

Supporting Information

Org. Commun. 16:4 (2023) 175-186

Water extract of onion: chemoselective synthesis of 2-substituted benzimidazole derivatives

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S1: Preparation and Standardization of Onion Extract¹

Two gram of cut pieces of onion were taken into 100 mL clean beaker. To this 10 mL of Milli-Q water was added and stirred for half an hour. The stirred suspension was allowed to stand for 10 min. followed by filtration. The filtrate was used as a catalyst and stored in refrigerator. The strength of the onion extract is 0.0034 N, which is determined by using acid-base titrations and the pH of the catalyst is 3.6. The strength and pH of the catalyst were examined periodically over the month and found to be consistent.

The main constituent of onion is 1-propenylcysteine sulfoxide (isoalliin, an alkylated cysteine sulfoxide) (Figure 1), when cutting the onion, isoalliin undergoes a series of rapid reactions. The enzyme Alliinase, catalyzes the conversion of (E)-(prop-1-en-1-ylsulfanyl)alanine to (E)-1-propenesulphenic acid, which is then rearranged to the volatile and highly reactive lachrymatory factor (LF) (Z)-propanethial S-oxide,^{65,66} which on treatment with water to produce acetaldehyde, sulphuric acid and hydrogen sulfide.^{67,68}

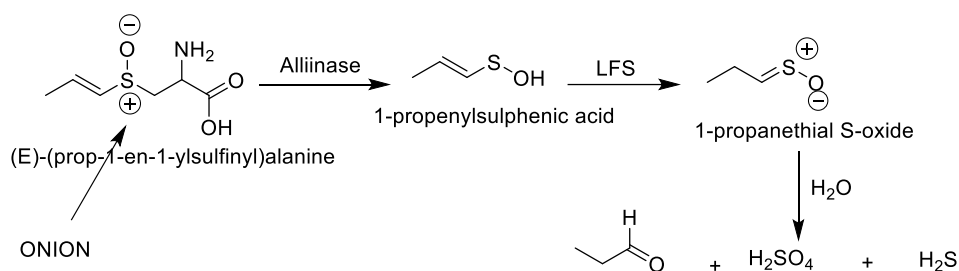


Figure S1: Metabolic pathway of onion

References

- [1] Prabakaran, K.; Sivakumar, M.; Perumal, M. S. A Simple, Efficient Green Protocol for the Synthesis of β -Enaminone and Enamino Ester Derivatives by Using Onion Extract as Green Catalyst. *ChemistrySelect*. **2017**, *2*, 2363-2372.
- [2] Thomson, S. J.; Rippon, P.; Butts, C.; Olsen, S.; Shaw, M.; Joyce, N. I.; Eady, C. C. Inhibition of platelet activation by lachrymatory factor synthase (LFS)-silenced (tearless) onion juice. *J. Agric. Food. Chem.* **2013**, *61*, 10574-10581.
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- [5] Eric B. The chemistry of garlic and onions. *Sci Am*, **1985**, *252*, 114-118.

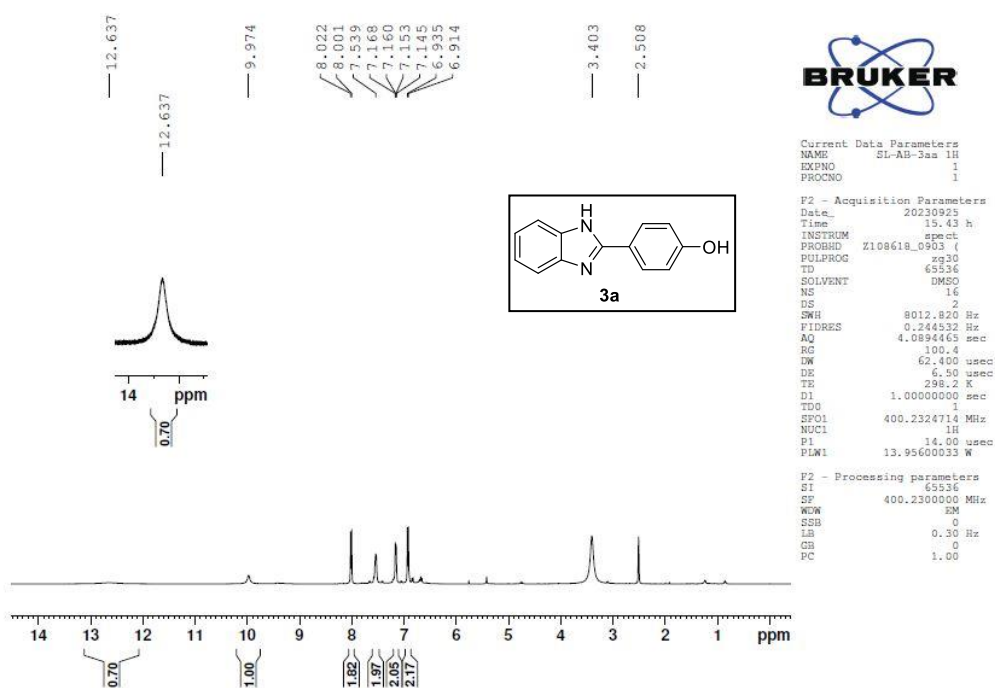


Figure S2: ¹H NMR (400 MHz, DMSO-*d*₆) Spectrum of compound **3a**

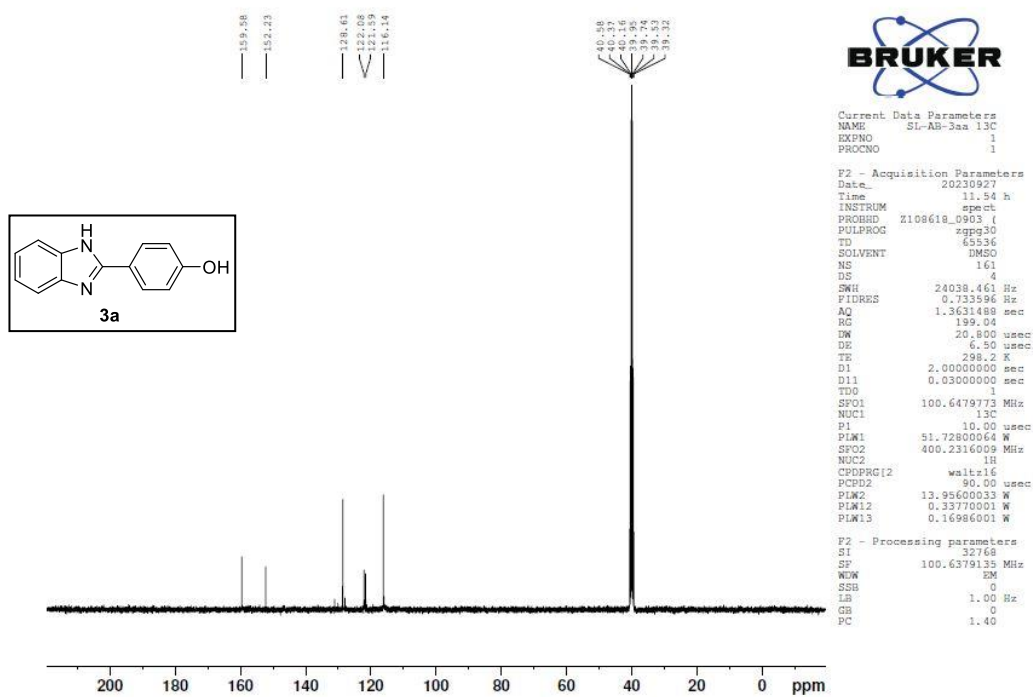


Figure S3: ¹³C NMR (100 MHz, DMSO-*d*₆) Spectrum of compound **3a**

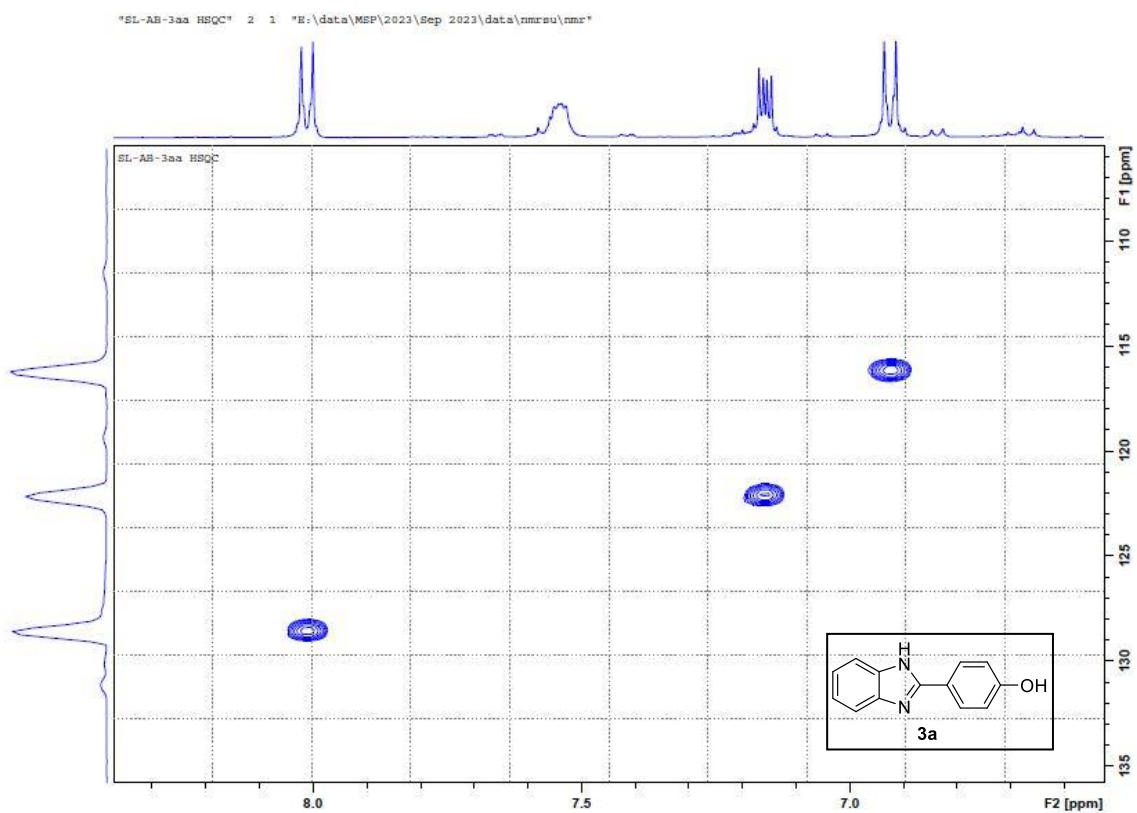
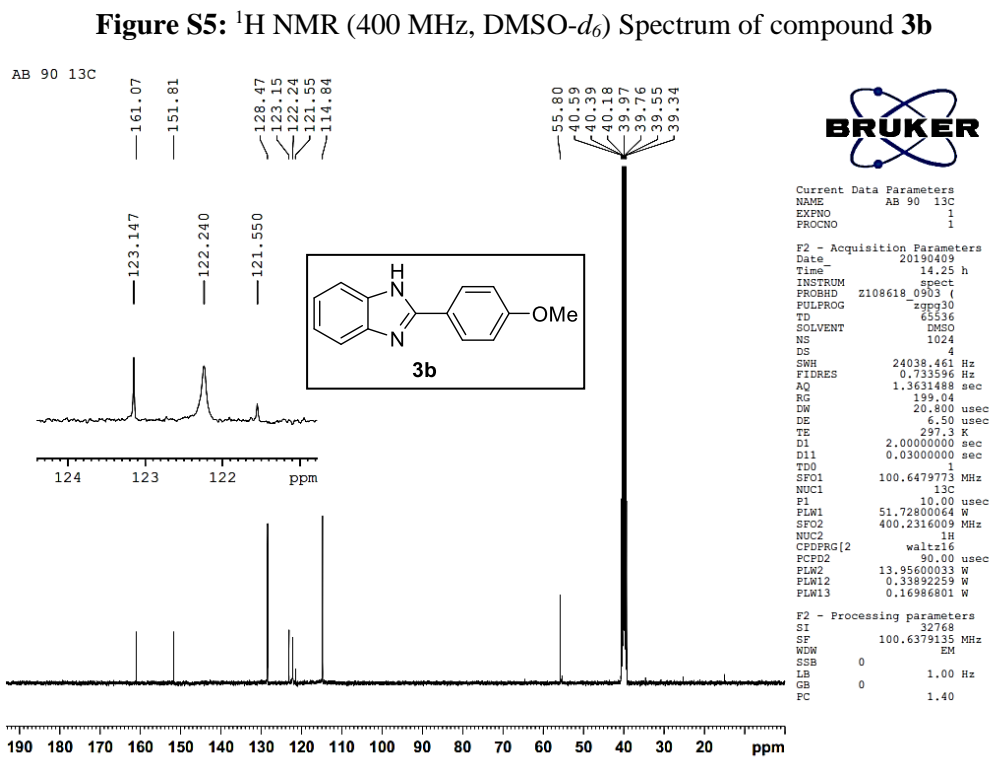
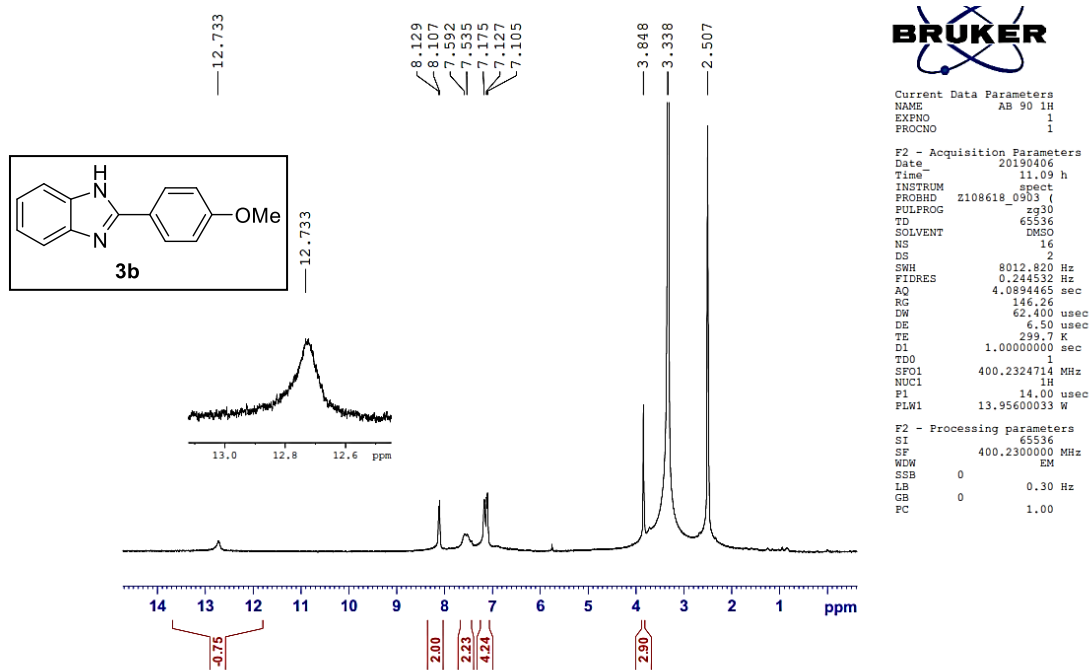


Figure S4: HSQC Spectrum of compound **3a**



P-321 #86 RT: 0.39 AV: 1 NL: 7.72E9
T: FTMS + p ESI Full ms [100.00-1500.00]

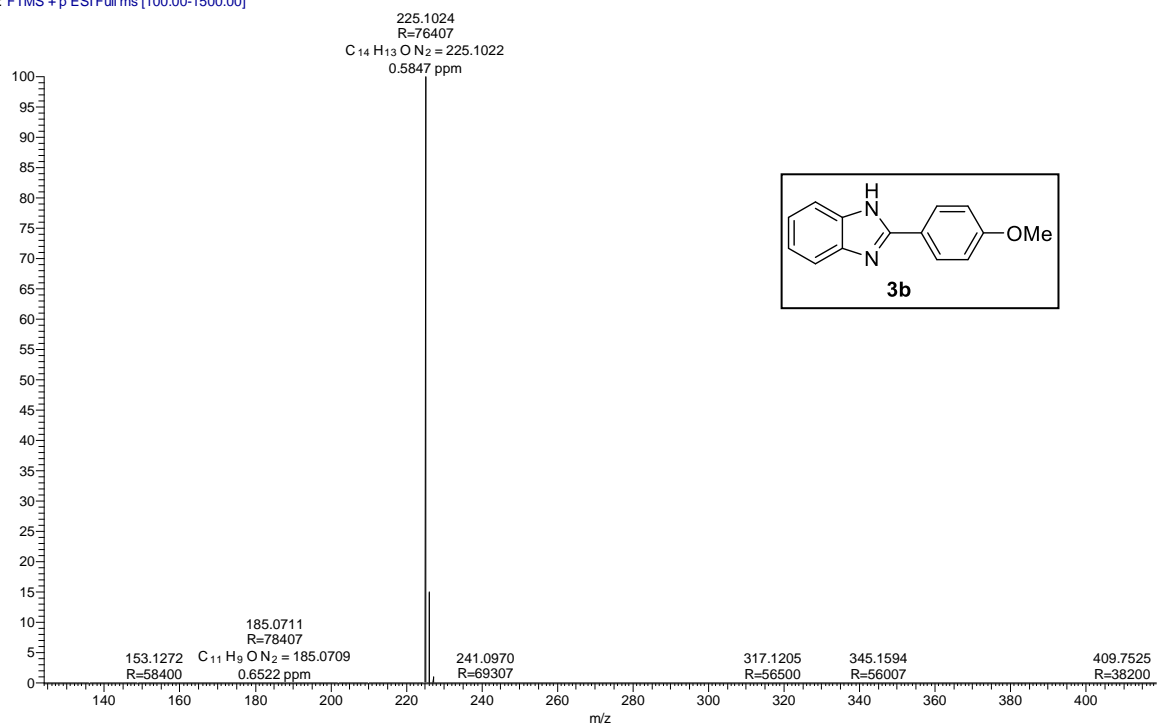


Figure S7: Mass Spectrum of compound **3b**

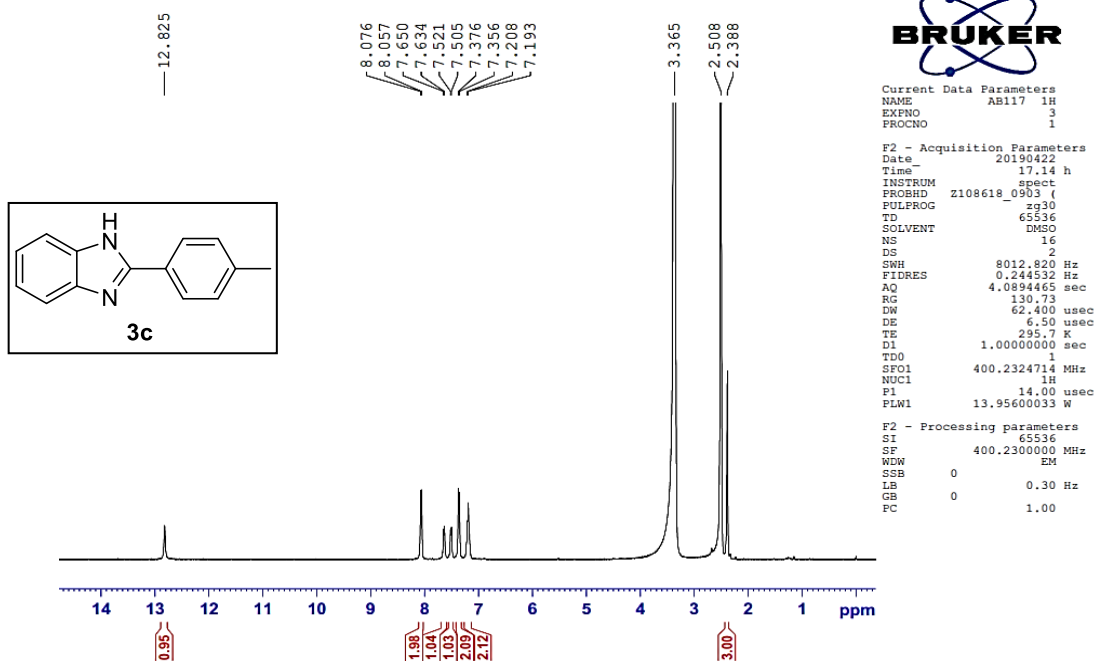


Figure S8: ¹H NMR (400 MHz, DMSO-*d*₆) Spectrum of compound 3c

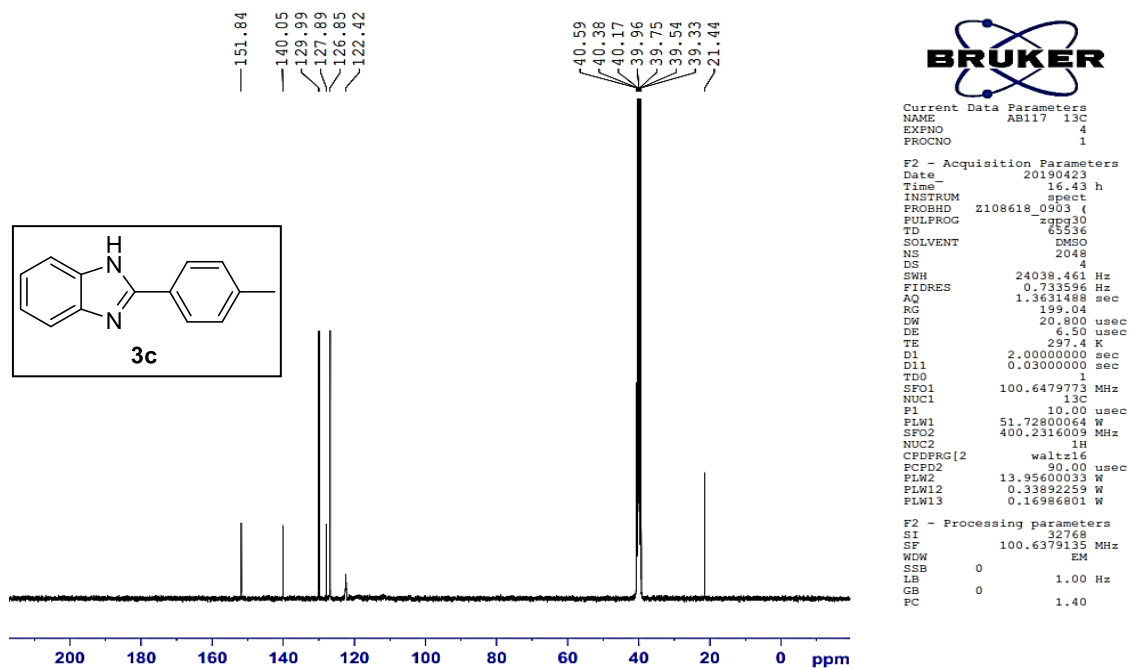


Figure S9: ¹³C NMR (100 MHz, DMSO-*d*₆) Spectrum of compound 3c

P-309 #107 RT: 0.48 AV: 1 NL: 1.96E10
T: FTMS + p ESI Full ms [100.00-1500.00]

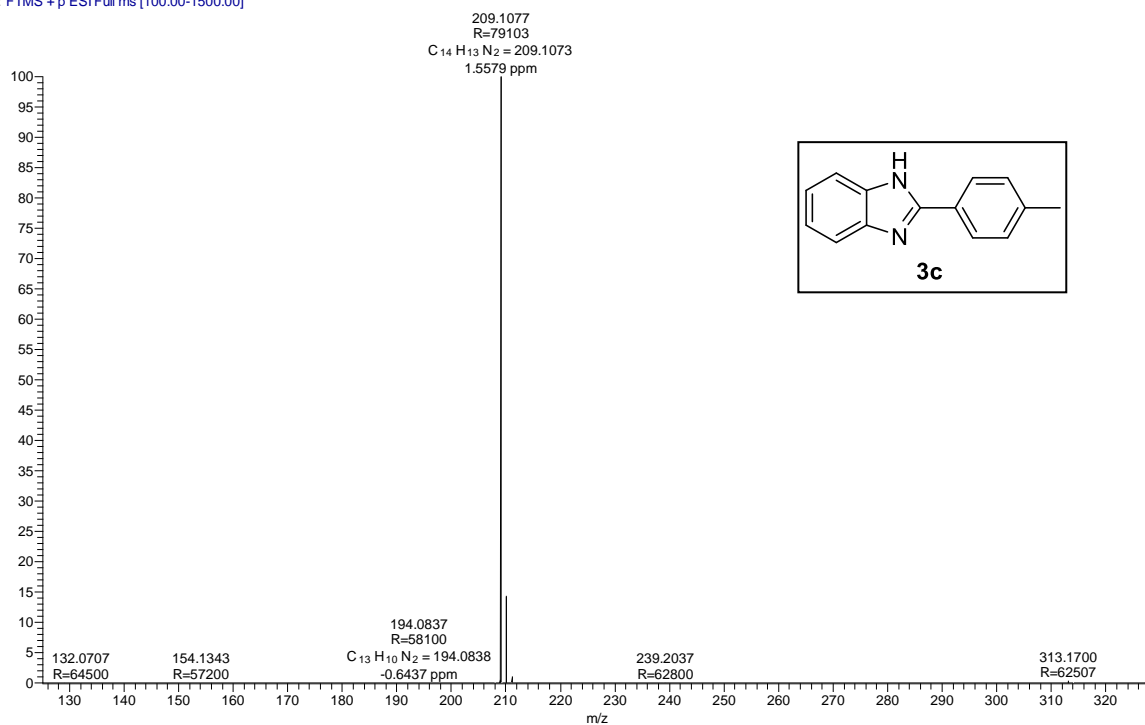


Figure S10: Mass Spectrum of compound **3c**

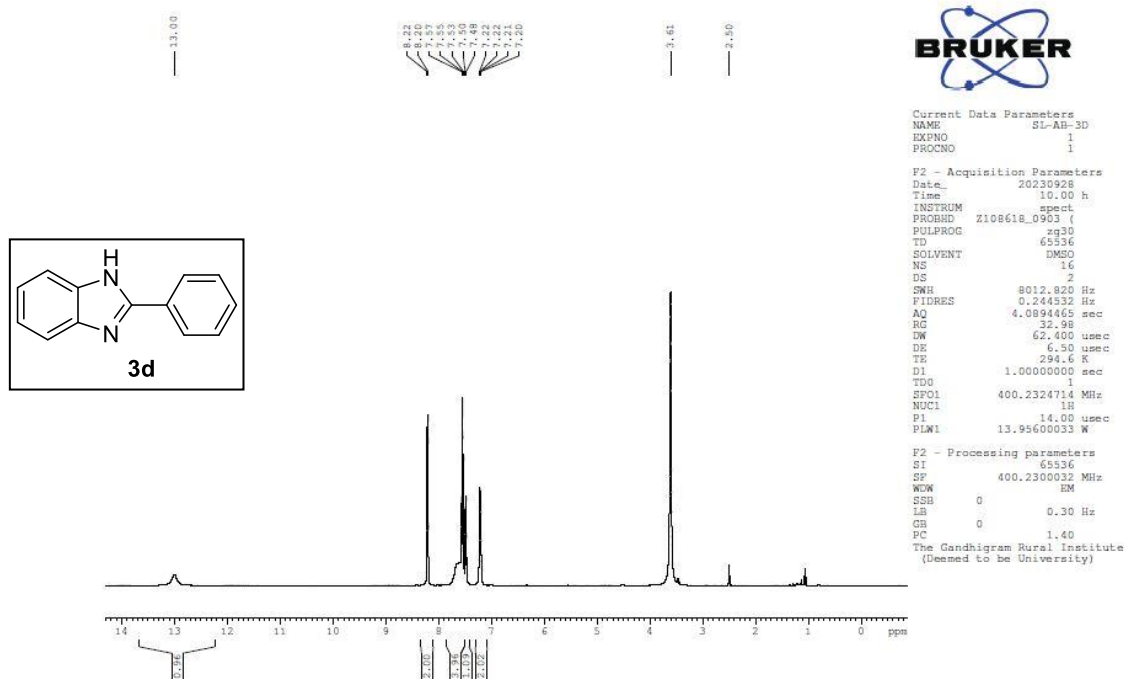


Figure S11: ^1H NMR (400 MHz, $\text{DMSO-}d_6$) Spectrum of compound **3d**

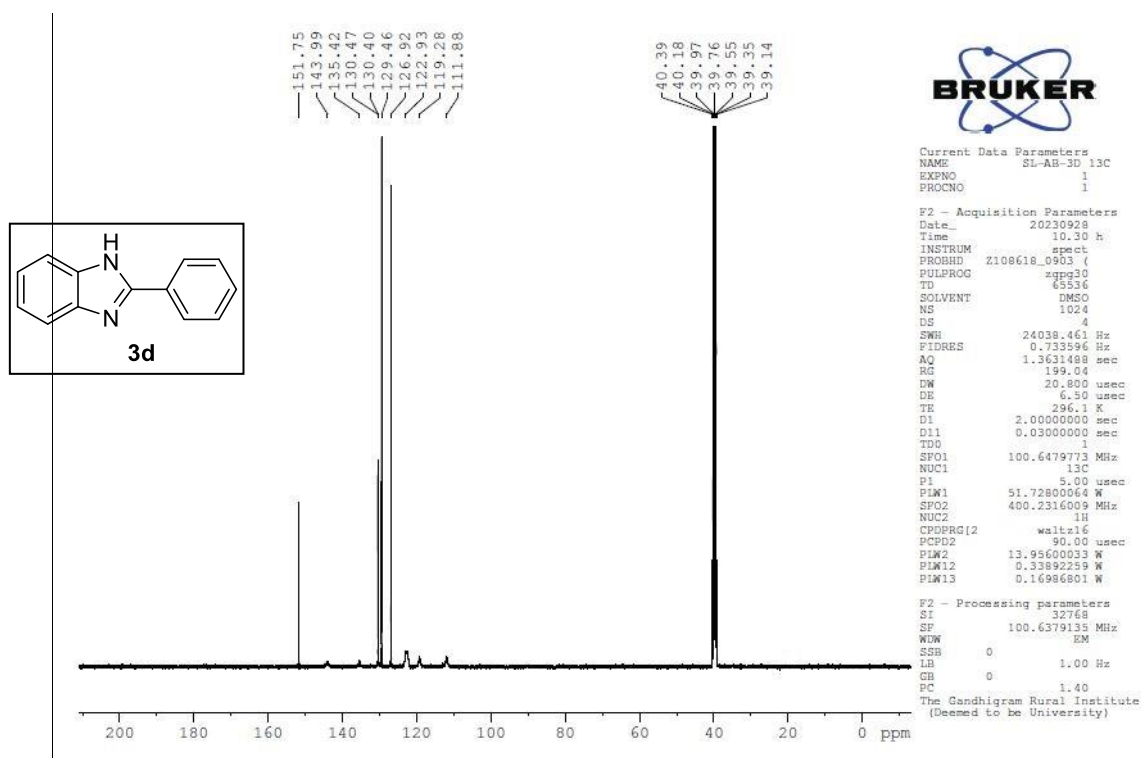


Figure S12: ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) Spectrum of compound **3d**

KP-322 #118 RT: 0.52 AV: 1 NL: 3.85E9
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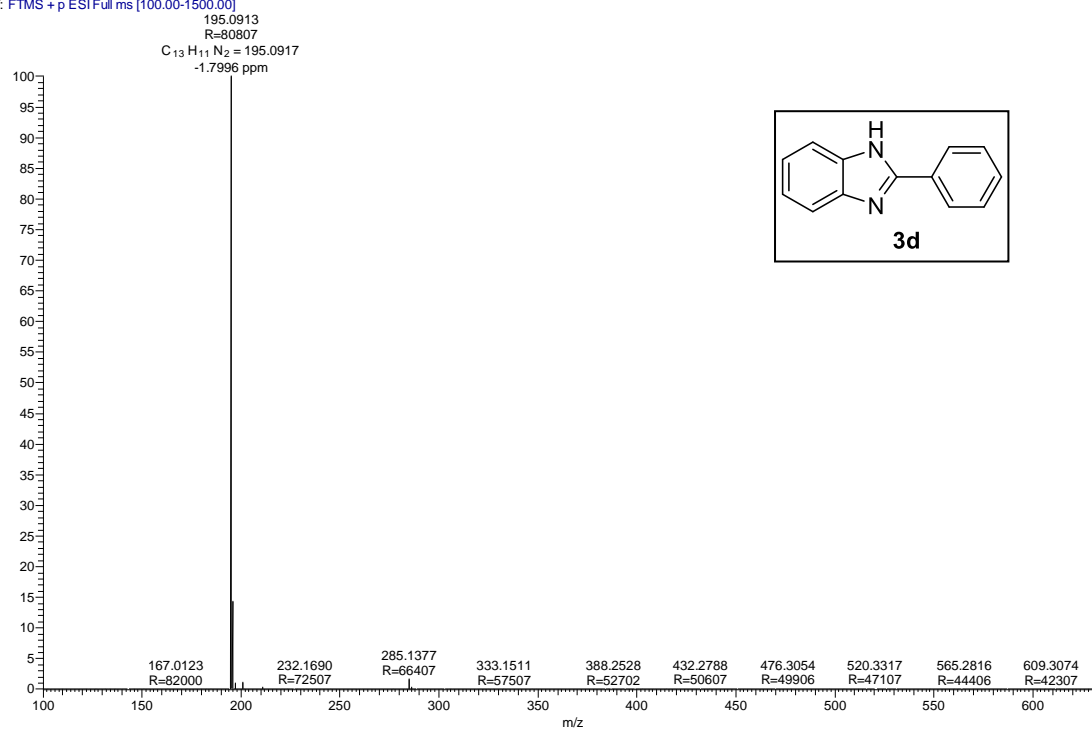
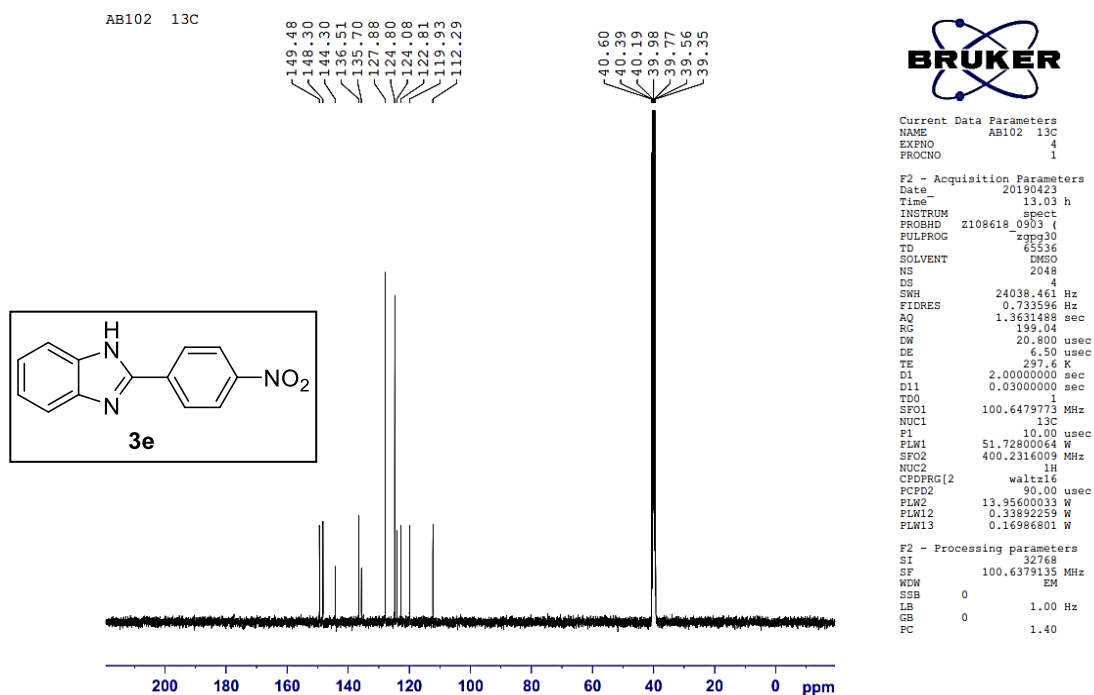
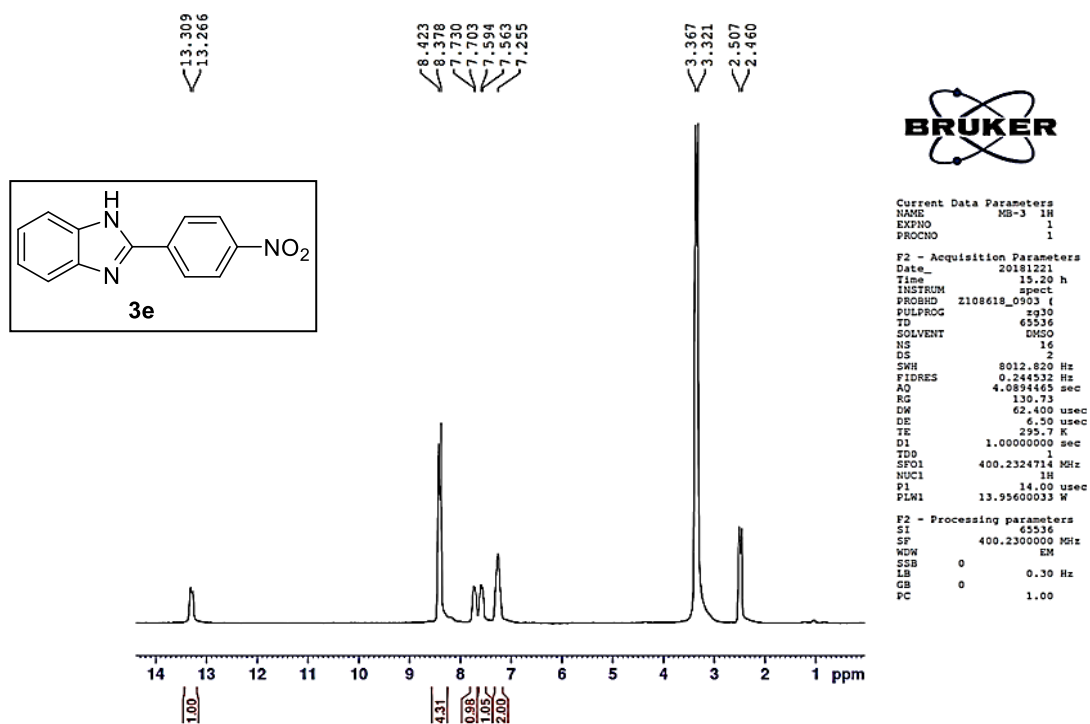


Figure S13: Mass Spectrum of compound **3d**



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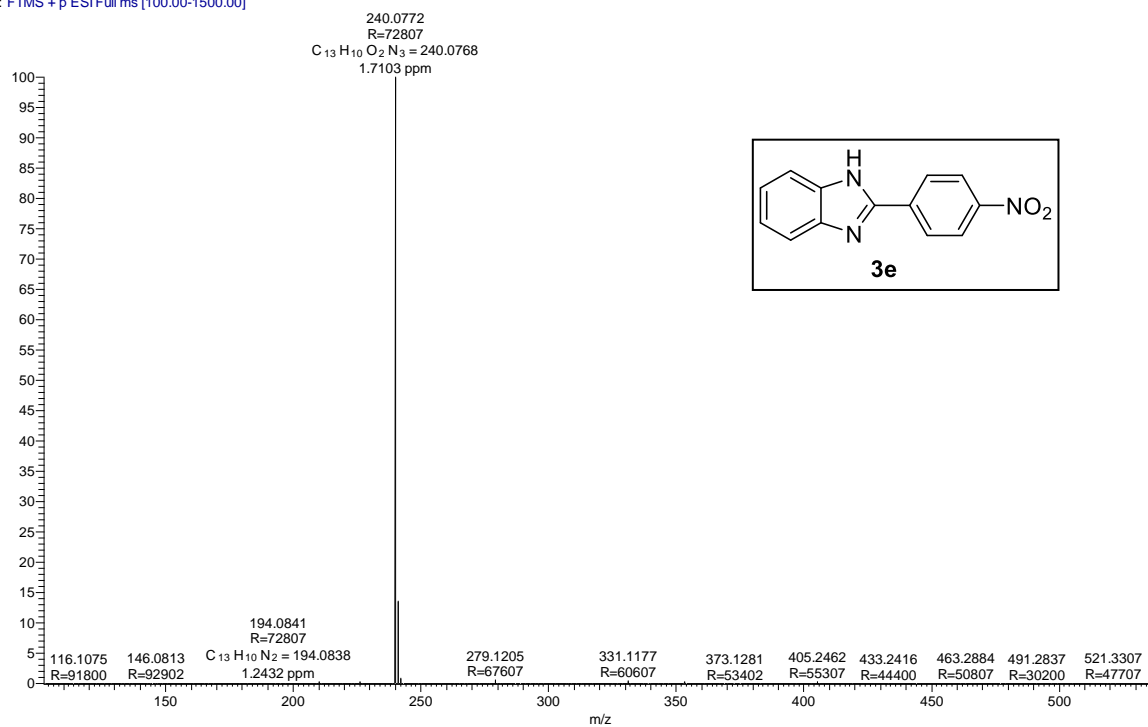


Figure S16: Mass Spectrum of compound **3e**

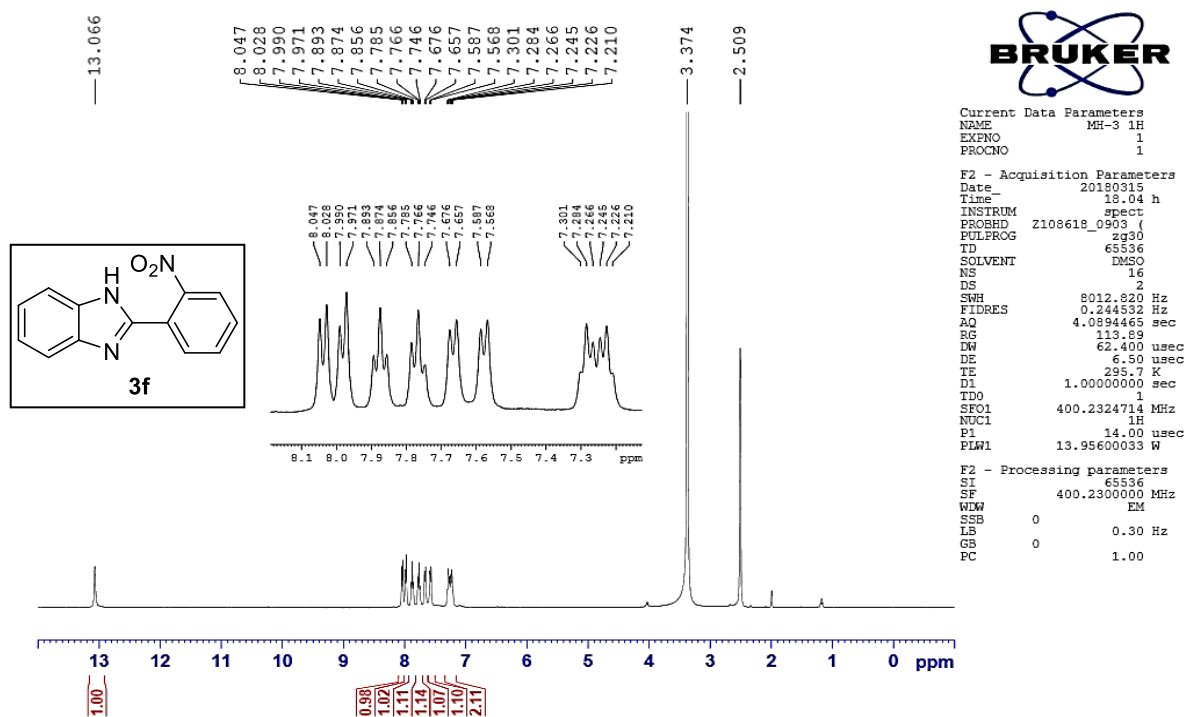


Figure S17: ¹H NMR (400 MHz, DMSO-*d*₆) Spectrum of compound 3f

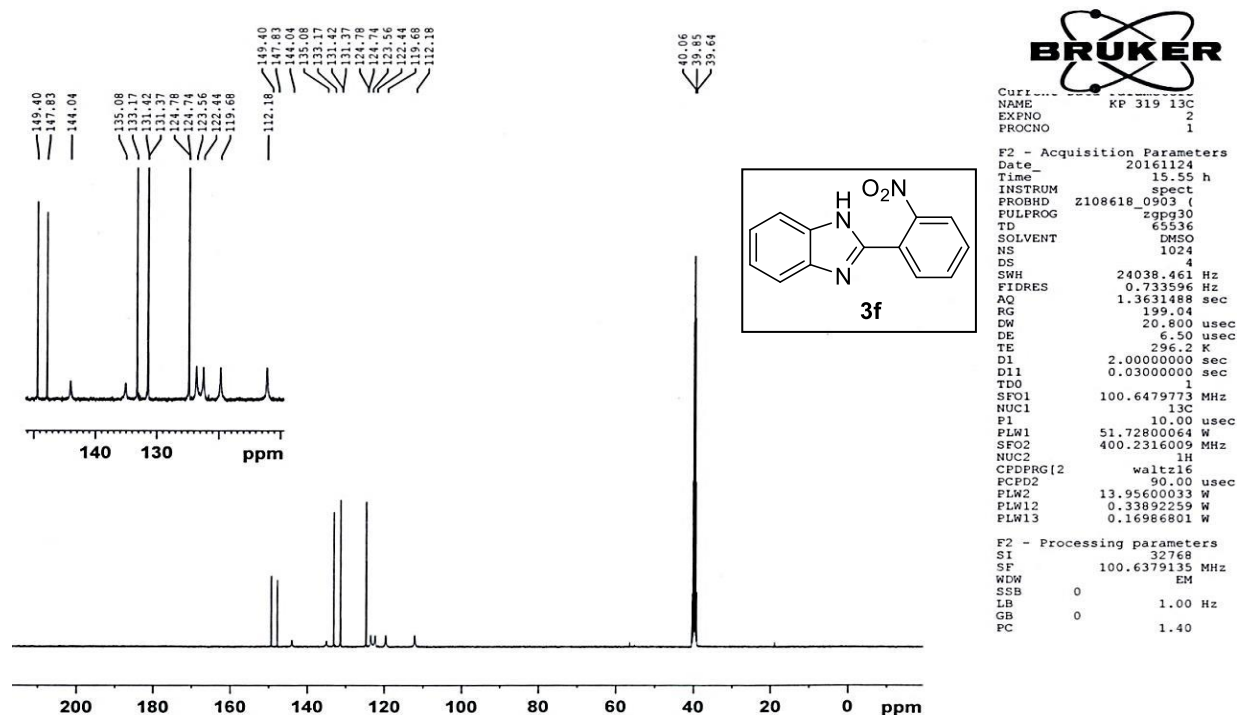


Figure S18: ¹³C NMR (100 MHz, DMSO-*d*₆) Spectrum of compound 3f

P-319 #127 RT: 0.56 AV: 1 NL: 1.32E9
T: FTMS + p ESI Full ms [100.00-1500.00]

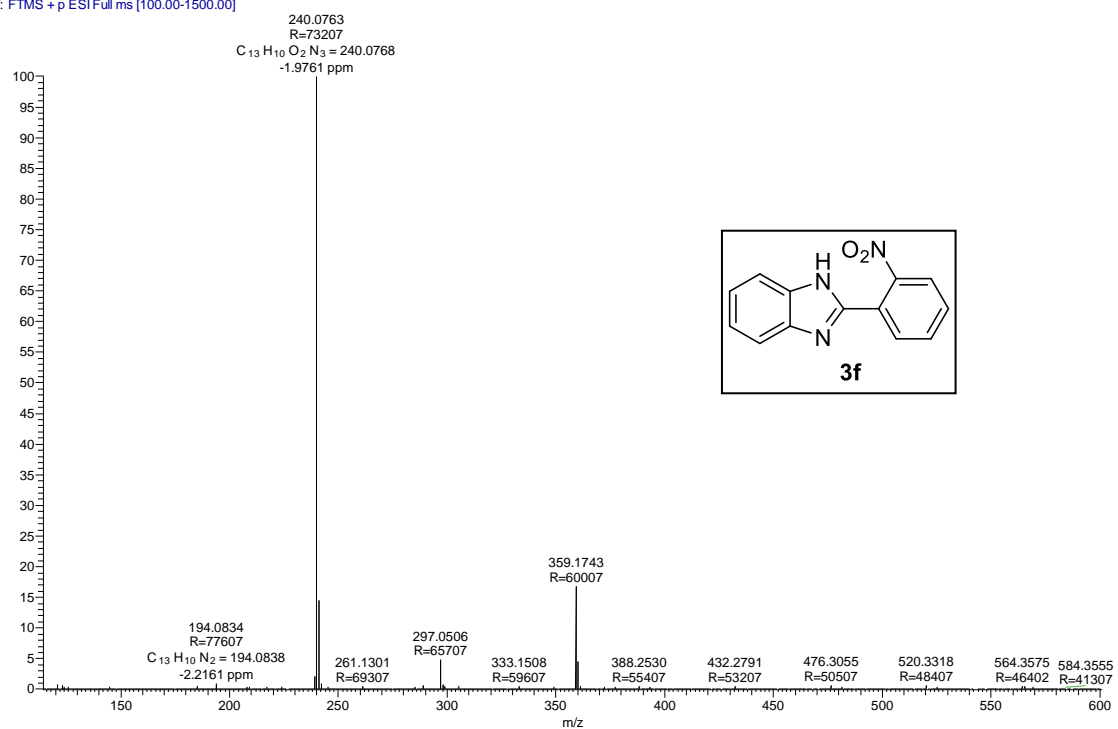


Figure S19: Mass Spectrum of compound **3f**

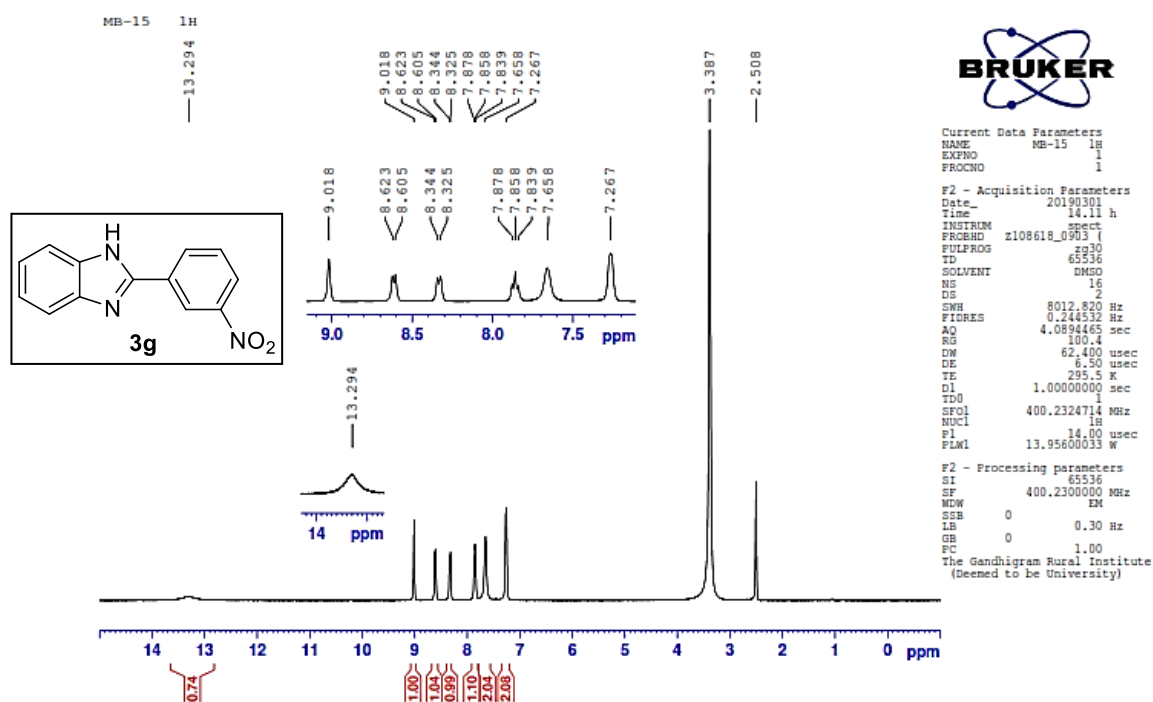


Figure S20: ^1H NMR (400 MHz, $\text{DMSO-}d_6$) Spectrum of compound **3g**

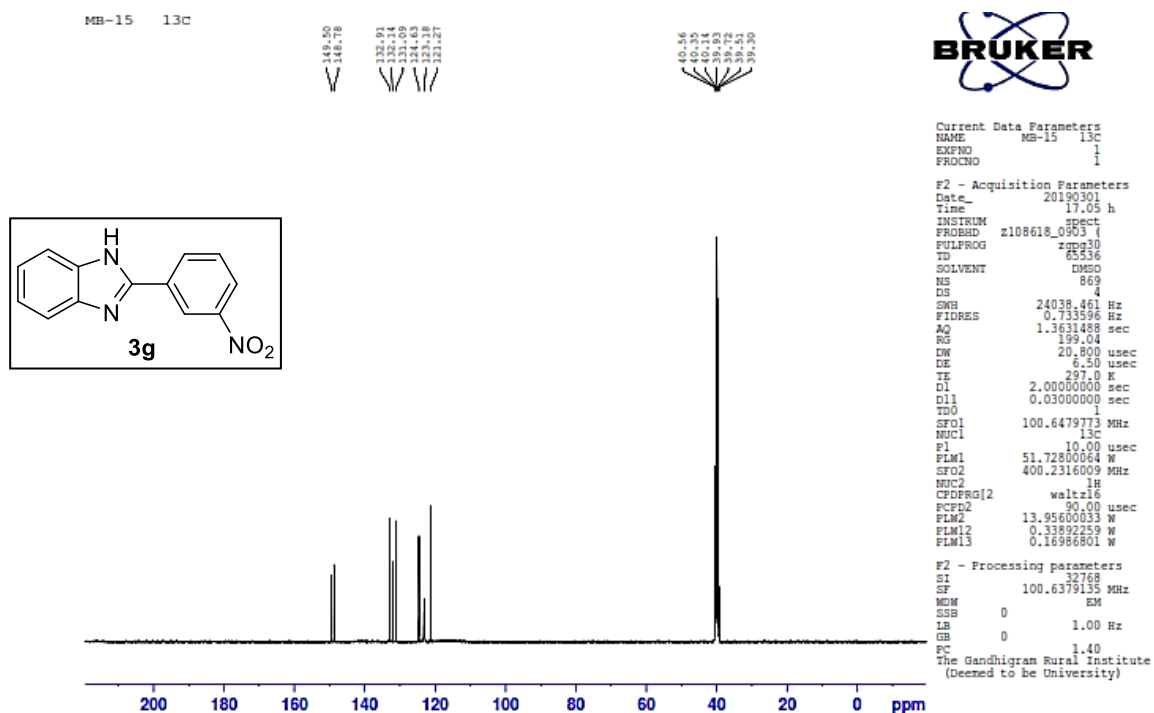


Figure S21: ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) Spectrum of compound **3g**

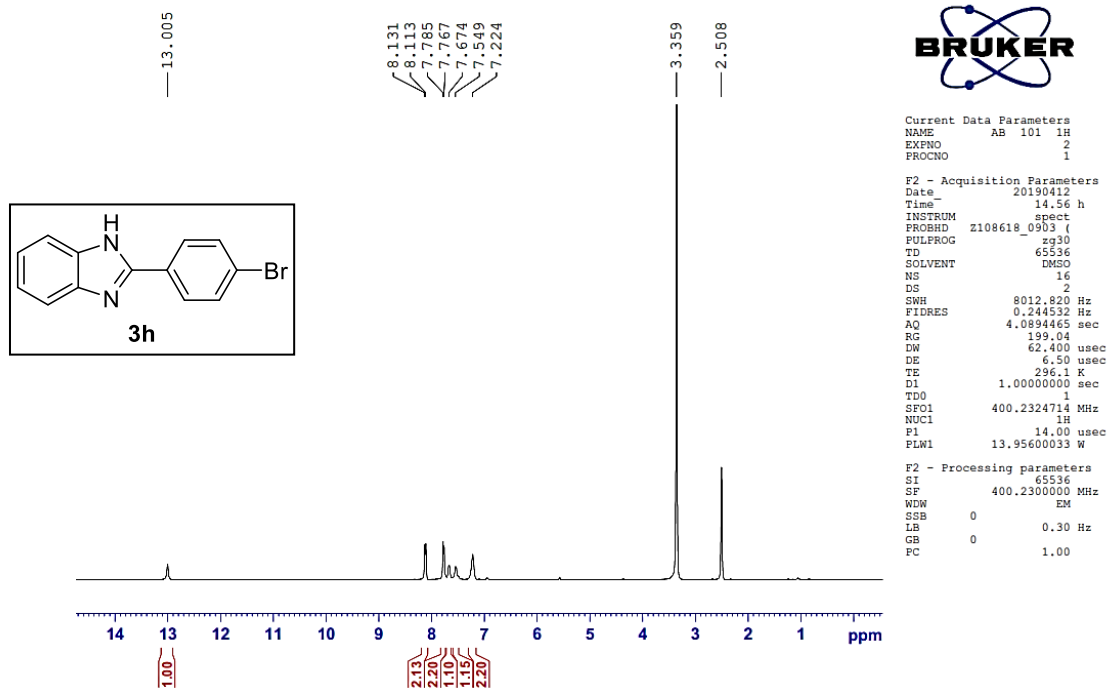


Figure S22: ¹H NMR (400 MHz, DMSO-*d*₆) Spectrum of compound **3h**

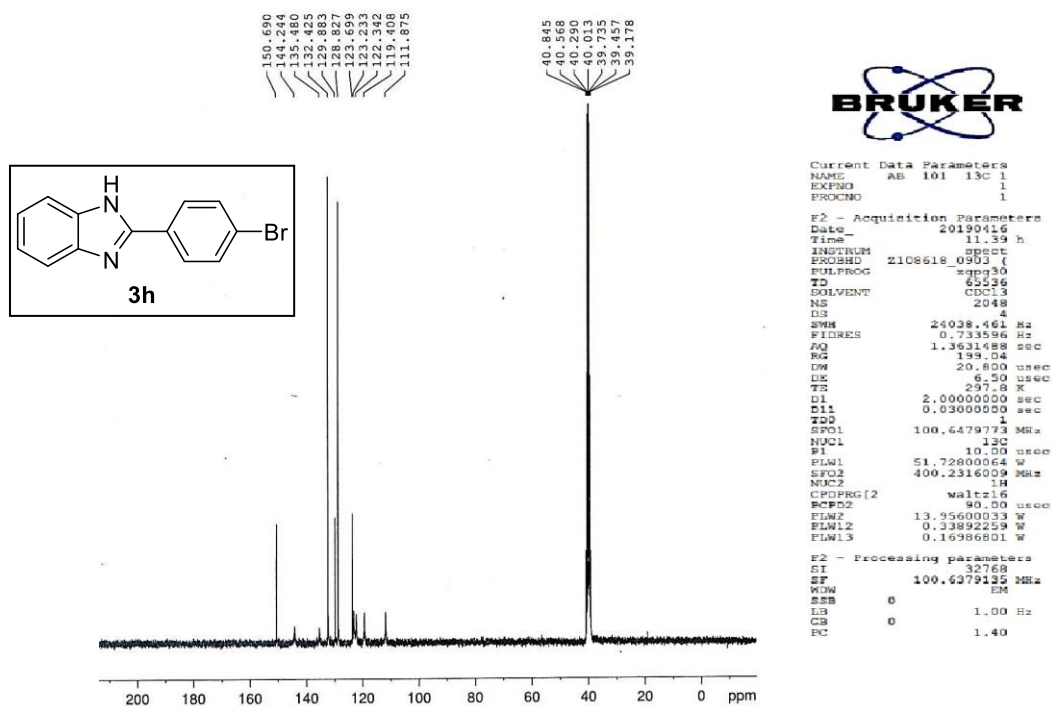


Figure S23: ¹³C NMR (100 MHz, DMSO-*d*₆) Spectrum of compound **3h**

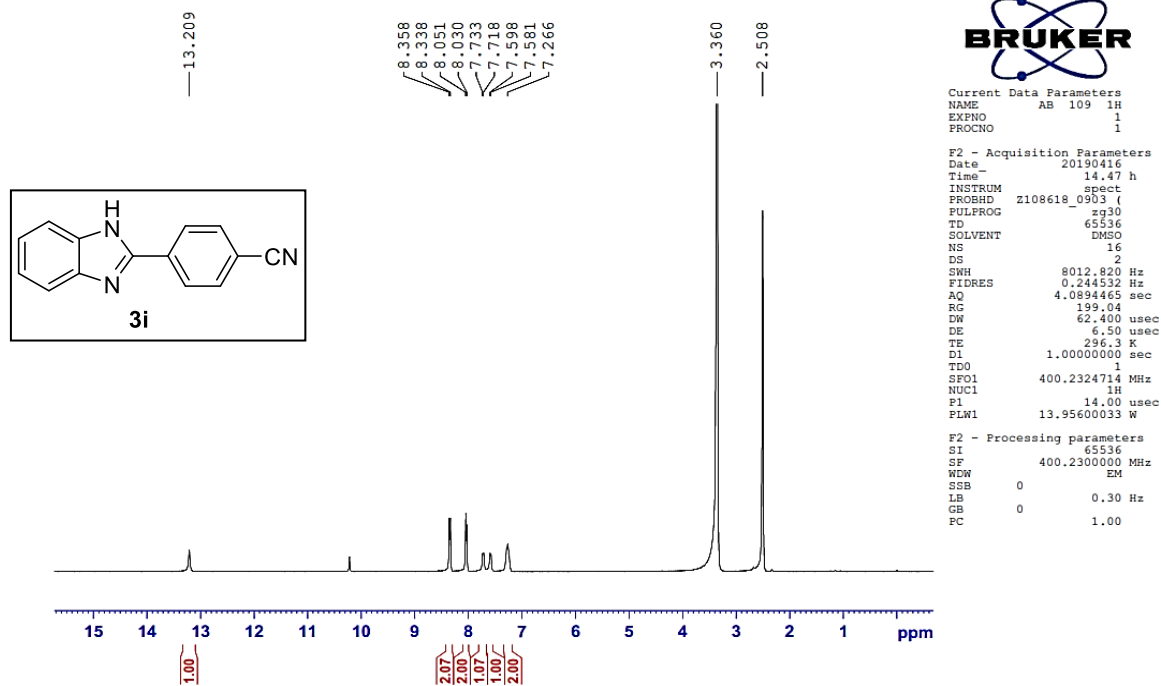


Figure S24: ¹H NMR (400 MHz, DMSO-*d*₆) Spectrum of compound **3i**

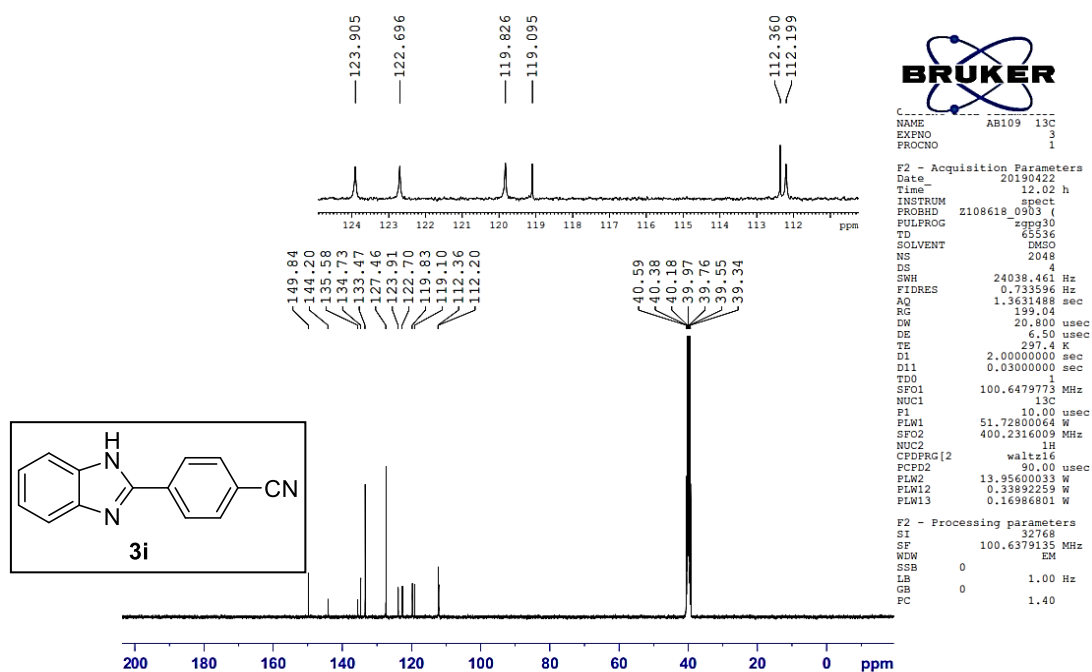


Figure S25: ¹³C NMR (100 MHz, DMSO-*d*₆) Spectrum of compound **3i**

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T: FTMS + p ESI Full ms [100.00-1500.00]

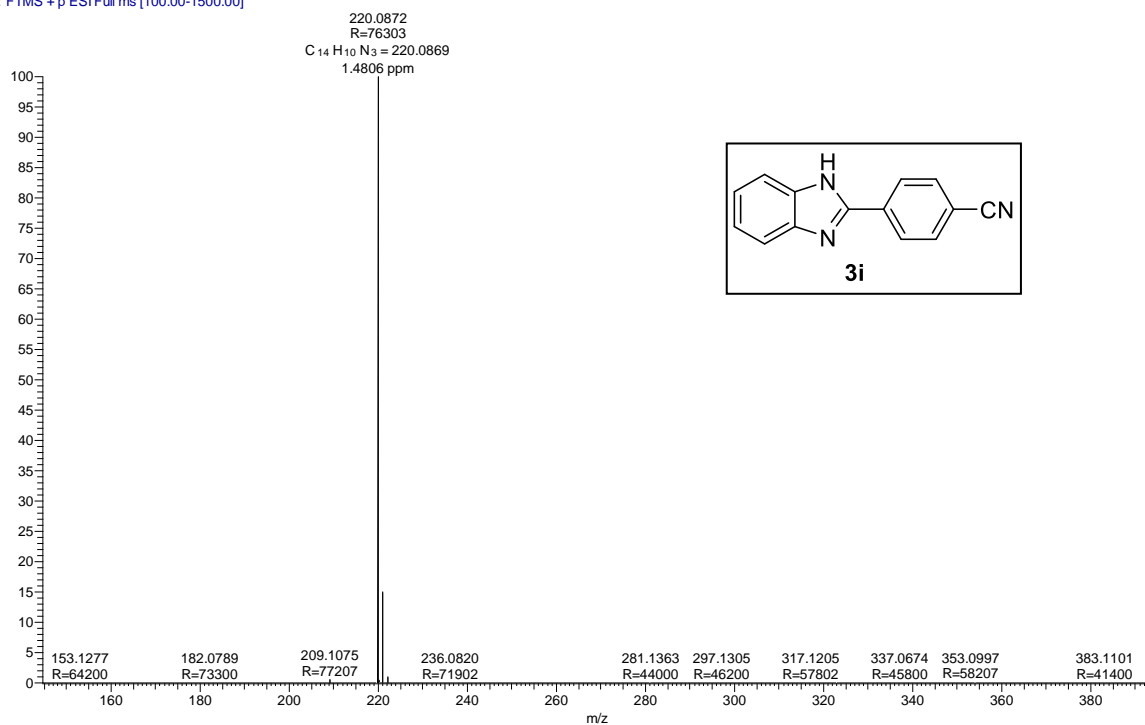
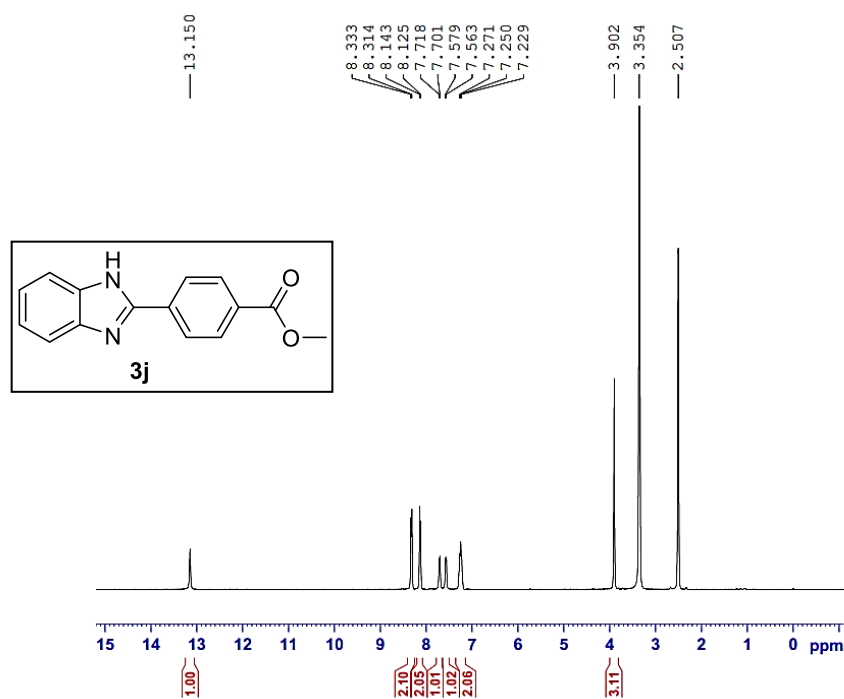


Figure S26: Mass Spectrum of compound **3i**

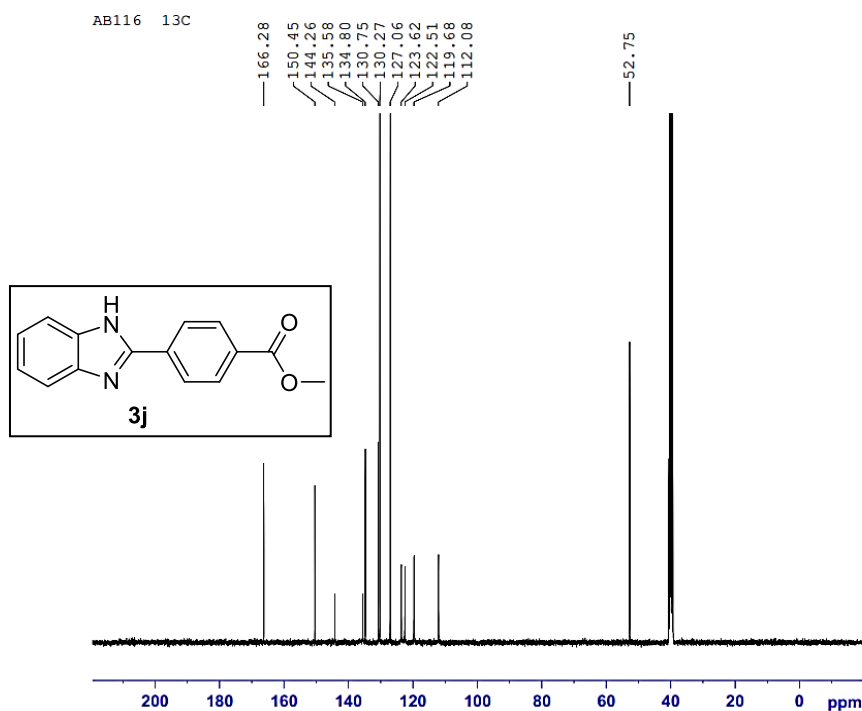


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 SOLVENT DMSO
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 DS 2
 SWH 8012.820 Hz
 FIDRES 0.244532 Hz
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 RG 199.04
 DW 62.400 usec
 DE 6.50 usec
 TE 296.2 K
 D1 1.0000000 sec
 TD0 1
 SFO1 400.2324714 MHz
 NUC1 1H
 P1 14.00 usec
 PLW1 13.95600033 W

F2 - Processing parameters
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Figure S27: ¹H NMR (400 MHz, DMSO-*d*₆) Spectrum of compound **3j**

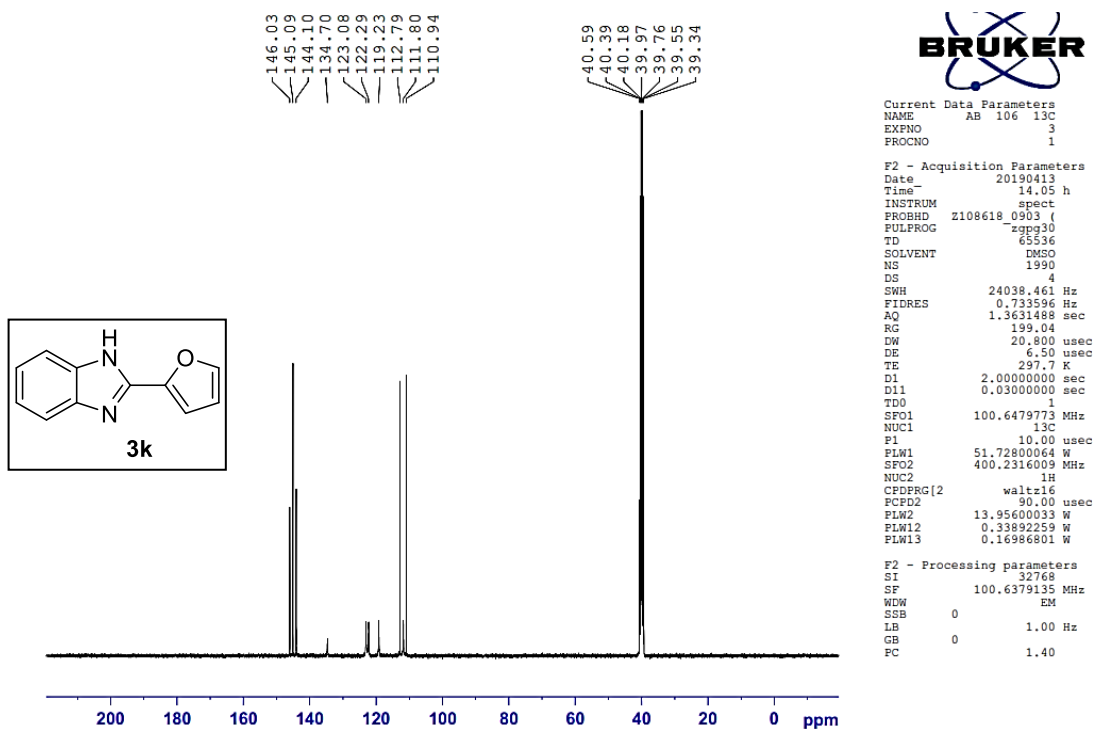
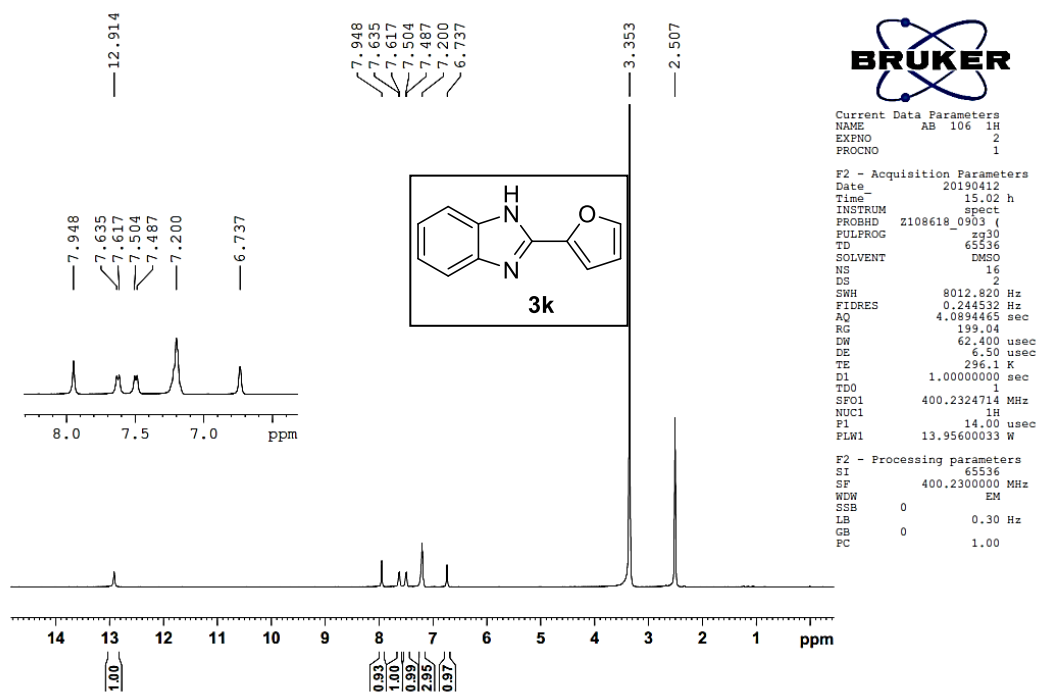


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 DE 6.50 usec
 TE 297.1 K
 D1 2.0000000 sec
 D11 0.0300000 sec
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 NUC1 13C
 P1 10.00 usec
 PLW1 51.72800064 W
 SFO2 400.2316009 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 13.95600033 W
 PLW12 0.33892259 W
 PLW13 0.16986801 W

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Figure S28: ¹³C NMR (100 MHz, DMSO-*d*₆) Spectrum of compound **3j**



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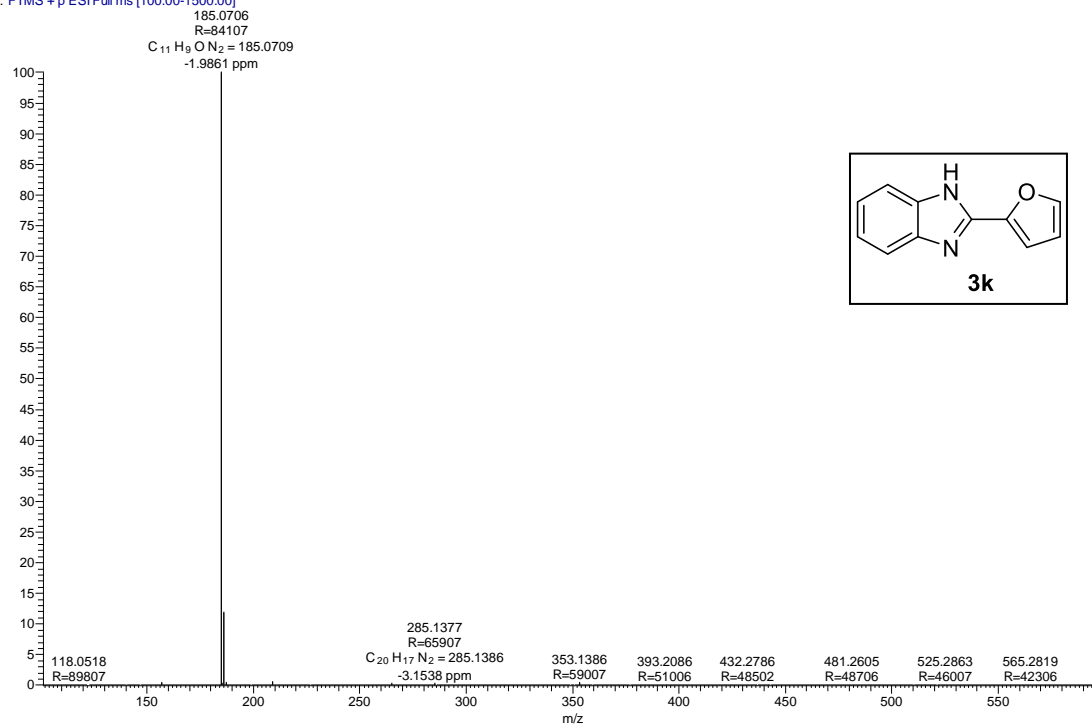
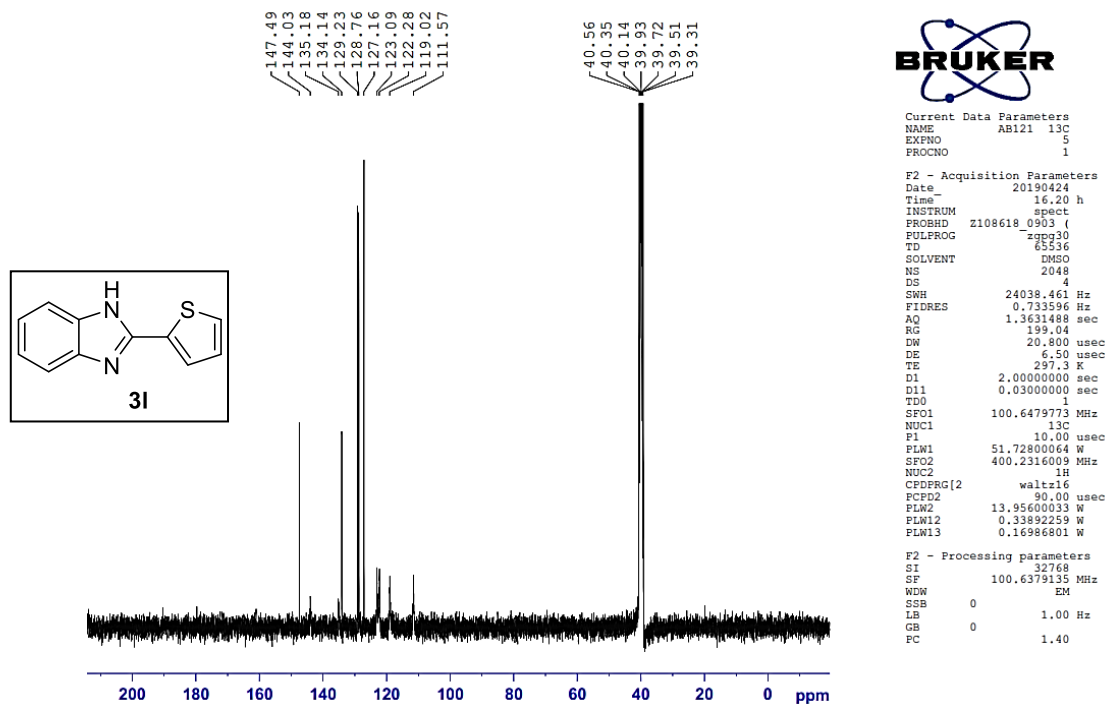
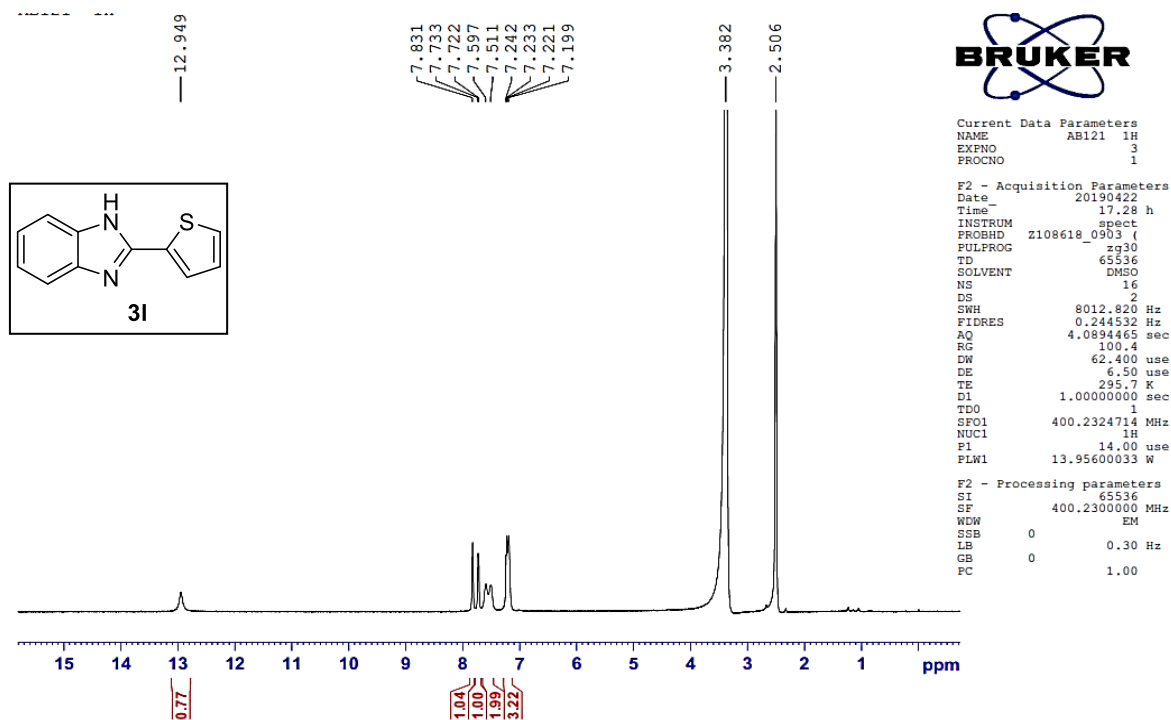


Figure S31: Mass Spectrum of compound **3k**



P-317 #91 RT: 0.41 AV: 1 NL: 1.00E10
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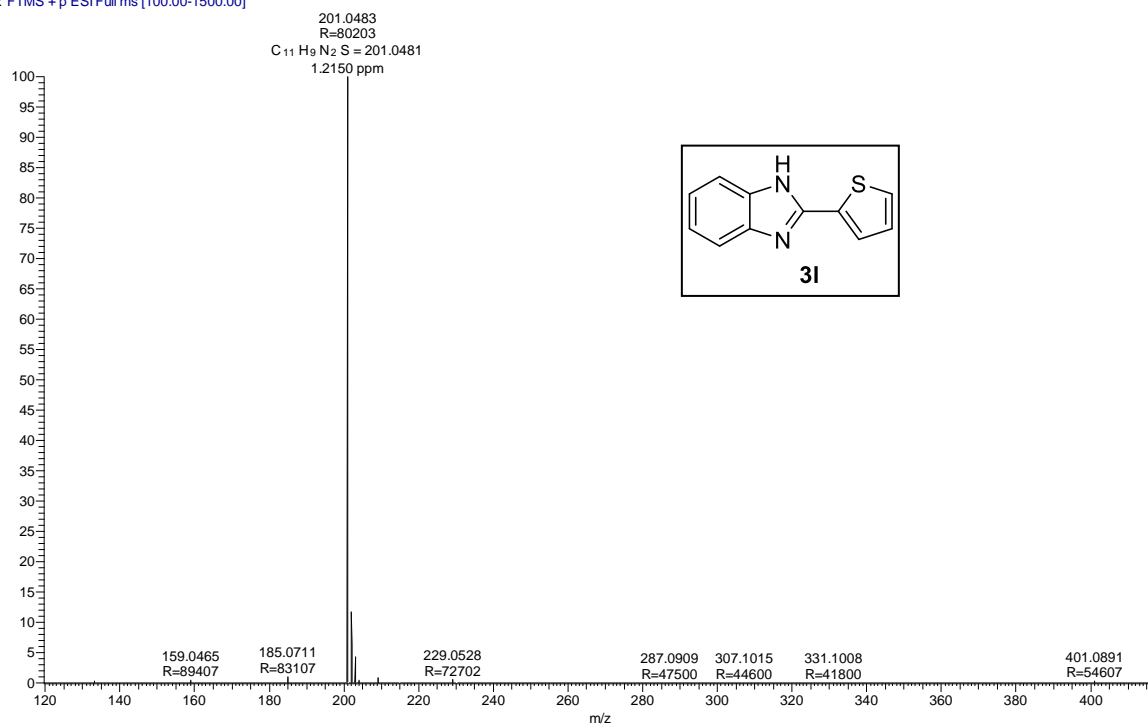


Figure S34: Mass Spectrum of compound 31

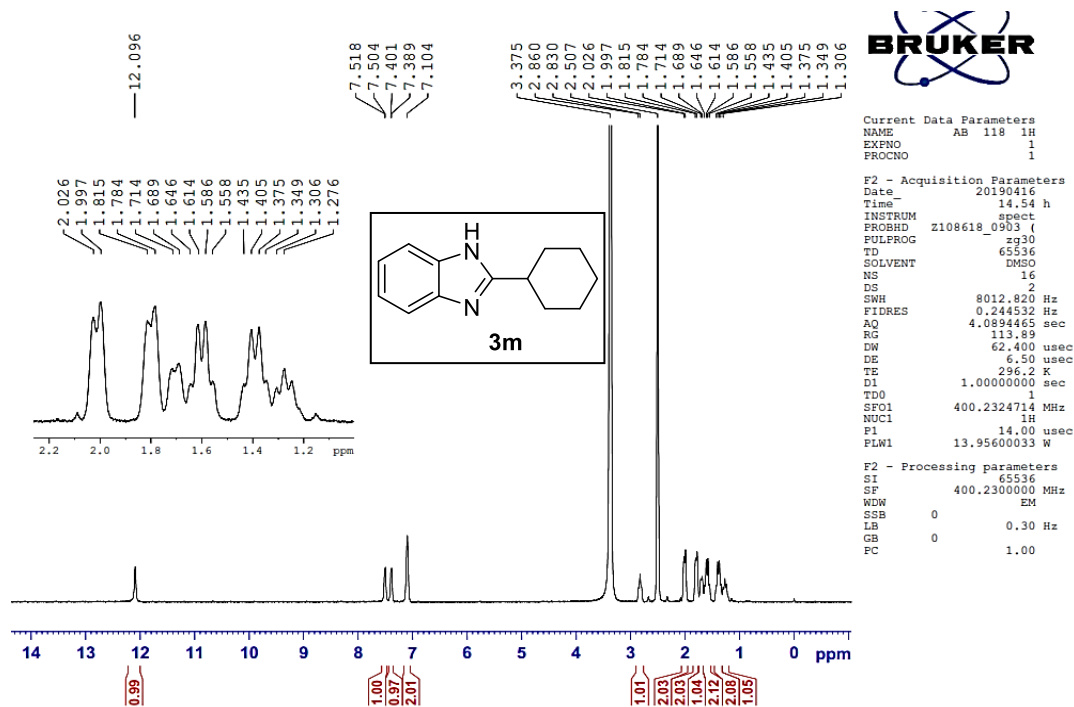


Figure S35: ^1H NMR (400 MHz, $\text{DMSO-}d_6$) Spectrum of compound **3m**

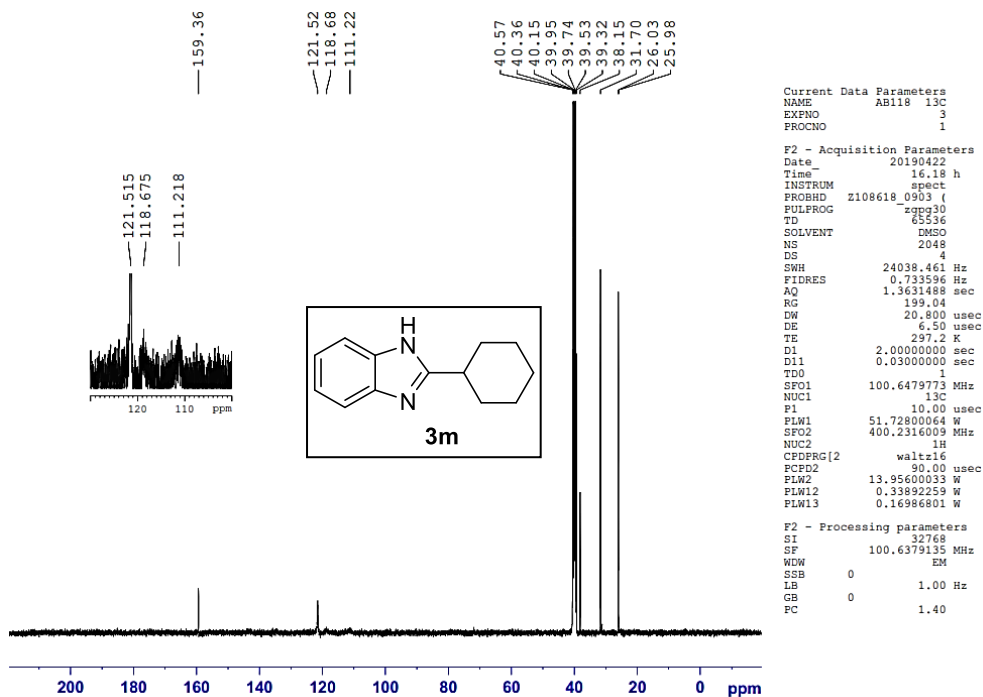


Figure S36: ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) Spectrum of compound **3m**

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-1.9675 ppm

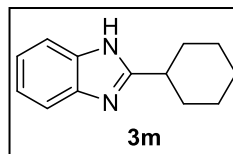
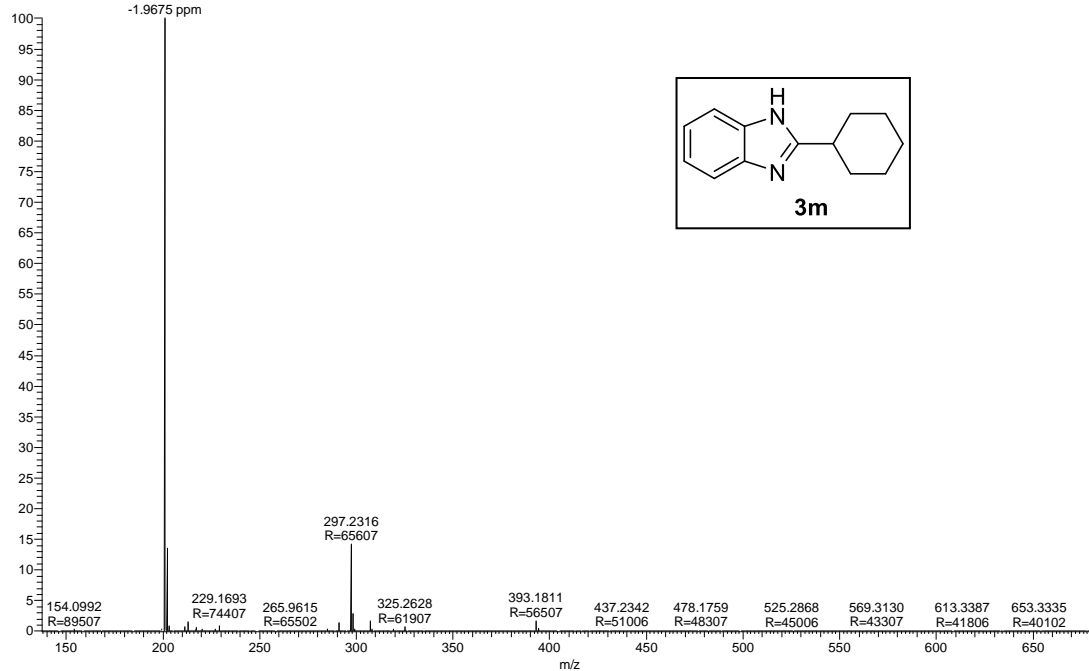
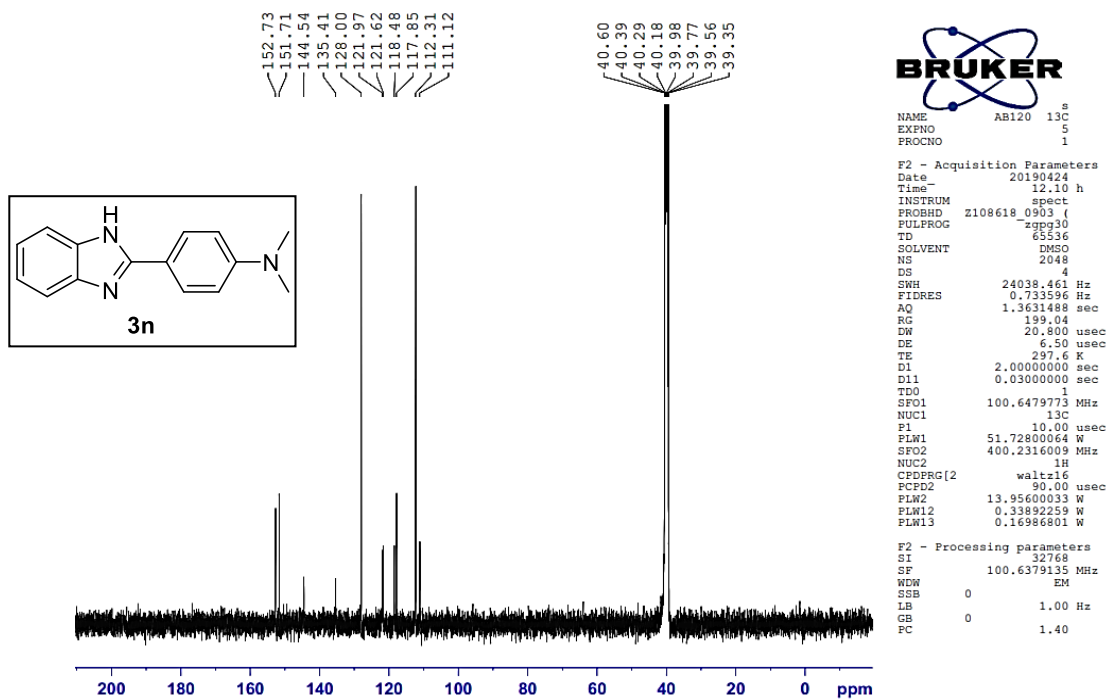
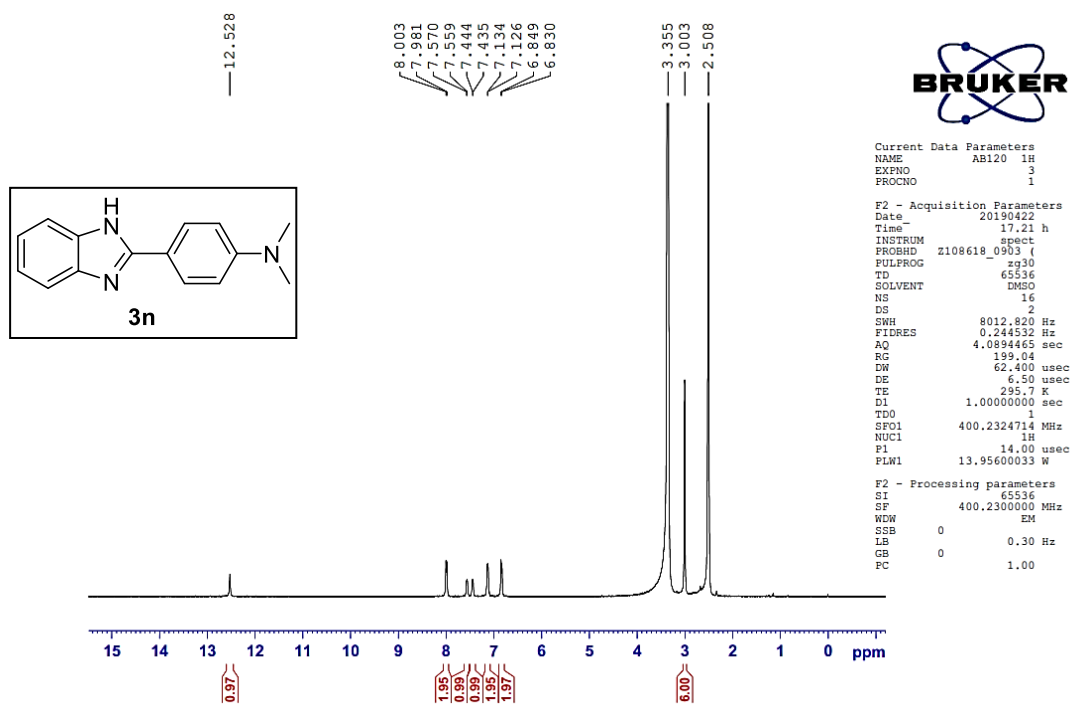


Figure S37: Mass Spectrum of compound **3m**



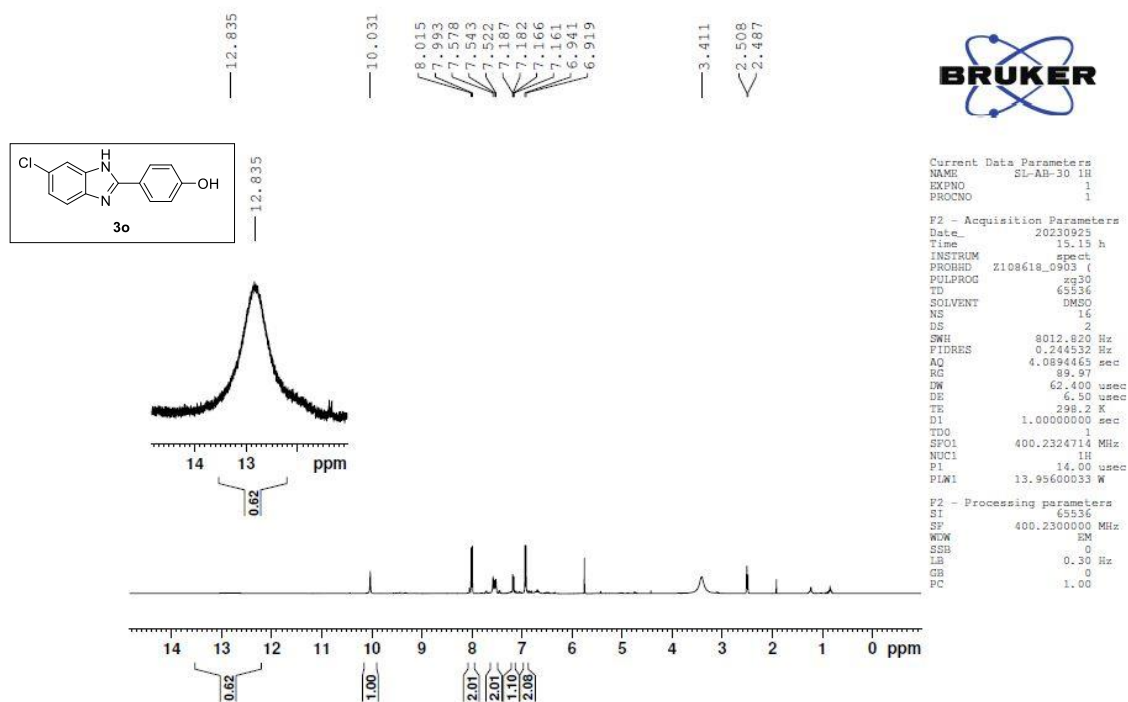


Figure S40: ¹H NMR (400 MHz, DMSO-*d*₆) Spectrum of compound **3o**

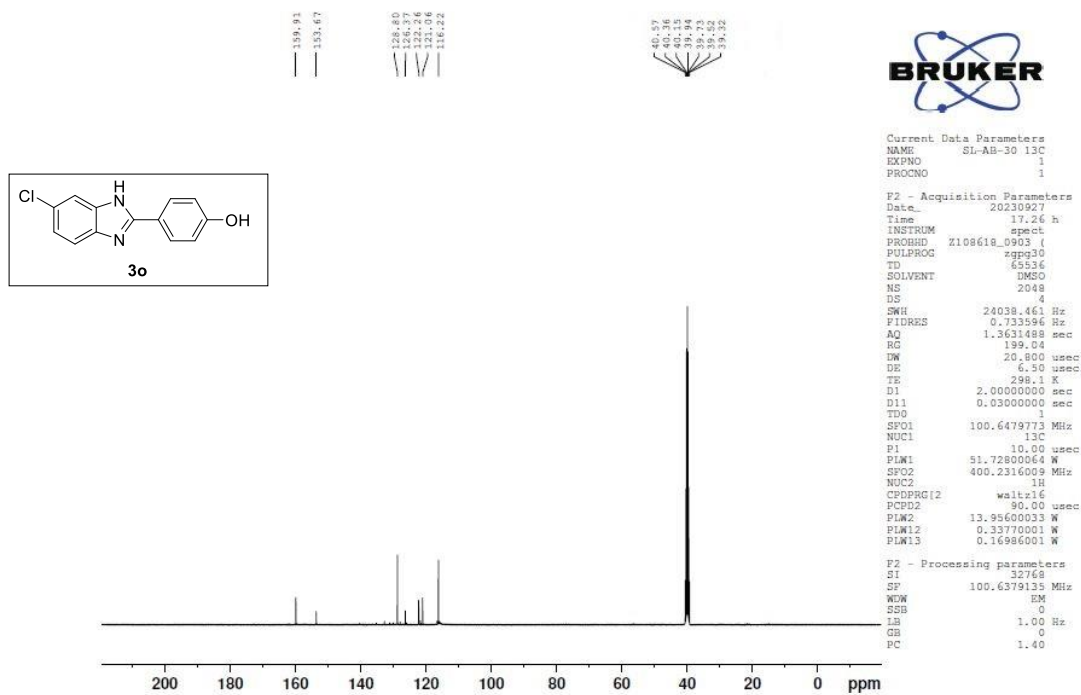


Figure S41: ¹³C NMR (100 MHz, DMSO-*d*₆) Spectrum of compound **3o**