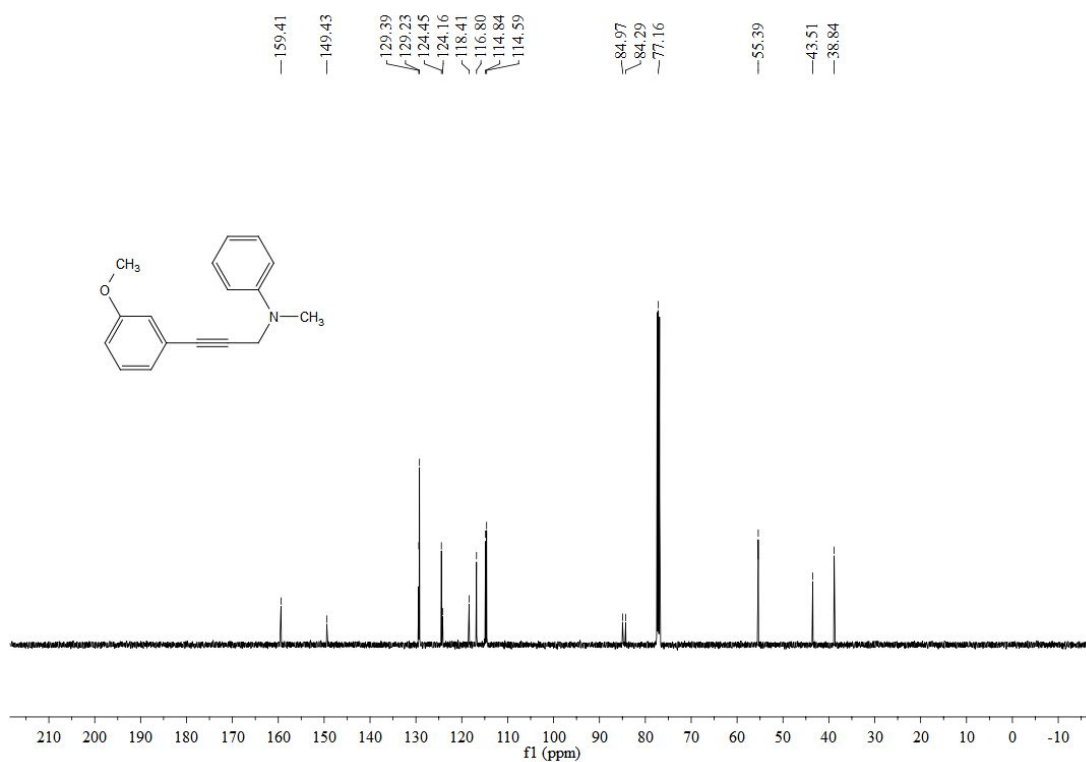




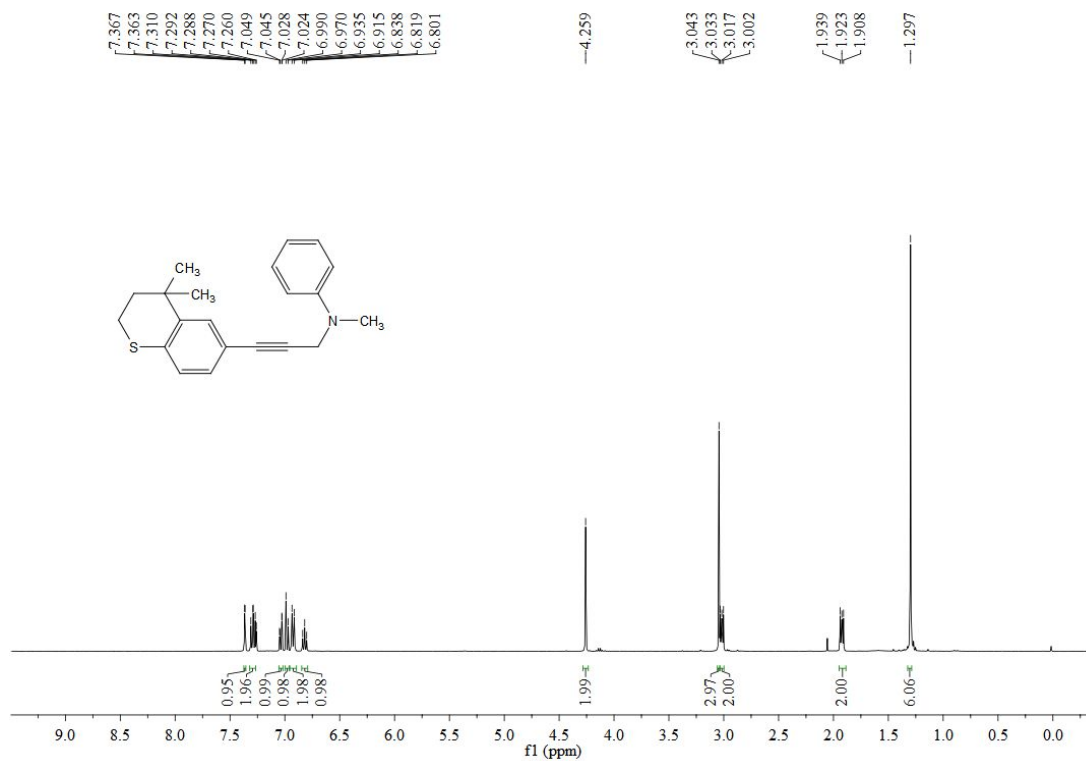
¹H NMR: N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-N-methylaniline (1g)



¹H NMR: N-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-N-methylaniline (1h)

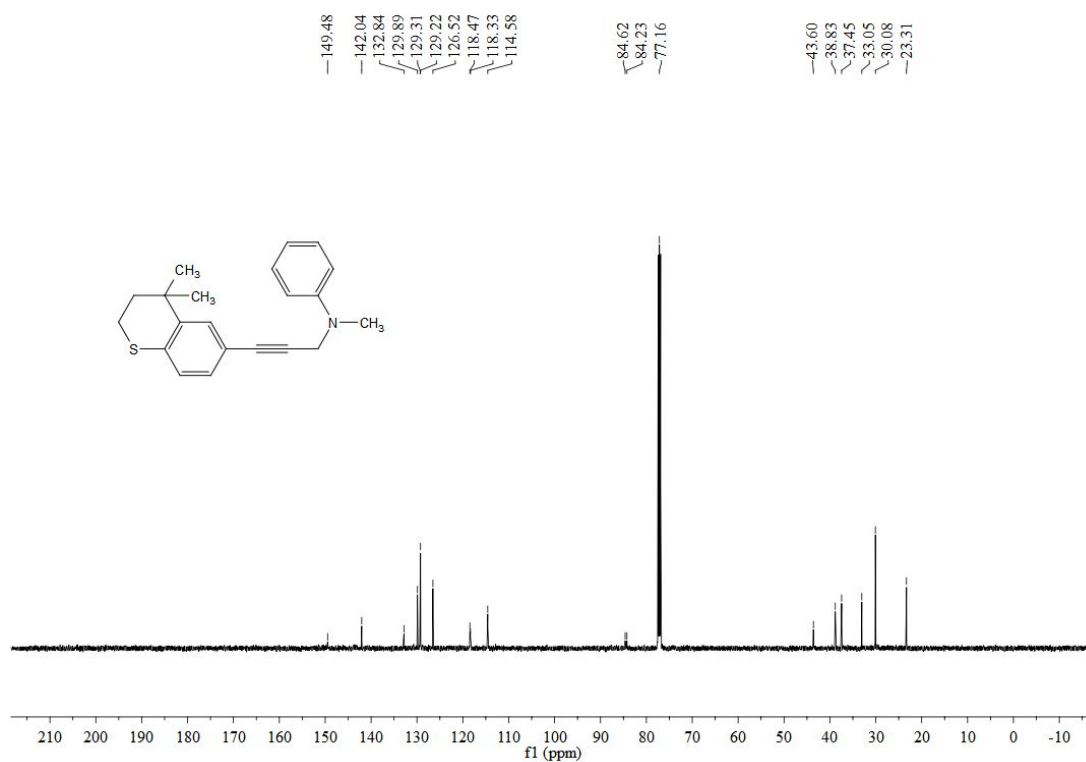


¹³C NMR: N-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-N-methylaniline (1h)

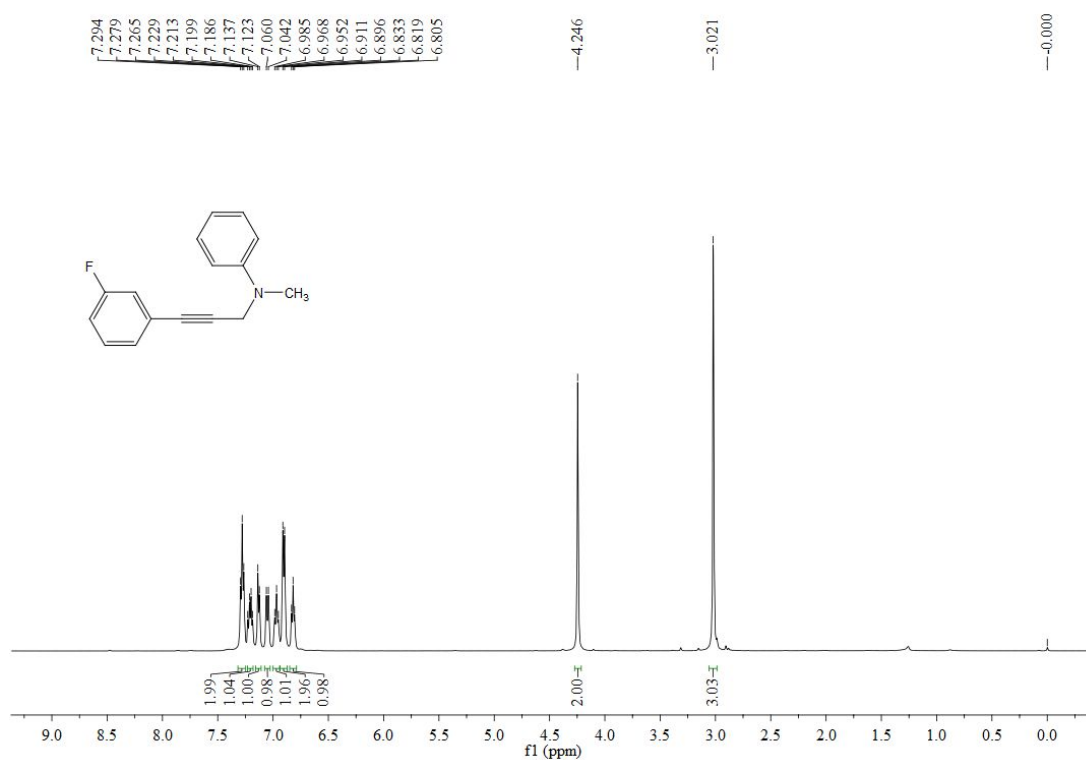


¹H NMR: N-(3-(4,4-dimethylthiochroman-6-yl)prop-2-yn-1-yl)-N-methylaniline

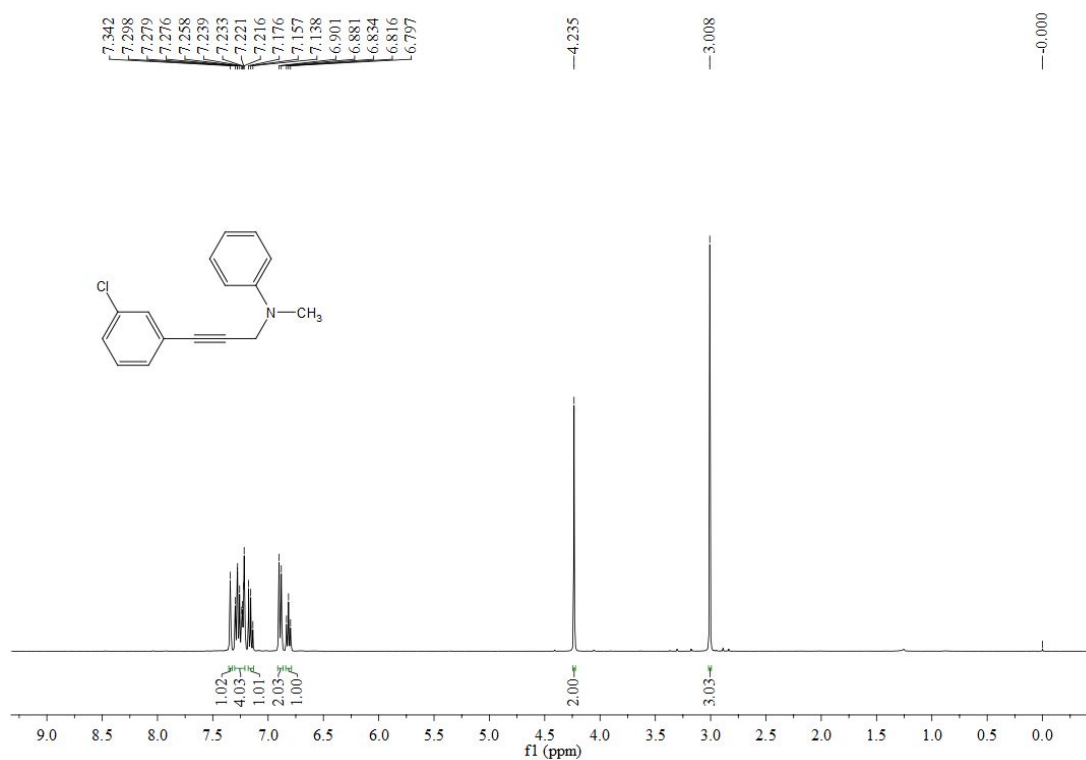
(1i)



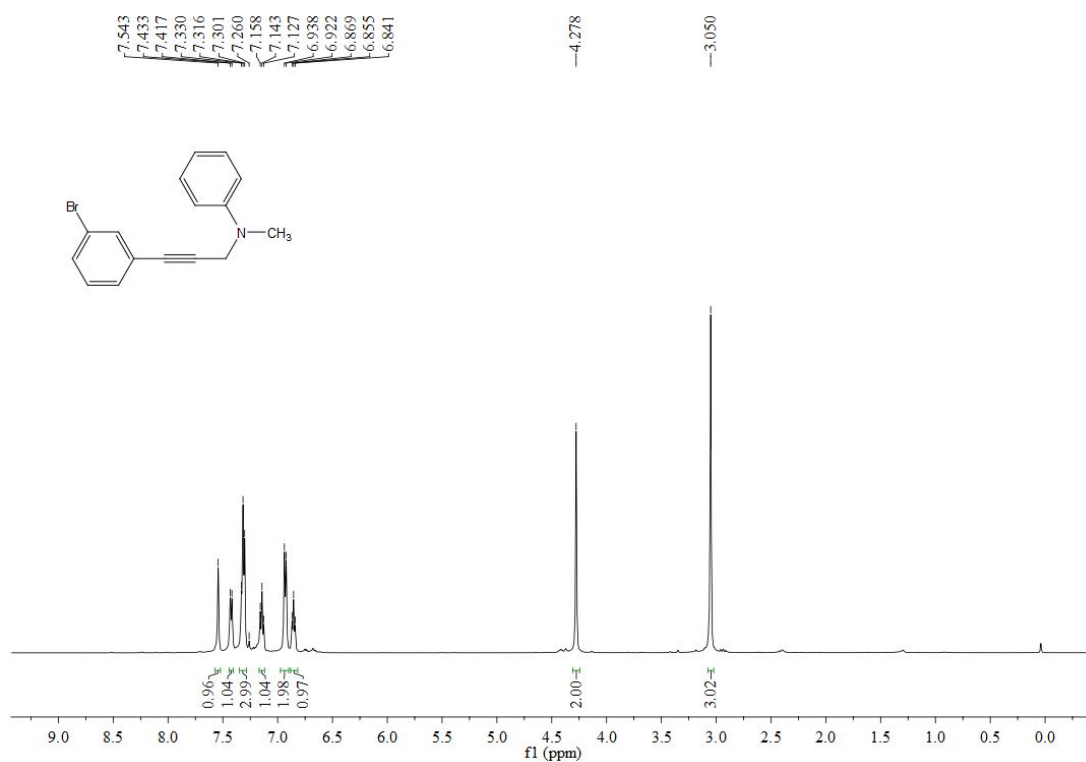
¹³C NMR: N-(3-(4,4-dimethylthiochroman-6-yl)prop-2-yn-1-yl)-N-methylaniline (1i)



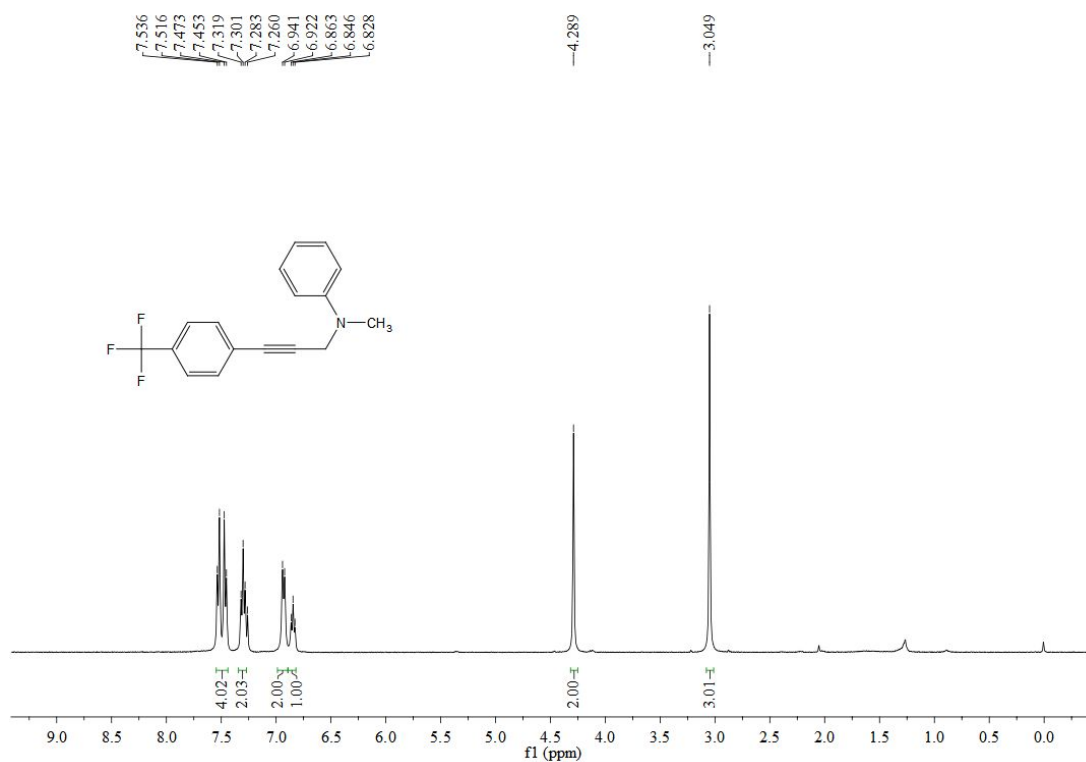
¹H NMR: N-(3-(3-fluorophenyl)prop-2-yn-1-yl)-N-methylaniline (1j)



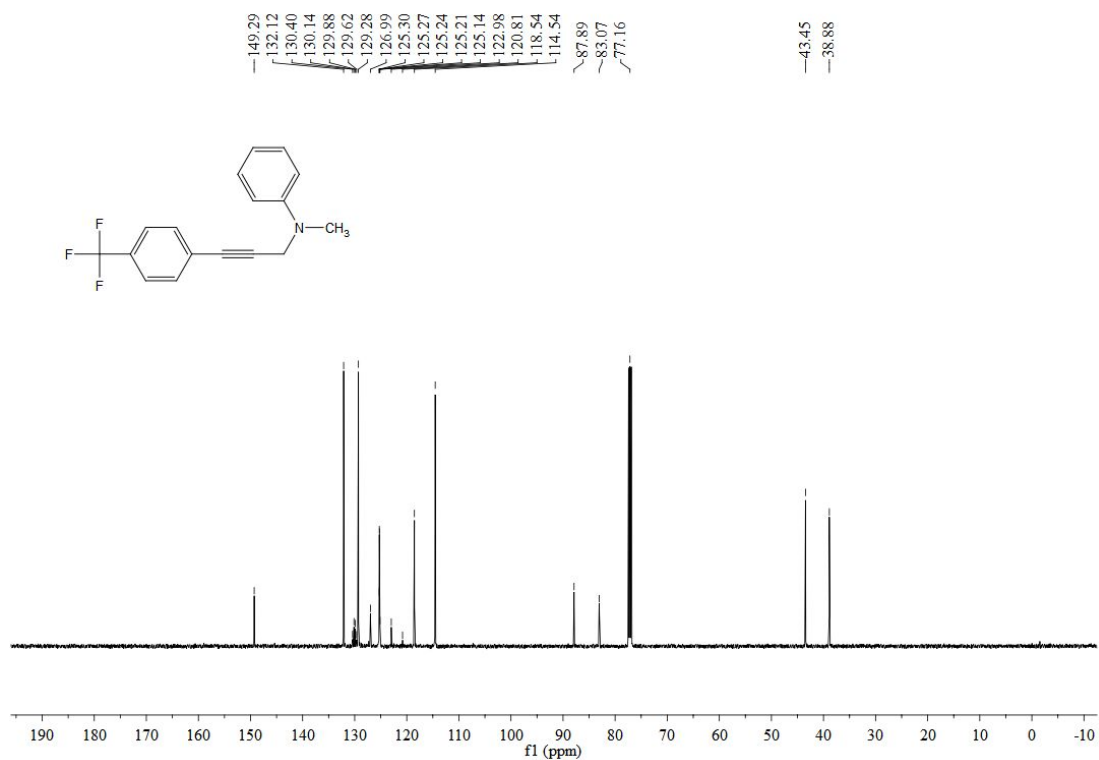
¹H NMR: N-(3-(3-chlorophenyl)prop-2-yn-1-yl)-N-methylaniline (1k)



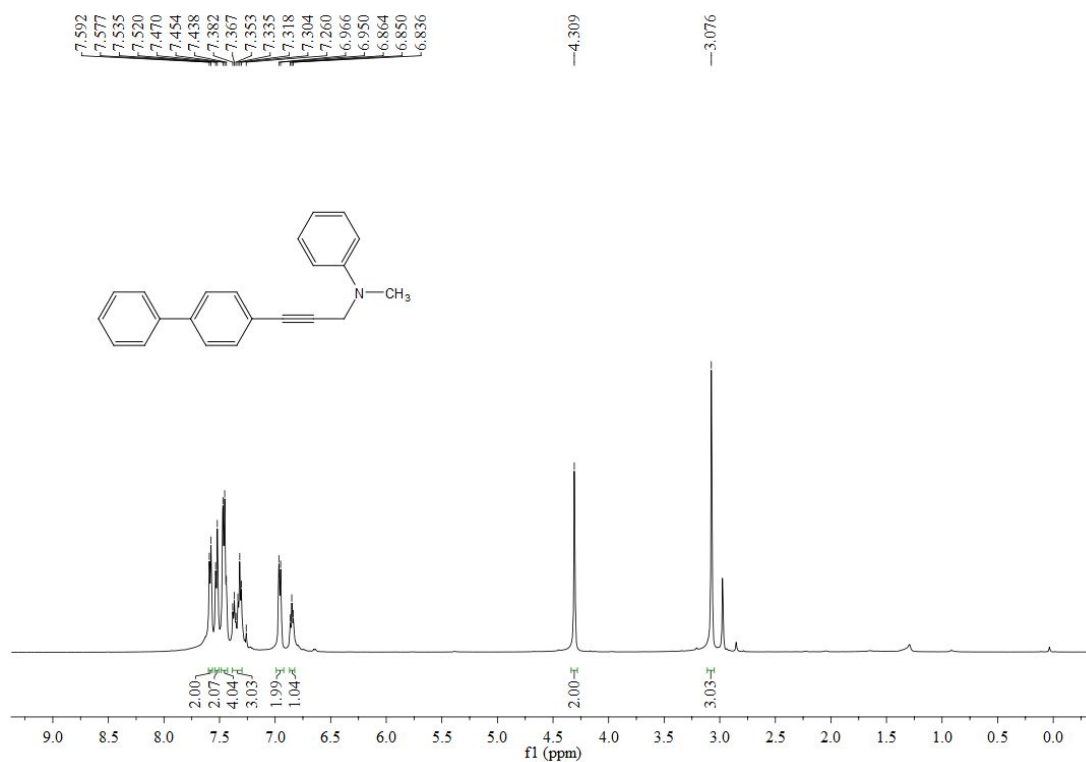
¹H NMR: N-(3-(3-bromophenyl)prop-2-yn-1-yl)-N-methylaniline (1l)



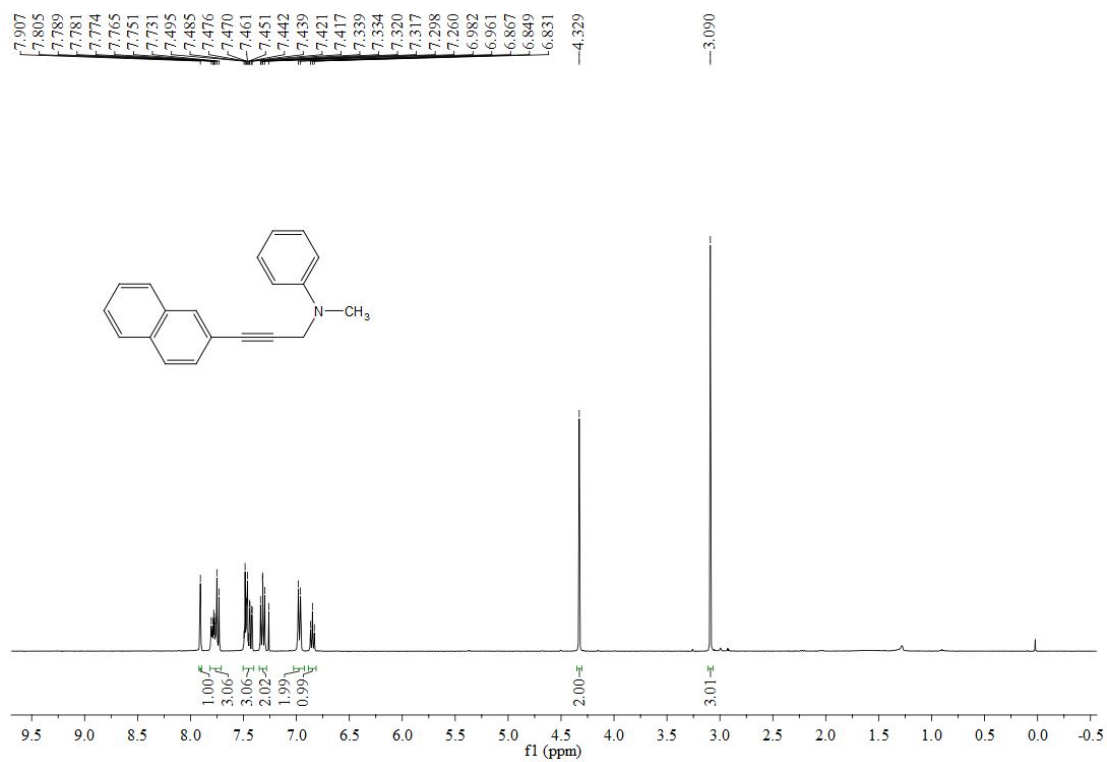
¹H NMR: N-methyl-N-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)aniline (1m)



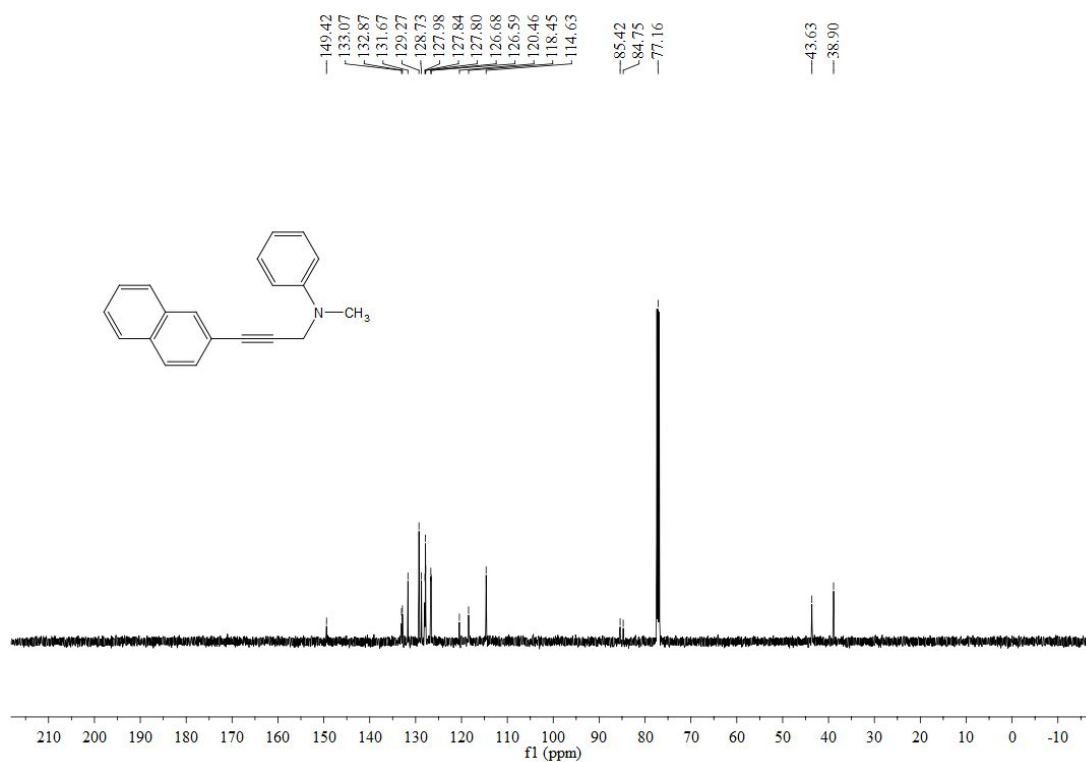
¹³C NMR: N-methyl-N-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)aniline (1m)



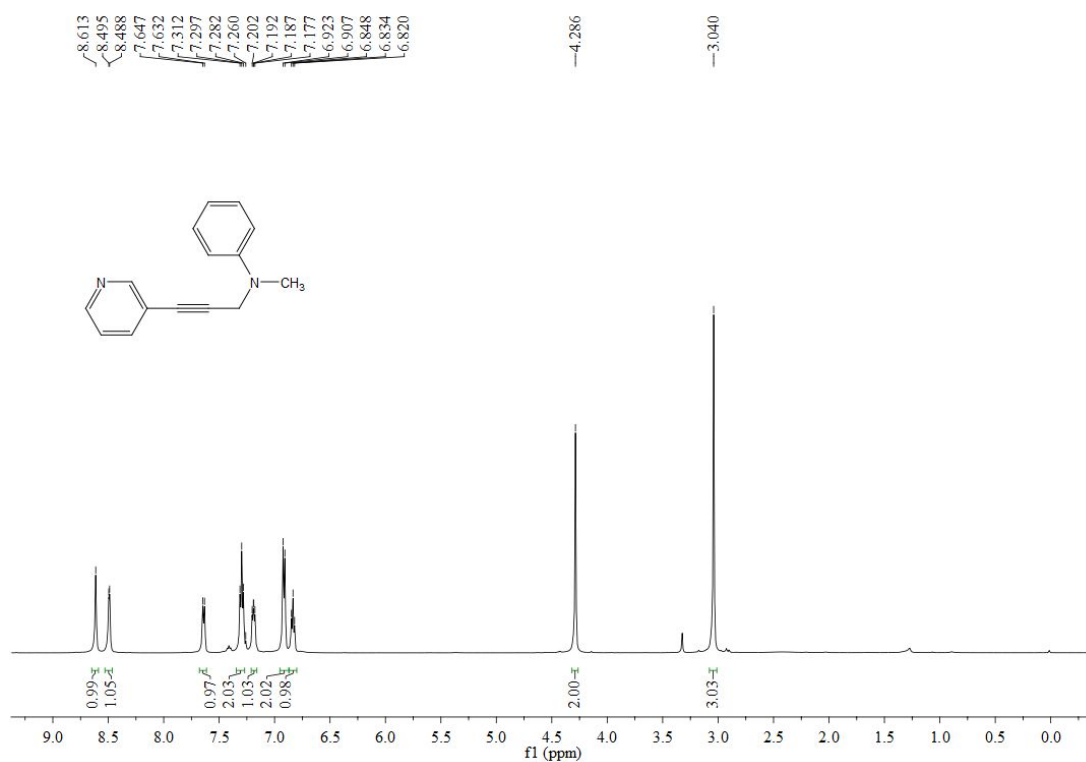
¹H NMR: N-(3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)-N-methylaniline (1n)



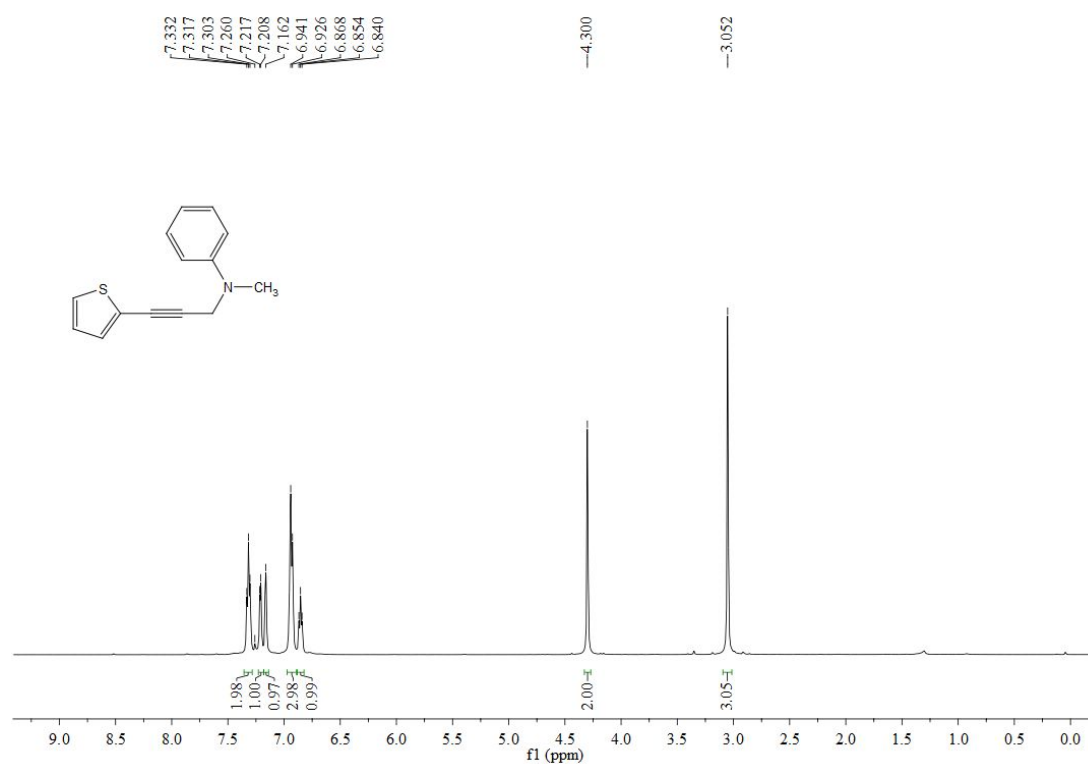
¹H NMR: N-methyl-N-(3-(naphthalen-2-yl)prop-2-yn-1-yl)aniline (1o)



¹³C NMR: N-methyl-N-(3-(naphthalen-2-yl)prop-2-yn-1-yl)aniline (1o)

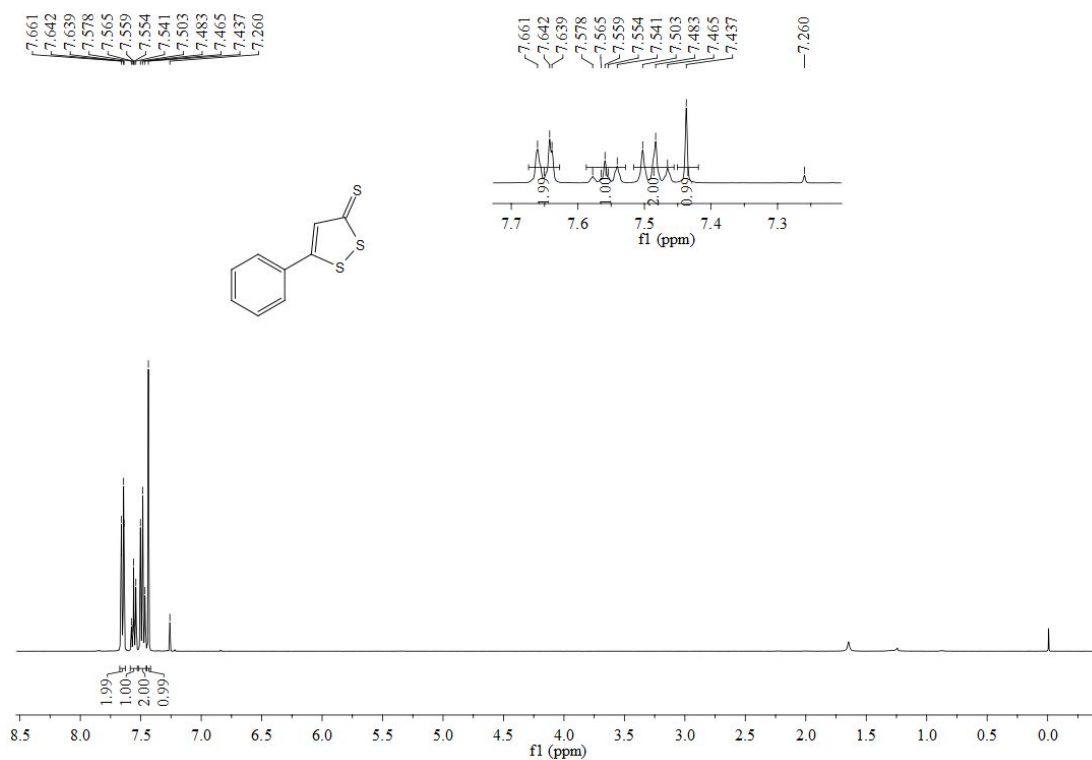


¹H NMR: N-methyl-N-(3-(pyridin-3-yl)prop-2-yn-1-yl)aniline (1p)

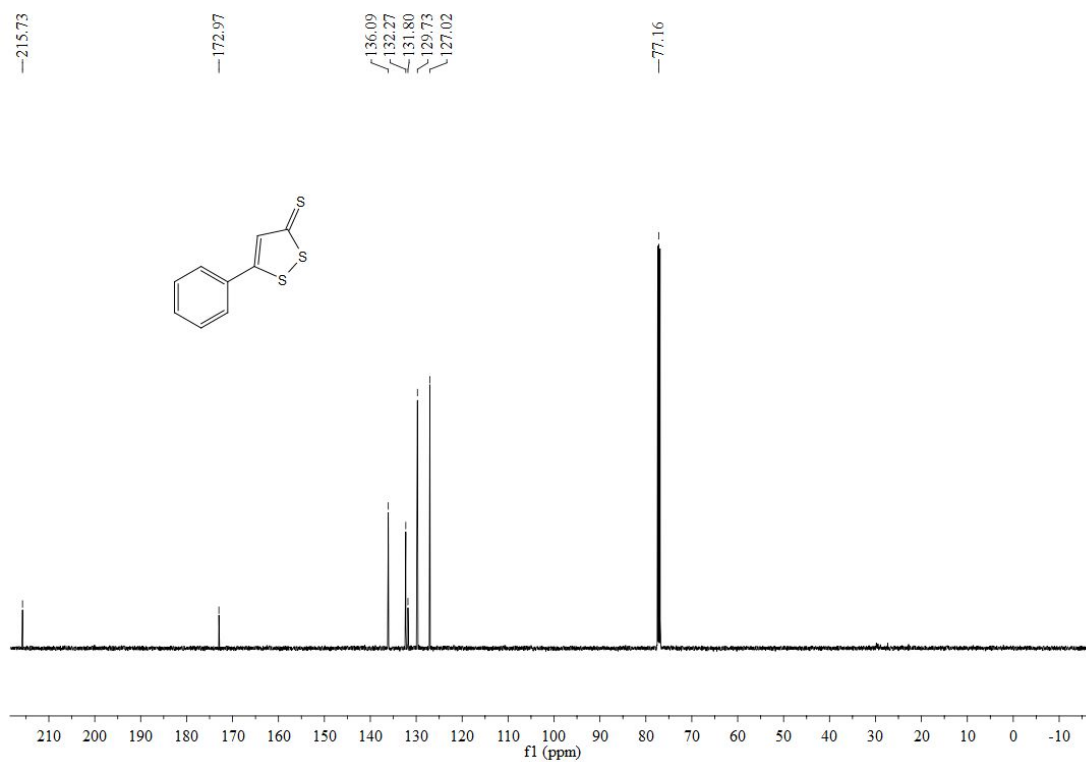


¹H NMR: N-methyl-N-(3-(thiophen-2-yl)prop-2-yn-1-yl)aniline (1q)

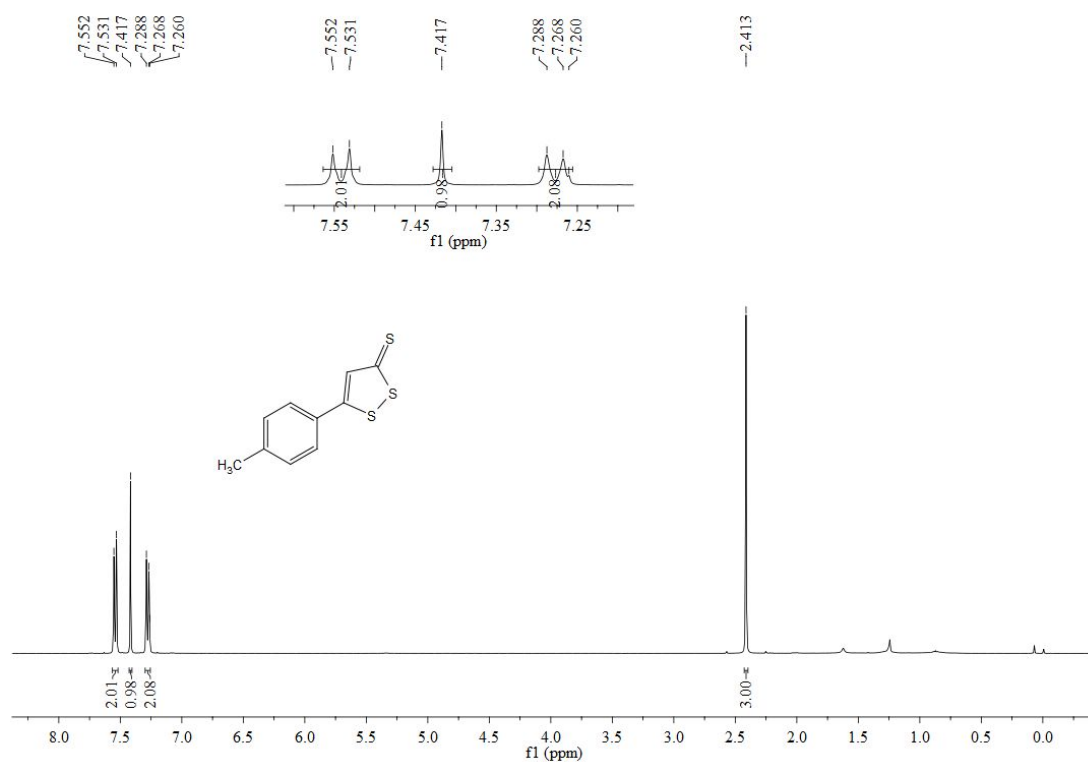
4. NMR Spectra for All Compounds 2a-2q.



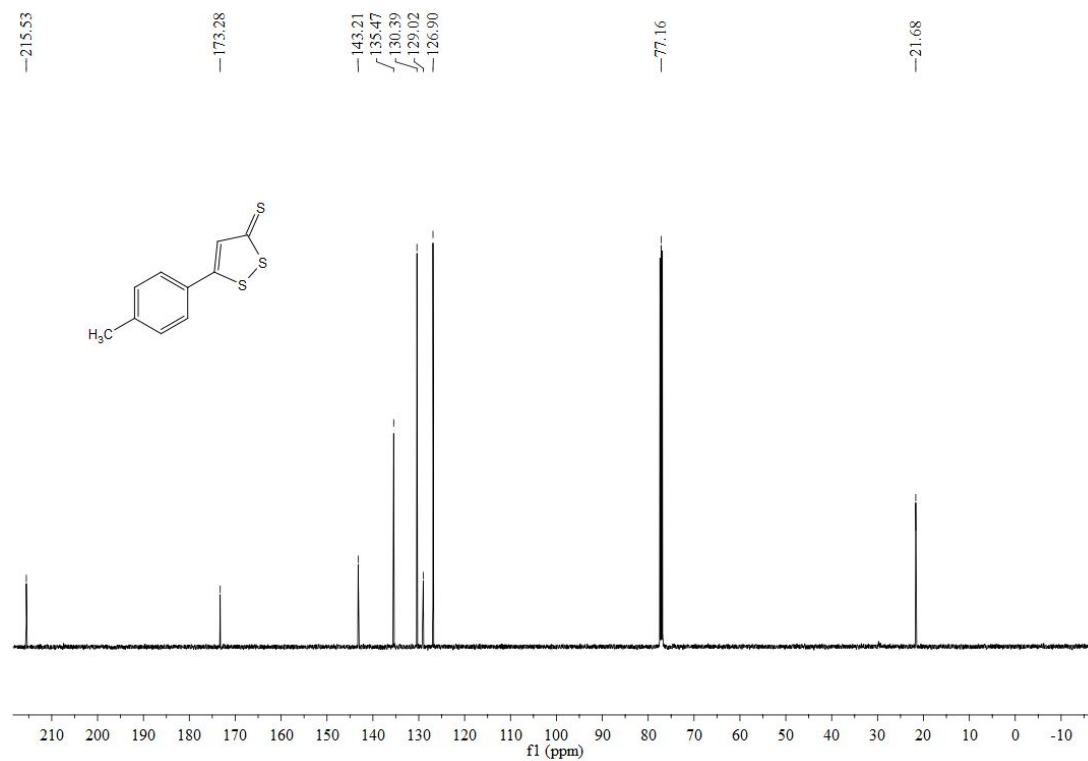
¹H NMR: 5-phenyl-3H-1,2-dithiole-3-thione (2a)



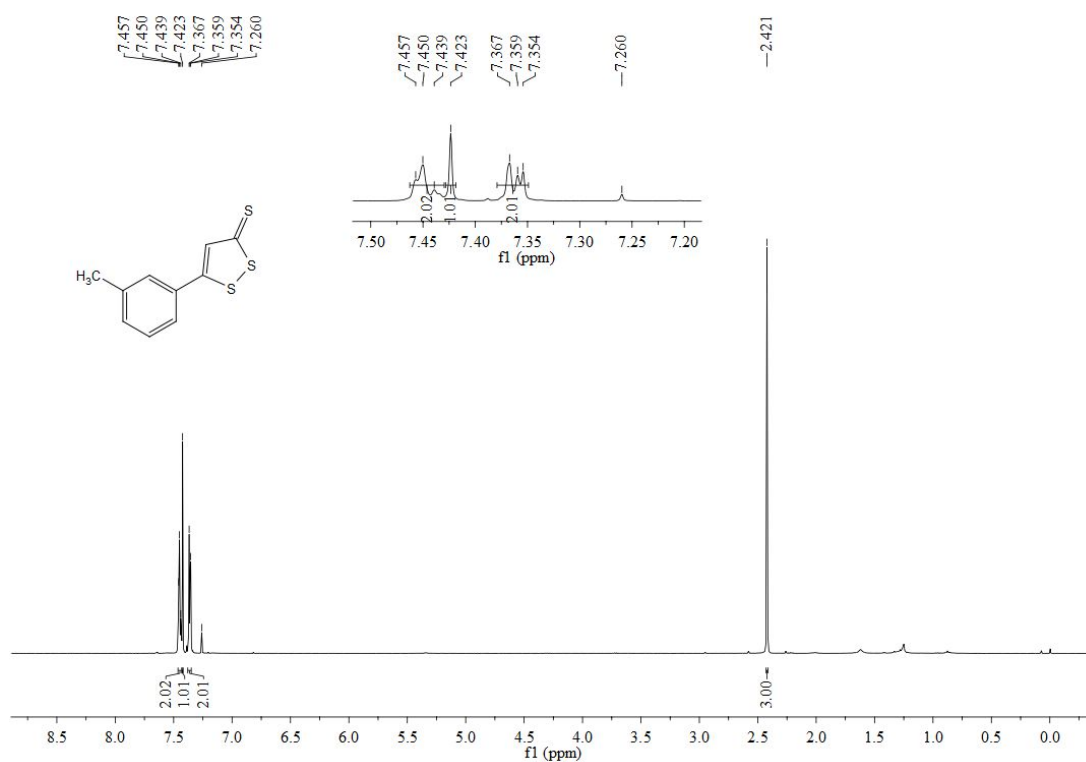
¹³C NMR: 5-phenyl-3H-1,2-dithiole-3-thione (2a)



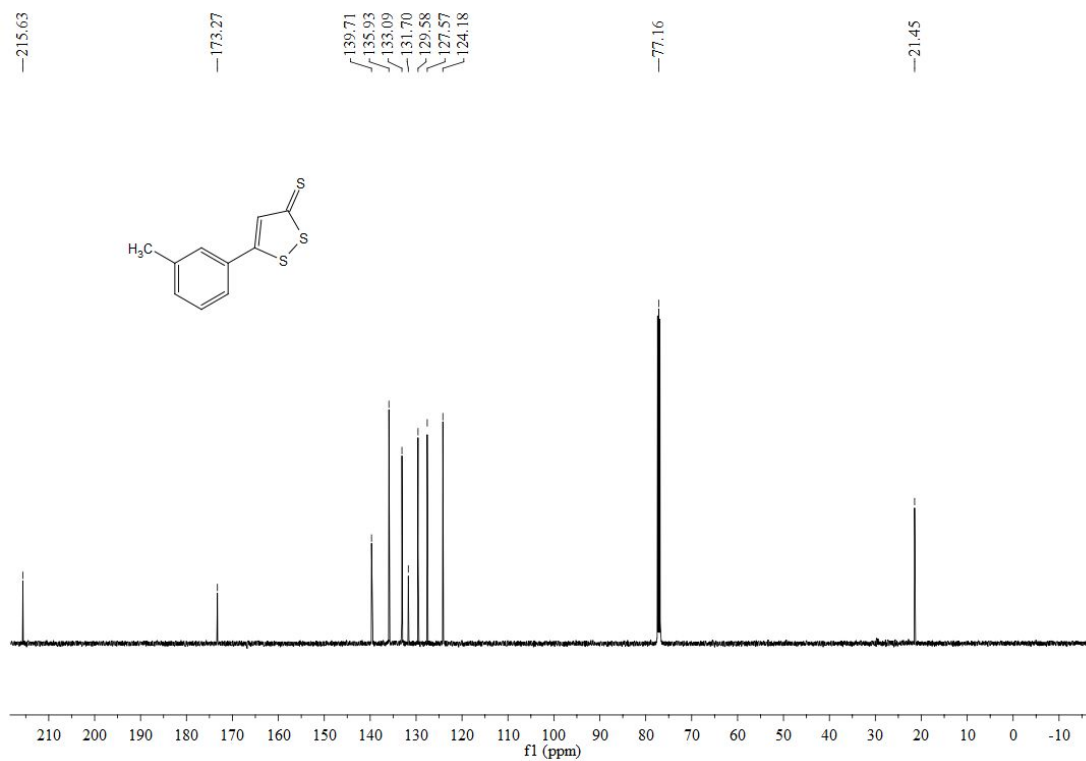
¹H NMR: 5-(p-tolyl)-3H-1,2-dithiole-3-thione (2b)



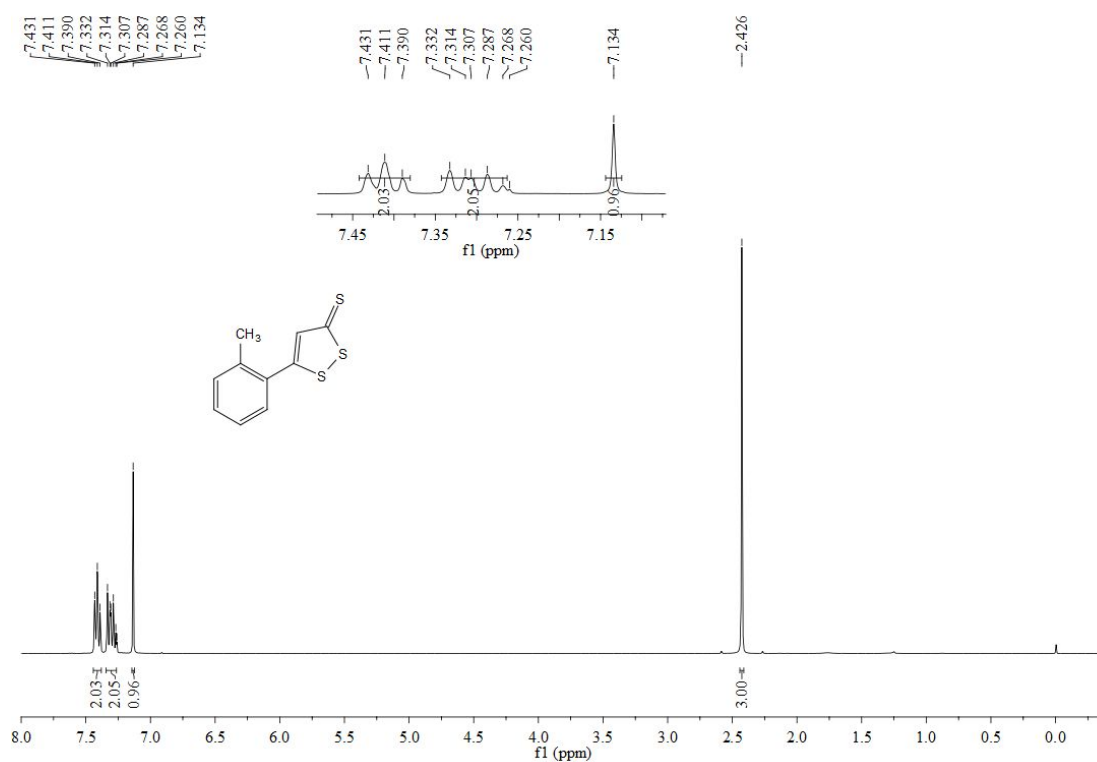
¹³C NMR: 5-(p-tolyl)-3H-1,2-dithiole-3-thione (2b)



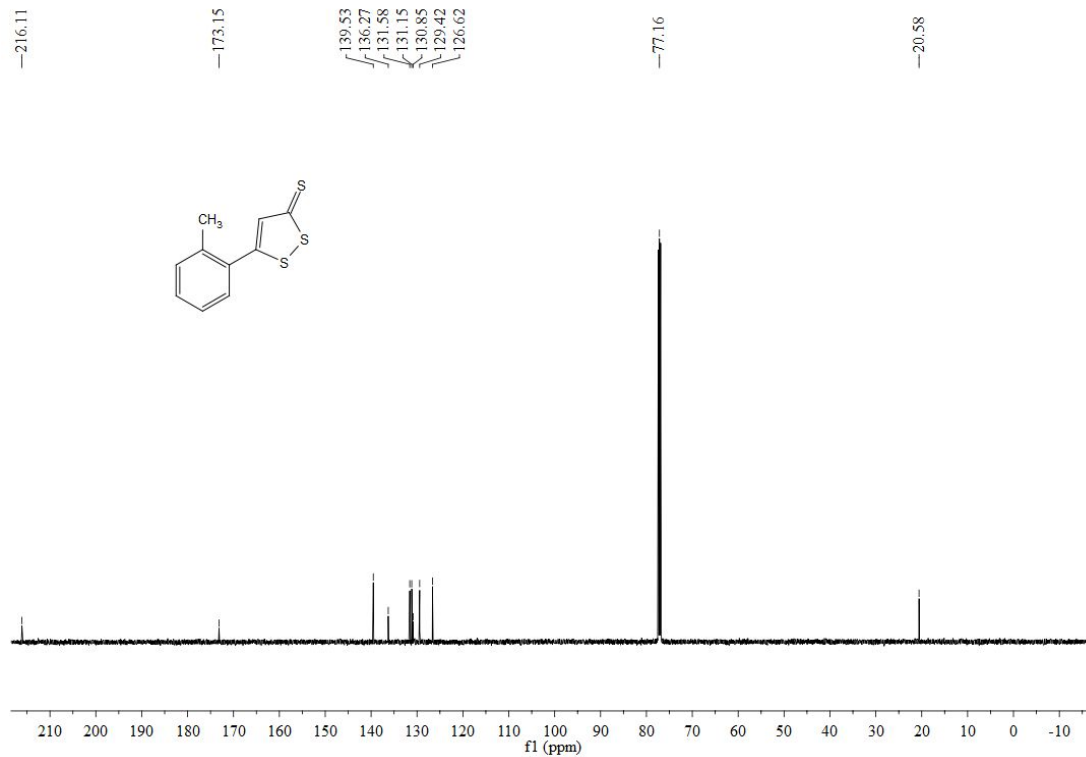
¹H NMR: 5-(m-tolyl)-3H-1,2-dithiole-3-thione (2c)



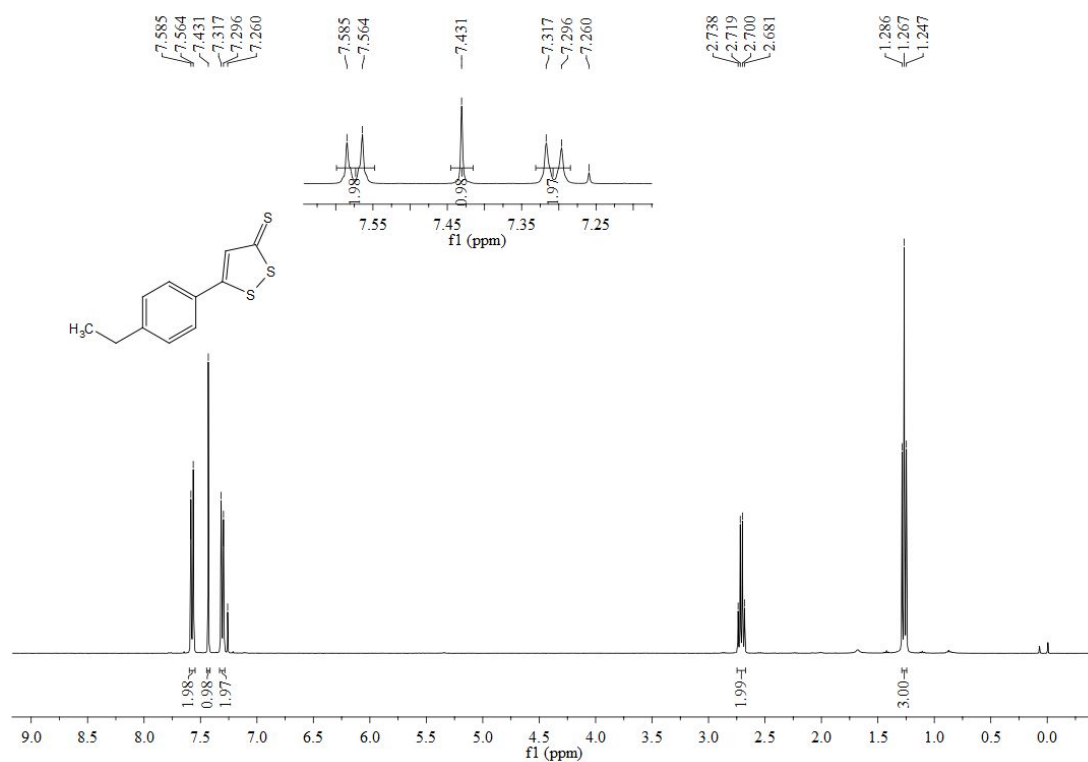
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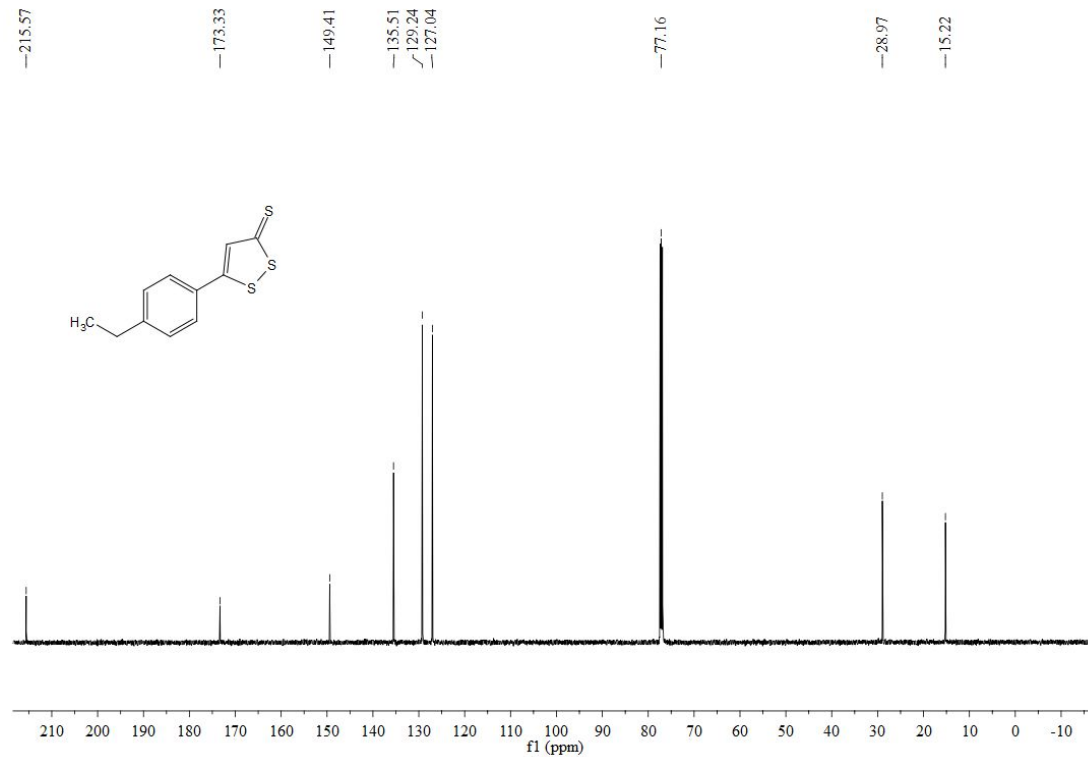
¹H NMR: 5-(o-tolyl)-3H-1,2-dithiole-3-thione (2d)



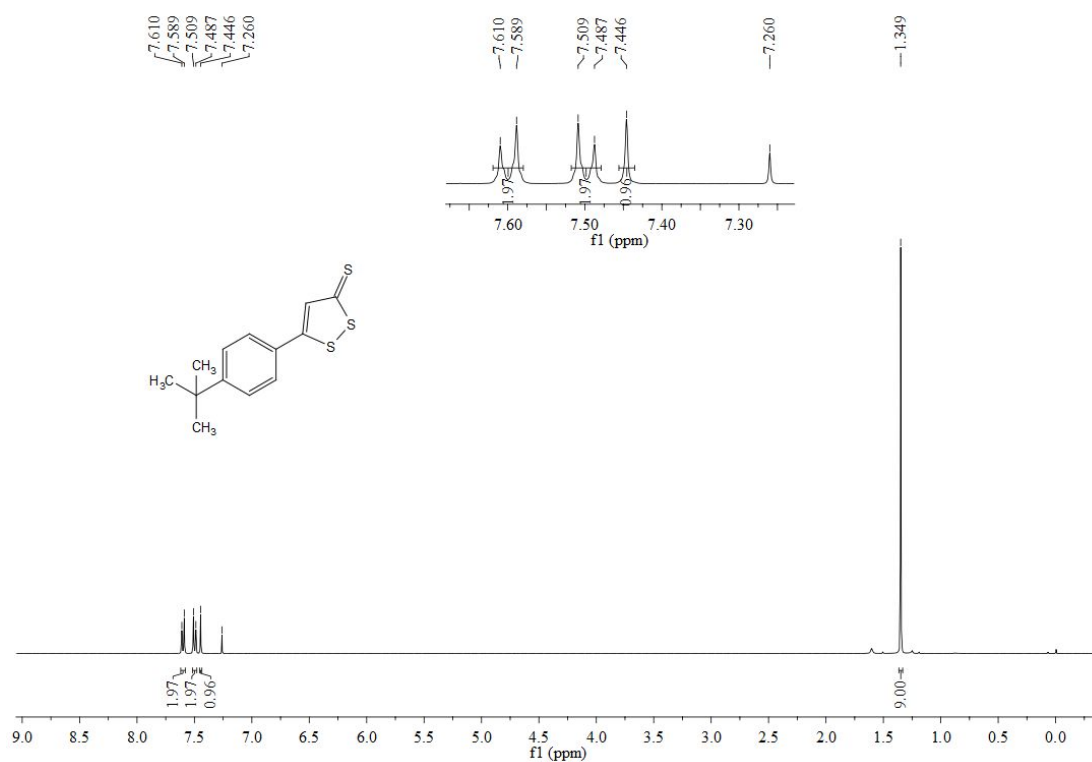
¹³C NMR: 5-(o-tolyl)-3H-1,2-dithiole-3-thione (2d)



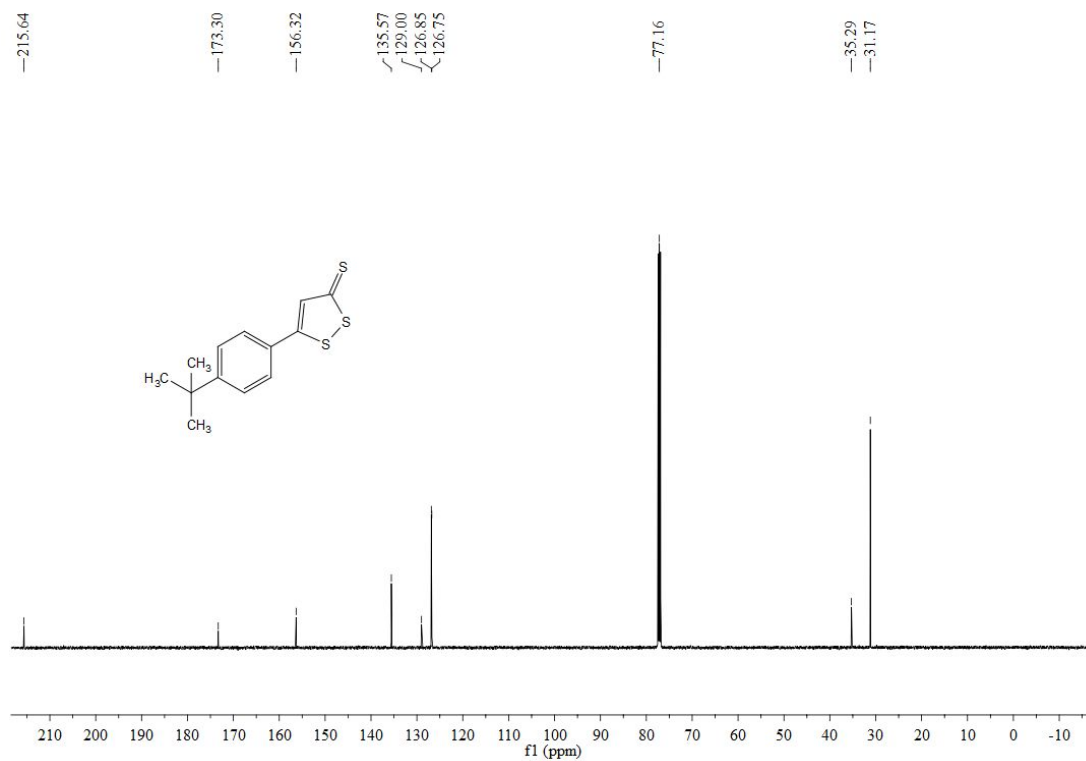
¹H NMR: 5-(4-ethylphenyl)-3H-1,2-dithiole-3-thione (2e)



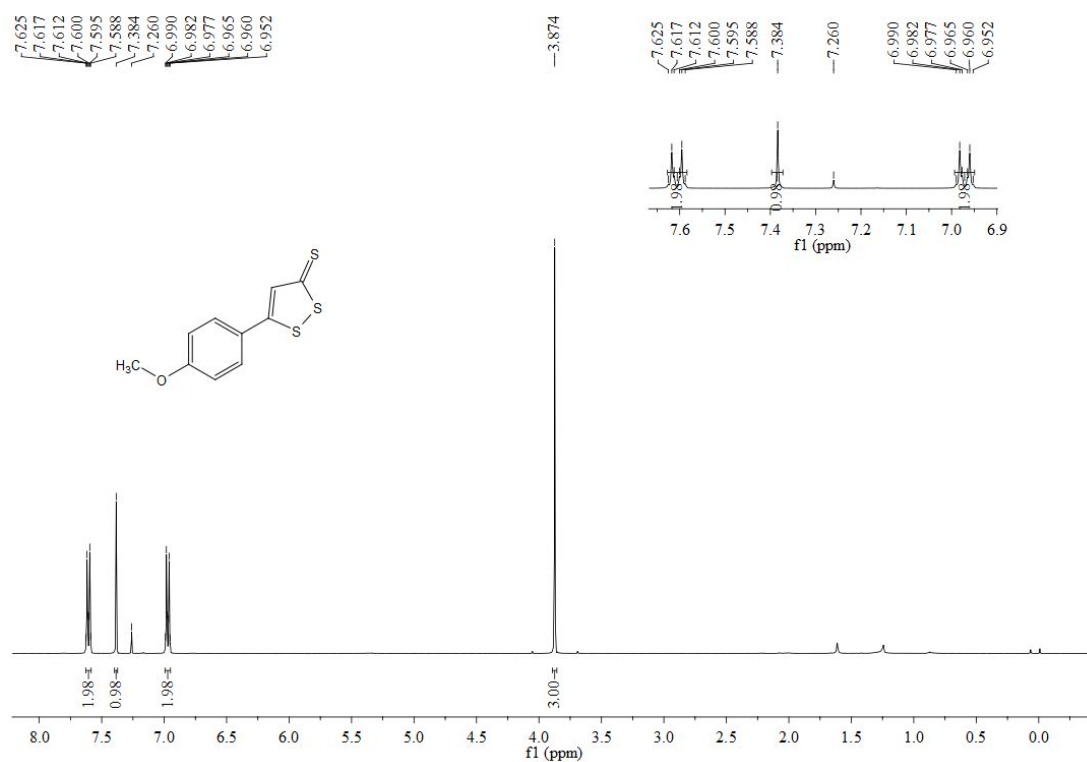
¹³C NMR: 5-(4-ethylphenyl)-3H-1,2-dithiole-3-thione (2e)



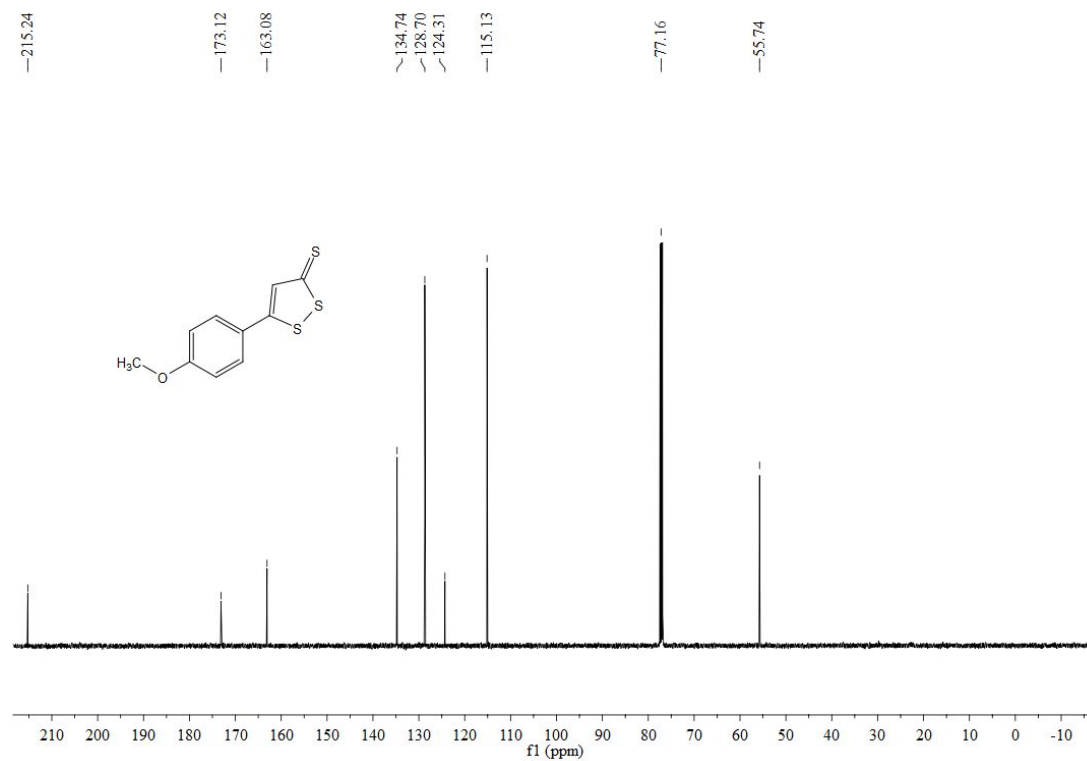
¹H NMR: 5-(4-(tert-butyl)phenyl)-3H-1,2-dithiole-3-thione (2f)



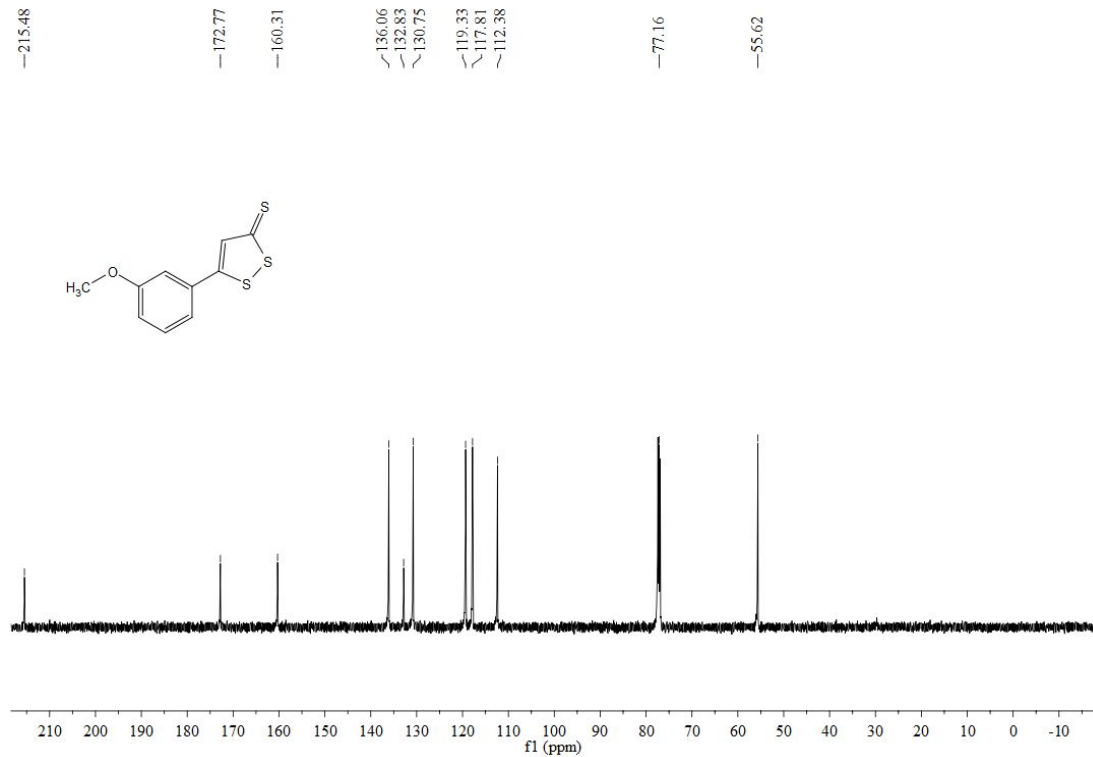
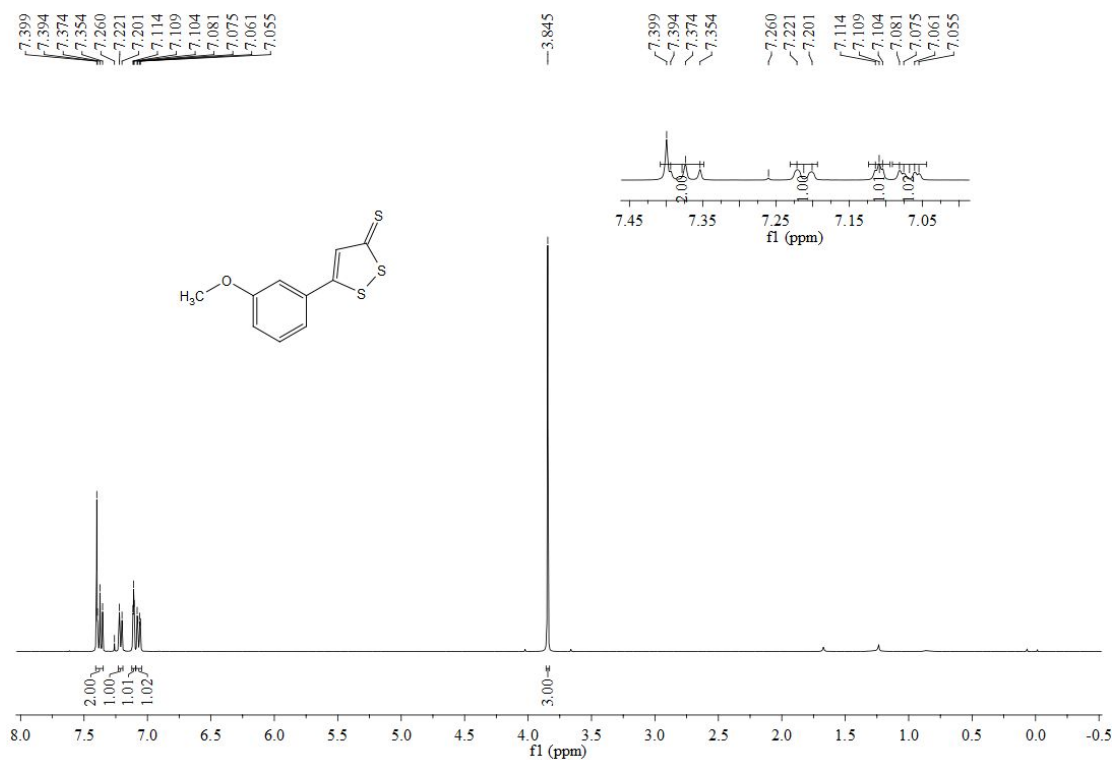
¹³C NMR: 5-(4-(tert-butyl)phenyl)-3H-1,2-dithiole-3-thione (2f)

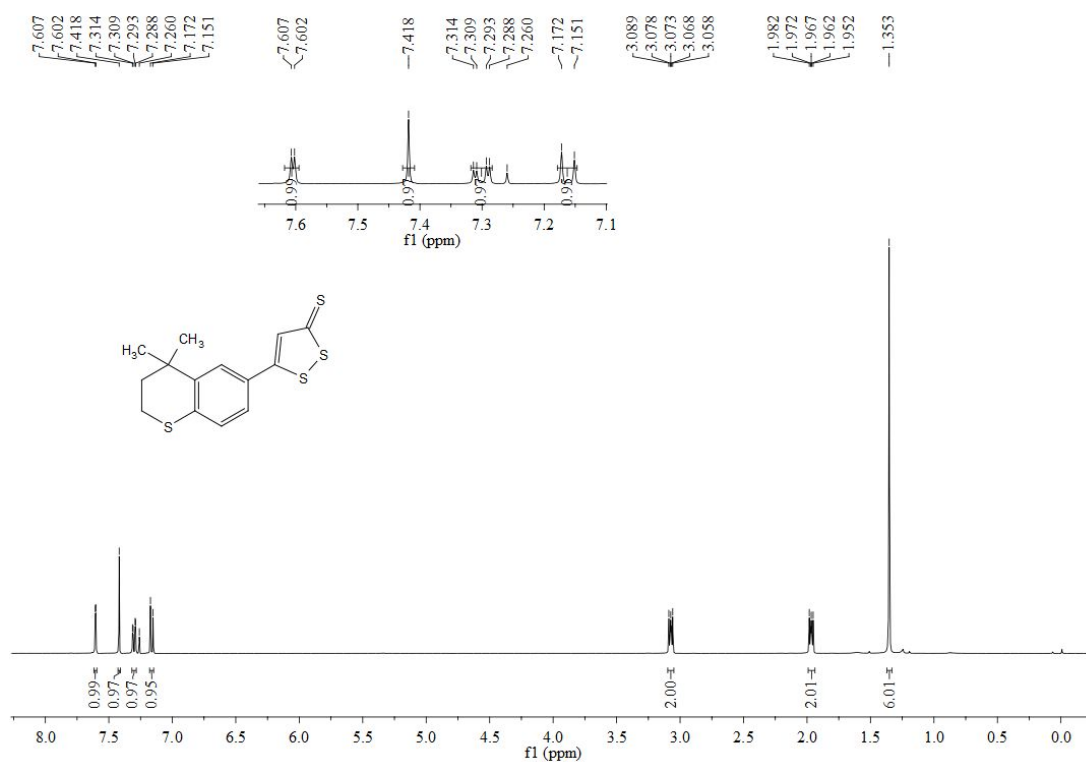


¹H NMR: 5-(4-methoxyphenyl)-3H-1,2-dithiole-3-thione (2g)

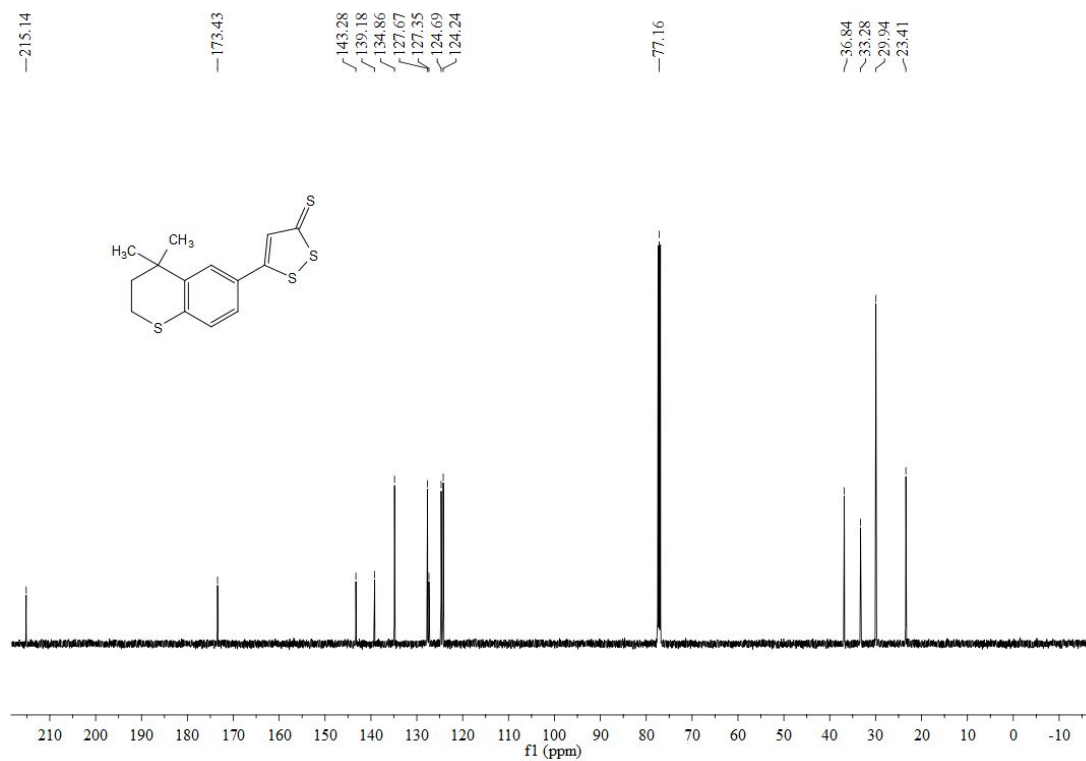


¹³C NMR: 5-(4-methoxyphenyl)-3H-1,2-dithiole-3-thione (2g)

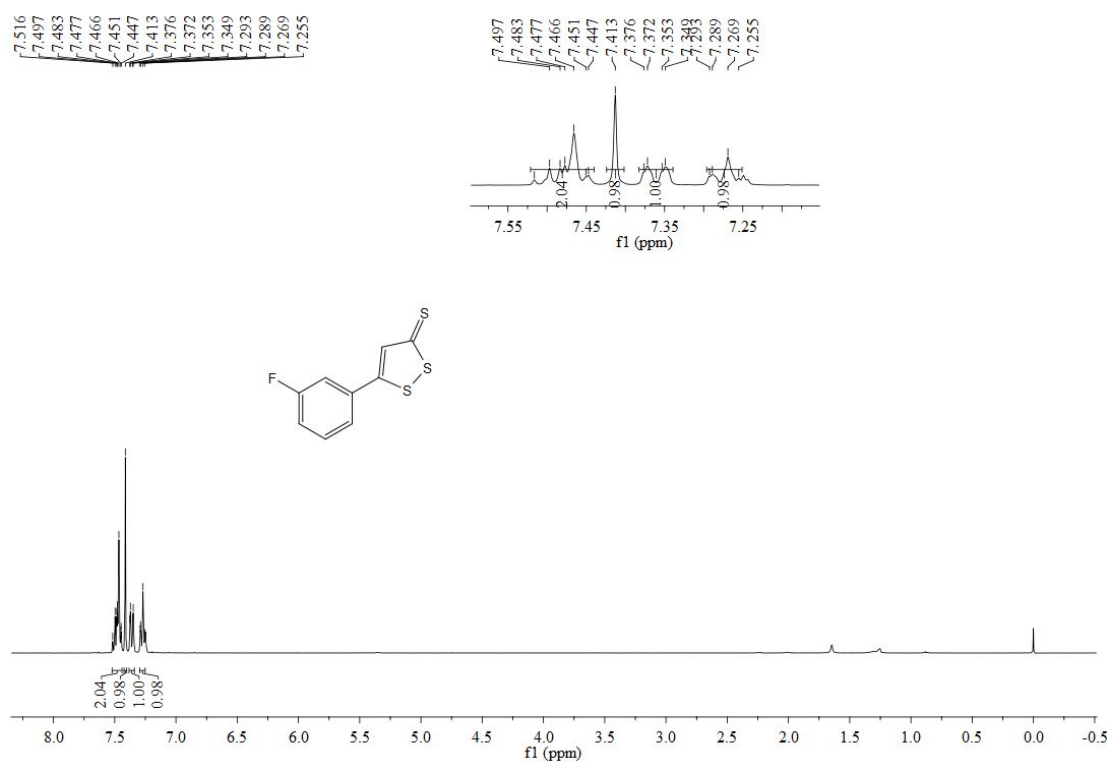




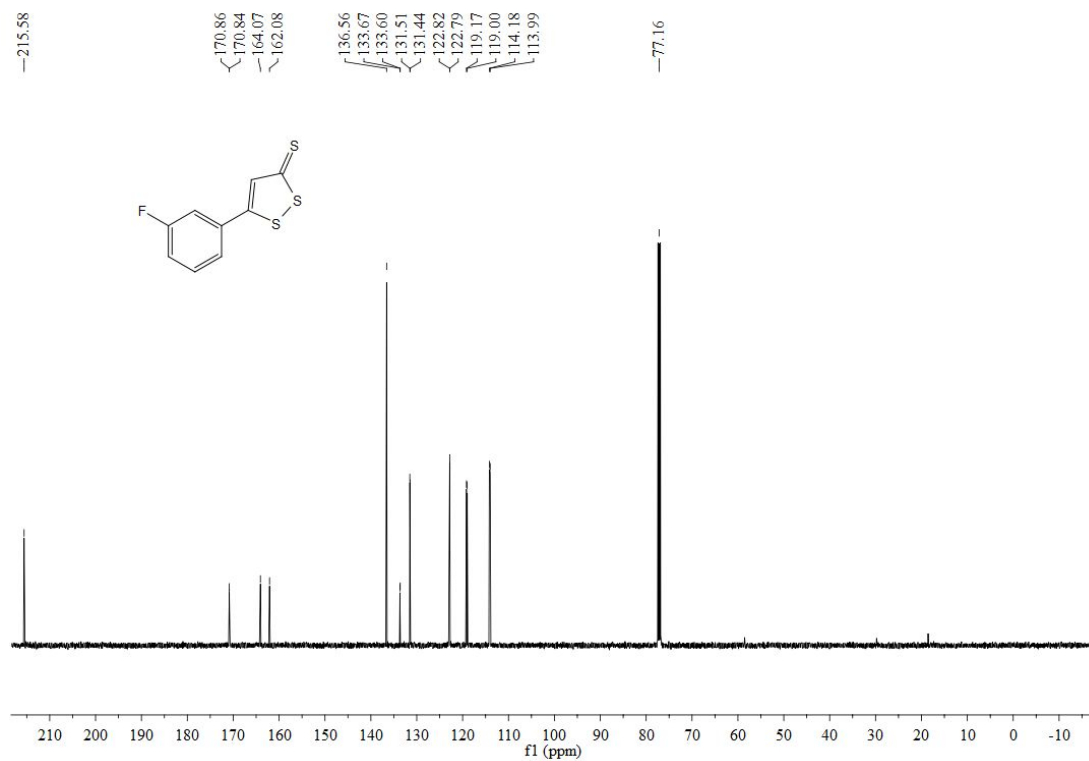
¹H NMR: 5-(4,4-dimethylthiochroman-6-yl)-3H-1,2-dithiole-3-thione (2i)



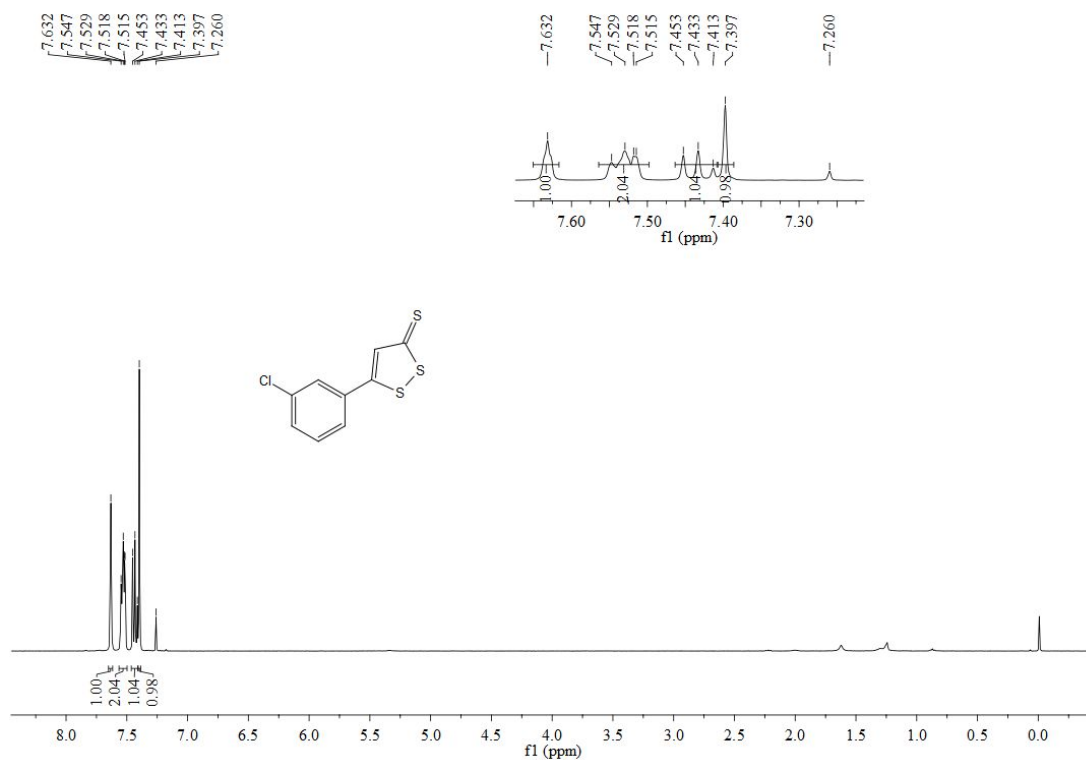
¹³C NMR: 5-(4,4-dimethylthiochroman-6-yl)-3H-1,2-dithiole-3-thione (2i)



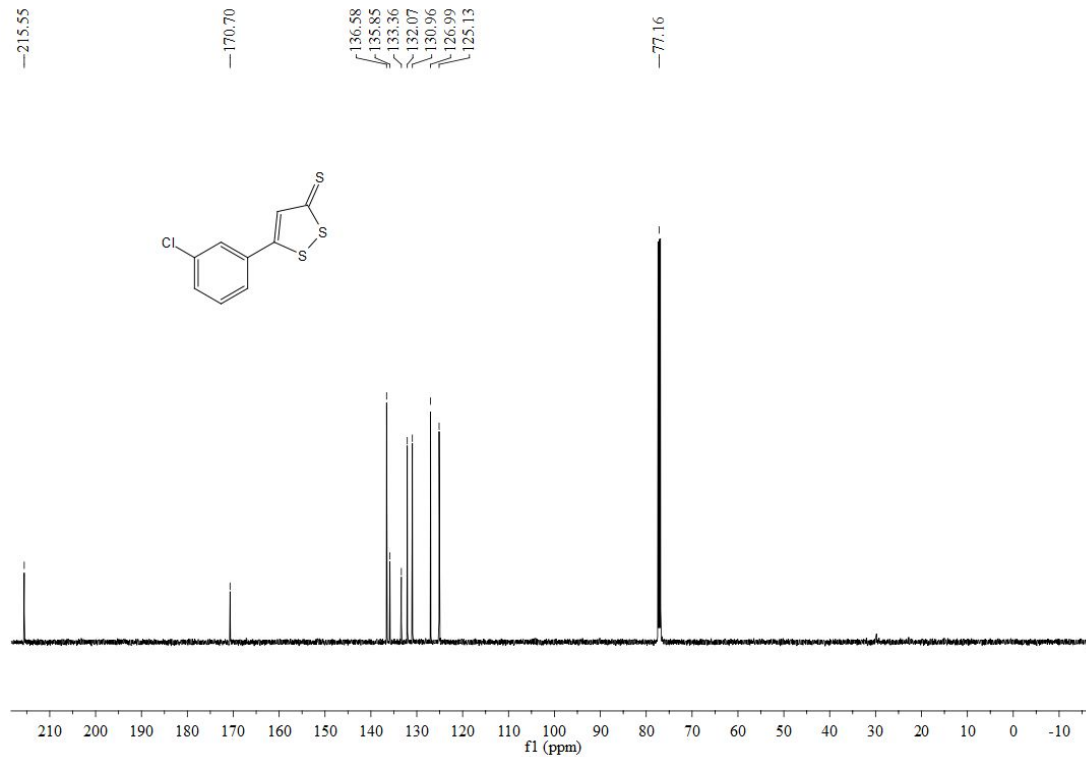
¹H NMR: 5-(3-fluorophenyl)-3H-1,2-dithiole-3-thione (2j)



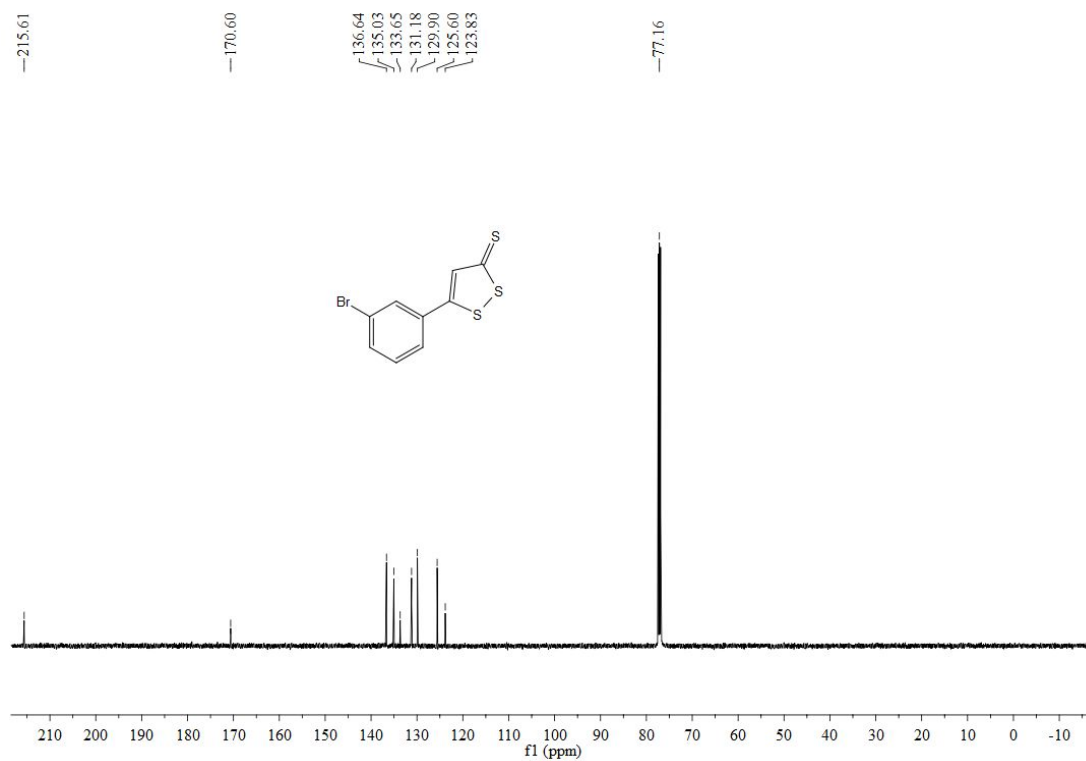
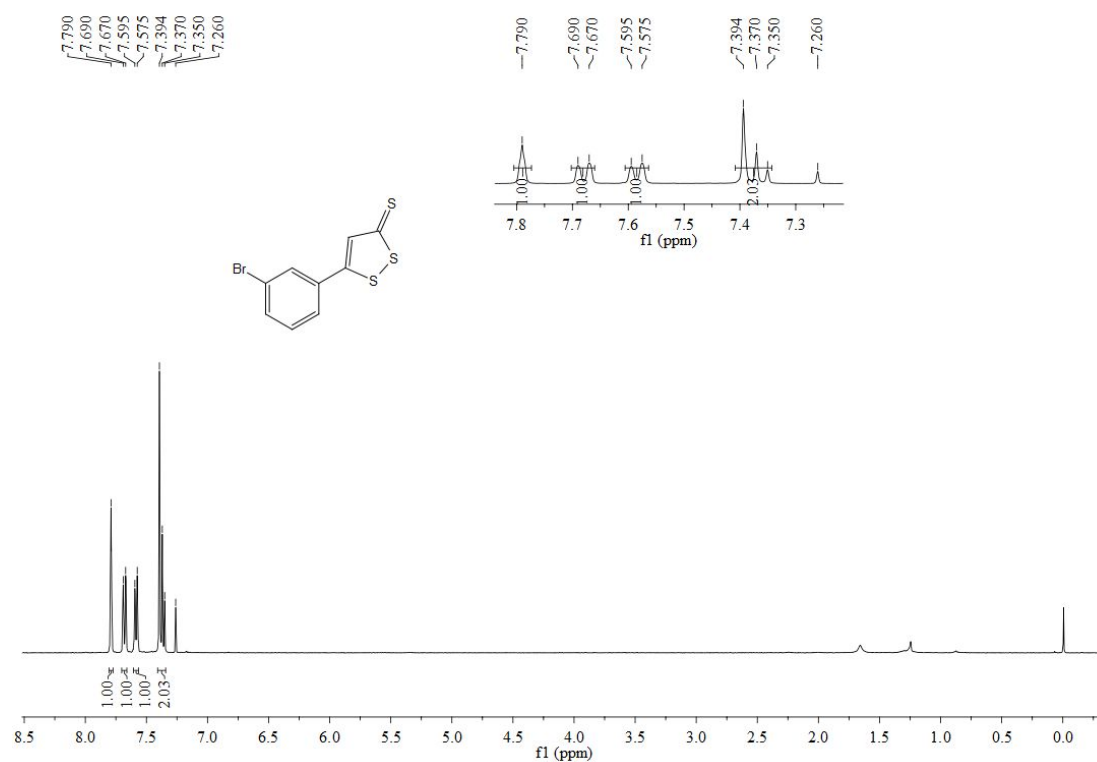
¹³C NMR: 5-(3-fluorophenyl)-3H-1,2-dithiole-3-thione (2j)

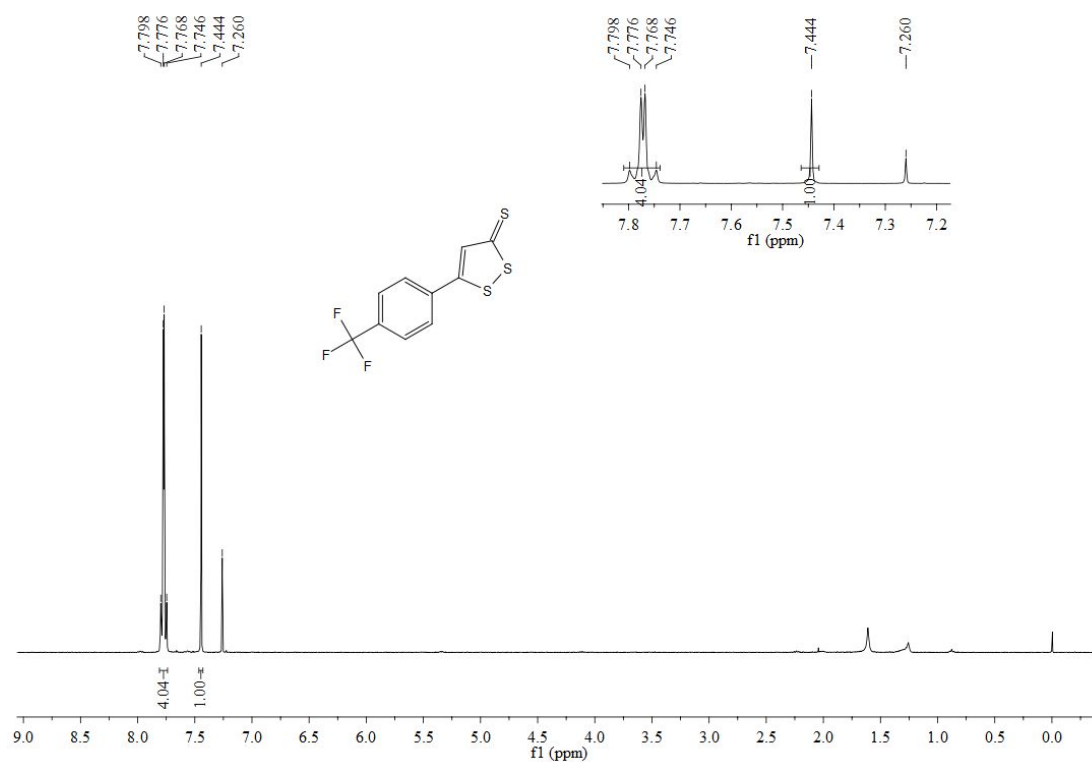


¹H NMR: 5-(3-chlorophenyl)-3H-1,2-dithiole-3-thione (2k)

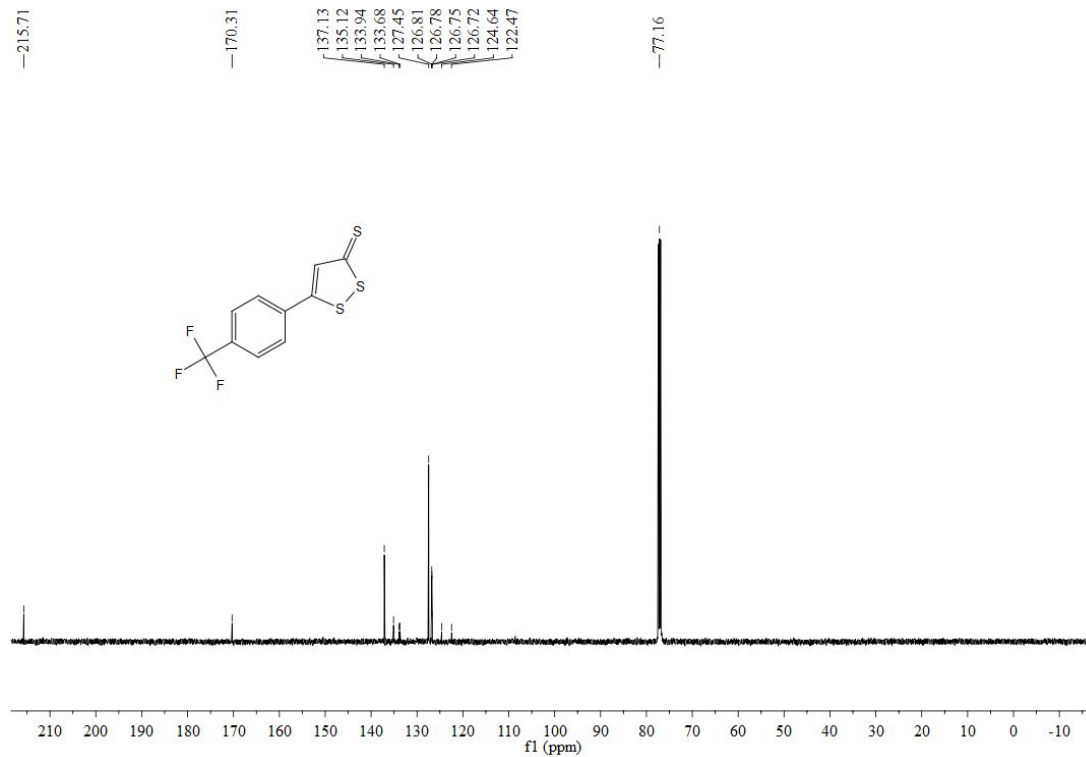


¹³C NMR: 5-(3-chlorophenyl)-3H-1,2-dithiole-3-thione (2k)

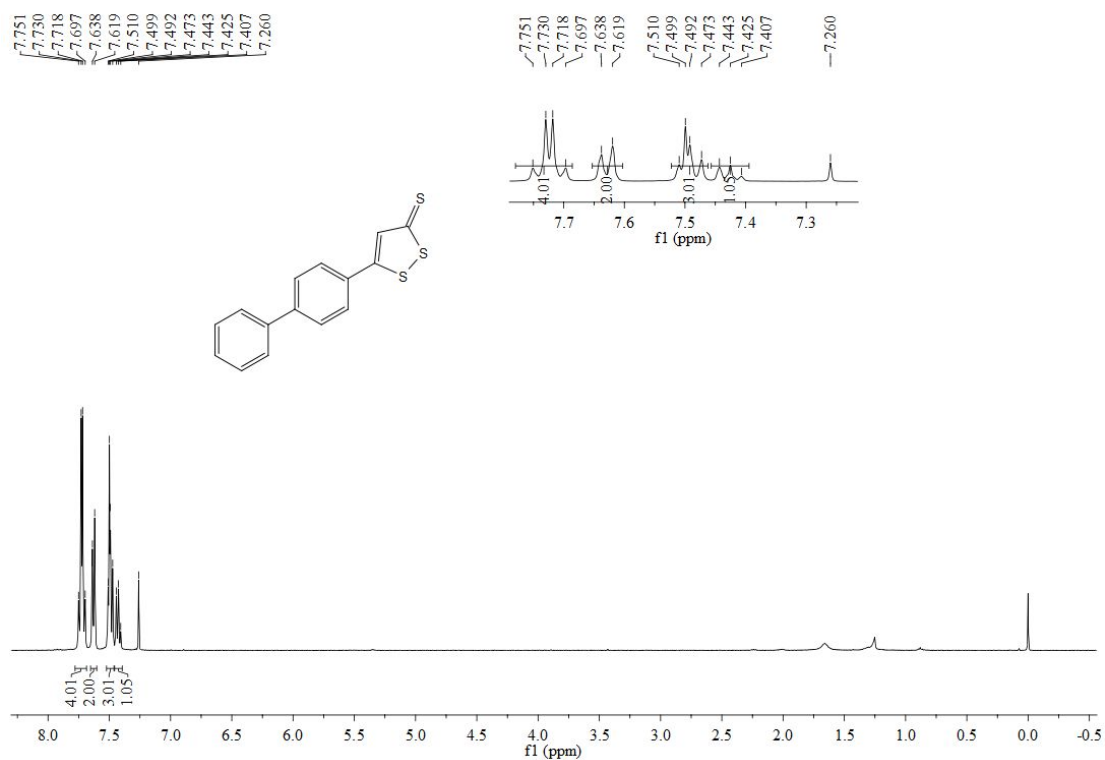




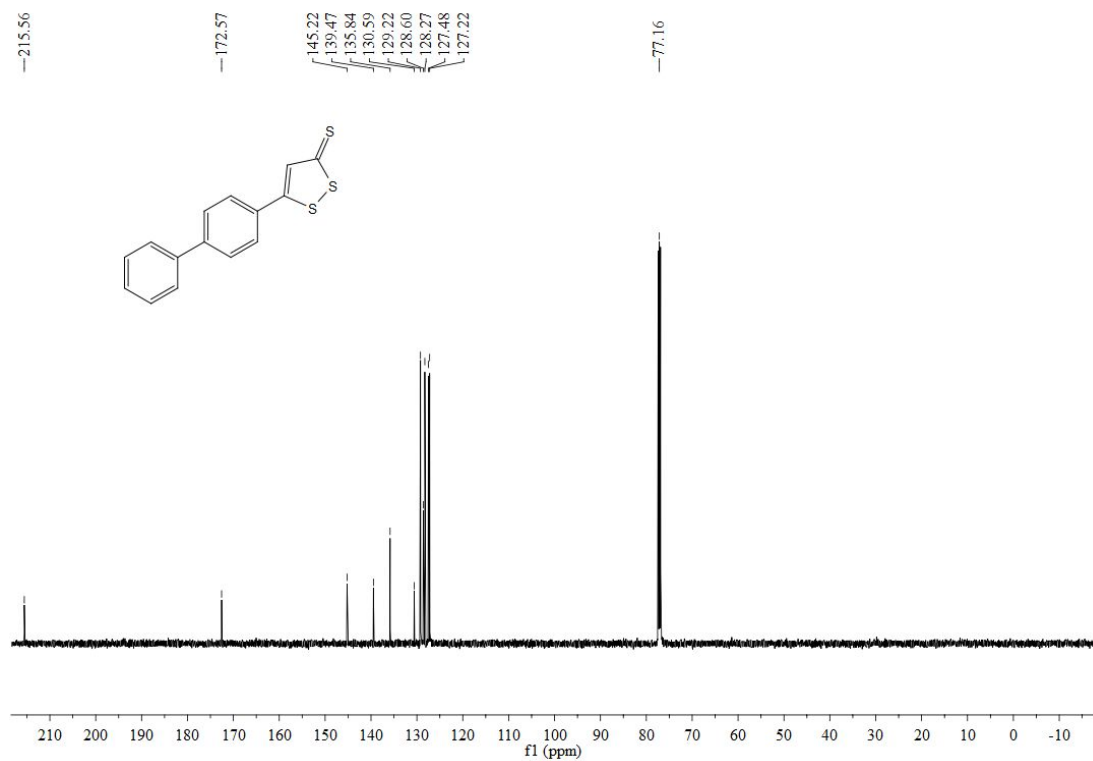
¹H NMR: 5-(4-(trifluoromethyl)phenyl)-3H-1,2-dithiole-3-thione (2m)



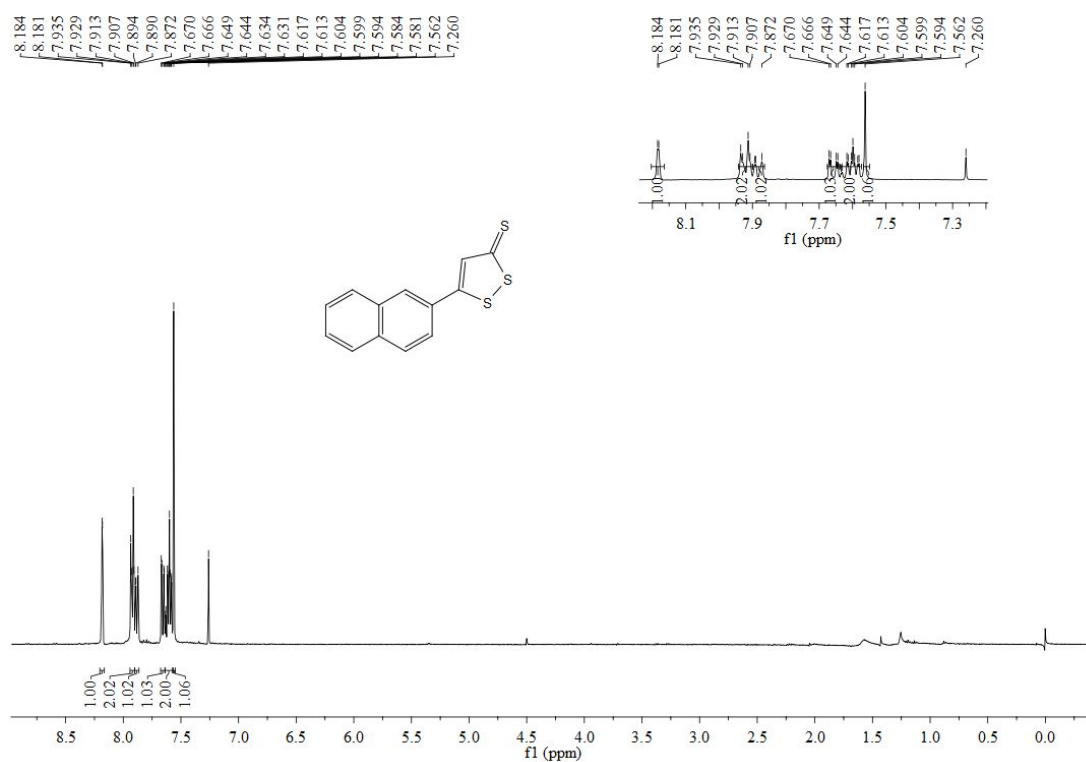
¹³C NMR: 5-(4-(trifluoromethyl)phenyl)-3H-1,2-dithiole-3-thione (2m)



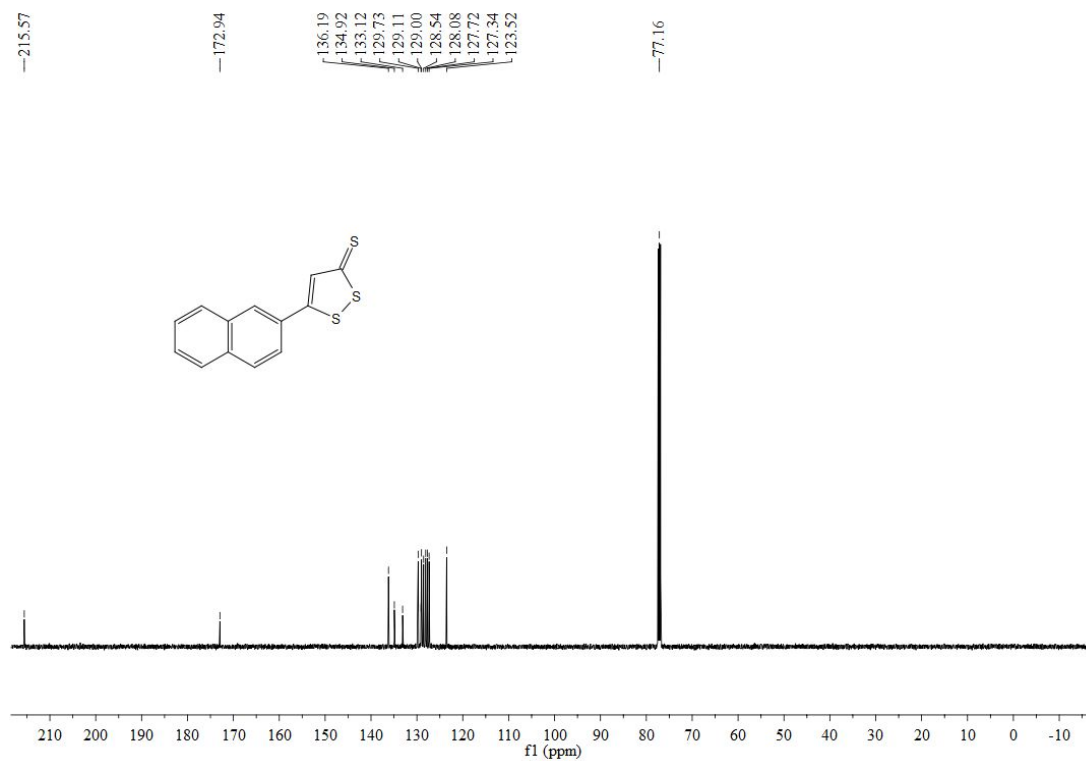
¹H NMR: 5-([1,1'-biphenyl]-4-yl)-3H-1,2-dithiole-3-thione (2n)



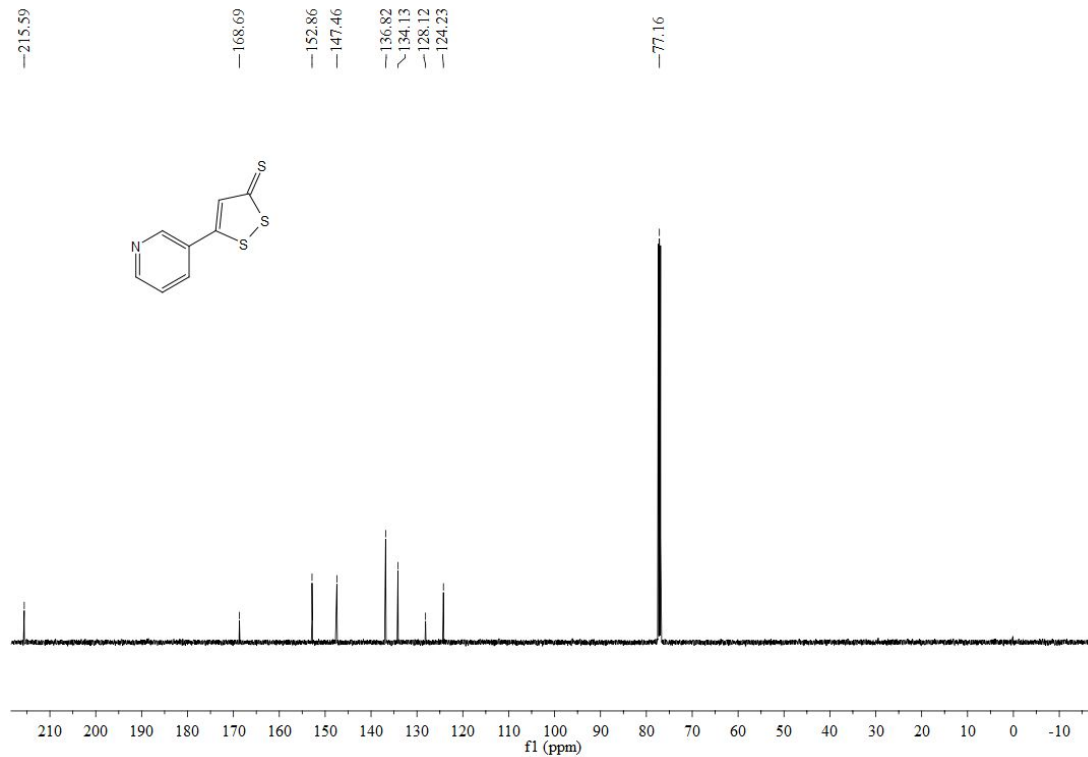
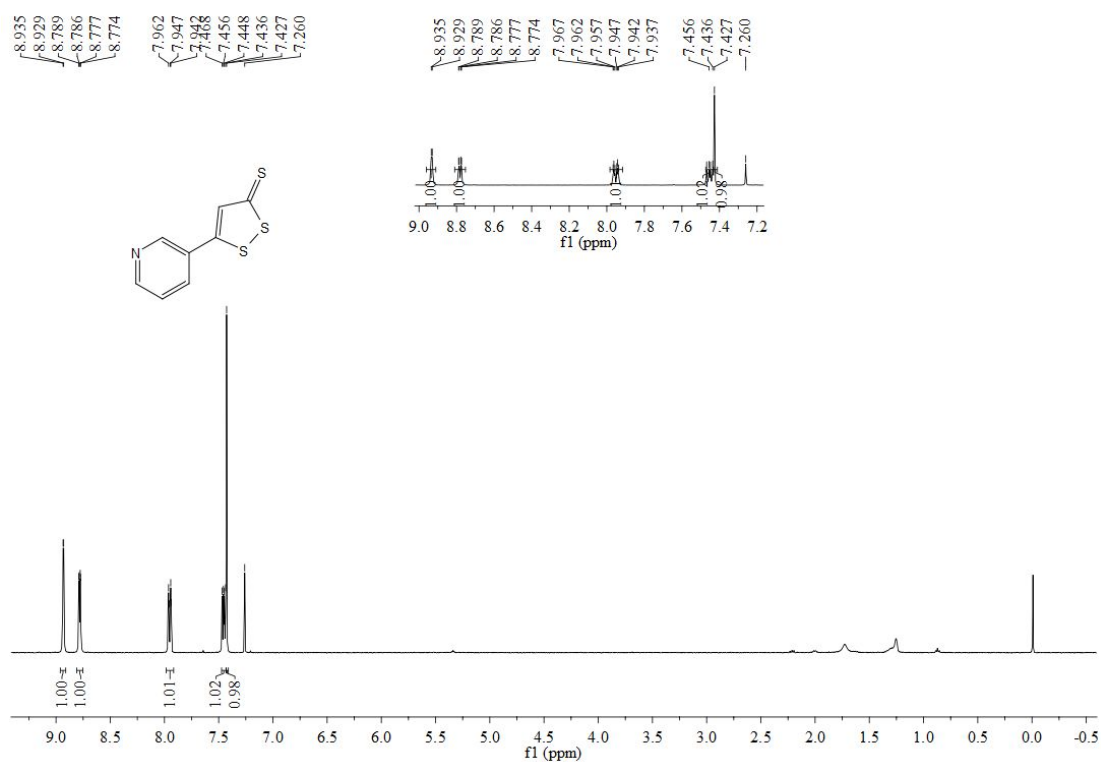
¹³C NMR: 5-([1,1'-biphenyl]-4-yl)-3H-1,2-dithiole-3-thione (2n)

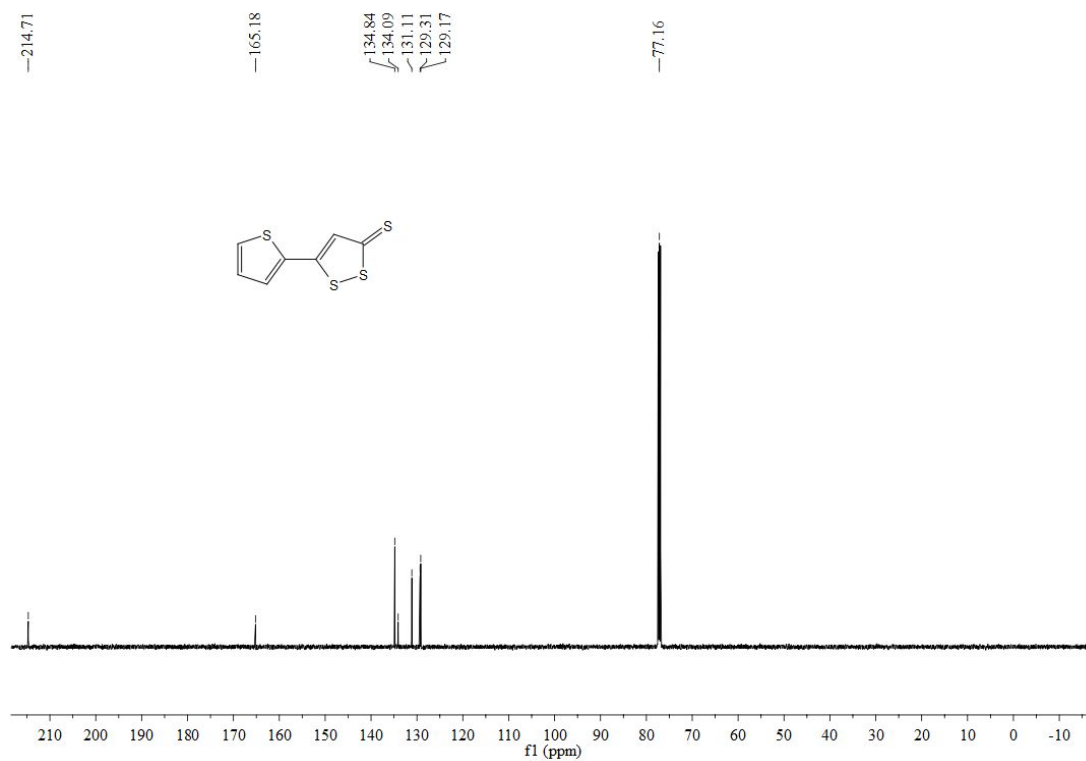
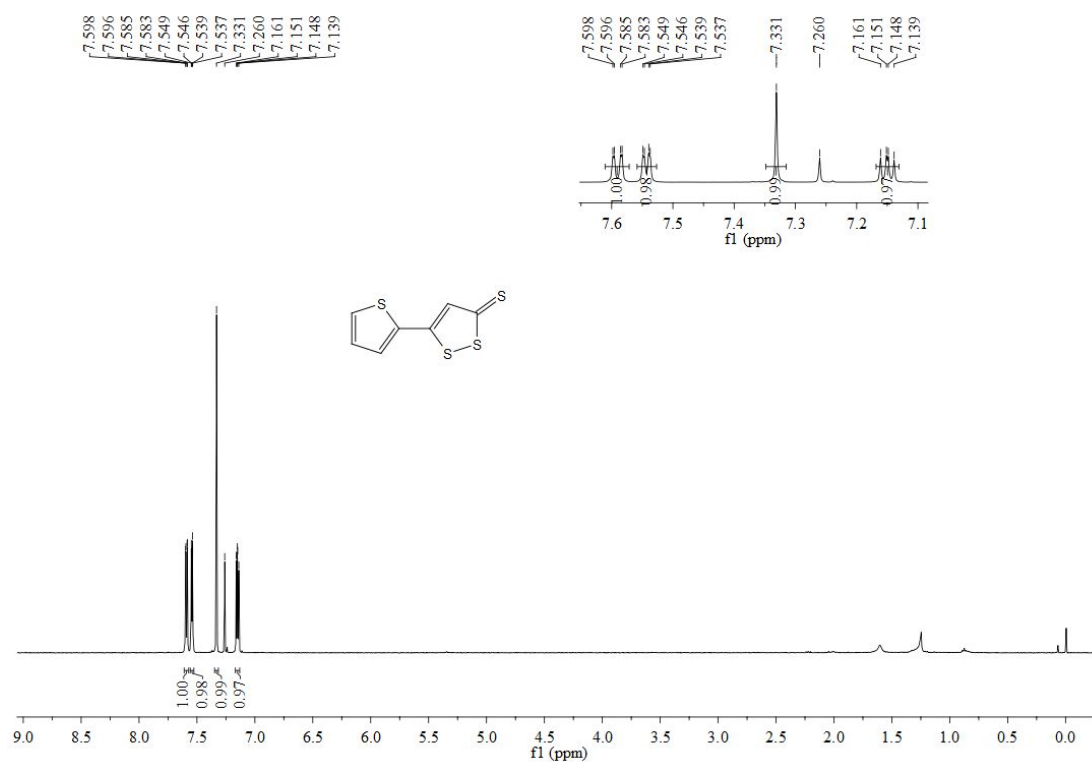


¹H NMR: 5-(naphthalen-2-yl)-3H-1,2-dithiole-3-thione (2o)

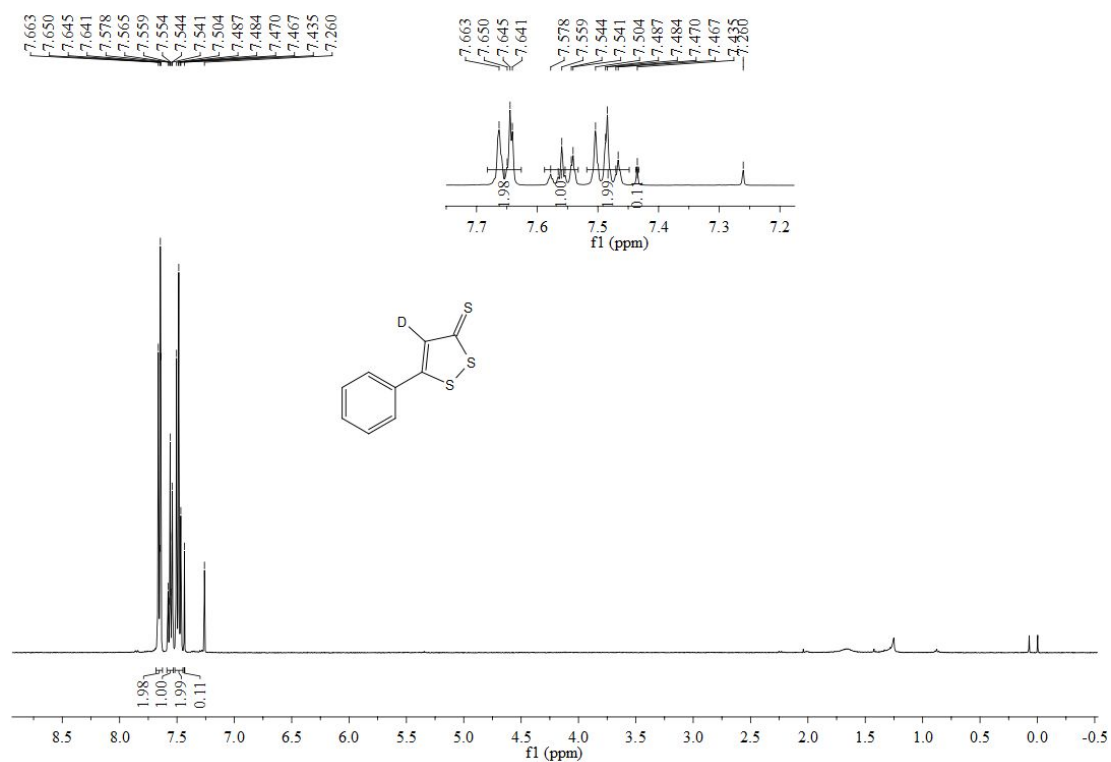


¹³C NMR: 5-(naphthalen-2-yl)-3H-1,2-dithiole-3-thione (2o)

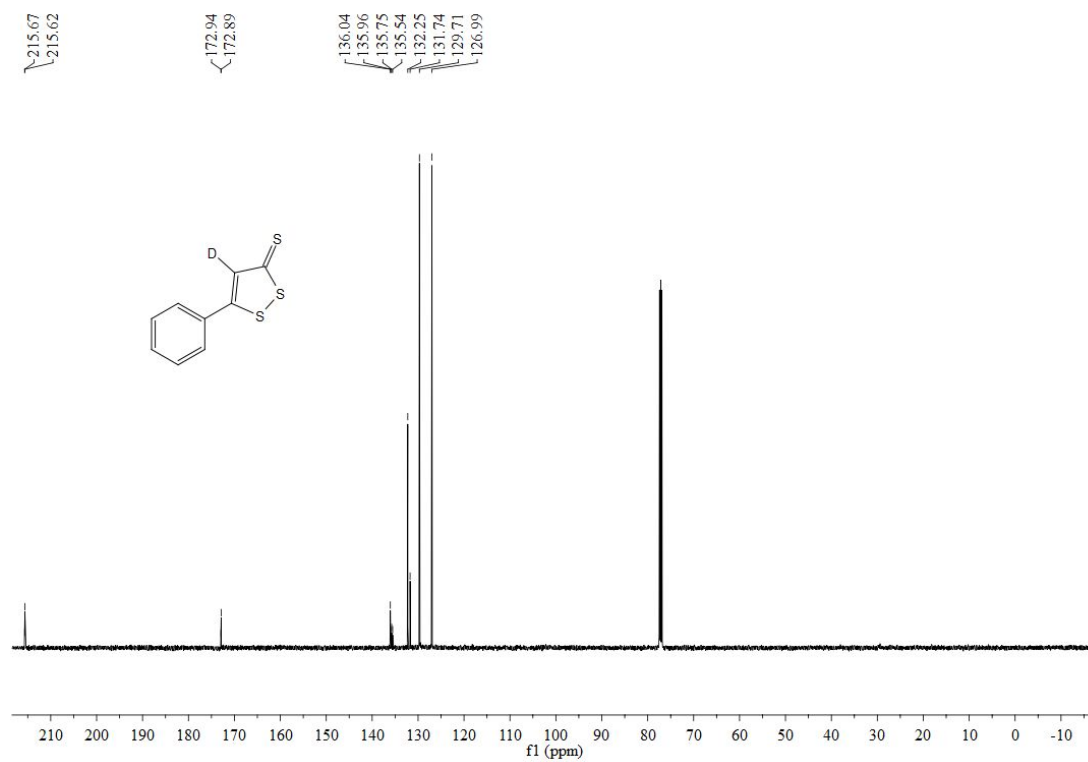




5. NMR Spectra for Compound D-2a

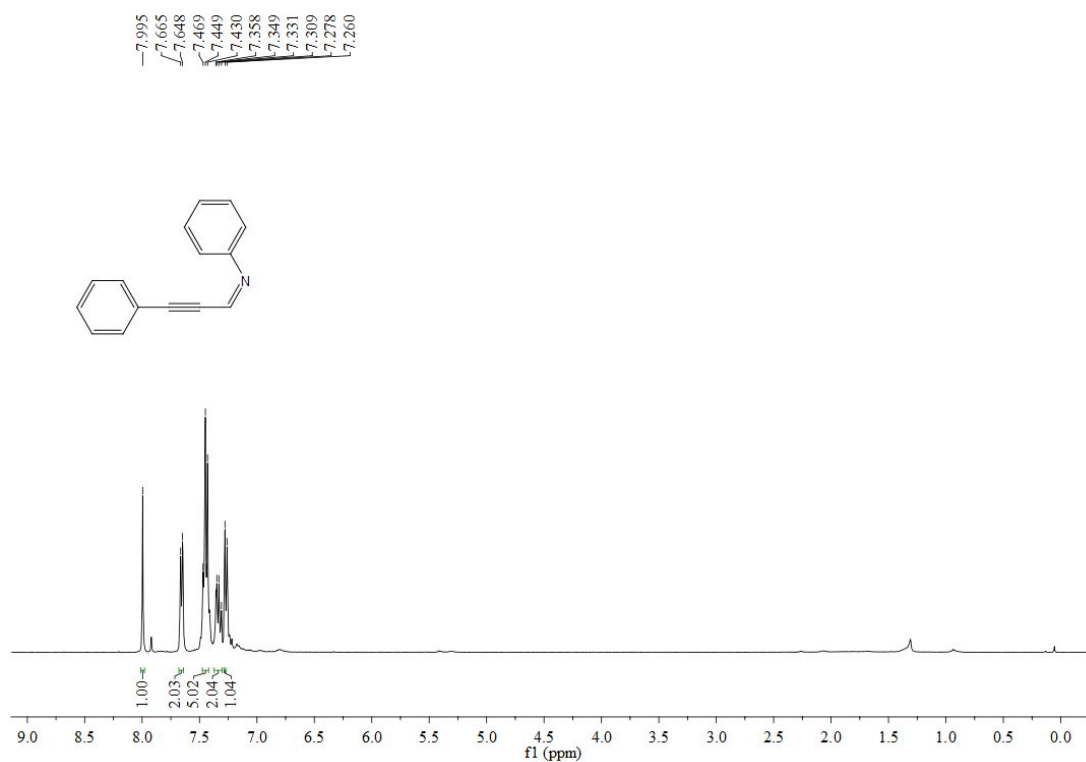


¹H NMR: 5-phenyl-3H-1,2-dithiole-3-thione-4-D (D-2a)

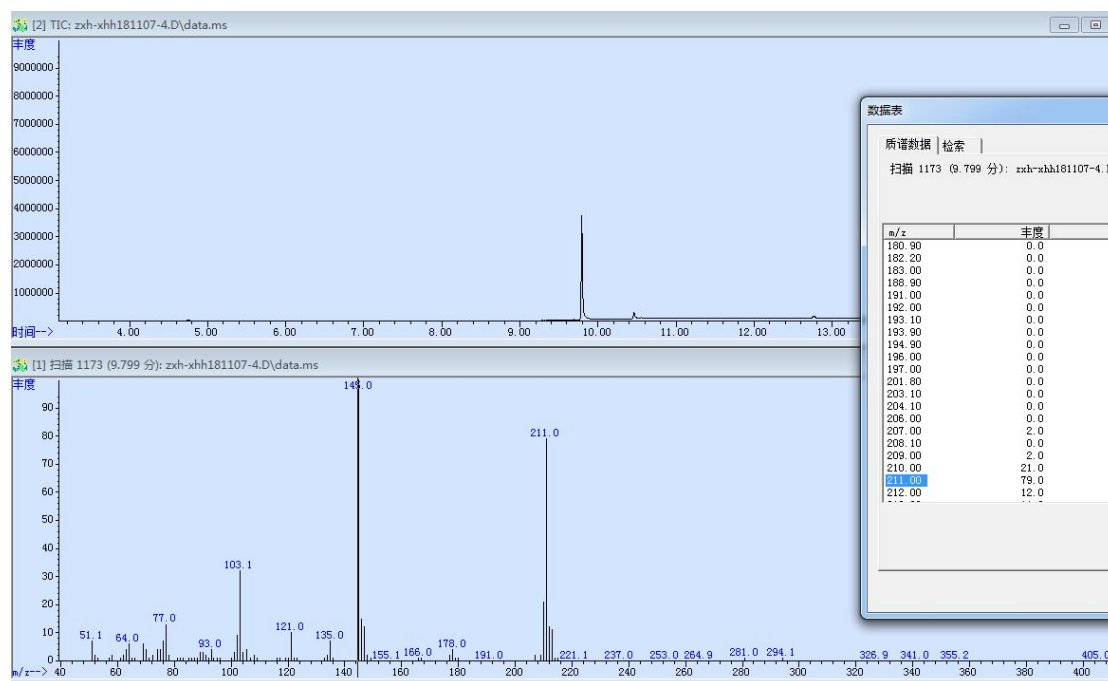


¹³C NMR: 5-phenyl-3H-1,2-dithiole-3-thione-4-D (D-2a)

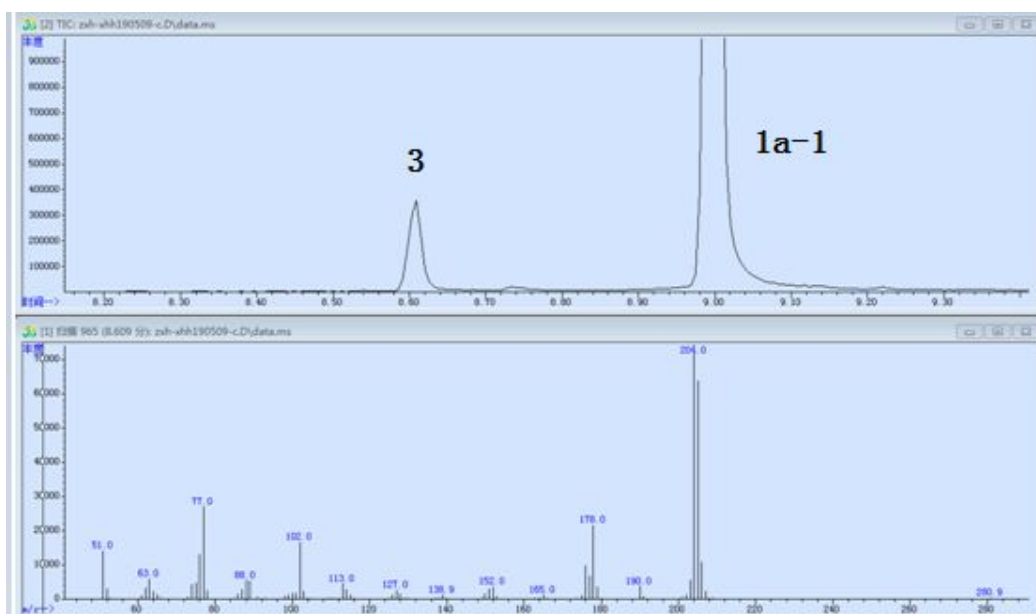
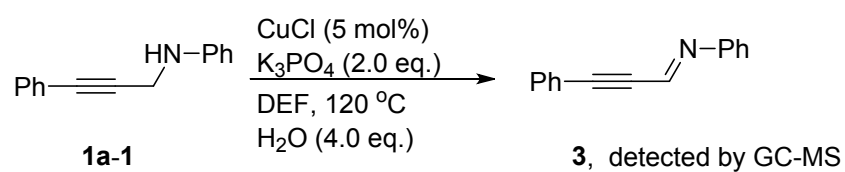
6. ^1H NMR: (Z)-N,3-diphenylprop-2-yn-1-imine (3)



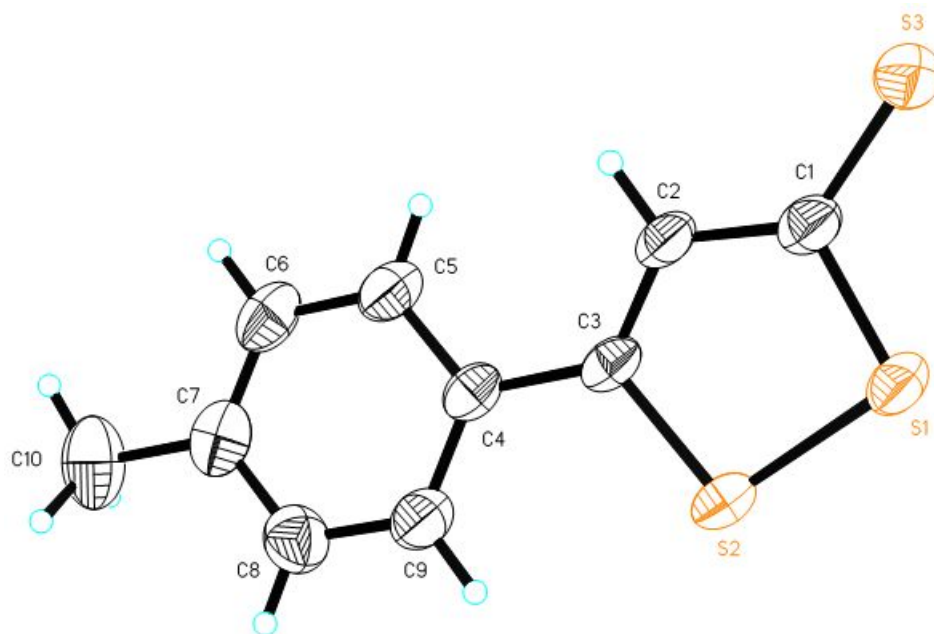
7. GC analysis for Compound D-2a.



8. GC analysis for Compound 3



9. X-ray crystal structure and data of compound 2b



The displacement ellipsoids are drawn at the 30% probability level

Single crystals suitable for X-ray analysis were obtained by slow evaporation of CH_2Cl_2 solvent.

Supplementary crystallographic data was deposited at the Cambridge Crystallographic Data Centre (CCDC) under the number CCDC-1883614 (**2b**) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request.cif.

Table S3: Crystal Structure and Data Refinement Parameters of compound 2b

Compound	2b
Empirical Formula	C ₁₀ H ₈ S ₃
Formula Weight	224.34
Crystal System / Space Group	Triclinic, P -1
a / Å	7.3636(8)
b / Å	8.0204(9)
c / Å	18.386(2)
α / °	90.452(2)
β / °	94.406(2)
γ / °	105.314(2)
V / Å ³	1043.8(2)
Z	4
D _{calc} (g/cm ³)	1.428
μ (mm ⁻¹)	0.658
Crystal size (mm)	0.180 x 0.150 x 0.120
Color / Shape	red
Temp (K)	298(2)
Theta range for collection	1.111 to 25.996
Reflections collected	7696
Independent reflections	4092
Data/restraints/parameters	4092 / 0 / 237
Goodness of fit on F ²	1.030
Final R indices [I > 2 σ (I)]	R1 = 0.0364, wR2 = 0.0884
R indices (all data)	R1 = 0.0587, wR2 = 0.1006
Largest difference peak/hole	0.226 and -0.279