Supporting Information

Ni(II)-catalyzed C–H hydroarylation of diarylacetylenes with imidazolium salts

Tianbao Wang, Xuesong Zheng, Qinze Zheng, Fulin Zhou, Linhua Wang and Ge Gao*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, P. R. China

*E-mails: gg2b@scu.edu.cn

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I. General Remarks

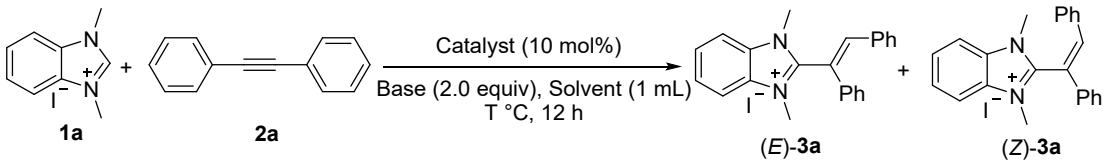
All commercial available reagents were used without further purification unless otherwise noted. $Ni(OAc)_2 \cdot 4H_2O$ (> 98.0%), NaOAc and DMSO were purchased from Chengdu Chron Chemicals (China) CO., Ltd. KOAc, $^nBu_3P$ and styrene were purchased from Energy Chemical (China) CO., Ltd.. Analytical thin layer chromatography was performed on HG/T2354-92 GF254 plates (Qingdao Haiyang Chemical Co., Ltd.). The imidazolium salts substrates[1] and diarylacetylene derivatives[2] were prepared according to the literature procedures.

NMR spectroscopy were obtained on a Bruker AV II-400 MHz or Agilent 400-MR DD2 spectrometer. The ^1H NMR (400 MHz) chemical shifts were recorded relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High resolution mass spectra (HR-MS) were measured on a Waters-Q-TOF-Premier (ESI).

II. Optimization of the Reaction Conditions

A Schlenk tube with a magnetic stirring bar was charged with 1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium **1a** (54.8 mg, 0.2 mmol), diphenylacetylene **2a** (53.4 mg, 0.3 mmol), a catalyst (10 mol%), a base (0.4 mmol), and solvent (1 mL) under N_2. The reaction mixture was heated at 100 ºC or 120 ºC for 12 h. After the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (v/v, 40/1−20/1) to provide product **3a**.

Table S1.Optimization of the Reaction Conditions[a]



Entry	Catalysts	Bases	Solevents	Temperature	Yield[b]	*E*/*Z*
1	$Ni(OAc)_2 \cdot 4H_2O$	NaOAc	DCE	120 ℃	ND	--
2	$Ni(OAc)_2 \cdot 4H_2O$	NaOAc	DMF	120 ℃	69%	8/1
3	$Ni(OAc)_2 \cdot 4H_2O$	NaOAc	Dioxane	120 ℃	ND	--

4	$Ni(OAc)_2·4H_2O$	NaOAc	THF	120 ℃	ND	--
5	$Ni(OAc)_2·4H_2O$	NaOAc	Toluene	120 ℃	ND	--
6	$Ni(OAc)_2·4H_2O$	NaOAc	DMSO	120 ℃	86%	9/1
7	$Ni(OAc)_2·4H_2O$	NaOAc	*t*-amylOH	120 ℃	ND	--
8	$Ni(OAc)_2·4H_2O$	NaOAc	MeCN	120 ℃	ND	--
9	$Ni(OAc)_2·4H_2O$	K_2CO_3	DMSO	120 ℃	46%	8/1
10	$Ni(OAc)_2·4H_2O$	KOAc	DMSO	120 ℃	91%	12/1
11	$Ni(OAc)_2·4H_2O$	K_3PO_4	DMSO	120 ℃	95%	5/1
12	$Ni(OAc)_2·4H_2O$	*t*-BuOK	DMSO	120 ℃	trace	--
13	$Ni(OAc)_2·4H_2O$	CsOAc	DMSO	120 ℃	57%	13/1
14	$Ni(OAc)_2$	KOAc	DMSO	120 ℃	94%	12/1
15	$NiBr_2$	KOAc	DMSO	120 ℃	87%	11/1
16	$Ni(acac)_2$	KOAc	DMSO	120 ℃	76%	14/1
17	$Ni(Cp)_2$	KOAc	DMSO	120 ℃	70%	9/1
18	$Ni(OAc)_2·4H_2O$	KOAc	DMSO	80 ℃	95%	9/1
19	**$Ni(OAc)_2·4H_2O$**	**KOAc**	**DMSO**	**100 ℃**	**95%**	**12/1**
20	$Ni(OAc)_2·4H_2O$	KOAc	DMSO	140 ℃	61%	13/1
21[c]	$Ni(OAc)_2·4H_2O$	KOAc	DMSO	100 ℃	59%	10/1
22[d]	$Ni(OAc)_2·4H_2O$	KOAc	DMSO	100 ℃	trace	--

[a]Reaction conditions: **1a** (54.8 mg, 0.2 mmol), **2a** (53.4 mg, 0.3 mmol), a catalyst (10 mol%), a base (0.4 mmol) and solvent (1.0 mL) at T ºC for 12 h under N_2. [b]Isolated yield. [c]$Ni(OAc)_2·4H_2O$ (5 mol%). [d]$Ni(OAc)_2·4H_2O$ (1 mol%). ND = not detected.

III. General Procedures

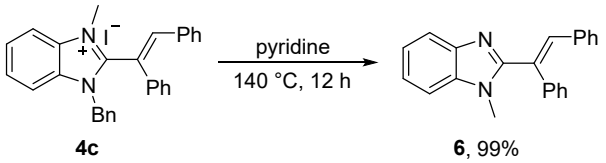
a) General procedure for the Ni-catalyzed alkenylation of 1 with 2

A Schlenk tube with a magnetic stirring bar was charged with an imidazolium salt **1** (0.2 mmol), a diarylacetylene **2** (0.3 mmol), $Ni(OAc)_2·4H_2O$ (5.0 mg, 10 mol%), KOAc (39.2 mg, 0.4 mmol) and DMSO (1 mL) under N_2. The reaction mixture was then heated at 100-140 ºC for 12 or 24 h. After the reaction was complete, DMSO was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (v/v, 40/1−20/1) to provide product **3** and **4**.

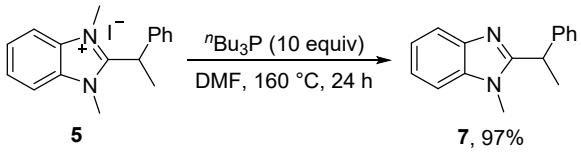
b) Procedure for the Ni-catalyzed alkylation of 1a with styrene

A Schlenk tube with a magnetic stirring bar was charged with *N*,*N*-dialkyl benzoimidazolium salts **1a** (54.8 mg, 0.2 mmol), styrene (69.0 μL, 0.6 mmol), $Ni(OAc)_2·4H_2O$ (5.0 mg, 10 mol%), NaOAc (32.8 mg, 0.4 mmol) and DMSO (1 mL) under N_2. The reaction mixture was then heated at 120 ºC for 24 h. After the reaction was complete, DMSO was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (v/v, 30/1−25/1) to provide product **9**.

c) General procedure for the synthesis of 6 and 7

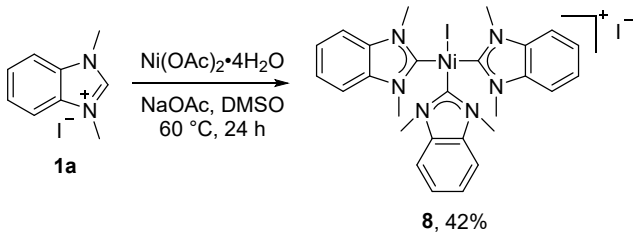


(1) A Schlenk tube with a magnetic stirring bar was charged with **4c** (105.6 mg, 0.2 mmol) and pyridine (1 mL) in air. The reaction mixture was heated at 140 ºC for 12 h. After the reaction was complete, the mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel with PE/EA (v/v = 3/1) to provide 2-(1,2-diphenylvinyl)-1-methylbenzimidazole **6** in 99% yield.



(2) A Schlenk tube with a magnetic stirring bar was charged with **5** (75.6 mg, 0.2 mmol), tributyl phosphine (495.3 μL, 2.0 mmol) and DMF (1 mL) under N_2. The reaction mixture was heated at 160 ºC for 24 h. After the reaction was complete, the mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel with PE/EA (v/v = 3/1) to afford 1-methyl-2-(1-phenylethyl)benzimidazole **7** in 97% yield.

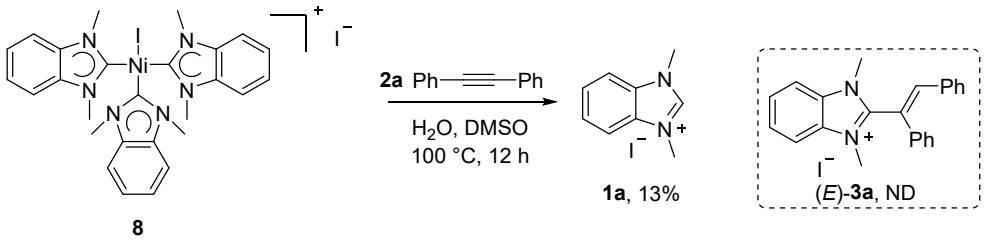
d) Synthesis of the tricarbene coordinated Ni(II) complex 8



A Schlenk tube with a magnetic stirring bar was charged with 1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium **1a** (54.8 mg, 0.2 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (5.0 mg, 0.01 mmol), NaOAc (32.8 mg, 0.4 mmol) and DMSO (1 mL) under N_2. The reaction mixture was then heated at 60 ºC for 24 h. After the reaction was cooled down to room temperature, DMSO was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (v/v, 50/1−30/1) to provide **8** as an orange solid (6.4 mg, 42% yield). Compound **8** in $CDCl_3$ gradually

decomposes in air. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.43 (m, 2H), 7.40-7.37 (m, 4H), 7.31-7.27 (m, 6H), 4.49 (s, 12H), 4.44 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.9, 179.6, 135.6, 135.0, 124.3, 123.7, 110.7, 110.2, 37.4, 36.9 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{33}IN_6Ni^+$ $[M-I^-]^+$ 623.0930, found 623.0922.

e) Reaction of the tricarbene coordinated Ni(II) complex 8 with diphenylacetylene 2a

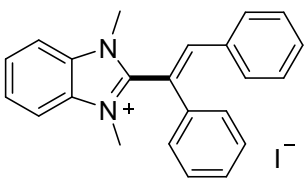


A flame dried Schlenk tube with a magnetic stirring bar was charged with **8** (32.0 mg, 0.043 mmol), **2a** (22.7 mg, 0.13 mmol), H_2O (3.8 μL, 0.22 mmol) and DMSO (0.5 mL) under N_2. The reaction mixture was then heated at 100 ºC for 12 h. After the reaction was cooled down to room temperature, DMSO was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (v/v, 40/1−10/1) to provide **1a** as a light yellow solid (3.0 mg, 13% yield). (*E*)-**3a** was not detected.

f) Experiments to detect the Ni–H intermediate

A flame dried Schlenk tube with a magnetic stirring bar was charged with **1a** (27.4 mg, 0.1 mmol), **2a** (26.7 mg, 0.15 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (25.0 mg, 0.1 mmol) and KOAc (19.2 mg, 0.2 mmol) in DMSO-d_6 (0.5 mL) under N_2. The reaction mixture was then heated at 100 ºC for 15 minutes. After cooling to room temperature, the mixture was filtered in the glove box. The filtrate was sealed in a NMR tube and directly subjected to ^{1}H NMR analysis. No characteristic signal of the Ni–H was detected.

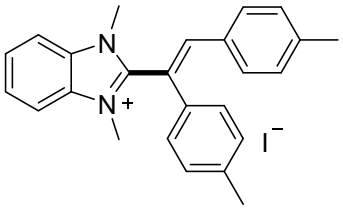
IV. Characterization of New Compounds



(*E*)-2-(1,2-diphenylvinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3a):

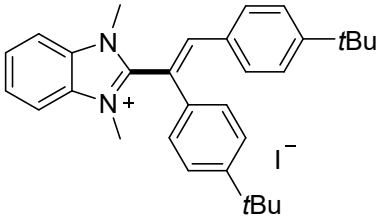
Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3a** as a

white solid of inseparable *E*/*Z* isomers (85.8 mg, 95% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 12:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.21 (s, 1H), 8.09-8.05 (m, 2H), 7.80-7.76 (m, 2H), 7.50 (br, 5H), 7.36 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 2H), 7.03 (d, J = 7.2 Hz, 2H), 3.71 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 141.9, 134.9, 133.4, 131.7, 130.9, 130.5, 130.3, 130.0, 128.4, 128.1, 126.1, 121.5, 114.2, 34.1 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{21}N_2^+$ [M−I$^-$]$^+$ 325.1699, found 325.1696.

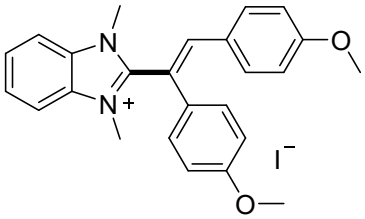


(*E*)-2-(1,2-di-*p*-tolylvinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3b):

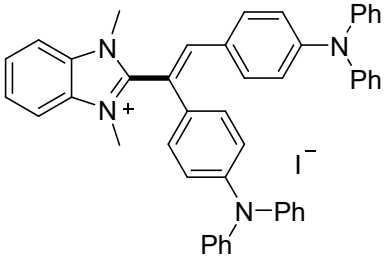
Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3b** as an offwhite solid of inseparable *E*/*Z* isomers (80.7 mg, 84% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be more than 20:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.10 (s, 1H), 8.09-8.06 (m, 2H), 7.79-7.77 (m, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 3.71 (s, 6H), 2.36 (s, 3H), 2.25 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 149.0, 140.5, 139.9, 139.3, 132.7, 131.7, 131.4, 130.1, 129.9, 128.2, 127.1, 126.2, 119.9, 113.9, 32.5, 20.9, 20.8 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{25}N_2^+$ [M−I$^-$]$^+$ 353.2012, found 353.2012.



(*E*)-2-(1,2-bis(4-(*tert*-butyl)phenyl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3c): Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3c** as a white solid of inseparable *E*/*Z* isomers (107.2 mg, 95% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be more than 20:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.12-8.09 (m, 3H), 7.81-7.79 (m, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 3.76 (s, 6H), 1.30 (s, 9H), 1.20 (s, 9H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.0, 152.2, 149.0, 140.1, 132.7, 131.8, 131.1, 128.2, 127.2, 126.3, 126.2, 125.8, 119.1, 114.0, 34.6, 34.5, 32.4, 30.9, 30.8 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{37}N_2$ [M−I$^-$]$^+$ 437.2951, found 437.2951.

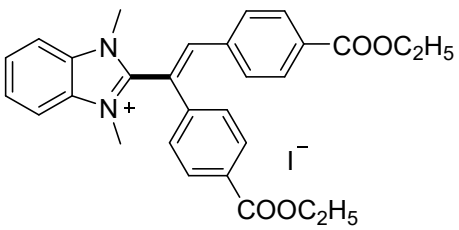


(*E*)-2-(1,2-bis(4-methoxyphenyl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3d): Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3d** as a yellow solid of inseparable *E*/*Z* isomers (92.1 mg, 90% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be more than 20:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07-8.02 (m, 2H), 7.75-7.71 (m, 2H), 7.68 (s, 1H), 7.19-7.15 (m, 2H), 6.97-6.95 (m, 2H), 6.80-6.75 (m, 4H), 3.84 (s, 6H), 3.82 (s, 3H), 3.75 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 161.0, 149.9, 139.4, 131.8, 129.8, 128.2, 127.7, 127.5, 126.2, 118.4, 115.6, 115.4, 114.1, 55.8, 55.6, 33.9 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{25}N_2O_2^+$ $[M-I^-]^+$ 385.1911, found 385.1911.



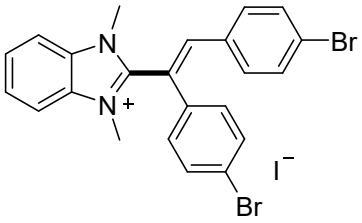
(*E*)-2-(1,2-bis(4-(diphenylamino)phenyl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3e):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3e** as a yellow solid of inseparable *E*/*Z* isomers (103.8 mg, 66% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 9:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.07-8.04 (m, 2H), 7.90 (s, 1H), 7.75-7.73 (m, 2H), 7.37-7.32 (m, 7H), 7.30-7.27 (m, 3H), 7.14-7.11 (m, 3H), 7.09-7.06 (m, 5H), 7.04-7.01 (m, 4H), 6.93 (d, J = 9.2 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 3.76 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 149.2, 148.5, 148.0, 146.4, 146.0, 138.4, 131.8, 129.8, 129.8, 129.6, 128.9, 127.1, 126.9, 126.6, 125.3, 124.8, 124.5, 124.0, 122.0, 120.5, 117.1, 113.9, 32.4 ppm. HRMS (ESI$^+$): calcd for $C_{47}H_{39}N_4^+$ $[M-I^-]^+$ 659.3169, found 659.3169.

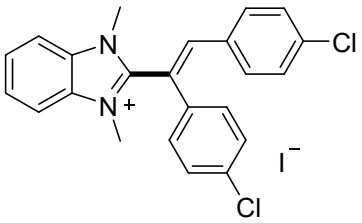


(*E*)-2-(1,2-bis(4-(ethoxycarbonyl)phenyl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3f):

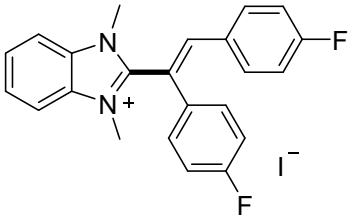
Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3f** as a yellow solid of inseparable *E*/*Z* isomers (52 mg, 55% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be more than 20:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.45 (s, 1H), 8.09-8.07 (m, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.81-7.79 (m, 2H), 7.69 (d, J = 8.0, Hz 2H), 7.22 (d, J = 7.6 Hz, 2H), 4.34 (d, J = 6.8 Hz, 2H), 4.26 (q, J = 6.8 Hz, 2H), 3.73 (s, 6H), 1.33 (t, J = 6.8 Hz, 3H), 1.27 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.1, 164.9, 147.5, 142.8, 139.4, 138.2, 131.9, 130.8, 130.7, 130.1, 129.9, 128.8, 127.3, 127.0, 121.9, 114.1, 61.1, 32.6, 14.2, 14.1 ppm. HRMS (ESI$^+$): calcd for $C_{29}H_{29}N_2O_4^+$ [M−I$^-$]$^+$ 469.2122, found 469.2118.



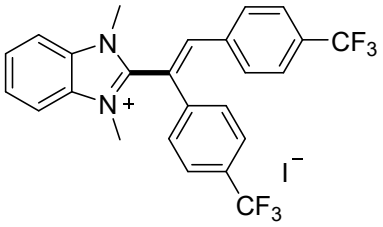
(*E*)-2-(1,2-bis(4-bromophenyl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3g): Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3g** as a white solid of inseparable *E*/*Z* isomers (55.9 mg, 46% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be more than 20:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.22 (s, 1H), 8.09-8.07 (m, 2H), 7.80-7.77 (m, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.52-7.46 (m, 4H), 6.99 (d, J = 8.4, Hz, 2H), 3.73 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 147.7, 141.3, 134.5, 133.1, 132.4, 132.3, 131.9, 130.4, 128.6, 127.2, 123.7, 123.2, 120.4, 114.0, 32.6 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{19}Br_2N_2^+$ [M−I$^-$]$^+$ 482.9889, 480.9910, found 482.9891, 480.9912.



(*E*)-2-(1,2-bis(4-chlorophenyl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3h): Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3h** as a white solid of inseparable *E*/*Z* isomers (80.1 mg, 77% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be more than 20:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.22 (s, 1H), 8.08-8.06 (m, 2H), 7.79-7.77 (m, 2H), 7.57-7.52 (m, 4H), 7.38 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 3.72 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 147.8, 141.2, 134.8, 134.4, 134.2, 132.8, 131.9, 130.2, 129.5, 129.4, 128.4, 127.2, 120.3, 114.0, 32.6 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{19}Cl_2N_2^+$ [M−I$^-$]$^+$ 393.0920, found 393.0924.

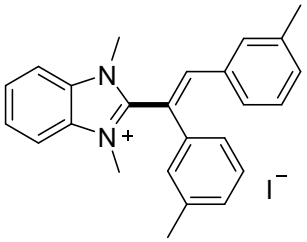


(*E*)-2-(1,2-bis(4-fluorophenyl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3i): Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3i** as a pale yellow solid of inseparable *E*/*Z* isomers (84.9 mg, 87% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 8:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.16 (s, 1H), 8.08-8.06 (m, 2H), 7.79-7.77 (m, 2H), 7.59-7.55 (m, 2H), 7.34 (t, J = 8.8 Hz, 2H), 7.19-7.08 (m, 4H), 3.93 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.7 (d, J_{CF} = 246.5 Hz), 162.6 (d, J_{CF} = 247.9 Hz), 148.2, 140.8, 132.0 (d, J_{CF} = 3.1 Hz), 131.8, 130.8 (d, J_{CF} = 8.6 Hz), 130.6 (d, J_{CF} = 3.2 Hz), 128.9 (d, J_{CF} = 8.6 Hz), 127.1, 119.8 (d, J_{CF} = 1.6 Hz), 116.5 (d, J_{CF} = 21.7 Hz), 116.4 (d, J_{CF} = 21.8 Hz), 113.9, 32.5 ppm. HRMS (ESI^{+}): calcd for $C_{23}H_{19}F_2N_2^{+}$ [M−I^{-}]$^{+}$ 361.1511, found 361.1506.



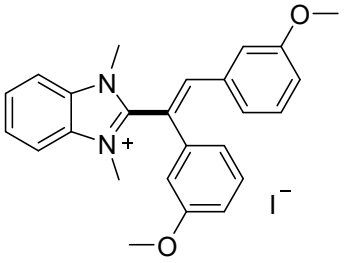
(*E*)-2-(1,2-bis(4-(trifluoromethyl)phenyl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3j):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3j** as a yellow solid of inseparable *E*/*Z* isomers (80.4 mg, 68% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 16:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.46 (s, 1H), 8.10-8.08 (m, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.81-7.77 (m, 4H), 7.69 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 3.75 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 147.2, 142.8, 139.0 (d, J_{CF} = 1.3 Hz), 137.6 (d, J_{CF} = 0.9 Hz), 131.9, 129.9 (d, J_{CF} = 31.8 Hz), 129.8 (d, J_{CF} = 31.9 Hz), 129.4, 127.6, 127.3, 126.4 (q, J_{CF} = 3.6 Hz), 126.2 (q, J_{CF} = 3.8 Hz), 124.0 (d, J_{CF} = 270.8 Hz), 123.8 (d, J_{CF} = 270.9 Hz), 121.6, 114.1, 32.7 ppm. HRMS (ESI^{+}): calcd for $C_{25}H_{19}F_6N_2^{+}$ [M−I^{-}]$^{+}$ 461.1447, found 461.1443.



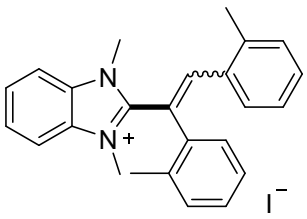
(*E*)-2-(1,2-di-*m*-tolylvinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3k):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3k** as a white solid of inseparable *E*/*Z* isomers (84 mg, 87% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 15:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.14 (s, 1H), 8.09-8.06 (m, 2H), 7.81-7.77 (m, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.18-7.11 (m, 2H), 6.87 (s, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 3.71 (s, 6H), 2.34 (s, 3H), 2.12 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 148.9, 141.4, 139.0, 138.5, 135.3, 134.1, 131.7, 130.7, 130.4, 129.4, 129.3, 129.2, 127.1, 126.7, 124.6, 123.5, 121.0, 113.9, 32.5, 21.0, 20.8 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{25}N_2^+$ [M−I$^-$]$^+$ 353.2012, found 353.2013.



(*E*)-2-(1,2-bis(3-methoxyphenyl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3l):

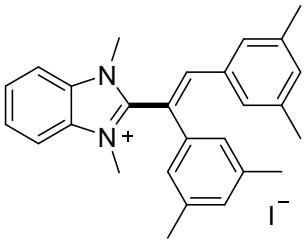
Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3l** as a light yellow solid of inseparable *E*/*Z* isomers (82.3 mg, 80% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 15:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-8.07 (m, 2H), 7.89 (s, 1H), 7.76-7.72 (m, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz,1H), 6.98 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 6.86-6.83 (m, 2H), 6.71 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 6.48 (t, *J* = 2.0 Hz, 1H), 6.31 (d, *J* = 7.6 Hz, 1H), 3.863-3.857 (m, 9H), 3.59 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 160.3, 149.2, 142.0, 136.2, 134.7, 131.7, 131.4, 131.1, 128.4, 121.4, 119.7, 118.5, 116.6, 115.5, 114.2, 113.8, 112.0, 56.0, 55.5, 34.1 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{25}N_2O_2^+$ [M−I$^-$]$^+$ 385.1911, found 385.1910.



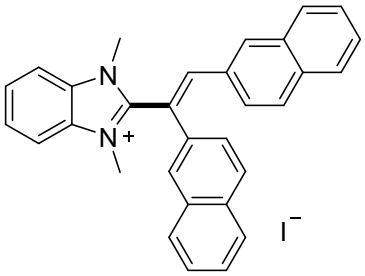
2-(1,2-di-*o*-tolylvinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3m):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3m** as a light yellow solid of inseparable *E*/*Z* isomers (70 mg, 73% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 1:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.10-8.07 (m, 1H), 7.99-7.97 (m, 1H), 7.96 (s, 0.59H, for (*Z*)-**3m**), 7.77 (s, 0.58H, for (*E*)-**3m**), 7.76-7.74 (m, 1H), 7.73-7.70

(m, 1H), 7.43-7.38 (m, 2H), 7.36-7.31 (m, 2.35H), 7.29-7.24 (m, 1.55H), 7.22-7.20 (m, 1H), 6.97 (t, J = 8.0 Hz, 0.66H), 6.89 (t, J = 7.6 Hz, 0.67H), 6.84 (d, J = 7.6 Hz, 0.58H), 6.60 (d, J = 7.6 Hz, 0.60H), 3.90 (s, 3H, for (*Z*)-**3m**), 3.58 (s, 3H, for (*E*)-**3m**), 2.49 (s, 1.54H), 2.38 (s, 1.50H), 2.16 (s, 1.56H), 1.87 (s, 1.50H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 150.8, 149.3, 145.8, 144.6, 137.8, 137.7, 136.3, 136.0, 135.5, 133.8, 133.7, 132.9, 131.8, 131.7, 131.38, 131.42, 130.9, 130.7, 130.5, 130.3, 130.2, 129.7, 129.5, 128.5, 127.2, 127.1, 127.0, 126.8, 126.5, 125.6, 122.1, 121.6, 113.7, 113.5, 32.9, 32.5, 19.74, 19.71, 19.69, 19.2 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{25}N_2^+$ [M−I$^-$]$^+$ 353.2012, found 353.2016.

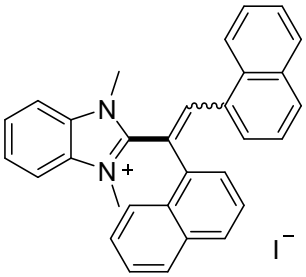


(*E*)-2-(1,2-bis(3,5-dimethylphenyl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3n): Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3n** as an offwhite solid of inseparable *E*/*Z* isomers (87.2 mg, 86% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 16:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17-8.14 (m, 2H), 7.75-7.72 (m, 3H), 7.07 (s, 1H), 6.93 (s, 1H), 6.82(s, 2H), 6.31 (s, 2H), 3.84 (s, 6H), 2.32 (s, 6H), 2.05 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6, 141.6, 140.1, 139.5, 135.0, 133.6, 132.6, 132.3, 131.6, 128.3, 125.6, 123.7, 121.4, 114.2, 34.2, 21.5, 21.3 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{29}N_2^+$ [M−I$^-$]$^+$ 381.2325, found 381.2320.

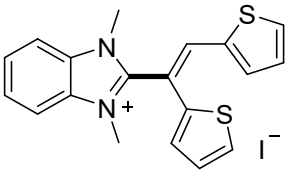


(*E*)-2-(1,2-di(naphthalen-2-yl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3o): Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3o** as a brown solid of inseparable *E*/*Z* isomers (93.4 mg, 85% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 12:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.53 (s, 1H), 8.12-8.09 (m, 3H), 8.01 (d, J = 7.6 Hz, 1H), 7.93-7.88 (m, 4H), 7.83-7.77 (m, 5H), 7.62-7.51 (m, 4H), 6.87 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H), 3.78 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 148.8, 141.7, 133.08, 133.07, 133.0, 132.8, 132.7, 131.9, 131.6, 129.5, 129.3, 129.0, 128.5, 128.4, 127.7, 127.3, 127.2, 127.1, 127.0, 126.0, 123.9, 123.7, 123.4, 121.1, 114.0, 32.6 ppm. HRMS (ESI$^+$): calcd for

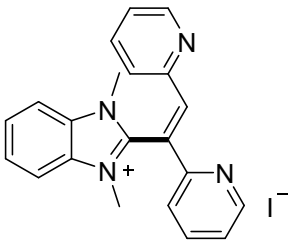
$C_{31}H_{25}N_2^+$ $[M-I^-]^+$ 425.2012, found 425.2007.



2-(1,2-di(naphthalen-1-yl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3p): Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3p** as a yellow solid of inseparable *E*/*Z* isomers (100.8 mg, 91% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 1:1.4 ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.06 (s, 0.55H, for (*Z*)-**3p**), 8.86 (d, *J* = 8.8 Hz, 0.6H), 8.50 (s, 0.45H, for (*E*)-**3p**), 8.12-8.09 (m, 0.55H), 8.02-7.98(m, 1.48H), 7.94-7.87 (m, 2.52H), 7.82-7.77 (m, 1.47H), 7.74-7.72 (m, 1H), 7.68-7.50 (m, 7.47H), 7.43 (t, *J* = 8.4 Hz, 1.23H), 7.36-7.30 (m, 1.72H), 7.12-7.08 (m, 1H), 6.99 (d, *J* = 7.2 Hz, 0.6H), 6.91 (t, *J* = 7.6 Hz, 0.65H), 3.98 (s, 3.5H, for (*Z*)-**3p**), 3.71 (s, 2.5H, for (*E*)-**3p**) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7, 149.8, 147.9, 146.4, 134.6, 134.0, 133.8, 133.6, 132.8, 132.3, 131.84, 131.78, 131.7, 131.2, 130.8, 130.67, 130.66, 130.6, 129.80, 129.78, 129.5, 129.2, 129.1, 128.7, 128.4, 128.21, 128.19, 128.1, 127.9, 127.8, 127.5, 127.4, 127.2, 126.7, 126.6, 126.3, 125.9, 125.79, 125.76, 124.6, 124.0, 123.1, 123.1, 122.0, 120.6, 114.0, 113.3, 34.3, 34.0 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{25}N_2^+$ $[M-I^-]^+$ 425.2012, found 425.2007.

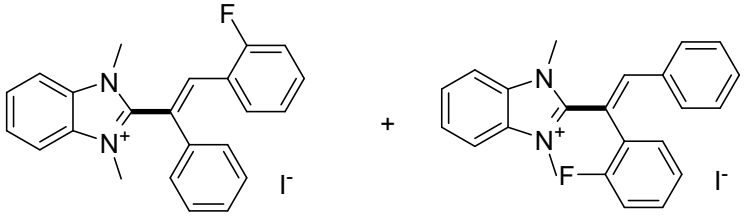


(*E*)-2-(1,2-di(thiophen-2-yl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3q): Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3q** as a brown solid of inseparable *E*/*Z* isomers (76.6 mg, 83% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be more than 20:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.25 (s, 1H), 8.22-8.20 (m, 2H), 7.87-7.85 (m, 2H), 7.75 (d, *J* = 4.8 Hz, 1H), 7.63 (t, *J* = 4.8 Hz, 1H), 7.56 (d, *J* = 3.2 Hz, 1H), 7.15 (t, *J* = 4.8 Hz, 1H), 7.10 (t, *J* = 5.2 Hz, 1H), 6.97 (d, *J* = 3.2 Hz, 1H), 3.93 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 146.0, 138.5, 136.0, 134.6, 132.2, 131.4, 129.9, 128.8, 128.6, 128.1, 127.6, 114.2, 111.3, 32.4 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{17}N_2S_2^+$ $[M-I^-]^+$ 337.0828, found 337.0824.



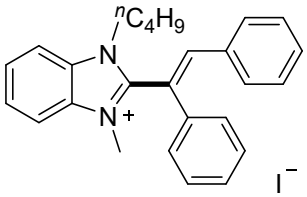
(*Z*)-2-(1,2-di(pyridin-2-yl)vinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3r):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3r** as a brown solid (51.3 mg, 56% yield). By ^{1}H NMR, the *Z*:*E* ratio was determined to be more than 20:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.68 (s, 1H), 8.51 (d, J = 4.8 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.12-8.04 (m, 3H), 8.00-7.91 (m, 3H), 7.78-7.74 (m, 2H), 7.48 (dd, J = 7.2 Hz, J = 4.8 Hz, 1H), 7.32-7.28 (m, 1H), 3.73 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9, 152.6, 151.0, 150.1, 149.7, 140.1, 138.3, 137.8, 131.9, 128.9, 126.8, 124.7, 124.3, 122.9, 122.0, 113.0, 32.4 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{19}N_4^+$ $[M-I^-]^+$ 327.1604, found 327.1601.



(*E*)-2-(2-(2-fluorophenyl)-1-phenylvinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3s) and (*E*)-2-(1-(2-fluorophenyl)-2-phenylvinyl)-1,3-dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (3s′):

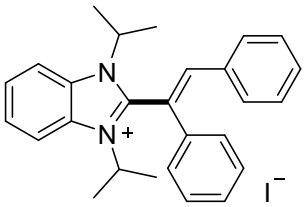
Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **3s** and **3s′** as a light yellow solid of inseparable mixture (78.0 mg, 83% yield). By ^{1}H NMR, the **3s**: **3s′** ratio was determined to be 1.3:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3.36H, for **3s**), 3.87 (s, 2.63H, for **3s′**), 6.96-7.02 (m, 2H), 7.33-7.43 (m, 4H), 7.50-7.52 (m, 2H), 7.72-7.78 (m, 3H), 7.88 (s, 0.59H, for **3s**), 7.89 (s, 0.45H, for **3s′**), 7.98-8.03 (m, 2H) ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{20}FN_2^+$ $[M-I^-]^+$ 343.1605, found 343.1611.



(*E*)-1-butyl-2-(1,2-diphenylvinyl)-3-methyl-1*H*-benzo[*d*]imidazol-3-ium iodide (4a):

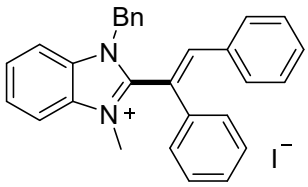
Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **4a** as a white solid of inseparable *E*/*Z* isomers (90.9 mg, 92% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 7:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.18 (s, 1H), 8.16-8.13 (m,

1H), 8.12-8.09 (m, 1H), 7.79-7.77 (m, 2H), 7.50 (br, 5H), 7.37-7.30 (m, 3H), 7.01 (d, J = 7.2 Hz, 2H), 4.21-4.14 (m, 2H), 3.77 (s, 3H), 1.35-1.29 (m, 2H), 1.15-1.08 (m, 2H), 0.62 (t, J = 7.2 Hz, 3H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5, 141.4, 135.2, 133.3, 131.9, 131.1, 131.0, 130.5, 130.2, 130.0, 128.4, 128.3, 128.2, 126.2, 121.4, 114.9, 113.9, 47.2, 34.3, 30.8, 20.0, 13.5 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{27}N_2^+$ [M−I$^-$]$^+$ 367.2169, found 367.2164.



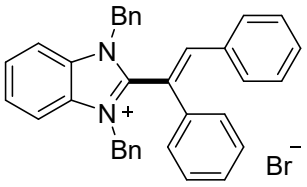
(*E*)-2-(1,2-diphenylvinyl)-1,3-diisopropyl-1*H*-benzo[*d*]imidazol-3-ium iodide (4b):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **4b** as a white solid of inseparable *E*/*Z* isomers (78.3 mg, 77% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 10:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.39-8.37 (m, 2H), 8.22 (s, 1H), 7.76-7.74 (m, 2H), 7.49 (br, 5H), 7.39-7.36 (m, 3H), 7.01-6.99 (m, 2H), 4.80-4.73 (m, 2H), 1.44 (d, J = 7.2 Hz, 6H), 1.28 (d, J = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 147.0, 140.7, 135.7, 133.8, 130.3, 130.1, 129.8, 129.6, 129.4, 128.6, 126.9, 126.3, 121.3, 116.1, 52.6, 20.3, 19.6 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{29}N_2^+$ [M−I$^-$]$^+$ 381.2325, found 381.2326.



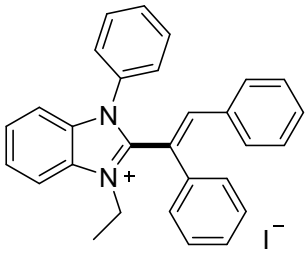
(*E*)-1-benzyl-2-(1,2-diphenylvinyl)-3-methyl-1*H*-benzo[*d*]imidazol-3-ium bromide (4c):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **4c** as a white solid of inseparable *E*/*Z* isomers (73.9 mg, 70% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 7:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.17 (s, 1H), 8.13 (d, J = 8.4, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.81-7.75 (m, 2H), 7.49-7.42 (m, 4H), 7.34 (t, J = 7.2 Hz, 2H), 7.25 (t, J = 7.2 Hz, 3H), 7.19 (d, J = 7.6 Hz, 2H), 7.06 (d, J = 7.2 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 5.56 (d, J = 16.0 Hz, 1H), 5.37 (d, J = 15.6 Hz, 1H), 3.76 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 148.9, 141.9, 135.3, 133.9, 133.1, 132.1, 131.3, 130.2, 129.7, 129.4, 129.3, 128.8, 128.6, 128.2, 127.9, 127.6, 127.3, 126.6, 120.8, 114.5, 114.2, 49.4, 32.6 ppm. HRMS (ESI$^+$): calcd for $C_{29}H_{25}N_2^+$ [M−Br$^-$]$^+$ 401.2012, found 401.2020.



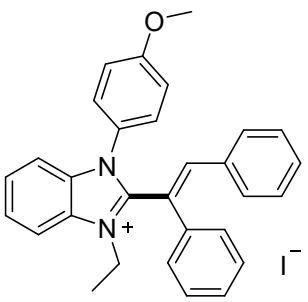
(*E*)-1,3-dibenzyl-2-(1,2-diphenylvinyl)-1*H*-benzo[*d*]imidazol-3-ium bromide (4d):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **4d** as a white solid of inseparable *E*/*Z* isomers (59.2 mg, 53% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 8:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-8.09 (m, 2H), 7.85 (s, 1H), 7.71-7.69 (m, 2H), 7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.21-7.09 (m, 14H), 6.71 (d, *J* = 7.6 Hz, 2H), 5.65 (d, *J* = 15.6 Hz, 2H), 5.38 (d, *J* = 15.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 141.6, 135.0, 133.1, 132.2, 131.8, 130.9, 130.5, 130.1, 129.9, 129.31, 129.28, 128.5, 128.40, 128.36, 126.3, 121.8, 115.1, 50.9 ppm. HRMS (ESI$^+$): calcd for $C_{35}H_{29}N_2^+$ [M−Br$^-$]$^+$ 477.2325, found 477.2326.



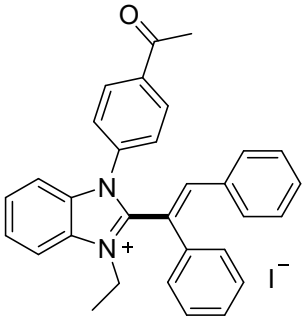
(*E*)-2-(1,2-diphenylvinyl)-3-ethyl-1-phenyl-1*H*-benzo[*d*]imidazol-3-ium iodide (4e):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **4e** as a light purple solid of inseparable *E*/*Z* isomers (94 mg, 89% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 5:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.32 (d, *J* = 8.4 Hz, 1H), 7.90 (s, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.62-7.49 (m, 5H), 7.46-7.38 (m, 6H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.08-7.06 (m, 1H), 6.90 (d, *J* = 7.6 Hz, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 148.3, 141.4, 136.0, 133.9, 132.6, 131.6, 131.0, 130.7, 130.2, 129.9, 129.6, 129.3, 128.5, 128.1, 127.7, 126.8, 125.8, 121.0, 114.5, 113.8, 42.2, 13.5 ppm. HRMS (ESI$^+$): calcd for $C_{29}H_{25}N_2^+$ [M−I$^-$]$^+$ 401.2012, found 401.2012.

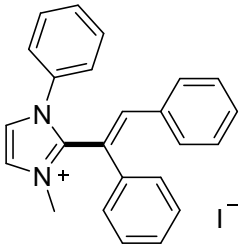


(*E*)-2-(1,2-diphenylvinyl)-3-ethyl-1-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazol-3-ium iodide (4f):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **4f** as a white solid of inseparable *E*/*Z* isomers (96 mg, 86% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 3:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.29 (d, J = 8.4 Hz, 1H), 7.91 (s, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.58-7.57 (m, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.46-7.44 (m, 3H), 7.32 (t, J = 7.6 Hz, 3H), 7.07 (d, J = 8.4 Hz, 1H), 6.93-6.90 (m, 5H), 4.41 (q, J = 7.2 Hz, 2H), 3.75 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.5, 148.5, 141.1, 136.0, 134.0, 133.0, 130.9, 130.2, 129.6, 129.4, 128.6, 128.0, 127.6, 127.3, 126.7, 124.1, 121.1, 115.0, 114.4, 113.9, 55.7, 42.2, 13.5 ppm. HRMS (ESI$^+$): calcd for $C_{30}H_{27}N_2O^+$ $[M-I^-]^+$ 431.2118, found 431.2119.



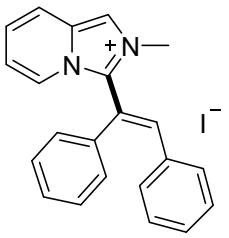
(*E*)-1-(4-acetylphenyl)-2-(1,2-diphenylvinyl)-3-ethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (4g): Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **4g** as a light yellow solid of inseparable *E*/*Z* isomers (34 mg, 30% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be approximately 3:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.33 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.8 Hz, 2H), 7.89 (s, 1H), 7.80-7.74 (m, 2H), 7.66-7.58 (m, 3H), 7.49-7.45 (m, 3H), 7.42-7.38 (m, 1H), 7.32-7.27 (m, 3H), 7.08-7.06 (m, 1H), 6.87 (d, J = 7.6 Hz, 2H), 4.43 (q, J = 7.2 Hz, 2H), 2.58 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 197.1, 148.2, 141.9, 137.9, 135.9, 135.2, 133.9, 132.4, 131.1, 130.3, 129.7, 129.6, 129.38, 129.35, 128.5, 128.2, 127.8, 126.9, 126.3, 120.9, 114.6, 113.8, 42.4, 27.0, 13.4 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{27}N_2O^+$ $[M-I^-]^+$ 443.2118, found 443.2110.



(*E*)-2-(1,2-diphenylvinyl)-3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (4h):

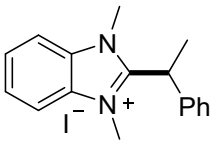
Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **4h** as a gray solid of inseparable *E*/*Z* isomers (53 mg, 57% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be more than 20:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.27 (s, 1H), 8.23 (s, 1H), 7.81 (s, 1H),

7.44-7.39 (m, 7H), 7.36-7.30 (m, 4H), 6.98 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 7.6 Hz, 2H), 3.61 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 142.5, 140.4, 135.8, 134.2, 134.2, 130.1, 129.8, 129.5, 129.4, 129.2, 128.1, 126.2, 125.2, 124.2, 121.2, 35.7 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{21}N_2^+$ [M−I$^-$]$^+$ 337.1699, found 337.1694.



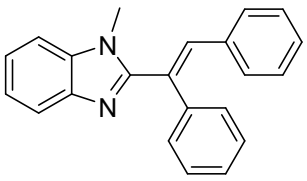
(*E*)-3-(1,2-diphenylvinyl)-2-methylimidazo[1,5-*a*]pyridin-2-ium iodide (4i):

Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **4i** as a brown solid of inseparable *E*/*Z* isomers (50.5 mg, 58% yield). By ^{1}H NMR, the *E*:*Z* ratio was determined to be more than 20:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.49 (s, 1H), 8.11 (s, 1H), 8.01 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 7.2 Hz, 1H), 7.48-7.40 (m, 5H), 7.30-7.23 (m, 4H), 7.04 (t, J = 6.8 Hz, 1H), 6.84 (d, J = 6.8 Hz, 2H), 3.78 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 141.2, 135.8, 134.4, 131.9, 129.7, 129.6, 129.5, 129.4, 129.1, 128.0, 126.4, 125.1, 122.4, 120.5, 118.9, 118.6, 116.2, 36.4 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{19}N_2^+$ [M−I$^-$]$^+$ 311.1543, found 311.1538.



1,3-dimethyl-2-(1-phenylethyl)-1*H*-benzo[*d*]imidazol-3-ium iodide (5):

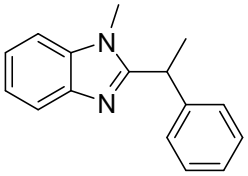
Purification via column chromatography on silica gel (DCM/MeOH = 30/1, v/v) afforded **5** as a light yellow solid (34.0 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81-7.76 (m, 2H), 7.66-7.62 (m, 2H), 7.43-7.39 (m, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 2H), 5.43 (q, J = 7.2 Hz, 1H), 4.08 (s, 6H), 2.10 (d, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 135.9, 131.9, 129.9, 128.7, 127.5, 127.1, 113.1, 35.4, 34.3, 17.5 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{19}N_2^+$ [M−I$^-$]$^+$ 251.1543, found 251.1540.



(*E*)-2-(1,2-diphenylvinyl)-1-methyl-1*H*-benzo[*d*]imidazole (6):

Purification via column chromatography on silica gel PE/EA (v/v = 3/1) afforded **6** as a white solid (61.5 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-7.84 (m, 1H), 7.45 (s, 1H), 7.36-7.30

(m, 8H), 7.19 (s, 1H), 7.16-7.14 (m, 2H), 6.95-6.93 (m, 2H), 3.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3, 143.4, 139.9, 136.0, 135.3, 134.0, 128.8, 128.765, 128.755, 128.4, 128.3, 126.8, 122.9, 122.4, 120.4, 109.8, 30.2 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{19}N_2^+$ $[M+H]^+$ 311.1543, found 311.1543.

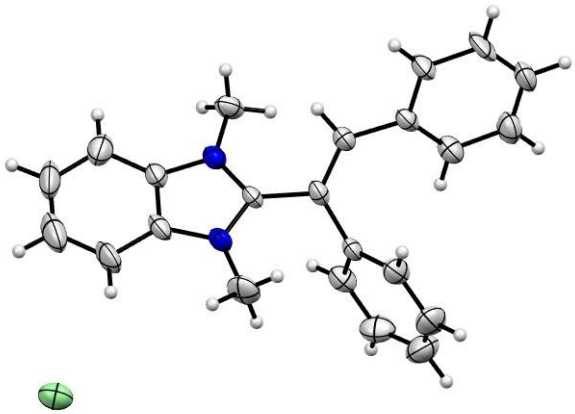


1-methyl-2-(1-phenylethyl)-1*H*-benzo[*d*]imidazole (7):

Purification via column chromatography on silica gel PE/EA (v/v = 3/1) afforded **7** as a white solid (45.8 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-7.83 (m, 1H), 7.31-7.19 (m, 8H), 4.35 (q, J = 7.2 Hz, 1H), 3.48 (s, 3H), 1.87 (d, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 143.0, 142.4, 136.2, 129.0, 127.5, 127.0, 122.4, 121.9, 119.7, 109.0, 39.1, 29.9, 21.8 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{17}N_2^+$ $[M+H]^+$ 237.1386, found 237.1386.

V. Single Crystal X-Ray Crystallographic Data

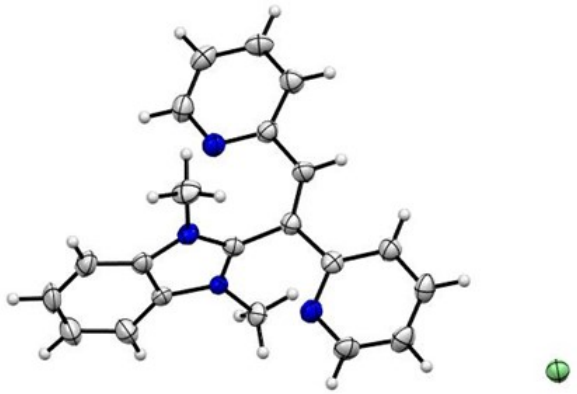
Table S7. Crystal data and structure refinement for **3a**



Identification code	2114144
Empirical formula	$C_{23}H_{21}IN_2$
Formula weight	452.32

Temperature/K	292.2(6)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.5543(4)
b/Å	8.6038(2)
c/Å	14.9273(4)
α/°	90
β/°	105.336(3)
γ/°	90
Volume/Å^3	2050.41(10)
Z	4
ρ_{calc}g/cm^3	1.465
μ/mm^{-1}	12.315
F(000)	904.0
Crystal size/mm^3	0.4 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.084 to 142.726
Index ranges	-20 ≤ h ≤ 19, -6 ≤ k ≤ 10, -14 ≤ l ≤ 18
Reflections collected	11549
Independent reflections	3936 [R_{int} = 0.0668, R_{sigma} = 0.0539]
Data/restraints/parameters	3936/0/237
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0618, wR_2 = 0.1693
Final R indexes [all data]	R_1 = 0.0677, wR_2 = 0.1795
Largest diff. peak/hole / e Å^{-3}	1.34/-2.03

Table S8. Crystal data and structure refinement for **3r**



Identification code	2114142
Empirical formula	$C_{21}H_{19}IN_4$
Formula weight	454.30
Temperature/K	150.0
Crystal system	triclinic

Space group	P-1
a/Å	7.887(3)
b/Å	10.676(5)
c/Å	11.448(4)
α/°	80.632(18)
β/°	89.145(17)
γ/°	86.29(2)
Volume/Å^3	949.1(7)
Z	2
ρ_{calc}g/cm^3	1.590
μ/mm^{-1}	1.699
F(000)	452.0
Crystal size/mm^3	0.3 × 0.3 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.846 to 51.358
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected	30470
Independent reflections	3565 [R_{int} = 0.1207, R_{sigma} = 0.0578]
Data/restraints/parameters	4495/4/289
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0498, wR_2 = 0.1222
Final R indexes [all data]	R_1 = 0.0555, wR_2 = 0.1258
Largest diff. peak/hole / e Å^{-3}	1.78/-1.94

VI. References

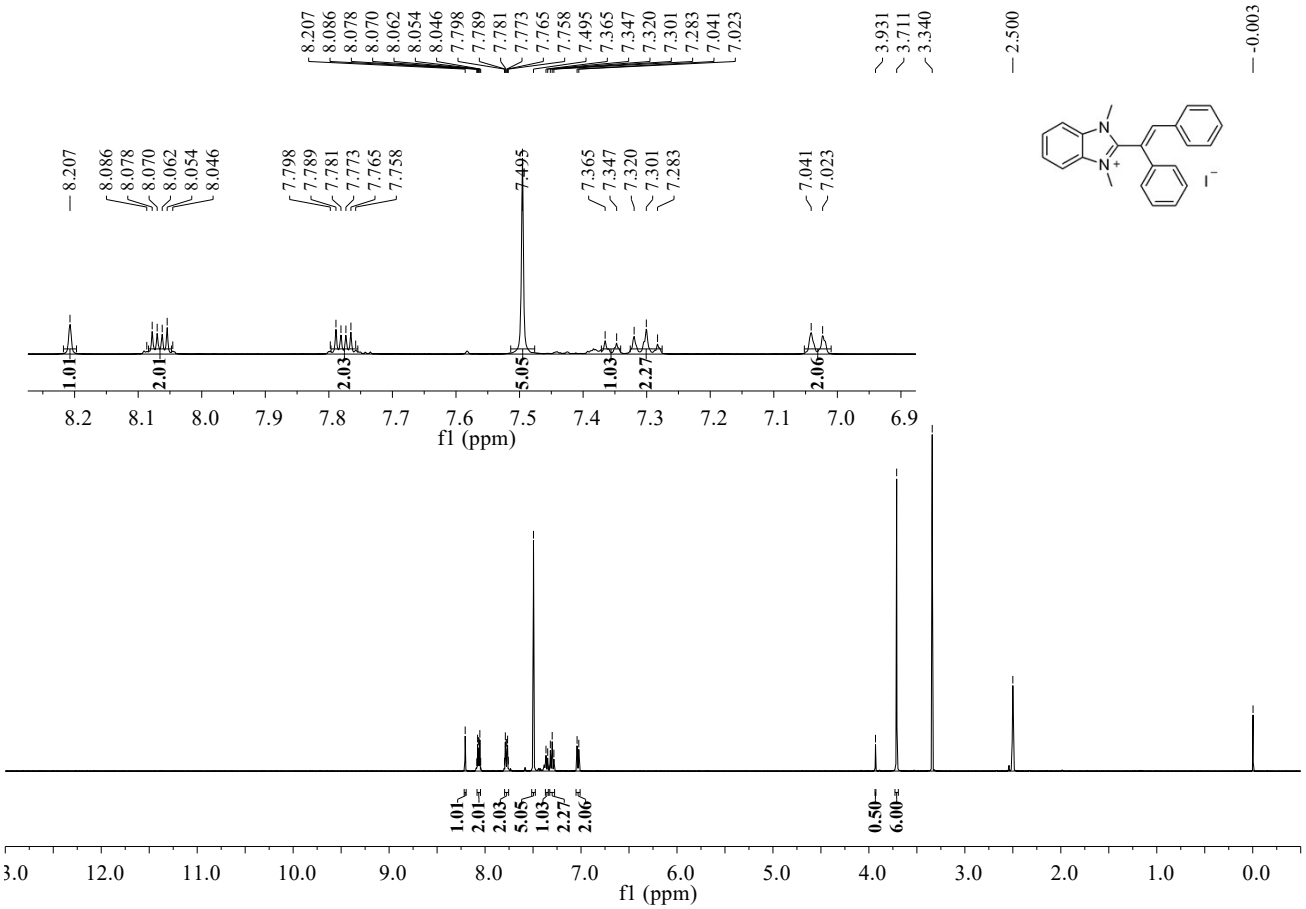
(1) (a) Zhang, H.; Cai, Q.; Ma, D. Amino Acid Promoted CuI-Catalyzed C−N Bond Formation between Aryl Halides and Amines or N-Containing Heterocycles. *J. Org. Chem.* **2005**, *70*, 5164-5173. (b) Zhu, L.; Cheng, L.; Zhang, Y.; Xie, R.; You, J. Highly Efficient Copper-Catalyzed *N*-Arylation of Nitrogen-Containing Heterocycles with Aryl and Heteroaryl Halides. *J. Org. Chem*. **2007**, *72*, 2737-2743. (c) Zhu, L.; Guo, P.; Li, G.; Lan, J.; Xie R.; You, J. Simple Copper Salt-Catalyzed N-Arylation of Nitrogen-Containing Heterocycles with Aryl and Heteroaryl Halides. *J. Org. Chem*. **2007**, *72*, 8535-8538. (d) Zhu, L.; Li, G.; Luo, L.; Guo, P.; Lan J.; You, J. Highly Functional Group Tolerance in Copper-Catalyzed *N*-Arylation of Nitrogen-Containing Heterocycles under Mild Conditions. *J. Org. Chem*. **2009**, *74*, 2200-2202.

(2) (a) Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. One-Pot Synthesis of Symmetrical and Unsymmetrical Bisarylethynes by A Modification of the Sonogashira Coupling Reaction. *Org. Lett*. **2002**, *4*, 3199-

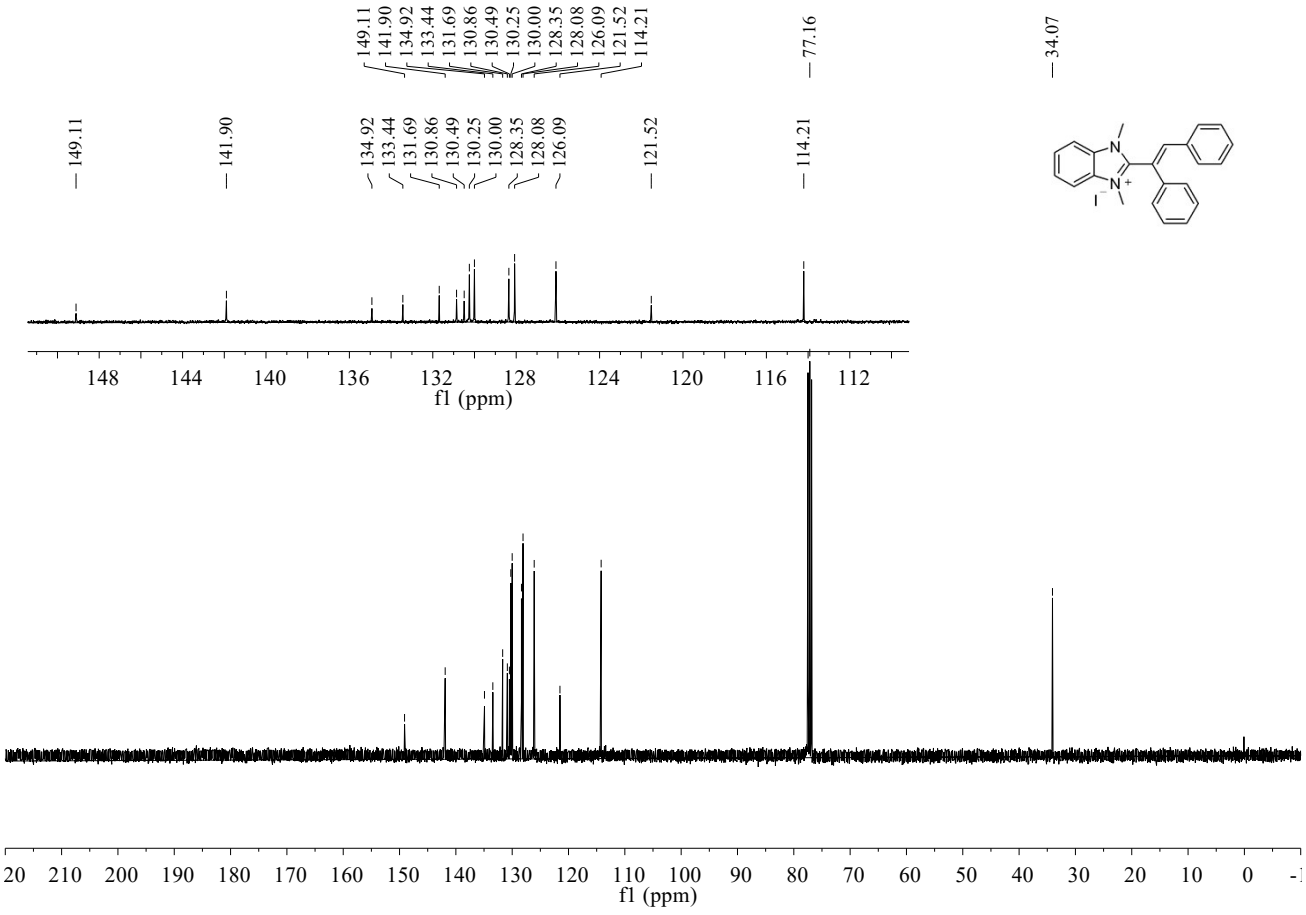
3202. (b) Park, K.; Bae, G.; Moon, J.; Choe, J.; Song, K. H.; Lee, S. Synthesis of Symmetrical and Unsymmetrical Diarylalkynes from Propiolic Acid Using Palladium-Catalyzed Decarboxylative Coupling. *J. Org. Chem.* **2010**, *75*, 6244-6251.

VII. Copies of ^{1}H, ^{1}H-^{1}H NOESY and ^{13}C NMR Spectra

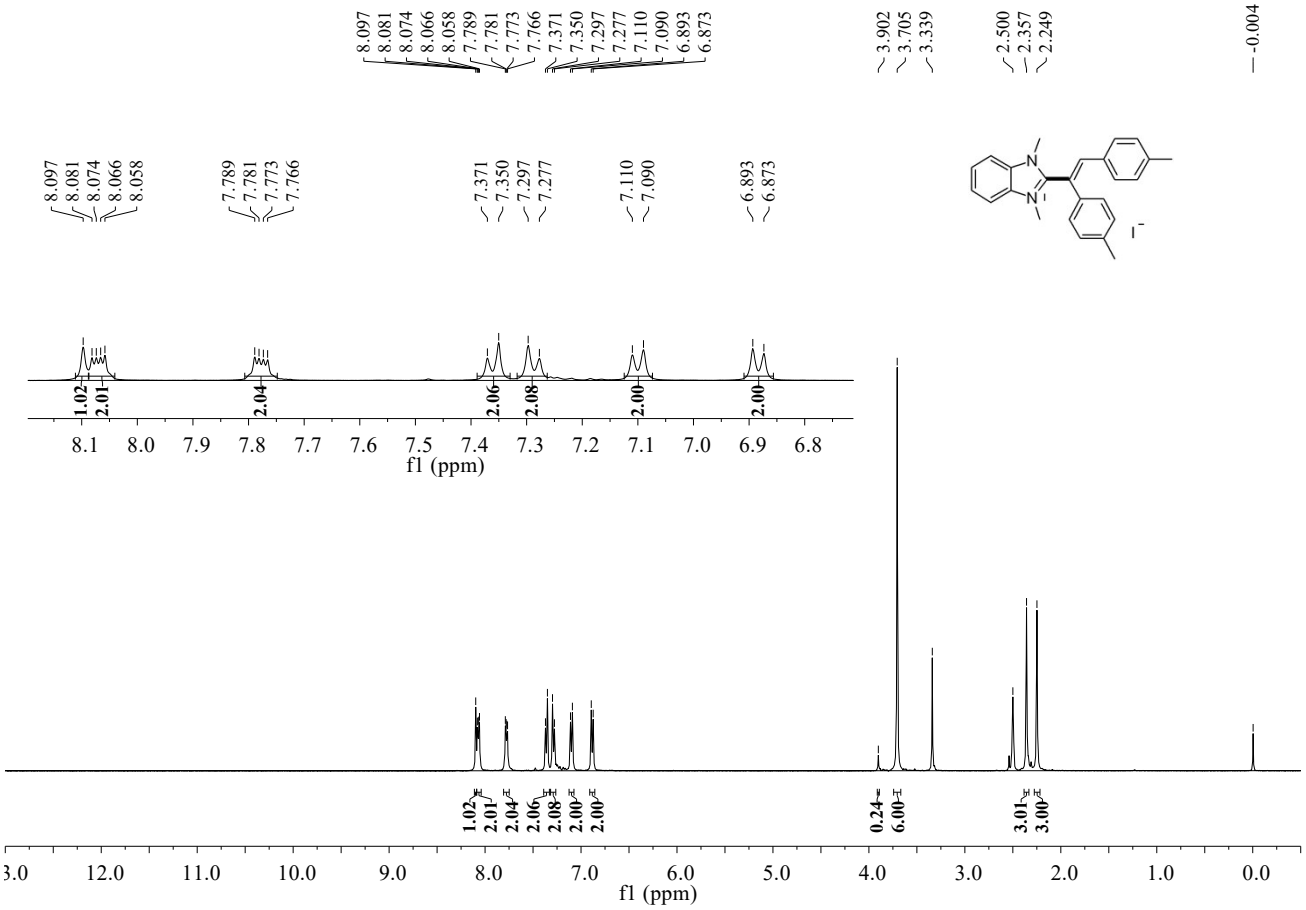
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3a



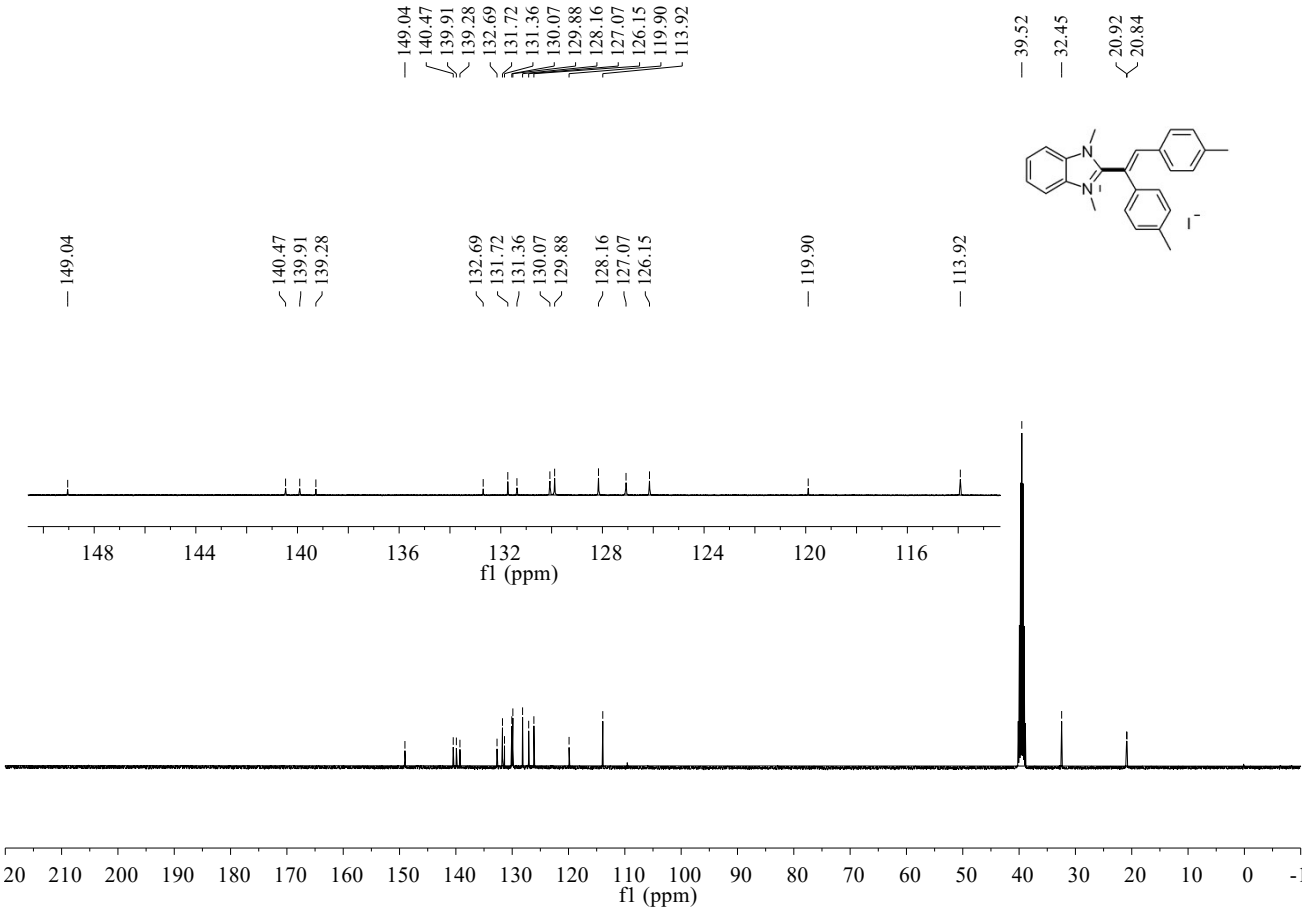
^{13}C NMR Spectra (100 MHz, $CDCl_3$) of 3a



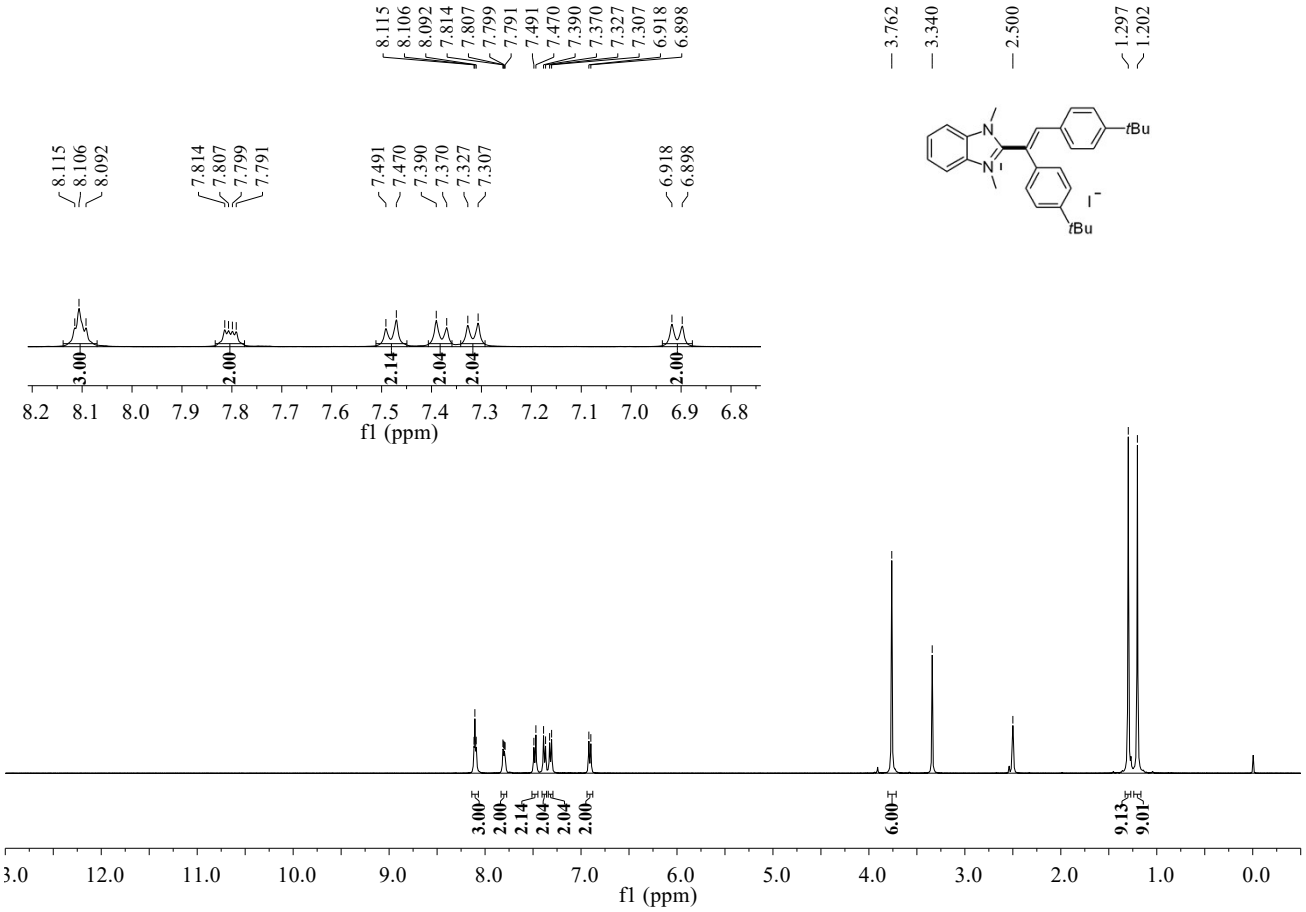
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3b



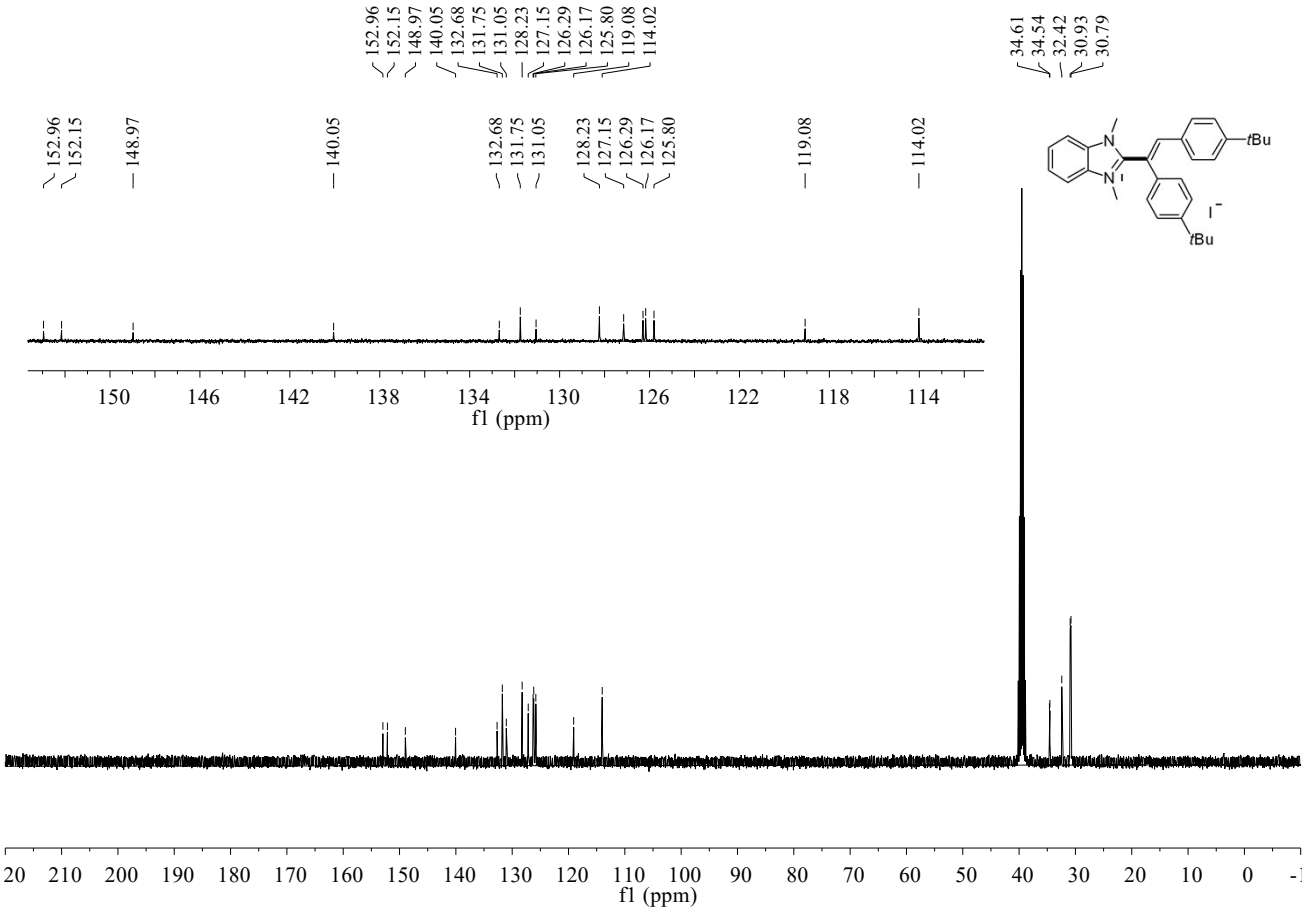
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3b



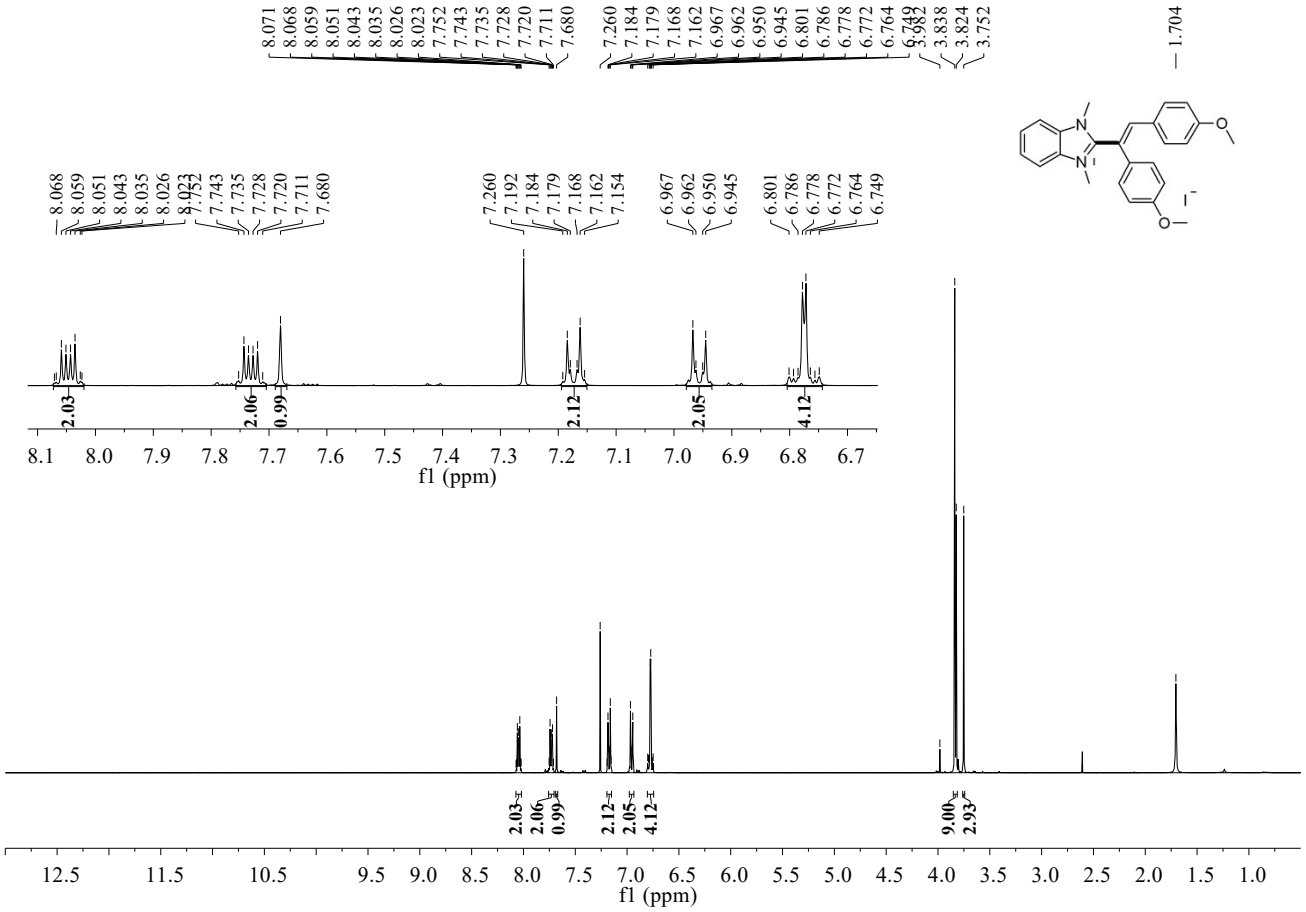
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3c



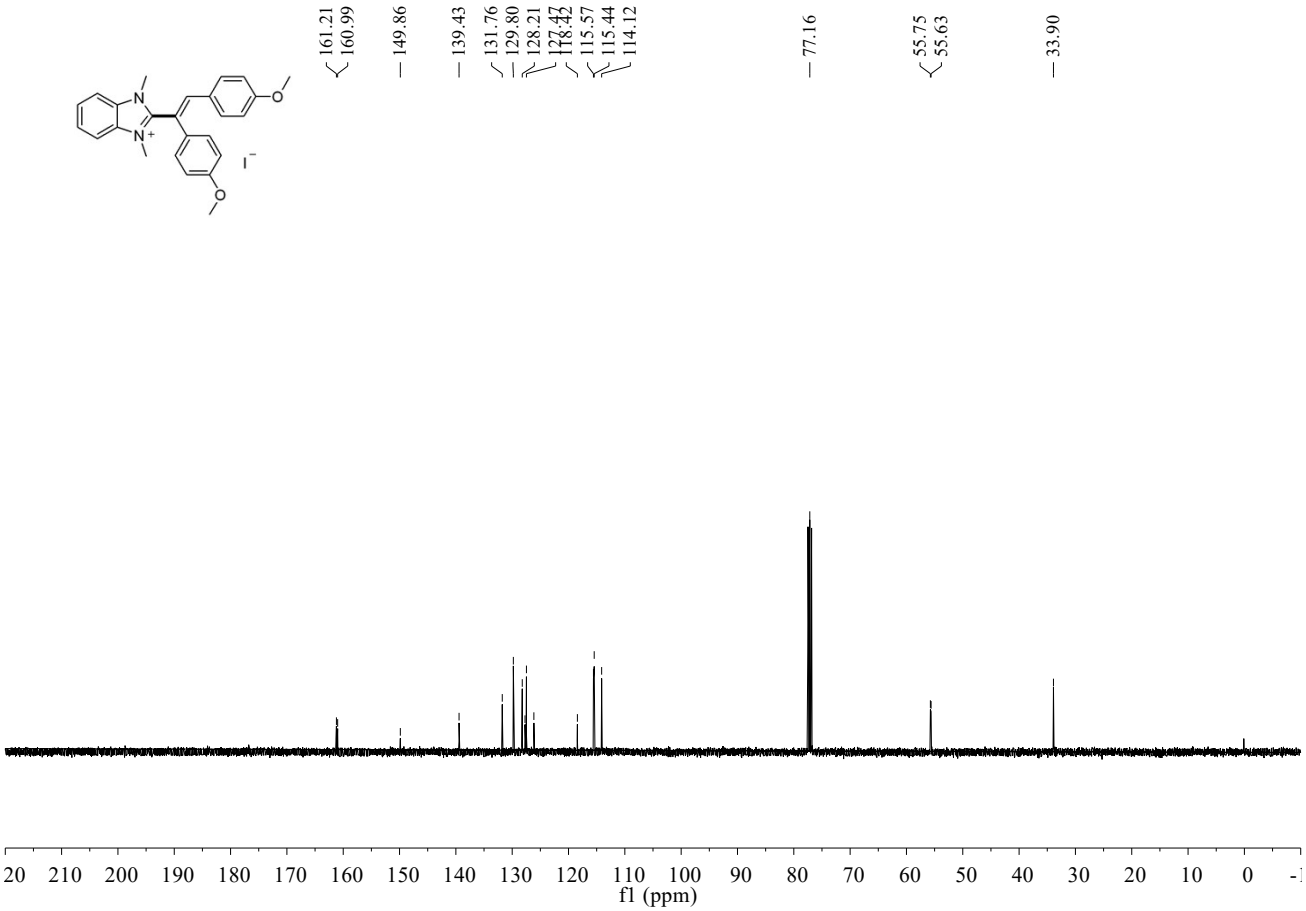
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3c



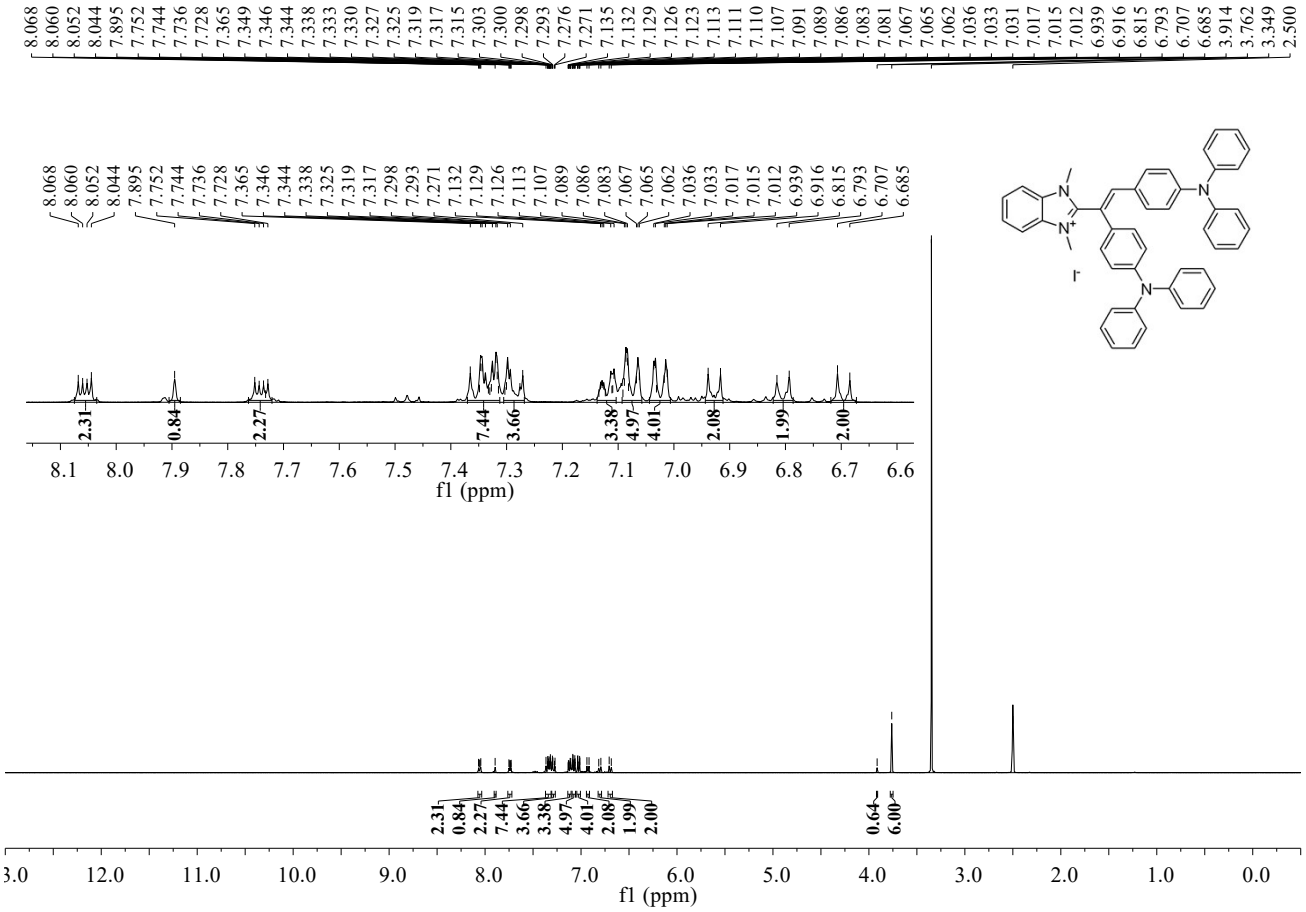
^{1}H NMR Spectra (400 MHz, $CDCl_3$) of 3d



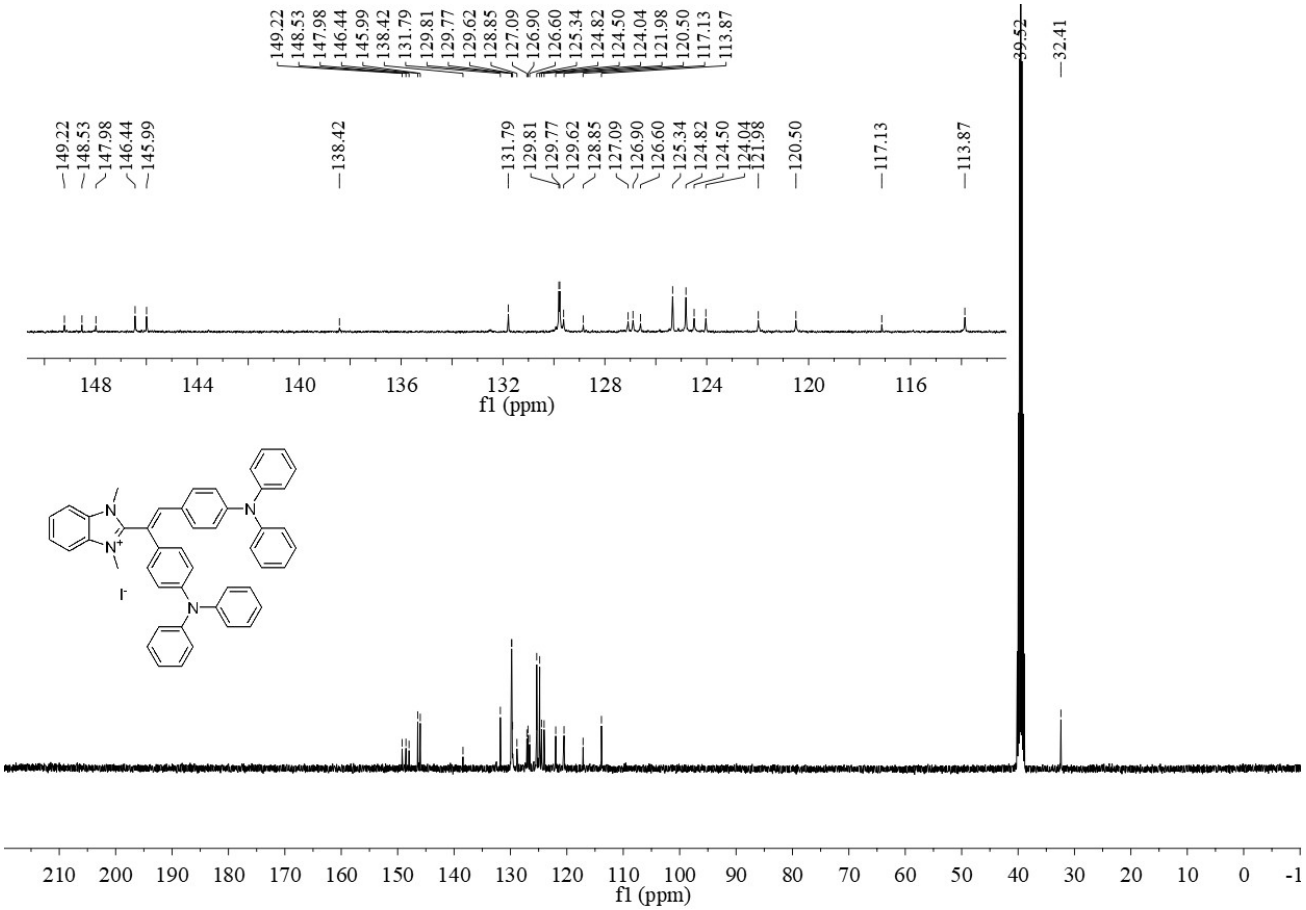
^{13}C NMR Spectra (100 MHz, $CDCl_3$) of 3d



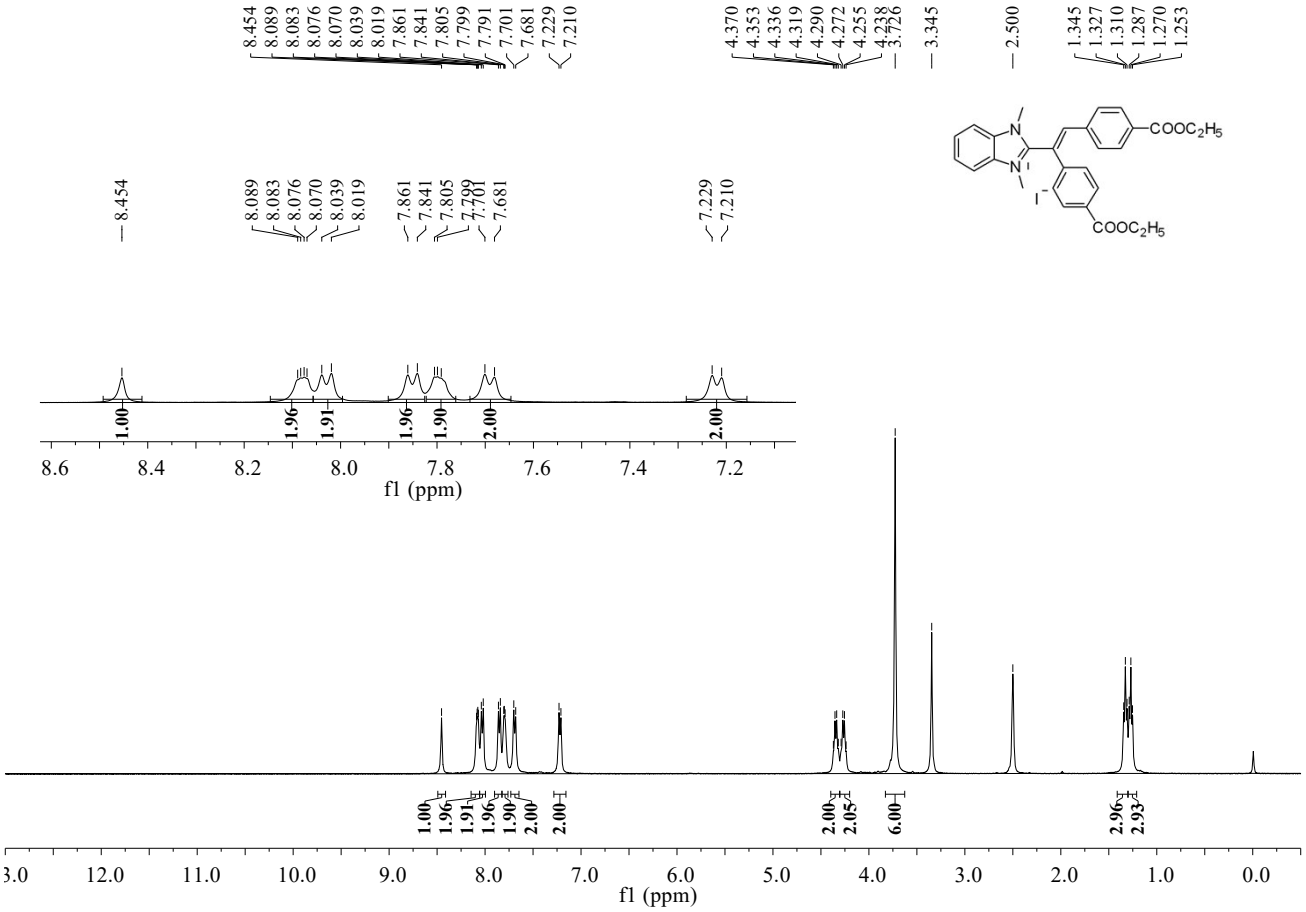
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3e



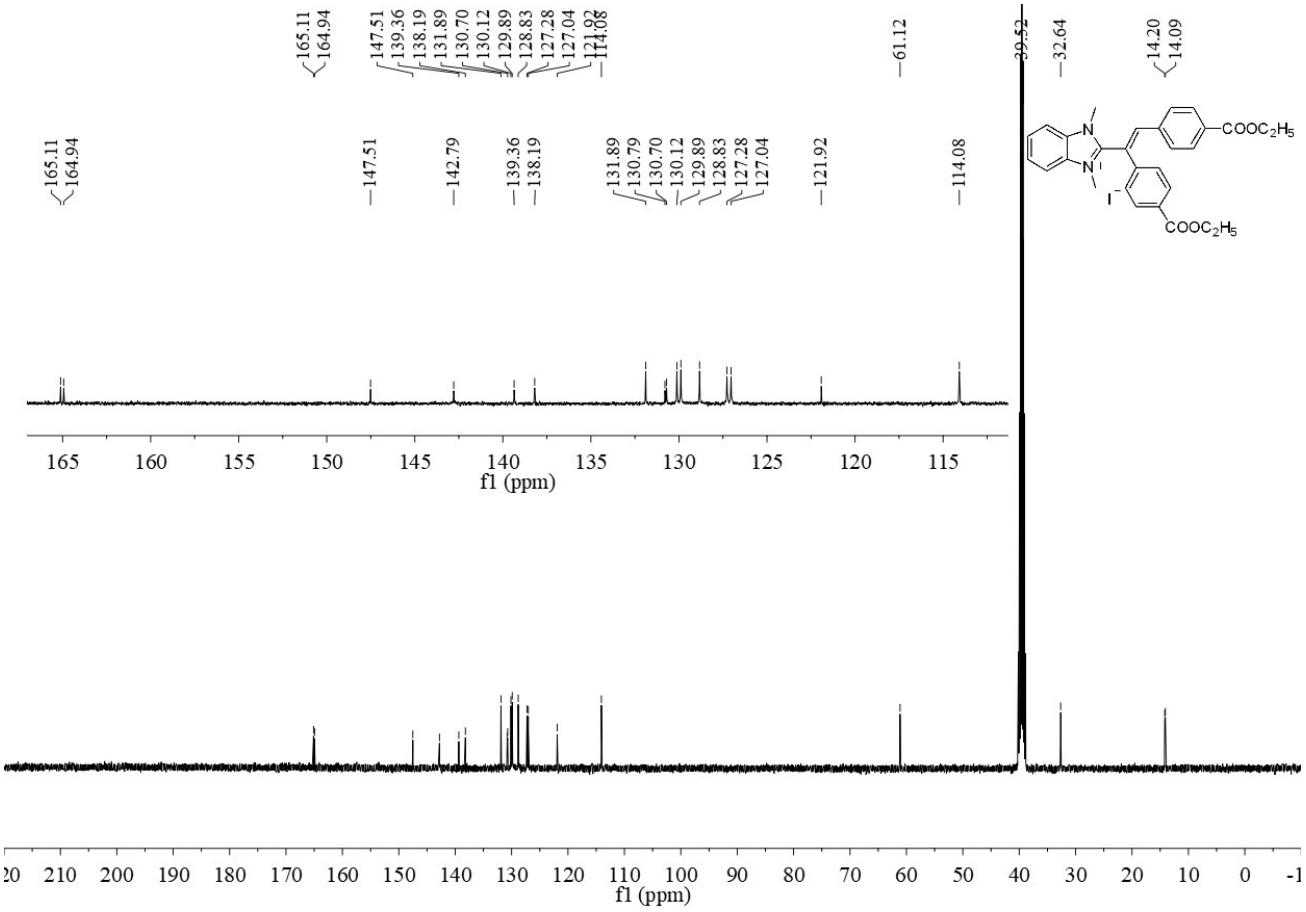
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3e



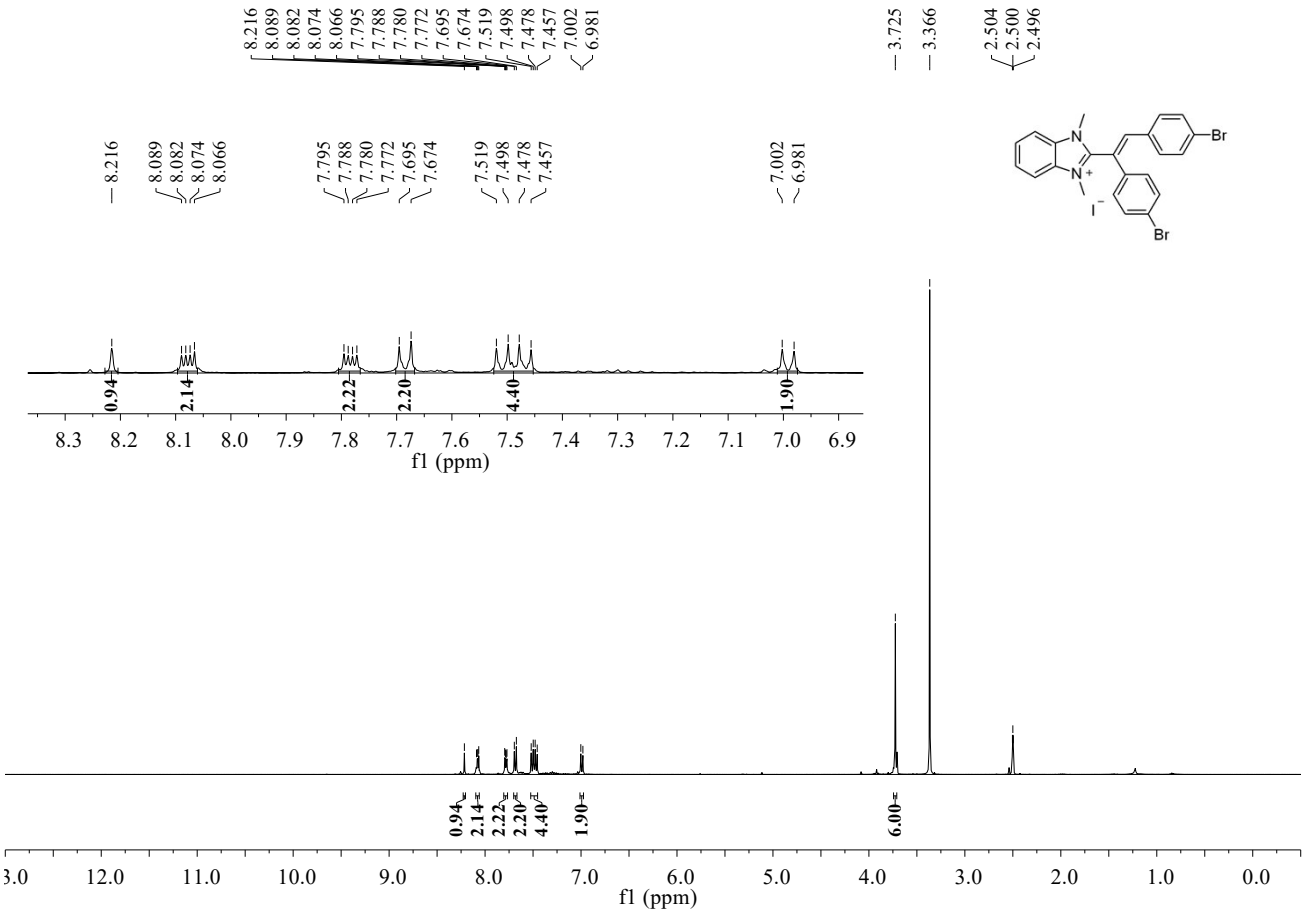
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3f



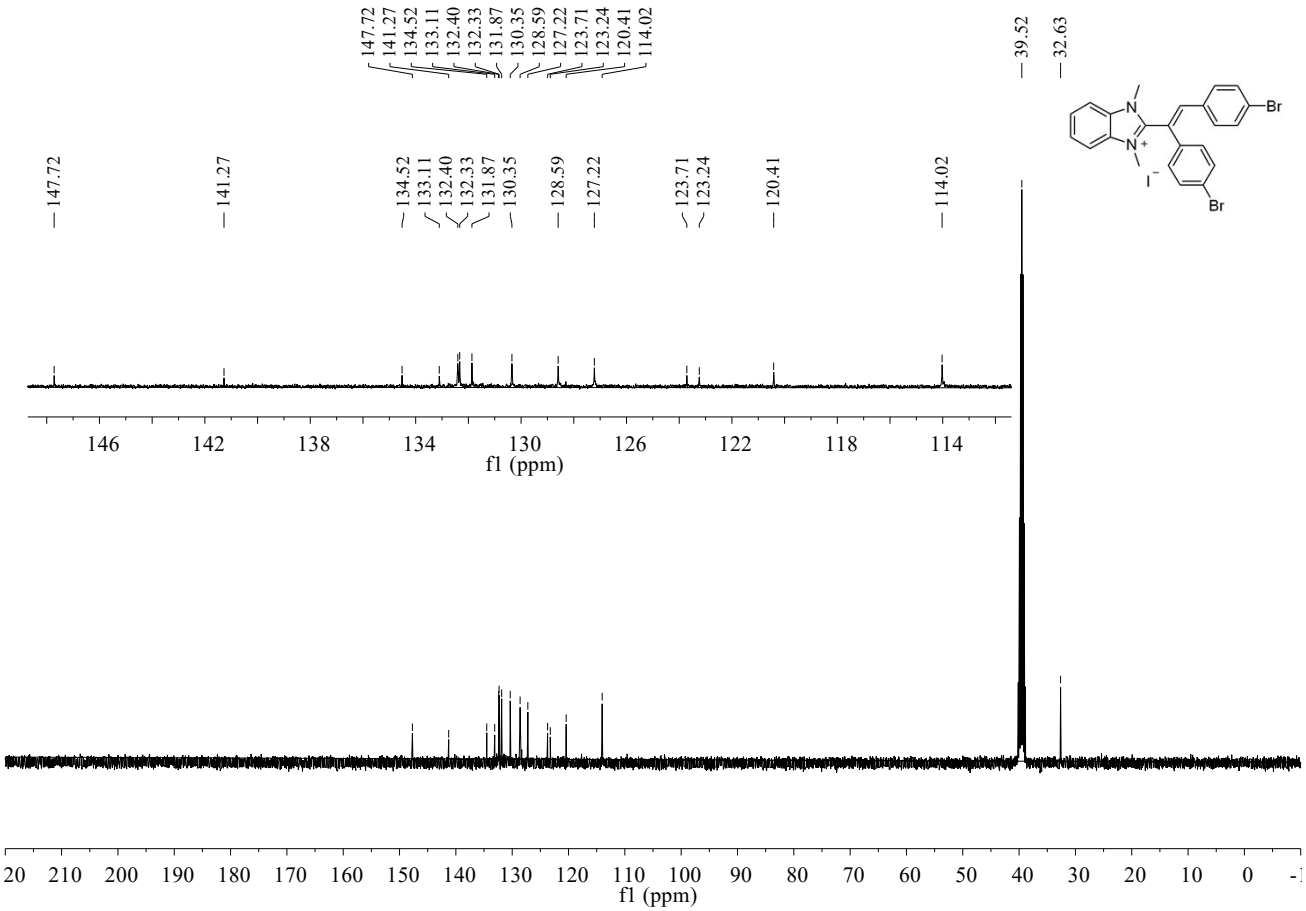
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3f



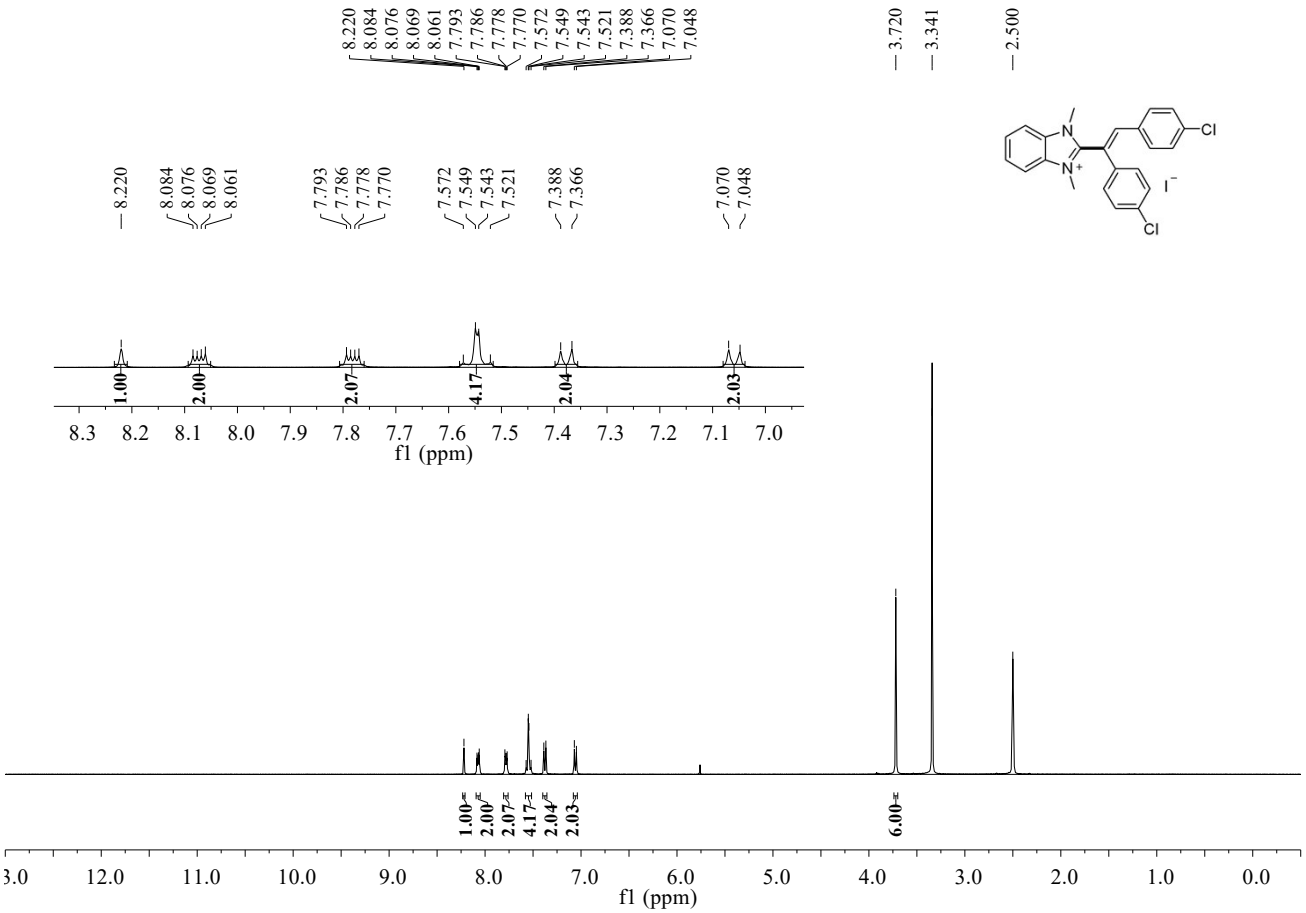
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3g



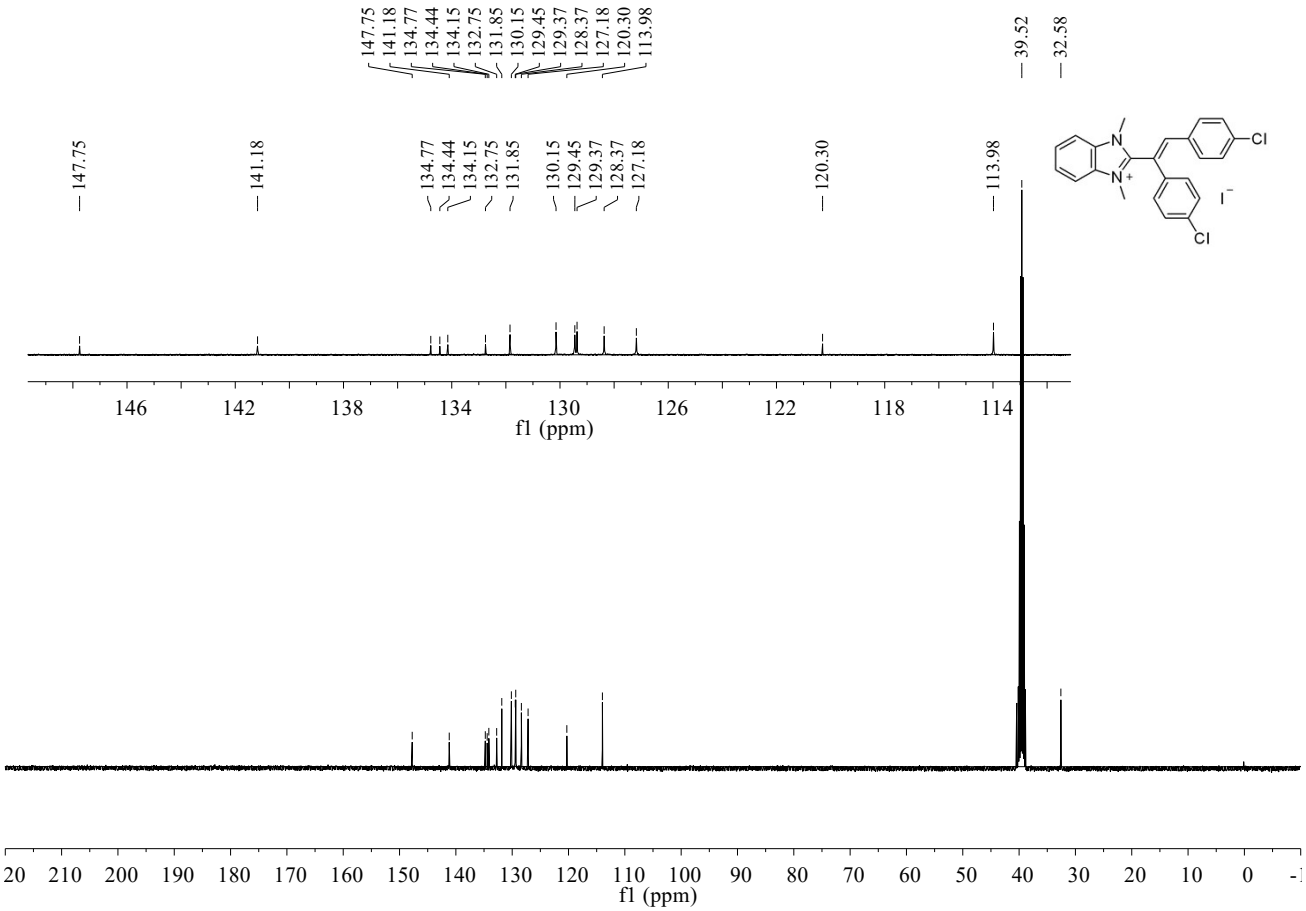
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3g



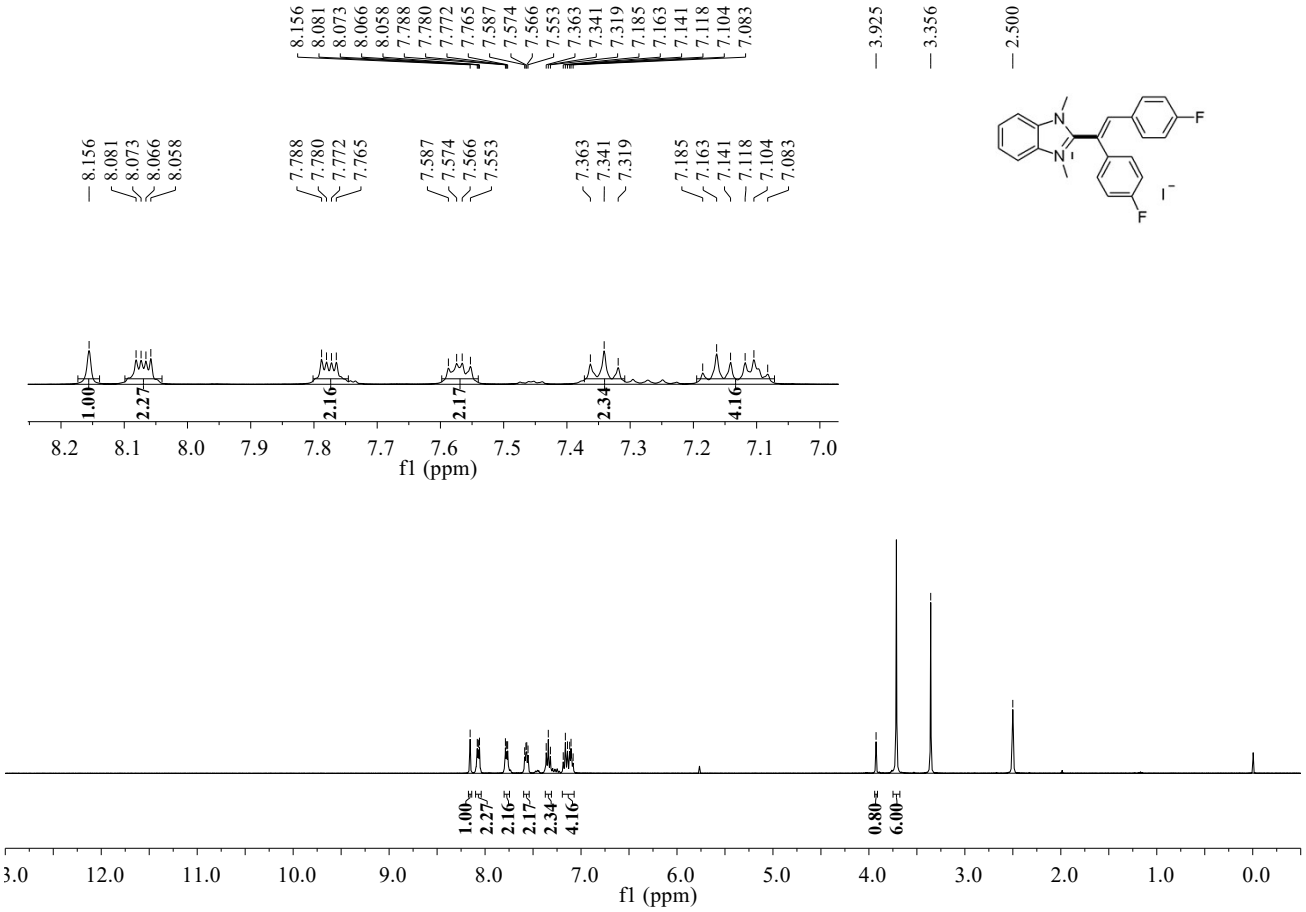
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3h



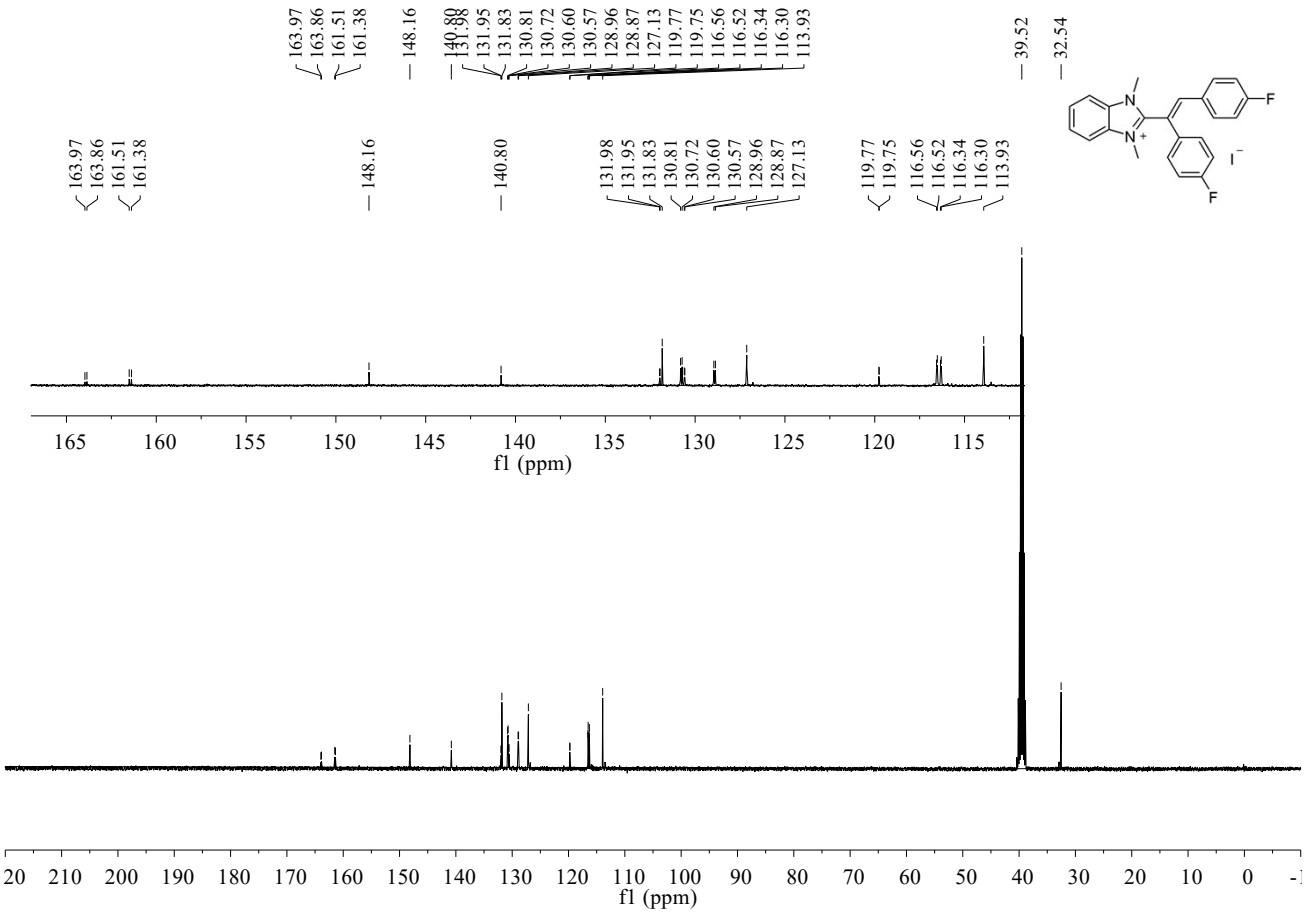
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3h



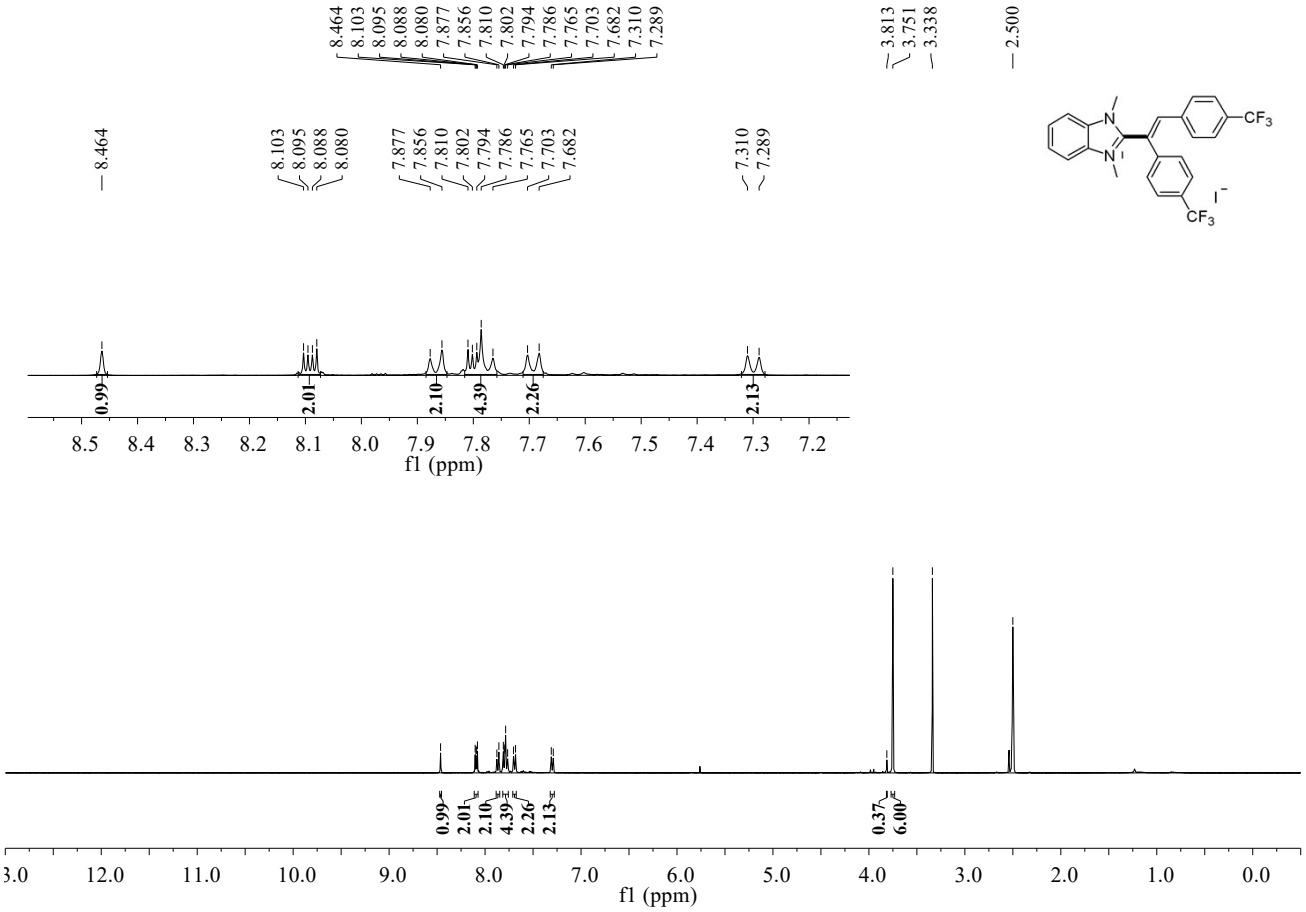
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3i



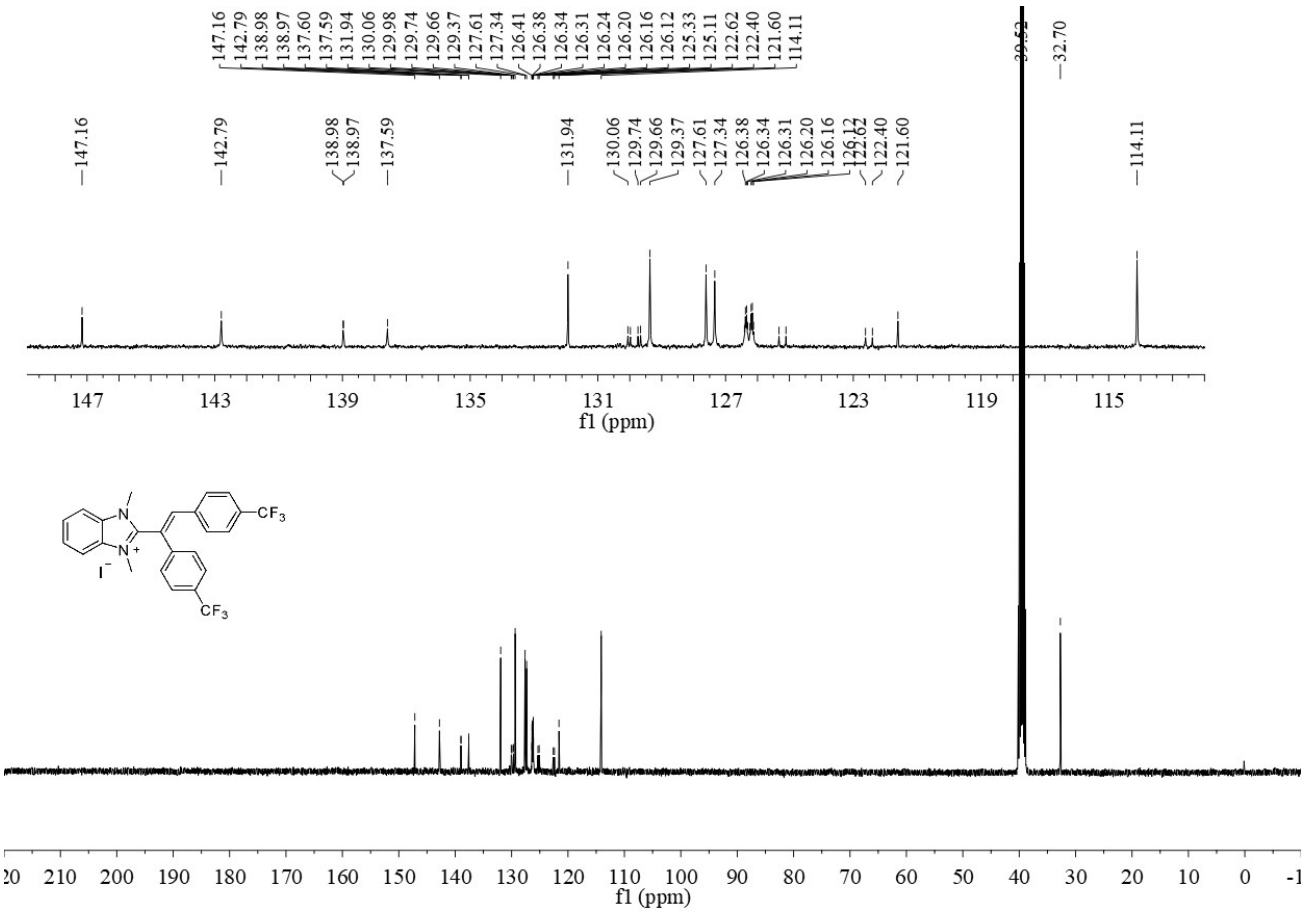
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3i



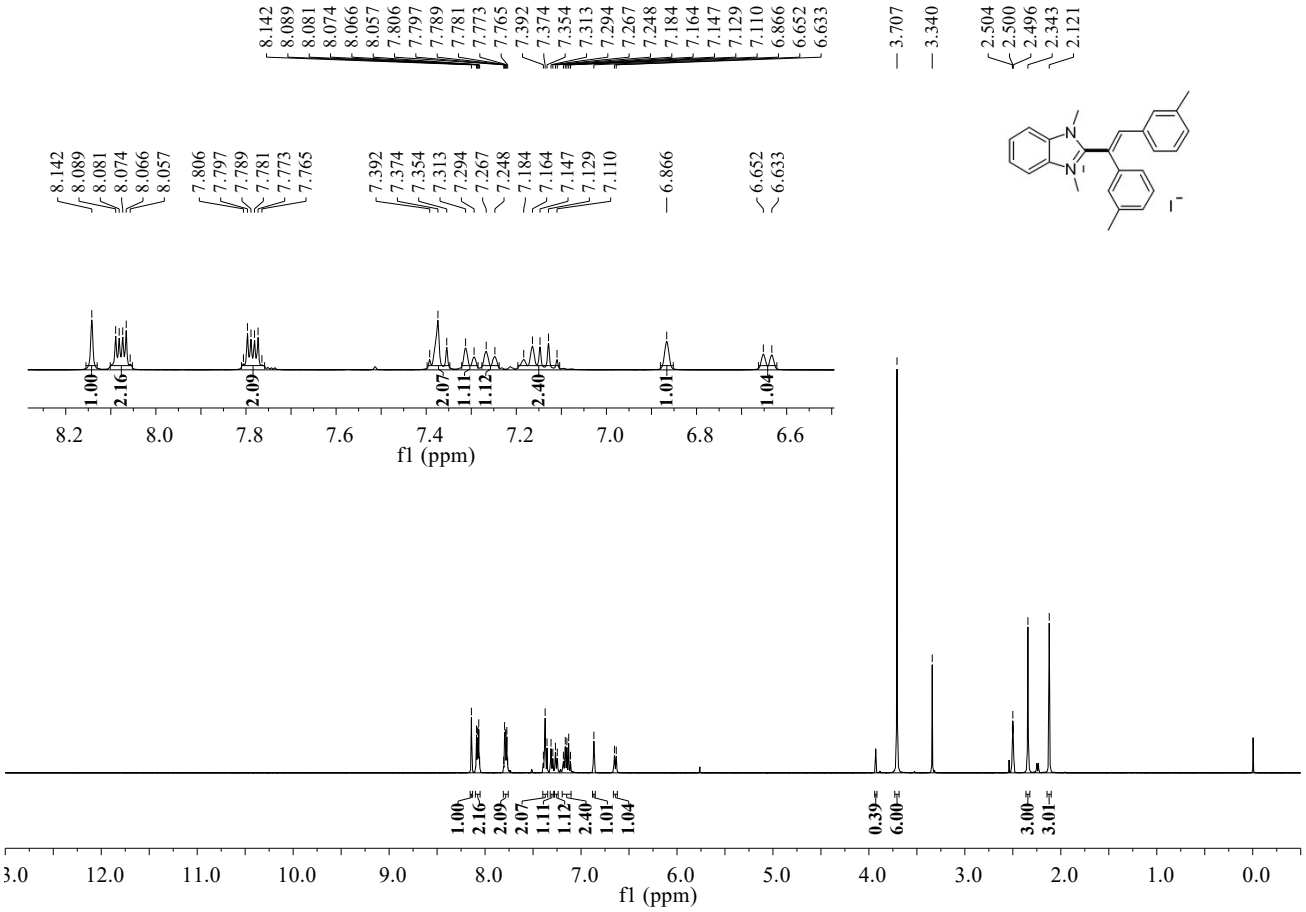
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3j



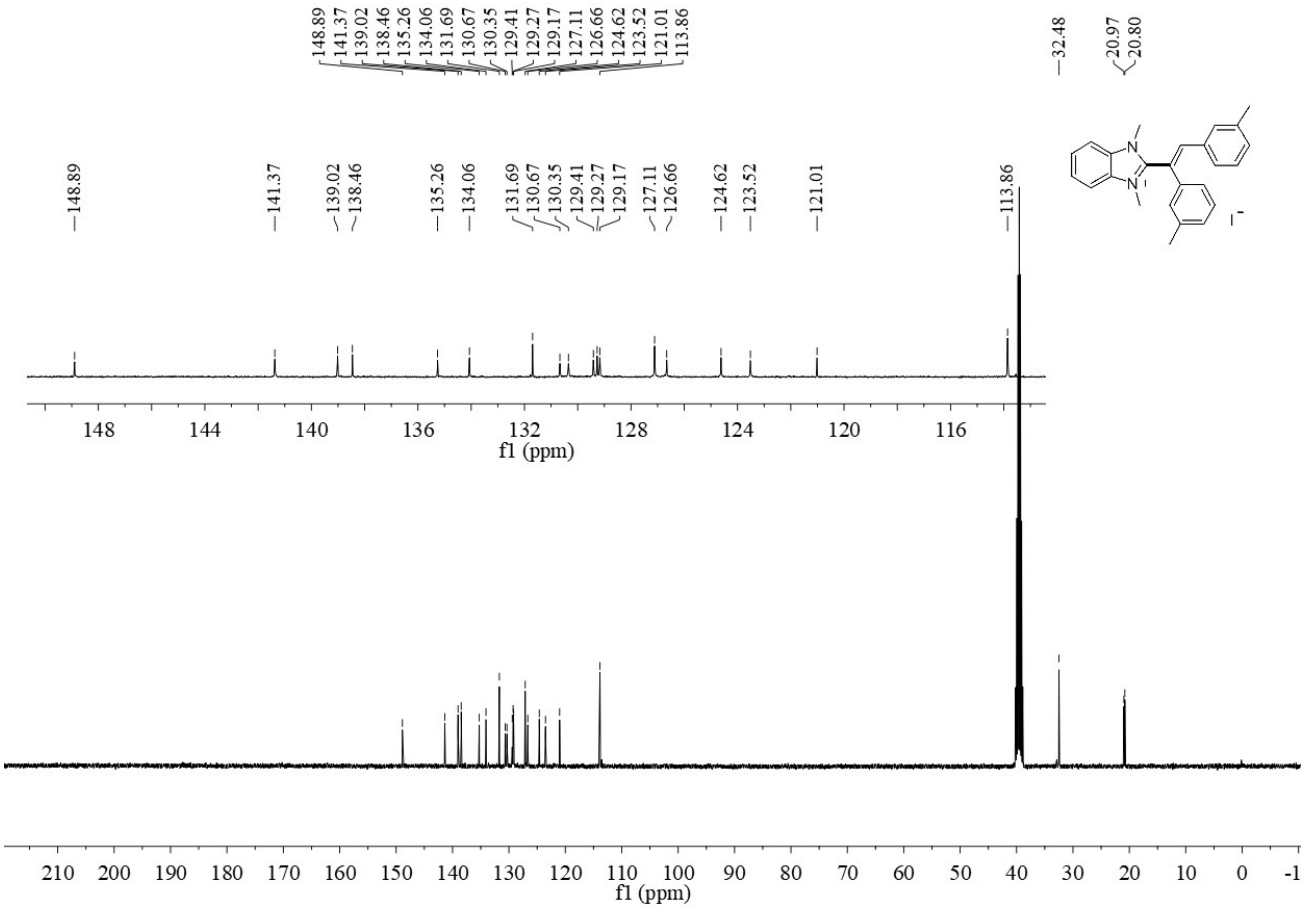
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3j



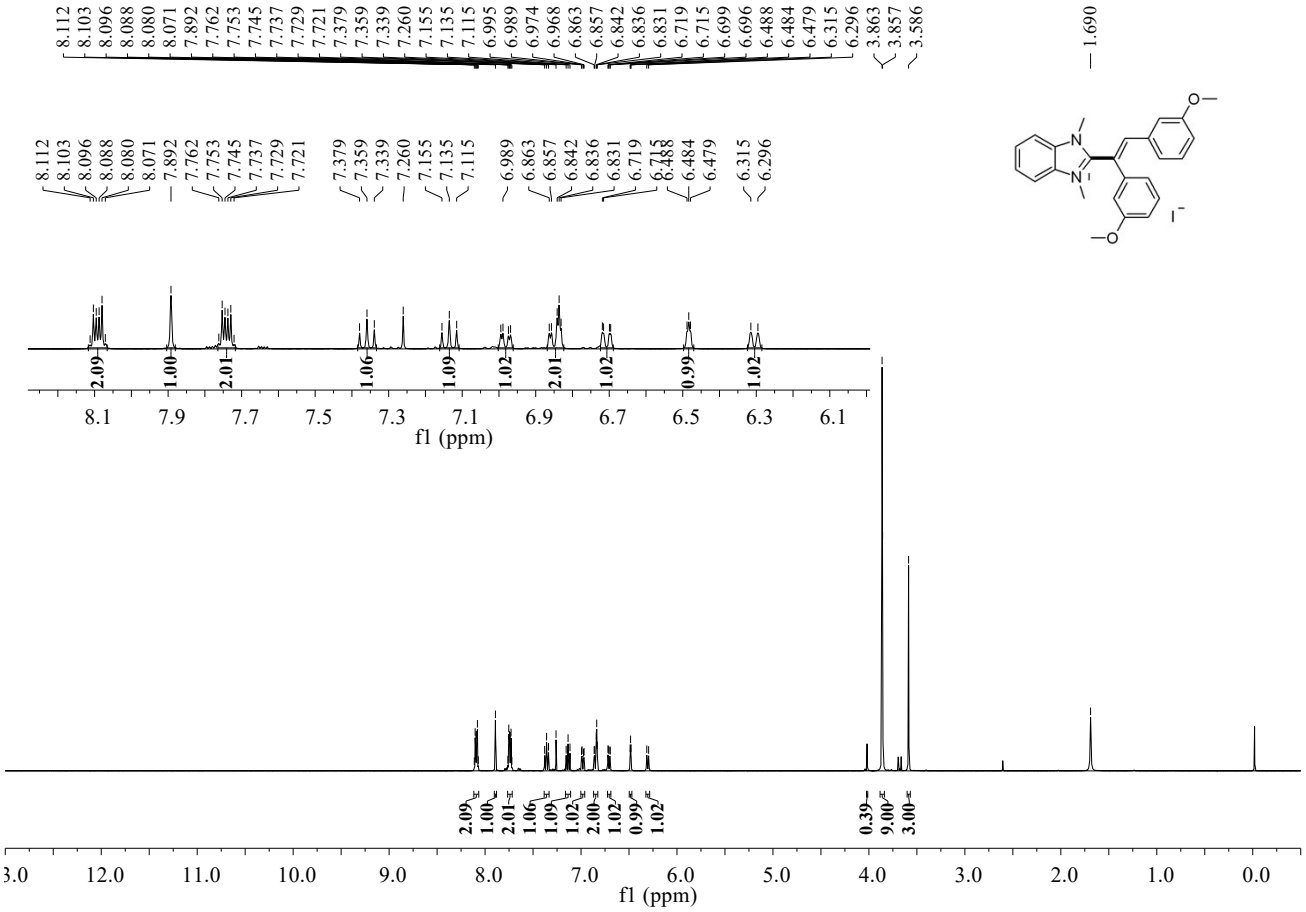
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3k



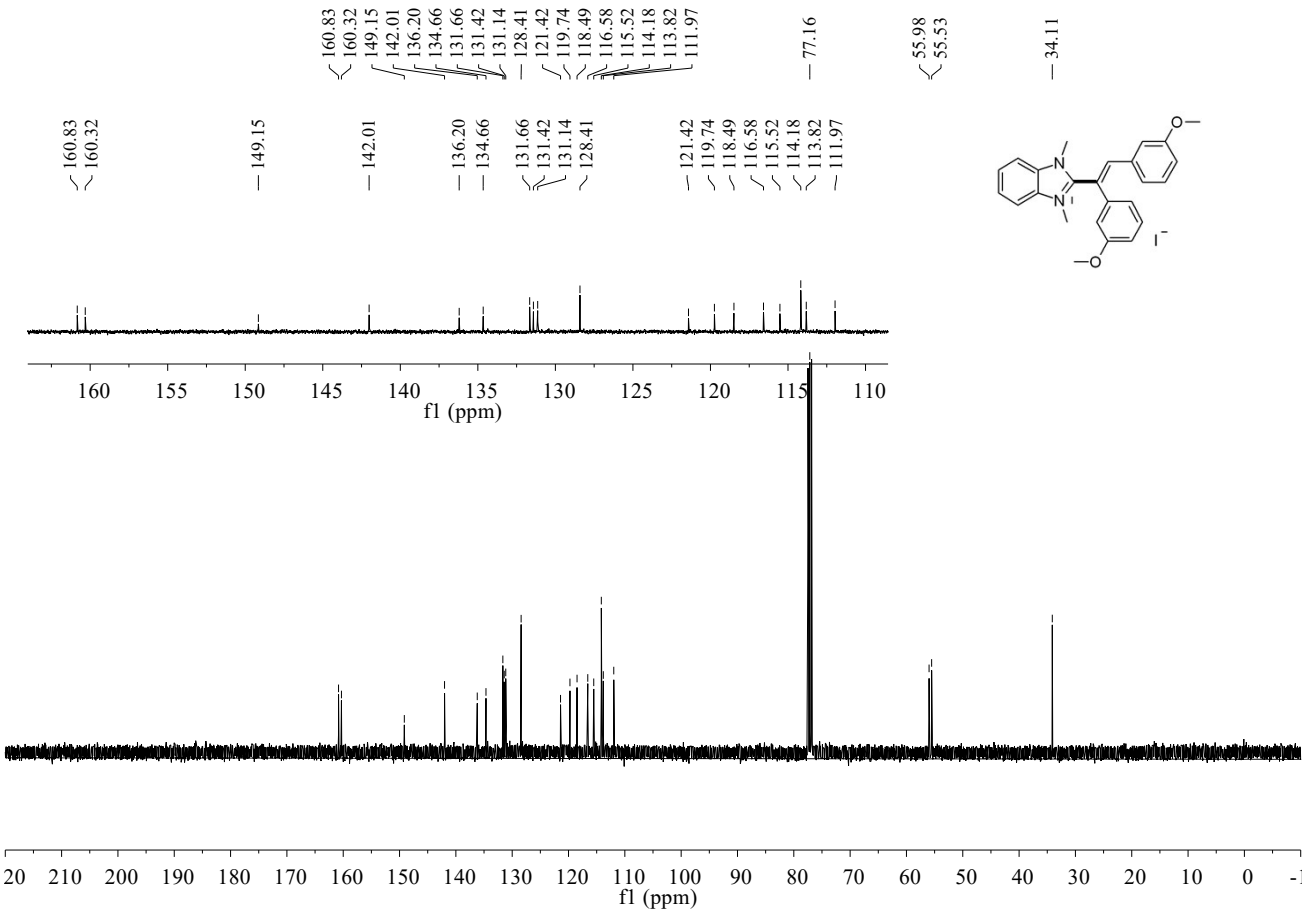
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3k



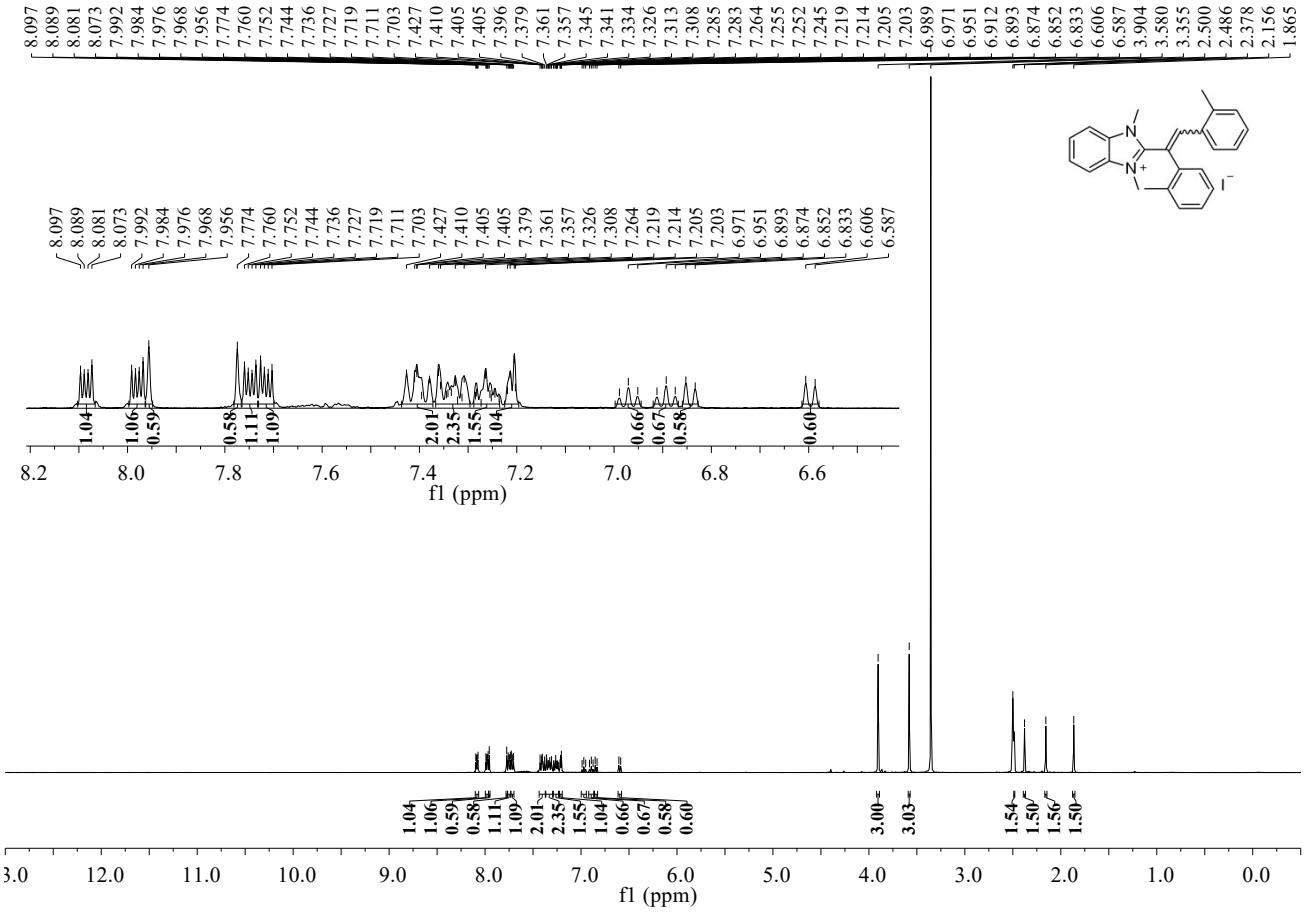
^{1}H NMR Spectra (400 MHz, $CDCl_3$) of 3l



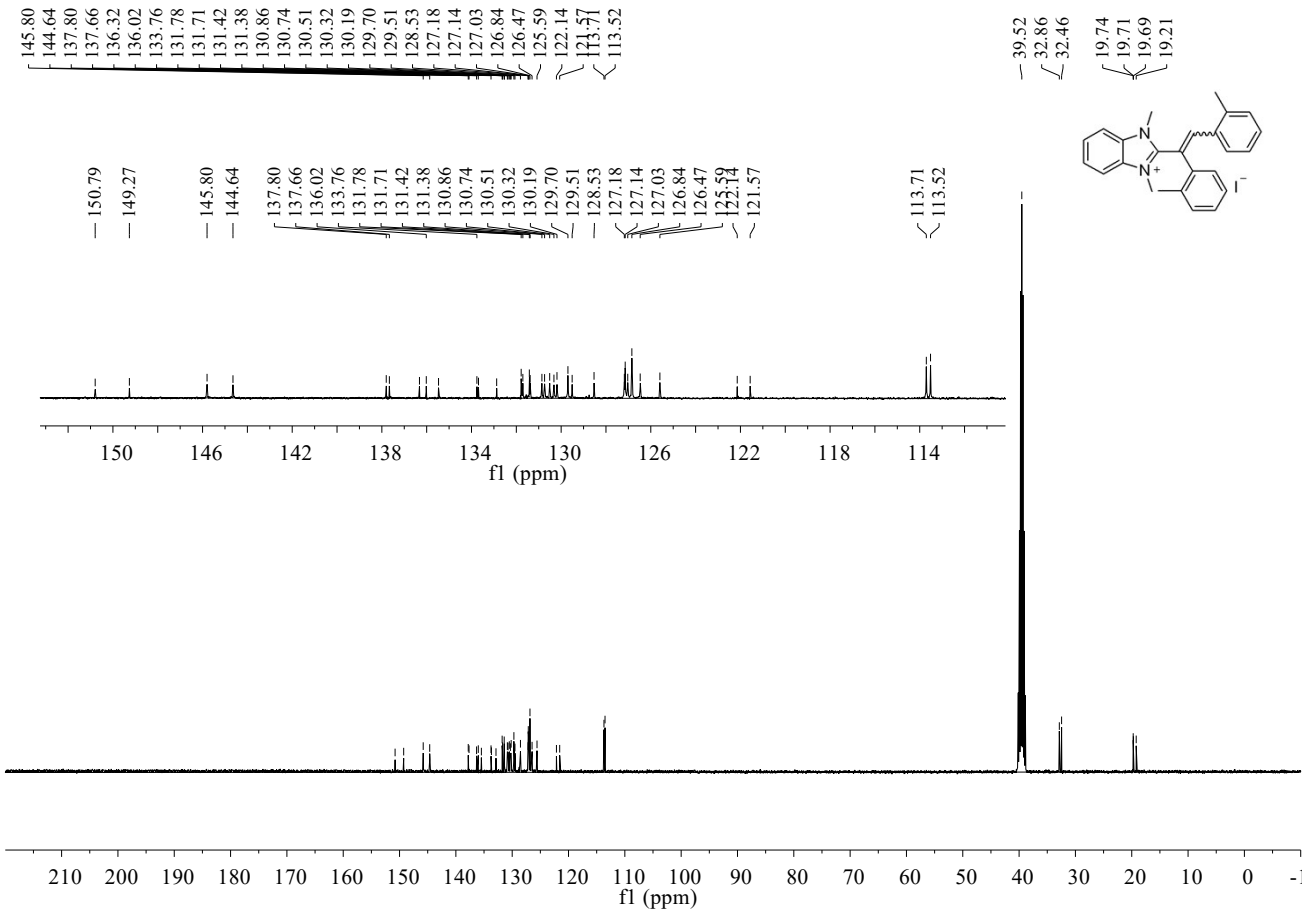
^{13}C NMR Spectra (100 MHz, $CDCl_3$) of 3l



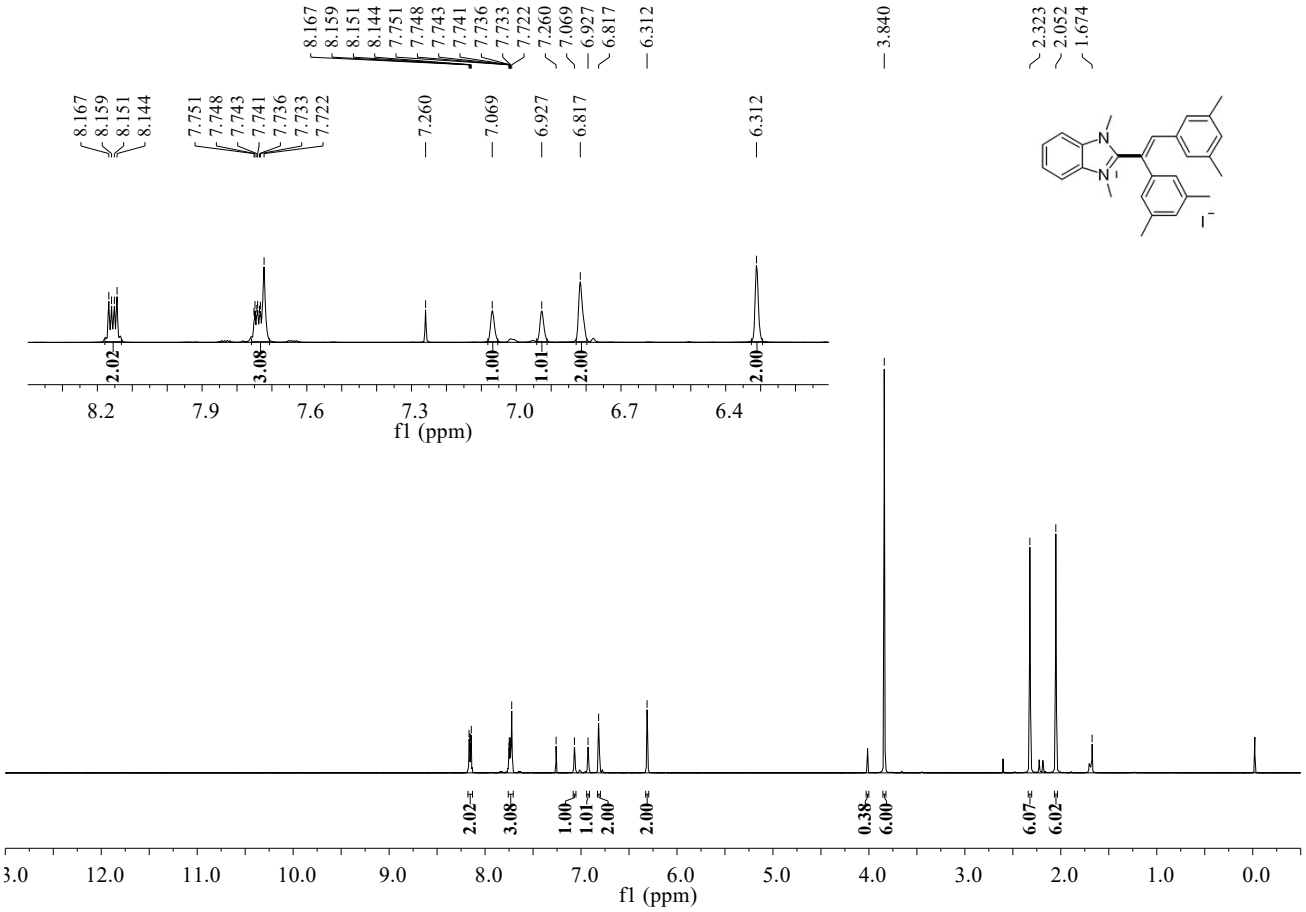
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3m



^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3m



^{1}H NMR Spectra (400 MHz, $CDCl_3$) of 3n



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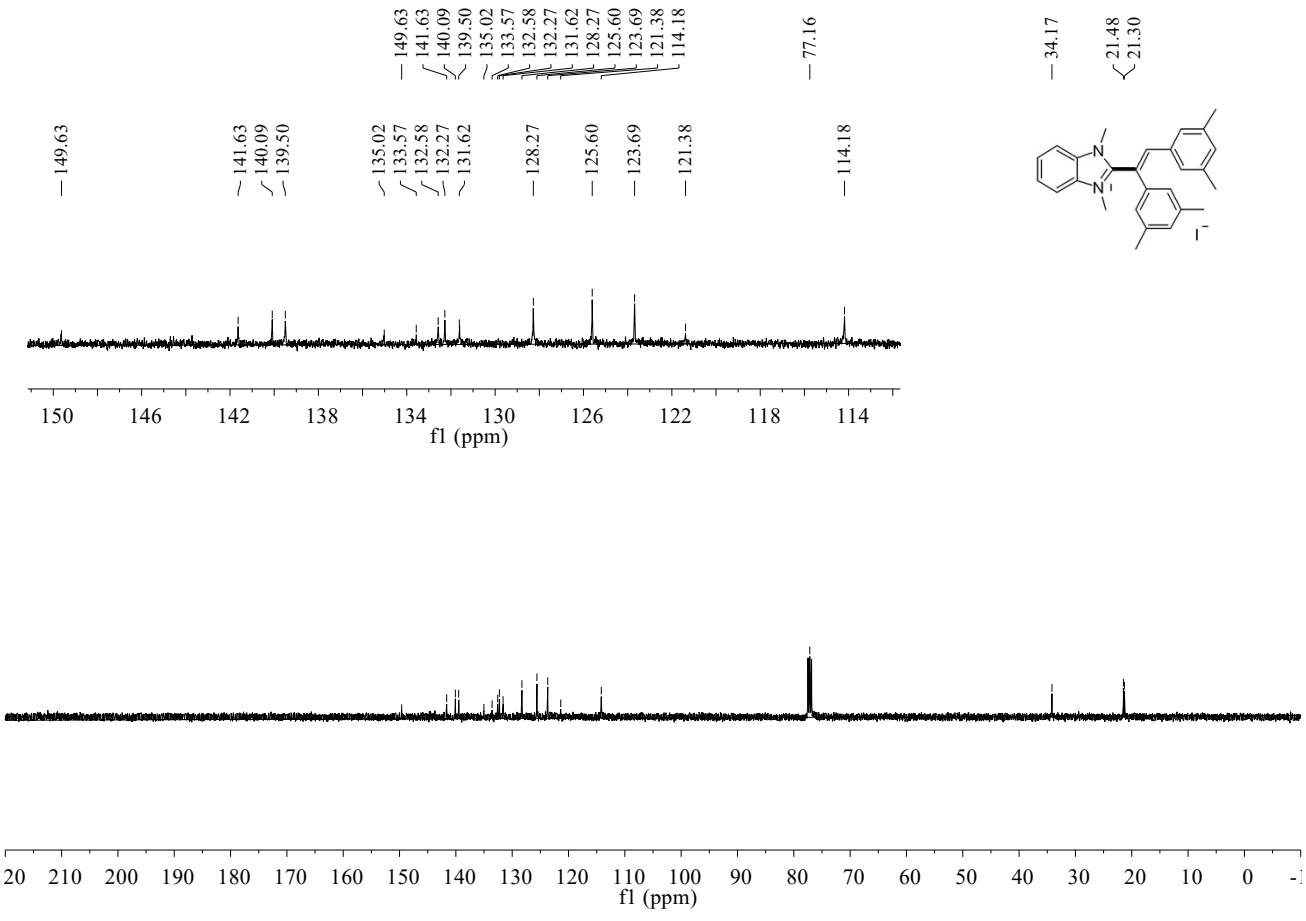
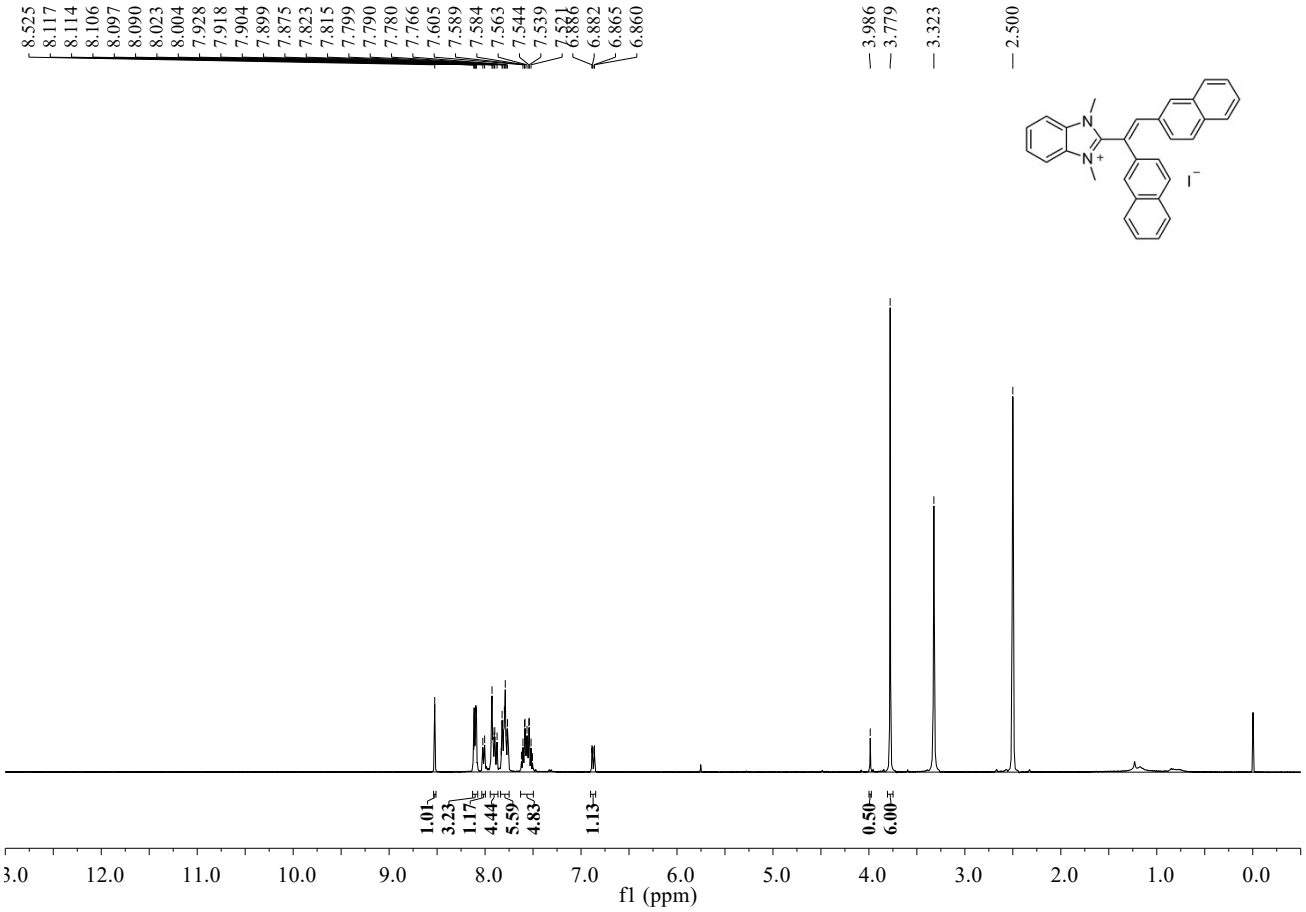
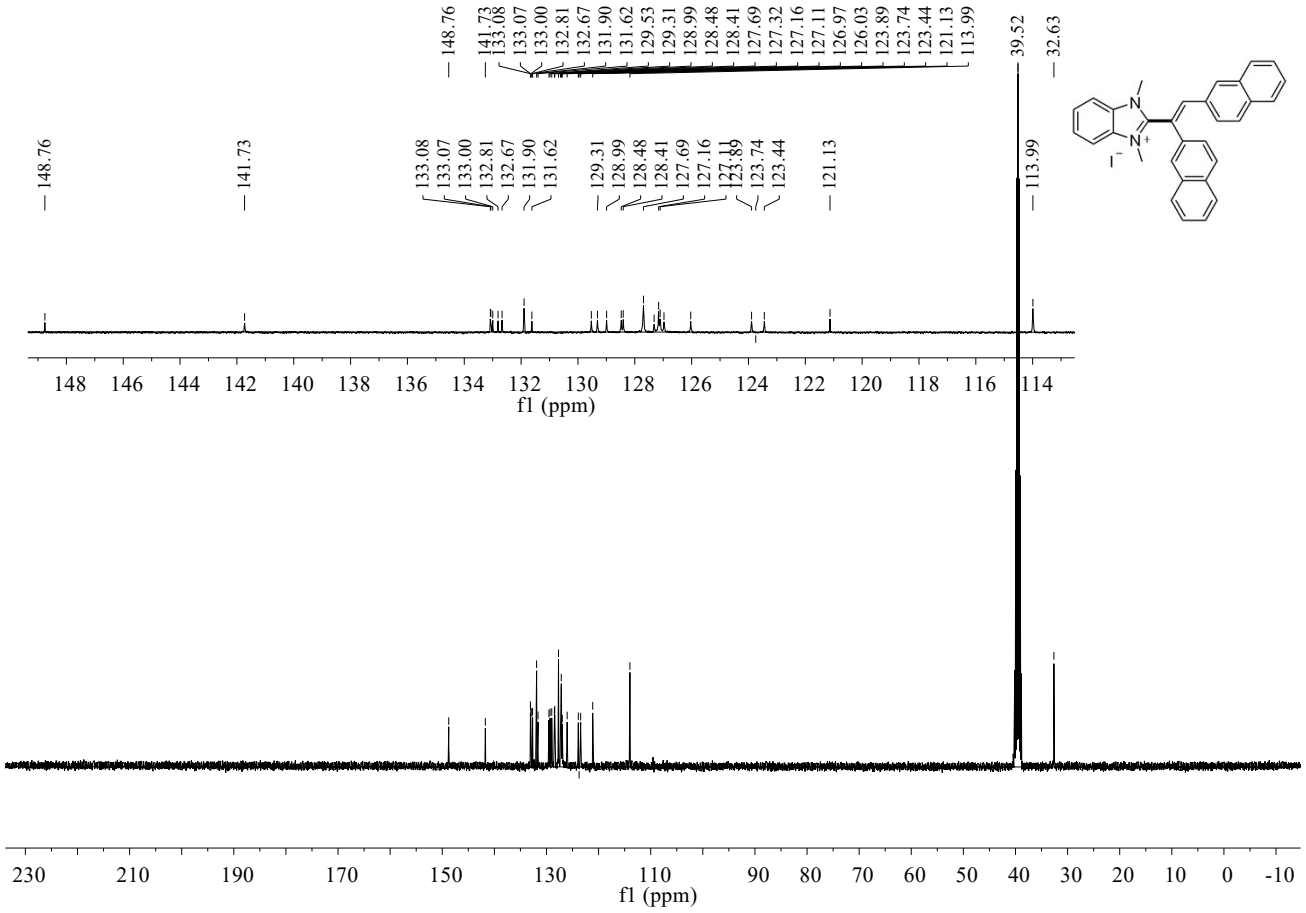


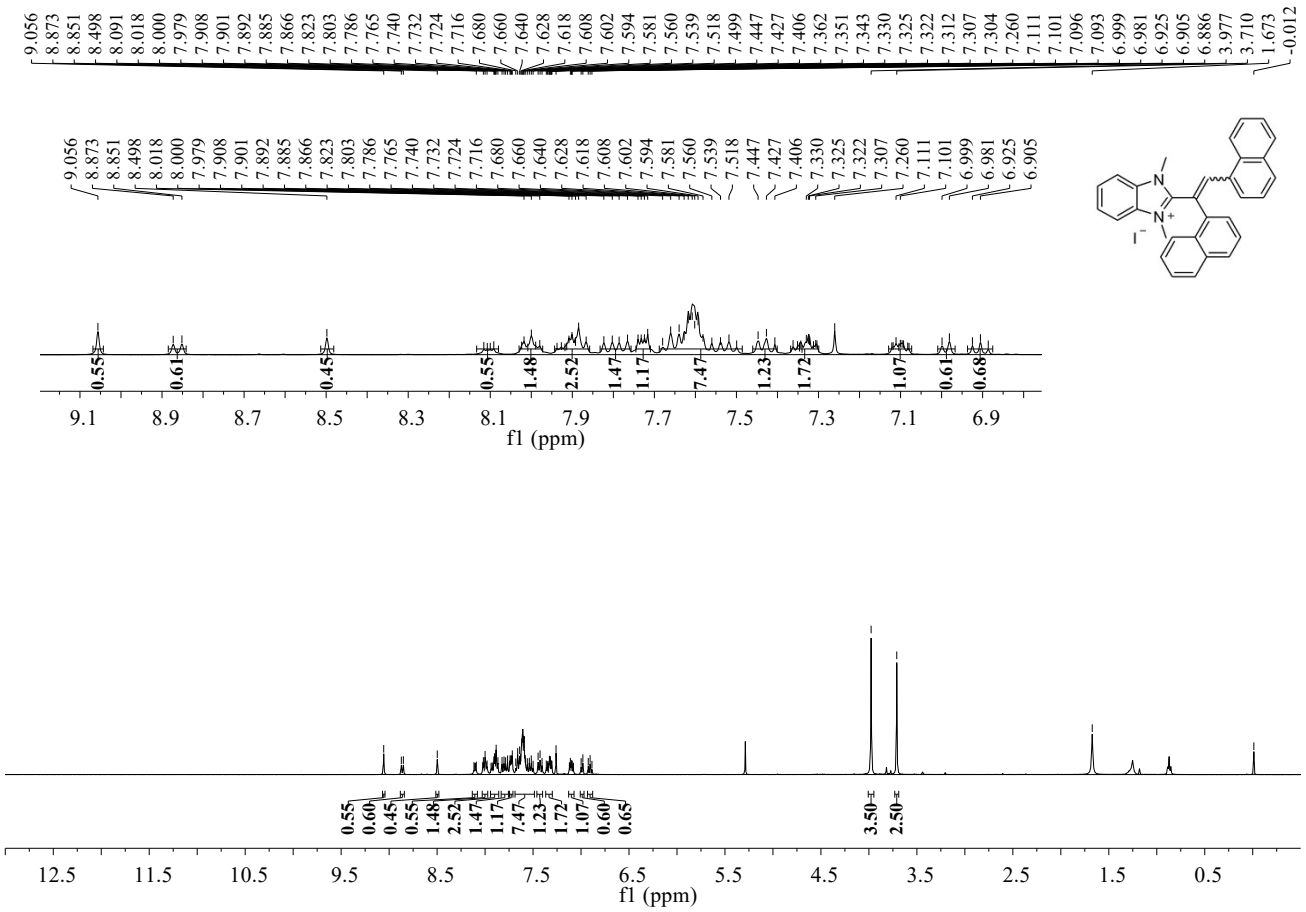
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3o



^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3o



^{1}H NMR Spectra (400 MHz, $CDCl_3$) of 3p



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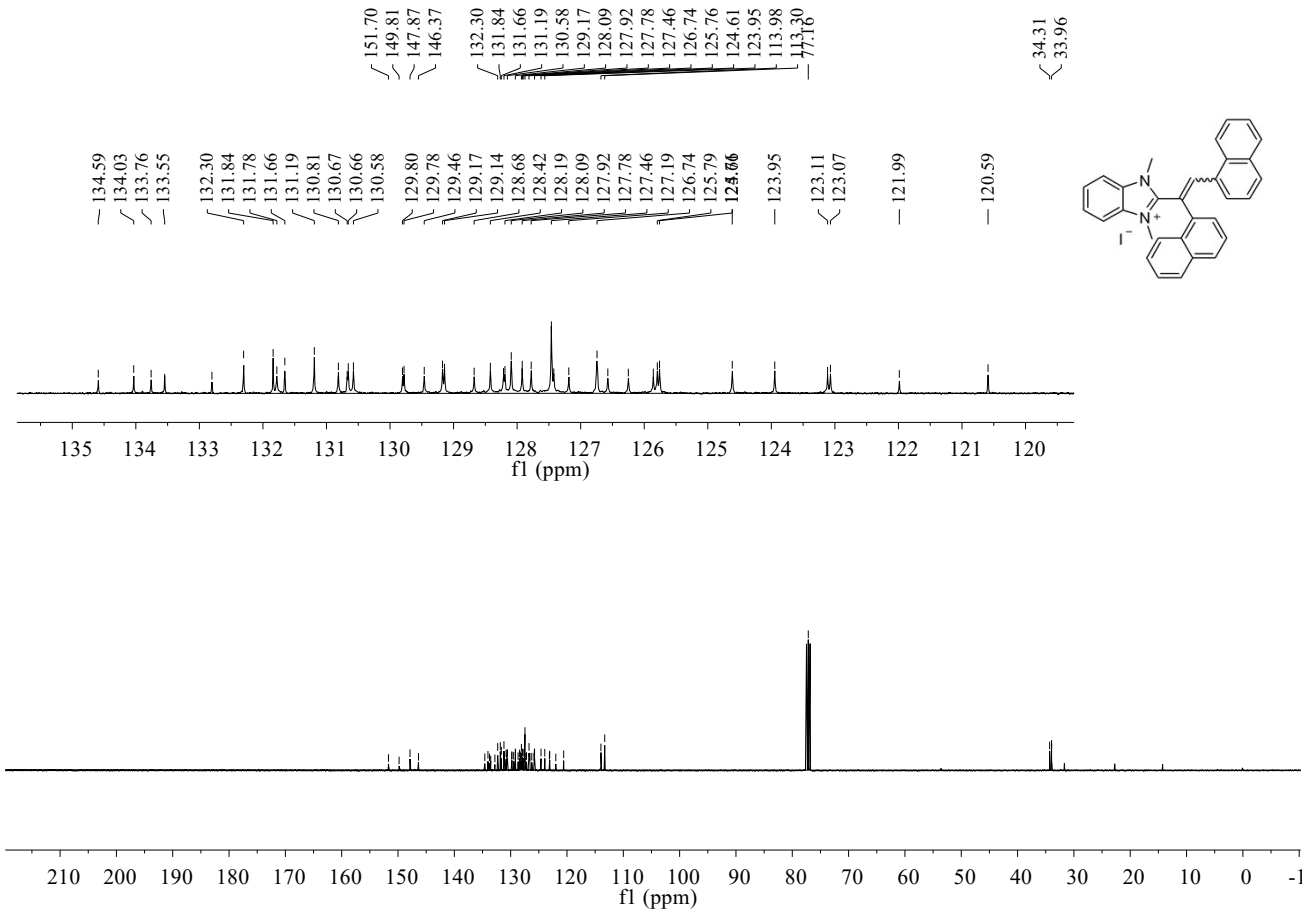
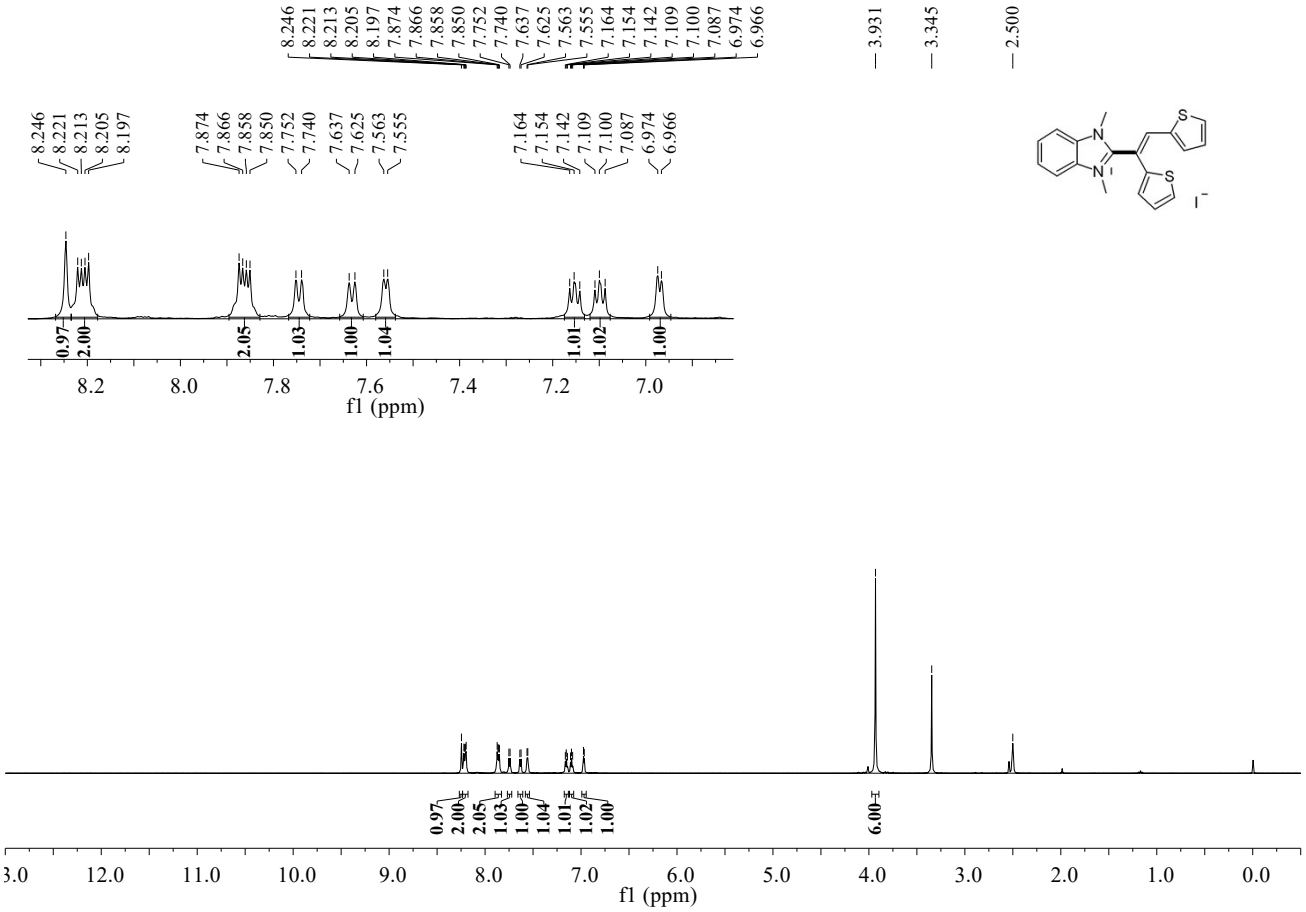
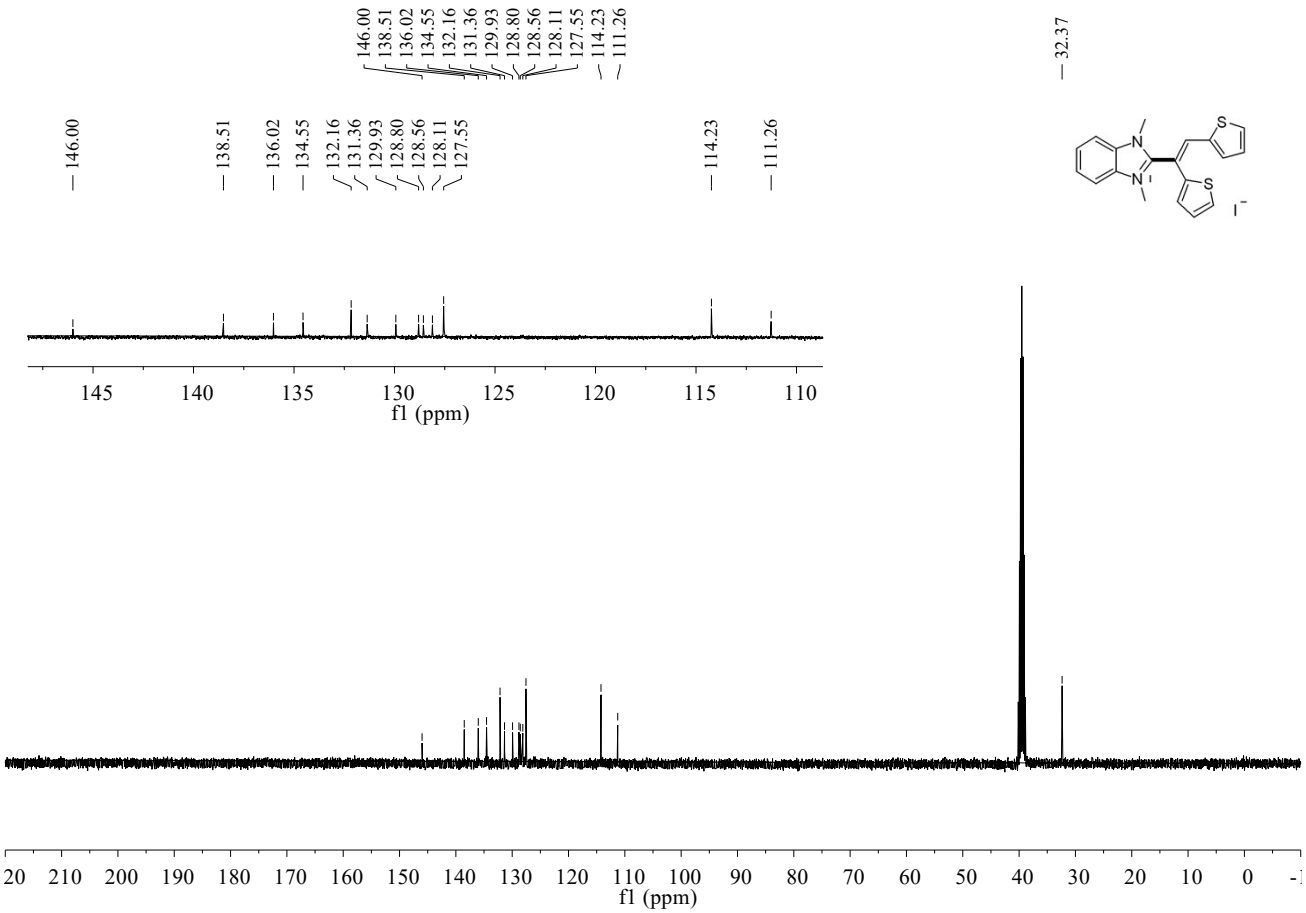


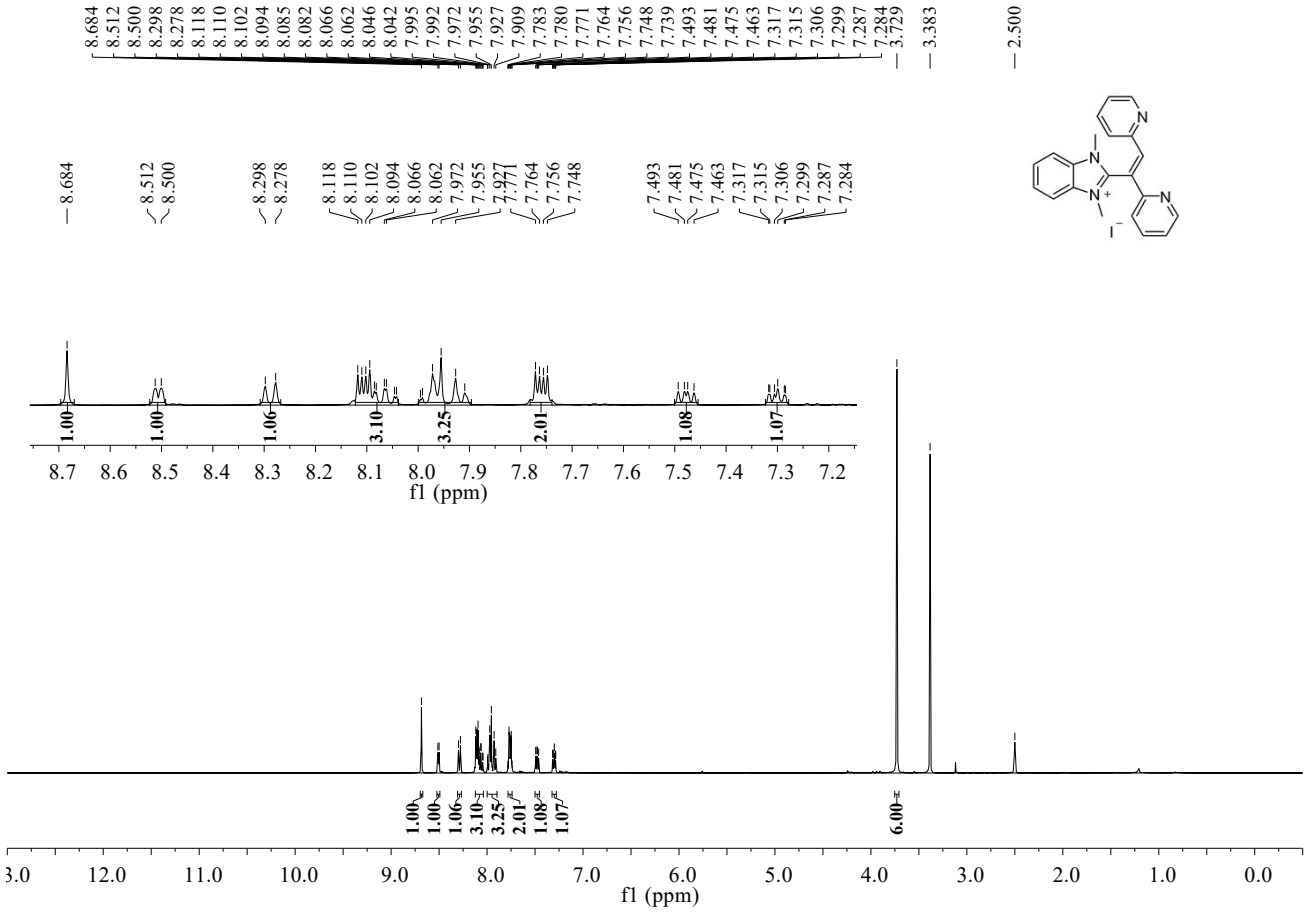
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3q



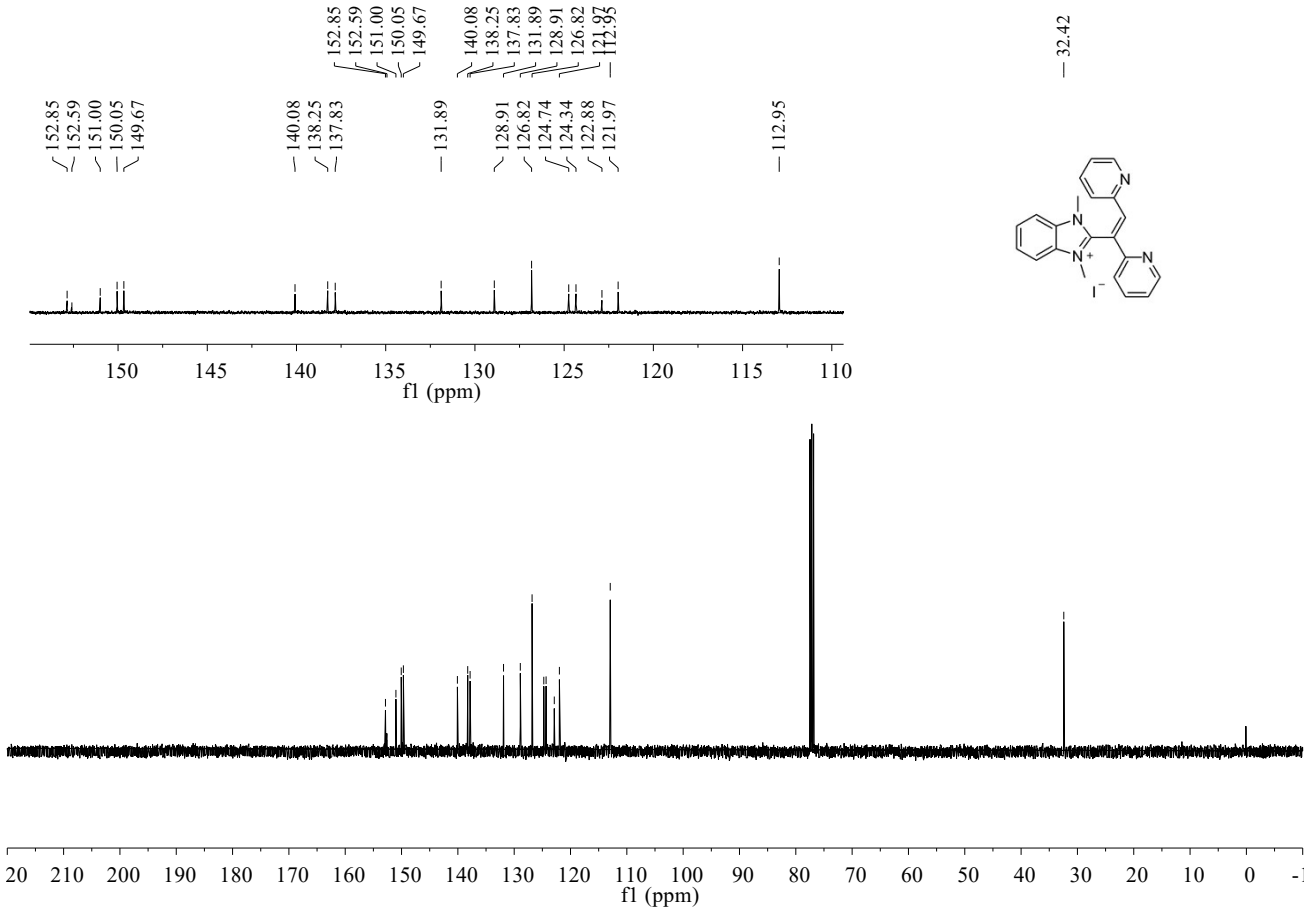
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 3q



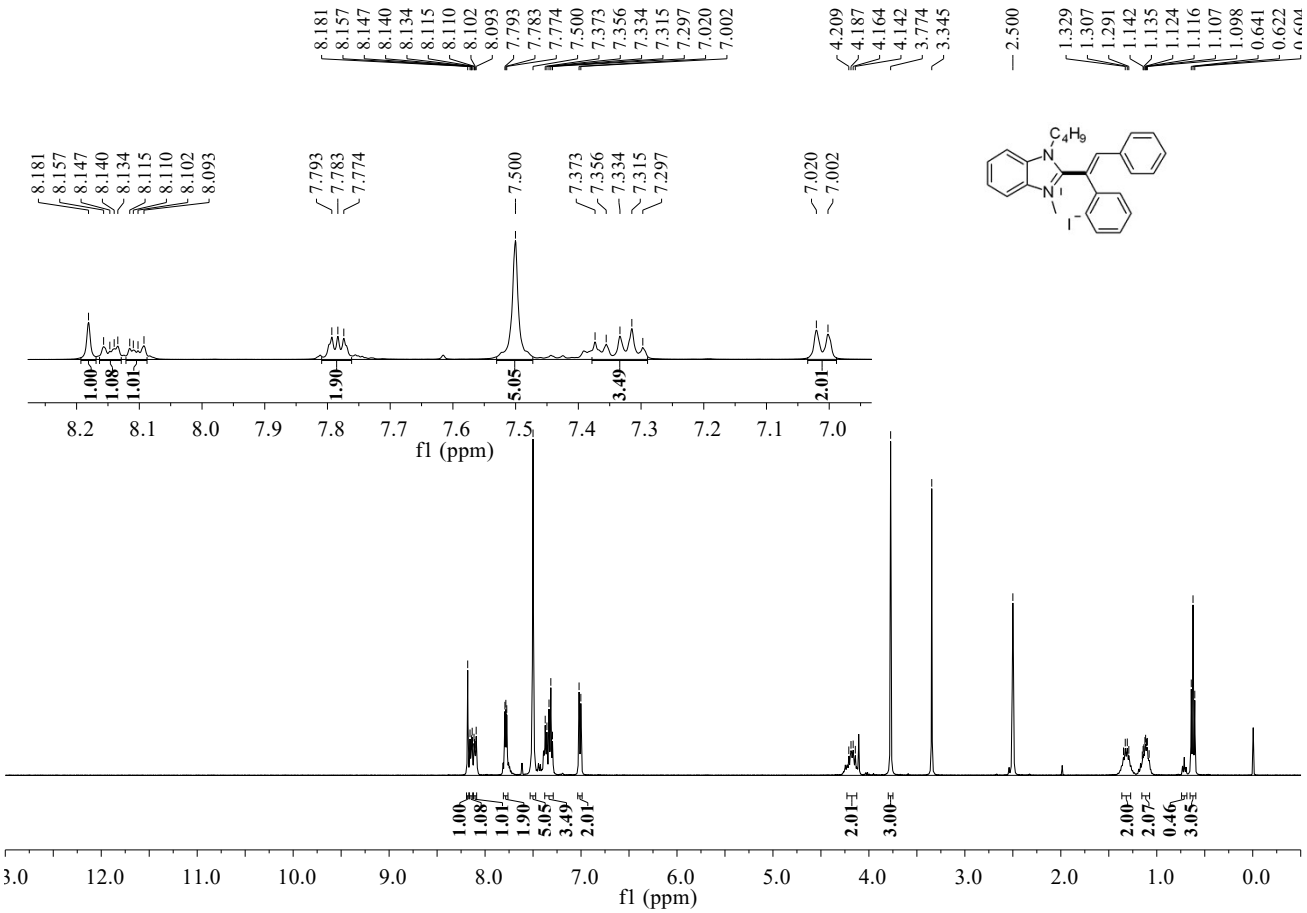
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 3r



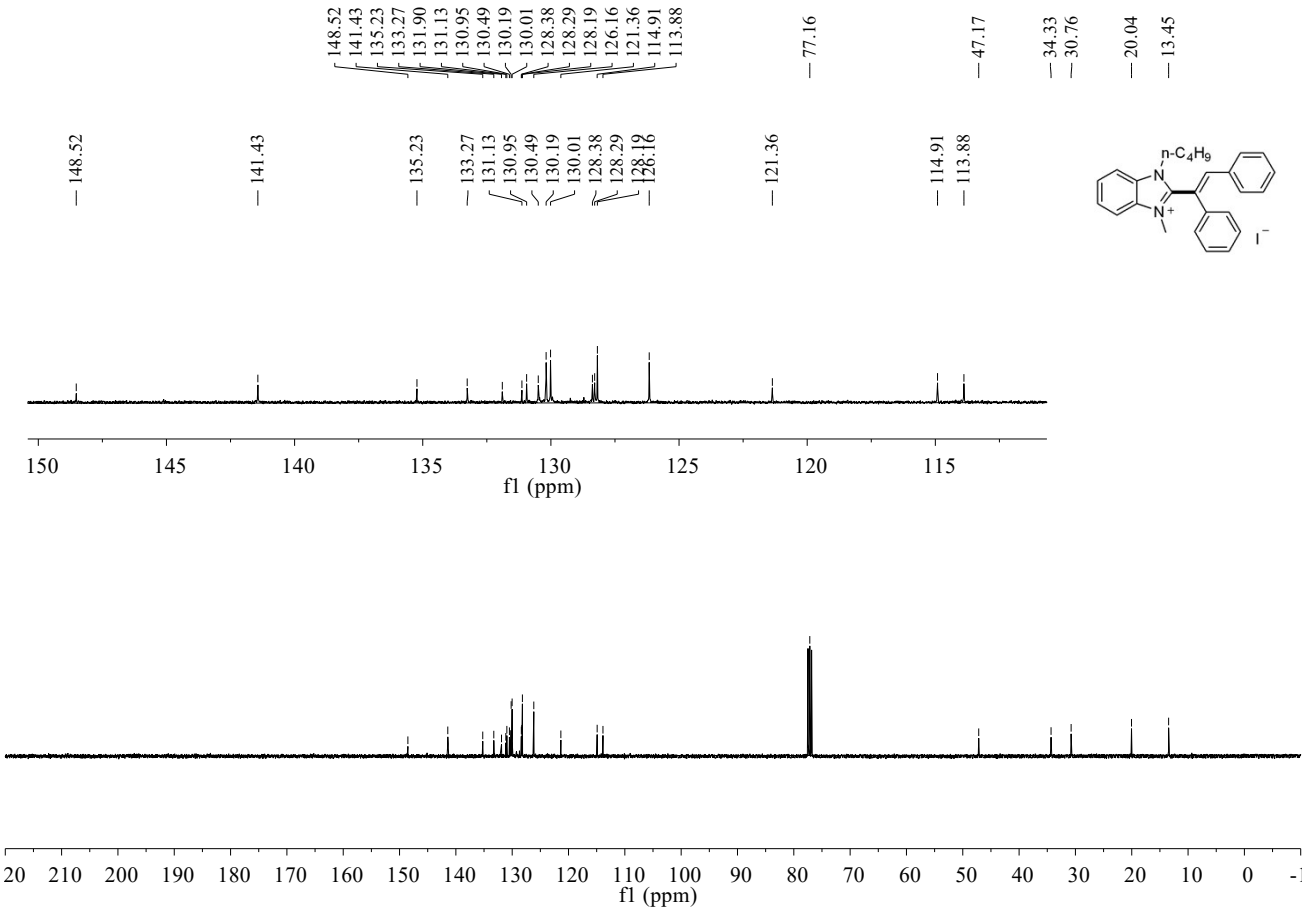
^{13}C NMR Spectra (100 MHz, $CDCl_3$) of 3r



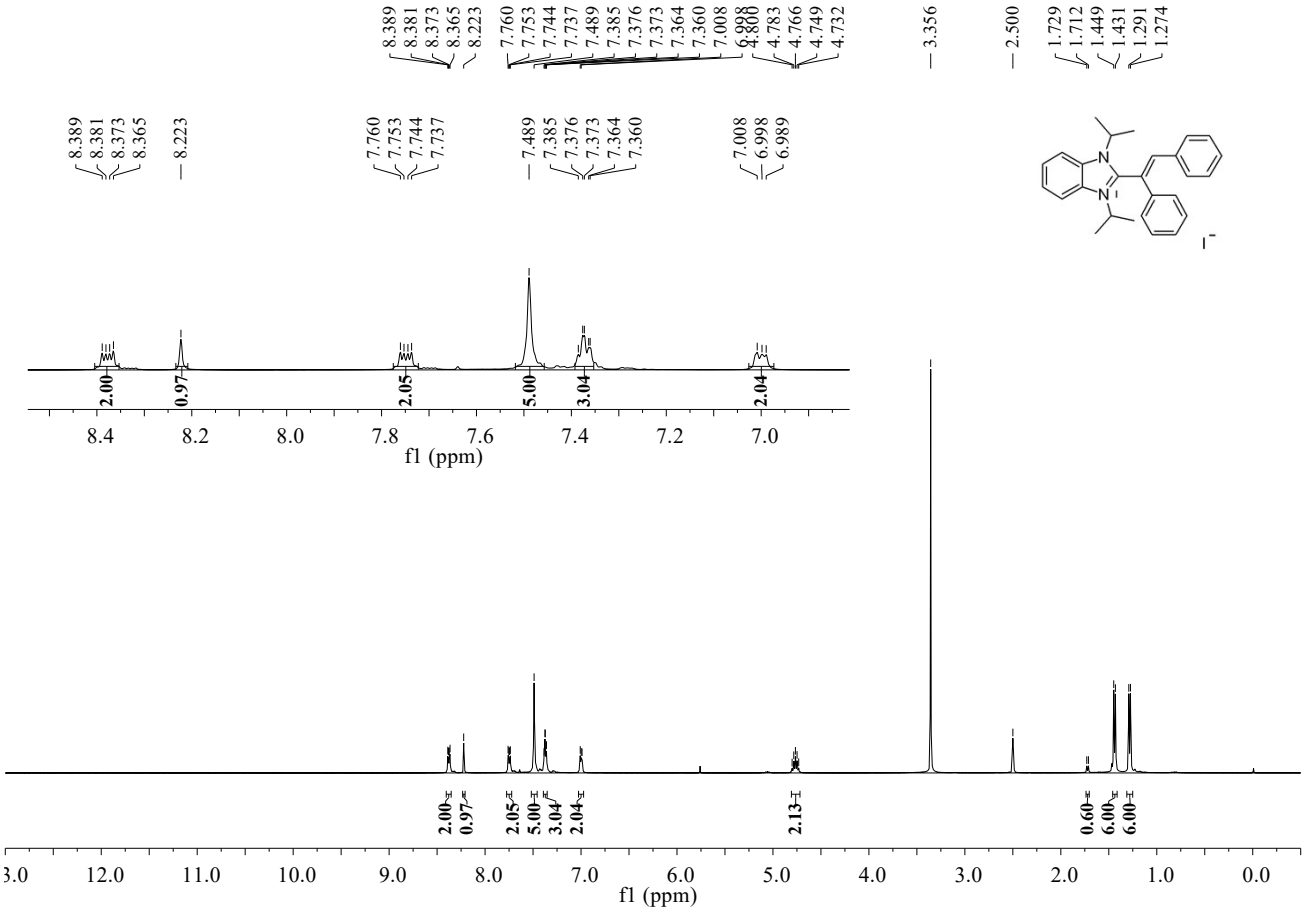
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 4a



^{13}C NMR Spectra (100 MHz, $CDCl_3$) of 4a



^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 4b



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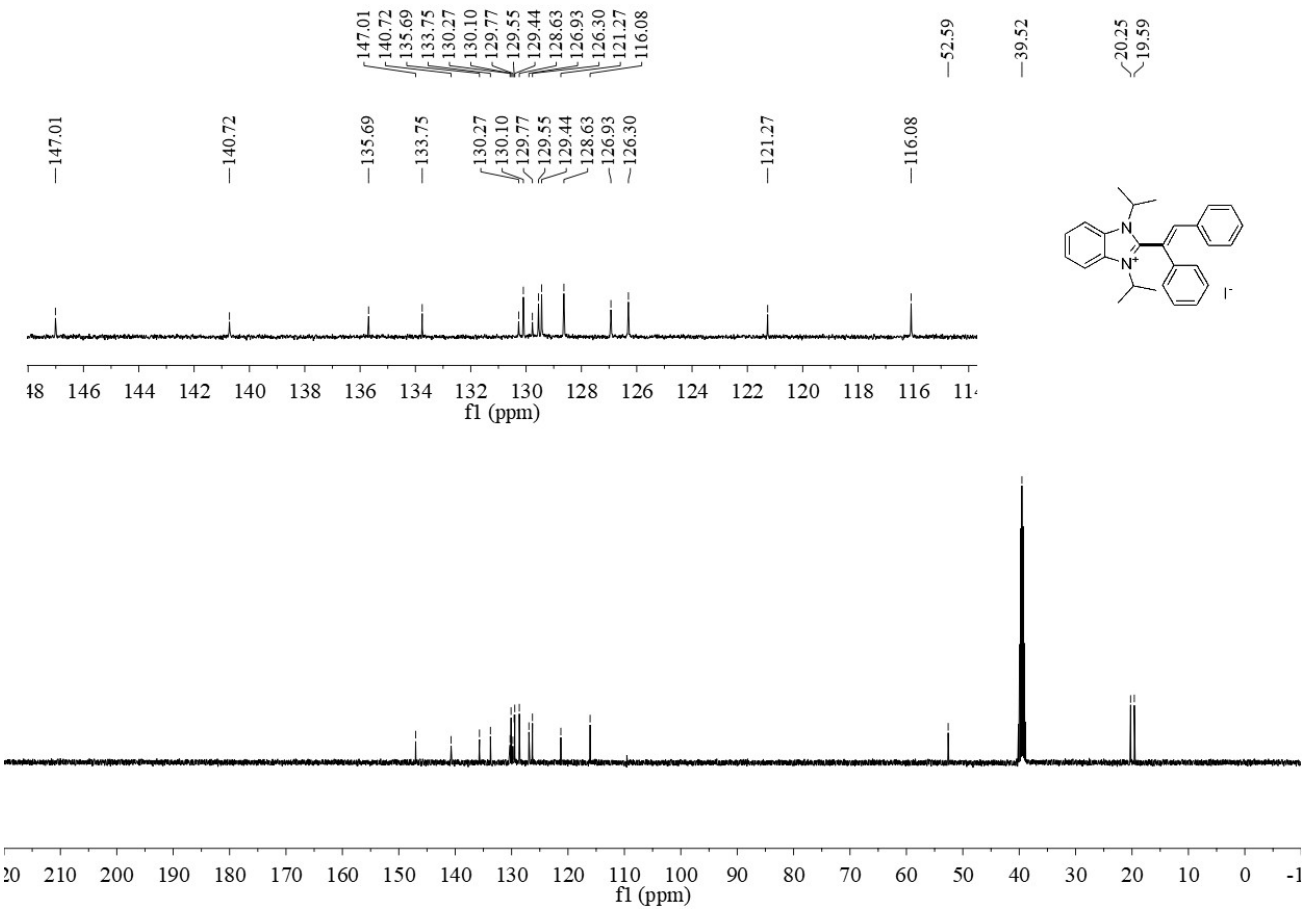
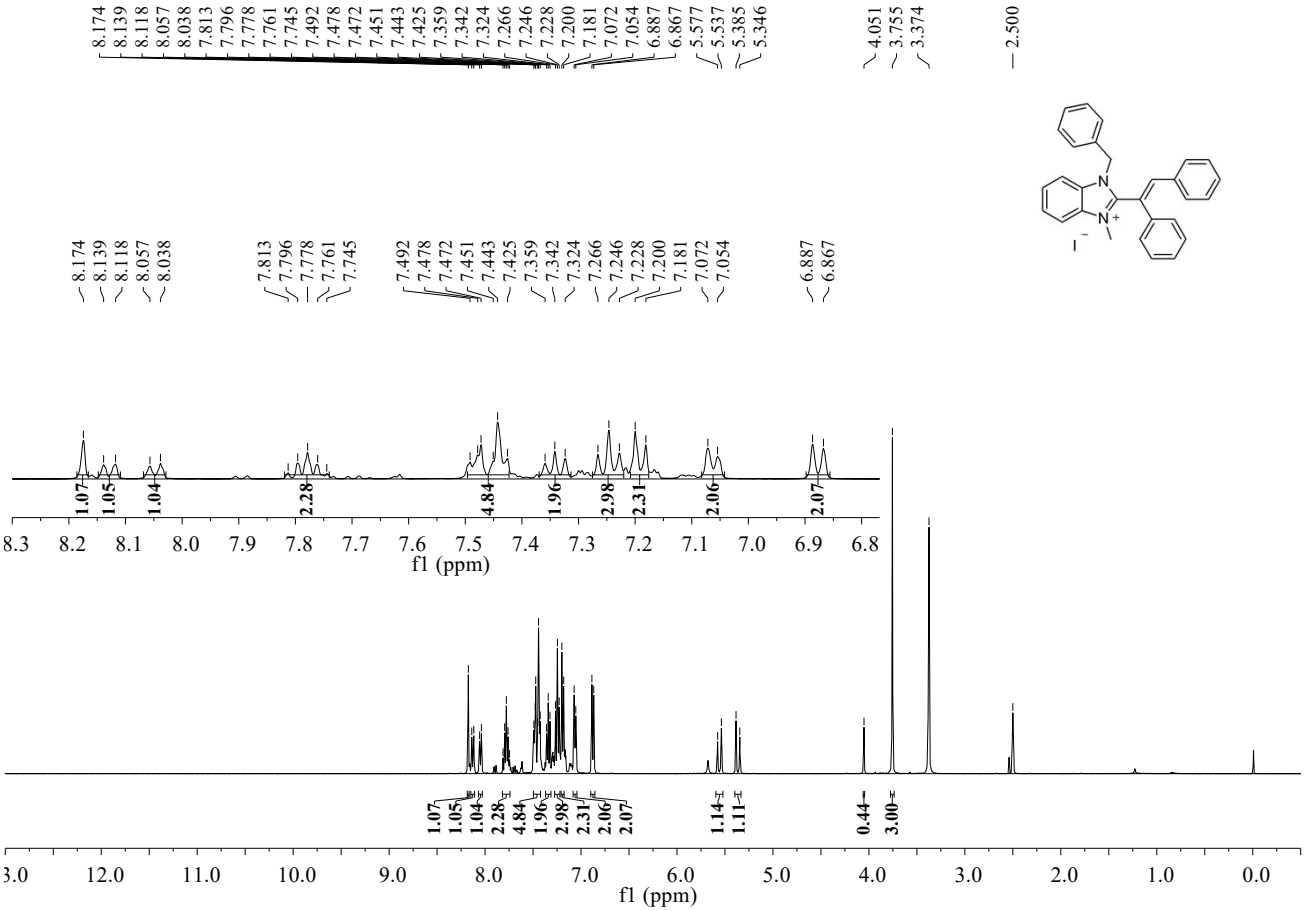


^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 4c



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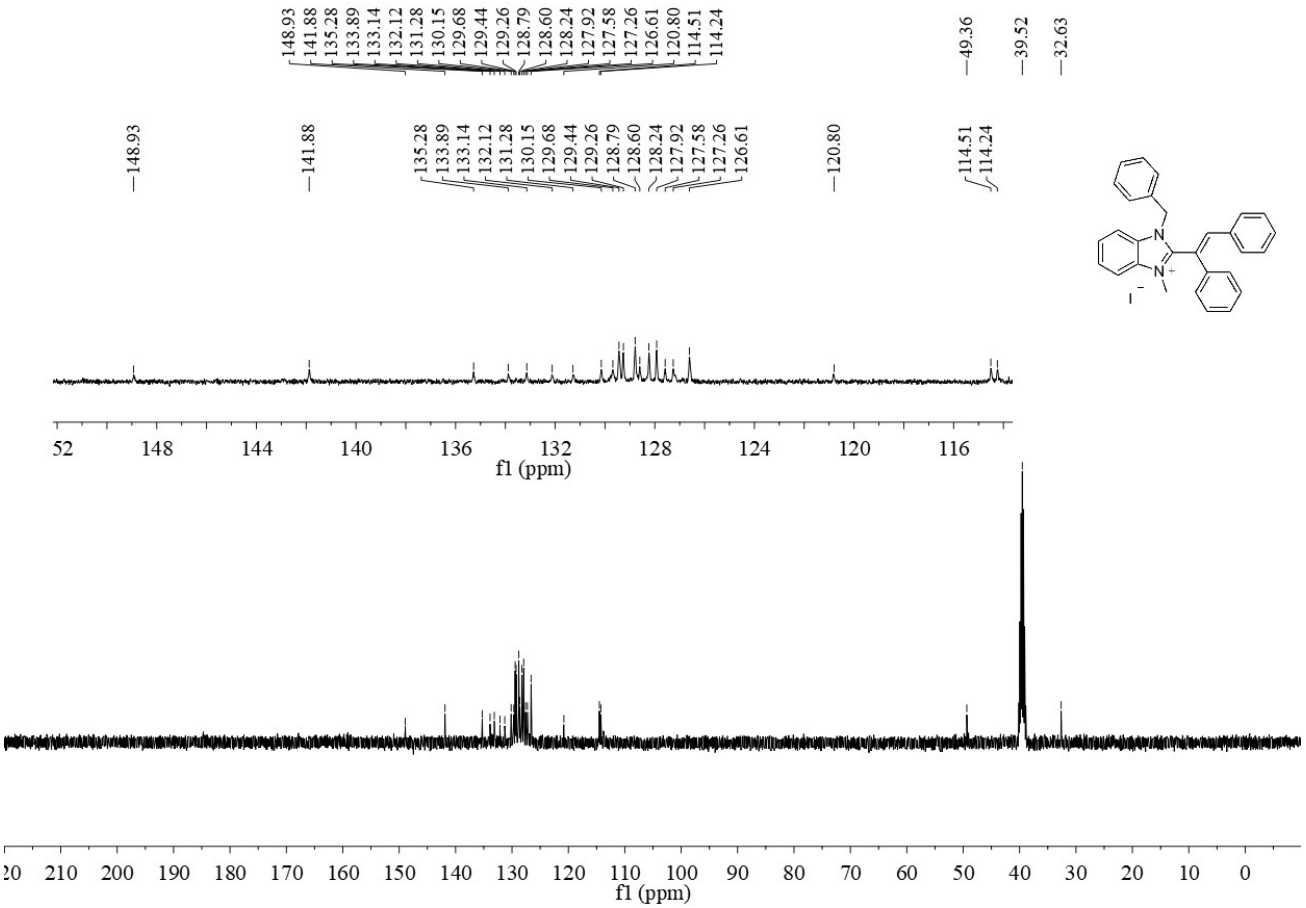
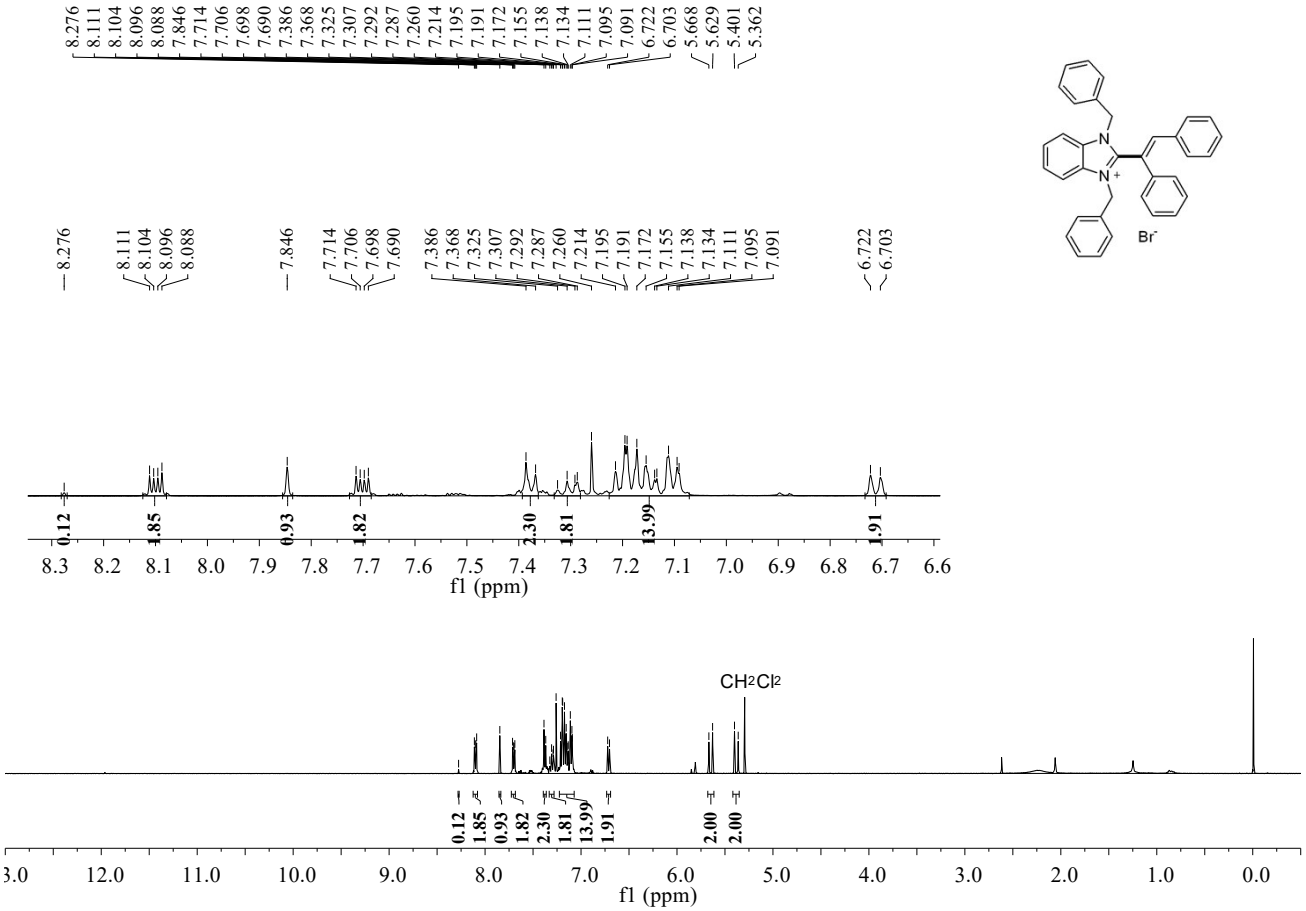
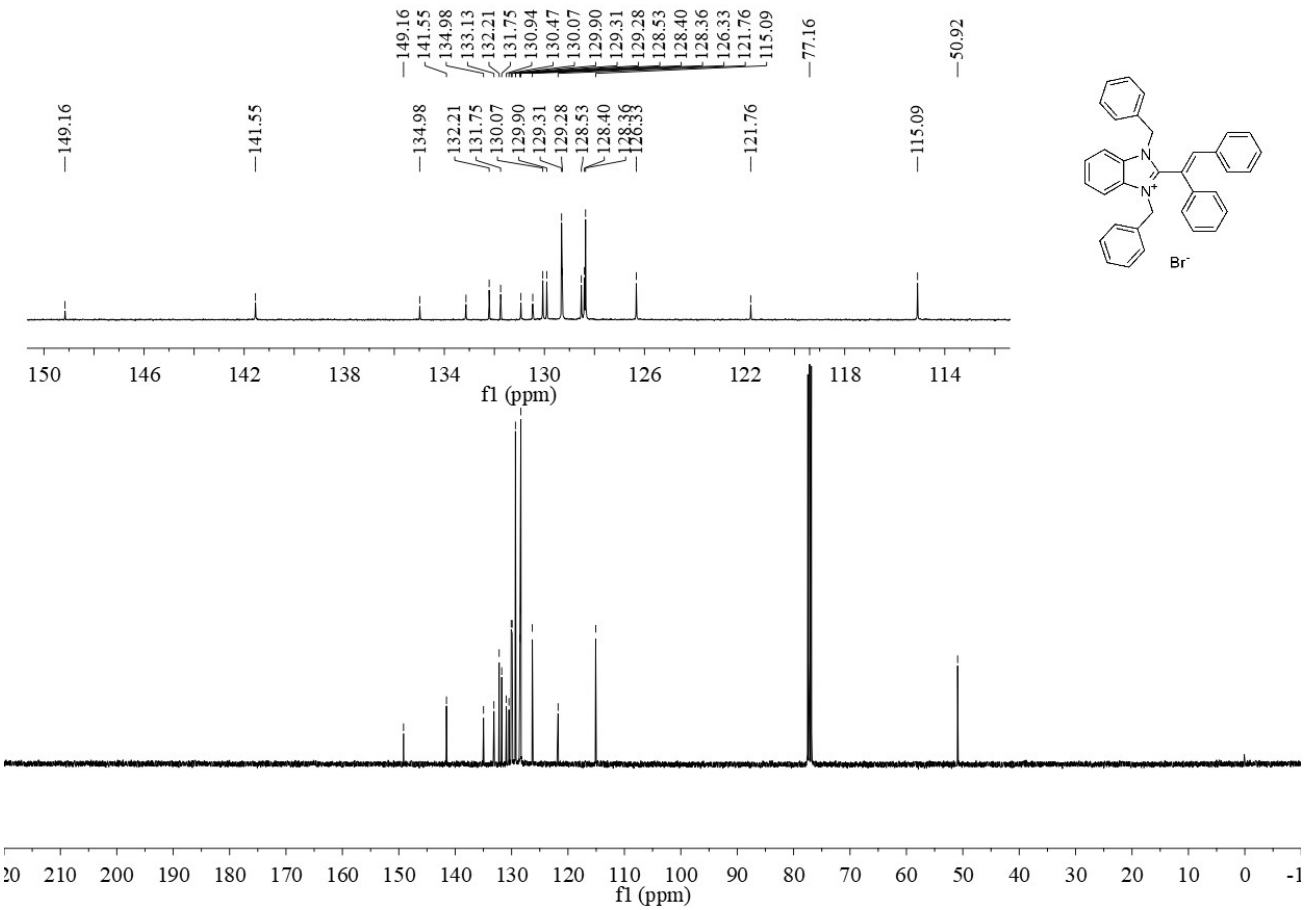


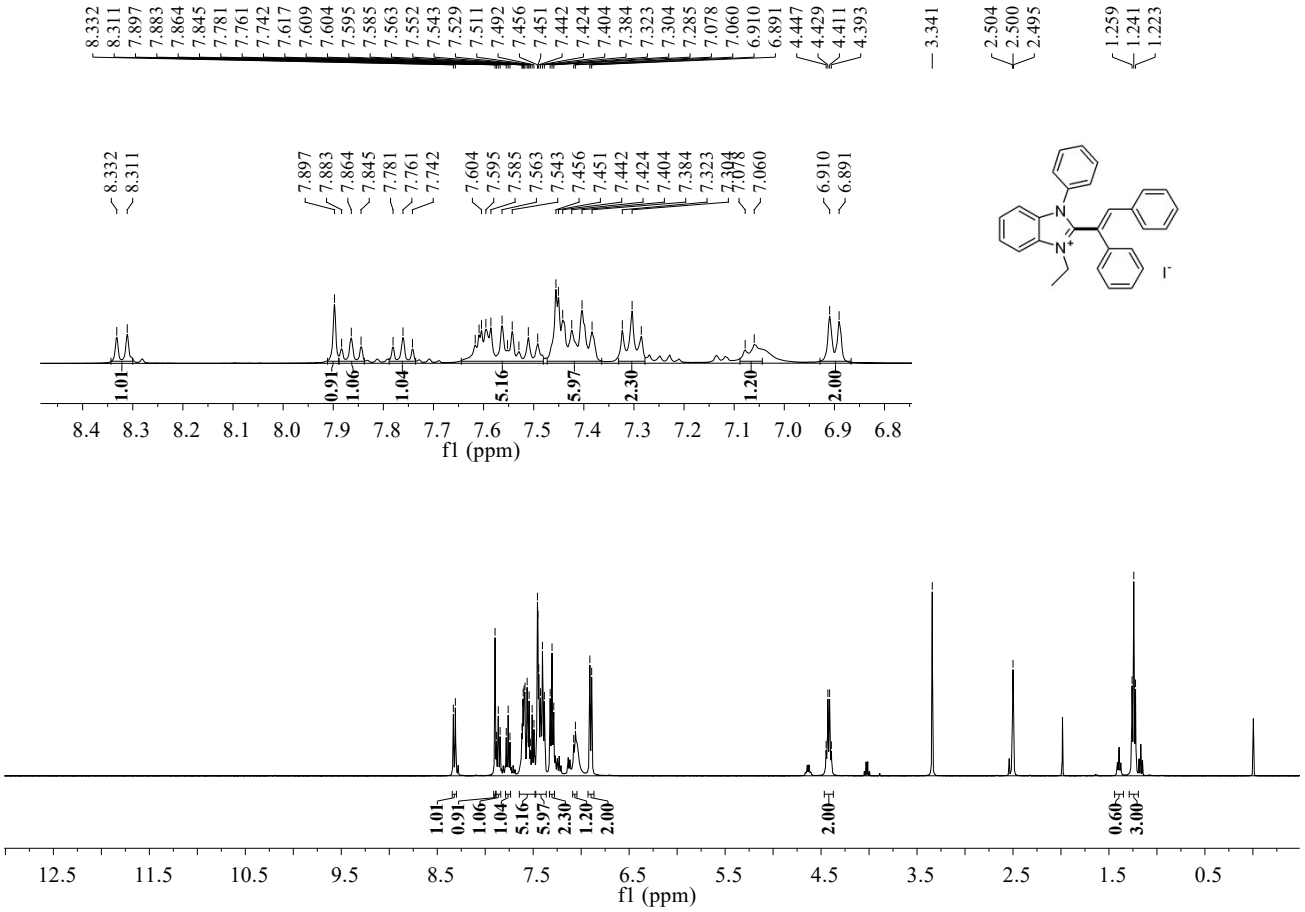
^{1}H NMR Spectra (400 MHz, $CDCl_3$) of 4d



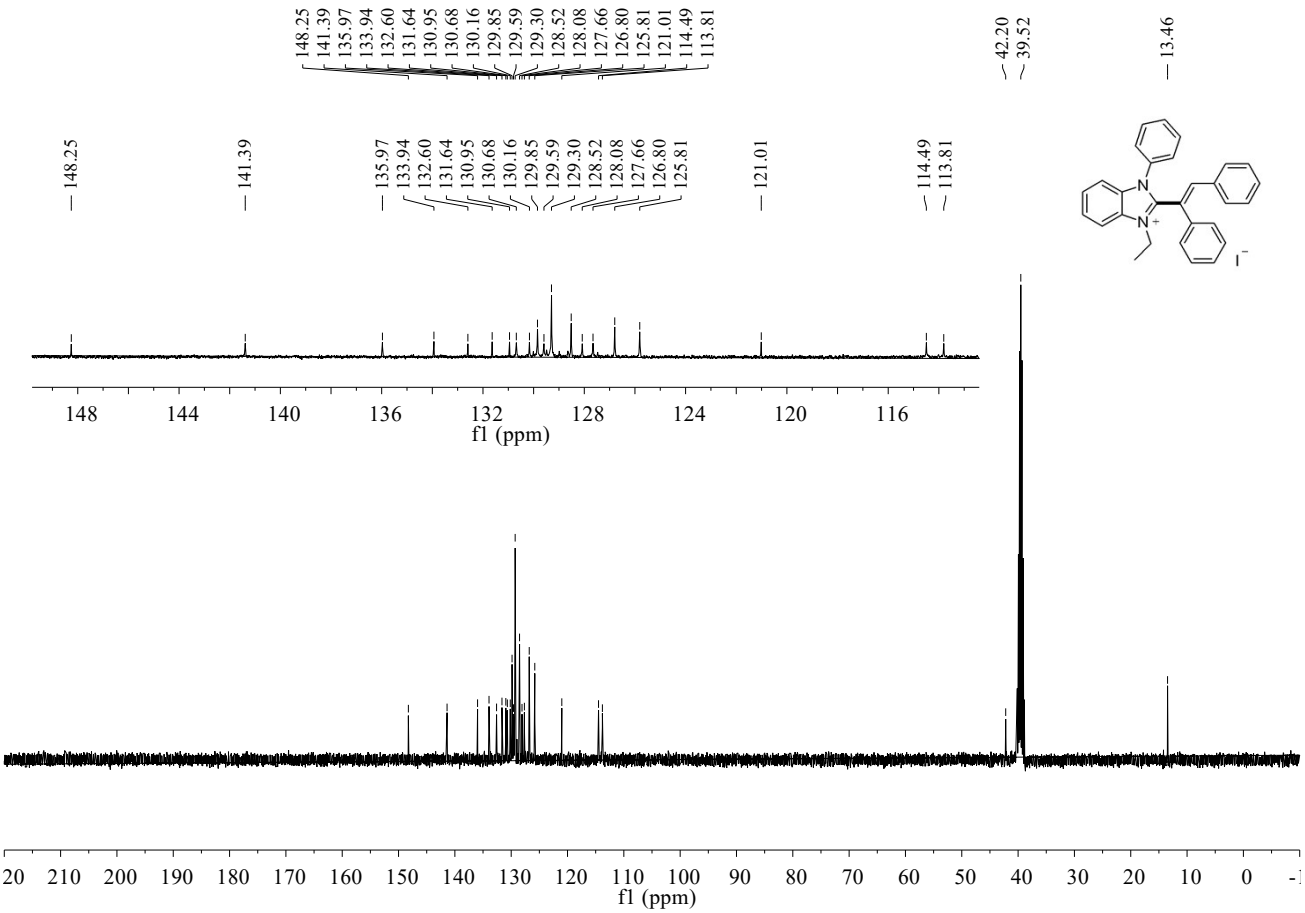
^{13}C NMR Spectra (100 MHz, $CDCl_3$) of 4d



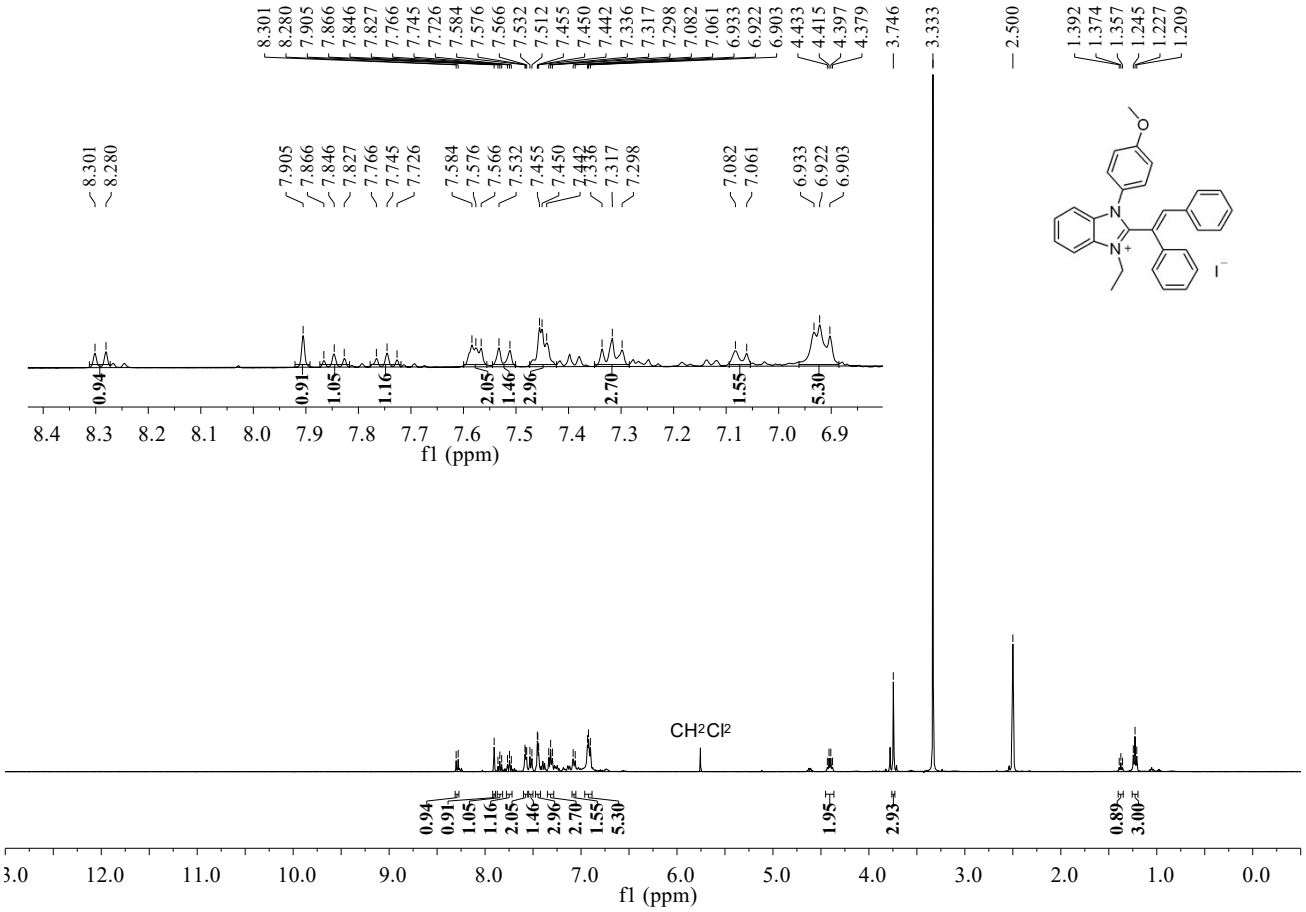
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 4e



^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 4e



^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 4f



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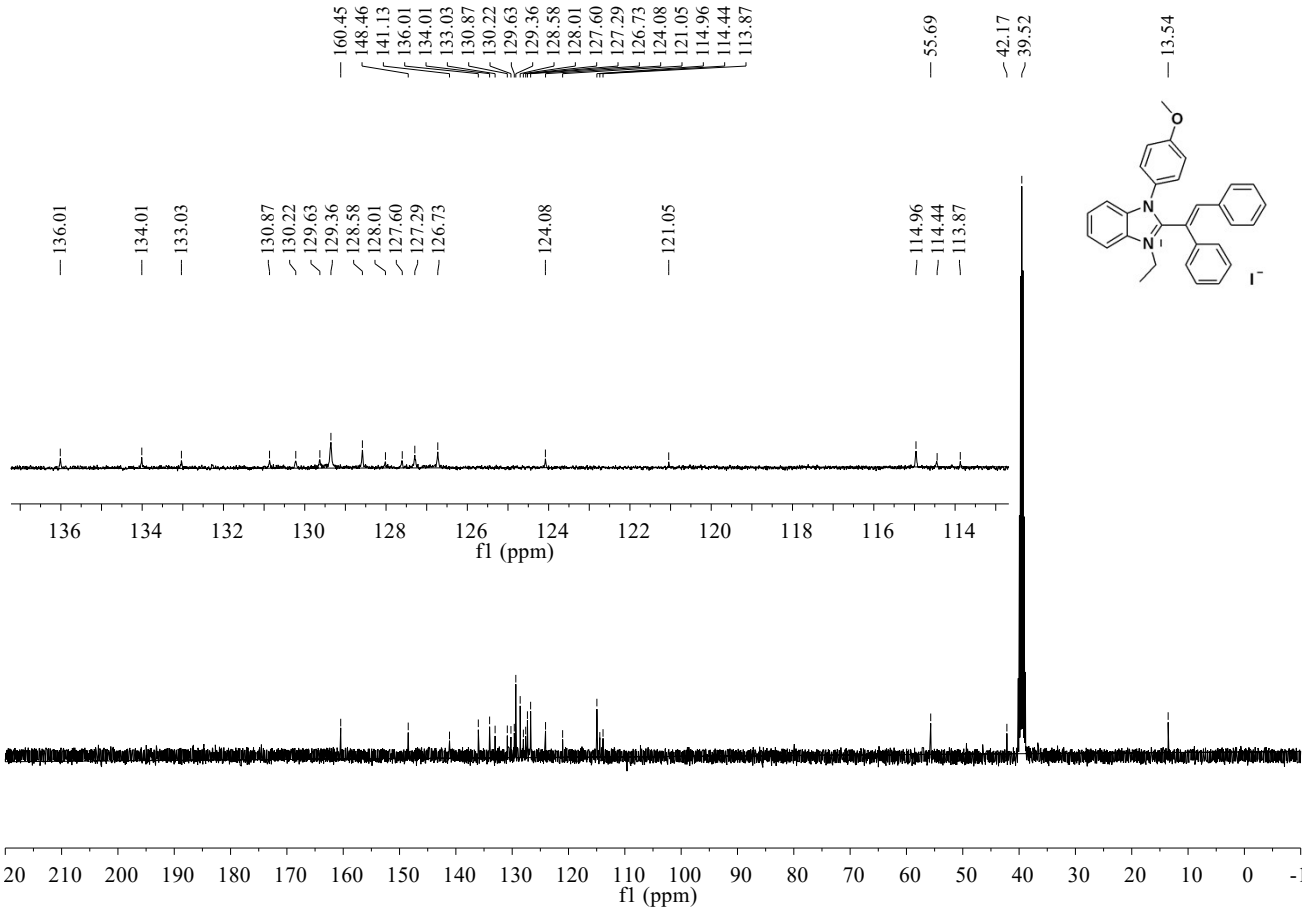
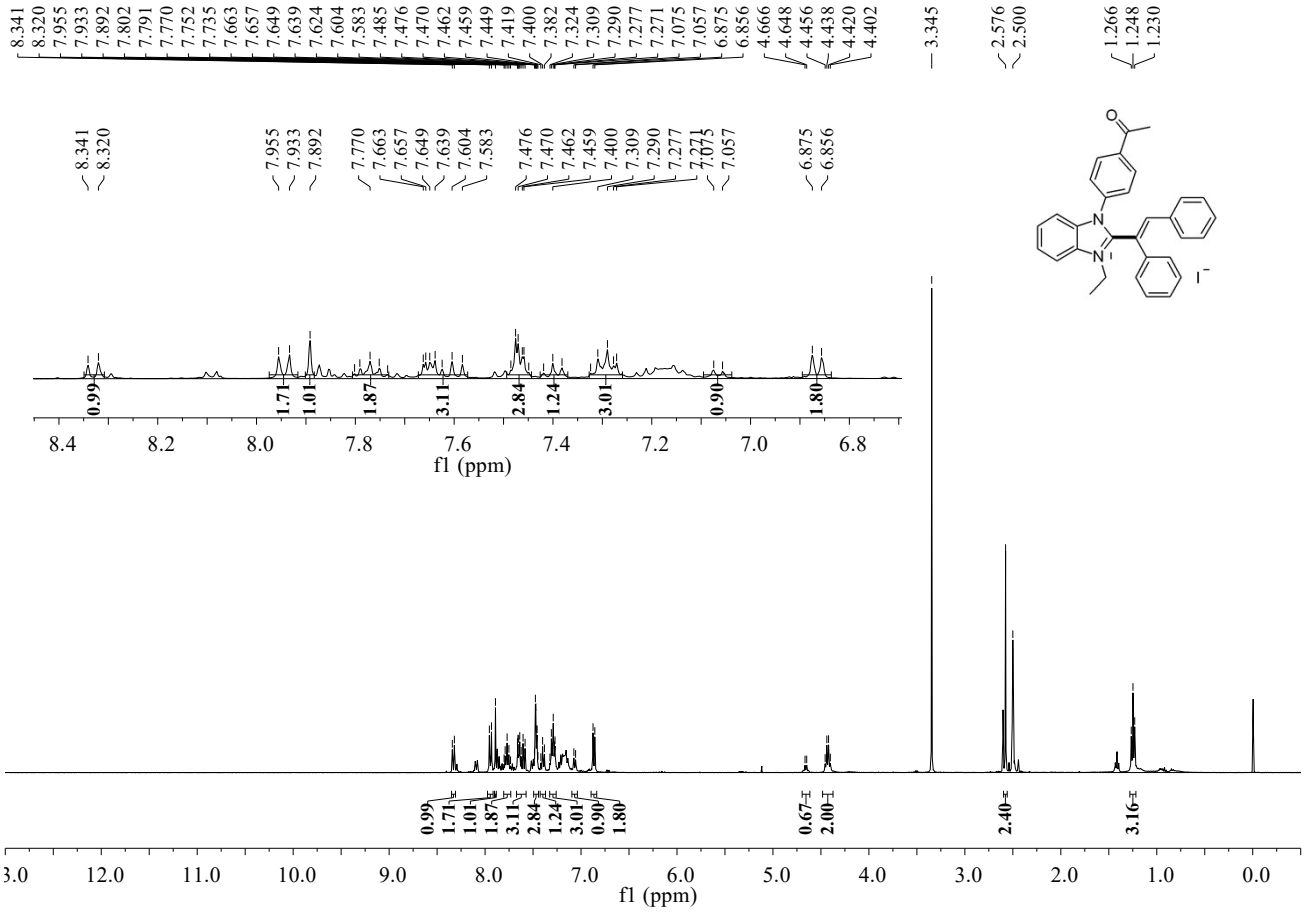
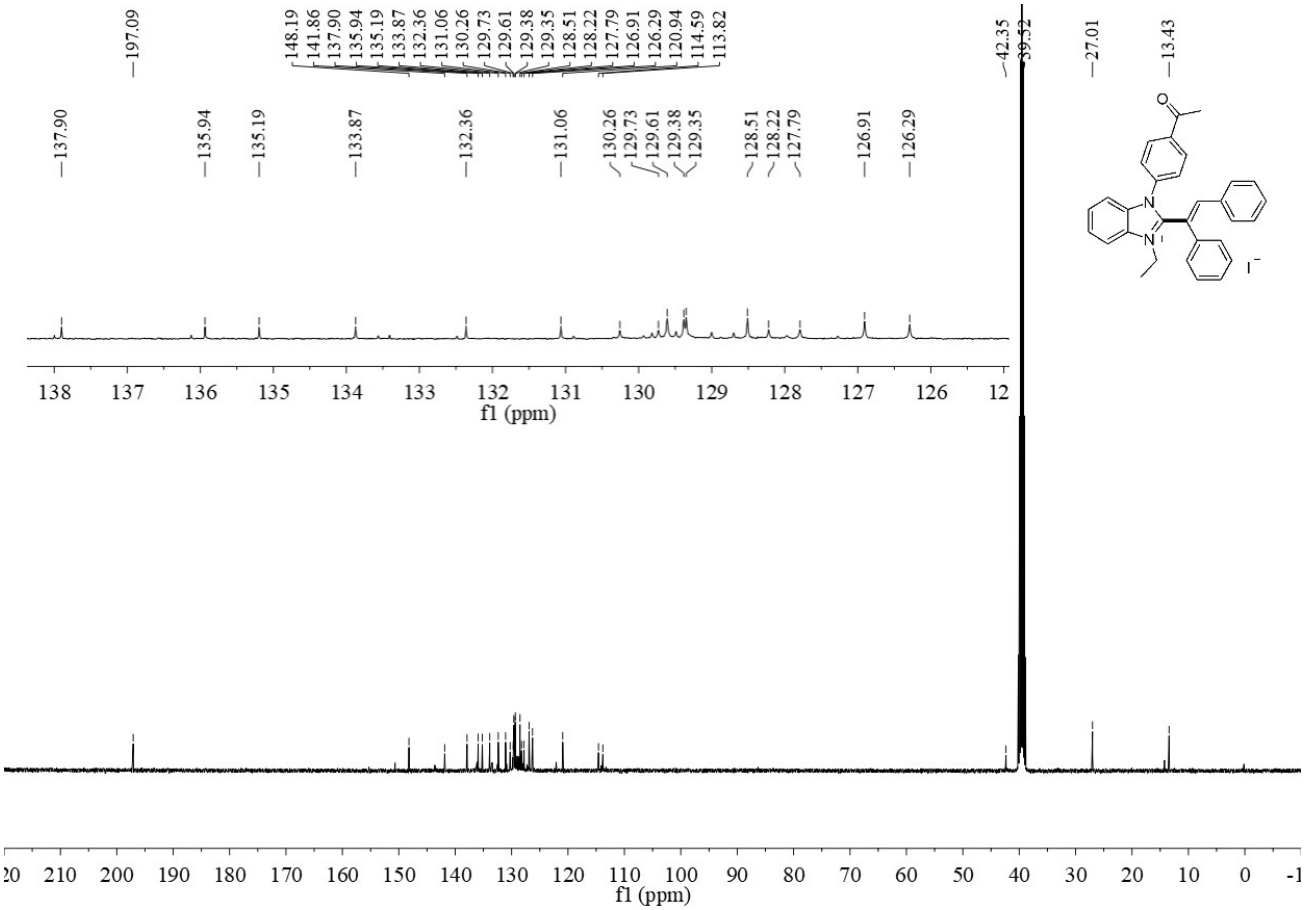


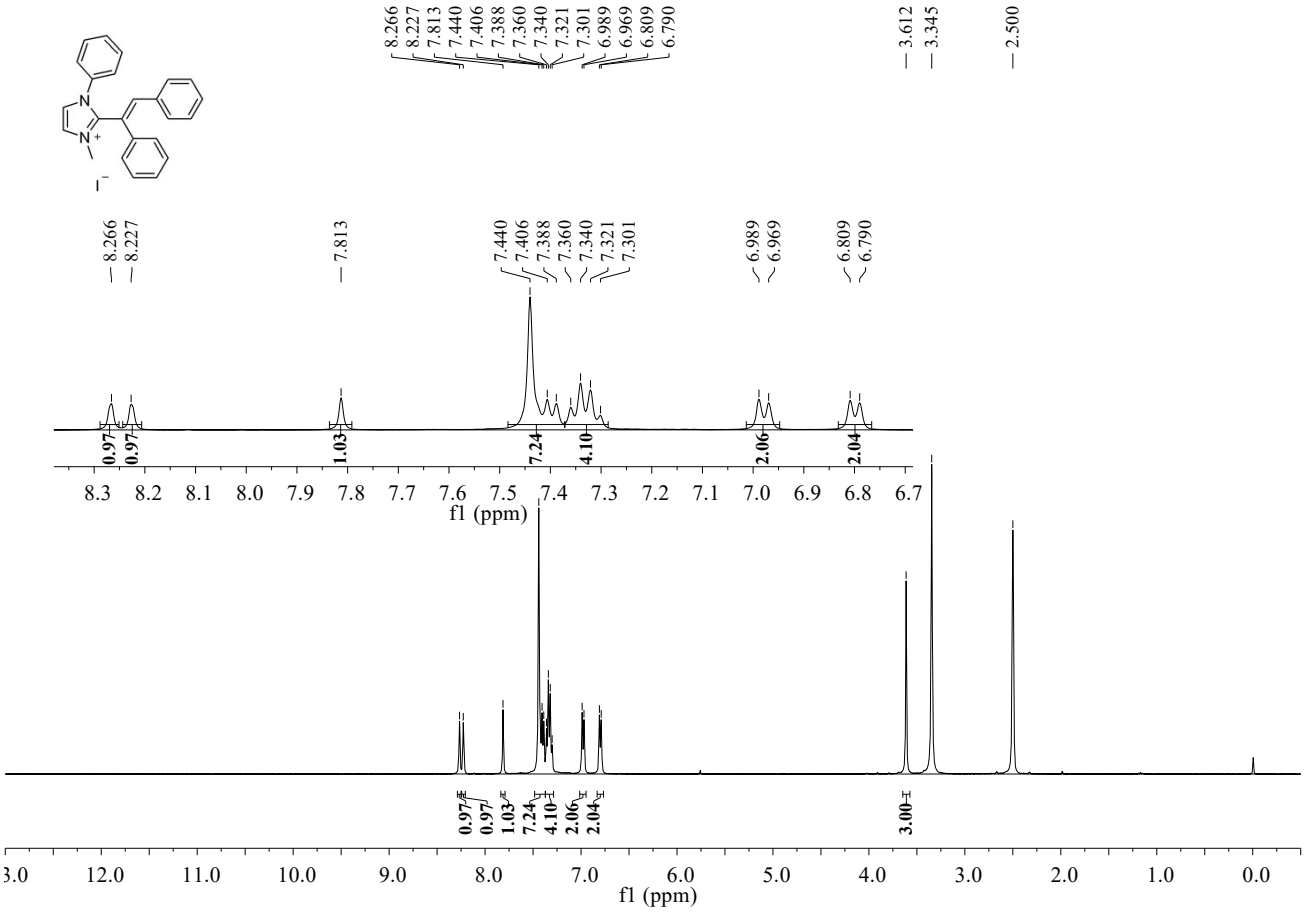
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 4g



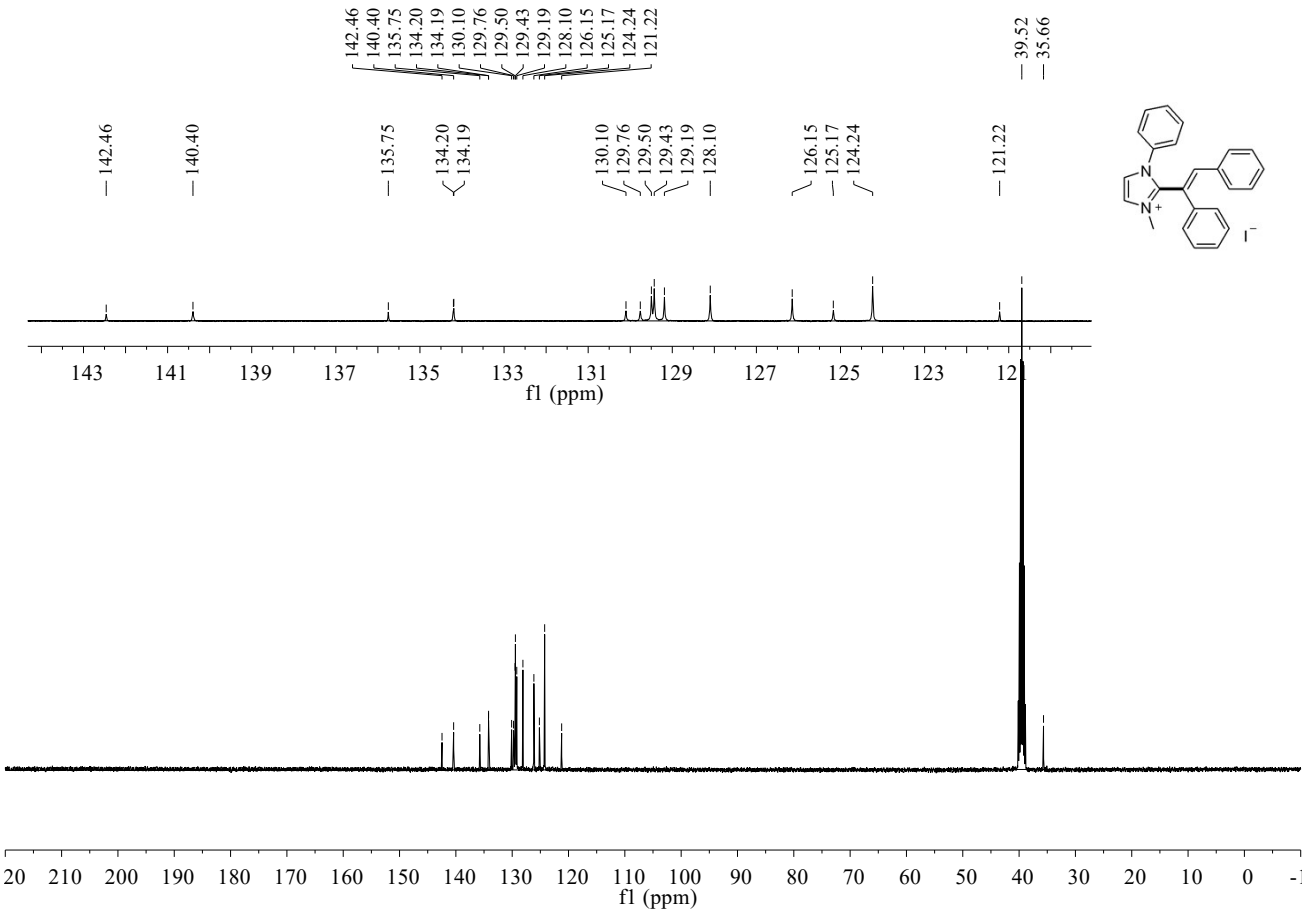
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 4g



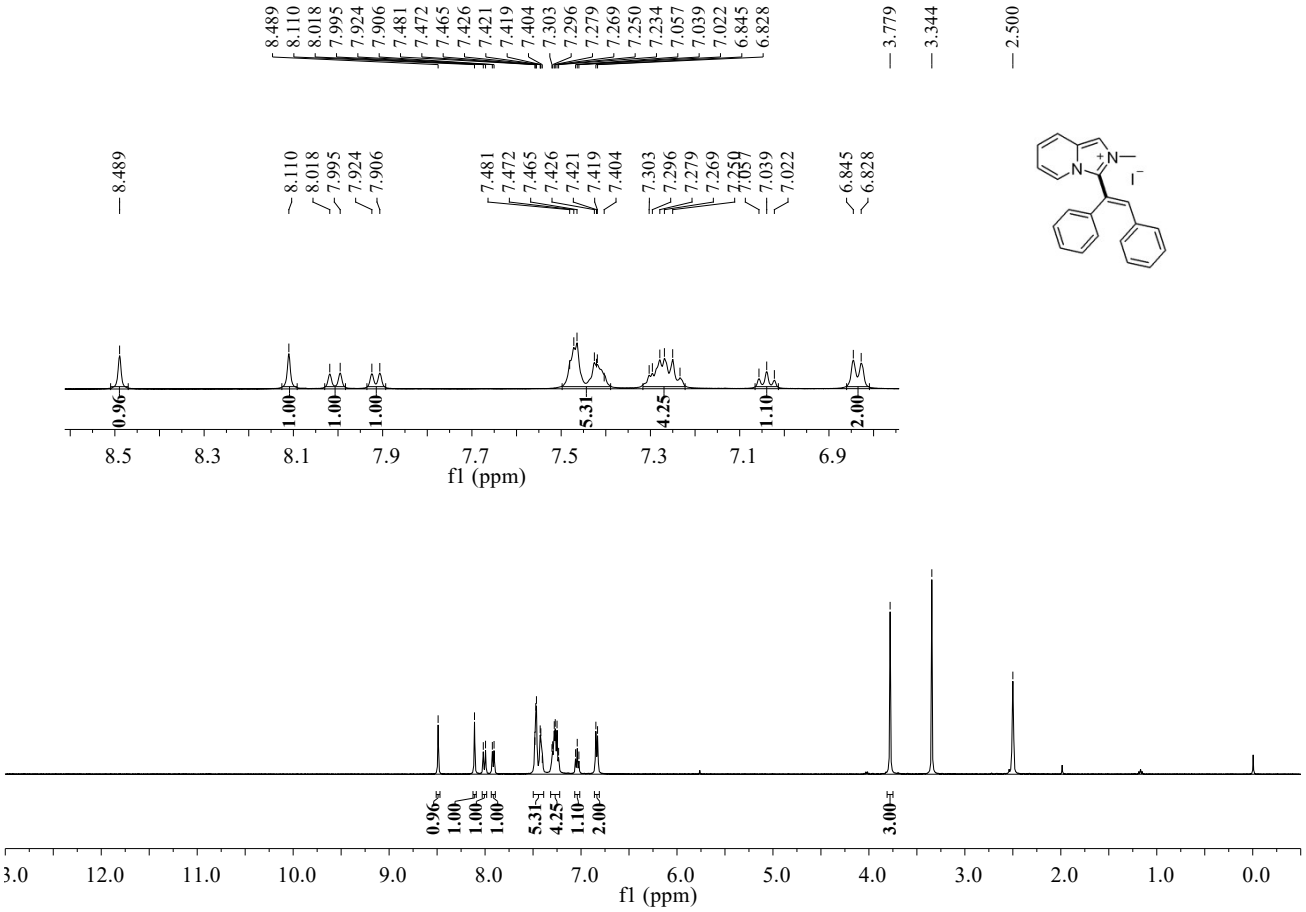
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 4h



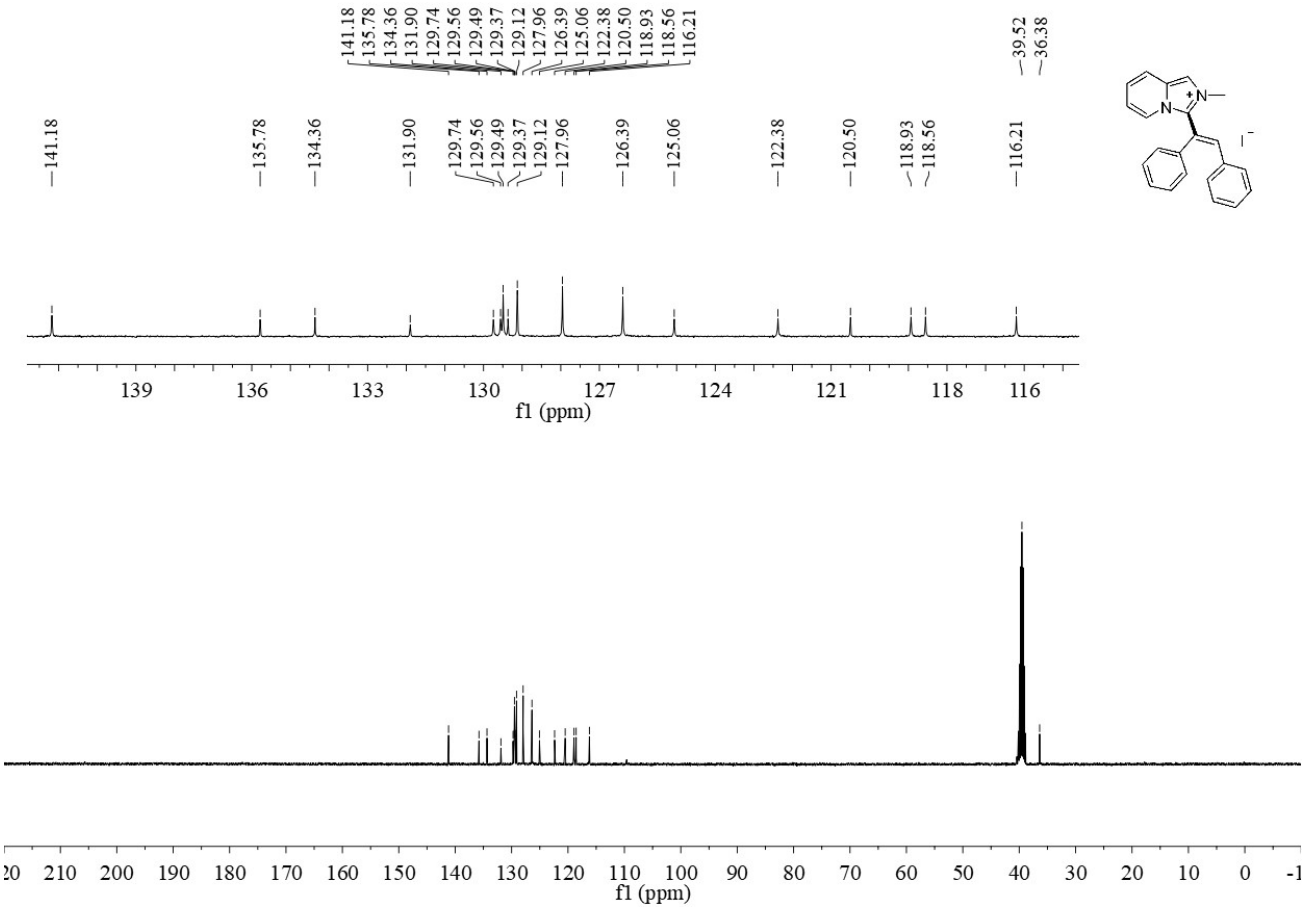
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 4h



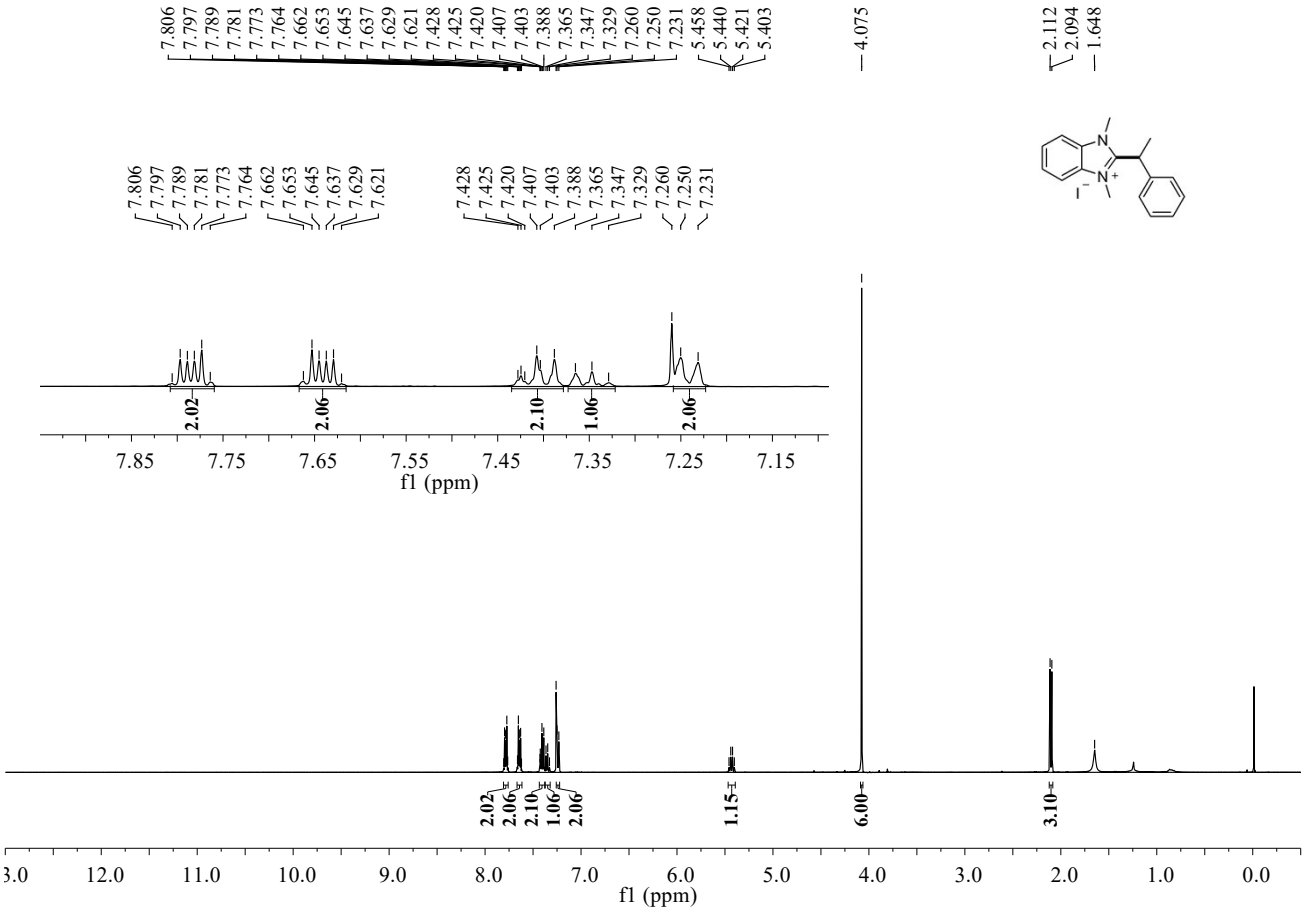
^{1}H NMR Spectra (400 MHz, DMSO-d_6) of 4i



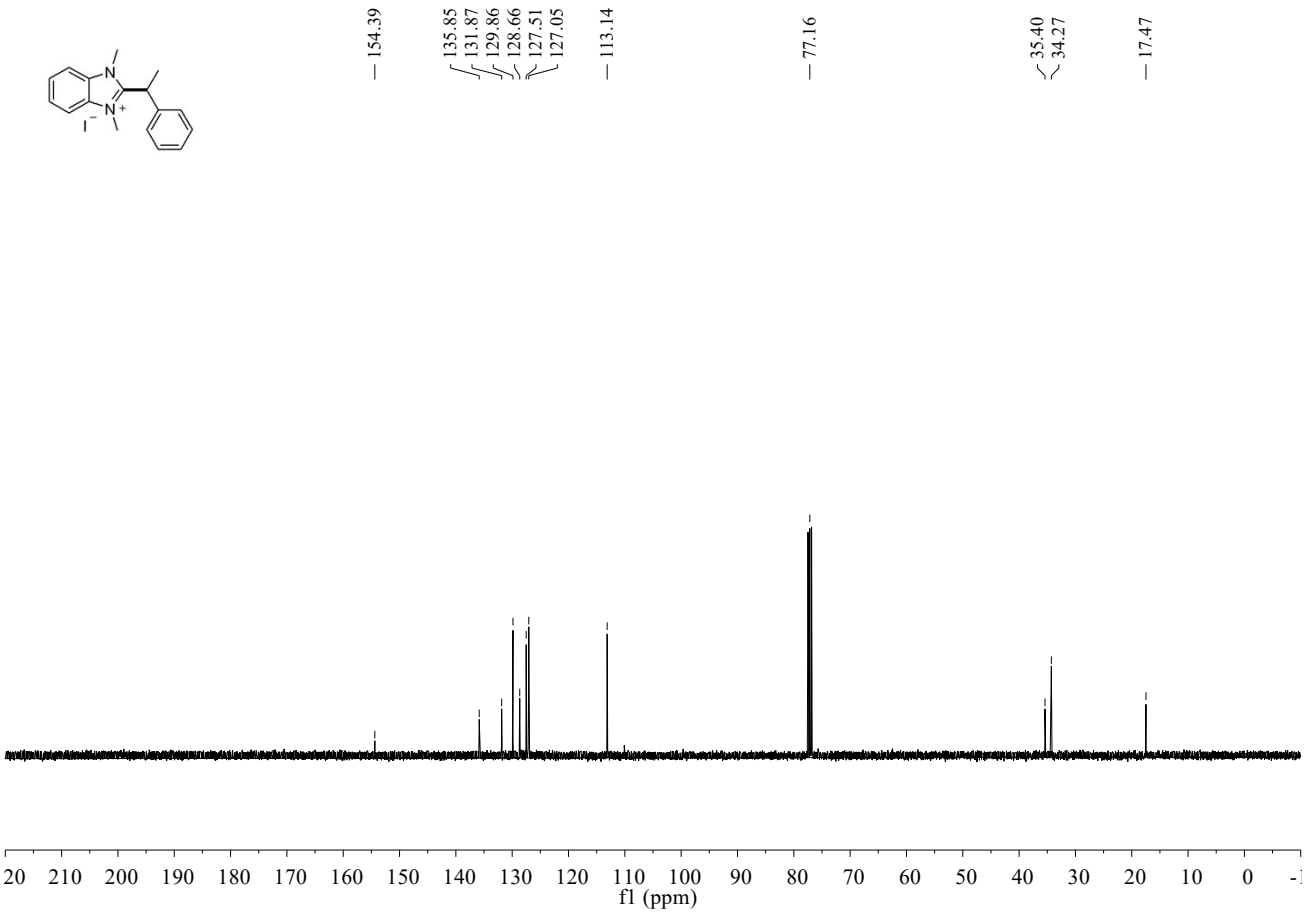
^{13}C NMR Spectra (100 MHz, DMSO-d_6) of 4i



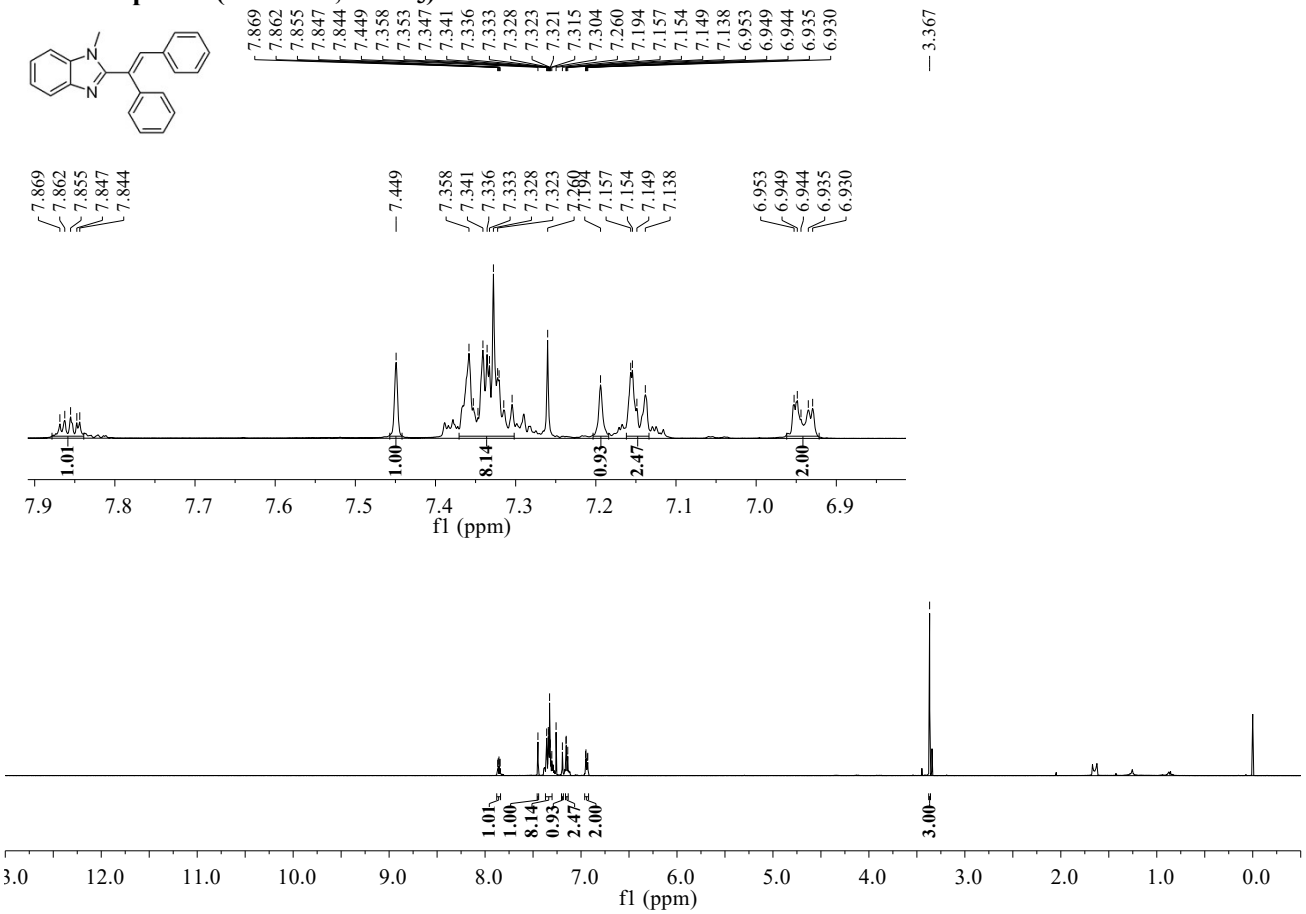
^{1}H NMR Spectra (400 MHz, $CDCl_3$) of 5



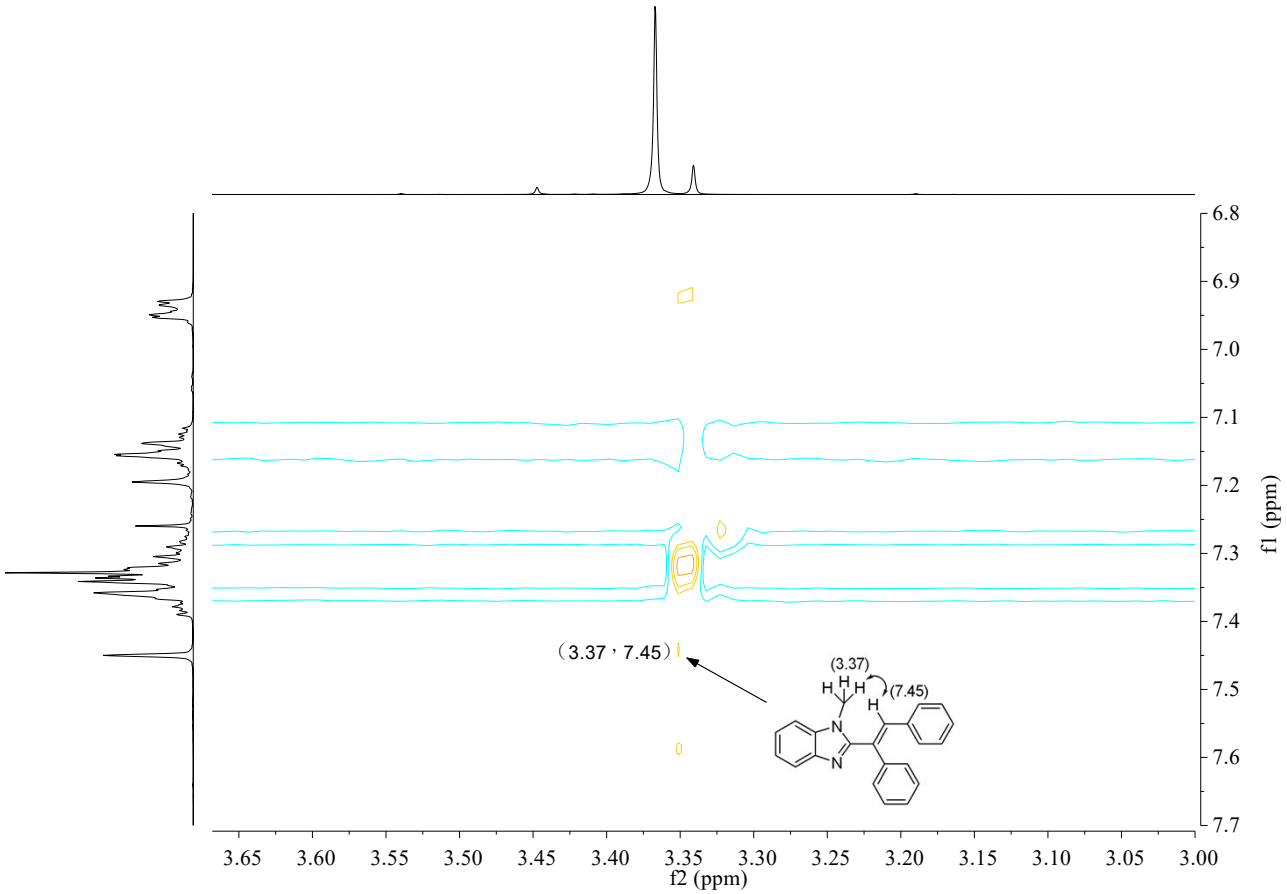
^{13}C NMR Spectra (100 MHz, $CDCl_3$) of 5



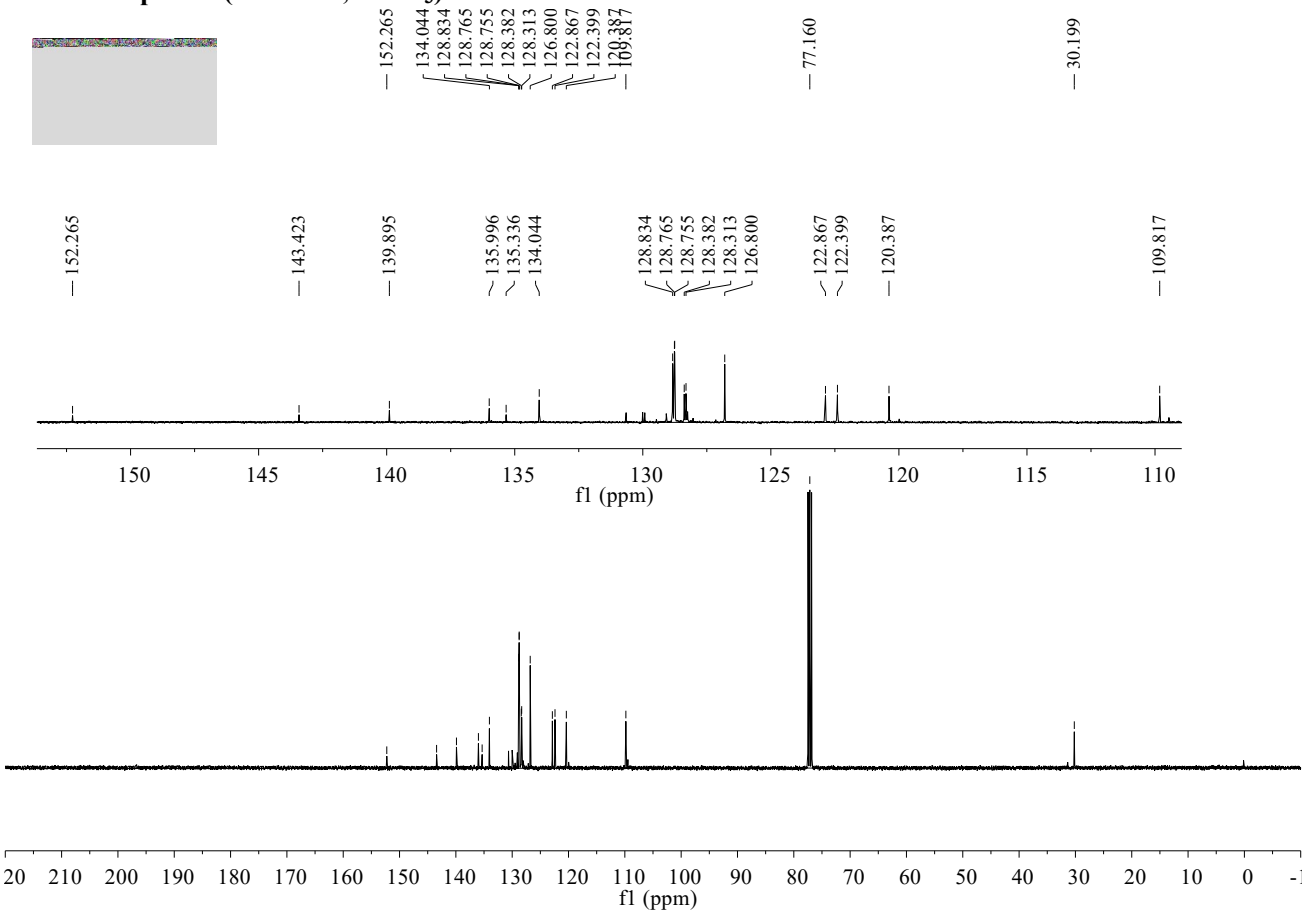
^{1}H NMR Spectra (400 MHz, $CDCl_3$) of 6



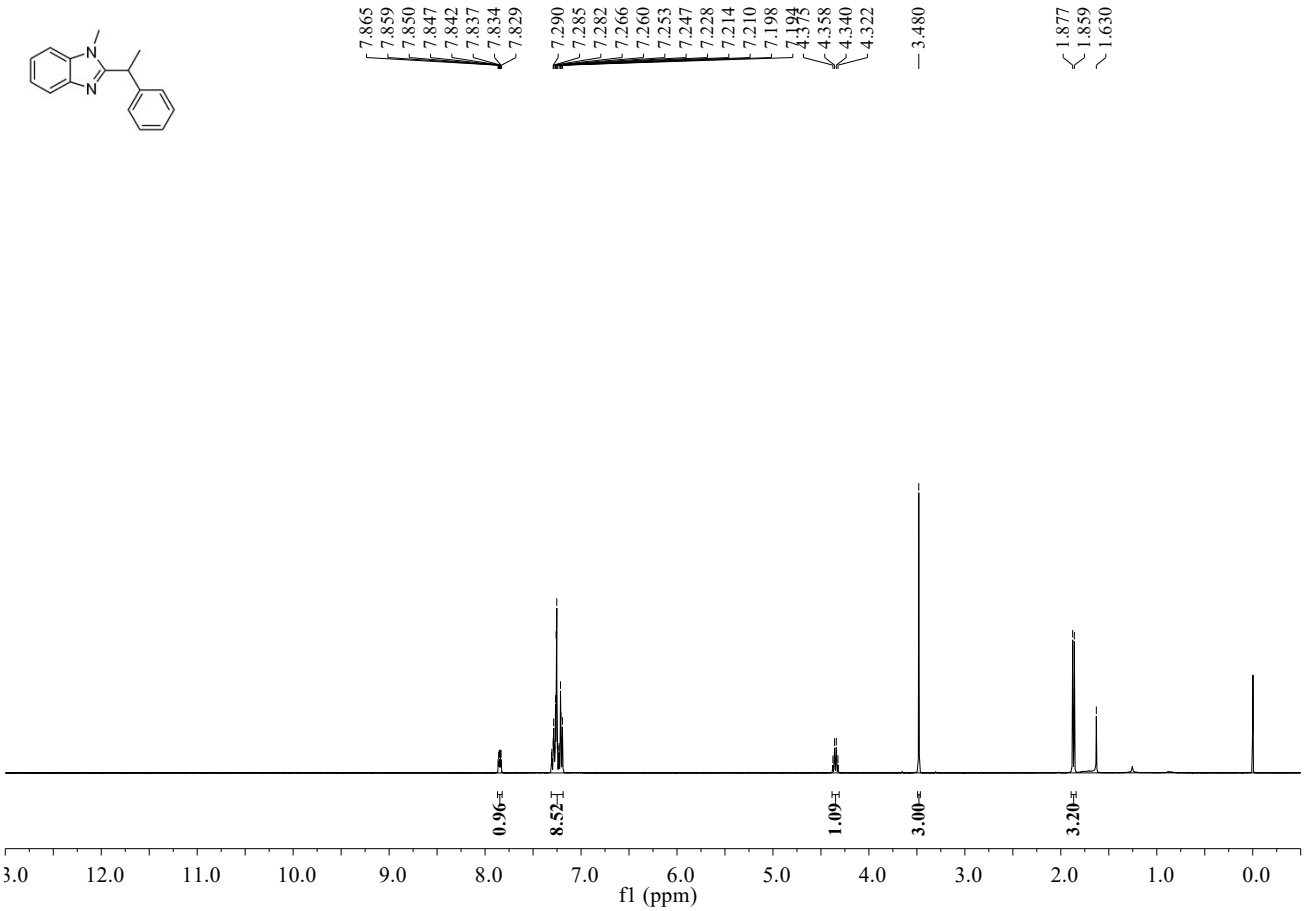
^{1}H–^{1}H NOESY NMR Spectra (400 MHz, $CDCl_3$) of 6



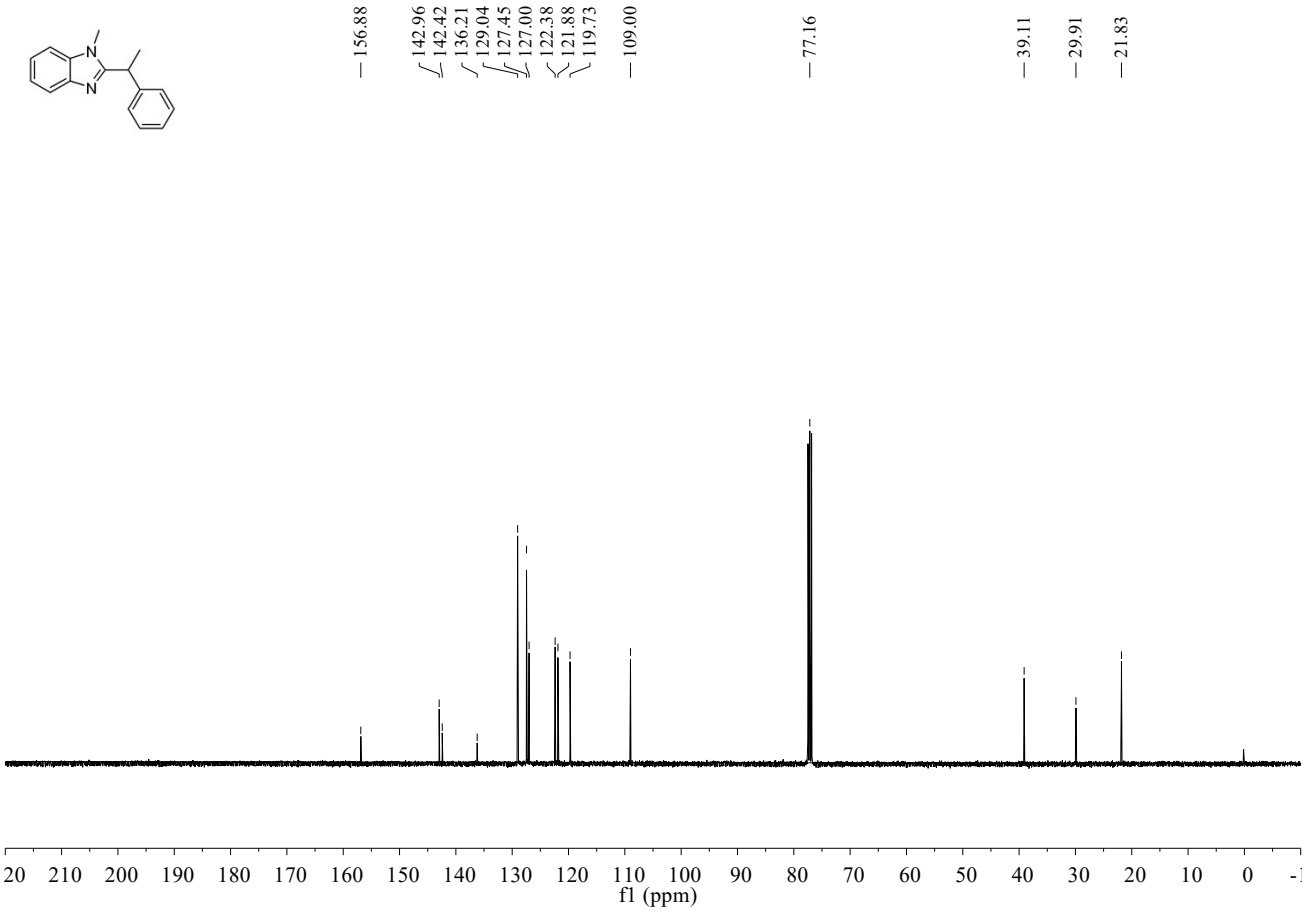
^{13}C NMR Spectra (100 MHz, $CDCl_3$) of 6



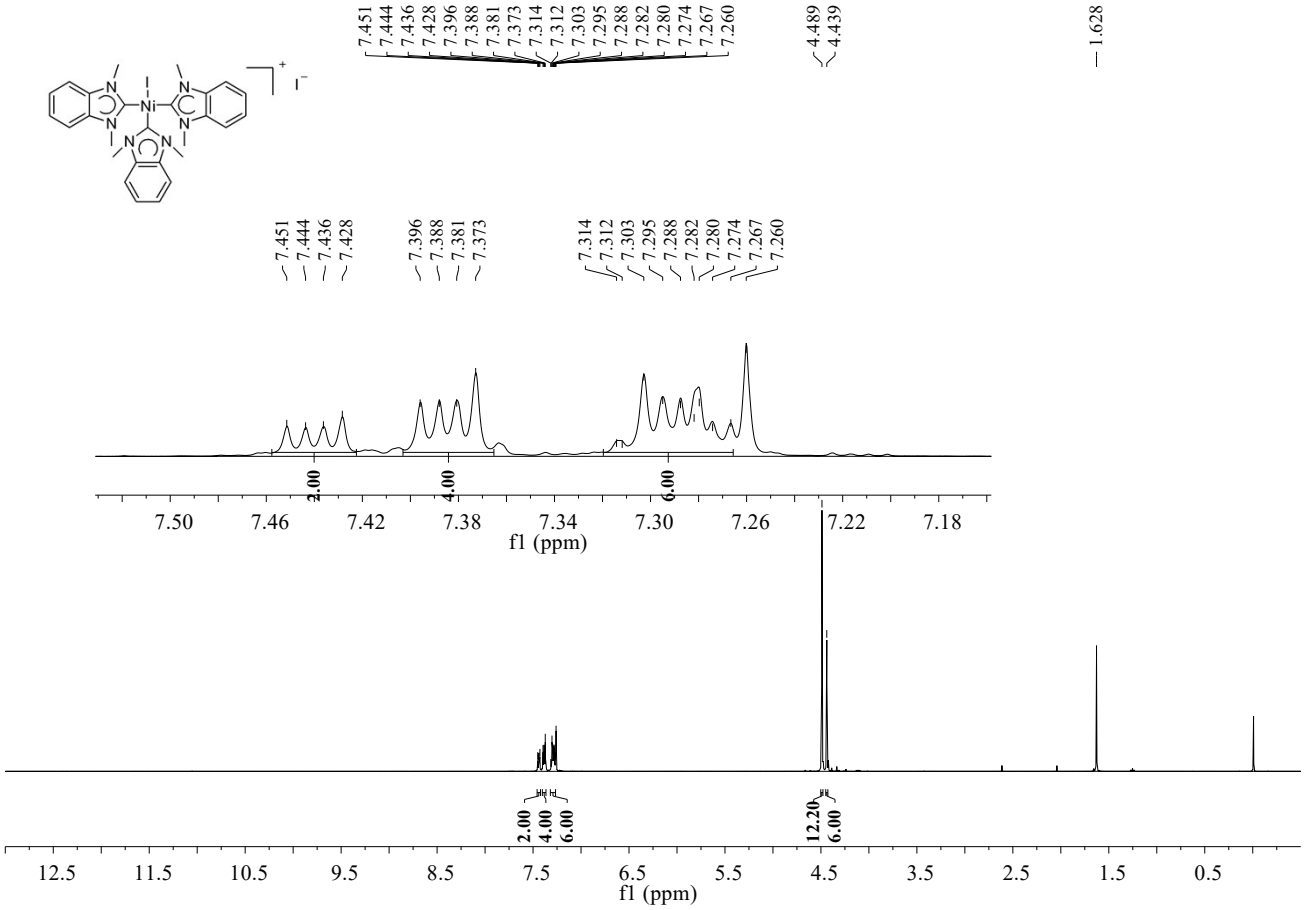
^{1}H NMR Spectra (400 MHz, $CDCl_3$) of 7



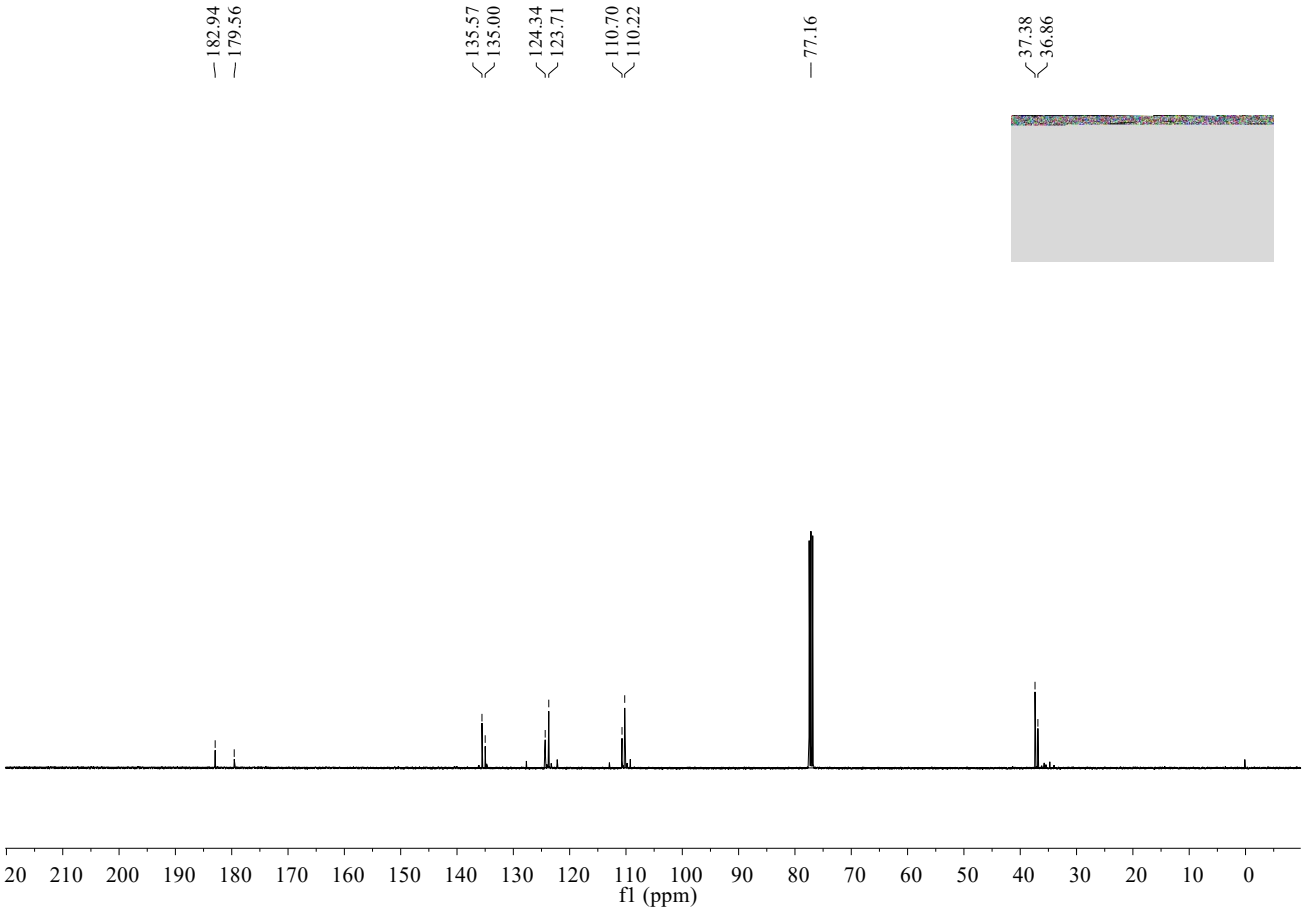
^{13}C NMR Spectra (100 MHz, $CDCl_3$) of 7



^{1}H NMR Spectra (400 MHz, $CDCl_3$) of 8



^{13}C NMR Spectra (100 MHz, $CDCl_3$) of 8



^{1}H NMR Spectra (400 MHz, $CDCl_3$) of the mixture of 3s and 3s′