Supporting Information

# Metal-free benzannulation of 1,7-diynes toward unexpected 1-aroyl-2-naphthaldehydes and their application in fused aza-heterocyclic synthesis

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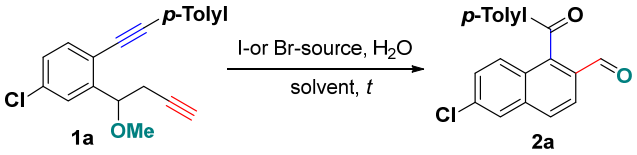
## Context

**General Information**

$^1$H NMR ($^{13}$C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (DMSO-$d_6$) with chemical shift ($\delta$) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

## Condition optimization

**Table 1. Optimization of Reaction Conditions**[a]




| Entry | I- or Br-source (equiv) | Solvent | *t* (°C) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | $I_2$ (2.0) | $CH_3CN$ | 50 | 27%[c] |
| 2 | $I_2$ (2.0) | $CH_3CN$ | 50 | 47% |
| 3 | $I_2$ (3.0) | $CH_3CN$ | 50 | 40% |
| 4 | $I_2$ (1.0) | $CH_3CN$ | 50 | 66% |
| 5 | $I_2$ (0.5) | $CH_3CN$ | 50 | 48% |
| 6 | $I_2$ (1.0) | EtOH | 50 | ND[d] |
| 7 | $I_2$ (1.0) | DMSO | 50 | trace |
| 8 | $I_2$ (1.0) | 1,4-dioxane | 50 | 21% |
| 9 | $I_2$ (1.0) | DCE | 50 | 24% |
| 10 | $I_2$ (1.0) | EA | 50 | trace |
| 11 | TBAI (1.0) | $CH_3CN$ | 50 | NR[e] |
| 12 | NIS (1.0) | $CH_3CN$ | 50 | 37% |
| 13 | $PhI(OAc)_2$ (1.0) | $CH_3CN$ | 80 | NR[e] |
| 14 | NBS (1.0) | $CH_3CN$ | 80 | NR[e] |
| 15 | $I_2$ (1.0) | $CH_3CN$ | 60 | 72% |
| 16 | $I_2$ (1.0) | $CH_3CN$ | 70 | 62% |
| 17 | $I_2$ (1.0) | $CH_3CN$ | 80 | 50% |
| 18 | $I_2$ (1.0) | $CH_3CN$ | 60 | 31%[f] |
| 19 | $I_2$ (1.0) | $CH_3CN$ | 60 | trace[g] |

[a]Reaction conditions: **1a** (0.5 mmol), I-source (X equiv) $H_2O$ (2.0 equiv), solvent (3.0 mL), under $O_2$ conditions, [b]Isolated yield. [c]Under air conditions. [d]Not detected (ND).[e]Not reaction (NR). [f]Use of TBHP (2.0 equiv) under Ar conditions. [g]Under Ar conditions

Our initial investigation was started with the treatment of benzene-tethered 1,7-diyne **1a** by water and 2.0 equivalents of $I_2$ under air conditions in acetonitrile at 50 °C, and the unexpected 2-naphthaldehyde **2a** was generated in a low 27% yield (Table 1, entry 1). To our delight, the reaction under $O_2$ conditions could work more efficiently, leading to the formation of 2-naphthaldehyde product **2a** in 47% yield (entry 2). We next optimized conditions by changing the amount of $I_2$. Increasing the loading of $I_2$ (3.0 equiv) was harmful to the yield of product **2a** (entry 3) whereas lowering the loading of $I_2$ to 1.0 equivalent

remarkably facilitated this reaction process and afforded a higher 66% yield (entry 4). Further decrease of the loading of $I_2$ did not improve the reaction efficiency (entry 5). Subsequently, we investigated the solvent effect for this transformation with use of various solvents such as EtOH, dimethylsulfoxide (DMSO), 1,4-dioxane, 1,2-dichloroethane (DCE), and ethyl acetate (EA). All these attempted solvents were inferior to acetonitrile in terms of reaction yields (entries 6-10). Screening other I- sources, such as tetrabutylammonium iodide (TBAI), *N*-iodosuccinimide (NIS) and $PhI(OAc)_2$, did not show any improvements (entries 11-13). The reaction did not proceed by using *N*-bromosuccinimide (NBS, entry 14). It was also found that the reaction temperature affected the reaction efficiency. Elevating reaction temperature to 60 $^oC$ facilitated this transformation, delivering the product **2a** in a higher 72% yield (entry 15). The lower conversion was detected with reaction temperature being at either higher 70 or 80°C (entries 16-17). Using *tert*-Butyl hydroperoxide (TBHP) as an oxidant, the reaction under Ar conditions gave the desired product **2a** in 31% yield whereas only trace amount of product **2a** was detected when the reaction was carried out under Ar conditions without any oxidant.

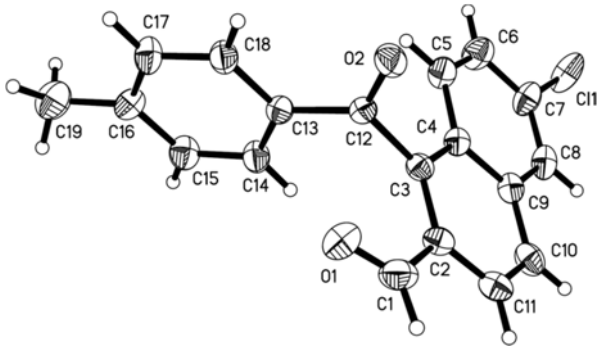



**Figure 1** The ORTEP Drawing of **2a** (Thermal ellipsoids are set at 30% probability level)

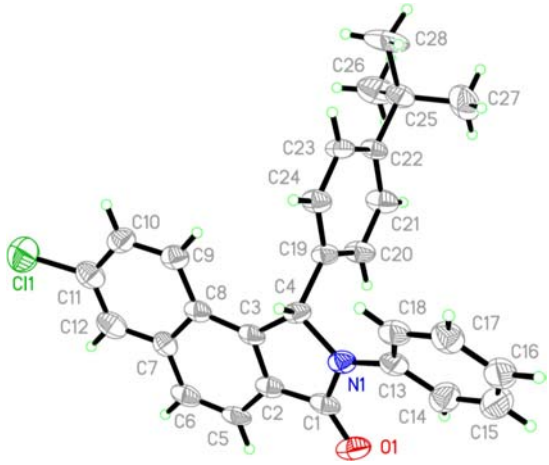



**Figure 2** The ORTEP Drawing of **4h** (Thermal ellipsoids are set at 30% probability level)

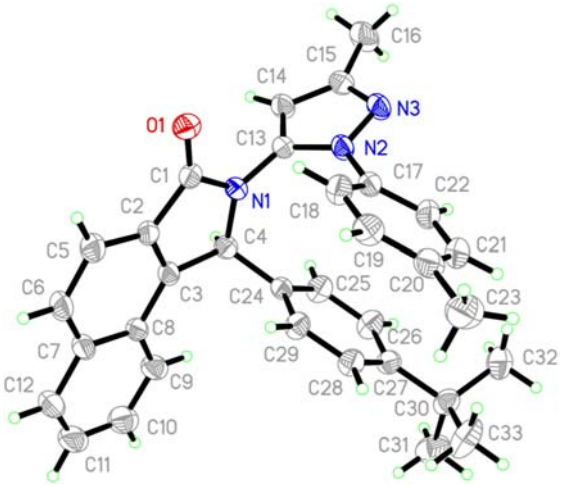
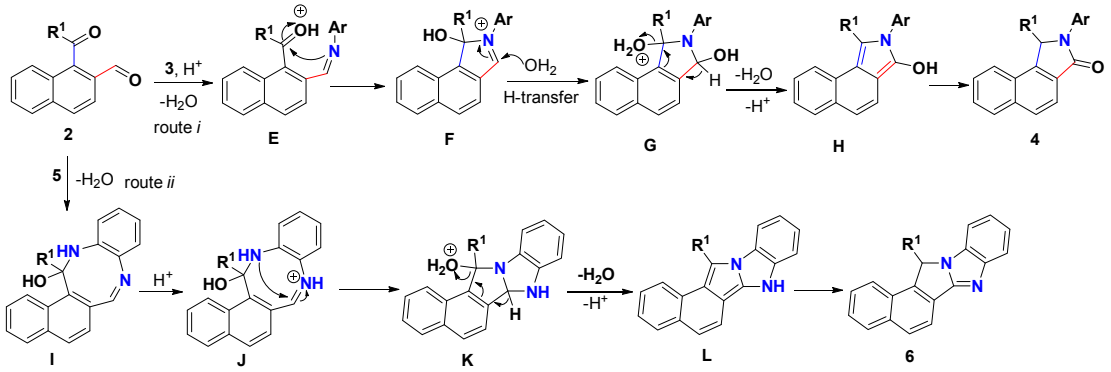


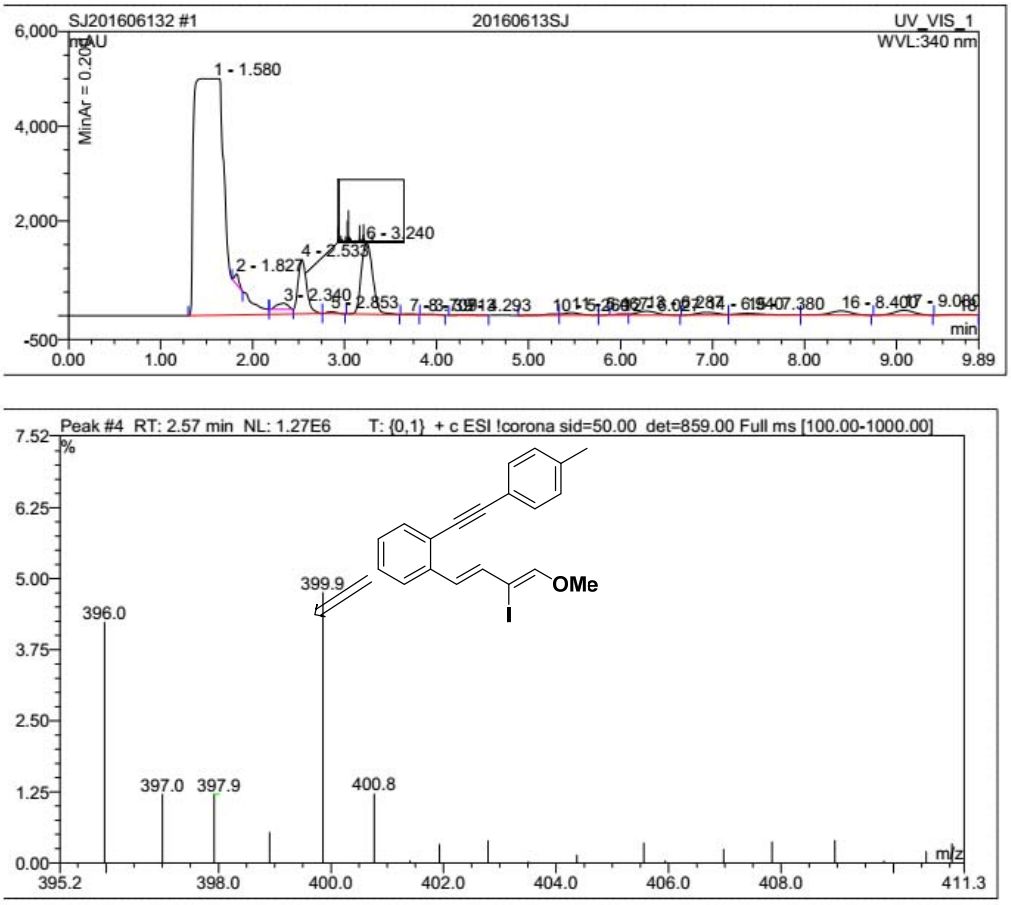

**Figure 3** The ORTEP Drawing of **4l** (Thermal ellipsoids are set at 30% probability level)

**Scheme 1**. Plausible mechanisms for forming **4** and **6**



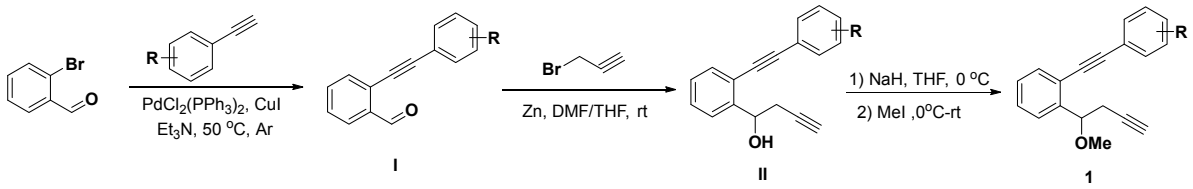

The formation of products **4** involved *in situ* formation of imines (**2** to **E**), 5-*exo*-*trig* cyclization (**E** to **F**), nucleophilic addition of $H_2O$ (**F** to **G**), dehydration and tautomerization (**G** to **4**) sequence (Scheme 1, route *i*). Similar to the above, the synthesis of products **6** is expected to consist of nucleophilic additions-dehydration (**2** to **I**), intramolecular cyclization (**I** to **K**), second dehydration and tautomerization (**K** to **6**) sequence (Scheme 1, route *ii*).

**Overlay of Samples and Spectra from Integration View**




LC-MS Spectra of Intermediate **B**

General Procedure for the Synthesis of Compounds **1**




Under Ar conditions, a mixture of 2-bromobenzaldehyde (10.0 mmol), CuI (2 mol%), $PdCl_2(PPh_3)_2$ (2 mol%) and $Et_3N$ (60 mL) as solvent were stirred at 50 °C，then ethynylbenzene (1.05 equiv) was added into the reaction system by dropwise. The resulting mixture was stirred until TLC indicated complete consumption of the starting material. Subsequent filtration through a pad of Celite® rinsing with $Et_2O$, The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford compound I (90%-100% yield).

Under Ar atmosphere, a mixture of compound I (5.0 mmol, 1.0 equiv), 3-bromoprop-1-yne (1.5 equiv) and zinc powder (4 equiv) in 60 mL of THF/DMF (1/1) was stirred at room temperature and the reaction system was detected by TLC . After completion of the reaction, the residue was quenched with saturated $NH_4Cl$ solution, extracted with ethyl acetate and dried on $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (EtOAc/hexanes, 1:10) to give compound II as white solid (80%-90% yield).

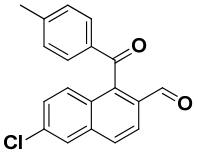
To a solution of compound II (4.0 mmol, 1.0 equiv) in anhydrous THF (20 mL), NaH (2.0 equiv) was added by dropwise at 0 °C. After stirring for 0.5 hours, $CH_3I$ (1.2 equiv) was added and then the reaction mixture was stirred at room temperature. After the mixture was stirred overnight. The reaction mixture was quenched with saturated $NH_4Cl$ solution, extracted with ethyl acetate and dried on $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (EtOAc/hexanes, 1:100) to give compound **1** (oil, 80%-95% yield).

General Procedure for the Synthesis of Products **2**

Example for the synthesis of **2a**: **6-chloro-1-(4-methylbenzoyl)-2-naphthaldehyde**

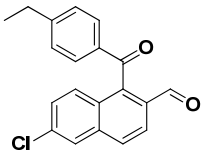
To a 10-mL Schlenk tube under $O_2$ conditions, 4-chloro-2-(1-methoxybut-3-yn-1-yl)-1- (*p*-tolylethynyl)benzene (**1a**, 0.5 mmol, 155 mg, 1.0 equiv) , $I_2$ (0.5 mmol, 127 mg, 1.0 equiv.) and $H_2O$ (1.0 mmol, 18 mg, 2.0 equiv) as well as acetonitrile (3.0 mL) were successively added. Then the tube was stirred at 60 °C for 8.0 hours until complete consumption of **1a** as monitored by TLC analysis. After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 50:1) to afford the desired product **2a** as a white solid.

**6-Chloro-1-(4-methylbenzoyl)-2-naphthaldehyde (2a)**



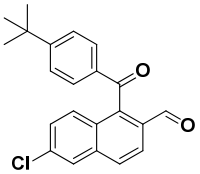

111 mg, 72%; white solid, mp 146-147 °C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.06 (s, 1H), 8.33-8.28 (m, 2H), 8.21 (d, $J$ = 8.8 Hz, 1H), 7.63-7.59 (m, 2H), 7.58 (d, $J$ = 2.4 Hz, 2H), 7.31 (d, $J$ = 8.0 Hz, 2H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 196.8, 192.2, 145.4, 140.5, 136.8, 135.1, 134.6, 131.2, 130.1, 129.7, 129.5, 129.3, 128.9, 128.2, 127.8(4), 127.8(1), 21.7. IR (film, ν, cm$^{-1}$) 2916, 1689, 1663, 1603, 1562, 1457, 1374, 921, 815. HRMS (ESI) m/z calcd for $C_{19}H_{13}ClO_2Na$ $[M+Na]^+$ 331.0502, found 331.0493.

**6-Chloro-1-(4-ethylbenzoyl)-2-naphthaldehyde (2b)**



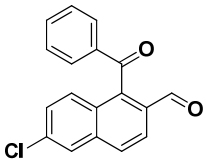
113 mg, 70%; white solid, mp 147-148 °C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.07 (s, 1H), 8.37- 8.28 (m, 2H), 8.21 (d, $J$ = 8.4Hz, 1H), 7.66-7.54 (m, 4H), 7.35 (d, $J$ = 7.6 Hz, 2H), 2.71-2.62 (m, 2H), 1.18 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 196.8, 192.3, 151.3, 140.5, 136.8, 135.3, 134.6, 131.2, 129.7, 129.6, 129.3, 129.0, 128.9, 128.2, 127.8, 28.7, 15.5. IR(film,ν,cm$^{-1}$) 2975, 2940, 1693, 1660, 1603, 1566, 1463, 1415, 1375, 812. HR-MS (ESI) m/z calcd for $C_{20}H_{15}ClO_2Na$ $[M+Na]^+$ 345.0658, found 345.0667.

**1-(4-(*tert*-Butyl)benzoyl)-6-chloro-2-naphthaldehyde (2c)**



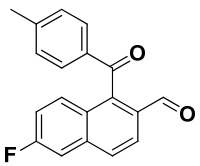
124 mg, 71%; white solid, mp 137-138 °C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.07 (s, 1H), 8.34 (d, $J$ = 1.6 Hz, 1H), 8.31 (d, $J$ = 8.4 Hz, 1H), 8.21 (d, $J$ = 8.4 Hz, 1H), 7.65-7.58 (m, 4H), 7.53 (d, $J$ = 8.4 Hz, 2H), 1.28 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 196.8, 192.3, 157.8, 140.5, 136.8, 135.0, 134.6, 131.1, 129.7, 129.3, 129.3, 128.9, 128.2, 127.9, 127.8, 126.4, 35.5, 31.2. IR (film, ν, cm$^{-1}$) 2964, 1700, 1660, 1605, 1458, 1375, 1361, 922, 778. HR-MS (ESI) m/z calcd for $C_{22}H_{19}ClO_2Na$ $[M+Na]^+$ 373.0971, found 373.0979.

**1-Benzoyl-6-chloro-2-naphthaldehyde (2d)**



90 mg, 61%; white solid, mp 154-155 °C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.08 (s, 1H), 8.32 (d, $J$ = 9.2Hz, 2H), 8.23 (d, $J$ = 8.4 Hz, 1H), 7.71-7.66 (m, 3H), 7.64-7.57 (m, 2H), 7.53-7.49 (m, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.4, 192.4, 140.0, 137.4, 136.8, 134.6, 134.6, 131.3, 129.8, 129.6, 129.4, 129.3, 128.8, 128.2(0), 128.2(6), 127.9. IR (film, ν, cm$^{-1}$) 3057, 2970, 1697, 1659, 1601, 1564, 1459, 913,852, 748. HR-MS (ESI) m/z calcd for $C_{18}H_{11}ClO_2Na$ $[M+Na]^+$ 317.0345, found 317.0350.

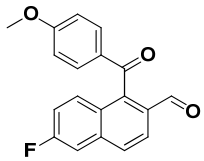
**6-Fluoro-1-(4-methylbenzoyl)-2-naphthaldehyde (2f)**



96 mg, 66%; white solid, mp 123-124 °C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.06 (s, 1H), 8.30 (d, $J$ = 8.8 Hz, 1H), 8.19 (d, $J$ = 8.8 Hz, 1H), 8.02-7.98 (m, 1H), 7.66-7.62 (m, 1H), 7.59 (d, $J$ = 8.0 Hz, 2H), 7.55-7.49 (m, 1H), 7.31 (d, $J$ = 8.0 Hz, 2H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 196.9, 192.1, 162.1 ($^1J_{CF}$ = 248.3 Hz), 145.3, 140.7, 137.5 ($^4J_{CF}$ = 10.2 Hz), 135.1, 130.5 ($^6J_{CF}$ = 2.5 Hz), 130.1, 130.0 ($^5J_{CF}$ = 9.7 Hz), 129.8, 129.8, 129.4, 127.6, 127.0, 119.1 ($^2J_{CF}$ = 25.7 Hz), 112.5 ($^3J_{CF}$ = 20.9 Hz), 21.7. $^1$F NMR (377 MHz, DMSO-$d_6$; $\delta$, ppm) -108.9. IR (film, ν,

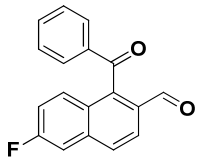
cm$^{-1}$) 3021, 1690, 1654, 1602, 1466, 1373, 958, 870. HR-MS (ESI) m/z calcd for $C_{19}H_{13}FO_2Na$ $[M+Na]^+$ 315.0797, found 315.0798.

**6-Fluoro-1-(4-methoxybenzoyl)-2-naphthaldehyde (2g)**



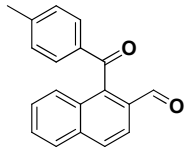
68 mg, 44%; Colorless oil ; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.09 (s, 1H), 8.38 (d, $J$ = 8.4 Hz, 1H), 8.31-8.13 (m, 4H), 7.72-7.68 (m, 1H), 7.55 (d, $J$ = 8.8 Hz, 1H), 7.25 (d, $J$ = 10.8 Hz, 1H), 7.04 (d, $J$ = 8.8 Hz, 1H), 3.91 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 195.4, 192.2, 164.4, 161.3 ($^1J_{CF}$ = 246.1 Hz), 140.3, 140.20, 133.24, 132.4 ($^4J_{CF}$ = 9.3 Hz), 131.91, 131.6, 130.6 ($^5J_{CF}$ = 7.6 Hz), 130.5, 127.8, 125.7 ($^6J_{CF}$ = 2.2 Hz), 120.2 ($^2J_{CF}$ = 25.2 Hz), 114.9, 114.5, 109.7 ($^3J_{CF}$ = 21.8 Hz), 56.1. $^1$F NMR (377 MHz, DMSO-$d_6$; $\delta$, ppm) -109.9. IR (film, ν, cm$^{-1}$) 3062, 1694, 1658, 1604, 1502, 1461, 1375, 914, 835. HR-MS (ESI) m/z calcd for $C_{19}H_{13}FO_3Na$ $[M+Na]^+$ 331.0746, found 331.0744.

**1-Benzoyl-6-fluoro-2-naphthaldehyde (2h)**



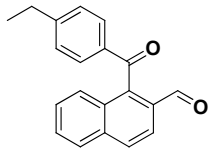
90 mg, 65%; white solid, mp 82-83 $^o$C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.07 (s, 1H), 8.33 (d, $J$ = 8.8 Hz, 1H), 8.22 (d, $J$ = 8.8 Hz, 1H), 8.03-7.99 (m, 1H), 7.70-7.63 (m, 4H), 7.56-7.49 (m, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.5, 192.4, 162.1 ($^1J_{CF}$ = 248.3 Hz), 140.2, 137.5 ($^4J_{CF}$ = 10.3 Hz), 137.4, 134.6, 130.6 ($^6J_{CF}$ = 2.5Hz), 130.0 ($^5J_{CF}$ = 9.9 Hz), 130.0, 129.6, 129.2, 128.0, 126.9, 119.2 ($^2J_{CF}$ = 25.8 Hz), 112.5 ($^3J_{CF}$ = 20.9 Hz). $^1$F NMR (377 MHz, DMSO-$d_6$; $\delta$, ppm) -108.9. IR (film, ν, cm$^{-1}$) 3065, 1697, 1661, 1623, 1470, 887, 792. R-MS (ESI) m/z calcd for $C_{18}H_{11}FO_2Na$ $[M+Na]^+$ 301.0641, found 301.0649.

**1-(4-Methylbenzoyl)-2-naphthaldehyde (2i)**



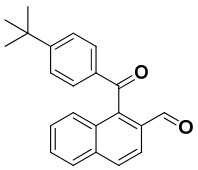
84 mg, 61%; white solid, mp 140-141 $^o$C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.07 (s, 1H), 8.31 (d, $J$ = 8.8 Hz, 1H), 8.18-8.12 (m, 2H), 7.77-7.72 (m, 1H), 7.62-7.54 (m, 4H), 7.30 (d, $J$ = 8.0 Hz, 2H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.3, 192.3, 145.2, 140.7, 136.0, 135.3, 130.8, 130.4, 130.1, 129.9, 129.8, 129.4, 129.1, 128.7, 126.7, 126.3, 21.7. IR (film, ν, cm$^{-1}$) 3061, 1693, 1662, 1601, 1462, 1375, 815, 742. HR-MS (ESI) m/z calcd for $C_{19}H_{14}O_2Na$ $[M+Na]^+$ 297.0891, found 297.0895.

**1-(4-Ethylbenzoyl)-2-naphthaldehyde (2j)**



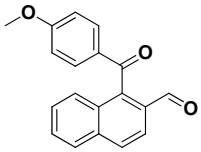
91 mg, 63%; white solid, mp 85-86 °C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.08 (s, 1H), 8.32 (d, $J$ = 8.4 Hz, 1H), 8.19-8.13 (m, 2H), 7.78-7.72 (m, 1H), 7.64 - 7.55 (m, 4H), 7.34 (d, $J$ = 8.0 Hz, 2H), 2.70-2.63 (m, 2H), 1.18 (t, $J$ =7.6Hz, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.3, 192.4, 151.1, 140.7, 136.0, 135.5, 130.8, 130.4, 129.9, 129.8, 129.5, 129.1, 128.9, 128.7, 126.7, 126.4, 28.7, 15.5. IR(film,ν,cm$^{-1}$) 3057, 2970, 1697, 1659, 1601, 1564, 1459, 1376, 913, 852, 748. HR-MS (ESI) m/z calcd for $C_{20}H_{16}O_2Na$ $[M+Na]^+$ 311.1048, found 311.1041.

**1-(4-(*tert*-Butyl)benzoyl)-2-naphthaldehyde (2k)**



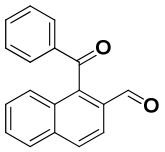
112 mg, 71%; white solid, mp 162-163 °C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.08 (s, 1H), 8.32 (d, $J$ = 8.4 Hz, 1H), 8.18-8.14 (m, 2H), 7.77-7.73 (m, 1H), 7.64-7.57 (m, 4H), 7.53 (d, $J$ = 8.4 Hz, 2H), 1.28 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.3, 192.4, 157.6, 140.7, 136.0, 135.2, 130.8, 130.4, 129.9, 129.8, 129.2, 129.1, 128.7, 126.8, 126.4, 35.4, 31.2. IR (film, ν, cm$^{-1}$) 2961, 1694, 1664, 1603, 1465, 1407, 1376, 825,761. HR-MS (ESI) m/z calcd for $C_{22}H_{20}O_2Na$ $[M+Na]^+$ 339.1361, found 339.1369.

**1-(4-Methoxybenzoyl)-2-naphthaldehyde (2l)**



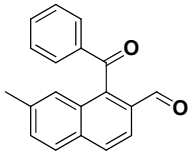
61 mg, 42%; Colorless oil; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.07 (s, 1H), 8.29 (d, $J$ = 8.4Hz, 1H), 8.16-8.11 (m, 2H), 7.76-7.71 (m, 1H), 7.66 (d, $J$ = 8.4 Hz, 2H), 7.59 (d, $J$ = 4.0 Hz, 2H), 7.02 (d, $J$ = 8.8 Hz, 2H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 196.0, 192.1, 164.3, 141.3, 136.0, 131.8, 130.9, 130.7, 130.3, 129.9, 129.8, 129.1, 128.6, 126.8, 125.8, 114.8, 56.1. IR (film, ν, cm$^{-1}$) 3052, 1693, 1655, 1602, 1547, 1451, 1382, 914, 832. HR-MS (ESI) m/z calcd for $C_{19}H_{14}O_3Na$ $[M+Na]^+$ 313.0841, found 313.0843.

**1-Benzoyl-2-naphthaldehyde (2m)**



75 mg, 58%; white solid, mp 96-97 °C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.09 (s, 1H), 8.34 (d, $J$ = 8.4 Hz, 1H), 8.17 (d, $J$ = 8.4 Hz, 2H), 7.78-7.73 (m, 1H), 7.72-7.64 (m, 3H), 7.63-7.55 (m, 2H), 7.54-7.46 (m, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.9, 192.6, 140.2, 137.5, 136.0, 134.5, 130.9, 130.5, 129.9, 129.7, 129.5, 129.2(1), 129.2(6), 128.8, 126.7(2), 126.7(0). IR (film, ν, cm$^{-1}$) 2981, 1692, 1661, 1602, 1553, 1457, 824, 738. HR-MS (ESI) m/z calcd for $C_{18}H_{12}O_2Na$ $[M+Na]^+$ 283.0735, found 283.0731.

**1-Benzoyl-7-methyl-2-naphthaldehyde (2n)**



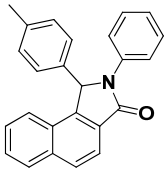
85 mg, 62%; white solid, mp 94-95 °C; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.06 (s, 1H), 8.28 (d, $J$ = 8.4 Hz, 1H), 8.12-8.06 (m, 2H), 7.72-7.64 (m, 3H), 7.60 (d, $J$ = 8.4 Hz, 1H), 7.53-7.48 (m, 2H), 7.33 (s, 1H), 2.38 (s, 3H).$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 198.0, 192.6, 139.4, 138.4, 137.6, 134.5, 134.4, 132.1, 131.0, 130.2, 130.0, 129.5, 129.2, 129.0, 126.0, 125.1, 21.9. IR (film, ν, cm$^{-1}$) 3061, 1697, 1664, 1603, 1465, 1375, 913, 809, 748. HR-MS (ESI) m/z calcd for $C_{19}H_{14}O_2Na$ $[M+Na]^+$ 297.0891, found 297.0887.

General procedure for the synthesis of Products **4**

Example for the synthesis of **4a**: **2-phenyl-1-(*p*-tolyl)-1*H*-benzo[e]isoindol-3(2*H*)-one**

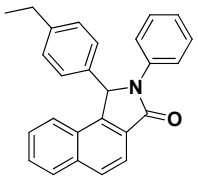
Microwave Heating: 1-(4-methylbenzoyl)-2-naphthaldehyde (**2i**, 0.2 mmol, 55 mg, 1.0 equiv) and aniline (**3a**, 0.3 mmol, 28 mg, 1.5 equiv) were introduced in a 10-mL Initiator$^{TM}$ reaction vial. Then *p*-toluenesulfonic acid (0.2 mmol, 35 mg, 1.0 equiv) and ethanol (2.0 mL) were successively added into the reaction system. Subsequently, the reaction vial was capped and then pre-stirring for 20 second. The mixture was irradiated (Time: 20 min, Temperature: 120 °C; Absorption Level: High; Fixed Hold Time: 30 min) until TLC (petroleum ether: ethyl acetate 5:1) revealed that conversion of the starting material **2i** was completed. The reaction mixture was then cooled to room temperature and then diluted with cold water (8.0 mL). The solid product was collected by Büchner filtration and was purified by recrystallization from 95% ethanol afford the desired pure **4a**

**2-Phenyl-1-(*p*-tolyl)-1*H*-benzo[*e*]isoindol-3(2*H*)-one (4a)**



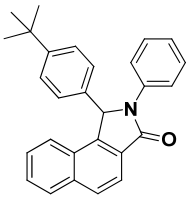

53 mg, 76%; white solid, mp 167-168 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.04-7.98 (m, 2H), 7.95 (d, $J$ = 8.0 Hz, 1H), 7.73 (d, $J$ = 8.0 Hz, 1H), 7.58-7.51 (m, 3H), 7.44-7.39 (m, 1H), 7.35-7.29 (m, 2H), 7.13 (d, $J$ = 7.6 Hz, 3H), 7.03 (d, $J$ = 7.6 Hz, 2H), 6.39 (s, 1H), 2.23 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 167.1, 143.6, 138.3, 137.3, 135.8, 130.0, 129.7, 129.3, 128.8, 128.0, 127.7, 127.6, 127.2, 125.4, 123.8(1), 123.8(6), 120.1, 65.7, 21.2. IR (film, ν, cm$^{-1}$) 3064, 1694, m1596, 1500, 1457, 1382, 1358, 770. HR-MS (ESI) m/z calcd for $C_{25}H_{19}NONa$ $[M+Na]^+$ 372.1364, found 372.1362.

**1-(4-Ethylphenyl)-2-phenyl-1*H*-benzo[*e*]isoindol-3(2*H*)-one (4b)**



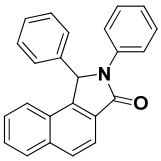

50 mg, 69%; white solid, mp 174-175 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.04 (d, $J$ = 6.8 Hz, 1H), 7.97 (d, $J$ = 8.0 Hz, 1H), 7.77 (d, $J$ = 8.8 Hz, 1H), 7.59 (d, $J$ = 8.4 Hz, 2H), 7.55 (d, $J$ = 7.6 Hz, 1H), 7.47-7.42 (m, 1H), 7.37-7.33 (m, 2H), 7.26 (s, 1H), 7.19-7.13 (m, 3H), 7.08 (d, $J$ = 8.0 Hz, 2H), 6.42 (s, 1H), 2.61-2.52 (m, 2H), 1.16 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 168.0, 144.5, 143.7, 137.3, 135.8, 134.4, 130.0, 129.5, 129.2, 129.1, 128.8, 128.4, 128.1, 127.6, 127.2, 125.3, 123.8, 123.7, 121.3, 120.0, 65.7, 28.4, 15.0. IR (film, ν, cm$^{-1}$) 3063, 2964, 1682, 1596, 1500, 1456, 1371, 850, 761. HR-MS (ESI) m/z calcd for $C_{26}H_{21}NONa$ $[M+Na]^+$ 386.1521, found 386.1515.

**1-(4-(*tert*-Butyl)phenyl)-2-phenyl-1*H*-benzo[*e*]isoindol-3(2*H*)-one (4c)**



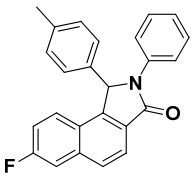
65 mg, 83%; white solid, mp 222-223 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) δ 8.07-8.00 (m, 2H), 7.97 (d, $J$ = 8.4 Hz, 1H), 7.78 (d, $J$ = 8.4 Hz, 1H), 7.61 (d, $J$ = 8.4 Hz, 2H), 7.58-7.53 (m, 1H), 7.47-7.42 (m, 1H), 7.38-7.33 (m, 2H), 7.26 (d, $J$ = 8.4 Hz, 2H), 7.21-7.13 (m, 3H), 6.42 (s, 1H), 1.23 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 168.1, 151.4, 143.7, 137.4, 135.8, 134.1, 129.9, 129.5, 129.2, 128.8, 127.8, 127.6(2), 127.6(8), 127.1, 125.9, 125.2, 123.9, 123.5, 120.1, 65.5, 34.5, 31.2. IR (film, ν, cm$^{-1}$) 3057, 2958, 1686, 1597, 1500, 1367, 837, 783, 756. HR-MS (ESI) m/z calcd for $C_{28}H_{25}NONa$ $[M+Na]^+$ 414.1834, found 414.1826.

**1,2-Diphenyl-1*H*-benzo[e]isoindol-3(2*H*)-one (4d)**



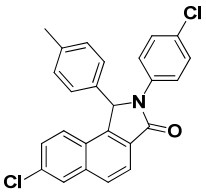
48 mg, 72%; white solid, mp 196-197 °C; $^1$H NMR (400 MHz, $CDCl_3$ ; $\delta$, ppm) 8.08-8.02 (m, 2H), 7.98 (d, $J$ = 8.4 Hz, 1H), 7.74 (d, $J$ = 8.4 Hz, 1H), 7.59-7.54 (m, 3H), 7.46 -7.42 (m, 1H), 7.37-7.32 (m, 2H), 7.28-7.24 (m, 5H), 7.17-7.13 (m, 1H), 6.44 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 168.0, 143.5, 137.4, 137.2, 135.8, 130.1, 129.6, 129.3, 129.0, 128.9, 128.6, 128.2, 127.7, 127.5, 127.2, 125.5, 123.8, 123.7, 120.1, 65.9. IR (film, ν, cm$^{-1}$) 3063, 3027, 1693, 1596, 1494, 1376, 1357, 759, 694. HR-MS (ESI) m/z calcd for $C_{24}H_{17}NONa$ $[M+Na]^+$ 358.1208, found 358.1207.

**7-Fluoro-2-phenyl-1-(*p*-tolyl)-1*H*-benzo[*e*]isoindol-3(2*H*)-one (4e)**



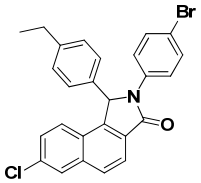
57 mg, 77%; white solid, mp 162-163 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) δ 8.07 (d, $J$ = 8.4 Hz, 1H), 7.95 (d, $J$ = 8.4 Hz, 1H), 7.77-7.72 (m, 1H), 7.61-7.57 (m, 1H), 7.55 (d, $J$ = 8.0 Hz, 2H), 7.38-7.31 (m, 2H), 7.24 - 7.19 (m, 1H), 7.18-7.11 (m, 3H), 7.06 (d, $J$ = 7.6 Hz, 2H), 6.39 (s, 1H), 2.26 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) δ 167.8, 161.5($^1J_{CF}$ = 248.0 Hz), 143.8, 138.6, 137.2, 137.1 ($^4J_{CF}$ = 9.2Hz), 134.0, 129.8, 129.3, 129.3, 129.0 ($^6J_{CF}$ = 2.4 Hz), 128.9, 128.0, 126.3 ($^5J_{CF}$ = 9.1 Hz), 125.5, 124.6, 123.8, 121.2, 117.5 ($^2J_{CF}$ = 25.1 Hz), 112.6 ($^3J_{CF}$ = 20.5 Hz), 65.7, 21.2. $^1$F NMR (377 MHz, DMSO-$d_6$; $\delta$, ppm) -111.2. IR (film, ν, cm$^{-1}$) 3044, 2920, 1685, 1598, 1499, 1365, 876, 762. HR-MS (ESI) m/z calcd for $C_{25}H_{18}FNONa$ $[M+Na]^+$ 390.1270, found 390.1277.

**7-Chloro-2-(4-chlorophenyl)-1-(*p*-tolyl)-1*H*-benzo[*e*]isoindol-3(2*H*)-one (4f)**



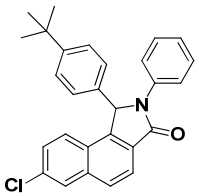
63 mg, 76%; white solid, mp 201-202 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) δ 8.02 (d, $J$ = 8.4 Hz, 1H), 7.93-7.88 (m, 2H), 7.65 (d, $J$ = 9.2 Hz, 1H), 7.49 (d, $J$ = 8.0 Hz, 2H), 7.36 (d, $J$ = 8.8 Hz, 1H), 7.28 (s, 1H), 7.16-7.02 (m, 5H), 6.31 (s, 1H), 2.25 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 167.6, 143.5, 138.8, 136.6, 135.7, 133.9, 133.6, 130.7, 130.0, 129.5, 129.3, 129.0, 128.3, 128.2, 128.1, 127.9, 125.7, 125.3, 124.6, 121.2, 65.5, 21.2. IR (film, ν, cm$^{-1}$) 3028, 2920, 1696, 1495, 1355, m882, 823, 793. HR-MS (ESI) m/z calcd for $C_{25}H_{17}Cl_2NONa$ $[M+Na]^+$ 440.0585, found 440.0587.

**2-(4-Bromophenyl)-7-chloro-1-(4-ethylphenyl)-1*H*-benzo[*e*]isoindol-3(2*H*)-one (4g)**



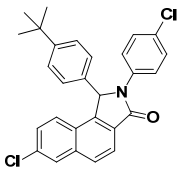

73 mg, 77%; white solid, mp 189-190 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.05 (d, $J$ = 8.0 Hz, 1H), 7.98-7.90 (m, 2H), 7.69 (d, $J$ = 8.4 Hz, 1H), 7.52-7.37 (m, 5H), 7.19-7.06 (m, 4H), 6.35 (s, 1H), 2.63-2.51 (m, 2H), 1.18 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 167.6, 145.0, 143.6, 136.6, 136.3, 133.9, 133.8, 131.9, 129.5, 129.3, 128.7, 128.3, 128.0, 127.9, 125.7, 125.3, 124.8, 121.2, 118.5, 65.4, 28.4, 15.0. IR (film, ν, cm$^{-1}$) 2967, 2930, 1695, 1492, 1459, 1355, 853, 821. HR-MS (ESI) m/z calcd for $C_{26}H_{19}BrClNONa$ $[M+Na]^+$ 498.0236, found 498.0228.

**1-(4-(*tert*-Butyl)phenyl)-7-chloro-2-phenyl-1*H*-benzo[*e*]isoindol-3(2*H*)-one(4h)**



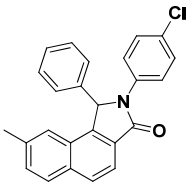

71 mg, 83%; white solid, mp 244-245 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.06 (d, $J$ = 8.4 Hz, 1H), 7.95-7.89 (m, 2H), 7.69 (d, $J$ = 8.8 Hz, 1H), 7.58 (d, $J$ = 8.0 Hz, 2H), 7.39-7.32 (m, 3H), 7.26 (d, $J$ = 8.0 Hz, 2H), 7.19 -7.13 (m, 3H), 6.38 (s, 1H), 1.24 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 167.7, 151.7, 143.7, 137.2, 136.5, 133.8, 133.7, 129.8, 129.1, 128.9, 128.1, 128.0, 127.7, 126.0, 125.8, 125.4(2), 125.4(8), 123.6, 121.3, 65.4, 34.5, 31.2. IR (film, ν, cm$^{-1}$) 3058, 2953, 1685, 1596, 1499, 1367, 855, 749. HR-MS (ESI) m/z calcd for $C_{28}H_{24}ClNONa$ $[M+Na]^+$ 448.1444, found 448.1448.

**1-(4-(*tert*-Butyl)phenyl)-7-chloro-2-(4-chlorophenyl)-1*H*-benzo[e]isoindol-3(2*H*)-one(4i)**



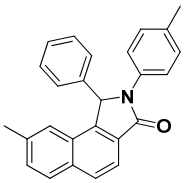

76 mg, 81%; white solid, mp 170-171 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) δ 8.05 (d, $J$ = 8.4 Hz, 1H), 7.96- 7.90 (m, 2H), 7.69 (d, $J$ = 8.8Hz, 1H), 7.55 (d, $J$ = 7.6 Hz, 2H), 7.39 (d, $J$ = 9.2Hz, 1H), 7.33-7.27 (m, 4H), 7.15 (d, $J$ = 7.6 Hz, 2H), 6.36 (s, 1H), 1.25 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 167.7, 151.9, 143.6, 136.6, 135.8, 133.8, 133.4, 130.6, 129.4, 129.2, 129.0, 128.2, 128.0, 127.6, 126.2, 125.8, 125.4, 124.5, 121.2, 65.4, 34.6, 31.2. IR (film, ν, cm$^{-1}$) 2963, 1698, 1495, 1363, 855, 830. HR-MS (ESI) m/z calcd for $C_{28}H_{23}Cl_2NONa$ $[M+Na]^+$ 482.1054, found 482.1050.

**2-(4-Chlorophenyl)-8-methyl-1-phenyl-1*H*-benzo[*e*]isoindol-3(2*H*)-one(4j)**



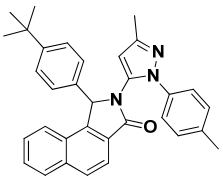
61 mg, 80%; white solid, mp 160-161 ºC; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) δ 7.97 (s, 2H), 7.87 (d, $J$ = 8.4 Hz, 1H), 7.57 - 7.48 (m, 3H), 7.39 (d, $J$ = 8.0 Hz, 1H), 7.33-7.23 (m, 7H), 6.36 (s, 1H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 168.1, 142.6, 137.2(5), 137.2(6), 135.9, 134.1, 130.6, 130.1, 129.9, 129.2, 129.1, 129.0, 128.7, 128.1, 127.6, 124.6, 122.7, 119.1, 65.8, 22.0. IR (film, ν, cm$^{-1}$) 3058, 2921, 1690, 1595, 1494, 1456, 1369, 850, 836. HR-MS (ESI) m/z calcd for $C_{25}H_{18}ClNONa$ $[M+Na]^+$ 406.0975, found 406.0971.

**8-Methyl-1-phenyl-2-(*p*-tolyl)-1H-benzo[*e*]isoindol-3(2*H*)-one (4k)**



54 mg, 74%; white solid, mp 219-220 ºC; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 7.98 (s, 2H), 7.87 (d, $J$ = 8.4 Hz, 1H), 7.48 (s, 1H), 7.43-7.35 (m, 4H), 7.27-7.25 (m, 4H), 7.14 (d, $J$ = 8.0 Hz, 2H), 6.35 (s, 1H), 2.40 (s, 3H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 168.1, 142.7, 137.6, 137.0, 135.2, 134.6, 134.0, 129.9, 129.7, 129.5, 129.0, 128.9, 128.5, 128.2, 127.7, 123.9, 122.8, 119.2, 66.1, 21.9, 21.0. IR (film, ν, cm$^{-1}$) 3061, 2972, 1694, 1597, 1500, 1376. 836, 783. HR-MS (ESI) m/z calcd for $C_{26}H_{21}NONa$ $[M+Na]^+$ 386.1521, found 386.1517.

**1-(4-(*tert*-Butyl)phenyl)-2-(3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-yl)-1*H*-benzo[*e*]isoindol-3(2*H*)-one (4l)**



64 mg, 66%; white solid, mp 229-230 ºC; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.02 (s, 2H), 7.97 (d, $J$ = 8.0 Hz, 1H), 7.57-7.52 (m, 1H), 7.44 (d, $J$ = 8.4 Hz, 1H), 7.40-7.35 (m, 1H), 7.19-7.12 (m, 4H), 7.06 (d, $J$ = 8.0 Hz, 2H), 6.76 (d, $J$ = 8.0 Hz, 2H), 5.99 (s, 1H), 5.78 (s, 1H), 2.30 (s, 6H), 1.27 (s, 9H).

$^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 168.9, 151.8, 148.8, 144.2, 137.3, 136.3, 135.9, 135.1, 132.7, 130.0, 129.6, 129.1, 128.6, 128.0, 127.8, 127.6, 127.2, 125.7, 124.3, 124.1, 120.1, 105.2, 67.1, 34.6, 31.2, 21.1, 14.1. IR (film, ν, cm$^{-1}$) 2960, 1698, 1561, 1517, 1382, 1365, 1352, 818, 783, 765. HR-MS (ESI) m/z calcd for $C_{33}H_{31}N_3ONa$ $[M+Na]^+$ 508.2365, found 508.2362.

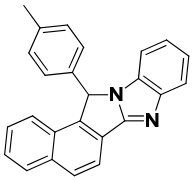
General procedure for the synthesis of **6**

Example for the synthesis of **6a**: **13-(*p*-tolyl)-13*H*-benzo[*e*]benzo[4,5]imidazo[2,1-*a*]isoindole**

Microwave Heating: 1-(4-methylbenzoyl)-2-naphthaldehyde (**2i**, 0.2 mmol, 55 mg, 1.0 equiv) was introduced in a 10-mL Initiator$^{TM}$ reaction vial, acetic acid (2.0 mL), benzene-1,2-diamine (**5**, 0.24 mmol, 26 mg, 1.2 equiv) and trifluoroacetic acid (0.4 mmol, 46 mg, 2.0 equiv) were then successively added into this reaction system. Subsequently, the reaction vial was capped and then pre-stirring for 20 second. The mixture was irradiated (Time: 30 min, Temperature: 120 ºC; Absorption Level: High; Fixed Hold Time: 25 min) until TLC (petroleum ether: acetone 2:1) revealed that

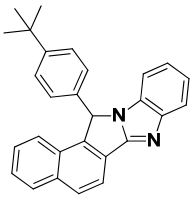
conversion of the starting material **2i** was completed. The reaction mixture was then cooled to room temperature and then diluted with cold water (8.0 mL). The solid product was collected by Büchner filtration and was purified by recrystallization from 95 % ethanol afford the desired pure **6a**.

**13-(*p*-Tolyl)-13H-benzo[*e*]benzo[4,5]imidazo[2,1-*a*]isoindole(6a)**



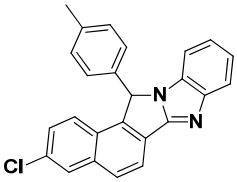
60 mg, 87%; white solid, mp 152-153 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.27 (s, 1H), 8.11-7.82 (m, 3H), 7.68 (s, 1H), 7.48 (d, $J$ = 36.8 Hz, 2H), 7.33 -6.89 (m, 7H), 6.53 (s, 1H), 2.34 (s, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 154.2, 146.8, 140.4, 135.4, 131.6, 130.8, 130.6, 129.6, 129.4, 128.6, 128.2, 128.1, 128.0, 125.5, 125.3, 123.7, 119.5, 117.4, 110.9, 65.9, 21.3. IR (film, ν, cm$^{-1}$) 3058, 1609, 1496, 1457, 1390, 846, 742, 700. HR-MS (ESI) m/z calcd for $C_{25}H_{18}N_2Na$ $[M+Na]^+$ 369.1368, found 369.1365.

**13-(4-(*tert*-Butyl)phenyl)-13*H*-benzo[*e*]benzo[4,5]imidazo[2,1-*a*]isoindole (6b)**



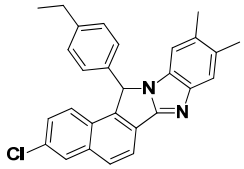
71 mg, 92%; white solid, mp 259-260 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.25 (d, $J$ = 8.0 Hz, 1H), 8.07 (d, $J$ = 8.4 Hz, 1H), 7.97 (d, $J$ = 8.4 Hz, 1H), 7.87 (d, $J$ = 8.0 Hz, 1H), 7.70 (d, $J$ = 8.4 Hz, 1H), 7.54-7.49 (m, 1H), 7.47-7.41 (m, 1H), 7.36 (d, $J$ = 8.0 Hz, 2H), 7.25 (d, $J$ = 8.0 Hz, 3H), 7.21-7.12 (m, 2H), 6.53 (s, 1H), 1.29 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 152.2, 145.3, 134.5, 130.5, 129.3, 128.8, 127.8, 127.4, 126.9, 126.4, 123.5, 122.7, 122.2, 120.4, 118.9, 109.7, 63.5, 34.7, 31.2. IR (film, ν, cm$^{-1}$) 3050, 2960, 1620, 1547, 1519, 1452, 1360, 1321, 827, 748. HR-MS (ESI) m/z calcd for $C_{28}H_{24}N_2Na$ $[M+Na]^+$ 411.1837, found 411.1844.

**3-Chloro-13-(*p*-tolyl)-13H-benzo[*e*]benzo[4,5]imidazo[2,1-*a*]isoindole (6c)**



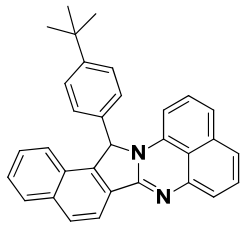
67 mg, 88%; white solid, mp 160-161 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) δ 8.41 (d, $J$ = 8.4 Hz, 1H), 7.89-7.79 (m, 3H), 7.63 (d, $J$ = 8.8 Hz, 1H), 7.44 (d, $J$ = 9.2 Hz, 1H), 7.30-7.19 (m, 7H), 6.86 (s, 1H), 2.35 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 146.8, 140.5, 135.9, 134.7, 130.7, 130.5, 129.5, 129.2, 128.3, 128.0, 126.2, 125.4, 125.2(5), 125.2(6), 120.6, 117.5, 110.9, 65.6, 21.3. IR (film, ν, cm$^{-1}$) 3057, 2924, 1623, 1514, 1452, 1380, 807, 741. HR-MS (ESI) m/z calcd for $C_{25}H_{17}ClN_2Na$ $[M+Na]^+$ 403.0978, found 403.0980.

**3-Chloro-13-(4-ethylphenyl)-9,10-dimethyl-13*H*-benzo[*e*]benzo[4,5]imidazo[2,1-*a*]isoindole (6d)**



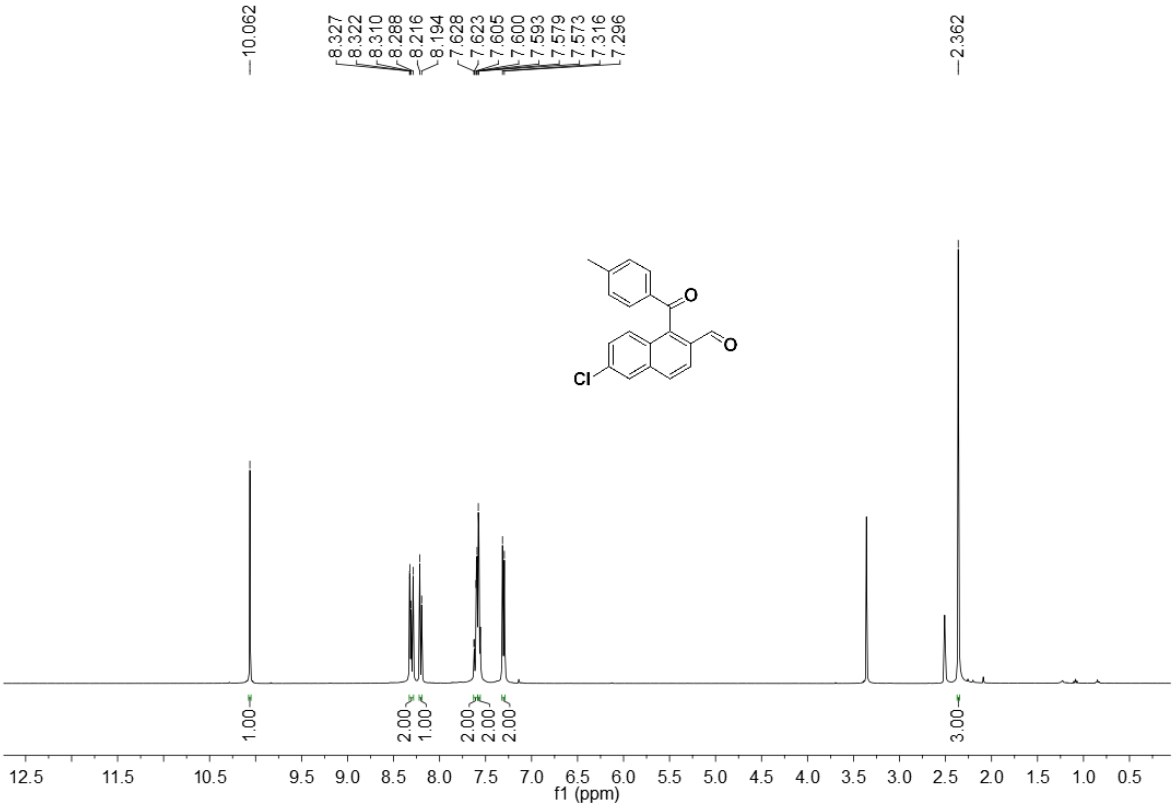
61 mg, 72%; white solid, mp 161-162 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.33 (d, $J$ = 8.0 Hz, 1H), 7.78 (s, 1H), 7.74-7.62 (m, 2H), 7.47 -7.38 (m, 2H), 7.20 (s, 4H), 6.97 (s, 1H), 6.96 (s, 1H), 2.70-2.60 (m, 2H), 2.28 (s, 3H), 2.19 (s, 3H), 1.25-1.17 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 146.8, 146.6, 135.8, 130.6, 130.4, 129.5, 129.3, 128.1, 128.0, 127.4, 126.1, 125.4, 120.6, 116.3, 111.2, 65.8, 28.5, 20.6, 20.2, 15.0. IR (film, ν, cm$^{-1}$) 2966, 1616, 1515, 1457, 1375, 1352, 852, 795, 718. HR-MS (ESI) m/z calcd for $C_{28}H_{23}ClN_2Na$ $[M+Na]^+$ 445.1447, found 445.1439.

**15-(4-(*tert*-Butyl)phenyl)-15*H*-benzo[4,5]isoindolo[2,1-*a*]perimidine (6e)**

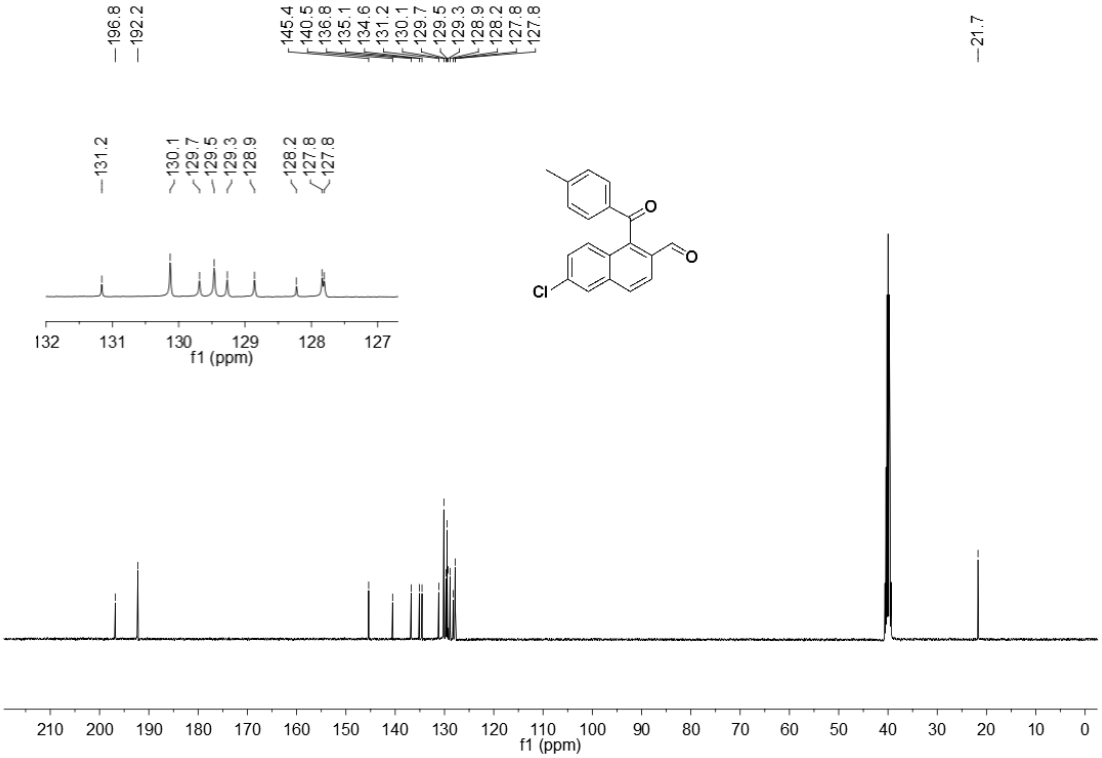


80 mg, 91%; white solid, mp 306-307 °C; $^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.33 (d, $J$ = 7.6 Hz, 1H), 7.92 (d, $J$ = 8.0 Hz, 1H), 7.70-7.61 (m, 2H), 7.54-7.48 (m, 2H), 7.39-7.29 (m, 4H), 7.20-7.01 (m, 5H), 6.90 (s, 1H), 6.57 (d, $J$ = 4.0 Hz, 1H), 1.22 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 156.5, 152.5, 136.0, 134.6, 130.9, 129.1, 128.5, 128.0, 127.6(3), 127.6(0), 126.6, 125.9, 125.8, 124.6, 122.2, 119.1, 68.1, 34.6, 31.1. IR (film, ν, cm$^{-1}$) 3058, 2958, 1615, 1500, 1460, 1434, 1382, 819, 755. HR-MS (ESI) m/z calcd for $C_{32}H_{26}N_2Na$ $[M+Na]^+$ 461.1994, found 416.1997.

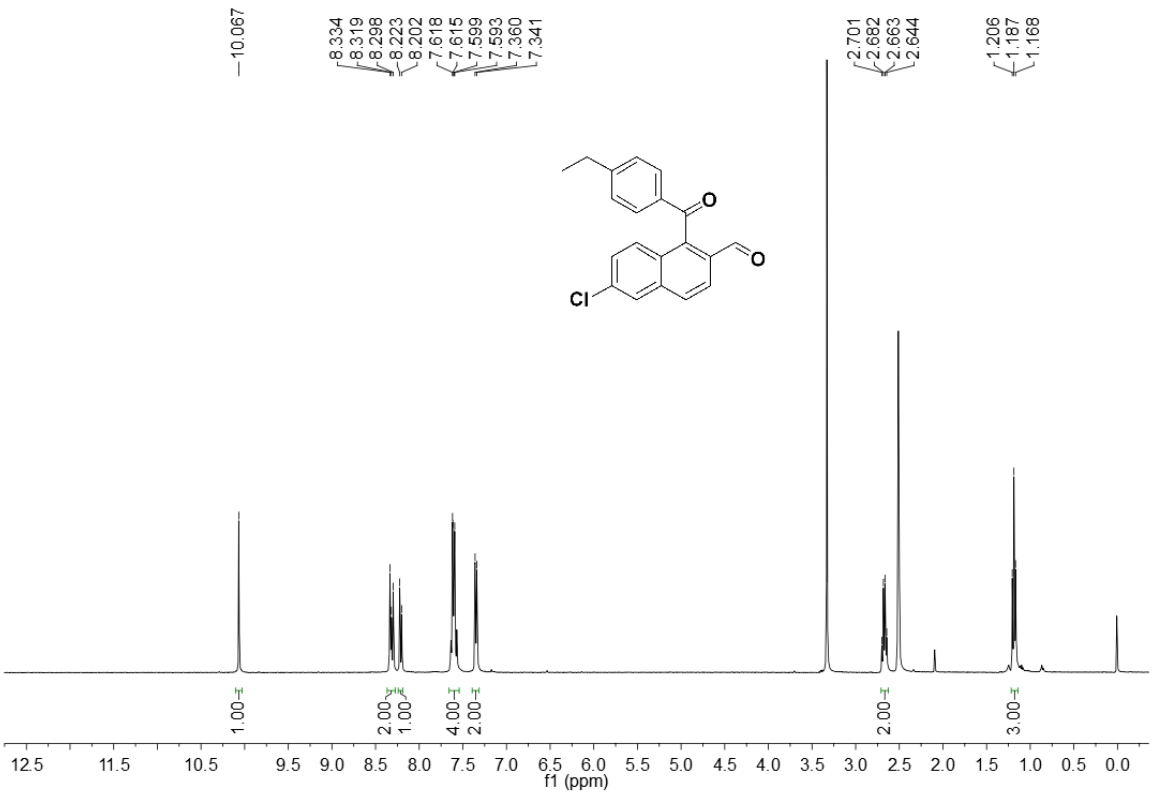
Copies of $^{1}H$ and $^{13}C$ NMR Spectra for Compounds **2, 4** and **6**



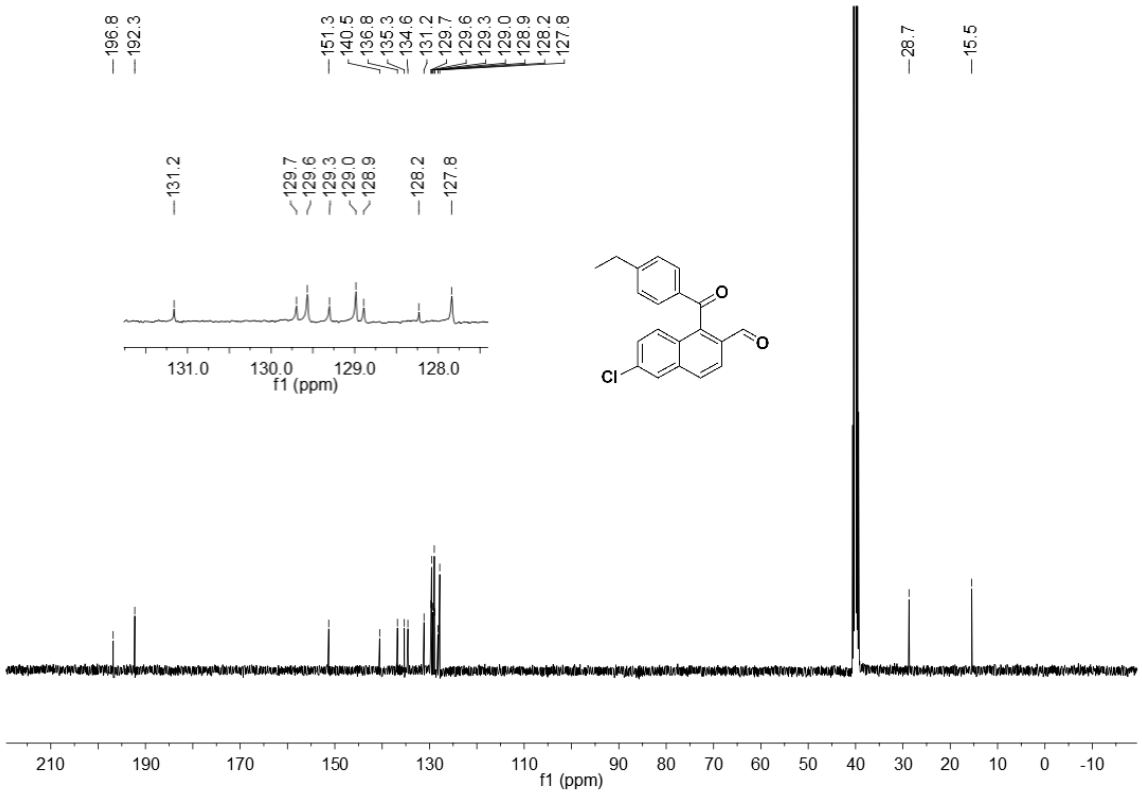

**$^{1}H$ NMR Spectrum of Compound 2a**



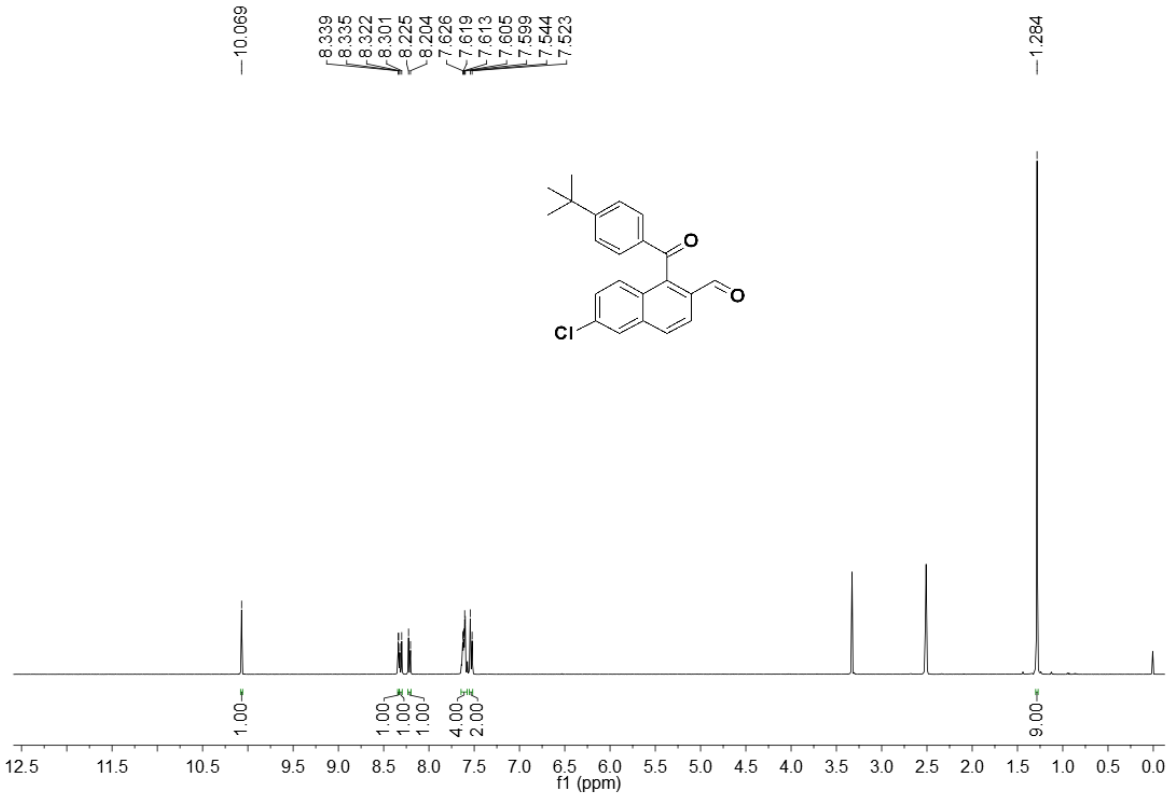

**$^{13}C$ NMR Spectrum of Compound 2a**



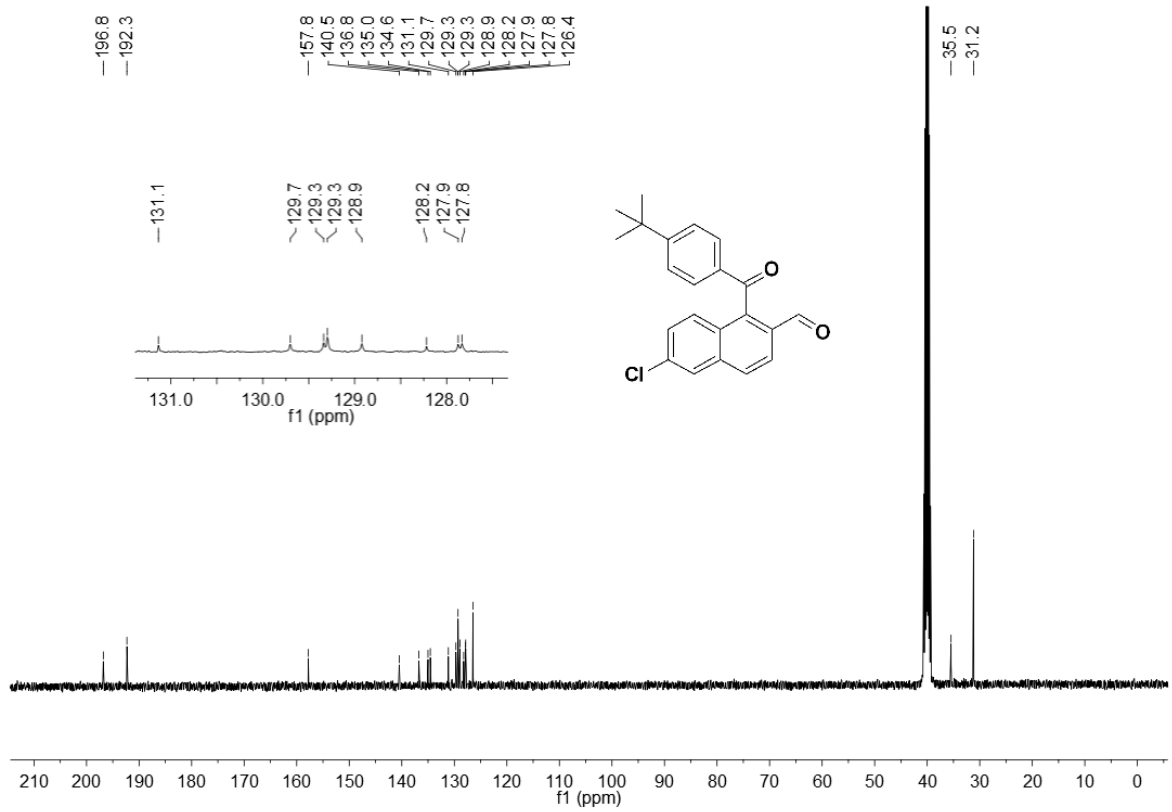

**$^{1}$H NMR Spectrum of Compound 2b**



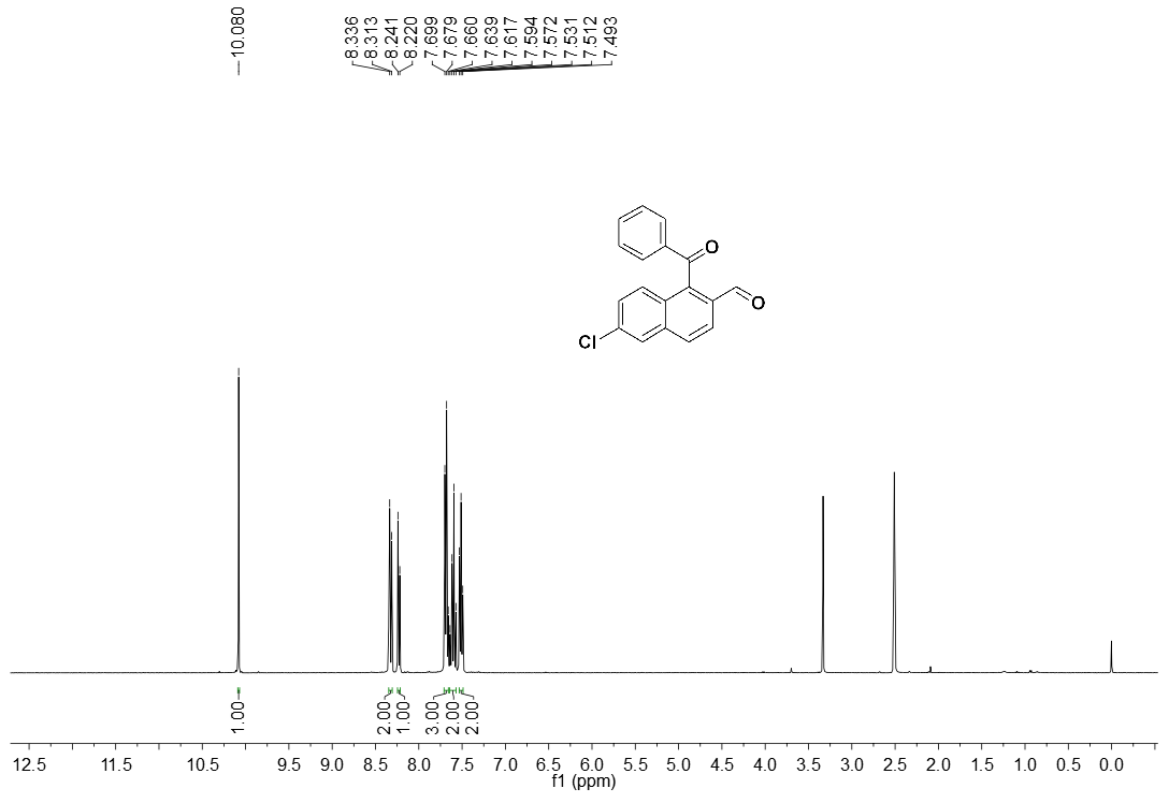

**$^{13}$C NMR Spectrum of Compound 2b**



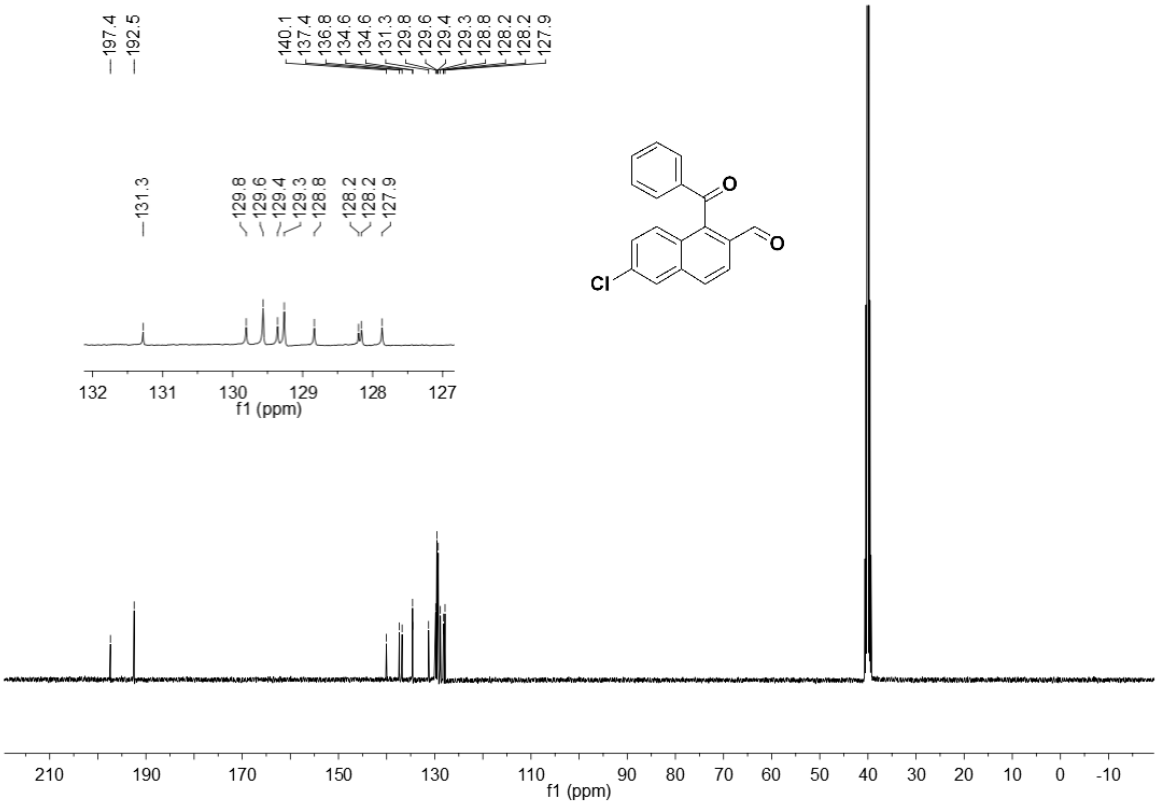

**[1]H NMR Spectrum of Compound 2c**



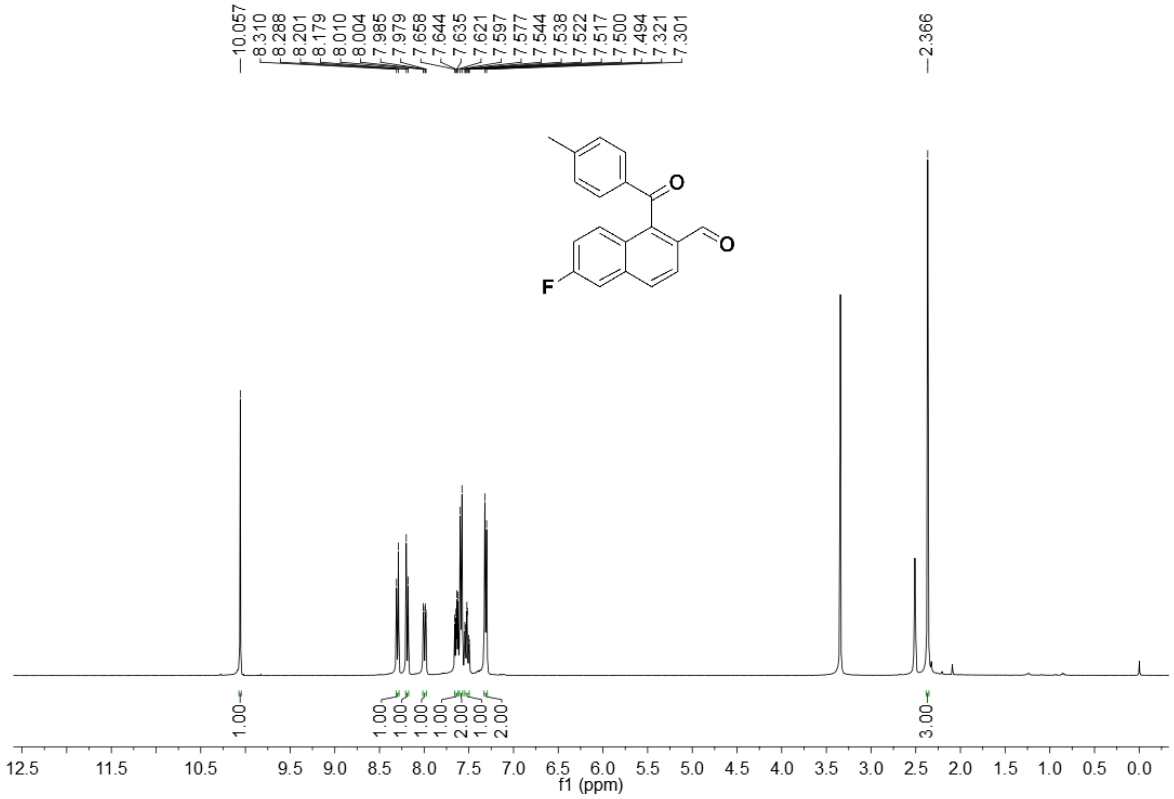

**[13]C NMR Spectrum of Compound 2c**



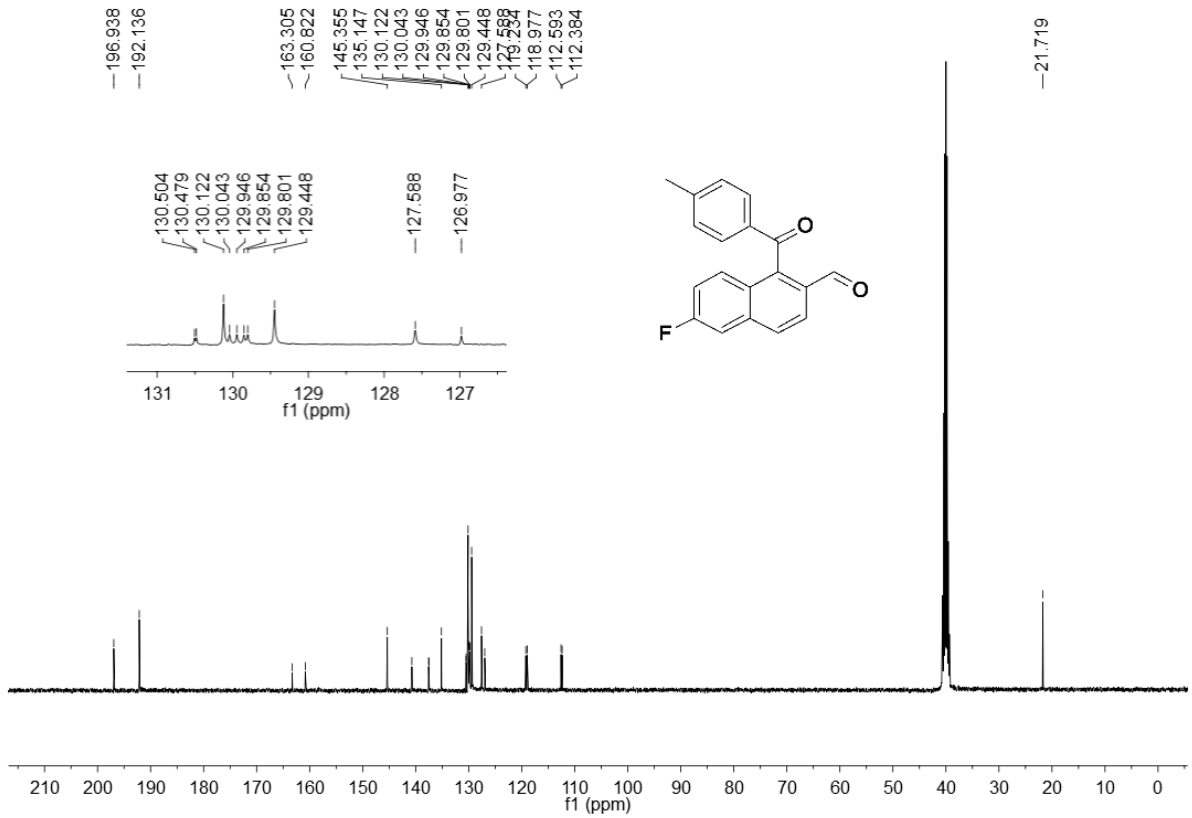

**$^{1}$H NMR Spectrum of Compound 2d**



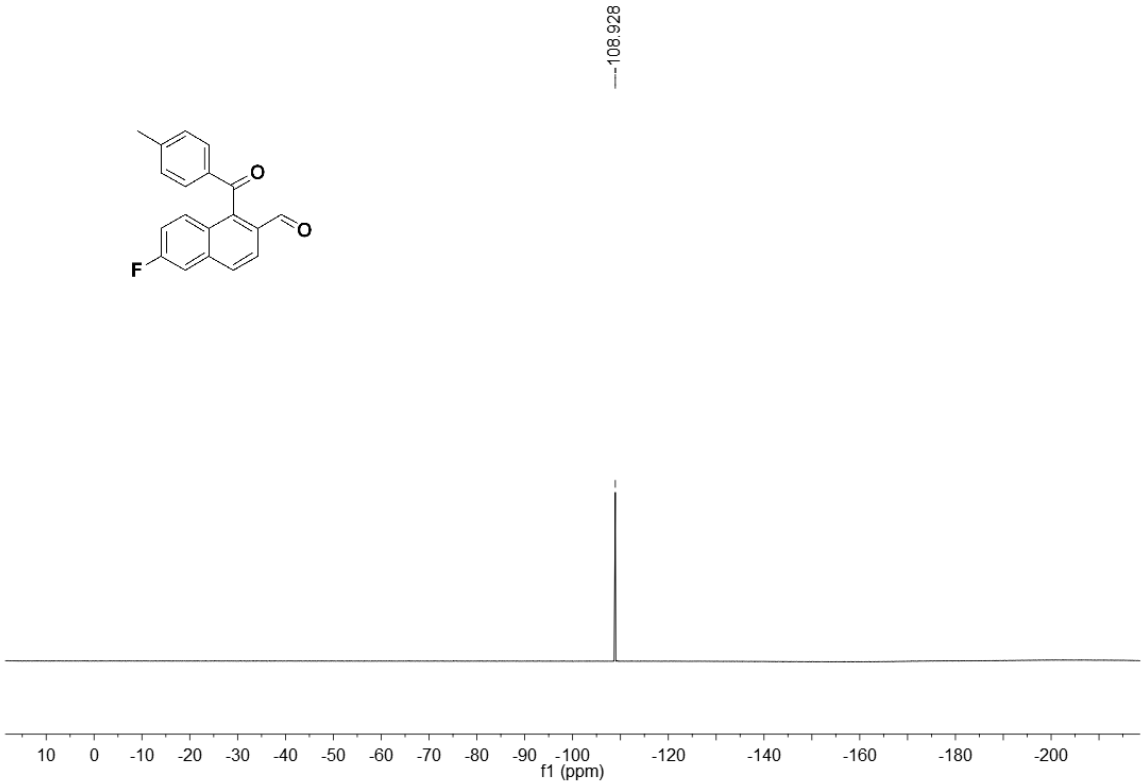

**$^{13}$C NMR Spectrum of Compound 2d**



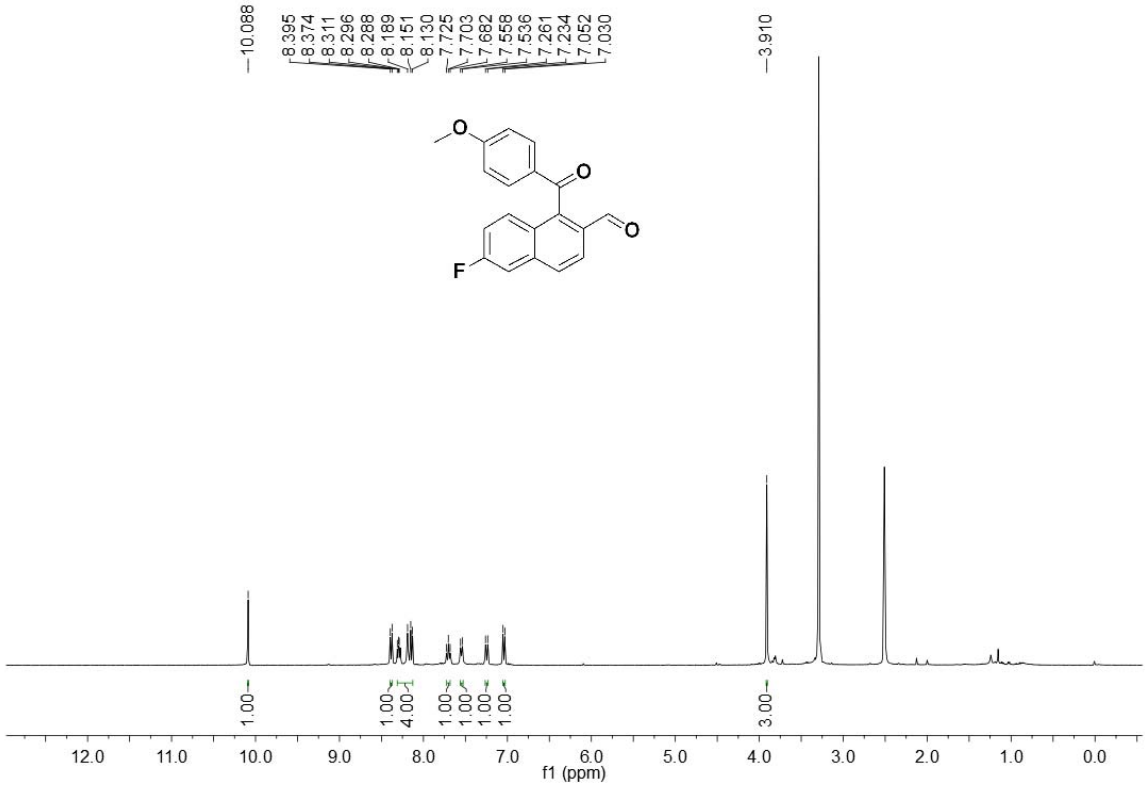

**$^{1}$H NMR Spectrum of Compound 2f**



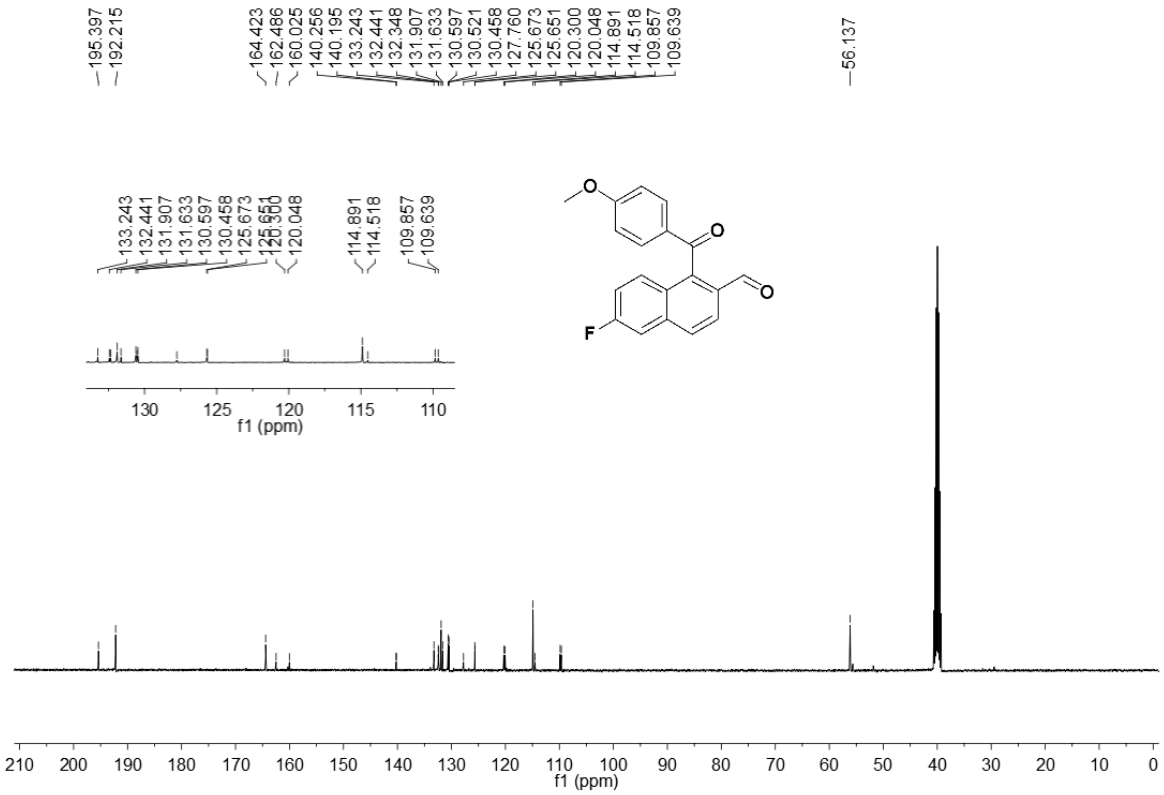

**$^{13}$C NMR Spectrum of Compound 2f**



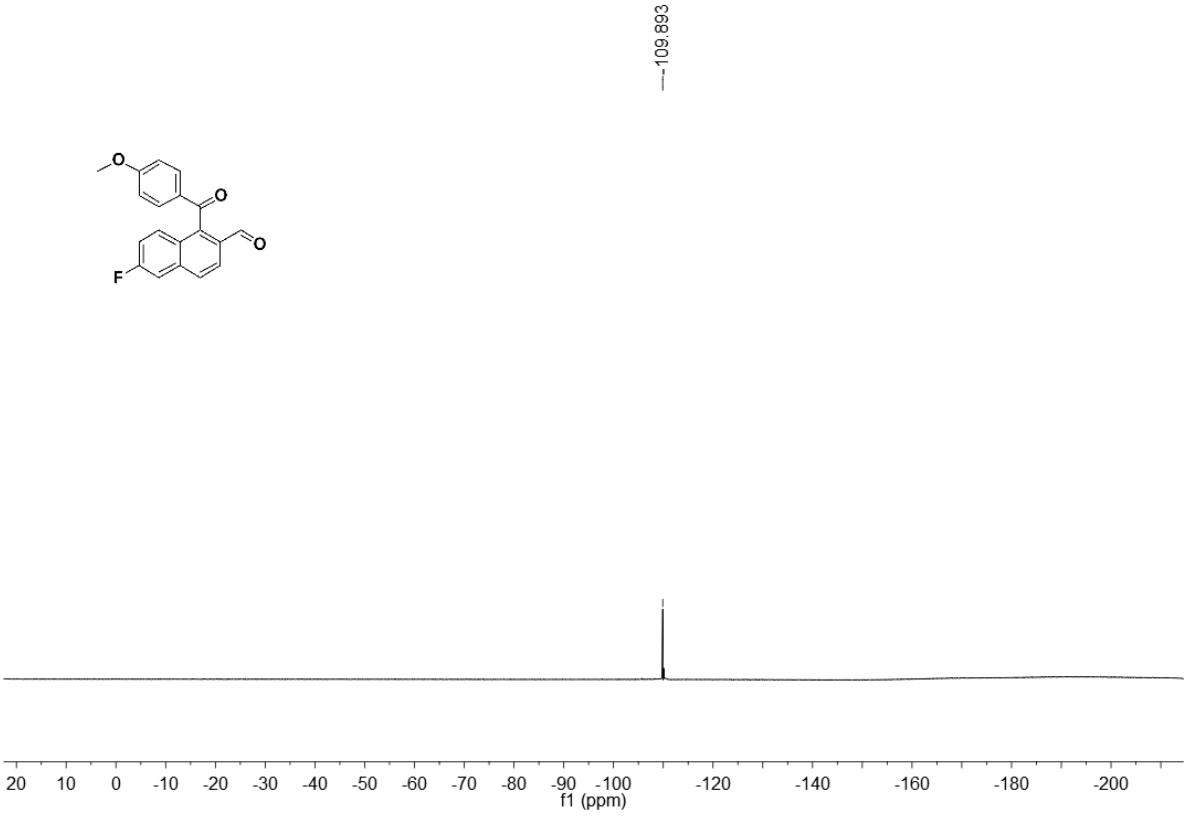

**$^{19}$F NMR Spectrum of Compound 2f**



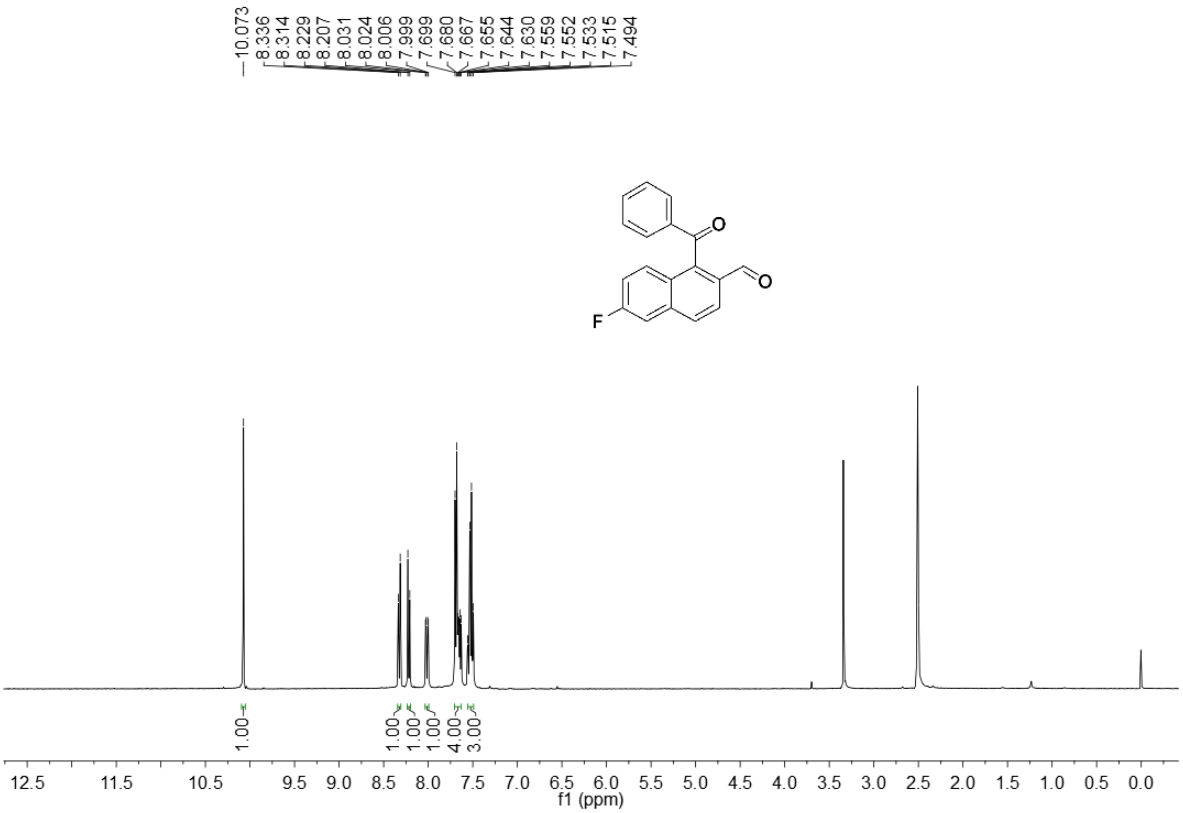

**$^{1}$H NMR Spectrum of Compound 2g**



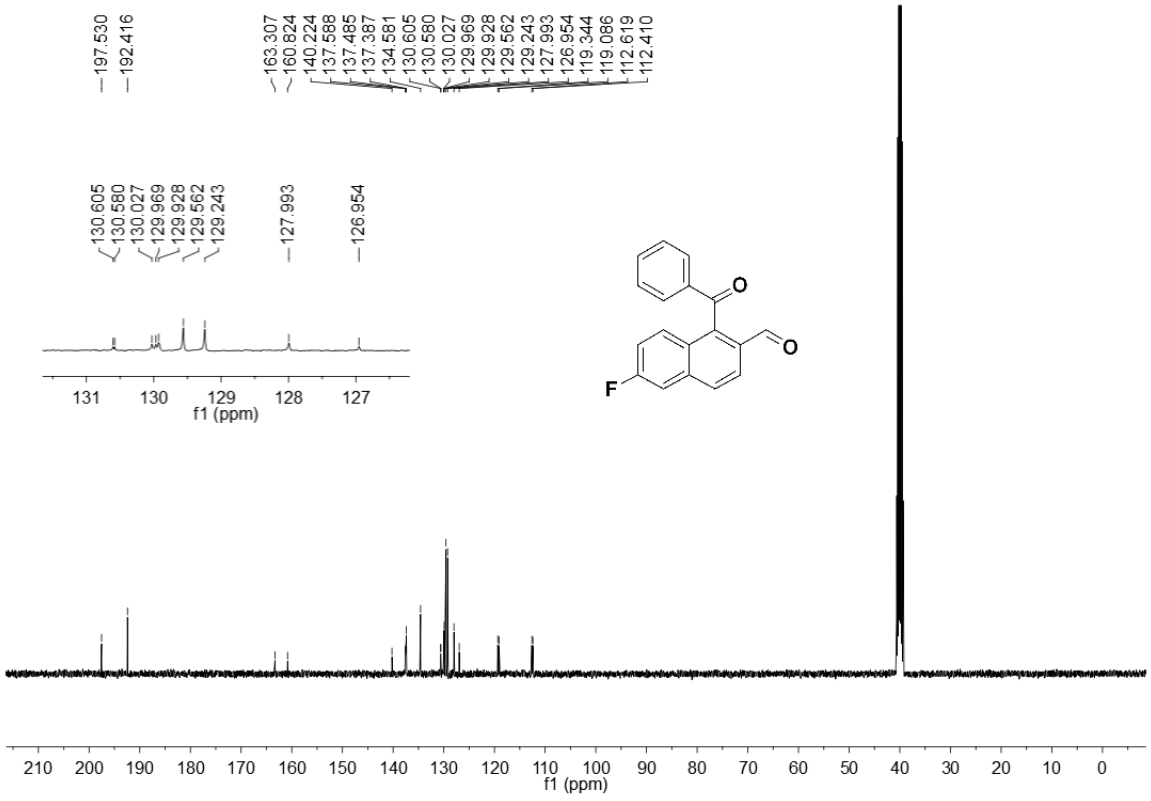

**$^{13}$C NMR Spectrum of Compound 2g**



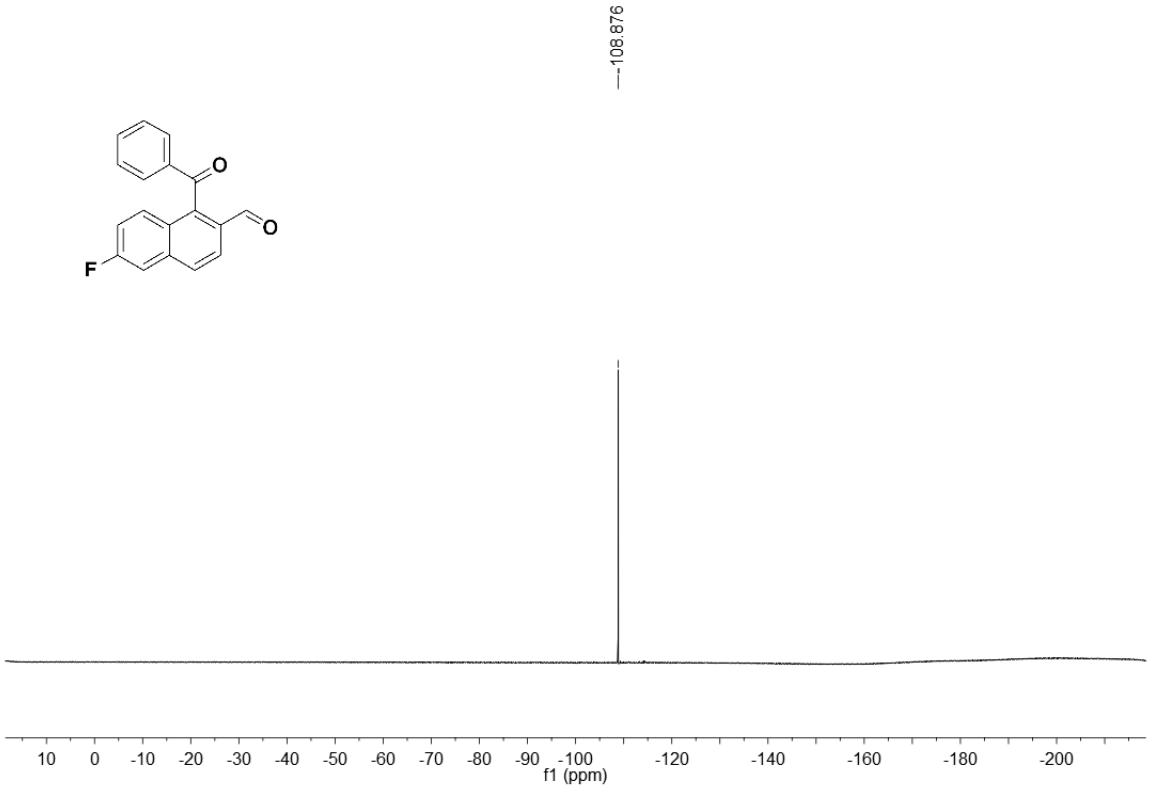

**$^{19}$F NMR Spectrum of Compound 2g**



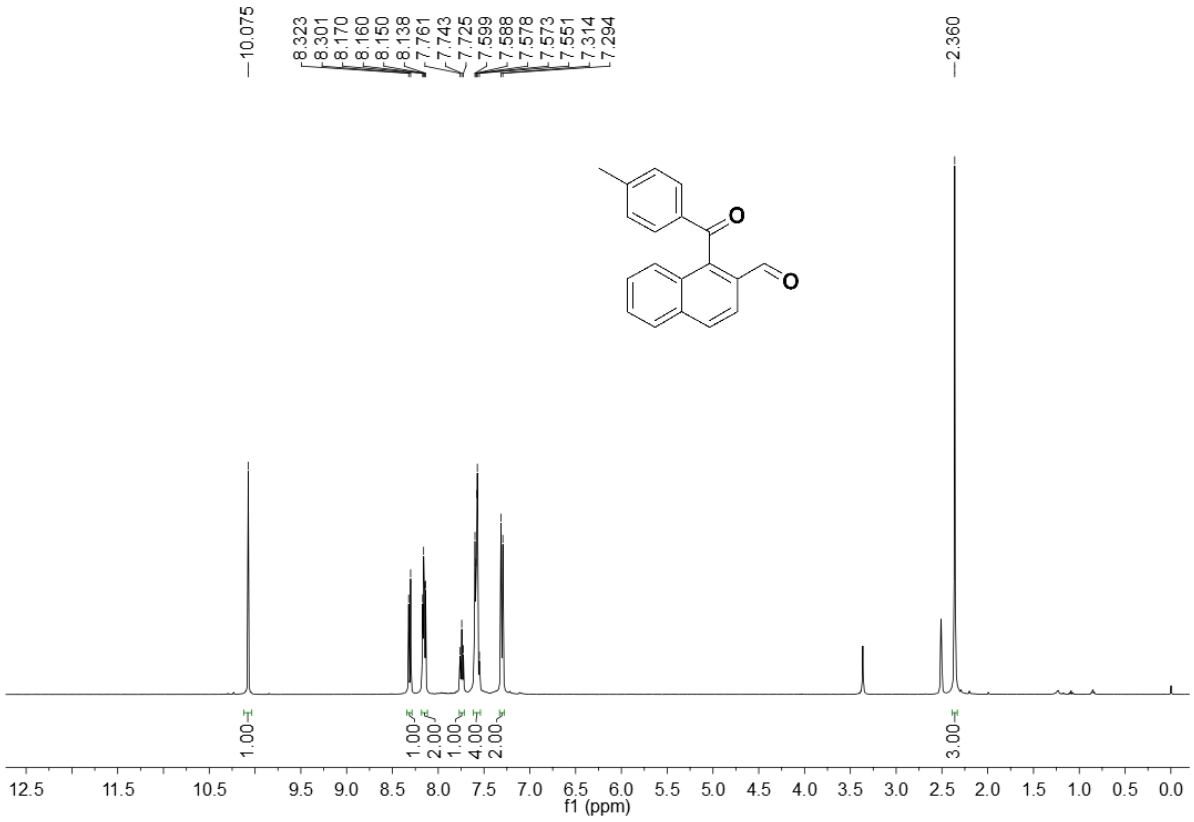

**$^{1}$H NMR Spectrum of Compound 2h**



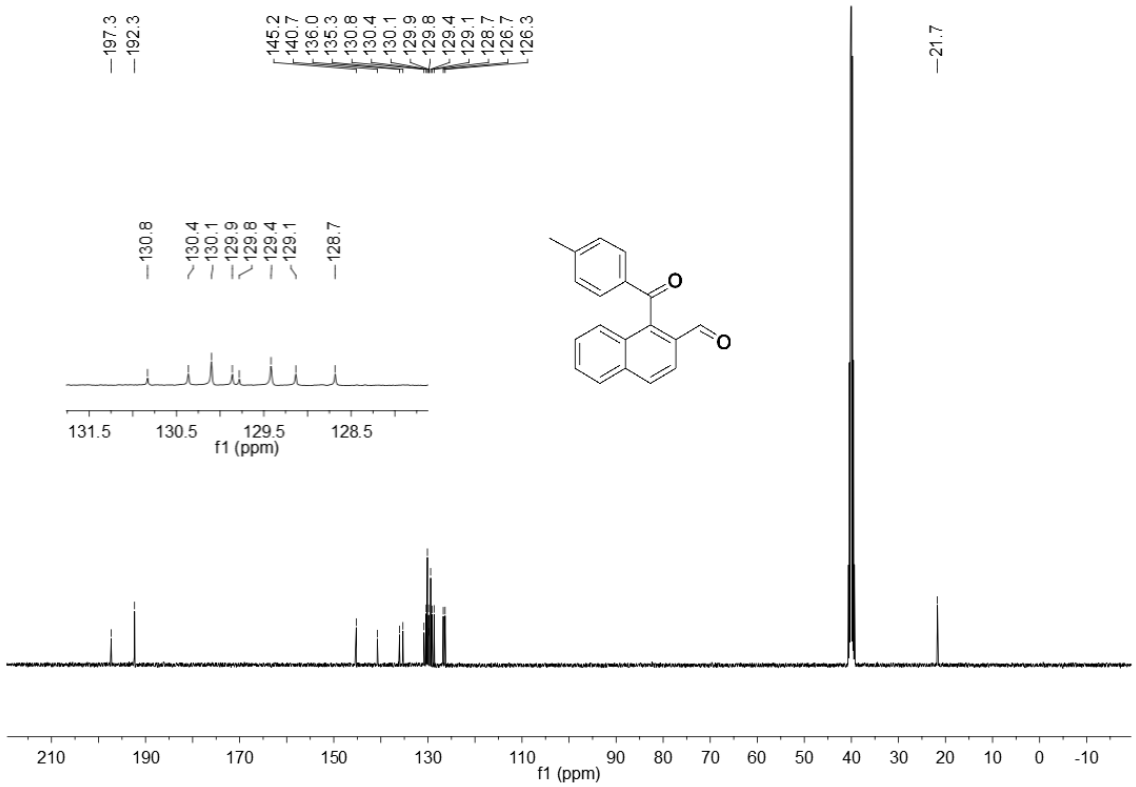

**$^{13}$C NMR Spectrum of Compound 2h**



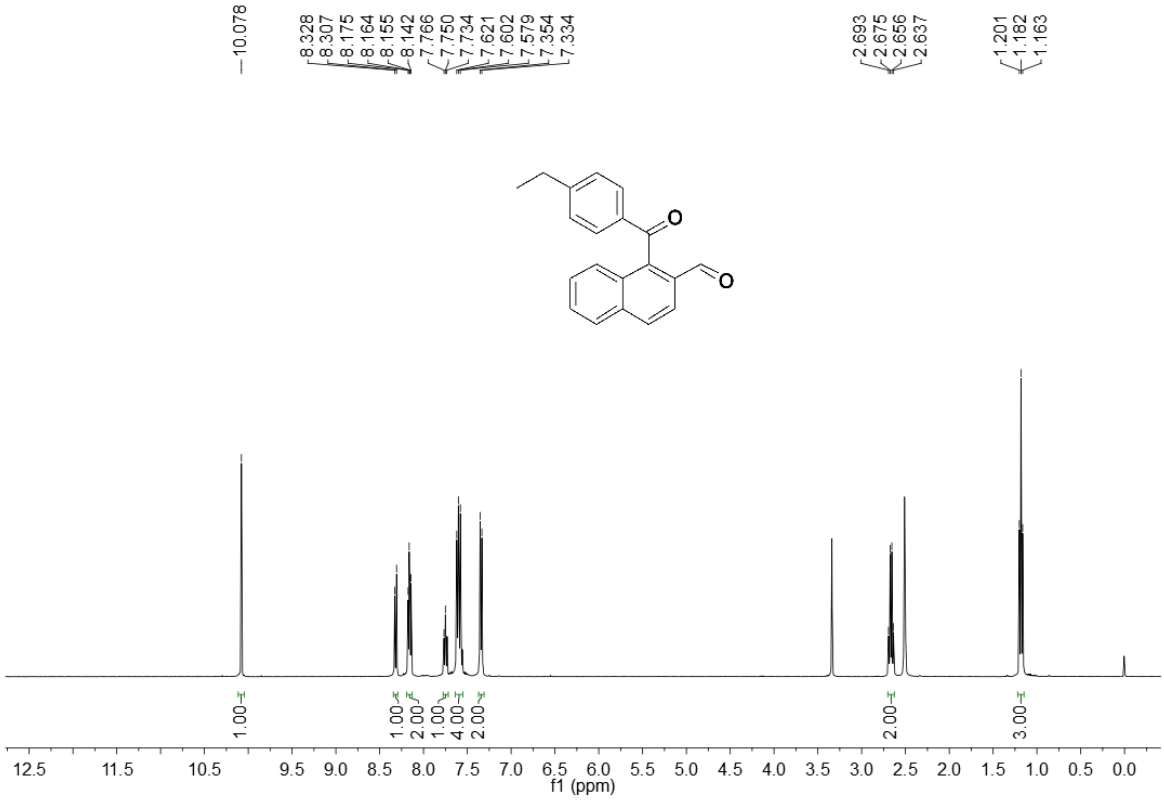

**$^{19}$F NMR Spectrum of Compound 2h**



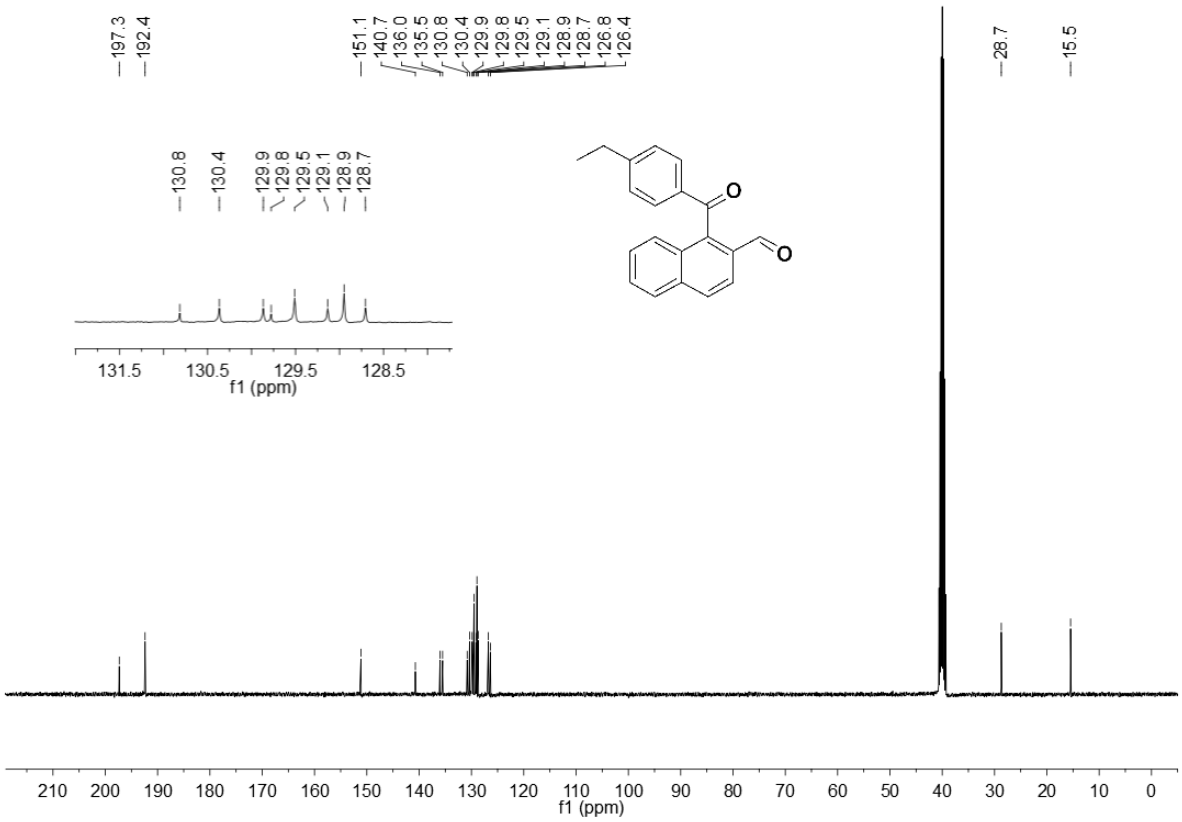

**$^{1}$H NMR Spectrum of Compound 2i**



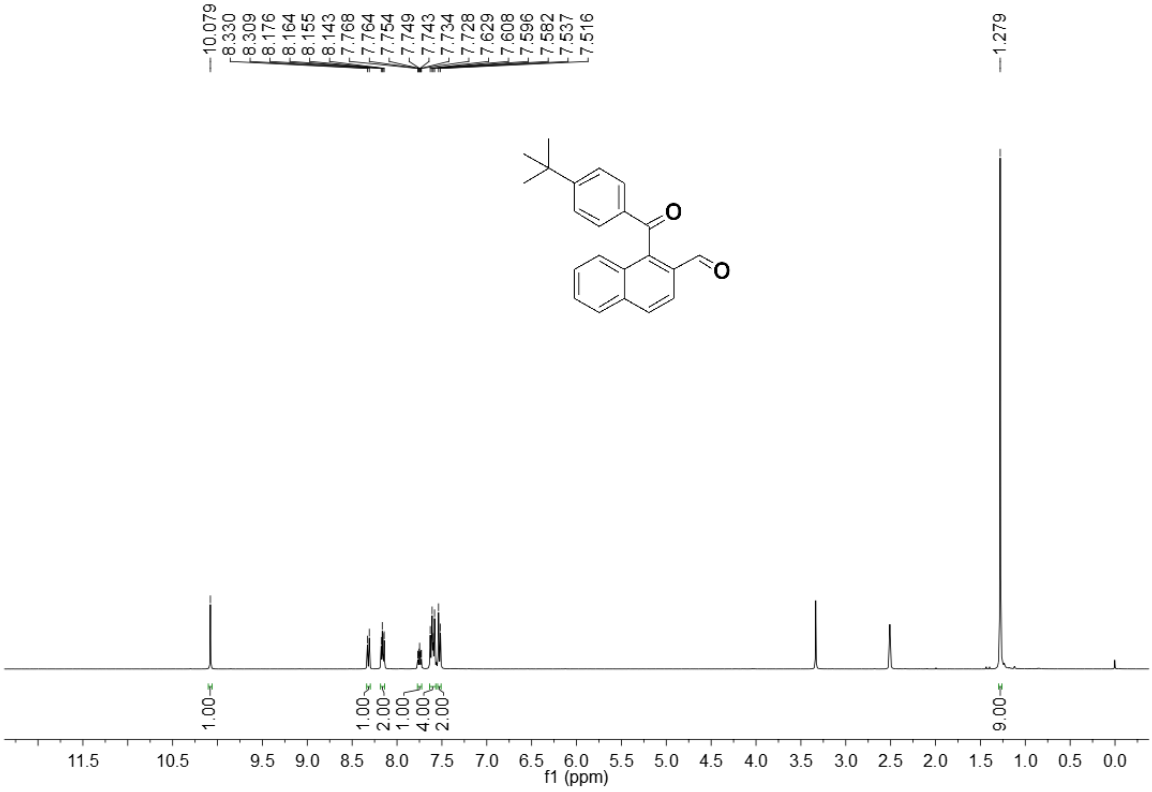

**$^{13}$C NMR Spectrum of Compound 2i**



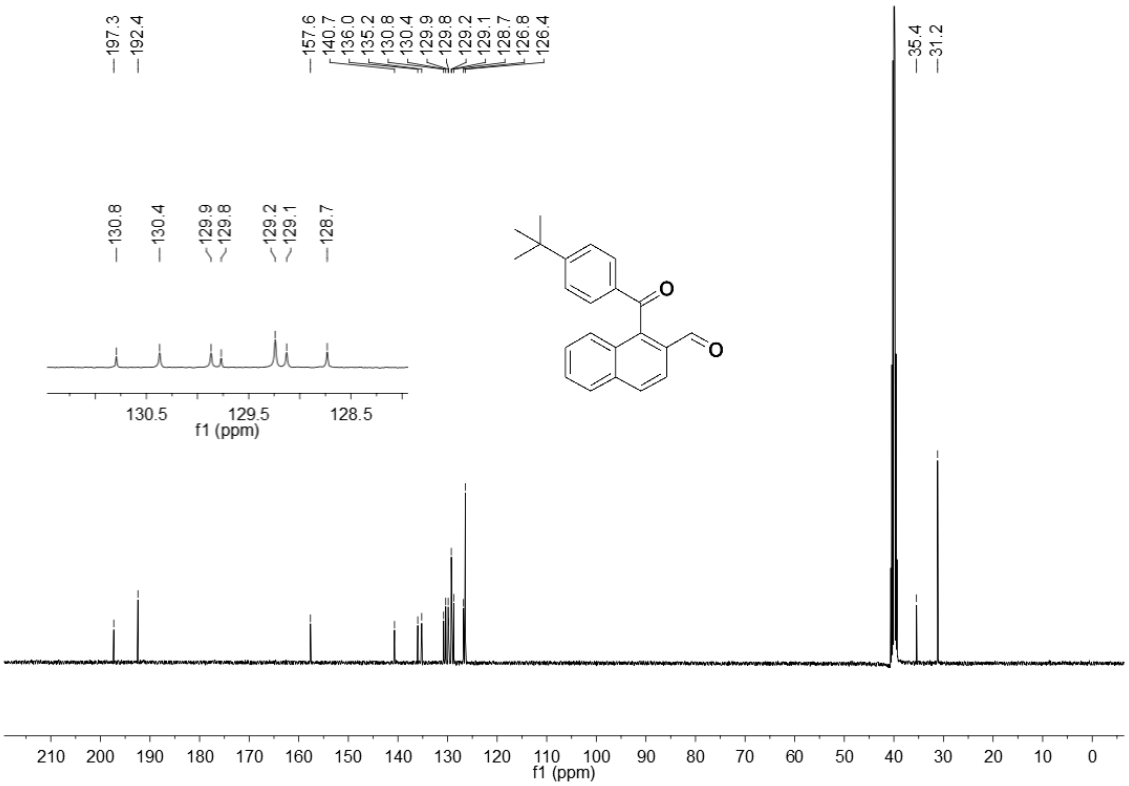

**$^{1}$H NMR Spectrum of Compound 2j**



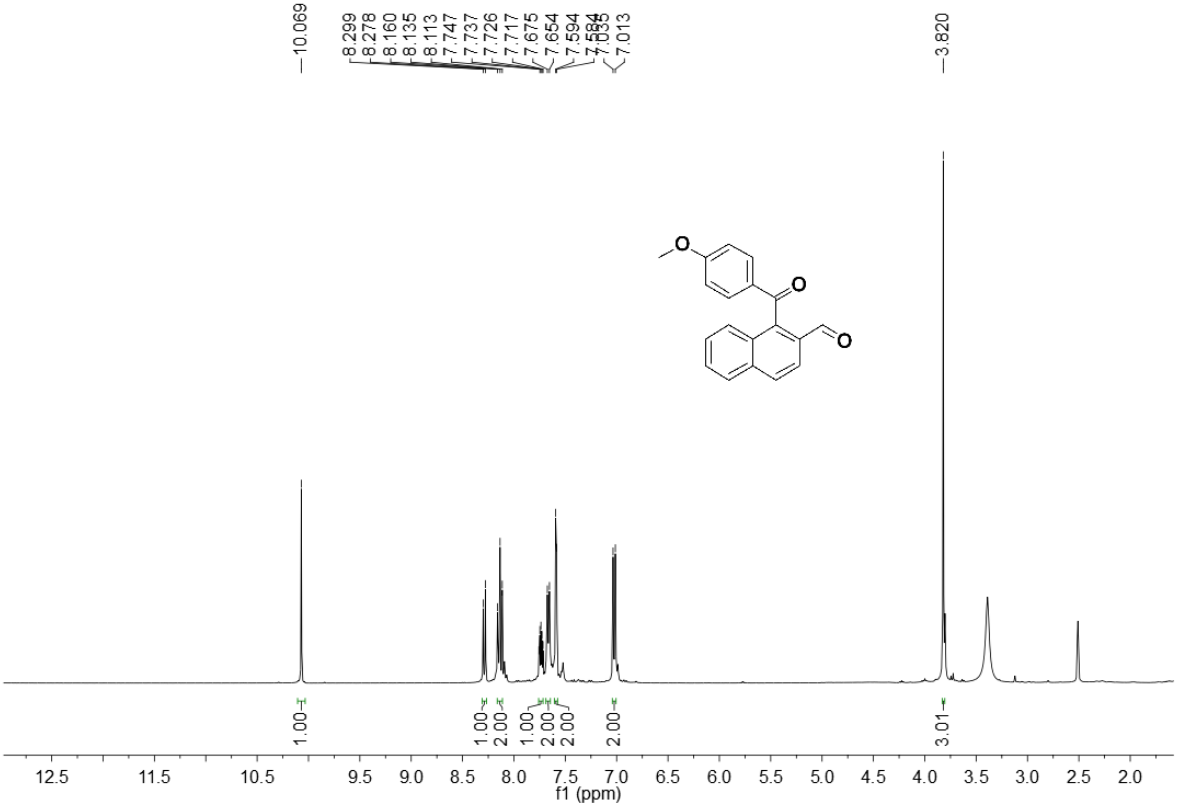

**$^{13}$C NMR Spectrum of Compound 2j**



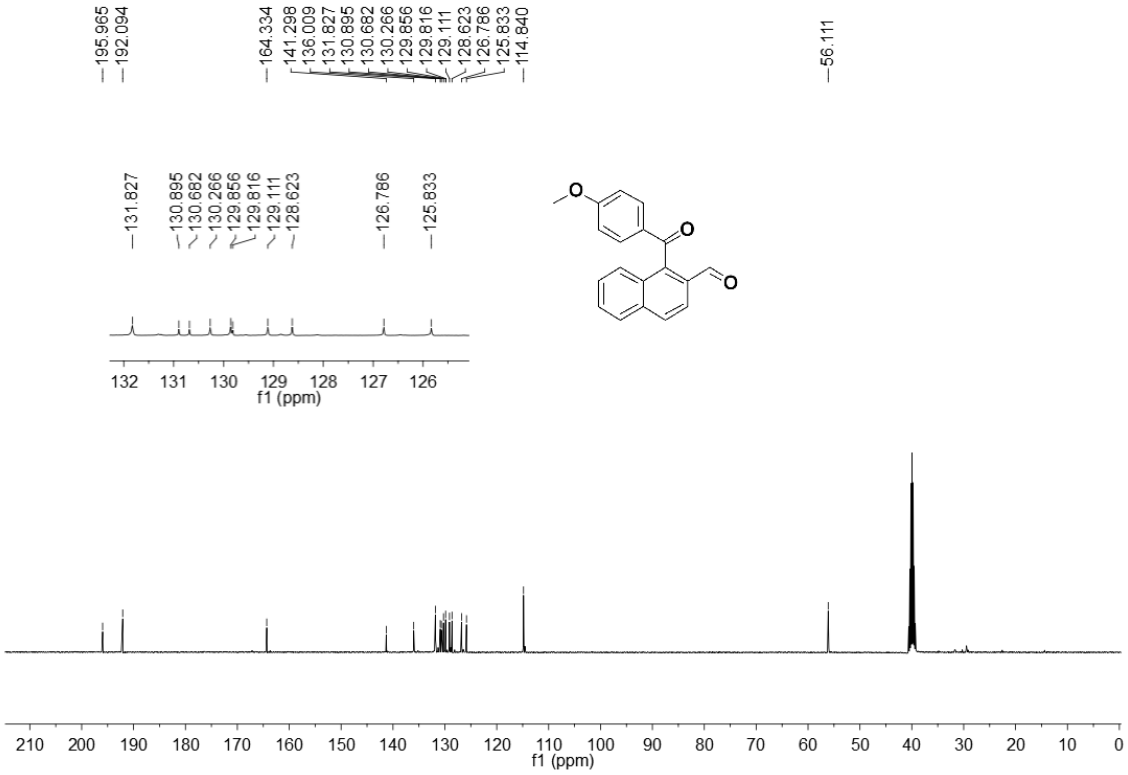

**$^{1}$H NMR Spectrum of Compound 2k**



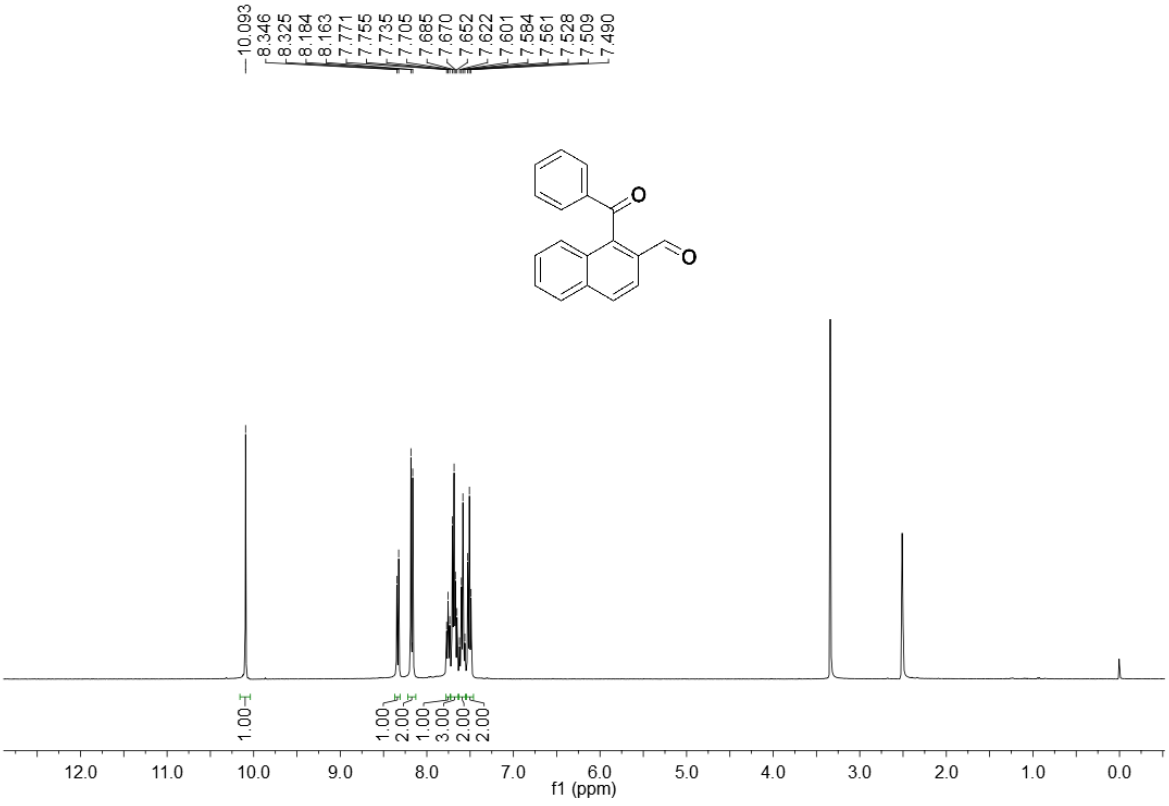

**$^{13}$C NMR Spectrum of Compound 2k**



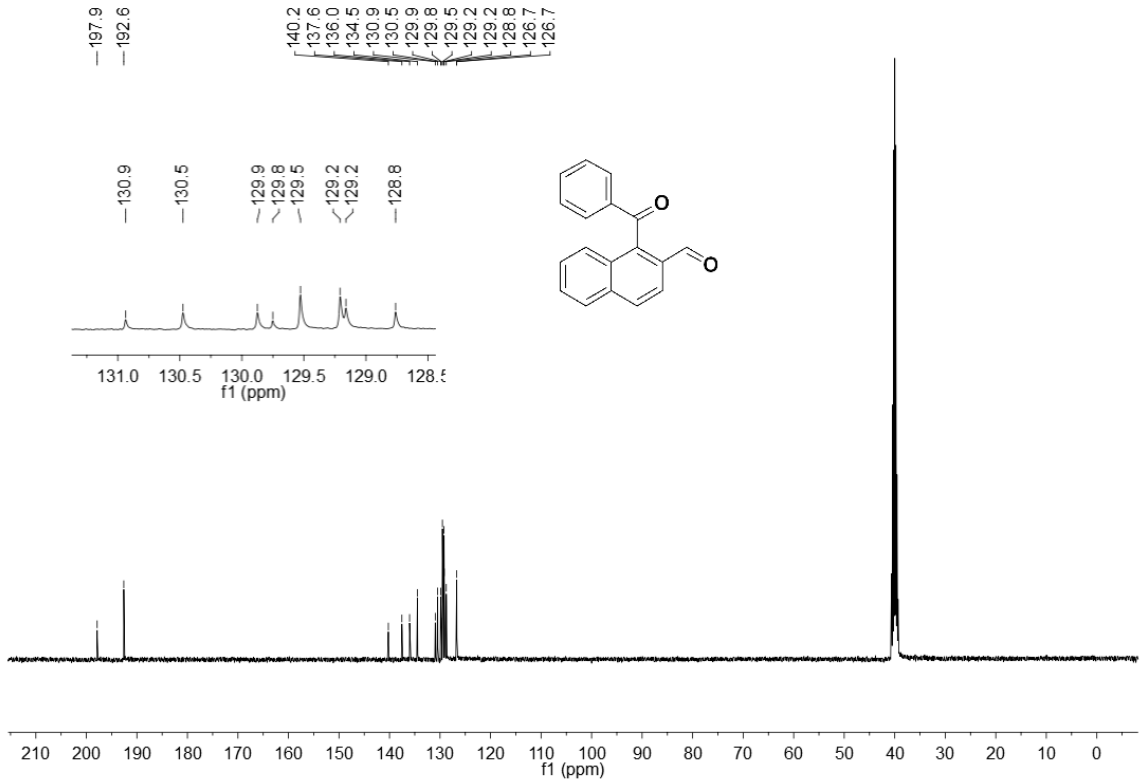

**$^{1}$H NMR Spectrum of Compound 2l**



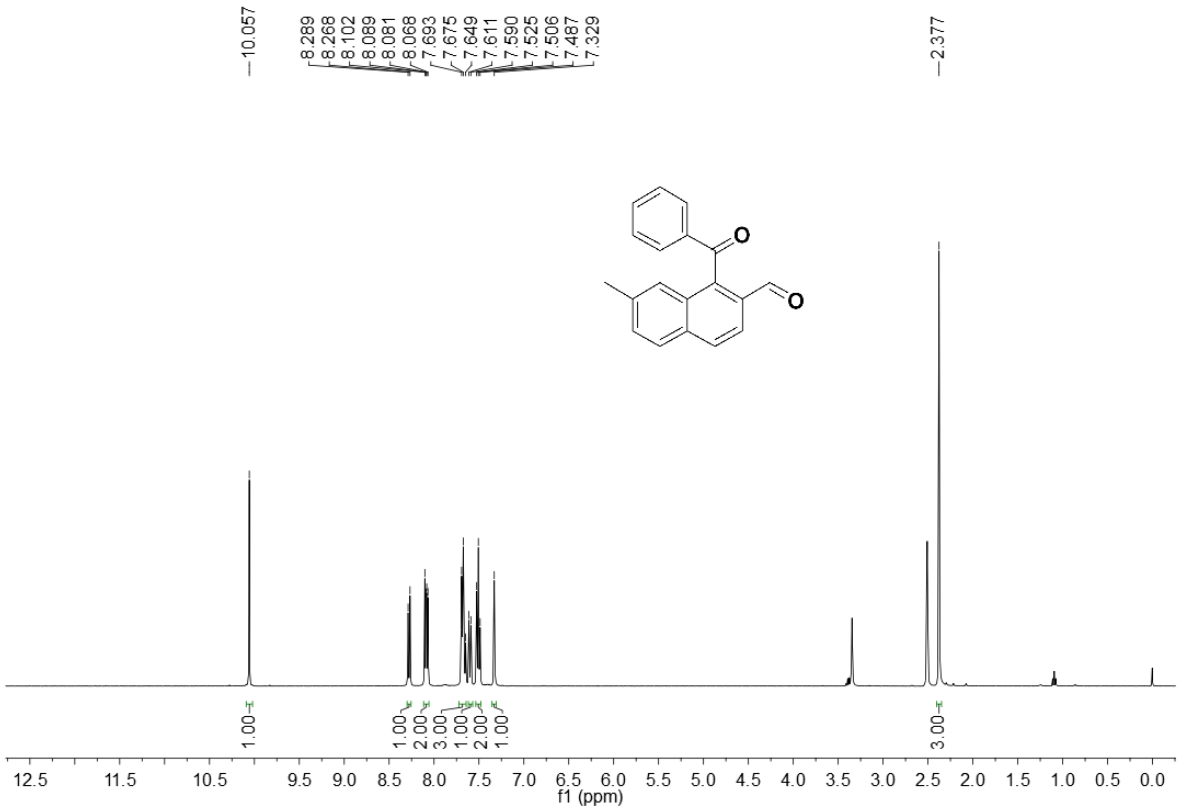

**$^{13}$C NMR Spectrum of Compound 2l**



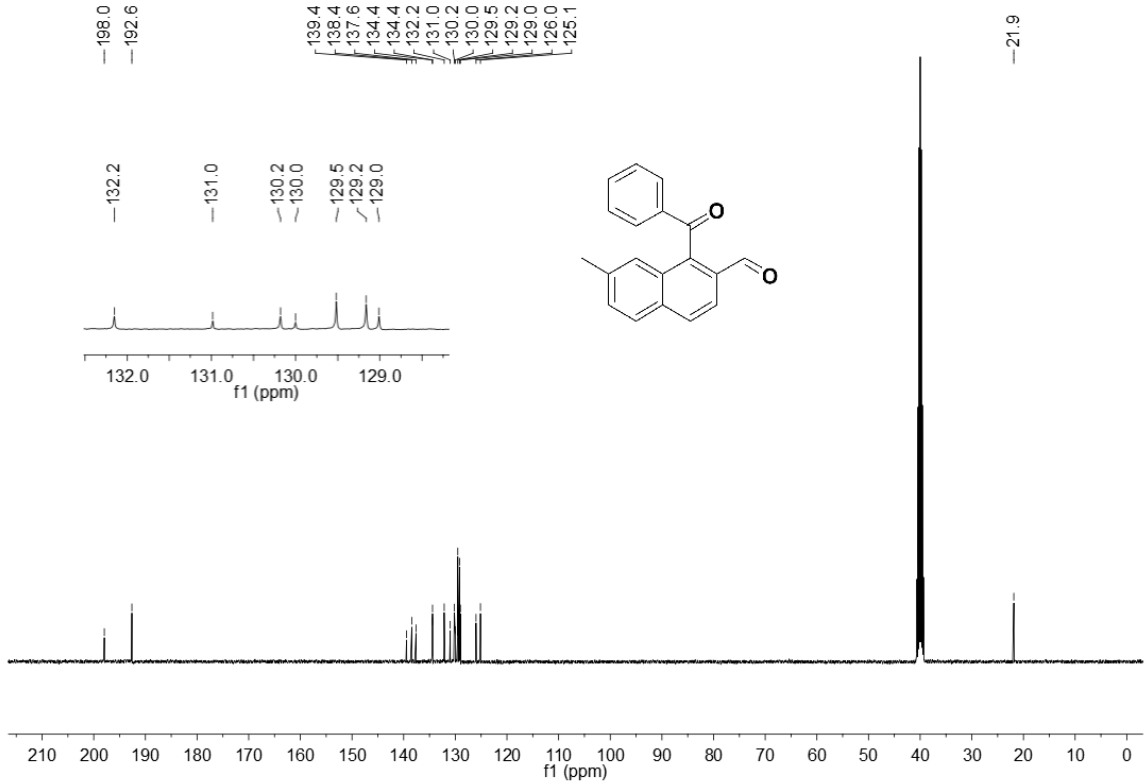

**$^{1}$H NMR Spectrum of Compound 2m**



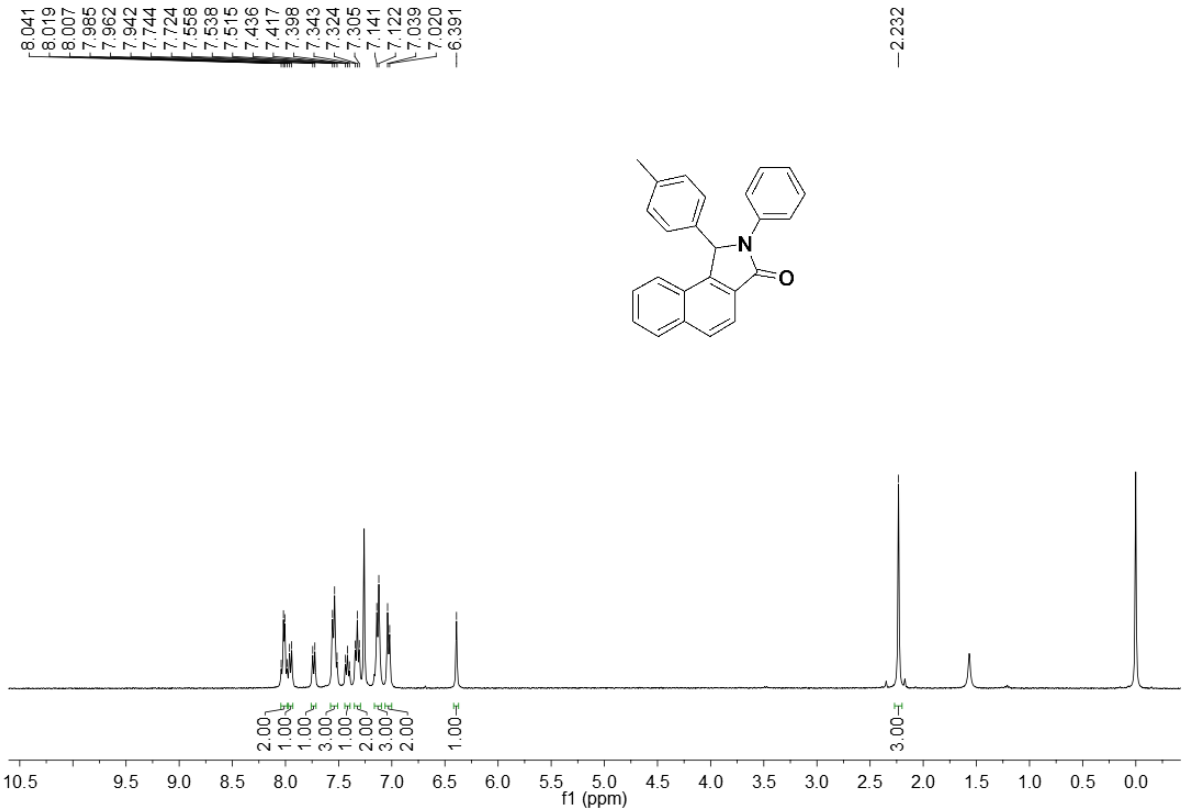

**$^{13}$C NMR Spectrum of Compound 2m**



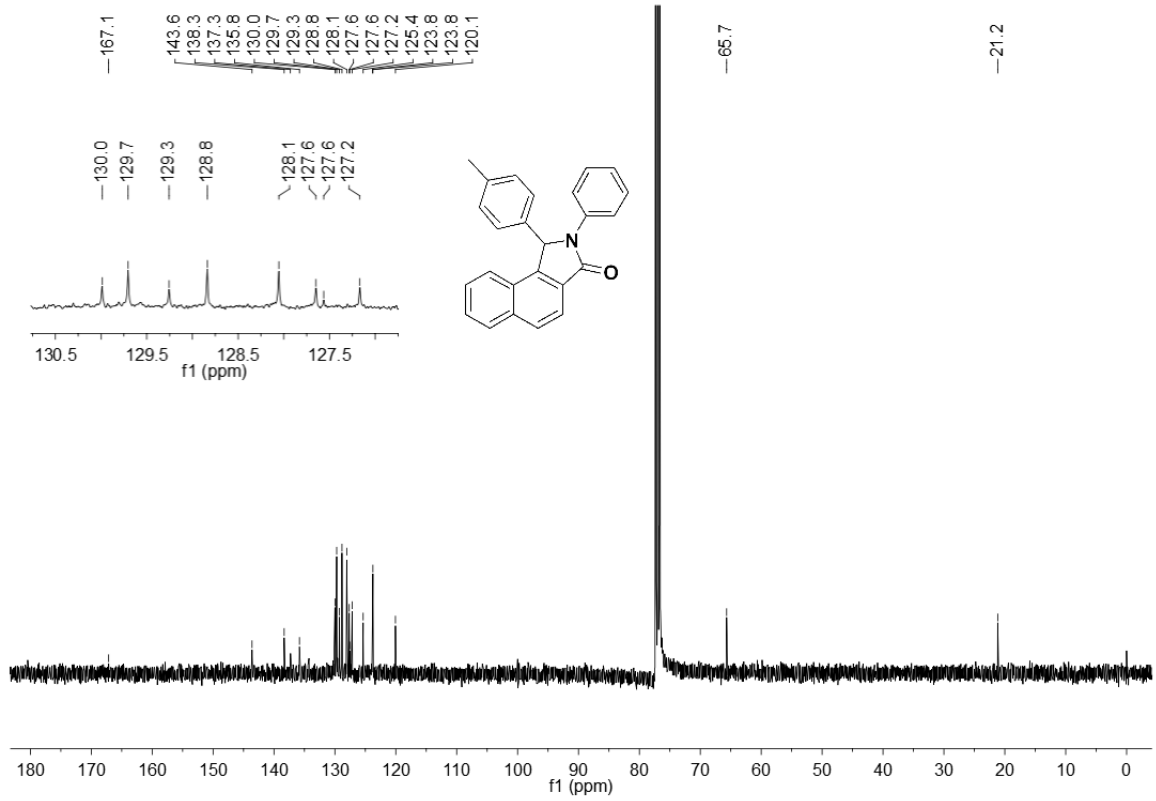

**$^{1}$H NMR Spectrum of Compound 2n**



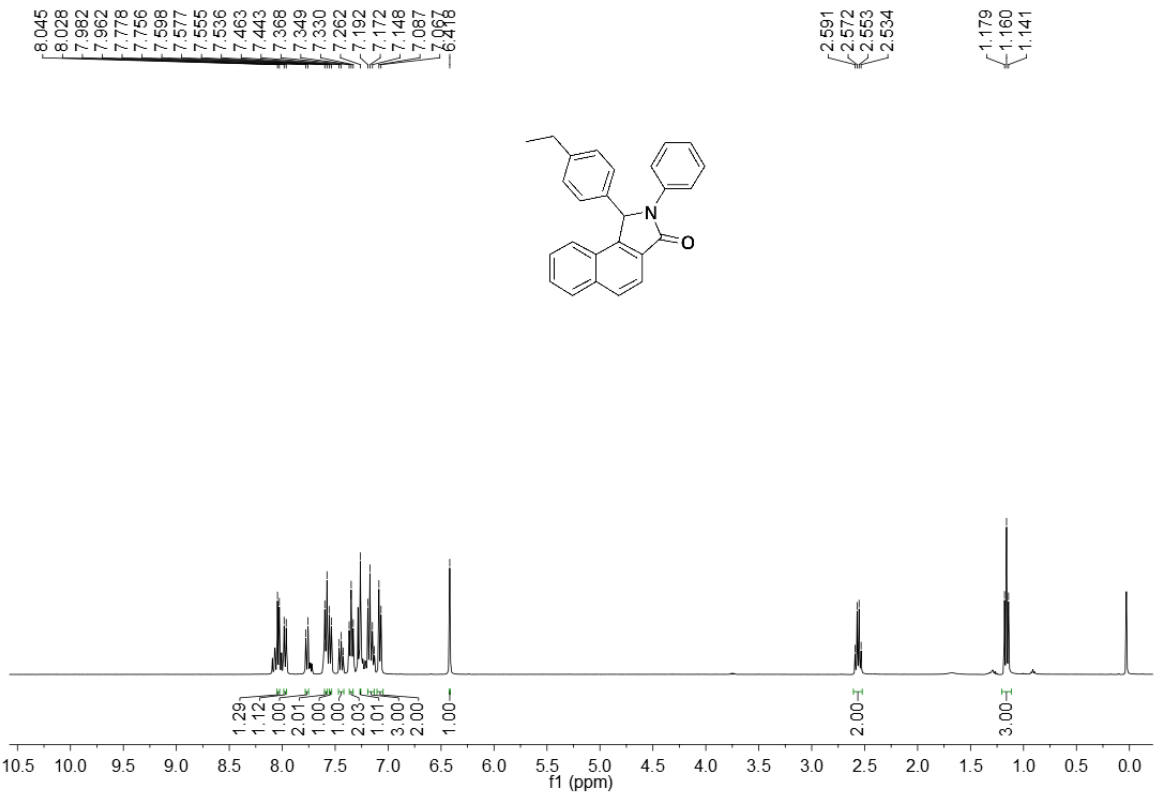

**$^{13}$C NMR Spectrum of Compound 2n**



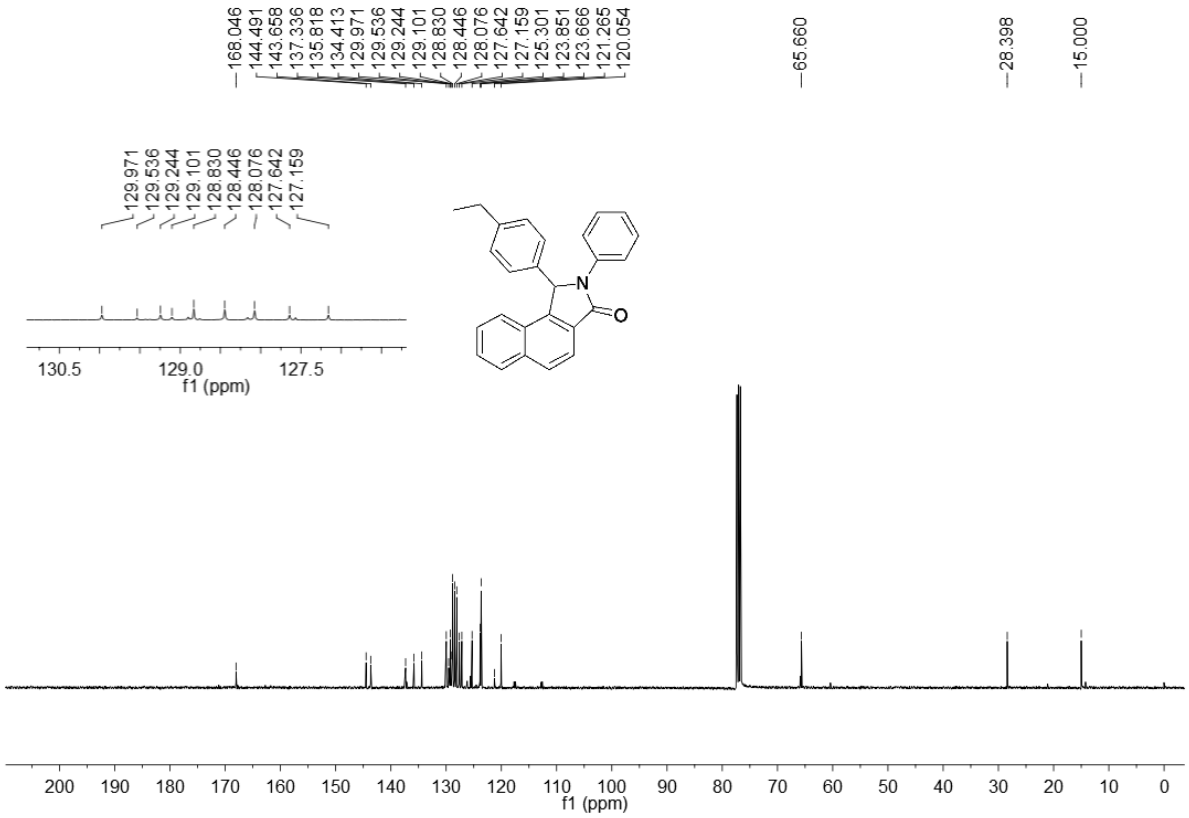

**$^{1}$H NMR Spectrum of Compound 4a**



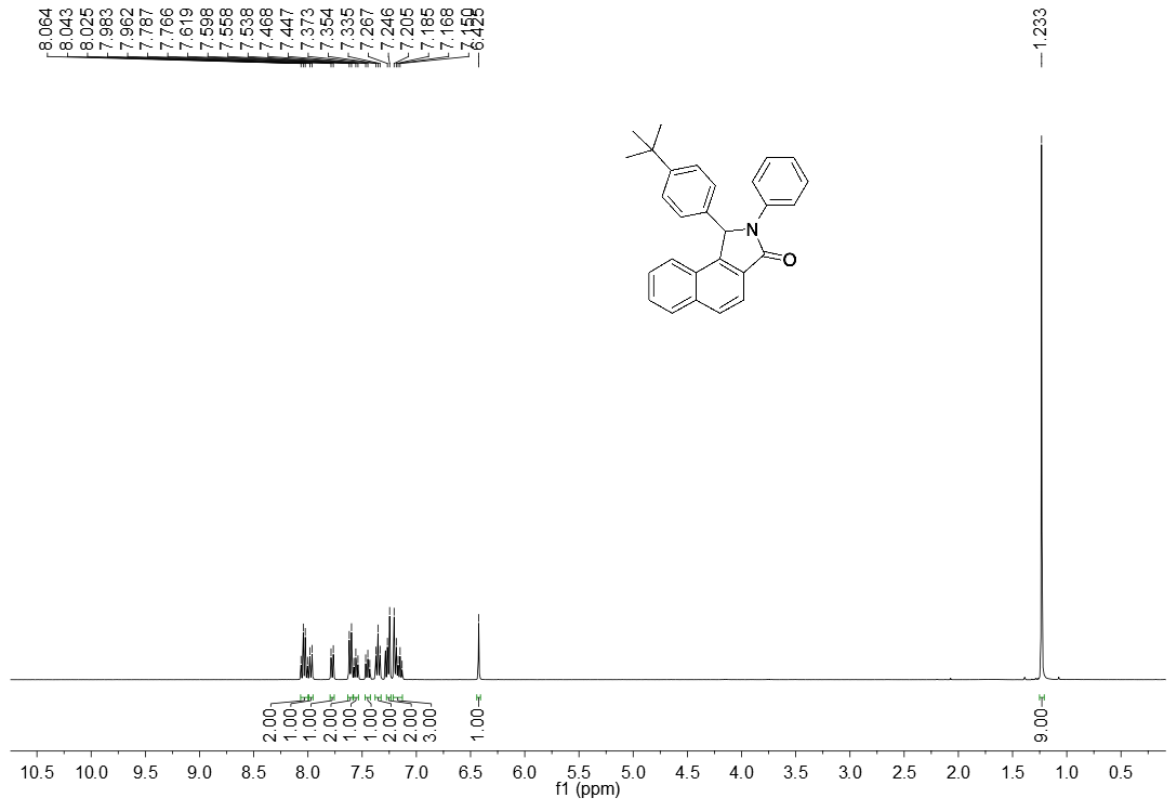

**$^{13}$C NMR Spectrum of Compound 4a**



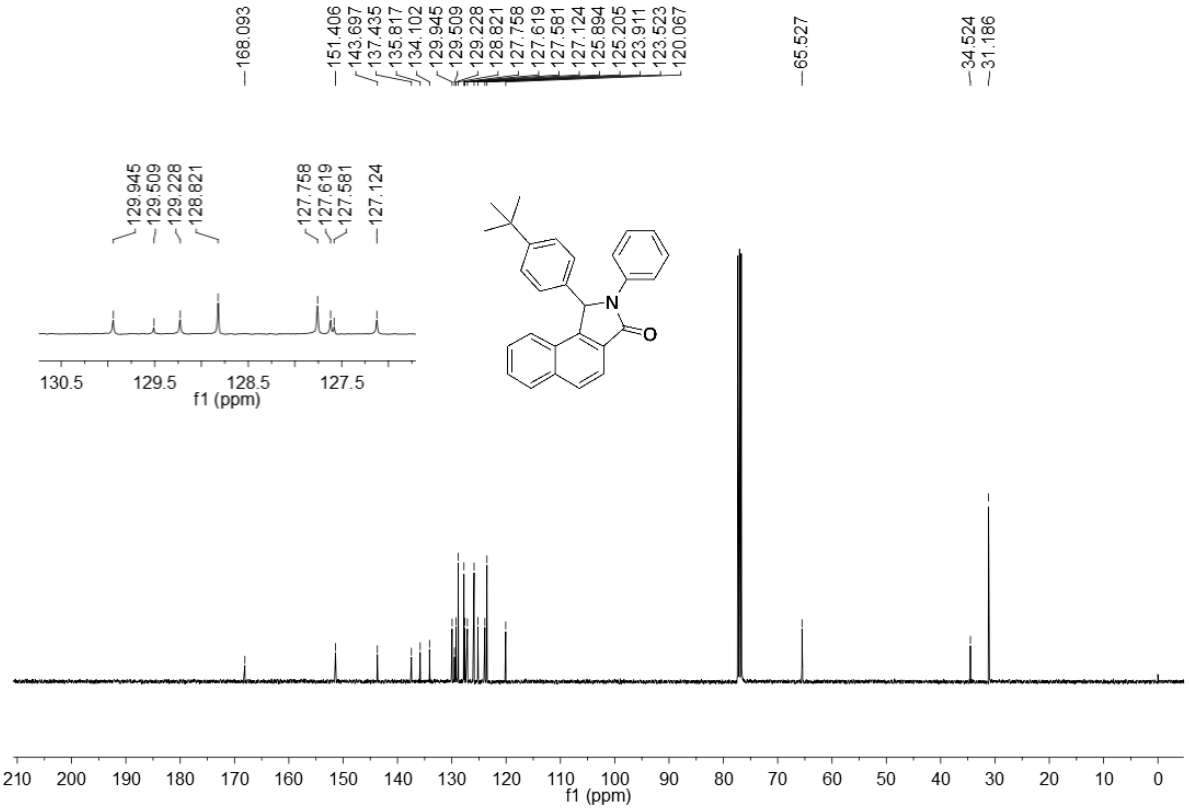

**$^{1}$H NMR Spectrum of Compound 4b**



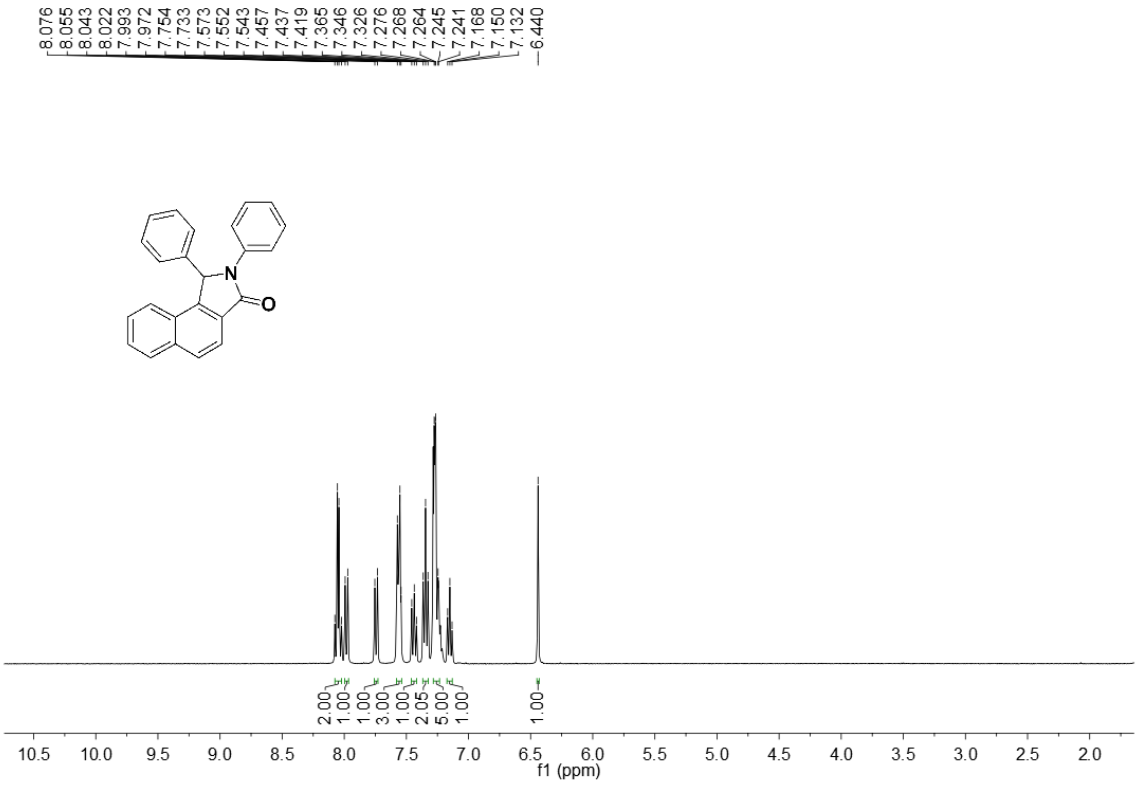

**$^{13}$C NMR Spectrum of Compound 4b**



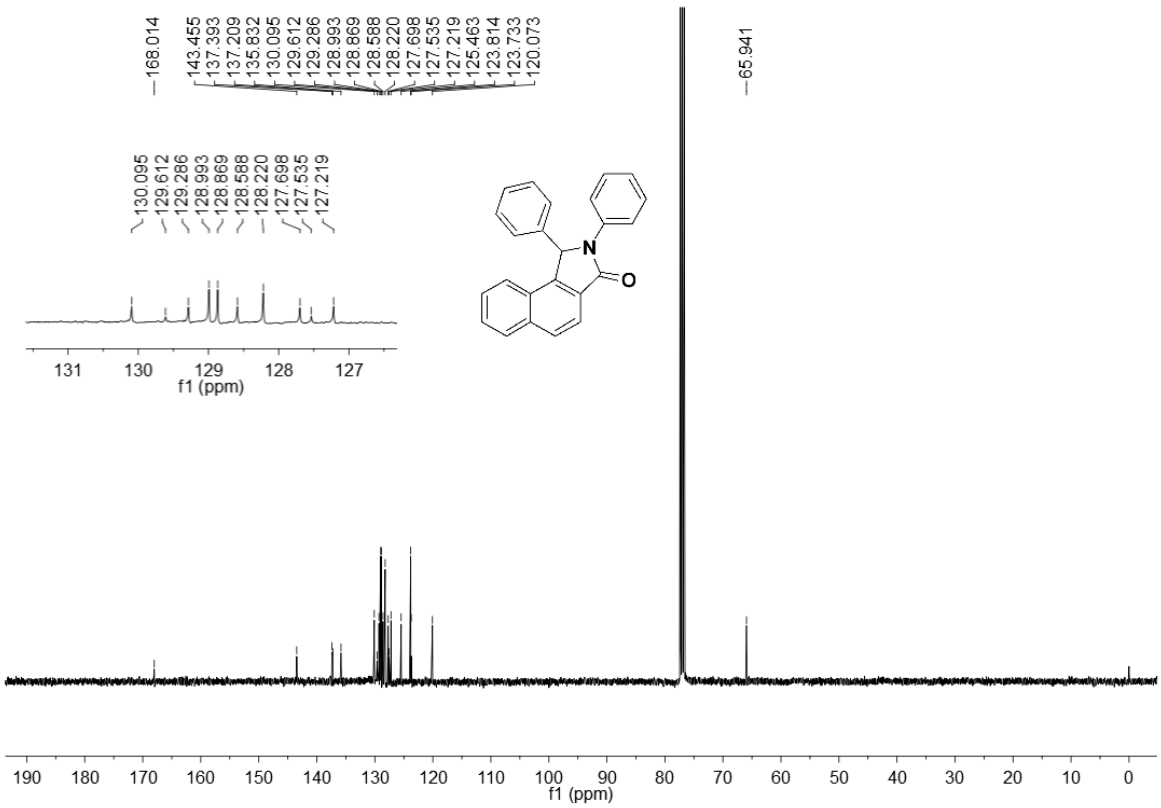

**$^{1}$H NMR Spectrum of Compound 4c**



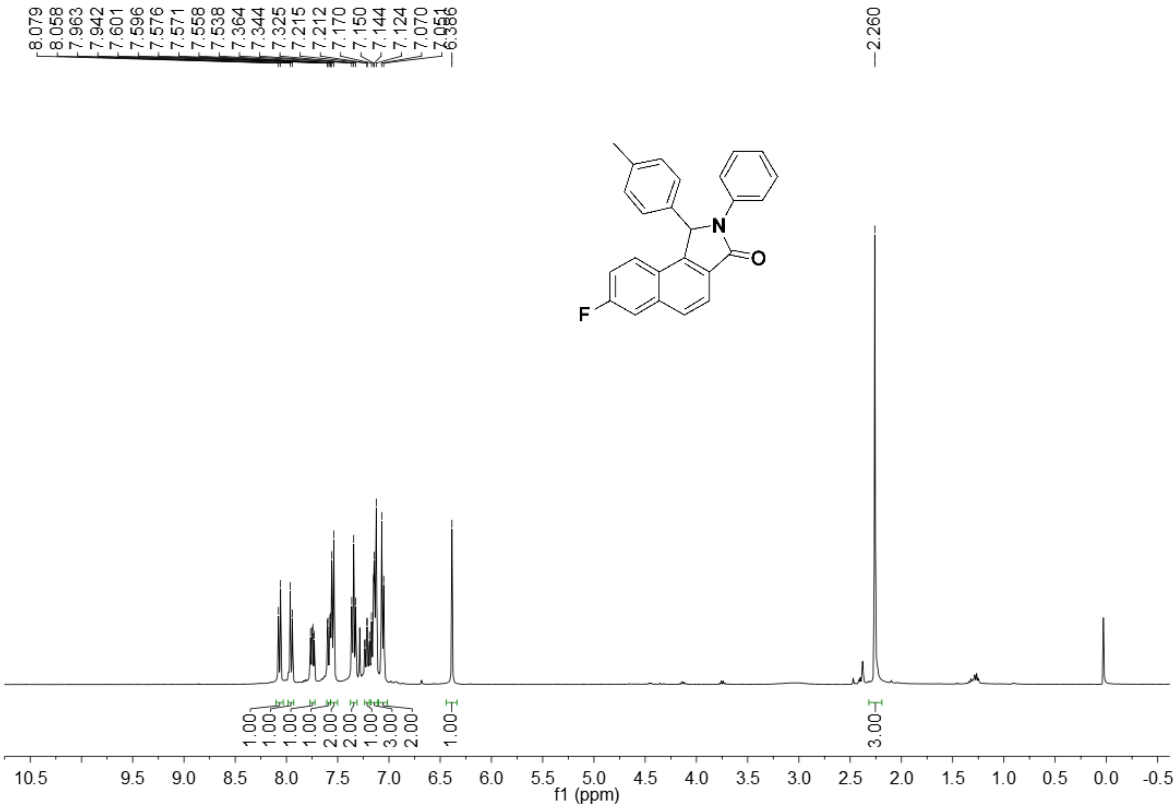

**$^{13}$C NMR Spectrum of Compound 4c**



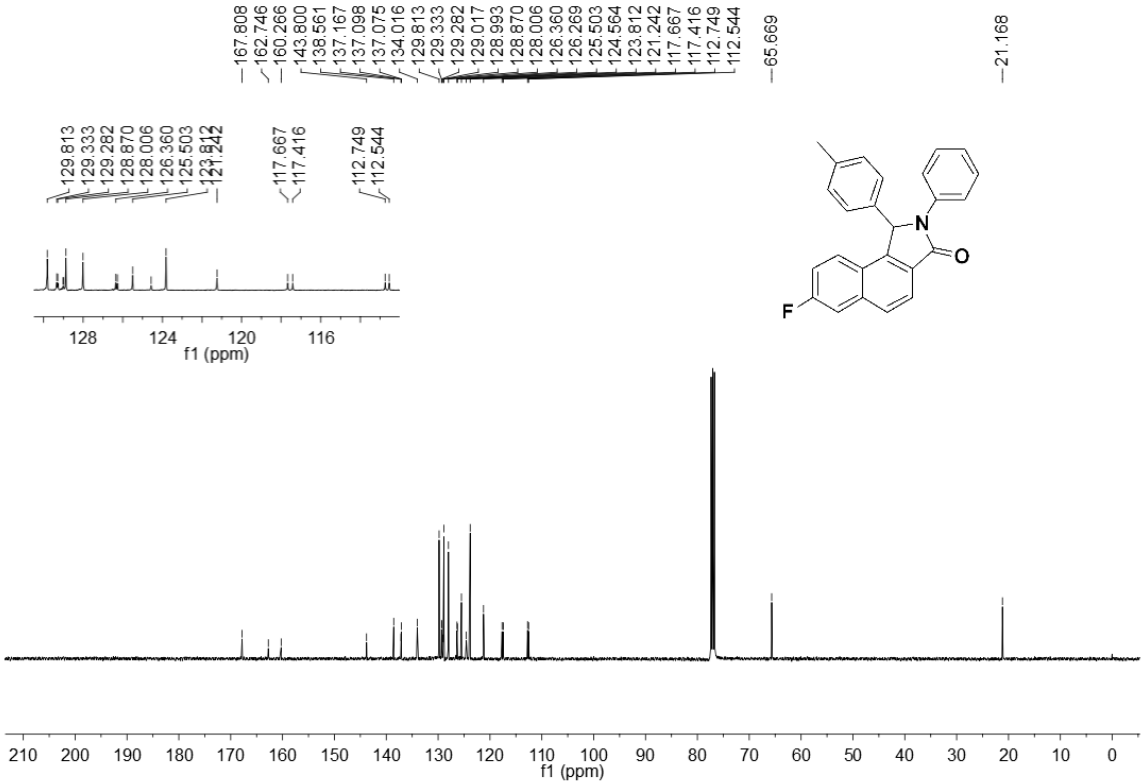

**$^{1}$H NMR Spectrum of Compound 4d**



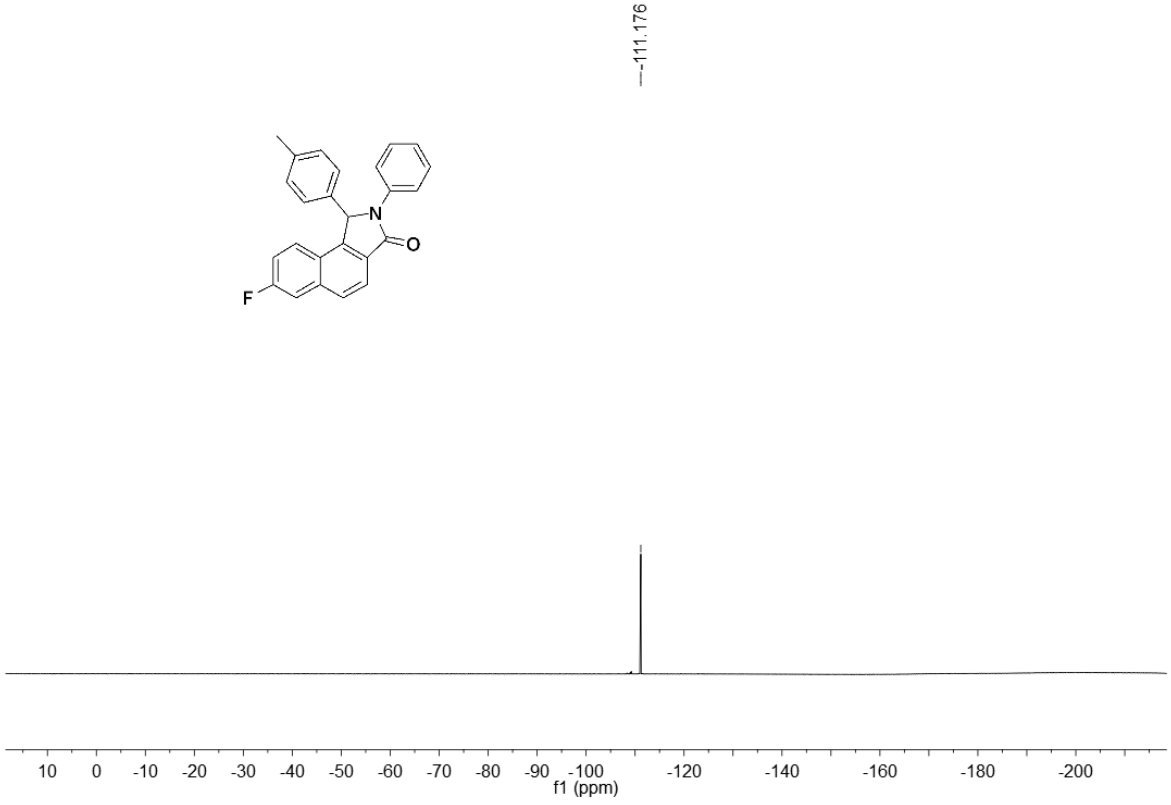

**$^{13}$C NMR Spectrum of Compound 4d**



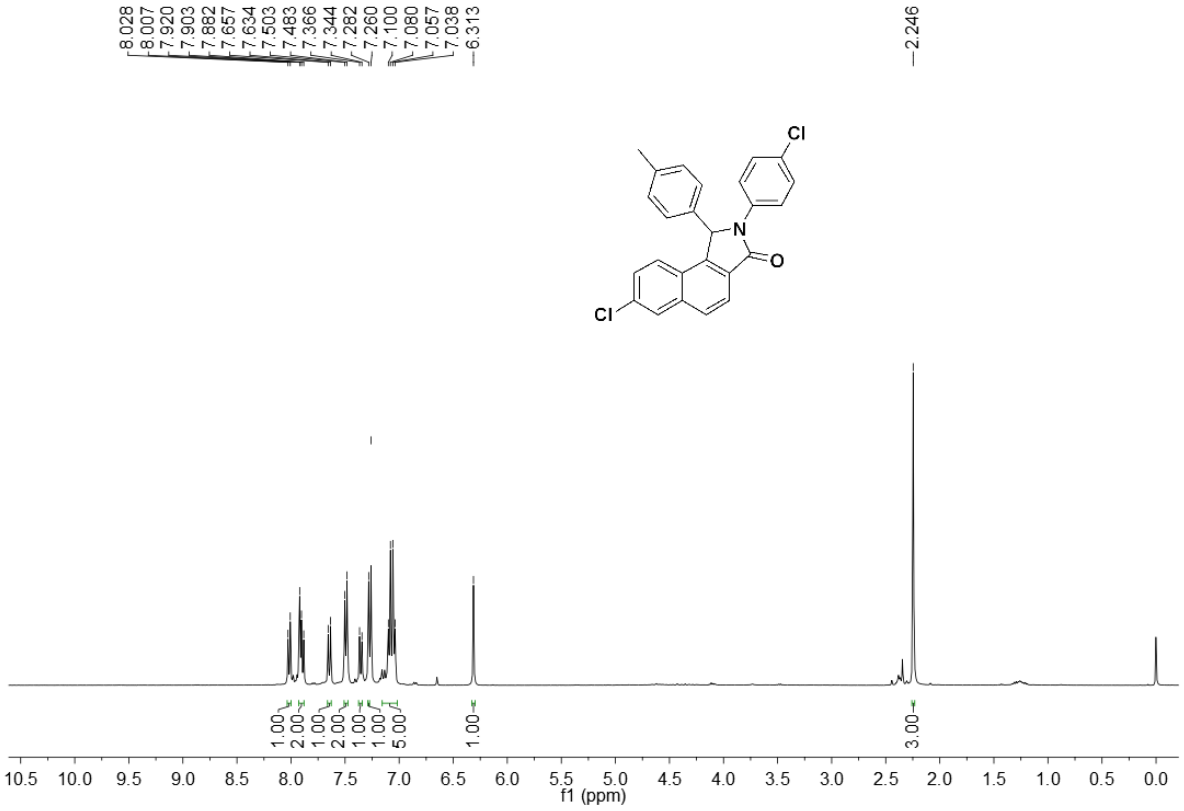

**$^{1}$H NMR Spectrum of Compound 4e**



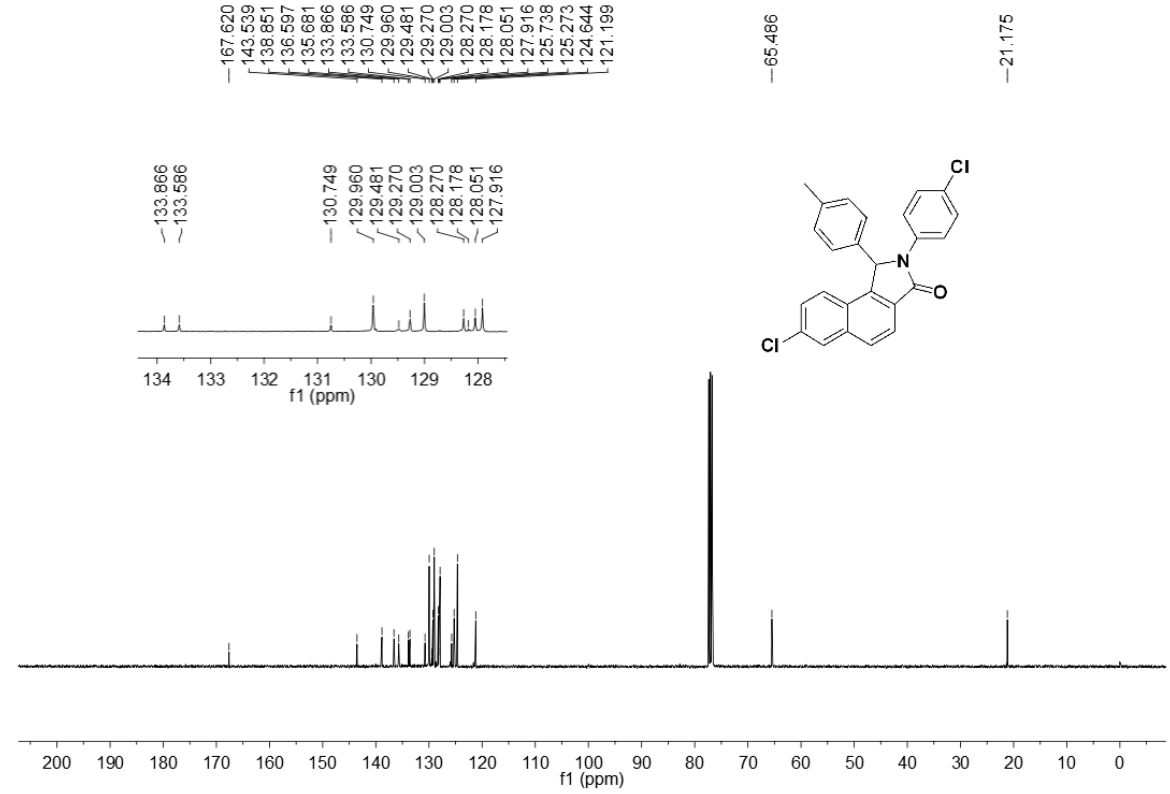

**$^{13}$C NMR Spectrum of Compound 4e**



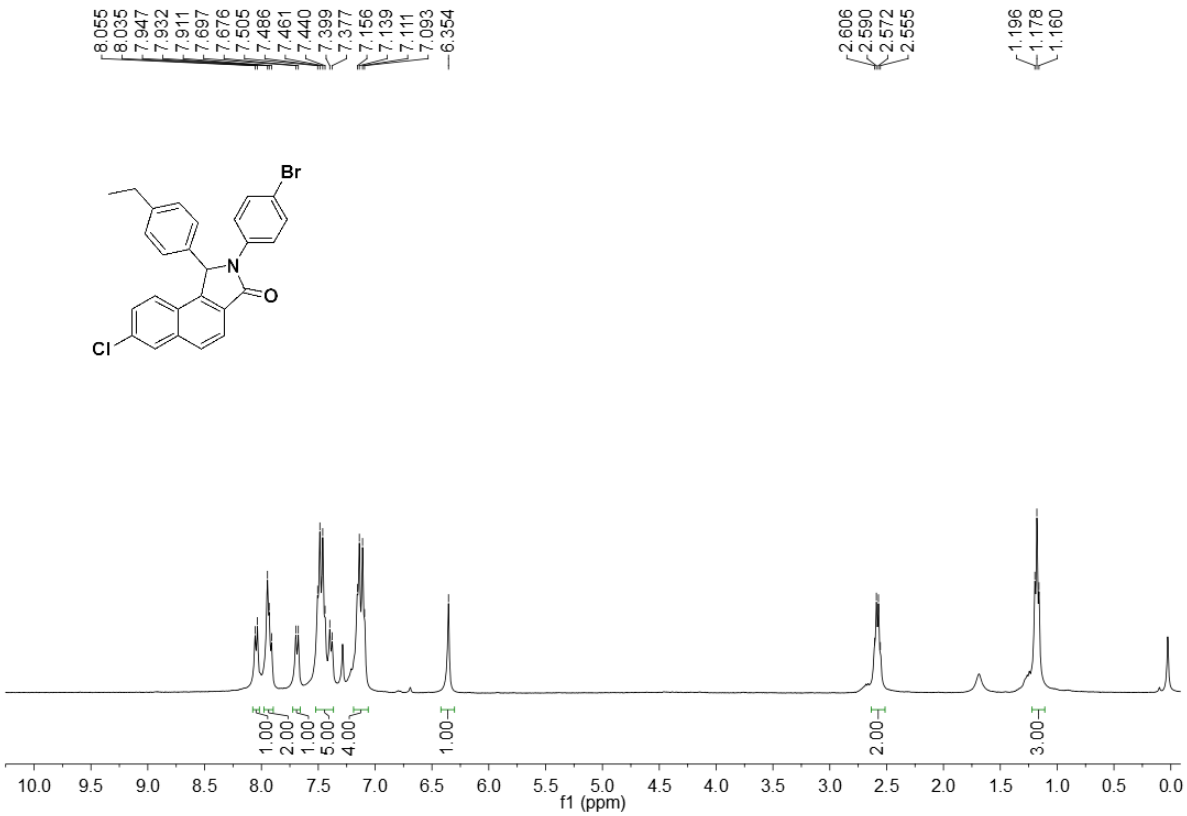

**$^{19}$F NMR Spectrum of Compound 4e**



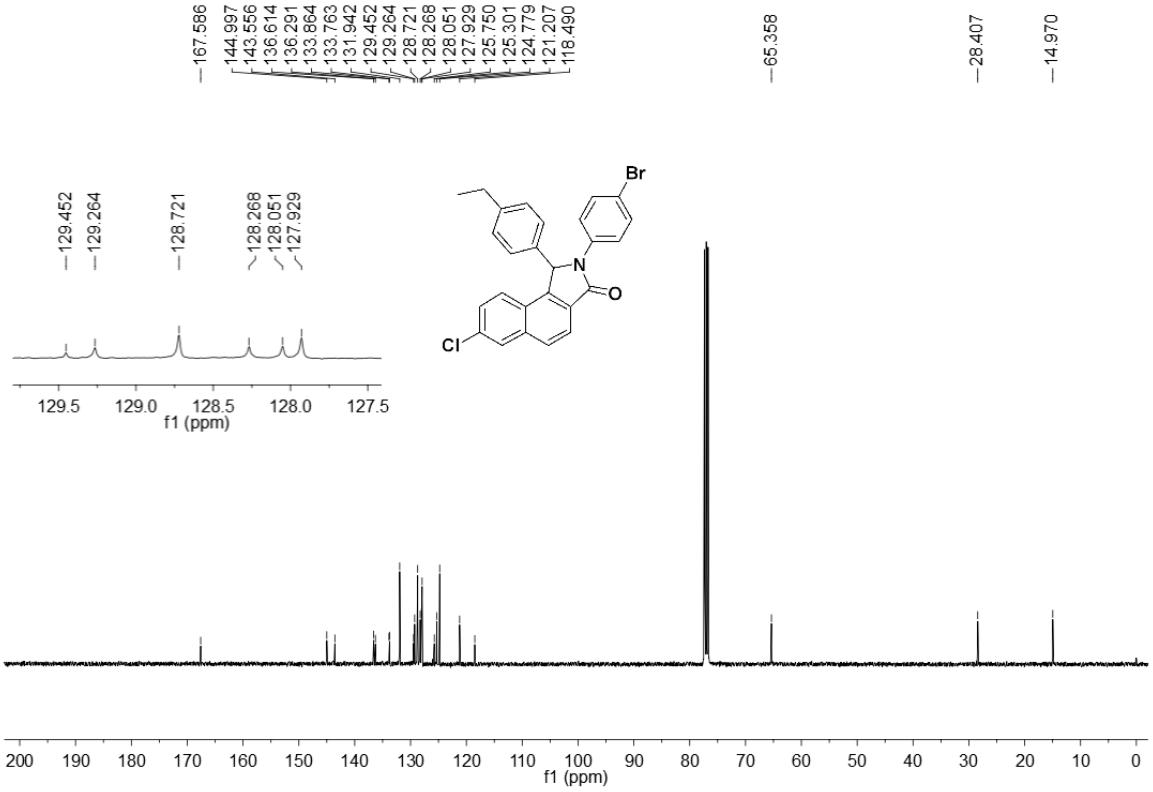

**$^{1}$H NMR Spectrum of Compound 4f**



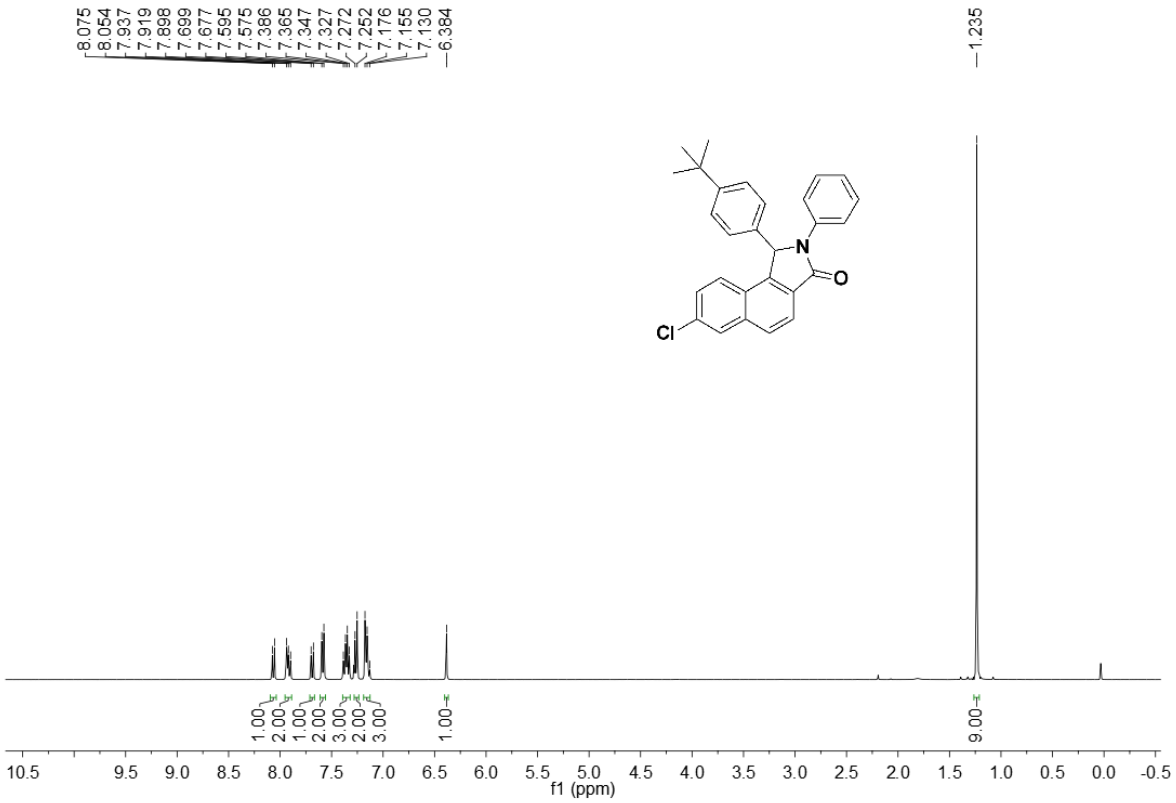

**$^{13}$C NMR Spectrum of Compound 4f**



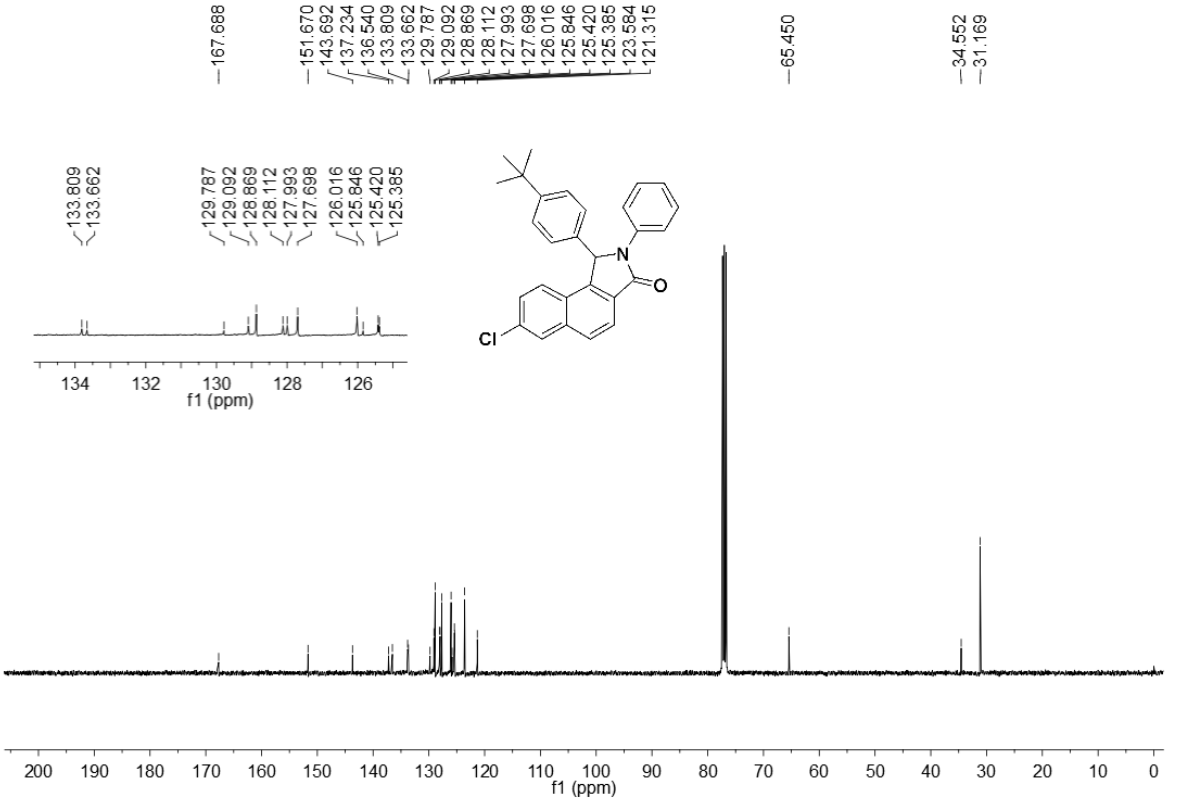

**[1]H NMR Spectrum of Compound 4g**



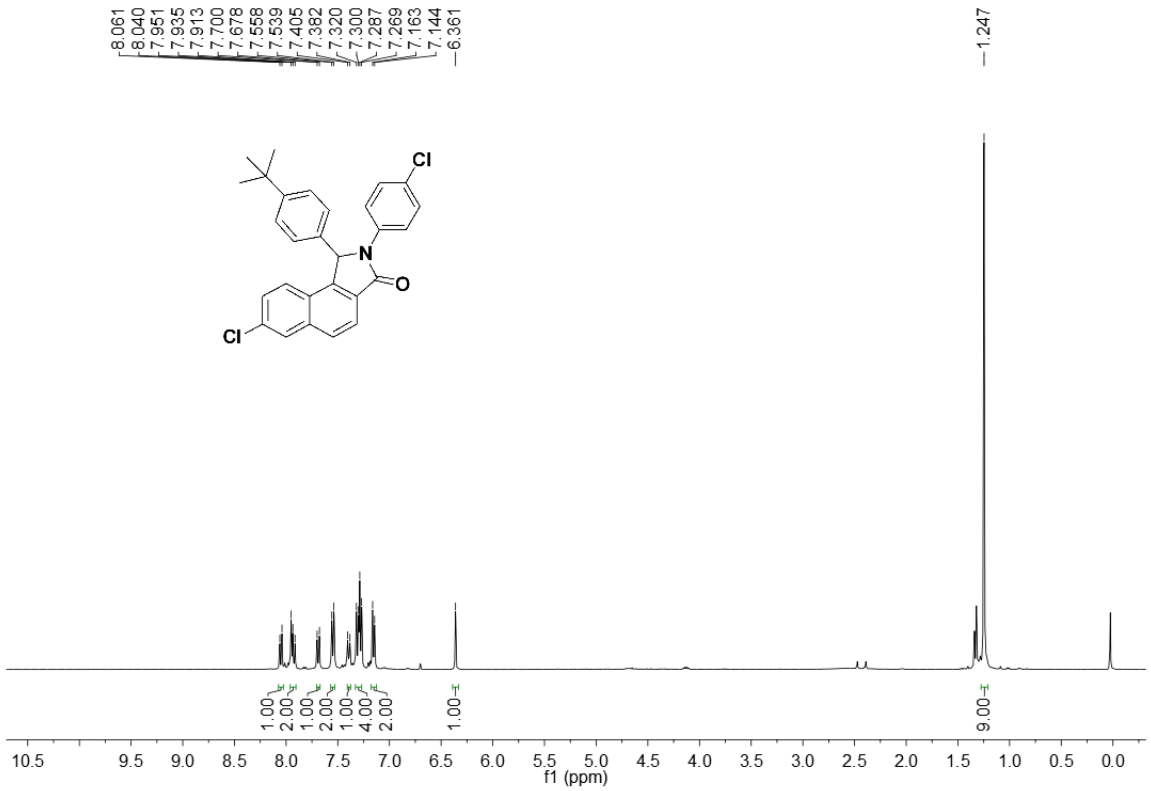

**[13]C NMR Spectrum of Compound 4g**



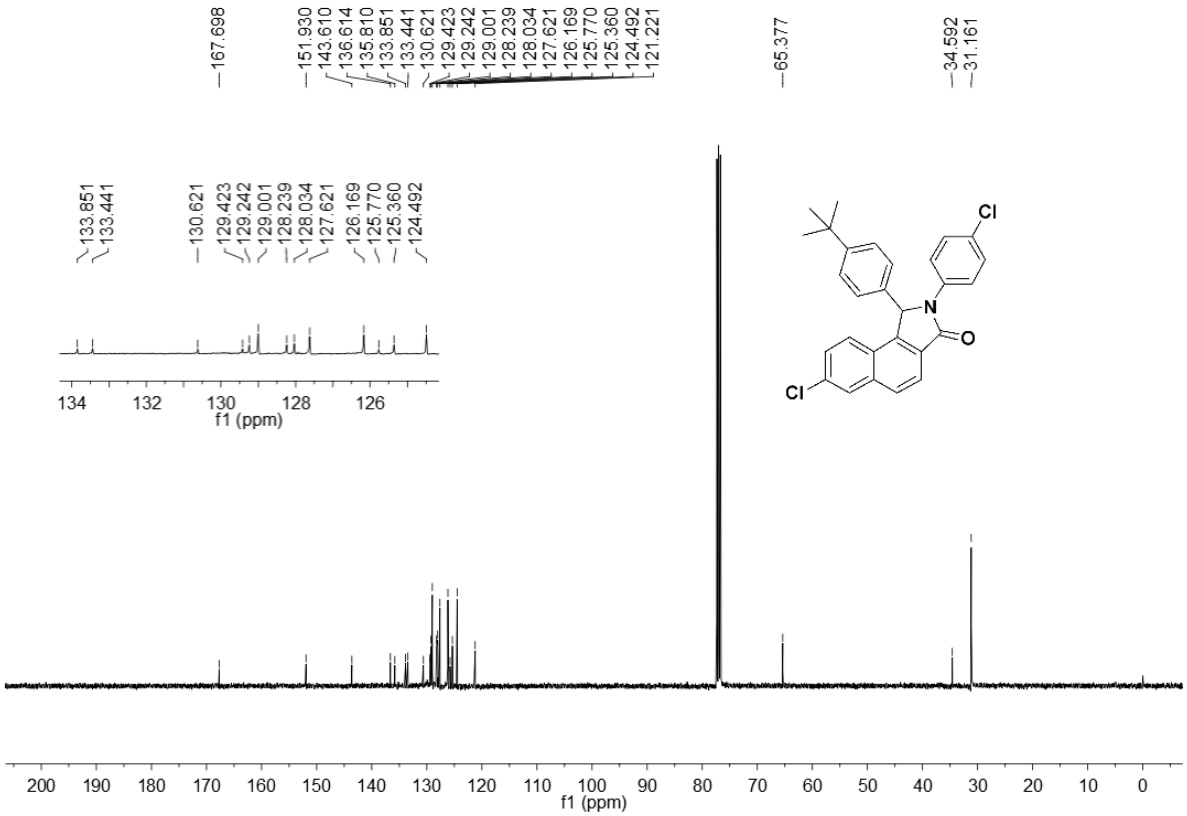

**$^{1}$H NMR Spectrum of Compound 4h**



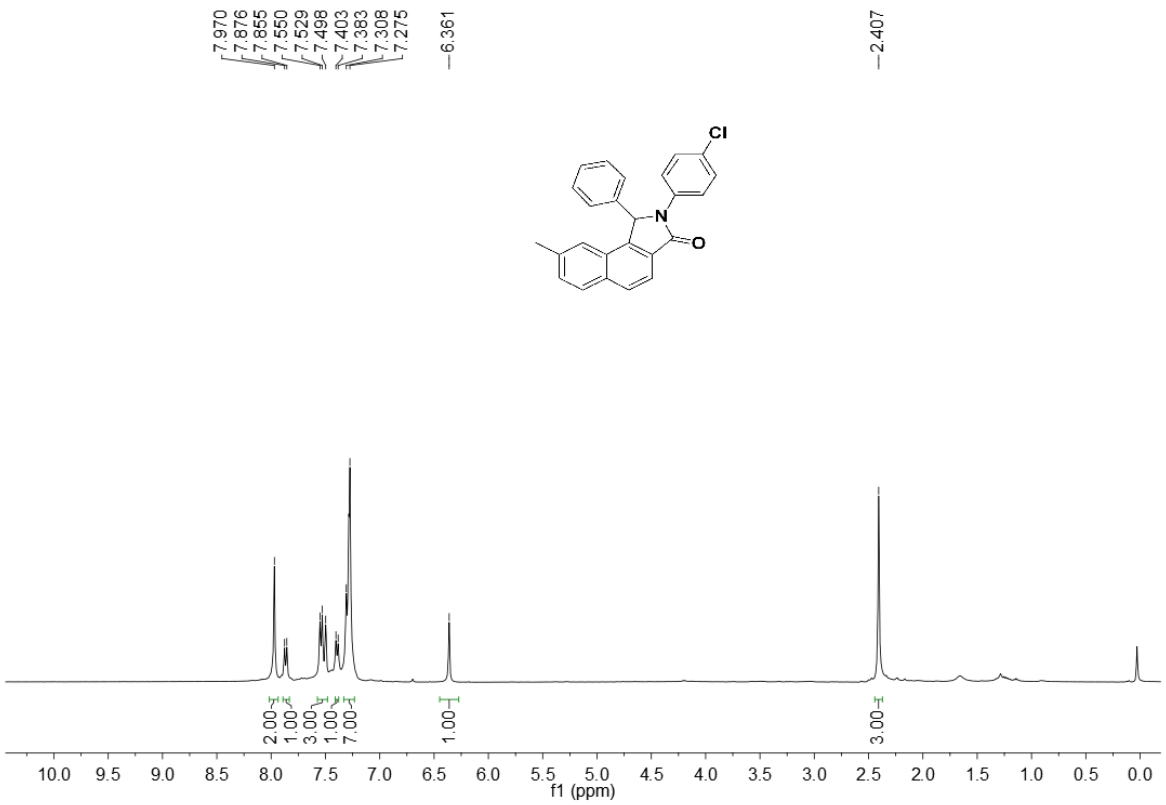

**$^{13}$C NMR Spectrum of Compound 4h**



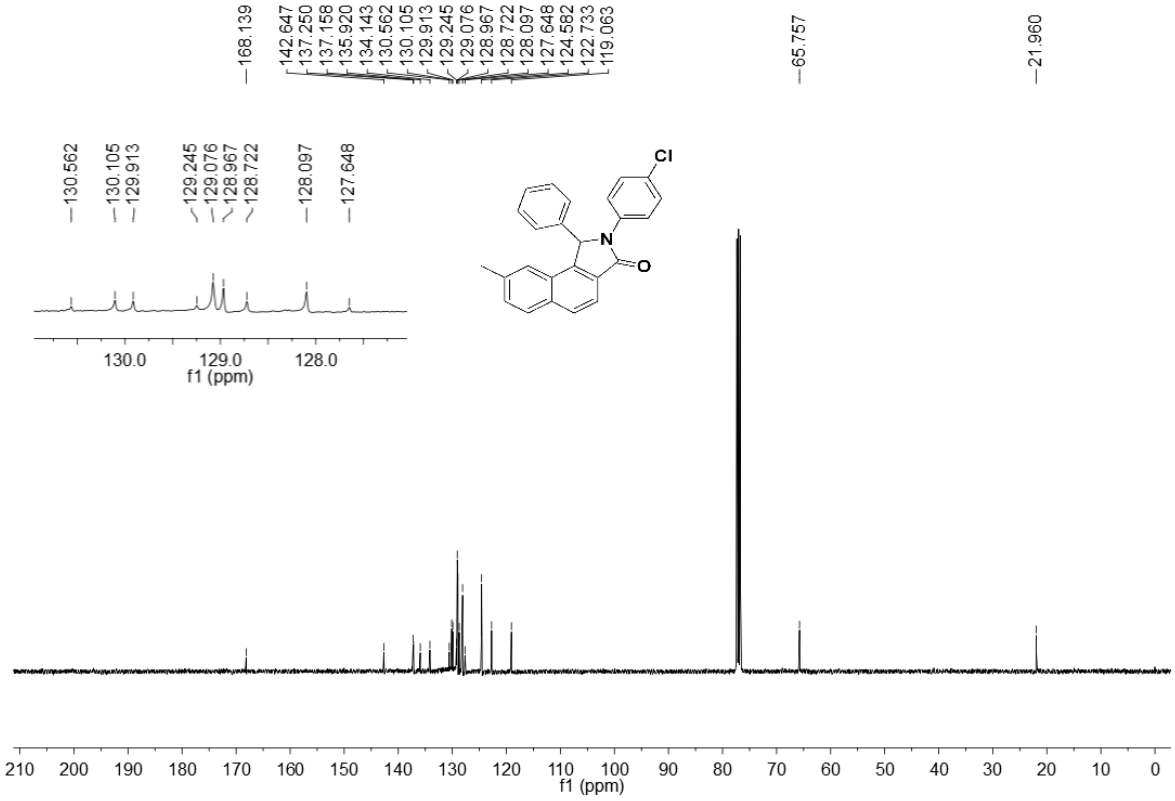

**[1]H NMR Spectrum of Compound 4i**



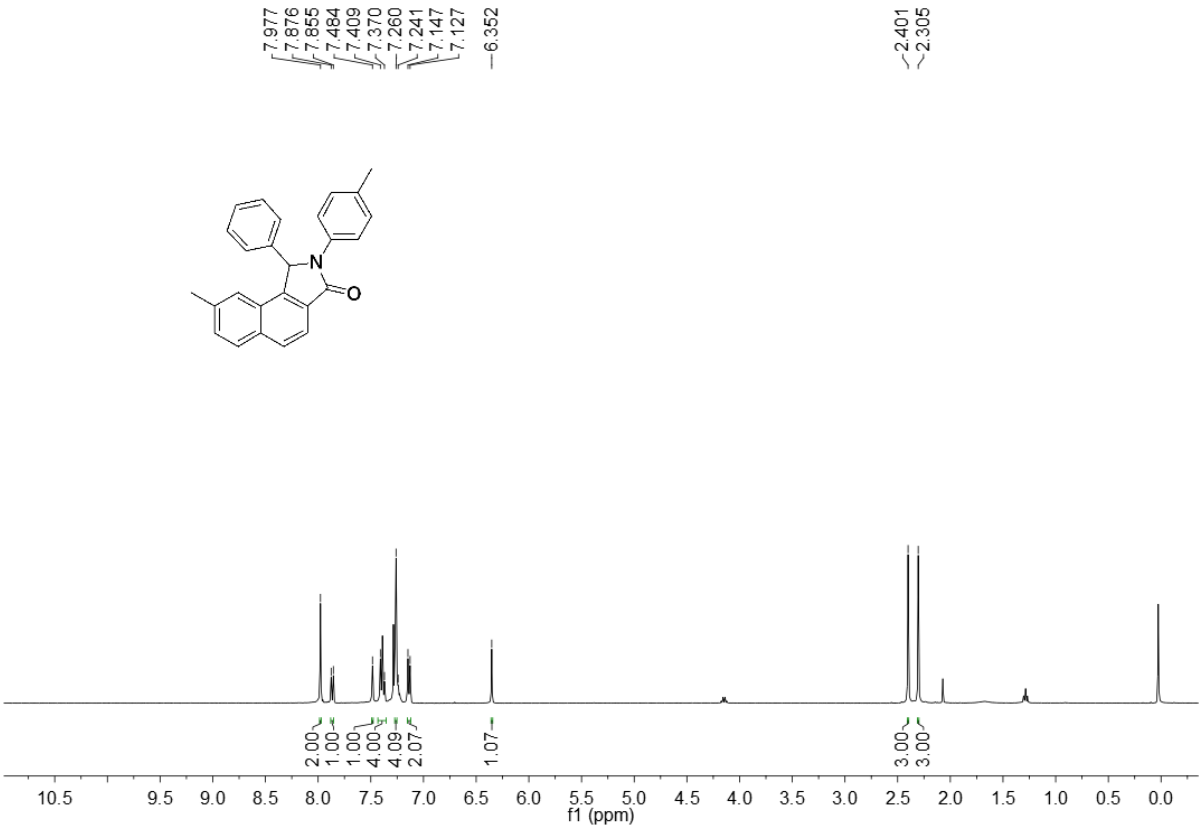

**[13]C NMR Spectrum of Compound 4i**



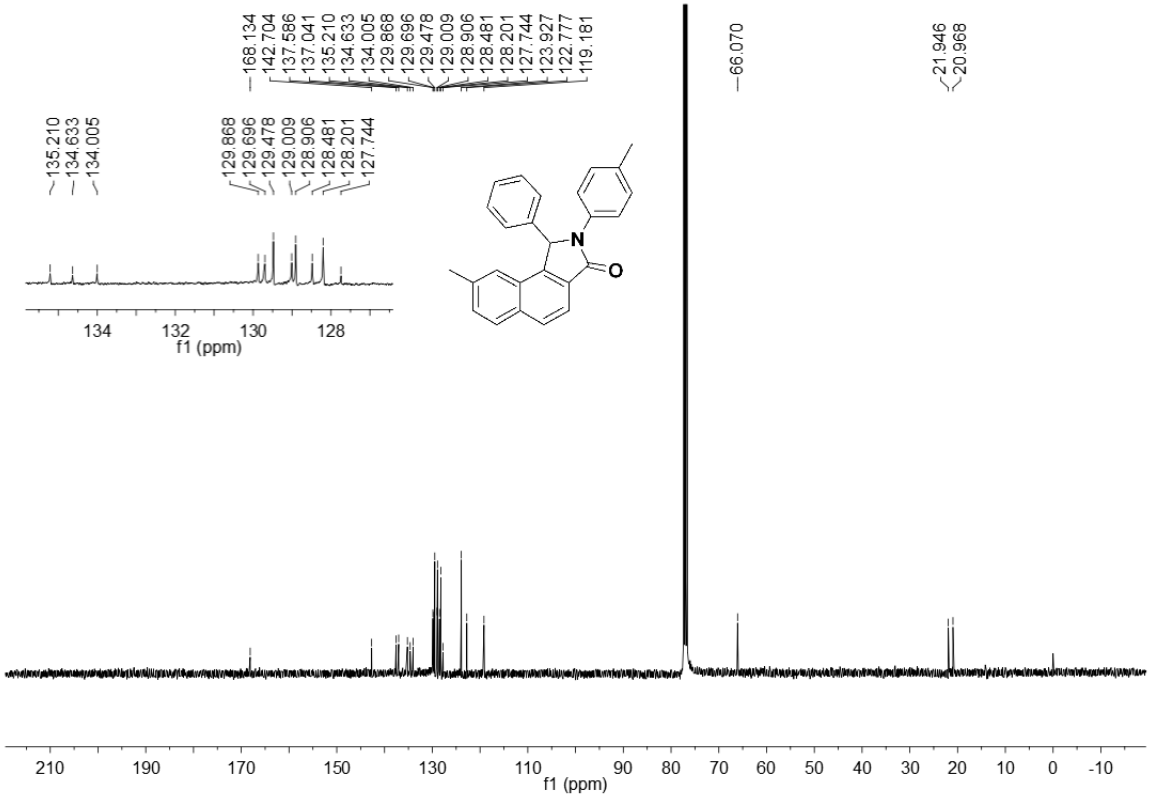

**[1]H NMR Spectrum of Compound 4j**



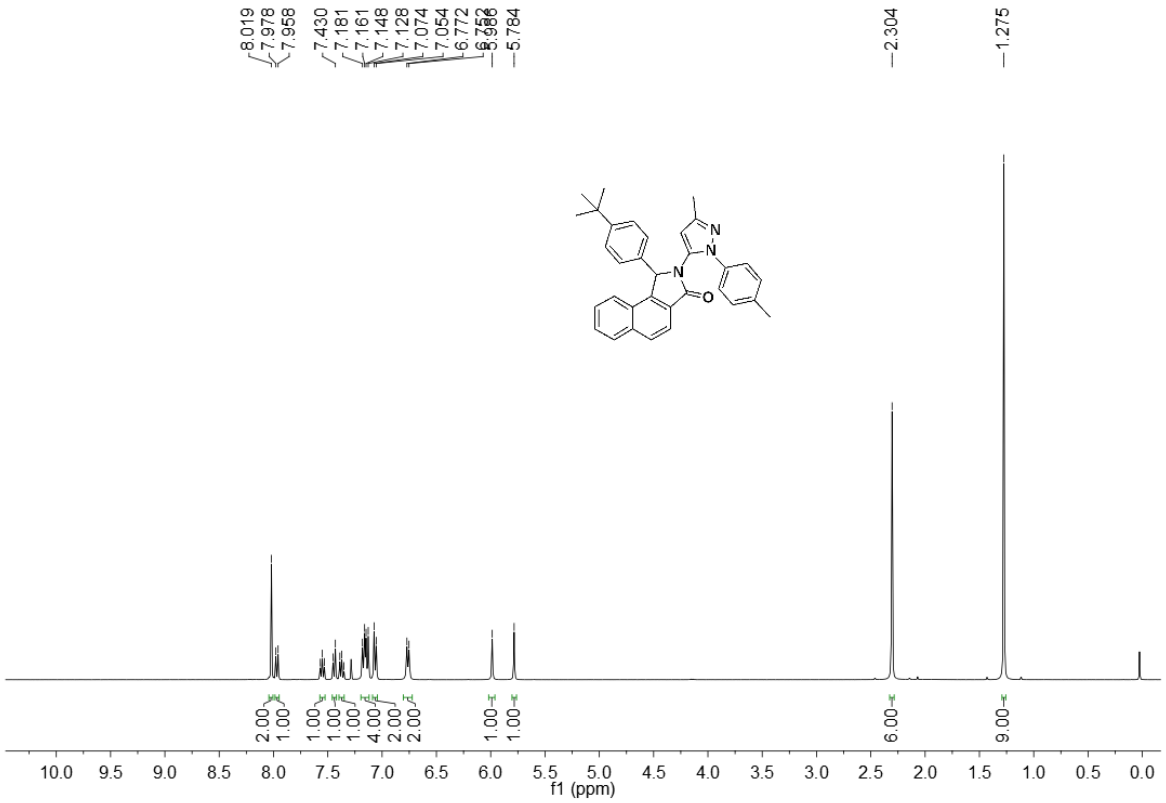

**[13]C NMR Spectrum of Compound 4j**



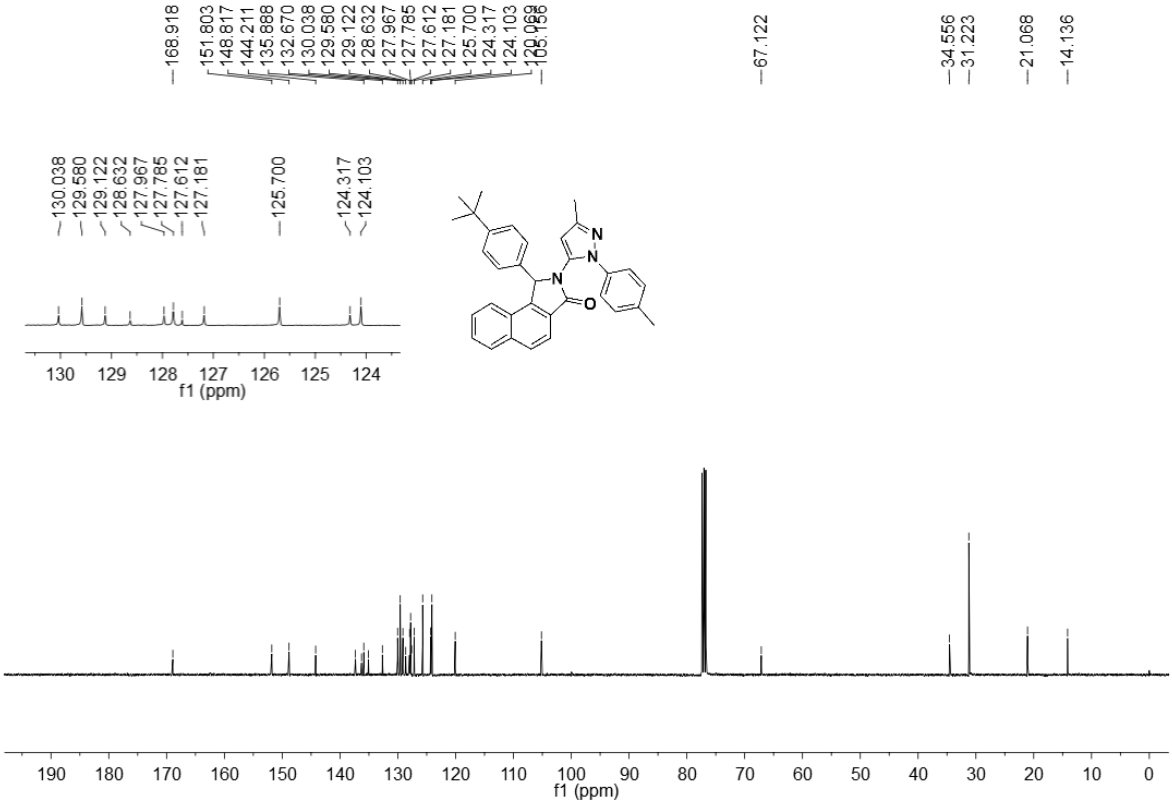

**$^{1}$H NMR Spectrum of Compound 4k**



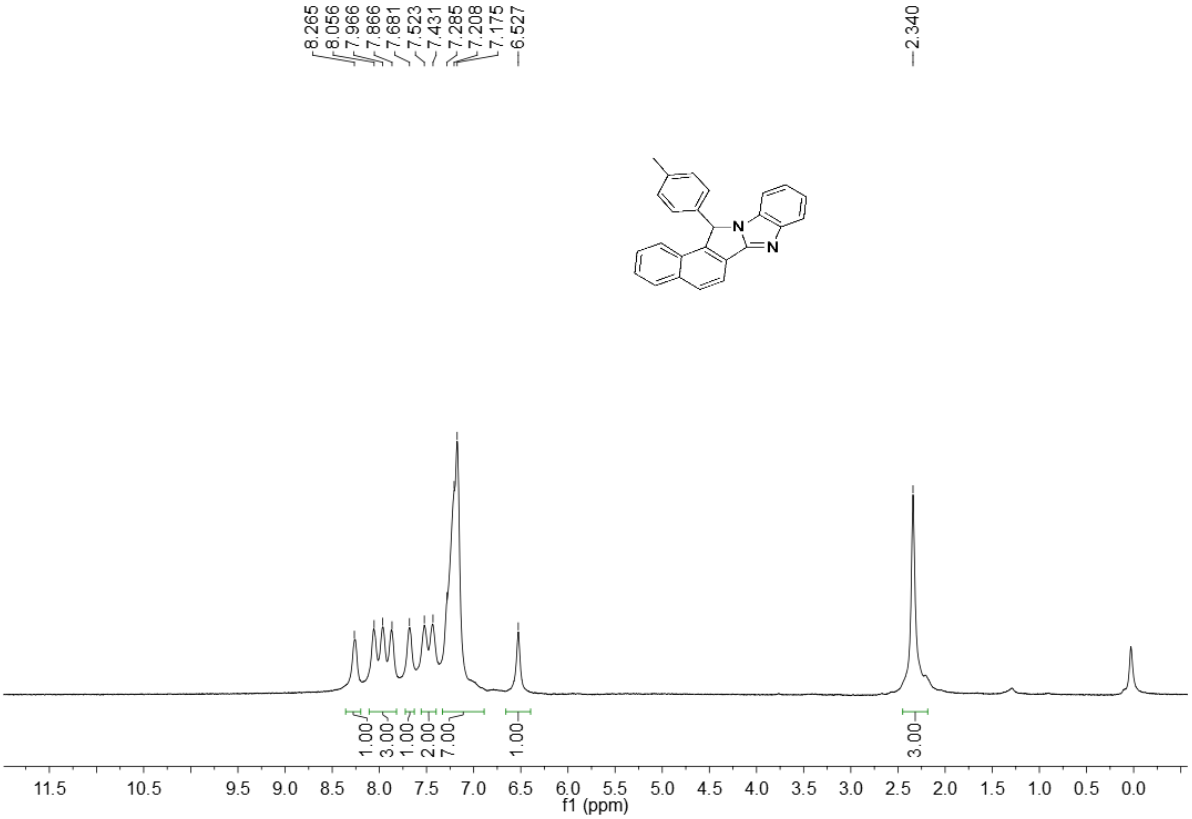

**$^{13}$C NMR Spectrum of Compound 4k**



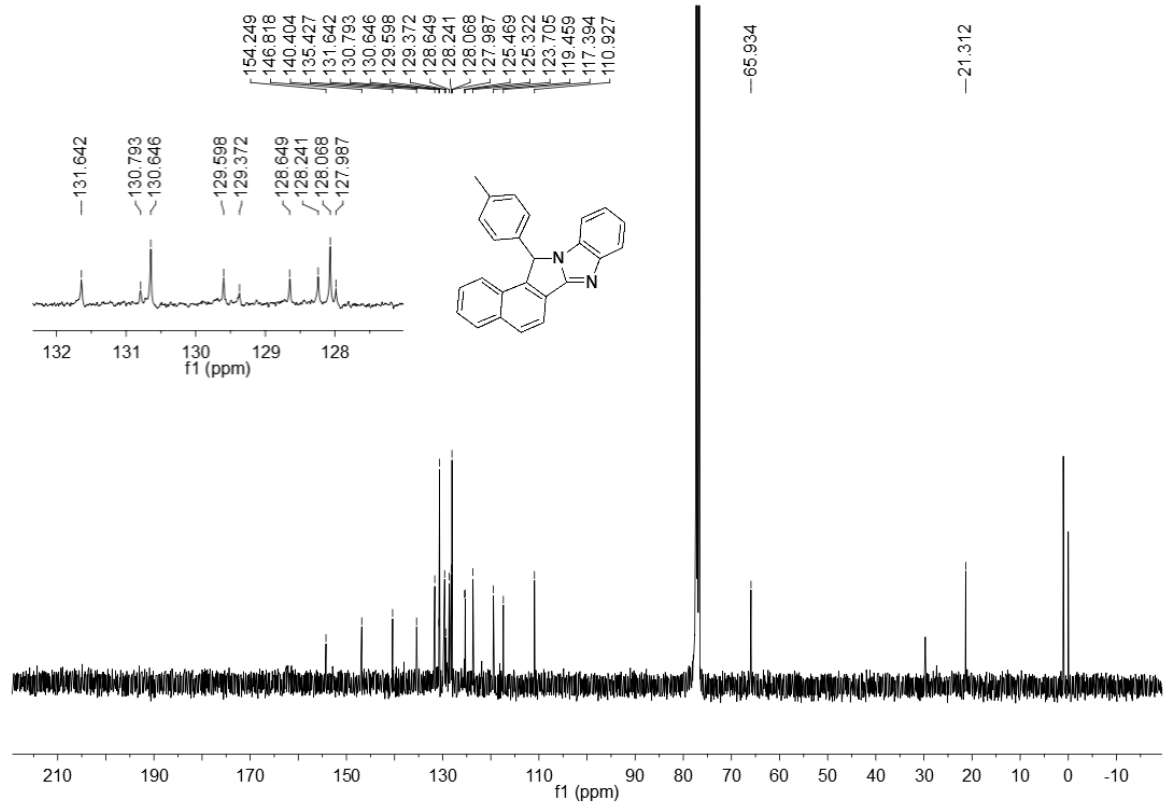

**[1]H NMR Spectrum of Compound 4l**



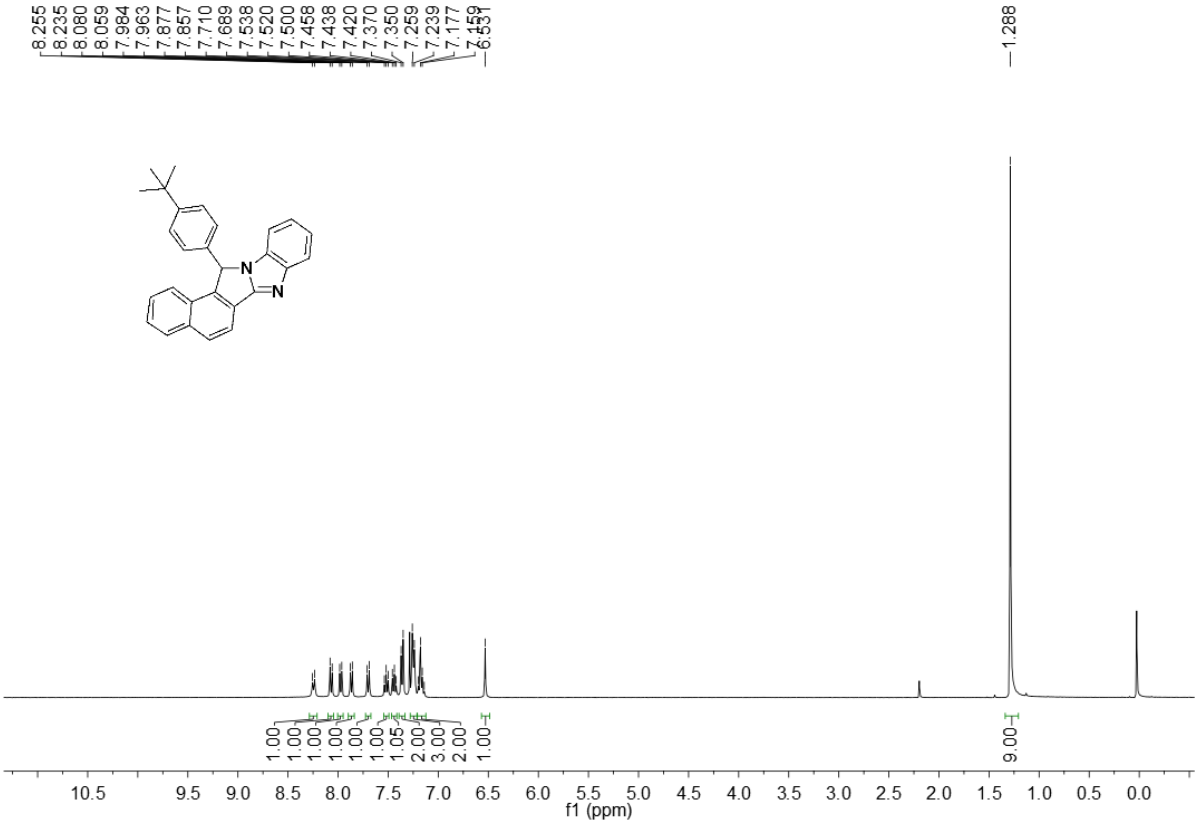

**[13]C NMR Spectrum of Compound 4l**



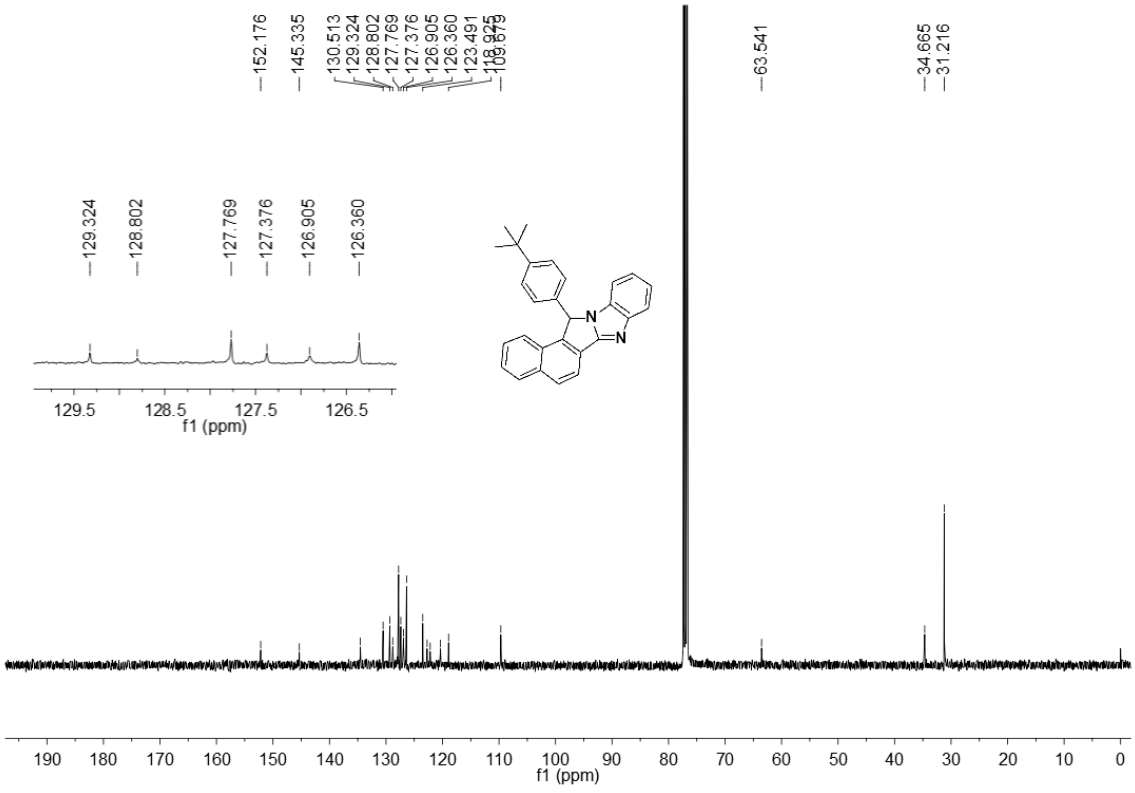

**$^{1}$H NMR Spectrum of Compound 6a**



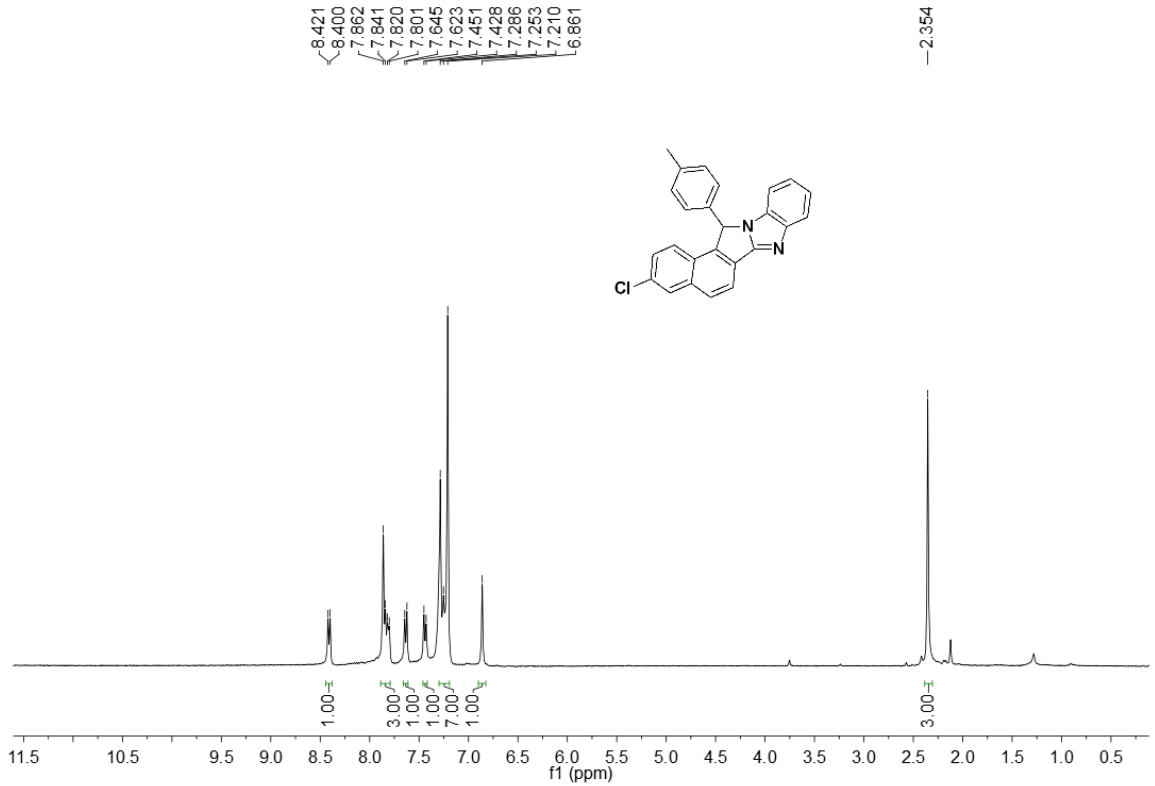

**$^{13}$C NMR Spectrum of Compound 6a**



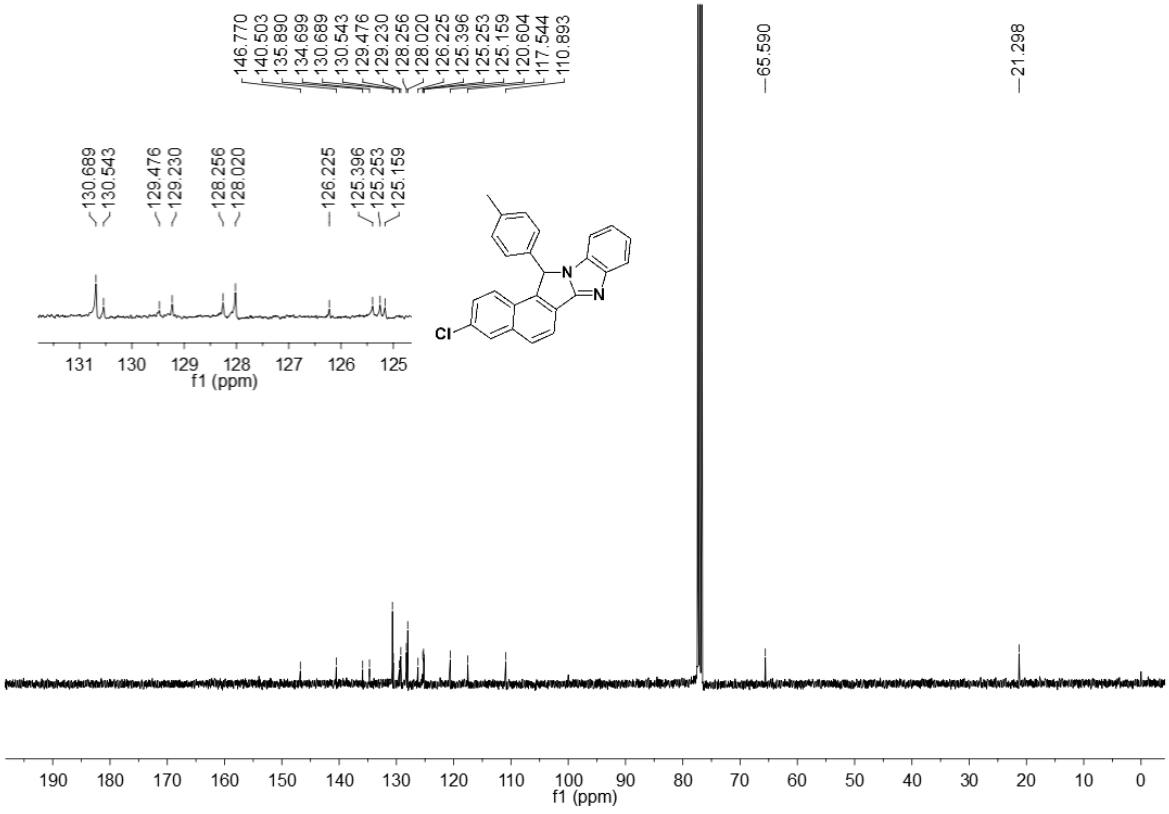

**$^{1}$H NMR Spectrum of Compound 6b**



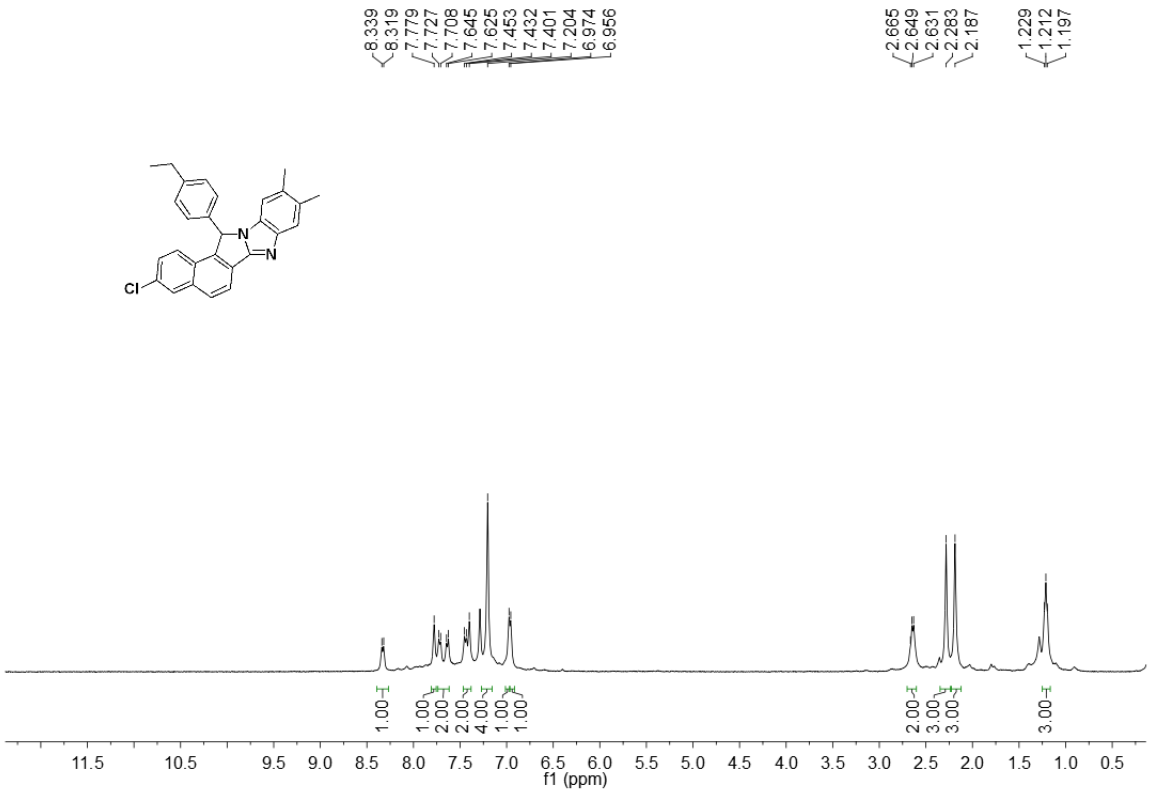

**$^{13}$C NMR Spectrum of Compound 6b**



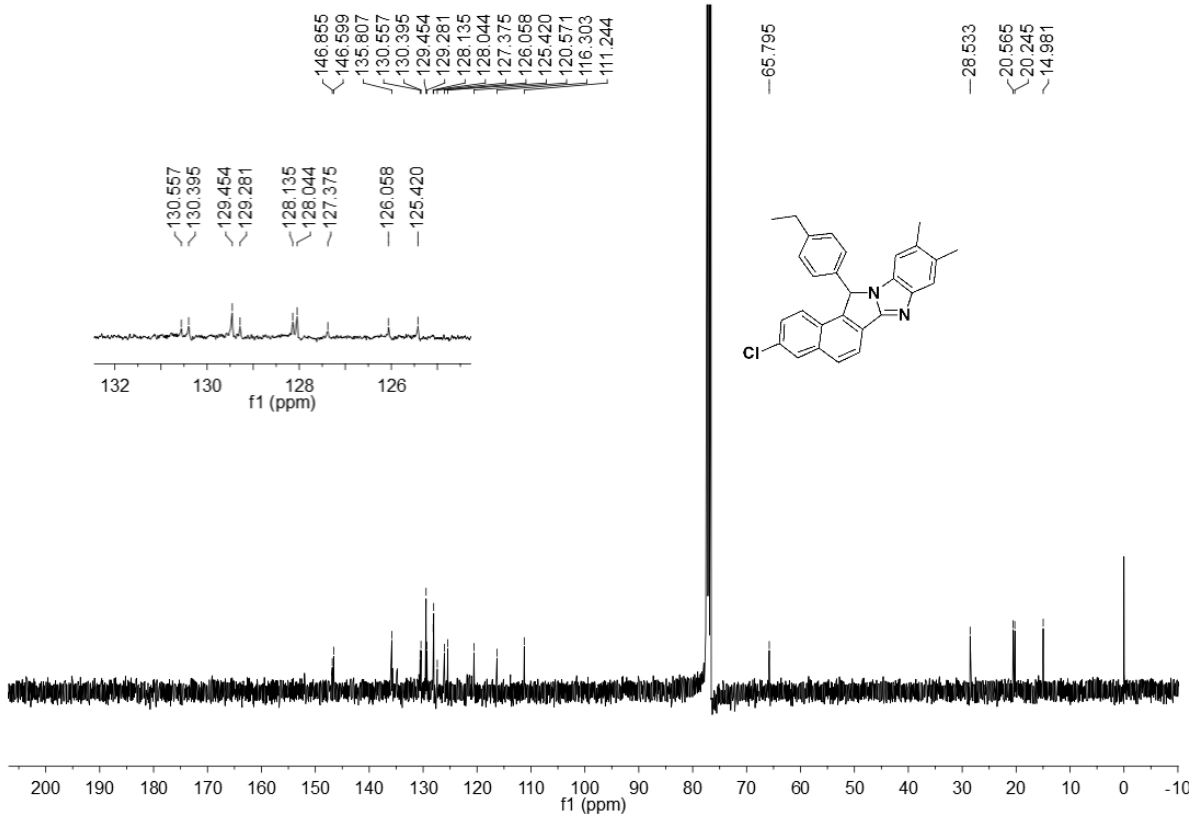

**$^{1}$H NMR Spectrum of Compound 6c**



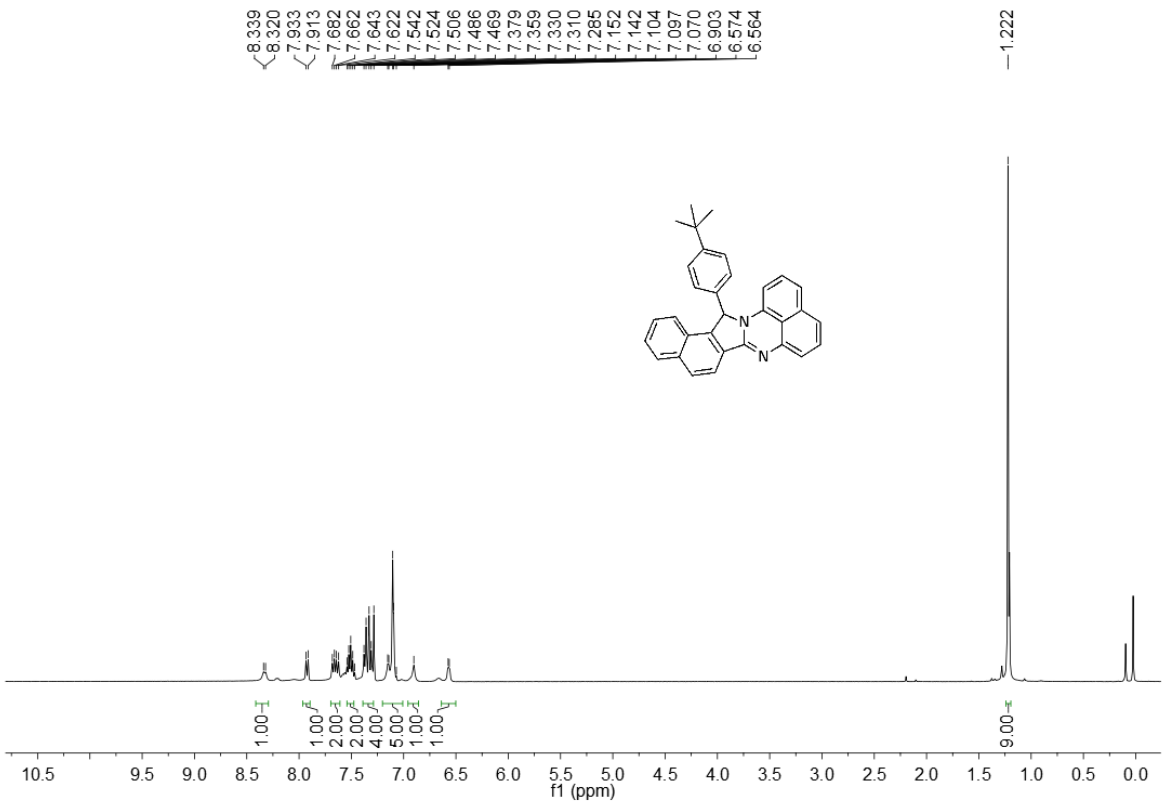

**$^{13}$C NMR Spectrum of Compound 6c**



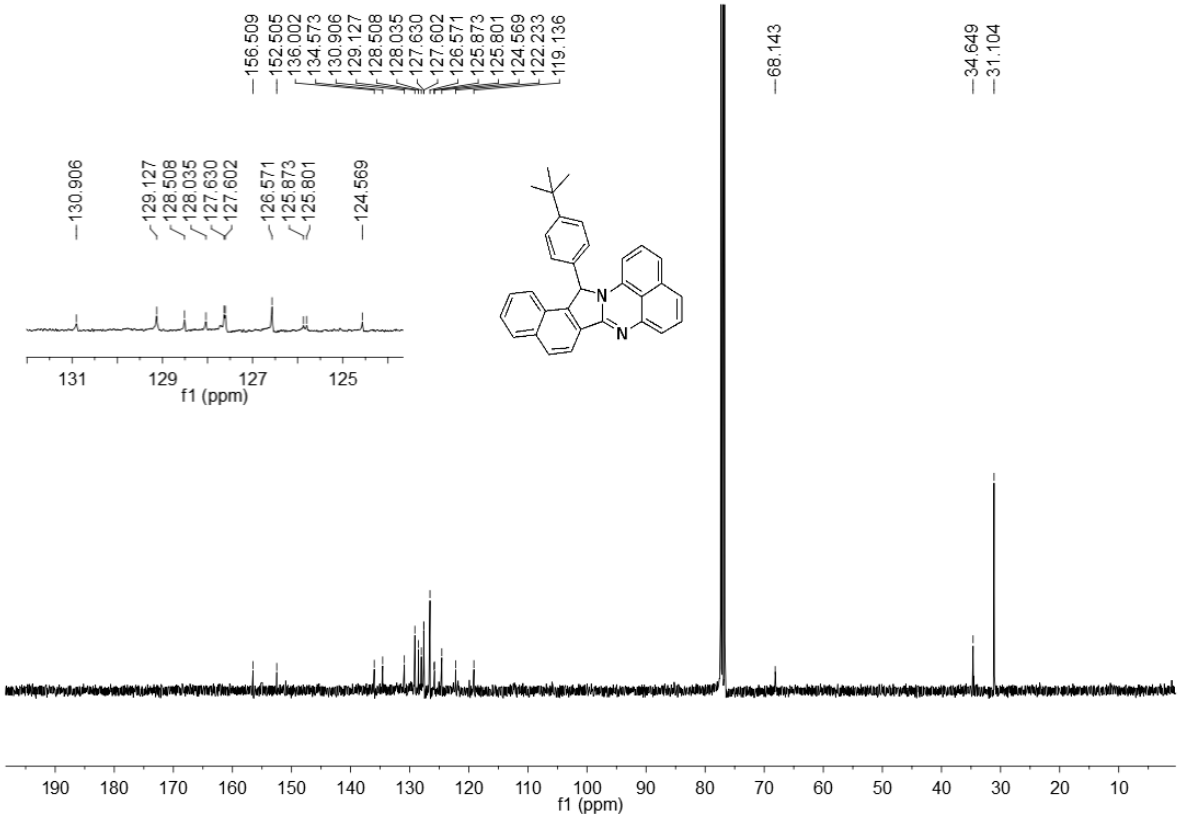

**[1]H NMR Spectrum of Compound 6d**




**[13]C NMR Spectrum of Compound 6d**




**[1]H NMR Spectrum of Compound 6e**




**[13]C NMR Spectrum of Compound 6e**