Supplementary Information (SI) for Catalysis Science & Technology.
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Regioselective direct synthesis of *mono*- and *bis*-substituted benzimidazoles *via* base-switchable aerobic N-heterocyclic carbene organocatalysis

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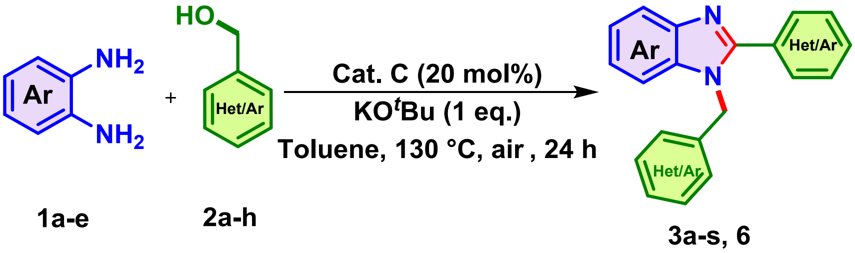
Supporting Information

1. General Information

Each component of the laboratory glassware was oven dried and then used for carrying out the general experimental procedures. ^{1}H NMR and ^{13}C NMR spectra were measured on JEOL RESONANCE ECZ500R operating at 500 MHz, and utilization of $CDCl_3$ and DMSO-d_6 were used as solvents for preparing the samples. Chemical shifts are reported in ppm and coupling constants are reported in Hz with TMS at 0.0 ppm (^{1}H and ^{13}C) or $CDCl_3$ referenced at 7.26 (1H) and 77.0 ppm (13C) and DMSO-d_6 referenced at 2.50 (^{1}H) and 39.5 (^{13}C). The pattern of the chemical shifts in proton NMR was described in parts per million (ppm). While peak splitting patterns were defined as singlet (s), broad singlet (brs), doublet (d), double doublet (dd), triplet (t), and multiplet (m). All Coupling constant (*J*) values were stated in Hertz (Hz). High-resolution mass spectrometry (HRMS) was carried out in an ESI quadrupole time-of-flight (QTOF) mass spectrophotometer. Column chromatography was done using a normal (particle size: 100-200 Mesh), which was obtained from Spectrochem (India) and Agnitio Pharma (India). TLC plates coated with silica gel (Kiesel 60-F254, Merck (India)) were used to track the progress of chemical reactions. The visualizing agents that were utilized for TLC were UV light. For drying and concentrating all the solvents, BUCHI's Rotavapor R-300 was used. EPR data were collected using BRUKER BIOSPIN, Germany (EMXmicro A200-9.5/12/S/W). All the supplied solvents were of analytical grade, such as Toluene, MeOH, EtOH, and they were used without any prior purification. The chemicals and reagents used for the chemical reactions were purchased from Sigma Aldrich chemicals company (USA), TCI (India) Pvt. Ltd., Merck (India), and/or Spectrochem (India), etc. were used without any purification before use.

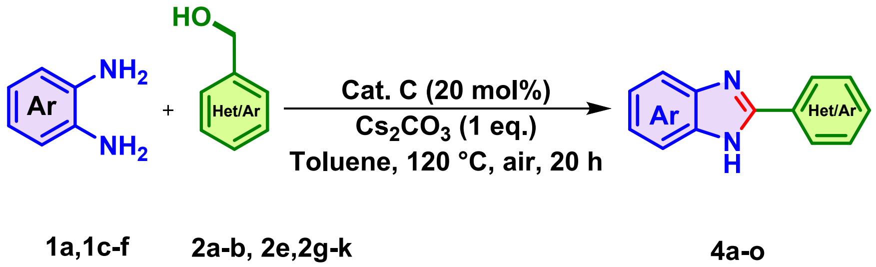
2. General procedure for the synthesis of *bis*-substituted benzimidazole derivatives (3a-s) and 6



1a-e **2a-h** **3a-s, 6**

In an oven-dried reaction tube, *o*-phenylenediamine (1.0 mmol), benzyl alcohol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled and dried under reduced pressure. Then, the ethyl acetate was added to the crude residue and washed with $NaHCO_3$ saturated solution (3 × 15 mL). The obtained organic fraction was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford a crude residue, which on subjection to purification by column chromatography using 10-12% EtOAc/hexane as eluent, furnished the compound **3a**. All the derivatives **3a-q** were synthesized by using the above-mentioned procedures.

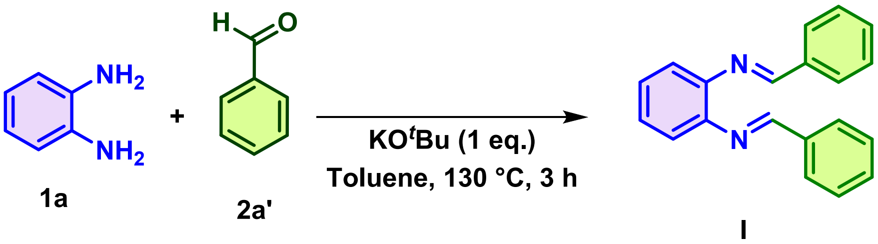
3. General procedure for the synthesis of *mono*-substituted benzimidazole derivatives (4a-o)



In an oven-dried reaction tube, *o*-phenylenediamine (1.0 mmol), benzyl alcohol (1.2 mmol), cat C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved under an atmosphere of air in toluene. The reaction mixture was heated and stirred at 120 °C for 20 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled and dried under reduced pressure. Then, the ethyl acetate was added to the crude residue and washed with $NaHCO_3$ saturated solution (3 × 15 mL). The obtained organic fraction was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford a crude residue, which on subjection to purification by column chromatography using 10-15% EtOAc/hexane as eluent furnished the compound **4a**. All the derivatives **4a-o** were synthesized by using the above-mentioned procedures.

4. General Procedure for the synthesis of intermediate imines (I and I')

(a)



In an oven-dried 10 mL reaction tube, *o*-phenylenediamine (1.0 mmol), benzaldehyde (2.2 mmol), and KO^tBu (1.0 mmol) were dissolved in toluene.[1] The reaction mixture was stirred at 130 °C. The progress of the reaction was monitored by TLC and run for 3 h. Then, the formation of intermediate **I** was confirmed from HRMS. Next, without further purification, 20 mol% of Cat. C was added to the reaction mixture and continued under aerobic conditions for 24 h.

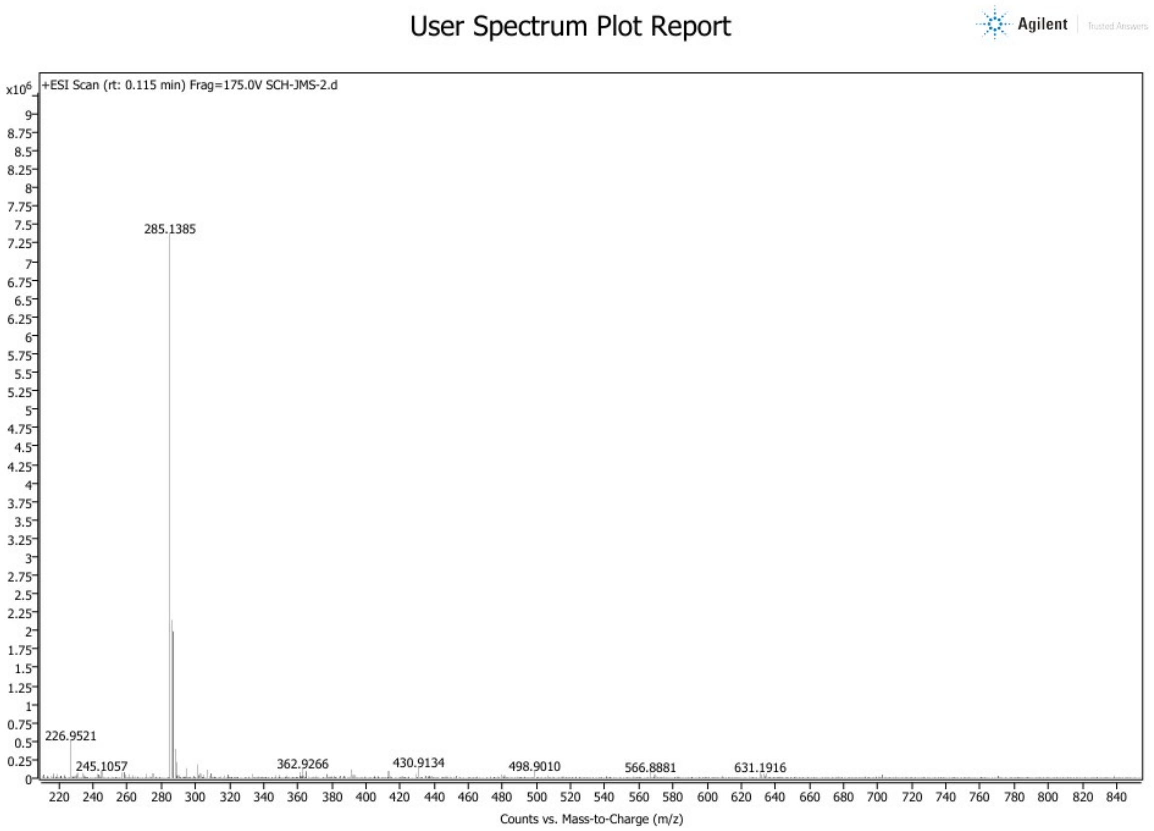
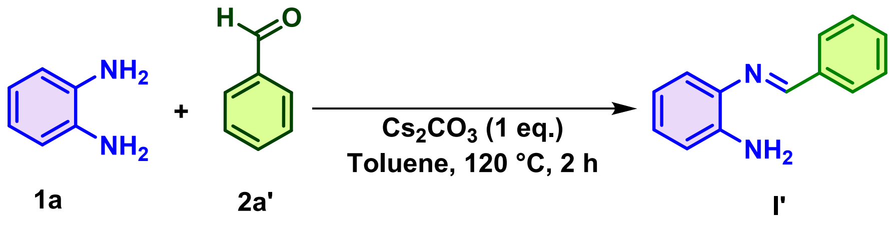


Figure S1. HRMS spectra of intermediate I

(b)



In an oven-dried 10 mL reaction tube, *o*-phenylenediamine (1.0 mmol), benzaldehyde (1.2 mmol), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene.[1] The reaction mixture was stirred at 130 °C. The progress of the reaction was monitored by TLC and run for 2 h. Then, the formation of intermediate **I'** was confirmed from HRMS. Next, without further purification, 20 mol% of Cat. C was added to the reaction mixture and continued under aerobic conditions for 20 h.

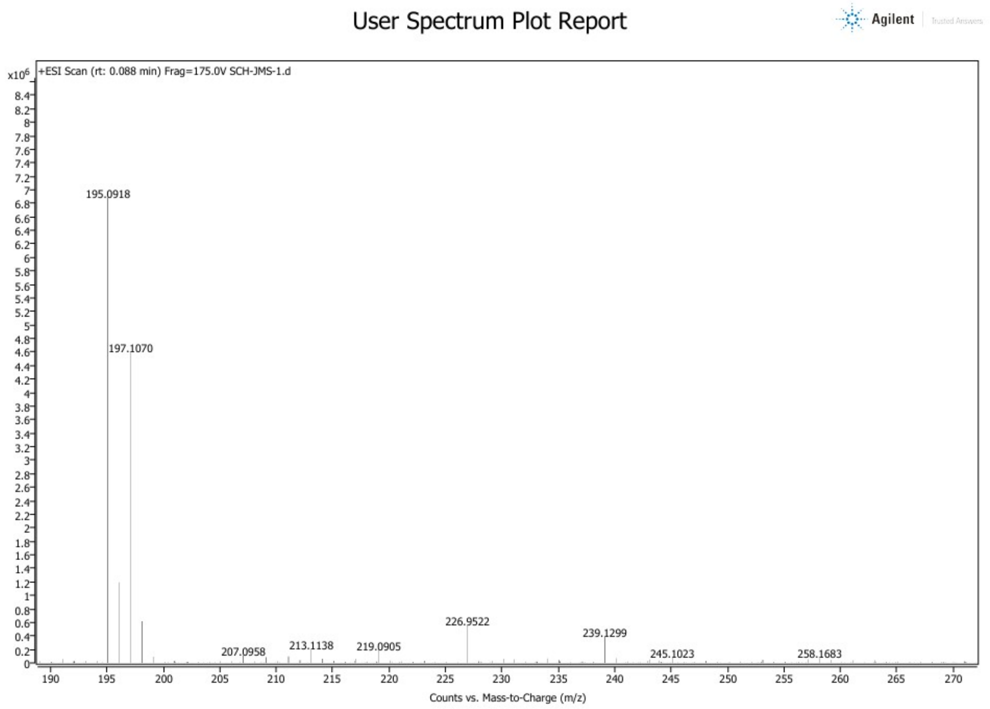
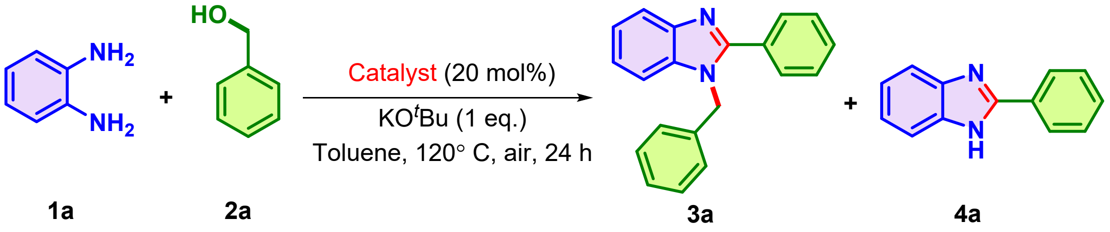


Figure S2. HRMS spectra of intermediate I'

5. Optimization of the reaction conditions

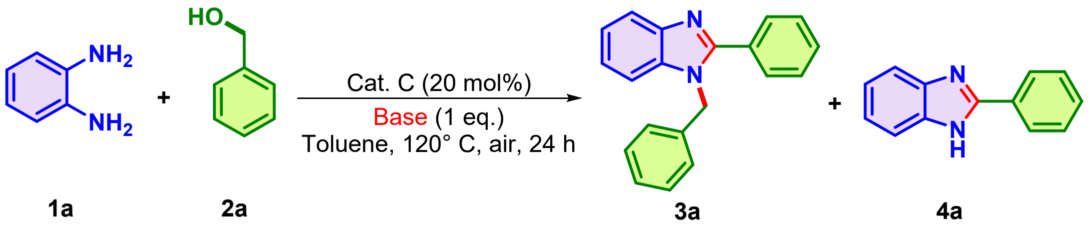
Table S1. Primary screening of catalyst



Entry	Catalyst 20 mol %	Yield (%)	
		3a	**4a**
1	Cat. A	41	33
2	Cat. B	43	31
3	**Cat. C**	**71**	**<5**
4	Cat. D	25	40
5	Cat. E	17	29
6	Cat. F	35	Trace
7	Cat. G	31	37
8	Cat. H	20	26
9	Cat. I	47	39
10	Cat. J	33	23

[a]*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (20 mol%), base (1 mmol), toluene, 120 °C, under air, 24 h . [b]Isolated yield.

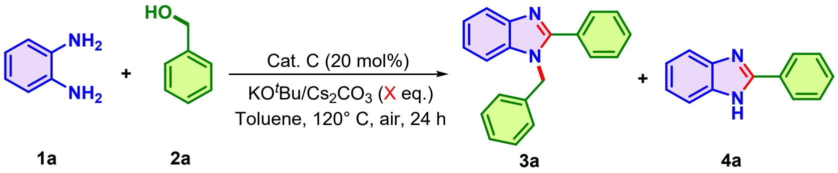
Table S2. Examination of bases



Entry	Base (1 eq.)	Yield (%)	
		3a	4a
1	**KO^tBu**	**71**	**<5**
2	NaOH	59	Trace
3	KOH	51	Trace
4	TEA	NR	NR
5	NaO^tBu	67	7
6	$NaHCO_3$	Trace	<5
7	Na_2CO_3	Trace	10
8	K_3PO_4	Trace	53
9	K_2CO_3	Trace	17
10	**Cs_2CO_3**	**Trace**	**66**
11	Imidazole	NR	Trace
12	DBU	NR	NR

[a]*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (20 mol%), base (1 mmol), toluene, 120 °C, under air, 24 h. [b]Isolated yield.

Table S3. Examination of base loading



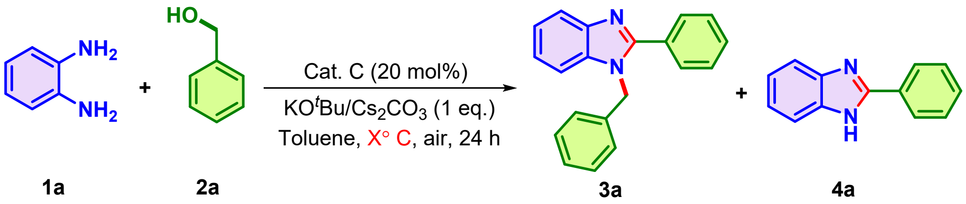
Entry	KO^tBu (eq.)	Yield 3a (%)
1	0	0
2	0.5	53
3	**1**	**71**
4	1.5	71
5	2	70

[a]*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (20 mol%), KO^tBu (X mmol), toluene, 120 °C, under air, 24 h. [b]Isolated yield.

Entry	Cs_2CO_3 (eq.)	Yield 4a (%)
1	0	0
2	0.5	Trace
3	**1**	**62**
4	1.5	59
5	2	60

[a]*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (20 mol%), Cs_2CO_3 (X mmol), toluene, 120 °C, under air, 24 h. [b]Isolated yield.

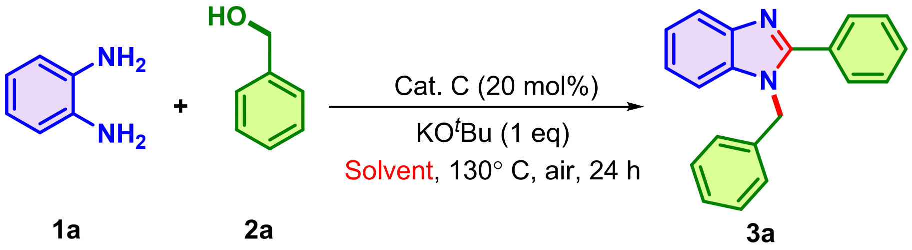
Table S4. Examination of different temperatures



Entry	Base (1 eq.)	Temp °C	Yield (%)	
			3a	4a
3	KO^tBu	110	51	23
4	KO^tBu	120	74	<5
5	**KO^tBu**	**130**	**82**	**Trace**
6	KO^tBu	140	80	NR
9	Cs_2CO_3	100	NR	41
9	Cs_2CO_3	110	NR	47
10	**Cs_2CO_3**	**120**	**NR**	**62**
11	Cs_2CO_3	130	NR	62

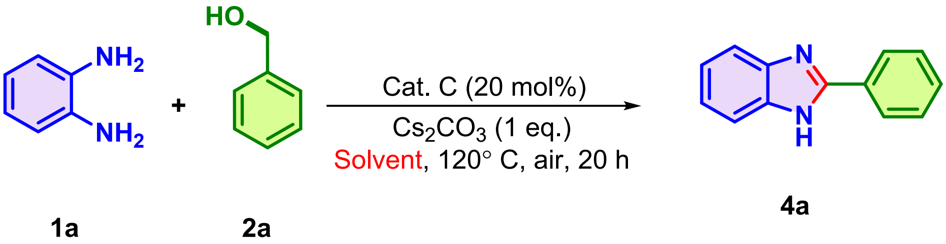
[a] *Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (20 mol%), base (1 mmol), solvent, temp. X °C, under air, 24 h. [b] Isolated yield.

Table S5. Examination of solvents



Entry	Solvent	Yield 3a (%)
1	**Toluene**	**82**
2	Chlorobenzene	16
3	1,4 Dioxane	Trace
4	O-Xylene	43
5	DMSO	25
6	DMA	19

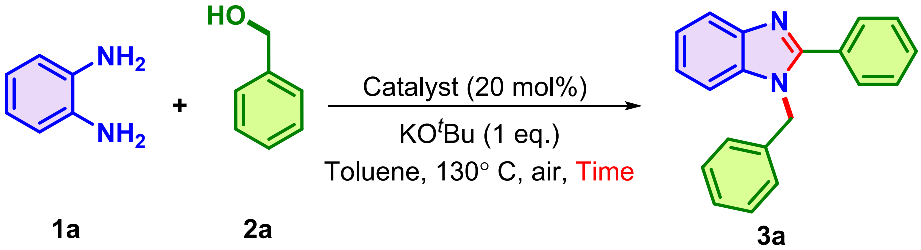
[a] *Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (20 mol%), KO^tBu (1 mmol), solvent, 130 °C, under air, 24 h. [b] Isolated yield.



Entry	Solvent	Yield 4a (%)
1	**Toluene**	**62**
1	Chlorobenzene	41
2	1,4 Dioxane	37
3	O-Xylene	35
4	DMSO	33
5	DMA	Trace

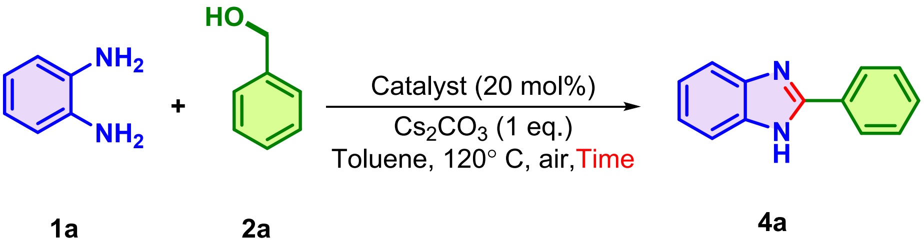
[a]*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (20 mol%), Cs_2CO_3 (1 mmol), solvent, 120 °C, under air, 24 h. [b]Isolated yield.

Table S6. Examination of time



Entry	Time (h)	Yield 3a (%)
1	6	51
2	12	64
3	20	76
4	**24**	**82**
5	30	79

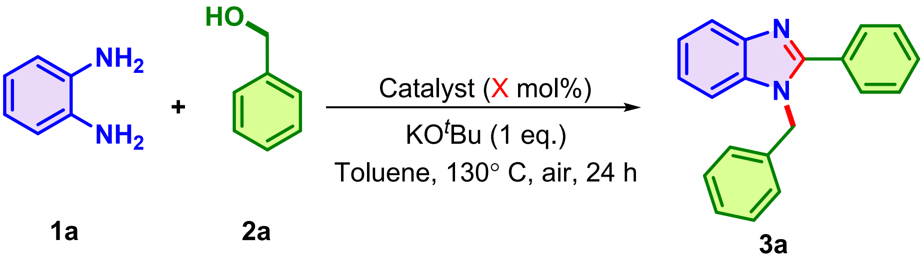
[a]*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (20 mol%), KO^{t}Bu (1 mmol), toluene, 130 °C, under air, time X h. [b]Isolated yield.



Entry	Time (h)	Yield 4a (%)
1	6	<5
2	12	57
3	**20**	**66**
4	24	66

[a]*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (20 mol%), Cs_2CO_3 (1 mmol), toluene, 120 °C, under air, time X h. [b]Isolated yield.

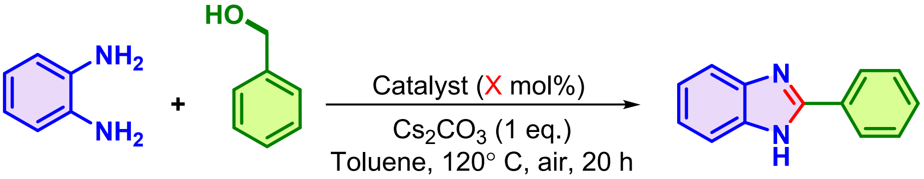
Table S7. Examination of catalyst loading



1a **2a** **3a**

Entry	Catalyst (mol%)	Yield 3a (%)
1	0	19
2	10	47
3	15	59
4	**20**	**82**
5	25	78

^{a}*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (X mol%), KO^{t}Bu (1 mmol), solvent, 130 °C, under air, 24 h. ^{b}Isolated yield.

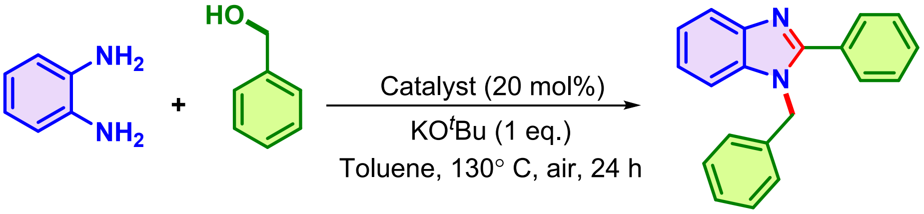


1a **2a** **4a**

Entry	Catalyst (mol%)	Yield 4a (%)
1	0	13
2	10	47
3	15	53
4	**20**	**66**
5	25	63

^{a}*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (2 mmol), cat. C (X mol%), Cs_2CO_3 (1 mmol), solvent, 120 °C, under air, 20 h. ^{b}Isolated yield.

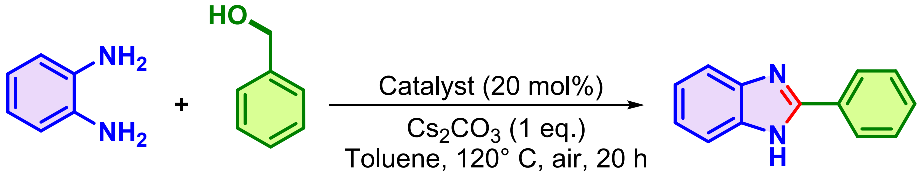
Table S8. Examination of the Stoichiometric ratio of benzyl alcohol



1a **2a** **3a**

Entry	2a (eq.)	Yield 3a (%)
1	1.5	73
2	2	80
3	**2.2**	**85**
4	2.5	82

[a]*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (X mmol), cat. C (20 mol%), KO^{t}Bu (1 mmol), toluene, 130 °C, under air, 24 h. [b]Isolated yield.



1a **2a** **4a**

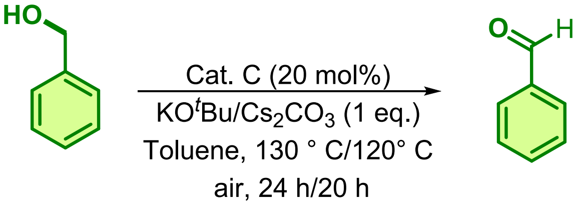
Entry	2a (eq.)	Yield 4a (%)
1	1	69
2	**1.2**	**74**
3	1.5	72
4	2	66

[a]*Reaction conditions until and unless mentioned*: Diamine 1a (1 mmol), benzyl alcohol 2a (X mmol), cat. C (20 mol%), Cs_2CO_3 (1 mmol), solvent, 120 °C, under air, 20 h. [b]Isolated yield.

6. Mechanistic studies

(i) Dehydrogenation of benzyl alcohol

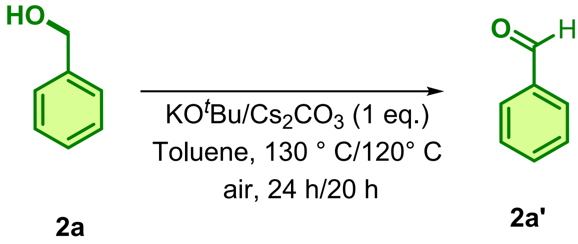
(a)



2a **2a'**

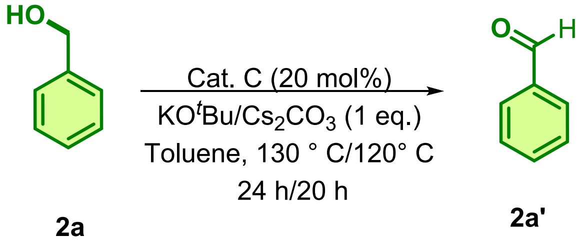
This experiment was performed by following the previous literature.[2] In an oven-dried reaction tube, benzyl alcohol **2a** (1 mmol) and KO^{t}Bu/ Cs_2CO_3 (1.0 mmol) were dissolved under an atmosphere of air in toluene. The reaction mixture was heated and stirred at 130 °C for 24 h or 120 °C for 20 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled and dried under reduced pressure. Then ethyl acetate was added to the crude residue and washed with a saturated solution of $NaHCO_3$ (3×15 mL). The obtained organic fraction was dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford a residue. After that, the residue was purified using column chromatography by the gradient elution method with (EtOAc/hexane, 0-7%) ratio as the eluting solvent to generate compound **2a'** in 87% yield, while KO^{t}Bu was used as the base and 75% when CS_2CO_3 was used as the base.

(b)



The compound 2a' was generated following the above procedure (i-a) without using Cat. C in 33% and 20%.

(c)

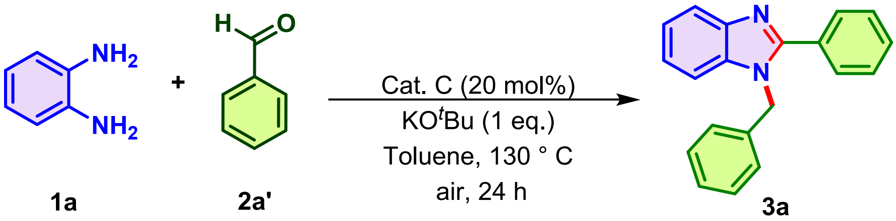


Again, following the same procedure (i-a) in the absence of air, 2a' was generated in 84% and 70%.

The above experiments indicate NHC is essential for the oxidation of benzyl alcohol and doesn't require air.

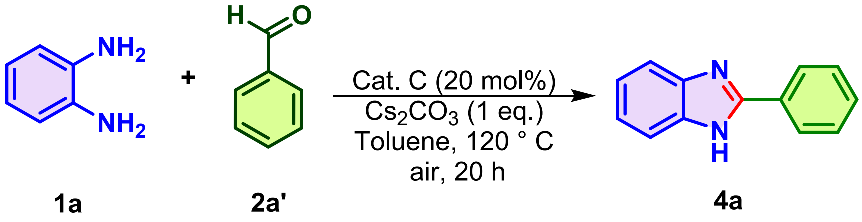
(ii) Reaction of damine with benzaldehyde

(a)



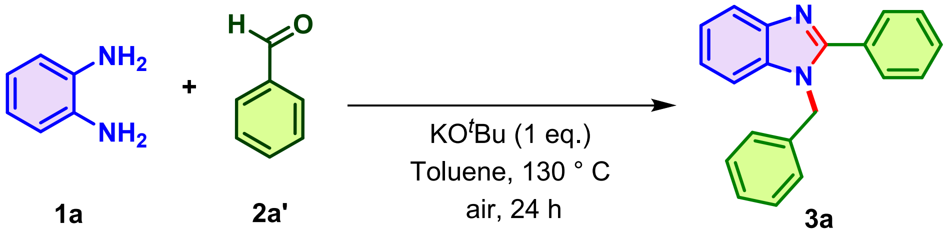
In an oven-dried reaction tube, *o*-phenylenediamine **1a** (1 mmol), benzaldehyde **2a'** (2.2 mmol), KO^{t}Bu (1.0 mmol), and cat. C (20 mol%) were dissolved under an atmosphere of air in toluene. The reaction mixture was heated and stirred at 130 °C for 24 h. Then after completion of the reaction, the reaction mixture was cooled and dried under reduced pressure. Then ethyl acetate was added to the crude residue and washed with a saturated solution of $NaHCO_3$ (3×15 mL). The obtained organic fraction was dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford a residue. After that, the residue was purified using column chromatography by the gradient elution method with (EtOAc/hexane, 10-12%) ratio as the eluting solvent to generate compound **2a'** in 84% yield.

(b)



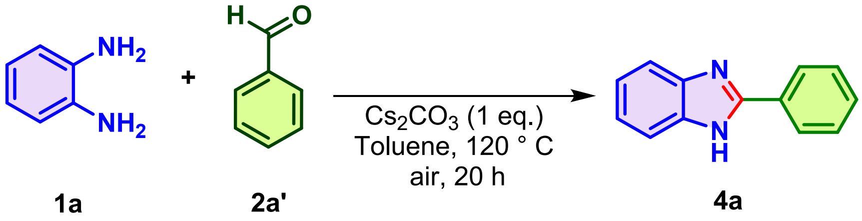
4a was generated by using the above procedure (ii- a) in 72% (EtOAc/hexane, 10-15% as eluant)

(c)



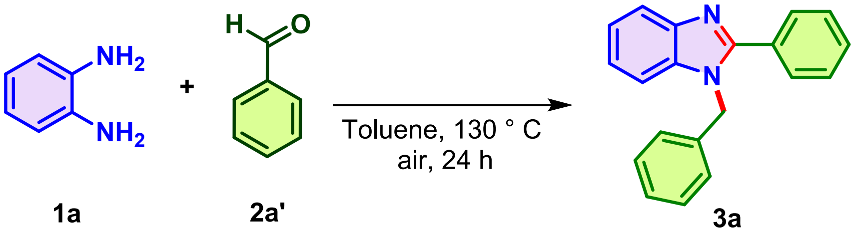
3a was generated by using the above procedure (ii- a) in 29% (EtOAc/hexane, 10-12% as eluant)

(d)



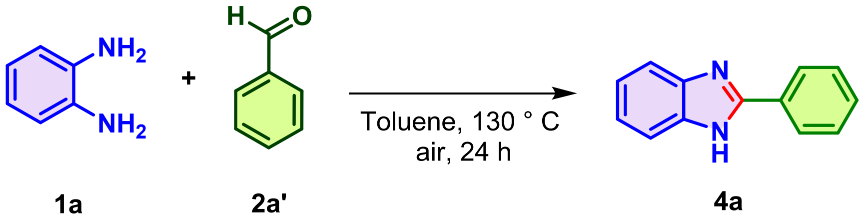
4a was generated by using the above procedure (ii- a) in 22% (EtOAc/hexane, 10-15% as eluant)

(e)



3a was generated by using the above procedure (ii- a) in 25% (EtOAc/hexane, 10-12% as eluant).

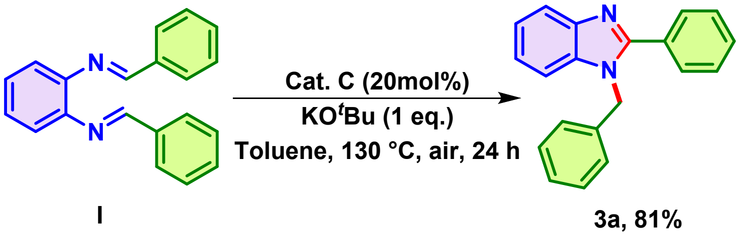
(f)



4a was generated by using the above procedure (ii- a) in 23% (EtOAc/hexane, 10-15% as eluant)

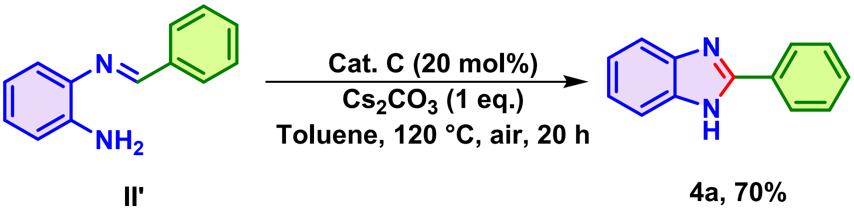
*The above experiments suggest that reactions proceed effectively in the presence of NHC, whereas in the absence of NHC, the selective formation of **3a** and **4a** is very poor. Also, the use of bases and air is not effective in getting the desired selective products without the use of NHC.*

(iii) Involvement of different intermediates



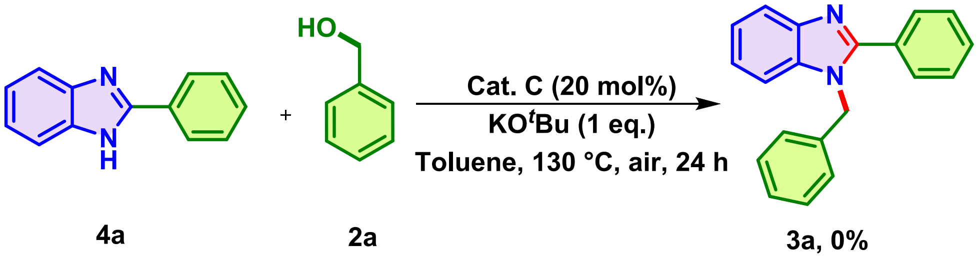
Following the previous literature (see SI, S3),[1] in an oven-dried reaction tube *(1E,1'E)-N,N'*-(1,2-phenylene)bis(1-phenylmethanimine) I (1 mmol), cat. C (20 mol%), were dissolved under an atmosphere of air in toluene. The reaction mixture was heated and stirred at 130 °C for 24 h. After the reaction was completed, the reaction mixture was cooled and dried under reduced pressure. Then ethyl acetate was added to the crude residue and washed with a saturated solution of $NaHCO_3$ (3×15 mL). The obtained organic fraction was dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford a residue. After that, the residue was purified using column chromatography by the gradient elution method with (EtOAc/hexane, 10-12%) ratio as the eluting solvent to generate compound **3a** in 81%.

*This experiment indicates the possibility of the formation of intermediate **I**, which could undergo cyclization in the presence of NHC under air to furnish product **3a**.*



Following the previous literature (see SI, S3),[1] in an oven-dried reaction tube (*E*)-2-(benzylideneamino)aniline **II'** (1 mmol), cat. C (20 mol%), were dissolved under an atmosphere of air in toluene. The reaction mixture was heated and stirred at 120 °C for 20 h. After the reaction was completed, the reaction mixture was cooled and dried under reduced pressure. Then ethyl acetate was added to the crude residue and washed with a saturated solution of $NaHCO_3$ (3×15 mL). The obtained organic fraction was dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford a residue. After that, the residue was purified using column chromatography by the gradient solution of $NaHCO_3$ (3×15 mL). The obtained organic fraction was dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford a residue. After that, the residue was purified using column chromatography by the gradient elution method with (n-hexane/ethyl acetate = 10-15%) ratio as the eluting solvent to generate the compound **4a** in 70% yield.

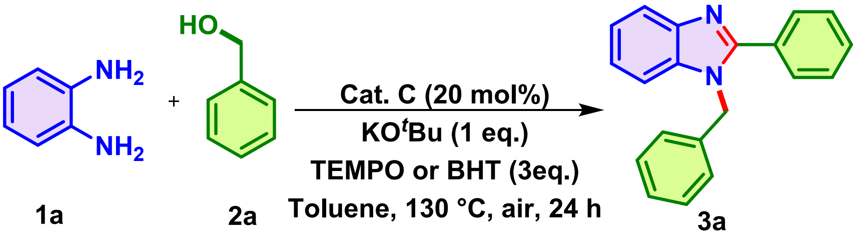
*This experiment indicates the possibility of the formation of intermediate II', which could undergo cyclization in the presence of NHC under air to furnish the product **4a**.*



In an oven-dried reaction tube, 2-phenylbenzimidazole **4a** (1 mmol), benzyl alcohol **2a** (2.2 mmol), KO^{t}Bu (1.0 mmol), and cat. C (20 mol%) were dissolved under an atmosphere of air in toluene. The reaction mixture was heated and stirred at 130 °C for 24 h. Then, after completion of the reaction, the reaction was monitored using TLC, which confirmed no formation of the product **3a**.

*This experiment indicates that there is no involvement of **4a** in the formation of **3a**.*

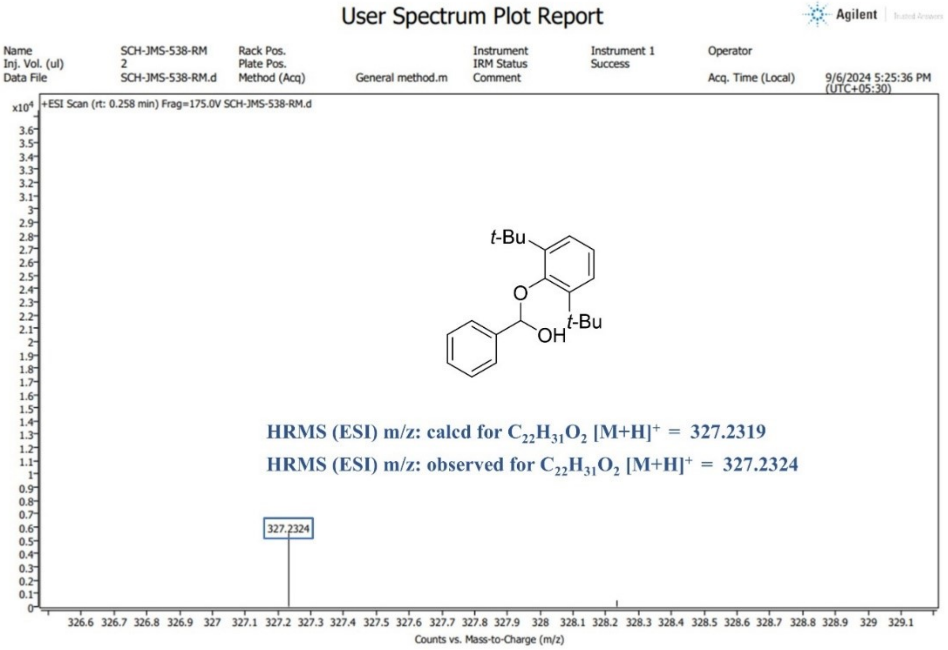
(iv) Radical scavenger reaction



For TEMPO (3 eq.) yield is 53%

BHT (3 eq.) yield is 34%

In an oven-dried reaction tube, *o*-phenylenediamines **1a** (1 mmol), benzyl alcohol **2a** (2.2 mmol), Cat. C (20 mol%), KO^{t}Bu (1 mmol), and TEMPO or BHT (3 mmol) were dissolved under an atmosphere of air in toluene. The reaction mixture was heated and stirred at 130 °C for 24 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled and dried under reduced pressure. Then ethyl acetate was added to the crude residue and washed with a saturated solution of $NaHCO_3$ (3×15 mL). The obtained organic fraction was dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford a residue. After that, the residue was purified using column chromatography by the gradient elution method with (EtOAc/hexane, 10-12%) ratio as the eluting solvent to generate compound **3a**.



User Spectrum Plot Report

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Data File	SCH-JMS-538-RM.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	9/6/2024 5:25:36 PM (UTC+05:30)

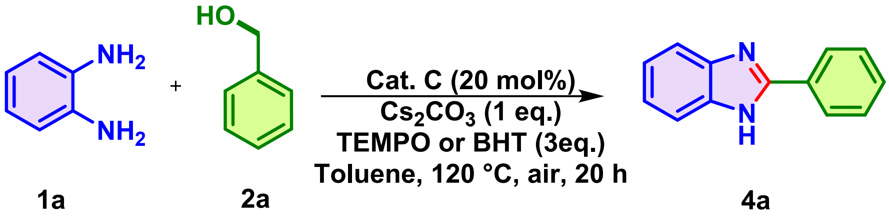
+ESI Scan (rt: 0.258 min) Frag=175.0V SCH-JMS-538-RM.d

HRMS (ESI) m/z: calcd for $C_{22}H_{31}O_2$ $[M+H]^+$ = 327.2319

HRMS (ESI) m/z: observed for $C_{22}H_{31}O_2$ $[M+H]^+$ = 327.2324

Figure S3. BHT adduct of benzylic radical in the formation of product 3a.

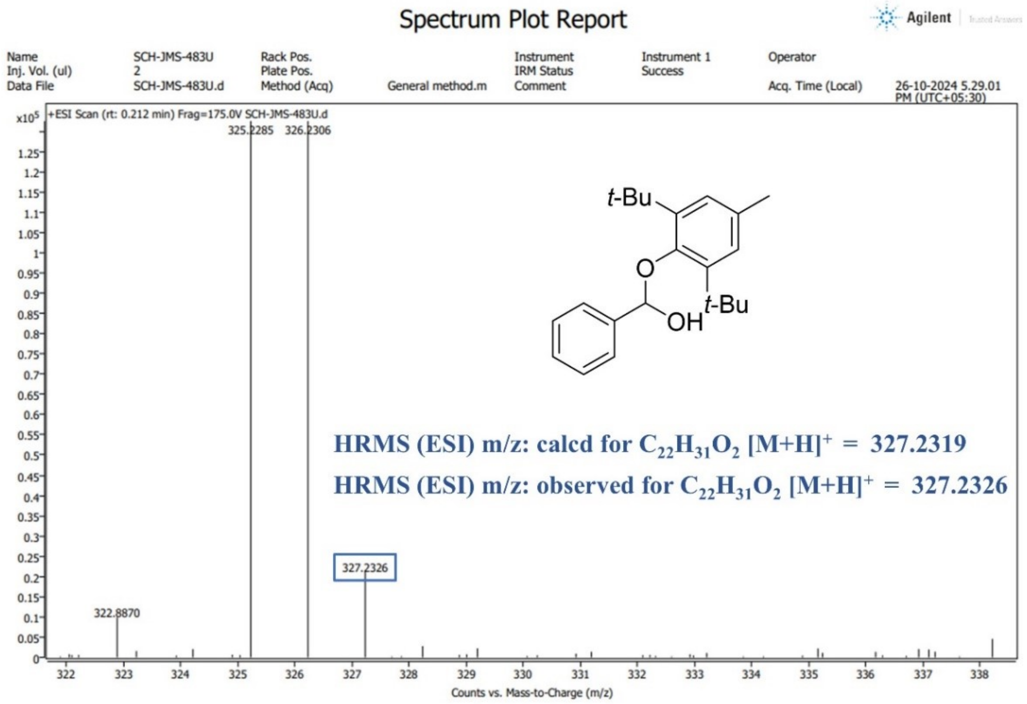
Also, the reaction mixture was analyzed immediately after the completion of the reaction in a high-resolution mass spectrometer. In the case of BHT, the HRMS was observed 327.2324, which corresponds to the calculated mass value $[M + H]^+$ (m/z) = 327.2319 of BHT adduct **J**. *These above experiments indicate that when TEMPO was used as a radical scavenger, it had minimal effect in reducing the product* ***3a*** *formation and the yield was observed in 53%. Also, the TEMPO-trapped benzylic adduct was not observed in HRMS. Whereas when BHT was used as a radical scavenger the yield of the reaction was decreased drastically and also the BHT trapped adduct was observed in HRMS analysis.*



For TEMPO (2 eq.) yield is 59%

BHT (2 eq.) Trace amount

In an oven-dried reaction tube *o*-phenylenediamines **1a** (1 mmol), benzyl alcohol **2a** (1.2 mmol), Cat. C (0.2 mmol), Cs_2CO_3 (1 mmol), and TEMPO or BHT (3 mmol) were dissolved under an atmosphere of air in toluene. The reaction mixture was heated and stirred at 120 °C for 20 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled and dried under reduced pressure. Then ethyl acetate was added to the crude residue and washed with a saturated solution of $NaHCO_3$ (3×15 mL). The obtained organic fraction was dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford a residue. After that, the residue was purified using column chromatography by the gradient elution method with (EtOAc/hexane, 10-15%) ratio as the eluting solvent to generate compound **4a**.



Spectrum Plot Report

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Plate Pos.
Method (Acq) General method.m
Instrument Instrument 1
IRM Status Success
Comment
Operator
Acq. Time (Local) 26-10-2024 5.29.01 PM (UTC+05:30)

HRMS (ESI) m/z: calcd for $C_{22}H_{31}O_2$ $[M+H]^+$ = 327.2319

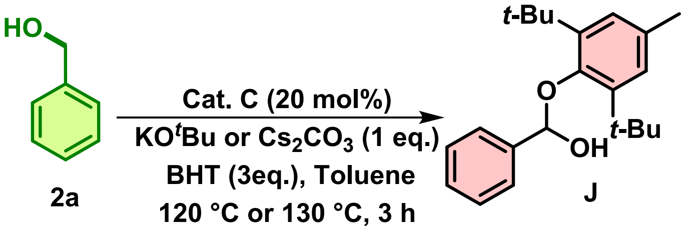
HRMS (ESI) m/z: observed for $C_{22}H_{31}O_2$ $[M+H]^+$ = 327.2326

Figure S4. BHT adduct of benzylic radical in the formation of product 4a.

Also, the reaction mixture was analyzed immediately after the completion of the reaction in a high-resolution mass spectrometer. In the case of BHT, the HRMS was observed 327.2326. that corresponds to the calculated mass value $[M + H]^+$ (m/z) = 327.2319 of BHT adduct **J**.

*The above experiments indicate that when TEMPO was used as a radical scavenger, it had minimal effect in reducing the product 4**a** formation, and the yield was observed in 59%. Also, the TEMPO-trapped benzylic adduct was not observed in HRMS. Whereas when BHT was used as a radical scavenger, only a trace amount of product 4a was produced, and the corresponding BHT-trapped adduct was observed in HRMS analysis.*

(v) Trapping of benzylic radical during the oxidation of benzyl alcohol



In an oven-dried reaction tube, benzyl alcohol **2a** (1 mmol), Cat. C (0.2 mmol), KO^{t}Bu (1 mmol) or Cs_2CO_3 (1 mmol), and BHT (3 mmol) were dissolved in toluene. The reaction mixture was heated and stirred at 130 °C or 120 °C for 3 h. After 3 h, the reaction mixture was analyzed using HRMS for both reactions.

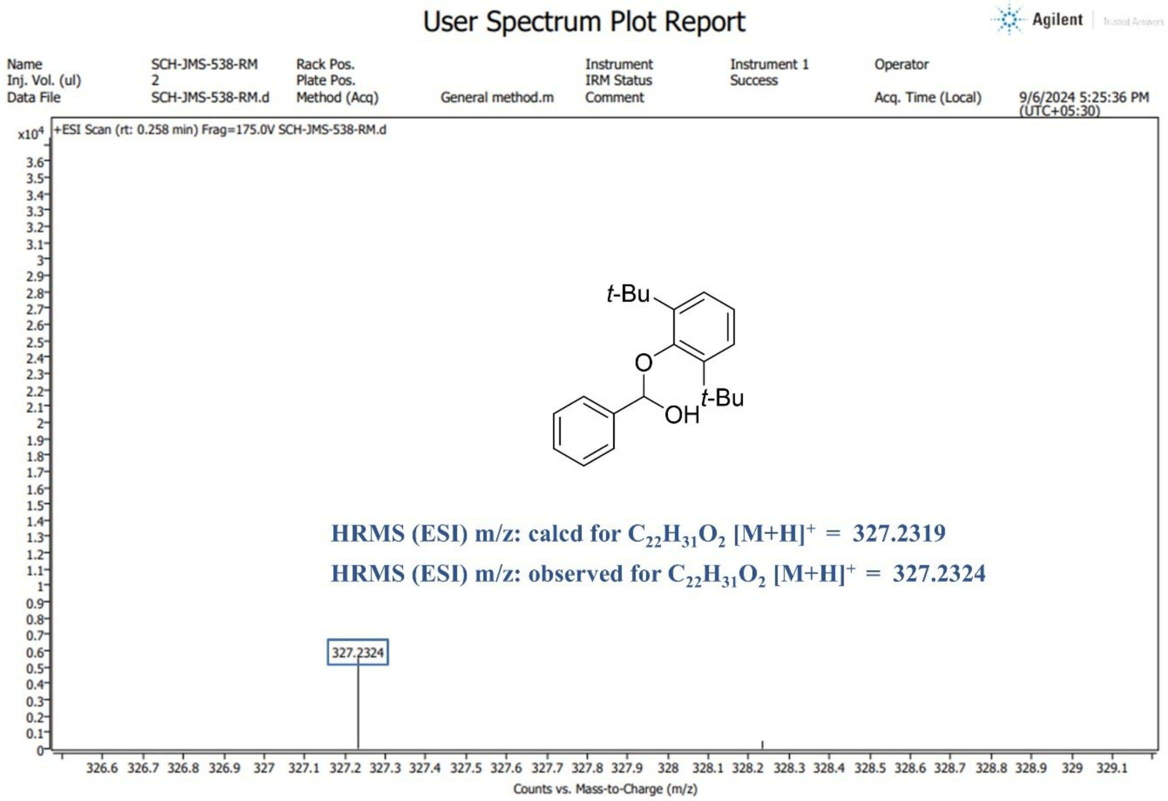

User Spectrum Plot Report

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Plate Pos.
Method (Acq) General method.m
Instrument Instrument 1
IRM Status Success
Comment
Operator
Acq. Time (Local) 9/6/2024 5:25:36 PM (UTC+05:30)

HRMS (ESI) m/z: calcd for $C_{22}H_{31}O_2$ $[M+H]^+$ = 327.2319

HRMS (ESI) m/z: observed for $C_{22}H_{31}O_2$ $[M+H]^+$ = 327.2324

Figure S5. Trapping of benzylic radical (KO^{t}Bu as the base).

In the case of the reaction, in which KO^{t}Bu was used as the base, HRMS was observed 327.2324 that corresponds to the calculated mass value [M + H]$^+$ (m/z) = 327.2319 of BHT adduct **J**.

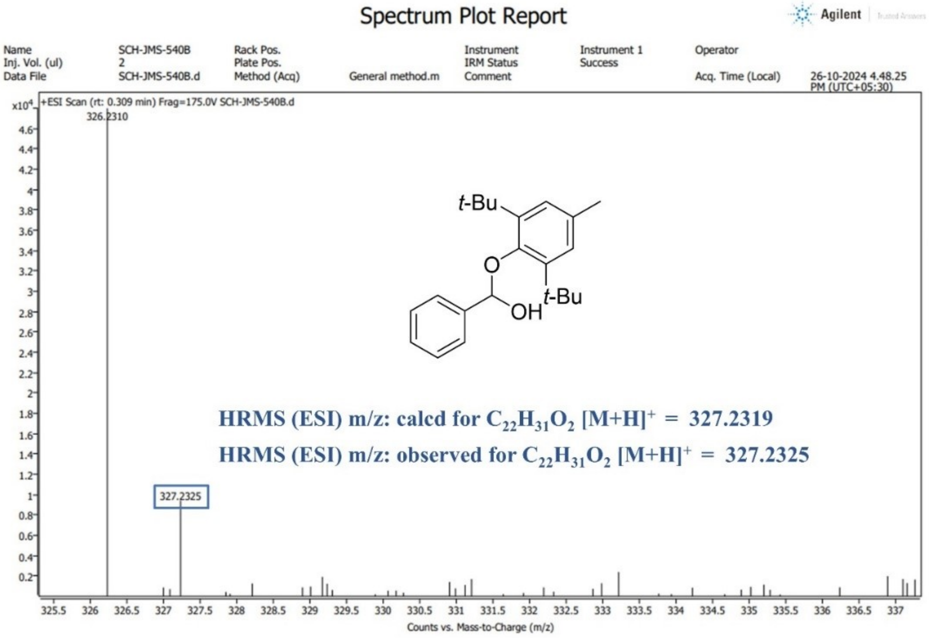


Figure S6. Trapping of benzylic radical (Cs_2CO_3 as the base).

Whereas, in the reaction using Cs2CO3, an HRMS value of 327.2325 was observed, which corresponds to the calculated mass value [M + H]$^+$ (m/z) = 327.2319 of the BHT adduct **J**.

The above experiments indicate that NHC caused the generation of a benzylic radical (organic radical) as per the previous report.[2,3] Later, with the aid of NHC, the benzyl alcohol is oxidized to benzaldehyde.

7. EPR studies

EPR studies were carried out to confirm free radical species in the reaction mixtures during the oxidation of benzyl alcohol to benzaldehyde.

(a) For Bis-Substituted benzimidazole

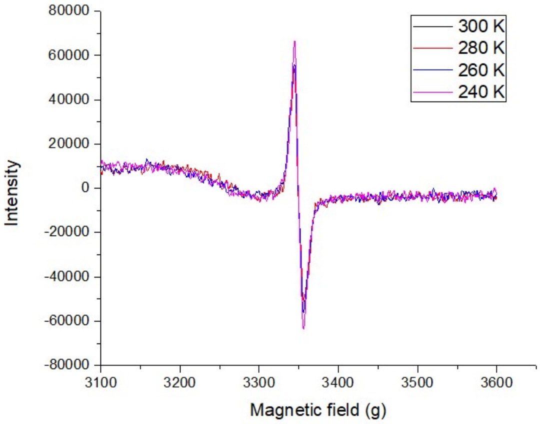


Figure S7. EPR spectrum of *o*-phenylenediamine, benzyl alcohol, Cat. C, and KO^{t}Bu, at a variable temperature.

To an oven-dried 10 mL pressure tube, *o*-phenylenediamine (1 mmol), benzyl alcohol (2.2 mmol), KO^{t}Bu (1 mmol), and cat. C (0.2 mmol) and toluene (1.5 mL) were taken under an atmosphere of air and heated at 130 °C for 3 h. Then a small aliquot was taken from the reaction mixture and analyzed for EPR at variable temperatures. The EPR signal was detected, which showed a sharp peak with a g-value of 2.00, which is close to those reported in the previous reports for ketyl radicals derived from the other different NHCs.[4–8]

This experiment indicates the formation of radical species during the reaction.

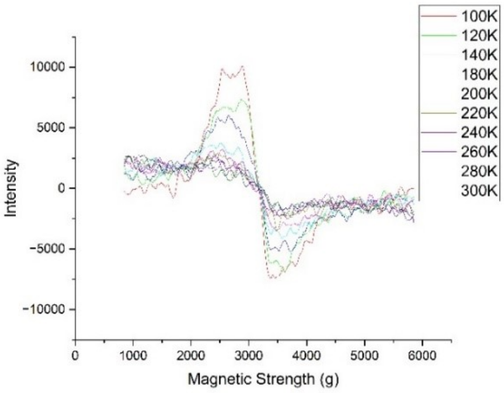


Figure S8. EPR spectrum of benzyl alcohol, Cat. C, and KO^{t}Bu at variable temperature.

Further benzyl alcohol (1 mmol), KO^{t}Bu (1 mmol), cat. C (0.2 mmol) were taken in toluene and stirred at 130 °C for 3 h. Then EPR experiment of the reaction mixture was performed at variable temperatures which showed a sharp peak with a g-value of 2.09.

This experiment indicates the formation of radical species during the oxidation from benzyl alcohol to benzaldehyde. Also, the observed g-value further confirms that the radical formed is a benzylic radical.

(b) For Mono-Substituted benzimidazole

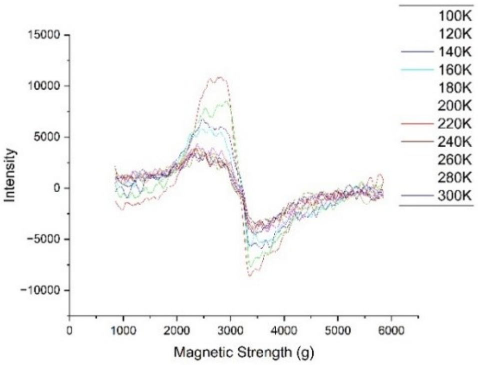


Figure S9. EPR spectrum of *o*-phenylenediamine, benzyl alcohol, Cat. C, and Cs_2CO_3, at variable temperature.

To an oven-dried 10 mL pressure tube *o*-phenylenediamine (1 mmol), benzyl alcohol (1.2 mmol), Cs_2CO_3 (1 mmol), cat. C (0.2 mmol) and toluene (1.5 mL) were taken under an atmosphere of air and heated at 120 °C for 3 h. Then a small aliquot was taken from the reaction mixture and analyzed for EPR at variable temperatures. The EPR signal was detected which shows a sharp peak with a g-value of 2.05.

This experiment indicates the formation of radical species during the reaction.

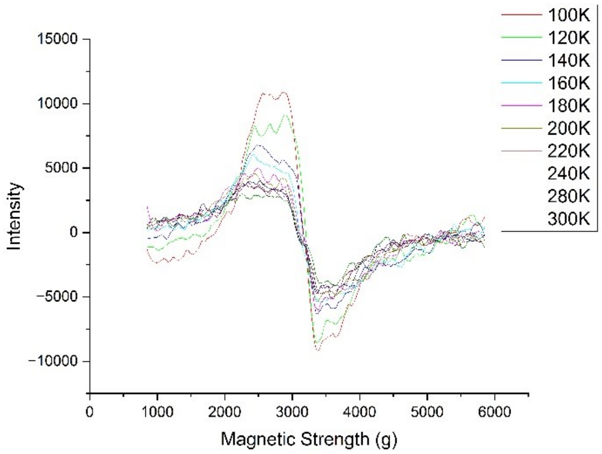


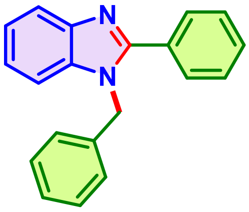
Figure S10. EPR spectrum of benzyl alcohol, Cs_2CO_3, and Cat. C at variable temperature.

Further benzyl alcohol (1 mmol), cat. C (0.2 mmol), Cs_2CO_3 (1 mmol), were dissolved in toluene and stirred at 120 °C for 3 h. Then EPR was performed at variable temperatures which shows a sharp peak with a g-value of 2.06.

This experiment indicates the formation of radical species during the oxidation from benzyl alcohol to benzaldehyde. Also, the observed g-value further confirms that the radical formed is a benzylic radical.

8. Synthesis and characterization of NHC-catalysed compounds

1-benzyl-2-phenyl-1*H*-benzo[*d*]imidazole (3a)

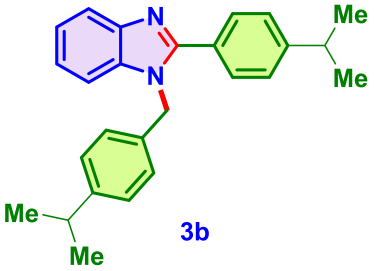


3a

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), benzyl alcohol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 1-benzyl-2-phenyl-1*H*-benzo[*d*]imidazole **3a**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 85%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.73-7.71 (m, 3H), 7.53-7.51 (m, 3H), 7.47-7.46 (m, 1H), 7.30-7.21 (m, 5H), 6.99 (d, J = 7.05 Hz, 2H), 5.58 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 153.78, 143.19, 137.46, 136.40, 130.65, 130.37, 129.56, 129.32, 128.01, 126.61, 123.23, 122.75, 119.80, 111.64, 47.96; HRMS (ESI/QTOF) m/z: calcd. for $C_{20}H_{17}N_2$ $[M + H]^+$ 285.1386, found 285.1394.

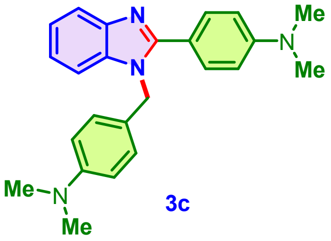
1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole (3b)


3b

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), (4-isopropylphenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole **3b**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 74%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.7 (d, J = 7.25 Hz, 1H), 7.66 (d, J = 7.7 Hz, 2H), 7.41-7.39 (m, 3H), 7.22 (qu, 2H), 7.15 (d, J = 7.6 Hz, 2H), 6.92 (d, J = 7.6 Hz, 2H), 5.53 (s, 2H), 2.96 (qu, 1H), 2.81 (qu, 1H), 1.24 (s, 3H), 1.22 (s, 3H), 1.13 (s, 3H), 1.12 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 153.82, 150.79, 148.08, 143.22, 136.36, 134.85, 129.55, 128.16, 127.31, 127.24, 126.51, 123.07, 122.66, 119.66, 111.61, 47.75, 33.82, 33.51, 24.29, 24.19; HRMS (ESI/QTOF) m/z: calcd. for $C_{26}H_{29}N_2$ $[[M + H]^+$ 369.2325, found 369.2323.

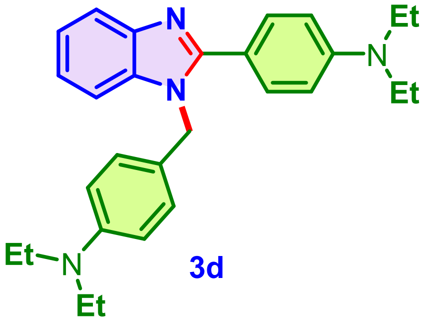
4-(1-(4-(dimethylamino)benzyl)-1*H*-benzo[*d*]imidazol-2-yl)-*N*,*N*-dimethylaniline (3c)


3c

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), (4-(dimethylamino)phenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 4-(1-(4-(dimethylamino)benzyl)-1*H*-benzo[*d*]imidazol-2-yl)-*N*,*N*-dimethylaniline **3c**.

Purification: column chromatography (EtOAc/hexane, 12-18%).Yield 85%, white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 7.95 Hz, 1H), 7.64 (s, 1H), 7.62 (s, 1H), 7.27-7.26 (m, 1H), 7.21-7.15 (m, 2H), 7.02 (d, J = 8.9 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 6.68 (d, J = 8.75 Hz, 2H), 5.37 (s, 2H), 3.00 (s, 6H), 2.93 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.12, 151.28, 150.06, 143.43, 136.48, 130.38, 127.01, 124.43, 122.20, 119.36, 117.54, 112.89, 111.89, 110.46, 48.13, 40.62, 40.28; HRMS (ESI/QTOF) m/z: calcd. for $C_{24}H_{27}N_4$ $[M + H]^+$ 371.2230, found 371.2237.

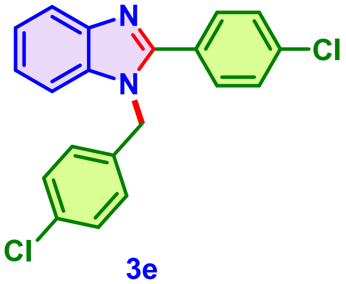
4-(1-(4-(diethylamino)benzyl)-1*H*-benzo[*d*]imidazol-2-yl)-*N*,*N*-diethylaniline (3d)


3d

Following the general procedure, treatment *o*-phenylenediamines (1 mmol), (4-(diethylamino)phenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 4-(1-(4-(diethylamino)benzyl)-1*H*-benzo[*d*]imidazol-2-yl)-*N*,*N*-diethylaniline **3d.**

Purification: column chromatography (EtOAc/hexane, 12-18%). Yield 87%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.61 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.75 Hz, 2H), 7.34 (d, J = 7.6 Hz, 1H), 7.18-7.12 (m, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 8.6 Hz, 2H), 5.39 (s, 2H), 3.40 (dd, J = 8.6 Hz, 4H), 3.26 (dd, , 4H), 1.13 (t, J = 7 Hz, 6H), 1.03 (t, J = 6.95 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 154.68, 148.97, 147.51, 143.58, 136.65, 130.70, 127.73, 123.67, 122.15, 122.10, 119.05, 116.84, 112.35, 111.69, 111.20, 47.77, 44.18, 44.08, 12.94, 12.91; HRMS (ESI/QTOF) m/z: calcd. for $C_{28}H_{35}N_4$ [M + H]$^+$ 427.2856, found 427.2859.

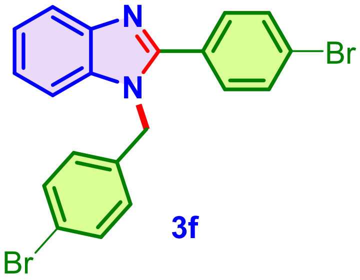
1-(4-chlorobenzyl)-2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole (3e)


3e

Following the general procedure, treatment *o*-phenylenediamines (1 mmol), (4-chlorophenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 1-(4-chlorobenzyl)-2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole **3e**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 63%, white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 1H), 7.59 (s, 1H), 7.58 (s, 1H), 7.44 (s, 1H), 7.43 (s, 1H), 7.35-7.30 (m, 3H), 7.28-7.27 (m, 1H), 7.20-7.18 (m, 1H), 7.03 (s, 1H), 7.01 (s, 1H), 5.40 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.97, 143.17, 136.43, 136.00, 134.72, 133.93, 130.52, 129.47, 129.24, 128.43, 127.32, 123.56, 123.14, 120.27, 110.39, 47.87; HRMS (ESI/QTOF) m/z: calcd. for $C_{20}H_{15}Cl_2N_2$ [M+H]$^+$ 353.0607, found 353.0609.

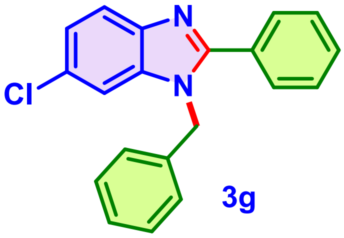
1-(4-bromobenzyl)-2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole (3f)


3f

Following the general procedure, treatment *o*-phenylenediamines (1 mmol), (4-bromophenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 1-(4-bromobenzyl)-2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole **3f**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 69%, white solid, ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.86 (d, *J* = 8 Hz, 1H), 7.60 (s, 1H), 7.59 (s, 1H), 7.52 (s, 1H), 7.50 (s, 1H), 7.47 (s, 1H), 7.46 (s, 1H), 7.35-7.32 (m, 1H), 7.28-7.27 (m, 1H), 7.20-7.18 (m, 1H), 6.96 (d, *J* = 8.35 Hz, 2H), 5.37 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) *δ* 153.01, 143.14, 135.99, 135.23, 132.43, 132.21, 130.72, 128.83, 127.63, 124.79, 123.61, 123.18, 121.98, 120.27, 110.40, 47.92; HRMS (ESI/QTOF) m/z: calcd. for $C_{20}H_{15}Br_2N_2$ $[M + H]^+$ 440.9597, found 440.9604.

1-benzyl-6-chloro-2-phenyl-1*H*-benzo[*d*]imidazole (3g)

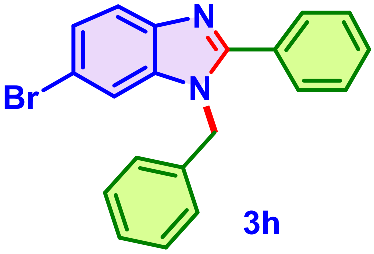


3g

Following the general procedure, treatment 4-chlorobenzene-1,2-diamine (1 mmol), benzyl alcohol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C temperature for 24 h, followed by purification to afford 1-benzyl-6-chloro-2-phenyl-1*H*-benzo[*d*]imidazole **3g**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 59%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) *δ* 7.74-7.71 (m, 3H), 7.64 (d, *J* = 1.85 Hz, 1H), 7.54-7.50 (m, 3H), 7.30-7.27 (m, 3H), 7.25-7.22 (m, 1H), 6.97 (s, 1H), 6.96 (s, 1H), 5.60 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) *δ* 154.90, 141.92, 137.22, 137.12, 130.61, 130.19, 129.57, 129.36, 128.10, 127.67, 126.60, 123.17, 121.13, 111.61, 48.01; HRMS (ESI/QTOF) m/z: calcd. for $C_{20}H_{16}ClN_2$ $[M + H]^+$ 319.0997, found 319.1004.

1-benzyl-6-bromo-2-phenyl-1*H*-benzo[*d*]imidazole (3h)

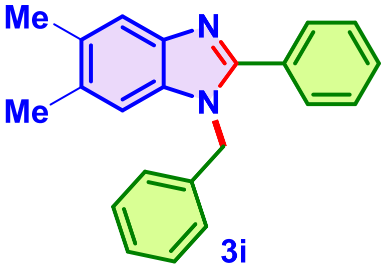


3h

Following the general procedure, treatment 4-bromobenzene-1,2-diamine (1 mmol), benzyl alcohol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 1-benzyl-6-bromo-2-phenyl-1*H*-benzo[*d*]imidazole **3h**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 57%, white solid, ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.00 (s, 1H), 7.67 (d, *J* = 7 Hz, 2H), 7.50-7.45 (m, 3H), 7.34-7.32 (m, 4H), 7.07-7.06 (m, 3H), 5.44 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) *δ* 155.18, 135.89, 134.97, 130.40, 129.34, 129.25, 128.97, 128.09, 126.23, 125.97, 122.83, 115.88, 111.89, 48.62; HRMS (ESI/QTOF) m/z: calcd. for $C_{20}H_{16}BrN_2$ $[M + H]^+$ 363.0491, found 363.0500.

1-benzyl-5,6-dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole (3i)

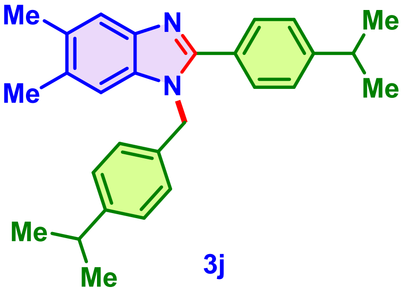


3i

Following the general procedure, treatment 4,5-dimethylbenzene-1,2-diamine (1 mmol), benzyl alcohol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 1-benzyl-5,6-dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole **3i**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 77%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.69-7.67 (m, 2H), 7.50-7.48 (m, 4H), 7.29-7.28 (m, 2H), 7.24-7.21 (m, 2H), 6.96 (d, J = 7.3 Hz, 2H), 5.52 (s, 2H), 2.31 (s, 3H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 152.84, 141.82, 137.67, 135.05, 131.96, 131.19, 130.85, 130.11, 129.38, 129.31, 129.26, 127.92, 126.43, 119.83, 111.48, 47.84, 20.70, 20.43; HRMS (ESI/QTOF) m/z: calcd. for $C_{22}H_{21}N_2$ $[M + H]^+$ 313.1699, found 313.1698.

1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3j)

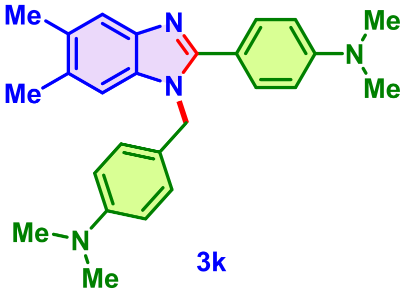


3j

Following the general procedure, treatment 4,5-dimethylbenzene-1,2-diamine (1 mmol), (4-isopropylphenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24, h followed by purification to afford 1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole **3j**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 71%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.62 (d, J = 7.95 Hz, 2H), 7.47 (s, 1H), 7.37 (d, J = 7.85 Hz, 2H), 7.19 (s, 1H), 7.15 (d, J = 7.85 Hz, 2H), 6.88 (d, J = 7.65 Hz, 2H), 5.48 (s, 2H), 2.94 (qu, 1H), 2.81 (qu, 1H), 2.30 (s, 3H), 2.27 (s, 3H), 1.22 (s, 3H), 1.21 (s, 3H), 1.14 (s, 3H), 1.13 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 153.00, 150.49, 148.03, 141.96, 135.09, 135.04, 131.67, 130.98, 129.40, 128.49, 127.17, 127.14, 126.43, 119.78, 111.41, 47.73, 33.76, 33.47, 24.22, 24.12, 20.57, 20.31; HRMS (ESI) m/z: calcd. for $C_{28}H_{33}N_2$ $[M + H]^+$ 397.2638, found 397.2642.

4-(1-(4-(dimethylamino)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)-*N*,*N*-dimethylaniline (3k)

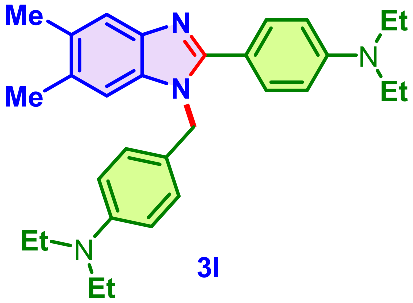


3k

Following the general procedure, treatment 4,5-dimethylbenzene-1,2-diamine (1 mmol), (4-(dimethylamino)phenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 4-(1-(4-(dimethylamino)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)-*N*,*N*-dimethylaniline **3k**.

Purification: column chromatography (EtOAc/hexane, 15-18%). Yield 79%, white solid, ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.60-7.57 (m, 3H), 7.01 (d, 8.6 Hz, 2H), 6.97 (s, 1H), 6.72-6.68 (m, 4H), 5.31 (s, 2H), 2.99 (s, 6H), 2.93 (s, 6H), 2.36 (s, 3H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) *δ* 154.30, 151.11, 149.95, 141.88, 135.02, 131.27, 130.99, 130.24, 126.89, 124.75, 119.46, 117.75, 112.91, 111.88, 110.60, 47.96, 40.68, 40.34, 20.66, 20.44; HRMS (ESI/QTOF) m/z: calcd. for $C_{26}H_{31}N_4$ $[M + H]^+$ 399.2543, found 399.2548.

4-(1-(4-(diethylamino)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)-*N*,*N*-diethylaniline (3l)

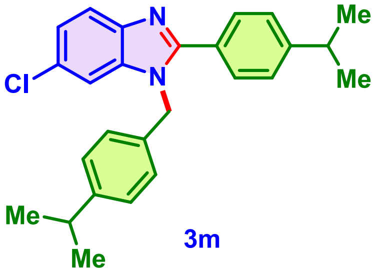


3l

Following the general procedure, treatment 4,5-dimethylbenzene-1,2-diamine (1 mmol), (4-(diethylamino)phenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 4-(1-(4-(diethylamino)benzyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)-*N*,*N*-diethylaniline **3l**.

Purification: column chromatography (EtOAc/hexane, 15 -18%). Yield 81%, white solid, ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.59-7.56 (m, 3H), 6.99-6.97 (m, 3H), 6.68-6.62 (m, 4H), 5.31 (s, 2H), 3.40-3.31 (m, 8H), 2.36 (s, 3H), 2.31 (s, 3H), 1.18-1.13 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) *δ* 154.40, 148.57,147.19, 141.82, 135.03, 131.08, 130.88, 130.48, 127.10, 123.49, 119.34, 116.64, 112.01, 111.25, 110.64, 47.99, 44.44, 44.38, 20.60, 20.38, 12.65; HRMS (ESI/QTOF) m/z: calcd. for $C_{30}H_{39}N_4$ $[M + H]^+$ 455.3169, found 455.3177.

6-chloro-1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole (3m)

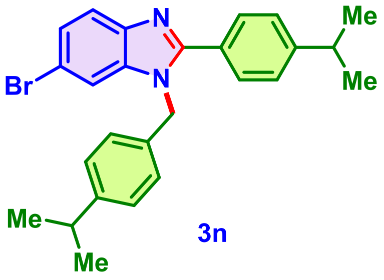


3m

Following the general procedure, treatment 4-chlorobenzene-1,2-diamine (1 mmol), (4-isopropylphenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 6-chloro-1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole **3m**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 55%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.70 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 7.9 Hz, 2H), 7.54 (s, 1H), 7.39 (d, J = 8 Hz, 2H), 7.24 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 7.95 Hz, 2H), 6.91 (d, J = 7.9 Hz, 2H), 5.53 (s, 2H), 2.97 (qu, 1H), 2.82 (qu, 1H), 1.25 (s, 3H), 1.23 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 155.07, 151.09, 148.30, 142.09, 137.25, 134.41, 129.59, 127.81, 127.55, 127.29, 126.63, 126.55, 123.08, 122.97, 120.98, 111.46, 47.96, 33.85, 33.51, 24.17, 24.07; HRMS (ESI/QTOF) m/z: calcd. for $C_{26}H_{28}ClN_2$ [M + H]$^+$ 403.1936, found 403.1941.

6-bromo-1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole (3n)

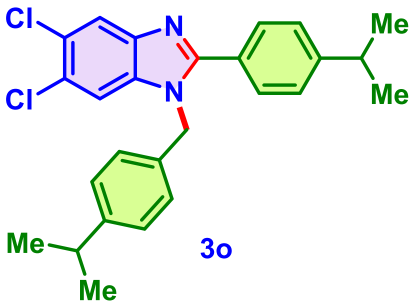


3n

Following the general procedure, treatment 4-bromobenzene-1,2-diamine (1 mmol), (4-isopropylphenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 6-bromo-1-(4- isopropylbenzyl)-2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole **3n**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 57%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.67-7.65 (m, 4H), 7.40-7.35 (m, 3H), 7.16 (d, J = 7.9 Hz, 2H), 6.91 (d, J = 7.95 Hz, 2H), 5.53 (s, 2H), 2.97 (qu, 1H), 2.83 (qu, 1H), 1.25 (s, 3H), 1.23 (s, 3H), 1.16 (s, 3H), 1.14 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 154.91, 151.10, 148.29, 142.40, 137.73, 134.43, 129.58, 127.78, 127.25, 126.58, 125.68, 121.42, 115.36, 114.34, 47.94, 33.79, 33.47, 24.17, 24.07; HRMS (ESI/QTOF) m/z: calcd. for $C_{26}H_{28}BrN_2$ [M + H]$^+$ 447.1430, found 447.1429.

5,6-dichloro-1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole (3o)

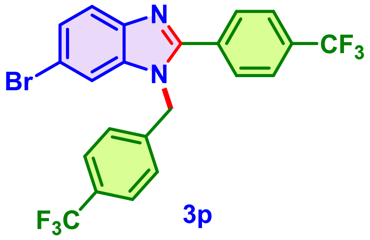


3o

Following the general procedure, treatment 4,5-dichlorobenzene-1,2-diamine (1 mmol), (4-isopropylphenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 5,6-dichloro-1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole **3o**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 51%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.96 (s, 1H), 7.80 (s, 1H), 7.67 (d, J = 7.85 Hz, 2H), 7.40 (d, J = 7.95 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 6.90 (d, J = 7.65 Hz, 2H), 5.56 (s, 2H), 2.97 (qu, 1H), 2.83 (qu, 1H), 1.25 (s, 3H), 1.24 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 156.36, 151.39, 148.36, 142.85, 136.12, 134.20, 129.63, 127.45, 127.30, 127.25, 126.62, 125.51, 125.38, 120.86, 113.24, 48.13, 33.80, 33.47, 24.17, 24.05; HRMS (ESI/QTOF) m/z: calcd. for $C_{26}H_{27}Cl_2N_2$ [M + H]$^+$ 437.1546, found 437.1553.

6-bromo-1-(4-(trifluoromethyl)benzyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole (3p)

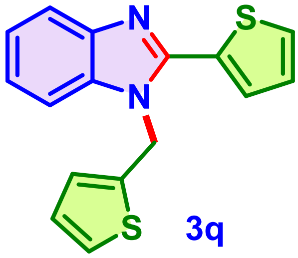


3p

Following the general procedure, treatment 4-bromobenzene-1,2-diamine (1 mmol), (4-(trifluoromethyl)phenyl)methanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 6-bromo-1-(4-(trifluoromethyl)benzyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole **3p**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 53%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.94-7.92 (m, 2H), 7.89-7.87 (m, 3H), 7.75 (d, J = 8.6 Hz, 1H), 7.67 (d, J = 8.25 Hz, 2H), 7.46-7.44 (m, 1H), 7.18 (d, J = 8.05 Hz, 2H), 5.76 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 153.20, 142.23, 141.67, 137.80, 134.02, 130.43, 127.44, 126.26, 121.93, 116.32, 114.54, 47.82; ^{19}F NMR (470 MHz, DMSO-d_6) δ -60.99 (s, 3F), -61.33 (s, 3F). HRMS (ESI/QTOF) m/z: calcd. for $C_{22}H_{14}BrF_6N_2$ [M + H]$^+$ 499.0239, found 499.0246.

2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1*H*-benzo[*d*]imidazole (3q)

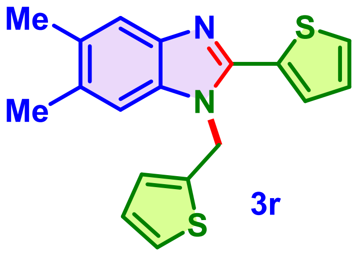


3q

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), thiophen-2-ylmethanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1*H*-benzo[*d*]imidazole **3q**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 54%, brown solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.82 (d, J = 5 Hz, 1H), 7.74-7.66 (m, 3H), 7.40 (d, J = 4.9 Hz, 1H), 7.30-7.24 (m, 3H), 7.02 (s, 1H), 6.96-6.94 (m, 1H), 5.94 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 147.27, 142.92, 139.88, 136.37, 132.61, 130.23, 128.96, 128.39, 127.59, 126.63, 126.51, 123.45, 123.12, 119.48, 111.35, 43.56; HRMS (ESI/QTOF) m/z: calcd. for $C_{16}H_{13}N_2S_2$ $[M + H]^+$ 297.0515, found 297.0523.

5,6-dimethyl-2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1*H*-benzo[*d*]imidazole (3r)

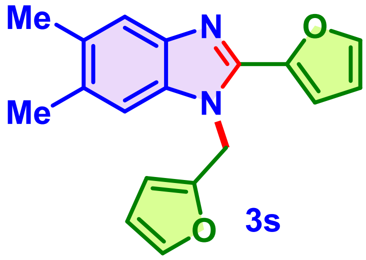


3r

Following the general procedure, treatment 4,5-dimethylbenzene-1,2-diamine (1 mmol), thiophen-2-ylmethanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 5,6-dimethyl-2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1*H*-benzo[*d*]imidazole **3r**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 51%, brown solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.77 (s, 1H), 7.64 (s, 1H), 7.45-7.39 (m, 3H), 7.21 (s, 1H), 6.97 (d, J = 14.8 Hz, 2H), 5.86 (s, 2H), 2.33-2.31 (m, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 146.35, 141.50, 140.11, 134.92, 132.91, 132.32, 131.61, 129.73, 128.88, 127.81, 127.60, 126.38, 119.48, 111.24, 43.53, 20.75, 20.42; HRMS (ESI/QTOF) m/z: calcd. for $C_{18}H_{17}N_2S_2$ $[M + H]^+$ 325.0828, found 325.0834.

2-(furan-2-yl)-1-(furan-2-ylmethyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (3s)

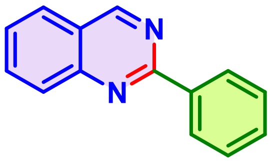


3s

Following the general procedure, treatment 4,5-dimethylbenzene-1,2-diamine (1 mmol), furan-2-ylmethanol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 2-(furan-2-yl)-1-(furan-2-ylmethyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole **3s**.

Purification: column chromatography (EtOAc/hexane, 10-12%). Yield 47%, brown solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.96 (s, 1H), 7.53 (s, 1H), 7.47 (s, 1H), 7.40 (s, 1H), 7.17 (s, 1H), 6.72 (s, 1H), 6.39 (d, J = 20.15 Hz, 2H), 5.68 (s, 2H), 2.34 (s, 3H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 150.46, 145.54, 145.21, 143.61, 143.12, 141.63, 134.40, 132.26, 131.53, 119.55, 112.73, 112.58, 111.32, 111.08, 109.02, 41.42, 20.76, 20.39; HRMS (ESI/QTOF) m/z: calcd. for $C_{18}H_{17}N_2O_2$ $[M + H]^+$ 293.1285, found 293.1294.

2-phenylquinazoline (6)

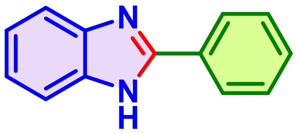


6

Following the general procedure, treatment 2-(aminomethyl)aniline (1 mmol), benzyl alcohol (2.2 mmol), cat. C (20 mol%), and KO^{t}Bu (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 24 h, followed by purification to afford 2-phenylquinazoline **6**.

Purification: column chromatography (EtOAc/hexane, 0-5%). Yield 53%, white solid, ^1H NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.62-8.60 (m, 2H), 8.09 (d, J = 8.45 Hz, 1H), 7.94-7.89 (m, 2H), 7.63-7.59 (m, 1H), 7.55-7.49 (m, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 161.16, 160.60, 150.86, 138.12, 134.21, 130.70, 128.73, 128.66, 127.37, 127.22, 123.69; HRMS (ESI/QTOF) m/z: calcd. for $C_{14}H_{11}N_2$ $[M + H]^+$ 207.0917, found 207.0923.

2-phenyl-1*H*-benzo[*d*]imidazole (4a)

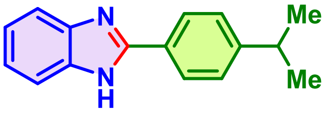


4a

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), benzyl alcohol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved under an atmosphere of air in toluene. The reaction mixture was heated and stirred at 130 °C for 20 h, followed by purification to afford 2-phenyl-1*H*-benzo[*d*]imidazole **4a**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 74%, white solid, ^1H NMR (500 MHz, DMSO-d_6) δ 12.92 (s, 1H), 8.17 (d, J = 7.15 Hz, 2H), 7.66 (d, J = 7.6 Hz, 1H), 7.56-7.47 (m, 4H), 7.23-7.17 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 151.73, 144.29, 135.50, 130.65, 130.39, 129.49, 126.94, 123.08, 122.21, 119.39, 111.86; HRMS (ESI/QTOF) m/z: calcd. for $C_{13}H_{11}N_2$ $[M + H]^+$ 195.0917, found 195.0922.

2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole (4b)

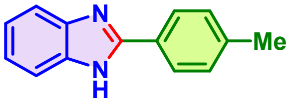


4b

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), (4-isopropylphenyl)methanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 130 °C for 20 h, followed by purification to afford 2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole **4b**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 65%, white solid, ^1H NMR (500 MHz, DMSO-d_6) δ 12.85 (s, 1H), 8.09 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.25 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.18 (qu, 2H), 2.95 (qu, 1H), 1.25 (s, 3H), 1.23 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 151.89, 150.92, 144.32, 135.47, 129.50, 128.32, 127.45, 127.03, 122.89, 122.11, 119.23, 111.75, 33.88, 24.22; HRMS (ESI/QTOF) m/z: calcd. for $C_{16}H_{17}N_2$ $[M + H]^+$ 237.1386, found 237.1391.

2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole (4c)



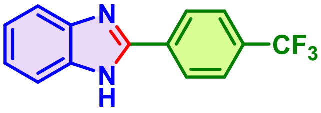
4c

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), *p*-tolylmethanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3

(1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole **4c**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 61%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.81 (s, 1H), 8.06 (t, J = 5.2 Hz, 2H), 7.63 (s, 1H), 7.50 (s, 1H), 7.35 (t, J = 5.45 Hz, 2H), 7.19-7.17 (m, 2H), 2.38-2.37 (m, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 151.91, 144.33, 140.09, 135.45, 130.03, 127.95, 126.91, 122.86, 122.09, 119.21, 111.71, 21.48; HRMS (ESI/QTOF) m/z: calcd. for $C_{14}H_{13}N_2$ $[M + H]^+$ 209.1073, found 209.1080.

2-(4-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole (4d)

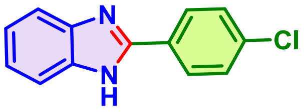


4d

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), (4-(trifluoromethyl)phenyl)methanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 2-(4-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole **4d**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 77%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.17 (s, 1H), 8.38 (d, J = 7.9 Hz, 2H), 7.93 (d, J = 8 Hz, 2H), 7.71 (d, J = 7.45 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.28-7.21 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 150.16, 144.23, 135.61, 134.46, 130.16 (q, $J_{C\text{-}F}$ =31.66), 127.57, 126.49, 124.65 (q, $^1J_{C\text{-}F}$ = 270.63Hz), 123.72, 122.60, 119.77, 112.18; ^{19}F NMR (470 MHz, DMSO-d_6) δ -61.14 (s, 3F). HRMS (ESI) m/z: calcd. for $C_{14}H_{10}F_3N_2$ $[M + H]^+$ 263.0791, found 263.0797.

2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole (4e)

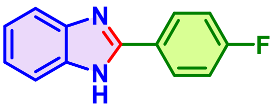


4e

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), (4-chlorophenyl)methanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole **4e**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 51%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.99 (s, 1H), 8.18 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 7.7 Hz, 1H), 7.63-7.62 (m, 2H), 7.53 (d, J = 7.65 Hz, 1H), 7.24-7.18 (m, 2H). ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ 150.67, 144.23, 135.53, 135.02, 129.60, 129.54, 128.65, 123.32, 122.38, 119.48, 111.95. HRMS (ESI/QTOF) m/z: calcd. for $C_{13}H_{10}ClN_2$ $[M + H]^+$ 229.0527, found 229.0536.

2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole (4f)

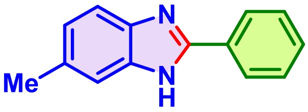


4f

Following the general procedure, treatment *o*-phenylenediamines (1 mmol), (4-fluorophenyl)methanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole **4f**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 71%, brown solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.76 (s, 1H), 8.23-8.20 (m, 2H), 7.65 (s, 1H), 7.53 (s, 1H), 7.37 (t, J = 8.75, 2H), 7.20 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 164.56, 162.60, 150.90, 144.26, 135.54, 129.24 (d, $J_{C\text{-}F}$ = 8.5 Hz), 127.32, 123.07, 122.26, 119.37, 116.54 (d, $J_{C\text{-}F}$ = 21.76 Hz), 111.86; ^{19}F NMR (470 MHz, DMSO-d_6) δ -110.67– -110.73 (m, 1F). HRMS (ESI/QTOF) m/z: calcd. for $C_{13}H_{10}FN_2$ $[M + H]^+$ 213.0823, found 213.0829.

6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole (4g)

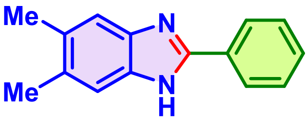


4g

Following the general procedure, treatment 4-methylbenzene-1,2-diamine (1 mmol), benzyl alcohol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole **4g**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 62%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.15-8.13 (m, 2H), 7.54-7.51 (m, 2H), 7.48-7.45 (m, 2H), 7.37 (s, 1H), 7.02 (d, J = 8.2 Hz, 1H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 151.48, 130.76, 130.21, 129.42, 126.85, 124.15, 21.81; HRMS (ESI/QTOF) m/z: calcd. for $C_{14}H_{13}N_2$ $[M + H]^+$ 209.1073, found 209.1080.

5,6-dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole (4h)

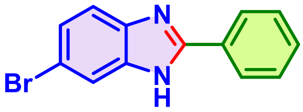


4h

Following the general procedure, treatment 4,5-dimethylbenzene-1,2-diamine (1 mmol), benzyl alcohol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 5,6-dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole **4h**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 63%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.63 (s, 1H), 8.12 (d, J = 8.1 Hz, 2H), 7.53 (t, J = 8.1 Hz, 2H), 7.46-7.44 (m, 1H), 7.35 (s, 2H), 2.31 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 150.93, 131.04, 129.93, 129.32, 126.77, 20.44; HRMS (ESI/QTOF) m/z: calcd. for $C_{15}H_{15}N_2$ $[M + H]^+$ 223.1230, found 223.1237.

6-bromo-2-phenyl-1*H*-benzo[*d*]imidazole (4i)

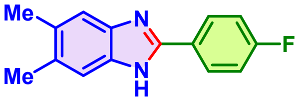


4i

Following the general procedure, treatment 4-bromobenzene-1,2-diamine (1 mmol), benzyl alcohol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 6-bromo-2-phenyl-1*H*-benzo[*d*]imidazole **4i**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 45%, white solid, ^{1}H NMR (500 MHz, DMSO-*d₆*) δ 13.0 (s, 1H), 8.11 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.24-7.18 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 150.79, 144.31, 135.57, 132.46, 129.99, 128.92, 123.74, 123.30, 122.38, 119.50, 111.92; HRMS (ESI/QTOF) m/z: calcd. for $C_{13}H_{10}BrN_2$ $[M + H]^+$ 273.0022, found 273.0026.

2-(4-fluorophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (4j)

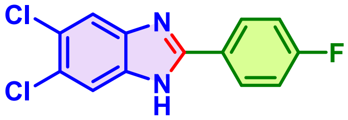


4j

Following the general procedure, treatment 4,5-dimethylbenzene-1,2-diamine (1 mmol), (4-fluorophenyl)methanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 2-(4-fluorophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole **4j**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 57%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.65 (s, 1H), 8.16-8.15 (m, 2H), 7.39- 7.35 (m, 4H), 2.31-2.29 (m, 6H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 164.34, 162.38, 150.00, 128.95 (d, $J_{C\text{-}F}$ = 8.11 Hz), 127.52, 116.44 (d, $J_{C\text{-}F}$ = 21.75 Hz), 20.53; ^{19}F NMR (470 MHz, DMSO-d_6) δ -111.56– -111.62 (m, 1F). HRMS (ESI/QTOF) m/z: calcd. for $C_{15}H_{14}FN_2$ $[M + H]^+$ 241.1136, found 241.1143.

5,6-dichloro-2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole (4k)



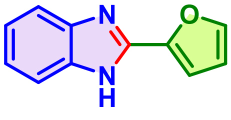
4k

Following the general procedure, treatment 4,5-dichlorobenzene-1,2-diamine (1 mmol), (4-fluorophenyl)methanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 5,6-dichloro-2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole **4k**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 59%, white solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.25 (s, 1H), 8.22-8.18 (m, 2H), 7.83 (s, 2H), 7.43-7.39 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 164.93, 162.96, 153.47, 129.64 (d, $J_{C\text{-}F}$ = 8.67 Hz), 126.42, 125.04, 116.65 (d, $J_{C\text{-}F}$ = 21.87 Hz); ^{19}F NMR (470 MHz, DMSO-d_6) δ -109.85–

-109.91 (m, 1F). HRMS (ESI/QTOF) m/z: calcd. for $C_{13}H_8Cl_2FN_2$ [M + H]$^+$ 281.0043, found 281.0046.

2-(furan-2-yl)-1*H*-benzo[*d*]imidazole (4l)

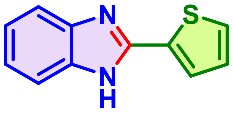


4l

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), furan-2-ylmethanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 2-(furan-2-yl)-1*H*-benzo[*d*]imidazole **4l**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 49%, white solid, ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 12.91 (s, 1H), 7.93 (s, 1H), 7.62-7.61 (m, 1H), 7.49-7.48 (m, 1H), 7.2-7.19 (m, 3H), 6.73-6.72 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-*d*$_6$) δ 146.05, 145.15, 144.15, 134.74, 123.17, 122.34, 119.27, 112.85, 111.87, 111.02; HRMS (ESI/QTOF) m/z: calcd. for $C_{11}H_9N_2O$ [M + H]$^+$ 185.0709, found 185.0716.

2-(thiophen-2-yl)-1*H*-benzo[*d*]imidazole (4m)

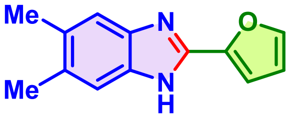


4m

Following the general procedure, treatment *o*-phenylenediamine (1 mmol), thiophen-2-ylmethanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 2-(thiophen-2-yl)-1*H*-benzo[*d*]imidazole **4m**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 53%, brown solid, ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 12.95 (s, 1H), 7.83-7.82 (m, 1H), 7.73-7.71 (m, 1H), 7.60-7.59 (m, 1H), 7.50-7.48 (m, 1H), 7.23-7.18 (m, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-*d*$_6$) δ 147.54, 134.17, 129.30, 128.83, 127.22, 123.16, 122.30, 119.05, 111.65; HRMS (ESI/QTOF) m/z: calcd. for $C_{11}H_9N_2S$ [M+H]$^+$ 201.0481, found 201.0486.

2-(furan-2-yl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (4n)

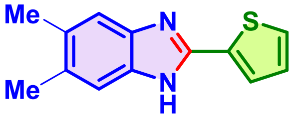


4n

Following the general procedure, treatment 4,5-dimethylbenzene-1,2-diamine (1 mmol), furan-2-ylmethanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at120°C for 20 h, followed by purification to afford 2-(furan-2-yl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole **4n**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 43%, brown solid, ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 12.65 (brs, 1H), 7.89-7.88 (m, 1H), 7.31 (s, 2H), 7.11-7.09 (m, 1H), 6.69-6.67 (m, 1H), 2.30-2.28 (m, 6H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-*d*$_6$) δ 146.29, 144.75, 143.33, 131.27, 112.76, 110.34, 20.50; HRMS (ESI/QTOF) m/z: calcd. for $C_{13}H_{13}N_2O$ $[M + H]^+$ 213.1022, found 213.1028.

5,6-dimethyl-2-(thiophen-2-yl)-1*H*-benzo[d]imidazole (4o)



4o

Following the general procedure, treatment 4,5-dimethylbenzene-1,2-diamine (1 mmol), thiophen-2-ylmethanol (1.2 mmol), cat. C (20 mol%), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene under an atmosphere of air. The reaction mixture was heated and stirred at 120 °C for 20 h, followed by purification to afford 5,6-dimethyl-2-(thiophen-2-yl)-1*H*-benzo[*d*]imidazole **4o**.

Purification: column chromatography (EtOAc/hexane, 10-15%). Yield 46%, brown solid, ^1H NMR (500 MHz, DMSO-d_6) δ 12.67 (s, 1H), 7.77-7.76 (m, 1H), 7.67 (t, $J = 3.95$ Hz, 1H), 7.35 (s, 1H), 7.24 (s, 1H), 7.19 (q, $J = 4.05$ Hz, 1H), 2.31-2.28 (m, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 146.68, 142.76, 134.56, 133.70, 131.81, 130.54, 128.69, 126.62, 119.11, 111.65, 20.52; HRMS (ESI/QTOF) m/z: calcd. for $C_{13}H_{13}N_2S$ $[M + H]^+$ 229.0794, found 229.0798.

9. References.

[1] Q. Zhou, S. Liu, M. Ma, H. Z. Cui, X. Hong, S. Huang, J. F. Zhang, X. F. Hou, "N-Heterocyclic Carbene (NHC)-Catalyzed One-Pot Aerobic Oxidative Synthesis of 2-Substituted Benzo[d]oxazoles, Benzo[d]thiazoles and 1,2-Disubstituted Benzo[d]imidazoles" *Synthesis (Stuttg)* 2018, *50*, 1315–1322.

[2] R. Sharma, A. Rahaman T A, J. Sen, I. V. Mashevskaya, S. Chaudhary, "Discovering the role of N-heterocyclic carbene as hydrogen borrowing organocatalyst: metal-free, direct N-alkylation of amines with benzyl alcohols" *Organic Chemistry Frontiers* 2023, *10*, 730–744.

[3] B. S. Li, Y. Wang, R. S. J. Proctor, Y. Zhang, R. D. Webster, S. Yang, B. Song, Y. R. Chi, "Carbene-catalysed reductive coupling of nitrobenzyl bromides and activated ketones or imines via single-electron-transfer process" *Nature Communications 2016 7:1* 2016, *7*, 1–8.

[4] J. K. Mahoney, R. Jazzar, G. Royal, D. Martin, G. Bertrand, "The Advantages of Cyclic Over Acyclic Carbenes To Access Isolable Capto-Dative C-Centered Radicals" *Chemistry – A European Journal* 2017, *23*, 6206–6212.

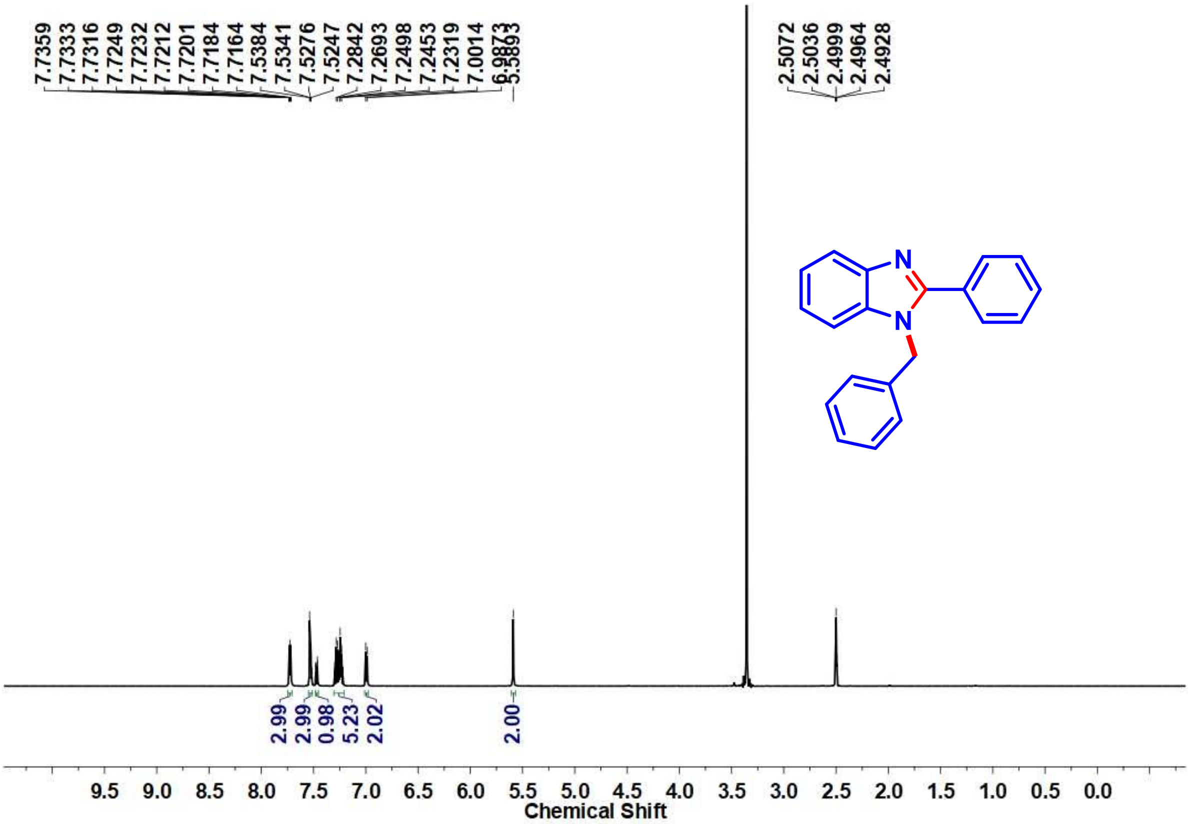
[5] J. L. Peltier, M. R. Serrato, V. Thery, J. Pecaut, E. Tomá S-Mendivil, G. Bertrand, R. Jazzar, D. Martin, "An air-stable radical with a redox-chameleonic amide †" *Chem. Commun* 2023, *59*, 595.

[6] X. Li, Y.-Y. Ren, C. Chen, L.-Y. Sun, Y.-F. Han, “Isolation and characterization of an annelated N-heterocyclic carbene stabilized Breslow enolate †” *Cite this: Org. Chem. Front* 2024, *11*, 1076.

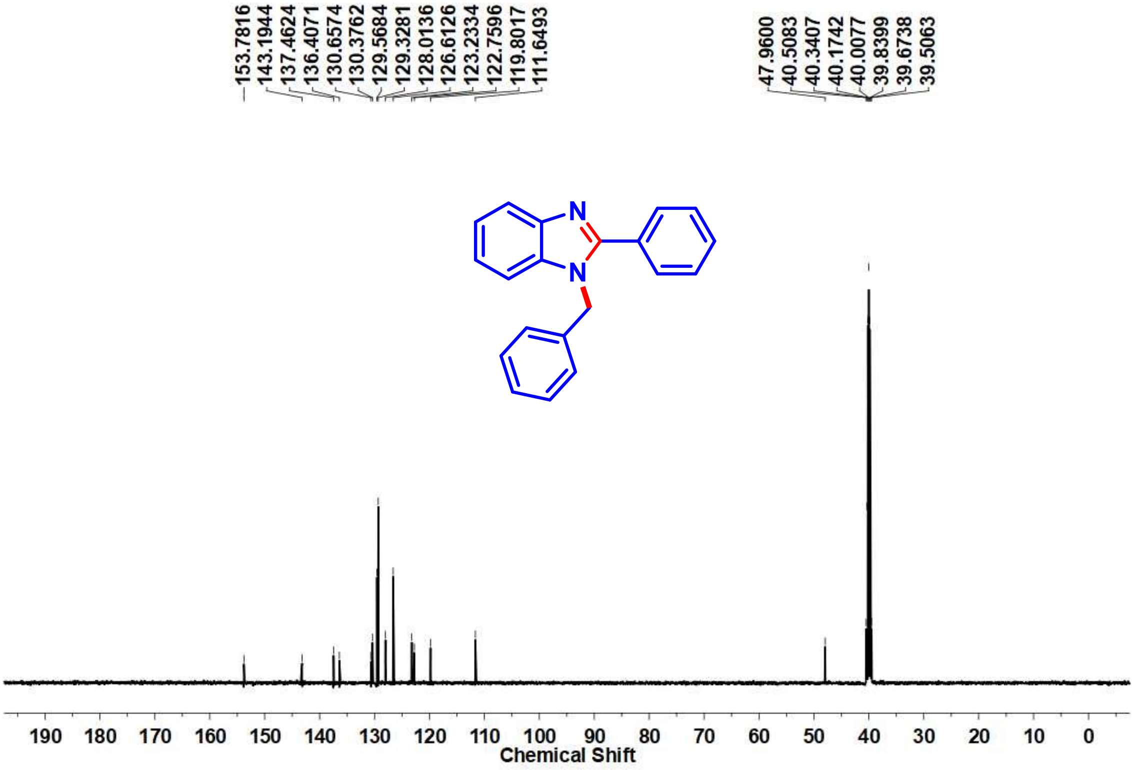
[7] C. L. Deardorff, R. E. Sikma, C. P. Rhodes, T. W. Hudnall, “Carbene-derived a-acyl formamidinium cations: organic molecules with readily tunable multiple redox processes † ChemComm” *Chem. Commun* 2016, *52*, 9024.

[8] J. K. Mahoney, D. Martin, F. Thomas, C. E. Moore, A. L. Rheingold, G. Bertrand, “Air-Persistent Monomeric (Amino)(carboxy) Radicals Derived from Cyclic (Alkyl)(Amino) Carbenes” *J Am Chem Soc* 2015, *137*, 7519–7525.

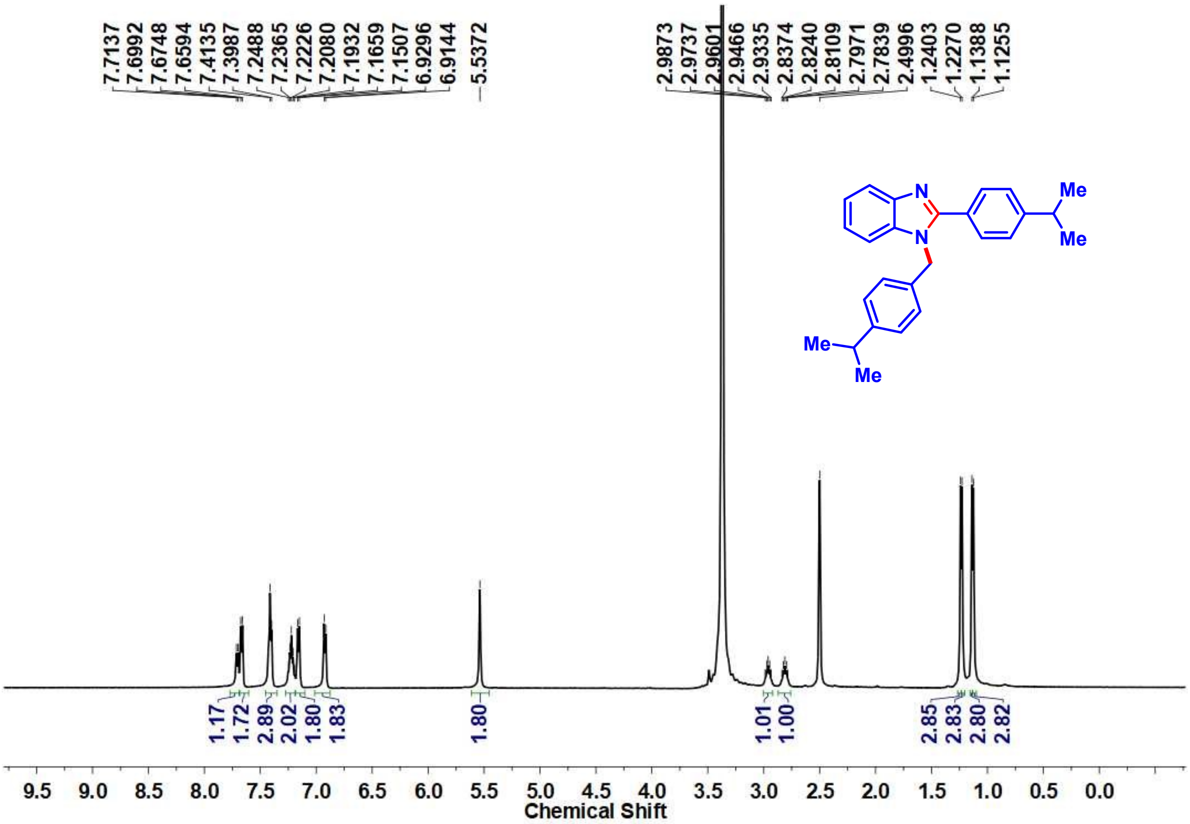
10. ^{1}H, ^{13}C, and ^{19}F NMR spectral data of NHC-catalysed compounds



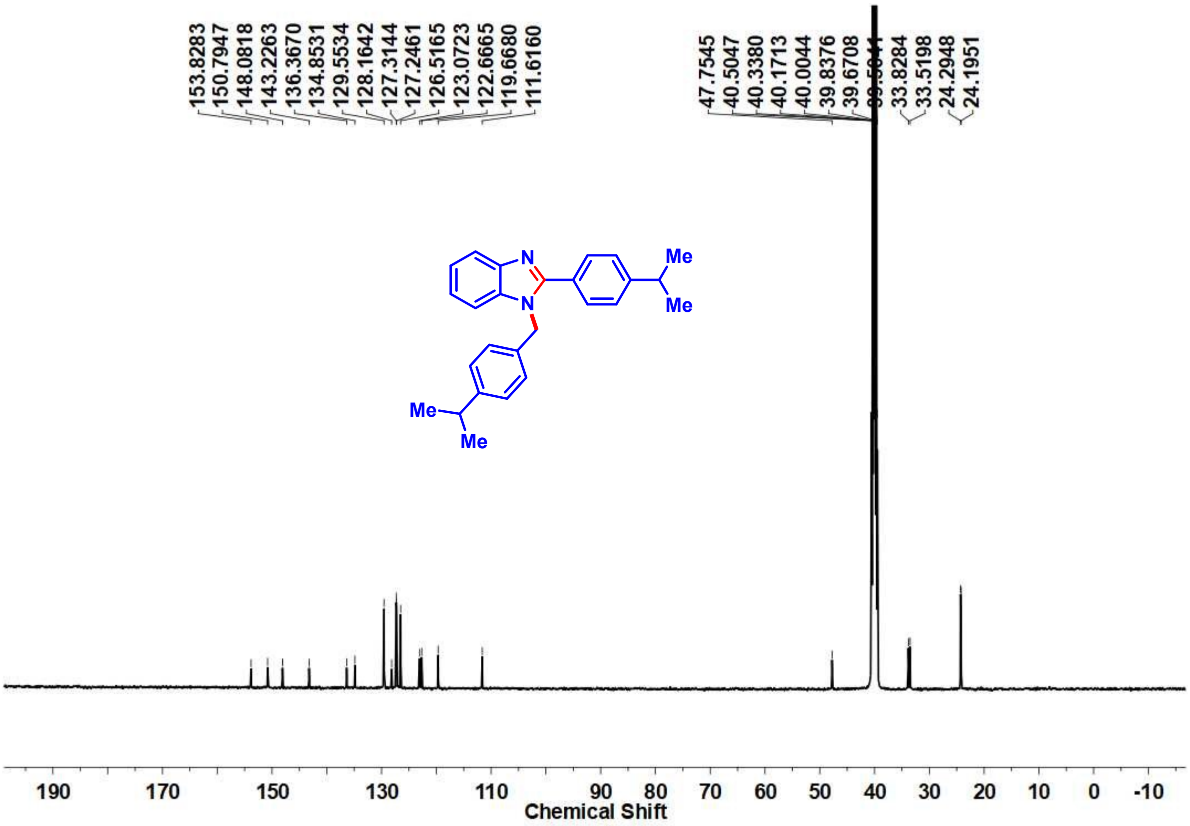
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3a



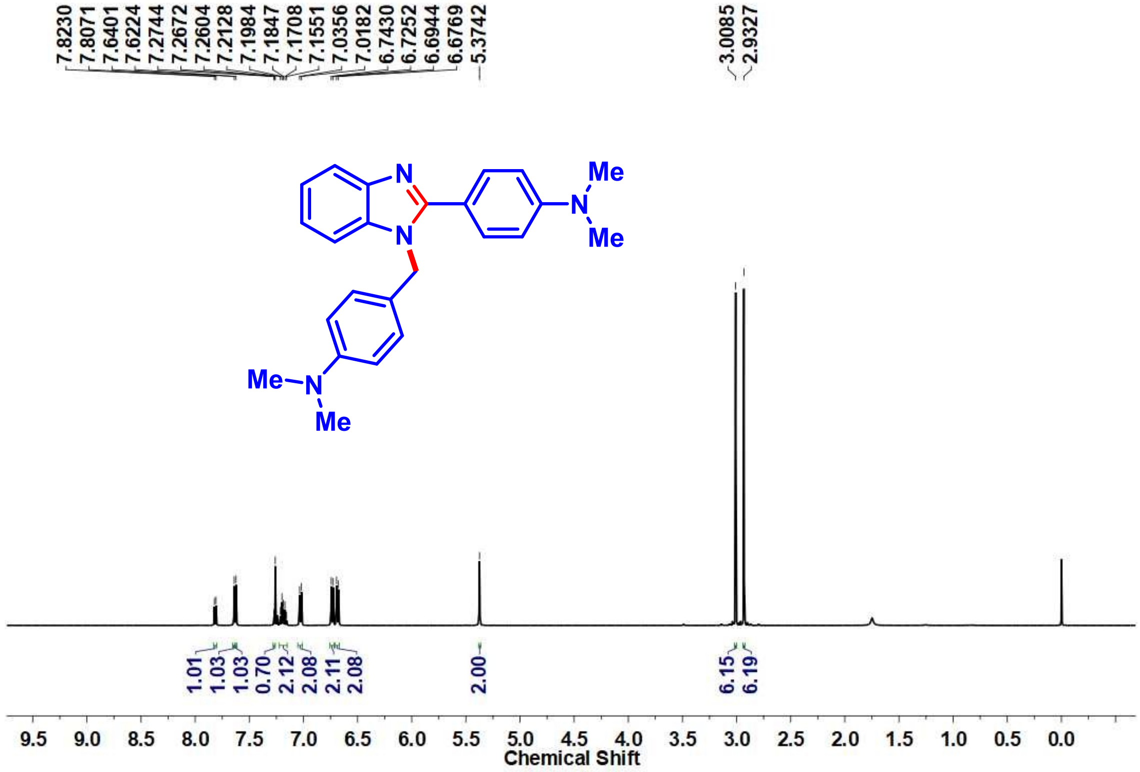
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 3a



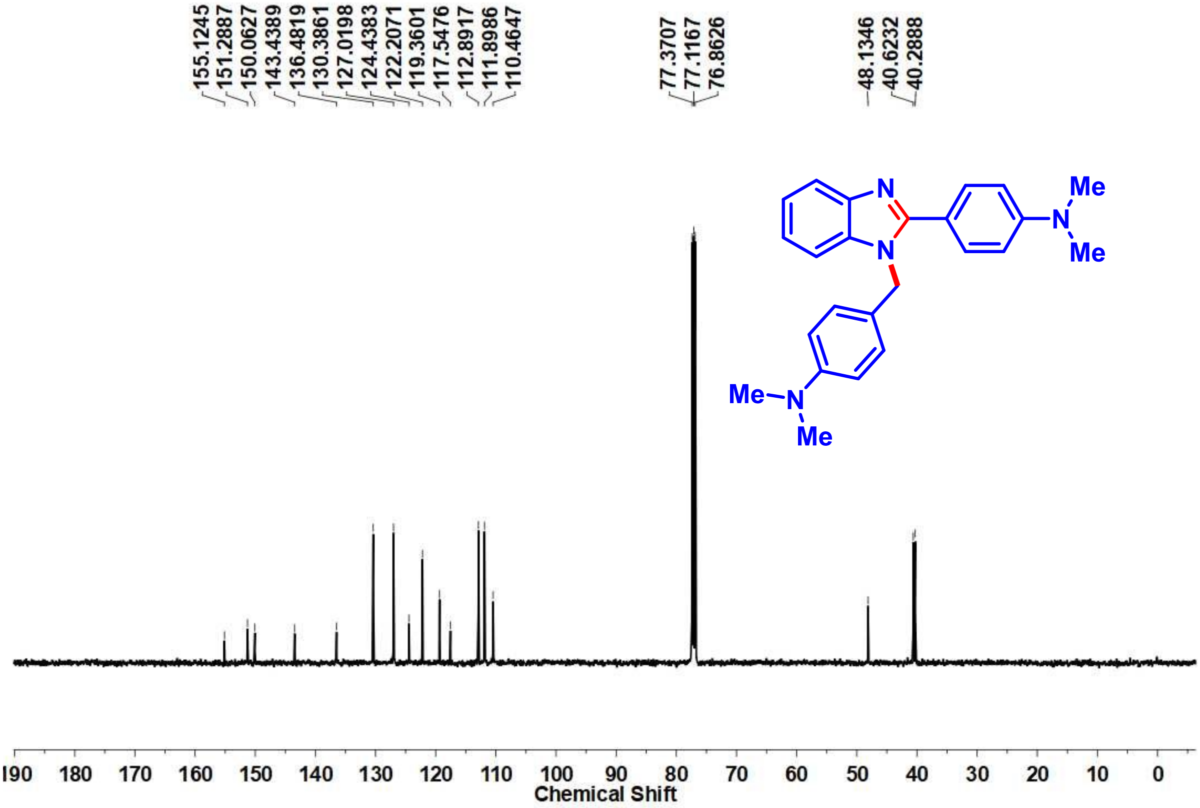
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3b



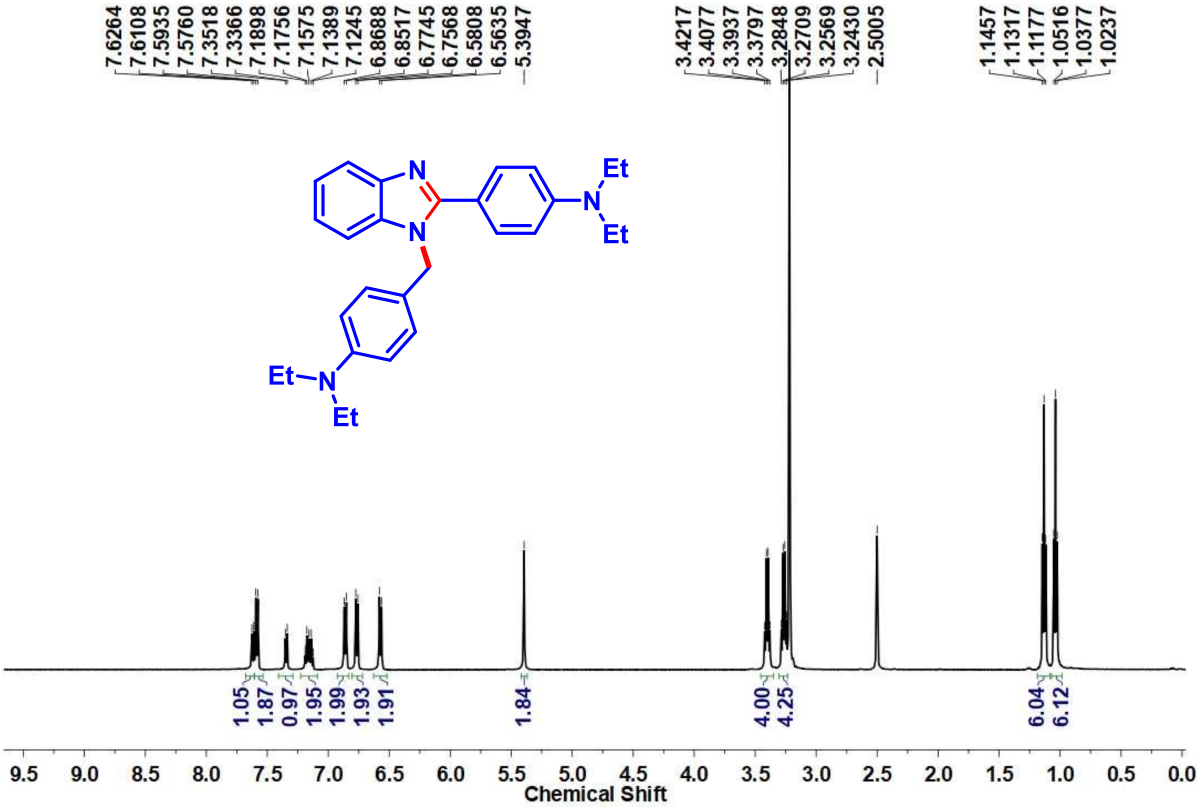
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 3b



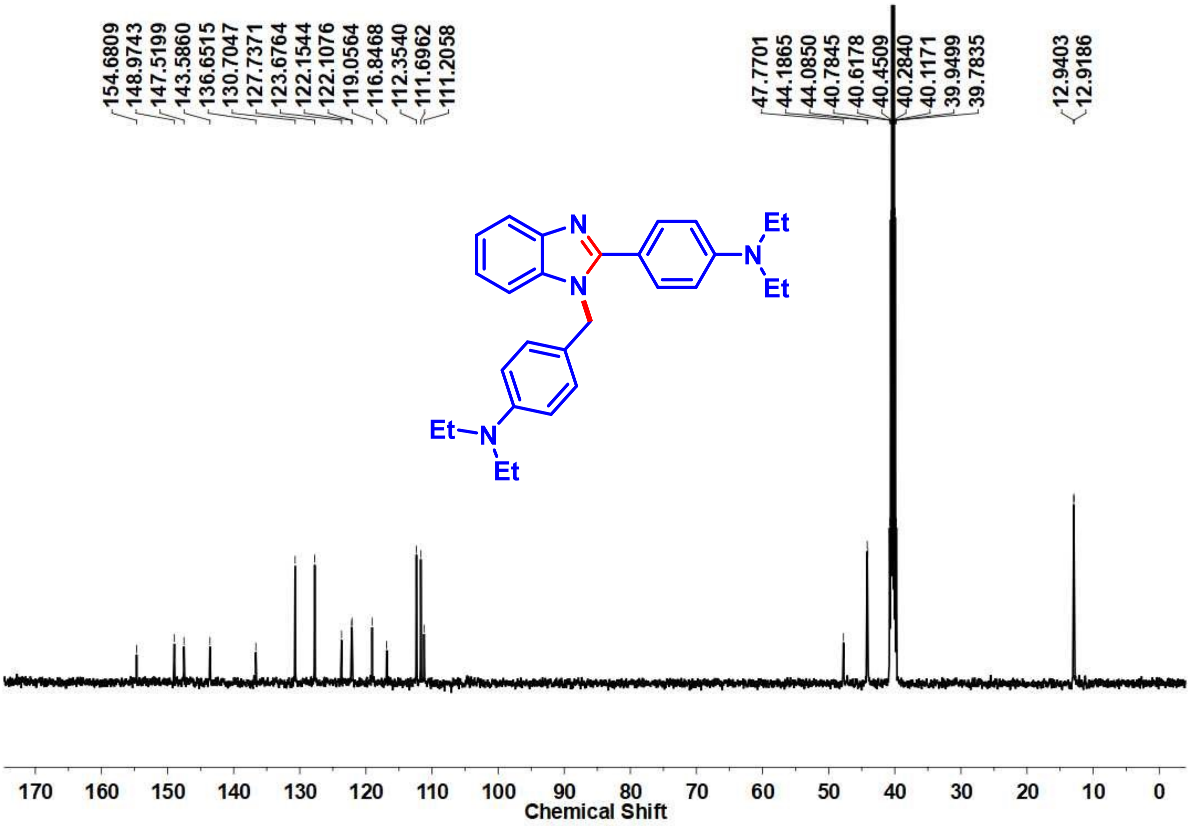
^{1}H NMR (CDCl$_3$, 500 MHz) Spectrum of 3c



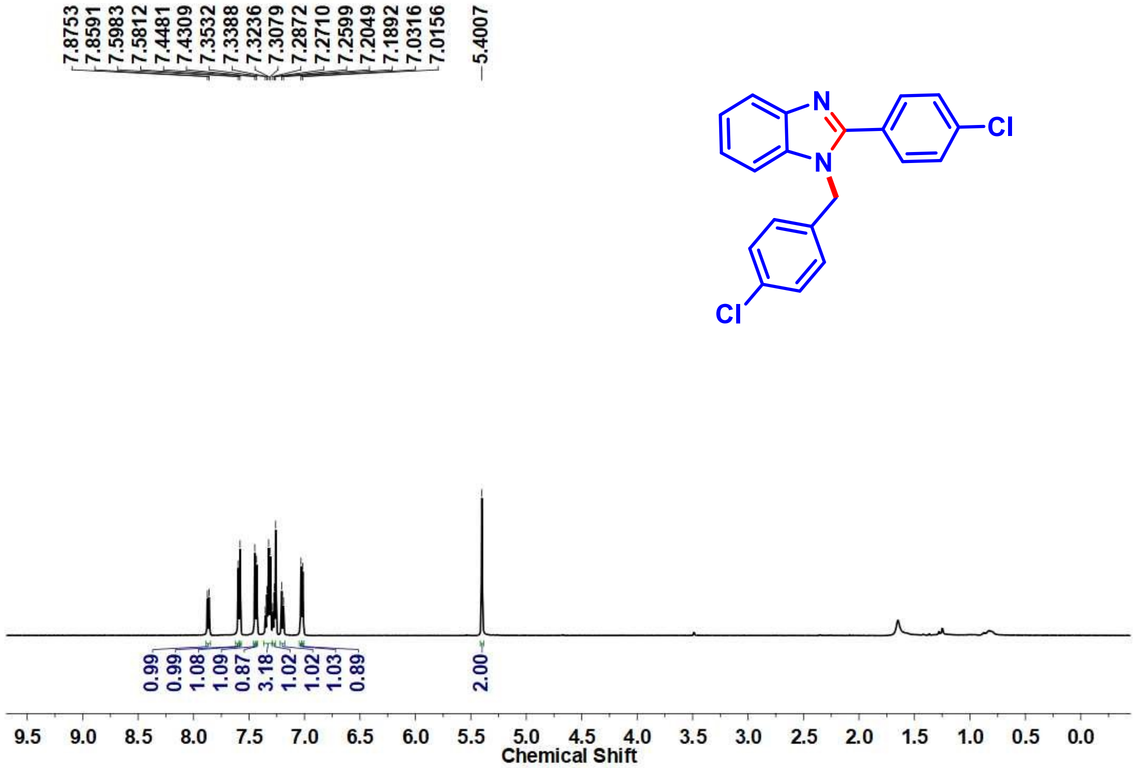
^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) Spectrum of 3c



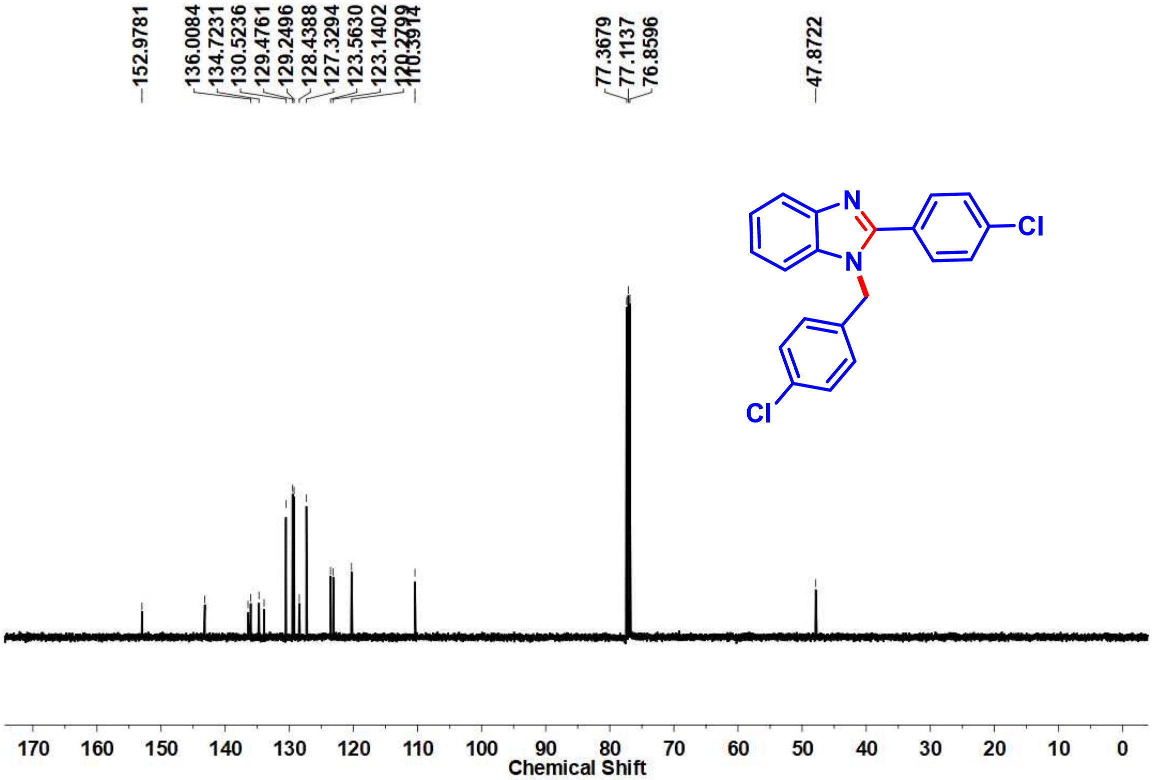
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3d



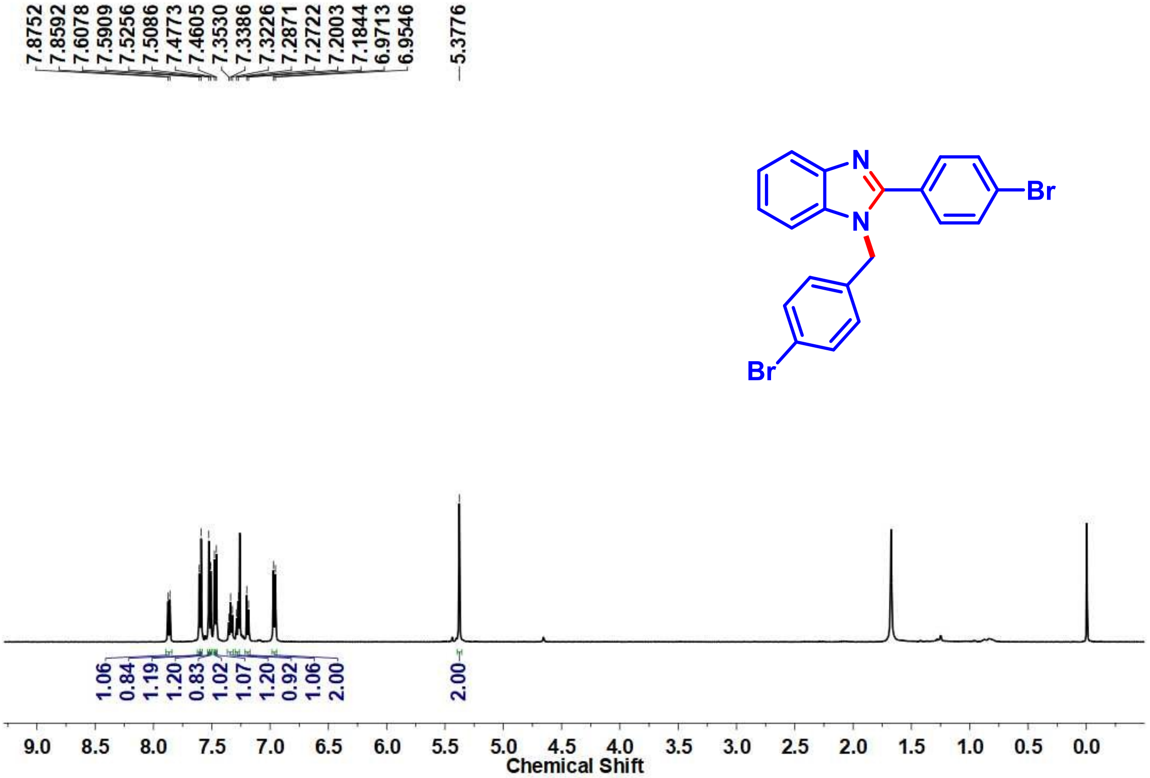
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 3d



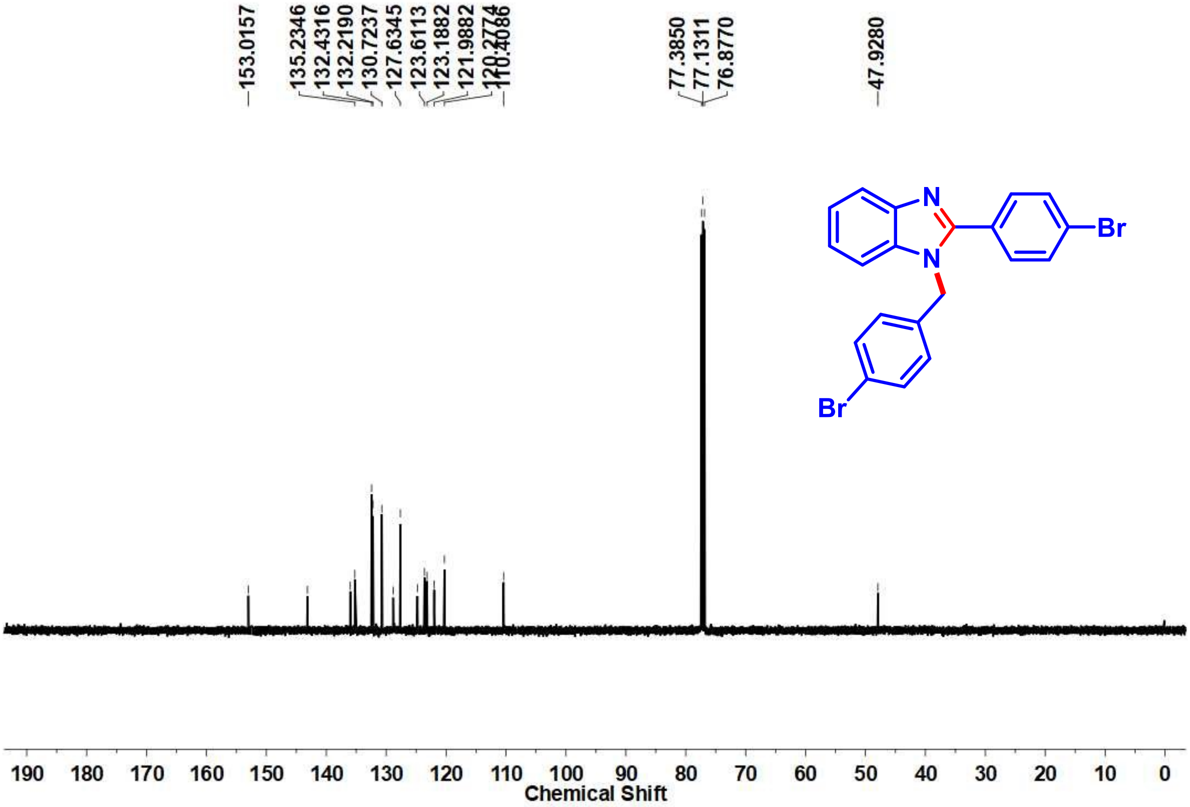
^{1}H NMR (CDCl$_3$, 500 MHz) Spectrum of 3e



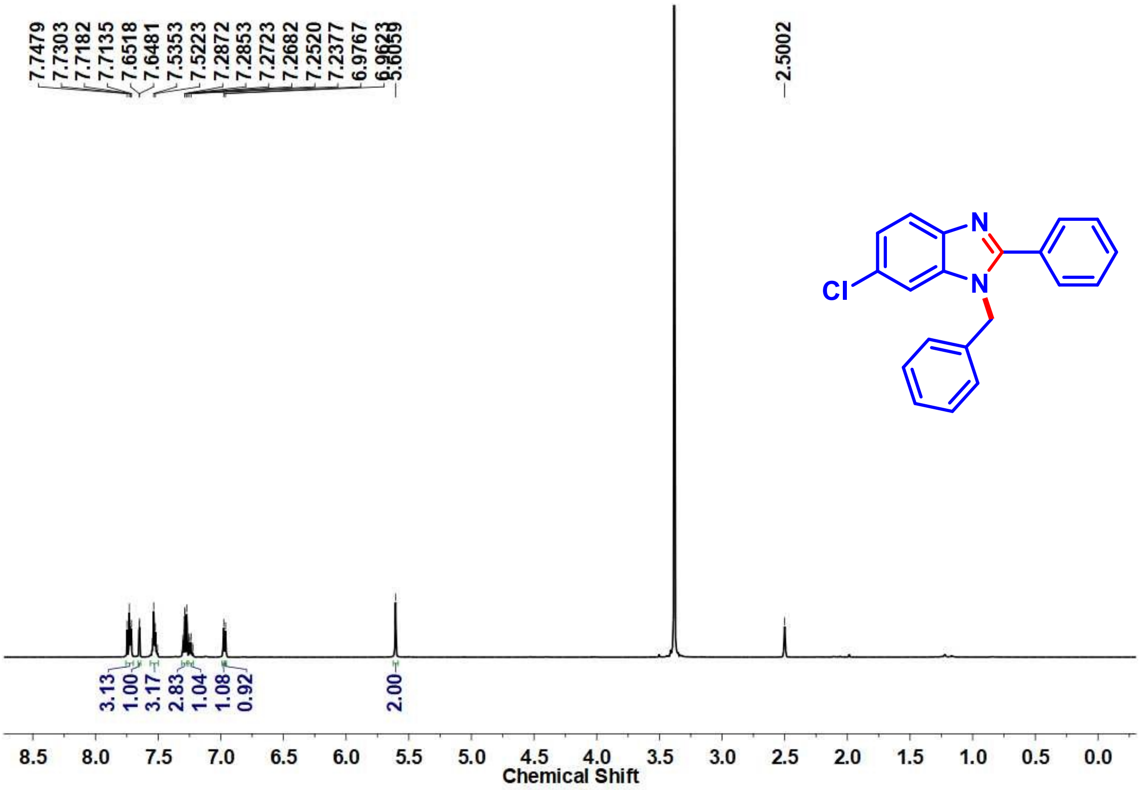
^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) Spectrum of 3e



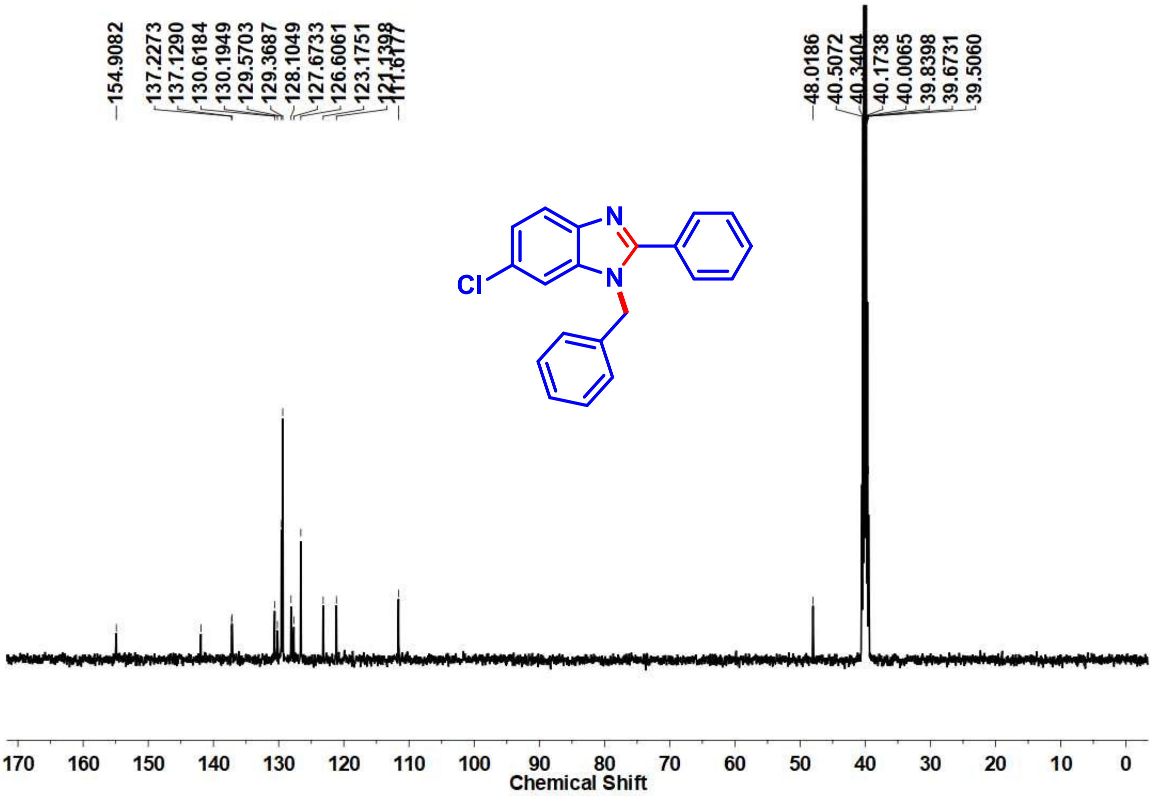
^{1}H NMR (CDCl$_3$, 500 MHz) Spectrum of 3f



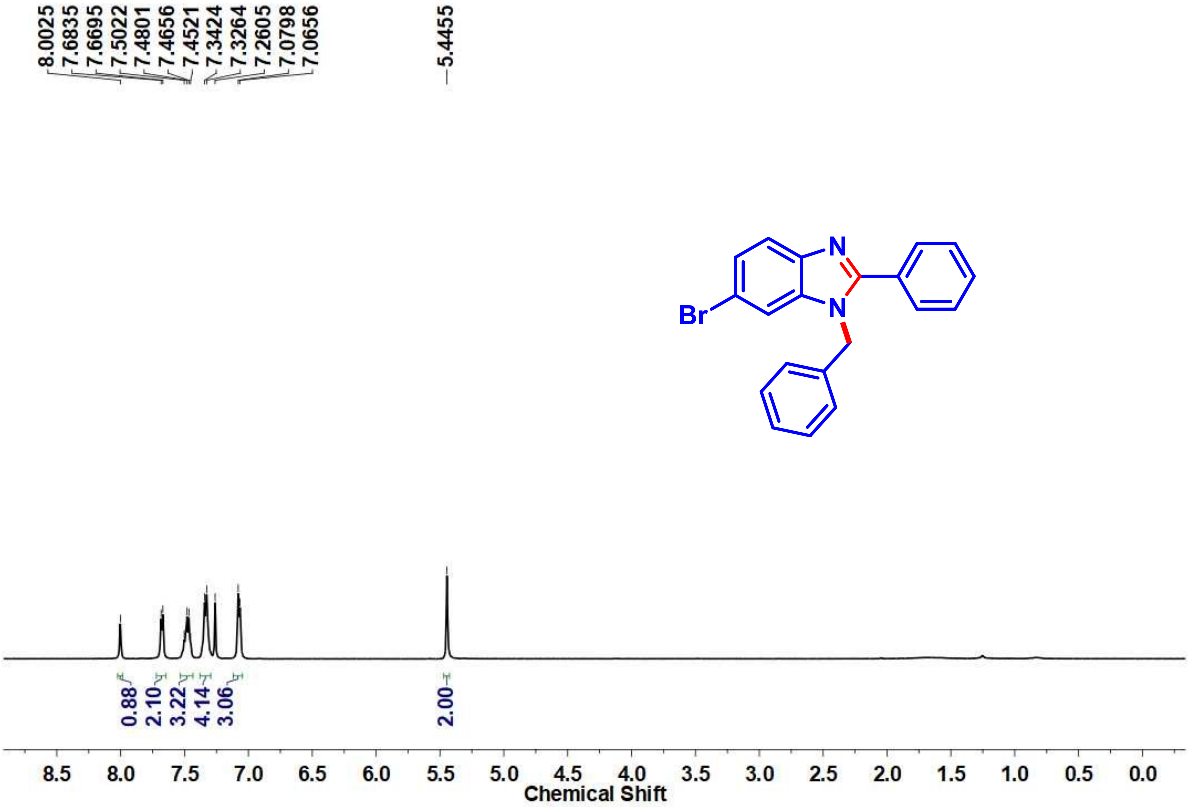
^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) Spectrum of 3f



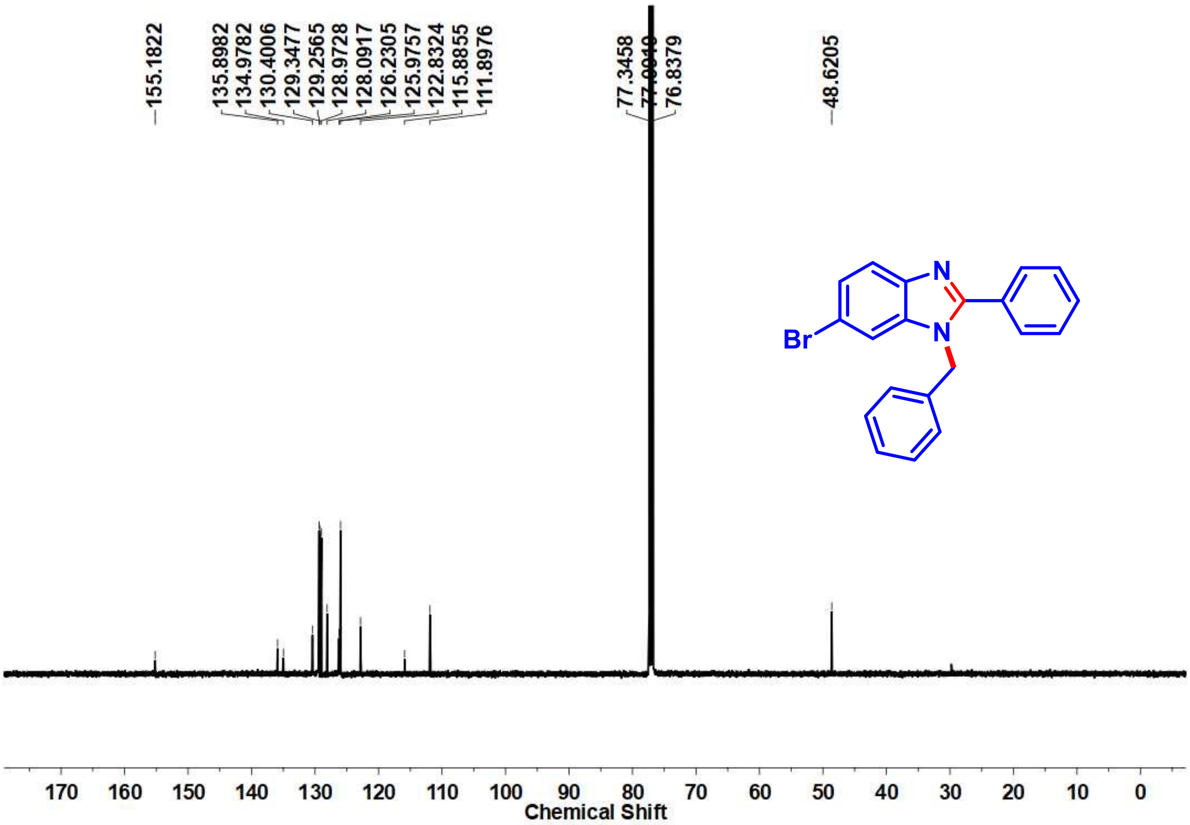
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3g



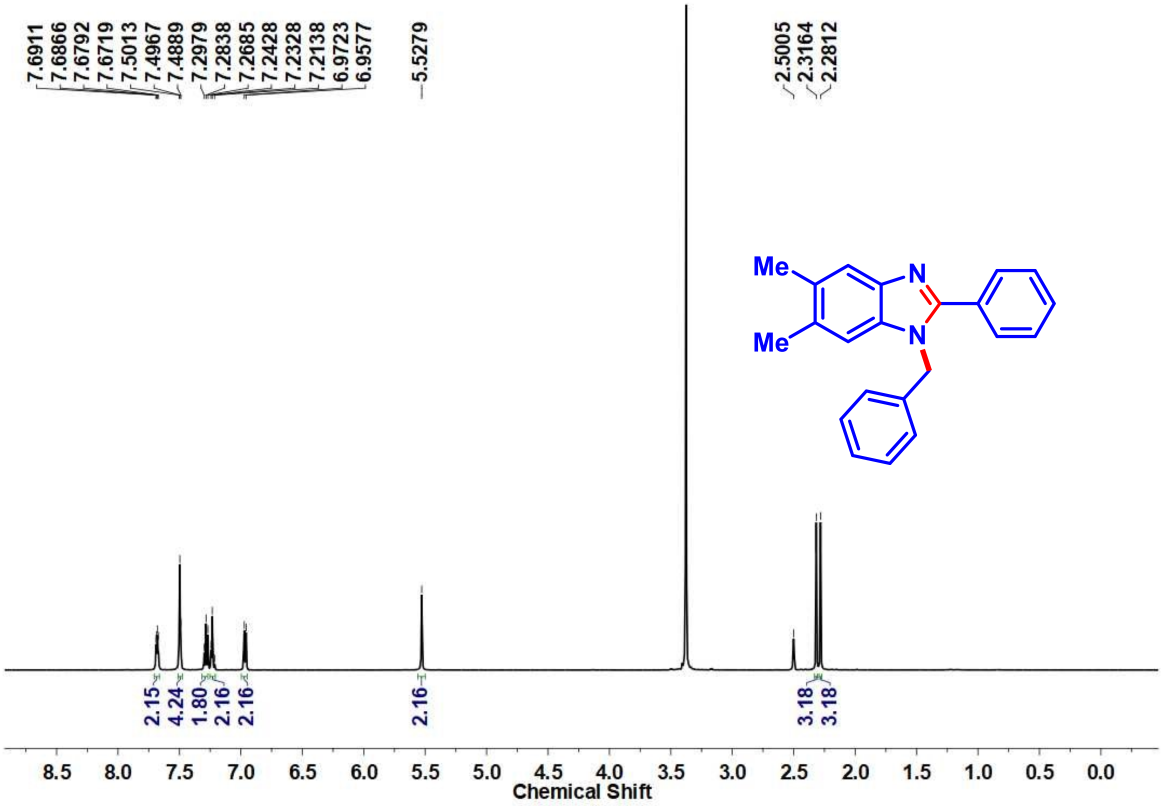
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) Spectrum of 3g



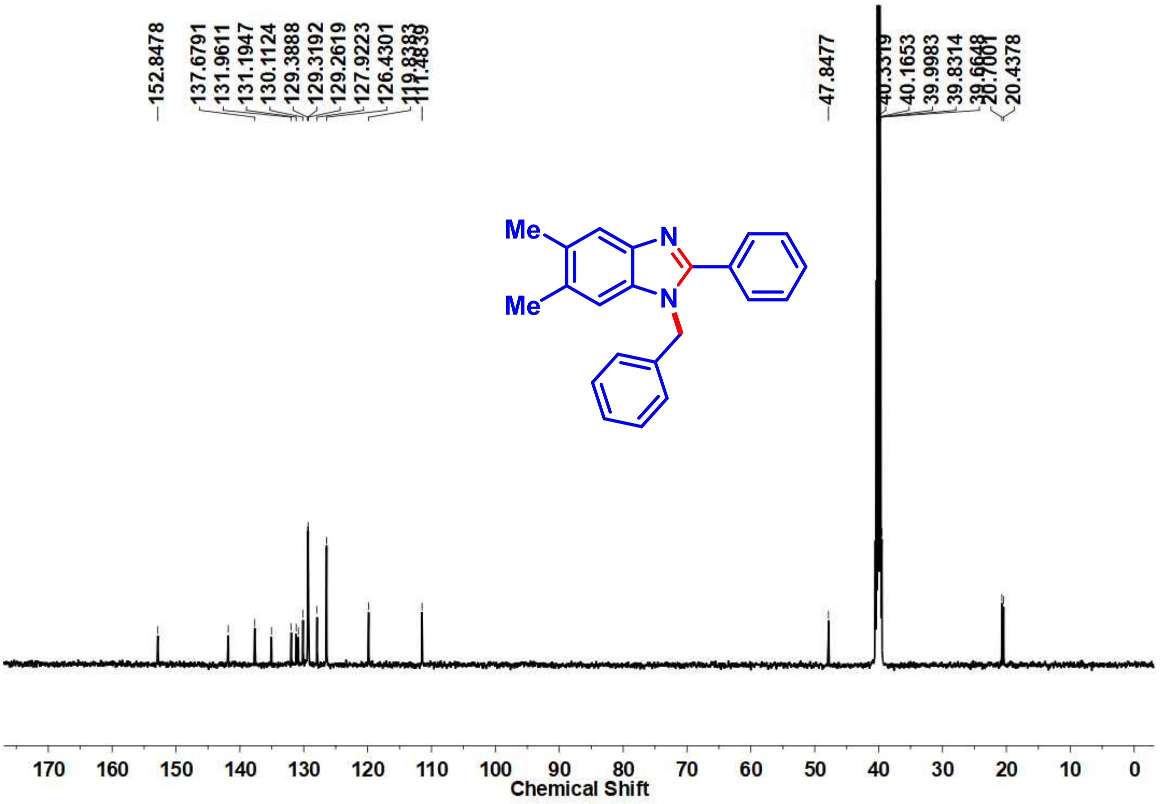
^{1}H NMR (CDCl$_3$, 500 MHz) Spectrum of 3h



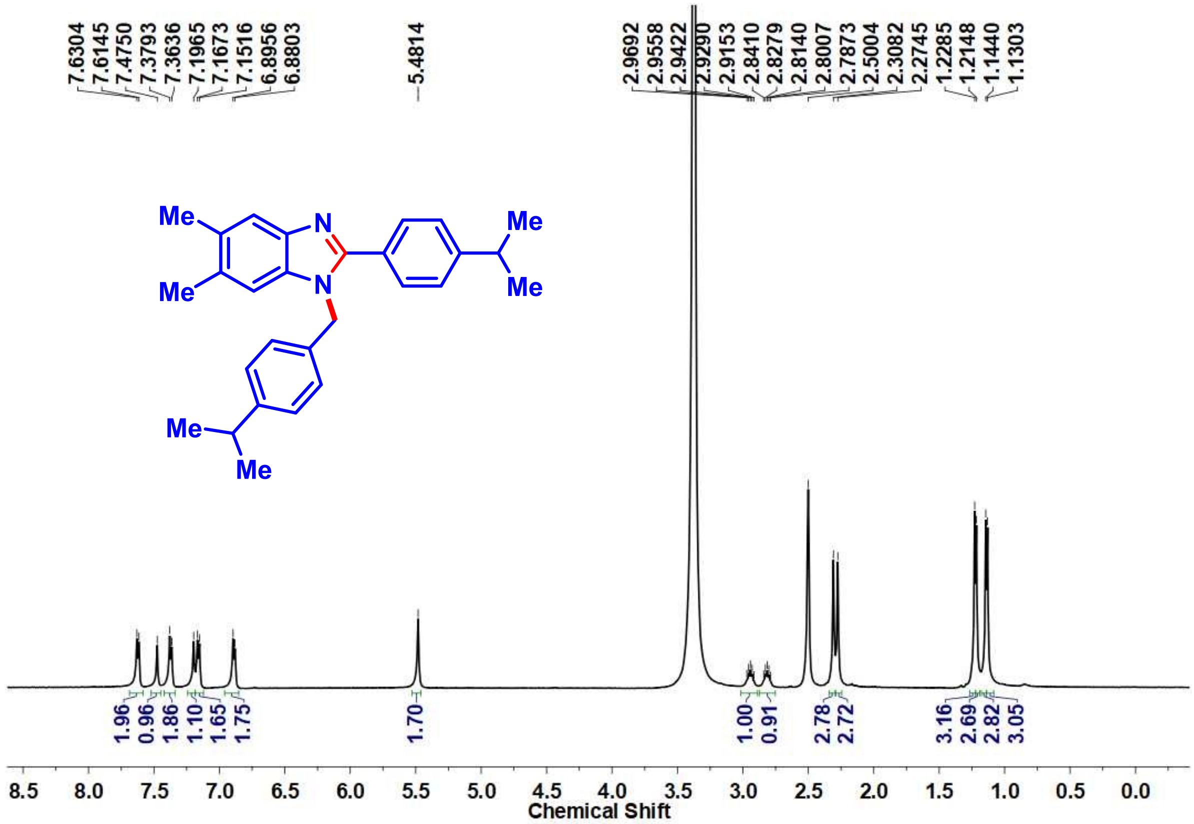
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) Spectrum of 3h



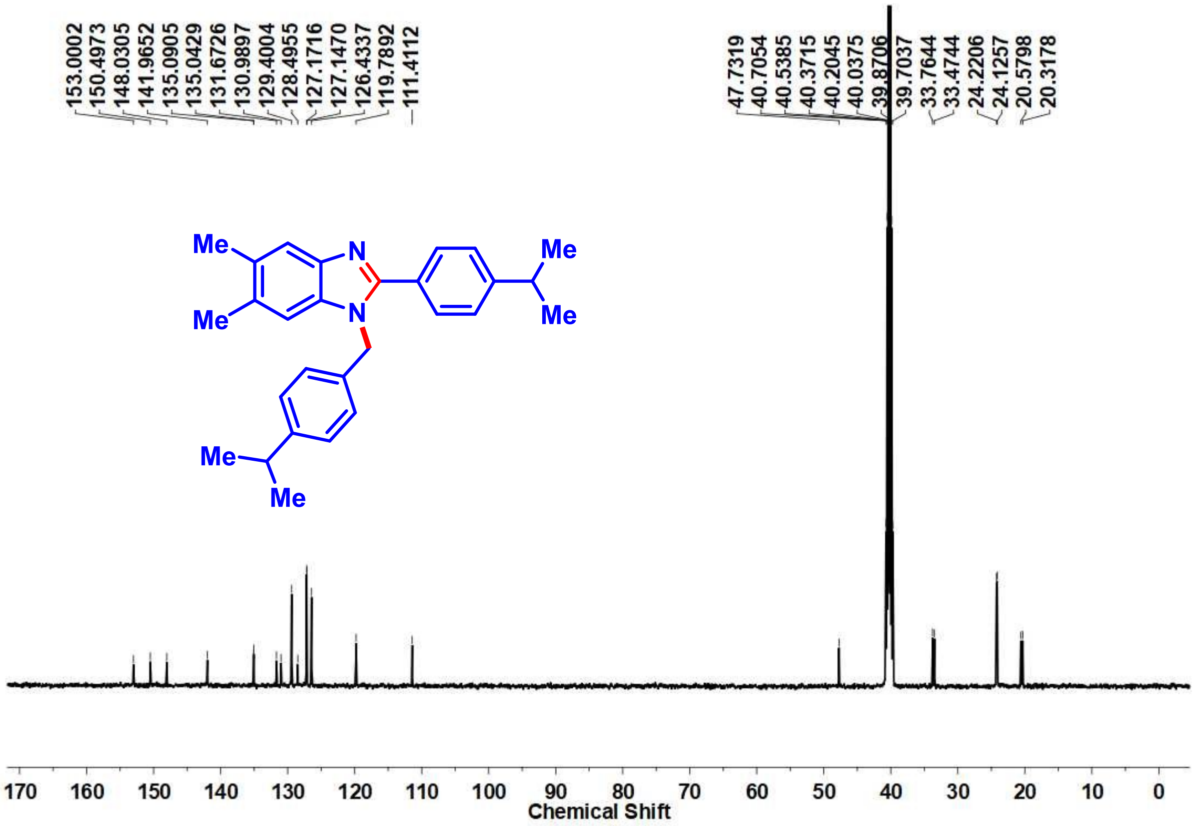
^1H NMR (DMSO-d_6, 500 MHz) Spectrum of 3i



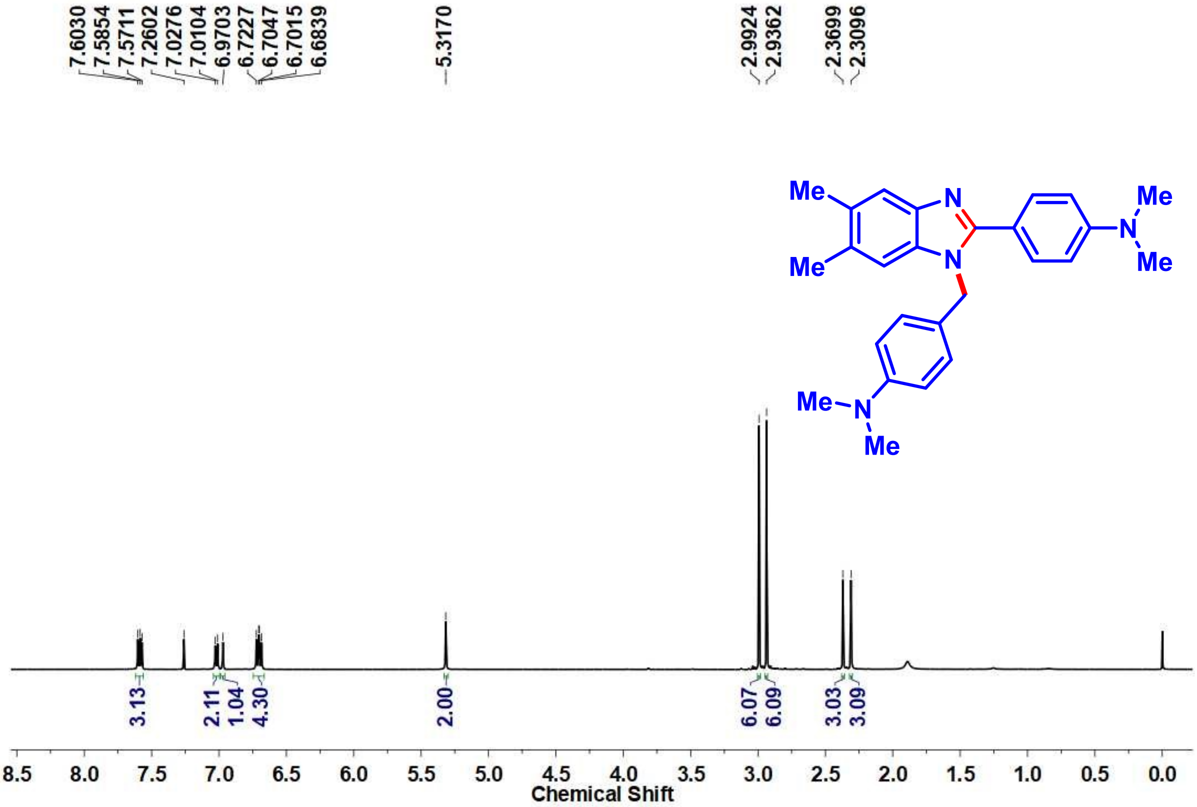
$^{13}C\{^1H\}$ NMR (DMSO-d_6, 125 MHz) Spectrum of 3i



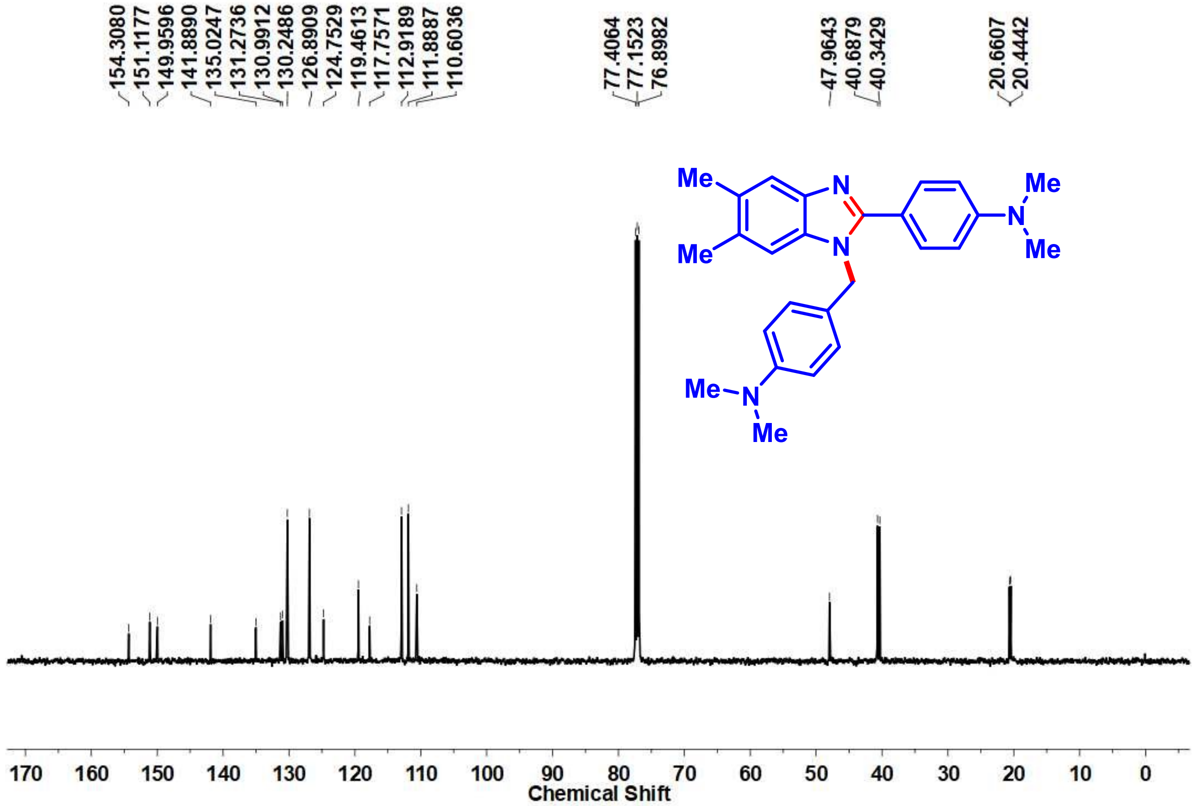
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3j



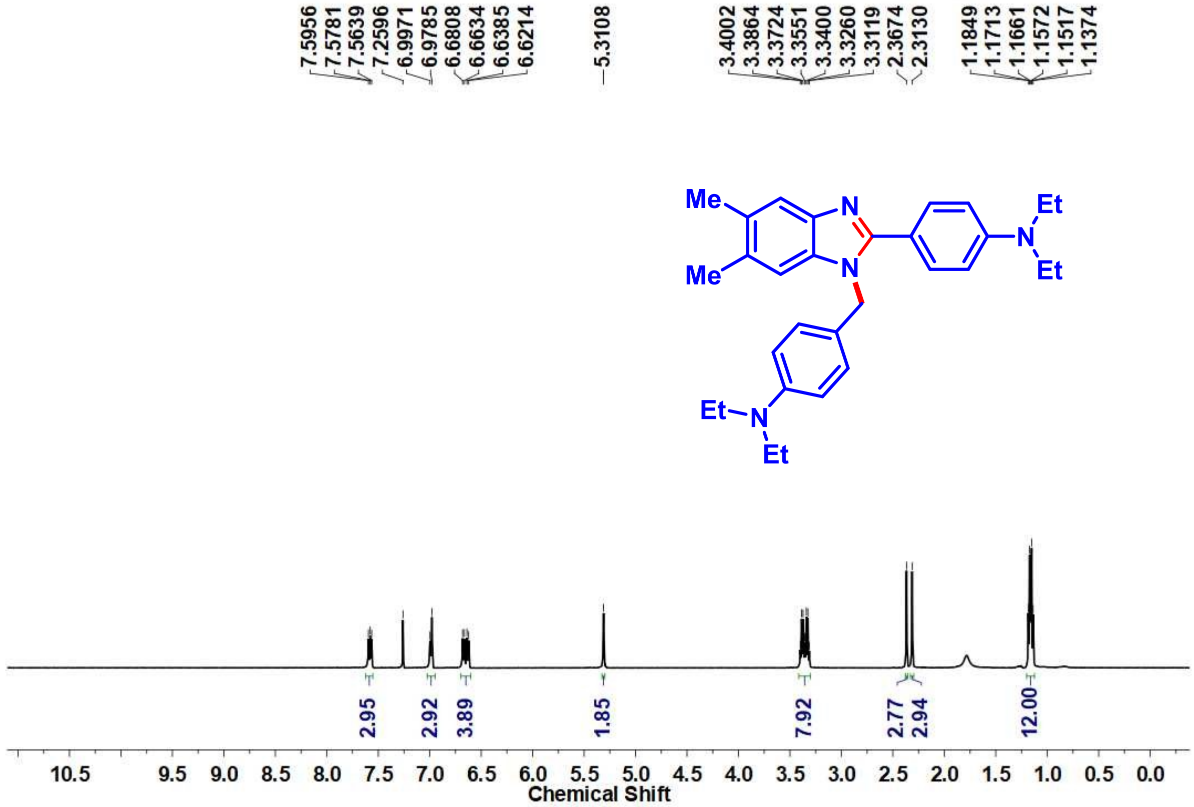
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 3j



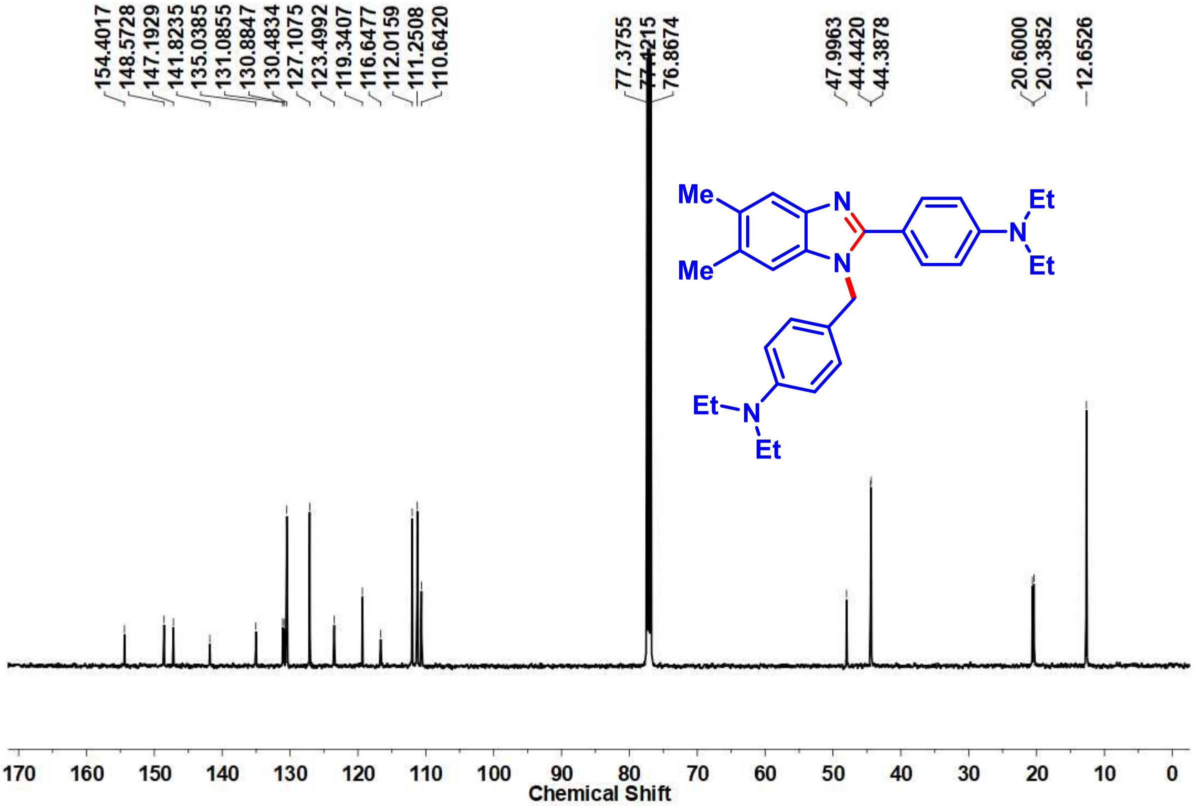
^{1}H NMR (CDCl$_3$, 500 MHz) Spectrum of 3k



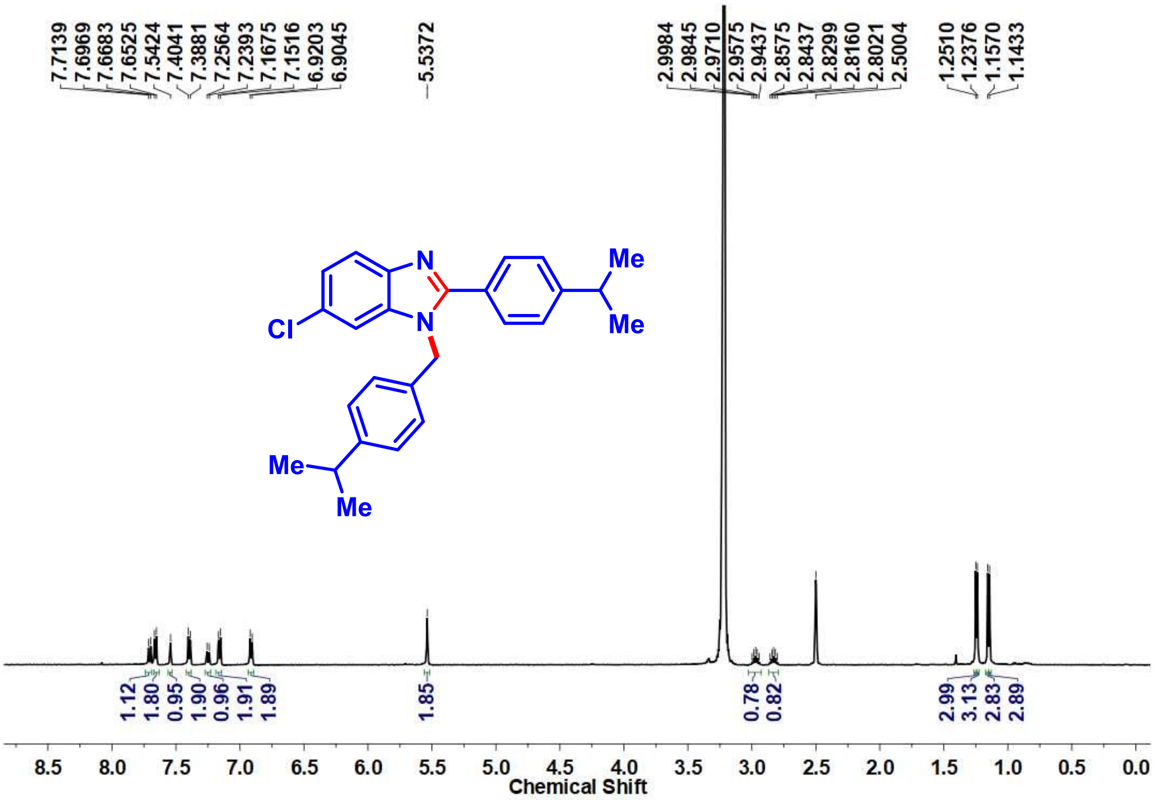
^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) Spectrum of 3k



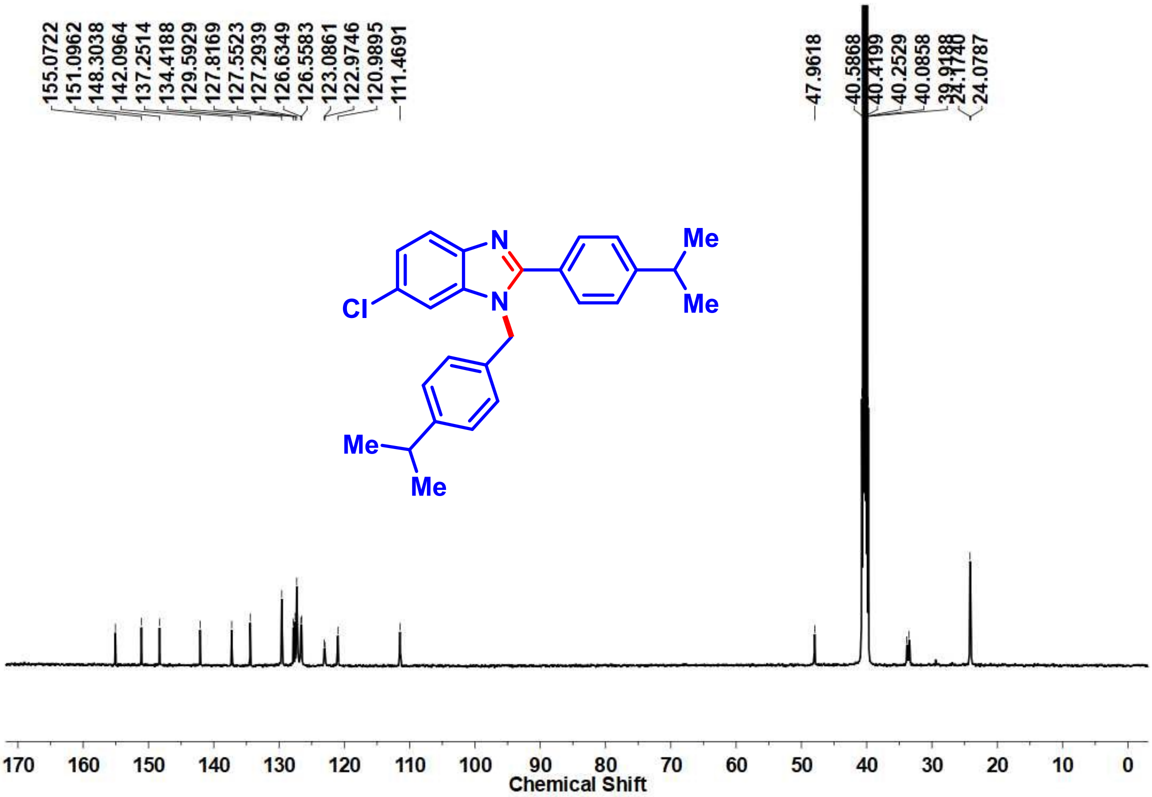
^{1}H NMR (CDCl$_3$, 500 MHz) Spectrum of 3l



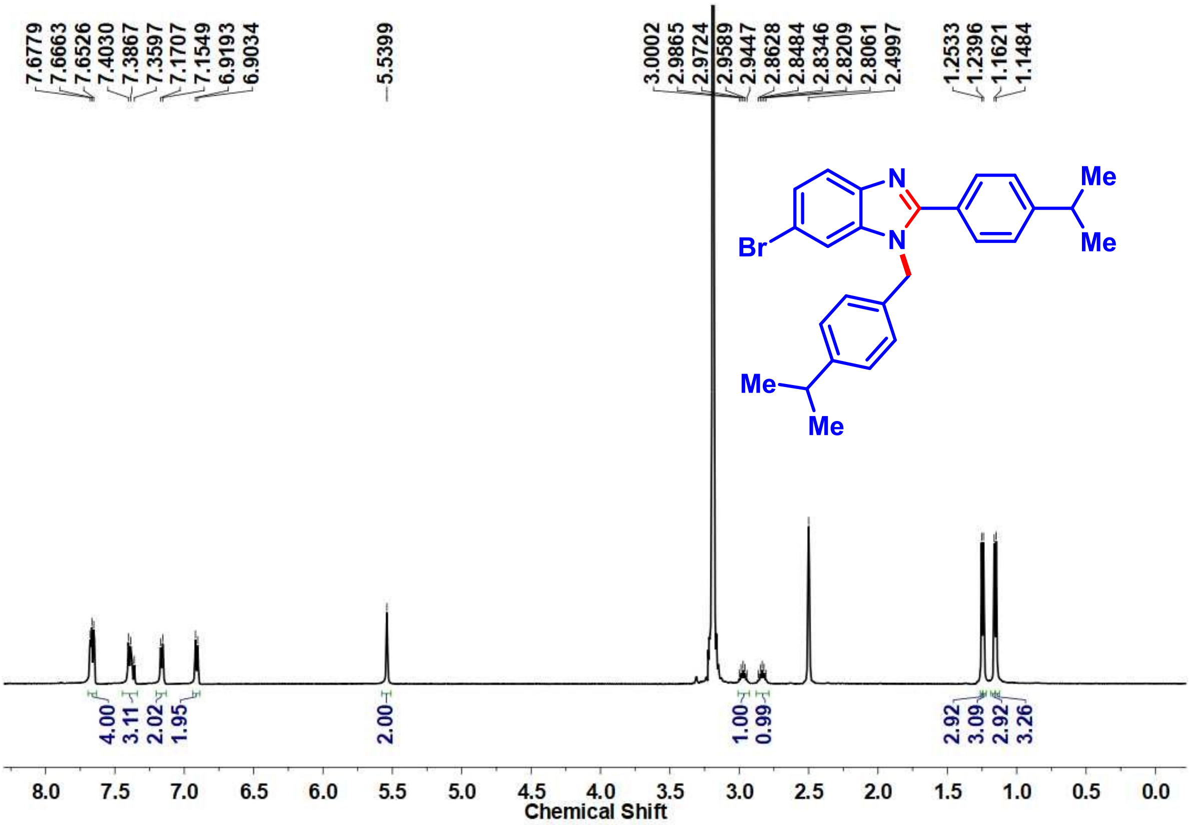
^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) Spectrum of 3l



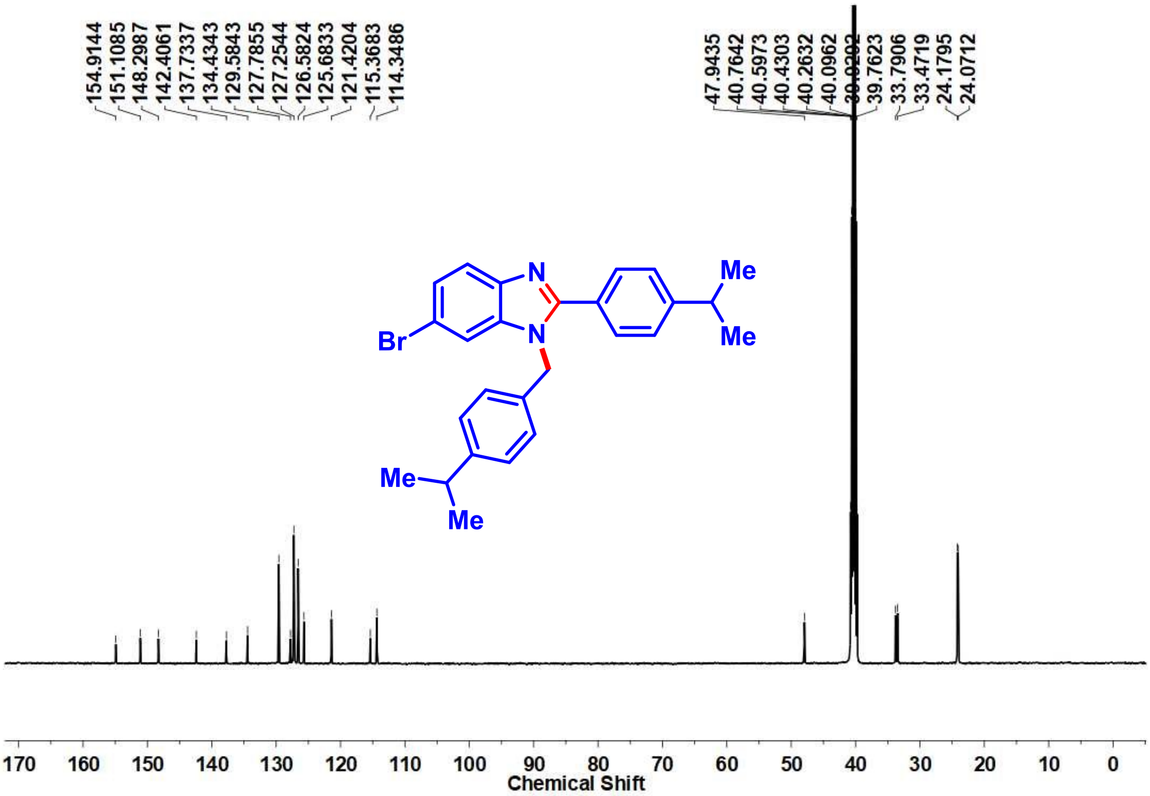
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3m



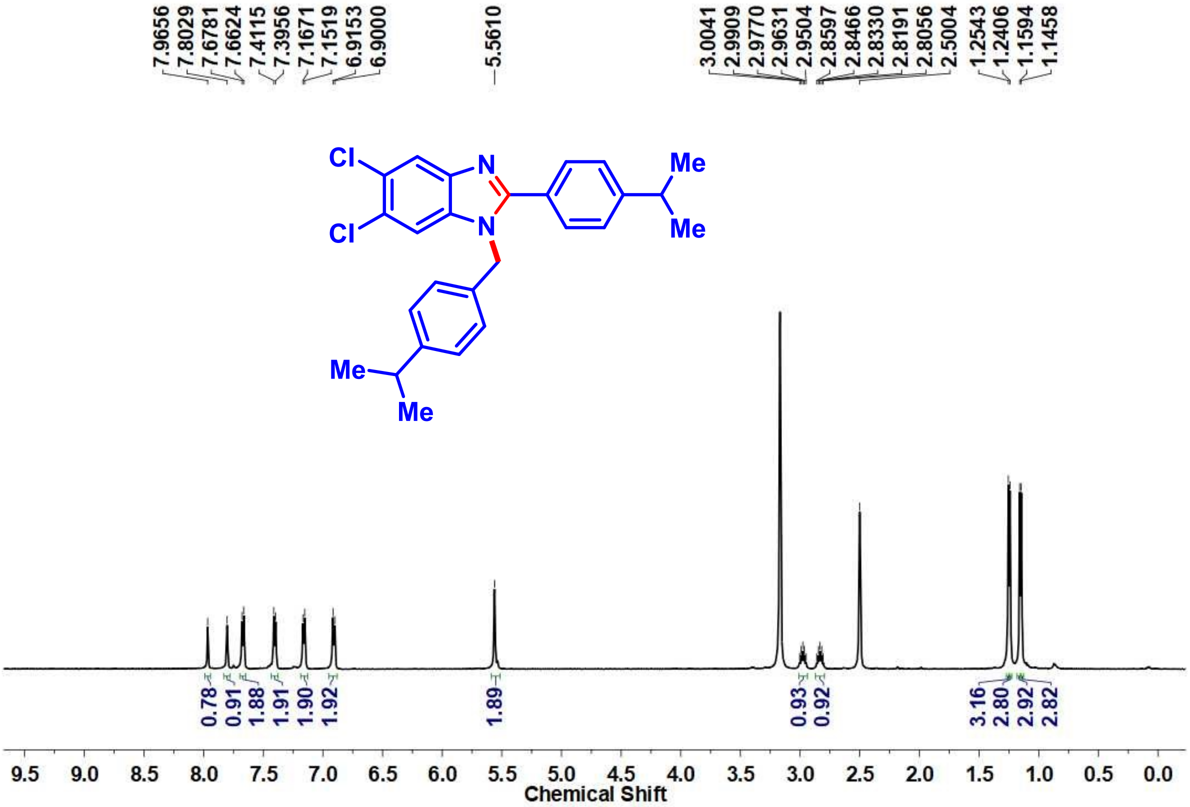
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 3m



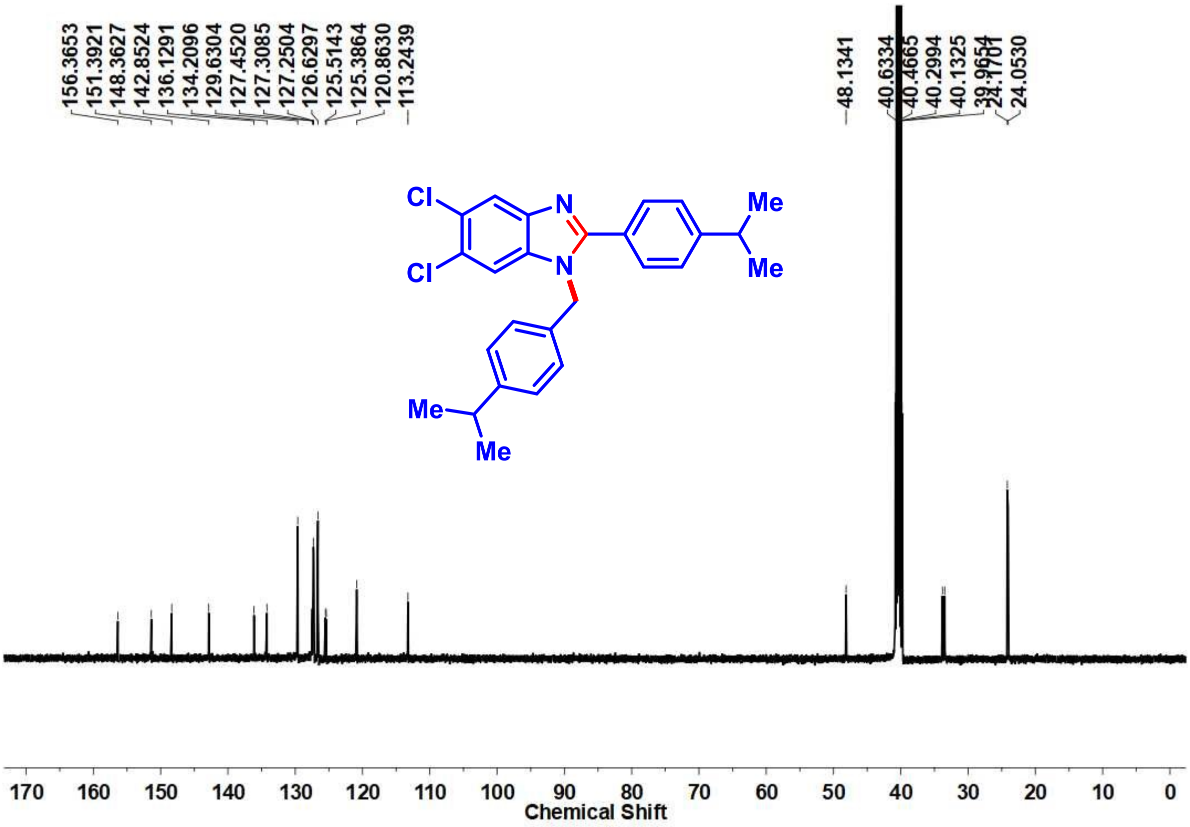
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3n



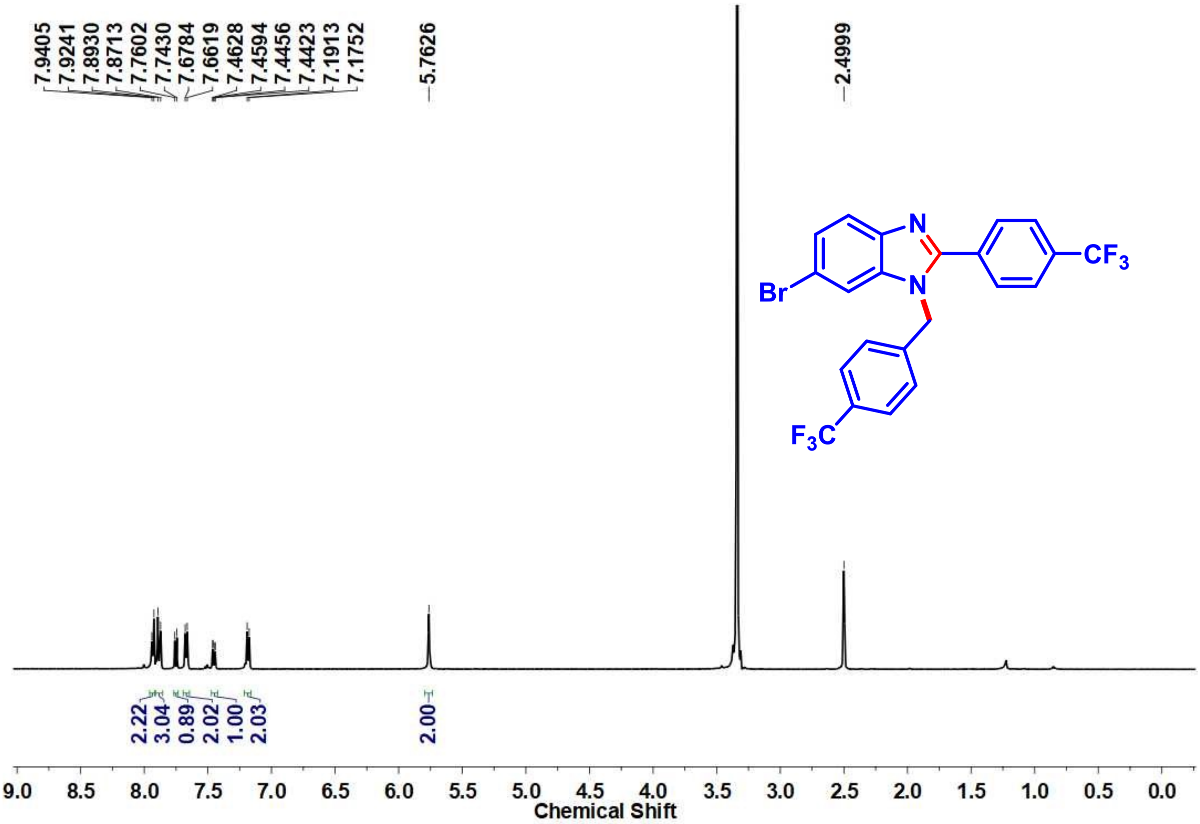
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 3n



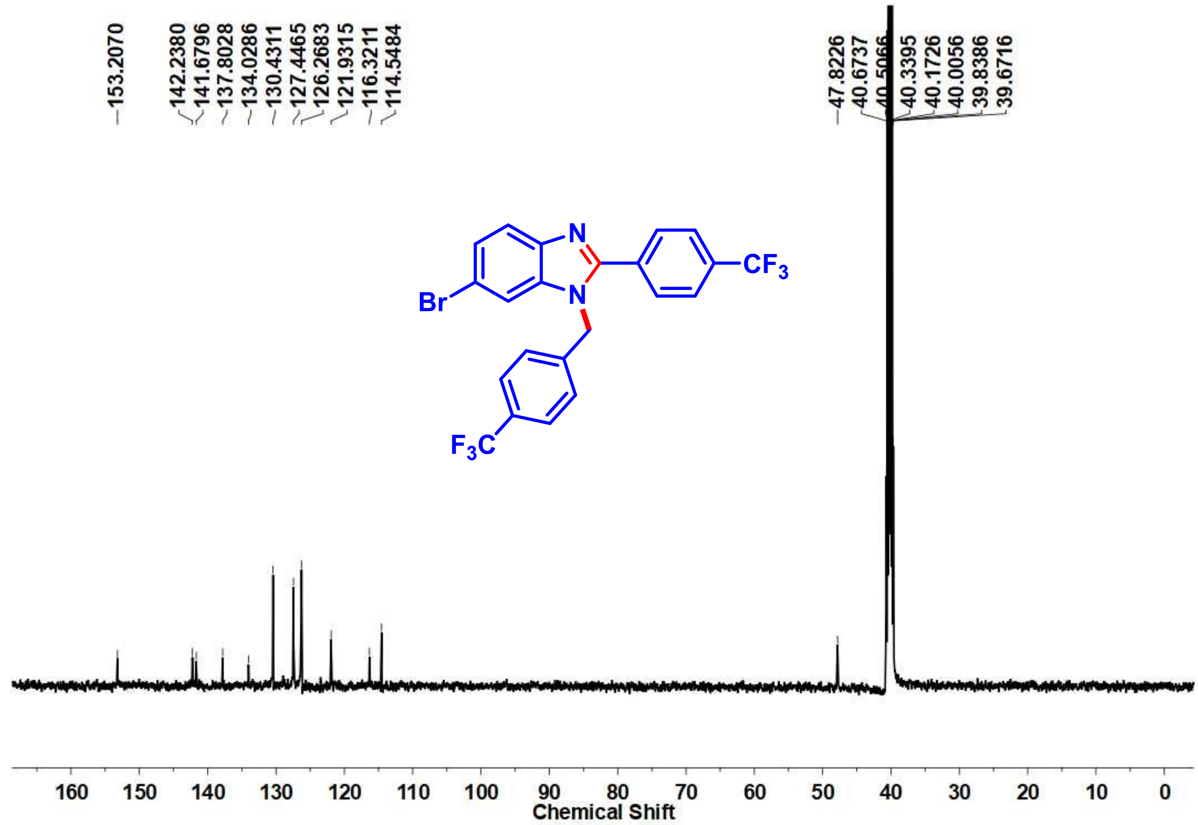
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3o



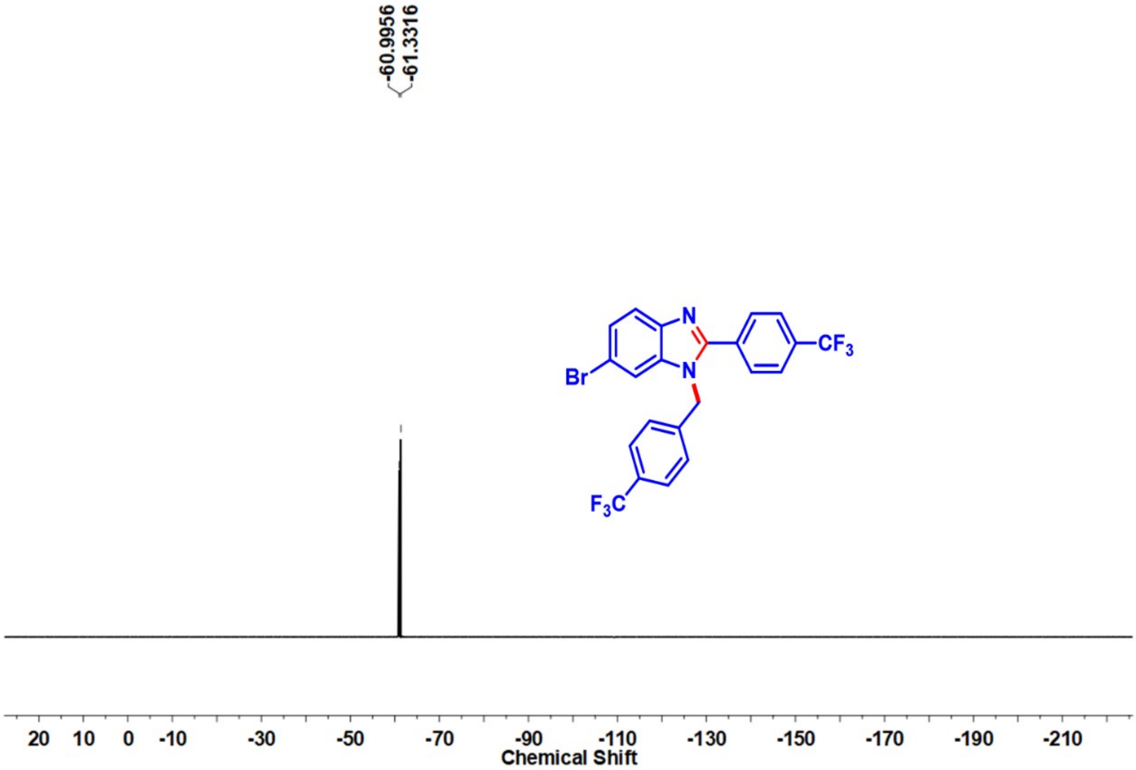
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 3o



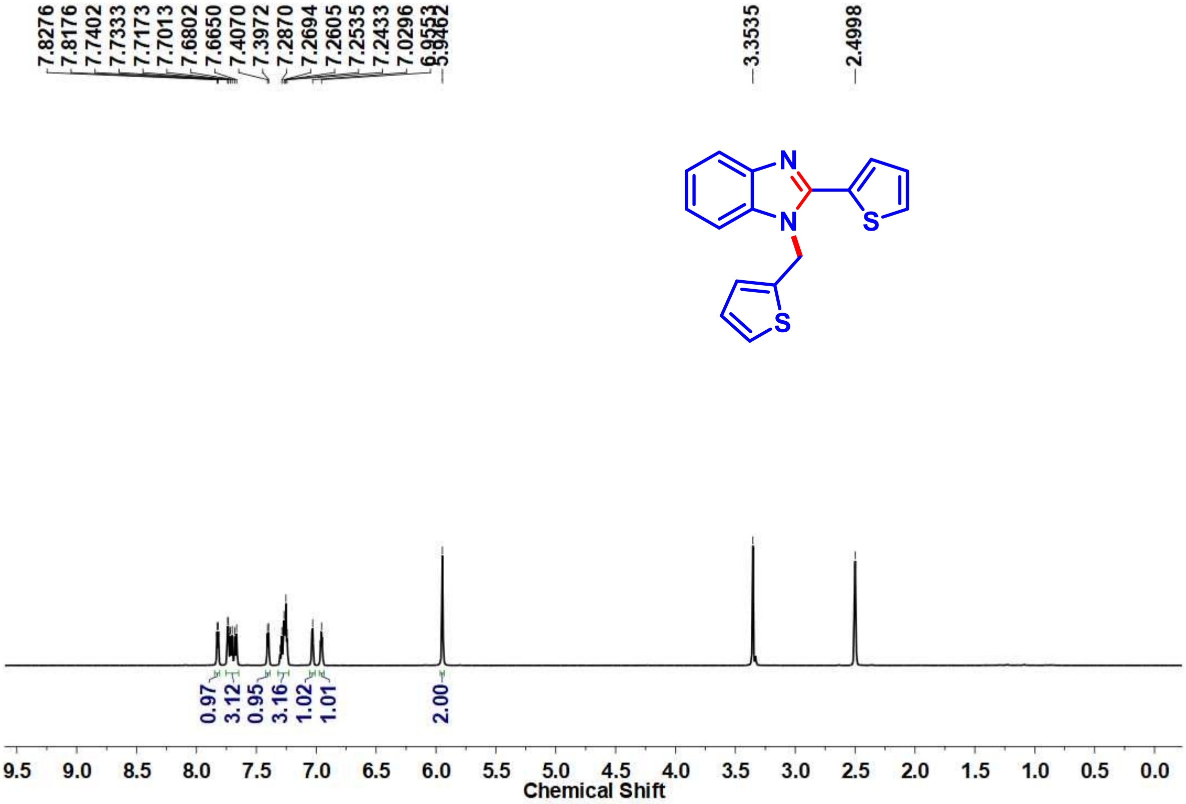
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3p



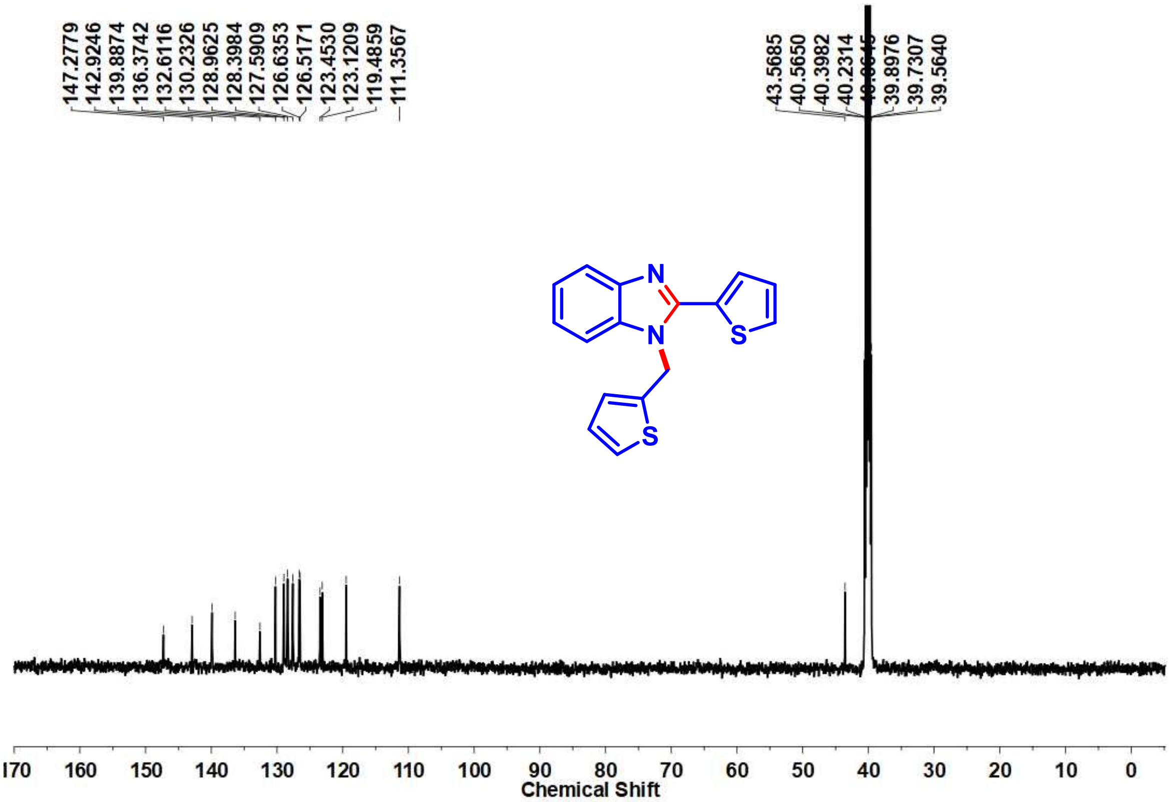
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 3p



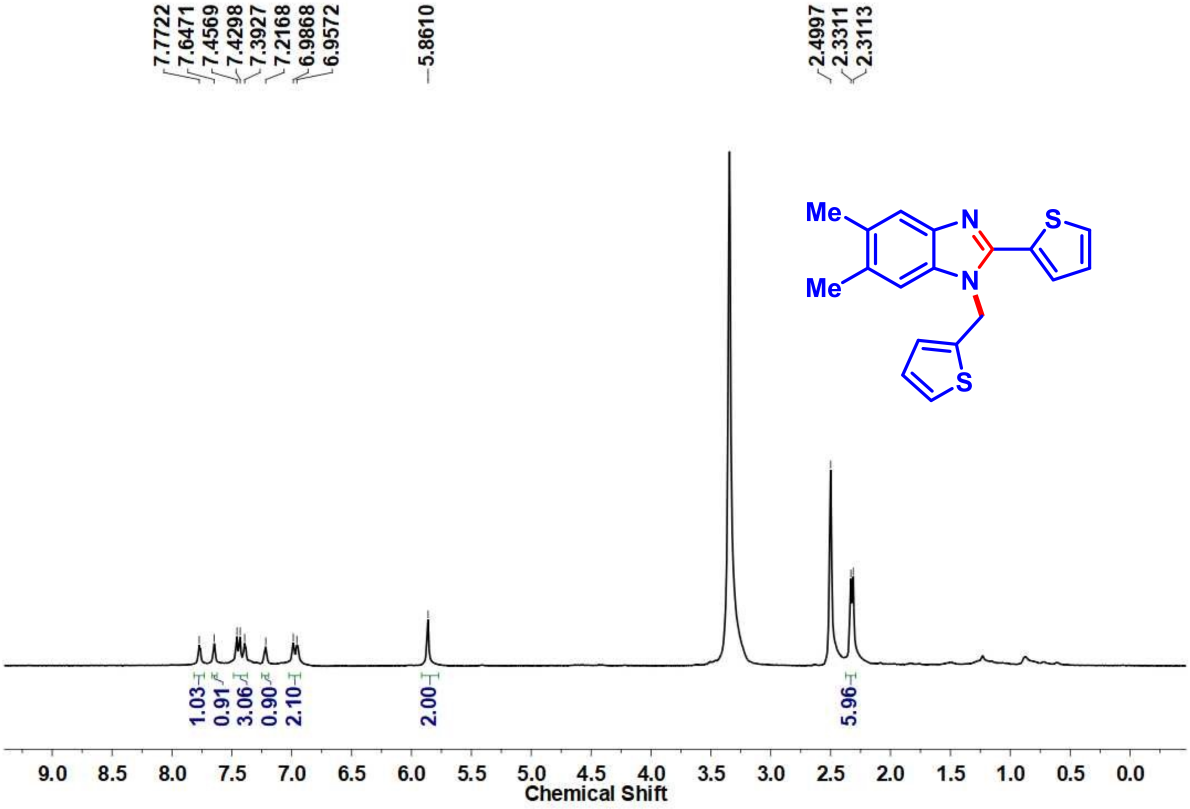
^{19}F NMR (DMSO-d_6, 125 MHz) Spectrum of 3p



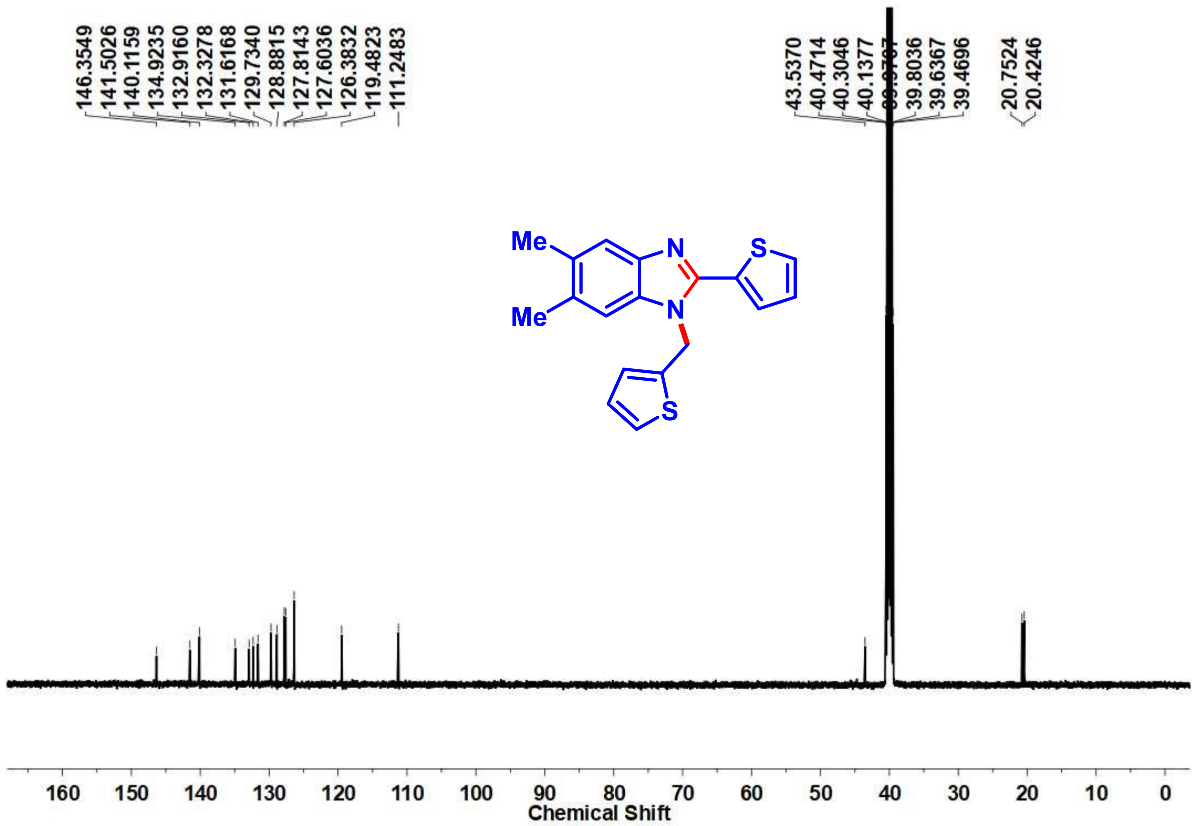
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3q



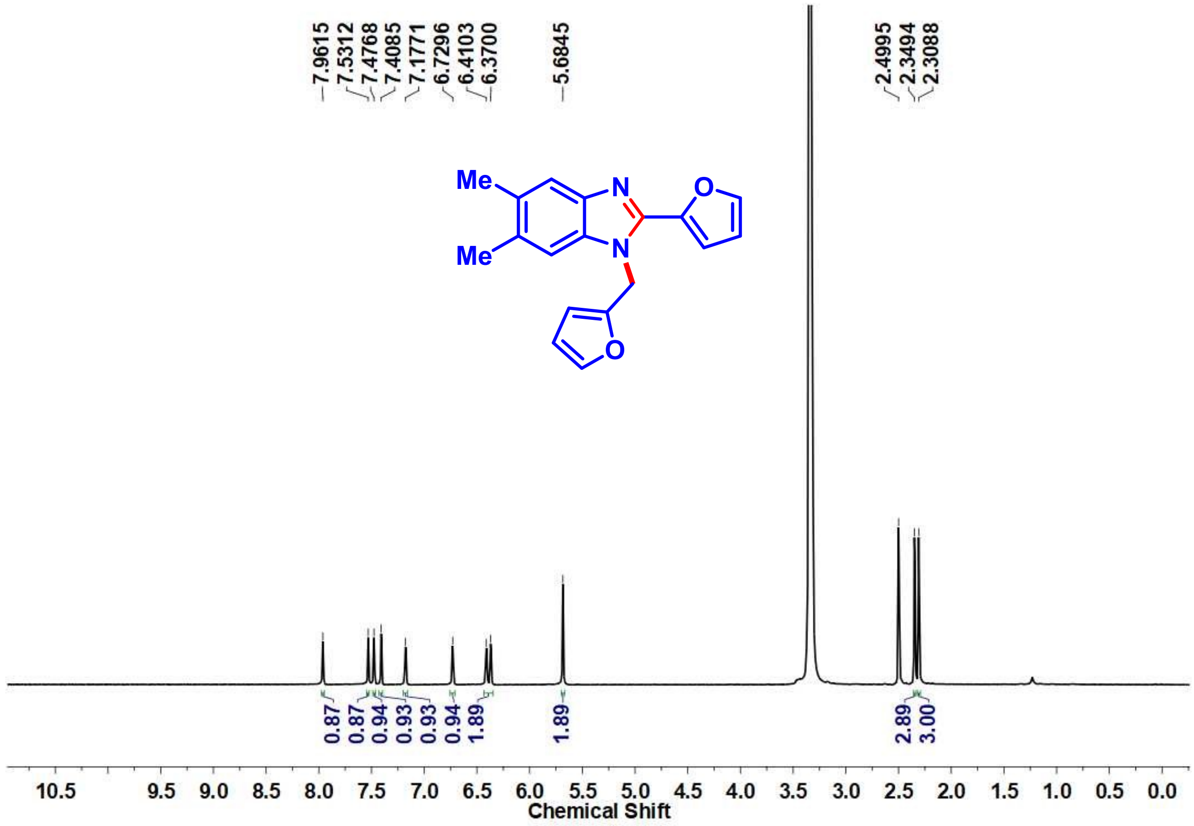
$^{13}C\{^1H\}$ NMR (DMSO-d_6, 125 MHz) Spectrum of 3q



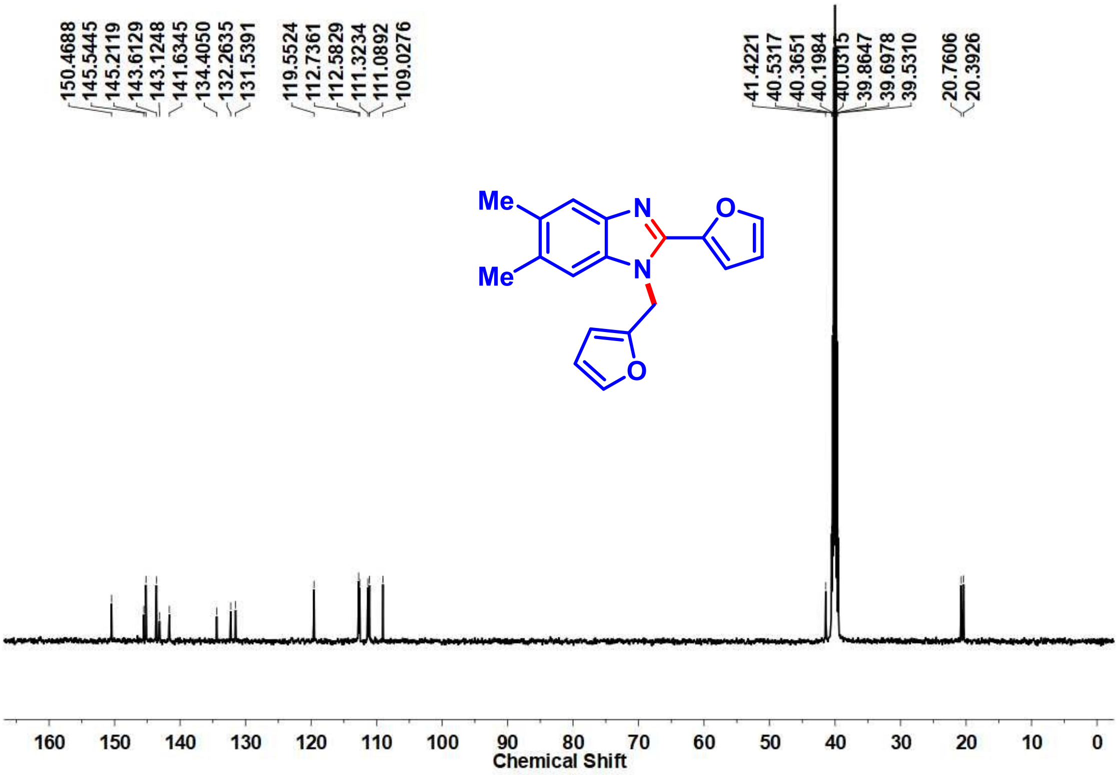
^1H NMR (DMSO-d_6, 500 MHz) Spectrum of 3r



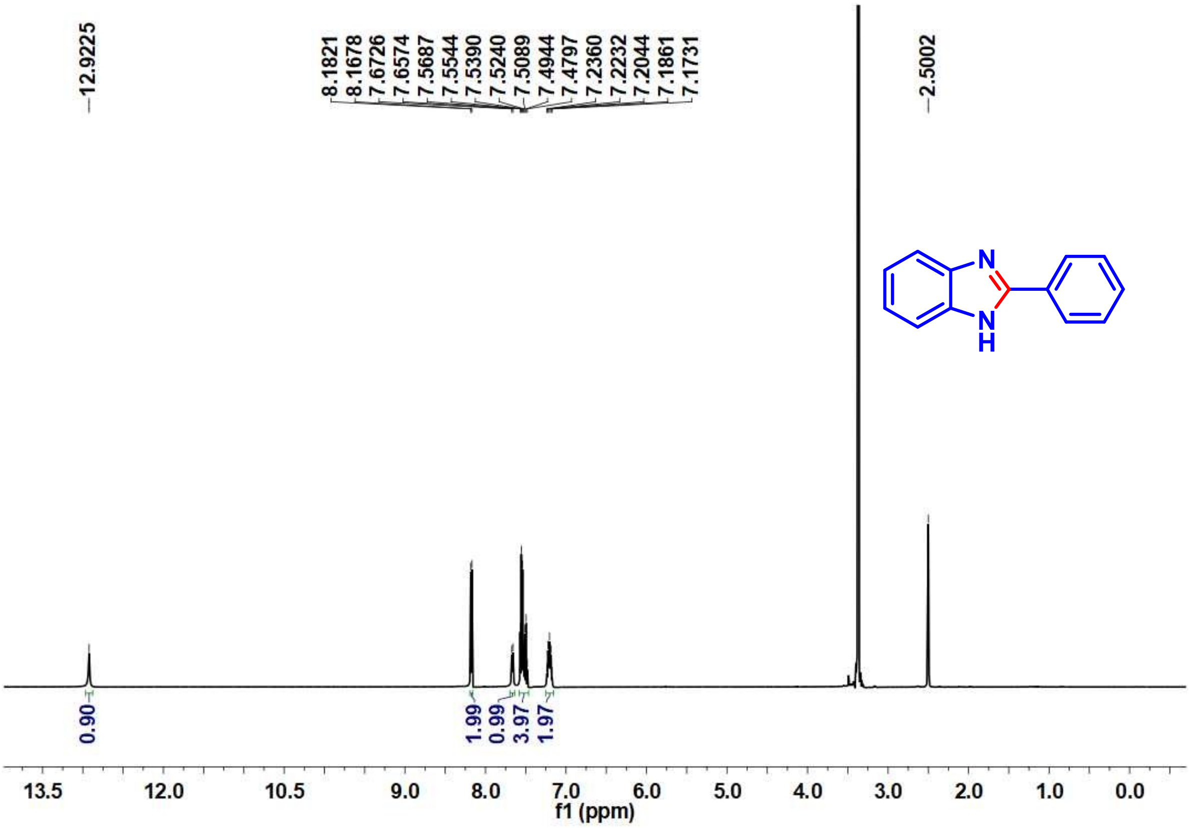
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 3r



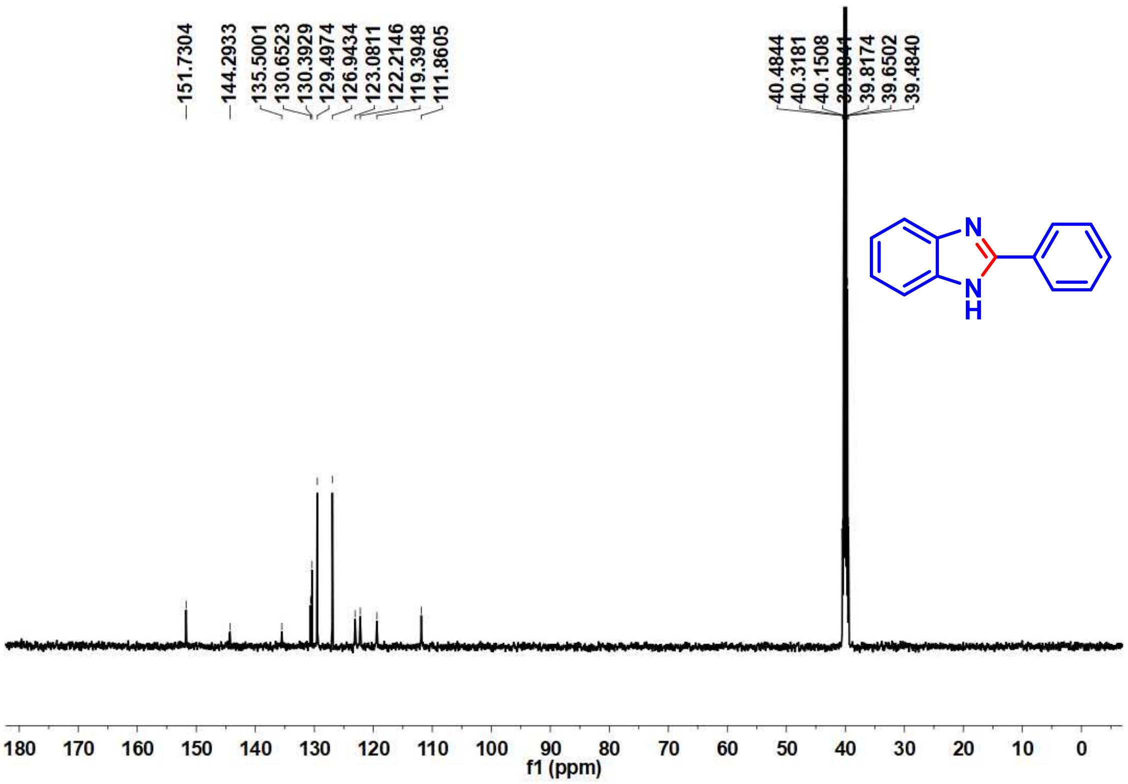
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 3s



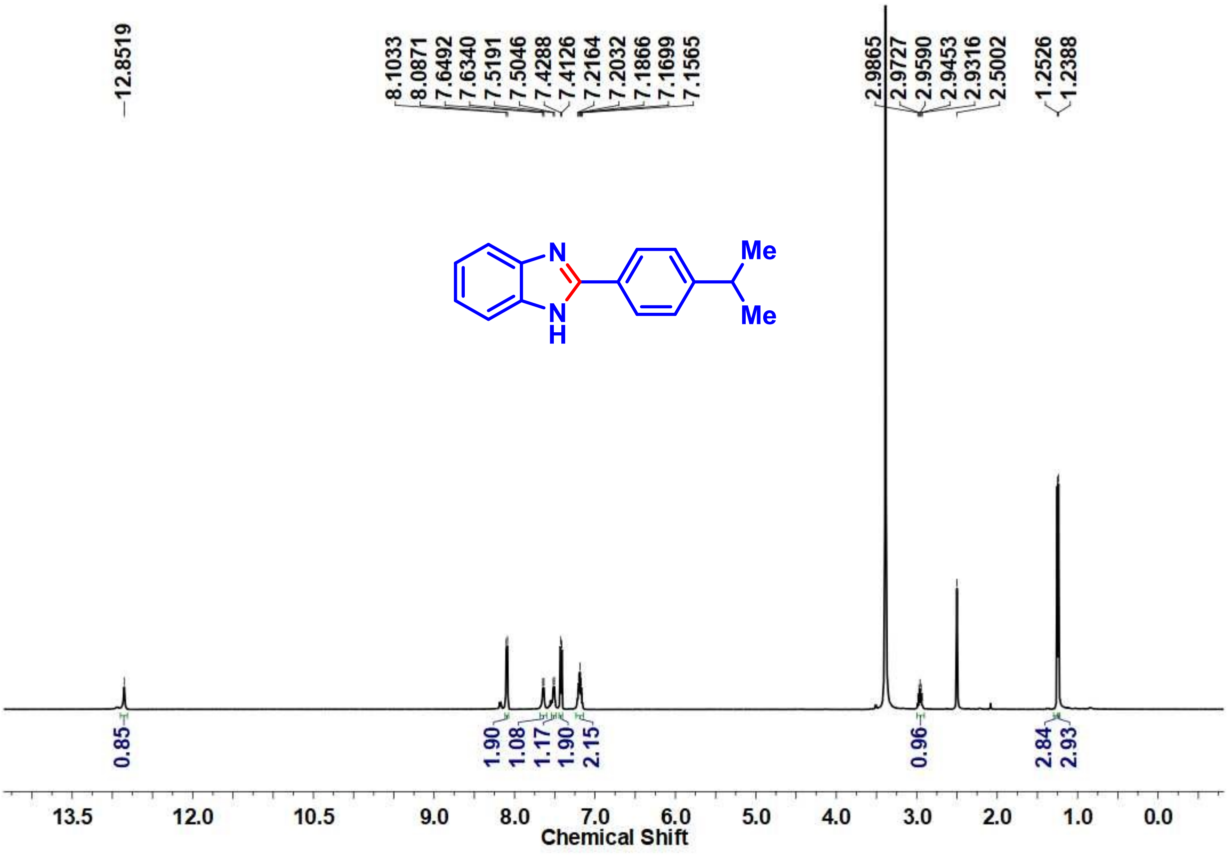
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 3s



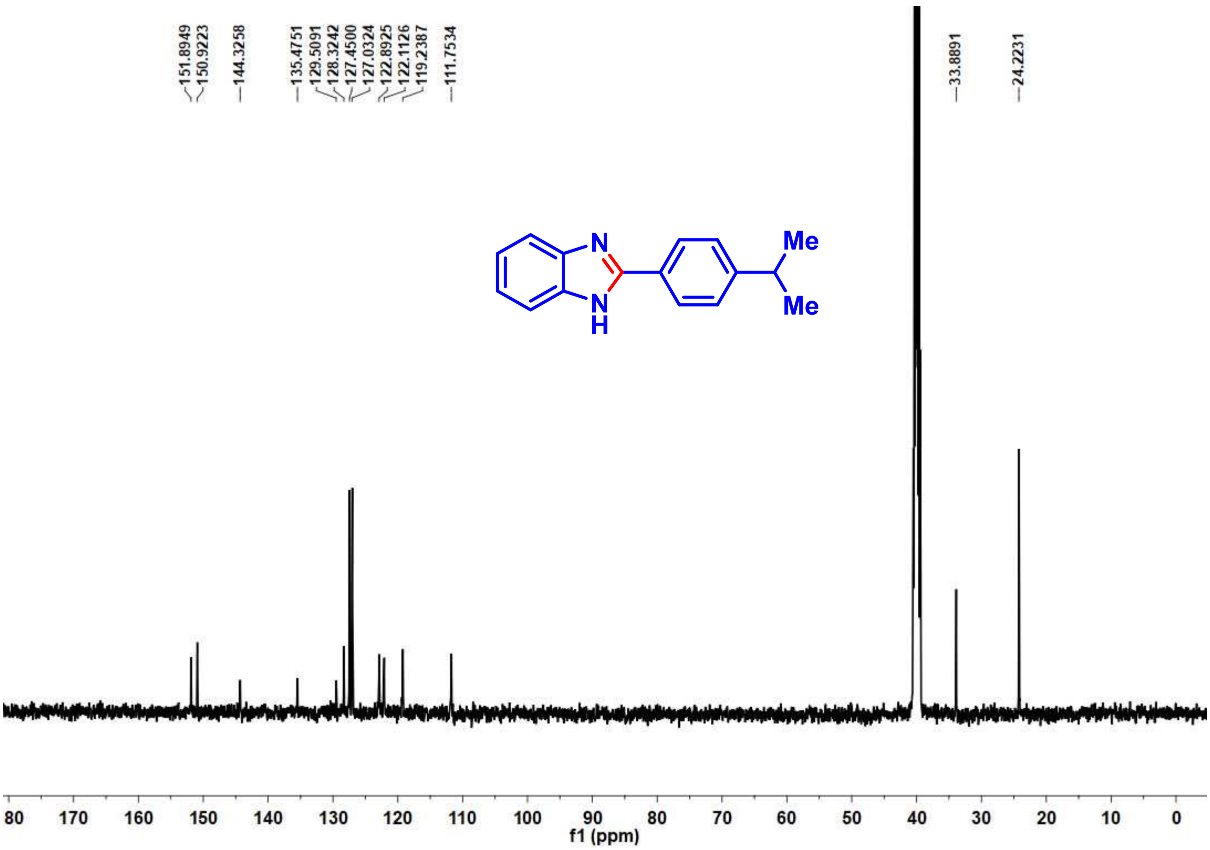
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4a



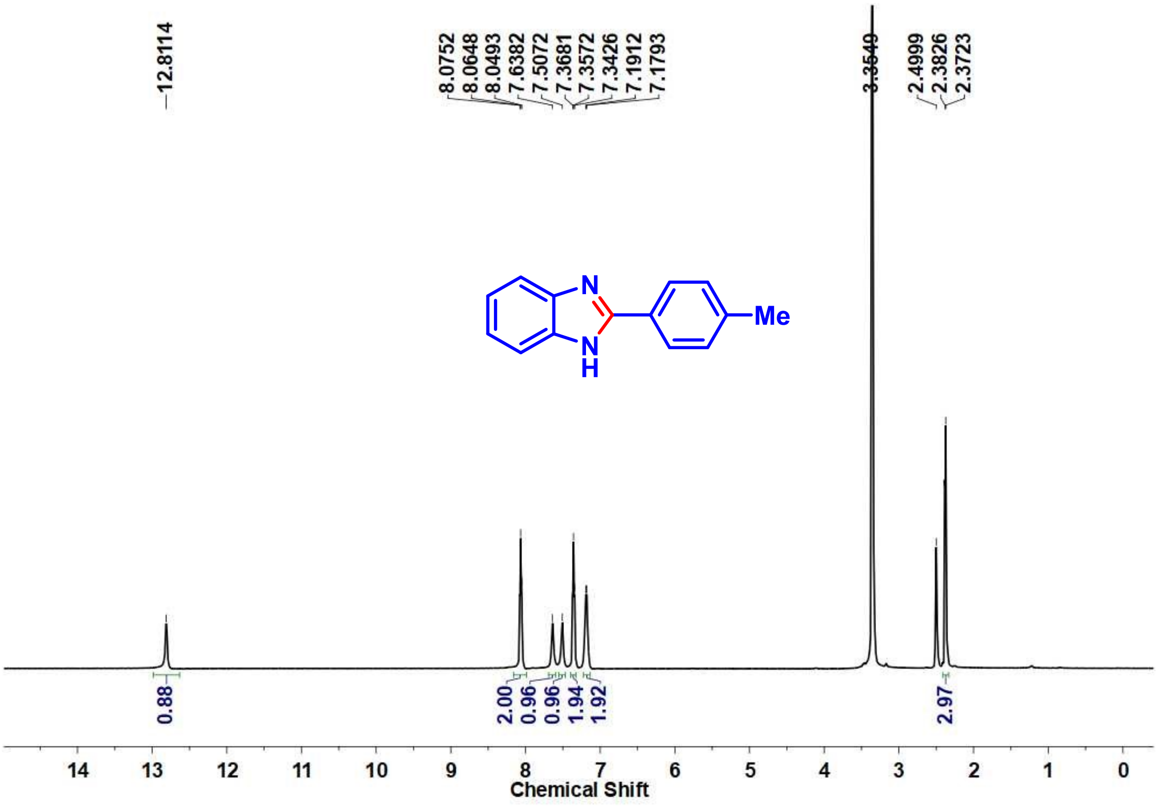
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 4a



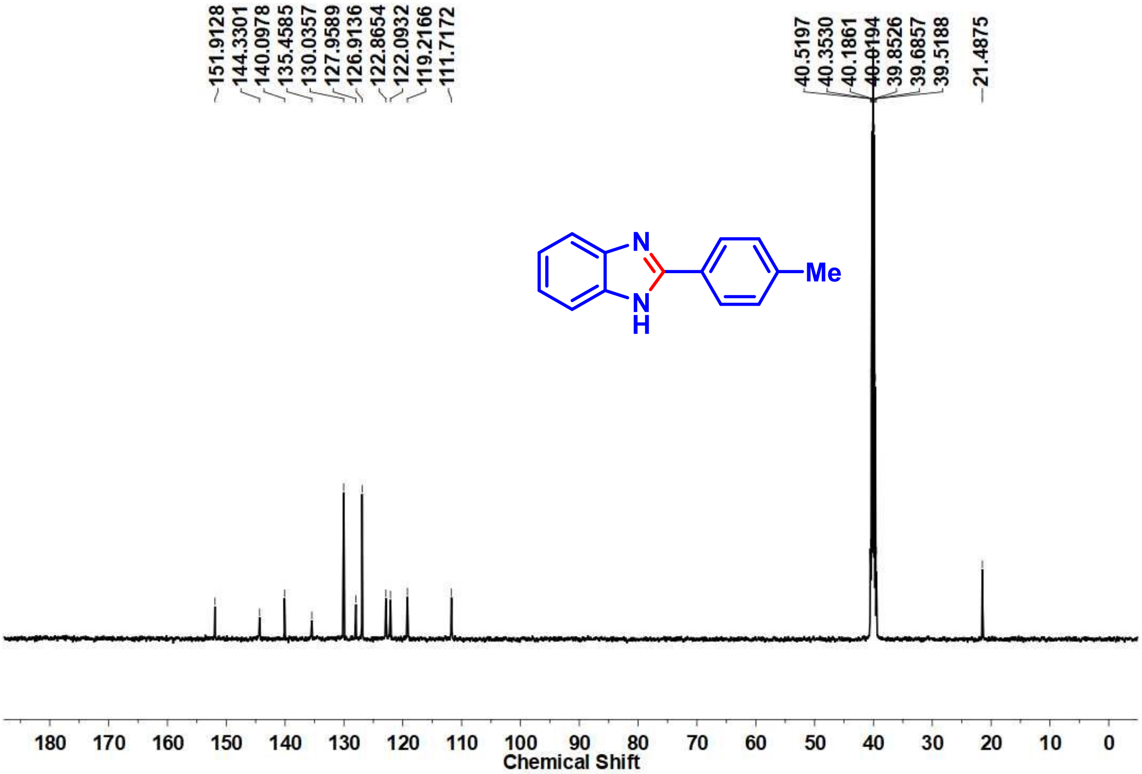
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4b



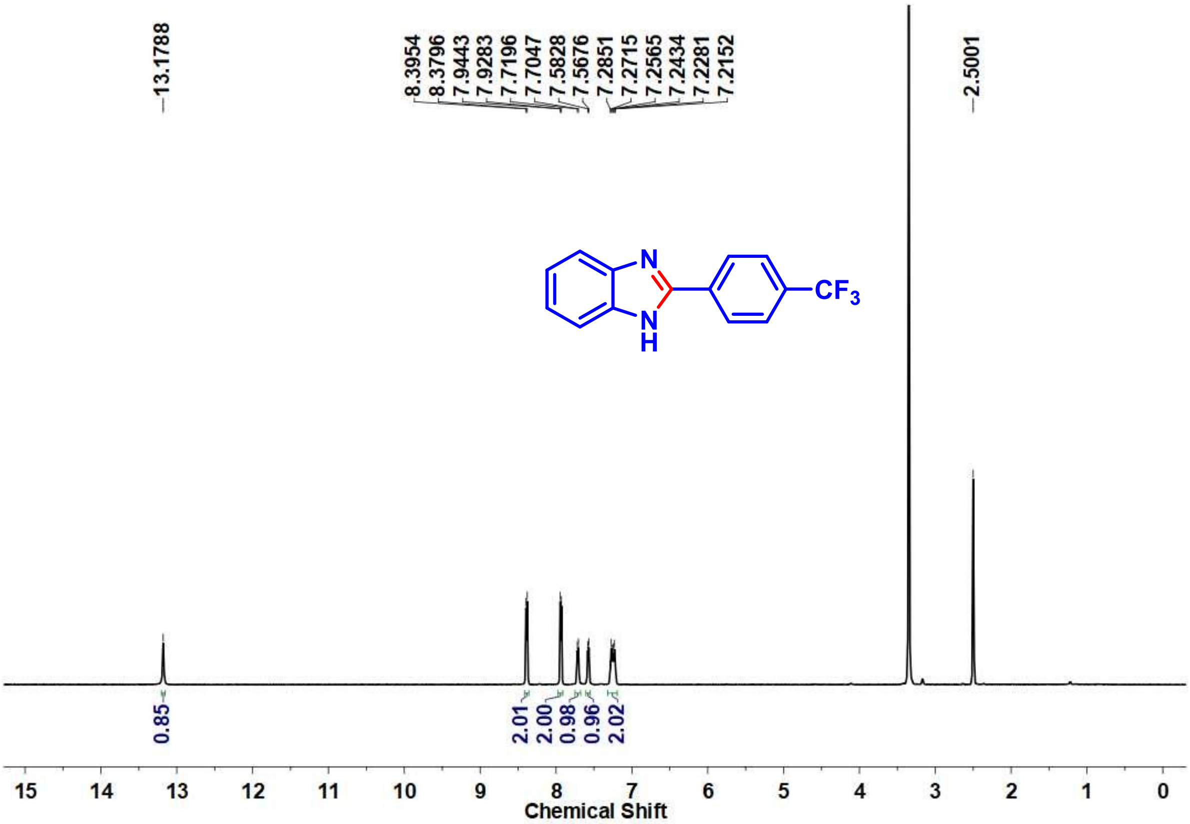
$^{13}C\{^1H\}$ NMR (DMSO-d_6, 125 MHz) Spectrum of 4b



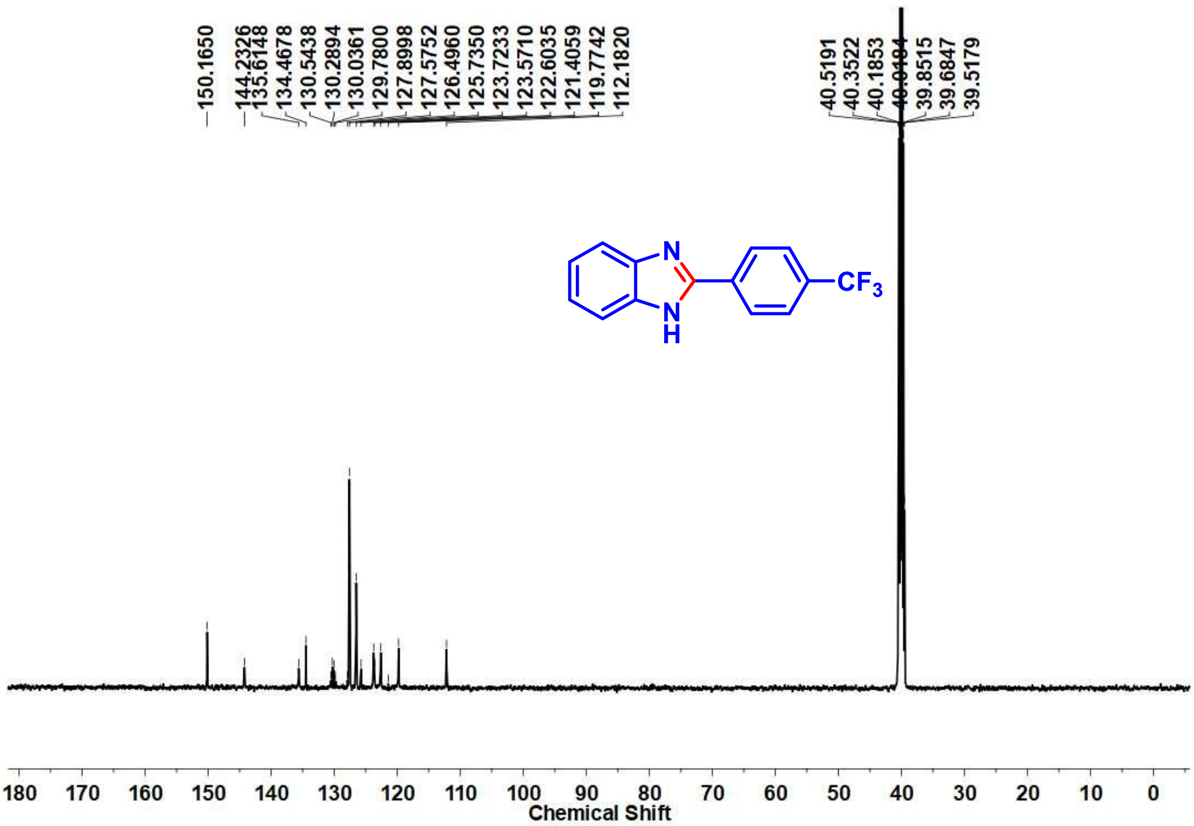
^1H NMR (DMSO-d_6, 500 MHz) Spectrum of 4c



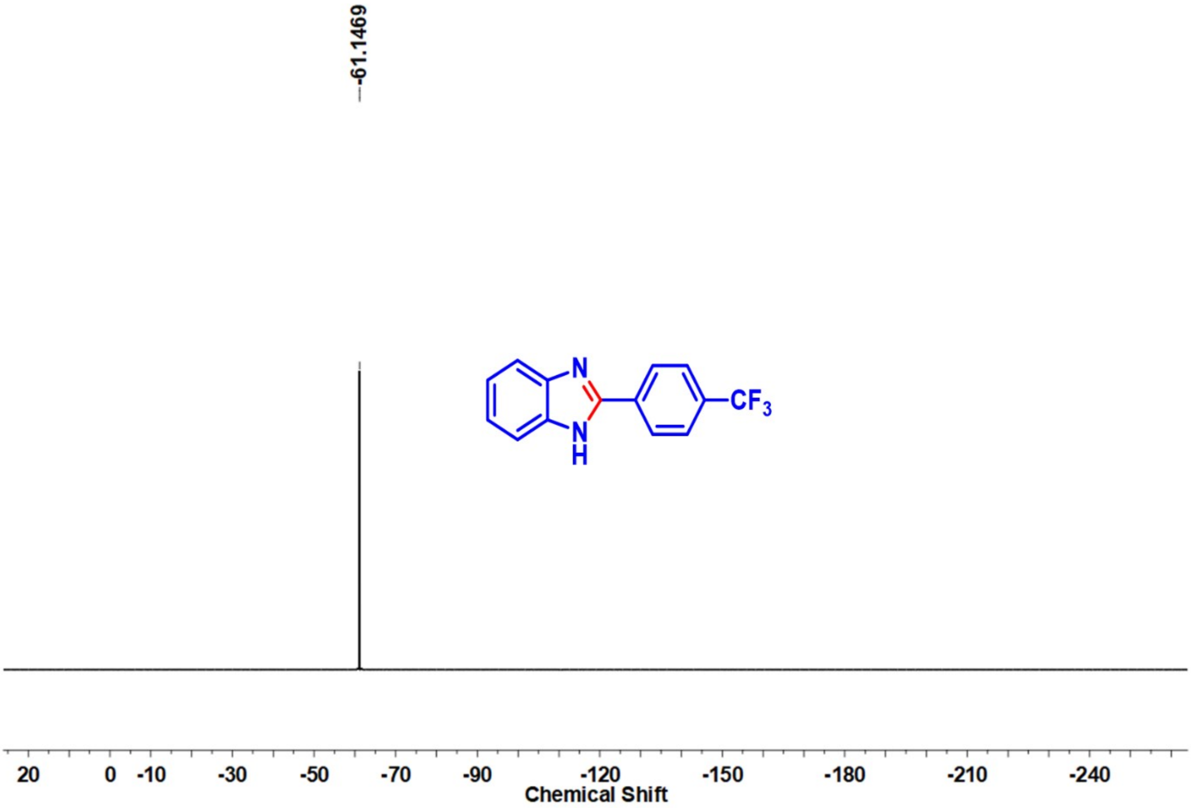
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 4c



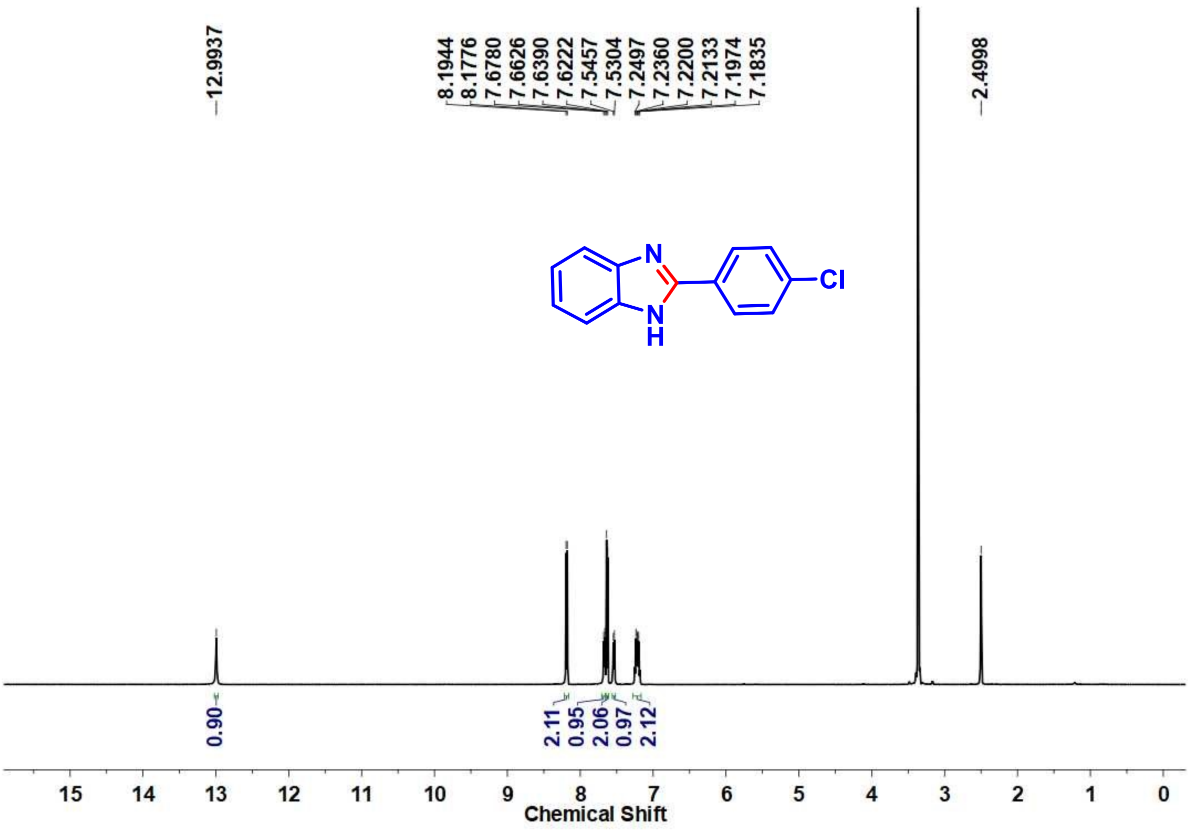
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4d



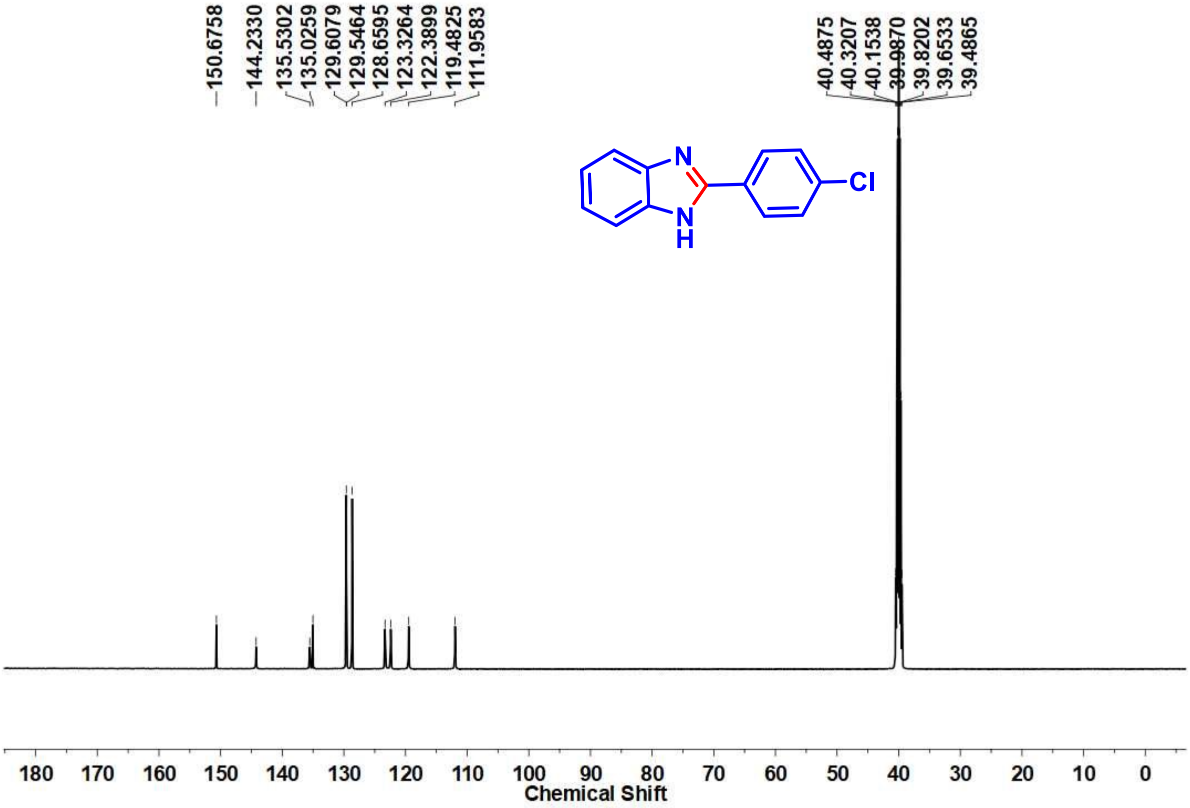
$^{13}C\{^{1}H\}$ **NMR (DMSO-*d*$_6$, 125 MHz) Spectrum of 4d**



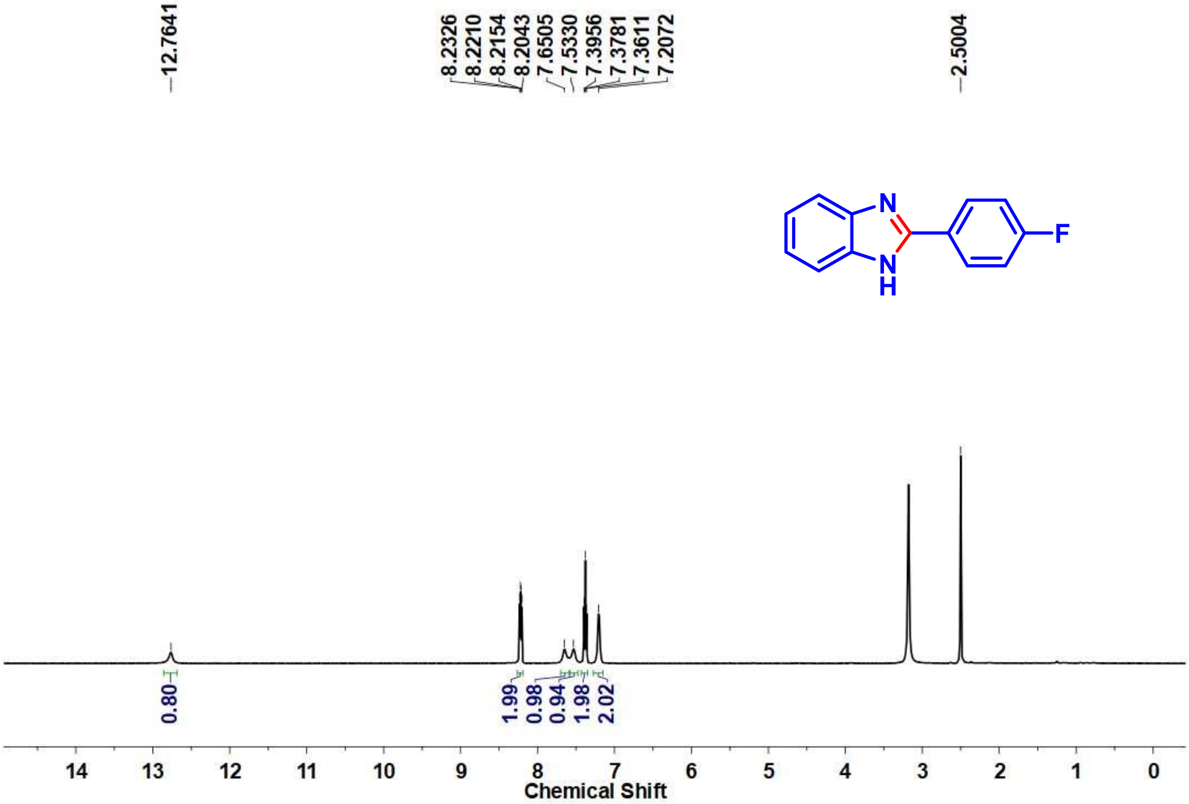
^{19}F **NMR (DMSO-*d*$_6$, 125 MHz) Spectrum of 4d**



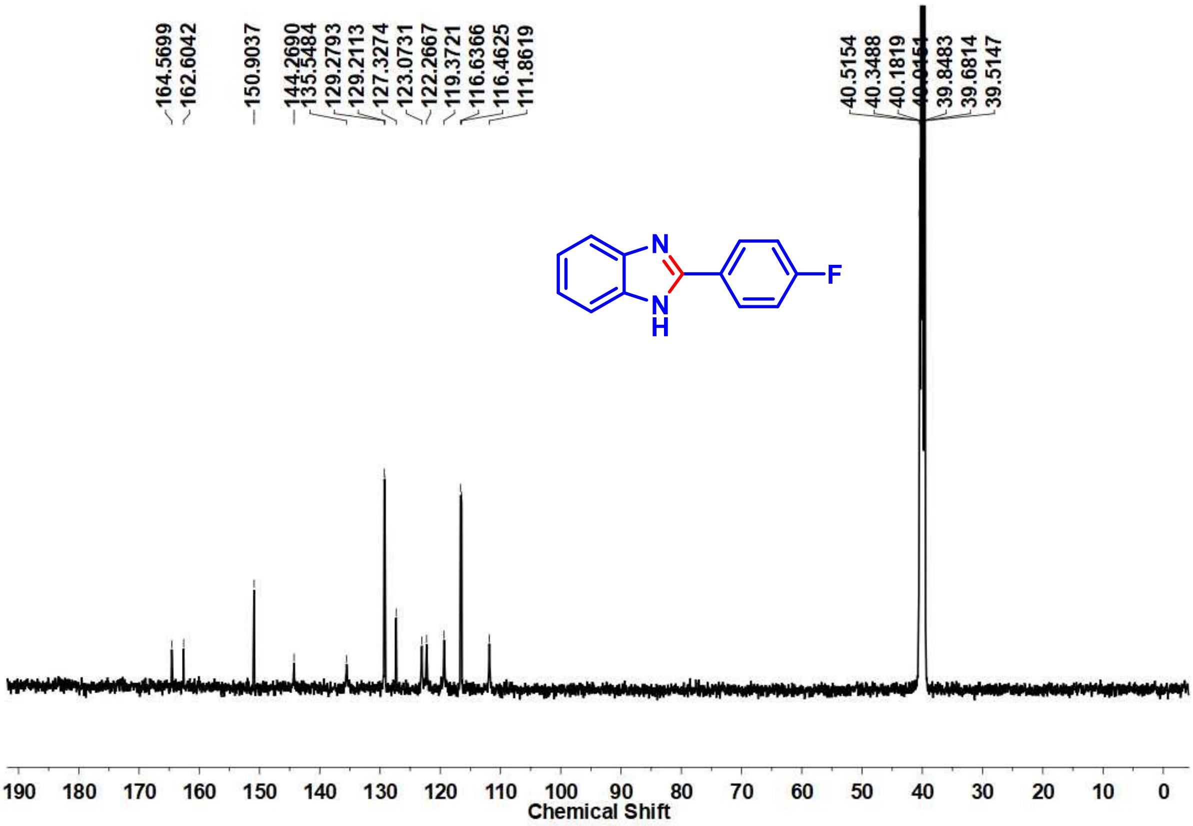
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4e



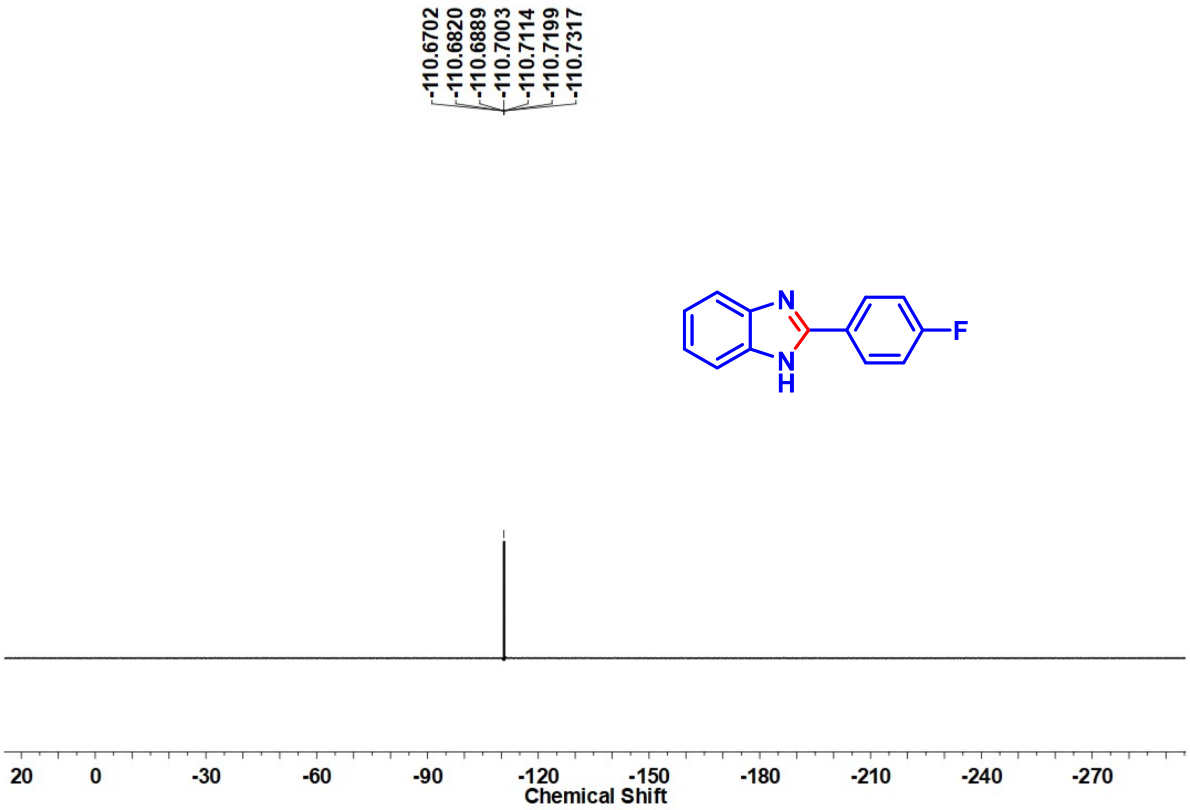
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 4e



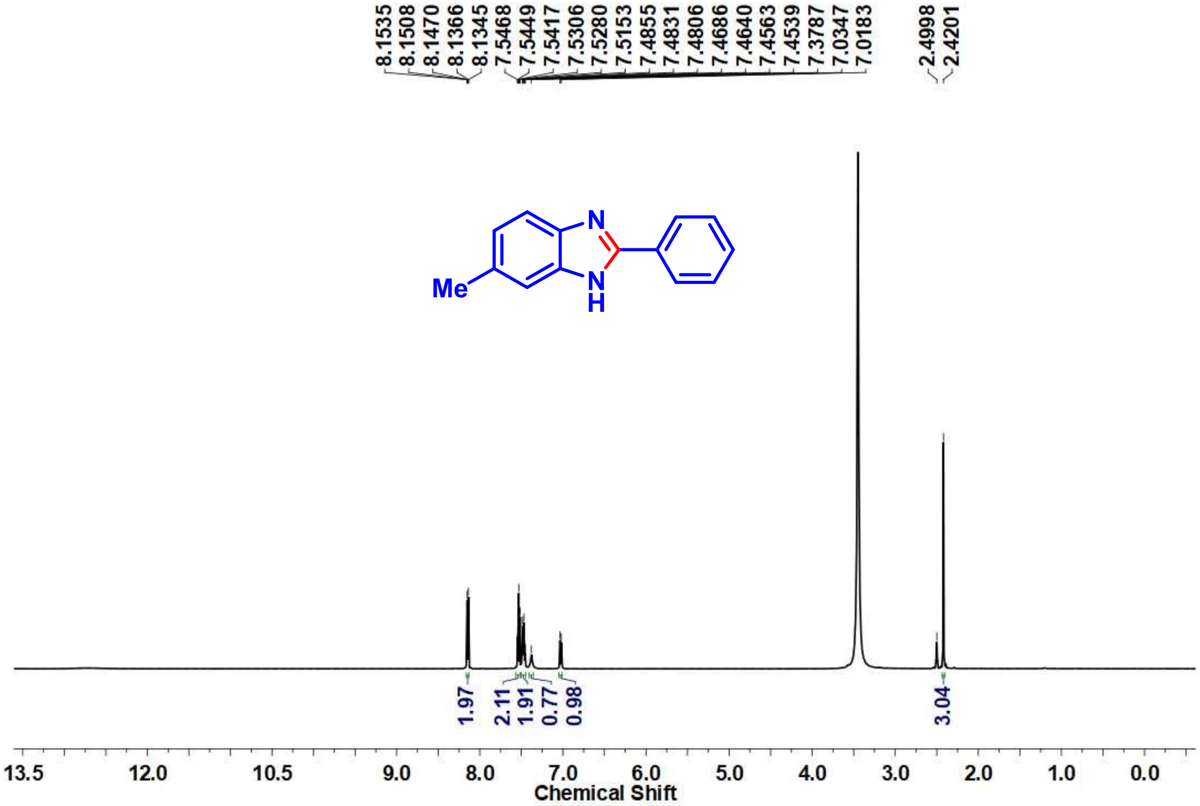
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4f



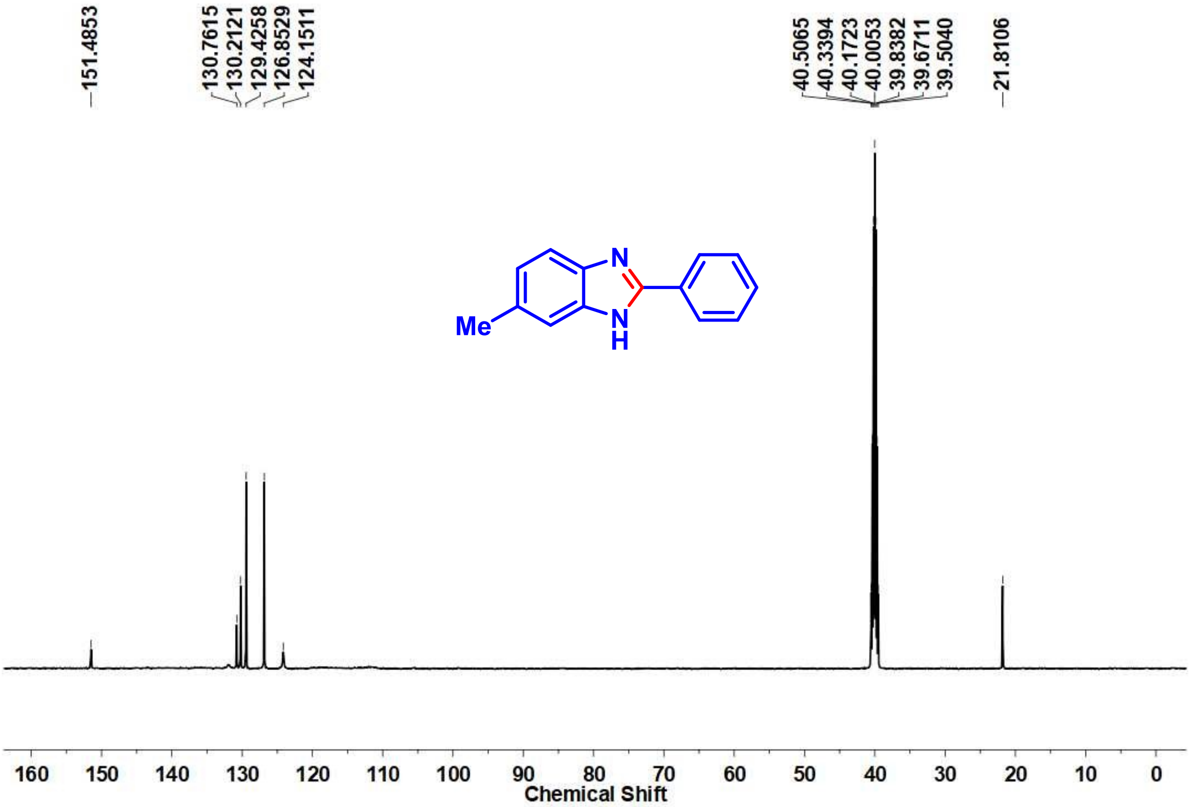
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 4f



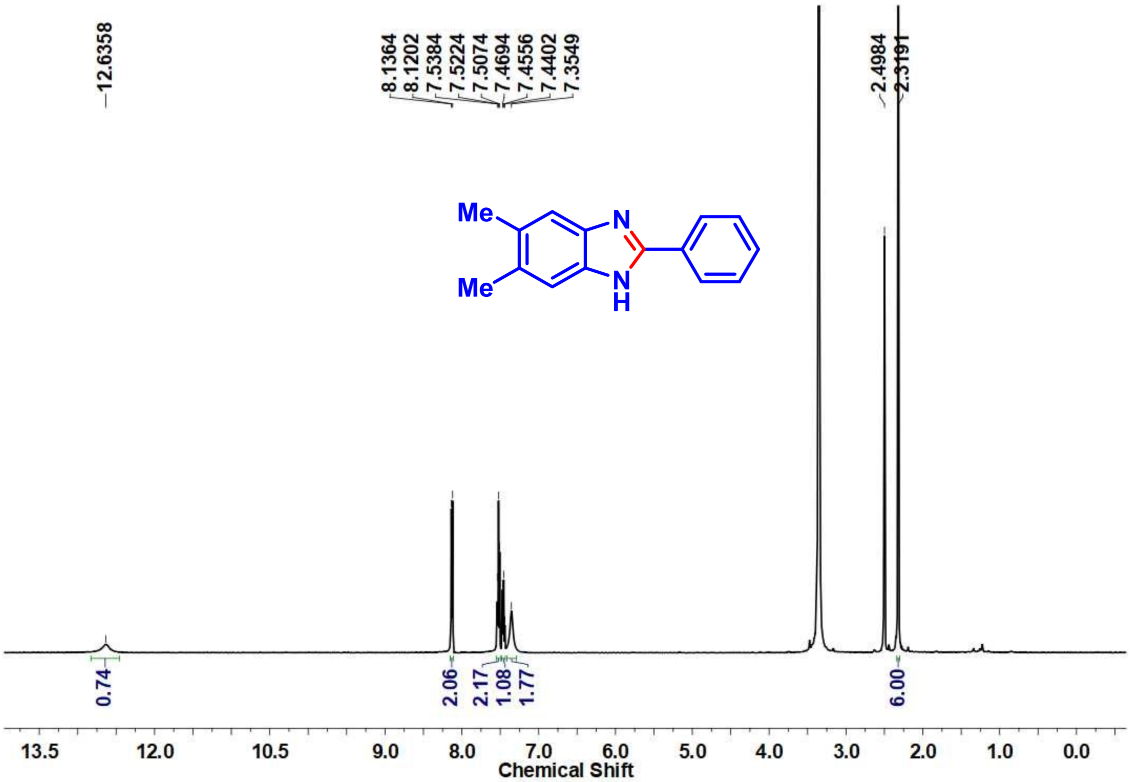
^{19}F NMR (DMSO-d_6, 125 MHz) Spectrum of 4f



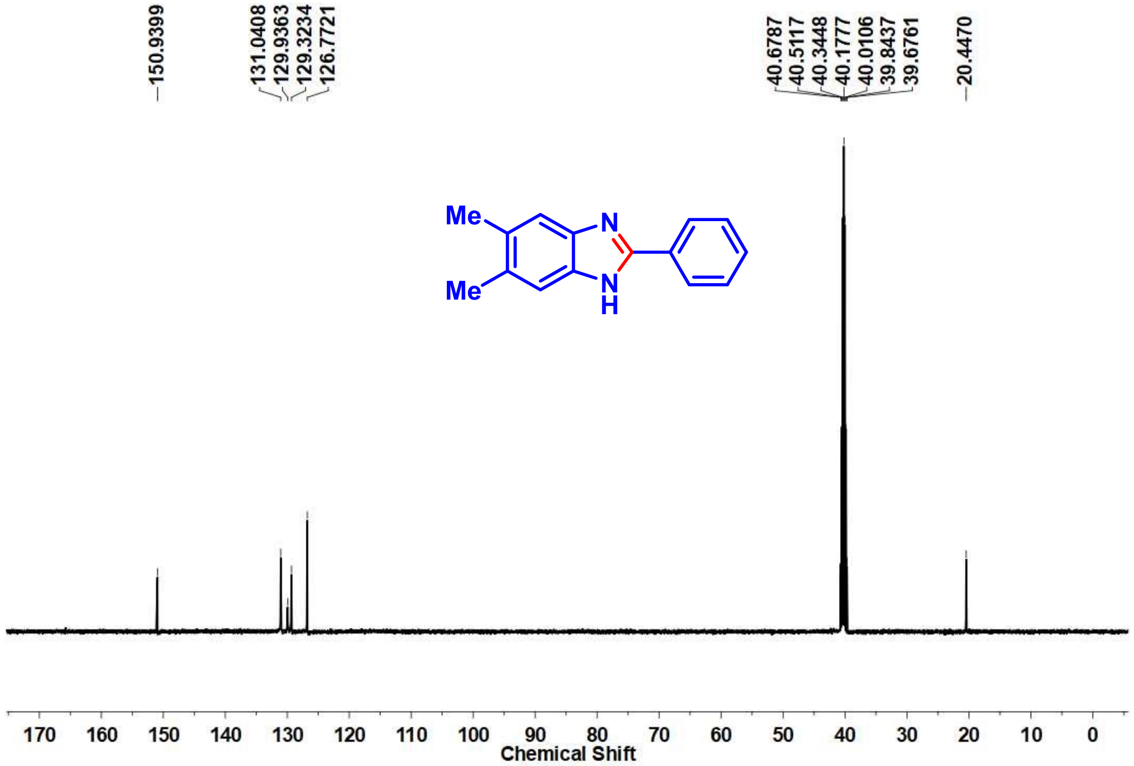
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4g



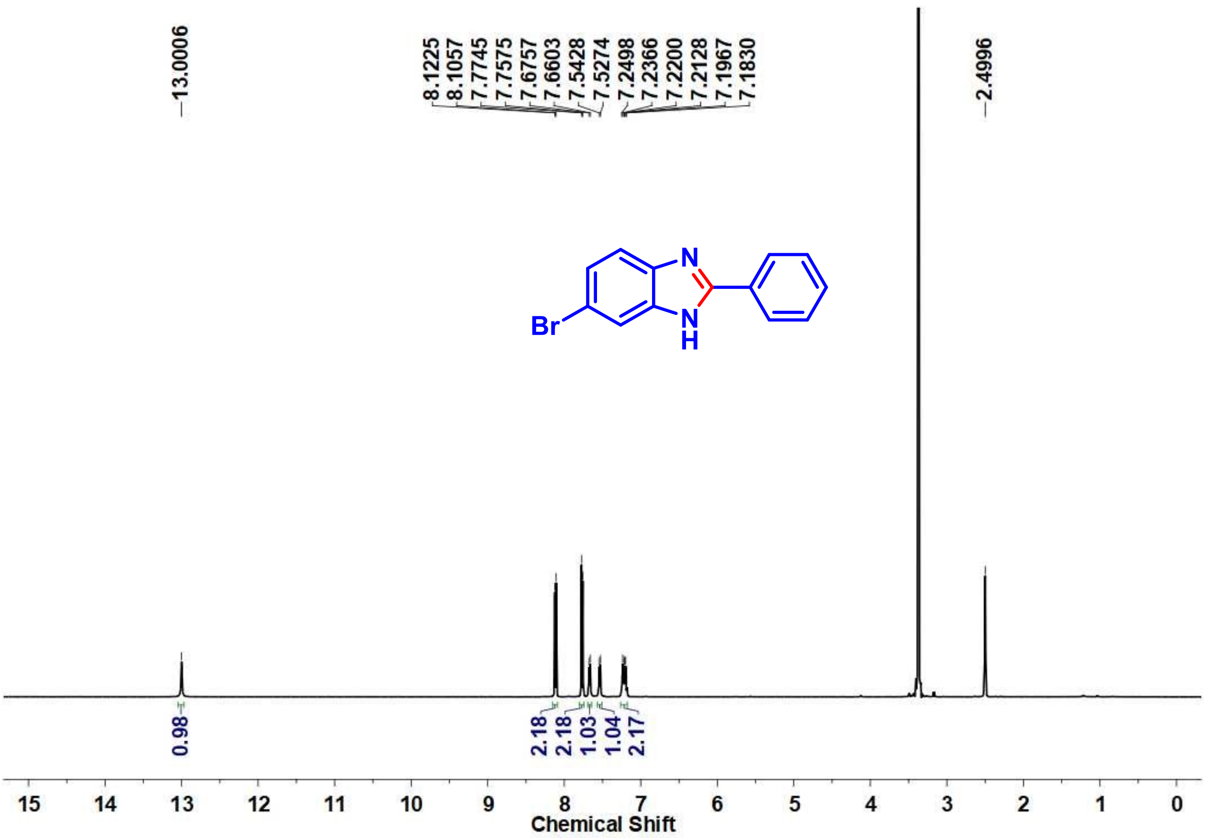
$^{13}C\{^1H\}$ NMR (DMSO-d_6, 125 MHz) Spectrum of 4g



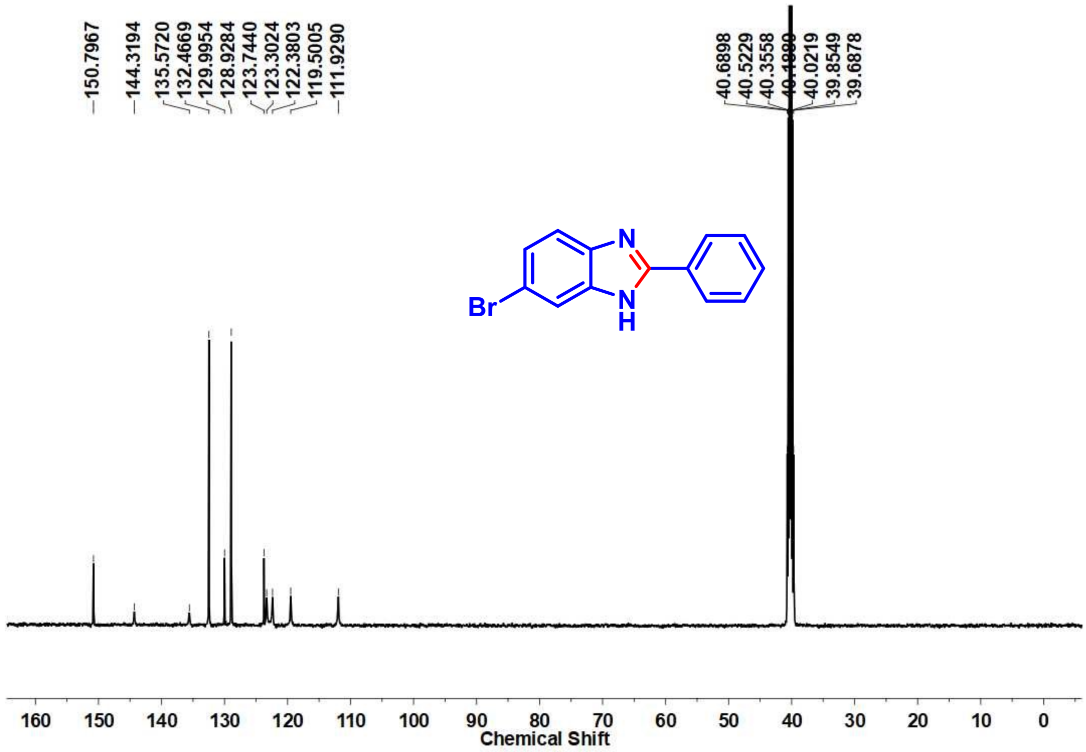
^1H NMR (DMSO-d_6, 500 MHz) Spectrum of 4h



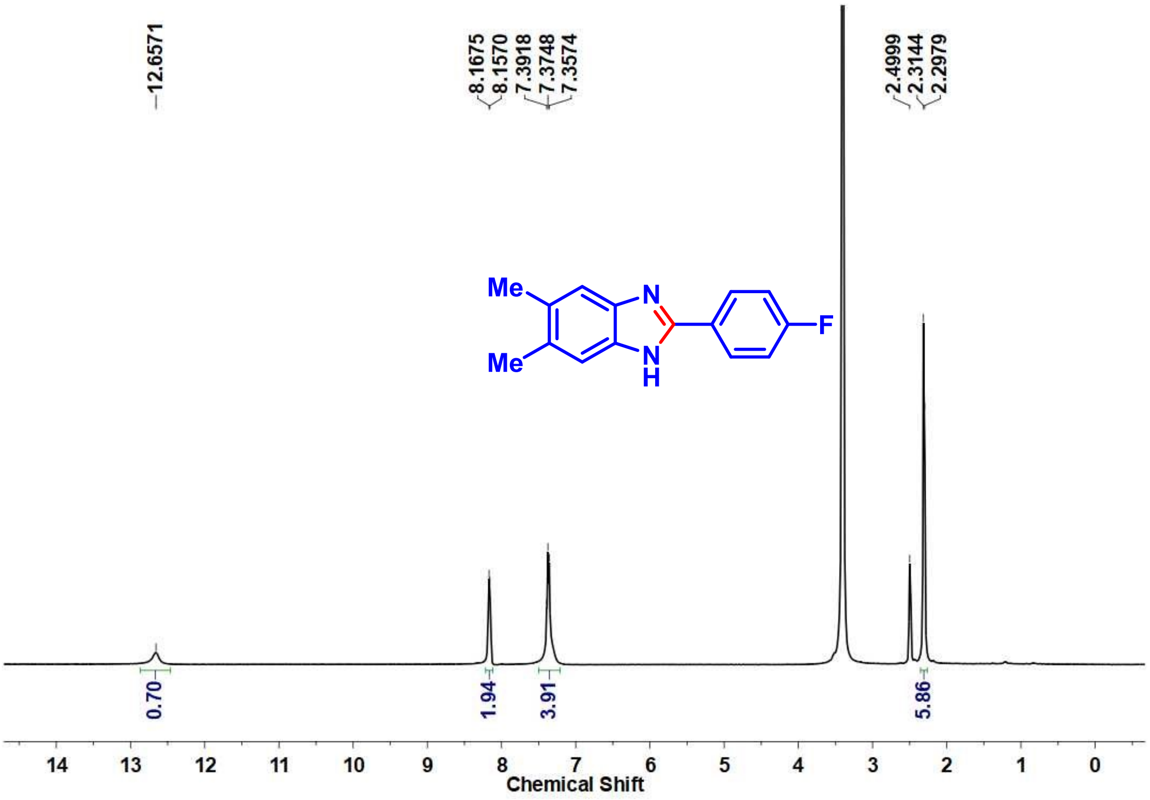
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 4h



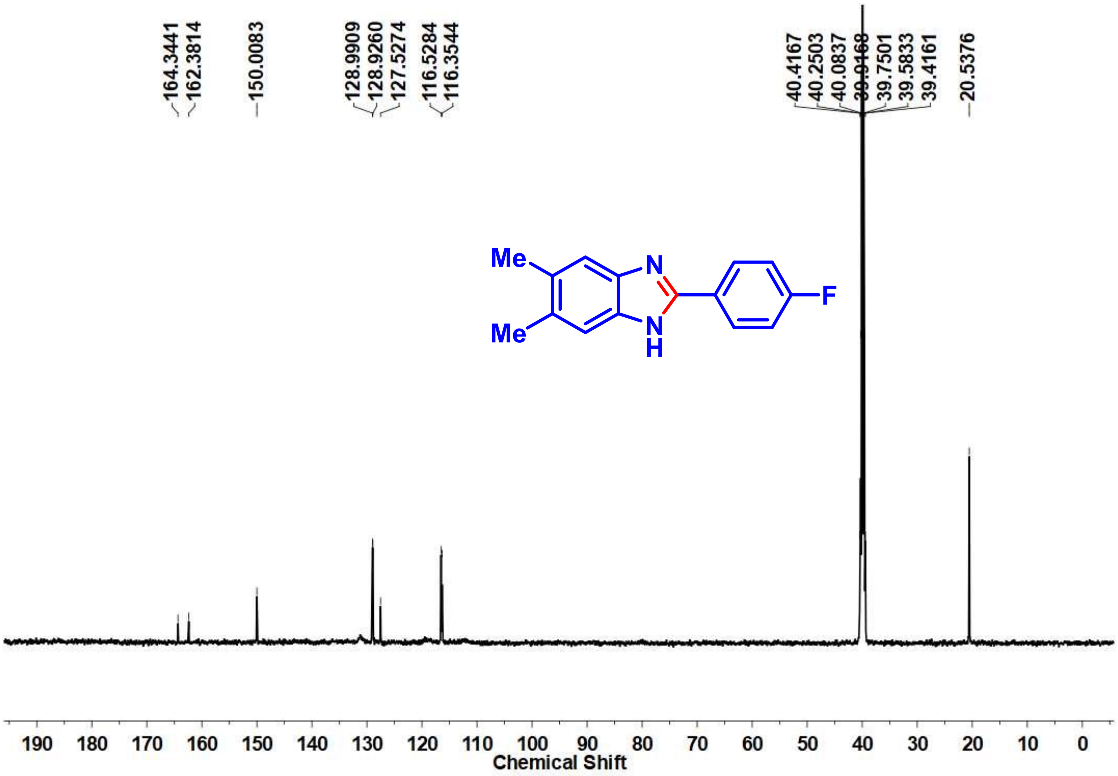
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4i



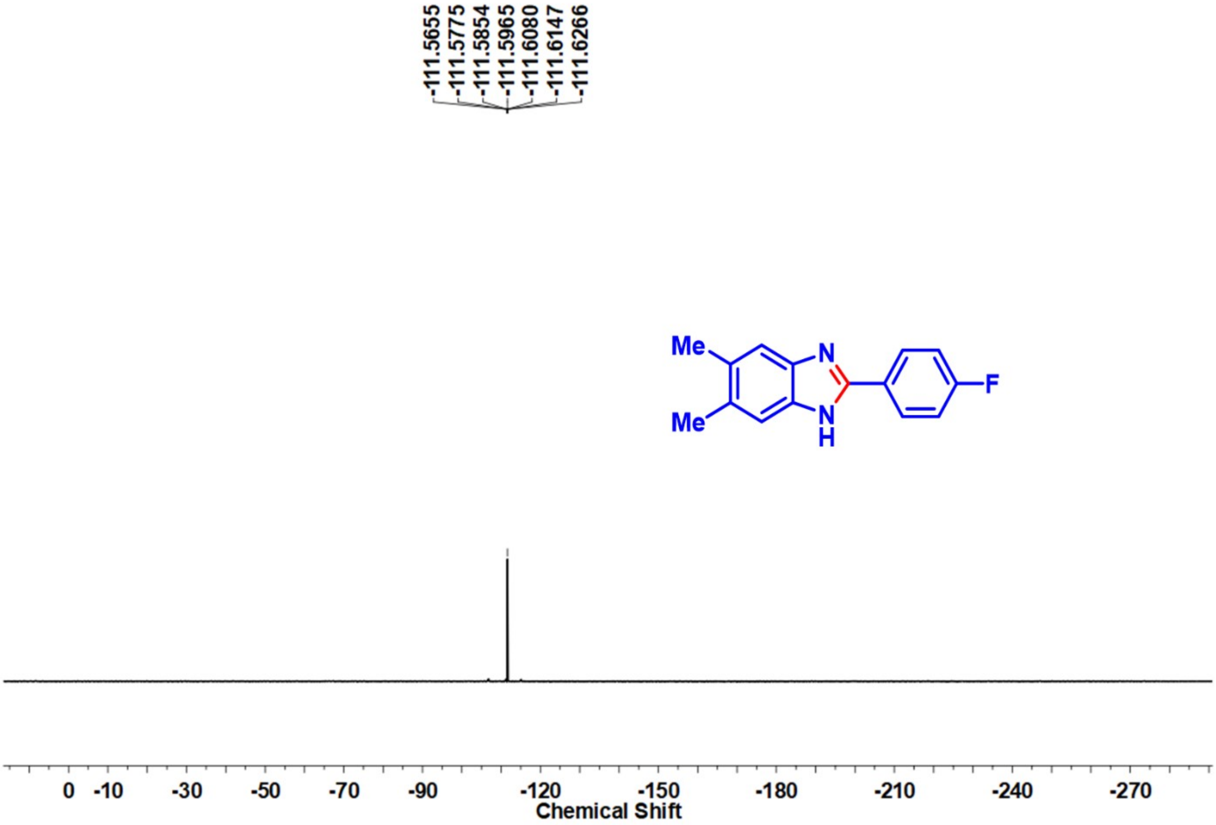
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 4i



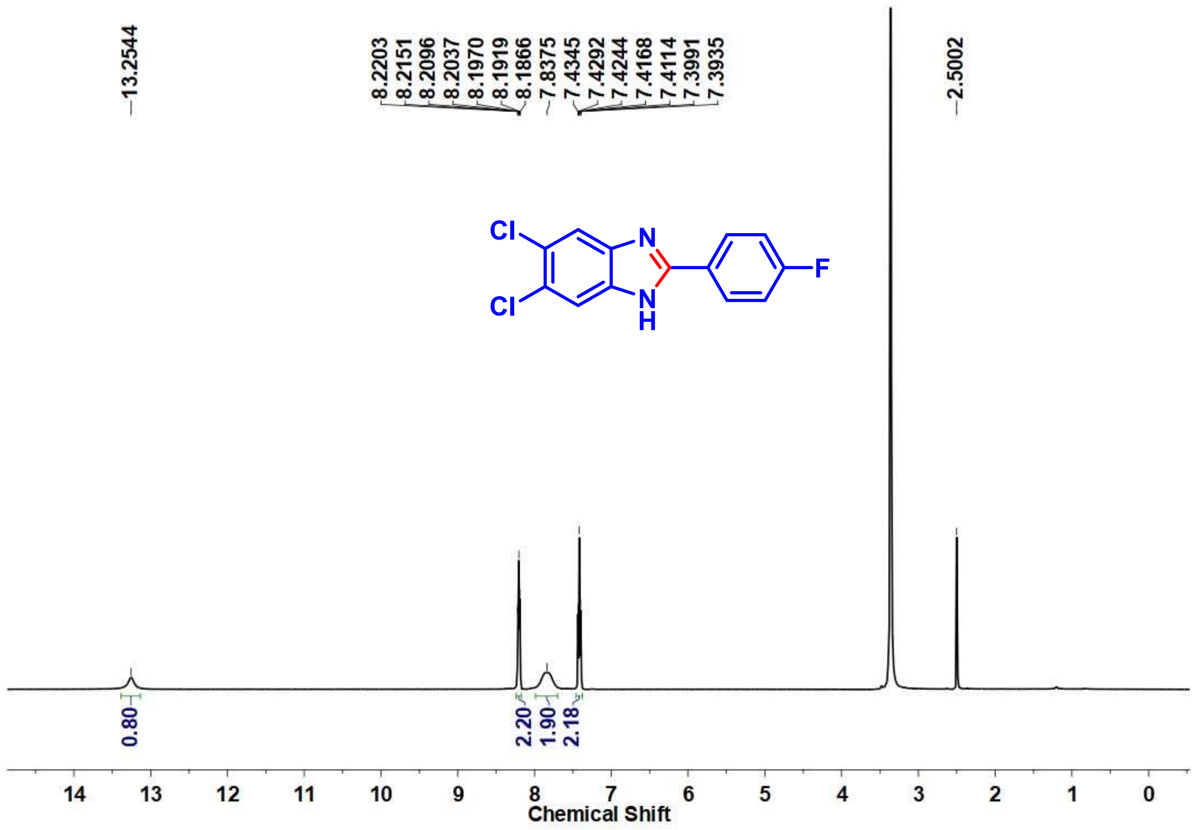
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4j



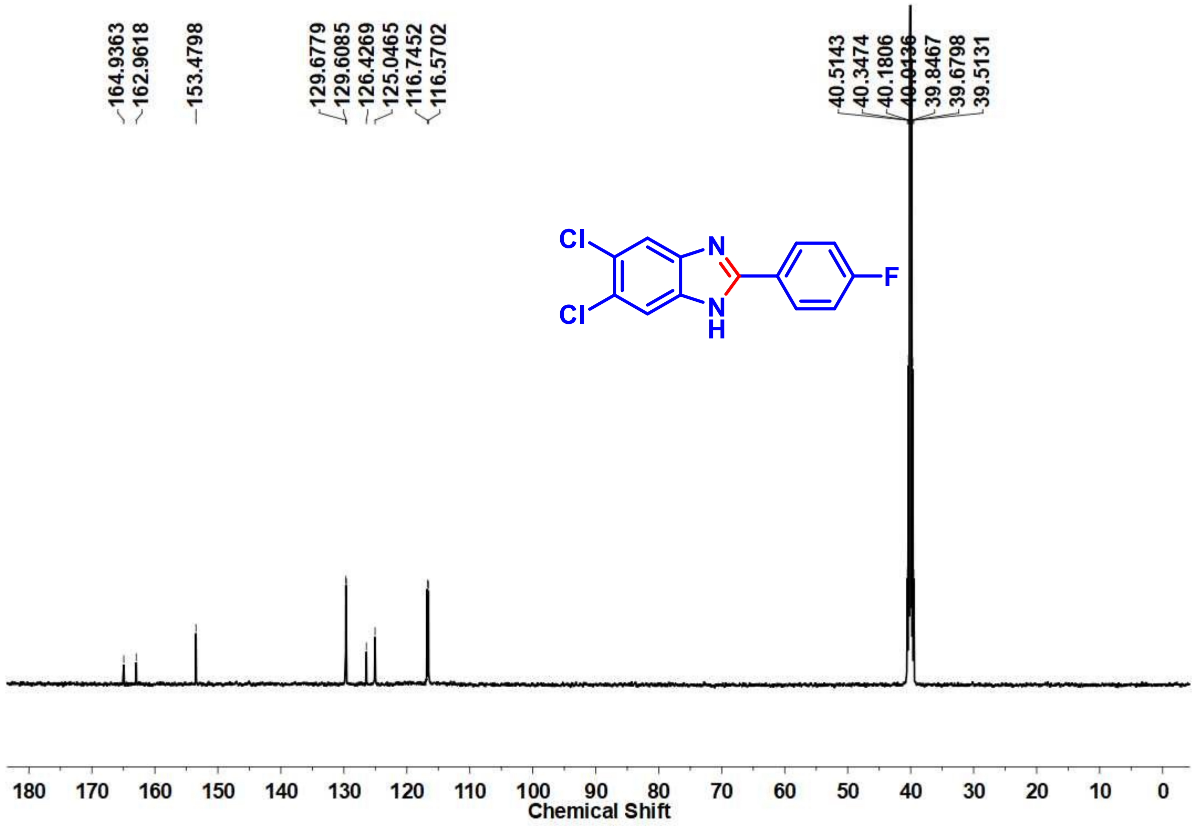
$^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 125 MHz) Spectrum of 4j



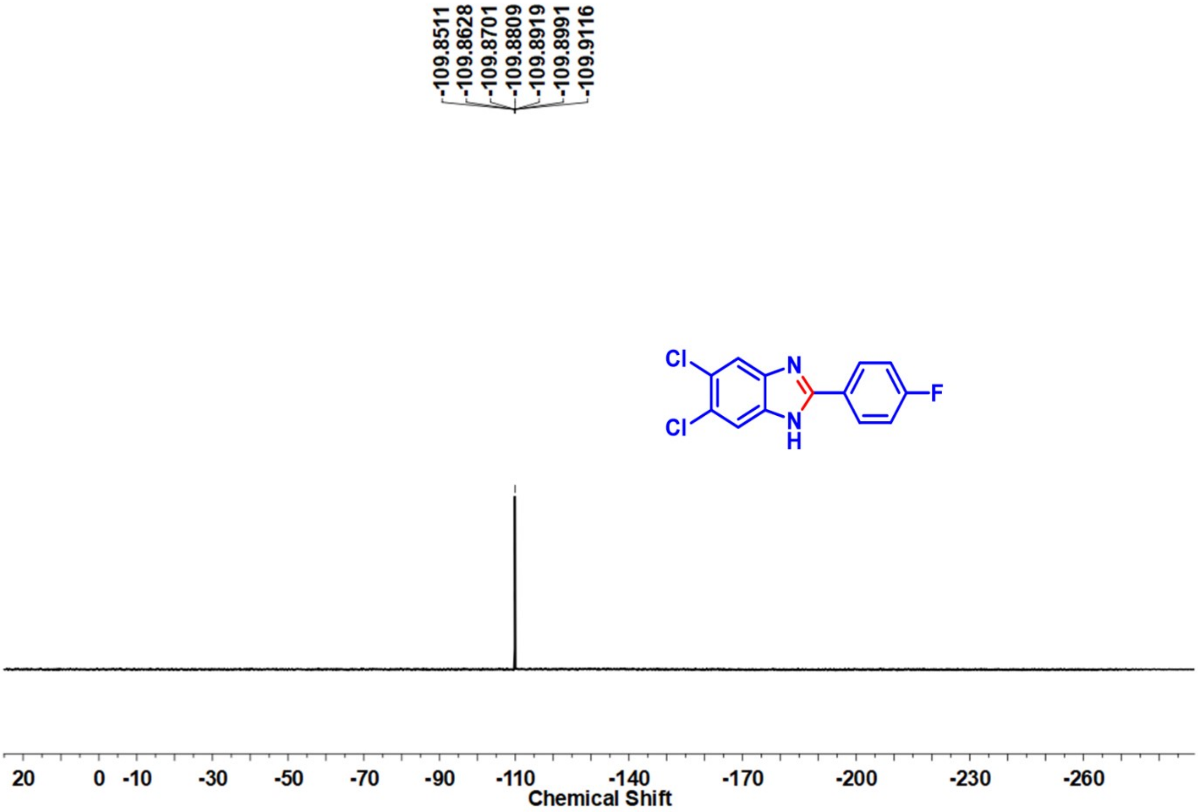
^{19}F NMR (DMSO-d_6, 125 MHz) Spectrum of 4j



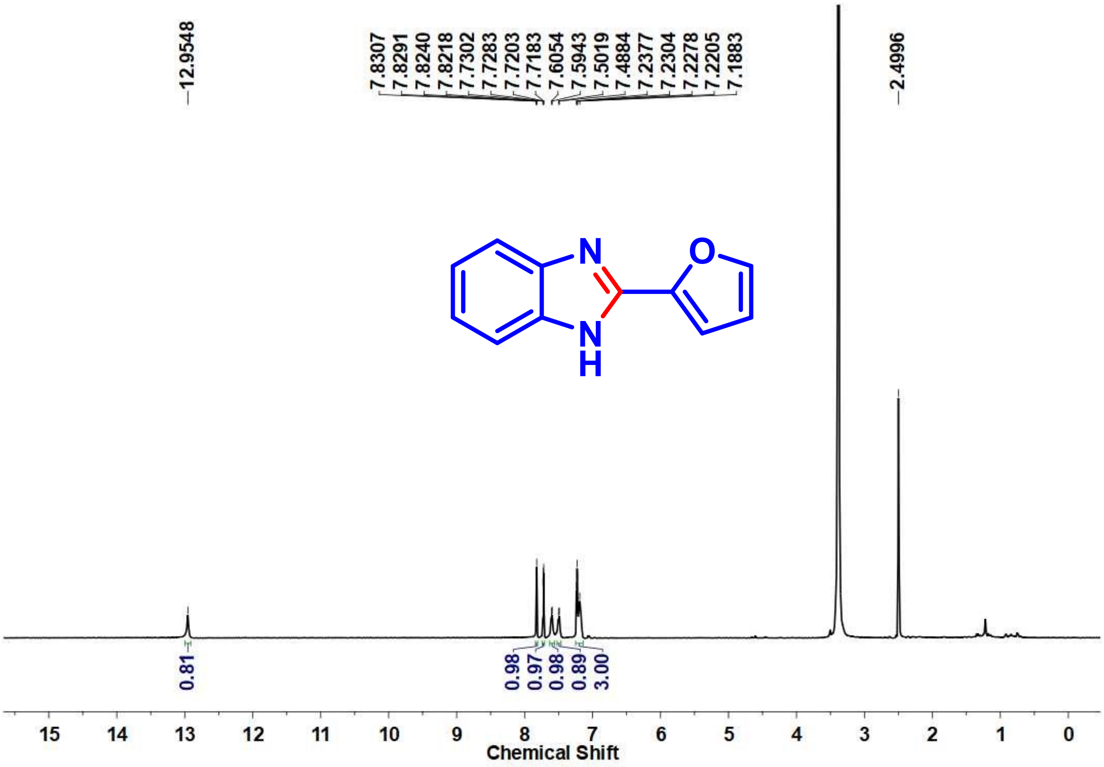
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4k



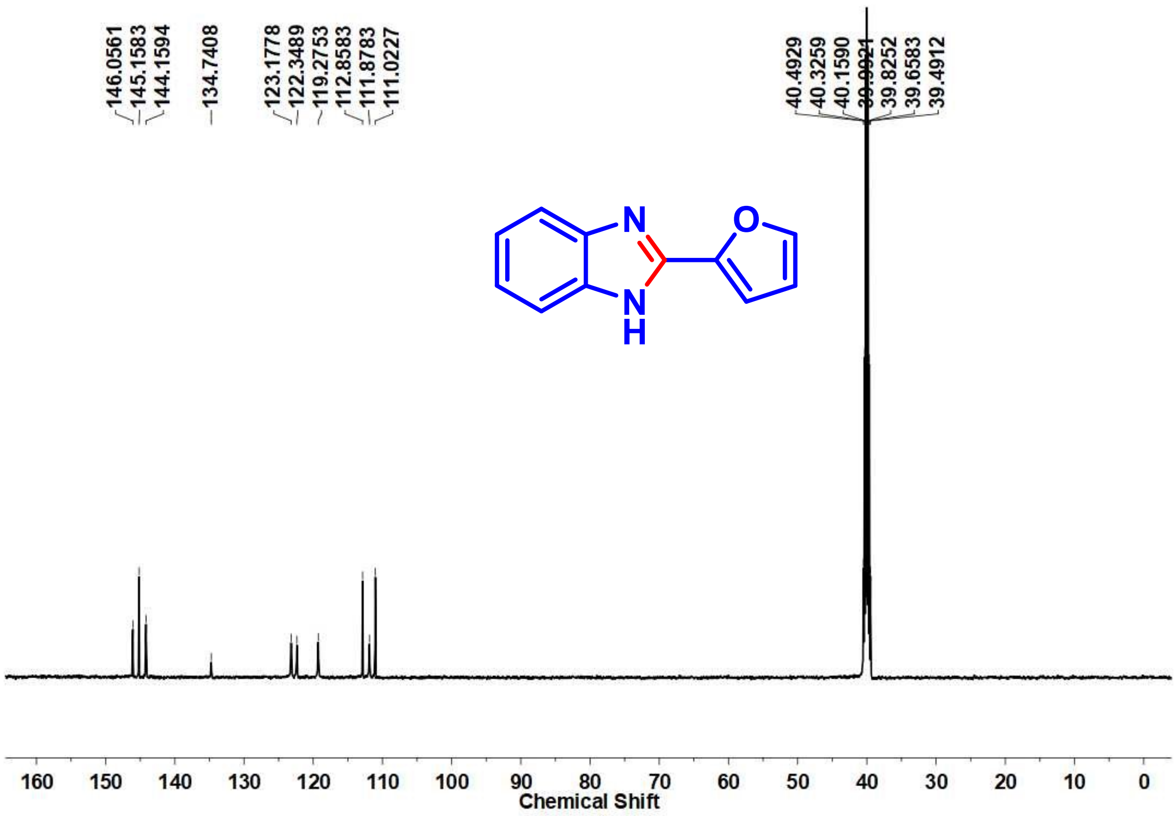
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 4k



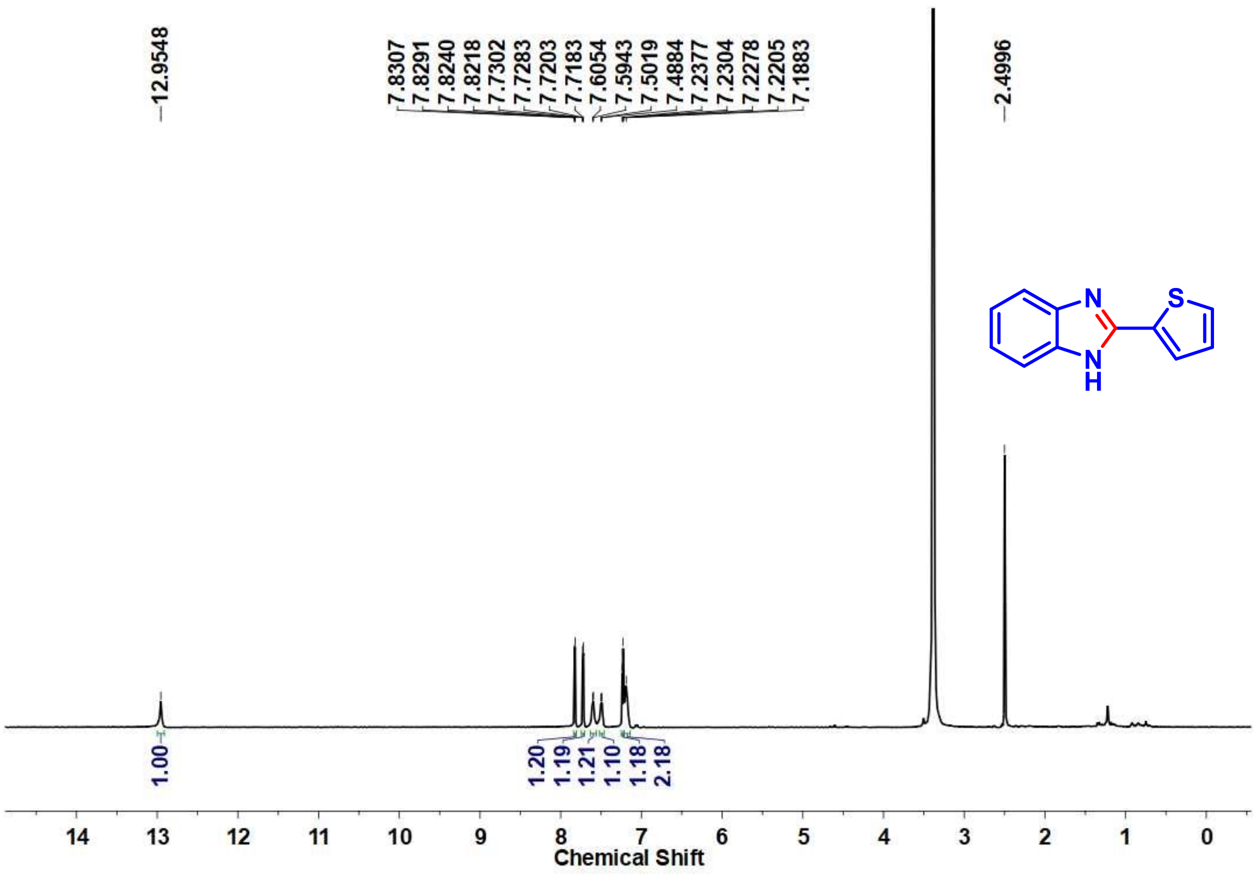
^{19}F NMR (DMSO-d_6, 125 MHz) Spectrum of 4k



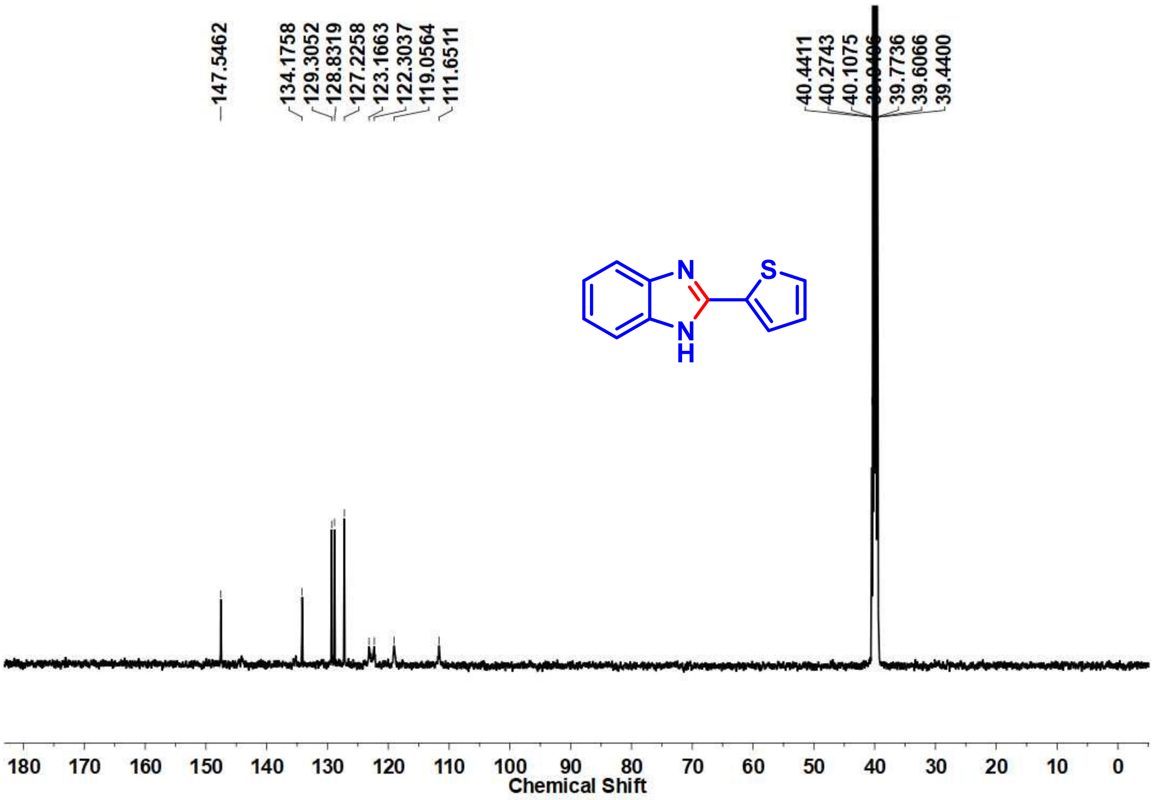
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4l



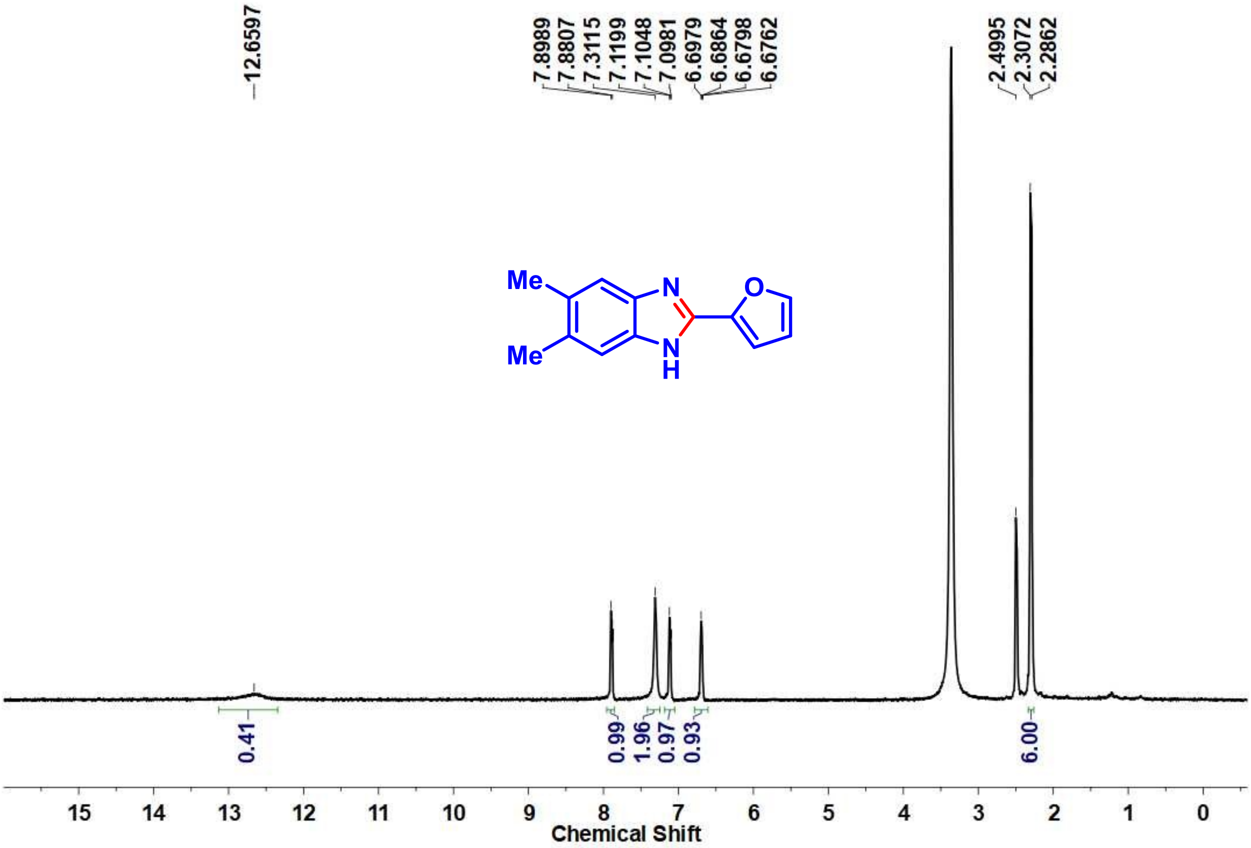
$^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 125 MHz) Spectrum of 4l



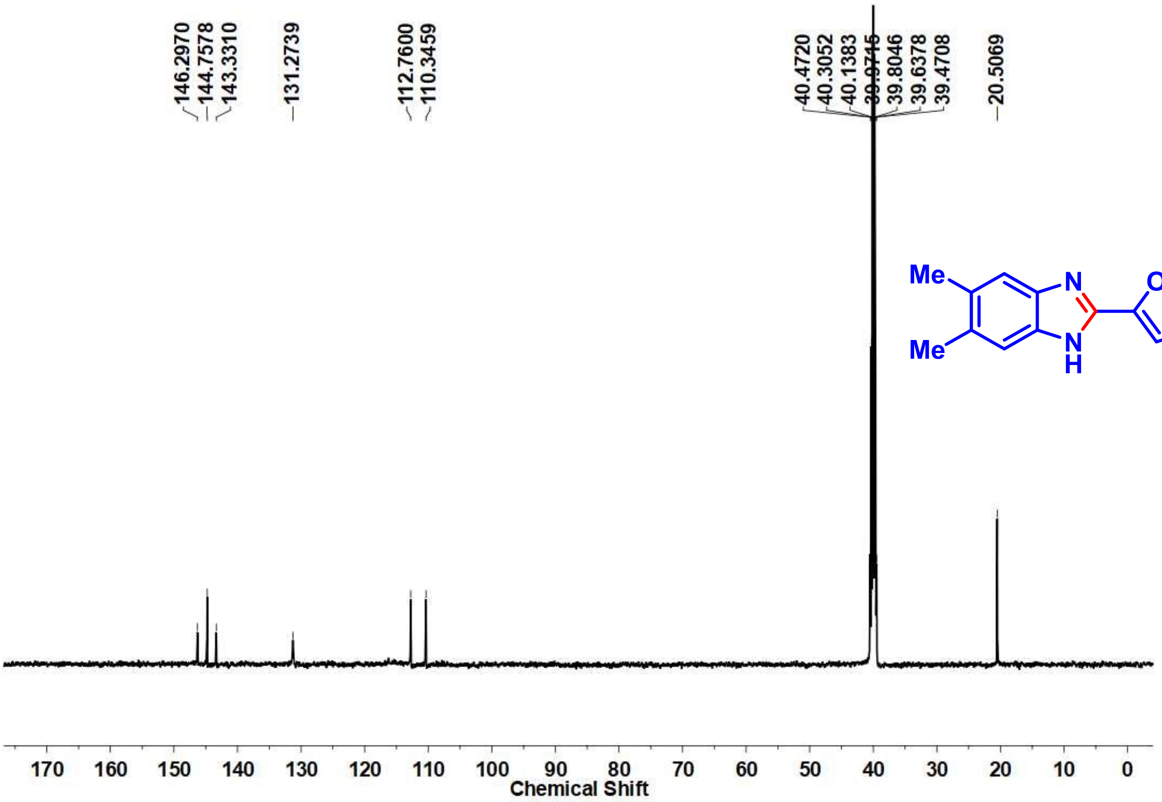
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4m



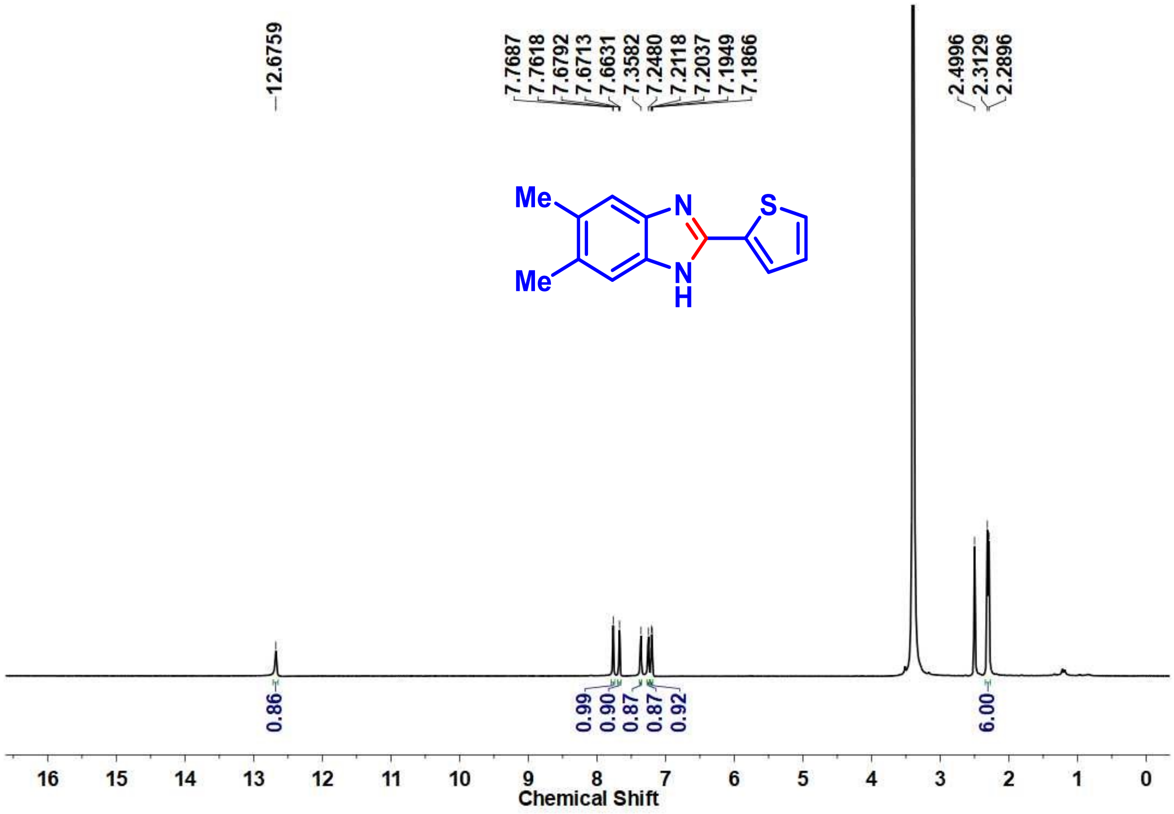
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 4m



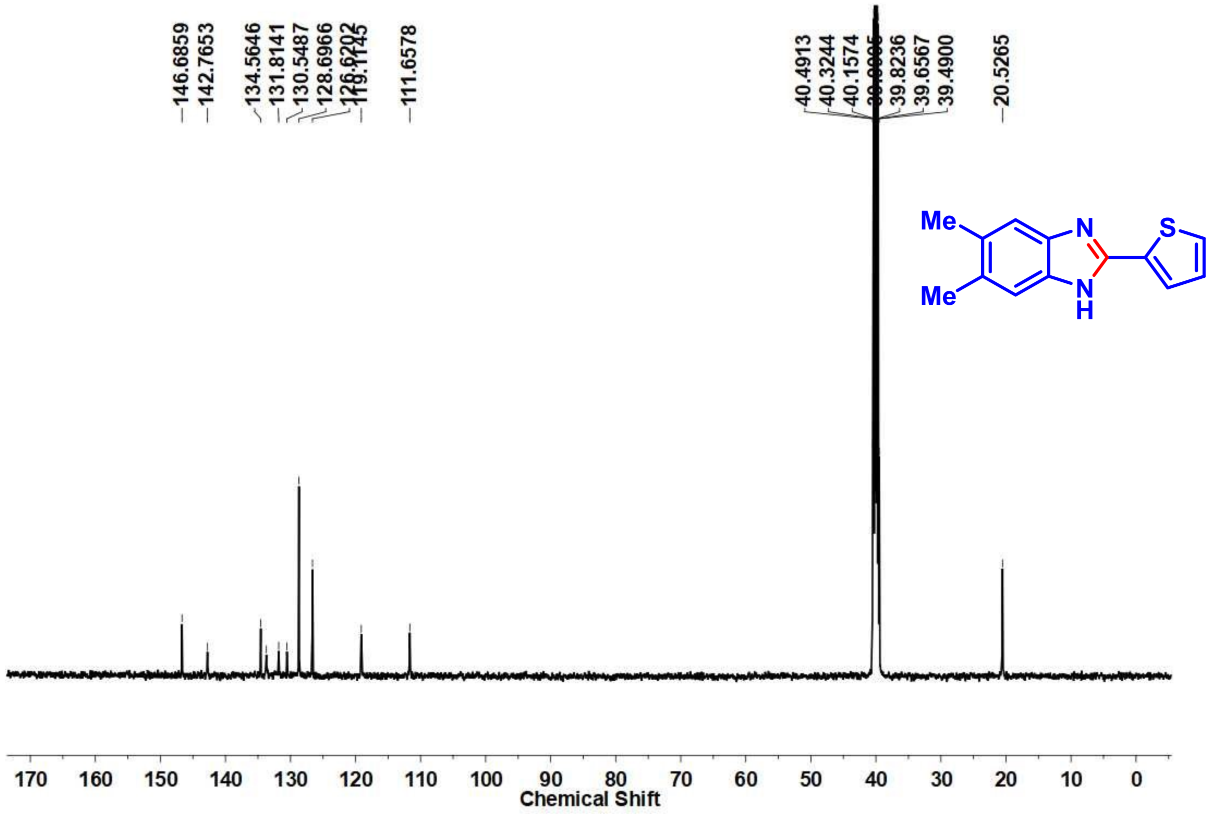
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4n



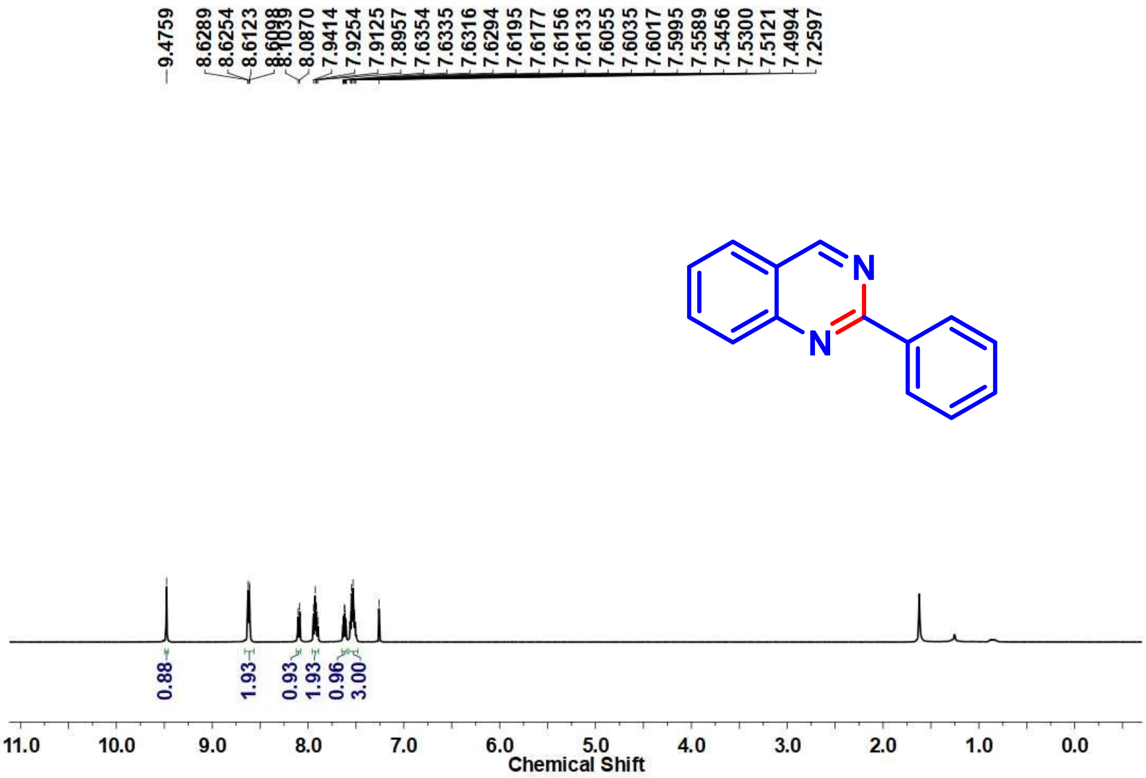
^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 4n



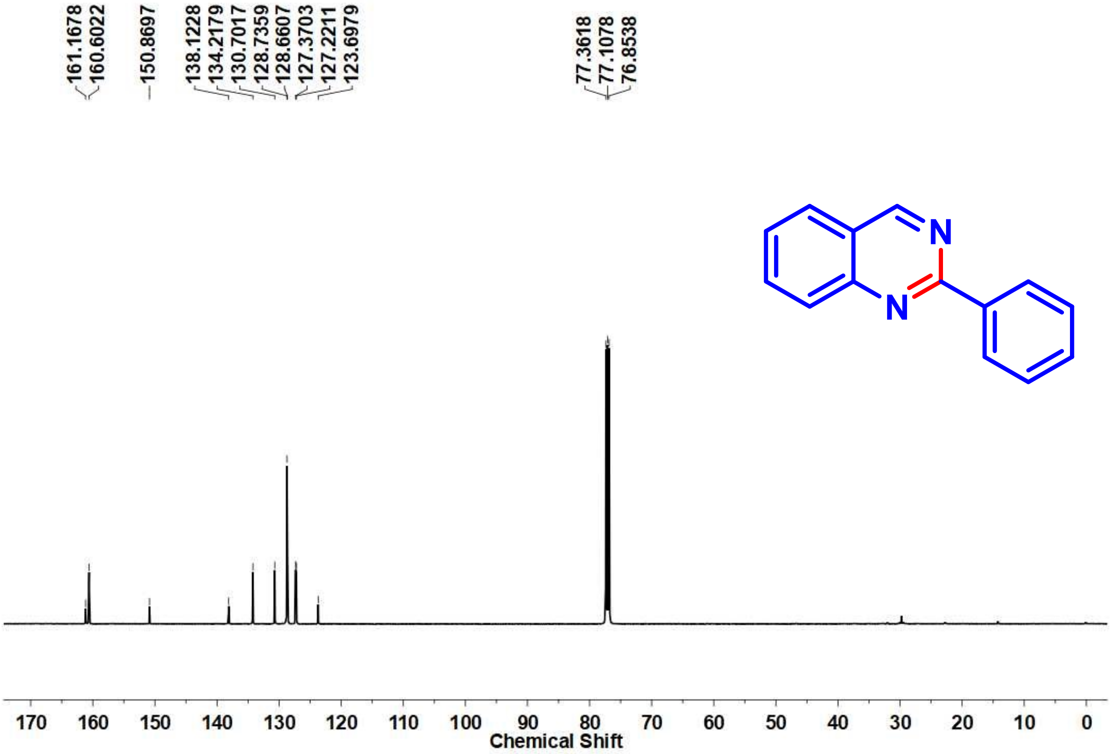
^{1}H NMR (DMSO-d_6, 500 MHz) Spectrum of 4o



^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) Spectrum of 4o

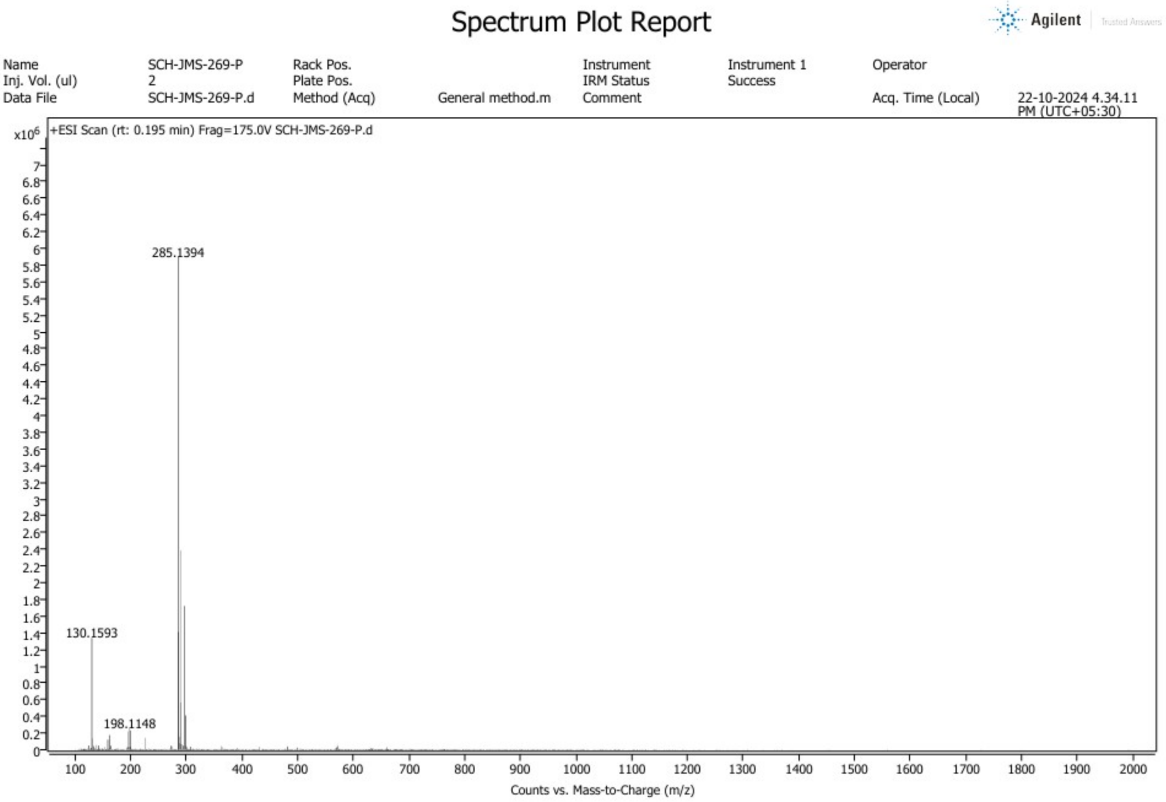


^{1}H NMR (CDCl$_3$, 500 MHz) Spectrum of 6



^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) Spectrum of 6

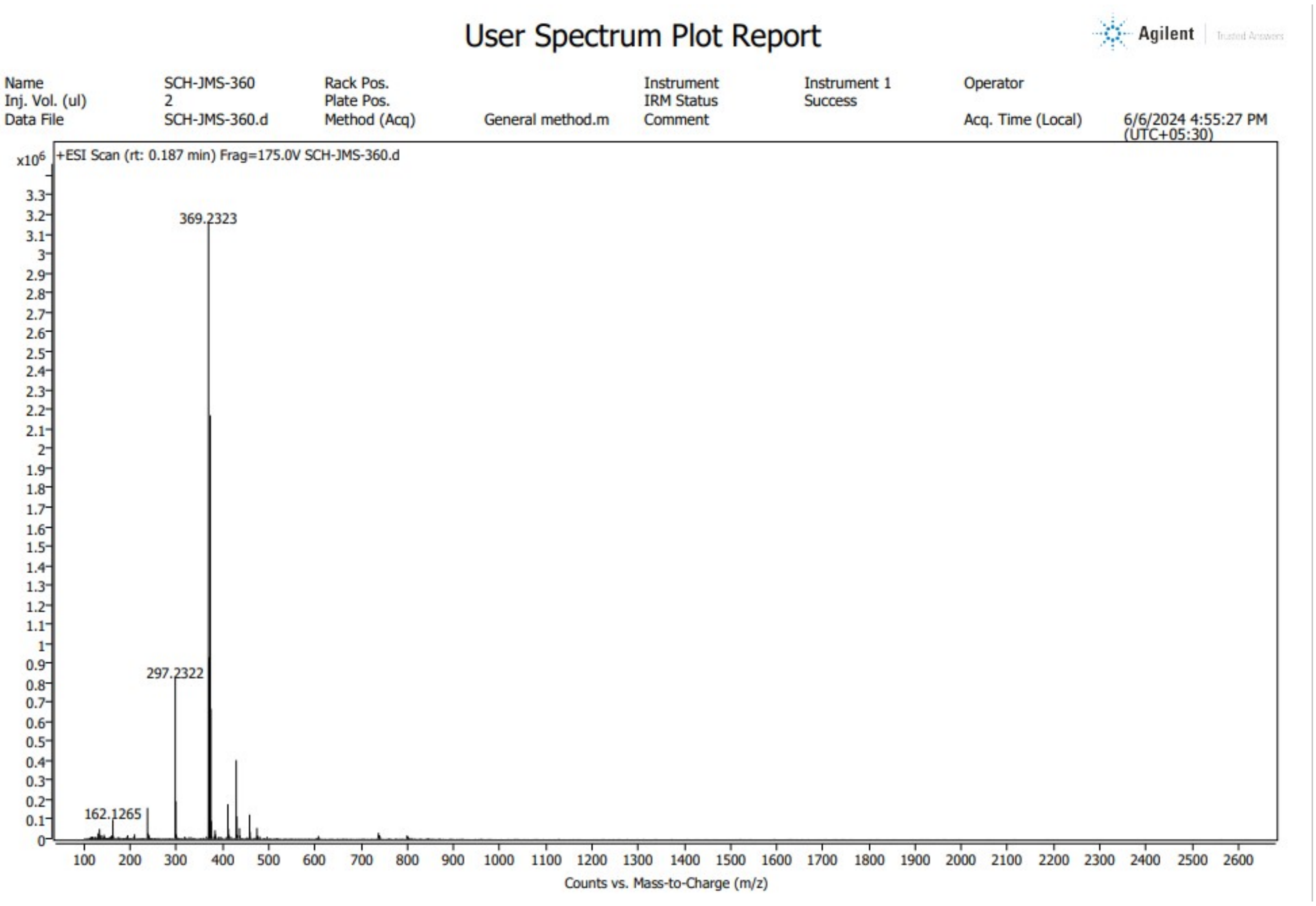
11. Mass Spectra NHC-catalysed compounds



Spectrum Plot Report

Name	SCH-JMS-269-P	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-269-P.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	22-10-2024 4.34.11 PM (UTC+05:30)

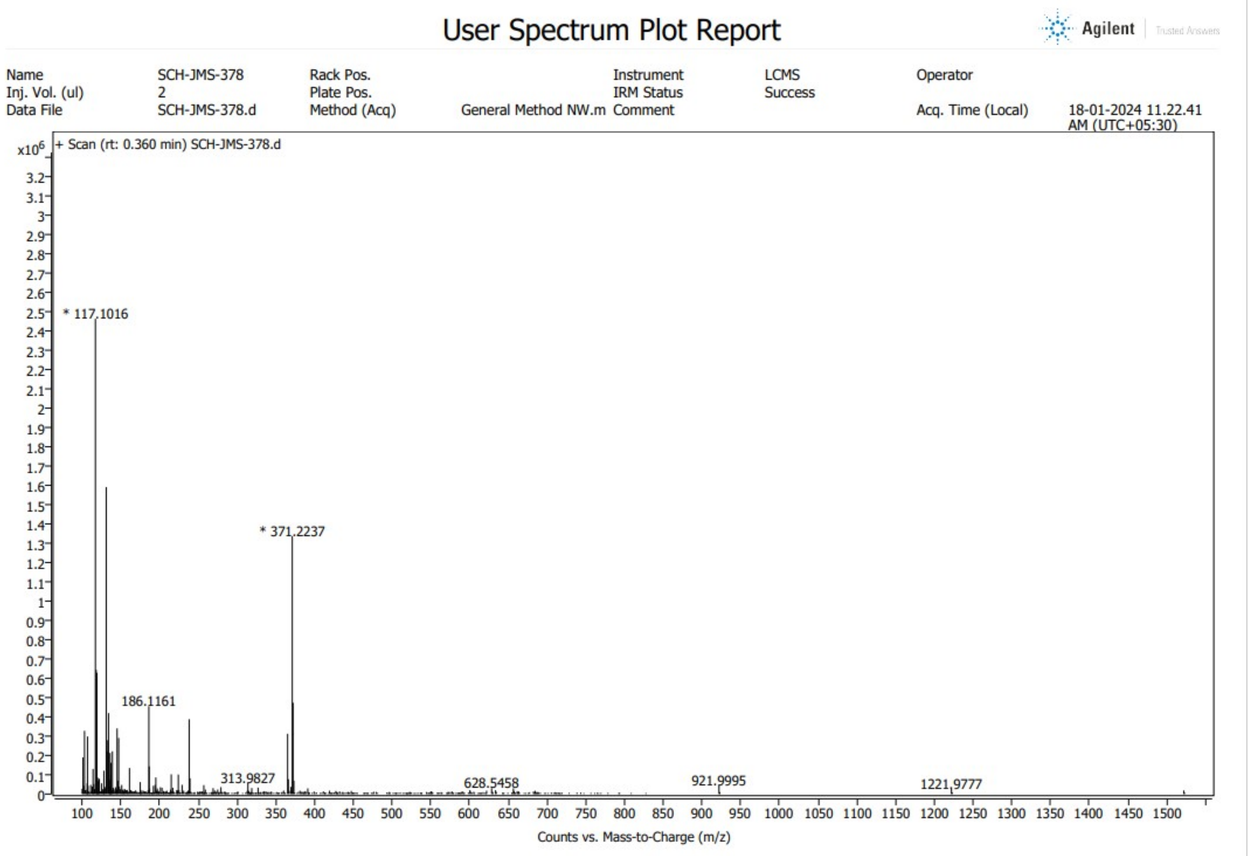
Mass spectrum of 3a



User Spectrum Plot Report

Name	SCH-JMS-360	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-360.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	6/6/2024 4:55:27 PM (UTC+05:30)

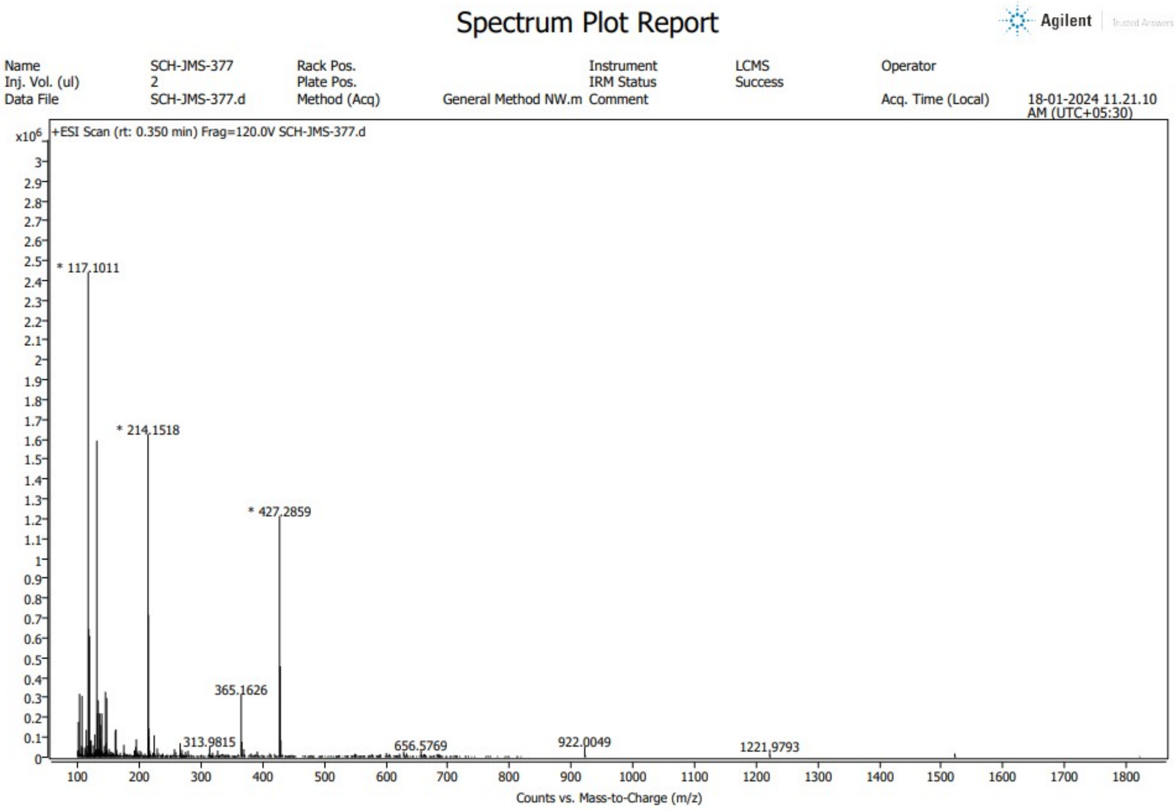
Mass spectrum of 3b



User Spectrum Plot Report

Name	SCH-JMS-378	Rack Pos.		Instrument	LCMS	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-378.d	Method (Acq)	General Method NW.m	Comment		Acq. Time (Local)	18-01-2024 11.22.41 AM (UTC+05:30)

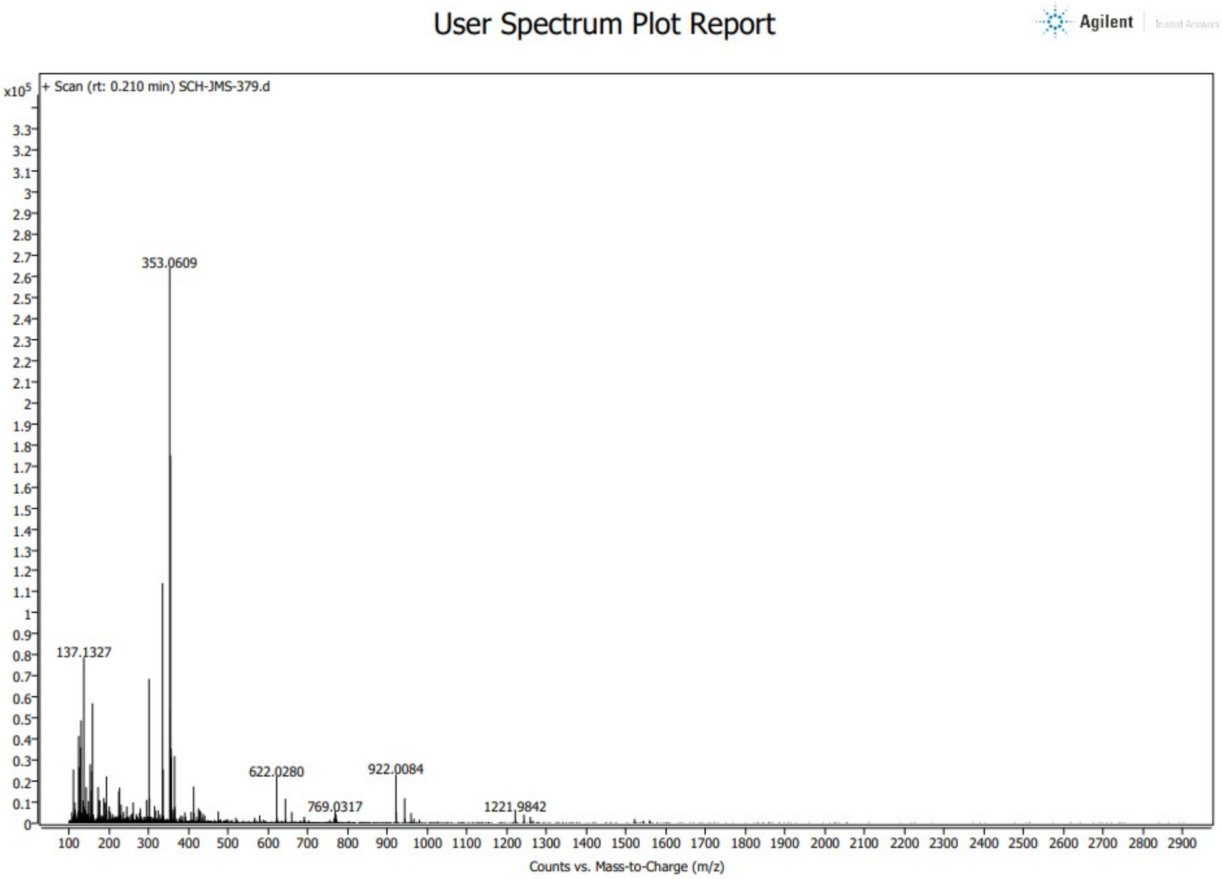
Mass spectrum of 3c



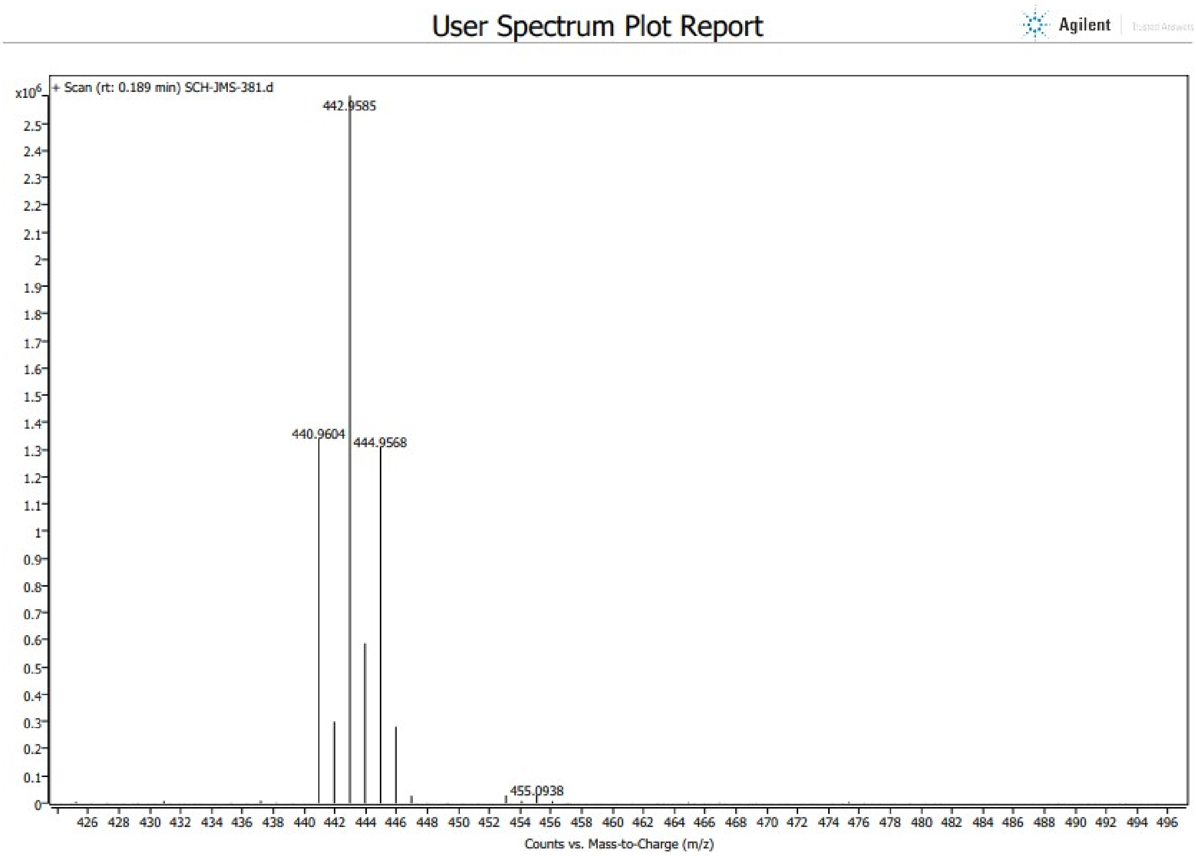
Spectrum Plot Report

Name SCH-JMS-377 Rack Pos. Instrument LCMS Operator
Inj. Vol. (ul) 2 Plate Pos. IRM Status Success
Data File SCH-JMS-377.d Method (Acq) General Method NW.m Comment Acq. Time (Local) 18-01-2024 11.21.10 AM (UTC+05:30)

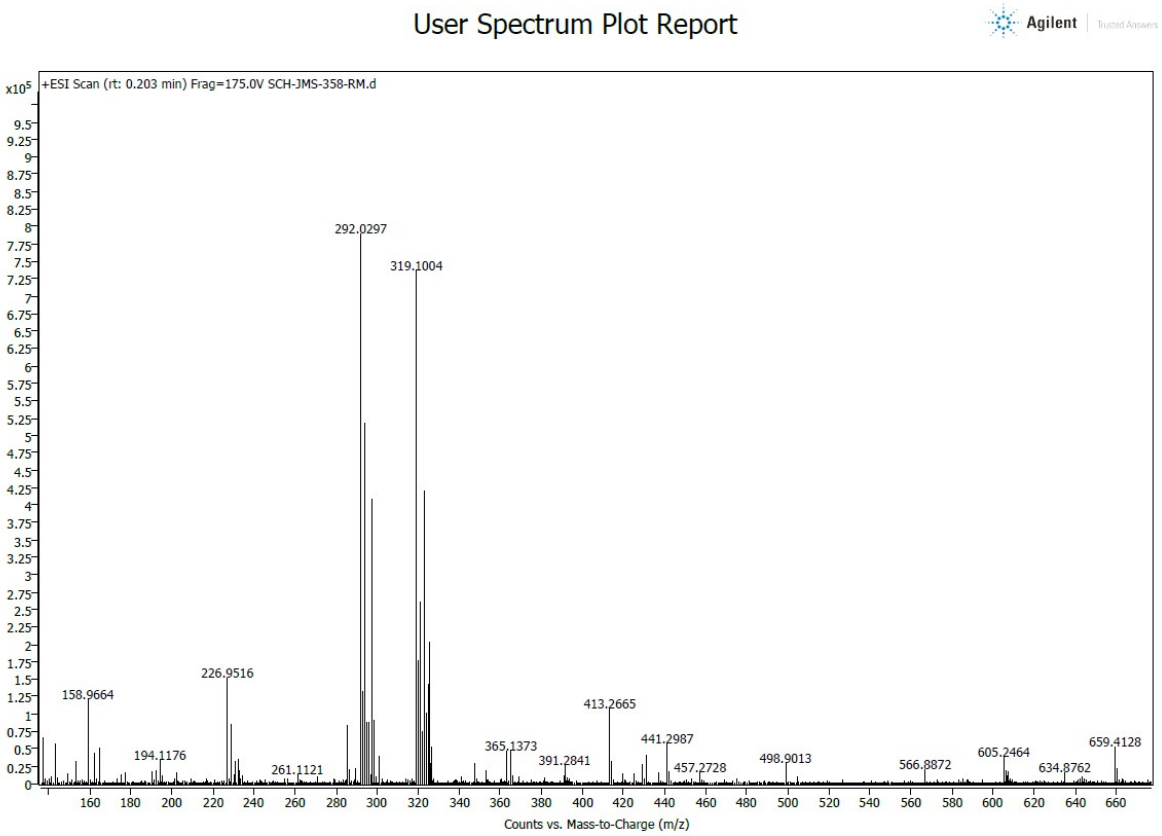
Mass spectrum of 3d



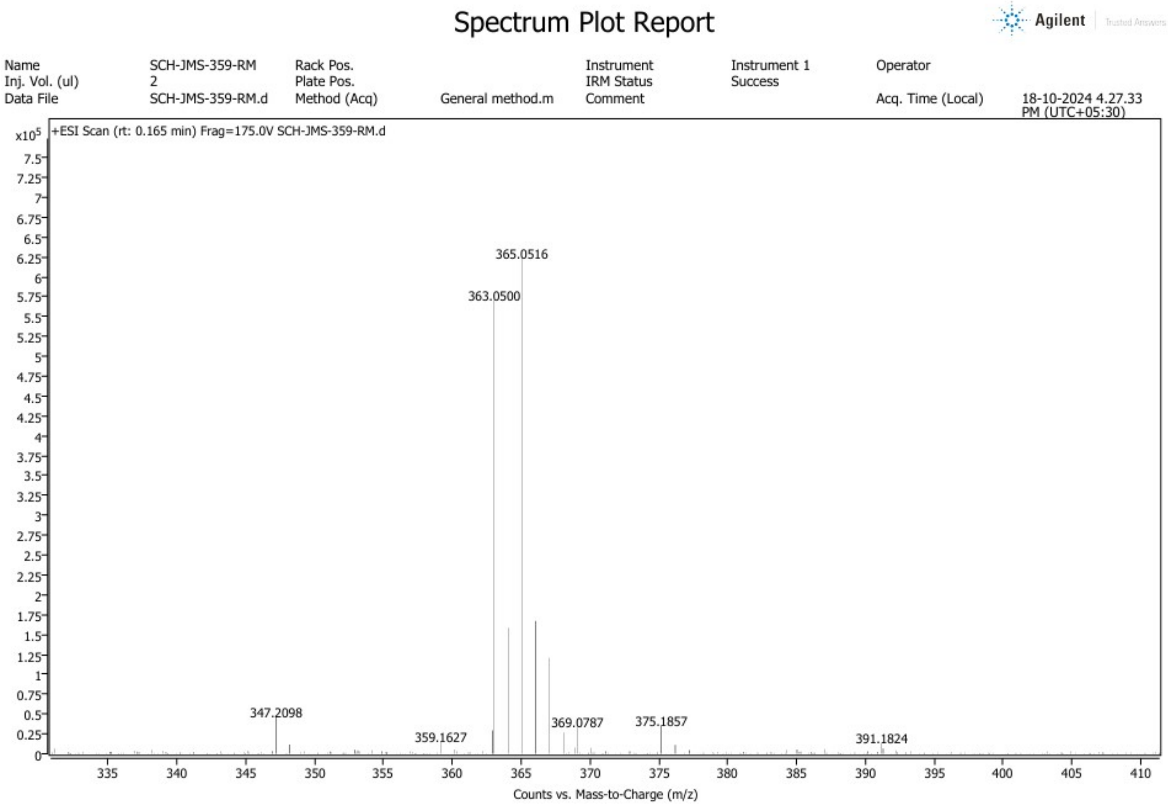
Mass spectrum of 3e



Mass spectrum of 3f



Mass spectrum of 3g



Spectrum Plot Report

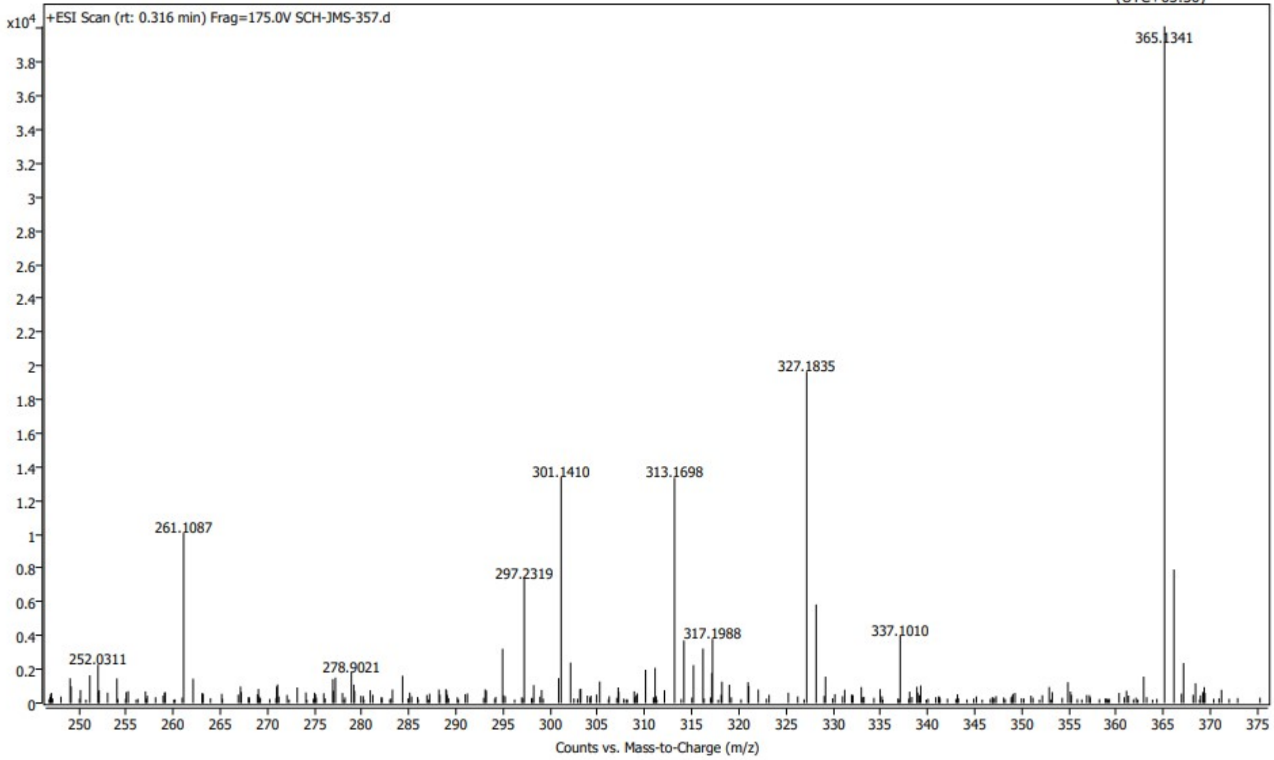
Name	SCH-JMS-359-RM	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-359-RM.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	18-10-2024 4.27.33 PM (UTC+05:30)

Mass spectrum of 3h

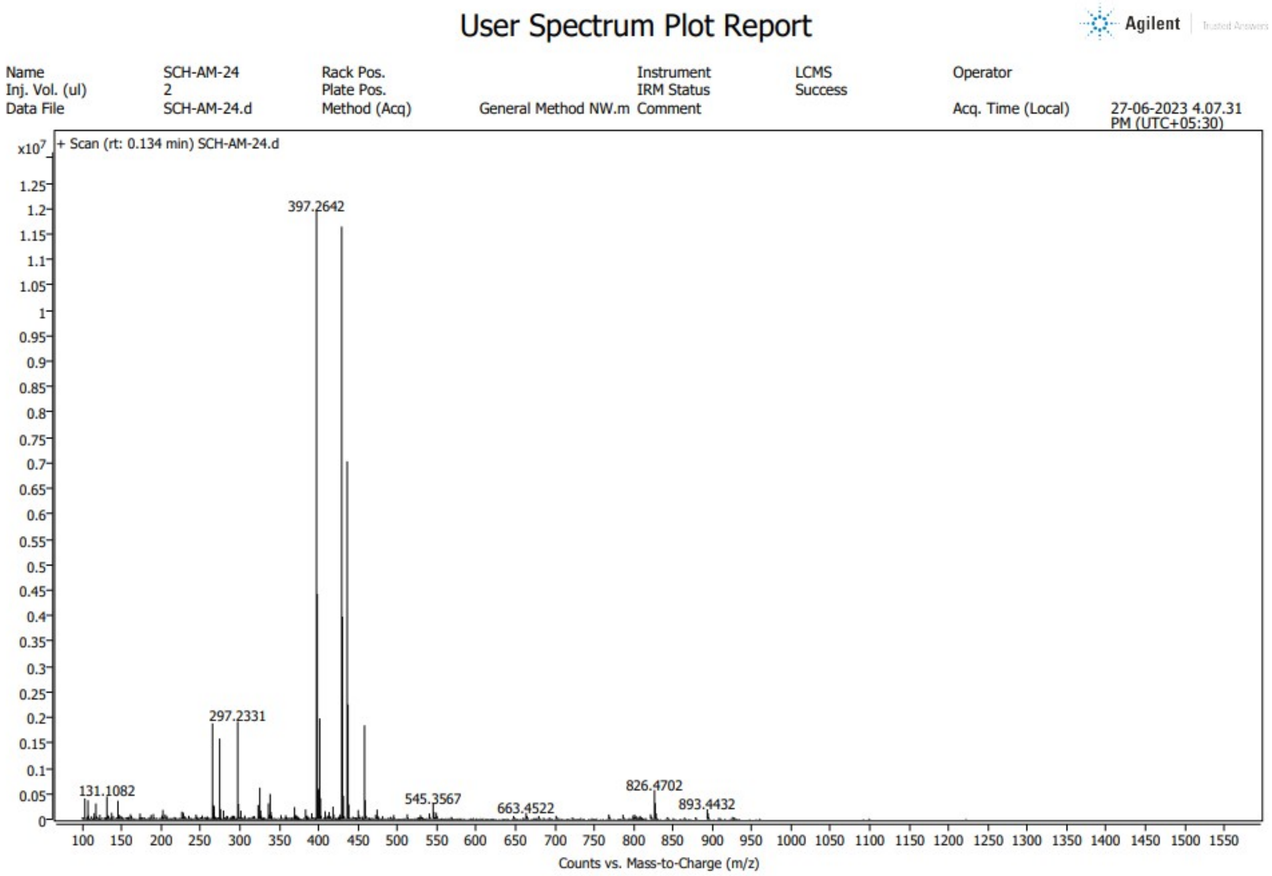
User Spectrum Plot Report

Agilent

Name	SCH-JMS-357	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-357.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	6/6/2024 4:52:36 PM (UTC+05:30)



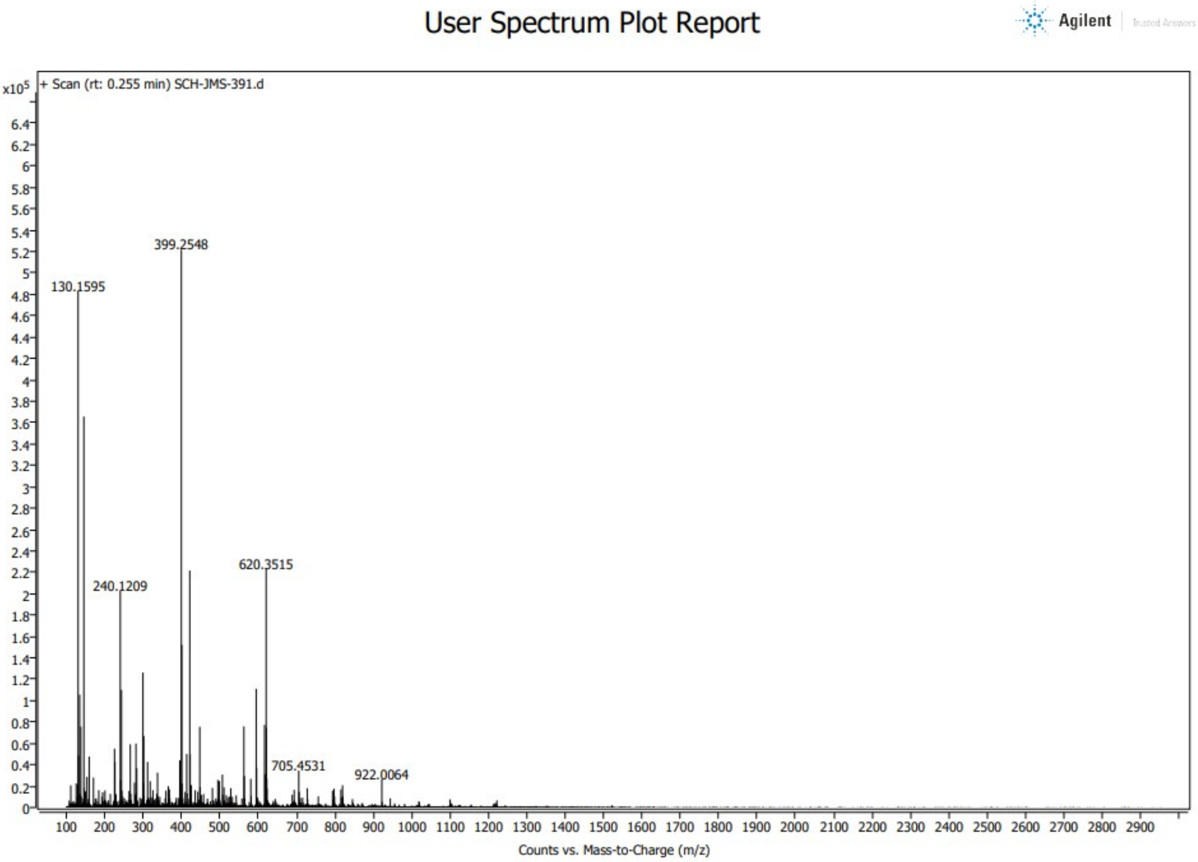
Mass spectrum of 3i



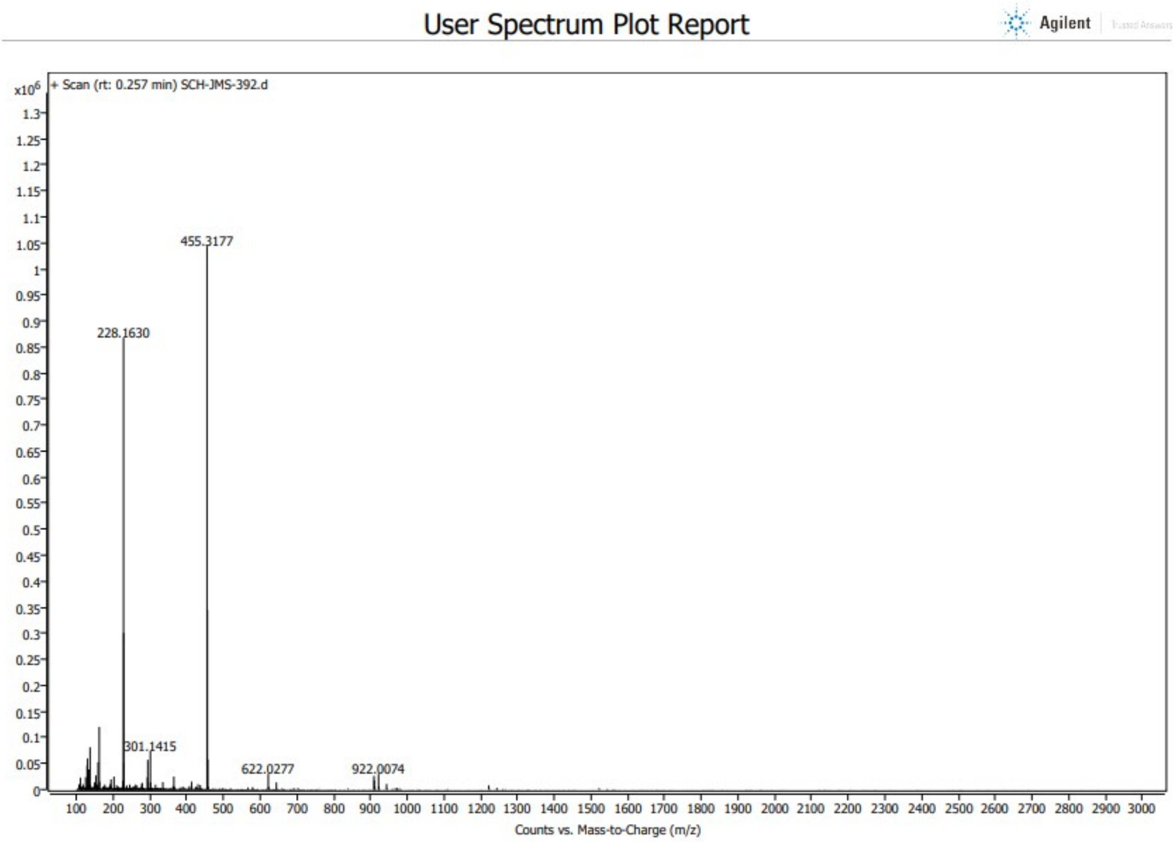
User Spectrum Plot Report

Name	SCH-AM-24	Rack Pos.		Instrument	LCMS	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-AM-24.d	Method (Acq)	General Method NW.m	Comment		Acq. Time (Local)	27-06-2023 4.07.31 PM (UTC+05:30)

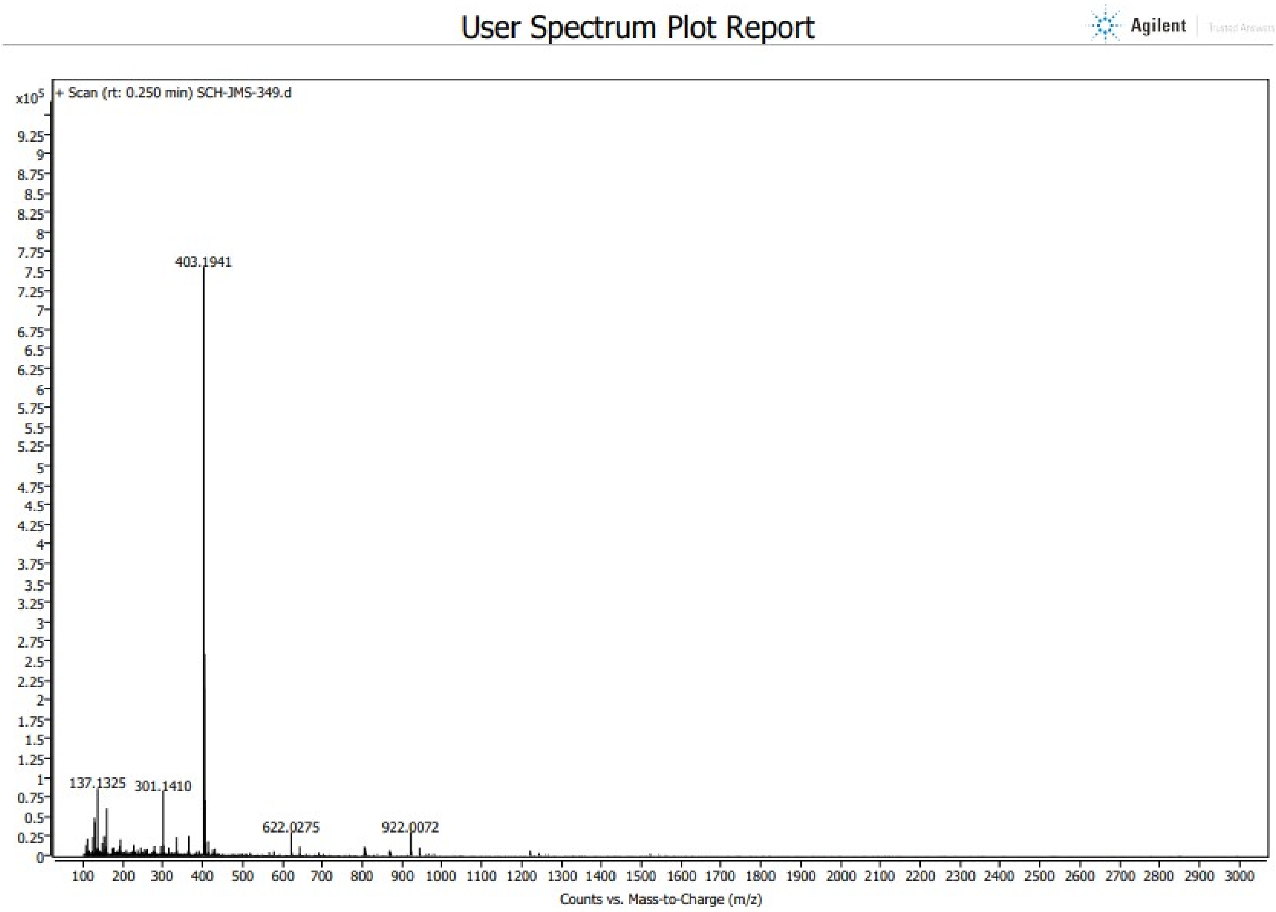
Mass spectrum of 3j



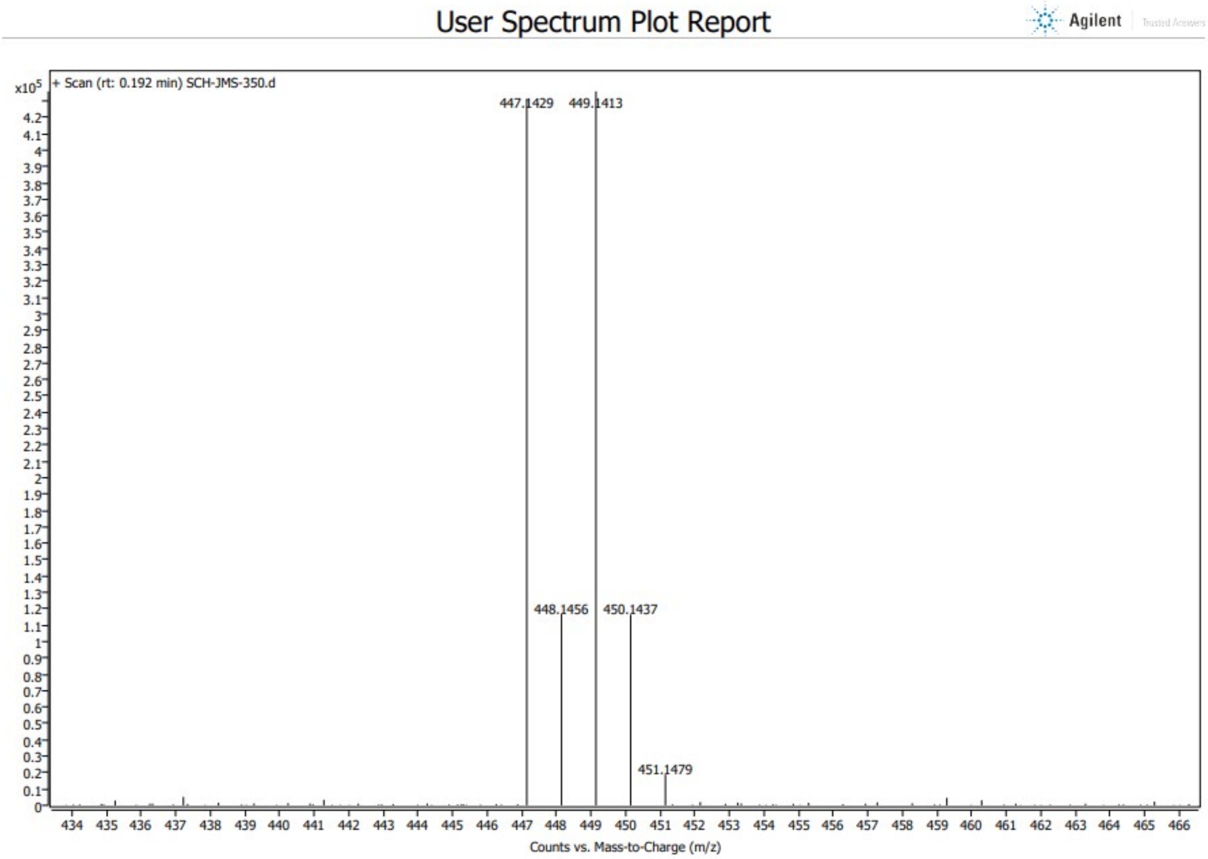
Mass spectrum of 3k



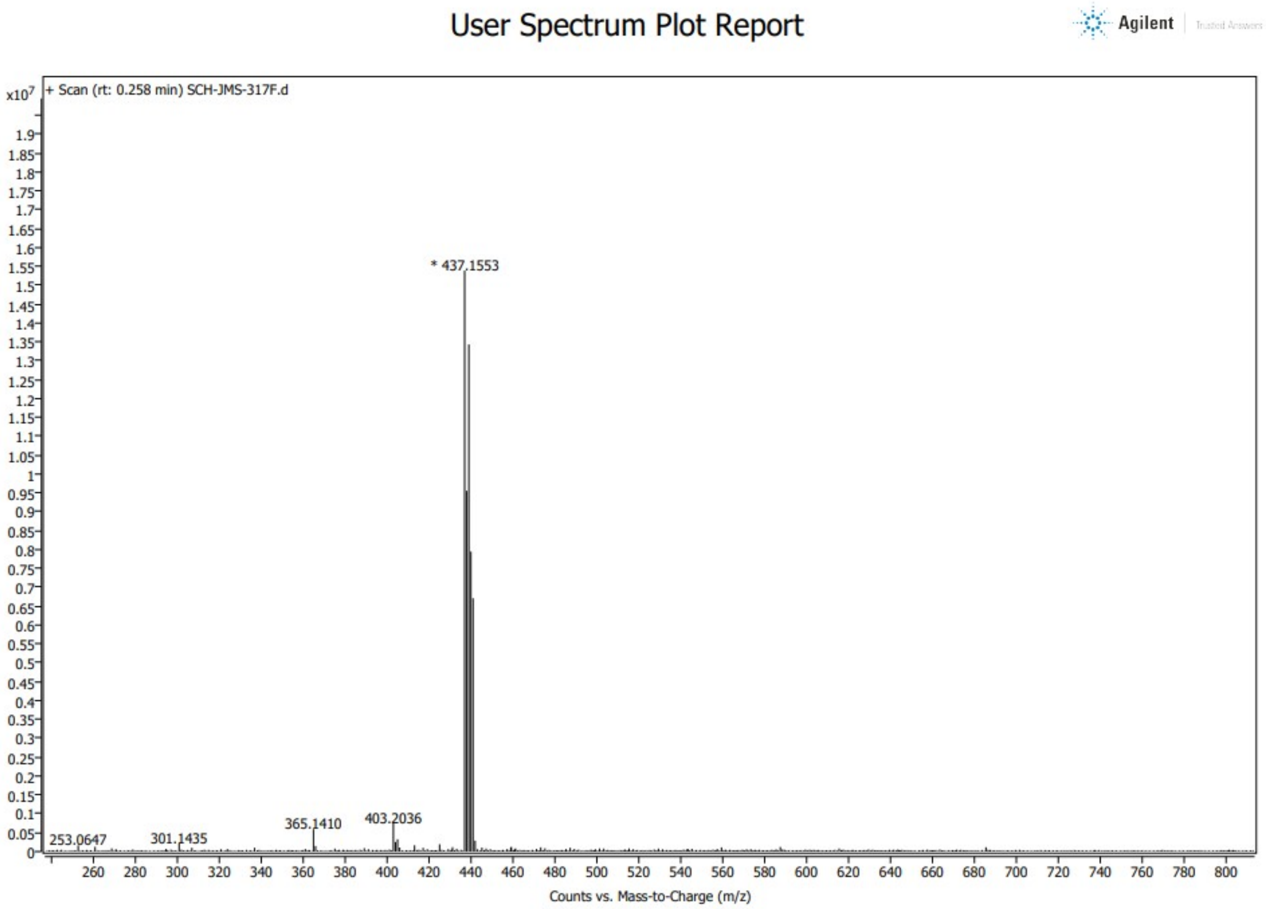
Mass spectrum of 3l



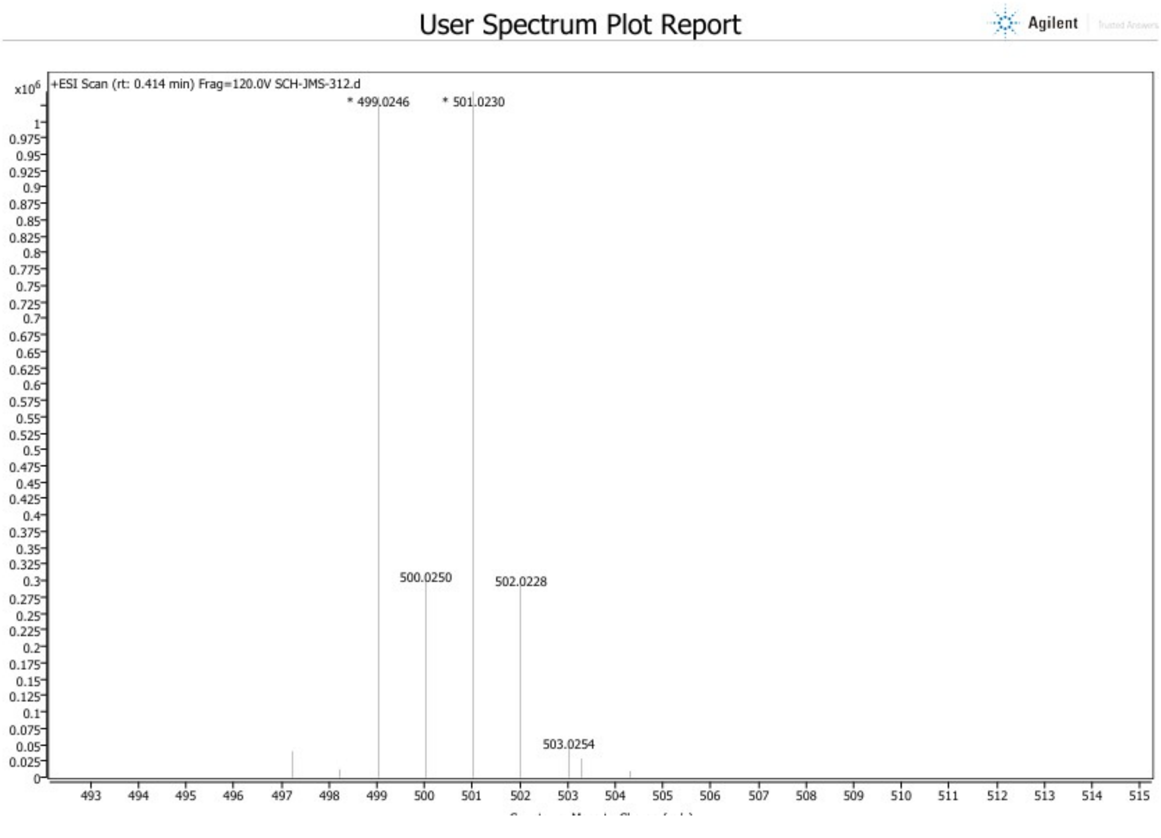
Mass spectrum of 3m



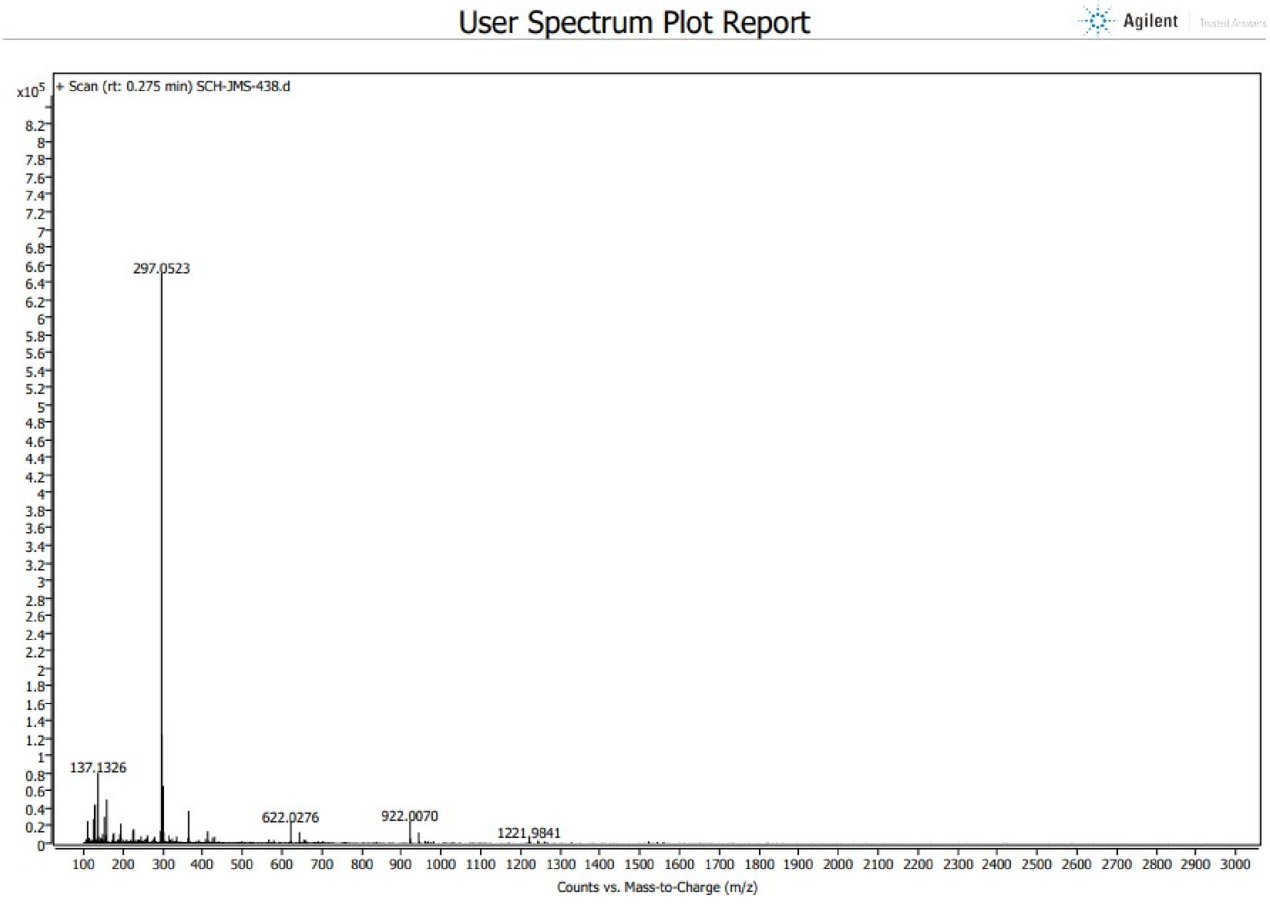
Mass spectrum of 3n



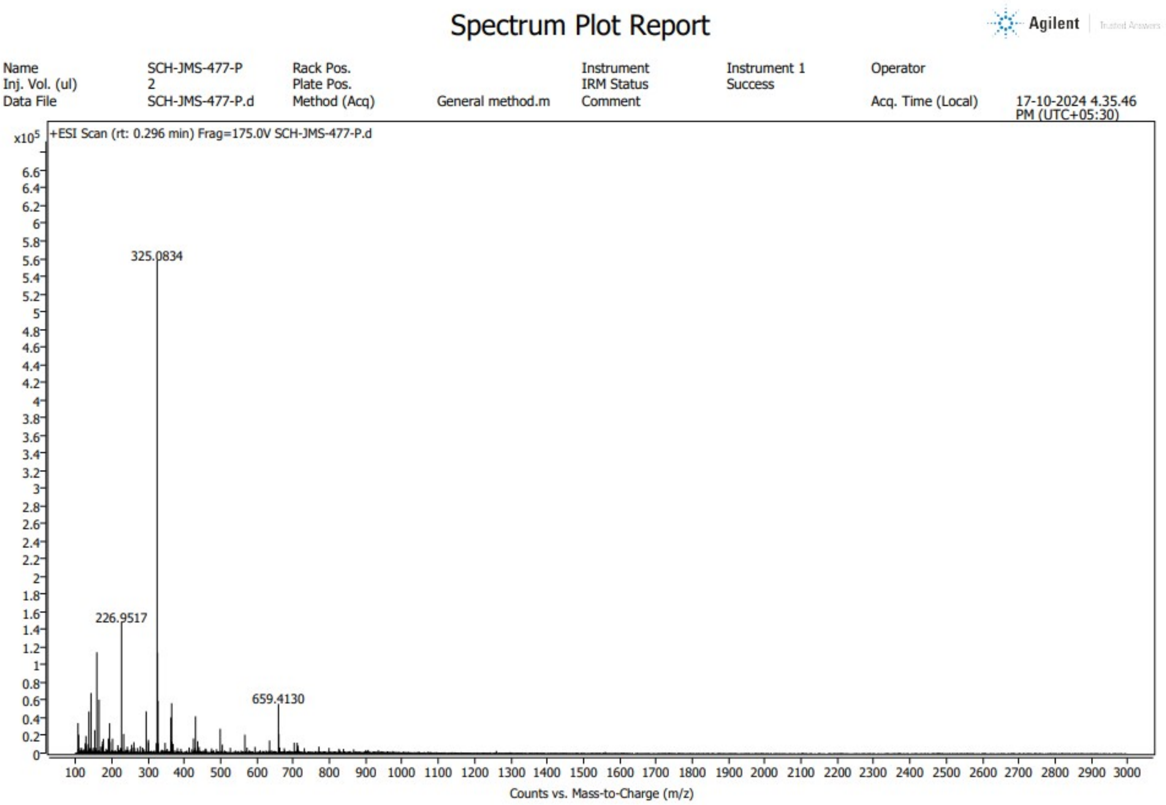
Mass spectrum of 3o



Mass spectrum of 3p



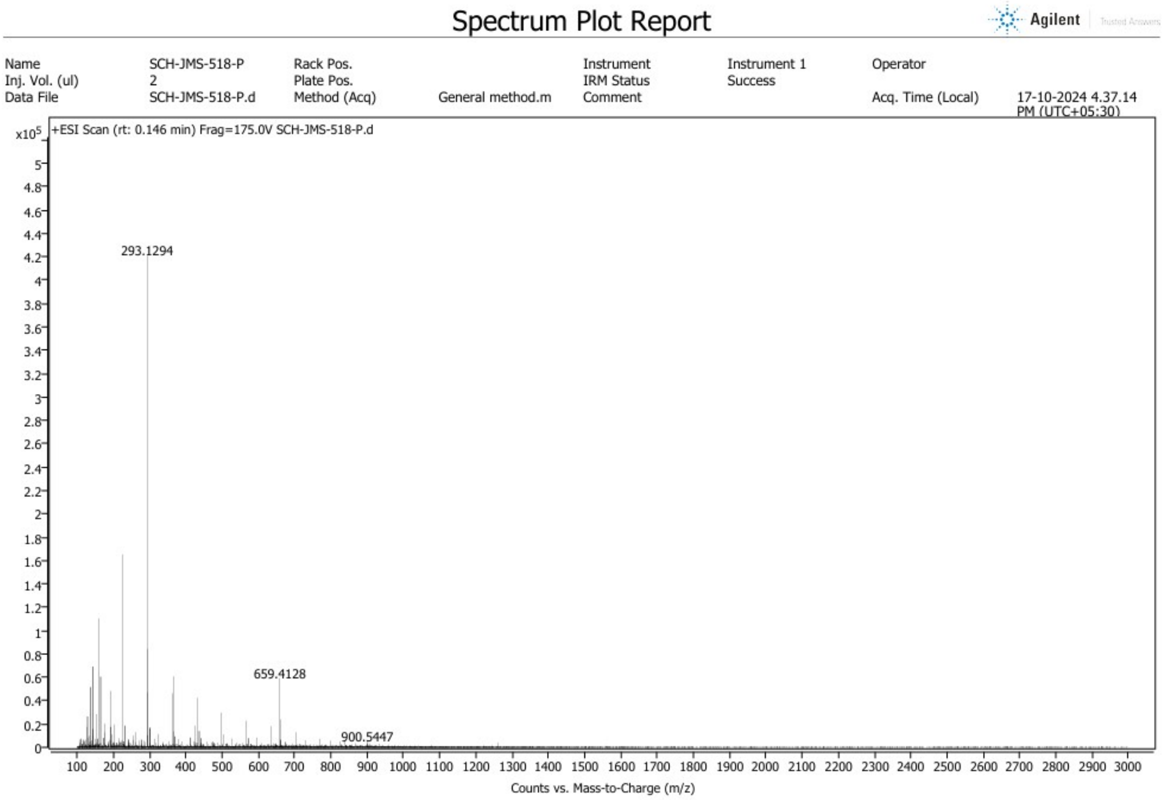
Mass spectrum of 3q



Spectrum Plot Report

Name	SCH-JMS-477-P	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-477-P.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	17-10-2024 4.35.46 PM (UTC+05:30)

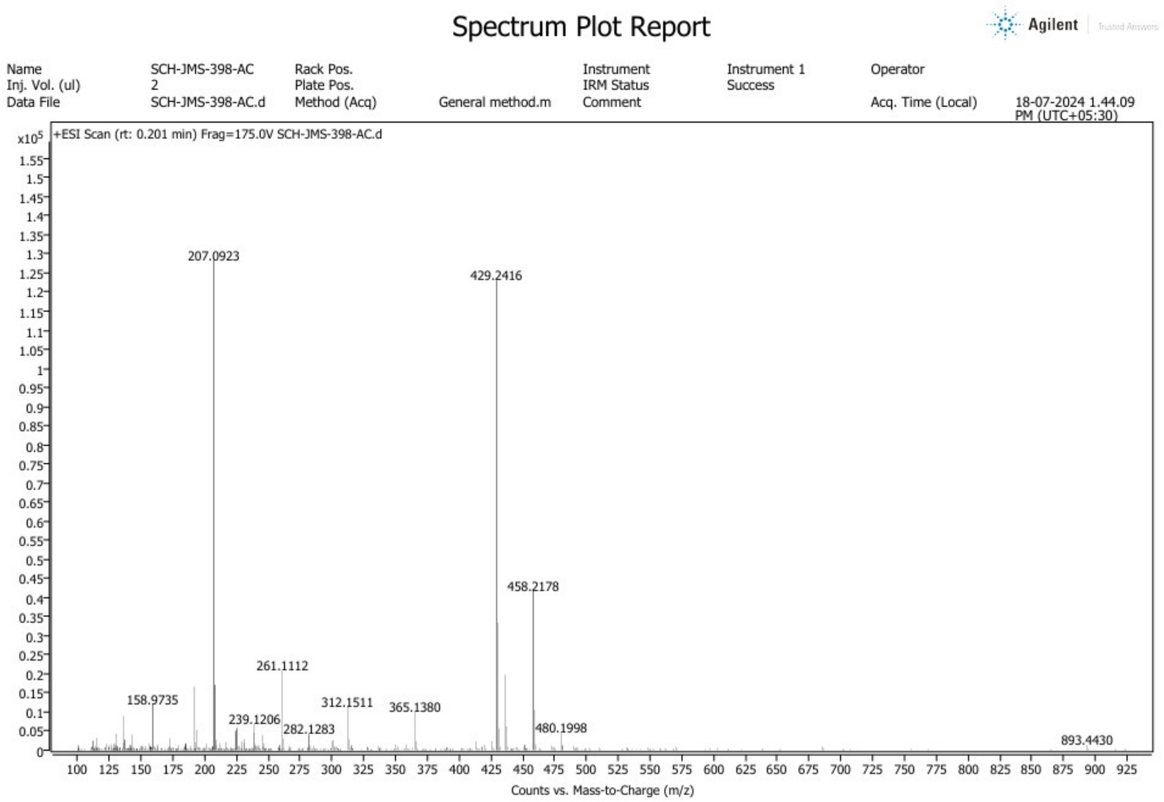
Mass spectrum of 3r



Spectrum Plot Report

Name	SCH-JMS-518-P	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-518-P.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	17-10-2024 4.37.14 PM (UTC+05:30)

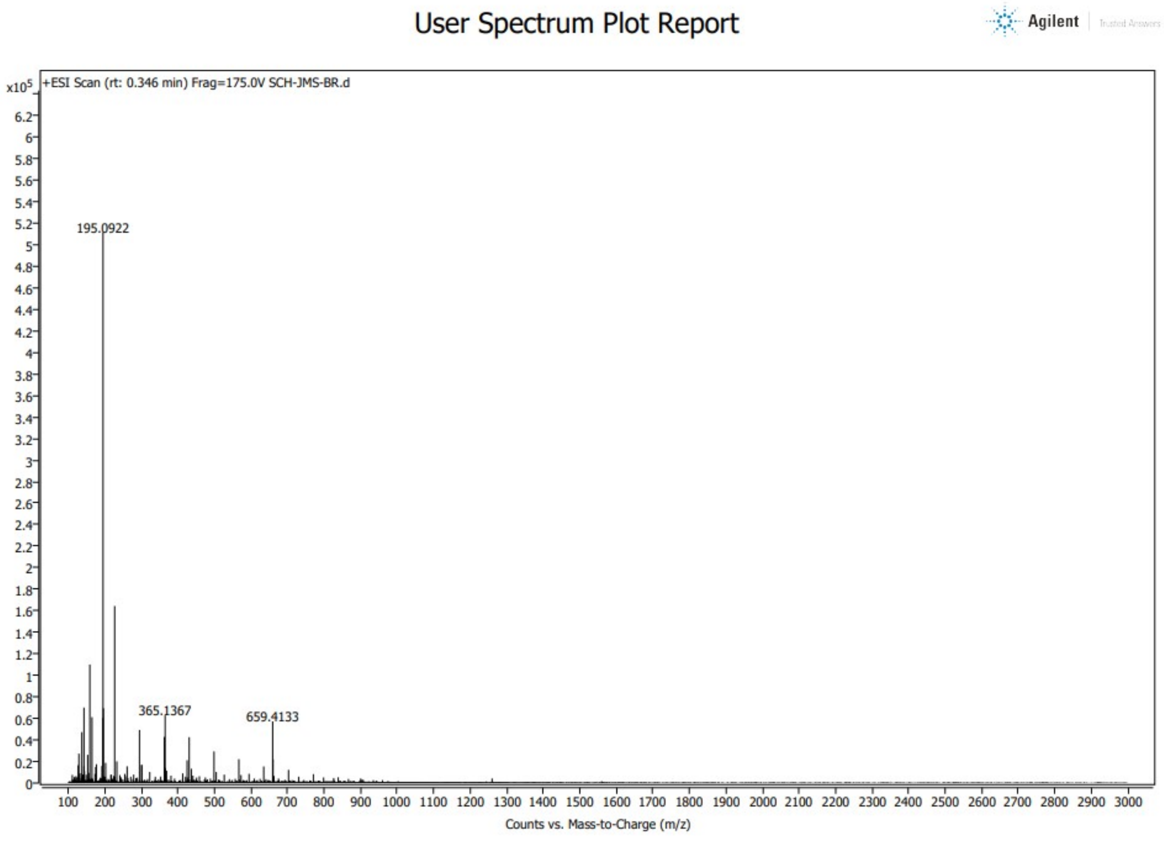
Mass spectrum of 3s



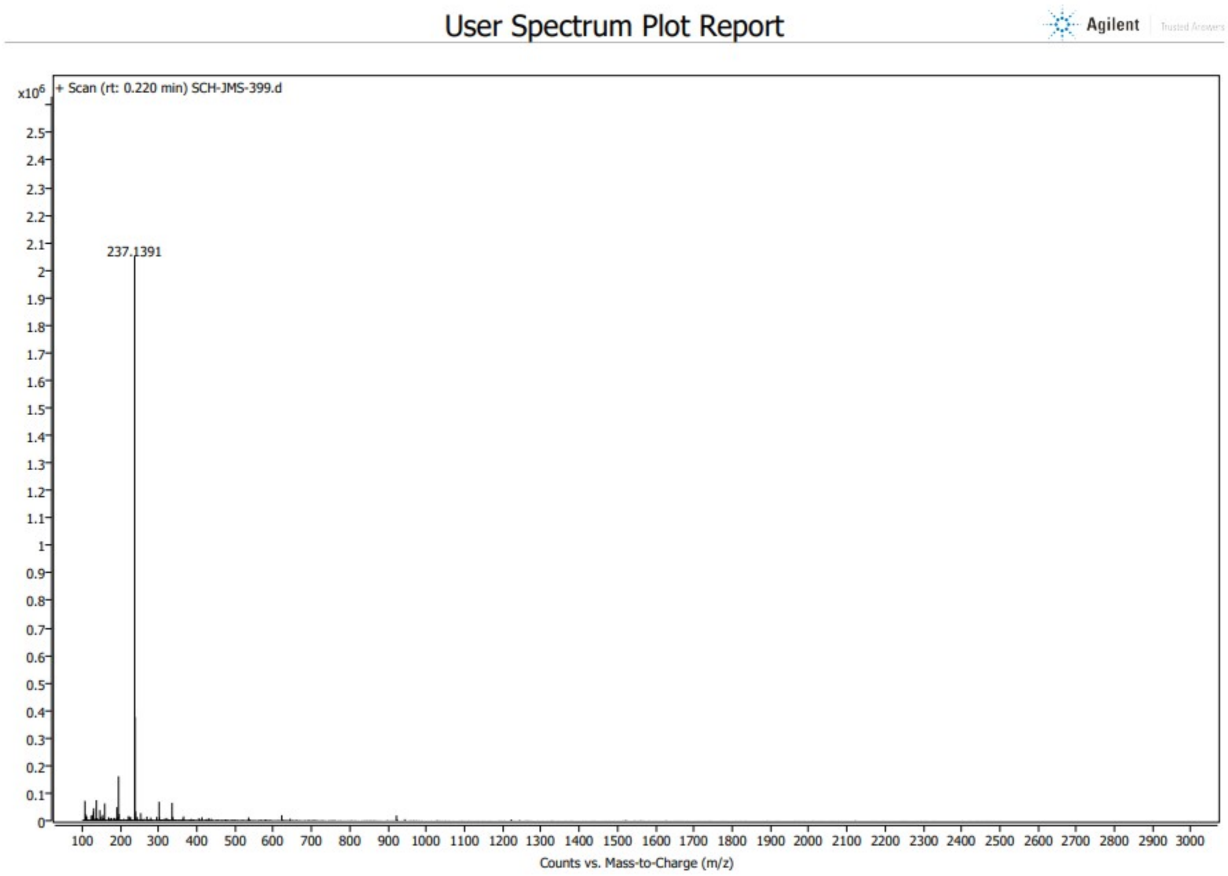
Spectrum Plot Report

Name	SCH-JMS-398-AC	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-398-AC.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	18-07-2024 1.44.09 PM (UTC+05:30)

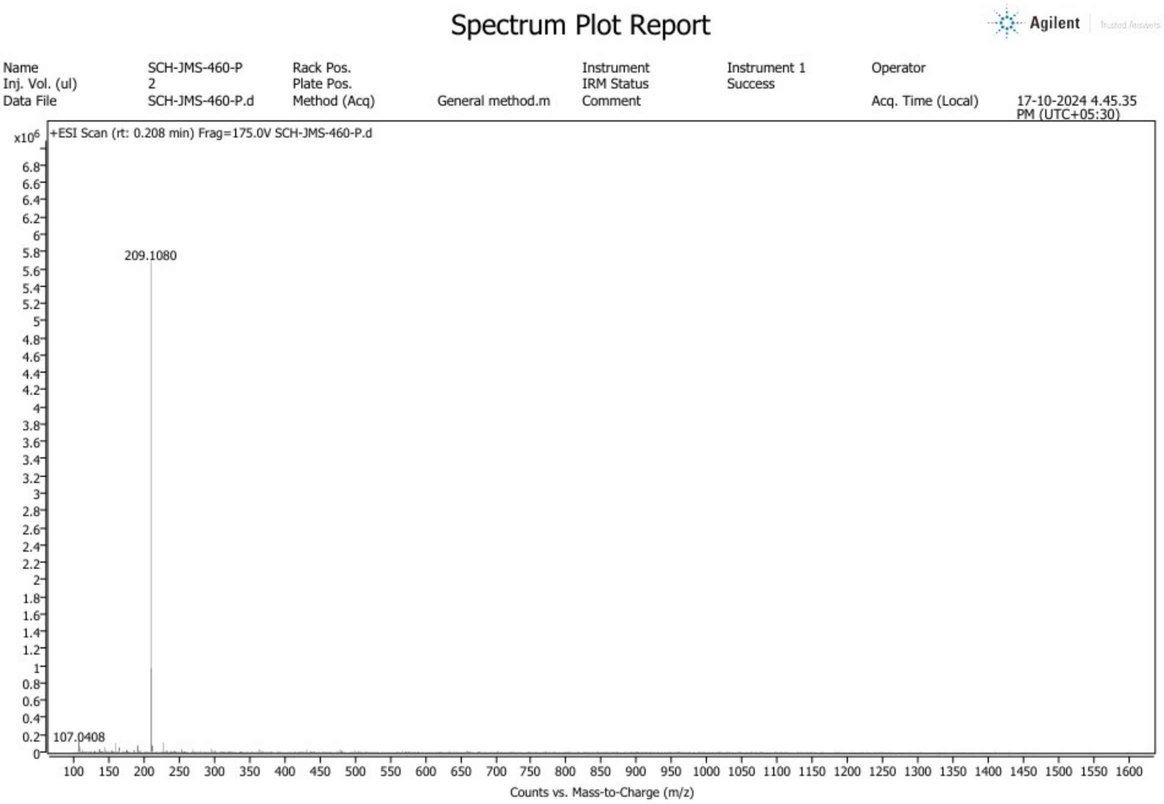
Mass spectrum of 3t



Mass spectrum of 4a



Mass spectrum of 4b

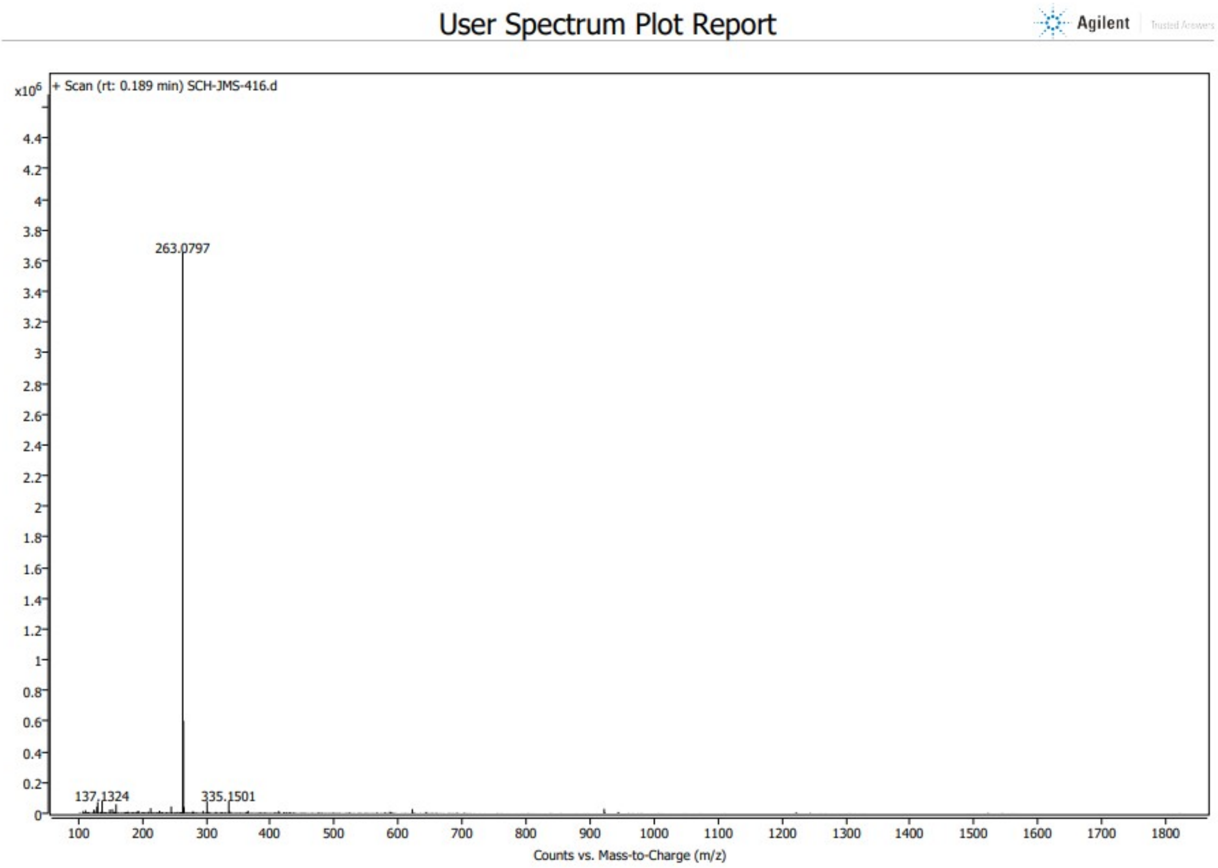


Spectrum Plot Report

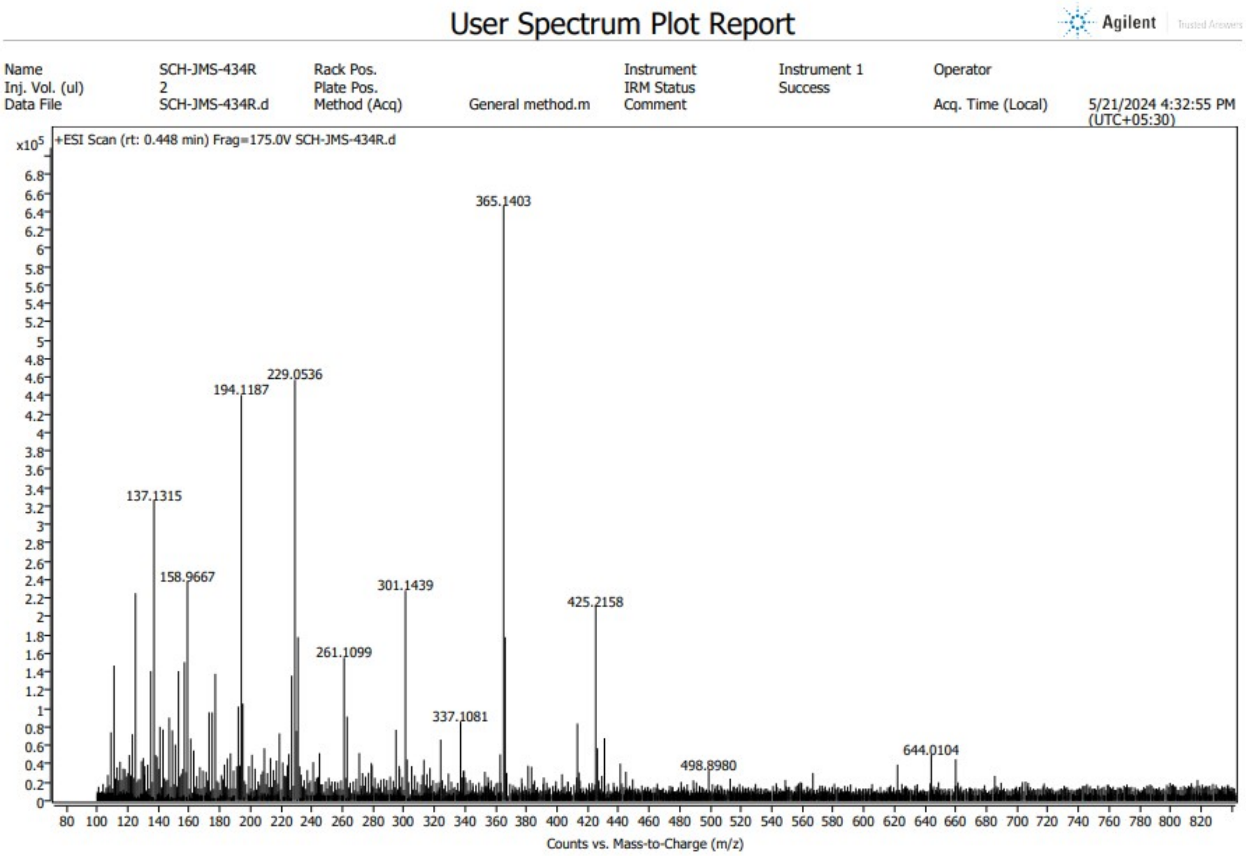
Name	SCH-JMS-460-P	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-460-P.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	17-10-2024 4.45.35 PM (UTC+05:30)

+ESI Scan (rt: 0.208 min) Frag=175.0V SCH-JMS-460-P.d

Mass spectrum of 4c



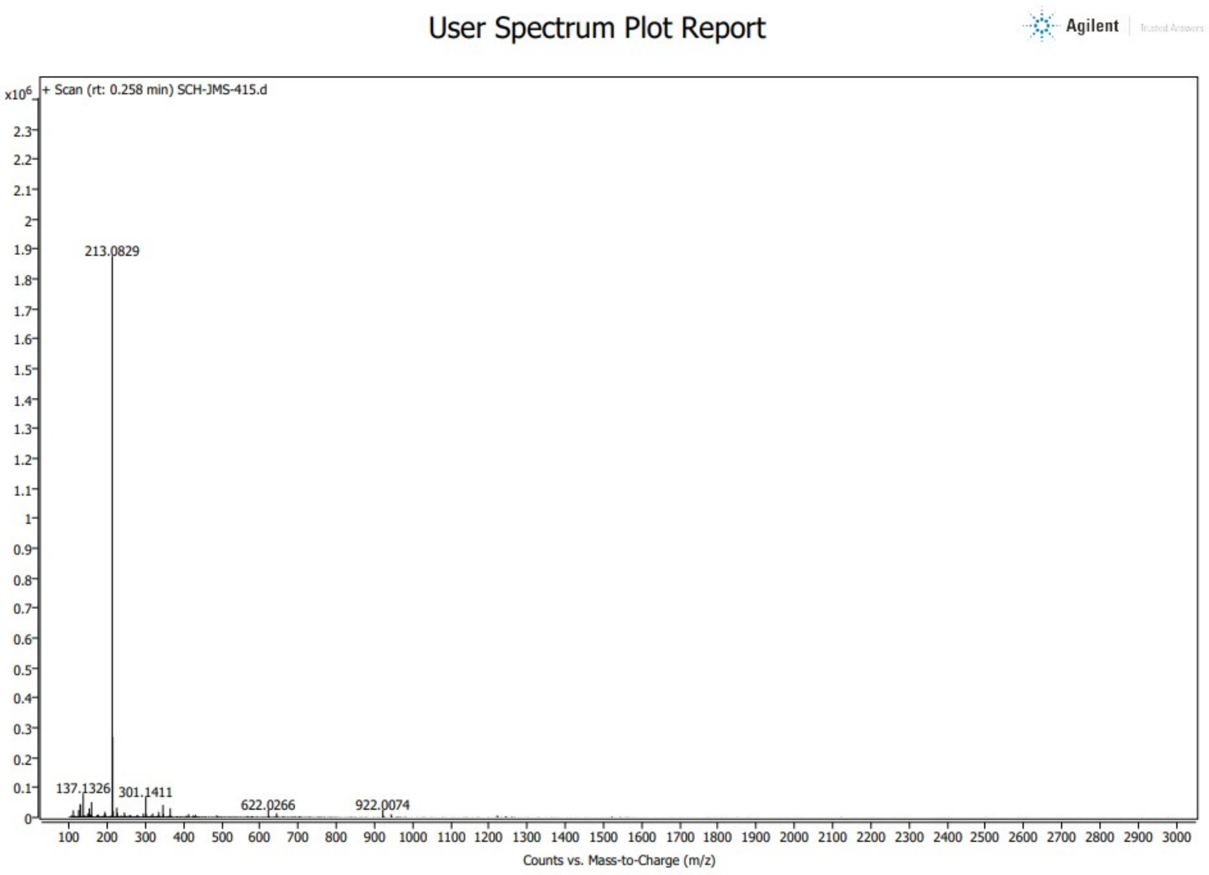
Mass spectrum of 4d



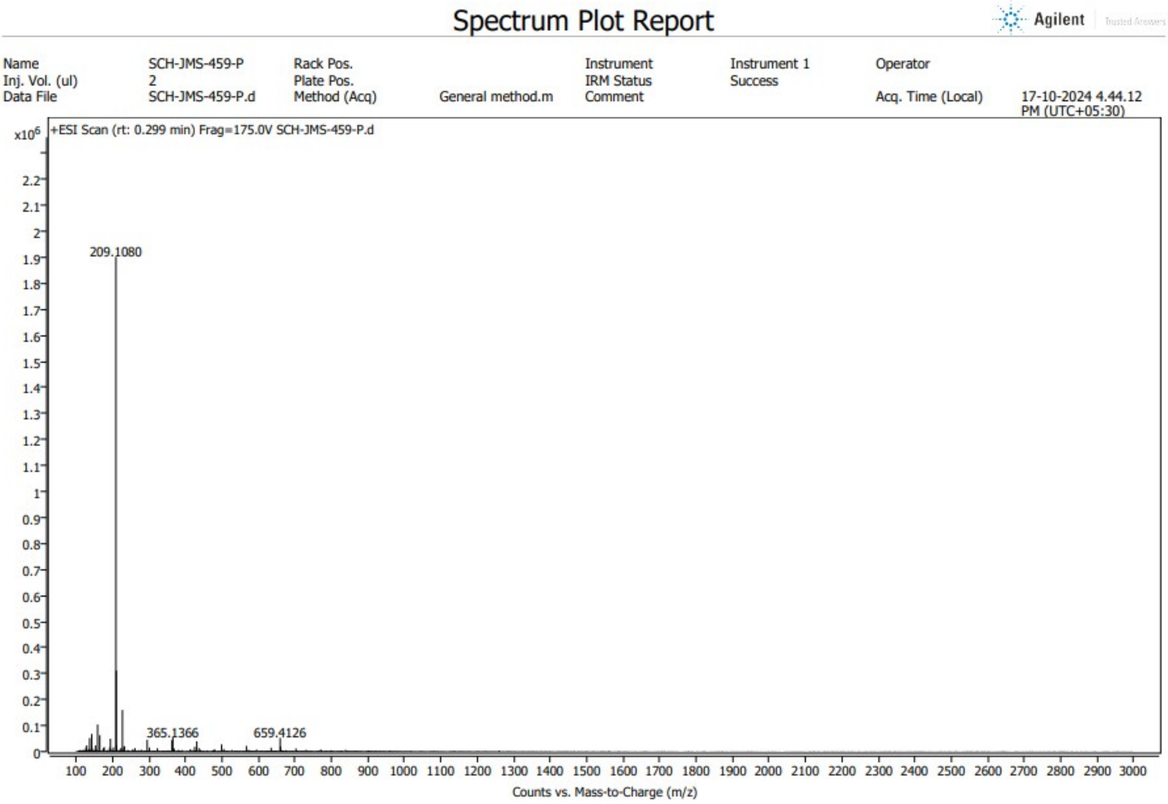
User Spectrum Plot Report

Name	SCH-JMS-434R	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-434R.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	5/21/2024 4:32:55 PM (UTC+05:30)

Mass spectrum of 4e



Mass spectrum of 4f

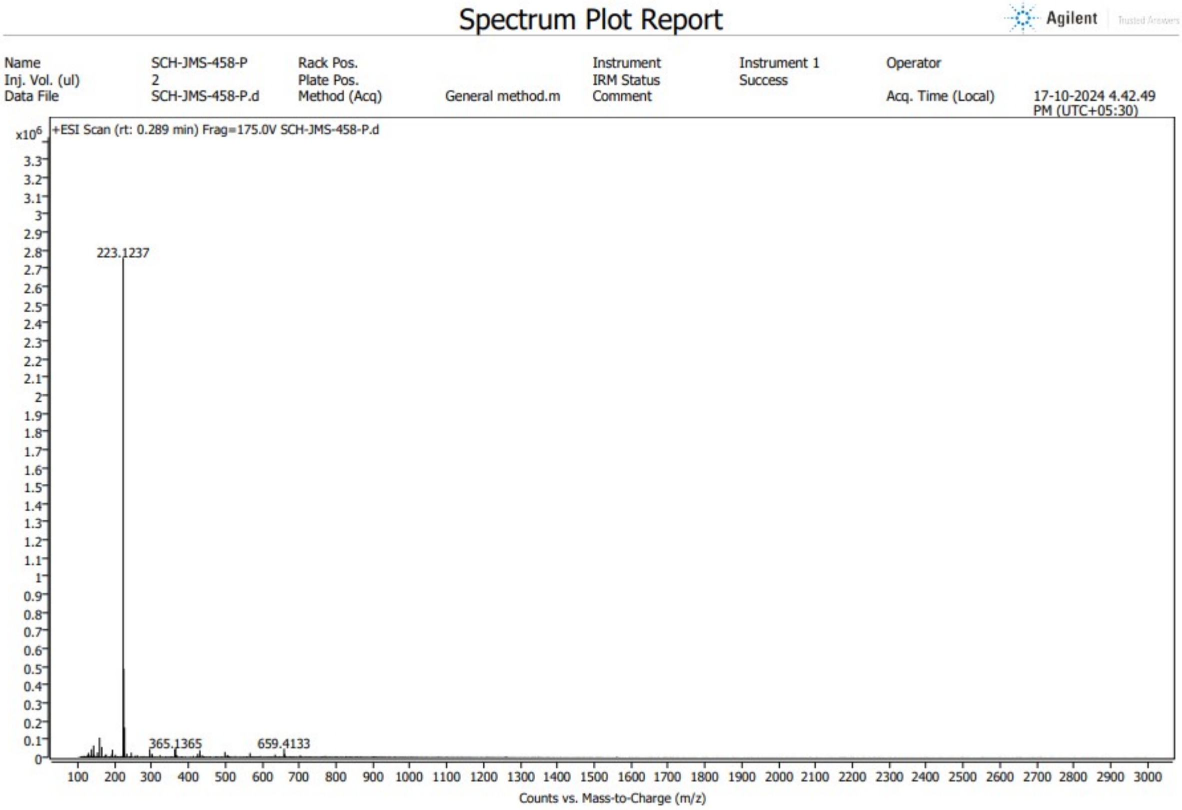


Spectrum Plot Report

Name	SCH-JMS-459-P	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-459-P.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	17-10-2024 4.44.12 PM (UTC+05:30)

+ESI Scan (rt: 0.299 min) Frag=175.0V SCH-JMS-459-P.d

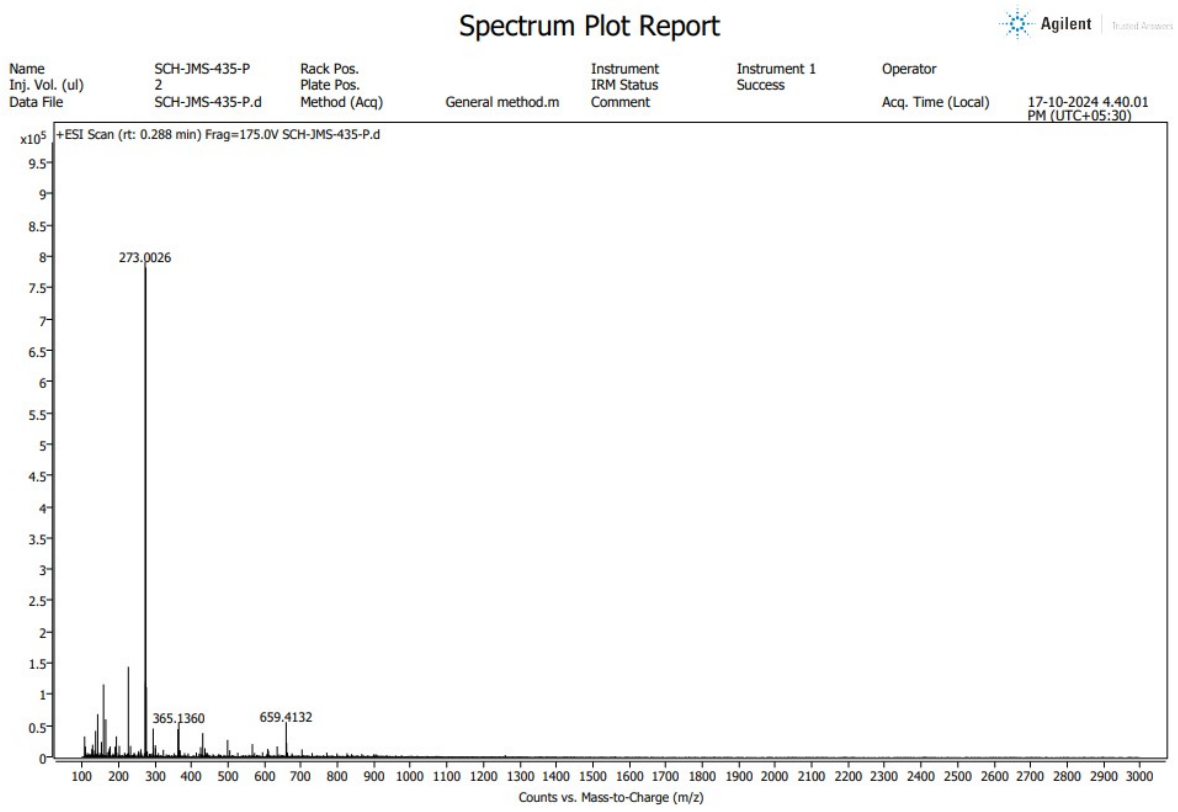
Mass spectrum of 4g



Spectrum Plot Report

Name	SCH-JMS-458-P	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-458-P.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	17-10-2024 4.42.49 PM (UTC+05:30)

Mass spectrum of 4h



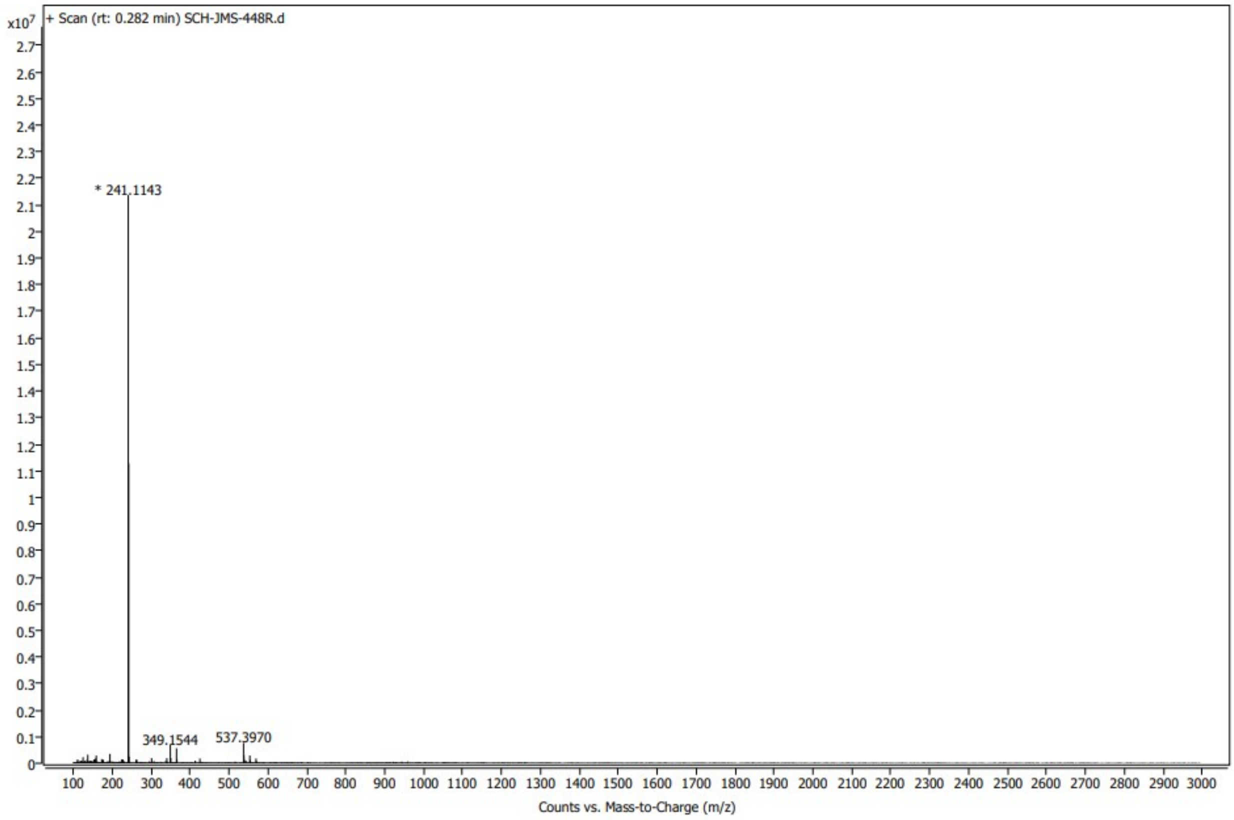
Spectrum Plot Report

Name	SCH-JMS-435-P	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-435-P.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	17-10-2024 4.40.01 PM (UTC+05:30)

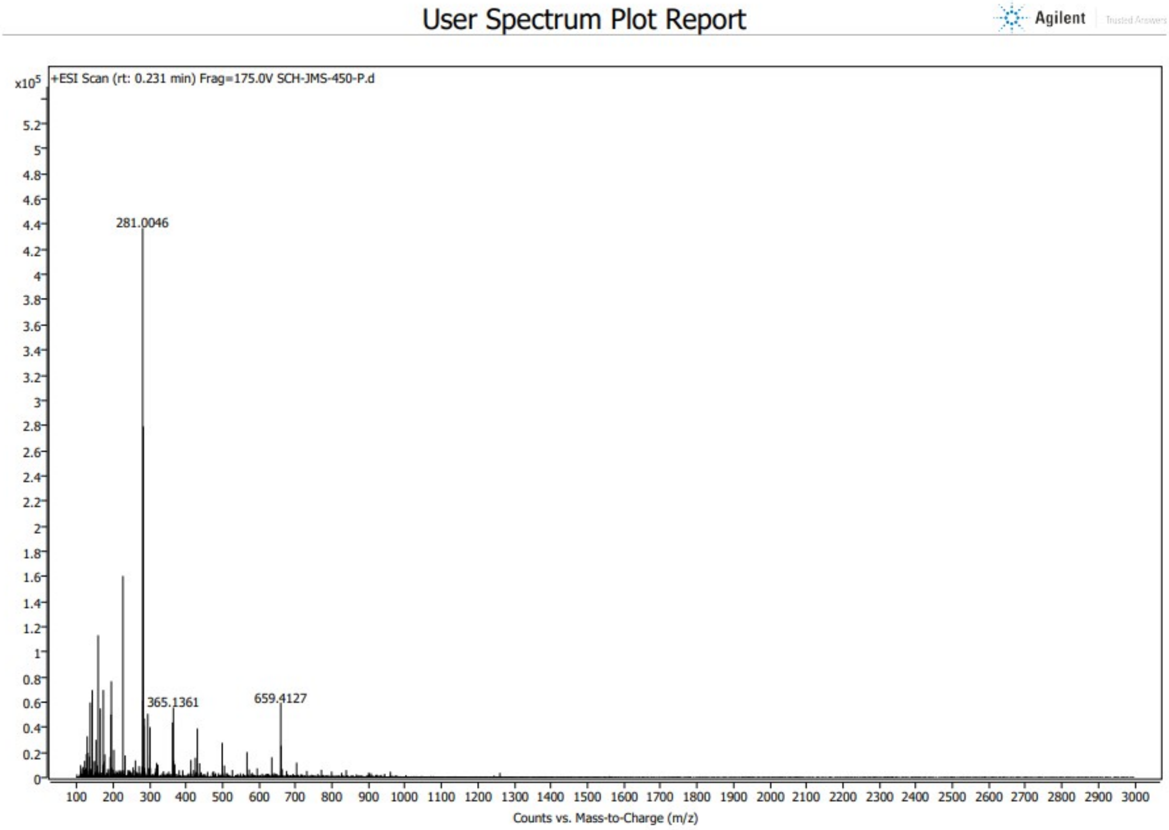
+ESI Scan (rt: 0.288 min) Frag=175.0V SCH-JMS-435-P.d

Mass spectrum of 4i

User Spectrum Plot Report



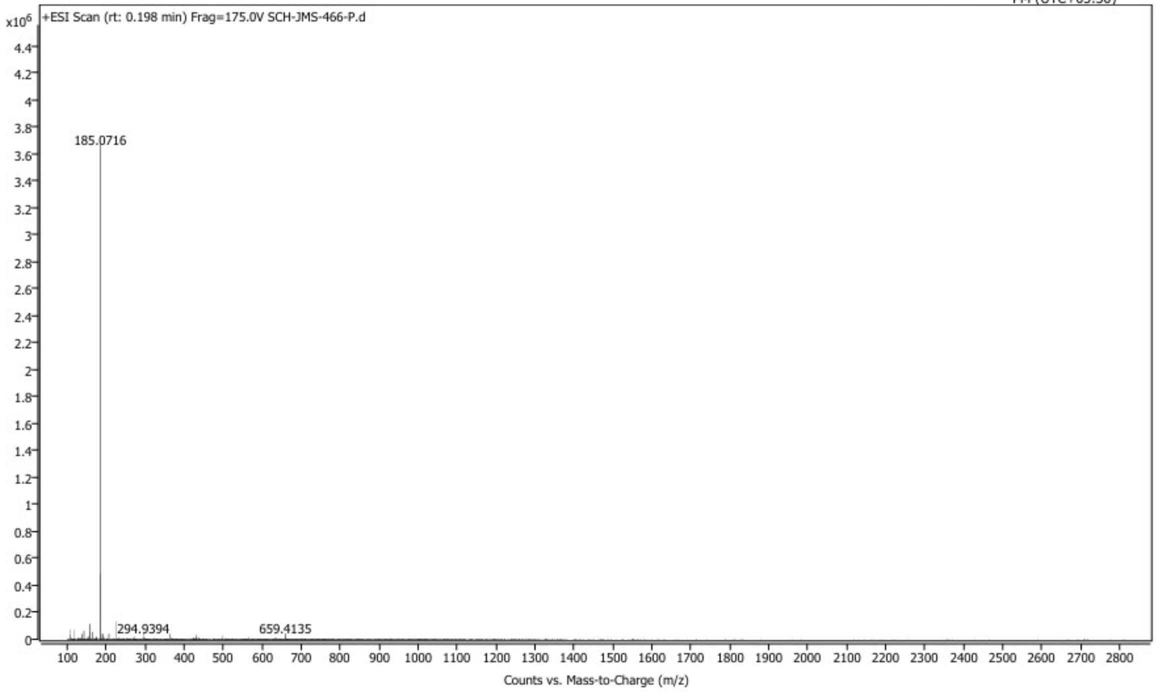
Mass spectrum of 4j



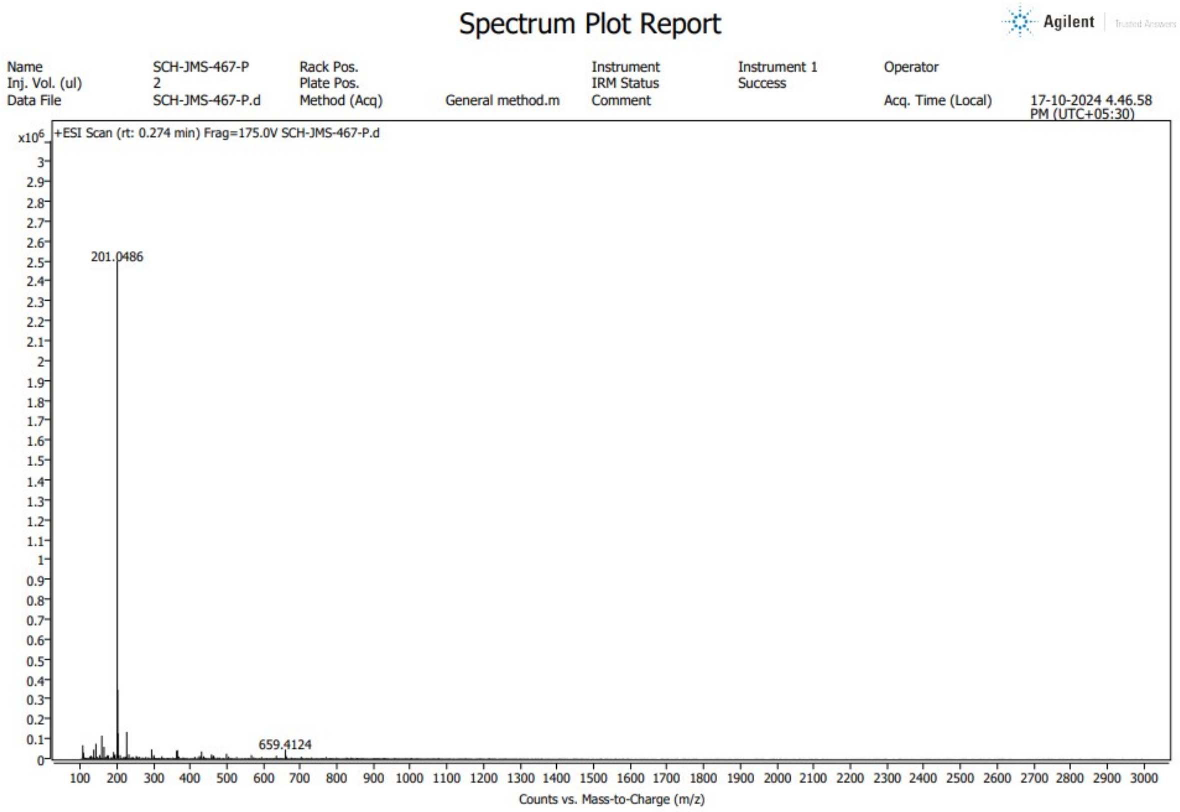
Mass spectrum of 4k

Spectrum Plot Report

Name	SCH-JMS-466-P	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-466-P.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	17-10-2024 4.41.25 PM (UTC+05:30)



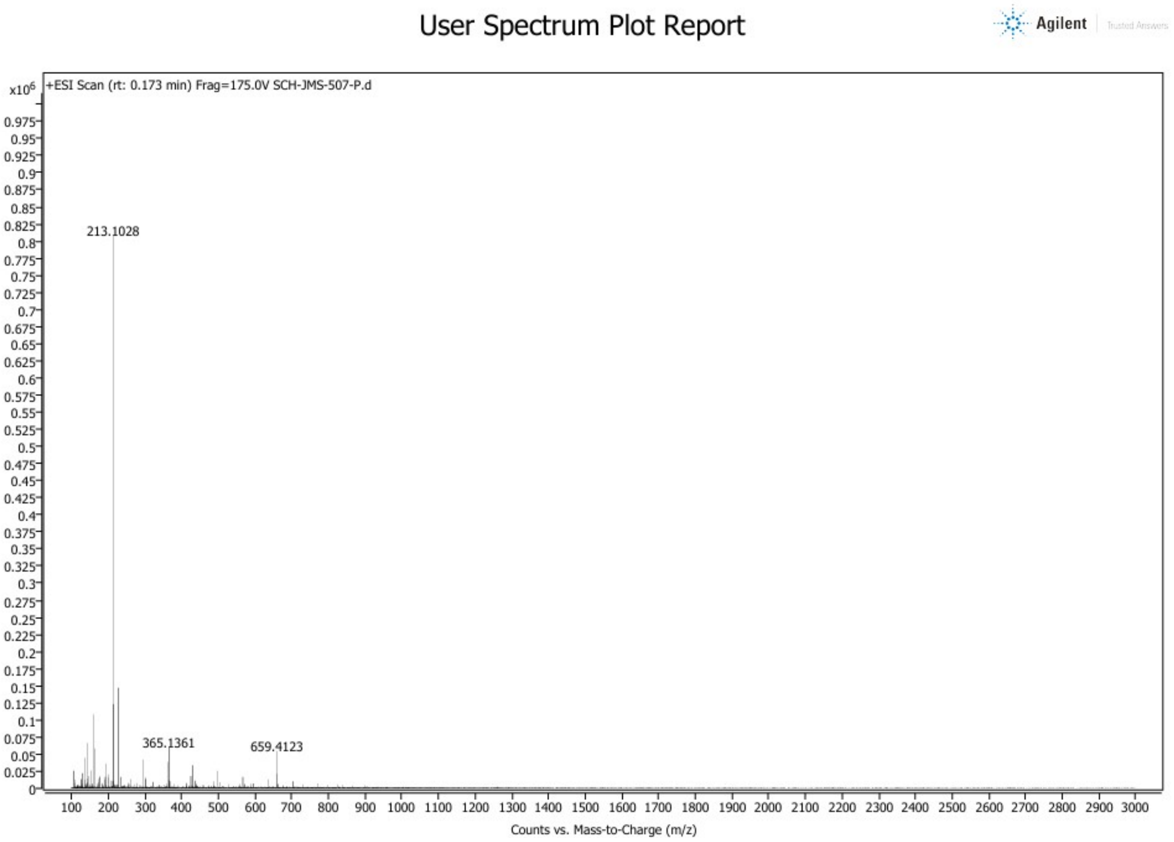
Mass spectrum of 4l



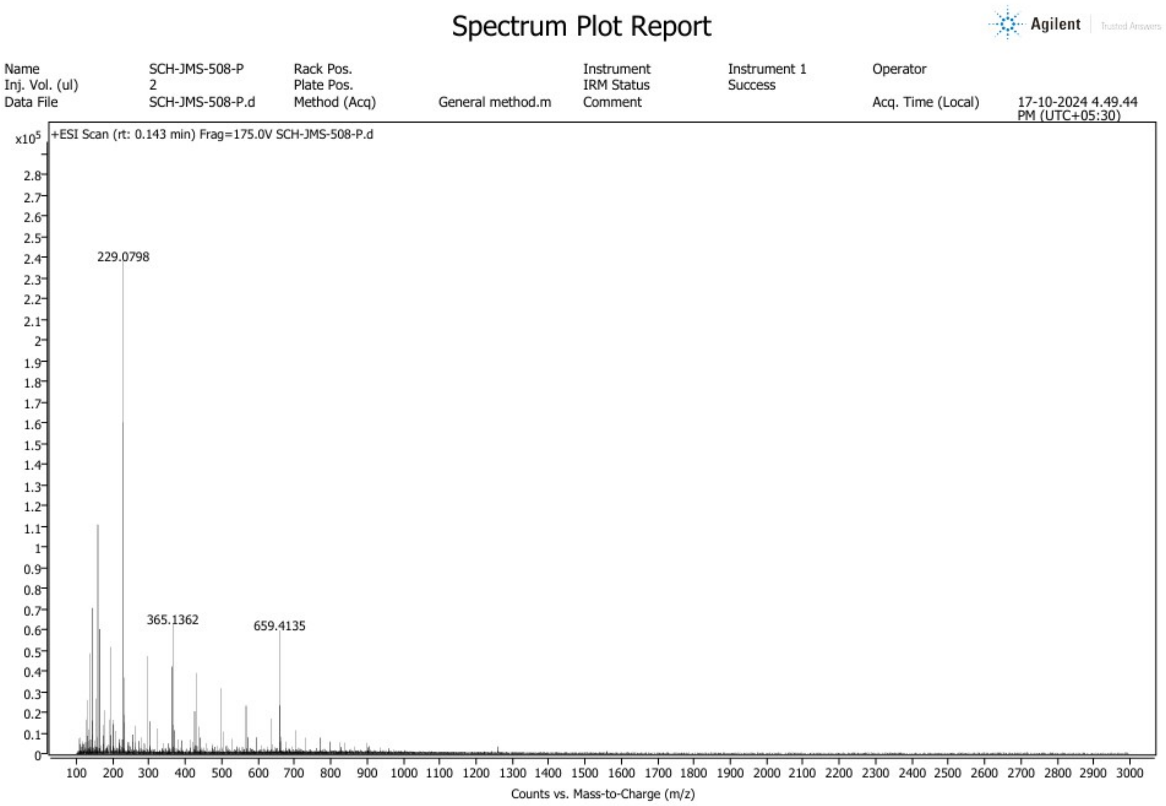
Spectrum Plot Report

Name	SCH-JMS-467-P	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-467-P.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	17-10-2024 4.46.58 PM (UTC+05:30)

Mass spectrum of 4m



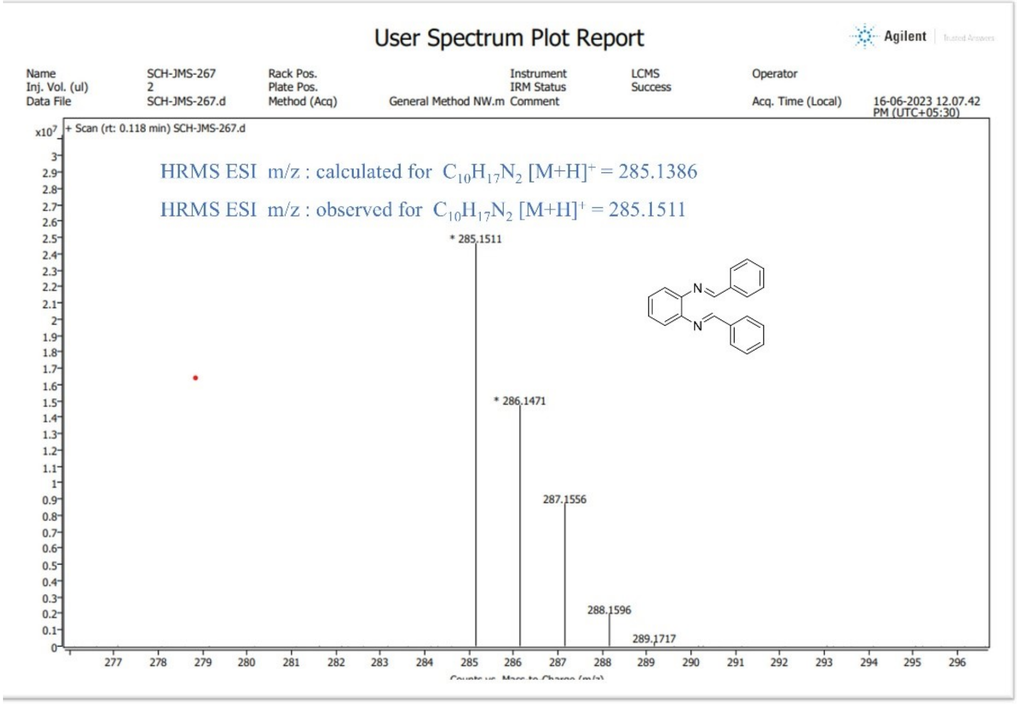
Mass spectrum of 4n



Spectrum Plot Report

Name	SCH-JMS-508-P	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-508-P.d	Method (Acq)	General method.m	Comment		Acq. Time (Local)	17-10-2024 4.49.44 PM (UTC+05:30)

Mass spectrum of 4o



User Spectrum Plot Report

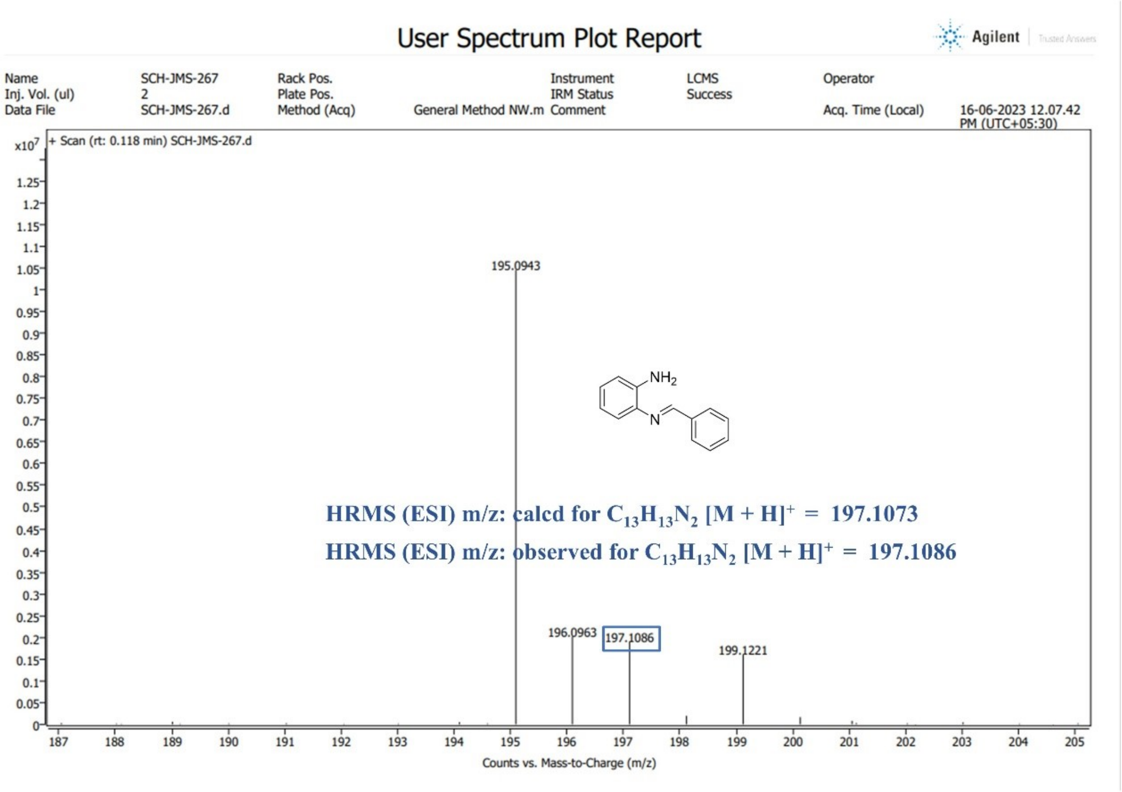
Name	SCH-JMS-267	Rack Pos.		Instrument	LCMS	Operator	
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	SCH-JMS-267.d	Method (Acq)	General Method NW.m	Comment		Acq. Time (Local)	16-06-2023 12.07.42 PM (UTC+05:30)

+ Scan (rt: 0.118 min) SCH-JMS-267.d

HRMS ESI m/z : calculated for $C_{10}H_{17}N_2$ $[M+H]^+$ = 285.1386

HRMS ESI m/z : observed for $C_{10}H_{17}N_2$ $[M+H]^+$ = 285.1511

Figure S11. Mass spectrum of intermediate I



User Spectrum Plot Report

Name SCH-JMS-267
Inj. Vol. (ul) 2
Data File SCH-JMS-267.d
Rack Pos.
Plate Pos.
Method (Acq) General Method NW.m
Instrument LCMS
IRM Status Success
Comment
Operator
Acq. Time (Local) 16-06-2023 12.07.42 PM (UTC+05:30)

HRMS (ESI) m/z: calcd for $C_{13}H_{13}N_2$ $[M + H]^+$ = 197.1073

HRMS (ESI) m/z: observed for $C_{13}H_{13}N_2$ $[M + H]^+$ = 197.1086

Figure S12. Mass spectrum of intermediate I'