Supplementary Material

A practical Cu(I)-catalyzed domino approach to 1,2-disubstituted indoles and its application for the assembly of indolophenanthridines

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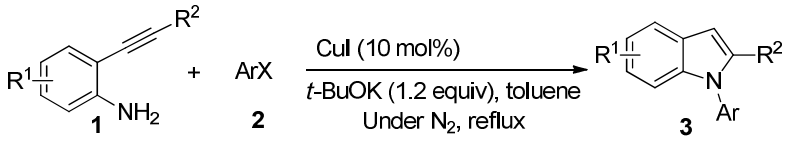
1. General Information

Unless otherwise noted, all one-pot reactions were carried out in an over-dried Schlenk tube equipped with a magnetic stir bar under N_2 atmosphere. Toluene, *o*-xylene and dioxane were distilled from Na; DCE and DMF were distilled from CaH_2. 2-alkynylanilines[1] and aryl halides[2] were synthesized according to the known literatures. All other reagents were obtained from commercial sources and utilized without further purification, if not stated otherwise. All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ on a 600 M Hz instrument with TMS as internal standard. Recorded shifts were reported in parts per million (δ) downfield from TMS. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant (*J*, Hz) and integration. TLC was carried out with 0.2 mm thick silica gel plates (GF254). Visualization was accomplished by UV light. The columns were hand packed with silica gel 60 (150-200 mesh). Unknown products were additionally confirmed by HRMS. Mass spectra were obtained using ESI ionization.

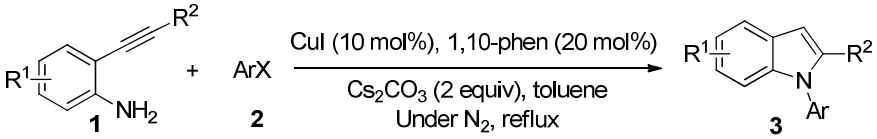
2. General Procedure

General Procedure for Cu(I)-Catalyzed One-Pot Synthesis of 1,2-Disubstituted Indoles 3 with *t*-BuOK as the base.



An oven-dried Schlenk tube was charged with a magnetic stir bar, 2-alkynylaniline **1** (1.0 mmol, 1 equiv), CuI (0.1 mmol, 10 mol %) and *t*-BuOK (1.2 mmol, 1.2 equiv). The tube was capped and then evacuated and backfilled with nitrogen (3 times). Under a positive pressure of nitrogen, a solution of aryl halide (1.1 mmol, 1.1 equiv) in toluene (3 mL) was added *via* syringe. The tube was sealed and allowed to stir at 110 °C (monitored by TLC). After being cooled to room temperature, the mixture was diluted with ethyl acetate (30 mL), filtered through a plug of silica gel and concentrated. The residue was purified by column chromatography on silica gel using petrol/EtOAc (50:1 → 20:1, v:v) as eluent to give product **3**.

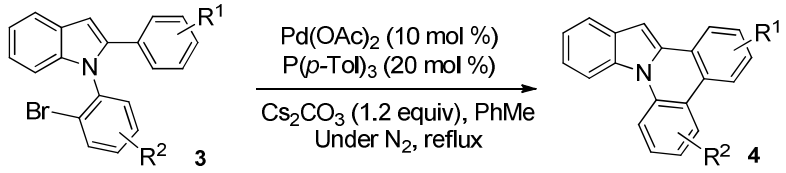
General Procedure for Cu(I)-Catalyzed One-Pot Synthesis of 1,2-Disubstituted Indoles 3 with Cs_2CO_3 as the base.



An oven-dried Schlenk tube was charged with a magnetic stir bar, 2-alkynylaniline **1** (1.0

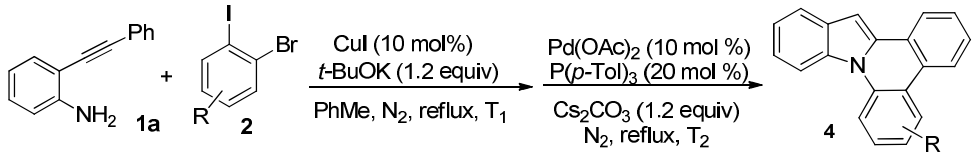
mmol, 1 equiv), CuI (0.1 mmol, 10 mol %), 1,10-phen (0.2 mmol, 20 mol) and Cs_2CO_3 (2 mmol, 2 equiv). The tube was capped and then evacuated and backfilled with nitrogen (3 times). Under a positive pressure of nitrogen, a solution of aryl halide (1.1 mmol, 1.1 equiv) in toluene (3 mL) was added *via* syringe. The tube was sealed and allowed to stir at 110 °C (monitored by TLC). After being cooled to room temperature, the mixture was diluted with ethyl acetate (30 mL), filtered through a plug of silica gel and concentrated. The residue was purified by column chromatography on silica gel using petrol/EtOAc (50:1 → 20:1, v:v) as eluent to give product **3**.

General Procedure for Pd-Catalyzed Synthesis of Indolo[1,2-*f*]phenanthridine 4.



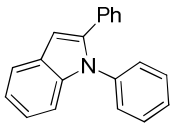
An oven-dried Schlenk tube was charged with a magnetic stir bar, brominated 1,2-diphenyl-1*H*-indole **3** (0.3 mmol, 1 equiv), $Pd(OAc)_2$ (0.03 mmol, 10 mol %), $(p\text{-Tol})_3P$ (0.06 mmol, 20 mol %) and Cs_2CO_3 (0.36 mmol, 1.2 equiv). The tube was capped and then evacuated and backfilled with nitrogen (3 times). Under a positive pressure of nitrogen, toluene (3 mL) was then added. The tube was sealed and allowed to stir at 110 °C (monitored by TLC). After being cooled to room temperature, the mixture was diluted with ethyl acetate (30 mL), filtered through a plug of silica gel and concentrated. The residue was purified by column chromatography on silica gel using petrol/EtOAc (20:1 → 10:1, v:v) as eluent to give product **4**.

General Procedure for One-Pot Tendem Synthesis of Indolo[1,2-*f*]phenanthridine.

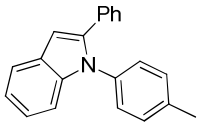


An oven-dried Schlenk tube was charged with a magnetic stir bar, 2-alkynylaniline **1** (1 mmol, 1equiv), CuI (0.1 mmol, 10 mol %) and *t*-BuOK (1.2 mmol, 1.2 equiv). The tube was capped and then evacuated and backfilled with nitrogen (3 times). Under a positive pressure of nitrogen, a solution of *o*-bromo iodobeneene **2** (1.1 mmol, 1.1 equiv) in toluene (3 mL) was added *via* syringe. The tube was sealed and allowed to stir at 110 °C (monitored by TLC). After being cooled to room temperature, $Pd(OAc)_2$ (0.03 mmol, 10 mol %), $(p\text{-Tol})_3P$ (0.06 mmol, 20 mol %) and Cs_2CO_3 (0.36 mmol, 1.2 equiv) was added. Filled with positive nitrogen stream (3 minutes), the tube was sealed and allowed to stir at 110 °C (monitored by TLC). After being cooled to room temperature, the mixture was diluted with ethyl acetate (30 mL), filtered through a plug of silica gel and concentrated. The residue was purified by column chromatography on silica gel using petrol/EtOAc (20:1 → 10:1, v:v) as eluent to give product **4**.

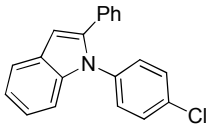
3. Characterization Data for the Products



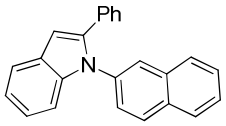
1,2-Diphenyl-1*H*-indole (**3a**).[3] White solid (87% yield), mp 78 - 79 °C (Lit. mp: 78 - 80 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 - 7.67 (m, 1H), 7.34 - 7.36 (m, 2H), 7.28 - 7.29 (m, 2H), 7.24 - 7.25 (m, 2H), 7.16 - 7.22 (m, 7H), 6.79 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.8, 139.1, 138.6, 132.6, 129.3 (2C), 129.0 (2C), 128.4, 128.3 (2C), 128.1 (2C), 127.4, 127.3, 122.5, 120.8, 120.7, 110.7, 103.8.



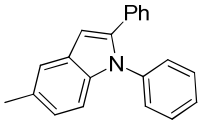
2-Phenyl-1-(*p*-tolyl)-1*H*-indole (**3b**).[4] Pale yellow solid (92% yield), mp 80 - 82 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67 - 7.69 (m, 1H), 7.20 - 7.29 (m, 8H), 7.15 - 7.18 (m, 2H), 7.12 - 7.14 (m, 2H), 6.79 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.9, 139.2, 137.2, 136.0, 132.8, 130.0 (2C), 129.0 (2C), 128.3 (2C), 128.27, 127.9 (2C), 127.4, 122.3, 120.7, 120.6, 110.8, 103.5, 21.3.



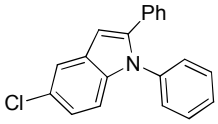
1-(4-Chlorophenyl)-2-phenyl-1*H*-indole (**3c**).[5] Yellow solid (72% yield), mp 100 - 102 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67 - 7.68 (m, 1H), 7.36 - 7.38 (m, 2H), 7.23 - 7.28 (m, 6H), 7.16 - 7.19 (m, 4H), 6.80 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.7, 138.9, 137.2, 133.0, 132.3, 129.6 (2C), 129.31 (2C), 129.30, 129.1 (2C), 128.5 (2C), 127.6, 122.7, 121.1, 120.8, 110.5, 104.3.



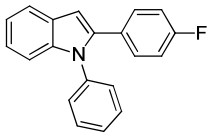
1-(Naphthalen-2-yl)-2-phenyl-1*H*-indole (**3d**). Yellow solid (70% yield), mp 112 - 114 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 - 7.84 (m, 4H), 7.71 - 7.72 (m, 1H), 7.48 - 7.50 (m, 2H), 7.30 - 7.34 (m, 3H), 7.22 - 7.25 (m, 1H), 7.16 - 7.19 (m, 5H), 6.86 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.9, 139.3, 136.2, 133.6, 132.6, 132.2, 129.3, 129.0 (2C), 128.5, 128.4 (2C), 128.0, 127.9, 127.4, 126.8, 126.5, 126.1, 122.5, 120.9, 120.7, 110.8, 104.0. HRMS (ESI) calcd. for $C_{24}H_{18}N$ ($M + H^+$): 320.1434; found: 320.1438.



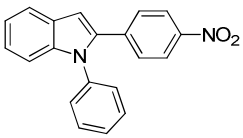
5-Methyl-1,2-diphenyl-1*H*-indole (**3e**).[6] Yellow solid (88% yield), mp 88 - 90 °C (Lit. mp: 89 - 92 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.37 - 7.40 (m, 2H), 7.30 - 7.33 (m, 1H), 7.18 - 7.26 (m, 8H), 6.99 - 7.01 (m, 1H), 6.72 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.9, 138.8, 137.6, 132.8, 130.1, 129.3 (2C), 129.0 (2C), 128.6, 128.3 (2C), 128.1 (2C), 127.3, 127.2, 124.0, 120.3, 110.4, 103.5, 21.5.



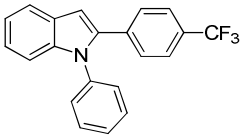
5-Chloro-1,2-diphenyl-1*H*-indole (**3f**). Yellow solid (72% yield), mp 136 - 137 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.35 - 7.37 (m, 1H), 7.21 - 7.24 (m, 7H), 7.17 - 7.19 (m, 1H), 7.10 - 7.12 (m, 1H), 6.73 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.1, 138.2, 137.5, 132.2, 129.5 (2C), 129.3, 129.0 (2C), 128.4 (2C), 128.1 (2C), 127.8, 127.7, 126.4, 122.6, 119.9, 111.8, 103.2. HRMS (ESI) calcd. for $C_{20}H_{15}ClN$ (M + H^+): 304.0888; found: 304.0897.



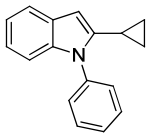
2-(4-Fluorophenyl)-1-phenyl-1*H*-indole (**3g**).[3] White solid (81% yield), mp 119 - 121 °C (Lit. mp: 121 - 122 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.39 - 7.41 (m, 2H), 7.33 - 7.35 (m, 1H), 7.27 (s, 1H), 7.17 - 7.22 (m, 6H), 6.92 (t, J = 8.2 Hz, 2H), 6.75 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.2 (d, $J_{C\text{-}F}$ = 246.8 Hz), 139.8, 139.0, 138.4, 130.7 (d, $J_{C\text{-}F}$ = 8.1 Hz) (2C), 129.5 (2C), 128.8, 128.3, 128.2 (2C), 127.5, 122.6, 120.9, 120.7, 115.4 (d, $J_{C\text{-}F}$ = 21.3 Hz) (2C), 110.8, 103.7.



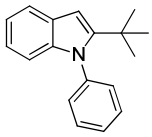
2-(4-Nitrophenyl)-1-phenyl-1*H*-indole (**3h**). Yellow solid (66% yield), mp 148 - 149 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 - 8.08 (m, 2H), 7.70 - 7.71 (m, 1H), 7.43 - 7.46 (m, 2H), 7.36 - 7.41 (m, 3H), 7.29 - 7.30 (m, 1H), 7.20 - 7.24 (m, 4H), 6.96 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.5, 139.9, 139.0, 138.0, 129.8 (2C), 129.0, 128.98 (2C), 128.0 (2C), 127.97, 127.95, 123.8, 123.7 (2C), 121.4, 121.2, 111.0, 106.4. HRMS (ESI) calcd. for $C_{20}H_{15}N_2O_2$ (M + H^+): 315.1128; found: 315.1122.



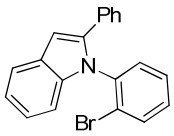
1-Phenyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indole (**3i**). Pale yellow solid (61% yield), mp 133 - 135 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 - 7.71 (m, 1H), 7.48 - 7.50 (m, 2H), 7.43 - 7.46 (m, 2H), 7.36 - 7.40 (m, 3H), 7.30 - 7.31 (m, 1H), 7.24 - 7.25 (m, 2H), 7.19 - 7.22 (m, 2H), 6.89 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.5, 139.1, 138.8 (d, *J* = 183 Hz), 138.2, 136.1, 129.7 (2C), 129.1, 128.9 (2C), 128.12, 128.09 (2C), 127.7, 125.3 (q, *J* = 3.8 Hz), 123.2 (2C), 121.0 (d, *J* = 25.6 Hz), 110.9, 105.1, 100.1. HRMS (ESI) calcd. for $C_{21}H_{15}F_3N_1$ ($M + H^+$): 338.1151; found: 315.1162.



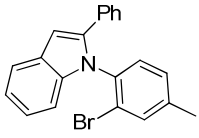
2-Cyclopropyl-1-phenyl-1*H*-indole (**3j**). Yellow oil (70% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (d, *J* = 6.8 Hz, 1H), 7.48 - 7.51 (m, 2H), 7.44 - 7.45 (m, 2H), 7.39 - 7.41 (m, 1H), 7.12 - 7.14 (m, 1H), 7.06 - 7.09 (m, 2H), 6.19 (s, 1H), 1.65 - 1.68 (m, 1H), 0.83 - 0.85 (m, 2H), 0.76 - 0.78 (m,2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.1, 138.3, 129.4 (2C), 128.19, 128.18 (2C), 128.1, 127.6, 121.2, 120.2, 119.9, 110.0, 97.4, 8.49, 8.45 (2C). HRMS (ESI) calcd. for $C_{17}H_{16}N$ ($M + H^+$): 234.1277; found: 234.1286.



2-(*Tert*-butyl)-1-phenyl-1*H*-indole (**3k**). Yellow oil (65% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 - 7.58 (m, 1H), 7.43 - 7.53 (m, 3H), 7.34 - 7.37 (m, 2H), 7.06 - 7.09 (m, 1H), 7.00 - 7.03 (m, 1H), 6.63 - 6.65 (m, 1H), 6.47 (s, 1H), 1.25 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.8, 140.3, 130.9 (2C), 129.5, 129.1 (2C), 128.7, 126.9, 121.3, 119.9, 119.7, 110.3, 99.3, 33.4, 31.1 (3C). HRMS (ESI) calcd. for $C_{18}H_{20}N$ ($M + H^+$): 250.1590; found: 250.1596.

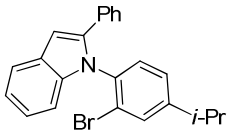


1-(2-Bromophenyl)-2-phenyl-1*H*-indole (**3l**). Yellow oil (76% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 - 7.70 (m, 2H), 7.29 - 7.32 (m, 3H), 7.17 - 7.25 (m, 7H), 6.96 - 6.98 (m, 1H), 6.82 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.3, 138.9, 138.2, 133.8, 132.5, 131.5, 130.9, 129.9, 128.6 (2C), 128.5, 128.4 (2C), 127.6, 124.1, 122.5, 120.9, 120.7, 111.1, 103.5. HRMS (ESI) calcd. for $C_{20}H_{15}{}^{81}BrN$ ($M + H^+$): 350.0367; found: 350.0376.

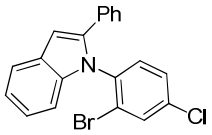


1-(2-Bromo-4-methylphenyl)-2-phenyl-1*H*-indole (**3m**). Yellow oil (71% yield). ^{1}H NMR (600

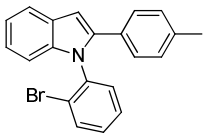
MHz, $CDCl_3$): δ 7.68 - 7.70 (m, 1H), 7.51 (s, 1H), 7.31 - 7.32 (m, 2H), 7.21 - 7.25 (m, 3H), 7.15 - 7.17 (m, 2H), 7.12 (s, 2H), 6.95 - 6.97 (m, 1H), 6.81 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.3, 140.2, 139.0, 135.4, 134.2, 132.6, 131.0, 129.3, 128.6 (2C), 128.3 (2C), 127.5, 123.7, 122.4, 120.8, 120.6, 111.1, 103.3, 21.0. HRMS (ESI) calcd. for $C_{21}H_{17}{}^{81}BrN$ ($M + H^+$): 364.0524; found: 364.0533.



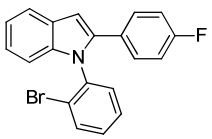
1-(2-Bromo-4-isopropylphenyl)-2-phenyl-1*H*-indole (**3n**). Yellow oil (68% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67 -7.68 (m, 1H), 7.54 (s, 1H), 7.29 - 7.31 (m, 2H), 7.19 - 7.22 (m, 3H), 7.14 - 7.17 (m, 4H), 6.97 - 6.98 (m, 1H), 6.81 (s, 1H), 2.92 (heptet, *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.1, 141.3, 139.0, 135.6, 132.6, 131.6, 131.1, 128.6 (2C), 128.3 (2C), 127.5, 126.7, 123.8, 122.4, 120.8, 120.6, 111.1, 103.3, 33.8, 23.9 (2C). HRMS (ESI) calcd. for $C_{23}H_{21}{}^{81}BrN$ ($M + H^+$): 392.0837; found: 392.0843.



1-(2-Bromo-4-chlorophenyl)-2-phenyl-1*H*-indole (**3o**). Yellow solid (65% yield), mp 112-114 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 - 7.71 (m, 2H), 7.23 - 7.29 (m, 6H), 7.17 - 7.19 (m, 2H), 7.12 - 7.13 (m, 1H), 6.94 - 6.96 (m, 1H), 6.82 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.2, 138.8, 137.0, 134.8, 133.5, 132.2, 132.1, 130.8, 128.7, 128.6 (2C), 128.5 (2C), 127.7, 124.6, 122.7, 121.1, 120.8, 110.9, 103.9. HRMS (ESI) calcd. for $C_{20}H_{14}{}^{81}BrClN$ ($M + H^+$): 383.9978; found: 383.9983.

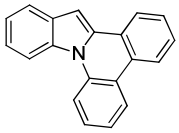


1-(2-Bromophenyl)-2-(*p*-tolyl)-1*H*-indole (**3p**). Yellow oil (67% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 - 7.71 (m, 2H), 7.33 - 7.35 (m, 1H), 7.25 - 7.27 (m, 2H), 7.16 - 7.20 (m, 4H), 7.03 - 7.05 (m, 2H), 6.94 - 6.97 (m, 1H), 6.80 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.4, 138.8, 138.4, 137.4, 133.8, 131.5, 129.8, 129.6, 129.1 (2C), 128.49 (2C), 128.47, 128.4, 124.2, 122.3, 120.9, 120.6, 111.0, 103.0, 21.3. HRMS (ESI) calcd. for $C_{21}H_{17}{}^{81}BrN$ ($M + H^+$): 364.0524; found: 364.0530.

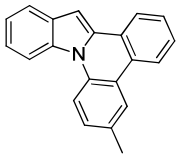


1-(2-Bromophenyl)-2-(4-fluorophenyl)-1*H*-indole (**3q**). Yellow solid (52% yield), mp 131-133 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 - 7.71 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.24 - 7.28 (m, 4H),

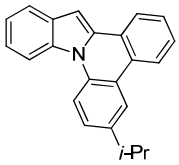
7.18 - 7.19 (m, 2H), 6.92 - 6.97 (m, 3H), 6.78 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.4 (d, J_{C-F} = 246.0 Hz), 140.3, 138.8, 138.0, 133.9, 131.5, 130.4 (d, J_{C-F} = 8.1 Hz) (2C), 130.0, 128.7, 128.5, 128.3, 124.1, 122.6, 121.0, 120.7, 115.4 (d, J_{C-F} = 21.3 Hz) (2C), 111.0, 103.4. HRMS (ESI) calcd. for $C_{20}H_{14}{}^{81}BrFN$ ($M + H^+$): 368.0273; found: 368.0277.



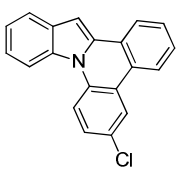
Indolo[1,2-*f*]phenanthridine (**4a**).[7] White solid (85% yield) mp 140 - 141 °C (Lit. mp: 140 - 142 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.3 Hz, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 8.10 - 8.12 (m, 1H), 8.03 - 8.05 (m, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 8.3 Hz, 1H), 7.38 - 7.42 (m, 2H), 7.31 - 7.36 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.18 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 136.1, 135.3, 134.0, 130.5, 128.8, 128.3, 127.9, 126.9, 126.2, 124.2, 124.1, 123.1, 122.5, 122.2, 122.1, 121.9, 121.2, 116.4, 114.4, 96.3.



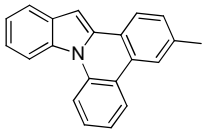
6-Methylindolo[1,2-*f*]phenanthridine (**4b**). White solid (83% yield), mp 165 - 167 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.42 (d, *J* = 8.5 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 8.21 - 8.22 (m, 1H), 8.12 -8.14 (m, 1H), 8.10 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.46 - 7.49 (m, 2H), 7.36 - 7.38 (m, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.24 - 7.25 (m, 1H), 2.50 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 135.3, 134.0, 133.9, 132.5, 130.3, 129.6, 128.1, 127.8, 127.0, 126.3, 124.3, 124.2, 122.5, 122.01, 122.0, 121.7, 121.1, 116.2, 114.3, 96.0, 21.2. HRMS (ESI) calcd. for $C_{21}H_{16}N$ ($M + H^+$): 282.1277; found: 282.1281.



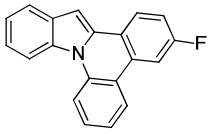
6-Isopropylindolo[1,2-*f*]phenanthridine (**4c**). White solid (79% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.6 Hz, 1H), 8.30 (d, *J* = 8.3 Hz, 1H), 8.16 - 8.18 (m, 1H), 8.09 (m, 1H), 8.02 - 8.04 (m, 1H), 7.78 (d, *J* = 7.4 Hz, 1H), 7.37 - 7.42 (m, 3H), 7.30 - 7.35 (m, 2H), 7.15 (s, 1H), 3.02 (heptet, *J* = 6.9 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.4, 135.3, 134.2, 133.9, 130.3, 128.1, 127.8, 127.1, 127.0, 126.3, 124.3, 122.4, 122.0, 121.95, 121.8, 121.7, 121.1, 116.4, 114.2, 96.0, 34.0, 24.3 (2C). HRMS (ESI) calcd. for $C_{23}H_{20}N$ ($M + H^+$): 310.1590; found: 310.1598.



6-Chloroindolo[1,2-*f*]phenanthridine (**4d**). Yellow solid (92% yield), mp 177 - 179 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.8 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.16 (s, 1H), 8.05 (m, 2H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.44 - 7.49 (m, 3H), 7.33 - 7.38 (m, 2H), 7.19 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 134.9, 134.5, 133.8, 130.4, 128.9, 128.5, 128.46, 128.0, 126.4, 125.8, 124.2, 123.9, 123.8, 122.6, 122.4, 122.1, 121.3, 117.5, 114.1, 96.8. HRMS (ESI) calcd. for $C_{20}H_{13}ClN$ ($M + H^+$): 302.0731; found: 302.0737.



3-Methylindolo[1,2-*f*]phenanthridine (**4e**). White solid (93% yield), mp 158 - 160 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.54 (d, *J* = 8.3 Hz, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 8.02 - 8.03 (m, 2H), 7.82 (d, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 8.2 Hz, 1 Hz), 7.31 - 7.38 (m, 4H), 7.21 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.9, 136.3, 135.7, 134.0, 130.6, 129.7, 128.8, 127.0, 124.3, 124.1, 123.9, 123.1, 122.7, 122.3, 121.9, 121.9, 121.0, 116.5, 114.3, 95.6, 22.0. HRMS (ESI) calcd. for $C_{21}H_{16}N$ ($M + H^+$): 282.1277; found: 282.1273.



3-Fluoroindolo[1,2-*f*]phenanthridine (**4f**). Yellow solid (87% yield), mp 168 - 169 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.3 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.82 - 7.85 (m, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.59 - 7.61 (m, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.28 - 7.32 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.01 - 7.04 (m, 1H), 6.95 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.6 (d, J_{C-F} = 244.8 Hz), 136.2, 134.6, 133.8, 130.4, 129.5, 129.4, 126.3 (d, J_{C-F} = 8.6 Hz), 124.2, 123.12, 123.09, 122.1, 122.0, 121.1, 116.4, 116.35, 116.2 (d, J_{C-F} = 22.9 Hz), 114.3, 108.5 (d, J_{C-F} = 23.0 Hz), 95.9. HRMS (ESI) calcd. for $C_{20}H_{13}FN$ ($M + H^+$): 286.1027; found: 286.1032.

4. References

1. Akira, T.; Shin, K.; Yoshinori, Y. *J. Am. Chem. Soc.* **2000**, *122*, 5662-5663.

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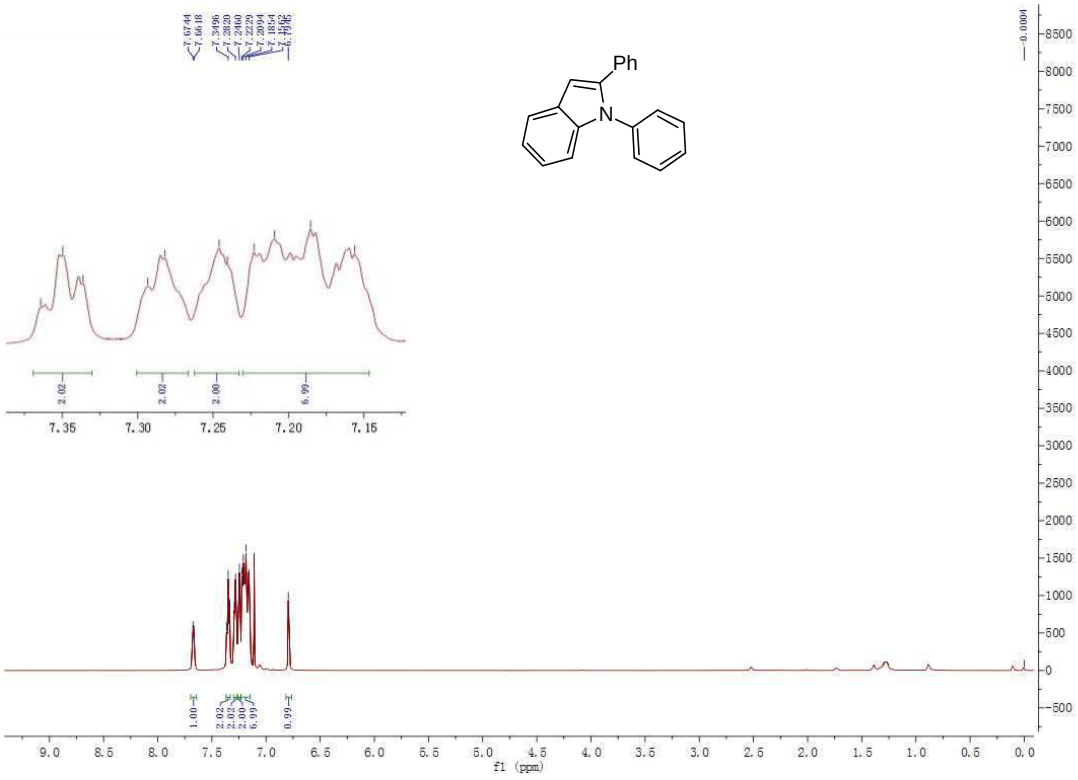
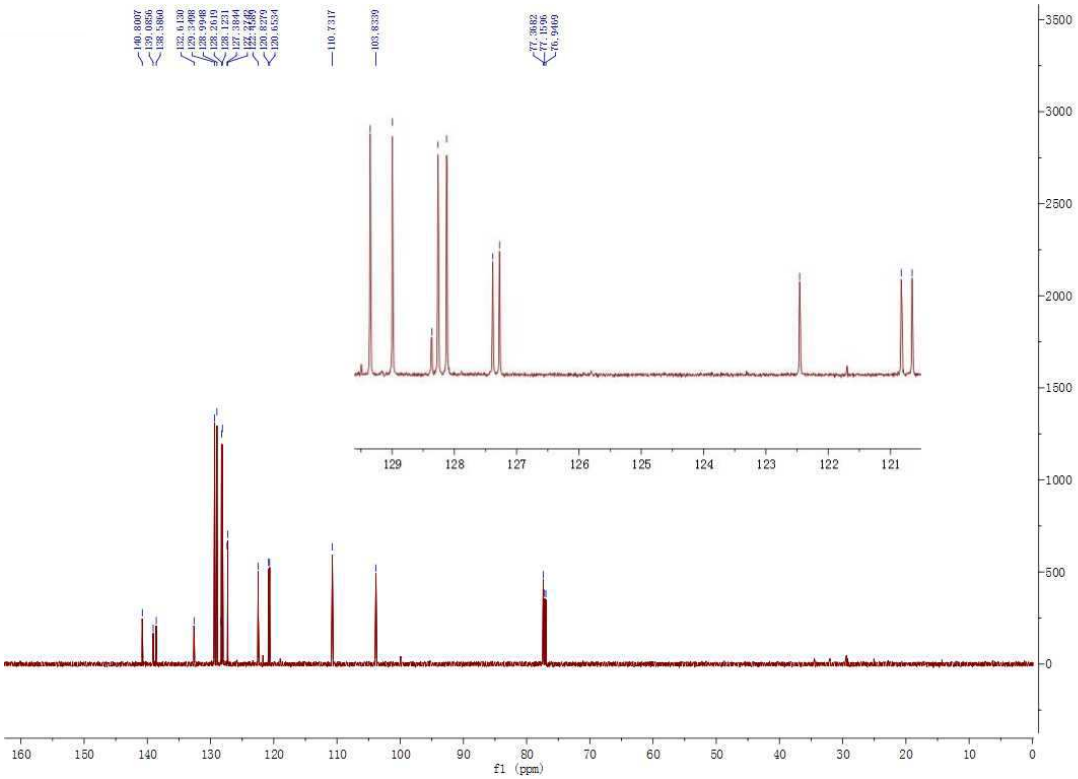
5. Spectra for the Compounds

Compound 3:

3a:





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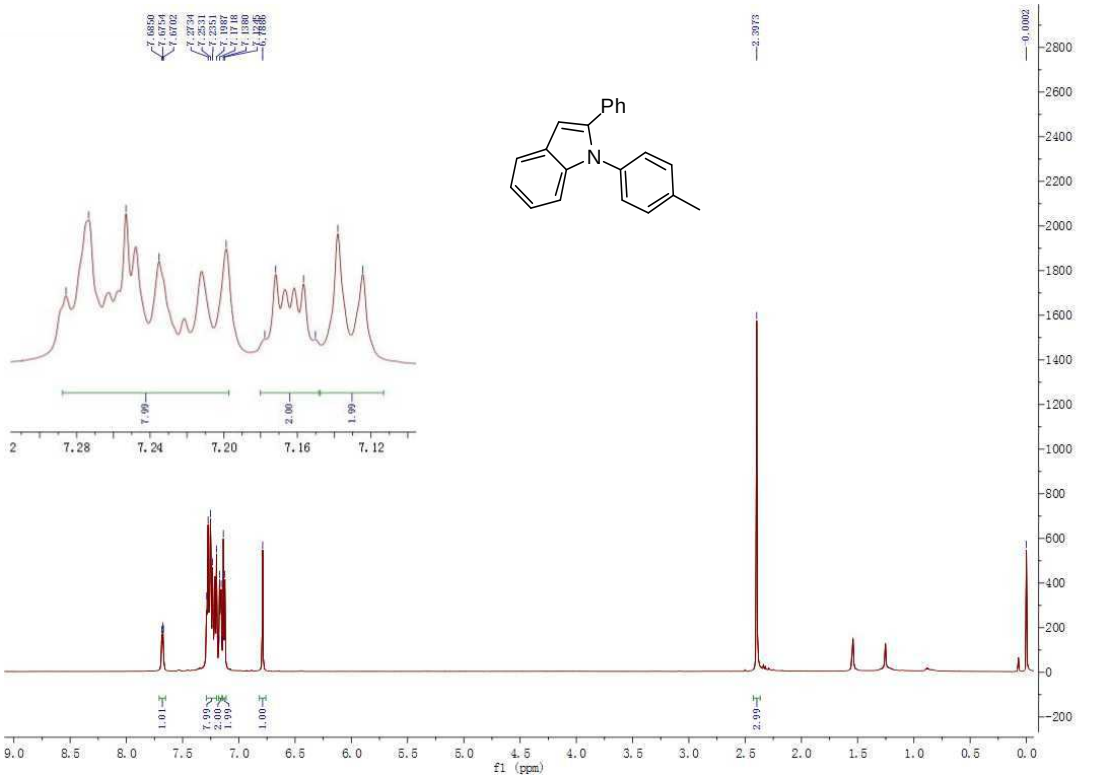

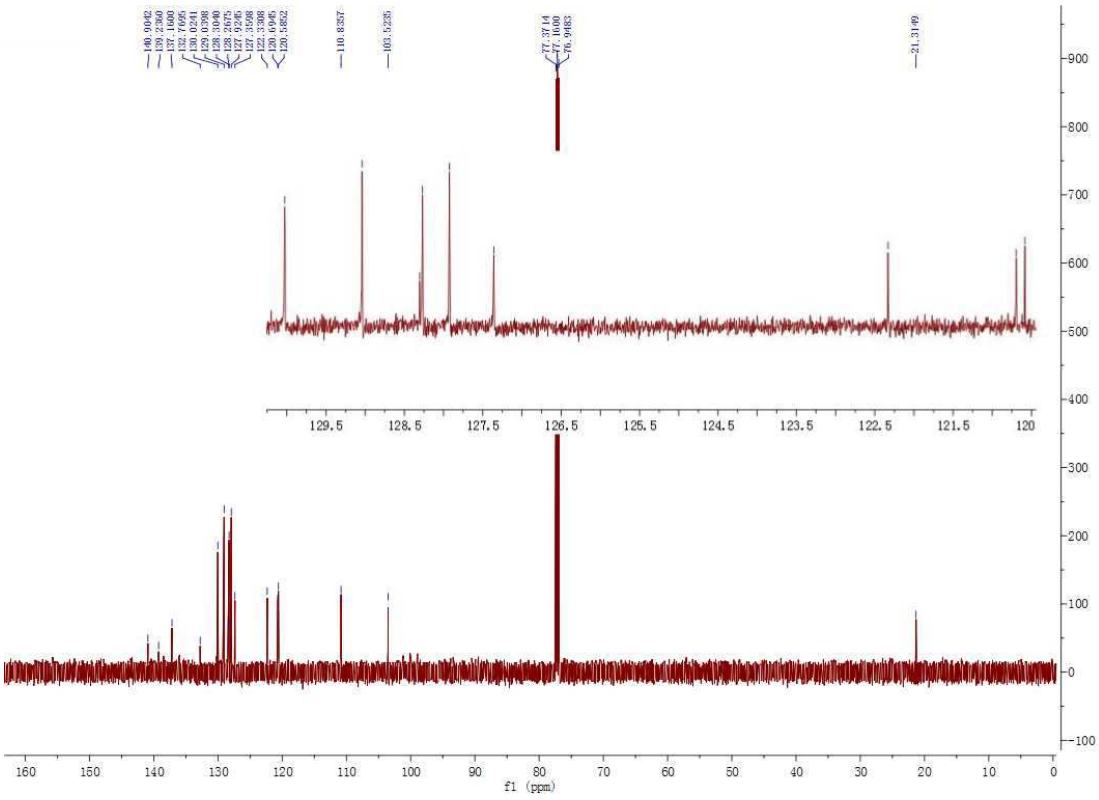

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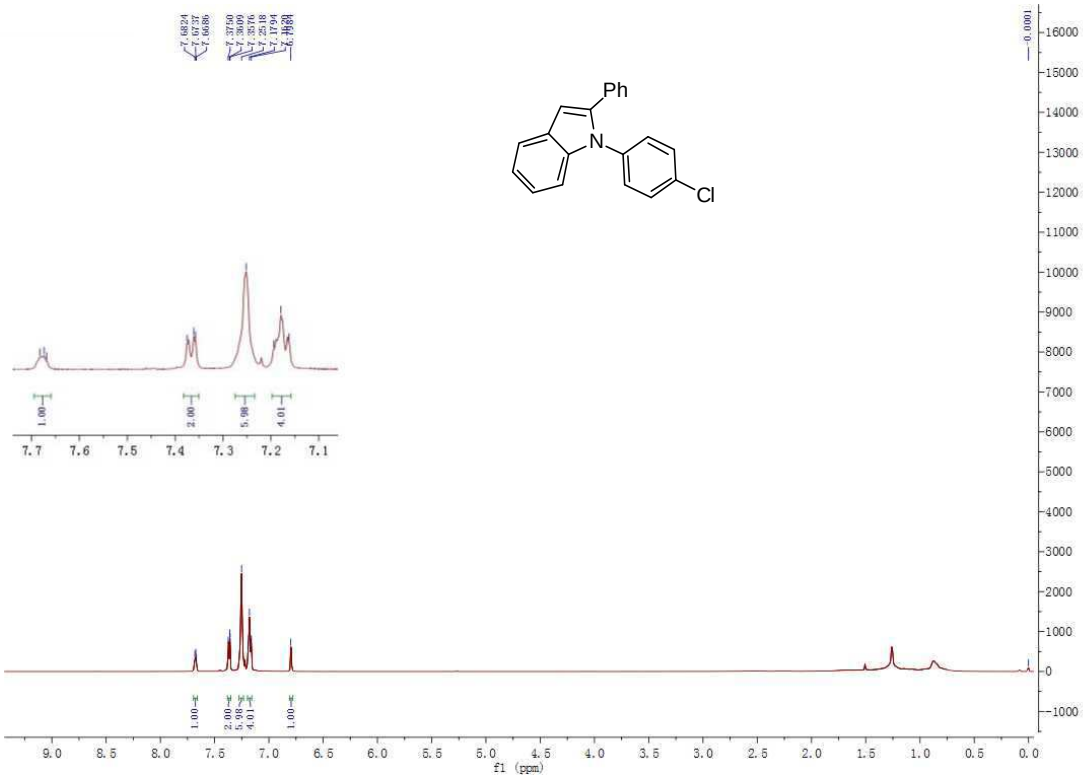

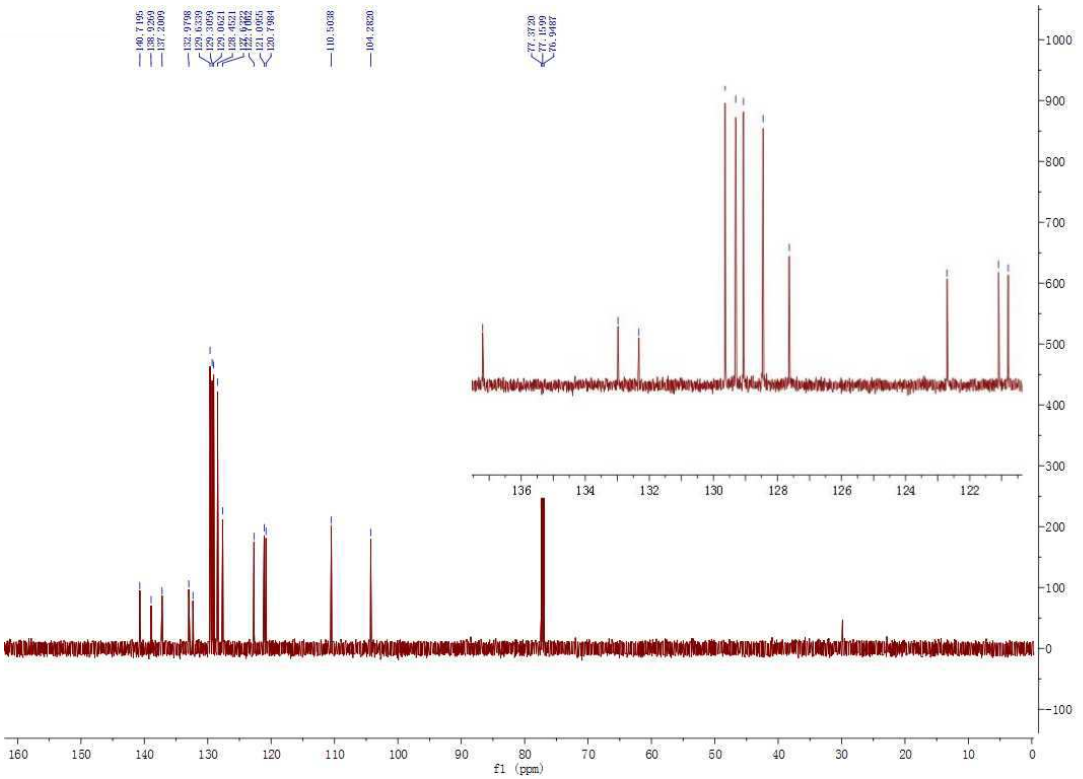

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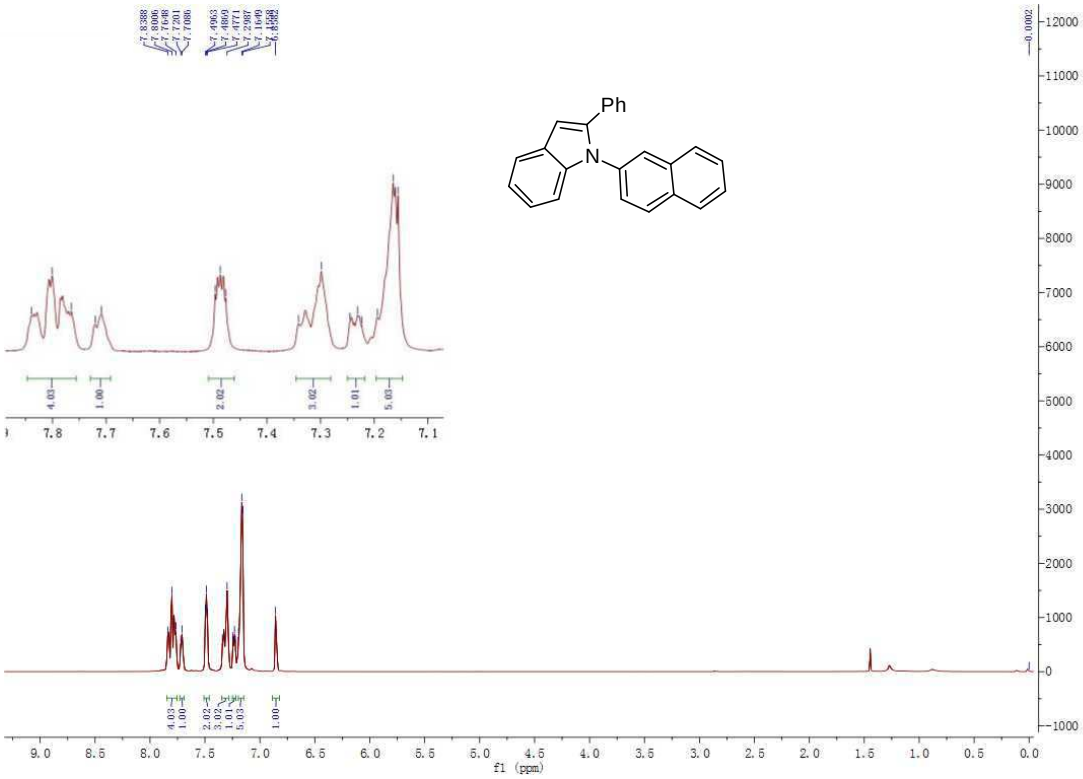

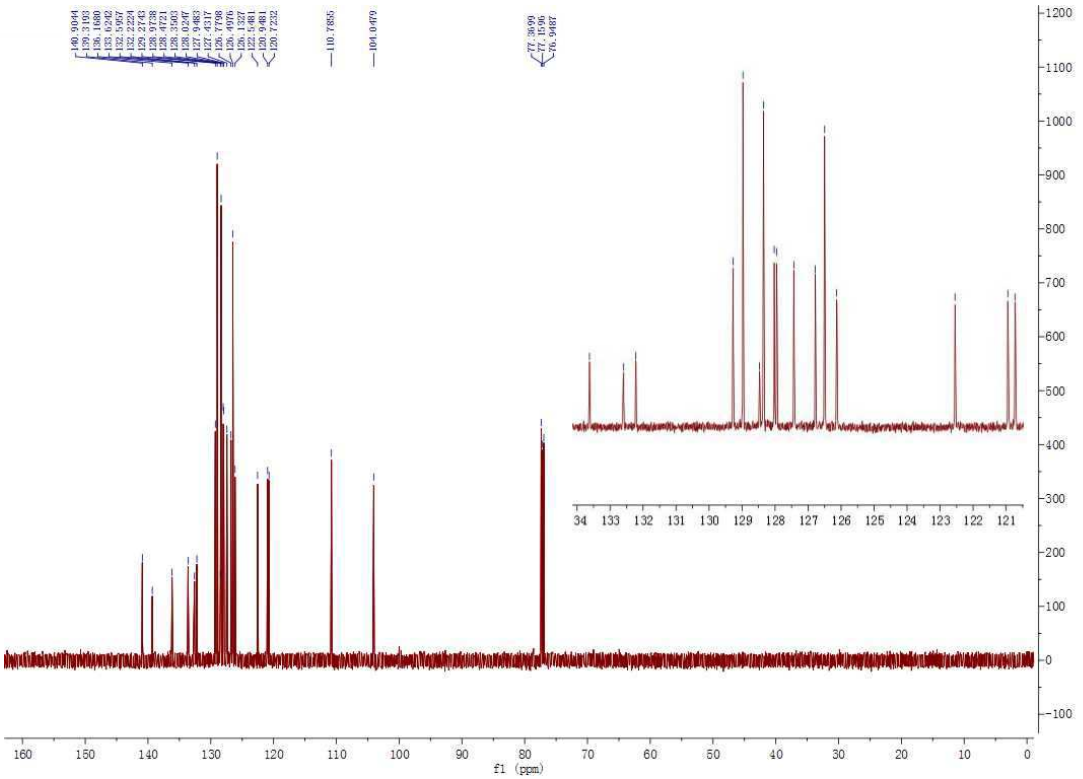

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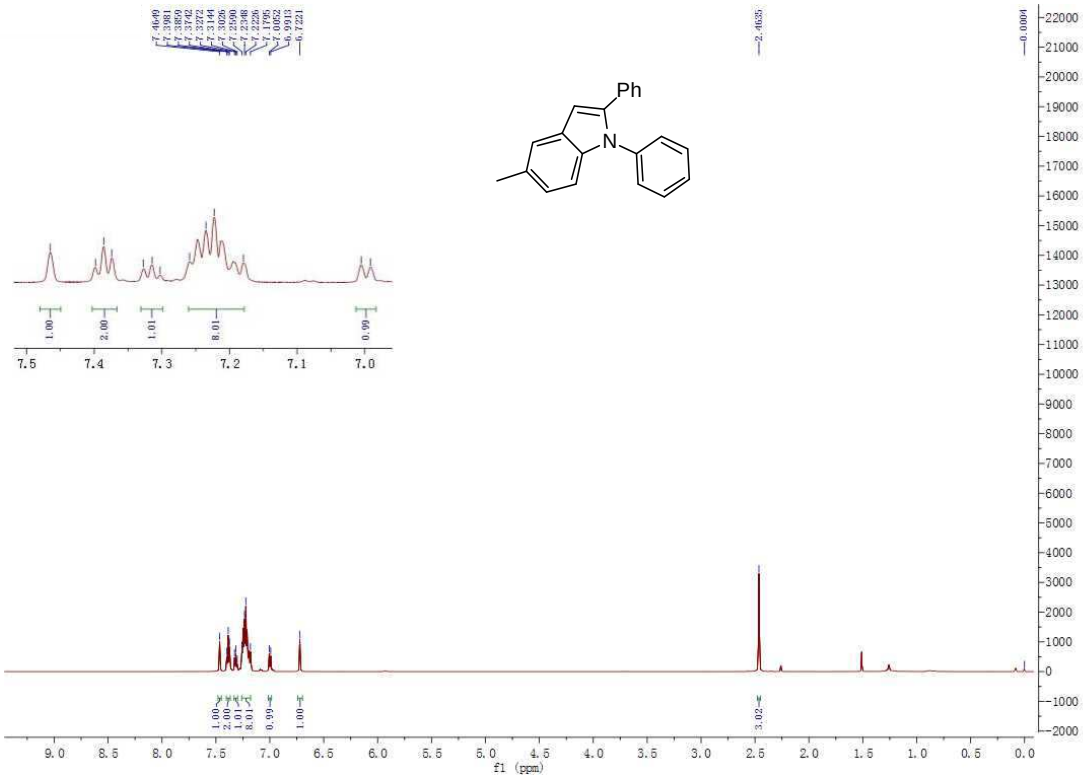

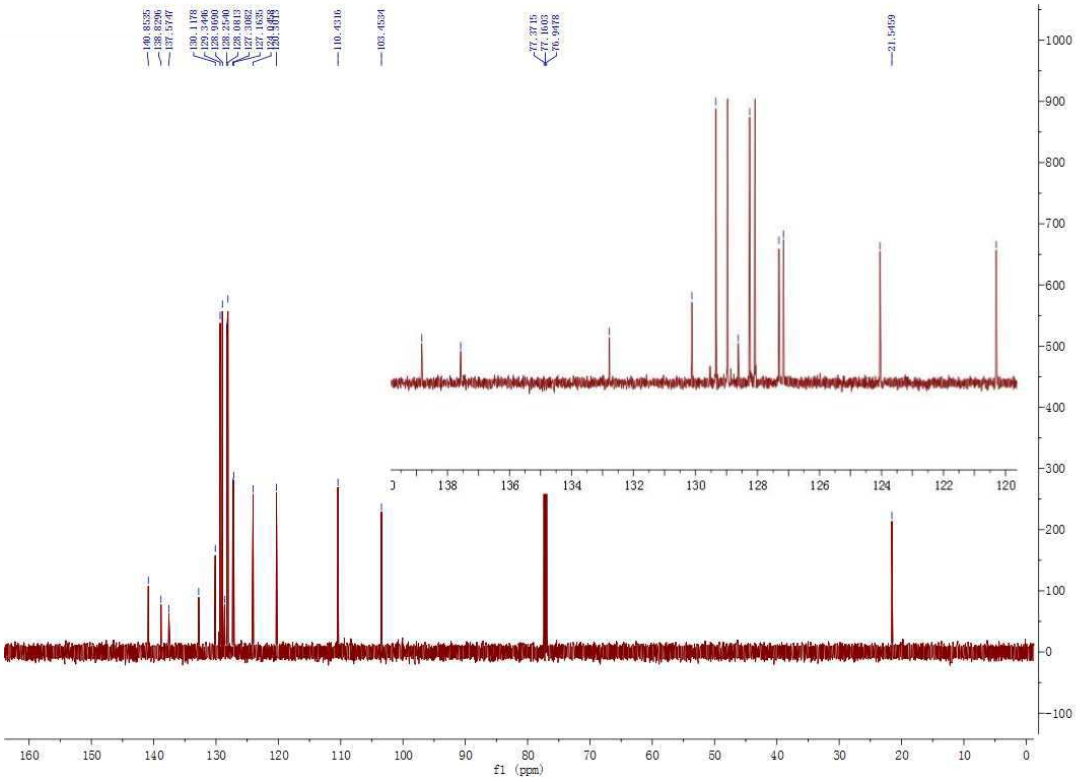

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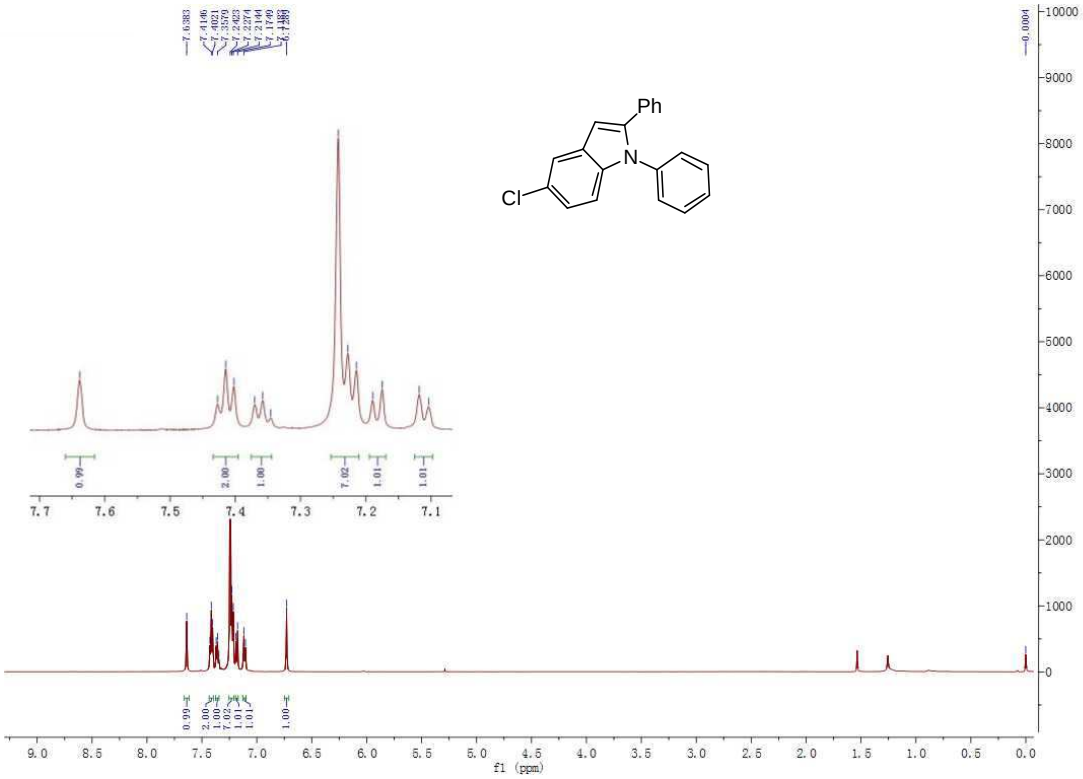

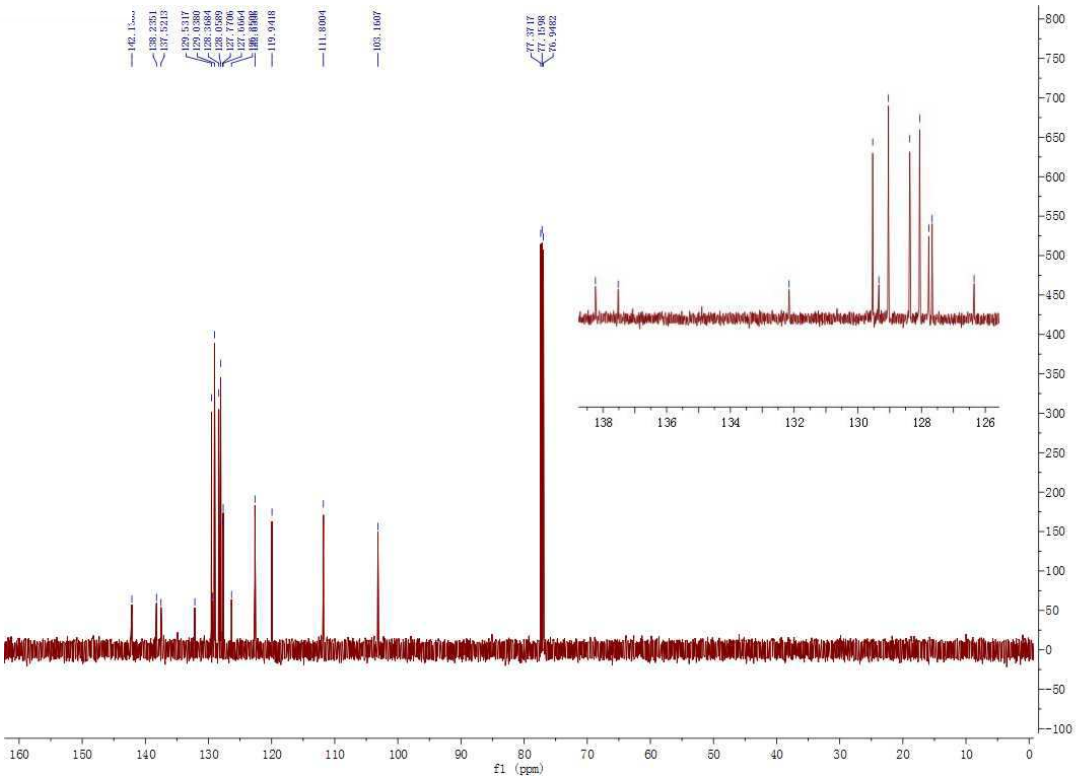

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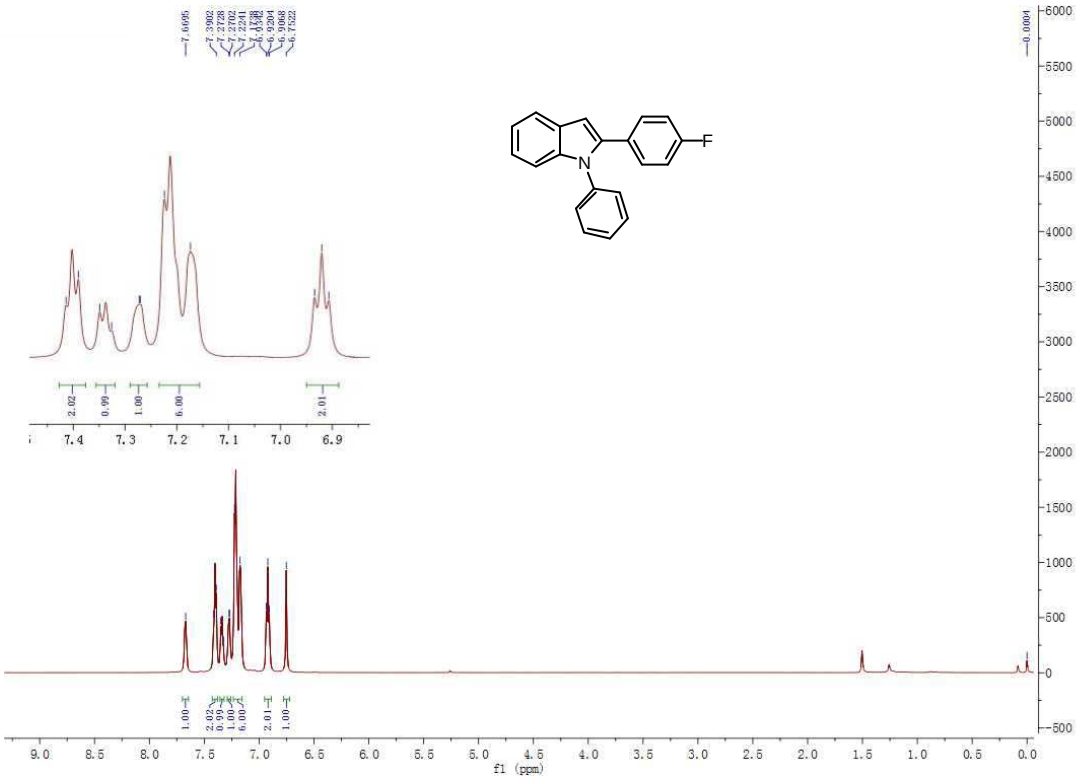

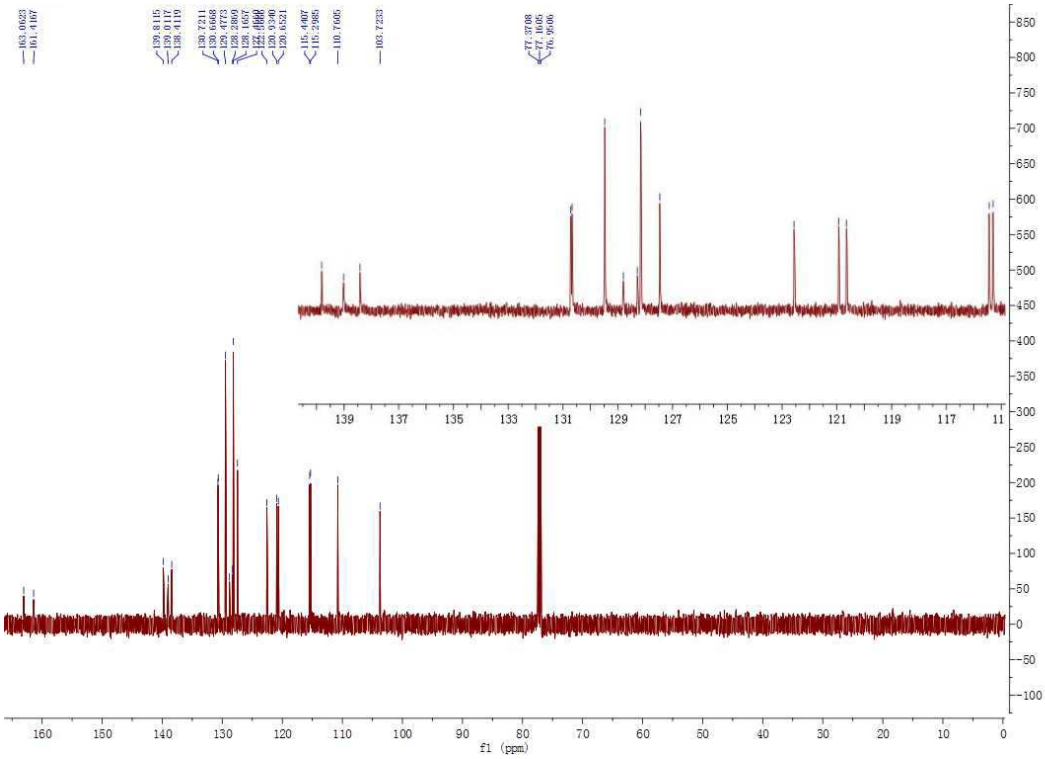

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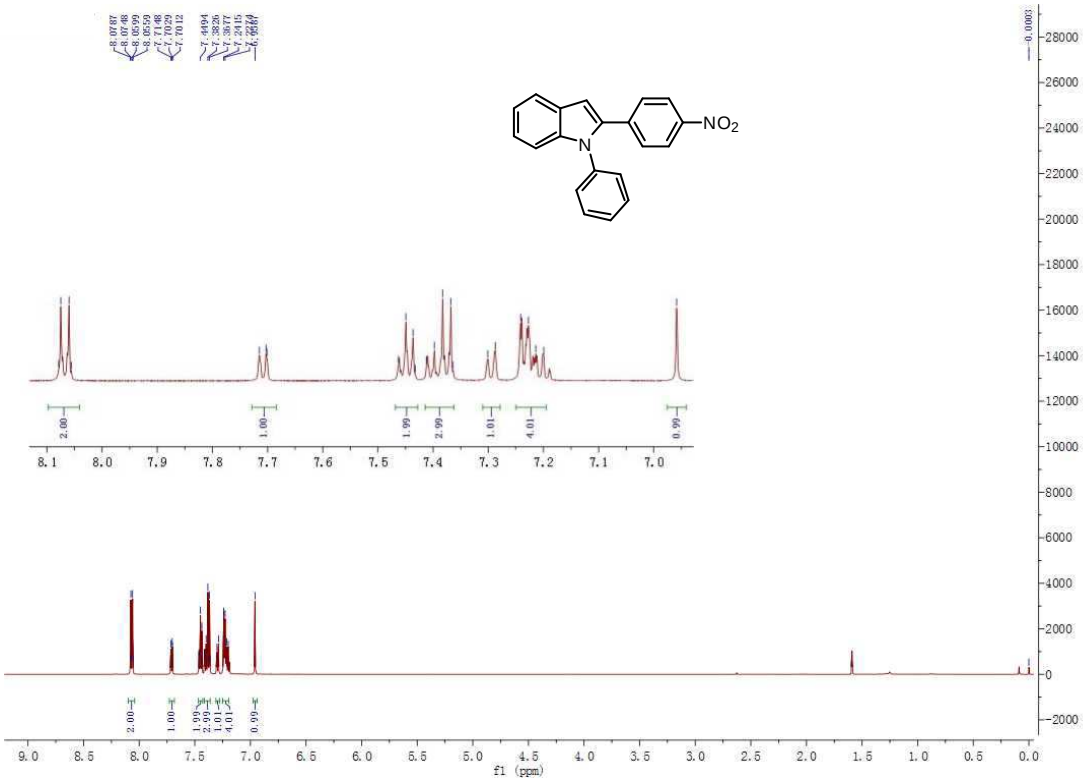

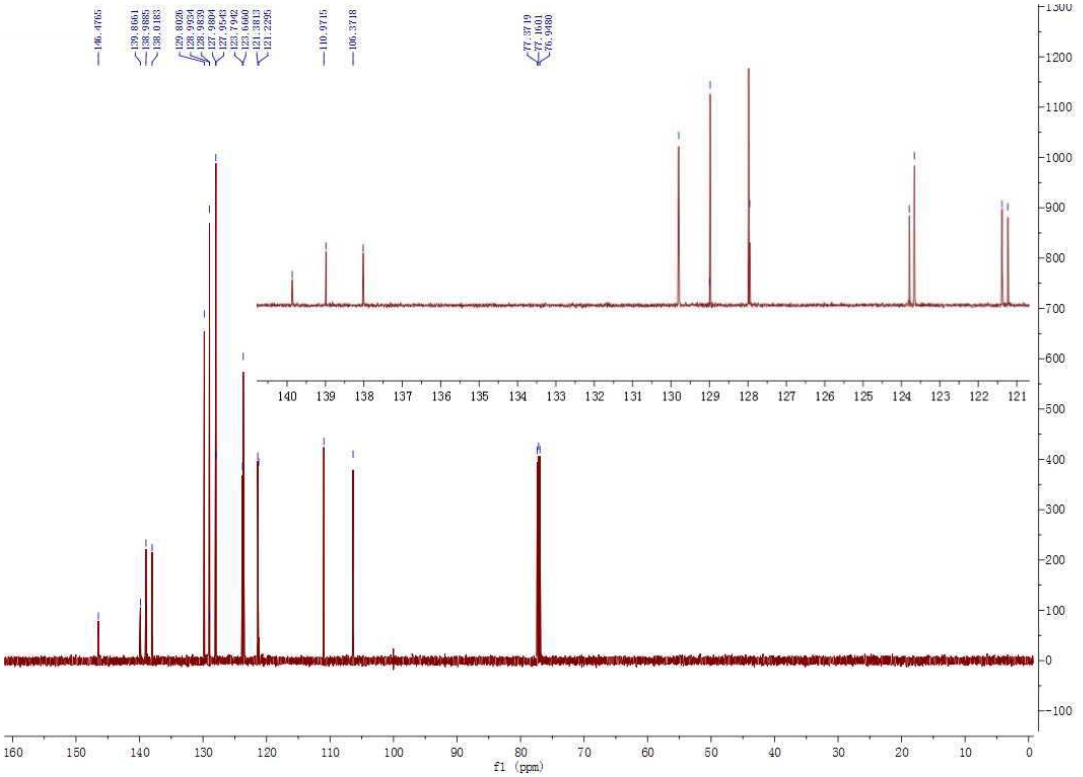

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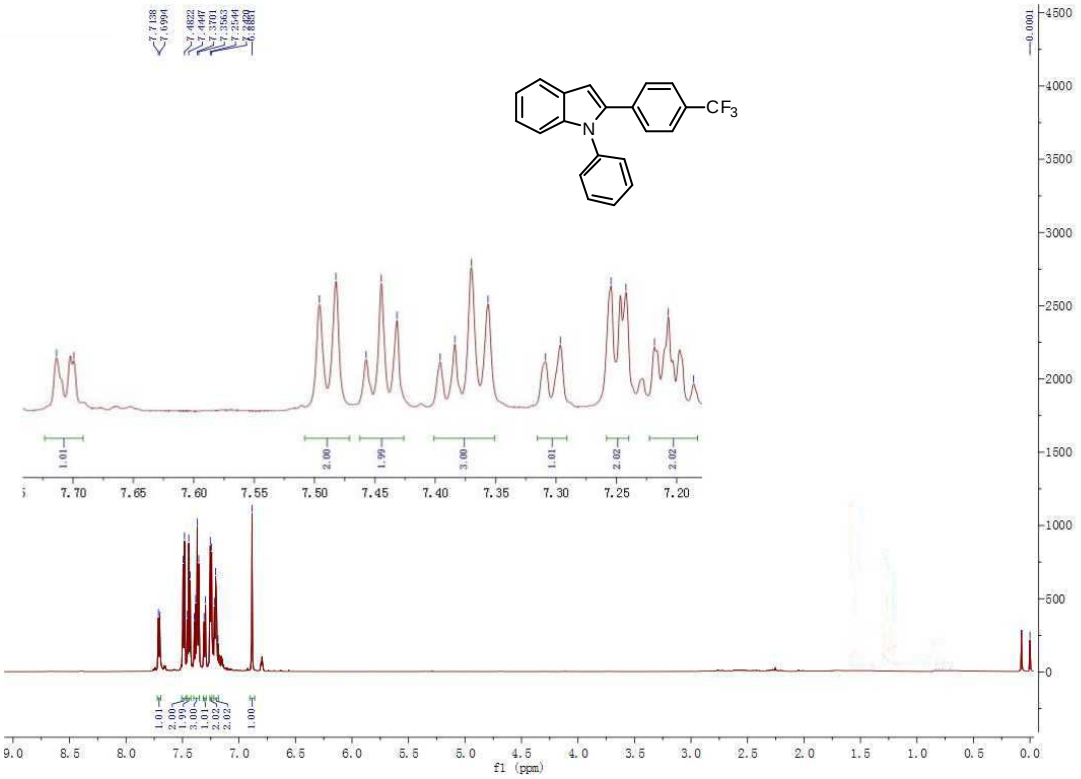

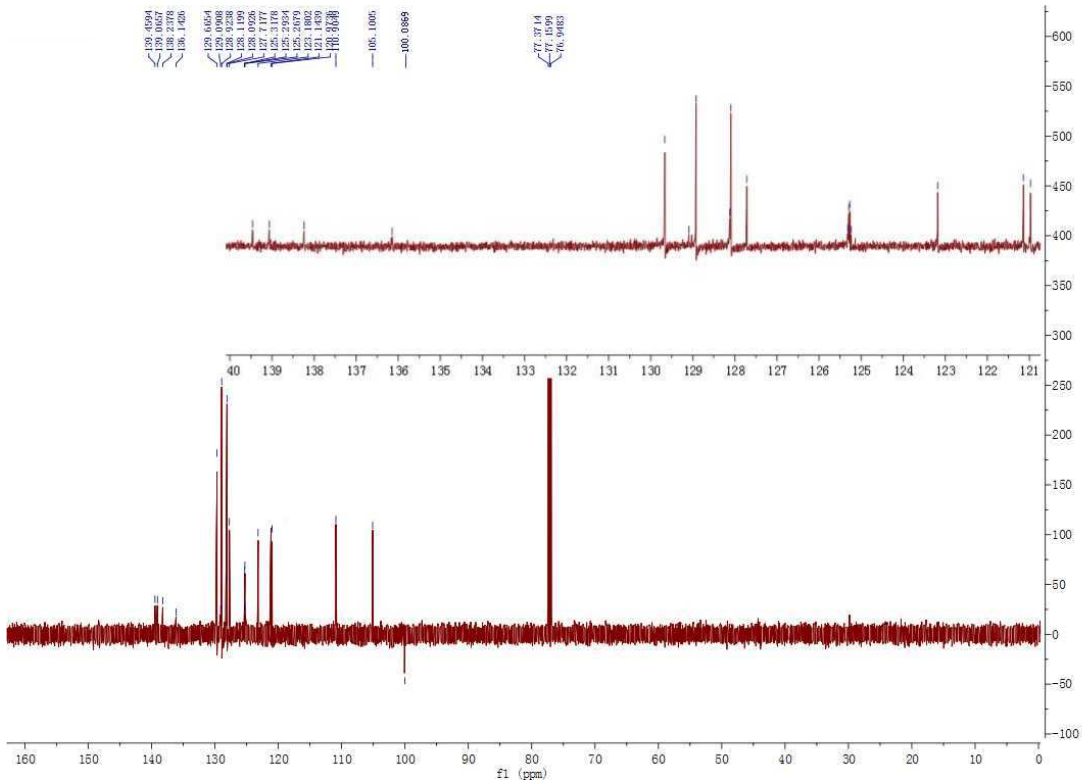

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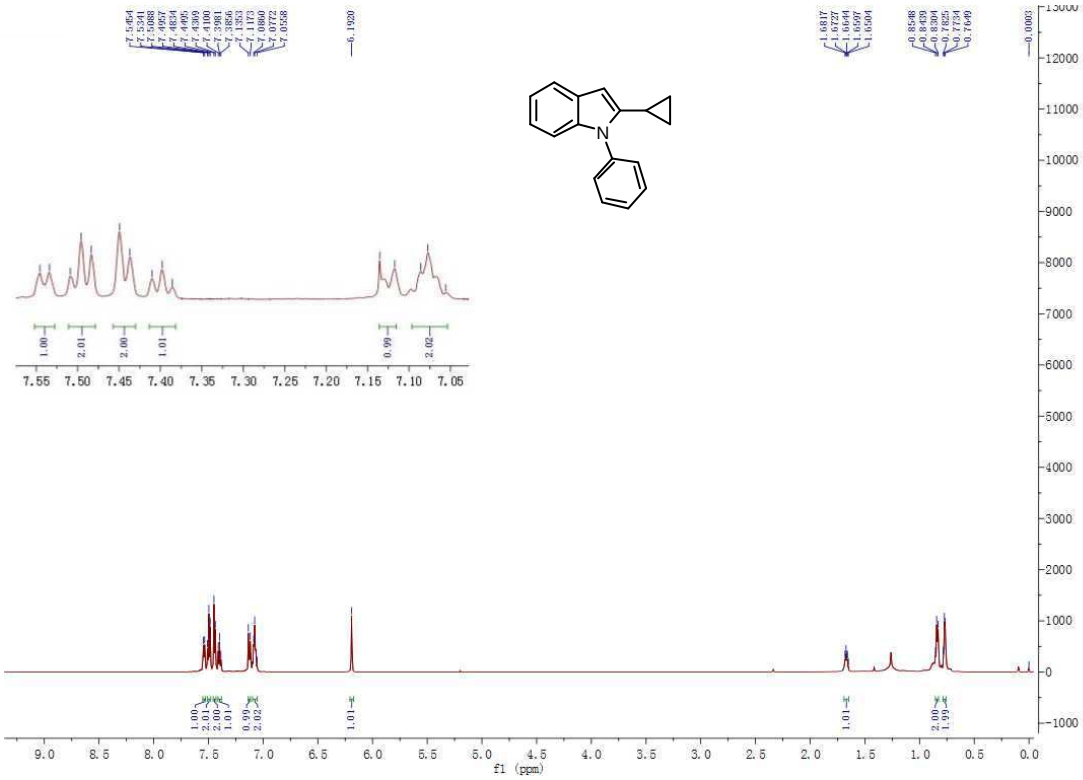

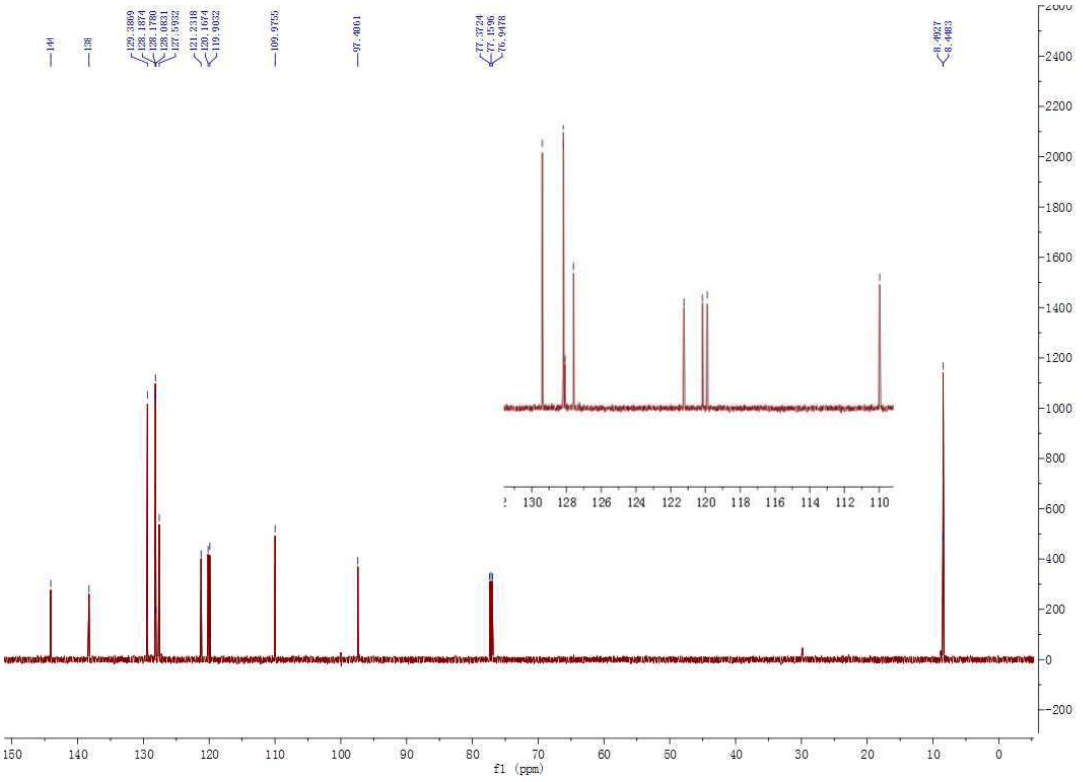

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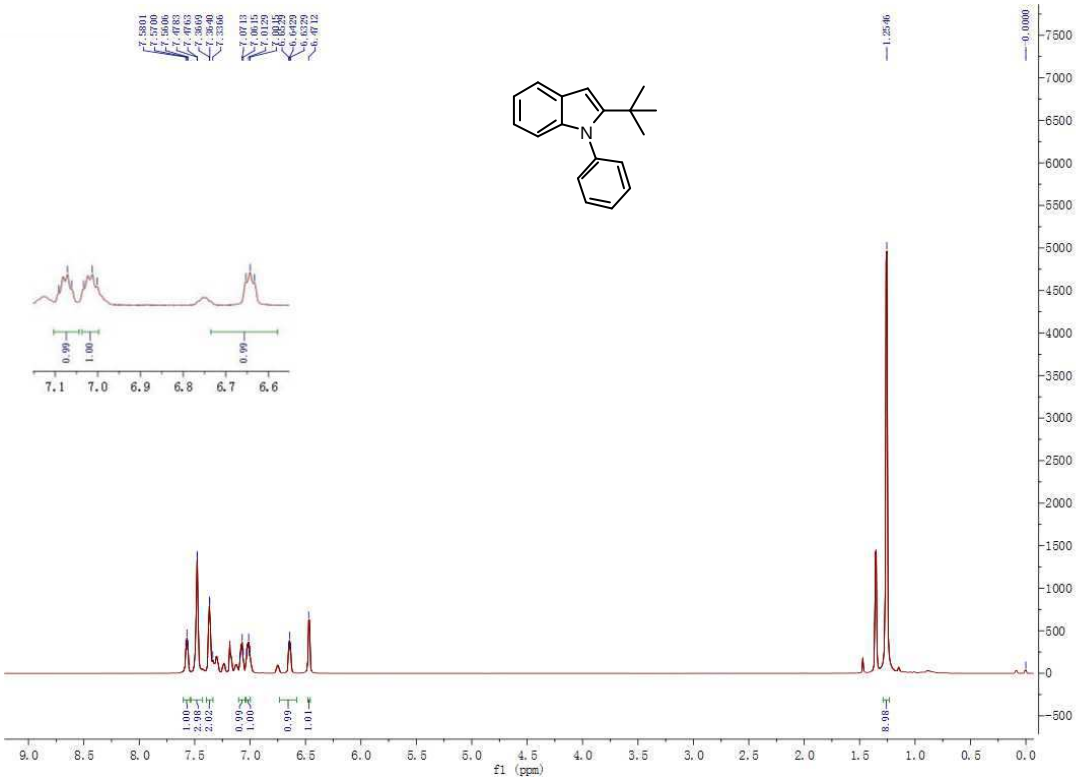

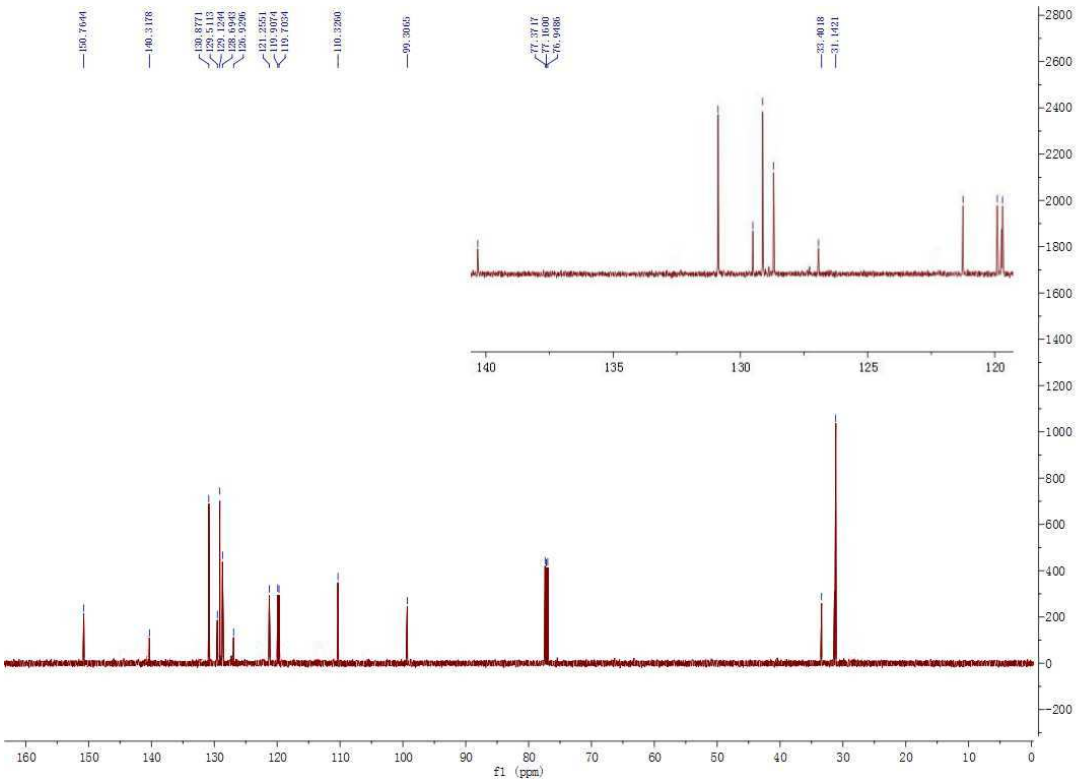

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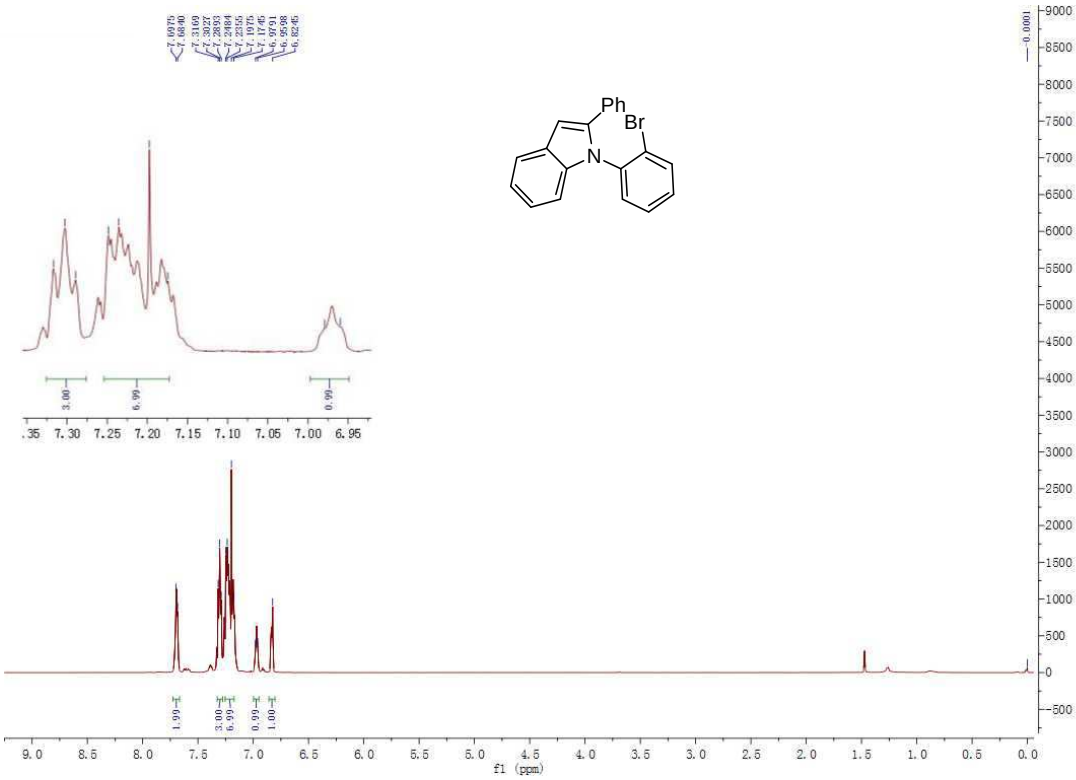

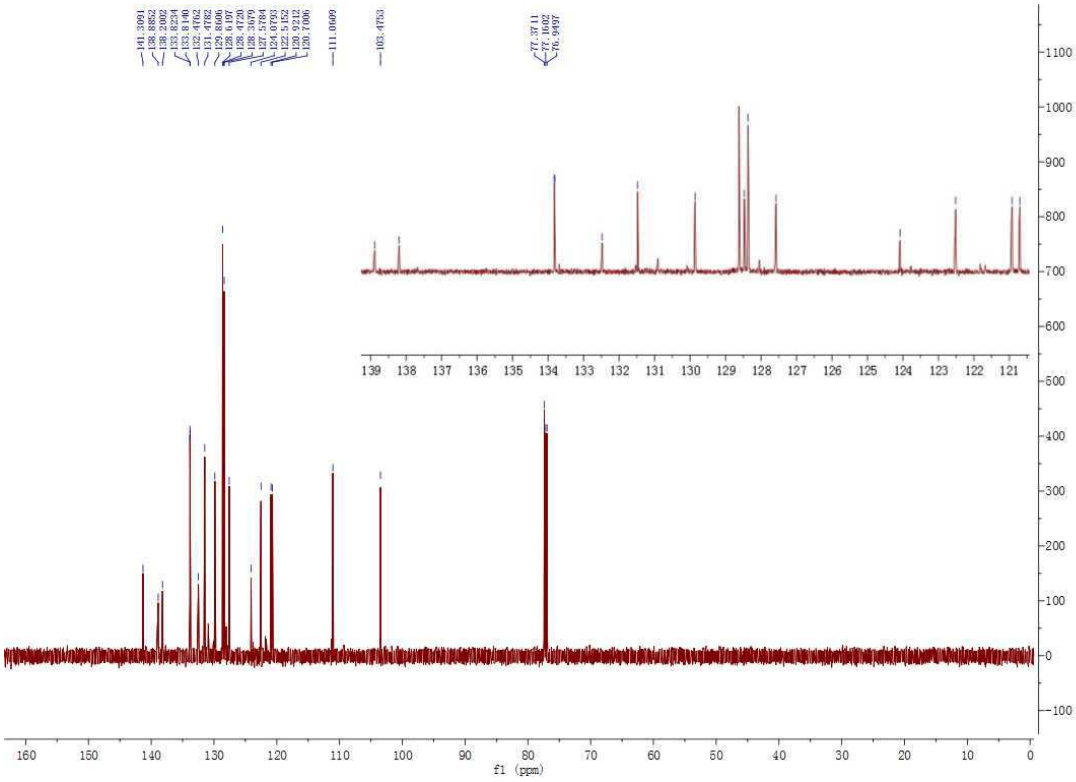

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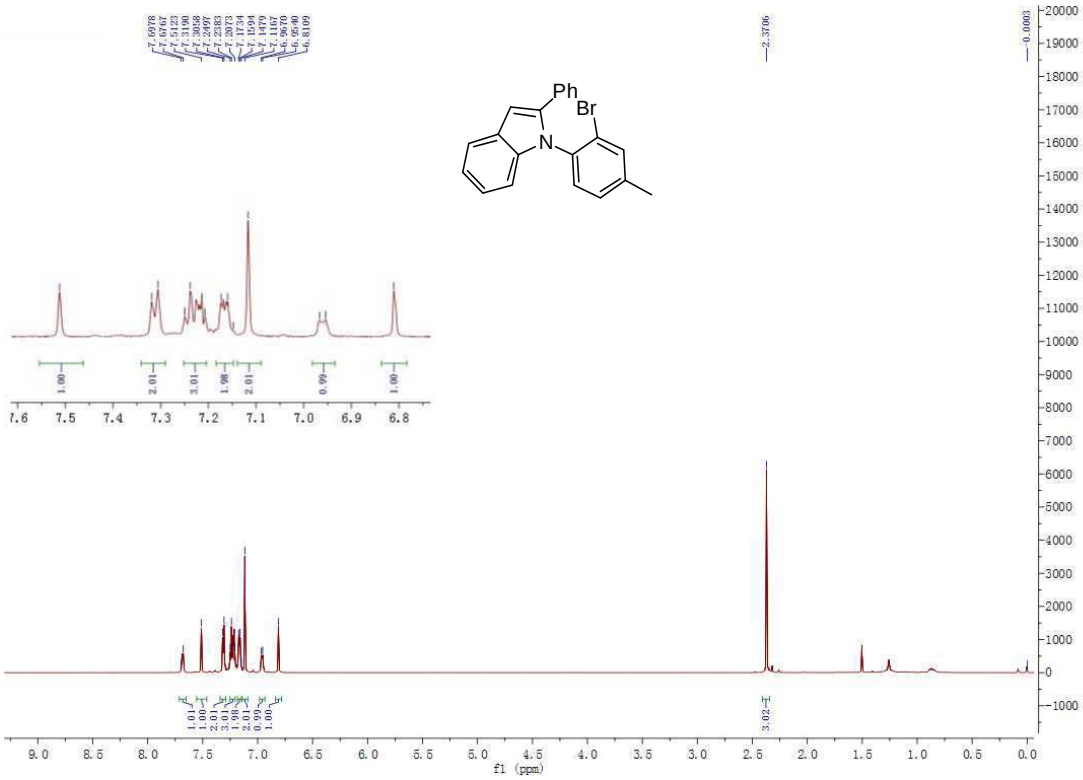

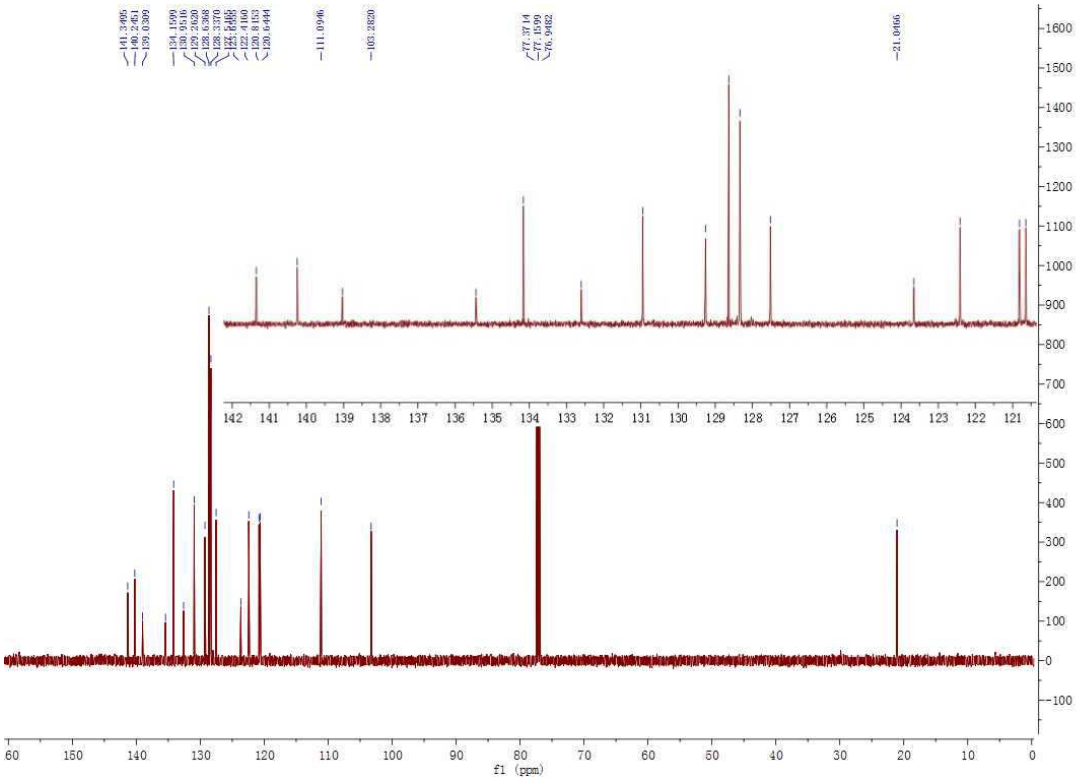

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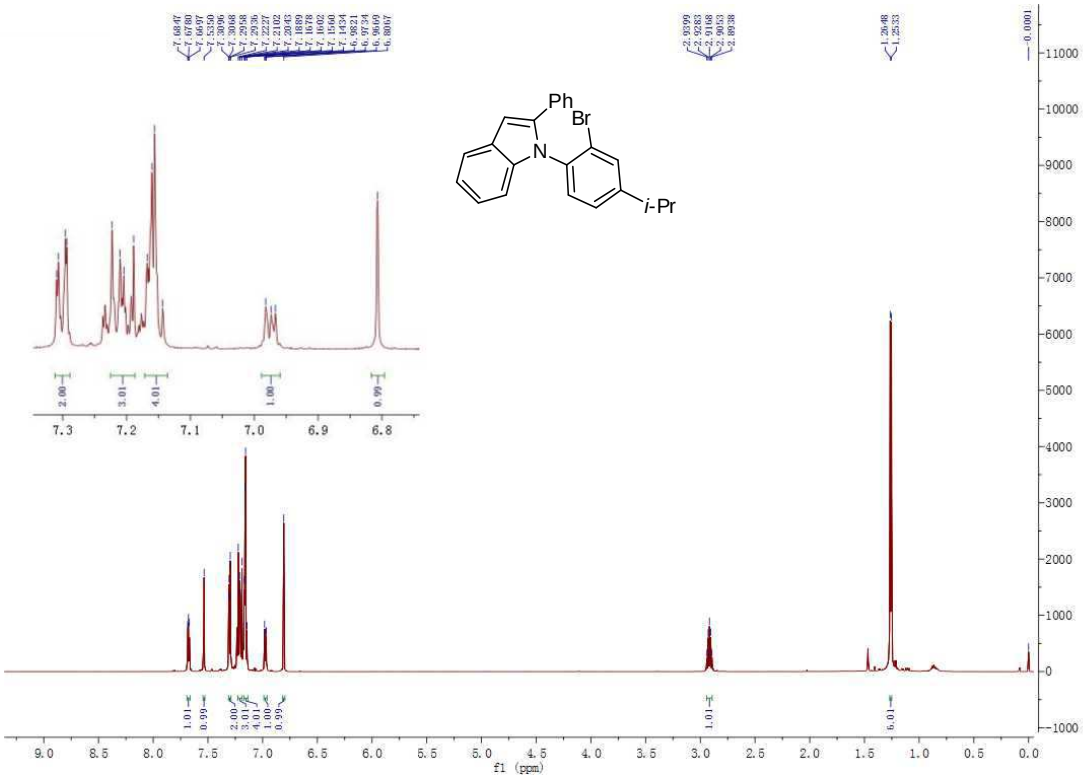

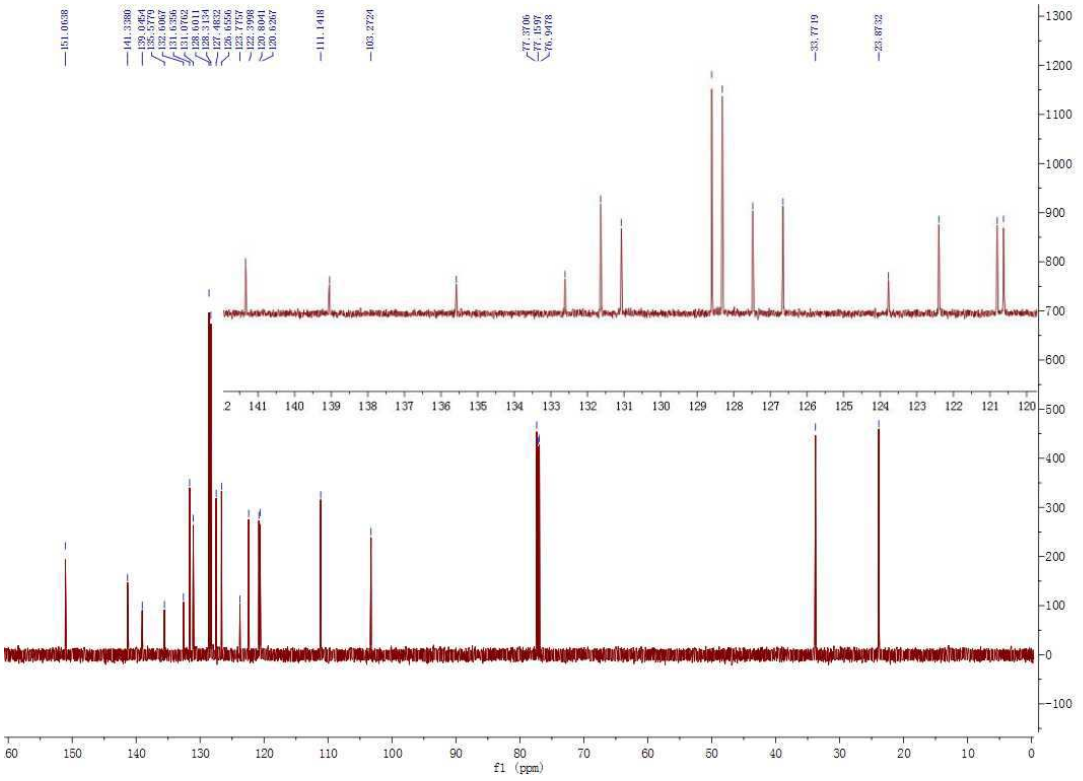

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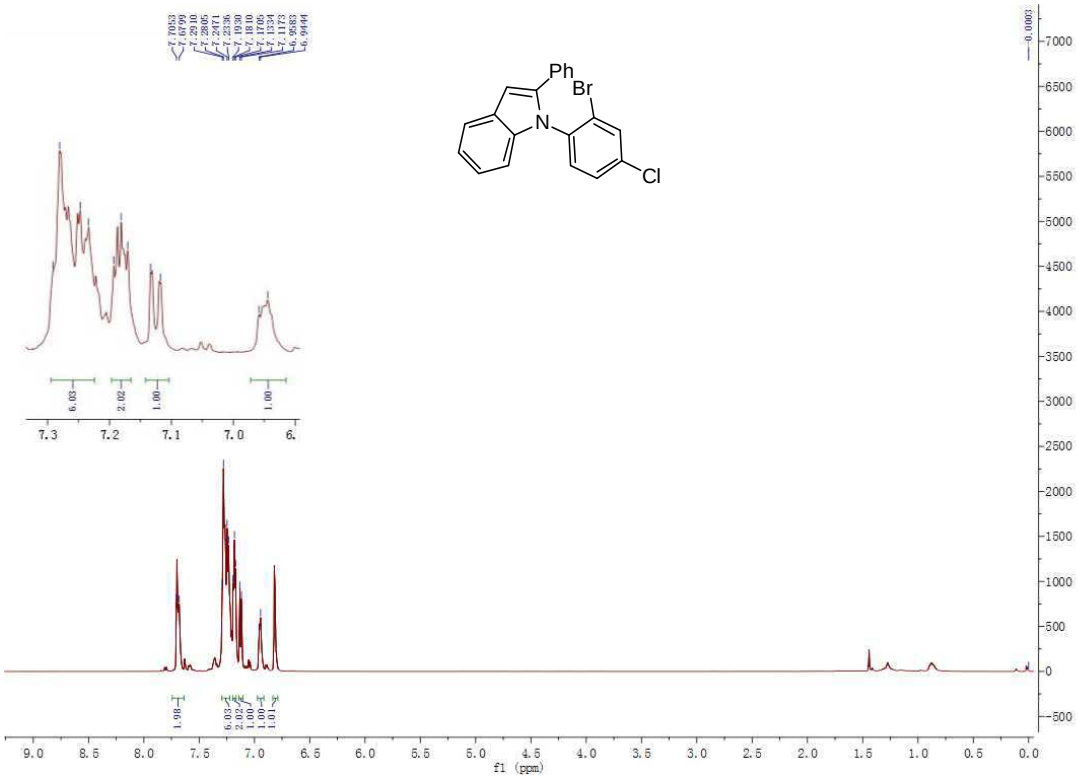

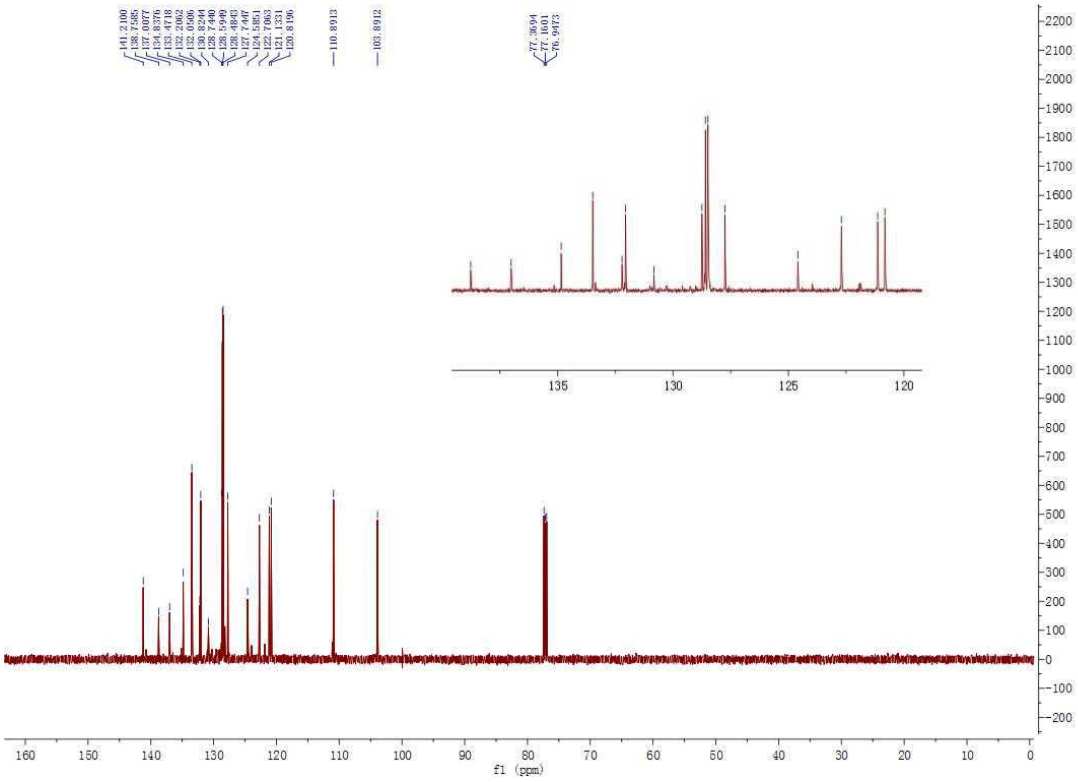

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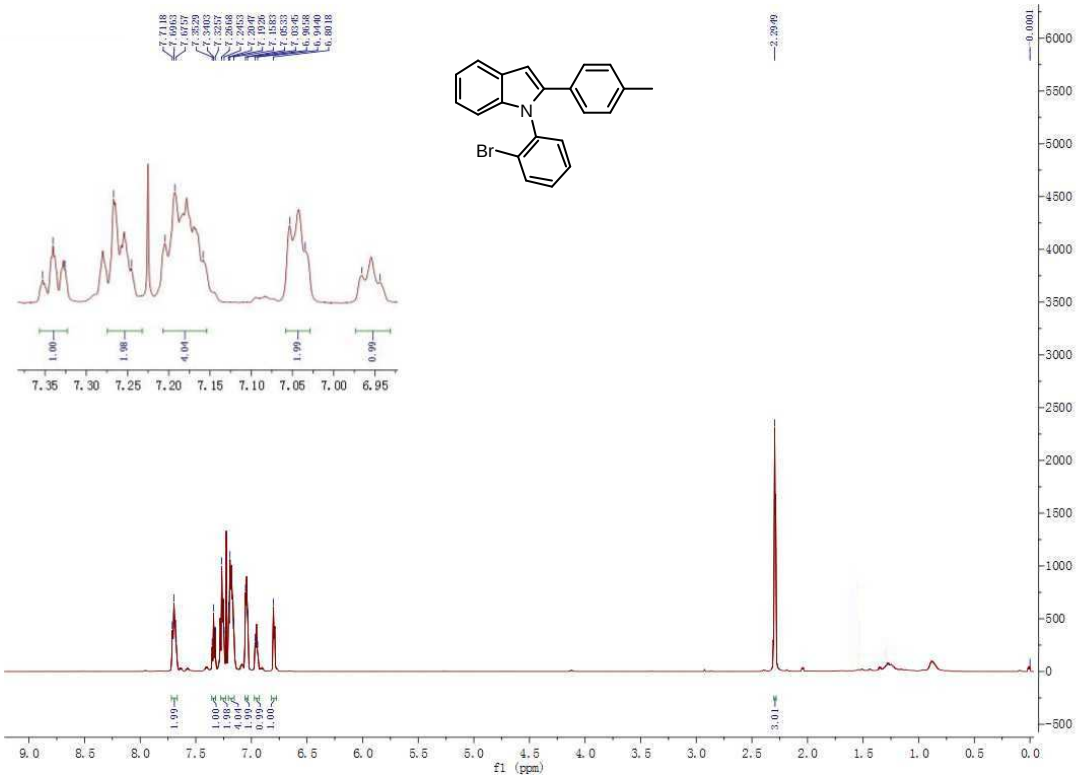

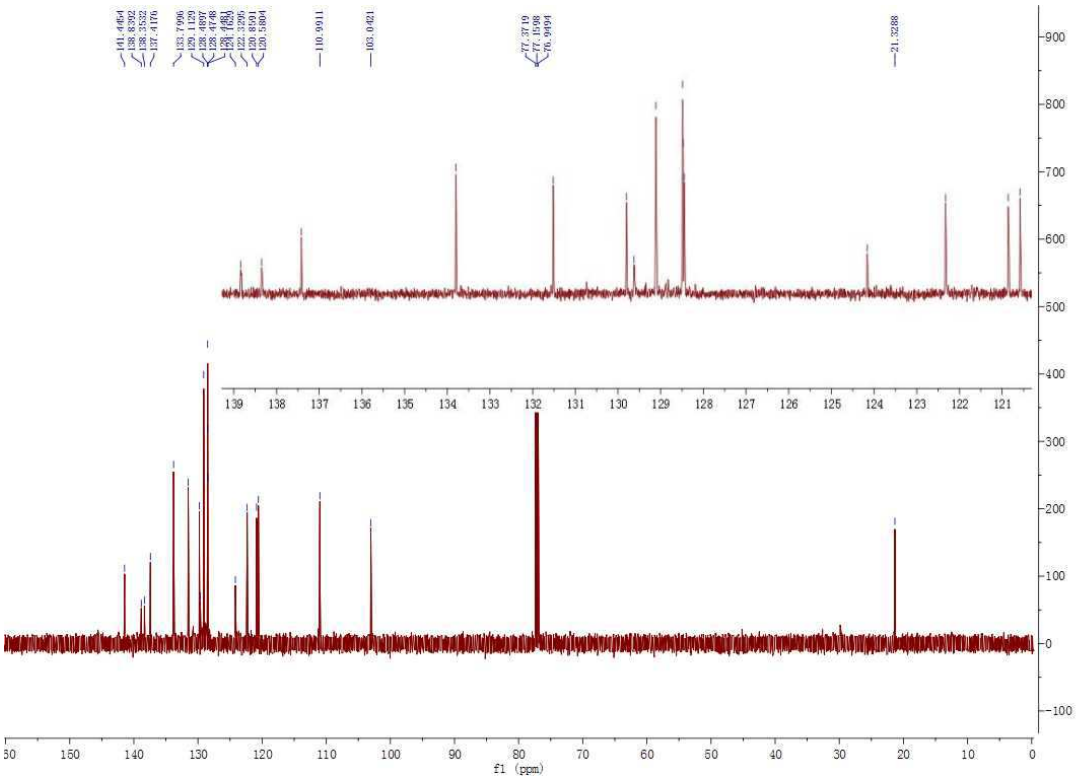

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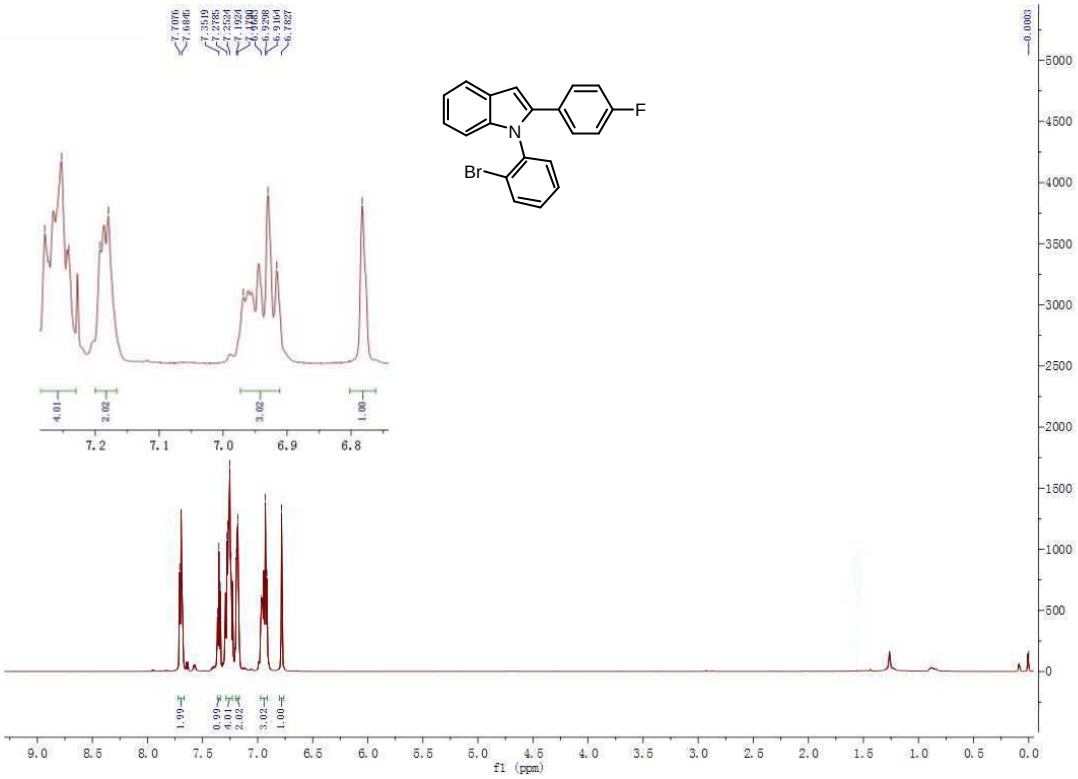

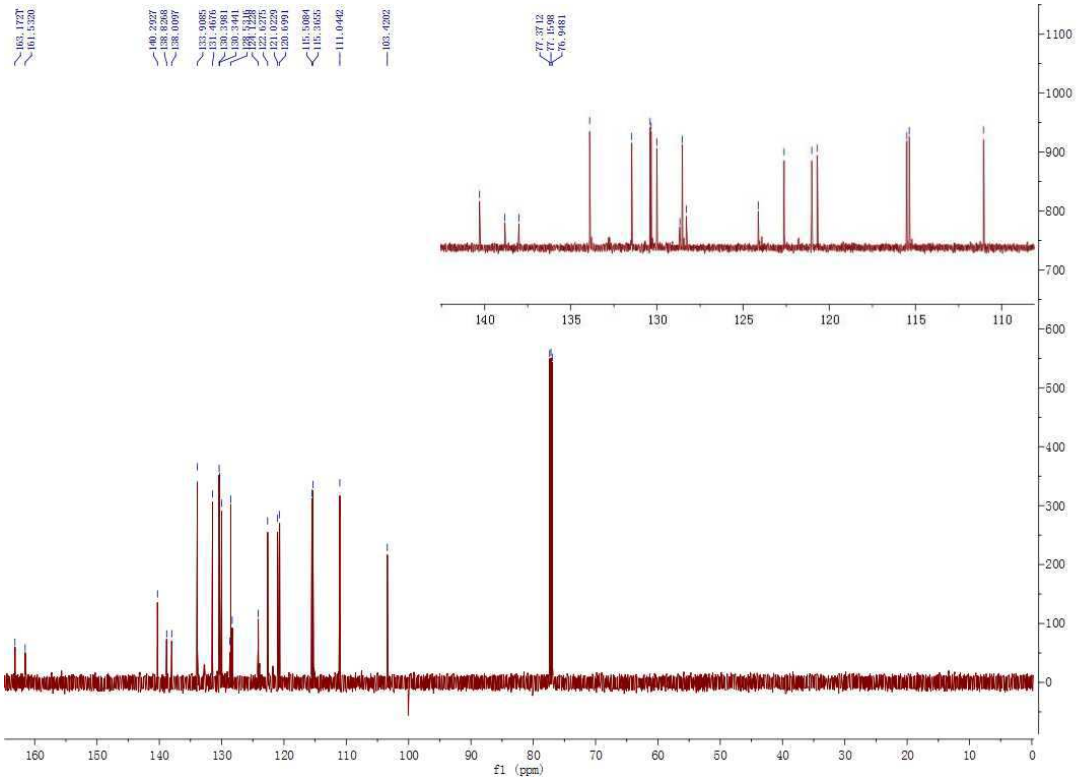

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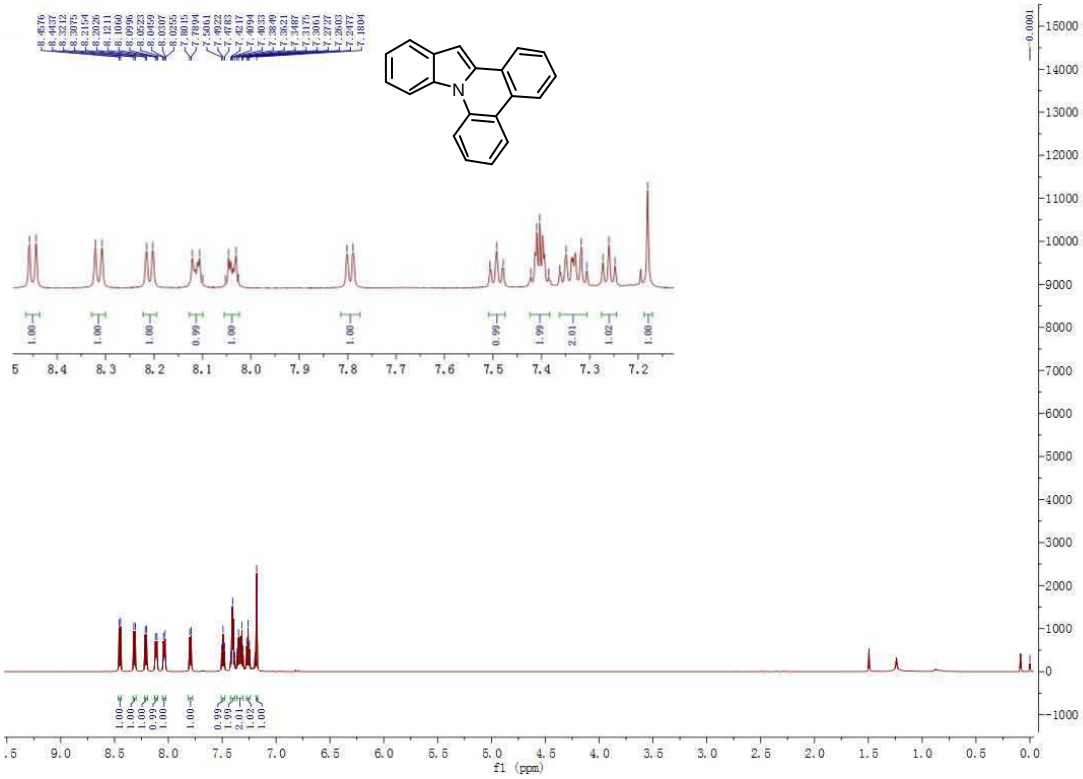

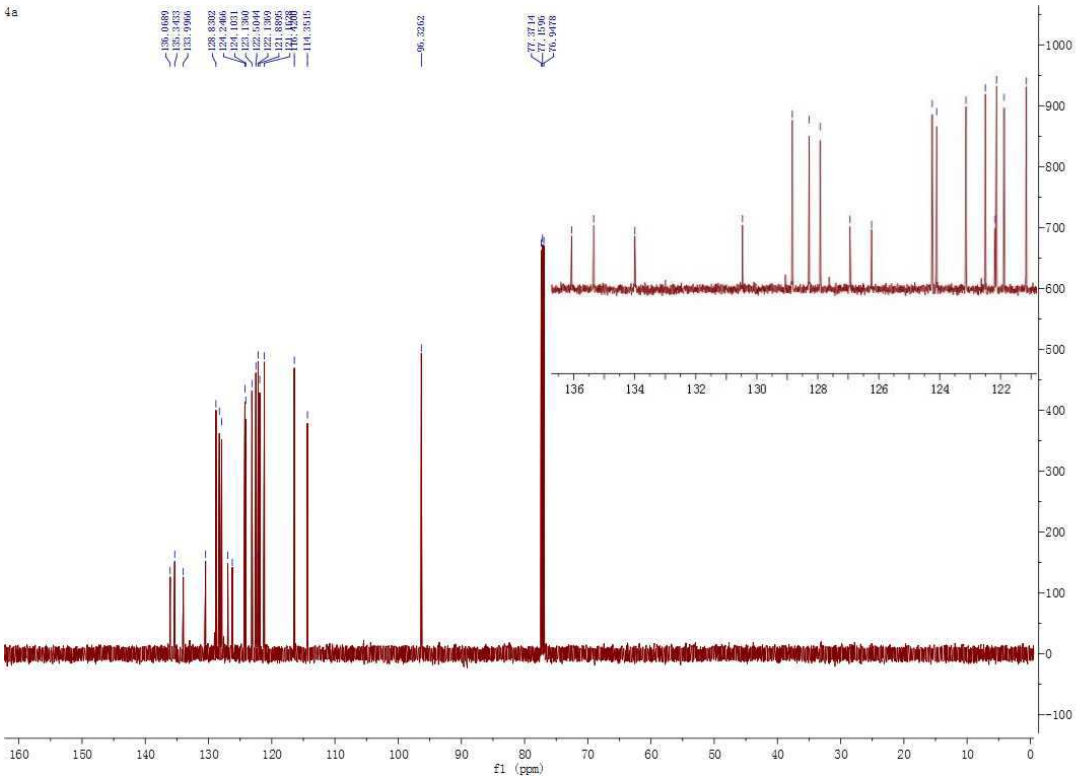

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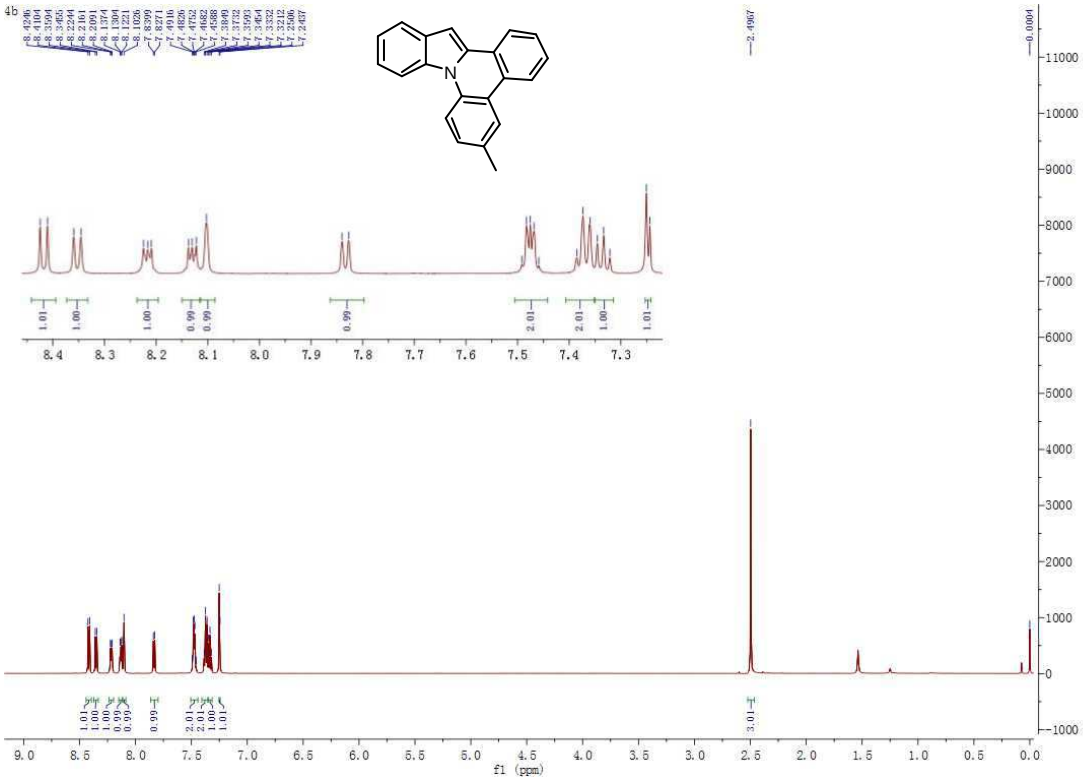

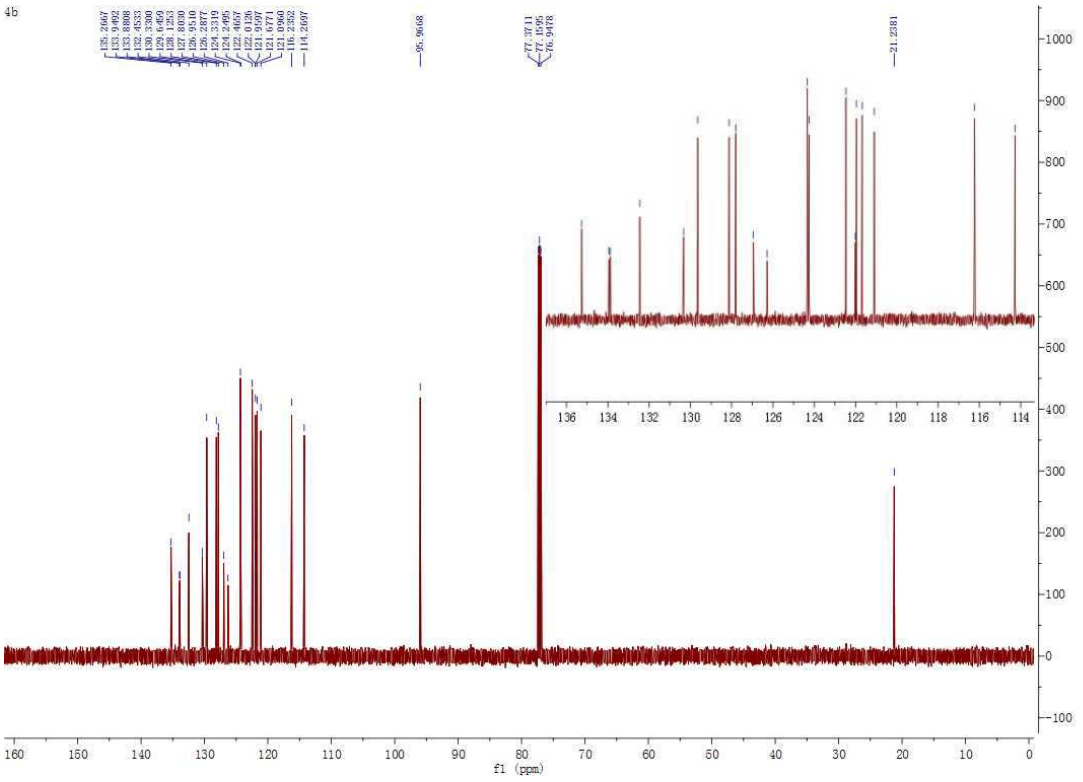

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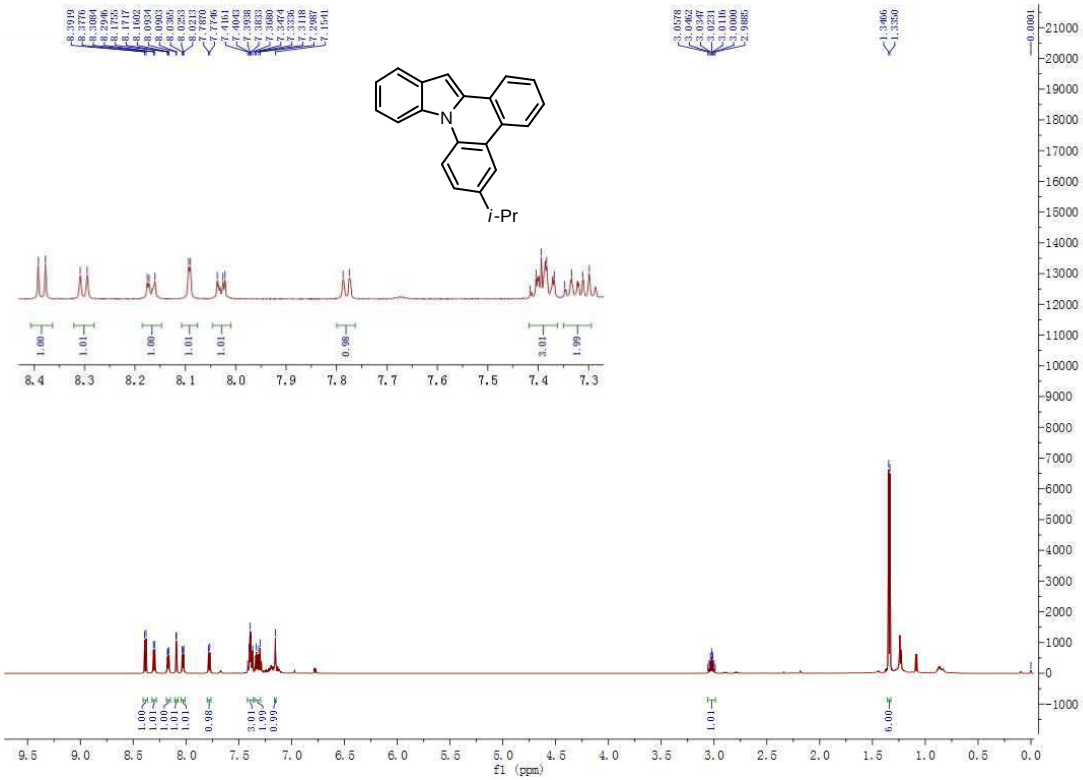

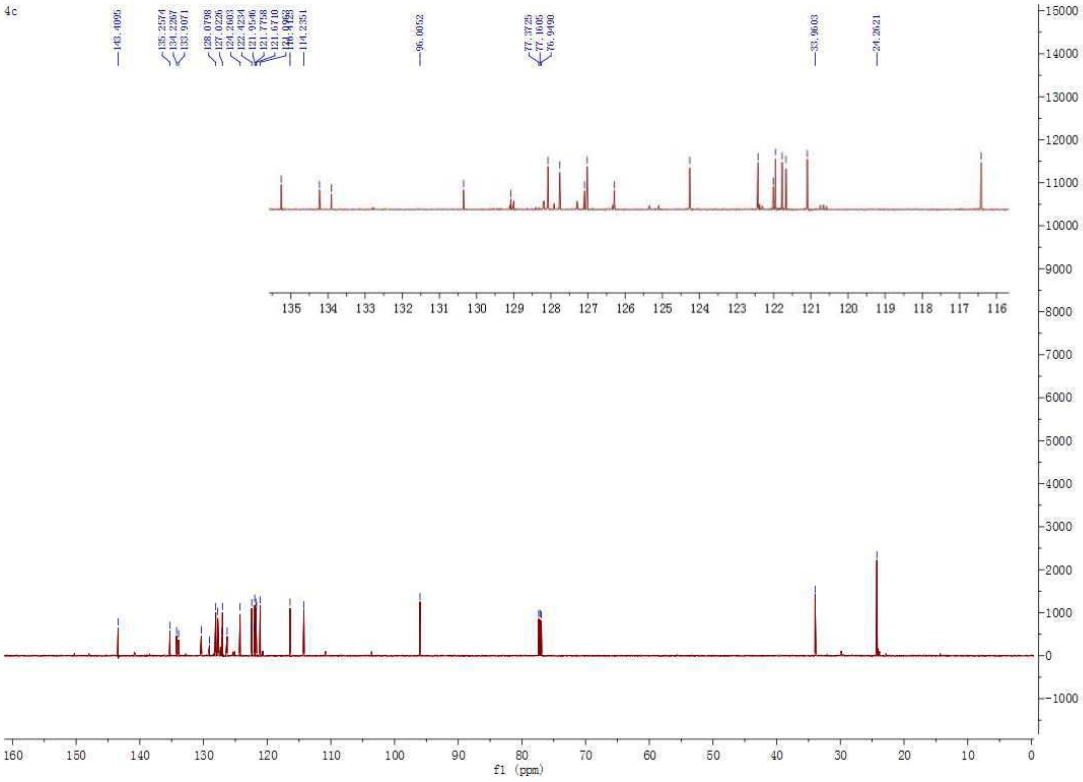

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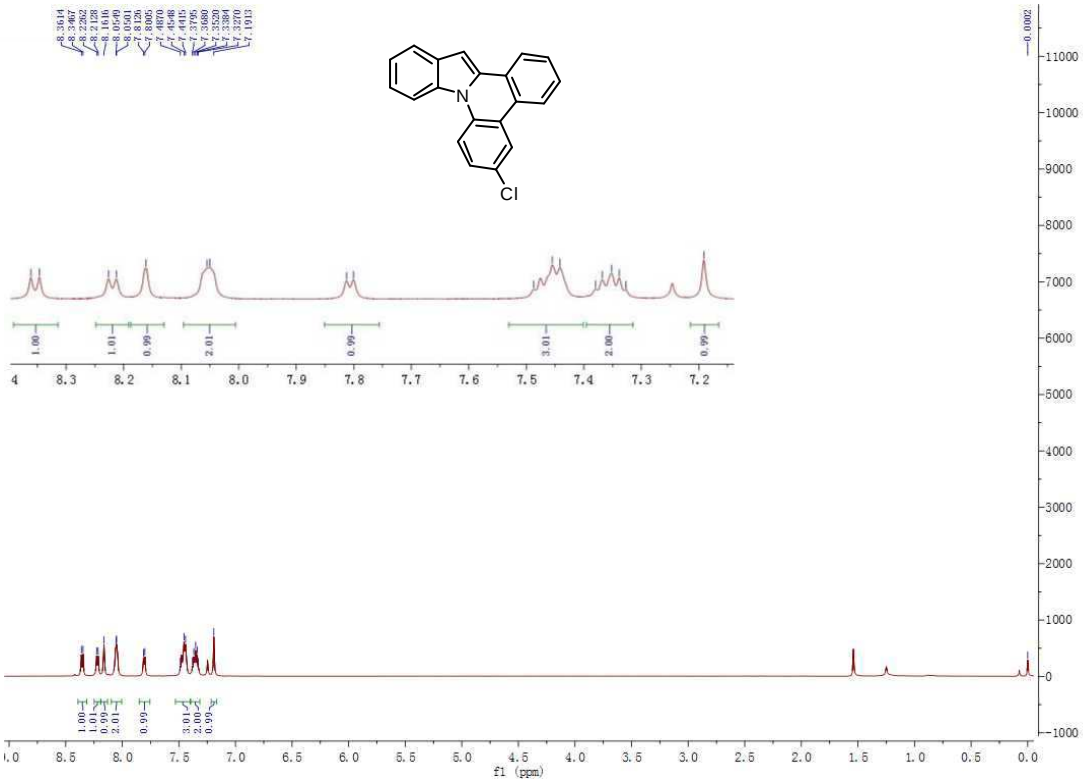

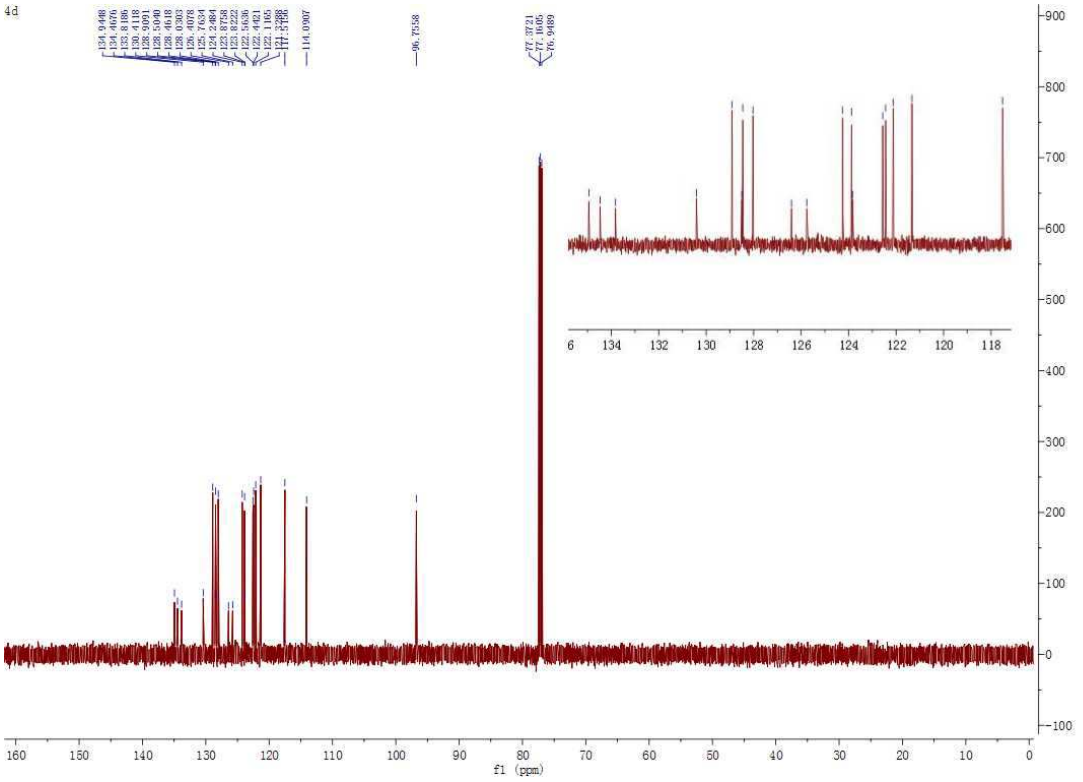

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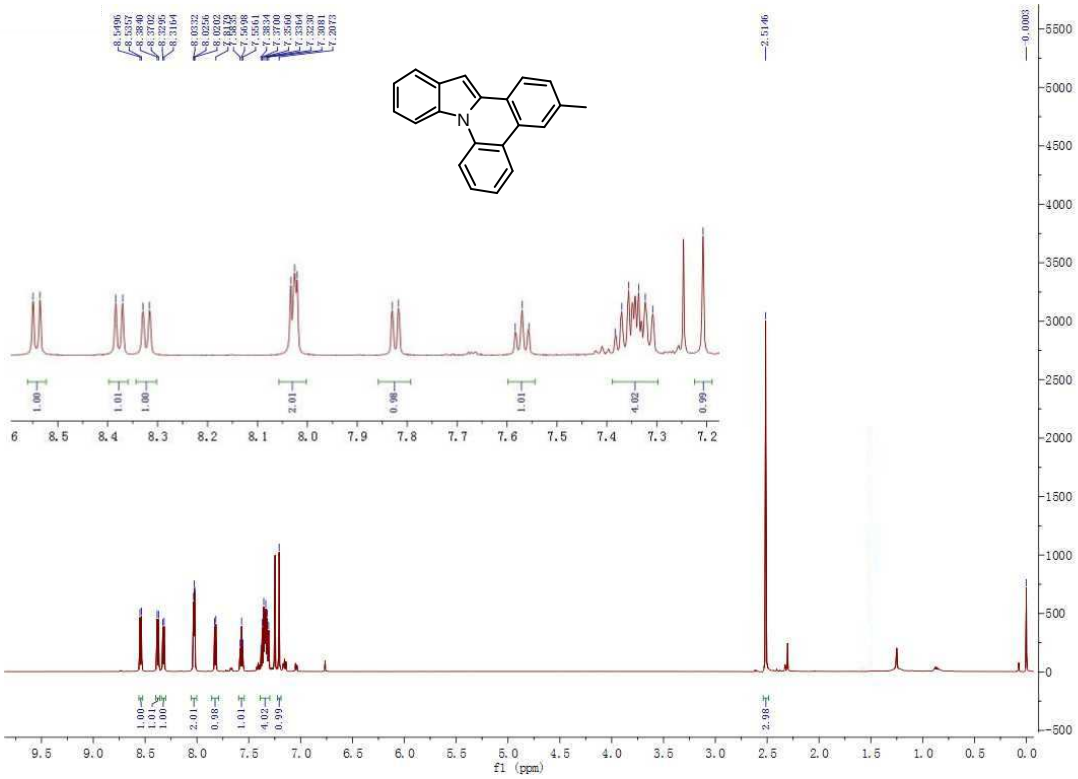

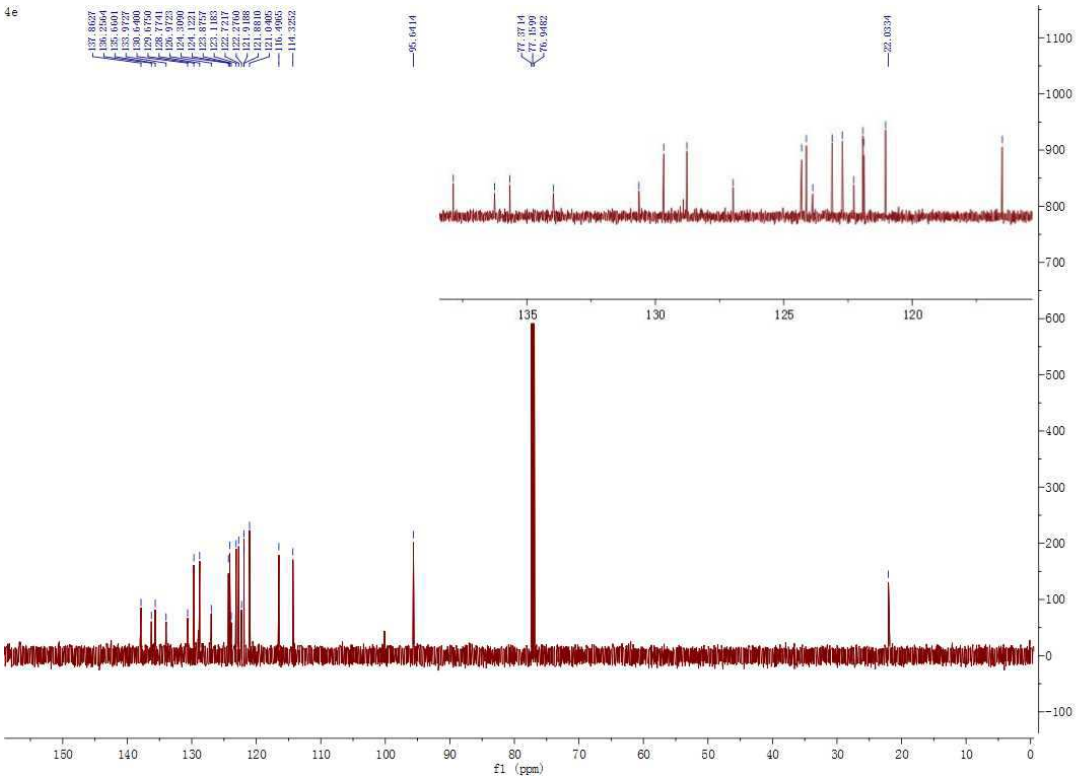

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