Supporting Information

Ir(III)-catalyzed quadruple C−H activation of *N*-arylimidazolium and diaryliodonium salts: facile access to polysubstituted imidazo[1,2-*f*]phenanthridiniums

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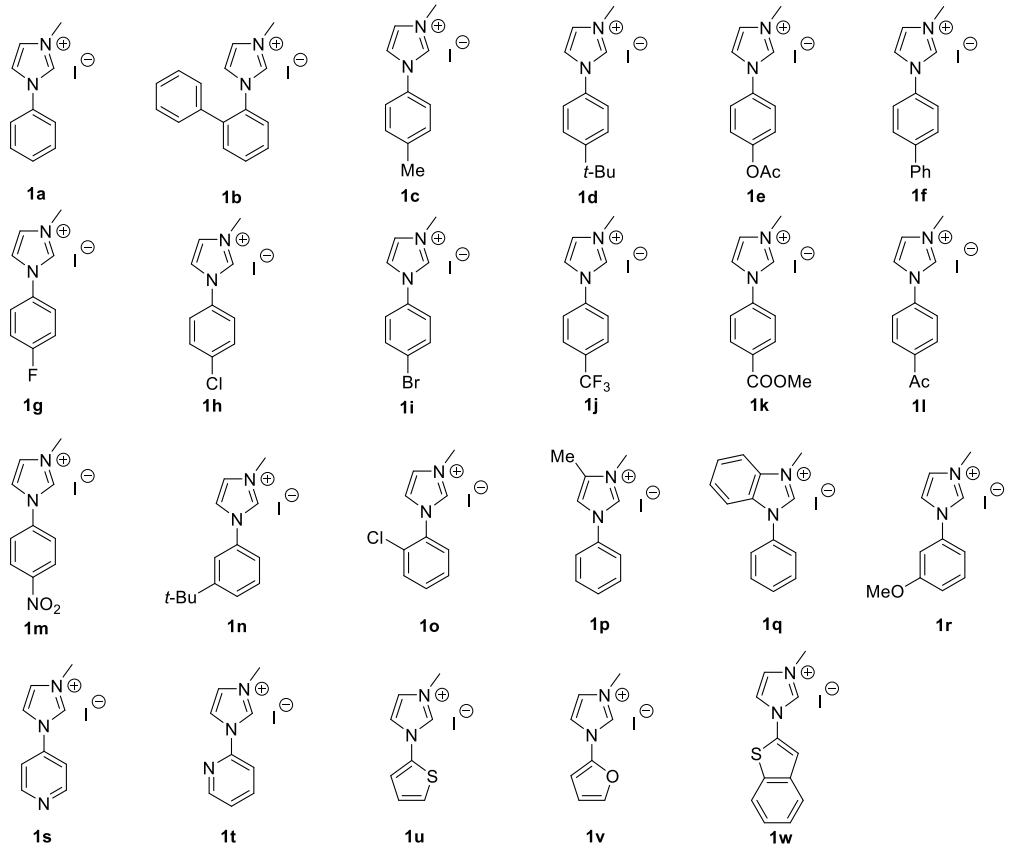
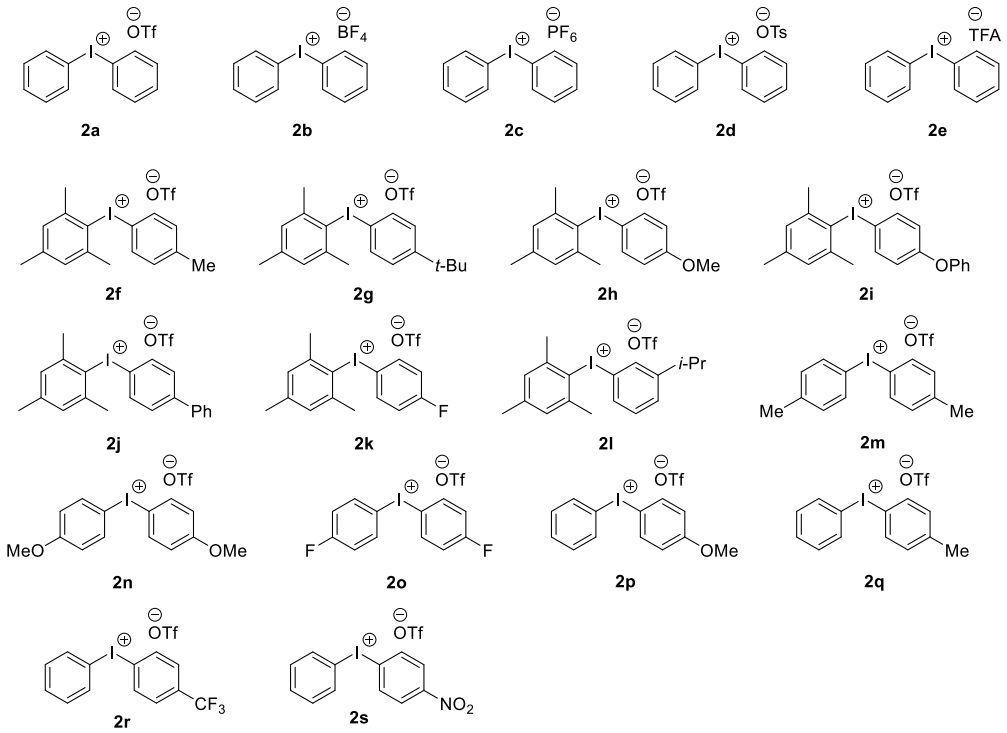
I. General remarks

NMR spectra were recorded on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference (DMSO-d_6: δ = 2.50 ppm; $CDCl_3$: δ = 7.26 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard (DMSO-d_6: δ = 39.52 ppm; $CDCl_3$: δ = 77.16 ppm). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-ITTOF (ESI). X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single-crystal diffractometer.

All reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. $IrCl_3 \cdot 3H_2O$ was purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. $AgSbF_6$ was purchased from Alfa Aesar, 2,2,2-trifluoroethanol was purchased from Shanghai Energy Chemical CO., Ltd. Ag_2CO_3 was purchased from Beijing Ou He Chemical Engineering (china) CO., Ltd.



Scheme S1 List of *N*-arylimidazolium salts **1**.

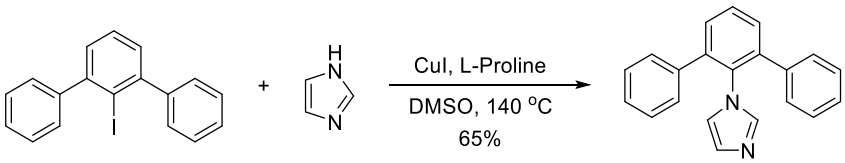


Scheme S2 List of diaryliodonium salts **2**.

$[Cp^*IrCl_2]_2$,[1] *N*-substituted aryl imidazole,[2] imidazolium salts iodide substrates,[3] 3-methyl-1-(pentadeuteriophenyl)-1*H*-imidazolium iodide ([D_5]-**1a**),[3] diaryliodonium trifluoromethanesulfonate,[4,5,6] duteriodiphenyliodonium trifluoromethanesulfonate ([D_{10}]-**4a**)[4,7] were prepared according to the literatures.

II. General procedure for the synthesis of 1-([1,1':3',1''-terphenyl]-2'-yl)-3-methyl-1*H*-imidazolium iodide

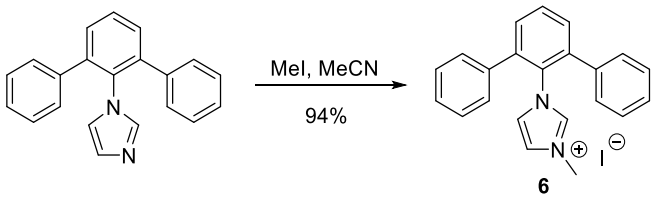
Synthesis of 1-([1,1':3',1''-terphenyl]-2'-yl)-1*H*-imidazole



A 100 mL three-necked flask equipped with a magnetic stir bar was charged with CuI (92.5 mg, 0.5 mmol), *L*-proline (115.1 mg, 1.0 mmol), 2'-iodo-1,1':3',1''-terphenyl (1.83 g, 5.1 mmol), imidazole (340 mg, 5.0 mmol), K_2CO_3 (1.38 g, 10.0 mmol), DMSO (5.0 mL), and the reaction mixture was heated at 150 °C in oil bath for 24 h. After cooling to room temperature, EtOAc (30 mL) was added to that solution and washed with water (2 × 30 mL). Then the whole organic solution was dried over

Na_2SO_4 and filtrate was evaporated under reduced pressure. Final product (963 mg, 3.25 mmol, 65% yield) was separated by silica gel column chromatography using EtOAc and hexane (1:2, v/v) solvent mixture as an eluting solvent.

Synthesis of 1-([1,1':3',1''-terphenyl]-2'-yl)-3-methyl-1*H*-imidazolium iodide 6



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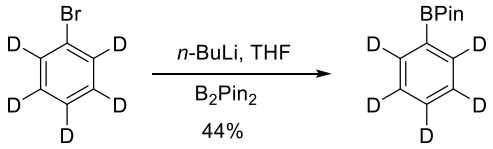
A 25 mL single-necked flask equipped with a magnetic stir bar was charged with 1-([1,1':3',1''-terphenyl]-2'-yl)-1*H*-imidazole (889.0 mg, 3.0 mmol) and iodomethane (852.0 mg, 6.0 mmol), THF (5.0 mL), and the reaction mixture was stirred for 24 h at room temperature. The resultant precipitate (1.24 g, 2.83 mmol, 94% yield) was collected by filtration and washed with hexane and then dried in vacuo. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.16-9.15 (m, 1H), 7.83 (t, J = 8.0, 1H), 7.71 (t, J = 1.7 Hz, 1H), 7.64 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 1.7 Hz, 1H), 7.39-9.35 (m, 6H), 7.24-7.22 (m, 4H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.5, 138.2, 136.5, 131.1, 130.5, 128.7, 128.3, 128.2, 125.8, 123.3, 36.0 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{19}N_2^+$: $[M\text{-}I]^+$, 311.1543, found: 311.1541.

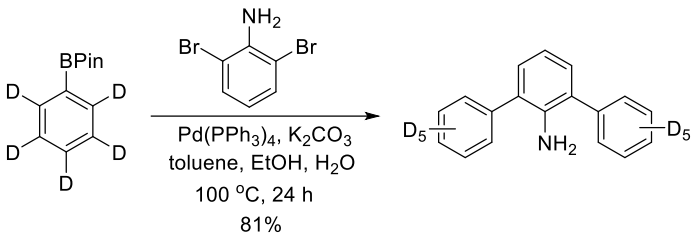
Synthesis of 4,4,5,5-tetramethyl-2-(phenyl-d_5)-1,3,2-dioxaborolane



A flame dried 100 mL three-necked flask equipped with a magnetic stir bar was charged with bromobenzene-d_5 (4.9 g, 30.0 mmol) and THF (40 mL). The solution was cooled to -78 °C and *n*-BuLi (2.5 mol/L in hexane, 36.0 mmol, 1.2 equiv) was added dropwise. After stirring for 0.5 h at the temperature, bis(pinacolato)diboron (36.0 mmol, 1.2 equiv) in THF (5 mL) was added. The mixture was allowed to warm to room temperature and stirred overnight, and saturated aqueous NH_4Cl solution was added. The organic layer was separated, washed with H_2O and aqueous $NaHCO_3$

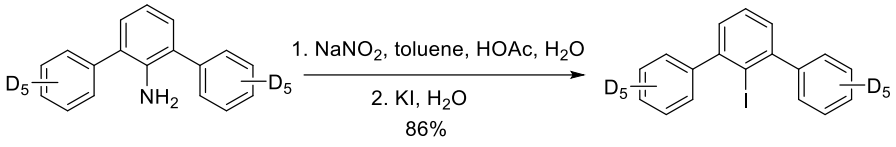
solution, dried over Na_2SO_4, and concentrated in vacuo. Final product (2.8 g, 13.3 mmol, 44% yield) was separated by silica gel column chromatography using DCM and hexane (1:40, v/v) solvent mixture as an eluting solvent.

Synthesis of [1,1':3',1''-terphenyl]-2,2'',3,3'',4,4'',5,5'',6,6''-d_{10}-2'-amine



A 100 mL three-necked flask equipped with a magnetic stir bar was charged with 4,4,5,5-tetramethyl-2-(phenyl-d_5)-1,3,2-dioxaborolane (2.8 g, 13.3 mmol), 2,6-dibromoaniline (1.3 g, 5.3 mmol), $Pd(PPh_3)_4$ (580 mg, 0.5 mmol), Na_2CO_3 (5.3 g, 50 mmol), toluene (25 mL), EtOH (5 mL), H_2O (10 mL), and the reaction mixture was heated at 100 °C in oil bath for 24 h. After cooling to room temperature, DCM (30 mL) was added to that solution and washed with water (2 × 30 mL). Then the whole organic solution was dried over Na_2SO_4 and filtrate was evaporated under reduced pressure. Final product (1.1 g, 4.3 mmol, 81% yield) was separated by silica gel column chromatography using EtOAc and hexane (1:30, v/v) solvent mixture as an eluting solvent.

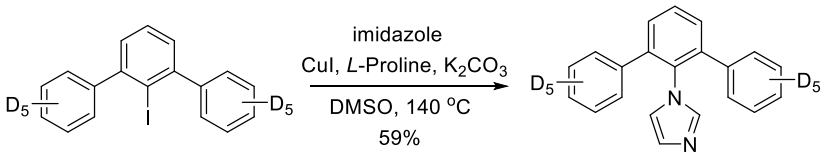
Synthesis of 2'-iodo-1,1':3',1''-terphenyl-2,2'',3,3'',4,4'',5,5'',6,6''-d_{10}



A 100 mL single-necked flask equipped with a magnetic stir bar was charged with [1,1':3',1''-terphenyl]-2,2'',3,3'',4,4'',5,5'',6,6''-d_{10}-2'-amine (1.1 g, 4.3 mmol), toluene and HOAc, The solution was cooled to -0 °C and $NaNO_2$ (840 mg, 12.2 mmol, 2.8 equiv) in H_2O (2 mL) was added dropwise. After stirring for 0.5 h at the temperature, KI (3.0 g, 18.0 mmol, 4.2 equiv) in H_2O (5 mL) was added. The mixture was allowed to warm to room temperature and stirred overnight, and saturated aqueous $NaHSO_3$

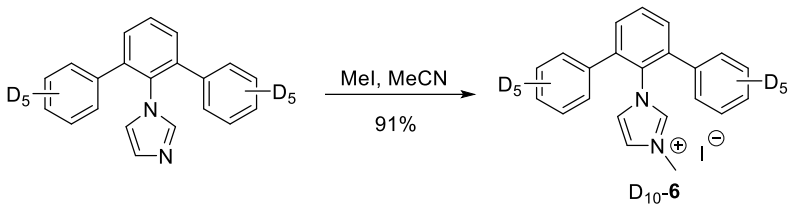
solution was added. The organic layer was separated, washed with H_2O, dried over Na_2SO_4, and concentrated in vacuo. Final product (1.35 g, 3.7 mmol, 86% yield) was separated by silica gel column chromatography using DCM and hexane (1:50, v/v) solvent mixture as an eluting solvent.

Synthesis of 1-([1,1':3',1''-terphenyl]-2'-yl-2,2'',3,3'',4,4'',5,5'',6,6''-*d*$_{10}$)-1H-imidazole



A 100 mL three-necked flask equipped with a magnetic stir bar was charged with CuI (70.5 mg, 0.37 mmol), *L*-proline (85.2 mg, 0.74 mmol), 2'-iodo-1,1':3',1''-terphenyl-2,2'',3,3'',4,4'',5,5'',6,6''-d_{10} (1.35 g, 3.7 mmol), imidazole (252 mg, 3.7 mmol), K_2CO_3 (1.02 g, 7.4 mmol), DMSO (5.0 mL), and the reaction mixture was heated at 150 °C in oil bath for 24 h. After cooling to room temperature, EtOAc (30 mL) was added to that solution and washed with water (2 × 30 mL). Then the whole organic solution was dried over Na_2SO_4 and filtrate was evaporated under reduced pressure. Final product (674 mg, 2.2 mmol, 59% yield) was separated by silica gel column chromatography using EtOAc and hexane (1:2, v/v) solvent mixture as an eluting solvent.

Synthesis of 1-([1,1':3',1''-terphenyl]-2'-yl-2,2'',3,3'',4,4'',5,5'',6,6''-*d*$_{10}$)-3-methyl-1*H*-imidazol-3-ium iodide D$_{10}$-6



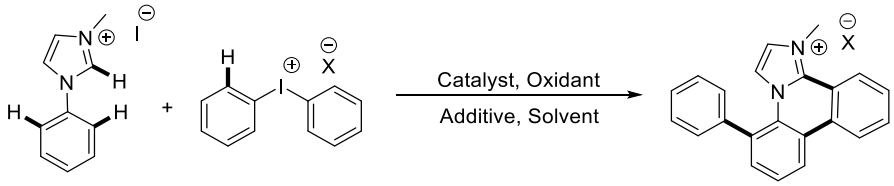
A 25 mL single-necked flask equipped with a magnetic stir bar was charged with 1-([1,1':3',1''-terphenyl]-2'-yl)-1*H*-imidazole (674 mg, 2.2 mmol) and iodomethane (625 mg, 4.4 mmol), THF (5.0 mL), and the reaction mixture was stirred for 24 h at room temperature. The resultant precipitate (897 mg, 2.0 mmol, 91% yield) was

collected by filtration and washed with hexane and then dried in vacuo. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.16 (s, 1H), 7.83 (t, J = 7.7 Hz, 1H), 7.71 (s, 1H), 7.64 (d, J = 7.7 Hz, 2H), 7.59 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.4, 138.2, 136.3, 131.1, 130.5, 128.0-128.3 (m), 128.2-128.1 (m), 127.9-127.8 (m), 127.6-127.5 (m), 125.8, 123.3, 36.0 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_9D_{10}N_2^+$: [M-I]$^+$, 321.2170, found: 321.2172.

III. Optimization of the NHC-directed cascade C−H arylation/annulation

A Schlenk tube with a magnetic stir bar was charged with 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 57.2 mg, 0.2 mmol), diphenyliodonium trifluoromethanesulfonate (**2a**, 215.0 mg, 0.5 mmol), the catalyst, oxidant, and solvent (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 3/1) to provide the desired product.

Table S1 Optimization of NHC-directed cascade C−H arylation/annulation[a].



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

entry	catalyst[b]	oxidant	additive	solvent	yield(%)[c]
1	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2O	—	TFE	66%
2	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2O	—	Toluene	29%
3	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2O	—	DCE	50%
4	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2O	—	1,4-dioxane	N.D.
5	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2O	—	MeOH	N.D.
6	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2O	—	*t*-BuOH	N.D.
7	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2O	—	HFIP	42%
8	—	Ag_2O	—	TFE	N.D.

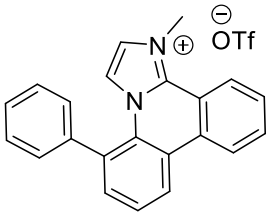
9	$IrCl_3 \cdot 3H_2O$	Ag_2O	—	TFE	N.D.
10	$[Cp^*RhCl_2]_2/AgSbF_6$	Ag_2O	—	TFE	22%
11	$Pd(OAc)_2$	Ag_2O	—	TFE	Trace
12	$[Ru(p\text{-cymene})Cl_2]_2$	Ag_2O	—	TFE	N.D.
13	$[Cp^*IrCl_2]_2/AgSbF_6$	—	—	TFE	Trace
14	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2CO_3	—	TFE	76
15[d]	$[Cp^*IrCl_2]_2/AgSbF_6$	AgOAc	—	TFE	65
16[e]	$[Cp^*IrCl_2]_2/AgSbF_6$	$Cu(OAc)_2$	—	TFE	Trace
17[f]	$[Cp^*IrCl_2]_2/AgSbF_6$	CuO	—	TFE	N.D.
18	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2CO_3	PivOH	TFE	33%
19	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2CO_3	TfOH	TFE	35%
20	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2CO_3	K_2CO_3	TFE	25%
21	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2CO_3	NaOAc	TFE	38%
22	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2CO_3	AgOTf	TFE	75%
23[g]	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2CO_3	—	TFE	51%
24[h]	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2CO_3	—	TFE	17%
25[i]	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2CO_3	—	TFE	N.D.
26[j]	$[Cp^*IrCl_2]_2/AgSbF_6$	Ag_2CO_3	—	TFE	N.D.

[a]Reaction conditions: 3-methyl-1-phenyl-1*H*-imidazolium iodide **1a** (57.2 mg, 0.2 mmol), diphenyliodonium trifluoromethanesulfonate **2a** (215.0 mg, 0.5 mmol), catalyst (2.5 mol%), oxidant (2.0 equiv), additive (1.0 equiv), and solvent (1.0 mL) at 120 °C for 24 h under the nitrogen atmosphere. [b]$AgSbF_6$ (10 mol%) was used. [c]Yield of isolated products. [d]AgOAc (4.0 equiv) was used. [e]$Cu(OAc)_2$ (4.0 equiv) was used. [f]CuO (4.0 equiv) was used. [g]Ph_2IBF_4 (**2b**, 0.5 mmol, 2.5 equiv) was used. [h]Ph_2IPF_6 (**2c**, 0.5 mmol, 2.5 equiv) was used. [i]Ph_2IOTs (**2d**, 0.5 mmol, 2.5 equiv) was used. [j]Ph_2ITFA (**2e**, 0.5 mmol, 2.5 equiv) was used. N.D. = not detected, TFE = 2,2,2-trifluoroethanol, DCE = 1,2-dichloroethane, HOAc = glacial acetic acid, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, MeOH = methanol, PivOH = pivalic acid.

IV. NHC-directed cascade C−H arylation/annulation of *N*-arylimidazolium salts with diaryliodoniums

A Schlenk tube with a magnetic stir bar was charged with $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.9 mg, 10 mol%), Ag_2CO_3 (110.5 mg, 2.0 equiv), *N*-arylimidazolium salts (**1**, 0.2 mmol), diaryliodonium salts (**2**, 0.5 mmol, 2.5 equiv), and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was

concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile) to provide the desired product.

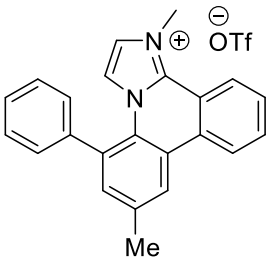


1-Methyl-5-phenylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3a)

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodine (**1a**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 3/1, v/v) afforded the desired product **3a** as a yellow solid (69.7 mg, 76% yield).

Synthesized from 1-([1,1'-biphenyl]-2-yl)-3-methyl-1*H*-imidazolium iodide (**1b**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.3 mmol, 1.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 3/1, v/v) afforded the desired product **3a** as a yellow solid (71.5 mg, 78% yield).

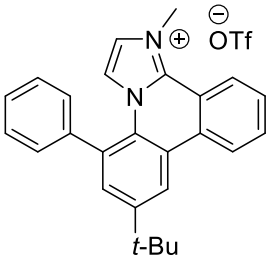
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.06-9.00 (m, 2H), 8.79 (d, J = 8.4 Hz, 1H), 8.14-8.10 (m, 1H), 8.02-7.97 (m, 1H), 7.95 (d, J = 2.4 Hz, 1H), 7.93-7.88 (m, 1H), 7.76 (dd, J = 7.4, 1.3 Hz, 1H), 7.64-7.60 (m, 3H), 7.56-7.53 (m, 2H), 7.06 (d, J = 2.3 Hz, 1H), 4.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.8, 137.9, 134.1, 132.6, 132.5, 130.2, 129.7, 129.1, 129.0, 127.8, 127.1, 125.6, 125.4, 124.4, 124.4, 123.6, 119.1, 117.2, 117.1 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{17}N_2^+$: [M-OTf]$^+$, 309.1386, found: 309.1381.



1,7-Dimethyl-5-phenylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3b)

Synthesized from 3-methyl-1-(*p*-tolyl)-1*H*-imidazol-3-ium iodine (**1c**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3b** as a white solid (68.8 mg, 73% yield).

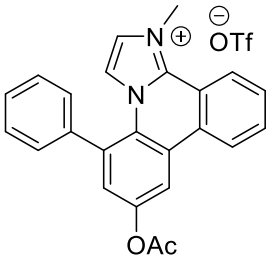
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.04 (d, J = 8.3 Hz, 1H), 8.84 (s, 1H), 8.77 (d, J = 8.3 Hz, 1H), 8.10 (t, J = 7.8 Hz, 1H), 7.98 (t, J = 7.8 Hz, 1H), 7.93 (d, J = 2.3 Hz, 1H), 7.66-7.57 (m, 4H), 7.56-7.49 (m, 2H), 7.02 (d, J = 1.6 Hz, 1H), 4.40 (s, 3H), 2.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.8, 137.7, 137.6, 135.2, 132.4, 132.4, 130.2, 129.7, 129.6, 129.0, 125.6, 125.4, 125.2, 124.4, 124.2, 123.5, 117.2, 116.9, 20.7 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{19}N_2^+$: [M-OTf]$^+$, 323.1543, found: 323.1543.



7-(*tert*-Butyl)-1-methyl-5-phenylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3c)

Synthesized from 1-(4-(*tert*-butyl)phenyl)-3-methyl-1*H*-imidazol-3-ium iodine (**1d**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3c** as a white solid (64.7 mg, 63% yield).

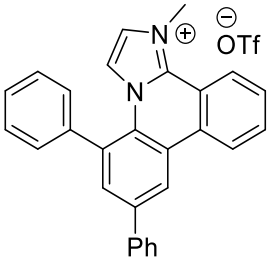
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.18 (d, J = 8.4 Hz, 1H), 8.87 (s, 1H), 8.77 (d, J = 8.5 Hz, 1H), 8.11 (t, J = 7.8 Hz, 1H), 7.98 (t, J = 7.7 Hz, 1H), 7.93 (s, 1H), 7.72 (s, 1H), 7.64-7.59 (m, 3H), 7.58-7.51 (m, 2H), 7.00 (d, J = 1.6 Hz, 1H), 4.41 (s, 3H), 1.49 (s, 9H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 150.5, 139.0, 137.7, 132.44, 132.41, 131.4, 130.3, 129.7, 129.6, 129.2, 129.1, 125.6, 125.4, 125.2, 124.7, 123.4, 120.6, 117.2, 116.9, 35.1, 31.0 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{25}N_2^+$: [M-OTf]$^+$, 365.2012, found: 365.2011.



7-Acetoxy-1-methyl-5-phenylimidazo[1,2-f]phenanthridinium trifluoromethanesulfonate (3d)

Synthesized from 1-(4-acetoxyphenyl)-3-methyl-1*H*-imidazol-3-ium iodine (**1e**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 3/1, v/v) afforded the desired product **3d** as a yellow solid (80.4 mg, 78% yield).

^{1}H NMR (400 MHz, DMSO-d_6): 9.41 (s, 1H), 9.13 (d, J = 8.3 Hz, 1H), 8.82 (d, J = 8.3 Hz, 1H), 8.22-8.10 (m, 2H), 8.04 (t, J = 7.7 Hz, 1H), 7.98 (d, J = 2.0 Hz, 1H), 7.64-7.59 (m, 5H), 7.11 (d, J = 1.9 Hz, 1H), 4.43 (s, 3H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.1, 138.5, 138.1, 133.4, 133.3, 132.9, 130.3, 130.0, 129.9, 129.7, 129.5, 129.0, 128.5, 126.0, 125.5, 125.0, 124.7, 124.0, 117.5, 117.4, 52.9 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{19}N_2O_2^+$: $[M\text{-}OTf]^+$, 367.1441, found: 367.1446.

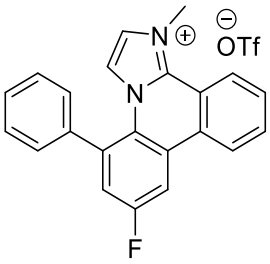


1-Methyl-5,7-diphenylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3e)

Synthesized from 1-([1,1'-biphenyl]-4-yl)-3-methyl-1*H*-imidazol-3-ium iodine (**1f**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3e** as a white solid (56.7 mg, 53% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.31 (d, J = 8.2 Hz, 1H), 9.21 (s, 1H), 8.80 (d, J = 8.5 Hz, 1H), 8.13 (t, J = 7.9 Hz, 1H), 8.08-7.99 (m, 4H), 7.96 (d, J = 1.6 Hz, 1H),

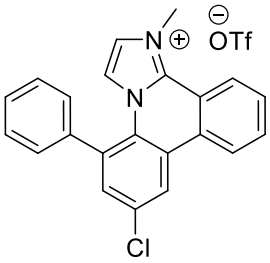
7.64 (s, 5H), 7.58 (t, J = 7.5 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.06 (d, J = 2.2 Hz, 1H), 4.43 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.3, 138.7, 138.0, 137.9, 133.3, 132.5, 132.2, 130.3, 129.8, 129.7, 129.2, 129.2, 128.6, 127.6, 126.5, 125.7, 125.4, 125.1, 124.3, 121.8, 117.4, 117.1 ppm. HRMS (ESI$^+$): calcd for $C_{28}H_{21}N_2^+$: [M-OTf]$^+$, 385.1699, found: 385.1693.



7-Fluoro-1-methyl-5-phenylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3f)

Synthesized from 1-(4-fluorophenyl)-3-methyl-1*H*-imidazol-3-ium iodine (**1g**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3f** as a white solid (51.5 mg, 54% yield).

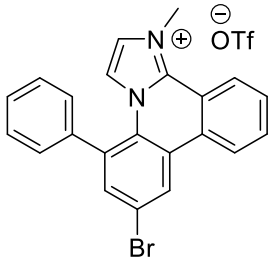
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.05 (d, J = 8.2 Hz, 1H), 8.93 (dd, J = 10.1, 2.5 Hz, 1H), 8.79 (d, J = 8.4 Hz, 1H), 8.12 (t, J = 7.9 Hz, 1H), 8.03 (t, J = 7.7 Hz, 1H), 7.94 (d, J = 2.1 Hz, 1H), 7.73 (dd, J = 8.3, 2.6 Hz, 1H), 7.66-7.60 (m, 3H), 7.58-7.56 (m, 2H), 7.00 (d, J = 2.2 Hz, 1H), 4.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.0 (d, J_{CF} = 245.6 Hz), 137.7 (d, J_{CF} = 3.6 Hz), 135.4 (d, J_{CF} = 9.2 Hz), 132.6, 130.4, 129.8, 129.7 (d, J_{CF} = 3.4 Hz), 129.5, 129.0, 126.0 (d, J_{CF} = 9.3 Hz), 125.6 (d, J_{CF} = 22.8 Hz), 125.0, 124.1 (d, J_{CF} = 2.9 Hz), 121.6, 121.3, 117.7, 117.5, 117.2, 110.3 (d, J_{CF} = 24.8 Hz) ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{16}FN_2^+$: [M-OTf]$^+$, 327.1292, found: 327.1290.



7-Chloro-1-methyl-5-phenylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3g)

Synthesized from 1-(4-chlorophenyl)-3-methyl-1*H*-imidazol-3-ium iodine (**1h**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3g** as a white solid (75.8 mg, 77% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.11 (d, J = 8.5 Hz, 2H), 8.79 (d, J = 8.2 Hz, 1H), 8.12 (t, J = 7.8 Hz, 1H), 8.02 (t, J = 7.7 Hz, 1H), 7.95 (d, J = 1.2 Hz, 1H), 7.83 (s, 1H), 7.63-7.62 (m, 3H), 7.61-7.55 (m, 2H), 7.00 (s, 1H), 4.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.0, 137.5, 134.6, 133.2, 132.6, 132.5, 130.4, 129.8, 129.6, 129.3, 129.0, 126.2, 125.8, 125.5, 125.0, 123.8, 117.6, 117.2 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{16}{}^{35}ClN_2^+$: $[M\text{-}OTf]^+$, 343.0997, found: 343.0995; calcd for $C_{22}H_{16}{}^{37}ClN_2^+$: $[M\text{-}OTf]^+$, 345.0968, found: 345.0975.

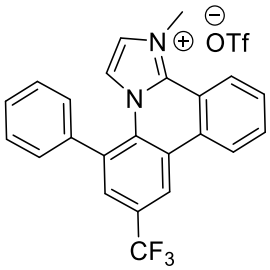


7-Bromo-1-methyl-5-phenylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3h)

Synthesized from 1-(4-bromophenyl)-3-methyl-1*H*-imidazol-3-ium iodine (**1i**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3h** as a white solid (68.8 mg, 64% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.23 (s, 1H), 9.12 (d, J = 8.3 Hz, 1H), 8.79 (d, J = 8.2 Hz, 1H), 8.11 (t, J = 7.7 Hz, 1H), 8.02 (t, J = 7.6 Hz, 1H), 7.94 (d, J = 5.5 Hz, 2H), 7.62 (d, J = 3.4 Hz, 3H), 7.59-7.53 (m, 2H), 7.00 (s, 1H), 4.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.0, 137.5, 134.6, 133.2, 132.6, 132.5, 130.4, 129.8, 129.6, 129.3, 129.0, 126.2, 125.8, 125.5, 125.0, 123.8, 117.6, 117.2 ppm.

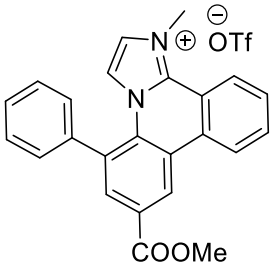
HRMS (ESI$^+$): calcd for $C_{22}H_{16}{}^{79}BrN_2^+$: $[M\text{-}OTf]^+$, 387.0492, found: 387.0491; calcd for $C_{22}H_{16}{}^{81}BrN_2^+$: $[M\text{-}OTf]^+$, 389.0491, found: 389.0484.



1-Methyl-5-phenyl-7-(trifluoromethyl)imidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3i)

Synthesized from 3-methyl-1-(4-(trifluoromethyl)phenyl)-1*H*-imidazol-3-ium iodine (**1j**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 3/1, v/v) afforded the desired product **3i** as a yellow solid (63.0 mg, 60% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.36 (s, 1H), 9.27 (d, J = 8.4 Hz, 1H), 8.83 (d, J = 8.3 Hz, 1H), 8.15 (t, J = 7.8 Hz, 1H), 8.10-8.03 (m, 2H), 7.98 (d, J = 2.1 Hz, 1H), 7.66-7.62 (m, 5H), 7.09 (d, J = 2.2 Hz, 1H), 4.44 (s, 3H). ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.6, 137.6, 134.1, 132.8, 130.6, 129.8, 129.6, 129.56 (q, J_{CF} = 3.1 Hz), 129.52, 129.1, 128.0 (q, J_{CF} = 32.8 Hz), 125.9, 125.5, 125.1, 124.6, 123.6 (q, J_{CF} = 271.7 Hz), 121.8 (q, J_{CF} = 3.7 Hz), 117.6, 117.5 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{16}F_3N_2^+$: $[M\text{-}OTf]^+$, 377.1260, found: 377.1263.

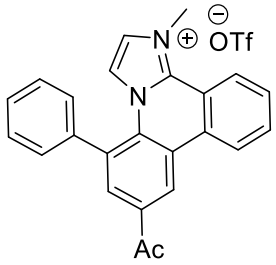


7-(Methoxycarbonyl)-1-methyl-5-phenylimidazo[1,2-*f*]phenanthridin-1-ium trifluoromethanesulfonate (3j)

Synthesized from 1-(4-(methoxycarbonyl)phenyl)-3-methyl-1*H*-imidazol-3-ium iodine (**1k**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5

mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3j** as a white solid (63.1 mg, 61% yield).

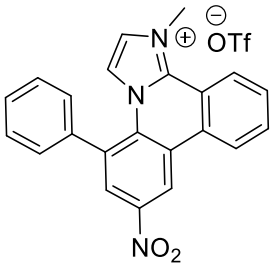
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.34 (s, 1H), 9.07 (d, J = 8.4 Hz, 1H), 8.80 (d, J = 8.2 Hz, 1H), 8.15-8.08 (m, 2H), 8.03 (t, J = 7.7 Hz, 1H), 7.99 (s, 1H), 7.68-7.62 (m, 3H), 7.60 (d, J = 4.6 Hz, 2H), 7.11 (s, 1H), 4.43 (s, 3H), 3.99 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.0, 138.5, 138.0, 133.4, 133.3, 132.9, 130.3, 129.9, 129.9, 129.6, 129.5, 129.0, 128.4, 126.0, 125.5, 124.9, 124.6, 124.0, 117.4, 117.4, 52.9 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{19}N_2O_2^+$: $[M\text{-}OTf]^+$, 367.1441, found: 367.1438.



7-Acetyl-1-methyl-5-phenylimidazo[1,2-*f*]phenanthridin-1-ium trifluoromethanesulfonate (3k)

Synthesized from 1-(4-acetylphenyl)-3-methyl-1*H*-imidazol-3-ium iodine (**1l**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3k** as a white solid (53.3 mg, 53% yield).

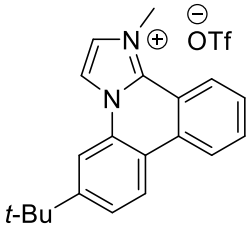
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.34 (s, 1H), 9.07 (d, J = 8.4 Hz, 1H), 8.80 (d, J = 8.2 Hz, 1H), 8.15-8.08 (m, 2H), 8.03 (t, J = 7.7 Hz, 1H), 7.99 (s, 1H), 7.68-7.62 (m, 3H), 7.60 (d, J = 4.6 Hz, 2H), 7.11 (s, 1H), 4.43 (s, 3H), 3.99 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 197.3, 138.5, 138.3, 135.1, 133.1, 132.7, 132.5, 130.2, 130.0, 129.82, 129.81, 129.4, 129.1, 126.0, 125.5, 124.9, 124.3, 124.0, 117.5, 117.3, 27.4 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{19}N_2O^+$: $[M\text{-}OTf]^+$, 351.1492, found: 351.1488.



1-Methyl-7-nitro-5-phenylimidazo[1,2-*f*]phenanthridin-1-ium trifluoromethanesulfonate (3l)

Synthesized from 3-methyl-1-(4-nitrophenyl)-1*H*-imidazol-3-ium iodine (**1m**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3l** as a white solid (35.2 mg, 35% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.72 (s, 1H), 9.25 (d, J = 8.4 Hz, 1H), 8.84 (d, J = 8.2 Hz, 1H), 8.42 (s, 1H), 8.18 (t, J = 7.8 Hz, 1H), 8.09 (t, J = 7.7 Hz, 1H), 7.99 (s, 1H), 7.66 (s, 5H), 7.12 (s, 1H), 4.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 145.6, 137.3, 134.3, 133.0, 130.9, 130.9, 129.94, 129.86, 129.4, 129.0, 127.3, 126.1, 125.6, 125.3, 124.9, 119.5, 117.8, 117.6 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{16}N_3O_2^+$: $[M\text{-}OTf]^+$, 354.1237, found: 354.1234.

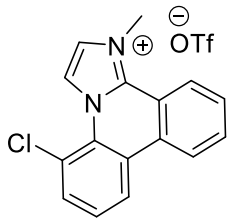


6-(*tert*-Butyl)-1-methylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3m)

Synthesized from 1-(3-(*tert*-butyl)phenyl)-3-methyl-1*H*-imidazol-3-ium iodine (**1n**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.3 mmol, 1.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3m** as a white solid (63.1 mg, 72% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.42 (d, J = 2.0 Hz, 1H), 8.97 (d, J = 8.3 Hz, 1H), 8.87 (d, J = 8.7 Hz, 1H), 8.79 (d, J = 8.4 Hz, 1H), 8.48 (s, 1H), 8.40 (d, J = 2.0 Hz, 1H), 8.07 (t, J = 7.8 Hz, 1H), 7.93 (dd, J = 17.9, 8.5 Hz, 2H), 4.50 (s, 3H), 1.47 (s,

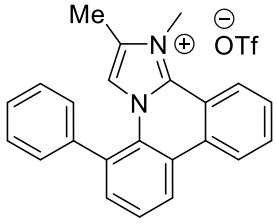
9H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 154.6, 136.6, 132.3, 129.7, 129.3, 129.2, 127.3, 125.9, 125.4, 124.6, 124.0, 119.3, 117.0, 114.5, 113.7, 35.5, 31.0 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{21}N_2^+$: [M-OTf]$^+$, 289.1699, found: 289.1695.



5-Chloro-1-methylimidazo[1,2-*f*]phenanthridin-1-ium trifluoromethanesulfonate (3n)

Synthesized from 1-(2-chlorophenyl)-3-methyl-1*H*-imidazol-3-ium iodine (**1o**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.3 mmol, 1.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3n** as a white solid (35.1 mg, 42% yield).

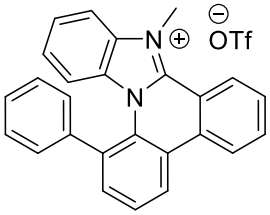
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.65 (d, J = 2.1 Hz, 1H), 9.00 (d, J = 8.3 Hz, 2H), 8.81 (d, J = 8.3 Hz, 1H), 8.35 (d, J = 2.1 Hz, 1H), 8.14-8.05 (m, 2H), 8.00 (t, J = 7.7 Hz, 1H), 7.84 (t, J = 8.0 Hz, 1H), 4.51 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.2, 133.8, 132.7, 130.2, 129.6, 128.7, 126.7, 126.3, 125.5, 125.4, 124.6, 124.5, 122.6, 117.9, 117.3 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{12}{}^{35}ClN_2^+$: [M-OTf]$^+$, 267.0684, found: 267.0683; calcd for $C_{16}H_{12}{}^{37}ClN_2^+$: [M-OTf]$^+$, 269.0655, found: 269.0650.



1,2-Dimethyl-5-phenylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3o)

Synthesized from 3,4-dimethyl-1-phenyl-1H-imidazol-3-ium iodine (**1p**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3o** as a white solid (42.5 mg, 45% yield).

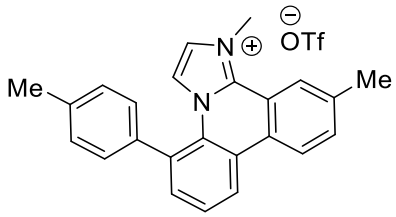
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.02 (dd, J = 16.2, 8.3 Hz, 2H), 8.83 (d, J = 8.4 Hz, 1H), 8.10 (t, J = 7.7 Hz, 1H), 7.98 (t, J = 7.7 Hz, 1H), 7.89 (t, J = 7.9 Hz, 1H), 7.76 (d, J = 7.3 Hz, 1H), 7.65-7.58 (m, 3H), 7.57-7.49 (m, 2H), 6.88 (s, 1H), 4.24 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.7, 138.1, 134.1, 132.6, 132.4, 132.3, 130.2, 129.7, 129.1, 129.0, 127.7, 126.8, 125.4, 124.4, 124.3, 123.5, 117.0, 114.7, 35.7, 9.8 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{19}N_2^+$: [M-OTf]$^+$, 323.1543, found: 323.1541.



9-Methyl-1-phenylbenzo[4,5]imidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (3p)

Synthesized from 3-methyl-1-phenyl-1*H*-benzo[*d*]imidazol-3-ium iodine (**1q**, 0.2 mmol) and diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **3p** as a white solid (55.8 mg, 55% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.05 (t, J = 8.5 Hz, 2H), 8.99 (d, J = 7.9 Hz, 1H), 8.21 (t, J = 8.6 Hz, 2H), 8.09-7.97 (m, 3H), 7.59-7.56 (m, 3H), 7.26 (d, J = 8.6 Hz, 4H), 7.13 (d, J = 7.9 Hz, 1H), 4.58 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.9, 134.2, 134.0, 133.1, 132.9, 132.4, 131.0, 130.2, 129.6, 129.2, 129.1, 128.5, 128.4, 128.1, 127.6, 126.8, 125.7, 124.4, 124.2, 123.5, 117.4, 116.7, 112.6, 35.5 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{29}N_2^+$: [M-OTf]$^+$, 359.1543, found: 359.1543.

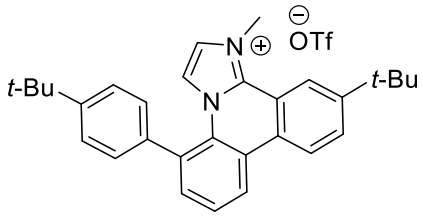


1,11-Dimethyl-5-(*p*-tolyl)imidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (4a)

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 0.2 mmol) and mesityl(*p*-tolyl)iodonium trifluoromethanesulfonate (**2f**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **4a** as a yellow solid (60.4 mg, 62% yield).

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 0.2 mmol) and di-*p*-tolyliodonium trifluoromethanesulfonate (**2m**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **4a** as a yellow solid (58.4 mg, 60% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.93 (t, J = 7.8 Hz, 2H), 8.55 (s, 1H), 8.00 (s, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.86 (t, J = 7.8 Hz, 1H), 7.68 (d, J = 7.3 Hz, 1H), 7.41 (s, 4H), 7.11 (d, J = 2.0 Hz, 1H), 4.44 (s, 3H), 2.66 (s, 3H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 140.3, 138.9, 138.1, 136.3, 134.2, 134.1, 133.0, 130.6, 129.3, 128.5, 128.3, 128.1, 127.2, 126.0, 125.2, 124.7, 124.4, 124.0, 117.6, 117.5, 21.6, 21.4 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{21}N_2^+$: $[M\text{-}OTf]^+$, 337.1699, found: 337.1699.

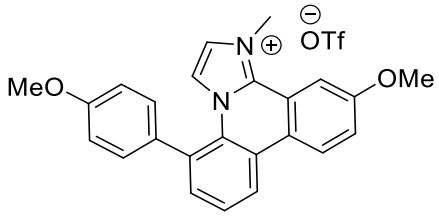


11-(*tert*-Butyl)-5-(4-(*tert*-butyl)phenyl)-1-methylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (4b)

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 0.2 mmol) and (4-(*tert*-butyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (**2g**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **4b** as a yellow solid (60.5 mg, 53% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.99-8.92 (m, 2H), 8.56 (s, 1H), 8.20 (d, J = 8.8 Hz, 1H), 7.98 (s, 1H), 7.87 (t, J = 7.8 Hz, 1H), 7.73 (d, J = 7.4 Hz, 1H), 7.62 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 7.06 (s, 1H), 4.46 (s, 3H), 1.49 (s, 9H), 1.39 (s, 9H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 152.4, 151.6, 138.0, 135.9, 133.8, 132.6, 130.6, 128.7, 128.1, 127.8, 127.0, 126.5, 125.6, 124.4, 124.0, 123.5, 121.0,

117.1, 117.0, 35.3, 34.6, 31.2, 30.8 ppm. HRMS (ESI^+): calcd for $C_{30}H_{33}N_2^+$: $[M\text{-}OTf]^+$, 421.2638, found: 421.2631.

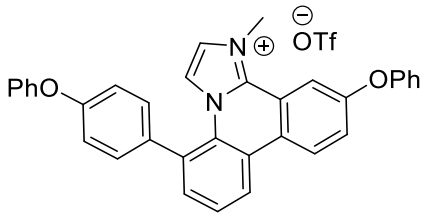


11-Methoxy-5-(4-methoxyphenyl)-1-methylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (4c)

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 0.2 mmol) and mesityl(4-methoxyphenyl)iodonium trifluoromethanesulfonate (**2h**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **4c** as a yellow solid (52.8 mg, 51% yield).

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 0.2 mmol) and bis(4-methoxyphenyl)iodonium trifluoromethanesulfonate (**2n**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **4c** as a yellow solid (57.0 mg, 55% yield).

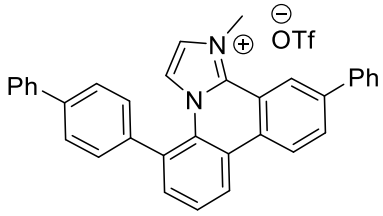
^1H NMR (400 MHz, DMSO-d_6): δ = 8.94 (d, J = 9.2 Hz, 1H), 8.86 (d, J = 7.6 Hz, 1H), 8.06 (d, J = 2.0 Hz, 1H), 7.94 (d, J = 2.0 Hz, 1H), 7.82 (t, J = 8.0 Hz, 1H), 7.72 (dd, J = 9.2, 2.4 Hz, 1H), 7.64 (d, J = 7.3 Hz, 1H), 7.44 (d, J = 8.7 Hz, 2H), 7.21-7.09 (m, 3H), 4.47 (s, 3H), 4.07 (s, 3H), 3.87 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.6, 159.5, 137.4, 133.1, 132.4, 130.8, 130.2, 129.5, 127.7, 126.4, 126.3, 125.7, 123.7, 123.6, 123.4, 120.7, 118.3, 117.2, 115.0, 114.0, 107.8, 56.0, 55.3 ppm. HRMS (ESI^+): calcd for $C_{24}H_{21}N_2O_2^+$: $[M\text{-}OTf]^+$, 369.1598, found: 369.1594.



1-Methyl-11-phenoxy-5-(4-phenoxyphenyl)imidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (4d)

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 0.2 mmol) and mesityl(4-phenoxyphenyl)iodonium trifluoromethanesulfonate (**2i**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 3/1, v/v) afforded the desired product **4d** as a yellow solid (51.4 mg, 40% yield).

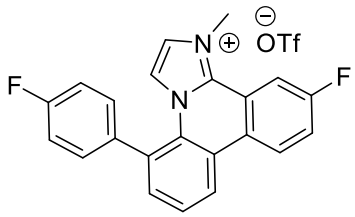
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.04 (d, J = 9.3 Hz, 1H), 8.91 (d, J = 8.1 Hz, 1H), 8.29 (d, J = 2.3 Hz, 1H), 7.99 (d, J = 2.2 Hz, 1H), 7.88 (t, J = 7.8 Hz, 1H), 7.74 (d, J = 7.3 Hz, 1H), 7.70 (dd, J = 9.2, 2.2 Hz, 1H), 7.55-7.46 (m, 6H), 7.30 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 2.2 Hz, 1H), 7.21 (m, 7H), 4.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 157.5, 157.3, 156.0, 155.5, 137.3, 133.7, 133.3, 132.1, 130.8, 130.6, 130.3, 127.9, 127.0, 126.7, 126.0, 125.7, 124.8, 124.2, 124.0, 122.9, 119.4, 119.4, 119.2, 118.6, 113.5 ppm. HRMS (ESI$^+$): calcd for $C_{34}H_{25}N_2O_2^+$: [M-OTf]$^+$, 493.1911, found: 493.1907.



5-([1,1'-Biphenyl]-4-yl)-1-methyl-11-phenylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (4e)

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 0.2 mmol) and [1,1'-biphenyl]-4-yl(mesityl)iodonium trifluoromethanesulfonate (**2j**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **4e** as a yellow solid (59.8 mg, 49% yield).

^{1}H NMR (400 MHz, DMSO-d_6):δ 9.13 (d, J = 8.8 Hz, 1H), 9.06 (d, J = 8.3 Hz, 1H), 8.89 (s, 1H), 8.43 (d, J = 8.7 Hz, 1H), 8.05-7.99 (m, 3H), 7.94 (t, J = 7.2 Hz, 3H), 7.83 (t, J = 7.2 Hz, 3H), 7.67-7.60 (m, 4H), 7.58-7.51 (m, 3H), 7.44 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 1.8 Hz, 1H), 4.58 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 141.0, 140.4, 139.0, 138.3, 137.8, 137.8, 134.1, 132.3, 131.0, 129.7, 129.4, 129.3, 129.2, 128.8, 128.1, 127.9, 127.8, 127.5, 127.1, 126.8, 125.9, 125.3, 124.5, 123.5, 122.7, 117.9, 117.5 ppm. HRMS (ESI$^+$): calcd for $C_{34}H_{25}N_2^+$: [M-OTf]$^+$, 461.2012, found: 461.2010.

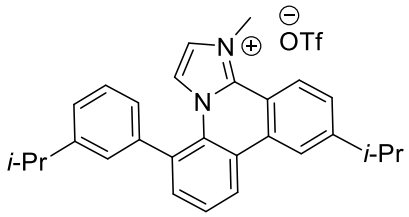


11-Fluoro-5-(4-fluorophenyl)-1-methylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (4f)

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 0.2 mmol) and (4-fluorophenyl)(mesityl)iodonium trifluoromethanesulfonate (**2k**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 3/1, v/v) afforded the desired product **4f** as a yellow solid (50.4 mg, 51% yield).

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 0.2 mmol) and bis(4-fluorophenyl)iodonium trifluoromethanesulfonate (**2o**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 3/1, v/v) afforded the desired product **4f** as a yellow solid (62.3 mg, 63% yield).

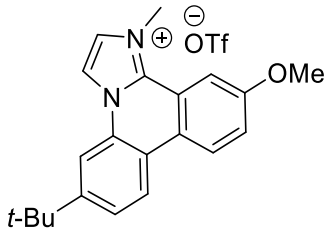
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.14 (dd, J = 9.2, 5.4 Hz, 1H), 8.99 (d, J = 8.3 Hz, 1H), 8.56 (d, J = 9.9 Hz, 1H), 8.05 (t, J = 8.4 Hz, 1H), 7.97 (s, 1H), 7.90 (t, J = 7.8 Hz, 1H), 7.75 (d, J = 7.4 Hz, 1H), 7.62-7.58 (m, 2H), 7.46 (t, J = 8.5 Hz, 1H), 7.19 (s, 1H), 4.44 (s, 3H). ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.5 (d, J_{CF} = 245.5 Hz), 161.8 (d, J_{CF} = 246.7 Hz), 137.1 (d, J_{CF} = 2.9 Hz), 134.9 (d, J_{CF} = 3.1 Hz), 134.2, 131.7, 131.3 (d, J_{CF} = 8.3 Hz), 127.9, 127.7 (d, J_{CF} = 9.2 Hz), 127.1 (d, J_{CF} = 2.4 Hz), 127.0, 126.1, 124.5, 123.3, 120.8 (d, J_{CF} = 22.6 Hz), 118.6 (d, J_{CF} = 9.8 Hz), 117.8, 116.7 (d, J_{CF} = 21.4 Hz), 111.4 (d, J_{CF} = 25.6 Hz) ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{15}F_2N_2^+$: $[M\text{-}OTf]^+$, 345.1198, found: 345.1195.



10-Isopropyl-5-(3-isopropylphenyl)-1-methylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (4g)

Synthesized from 3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (**1a**, 0.2 mmol) and (3-isopropylphenyl)(mesityl)iodonium trifluoromethanesulfonate (**2l**, 0.5 mmol, 2.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **4g** as a yellow solid (44.5 mg, 41% yield).

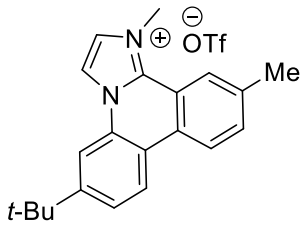
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.09 (d, J = 8.3 Hz, 1H), 8.88 (s, 1H), 8.70 (d, J = 8.7 Hz, 1H), 7.94-7.84 (m, 3H), 7.76 (d, J = 7.2 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.37 (d, J = 6.8 Hz, 2H), 6.99-6.94 (m, 1H), 4.39 (s, 3H), 3.32-3.27 (m, 1H), 2.99-2.89 (m, 1H), 1.41 (d, J = 6.9 Hz, 6H), 1.22 (d, J = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.7, 150.0, 138.7, 138.1, 133.9, 132.8, 130.5, 129.8, 128.2, 127.6, 127.2, 127.0, 126.4, 125.6, 125.2, 124.5, 123.6, 121.9, 116.8, 115.3, 34.1, 33.5, 23.8, 23.6 ppm. HRMS (ESI$^+$): calcd for $C_{28}H_{29}N_2^+$: [M-OTf]$^+$, 393.2325, found: 393.2318.



6-(*tert*-Butyl)-11-methoxy-1-methylimidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonate (4h)

Synthesized from 1-(3-(*tert*-butyl)phenyl)-3-methyl-1*H*-imidazol-3-ium iodide (**1n**, 0.2 mmol) and mesityl(4-methoxyphenyl)iodonium trifluoromethanesulfonate (**2h**, 0.3 mmol, 1.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **4h** as a white solid (45.2 mg, 48% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.38 (d, J = 1.6 Hz, 1H), 8.89 (d, J = 9.2 Hz, 1H), 8.77 (d, J = 8.7 Hz, 1H), 8.43 (s, 1H), 8.36 (s, 1H), 8.07 (d, J = 2.3 Hz, 1H), 7.87 (d, J = 8.7 Hz, 1H), 7.70 (dd, J = 9.1, 2.1 Hz, 1H), 4.55 (s, 3H), 4.06 (s, 3H), 1.46 (s, 9H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.3, 153.3, 136.2, 128.4, 127.4, 126.0, 125.9, 124.2, 123.3, 120.5, 119.4, 118.1, 114.5, 113.6, 107.8, 56.0, 35.4, 31.1 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{23}N_2O^+$: [M-OTf]$^+$, 319.1805, found: 319.1805.

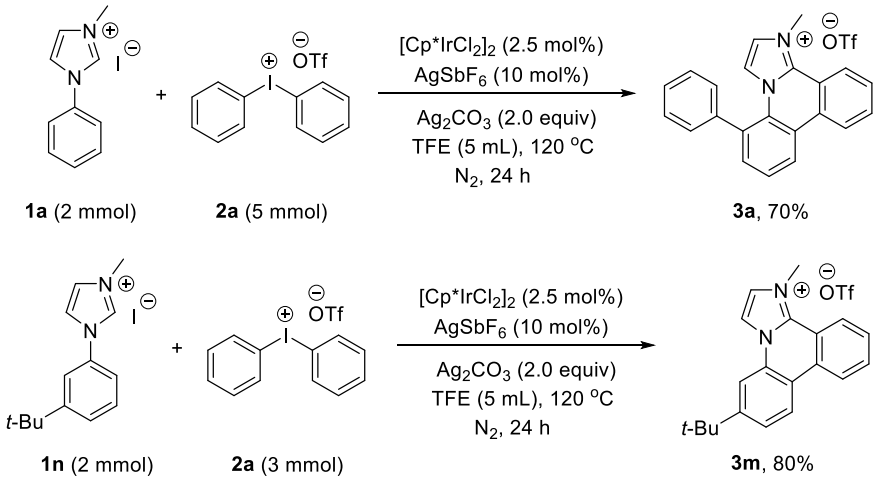


6-(*tert*-Butyl)-1,11-dimethylimidazo[1,2-*f*]phenanthridin-1-ium trifluoromethanesulfonate (4i)

Synthesized from 1-(3-(*tert*-butyl)phenyl)-3-methyl-1*H*-imidazol-3-ium iodide (**1n**, 0.2 mmol) and mesityl(p-tolyl)iodonium trifluoromethanesulfonate (**2f**, 0.3 mmol, 1.5 equiv), and purification *via* silica gel column chromatography (CH_2Cl_2/acetonitrile = 4/1, v/v) afforded the desired product **4i** as a white solid (57.8 mg, 64% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.36 (d, J = 1.8 Hz, 1H), 8.82 (dd, J = 13.9, 8.6 Hz, 2H), 8.52 (s, 1H), 8.44 (s, 1H), 8.35 (d, J = 2.1 Hz, 1H), 7.89 (dd, J = 8.4, 4.8 Hz, 2H), 4.50 (s, 3H), 2.64 (s, 3H), 1.47 (s, 9H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 154.1, 139.3, 133.6, 129.0, 127.5, 127.3, 125.8, 124.7, 124.5, 123.9, 119.3, 117.0, 114.4, 113.6, 31.0, 30.6, 21.3 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{23}N_2^+$: [M-OTf]$^+$, 303.1856, found: 303.1852.

V. Scale-up synthesis

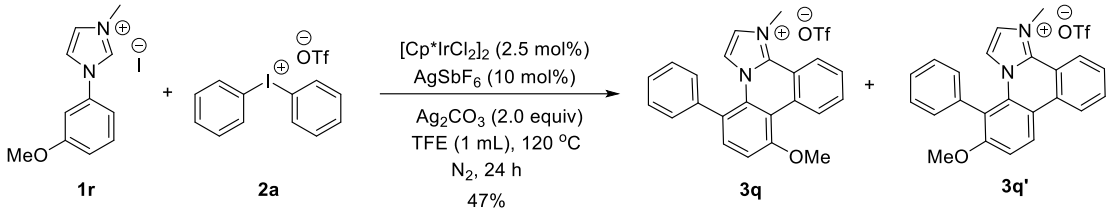


Scheme S3 Scale-up synthesis of **3a** and **3m**.

A 100 mL Schlenk tube with a magnetic stir bar was charged with *N*-methyl-*N*-phenylimidazolium iodide **1a** or **1n** (2.0 mmol), diphenyliodonium trifluoromethanesulfonate **2a**, $[Cp^*IrCl_2]_2$ (40.0 mg, 0.05 mmol, 2.5 mol%), $AgSbF_6$

(69.0 mg, 0.20 mmol, 10 mol%), Ag_2CO_3 (1.11 g, 4.0 mmol, 2.0 equiv) and TFE (5.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 20 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 80-100 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 3/1, v/v) to provide **3a** in 70% yield or **3m** in 80% yield.

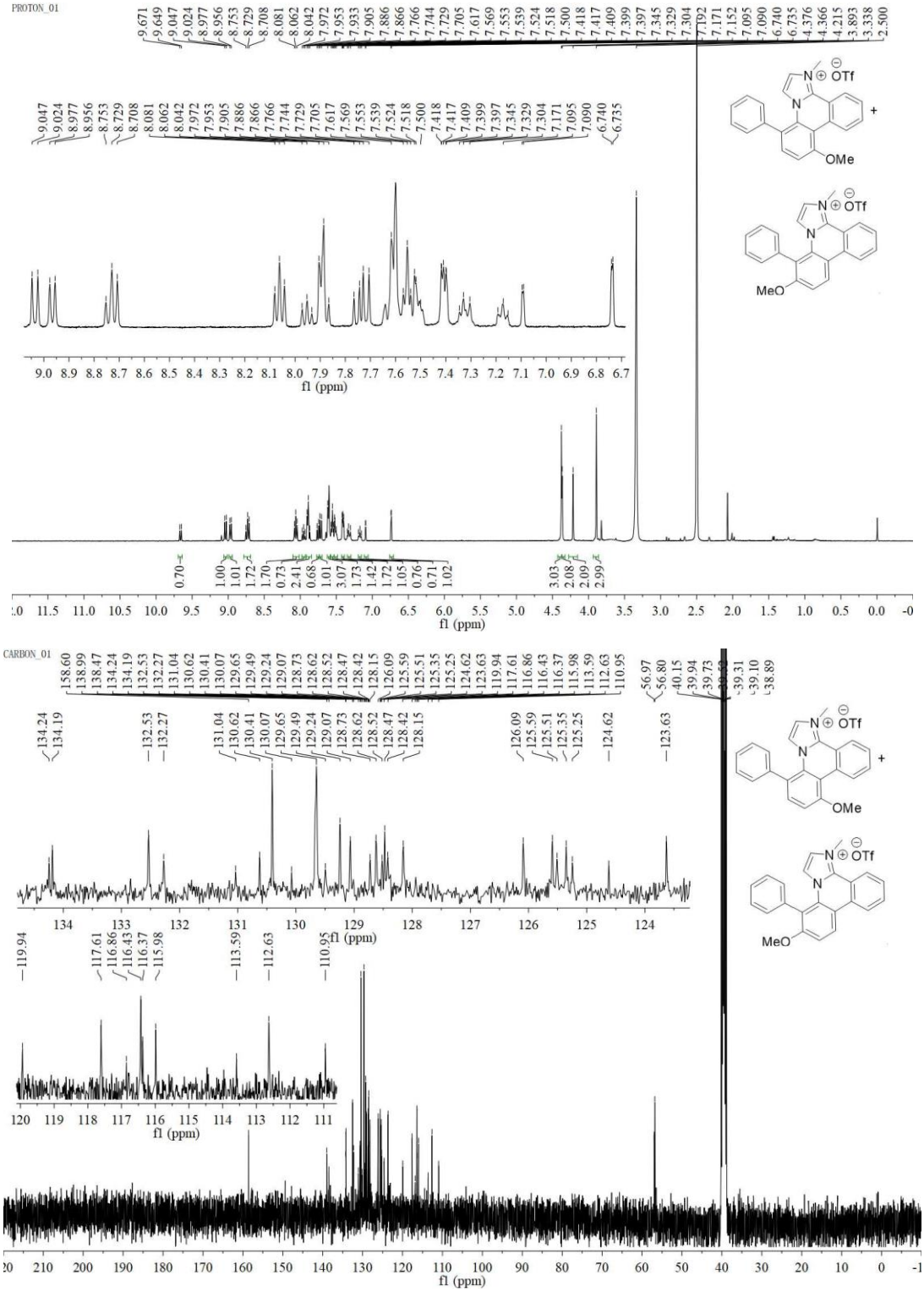
VI. Arylation/annulation of 1-(3-methoxyphenyl)-3-methyl-1*H*-imidazol-3-ium iodide with 2a



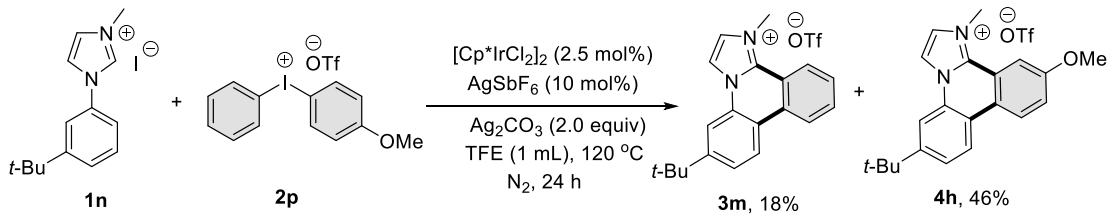
Scheme S4 Arylation/annulation of **1r** with **2a**.

A Schlenk tube with a magnetic stir bar was charged with $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.9 mg, 10 mol%), Ag_2CO_3 (110.5 mg, 2.0 equiv), 1-(3-methoxyphenyl)-3-methyl-1*H*-imidazol-3-ium iodide (**1r**, 0.2 mmol), diphenyliodonium trifluoromethanesulfonate (**2a**, 0.5 mmol, 2.5 equiv), and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 4/1, v/v) to provide mixture of **3q** and **3q'** as a white solid (45.7 mg, 47% yield), the product ratio is 1:0.7. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.66 (d, J = 8.8 Hz, 0.7H), 9.04 (d, J = 9.2 Hz, 1H), 8.97 (d, J = 8.4 Hz, 1H), 8.73 (t, J = 8.4 Hz, 1.7H), 8.06 (t, J = 8.0 Hz, 1.7H), 7.95 (t, J = 8.0 Hz, 0.7H), 7.91-7.87 (m, 2.4H), 7.76 (d, J = 8.8 Hz, 0.7H), 7.72 (d, J = 9.6 Hz, 1H), 7.62-7.60 (m, 3H), 7.57-7.54 (m, 1.7H), 7.52-7.50 (m, 1.4H), 7.42-7.40 (m, 1.7H), 7.35-7.30 (m, 1H), 7.17 (t, J = 7.6 Hz, 0.7H), 7.09 (d, J = 2.0 Hz, 0.7H), 6.74 (d, J = 2.0 Hz, 1H), 4.38 (s, 3H), 4.37 (s, 2.1H), 4.22 (s, 2.1H), 3.89 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6):

δ = 158.6, 139.0, 138.5, 134.2, 134.2, 132.5, 132.3, 131.0, 130.6, 130.4, 130.1, 129.7, 129.5, 129.2, 129.1, 128.7, 128.6, 128.52, 128.47, 128.4, 128.2, 126.1 125.6, 125.5, 125.4, 125.3, 124.6, 123.6, 119.9, 117.6, 116.9, 116.4, 116.4, 116.0, 113.6, 112.6, 111.0, 57.0, 56.8 ppm. HRMS (ESI^+): calcd for $C_{23}H_{19}N_2O^+$: $[M\text{-}OTf]^+$, 339.1492, found: 339.1486.

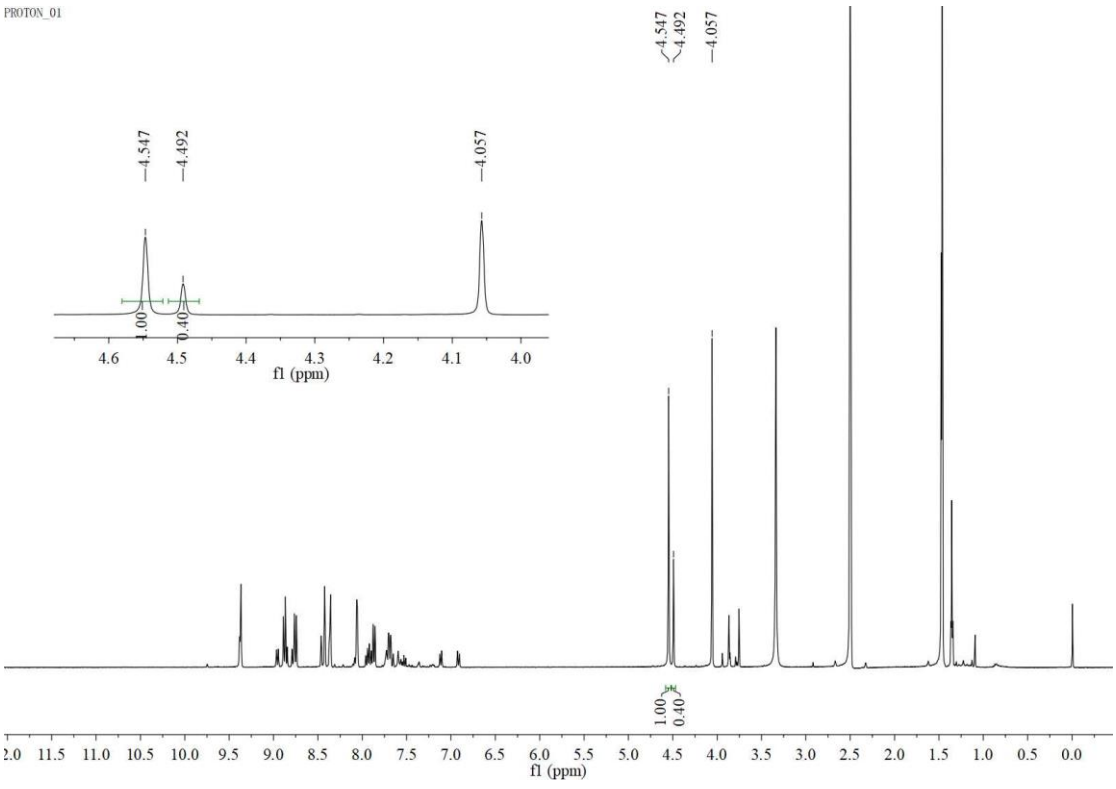


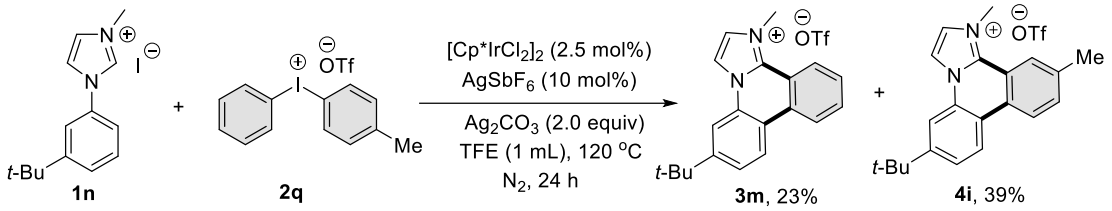
VII. Arylation/annulation of unsymmetrical diaryliodonium salts



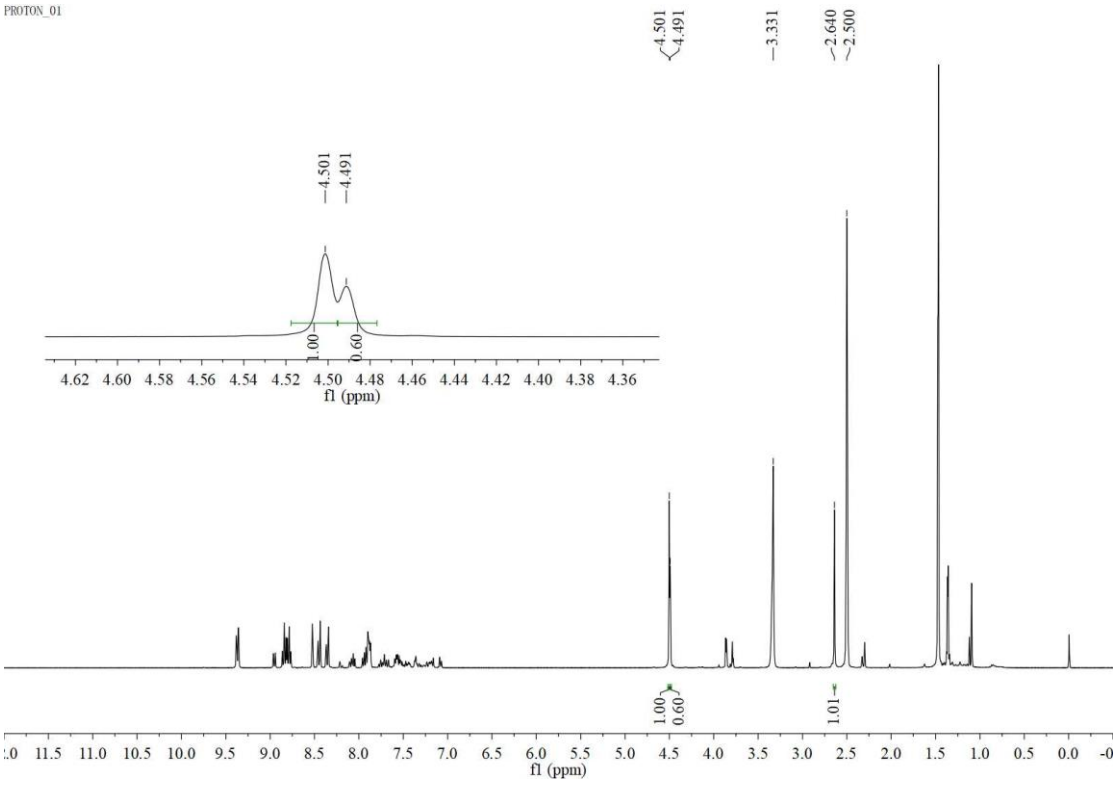
1n **2p** **3m**, 18% **4h**, 46%

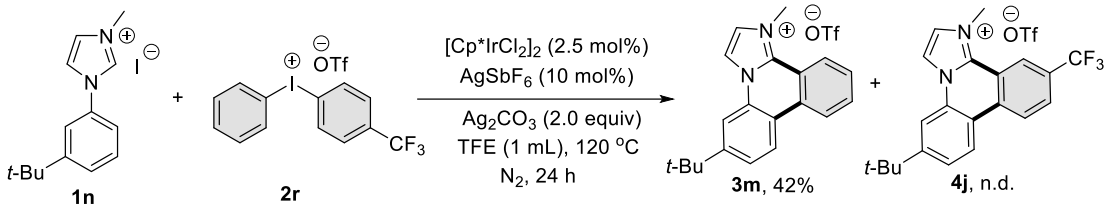
A Schlenk tube with a magnetic stir bar was charged with $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.9 mg, 10 mol%), Ag_2CO_3 (110.5 mg, 2.0 equiv), 1-(3-(*tert*-butyl)phenyl)-3-methyl-1*H*-imidazol-3-ium iodide (**1o**, 0.2 mmol), (4-methoxyphenyl)(phenyl)iodonium trifluoromethanesulfonate (**2p**, 0.3 mmol, 1.5 equiv), and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 4/1, v/v) to provide 58.7 mg white solid, The ratio of **3m** and **4h** was determined to be 0.4:1 by ^1H NMR spectrum, and the yields of **3m** and **4h** were 18% and 46%, respectively.



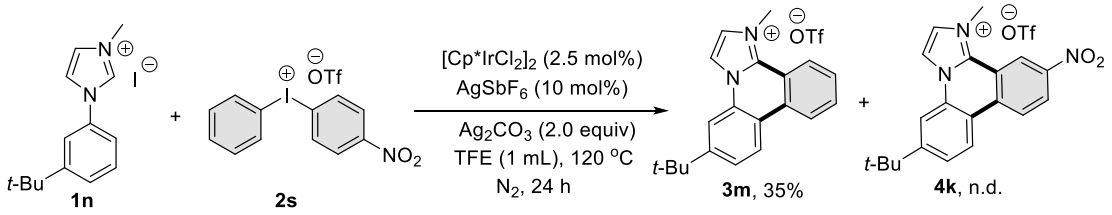


A Schlenk tube with a magnetic stir bar was charged with $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.9 mg, 10 mol%), Ag_2CO_3 (110.5 mg, 2.0 equiv), 1-(3-(*tert*-butyl)phenyl)-3-methyl-1*H*-imidazol-3-ium iodide (**1o**, 0.2 mmol), phenyl(*p*-tolyl)iodonium trifluoromethanesulfonate (**2q**, 0.3 mmol, 1.5 equiv), and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 4/1, v/v) to provide 55.4 mg white solid, The ratio of **3m** and **4i** was determined to be 0.6:1 by ^{1}H NMR spectrum, and the yields of **3m** and **4i** were 23% and 39%, respectively.



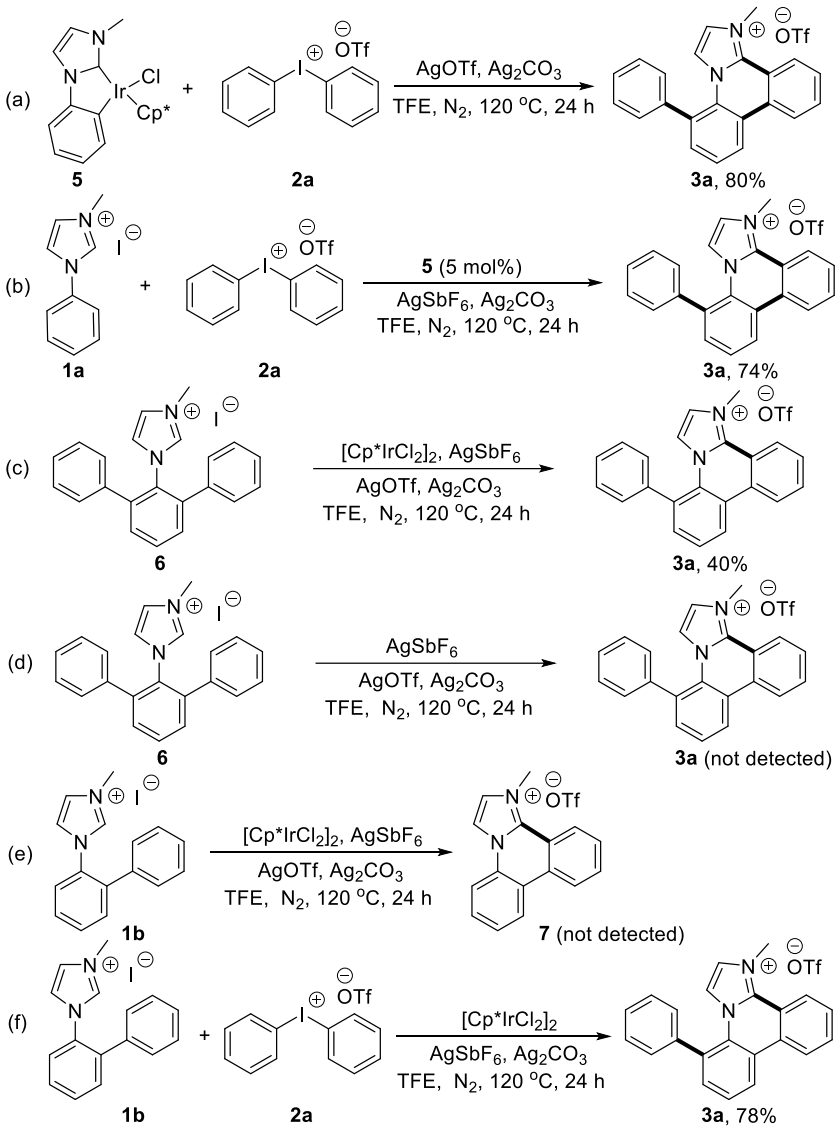


A Schlenk tube with a magnetic stir bar was charged with $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.9 mg, 10 mol%), Ag_2CO_3 (110.5 mg, 2.0 equiv), 1-(3-(*tert*-butyl)phenyl)-3-methyl-1*H*-imidazol-3-ium iodide (**1o**, 0.2 mmol), phenyl(4-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (**2r**, 0.3 mmol, 1.5 equiv), and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 4/1, v/v) to provide **3m** (36.9 mg, 42%).



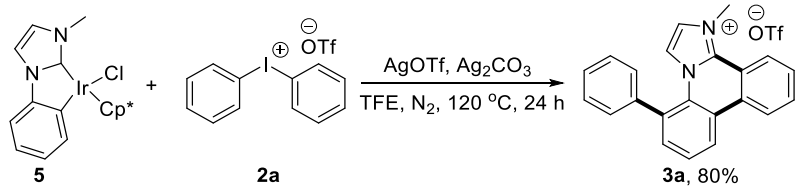
A Schlenk tube with a magnetic stir bar was charged with $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.9 mg, 10 mol%), Ag_2CO_3 (110.5 mg, 2.0 equiv), 1-(3-(*tert*-butyl)phenyl)-3-methyl-1*H*-imidazol-3-ium iodide (**1o**, 0.2 mmol), (4-nitrophenyl)(phenyl)iodonium trifluoromethanesulfonate (**2s**, 0.3 mmol, 1.5 equiv), and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 4/1, v/v) to provide **3m** (30.5 mg, 35%).

VIII. Mechanistic study



Scheme S5 Mechanistic studies.

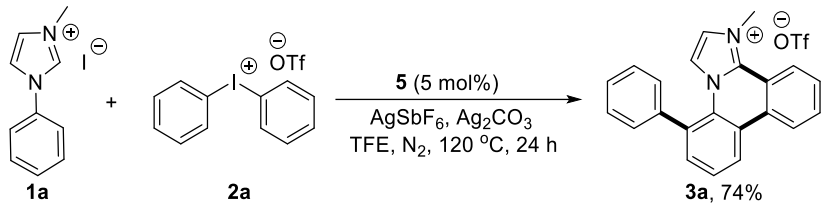
i) Stoichiometric reaction of Cp*-Ir(III) cyclometalated complex 5 with 2a



The Cp*-Ir(III) cyclometalated complex (**5**) was prepared by the synthesis steps reported previously.[3] A Schlenk tube with a magnetic stir bar was charged with Cp*-Ir(III) cyclometalated complex **5** (104.4 mg, 0.2 mmol), diphenyliodonium trifluoromethanesulfonate **2a** (215.0 mg, 0.5 mmol), AgOTf (51.4 mg, 0.2 mmol),

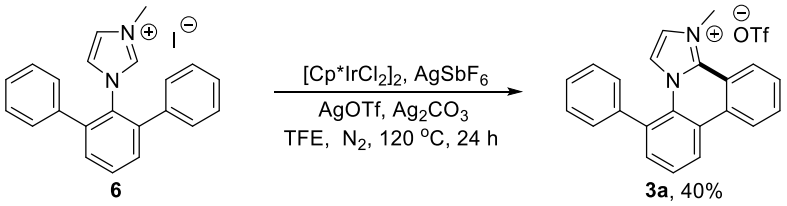
Ag_2CO_3 (110.5 mg, 2.0 equiv) and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 3/1, v/v) to provide **3a** in 80% yield.

ii) Cascade reaction using NHC-cyclometalated Ir(III) intermediate 5 as a catalyst



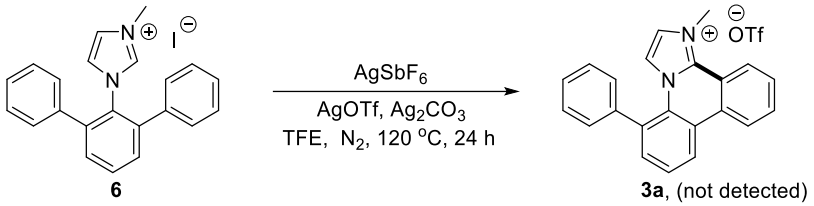
A Schlenk tube with a magnetic stir bar was charged with 3-methyl-1-phenyl-1*H*-imidazolium iodide **1a** (57.2 mg, 0.2 mmol), diphenyliodonium trifluoromethanesulfonate **2a** (215.0 mg, 0.5 mmol), The Cp*-Ir(III) cyclometalated complex **5** (5.2 mg, 5.0 mol%), $AgSbF_6$ (6.90 mg, 10 mol%), Ag_2CO_3 (110.5 mg, 2.0 equiv) and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 3/1, v/v) to provide **3a** in a 74% yield.

iii) Intramolecular cyclization of diarylation intermediate 6



A Schlenk tube with a magnetic stir bar was charged with 1-([1,1':3',1"-terphenyl]-2'-yl)-3-methyl-1*H*-imidazolium iodide **6** (87.7 mg, 0.2

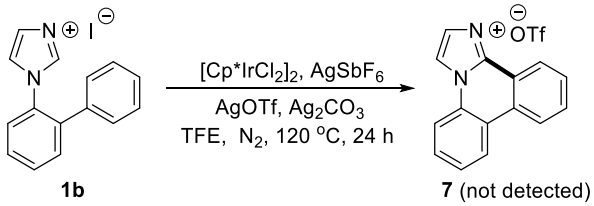
mmol), $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.90 mg, 10 mol%), AgOTf (51.4 mg, 1.0 equiv), Ag_2CO_3 (110.5 mg, 2.0 equiv) and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 3/1, v/v) to provide **3a** in a 40% yield.



6 **3a**, (not detected)

A Schlenk tube with a magnetic stir bar was charged with 1-([1,1':3',1''-terphenyl]-2'-yl)-3-methyl-1*H*-imidazolium iodide **6** (87.7 mg, 0.2 mmol), $AgSbF_6$ (6.90 mg, 10 mol%), AgOTf (51.4 mg,1.0 equiv), Ag_2CO_3 (110.5 mg, 2.0 equiv) and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and no production of **3a** was detected by TLC monitoring.

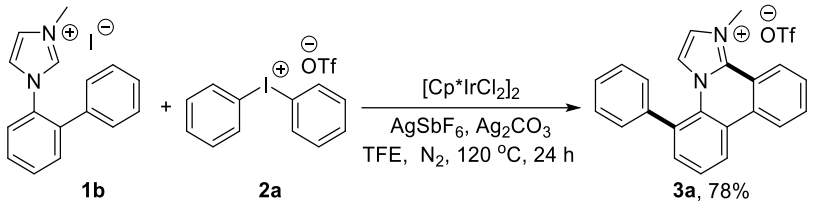
iv) Intramolecular cyclization of 1b



1b **7** (not detected)

A Schlenk tube with a magnetic stir bar was charged with 1-([1,1'-biphenyl]-2-yl)-3-methyl-1*H*-imidazolium iodide **1b** (72.4 mg, 0.2 mmol), $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.90 mg, 10 mol%), AgOTf (51.4 mg, 1.0 equiv), Ag_2CO_3 (110.5 mg, 2.0 equiv) and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and no production of **7** was detected by TLC monitoring.

v) Cascade reaction using 1b as a substrate



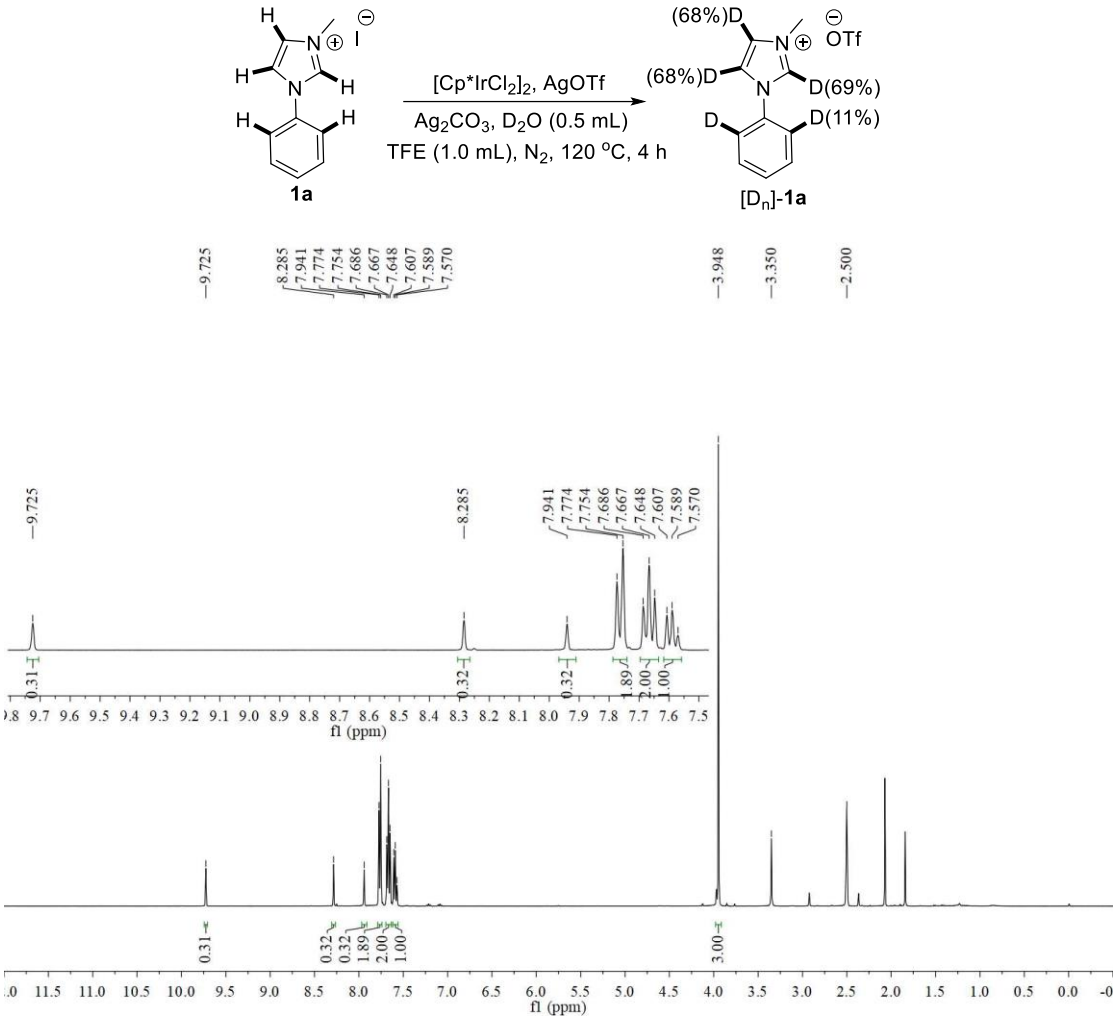
1b **2a** **3a**, 78%

A Schlenk tube with a magnetic stir bar was charged with 1-([1,1'-biphenyl]-2-yl)-3-methyl-1*H*-imidazolium iodide **1b** (72.4 mg, 0.2 mmol), diphenyliodonium trifluoromethanesulfonate **2a** (129.0 mg, 0.3 mmol), $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.90 mg, 10 mol%), Ag_2CO_3 (110.5 mg, 2.0 equiv) and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 3/1, v/v) to provide **3a** in a 78% yield.

vi) H/D exchange experiment

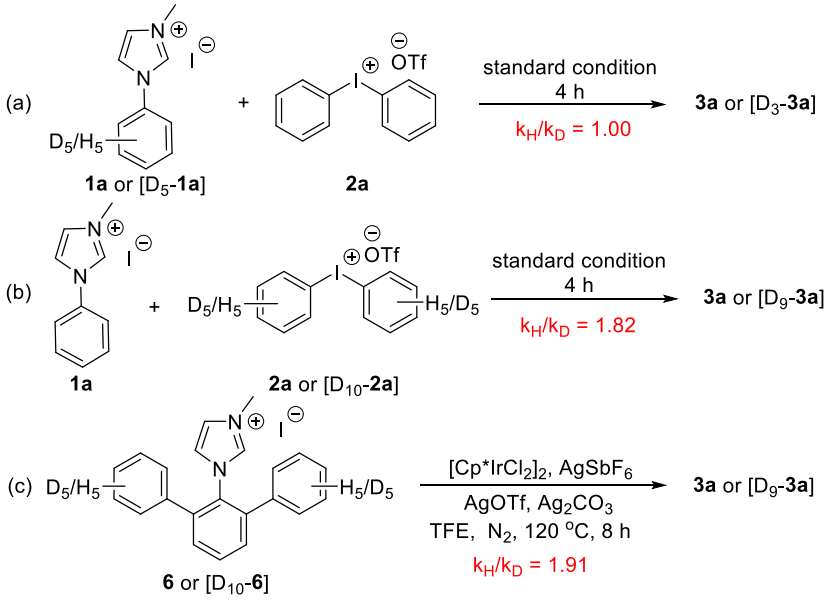
A Schlenk tube with a magnetic stir bar was charged with $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), AgOTf (51.4 mg, 0.2 mmol), Ag_2CO_3 (110.5 mg, 2.0 equiv), 3-methyl-1-phenyl-1*H*-imidazolium iodide **1a** (57.2 mg, 0.2 mmol), D_2O (0.5 mL) and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 4 h and then diluted with 10 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel to provide the designed product. The deuterated ratio was calculated from ^{1}H NMR analysis.

According to the ^{1}H NMR spectrum, the 11% deuteration at the phenyl *ortho*-C−H of **1a** was observed, the 69% deuteration, 68% deuteration and 68% deuteration at the imidazole C2−H, C4−H and C5−H of **1a** was observed respectively.



Scheme S6 H/D exchange experiment.

vii) Determination of intermolecular kinetic isotope effect (KIE)



Scheme S7 Determination of intermolecular kinetic isotope effect.

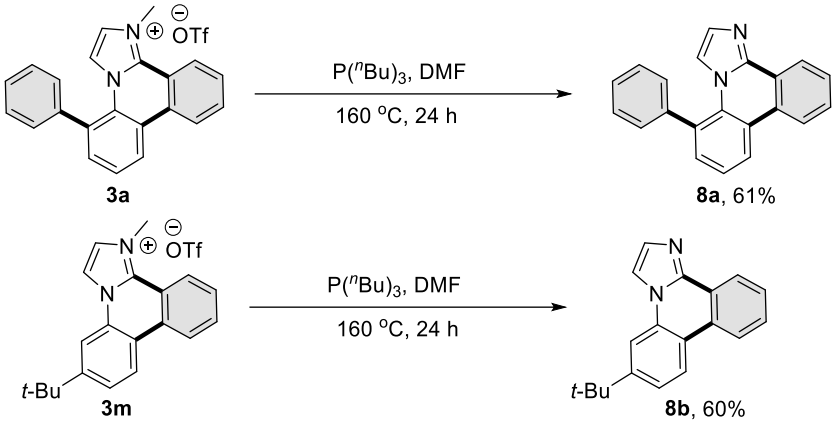
A Schlenk tube with a magnetic stir bar was charged with $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.9 mg, 10 mol%), Ag_2CO_3 (110.5 mg, 2.0 equiv), 3-methyl-1-phenyl-1*H*-imidazolium iodide **1a** (57.2 mg, 0.2 mmol) or [D_5-**1a**] (58.2 mg, 0.2 mmol), diphenyliodonium trifluoromethanesulfonate **2a** (215.0 mg, 0.5 mmol, 2.5 equiv), and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 4 h and then diluted with 5 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 3/1) to provide the desired product, the KIE value was found to be 1.00.

A Schlenk tube with a magnetic stir bar was charged with $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.9 mg, 10 mol%), Ag_2CO_3 (110.5 mg, 2.0 equiv), 3-methyl-1-phenyl-1*H*-imidazolium iodide **1a** (57.2 mg, 0.2 mmol), diphenyliodonium trifluoromethanesulfonate **2a** (215.0 mg, 0.5 mmol, 2.5 equiv) or [D_{10}-**2a**] (220.1 mg, 0.5 mmol, 2.5 equiv), and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 4 h and then diluted with 5 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 3/1) to provide the desired product, the KIE value was found to be 1.82.

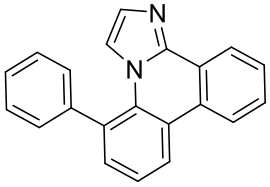
A Schlenk tube with a magnetic stir bar was charged with 1-([1,1':3',1"-terphenyl]-2'-yl)-3-methyl-1*H*-imidazolium iodide **6** (87.7 mg, 0.2 mmol) or 1-([1,1':3',1"-terphenyl]-2'-yl-2,2",3,3",4,4",5,5",6,6"-d_{10})-3-methyl -1H-imidazol-3-ium iodide D_{10}-**6** (89.7 mg, 0.2 mmol), $[Cp^*IrCl_2]_2$ (3.9 mg, 2.5 mol%), $AgSbF_6$ (6.90 mg, 10 mol%), AgOTf (51.4 mg, 1.0 equiv), Ag_2CO_3 (110.5 mg, 2.0 equiv) and TFE (1.0 mL) under the N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 8 h and then diluted with 5 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column

chromatography on silica gel (CH_2Cl_2/acetonitrile = 3/1) to provide the desired product, the KIE value was found to be 1.91.

IX. Dequaternization of 1-methylimidazo[1,2-*f*]phenanthridin-1-ium salts



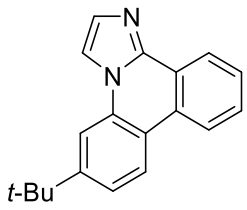
A Schlenk tube with a magnetic stir bar was charged with imidazo[1,2-*f*]phenanthridinium trifluoromethanesulfonates (**3**, 3.0 mmol), P(^{n}Bu)$_3$ (10 equiv, 7.5 mL) and DMF (15 mL) under the N_2 atmosphere. The resulting mixture was stirred at 160 ºC in oil bath for 24 h and then concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2/ethyl acetate = 10/10/1, v/v/v) to provide the desired product.



5-Phenylimidazo[1,2-*f*]phenanthridine (8a)

Purification *via* silica gel column chromatography (petroleum ether/CH_2Cl_2/ethyl acetate = 10/10/1, v/v/v) afforded the desired product **8a** as a white solid (538.6 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69-8.65 (m, 1H), 8.54 (dd, J = 8.1, 1.3 Hz, 1H), 8.45-8.41 (m, 1H), 7.68-7.64 (m, 2H), 7.57-7.50 (m, 4H), 7.46 (dd, J = 7.4, 1.5 Hz, 1H), 7.42-7.39 (m, 2H), 7.20 (d, J = 1.4 Hz, 1H), 6.75 (d, J = 1.4 Hz, 1H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 143.4, 141.0, 132.5, 132.4, 130.1, 129.8, 129.4, 129.2, 128.8, 128.8, 128.4, 127.8, 124.4, 124.3, 124.0, 123.7, 123.4, 122.7,

117.6 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{15}N_2^+$: $[M+Na]^+$, 317.1049, found: 317.1047.



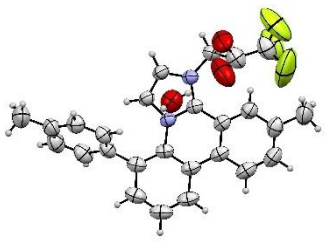
6-(*tert*-Butyl)imidazo[1,2-*f*]phenanthridine (8b)

Purification *via* silica gel column chromatography (petroleum ether/CH_2Cl_2/Ethyl acetate = 10/10/1, v/v/v) afforded the desired product **8b** as a white solid (493.7 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68-8.61 (m, 1H), 8.42-8.31 (m, 2H), 8.04 (s, 1H), 7.84 (s, 1H), 7.69-7.59 (m, 3H), 7.58-7.55 (m, 1H), 1.46 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 142.8, 131.7, 131.5, 128.7, 128.3, 127.6, 124.2, 124.1, 123.5, 123.1, 122.3, 119.4, 112.4, 112.0, 35.3, 31.4 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{19}N_2^+$: $[M+Na]^+$, 297.1362, found: 297.1352

X. Single crystal X-ray structure of 4a

Compound **4a** (0.2 mmol) was dissolved in acetonitrile, sodium trifluoroacetate (544.0 mg, 20.0 equiv) were added, and the mixture was stirred at room temperature for 20 h. The reaction system was concentrated under vacuum and the residue was purified by column chromatography on silica gel (CH_2Cl_2/acetonitrile = 3/1) to provide **4a**.TFA. Single crystal of **4a**.TFA was grown from saturated dichloromethane/heptane (*v*/*v*, 1/2) solutions.

Table S2 Crystal data and structure refinement for **4a**.TFA.



Identification code	zxs-ag2o
Empirical formula	$C_{26}H_{23}F_3N_2O_3$
Formula weight	468.46

Temperature/K	297.4(3)
Crystal system	triclinic
Space group	P-1
a/Å	7.9876(4)
b/Å	10.9369(6)
c/Å	13.1476(7)
α/°	84.081(5)
β/°	83.827(5)
γ/°	81.200(5)
Volume/Å^3	1124.07(11)
Z	2
ρ_{calc}g/cm^3	1.384
μ/mm^{-1}	0.908
F(000)	488.0
Crystal size/mm3	0.5 × 0.3 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.212 to 142.66
Index ranges	-9 ≤ h ≤ 7, -13 ≤ k ≤ 13, -15 ≤ l ≤ 16
Reflections collected	12035
Independent reflections	4283 [R_{int} = 0.0433, R_{sigma} = 0.0327]
Data/restraints/parameters	4283/0/323
Goodness-of-fit on F_2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0811, wR_2 = 0.2433
Final R indexes [all data]	R_1 = 0.0968, wR_2 = 0.2704
Largest diff. peak/hole / e Å^{-3}	0.44/-0.38

XI. References

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(2) A. K. Verma, J. Singh, V. K. Sankar, R. Chaudhary and R. Chandra, *Tetrahedron Lett.*, 2007, **48**, 4207-4210.

(3) R. Thenarukandiyil, S. K. Gupta and J. Choudhury, *ACS Catal.*, **2016**, *6*, 5132-5137.

(4) M. Bielawski, M. Zhu and B. Olofsson, *Adv. Synth. Catal.*, **2007**, *349*, 2610-2618.

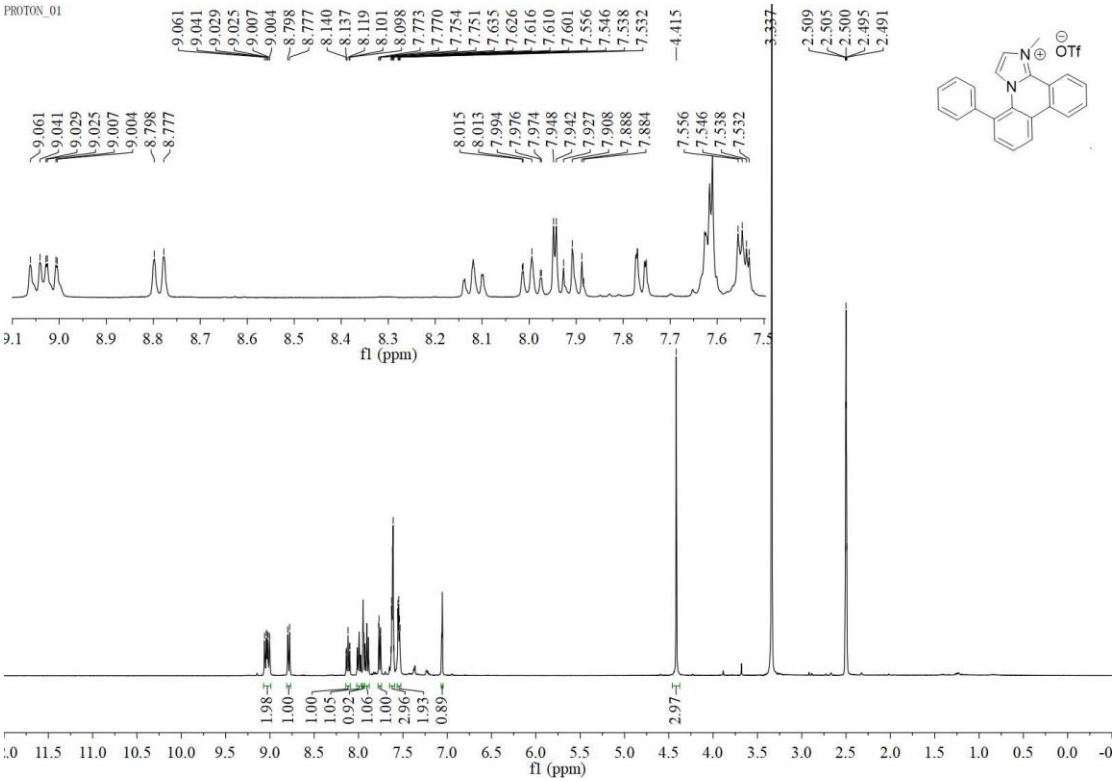
(5) A. Bigot, A. Williamson and M. Gaunt, *J. Am. Chem. Soc.*, **2011**, *133*, 13778-13781.

(6) M. Bielawski and B. Olofsson, *Chem. Commun.*, **2007**, 2521-2523.

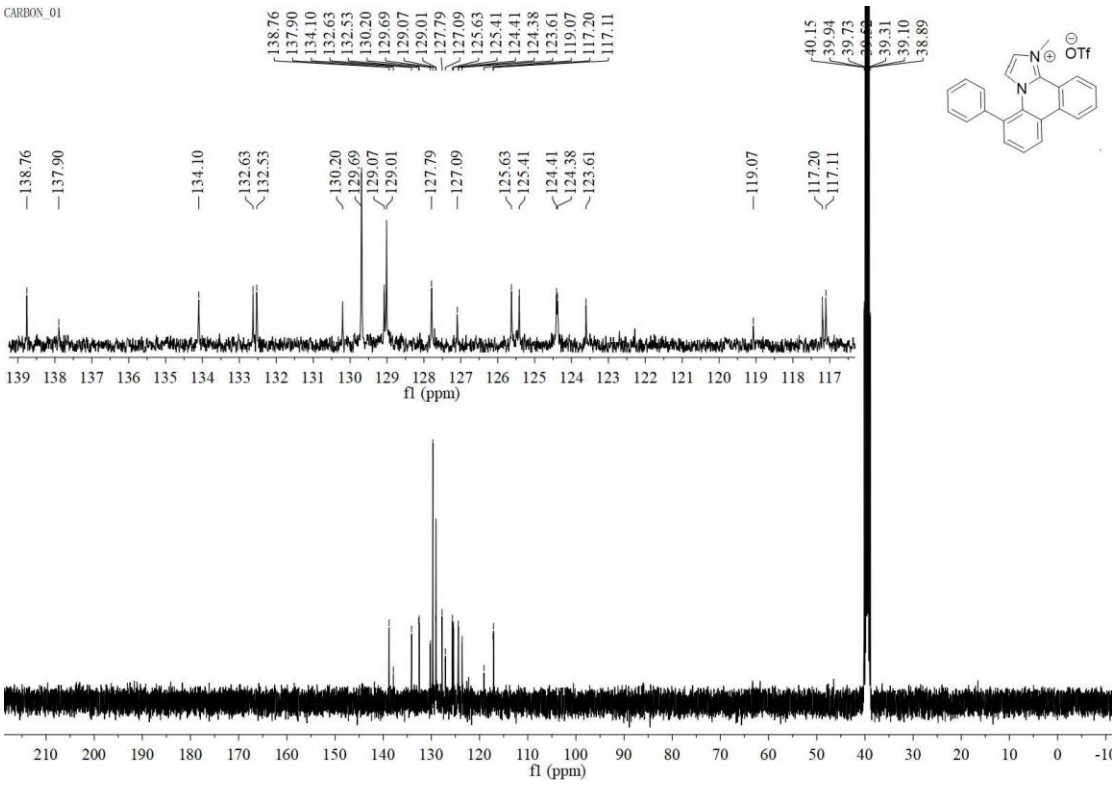
(7) P. P. Kaishap, G. Duarah, B. Sarma, Chetia, D. and S. Gogoi, *Angew. Chem., Int. Ed.*, **2018**, *57*, 456-460.

XII. Copies of ^{1}H and ^{13}C NMR spectra

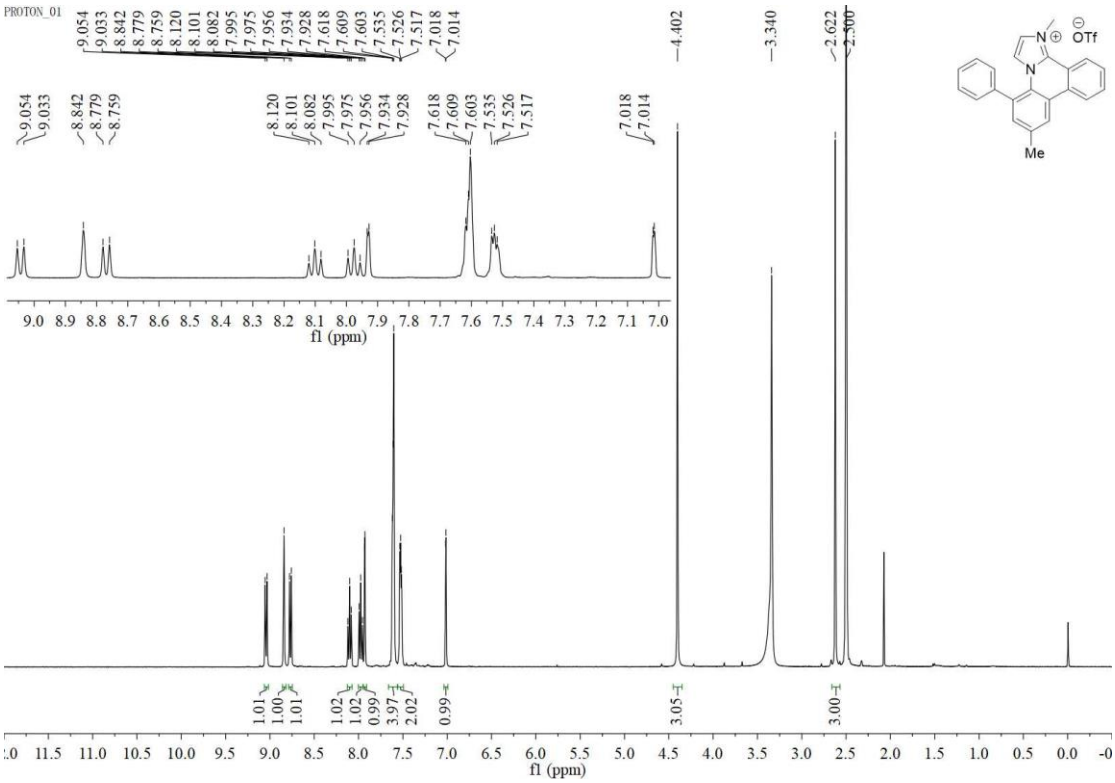
^{1}H NMR (400 MHz) spectrum of **3a** in DMSO-d_6



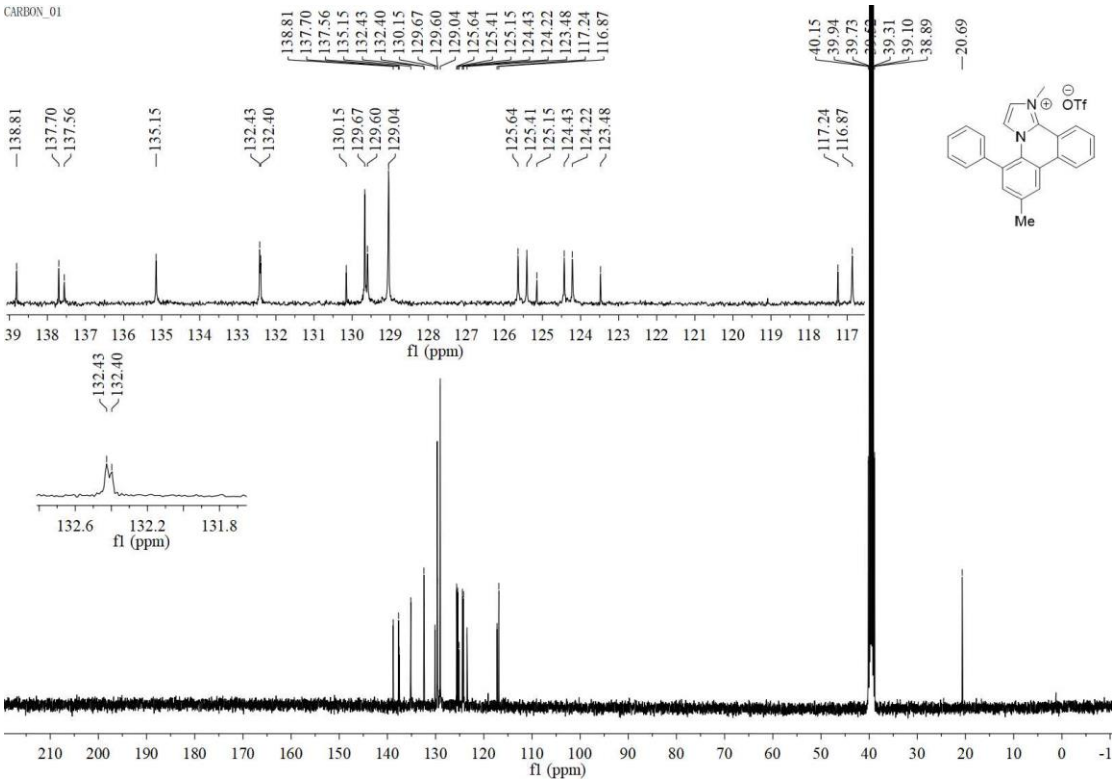
^{13}C NMR (100 MHz) spectrum of **3a** in DMSO-d_6



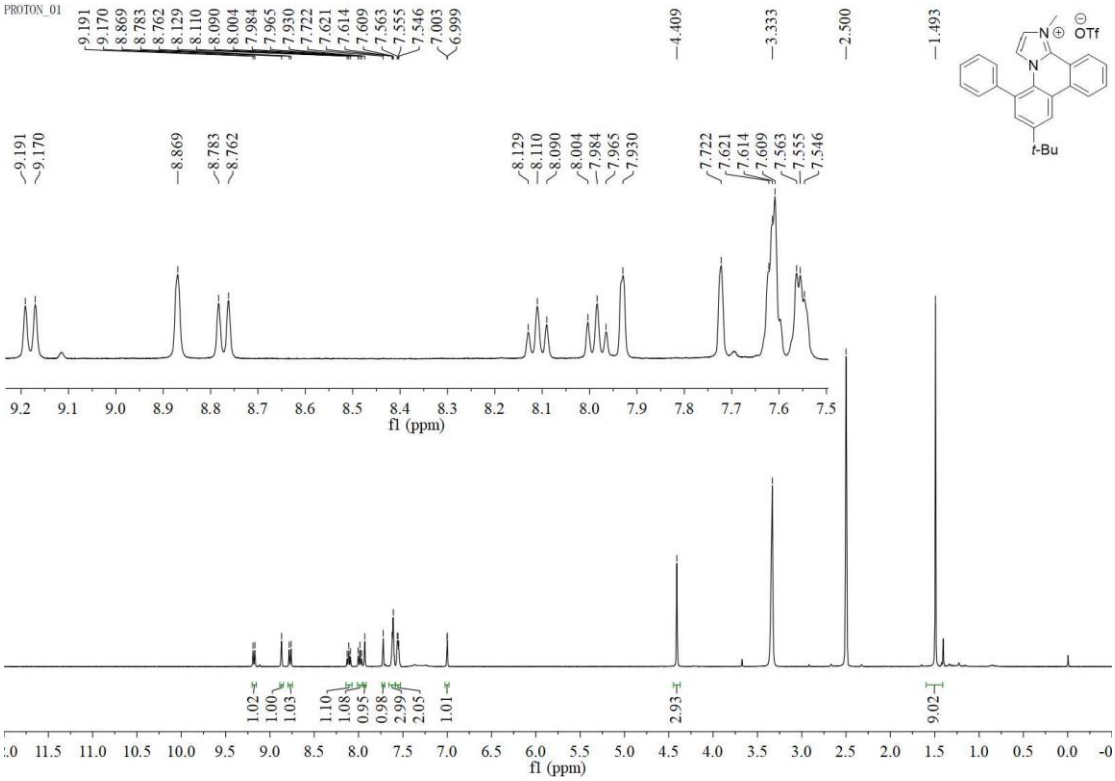
^{1}H NMR (400 MHz) spectrum of **3b** in DMSO-d_6



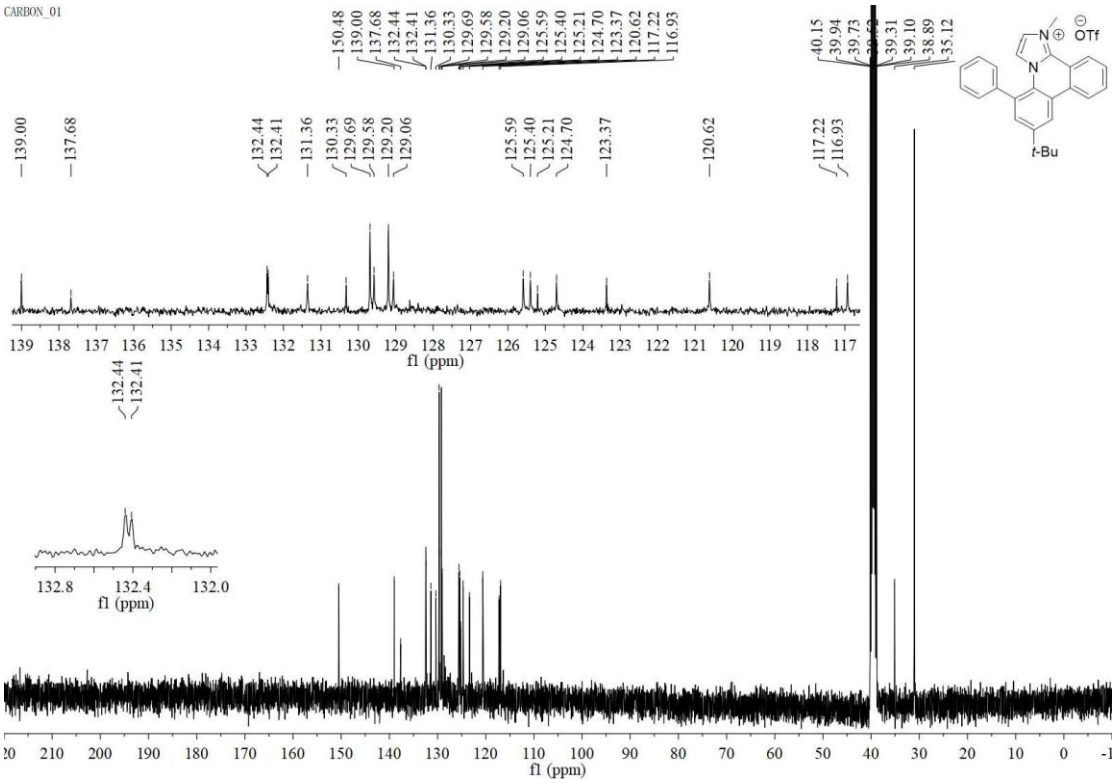
^{13}C NMR (100 MHz) spectrum of **3b** in DMSO-d_6



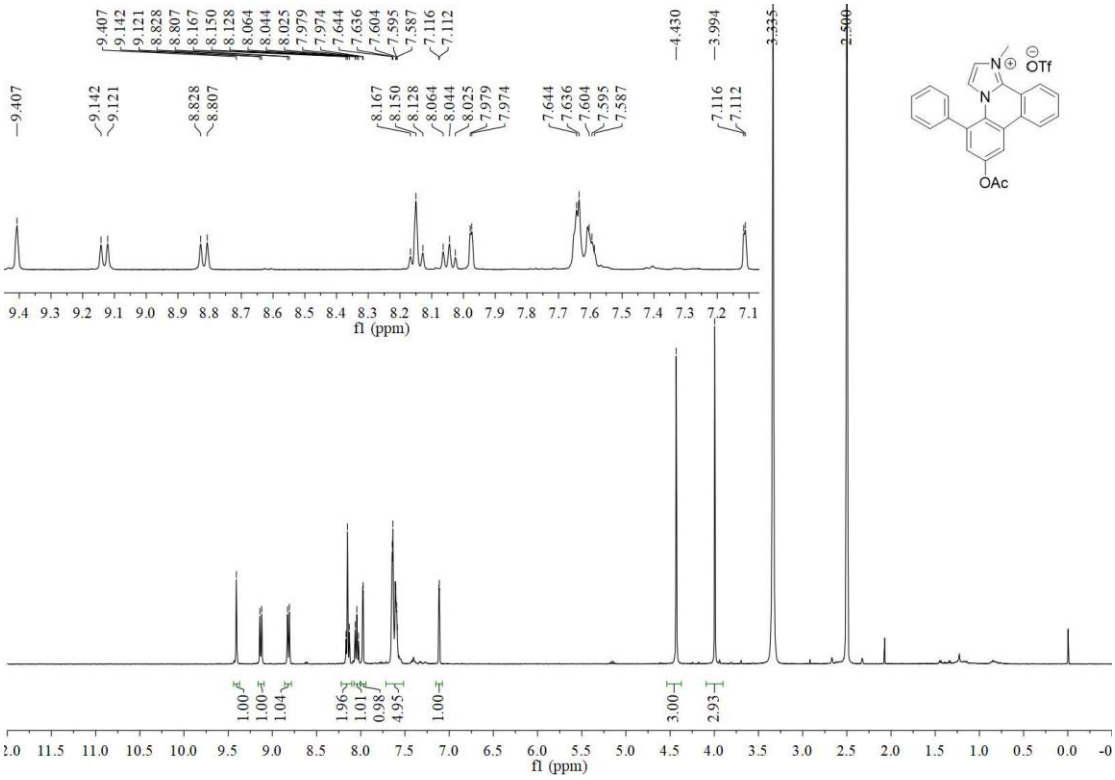
^{1}H NMR (400 MHz) spectrum of **3c** in DMSO-d_6



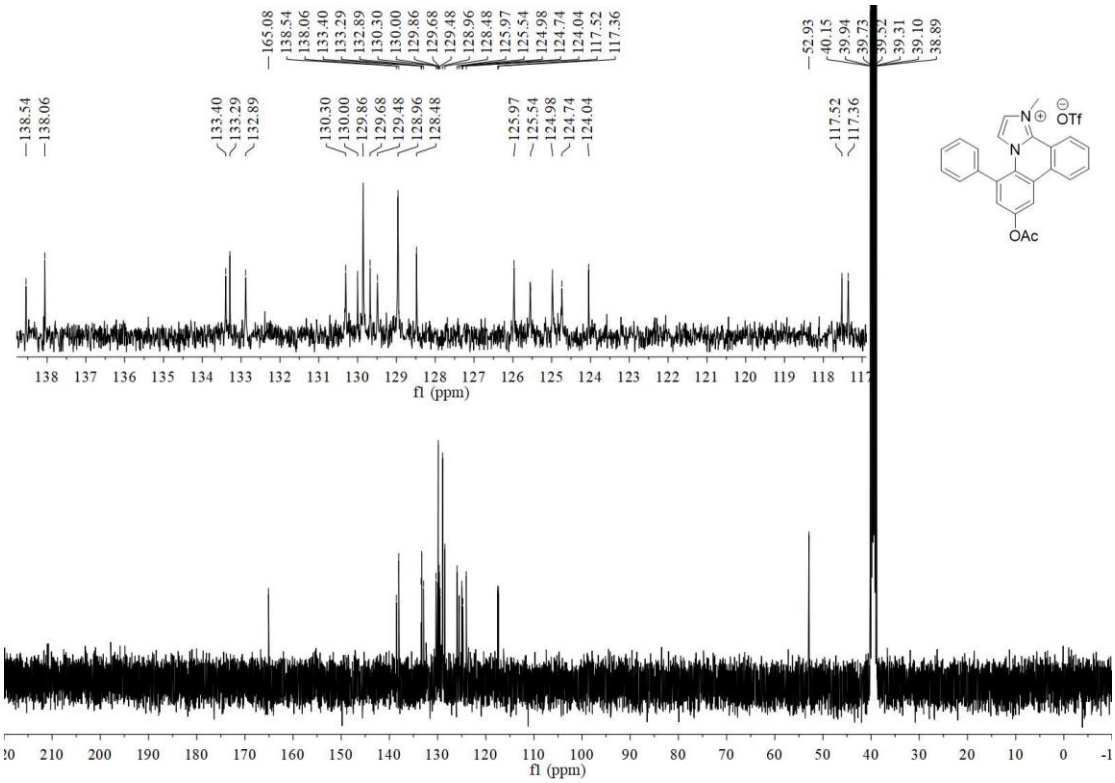
^{13}C NMR (100 MHz) spectrum of **3c** in DMSO-d_6



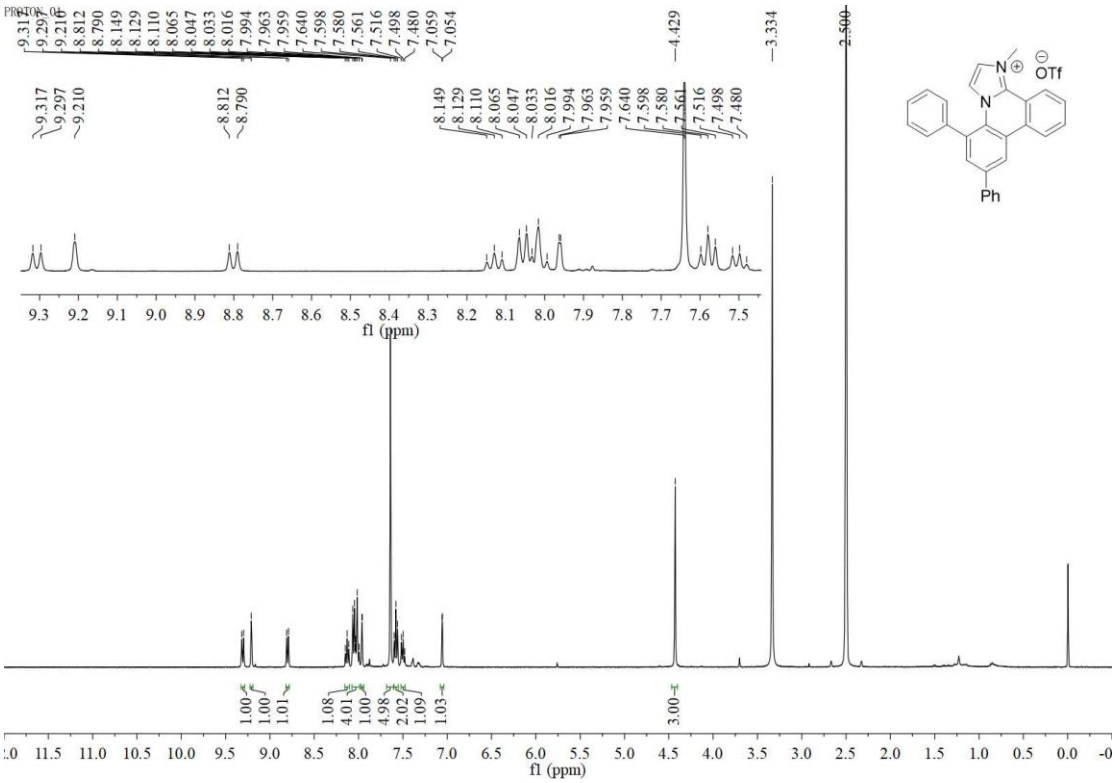
^{1}H NMR (400 MHz) spectrum of **3d** in DMSO-d_6



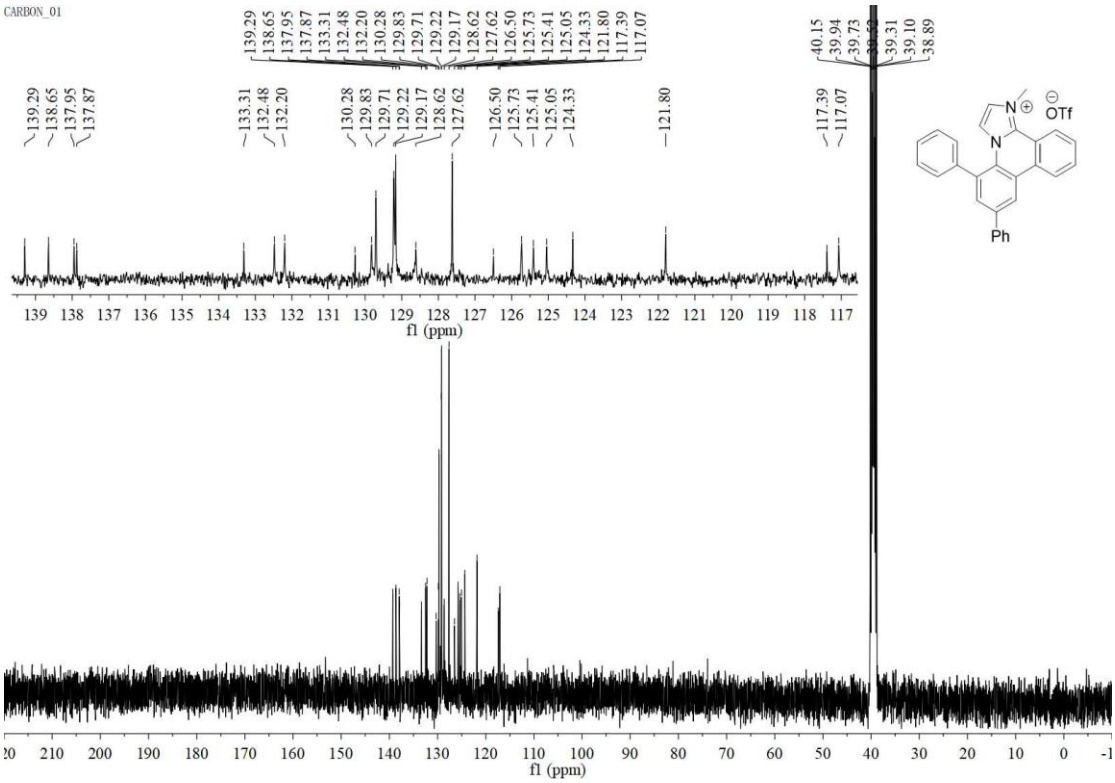
^{13}C NMR (100 MHz) spectrum of **3d** in DMSO-d_6



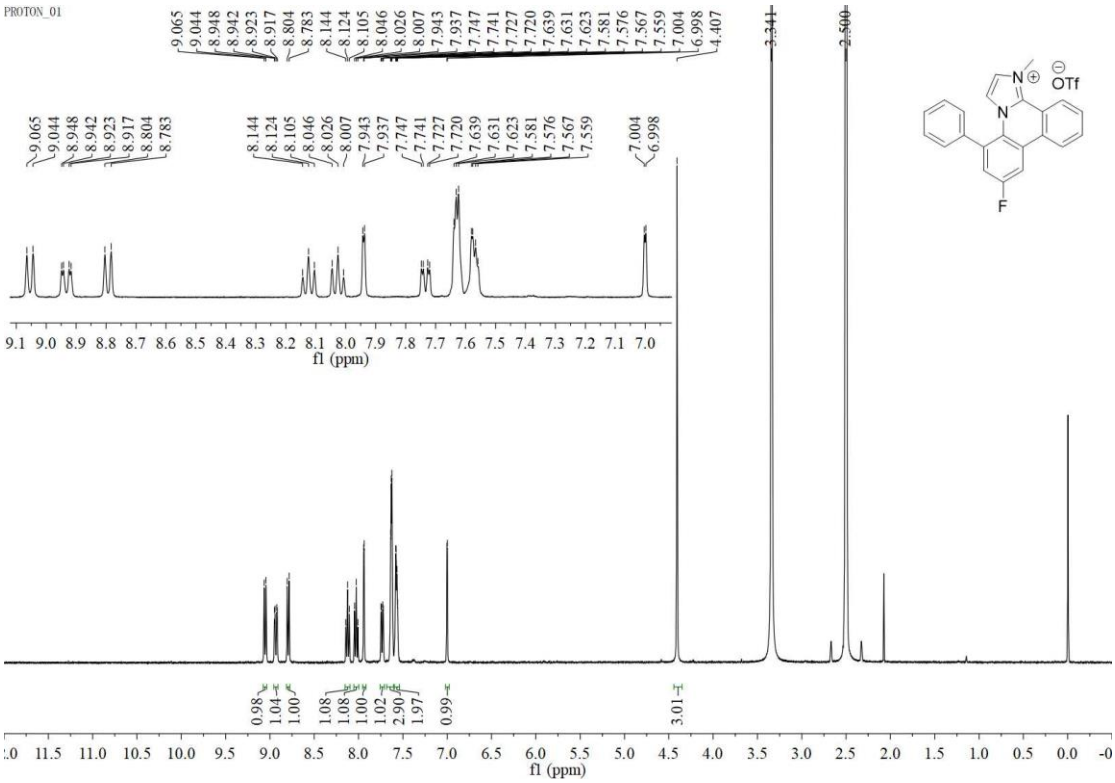
^{1}H NMR (400 MHz) spectrum of **3e** in DMSO-d_6



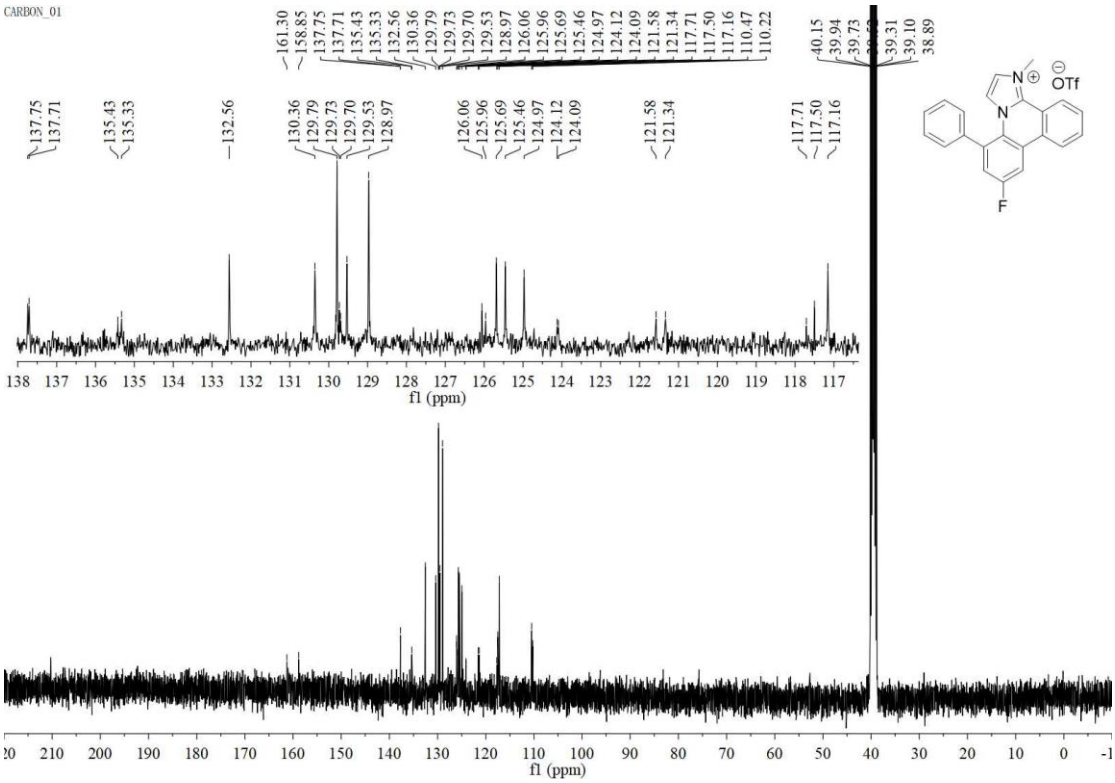
^{13}C NMR (100 MHz) spectrum of **3e** in DMSO-d_6



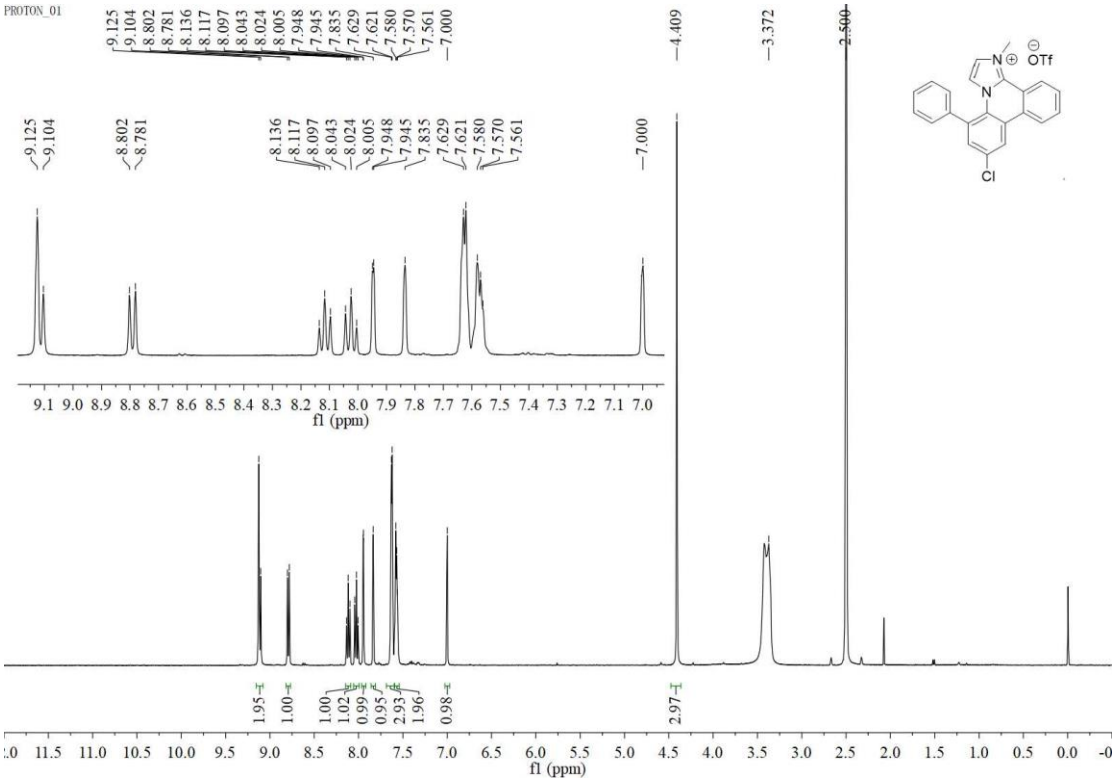
^{1}H NMR (400 MHz) spectrum of **3f** in DMSO-d_6



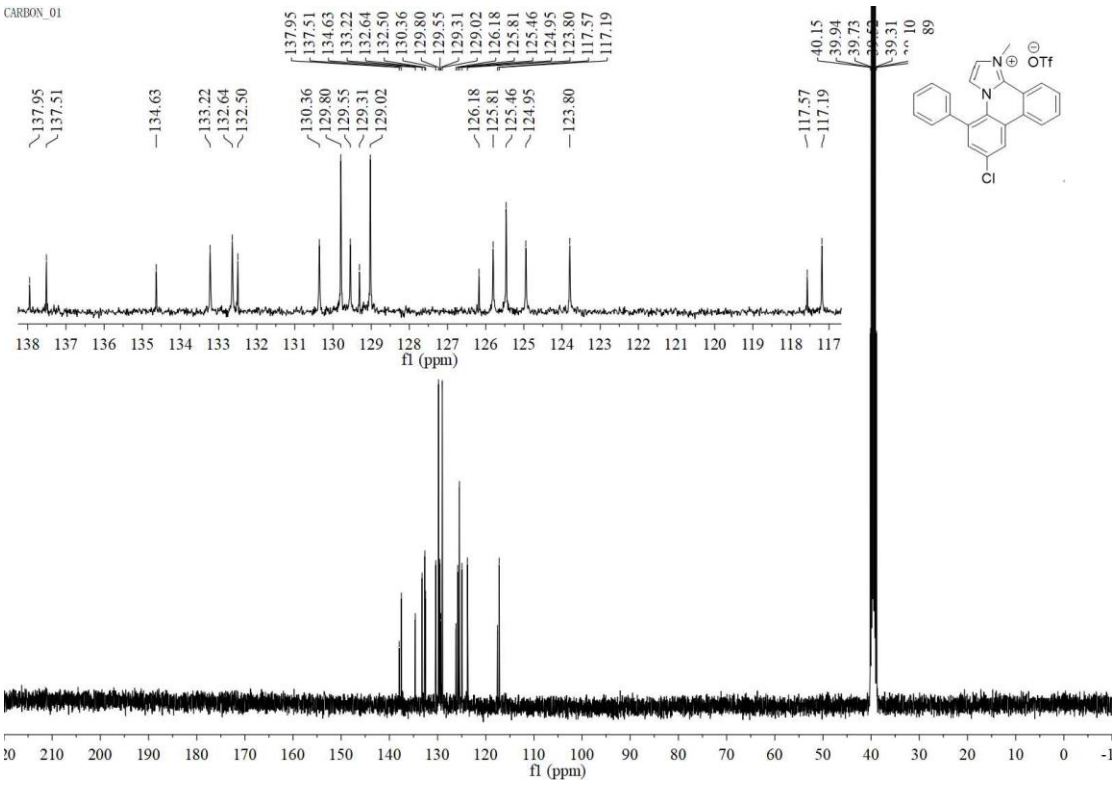
^{13}C NMR (100 MHz) spectrum of **3f** in DMSO-d_6



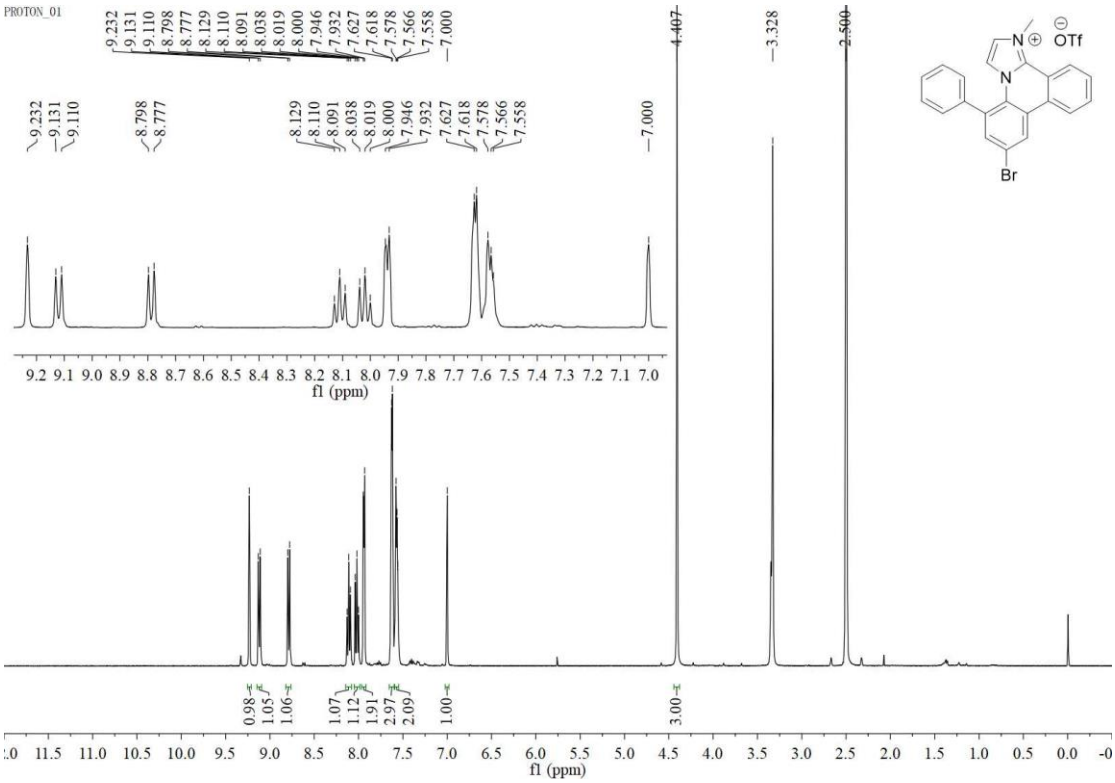
^{1}H NMR (400 MHz) spectrum of **3g** in DMSO-d_6



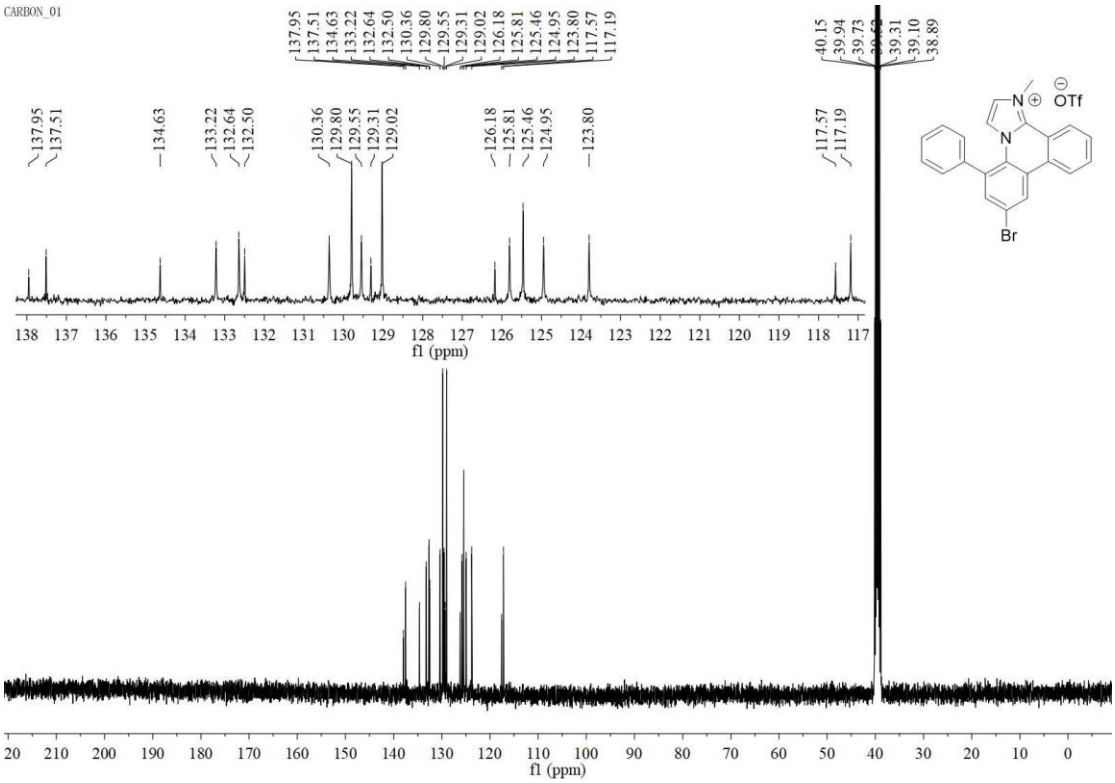
^{13}C NMR (100 MHz) spectrum of **3g** in DMSO-d_6



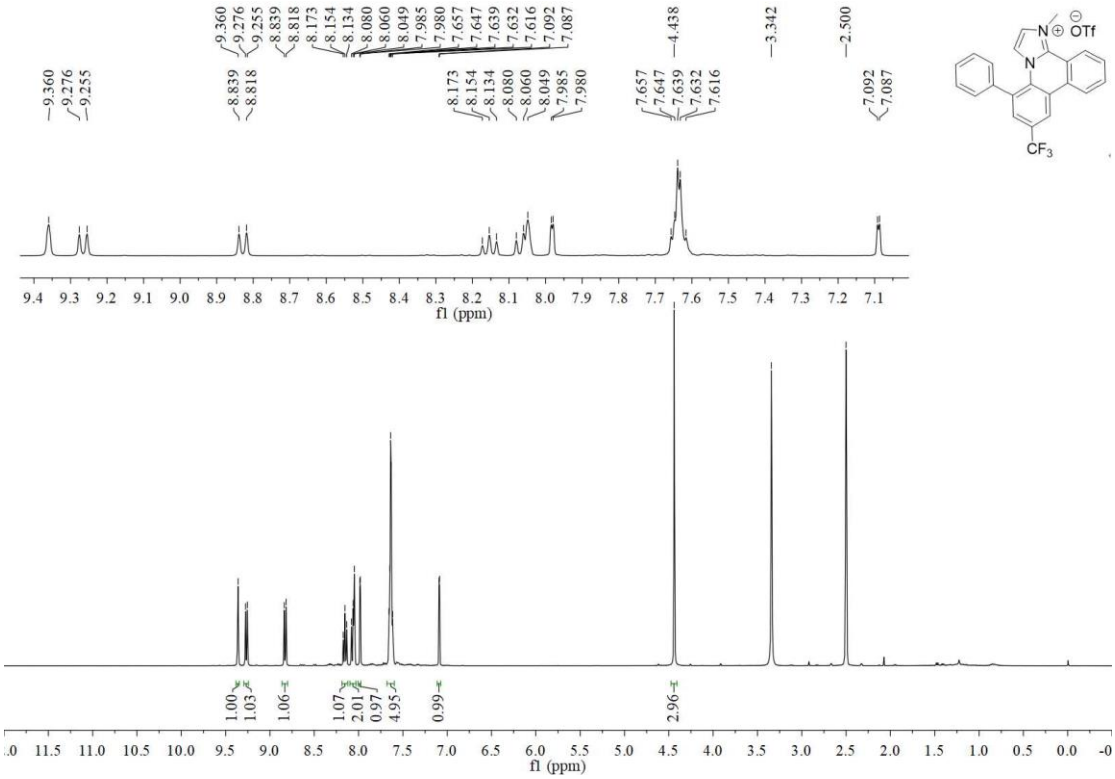
^{1}H NMR (400 MHz) spectrum of **3h** in DMSO-d_6



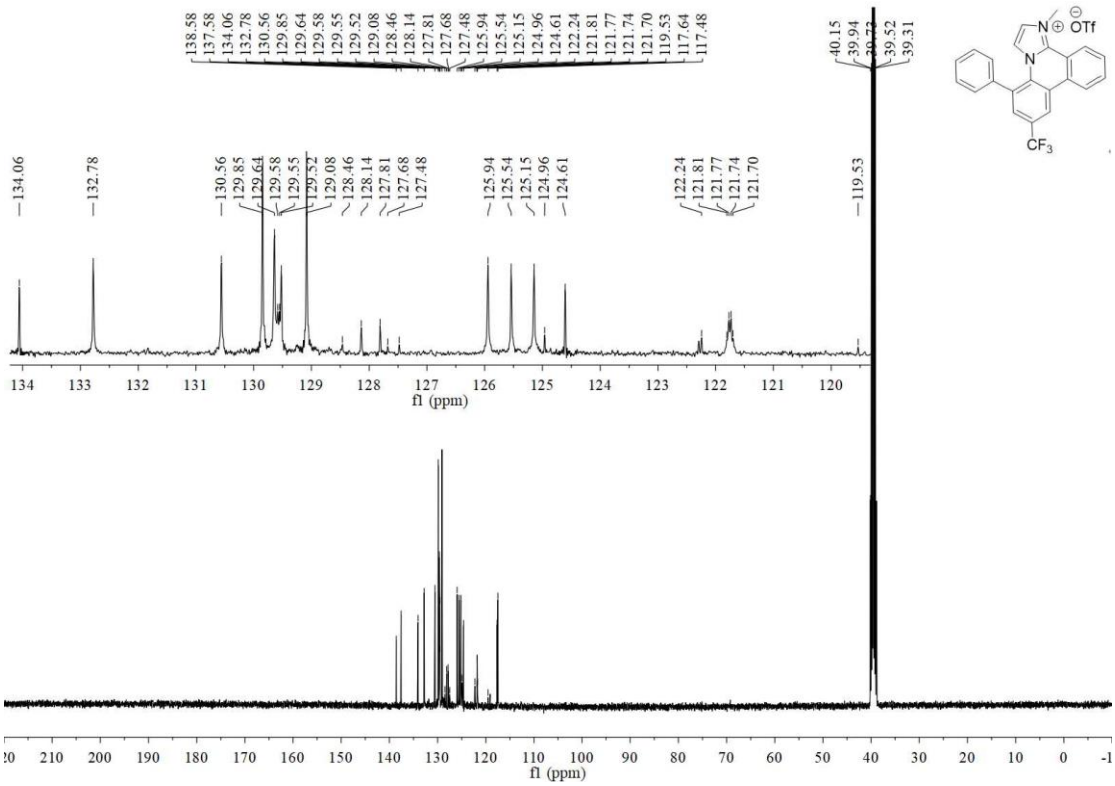
^{13}C NMR (100 MHz) spectrum of **3h** in DMSO-d_6



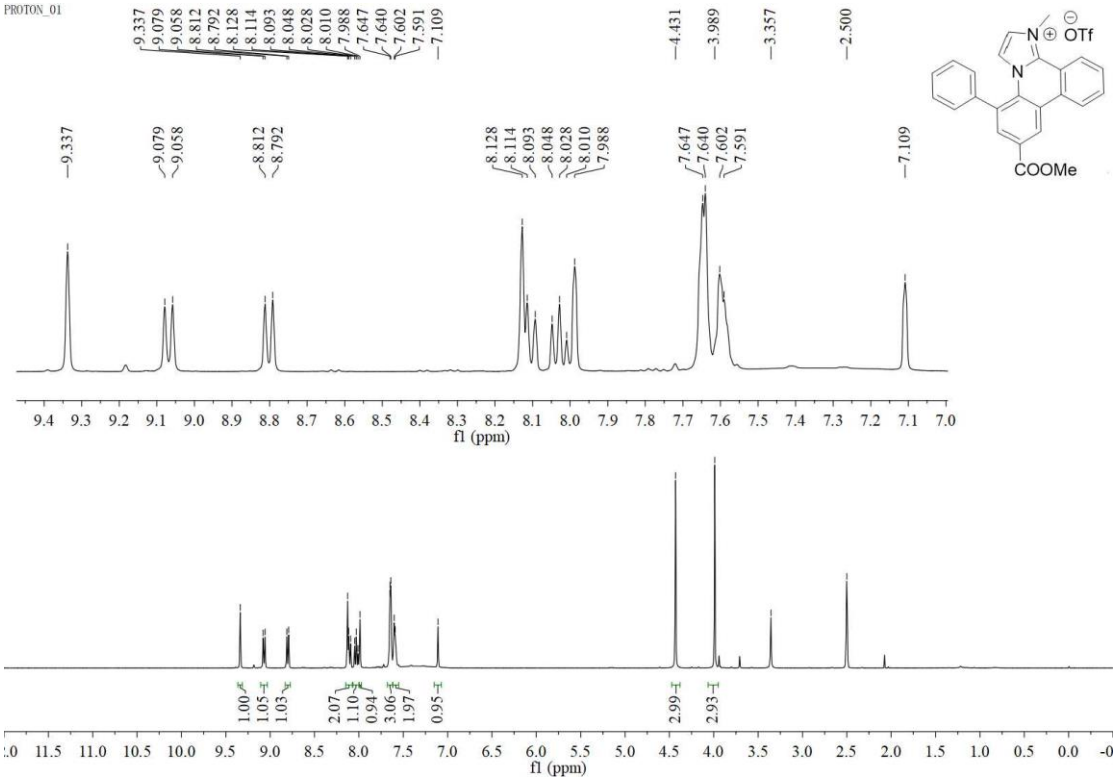
^{1}H NMR (400 MHz) spectrum of **3i** in DMSO-d_6



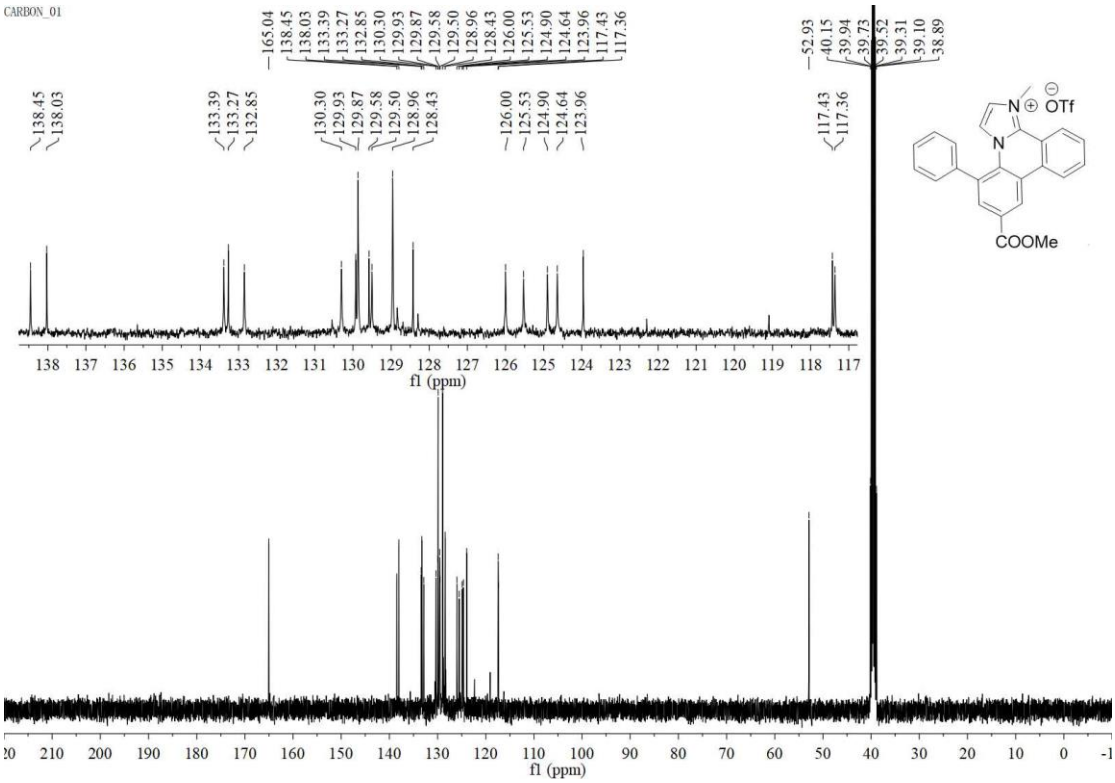
^{13}C NMR (100 MHz) spectrum of **3i** in DMSO-d_6



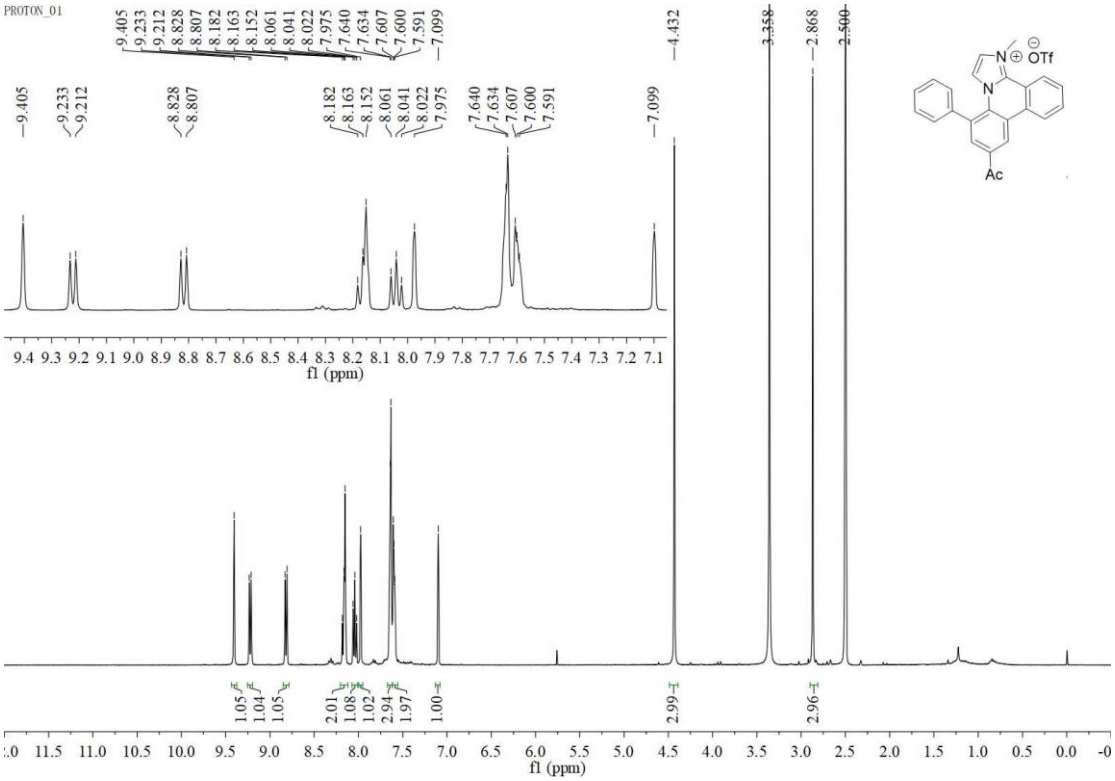
^{1}H NMR (400 MHz) spectrum of **3j** in DMSO-d_6



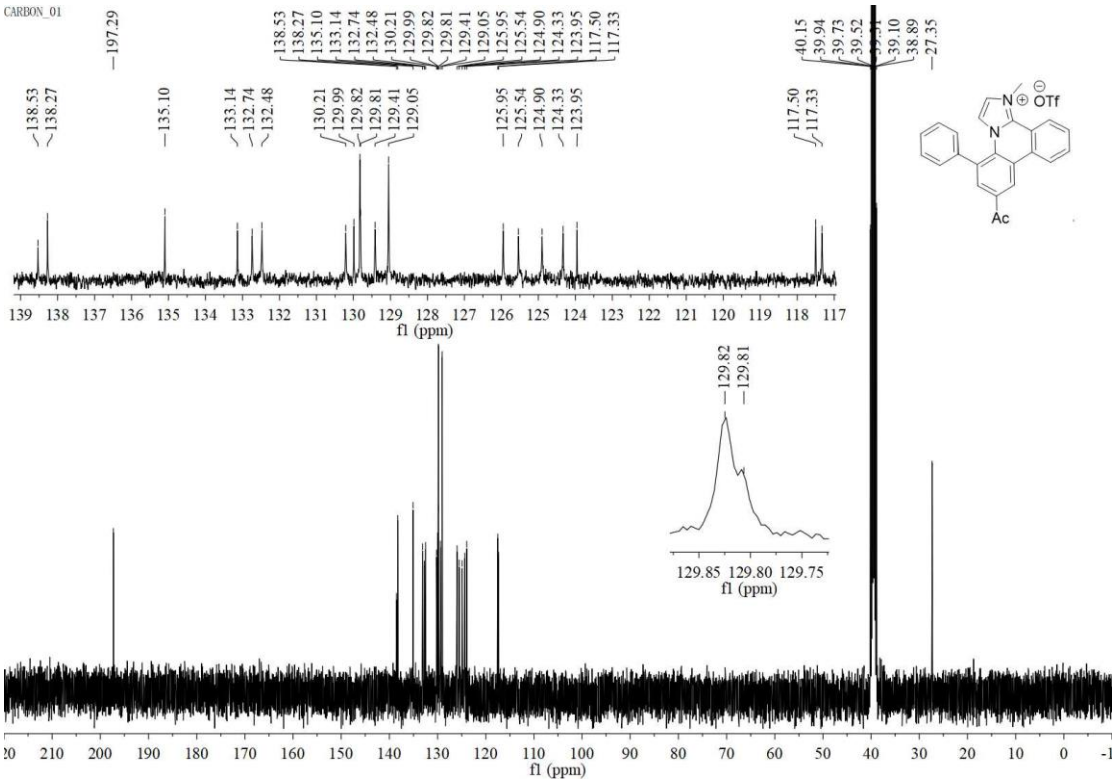
^{13}C NMR (100 MHz) spectrum of **3j** in DMSO-d_6



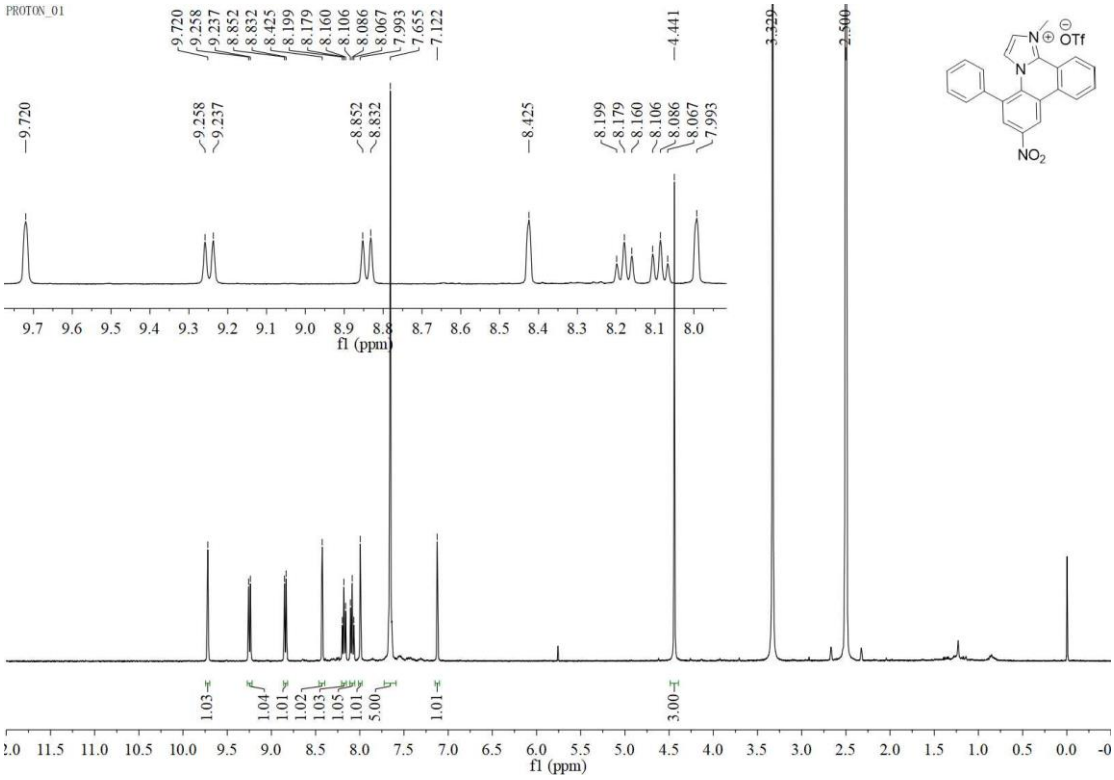
^{1}H NMR (400 MHz) spectrum of **3k** in DMSO-d_6



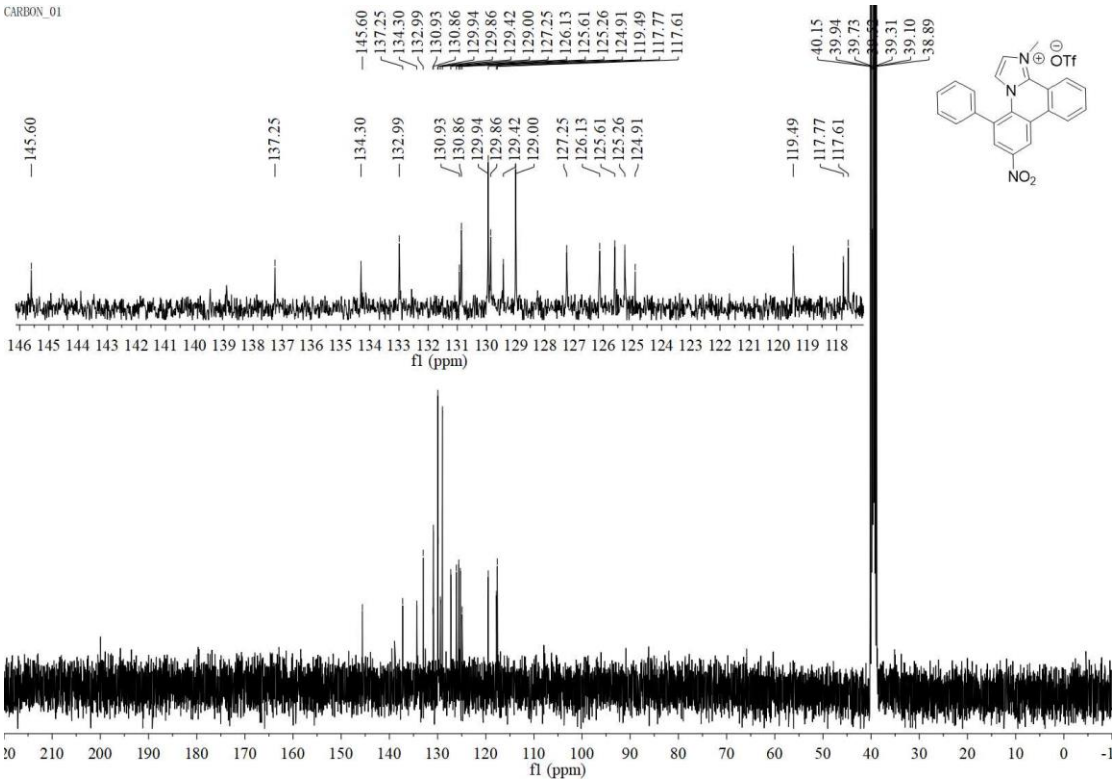
^{13}C NMR (100 MHz) spectrum of **3k** in DMSO-d_6



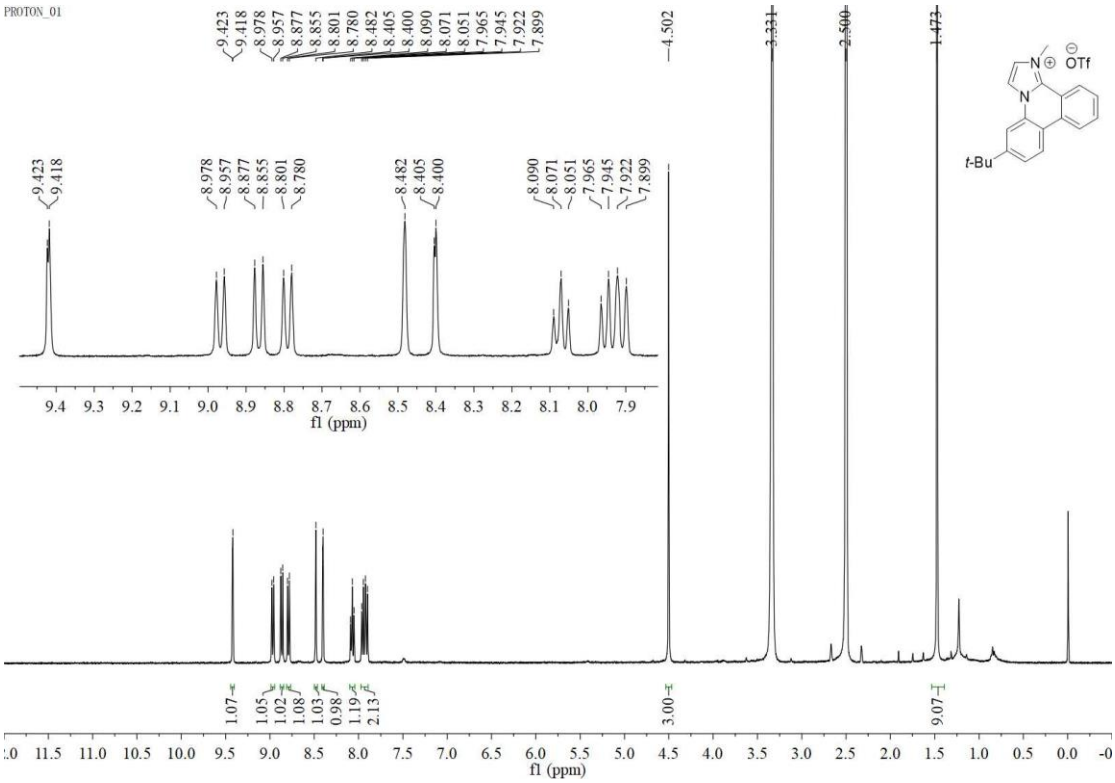
^{1}H NMR (400 MHz) spectrum of **3l** in DMSO-d_6



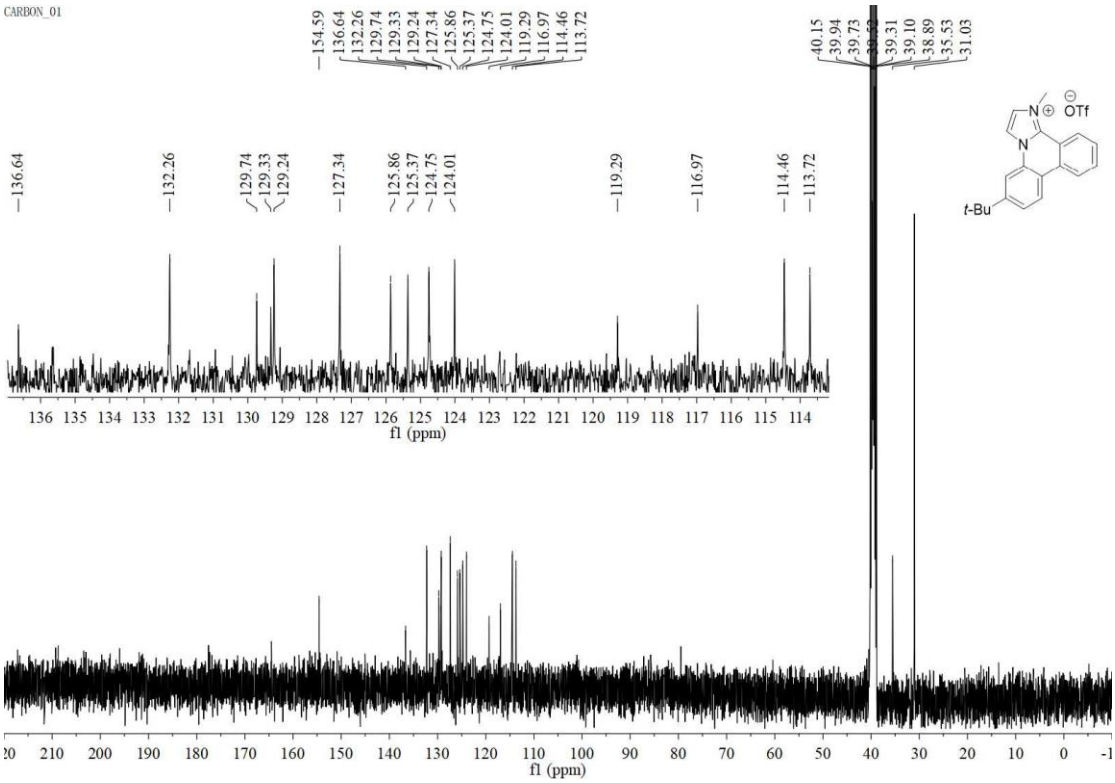
^{13}C NMR (100 MHz) spectrum of **3l** in DMSO-d_6



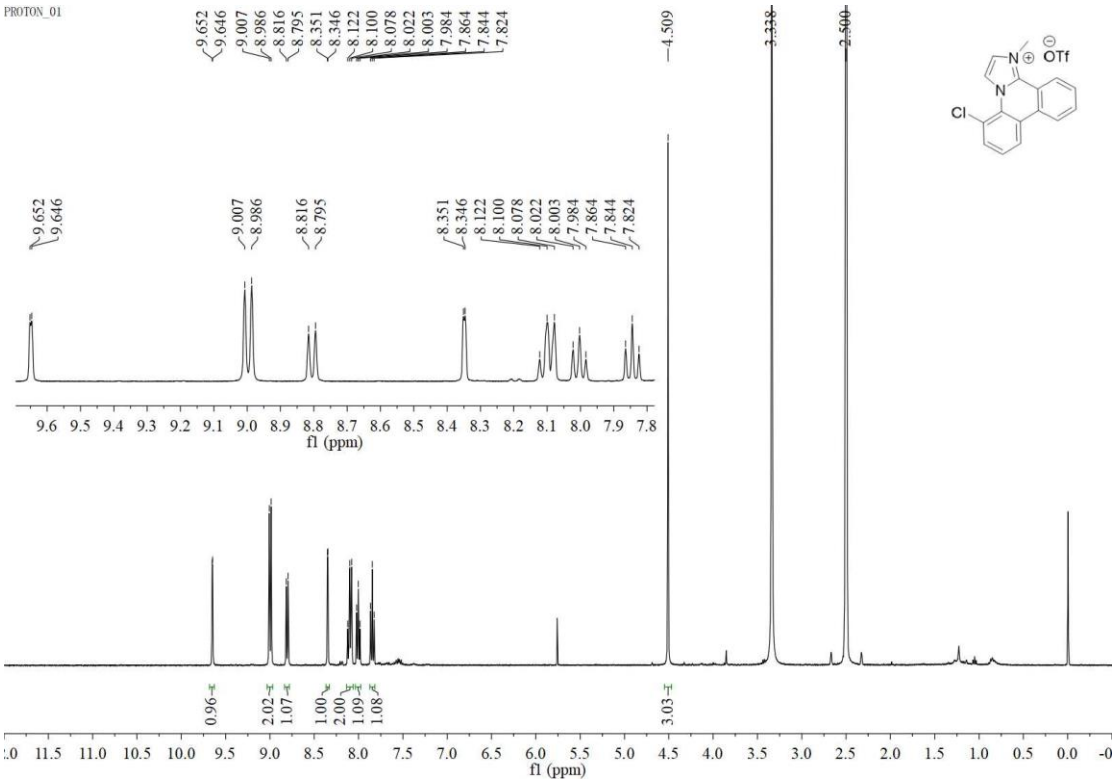
^{1}H NMR (400 MHz) spectrum of **3m** in DMSO-*d*$_6$



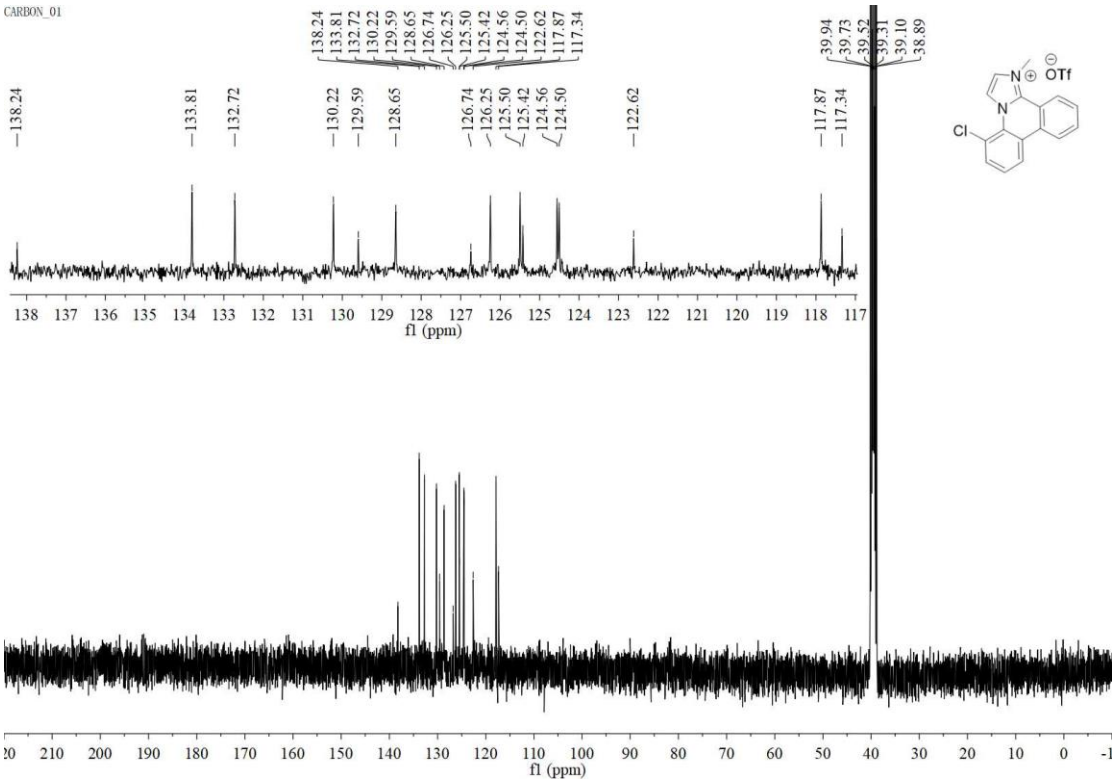
^{13}C NMR (100 MHz) spectrum of **3m** in DMSO-*d*$_6$



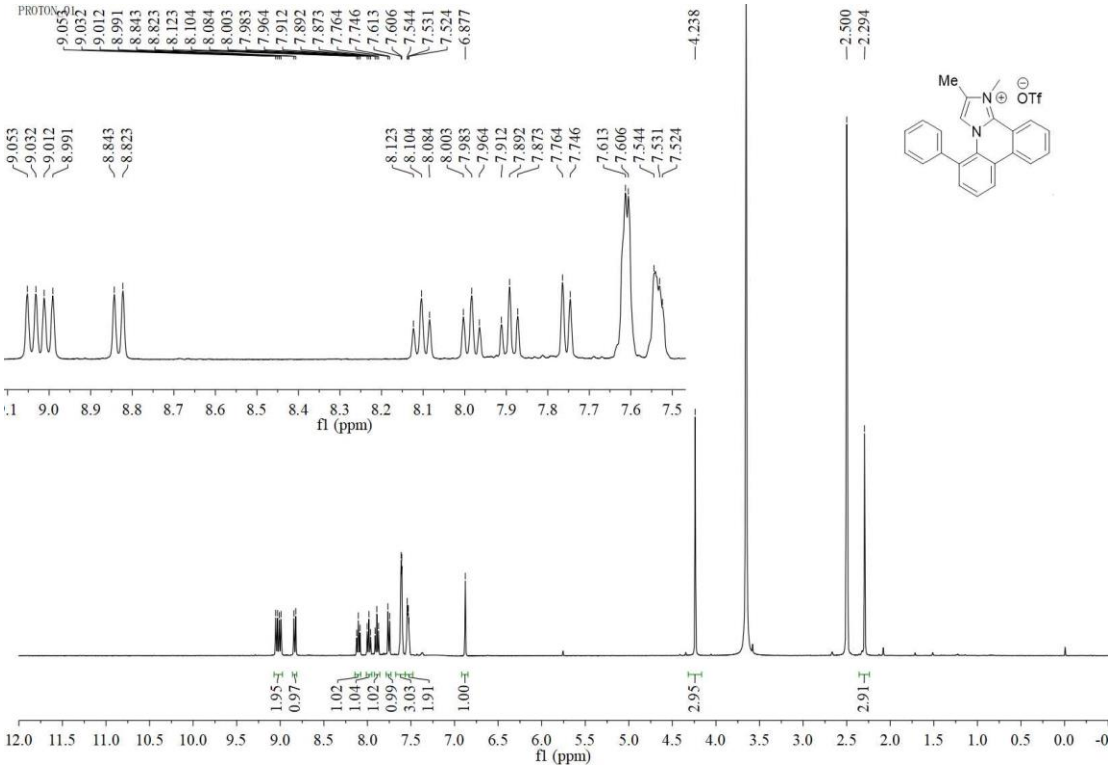
^{1}H NMR (400 MHz) spectrum of **3n** in DMSO-d_6



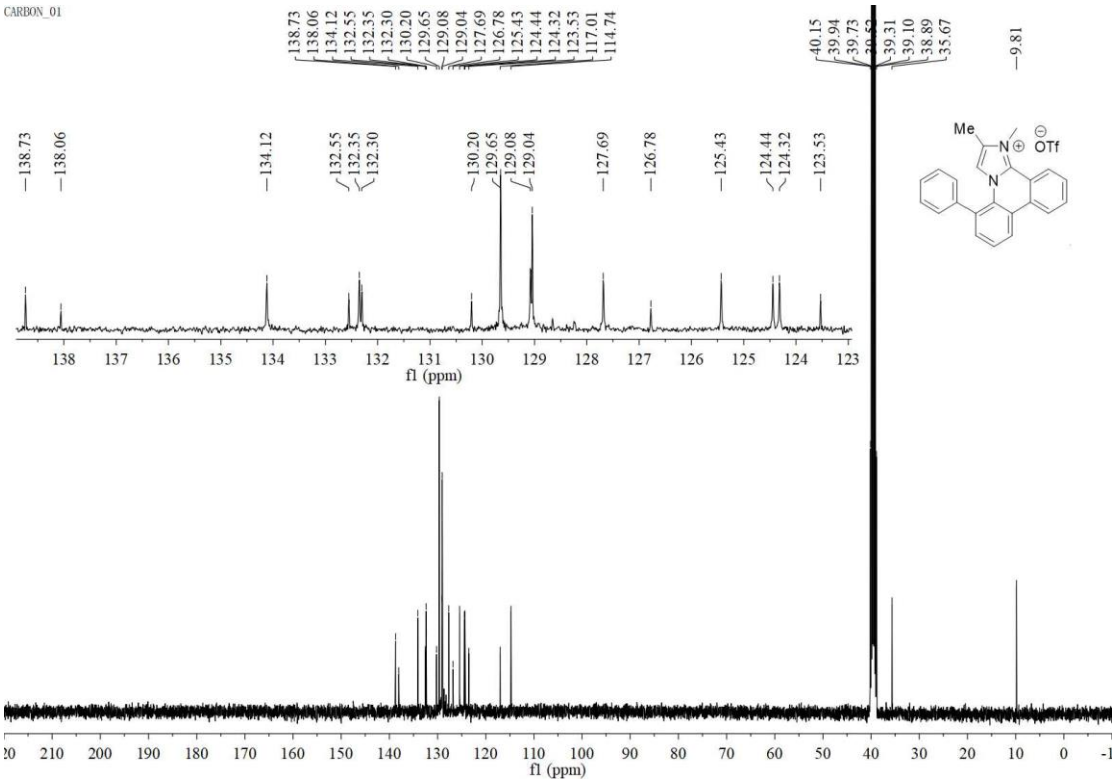
^{13}C NMR (100 MHz) spectrum of **3n** in DMSO-d_6



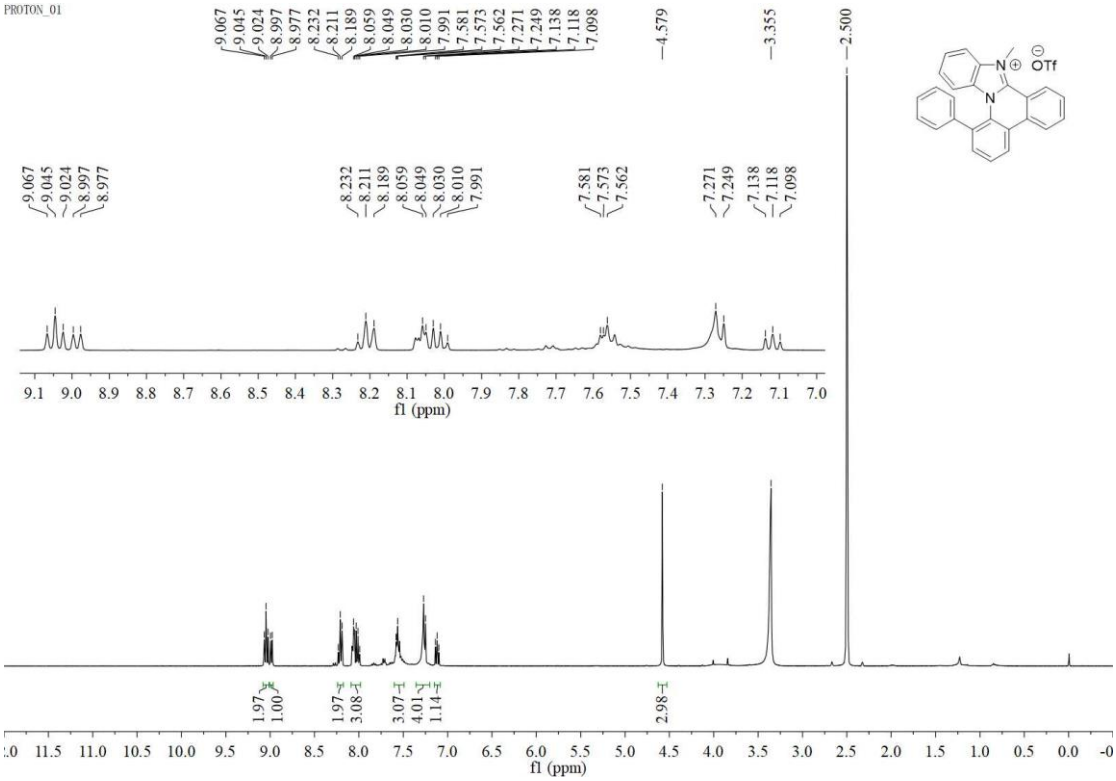
^{1}H NMR (400 MHz) spectrum of **3o** in DMSO-d_6



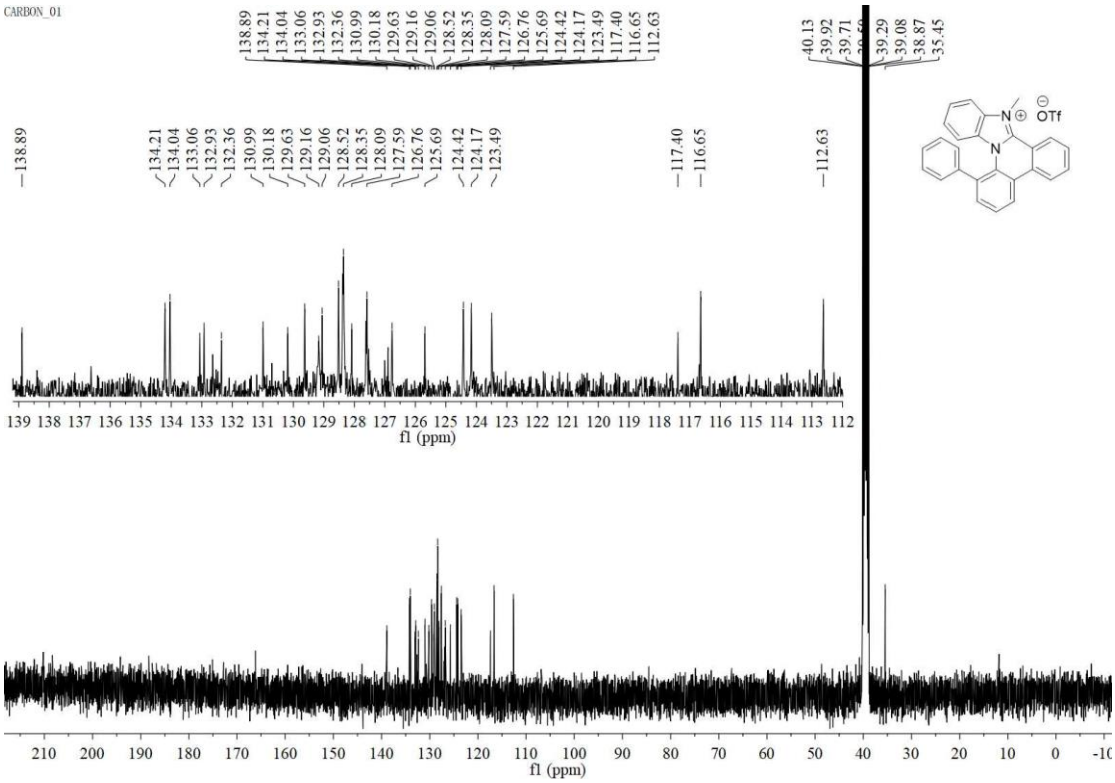
^{13}C NMR (100 MHz) spectrum of **3o** in DMSO-d_6



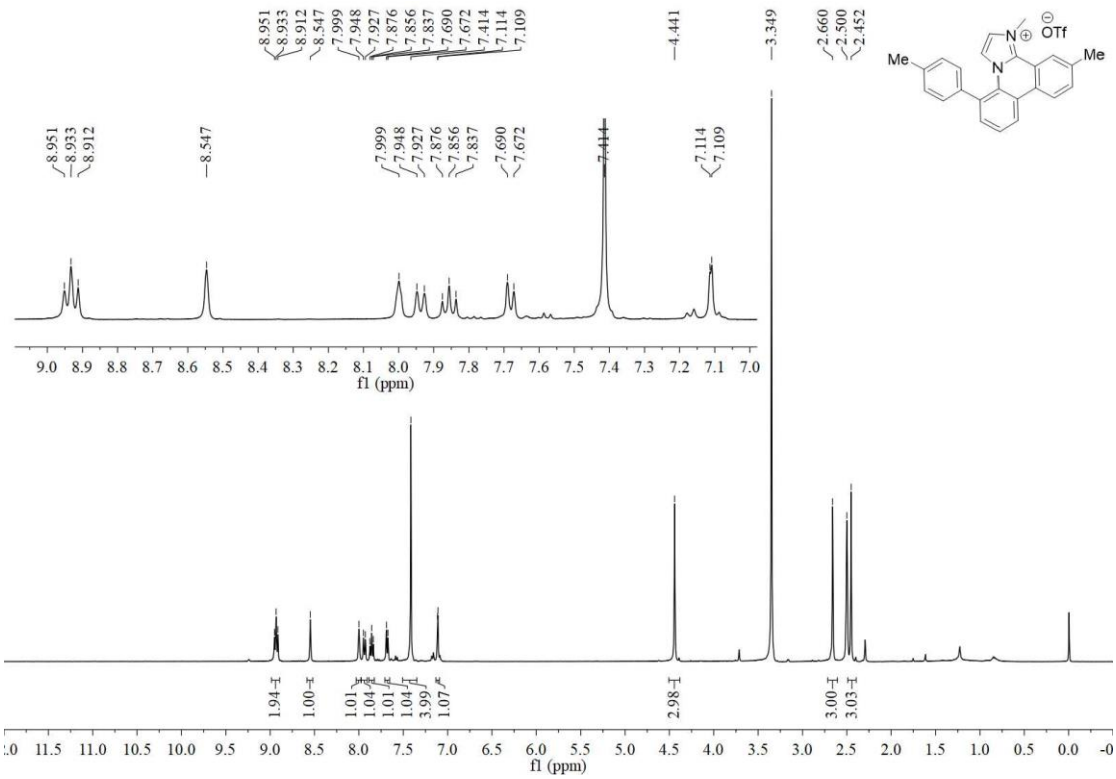
^{1}H NMR (400 MHz) spectrum of **3p** in DMSO-d_6



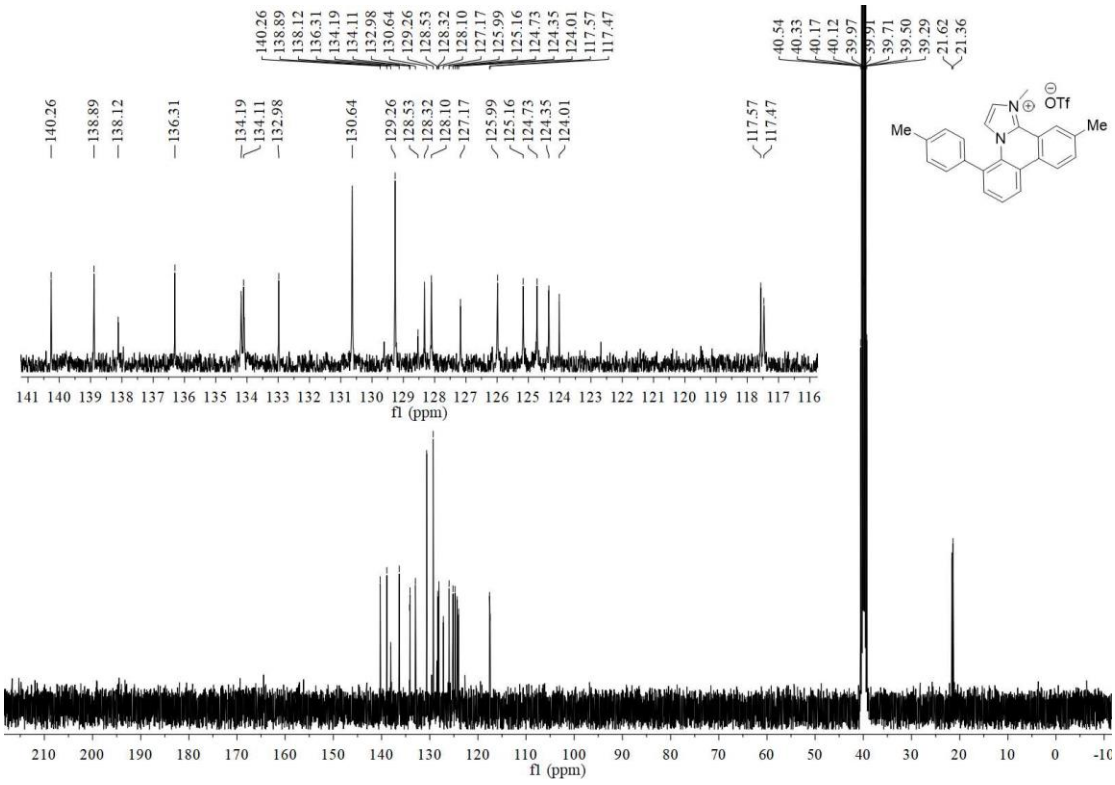
^{13}C NMR (100 MHz) spectrum of **3p** in DMSO-d_6



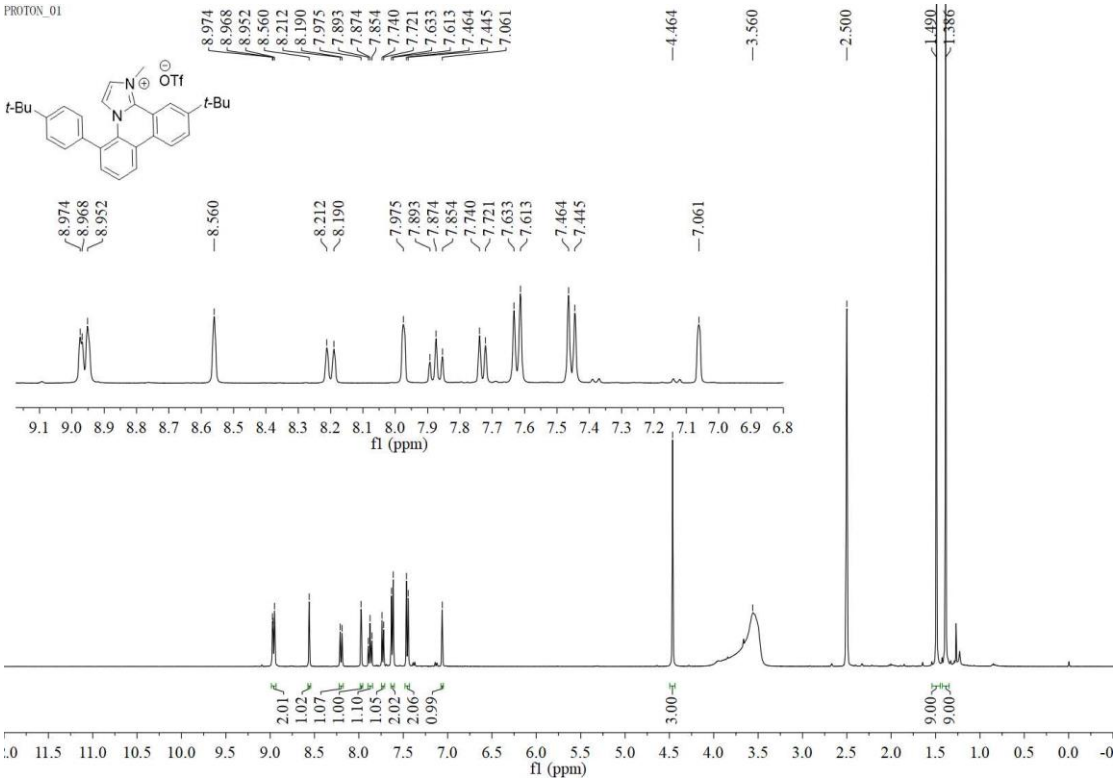
^{1}H NMR (400 MHz) spectrum of **4a** in DMSO-d_6



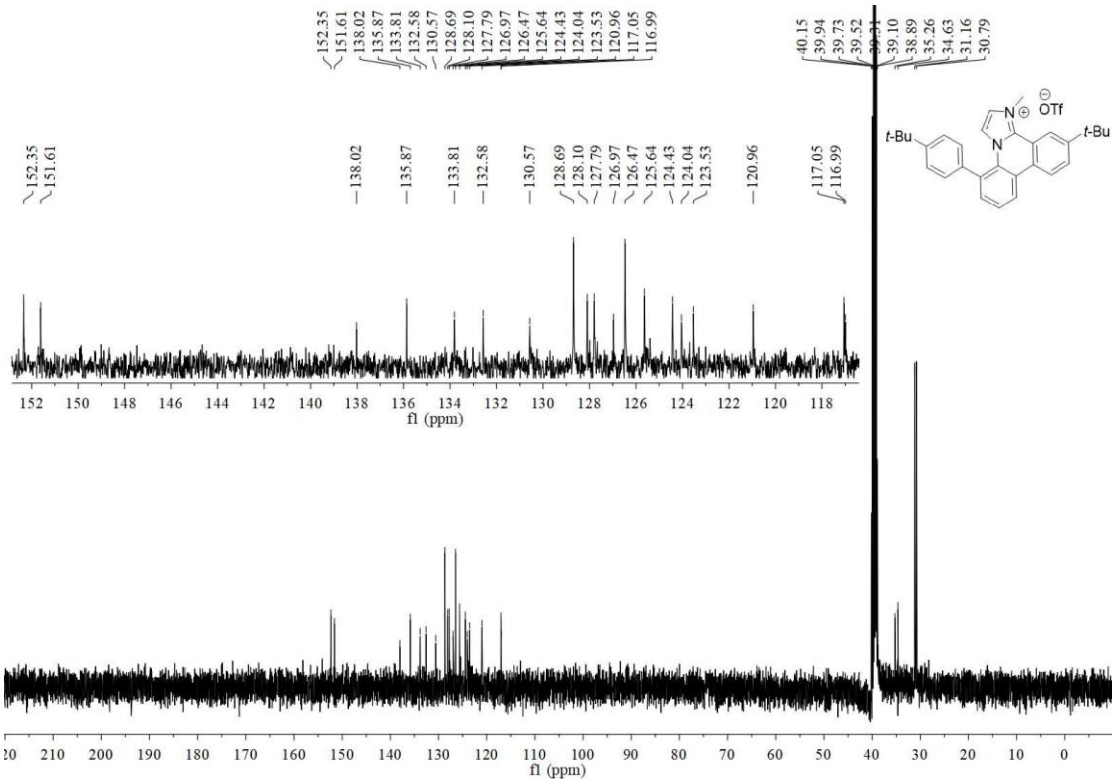
^{13}C NMR (100 MHz) spectrum of **4a** in DMSO-d_6



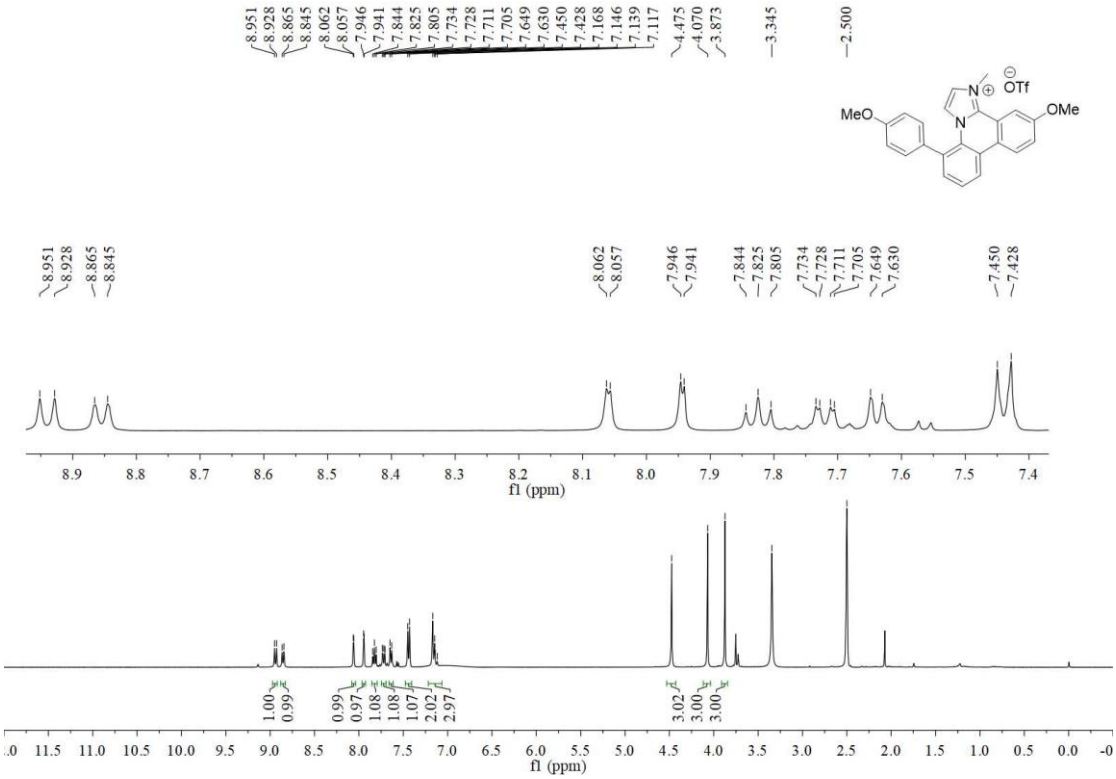
^{1}H NMR (400 MHz) spectrum of **4b** in DMSO-d_6



^{13}C NMR (100 MHz) spectrum of **4b** in DMSO-d_6



^{1}H NMR (400 MHz) spectrum of **4c** in DMSO-d_6



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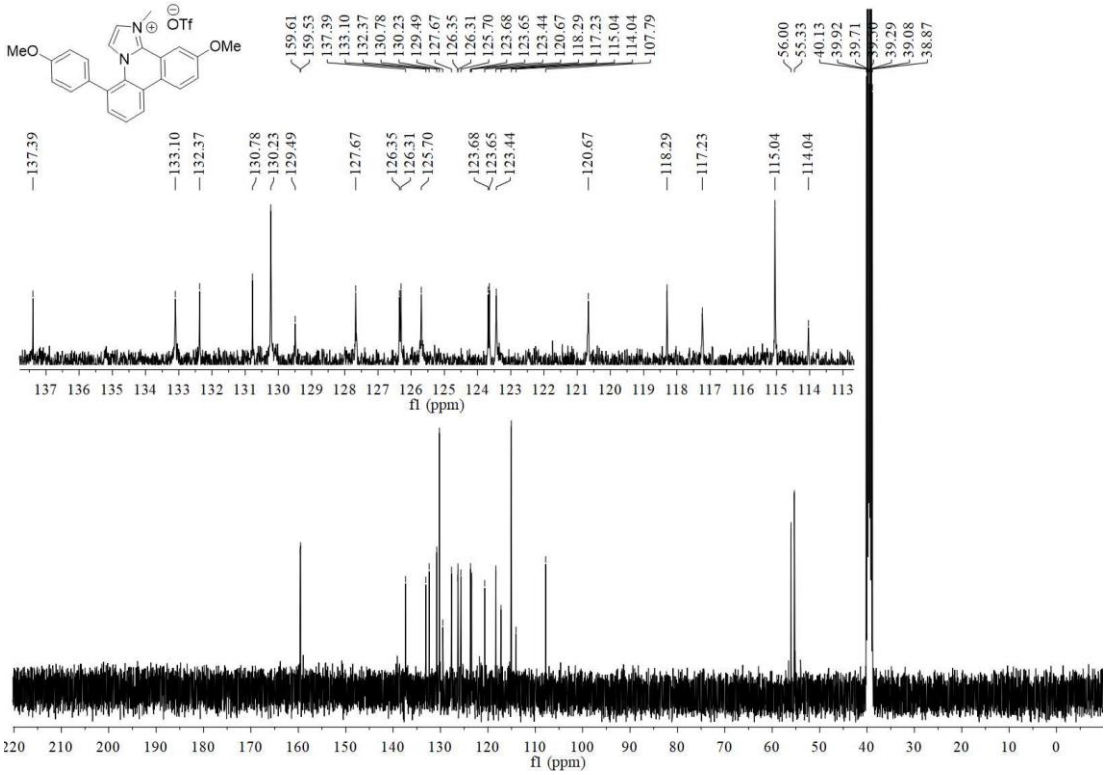
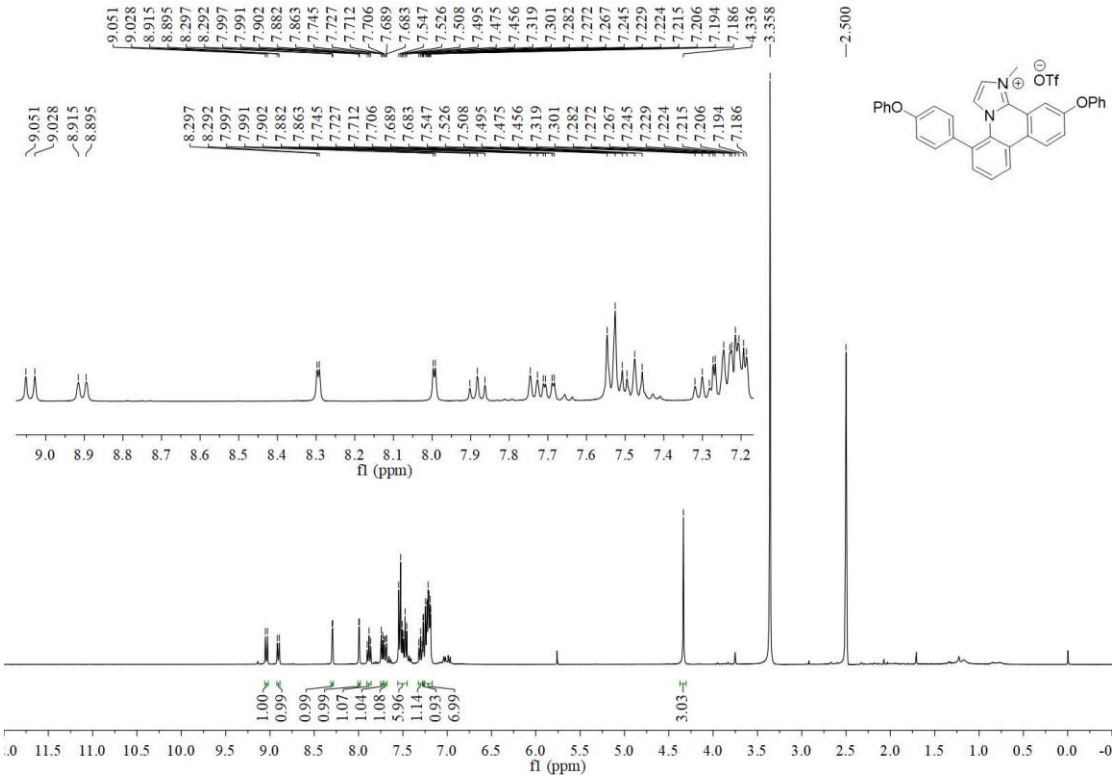
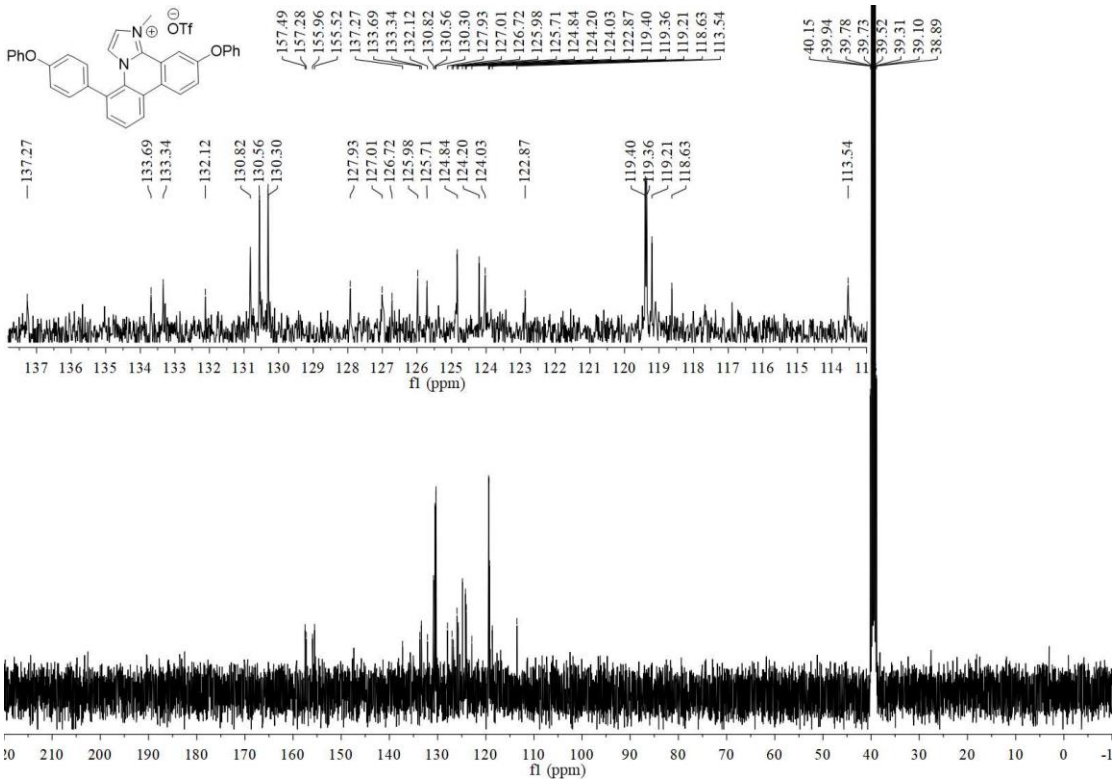


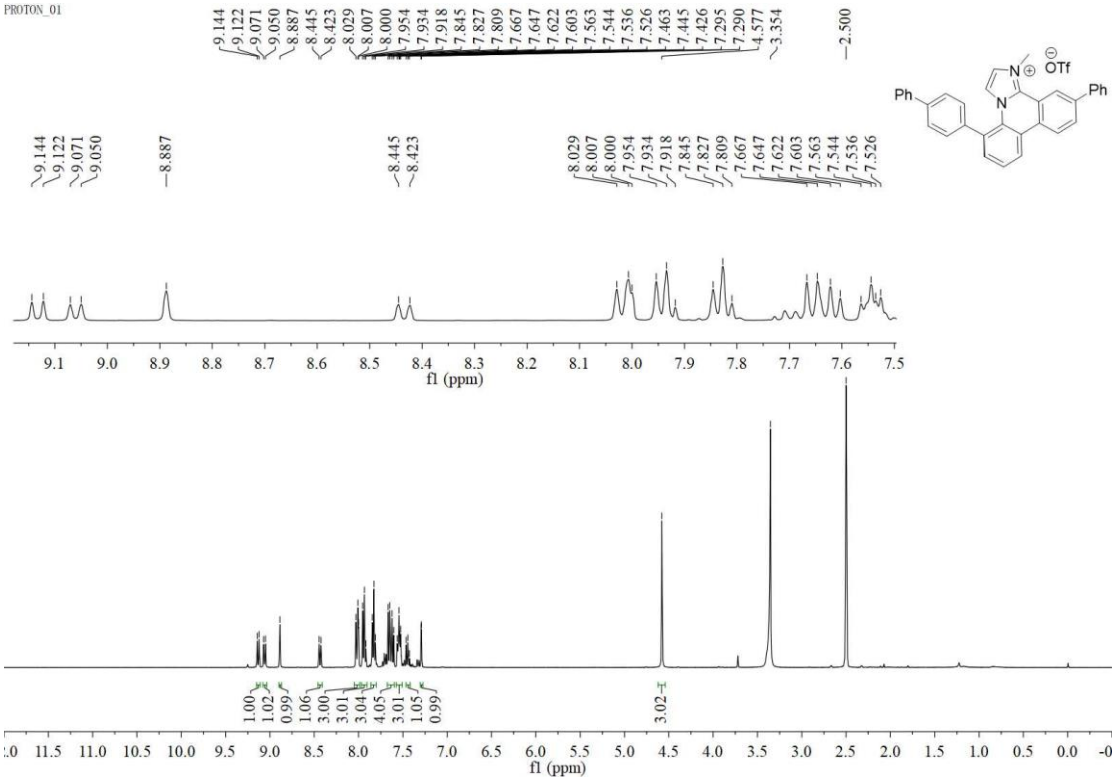
^{1}H NMR (400 MHz) spectrum of **4d** in DMSO-d_6



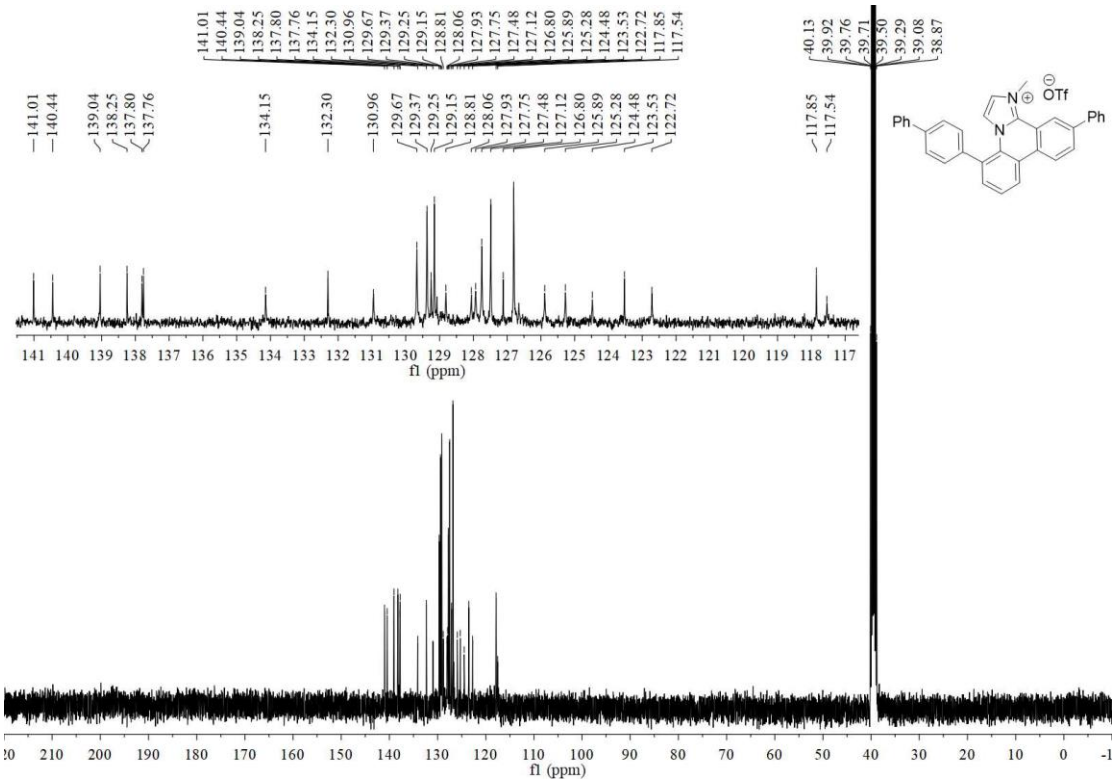
^{13}C NMR (100 MHz) spectrum of **4d** in DMSO-d_6



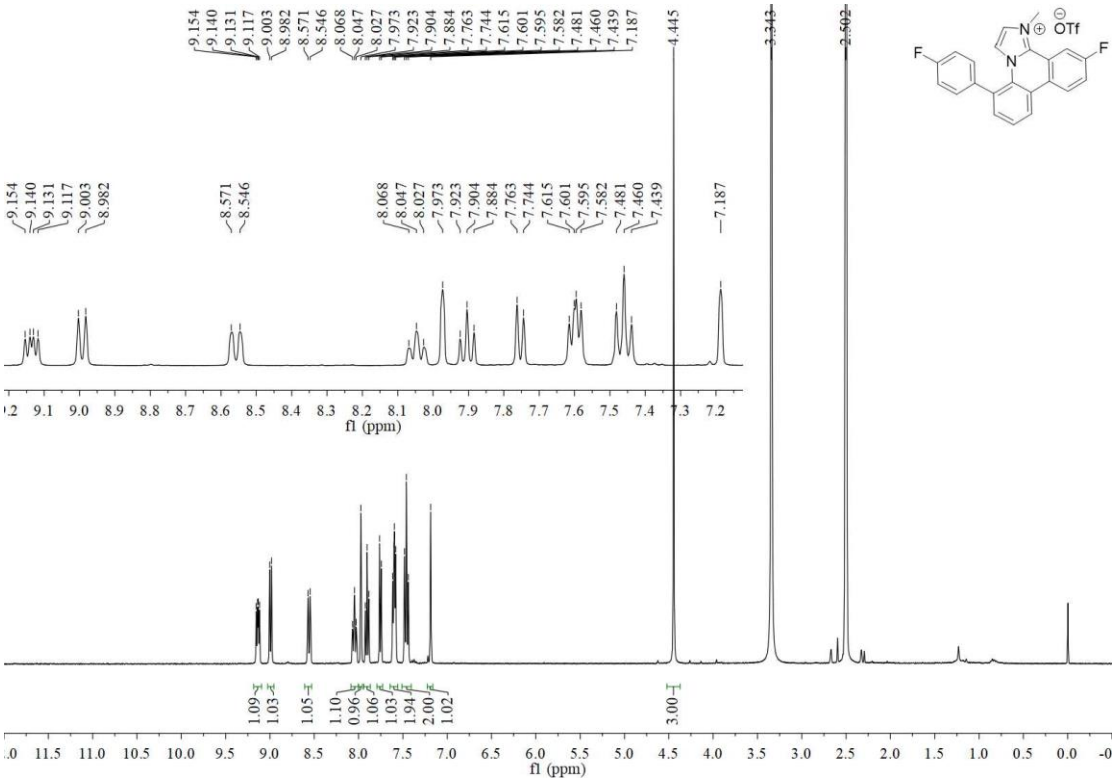
^{1}H NMR (400 MHz) spectrum of **4e** in DMSO-d_6



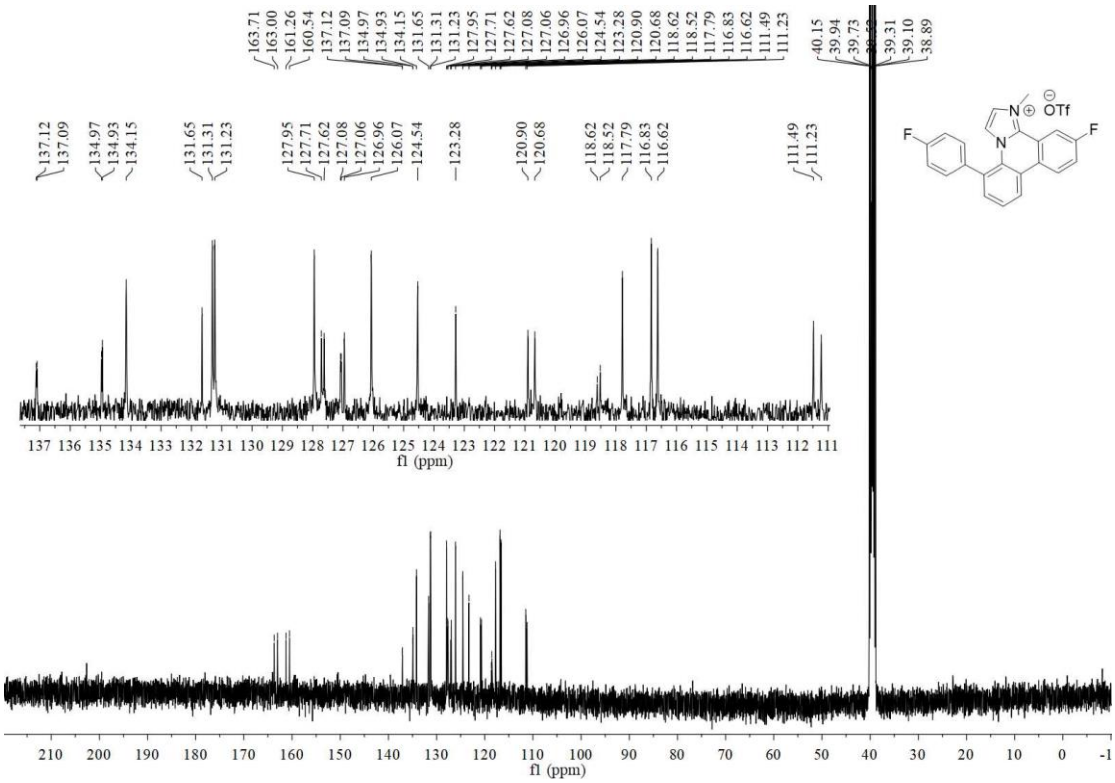
^{13}C NMR (100 MHz) spectrum of **4e** in DMSO-d_6



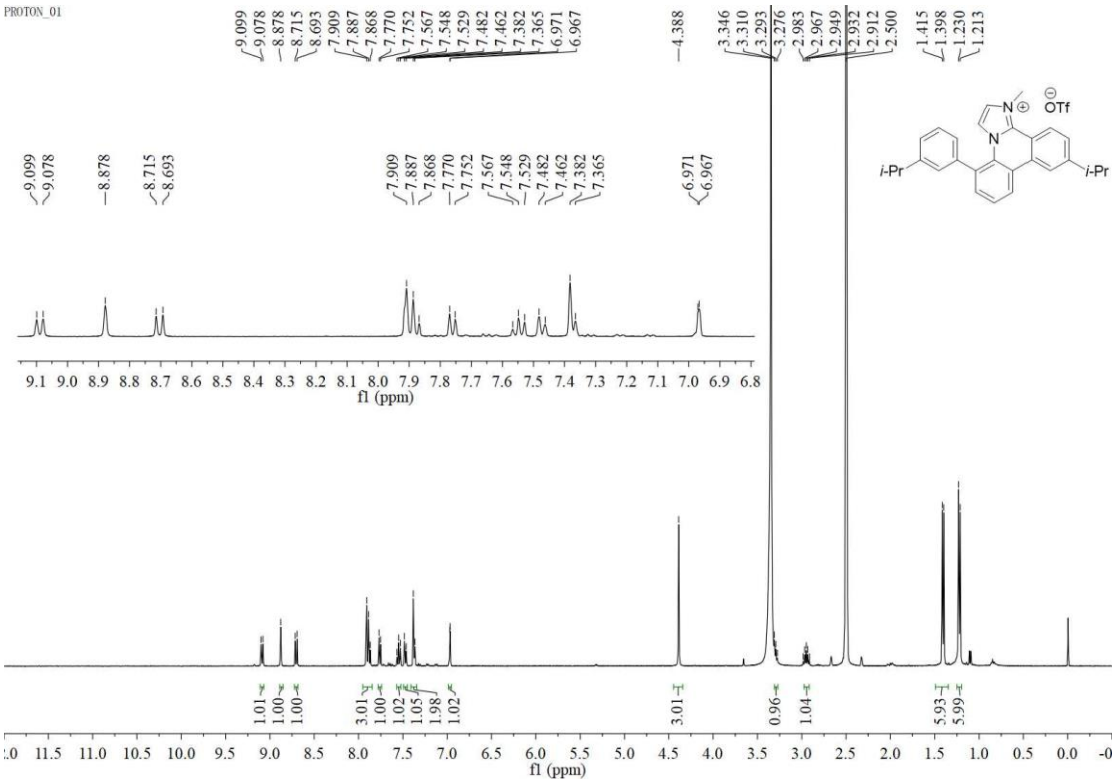
^{1}H NMR (400 MHz) spectrum of **4f** in DMSO-d_6



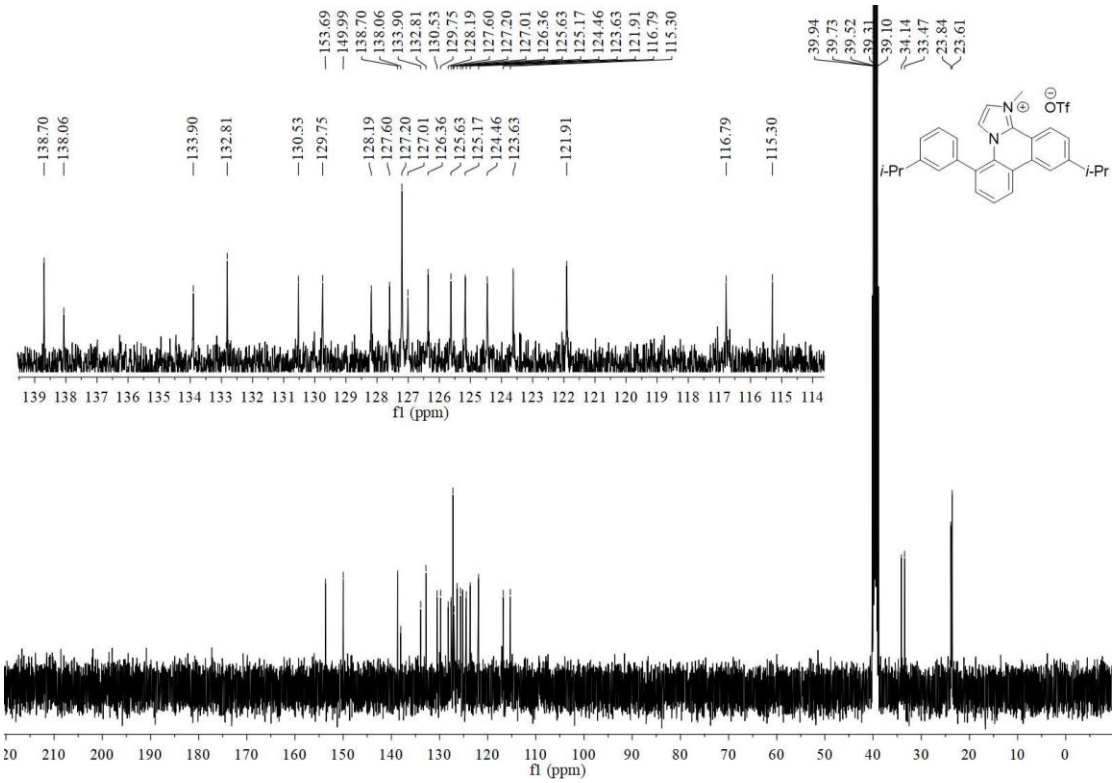
^{13}C NMR (100 MHz) spectrum of **4f** in DMSO-d_6



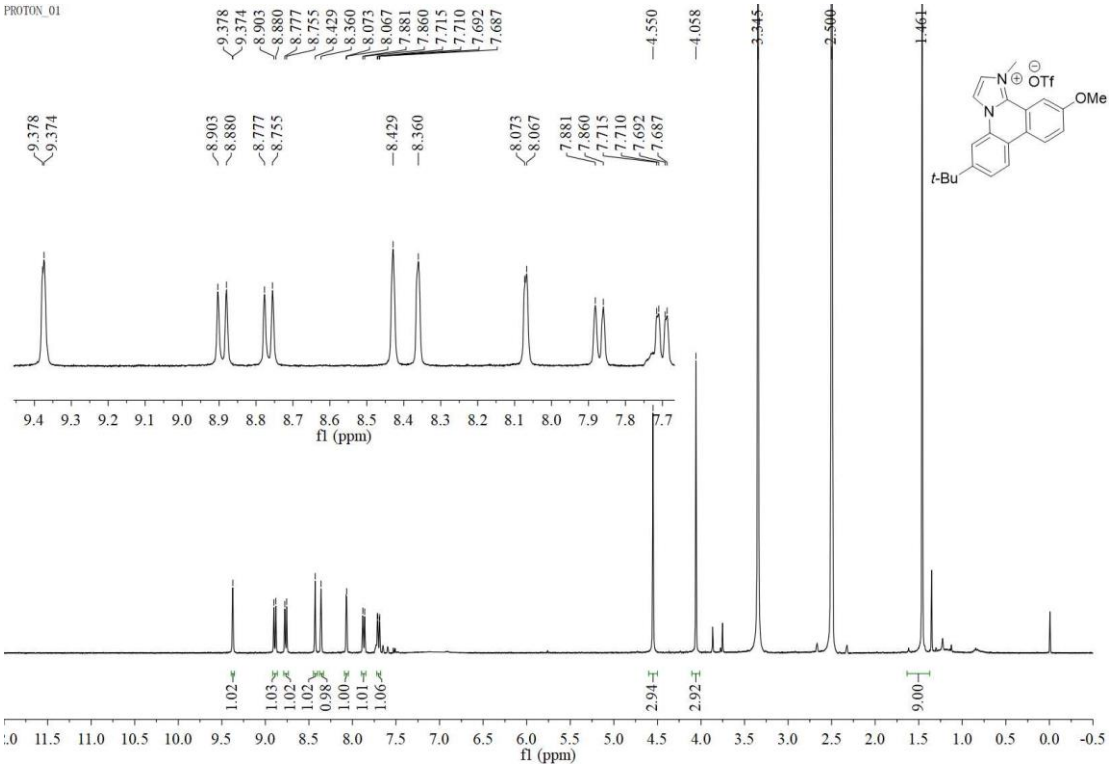
^{1}H NMR (400 MHz) spectrum of **4g** in DMSO-d_6



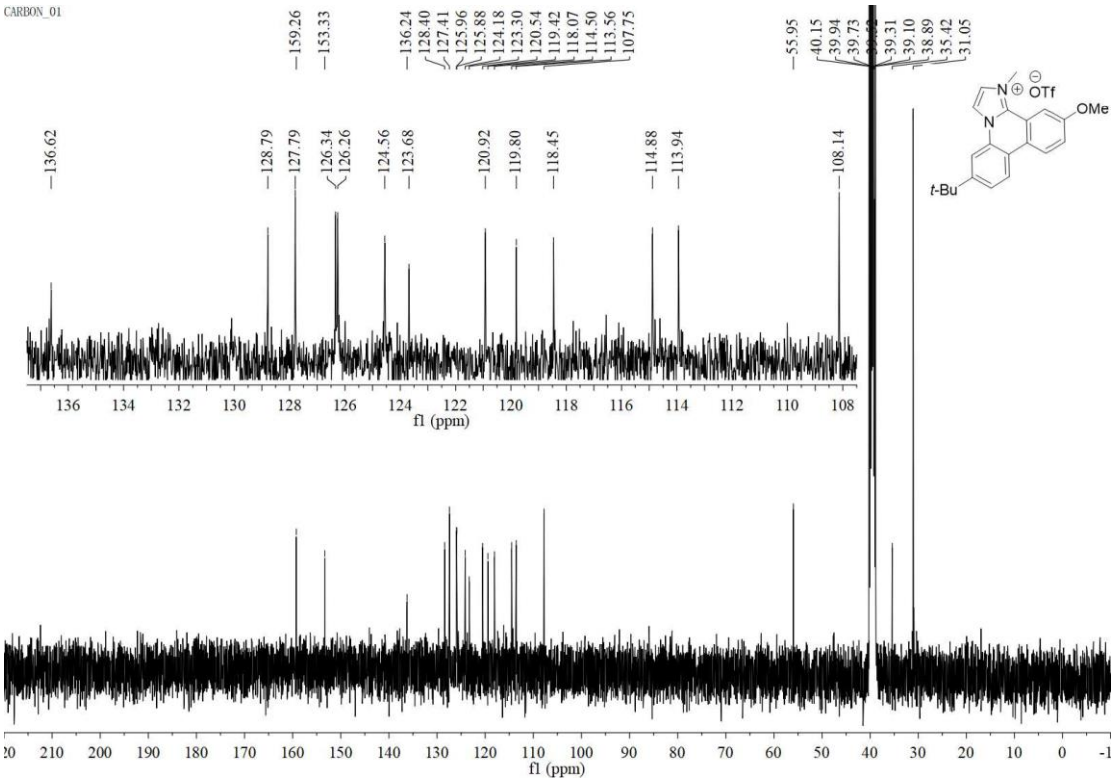
^{13}C NMR (100 MHz) spectrum of **4g** in DMSO-d_6



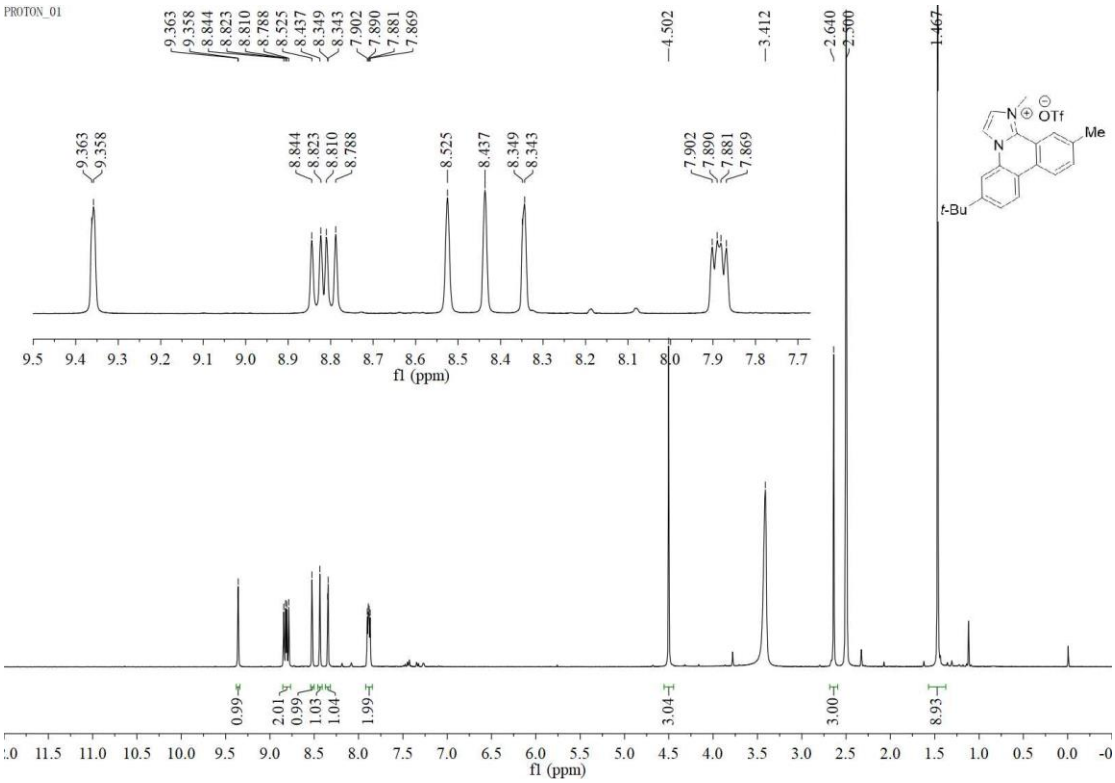
^{1}H NMR (400 MHz) spectrum of **4h** in DMSO-d_6



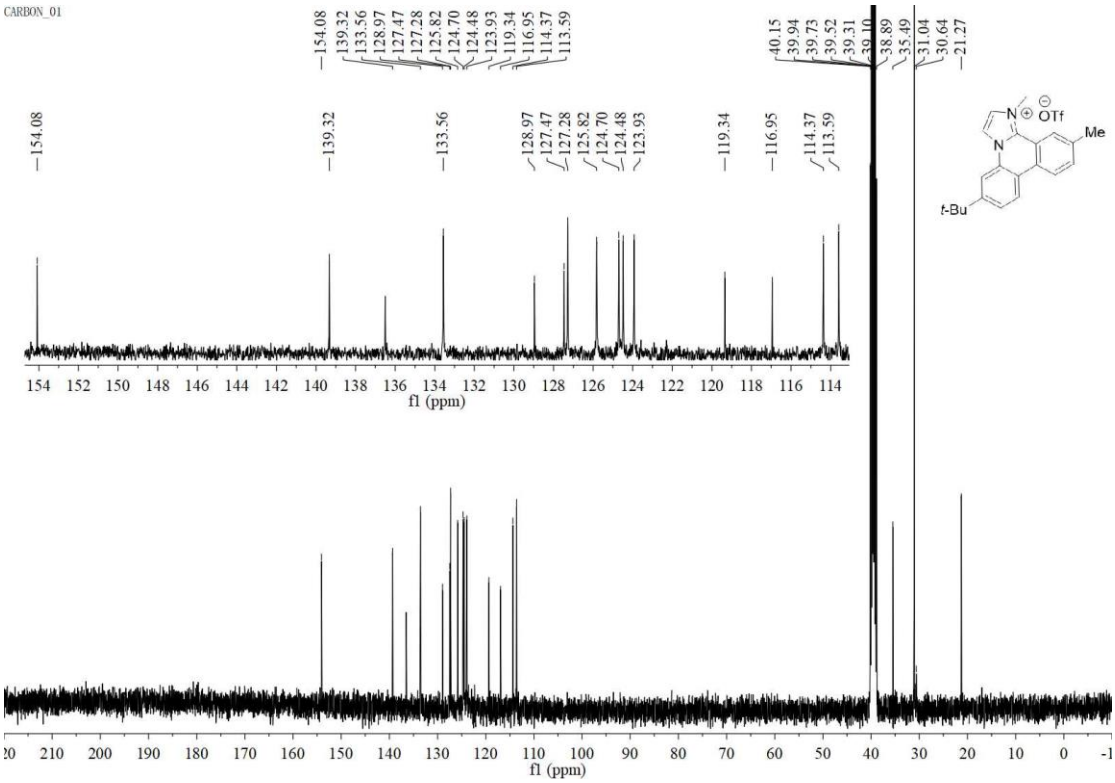
^{13}C NMR (100 MHz) spectrum of **4h** in DMSO-d_6



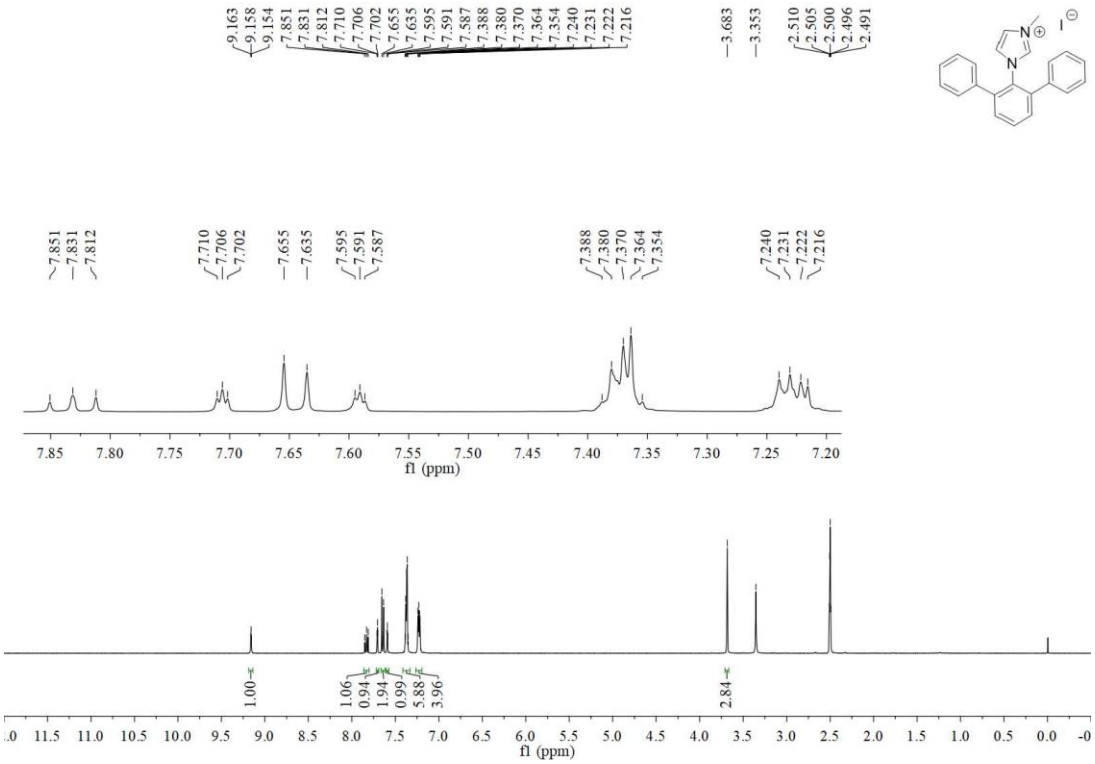
^{1}H NMR (400 MHz) spectrum of **4i** in DMSO-d_6



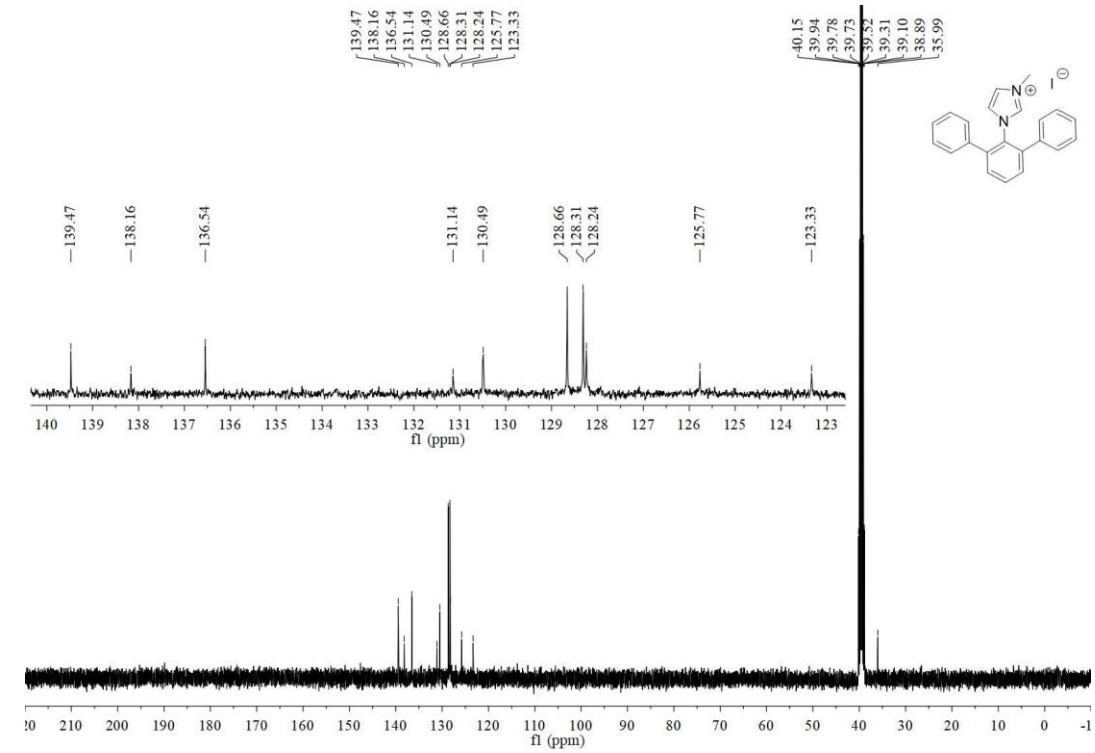
^{13}C NMR (100 MHz) spectrum of **4i** in DMSO-d_6



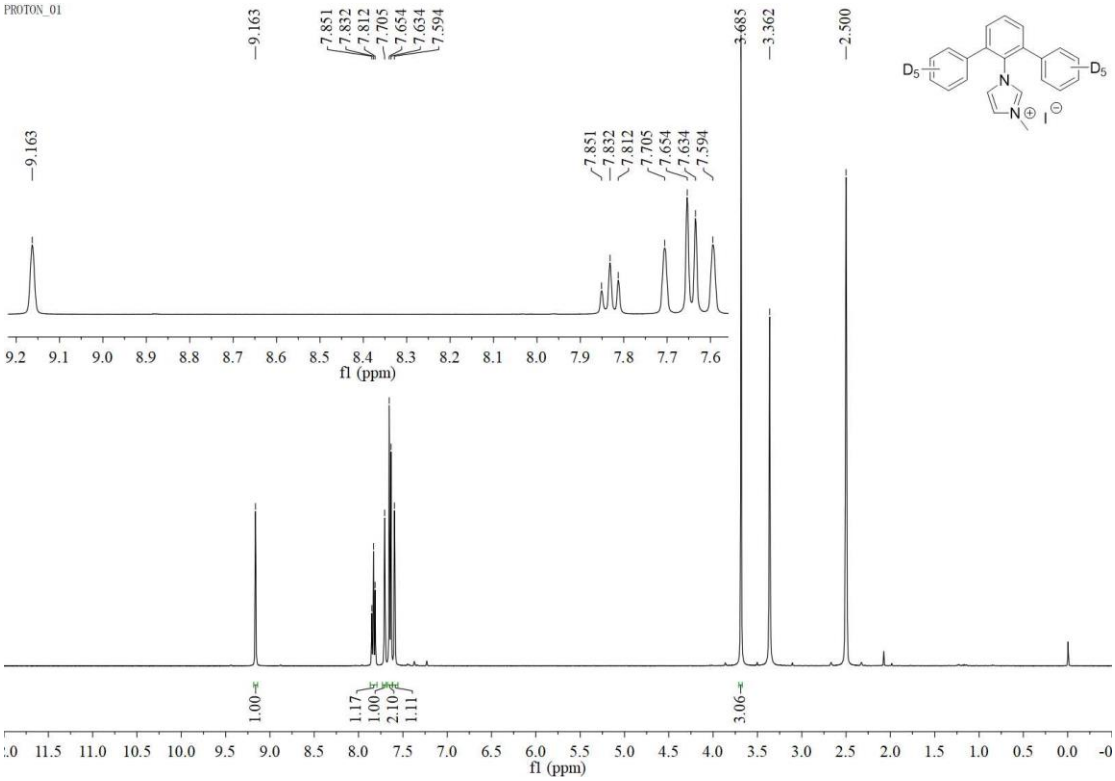
^{1}H NMR (400 MHz) spectrum of **6** in DMSO-d_6



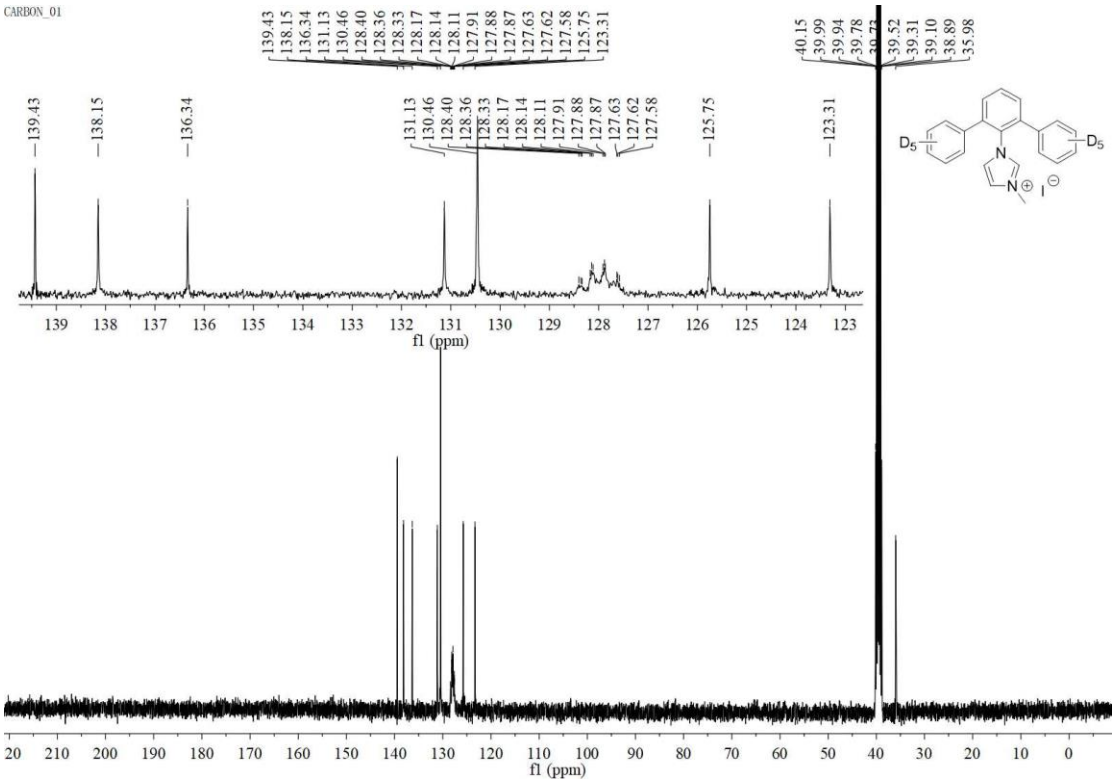
^{13}C NMR (100 MHz) spectrum of **6** in DMSO-d_6



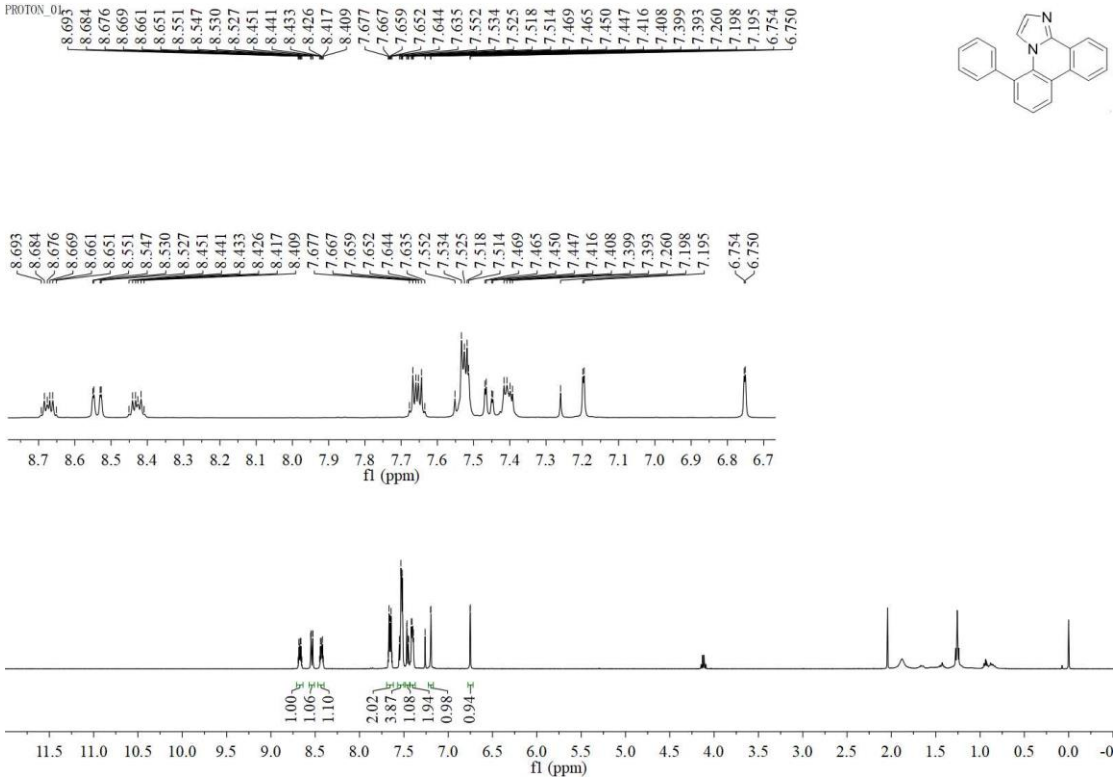
^{1}H NMR (400 MHz) spectrum of **D$_{10}$-6** in DMSO-*d*$_6$



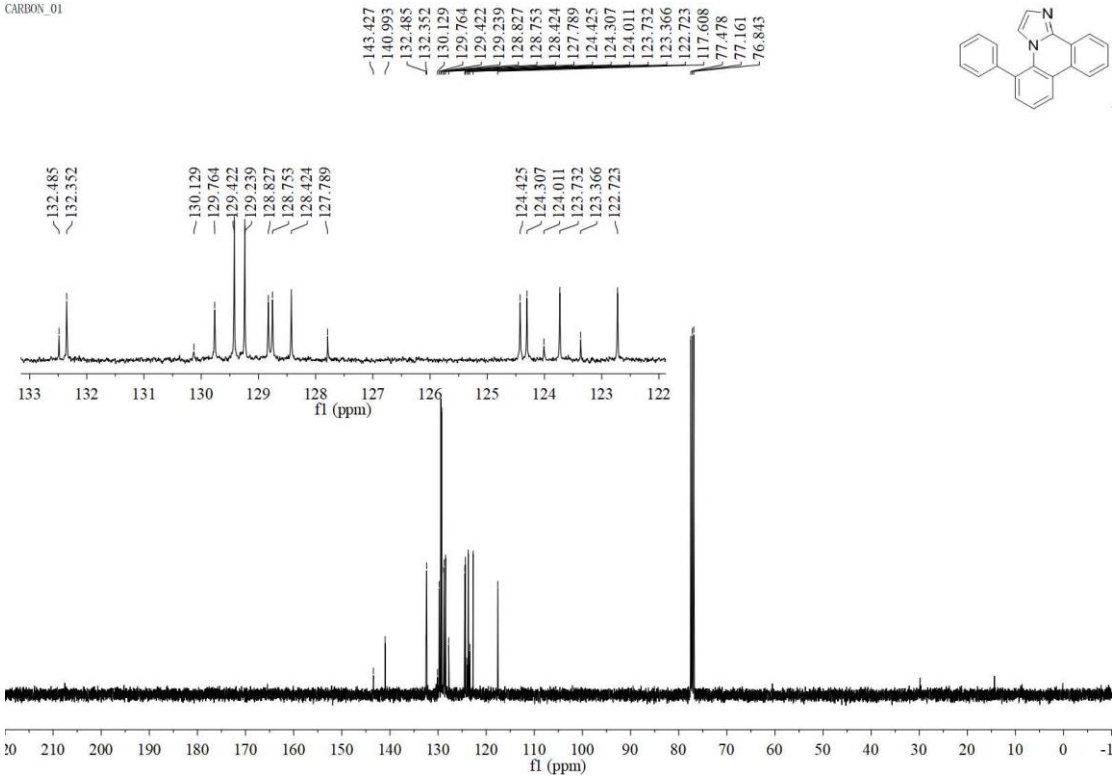
^{13}C NMR (100 MHz) spectrum of **D$_{10}$-6** in DMSO-*d*$_6$



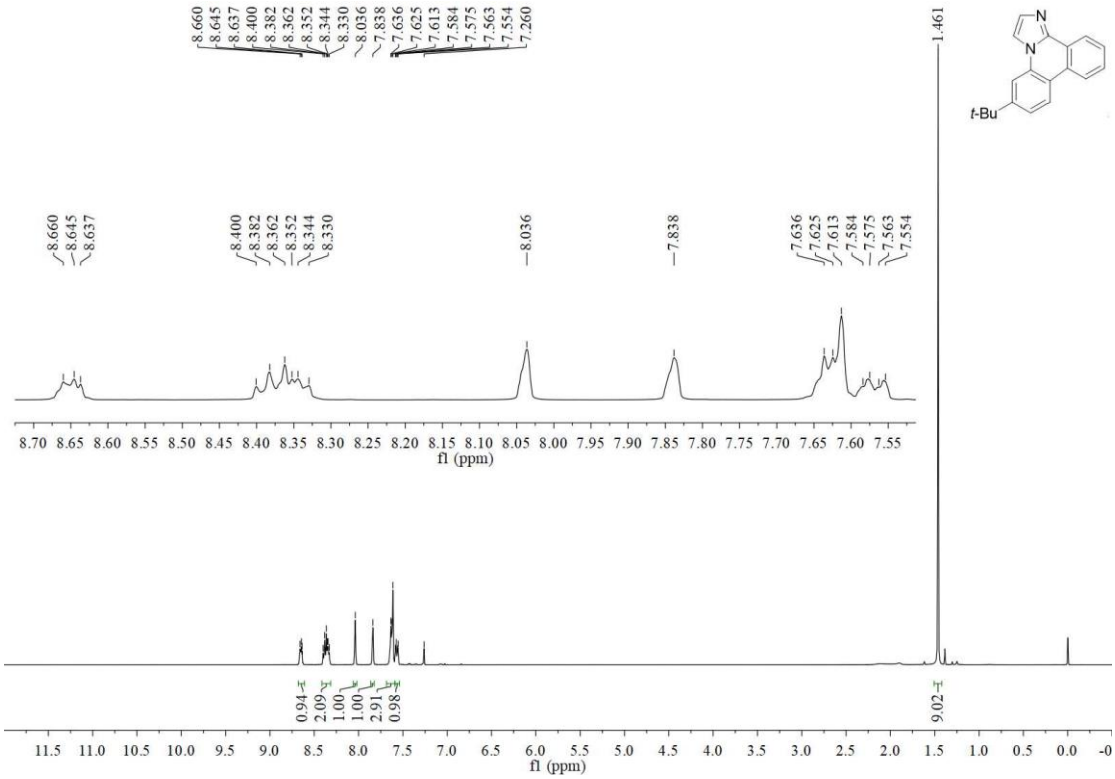
^{1}H NMR (400 MHz) spectrum of **8a** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **8a** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of **8b** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **8b** in $CDCl_3$