

Supplementary Information

Direct Construction of Carbazoles from 2-Methyl-indole-3-carbaldehydes and Enals

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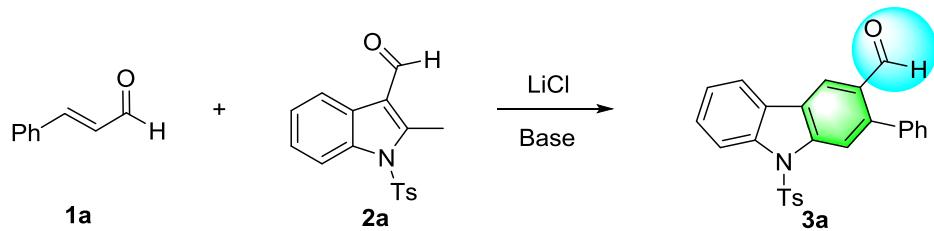
I: General Information

Commercially available materials were purchased from Alfa Aesar and Sigma-Aldrich. Toluene and DCM was dried over Pure Solv solvent purification system. THF was distilled over sodium. Other solvents were dried over 4 \AA molecular sieve prior use. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on a Waters Q-TOF Premier Spectrometer. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness).

II. General procedure

a) Optimized conditions:

Table S1. Optimized conditions.



Entry ^[a]	Base	Lewis acid	Solvent	Yield[%] ^[b]
1	K ₂ CO ₃	-	THF	n.d.
2	DBU	-	THF	n.d.
3	NaO <i>t</i> Bu	-	THF	n.d.
4	Et ₃ N	-	THF	n.d.
5	DBN	-	THF	n.d.
6	DBU	Cu(OTf) ₂	THF	<10
7	DBU	Zn(OTf) ₂	THF	<10
8	DBU	Sc(OTf) ₃	THF	<10
9	DBU	FeCl ₃	THF	n.d.
10	DBU	Mg(OTf) ₂	THF	<10
11	DBU	ZnCl ₂	THF	n.d.
12	DBU	LiCl	THF	63
13	DBU	LiF	THF	30
14	DBU	LiBr	THF	57
15	DBU	NaCl	THF	<10
16	K ₂ CO ₃	LiCl	THF	n.d.
17	DBN	LiCl	THF	n.d.
18	NaO <i>t</i> Bu	LiCl	THF	n.d.
19	Et ₃ N	LiCl	THF	n.d.
20	DBU	LiCl	1,4-dioxane	55
21	DBU	LiCl	DMF	45
22	DBU	LiCl	CH ₃ CN	60
23	DBU	LiCl	Toluene	50
24 ^[c]	DBU	LiCl	THF	45
25 ^[d]	DBU	LiCl	THF	58
26 ^[e]	DBU	LiCl	THF	40
27 ^[f]	DBU	LiCl	THF	75
28 ^{[f],[g]}	DBU	LiCl	THF/CH ₃ CN	79

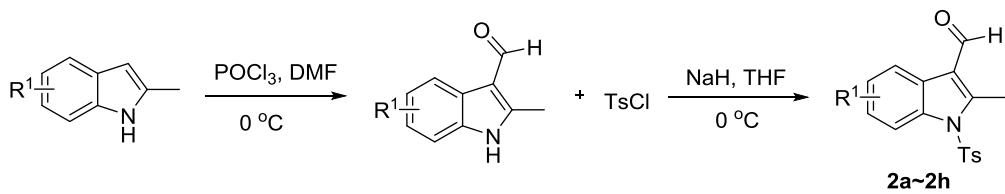
29 ^{[f],[h]}	DBU	LiCl	THF/CH ₃ CN	76
30 ^{[f],[i]}	DBU	LiCl	THF/CH₃CN	82
31 ^{[f],[j]}	DBU	LiCl	THF/CH ₃ CN	64
32 ^{[f],[i],[k]}	DBU	LiCl	THF/CH ₃ CN	64
33 ^{[f],[i],[l]}	DBU	LiCl	THF/CH ₃ CN	72
34 ^{[f],[i]}	-	LiCl	THF/CH ₃ CN	n.d.

[a] optimized conditions: **1a** (0.1 mmol), cinnamaldehyde **2a** (1.5 equiv), base (2.0 equiv), Lewis acid (0.2 or 3.0 equiv), solvent (1.0 mL), 30 °C, 24 h. [b] Yields of products isolated after column chromatography. [c] At 0 °C. [d] At 50 °C. [e] At 70 °C. [f] Under an O₂ balloon. [g] THF/CH₃CN=1:1. [h] 50 µL of t-BuOH was added [i] 100 µL of t-BuOH was added [j] 200 µL of t-BuOH was added. [k] LiCl (1.0 equiv). [l] LiCl (2.0 equiv). n.d. = not detected.

b) General procedure for the synthesis of α, β -unsaturated aldehydes (1a~1p**):**

1a, 1b, 1e, 1f, 1j and **1k** were purchased. **1c, 1d, 1g, 1h, 1i, 1l, 1m, 1n, 1o, 1p** and **1q** were prepared according to the literature.^[1-3]

c) General procedure for the synthesis of substrates **2^[4-10] (**2a** as an example):**

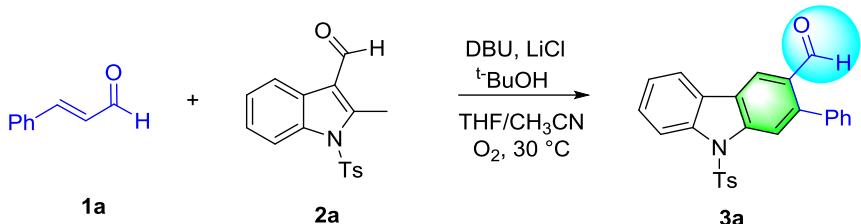


$R^1 = H, 4\text{-Br}, 5\text{-F}, 5\text{-Cl}, 5\text{-Br}, 5\text{-CH}_3, 6\text{-Cl}, 6\text{-Br}$

To a dried round bottom flask with anhydrous DMF (12.0 mmol, 0.94 mL), was dropwise added POCl₃ (11.0 mmol, 1.0 mL) at 0 °C. After stirring for 30 minutes at 0 °C, a solution of 2-methyl-1*H*-indole (10 mmol, 1.31 g) in DMF (5.0 mL) was added dropwise to the reaction mixture. Upon completion of the reaction, which was monitored by TLC, a solution of NaOH was added slowly. The formed solid was filtered and dried under vacuum to afford 2-methyl-1*H*-indole-3-carbaldehyde.

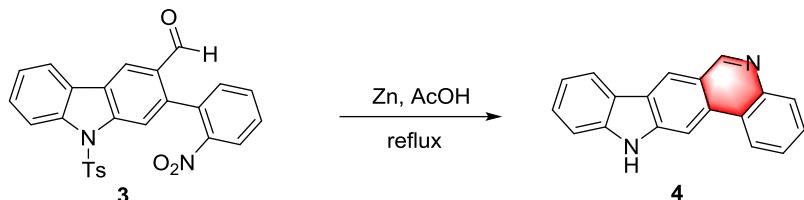
To a solution of 2-methyl-1*H*-indole-3-carbaldehyde (9.0 mmol, 1.43 g) in dry THF (20.0 mL) was added sodium hydride (60% in oil, 22.5 mmol) at 0 °C. After stirring for 20 minutes, TsCl (10.8 mmol, 2.06 g) was added to the reaction mixture, then stirred at 0 °C until the substrate was consumed completely. The resulting mixture was poured into saturated aqueous NaCl (50 mL), extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel with elution (30% v/v EtOAc in hexane) to afford 2-methyl-1-tosyl-1*H*-indole-3-carbaldehyde **2a** in 60% overall yield.

d) General procedure for the synthesis of carbazoles 3 (3a as an example):



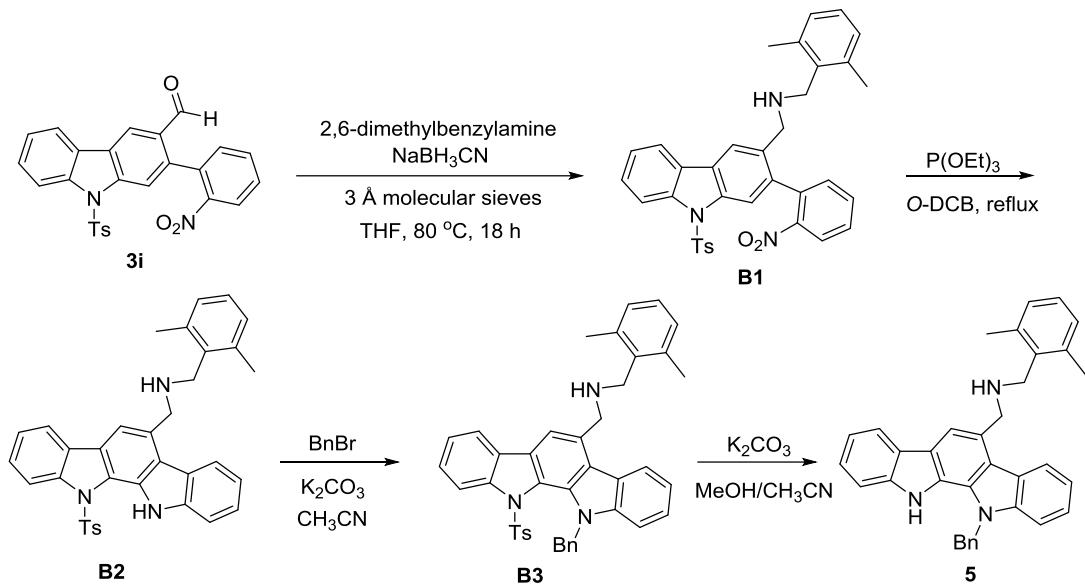
To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar under O₂ atmosphere was added **1a** (0.15 mmol, 19.0 μL), **2a** (0.10 mmol, 31.4 mg), LiCl (0.30 mmol, 13.0 mg). Then dry THF/CH₃CN (v/v=1:1, 1.0 mL), *t*BuOH (0.1M, 100.0 μL) and DBU (0.20 mmol, 30.0 μL) was added via a micro syringe. The reaction mixture was stirred at 30 °C until **2a** disappeared (detected by TLC), the residue was purified by silica gel column chromatography with elution (50% v/v DCM in hexane) to afford carbazole **3a** as a white solid in 82% yield.

e) General procedure for the synthesis of 4 (4a as an example):



To a solution of **3i** (0.10 mmol, 49.1 mg) in AcOH (3.0 mL) was added zinc powder (2.0 mmol, 0.13 g). The reaction mixture was stirred at refluxing temperature for overnight. After completion of reaction, a saturated sodium bicarbonate solution was added slowly, until the pH was adjusted to neutral. Then the resulting mixture was extracted with CH₂Cl₂ (3 × 15 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel with elution (20% v/v CH₂Cl₂ in MeOH) to afford the product **4a** in 88% yield.

f) Procedures for the synthesis of 5:



To a solution of **3i** (5.00 mmol, 2.46 g), 3 Å molecular sieves (5.00 g), NaBH_3CN (10.0 mmol, 0.63 g) and 2,6-dimethylbenzylamine (3.38 g, 10.0 mmol, 2.0 equiv) were suspended in THF (15.0 mL) and heated at 80 °C for 18 hours. The reaction mixture was cooled, diluted with CH_2Cl_2 (3×20 mL) and washed with saturated aqueous NaCl (20 mL) before drying over Na_2SO_4 , filtering, and concentrating in vacuo. Purification by column chromatography (30% v/v EtOAc in hexane) to afford the product **B1** in 70% yield.

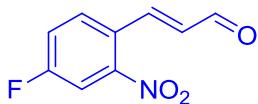
To a solution of **B1** (3.50 mmol, 2.06 g), $\text{P}(\text{OEt})_3$ (35.0 mmol, 5.50 g) were suspended in ortho-dichlorobenzene (15.0 mL) and reflux for overnight. After completion of reaction, the solvent was concentrated under reduced pressure, and the crude residue was purified by column chromatography (20% v/v EtOAc in hexane) to afford product **B2** in 62% yield. **B2** (2.0 mmol, 1.11 g), K_2CO_3 (4.0 mmol, 0.55 g) and benzyl bromide (2.2 mmol, 0.38 g) were added in CH_3CN (20.0 mL). The reaction mixture was stirred at room temperature for overnight. When the reaction is complete, the solvent was concentrated under reduced pressure, and the crude residue was purified by column chromatography (20% v/v EtOAc in hexane) to afford product **B3** in 87% yield.

B3 (0.5 mmol, 0.33 g) was refluxed overnight in MeOH-THF (1:1=10.0 mL) solvent mixture after addition of K_2CO_3 (0.5 mmol, 0.17 g). Once completion of the reaction, the solvent was removed under vacuo, the crude product was purified by column chromatography (50% v/v EtOAc in hexane) to afford product **5** in 82% yield as a brown solid.

III. Characterizations of substrates and products, reference

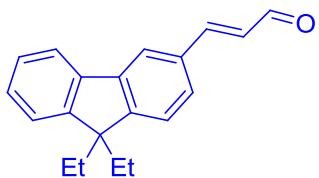
Structure of known compounds **1c**,^[11] **1d**,^[11] **1h**,^[13] **1i**,^[11] **1l**,^[12] **1m**,^[10] **1n**,^[13] **1o**,^[14] **1q**,^[15] **2a**,^[16] **2b**,^[17] **4a**,^[18] **4c**^[18] and **5**^[19] were confirmed by NMR spectral comparison with literature data. For compounds not reported before, ¹H NMR and ¹³C NMR characterization and the corresponding spectra are provided.

a) Characterizations of substrates and products



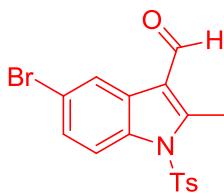
1g

(E)-3-(4-fluoro-2-nitrophenyl)acrylaldehyde (1g): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ = 9.71 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 16.0 Hz, 1H), 7.79 (dd, *J* = 8.2, 2.8 Hz, 1H), 7.71 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.41-7.45 (m, 1H), 6.57 (dd, *J* = 16.0, 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ = 193.0, 164.3, 161.7, 148.7, 146.1, 132.7, 132.6, 131.1, 131.0, 126.3, 126.2, 121.5, 121.3, 113.2, 112.9; HRMS(ESI) calcd for C₉H₇FNO₃ (M+H)⁺: 196.0404, Found: 196.0406.



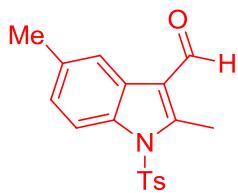
1p

(E)-3-(9,9-diethyl-9H-fluoren-3-yl)acrylaldehyde (1p): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ = 9.73 (d, *J* = 7.6 Hz, 1H), 7.73-7.76 (m, 2H), 7.54-7.59 (m, 3H), 7.35-7.38 (m, 3H), 6.79 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.06 (q, *J* = 7.2 Hz, 4H), 0.32 (t, *J* = 7.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ = 193.8, 153.6, 150.8, 150.7, 145.1, 140.3, 132.8, 128.3, 128.2, 127.7, 127.2, 123.1, 122.7, 120.4, 120.2, 56.2, 32.7, 8.5; HRMS(ESI) calcd for C₂₀H₂₁O (M+H)⁺: 277.1587, Found: 277.1583.



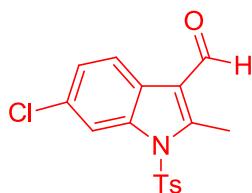
2d

5-bromo-2-methyl-1-tosyl-1H-indole-3-carbaldehyde (2d): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ = 10.21 (s, 1H), 8.44 (d, *J* = 2.4 Hz, 1H), 8.08 (d, *J* = 9.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.47 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.92 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 185.1, 148.4, 146.3, 135.2, 134.6, 130.4, 128.5, 127.7, 126.7, 124.1, 118.8, 118.2, 115.5, 21.7, 12.7; HRMS(ESI) calcd for C₁₇H₁₅BrNO₃S (M+H)⁺: 391.9951, Found: 391.9957.



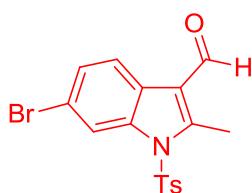
2e

2,6-dimethyl-1-tosyl-1*H*-indole-3-carbaldehyde (2e): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.26 (s, 1H), 8.09 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.27-7.29 (m, 2H), 7.20 (d, J = 9.6 Hz, 1H), 2.93 (s, 3H), 2.46 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 185.7, 147.7, 145.8, 135.6, 134.9, 134.1, 130.2, 126.8, 126.6, 126.3, 121.2, 118.8, 113.7, 100.0, 21.7, 21.3, 12.7; HRMS(ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 328.1002, Found: 328.1005.



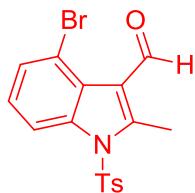
2f

6-chloro-2-methyl-1-tosyl-1*H*-indole-3-carbaldehyde (2f): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.20 (s, 1H), 8.23 (d, J = 2.0 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 3H), 2.89 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 185.3, 148.1, 146.3, 136.2, 135.2, 131.6, 130.4, 126.7, 125.6, 124.6, 122.1, 118.6, 114.3, 21.7, 12.6; HRMS(ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 348.0456, Found: 348.0448.



2g

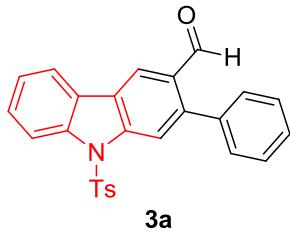
6-bromo-2-methyl-1-tosyl-1*H*-indole-3-carbaldehyde (2g): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.23 (s, 1H), 8.42 (d, J = 1.6 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.47 (dd, J = 8.8, 2.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 2.91 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 185.2, 147.9, 146.3, 136.5, 135.2, 130.5, 128.3, 126.7, 125.0, 122.5, 119.3, 118.6, 117.1, 21.7, 12.6; HRMS(ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{BrNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 391.9951, Found: 391.9957.



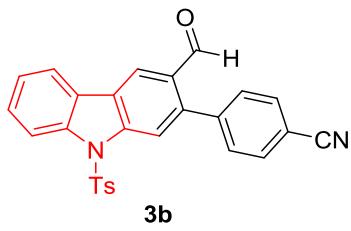
2h

4-bromo-2-methyl-1-tosyl-1*H*-indole-3-carbaldehyde (2h): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 11.18 (s, 1H), 8.33 (dd, J = 8.4, 0.8 Hz, 1H), 7.75 (d, J = 8.4

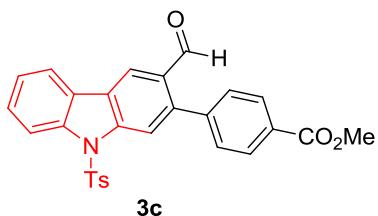
Hz, 2H), 7.56 (dd, J = 8.0, 0.8 Hz, 1H), 7.31 (d, J = 7.6 Hz, 2H), 7.23(t, J = 8.4 Hz, 1H), 3.00 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 188.6, 146.2, 145.6, 137.0, 135.4, 130.3, 129.2, 126.7, 125.5, 118.6, 113.7, 112.6, 21.7, 14.0; HRMS(ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{BrNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 391.9951, Found: 391.9957.



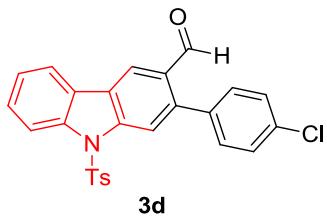
2-phenyl-9-tosyl-9*H*-carbazole-3-carbaldehyde (3a): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.02 (s, 1H), 8.60 (s, 1H), 8.39 (s, 1H), 8.34 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.48-7.58 (m, 6H), 7.43 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 191.9, 145.5, 145.4, 141.3, 139.2, 138.0, 134.8, 130.5, 130.0, 129.9, 128.6, 128.4, 128.3, 126.6, 125.9, 125.6, 124.5, 120.7, 120.0, 116.4, 115.1, 21.6; HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{20}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 426.1158, Found: 426.1159.



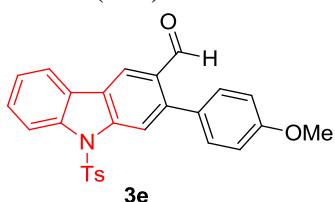
4-(3-formyl-9-tosyl-9*H*-carbazol-2-yl)benzonitrile (3b): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 9.97 (s, 1H), 8.62 (s, 1H), 8.33 (d, J = 9.2 Hz, 2H), 8.03 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.57-7.62 (m, 3H), 7.45 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 190.6, 145.8, 143.3, 143.0, 142.8, 141.1, 139.2, 134.7, 132.3, 131.1, 130.0, 129.7, 129.6, 128.8, 127.0, 126.6, 126.5, 125.2, 124.7, 120.9, 120.8, 118.5, 116.3, 115.1, 112.3, 21.6; HRMS(ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{N}_2\text{O}_3\text{S}$ ($\text{M}+\text{K}$) $^+$: 489.0670, Found: 489.0672.



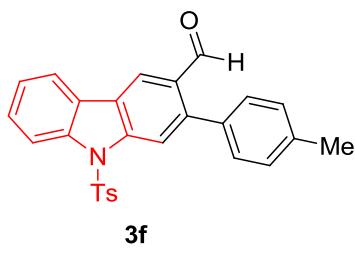
methyl 4-(3-formyl-9-tosyl-9*H*-carbazol-2-yl)benzoate (3c): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 9.99 (s, 1H), 8.62 (s, 1H), 8.37 (s, 1H), 8.34 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 8.0 Hz, 2H), 8.03 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.55-7.60 (m, 3H), 7.44 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 4.00 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 191.2, 166.7, 145.6, 144.0, 142.7, 141.2, 139.2, 134.7, 130.5, 123.0, 129.9, 129.8, 128.6, 126.6, 126.3, 125.4, 124.6, 120.8, 120.3, 116.3, 115.1, 52.4, 21.6; HRMS(ESI) calcd for $\text{C}_{28}\text{H}_{22}\text{NO}_5\text{S}$ ($\text{M}+\text{H}$) $^+$: 484.1213, Found: 484.1222.



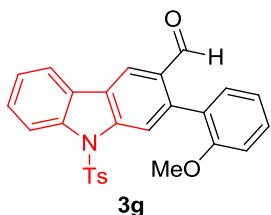
2-(4-chlorophenyl)-9-tosyl-9H-carbazole-3-carbaldehyde (3d): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.00 (s, 1H), 8.59 (s, 1H), 8.33 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.56 (td, J = 7.6, 1.2 Hz, 1H), 7.52 (dt, J = 8.4, 2.4 Hz, 2H), 7.40-7.45 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 191.4, 145.6, 143.9, 141.2, 139.2, 136.5, 134.7, 134.7, 131.7, 123.0, 129.9, 128.8, 128.5, 126.5, 126.1, 125.4, 124.6, 120.7, 120.3, 116.3, 115.1, 21.6; HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{19}\text{ClNO}_3\text{S} (\text{M}+\text{H})^+$: 460.0769, Found: 460.0765.



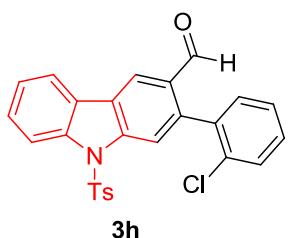
2-(4-methoxyphenyl)-9-tosyl-9H-carbazole-3-carbaldehyde (3e): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.03 (s, 1H), 8.57 (s, 1H), 8.36 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 7.2 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.54 (td, J = 7.2, 1.2 Hz, 1H), 7.40-7.44 (m, 3H), 7.15 (d, J = 8.0 Hz, 2H), 7.07 (dt, J = 9.6, 2.8 Hz, 2H), 3.91 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 192.1, 159.9, 145.5, 145.2, 141.3, 139.1, 134.8, 131.7, 130.3, 130.1, 129.9, 128.3, 126.6, 125.6, 125.5, 124.5, 120.6, 120.0, 116.3, 115.1, 114.0, 55.5, 21.6; HRMS(ESI) calcd for $\text{C}_{27}\text{H}_{22}\text{NO}_4\text{S} (\text{M}+\text{H})^+$: 456.1264, Found: 456.1261.



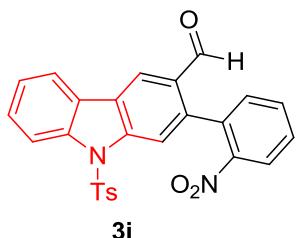
2-(p-tolyl)-9-tosyl-9H-carbazole-3-carbaldehyde (3f): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.03 (s, 1H), 8.59 (s, 1H), 8.38 (s, 1H), 8.34 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 7.2 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.55 (td, J = 7.2, 1.2 Hz, 1H), 7.42 (td, J = 7.6, 0.8 Hz, 1H), 7.34-7.40 (m, 4H), 7.15 (d, J = 8.4 Hz, 2H), 2.48 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 192.1, 145.5, 145.4, 141.3, 139.1, 138.3, 135.1, 134.8, 130.4, 130.1, 130.0, 129.3, 128.3, 126.6, 125.7, 125.6, 124.5, 120.6, 120.0, 116.4, 115.1, 21.6, 21.3; HRMS(ESI) calcd for $\text{C}_{27}\text{H}_{22}\text{NO}_3\text{S} (\text{M}+\text{H})^+$: 440.1315, Found: 440.1324.



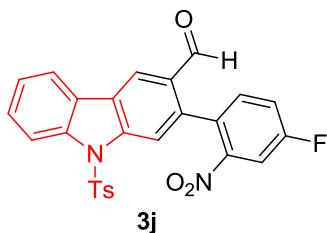
2-(2-methoxyphenyl)-9-tosyl-9H-carbazole-3-carbaldehyde (3g): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 9.83 (s, 1H), 8.57 (s, 1H), 8.34 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 7.2 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.54 (td, J = 7.6, 1.6 Hz, 1H), 7.48 (td, J = 8.4, 1.6 Hz, 1H), 7.38-7.44 (m, 2H), 7.15-7.19 (m, 3H), 7.04 (d, J = 8.0 Hz, 1H), 3.78 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 192.1, 156.6, 145.4, 141.5, 141.3, 139.0, 134.8, 131.9, 130.3, 130.2, 129.9, 128.2, 127.0, 126.6, 125.9, 124.5, 121.2, 120.6, 119.0, 117.1, 115.1, 110.8, 55.5, 21.6; HRMS(ESI) calcd for $\text{C}_{27}\text{H}_{22}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) $^+$: 456.1264, Found: 456.1263.



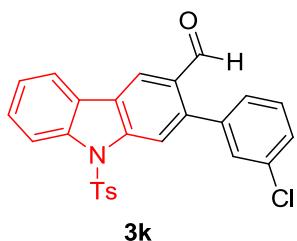
2-(2-chlorophenyl)-9-tosyl-9H-carbazole-3-carbaldehyde (3h): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 9.82 (s, 1H), 8.61 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H), 8.31 (s, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.55-7.59 (m, 2H), 7.42-7.48 (m, 4H), 7.15 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 190.9, 145.6, 142.0, 141.2, 139.2, 137.0, 134.5, 133.8, 132.1, 130.1, 130.0, 129.9, 129.7, 128.5, 127.0, 126.6, 126.5, 125.6, 124.6, 120.7, 119.7, 117.0, 115.2, 21.6; HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{19}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 460.0769, Found: 460.0766.



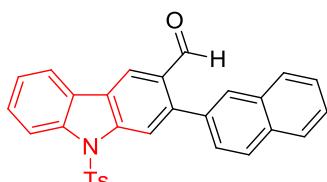
2-(2-nitrophenyl)-9-tosyl-9H-carbazole-3-carbaldehyde (3i): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 9.89 (s, 1H), 8.55 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.26 (s, 1H), 8.17 (dd, J = 8.0, 1.2 Hz, 1H), 8.01 (d, J = 7.2 Hz, 1H), 7.74 (td, J = 7.6, 1.2 Hz, 1H), 7.65-7.70 (m, 3H), 7.58 (td, J = 7.6, 1.2 Hz, 1H), 7.42-7.48 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 190.3, 149.2, 145.8, 141.0, 139.6, 139.2, 134.2, 133.9, 132.8, 130.0, 129.9, 129.5, 128.6, 126.7, 126.5, 125.5, 124.7, 124.6, 122.0, 120.7, 116.1, 115.3, 21.6; HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{19}\text{N}_2\text{O}_5\text{S}$ ($\text{M}+\text{H}$) $^+$: 471.1009, Found: 471.1003.



2-(4-fluoro-2-nitrophenyl)-9-tosyl-9H-carbazole-3-carbaldehyde (3j): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 9.90 (s, 1H), 8.51 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.24 (s, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.91 (dd, J = 8.4, 1.6 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.43-7.50 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 190.2, 163.2, 160.7, 149.5, 145.8, 141.0, 139.2, 138.2, 134.2, 134.1, 134.0, 130.3, 130.0, 129.9, 128.7, 126.8, 126.5, 125.3, 124.8, 123.1, 120.7, 120.3, 120.1, 116.4, 115.3, 112.4, 112.2, 21.6; HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{18}\text{FN}_2\text{O}_5\text{S} (\text{M}+\text{H})^+$: 489.0915, Found: 489.0913.

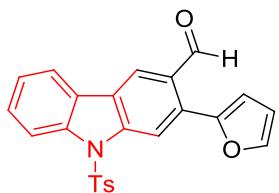


2-(3-chlorophenyl)-9-tosyl-9H-carbazole-3-carbaldehyde (3k): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.01 (s, 1H), 8.61 (s, 1H), 8.33 (d, J = 7.6 Hz, 2H), 8.02 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.42-7.51 (m, 4H), 7.34-7.37 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 191.3, 145.6, 143.7, 141.2, 139.9, 139.2, 134.7, 134.6, 130.3, 130.0, 129.9, 129.8, 128.7, 128.6, 128.5, 126.6, 126.2, 125.4, 124.6, 120.8, 120.2, 116.3, 115.1, 21.6; HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{19}\text{ClNO}_3\text{S} (\text{M}+\text{H})^+$: 460.0769, Found: 460.0765.



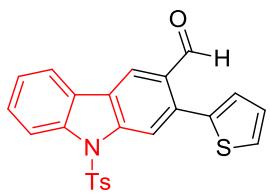
3l

2-(naphthalen-2-yl)-9-tosyl-9H-carbazole-3-carbaldehyde (3l): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.08 (s, 1H), 8.65 (s, 1H), 8.50 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H), 8.00-8.04 (m, 2H), 7.94-7.97 (m, 3H), 7.77 (d, J = 8.4 Hz, 2H), 7.64 (dd, J = 8.4, 2.0 Hz, 1H), 7.55-7.63 (m, 3H), 7.44 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 191.9, 145.5, 145.3, 141.2, 139.2, 135.4, 134.8, 133.0, 132.8, 130.2, 130.0, 129.9, 128.4, 128.3, 128.2, 128.1, 127.8, 127.0, 126.8, 126.6, 125.9, 125.6, 124.6, 120.7, 120.1, 116.6, 115.1, 21.6; HRMS(ESI) calcd for $\text{C}_{30}\text{H}_{22}\text{NO}_3\text{S} (\text{M}+\text{Na})^+$: 498.1134, Found: 498.1125.



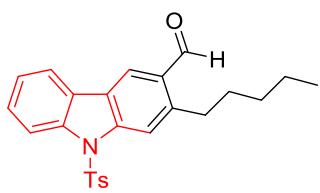
3m

2-(thiophen-2-yl)-9-tosyl-9H-carbazole-3-carbaldehyde (3m): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.41 (s, 1H), 8.61 (s, 1H), 8.53 (s, 1H), 8.30 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 0.8 Hz, 1H), 7.54 (td, J = 7.6, 1.2 Hz, 1H), 7.40 (td, J = 7.6, 0.8 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 2.8 Hz, 1H), 6.64 (dd, J = 3.2, 2.0 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 191.8, 151.2, 145.5, 144.2, 141.3, 139.3, 134.7, 132.6, 130.0, 129.5, 128.5, 126.6, 126.0, 125.5, 124.6, 120.7, 120.4, 115.1, 114.2, 112.2, 111.9, 21.6; HRMS(ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{NO}_4\text{S} (\text{M}+\text{H})^+$: 416.0951, Found: 416.0949.



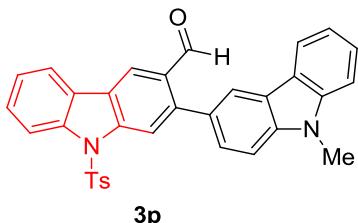
3n

2-(thiophen-2-yl)-9-tosyl-9H-carbazole-3-carbaldehyde (3n): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.22 (s, 1H), 8.57 (s, 1H), 8.47 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.53-7.58 (m, 2H), 7.43 (td, J = 7.6, 0.8 Hz, 1H), 7.21 (dd, J = 5.2, 3.6 Hz, 1H), 7.15-7.18 (m, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 191.6, 145.6, 141.1, 139.2, 139.1, 137.3, 134.7, 130.5, 130.0, 129.9, 128.6, 127.9, 127.6, 126.6, 126.2, 125.4, 124.6, 120.7, 120.1, 116.9, 115.1, 21.6; HRMS(ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{NO}_3\text{S}_2 (\text{M}+\text{H})^+$: 432.0723, Found: 432.0724.

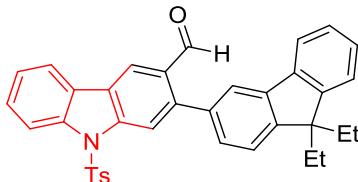


3o

2-pentyl-9-tosyl-9H-carbazole-3-carbaldehyde (3o): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.38 (s, 1H), 8.40 (s, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.21 (s, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.51 (td, J = 7.2, 1.2 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 3.21 (t, J = 7.6 Hz, 2H), 2.28 (s, 3H), 1.68-1.75 (m, 2H), 1.37-1.45 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 191.2, 145.6, 145.4, 141.6, 138.9, 134.8, 130.0, 129.9, 127.9, 126.5, 125.7, 124.80, 124.4, 123.2, 120.2, 116.6, 115.1, 33.3, 32.7, 31.6, 22.6, 21.6, 14.1; HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{26}\text{NO}_3\text{S} (\text{M}+\text{K})^+$: 458.1187, Found: 458.1196.

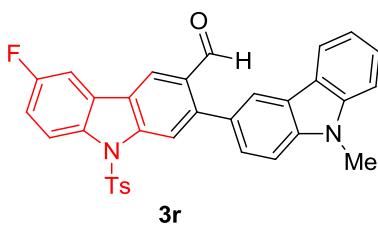


9'-methyl-9-tosyl-9H,9'H-[2,3'-bicarbazole]-3-carbaldehyde (3p): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.08 (s, 1H), 8.63 (s, 1H), 8.50 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 1.6 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 8.8 Hz, 2H), 7.61 (dd, J = 8.4, 2.0 Hz, 1H), 7.54-7.58 (m, 3H), 7.48 (d, J = 8.0 Hz, 1H), 7.44 (td, J = 7.6, 1.2 Hz, 1H), 7.31 (td, J = 6.8, 1.2 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 3.96 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 192.5, 146.5, 145.4, 141.6, 141.3, 140.8, 139.2, 134.8, 130.4, 129.9, 128.6, 128.2, 128.1, 126.6, 126.4, 125.8, 125.4, 124.5, 122.9, 122.4, 120.7, 120.6, 119.9, 119.5, 116.8, 115.1, 108.8, 108.5, 29.4, 21.6; HRMS(ESI) calcd for $\text{C}_{33}\text{H}_{25}\text{N}_2\text{O}_3\text{S} (\text{M}+\text{Na})^+$: 551.1400, Found: 551.1402.



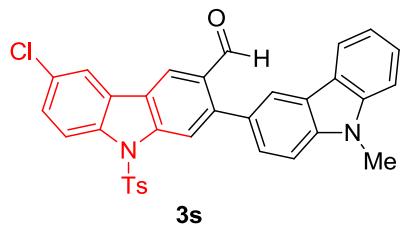
2-(9,9-diethyl-9H-fluoren-3-yl)-9-tosyl-9H-carbazole-3-carbaldehyde (3q):

yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.07 (s, 1H), 8.64 (s, 1H), 8.46 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 6.8 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.77-7.84 (m, 3H), 7.57 (td, J = 7.6, 1.6 Hz, 1H), 7.49 (dd, J = 7.6, 1.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.36-7.42 (m, 4H), 7.18 (d, J = 8.4 Hz, 2H), 2.31 (s, 3H), 2.10 (q, J = 7.2 Hz, 4H), 0.43 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ = 192.0, 150.3, 150.2, 146.0, 145.5, 141.8, 141.3, 140.7, 139.2, 136.6, 134.8, 130.2, 130.0, 129.2, 128.4, 127.7, 127.1, 126.6, 125.7, 125.6, 125.3, 124.6, 123.1, 120.7, 120.1, 120.0, 119.8, 116.4, 115.1, 56.3, 32.8, 21.6, 8.7; HRMS(ESI) calcd for $\text{C}_{37}\text{H}_{32}\text{NO}_3\text{S} (\text{M}+\text{Na})^+$: 592.1917, Found: 570.2093592.1915.

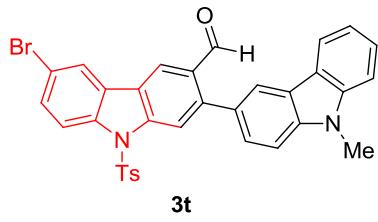


6-fluoro-9'-methyl-9-tosyl-9H,9'H-[2,3'-bicarbazole]-3-carbaldehyde (3r): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.06 (s, 1H), 8.56 (s, 1H), 8.48 (s, 1H), 8.30 (dd, J = 9.2, 4.0 Hz, 1H), 8.15 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 7.2 Hz, 1H), 7.53-7.60 (m, 3H), 7.48 (d, J = 8.0 Hz, 1H), 7.25-7.32 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 3.95 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 192.2, 147.0, 145.6, 142.0, 141.6, 140.9, 135.3, 134.6, 130.5, 129.9, 128.4, 128.1, 127.3, 127.2, 126.6, 126.4, 123.0, 122.5, 122.4, 120.6, 120.2, 119.5, 117.1, 116.4, 116.3, 115.8, 115.5,

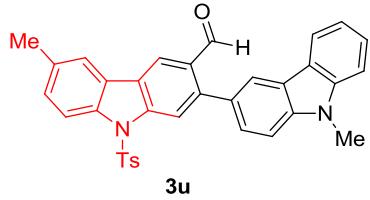
108.8, 108.5, 106.9, 106.7, 29.3, 21.6; HRMS(ESI) calcd for $C_{33}H_{24}FN_2O_3S$ ($M+Na$) $^+$: 569.1306, Found: 569.1303.



6-chloro-9'-methyl-9H,9'H-[2,3'-bicarbazole]-3-carbaldehyde (3s): white solid; 1H NMR (400 MHz, $CDCl_3$) δ = 10.06 (s, 1H), 8.58 (s, 1H), 8.48 (s, 1H), 8.28 (d, J = 8.8 Hz, 1H), 8.16 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.54-7.61 (m, 3H), 7.48-7.52 (m, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 3.96 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.2, 147.1, 145.7, 141.6, 140.9, 137.5, 134.6, 130.7, 130.4, 130.0, 128.4, 128.2, 128.1, 127.3, 126.6, 126.5, 124.3, 123.0, 122.5, 122.4, 120.6, 120.5, 120.2, 119.5, 116.9, 116.2, 108.8, 108.6, 29.3, 21.6; HRMS(ESI) calcd for $C_{33}H_{24}ClN_2O_3S$ ($M+H$) $^+$: 563.1191, Found: 563.1193.

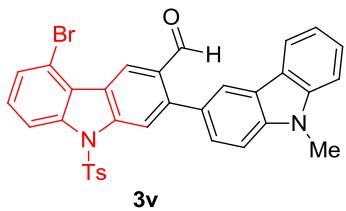


6-bromo-9'-methyl-9H,9'H-[2,3'-bicarbazole]-3-carbaldehyde (3t): white solid; 1H NMR (400 MHz, $CDCl_3$) δ = 10.06 (s, 1H), 8.56 (s, 1H), 8.48 (s, 1H), 8.22 (d, J = 8.8 Hz, 1H), 8.12-8.16 (m, 3H), 7.74 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.54-7.60 (m, 3H), 7.48 (d, J = 8.4 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 3.95 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.2, 147.1, 145.7, 141.6, 141.4, 140.8, 137.9, 134.5, 130.9, 130.6, 130.0, 128.3, 128.1, 127.7, 126.6, 126.5, 124.1, 123.5, 123.0, 122.4, 120.6, 120.2, 119.5, 117.9, 116.9, 116.5, 108.8, 108.6, 29.4, 21.6; HRMS(ESI) calcd for $C_{33}H_{24}BrN_2O_3S$ ($M+H$) $^+$: 607.0686, Found: 607.0689.

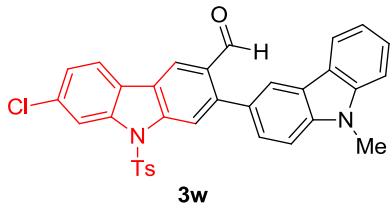


6,9'-dimethyl-9H,9'H-[2,3'-bicarbazole]-3-carbaldehyde (3u): white solid; 1H NMR (400 MHz, $CDCl_3$) δ = 10.07 (s, 1H), 8.59 (s, 1H), 8.48 (s, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 1.2 Hz, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.81 (s, 1H), 7.75 (d, J = 8.8 Hz, 2H), 7.60 (dd, J = 8.4, 1.6 Hz, 1H), 7.53-7.57 (m, 2H), 7.47 (d, J = 8.0 Hz, 1H), 7.36 (dd, J = 8.4, 1.2 Hz, 1H), 7.30 (td, J = 8.0, 1.2 Hz, 1H), 7.15 (d, J = 7.6 Hz, 2H), 3.94 (s, 3H), 2.52 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.5, 146.4, 145.3, 141.6, 141.5, 140.8, 137.3, 134.8, 134.3, 130.4, 129.9, 129.4, 128.6, 128.2, 126.6, 126.4, 125.9, 125.5, 122.9, 122.5, 122.4, 120.7, 120.6, 119.8, 119.4, 116.8, 114.8,

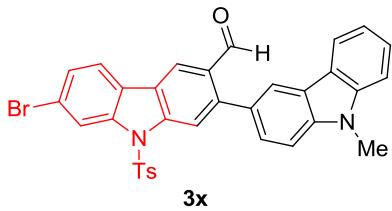
108.8, 108.5, 29.3, 21.6, 21.4; HRMS(ESI) calcd for C₃₄H₂₇N₂O₃S (M+H)⁺: 543.1737, Found: 543.1741.



5-bromo-9'-methyl-9H,9'H-[2,3'-bicarbazole]-3-carbaldehyde (3v): white solid; ¹H NMR (400 MHz, CDCl₃) δ = 10.10 (s, 1H), 9.37 (s, 1H), 8.55 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 1.2 Hz, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.53-7.62 (m, 4H), 7.48 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 3.96 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 192.3, 146.9, 145.8, 141.6, 141.4, 140.9, 140.3, 134.5, 130.3, 130.0, 128.9, 128.4, 128.3, 128.2, 126.6, 126.4, 124.8, 124.5, 123.0, 122.6, 122.5, 122.4, 120.6, 119.5, 116.9, 116.5, 113.9, 108.8, 108.6, 29.4, 21.6; HRMS(ESI) calcd for C₃₃H₂₄BrN₂O₃S (M+H)⁺: 607.0686, Found: 607.0689.

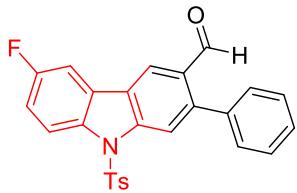


7-chloro-9'-methyl-9H,9'H-[2,3'-bicarbazole]-3-carbaldehyde (3w): white solid; ¹H NMR (400 MHz, CDCl₃) δ = 10.06 (s, 1H), 8.59 (s, 1H), 8.46 (s, 1H), 8.38 (d, J = 1.6 Hz, 1H), 8.16 (d, J = 6.8 Hz, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.54-7.60 (m, 3H), 7.49 (d, J = 8.0 Hz, 1H), 7.42 (dd, J = 8.0, 1.6 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 3.96 (s, 3H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 192.4, 146.7, 145.8, 141.6, 141.3, 140.8, 140.1, 139.6, 134.6, 134.0, 130.6, 130.1, 128.3, 128.1, 126.7, 126.5, 125.1, 124.6, 124.3, 123.0, 122.4, 121.3, 120.6, 119.9, 119.5, 116.8, 115.4, 108.8, 108.6, 29.4, 21.7; HRMS(ESI) calcd for C₃₃H₂₄ClN₂O₃S (M+H)⁺: 563.1191, Found: 563.1193.



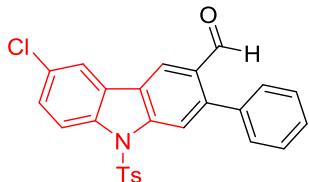
7-bromo-9'-methyl-9H,9'H-[2,3'-bicarbazole]-3-carbaldehyde (3x): white solid; ¹H NMR (400 MHz, CDCl₃) δ = 10.06 (s, 1H), 8.59 (s, 1H), 8.54 (d, J = 1.6 Hz, 1H), 8.46 (s, 1H), 8.15 (d, J = 6.8 Hz, 2H), 7.89 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.54-7.60 (m, 4H), 7.49 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 3.96 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 192.3, 146.8, 145.8, 141.6, 141.2, 140.9, 139.9, 134.6, 130.7, 130.1, 128.4, 128.1, 127.8, 126.6, 126.5,

124.7, 124.6, 123.0, 122.4, 122.3, 121.8, 121.6, 120.6, 119.9, 119.5, 118.2, 116.8, 108.8, 108.5, 29.3, 21.6; HRMS(ESI) calcd for $C_{33}H_{24}BrN_2O_3S$ ($M+H$) $^+$: 629.0505, Found: 629.0500.



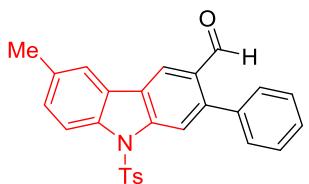
3y

6-fluoro-2-phenyl-9-tosyl-9H-carbazole-3-carbaldehyde (3y): white solid; 1H NMR (400 MHz, $CDCl_3$) δ = 10.03 (s, 1H), 8.55 (s, 1H), 8.39 (s, 1H), 8.31 (dd, J = 9.2, 4.4 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.63 (dd, J = 8.0, 2.4 Hz, 1H), 7.54-7.60 (m, 3H), 7.49-7.52 (m, 2H), 7.28 (td, J = 9.2, 2.4 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.7, 161.3, 158.9, 145.9, 145.7, 141.9, 137.8, 135.3, 135.2, 134.5, 130.4, 130.1, 130.0, 128.6, 128.5, 128.4, 127.0, 126.9, 126.5, 125.3, 125.2, 120.3, 116.7, 116.4, 116.3, 116.0, 115.8, 107.0, 106.7, 21.6; HRMS(ESI) calcd for $C_{26}H_{19}FNO_3S$ ($M+H$) $^+$: 444.1064, Found: 444.1060.



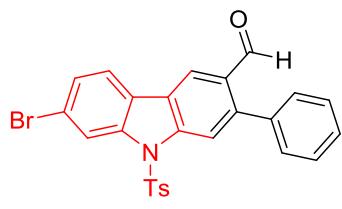
3z

6-chloro-2-phenyl-9-tosyl-9H-carbazole-3-carbaldehyde (3z): white solid; 1H NMR (400 MHz, $CDCl_3$) δ = 10.00 (s, 1H), 8.53 (s, 1H), 8.36 (s, 1H), 8.26 (d, J = 9.2 Hz, 1H), 7.93 (d, J = 2.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.51-7.57 (m, 3H), 7.47-7.52 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.6, 146.0, 145.8, 141.6, 137.8, 137.5, 134.5, 130.4, 130.3, 130.2, 130.0, 128.6, 128.5, 128.4, 127.0, 126.6, 124.8, 120.5, 120.2, 116.6, 116.2, 21.6; HRMS(ESI) calcd for $C_{26}H_{19}ClNO_3S$ ($M+H$) $^+$: 460.0769, Found: 460.0767.



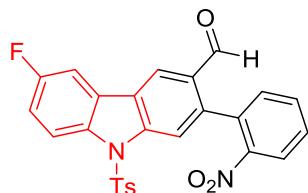
3aa

6-methyl-2-phenyl-9-tosyl-9H-carbazole-3-carbaldehyde (3aa): white solid; 1H NMR (400 MHz, $CDCl_3$) δ = 10.01 (s, 1H), 8.56 (s, 1H), 8.36 (s, 1H), 8.20 (d, J = 8.8 Hz, 1H), 7.78 (s, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.48-7.57 (m, 5H), 7.36 (dd, J = 8.8, 1.6 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 2.50 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.9, 145.4, 145.3, 141.5, 138.1, 137.3, 134.8, 134.4, 130.5, 130.0, 129.9, 129.6, 128.5, 128.3, 126.5, 125.9, 125.7, 120.7, 119.8, 116.4, 114.8, 21.6, 21.3; HRMS(ESI) calcd for $C_{27}H_{22}NO_3S$ ($M+H$) $^+$: 440.1315, Found: 440.1324.



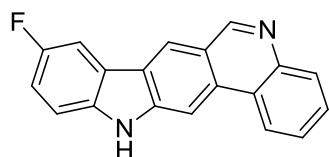
3ab

7-bromo-2-phenyl-9-tosyl-9H-carbazole-3-carbaldehyde (3ab): white solid; ^1H NMR (400 MHz, CDCl_3) δ = 10.00 (s, 1H), 8.55 (s, 1H), 8.51 (d, J = 1.6 Hz, 1H), 8.34 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.51-7.57 (m, 4H), 7.46-7.50 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 191.7, 145.9, 145.7, 141.1, 139.8, 137.8, 134.5, 130.4, 130.3, 130.1, 128.6, 128.5, 127.9, 126.6, 125.0, 124.5, 122.0, 121.7, 120.0, 118.2, 116.4, 21.7; HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{19}\text{BrNO}_3\text{S} (\text{M}+\text{H})^+$: 504.0264, Found: 504.0262.



3ac

6-fluoro-2-(2-nitrophenyl)-9-tosyl-9H-carbazole-3-carbaldehyde (3ac): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ = 9.88 (s, 1H), 8.49 (s, 1H), 8.31 (dd, J = 9.2, 4.0 Hz, 1H), 8.24 (s, 1H), 8.17 (dd, J = 8.0, 1.2 Hz, 1H), 7.75 (td, J = 7.6, 1.2 Hz, 1H), 7.69 (td, J = 8.0, 1.6 Hz, 1H), 7.63-7.65 (m, 3H), 7.47 (dd, J = 7.2, 1.2 Hz, 1H), 7.27-7.31 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 190.0, 161.4, 159.0, 149.1, 145.9, 141.7, 140.2, 135.3, 133.9, 133.7, 132.9, 132.7, 130.1, 130.0, 129.6, 126.9, 126.8, 126.5, 126.2, 124.6, 122.3, 116.7, 116.6, 116.4, 116.1, 107.0, 106.8, 21.6; HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{18}\text{FN}_2\text{O}_5\text{S} (\text{M}+\text{H})^+$: 489.0915, Found: 489.0910.



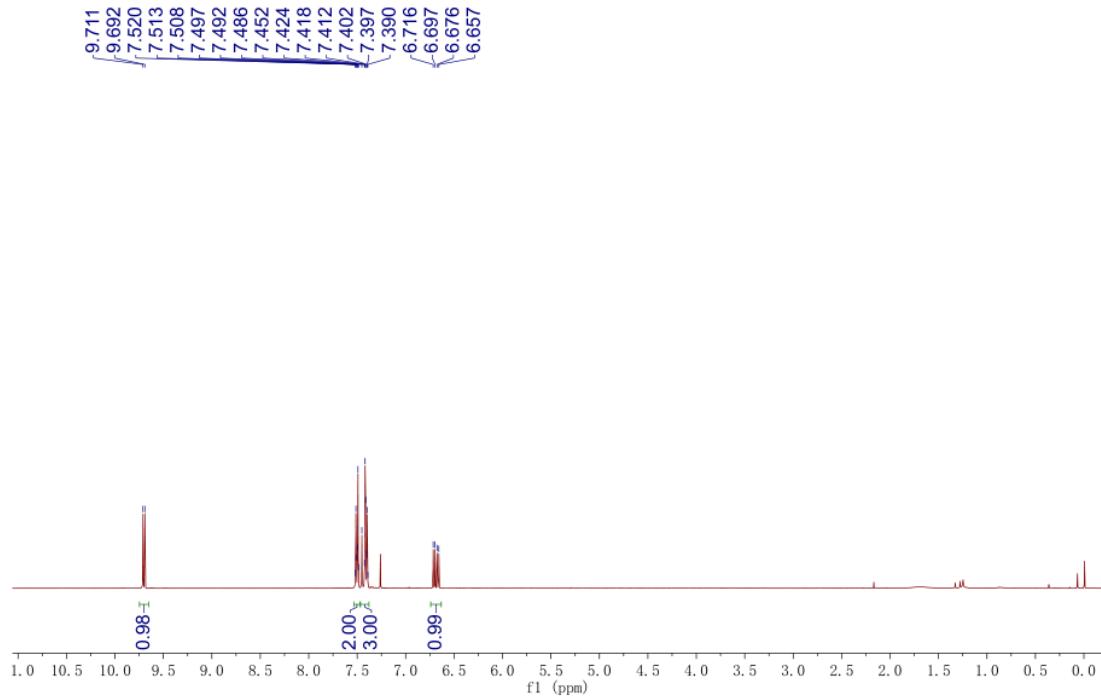
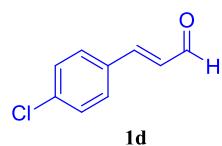
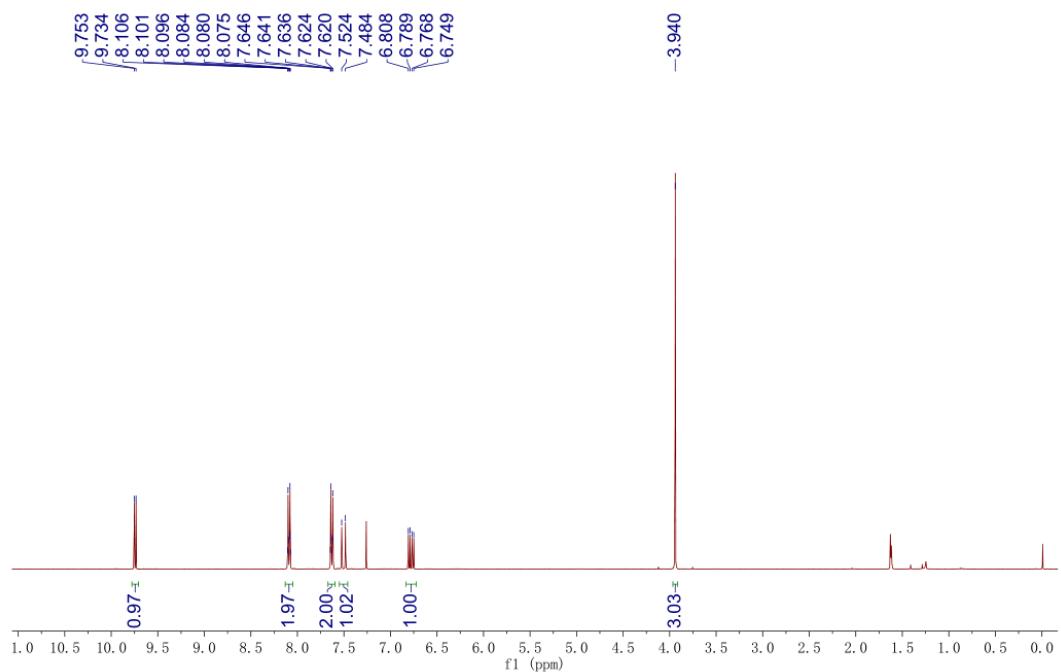
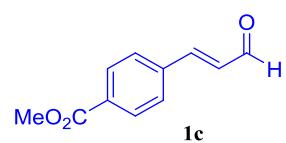
4b

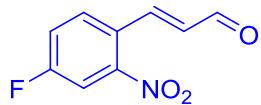
9-fluoro-12-tosyl-12H-indolo[3,2-j]phenanthridine (4b): brown solid; ^1H NMR (400 MHz, DMSO-d_6) δ = 11.83 (s, 1H), 9.39 (s, 1H), 9.02 (s, 1H), 8.84 (dd, J = 8.0, 1.2 Hz, 1H), 8.73 (s, 1H), 8.20 (dd, J = 9.2, 2.8 Hz, 1H), 8.08 (dd, J = 8.0, 1.6 Hz, 1H), 7.70-7.78 (m, 2H), 7.63 (q, J = 8.8, 4.4 Hz, 1H), 7.41 (td, J = 9.2, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 154.7, 144.1, 143.6, 138.8, 131.0, 129.9, 128.8, 127.0, 124.7, 124.5, 123.4, 123.2, 123.1, 122.1, 120.5, 115.6, 115.4, 112.7, 112.6, 107.6, 107.3, 102.1; HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{12}\text{FN}_2 (\text{M}+\text{H})^+$: 287.0979, Found: 287.0975.

b) References

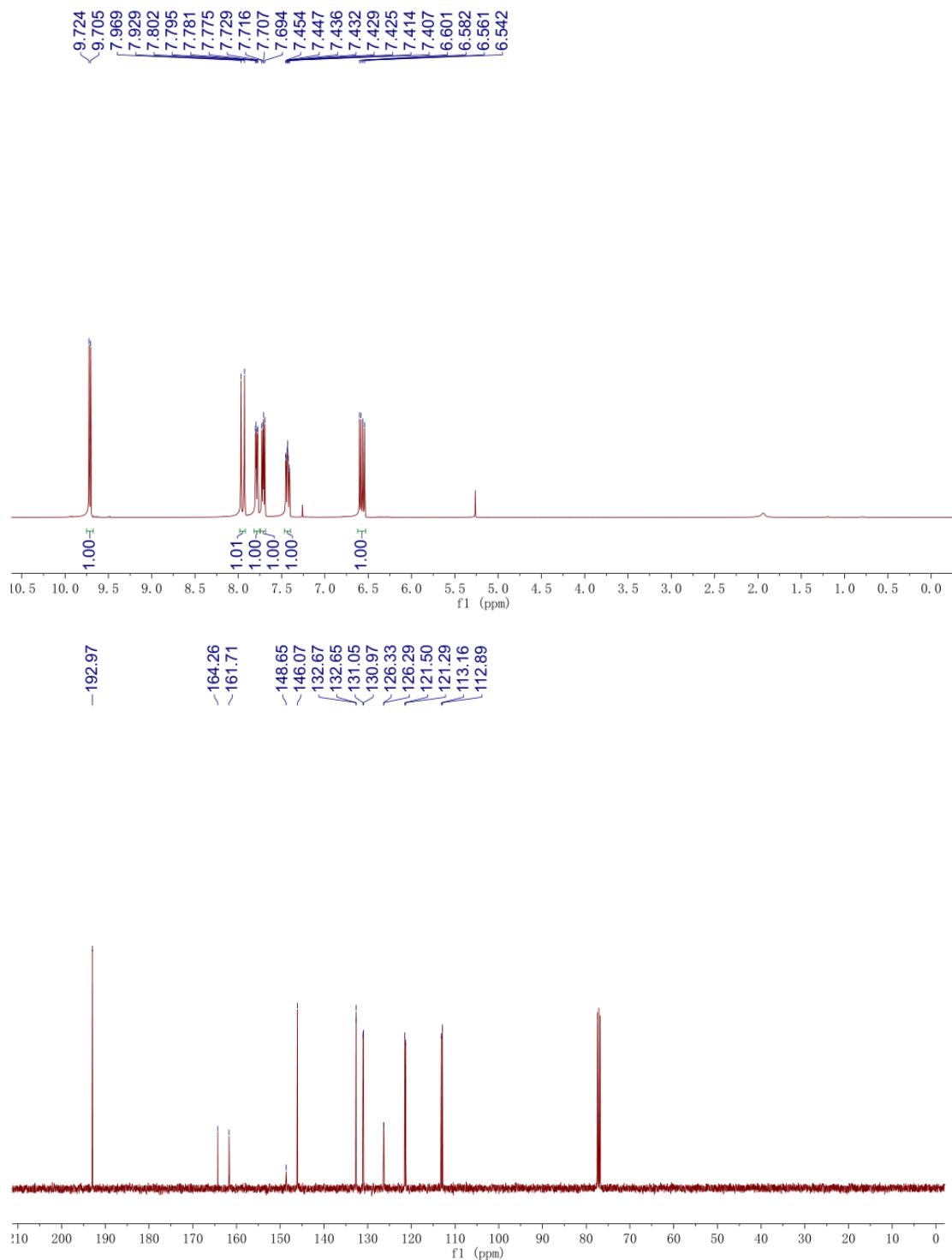
- [1] Meazza, M.; Light, M. E.; Mazzanti, A.; Rios, R. *Chem. Sci.* **2016**, *7*, 984-988.
- [2] Joshi, P. R.; Nanubolu, J. B.; Menon, R. S. *Org. Lett.* **2016**, *18*, 752-755.
- [3] Rodrigo, E.; Garcia Ruano, J. L.; Cid, M. B. *J. Org. Chem.* **2013**, *78*, 10737-10746.
- [4] Robinson, M. W.; Overmeyer, J. H.; Young, A. M.; Erhardt, P. W. *J. Med. Chem.* **2012**, *55*, 1940-1956.
- [5] Gu, W.; Hao, Y.; Zhang, G.; Wang, S.-F.; Miao, T.-T. *Bioorg. Med. Chem. Lett.* **2015**, *25*, 554-557.
- [6] Bhunia, S. K.; Polley, A.; Natarajan, R.; Jana, R. *Chem. Eur. J.* **2015**, *21*, 16786-16791.
- [7] Song, X.; Xu, C.; Du, D.; Zhao, Z.; Zhu, D.; Wang, M. *Org. Lett.* **2017**, *19*, 6542-6545.
- [8] Colley, H. E.; Muthana, M.; Danson, S. J.; Jackson, L. V.; Brett, M. L.; Harrison, J.; Coole, S. F.; Mason, D. P.; Jennings, L. R.; Wong, M.; Tulasi, V.; Norman, D.; Lockey, P. M.; Williams, L.; Dossetter, A. G.; Griffen, E. J.; Thompson, M. J. *J. Med. Chem.* **2015**, *58*, 9309-9333.
- [9] Han, L.; Liu, C.; Zhang, W.; Shi, X.-X.; You, S.-L. *Chem. Commun.* **2014**, *50*, 1231-1233.
- [10] Deng, Z.; Wei, J.; Liao, L.; Huang, H.; Zhao, X. *Org. Lett.* **2015**, *17*, 1834-1837.
- [11] Huang, H.; Yu, C.; Li, X.; Zhang, Y.; Zhang, Y.; Chen, X.; Mariano, P. S.; Xie, H.; Wang, W. *Angew. Chem., Int. Ed.* **2017**, *56*, 8201-8205.
- [12] Avery, T. D.; Caiazza, D.; Culbert, J. A.; Taylor, D. K.; Tiekkink, E. R. T. *J. Org. Chem.* **2005**, *70*, 8344-8351.
- [13] Liu, J.; Zhu, J.; Jiang, H.; Wang, W.; Li, J. *Chem. Commun.* **2010**, *46*, 415-417.
- [14] Kolehmainen, E.; Laihia, K.; Manttari, P. *Magn. Reson. Chem.* **1991**, *29*, 1109-1113.
- [15] W. Debrouwer, D. Hertsen, T. S. A. Heugebaert, E. B. Boydas, V. V. Speybroeck, S. Catak, C.V. Stevens, *J. Org. Chem.*, **2017**, *82*, 188-201.
- [16] Marcin, L. R.; Denhart, D. J.; Mattson, R. J. *Org. Lett.* **2005**, *7*, 2651-2654.
- [17] Vangveravong, S.; Kanthasamy, A.; Lucaites, V. L.; Nelson, D. L.; Nichols, D. E. *J. Med. Chem.* **1998**, *41*, 4995-5001.
- [18] Ramalingam, B. M.; Moorthy, N. D.; Chowdhury, S. R.; Mageshwaran, T.; Vellaichamy, E.; Saha, S.; Ganesan, K.; Rajesh, B. N.; Iqbal, S.; Majumder, H. K.; Gunasekaran, K.; Siva, R.; Mohanakrishnan, A. K.,. *J. Med. Chem.* **2018**, *61*, 1285-1315.
- [19] Y. Wada, H. Nagasaki, M. Tokuda, K. Orito, *J. Org. Chem.* **2007**, *72*, 2008.

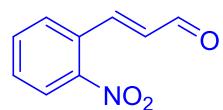
III: ^1H and ^{13}C NMR spectra of the products



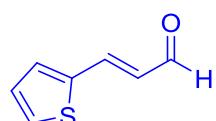
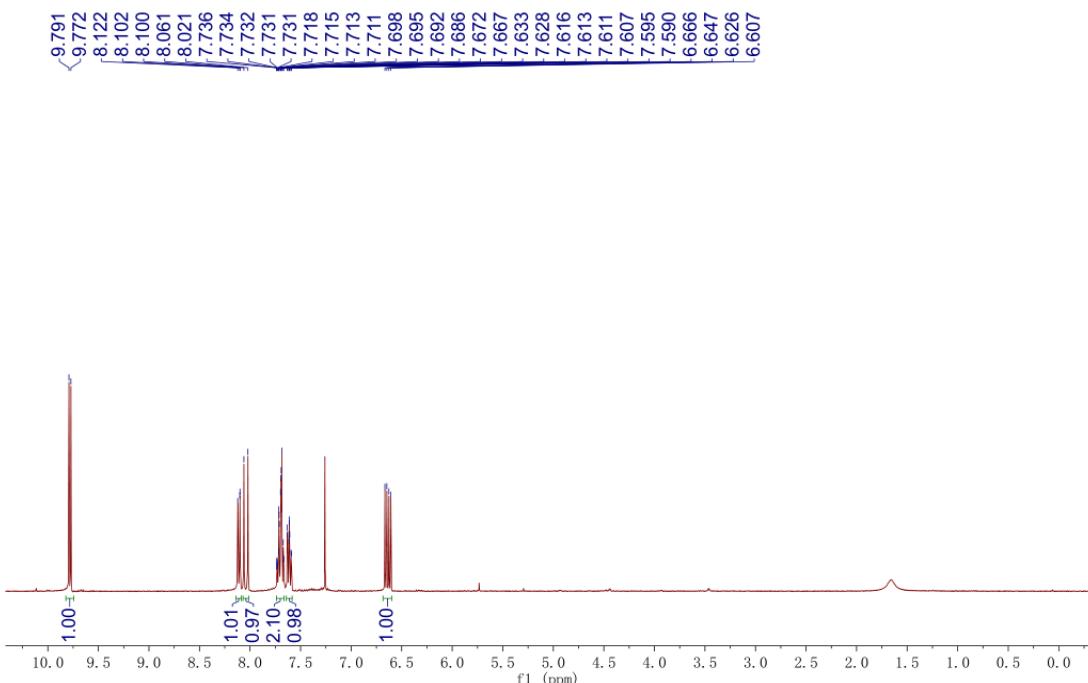


1g

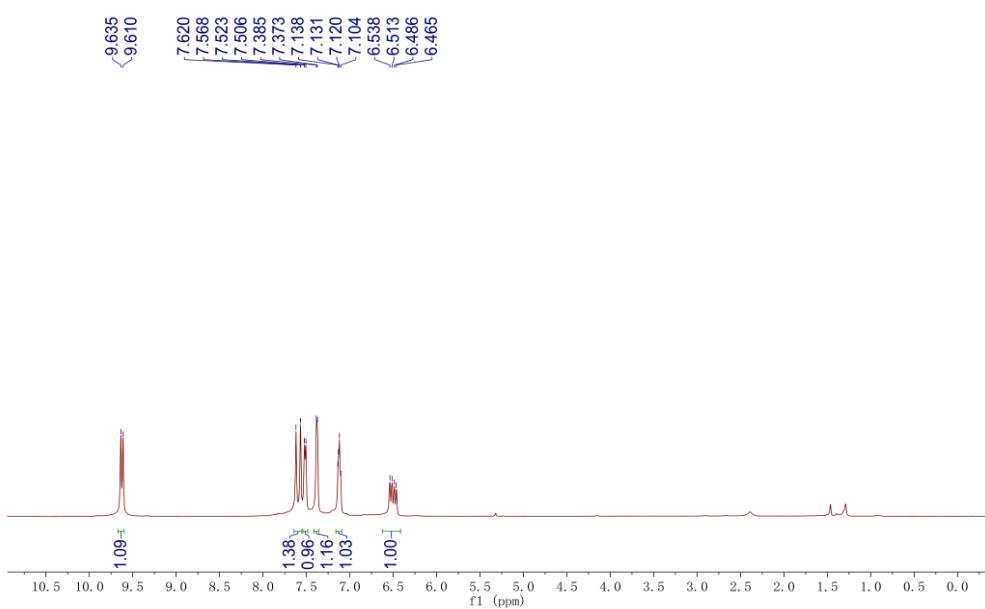


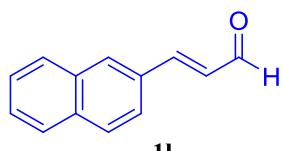


1h

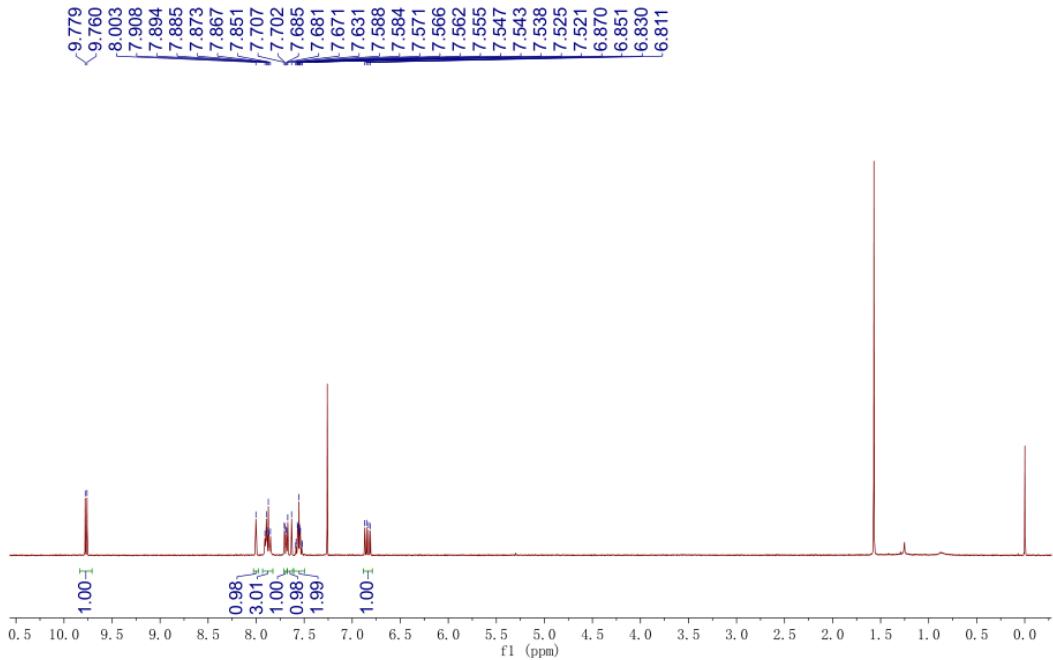


1i

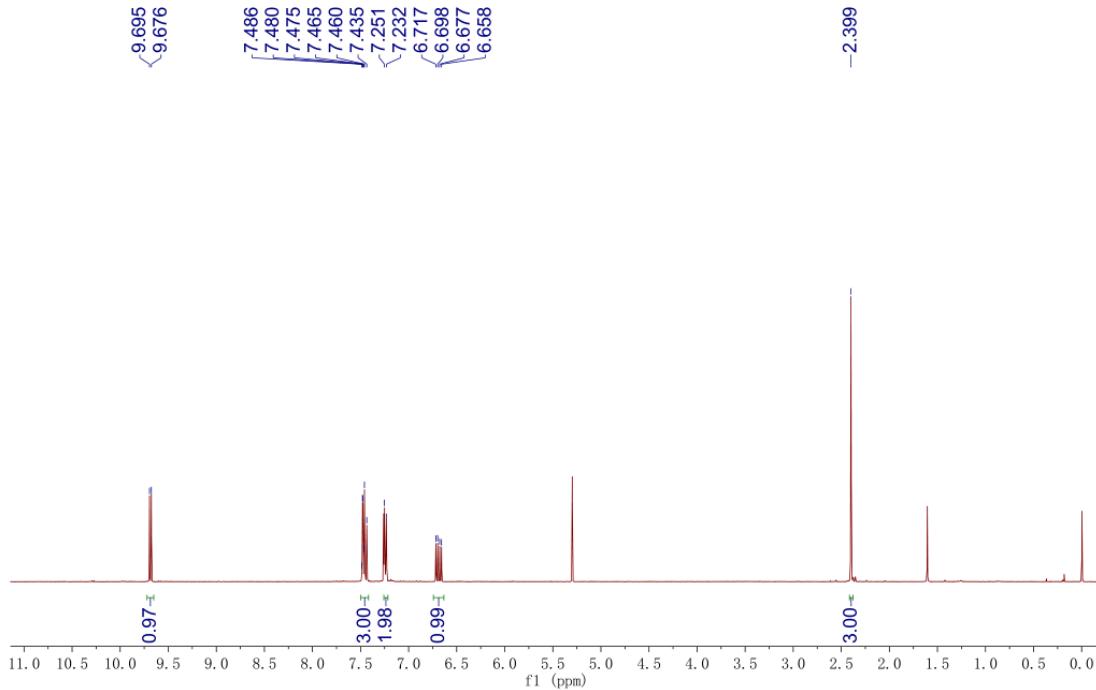


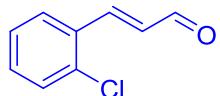


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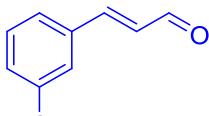
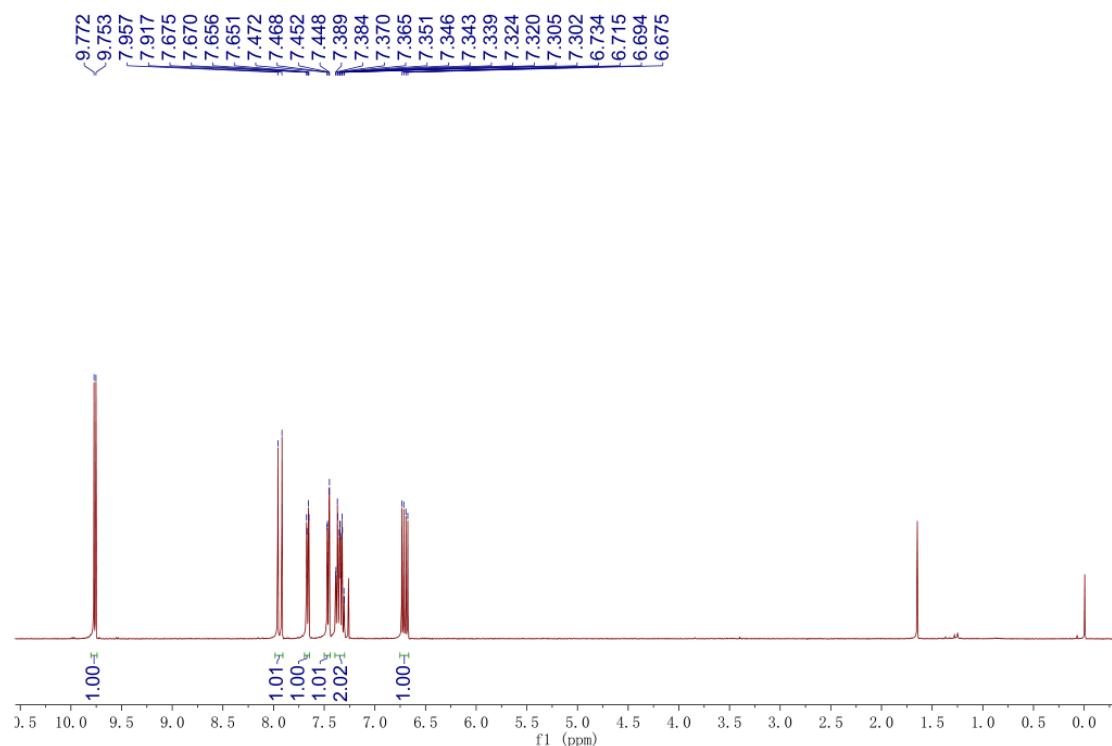


1m

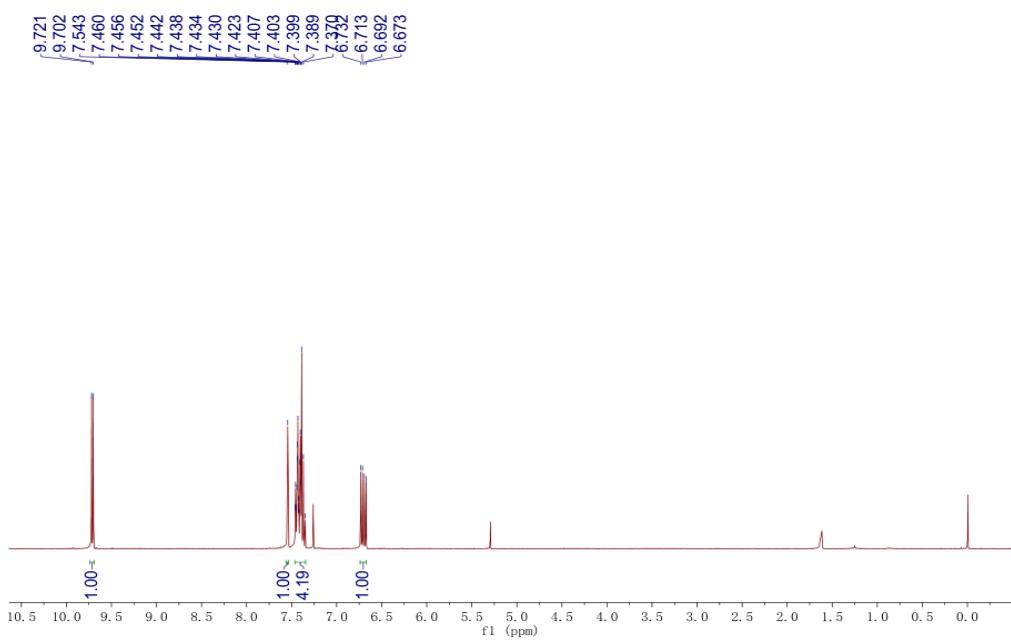


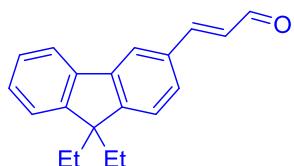


1n

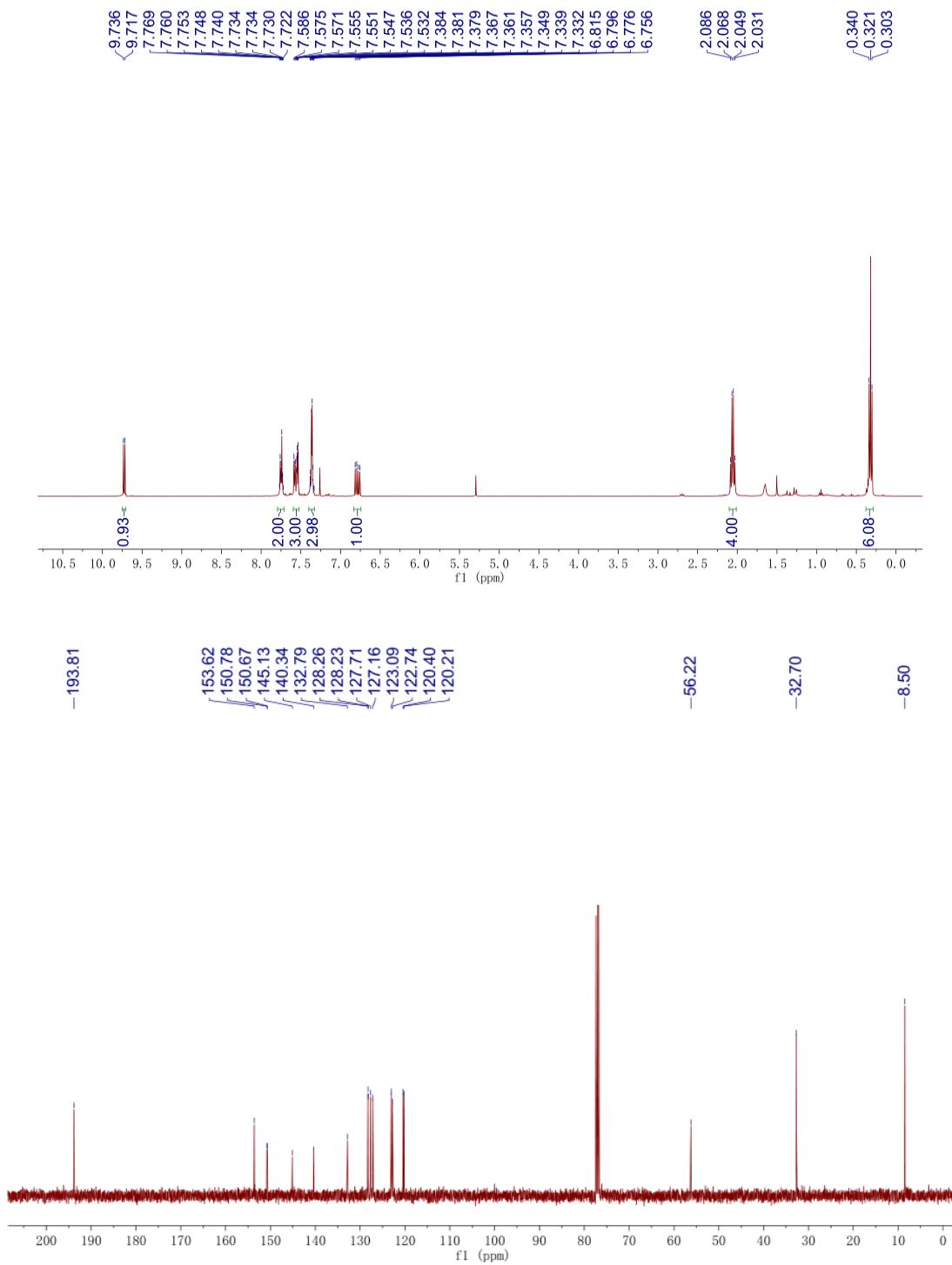


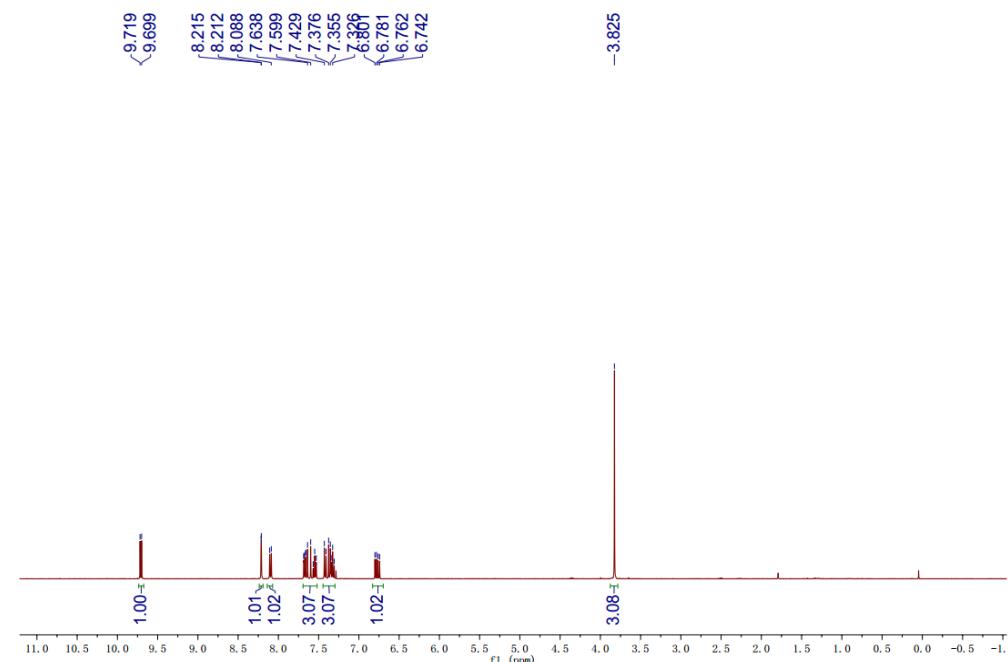
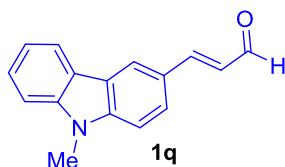
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1p



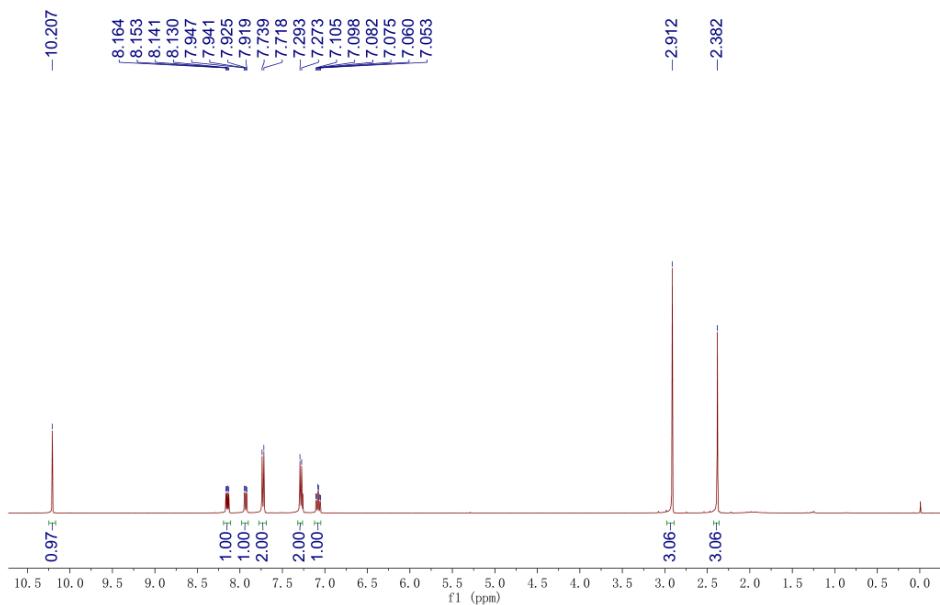


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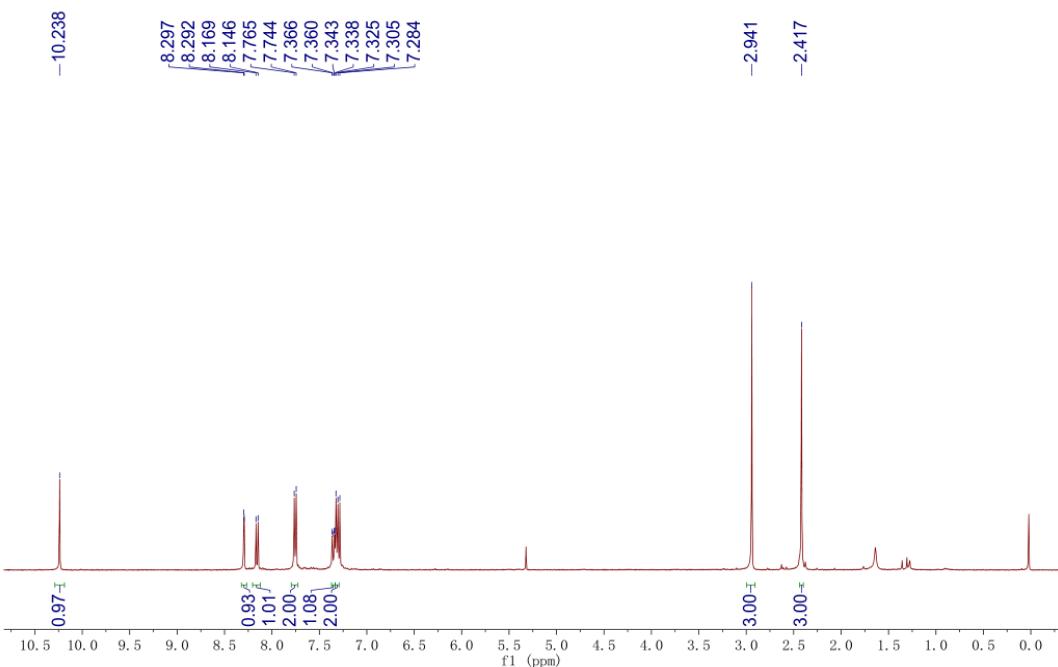


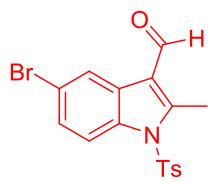


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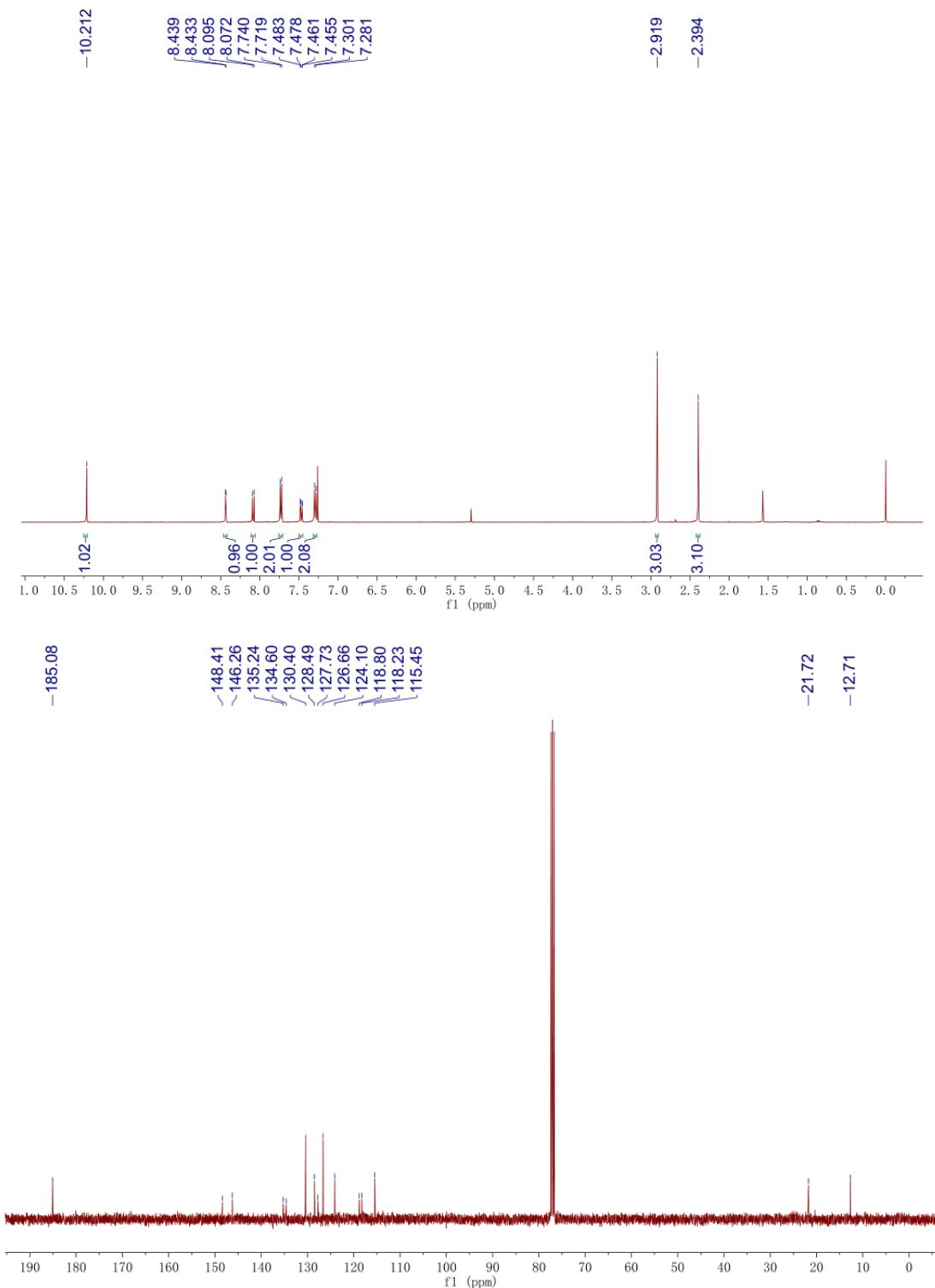


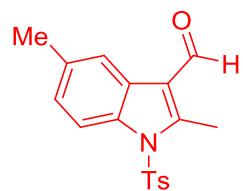
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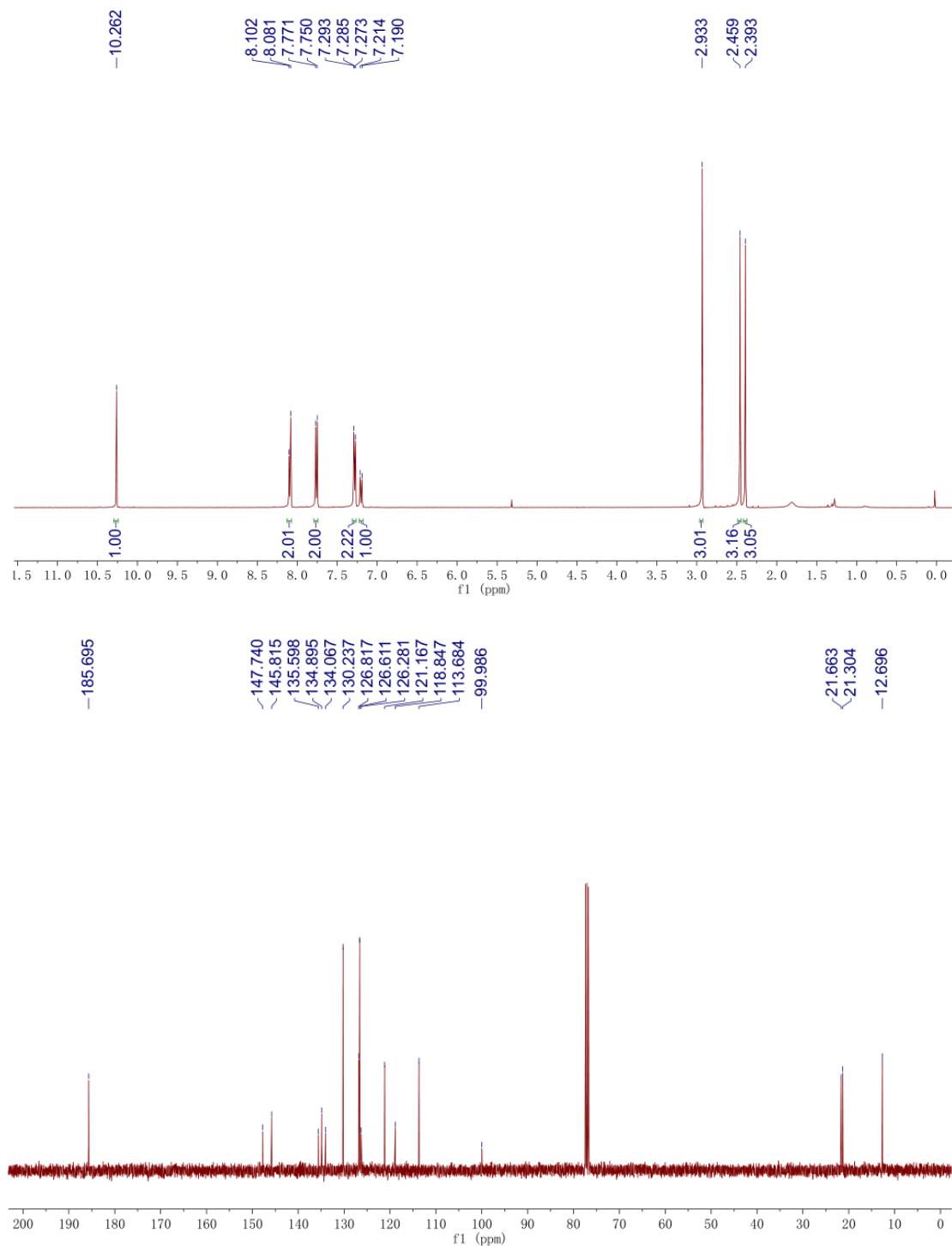


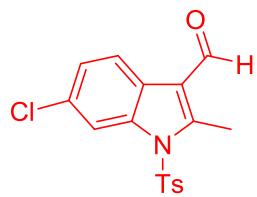
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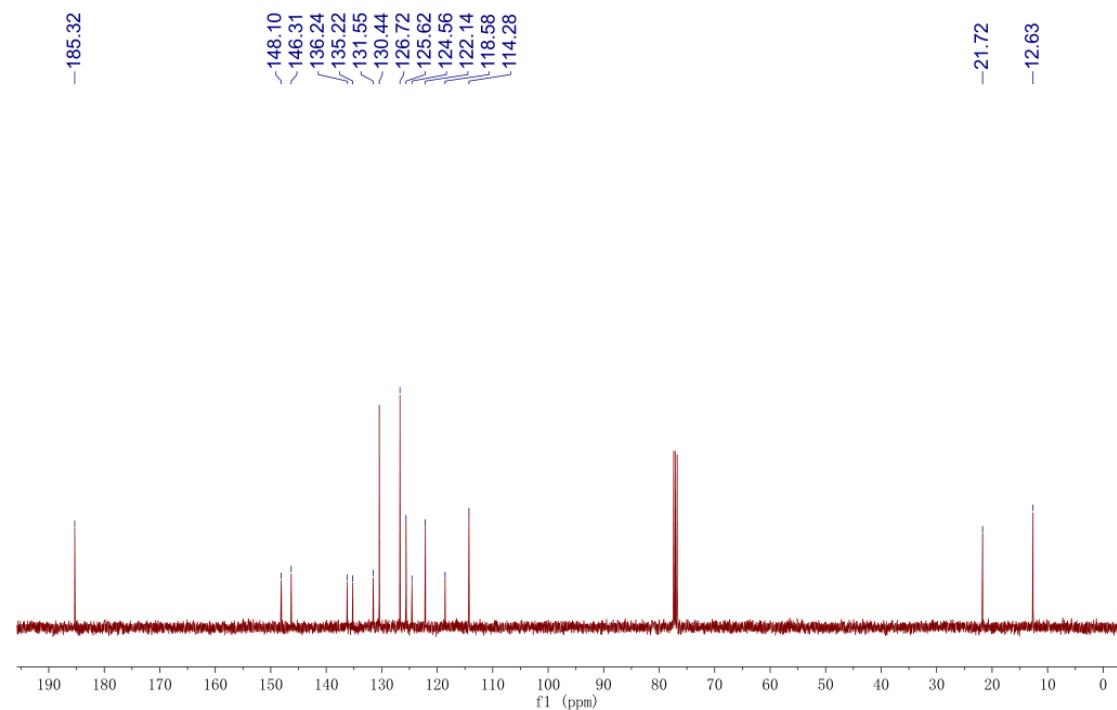
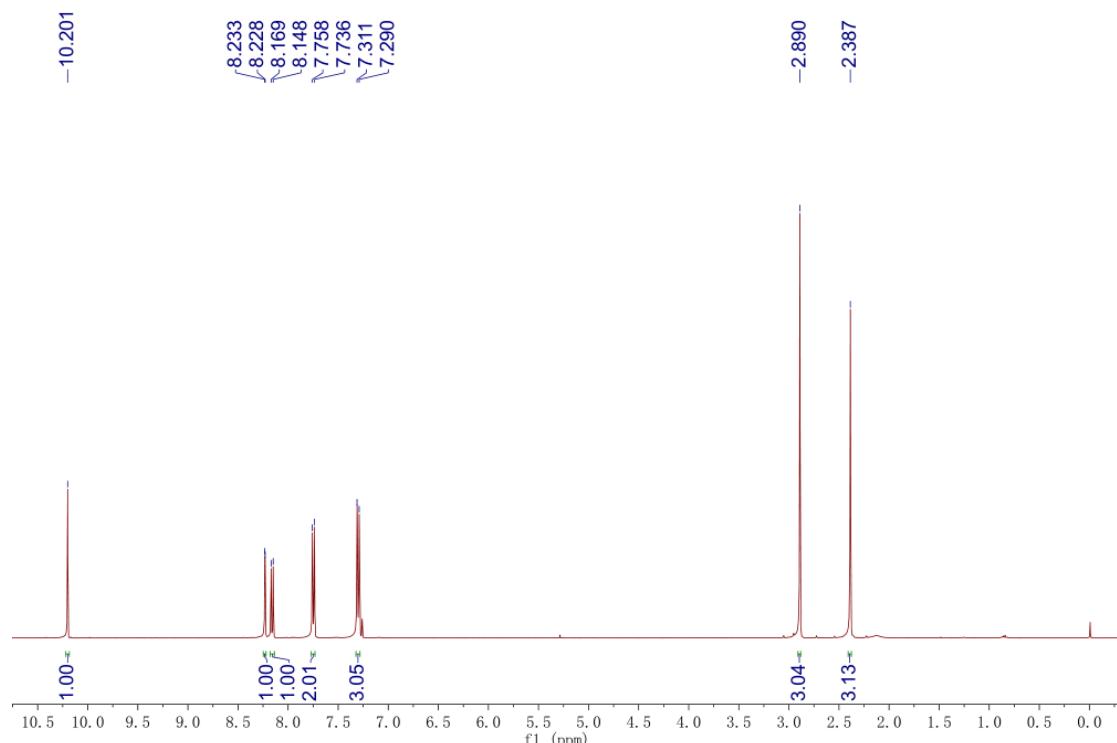


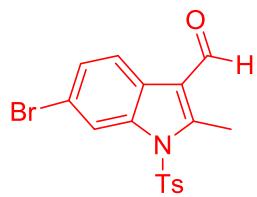
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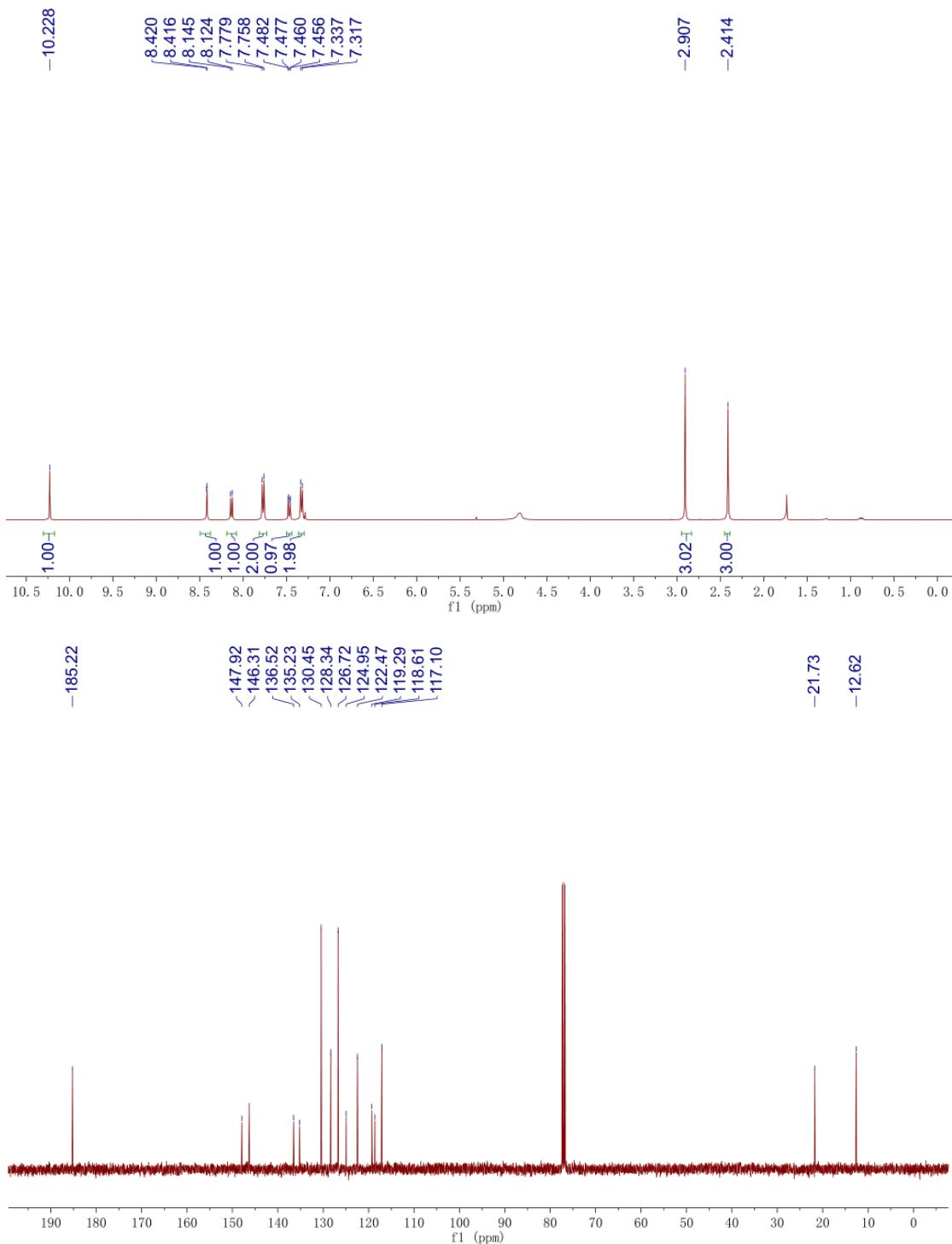


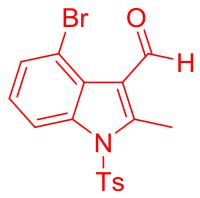
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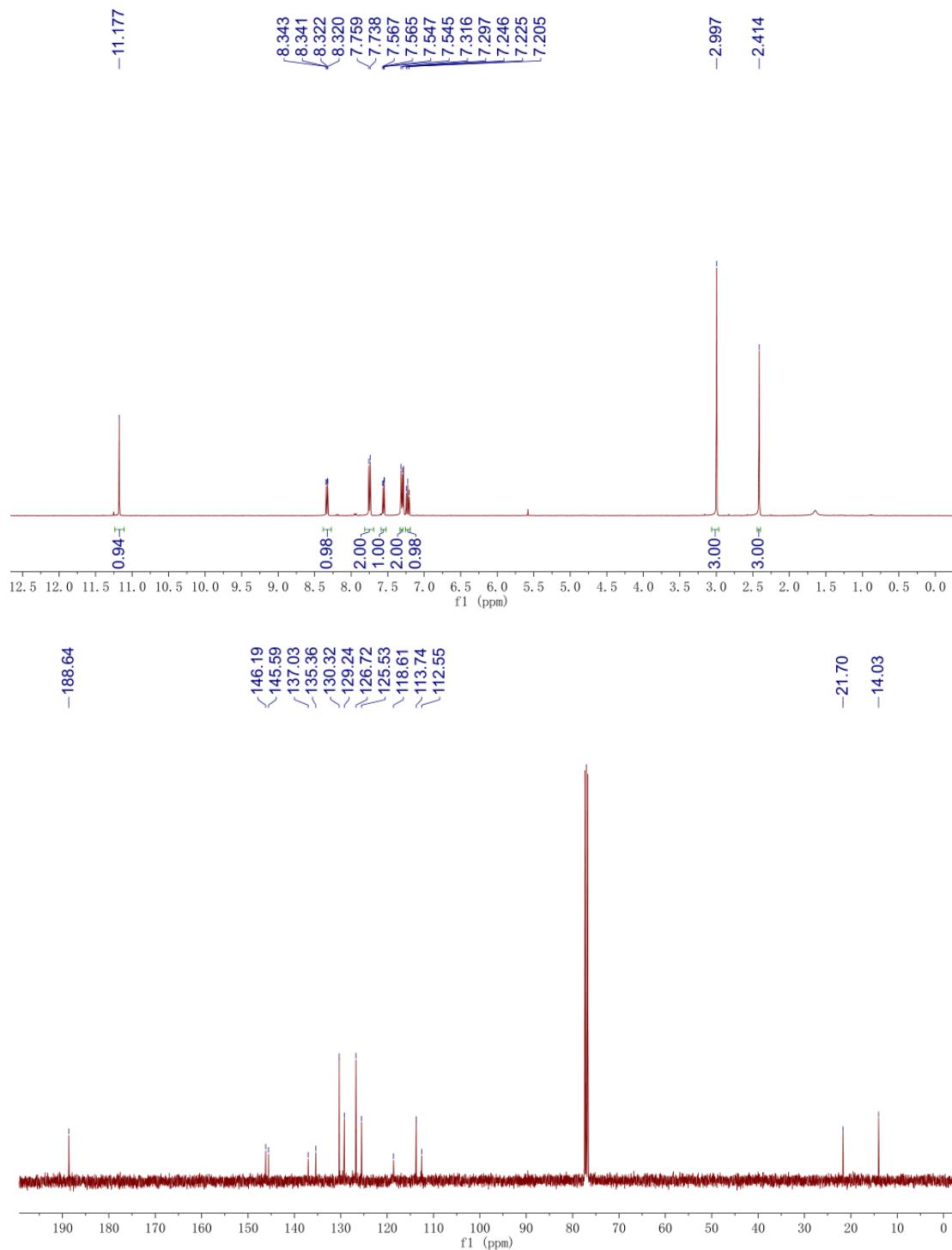


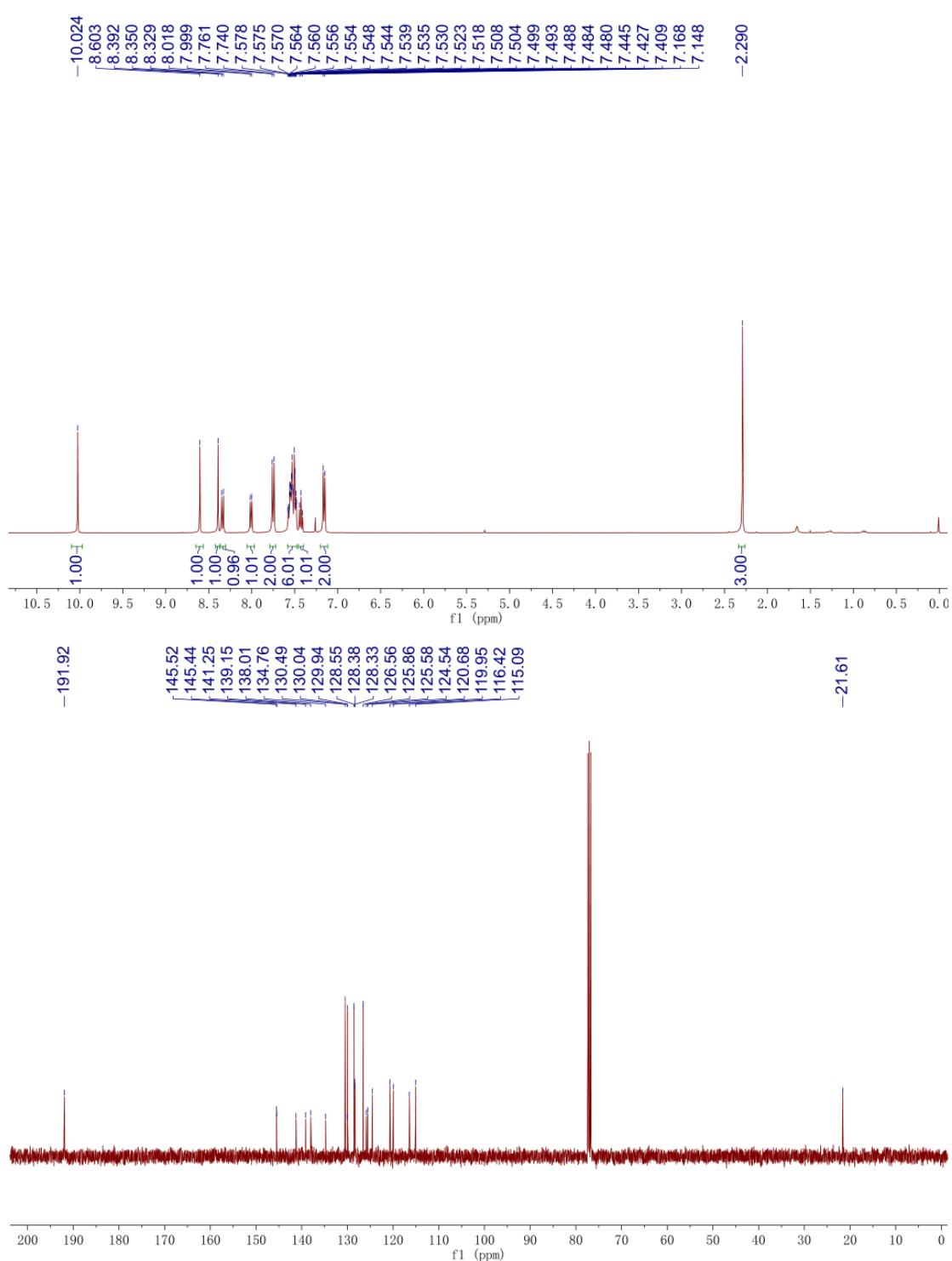
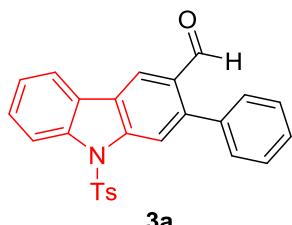
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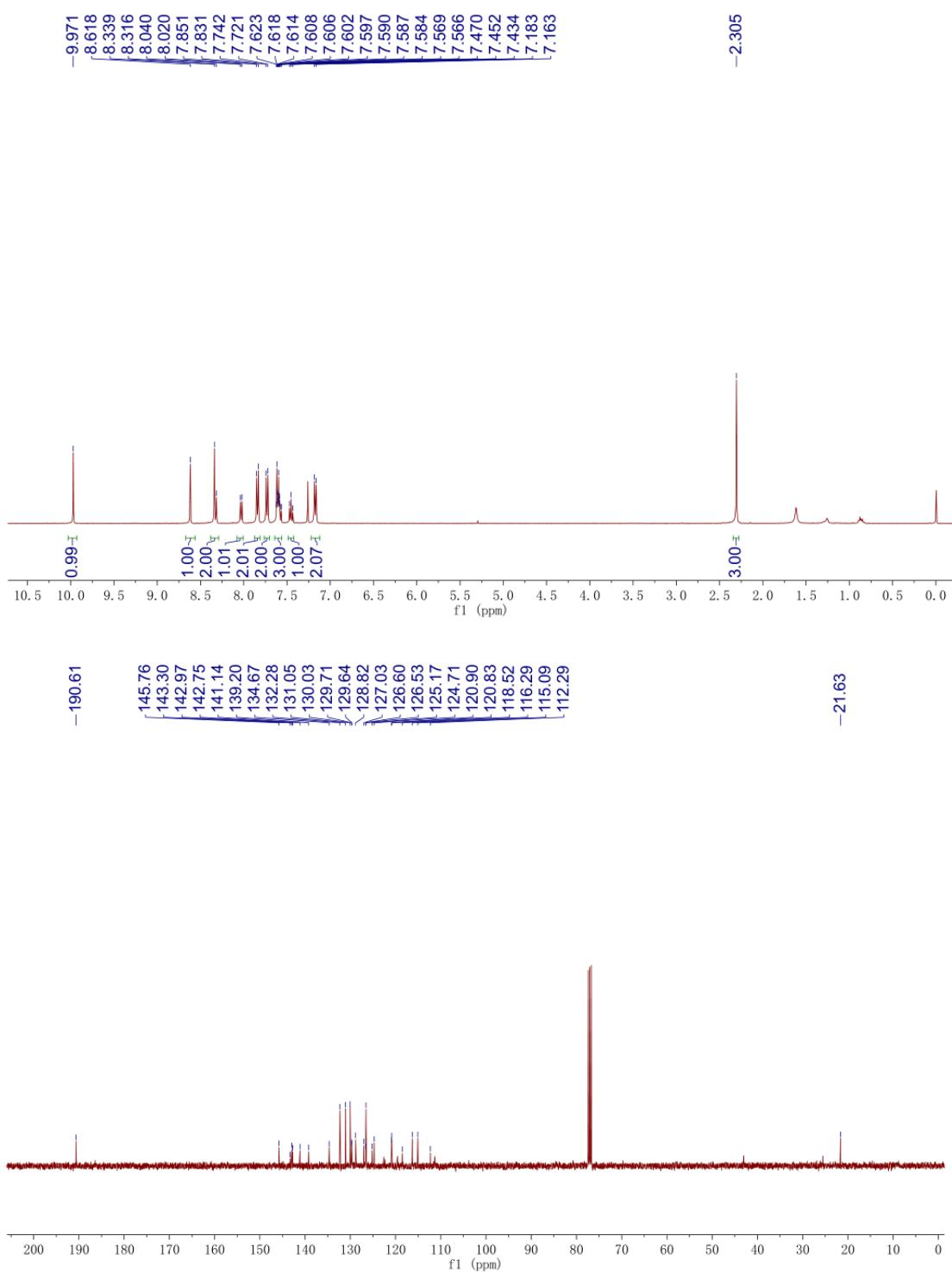
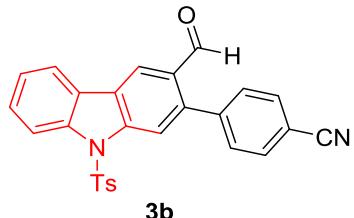


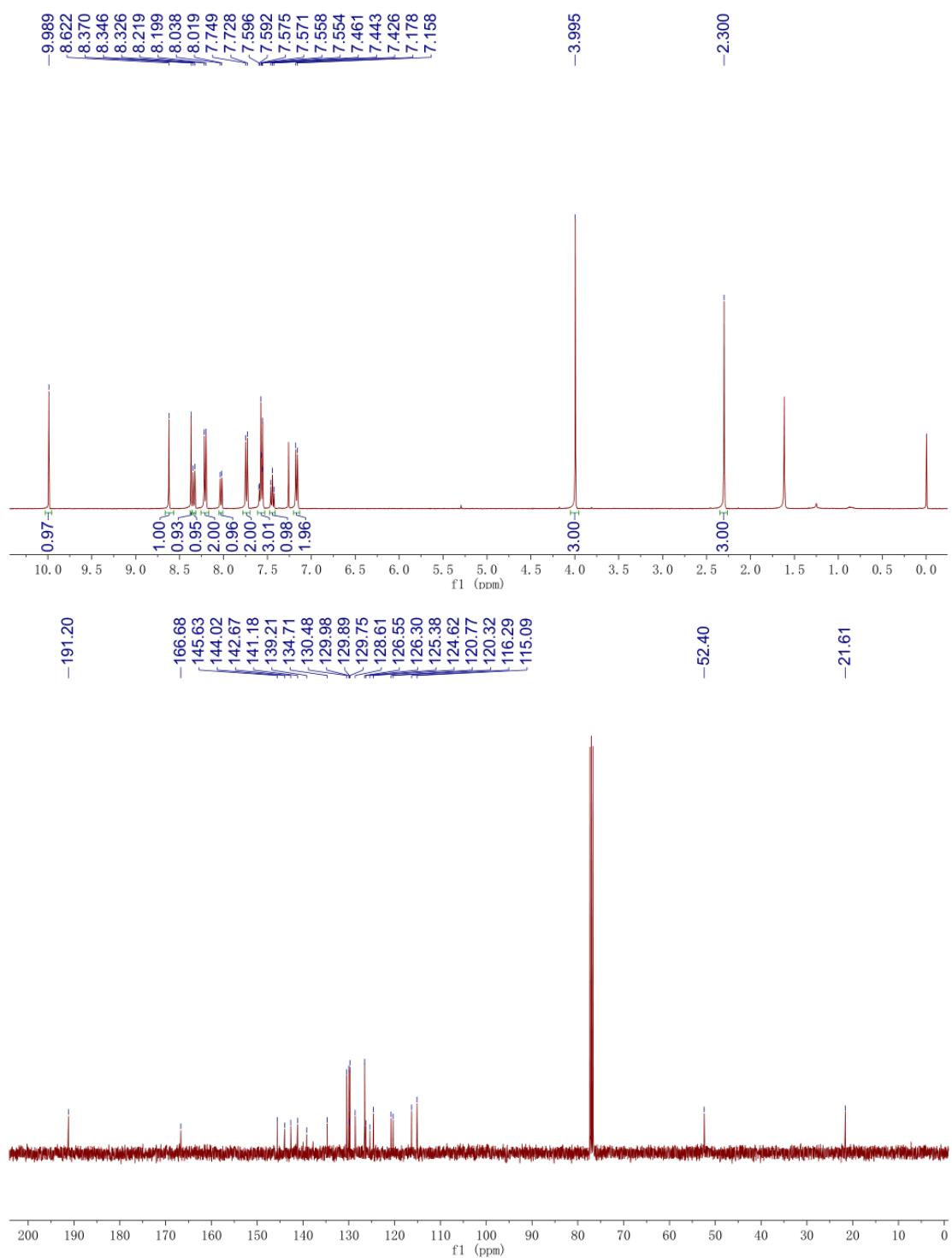
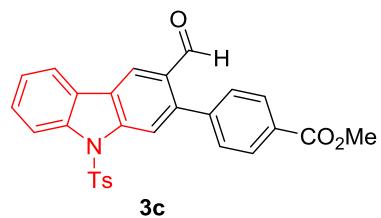


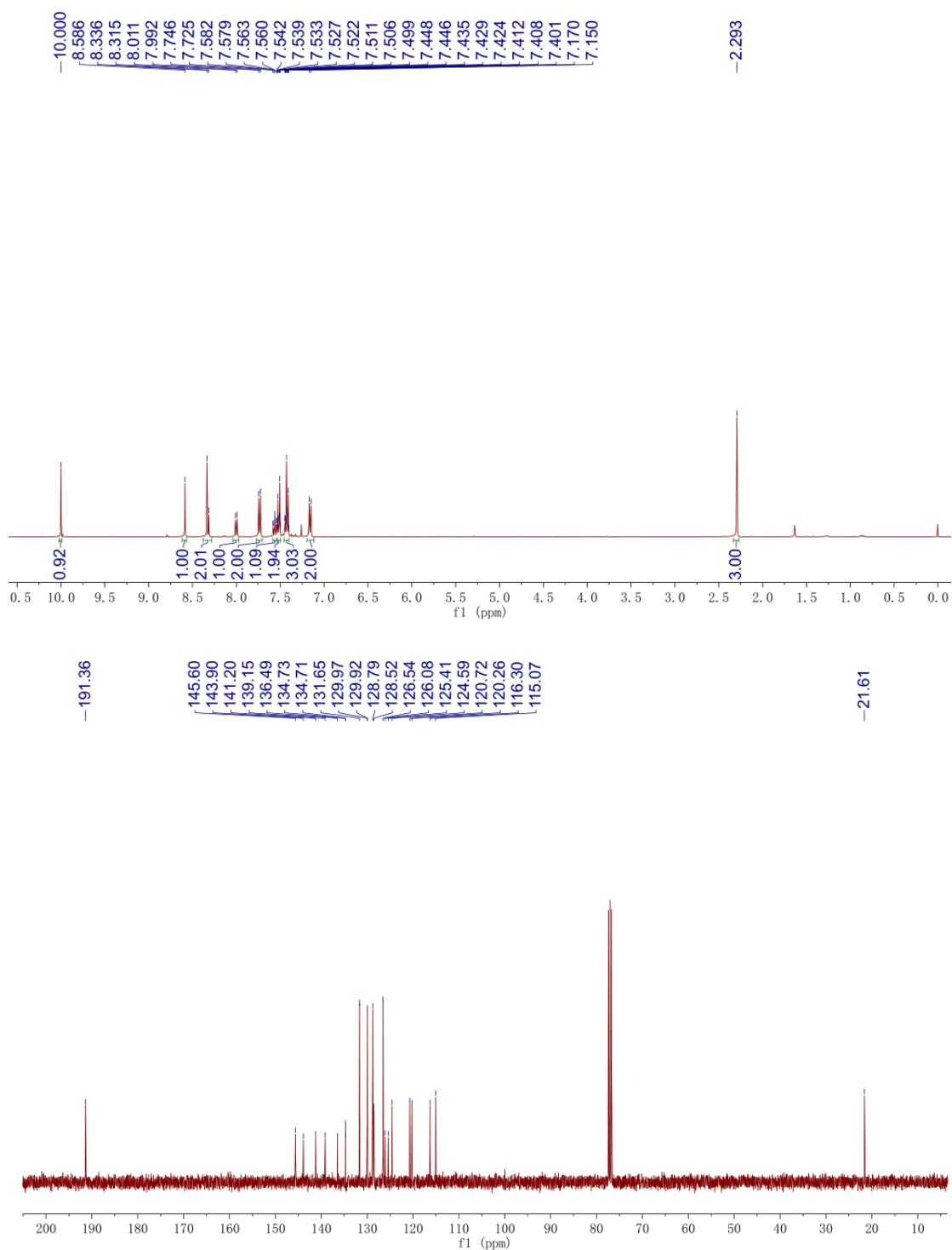
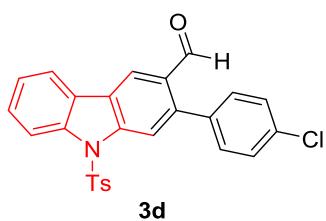
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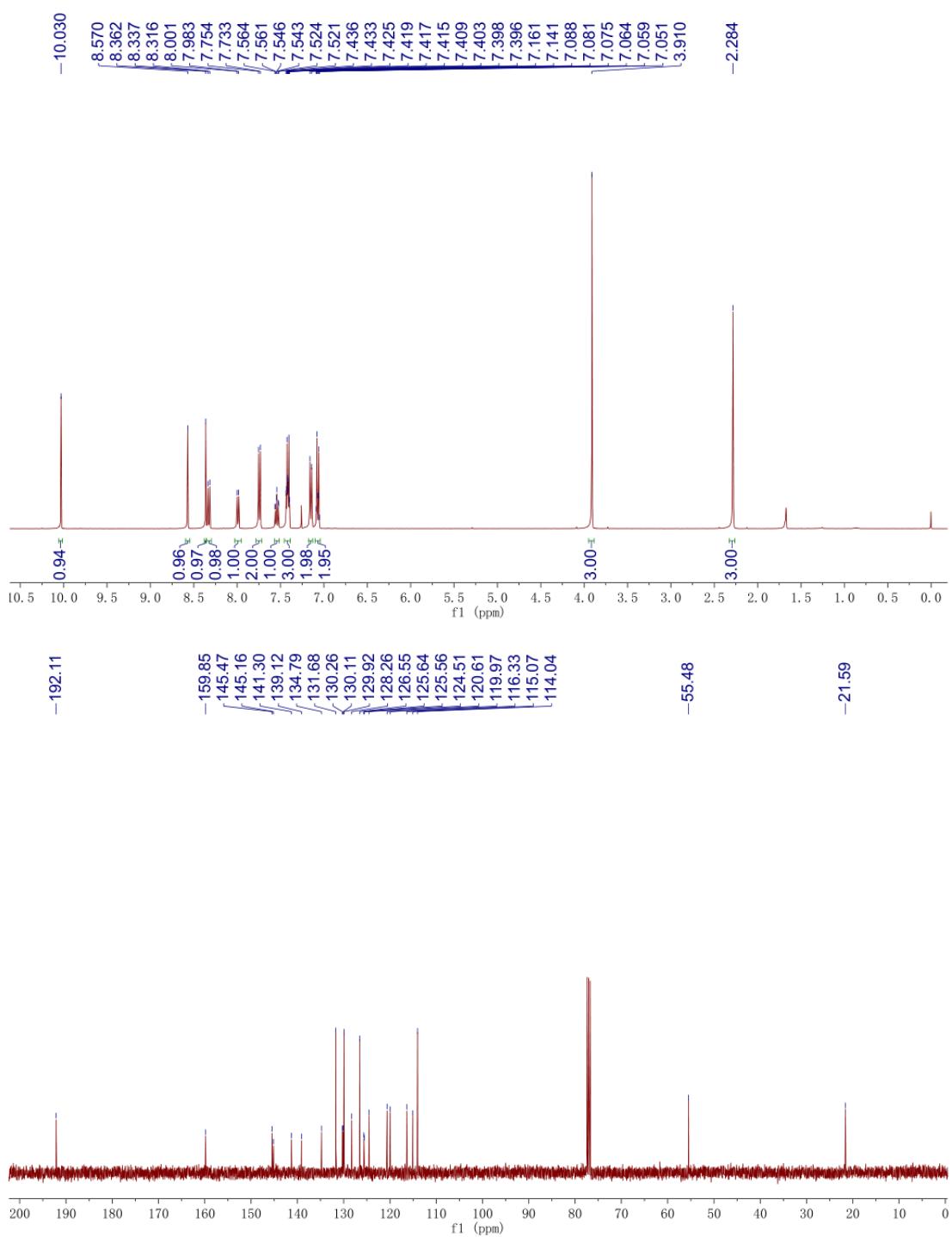
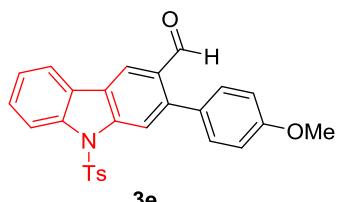


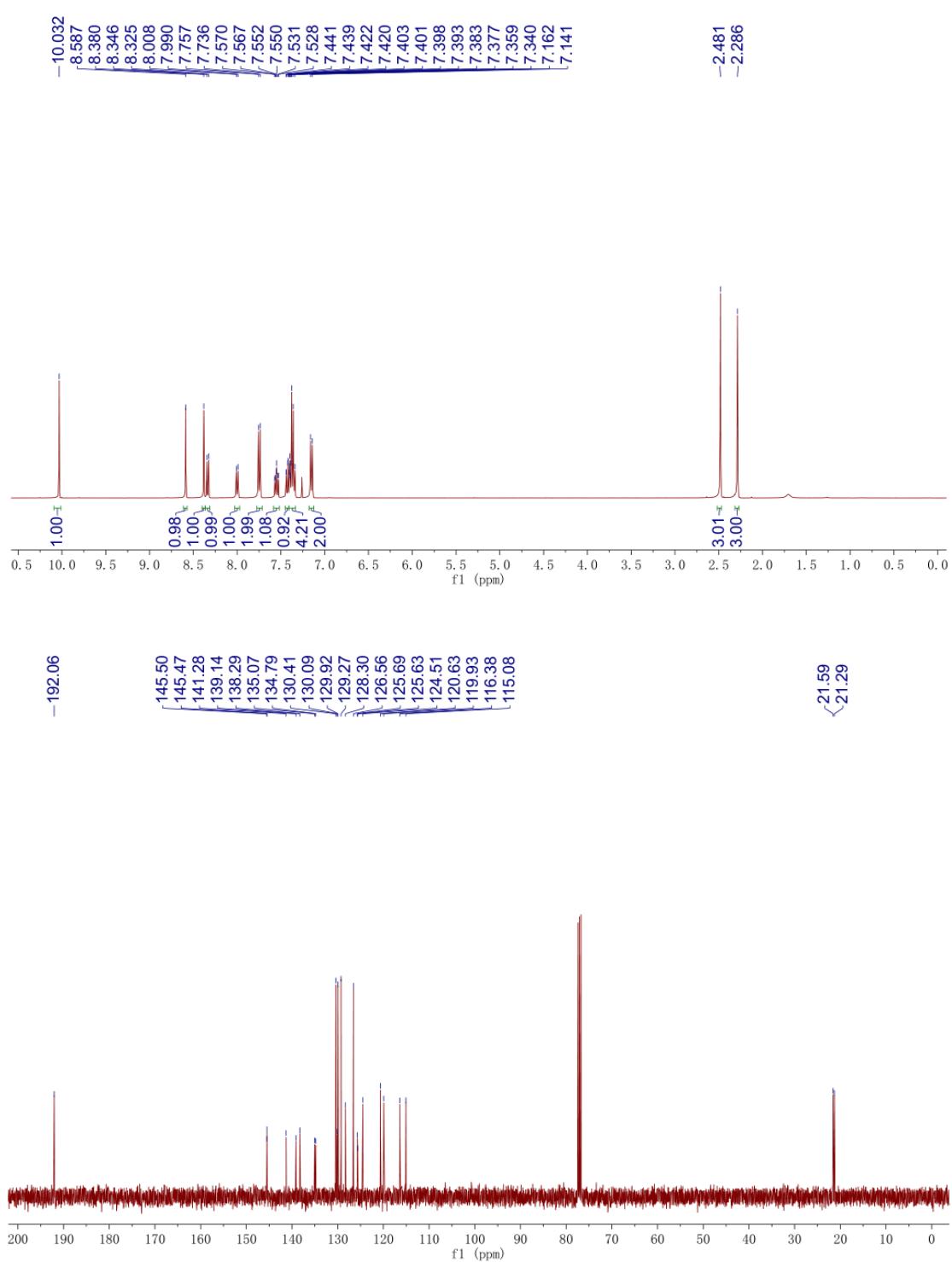
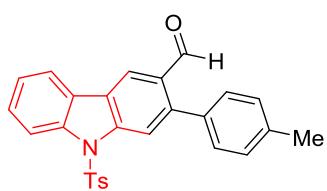


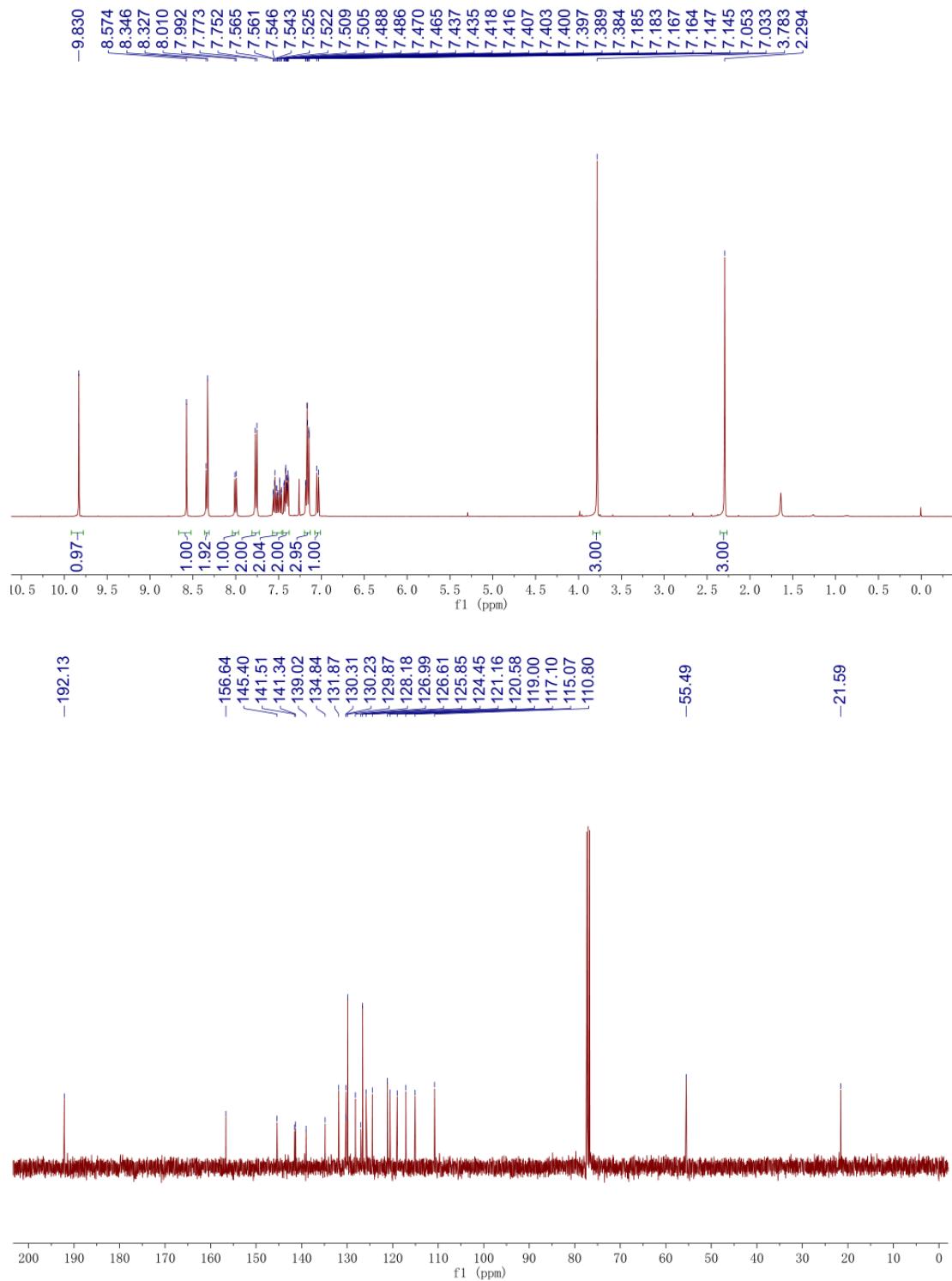
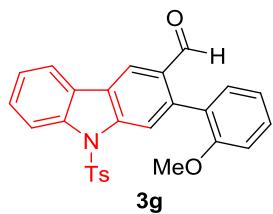


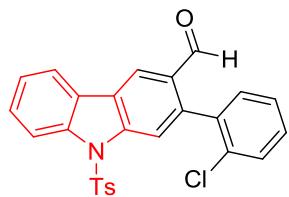




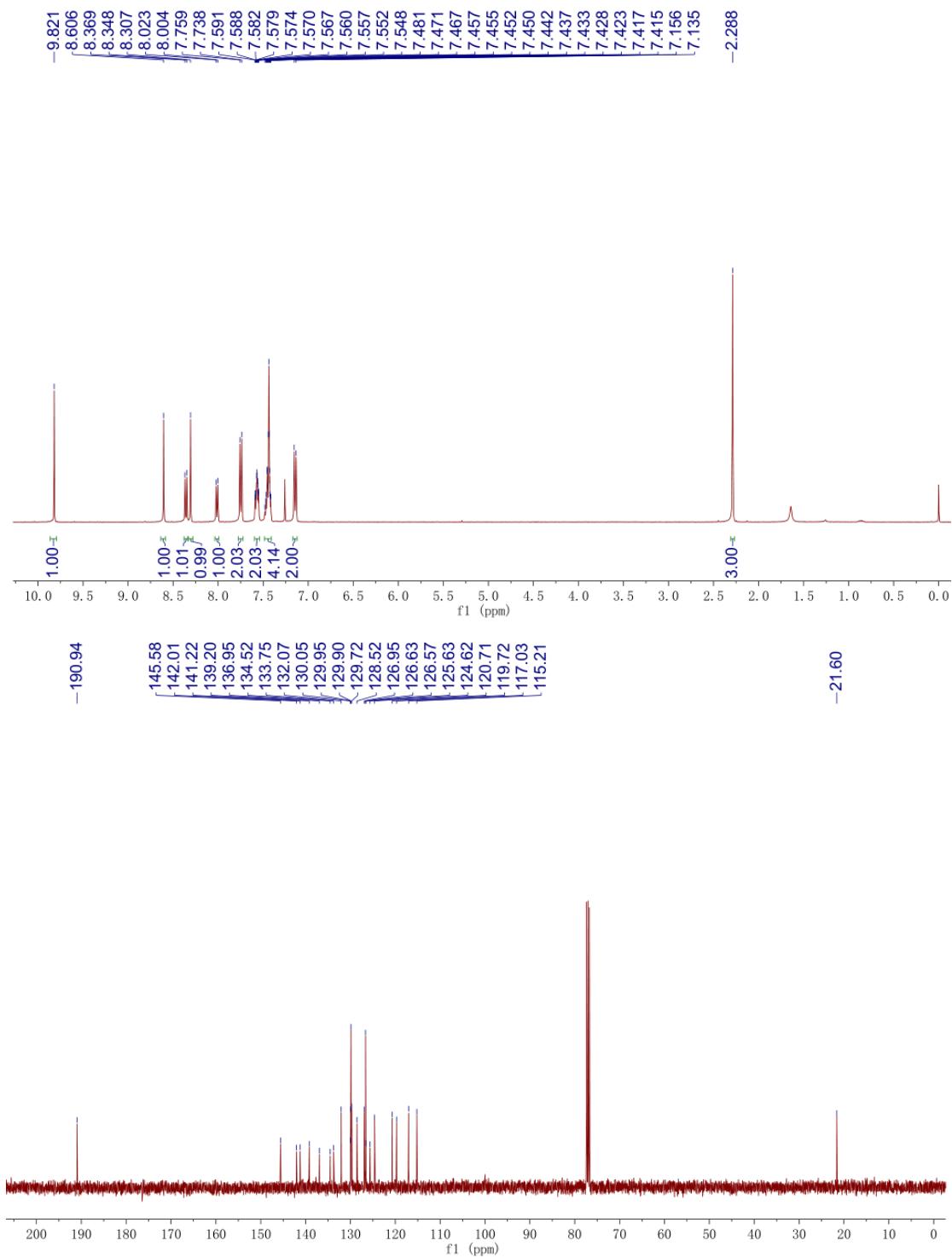


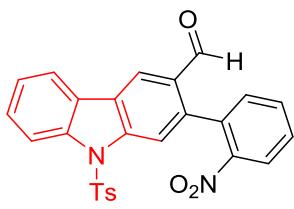




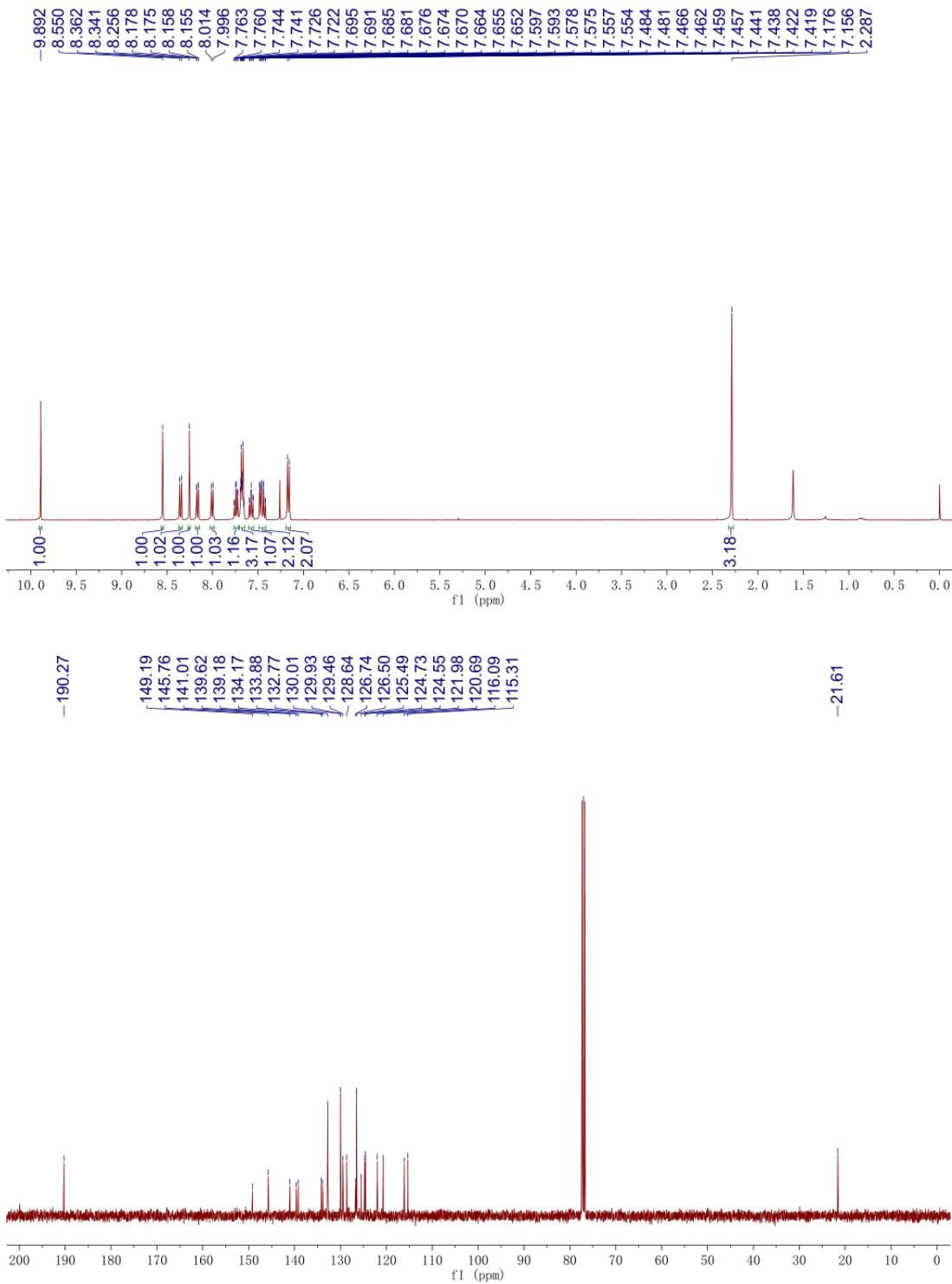


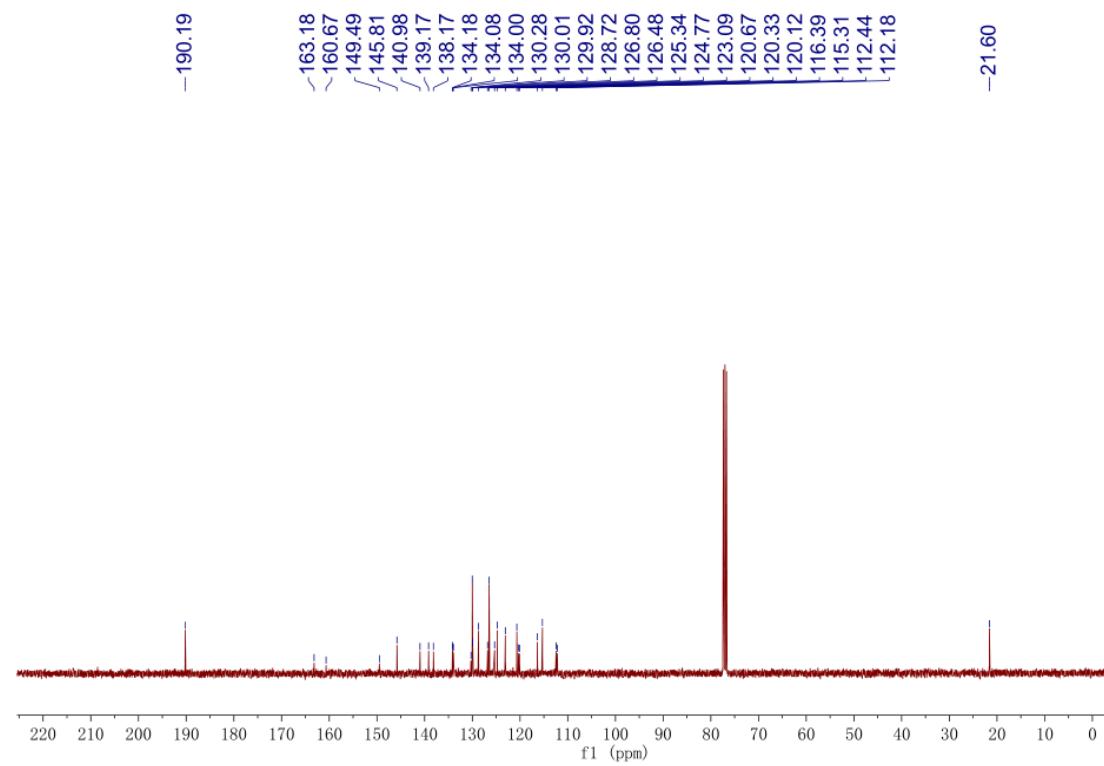
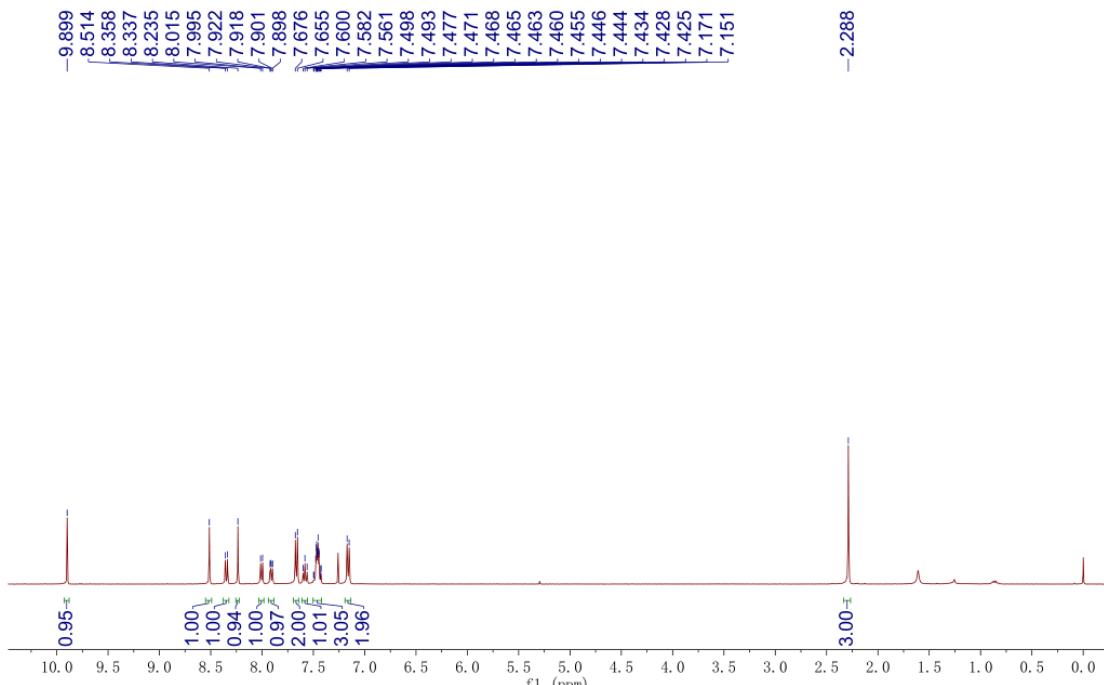
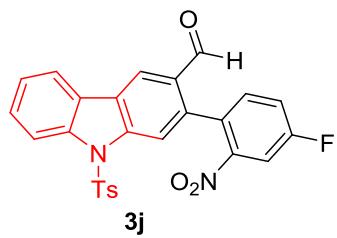
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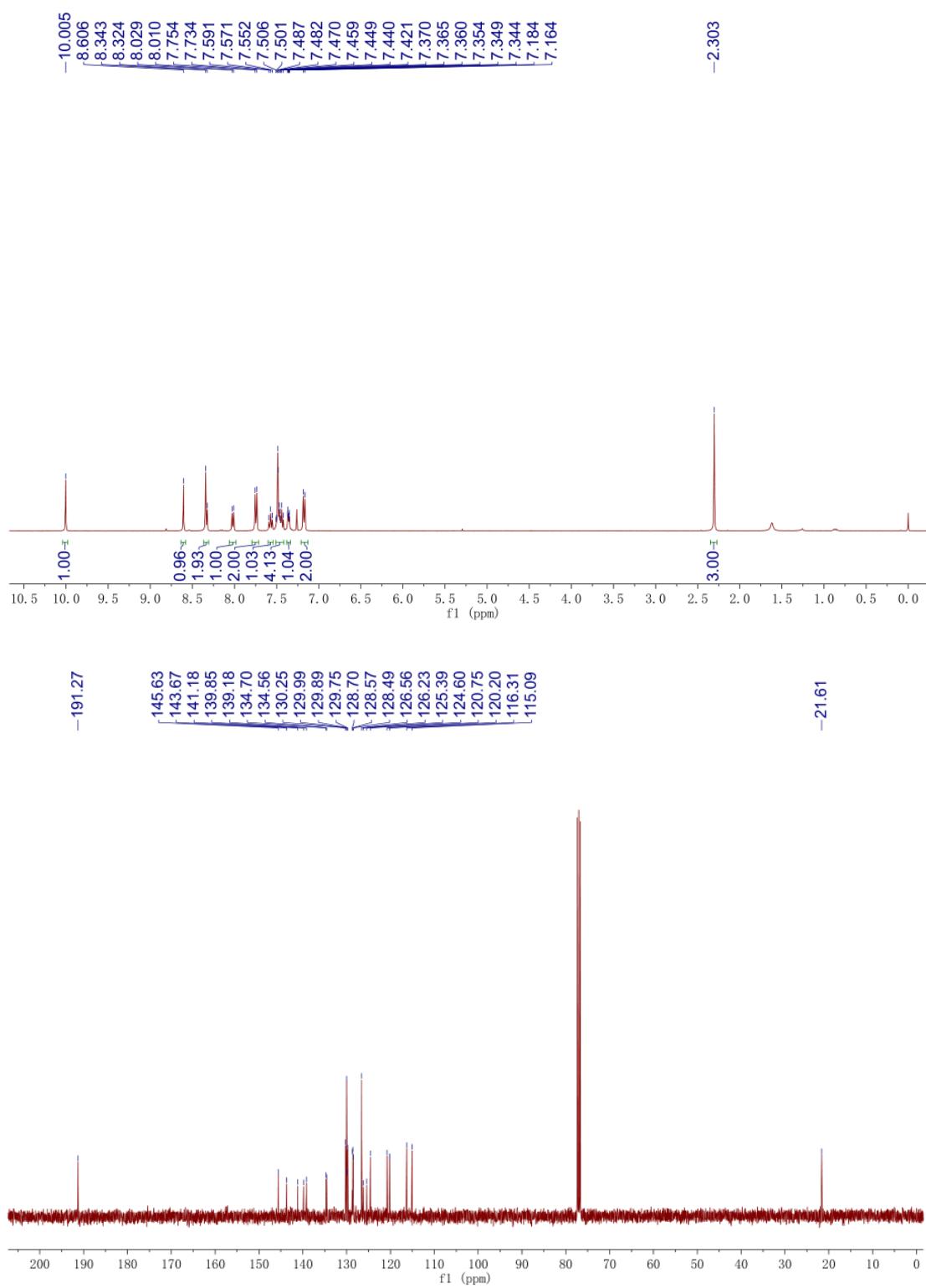
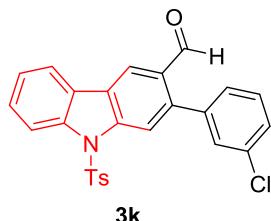


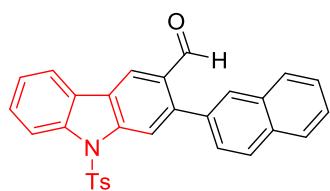


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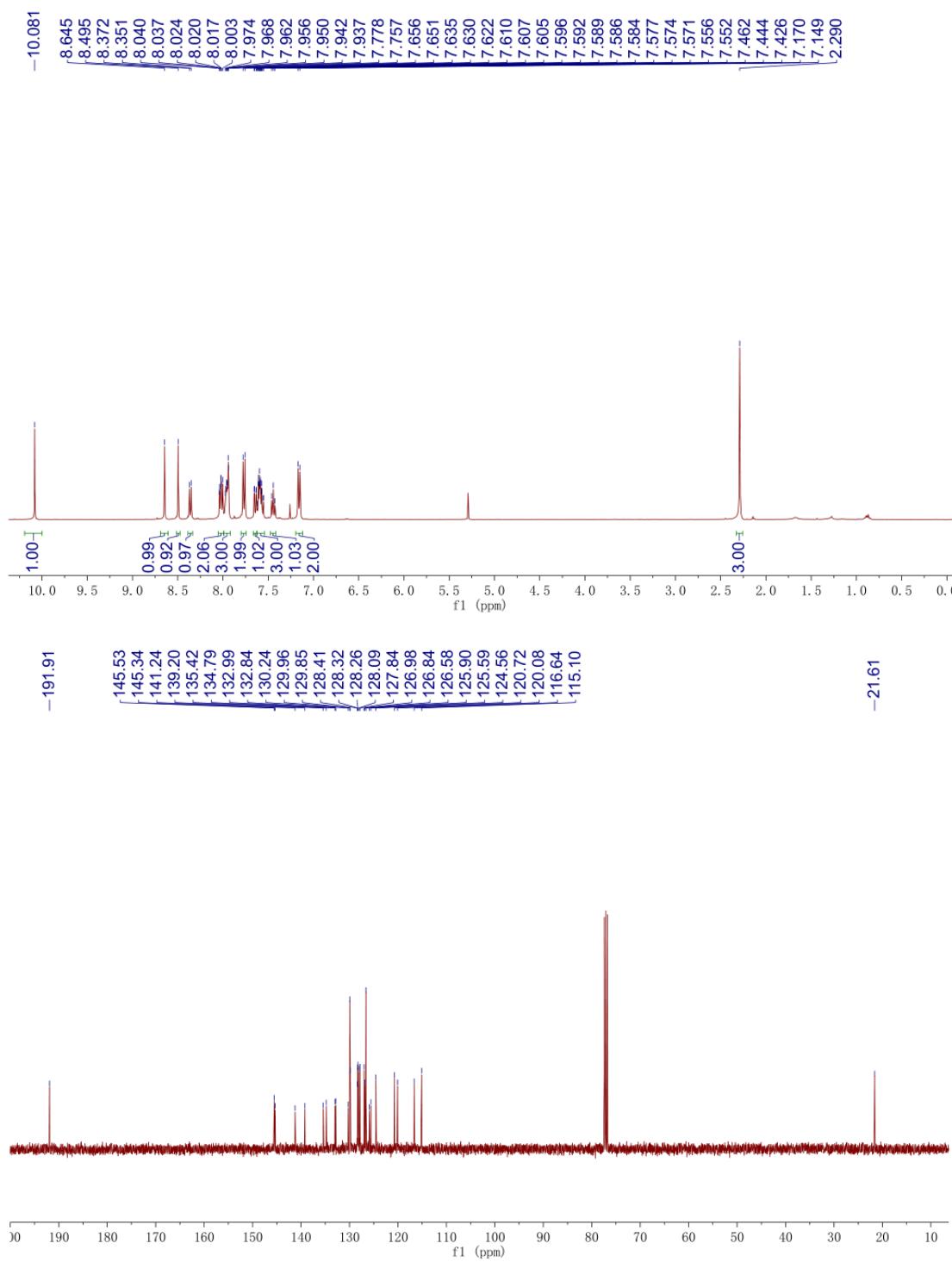


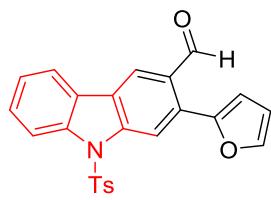




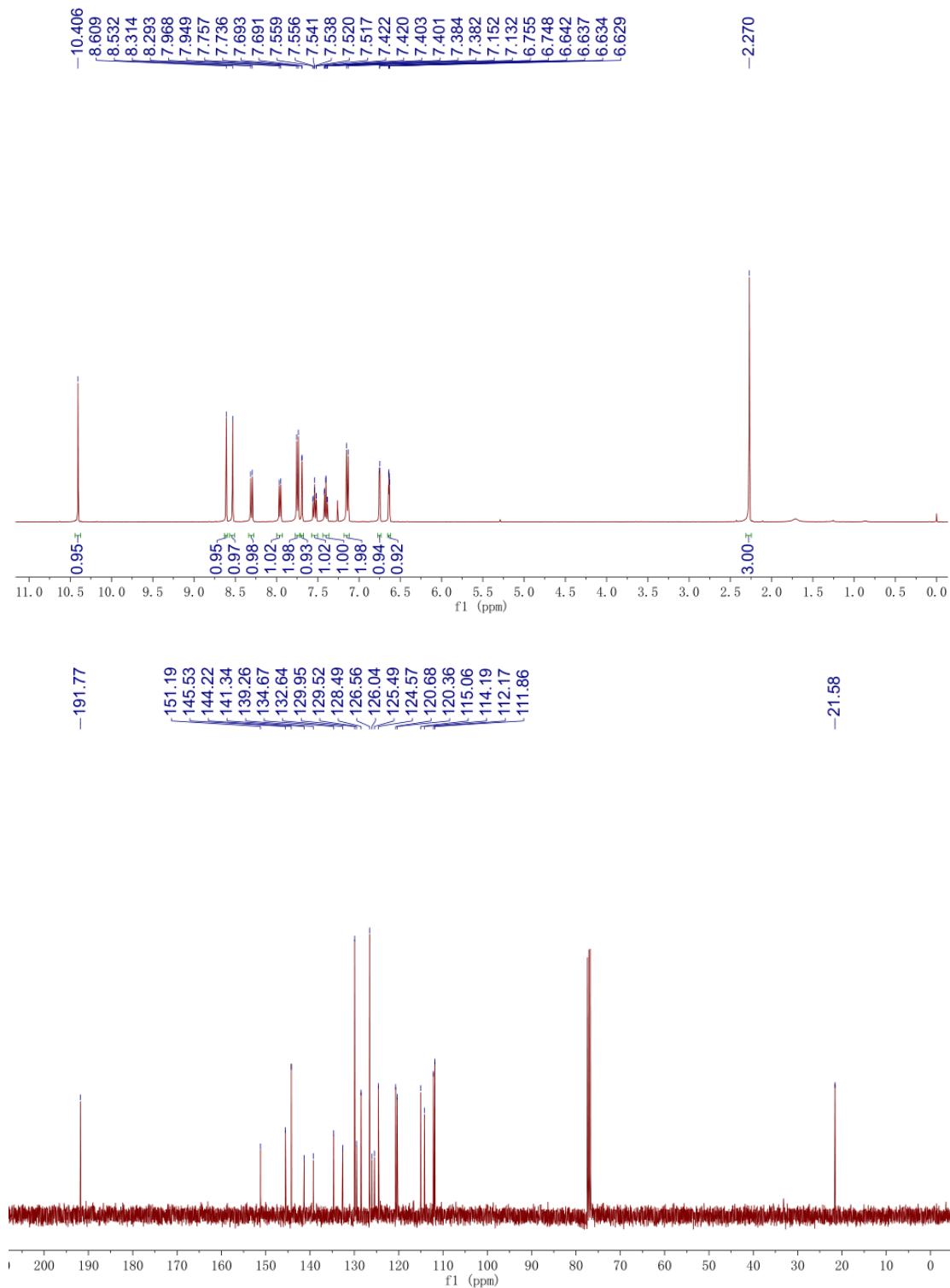


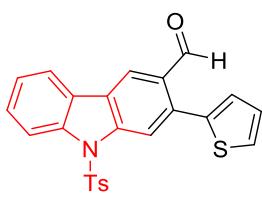
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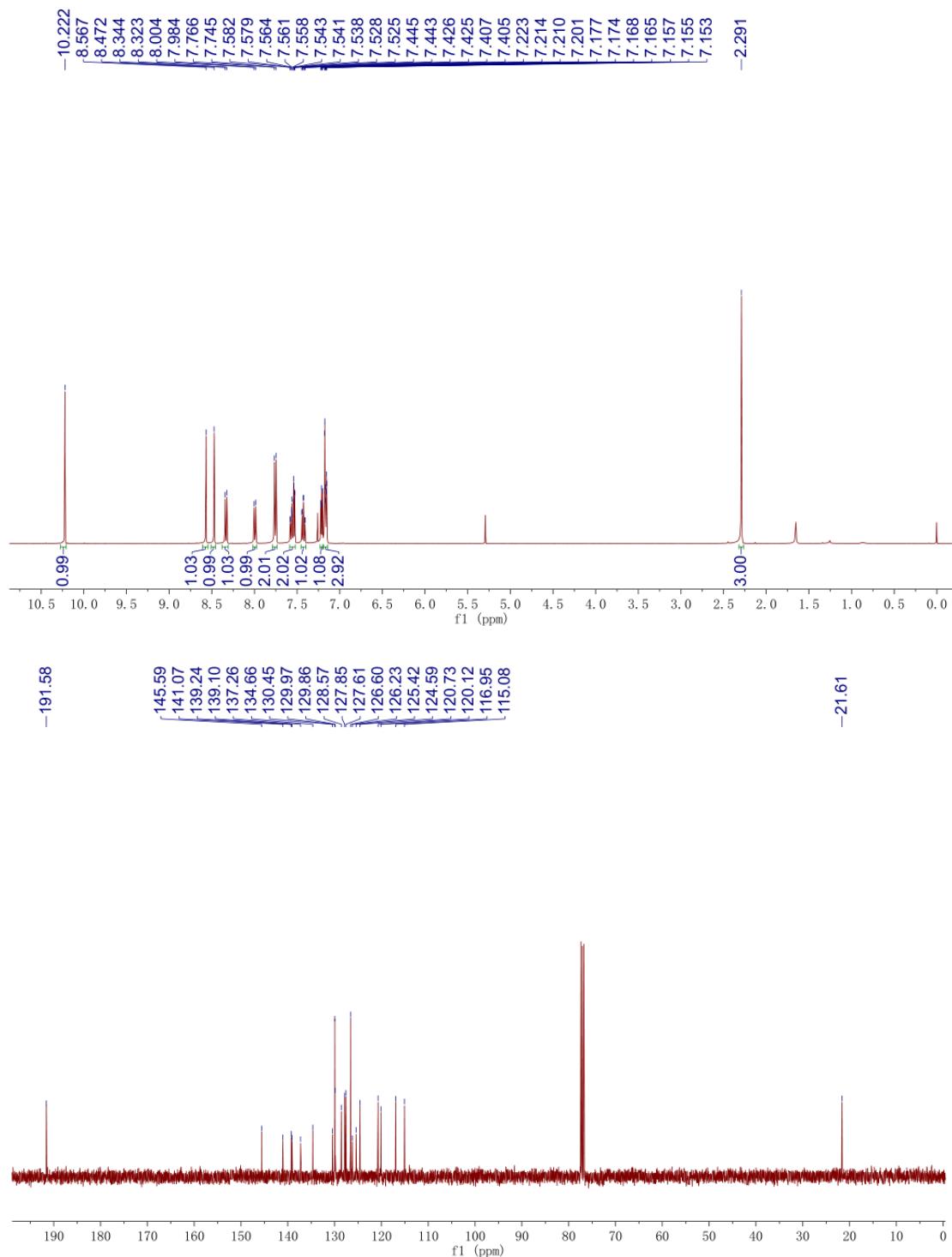


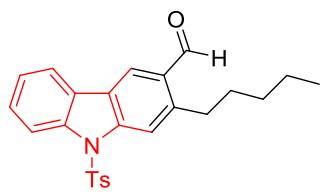
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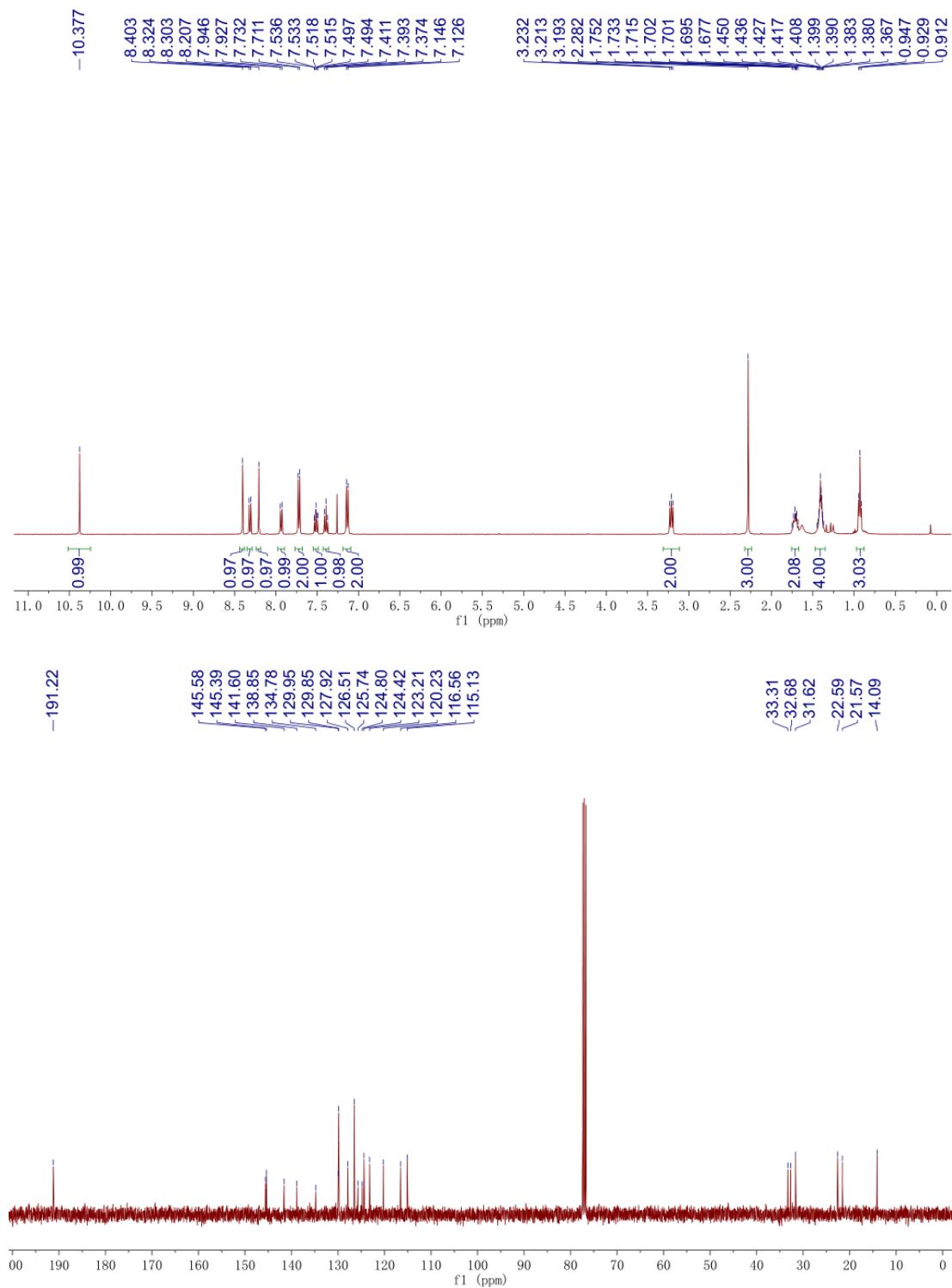


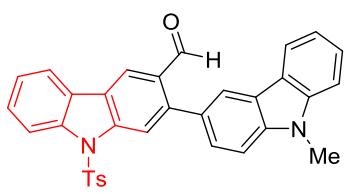
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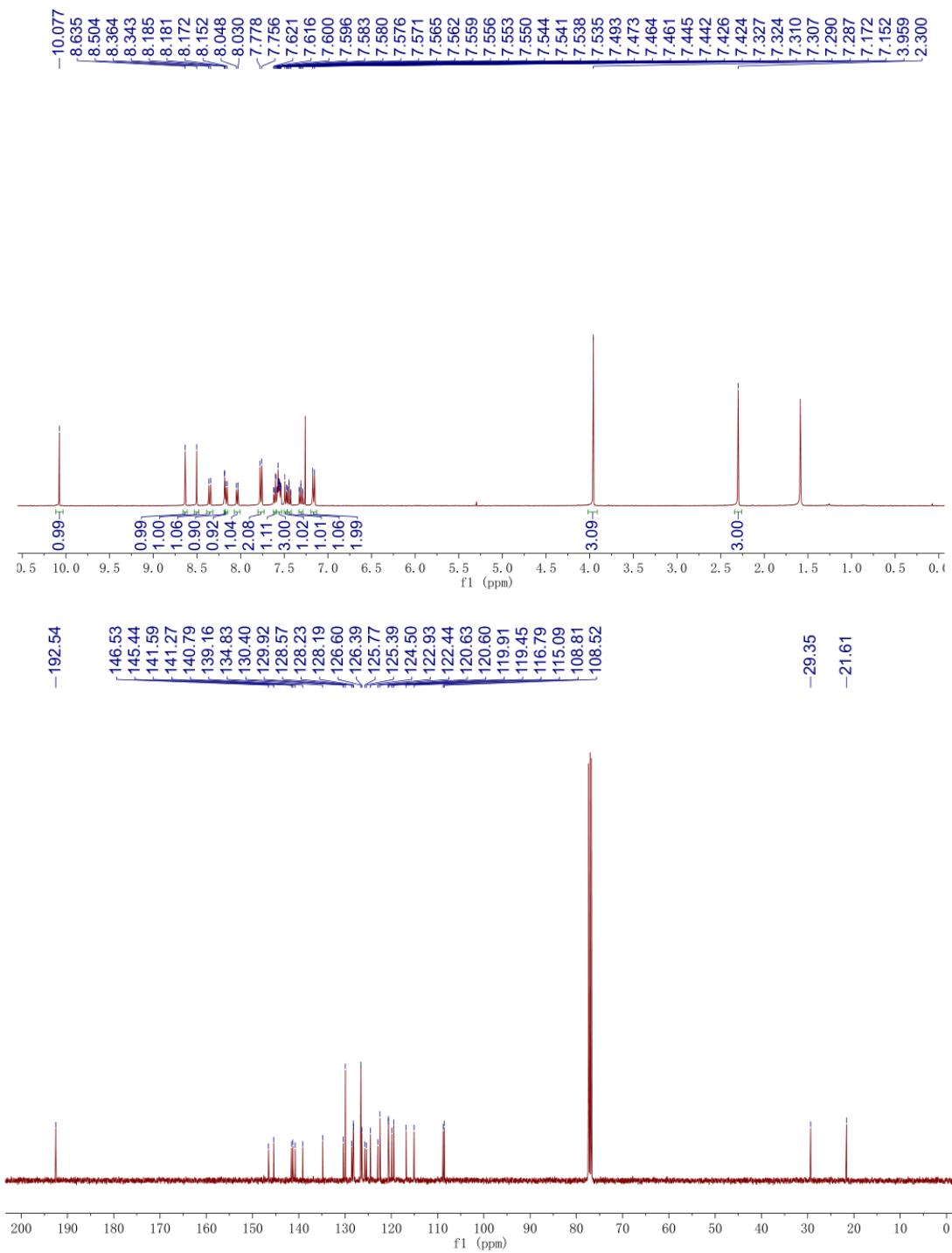


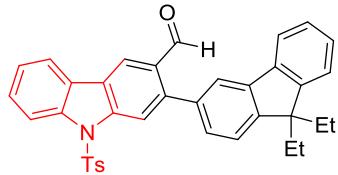
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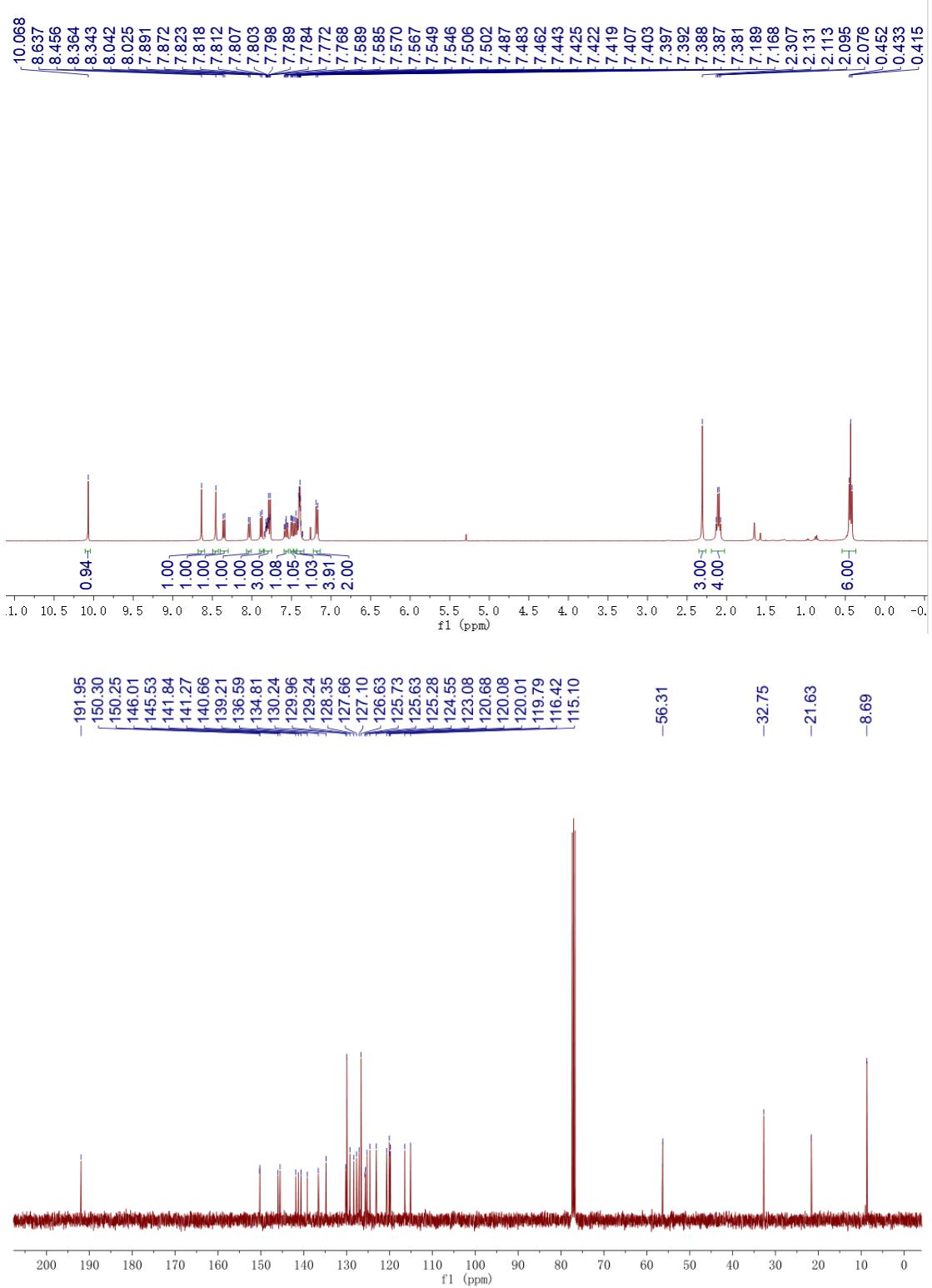


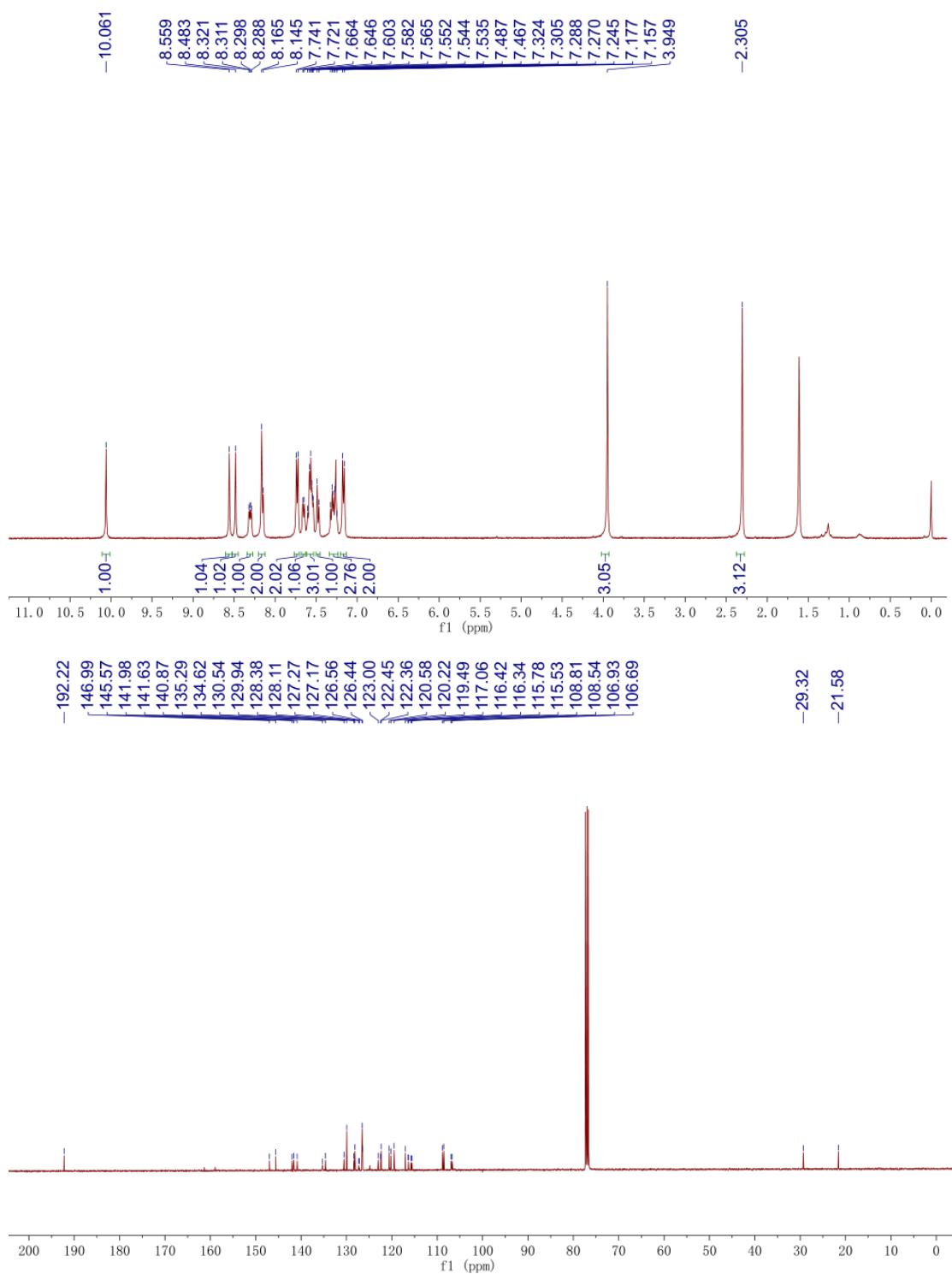
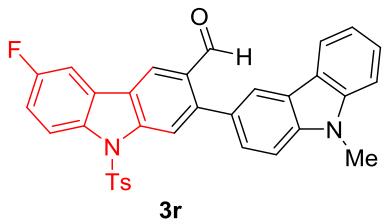
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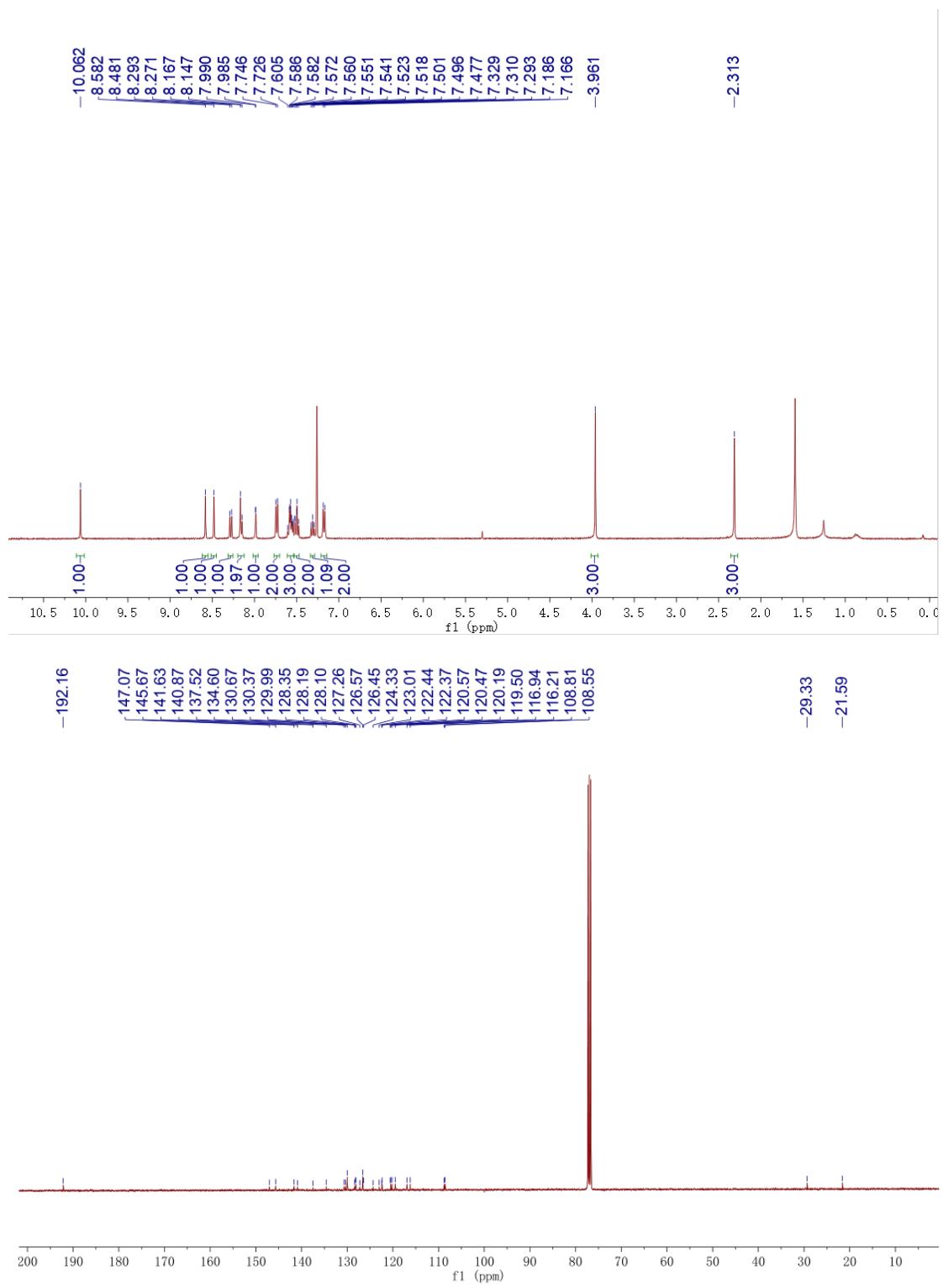
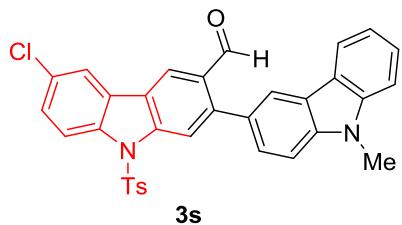


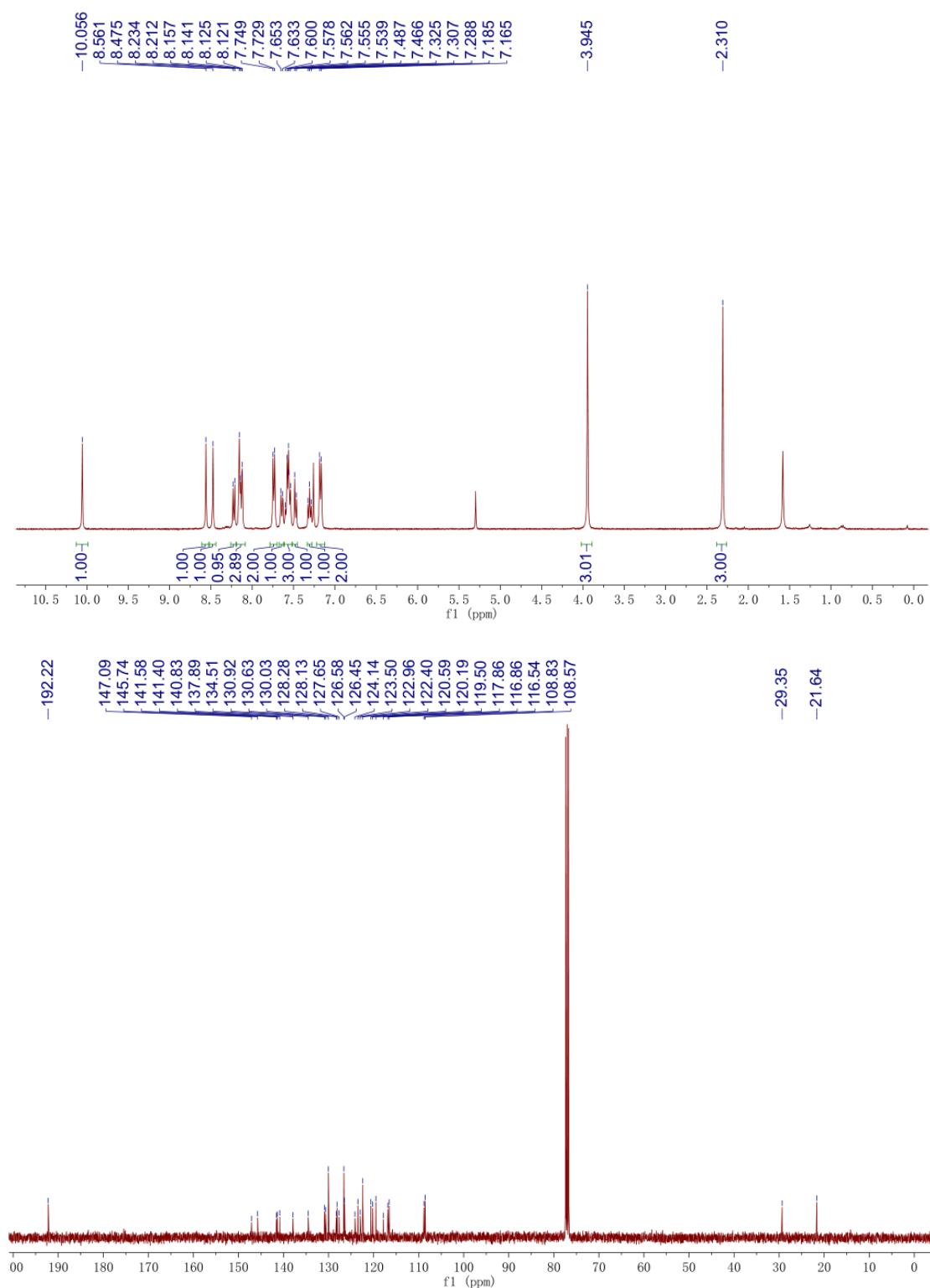
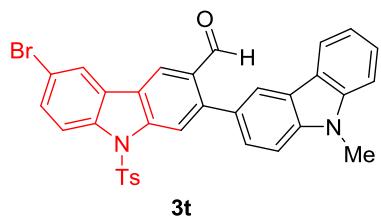


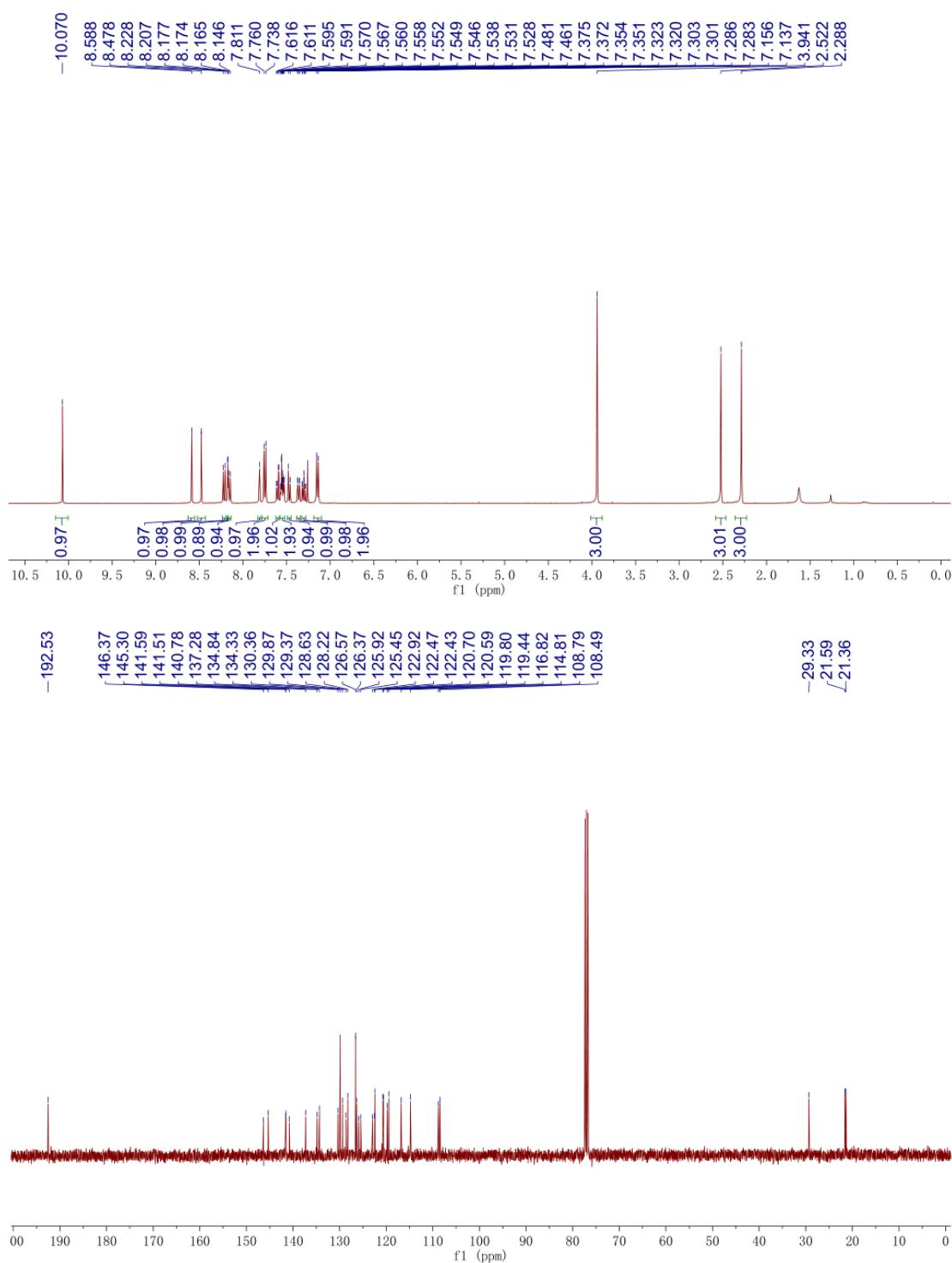
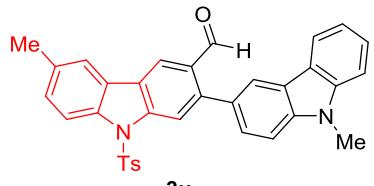
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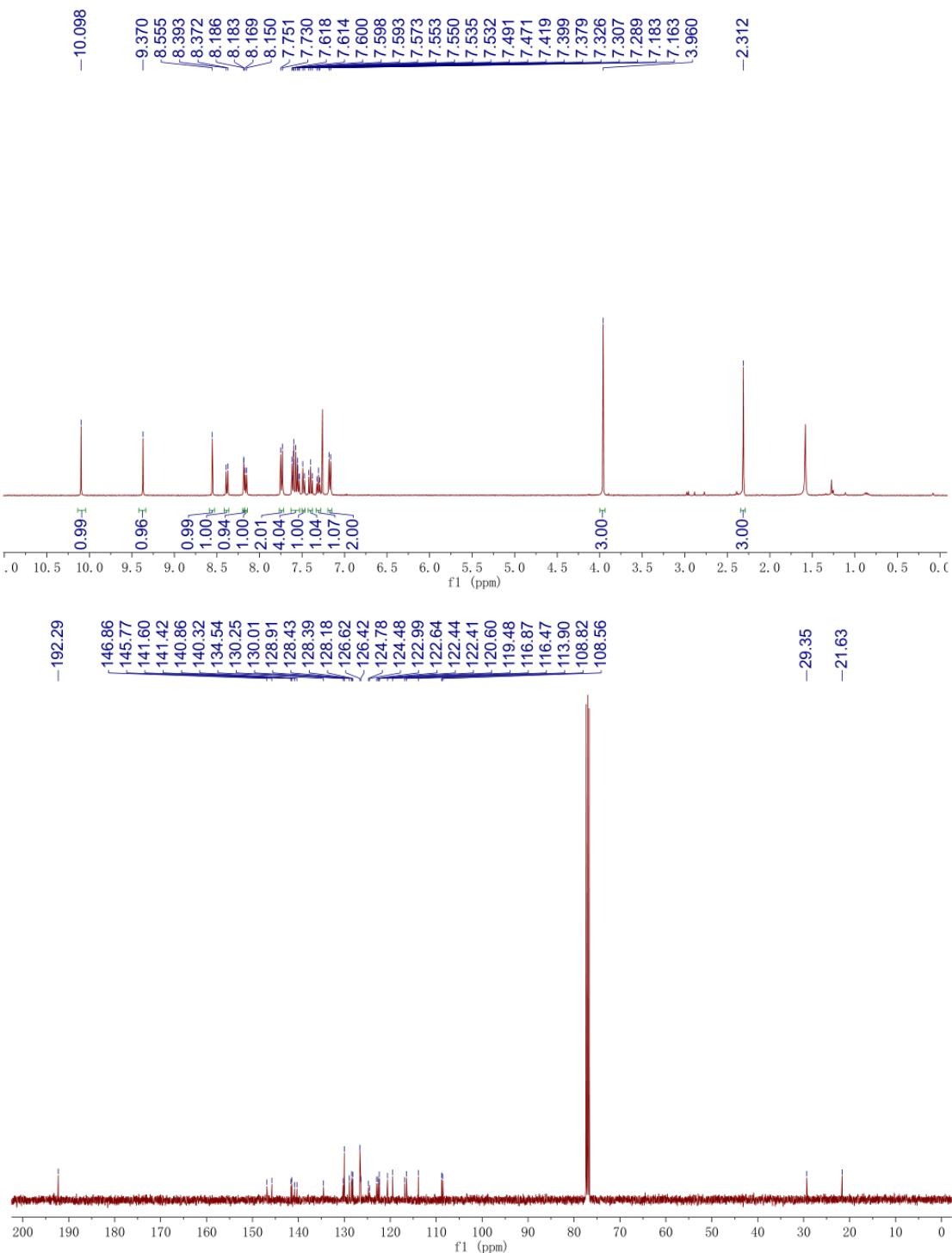
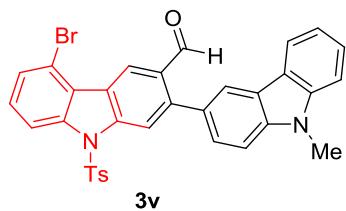


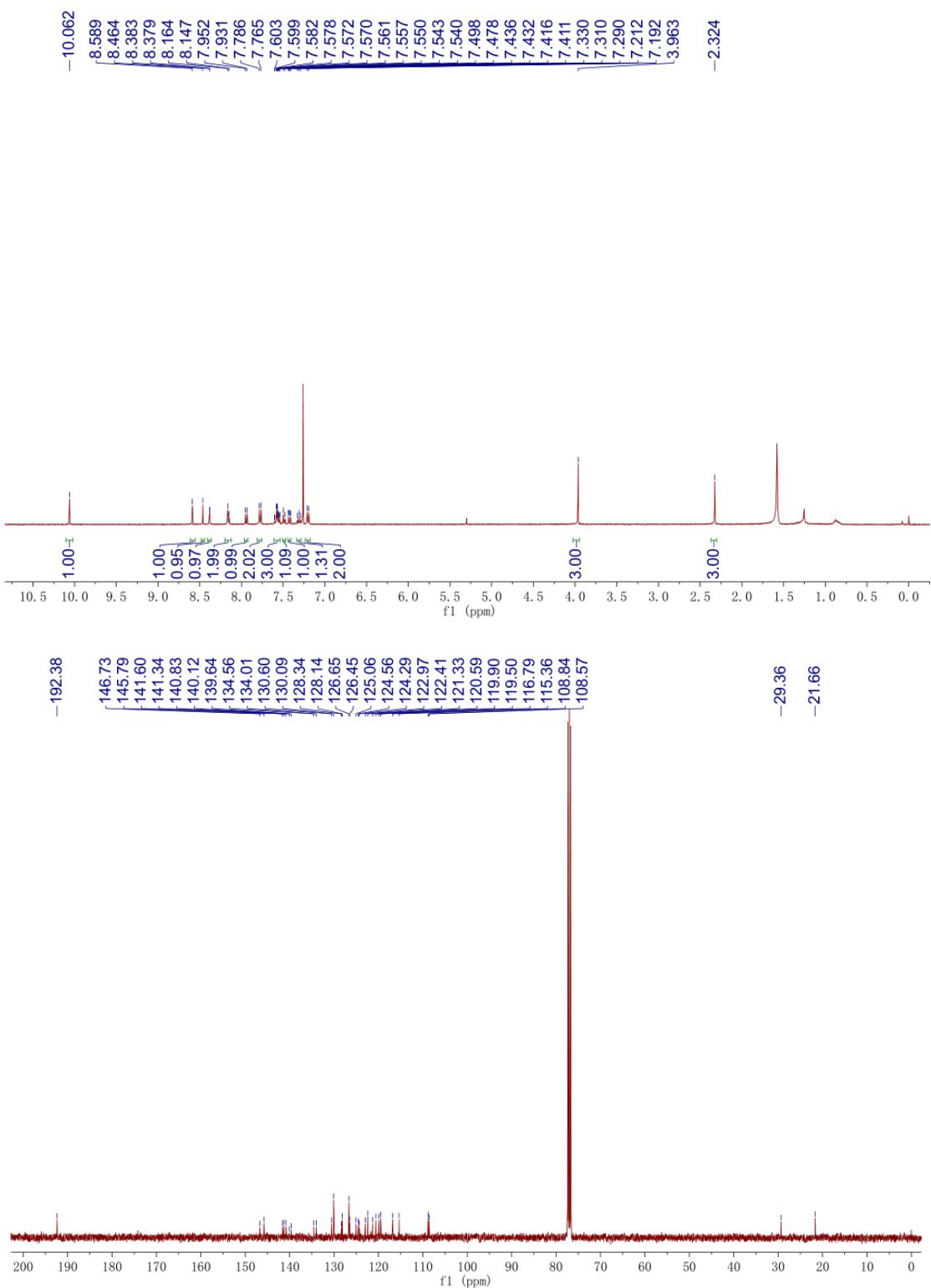
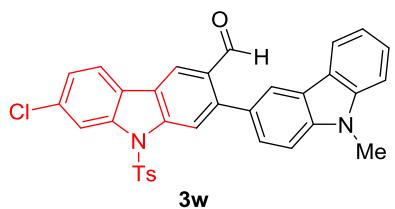


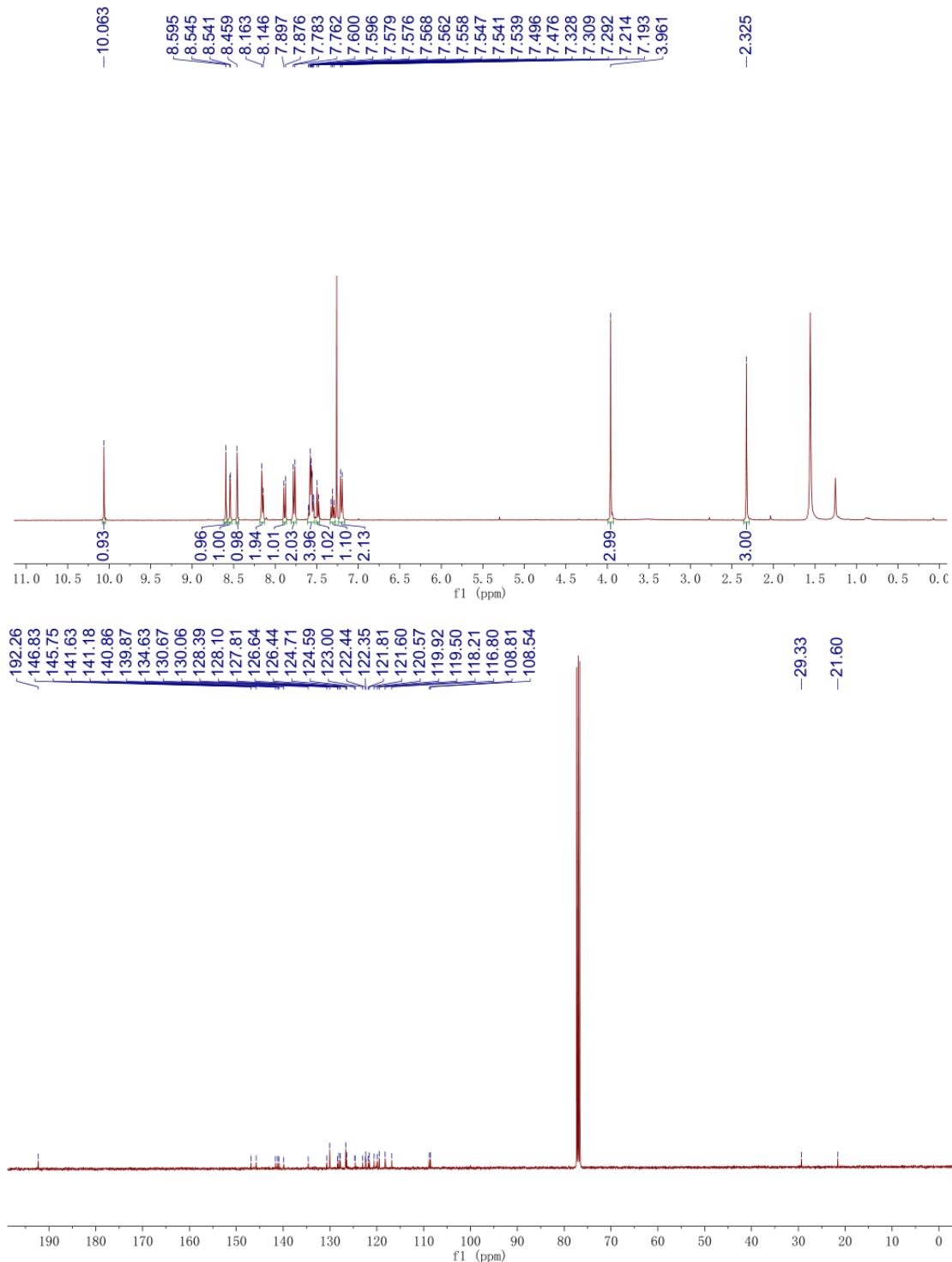
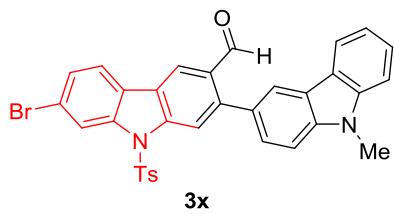


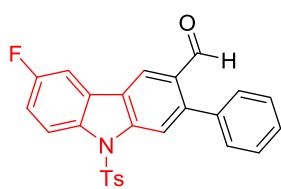




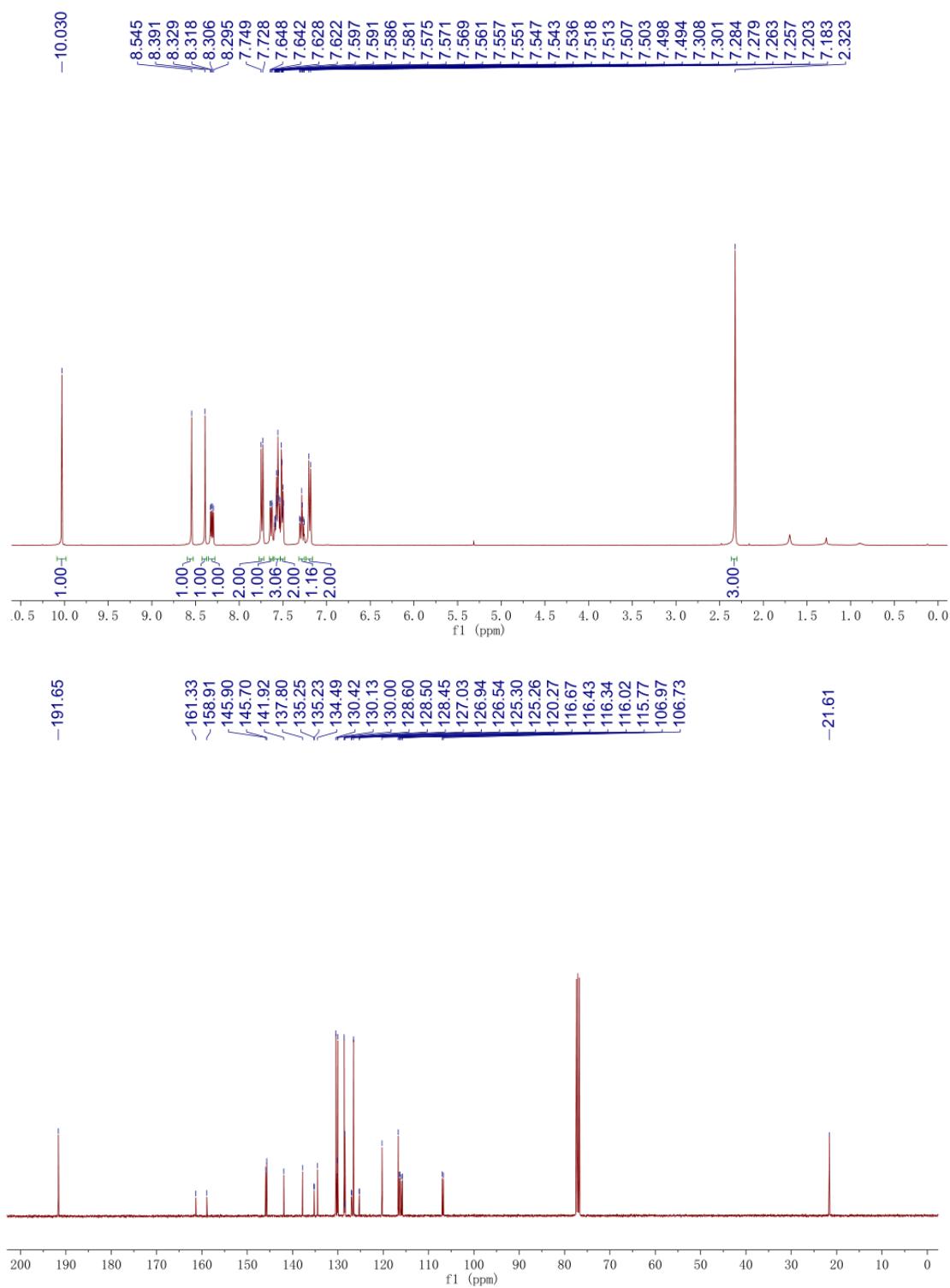


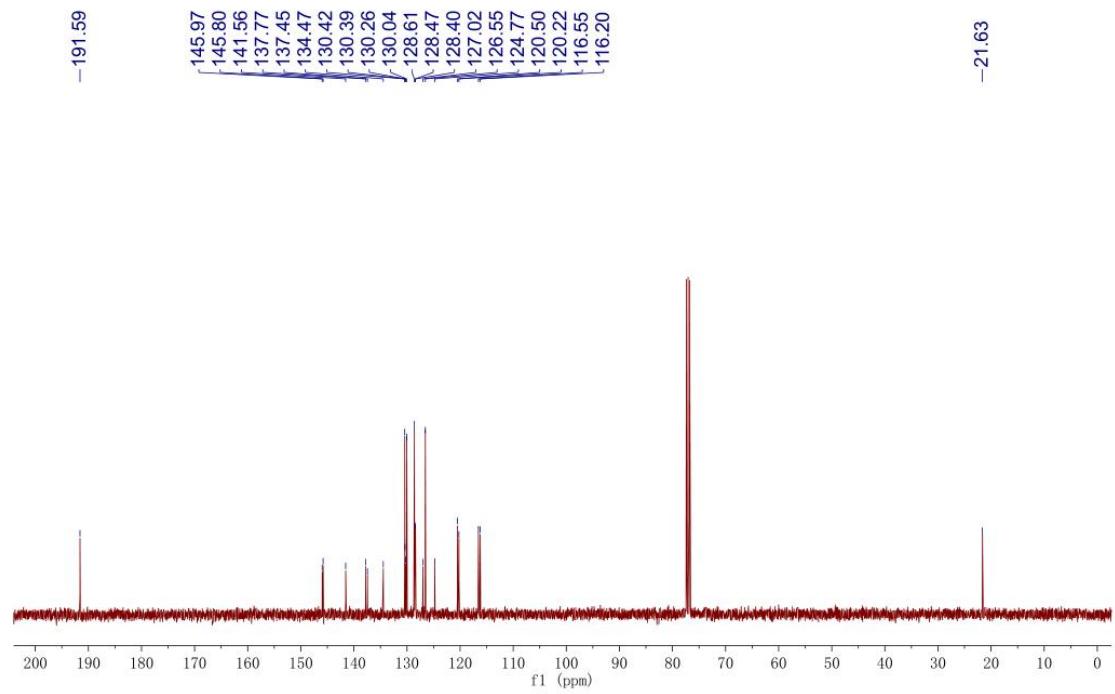
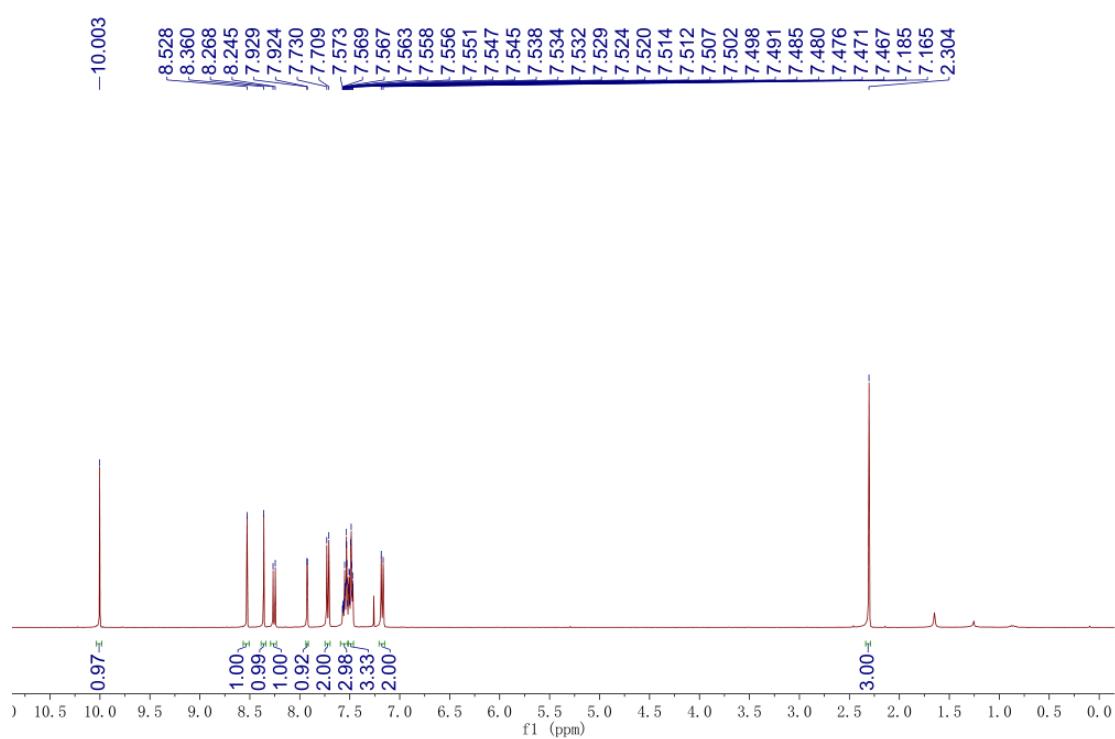
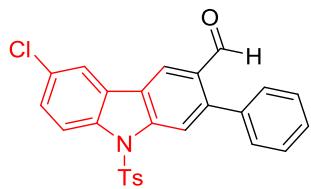


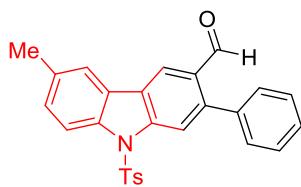




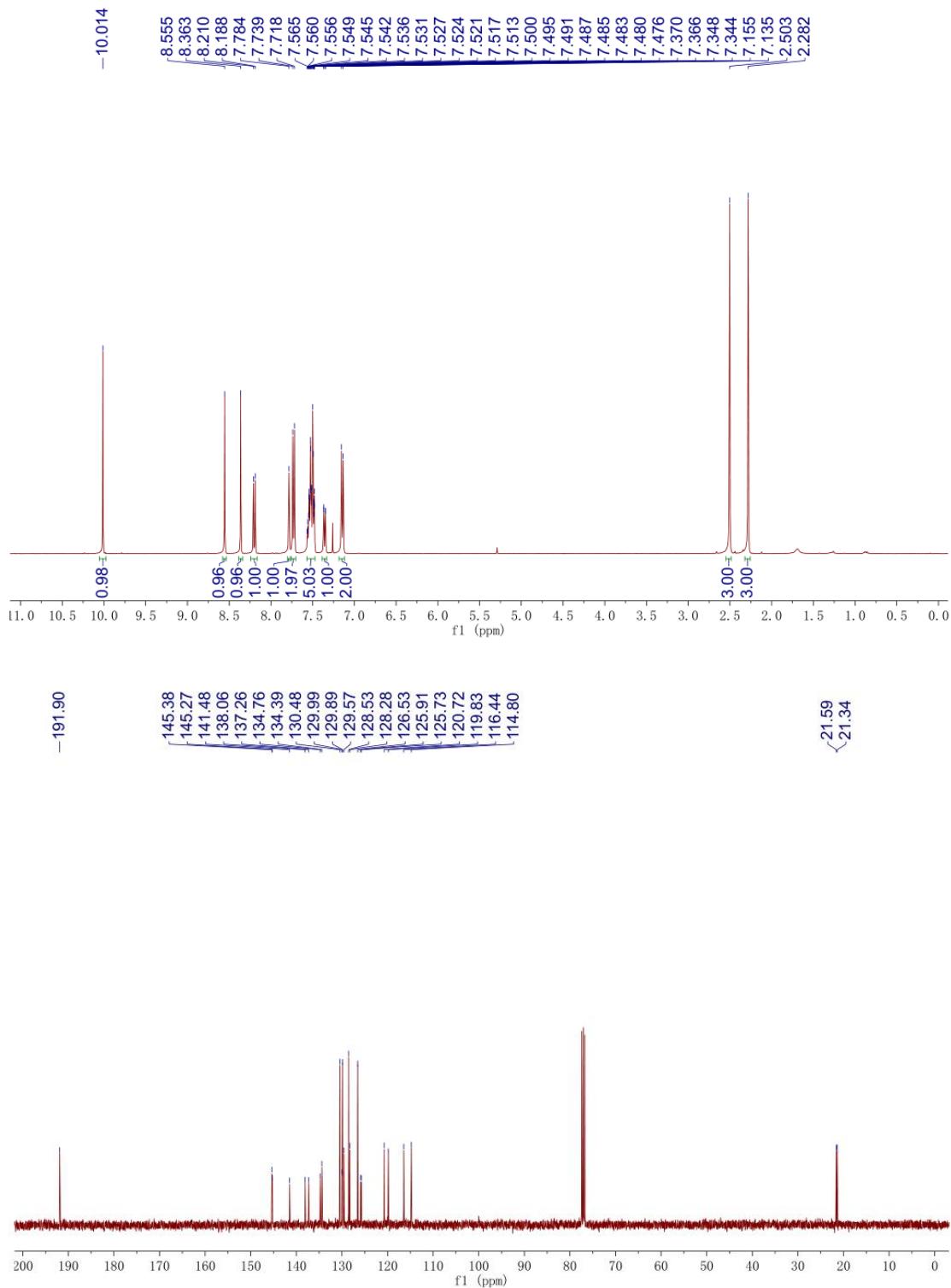
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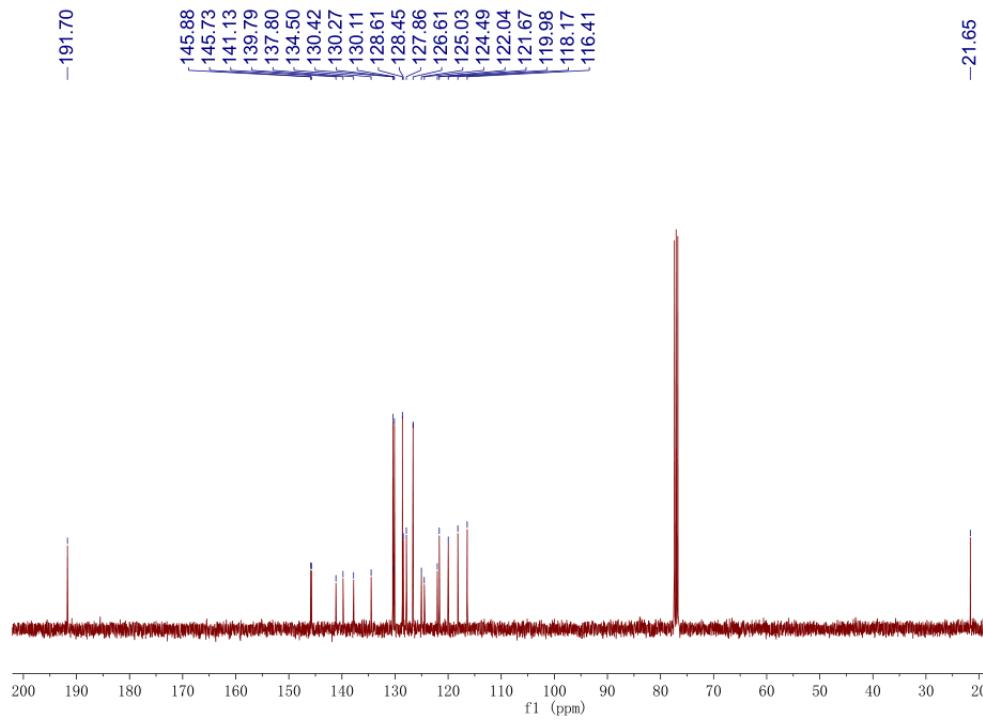
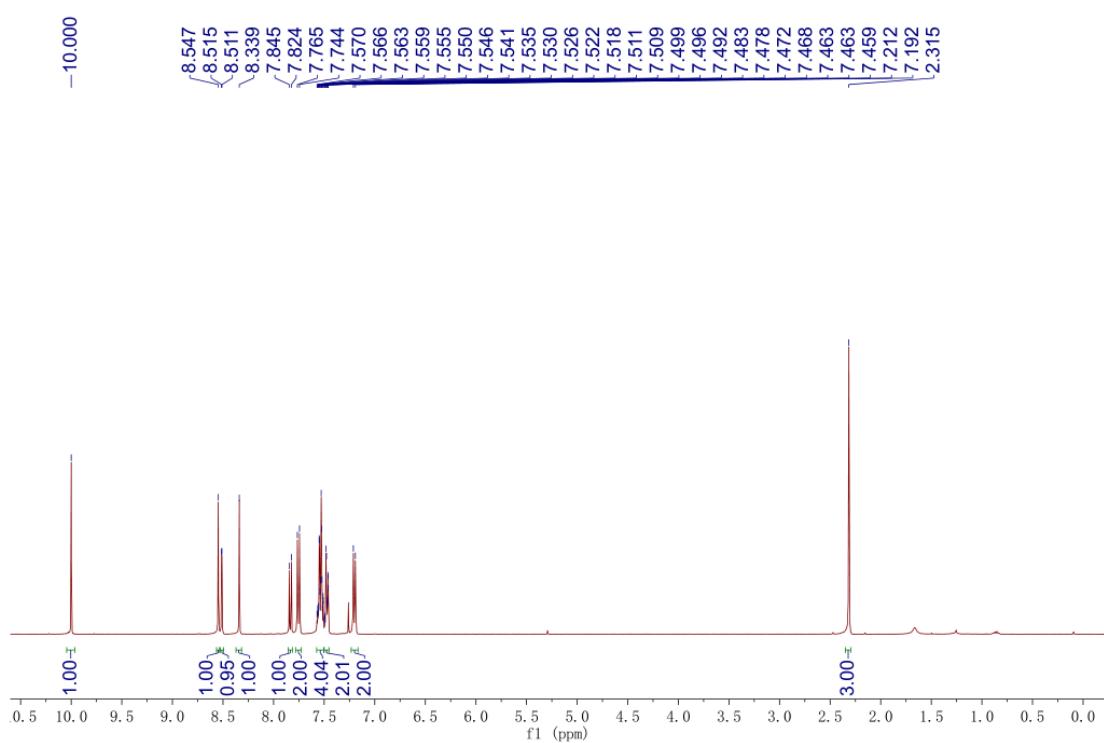
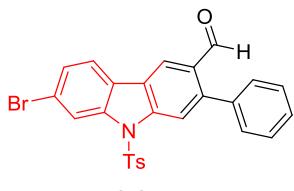


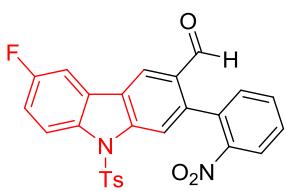




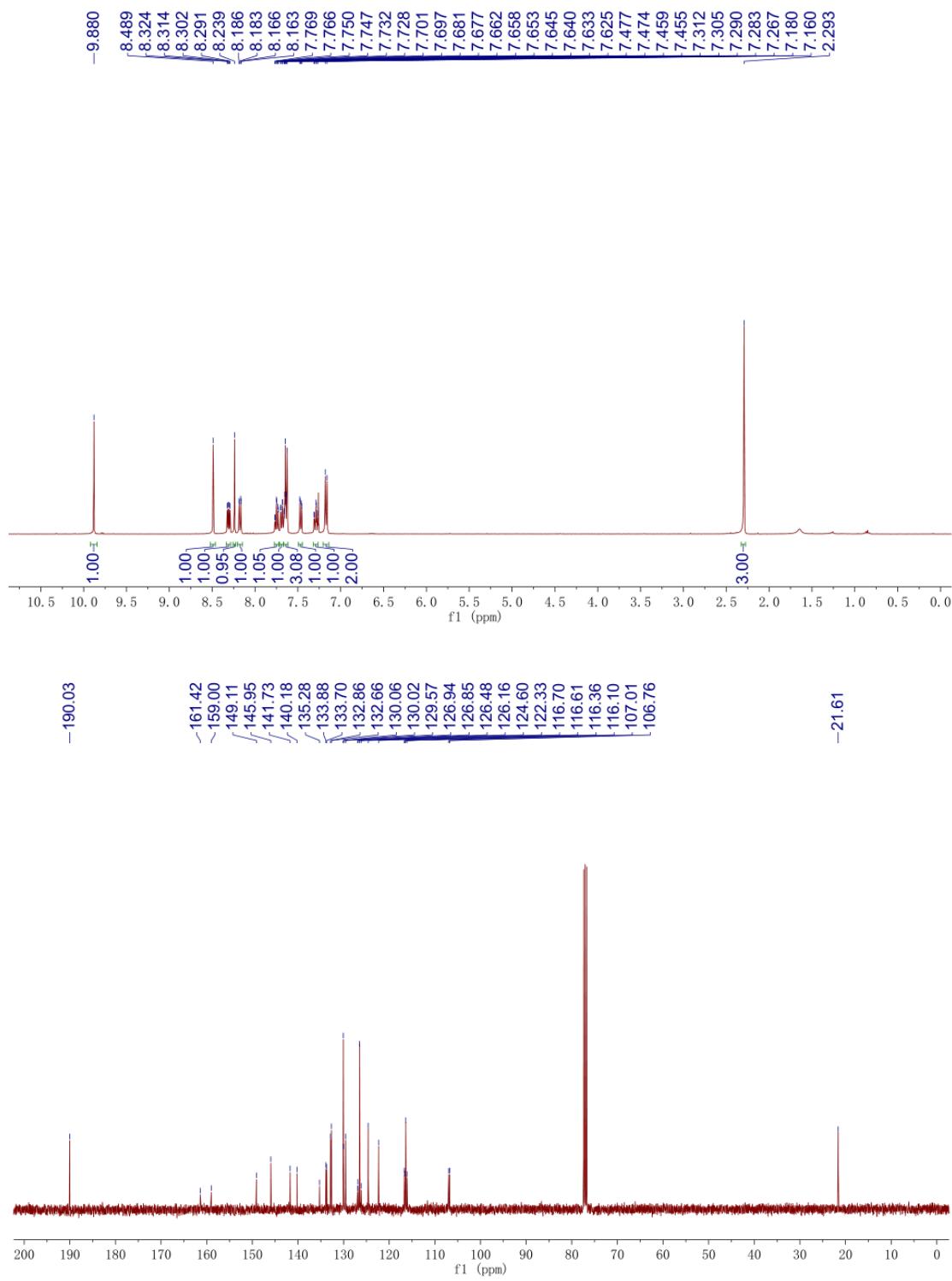
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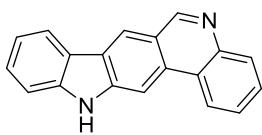




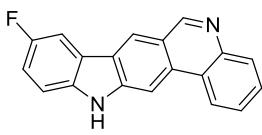
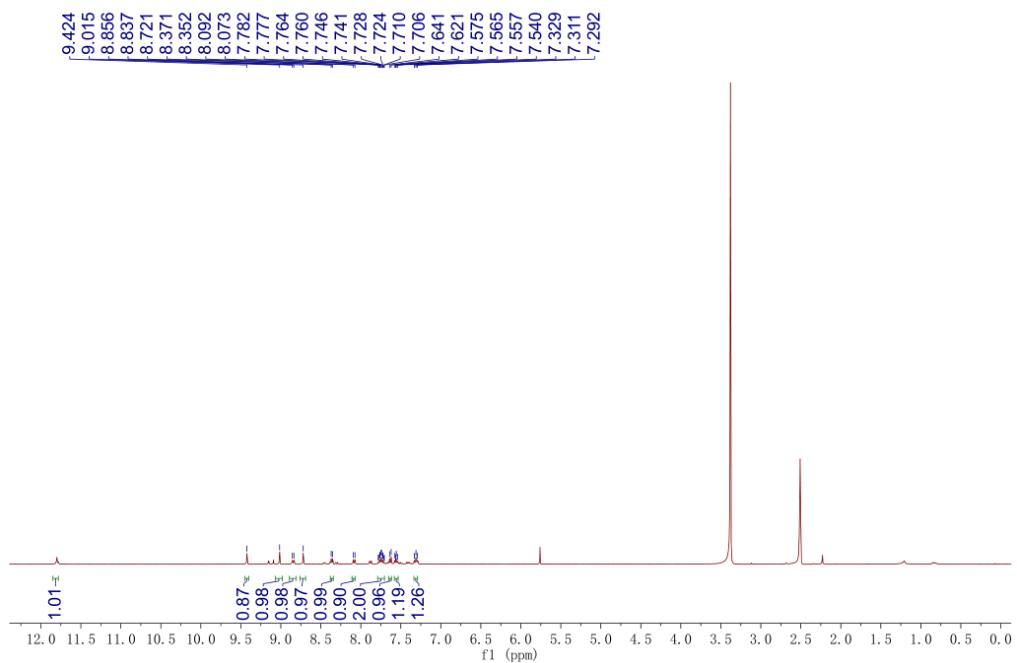


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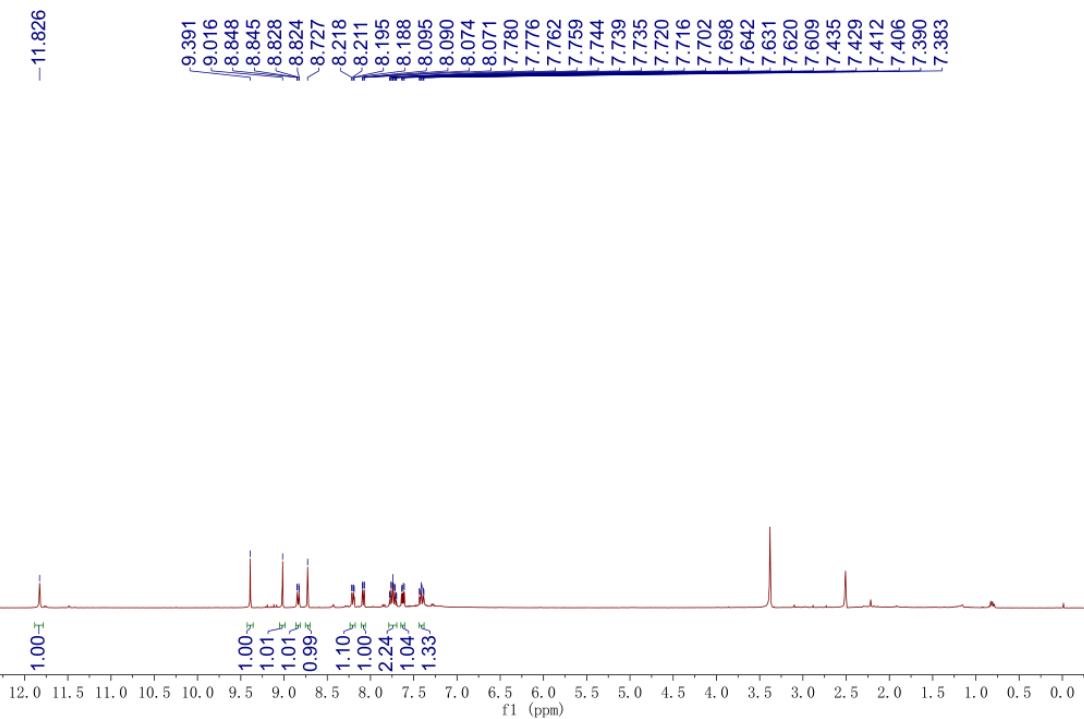


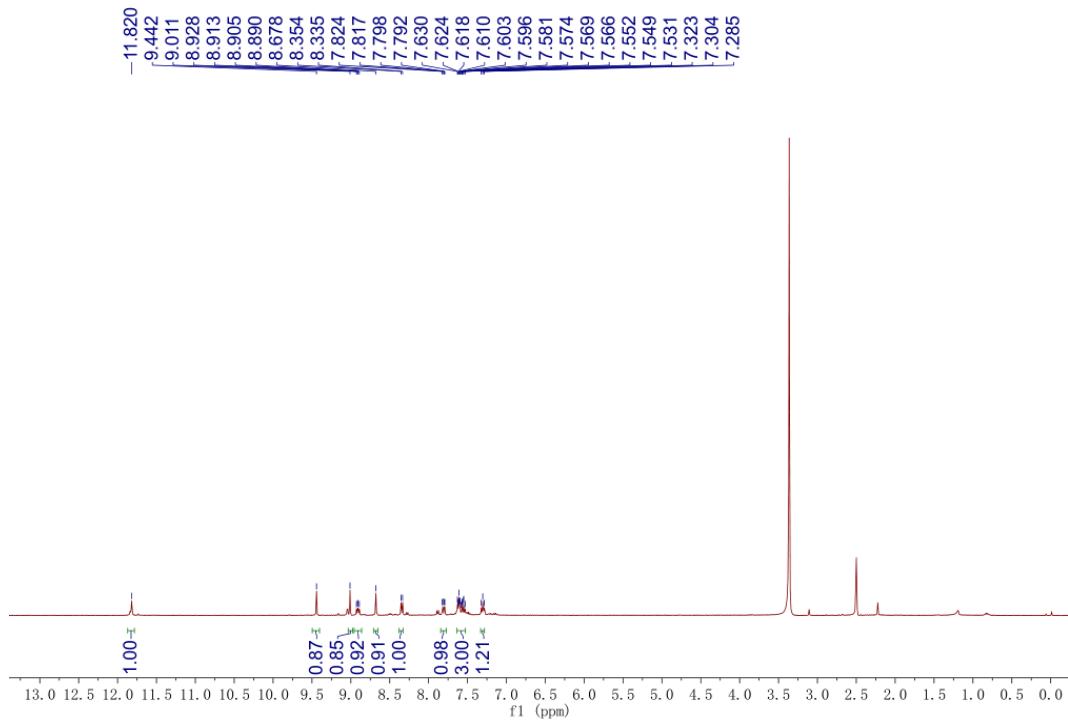
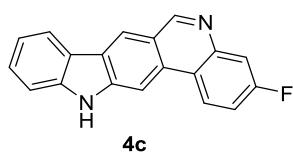
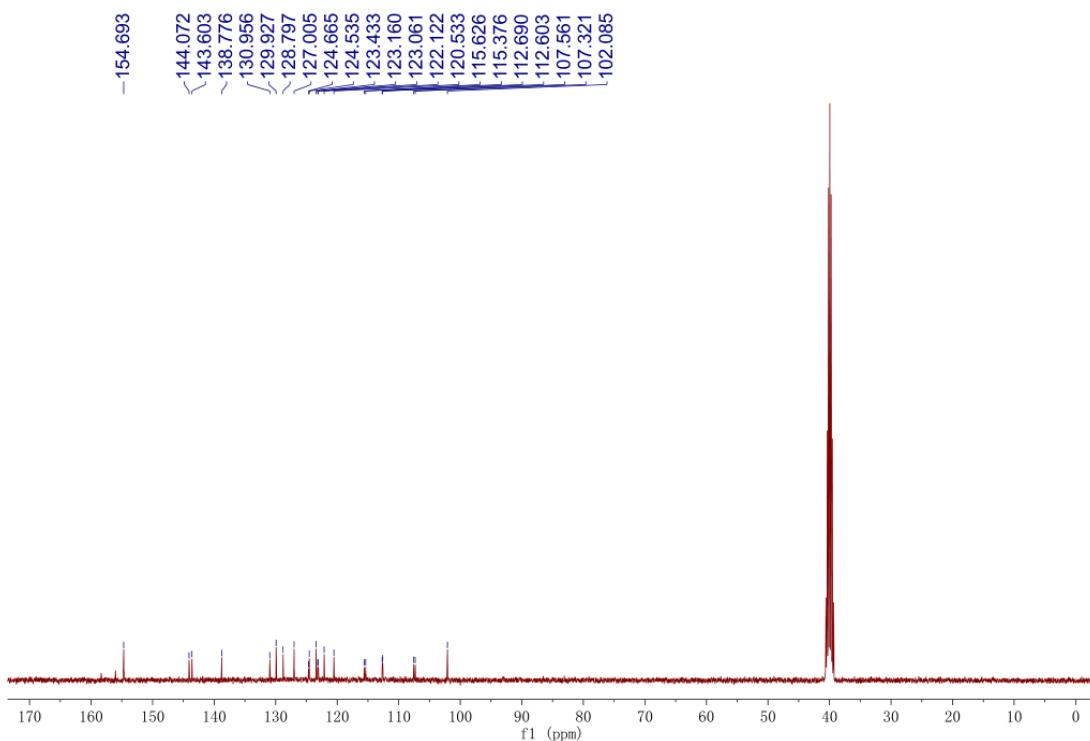


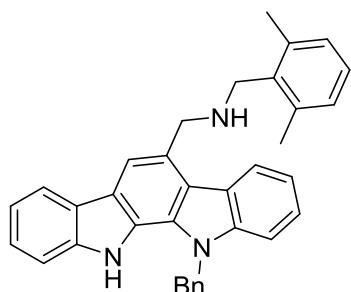
4a



4b







5

