Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-Catalyzed Domino Heck-Disilylation and -Borylation of Alkene-Tethered 2-(2-halophenyl)-1*H*-indoles: Access to Diverse Disilylated and Borylated Indolo[2,1-*a*]isoquinolines

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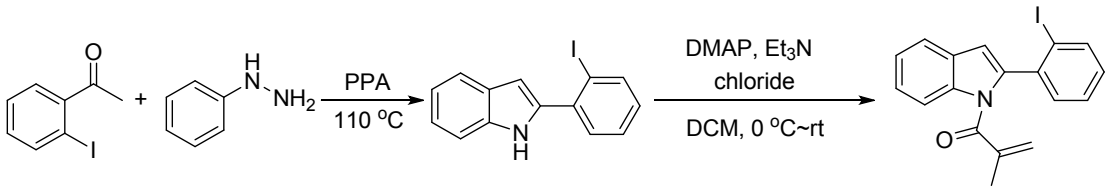
1 General Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance-500 instruments or Avance-400 instruments (^{1}H NMR at 500 or 400 MHz and ^{13}C NMR at 125 or 100 MHz), NMR spectra of all products were reported in ppm with reference to solvent signals [^{1}H NMR: $CD(H)Cl_3$ (7.26 ppm), ^{13}C NMR: $CD(H)Cl_3$ (77.00 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; dd, doublets of doublet; t, triplet, and m, multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC system coupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated.

2 Preparation of Substrates

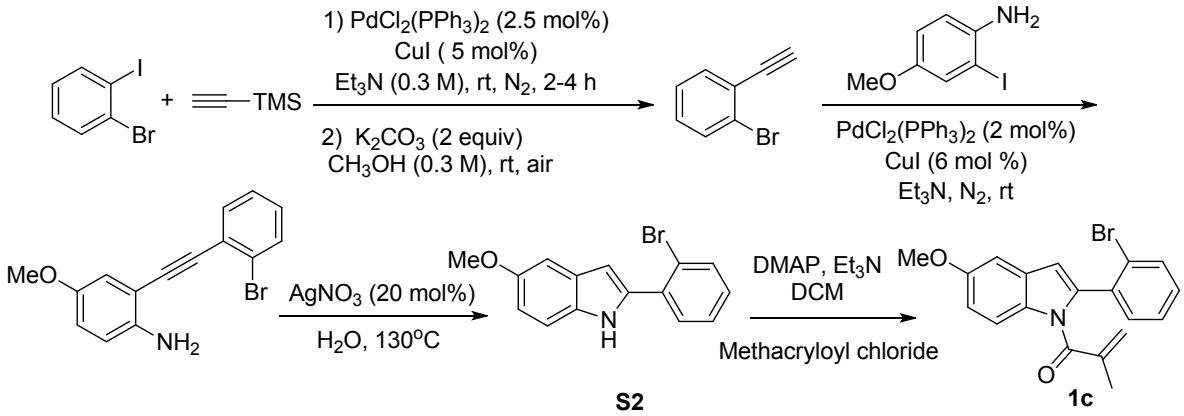
2.1 General Procedure for the Synthesis of Substrates 1a, 1b, 1d-1f, 1h and 1j-1l[1,2,3]



Step I: A mixture of 2-iodoacetophenone (5.0 mmol, 1.23 g), phenylhydrazine (6.0 mmol, 1.2 equiv, 648 mg) and polyphosphoric acid (PPA, 15.00 g) was added to a round bottom flask and stirred at 110 °C for 6 h. After the completion of the reaction, the residue was quenched with ice water and extracted into ethyl acetate. The organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc) to give the corresponding substituted indole **S1** (70%, 1.12 g)**.**

Step II: According to a literature procedure, to the solution of indole **S1** (3.5 mmol, 1.12 g) and DMAP (0.7 mmol, 0.2 equiv, 85 mg) in DCM (0.5 M) was added Et_3N (7mmol, 2.0 equiv, 707 mg) and chloride (4.2 mmol, 1.2 equiv, 437 mg) at 0 °C. The solution was warmed up to room temperature and stirred for overnight. The mixture was diluted with DCM (20 mL). The organic and aqueous layers were separated. The aqueous layer was extracted with DCM (20 mL x 2 times). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to give a residue, which was purified by flash chromatography and then recrystallized from n-hexane/EtOAc to afford the product **1a** (50%, 677 mg). The synthesis process of substrates **1b, 1d-1f, 1h** and **1j-1l** is similar to **1a**.

2.2 Synthesis of Substrates 1c and 1g[4,5]



Under nitrogen atmosphere, to a sealed tube (50 mL) was added $PdCl_2(PPh_3)_2$ (0.125 mmol, 2.5 mol%, 88 mg), CuI (0.25 mmol, 5 mol%, 48 mg) and Et_3N (15 mL), 2-iodobromobenzene (5.0 mmol, 1.48 g) and trimethylsilylacethylene (6.0 mmol, 1.2 equiv, 588 mg). After stirring at room temperature for 2-4 h, The filtrate was washed with H_2O and brine, dried over Na_2SO_4 and concentrated in vacuo and The crude product obtained was used in the next step without further purification.

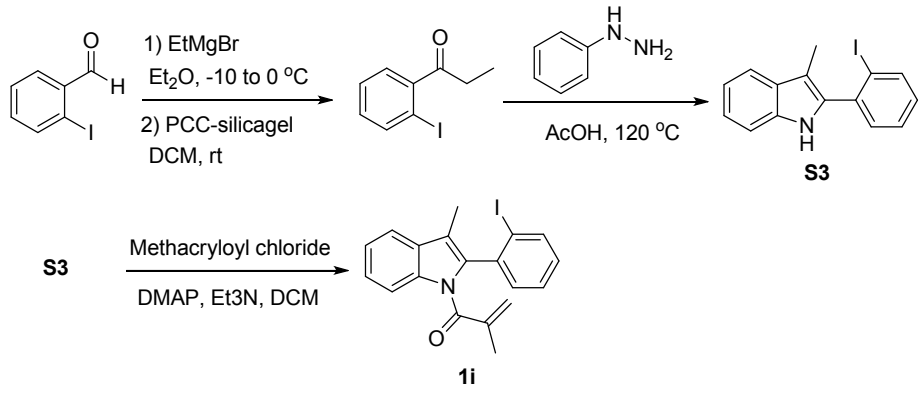
To the solution of crude product ((2-bromophenyl)ethynyl)trimethylsilane (5.0 mmol, 1.26 g) in MeOH (10 mL) was added K_2CO_3 (12.0 mmol, 1.66 g). After stirring at room temperature for 4 h, the mixture was diluted with Et_2O and filtered. The filtrate was washed with H_2O and brine, dried over Na_2SO_4 and concentrated in

vacuo. The residue was chromatographed on silica gel (hexane/EtOAc = 40/1) to afford the title compound 1-bromo-2-ethynylbenzene (90%, 810 mg) as a yellow oil.

A mixture of 2-iodo-4-methoxyaniline (3.0 mmol, 747 mg), 1-bromo-2-ethynylbenzene (4.5 mmol, 1.5 equiv, 810 mg), CuI (0.18 mmol, 6 mol%, 34 mg) and $PdCl_2(PPh_3)_2$ (0.06 mmol, 2 mol%, 42 mg) in Et_3N (3 ml) and THF (12 ml) was reacted at room temperature for 2-4 h under an nitrogen atmosphere. The filtrate was concentrated in vacuo. The solvent was evaporated and the residue was purified by column chromatography on silica gel to afford the desired products.

To a sealed tube (50 mL) was added 2-((2-bromophenyl)ethynyl)-4-methoxyaniline (1.5 mmol, 510 mg), H_2O (15 mL), and $AgNO_3$ (0.3 mmol, 20 mol%, 51 mg). The mixture was stirred at 130 °C for about 18-24 h. The reaction product was filtered, washed with H_2O, and dried to give a brown solid **S2** (78%, 353 mg). The following acylation procedure (similar to **1a**) will deliver substrate **1c** (52%, 216 mg). The synthesis process of substrate **1g** is similar to **1c**.

2.3 Synthesis of Substrate 1i[3,6]



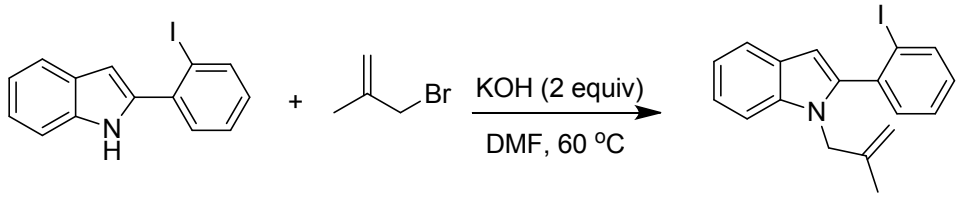
According to a modified literature procedure[6],To a cold (−10 °C), magnetically stirred solution of a 2-iodobenzaldehyde (5 mmol, 2.32 g) in dry ether (20 mL) was added ethylmagnesium bromide (10 mmol, 1.0M) The reaction mixture was stirred at −10 °C to 0 °C for 3 h. It was then poured into saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 15). The ethyl acetate extract was dried with Na_2SO_4 and concentrated in vacuo and The crude product obtained was used in the next step without further purification

To a magnetically stirred solution of the crude product secondary alcohol (5

mmol) in dry CH_2Cl_2 (10 mL) was added a homogeneous mixture of PCC (10 mmol) and silica gel. The resulted reaction mixture was stirred at room temperature for 2 h. The reaction mixture was then filtered through a short silica gel column and eluted with excess CH_2Cl_2 .Evaporation of the solvent furnished the ketone.

According to a modified literature procedure, a mixture of phenylhydrazine (6.6 mmol, 1.1 equiv, 712 mg), 1-(2-iodophenyl)propan-1-one (5.0 mmol, 1.0 equiv, 1.30 g) and acetic acid (10 mL, 1.0 M) was heated to 120 ºC for 24 h in a 100 mL schlenk tube under N_2 atmosphere. The reaction mixture was cooled to rt., AcOH was removed by rotory evaporation and the residue was portioned between water (50 mL) and EtOAc (20 mL). The organic and aqueous layers were separated. The aqueous layer was extracted with EtOAc (20 mL x 2 times), and the combined organic phase was washed with a saturated solution of sodium bicarbonate (20 mL) and brine (20 mL), dried with Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography to afford the desired product indole **S3** (60%, 999 mg)**.** The following acylation procedure (similar to **1a**) will deliver substrate **1i** (56%, 675 mg).

2.4 Synthesis of Substrates 2a, 2b, 2d, 2e and 2h[1,2,7]

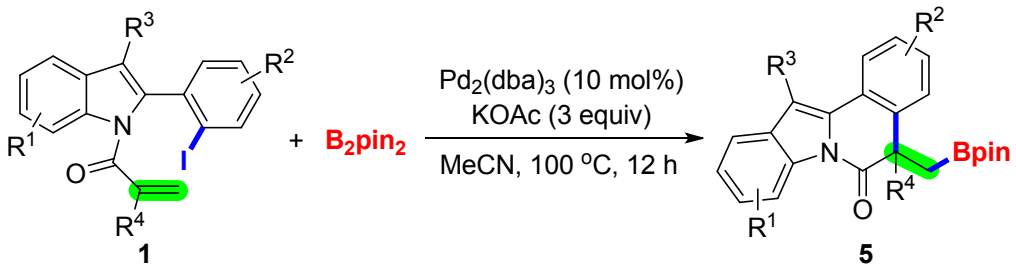


S1 **4a**

According to a literature procedure[7], a solution of **S1** (3.0 mmol, 955 mg) in DMF (5 mL) and powdered KOH (3.9 mmol, 1.3 equiv, 218 mg) was stirred at 60 °C for 10 min, cooled to room temperature, and treated with 3-bromo-2-methylprop-1-ene (4.5 mmol, 1.5 equiv, 600 mg). The reaction mixture was stirred at 60 °C for 12-18 h, poured onto ice and diluted with 15 mL of EtOAc. The combined organic layers were washed with H_2O, brine, dried Na_2SO_4, concentrated in vacuo and purified by chromatography on SiO_2 (hexane) to afford the desired product **2a** (63%, 700 mg). The synthesis process of substrates **2b, 2d, 2e** and **2h** is similar to **2a**.

3 Typical Procedures

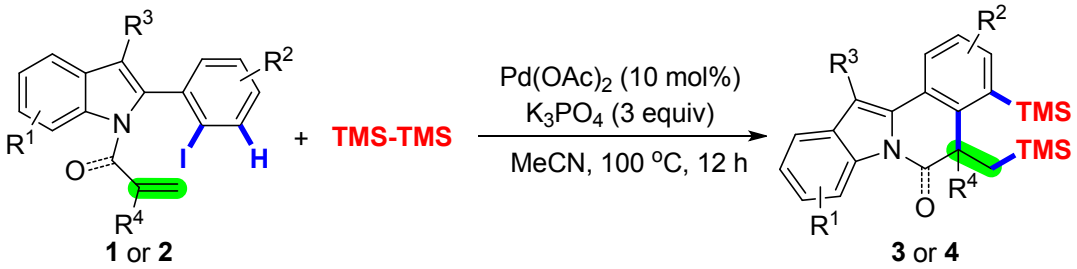
3.1 Table S1. Screening of Optimal Reaction Conditions[a]



Entry	Pd catalyst	Ligand	Base	Solvent	Yield/%[b]
1	$Pd(OAc)_2$		K_3PO_4	MeCN	38
2	$[Pd(\pi\text{-ally})Cl]_2$		K_3PO_4	MeCN	52
3	$PdCl_2$		K_3PO_4	MeCN	55
4	$Pd_2(dba)_3$		K_3PO_4	MeCN	62
5	$Pd(PPh_3)_4$		K_3PO_4	MeCN	50
6	$Pd_2(dba)_3$	PPh_3	K_3PO_4	MeCN	42
7	$Pd_2(dba)_3$	$P(^tBu)_3$	K_3PO_4	MeCN	52
8	$Pd_2(dba)_3$	X-Phos	K_3PO_4	MeCN	15
9	$Pd_2(dba)_3$		Na_2CO_3	MeCN	35
10	$Pd_2(dba)_3$		NaOAc	MeCN	62
11	$Pd_2(dba)_3$		KOAc	MeCN	74
12	$Pd_2(dba)_3$		KOAc	Tol	60
13	$Pd_2(dba)_3$		KOAc	Dioxane	56
14	$Pd_2(dba)_3$		KOAc	DMF	45

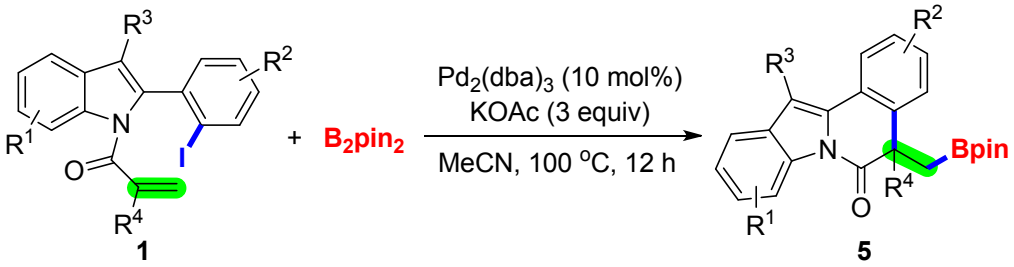
[a]Reaction conditions: 1 (0.2 mmol), B_2pin_2 (3 equiv), $Pd_2(dba)_3$ (10 mol%), KOAc (3 equiv), and MeCN (2 mL) at 100 °C under N_2 for 12 h. [b] Isolated yield.

3.2 General Procedure for the Synthesis of Disilyated Indolo[2,1-*a*]isoquinolinones 3 and 4



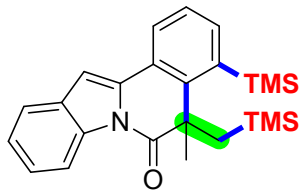
To a Schlenk tube were added alkene-tethered aryl iodides **1** or **2** (0.2 mmol, 1.0 equiv), Hexamethyldisilane (0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (0.02 mmol, 10 mol%, 4.5 mg), K_3PO_4 (0.6 mmol, 3.0 equiv, 127.2 mg), and MeCN (2 mL). Then the tube was charged with nitrogen, and was stirred at 100 °C (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (petroleum ether/EtOAc) to give product **3 or 4.**

3.3 General Procedure for the Synthesis of Borlyated Indolo[2,1-*a*]isoquinolines 5

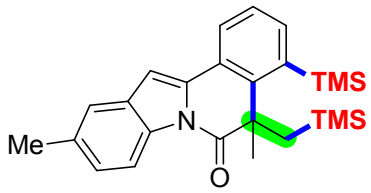


To a Schlenk tube were added alkene-tethered aryl iodides **1** (0.2 mmol, 1.0 equiv), Bis(pinacolato)diborane (0.6 mmol, 3.0 equiv), $Pd_2(dba)_3$ (0.02 mmol, 10 mol%, 18.3 mg), KOAc (0.6 mmol, 3.0 equiv, 58.9 mg), and MeCN (2 mL). Then the tube was charged with nitrogen, and was stirred at 100 °C (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (petroleum ether/EtOAc) to give product **5.**

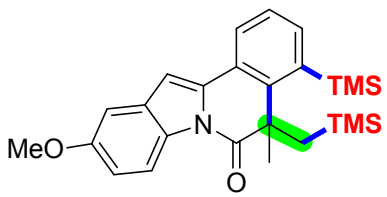
4 Characterization Data



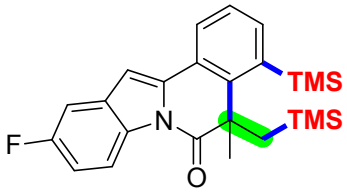
5-methyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3a): white solid, isolated yield 94% (76.27 mg), 90% (72.02 mg, alkene-tethered aryl bromides was used); mp: 83.1-85.8 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.61 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.40-7.36 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.05 (s, 1H), 1.90 (s, 3H), 1.75 (dd, *J* = 26.5 Hz, 14.5 Hz, 2H), 0.54 (s, 9H), -0.45 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.0, 145.2, 140.1, 138.2, 136.1, 134.9, 130.9, 126.1, 124.9, 124.7, 124.5, 123.5, 120.2, 116.8, 102.8, 47.6, 32.4, 32.0, 4.6, -1.2. HRMS (ESI) m/z calcd for $C_{24}H_{32}NOSi_2^+$ $(M+H)^+$ 406.2017, found 406.2030.



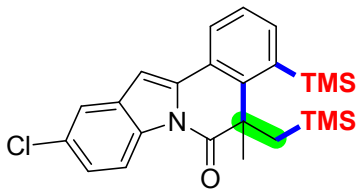
5,10-dimethyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3b): white solid, isolated yield 73% (62.27 mg); mp: 98.4-100.2 °C (uncorrected); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.48 (d, *J* = 8.2 Hz, 1H) , 7.88 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.39 (s, 1H), 7.33(t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.98 (s, 1H), 2.49 (s, 3H), 1.91 (s, 3H), 1.76 (dd, J = 14.4 Hz, *J* = 24.0 Hz, 2H), 0.54 (s, 9H), -0.44 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 173.7, 145.2, 140.1, 138.1, 136.2, 134.1, 133.1, 131.2, 126.2, 126.1, 124.7, 123.6, 120.2, 116.5, 102.6, 47.5, 32.4, 31.9, 21.5, 4.6, -1.2. HRMS (ESI) m/z calcd for $C_{25}H_{34}NOSi_2^+$ $(M+H)^+$ 420.2173, found 420.2185.



10-methoxy-5-methyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3c): white solid, isolated yield 90% (78.42 mg, alkene-tethered aryl bromides was used); mp: 58.8-60.6°C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.47 (d, *J* = 9.0 Hz, 1H), 7.86 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.76 (dd, *J* = 7.5 Hz, *J* = 1 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.97-6.95 (m, 2H), 3.88 (s, 3H), , 1.88 (s, 3H), 1.76-1.72 (m, 2H), 0.52 (s, 9H), -0.47 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 173.5, 157.1, 145.3, 140.2, 138.2, 136.8, 132.0, 129.6, 126.1, 124.7, 123.5, 117.6, 113.1, 103.1, 102.6, 55.6, 47.5, 32.4, 32.0, 4.6, -1.2. HRMS (ESI) m/z calcd for $C_{25}H_{34}NO_2Si_2^+$ $(M+H)^+$ 436.2123, found 436.2134.

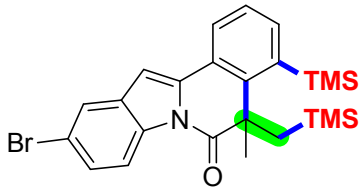


10-fluoro-5-methyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3d): white solid, isolated yield 92% (77.86 mg); mp: 104.1-105.9 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.54 (dd, *J* = 9.0 Hz, *J* = 4.5 Hz, 1H), 7.87 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.79 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.24 (dd, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H), 7.07 (td, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H) 6.99(s, 1H), 1.89 (s, 3H), 1.77-1.70 (m, 2H), 0.53 (s, 9H), -0.47 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 173.8, 160.3 (d, *J* = 239.8 Hz), 145.4, 140.3, 138.6, 137.7, 132.1 (d, *J* = 10.1 Hz), 131.2, 126.2, 124.8, 123.2, 117.8 (d, *J* = 9.0 Hz), 112.5 (d, *J* = 24.8 Hz), 105.9 (d, *J* = 24.0 Hz), 102.3 (d, *J* = 3.9 Hz), 47.6, 32.4, 31.9, 4.6, -1.2. HRMS (ESI) m/z calcd for $C_{24}H_{31}FNOSi_2^+$ $(M+H)^+$ 424.1923, found 424.1934.

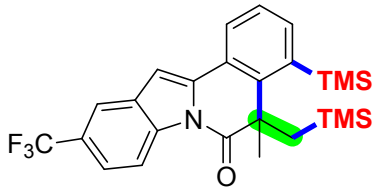


10-chloro-5-methyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3e): white solid, isolated yield 88% (77.46 mg); mp: 103.1-104.5 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.51 (d, *J* = 9.0 Hz, 1H), 7.87 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.80 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.55 (d, *J* =

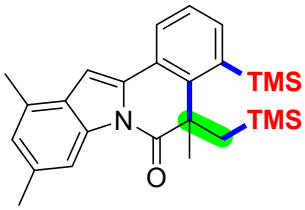
2.0 Hz, 1H), 7.35-7.30 (m, 2H), 6.96 (s, 1H), 1.89 (s, 3H), 1.77-1.73 (m, 2H), 0.53 (s, 9H), -0.47 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 173.9, 145.3, 140.2, 138.7, 137.5, 133.1, 132.2, 130.1, 126.2, 124.9, 124.8, 123.0, 119.8, 117.8, 101.8, 47.6, 32.5, 31.8, 4.5, -1.2. HRMS (ESI) m/z calcd for $C_{24}H_{31}ClNOSi_2^+$ $(M+H)^+$ 440.1627, found 440.1640.



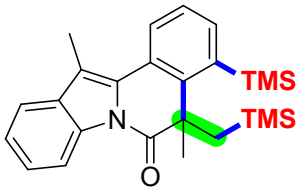
10-bromo-5-methyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3f): white solid, isolated yield 52% (50.39 mg); mp: 103.0-104.4 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.44 (d, *J* = 8.5 Hz, 1H), 7.87 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.79 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.45 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 1.88 (s, 3H), 1.72 (dd, *J* = 17.5 Hz, *J* = 14.0 Hz, 2H), 0.52 (s, 9H), -0.49 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.0, 145.4, 140.3, 138.7, 137.4, 133.6, 132.7, 127.7, 126.3, 124.9, 123.0, 122.9, 118.2, 118.0, 101.7, 47.7, 32.5, 31.9, 4.6, -1.2. HRMS (ESI) m/z calcd for $C_{24}H_{31}BrNOSi_2^+$ $(M+H)^+$ 484.1122, found 482.1134.



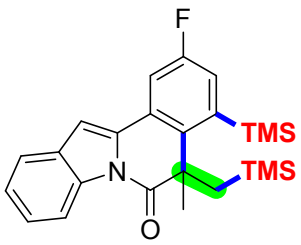
5-methyl-10-(trifluoromethyl)-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3g): colorless oil, isolated yield 30% (28.42 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.71 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 10.4 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 1.92 (s, 3H), 1.76 (t, *J* = 16.0 Hz, 2H), 0.55 (s, 9H), -0.44 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 174.2, 145.4, 140.4, 138.9, 138.0, 136.4, 130.7, 127.3, 126.6 (d, *J* = 32.0 Hz), 126.4, 125.0, 124.6 (q, *J* = 270.6 Hz), 122.9, 121.6 (q, *J* = 3.2 Hz), 117.5 (q, *J* = 4.6 Hz), 117.0, 102.4, 47.8, 32.5, 31.9, 4.5, -1.2. HRMS (ESI) m/z calcd for $C_{25}H_{31}F_3NOSi_2^+$ $(M+H)^+$ 474.1891, found 474.1902.



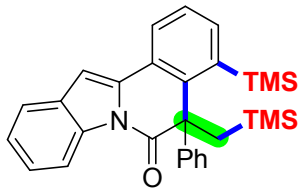
5,9,11-trimethyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3h): white solid, isolated yield 84% (72.86 mg); mp: 149.1-151.3 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.27 (s, 1H), 7.91 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.75 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 6.99 (s, 1H), 2.56 (s, 3H), 2.49 (s, 3H), 1.89 (s, 3H), 1.74 (dd, *J* = 25.0 Hz, *J* = 14.0 Hz, 2H), 0.53 (s, 9H), -0.45 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.1, 144.8, 140.0, 137.8, 135.2, 135.1, 134.9, 129.1, 128.2, 126.6, 126.1, 124.5, 123.8, 114.6, 101.3, 47.6, 32.3, 32.1, 21.9, 18.5, 4.6, -1.1. HRMS (ESI) m/z calcd for $C_{26}H_{36}NOSi_2^+$ $(M+H)^+$ 434.2330, found 434.2343.



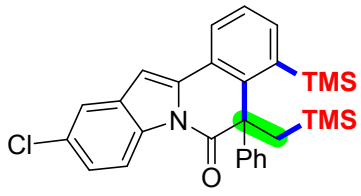
5,12-dimethyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3i): white solid, isolated yield 90% (75.54 mg); mp: 97.4-99.2 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.42-7.38 (m, 3H), 2.67 (s, 3H), 1.93(s, 3H), 1.74 (dd, *J* = 25.0 Hz, *J* = 14.0 Hz, 2H), 0.57 (s, 9H), -0.39 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 173.8, 146.0, 139.9, 137.1, 133.7, 132.8, 130.3, 126.1, 125.6, 125.3, 124.1, 118.2, 116.8, 113.5, 47.5, 32.6, 31.8, 11.9, 4.7, -1.0. HRMS (ESI) m/z calcd for $C_{25}H_{34}NOSi_2^+$ $(M+H)^+$ 420.2173, found 420.2185.



2-fluoro-5-methyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3j): white solid, isolated yield 55% (46.60 mg); mp: 98.7-100.3 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.57 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 7.46 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 7.40-7.33 (m, 2H), 7.02 (s, 1H), 1.86 (s, 3H), 1.73 (d, *J* = 14.0 Hz, 1H), 1.66 (d, *J* = 14.0 Hz, 1H), 0.52 (s, 9H), -0.47 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 173.7, 160.5 (d, *J* = 246.5 Hz), 144.1 (d, *J* = 3.1 Hz), 141.0 (d, *J* = 3.6 Hz), 135.0 (d, *J* = 3.8 Hz), 134.9, 130.6, 125.5 (d, *J* = 7.3 Hz), 125.4, 125.1, 124.9, 124.7, 120.5, 116.8, 110.3 (d, *J* = 21.4 Hz), 103.7, 47.4, 32.6, 32.0, 4.4, -1.1. HRMS (ESI) m/z calcd for $C_{24}H_{31}FNOSi_2^+$ $(M+H)^+$ 424.1923, found 424.1934.

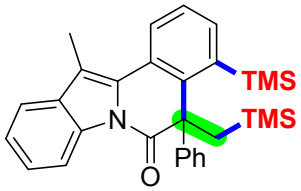


5-phenyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3k): white solid, isolated yield 73% (68.29 mg); mp: 230.1-232.0 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.44-8.43 (m, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.60-7.58 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31-7.21 (m, 6H), 7.10 (s, 1H), 2.69 (d, *J* = 14.0 Hz, 1H), 1.84 (d, *J* = 14.0 Hz, 1H), -0.04 (s, 9H), -0.43 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 171.4, 145.0, 143.6, 142.8, 138.6, 135.9, 135.1, 130.9, 129.2, 128.0, 127.3, 126.5, 124.9, 124.9, 124.6, 124.4, 120.2, 117.0, 103.1, 55.8, 30.5, 2.9, -1.2. HRMS (ESI) m/z calcd for $C_{29}H_{34}NOSi_2^+$ $(M+H)^+$ 468.2173, found 468.2185.

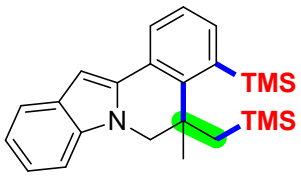


10-chloro-5-phenyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3l): white solid, isolated yield 70% (70.31 mg); mp: 234.2-236.0 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.32 (d, *J* = 8.0 Hz, 1H), 7.96 (dd, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.64 (dd, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.53 (d, *J*

= 2.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 3H), 7.23-7.20 (m, 4H), 2.63 (d, *J* = 14.0 Hz, 1H), 1.81 (d, *J* = 14.0 Hz, 1H), -0.08 (s, 9H), -0.48 (s,9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.4, 144.8, 143.8, 143.0, 139.0, 137.3, 133.4, 132.2, 130.2, 129.2, 128.1, 127.4, 126.6, 124,9, 124.6, 124.5, 119.8, 117.9, 102.1, 55.8, 30.9, 2.9, -1.2. HRMS (ESI) m/z calcd for $C_{29}H_{33}ClNOSi_2^+$ $(M+H)^+$ 502.1784, found 502.1796.

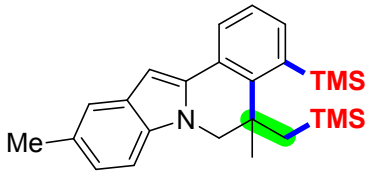


12-methyl-5-phenyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3m): white solid, isolated yield 84% (78.58 mg); mp: 132.3-135.5 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.46-8.44 (m, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.0 Hz, 1H), 7.58-7.56 (m, 1H), 7.47 (t, *J* = 7.5 Hz, 3H), 7.33-7.28 (m, 2H), 7.24-7.17 (m, 3H), 2.70 (d, *J* = 13.5 Hz, 1H), 2.69 (s, 3H), 1.78 (d, *J* = 13.5 Hz, 1H), -0.06 (s, 9H), -0.43 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =171.4, 145.3, 144.1, 142.9, 137.4, 133.8, 132.8, 130.1, 129.2, 127.9, 127.1, 126.8, 126.0, 125.7, 125.3, 124.1, 118.1, 116.9, 113.8, 55.7, 30.7, 12.0, 2.9, -1.0. HRMS (ESI) m/z calcd for $C_{30}H_{36}NOSi_2^+$ $(M+H)^+$ 482.2330, found 482.2344.

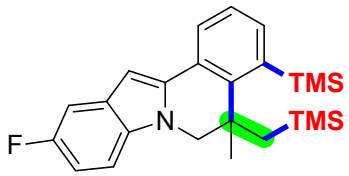


5-methyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)-5,6-dihydroindolo[2,1-a]isoquinoline (4a): white solid, isolated yield 84% (65.80 mg); mp: 123.0-124.9 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.84 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.71 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.83(s, 1H), 4.16 (d, *J* = 12.5 Hz, 1H), 3.90 (d, *J* = 12.0 Hz, 1H), 1.67 (s, 3H) 1.37 (d, *J* = 15.0 Hz, 1H), 1.14 (d, *J* = 15.0 Hz, 1H) 0.52 (s, 9H) 0.13 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =150.7, 137.1, 136.3, 136.2, 136.0, 129.0, 127.5, 126.9, 125.6, 121.1, 120.5, 119.7, 109.0, 96.2, 52.7, 41.0, 28.3, 27.1, 4.2, 1.2. HRMS (ESI) m/z calcd for

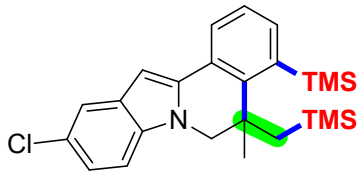
$C_{24}H_{34}NSi_2^+$ $(M+H)^+$ 392.2224, found 392.2235.



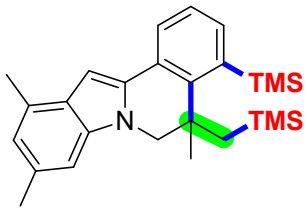
5,10-dimethyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)-5,6-dihydroindolo[2,1-a]isoquinoline (4b): white solid, isolated yield 88% (71.41 mg); mp: 137.0-139.4 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.85 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.73 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.48 (s, 1H), 7.31-7.27 (m, 2H), 7.08 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 6.78 (s, 1H), 4.16 (d, *J* = 12,5 Hz, 1H), 3.89 (d, *J* = 12.5 Hz, 1H), 2.52 (s, 3H), 1.70 (s, 3H), 1.39 (d, *J* = 15 Hz, 1H), 1.18 (d, *J* = 15 Hz, 1H), 0.56 (s, 9H), 0.16 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 150.6, 136.9, 136.3, 135.9, 134.7, 129.2 128.8, 127.6, 126.9, 125.6, 122.8, 120.2, 108.9, 95.7, 52.9, 41.0, 28.3, 27.1, 21.5, 4.2, 1.2. HRMS (ESI) m/z calcd for $C_{25}H_{36}NSi_2^+$ $(M+H)^+$ 406.2381, found 406.2392.



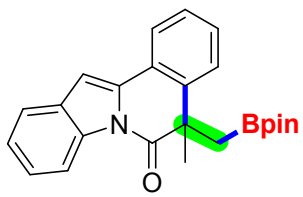
5-chloro-8a-methyl-8,8a-dihydro-9*H*-dibenzo[*de,g*]indolo[1,2-*b*]isoquinolin-9-one (4d): white solid, isolated yield 84% (68.82 mg); mp: 145.1-147.5 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.0 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.30-7.22 (m, 3H),6.95 (td, *J* =9.5 Hz, *J* = 2.5 Hz, 1H), 6.77 (s, 1H), 4.11 (d, *J* = 12,5 Hz, 1H), 3.86 (d, *J* = 12.5 Hz, 1H), 1.66(s, 3H), 1.34 (d, *J* = 15Hz, *I*H), 1.09 (d, *J* = 15 Hz, 1H), 0.51 (s, 9H), 0.10 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 157.9 (d, *J* = 232.5 Hz), 150.6, 137.9, 137.4, 136.1, 132.9, 129.1 (d, *J* = 10.6 Hz), 127.2, 127.0, 125.7, 109.5 (d, *J* = 13 Hz), 109.4 (d, *J* = 3.4 Hz), 105.2 (d, *J* = 23.5 Hz), 96.1 (d, *J* = 4.8 Hz), 52.8, 41.0, 28.3, 27.0, 4.2, 1.2. HRMS (ESI) m/z calcd for $C_{24}H_{33}FNSi_2^+$ $(M+H)^+$ 410.2130, found 410.2141.



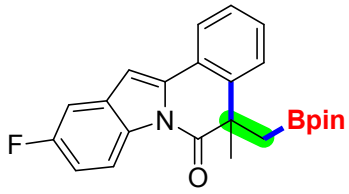
10-chloro-5-methyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)-5,6-dihydroindolo[2,1-a]isoquinoline (4e): white solid, isolated yield 81% (69.03 mg); mp: 144.6-145.5 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.29-7.23 (m, 2H), 6.75 (s, 1H), 4.12 (d, *J* = 12,5 Hz, 1H), 3.86 (d, *J* = 12.5 Hz, 1H), 1.67 (s, 3H), 1.35 (d, *J* = 15 Hz, *1*H), 1.09 (d, *J* = 15 Hz, 1H), 0.53 (s, 9H), 0.11 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 150.7, 137.6, 137.5, 136.1, 134.6, 129.9, 127.0, 125.7, 125.3, 121.4, 119.8, 109.9, 95.8, 52.7, 41.0, 28.3, 27.0, 4.1, 1.2. HRMS (ESI) m/z calcd for $C_{24}H_{33}ClNSi_2^+$ $(M+H)^+$ 426.1835, found 426.1846.



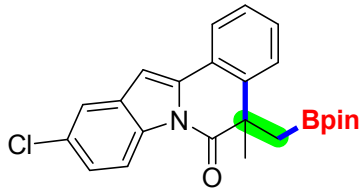
5,9,11-trimethyl-4-(trimethylsilyl)-5-((trimethylsilyl)methyl)-5,6-dihydroindolo[2,1-a]isoquinoline (4h): white solid, isolated yield 80% (67.16 mg); mp: 107.0-109.5 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.87 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.71 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.30-7.27 (m, 1H), 7.00 (s, 1H), 6.82 (s, 2H), 4.12 (d, *J* = 12,5 Hz, 1H), 3.89 (d, *J* = 12.5 Hz, 1H), 2.61 (s, 3H), 2.53 (s, 3H), 1.67 (s, 3H), 1.42 (d, *J* = 15.0 Hz, 1H), 1.20 (d, *J* = 15.0 Hz, 1H), 0.55 (s, 9H), 0.17 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 150.4, 136.7, 136.4, 135.9, 135.2, 131.2 129.6, 127.8 126.7, 126.7, 125.6, 121.9, 106.6, 94.7, 52.8, 41.0, 28.3, 27.1, 21.9, 18.7, 4.2, 1.3. HRMS (ESI) m/z calcd for $C_{26}H_{38}NSi_2^+$ $(M+H)^+$ 420.2537, found 420.2546.



5-methyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (5a): white solid, isolated yield 74% (57.32 mg); mp: 100.0-101.9 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.60 (d, *J* = 8.0 Hz, 1H), 7.83-1.81 (m, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.37-7.30 (m, 4H), 7.00 (s, 1H), 2.02 (d, *J* = 15,5 Hz, 1H), 1.71 (s, 3H), 1.59 (d, *J* = 15.5 Hz, 1H), 0.91 (s, 6H), 0.85 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.0, 140.5, 136.0, 135.5, 130.6, 128.6 126.9, 126.4, 124.8, 124.1, 124.1, 123.4, 120.1, 116.7, 102.1, 83.1, 46.3, 31.8, 24.5, 24.2. HRMS (ESI) m/z calcd for $C_{24}H_{27}BNO_3^+$ $(M+H)^+$ 388.2079, found 388.2087.

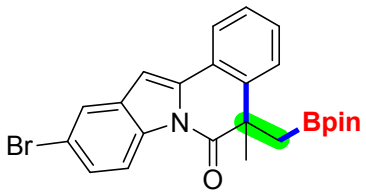


10-fluoro-5-methyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (5d): white solid, isolated yield 67% (54.31 mg); mp: 113.0-114.7 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.53 (dd, *J* = 9.0 Hz, *J* = 5.0 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.37-7.31 (m, 2H), 7.23 (dd, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H), 7.05 (td, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H) 6.95 (s, 1H), 1.99 (d, *J* = 15.5 Hz, 1H), 1.70 (s, 3H), 1.58 (d, *J* = 15.5 Hz, 2H), 0.89 (s, 6H), 0.82 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 173.9, 160.0 (d, *J* = 239.1 Hz), 140.6, 137.6, 131.8, 131.7 (d, *J* = 9.8 Hz), 129.0, 127.0, 126.5, 123.8, 123.5, 117.7 (d, *J* = 8.9 Hz), 112.3 (d, *J* = 24.3 Hz), 105.7 (d, *J* = 24.5 Hz), 101.6 (d, *J* = 4.5 Hz), 83.1, 46,1, 31.7, 24.5, 24.2. HRMS (ESI) m/z calcd for $C_{24}H_{26}BFNO_3^+$ $(M+H)^+$ 406.1984, found 406.1997.

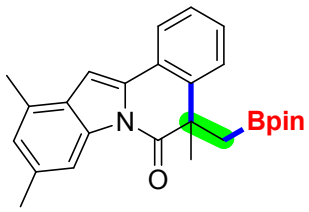


10-chloro-5-methyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (5e): white solid, isolated yield 73% (61.57 mg); mp: 107.4-109.7 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.50

(d, J = 9.0 Hz, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 1.5 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.37-7.28(m, 3H), 6.93 (s, 1H), 1.99 (d, J = 15,5 Hz, 1H), 1.70 (s, 3H), 1.58 (d, J = 15.5 Hz, 1H), 0.88 (s, 6H), 0.81 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.0, 140.5, 137.4, 133.7, 131.9, 129.6, 129.1, 127.0, 126.4, 124.7, 123.8, 123.5, 119.7, 117.6, 101.1, 83.1, 46.1, 31.7, 24.5, 24.1. HRMS (ESI) m/z calcd for $C_{24}H_{26}BClNO_3^+$ $(M+H)^+$ 422.1689, found 422.1698.

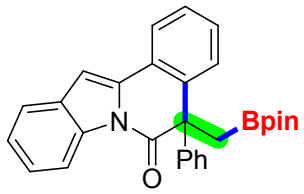


10-bromo-5-phenyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (5f): white solid, isolated yield 70% (65.26 mg); mp: 115.1-117.7 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.46 (d, J = 9.0Hz, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.70 (s, 1H), 7.43-7.41 (m, 2H), 7.37-7.30 (m, 2H), 6.92 (s, 1H), 1.99 (d, J = 16.0 Hz, 1H), 1.70 (s, 3H), 1.59 (d, J = 16.0 Hz, 1H), 0.87 (s, 6H), 0.81 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =174.0, 140.6, 137.2, 134.0, 132.4, 129.1, 127.5, 127.0, 126.4, 123.6, 123.5, 122.7, 118.0, 117.4, 100.9, 83.1, 46.1, 31.7, 24.5, 24.1. HRMS (ESI) m/z calcd for $C_{24}H_{26}BBrNO_3^+$ $(M+H)^+$ 466.1184, found 466.1192.

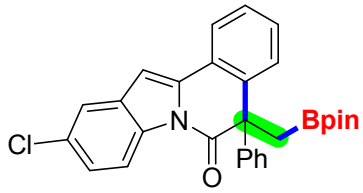


5,9,11-trimethyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (5h): white solid, isolated yield 80% (66.45 mg); mp: 118.1-120.2°C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.28 (s, 1H), 7.83-7.81 (m, 1H), 7.42-7.40 (m, 1H), 7.31 (t, J = 3.5 Hz, 2H), 7.00 (s, 1H), 6.97 (s, 1 H), 2.55 (s, 3H), 2.48 (s, 3H), 2.04 (d, J = 15.5 Hz, 1H), 1.67 (s, 3H), 1.59 (d, J = 15.5 Hz, 1H), 0.92 (s, 6H), 0.83 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.1, 140.1, 135.6, 135.1, 134.8, 129.1, 128.2, 127.8, 126.8, 126.3, 126.1, 124.5,

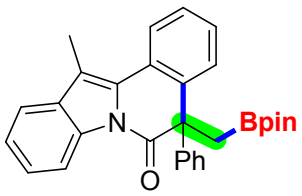
123.2, 114.5, 100.7, 83.1, 46.3, 32.2, 24.6, 24.1, 21.9, 18.5. HRMS (ESI) m/z calcd for $C_{26}H_{31}BNO_3^+$ $(M+H)^+$ 416.2392, found 416.2401.



5-phenyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (5k): white solid, isolated yield 73% (65.60 mg); mp: 158.7-160.3 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.47-8.45 (m, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.57-7.56 (m, 1H), 7.31-7.17 (m, 8H), 7.13 (t, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.04 (s, 1H), 2.70 (d, *J* = 15,5 Hz, 1H), 1.98 (d, *J* = 15.5 Hz, 1H), 0.80 (s, 6H), 0.73 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 171.7, 145.1, 139.9, 136.2, 135.7, 130.6, 128.8, 128.6, 128.5, 127.1, 127.0, 125.4, 124.9, 124.1, 123.1, 120.1, 116.8, 102.5, 83.2, 53.8, 24.4, 24.1. HRMS (ESI) m/z calcd for $C_{29}H_{29}BNO_3^+$ $(M+H)^+$ 450.2235, found 450.2246.



10-chloro-5-phenyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (5l): white solid, isolated yield 72% (69.67 mg); mp: 203.2-204.9 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.42 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.36-7.33 (m, 1H), 7.30-7.22 (m, 6H), 7.20-7.17 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 2.70 (d, *J* = 15,5 Hz, 1H), 2.02 (d, *J* = 15.5 Hz, 1H), 0.82(s, 6H), 0.77(s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 171.7, 144.8, 140.2, 137.6, 134.0, 131.9, 129.7, 129.2, 128.7, 128.5, 127.2, 127.1, 127.1, 124.9, 124.9, 123.3, 119.7, 117.8, 101.5, 83.3, 53.7, 24.4, 24.1. HRMS (ESI) m/z calcd for $C_{29}H_{28}BClNO_3^+$ $(M+H)^+$ 484.1845, found 484.1854.



12-methyl-5-phenyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one(5m): white solid, isolated yield 75% (69.51 mg); mp: 188.1-190.0 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.56-8,54 (m, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.61-7.59 (m, 1H), 7.42-7.38 (m, 1H), 7.34 (t, *J* = 4.0 Hz, 2H), 7.30-7.25 (m, 3H), 7.23-7.20 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 2.75 (d, *J* = 15.0 Hz, 1H), 2.70 (s, 3H), 2.02 (d, *J* = 15.0 Hz, 1H), 0.88 (s, 6H), 0.78 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =171.4, 145.5, 140.0, 134.6, 132.3, 130.4, 128.8, 128.4, 127.7, 127.1, 127.0, 126.9, 126.8, 125.3, 124.4, 123.7, 118.0, 116.7, 113.7, 83.1, 53.8, 24.5, 24.0, 11.4. HRMS (ESI) m/z calcd for $C_{30}H_{31}BNO_3^+$ $(M+H)^+$ 464.2392, found 464.2401.

5 References

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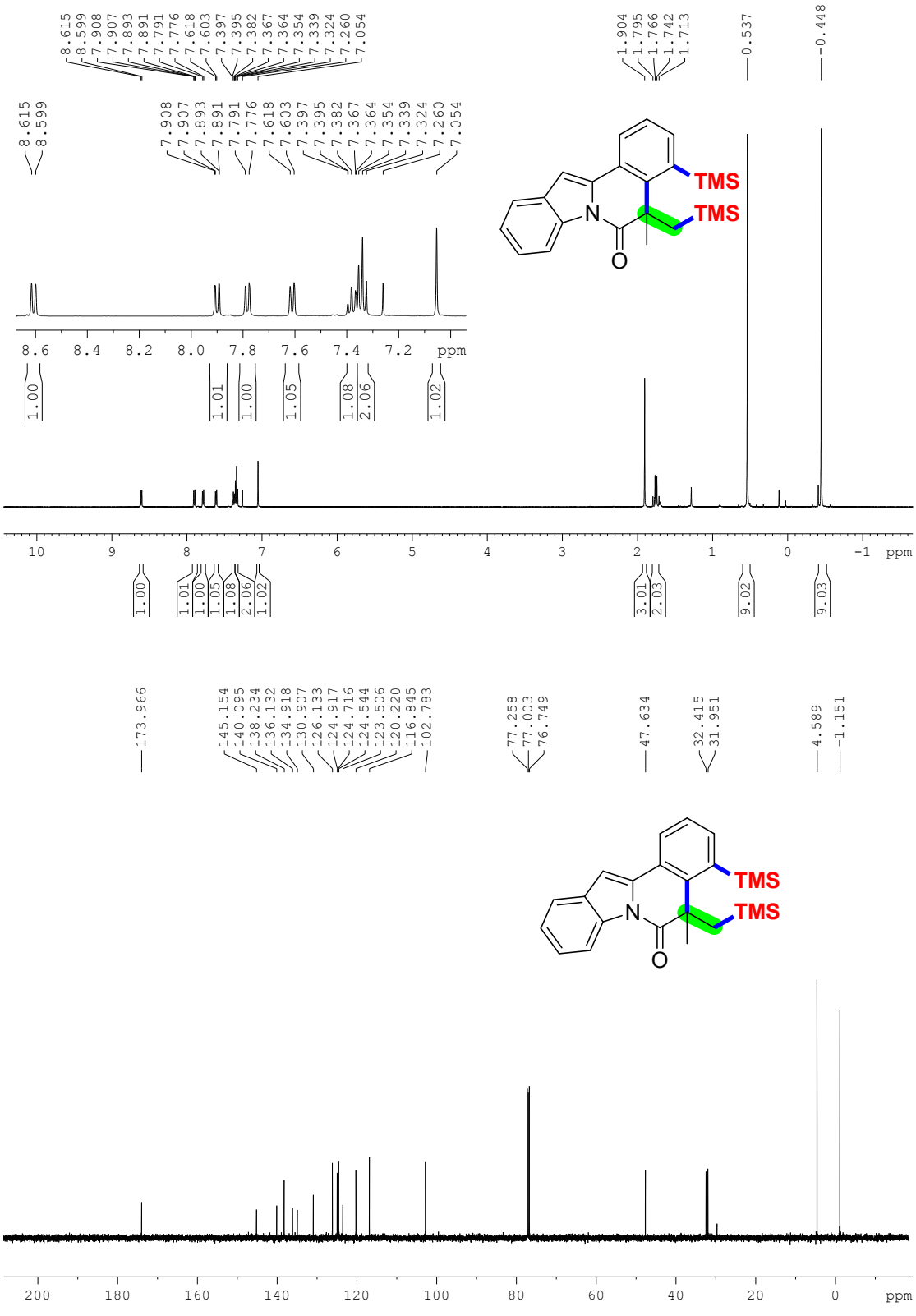
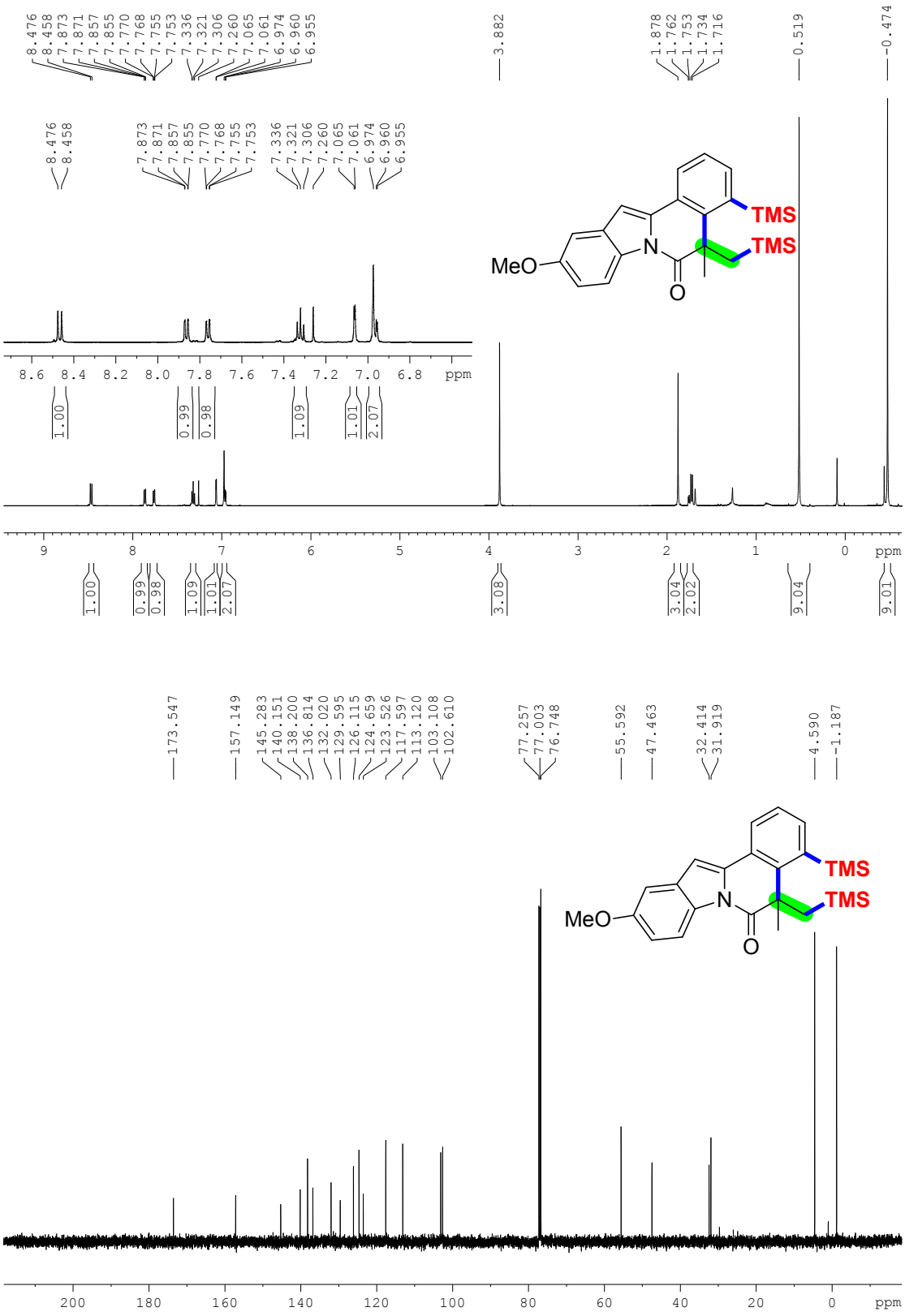
6 Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

^{1}H and ^{13}C Spectrum of Compound **3a**

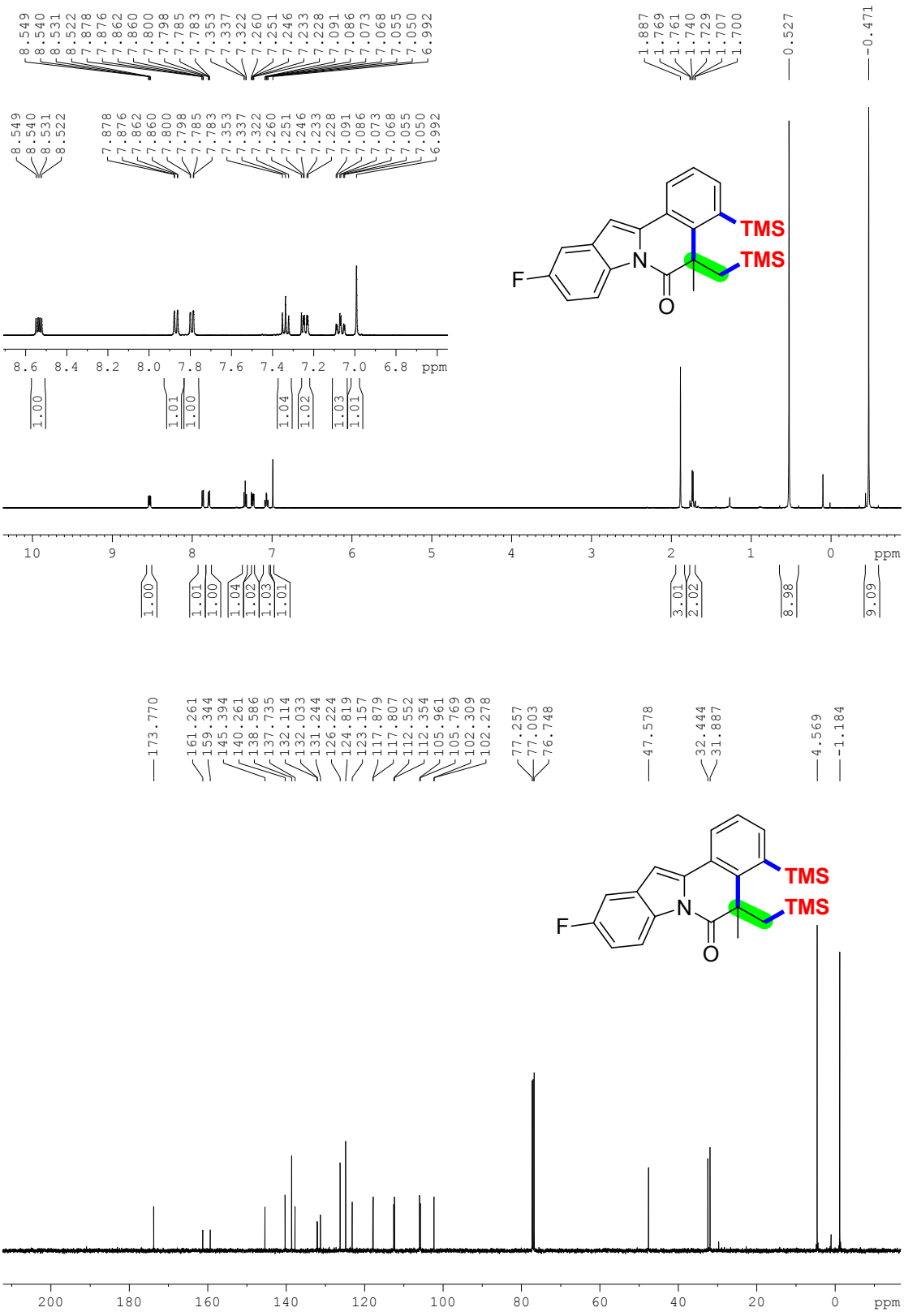


^{1}H and ^{13}C Spectrum of Compound **3b**

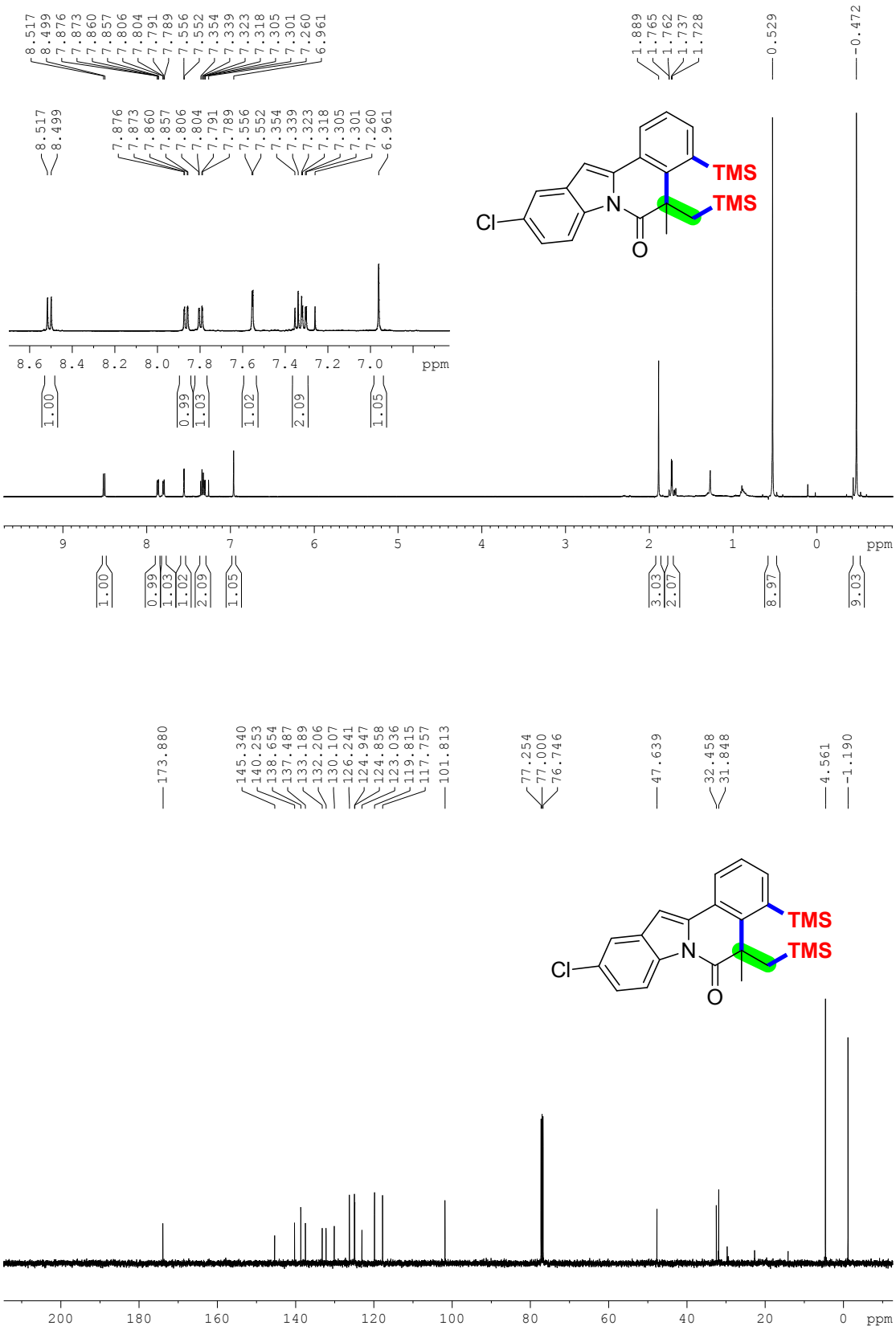
^{1}H and ^{13}C Spectrum of Compound **3c**



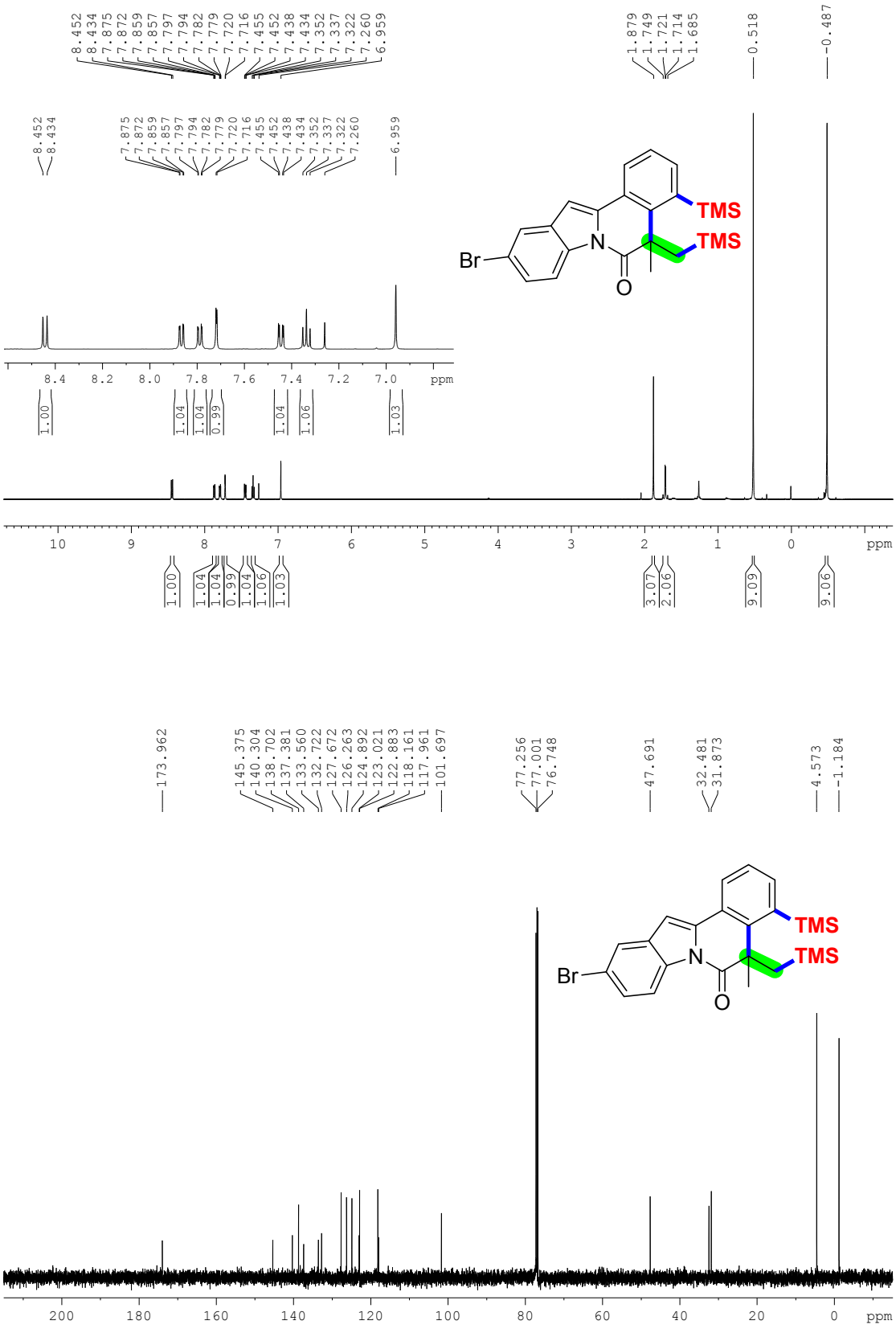
^{1}H and ^{13}C Spectrum of Compound **3d**



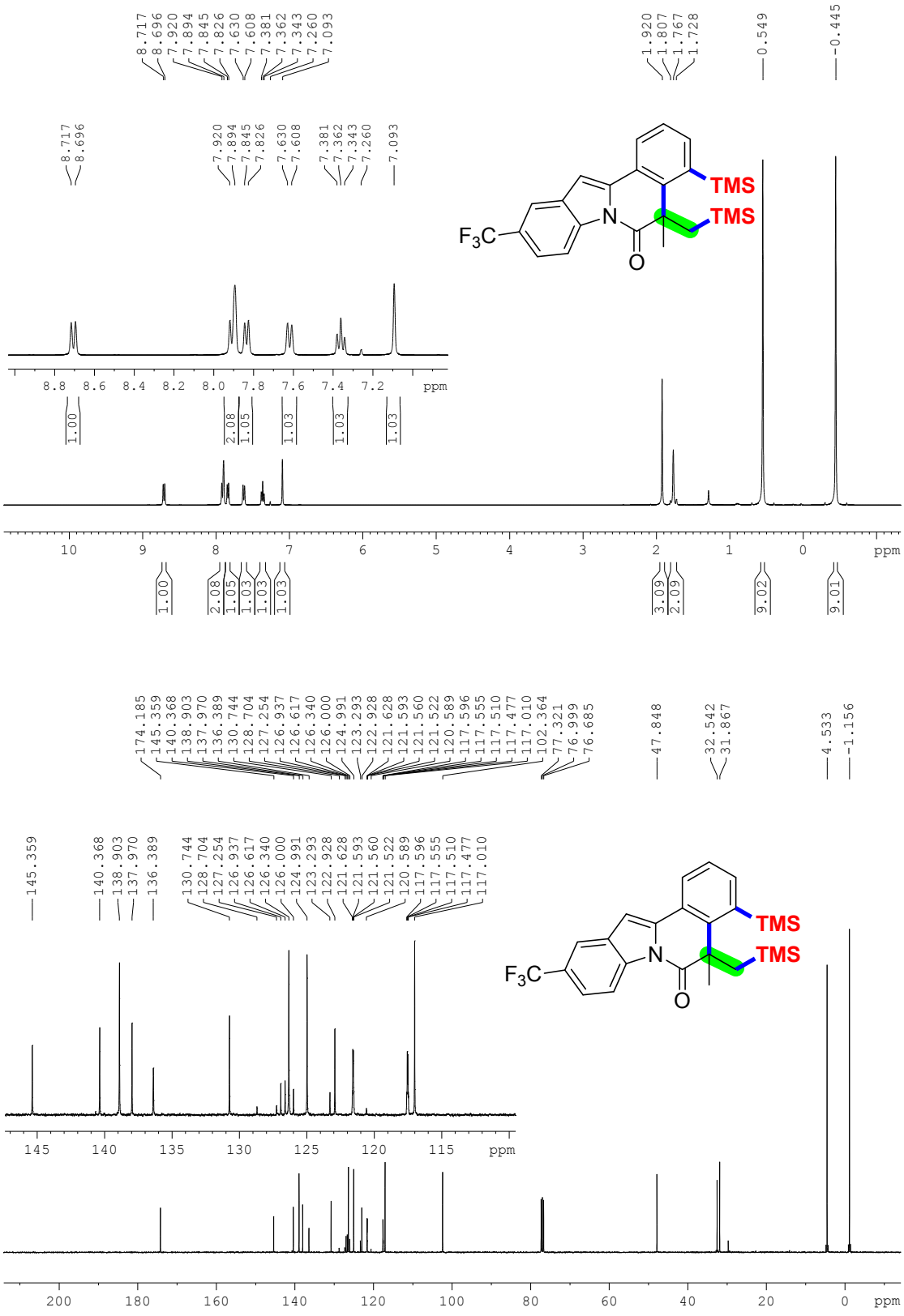
^{1}H and ^{13}C Spectrum of Compound **3e**



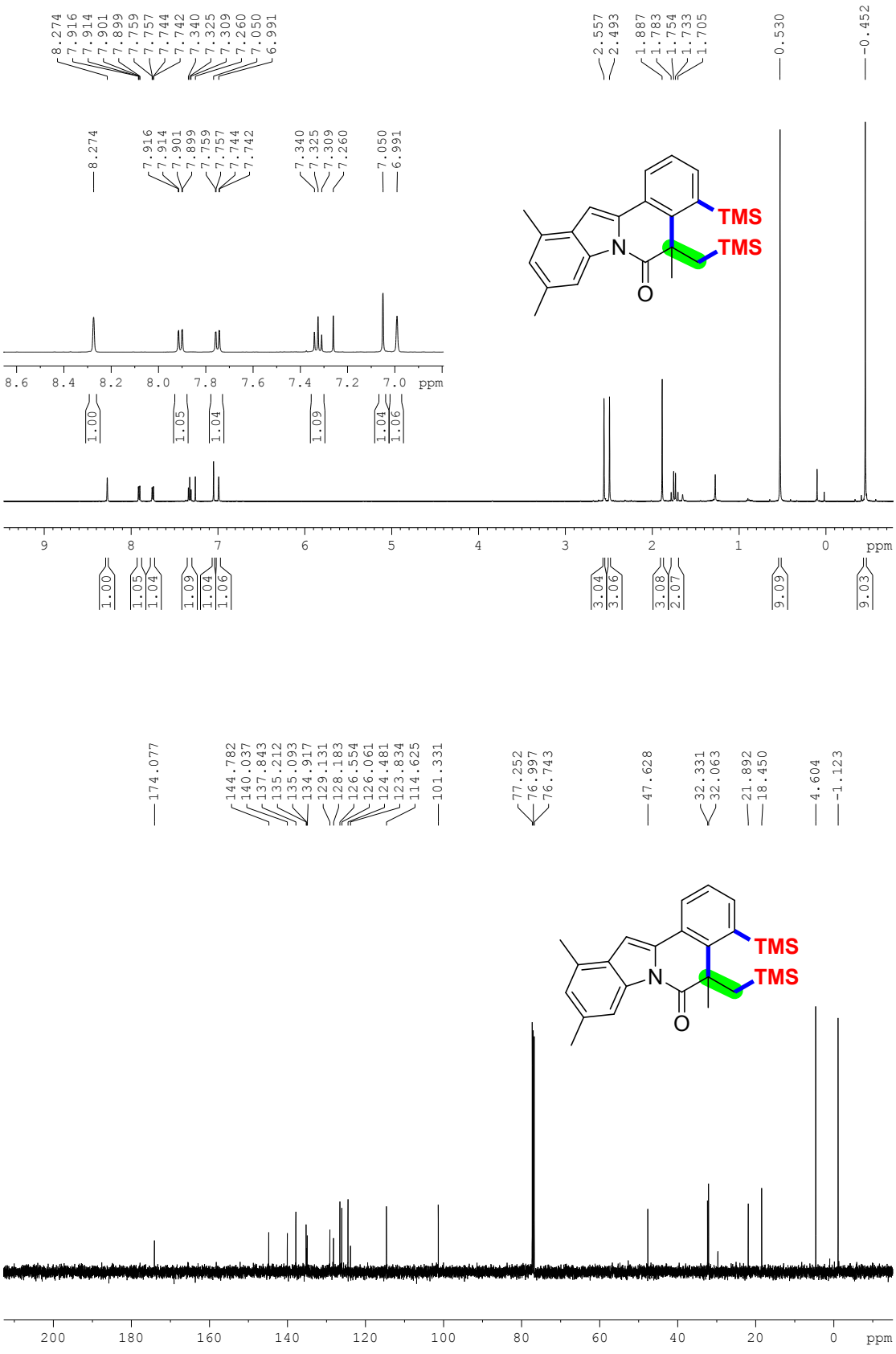
^{1}H and ^{13}C Spectrum of Compound **3f**



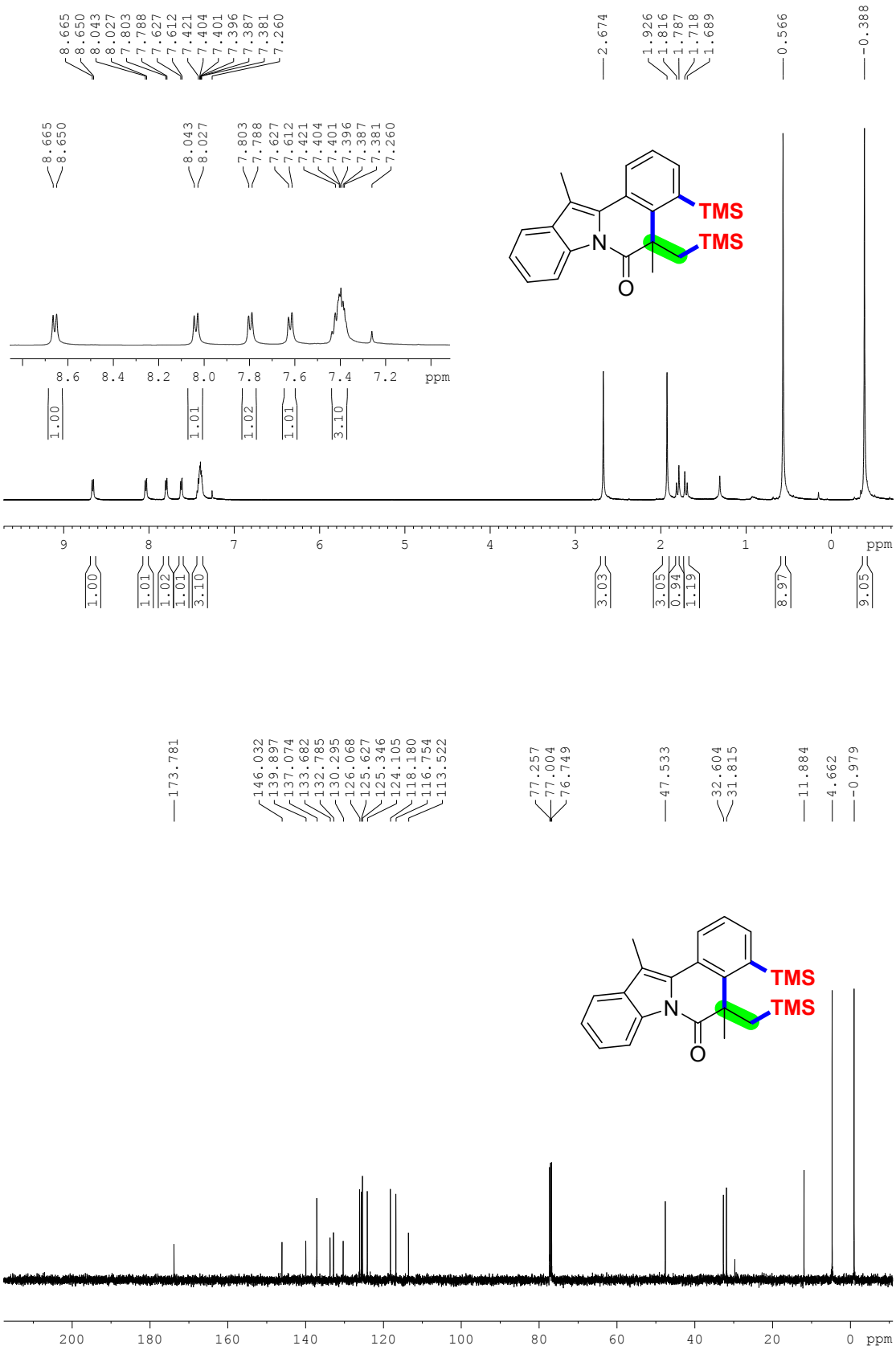
^{1}H and ^{13}C Spectrum of Compound **3g**



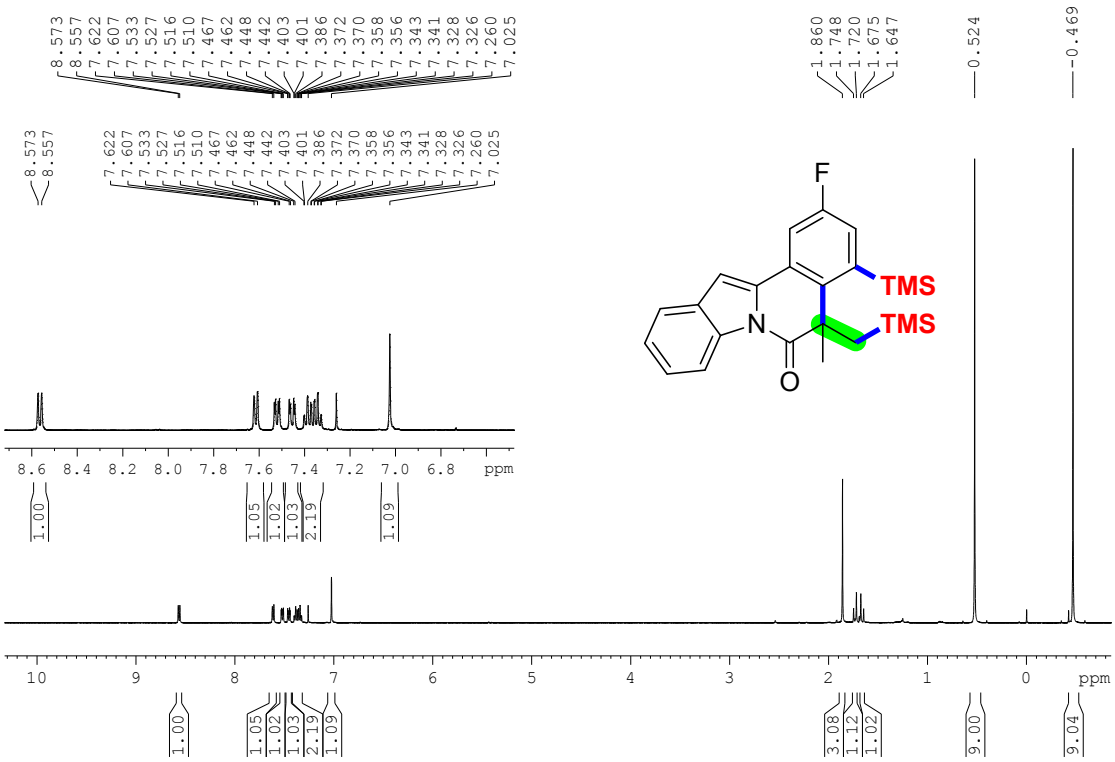
^{1}H and ^{13}C Spectrum of Compound **3h**

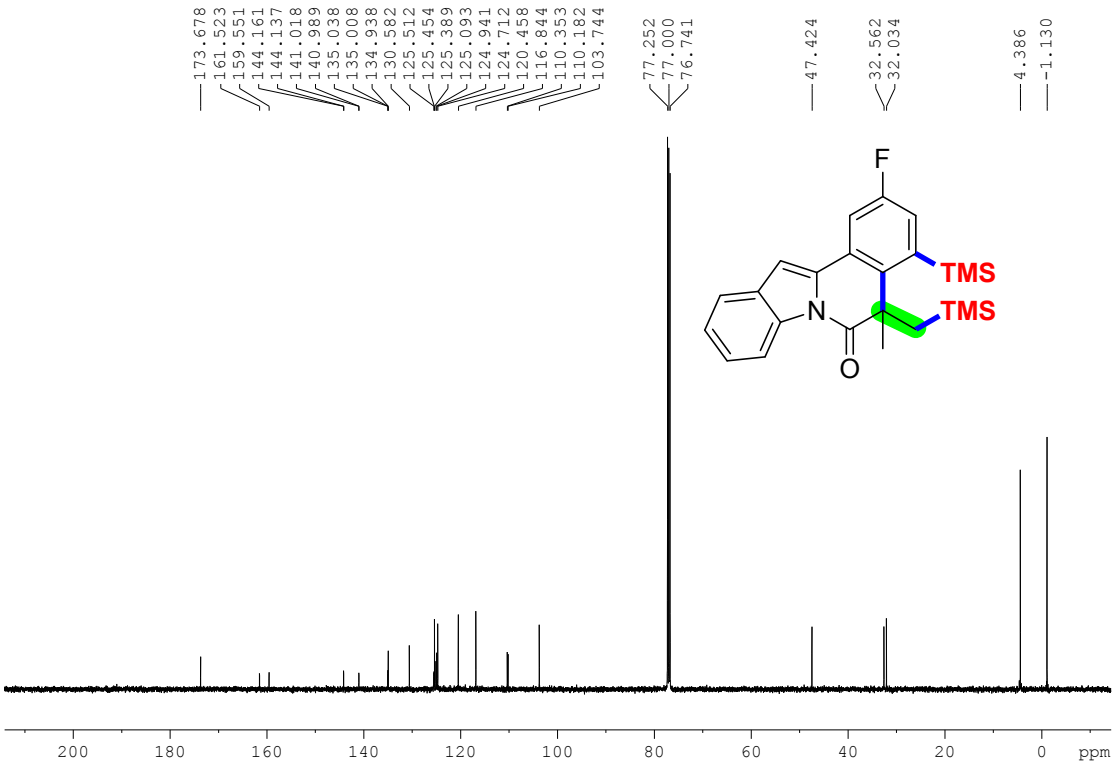


^{1}H and ^{13}C Spectrum of Compound **3i**

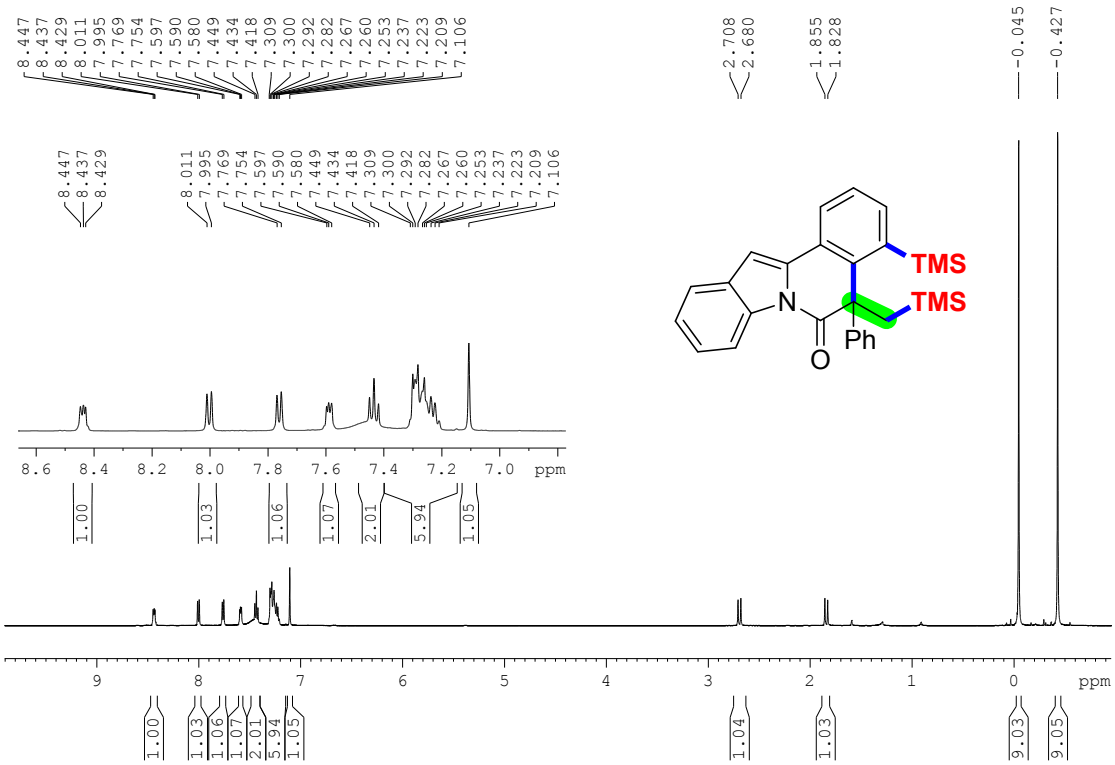


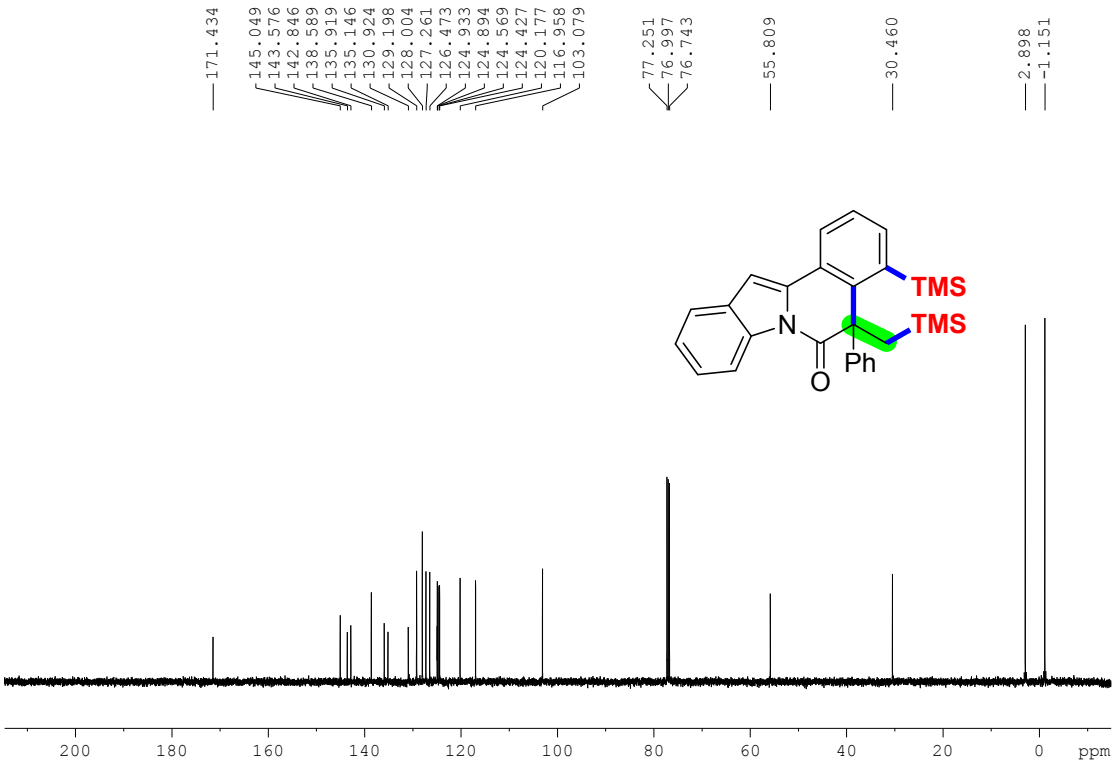
^{1}H and ^{13}C Spectrum of Compound **3j**



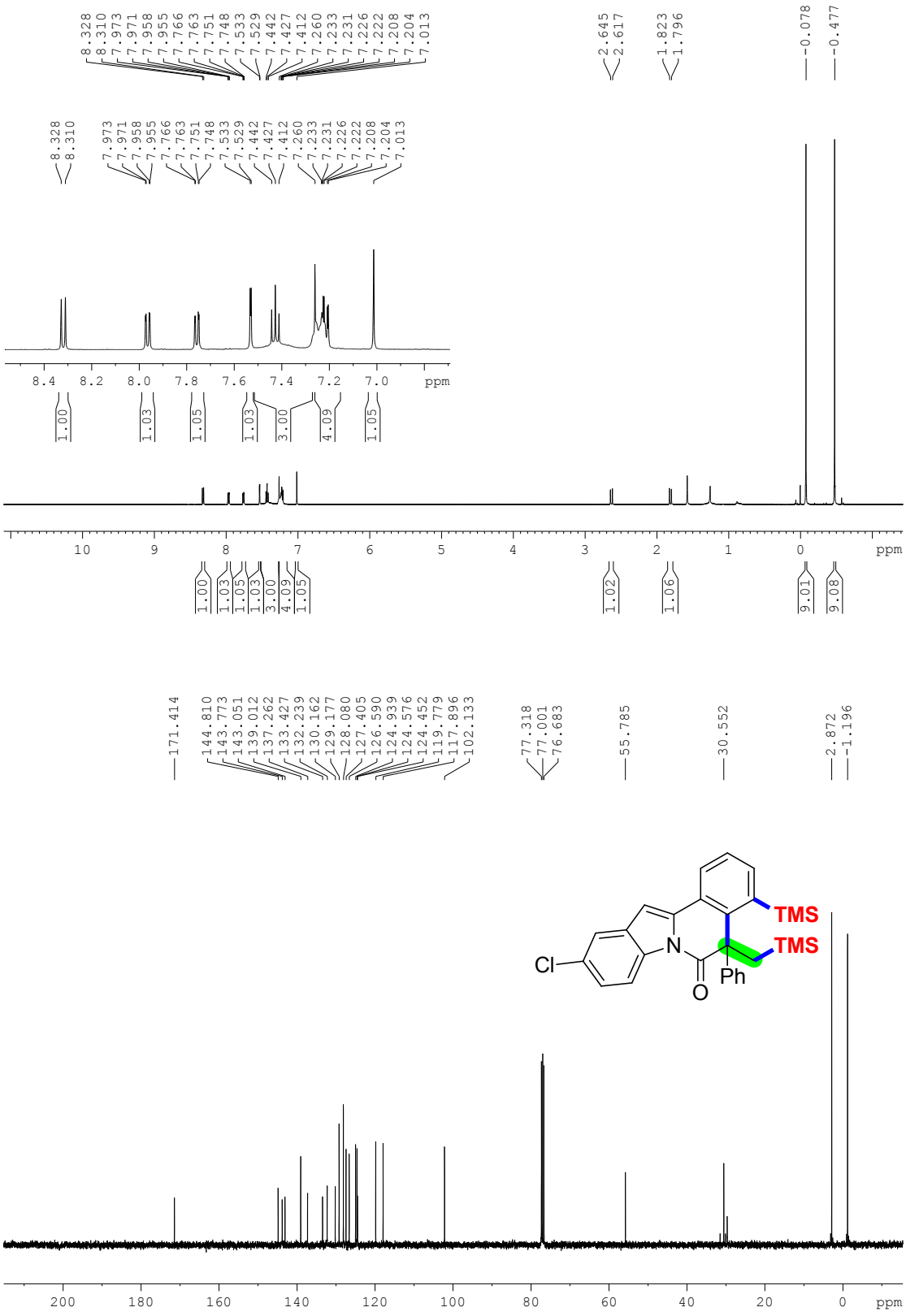


^{1}H and ^{13}C Spectrum of Compound **3k**

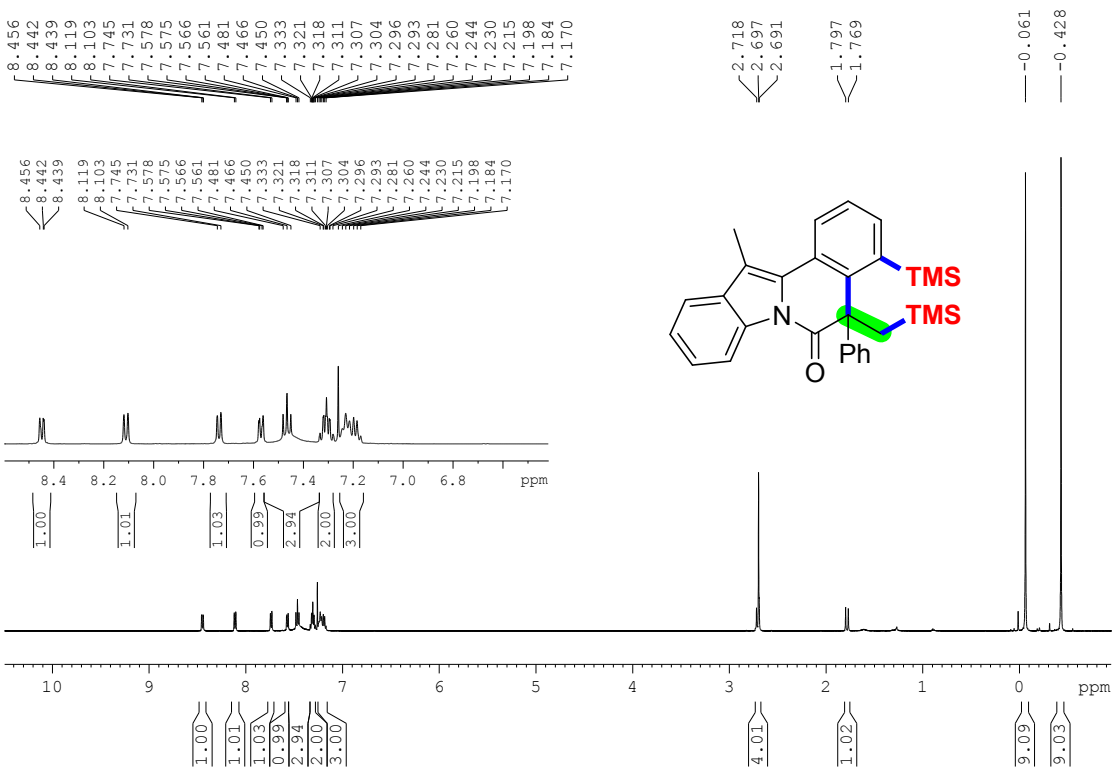


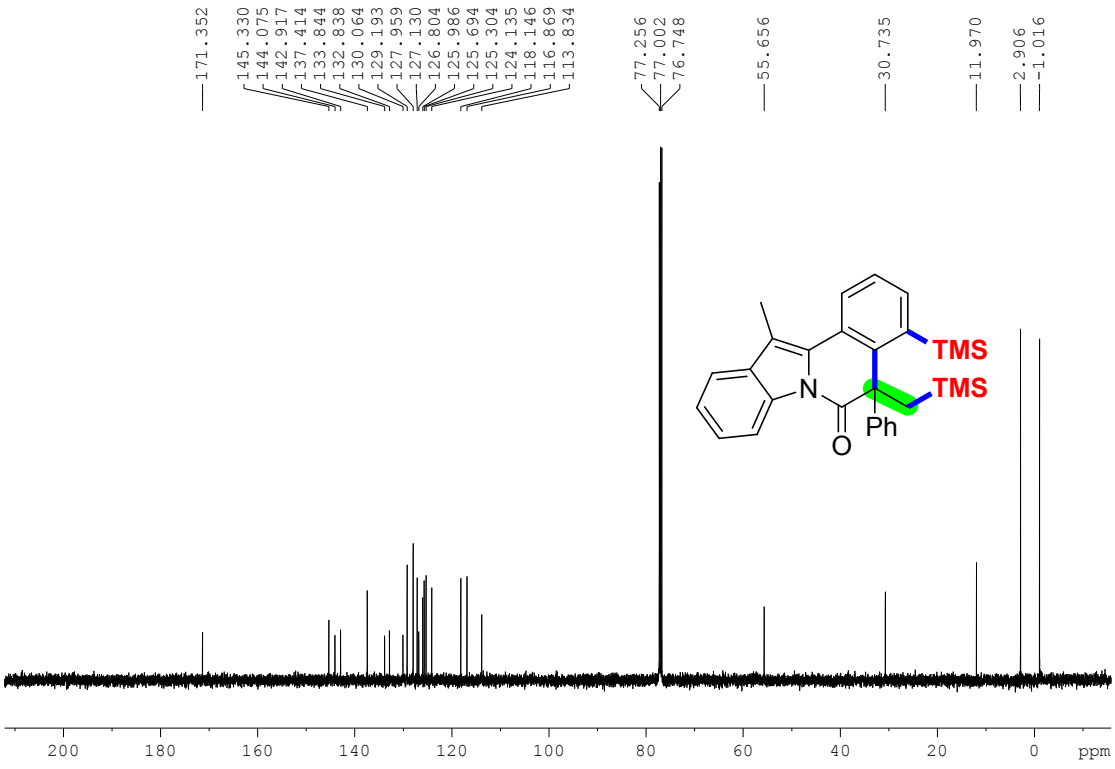


^{1}H and ^{13}C Spectrum of Compound **3l**

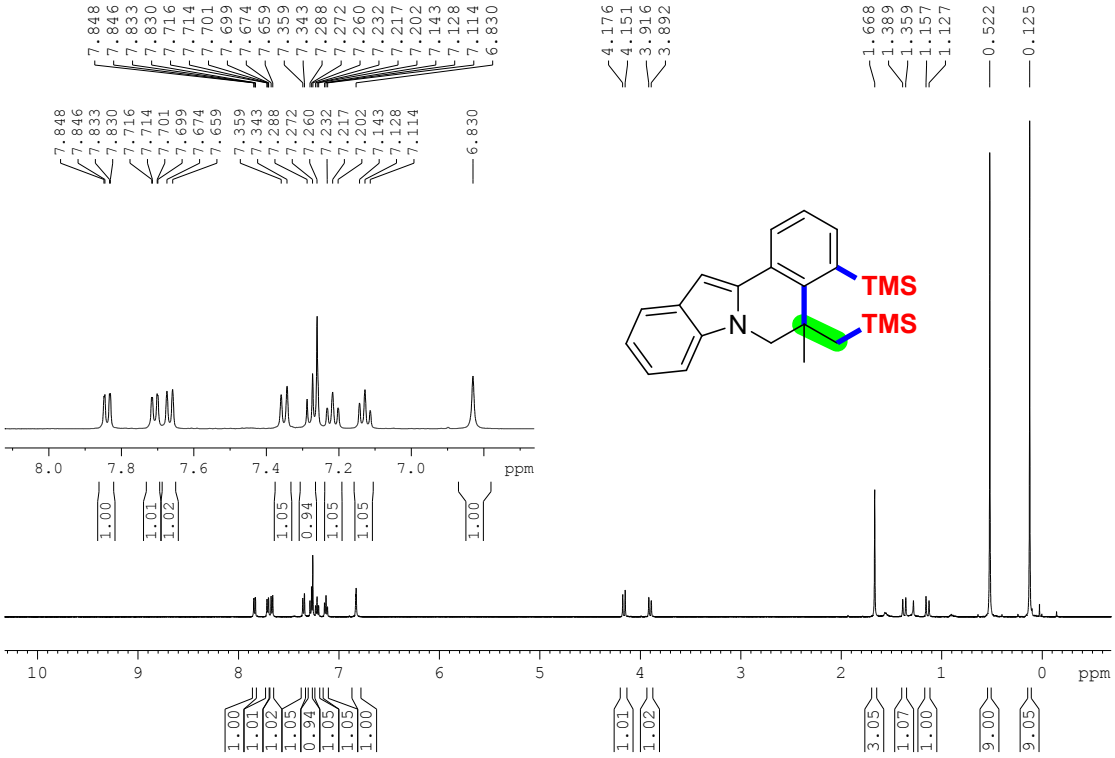


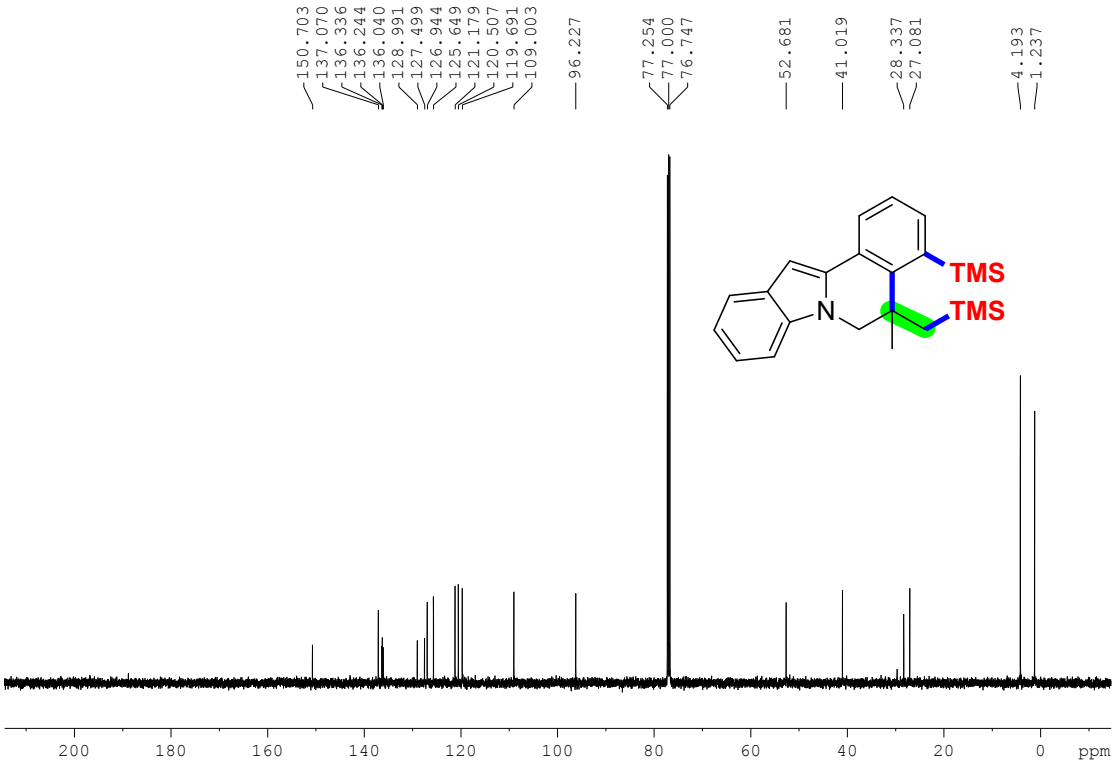
^{1}H and ^{13}C Spectrum of Compound **3m**



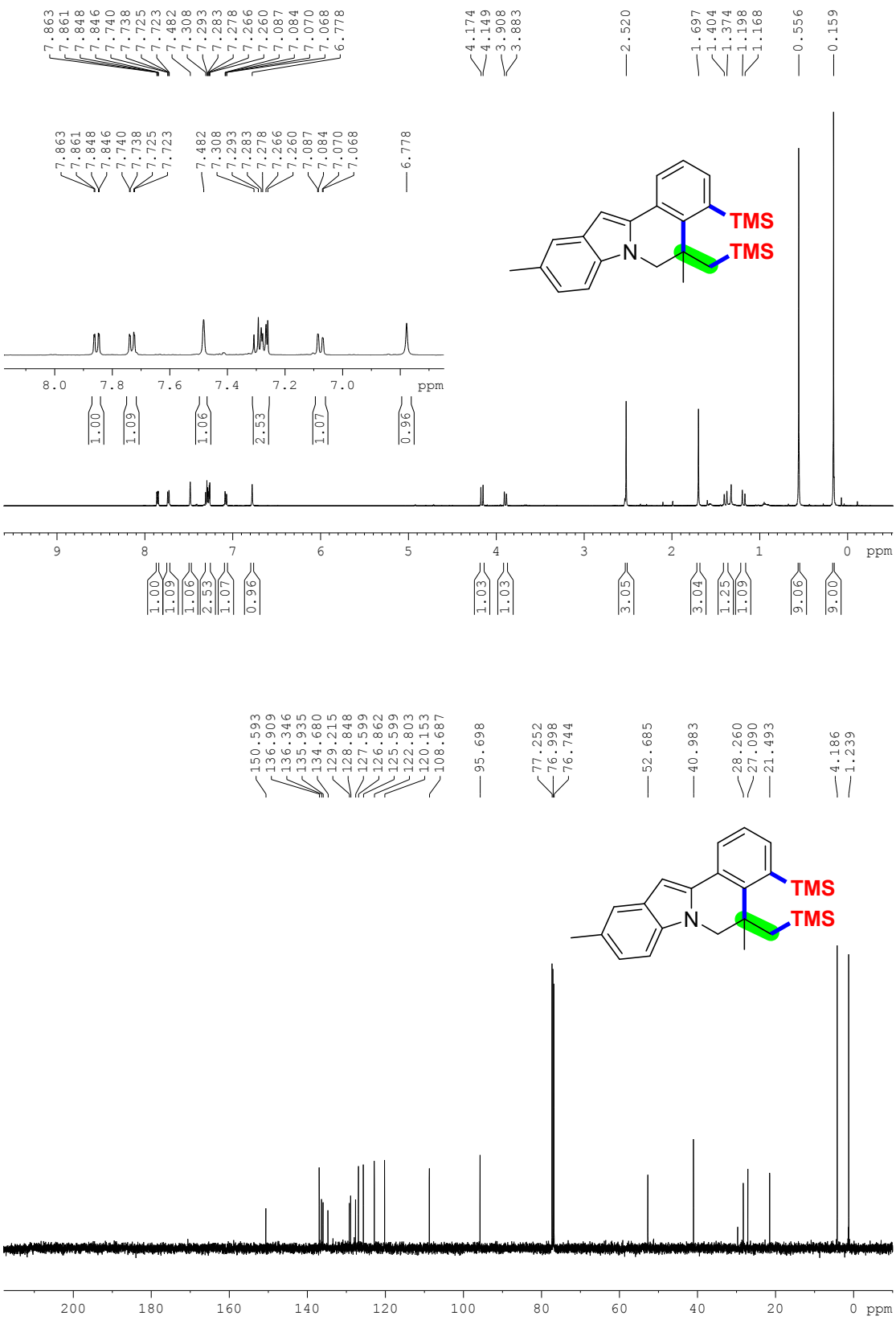


^{1}H and ^{13}C Spectrum of Compound **4a**

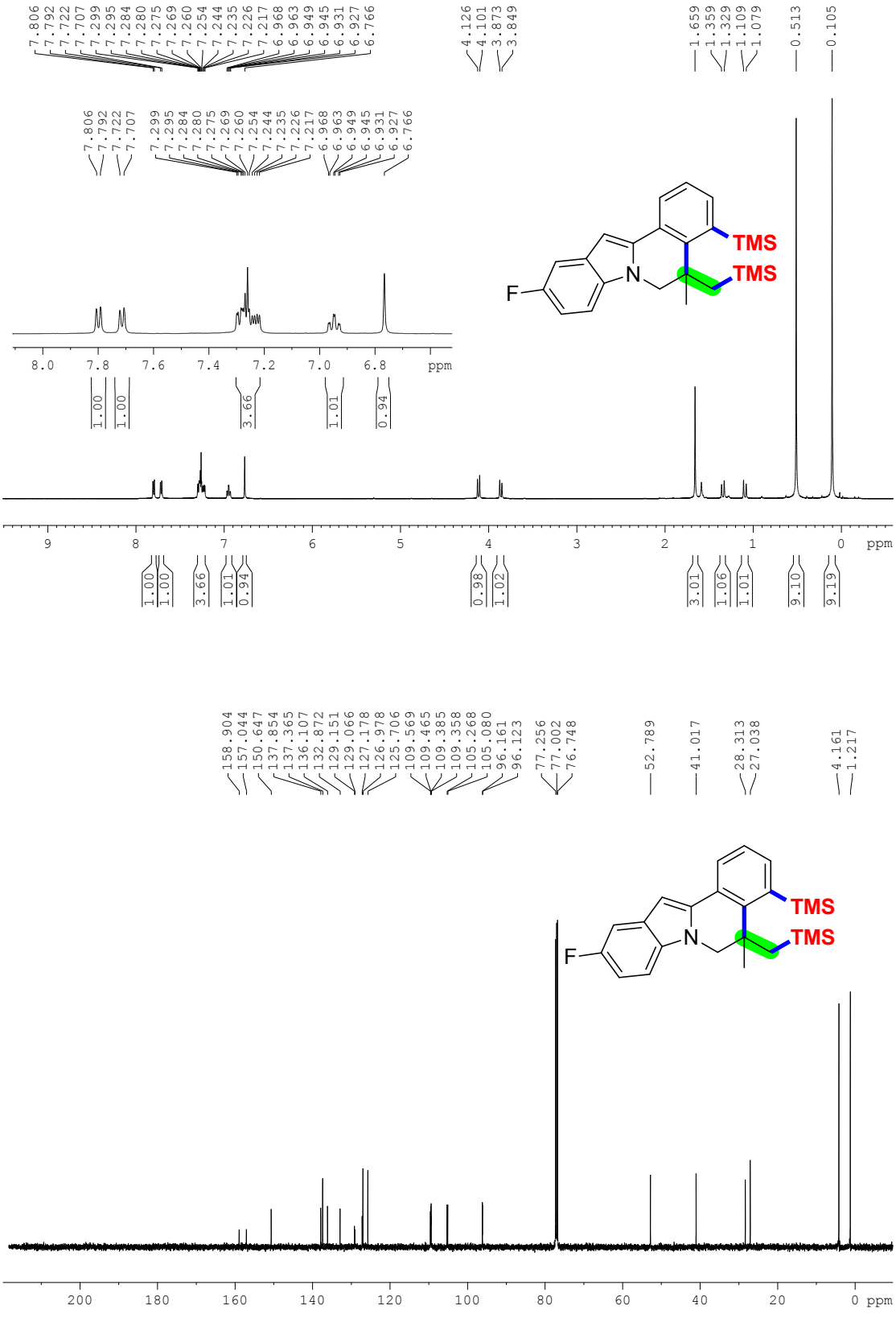




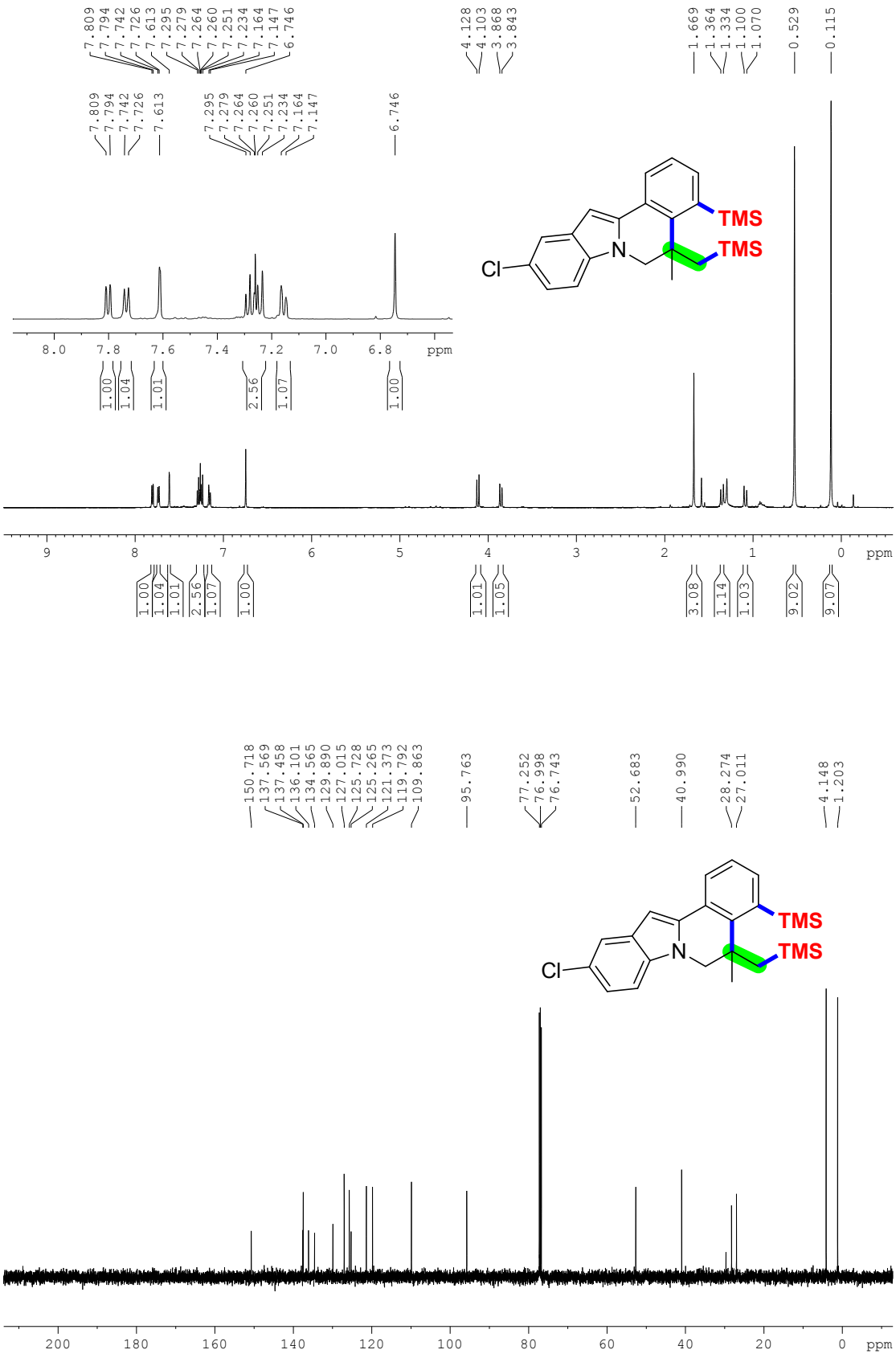
^{1}H and ^{13}C Spectrum of Compound **4b**



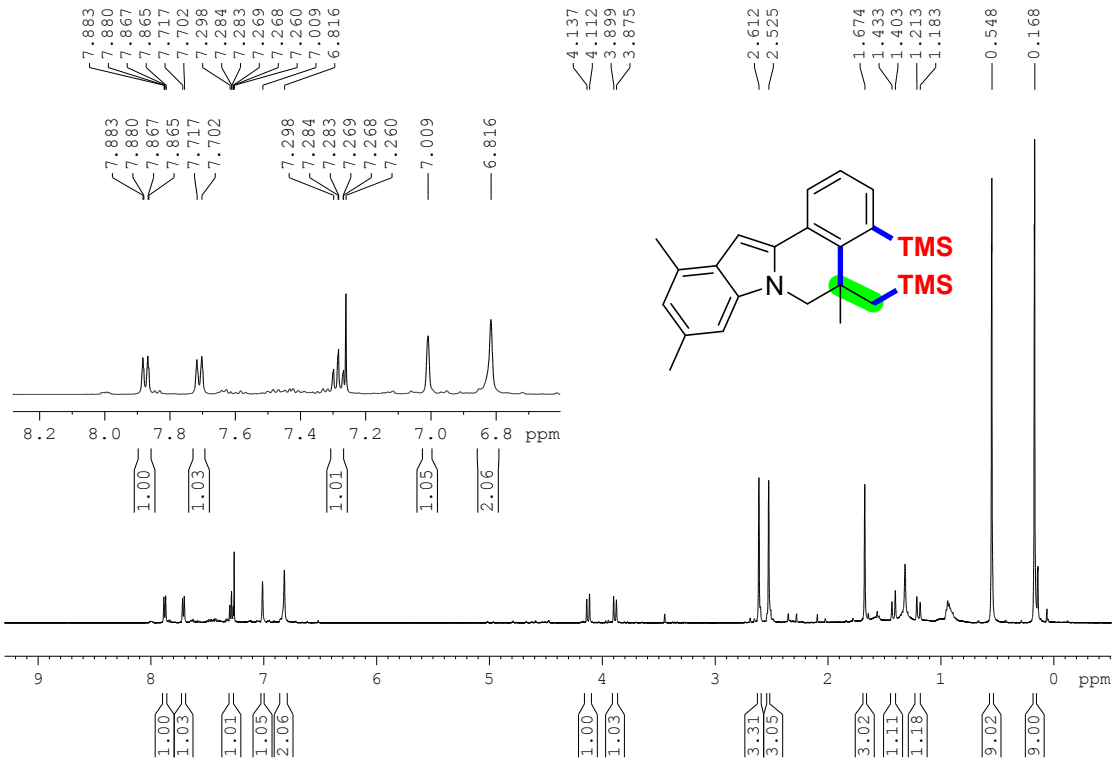
^{1}H and ^{13}C Spectrum of Compound **4d**

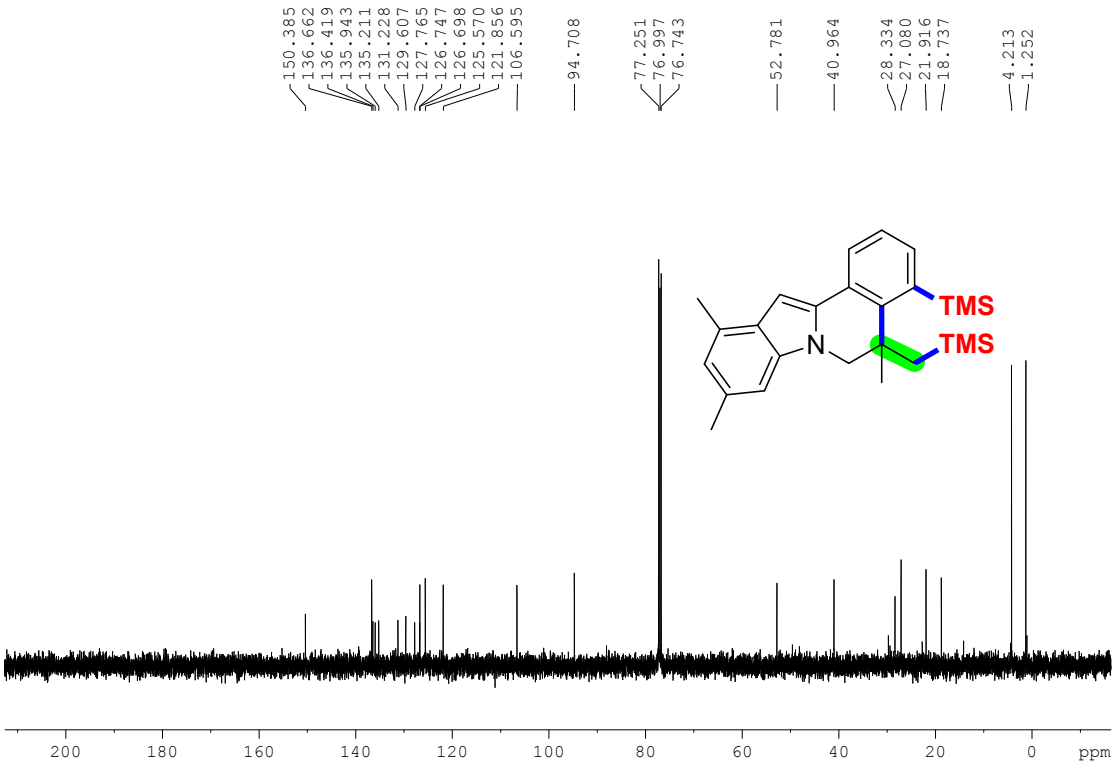


^{1}H and ^{13}C Spectrum of Compound **4e**

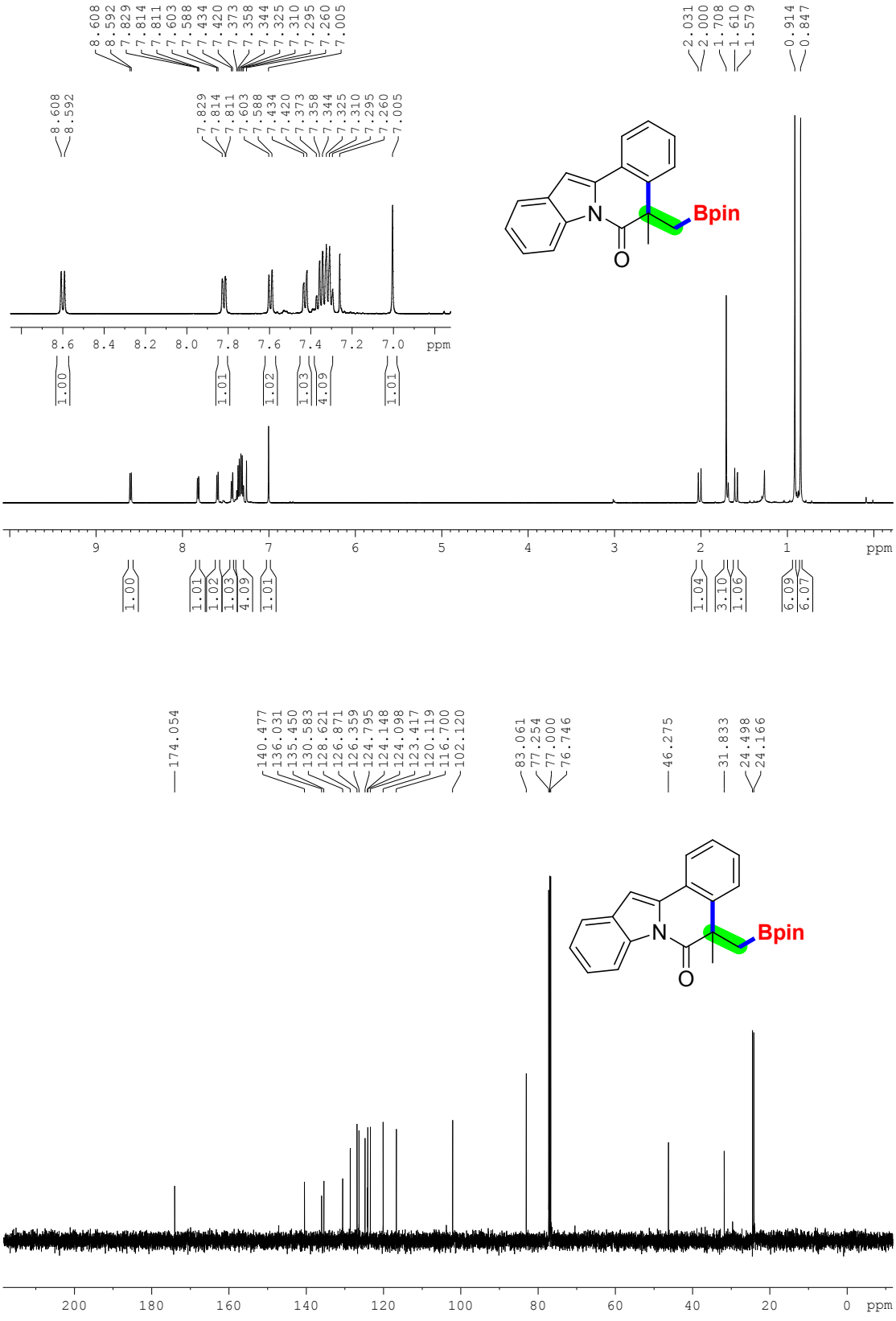


^{1}H and ^{13}C Spectrum of Compound **4h**

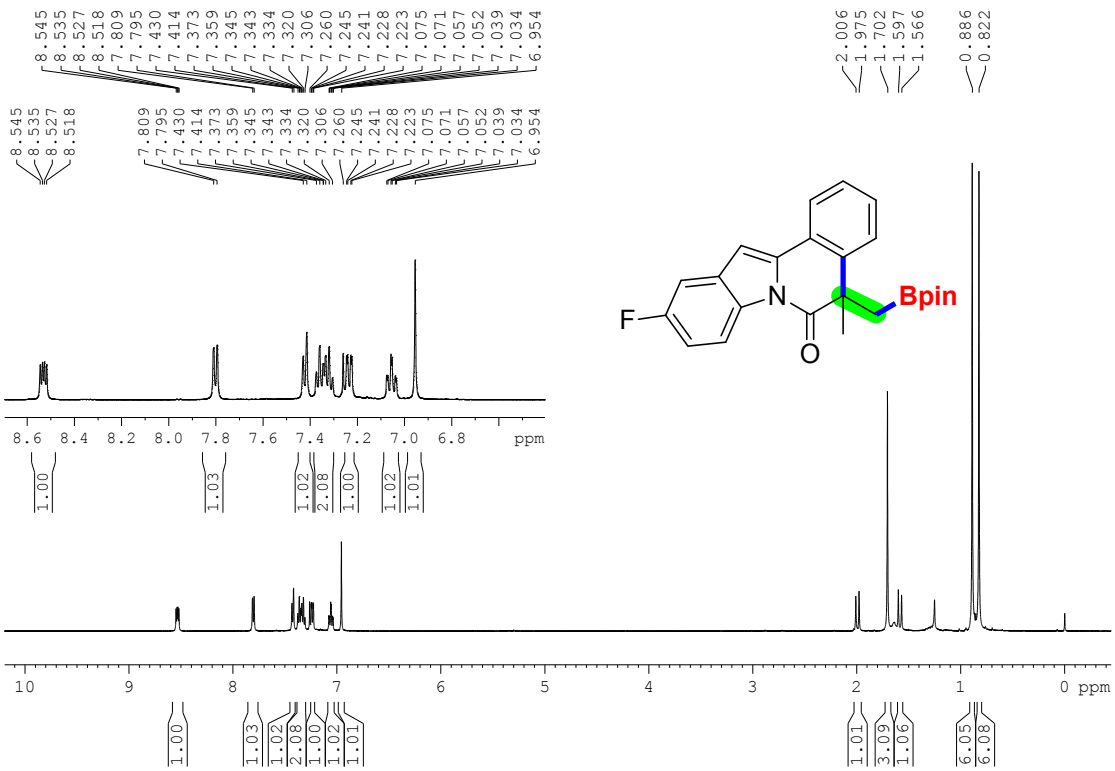


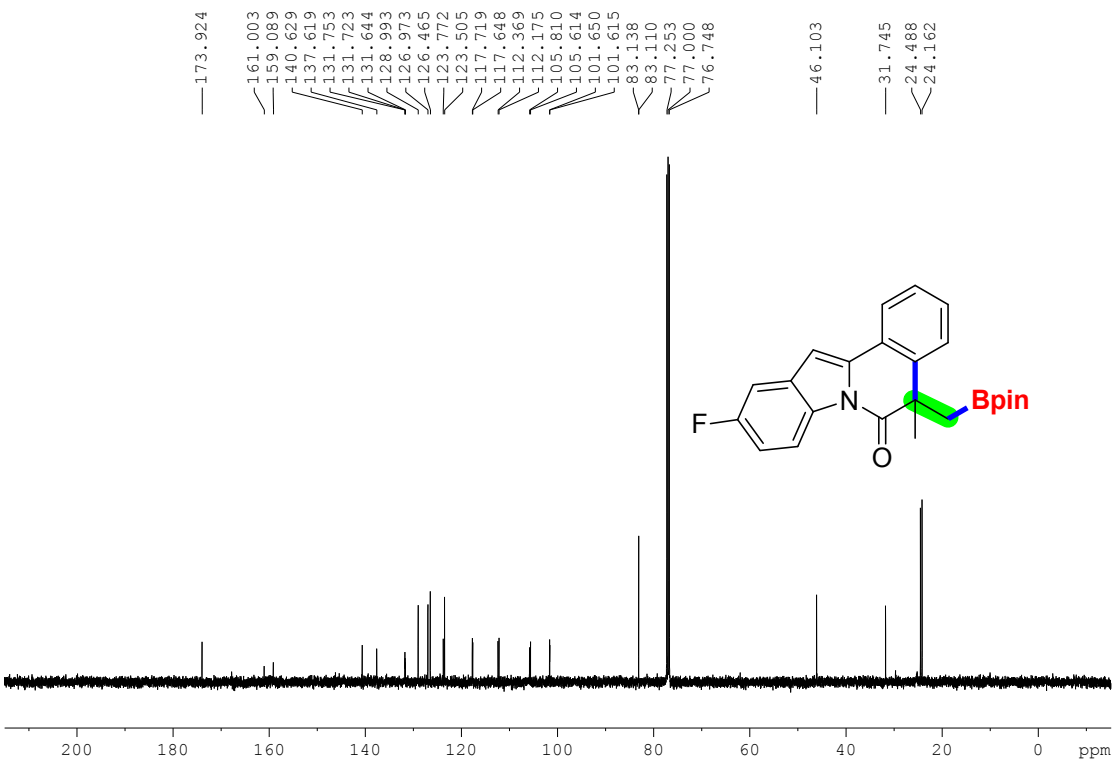


^{1}H and ^{13}C Spectrum of Compound **5a**

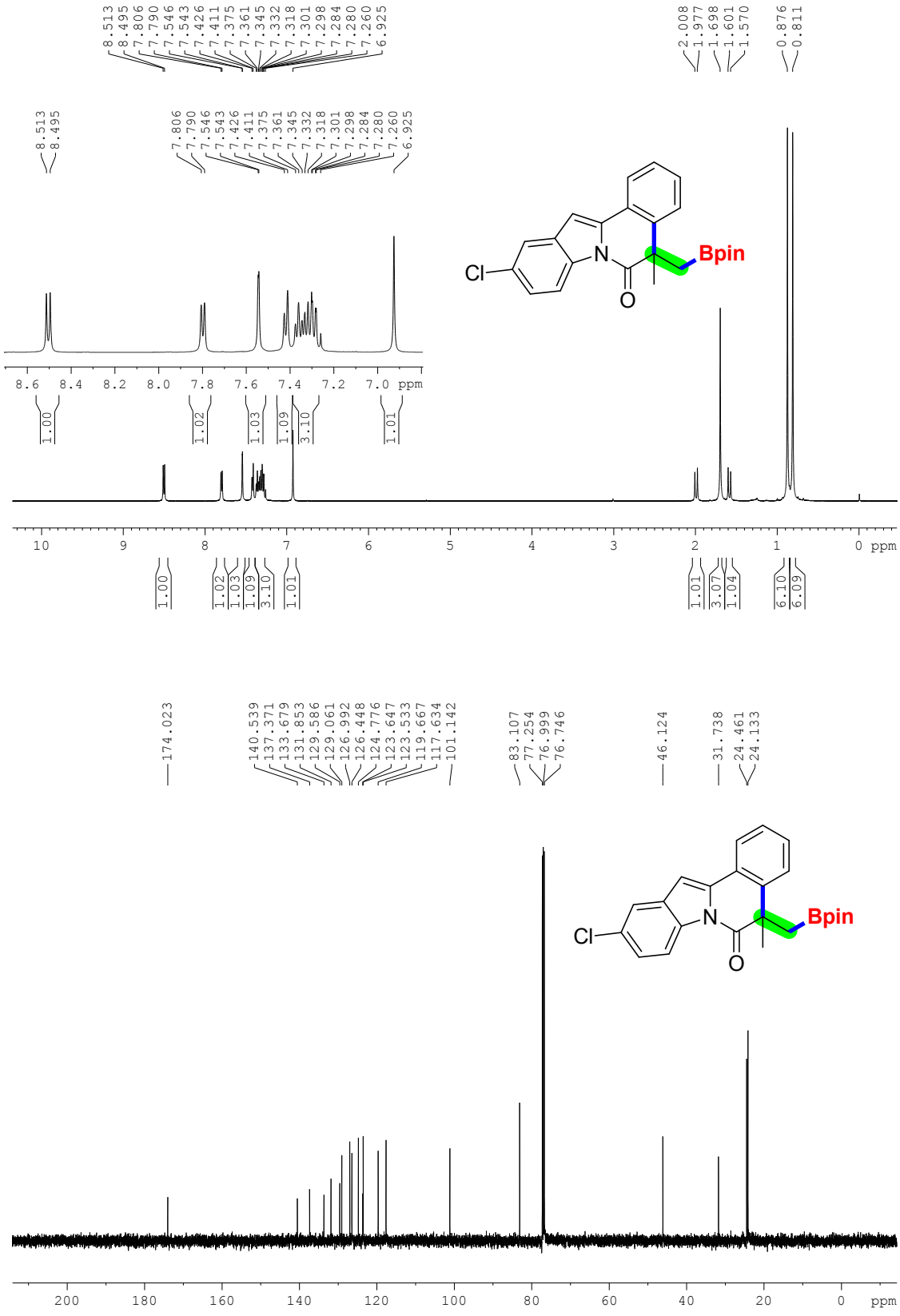


^{1}H and ^{13}C Spectrum of Compound **5d**

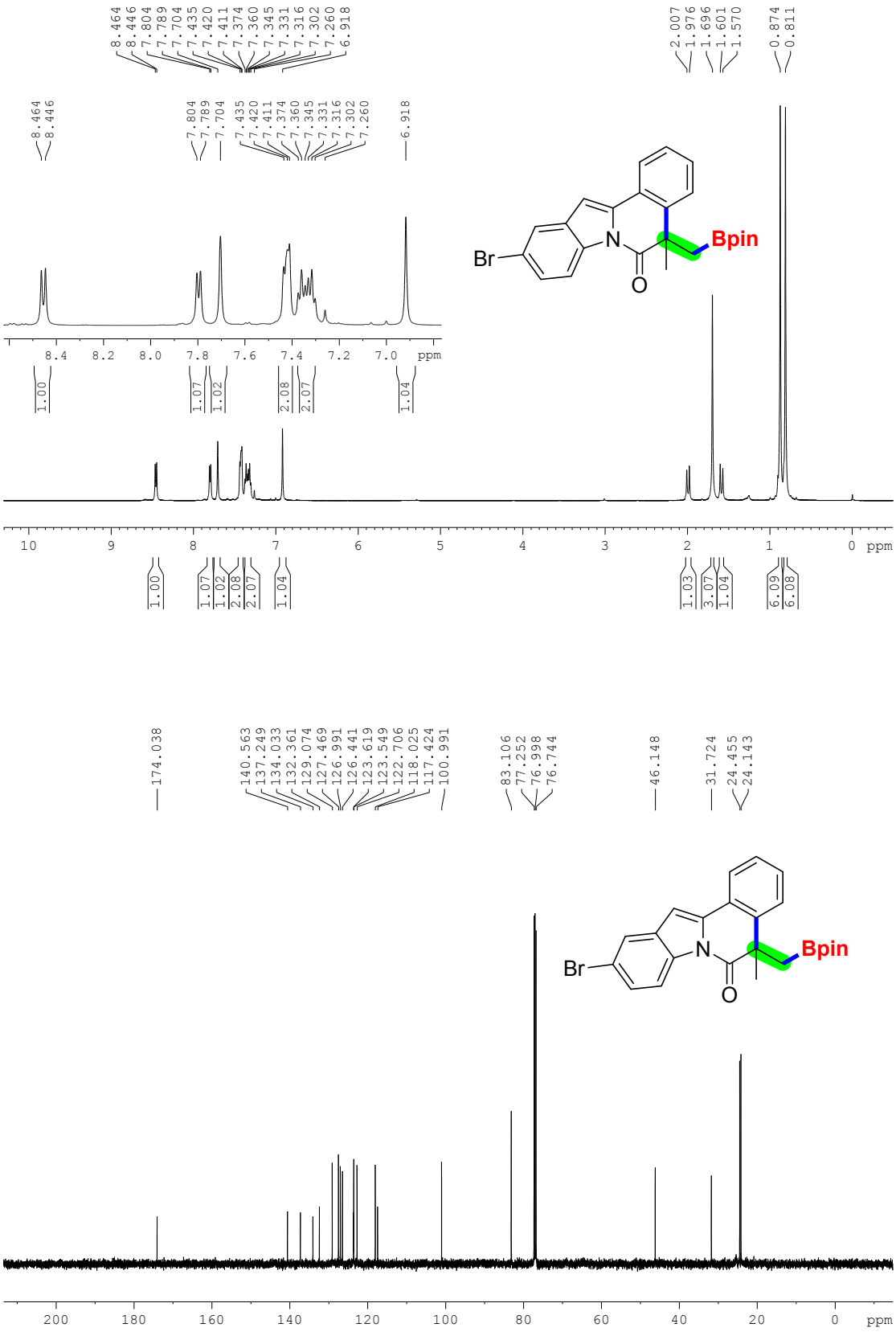




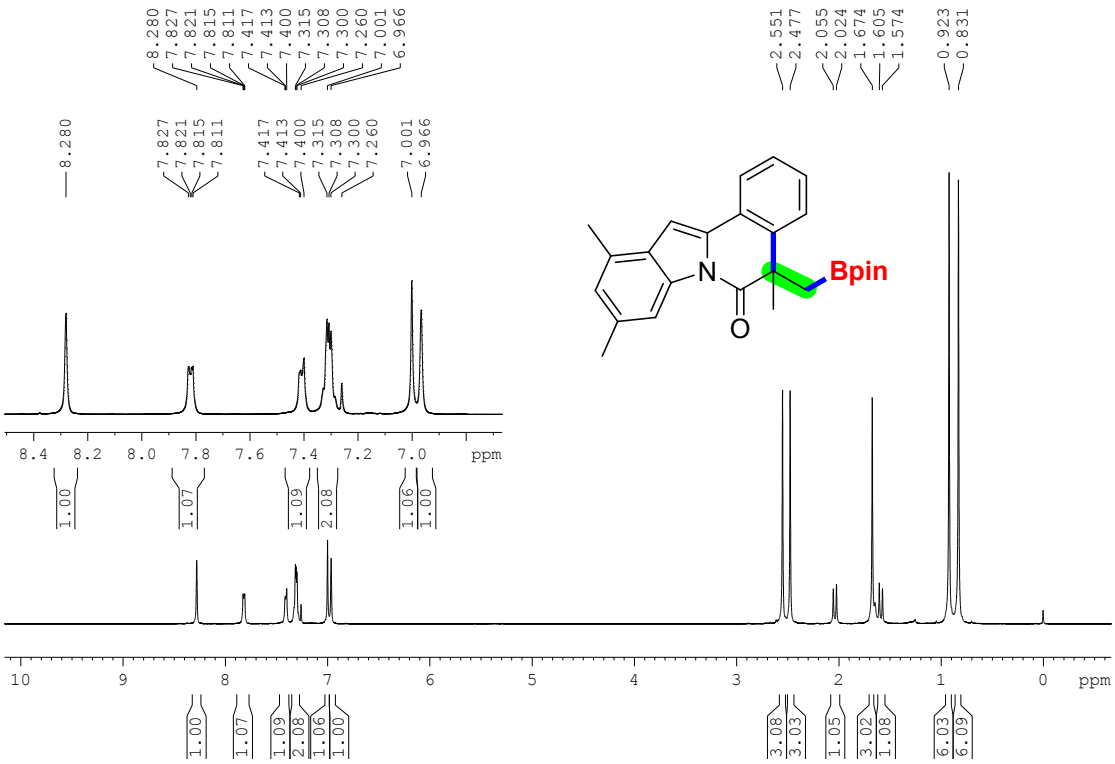
^{1}H and ^{13}C Spectrum of Compound **5e**

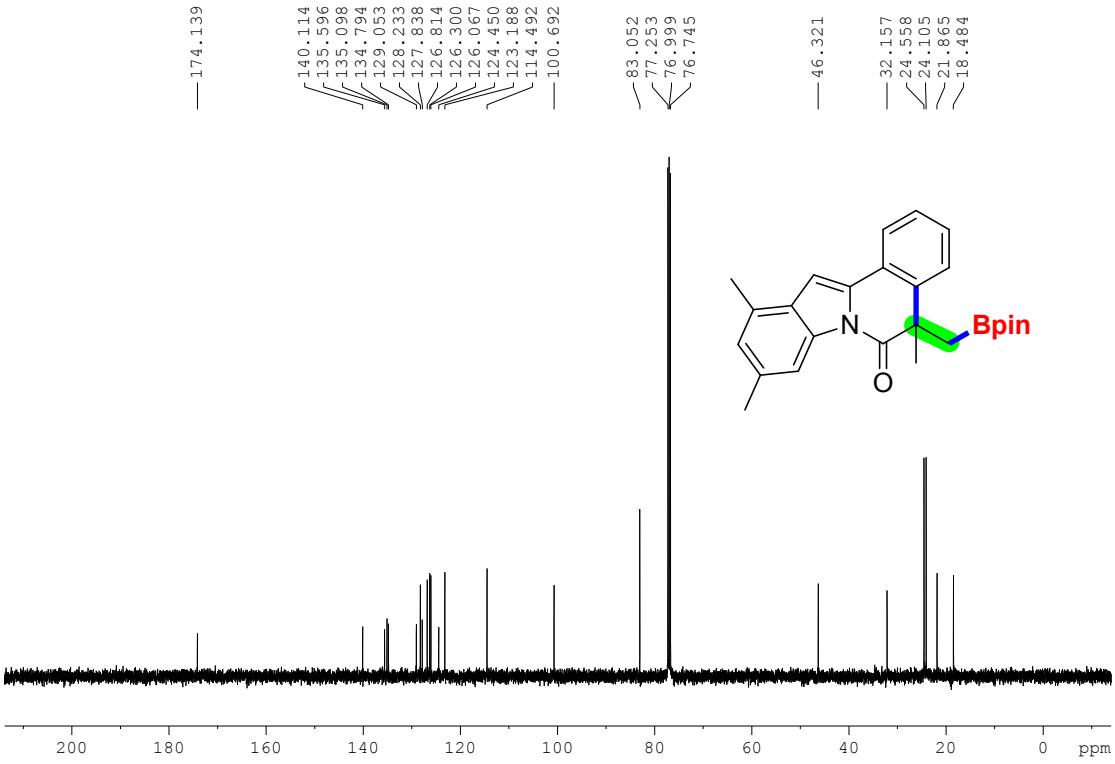


^{1}H and ^{13}C Spectrum of Compound **5f**

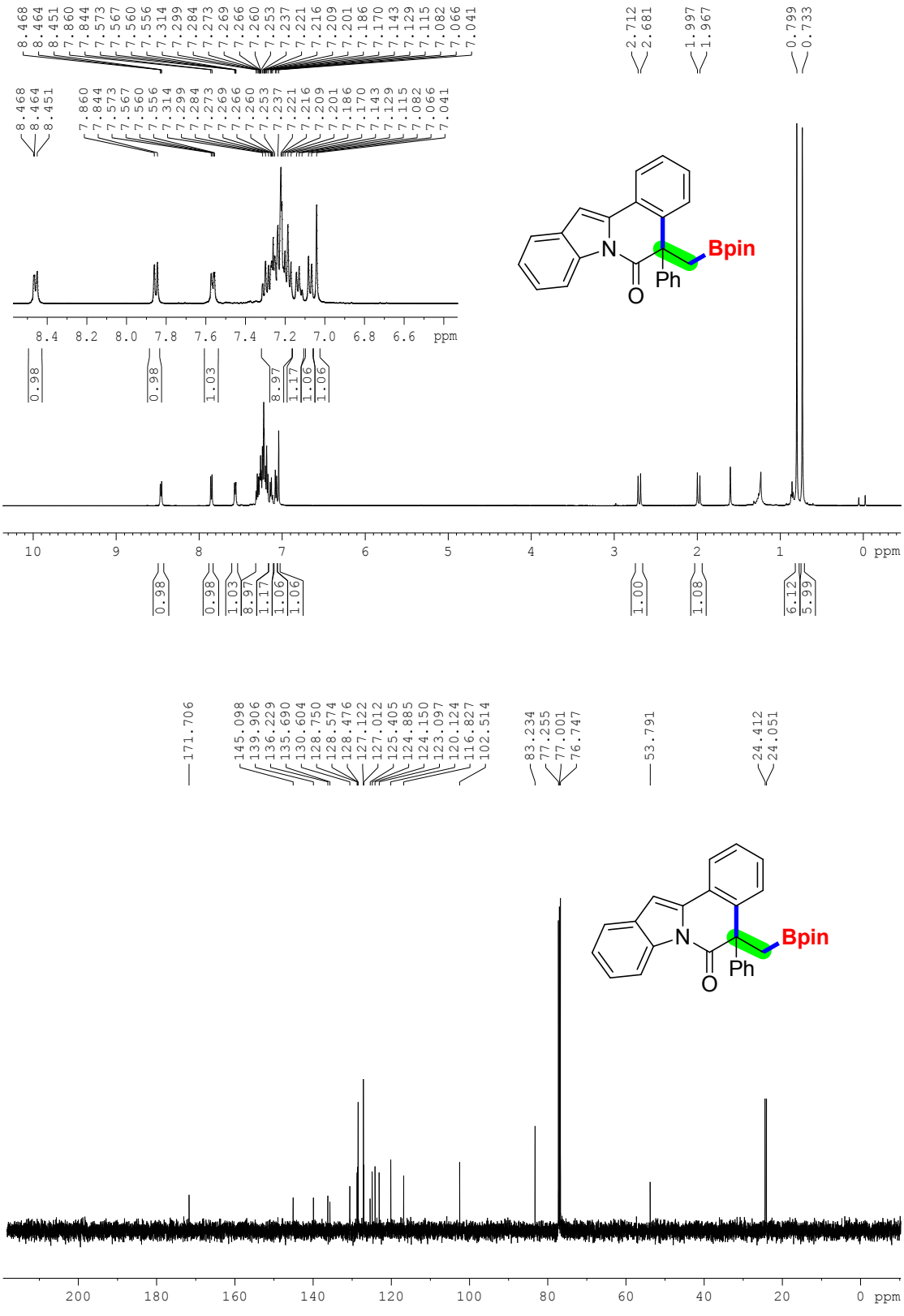


^{1}H and ^{13}C Spectrum of Compound **5h**

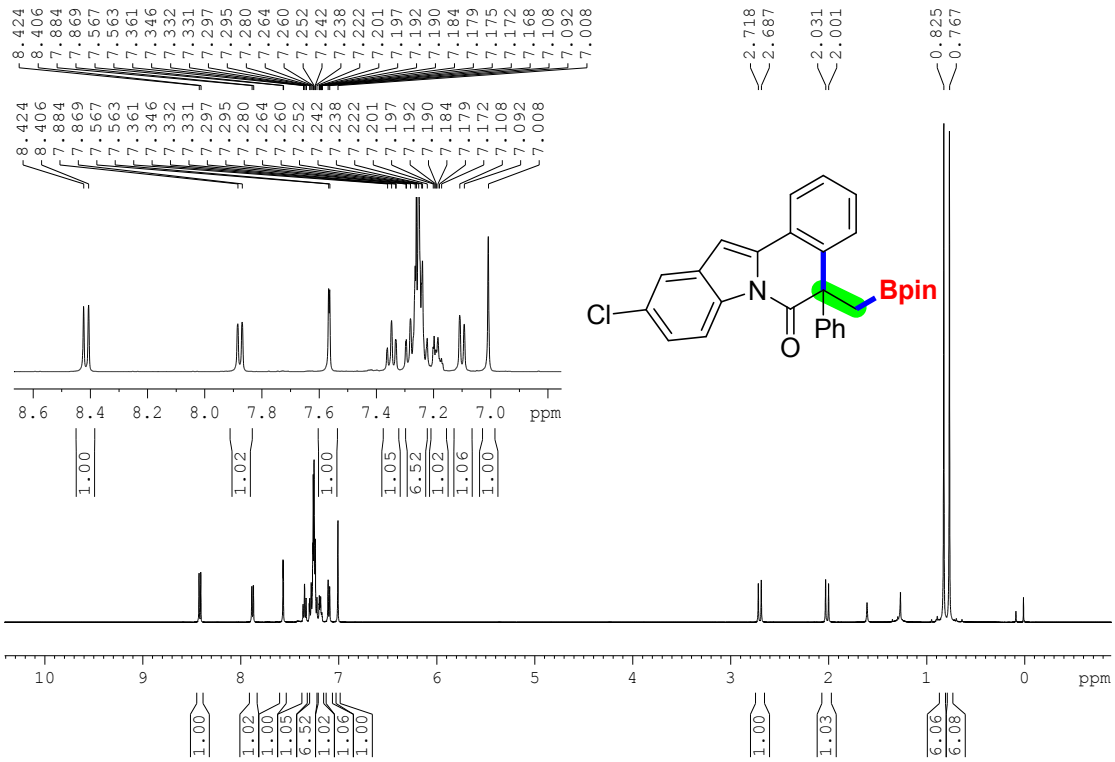


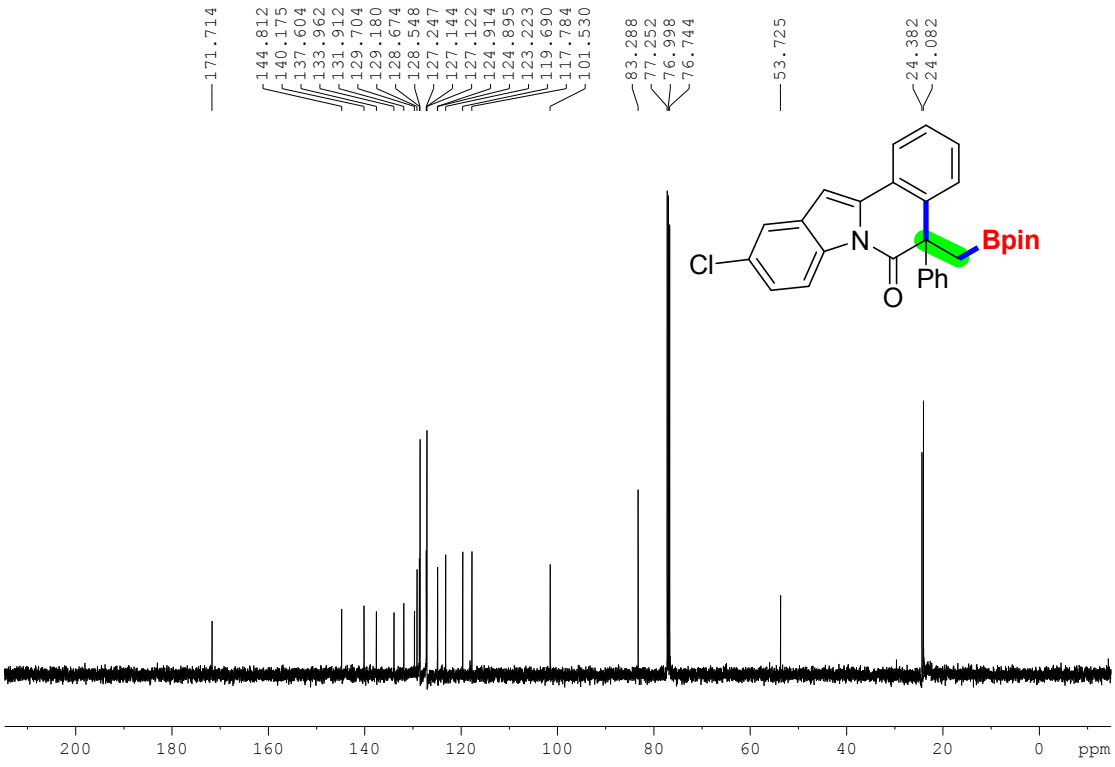


^{1}H and ^{13}C Spectrum of Compound **5k**

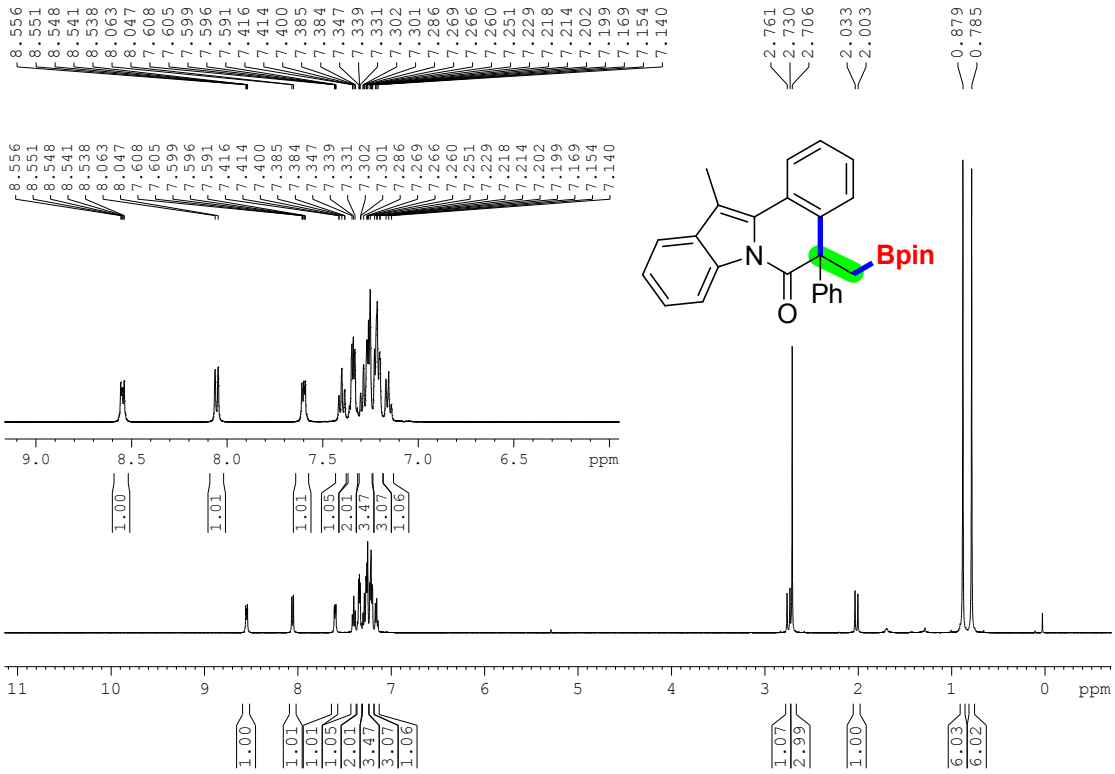


^{1}H and ^{13}C Spectrum of Compound **5l**





^{1}H and ^{13}C Spectrum of Compound **5m**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8.047
7.608
7.605
7.599
7.596
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7.416
7.414
7.400
7.385
7.384
7.347
7.339
7.331
7.302
7.301
7.286
7.269
7.266
7.260
7.251
7.229
7.218
7.214
7.202
7.199
7.169
7.154
7.140
2.761
2.730
2.706
2.033
2.003
0.879
0.785
N
O
Ph
Bpin
9.0
8.5
8.0
7.5
7.0
6.5
ppm
1.00
1.01
1.01
1.05
2.01
3.47
3.07
1.06
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
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1.01
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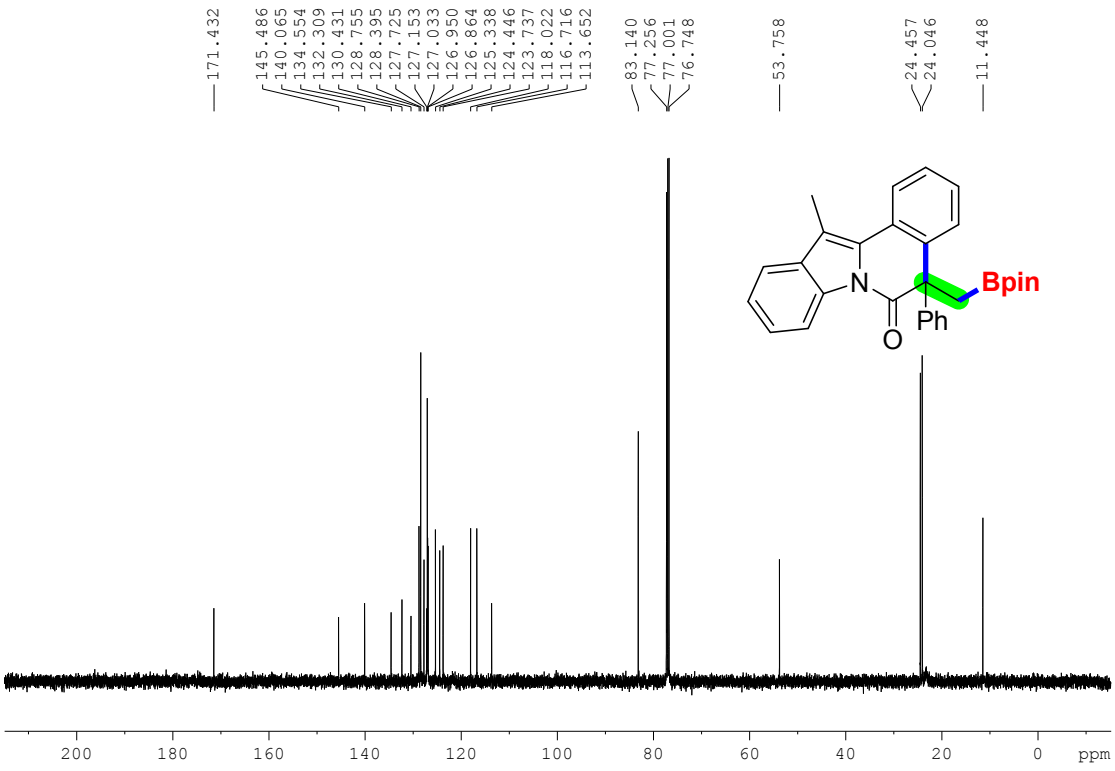
2.01
3.47
3.07
1.06
1.07
2.99
1.00
6.03
6.02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132.309
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128.755
128.395
127.725
127.153
127.033
126.950
126.864
125.338
124.446
123.737
118.022
116.716
113.652
83.140
77.256
77.001
76.748
53.758
24.457
24.046
11.448
N
O
Ph
Bpin
200
180
160
140
120
100
80
60
40
20
0
ppm