

Supporting Information

Access to Quaternary Stereogenic Centers via Rhodium(III)-Catalyzed Annulations between 2-Phenylindoles and Ketenes

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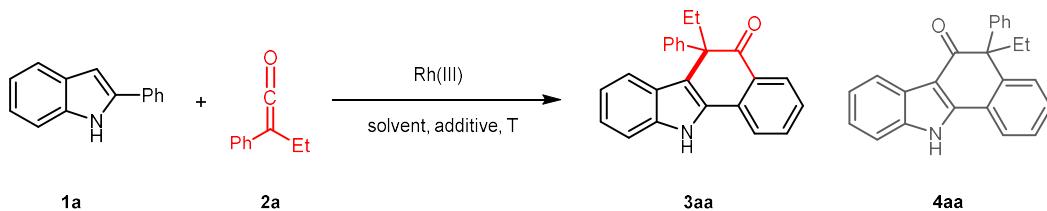
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1. General Information

Unless otherwise noted, all the coupling reactions were carried out in flame-dried pressure tubes with a Teflon screw cap under nitrogen atmosphere. Solvents were purified and dried by standard procedures. All chemicals were obtained from commercial sources and were used as received unless otherwise noted. 2-Phenylindoles¹⁻³ and ketenes⁴ were prepared by following literature reports. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 spectrometer (400 MHz for ¹H, 101 MHz for ¹³C, and 376 MHz for ¹⁹F). All coupling constants were reported in Hz. The residual solvent signals were used as references for ¹H and ¹³C NMR spectra and the chemical shifts were converted to the TMS scale {CDCl₃: δ ¹H = 7.26 ppm, δ ¹³C = 77.16 ppm; CD₂Cl₂: δ ¹H = 5.32 ppm, δ ¹³C = 53.84 ppm; (CD₃)₂SO: δ ¹H = 2.50 ppm, δ ¹³C = 39.52 ppm; CD₃CN: δ ¹H = 1.94 ppm, δ ¹³C = 1.32, 118.26}. HRMS data were obtained using a TOF mode. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

2. Optimization Studies

Table S1. Optimization Studies of Coupling of 2-Phenylindoles with Ketenes.^a



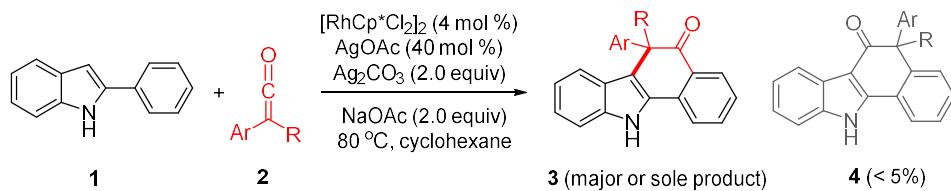
entry	oxidant (equiv)	base	solvent	yield (%)	yield (%)
				3aa	4aa
1	AgOAc (2.2)	Na ₂ CO ₃	DCE	ND	36
2	AgOAc (2.2)	K ₂ CO ₃	DCE	ND	28
3	AgOAc (2.2)	LiOAc	DCE	ND	45
4	AgOAc (2.2)	KOAc	DCE	trace	ND
5	AgOAc (2.2)	Li ₂ CO ₃	DCE	ND	41
6	Ag ₂ CO ₃ (2.0)	CS ₂ CO ₃	DCE	NR	
7 ^b	AgOAc (2.2)	K ₂ CO ₃	EtOH	ND	<5
8 ^b	AgOAc (2.2)	NaOAc	MeOH	ND	<5
9 ^b	AgOAc (2.2)	Li ₂ CO ₃	MeOH	ND	<5
10	AgOAc (2.2)	Li ₂ CO ₃	DCE	ND	17
11	AgOAc (2.2)	Na ₂ CO ₃	CF ₃ Ph	8	10
12 ^c	AgOAc (2.2)	Na ₂ CO ₃	DCE	15	5
13	AgOAc (2.2)	Na ₂ CO ₃	cyclohexane	17	ND
14	AgOAc (2.2)	Na ₂ CO ₃	THF	22	ND
15	AgOAc (2.2)	Na ₂ CO ₃	σ -xylene	18	ND
16	AgOAc (2.2)	CS ₂ CO ₃	DCE	20	ND
17	Cu(OAc) ₂ (2.0)	Na ₂ CO ₃	CH ₃ Ph	ND	ND
18 ^d	Ag ₂ CO ₃ (2.2)	NaOAc	DCE	43	ND
19	Ag ₂ CO ₃ (2.0)	KOAc	DCE	NR	
20	Ag ₂ CO ₃ (2.0)	CsOAc	DCE	NR	
21	Ag ₂ CO ₃ (2.0)	NaOAc	DCE	45	ND
22 ^b	Ag ₂ CO ₃ (2.0)	NaOAc	DCE	38	ND
23 ^e	Ag ₂ CO ₃ (2.0)	NaOAc	DCE	NR	
24 ^f	Ag ₂ CO ₃ (2.0)	NaOAc	DCE	trace	ND
25	Ag ₂ CO ₃ (2.0)	NaOAc	CF ₃ Ph	50	ND
26	Ag ₂ CO ₃ (2.0)	NaOAc	PhCl	50	ND
27	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	53	ND
28	Ag ₂ CO ₃ (2.0)	NaOAc	<i>n</i> -hexane	NR	
29 ^g	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	35	ND
30 ^h	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	57	ND
31 ^h	Ag ₂ O	NaOAc	cyclohexane	39	ND
32 ⁱ	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	43	ND
33 ^{h,j}	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	38	ND
34 ^k	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	57	ND
35 ^l	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	39	ND
36 ^m	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	10	ND

37 ^{n,o}	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	10	ND
38 ^h	Cu(OAc) ₂	NaOAc	cyclohexane	NR	
39 ⁿ	MesCOOAg (2.2)	NaOAc	cyclohexane	ND	20
40 ^p	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	56	ND
41 ^q	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	66	ND
42 ⁿ	Ag ₂ CO ₃ (2.0)	NaOAc (3.0)	cyclohexane	61	ND
43 ⁿ	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	67	ND
44^{n,r}	Ag₂CO₃ (2.0)	NaOAc	cyclohexane	70	ND
45 ⁿ	Ag ₂ CO ₃ (2.0)	NaOAc (1.5)	cyclohexane	22	ND
46 ⁿ	Ag ₂ CO ₃ (2.0)	HCOONa	cyclohexane	41	ND
47 ⁿ	Ag ₂ CO ₃ (2.0)	C ₂ H ₅ COONa	cyclohexane	43	ND
48 ⁿ	Ag ₂ CO ₃ (2.0)	CF ₃ COONa	cyclohexane	55	ND
49 ⁿ	Ag ₂ CO ₃ (2.0)	TsONa	cyclohexane	44	ND
50 ^s	Ag ₂ CO ₃ (2.0)	NaOAc	cyclohexane	62	ND
51 ^{h,q}	Ag ₂ CO ₃ (2.0)	Ba(OAc) ₂ (0.1)	cyclohexane	64	ND
52 ^{n,s}	Ag ₂ CO ₃ (2.0)	C ₂ H ₅ COONa	cyclohexane	58	ND

^aReaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [RhCp^{*}Cl₂]₂ (4 mol %), AgSbF₆ (16 mol %), base (2.0 equiv) unless otherwise noted, solvent (2.0 mL) under N₂ for 10 h, 80 °C, isolated yield after column chromatography. ^b[RhCp^{*}(MeCN)₃]₂(SbF₆)₂ (8 mol %) was used instead of [RhCp^{*}Cl₂]₂/AgSbF₆. ^cPivOH (1.0 equiv), 60 °C. ^dHOAc (0.2 mmol). ^eZn(NTf)₂ 20 mol %. ^fZn(OAc)₂ 20 mol %. ^gFe(OAc)₂ 20 mol %. ^hAgOAc was used instead of AgSbF₆. ⁱAgPF₆ 16 mol %. ^jCp^{*}Rh(OAc)₂. ^kAgNO₃ 40 mol %. ^lAgOTf 40 mol %. ^mAgBF₄ 40 mol %. ⁿAgOAc 40 mol % instead of AgSbF₆, 15 h. ^oTBAA (0.4 mmol). ^psilver cyclohexanecarboxylate (40 mol %). ^qAgOAc (0.2 mmol), 15 h. ^rSolvent (3.0 mL). ^sAg₂WO₄ (20 mol %).

3 The Synthesis Products

3.1 General Procedure for Synthesis of **3**.



2-Phenylindole (**1**, 0.2 mmol), ketene (**2**, 0.4 mmol), [RhCp^{*}Cl₂]₂ (4 mol %), AgOAc (0.08 mmol), Ag₂CO₃ (0.4 mmol), NaOAc (0.4 mmol), and cyclohexane (3.0 mL) were charged into a pressure tube. The reaction mixture was stirred at 80 °C for 15 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (8:1) to afford product **3**.

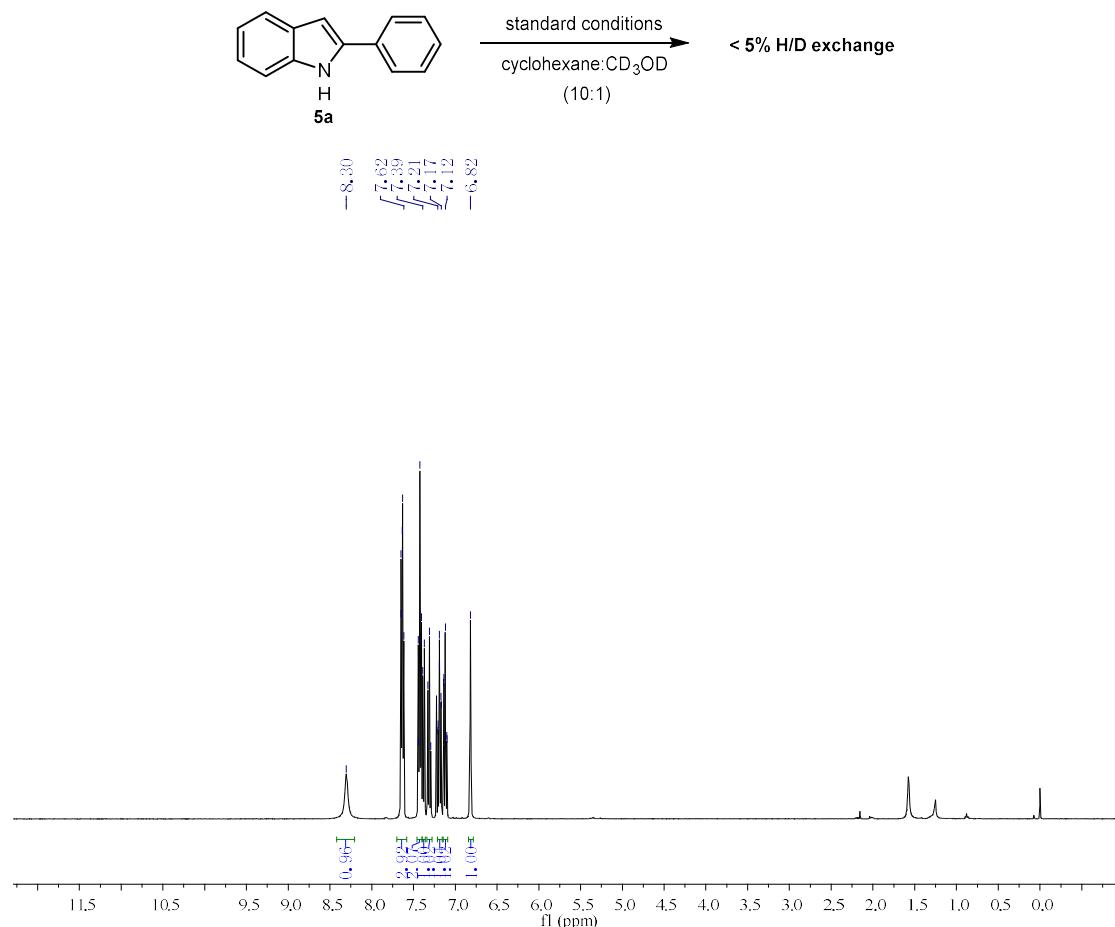
3.2 Synthesis of **3aa** at a 1 mmol scale

2-Phenylindole (**1a**, 193 mg, 1 mmol), phenyl ethyl ketene (**2a**, 292 mg, 2 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (4 mol %), AgOAc (0.08 mmol), Ag_2CO_3 (2 mmol), NaOAc (2 mmol), and cyclohexane (15.0 mL) were charged into a pressure tube. The reaction mixture was stirred at 80 °C for 15 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (8:1) to afford product **3aa** (229 mg, 68%).

4. Mechanistic Studies on Annulation between 2-Phenylindoles and Ketenes

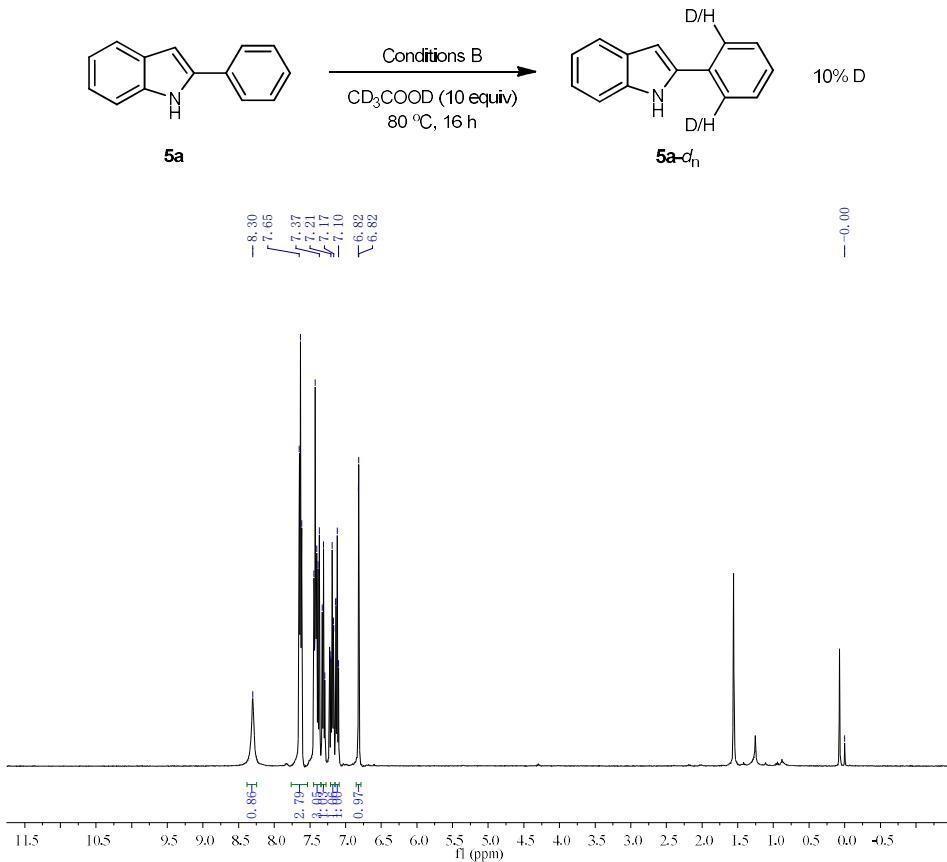
4.1 H/D Exchange of 2-Phenylindole

2-Phenyl-1*H*-indole (0.2 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (4 mol%), AgOAc (0.08 mmol), Ag_2CO_3 (0.4 mmol), NaOAc (0.4 mmol), and cyclohexane/ CD_3OD (10:1) were charged into a pressure tube. The reaction mixture was stirred at 80 °C for 15 h. The 2-phenylindole was isolated after chromatography using EA/PE (1:10), and only slight H/D exchange (< 5%) was observed on the basis of ^1H NMR analysis.



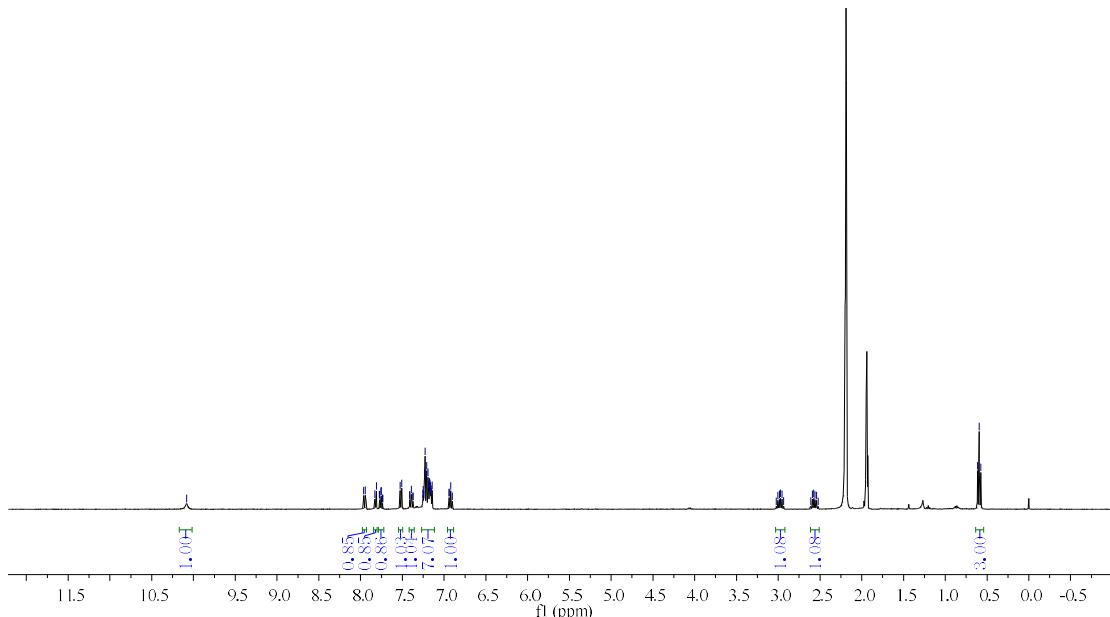
2-Phenylindole (0.2 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (4 mol%), AgOAc (0.08 mmol), Ag_2CO_3 (0.4 mmol), NaOAc (0.4 mmol), CD_3COOD (2 mmol), and cyclohexane were charged into a pressure tube. The mixture was

stirred at 80 °C for 15 h. The recovered 2-phenylindole was isolated after chromatography using EA/PE (1:10). Only slight H/D exchange was observed on the basis of ¹H NMR analysis.



4.2 KIE Experiments

Two independent reactions with **1a** or deuterated substrate **1a-d₅** were performed under the standard conditions. Suspensions of **1a** (0.1 mmol) or **1a-d₅** (0.1 mmol), [RhCp*(MeCN)₃]₂(SbF₆)₂ (8 mol%), ketene **2a** (0.2 mmol), Ag₂CO₃ (0.2 mmol), AgOAc (0.04 mmol), NaOAc (0.2 mmol), and cyclohexane (2 mL) were stirred side-by-side in an oil bath at 80 °C for 40 min under nitrogen. Both reactions were quenched and the two reactions mixtures were rapidly combined, and the volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography. KIE value ($k_H/k_D = 6.0$) was determined on the basis of ¹H NMR analysis.



5. Crystal Structure of 3aa

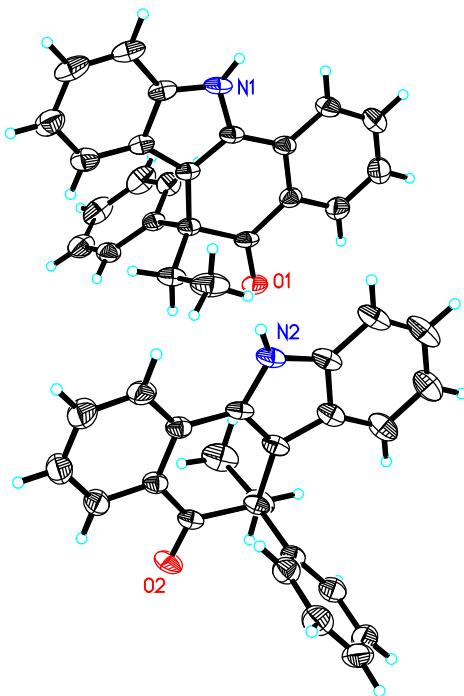


Table S3. Crystal data and structure refinement for cd17084.

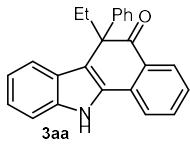
Identification code	cd17084		
Empirical formula	C ₂₄ H ₁₉ N ₂ O ₂		
Formula weight	337.40		
Temperature	293(2) K		
Wavelength	0.71073 Å		
Crystal system	Orthorhombic		
Space group	Pna21		
Unit cell dimensions	a = 15.9550(15) Å	α= 90°.	
	b = 8.8361(9) Å	β= 90°.	
	c = 25.229(2) Å	γ = 90°.	
Volume	3556.8(6) Å ³		
Z	8		
Density (calculated)	1.260 Mg/m ³		
Absorption coefficient	0.076 mm ⁻¹		

F(000)	1424
Crystal size	0.200 x 0.170 x 0.140 mm ³
Theta range for data collection	2.442 to 25.498°.
Index ranges	-19<=h<=19, -8<=k<=10, -30<=l<=30
Reflections collected	19259
Independent reflections	6605 [R(int) = 0.0373]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6554
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6605 / 3 / 480
Goodness-of-fit on F ²	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.0989
R indices (all data)	R1 = 0.0622, wR2 = 0.1083
Absolute structure parameter	0.2(10)
Largest diff. peak and hole	0.135 and -0.120 e.Å ⁻³

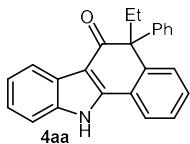
6. References

1. Kim, D.; Kang, M. S.; Song, K.; Kang, S. O.; Ko, J. *Tetrahedron* **2008**, *64*, 10417.
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4. (a) Douglas, J.; Taylor, J. E.; Churchill, G.; Slawin, A. M.; Smith, A. D. *J. Org. Chem.* **2013**, *78*, 3925. (b) Lv, H.; Zhang, Y. R.; Huang, X. L.; Ye, S. *Adv. Synth. Catal.* **2008**, *350*, 2715.
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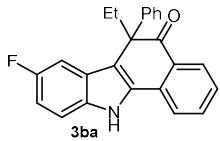
7. Characterization Data



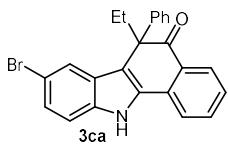
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 70% (47.2 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.73 (s, 1H), 8.06 (d, $J = 7.8$ Hz, 1H), 7.63 – 7.56 (m, 2H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.33 – 7.31 (m, 3H), 7.22 – 7.13 (m, 5H), 6.99 – 6.96 (m, 1H), 3.09 (dq, $J = 14.3, 7.2$ Hz, 1H), 2.56 (dq, $J = 14.8, 7.4$ Hz, 1H), 0.66 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.0, 142.5, 137.9, 134.6, 132.4, 130.5, 129.2, 128.7, 128.6, 127.6, 127.6, 127.1, 126.9, 123.6, 120.8, 120.5, 120.4, 117.8, 111.7, 58.5, 32.4, 10.1. HRMS: [M + H] $^+$ calculated for $\text{C}_{24}\text{H}_{20}\text{NO}^+$: 338.1539, found: 338.1547.



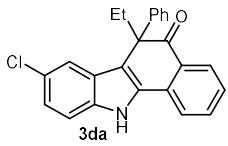
Purified by column chromatography using ethyl acetate/petroleum ether, Gray solid, 45% (30.3 mg). ^1H NMR {400 MHz, $(\text{CD}_3)_2\text{SO}$ } δ 12.7 (s, 1H), 8.19 (d, $J = 6.7$ Hz, 1H), 8.03 (d, $J = 8.7$ Hz, 1H), 7.58 (d, $J = 9.8$ Hz, 1H), 7.50 – 7.4 (m, 1H), 7.43 – 7.40 (m, 1H), 7.34 – 7.30 (m, 1H), 7.23 – 7.10 (m, 7H), 2.91 – 2.86 (m, 1H), 2.37 – 2.32 (m, 1H), 0.48 (bs, 3H). ^{13}C NMR {400 MHz, $(\text{CD}_3)_2\text{SO}$ } δ 193.3, 146.1, 145.5, 145.0, 137.7, 129.8, 129.4, 128.3, 127.1, 127.0, 126.4, 125.5, 124.6, 124.1, 122.6, 122.6, 120.9, 112.2, 110.4, 60.2, 31.4, 8.8. HRMS: [M + H] $^+$ calculated for $\text{C}_{24}\text{H}_{20}\text{NO}^+$: 338.1539, found: 338.1545.



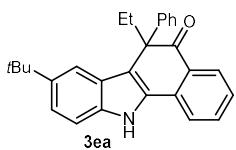
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 69% (49.0 mg). ^1H NMR (400 MHz, CD_3CN) δ 10.18 (s, 1H), 7.96 (d, $J = 7.8$ Hz, 1H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.77 – 7.73 (m, 1H), 7.49 (dd, $J = 8.8, 4.5$ Hz, 1H), 7.43 – 7.39 (m, 1H), 7.26 – 7.14 (m, 5H), 6.98 – 6.93 (m, 1H), 6.80 (dd, $J = 10.0, 2.0$ Hz, 1H), 2.94 (dq, $J = 14.5, 7.2$ Hz, 1H), 2.56 – 2.47 (m, 1H), 0.60 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 202.0, 158.4 (d, $J = 233.3$ Hz), 143.8, 136.0, 135.7, 133.5, 133.1, 129.4, 129.4, 129.1, 128.9, 128.1, 128.0, 127.3 (d, $J = 10.1$ Hz), 122.4, 117.6 (d, $J = 8.1$ Hz), 113.9 (d, $J = 9.8$ Hz), 112.2 (d, $J = 26.4$ Hz), 105.3 (d, $J = 24.2$ Hz), 58.6, 31.7, 9.9. HRMS: [M + H] $^+$ calculated for $\text{C}_{24}\text{H}_{19}\text{FNO}^+$: 356.1445, found: 356.1451.



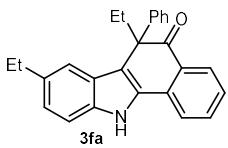
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 52% (43.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.76 (s, 1H), 8.06 (d, $J = 7.8$ Hz, 1H), 7.67 – 7.63 (m, 1H), 7.58 (d, $J = 7.7$ Hz, 1H), 7.42 – 7.15 (m, 9H), 3.09 (dq, $J = 13.7, 6.9$ Hz, 1H), 2.49 (dq, $J = 14.7, 7.4$ Hz, 1H), 0.65 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR {101 MHz, $(\text{CD}_3)_2\text{SO}$ } δ 200.4, 142.4, 136.7, 135.2, 132.0, 128.5, 128.2, 128.0, 127.9, 127.5, 127.0, 126.9, 125.3, 124.4, 122.2, 121.4, 115.1, 114.1, 112.1, 57.4, 30.6, 9.7. HRMS: $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{19}\text{BrNO}^+$: 416.0645, 416.0638.



Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 67% (49.7 mg). ^1H NMR {400 MHz, $(\text{CD}_3)_2\text{SO}$ } δ 12.21 (s, 1H), 8.07 (d, $J = 7.8$ Hz, 1H), 7.91 (d, $J = 7.7$ Hz, 1H), 7.85 – 7.81 (m, 1H), 7.53 (d, $J = 8.6$ Hz, 1H), 7.47 – 7.43 (m, 1H), 7.26 – 7.22 (m, 2H), 7.20 – 7.15 (m, 4H), 7.08 (d, $J = 1.7$ Hz, 1H), 2.91 (dq, $J = 13.9, 7.0$ Hz, 1H), 2.51 – 2.44(m, 1H), 0.54 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR {101 MHz, $(\text{CD}_3)_2\text{SO}$ } δ 200.5, 142.5, 136.5, 135.3, 132.2, 132.1, 128.6, 128.2, 128.1, 127.9, 127.0, 127.0, 126.8, 124.1, 122.8, 122.2, 118.4, 115.3, 113.7, 57.4, 30.6, 9.7. HRMS: $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{19}\text{ClNO}^+$: 372.1150, found: 372.1147.

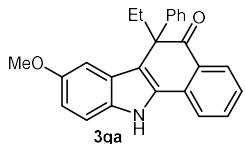


Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 50% (39.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.53 (s, 1H), 8.05 (d, $J = 8.5$ Hz, 1H), 7.65 – 7.61 (m, 1H), 7.55 (d, $J = 7.7$ Hz, 1H), 7.39 – 7.25 (m, 5H), 7.23 – 7.13 (m, 4H), 3.15 – 2.92 (m, 1H), 2.60 – 2.51 (m, 1H), 1.23 (s, 9H), 0.69 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.3, 143.2, 142.7, 136.1, 134.6, 132.6, 130.54, 129.1, 128.8, 128.5, 127.7, 127.4, 127.0, 126.8, 121.9, 120.3, 118.0, 116.6, 111.0, 58.5, 34.6, 32.4, 31.8, 10.0. HRMS: $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{28}\text{H}_{28}\text{NO}^+$: 394.2165, found: 394.2167.

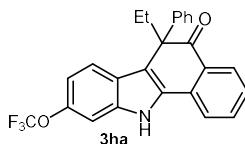


Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 50% (36.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.56 (s, 1H), 7.97 (d, $J = 7.8$ Hz, 1H), 7.55

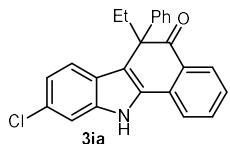
– 7.47 (m, 2H), 7.30 – 7.21 (m, 4H), 7.14 – 7.06 (m, 3H), 7.01 – 6.98 (d, J = 8.4 Hz, 1H), 6.93 (s, 1H), 3.01 (dq, J = 14.3, 7.2 Hz, 1H), 2.55 – 2.44 (m, 3H), 1.09 (t, J = 7.6 Hz, 3H), 0.60 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.0, 142.5, 136.5, 136.4, 134.6, 132.5, 130.6, 129.2, 128.7, 128.5, 127.6, 127.4, 127.2, 127.0, 124.2, 120.3, 119.3, 117.4, 111.5, 58.6, 32.3, 29.1, 16.4, 10.1. HRMS: [M + H]⁺ calculated for $\text{C}_{26}\text{H}_{24}\text{NO}^+$: 366.1852, found: 366.1860.



Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 54% (42.4 mg). ^1H NMR (400 MHz, CD_3CN) δ 9.96 (s, 1H), 7.94 (dd, J = 7.8, 0.8 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.76 – 7.71 (m, 1H), 7.42 – 7.36 (m, 2H), 7.27 – 7.15 (m, 5H), 6.83 (dd, J = 8.9, 2.5 Hz, 1H), 6.56 (d, J = 2.4 Hz, 1H), 3.62 (s, 3H), 2.93 (dq, J = 13.3, 7.2 Hz, 1H), 2.58 (dq, J = 13.0, 7.4 Hz, 1H), 0.61 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 201.9, 154.7, 143.2, 135.0, 133.5, 132.7, 131.6, 129.1, 129.0, 128.8, 127.8, 127.6, 127.3, 120.8, 117.6, 113.5, 112.7, 102.7, 58.5, 56.0, 31.9, 10.0. HRMS: [M + H]⁺ calculated for $\text{C}_{25}\text{H}_{22}\text{NO}_2^+$: 394.1645, found: 394.1646.

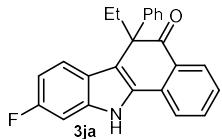


Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 38% (32.0 mg). ^1H NMR (400 MHz, CD_3CN) δ 10.30 (s, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.79 – 7.75 (m, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.25 – 7.17 (m, 5H), 7.10 (d, J = 8.8 Hz, 1H), 7.00 (s, 1H), 2.95 (dq, J = 14.4, 7.2 Hz, 1H), 2.50 (dq, J = 14.8, 7.4 Hz, 1H), 0.60 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 202.0, 143.8, 143.6, 143.5, 137.5, 136.0, 133.9, 132.9, 129.5, 129.4, 129.2, 128.2, 128.0, 127.2, 122.7, 121.6, (q, J = 260.3 Hz), 117.9, 117.7, 113.9, 113.0, 58.7, 31.9, 9.9. HRMS: [M + H]⁺ calculated for $\text{C}_{25}\text{H}_{19}\text{F}_3\text{NO}_2^+$: 422.1362, found: 422.1363.

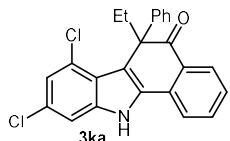


Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 60% (44.5 mg). ^1H NMR (400 MHz, CD_3CN) δ 10.19 (s, 1H), 7.95 (d, J = 6.6 Hz, 1H), 7.80 (d, J = 9.5 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.53 (s, 1H), 7.45 – 7.34 (m, 1H), 7.26 – 7.13 (m, 5H), 7.07 (d, J = 9.8 Hz, 1H), 6.89 (d, J = 9.9 Hz, 1H), 3.00 – 2.91 (m, 1H), 2.51 – 2.46 (m, 1H), 0.56 (t, J =

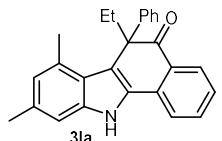
6.4 Hz, 3H). ^{13}C NMR {101 MHz, $(\text{CD}_3)_2\text{SO}$ } δ 200.5, 142.5, 138.4, 135.2, 132.1, 131.6, 128.4, 128.0, 127.9, 127.8, 127.4, 126.9, 126.9, 124.6, 122.0, 120.9, 120.0, 115.8, 111.6, 57.4, 30.7, 9.6. HRMS: [M + H] $^+$ calculated for $\text{C}_{24}\text{H}_{19}\text{ClNO}^+$: 372.1150, found: 372.1147.



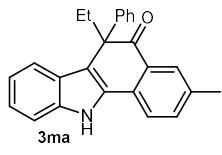
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 68% (48.2 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.70 (s, 1H), 8.05 (d, $J = 7.7$ Hz, 1H), 7.66 – 7.62 (m, 1H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.35 – 7.08 (m, 8H), 6.77 – 6.72 (m, 1H), 3.12 – 3.04 (m, 1H), 2.54 – 2.45 (m, 1H), 0.66 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 202.1, 161.3 (d, $J = 237.7$ Hz), 144.1, 139.4 (d, $J = 12.6$ Hz), 136.0, 133.4, 132.4 (d, $J = 3.4$ Hz), 129.4, 129.2, 129.1, 128.6, 128.1, 127.9, 123.9, 122.3, 121.9 (d, $J = 10.3$ Hz), 117.9, 109.3 (d, $J = 24.7$ Hz), 99.0 (d, $J = 26.1$ Hz), 58.7, 32.0, 9.9. HRMS: [M + H] $^+$ calculated for $\text{C}_{24}\text{H}_{19}\text{FNO}^+$: 356.1445, found: 356.1447.



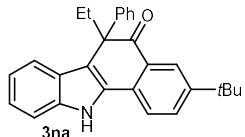
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 43% (34.8 mg). ^1H NMR (400 MHz, CD_3CN) δ 10.55 (s, 1H), 7.97 (d, $J = 7.7$ Hz, 1H), 7.87 (d, $J = 7.4$ Hz, 1H), 7.82 – 7.78 (m, 1H), 7.53 (s, 1H), 7.48 – 7.44 (m, 1H), 7.25 – 7.18 (m, 5H), 7.01 (bs, 1H), 3.06 (dq, $J = 14.0, 7.3$ Hz, 1H), 2.87 (dq, $J = 14.0, 7.1$ Hz, 1H), 0.51 (t, $J = 7.1$ Hz, 1H). ^{13}C NMR {101 MHz, $(\text{CD}_3)_2\text{SO}$ } δ 199.8, 143.5, 140.1, 135.5, 133.1, 131.7, 128.6, 128.2, 128.0, 127.3, 127.3, 127.2, 126.6, 125.1, 122.5, 122.3, 121.0, 115.4, 110.7, 57.6, 33.0, 9.2. HRMS: [M + H] $^+$ calculated for $\text{C}_{24}\text{H}_{18}\text{Cl}_2\text{NO}^+$: 406.0760, found: 406.0760.



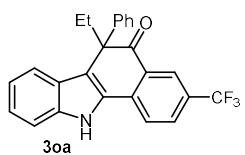
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 45% (32.9 mg). ^1H NMR (400 MHz, CD_3CN) δ 9.99 (s, 1H), 7.91 (d, $J = 7.7$ Hz, 1H), 7.82 (d, $J = 7.7$ Hz, 1H), 7.75 – 7.71 (m, 1H), 7.34 – 7.17 (m, 7H), 6.56 (s, 1H), 3.11 – 3.02 (m, 1H), 2.45 – 2.42 (m, 1H), 2.34 (s, 3H), 1.78 (s, 3H), 0.49 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 202.1, 145.3, 140.8, 136.1, 134.3, 134.1, 131.1, 131.0, 129.3, 128.9, 128.6, 128.1, 127.8, 125.3, 124.5, 122.3, 110.4, 59.3, 34.5, 22.4, 21.3, 9.5. (two signals are missing due to overlap). HRMS: [M + H] $^+$ calculated for $\text{C}_{26}\text{H}_{24}\text{NO}^+$: 366.1852, found: 366.1854.



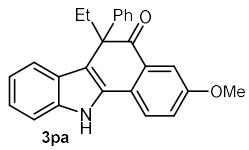
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 54% (37.9 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.60 (s, 1H), 7.87 (s, 1H), 7.50 – 7.44 (m, 3H), 7.30 (d, J = 7.8 Hz, 2H), 7.22 – 7.13 (m, 5H), 7.00 – 6.96 (m, 1H), 3.08 (dq, J = 14.3, 7.1 Hz, 1H), 2.54 (dq, J = 14.7, 7.3 Hz, 1H), 2.38 (s, 3H), 0.65 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.0, 142.6, 137.7, 135.4, 130.8, 129.8, 129.5, 128.7, 128.5, 127.6, 127.1, 127.0, 123.3, 120.6, 120.4, 120.3, 117.0, 111.6, 58.5, 32.2, 21.4, 10.0. HRMS: [M + H] $^+$ calculated for $\text{C}_{25}\text{H}_{22}\text{NO}^+$: 352.1696, found: 352.1699.



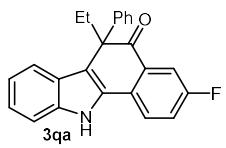
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 46% (36.2 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.62 (s, 1H), 8.10 (s, 1H), 7.69 – 7.66 (m, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.34 – 7.32 (m, 2H), 7.22 – 7.15 (m, 5H), 6.99 – 6.69 (t = 1H), 3.15 – 3.06 (m, 1H), 2.55 (dq, J = 14.8, 7.4 Hz, 1H), 1.32 (s, 9H), 0.66 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.2, 151.0, 142.7, 137.8, 132.0, 130.8, 129.8, 128.5, 128.4, 127.7, 127.0, 127.0, 125.9, 123.3, 120.7, 120.4, 120.3, 117.2, 111.6, 58.5, 35.1, 32.5, 31.2, 10.1. HRMS: [M + H] $^+$ calculated for $\text{C}_{28}\text{H}_{28}\text{NO}^+$: 394.2167, found: 394.2168.



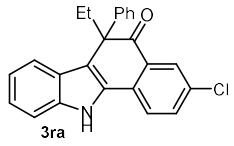
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 60% (48.6 mg). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.78 (s, 1H), 8.79 (s, 1H), 8.60 – 8.54 (m, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.95 – 7.72 (m, 7H), 7.54 – 7.50 (m, 1H), 3.58 (dq, J = 14.3, 7.2 Hz, 1H), 3.17 (dq, J = 14.7, 7.4 Hz, 1H), 1.18 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 201.5, 143.7, 139.7, 136.8, 132.22 (q, J = 3.7 Hz), 130.4, 129.9, 129.5, 129.4 (d, J = 32.9 Hz), 129.3, 128.2, 128.1, 126.9, 126.2 (q, 3.9 Hz), 125.1, 125.0 (q, J = 271.3 Hz) 123.4, 121.2 (d, J = 2.6 Hz), 119.9, 113.2, 59.2, 32.2, 10.0. HRMS: [M + H] $^+$ calculated for $\text{C}_{25}\text{H}_{19}\text{F}_3\text{NO}^+$: 406.1413, found: 406.1417.



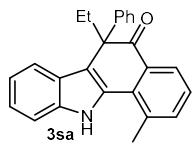
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 35% (25.7 mg). ^1H NMR (400 MHz, CD_3CN) δ 9.99 (s, 1H), 7.77 (d, $J = 8.6$ Hz, 1H), 7.53 – 7.45 (m, 2H), 7.33 (dd, $J = 8.6, 2.8$ Hz, 1H), 7.25 – 7.11 (m, 7H), 6.92 – 6.88 (m, 1H), 3.85 (s, 3H), 2.97 (dq, $J = 14.4, 7.2$ Hz, 1H), 2.64 – 2.46 (m, 1H), 0.58 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 201.9, 159.3, 142.6, 137.7, 130.8, 130.2, 128.6, 127.6, 127.1, 127.1, 125.8, 123.0, 122.5, 122.0, 120.4, 120.4, 115.9, 111.7, 111.5, 58.5, 55.7, 32.4, 10.0. HRMS: [M + H] $^+$ calculated for $\text{C}_{25}\text{H}_{22}\text{NO}_2^+$: 368.1645, found: 368.1648.



Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 61% (43.3 mg). ^1H NMR {400 MHz, $(\text{CD}_3)_2\text{SO}$ } δ 10.63 (s, 1H), 8.43 (dd, $J = 8.6, 5.0$ Hz, 1H), 8.24 (dd, $J = 9.3, 2.7$ Hz, 1H), 8.11 – 8.06 (m, 2H), 7.84 – 7.71 (m, 7H), 7.52 – 7.48 (m 1H), 3.56 (dq, $J = 14.4, 7.2$ Hz, 1H), 3.15 (dq, $J = 14.5, 7.4$ Hz, 1H), 1.17 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN). δ 201.6, 162.8 (d, $J = 246.5$ Hz), 143.8, 139.1, 131.2, 131.2, 131.0, 130.3 (d, $J = 2.9$ Hz), 129.3, 128.1, 128.0, 127.0, 124.8 (d, $J = 7.5$ Hz), 123.1, 122.9 (d, $J = 23.1$ Hz), 120.8 (d, $J = 18.2$ Hz), 117.0, 115.21 (d, $J = 23.0$ Hz), 112.9, 58.9, 32.1, 9.9. HRMS: [M + H] $^+$ calculated for $\text{C}_{24}\text{H}_{19}\text{FNO}^+$: 356.1445, found: 356.1446.

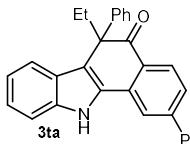


Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 63% (46.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.70 (s, 1H), 8.01 (s, 1H), 7.55 – 6.99 (m, 11H), 3.07 (bs, 1H), 2.56 (bs, 1H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 201.0, 142.1, 138.0, 134.5, 133.5, 130.8, 129.9, 129.7, 129.1, 128.7, 127.6, 127.3, 126.8, 123.9, 121.9, 120.8, 120.7, 118.0, 111.8, 58.7, 32.3, 10.0. HRMS: [M + H] $^+$ calculated for $\text{C}_{24}\text{H}_{19}\text{ClNO}^+$: 372.1150, found: 372.1147.

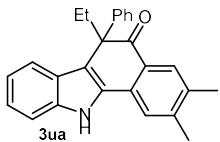


Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 44% (30.9 mg). ^1H NMR (400 MHz, CD_3CN) δ 10.18 (s, 1H), 7.96 (d, $J = 7.8$ Hz, 1H),

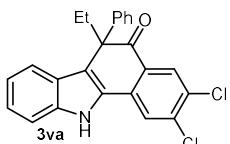
7.82 (d, $J = 7.6$ Hz, 1H), 7.77 – 7.73 (m, 1H), 7.49 (dd, $J = 8.8, 4.5$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.23 – 7.17 (m, 5H), 6.98 – 6.93 (m, 1H), 6.80 (dd, $J = 10.0, 2.0$ Hz, 1H), 2.94 (dq, $J = 14.3, 7.2$ Hz, 1H), 2.51 (m, 2.47 – 2.56, 1H), 2.2 (s, 3H), 0.60 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.0, 142.7, 138.0, 137.5, 131.6, 131.2, 131.2, 130.1, 128.5, 127.9, 127.6, 127.3, 127.0, 125.9, 123.4, 120.9, 120.5, 118.0, 111.7, 58.0, 32.4, 23.0, 10.1. HRMS: [M + H]⁺ calculated for $\text{C}_{25}\text{H}_{22}\text{NO}^+$: 352.1696, found: 352.1692.



Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 51% (42.1 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.73 (s, 1H), 8.12 (d, $J = 8.1$ Hz, 1H), 7.77 (s, 1H), 7.69 (d, $J = 7.3$ Hz, 2H), 7.55 – 7.44 (m, 5H), 7.33 (d, $J = 7.0$ Hz, 2H), 7.28 – 7.16 (m, 5H), 7.00 – 6.97 (m, 1H), 3.15 – 3.06 (m, 1H), 2.61 – 2.53 (m, 1H), 0.68 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 201.5, 147.5, 142.6, 140.0, 138.0, 132.8, 130.5, 129.9, 129.2, 128.7, 128.6, 127.6, 127.5, 127.4, 127.1, 126.9, 126.5, 123.7, 120.9, 120.5, 119.0, 118.3, 111.7, 58.5, 32.4, 10.1. HRMS: [M + H]⁺ calculated for $\text{C}_{30}\text{H}_{24}\text{NO}^+$: 414.1852, found: 414.1853.

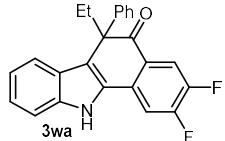


Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 63% (46.0 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.61 (s, 1H), 7.83 (s, 1H), 7.43 (d, $J = 8.5$ Hz, 1H), 7.38 (s, 1H), 7.30 (d, $J = 7.1$ Hz, 2H), 7.22 – 7.10 (m, 5H), 6.98 – 6.94 (m, 1H), 3.07 (dq, $J = 14.3, 7.1$ Hz, 1H), 2.53 (dq, $J = 14.8, 7.4$ Hz, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 0.64 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 201.9, 144.4, 142.8, 137.8, 136.6, 130.8, 130.3, 130.0, 128.5, 127.6, 127.0, 126.9, 126.8, 123.2, 121.7, 120.6, 120.3, 117.3, 111.6, 58.3, 32.2, 20.6, 19.8, 10.0. HRMS: [M + H]⁺ calculated for $\text{C}_{26}\text{H}_{24}\text{NO}^+$: 366.1852, found: 366.1854.

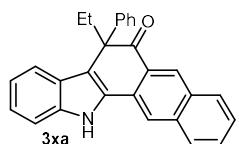


Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 82% (66.4 mg). ^1H NMR (400 MHz, CD_3CN) δ 10.01 (s, 1H), 7.99 (d, $J = 8.7$ Hz, 2H), 7.51 (d, $J = 8.2$ Hz, 1H), 7.29 – 7.04 (m, 7H), 6.94 – 6.91 (m, 1H), 3.00 – 2.91 (m, 1H), 2.60 – 2.52 (m,

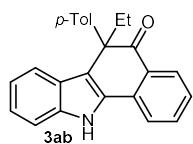
1H), 0.58 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CD₃CN) δ 200.7, 143.6, 139.6, 139.4, 133.4, 131.7, 131.1, 129.7, 129.5, 128.9, 128.2, 128.1, 126.8, 124.9, 124.7, 121.2, 121.1, 119.4, 113.1, 59.1, 32.2, 9.9. HRMS: [M + H]⁺ calculated for C₂₄H₁₈Cl₂NO⁺: 406.0760, found: 406.0758.



Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 54% (42.3 mg). ^1H NMR (400 MHz, CD₃CN) δ 10.01 (s, 1H), 7.99 (d, $J = 8.7$ Hz, 2H), 7.51 (d, $J = 8.2$ Hz, 1H), 7.22 – 7.13 (m, 7H), 6.95 – 6.91 (t, $J = 7.5$ Hz, 1H), 3.00 – 2.91 (m, 1H), 2.60 – 2.52 (m, 1H), 0.58 (m, 3H). ^{13}C NMR (101 MHz, CD₃CN) δ 200.6, 155.7 (dd, $J = 255.5, 13.9$ Hz), 150.4 (dd, $J = 248.8, 13.6$ Hz), 143.7, 139.3, 132.0 (dd, $J = 8.5, 3.3$ Hz), 130.0, 129.5, 128.2, 128.1, 126.9, 126.7 (dd, $J = 4.0, 3.5$ Hz), 124.7, 121.1, 121.1, 118.6 (dd, $J = 15.0, 1.9$ Hz), 113.8, 111.7, 111.5, 58.8, 32.3, 9.9. HRMS: [M + H]⁺ calculated for C₂₄H₁₈F₂NO⁺: 374.1351, found: 374.1352.

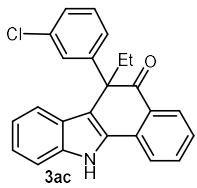


Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 50% (38.6 mg). ^1H NMR (400 MHz, CD₃CN) δ 10.20 (s, 1H), 8.57 (s, 1H), 8.24 (s, 1H), 8.05 – 7.92 (m, 2H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.56 (d, $J = 8.1$ Hz, 1H), 7.50 (d, $J = 7.3$ Hz, 1H), 7.30 (d, $J = 7.2$ Hz, 2H), 7.19 (dd, $J = 15.8, 7.4$ Hz, 5H), 6.93 (t, $J = 7.4$ Hz, 1H), 3.04 (dq, $J = 14.0, 7.0$ Hz, 1H), 2.66 – 2.51 (m, 1H), 0.64 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CD₃CN) δ 201.8, 144.5, 139.4, 137.3, 133.0, 132.3, 131.3, 131.1, 130.4, 129.3, 129.0, 128.7, 128.2, 128.2, 127.8, 127.6, 127.2, 124.2, 120.9, 120.8, 120.5, 117.1, 112.8, 58.7, 31.6, 10.1. HRMS: [M + H]⁺ calculated for C₂₈H₂₂NO⁺: 388.1696, found: 388.1704.

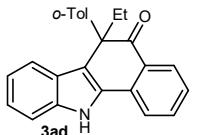


Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 50% (35.3 mg). ^1H NMR (400 MHz, CDCl₃) δ 9.01 (s, 1H), 8.06 (d, $J = 7.9$ Hz, 1H), 7.57 – 7.53 (m, 2H), 7.39 (d, $J = 8.2$ Hz, 1H), 7.31 – 7.26 (m, 1H), 7.24 – 7.16 (m, 4H), 6.99 – 6.95 (m, 3H), 3.08 (dq, $J = 14.3, 7.2$ Hz, 1H), 2.55 (dq, $J = 14.8, 7.4$ Hz, 1H), 2.19 (s, 3H), 0.67 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl₃) δ 202.5, 139.5, 138.0, 136.7, 134.6, 132.6, 130.5, 129.3, 129.1, 128.7, 127.5, 127.4, 126.9, 123.5, 120.7, 120.6, 120.3, 117.8, 111.8, 58.2, 32.3, 21.0, 10.0. HRMS: [M + H]⁺ calculated

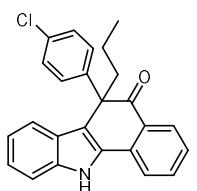
for $C_{25}H_{22}NO^+$: 352.1696, found: 352.1701.



Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 44% (32.5 mg). 1H NMR (400 MHz, CD_3CN) δ 10.13 (s, 1H), 7.97 (d, $J = 7.5$ Hz, 1H), 7.84 – 7.82 (d, $J = 7.6$ Hz, 1H), 7.78 – 7.74 m, 1H), 7.53 (d, $J = 8.2$ Hz, 1H), 7.42 – 7.38 (m, 1H), 7.25 – 7.12 (m, 6H), 6.96 – 6.92 (m, 1H), 3.04 – 2.85 (m, 1H), 2.58 – 2.49 (td, $J = 14.1, 8.0$ Hz, 1H), 0.57 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 201.8, 146.6, 139.2, 136.2, 134.7, 134.5, 133.5, 131.8, 130.9, 129.2, 129.1, 128.7, 128.2, 127.9, 126.9, 124.3, 122.5, 121.0, 120.6, 116.8, 113.0, 58.6, 32.3, 9.9. HRMS: $[M + H]^+$ calculated for $C_{24}H_{19}ClNO^+$: 372.1150, found: 372.1147.



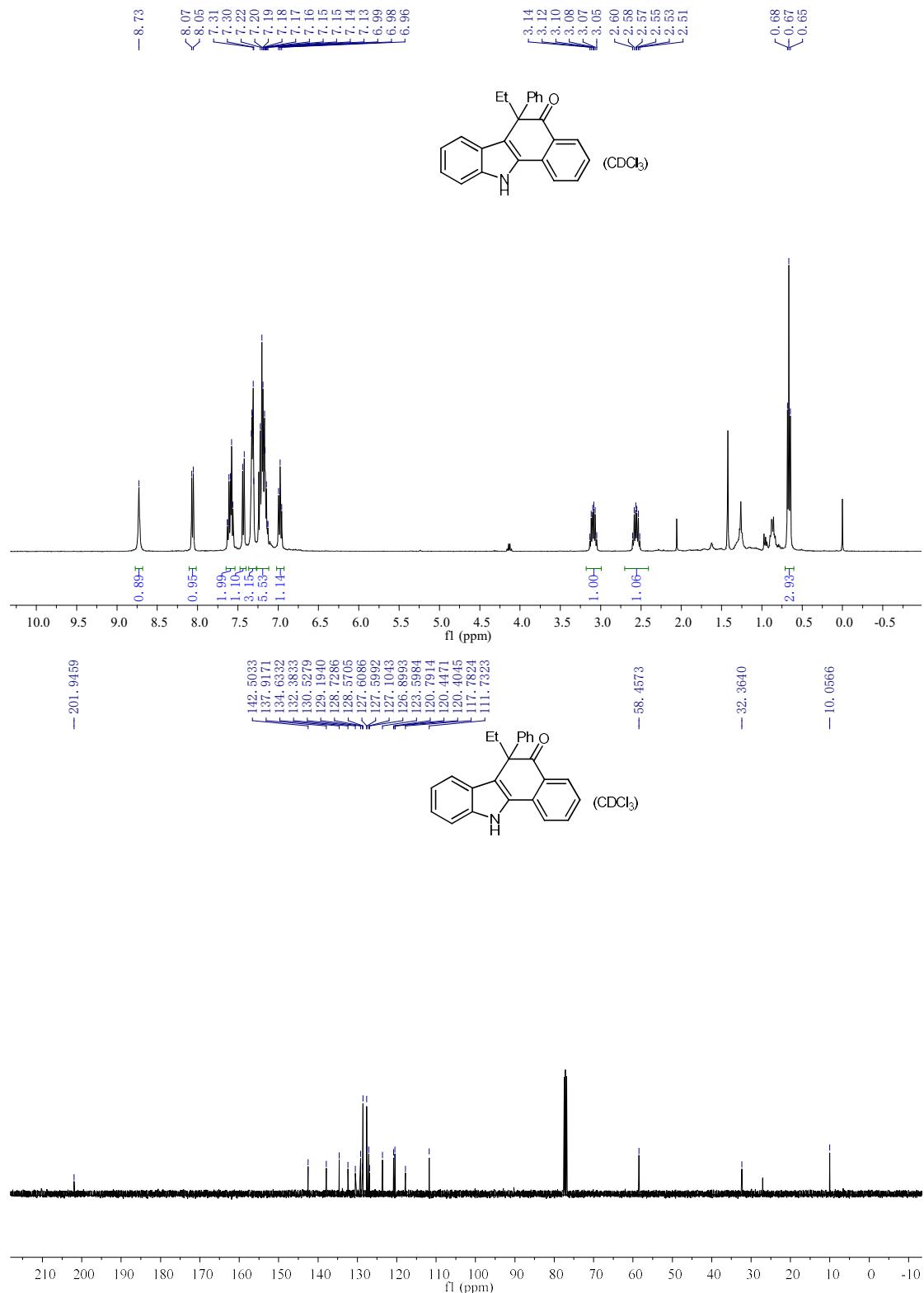
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 38% (26.5 mg). 1H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.20 (d, $J = 7.7$ Hz, 1H), 7.94 (d, $J = 7.8$ Hz, 1H), 7.69 – 7.66 (m, 1H), 7.61 (d, $J = 7.5$ Hz, 1H), 7.42 – 7.35 (m, 3H), 7.20 – 7.16 (m, 1H), 7.20 – 7.10 (m, 1H), 6.98 (d, $J = 7.2$ Hz, 1H), 6.85 – 6.79 (m, 2H), 2.58 (qd, $J = 12.4, 7.2$ Hz, 2H), 1.60 (s, 3H), 0.67 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 203.6, 144.2, 139.0, 137.9, 135.7, 133.4, 132.3, 131.1, 130.9, 128.5, 128.4, 128.2, 127.9, 126.5, 126.5, 124.0, 122.6, 120.4, 120.0, 117.9, 112.7, 57.7, 35.1, 20.2, 8.8. HRMS: $[M + H]^+$ calculated for $C_{25}H_{22}NO^+$: 352.1696, found: 352.1697.



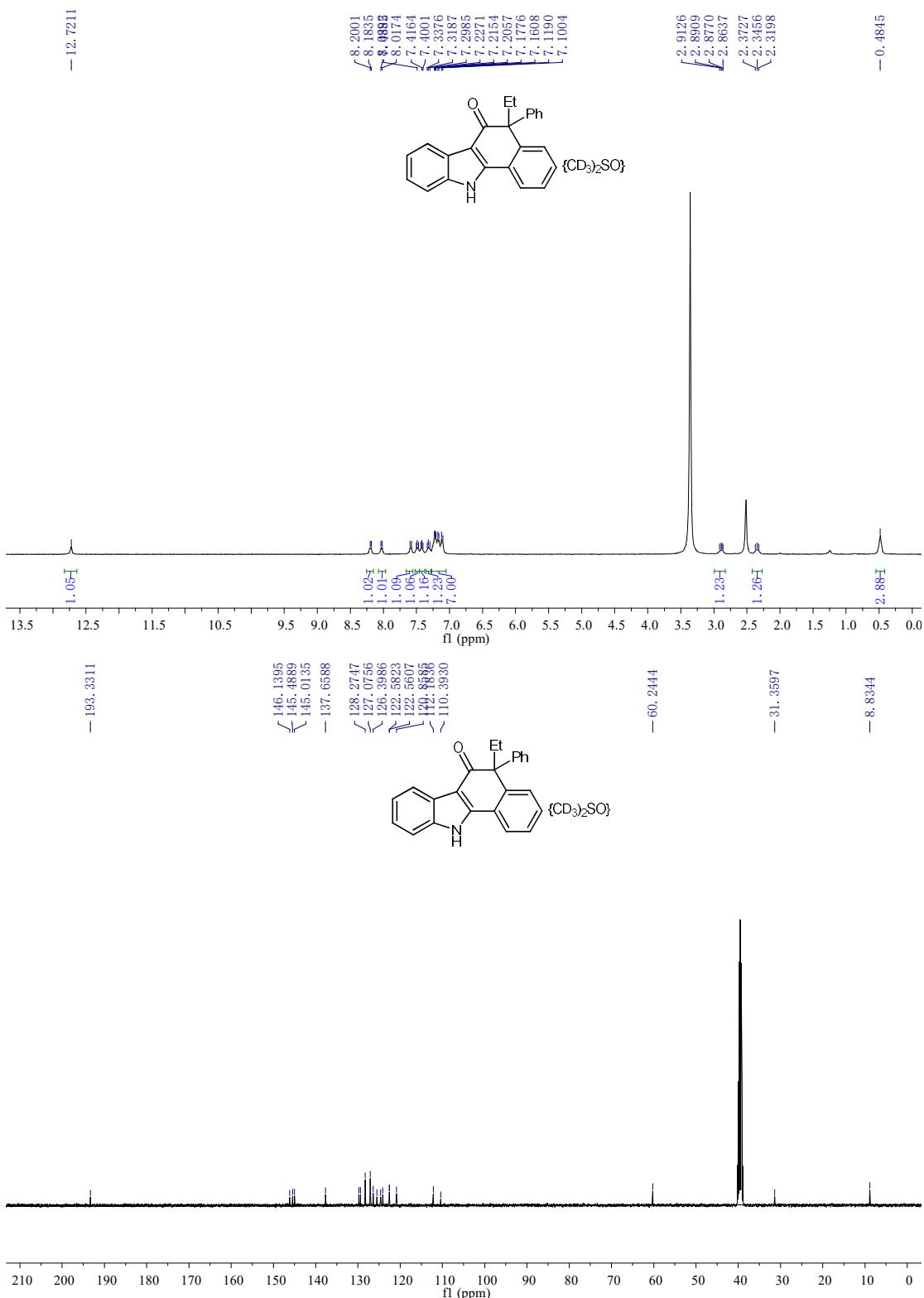
Purified by column chromatography using ethyl acetate/petroleum ether, Yellow solid, 61% (47.1 mg). 1H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.07 (d, $J = 7.1$ Hz, 1H), 7.62 – 7.57 (m, 2H), 7.41 (d, $J = 8.2$ Hz, 1H), 7.34 – 7.30 (m, 1H), 7.27 – 7.14 (m, 6H), 7.00 – 6.97 (m, 1H), 2.98 – 2.91 (m, 1H), 2.51 – 2.44 (m, 1H), 1.03 – 0.98 (m, 2H), 0.76 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 141.2, 137.9, 134.9, 133.0, 132.4, 130.2, 129.2, 129.1, 128.7, 127.7, 126.7, 123.7, 120.6, 120.5, 117.6, 111.8, 57.4, 42.0, 18.8, 14.6. (one signal is missing due to overlap). HRMS: $[M + H]^+$ calculated for $C_{25}H_{21}ClNO^+$: 386.1306, found: 386.1304.

8. NMR Spectra of Coupled Products

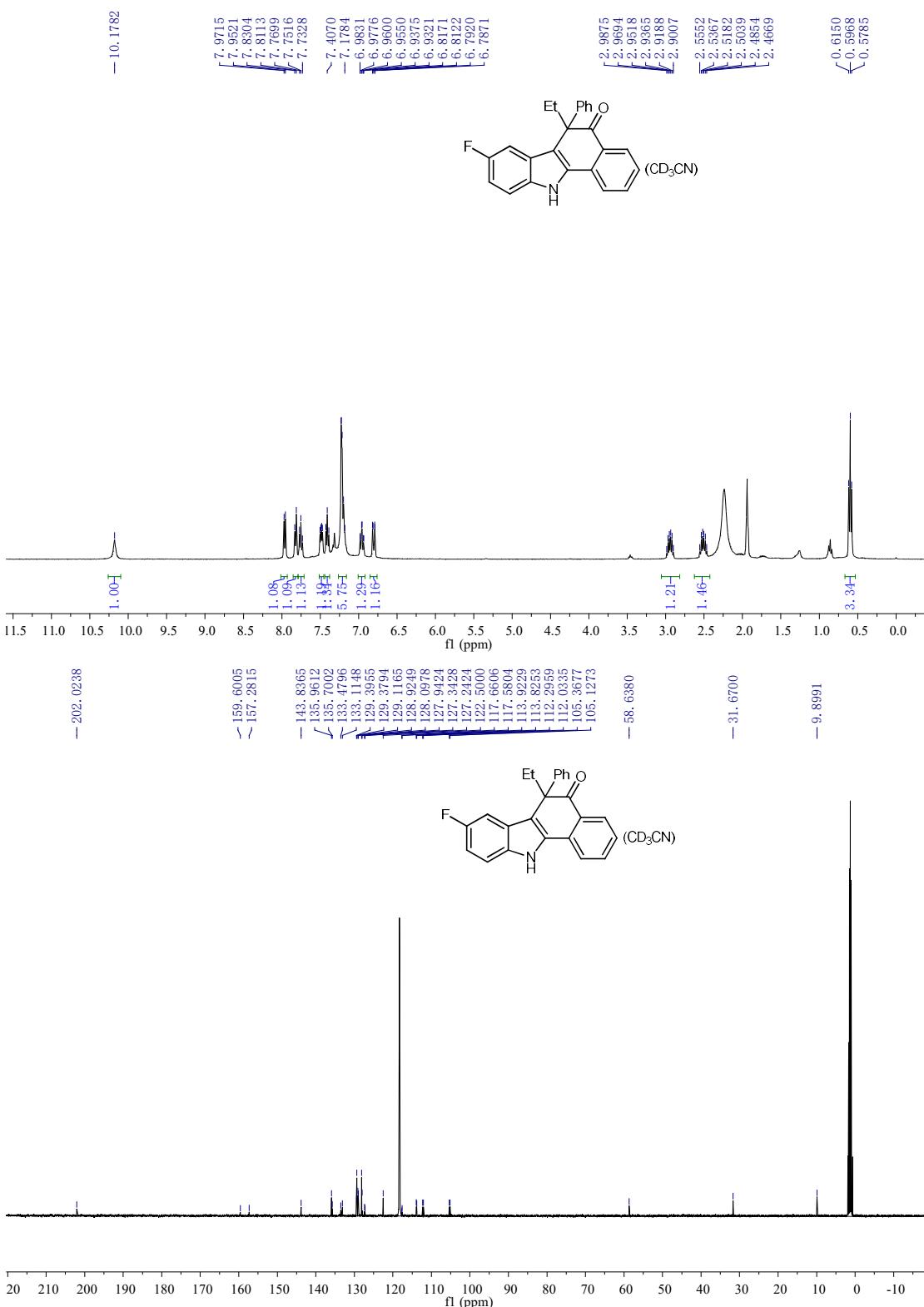
¹H and ¹³C NMR Spectra of compound 3aa



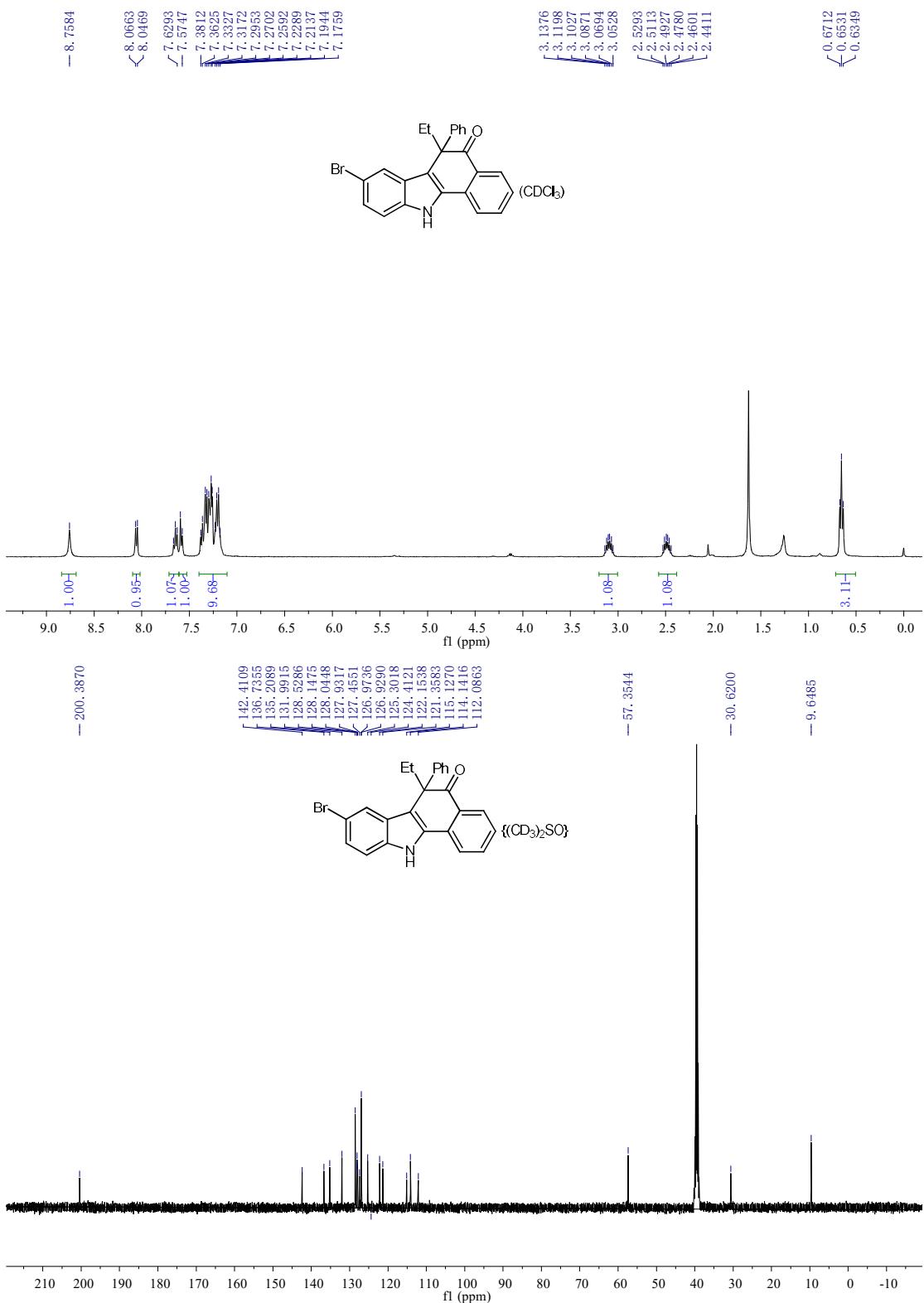
¹H and ¹³C NMR Spectra of compound 4aa



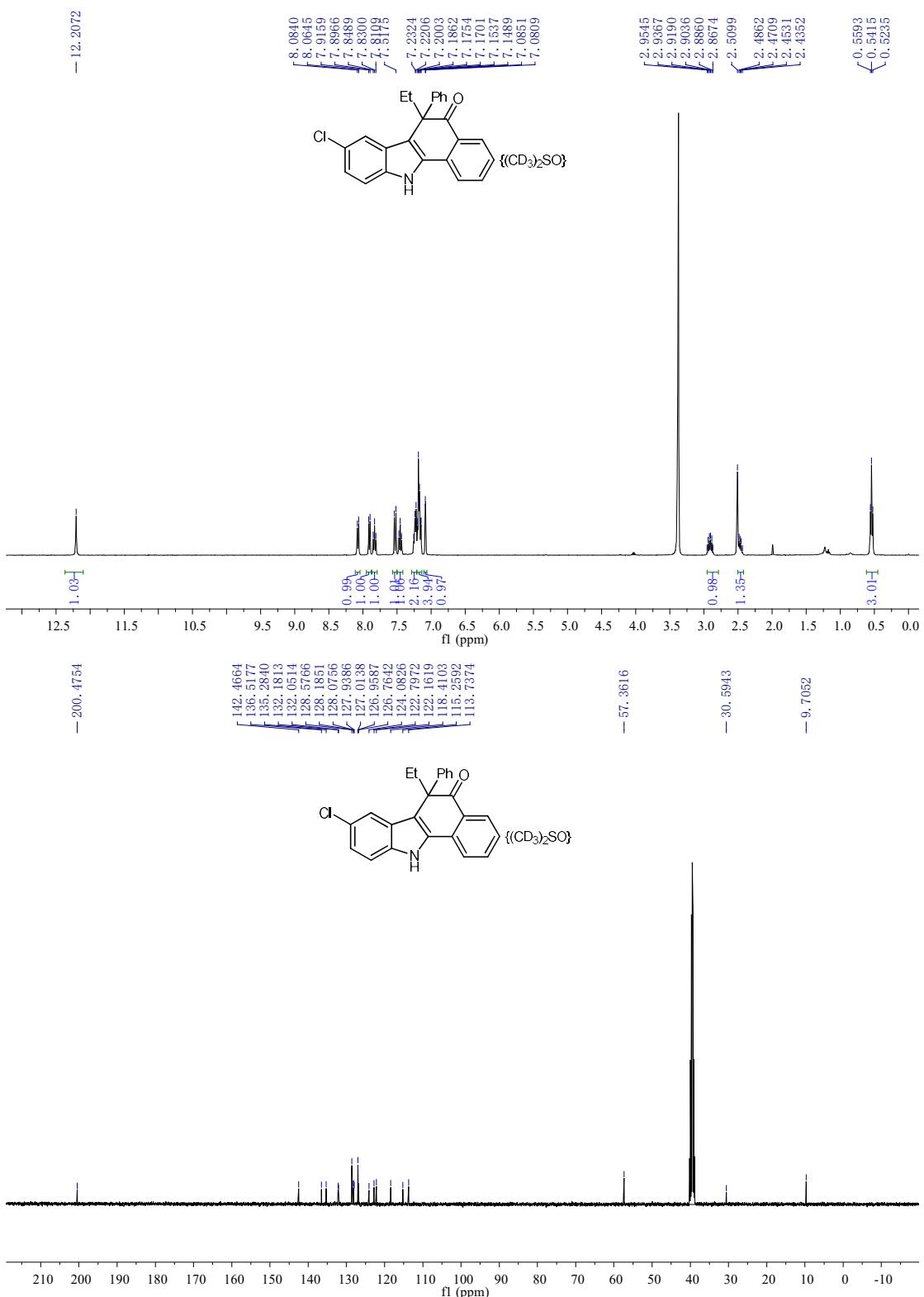
¹H and ¹³C NMR Spectra of compound **3ba**



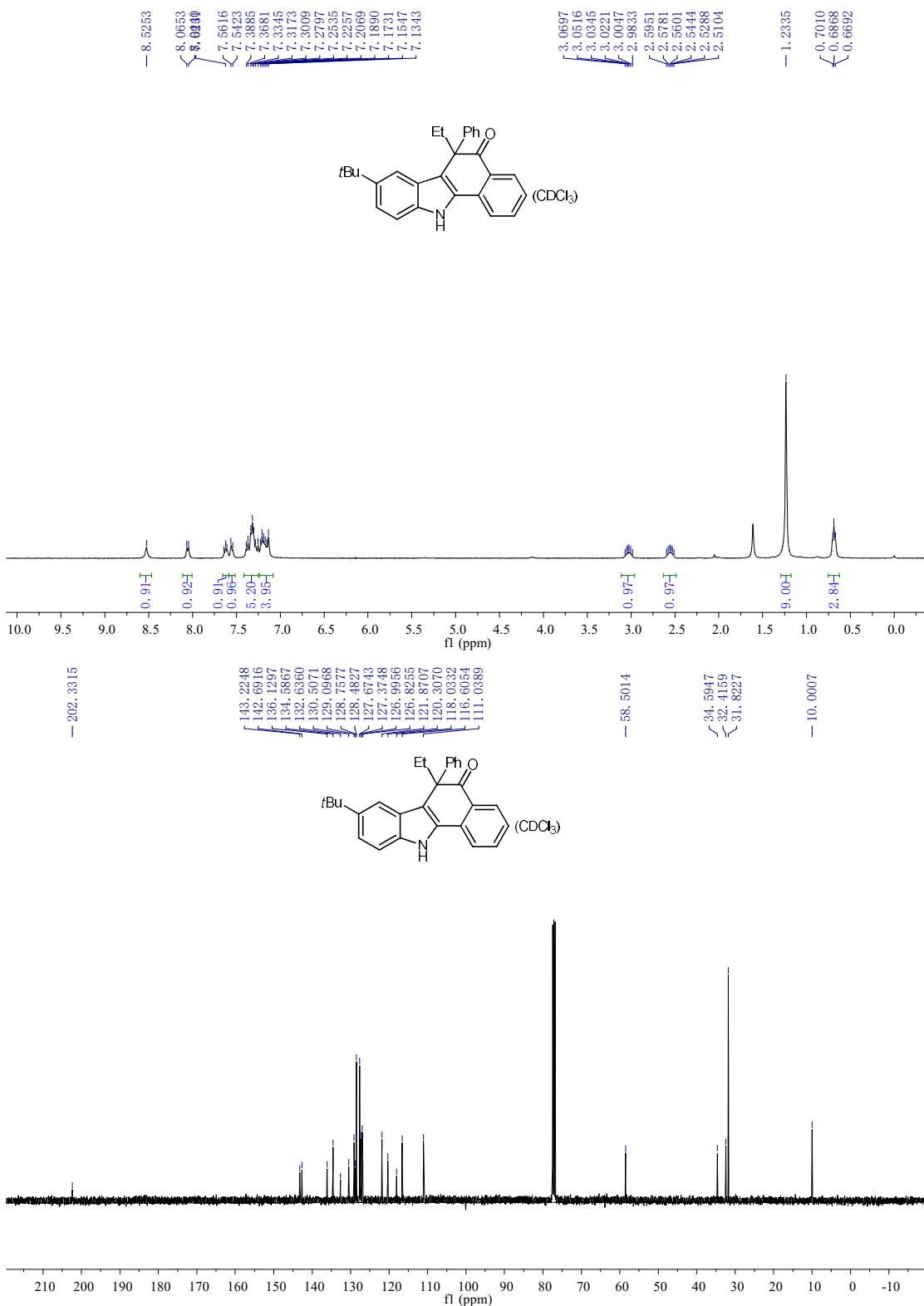
¹H and ¹³C NMR Spectra of compound 3ca



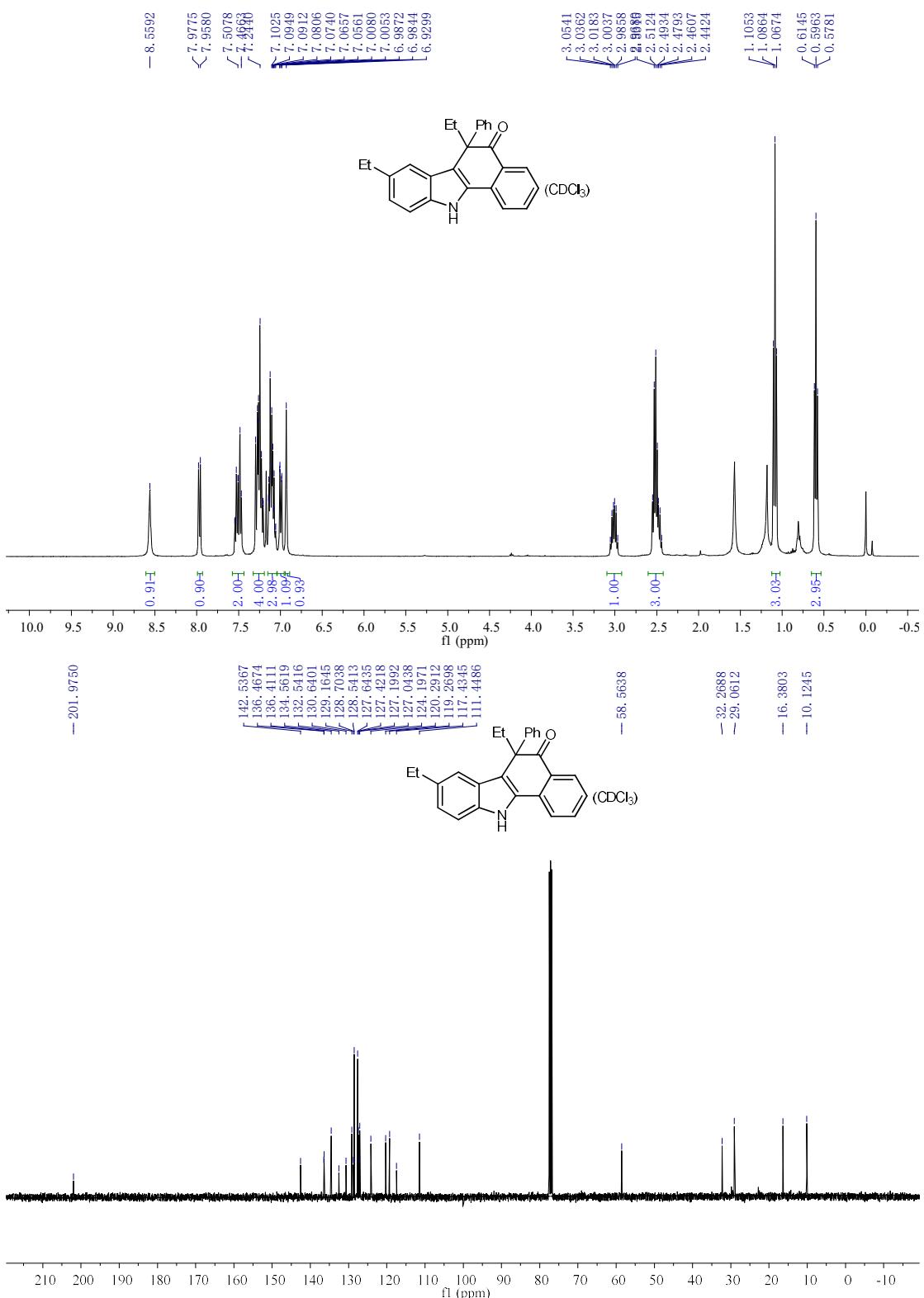
¹H and ¹³C NMR Spectra of compound 3da



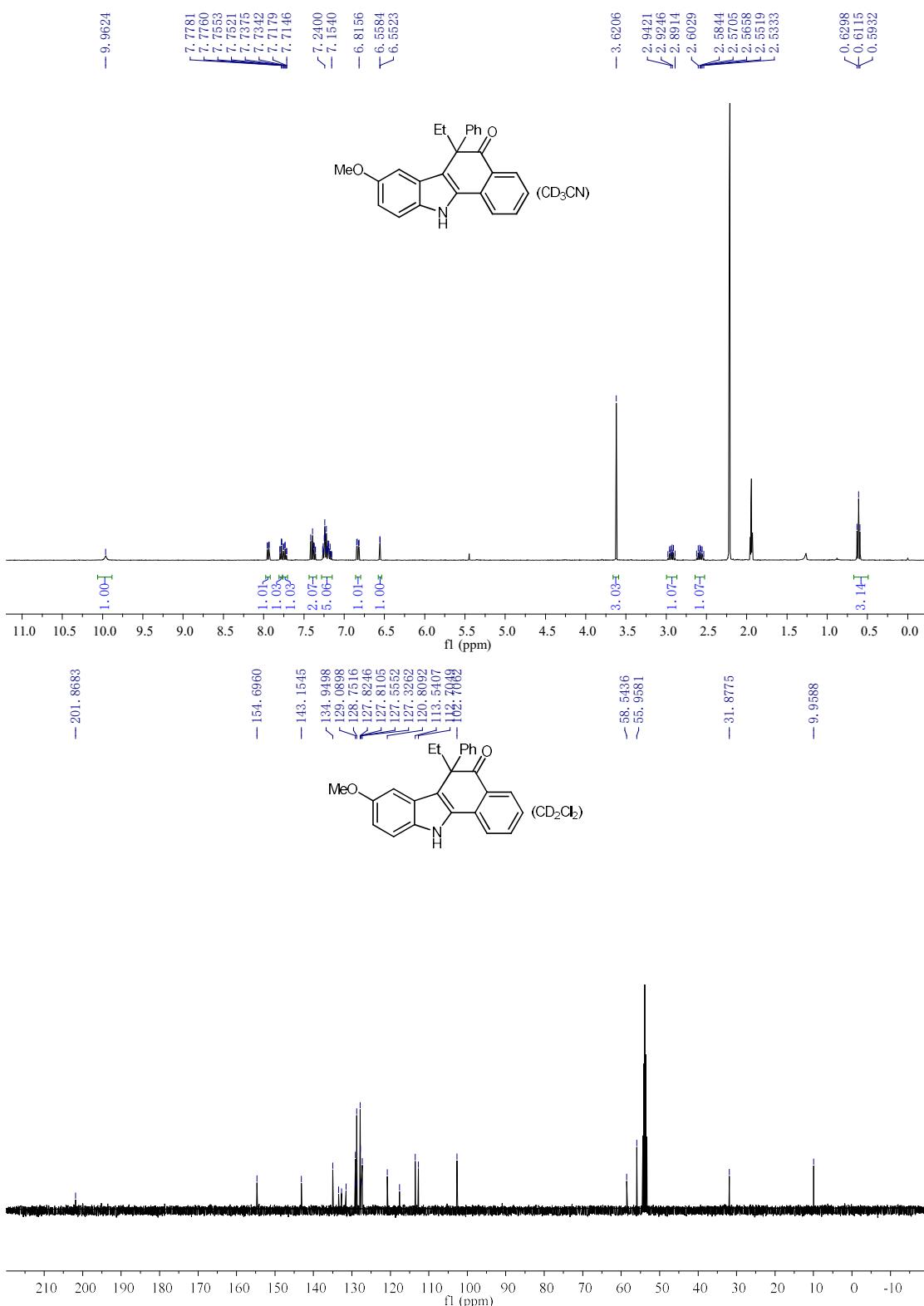
¹H and ¹³C NMR Spectra of compound 3ea



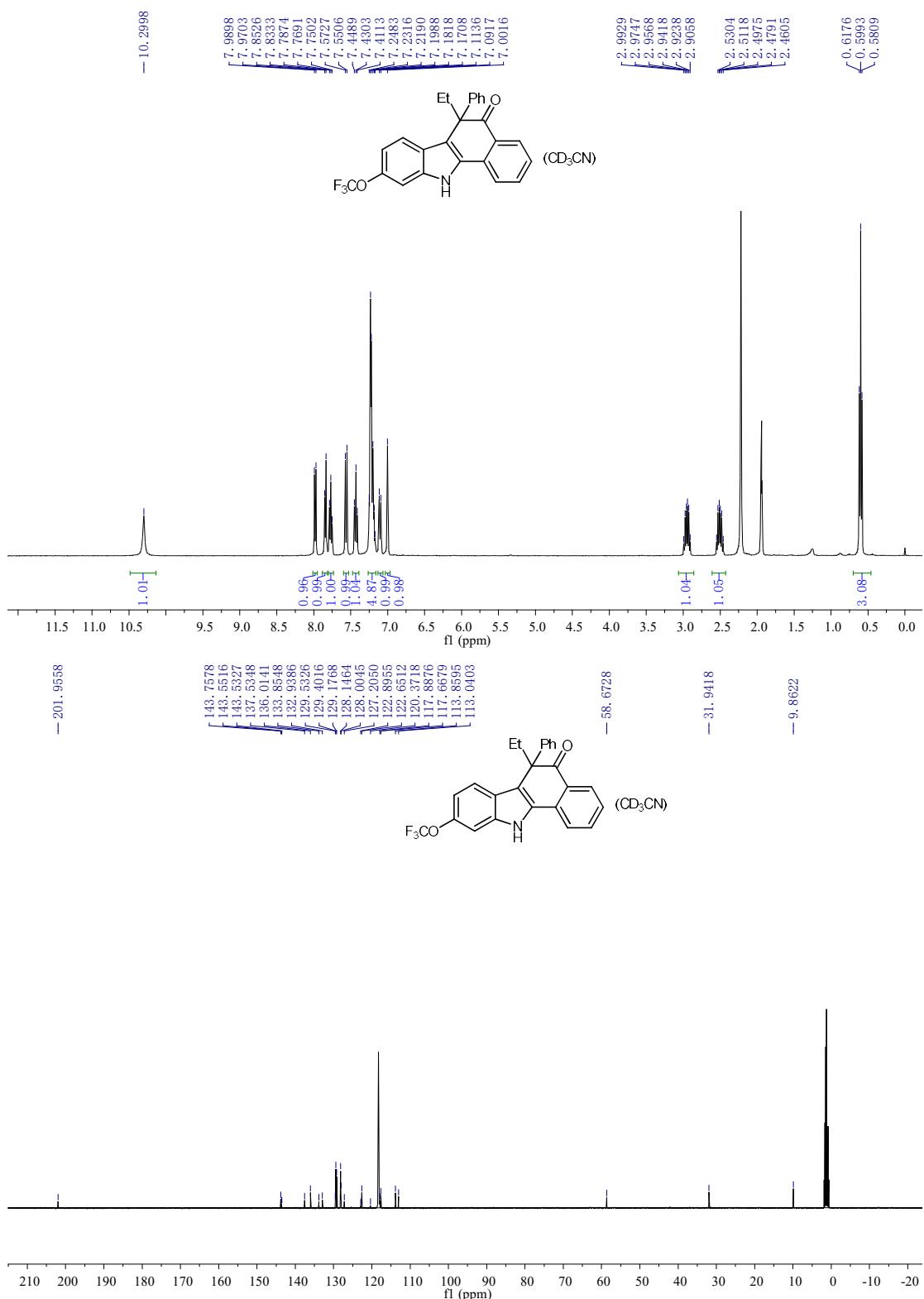
¹H and ¹³C NMR Spectra of compound 3fa



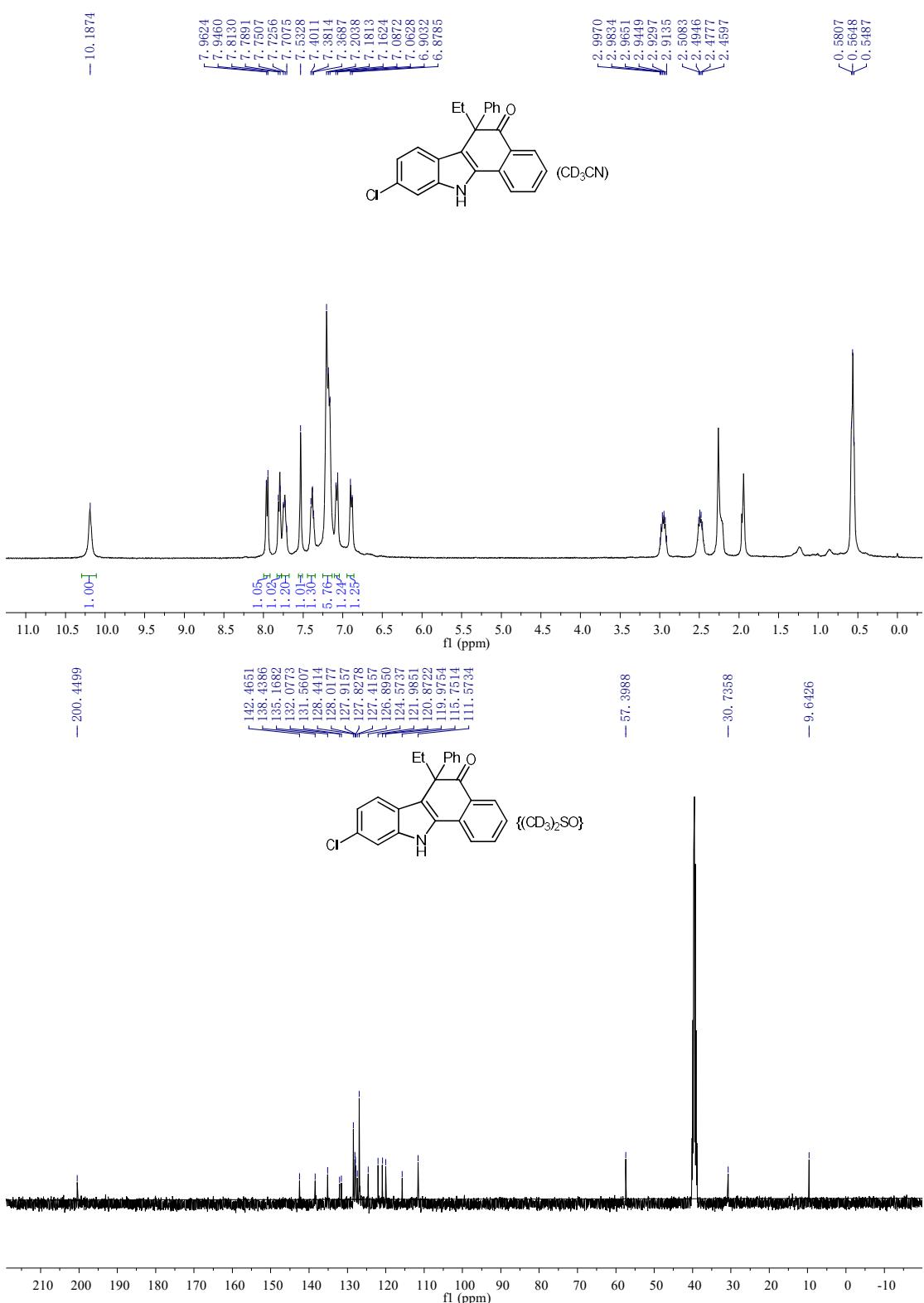
¹H and ¹³C NMR Spectra of compound 3ga



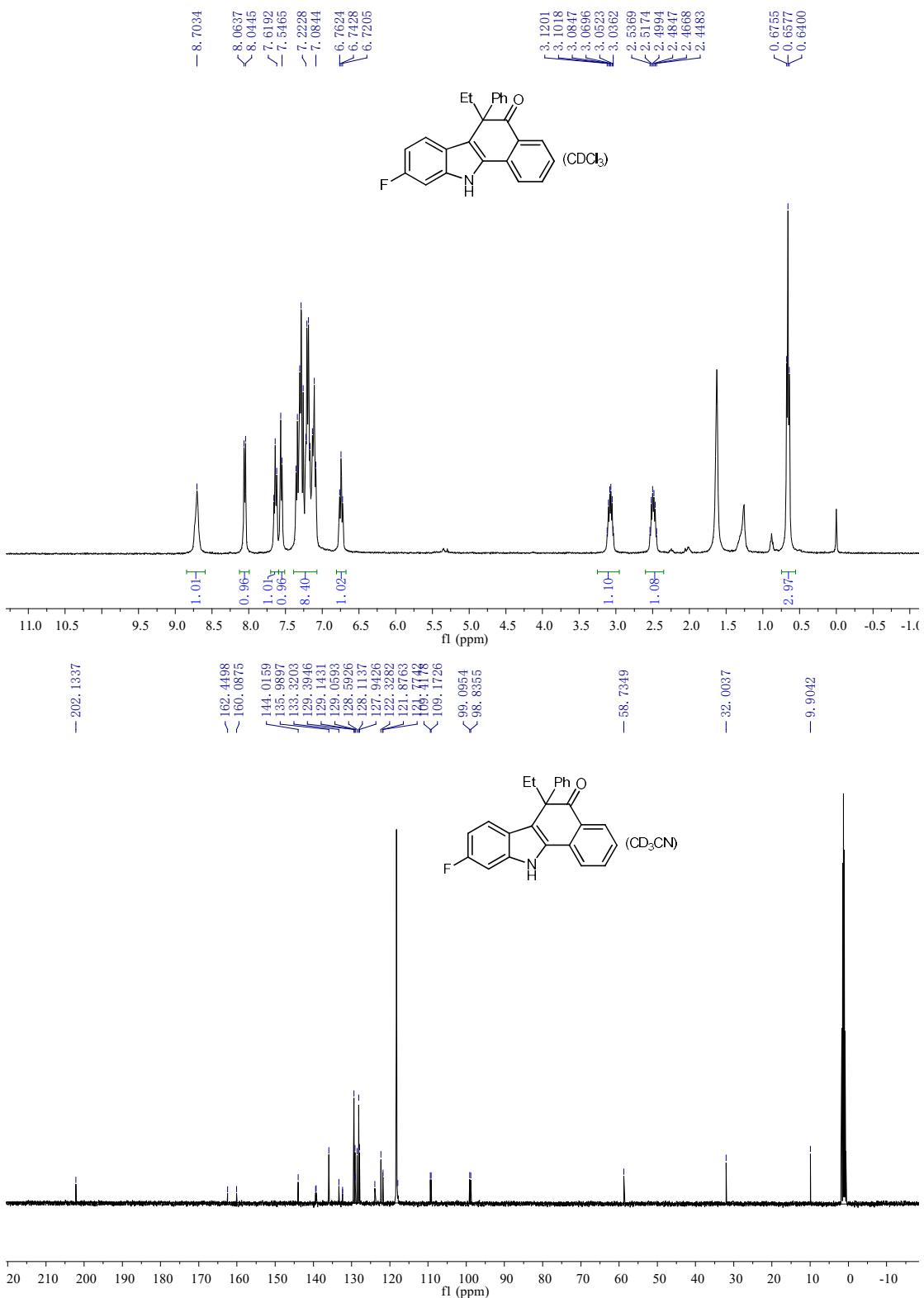
¹H and ¹³C NMR Spectra of compound 3ha



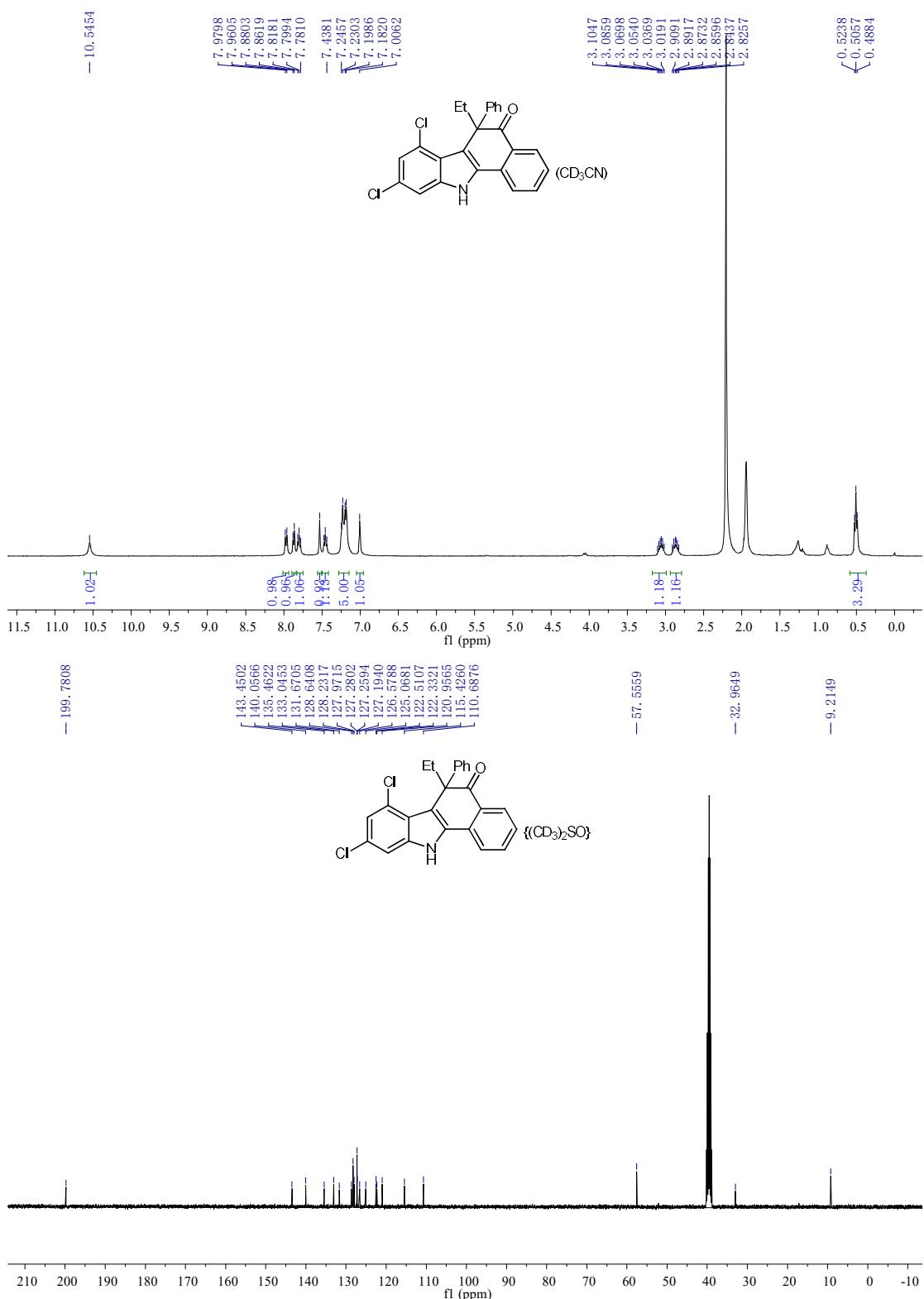
¹H and ¹³C NMR Spectra of compound 3ia



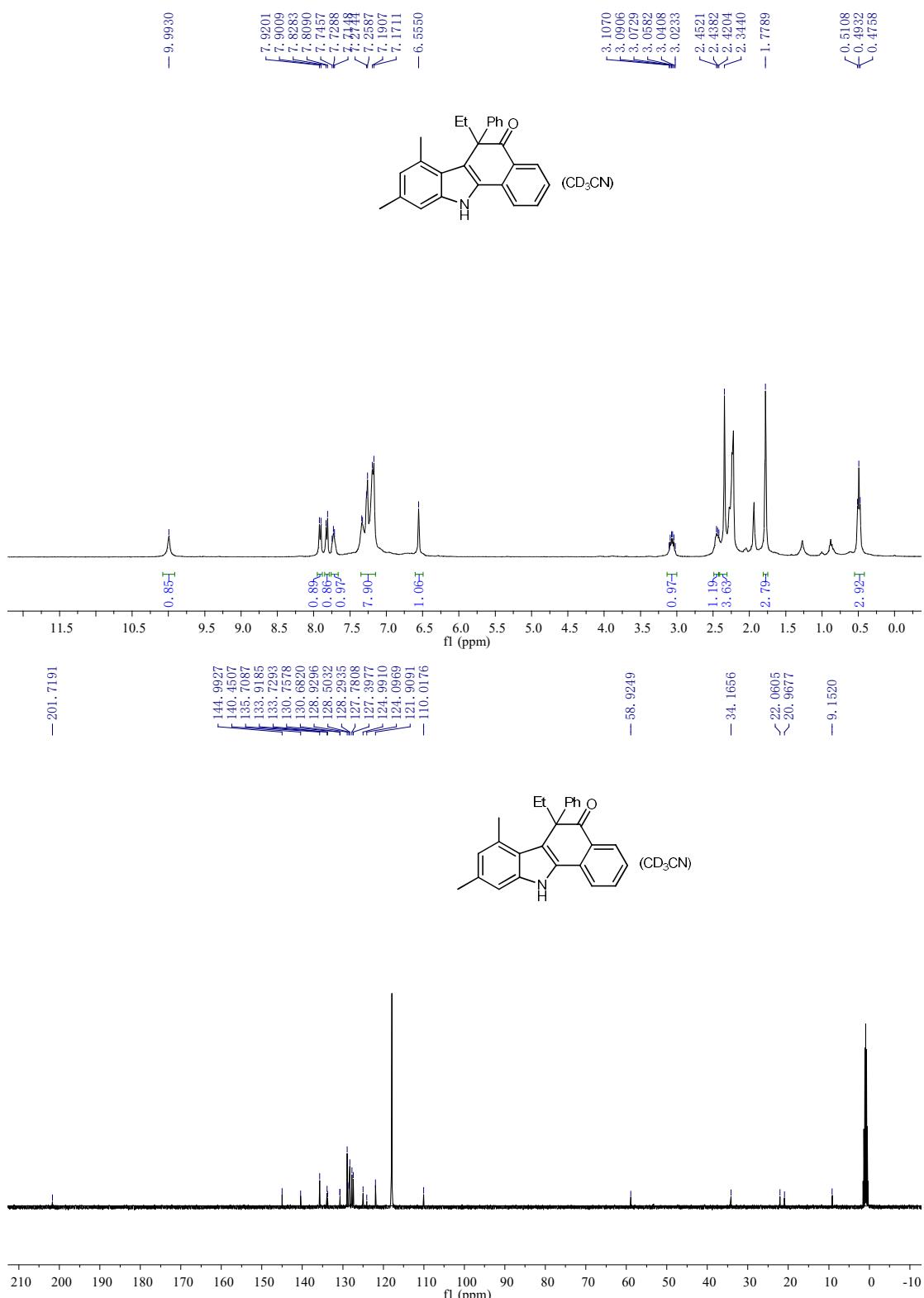
¹H and ¹³C NMR Spectra of compound 3ja



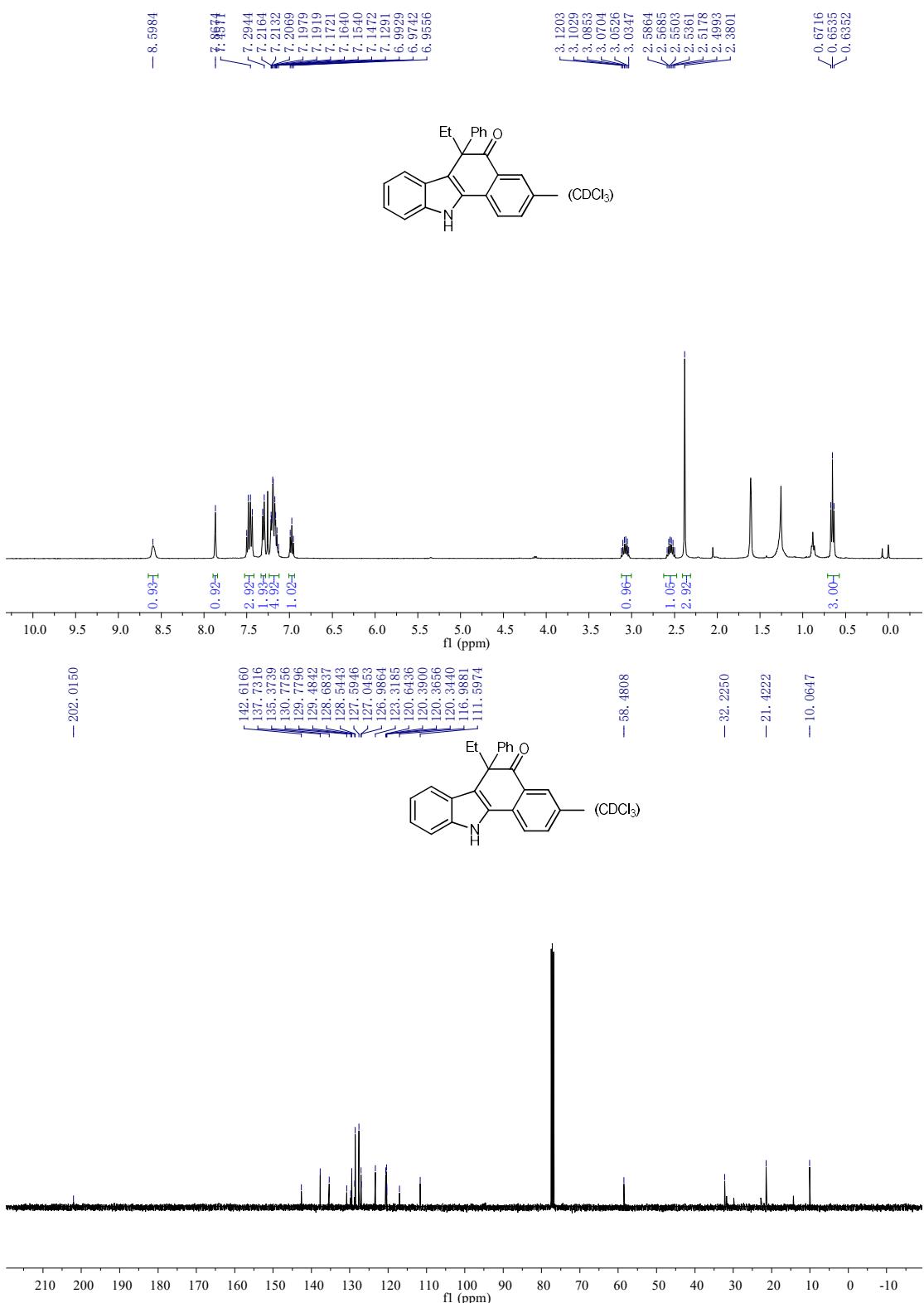
¹H and ¹³C NMR Spectra of compound 3ka



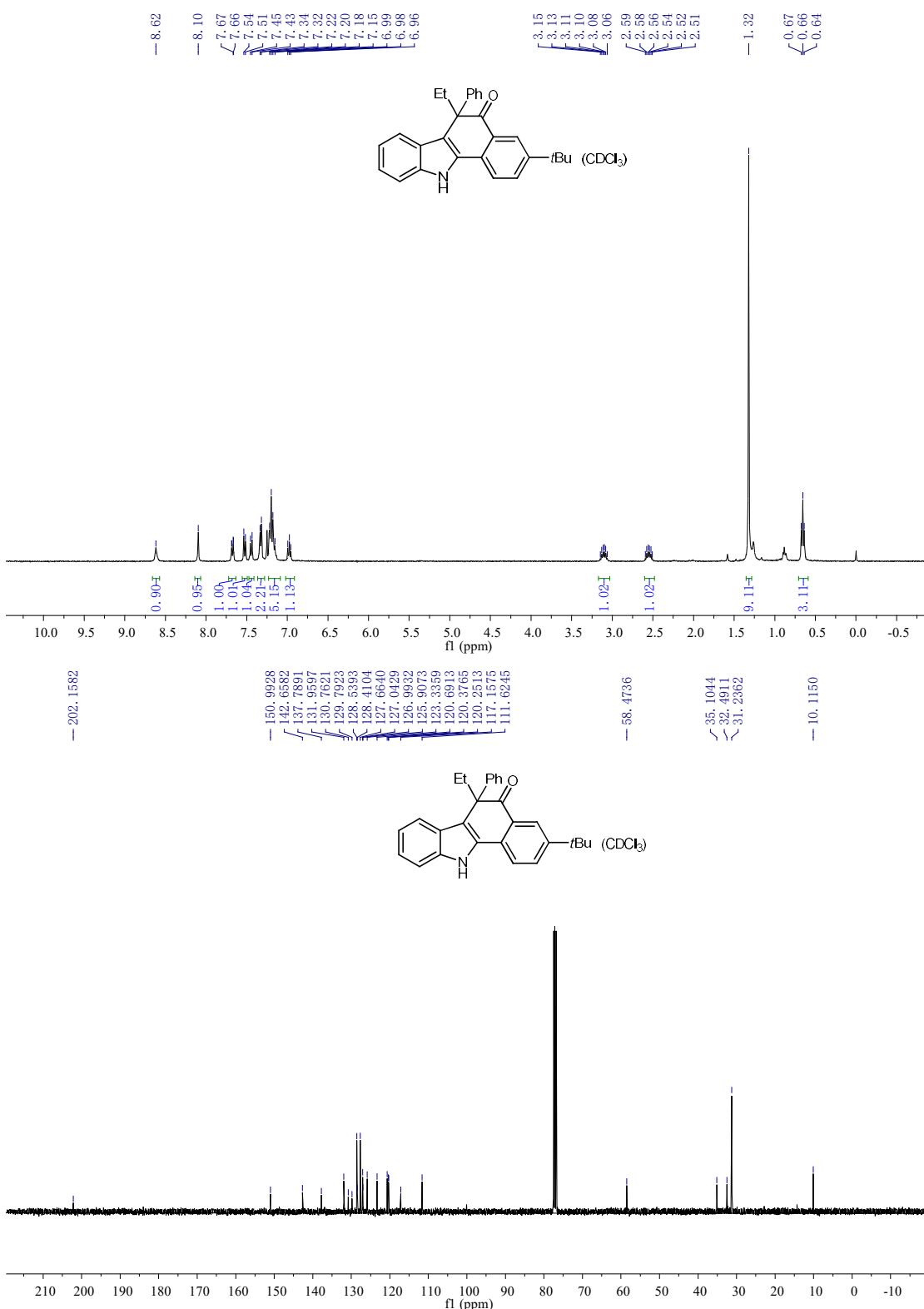
¹H and ¹³C NMR Spectra of compound 3la



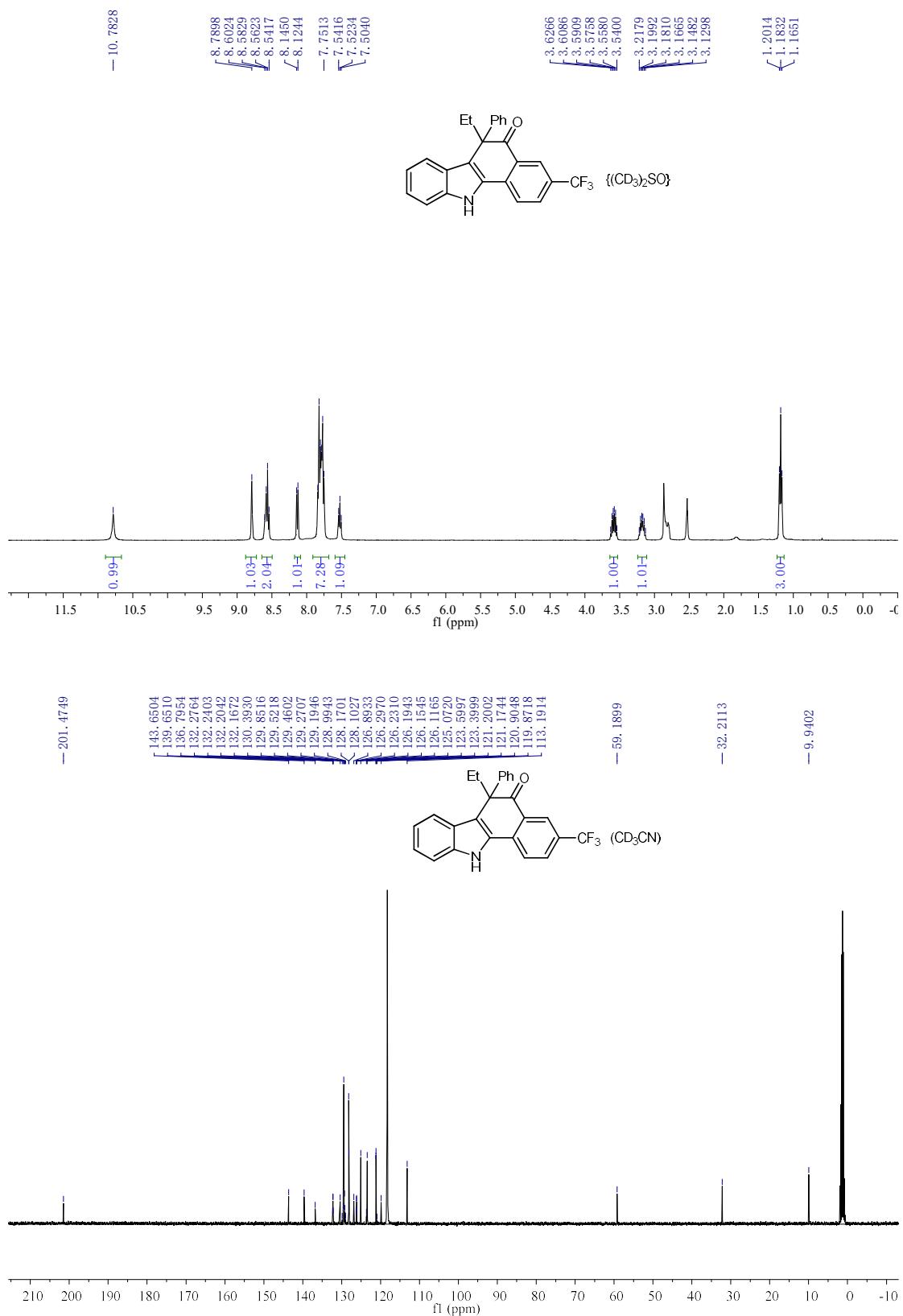
¹H and ¹³C NMR Spectra of compound 3ma



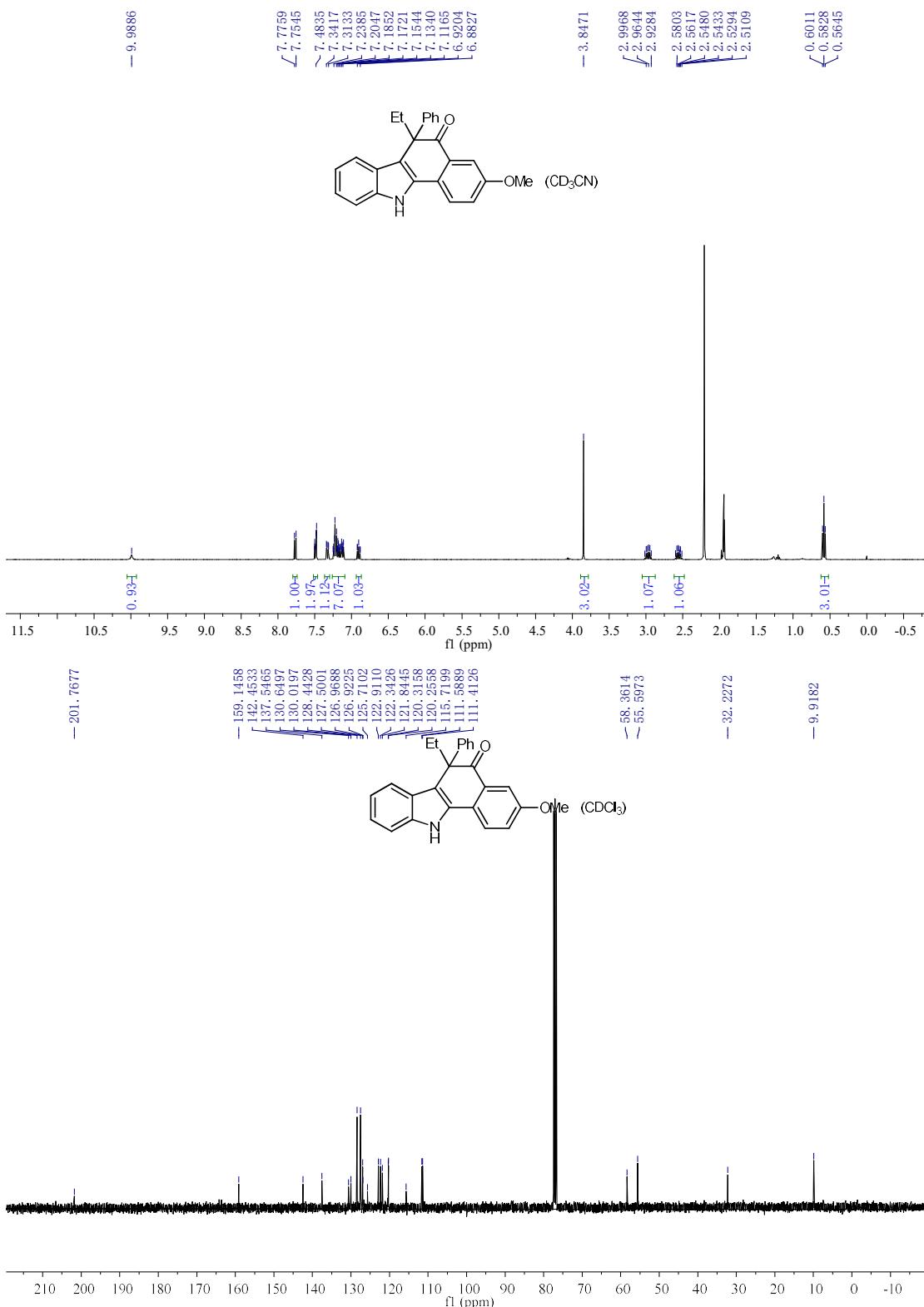
¹H and ¹³C NMR Spectra of compound 3na



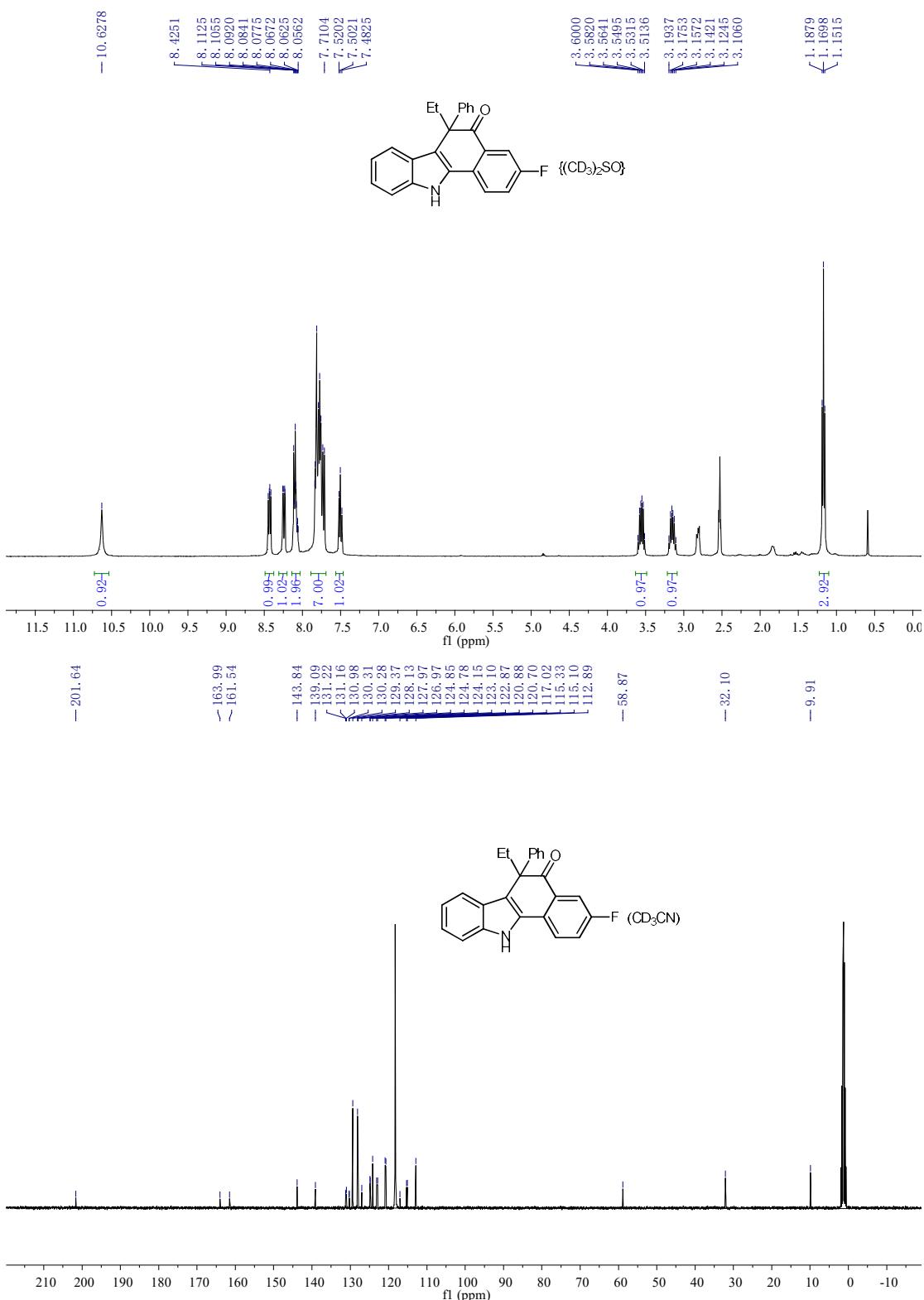
¹H and ¹³C NMR Spectra of compound **3oa**



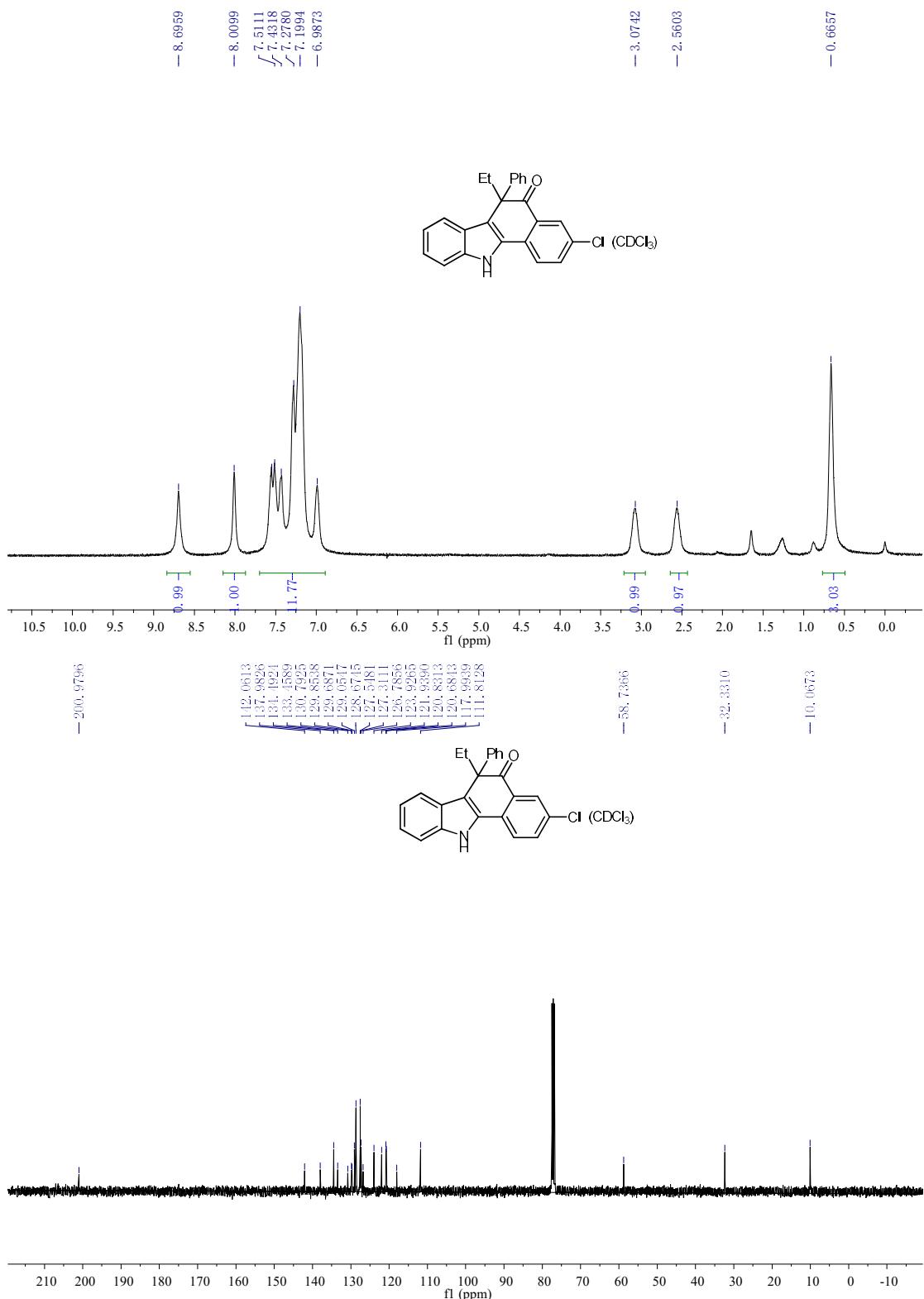
¹H and ¹³C NMR Spectra of compound 3pa



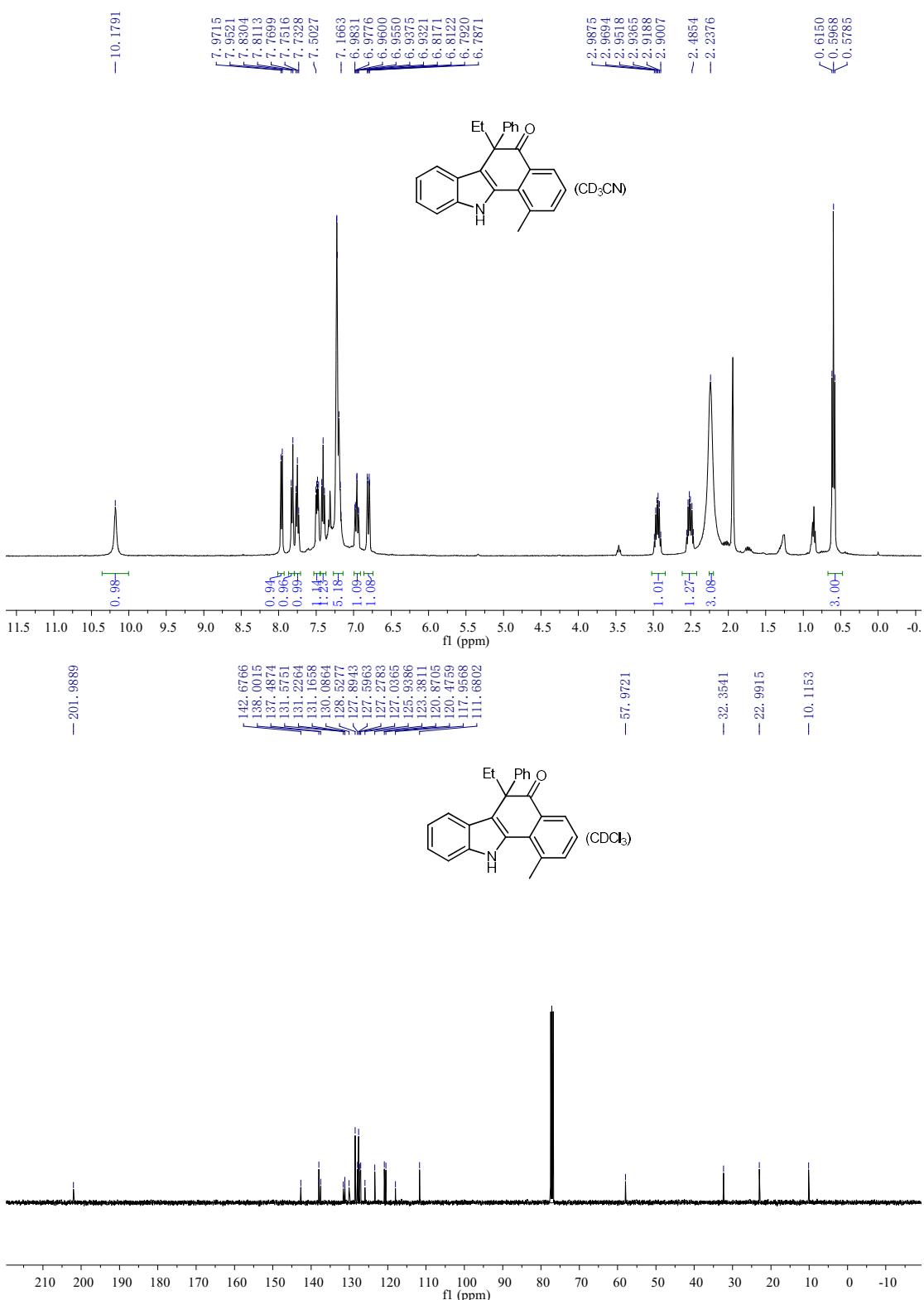
¹H and ¹³C NMR Spectra of compound 3qa



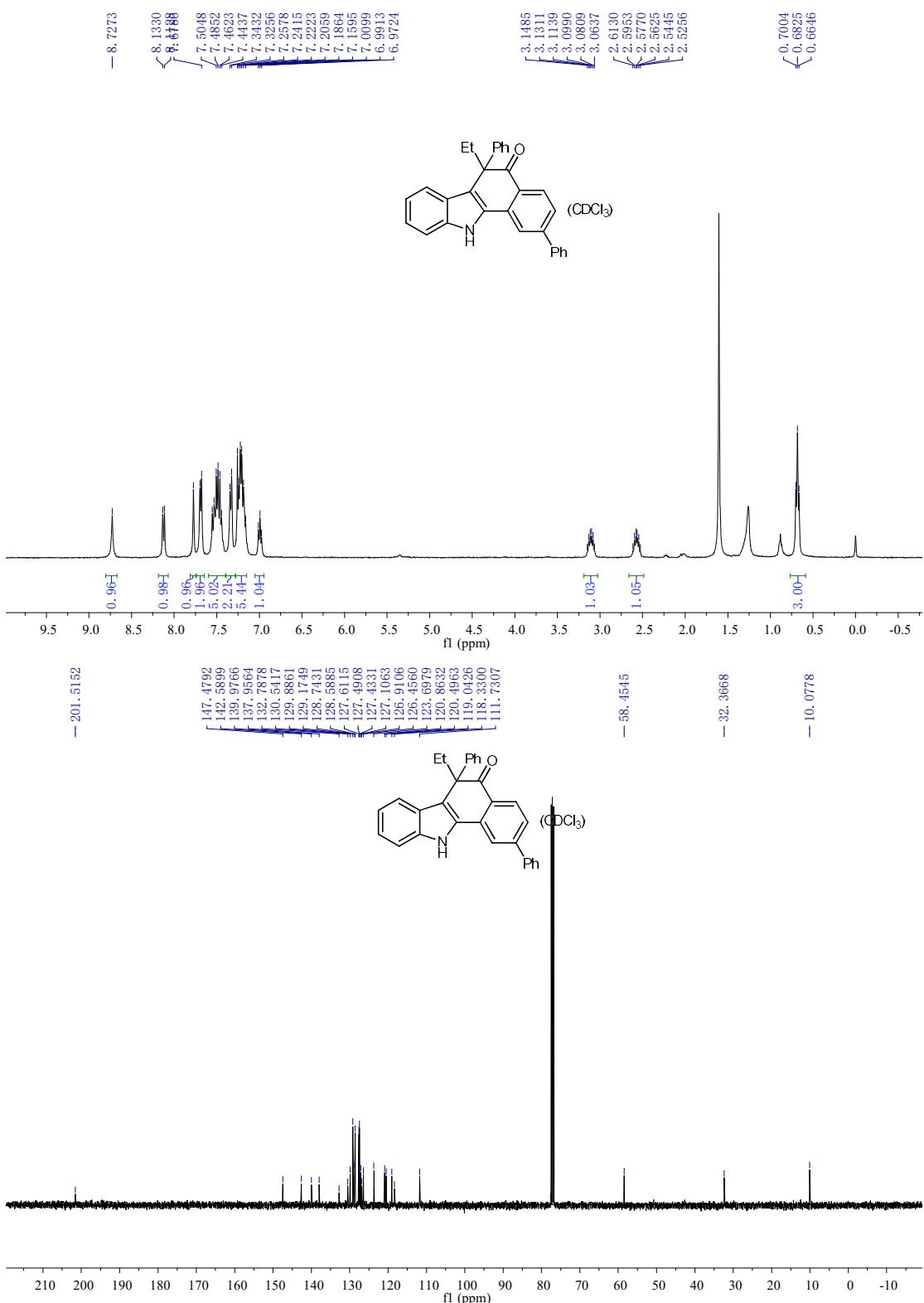
¹H and ¹³C NMR Spectra of compound 3ra



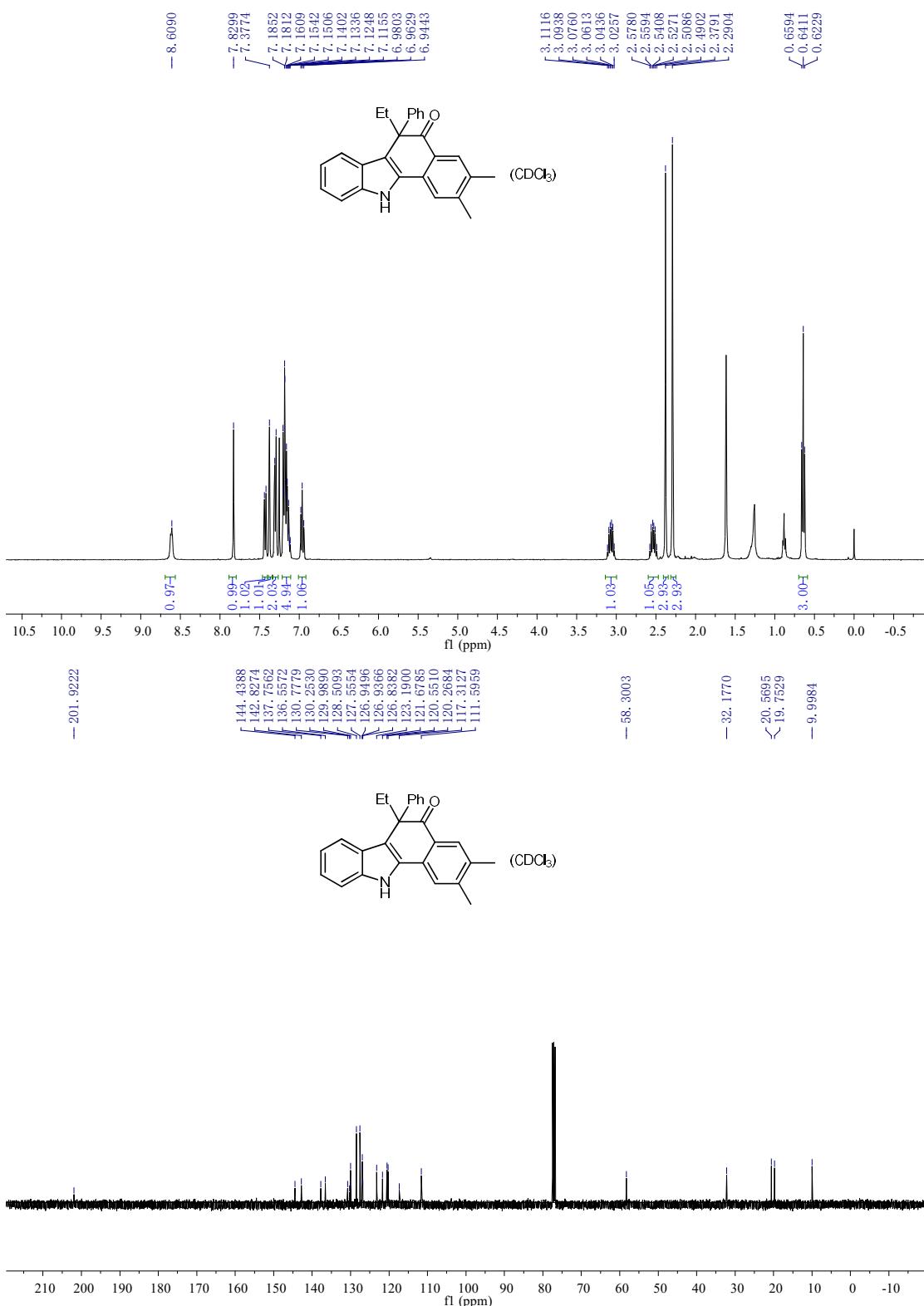
¹H and ¹³C NMR Spectra of compound 3sa



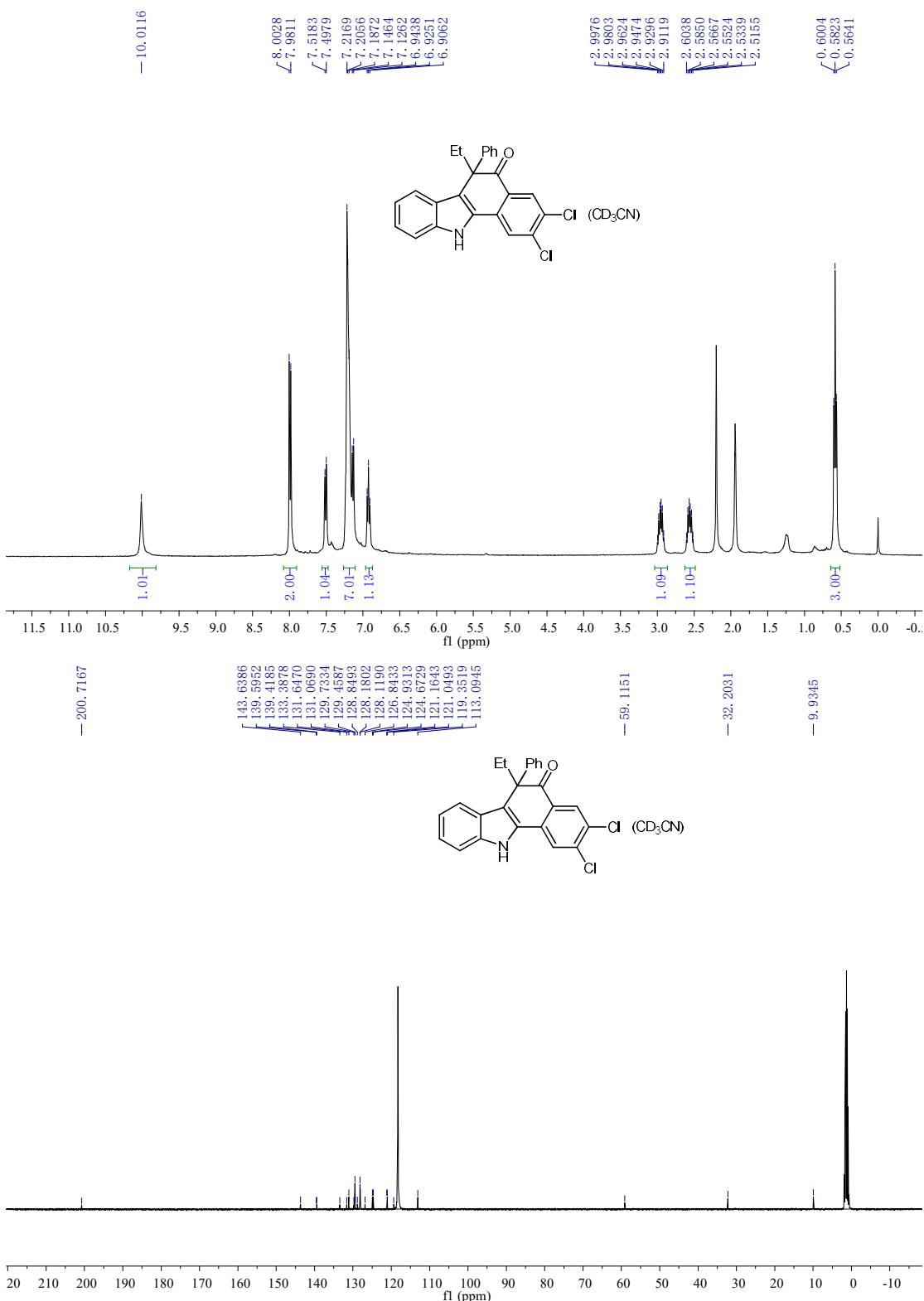
¹H and ¹³C NMR Spectra of compound 3ta



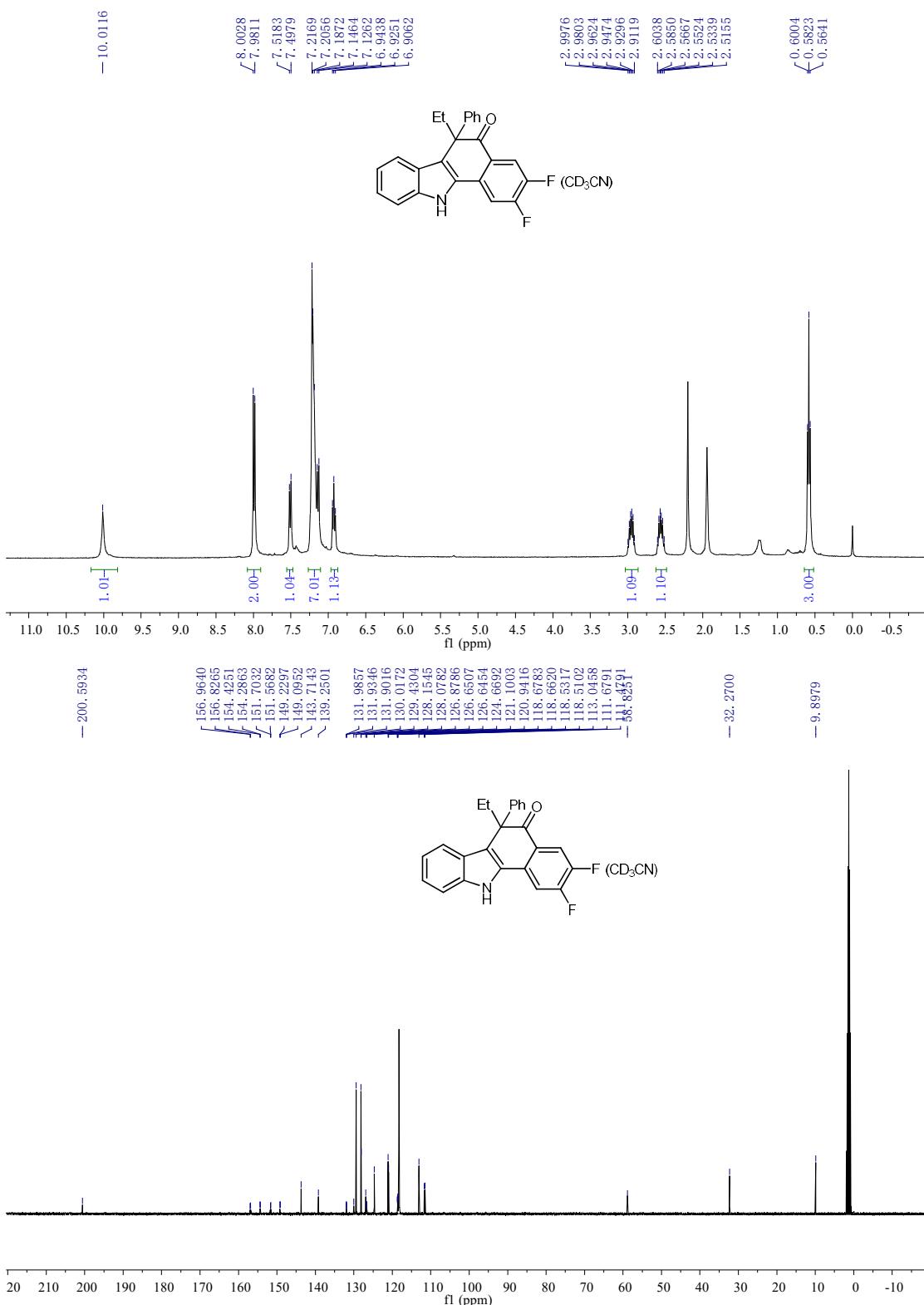
¹H and ¹³C NMR Spectra of compound 3ua



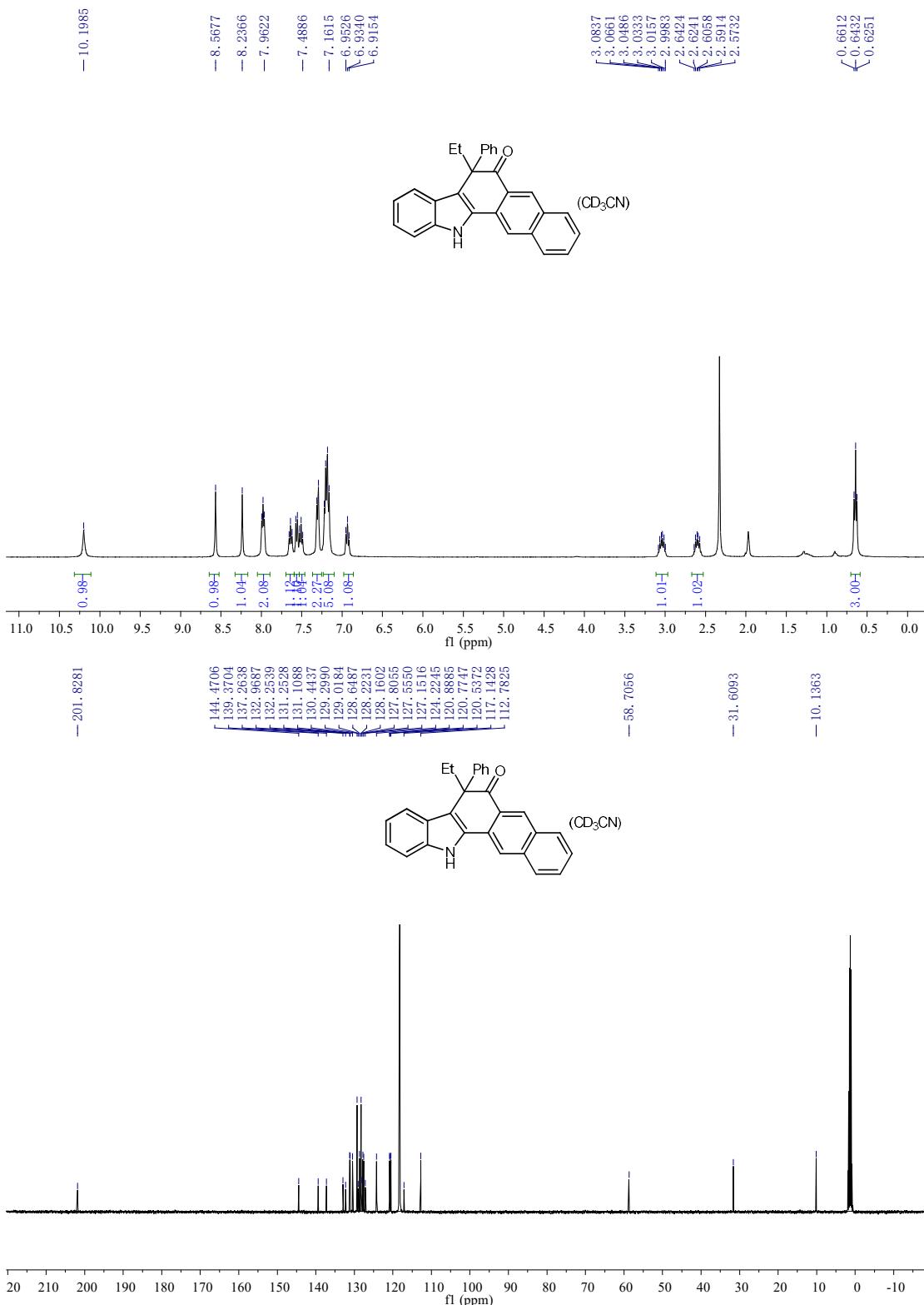
¹H and ¹³C NMR Spectra of compound 3va



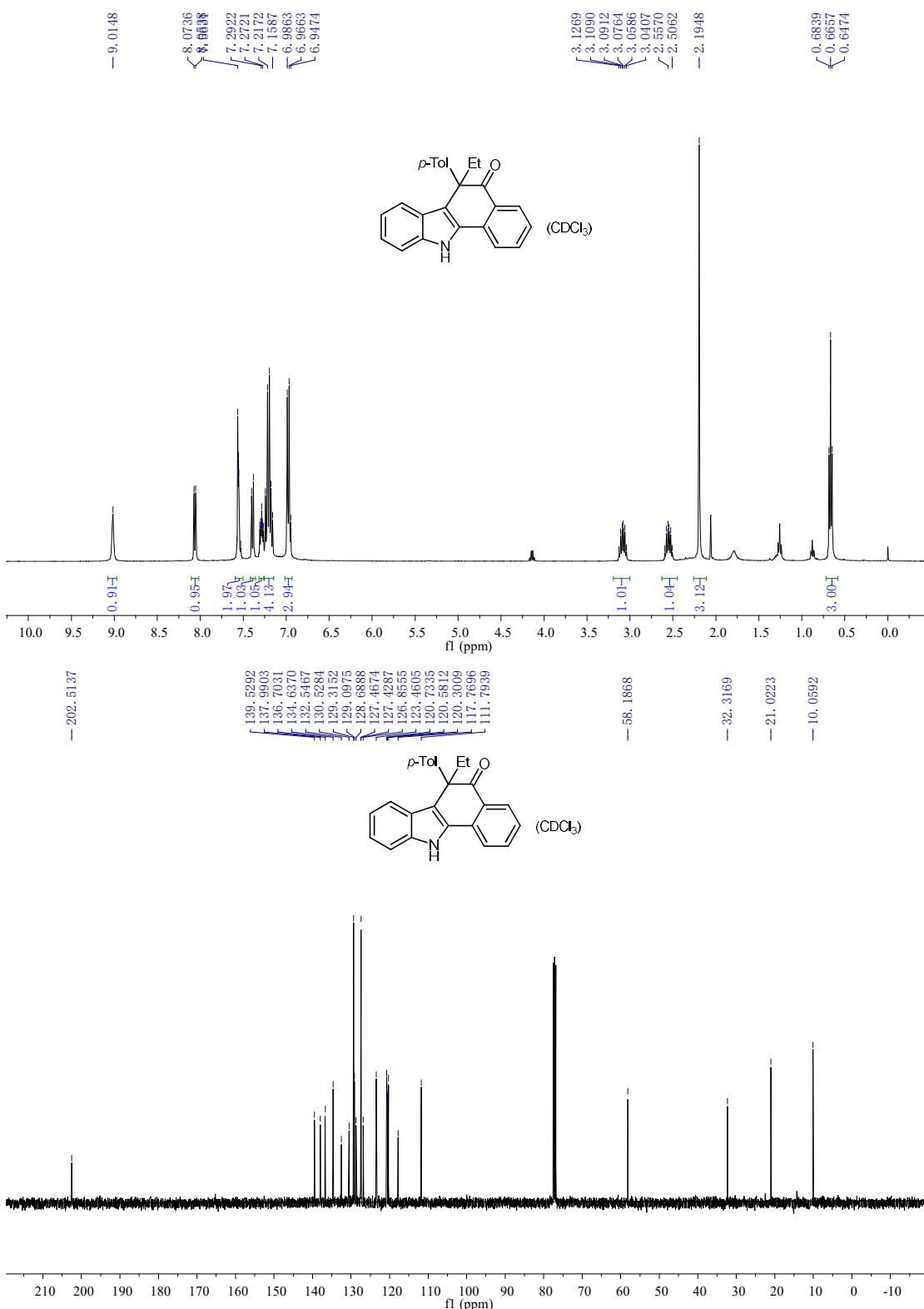
¹H and ¹³C NMR Spectra of compound 3wa



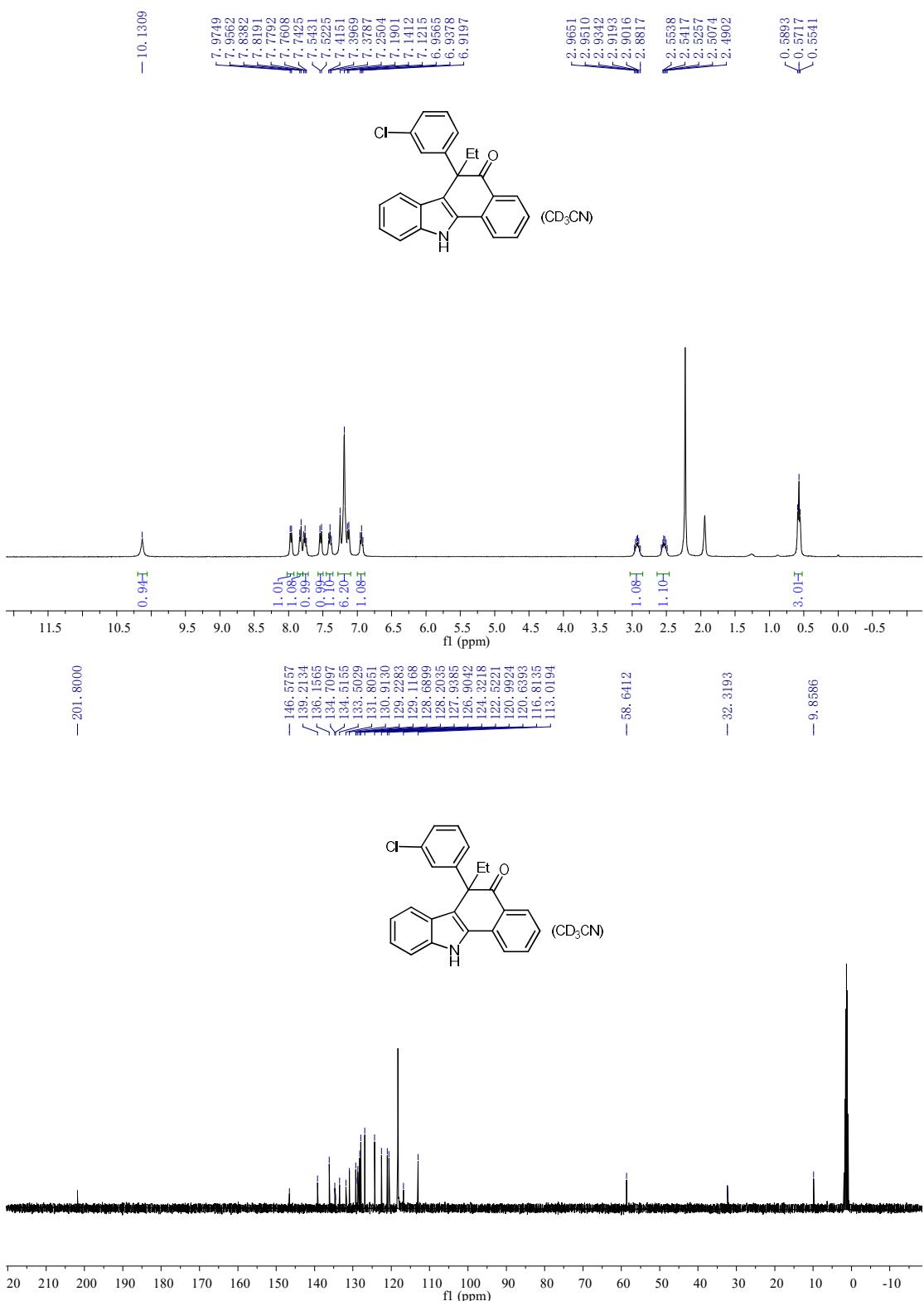
¹H and ¹³C NMR Spectra of compound **3xa**



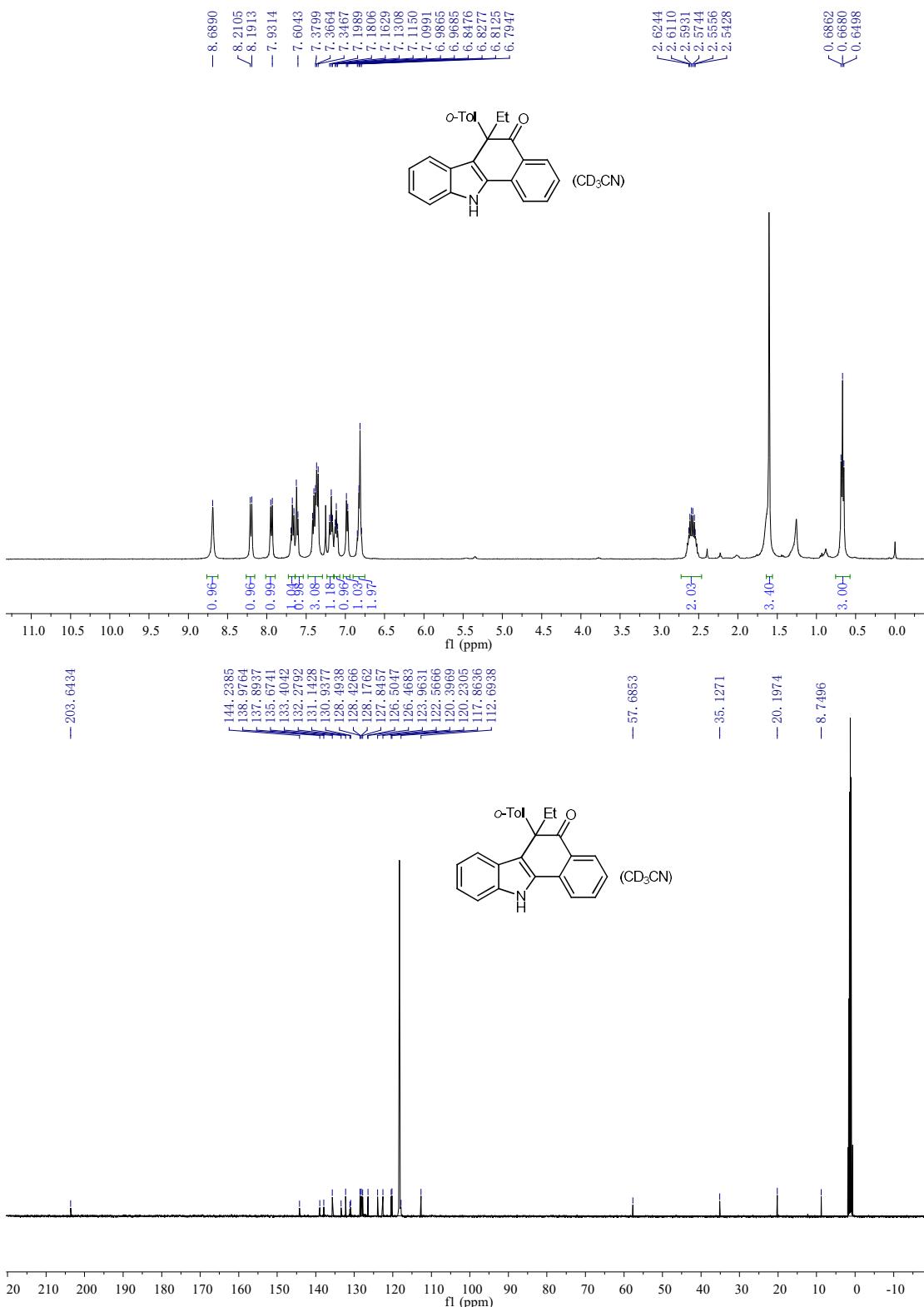
¹H and ¹³C NMR Spectra of compound 3ab



¹H and ¹³C NMR Spectra of compound 3ac



¹H and ¹³C NMR Spectra of compound 3ad



¹H and ¹³C NMR Spectra of compound 3ae

