Catalyst-controlled regio- and chemodivergent C–H functionalization of imidazopyridines with TIPS-protected terminal alkynes

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1. General information

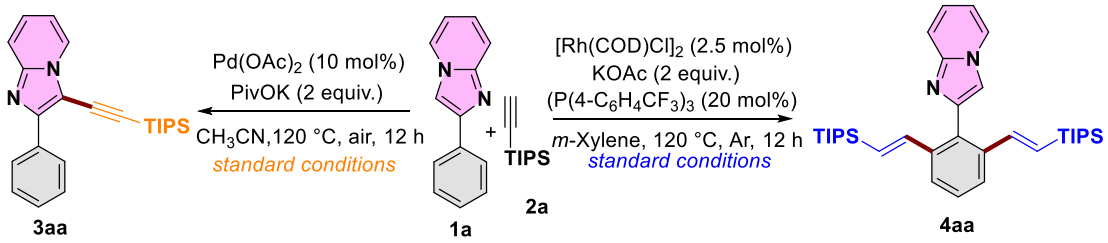
All the reagents were purchased from Bide Pharmatech Ltd. and Energy Chemical. All solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification. Unless otherwise stated, all reactions were carried out in oven-dried glassware under air atmosphere. All heating reactions were heated by metal sand bath (WATTCAS, LAB-600).^{1}H-NMR spectra were obtained on Bruker-600. NMR spectra for all the samples were recorded in deuterochloroform ($CDCl_3$) and deuterated methanol (CD_3OD). Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.28 ppm for ^{1}H; 77.23 ppm for ^{13}C) and deuterated methanol (4.87 ppm for ^{1}H; 49.00 ppm for ^{13}C), constants were reported in Hertz. ^{1}H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublets of doublet (dd), doublets of triplet(dt), triplets of doublet(td), triplets of triplet (tt) and multiplet (m), integration and coupling constant(s) *J* in hertz (Hz). ^{13}C NMR spectra were recorded at 151 MHz on the same spectrometer and reported in ppm. All spectra were processed using the MestReNova program.

High-resolution mass spectra (HRMS) were recorded on a mass spectrometer (Thermo fisher Q Exactive HRMS) using electrospray ionization-time of flight (ESI-TOF) reflection experiments.

2. Optimization of the reaction conditions

We first optimized the C3-alkynylation under Pd catalysis. With $Pd(OAc)_2$ as the catalyst and PivOK as the base in acetonitrile, the desired product **3aa** was obtained in 80% yield (see Table S1). Control experiments revealed that omission of either the Pd catalyst or the base completely suppressed the reaction (entries 2–3). Screening of alternative bases, including Na_2CO_3, KOAc, $NaHCO_3$, and Cs_2CO_3, resulted in lower yields, indicating the superiority of PivOK (entries 4–7). Solvent evaluation showed that toluene, DCE, and 1,4-dioxane were less effective than CH_3CN (entries 8–10). Notably, the addition of CH_3COOH as a co-solvent (CH_3CN/CH_3COOH, 10/1) did not significantly affect the reaction yield (entry 11). In addition, lowering the reaction temperature or shortening the reaction time led to diminished yields of **3aa** (entries 12–13).We next investigated the *ortho*-alkenylation using a Rh-catalyzed system. Gratifyingly, employing $[Rh(COD)Cl]_2$ as the catalyst afforded the desired product **4aa** in 90% yield with excellent regioselectivity (entry 14). Control experiments confirmed that both KOAc and the Rh catalyst were essential for the transformation (entries 15–16). Further optimization demonstrated the critical roles of additives and solvents in achieving optimal efficiency (entries 17–23). Similarly, the addition of CH_3COOH as a co-solvent (m-xylene/CH_3COOH, 10/1) showed no significant influence on the reaction outcome (entry 24). As observed in the Rh system, decreasing the reaction temperature or reducing the reaction time resulted in inferior yields (entries 25–26). Moreover, the reaction failed to proceed under aerobic conditions, underscoring the necessity of an inert atmosphere (entry 27).

Table S1. Optimization of the reaction conditions [a]



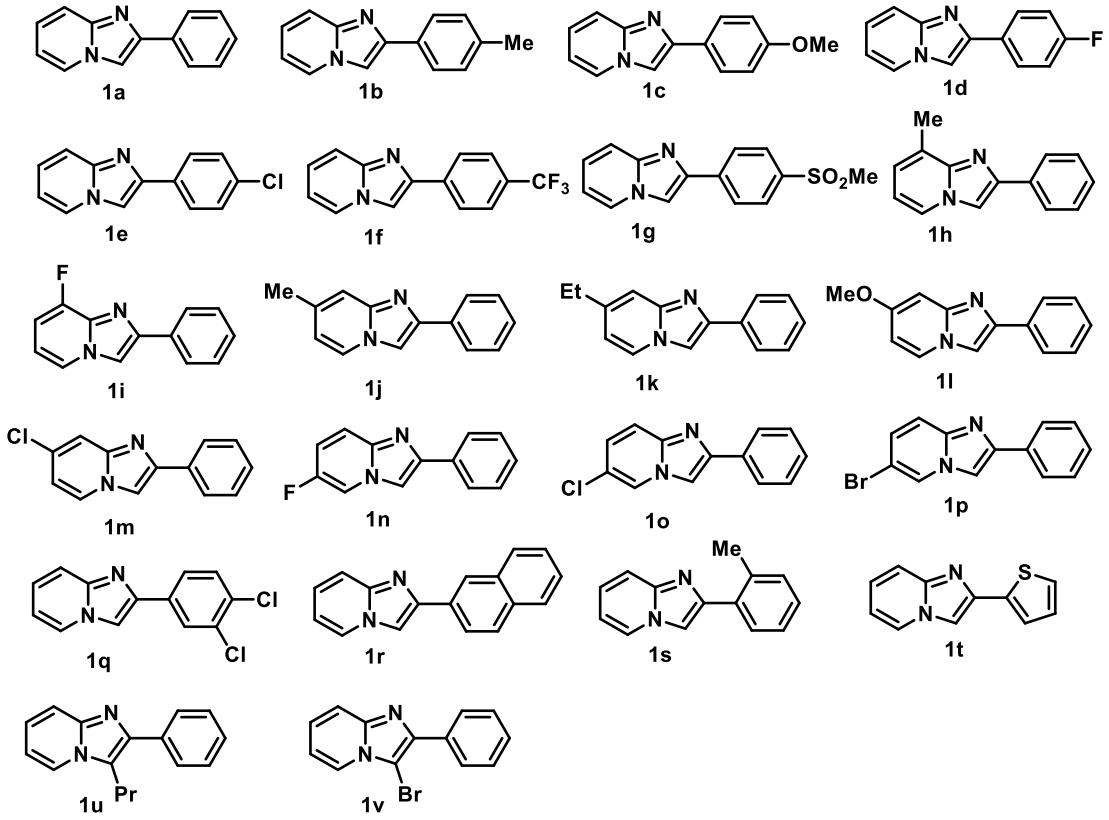
entry	variation from "standard conditions"	yield[%][b] 3aa/4aa
1	none	80/–
2	without $Pd(OAc)_2$	0/–
3	without PivOK	trace/–
4	Na_2CO_3 (2 equiv.) instead of PivOK	56/–
5	KOAc (2 equiv.) instead of PivOK	20/–
6	$NaHCO_3$ (2 equiv.) instead of PivOK	38/–
7	Cs_2CO_3 (2 equiv.) instead of PivOK	0/–
8	toluene instead of CH_3CN	61
9	DCE instead of CH_3CN	58
10	1,4-dioxane instead of CH_3CN	63
11	CH_3CN/CH_3COOH (10/1)	76/–
12	carried out at 100 °C	47/–
13	carried out for 8 h	64/–
14	none	–/90
15	without $[Rh(COD)Cl]_2$	–/0
16	without KOAc	–/trace
17	PPh_3 instead of $(P(4\text{-}C_6H_4CF_3)_3$	–/28
18	PCy_3 instead of $(P(4\text{-}C_6H_4CF_3)_3$	–/trace
19	K_2CO_3 (2 equiv.) instead of KOAc	–/12
20	$NaHCO_3$ (2 equiv.) instead of KOAc	–/trace
21	PivOH (2 equiv.) instead of KOAc	–/48
22	DCE instead of *m*-Xylene	–/36
23	1.4-dioxane instead of *m*-Xylene	–/41
24	*m*-Xylene/CH_3COOH (10/1)	–/87
25	carried out at 100 °C	–/62
26	carried out for 8 h	–/67
27	air instead of Ar	–/0

[a]Reaction conditions for **3aa**: **1a** (0.2 mmol), **2a** (entries 1–13, 0.3 mmol), $Pd(OAc)_2$ (10 mol%), PivOK (0.4 mmol) and CH_3CN (1.5 mL). Reaction conditions for **4aa**: **1a** (0.2 mmol), **2a** (entries 14–26, 0.5 mmol), $[Rh(COD)Cl]_2$ (2.5 mol%), $(P(4\text{-}C_6H_4CF_3)_3$ (0.04 mmol), KOAc (0.4 mmol) and *m*-Xylene (1.5 mL). [b]Isolated yield.

3. Experimental procedure

3.1 Procedure for the synthesis of starting materials

All known 2-aryl imidazopyridines (**1a–1t**) were synthesized following the reported procedure.[1] Notably, substrates **1u** and **1v** were prepared according to a different literature method.[2,3] All alkynes (**2a–2b**) were purchased from Bide Pharmatech Ltd.



3.2 Pd(II)-catalyzed oxidative C3-alkynylation of imidazo[1,2-*a*]pyridines

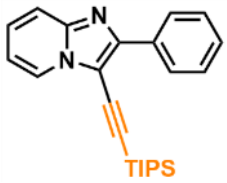
General Procedure A: To a 15 mL oven dried Schlenk tube, PivOK (0.4 mmol, 2 equiv.), imidazo[1,2-*a*]pyridines (0.2 mmol, 1 equiv.), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), terminal alkyne (0.3 mmol, 1.5 equiv.) and CH_3CN (1.5 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired alkynylated products **3**.

3.3 Rh(I)-catalyzed *ortho*-alkenylation of imidazo[1,2-*a*]pyridines

General Procedure B: To a 15 mL oven dried Schlenk tube, $(P(4\text{-}C_6H_4CF_3)_3$ (18.7 mg, 0.04 mmol, 20 mol%), imidazo[1,2-*a*]pyridines (0.2 mmol, 1 equiv.), $[Rh(cod)Cl]_2$ (2.5 mg, 0.005 mmol, 2.5 mol%), KOAc (0.4 mmol, 2 equiv.), terminal alkyne (0.5 mmol, 2.5 equiv.), and *m*-xylene (1.5 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under Ar. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the

desired alkenylated products **4**.

General Procedure C: To a 15 mL oven dried Schlenk tube, $(P(4\text{-}C_6H_4CF_3)_3$ (18.7 mg, 0.04 mmol, 20 mol%), imidazo[1,2-*a*]pyridines (0.2 mmol, 1 equiv.), $[Rh(cod)Cl]_2$ (2.5 mg, 0.005 mmol, 2.5 mol%), KOAc (0.4 mmol, 2 equiv.), terminal alkyne (0.5 mmol, 2.5 equiv.), and *m*-xylene (1.5 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 4 hours under Ar. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired alkenylated products **4**.

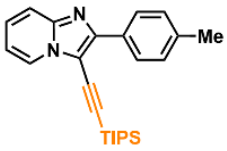


2-Phenyl-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3aa). Following the general procedure **A** using 2-phenylimidazopyridine (38.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3aa** (59.9 mg, 80%) as a white solid. Mp: 106-108 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, *J* = 7.2 Hz, 2H), 8.27 (d, *J* = 6.7 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.29 – 7.24 (m, 1H), 6.92 (t, *J* = 6.8 Hz, 1H), 1.26 – 1.19 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 145.0, 133.4, 128.6, 128.4, 127.3, 126.2, 125.2, 117.5, 113.1, 105.3, 104.8, 95.3, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{31}N_2Si$ 375.2251; Found 375.2243.

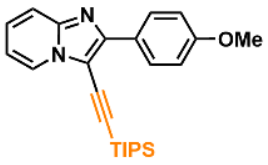


2-(*p*-Tolyl)-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3ba). Following the general procedure **A** using 2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (41.6 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ba** (58.2 mg, 75%) as a white solid. Mp: 118-120 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 – 8.32 (m, 2H), 8.25 (d, *J* = 6.7 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.24 (d, *J* = 3.3 Hz, 2H), 7.23 – 7.21 (m, 1H), 6.89 (td, *J* = 6.8, 1.0 Hz, 1H), 2.40 (s, 3H), 1.26 – 1.15 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.4, 144.9, 138.4, 130.6, 129.13, 127.2, 126.1, 125.1, 117.4, 112.9, 104.9, 104.7, 95.5, 21.4, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}N_2Si$ 389.2407; Found 389.2401.

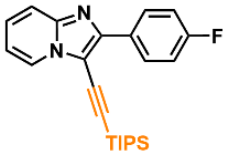


2-(4-Methoxyphenyl)-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3ca). Following the general procedure **A** using 2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (44.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ca** (63.1 mg, 78%) as a white solid. Mp: 124-126 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.8 Hz, 2H), 8.25 (d, *J* = 6.8 Hz, 1H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.90 (t, *J* = 6.5 Hz, 1H), 3.86 (s, 3H), 1.31 – 1.16 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 148.3, 144.9, 128.7, 126.1, 126.1, 125.1, 117.2, 113.8, 112.9, 104.6, 104.4, 95.6, 55.3, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}N_2OSi$ 405.2356; Found 405.2351.



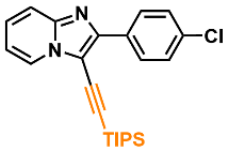
2-(4-Fluorophenyl)-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3da). Following the general procedure **A** using 2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (42.4 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3da** (54.1 mg, 69%) as a brown solid. Mp: 119-121 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 8.6, 5.5 Hz, 2H), 8.26 (d, *J* = 6.7 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.12 (t, *J* = 8.7 Hz, 2H), 6.94 (t, *J* = 6.7 Hz, 1H), 1.23 – 1.17 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.8 (d, *J* = 249.3 Hz), 162.2, 147.4, 144.9, 129.1 (d, *J* = 8.3 Hz), 126.4, 125.2 (d, *J* = 3.2 Hz), 117.4, 115.4 (d, *J* = 21.6 Hz), 113.2, 95.1, 18.7, 11.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.81 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}FN_2Si$ 393.2156; Found 393.2158.

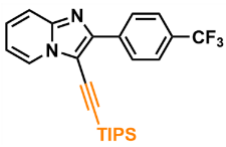


2-(4-Chlorophenyl)-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3ea). Following the general procedure **A** using 2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine (45.6 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ea** (53.1 mg, 65%) as a white solid. Mp: 130-132 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.6 Hz, 2H), 8.24 (d, *J* = 6.8 Hz, 1H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.91 (td, *J* = 6.7, 1.1 Hz, 1H), 1.25 – 1.17 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.0, 145.0, 134.3, 132.0, 128.6, 128.5, 126.4, 125.1, 117.5, 113.2, 105.4, 105.3, 95.0, 18.8, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}N_2ClSi$ 409.1861; Found 409.1853.



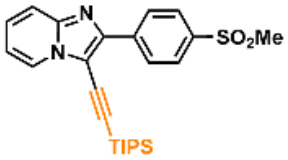
2-(4-(Trifluoromethyl)phenyl)-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3fa). Following the general procedure **A** using 2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine (52.4 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3fa** (51.3 mg, 58%) as a white solid. Mp: 136-138 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.2 Hz, 2H), 8.28 (d, *J* = 6.8 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.32 – 7.27 (m, 1H), 6.95 (t, *J* = 6.7 Hz, 1H), 1.27 – 1.18 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.4, 145.1, 136.9, 127.3, 126.7, 125.3 (q, *J* = 3.6 Hz), 117.7, 113.4, 106.0 (q, *J* = 33.5 Hz), 94.7, 18.7, 11.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.50 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{30}F_3N_2Si$ 443.2124; Found 443.2117.

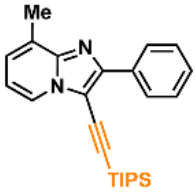


2-(4-Sulfonylphenyl)-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3ga). Following the general procedure **A** using 2-(4-sulfonylphenyl)imidazo[1,2-*a*]pyridine (54.2 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ga** (38.0 mg, 42%) as a brown solid. Mp: 166-168 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.1 Hz, 2H), 8.30 (d, *J* = 6.7 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.40 – 7.32 (m, 1H), 7.01 (t, *J* = 6.7 Hz, 1H), 3.10 (s, 3H), 1.25 – 1.19 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.6, 145.1, 139.7, 138.8, 127.7, 127.5, 127.0, 125.3, 117.8, 113.7, 106.6, 106.4, 44.6, 29.7, 18.8, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{32}N_2O_2SSi$ 453.2023; Found 453.2026.

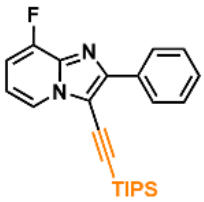


8-Methyl-2-phenyl-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3ha). Following the general procedure **A** using 8-methyl-2-phenylimidazo[1,2-*a*]pyridine (41.6 mg, 0.2 mmol) and TIPS-protected terminal alkyne (78.3 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ha** (52.0 mg, 67%) as a yellow solid. Mp: 118-120 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.2 Hz, 2H), 8.16 (d, *J* = 6.7 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.01 (dt, *J* = 6.9, 1.4 Hz, 1H), 6.81 (t, *J* = 6.8 Hz, 1H), 2.68 (s, 3H), 1.24 (dq, *J* = 11.9, 7.3, 5.4 Hz, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 145.4, 133.8, 128.37, 128.35, 127.6, 127.4, 125.0, 122.9, 113.0, 105.6, 104.3, 95.8, 18.8, 16.9, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}N_2Si$ 389.2407; Found 389.2400.



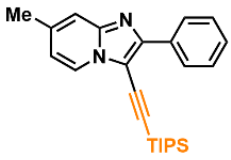
8-Fluoro-2-phenyl-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3ia). Following the general procedure **A** using 8-fluoro-2-phenylimidazo[1,2-*a*]pyridine (42.4 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ia** (46.3 mg, 59%) as a yellow solid. Mp: 128-130 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.1 Hz, 2H), 8.10 (dd, *J* = 6.7, 0.8 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.40 – 7.37 (m, 1H), 6.97 (ddd, *J* = 10.1, 7.7, 1.0 Hz, 1H), 6.85 (ddd, *J* = 7.6, 6.7, 4.4 Hz, 1H), 1.25 – 1.19 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.3, 150.6, 148.4, 137.3 (d, *J* = 27.2 Hz), 132.9, 128.8, 128.4, 127.4, 121.4 (d, *J* = 4.5 Hz), 112.1 (d, *J* = 6.0 Hz), 108.9 (d, *J* = 16.6 Hz), 106.7, 105.5, 94.8, 18.7, 11.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -129.91 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}FN_2Si$ 393.2156; Found 393.2148.

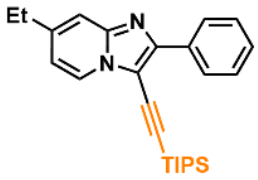


7-Methyl-2-phenyl-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3ja). 7-methyl-2-phenylimidazo[1,2-*a*]pyridine (41.6 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ja** (54.4 mg, 70%) as a brown oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.6 Hz, 2H), 8.13 (d, *J* = 6.9 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.35 (t, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 6.8 Hz, 1H), 2.40 (s, 3H), 1.25 – 1.17 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 145.4, 137.4, 133.5, 128.39, 128.36, 127.2, 124.3, 116.0, 115.7, 104.7, 104.4, 95.6, 21.5, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}N_2Si$ 389.2407; Found 389.2400.

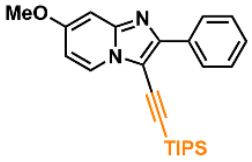


7-Ethyl-2-phenyl-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3ka). Following the general procedure **A** using 7-ethyl-2-phenylimidazo[1,2-*a*]pyridine (44.2 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ka** (53.1 mg, 66%) as a brown oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.4 Hz, 2H), 8.17 (d, *J* = 6.9 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.36 (d, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H), 1.25 – 1.18 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 145.5, 143.6, 133.5, 128.38, 128.36, 127.2, 124.5, 114.7, 114.6, 104.7, 104.4, 95.6, 28.5, 18.8, 14.4, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{34}N_2Si$ 403.2564; Found 403.2565.

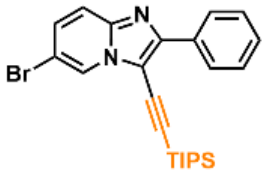


7-Methoxy-2-phenyl-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3la). Following the general procedure **A** using 7-methoxy-2-phenylimidazo[1,2-*a*]pyridine (44.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3la** (59.8 mg, 74%) as a yellow solid. Mp: 132-134 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.2 Hz, 2H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 2.3 Hz, 1H), 6.63 (dd, *J* = 7.4, 2.5 Hz, 1H), 3.86 (s, 3H), 1.22 – 1.18 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 148.2, 146.5, 133.5, 128.4, 128.3, 127.0, 125.4, 107.9, 104.22, 104.17, 95.6, 95.1, 55.6, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}N_2OSi$ 405.2356; Found 405.2349.

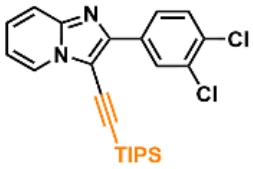


6-Bromo-2-phenyl-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3pa). Following the general procedure **A** using 6-bromo-2-phenylimidazo[1,2-*a*]pyridine (54.4 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3pa** (54.3 mg, 60%) as a yellow solid. Mp: 95-97 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 3H), 7.55 (d, *J* = 9.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.34 (dd, *J* = 9.4, 1.8 Hz, 1H), 1.26 – 1.20 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.7, 143.3, 132.9, 129.6, 128.8, 128.5, 127.3, 125.4, 118.0, 107.8, 105.9, 18.7, 17.7, 12.3, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}BrN_2Si$ 453.1356; Found 453.1357.

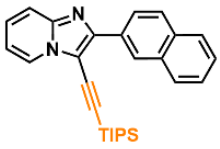


2-(3,4-Dichlorophenyl)-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3qa). Following the general procedure **A** using 2-(3,4-dichlorophenyl)imidazo[1,2-*a*]pyridine (52.4 mg, 0.2 mmol)and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3qa** (59.2 mg, 67%) as a brown solid. Mp: 156-158 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.0 Hz, 1H), 8.25 – 8.22 (m, 2H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.93 (td, *J* = 6.8, 1.1 Hz, 1H), 1.23 – 1.18 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.6, 145.0, 133.5, 132.7, 132.3, 130.3, 128.7, 126.7, 126.3, 125.2, 117.6, 113.4, 106.1, 105.7, 94.5, 18.8, 11.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}N_2Cl_2Si$ 443.1471; Found 443.1463.

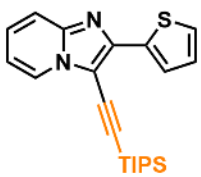


2-(Naphthalen-2-yl)-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3ra). Following the general procedure **A** using 2-(naphthalen-2-yl)imidazo[1,2-*a*]pyridine (48.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ra** (63.6 mg, 75%) as a white solid. Mp: 151-153 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.60 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.31 (d, *J* = 6.7 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.88 – 7.85 (m, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.30 – 7.25 (m, 1H), 6.93 (t, *J* = 6.7 Hz, 1H), 1.30 – 1.24 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.1, 145.1, 133.5, 133.5, 130.9, 128.5, 128.0, 127.7, 126.5, 126.4, 126.3, 126.2, 125.1, 125.1, 117.5, 113.2, 105.6, 105.0, 95.4, 18.9, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{33}N_2Si$ 425.2407; Found 425.2401.

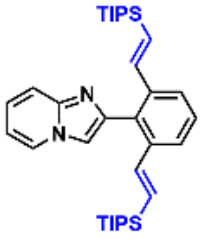


2-(Thiophen-2-yl)-3-((triisopropylsilyl)ethynyl)imidazo[1,2-*a*]pyridine (3ta). Following the general procedure **A** using 2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine (40.0 mg, 0.2 mmol) and TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3ta** (57.8 mg, 76%) as a orange solid. Mp: 105--107 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 6.7 Hz, 1H), 8.00 (d, *J* = 2.8 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.38 (d, *J* = 5.0 Hz, 1H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.14 – 7.11 (m, 1H), 6.93 (t, *J* = 6.8 Hz, 1H), 1.25 – 1.20 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 144.0, 136.9, 127.6, 126.4, 126.2, 125.8, 125.1, 117.3, 113.2, 106.3, 104.2, 94.4, 18.8, 11.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{28}N_2SSi$ 381.1815; Found 381.1816.

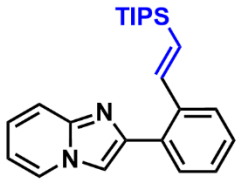


2-(4-Methoxy-2-((triisopropylsilyl)ethynyl)phenyl)imidazo[1,2-*a*]pyridine (4aa). Following the general procedure **B** using 2-phenylimidazopyridine (38.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4aa** (100.5 mg, 90%) as a white solid. Mp: 159-161 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.7 Hz, 1H), 7.60 – 7.56 (m, 3H), 7.49 (s, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.20 – 7.15 (m, 1H), 6.90 (d, *J* = 19.4 Hz, 2H), 6.79 (t, *J* = 6.7 Hz, 1H), 6.22 (d, *J* = 19.4 Hz, 2H), 1.00 – 0.93 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 144.8, 139.8, 131.0, 128.3, 125.4, 125.1, 124.9, 124.2, 117.7, 113.1, 112.2, 18.5, 11.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{54}N_2Si_2$ 559.3898; Found 559.3901.

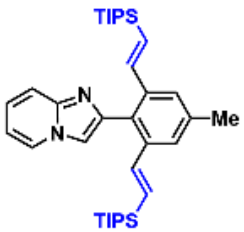


(*E*)-2-(2-(2-(triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine ($4aa_1$). Following the general procedure **C** using 2-phenylimidazopyridine (38.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **$4aa_1$** (28.6 mg, 38%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.7 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.68 (s, 1H), 7.66 – 7.61 (m, 2H), 7.42 – 7.34 (m, 3H), 7.20 – 7.16 (m, 1H), 6.79 (t, *J* = 6.7 Hz, 1H), 6.38 (d, *J* = 19.3 Hz, 1H), 1.20 – 1.10 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 145.0, 144.5, 138.3, 132.1, 129.7, 128.0, 127.8, 126.9, 126.2, 125.4, 124.6, 117.7, 112.4, 112.0, 18.8, 11.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{32}N_2Si$ 377.2407; Found 377.2404.



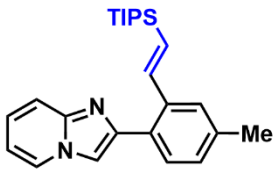
2-(4-Methyl-2,6-bis((triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (4ba). Following the general procedure **B** using 2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (41.6 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol),the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ba** (105.3 mg, 92%) as a white solid. Mp: 149-151 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (t, *J* = 6.3 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.47 (d, J = 3.4 Hz, 1H), 7.40 (s, 2H), 7.17 – 7.13 (m, 1H), 6.91 (dd, *J* = 18.7, 11.2 Hz, 2H), 6.76 (t, *J* = 6.3 Hz, 1H), 6.22 (dd, *J* = 19.4, 4.2 Hz, 2H), 2.45 (s, 3H), 1.04 – 0.90 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 145.4, 144.7, 142.9, 141.2, 125.5, 125.1, 124.3, 124.1,

117.6, 113.2, 112.2, 110.3, 55.4, 18.5, 10.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{56}F_3N_2Si_2$ 573.4003; Found 573.4002.

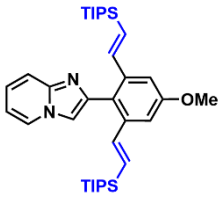


(*E*)-2-(4-methyl-2-(2-(triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (4ba$_1$). Following the general procedure **C** using 2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (41.6 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol),the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ba$_1$** (31.2 mg, 40%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.7 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 9.3 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.22 – 7.14 (m, 2H), 6.77 (t, *J* = 6.5 Hz, 1H), 6.36 (d, *J* = 19.3 Hz, 1H), 2.43 (s, 3H), 1.22 – 1.10 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 145.0, 144.6, 138.1, 137.7, 129.7, 129.4, 128.8, 127.4, 125.8, 125.3, 124.5, 117.6, 112.3, 111.8, 21.4, 18.8, 11.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{34}N_2Si$ 391.2564; Found 391.2560.

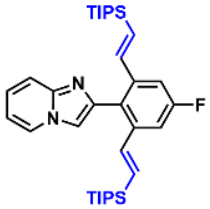


2-(4-Methoxy-2,6-bis((*E*)-2-(triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (4ca). Following the general procedure **B** using 2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (44.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ca** (105.7 mg, 95%) as a white solid. Mp: 142-144 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 5.7 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.45 (s, 1H), 7.18 – 7.14 (m, 1H), 7.11 (s, 2H), 6.89 (d, *J* = 19.4 Hz, 2H), 6.76 (t, *J* = 6.7 Hz, 1H), 6.21 (d, *J* = 19.4 Hz, 2H), 3.92 (s, 3H), 1.03 – 0.90 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 145.5, 144.7, 143.0, 141.2, 125.4, 125.1, 124.4, 124.1, 117.6, 113.2, 112.1, 110.3, 55.4, 18.5, 11.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{52}N_2Si_2$ 557.3741; Found 557.3738.



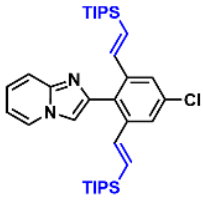
2-(4-Fluoro-2,6-bis((triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (4da). Following the general procedure **B** using 2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (42.4 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4da** (102.6mg, 89%) as a brown solid. Mp: 135-137 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.7 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.47 (s, 1H), 7.25 (d, *J* = 9.7 Hz, 2H), 7.20 – 7.16 (m, 1H), 6.85 (d, *J* = 19.4 Hz, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.24 (d, *J* = 19.3 Hz, 2H), 1.04 – 0.91 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.6 (d, *J* = 22.3 Hz), 142.1(d, *J* = 6.5 Hz), 126.8, 125.2, 124.4, 117.7, 113.2, 111.6 (d, *J* = 8.1 Hz), 18.5, 10.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.20 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{53}FN_2Si_2$ 577.3804; Found 577.3807.

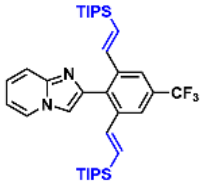


2-(4-Chloro-2,6-bis((triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (4ea). Following the general procedure **B** using 2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine (45.6 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ea** (103.1 mg, 87%) as a white solid. Mp: 156-158 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 6.7 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 22.5 Hz, 3H), 7.19 – 7.14 (m, 1H), 6.84 (d, *J* = 19.4 Hz, 2H), 6.77 (t, *J* = 7.1 Hz, 1H), 6.24 (d, *J* = 19.4 Hz, 2H), 1.02 – 0.90 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 144.2, 142.1, 141.5, 134.4, 129.5, 127.1, 125.2, 124.6, 124.4, 117.7, 113.2, 112.4, 18.5, 10.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{53}ClN_2Si_2$ 593.3508; Found 593.3511.



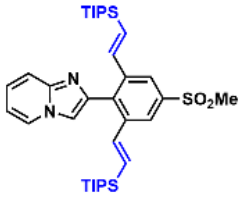
2-(4-(Trifluoromethyl)-2,6-bis((triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (4fa). Following the general procedure **B** using 2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine (52.4 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4fa** (105.2 mg, 84%) as a white solid. Mp: 133-135 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.7 Hz, 1H), 7.76 (s, 2H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 3.3 Hz, 1H), 7.21 – 7.17 (m, 1H), 6.91 (d, *J* = 19.4 Hz, 2H), 6.80 (t, *J* = 6.7 Hz, 1H), 6.30 (d, *J* = 19.4 Hz, 2H), 1.06 – 0.89 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 144.3, 141.9, 140.6, 134.2, 127.7, 125.2, 124.6, 121.2, 117.7, 112.9 (q, *J* = 89.0 Hz), 18.5, 10.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.54 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{53}F_3N_2Si_2$ 627.3772; Found 627.3775.

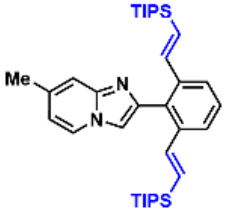


2-(4-Sulfonyl-2,6-bis((triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (4ga). Following the general procedure **B** using 2-(4-sulfonylphenyl)imidazo[1,2-*a*]pyridine (54.2 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ga** (99.3 mg, 78%) as a brown solid. Mp: 157-159 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 6.8 Hz, 1H), 8.05 (s, 2H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.52 (s, 1H), 7.23 – 7.19 (m, 1H), 6.89 – 6.80 (m, 3H), 6.35 (d, *J* = 19.4 Hz, 2H), 3.12 (s, 3H), 1.03 – 0.88 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 143.5, 141.37, 141.35, 140.4, 136.1, 129.1, 125.3, 124.9, 123.0, 117.8, 113.2, 112.8, 44.7, 18.5, 10.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{56}N_2O_2SSi_2$ 637.3673; Found 637.3672.

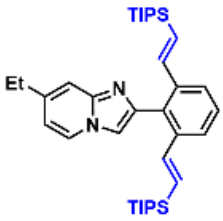


2-(2,6-Bis((triisopropylsilyl)vinyl)phenyl)-7-methylimidazo[1,2-*a*]pyridine (4ja). Following the general procedure **B** using 7-methyl-2-phenylimidazo[1,2-*a*]pyridine (41.6 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ja** (104.2 mg, 91%) as a yellow solid. Mp: 125-127 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 6.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.42 – 7.31 (m, 3H), 6.92 (d, *J* = 19.4 Hz, 2H), 6.61 (d, *J* = 6.3 Hz, 1H), 6.22 (d, *J* = 19.4 Hz, 2H), 2.41 (s, 3H), 1.03 – 0.92 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.7, 145.3, 142.7, 139.8, 135.0, 131.3, 128.2, 125.1, 124.9, 124.3, 116.0, 114.9, 112.6, 21.4, 18.5, 11.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{56}N_2Si_2$ 573.4003; Found 573.4001.

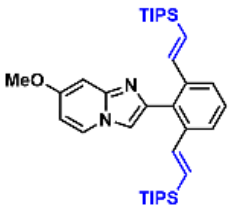


2-(2,6-Bis((triisopropylsilyl)vinyl)phenyl)-7-ethylimidazo[1,2-*a*]pyridine (4ka). Following the general procedure **B** using 7-ethyl-2-phenylimidazo[1,2-*a*]pyridine (44.3 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ka** (104.4mg, 89%) as a yellow solid. Mp: 129-131 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.42 (s, 1H), 7.39 – 7.33 (m, 2H), 6.94 (d, *J* = 19.4 Hz, 2H), 6.64 (d, *J* = 5.7 Hz, 1H), 6.23 (d, *J* = 19.4 Hz, 2H), 2.71 (q, *J* = 7.5 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H), 1.04 – 0.92 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.7, 145.4, 142.7, 141.2, 139.8, 131.3, 128.1, 125.1, 124.9, 124.5, 114.6, 113.9, 112.5, 28.5, 18.6, 14.6, 11.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{58}N_2Si_2$ 587.4211; Found 587.4214.

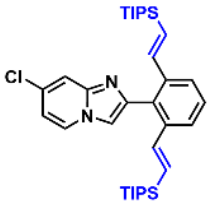


2-(2,6-Bis((triisopropylsilyl)vinyl)phenyl)-7-methoxyimidazo[1,2-*a*]pyridine (4la). Following the general procedure **B** using 7-methoxy-2-phenylimidazo[1,2-*a*]pyridine (44.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4la** (109.4 mg, 93%) as a white solid. Mp: 154-157 °C.

^{1}H NMR (600 MHz, CD_3OD) δ 7.87 (d, *J* = 7.3 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 3.4 Hz, 1H), 6.94 (d, *J* = 19.4 Hz, 2H), 6.83 (d, *J* = 2.3 Hz, 1H), 6.51 (dd, *J* = 7.4, 2.4 Hz, 1H), 6.26 – 6.19 (m, 2H), 3.86 (s, 3H), 1.03 – 0.92 (m, 42H).

^{13}C NMR (151 MHz, CD_3OD) δ 157.6, 146.2, 145.7, 142.5, 139.8, 131.2, 128.2, 125.5, 125.1, 124.9, 111.9, 107.3, 94.7, 55.5, 18.6, 11.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{56}N_2OSi_2$ 589.4003; Found 589.4003.

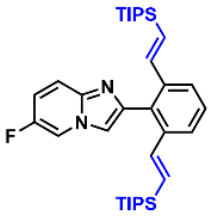


2-(2,6-Bis((triisopropylsilyl)vinyl)phenyl)-7-chloroimidazo[1,2-*a*]pyridine (4ma). Following the general procedure **B** using 7-chloro-2-phenylimidazo[1,2-*a*]pyridine (45.6 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ma** (101.9 mg, 86%) as a white solid. Mp: 158-160 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.1 Hz, 1H), 7.60 – 7.56 (m, 3H), 7.48 (s, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 19.4 Hz, 2H), 6.80 (dd, *J* = 7.2, 2.0 Hz, 1H), 6.24 (d, *J* = 19.4 Hz, 2H), 1.03 – 0.94 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.3, 144.6, 144.2, 139.8, 130.7, 130.4, 128.5, 125.8, 125.4, 125.0, 116.4, 114.0, 113.3, 18.5, 10.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{35}ClN_2Si_2$ 593.3508; Found 593.3511.



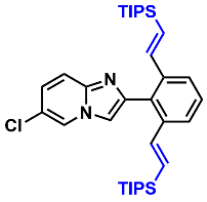
2-(2,6-Bis((triisopropylsilyl)vinyl)phenyl)-6-fluoroimidazo[1,2-*a*]pyridine (4na). Following the general procedure **B** using 6-fluoro-2-phenylimidazo[1,2-*a*]pyridine (42.4 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4na** (99.1 mg, 86%) as a white solid. Mp: 138-140 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.02 (m, 1H), 7.57 (t, *J* = 7.4 Hz, 3H), 7.51 (d, *J* = 3.5 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.12 (ddd, *J* = 10.2, 8.1, 2.3 Hz, 1H), 6.86 (d, *J* = 19.4 Hz, 2H), 6.23 (d, *J* = 19.4 Hz, 2H), 1.04 – 0.93 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.3, 142.6, 139.8, 130.6, 128.5, 125.7, 125.0, 118.1 (d, *J* = 9.1 Hz), 116.3 (d, *J* = 24.2 Hz)., 114.4 (d, *J* = 3.0 Hz), 111.7 (d, *J* = 40.8 Hz), 18.5, 11.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -140.96 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{53}FN_2Si_2$ 577.3804; Found 577.3807.

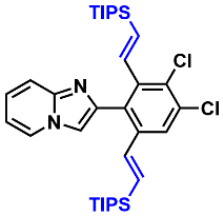


2-(2,6-Bis((triisopropylsilyl)vinyl)phenyl)-6-chloroimidazo[1,2-*a*]pyridine (4oa). Following the general procedure **B** using 6-chloro-2-phenylimidazo[1,2-*a*]pyridine (45.6 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4oa** (97.1 mg, 82%) as a white solid. Mp: 93-95 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 1.9, 0.7 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 9.5 Hz, 1H), 7.48 (s, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.16 (dd, *J* = 9.5, 1.9 Hz, 1H), 6.85 (d, *J* = 19.4 Hz, 2H), 6.24 (d, *J* = 19.4 Hz, 2H), 1.00 – 0.95 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.2, 144.2, 143.2, 139.8, 130.4, 128.5, 125.8, 125.7, 125.1, 122.9, 120.5, 118.0, 113.5, 18.5, 10.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{53}ClN_2Si_2$ 593.3508; Found 593.3510.

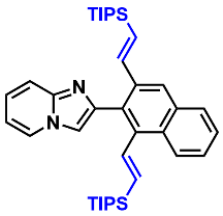


2-(3,4-Dichloro-2,6-bis((triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (4qa). Following the general procedure **B** using 2-(3,4-dichlorophenyl)imidazo[1,2-*a*]pyridine (52.4 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4qa** (67.6 mg, 54%) as a white solid. Mp: 148-151 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.7 Hz, 1H), 7.61 (s, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.37 (s, 1H), 7.16 – 7.12 (m, 1H), 6.83 (d, *J* = 19.7 Hz, 1H), 6.75 (t, *J* = 6.7 Hz, 1H), 6.67 (d, *J* = 19.4 Hz, 1H), 6.21 (d, *J* = 19.4 Hz, 1H), 5.71 (d, *J* = 19.7 Hz, 1H), 0.95 – 0.78 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 143.3, 142.3, 142.0, 139.6, 133.8, 133.1, 129.8, 127.4, 125.2, 117.7, 112.4, 112.1, 18.4, 18.2, 10.9, 10.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{52}Cl_2N_2Si_2$ 627.3118; Found 627.3121.

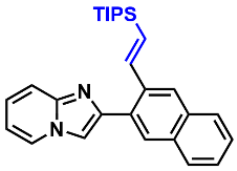


2-(1,3-Bis(2-(triisopropylsilyl)vinyl)naphthalen-2-yl)imidazo[1,2-*a*]pyridine (4ra). Following the general procedure **B** using 2-(naphthalen-2-yl)imidazo[1,2-*a*]pyridine (48.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ra** (48.7 mg, 40%) as a white solid. Mp: 144-146 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 1H), 8.07 – 8.00 (m, 2H), 7.91 (d, *J* = 9.1 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.23 (s, 1H), 7.18 – 7.14 (m, 1H), 6.95 (d, *J* = 19.3 Hz, 1H), 6.76 (t, *J* = 6.7 Hz, 1H), 6.35 (d, *J* = 19.3 Hz, 1H), 5.93 (d, *J* = 19.8 Hz, 1H), 1.07 – 0.90 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 144.0, 139.5, 137.9, 133.7, 133.0, 130.8, 128.5, 126.1, 126.0, 125.9, 125.7, 125.1, 123.4, 117.7, 112.5, 112.1, 18.5, 18.4, 11.0, 10.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{39}H_{56}N_2Si_2$ 609.4054; Found 609.4056.

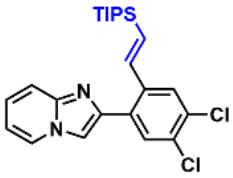


2-(3-((Triisopropylsilyl)vinyl)naphthalen-2-yl)imidazo[1,2-*a*]pyridine (4ra$_1$). Following the general procedure **B** using 2-(naphthalen-2-yl)imidazo[1,2-*a*]pyridine (48.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ra$_1$** (46.9 mg, 55%) as a white solid. Mp: 117-119 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.9 Hz, 1H), 8.08 (t, *J* = 6.2 Hz, 1H), 8.02 (s, 1H), 7.89 (t, *J* = 7.8 Hz, 2H), 7.79 – 7.73 (m, 1H), 7.70 (dd, *J* = 8.8, 3.4 Hz, 1H), 7.54 – 7.44 (m, 3H), 7.23 – 7.18 (m, 1H), 6.80 (t, *J* = 6.6 Hz, 1H), 6.52 (dd, *J* = 19.1, 8.9 Hz, 1H), 1.25 – 0.98 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.3, 146.1, 145.1, 144.5, 137.0, 133.0, 130.5, 128.7, 128.1, 127.8, 126.9, 126.3, 126.1, 125.4, 124.8, 117.6, 112.5, 112.1, 18.8, 11.5, 11.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{34}N_2Si$ 427.2564; Found 427.2567.

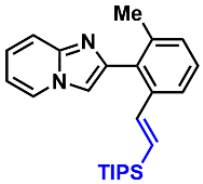


2-(4,5-Dichloro-2-((triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (4qa$_1$). Following the general procedure **B** using 2-(3,4-dichlorophenyl)imidazo[1,2-*a*]pyridine (52.4 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4qa$_1$** (36.4 mg, 41%) as a white solid. Mp: 121-123 °C.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.07 (t, *J* = 6.0 Hz, 1H), 8.00 (d, *J* = 3.9 Hz, 1H), 7.68 – 7.62 (m, 3H), 7.28 (dd, *J* = 19.2, 14.1 Hz, 1H), 7.24 – 7.19 (m, 1H), 6.82 (t, *J* = 6.7 Hz, 1H), 6.39 (d, *J* = 19.3 Hz, 1H), 1.25 – 1.03 (m, 21H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 145.1, 143.4, 137.9, 131.9, 131.8, 131.6, 131.18, 131.17, 128.7, 128.6, 125.5, 125.2, 117.7, 112.8, 112.2, 18.7, 11.1.

HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{24}H_{30}Cl_2N_2Si$ 445.1628; Found 445.1629.

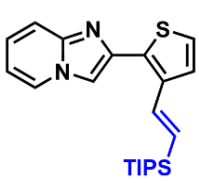


2-(2-Methyl-6-(2-(triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (4sa). Following the general procedure **B** using 2-(*o*-tolyl)imidazo[1,2-*a*]pyridine (41.7 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4sa** (68.7 mg, 88%) as a yellow solid. Mp: 140-141 °C.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.11 (d, *J* = 6.7 Hz, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.48 (d, *J* = 10.1 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.19 (dd, *J* = 14.1, 7.6 Hz, 2H), 6.82 – 6.74 (m, 2H), 6.18 (d, *J* = 19.4 Hz, 1H), 2.25 (s, 3H), 0.98 – 0.91 (m, 21H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 145.7, 144.9, 143.7, 139.9, 137.9, 132.4, 129.2, 128.2, 125.3, 125.1, 124.3, 123.1, 117.6, 112.3, 112.2, 20.7, 18.5, 10.9.

HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{25}H_{34}N_2Si$ 391.2564; Found 391.2565.

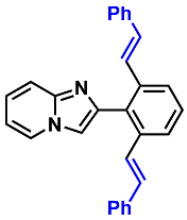


2-(3-(2-(Triisopropylsilyl)vinyl)thiophen-2-yl)imidazo[1,2-*a*]pyridine (4ta). Following the general procedure **B** using 2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine (40.0 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ta** (65.7 mg, 86%) as a white solid. Mp: 125-127 °C.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.09 (d, *J* = 6.7 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.38 – 7.32 (m, 2H), 7.27 (s, 1H), 7.20 – 7.16 (m, 1H), 6.79 (t, *J* = 6.7 Hz, 1H), 6.29 (d, *J* = 19.3 Hz, 1H), 1.19 – 1.10 (m, 21H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 145.2, 140.0, 139.0, 138.2, 133.1, 126.6, 125.5, 125.4, 125.1, 125.0, 117.5, 112.6, 109.4, 18.8, 11.1.

HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{22}H_{30}N_2SSi$ 383.1971; Found 383.1974



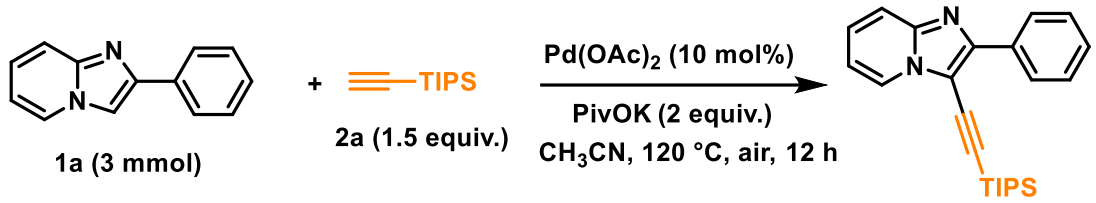
2-(2,6-Di((styrylphenyl)imidazo[1,2-*α*]pyridine (4ab). Following the general procedure **B** using 2-phenylimidazopyridine (38.8 mg, 0.2 mmol) and TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ab** (29.5 mg, 37%) as a yellow solid. Mp: 172-174 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.23 (d, *J* = 4.0 Hz, 1H), 7.79 (dd, *J* = 15.2, 7.8 Hz, 5H), 7.49 (dd, *J* = 15.4, 8.0 Hz, 7H), 7.40 (dd, *J* = 16.0, 8.1 Hz, 4H), 6.95 (d, J = 8.4 Hz, 2H), 6.78 – 6.74 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 148.3, 138.5, 137.7, 135.8, 133.7, 129.8, 129.6, 128.9, 127.9, 127.6, 126.9, 126.4, 124.6, 115.5, 115.3, 109.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{22}N_2$ 399.1855; Found 399.1857.

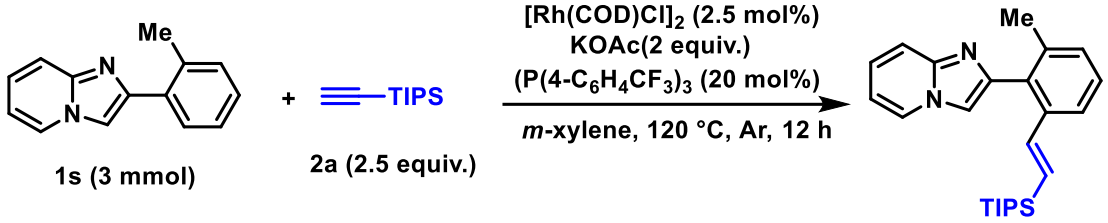
3.4 Pd(II) -catalyzed oxidative C3-alkylation: reaction on 3 mmol scale



3aa, 76%

To a 100 mL oven dried Schlenk tube, PivOK (853.4 mg, 6 mmol, 2 equiv.), 2-phenylimidazopyridine (582.7 mg, 3 mmol, 1 equiv.), $Pd(OAc)_2$ (67.4 mg, 0.3 mmol, 10 mol%), TIPS-protected terminal alkyne (820.7 mg, 4.5 mmol, 1.5 equiv.) and CH_3CN (20 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired alkynylated product **3aa** (0.85 g, 76%).

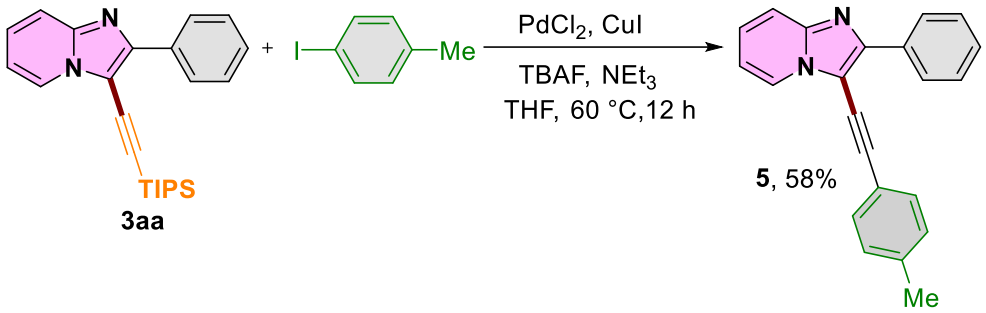
3.5 Rh(I)-catalyzed *ortho*-alkenylation: reaction on 3 mmol scale



4sa, 82%

To a 100 mL oven dried Schlenk tube, $(P(4\text{-}C_6H_4CF_3)_3$ (279.8 mg, 0.6 mmol, 20 mol%), 2-(*o*-tolyl)imidazo[1,2-*a*]pyridine (624.8 mg, 3 mmol, 1 equiv.), $[Rh(COD)Cl]_2$ (37.0 mg, 0.075 mmol, 2.5 mol%), TIPS-protected alkyne (1.4 g, 7.5 mmol, 2.5 equiv.), and *m*-xylene (20 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under Ar. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired alkenylated product **4sa** (0.96 g, 82%).

3.6 Preparation and characterization of products 5, 6, 7, 8, 9, 10, 11

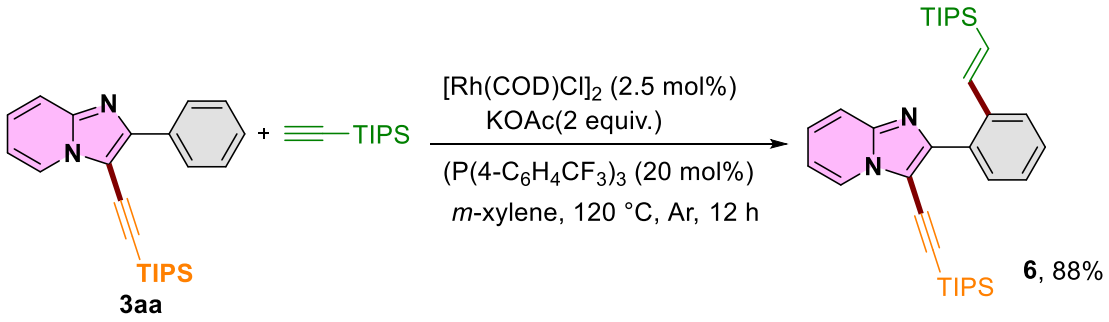


2-Phenyl-3-(*p*-tolylethynyl)imidazo[1,2-*a*]pyridine (5). To oven dried Schlenk tube equipped with magnetic stir bar was introduced 1-methyl-4-iodobenzene (43.6 mg, 0.2 mmol), $PdCl_2$ (1.8 mg, 0.01 mmol, 5 mol%), CuI (1.1 mg, 0.006 mmol, 3.0 mol%) and Et_3N (1.5 mL). To this mixture, a solution of **3aa** (74.9 mg, 0.2 mmol) in THF/Et_3N (1/0.5 mL) was added dropwise at room temperature. Then, the reaction mixture was stirred at 60 °C in a pre-heated metal sand bath for 12 hours. At ambient temperature, H_2O (5 mL) was added and the compound was extracted with EtOAc (15 mL × 3). The combined organic extract was dried over $MgSO_4$ and the volatiles were evaporated in vacuo. The remaining residue was purified by column chromatography (petroleum ether/ethyl acetate = 9:1) to afford the white solid **5** (35.7 mg, 58%). Mp: 111-113 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (t, *J* = 7.9 Hz, 3H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.52 – 7.47 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.93 (t, *J* = 6.7 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 145.2, 139.1, 133.5, 131.2, 129.4, 128.6, 128.5, 127.3, 126.2, 125.2, 119.7, 117.5, 112.9, 104.9, 101.4, 29.7, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{16}N_2$ 309.1386; Found 309.1387.

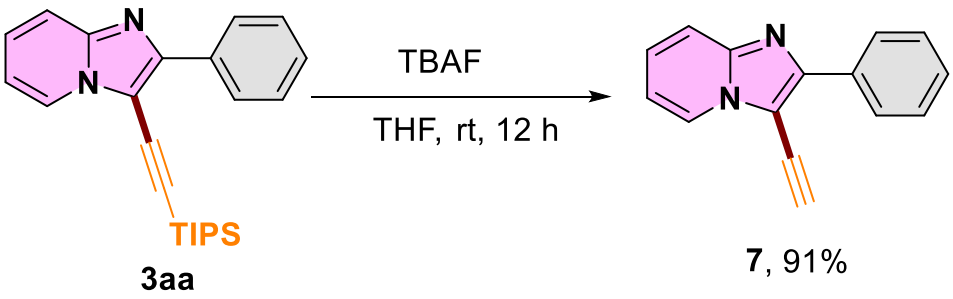


(*E*)-3-((triisopropylsilyl)ethynyl)-2-(2-(2-(triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (6). To a 15 mL oven dried Schlenk tube, **3aa** (74.9 mg, 0.2 mmol), $(P(4\text{-}C_6H_4CF_3)_3$ (18.7 mg, 0.04 mmol, 20 mol%), $[Rh(cod)Cl]_2$ (2.5 mg, 0.005 mmol, 2.5 mol%), KOAc (0.4 mmol, 2 equiv.), TIPS-protected alkyne (0.5 mmol, 2.5 equiv.), and *m*-xylene (1.5 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under Ar. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the brown liquid **6** (100.7 mg, 88%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 6.7 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.21 (m, 1H), 6.91 (t, *J* = 6.7 Hz, 1H), 6.38 (d, *J* = 19.3 Hz, 1H), 1.18 – 1.03 (m, 42H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 145.8, 144.4, 138.7, 131.5, 130.7, 128.5, 127.1, 126.4, 125.7, 125.2, 124.6, 117.6, 113.0, 107.1, 103.3, 94.7, 18.8, 18.7, 11.3, 11.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{56}N_2Si_2$ 573.4003; Found 573.3998.



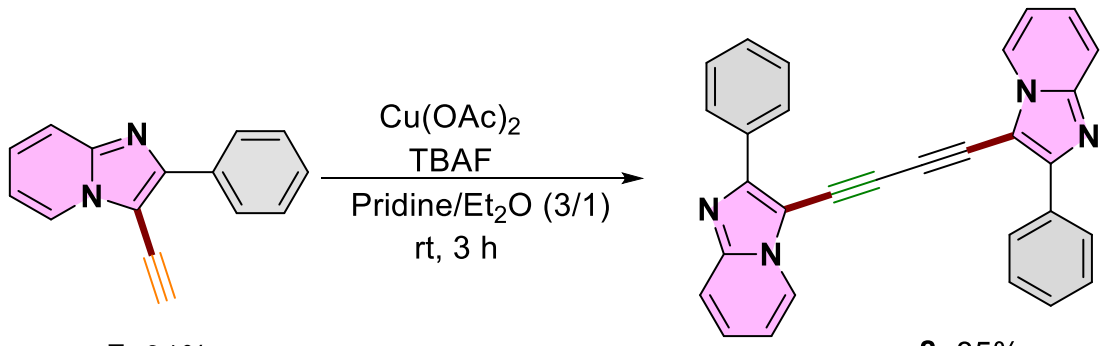
3aa **7**, 91%

3-Ethynyl-2-phenylimidazo[1,2-*a*]pyridine (7). The alkynylated product **3aa** (74.9 mg, 0.2 mmol) was dissolved in THF (1.5 mL). TBAF (1.0 M in THF, 0.6 mL) were then added. The resulting solution was allowed to stir at room temperature. After 12 hours, the mixture was concentrated in vacuo. The residue was extracted with EtOAc (3 × 15 mL), and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and evaporated in vacuo. The obtained crude product was purified by column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the white solid **7** (39.7 mg, 91%). Mp: 122-124 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.2 Hz, 2H), 8.25 (d, *J* = 6.8 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.85 (t, *J* = $CDCl_3$ 7.3 Hz, 1H), 4.05 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.8, 145.2, 133.2, 128.7, 128.6, 127.3, 126.5, 125.2, 117.5, 113.1, 103.8, 89.9, 73.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}N_2$ 219.0916; Found 219.0912.



7, 91% **8**, 85%

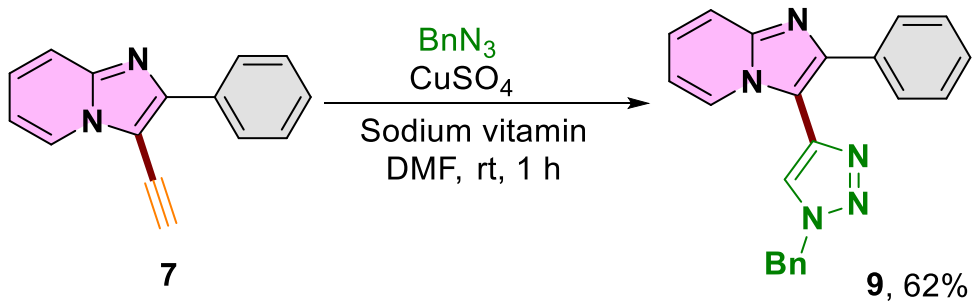
1,4-Bis(2-phenylimidazo[1,2-*a*]pyridin-3-yl)buta-1,3-diyne (8). To a 15 mL oven dried Schlenk tube, **7** (43.7 mg, 0.2 mmol), $Cu(OAc)_2$ (109 mg, 0.6 mmol, 3 equiv.), TBAF (1 M in THF, 0.4 ml), and pyridine/ether (3:1, 2 mL) were successively added. The reaction mixture was stirred at room temperature for 3 hours under the air. Afterwards, the reaction mixture was poured into

ether and HCl (1M), the organic phase was washed with an excess of HCl (1M) to remove the pyridine, and the organic phase was dried with anhydrous magnesium sulfate, after which the organic phase was concentrated, the crude product was purified by silica column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the desired product **8** (73.8 mg, 85%) as a reddish brown solid. Mp: 164-166 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, *J* = 6.7 Hz, 2H), 8.34 (d, *J* = 7.2 Hz, 4H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 4H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.33 (m, 2H), 6.98 (td, *J* = 6.8, 1.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 145.8, 132.9, 129.2, 128.8, 127.5, 127.4, 125.7, 117.8, 113.6, 104.1, 86.7, 75.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{18}N_4$ 435.1604; Found 435.1603.

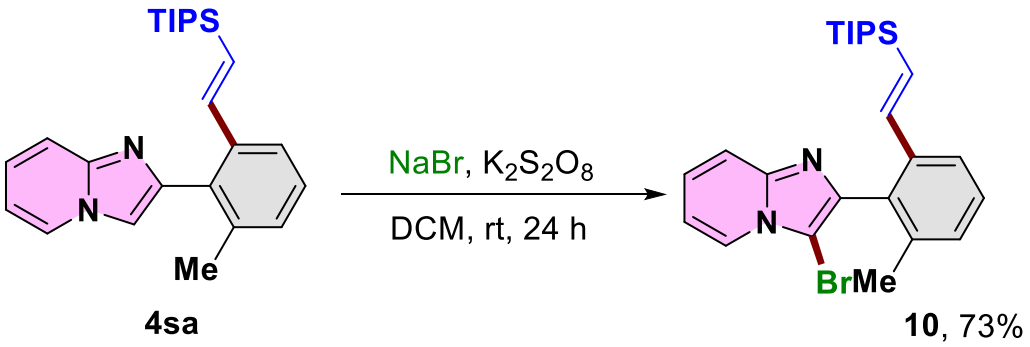


3-(1-Benzyl-1H-1,2,3-triazol-4-yl)-2-phenylimidazo[1,2-*a*]pyridine (9). To a 15 mL oven dried Schlenk tube, **7** (43.7 mg, 0.2 mmol), BnN_3 (77.7 mg. 0.4 mmol), $CuSO_4$ (43.8 mg, 0.4 mmol), sodium vitamin (19.8 mg, 0.1 mmol), and DMF (1.5 mL) were successively added. The reaction mixture was stirred at room temperature for 1 hour under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the white solid **9** (43.5 mg, 62%). Mp: 151-153 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (d, *J* = 6.9 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.64 – 7.60 (m, 2H), 7.41 (s, 1H), 7.37 – 7.32 (m, 3H), 7.31 – 7.28 (m, 3H), 7.27 – 7.24 (m, 1H), 7.24 – 7.21 (m, 2H), 6.86 (t, *J* = 6.8 Hz, 1H), 5.53 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 144.4, 138.9, 134.5, 134.1, 129.1, 128.8, 128.6, 128.5, 128.2, 127.8, 126.1, 125.6, 122.5, 117.2, 112.8, 111.6, 54.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}N_5$ 352.1556; Found 352.1556.



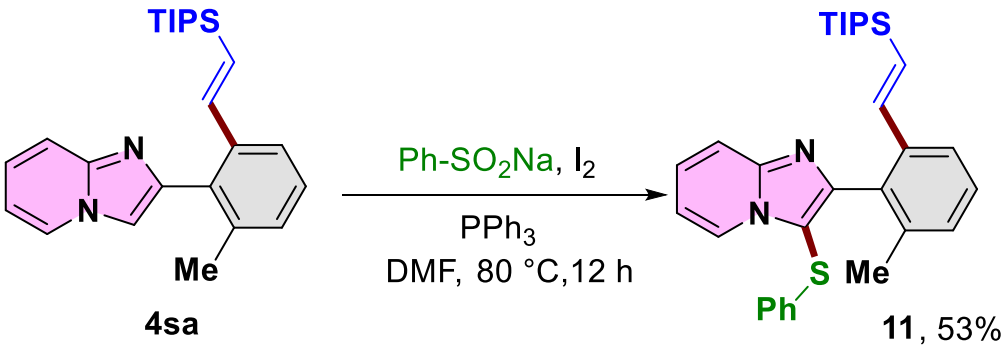
(*E*)-3-Bromo-2-(2-methyl-6-(2-(triisopropylsilyl)vinyl)phenyl)imidazo[1,2-*a*]pyridine (10). To a 15 mL oven dried Schlenk tube, **4sa** (78.1 mg, 0.2 mmol), NaBr (41.2 mg. 0.4 mmol), $K_2S_2O_8$

(108.1 mg, 0.4 mmol), and DCM (1.5 mL) were successively added. The reaction mixture was stirred at room temperature for 24 hours under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the grey solid **10** (68.4 mg, 73%). Mp: 116-118 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 6.8 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 9.1 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 6.4 Hz, 1H), 6.58 (d, *J* = 19.4 Hz, 1H), 6.16 (d, *J* = 19.4 Hz, 1H), 2.15 (s, 3H), 0.92 – 0.82 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 144.6, 143.1, 139.9, 138.0, 130.6, 129.0, 128.9, 125.9, 124.9, 123.8, 122.9, 117.6, 113.1, 95.1, 18.5, 18.4, 10.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{33}BrN_2Si$ 469.1669; Found 469.1671.



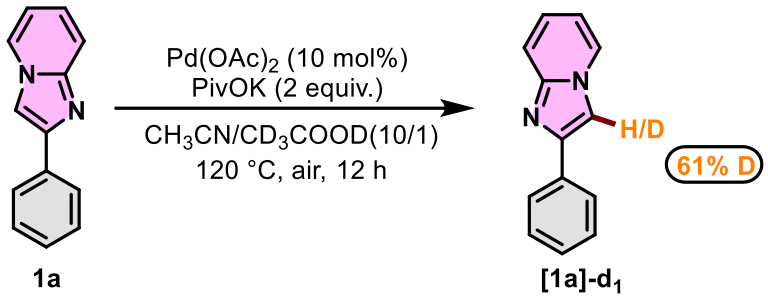
(*E*)-2-(2-methyl-6-(2-(triisopropylsilyl)vinyl)phenyl)-3-(phenylthio)imidazo[1,2-*a*]pyridine (11). To a 15 mL oven dried Schlenk tube, **4sa** (78.1 mg, 0.2 mmol), Ph-SO_2Na (65.7 mg. 0.4 mmol), I_2 (50.8 mg, 0.2 mmol), PPh_3(104.9 mg, 0.4 mmol), and DMF (1.5 mL) were successively added. The reaction mixture was stirred at 80 °C (metal sand bath temperature) for 12 hours under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the grey solid **11** (52.8 mg, 53%). Mp: 152-154 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 6.8 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.3 Hz, 3H), 6.63 (d, *J* = 19.4 Hz, 1H), 6.20 (d, *J* = 19.4 Hz, 1H), 2.14 (s, 3H), 0.96 – 0.89 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.5, 147.0, 144.8, 139.9, 137.7, 134.8, 131.5, 129.2, 129.0, 128.6, 126.6, 126.2, 126.1, 125.6, 124.4, 122.9, 117.8, 113.1, 110.0, 20.5, 18.5, 10.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{38}N_2SSi$ 499.2597; Found 499.2596.

3.7 H/D exchange experiment.



To a 15 mL oven dried Schlenk tube, PivOK (56.9 mg, 0.4 mmol), 2-phenylimidazopyridine **1a** (38.8 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), CD_3COOD (0.2 mL) and CH_3CN (2 mL) were charged into a Schlenk tube. The mixture was then stirred at 120 °C under the air for 12 hours. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1) to afford **[1a]-d_1** as grey solid in 80% isolated yield. Upon analyzing the ^1H NMR spectra as shown in **Figure S1**, the estimated deuterium incorporation at the C3-position of the 2-phenylimidazopyridine was 61%.

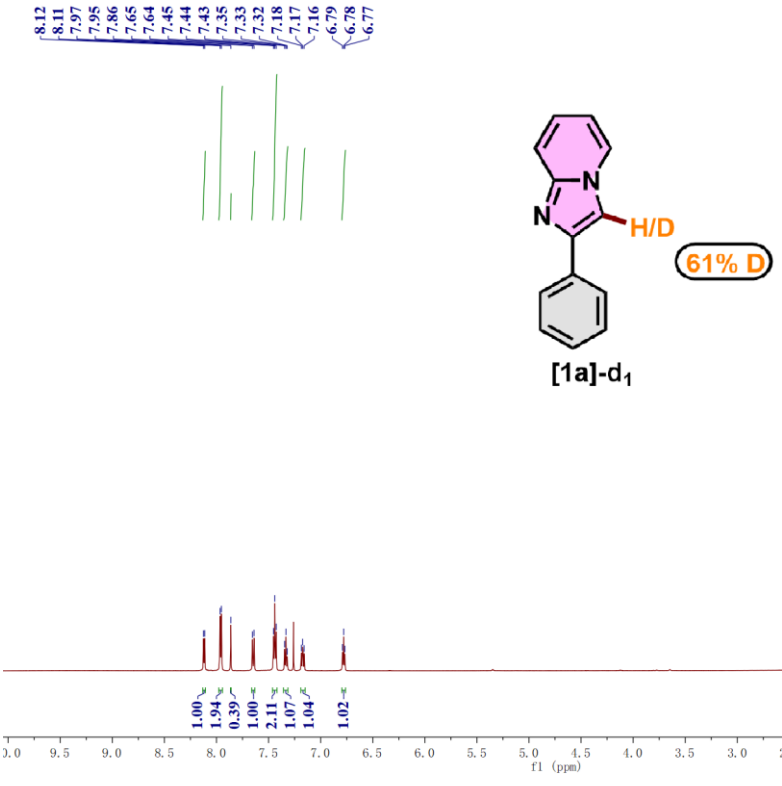
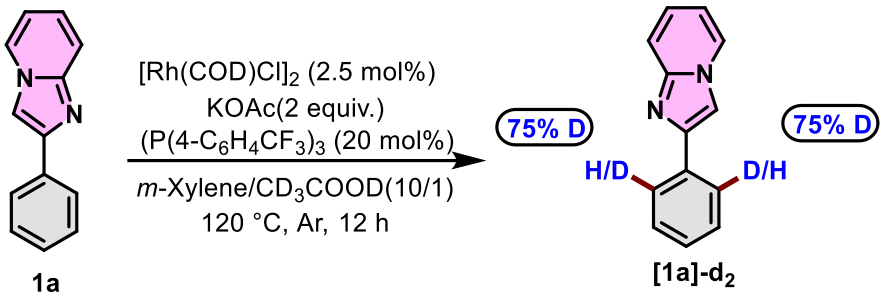


Figure S1. The ^1H NMR spectra of **[1a]-d_1**



To a 15 mL oven dried Schlenk tube, $(P(4\text{-}C_6H_4CF_3)_3$ (18.7 mg, 0.04 mmol, 20 mol%), 2-phenylimidazopyridine **1a** (38.8 mg, 0.2 mmol), $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol, 2.5 mol%), CD_3COOD (0.2 mL) and *m*-xylene (2 mL) were charged into a Schlenk tube. The mixture was then stirred at 120 °C under the Ar for 12 hours. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1) to afford **[1a]-d_2** as grey solid in 86% isolated yield. Upon analyzing the ^{1}H NMR spectra as shown in **Figure S2**, the estimated deuterium incorporation at the *ortho*-position of the 2-phenylimidazopyridine was 75%.

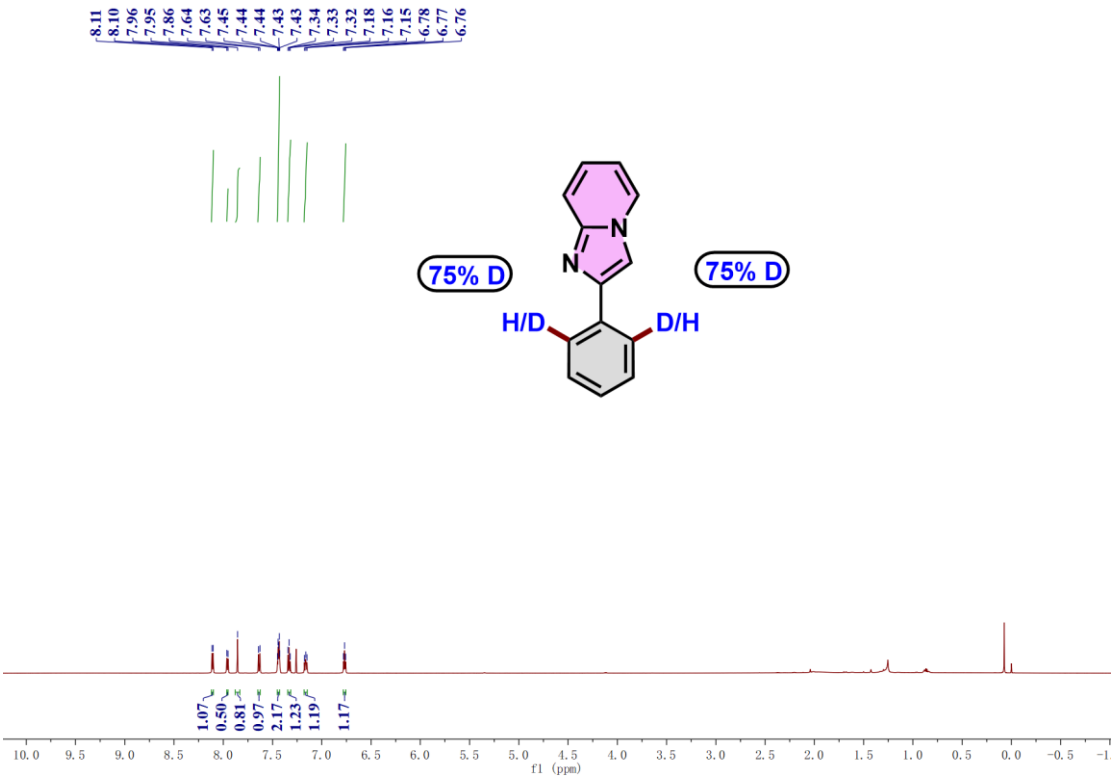
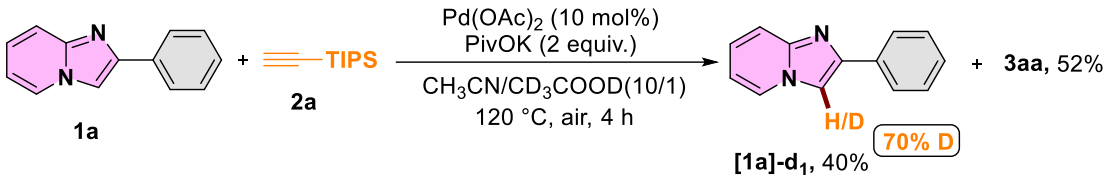


Figure S2. The ^{1}H NMR spectra of **[1a]-d_2**



To a 15 mL oven dried Schlenk tube, PivOK (56.9 mg, 0.4 mmol), 2-phenylimidazopyridine **1a** (38.8 mg, 0.2 mmol), TIPS-protected terminal alkyne (54.7 mg, 0.3 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), CD_3COOD (0.2 mL) and CH_3CN (2 mL) were charged into a Schlenk tube. The mixture was then stirred at 120 °C under the air for 4 hours. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1) to afford **[1a]-d_1** as grey solid in 40% isolated yield. Upon analyzing the ^1H NMR spectra as shown in **Figure S3**, the estimated deuterium incorporation at the C3-position of the 2-phenylimidazopyridine was 70%.

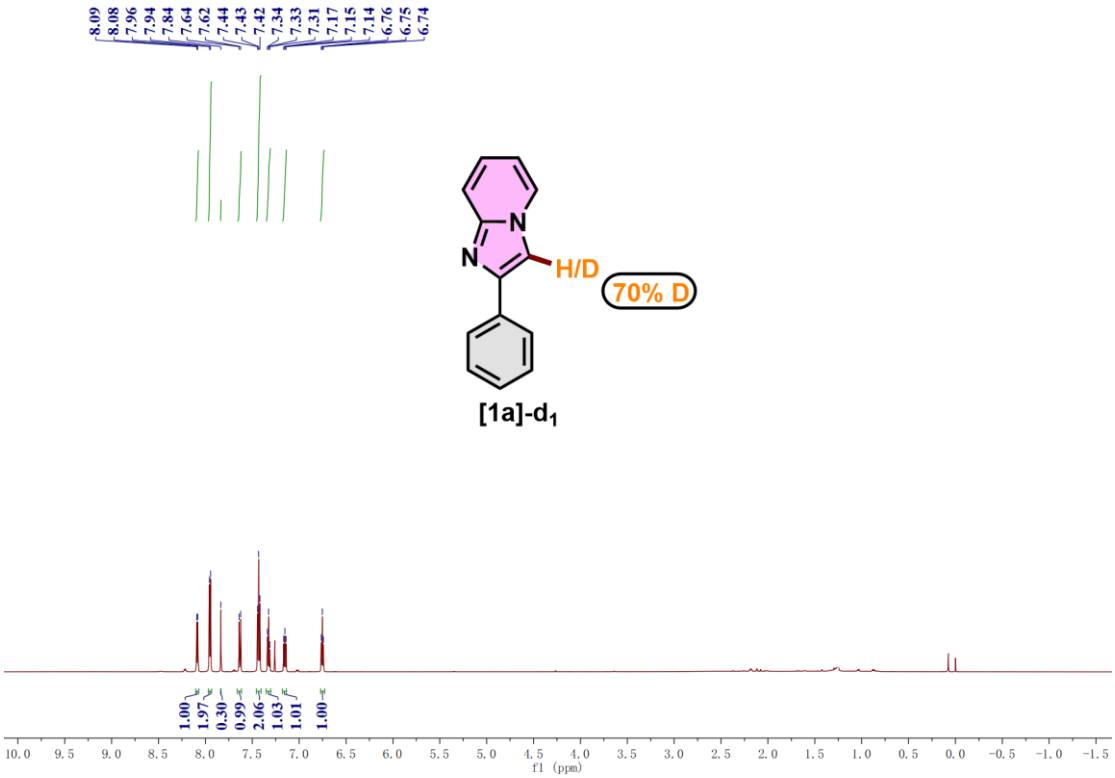
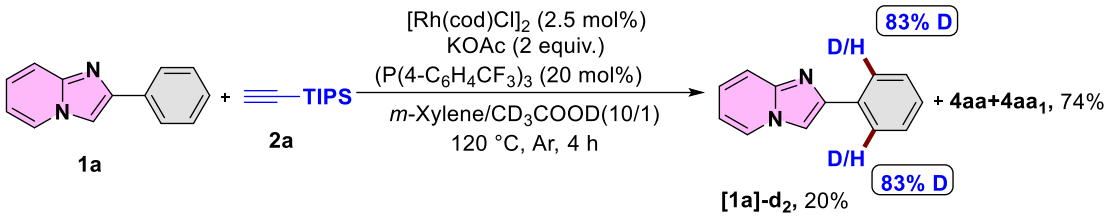


Figure S3. The ^1H NMR spectra of **[1a]-d_1**



To a 15 mL oven dried Schlenk tube, $(P(4\text{-}C_6H_4CF_3)_3$ (18.7 mg, 0.04 mmol, 20 mol%), 2-phenylimidazopyridine **1a** (38.8 mg, 0.2 mmol), TIPS-protected terminal alkyne (91.2 mg, 0.5 mmol), $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol, 2.5 mol%), CD_3COOD (0.2 mL) and *m*-xylene (2 mL) were charged into a Schlenk tube. The mixture was then stirred at 120 °C under the Ar for 4 hours. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1) to afford **[1a]-d$_2$** as grey solid in 20% isolated yield. Upon analyzing the ^{1}H NMR spectra as shown in **Figure S4**, the estimated deuterium incorporation at the *ortho*-position of the 2-phenylimidazopyridine was 83%.

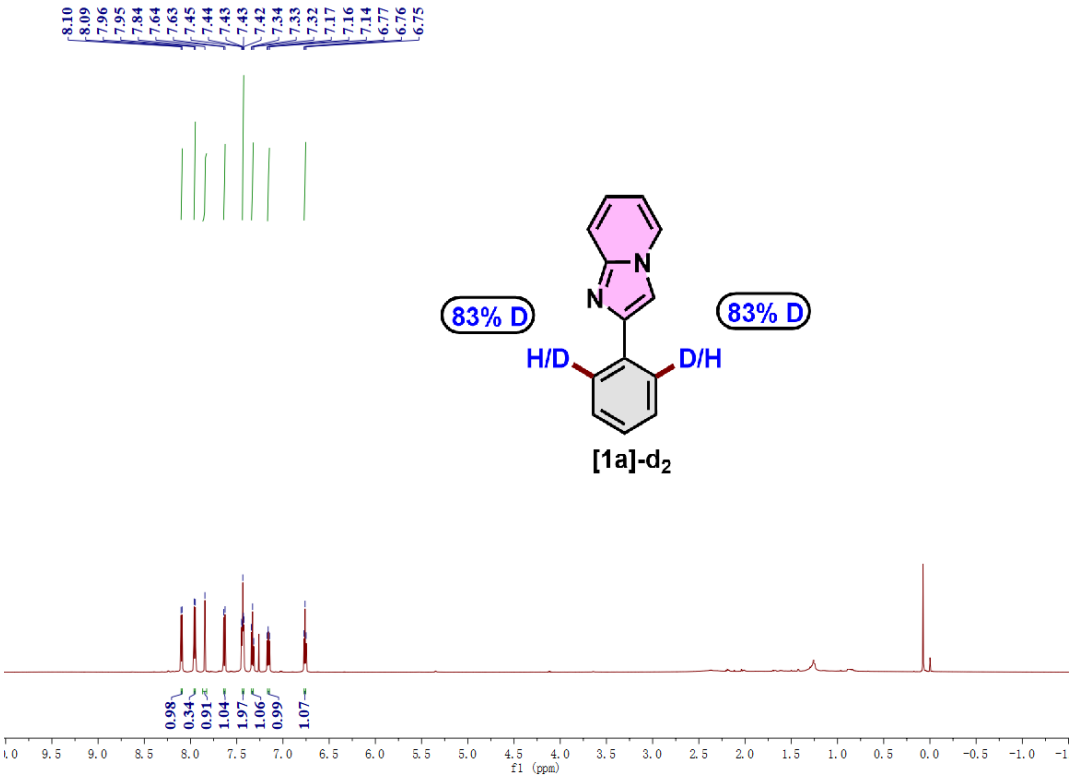
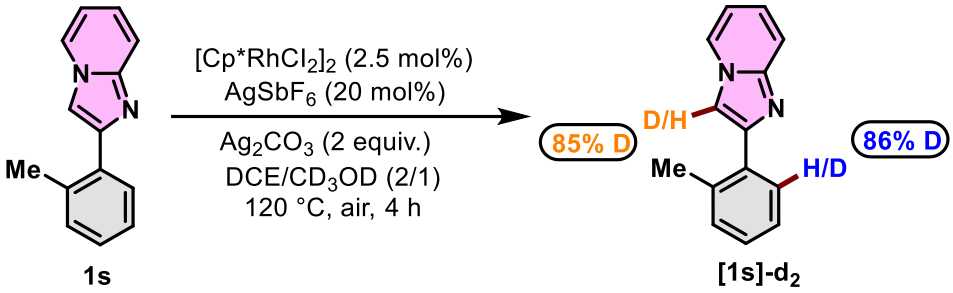


Figure S4. The ^{1}H NMR spectra of **[1a]-d$_2$**

3.8 KIE determination



2-(*o*-Tolyl)imidazo[1,2-*a*]pyridine **1s** (62.5 mg, 0.3 mmol), $[Cp^*RhCl_2]_2$ (4.6 mg, 0.0075 mmol, 2.5 mol%), Ag_2CO_3 (165.5 mg, 0.6 mmol), CD_3OD (0.7 mL) and DCE (1.4 mL) were charged into a Schlenk tube. The mixture was then stirred at 120 °C under air for 4 hours. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1) to afford **[1s]-d$_2$** in 87% yield. Upon analyzing the ^{1}H NMR spectra as shown in **Figure S5**, the estimated deuterium incorporation at the *ortho*-position of the 2-phenyl ring was 86% and at the C3-position of 2-(*o*-tolyl)imidazo[1,2-*a*]pyridine scaffold was 85%.

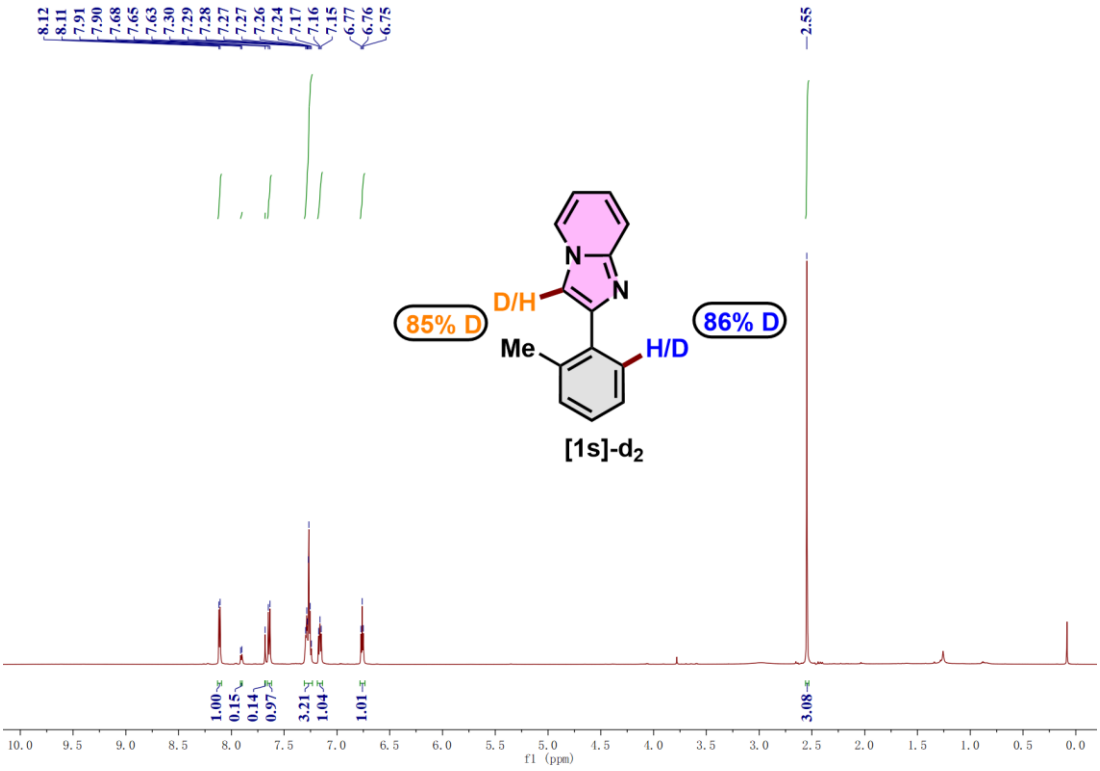
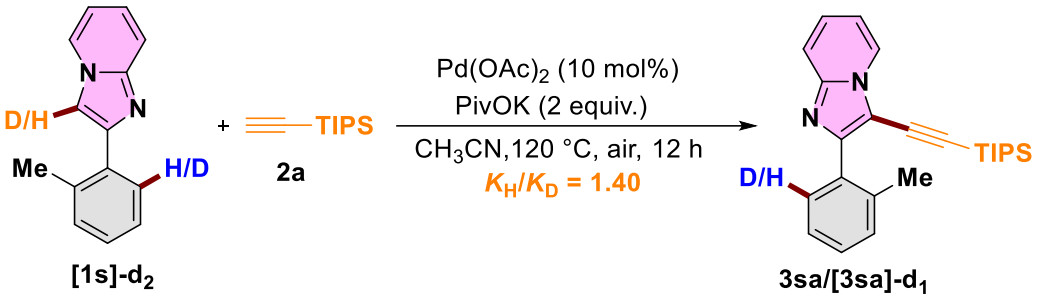


Figure S5. The ^{1}H NMR spectra of **[1s]-d$_2$**



To a 15 mL oven dried Schlenk tube, PivOK (0.6 mmol, 85.3 mg), 2-(*o*-tolyl)imidazo[1,2-*a*]pyridine **1s** (31.3 mg, 0.15 mmol), **[1s]-d$_2$** (0.15 mmol, 31.8 mg), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 10 mol%), TIPS-protected terminal alkyne (41.0 mg, 0.225 mmol) and CH_3CN (2 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified over a column of silica gel (petroleum ether/ethyl acetate = 30:1) to afford the mixture of products **3sa** and **[3sa]-d$_1$** as white solid. By analyzing the ^{1}H NMR of the mixture **3sa** and **[3sa]-d$_1$** as shown in **Figure S6**, the ratio of **3sa** and **[3sa]-d$_1$** was determined to be 0.58:0.42. Accordingly, the intermolecular **KIE** (k_H/k_D) = 0.58/1.00-0.58 = 1.40.

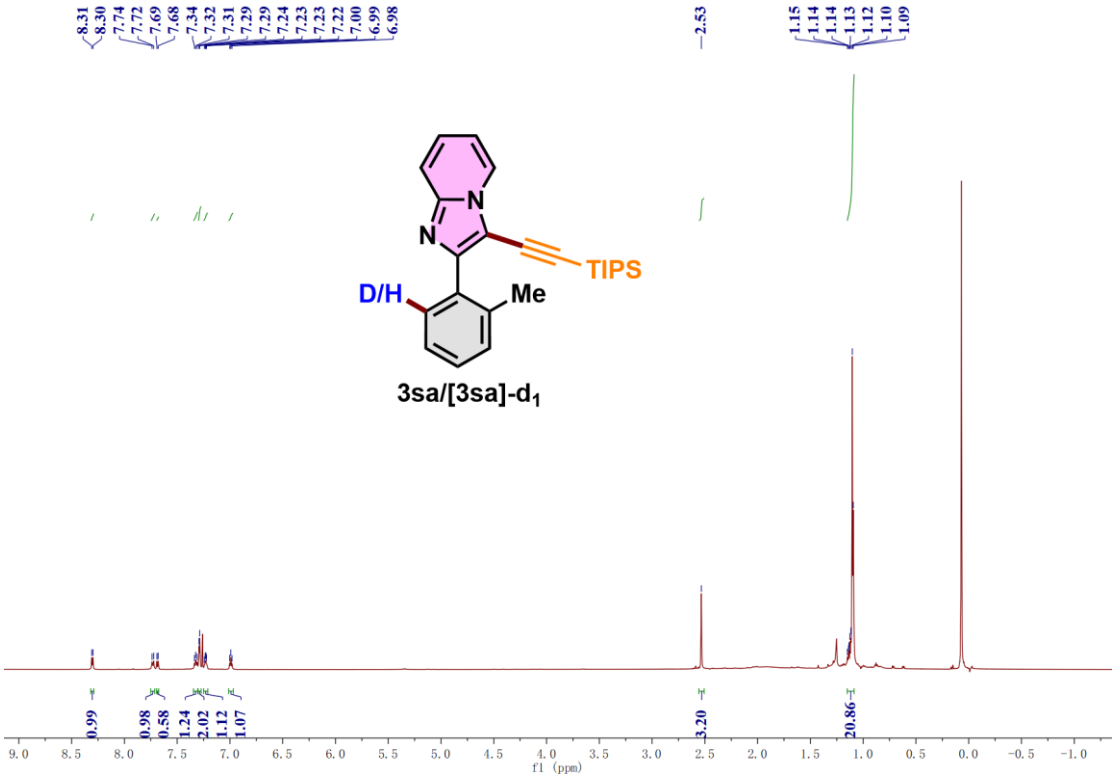
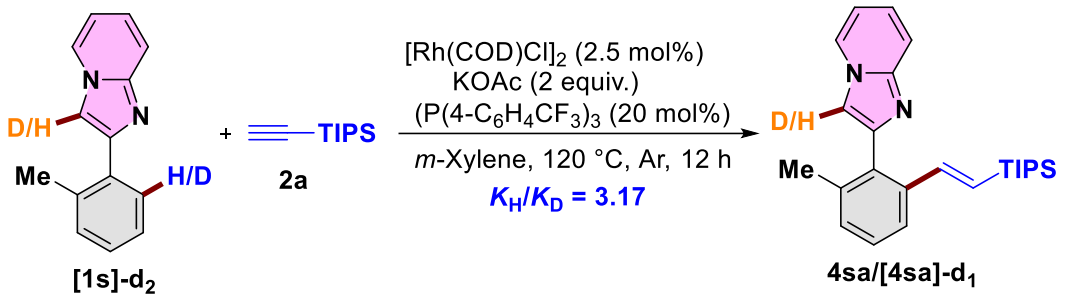


Figure S6. The ^{1}H NMR spectra of **3sa** and **[3sa]-d$_1$**



To a 15 mL oven dried Schlenk tube, 2-(*o*-tolyl)imidazo[1,2-*a*]pyridine **1s** (31.3 mg, 0.15 mmol), **[1s]-d$_2$** (0.15 mmol, 31.8 mg), (P(4-$C_6H_4CF_3$)$_3$ (28.0 mg, 0.06 mmol, 20 mol%), and [Rh(COD)Cl]$_2$ (3.7 mg, 0.0075 mmol, 2.5 mol%), TIPS-protected terminal alkyne (41.0 mg, 0.225 mmol), *m*-xylene (2 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under Ar. After cooling the reaction at room temperature and concentration, the crude mixture was purified over a column of silica gel (petroleum ether/ethyl acetate = 30:1) to afford the mixture of products **4sa** and **[4sa]-d$_1$** as yellow solid. By analyzing the ^{1}H NMR of the mixture **4sa** and **[4sa]-d$_1$** as shown in **Figure S7**, the ratio of **4sa** and **[4sa]-d$_1$** was determined to be 0.76:0.24. Accordingly, the intermolecular **KIE** (k_H/k_D) = 0.76/1.00-0.76= 3.17.

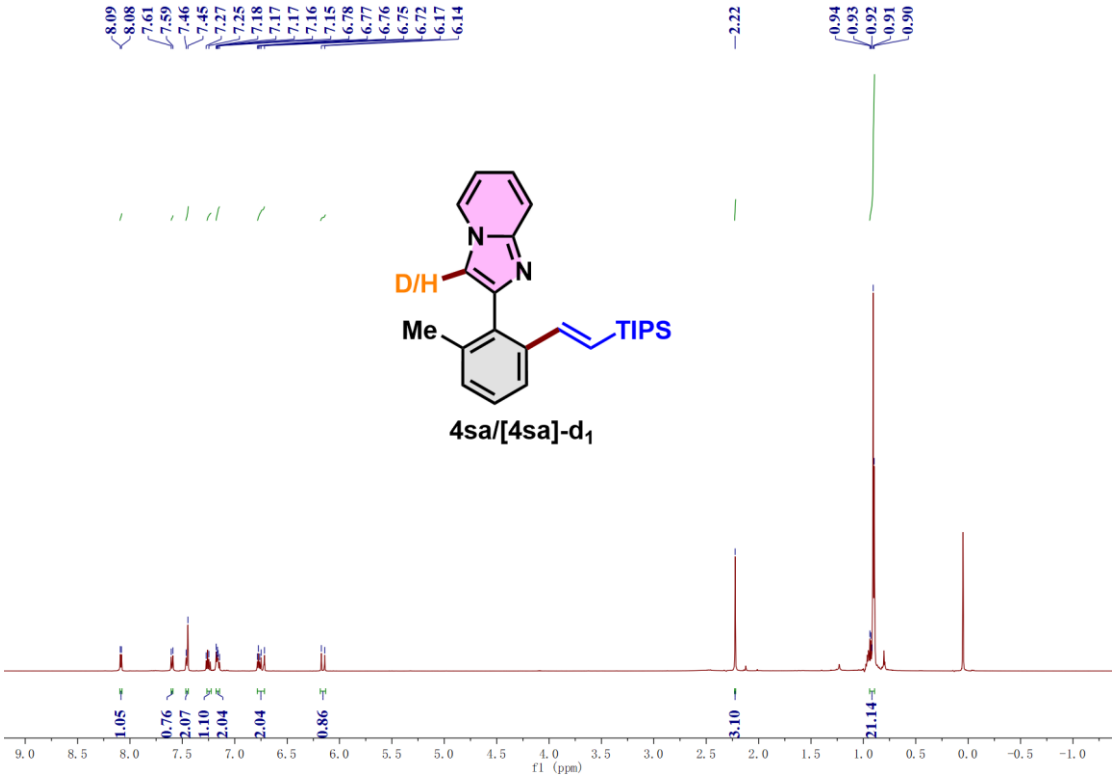


Figure S7. The ^{1}H NMR spectra of **4sa** and **[4sa]-d$_1$**

4. Crystallographic description

White block-like single crystals of **3da** were grown by layering a dichlormethane solution with hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 298(2) K, using the *ω*- and *φ*- scans to a maximum θ value of 28.327°. The data were refined by full-matrix least-squares techniques on F^2 with SHELXL-2018/3. And the structures were solved by direct methods SHELXL-2018/3. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. And an ORTEP representation of the structure is shown below. CCDC: 2522537.

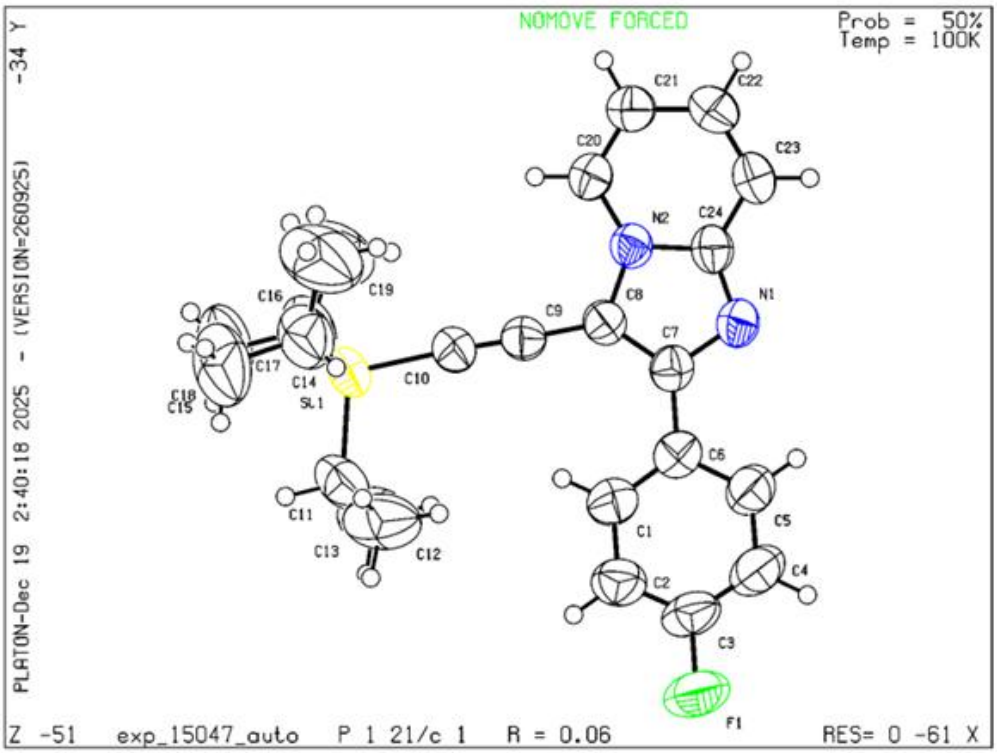


Figure S8. ORTEP diagram of **3da** with the thermal ellipsoids set at 50% probability.

Table 2 Crystal data and structure refinement for **3da.**

Identification code	exp_15047_auto
Empirical formula	C24H29FN2Si
Formula weight	392.58
Temperature/K	100
Crystal system	monoclinic
Space group	P21/c
a/Å	12.7706(8)
b/Å	14.9937(10)
c/Å	12.2093(8)
α/°	90
β/°	96.322(6)
γ/°	90

Volume/Å3	2323.6(3)
Z	4
ρcalcg/cm3	1.122
μ/mm 1	1.031
F(000)	840.0
Crystal size/mm3	0.12 × 0.1 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.964 to 142.16
Index ranges	-15 ≤ h ≤ 15, -17 ≤ k ≤ 10, -14 ≤ l ≤ 11
Reflections collected	8506
Independent reflections	4379 [Rint = 0.0272, Rsigma = 0.0396]
Data/restraints/parameters	4379/0/260
Goodness-of-fit on F2	1.043
Final R indexes [I>=2σ (I)]	R1 = 0.0649, wR2 = 0.1766
Final R indexes [all data]	R1 = 0.0840, wR2 = 0.1970
Largest diff. peak/hole / e Å-3	0.34/-0.27

Table 3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3da**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Si1	1819.6(6)	6239.4(6)	1690.0(7)	71.7(3)
N2	5177.1(16)	6996.3(14)	4467.1(16)	57.7(5)
F1	2038.8(16)	3487.7(18)	7410(2)	126.8(9)
N1	5428.2(18)	6303.5(15)	6107.5(17)	65.2(6)
C8	4333(2)	6419.5(17)	4512(2)	58.2(6)
C7	4516(2)	6007.3(17)	5534(2)	58.3(6)
C6	3866(2)	5329.8(18)	6013(2)	62.1(6)
C9	3531(2)	6370.3(18)	3622(2)	62.1(6)
C24	5819(2)	6900.2(18)	5449(2)	63.1(6)
C20	5400(2)	7571.4(19)	3651(2)	65.7(7)
C10	2856(2)	6349(2)	2850(2)	70.1(7)
C21	6284(2)	8070(2)	3813(2)	75.8(8)
C23	6747(2)	7416(2)	5606(2)	77.8(8)
C1	2969(2)	4982(2)	5436(3)	78.6(8)
C5	4153(2)	5024(2)	7076(3)	81.2(9)
C22	6971(3)	7984(2)	4798(3)	83.1(9)
C3	2654(3)	4101(2)	6953(3)	87.0(10)
C2	2352(3)	4366(2)	5910(3)	85.7(9)
C4	3542(3)	4403(3)	7549(3)	98.7(11)
C11	898(3)	5353(3)	2112(3)	97.2(11)
C14	1106(3)	7338(3)	1539(4)	121.7(15)
C12	433(3)	5595(4)	3170(5)	136.9(18)
C17	2476(3)	5839(4)	484(3)	128.4(17)
C13	1399(4)	4430(3)	2238(5)	136.0(17)
C15	87(4)	7306(4)	754(5)	157(2)

C18	1718(4)	5615(5)	-510(4)	171(3)
C19	3455(4)	6216(5)	290(5)	178(3)
C16	1716(5)	8117(4)	1477(6)	189(3)

Table 4 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3da. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	55.3(4)	82.3(6)	74.2(5)	-3.8(4)	-7.7(3)	-5.2(4)
N2	59.8(12)	61.7(12)	51.5(10)	-3.6(9)	5.4(9)	-1.6(9)
F1	81.6(13)	144.7(19)	157(2)	81.5(17)	26.1(13)	-4.3(12)
N1	70.9(14)	72.7(14)	51.0(11)	-3.0(10)	2.6(10)	-1.5(11)
C8	55.0(13)	67.3(15)	53.0(13)	-6.0(11)	9.1(10)	-1.8(11)
C7	61.4(14)	63.9(14)	50.7(12)	-6.4(11)	10.8(11)	3.7(11)
C6	62.5(15)	64.7(15)	61.5(14)	-1.3(11)	18.0(12)	11.2(12)
C9	57.1(14)	69.3(16)	60.4(14)	1.4(12)	9.0(12)	-3.3(11)
C24	68.0(16)	66.9(15)	53.1(13)	-8.3(11)	0.5(12)	-2.3(12)
C20	68.9(16)	72.6(16)	55.2(13)	1.1(12)	5.1(12)	-2.8(13)
C10	58.1(15)	86.1(19)	64.9(16)	6.0(13)	1.4(13)	-9.3(13)
C21	80.2(19)	77.4(18)	69.5(17)	2.7(14)	7.3(15)	-14.2(15)
C23	77.2(19)	87(2)	65.7(16)	-6.5(14)	-9.9(14)	-13.9(15)
C1	77.4(19)	88(2)	72.2(17)	8.2(15)	15.6(15)	-6.2(16)
C5	73.1(18)	98(2)	73.5(18)	18.1(16)	11.1(15)	5.0(16)
C22	81(2)	81(2)	85(2)	-3.9(16)	-0.2(16)	-24.3(16)
C3	68.4(18)	93(2)	105(2)	38.0(19)	31.6(18)	11.9(16)
C2	69.4(18)	91(2)	98(2)	14.8(18)	17.0(17)	-3.6(16)
C4	86(2)	119(3)	93(2)	45(2)	18.7(19)	7(2)
C11	63.8(18)	98(2)	126(3)	-3(2)	-8.0(19)	-10.5(17)
C14	111(3)	89(3)	154(4)	16(3)	-35(3)	1(2)
C12	83(3)	145(4)	191(5)	26(4)	58(3)	6(3)
C17	92(3)	207(5)	86(3)	-32(3)	7(2)	-30(3)
C13	148(4)	81(3)	179(5)	-1(3)	20(4)	-11(3)
C15	122(4)	143(4)	189(5)	10(4)	-55(4)	42(3)
C18	143(4)	263(8)	100(3)	-63(4)	-16(3)	12(5)
C19	145(5)	261(8)	139(4)	-56(5)	69(4)	-78(5)
C16	155(5)	100(4)	301(9)	36(5)	-22(6)	-14(3)

Table 5 Bond Lengths for **3da**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	C10	1.836(3)	C9	C10	1.206(4)
Si1	C11	1.884(4)	C24	C23	1.410(4)
Si1	C14	1.881(4)	C20	C21	1.351(4)
Si1	C17	1.871(4)	C21	C22	1.414(4)
N2	C8	1.388(3)	C23	C22	1.357(4)
N2	C24	1.383(3)	C1	C2	1.382(4)
N2	C20	1.371(3)	C5	C4	1.381(5)
F1	C3	1.368(4)	C3	C2	1.350(5)

N1	C7	1.366(3)	C3	C4	1.356(5)
N1	C24	1.336(3)	C11	C12	1.524(6)
C8	C7	1.389(3)	C11	C13	1.524(6)
C8	C9	1.411(4)	C14	C15	1.530(6)
C7	C6	1.473(4)	C14	C16	1.412(6)
C6	C1	1.380(4)	C17	C18	1.505(6)
C6	C5	1.387(4)	C17	C19	1.416(6)

Table 6 Bond Angles for **3da**.

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C10	Si1	C11	105.73(15)	N1	C24	C23	130.6(3)
C10	Si1	C14	107.32(17)	C21	C20	N2	118.6(3)
C10	Si1	C17	106.75(16)	C9	C10	Si1	176.3(3)
C14	Si1	C11	109.50(19)	C20	C21	C22	120.3(3)
C17	Si1	C11	109.6(2)	C22	C23	C24	119.2(3)
C17	Si1	C14	117.2(3)	C6	C1	C2	121.2(3)
C24	N2	C8	106.8(2)	C4	C5	C6	120.7(3)
C20	N2	C8	130.2(2)	C23	C22	C21	121.0(3)
C20	N2	C24	123.0(2)	C2	C3	F1	117.7(3)
C24	N1	C7	105.3(2)	C2	C3	C4	122.9(3)
N2	C8	C7	105.0(2)	C4	C3	F1	119.3(3)
N2	C8	C9	120.2(2)	C3	C2	C1	118.4(3)
C7	C8	C9	134.8(2)	C3	C4	C5	118.6(3)
N1	C7	C8	111.4(2)	C12	C11	Si1	112.2(3)
N1	C7	C6	120.5(2)	C12	C11	C13	109.2(4)
C8	C7	C6	128.1(2)	C13	C11	Si1	113.6(3)
C1	C6	C7	122.0(2)	C15	C14	Si1	113.8(3)
C1	C6	C5	118.2(3)	C16	C14	Si1	117.8(4)
C5	C6	C7	119.8(3)	C16	C14	C15	115.4(4)
C10	C9	C8	178.2(3)	C18	C17	Si1	113.7(3)
N2	C24	C23	118.0(2)	C19	C17	Si1	119.0(4)
N1	C24	N2	111.5(2)	C19	C17	C18	117.1(4)

Table 7 Torsion Angles for **3da**.

A	**B**	**C**	**D**	**Angle/˚**	**A**	**B**	**C**	**D**	**Angle/˚**
N2	C8	C7	N1	-0.2(3)	C20	N2	C8	C7	-179.7(2)
N2	C8	C7	C6	-179.9(2)	C20	N2	C8	C9	-0.4(4)
N2	C24	C23	C22	0.3(4)	C20	N2	C24	N1	179.7(2)
N2	C20	C21	C22	1.0(4)	C20	N2	C24	C23	-0.4(4)
F1	C3	C2	C1	-179.6(3)	C20	C21	C22	C23	-1.2(5)
F1	C3	C4	C5	-179.9(3)	C10	Si1	C11	C12	58.8(3)
N1	C7	C6	C1	-176.6(2)	C10	Si1	C11	C13	-65.6(3)
N1	C7	C6	C5	3.3(4)	C10	Si1	C14	C15	-168.9(4)
N1	C24	C23	C22	-179.9(3)	C10	Si1	C14	C16	51.5(5)
C8	N2	C24	N1	-0.3(3)	C10	Si1	C17	C18	173.6(4)
C8	N2	C24	C23	179.5(2)	C10	Si1	C17	C19	-42.1(6)

C8	N2	C20	C21	179.8(3)	C1	C6	C5	C4	-1.5(5)
C8	C7	C6	C1	3.1(4)	C5	C6	C1	C2	2.0(4)
C8	C7	C6	C5	-177.0(3)	C2	C3	C4	C5	1.3(6)
C7	N1	C24	N2	0.2(3)	C4	C3	C2	C1	-0.9(6)
C7	N1	C24	C23	-179.6(3)	C11	Si1	C14	C15	-54.6(5)
C7	C6	C1	C2	-178.1(3)	C11	Si1	C14	C16	165.8(5)
C7	C6	C5	C4	178.5(3)	C11	Si1	C17	C18	59.5(5)
C6	C1	C2	C3	-0.9(5)	C11	Si1	C17	C19	-156.2(5)
C6	C5	C4	C3	-0.1(5)	C14	Si1	C11	C12	-56.5(3)
C9	C8	C7	N1	-179.3(3)	C14	Si1	C11	C13	179.0(3)
C9	C8	C7	C6	0.9(5)	C14	Si1	C17	C18	-66.1(5)
C24	N2	C8	C7	0.3(3)	C14	Si1	C17	C19	78.2(6)
C24	N2	C8	C9	179.6(2)	C17	Si1	C11	C12	173.5(3)
C24	N2	C20	C21	-0.2(4)	C17	Si1	C11	C13	49.1(4)
C24	N1	C7	C8	0.0(3)	C17	Si1	C14	C15	71.1(5)
C24	N1	C7	C6	179.7(2)	C17	Si1	C14	C16	-68.6(5)
C24	C23	C22	C21	0.6(5)					

Table 8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3da.**

Atom	***x***	***y***	***z***	**U(eq)**
H20	4941.33	7618.43	2985.74	79
H21	6446.36	8479.7	3262.23	91
H23	7208.99	7366.95	6267.77	93
H1	2771.57	5169.48	4698.31	94
H5	4777.36	5242.71	7482.18	97
H22	7597.66	8329.93	4896.64	100
H2	1729.67	4135.46	5511.54	103
H4	3739.12	4192.89	8276.4	118
H11	299.02	5311.02	1513.76	117
H14	835.88	7404.95	2273.09	146
H12A	988.96	5582.58	3790.2	205
H12B	-116.8	5163.6	3299.76	205
H12C	126.45	6194.24	3099.42	205
H17	2702.35	5228.82	740.71	154
H13A	1669.94	4260.23	1547.14	204
H13B	868.82	3995.79	2413.5	204
H13C	1979.22	4441.78	2833.76	204
H15A	253.41	7177.38	5.41	235
H15B	-273.22	7882.54	762.31	235
H15C	-373.04	6836.69	991.02	235
H18A	1060.71	5387.12	-271.48	256
H18B	2030.16	5160	-950.08	256
H18C	1569.51	6152.85	-957.2	256
H19A	3358.5	6848.46	103.8	266
H19B	3729.57	5902.63	-322.61	266

H19C 3955.98	6157.06	954.48	266
H16A 2313.91	8102.31	2052.88	283
H16B 1280.39	8642.2	1581.68	283
H16C 1976.74	8149.09	752.34	283

White block-like single crystals of **4da** were grown by layering a dichlormethane solution with hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 298(2) K, using the *ω*- and *φ*- scans to a maximum θ value of 28.327°. The data were refined by full-matrix least-squares techniques on F^2 with SHELXL-2018/3. And the structures were solved by direct methods SHELXL-2018/3. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. And an ORTEP representation of the structure is shown below. CCDC: 2528406.

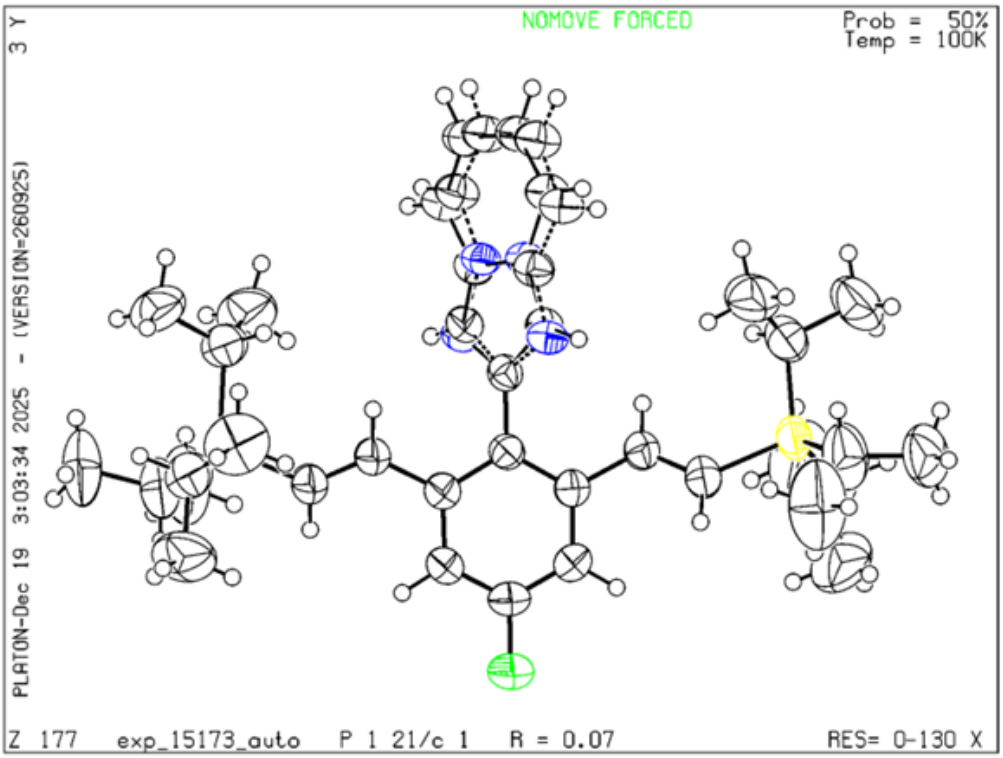


Figure S9. ORTEP diagram of **4da** with the thermal ellipsoids set at 50% probability.

Table 9 Crystal data and structure refinement for **4da**.

Identification code	exp_15173_auto
Empirical formula	C35H53FN2Si2
Formula weight	576.97
Temperature/K	100
Crystal system	monoclinic
Space group	P21/c
a/Å	18.0162(10)
b/Å	14.2172(11)

c/Å	14.0720(11)
α/°	90
β/°	92.780(6)
γ/°	90
Volume/Å3	3600.2(4)
Z	4
ρcalcg/cm3	1.064
μ/mm 1	1.107
F(000)	1256.0
Crystal size/mm3	0.13 × 0.1 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.91 to 141.908
Index ranges	-21 ≤ h ≤ 22, -17 ≤ k ≤ 17, -17 ≤ l ≤ 11
Reflections collected	23967
Independent reflections	6843 [Rint = 0.0613, Rsigma = 0.0543]
Data/restraints/parameters	6843/433/447
Goodness-of-fit on F2	1.050
Final R indexes [I>=2σ (I)]	R1 = 0.0651, wR2 = 0.1702
Final R indexes [all data]	R1 = 0.0893, wR2 = 0.1944
Largest diff. peak/hole / e Å-3	0.31/-0.32

Table 10 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4da**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Si1	7147.1(4)	5359.4(6)	2885.6(5)	57.4(2)
Si2	1165.1(4)	5410.0(6)	2456.0(6)	61.9(3)
F1	4142.6(11)	3137.4(18)	596.3(17)	121.1(9)
C7	4559(13)	5906(13)	4317(14)	49(2)
N2	4385(10)	6668(9)	4784(13)	48.0(17)
N1	3725(11)	6674(13)	3344(10)	49.5(19)
C5	3852(12)	7131(17)	4169(12)	52.4(18)
C6	4159.3(12)	5898.1(17)	3435.9(17)	46.3(5)
C9	3477.3(13)	4817.1(18)	2288.2(18)	50.1(6)
C8	4152.9(12)	5186.2(17)	2668.9(16)	46.6(5)
C25	2745.4(13)	5131.5(18)	2612.9(18)	53.1(6)
C13	4829.3(14)	4871.6(18)	2314.1(18)	53.1(6)
C14	5554.7(14)	5266.4(19)	2643.9(18)	55.4(6)
C15	6210.7(14)	4873(2)	2557(2)	63.8(7)
C10	3481.2(15)	4121(2)	1591(2)	66.4(8)
C1	3561(7)	7976(10)	4508(8)	57.6(19)
C26	2118.5(15)	5143(2)	2082(2)	68.9(8)
C12	4813.9(16)	4175(2)	1609(2)	73.2(9)
C4	4616(7)	7012(8)	5680(10)	60(2)
C11	4147.8(17)	3825(2)	1270(2)	77.1(9)
C27	1224.0(18)	6091(2)	3604(2)	77.8(9)

C16	7497(2)	6014(3)	1836(2)	80.8(9)
C22	7077.7(19)	6216(2)	3897(2)	76.0(9)
C3	4323(7)	7829(8)	5965(9)	66(2)
C2	3794(7)	8317(9)	5391(8)	65(2)
C19	7752.2(18)	4293(3)	3122(3)	93.7(11)
C30	696(2)	4255(3)	2663(3)	97.9(12)
C24	7774(2)	6810(3)	4085(3)	110.4(15)
C29	1588(2)	7057(3)	3517(3)	113.6(15)
C23	6819(2)	5780(3)	4814(2)	115.9(16)
C34	-181(2)	6045(4)	1474(3)	117.5(15)
C18	7561(3)	5400(4)	953(3)	124.5(17)
C28	475(2)	6176(3)	4083(3)	111.8(14)
C17	7011(3)	6884(3)	1588(3)	120.2(16)
C33	660(2)	6114(4)	1476(3)	117.2(16)
C21	8561(2)	4506(3)	3362(4)	131.3(18)
C20	7463(2)	3573(3)	3775(4)	135.6(19)
C32	671(3)	3641(4)	1756(5)	167(3)
C31	1068(3)	3730(3)	3519(4)	151(2)
C35	973(3)	6189(5)	591(4)	178(3)
C0	3756(13)	6740(15)	3500(12)	47(2)
N0	3934(9)	7148(13)	4328(8)	48.6(16)
N3	4598(11)	5779(11)	4230(12)	49.4(19)
C36	4459(12)	6529(12)	4773(17)	50.2(18)
C37	4757(7)	6790(8)	5677(10)	59.4(19)
C38	3706(7)	7981(10)	4758(8)	59.2(19)
C39	3997(6)	8200(8)	5618(7)	62(2)
C40	4527(6)	7619(8)	6086(9)	66(2)

Table 11 Anisotropic Displacement Parameters ($Å^2×10^3$) for **4da**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Si1	44.5(4)	62.8(5)	65.4(5)	0.2(3)	8.7(3)	-6.6(3)
Si2	43.7(4)	68.3(5)	74.0(5)	-0.7(4)	4.9(3)	3.9(3)
F1	77.6(13)	136.6(19)	150(2)	-98.0(17)	9.8(12)	-5.7(12)
C7	50(3)	48(5)	49(4)	0(3)	5(3)	5(3)
N2	56(4)	41(3)	48(2)	-8(3)	13(3)	-5(3)
N1	61(3)	47(3)	42(4)	-4(3)	7(3)	1(3)
C5	60(4)	48(3)	49(4)	0(3)	10(3)	-3(3)
C6	44.2(11)	45.9(12)	49.1(13)	1.7(10)	6.9(10)	-1.1(10)
C9	46.3(12)	52.5(14)	51.8(14)	-2.0(11)	4.3(10)	-2.0(11)
C8	46.1(12)	45.8(13)	48.2(13)	-1.0(10)	4.4(10)	0.1(10)
C25	46.5(13)	59.4(15)	53.7(15)	-1.6(12)	6.0(11)	-2.5(11)
C13	48.4(13)	52.5(14)	58.5(15)	-6.9(11)	3.6(11)	0.4(11)
C14	46.7(13)	57.1(15)	62.7(16)	-9.1(12)	6.6(11)	-3.3(11)
C15	48.0(14)	63.6(17)	80(2)	-14.3(14)	8.2(13)	-3.6(12)
C10	53.1(15)	69.6(18)	76.3(19)	-22.0(15)	-0.8(13)	-6.5(13)

C1	72(4)	50(3)	51(4)	-6(3)	7(3)	0(3)
C26	48.3(14)	93(2)	65.6(18)	-11.4(15)	3.2(13)	4.1(14)
C12	50.8(15)	80(2)	89(2)	-34.7(17)	8.1(14)	2.7(14)
C4	71(4)	54(4)	56(3)	-7(3)	5(3)	9(3)
C11	65.3(18)	80(2)	86(2)	-42.2(18)	4.7(15)	-3.1(16)
C27	67.5(19)	80(2)	87(2)	-4.3(17)	15.3(16)	9.0(16)
C16	81(2)	92(2)	70(2)	-0.6(17)	14.4(16)	-20.4(19)
C22	78(2)	84(2)	67.6(18)	-7.6(16)	11.8(15)	-17.7(17)
C3	80(5)	59(4)	58(4)	-11(3)	2(4)	9(3)
C2	79(5)	59(3)	58(4)	-7(3)	3(4)	8(3)
C19	56.7(18)	86(2)	139(3)	21(2)	10.6(19)	3.6(17)
C30	62(2)	80(2)	151(4)	-1(2)	-1(2)	-9.6(17)
C24	111(3)	122(3)	99(3)	-33(2)	13(2)	-52(3)
C29	110(3)	90(3)	144(4)	-39(3)	26(3)	-12(2)
C23	130(4)	151(4)	69(2)	-10(2)	27(2)	-45(3)
C34	80(3)	143(4)	128(3)	13(3)	-14(2)	39(3)
C18	151(4)	146(4)	79(3)	-14(3)	40(3)	-16(3)
C28	98(3)	137(4)	103(3)	-8(3)	38(2)	19(3)
C17	157(4)	106(3)	98(3)	37(3)	6(3)	-13(3)
C33	78(2)	173(5)	101(3)	35(3)	2(2)	22(3)
C21	55(2)	127(4)	211(5)	42(4)	-3(3)	8(2)
C20	86(3)	107(3)	214(5)	65(4)	8(3)	5(2)
C32	140(5)	97(4)	259(7)	-64(4)	-40(5)	-11(3)
C31	138(4)	94(3)	218(6)	56(4)	-19(4)	-24(3)
C35	122(4)	263(8)	148(5)	106(5)	2(4)	9(5)
C0	52(3)	45(4)	44(5)	0(3)	0(4)	5(3)
N0	58(4)	45(2)	44(4)	-5(3)	11(3)	-5(3)
N3	56(3)	41(3)	52(3)	-9(3)	9(3)	1(3)
C36	56(4)	47(4)	49(3)	-1(3)	10(3)	1(3)
C37	71(4)	54(4)	53(3)	-10(3)	10(3)	5(3)
C38	70(4)	54(3)	54(4)	-5(3)	3(3)	4(3)
C39	72(5)	58(4)	55(4)	-11(3)	1(3)	10(3)
C40	75(4)	64(4)	57(3)	-13(3)	0(3)	10(3)

Table 12 Bond Lengths for **4da.**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Si1	C15	1.861(3)	C14	C15	1.319(4)
Si1	C16	1.880(3)	C10	C11	1.370(4)
Si1	C22	1.882(3)	C1	C2	1.381(11)
Si1	C19	1.888(4)	C12	C11	1.364(4)
Si2	C26	1.860(3)	C4	C3	1.345(11)
Si2	C27	1.881(3)	C27	C29	1.530(5)
Si2	C30	1.876(4)	C27	C28	1.542(4)
Si2	C33	1.900(4)	C16	C18	1.527(5)
F1	C11	1.361(3)	C16	C17	1.546(6)
C7	N2	1.313(16)	C22	C24	1.525(5)

C7	C6	1.403(19)	C22	C23	1.525(4)
N2	C5	1.422(10)	C3	C2	1.402(9)
N2	C4	1.398(17)	C19	C21	1.511(5)
N1	C5	1.341(16)	C19	C20	1.487(5)
N1	C6	1.355(16)	C30	C32	1.544(6)
C5	C1	1.40(2)	C30	C31	1.542(6)
C6	C8	1.479(3)	C34	C33	1.517(5)
C6	C0	1.406(18)	C33	C35	1.396(6)
C6	N3	1.348(15)	C0	N0	1.326(15)
C9	C8	1.407(3)	N0	C36	1.417(10)
C9	C25	1.485(3)	N0	C38	1.400(17)
C9	C10	1.393(4)	N3	C36	1.341(17)
C8	C13	1.412(3)	C36	C37	1.40(2)
C25	C26	1.324(4)	C37	C40	1.385(10)
C13	C14	1.476(3)	C38	C39	1.332(10)
C13	C12	1.401(4)	C39	C40	1.403(9)

Table 13 Bond Angles for **4da.**

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C15	Si1	C16	108.86(15)	C2	C1	C5	120.2(9)
C15	Si1	C22	109.62(13)	C25	C26	Si2	128.1(2)
C15	Si1	C19	104.70(15)	C11	C12	C13	119.5(2)
C16	Si1	C22	108.11(15)	C3	C4	N2	117.8(9)
C16	Si1	C19	108.86(17)	F1	C11	C10	118.3(3)
C22	Si1	C19	116.48(19)	F1	C11	C12	118.8(3)
C26	Si2	C27	109.48(14)	C12	C11	C10	122.9(3)
C26	Si2	C30	107.10(17)	C29	C27	Si2	113.6(3)
C26	Si2	C33	108.59(16)	C29	C27	C28	110.6(3)
C27	Si2	C33	110.9(2)	C28	C27	Si2	113.7(3)
C30	Si2	C27	108.92(18)	C18	C16	Si1	113.5(3)
C30	Si2	C33	111.7(2)	C18	C16	C17	109.7(3)
N2	C7	C6	108.8(13)	C17	C16	Si1	111.5(2)
C7	N2	C5	104.4(19)	C24	C22	Si1	113.9(2)
C7	N2	C4	132.2(12)	C23	C22	Si1	114.2(3)
C4	N2	C5	123.3(14)	C23	C22	C24	111.2(3)
C5	N1	C6	103.8(12)	C4	C3	C2	121.5(10)
N1	C5	N2	113(2)	C1	C2	C3	120.9(10)
N1	C5	C1	131.1(13)	C21	C19	Si1	114.9(3)
C1	C5	N2	116.3(15)	C20	C19	Si1	116.4(3)
C7	C6	C8	129.4(7)	C20	C19	C21	111.3(4)
N1	C6	C7	110.3(7)	C32	C30	Si2	111.2(3)
N1	C6	C8	120.2(6)	C31	C30	Si2	111.3(3)
C0	C6	C8	130.1(7)	C31	C30	C32	111.5(4)
N3	C6	C8	120.2(6)	C34	C33	Si2	114.2(3)
N3	C6	C0	109.7(6)	C35	C33	Si2	119.2(4)
C8	C9	C25	122.3(2)	C35	C33	C34	116.7(4)

C10	C9	C8	119.9(2)	N0	C0	C6	109.0(12)
C10	C9	C25	117.7(2)	C0	N0	C36	104.2(18)
C9	C8	C6	120.6(2)	C0	N0	C38	133.3(12)
C9	C8	C13	119.5(2)	C38	N0	C36	122.5(14)
C13	C8	C6	119.9(2)	C36	N3	C6	104.8(12)
C26	C25	C9	125.2(2)	N3	C36	N0	112(2)
C8	C13	C14	122.3(2)	N3	C36	C37	130.7(13)
C12	C13	C8	119.1(2)	C37	C36	N0	117.0(15)
C12	C13	C14	118.6(2)	C40	C37	C36	119.6(9)
C15	C14	C13	126.4(3)	C39	C38	N0	118.7(9)
C14	C15	Si1	128.7(2)	C38	C39	C40	121.2(9)
C11	C10	C9	119.0(3)	C37	C40	C39	121.1(9)

Table 14 Torsion Angles for **4da**.

A	**B**	**C**	**D**	**Angle/˚**	**A**	**B**	**C**	**D**	**Angle/˚**
C7	N2	C5	N1	-2(2)	C10	C9	C25	C26	-30.5(4)
C7	N2	C5	C1	179.1(18)	C26	Si2	C27	C29	64.1(3)
C7	N2	C4	C3	-179(2)	C26	Si2	C27	C28	-168.3(3)
C7	C6	C8	C9	128.4(15)	C26	Si2	C30	C32	-58.6(3)
C7	C6	C8	C13	-51.5(15)	C26	Si2	C30	C31	66.4(4)
N2	C7	C6	N1	0(2)	C12	C13	C14	C15	-20.6(5)
N2	C7	C6	C8	-178.8(10)	C4	N2	C5	N1	179.3(16)
N2	C5	C1	C2	0(2)	C4	N2	C5	C1	0(3)
N2	C4	C3	C2	1.0(17)	C4	C3	C2	C1	-0.6(16)
N1	C5	C1	C2	-179(2)	C27	Si2	C26	C25	20.4(4)
N1	C6	C8	C9	-50.5(12)	C27	Si2	C30	C32	-176.9(3)
N1	C6	C8	C13	129.6(12)	C27	Si2	C30	C31	-51.9(4)
C5	N2	C4	C3	-1(2)	C16	Si1	C15	C14	-89.7(3)
C5	N1	C6	C7	-1(2)	C16	Si1	C22	C24	-49.2(3)
C5	N1	C6	C8	177.9(11)	C16	Si1	C22	C23	-178.5(3)
C5	C1	C2	C3	-0.1(17)	C16	Si1	C19	C21	61.1(4)
C6	C7	N2	C5	1(2)	C16	Si1	C19	C20	-166.3(4)
C6	C7	N2	C4	179.7(17)	C22	Si1	C15	C14	28.4(3)
C6	N1	C5	N2	2(2)	C22	Si1	C16	C18	-178.6(3)
C6	N1	C5	C1	-179(2)	C22	Si1	C16	C17	-54.1(3)
C6	C8	C13	C14	-3.5(4)	C22	Si1	C19	C21	-61.4(4)
C6	C8	C13	C12	178.0(3)	C22	Si1	C19	C20	71.2(4)
C6	C0	N0	C36	0(2)	C19	Si1	C15	C14	154.0(3)
C6	C0	N0	C38	-179.9(16)	C19	Si1	C16	C18	54.0(3)
C6	N3	C36	N0	-1(2)	C19	Si1	C16	C17	178.5(3)
C6	N3	C36	C37	-179(2)	C19	Si1	C22	C24	73.7(3)
C9	C8	C13	C14	176.6(2)	C19	Si1	C22	C23	-55.6(3)
C9	C8	C13	C12	-2.0(4)	C30	Si2	C26	C25	-97.5(3)
C9	C25	C26	Si2	173.4(2)	C30	Si2	C27	C29	-179.1(3)
C9	C10	C11	F1	179.3(3)	C30	Si2	C27	C28	-51.5(3)
C9	C10	C11	C12	0.7(6)	C33	Si2	C26	C25	141.7(3)

C8	C6	C0	N0	179.1(9)	C33	Si2	C27	C29	-55.8(3)
C8	C6	N3	C36	-178.8(11)	C33	Si2	C27	C28	71.9(3)
C8	C9	C25	C26	150.4(3)	C33	Si2	C30	C32	60.2(4)
C8	C9	C10	C11	-1.7(4)	C33	Si2	C30	C31	-174.8(3)
C8	C13	C14	C15	160.9(3)	C0	C6	C8	C9	-49.7(15)
C8	C13	C12	C11	0.9(5)	C0	C6	C8	C13	130.3(15)
C25	C9	C8	C6	1.4(4)	C0	C6	N3	C36	1(2)
C25	C9	C8	C13	-178.6(2)	C0	N0	C36	N3	1(2)
C25	C9	C10	C11	179.2(3)	C0	N0	C36	C37	179.4(18)
C13	C14	C15	Si1	175.8(2)	C0	N0	C38	C39	-180.0(19)
C13	C12	C11	F1	-178.9(3)	N0	C36	C37	C40	0(2)
C13	C12	C11	C10	-0.3(6)	N0	C38	C39	C40	0.7(16)
C14	C13	C12	C11	-177.7(3)	N3	C6	C8	C9	129.6(11)
C15	Si1	C16	C18	-59.6(3)	N3	C6	C8	C13	-50.3(12)
C15	Si1	C16	C17	64.9(3)	N3	C6	C0	N0	0(2)
C15	Si1	C22	C24	-167.7(3)	N3	C36	C37	C40	179(2)
C15	Si1	C22	C23	63.0(3)	C36	N0	C38	C39	0(2)
C15	Si1	C19	C21	177.3(3)	C36	C37	C40	C39	0.6(17)
C15	Si1	C19	C20	-50.1(4)	C38	N0	C36	N3	-179.6(16)
C10	C9	C8	C6	-177.6(2)	C38	N0	C36	C37	-1(3)
C10	C9	C8	C13	2.3(4)	C38	C39	C40	C37	-1.2(15)

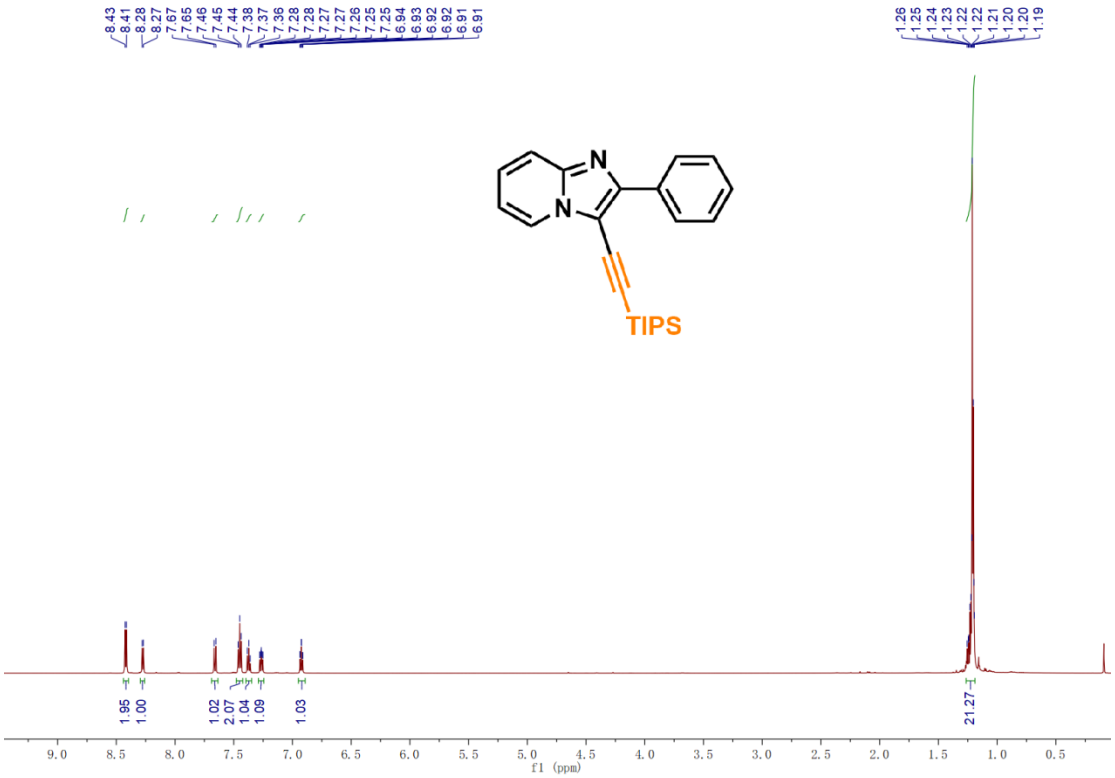
Table 15 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4da**.

Atom	***x***	***y***	***z***	**U(eq)**
H7	4900.54	5436.2	4539.18	59
H25	2725.62	5340.96	3252.27	64
H14	5548.28	5862.6	2948.25	66
H15	6204.34	4258.17	2291.97	77
H10	3028.28	3856.43	1342.68	80
H1	3201.14	8313.72	4128.12	69
H26	2160.84	4996.37	1428.44	83
H12	5264.07	3948.56	1368.34	88
H4A	4968.41	6679.45	6076.08	72
H27	1557.51	5719.62	4051.65	93
H16	8006.7	6246.85	2022.22	97
H22	6678.74	6670.2	3687.18	91
H3A	4477.59	8081.73	6567.09	79
H2	3593.1	8889.64	5613.69	79
H19	7755.13	3965.88	2492.57	112
H30	171.6	4391.56	2819.27	118
H24A	8186.97	6402.6	4304.2	166
H24B	7682.15	7279.93	4574.38	166
H24C	7901.72	7127.65	3496.76	166
H29A	2056.92	6991.5	3198.7	170
H29B	1685.7	7323.46	4153.15	170

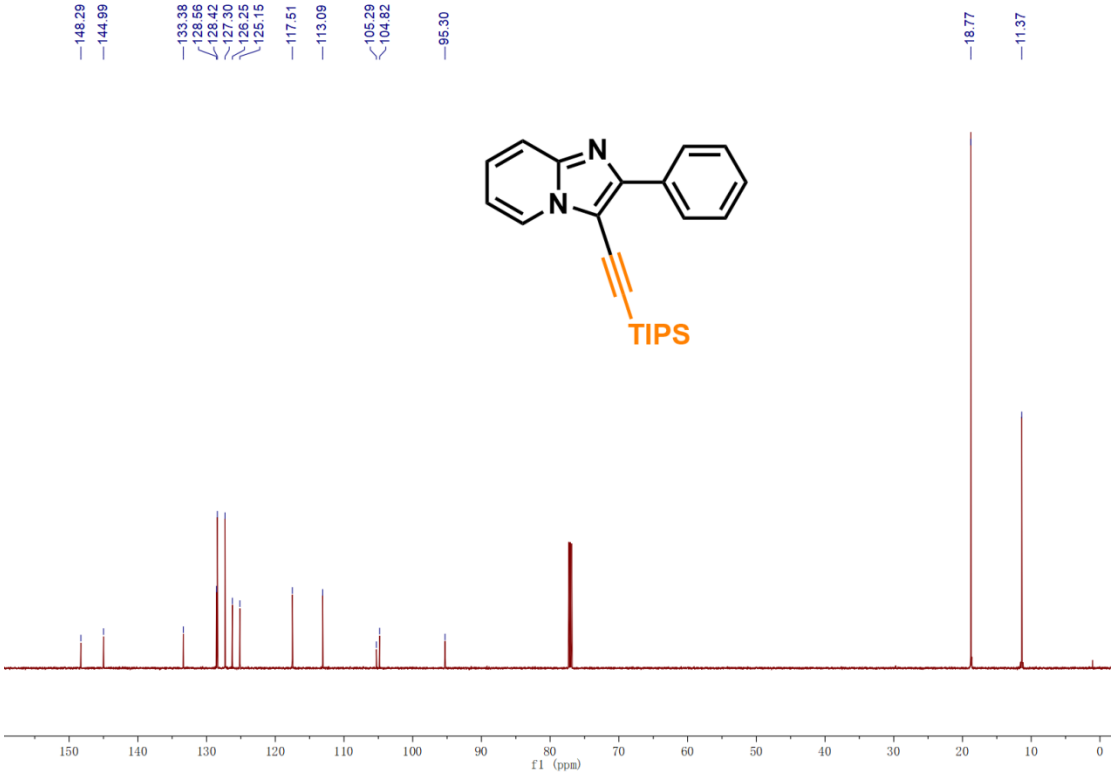
H29C	1253.93	7475.26	3144.03	170
H23A	6401.39	5354.68	4665.06	174
H23B	6660.92	6278.43	5239.88	174
H23C	7229.33	5425.52	5125.43	174
H34A	-401.72	6481.39	1001.02	176
H34B	-347.73	6208.07	2105.42	176
H34C	-335.41	5401.16	1313.42	176
H18A	7861.52	4843.45	1116.1	187
H18B	7799.36	5760.65	457.79	187
H18C	7064.39	5203.56	717.47	187
H28A	128.31	6545.48	3676.14	168
H28B	552.79	6488.65	4700.18	168
H28C	268.94	5546.48	4177.1	168
H17A	6509.5	6679.3	1380.02	180
H17B	7231.16	7238.58	1074.95	180
H17C	6984.01	7285.63	2151.02	180
H33	737.31	6767.56	1723.11	141
H21A	8747.07	4942.43	2890.2	197
H21B	8848.96	3921.36	3357.12	197
H21C	8611.51	4792.48	3995.49	197
H20A	7448.9	3836.16	4417.79	203
H20B	7788.4	3020.65	3786.19	203
H20C	6959.93	3387.92	3552.41	203
H32A	393.8	3972.72	1241.34	251
H32B	423.43	3043.76	1884.3	251
H32C	1178.02	3518.56	1567.71	251
H31A	1570.94	3539.48	3366.36	226
H31B	774.78	3170.55	3660.18	226
H31C	1093.39	4146.1	4074.79	226
H35A	1471.96	6459.8	673.04	267
H35B	661.41	6597.02	175.77	267
H35C	1004.36	5563.77	303.05	267
H0	3411.8	6978.87	3027.29	57
H2A	5112.86	6399.81	6004.01	71
H3	3351.72	8381.54	4443.01	71
H4	3841.93	8759.88	5919.62	74
H5	4732.29	7797.99	6694.35	79
C7	0.497(12)		H7	0.497(12)
N1	0.497(12)		C5	0.497(12)
H1	0.497(12)		C4	0.497(12)
C3	0.497(12)		H3A	0.497(12)
H2	0.497(12)		C0	0.503(12)
N0	0.503(12)		N3	0.503(12)
C37	0.503(12)		H2A	0.503(12)
H3	0.503(12)		C39	0.503(12)
C40	0.503(12)		H5	0.503(12)

5. NMR charts

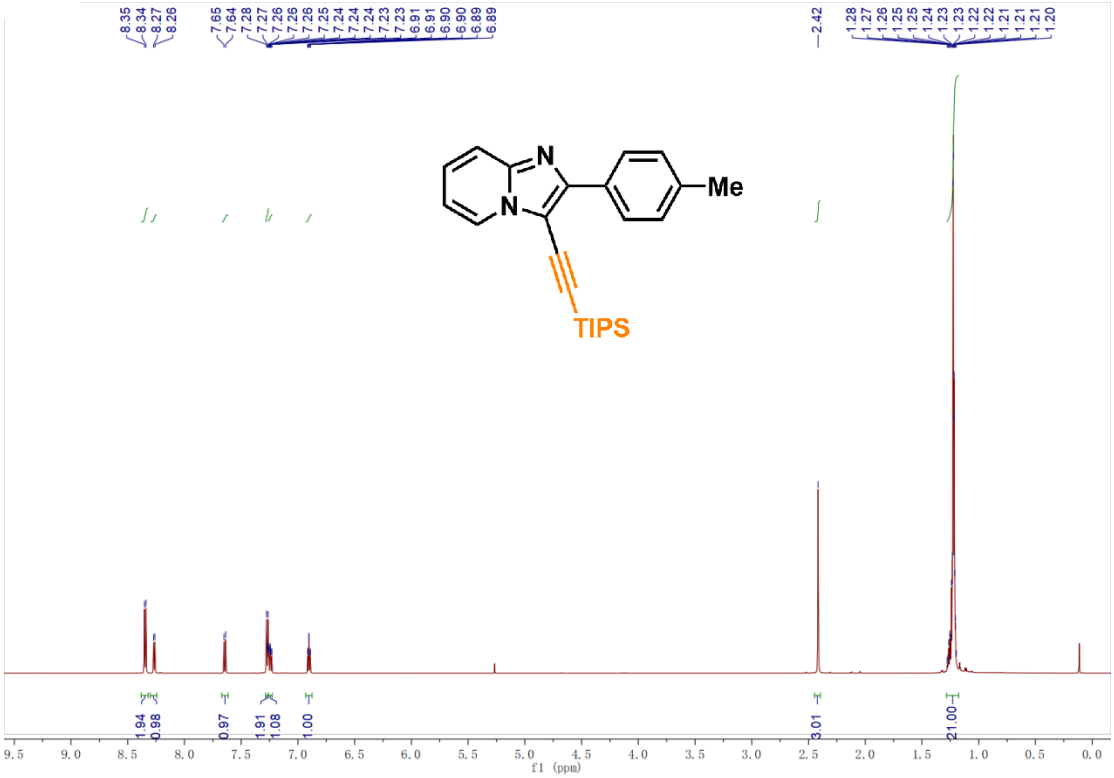
3aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



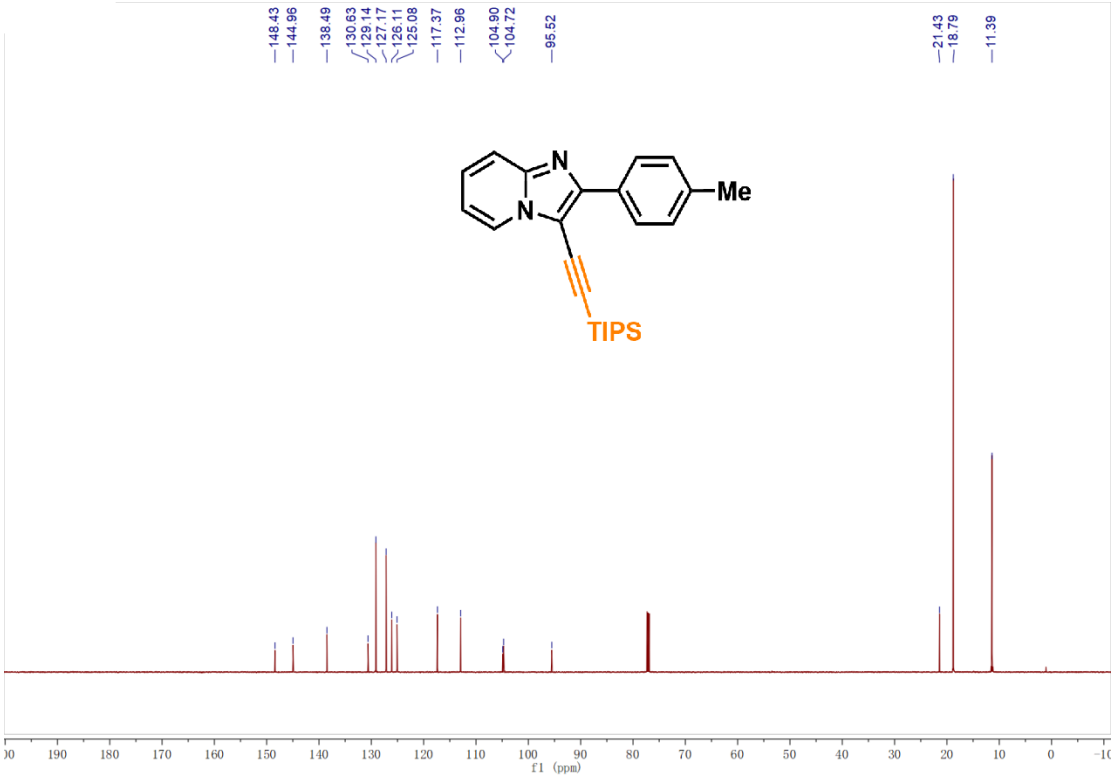
3aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



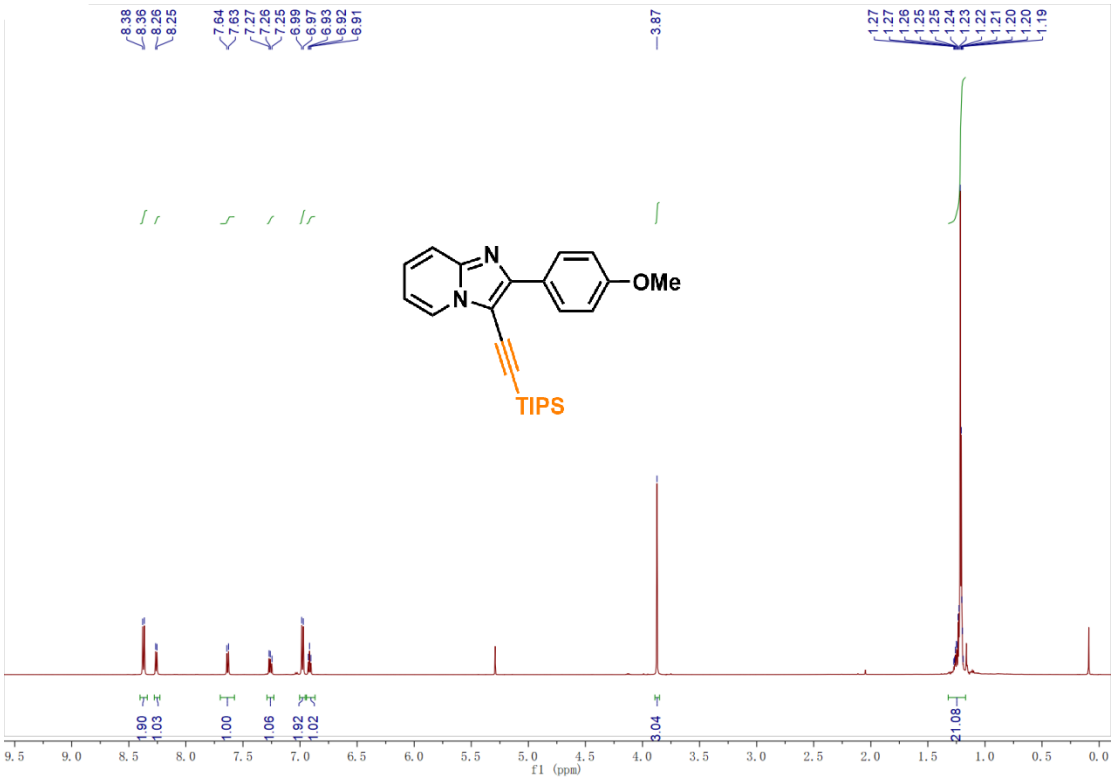
3ba | ^{1}H NMR ($CDCl_3$, 600 MHz)



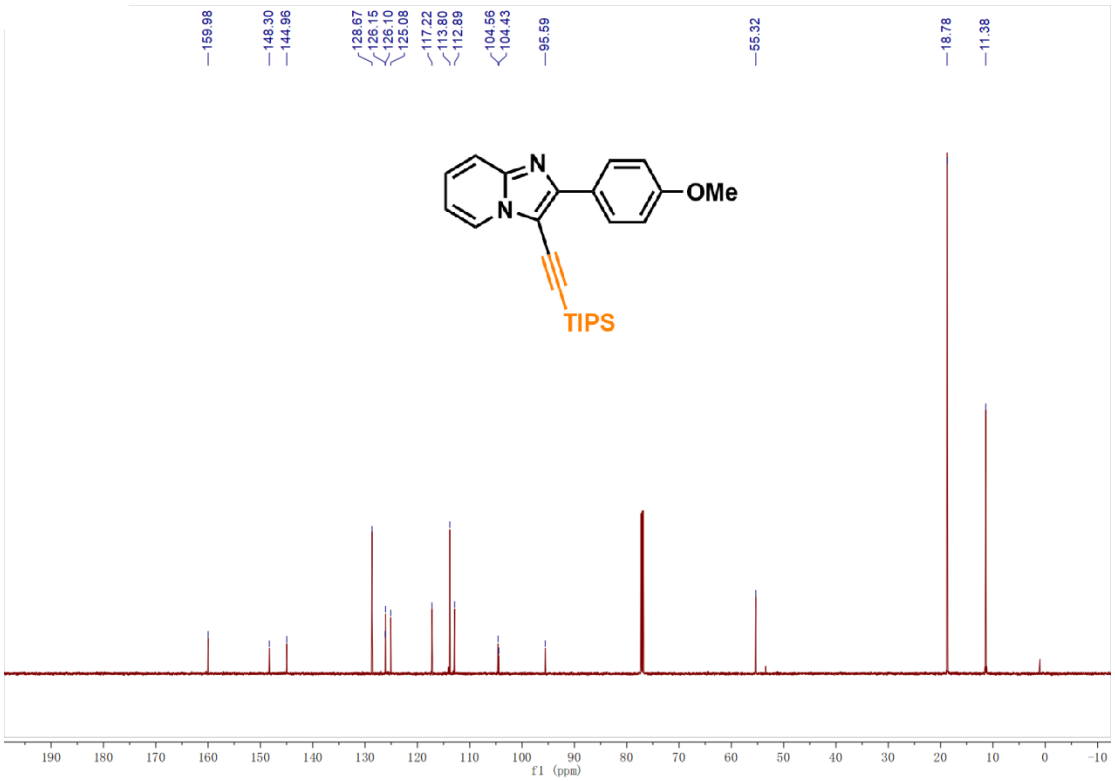
3ba | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



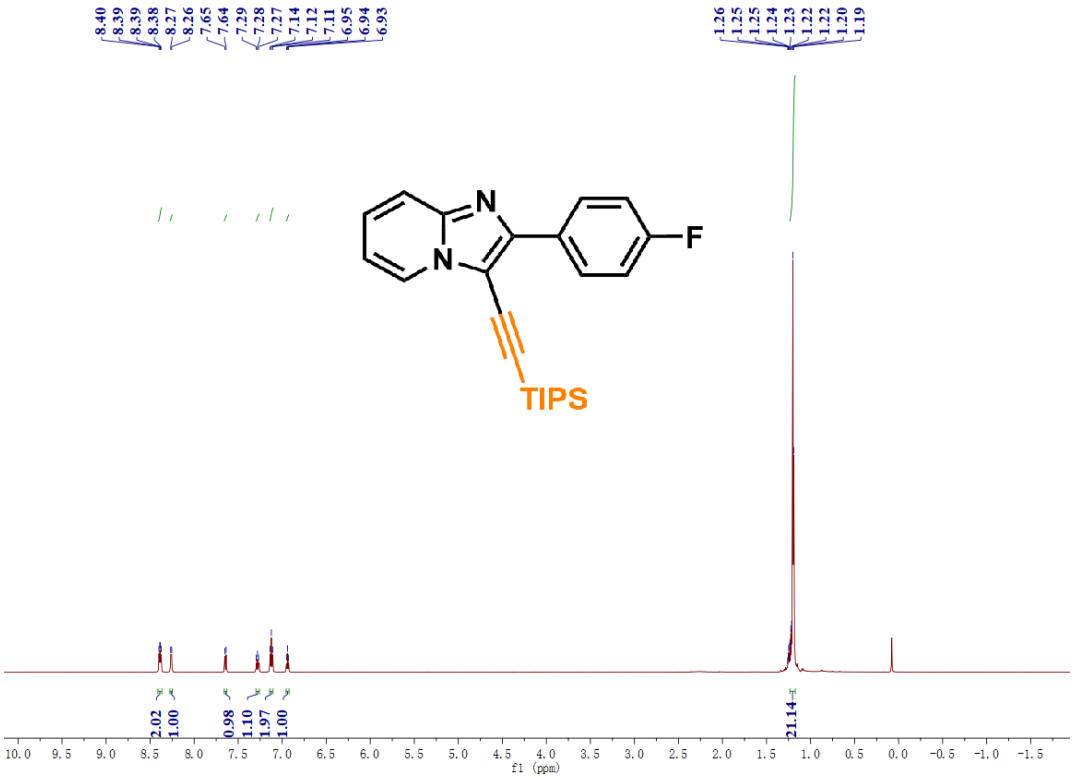
3ca | ^{1}H NMR ($CDCl_3$, 600 MHz)



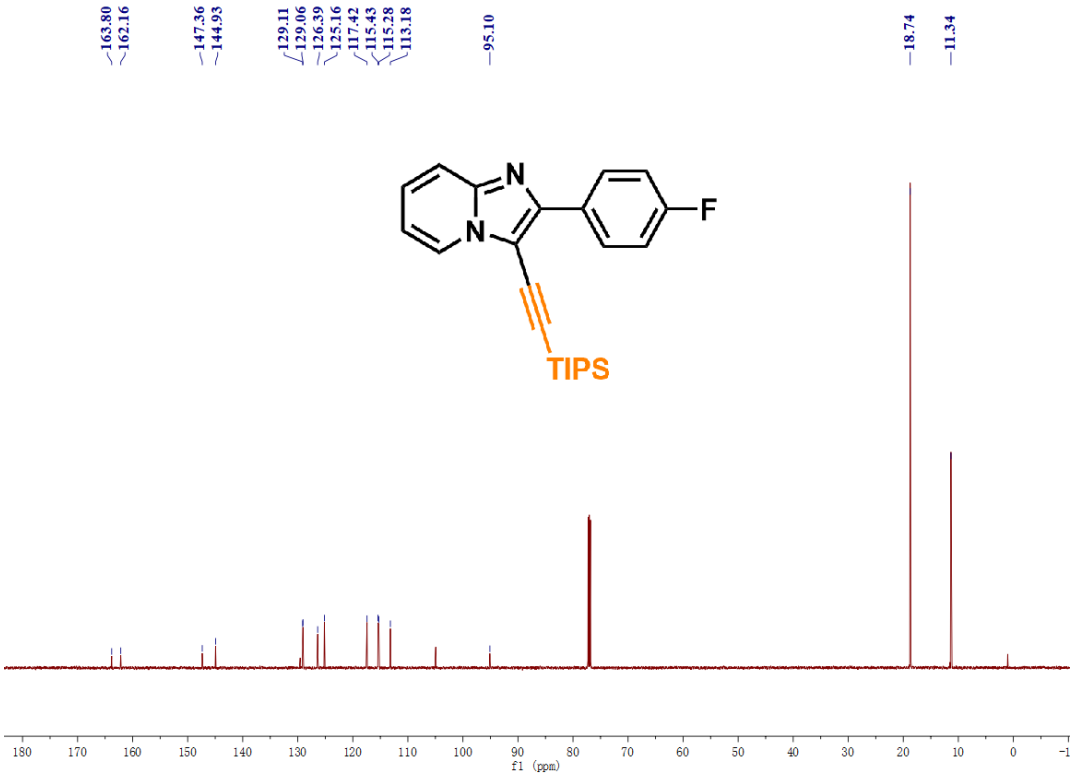
3ca | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



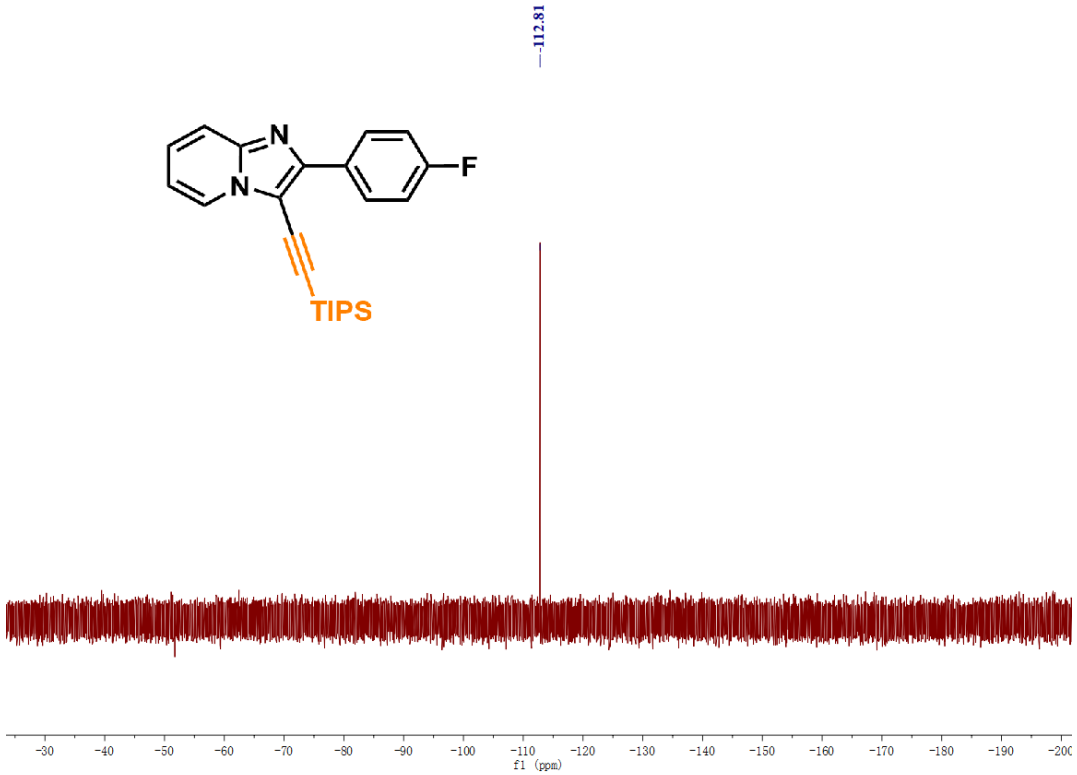
3da | ^{1}H NMR ($CDCl_3$, 600 MHz)



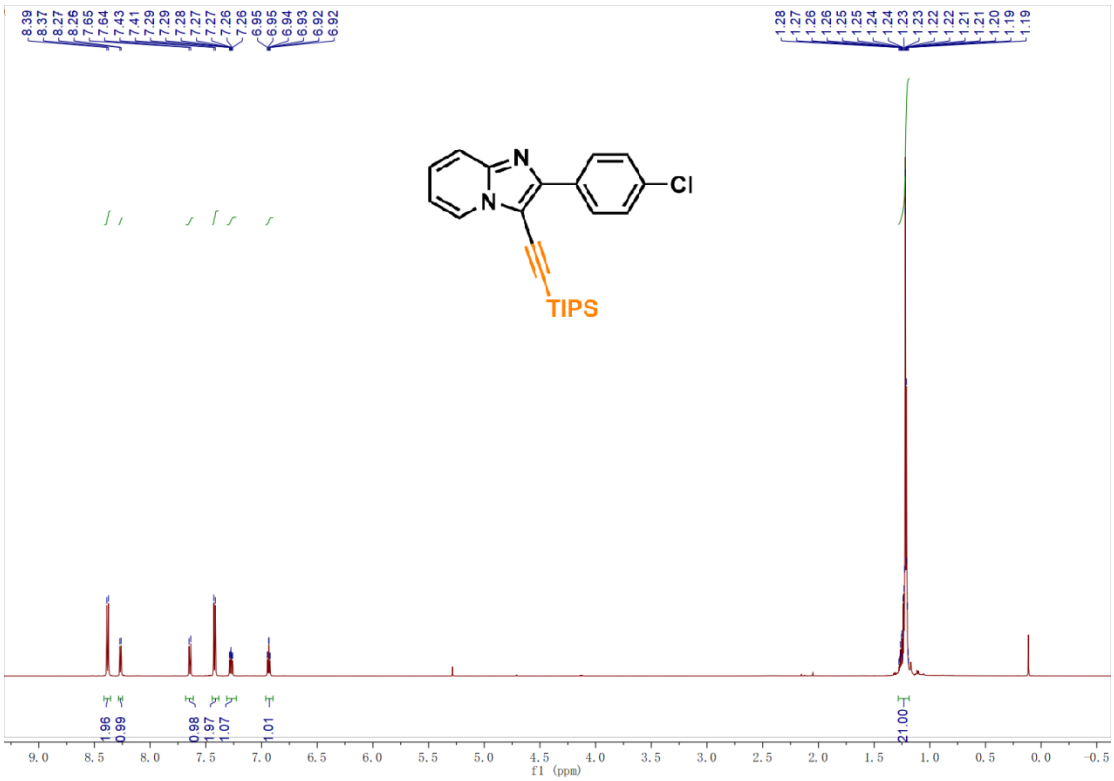
3da | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



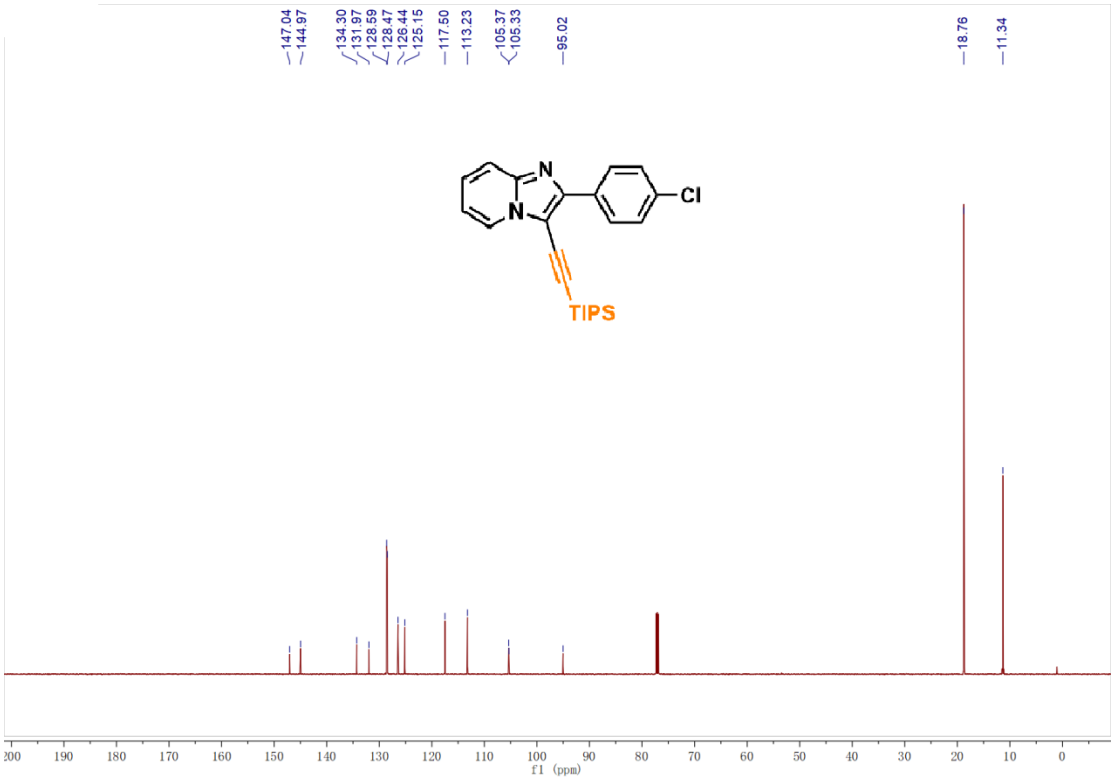
3da | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



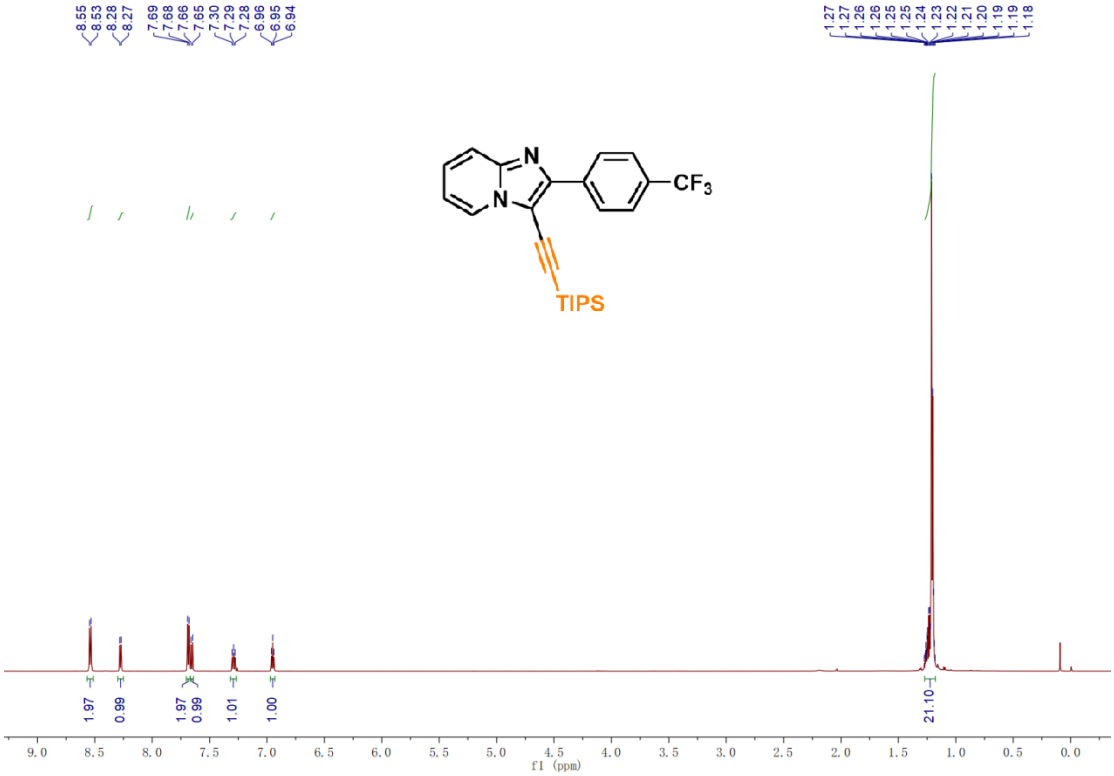
3ea | ^{1}H NMR ($CDCl_3$, 600 MHz)



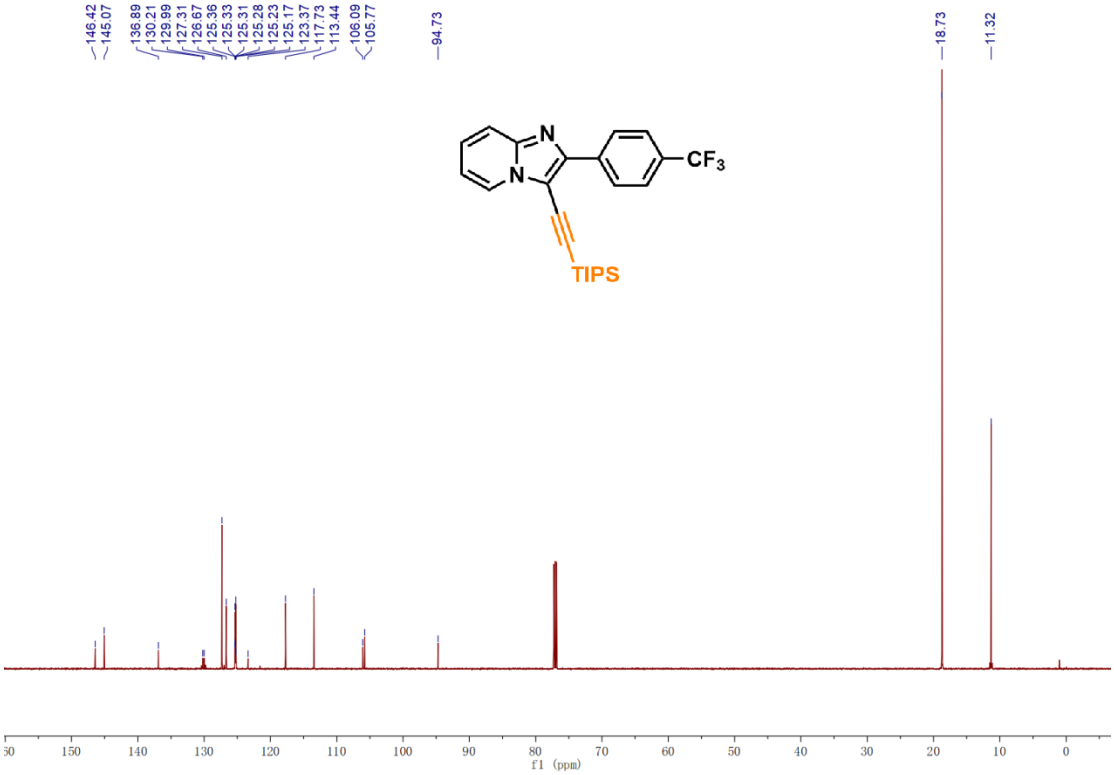
3ea | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



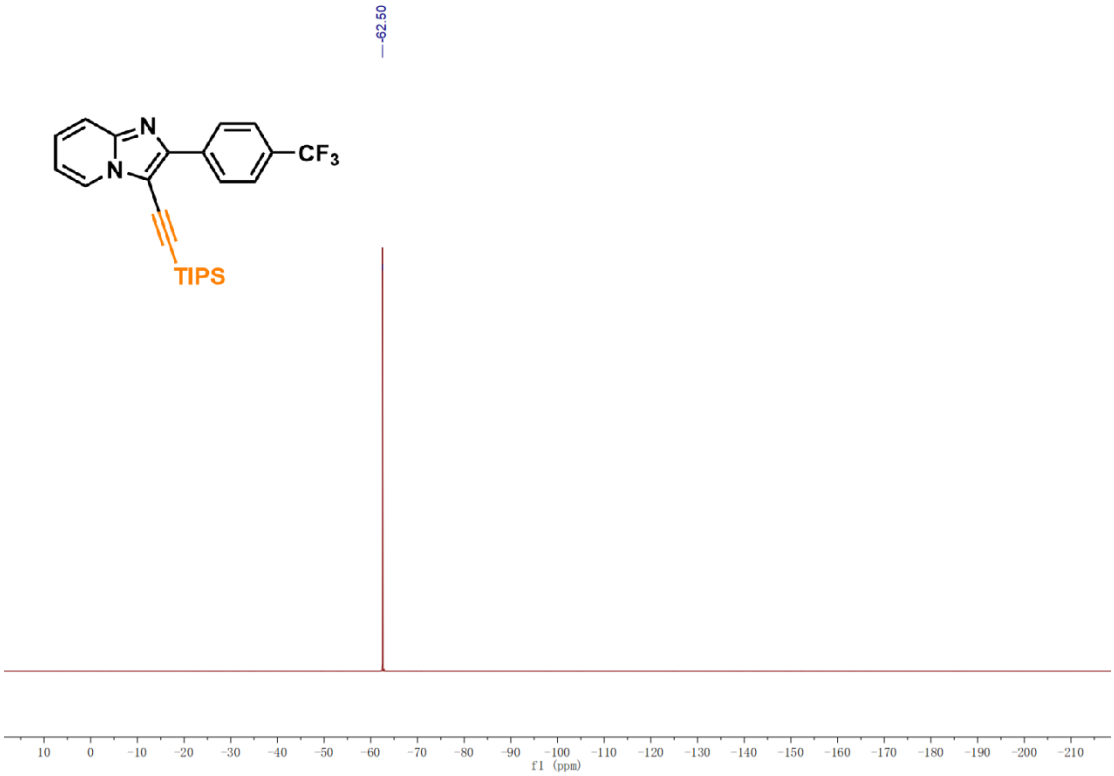
3fa | ^{1}H NMR ($CDCl_3$, 600 MHz)



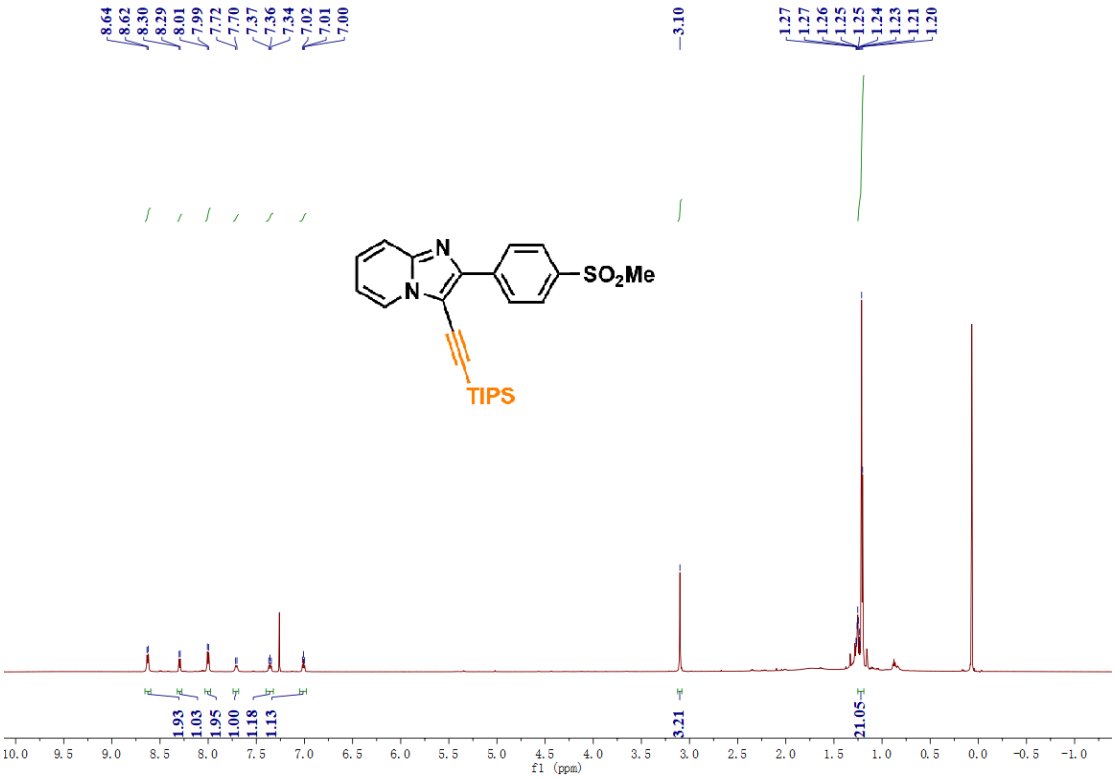
3fa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



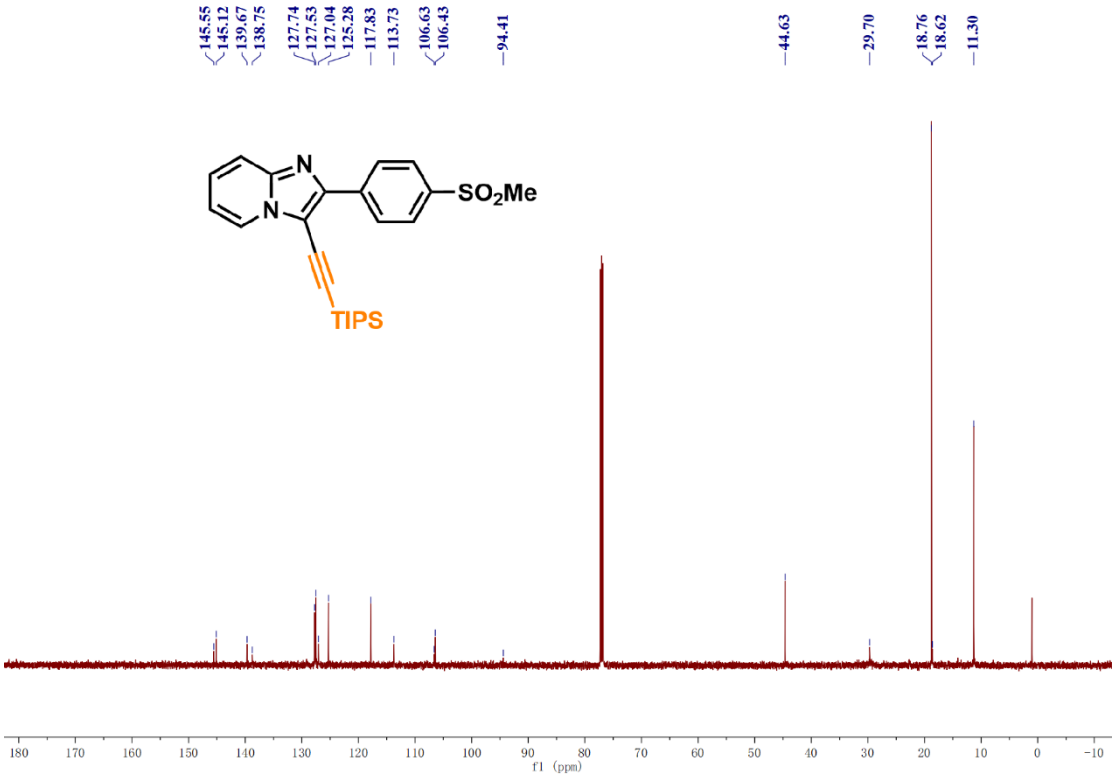
3fa | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



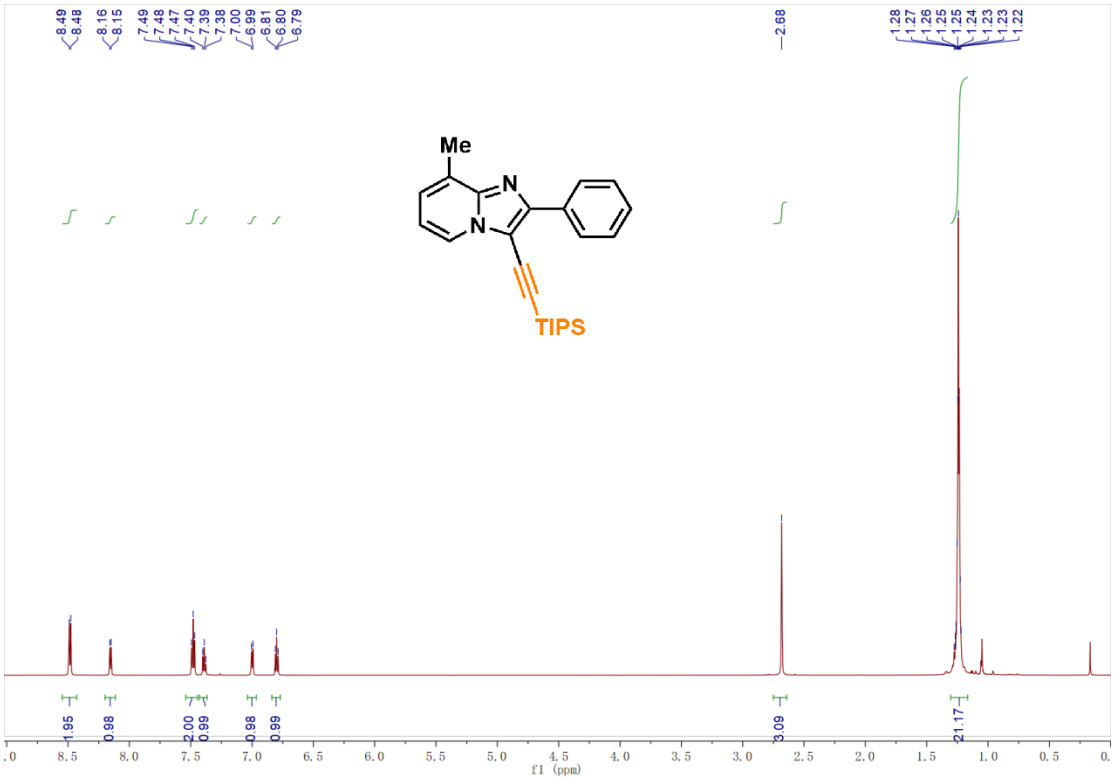
3ga | ^{1}H NMR ($CDCl_3$, 600 MHz)



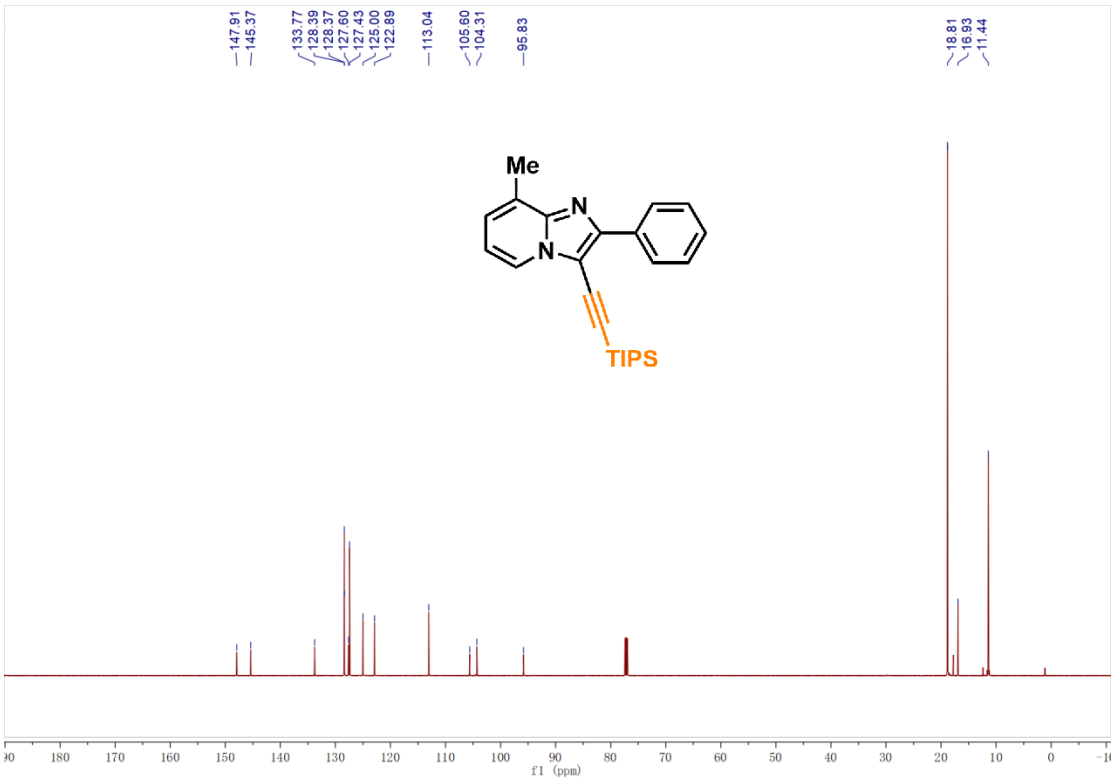
3ga | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



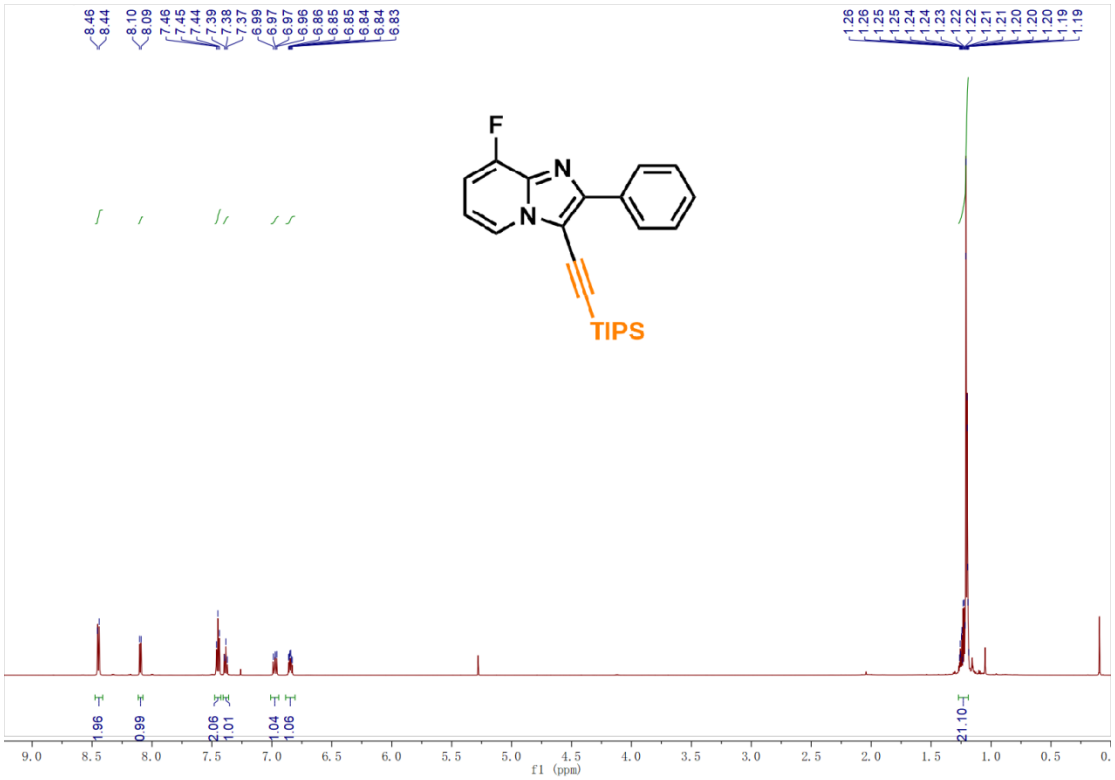
3ha | ^{1}H NMR ($CDCl_3$, 600 MHz)



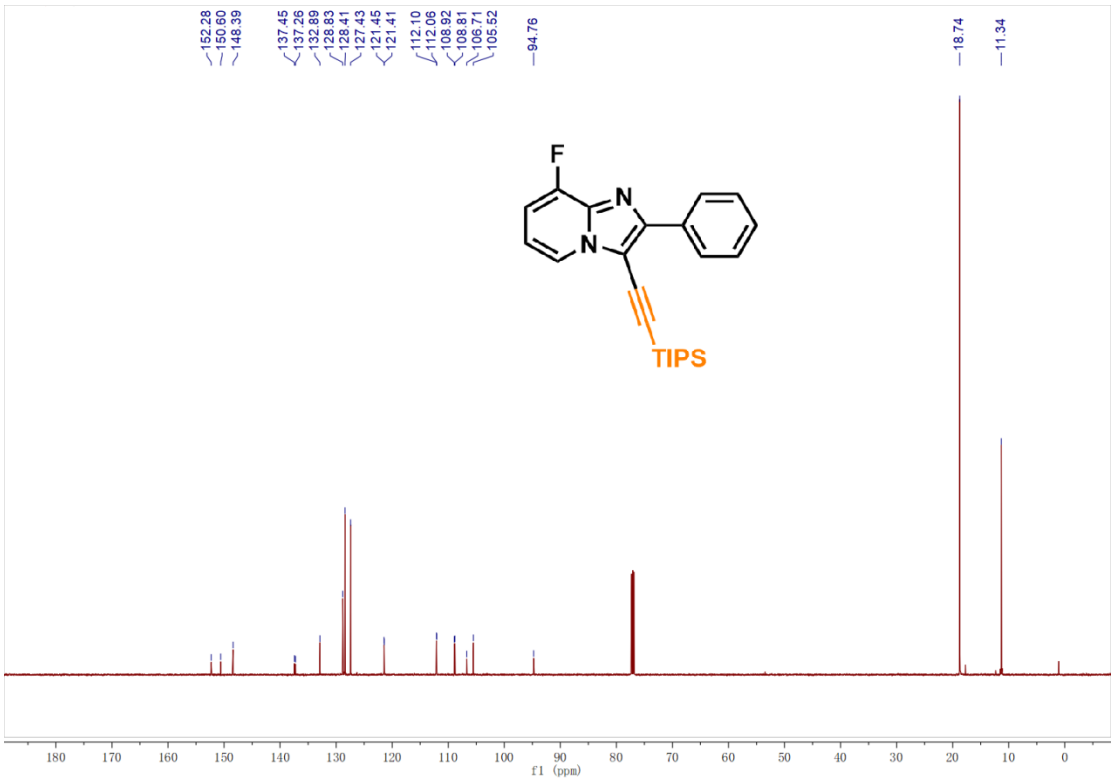
3ha | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



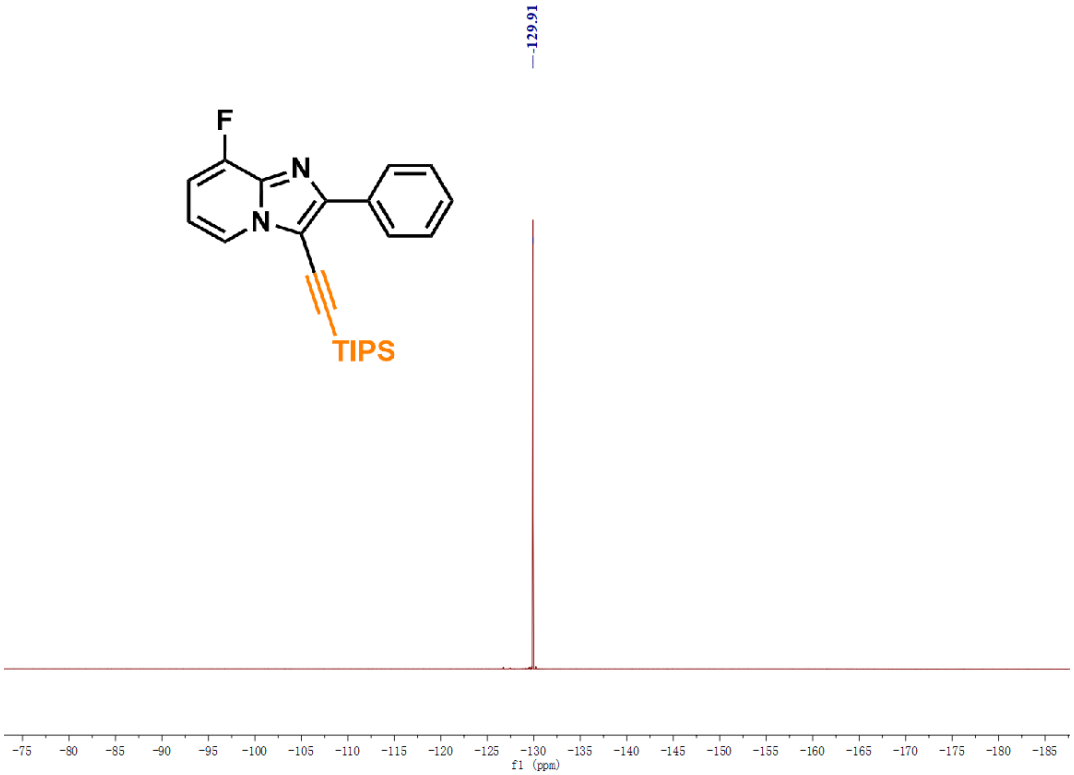
3ia | ^{1}H NMR ($CDCl_3$, 600 MHz)



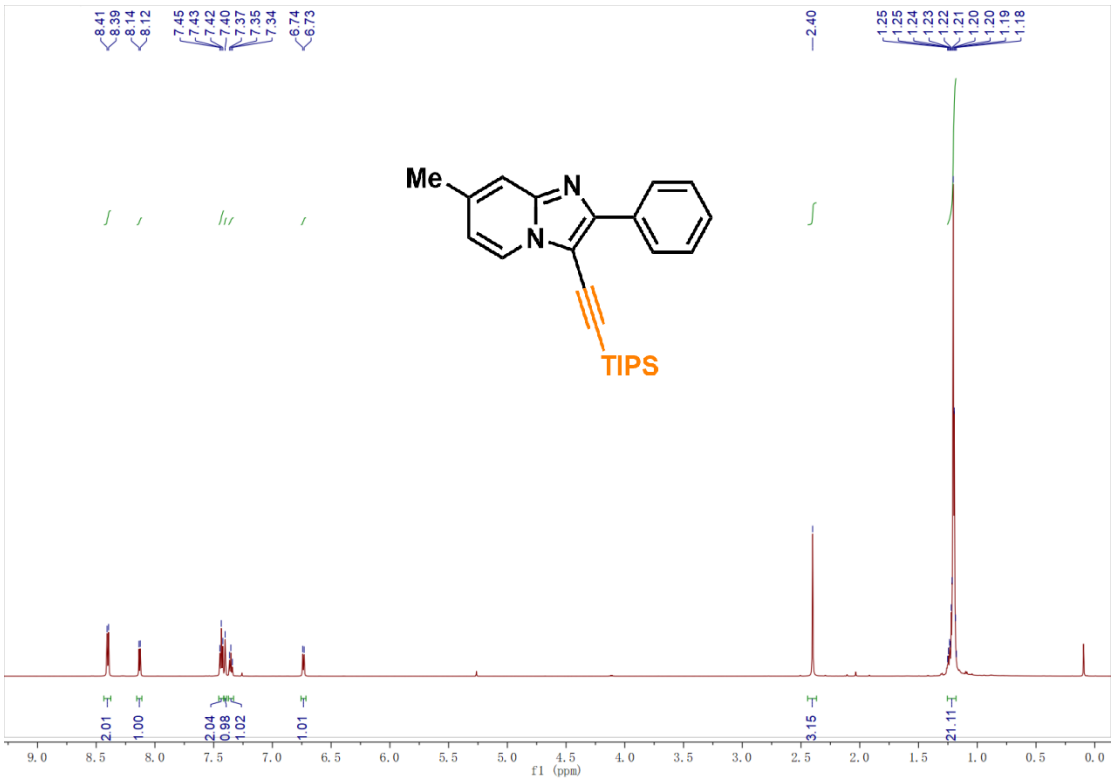
3ia | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



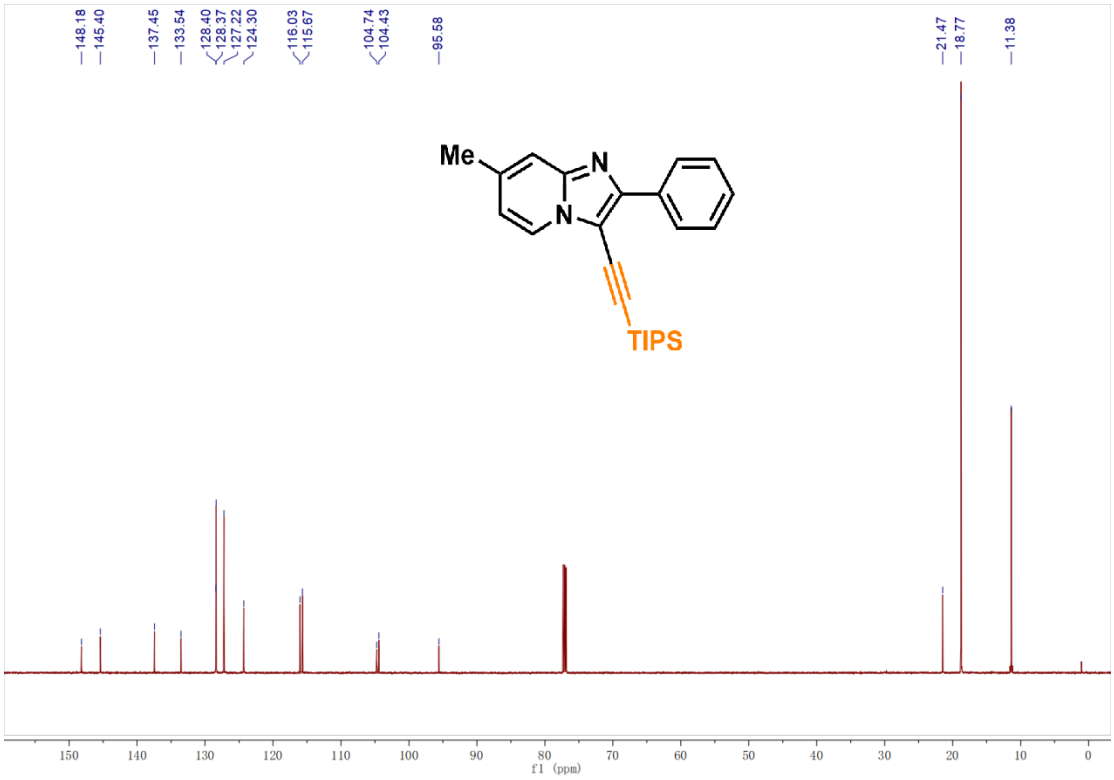
3ia | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



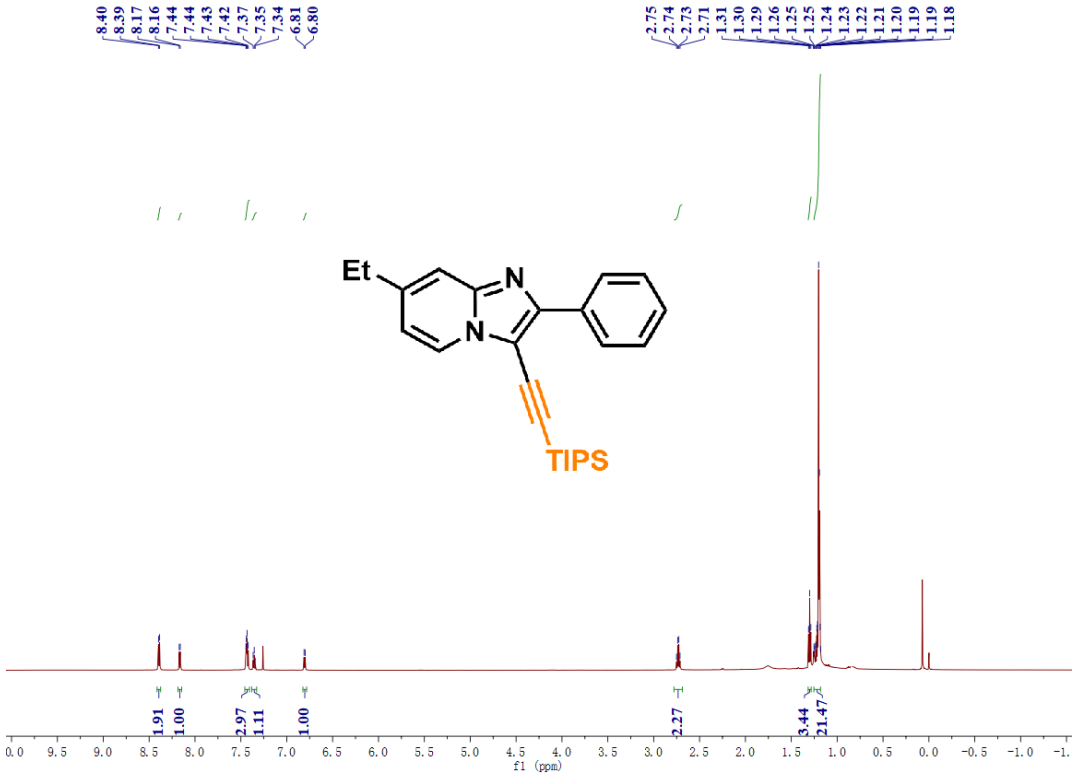
3ja | ^{1}H NMR ($CDCl_3$, 600 MHz)



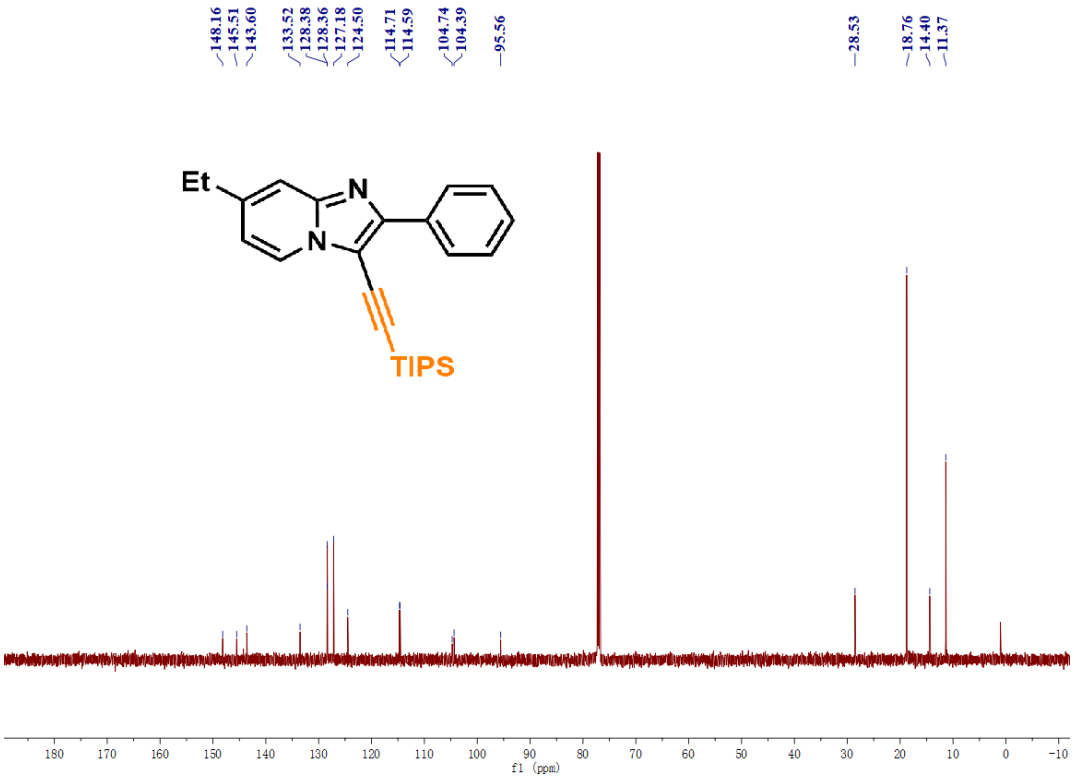
3ja | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



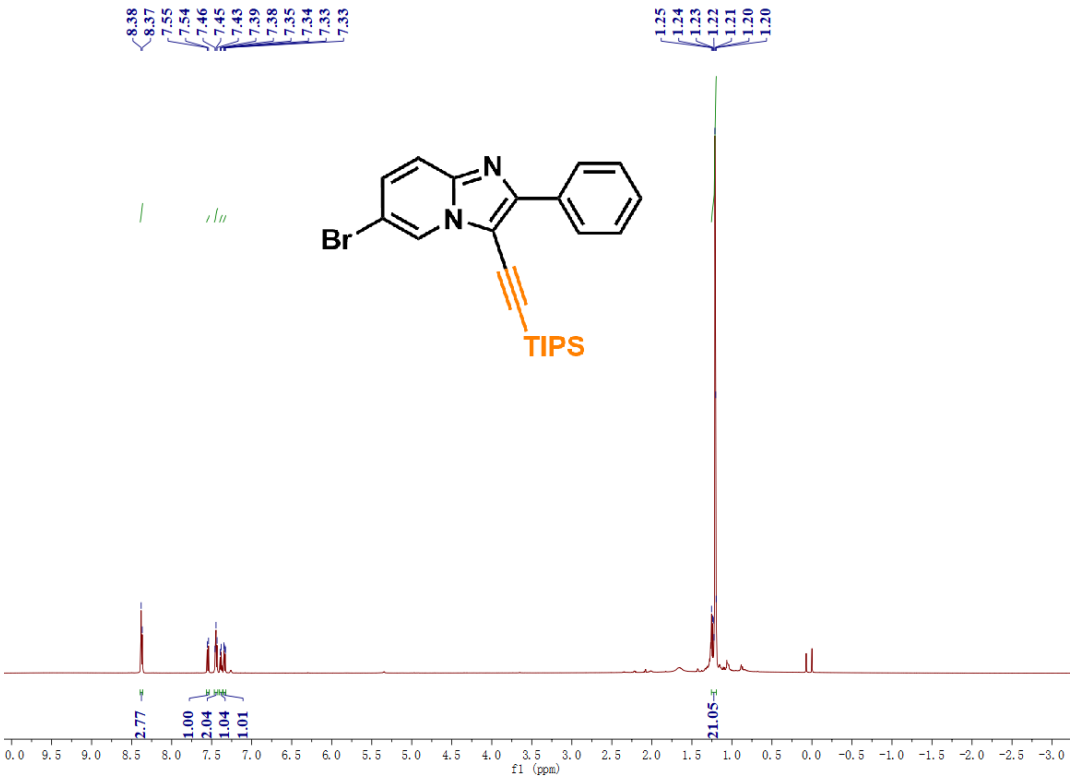
3ka | ^{1}H NMR ($CDCl_3$, 600 MHz)



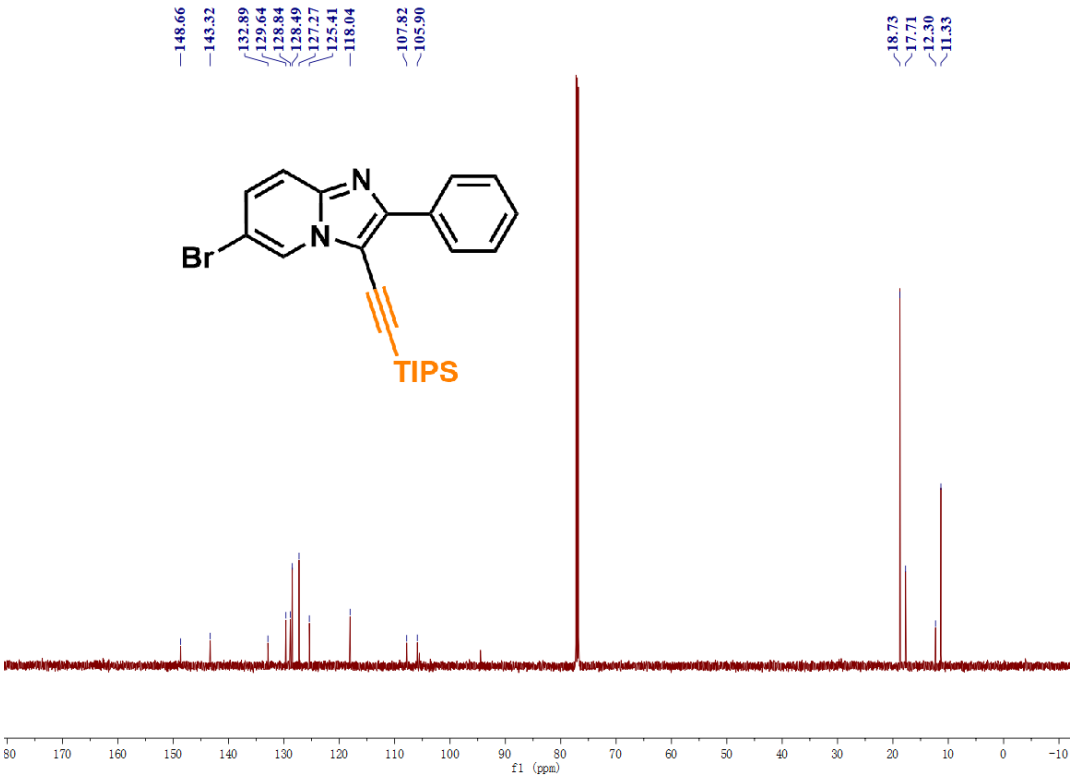
3ka | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



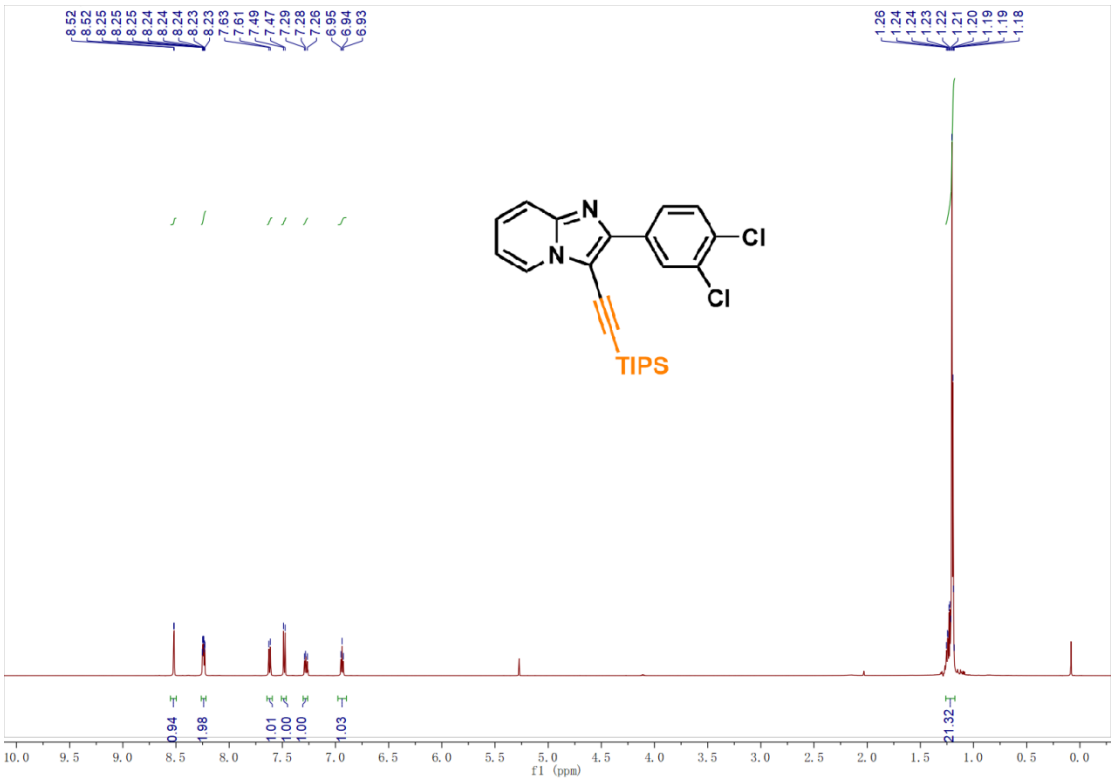
3pa | ^{1}H NMR ($CDCl_3$, 600 MHz)



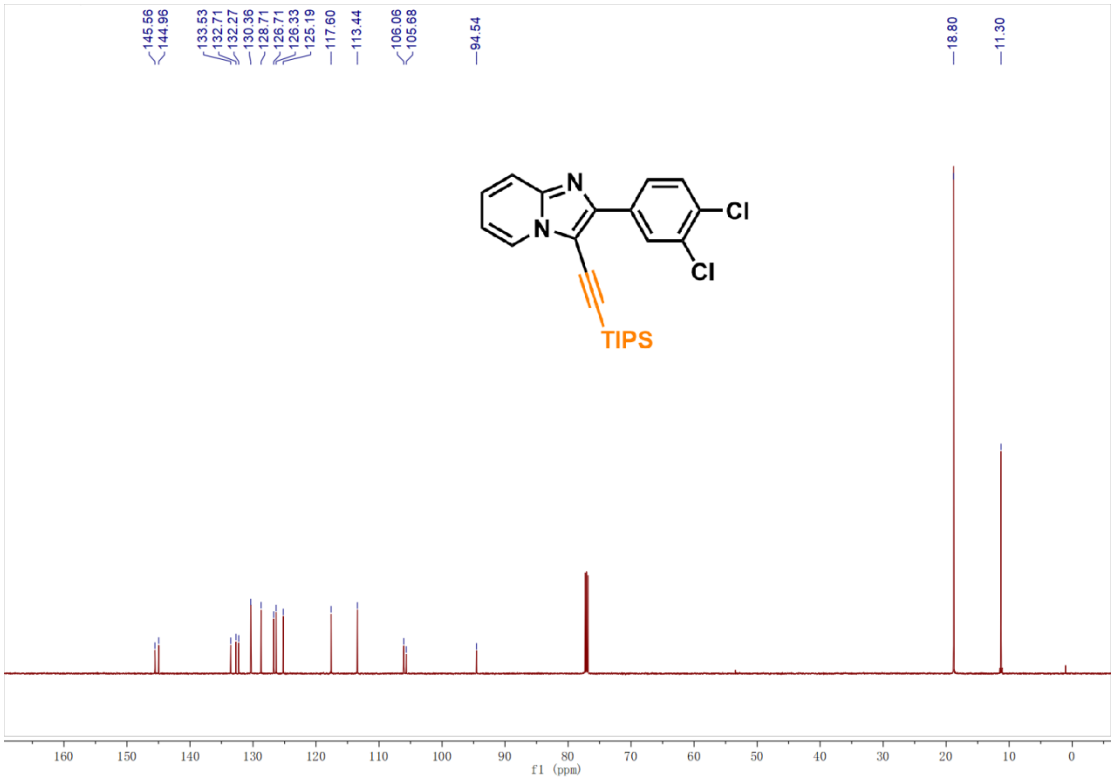
3pa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



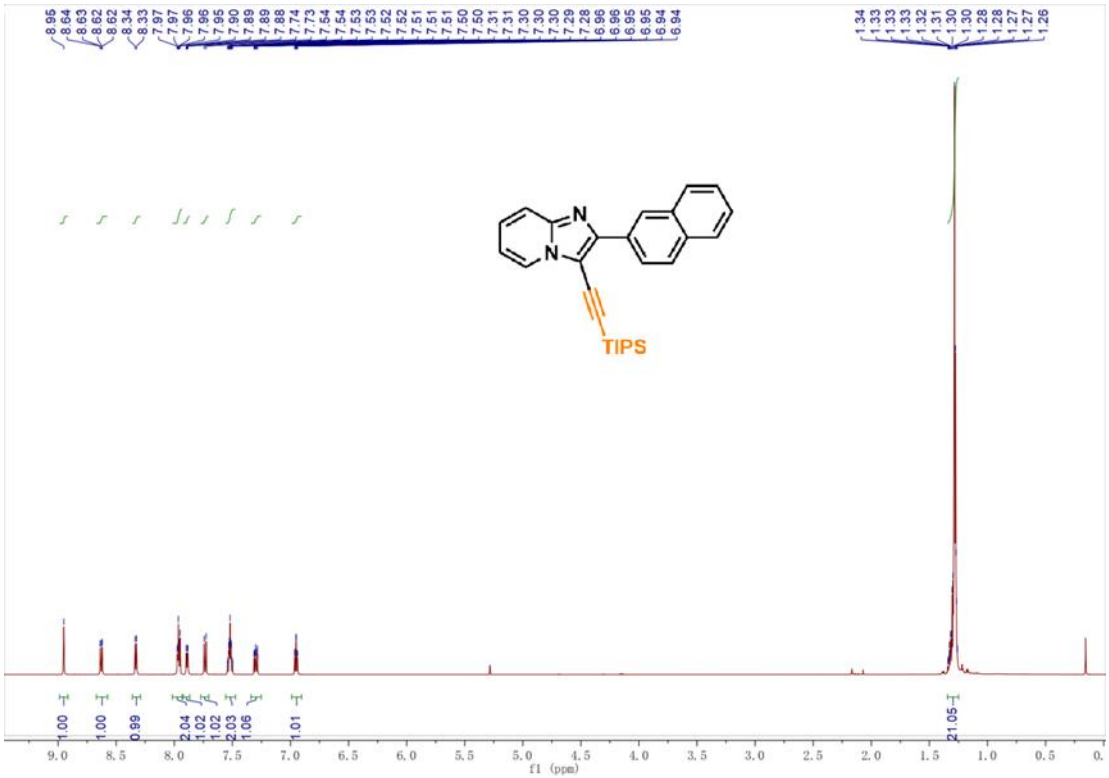
3qa | ^{1}H NMR ($CDCl_3$, 600 MHz)



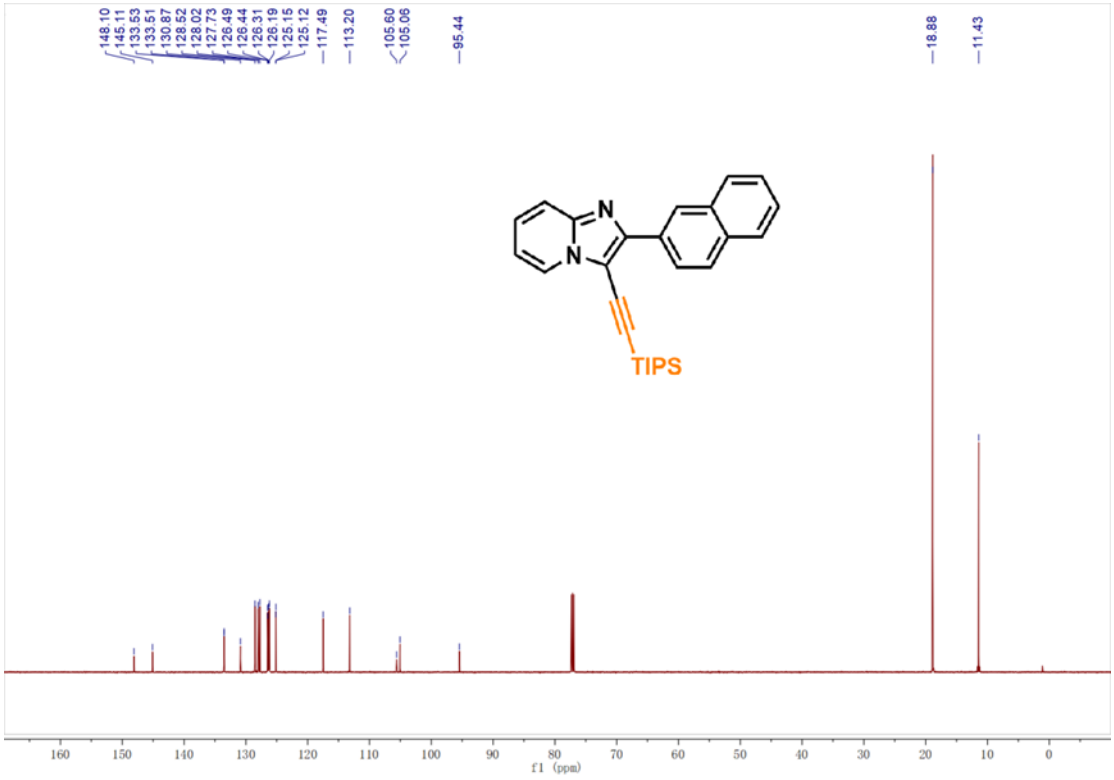
3qa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



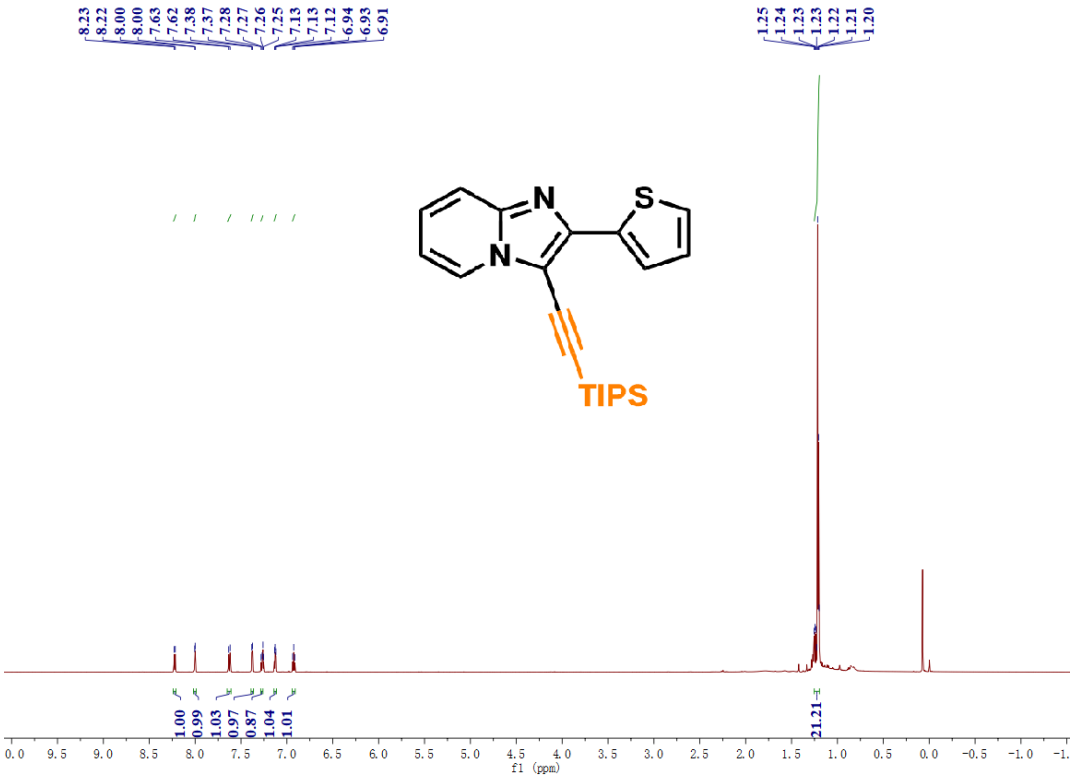
3ra | ^{1}H NMR ($CDCl_3$, 600 MHz)



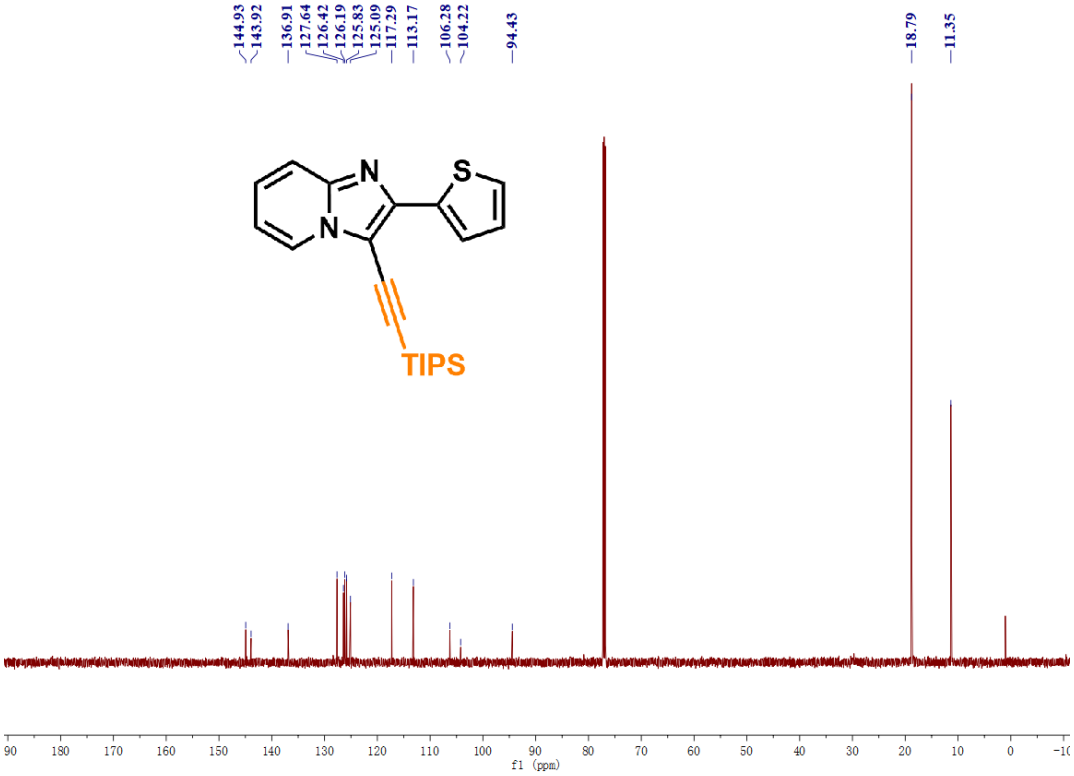
3ra | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



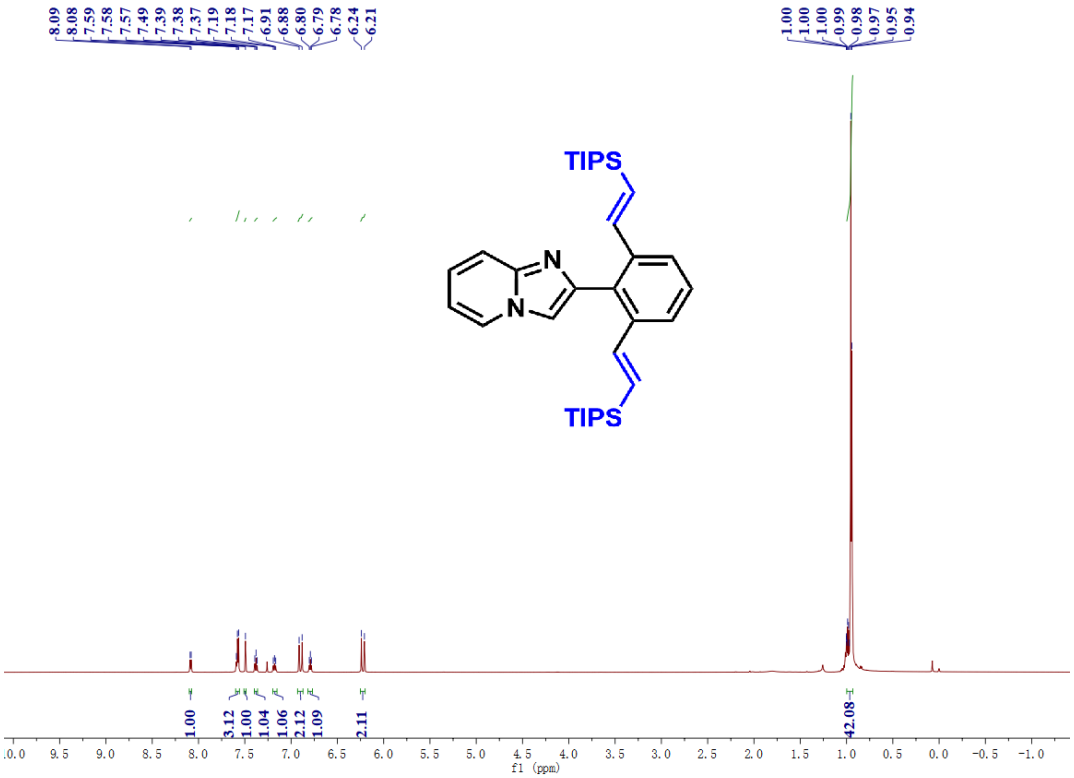
3ta | ^{1}H NMR ($CDCl_3$, 600 MHz)



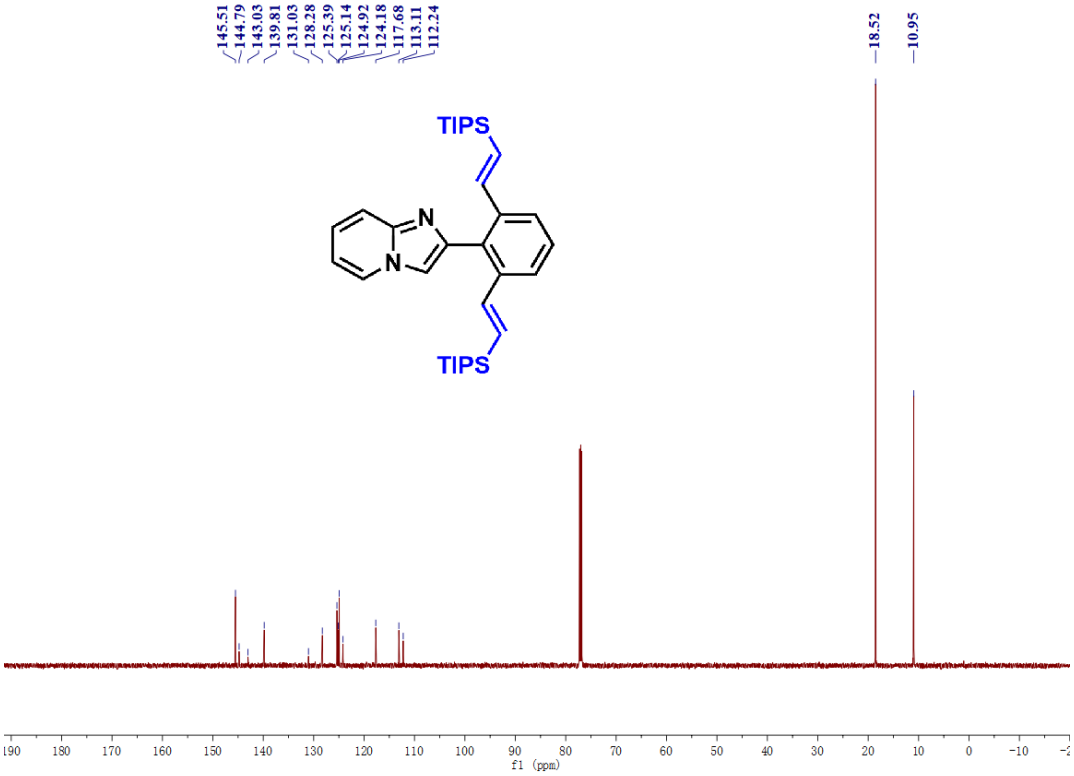
3ta | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



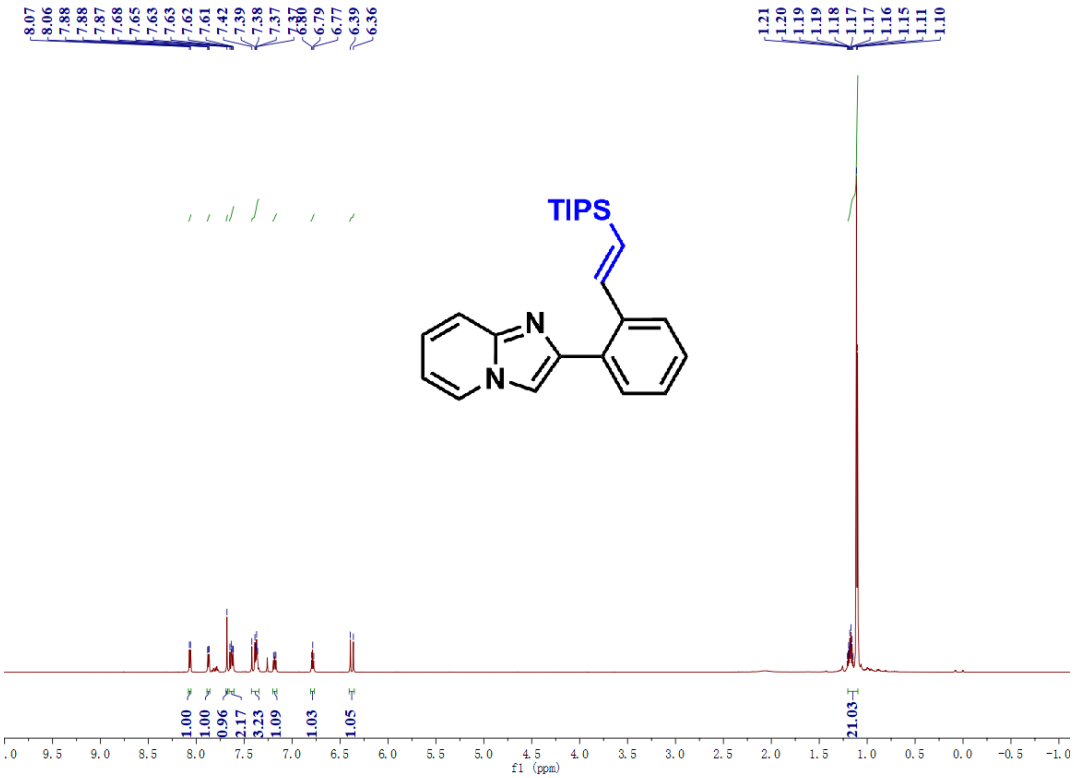
4aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



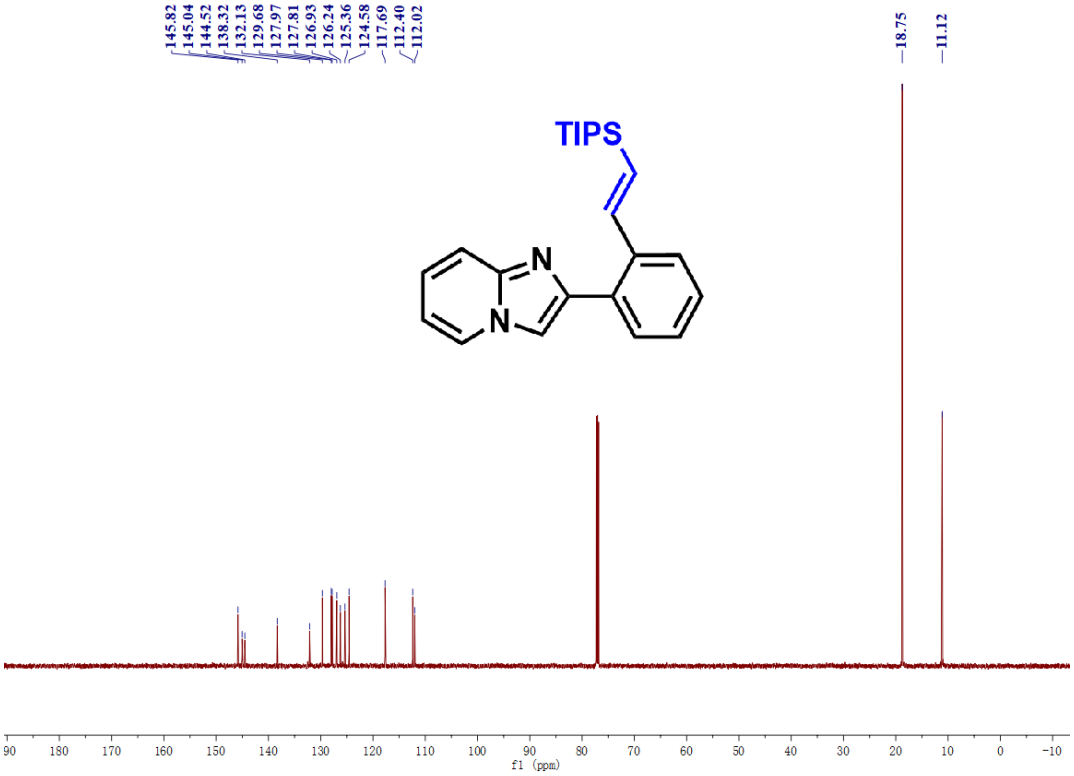
4aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



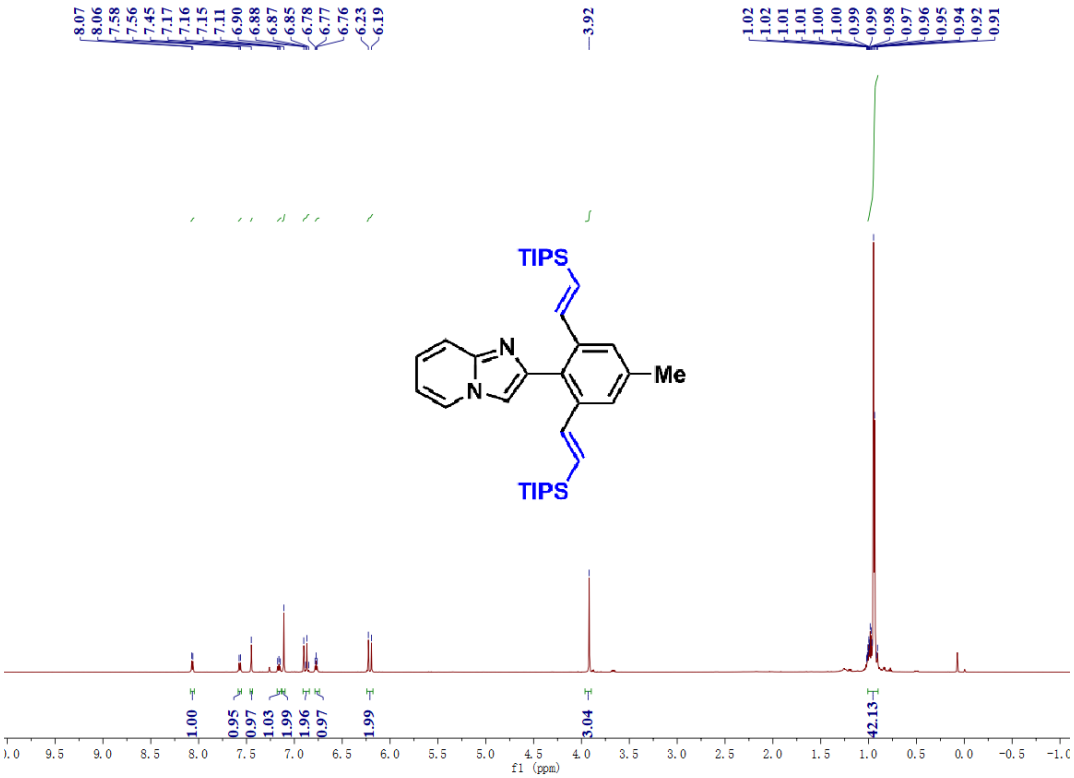
4aa$_1$ | ^{1}H NMR ($CDCl_3$, 600 MHz)



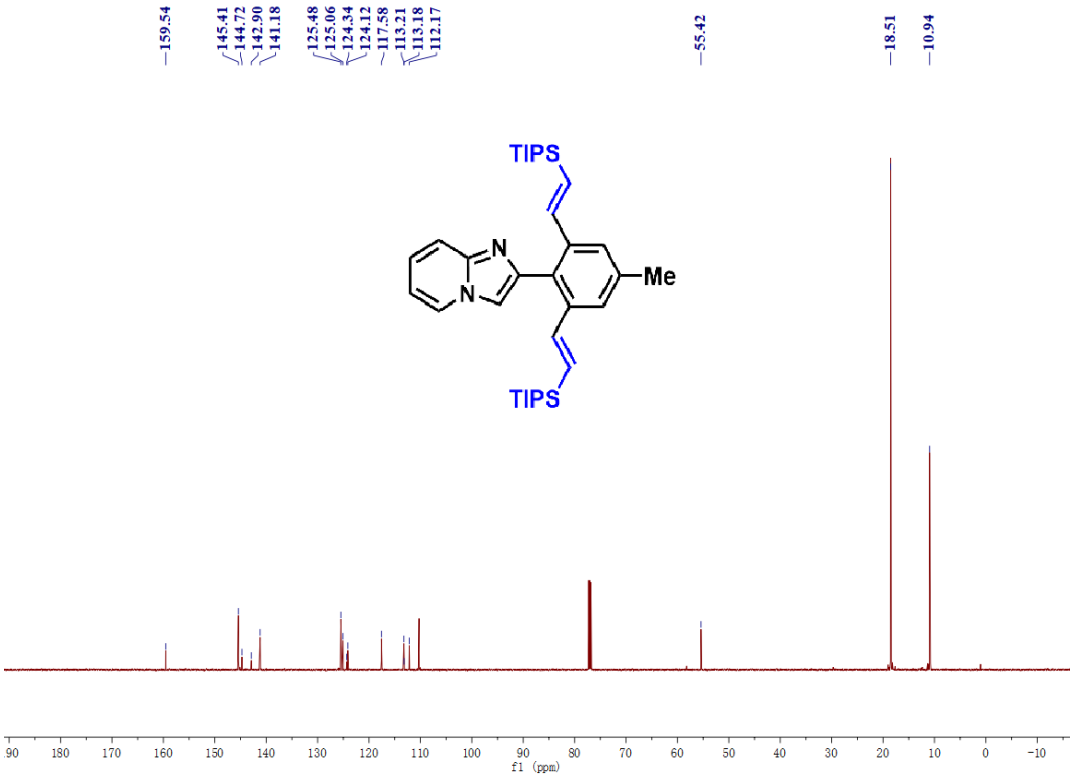
4aa$_1$ | $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz)



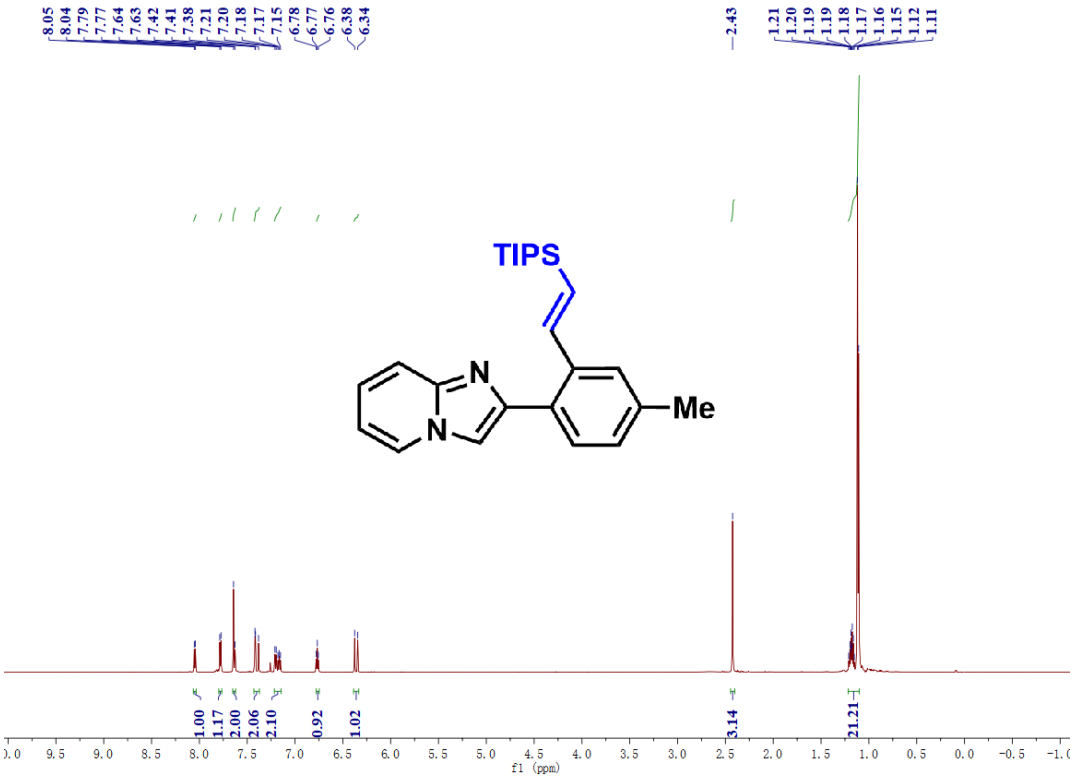
4ba | ^1H NMR ($CDCl_3$, 600 MHz)



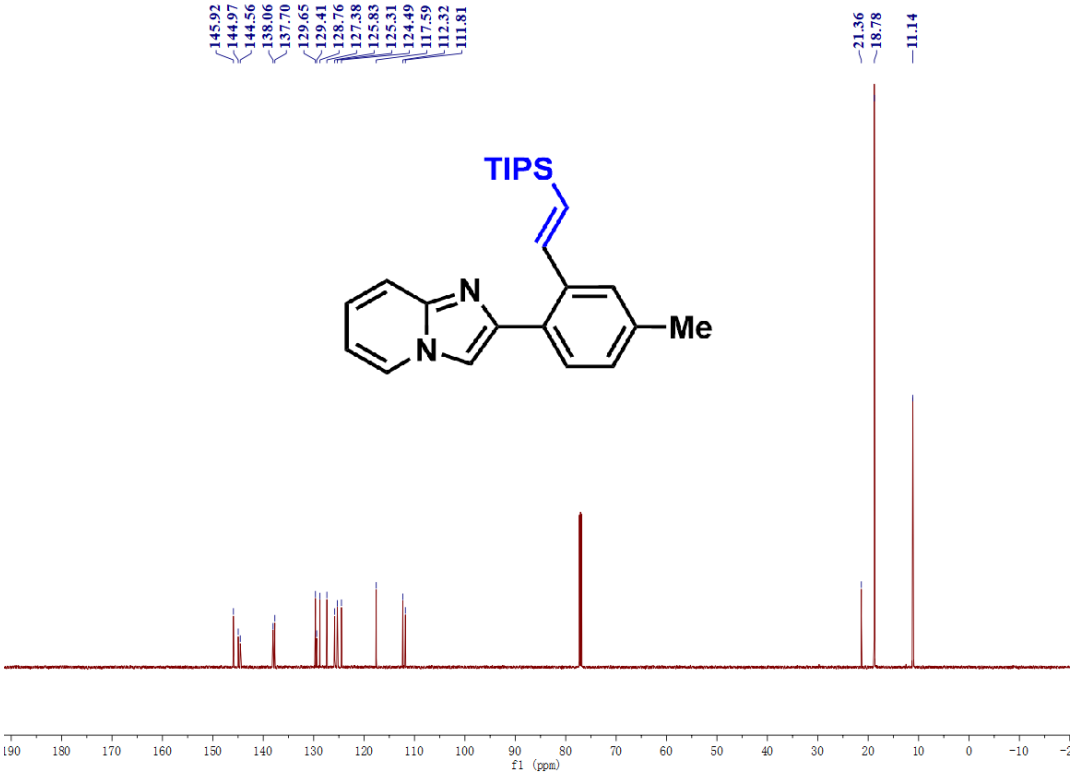
4ba | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



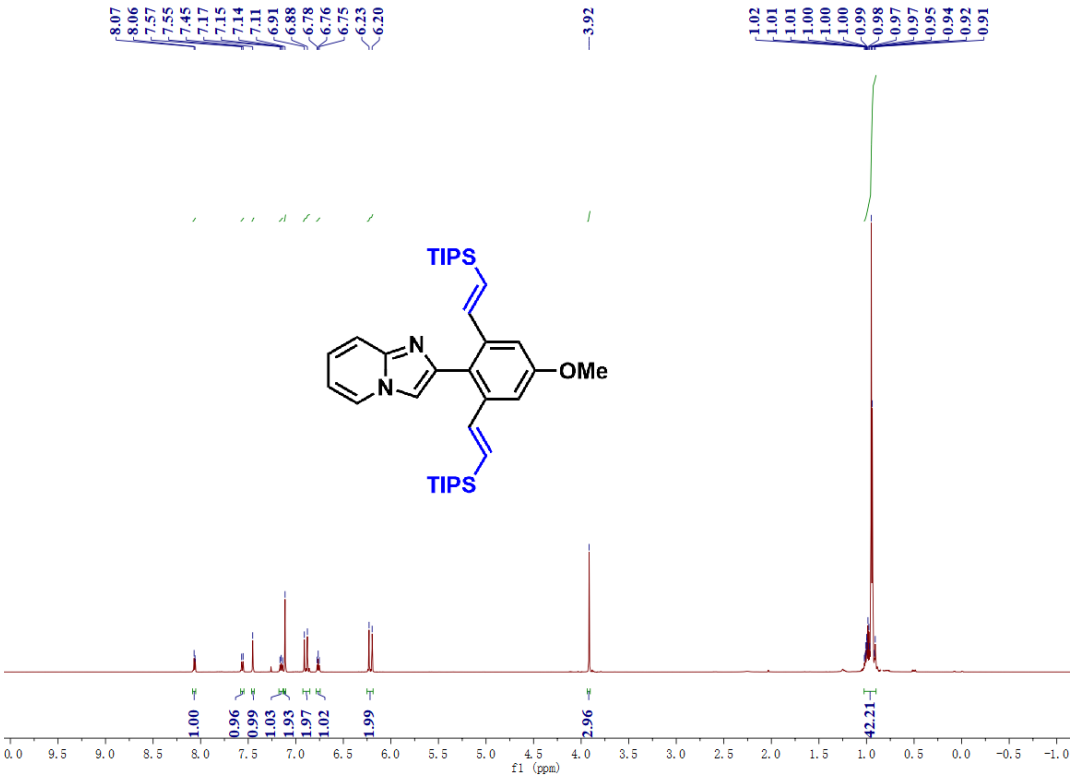
4ba$_1$ | ^{1}H NMR ($CDCl_3$, 600 MHz)



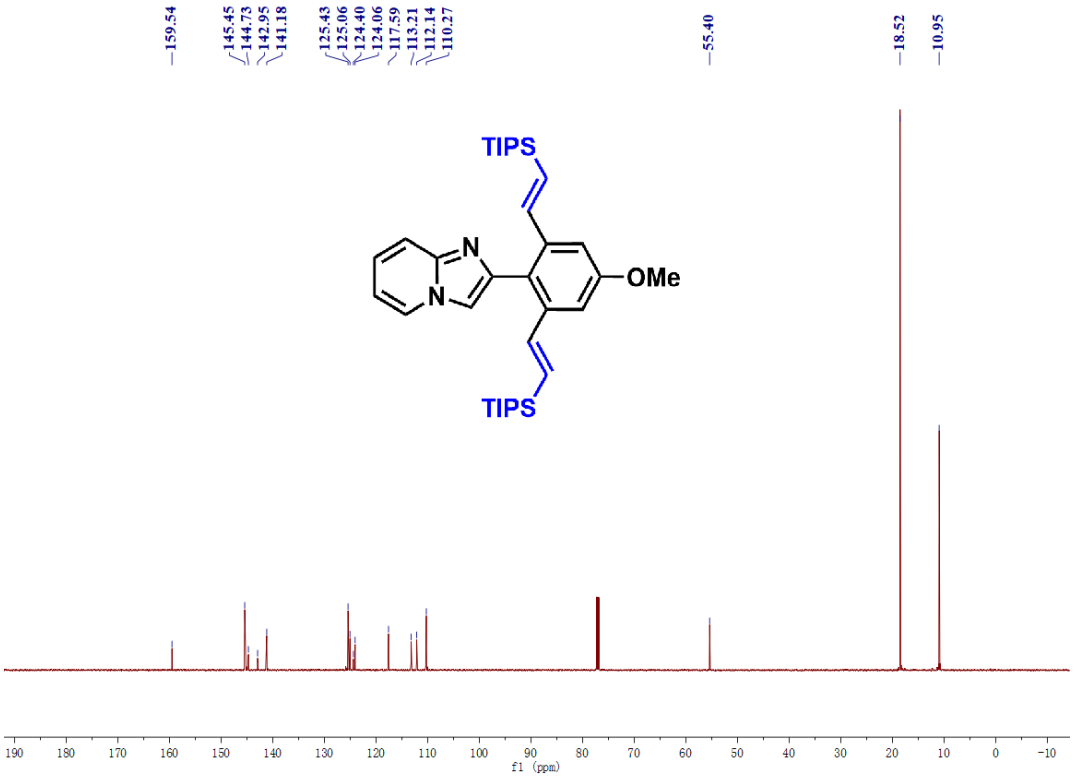
4ba$_1$ | $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz)



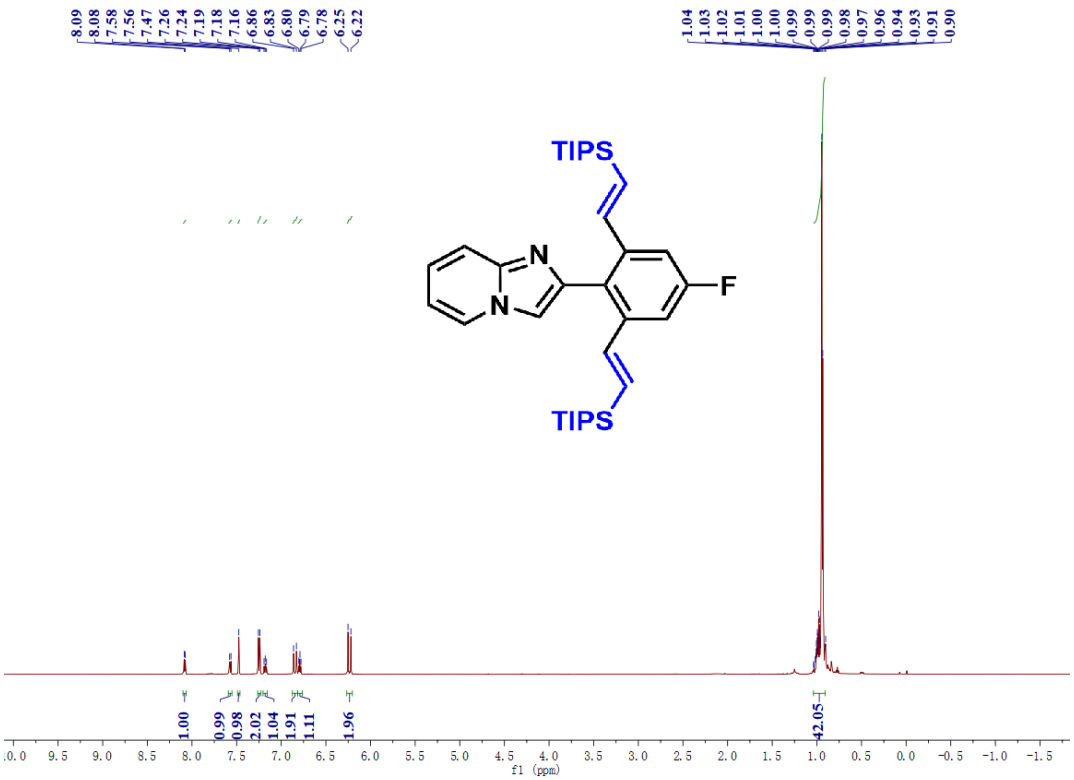
4ca | ^1H NMR ($CDCl_3$, 600 MHz)



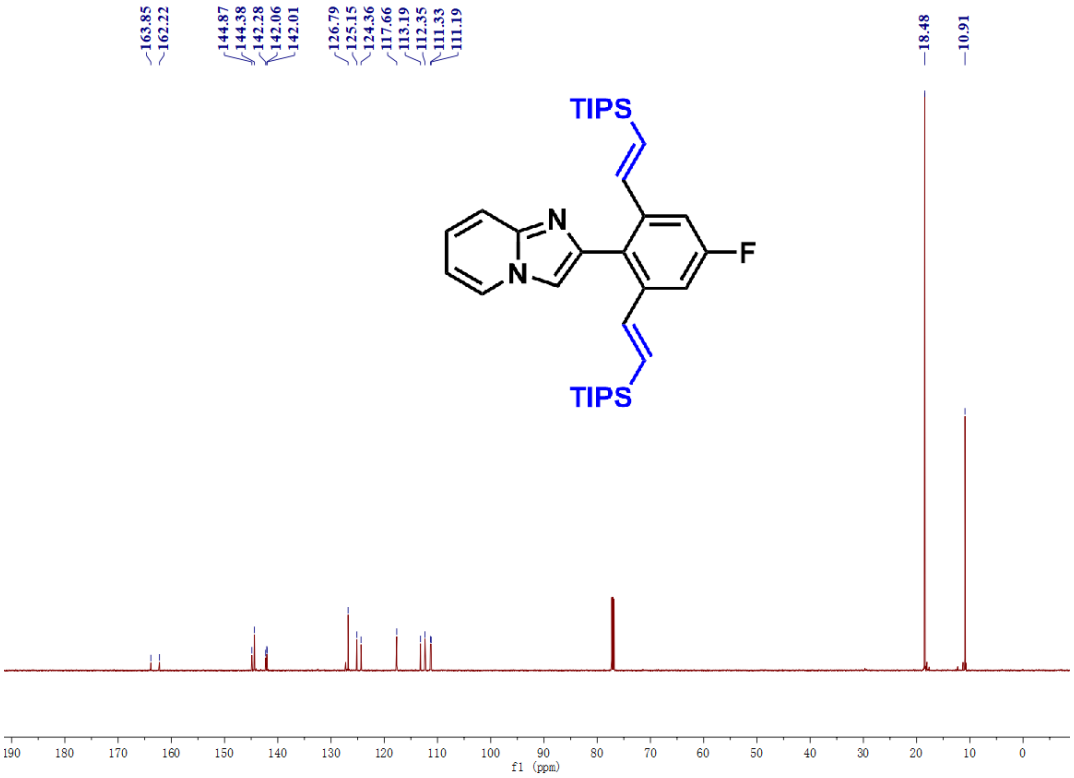
4ca | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



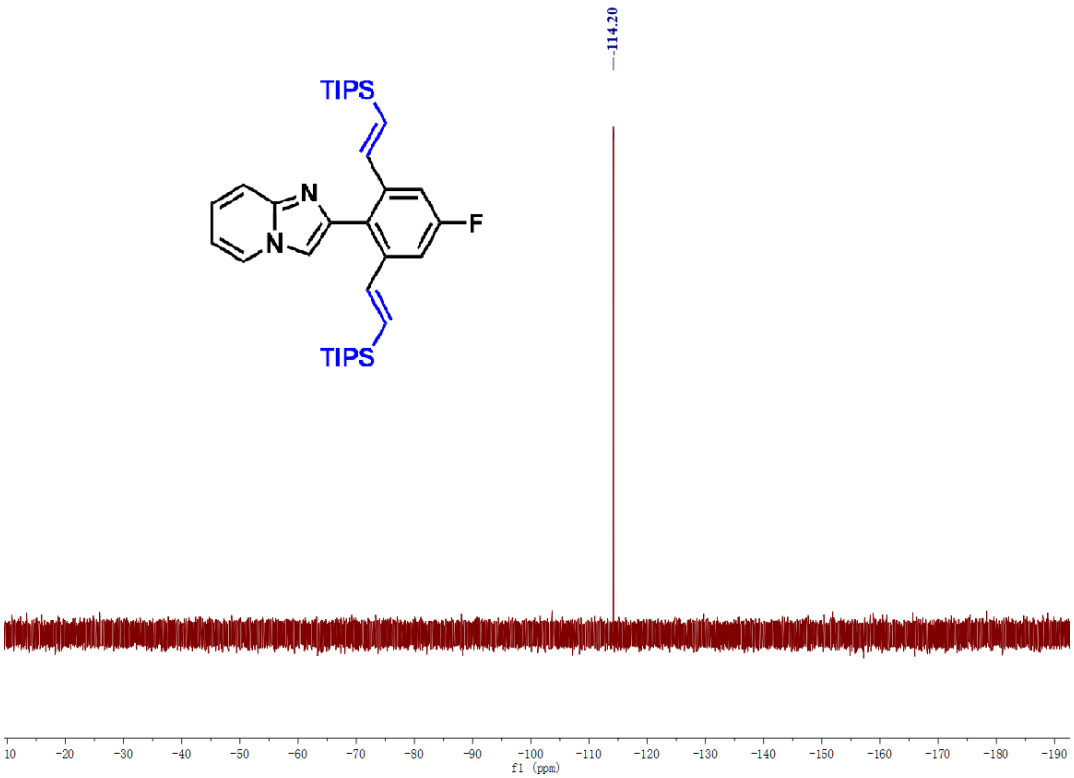
4da | ^{1}H NMR ($CDCl_3$, 600 MHz)



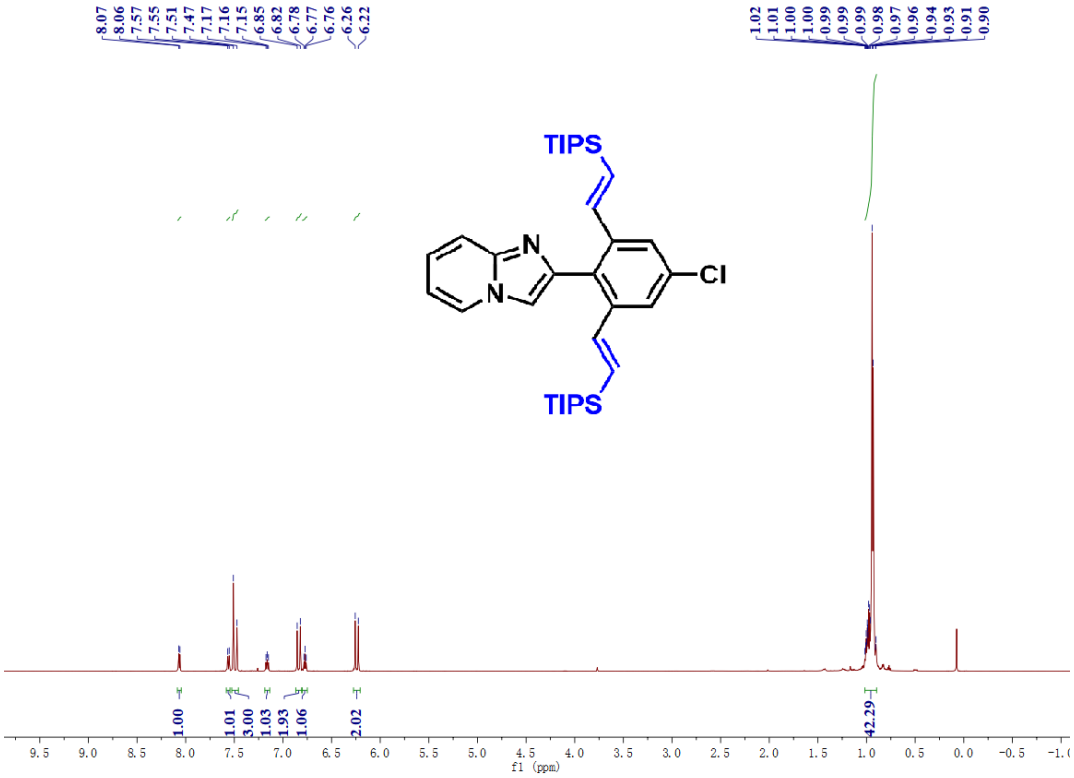
4da | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



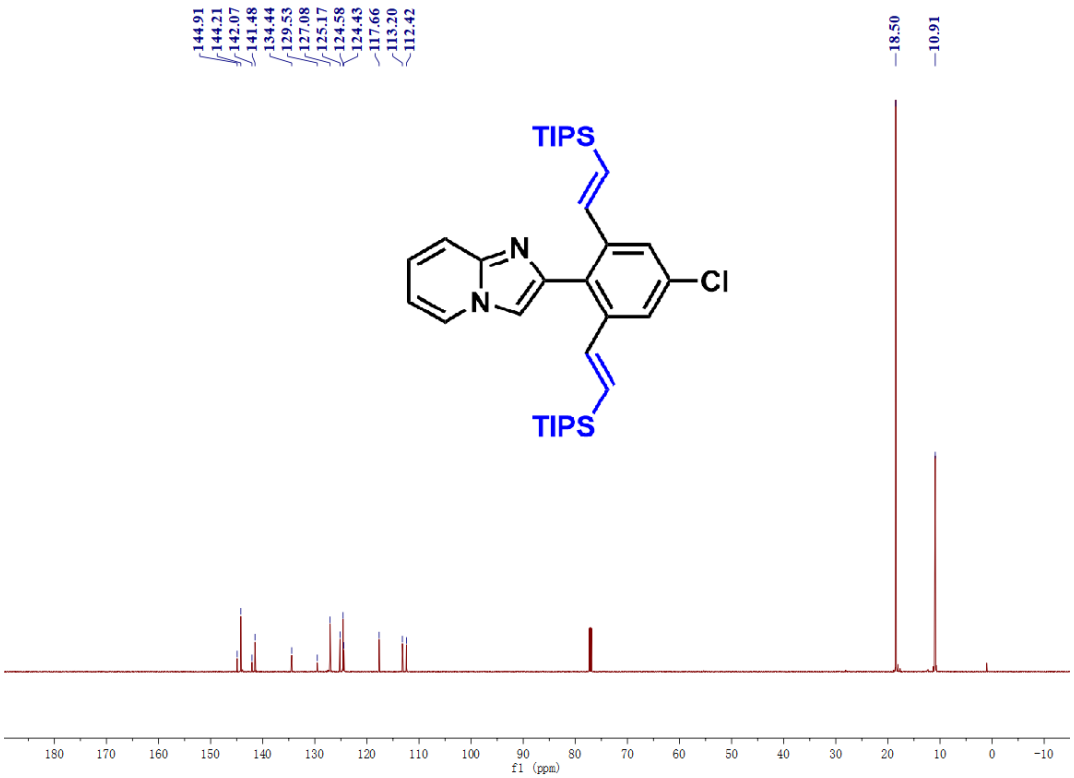
4da | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



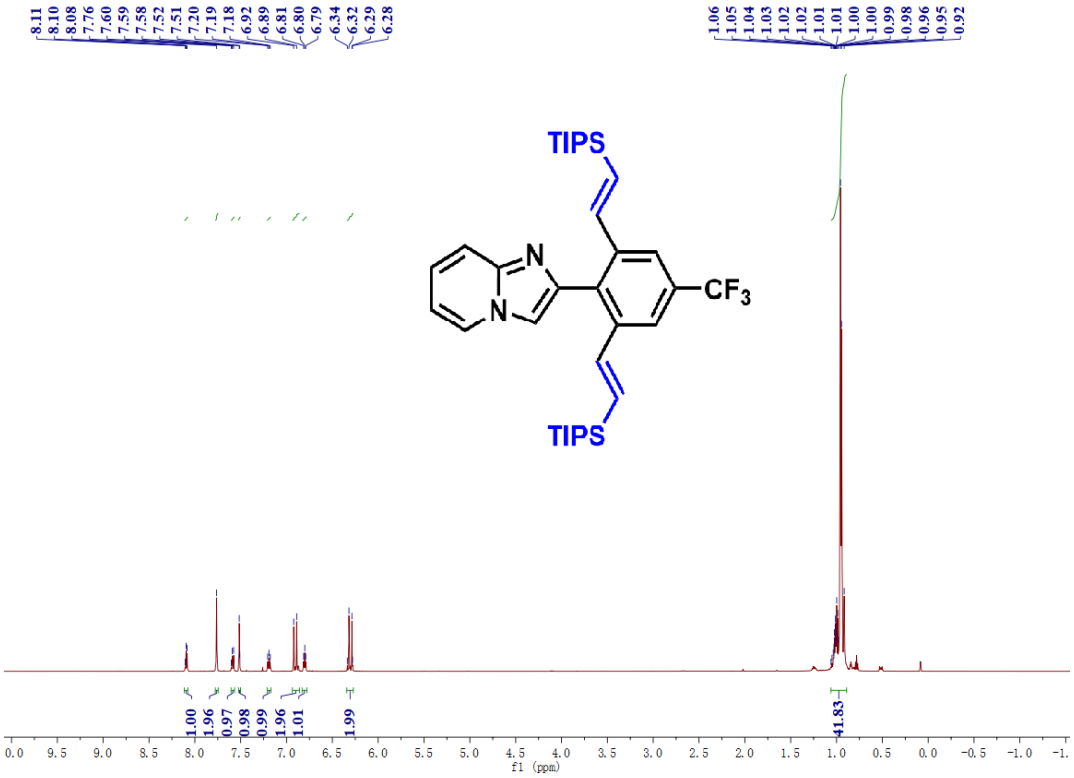
4ea | ^{1}H NMR ($CDCl_3$, 600 MHz)



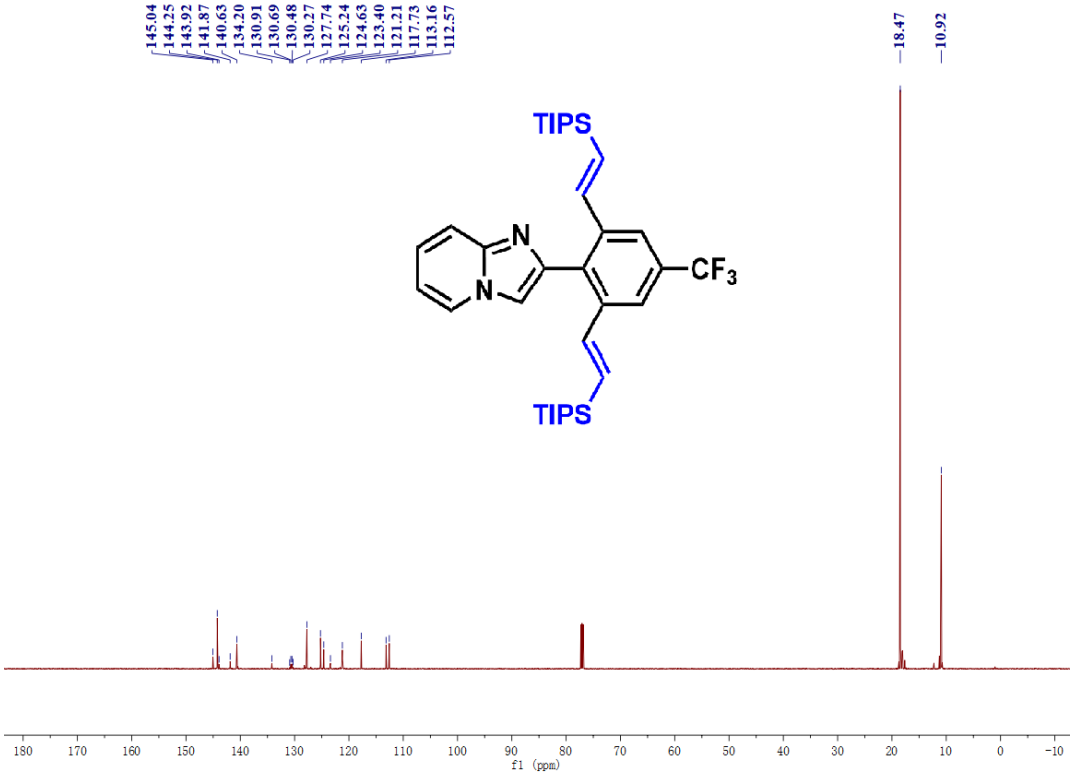
4ea | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



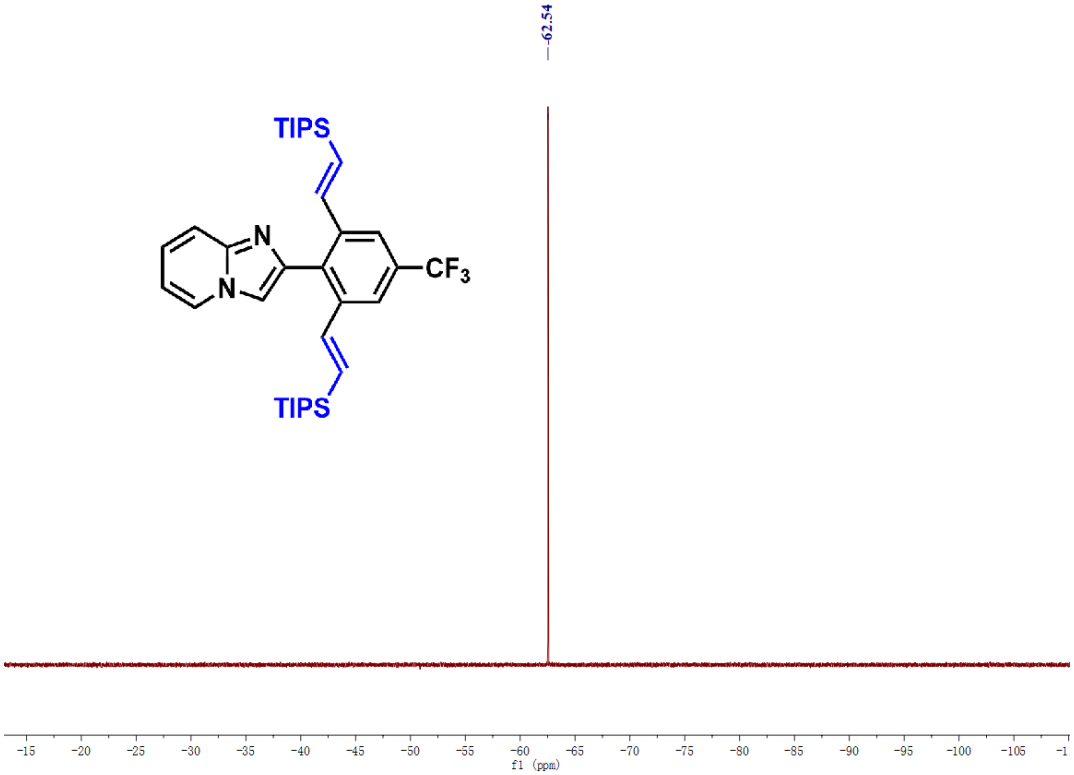
4fa | ^{1}H NMR ($CDCl_3$, 600 MHz)



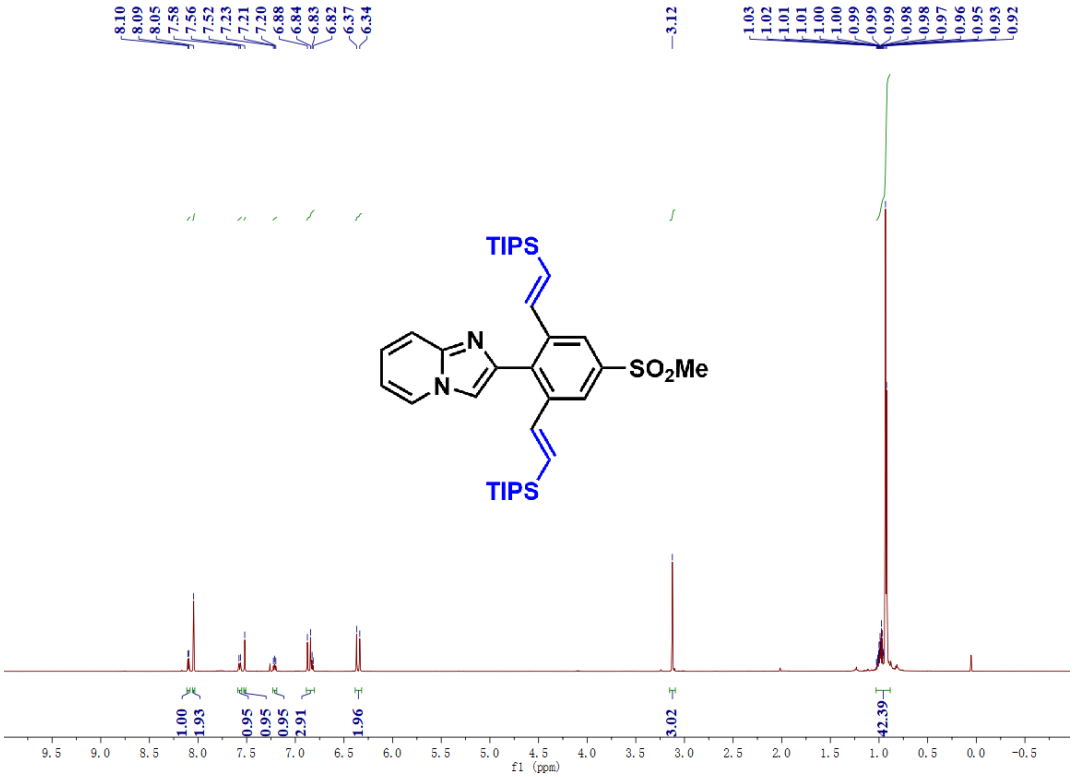
4fa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



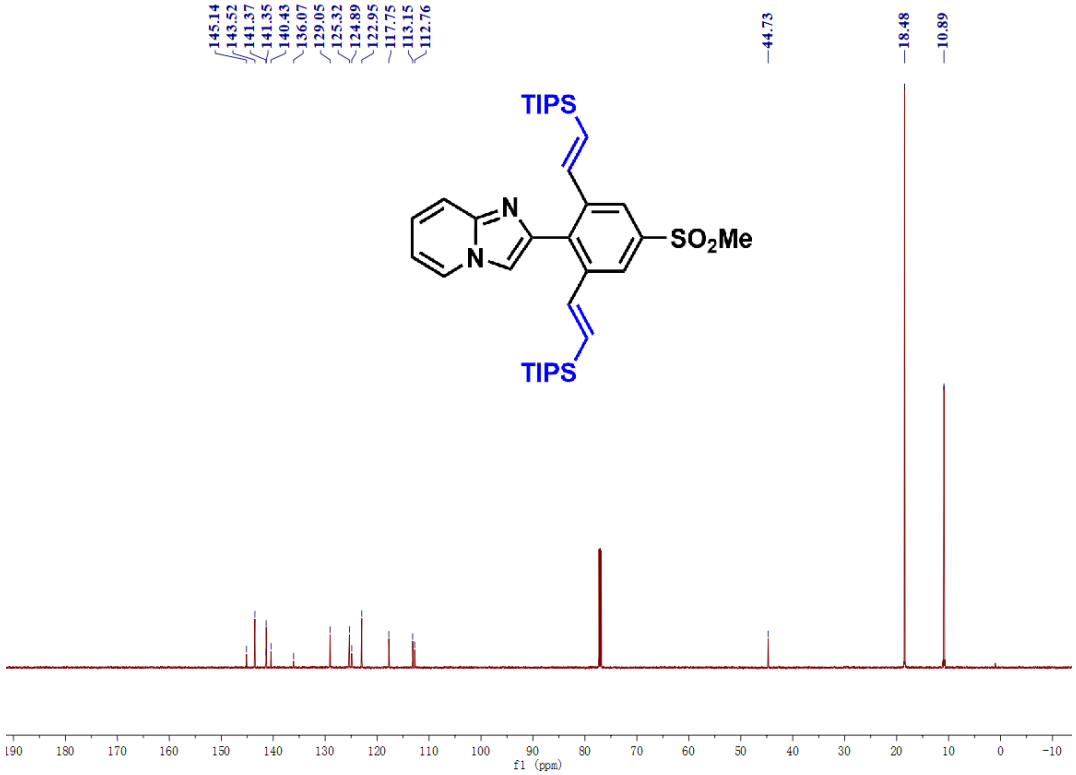
4fa | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



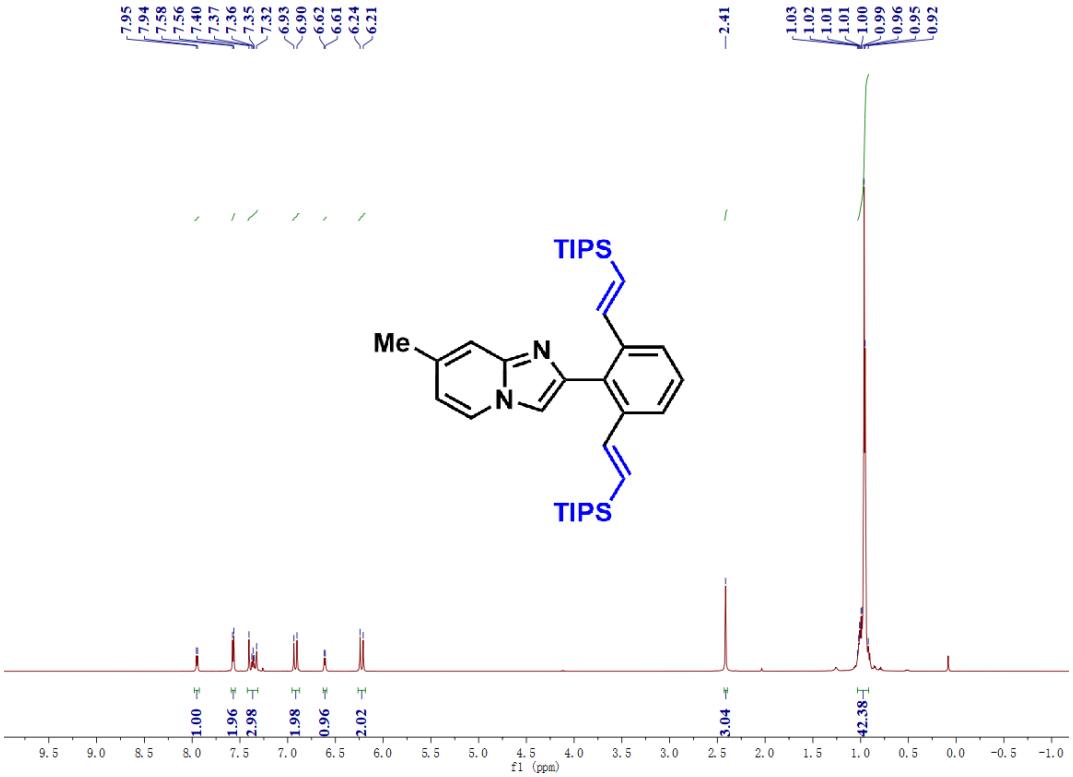
4ga | ^{1}H NMR ($CDCl_3$, 600 MHz)



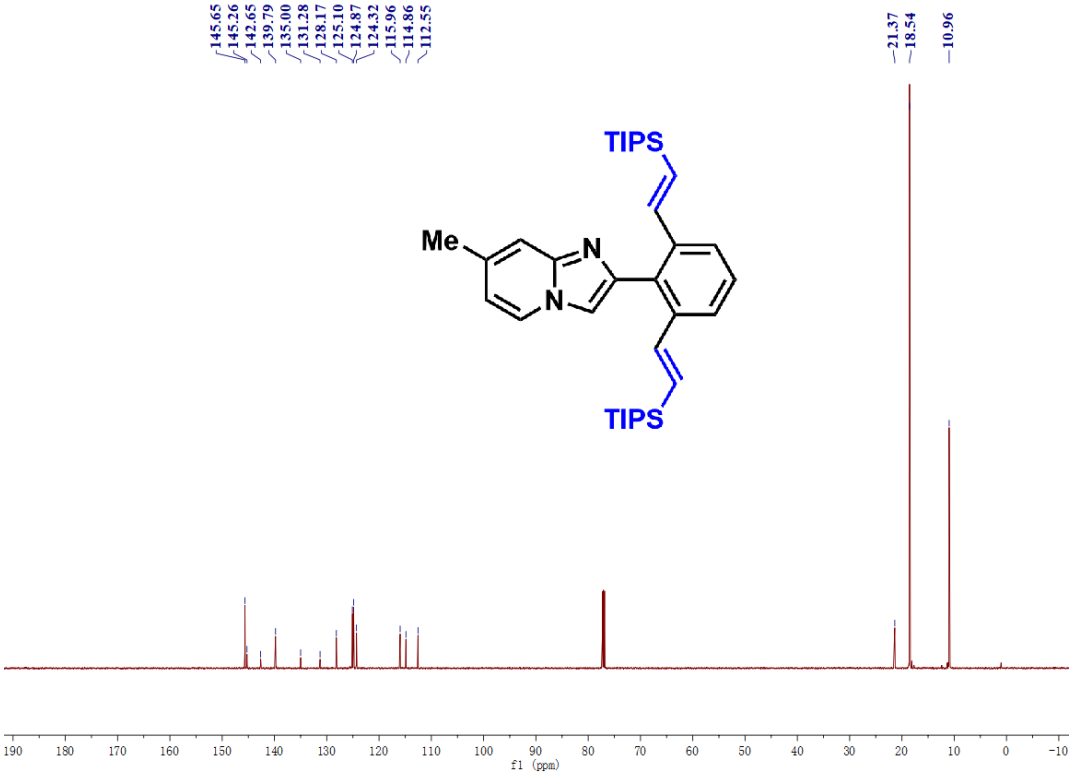
4ga | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



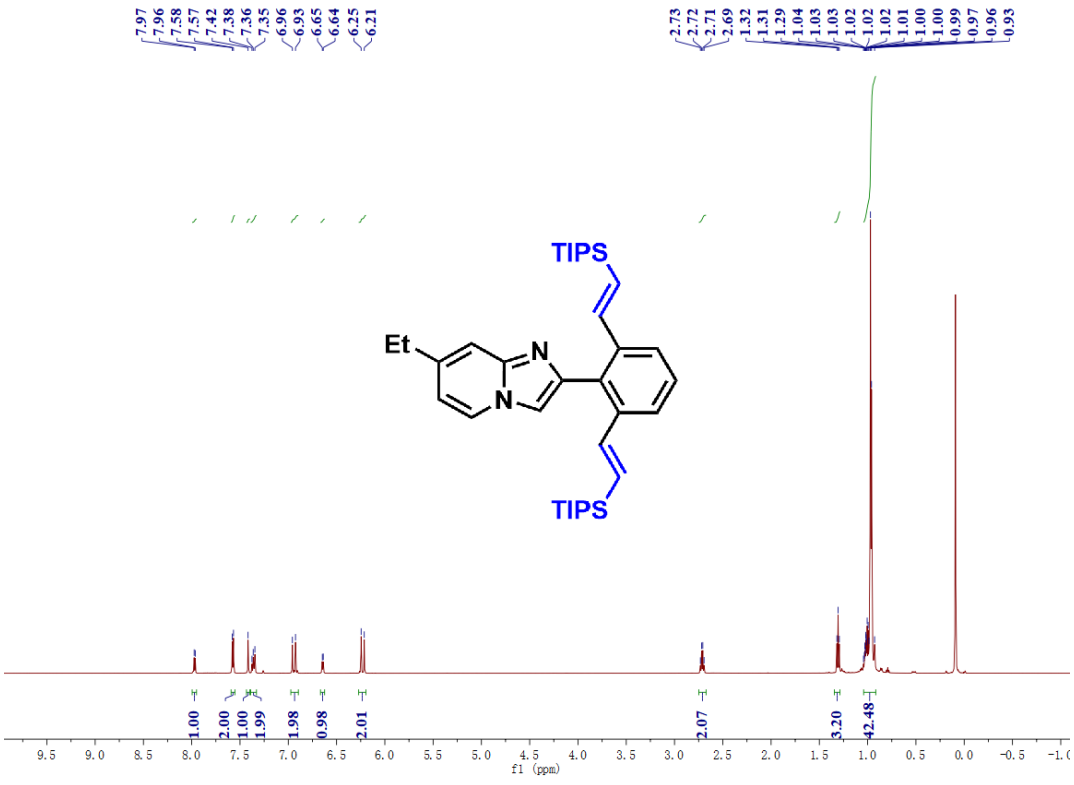
4ja | ^{1}H NMR ($CDCl_3$, 600 MHz)



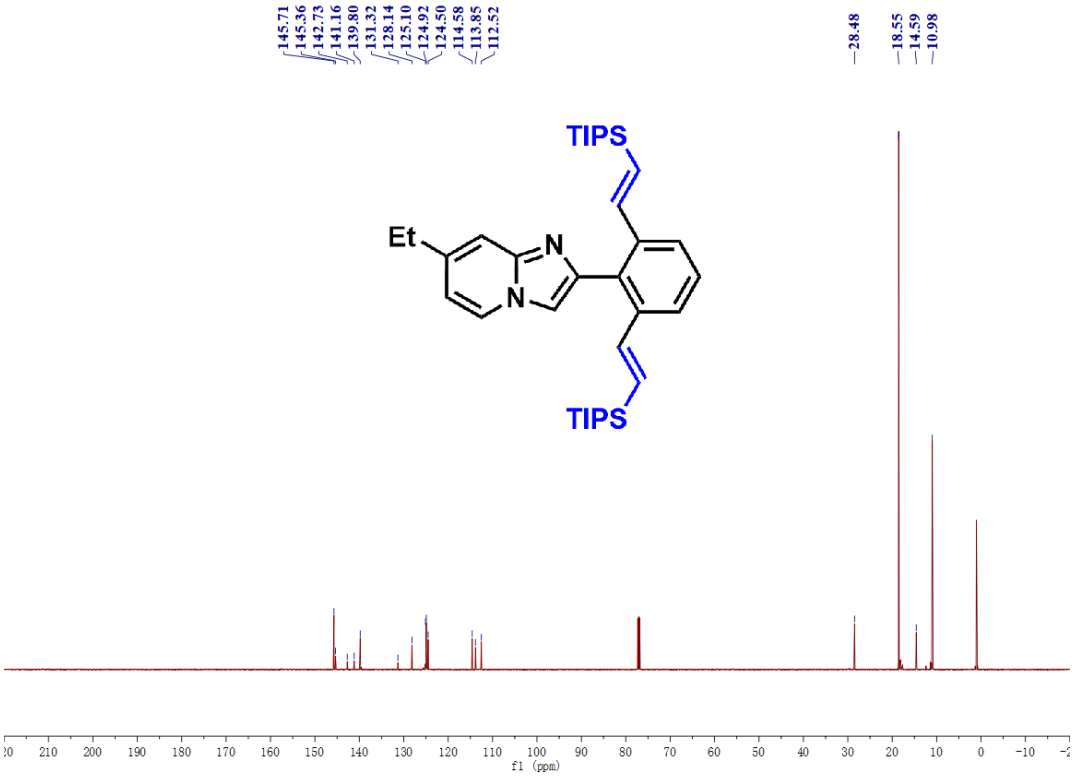
4ja | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



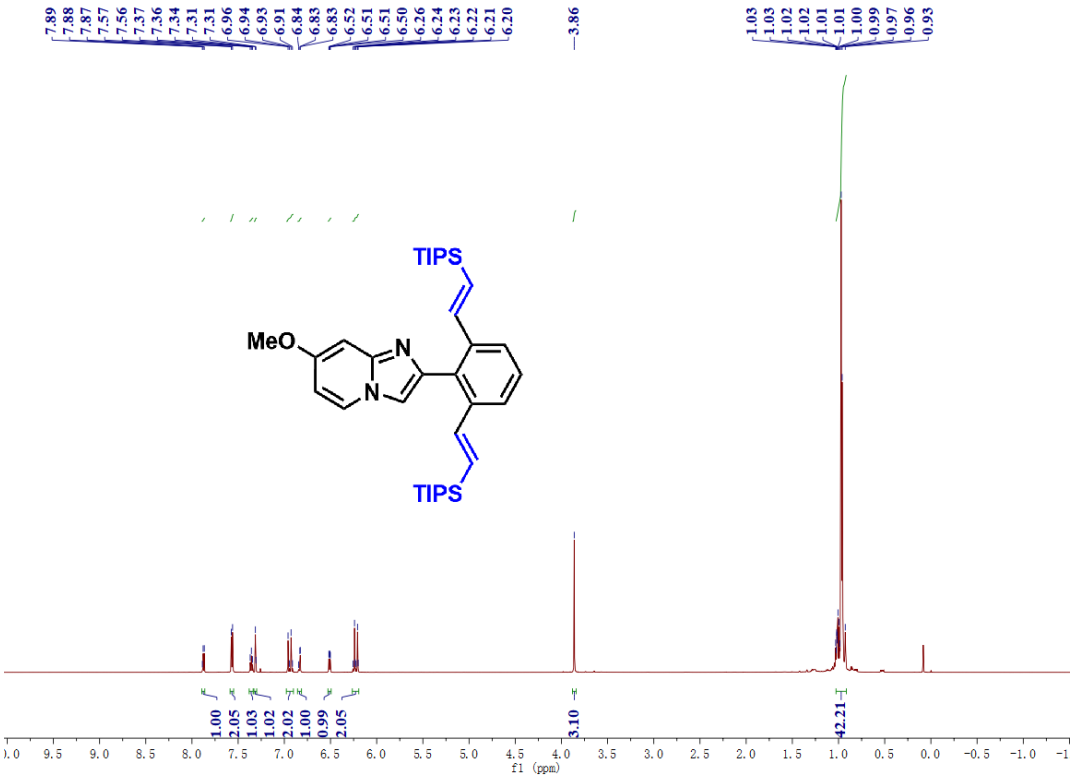
4ka | ^{1}H NMR ($CDCl_3$, 600 MHz)



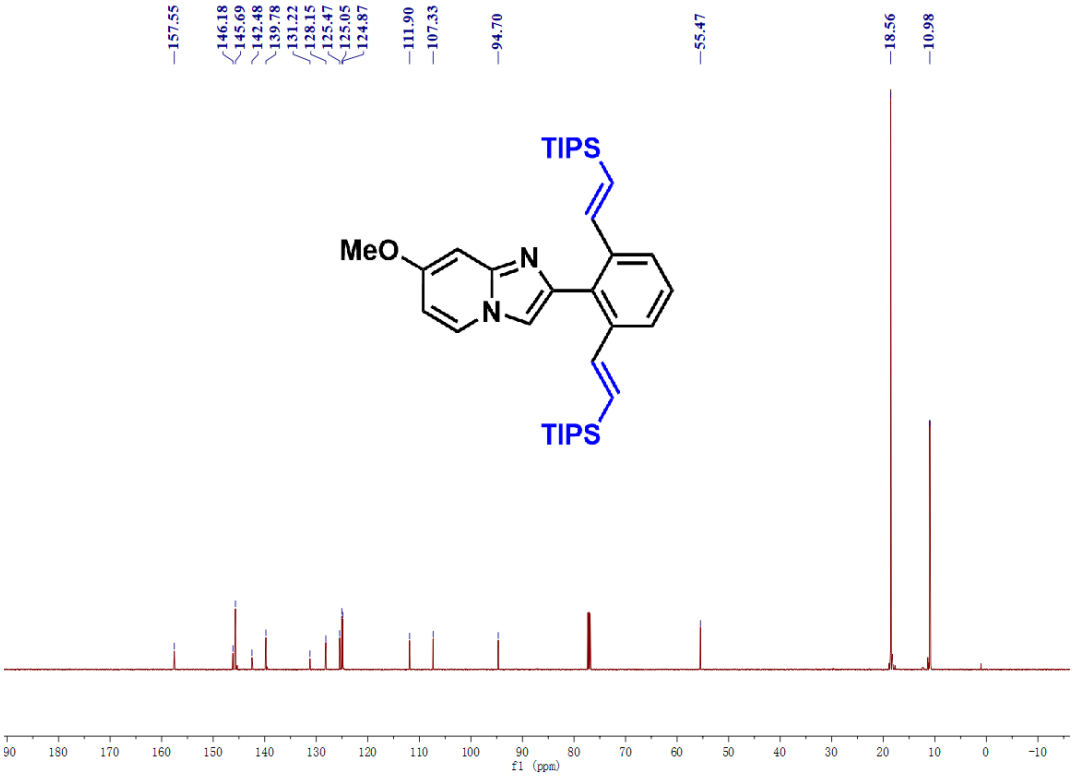
4ka | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



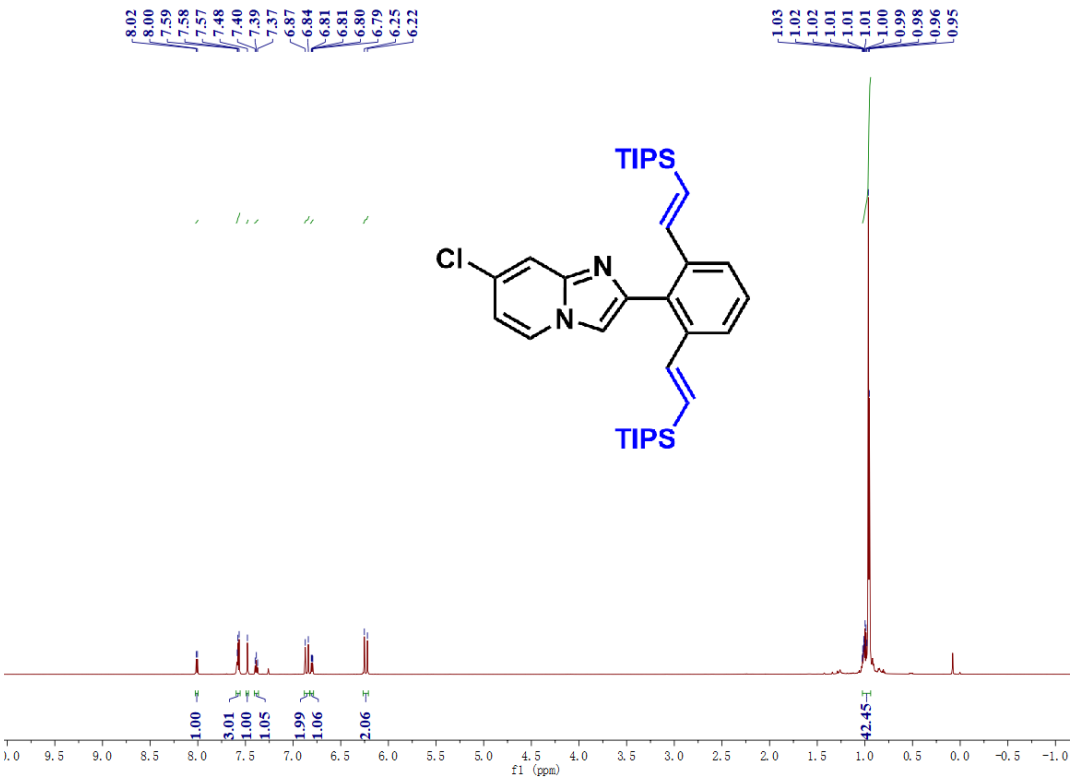
4la | ^{1}H NMR ($CDCl_3$, 600 MHz)



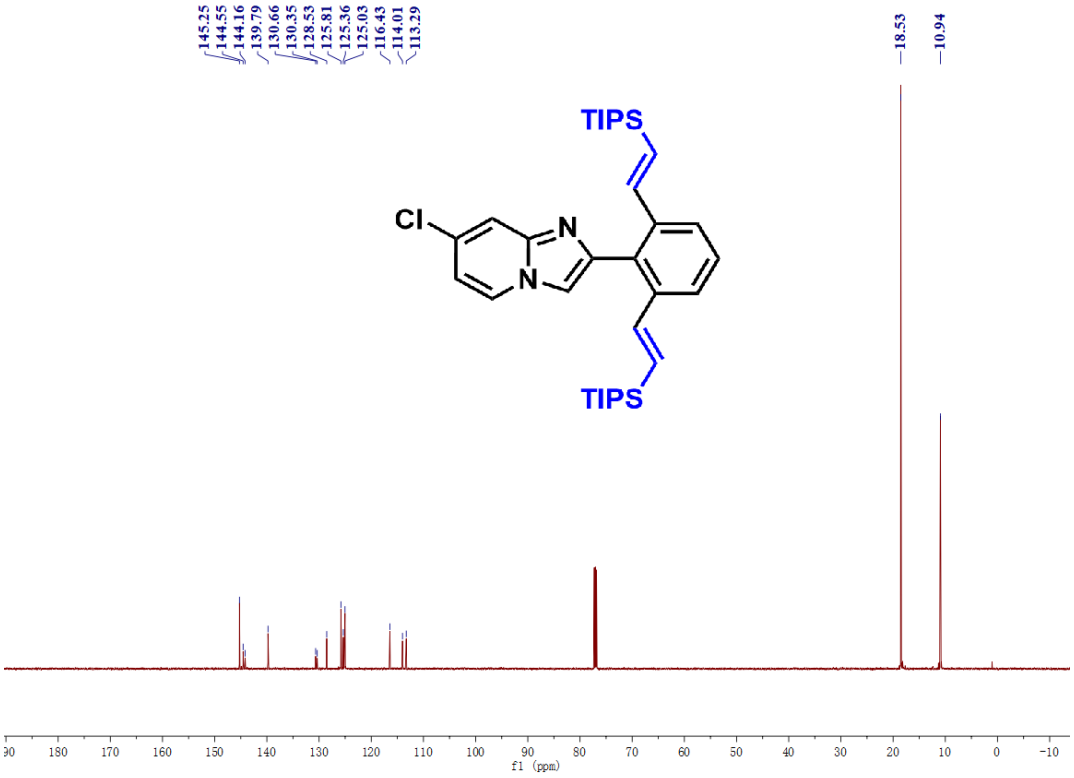
4la | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



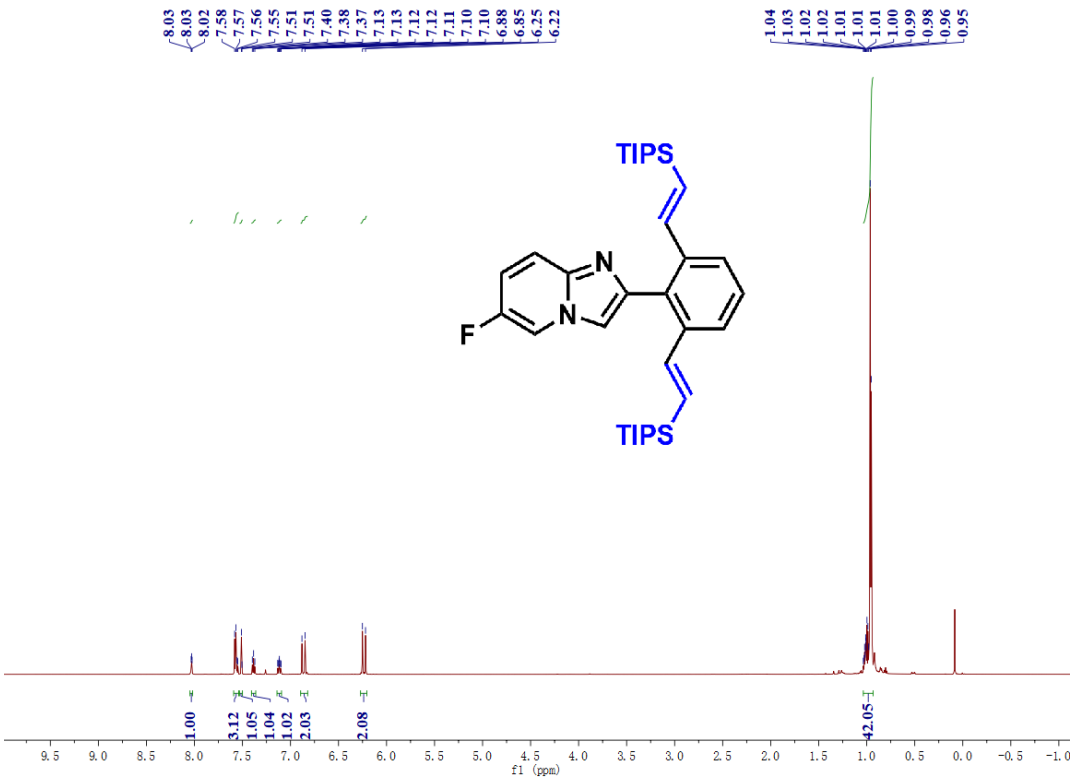
4ma | ^{1}H NMR ($CDCl_3$, 600 MHz)



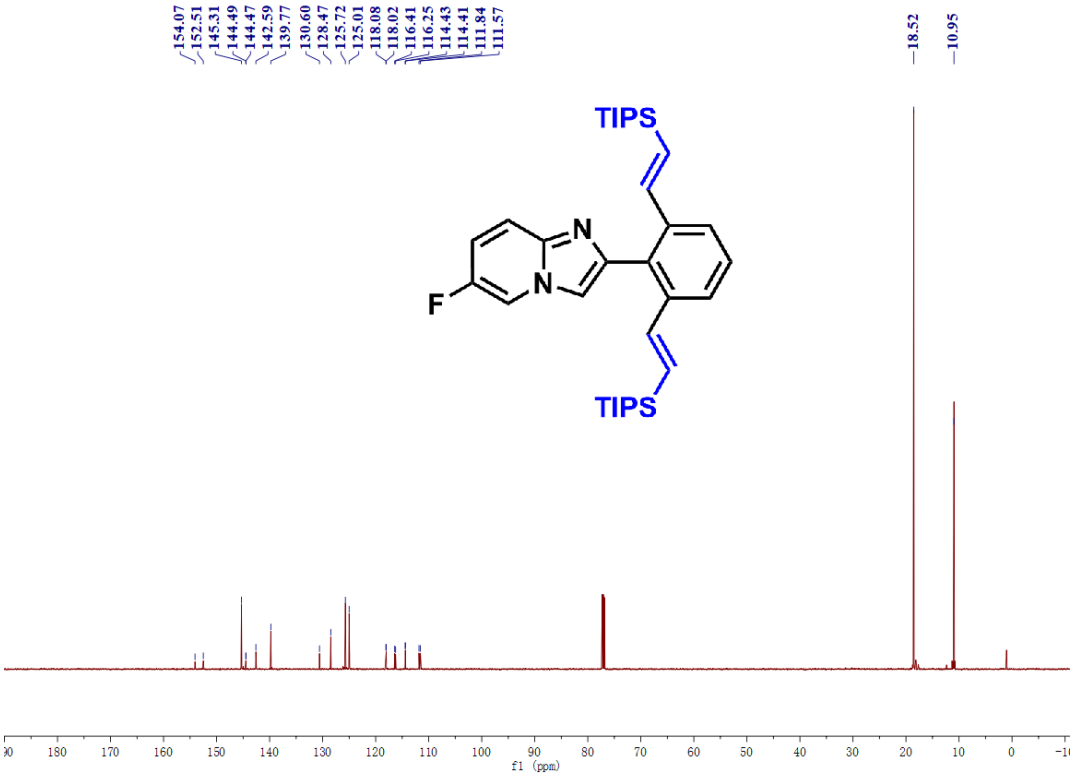
4ma | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



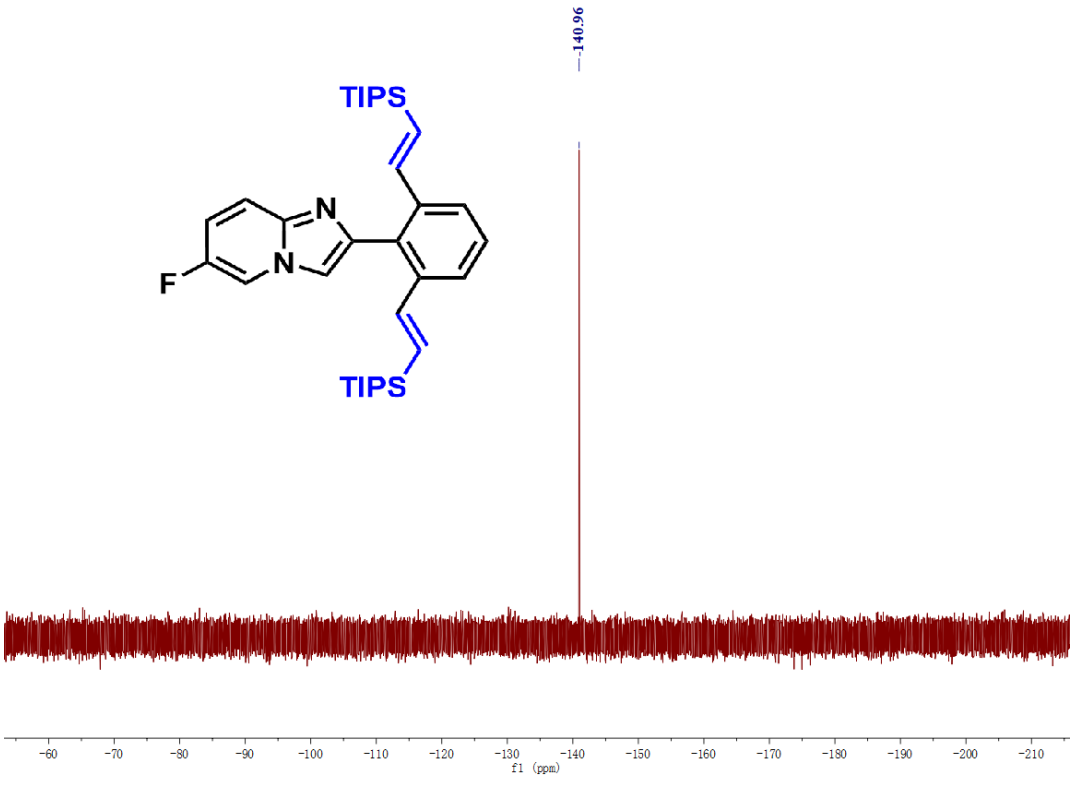
4na | ^{1}H NMR ($CDCl_3$, 600 MHz)



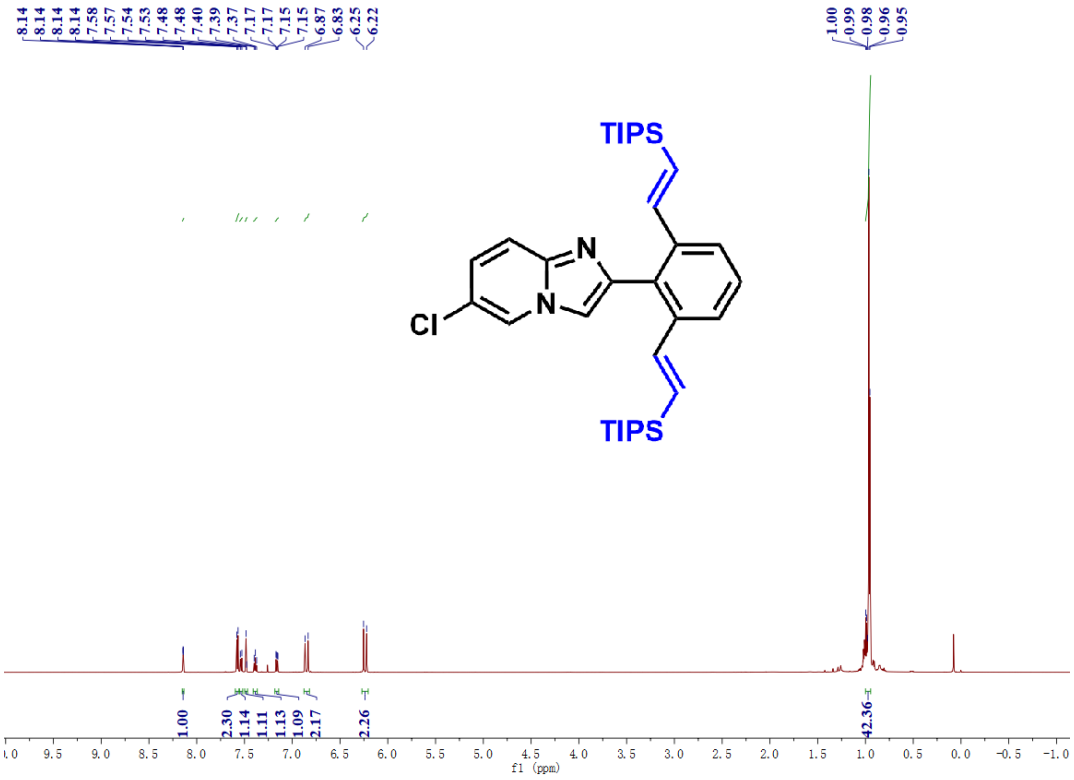
4na | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



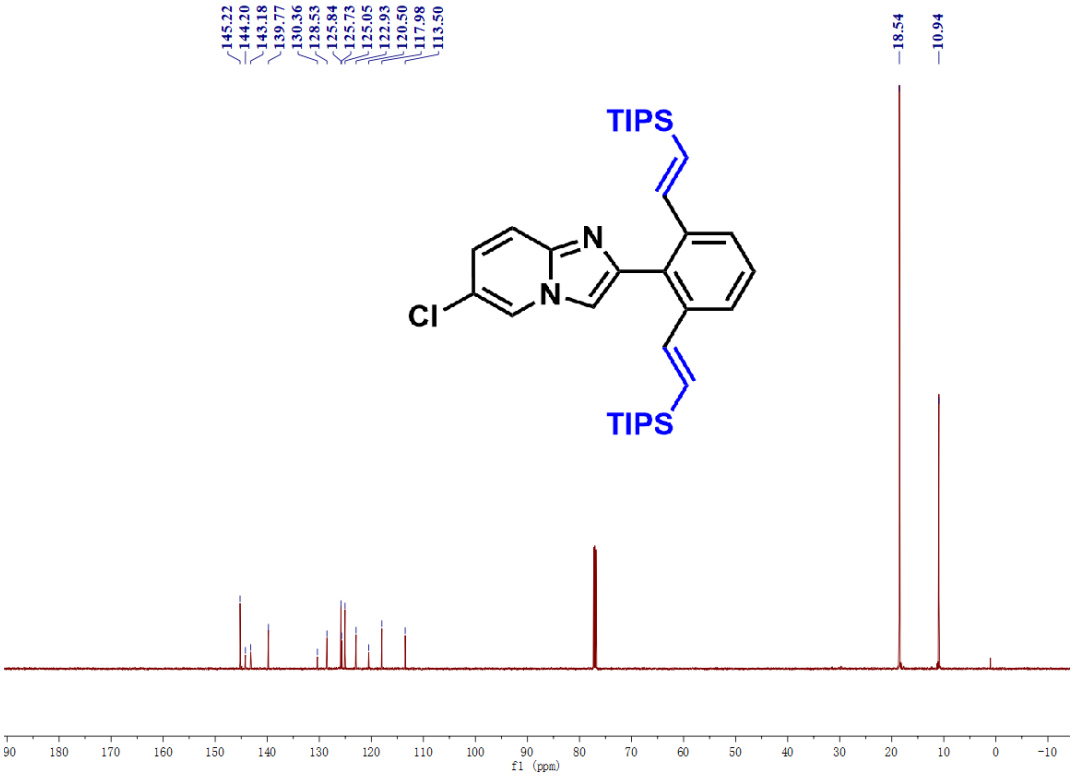
4na | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



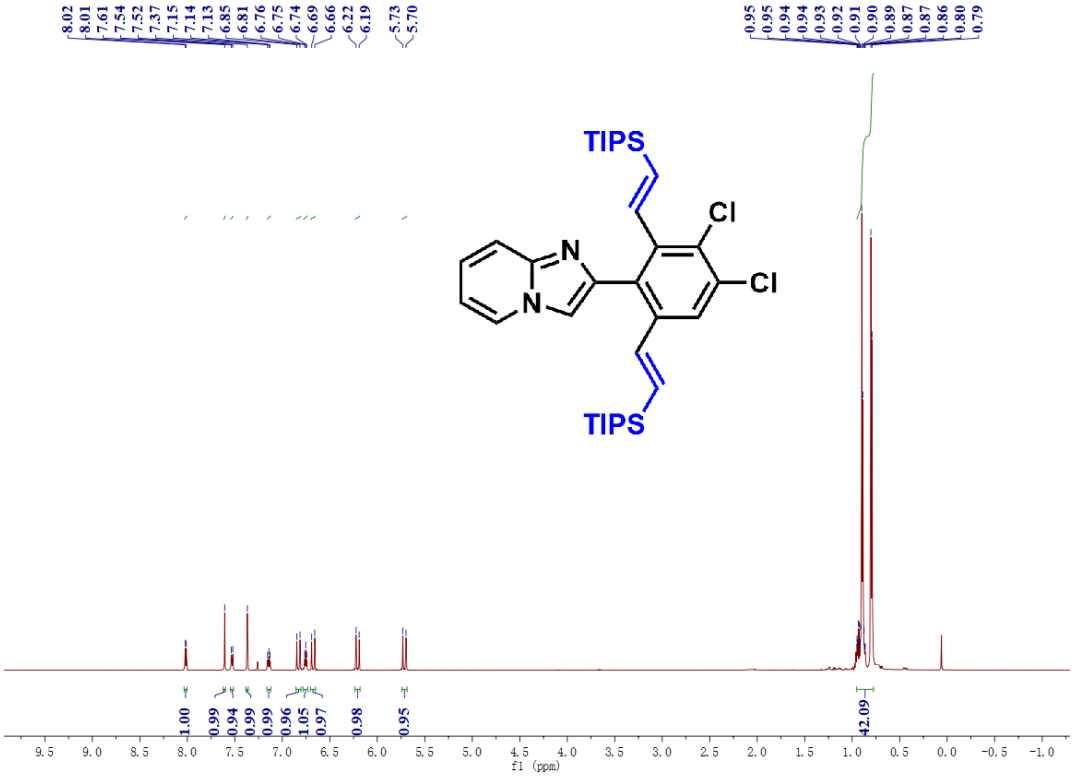
4oa | ^{1}H NMR ($CDCl_3$, 600 MHz)



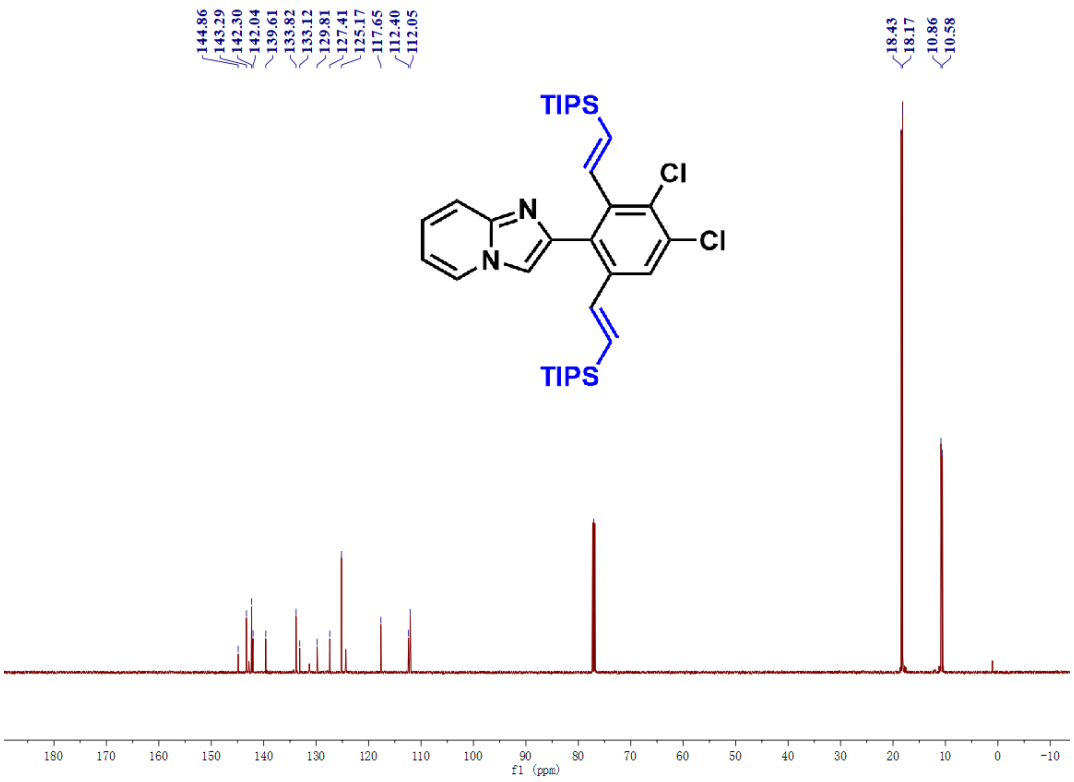
4oa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



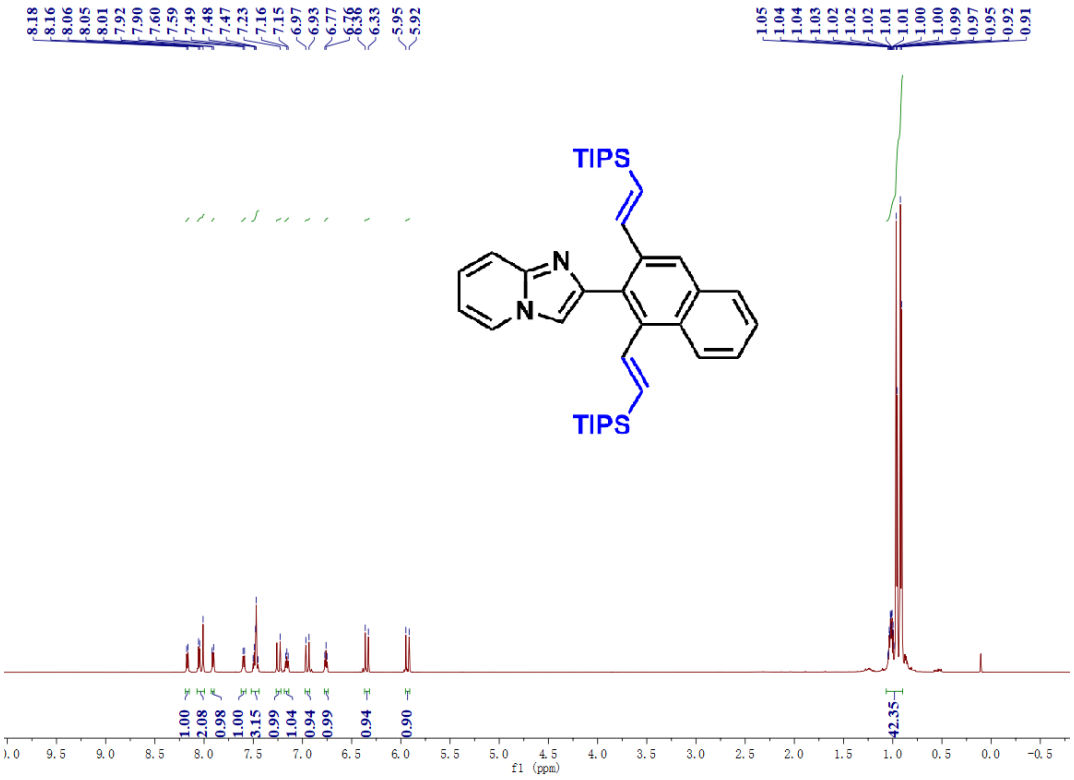
4qa | ^{1}H NMR ($CDCl_3$, 600 MHz)



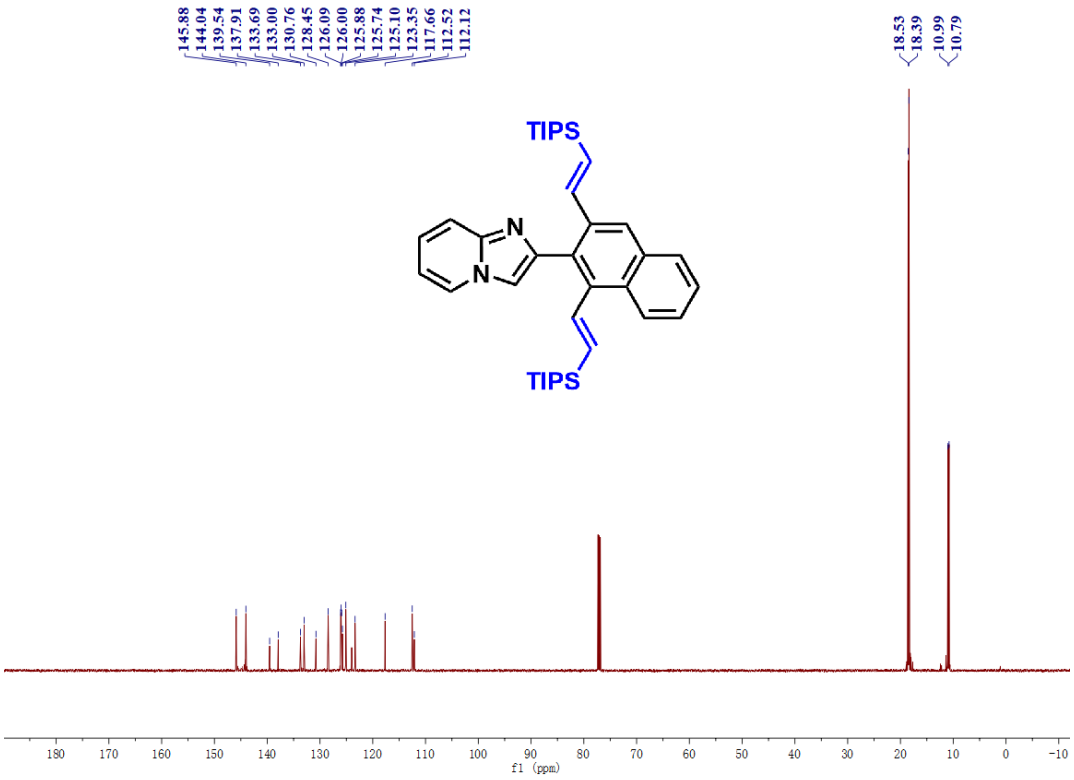
4qa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



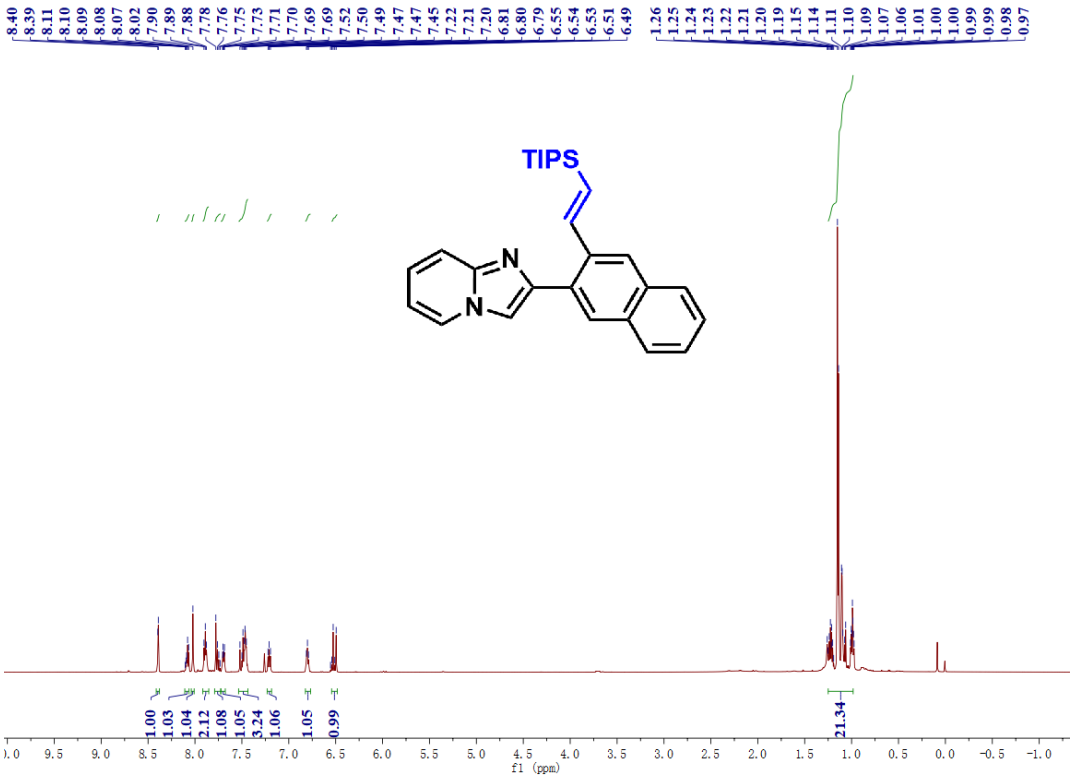
4ra | ^{1}H NMR ($CDCl_3$, 600 MHz)



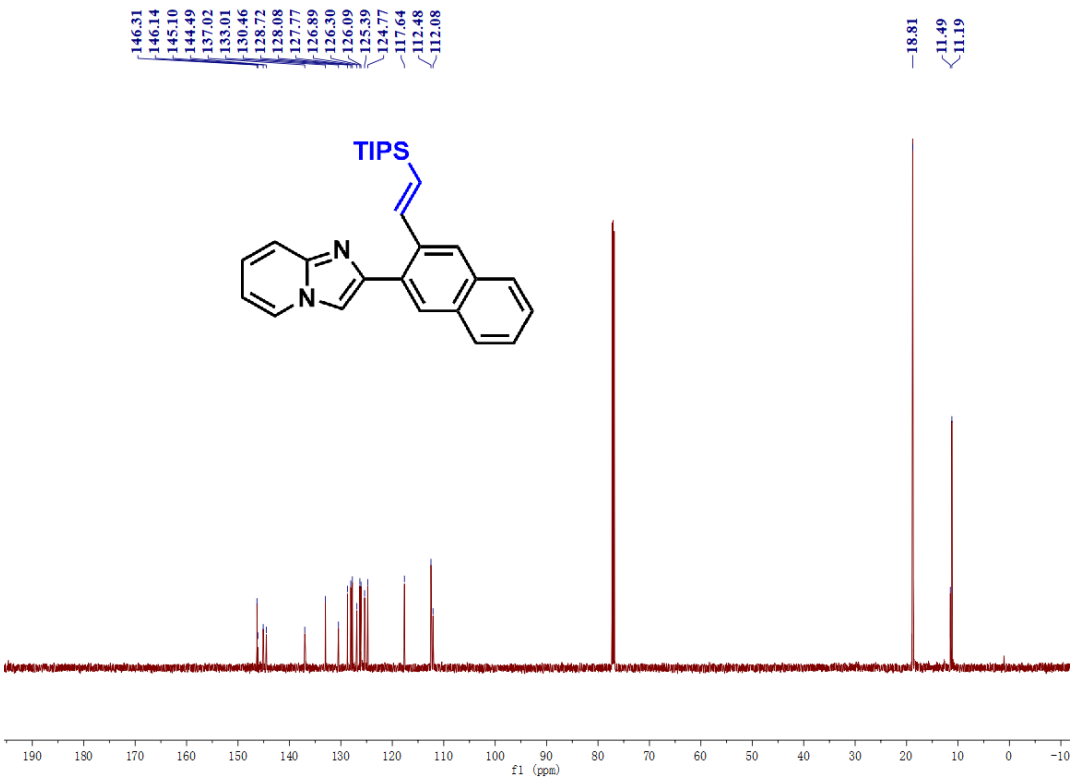
4ra | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



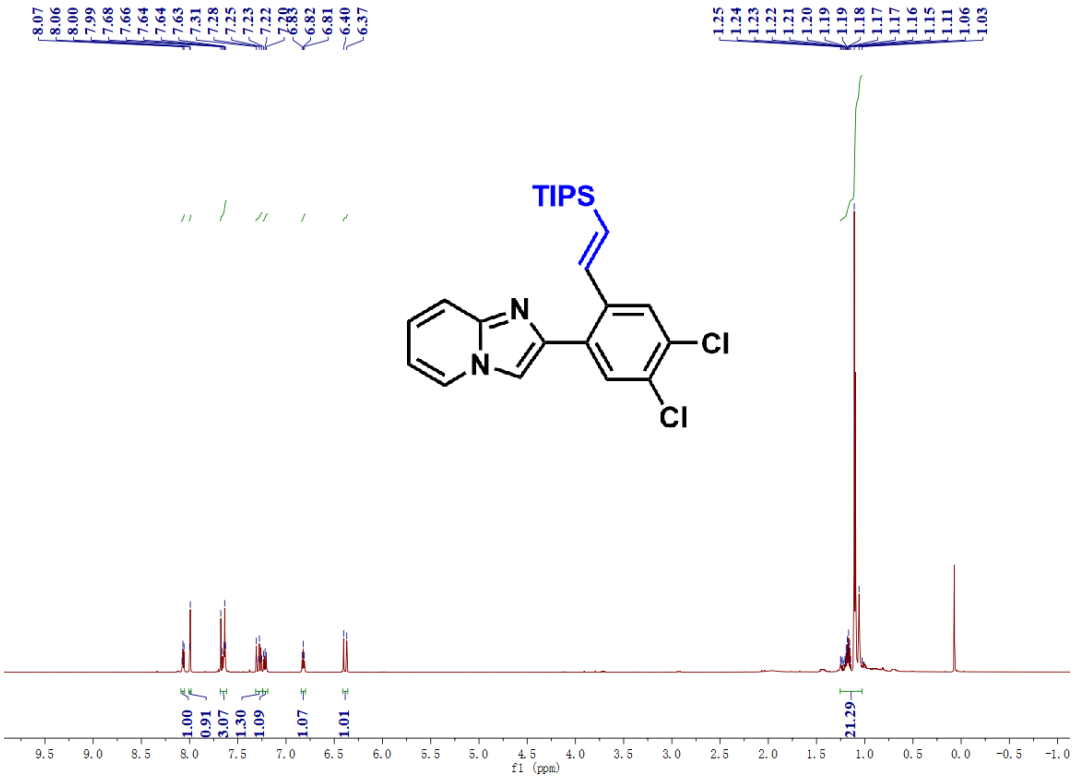
4ra$_1$ | ^{1}H NMR ($CDCl_3$, 600 MHz)



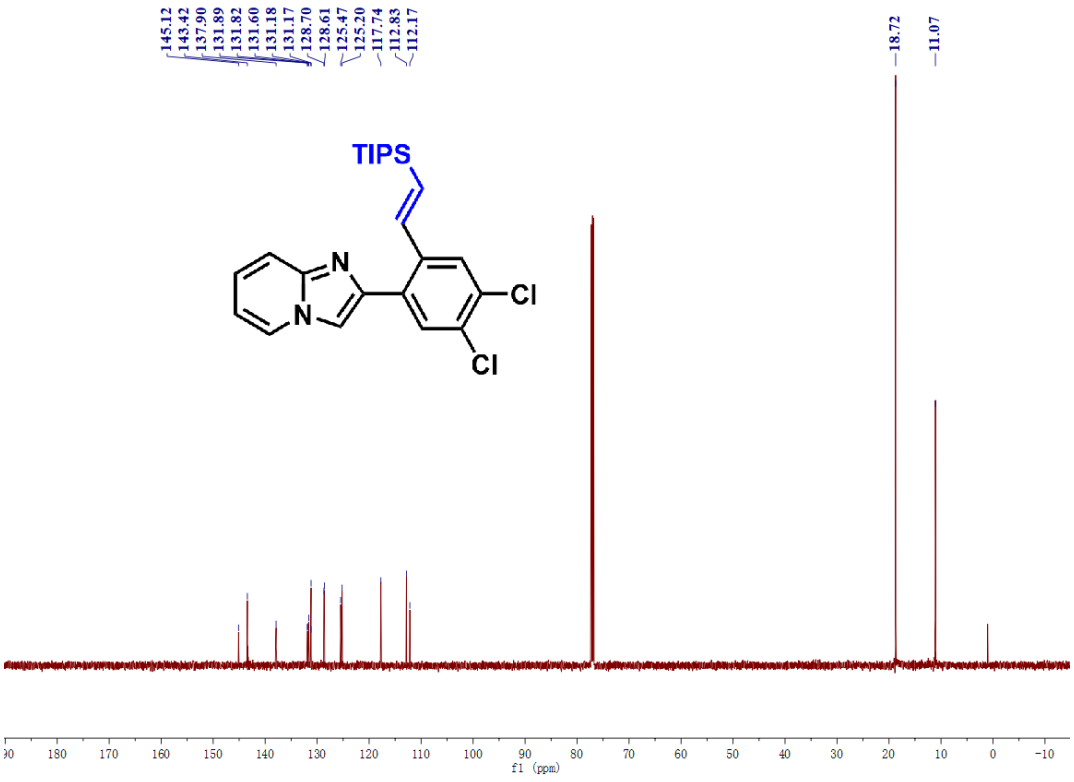
4ra$_1$ | $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz)



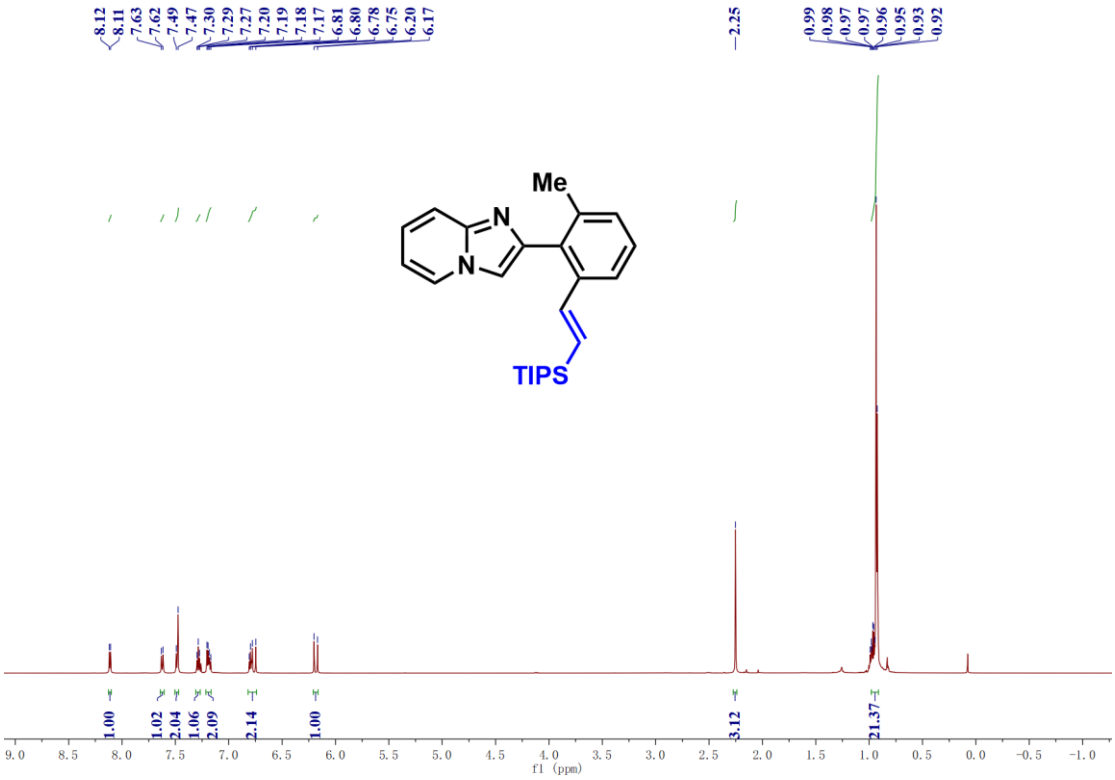
4qa$_1$ | ^{1}H NMR ($CDCl_3$, 600 MHz)



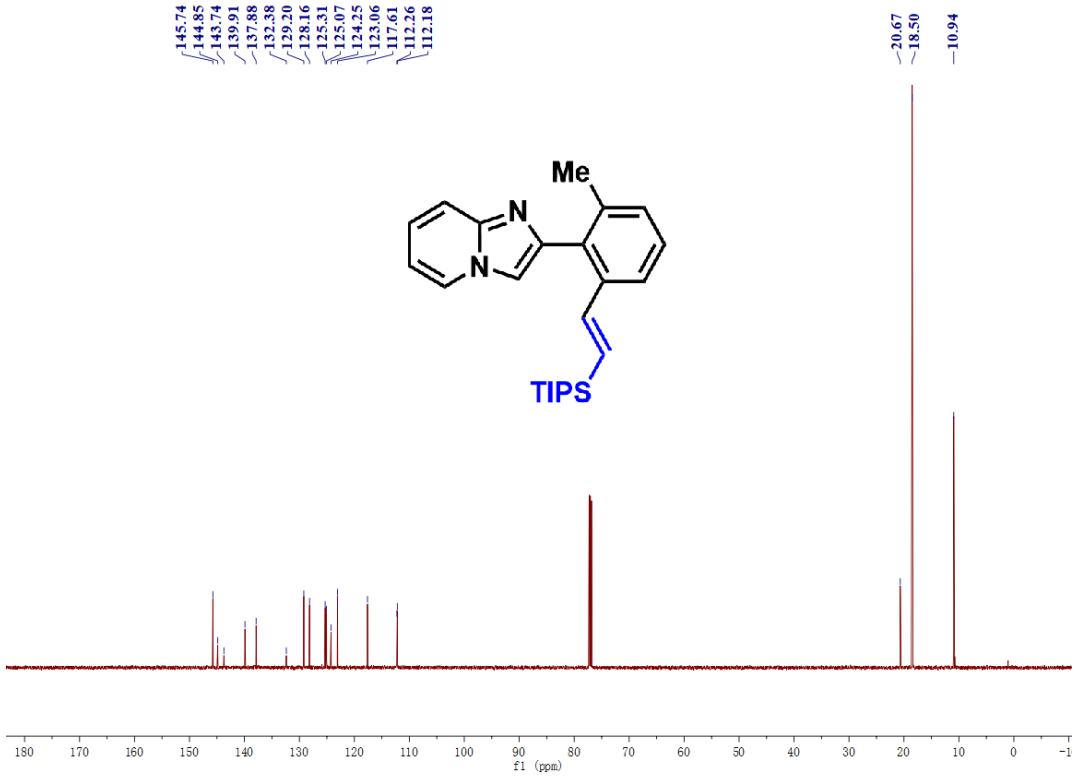
4qa$_1$ | $^{13}C\{^1H\}$ NMR (CCl_3, 151 MHz)



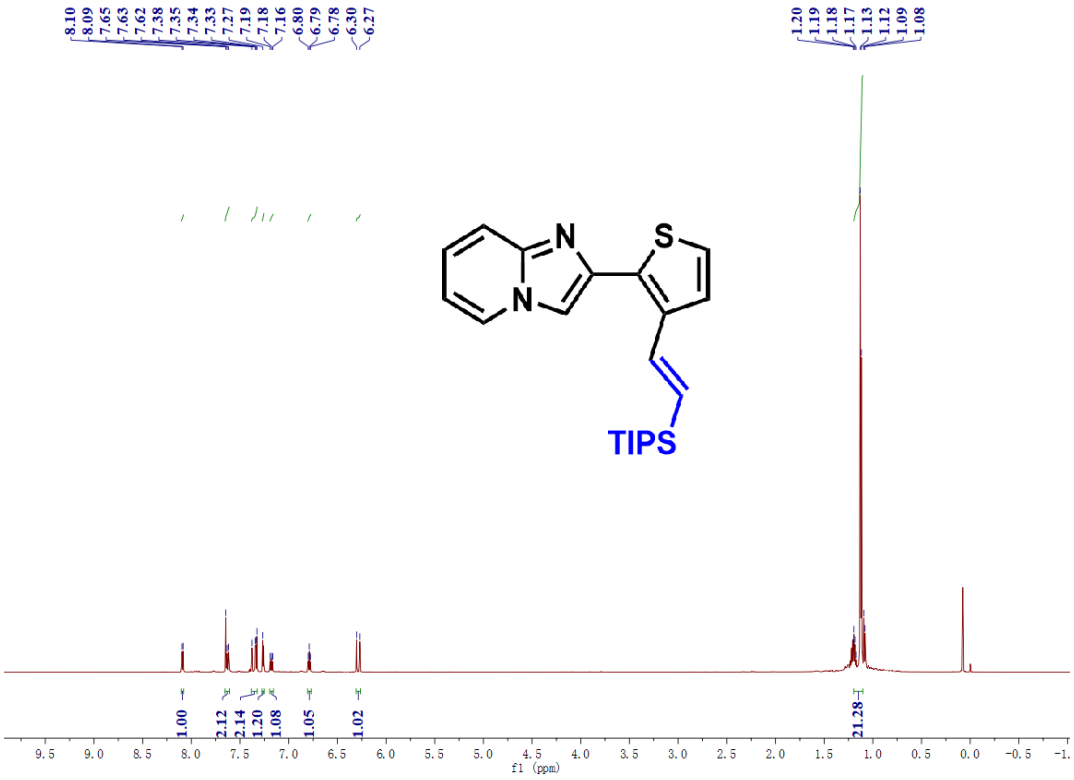
4sa | ^{1}H NMR ($CDCl_3$, 600 MHz)



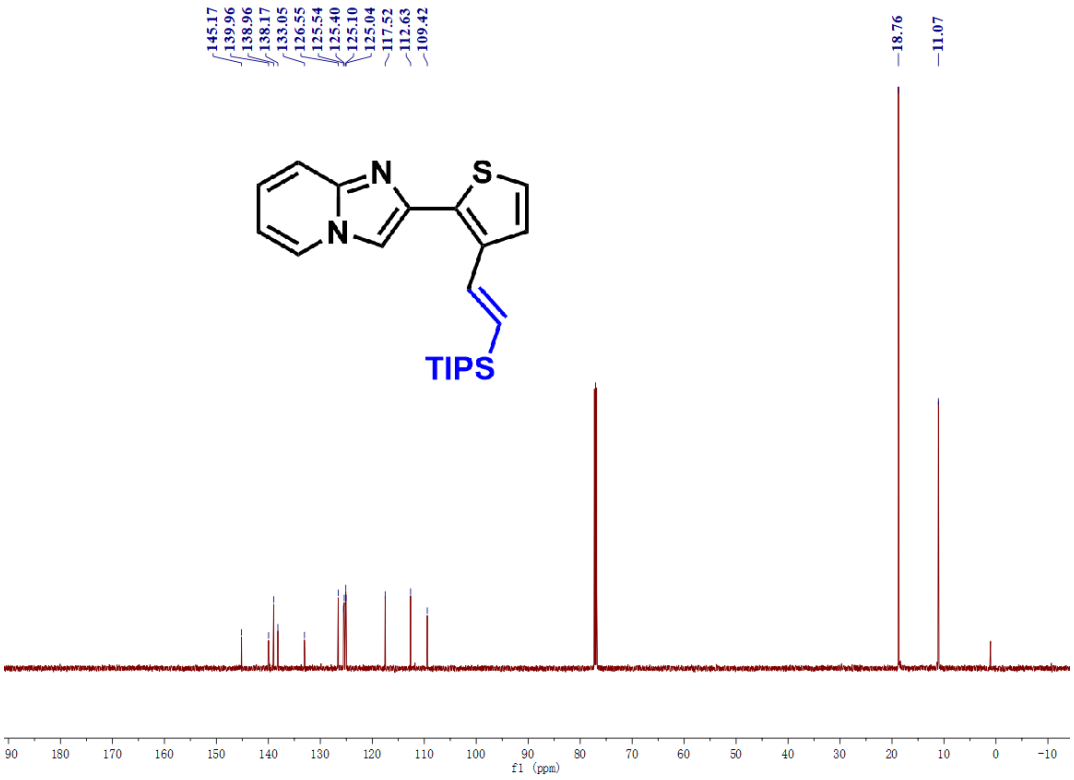
4sa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



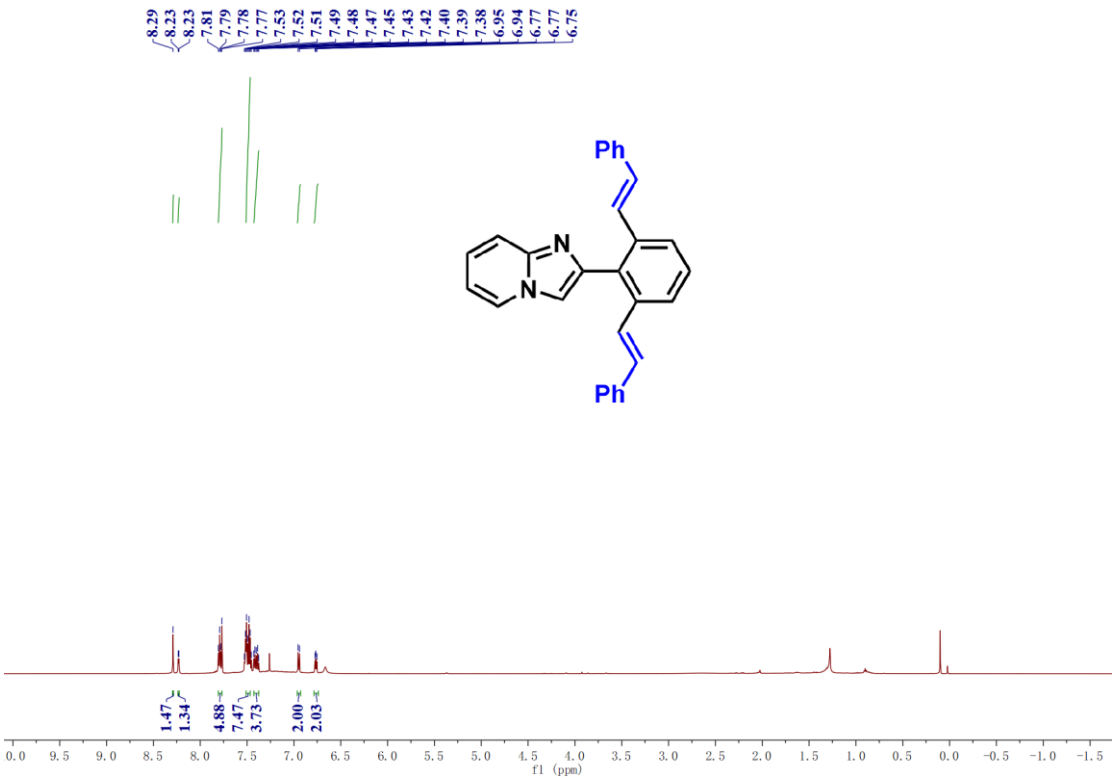
4ta | ^{1}H NMR ($CDCl_3$, 600 MHz)



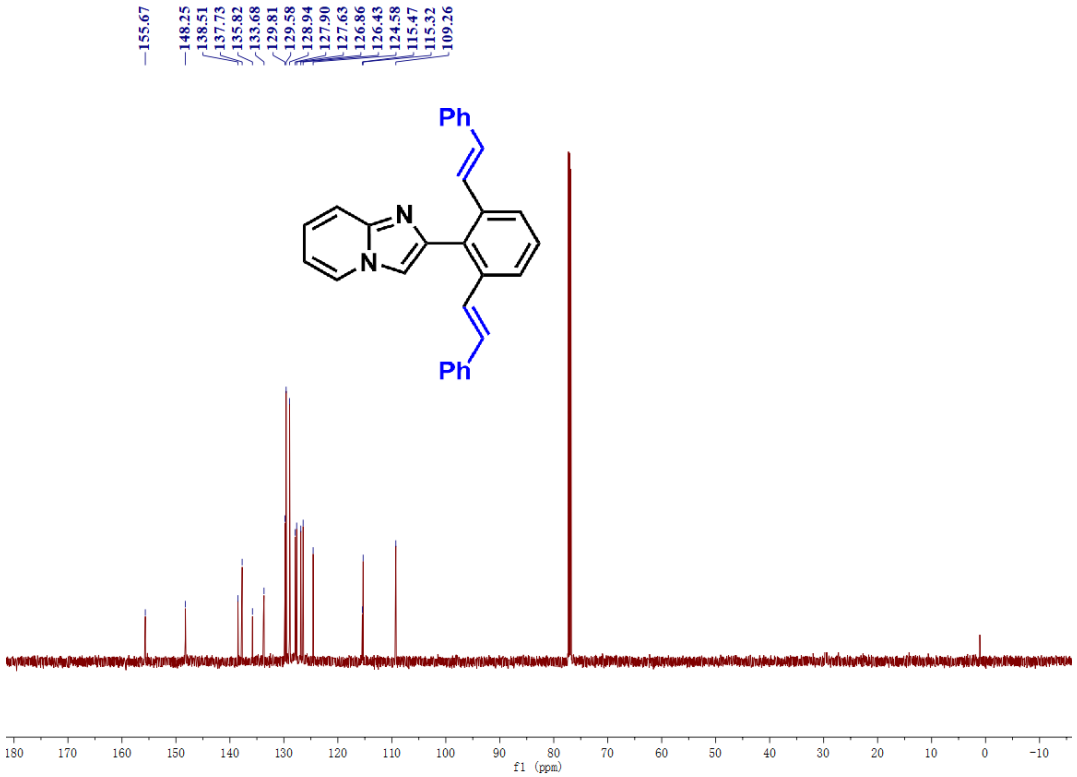
4ta | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



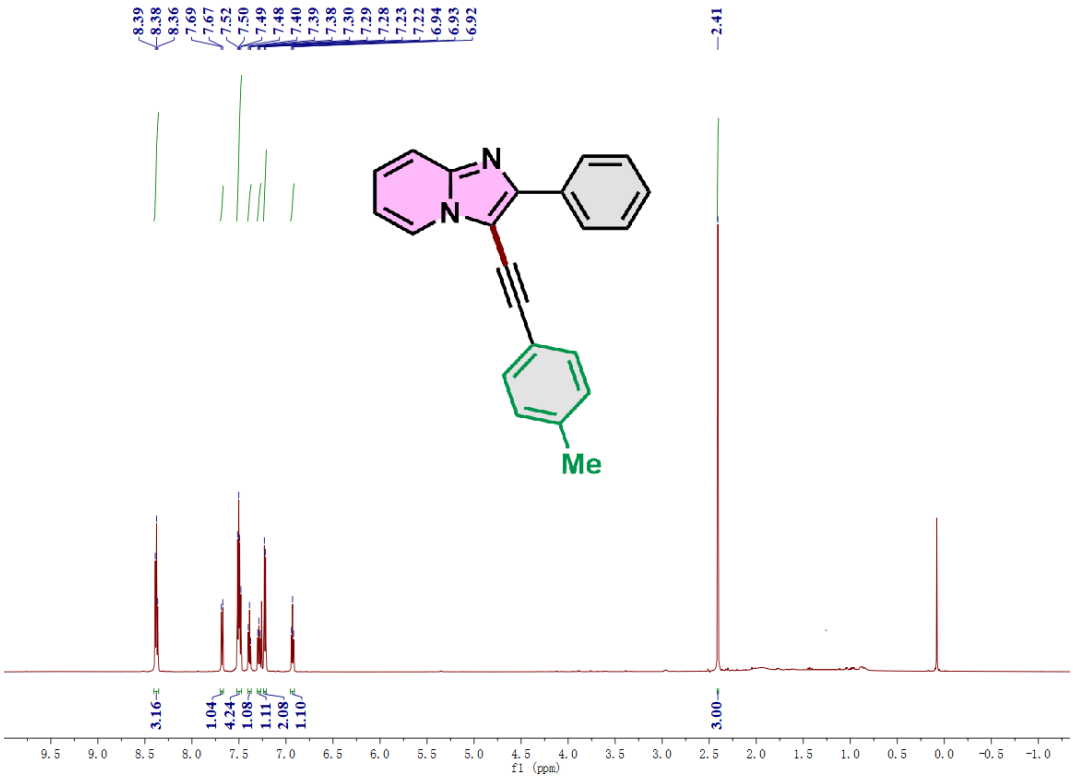
4ab | ^{1}H NMR ($CDCl_3$, 600 MHz)



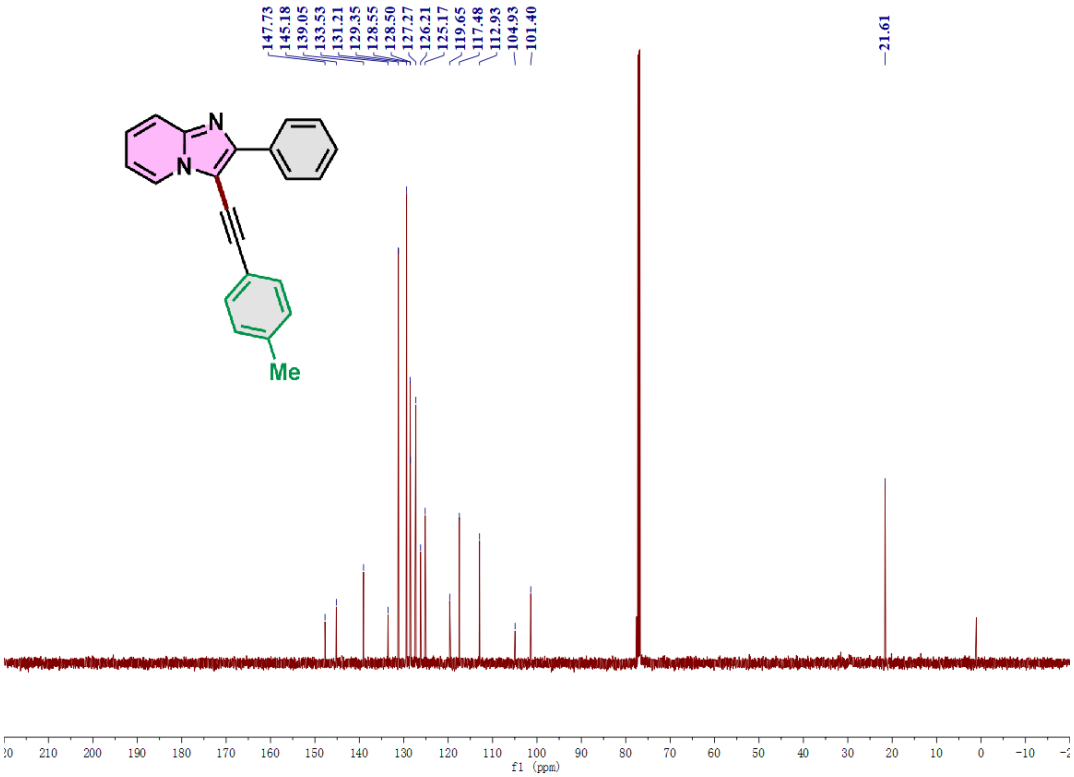
4ab | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



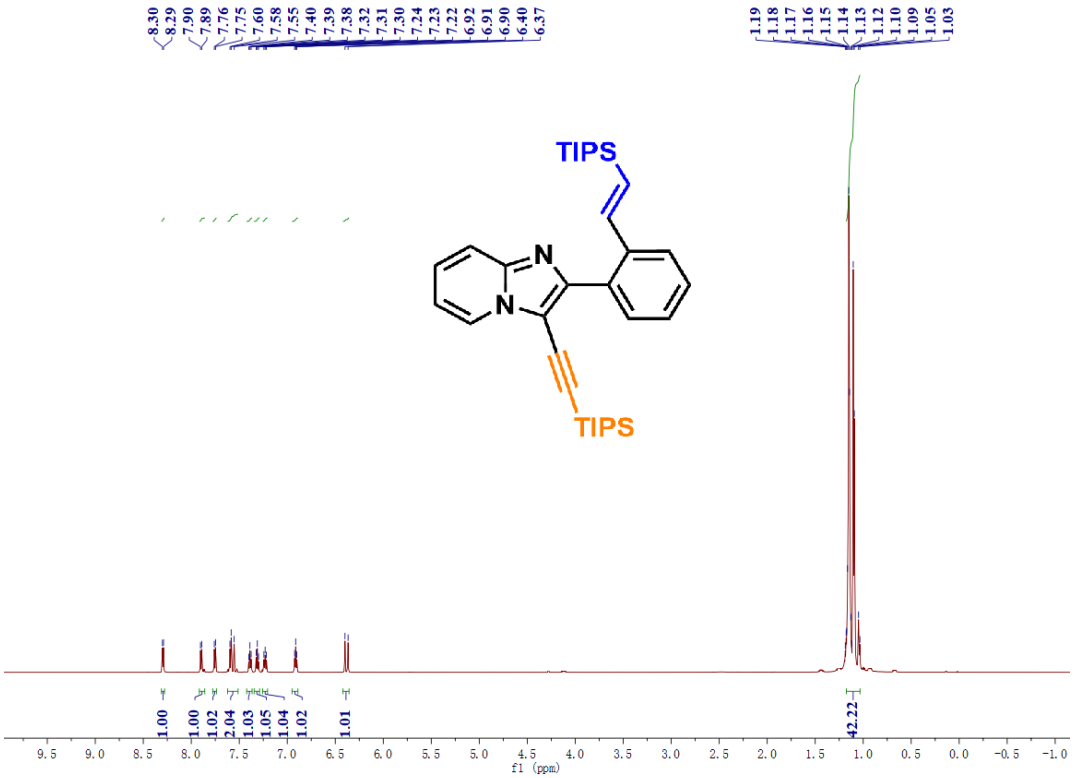
5 | ^{1}H NMR ($CDCl_3$, 600 MHz)



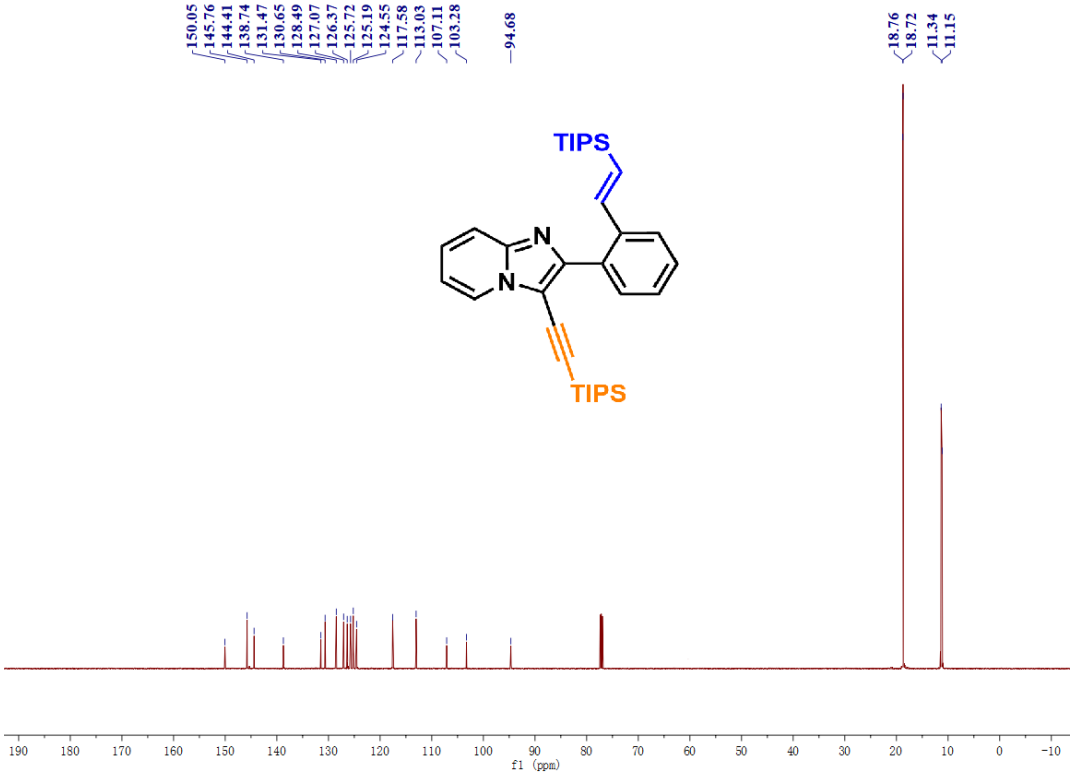
5 | $^{13}C\{^{1}H\}$ NMR (CCl_3, 151 MHz)



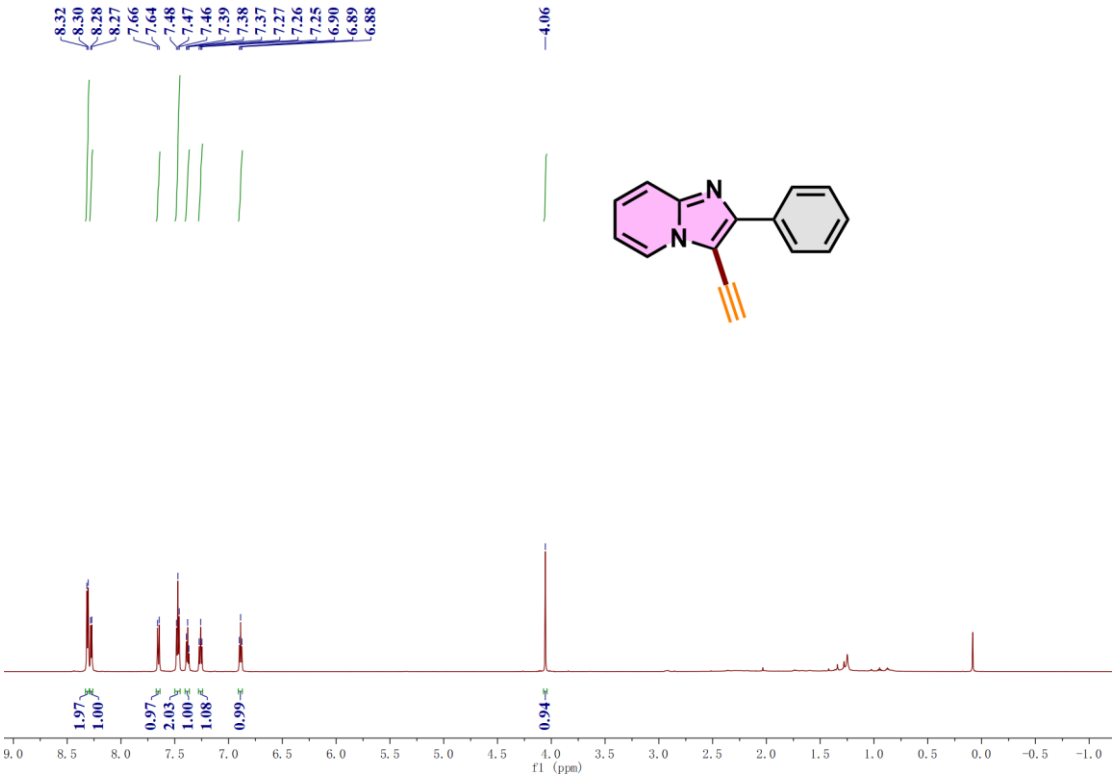
6 | ^{1}H NMR ($CDCl_3$, 600 MHz)



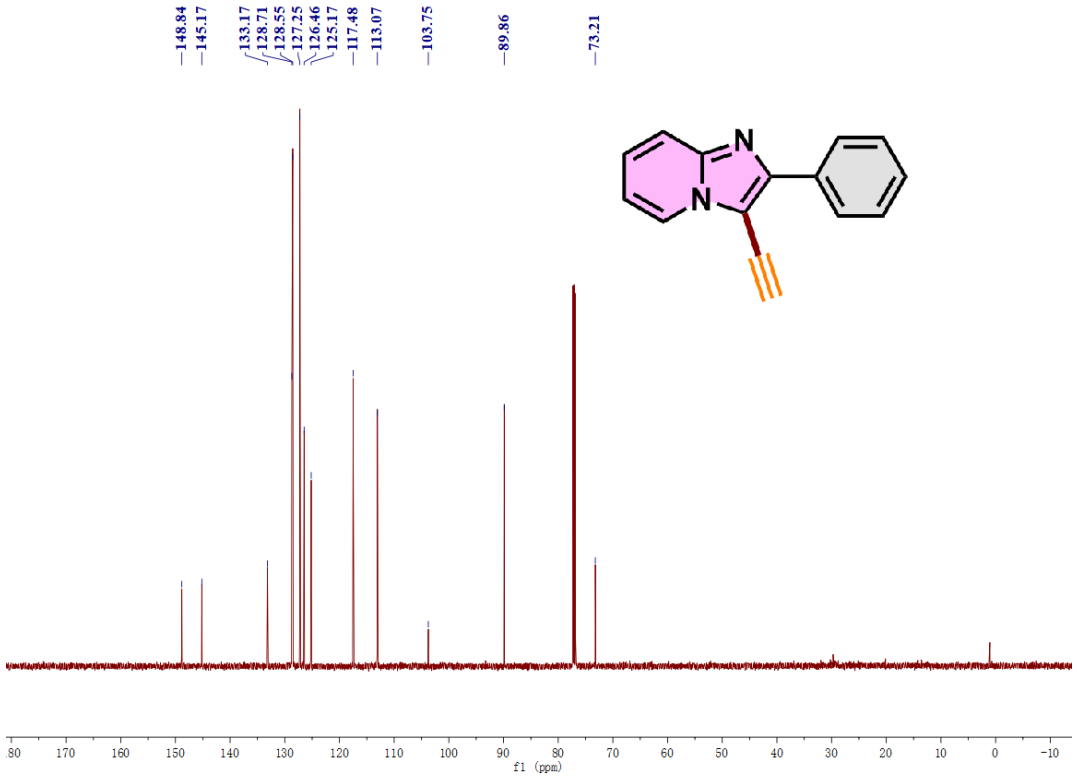
6 | ^{13}C{^{1}H} NMR (CCl_3, 151 MHz)



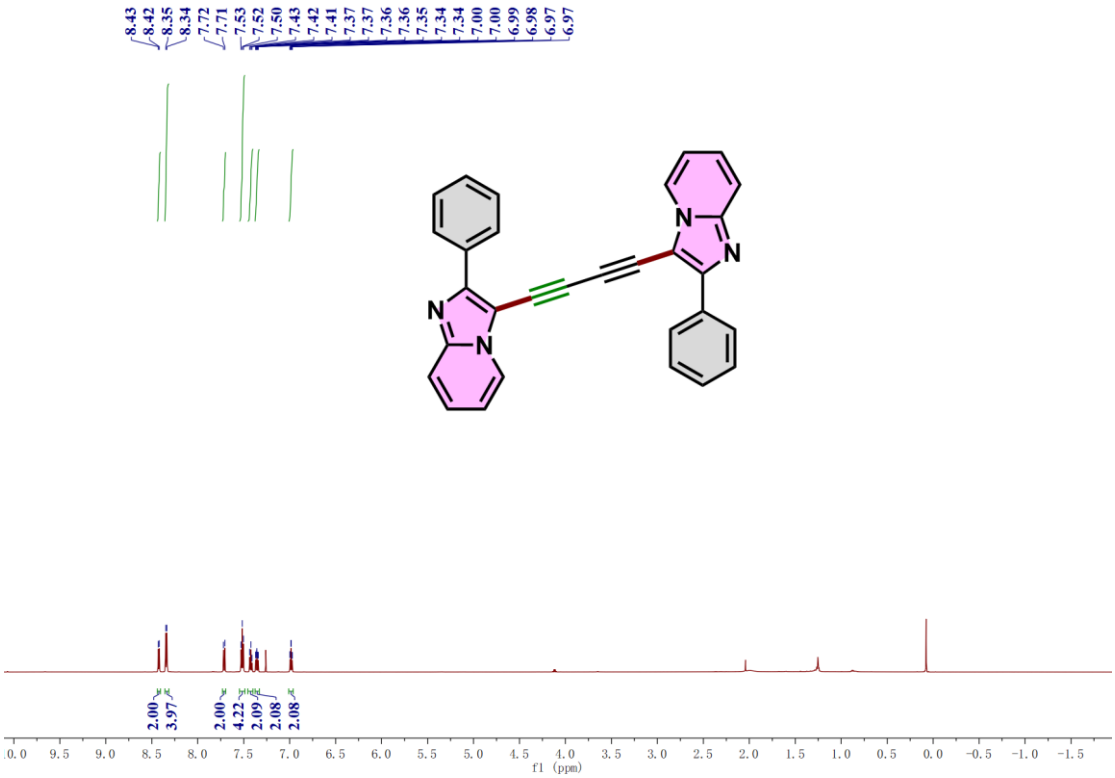
7 | ^{1}H NMR ($CDCl_3$, 600 MHz)



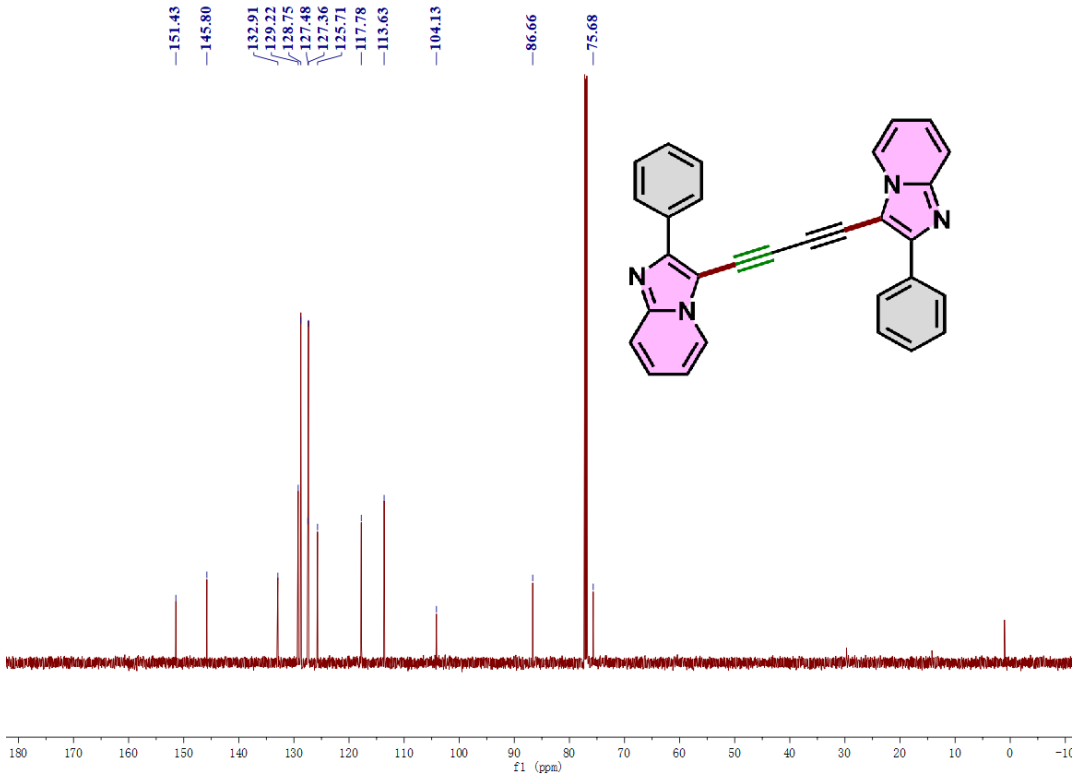
7 | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



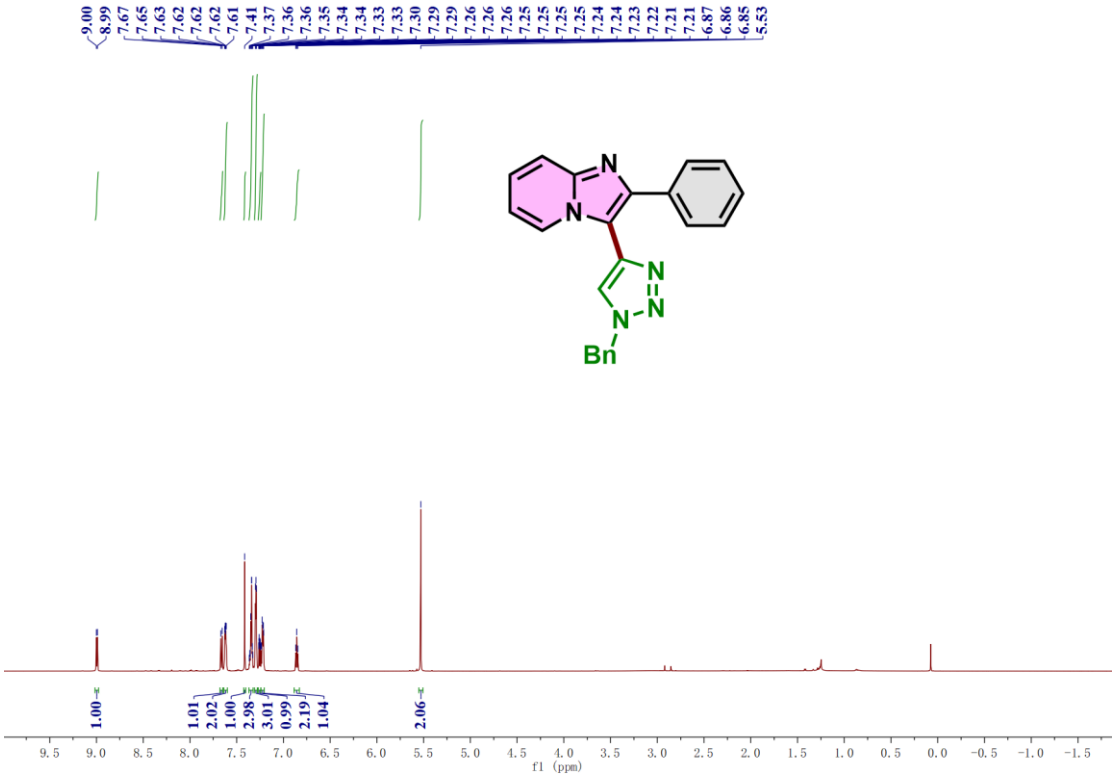
8 | ^{1}H NMR ($CDCl_3$, 600 MHz)



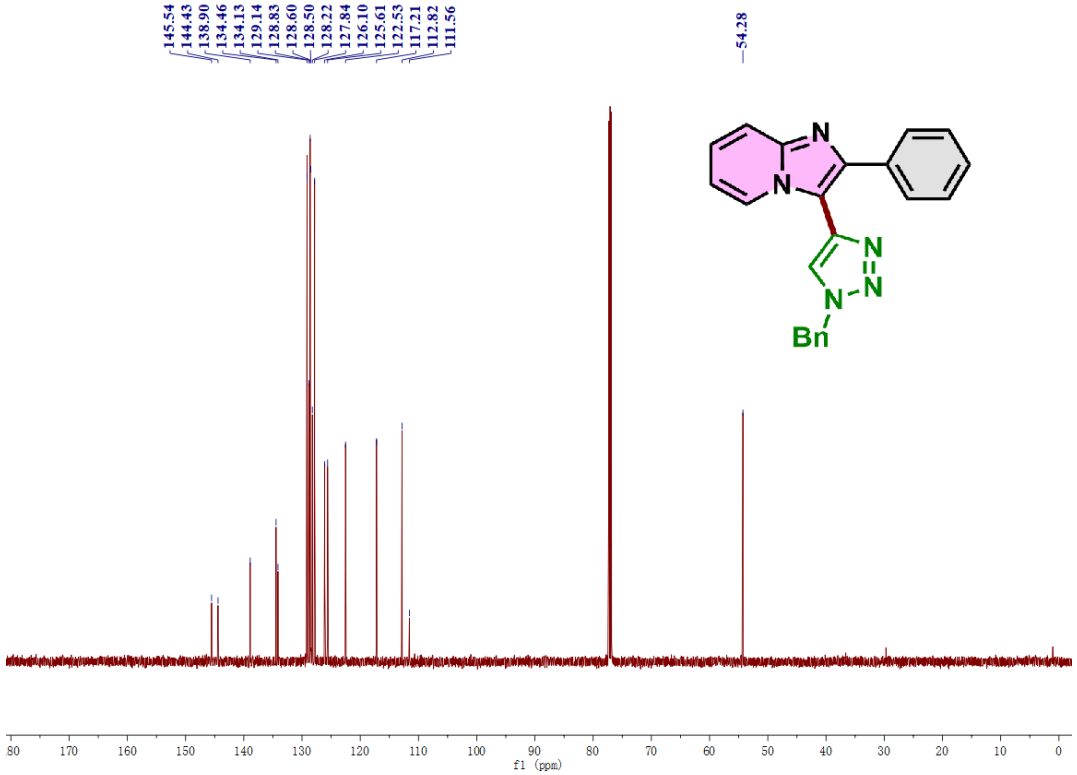
8 | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



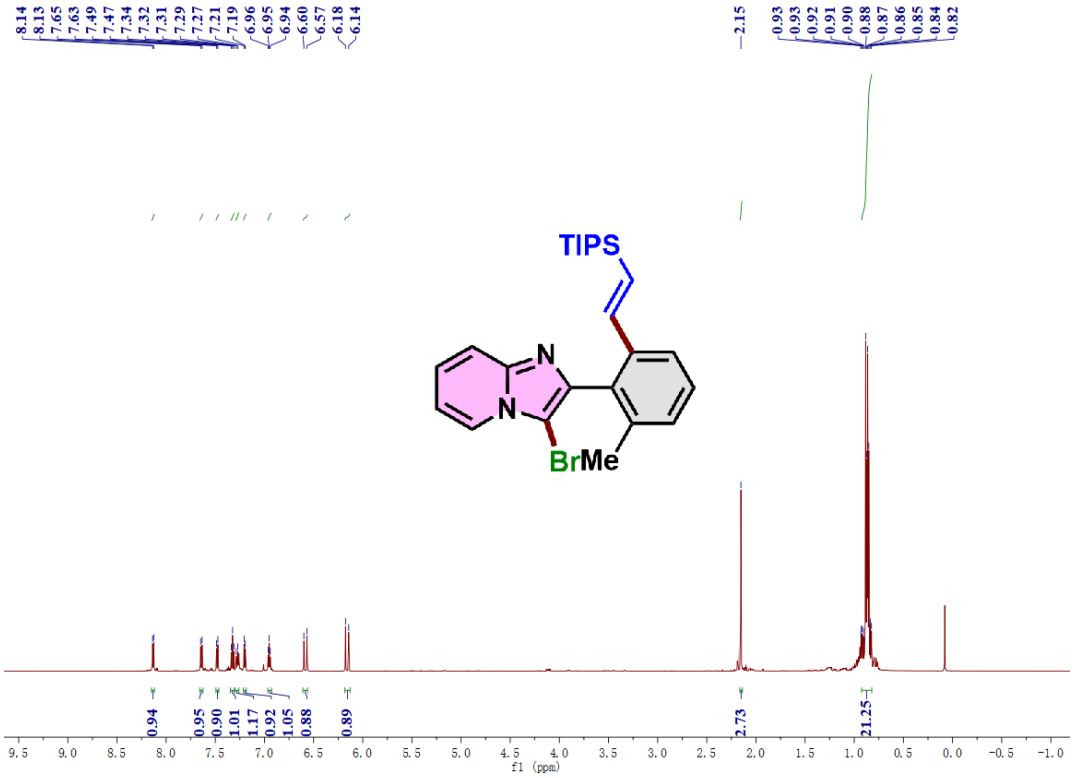
9 | ^{1}H NMR ($CDCl_3$, 600 MHz)



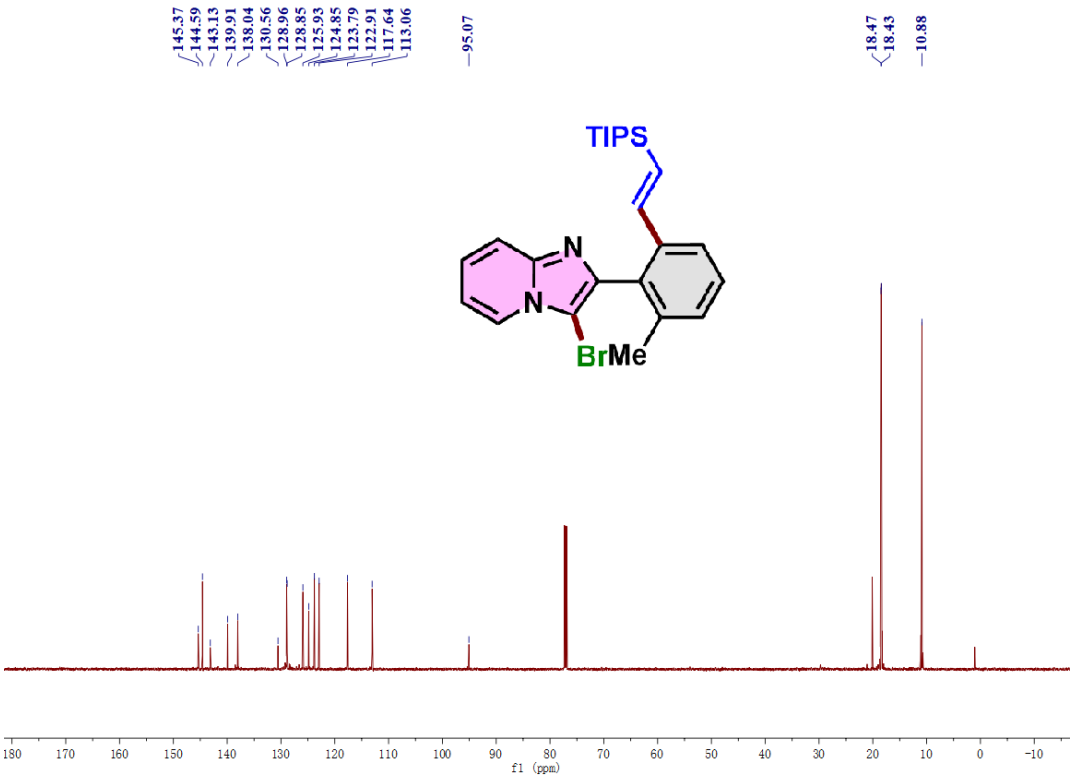
9 | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



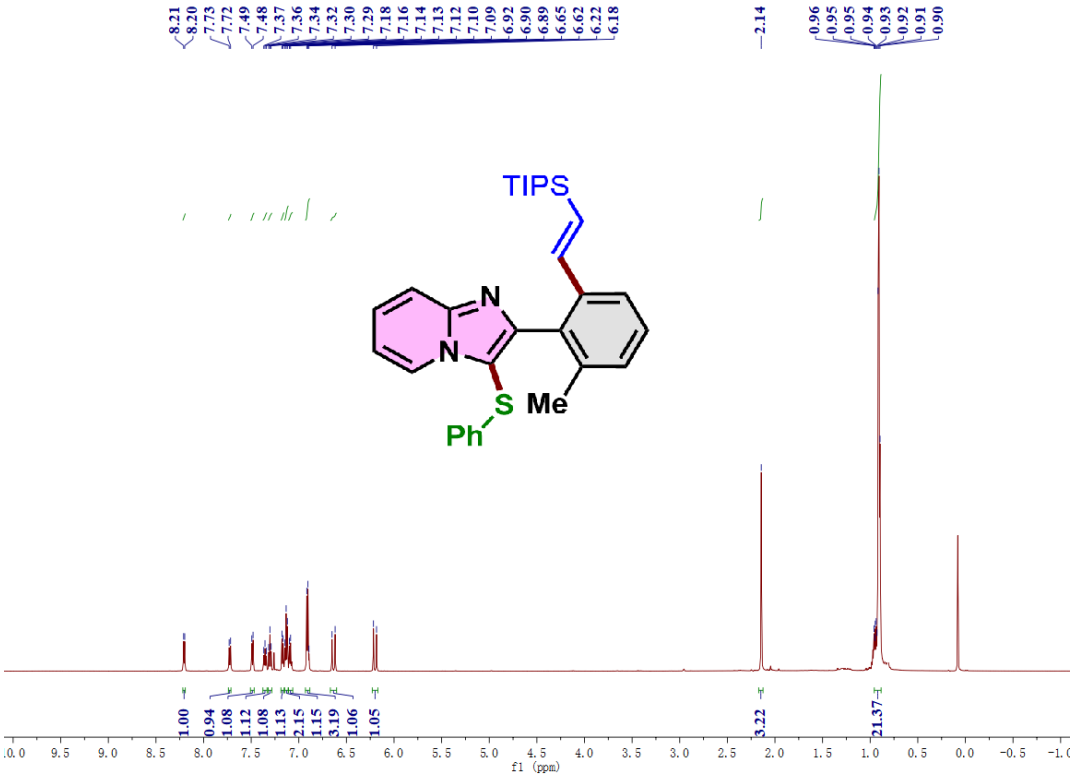
10 | ^{1}H NMR ($CDCl_3$, 600 MHz)



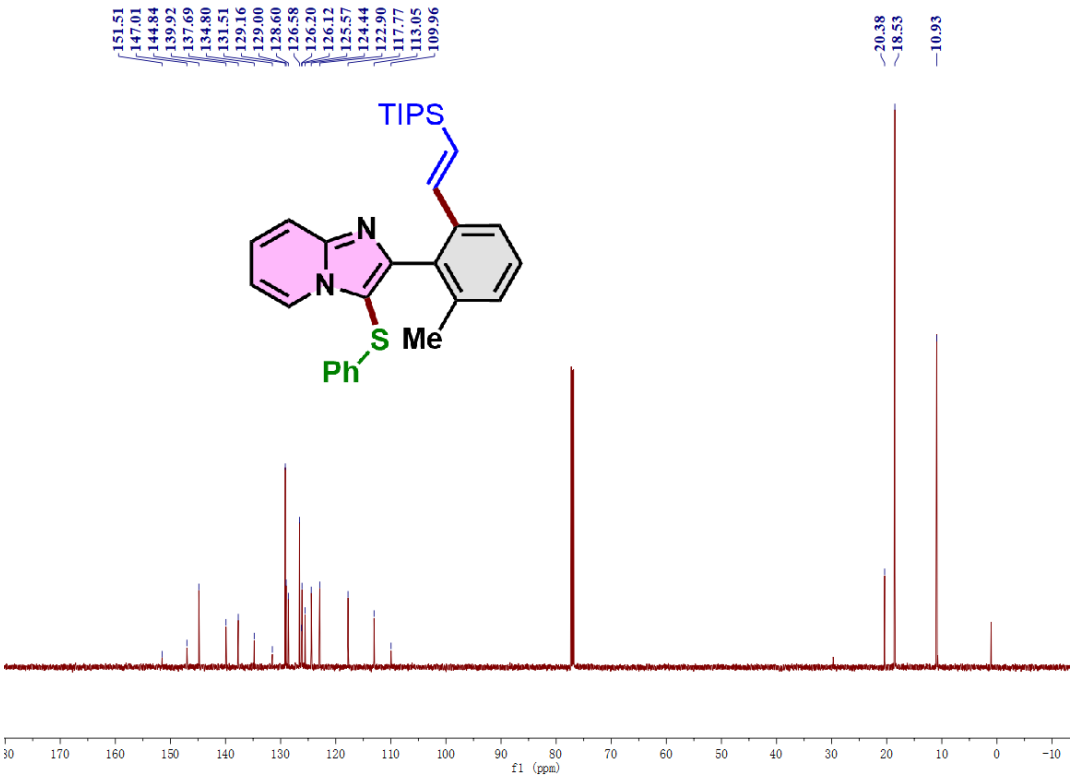
10 | ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz)



11 | ^{1}H NMR ($CDCl_3$, 600 MHz)



11 | ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz)



6. References

1. Su, H.; Wang, L.; Rao, H.; Xu, H. Iron-Catalyzed Dehydrogenative sp^3–sp^2 Coupling *via* Direct Oxidative C−H Activation of Acetonitrile. *Org. Lett.* **2017**, 19, 2226−2229.
2. Ge, W. L.; Zhu, X.; Wei, Y. Y. Aerobic Multicomponent Tandem Synthesis of 3-Sulfenylimidazo[1,2-*a*] pyridines from Ketones, 2-Aminopyridines, and Disulfides. *Eur. J. Org. Chem*. **2013**, 27, 6015–6020.
3. Liu, Y. P.; Lu, L. X.; Zhou, H. P.; Xu, F. J.; Ma, C.; Huang, Z. J.; Xu, J. Y.; Xu, S. T. Chemodivergent synthesis of *N*-(pyridin-2-yl)amides and 3-bromoimidazo[1,2-*a*]pyridines from *α*-bromoketones and 2-aminopyridines. *RSC Adv.* **2019**, 9, 34671–34676.