

Supporting Information

Visible Light Initiated Amino Group *Ortho*-Directed Copper (I)-Catalysed Aerobic Oxidative C(*sp*)-S
Coupling Reaction: Synthesis of 2-phenylbenzothiazoles *via* Thia-Wolff rearrangement

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1. General experimental details:

The ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker spectrometers 300, 400 and 500 MHz NMR spectrometer (300, 400 and 500 MHz for ^1H NMR and 75, 100 and 125 MHz for ^{13}C NMR) respectively with TMS as an internal standard. Mass spectra were recorded on Xevo G2S Q-TOF spectrometer. TLC was performed on using Merck pre-coated TLC plates (Merck 60 F_{254}) and detected under UV light. Column chromatography was carried out with silica gel (100-200 mesh). Reagents and solvents were purified as per standard procedures. Absorption spectra were recorded using Shimadzu UV-1601 UV-VIS spectrophotometer in ACN solvent. Steady-state fluorescence spectra were recorded on Perkin Elmer LS 45 Fluorescence spectrometer by excitation at 420 nm.

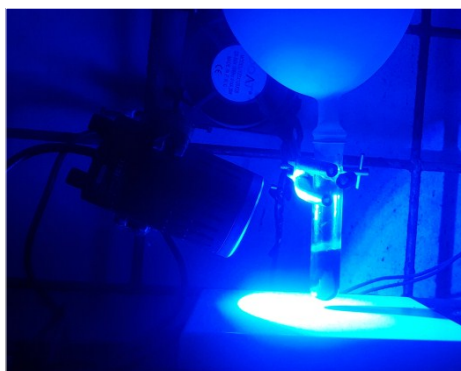


Figure I. Reaction setup for S-alkynylation reactions.

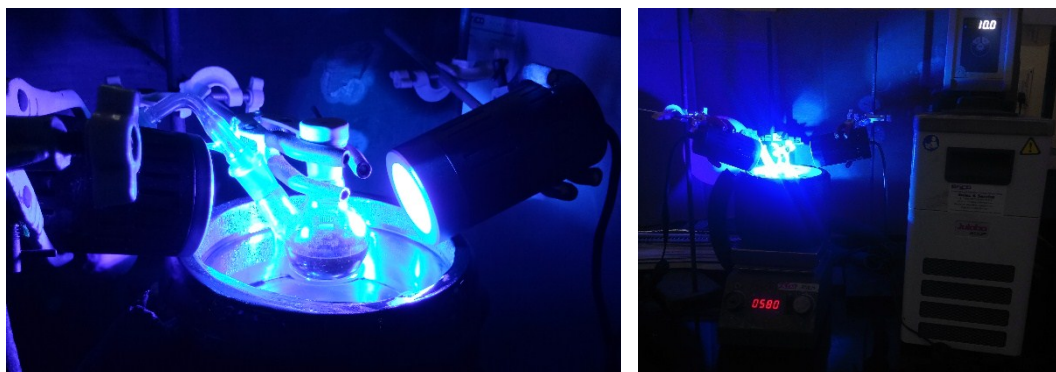


Figure 2. Reaction setup for synthesis of 2-phenylbenzothiazoles.

2. X-ray crystallographic studies of compound 3ai

Figure 3. ORTEP structure of compound **3ai** (CCDC 1951215).

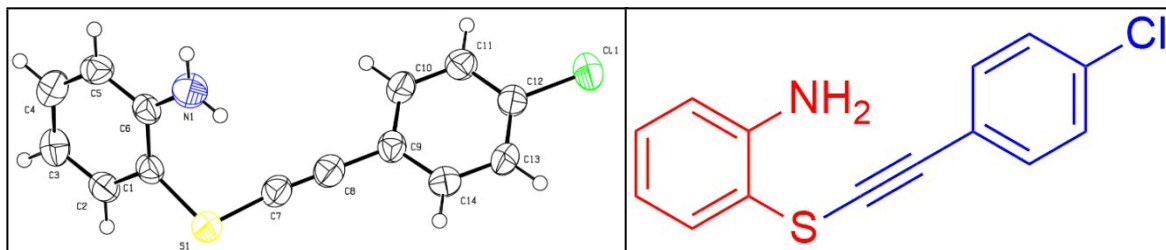


Table 1. Crystal data and structure refinement for Compound **3ai**.

Identification code Compound	3ai
Empirical formula	C ₁₄ H ₁₀ Cl N S
Formula weight	259.74
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 7.9940(9) Å α = 90 ° b = 5.8548(6) Å β = 92.333 (10)° c = 25.946(2) Å γ = 90 (3)°
Volume	1213.4(2) Å ³
Z	4
Density (calculated)	1.422 g/cm ³
Absorption coefficient	0.460 mm ⁻¹
F(000)	536.0
Crystal size	0.280x 0.210 x 0.170 mm ³

Theta range for data collection	1.571 to 31.224°.
Index ranges	-11<=h<=11, -8<=k<=7, -37<=l<=37
Reflections collected	16223
Independent reflections	3648 [R(int) = 0.0763]
Completeness to theta	25.242° 100 %
Absorption correction	Multi-scan
Max. and min. transmission	0.925 and 0.891
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3648 / 0 / 154
Goodness-of-fit on F2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0675, wR2 = 0.1397
R indices (all data)	R1 = 0.1275, wR2 = 0.1724

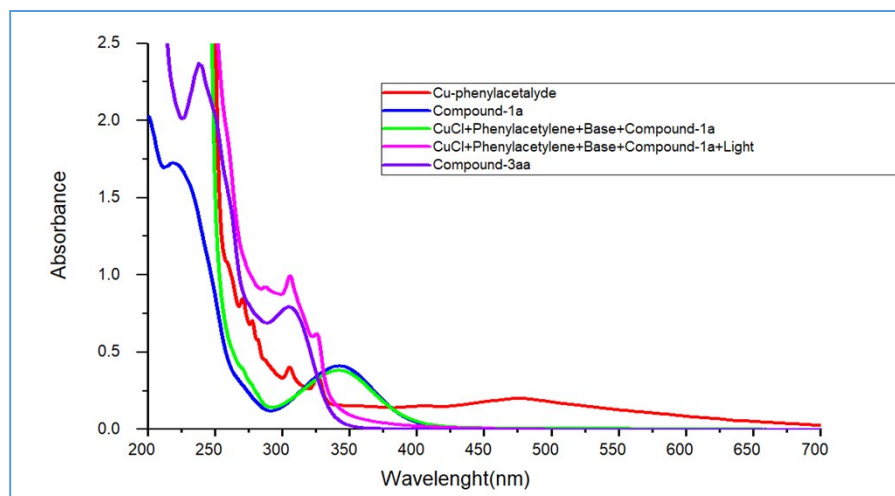


Figure 4. UV-visible absorption spectra of copper phenylacetylide (red), substrate **1a** (blue), phenylacetylene with CuCl before (green) and after irradiation in ACN solvent (purple).

a) b)

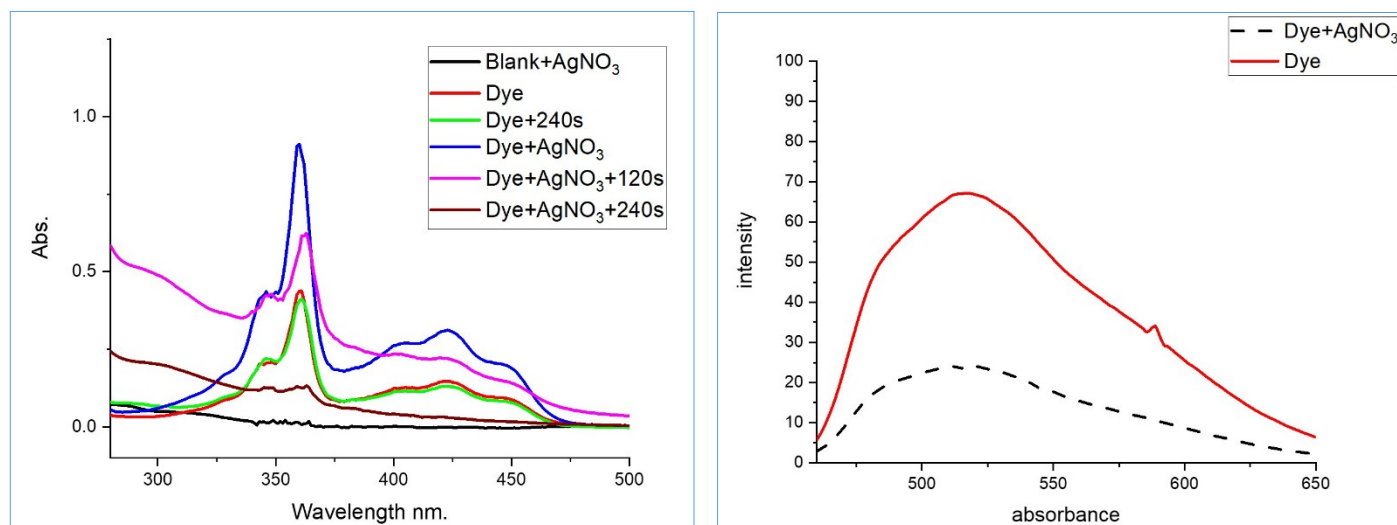


Figure 5. Spectra of the reduced catalyst $\text{Acr}^{\bullet}\text{-Mes}$ formed upon irradiation in the presence of AgNO_3 under inert atmosphere after 120s (purple) and 240s (wine). **b)** Quenching of the fluorescence of excited $\text{Acr}^{\bullet}\text{-Mes}$ by AgNO_3 (50 equiv.).

HRMS DST-FIST Funded, Department of Chemistry, IIT Madras

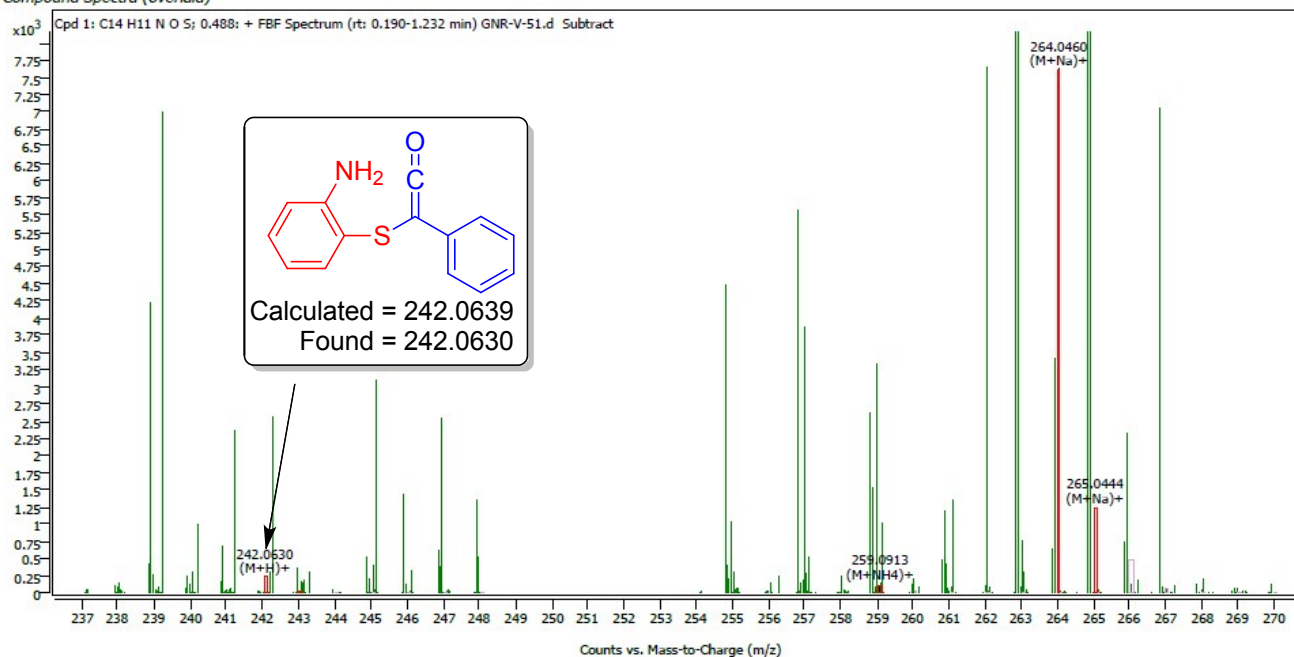
ESI Mass Report

Name	19022020-46-GSK	Data File Path	D:\MassHunter\Data\2020\FEB-2020\GSK\GNR-V-51.d
Sample ID		Acq. Time (Local)	19-02-2020 17:38:18 (UTC+05:30)
Instrument	Instrument 1	Method Path (Acq)	D:\MassHunter\Methods\Direct Infusion_HPLC.m
MS Type	QTOF	Version (Acq SW)	6200 series TOF/6500 series Q-TOF 10.1 (48.0)
Inj. Vol. (ul)	2	IRM Status	Success
Position	P2-D5	Method Path (DA)	D:\MassHunter\Methods\10.0\Default.m
Plate Pos.		Target Source Path	
Operator		Result Summary	1 qualified (1 targets)

Compound Details

Cpd. 1: C₁₄H₁₁N O S

Compound Spectra (overlaid)

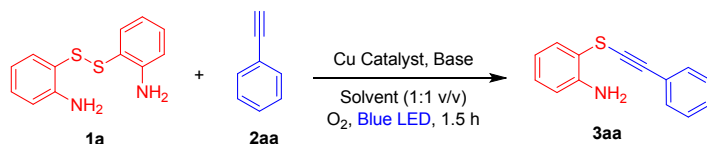


Compound ID Table

Cpd	Formula	Mass (Tqt)	Calc. Mass	Mass	Species	Diff(Tqt.ppm)	mDa
1	C ₁₄ H ₁₁ N O S	241.0561	241.0563	242.0630	(M+H)+	0.75	0.18
				259.0913	(M+NH ₄)+		
				264.0460	(M+Na)+		

HRMS spectrum of compound of ketene intermediate **14** (Mass recorded after irradiation of 1.5 h)

Table S1: Optimization table for alkynylsulfide **3aa** from 2-aminothiophenol dimer **1a** and phenylacetylene **2aa**^a



Entry	Cat. (mol %)	Base	Solvent	Yield (%) ^b
1	CuCl (5)	K ₂ CO ₃	MeOH	88
2	CuCl (5)	K ₂ CO ₃	ACN	85
3	CuCl (5)	K ₂ CO ₃	DMSO	55
4	CuCl (5)	K ₂ CO ₃	ACN:MeOH	92
5	CuCl (10)	K ₂ CO ₃	ACN:MeOH	85
6	CuCl(5)	Cs ₂ CO ₃	ACN:MeOH	90
7	CuCl(5)	Na ₂ CO ₃	ACN:MeOH	81
8	CuCl(5)	K(OAc)	ACN:MeOH	75
9	CuI(5)	K ₂ CO ₃	ACN:MeOH	91
10	CuBr(5)	K ₂ CO ₃	ACN:MeOH	90
11	Cu(OAc) (5)	K ₂ CO ₃	ACN:MeOH	78
12	CuCl ₂ (5)	K ₂ CO ₃	ACN:MeOH	40
13	CuSO ₄ (5)	K ₂ CO ₃	ACN:MeOH	15
14	CuCl (5)	K ₂ CO ₃	H ₂ O:MeOH	n.r. ^c
15	-	K ₂ CO ₃	ACN:MeOH	n.r. ^c
16	CuCl(5)	-	ACN:MeOH	n.r. ^c
17 ^c	CuCl(5)	K ₂ CO ₃	ACN:MeOH	n.r. ^c
18 ^d	CuCl(5)	K ₂ CO ₃	ACN:MeOH	trace

^aReaction conditions: **1a** (0.2 mmol), **2aa** (0.42 mmol), base (0.43 mmol.) and CuCl (5mol%) in solvent (1:1, 8 mL). ^bYields were determined after purification. ^cIn the presence of N₂. ^dIn the absence of light.

^enr = No reaction.

Table S2: Optimization table for 2-phenylbenzothiazoles **5a** from alkynyl sulfide **3aa**^a

3aa $\xrightarrow[\text{Blue LED, O}_2, 6\text{h}]{\text{PC, Oxidant, Solvent}}$ **5a**

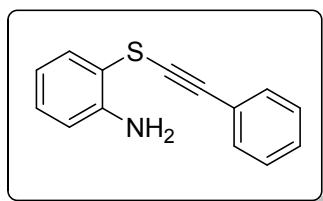
Entry	PC	Oxidant	Temp.	Solvent	Condition (light/thermal)	Yield ^b (%)
1	-	AgNO ₃	rt	ACN	thermal	nr ^d
2	-	AgOAc	rt	ACN	thermal	nr ^d
3	-	AgNO ₃	rt	ACN	light	10
4	-	AgOAc	rt	ACN	light	nr ^d
5	Acr ⁺ -Mes	AgNO ₃	rt	ACN	light	50 ^c
6	Acr ⁺ -Mes	AgOAc	rt	ACN	light	nr ^d
7	Acr ⁺ -Mes	AgNO ₃	10 °C	ACN	light	66
8	Acr ⁺ -Mes	AgNO ₃	0 °C	ACN	light	46
9	Acr ⁺ -Mes	AgNO ₃	10 °C	DMSO	light	40
10	Acr ⁺ -Mes	AgNO ₃	10 °C	MeOH	light	22
11	Acr ⁺ -Mes	AgNO ₃	10 °C	DCE	light	30
12	Rose Bengal	AgNO ₃	10 °C	ACN	light	31
13	Eosin Y	AgNO ₃	10 °C	ACN	light	15
14	Benzophenone	AgNO ₃	10 °C	ACN	light	10

^aReaction conditions: **3aa** (0.22 mmol), 2 equiv. of oxidant and 5 mol% of Acr⁺-Mes used in blue LED and 8 mL of solvent. ^bYields were determined after column purification. ^cNo reaction was observed under thermal condition. ^dnr = No reaction.

General procedure for the synthesis of S-alkynylated compounds

Reaction tube was charged with Dimer (0.2 mmol), Acetylene (0.42 mmol), K_2CO_3 (0.21 mmol) and CuCl (5 mol%) in ACN: MeOH (1:1) 8 mL. The reaction mixture was stirred under blue light for 1.5 hour. After the reaction completion, mixture was passed through celite and solvent was evaporated under reduced pressure. The crude was purified by column chromatography using EtOAc/Hexane (5: 95) as eluent to furnish the afforded S-alkynylated compounds.

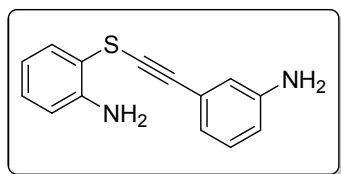
2-((phenylethynyl)thio)aniline 3aa



Yield 92%, yellow liquid.

1H NMR (300 MHz, $CDCl_3$): δ_H 4.20 (br s, 2H), 6.66-6.71 (m, 2H), 7.09 (dt, $J = 3\text{Hz}$, $J = 6\text{Hz}$, 1H), 7.18-7.23 (m, 3H), 7.33-7.36 (m, 2H), 7.43 (dd, $J = 3\text{Hz}$, $J = 6\text{Hz}$, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 93.5, 114.5, 115.9, 119.0, 123.2, 128.1, 129.9, 131.5, 132.8, 146.5; HRMS: $(M+H)^+$ calculated for $C_{14}H_{12}NS$: 226.0690, Found: 226.0688.

2-(((4-methoxyphenyl)ethynyl)thio)aniline 3ab

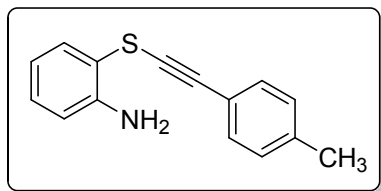


Yield 65%, brown solid.

1H NMR (300 MHz, $CDCl_3$): δ_H 3.66 (br s, 4H), 6.57 (dd, $J = 2.4\text{Hz}$, $J = 5.7\text{Hz}$, 1H), 6.69-6.75 (m, 3H), 6.80 (d, $J = 6.2\text{Hz}$, 1H), 7.03 (t, $J = 7.8\text{Hz}$, 1H), 7.12 (dt, $J = 1.2\text{Hz}$, $J = 6.6\text{Hz}$, 1H), 7.48 (dd, $J = 1.5\text{Hz}$,

$J = 6.3\text{Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 75.9, 93.9, 114.4, 115.4, 115.9, 117.8, 119.0, 122.0, 123.7, 129.2, 130.0, 132.7, 146.3, 146.5.

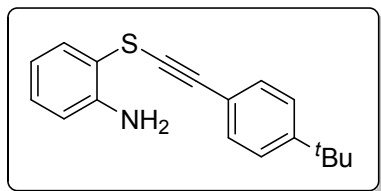
2-((p-tolylethynyl)thio)aniline 3ac



Yield 91%, yellow solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 2.26 (s, 3H), 4.19 (br s, 2H), 6.68 (t, $J = 7.8\text{Hz}$, 2H), 7.01-7.10 (m, 3H), 7.24 (d, $J = 9\text{Hz}$, 2H), 7.43 (d, $J = 9\text{Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 21.5, 75.5, 93.6, 114.4, 115.9, 119.0, 119.8, 129.0, 130.0, 131.7, 132.8, 138.7, 146.4; **HRMS**: $(\text{M}+\text{H})^+$ calculated for $\text{C}_{15}\text{H}_{14}\text{NS}$: 240.0846, Found: 240.0894.

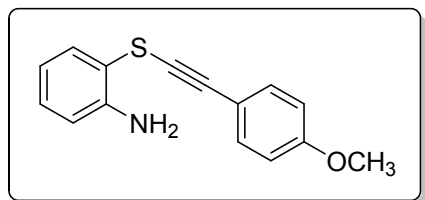
2-((p-tert-butylethynyl)thio)aniline 3ad



Yield 90%, yellow oily liquid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 1.21 (s, 9H), 4.17 (br s, 2H), 6.64-6.69 (m, 2H), 7.01-7.09 (m, 1H), 7.22-7.24 (m, 2H), 7.27-7.30 (m, 2H), 7.41 (dd, $J = 1.6\text{Hz}$, $J = 6.4\text{Hz}$, 1H); ^{13}C NMR (100MHz, CDCl_3): δ_{C} 30.1, 33.7, 74.5, 92.7, 113.4, 114.8, 118.0, 118.8, 124.2, 128.9, 130.5, 131.6, 145.3, 150.8.

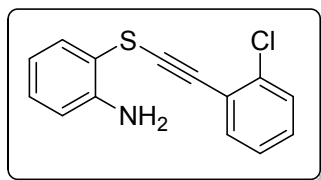
2-(((4-methoxyphenyl)ethynyl)thio)aniline 3ae



Yield 75%, yellow crystalline solid.

^1H NMR (500 MHz, CDCl_3): δ_{H} 3.71 (s, 3H), 4.18 (br s, 2H), 6.64-6.69 (m, 2H), 6.72-6.74 (m, 2H), 7.06 (dt, $J=1\text{Hz}$, $J=3\text{Hz}$, 1H), 7.29-7.31 (m, 2H), 7.42 (dd, $J=1\text{Hz}$, $J=3\text{Hz}$, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 55.3, 74.6, 93.5, 113.9, 114.6, 115.0, 115.9, 119.0, 130.0, 132.7, 133.6, 146.4, 159.8.

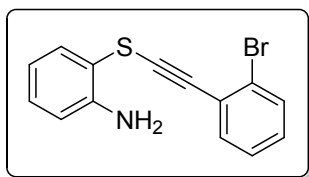
2-(((2-chlorophenyl)ethynyl)thio)aniline 3af



Yield 86%, yellow oil.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.22 (br s, 2H), 6.68 (t, $J=9\text{Hz}$, 2H), 7.07-7.17 (m, 3H), 7.28 (d, $J=9\text{Hz}$, 1H), 7.35 (dd, $J=2\text{Hz}$, $J=6\text{Hz}$, 1H), 7.46 (d, $J=9\text{Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 82.5, 90.3, 115.9, 119.0, 123.2, 126.2, 129.0, 129.18, 130.0, 132.9, 133.0, 135.9, 146.6.

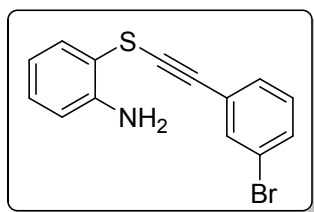
2-(((2-bromophenyl)ethynyl)thio)aniline 3ag



Yield 75%, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 4.21 (br s, 2H), 6.63-6.69 (m, 2H), 7.01-7.19 (m, 3H), 7.31-7.33 (m, 1H), 7.44-7.48 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 82.0, 92.1, 116.0, 119.1, 125.3, 127.0, 127.6, 128.9, 129.4, 130.3, 132.3, 133.0, 133.3, 146.6.

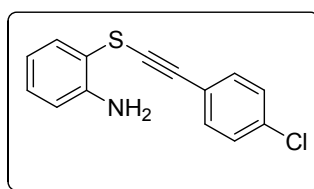
2-(((2-chlorophenyl)ethynyl)thio)aniline 3ah



Yield 85%, yellow oil.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.19 (br s, 2H), 6.68 (t, $J=9\text{Hz}$, 2H), 7.03-7.12 (m, 2H), 7.24 (d, $J=9\text{Hz}$, 1H), 7.34 (d, $J=9\text{Hz}$, 1H), 7.42 (dd, $J=1.5\text{Hz}$, $J=6\text{Hz}$, 1H), 7.47 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 78.8, 91.5, 113.5, 115.9, 119.1, 122.0, 124.9, 129.7, 130.0, 130.4, 131.4, 133.2, 134.2, 146.7.

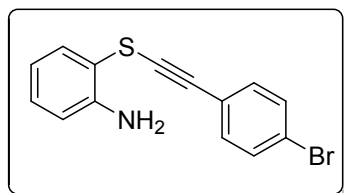
2-(((4-chlorophenyl)ethynyl)thio)aniline 3ai



Yield 89%, White solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.20 (br s, 2H), 6.68 (t, $J=9\text{Hz}$, 2H), 7.11 (dt, $J=1.5\text{Hz}$, $J=6\text{Hz}$, 1H), 7.17-7.19 (m, 2H), 7.25-7.28 (m, 2H), 7.42 (dd, $J=1.5\text{Hz}$, $J=6\text{Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 78.3, 92.1, 115.9, 116.5, 119.1, 121.7, 128.5, 130.1, 132.7, 133.0, 134.4, 146.6.

2-(((4-bromophenyl)ethynyl)thio)aniline 3aj

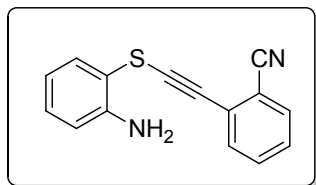


Yield 88%, yellow solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.19 (br s, 2H), 6.67 (t, $J=9\text{Hz}$, 2H), 7.08 (t, $J=9\text{Hz}$, 1H), 7.18

(d, J = 6Hz, 2H), 7.33 (d, J = 6Hz, 2H), 7.41 (d, J = 9Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 78.6, 92.2, 114.0, 115.9, 119.1, 122.1, 122.5, 130.1, 130.8, 131.5, 132.8, 146.6.

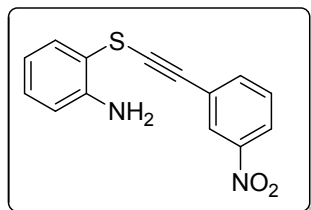
2-(((2-aminophenyl)thio)ethynyl)benzonitrile 3ak



Yield 65%, Red liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.28 (br s, 2H), 6.69 (d, J = 9Hz, 2H), 7.05-7.13 (m, 1H), 7.18-7.19 (m, 1H), 7.25-7.31 (m, 1H), 7.41-7.47 (m, 2H), 7.46 (d, J = 9Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 85.1, 89.1, 112.5, 114.9, 116.1, 117.5, 119.0, 126.9, 128.2, 130.8, 132.2, 132.3, 132.6, 133.5, 147.0.

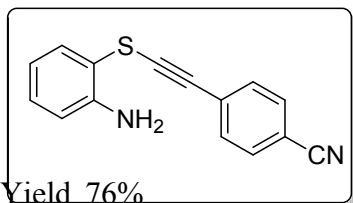
2-(((3-nitrophenyl)ethynyl)thio)aniline 3al



Yield 75%, yellow oil.

^1H NMR (500 MHz, CDCl_3): δ_{H} 4.24 (br s, 2H), 6.69 (dt, J = 0.6, J = 3Hz, 2H), 7.12 (dt, J = 0.9Hz, J = 3Hz, 1H), 7.11-7.14 (m, 1H), 7.37 (t, J = 6Hz, 1H), 7.42 (dd, J = 0.9Hz, J = 3Hz, 1H), 7.59-7.61 (m, 1H), 8.03 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 80.9, 90.4, 112.7, 116.0, 119.1, 122.8, 124.8, 126.1, 129.33, 130.85, 133.6, 136.9, 146.9, 148.0.

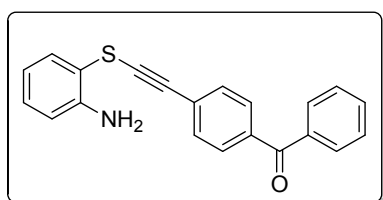
2-(((4-bromophenyl)ethynyl)thio)aniline 3am



Yield 76%, yellow solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 4.21 (br s, 2H), 6.67-6.7 (m, 2H), 7.12 (dt, $J = 1.6\text{Hz}, J = 5.6\text{Hz}$, 1H), 7.35-7.36 (m, 2H), 7.41 (dd, $J = 1.2\text{Hz}, J = 1.6\text{Hz}$, 1H), 7.47-7.49 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 83.1, 91.5, 111.2, 112.8, 116.0, 118.4, 119.1, 127.9, 130.8, 131.5, 131.9, 133.5, 146.8.

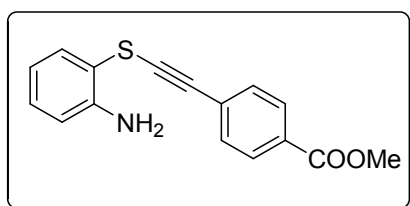
(4-(((2-aminophenyl)thio)ethynyl)phenyl)(phenyl)methanone 3an



Yield 83%, yellow solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.23 (br s, 2H), 6.69 (t, $J = 6\text{Hz}$, 2H), 7.10 (t, $J = 6\text{Hz}$, 1H), 7.40 (q, $J = 6\text{Hz}, J = 9\text{Hz}$, 5H), 7.50 (t, $J = 6\text{Hz}$, 1H), 7.66 (t, $J = 9\text{Hz}$, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 81.1, 92.6, 113.3, 116.0, 119.1, 127.2, 128.3, 129.9, 130.0, 130.5, 131.0, 132.5, 133.3, 136.6, 137.3, 146.8, 195.8.

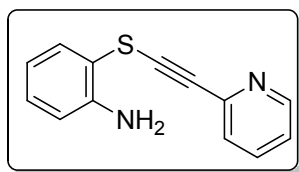
2-(((4-bromophenyl)ethynyl)thio)aniline 3ao



Yield 78%, white solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 3.82 (s, 3H), 4.21 (br s, 2H), 6.67-6.70 (m, 2H), 7.10 (dt, $J = 1.2\text{Hz}, J = 5.6\text{Hz}$, 1H), 7.34-7.37 (m, 2H), 7.42 (dd, $J = 1.6\text{Hz}, J = 6.4\text{Hz}$, 1H), 7.85-7.88 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 52.2, 80.8, 92.5, 113.3, 115.9, 119.1, 127.6, 129.3, 129.4, 130.5, 131.1, 133.3, 146.7, 166.4.

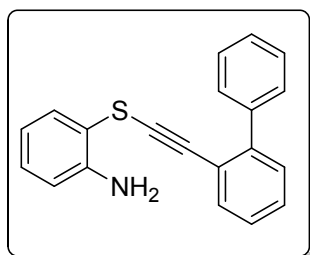
2-((pyridin-2-ylethynyl)thio)aniline 3ap



Yield 67%, brown liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.26 (br s, 2H), 6.63-6.67 (m, 2H), 7.04-7.10 (m, 2H), 7.27 (d, $J=8.1\text{Hz}$, 1H), 7.42 (dd, $J=1.2\text{Hz}$, $J=6.6\text{Hz}$, 1H), 7.47-7.53 (m, 1H), 8.42 (d, $J=4.2\text{Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 78.7, 92.4, 112.6, 115.9, 119.0, 1226, 126.8, 130.6, 133.6, 136.1, 143.0, 147.0, 149.9.

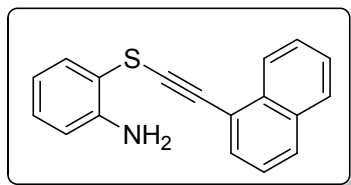
2-((1,1'-biphenyl)-2-ylethynyl)thio)aniline 3aq



Yield 86%, yellow liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 3.87 (br s, 2H), 6.60 (t, $J=9\text{Hz}$, 2H), 7.05 (dt, $J=1.2\text{Hz}$, $J=6.4\text{Hz}$, 1H), 7.17-7.28 (m, 7H), 7.41-7.44 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 79.2, 93.3, 113.7, 115.9, 118.9, 121.4, 127.0, 127.3, 128.0, 128.4, 129.1, 129.4, 130.0, 132.7, 132.9, 140.4, 143.8, 146.5.

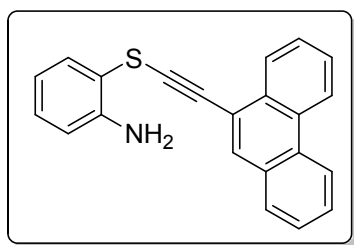
2-((naphthalen-1-ylethynyl)thio)aniline 3ar



Yield 88%, yellow liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.22 (br s, 2H), 6.64-6.70 (m, 2H), 7.07 (dt, $J=1.2\text{Hz}, J=6.2\text{Hz}$, 1H), 7.27 (t, $J=6.1\text{Hz}$, 1H), 7.36-7.45 (m, 2H), 7.49 (dd, $J=1.2\text{Hz}, J=6\text{Hz}$, 1H), 7.54 (d, $J=10.8\text{Hz}$, 1H), 7.67-7.72 (m, 2H), 8.16 (d, $J=10.2\text{Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 81.5, 91.7, 114.3, 115.9, 119.1, 120.6, 125.1, 126.1, 126.4, 126.8, 128.8, 128.8, 130.2, 130.5, 132.9, 133.1, 133.4, 146.5.

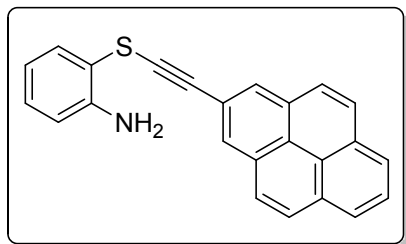
2-((phenanthren-9-ylethynyl)thio)aniline **3as**



Yield 85%, white solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.29 (br s, 2H), 6.71 (t, $J=9\text{Hz}$, 2H), 7.11 (t, $J=7.5\text{Hz}$, 1H), 7.45-7.55 (m, 5H), 7.72 (d, $J=7.8\text{Hz}$, 1H), 7.91 (s, 1H), 8.27 (d, $J=7.5\text{Hz}$, 1H), 8.54 (t, $J=9\text{Hz}$, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 81.2, 91.8, 114.2, 116.0, 119.1, 119.4, 122.6, 122.7, 126.8, 126.9, 127.1, 127.5, 128.5, 130.0, 130.2, 130.3, 131.1, 132.0, 133.1, 146.6.

2-((pyren-2-ylethynyl)thio)aniline **3at**

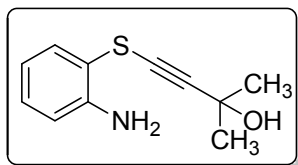


Yield 75%, yellow solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 4.31 (br s, 2H), 6.70-6.75 (m, 2H), 7.10-7.15 (m, 1H), 7.57 (d, $J=6.4\text{Hz}$, 1H), 7.84-8.02 (m, 6H), 8.08 (t, $J=9.2\text{Hz}$, 2H), 8.38 (d, $J=9.2\text{Hz}$, 1H); ^{13}C NMR (100 MHz,

CDCl₃): δ_C 82.1, 92.7, 114.4, 116.0, 117.4, 119.2, 124.2, 124.4, 125.4, 125.6, 126.2, 127.1, 128.2, 128.4, 129.6, 130.3, 131.0, 131.2, 131.3, 132.1, 133.0, 146.6.

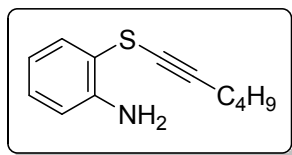
4-((2-aminophenyl)thio)-2-methylbut-3-yn-2-ol 3au



Yield 63%, yellow liquid.

¹H NMR (400 MHz, CDCl₃): δ_H 1.43 (s, 6H), 6.64-6.69 (m, 2H), 7.07 (dt, J = 1.2Hz, J = 6Hz, 1H), 7.35 (dd, J = 0.9Hz, J = 6Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ_C 31.2, 65.8, 69.7, 98.6, 114.1, 116.0, 119.1, 130.1, 132.8, 146.4.

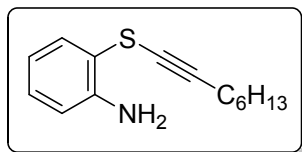
2-(hex-1-yn-1-ylthio)aniline 3av



Yield 83%, yellow liquid.

¹H NMR (400 MHz, CDCl₃): δ_H 0.80 (t, J = 7.2Hz, 3H), 1.28-1.34 (m, 2H), 1.39-1.44 (m, 2H), 2.24 (t, J = 6Hz, 2H), 4.11 (br s, 2H), 6.61-6.65 (m, 2H), 7.04-7.05 (m, 1H), 7.35-7.37 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ_C 13.5, 19.8, 21.9, 30.7, 65.5, 95.5, 115.1, 115.7, 118.9, 129.6, 132.3, 146.2.

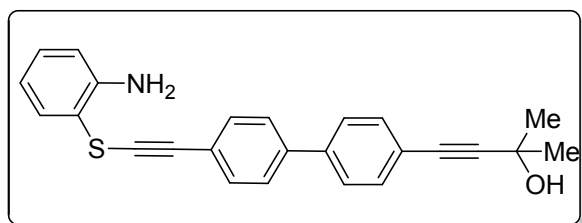
2-(oct-1-yn-1-ylthio)aniline 3aw



Yield 85%, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 0.80 (t, $J = 7.2\text{Hz}$, 3H), 1.17-1.29 (m, 6H), 1.42-1.45 (m, 2H), 2.22-2.25 (t, $J = 1.2\text{Hz}$, 2H), 4.10 (br s, 2H), 6.62-6.67 (m, 2H), 7.02-7.06 (m, 1H), 7.36-7.38 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 14.0, 20.1, 22.5, 28.5, 28.6, 31.3, 65.6, 95.6, 115.2, 115.7, 118.9, 129.6, 132.3, 146.1.

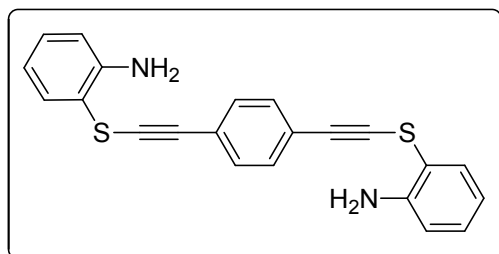
4-(4'-(((2-aminophenyl)thio)ethynyl)-[1,1'-biphenyl]-4-yl)-2-methylbut-3-yn-2-ol 3ax



Yield 73%, brown solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 1.55 (s, 6H), 2.0 (br s, 1H), 4.22 (br s, 2H), 6.69 (t, $J = 7.8\text{Hz}$, 2H), 7.10-7.12 (m, 1H), 7.38-7.46 (m, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 31.5, 65.6, 77.8, 81.9, 93.2, 94.8, 114.0, 116.0, 119.1, 122.1, 122.2, 126.7, 126.8, 130.2, 132.1, 133.0, 139.9, 140.0, 146.5.

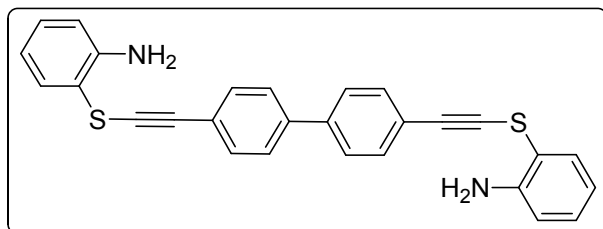
2,2'-((1,4-phenylenebis(ethyne-2,1-diyl))bis(sulfanediyl))dianiline 3ba



Yield 82%, brown solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.20 (br s, 4H), 6.65-6.70 (m, 4H), 7.06-7.11 (m, 2H), 7.23 (s, 4H), 7.41 (dd, $J = 1.2\text{Hz}$, $J = 6.4\text{Hz}$, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 79.2, 92.9, 113.7, 115.9, 119.1, 122.8, 130.4, 131.3, 133.1, 146.6; **HRMS:** ($\text{M}+\text{H}$) $^+$ calculated for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{S}_2$: 373.0833, Found: 373.0851.

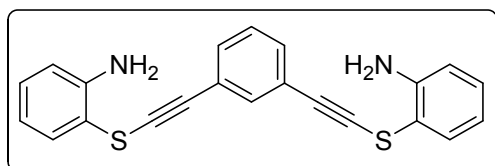
2,2'-((([1,1'-biphenyl]-4,4'-diylbis(ethyne-2,1-diyl))bis(sulfanediyl))dianiline 3bb



Yield 83%, brown solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.20 (br s, 4H), 6.66-6.72 (m, 4H), 7.06-7.12 (m, 2H), 7.37-7.45 (m, 10H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 77.8, 93.1, 113.9, 115.8, 119.0, 122.2, 126.7, 130.1, 132.0, 132.9, 139.9, 146.5.

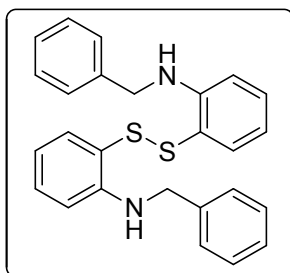
2,2'-((1,3-phenylenebis(ethyne-2,1-diyl))bis(sulfanediyl))dianiline 3bc



Yield 75%, brown liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.22 (br s, 4H), 6.70-6.76 (m, 4H), 7.11-7.17 (m, 3H), 7.20-7.31 (m, 2H), 7.44-7.48 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 78.0, 92.3, 113.9, 115.9, 119.1, 123.4, 128.3, 130.2, 131.2, 133.1, 134.4, 146.6.

2,2'-disulfanediylbis(N-benzylaniline) 1b:

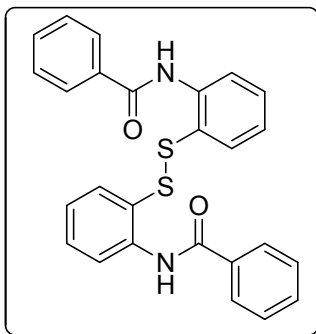


Yield 40%, yellow liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.20 (s, 4H), 5.30 (br s, 2H), 6.43-6.46 (m, 4H), 7.10-7.30 (m, 14H);

^{13}C NMR (75 MHz, CDCl_3): δ_{C} 47.6, 110.7, 116.6, 118.4, 127.1, 127.2, 128.6, 131.9, 137.1, 138.9, 149.1.

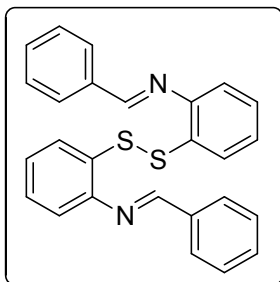
N,N'-(disulfanediy)lbis(2,1-phenylene))dibenzamide 1c¹:



Yield 91%, White solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 6.93-6.98 (m, 2H), 7.31 (dt, $J = 1.2\text{Hz}$, $J = 6.4\text{Hz}$, 2H), 7.42-7.49 (m, 6H), 7.54-7.59 (m, 2H), 7.70 (d, $J = 7.5\text{Hz}$, 4H), 8.50 (d, $J = 8.1\text{Hz}$, 2H), 8.95 (br s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 120.6, 123.5, 124.3, 127.0, 128.8, 132.0, 132.3, 134.3, 136.6, 139.9, 164.9.

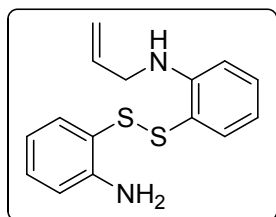
(NE,N'E)-2,2'-disulfanediy)lbis(N-benzylideneaniline) 1d²:



Yield 88%, White solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 7.16-7.19 (m, 2H), 7.22-7.28 (m, 4H), 7.51-7.54 (m, 6H), 7.71-7.74 (m, 2H), 8.01-8.05 (m, 4H), 8.52 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 117.2, 126.0, 126.9, 128.8, 129.2, 131.7, 132.1, 136.0, 148.9, 160.0.

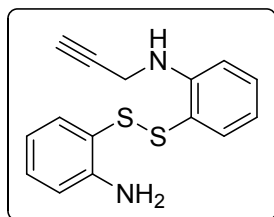
N-allyl-2-((2-aminophenyl)disulfanyl)aniline 1i:



Yield 35%, yellow liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 3.72 (d, J = 4.5Hz, 2H), 4.26 (br s, 2H), 5.06 (br s, 1H), 5.12 (dd, J = 1.2Hz, J = 9Hz, 1H), 5.25 (dd, J = 1.2Hz, J = 15Hz, 1H), 5.78-5.90 (m, 1H), 6.48-6.68 (m, 4H), 7.09-7.21 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 46.0, 110.6, 115.1, 116.0, 116.5, 118.2, 118.6, 119.0, 131.4, 131.8, 134.8, 136.7, 137.0, 148.6, 149.2.

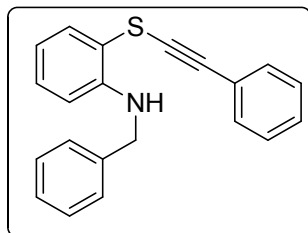
2-((2-aminophenyl)disulfanyl)-N-(prop-2-yn-1-yl)aniline 1j:



Yield 33%, yellow liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 2.19 (t, J = 2.4Hz, 1H), 3.88 (s, 2H), 4.31 (br s, 2H), 5.13 (br s, 1H), 6.56-6.62 (m, 2H), 6.67-6.73 (m, 2H), 7.11-7.30 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 33.2, 71.2, 80.5, 111.0, 115.2, 117.6, 118.3, 118.7, 119.4, 131.6, 131.9, 136.8, 137.1, 148.2, 148.6.

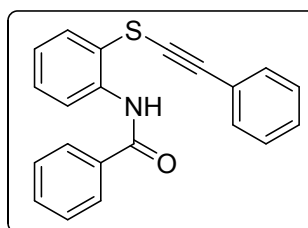
N-benzyl-2-((phenylethynyl)thio)aniline 4b:



Yield 60%, yellow liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 4.36 (s, 2H), 5.07 (br s, 1H), 6.53-6.62 (m, 2H), 7.08-7.19 (m, 7H), 7.24-7.29 (m, 4H) 7.45 (dd, $J=1.2\text{Hz}$, $J=6.6\text{Hz}$, 1H) ; ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 47.8, 77.5, 92.9, 111.2, 113.0, 117.4, 123.0, 127.2, 127.3, 128.3, 128.4, 128.7, 130.8, 131.7, 133.7, 138.8, 147.5.

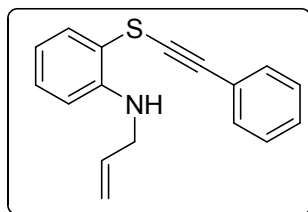
N-(2-((phenylethynyl)thio)phenyl)benzamide 4c:



Yield 75%, White solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 7.20 (dt, $J=1.2\text{Hz}$, $J=6.3\text{Hz}$, 1H), 7.27-7.34 (m, 3H), 7.36-7.39 (m, 2H), 7.44-7.51 (m, 3H), 7.55-7.60 (m, 1H), 8.01-8.04 (m, 2H), 8.44 (dd, $J=0.6\text{Hz}$, $J=7.5\text{Hz}$, 1H), 8.84 (br s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 75.6, 94.6, 120.9, 122.2, 122.6, 125.1, 127.2, 128.4, 128.9, 129.0, 130.3, 131.8, 132.1, 132.5, 134.5, 137.9, 165.4.

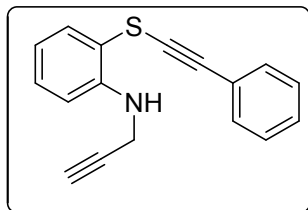
N-allyl-2-((phenylethynyl)thio)aniline 4i:



Yield 35%, yellow liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 3.90 (d, $J = 4.8\text{Hz}$, 2H), 4.86 (br s, 1H), 5.18 (dd, $J = 1.2\text{Hz}$, $J = 9\text{Hz}$, 1H), 5.33 (dd, $J = 1.2\text{Hz}$, $J = 15\text{Hz}$, 1H), 5.91-6.02 (m, 1H), 6.64-6.71 (m, 2H), 7.21-7.28 (m, 4H), 7.36-7.54 (m, 2H), 7.52 (d, $J = 1.2\text{Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 46.1, 77.4, 92.8, 111.2, 113.4, 116.2, 117.3, 123.0, 128.2, 128.3, 130.6, 131.6, 133.5, 134.6, 147.4.

2-((phenylethynyl)thio)-N-(prop-2-yn-1-yl)aniline 4j:



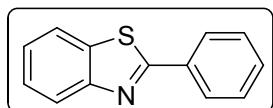
Yield 37%, yellow liquid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 2.13 (t, $J = 2.1\text{Hz}$, 1H), 3.94 (d, $J = 2.7\text{Hz}$, 2H), 4.76 (br s, 1H), 6.66-6.71 (m, 2H), 7.15-7.22 (m, 4H), 7.31-7.34 (m, 2H), 7.46-7.49 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 33.5, 71.4, 77.4, 80.4, 93.4, 111.9, 115.1, 118.6, 123.0, 128.2, 128.3, 130.3, 131.6, 133.2, 146.4.

General procedure for synthesis of 2-phenylbenzothiazoles:

Reaction tube was charged with S-alkynylated compound (0.2 mmol), AgNO₃(0.4 mmol), and 9-mesityl-10-methylacridinium tetrafluoroborate (5 mol%) in ACN 8 mL. The reaction mixture was stirred under blue light in presence of O₂ atmosphere at 10 °C for 6 hour. After the reaction completion, mixture was passed through celite and solvent was evaporated under reduced pressure. The crude was purified by column chromatography using EtOAc/Hexane (2: 98) as eluent to furnish the afforded 2-phenylbenzothiazoles

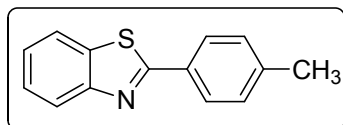
2-phenylbenzo[d]thiazole 5a³:



Yield 66%, half white solid.

¹H NMR (300 MHz, CDCl₃): δ_H7.29 (t, *J* = 6.9 Hz, 1H), 7.40-7.43 (m, 4H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.99-8.04 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ_C121.4, 123.3, 125.0, 126.1, 127.5, 128.8, 130.7, 133.9, 135.2, 154.4, 167.8; **HRMS:** (M+H)⁺ calculated for C₁₃H₁₀NS: 212.0533, Found: 212.0543.

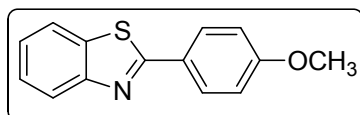
2-(p-tolyl)benzo[d]thiazole 5b³:



Yield 68%, pale yellow solid.

¹H NMR (300 MHz, CDCl₃): δ_H2.35 (s, 3H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.38-7.43 (m, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ_C20.4, 120.5, 122.0, 123.9, 125.2, 126.4, 128.6, 129.9, 133.8, 140.4, 153.1, 167.2.

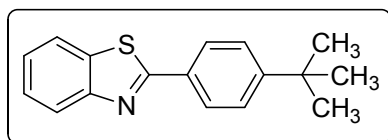
2-(4-methoxyphenyl)benzo[d]thiazole 5c³:



Yield 70%, pale yellow solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 3.86 (s, 3H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.29-7.31 (m, 1H), 7.40-7.43 (m, 1H), 7.82 (d, $J = 7.8$ Hz, 1H), 7.98-7.81 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 55.5, 114.3, 120.0, 121.5, 122.7, 124.9, 126.2, 129.2, 134.6, 154.1, 162.0, 167.3.

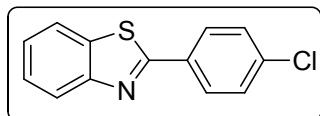
2-(4-(tert-butyl)phenyl)benzo[d]thiazole 5d⁴:



Yield 68%, pale yellow solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 1.31 (s, 9H), 7.29-7.32 (m, 1H), 7.40-7.45 (m, 2H), 7.81-7.83 (m, 1H), 7.93-7.96 (m, 3H), 7.98-7.80 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 30.1, 33.9, 120.5, 122.0, 123.9, 124.9, 125.1, 126.3, 128.5, 132.1, 133.9, 153.5, 167.4.

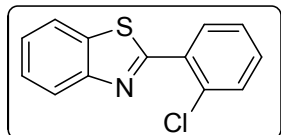
2-(4-chlorophenyl)benzo[d]thiazole 5e³:



Yield 64%, half white solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 7.33 (t, $J = 7.5$ Hz, 1H), 7.38-7.45 (m, 3H), 7.83 (d, $J = 8.1$ Hz, 1H), 8.94-8.02 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 121.6, 123.0, 125.4, 126.5, 128.7, 129.2, 1321, 135.0, 137.0, 154.0, 166.6.

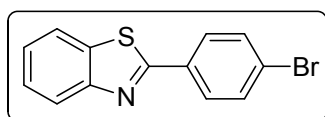
2-(2-chlorophenyl)benzo[d]thiazole 5f³:



Yield 55%, white solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 7.33-7.38 (m, 3H), 7.44-7.48 (m, 2H), 7.97-7.99 (m, 1H), 8.05-8.08 (m, 1H), 8.13-8.15 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 120.3, 122.4, 124.4, 125.2, 126.0, 129.7, 130.1, 130.7, 131.2, 131.7, 135.0, 151.4, 163.1.

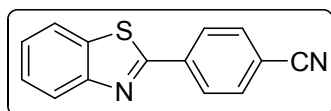
2-(4-bromophenyl)benzo[d]thiazole **5g³:**



Yield 65%, pale yellow solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 7.33 (t, $J = 7.5$ Hz, 1H), 7.40-7.45 (m, 1H), 7.51-7.57 (m, 2H), 7.82-8.7.94 (m, 3H), 8.01 (d, $J = 8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 121.6, 123.3, 125.4, 126.5, 128.9, 131.4, 132.2, 133.3, 135.0, 154.0, 166.7.

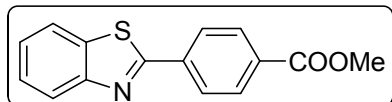
4-(benzo[d]thiazol-2-yl)benzonitrile **5h⁵:**



Yield 58%, pale yellow solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 7.36-7.40 (m, 1H), 7.45-7.49 (m, 1H), 7.72 (d, $J = 6.5$ Hz, 2H), 7.86-7.88 (m, 1H), 8.03-8.05 (m, 1H), 8.14 (d, $J = 6.5$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 114.1, 118.2, 121.8, 123.8, 126.0, 126.8, 127.9, 132.7, 135.3, 137.5, 154.0, 165.3.

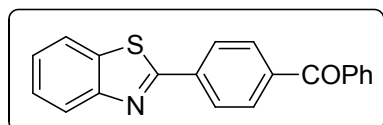
Methyl 4-(benzo[d]thiazol-2-yl)benzoate **5i⁴:**



Yield 61%, white solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 3.89 (s, 3H), 7.33-7.37 (m, 1H), 7.43-7.47 (m, 1H), 7.85-7.87 (m, 1H), 8.02-8.04 (m, 1H), 8.09 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 52.3, 121.7, 123.6, 125.7, 126.6, 127.4, 130.2, 132.0, 135.2, 137.4, 154.1, 166.4, 166.6.

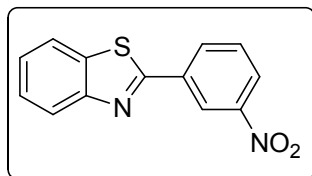
(4-(benzo[d]thiazol-2-yl)phenyl)(phenyl)methanone 5j:



Yield 56%, pale yellow solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 7.34-7.38 (m, 1H), 7.42-7.48 (m, 3H), 7.53-7.57 (m, 1H), 7.75-7.78 (m, 2H), 7.85-7.88 (m, 3H), 8.05 (d, $J = 8.1\text{ Hz}$, 1H), 8.13-8.15 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 121.7, 123.6, 125.7, 126.6, 127.3, 128.4, 130.0, 130.7, 132.7, 135.3, 136.9, 137.2, 139.3, 154.1, 166.5, 195.9, **HRMS**: $(\text{M}+\text{H})^+$ calculated for $\text{C}_{20}\text{H}_{14}\text{NOS}$: 316.0796, Found: 316.0843.

2-(3-nitrophenyl)benzo[d]thiazole 5k⁵:

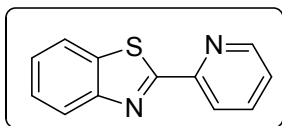


Yield 64%, yellow solid.

^1H NMR (500 MHz, CDCl_3): δ_{H} 7.38 (t, $J = 7.5\text{ Hz}$, 1H), 7.47 (t, $J = 8.0\text{ Hz}$, 1H), 7.62 (t, $J = 8.0\text{ Hz}$, 1H), 7.88 (d, $J = 8.0\text{ Hz}$, 1H), 8.05 (d, $J = 8.0\text{ Hz}$, 1H), 8.26 (d, $J = 7.5\text{ Hz}$, 1H), 8.35 (d, $J = 8\text{ Hz}$, 1H),

8.86 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 120.8, 121.3, 122.7, 124.1, 125.0, 125.8, 129.0, 131.9, 134.1, 134.2, 147.7, 152.9, 163.8.

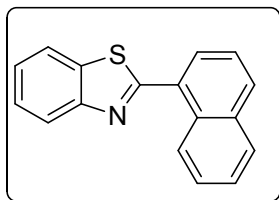
2-(pyridin-2-yl)benzo[d]thiazole 5l⁶:



Yield 59%, brown solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 7.29-7.36 (m, 2H), 7.41-7.45 (m, 1H), 7.75-7.80 (m, 1H), 7.88-7.90 (m, 1H), 8.01-8.03 (m, 1H), 8.29-8.31 (m, 1H), 8.60-8.62 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 120.8, 122.0, 123.5, 125.2, 125.6, 126.2, 136.1, 137.0, 149.6, 151.4, 154.2, 169.4.

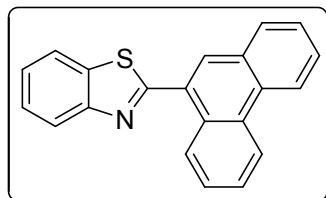
2-(naphthalen-1-yl)benzo[d]thiazole 5m³:



Yield 76%, half white solid.

^1H NMR (300 MHz, CDCl_3): δ_{H} 7.43 (t, J = 3.3 Hz, 1H), 7.45-7.65 (m, 4H), 7.86-8.01 (m, 4H), 8.20 (d, J = 8.1Hz, 1H), 8.92 (d, J = 8.1Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 121.4, 123.5, 125.0, 125.3, 125.9, 126.2, 126.5, 127.6, 128.4, 129.4, 130.6, 130.8, 131.0, 134.0, 135.4, 154.1, 167.6.

2-(phenanthren-9-yl)benzo[d]thiazole 5n⁶:



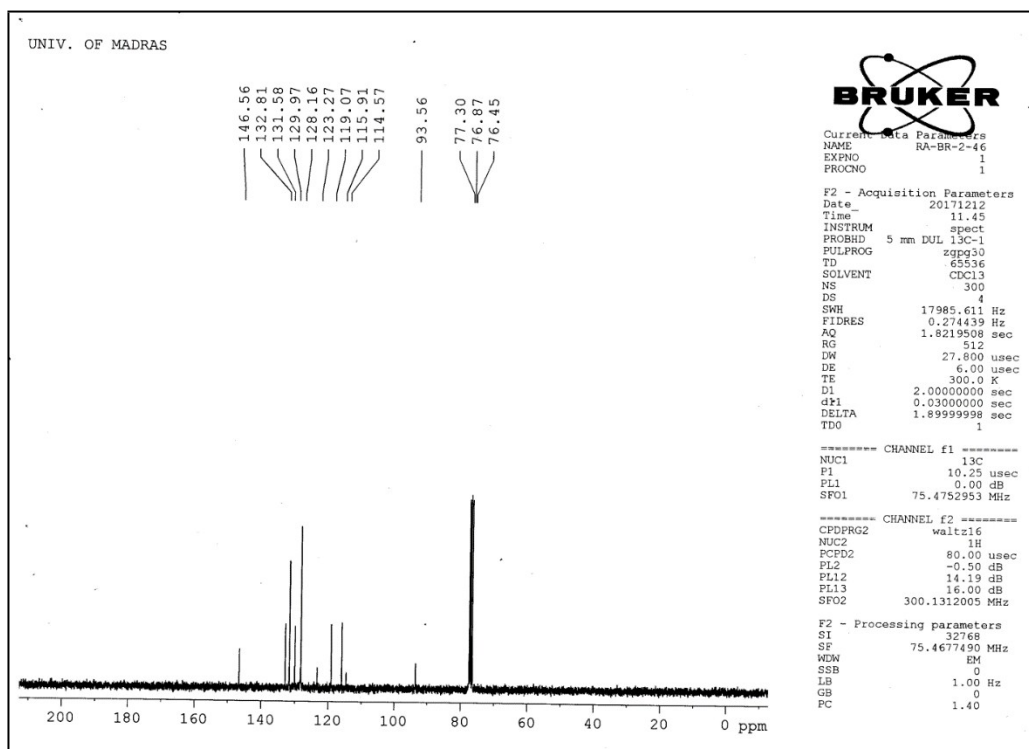
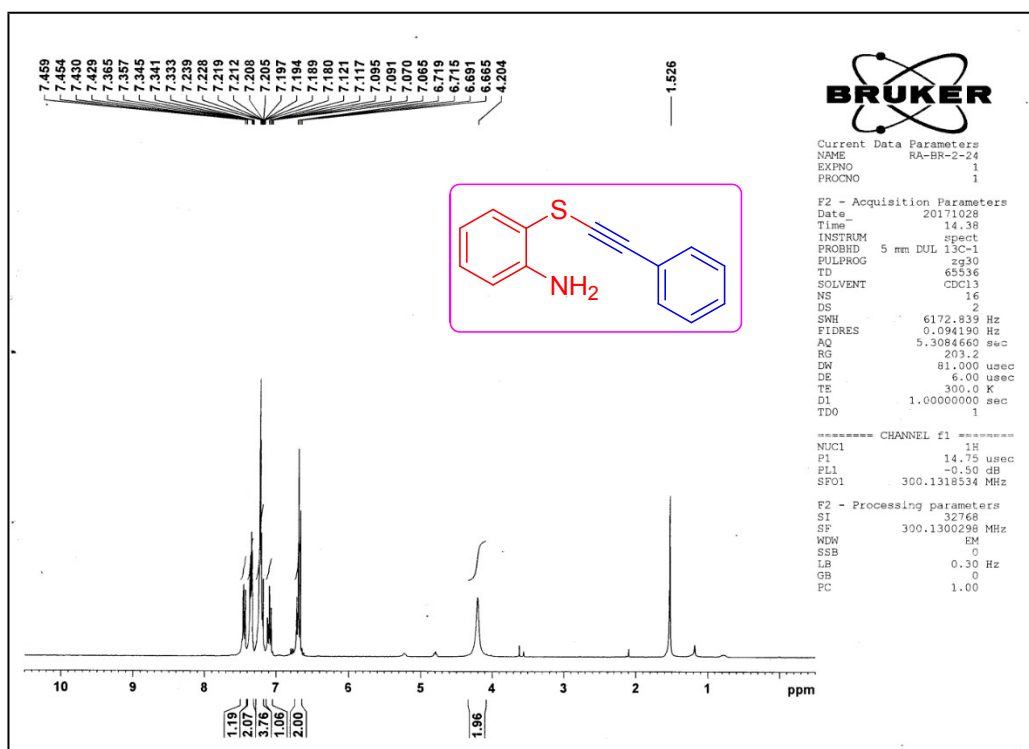
Yield 79%, white solid.

^1H NMR (400 MHz, CDCl_3): δ_{H} 7.38-7.42 (m, 1H), 7.48-7.52 (m, 1H), 7.58-7.69 (m, 4H), 7.89-7.93 (m, 2H), 8.13-8.15 (m, 2H), 8.65-8.73 (m, 2H), 8.82-8.85 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 121.4, 122.7, 122.9, 123.6, 125.4, 126.3, 126.7, 127.1, 127.2, 127.4, 128.1, 129.2, 129.4, 129.8, 130.7, 130.8, 131.0, 131.2, 135.4, 154.1, 167.5; **HRMS**: $(\text{M}+\text{H})^+$ calculated for $\text{C}_{21}\text{H}_{14}\text{NS}$: 312.0846, Found: 312.0857.

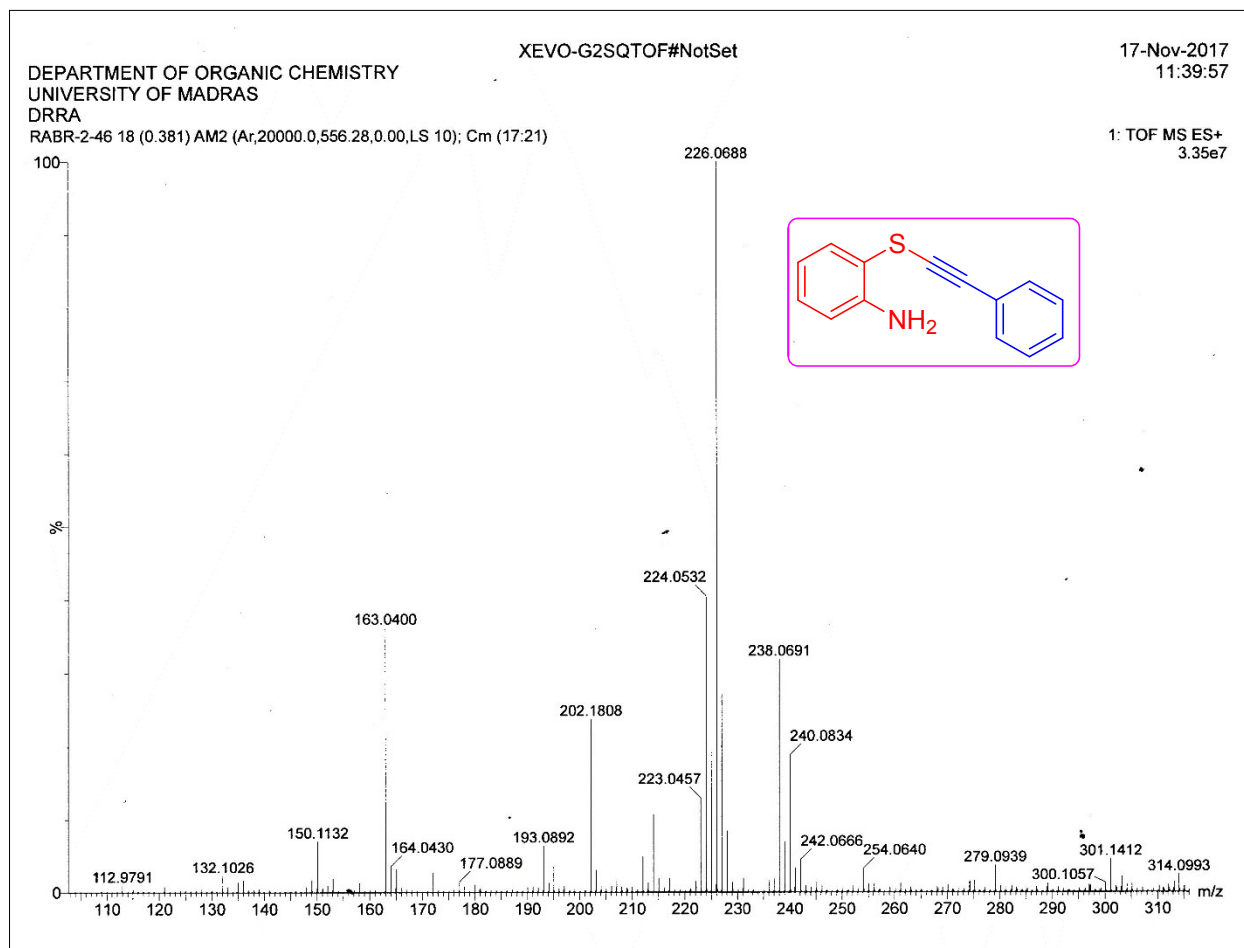
References:

1. S. Uesato, Y. Matsuura, S. Matsue, T. Sumiyoshi, Y. Hirata, S. Takemoto, Y. Kawaratani, Y. Yamai, K. Ishida, T. Sasaki and M. Enari, *Bioorg. Med. Chem.*, 2016, **24**, 1919.
2. J. Srogl, J. Hyvl, A. Revesz and D. Schroder, *Chem. Commun.*, 2009, **23**, 3463.
3. H. Deng, Z. Li, F. Ke and X. Zhou, *Chem. Eur. J.*, 2012, **18**, 4840.
4. X. Zhang, W. Zeng, Y. Yang, Hui Huang and Y. Liang, *Org. Lett.*, 2014, **16**, 876.
5. A. A. Weekes, J. Frydrych, and A. D. Westwell, *Synth. Comm.*, 2013, **43**, 2656.
6. T. Yamamoto, K. Muto, M. Komiyama, J. Canivet, J. Yamaguchi and K. Itami, *Chem. Eur. J.*, 2011, **17**, 10113.

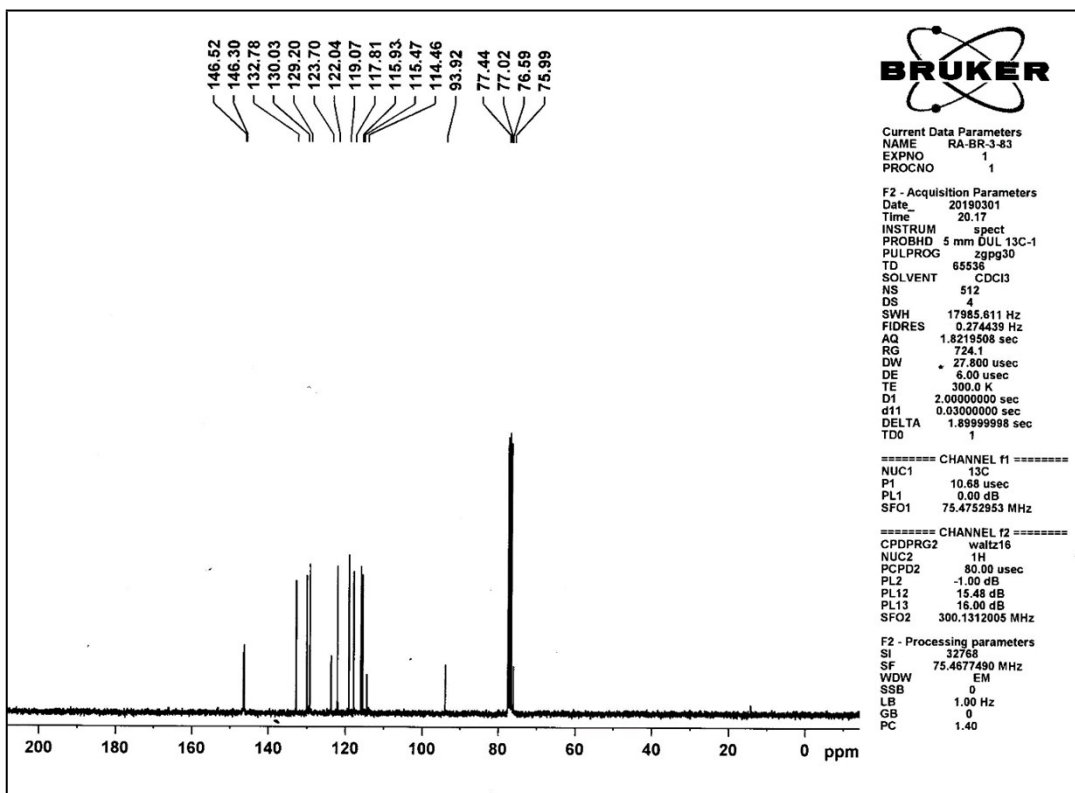
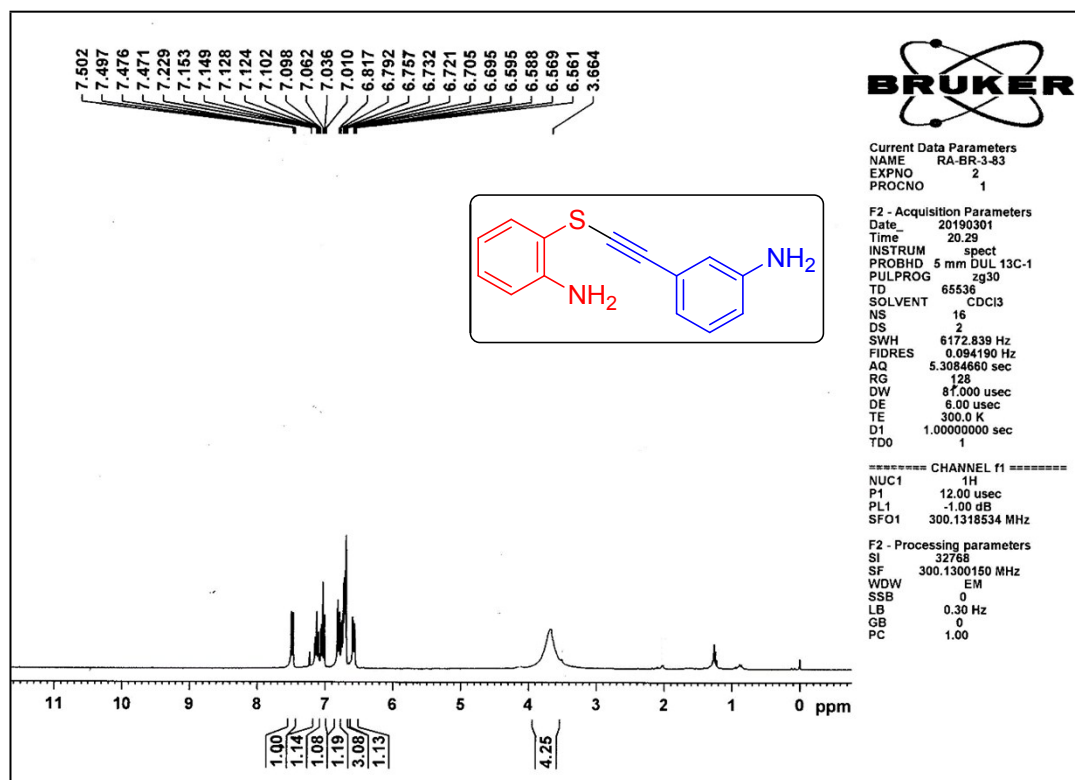
Spectral Data:



¹H & ¹³C NMR (CDCl₃) spectra of compound 3aa



HRMS spectrum of compound 3aa



¹H & ¹³C NMR (CDCl₃) spectra of compound 3ab

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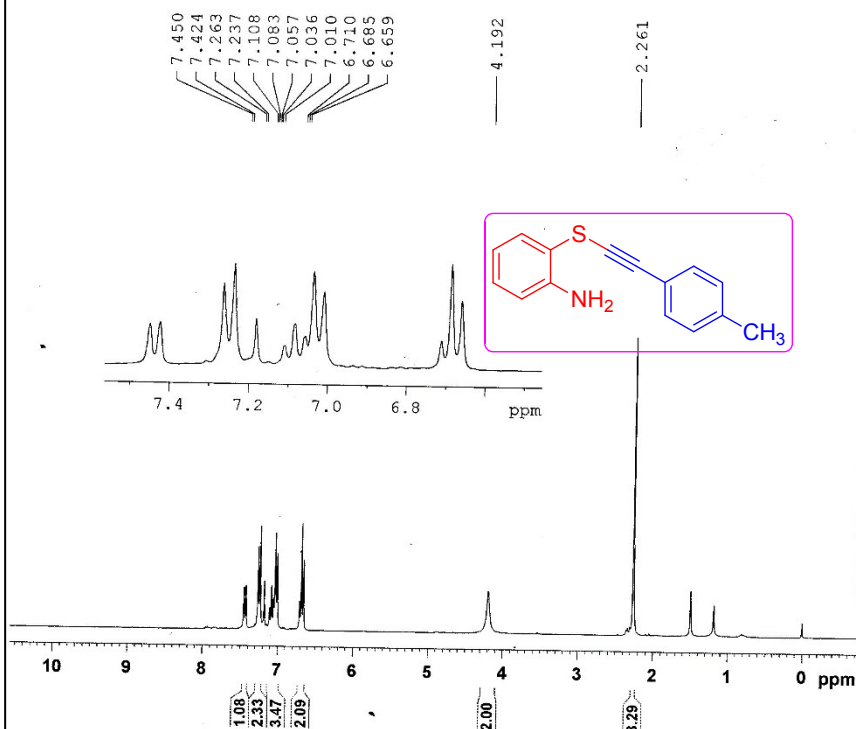


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PROCNO 1

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DS 2
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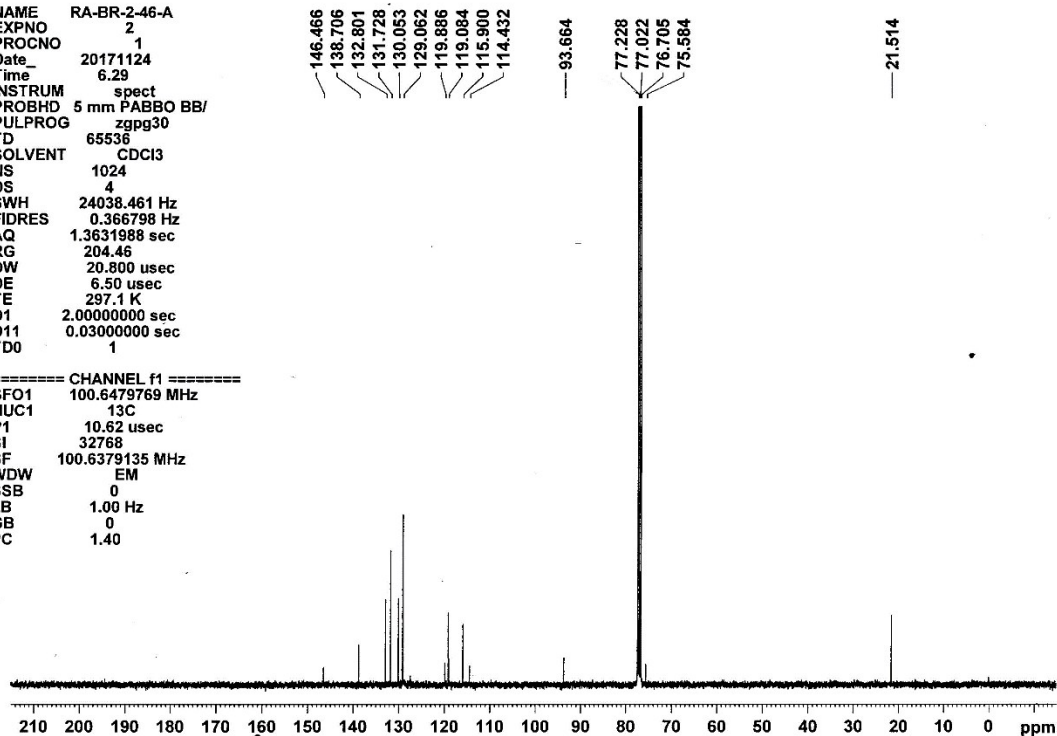
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LB 0.30 Hz
GB 0
PC 1.00



NAME RA-BR-2-46-A
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¹H & ¹³C NMR (CDCl₃) spectra of compound 3ac

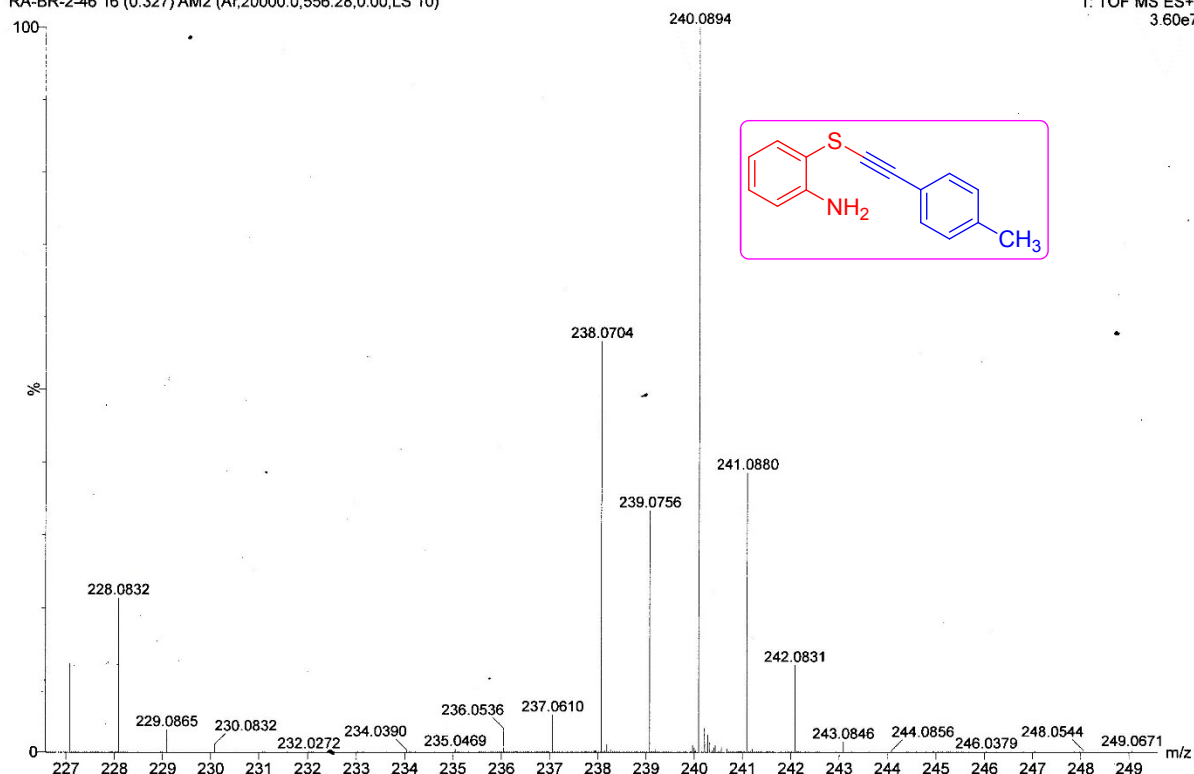
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UNIVERSITY OF MADRAS
DRRA

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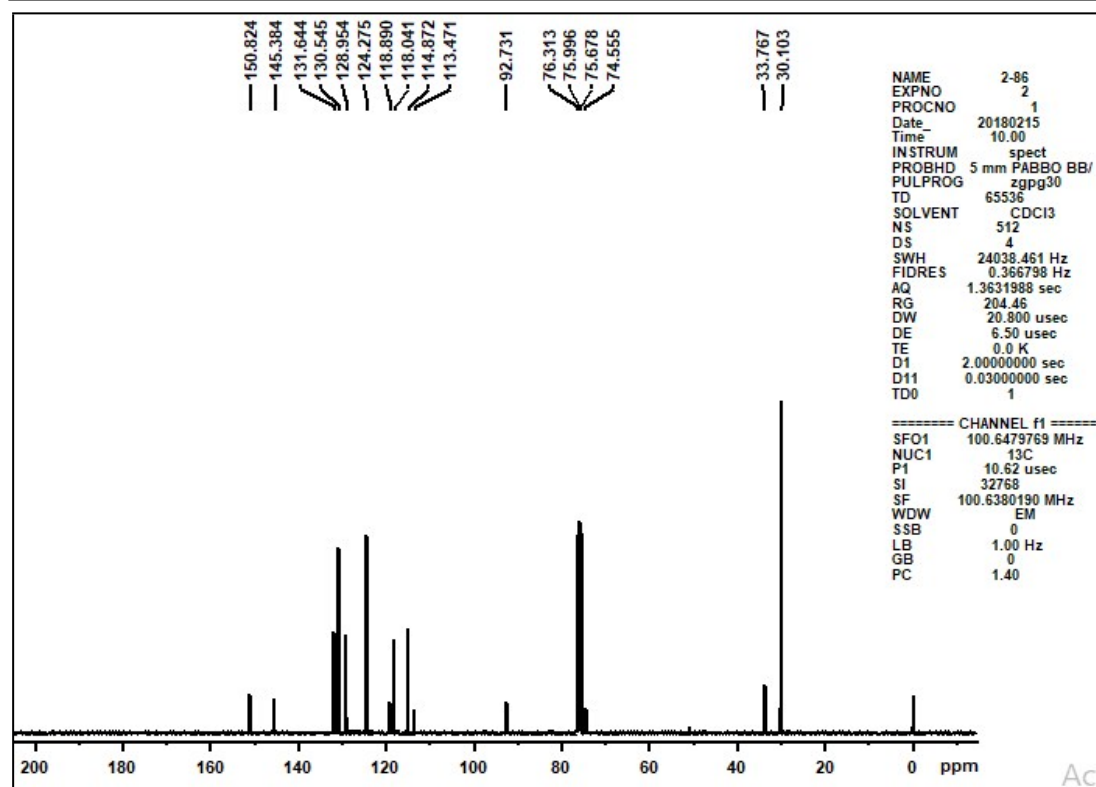
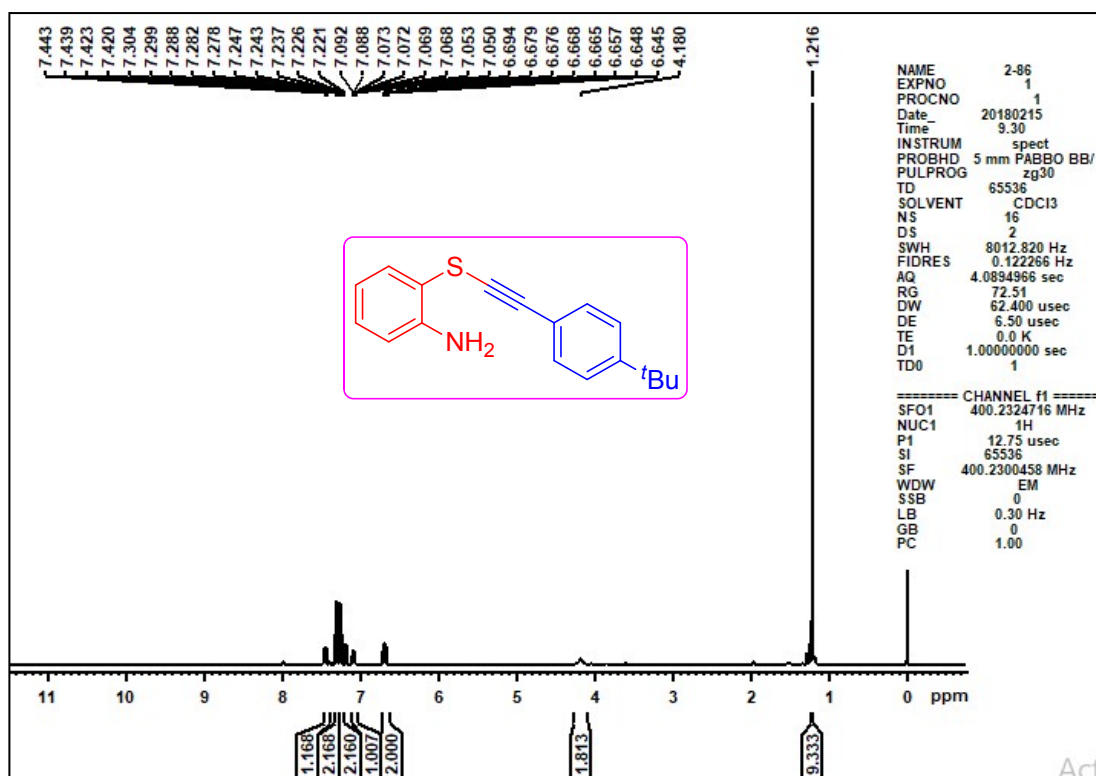
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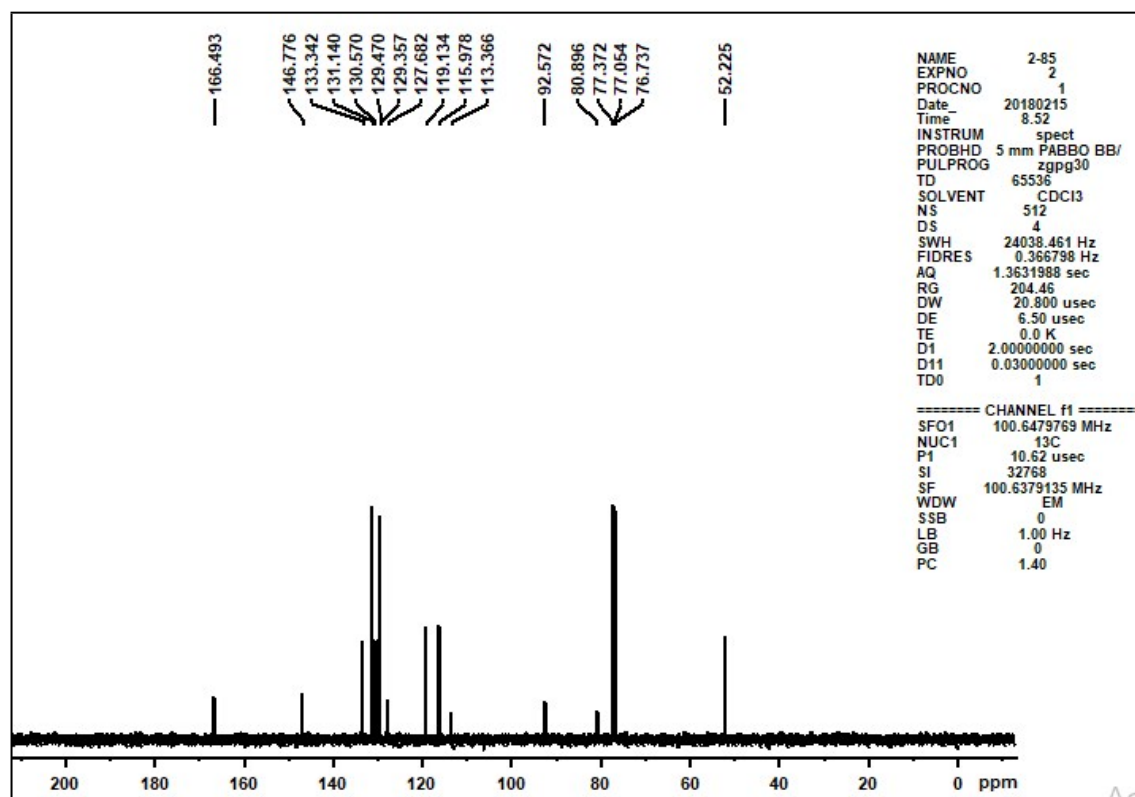
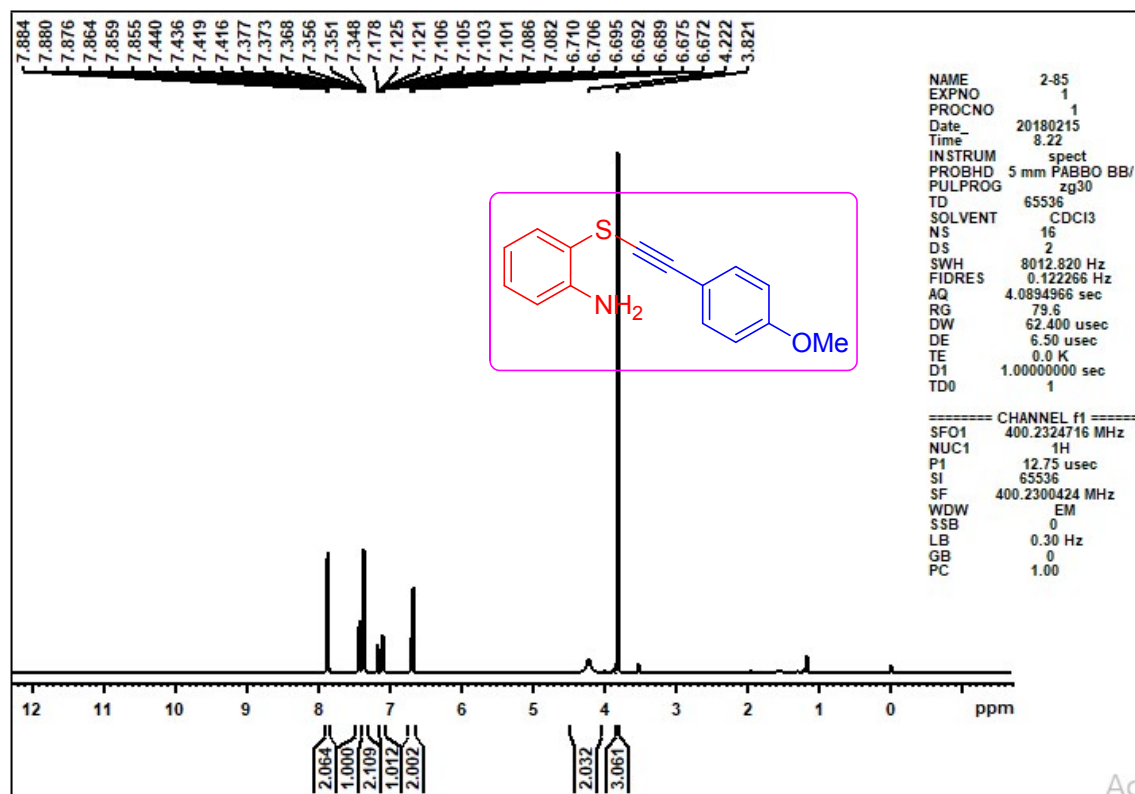
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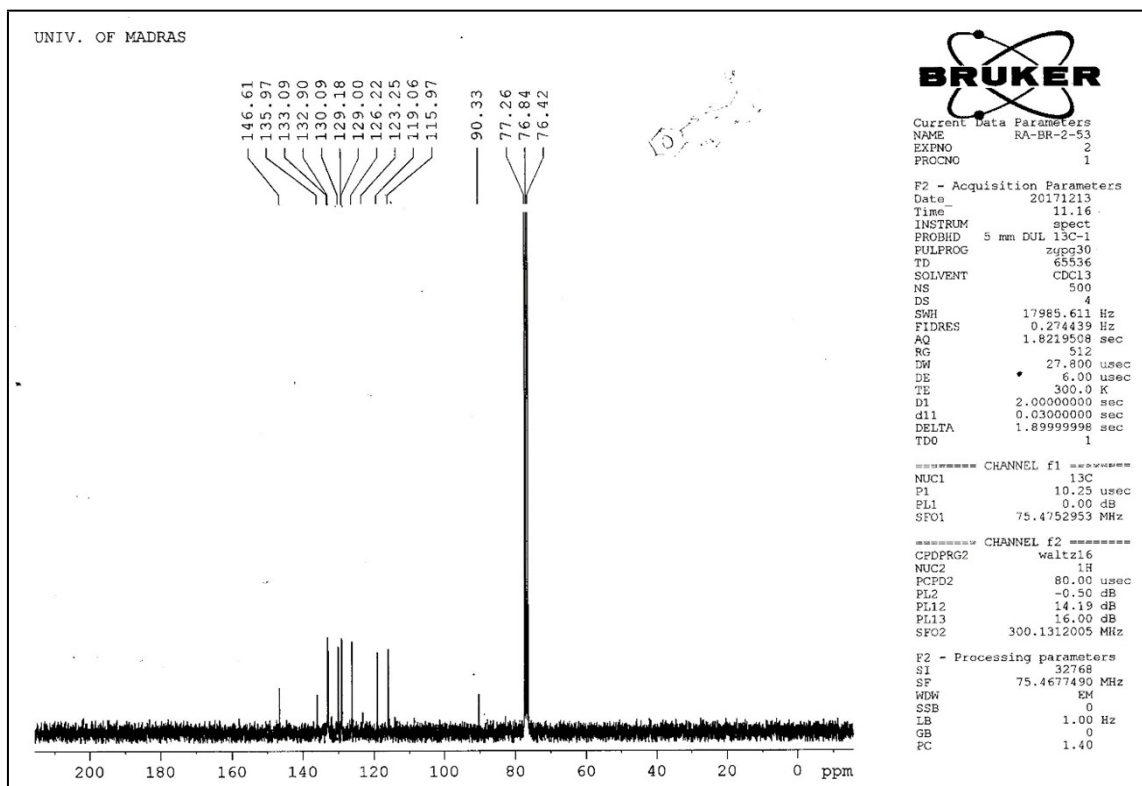
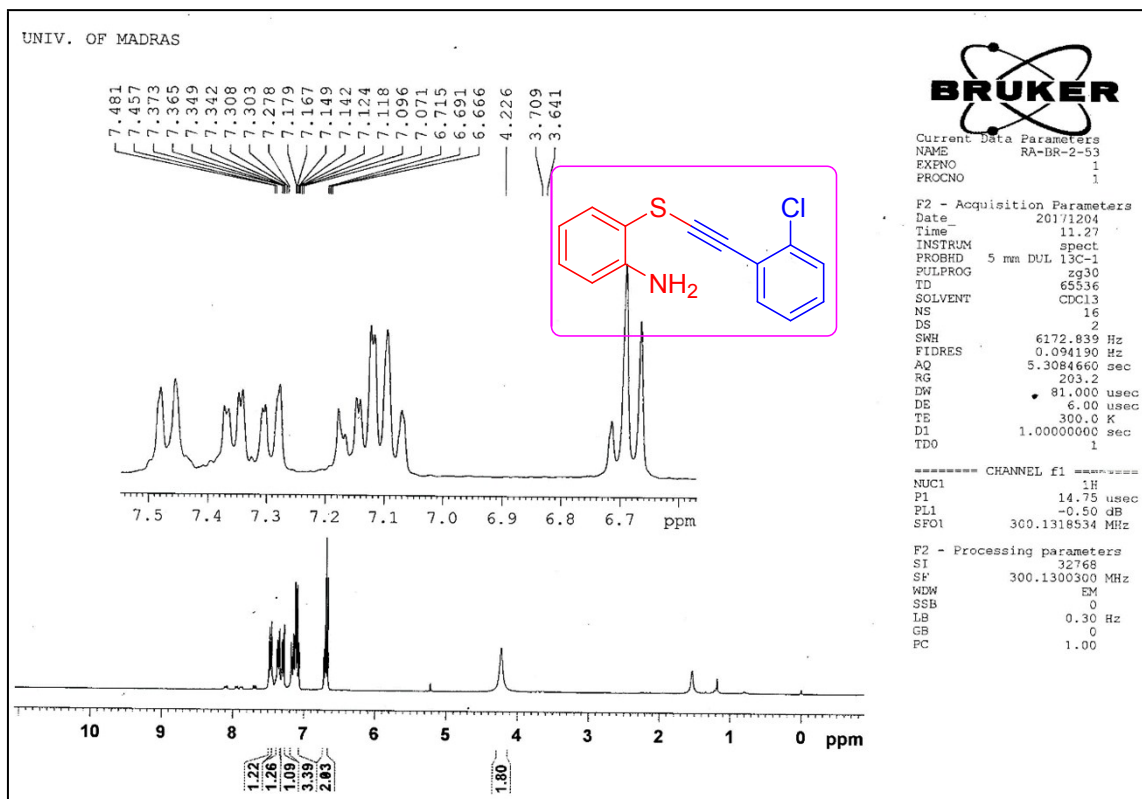
HRMS spectrum of compound 3ac



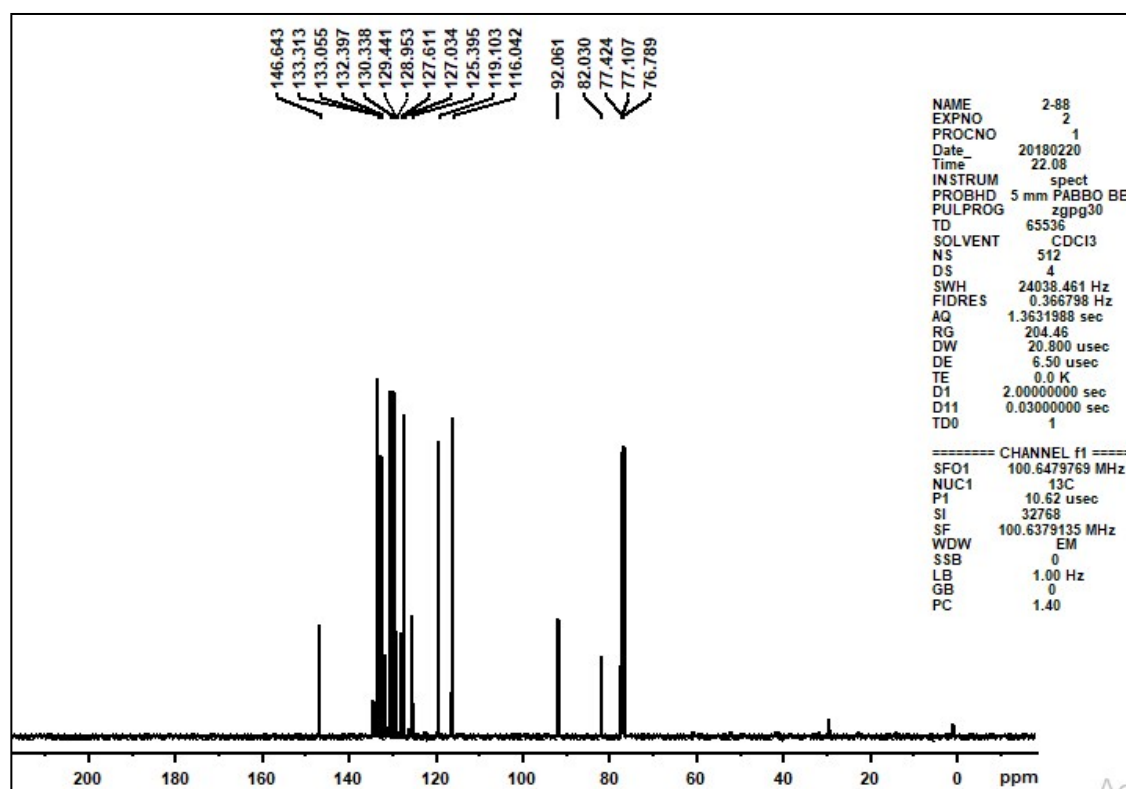
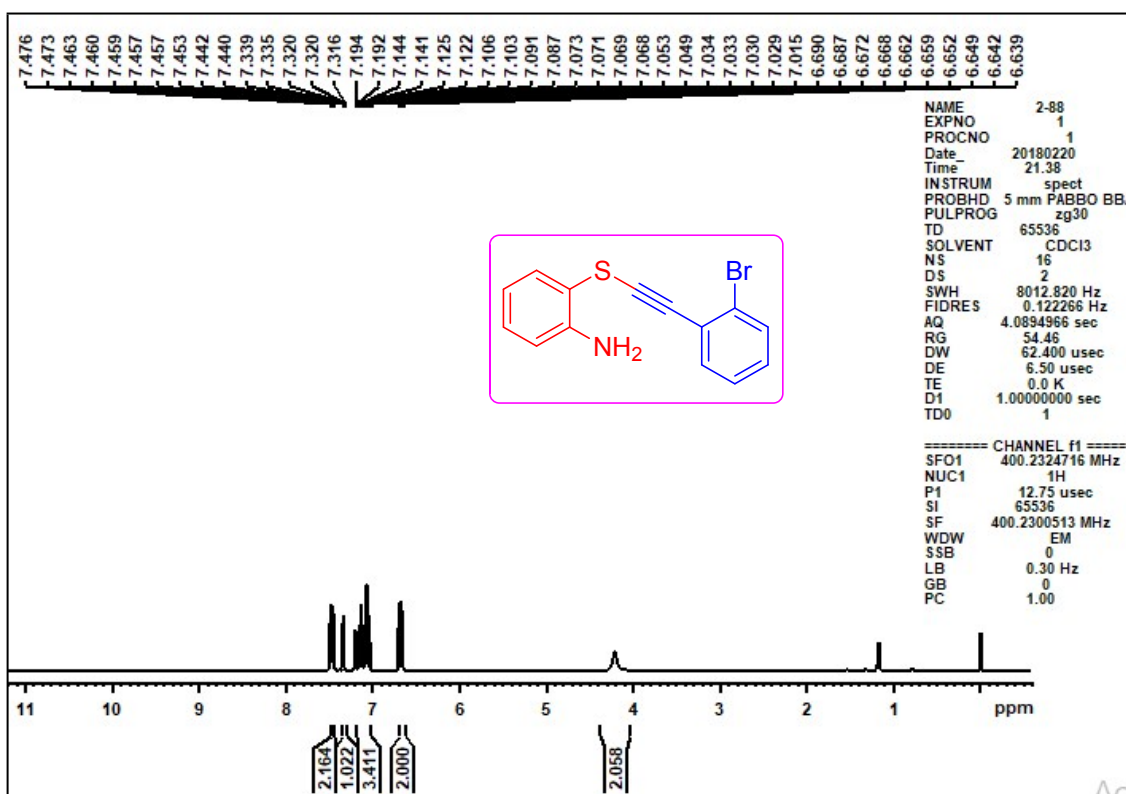
¹H & ¹³C NMR (CDCl₃) spectra of compound 3ad



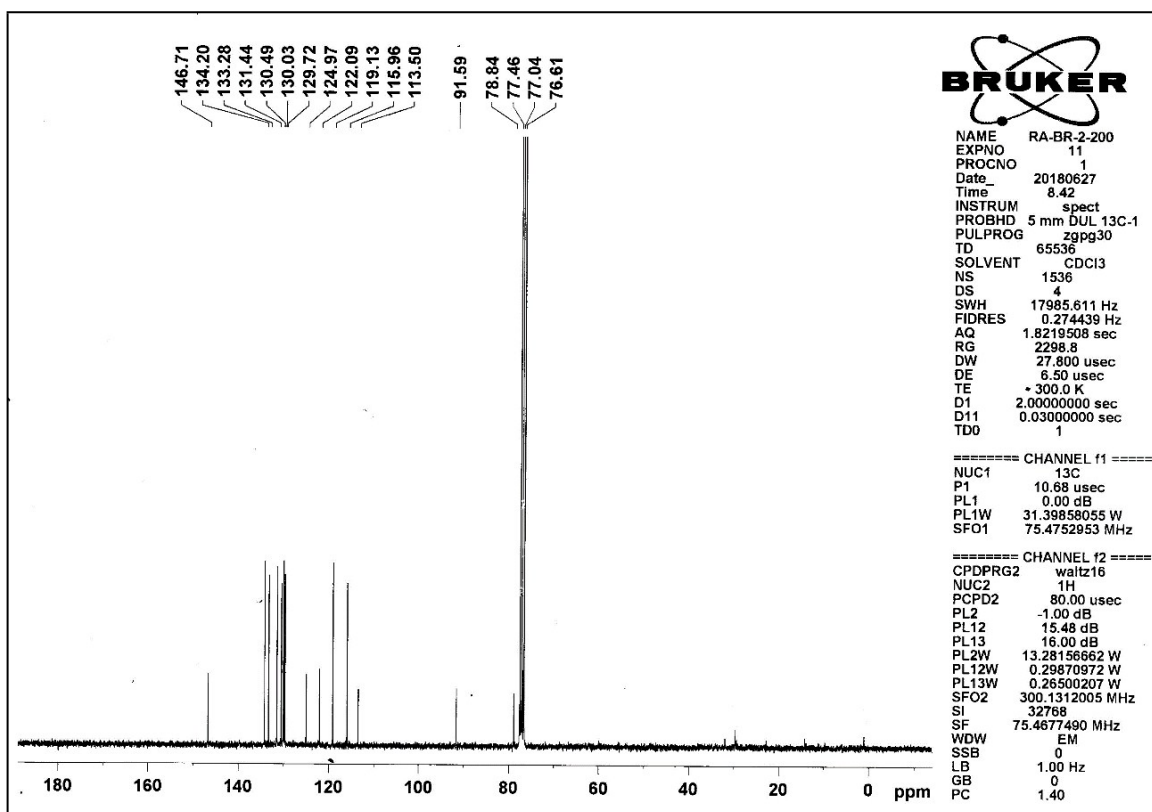
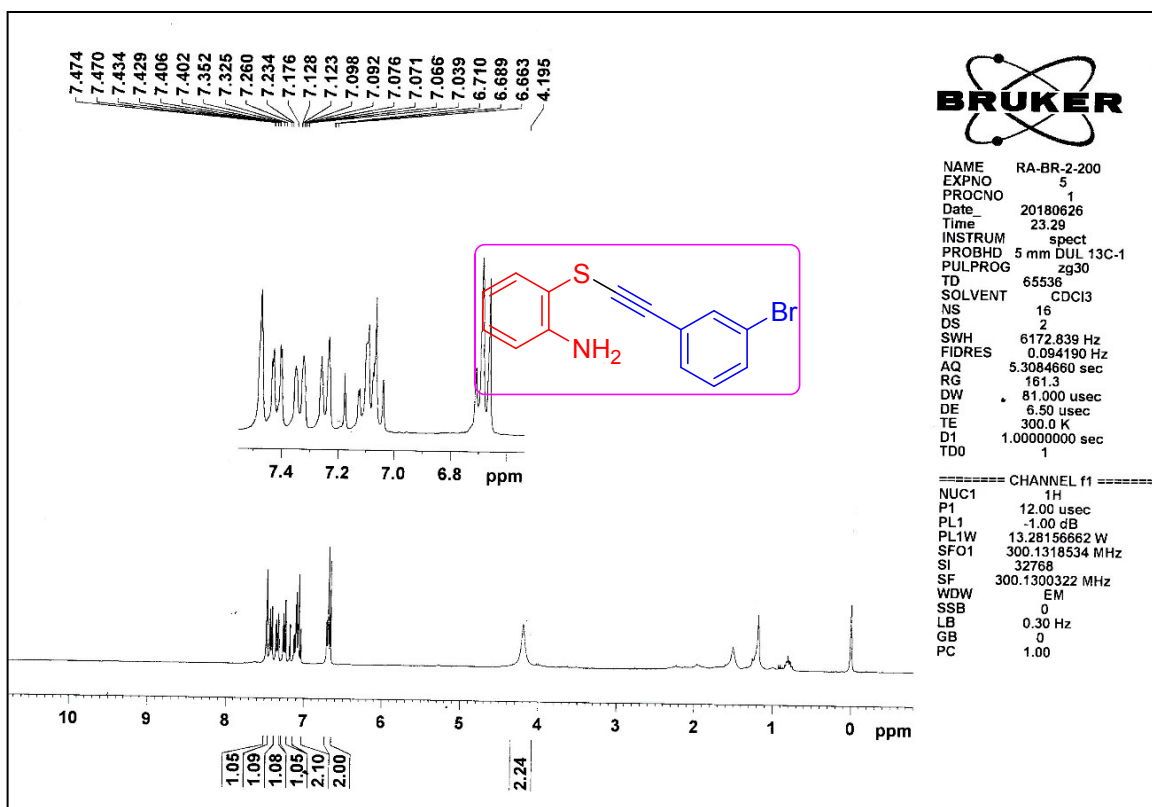
¹H & ¹³C NMR (CDCl₃) spectra of compound 3ae



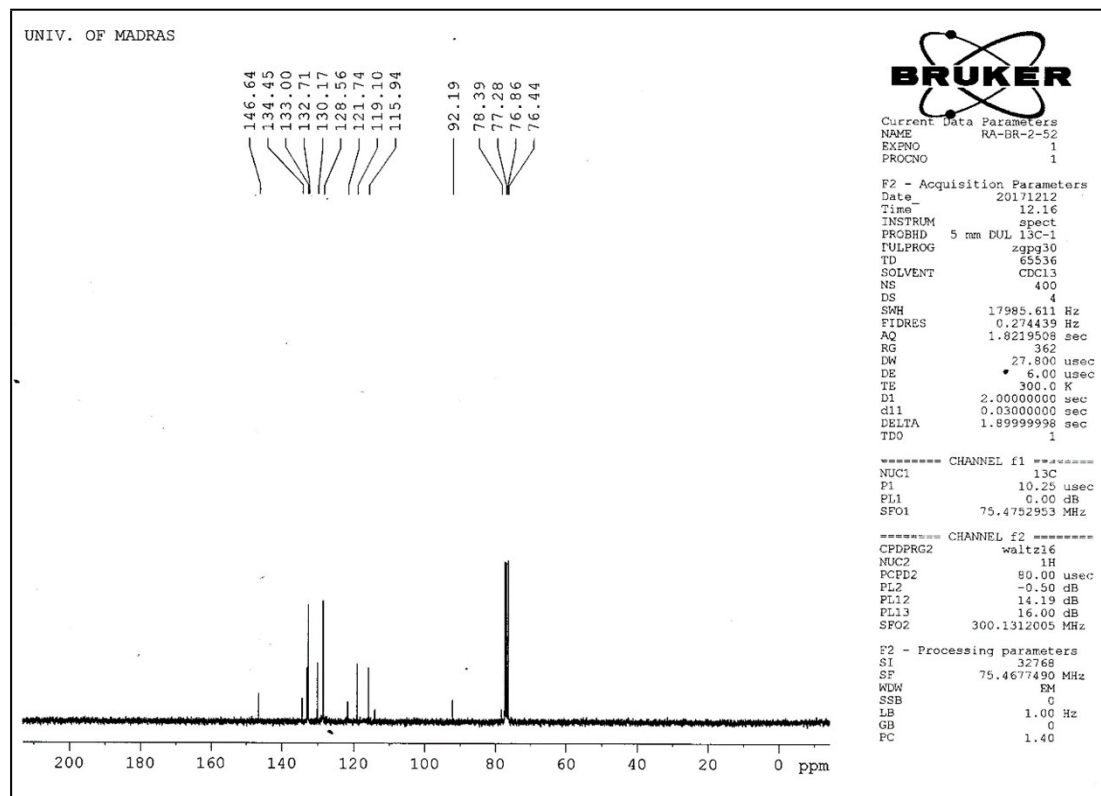
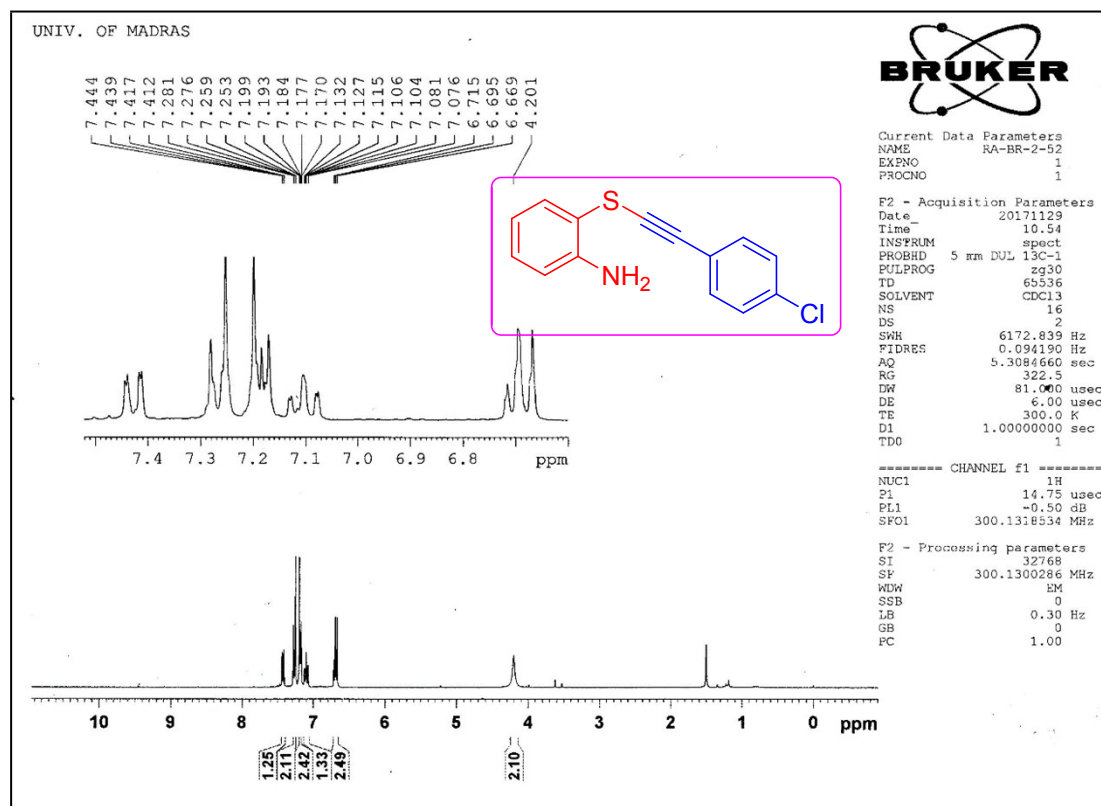
¹H & ¹³C NMR (CDCl₃) spectra of compound 3af



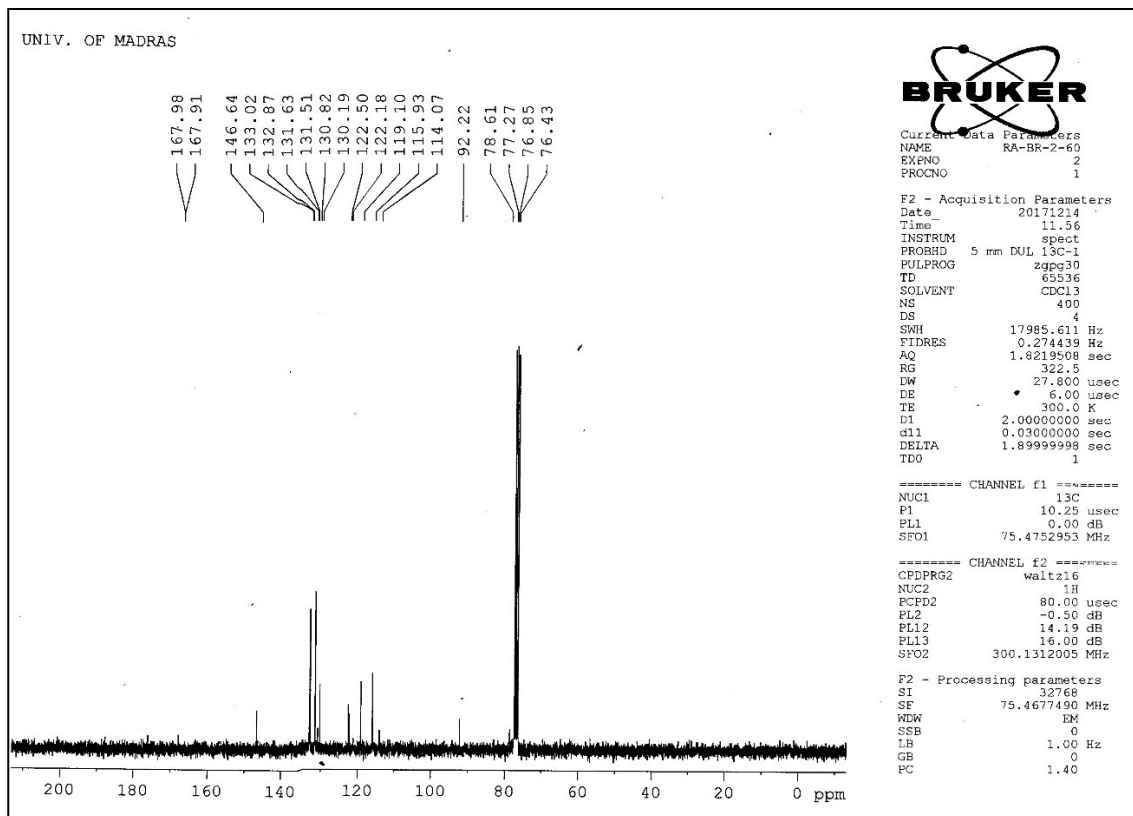
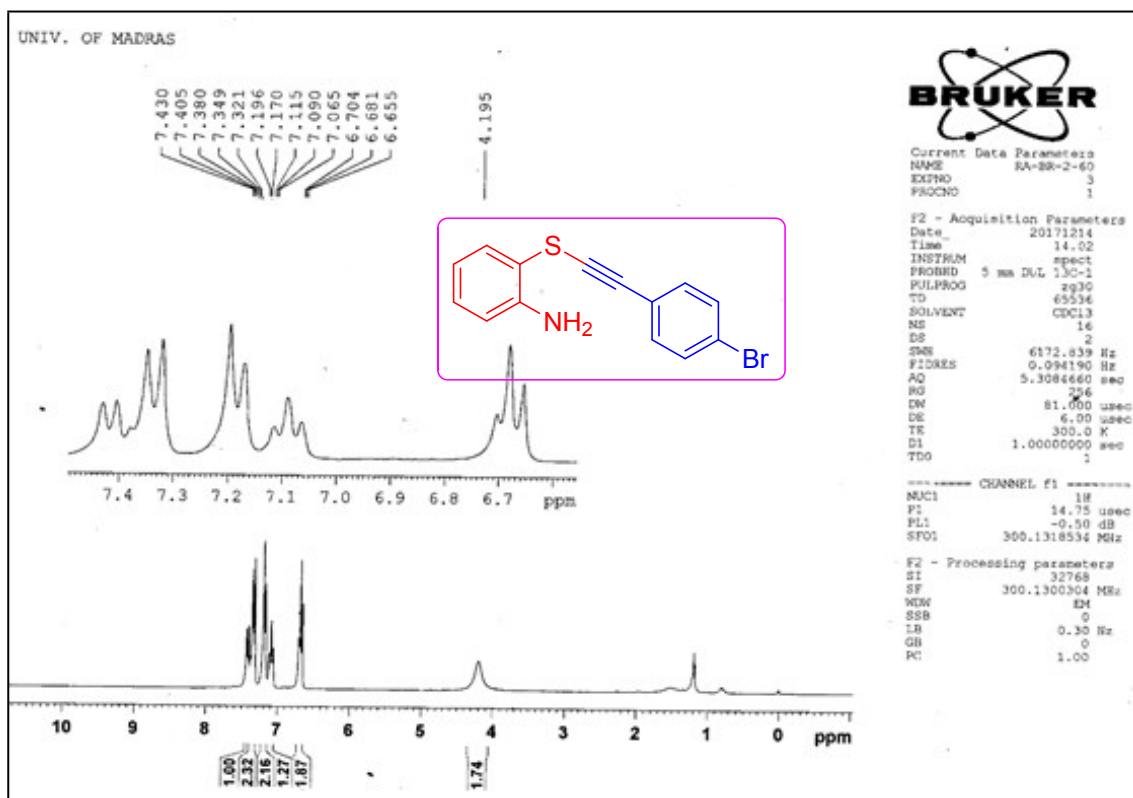
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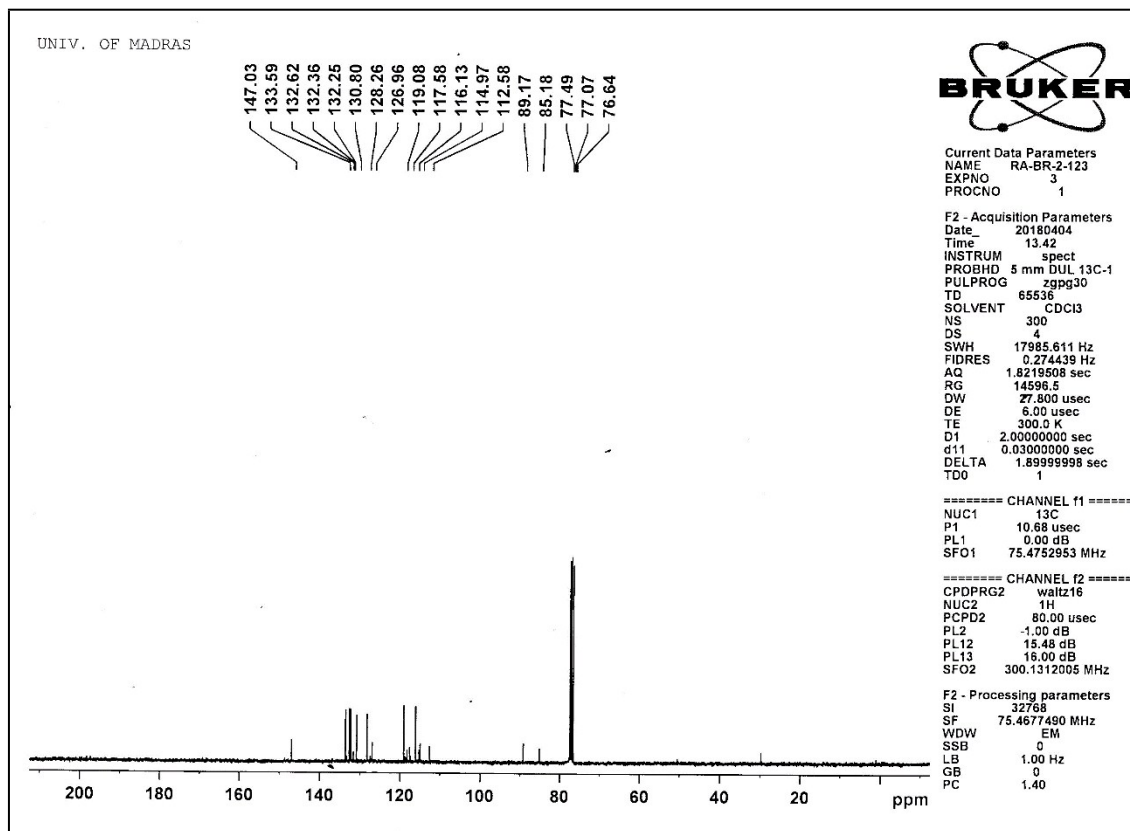
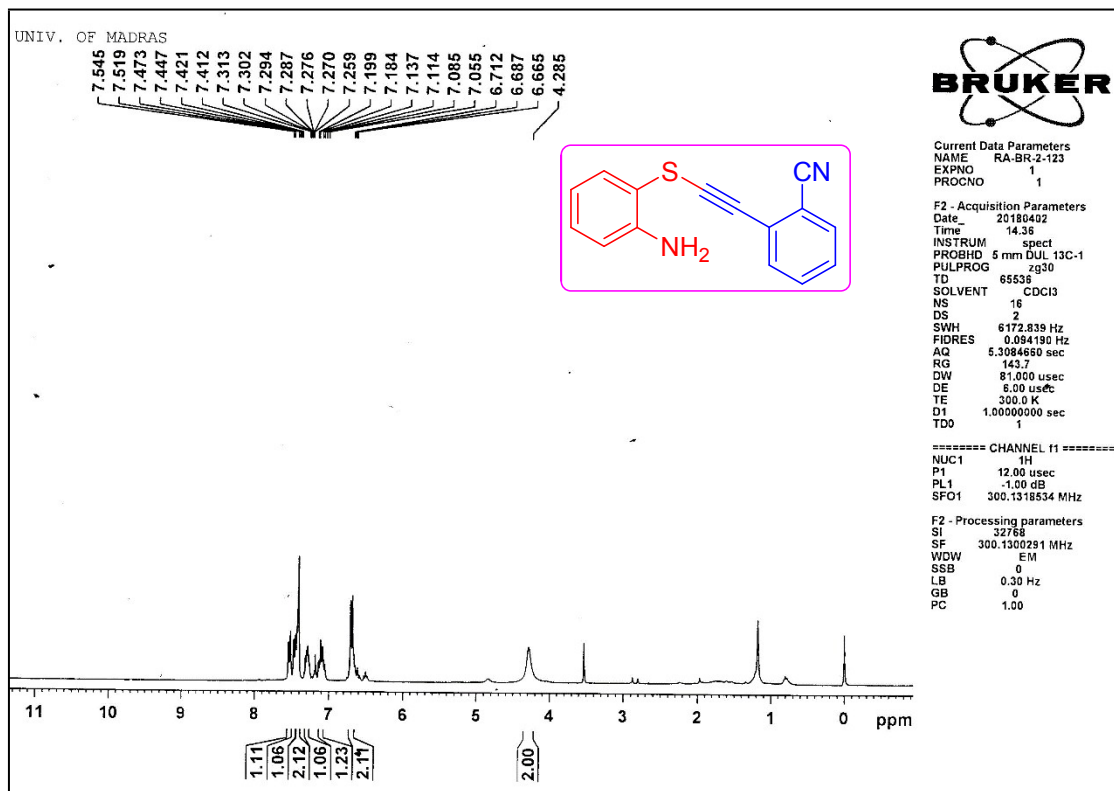
¹H & ¹³C NMR (CDCl₃) spectra of compound 3ah



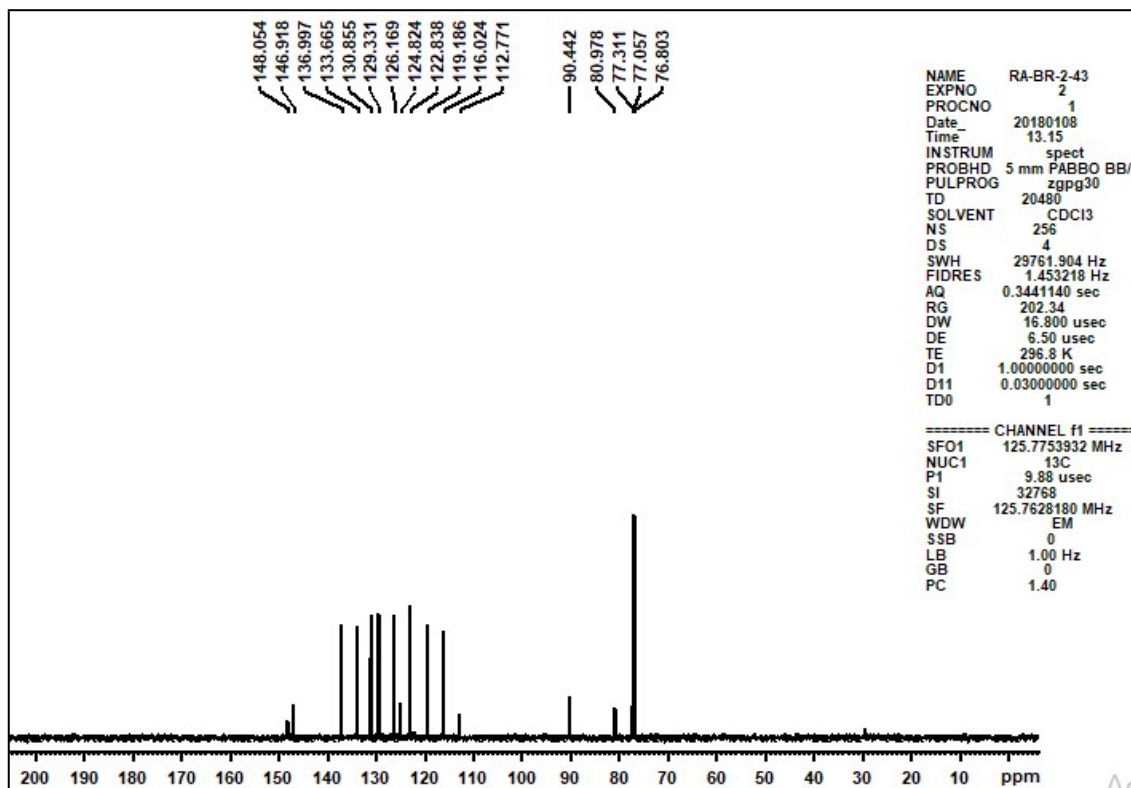
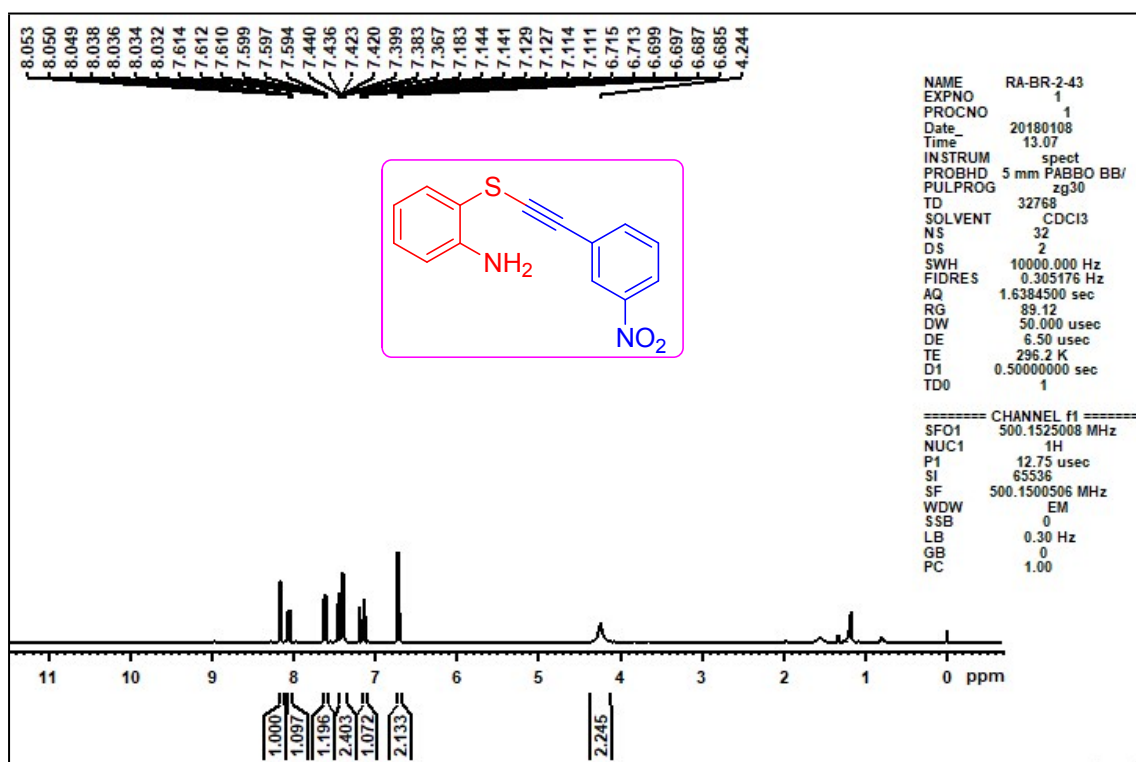
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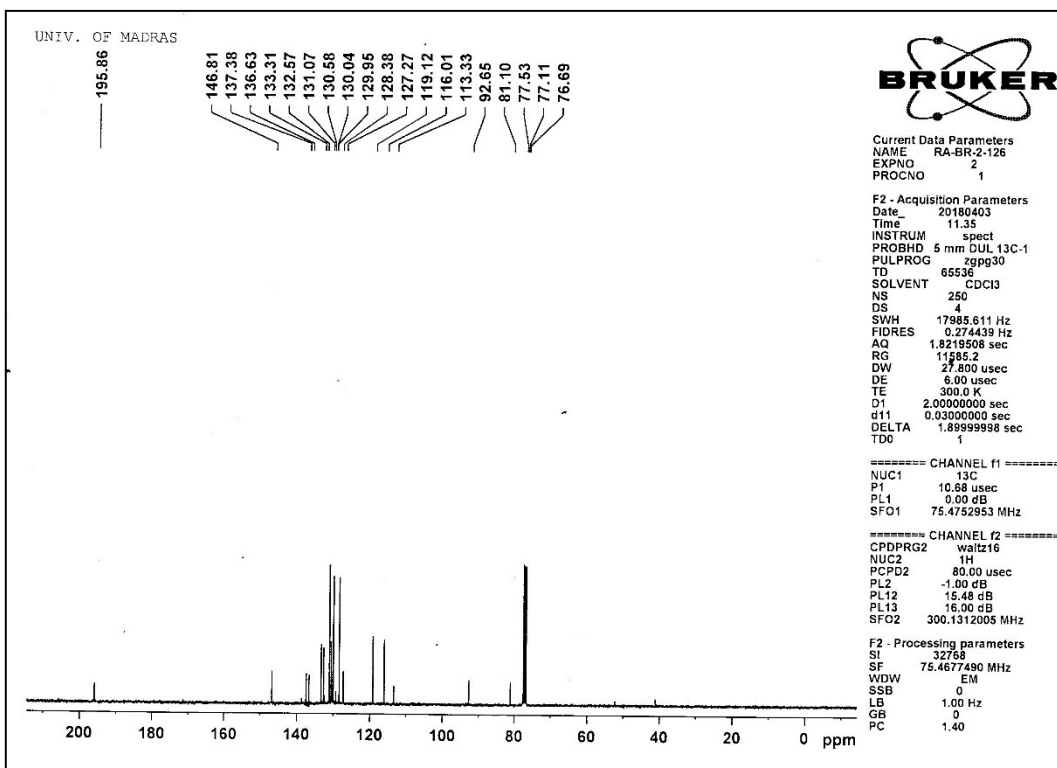
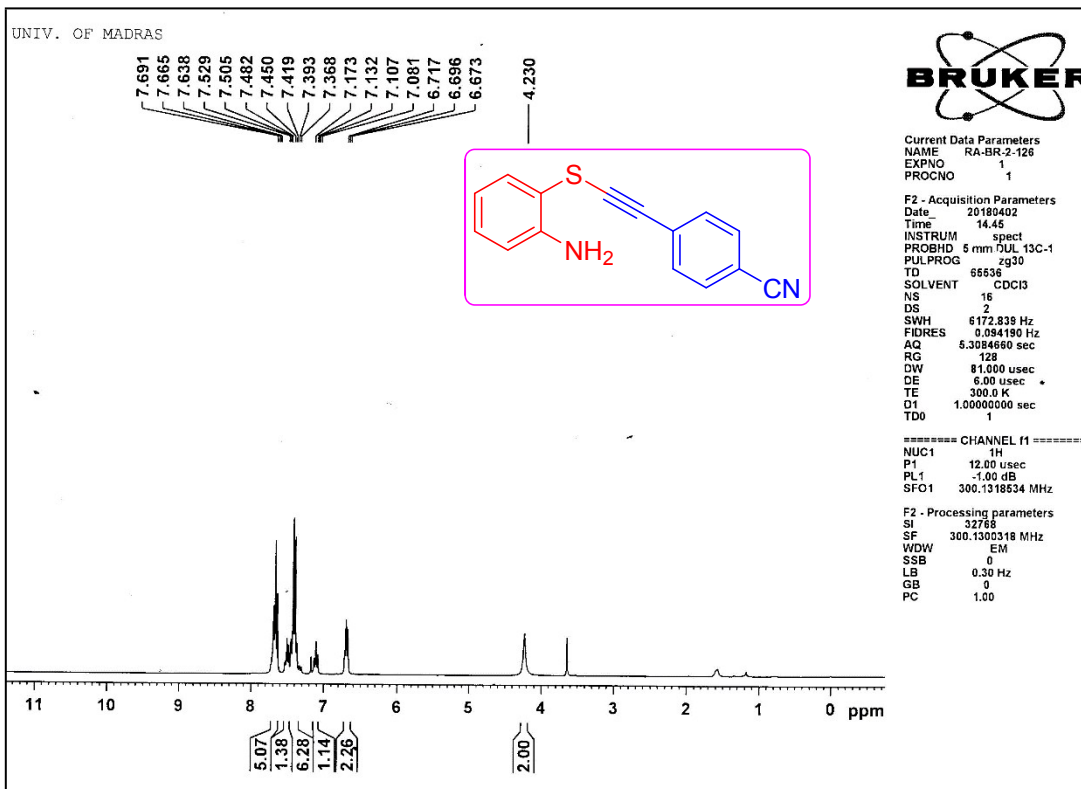
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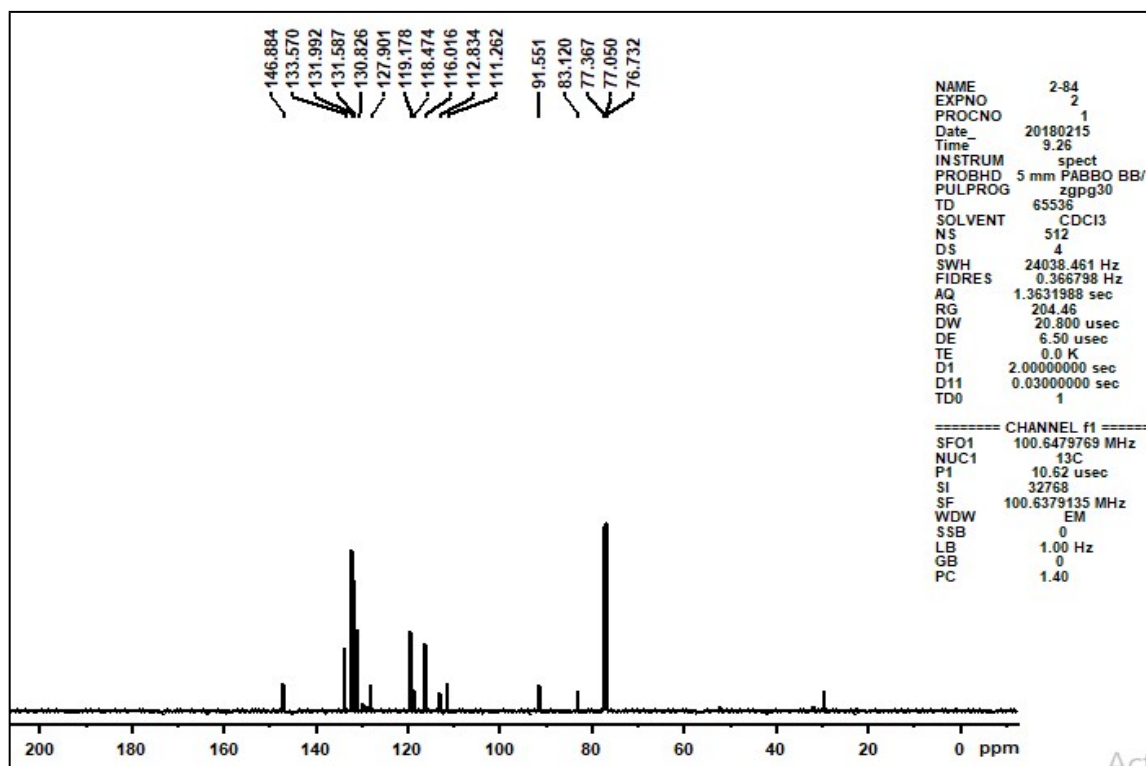
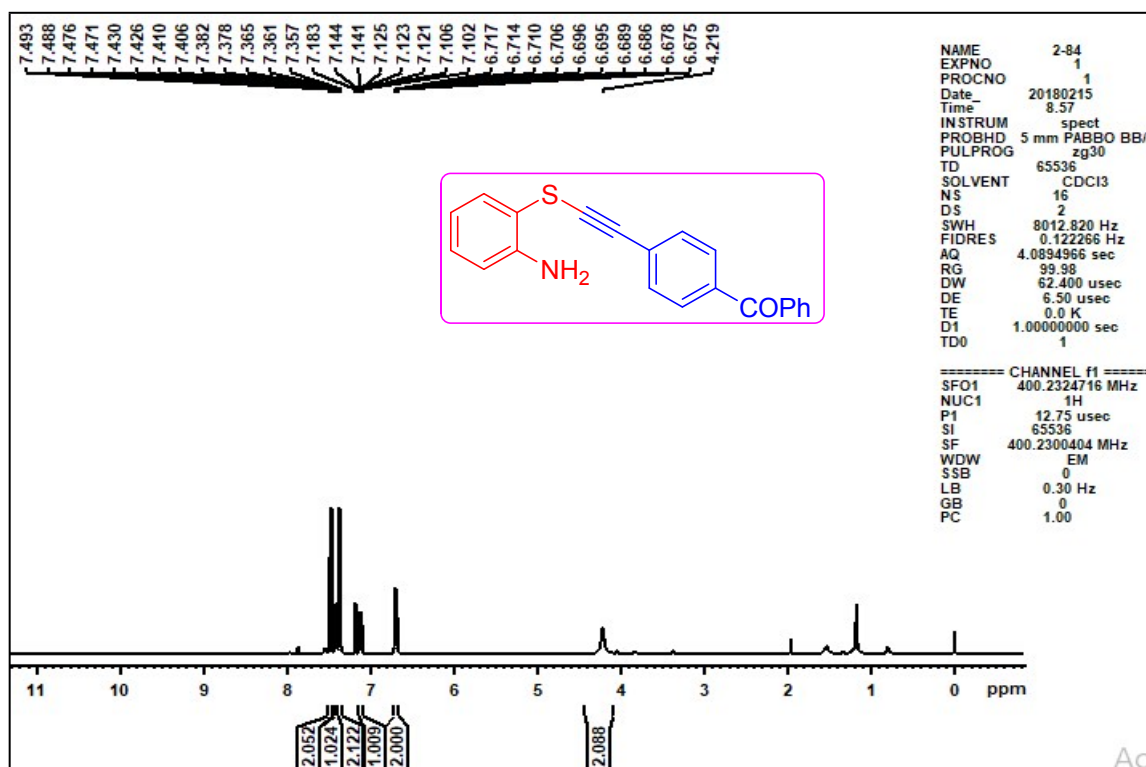
¹H & ¹³C NMR (CDCl₃) spectra of compound 3ak



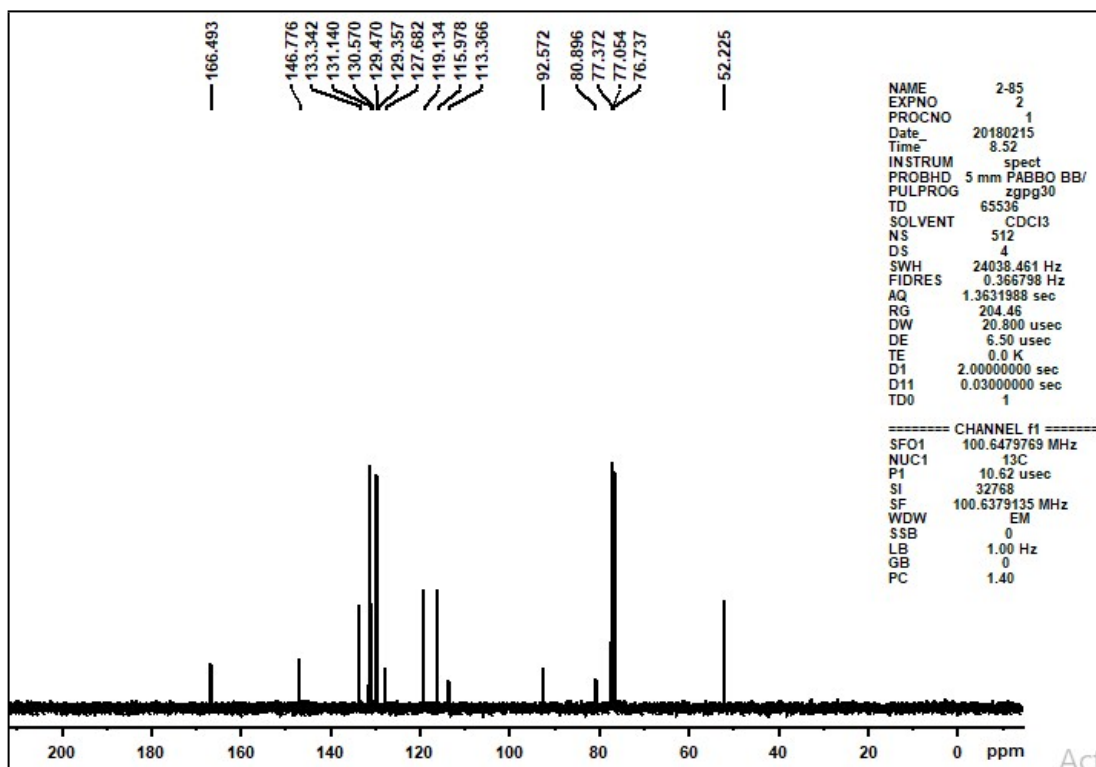
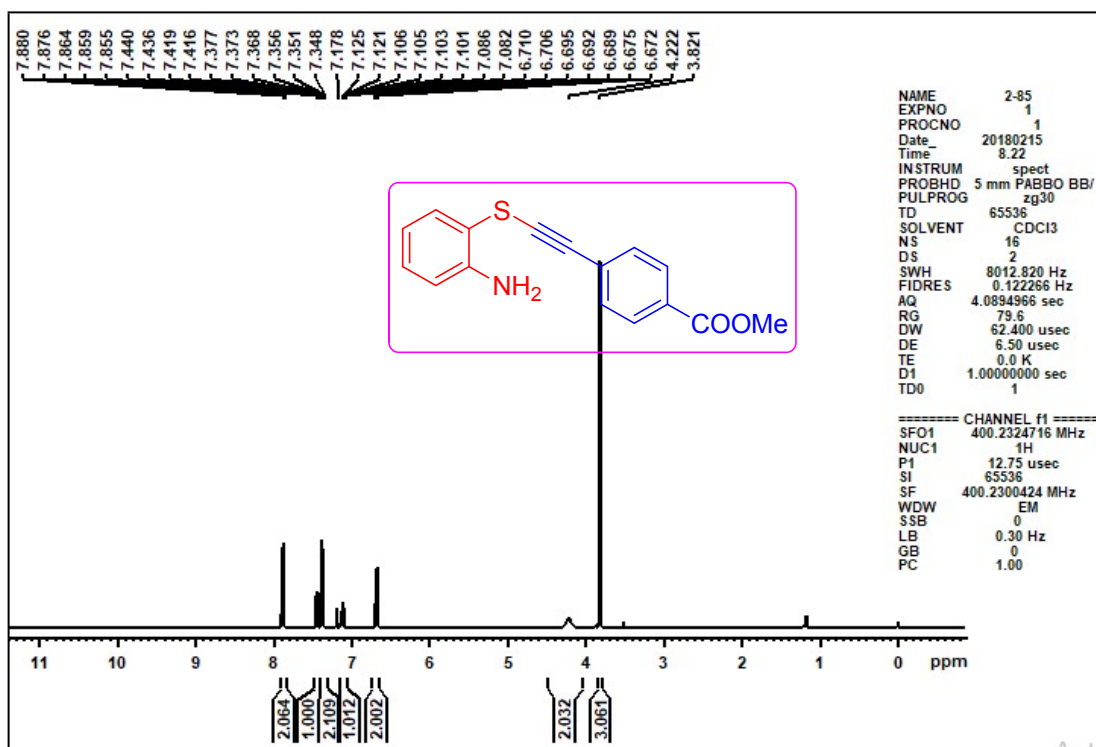
¹H & ¹³C NMR (CDCl₃) spectra of compound 3aI



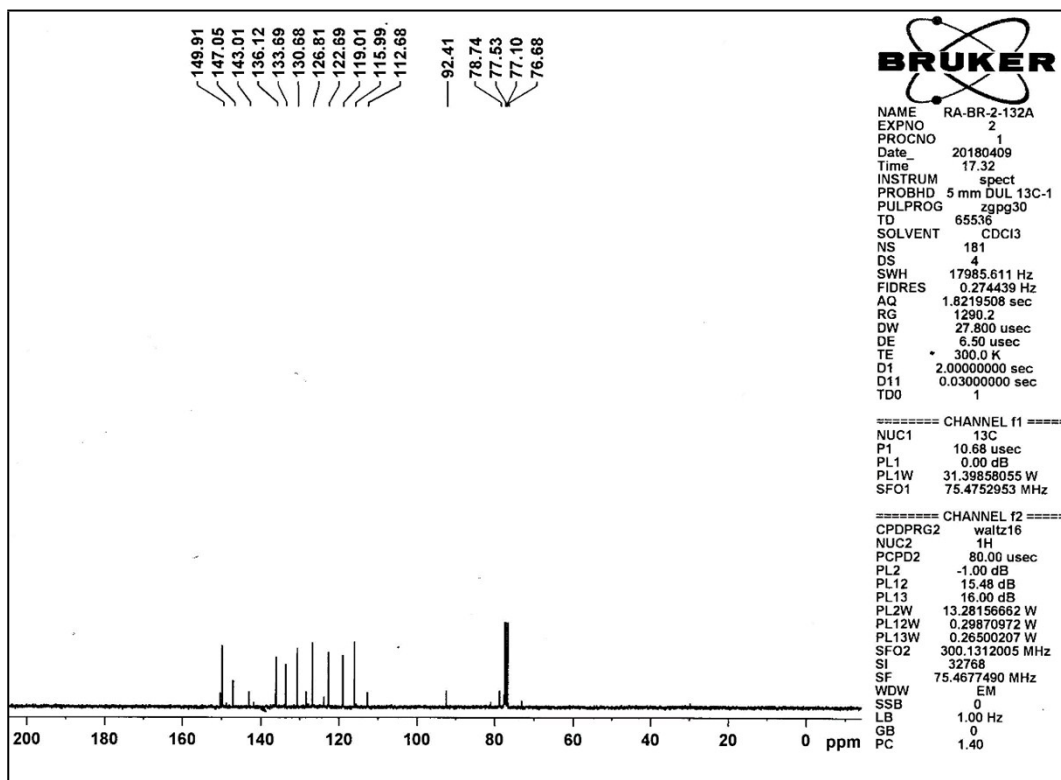
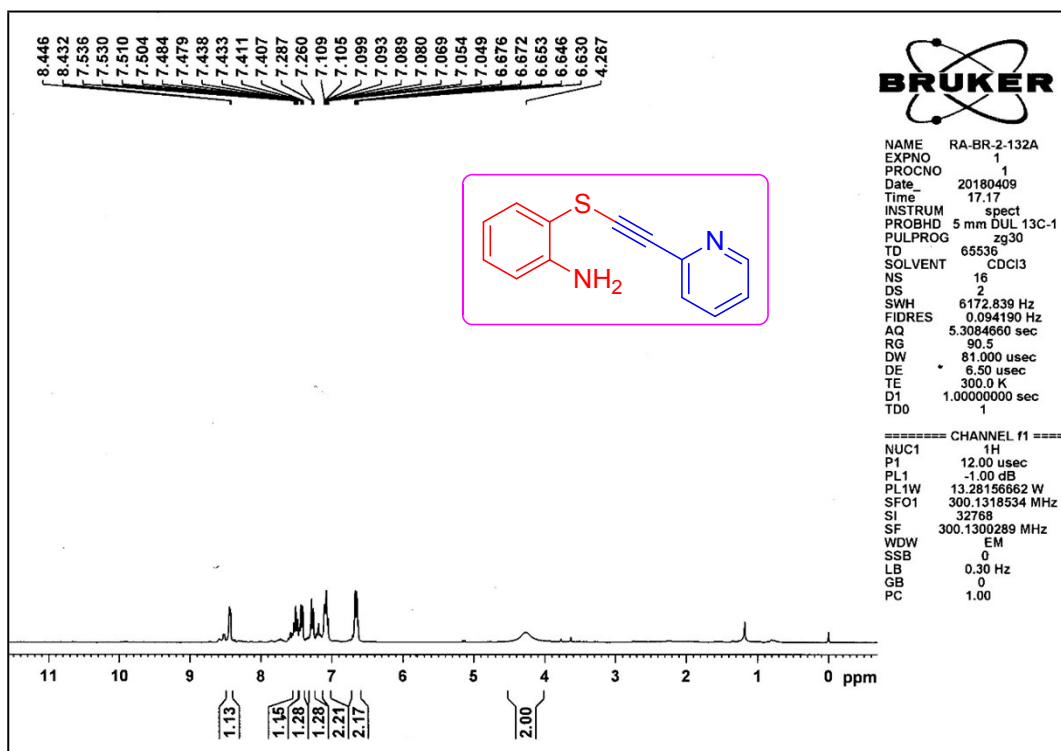
^1H & ^{13}C NMR (CDCl_3) spectra of compound 3am



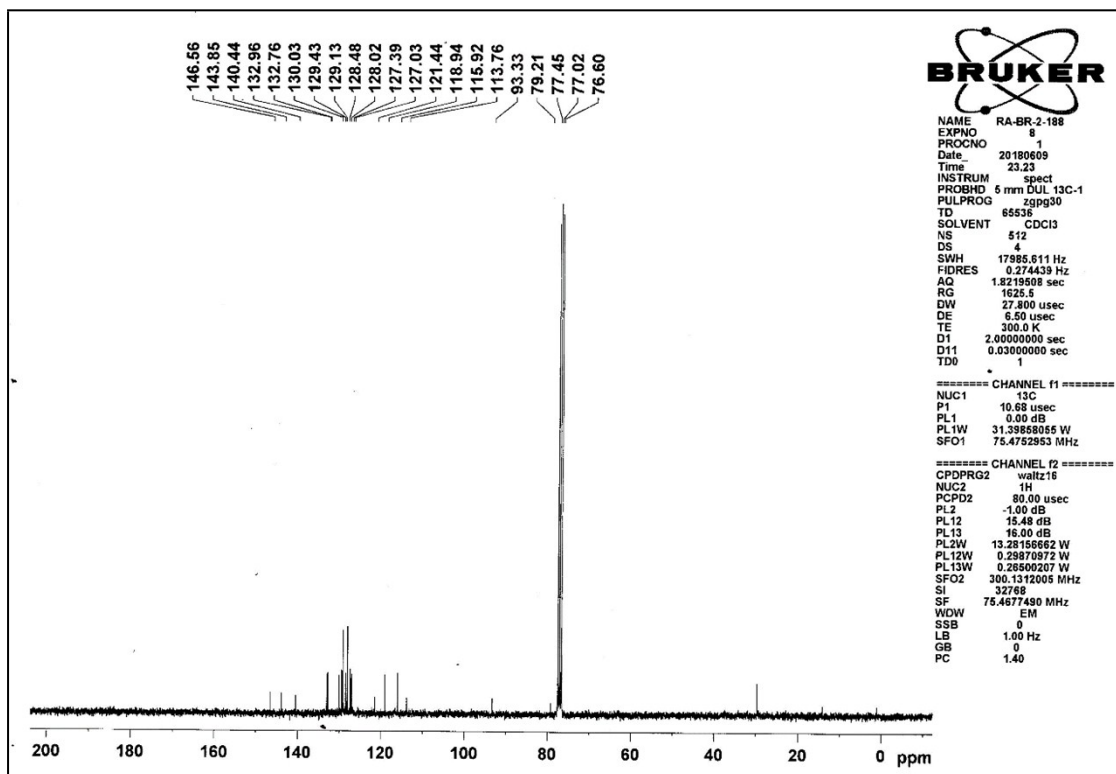
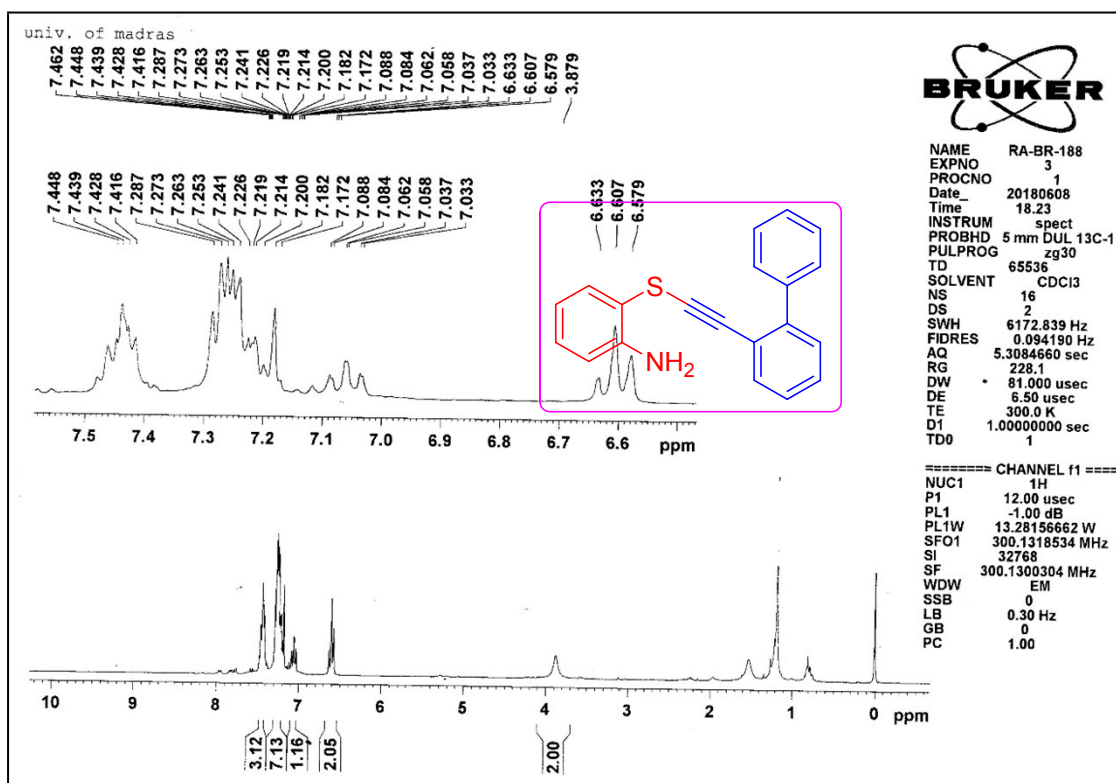
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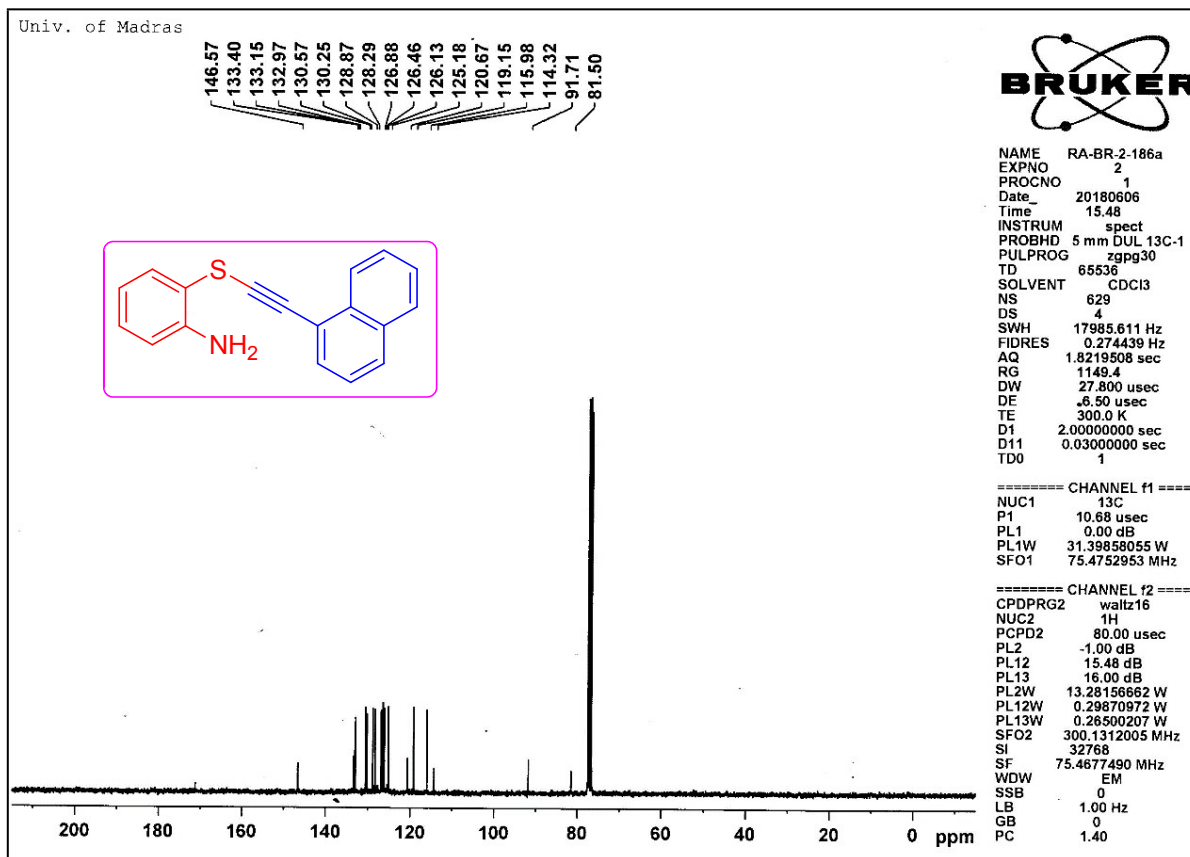
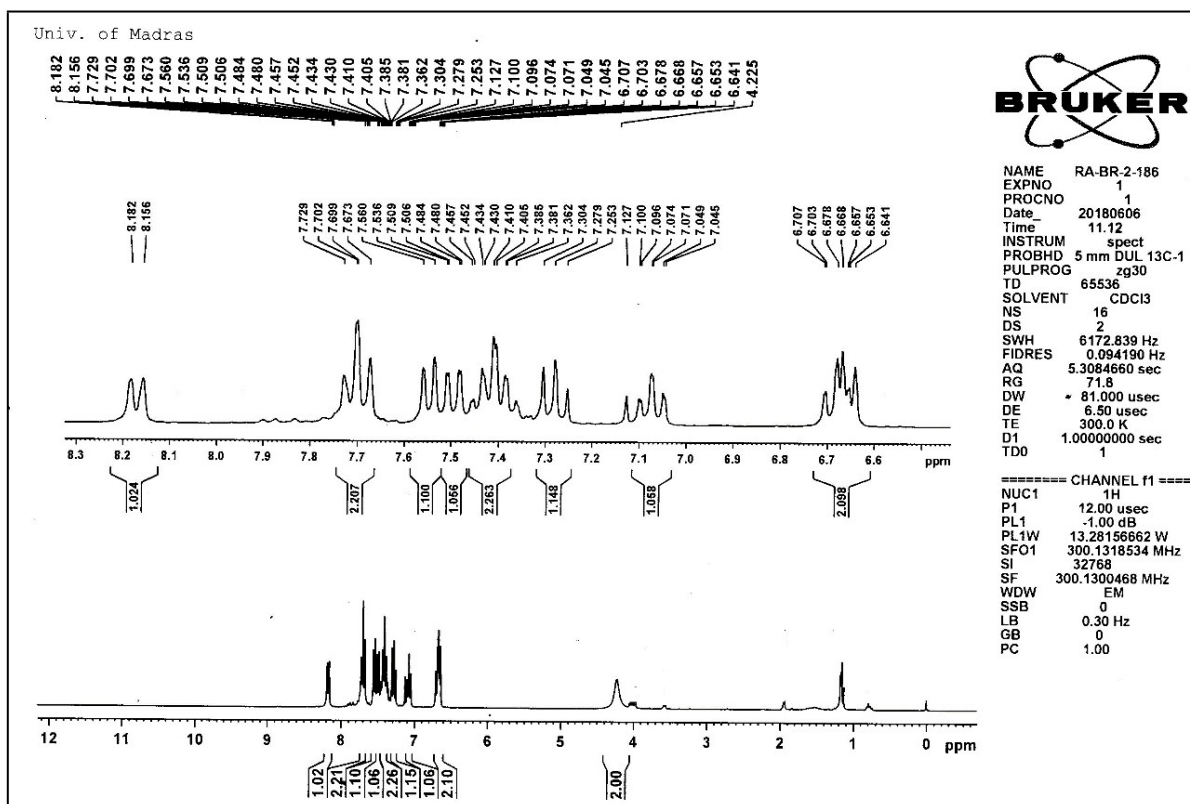
¹H & ¹³C NMR (CDCl₃) spectra of compound 3ao



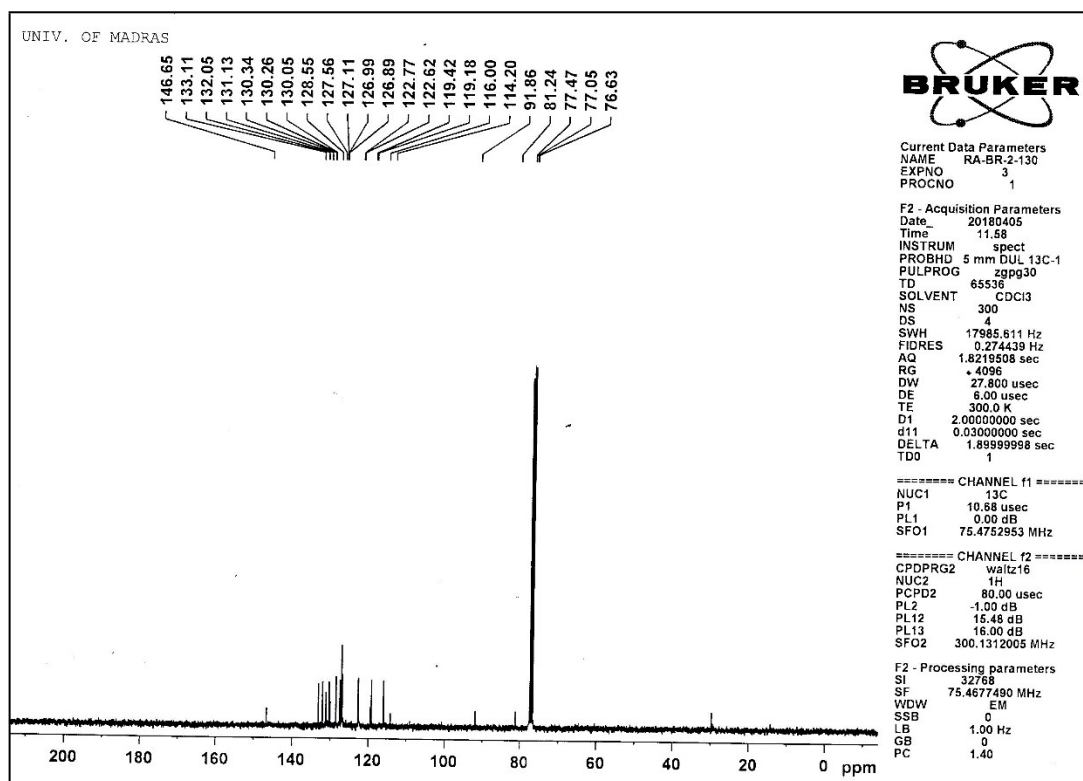
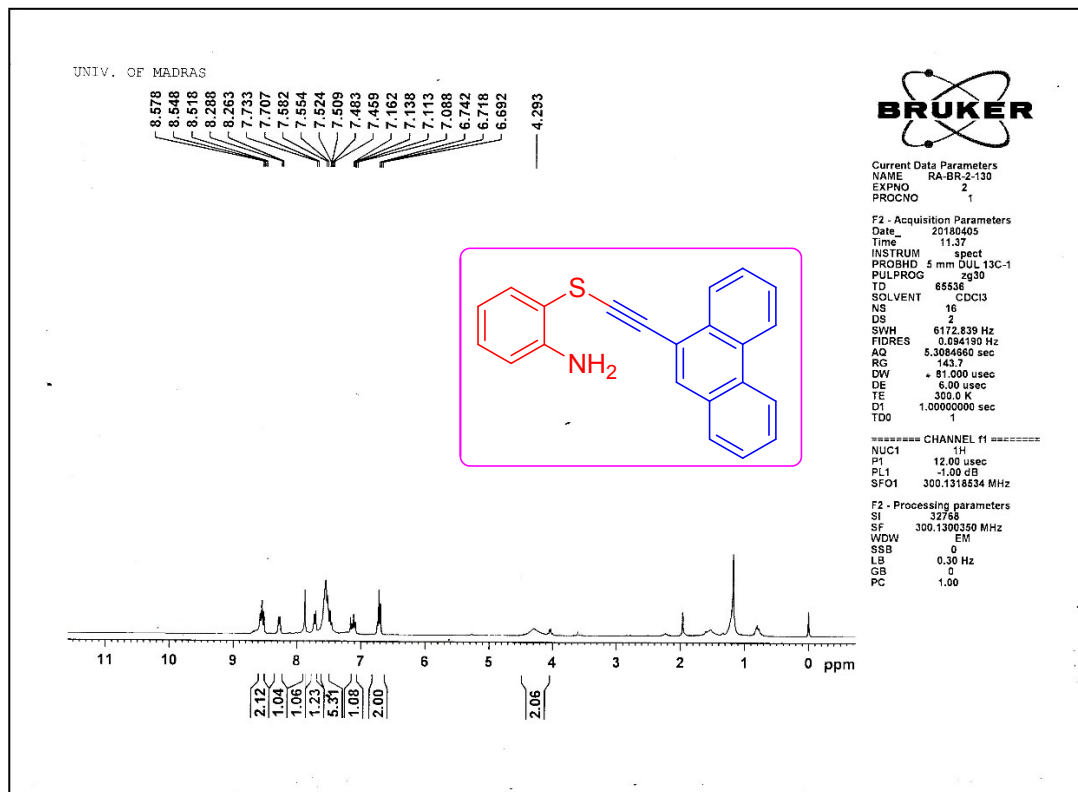
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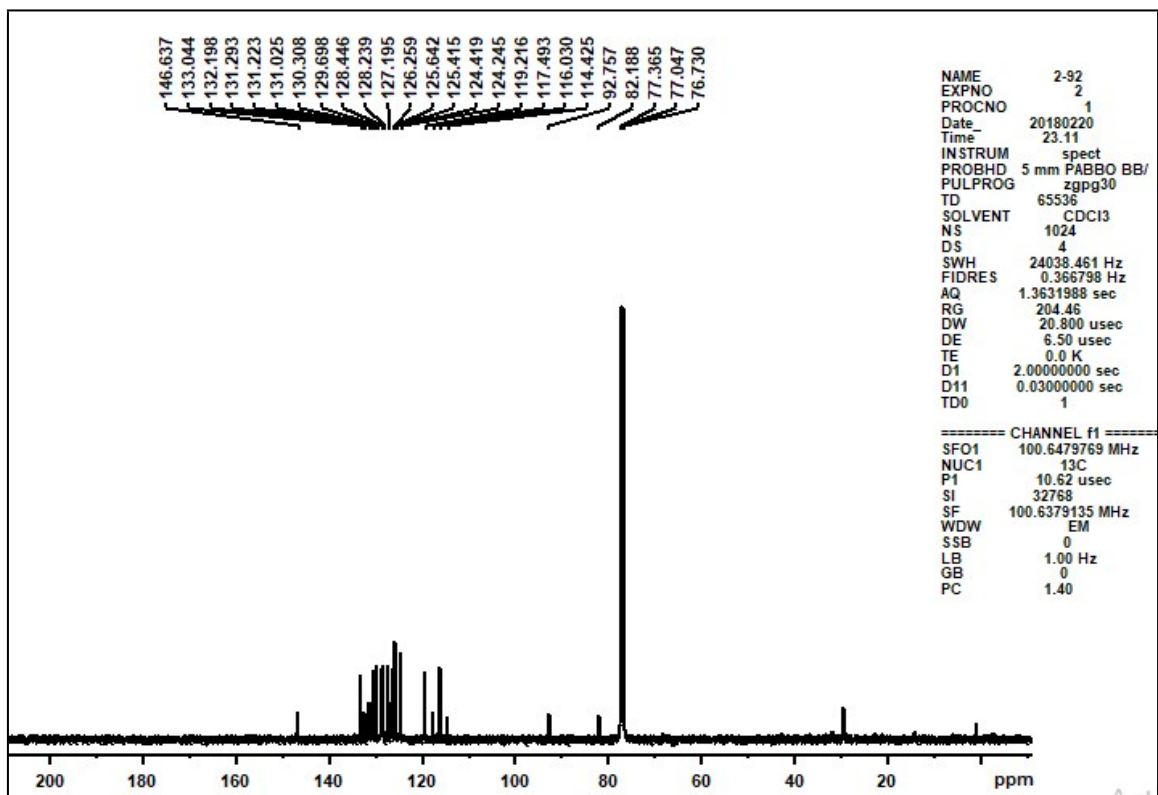
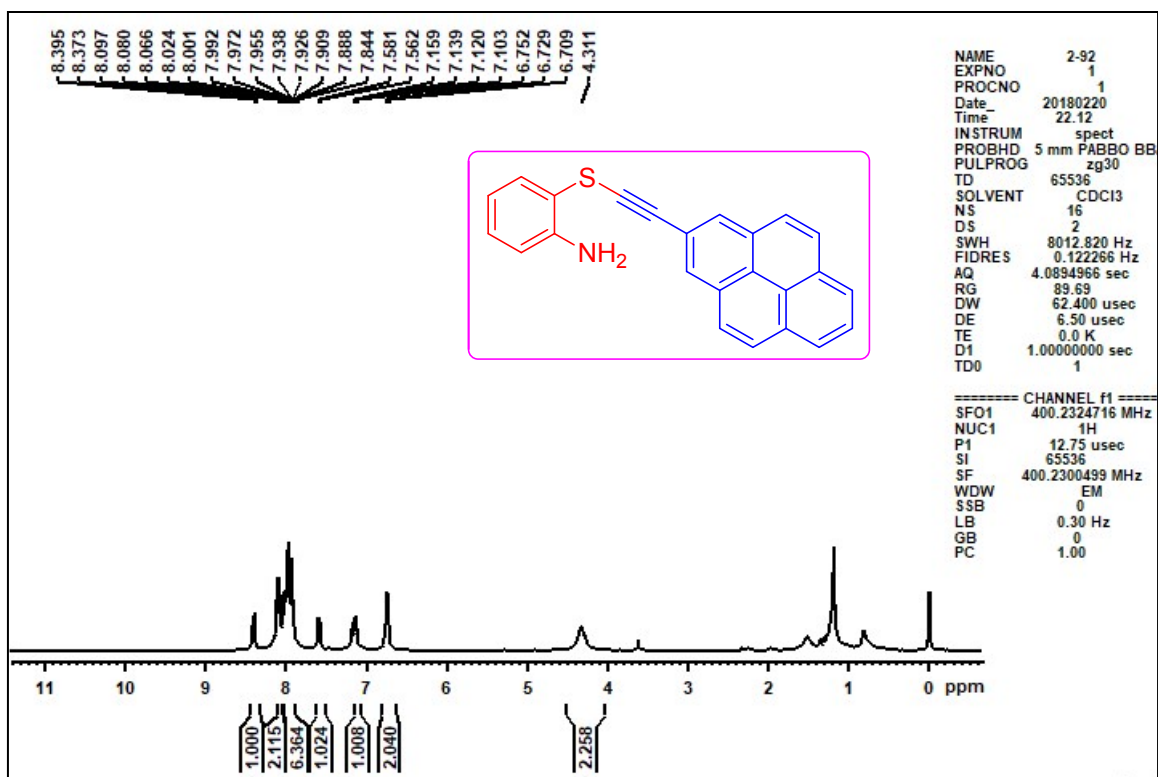
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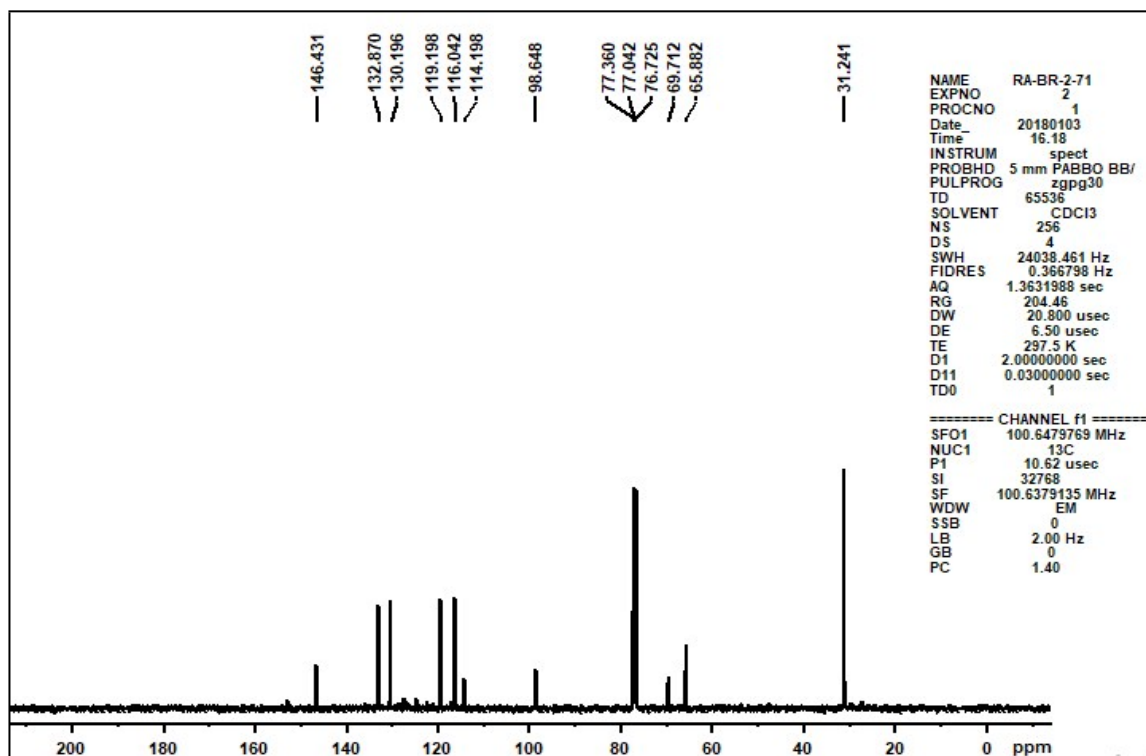
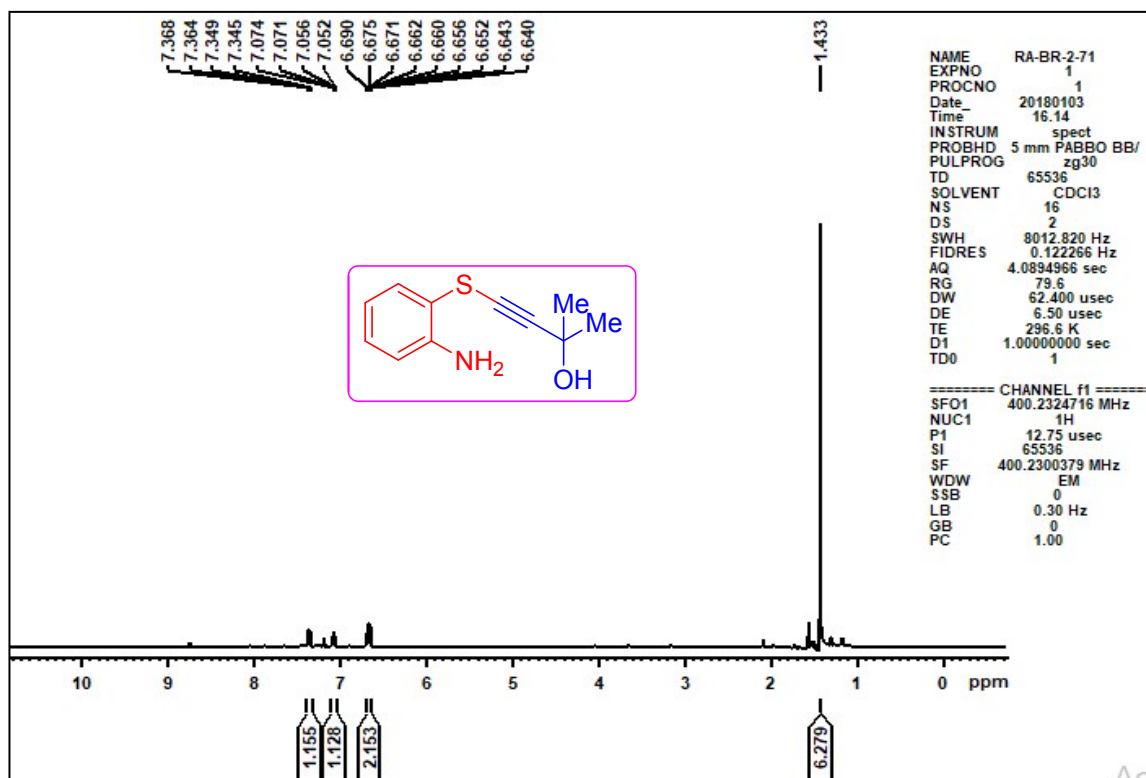
¹H & ¹³C NMR (CDCl₃) spectra of compound 3ar



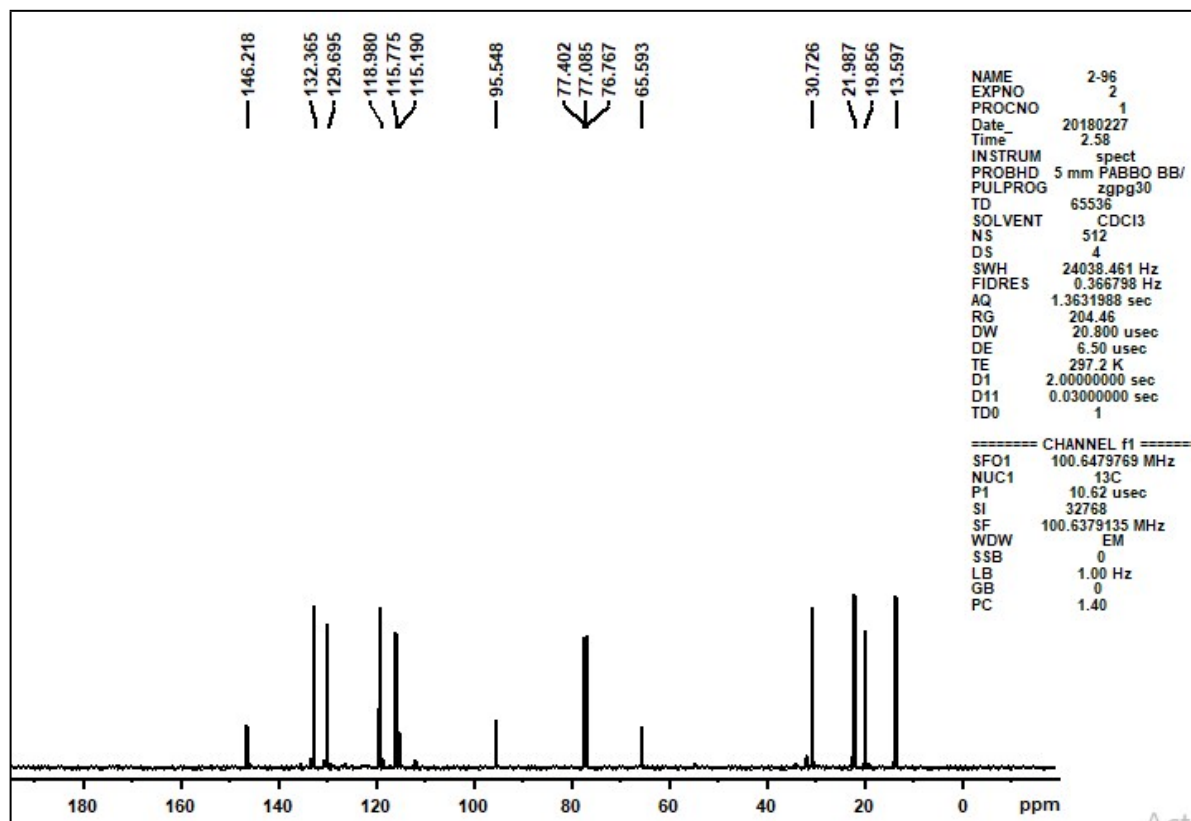
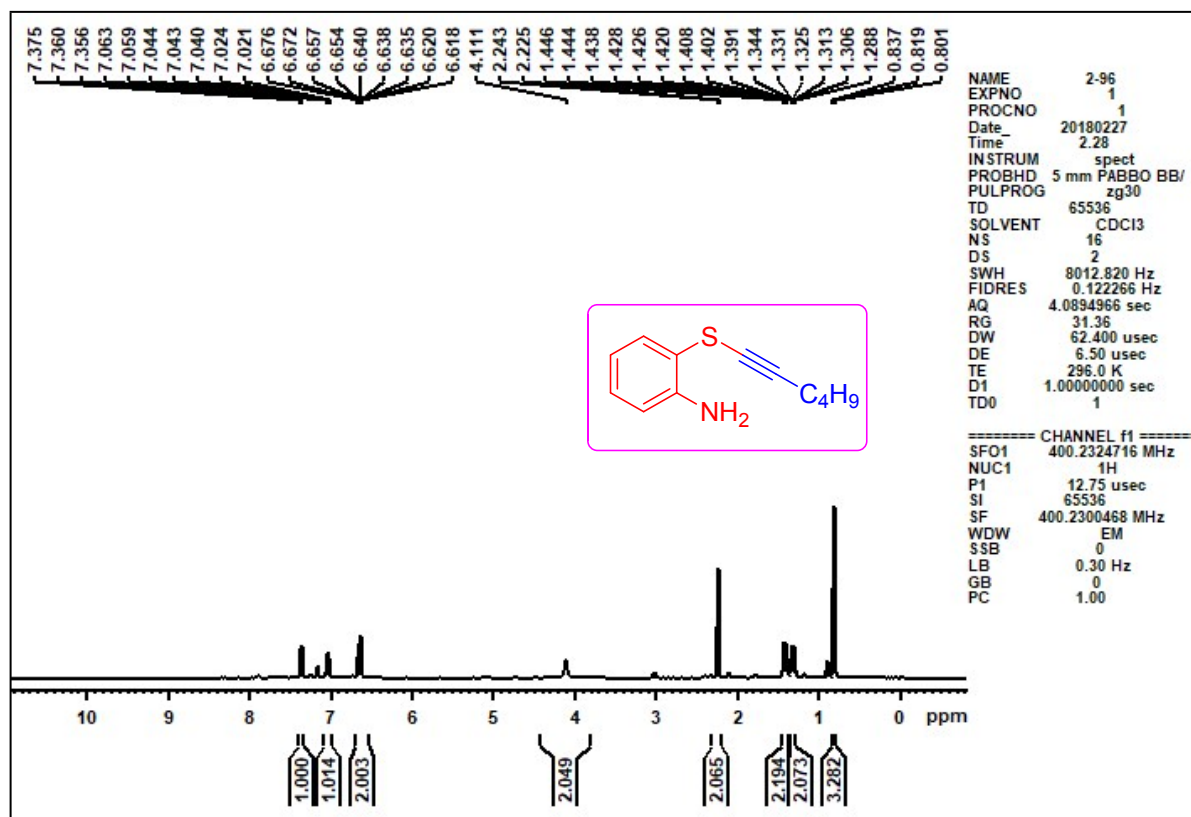
¹H & ¹³C NMR (CDCl₃) spectra of compound 3as



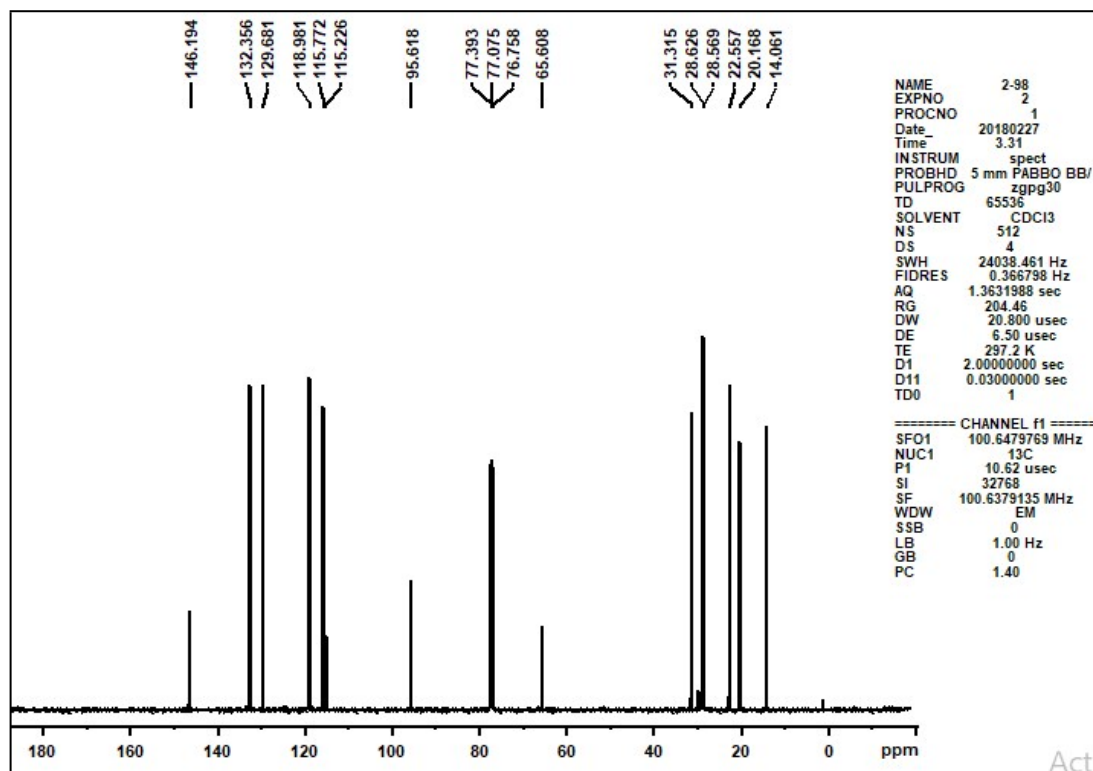
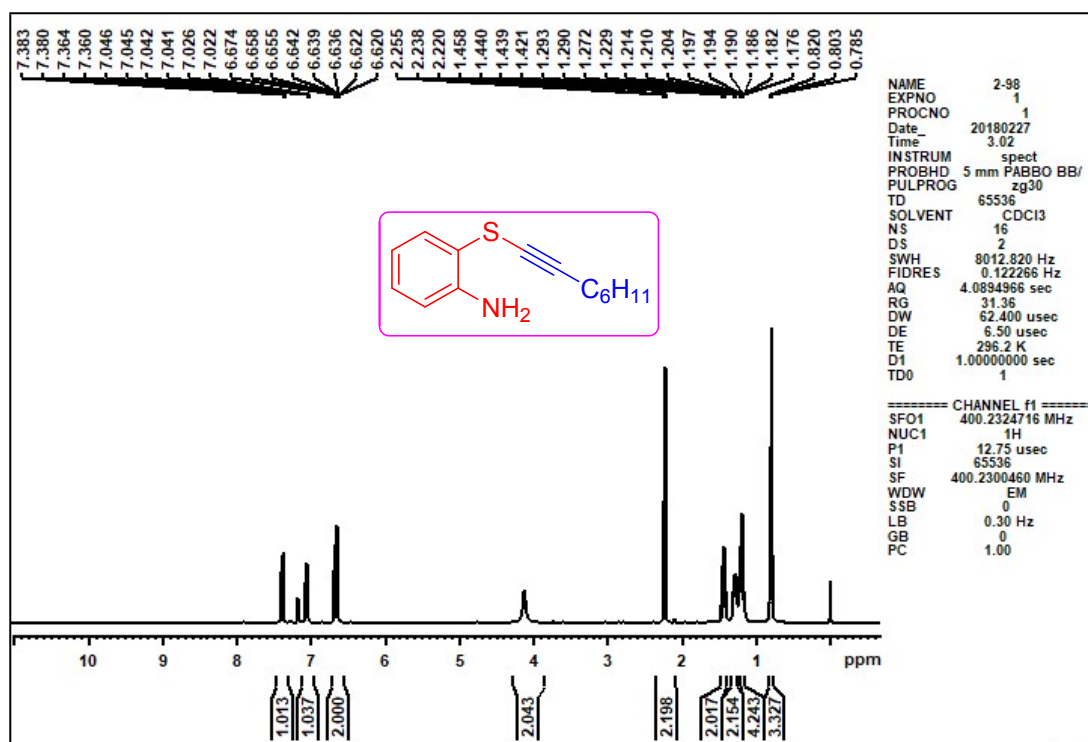
¹H & ¹³C NMR (CDCl₃) spectra of compound 3at



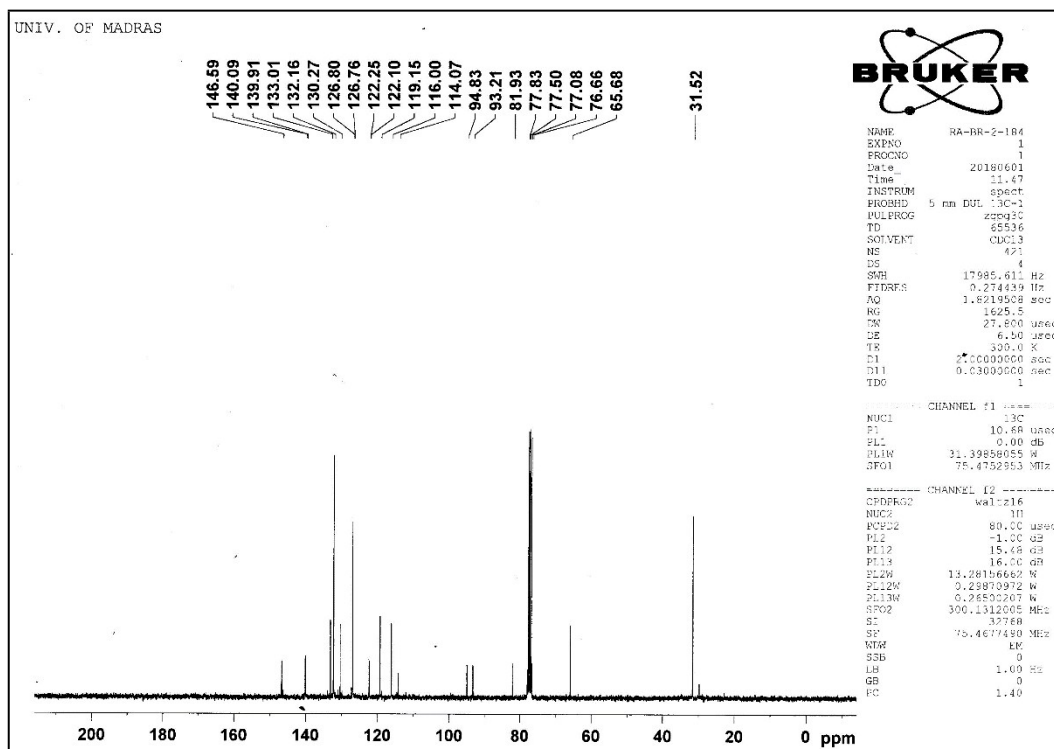
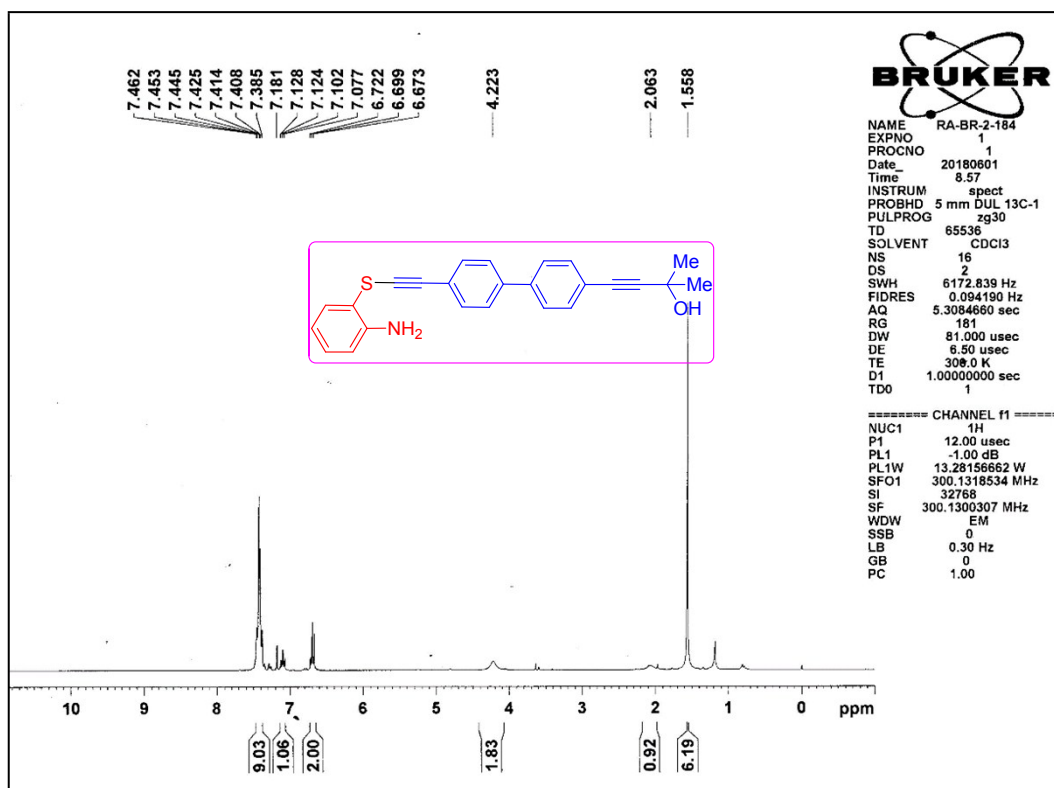
¹H & ¹³C NMR (CDCl₃) spectra of compound 3au



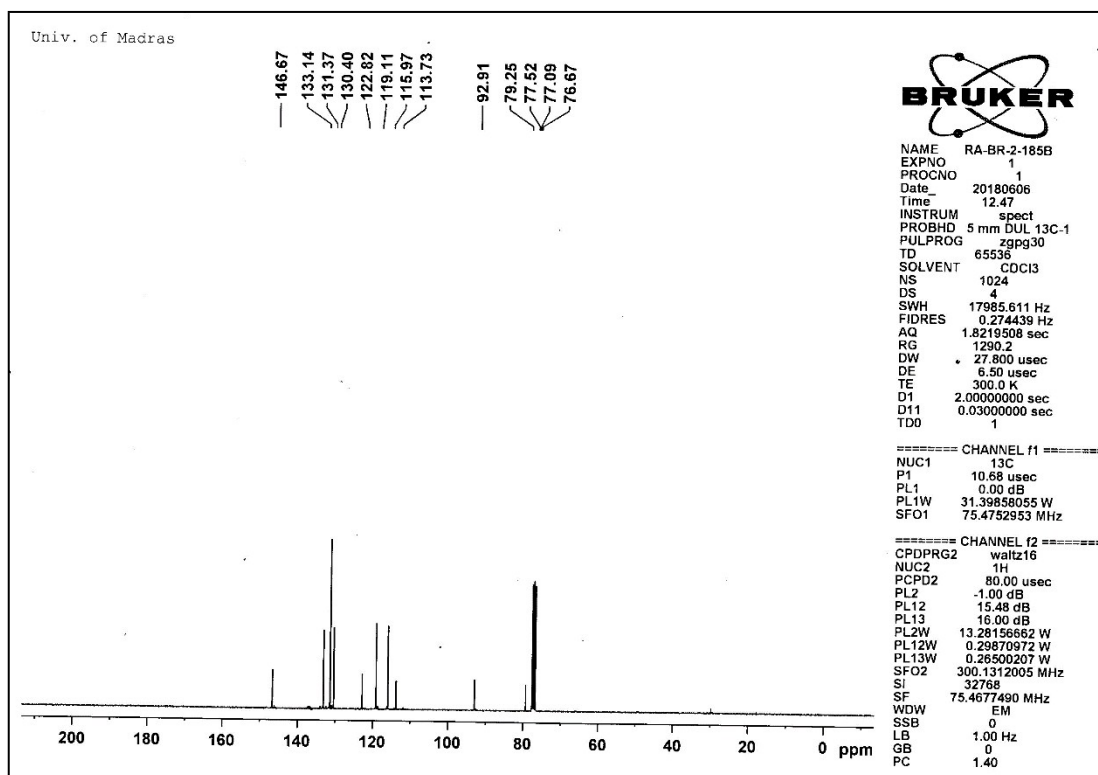
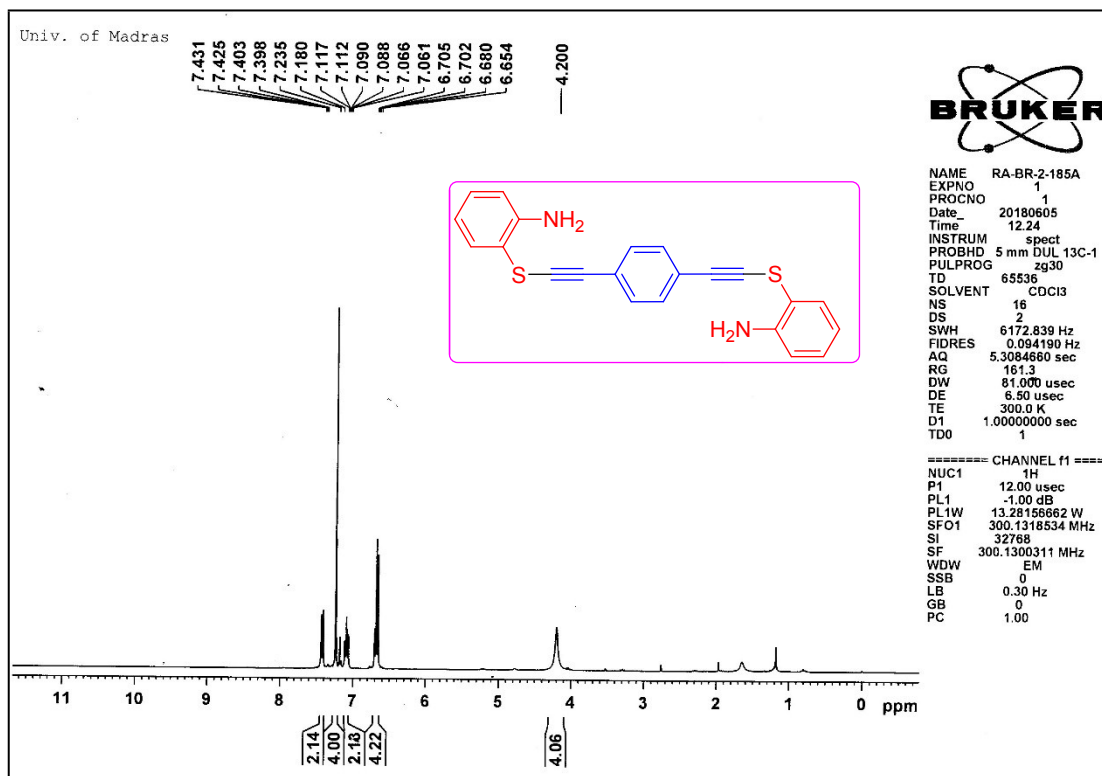
¹H & ¹³C NMR (CDCl₃) spectra of compound 3av



¹H & ¹³C NMR (CDCl₃) spectra of compound 3aw



¹H & ¹³C NMR (CDCl₃) spectra of compound 3ax



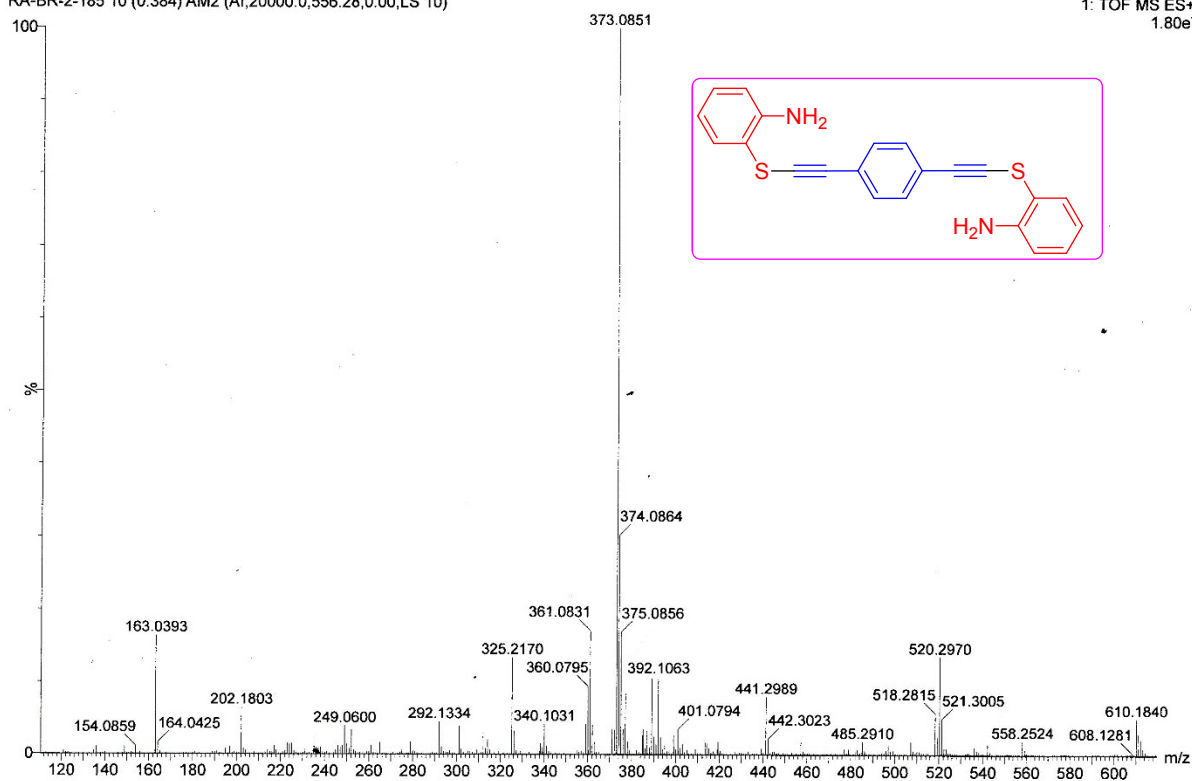
¹H & ¹³C NMR (CDCl₃) spectra of compound 3ba

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DRRA
RA-BR-2-185 10 (0.384) AM2 (Ar,20000.0,556.28,0.00,LS 10)

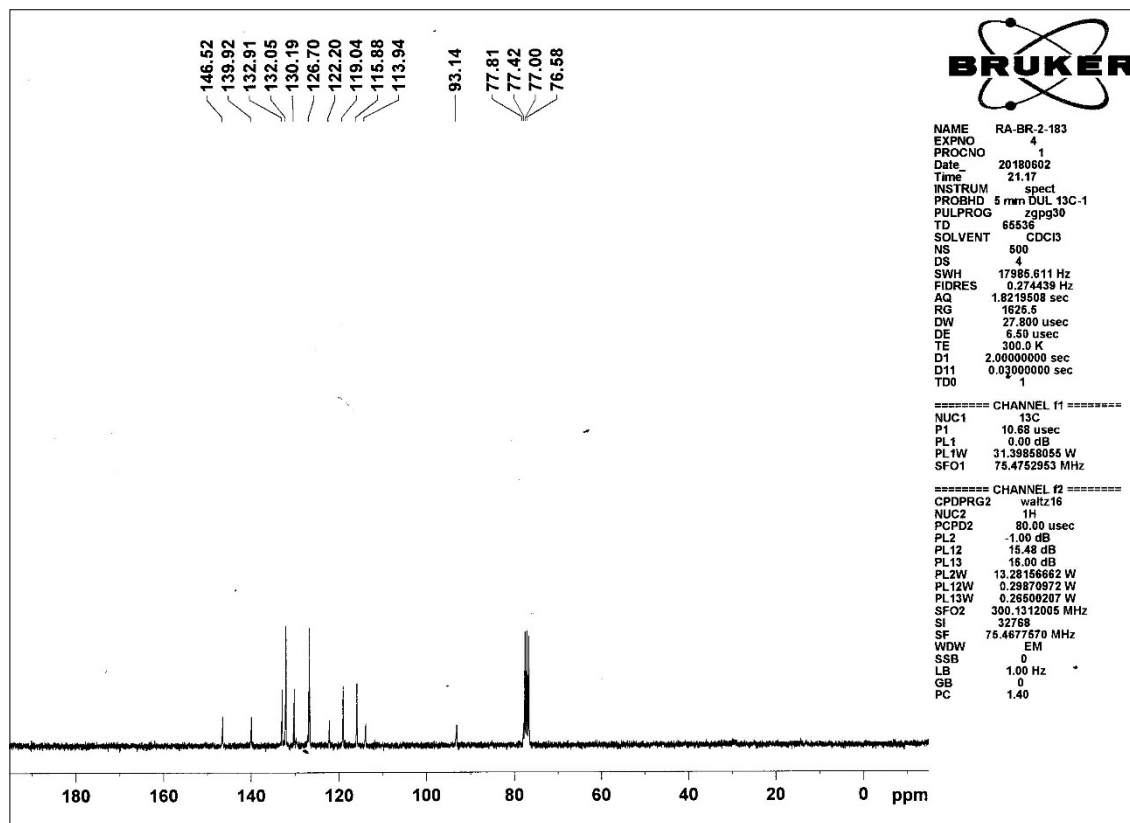
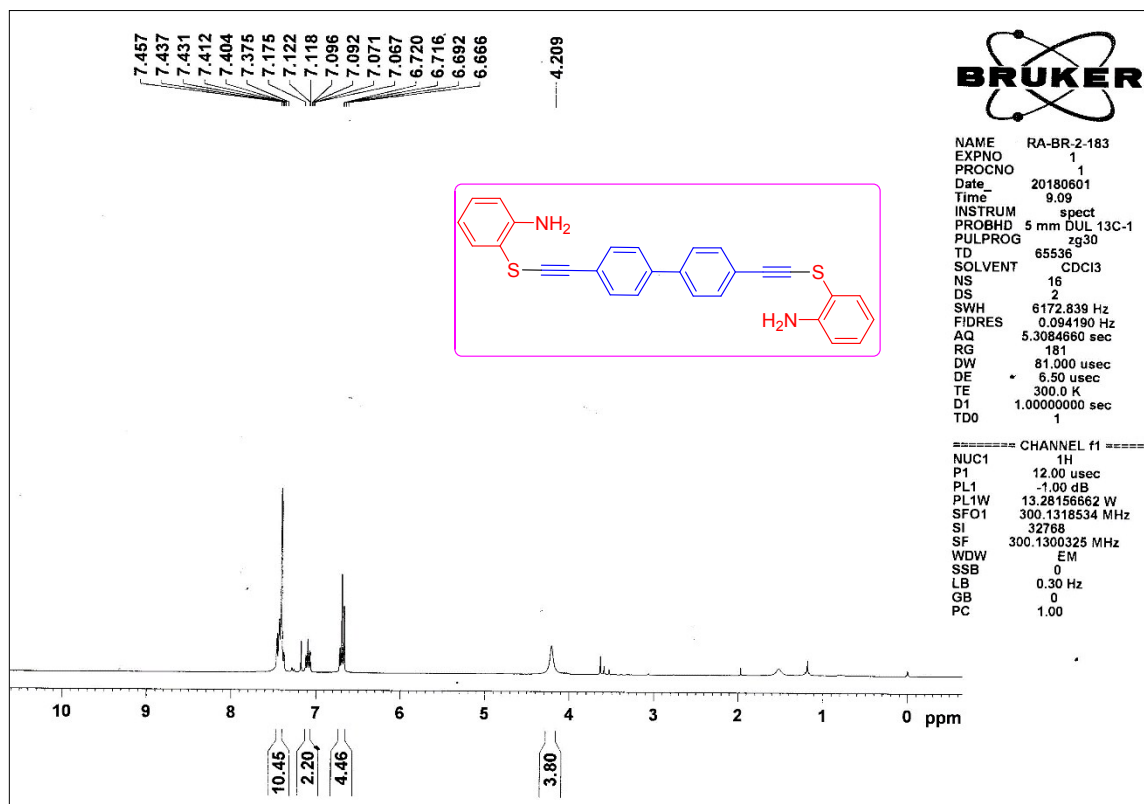
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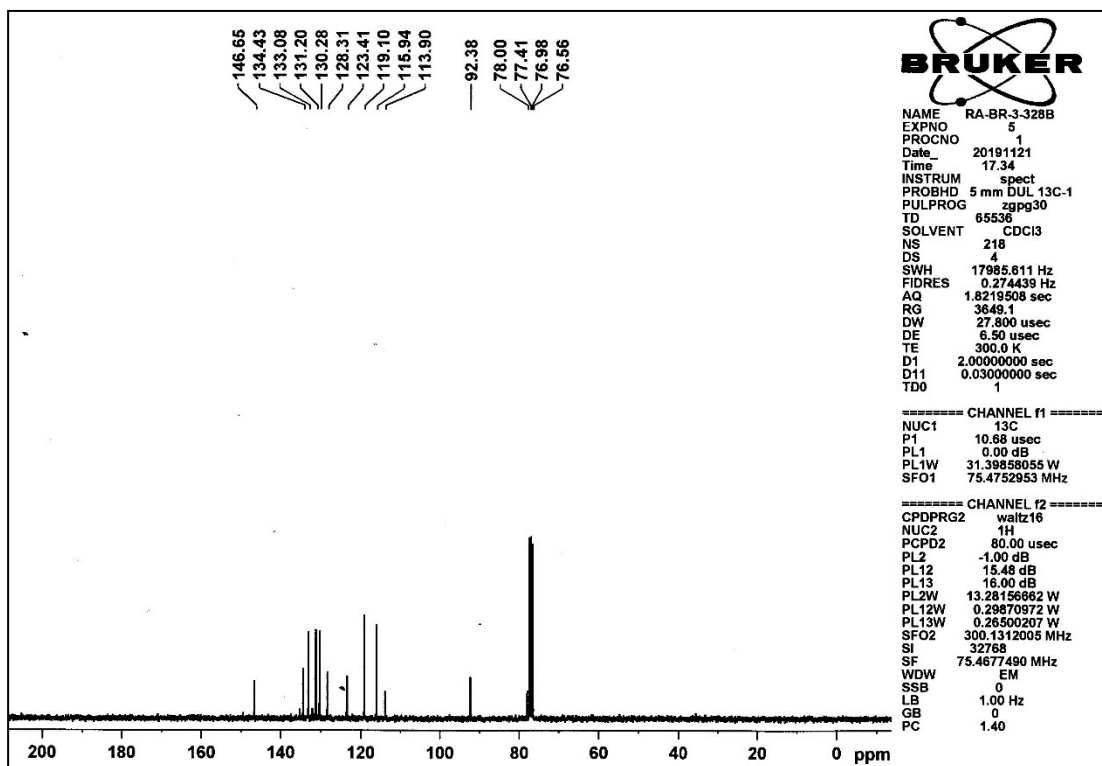
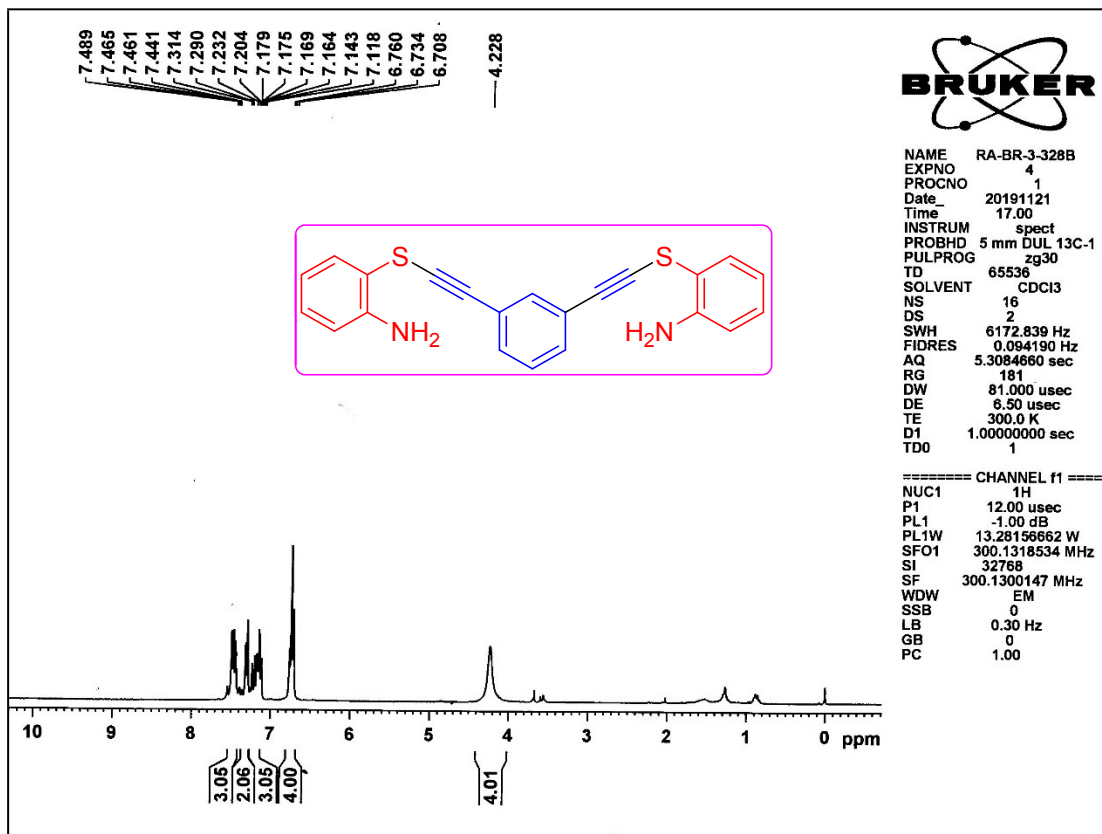
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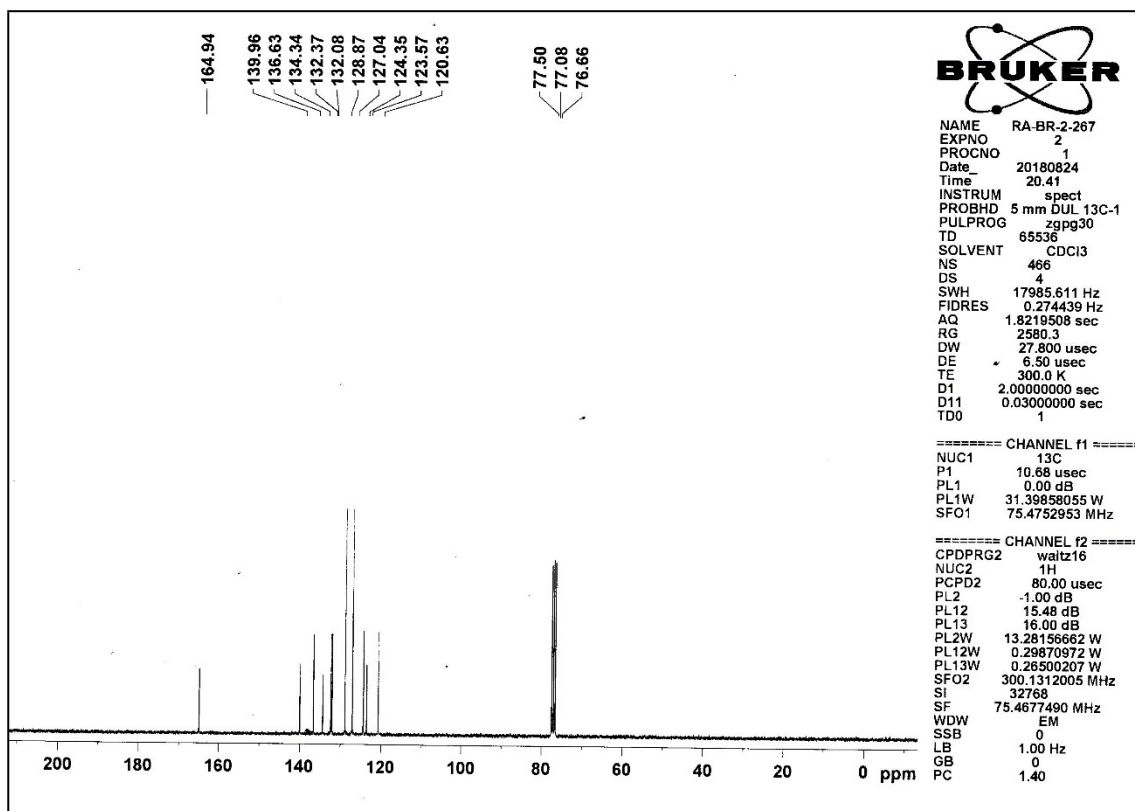
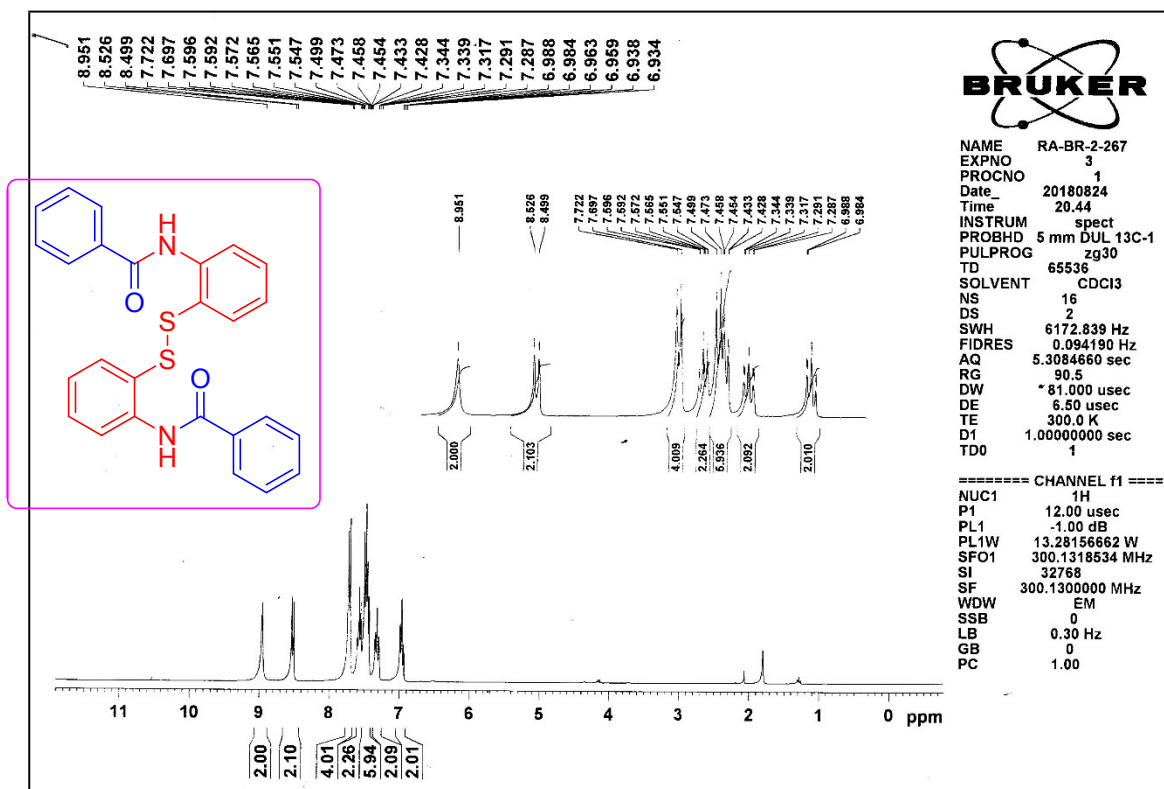
HRMS spectrum of compound 3ba



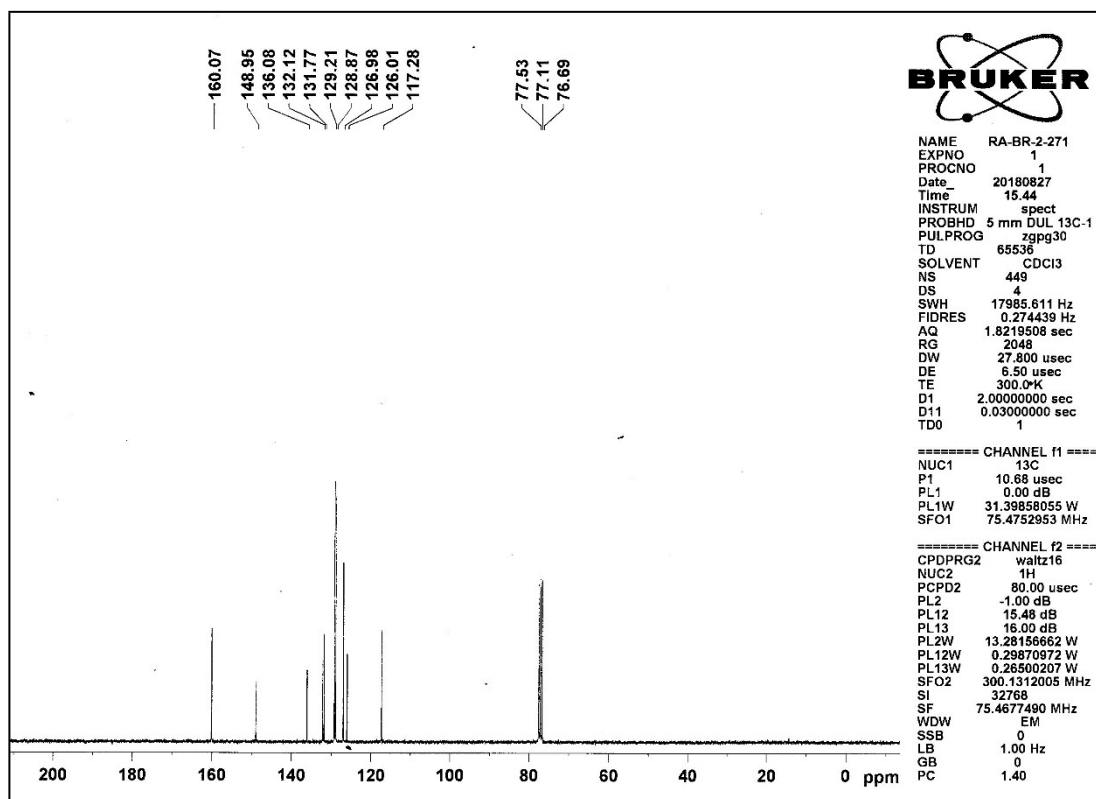
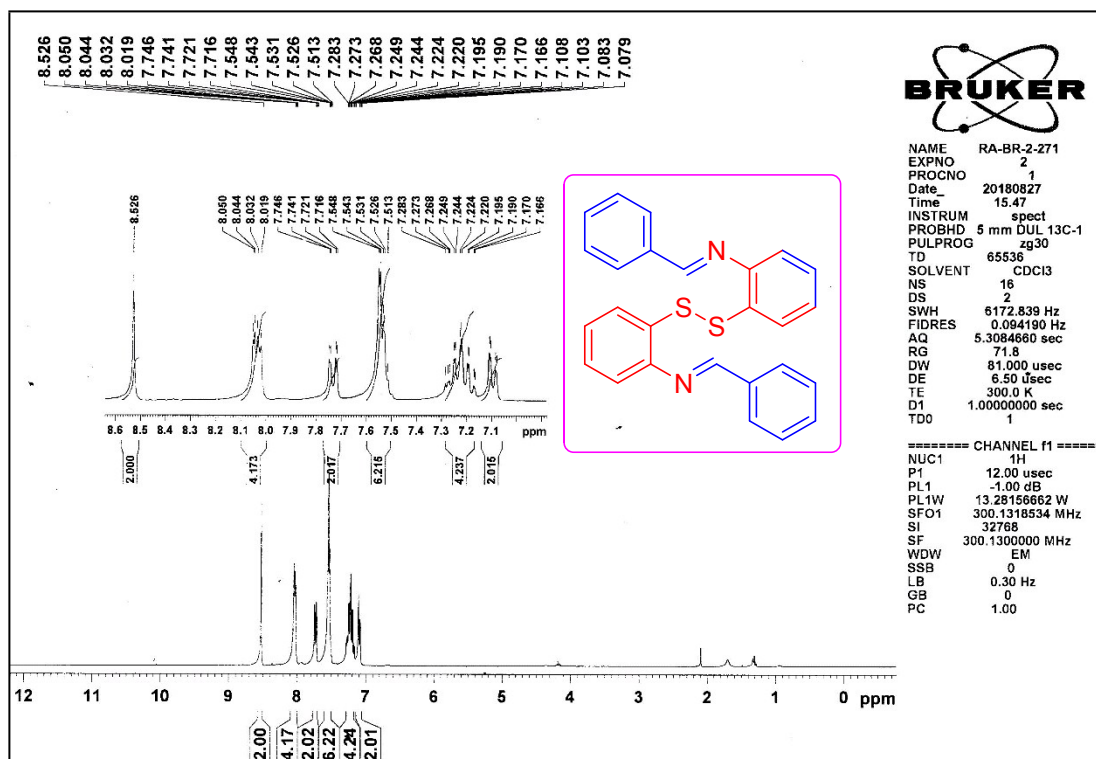
^1H & ^{13}C NMR (CDCl_3) spectra of compound 3bb



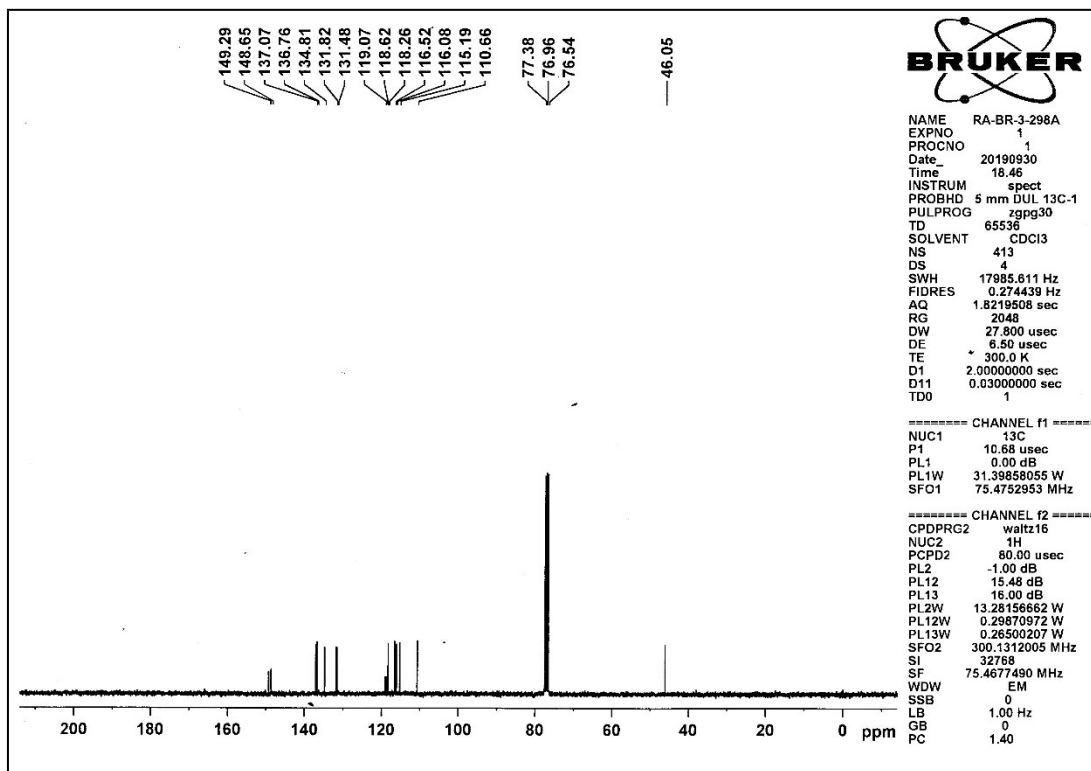
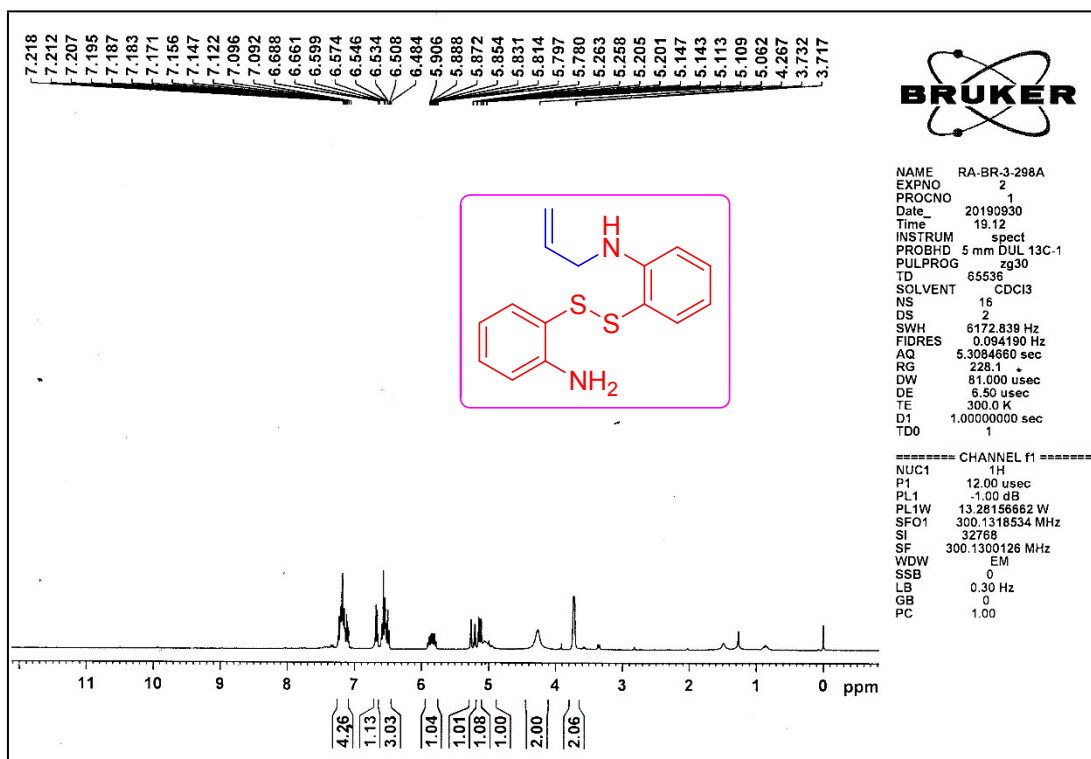
¹H & ¹³C NMR (CDCl₃) spectra of compound 3bc



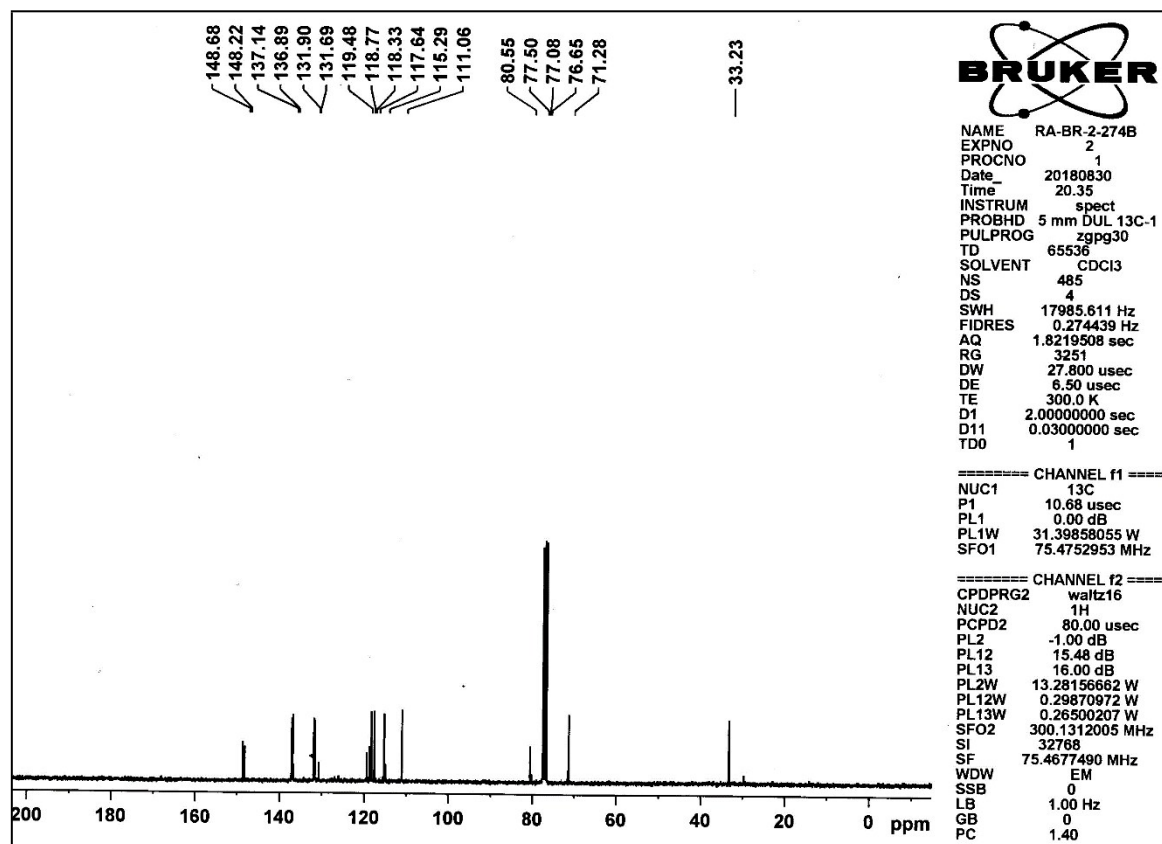
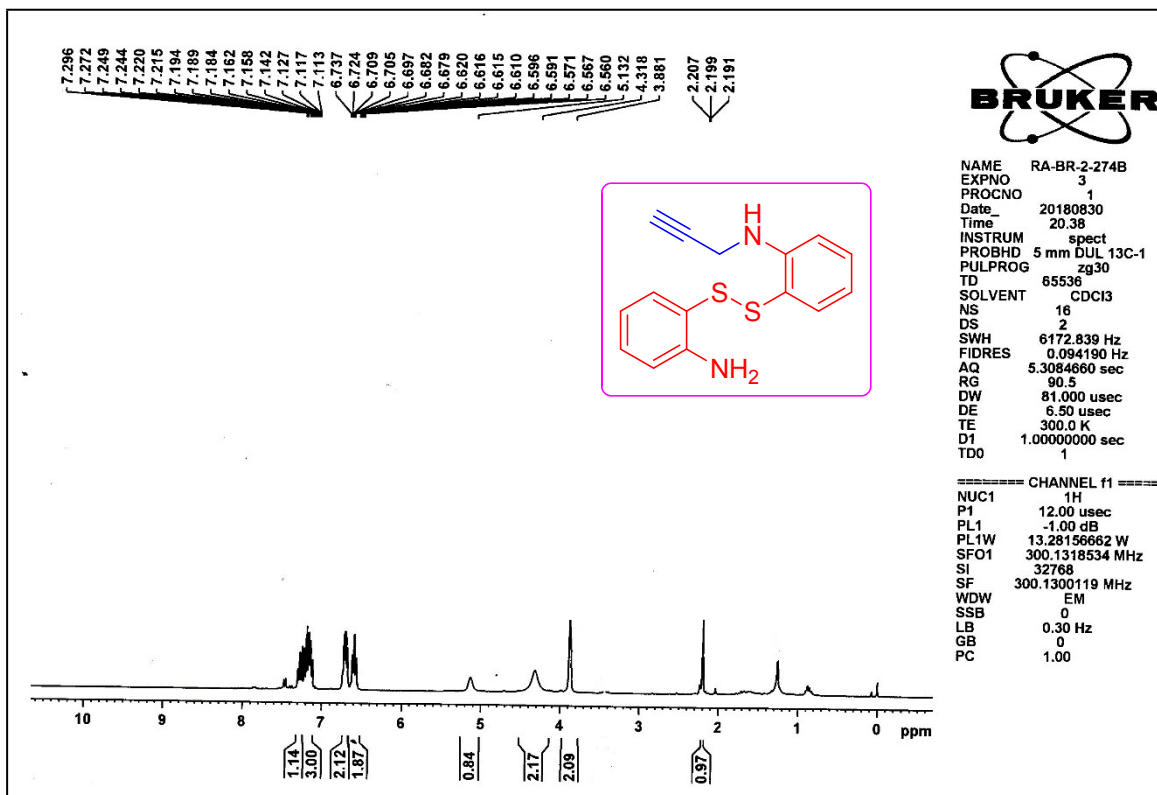
¹H & ¹³C NMR (CDCl₃) spectra of compound 1c



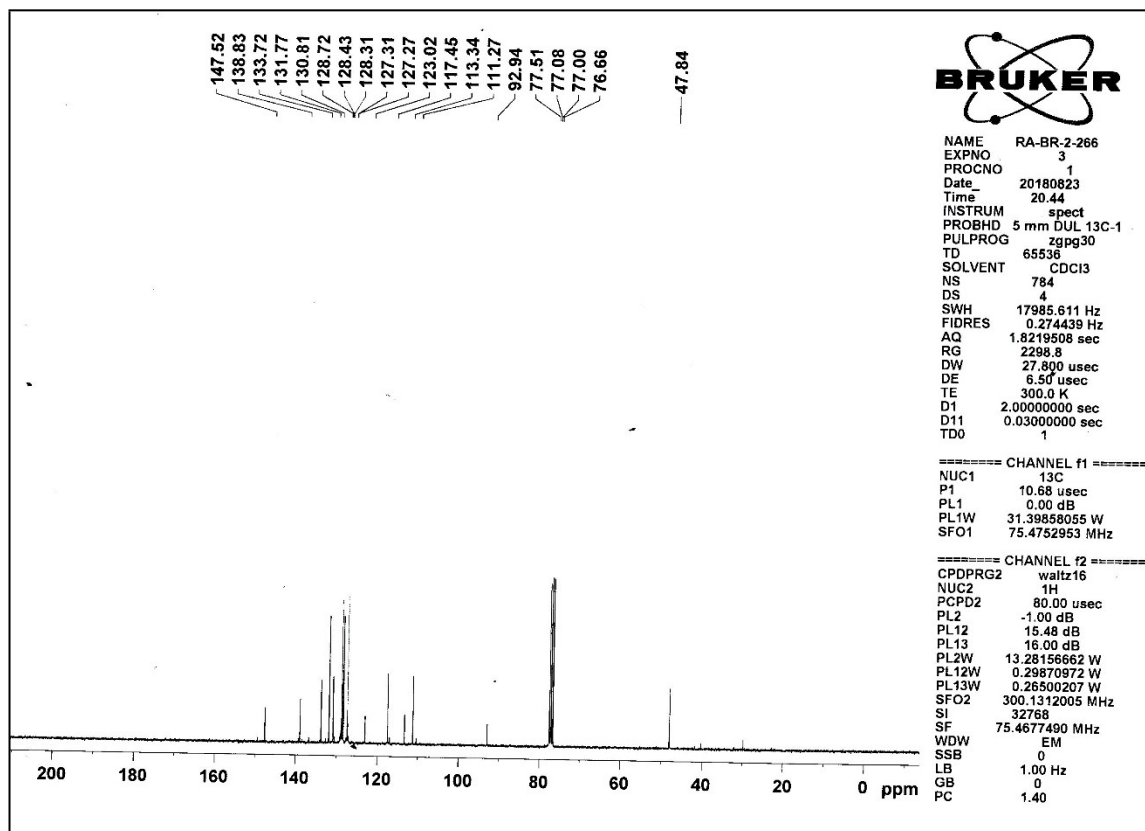
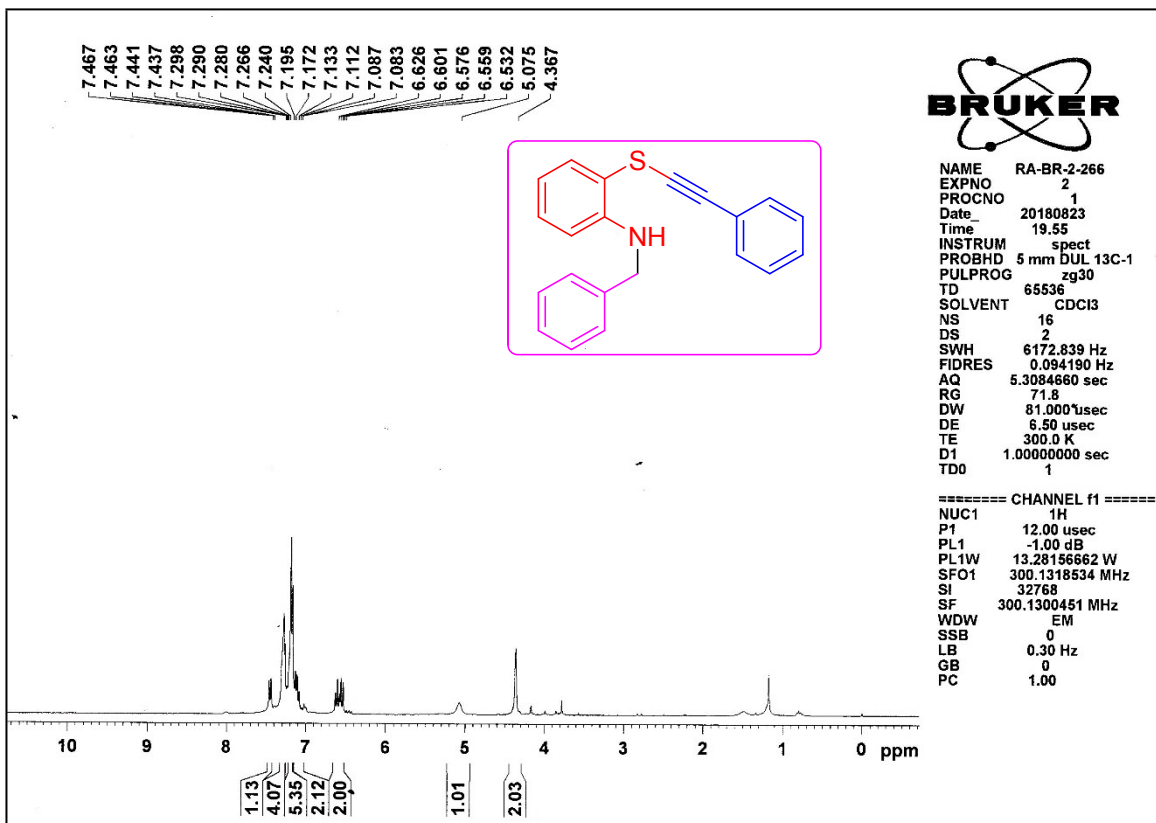
¹H & ¹³C NMR (CDCl₃) spectra of compound 1d



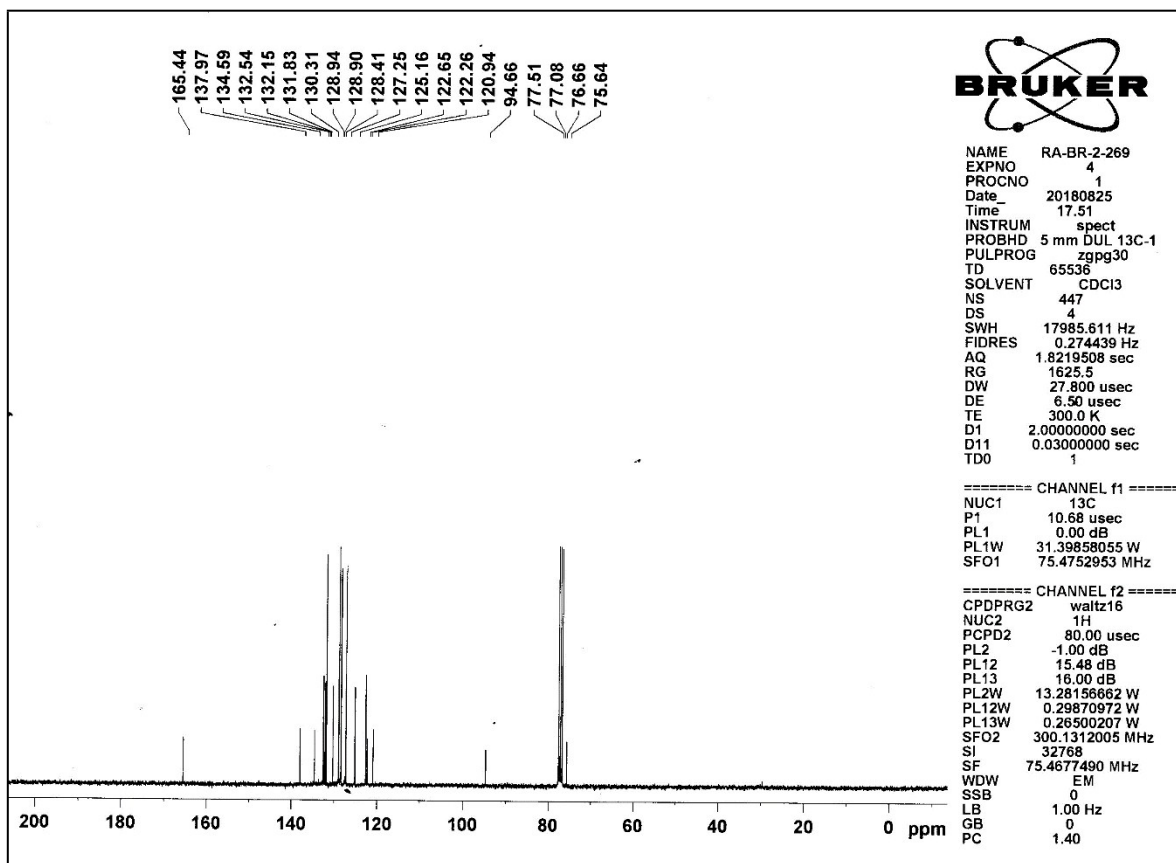
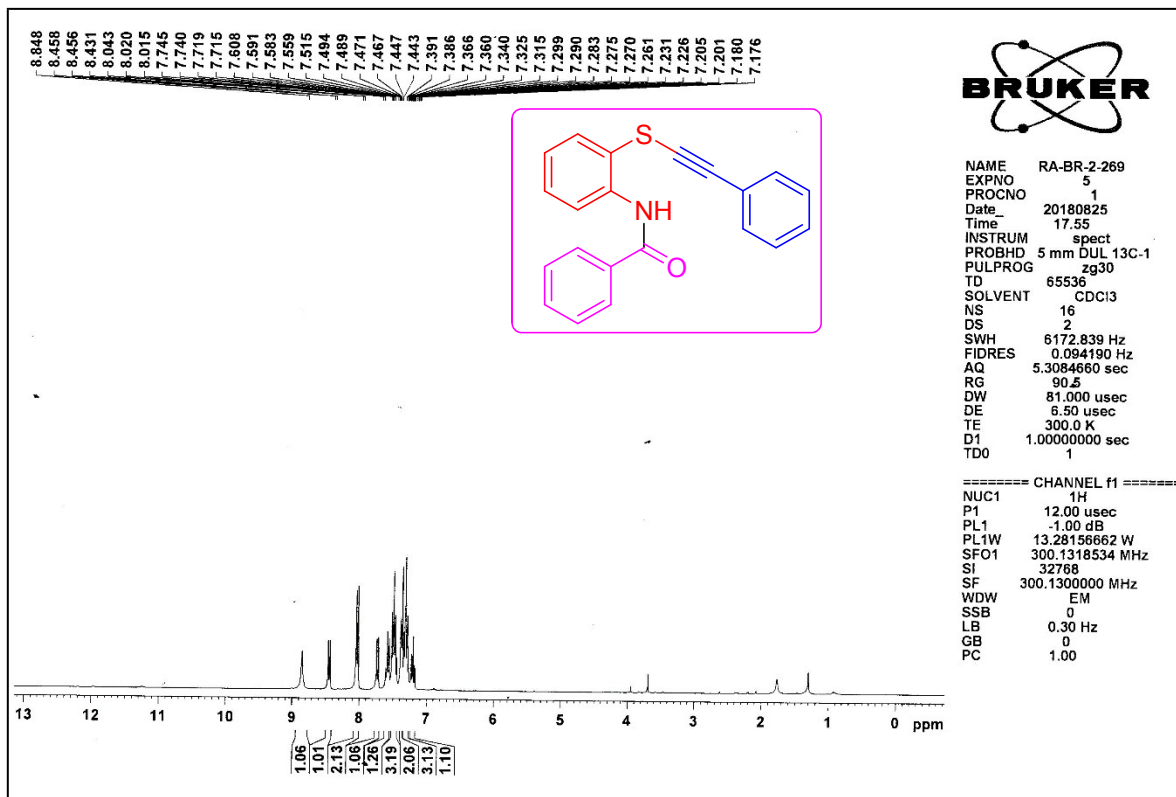
^1H & ^{13}C NMR (CDCl_3) spectra of compound 1i



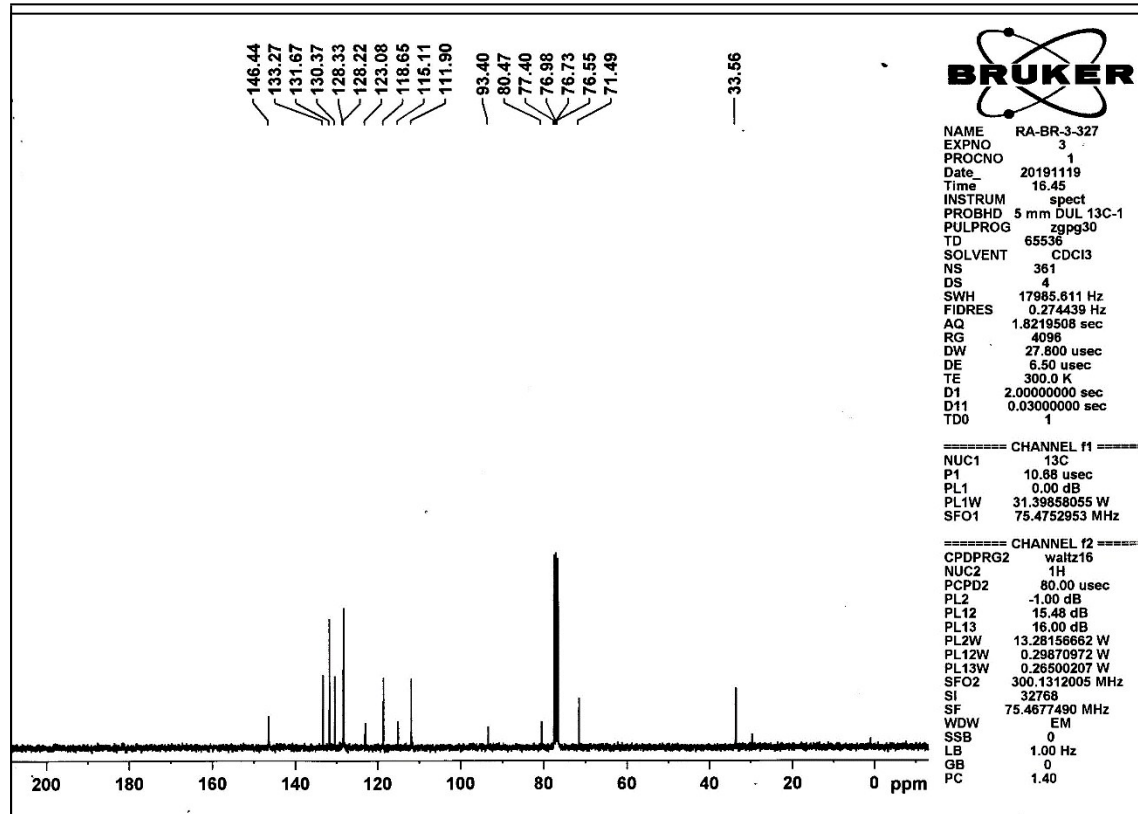
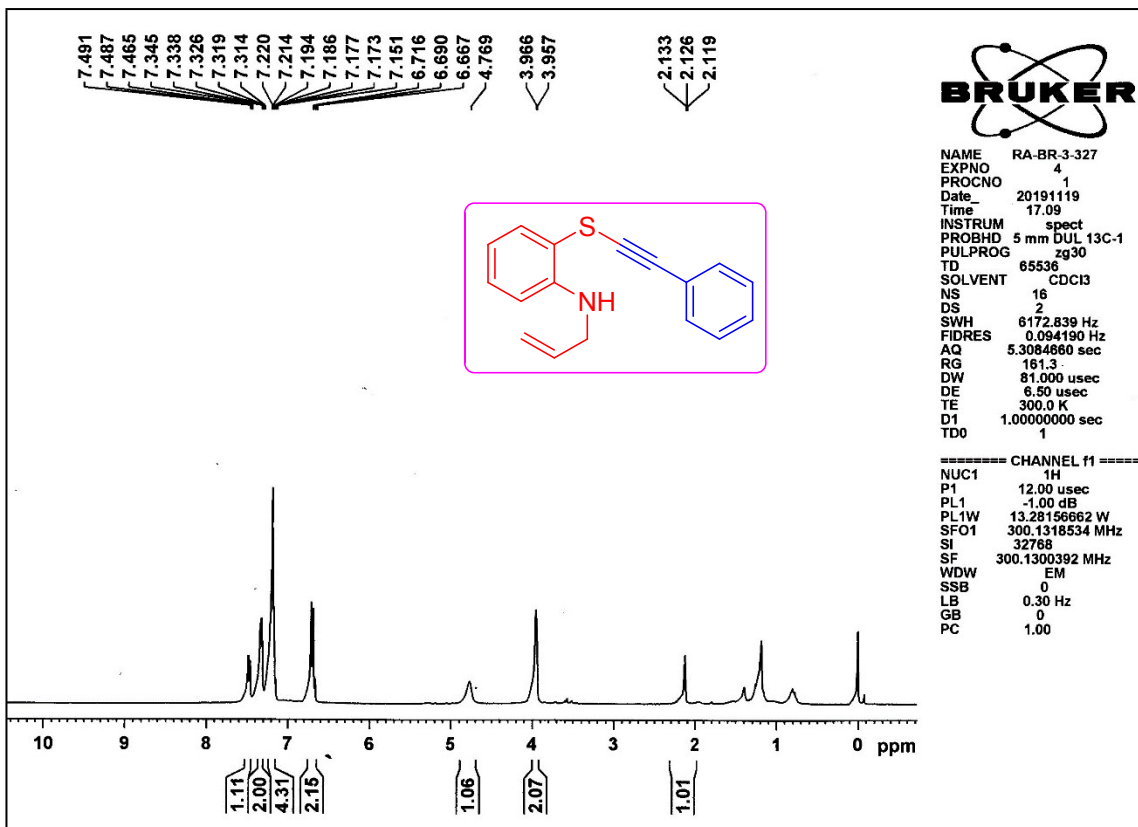
¹H & ¹³C NMR (CDCl₃) spectra of compound 1j



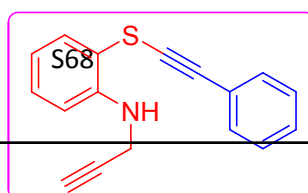
¹H & ¹³C NMR (CDCl₃) spectra of compound 4b



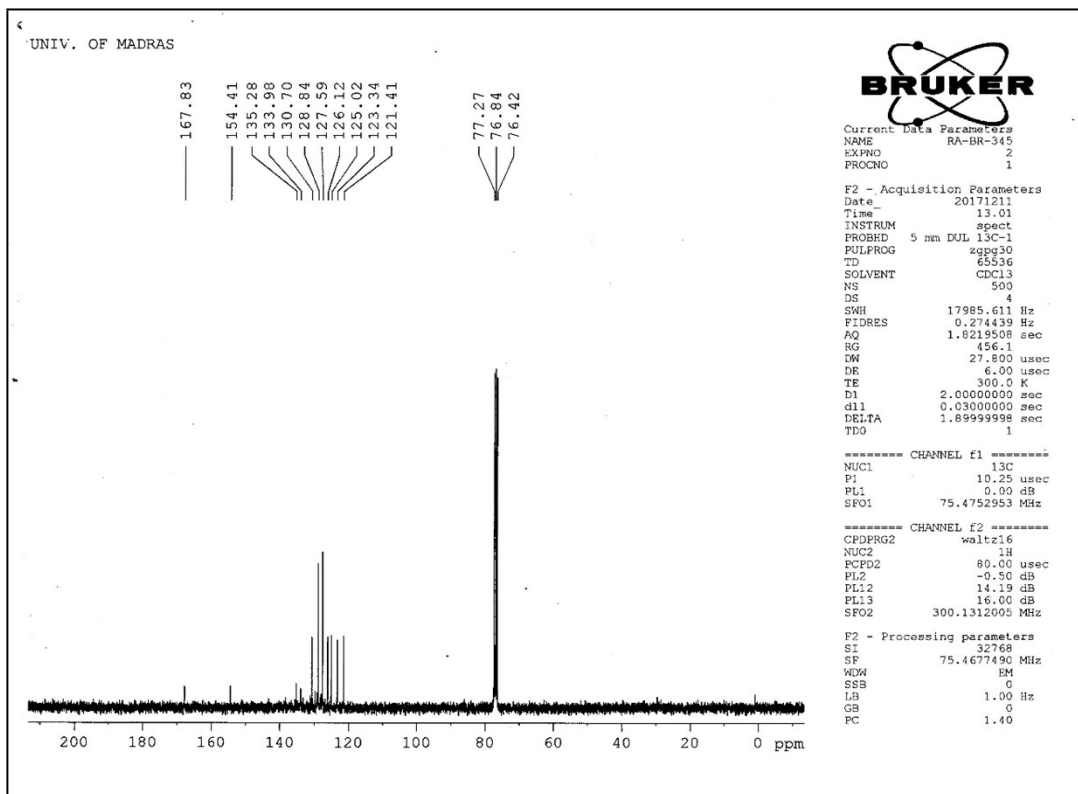
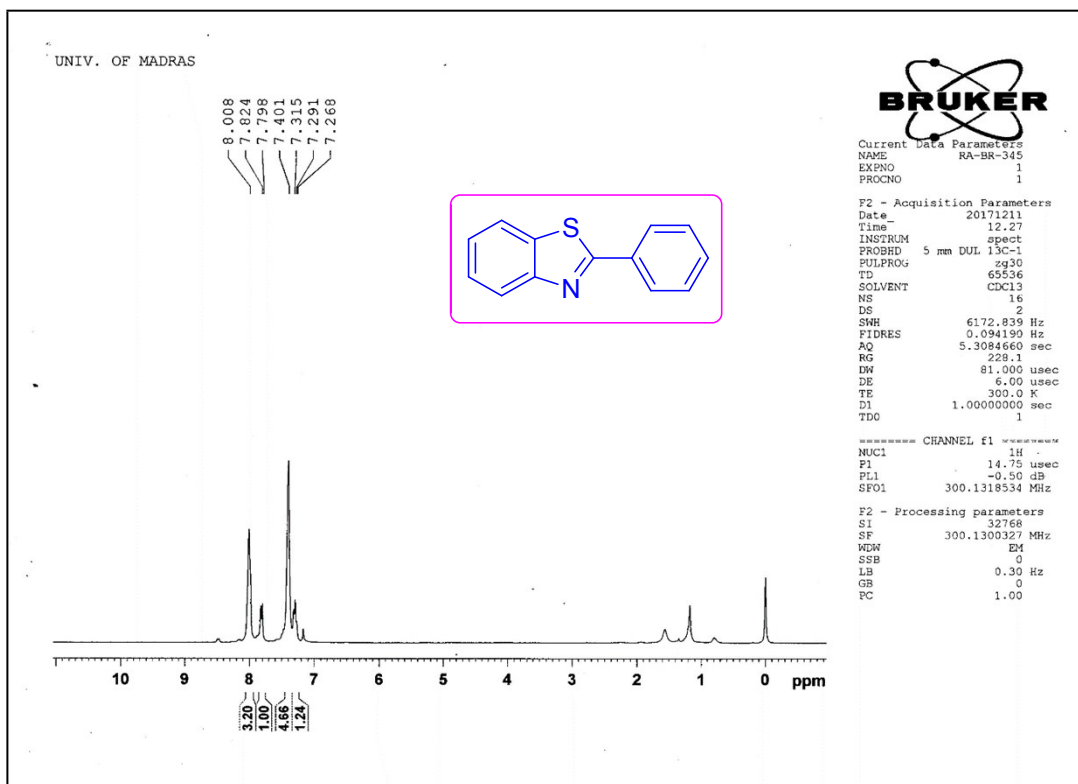
¹H & ¹³C NMR (CDCl₃) spectra of compound 4c



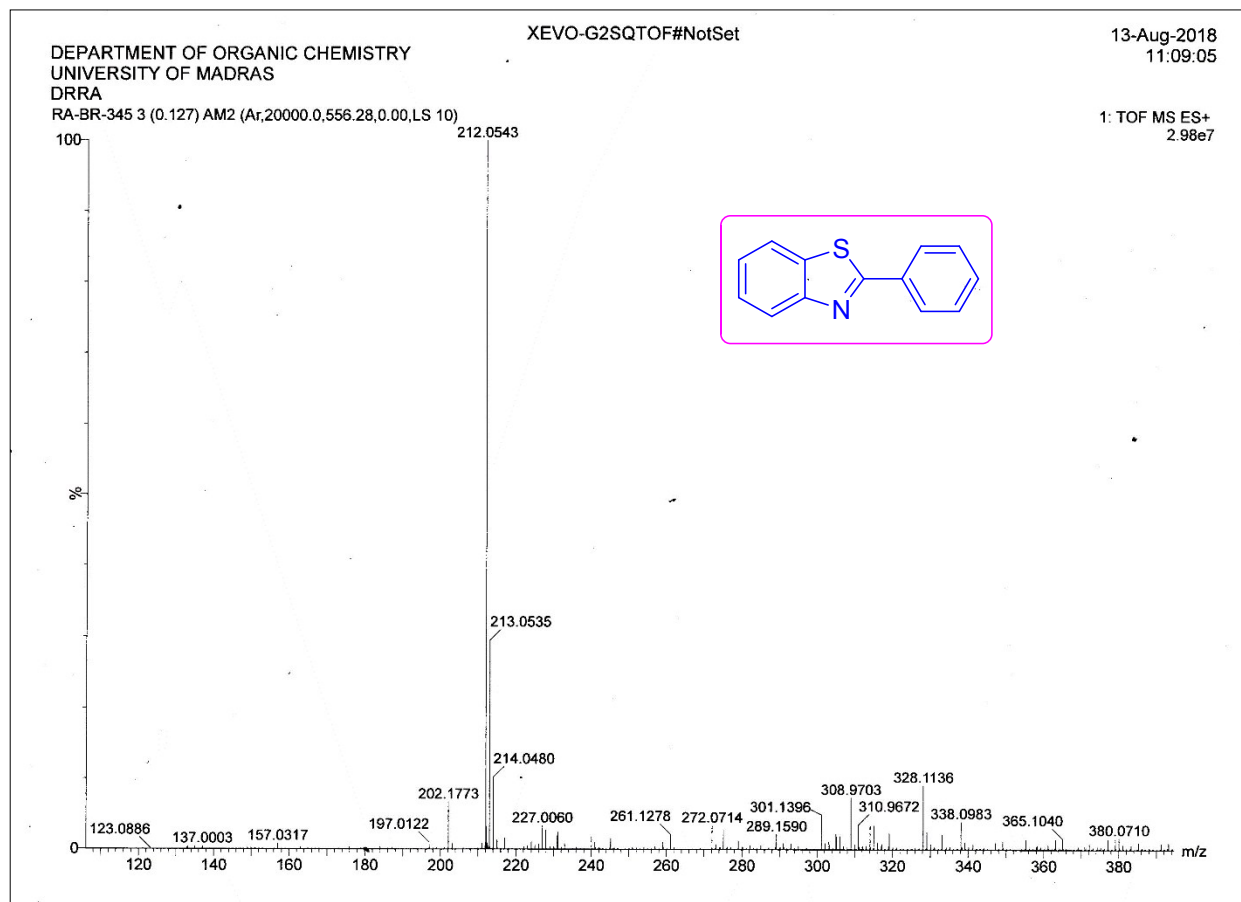
^1H & ^{13}C NMR (CDCl_3) spectra of compound 4i



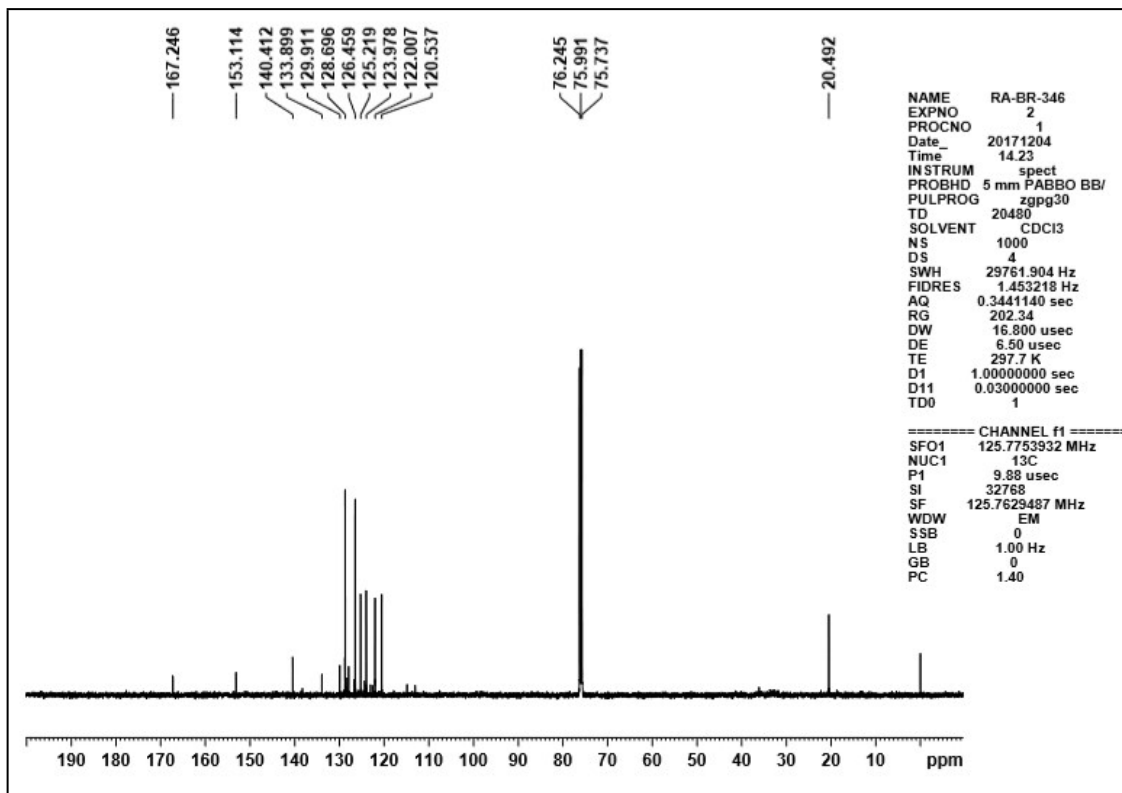
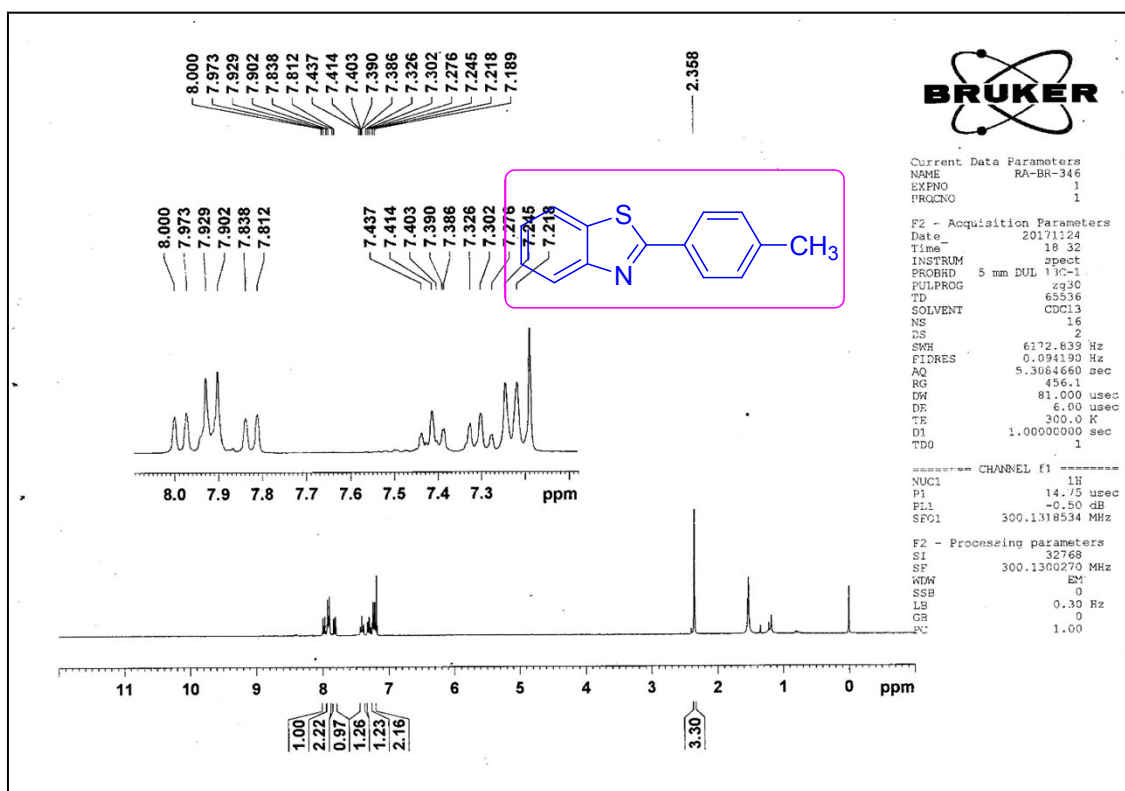
^1H & ^{13}C NMR (CDCl_3) spectra of compound 4j



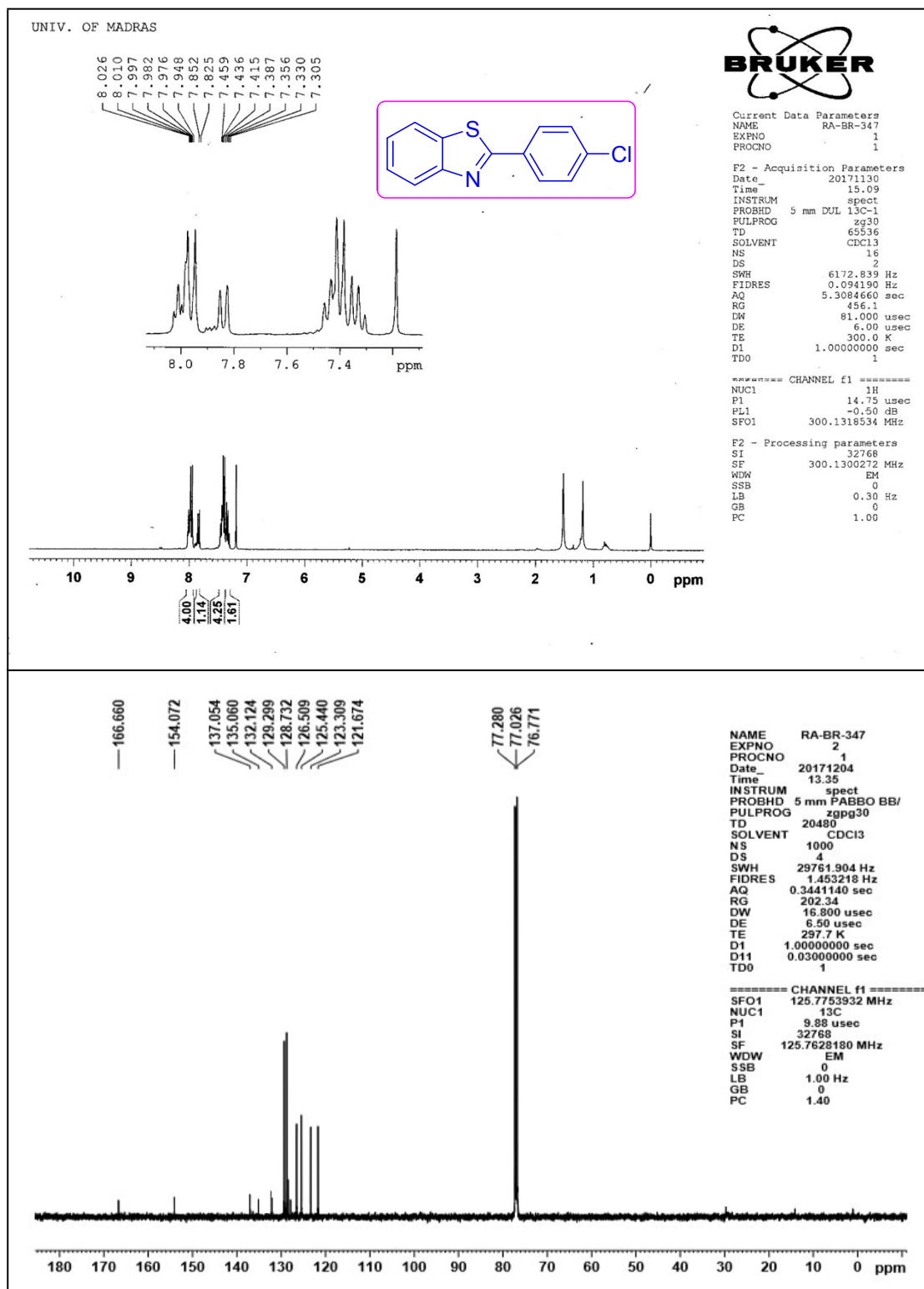
^1H & ^{13}C NMR (CDCl_3) spectra of compound 5a



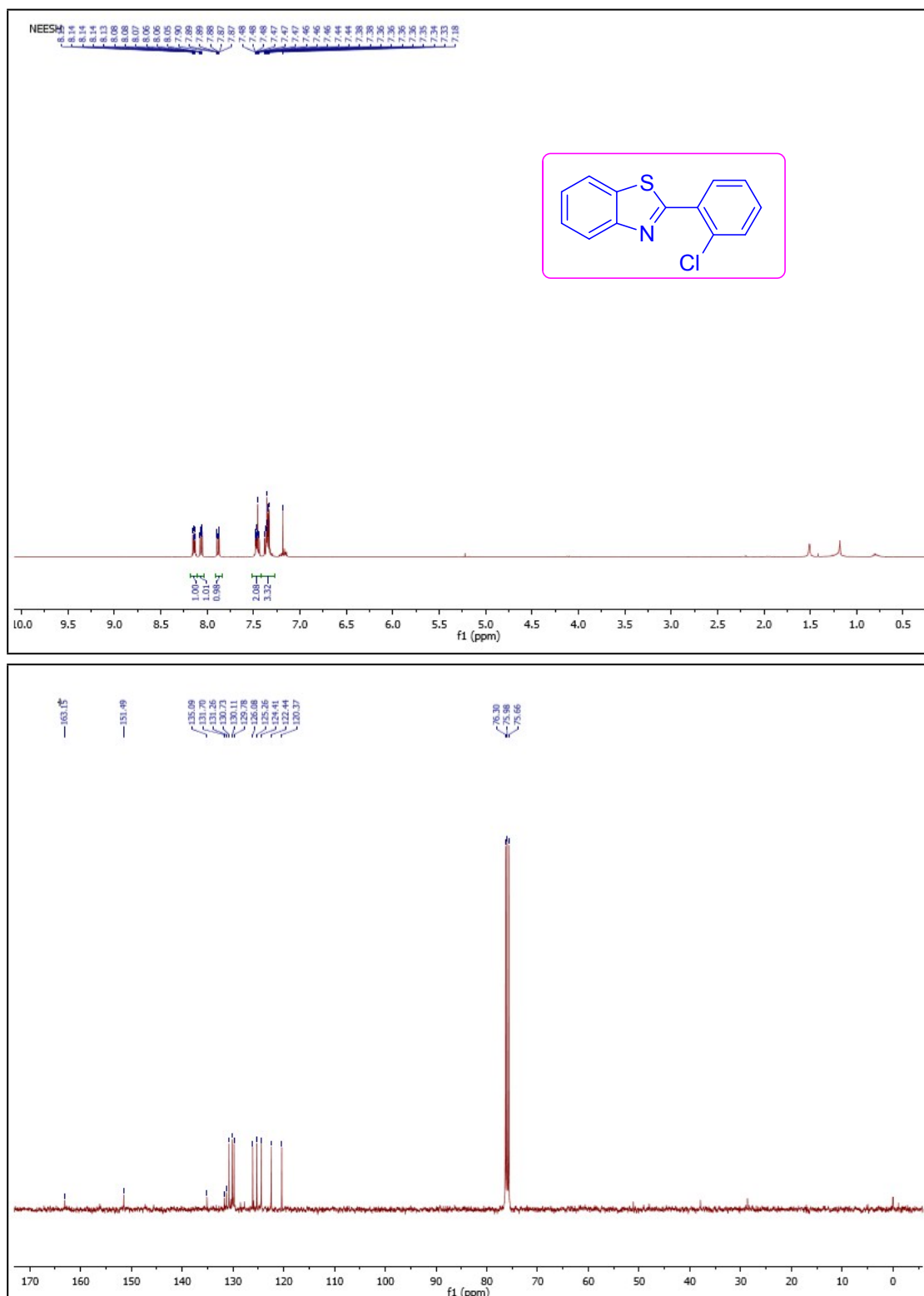
HRMS spectrum of compound 5a



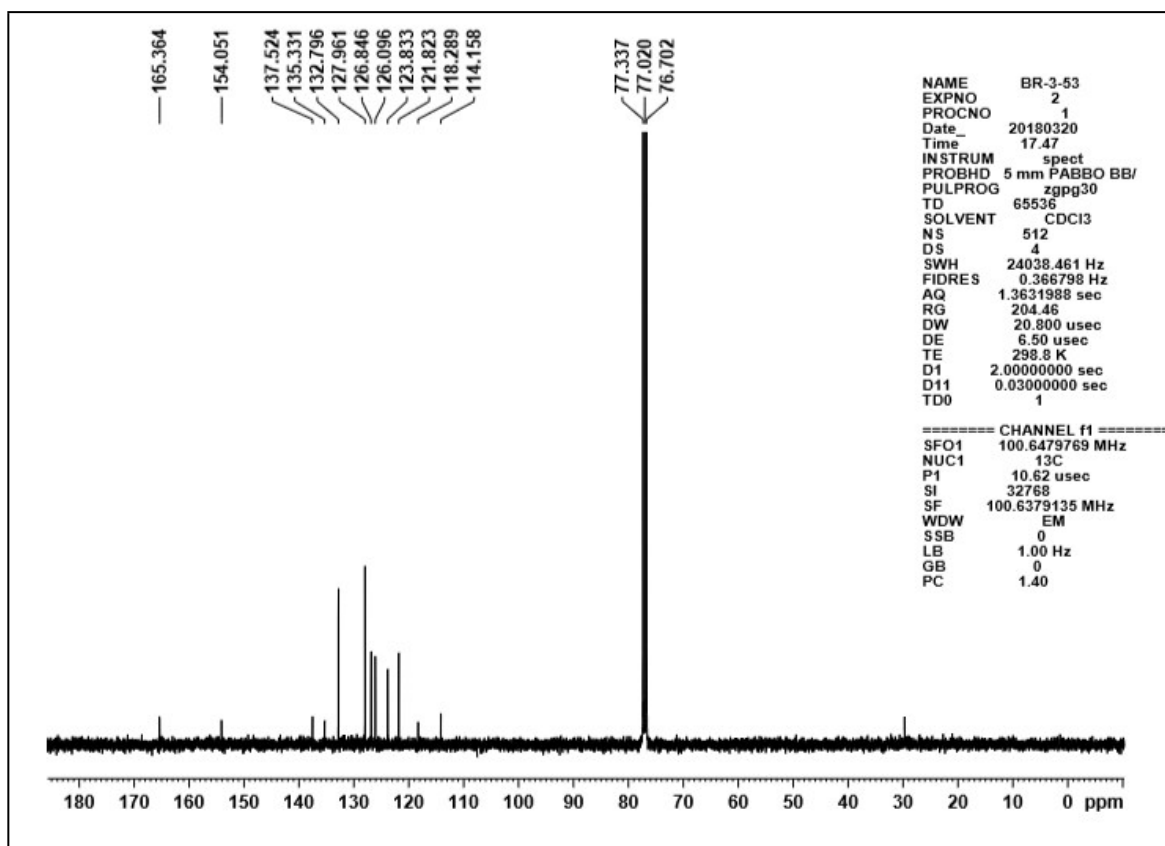
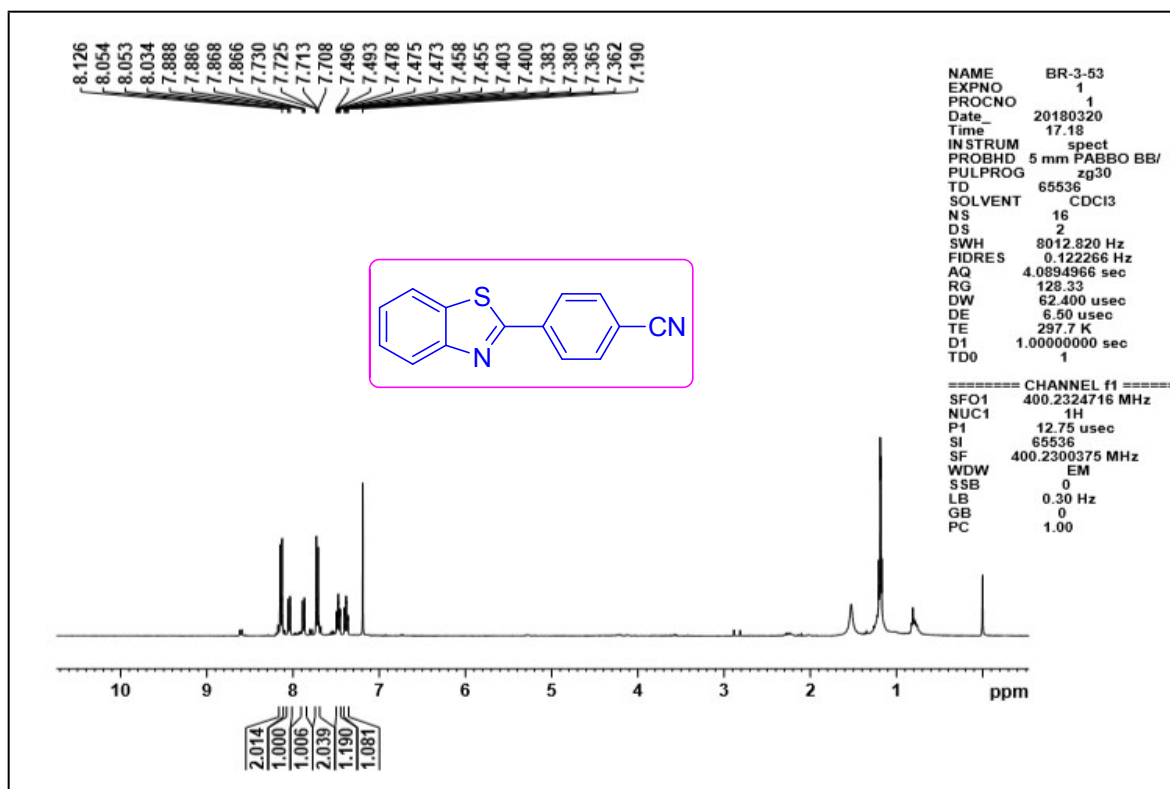
¹H & ¹³C NMR (CDCl₃) spectra of compound 5b



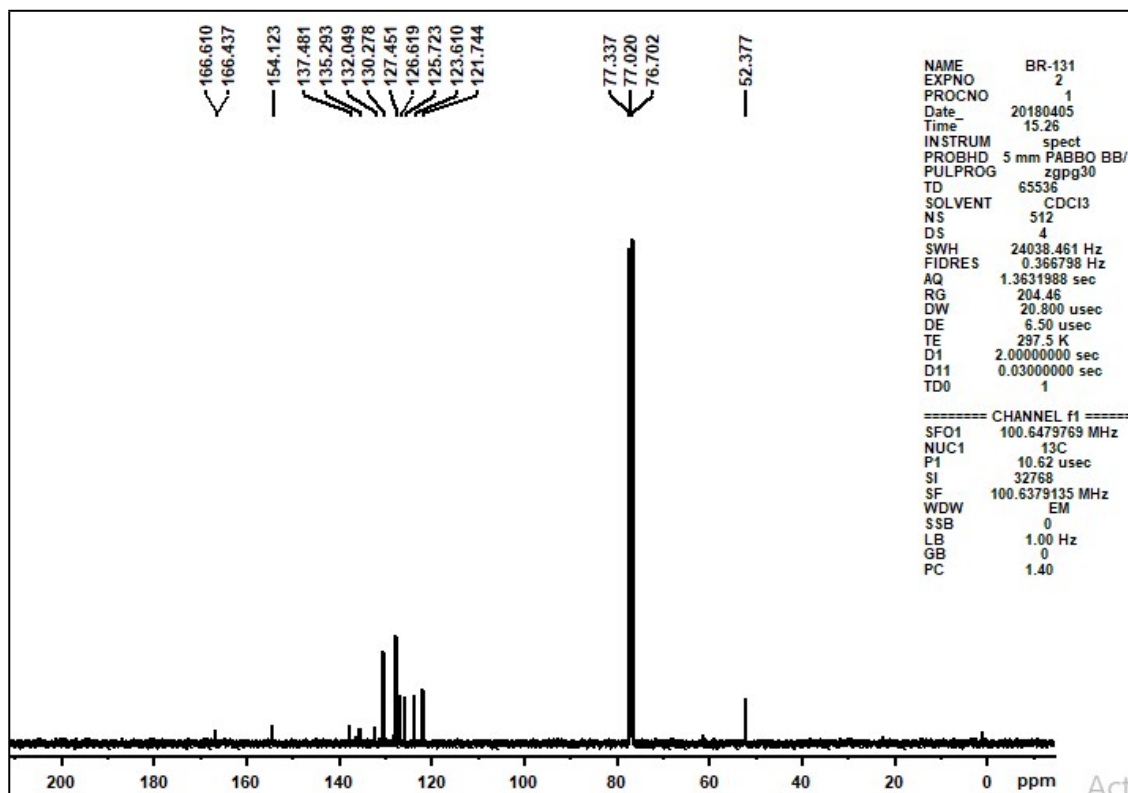
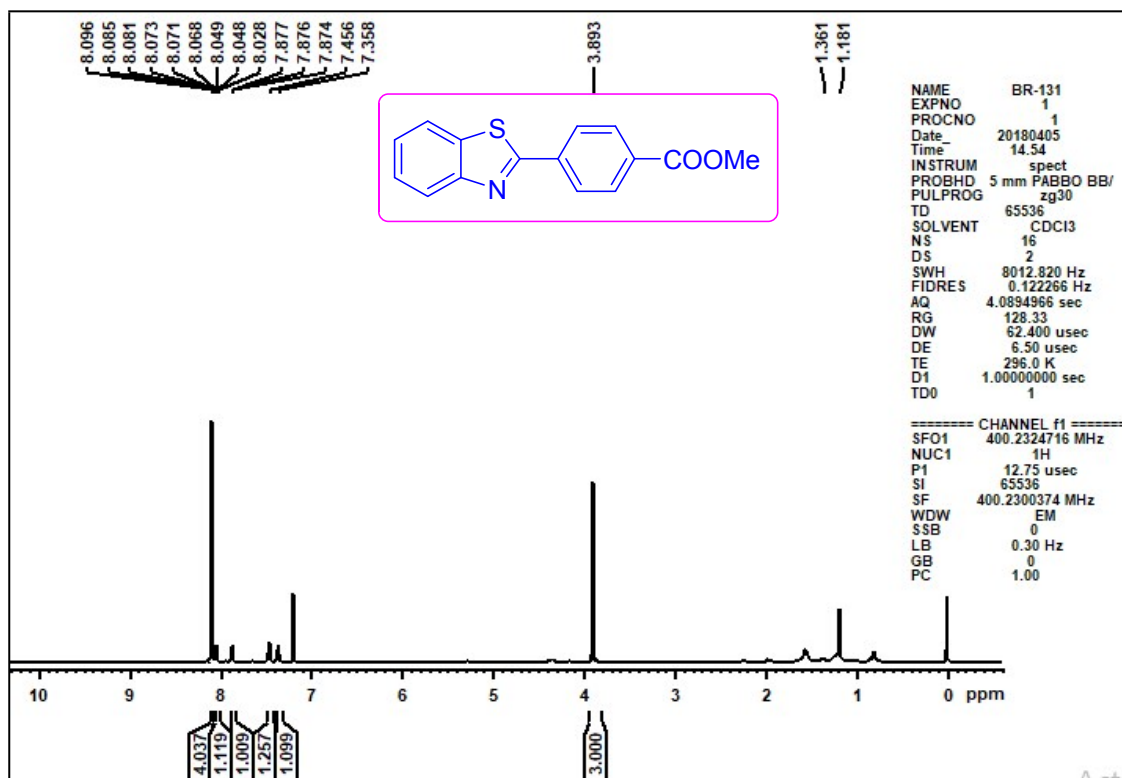
¹H & ¹³C NMR (CDCl₃) spectra of compound 5e



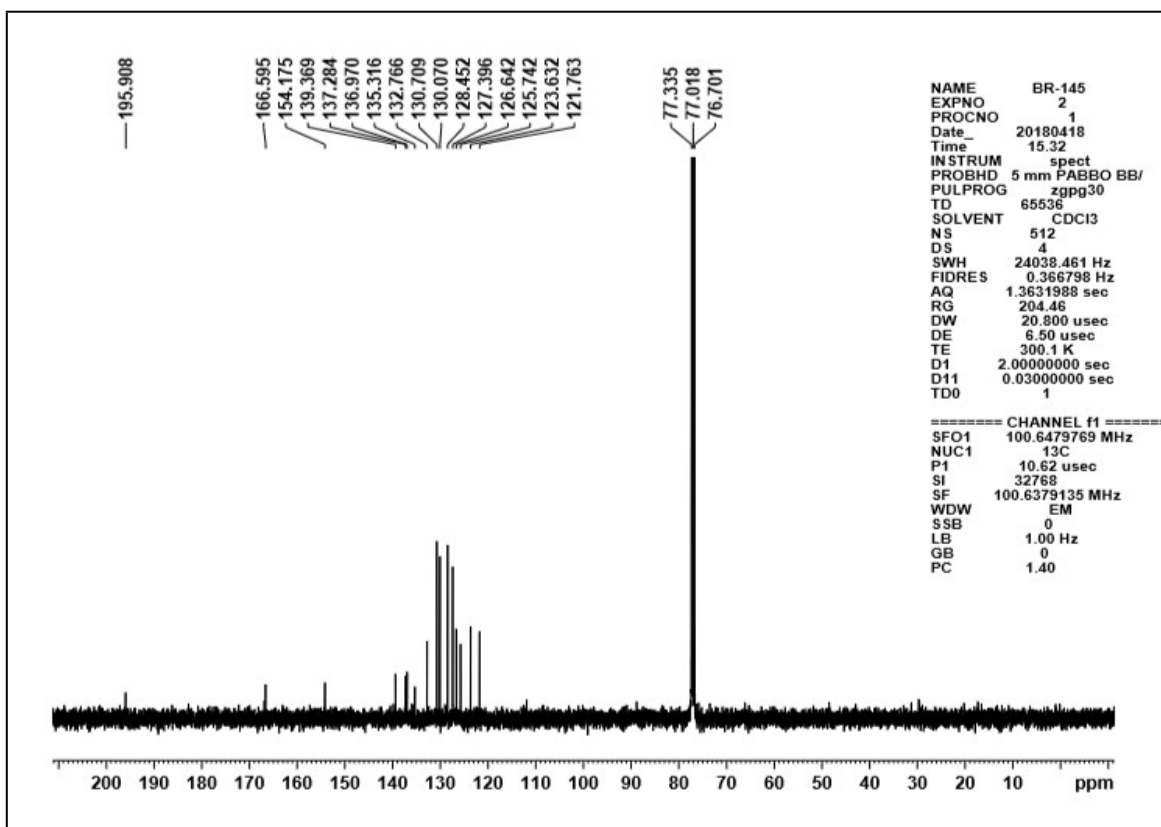
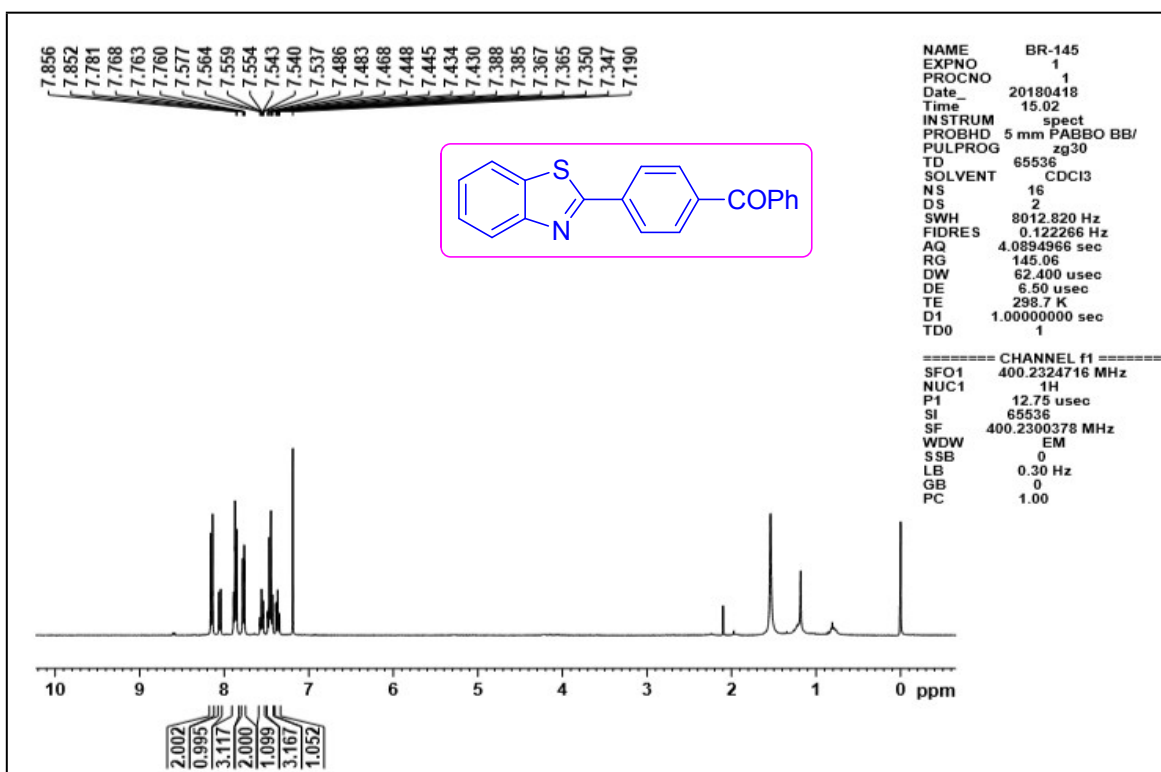
¹H & ¹³C NMR (CDCl₃) spectra of compound 5f



¹H & ¹³C NMR (CDCl₃) spectra of compound 5h



¹H & ¹³C NMR (CDCl₃) spectra of compound 5i

¹H

&¹³C NMR (CDCl₃) spectra of compound 5j

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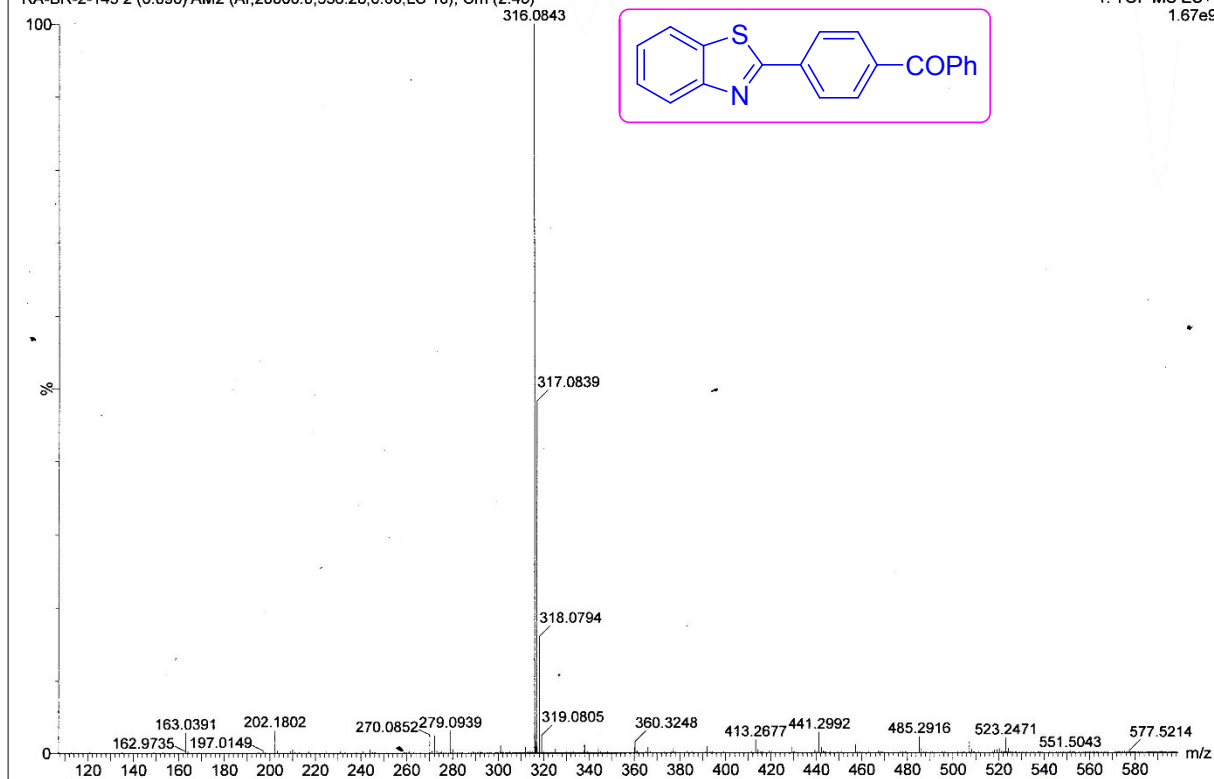
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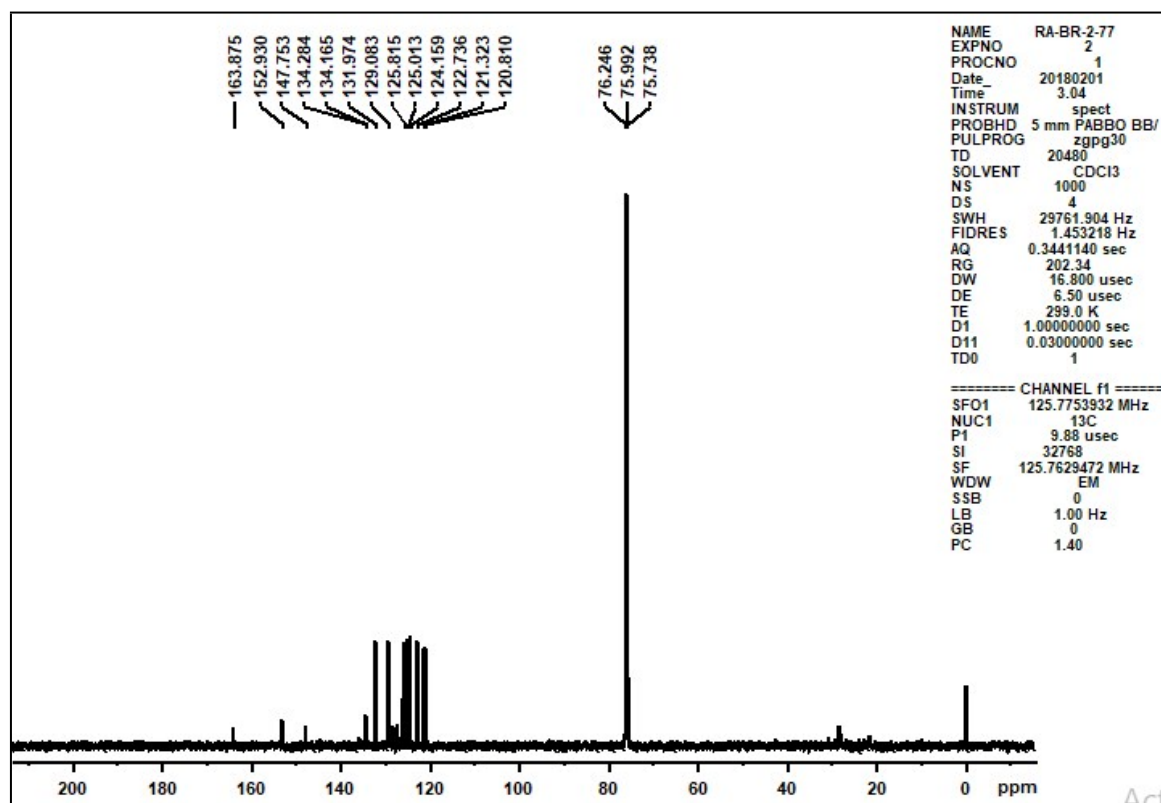
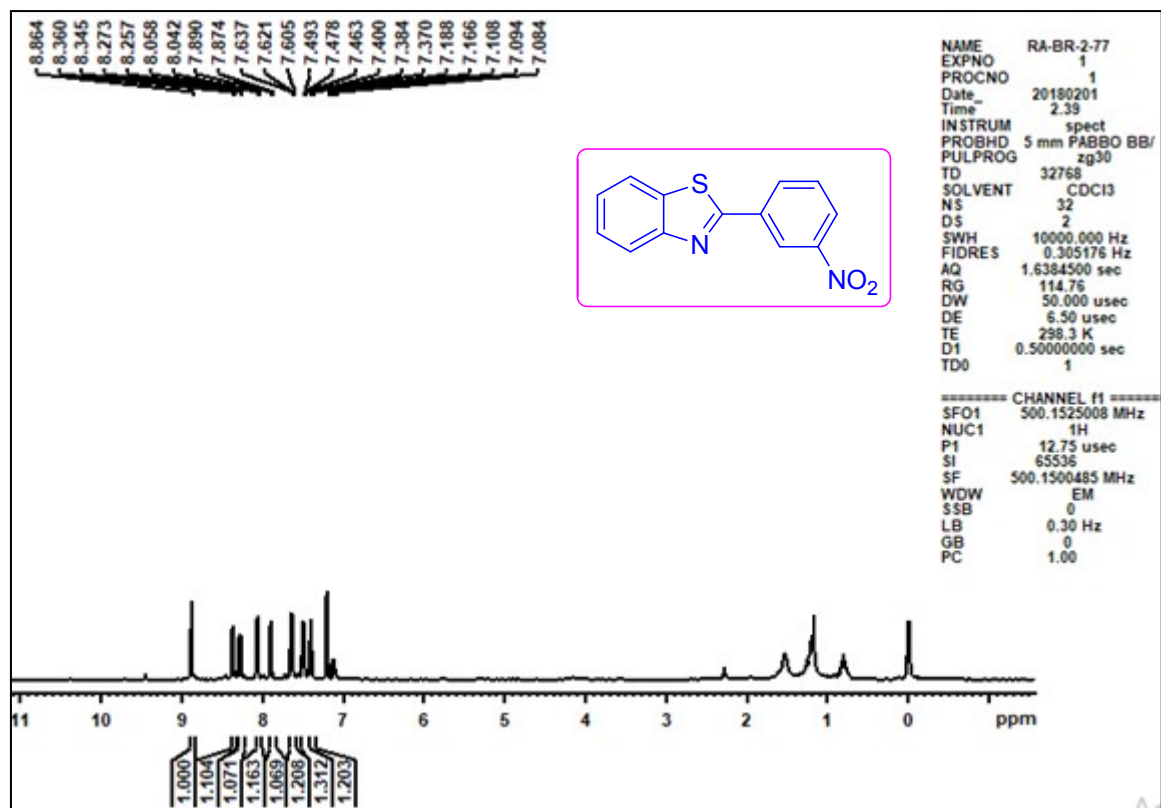
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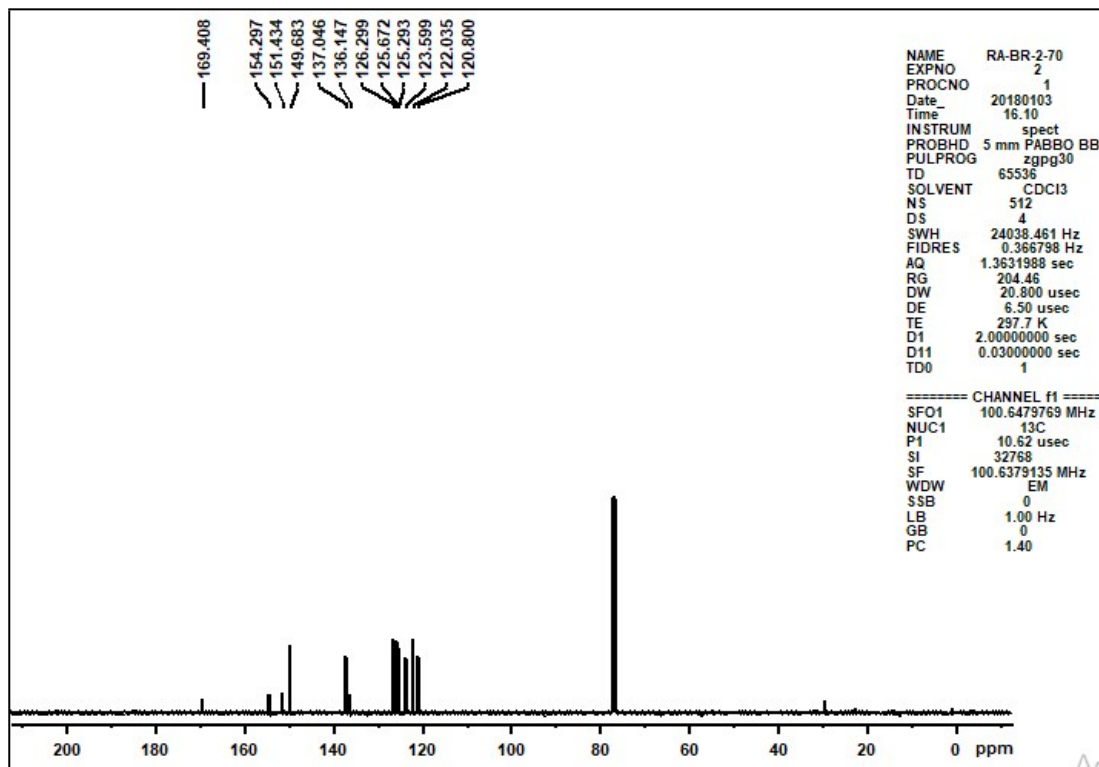
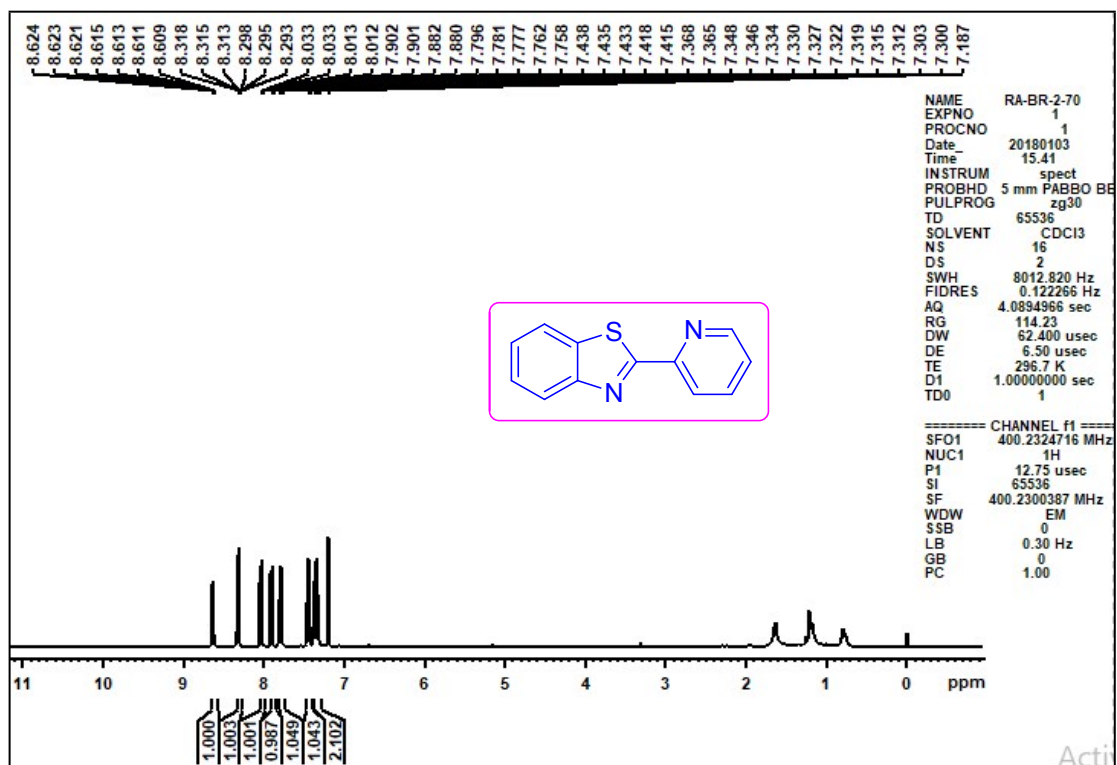
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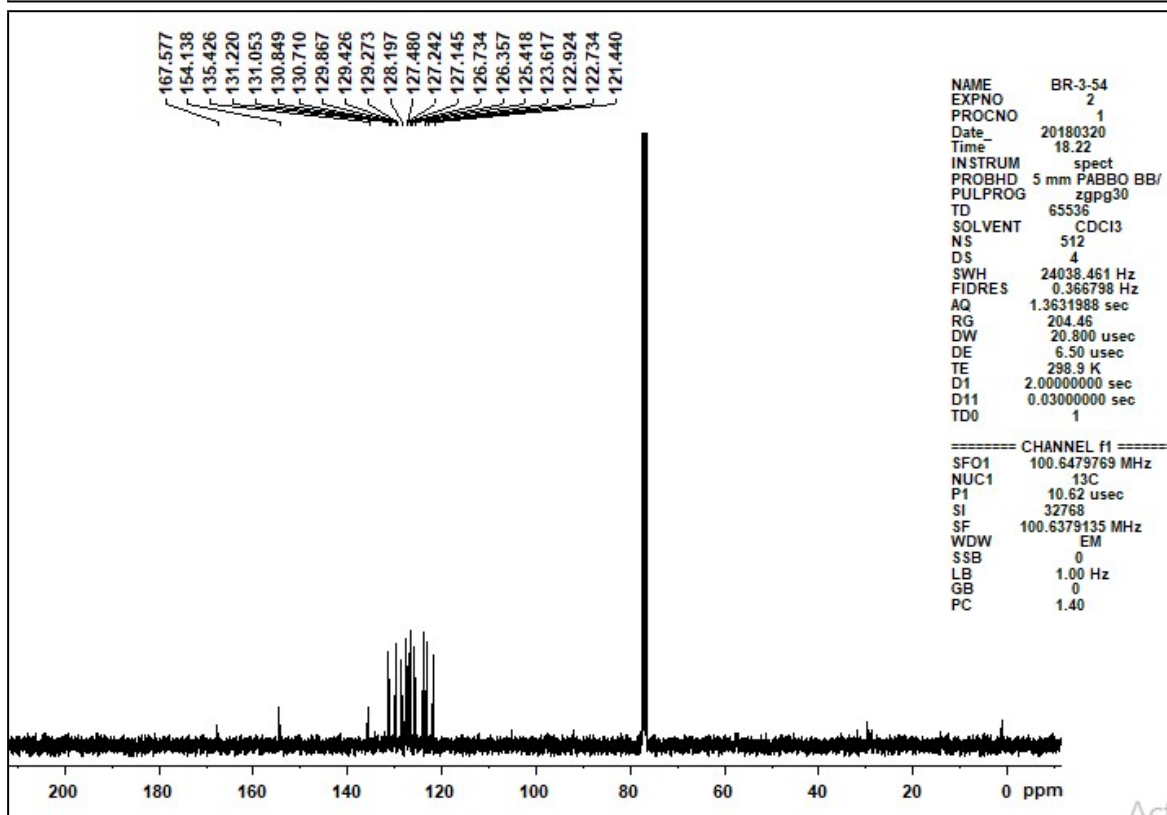
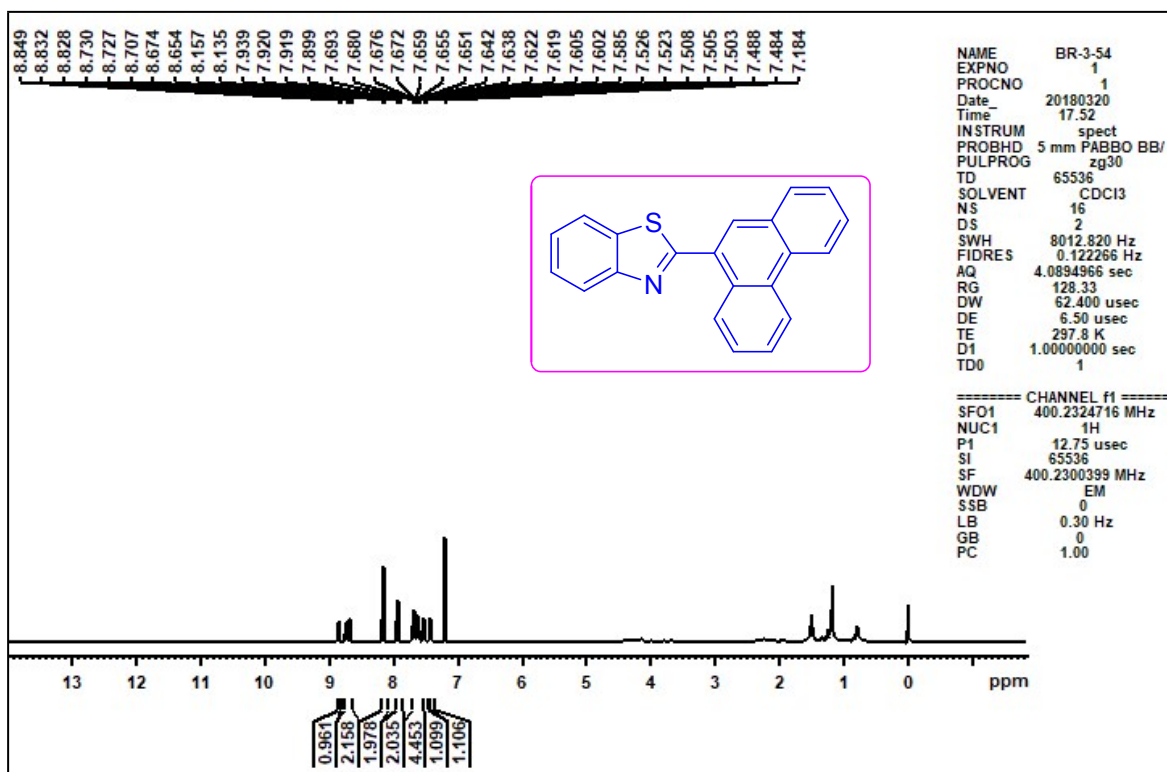
HRMS spectrum of compound 5j



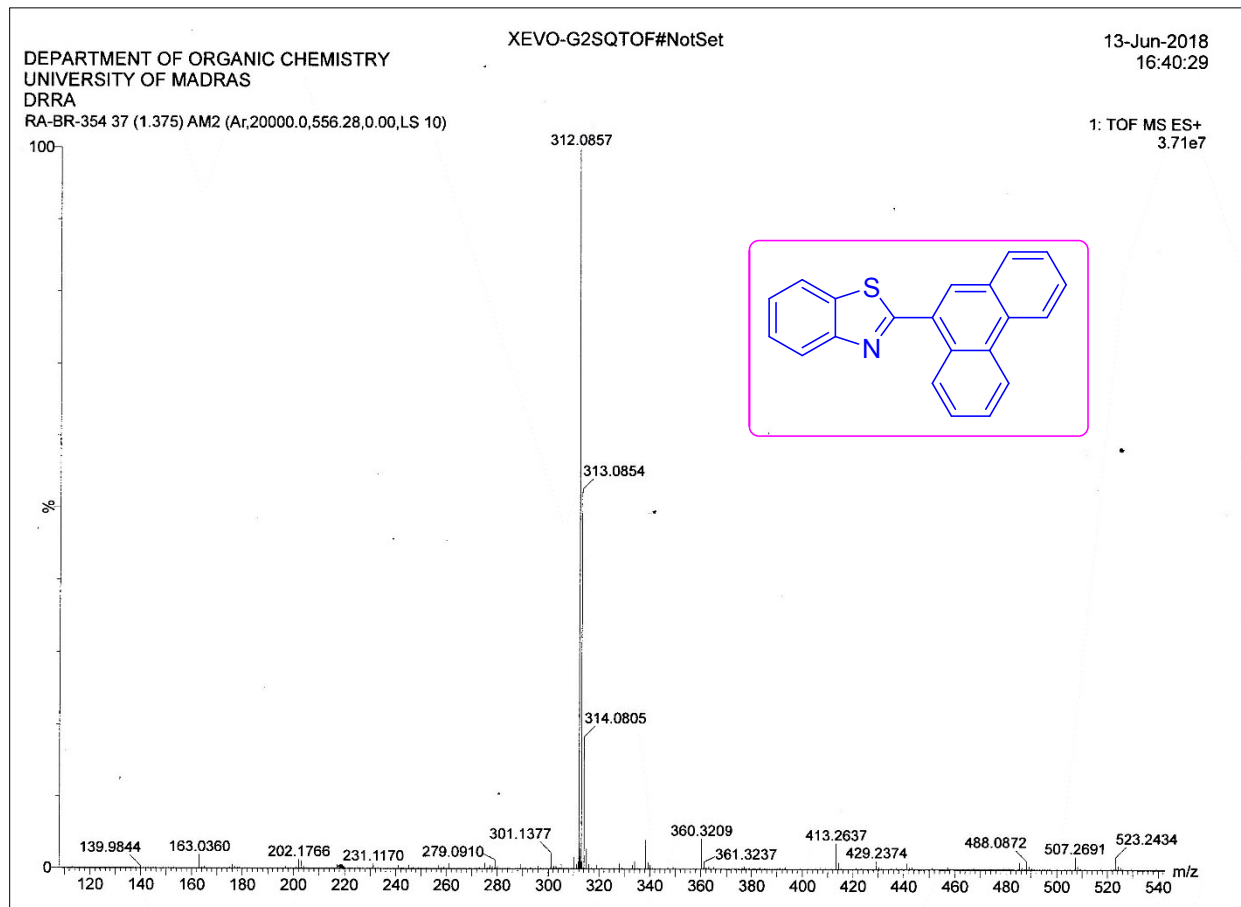
¹H & ¹³C NMR (CDCl₃) spectra of compound 5k



¹H & ¹³C NMR (CDCl₃) spectra of compound 5l



¹H & ¹³C NMR (CDCl₃) spectra of compound 5n



HRMS spectrum of compound 5n