Supporting Information

Tertiary amine self-catalyzed intramolecular C_{sp3}-H functionalization with *in situ* generated allenes for the formation of 3-alkenyl indolines

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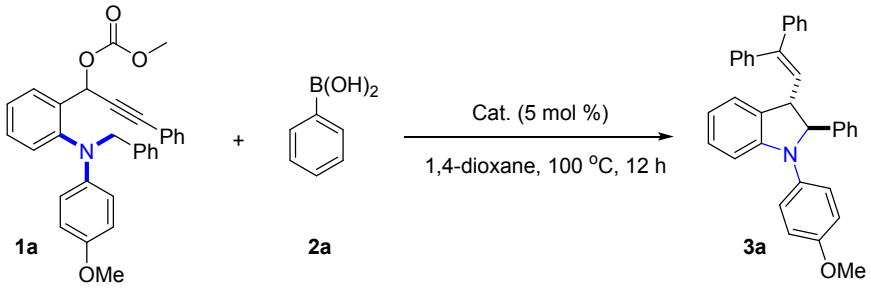
General Methods. All reactions were carried out under N_2 except noted. Anhydrous MeCN were prepared by distillation from P_2O_5. Anhydrous toluene, THF, 1,4-dioxane, $(MeOCH_2)_2$ and MeO^tBu was distilled from sodium and benzophenone. MeOH were prepared by distillation from Mg and I_2. Unless noted, all commercial reagents were used without further purification. Column chromatographic purification of products was carried out using silica gel (300-400 mesh). NMR spectra were recorded at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) respectively, referenced to tetramethylsilane (δ = 0.00 ppm) and the residual solvent peak (δ = 77.00 ppm) in $CDCl_3$ or $(CD_3)_2SO$ (containing 0.03% TMS) solutions. *J* values are in hertz. High-resolution mass spectra were performed on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single crystal X-ray diffraction data was collected in Bruker SMARTAPEX diffractiometers.

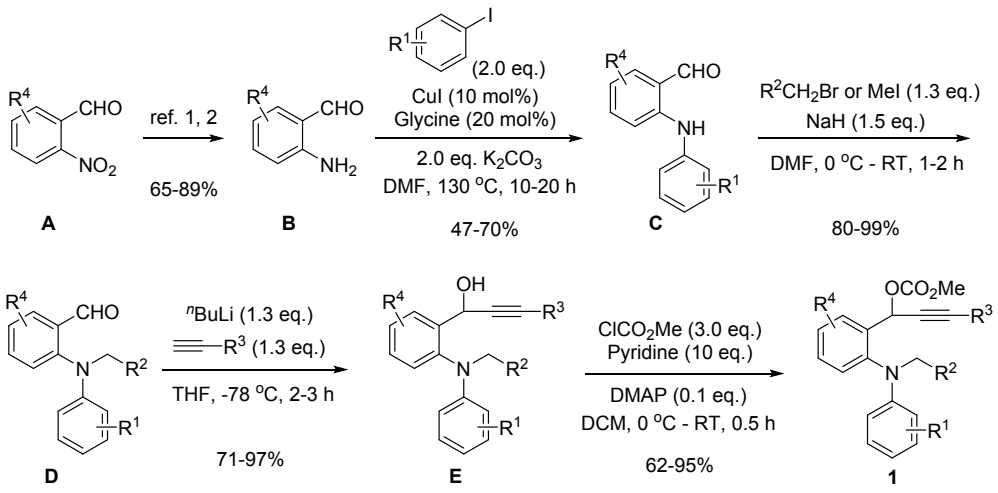
Table S1 Optimization of the reaction conditions with Pd catalysts



Entry	Catalyst	Yield (%)
1	$Pd(OAc)_2$	-
2	$Pd_2(dba)_3$	-
3	$Pd(Ph_3P)_2Cl_2$	trace
4	$Pd(Ph_3P)_4$	90

We screened common palladium catalysts, such as $Pd(OAc)_2$, $Pd_2(dab)_3$, $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$. However, no desired product was detected with 5 mol% of $Pd(OAc)_2$ or $Pd_2(dab)_3$ and a large number of starting material **1a** remained unreacted. With 5 mol% of $PdCl_2(PPh_3)_2$ as the catalyst, only trace of **3a** was generated. Interestingly, **3a** could be obtained in a 90% yield with 5 mol% of Pd $(PPh_3)_4$. So, we chose Pd $(PPh_3)_4$ as the catalyst for further investigation.

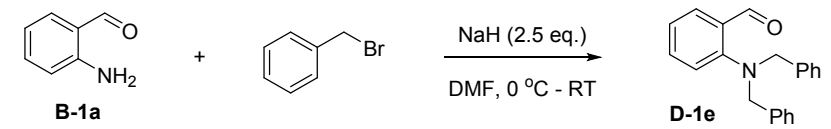
Synthesis and characterization of 1



The intermediate **B** was prepared according to the literature methods.[1,2]

Synthesis of the intermediate C: Under an atmosphere of N_2, to a 100 mL Schlenk tube were added **B** (1.29 g, 10.7 mmol), the corresponding iodobenzene (1.2 eq.), CuI (203.8 mg, 0.1 eq.), Glycine (160.6 mg, 0.2 eq.), K_2CO_3 (2.96 g, 2.0 eq.) and DMF (50 mL). Then, the reaction temperature was increased to 130 °C. After **C** was almost consumed by TLC analysis, the reaction was cooled to room temperature, and 100 mL ethyl acetate was added. Subsequently, the organic layers were washed with brine (80 mL×5) and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography with petroleum ether/ethyl acetate = 40/1-30/1 as the eluent afforded **C** with 47-70% yields

Synthesis of the intermediate D: Under an atmosphere of N_2, to a 100 mL Schlenk tube were added **C** (6.6 mmol) and DMF (50 mL). After the mixture was cooled to 0 °C, NaH (345.0 mg, 1.3 eq.) was added. 20 min latter, MeI or the corresponding bromide (1.2 eq.) was added dropwise. The mixture was slowly warmed to room temperature. About 30 min latter，after full conversion of **C** by TLC analysis, the resulting mixture was quenched with saturated solution of ammonium chloride, and extracted with ethyl acetate (100 mL). The organic layers were washed with brine and dried over anhydrous Na2SO4, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel with petroleum ether/ethyl acetate = 30/1-10/1 as the eluent afforded the intermediate **D** with 80-99% yields.

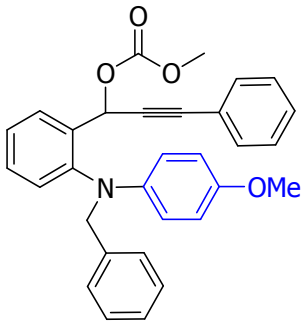


Synthesis of the intermediate D-1e (only for 1e): Under an atmosphere of N_2, to a 100 mL Schlenk tube were added **B-1a** (1.21 g, 20 mmol), DMF (40 mL) and benzyl bromide (3 mL, 2.5 eq.). After the mixture was cooled to 0 °C, NaH (1.0 g, 2.5

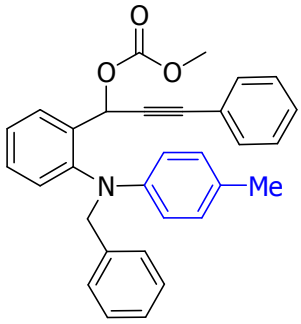
eq.) was added. 20 min latter, the mixture was slowly warmed to room temperature. After full conversion by TLC analysis, the resulting mixture was quenched with saturated solution of ammonium chloride, and extracted with ethyl acetate (150 mL). The organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel with petroleum ether/ethyl acetate = 150/2 as the eluent afforded the intermediate **D-1e** (yellow oil) with 72% yield.

Synthesis of the intermediate E：To a solution of the corresponding terminal alkyne (1.3 eq.) in THF (40 mL) in Schlenk tube was added *n*-BuLi (2.5 M, 3.2 mL, 1.3 eq.) at -78 ^oC and then stirred at -78 ^oC under nitrogen for 30 min. Then, a solution of **D** in THF (5 mL) was added dropwise and stirred at -78 ^oC for 1-2 h. After full conversion of **D** monitored by thin-layer chromatography, the resulting mixture was quenched with saturated solution of ammonium chloride, and extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel with petroleum ether/ethyl acetate = 20:1-5:1 as the eluent afforded the intermediate **E** with 71-93% yields.

Synthesis of the substrate 1：To a solution of the corresponding intermediate **E** (1.5 mmol) in DCM (40 mL) in Schlenk tube was added DMAP (17.0 mg, 0.1 eq.), pyridine (1.2 mL, 10.0 eq.) at 0 ^oC. Then $ClCO_2Me$ (352 uL, 3.0 eq.) was added dropwise at 0 ^oC under nitrogen. The mixture was slowly warmed to room temperature. About 30 min latter，after full conversion of **E** by TLC analysis, the resulting mixture was quenched with saturated solution of ammonium chloride, and extracted with ethyl acetate (100 mL). The organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel with petroleum ether/ethyl acetate/Et_3N = 100/10/1 as the eluent afforded the substrate **1**.

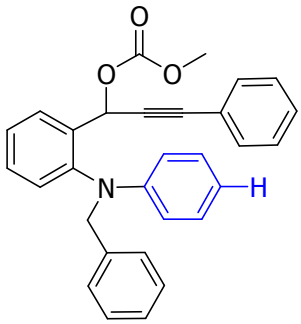


1-(2-(benzyl(4-methoxyphenyl)amino)phenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1a): yellow oil, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.41-7.18 (m, 13H), 6.80 (s, 1H), 6.70 (d, *J* = 9.2 Hz, 2H), 6.63 (d, *J* = 9.2 Hz, 2H), 4.83 (s, 2H), 3.69 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.76, 153.23, 147.31, 143.48, 138.91, 135.22, 132.05, 130.92, 129.67, 128.88, 128.66, 128.60, 128.36, 127.41, 127.00, 126.83, 122.27, 117.98, 114.42, 87.34, 85.42, 65.97, 57.35, 55.35, 54.74; HRMS (ESI) calcd for $C_{31}H_{28}NO_4$ $[M+H]^+$: 478.2013, found 478.2010.

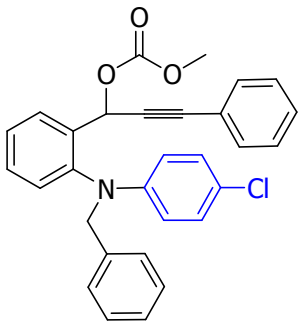


1-(2-(benzyl(p-tolyl)amino)phenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1b): yellowish oil, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.41-7.18 (m, 13H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.73 (s, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.86 (s, 2H), 3.66 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ154.74, 146.98, 146.66, 138.88, 135.69, 132.07, 131.06, 129.78, 129.63, 129.39,

128.90, 128.68, 128.37, 127.82, 127.38, 127.29, 126.99, 122.31, 115.70, 100.64, 87.46, 85.42, 66.04, 56.71, 54.74, 20.05; HRMS (ESI) calcd for $C_{31}H_{28}NO_3$ $[M+H]^+$: 462.2064, found 462.2061.

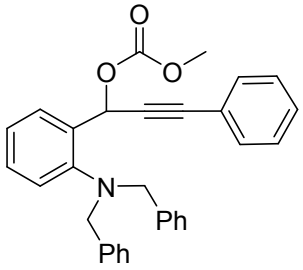


1-(2-(benzyl(phenyl)amino)phenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1c): yellowish oil, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.46-7.18 (m, 13H), 7.16-7.08 (m, 2H), 6.78-6.71 (m, 1H), 6.69 (s, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.91 (s, 2H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.75, 149.08, 146.07, 138.66, 135.86, 132.08, 131.19, 129.95, 129.76, 129.10, 128.95, 128.72, 128.40, 127.62, 127.39, 127.07, 122.27, 118.41, 115.11, 87.59, 85.32, 66.01, 56.44, 54.78; HRMS (ESI) calcd for $C_{30}H_{26}NO_3$ $[M+H]^+$: 448.1907, found 448.1904.

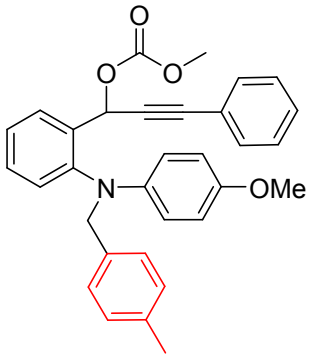


1-(2-(benzyl(4-chlorophenyl)amino)phenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1d): yellowish oil, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J*

= 7.2, 2.0 Hz, 1H), 7.44-7.21 (m, 13H), 7.05 (d, J = 9.2 Hz, 2H), 6.65 (s, 1H), 6.53 (d, J = 9.2 Hz, 2H), 4.88 (s, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ154.77, 147.60, 145.64, 138.12, 135.73, 132.06, 131.31, 130.06, 129.61, 129.05, 128.93, 128.83, 128.45, 127.95, 127.27, 123.32, 122.09, 116.27, 87.78, 85.01, 65.90, 56.52, 54.88; HRMS (ESI) calcd for $C_{30}H_{25}ClNO_3$ $[M+H]^+$: 482.1517, found 482.1515.

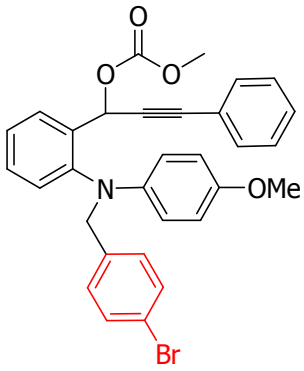


1-(2-(dibenzylamino)phenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1e): yellow oil, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 7.6 Hz, 1H), 7.44-7.13 (m, 18H), 7.05 (d, J = 7.6 Hz, 1H), 4.25-3.85 (m, 4H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.12, 149.14, 137.88, 133.81, 132.09, 129.56, 129.32, 129.04, 128.84, 128.44, 128.38, 127.32, 125.36, 124.08, 122.41, 87.03, 86.17, 65.43, 58.13, 54.83.

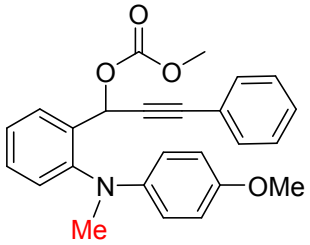


1-(2-((4-methoxyphenyl)(4-methylbenzyl)amino)phenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1f): yellowish oil, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84

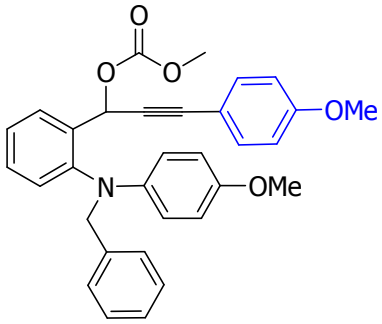
(d, J = 7.6 Hz, 1H), 7.40-7.21 (m, 10H), 7.09 (d, J = 7.6 Hz, 2H), 6.78 (s, 1H), 6.70 (d, J = 9.2 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 4.79 (s, 2H), 3.69 (s, 3H), 3.67 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.78, 153.20, 147.31, 143.63, 136.58, 135.82, 135.28, 132.08, 130.90, 129.68, 129.35, 128.88, 128.64, 128.36, 127.45, 126.78, 122.35, 117.99, 114.46, 87.31, 85.51, 66.00, 57.13, 55.39, 54.73, 20.79; HRMS (ESI) calcd for $C_{32}H_{30}NO_4$ $[M+H]^+$: 492.2169, found 492.2166.



1-(2-((4-bromobenzyl)(4-methoxyphenyl)amino)phenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1g): yellowish oil, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 7.6 Hz, 1H), 7.44-7.16 (m, 12H), 6.77 (s, 1H), 6.70 (d, J = 8.8 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 4.76 (s, 2H), 3.70 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ154.80, 153.54, 147.25, 143.24, 137.99, 135.25, 132.08, 131.79, 130.97, 129.69, 129.25, 128.96, 128.40, 126.99, 122.22, 120.78, 118.27, 114.54, 87.46, 85.29, 65.96, 56.91, 55.40, 54.81; HRMS (ESI) calcd for $C_{31}H_{27}BrNO_4$ $[M+H]^+$: 556.1118, found 556.1116.

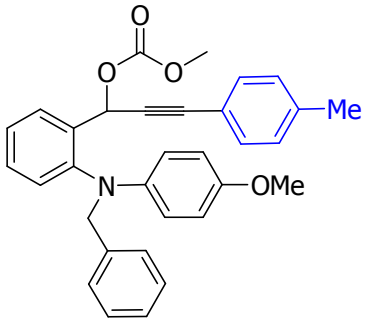


1-(2-((4-methoxyphenyl)(methyl)amino)phenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1h): yellowish oil, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.2 Hz, 1H), 7.43-7.25 (m, 7H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 6.76 (d, *J* = 9.2 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 3.73 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ154.93, 152.95, 148.29, 144.66, 135.54, 132.09, 131.10, 129.24, 128.94, 128.42, 127.98, 126.88, 122.34, 116.48, 114.54, 87.41, 85.51, 66.04, 55.55, 54.82, 40.75; HRMS (ESI) calcd for $C_{25}H_{24}NO_4$ $[M+H]^+$: 402.1700, found 402.1696.

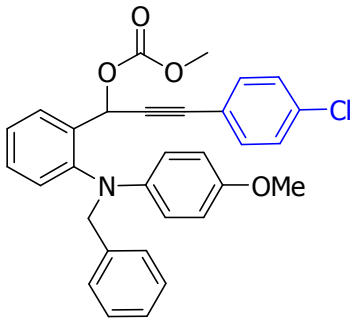


1-(2-(benzyl(4-methoxyphenyl)amino)phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-yl methyl carbonate (1i): yellowish oil, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.2 Hz, 1H), 7.40-7.19 (m, 10H), 6.83-6.74 (m, 3H), 6.70 (d, *J* = 9.2 Hz, 2H), 6.62 (d, *J* = 9.2 Hz, 2H), 4.83 (s, 2H), 3.79 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.25, 154.80, 153.20, 147.30, 143.51, 138.97, 135.47, 133.62, 130.84, 129.68, 128.66, 127.43, 126.98, 126.83, 117.93, 114.44, 113.92,

87.45, 84.09, 66.17, 57.33, 55.39, 55.14, 54.70; HRMS (ESI) calcd for $C_{32}H_{30}NO_5$ $[M+H]^+$: 508.2118, found 508.2117.

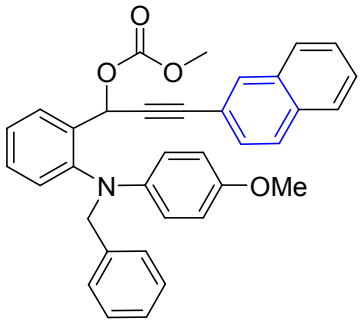


1-(2-(benzyl(4-methoxyphenyl)amino)phenyl)-3-(p-tolyl)prop-2-yn-1-yl methyl carbonate (1j): yellowish oil, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.40-7.33 (m, 3H), 7.33-7.27 (m, 3H), 7.25-7.15 (m, 4H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.78 (s, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 9.2 Hz, 2H), 4.83 (s, 2H), 3.70 (s, 3H), 3.66 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.80, 153.24, 147.32, 143.53, 139.12, 138.98, 135.43, 132.00, 130.87, 129.72, 129.14, 128.67, 127.46, 127.01, 126.85, 119.25, 117.95, 114.48, 87.60, 84.77, 66.12, 57.36, 55.41, 54.72, 21.22; HRMS (ESI) calcd for $C_{32}H_{30}NO_4$ $[M+H]^+$: 492.2169, found 492.2168.

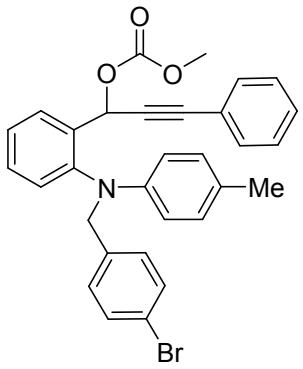


1-(2-(benzyl(4-methoxyphenyl)amino)phenyl)-3-(4-chlorophenyl)prop-2-yn-1-yl methyl carbonate (1k): yellowish oil, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ

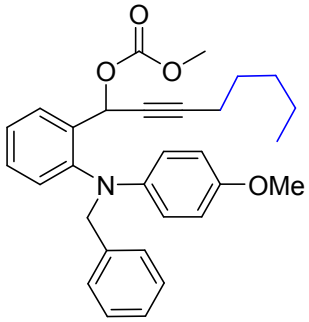
7.81 (d, J = 7.2 Hz, 1H), 7.40-7.18 (m, 12H), 6.79 (s, 1H), 6.69 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H), 4.90-4.75 (m, 2H), 3.69 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ154.76, 153.32, 147.36, 143.52, 138.89, 135.02, 133.30, 130.99, 129.54, 128.73, 128.68, 128.60, 127.44, 127.04, 126.84, 120.76, 118.14, 114.45, 86.42, 86.12, 65.88, 57.44, 55.38, 54.80; HRMS (ESI) calcd for $C_{31}H_{27}ClNO_4$ $[M+H]^+$: 512.1623, found 512.1620.



1-(2-(benzyl(4-methoxyphenyl)amino)phenyl)-3-(naphthalen-2-yl)prop-2-yn-1-yl methyl carbonate (1l): white solid, 65% yield, mp 41-43 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 7.5 Hz, 1H), 7.85-7.62 (m, 4H), 7.55-7.13 (m, 11H), 6.86 (s, 1H), 6.71 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 4.85 (s, 2H), 3.69 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.82, 153.27, 147.38, 143.54, 138.96, 135.28, 133.17, 132.97, 132.25, 130.93, 129.62, 128.70, 128.65, 128.53, 128.00, 127.93, 127.45, 127.03, 126.88, 126.73, 119.54, 118.09, 114.46, 87.67, 85.67, 66.10, 57.41, 55.36, 54.79; HRMS (ESI) calcd for $C_{35}H_{30}NO_4$ $[M+H]^+$: 528.2169, found 528.2163.

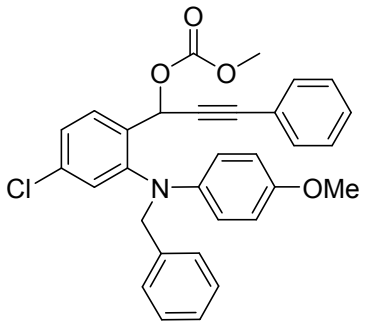


1-(2-((4-bromobenzyl)(p-tolyl)amino)phenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1m): yellowish oil, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.44-7.18 (m, 12H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 4.79 (s, 2H), 3.67 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.74, 146.72, 146.59, 137.91, 135.63, 132.06, 131.77, 131.13, 129.77, 129.70, 129.15, 128.96, 128.39, 128.24, 127.43, 122.17, 120.75, 115.89, 87.55, 85.24, 65.96, 56.21, 54.80, 20.05; HRMS (ESI) calcd for $C_{31}H_{27}BrNO_3$ $[M+H]^+$: 540.1169, found 540.1162.

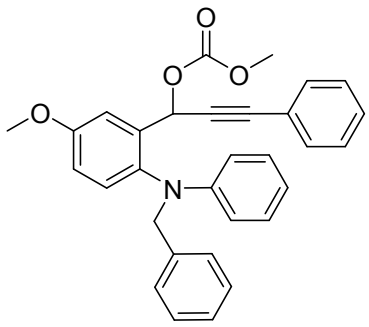


1-(2-(benzyl(4-methoxyphenyl)amino)phenyl)oct-2-yn-1-yl methyl carbonate (1n): yellowish oil, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 6.4 Hz, 1H), 7.40-7.16 (m, 8H), 6.69 (d, *J* = 9.2 Hz, 2H), 6.60-6.50 (m, 3H), 4.79 (s, 2H), 3.71 (s, 3H), 3.63 (s, 3H), 2.21-2.10 (m, 2H), 1.49-1.38 (m, 2H), 1.34-1.20 (m, 4H), 0.86 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ154.80, 153.09, 147.28,

143.50, 138.98, 135.84, 130.73, 129.66, 128.74, 128.63, 127.36, 126.95, 126.79, 117.70, 114.37, 88.95, 65.99, 57.26, 55.41, 54.60, 30.75, 27.72, 21.84 18.51, 13.63; HRMS (ESI) calcd for $C_{30}H_{34}NO_4$ $[M+H]^+$: 472.2482, found 472.2481.



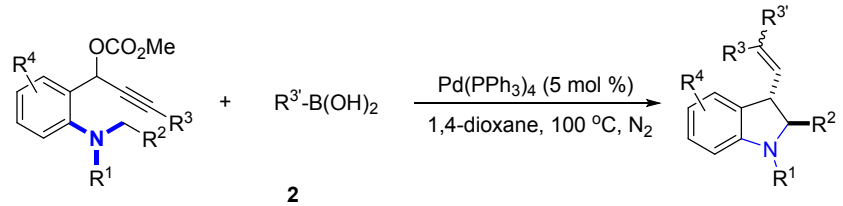
1-(2-(benzyl(4-methoxyphenyl)amino)-4-chlorophenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1o): yellow solid, 81% yield, mp 34-36 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.40-7.18 (m, 12H), 6.80-6.60 (m, 5H), 4.58-4.54 (m, 2H), 3.70 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.67, 154.01, 148.63, 142.90, 138.41, 136.10, 133.50, 132.08, 130.87, 129.03, 128.78, 128.41, 128.03, 127.48, 127.22, 126.73, 122.10, 119.33, 114.56, 87.48, 84.97, 65.45, 57.66, 55.34, 54.83.



1-(2-(benzyl(phenyl)amino)-5-methoxyphenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (1p): yellow oil, 95% yield; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42-7.20 (m, 11H), 7.17-7.08 (m, 3H), 6.93 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.76-6.69 (m, 1H), 6.64 (s,

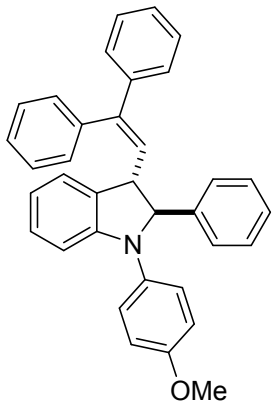
1H), 6.60 (d, J = 8.0 Hz, 2H), 4.87 (s, 2H), 3.85 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.85, 154.70, 149.39, 138.72, 138.54, 137.12, 132.06, 131.15, 129.06, 128.97, 128.69, 128.40, 127.46, 127.04, 122.21, 117.94, 116.87, 114.51, 114.21, 87.69, 85.19, 66.03, 56.36, 55.43, 54.83.

Synthesis and characterization of 3



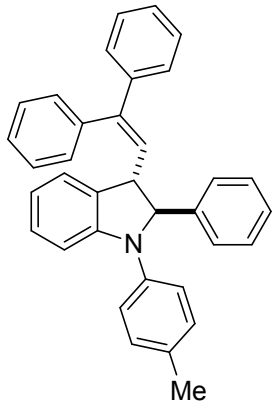
1 **2** **3**

To a solution of **1** (0.2 mmol) in 1,4-dioxane (4 mL) in Schlenk tube was added **2** (2.0 eq.) and $Pd(Ph_3P)_4$ (11.6 mg, 0.05 eq.) at room temperature under nitrogen and then stirred at 100 °C. After the corresponding reaction time (see Table 2 in the text), the solution was cooled to room temperature and concentrated under reduced pressure directly. The residue was purified by flash chromatography on silica gel with petroleum ether/DCM = 20/1-5/1 as the eluent afforded the 3-alkenyl indoline **3**.



(2S,3S)-3-(2,2-diphenylvinyl)-1-(4-methoxyphenyl)-2-phenylindoline (3a)

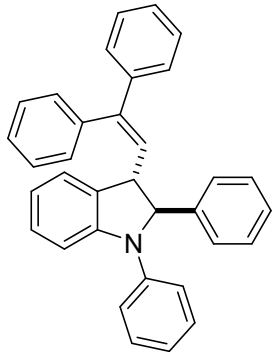
White solid, 92% yield (88 mg), mp 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.16 (m, 10H), 7.14-7.09 (m, 1H), 7.09-6.96 (m, 6H), 6.84-6.71 (m, 3H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.2 Hz, 2H), 6.31 (d, *J* = 10.4 Hz, 1H), 4.99 (d, *J* = 10.0 Hz, 1H), 4.02 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.56, 150.76, 145.71, 142.10, 140.87, 139.43, 137.02, 131.72, 129.87, 128.73, 128.57, 128.36, 128.18, 127.82, 127.80, 127.62, 127.33, 127.21, 125.12, 124.57, 119.30, 114.67, 108.09, 76.68, 55.34, 53.03; HRMS (ESI) calcd for $C_{35}H_{29}NNaO$ $[M+Na]^+$: 502.2141, found 502.2154.



(2S,3S)-3-(2,2-diphenylvinyl)-2-phenyl-1-(p-tolyl)indoline (3b)

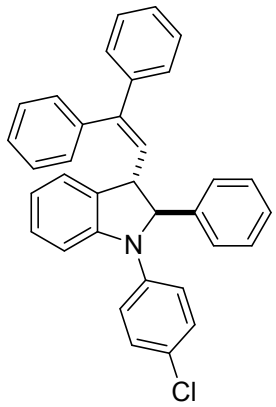
White solid, 89% yield (83 mg), mp 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.18 (m, 10H), 7.16-6.97 (m, 9H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.81-6.72 (m, 1H), 6.62 (d, *J* = 7.2 Hz, 2H), 6.31 (d, *J* = 10.0 Hz, 1H), 5.07 (d, *J* = 9.6 Hz, 1H), 4.01 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.77, 145.53, 142.09, 141.06, 141.01, 139.46, 133.05, 131.92, 129.98, 129.89, 128.80, 128.57, 128.40, 128.31, 127.91, 127.80, 127.76, 127.63, 127.49, 127.24, 124.73, 122.54,

119.50, 108.14, 75.62, 53.05, 20.70; HRMS (ESI) calcd for $C_{35}H_{30}N$ $[M+H]^+$: 464.2373, found 464.2353.



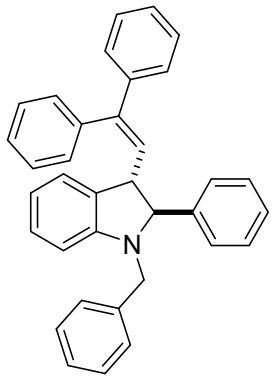
(2S,3S)-3-(2,2-diphenylvinyl)-1,2-diphenylindoline (3c)

White solid, 71% yield (64 mg), mp 166-168 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.18 (m, 12H), 7.17-7.03 (m, 7H), 7.00-6.90 (m, 2H), 6.87-6.75 (m, 1H), 6.66 (d, *J* = 7.2 Hz, 2H), 6.31 (d, *J* = 10.4 Hz, 1H), 5.11 (d, *J* = 9.2 Hz, 1H), 4.01 (dd, *J* = 9.6, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.09, 145.43, 143.51, 142.05, 140.98, 139.46, 132.10, 129.90, 129.34, 128.86, 128.59, 128.44, 128.30, 127.83, 127.78, 127.75, 127.64, 127.57, 127.28, 124.90, 123.17, 121.99, 119.82, 108.25, 75.24, 53.02; HRMS (ESI) calcd for $C_{34}H_{28}N$ $[M+H]^+$: 450.2216, found 450.2221.



(2S,3S)-1-(4-chlorophenyl)-3-(2,2-diphenylvinyl)-2-phenylindoline (3d)

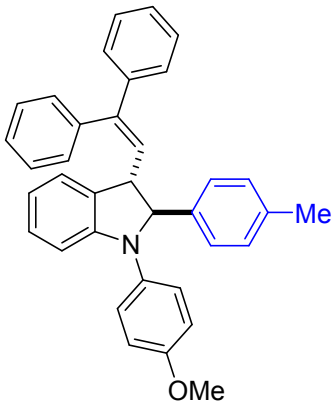
White solid, 54% yield (52 mg), mp 182-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.20 (m, 10H), 7.20-7.00 (m, 9H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.86-6.79 (m, 1H), 6.63 (d, *J* = 7.2 Hz, 2H), 6.28 (d, *J* = 10.0 Hz, 1H), 5.06 (d, *J* = 9.2 Hz, 1H), 4.02 (dd, *J* = 10.0, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.65, 145.75, 142.05, 141.96, 140.46, 139.37, 132.14, 129.85, 129.43, 128.97, 128.60, 128.45, 128.36, 128.04, 128.00, 127.90, 127.76, 127.63, 127.32, 127.20, 125.00, 123.22, 120.22, 108.10, 75.33, 52.99; HRMS (ESI) calcd for $C_{34}H_{27}ClN$ $[M+H]^+$: 484.1827, found 484.1830.



(2S,3S)-1-benzyl-3-(2,2-diphenylvinyl)-2-phenylindoline (3e)

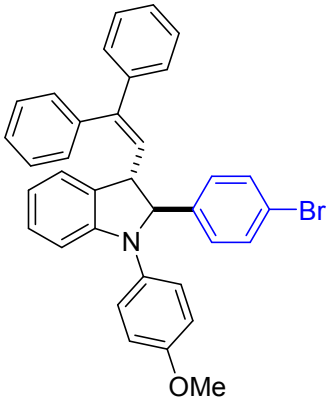
White solid, 74% yield (96.9 mg), mp 149-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.35 (m, 2H), 7.35-7.29 (m, 3H), 7.28-7.19 (m, 10H), 7.16-7.10 (m, 1H), 7.09-6.94 (m, 4H), 6.77-6.68 (m, 1H), 6.54 (d, *J* = 7.2 Hz, 2H), 6.40 (d, *J* = 7.6 Hz, 1H), 6.19 (d, *J* = 10.4 Hz, 1H), 4.43 (d, *J* = 11.2 Hz, 1H), 4.35 (d, *J* = 15.6 Hz, 1H), 4.10-3.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.06, 145.51, 141.99, 140.43, 139.30, 138.37, 131.88, 129.74, 128.73, 128.59, 128.47, 128.37, 128.28, 128.17, 128.04, 127.84, 127.57, 127.44, 127.19, 127.09, 127.00, 124.04, 118.60, 108.38,

76.84, 52.55, 51.36; HRMS (ESI) calcd for $C_{35}H_{30}N$ $[M+H]^+$: 464.2373, found 464.2381.



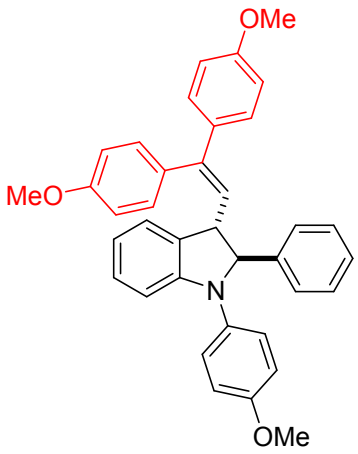
(2S,3S)-3-(2,2-diphenylvinyl)-1-(4-methoxyphenyl)-2-(p-tolyl)indoline (3f)

White solid, 94% yield (93 mg), mp 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.21 (m, 5H), 7.20-7.11 (m, 3H), 7.10-6.96 (m, 8H), 6.81-6.71 (m, 3H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 7.2 Hz, 2H), 6.30 (d, *J* = 10.4 Hz, 1H), 4.96 (d, *J* = 10.0 Hz, 1H), 4.01 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.71 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.49, 150.74, 145.60, 142.20, 139.49, 137.78, 137.40, 137.06, 131.81, 129.96, 129.39, 128.55, 128.31, 128.08, 127.76, 127.64, 127.50, 127.19, 125.07, 124.56, 119.21, 114.64, 108.01, 76.41, 55.34, 52.99, 21.06; HRMS (ESI) calcd for $C_{36}H_{32}NO$ $[M+H]^+$: 494.2478, found 494.2491.



(2S,3S)-2-(4-bromophenyl)-3-(2,2-diphenylvinyl)-1-(4-methoxyphenyl)indoline

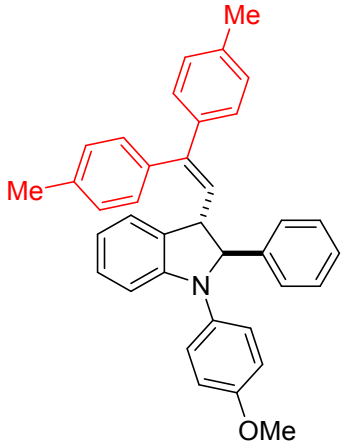
(3g): white solid, 84% yield (94 mg), mp 206-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.4 Hz, 2H), 7.31-7.21 (m, 5H), 7.20-7.00 (m, 9H), 6.86-6.71 (m, 3H), 6.70-6.52 (m, 3H), 6.29 (d, *J* = 10.0 Hz, 1H), 4.92 (d, *J* = 10.0 Hz, 1H), 3.99 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.82, 150.73, 146.17, 141.86, 140.11, 139.32, 136.75, 131.85, 131.49, 129.87, 129.76, 128.62, 128.46, 127.93, 127.58, 127.36, 126.77, 125.28, 124.52, 121.58, 119.54, 114.79, 108.23, 76.20, 55.38, 52.99; HRMS (ESI) calcd for $C_{35}H_{29}BrNO$ $[M+H]^+$: 558.1427, found 558.1423.



(2S,3S)-3-(2,2-bis(4-methoxyphenyl)vinyl)-1-(4-methoxyphenyl)-2-phenylindoline

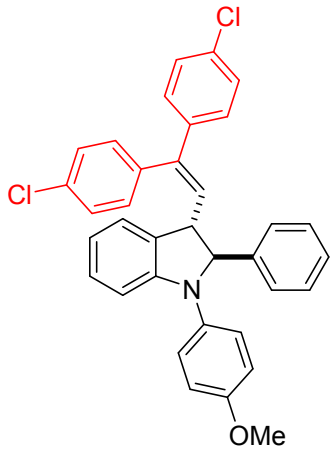
(3i): white solid, 76% yield (82 mg), mp 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.15 (m, 7H), 7.12-6.96 (m, 4H), 6.89-6.70 (m, 5H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 7.6 Hz, 2H), 6.17 (d, *J* = 10.4 Hz, 1H), 4.97 (d, *J* = 10.4 Hz, 1H), 4.03 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.61, 158.91, 156.52, 150.73, 144.72, 141.05, 137.10, 135.19, 132.04, 132.01, 130.99, 128.81, 128.71, 128.26, 128.21, 125.49,

125.11, 124.55, 119.26, 114.65, 113.82, 113.65, 108.02, 76.77, 55.36, 55.20, 53.05; HRMS (ESI) calcd for $C_{37}H_{33}NNaO_3$ $[M+Na]^+$: 562.2353, found 562.2358.

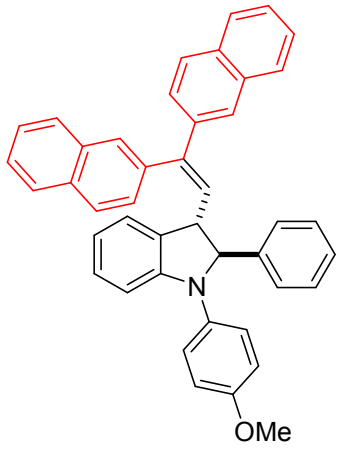


(2S,3S)-3-(2,2-di-p-tolylvinyl)-1-(4-methoxyphenyl)-2-phenylindoline (3j)

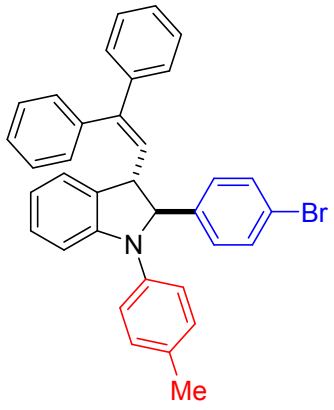
White solid, 89% yield (90 mg), mp 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.14 (m, 7H), 7.11-6.97 (m, 6H), 6.86 (d, *J* = 7.2 Hz, 2H), 6.81-6.71 (m, 3H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 7.2 Hz, 2H), 6.24 (d, *J* = 10.0 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 4.03 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.71 (s, 3H), 2.32 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.52, 150.71, 145.45, 140.99, 139.62, 137.62, 137.13, 136.76, 136.62, 131.93, 129.77, 129.24, 129.02, 128.70, 128.26, 128.20, 127.76, 127.56, 126.41, 125.08, 124.61, 119.28, 114.66, 108.04, 76.73, 55.35, 52.98, 20.98, 20.95; HRMS (ESI) calcd for $C_{37}H_{34}NO$ $[M+H]^+$: 508.2635, found 508.2635.



(2S,3S)-3-(2,2-bis(4-chlorophenyl)vinyl)-1-(4-methoxyphenyl)-2-phenylindoline (**3k**): white solid, 99% yield (109 mg), mp 163-165 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.19 (m, 7H), 7.19-7.10 (m, 2H), 7.10-6.92 (m, 6H), 6.85-6.71 (m, 3H), 6.66 (d, J = 7.2 Hz, 1H), 6.46 (d, J = 7.6 Hz, 2H), 6.30 (d, J = 10.0 Hz, 1H), 4.96 (d, J = 10.0 Hz, 1H), 3.98 (dd, J = 10.0, 10.0 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.74, 150.86, 143.58, 140.73, 140.17, 137.36, 136.87, 133.96, 133.54, 131.19, 128.83, 128.73, 128.60, 128.32, 128.18, 128.03, 125.29, 124.36, 119.37, 114.73, 108.29, 76.64, 55.35, 53.16; HRMS (ESI) calcd for $C_{35}H_{28}Cl_2NO$ $[M+H]^+$: 548.1542, found 548.1542.



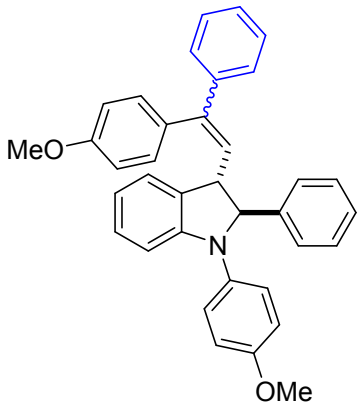
(2S,3S)-3-(2,2-di(naphthalen-2-yl)vinyl)-1-(4-methoxyphenyl)-2-phenylindoline (3l): white solid, 85% yield (99 mg), mp 123-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.70 (m, 3H), 7.69-7.52 (m, 4H), 7.49-7.37 (m, 5H), 7.37-7.24 (m, 5H), 7.15-7.01 (m, 4H), 6.97 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.84-6.71 (m, 3H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 10.4 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.19 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.61, 150.78, 145.58, 141.05, 139.42, 137.02, 136.85, 133.68, 133.38, 133.20, 132.79, 131.60, 128.93, 128.80, 128.59, 128.52, 128.42, 128.35, 128.28, 128.16, 128.12, 127.97, 127.87, 127.24, 126.58, 126.37, 126.21, 126.18, 125.53, 125.20, 124.62, 119.34, 114.69, 108.15, 76.72, 55.34, 53.17; HRMS (ESI) calcd for $C_{43}H_{33}NNaO$ $[M+Na]^+$: 602.2454, found 602.2460.



(2S,3S)-2-(4-bromophenyl)-3-(2,2-diphenylvinyl)-1-(p-tolyl)indoline (3m)

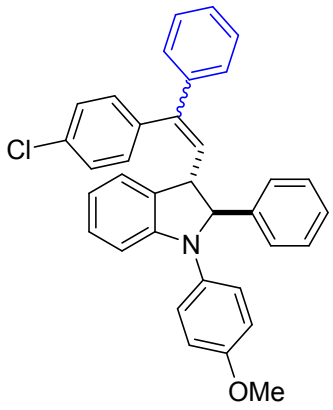
White solid, 75% yield (81 mg), mp 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.30-7.22 (m, 5H), 7.19-6.95 (m, 11H), 6.85-6.75 (m, 2H), 6.66 (d, *J* = 6.8 Hz, 2H), 6.29 (d, *J* = 10.4 Hz, 1H), 5.01 (d, *J* = 10.0 Hz, 1H), 3.98 (dd, *J* = 10.0, 10.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.76, 146.03,

141.84, 140.80, 140.22, 139.34, 133.49, 131.92, 131.67, 130.11, 129.77, 129.63, 128.62, 128.49, 128.42, 127.94, 127.59, 127.38, 126.91, 124.67, 122.71, 121.52, 119.72, 108.22, 75.11, 53.02, 20.72; HRMS (ESI) calcd for $C_{35}H_{29}BrN$ $[M+H]^+$: 542.1478, found 542.1473.

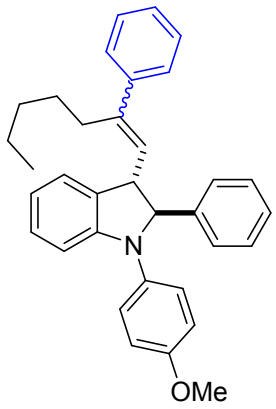


(2S,3S)-1-(4-methoxyphenyl)-3-(2-(4-methoxyphenyl)-2-phenylvinyl)-2-phenylindoline (3n): white solid, 91% yield (1.2/1.0, 93 mg), mp 65-68 °C; ^{1}H NMR (400 MHz, $CDCl_3$): major isomer: δ 7.35-7.15 (m, 9H), 7.14-7.00 (m, 5H), 6.84-6.72 (m, 4H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.62-6.54 (m, 2H), 6.21 (d, *J* = 10.4 Hz, 1H), 4.97 (d, *J* = 10.4 Hz, 1H), 3.98 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H); minor isomer: 6.50 (d, *J* = 8.4 Hz, 2H), 6.27 (d, *J* = 10.4 Hz, 1H), 4.98 (d, *J* = 10.0 Hz, 1H), 4.07 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H) other peaks are overlapped with the signals of the major isomer; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.65, 158.99, 156.58, 156.56, 150.78, 150.74, 145.32, 145.13, 142.56, 141.01, 140.96, 139.70, 137.09, 134.79, 131.94, 131.85, 131.04, 129.86, 128.75, 128.71, 128.54, 128.33, 128.30, 128.22, 128.20, 127.82, 127.78, 127.75, 127.71, 127.31, 127.13, 125.55, 125.16, 125.12, 124.58, 119.28, 114.68, 113.88, 113.71, 108.09,

108.06, 76.78, 76.74, 55.36, 55.20, 53.06, 53.02; HRMS (ESI) calcd for $C_{36}H_{32}NO_2$ $[M+H]^+$: 510.2428, found 510.2439.

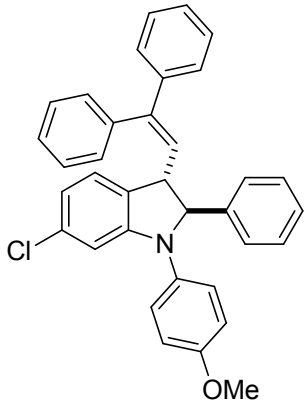


(2S,3S)-3-(2-(4-chlorophenyl)-2-phenylvinyl)-1-(4-methoxyphenyl)-2-phenylindoline (3o): white solid, 82% yield (1.2/1.0, 84 mg), mp 96-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): major isomer: δ 7.35-7.12 (m, 10H), 7.11-6.95 (m, 6H), 6.83-6.70 (m, 3H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 7.2 Hz, 2H), 6.28 (d, *J* = 10.4 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 4.20-3.80 (m, 1H), 3.72 (s, 3H); minor isomer: 6.66 (d, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 8.4 Hz, 2H), 6.32 (d, *J* = 10.0 Hz, 1H) other peaks are overlapped with the signals of the major isomer; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.69, 156.63, 150.87, 150.76, 144.68, 144.62, 141.70, 140.82, 140.79, 140.60, 138.95, 137.87, 136.97, 136.93, 133.69, 133.27, 131.48, 131.39, 131.27, 129.80, 128.88, 128.84, 128.78, 128.71, 128.68, 128.59, 128.51, 128.46, 128.22, 128.15, 128.04, 127.97, 127.89, 127.86, 127.78, 127.61, 127.46, 125.29, 125.14, 124.53, 124.41, 119.32, 114.70, 108.20, 76.68, 76.56, 55.36, 53.17, 53.03; HRMS (ESI) calcd for $C_{35}H_{29}ClNO$ $[M+H]^+$: 514.1932, found 514.1934.



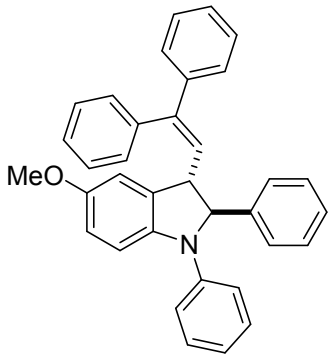
(2S,3S)-1-(4-methoxyphenyl)-2-phenyl-3-(2-phenylhept-1-en-1-yl)indoline (3p)

Yellow oil, 86% yield (1.6/1.0, 81 mg); ^{1}H NMR (400 MHz, $CDCl_3$): major isomer: δ 7.50-7.35 (m, 2H), 7.35-7.15 (m, 7H), 7.12-6.95 (m, 5H), 6.82-6.70 (m, 3H), 6.50 (d, *J* = 7.2 Hz, 1H), 5.88 (d, *J* = 10.0 Hz, 1H), 4.90 (d, *J* = 9.6 Hz, 1H), 4.29 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.71 (s, 3H), 2.50-2.20 (m, 2H), 1.35-1.20 (m, 2H), 1.20-0.90 (m, 2H), 0.90-0.80 (m, 2H), 0.72 (t, *J* = 6.8 Hz, 3H); minor isomer: 6.64 (d, *J* = 8.0 Hz, 1H), 5.60 (d, *J* = 10.0 Hz, 1H), 4.85 (d, *J* = 10.4 Hz, 1H), 3.83 (dd, *J* = 10.4, 10.4 Hz, 1H), 3.70 (s, 3H), 2.90-2.50 (m, 2H) other peaks are overlapped with the signals of the major isomer; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.53, 156.46, 150.98, 150.68, 146.34, 144.35, 143.18, 141.59, 141.09, 140.85, 137.20, 132.22, 131.90, 128.76, 128.60, 128.37, 128.30, 128.14, 128.12, 127.79, 127.70, 127.35, 126.88, 126.63, 125.30, 125.01, 124.53, 124.39, 119.36, 119.17, 114.69, 114.62, 108.17, 107.92, 76.84, 76.76, 55.35, 55.34, 52.19, 52.10, 39.36, 31.58, 31.10, 29.82, 28.64, 27.21, 22.36, 22.19, 14.00, 13.82; HRMS (ESI) calcd for $C_{34}H_{36}NO$ $[M+H]^+$: 474.2791, found 474.2798.



(2S,3S)-6-chloro-3-(2,2-diphenylvinyl)-1-(4-methoxyphenyl)-2-phenylindoline

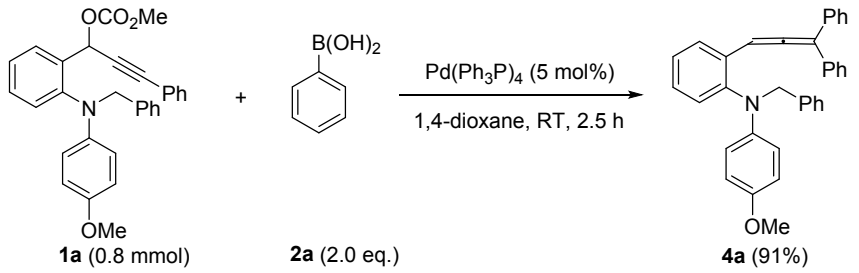
(3q) White solid, 96% yield (99 mg), mp 75-77 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.20 (m, 10H), 7.16-7.11 (m, 1H), 7.10-6.98 (m, 4H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.63-6.50 (m, 3H), 6.25 (d, *J* = 10.0 Hz, 1H), 5.00 (d, *J* = 10.0 Hz, 1H), 3.97 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.86, 151.85, 145.89, 141.77, 140.19, 139.10, 135.94, 134.04, 130.11, 129.65, 128.66, 128.45, 128.27, 127.97, 127.87, 127.78, 127.47, 127.17, 126.59, 125.22, 125.05, 118.75, 114.71, 108.13, 77.0, 55.22, 52.27; HRMS (ESI) calcd for $C_{35}H_{29}ClNO$ $[M+H]^+$: 514.1932, found 514.1930.



(2S,3S)-3-(2,2-diphenylvinyl)-5-methoxy-1,2-diphenylindoline (3r)

White solid, 48% yield (65 mg), mp 203-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.02 (m, 18H), 6.98-6.85 (m, 2H), 6.70-6.60 (m, 3H), 6.29 (d, *J* = 10.0 Hz, 1H), 5.05 (d, *J* = 8.8 Hz, 1H), 3.96 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.22, 145.23, 144.06, 142.79, 141.81, 140.97, 139.28, 133.59, 129.73, 129.16, 128.71, 128.43, 128.33, 127.71, 127.59, 127.47, 127.44, 127.17, 122.36, 120.98, 112.12, 112.03, 108.57, 75.27, 55.89, 52.81; HRMS (ESI) calcd for $C_{35}H_{30}NO$ $[M+H]^+$: 480.2322, found 480.2320.

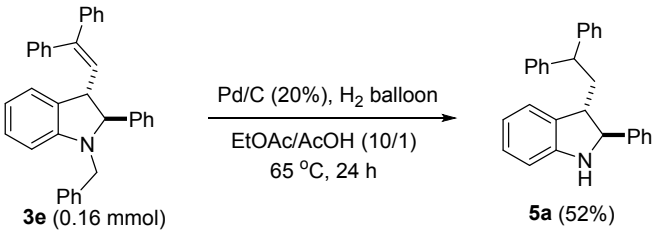
Synthesis and characterization of 4a.



To a solution of **1a** (382.0 mg, 0.8 mmol) in 1,4-dioxane (15 mL; THF also worked well) in Schlenk tube was added **2a** (195.0 mg, 2.0 eq.) and $Pd(Ph_3P)_4$ (46.2 mg, 0.05 eq.) at room temperature under nitrogen. 2.5 h latter, the solution was concentrated under reduced pressure directly. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/Et_3N = 120/3/1 as the eluent afforded the allene **4a**. Yellow solid, 91% yield, mp 58-60 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.48 (d, *J* = 7.2 Hz, 1H), 7.40-7.25 (m, 12H), 7.25-7.16 (m, 6H), 6.87 (s, 1H), 6.76 (d, *J* = 9.2 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 4.85 (s, 2H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 208.72, 152.89, 145.67, 143.76, 139.51, 135.81, 131.26, 129.48, 129.13, 128.80, 128.61, 128.38, 128.14, 127.69, 127.21,

126.42, 117.42, 114.86, 112.82, 94.31, 56.63, 55.29; HRMS (ESI) calcd for $C_{35}H_{30}NO$ $[M+H]^+$: 480.2322, found 480.2320.

Synthesis and characterization of 5a.



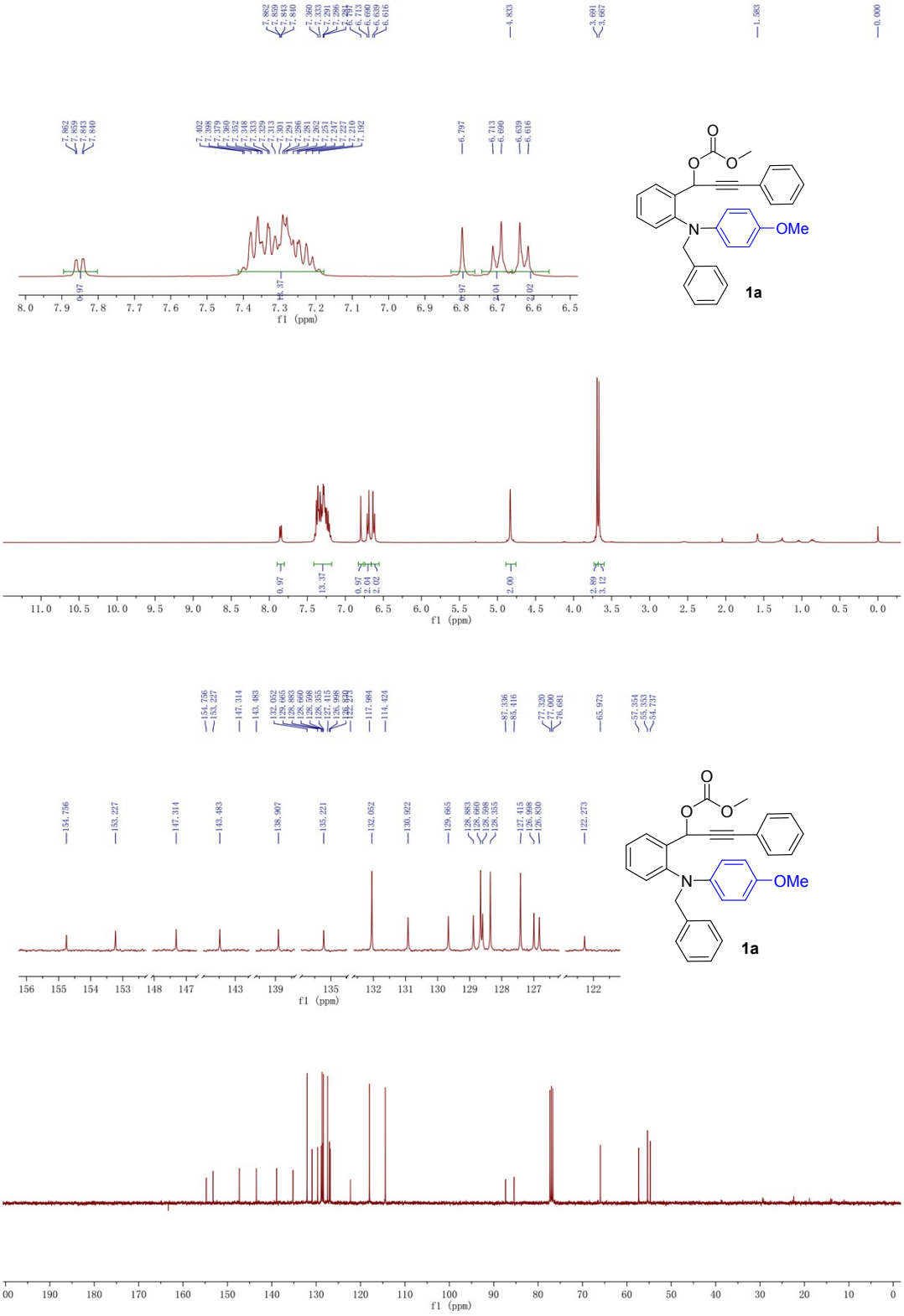
3e (0.16 mmol) **5a** (52%)

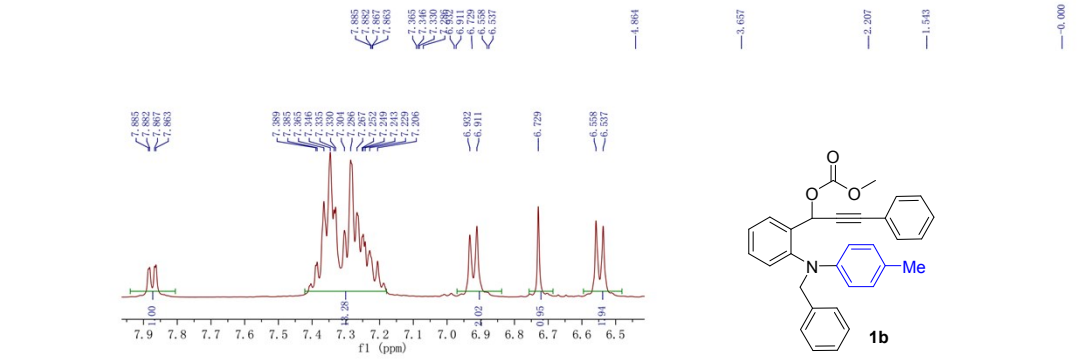
A mixture of **3e** (74.2 mg, 0.16 mmol), EtOAc/AcOH (0.55 mL; 10/1) and Pd/C (15.0 mg, 20%) in Schlenk tube was purged three times with hydrogen gas and stirred at 65 °C under an atmosphere of hydrogen (balloon). After 24 hours**,** the reaction was cooled to room temperature and filtered to remove Pd/C. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 20/1 as the eluent afforded **5a**. Colorless oil, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.05 (m, 15H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.80-6.70 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.56 (d, *J* = 7.6 Hz, 1H), 4.26-3.90 (m, 2H), 3.24-3.05 (m, 1H), 2.70-2.55 (m, 1H), 2.50-2.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.59, 144.69, 144.51, 144.30, 132.03, 128.78, 128.69, 128.63, 128.13, 128.01, 127.96, 127.89, 127.29, 126.36, 124.04, 118.92, 108.88, 70.84, 48.68, 48.46, 40.67; HRMS (ESI) calcd for $C_{28}H_{26}N$ $[M+H]^+$: 376.2060, found 376.2064.

References

1. X. Pang, Z. Lou, M. Li, L. Wen, C. Chen, *Eur. J. Org. Chem.*, 2015, 3361-3369.
2. L. Munoz, M. E. Kavanagh, A. F. Phoa, B. Heng, N. Dzamko, E.-J. Chen, M. R. Doddareddy, G. J. Guillemin, M. Kassiou, *Eur. J. Med. Chem.*, 2015, **95**, 29-34.

NMR spectra of new compounds (1)

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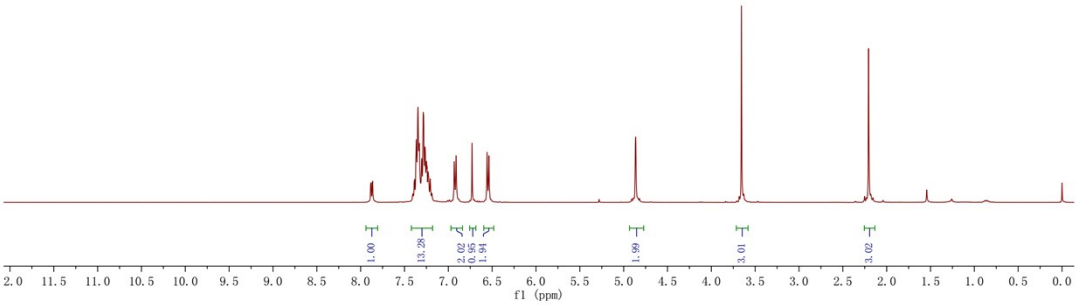
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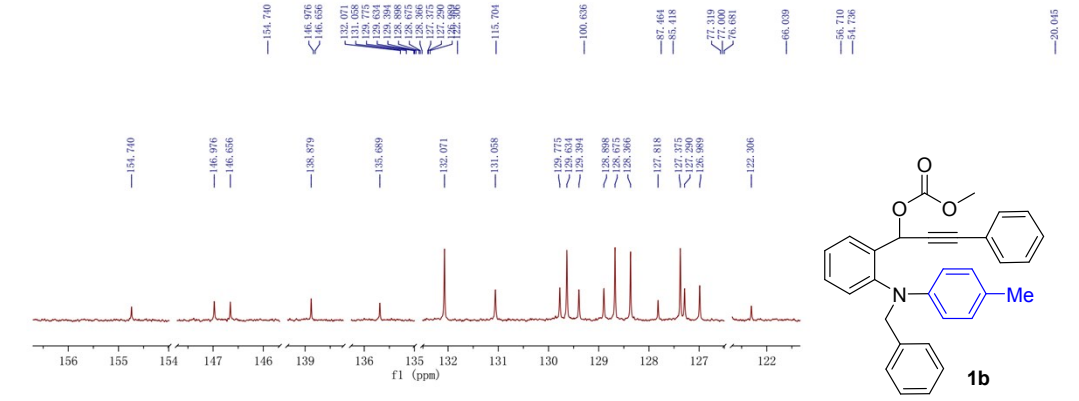
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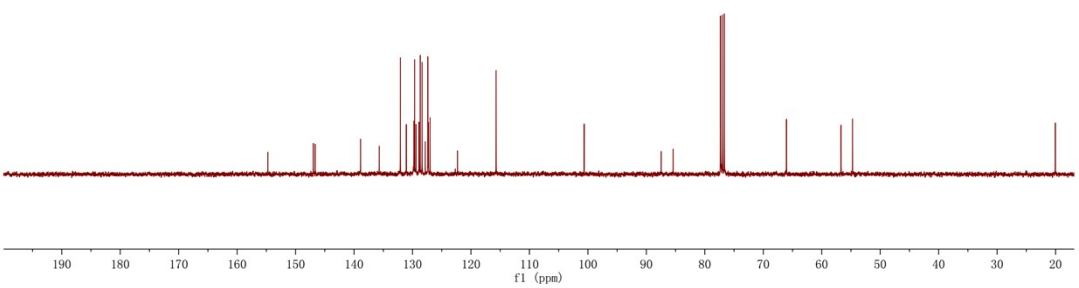
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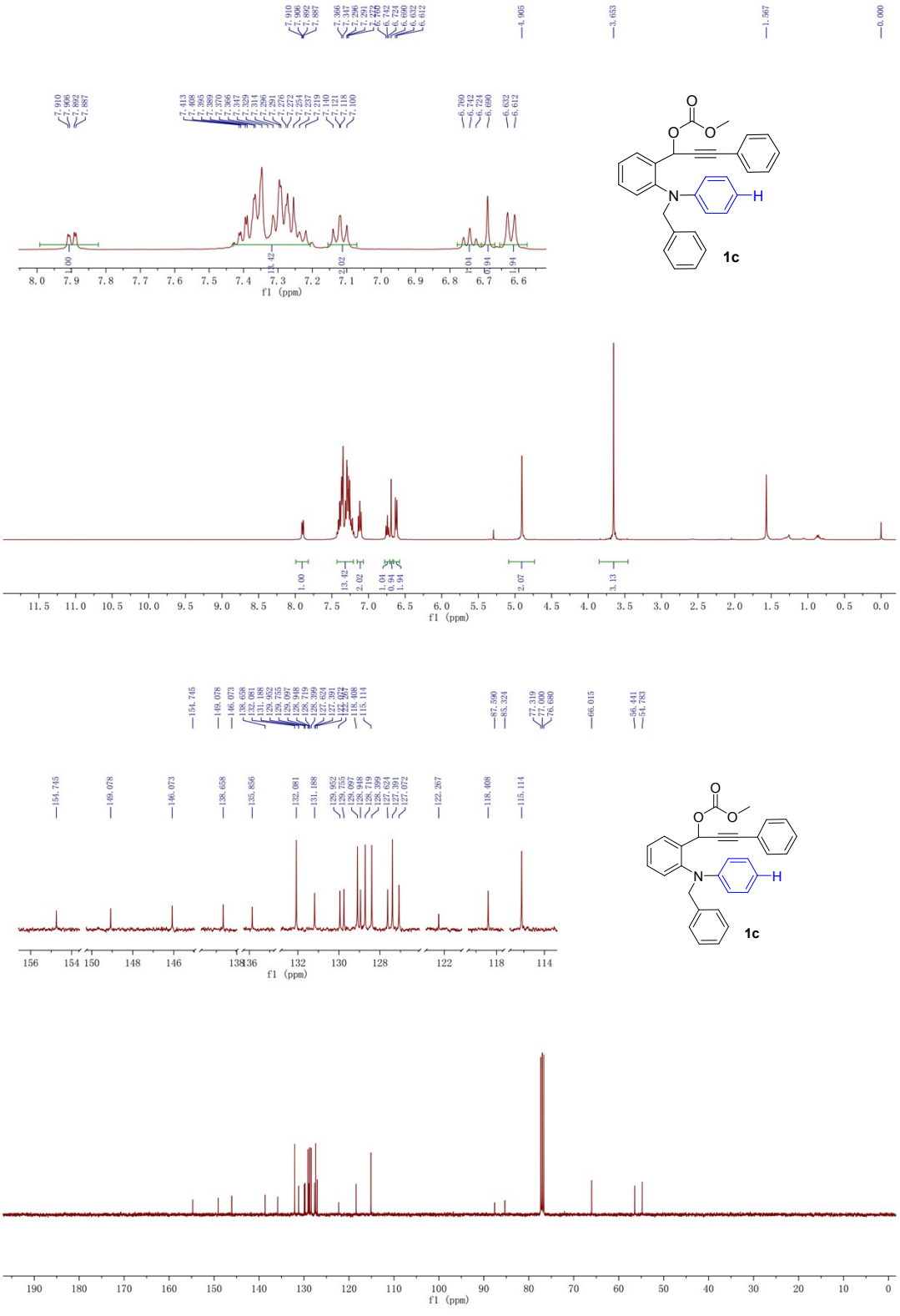
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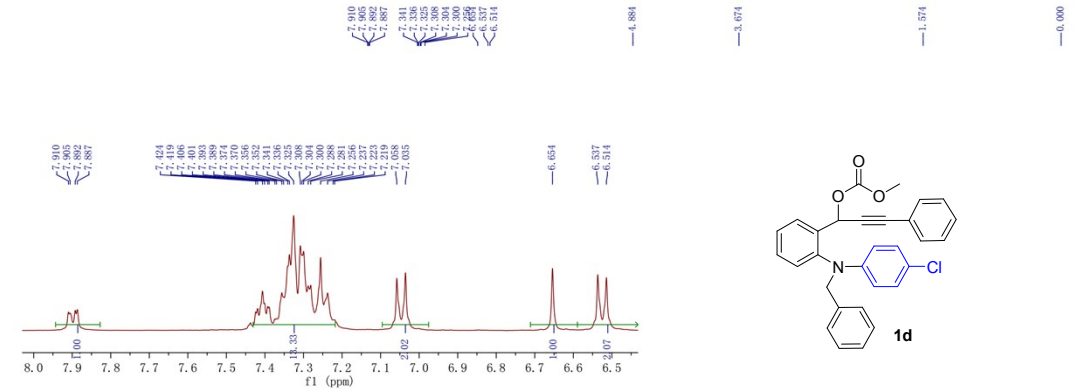
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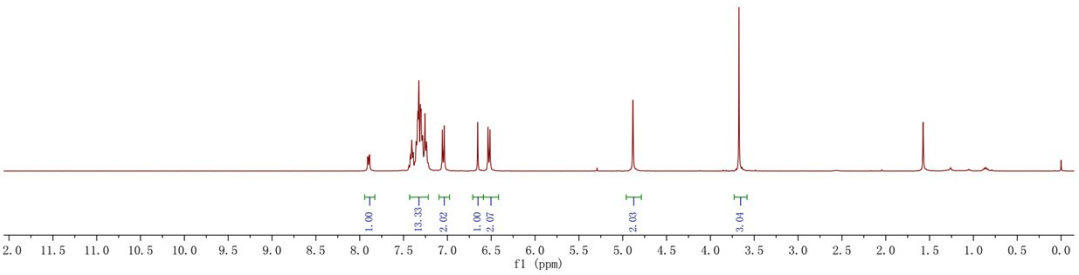
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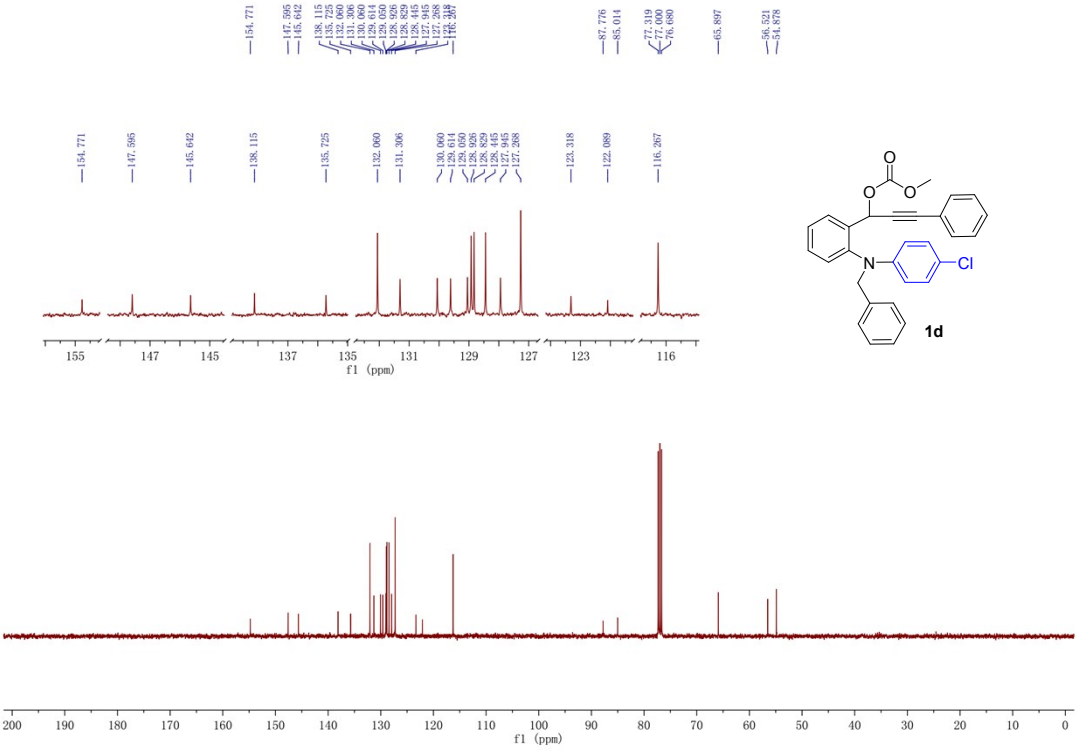
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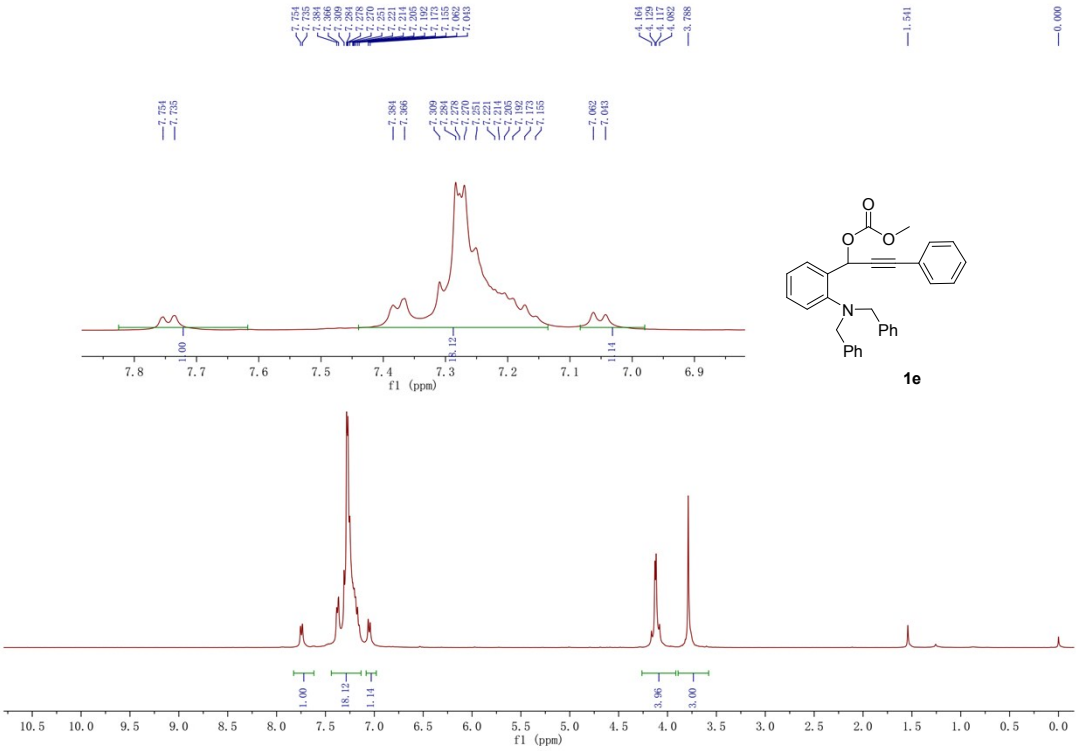
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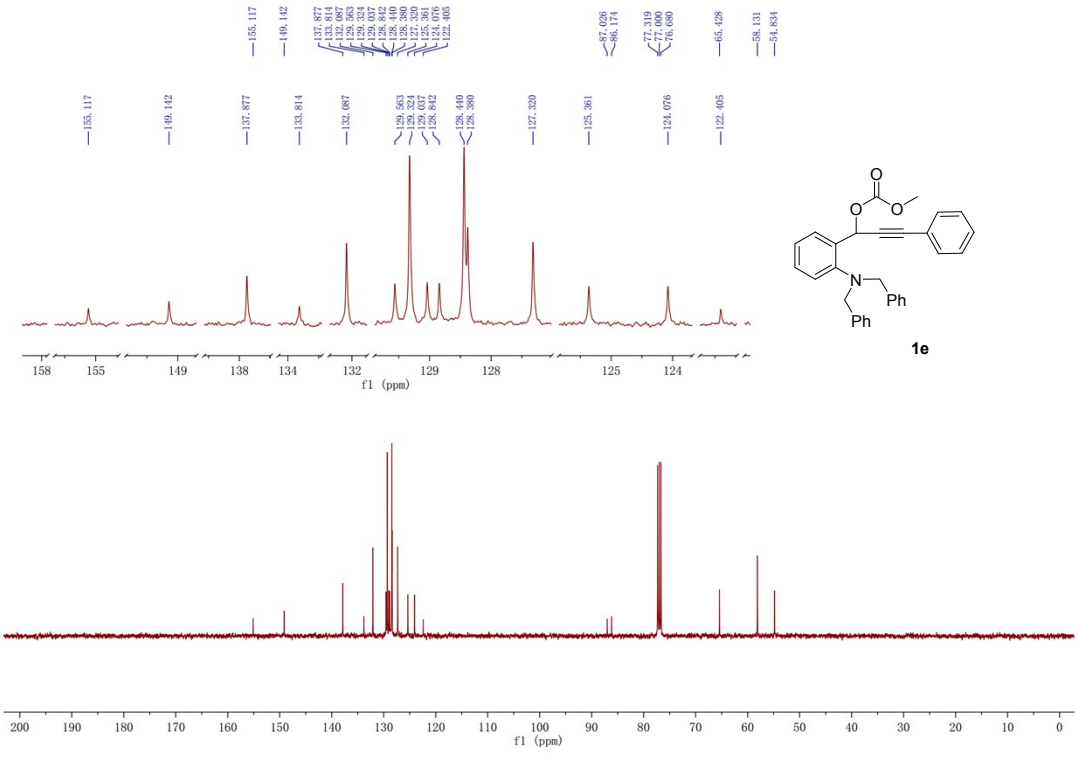
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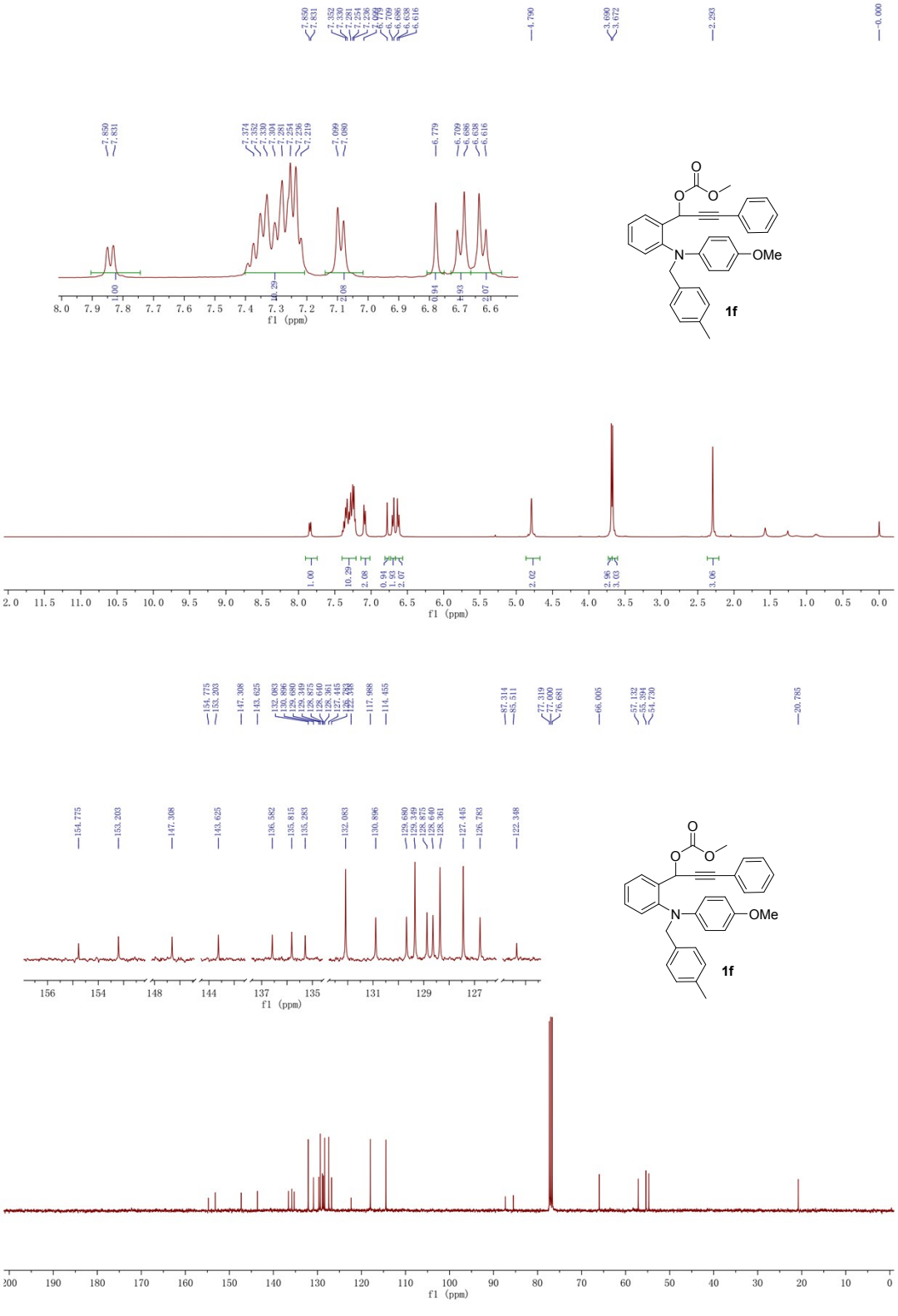
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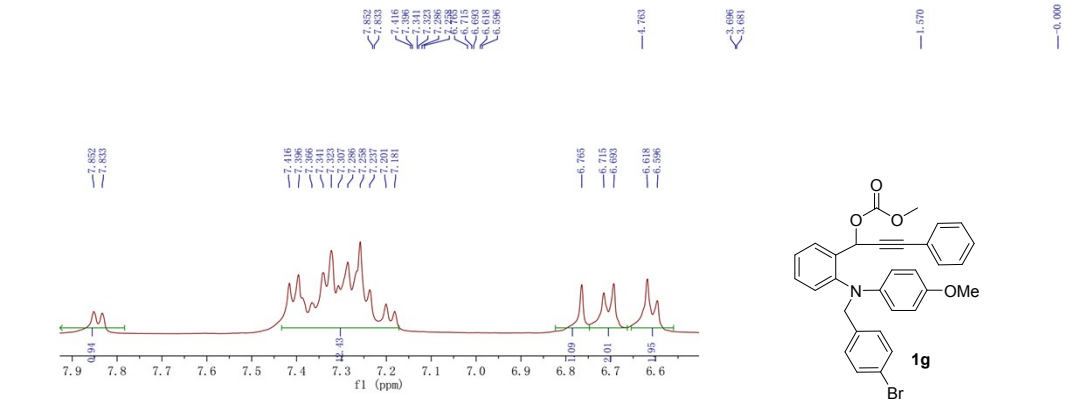
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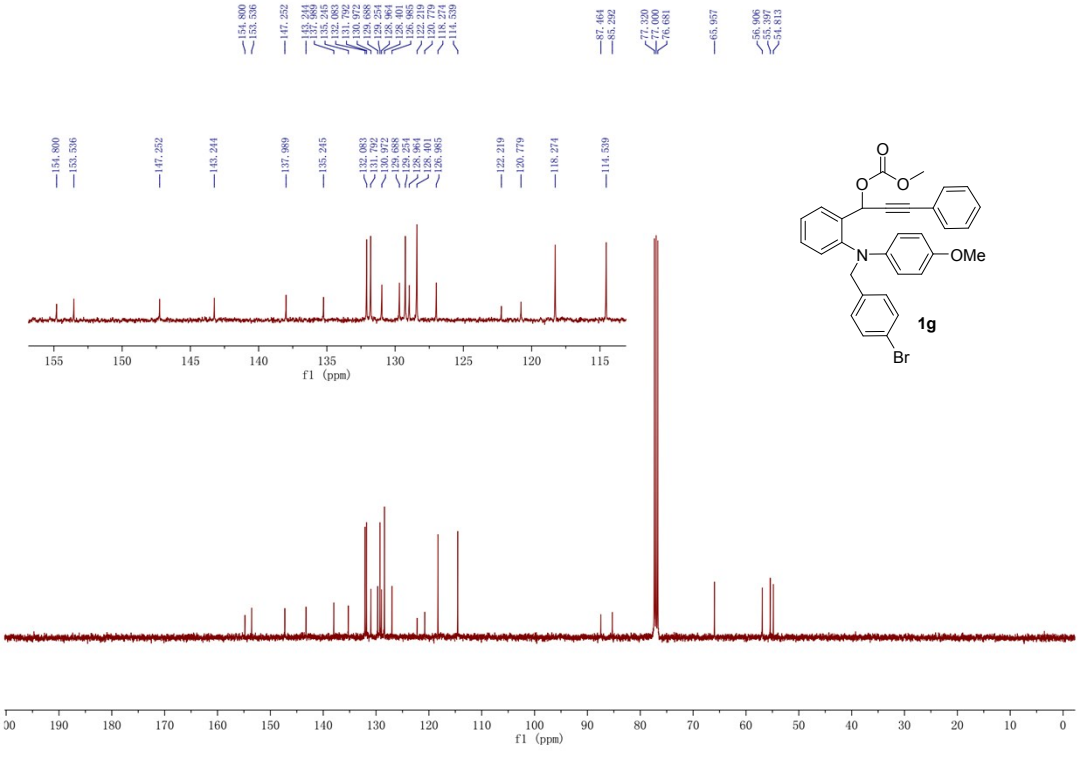
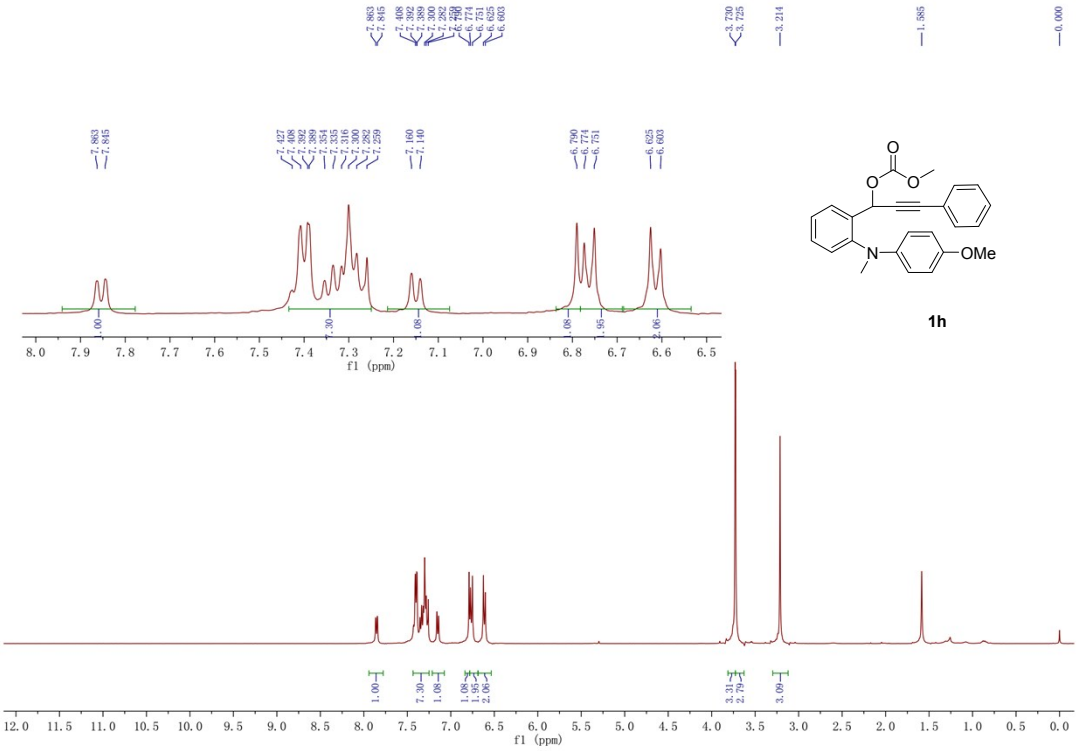
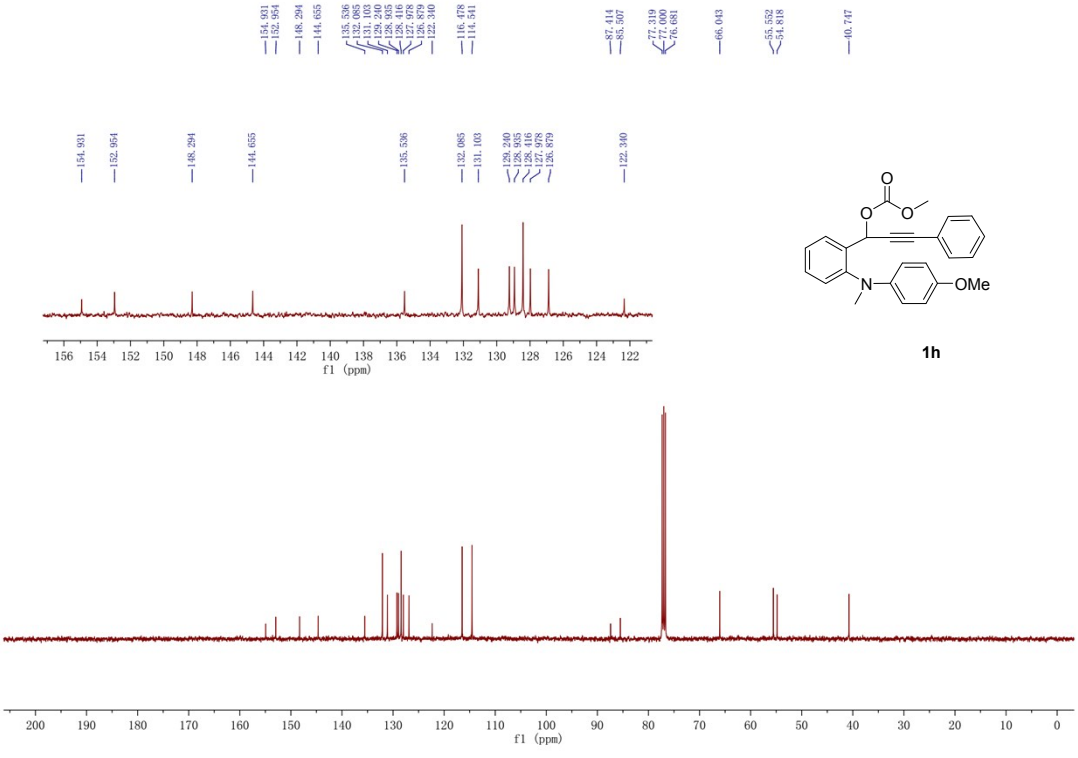
3.681
1.570
0.000
0.94
12.43
1.09
2.01
1.95
2.00
3.41
2.78
f1 (ppm)
OMe
1g
Br

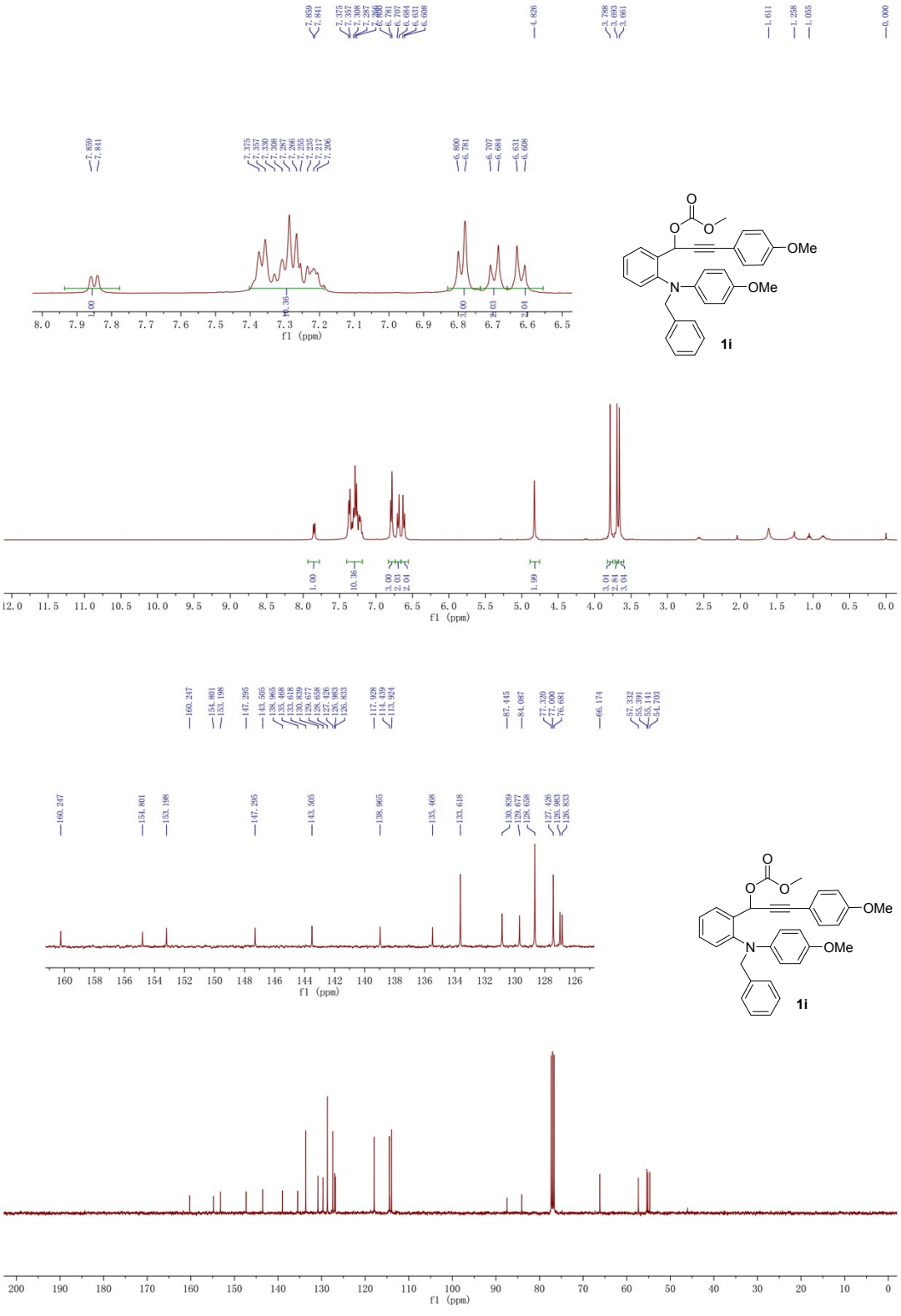

154.800
153.536
147.252
143.244
137.989
135.245
132.063
131.792
130.972
129.688
129.254
128.964
128.401
126.985
122.219
120.779
118.274
114.539
87.464
85.292
77.320
77.000
76.681
65.957
56.906
55.397
54.813
f1 (ppm)
OMe
1g
Br

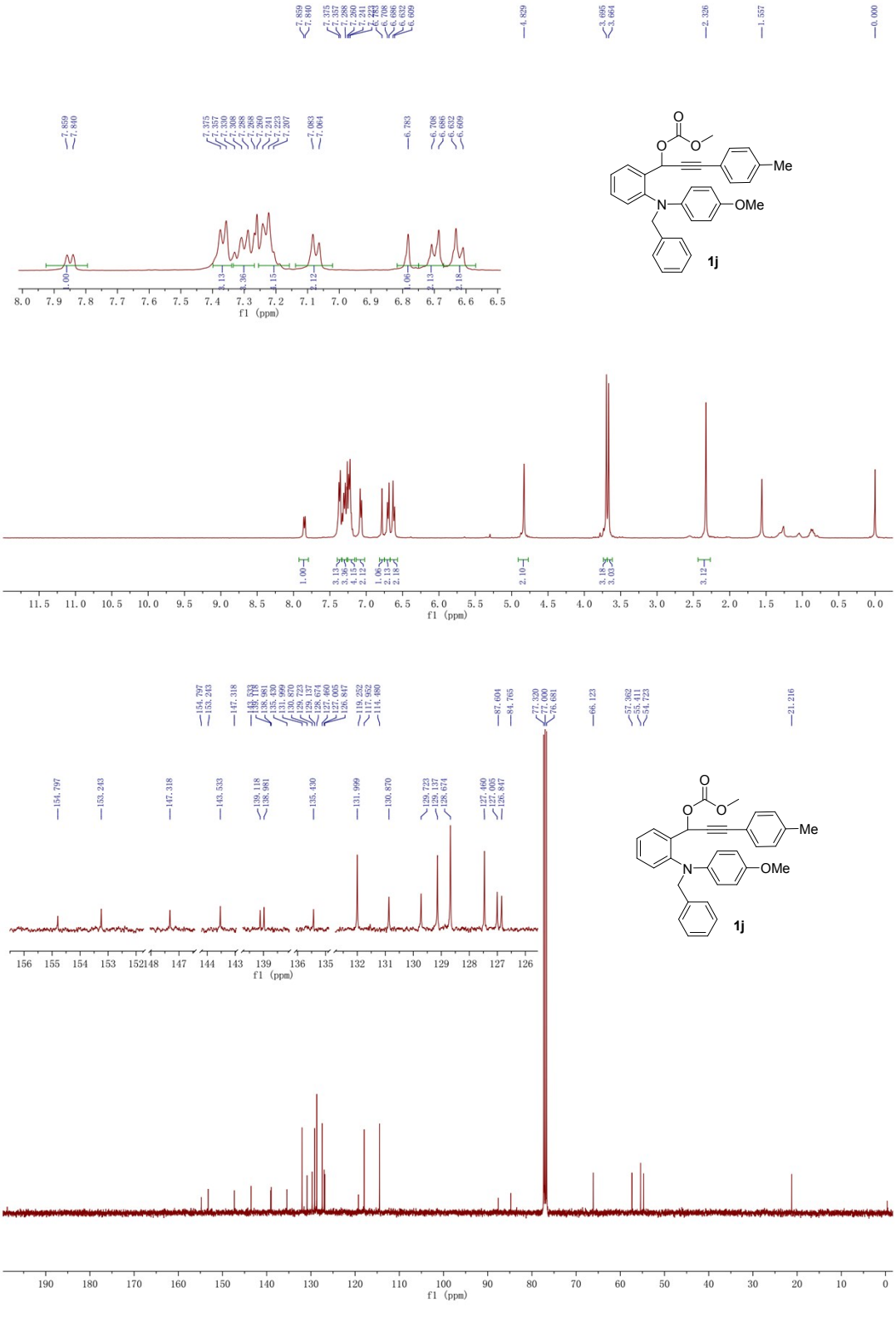

7.863
7.845
7.427
7.408
7.392
7.389
7.354
7.335
7.316
7.300
7.282
7.259
7.160
7.140
6.790
6.774
6.751
6.625
6.603
3.730
3.725
3.214
1.585
0.000
1.00
7.30
1.08
1.08
1.95
2.06
3.31
2.79
3.09
f1 (ppm)
O
O
O
N
OMe

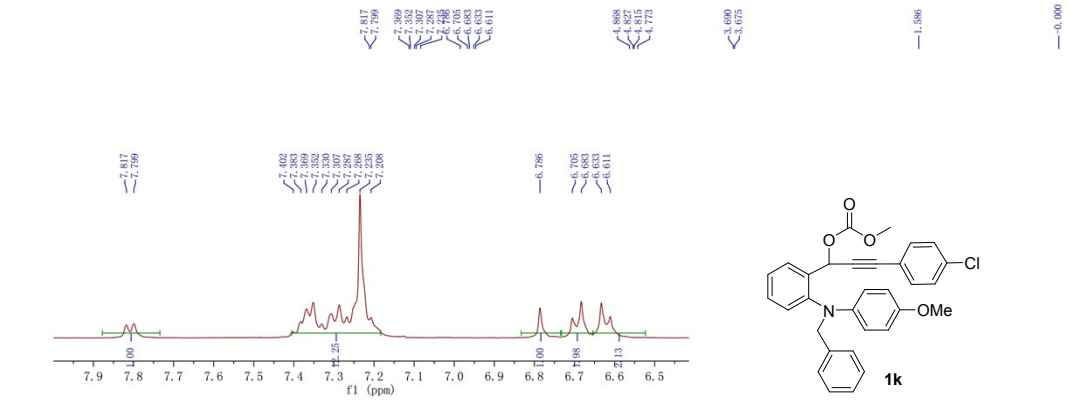
1h

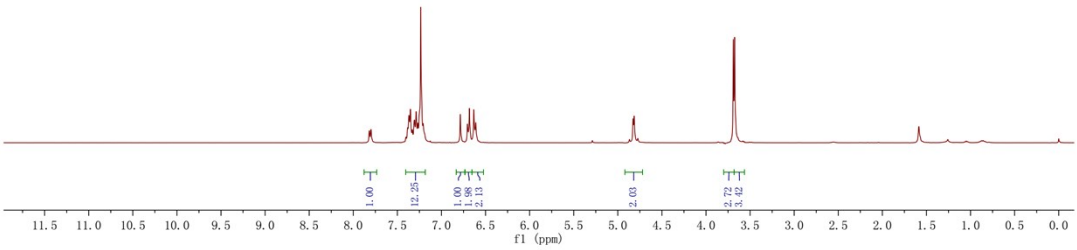

154.931
152.954
148.294
144.655
135.536
132.085
131.103
129.240
128.935
128.416
127.978
126.879
122.340
116.478
114.541
87.414
85.507
77.319
77.000
76.681
68.043
55.552
54.818
40.747
f1 (ppm)
O
O
O
N
OMe

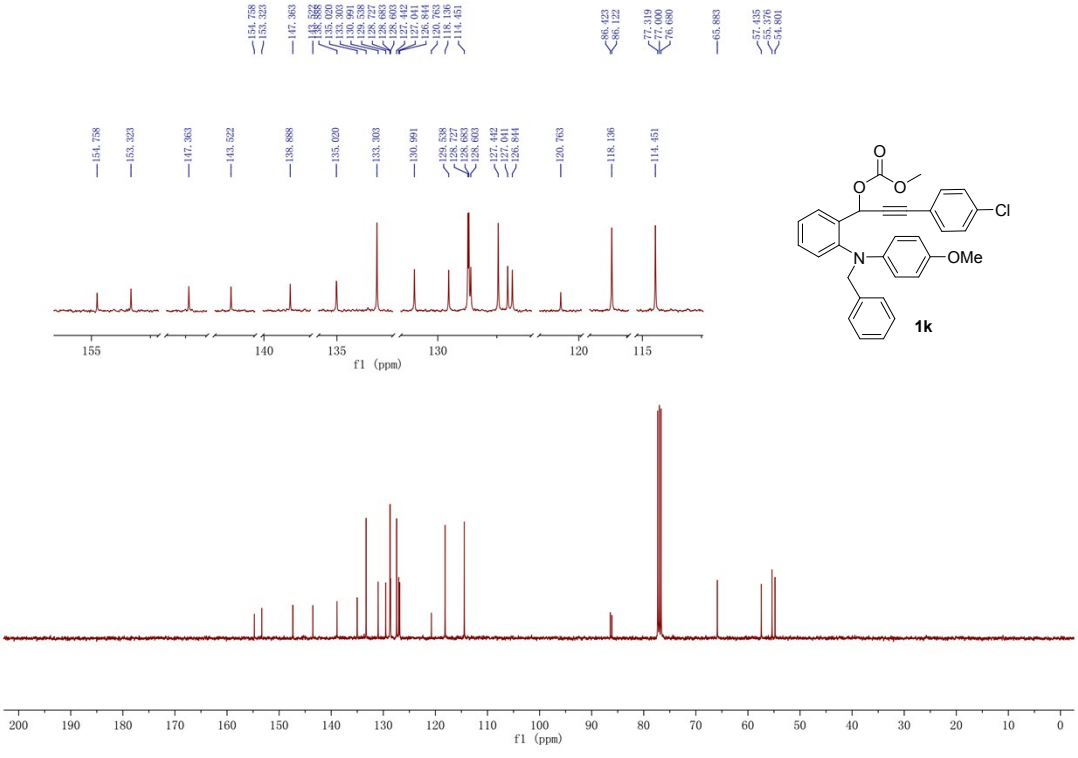
1h

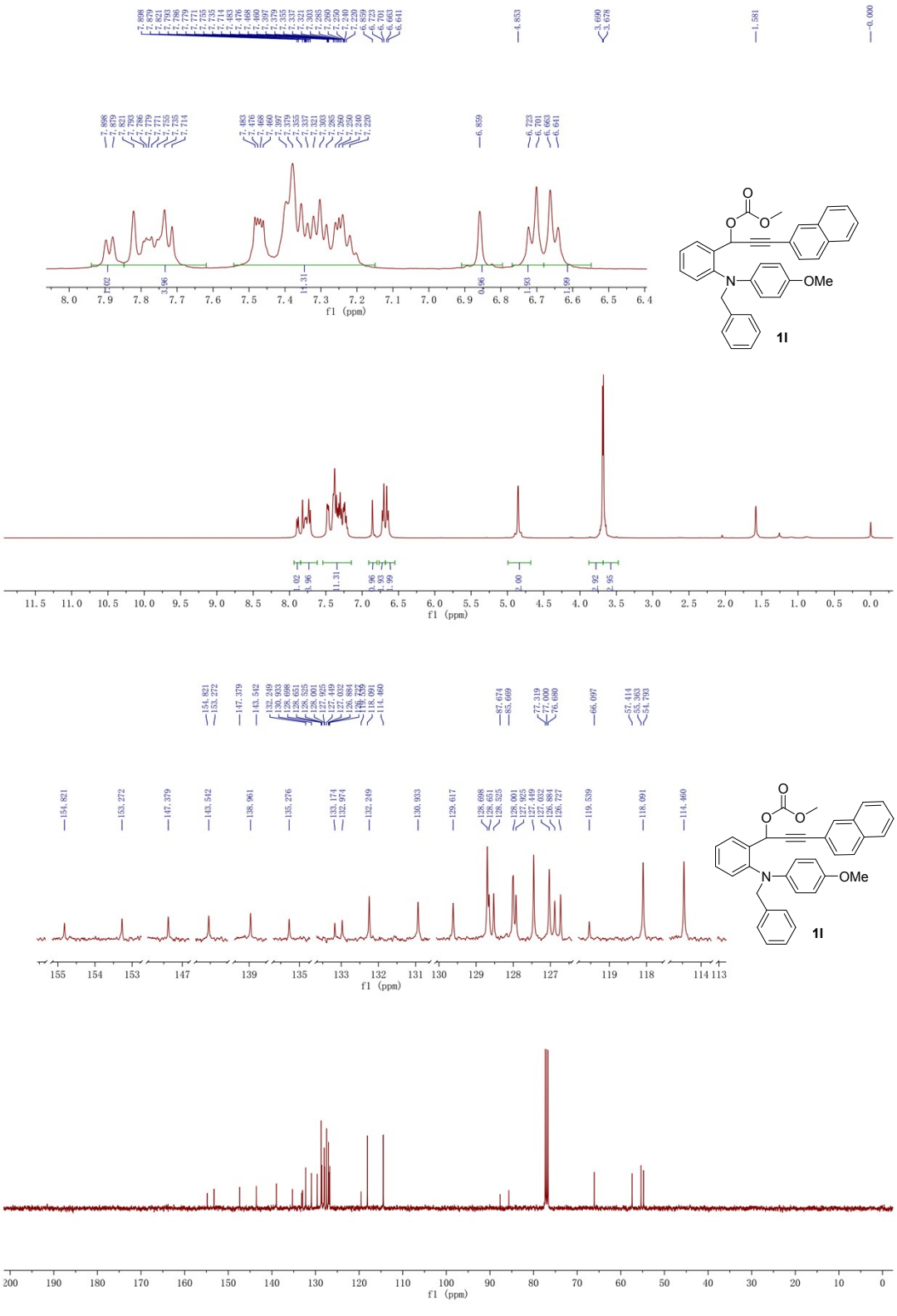

7.859
7.841
7.375
7.357
7.339
7.308
7.287
7.266
7.255
7.235
7.217
7.206
6.800
6.781
6.707
6.684
6.631
6.608
4.826
3.788
3.693
3.661
1.611
1.258
1.055
0.000
1.00
10.36
3.00
2.03
2.04
1.99
3.04
2.84
3.04
f1 (ppm)
OMe
OMe
1i
160.247
154.801
153.198
147.295
143.505
138.965
135.468
132.618
130.839
129.677
128.658
127.426
126.983
126.833
117.928
114.039
113.924
87.445
84.087
77.320
77.000
76.681
68.174
57.332
55.391
55.141
54.703
f1 (ppm)
OMe
OMe
1i
f1 (ppm)

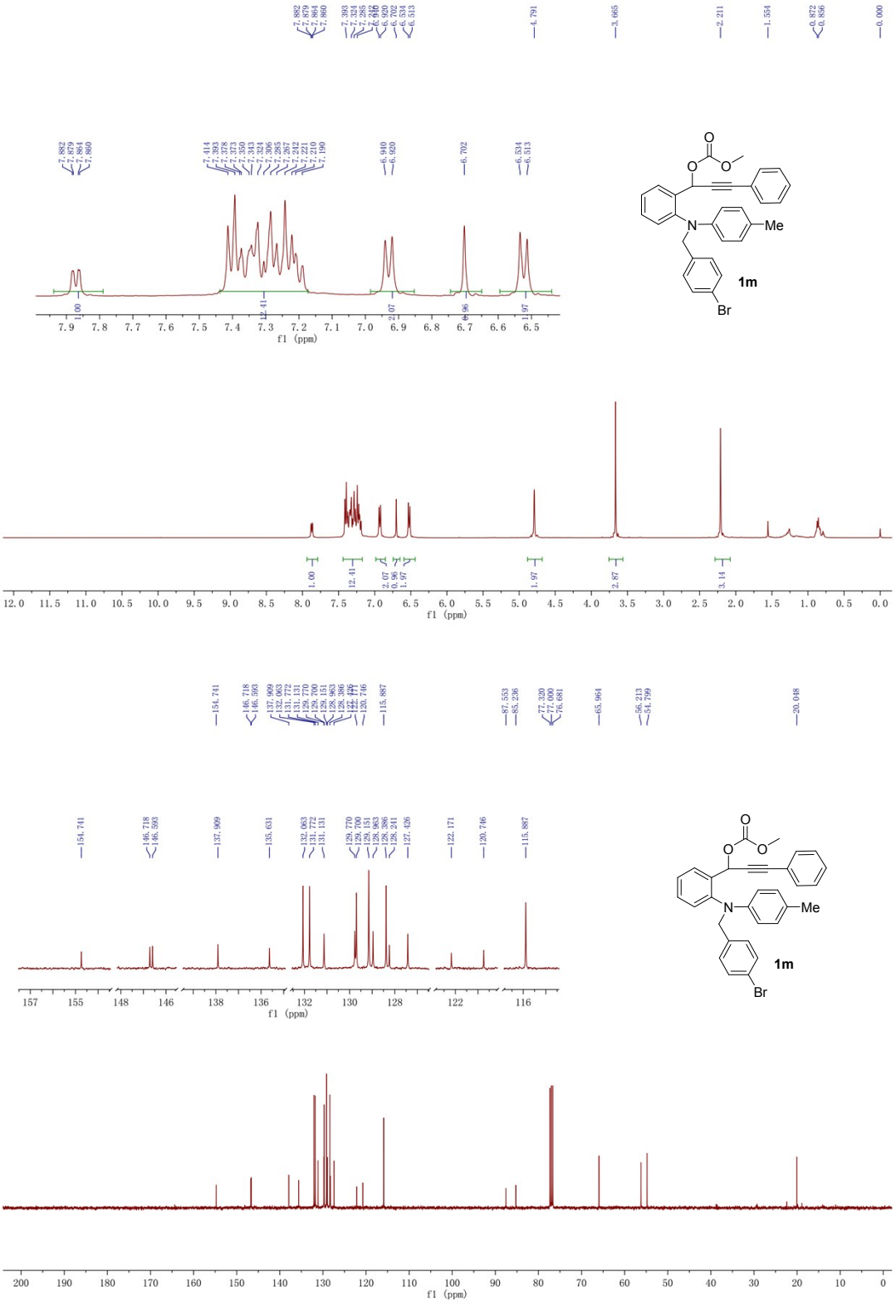

7.859
7.840
7.375
7.357
7.330
7.308
7.288
7.260
7.241
7.223
7.207
7.083
7.064
6.783
6.708
6.686
6.632
6.609
4.829
3.695
3.664
2.326
1.557
0.000
O
O
O
Me
N
OMe
1j
f1 (ppm)
154.797
153.243
147.318
143.533
139.118
138.981
135.430
131.999
130.870
129.723
129.137
128.674
127.460
127.005
126.847
119.252
117.252
114.480
87.604
84.765
77.320
77.000
76.681
66.123
57.362
55.411
54.723
21.216

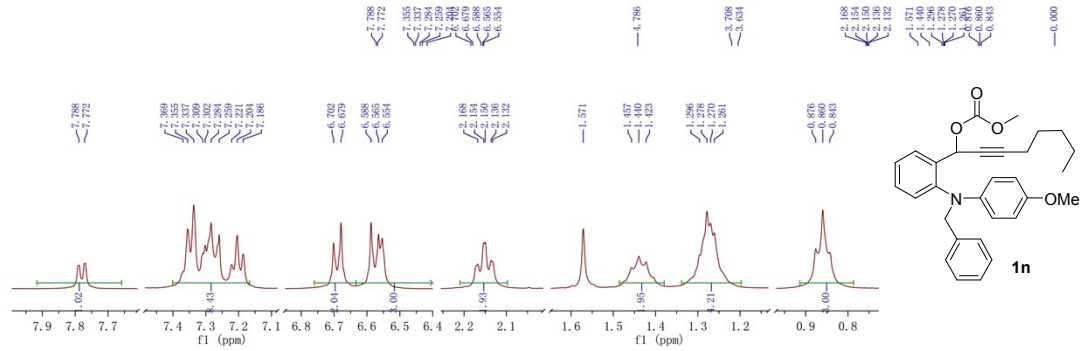

7.817
7.799
7.402
7.383
7.369
7.352
7.330
7.307
7.297
7.288
7.235
7.208
6.786
6.705
6.683
6.633
6.611
1.00
2.25
1.00
1.98
2.13
f1 (ppm)
O
O
O
Cl
N
OMe
1k

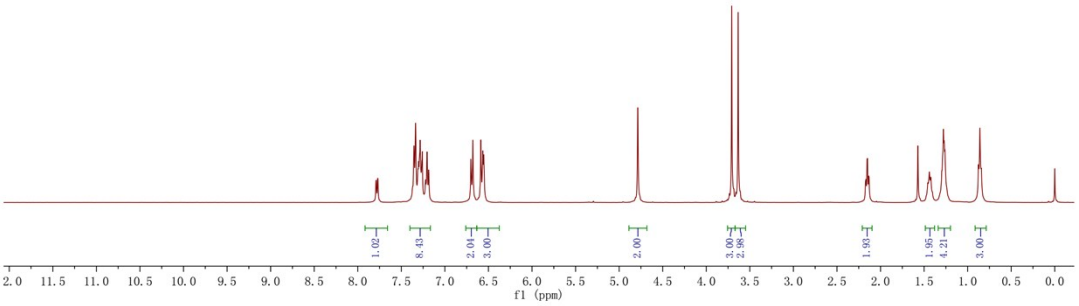

1.00
12.25
1.00
1.98
2.13
2.03
2.72
3.42
f1 (ppm)

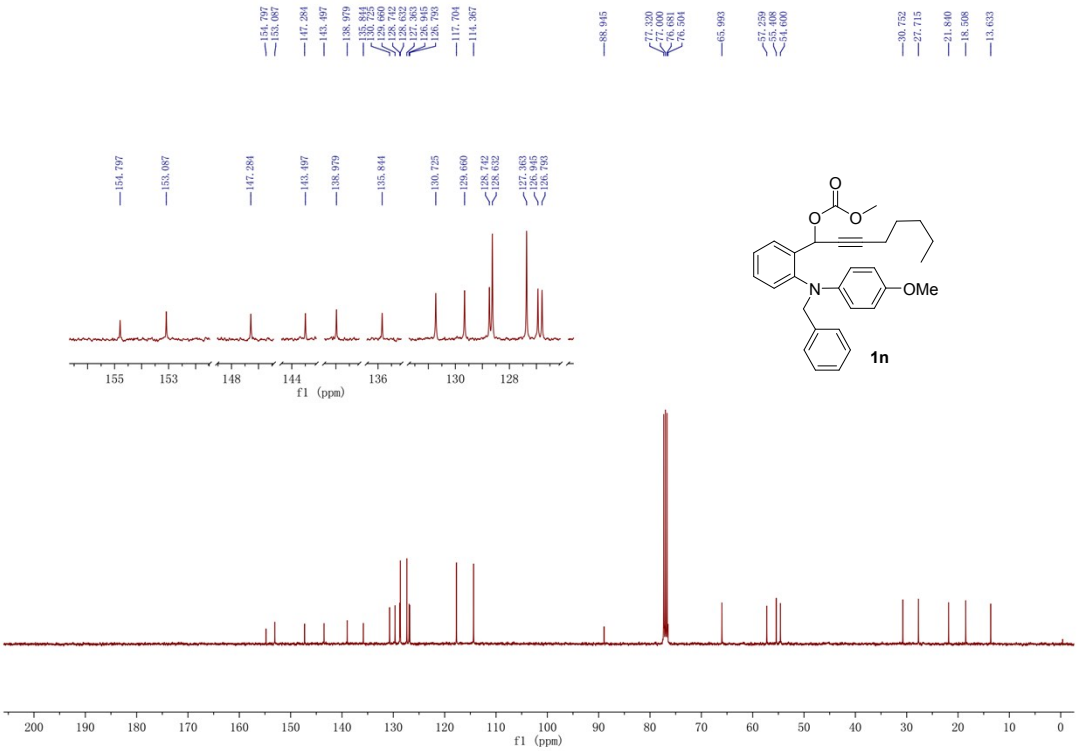

154.738
153.323
147.363
143.522
138.888
135.020
133.303
130.991
129.538
128.727
128.683
128.603
127.442
127.041
126.844
120.763
118.136
114.451
88.423
86.122
77.319
77.000
76.680
65.883
57.435
55.576
54.801
155
140
135
130
120
115
f1 (ppm)
O
O
O
Cl
N
OMe
1k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

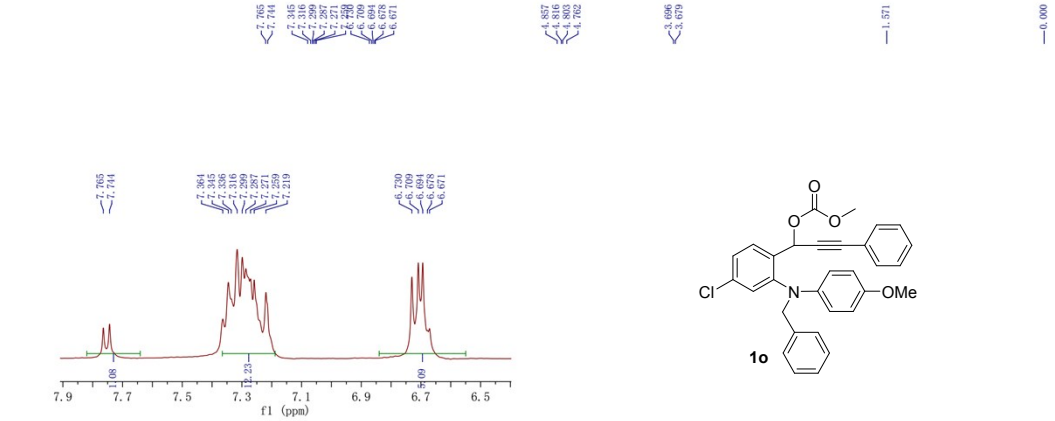

1l
f1 (ppm)

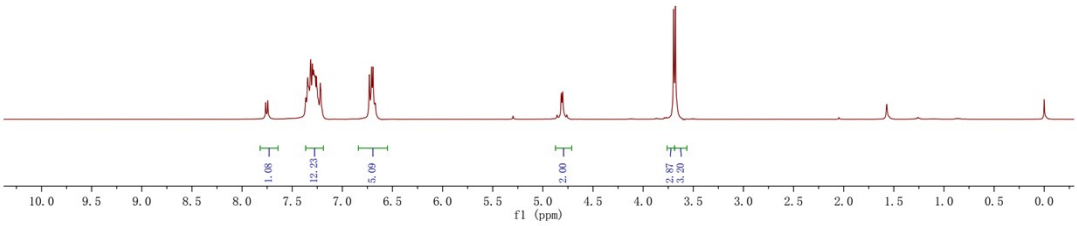

1m
Br
Me
f1 (ppm)

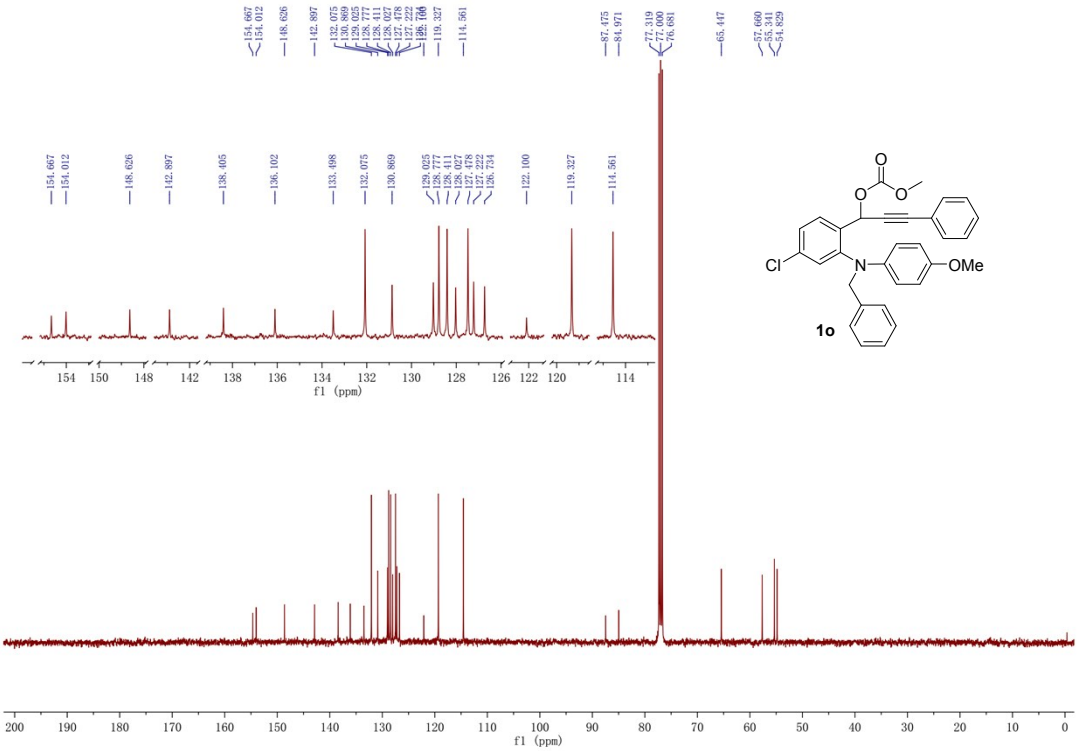

1n
f1 (ppm)

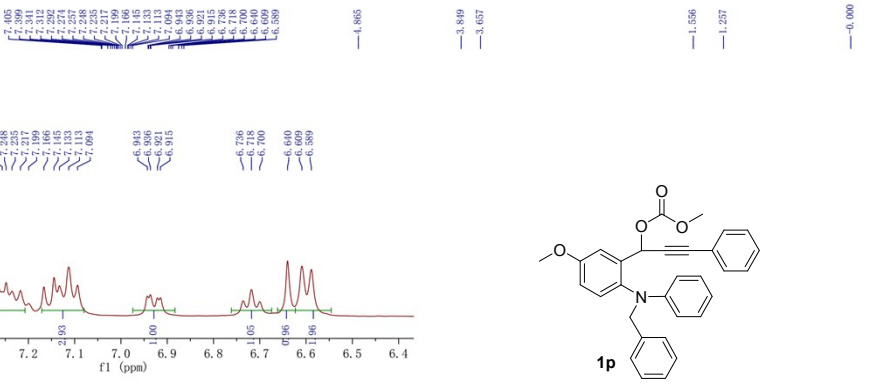

f1 (ppm)


1n
f1 (ppm)
f1 (ppm)

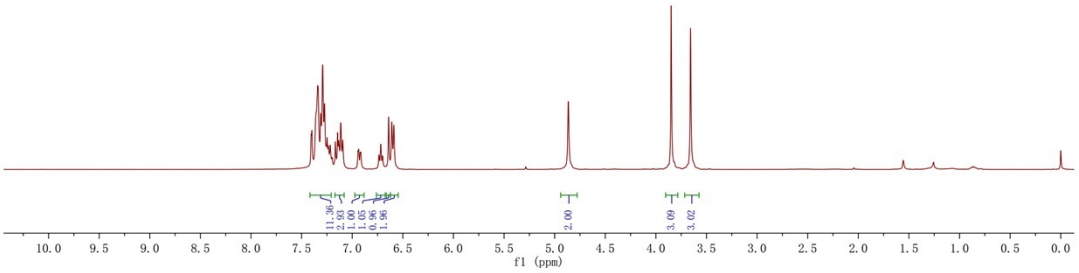

7.765
7.744
7.364
7.345
7.336
7.316
7.299
7.287
7.271
7.259
7.219
6.730
6.709
6.694
6.678
6.671
1.08
12.23
5.09
f1 (ppm)
Cl
N
OMe
1o

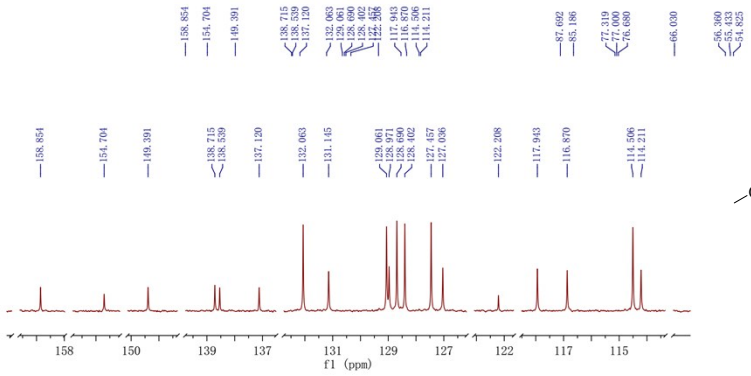

1.08
12.23
5.09
2.00
2.87
3.20
f1 (ppm)

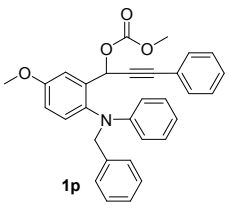

154.667
154.012
148.626
142.897
138.405
136.102
133.498
132.075
130.869
129.025
128.777
128.411
128.057
127.478
127.222
126.734
122.100
119.327
114.561
87.475
84.971
77.319
77.000
76.681
65.447
57.660
55.341
54.829
f1 (ppm)
Cl
N
OMe
1o

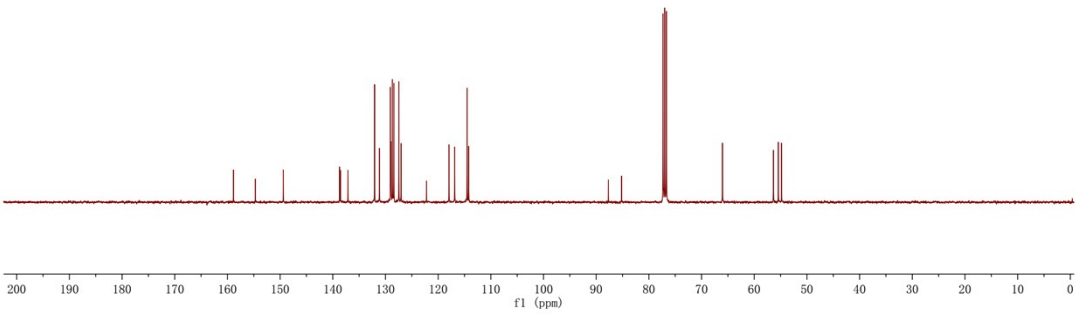

7.405
7.399
7.341
7.312
7.292
7.274
7.257
7.248
7.235
7.217
7.199
7.166
7.145
7.133
7.113
7.094
6.943
6.936
6.921
6.915
6.736
6.718
6.700
6.640
6.609
6.589
4.865
3.849
3.657
1.556
1.257
0.000
11.36
2.93
1.00
1.05
0.96
1.96
f1 (ppm)

1p

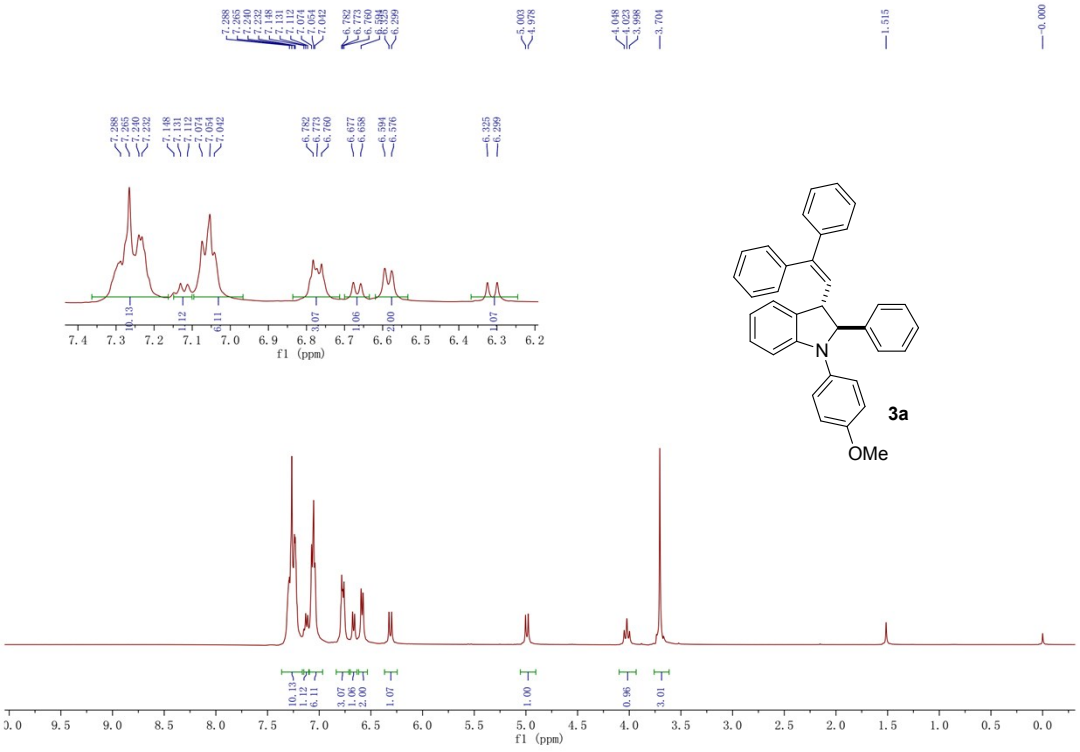

11.36
2.93
1.00
1.05
0.96
1.96
2.00
3.09
3.02
f1 (ppm)

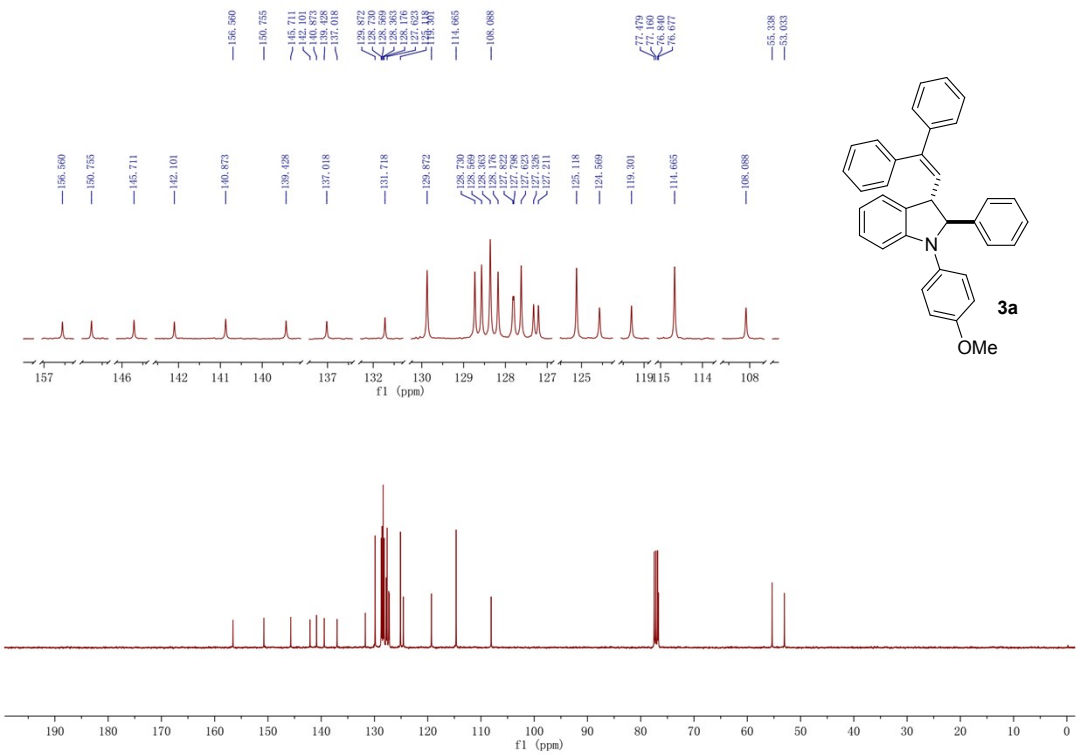

158.854
154.704
149.391
138.715
138.539
137.120
132.063
131.145
129.061
128.971
128.690
128.402
127.457
127.036
122.208
117.943
116.870
114.506
114.211
87.692
85.186
77.319
77.000
76.680
66.030
56.360
55.433
54.825
f1 (ppm)

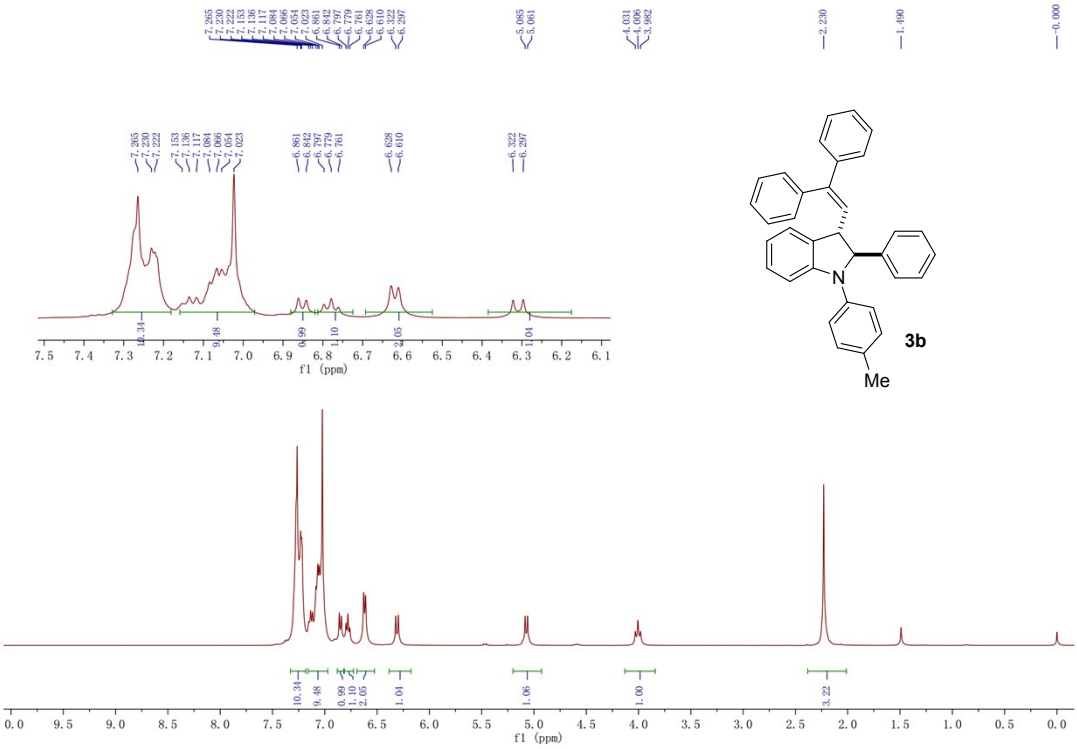

1p

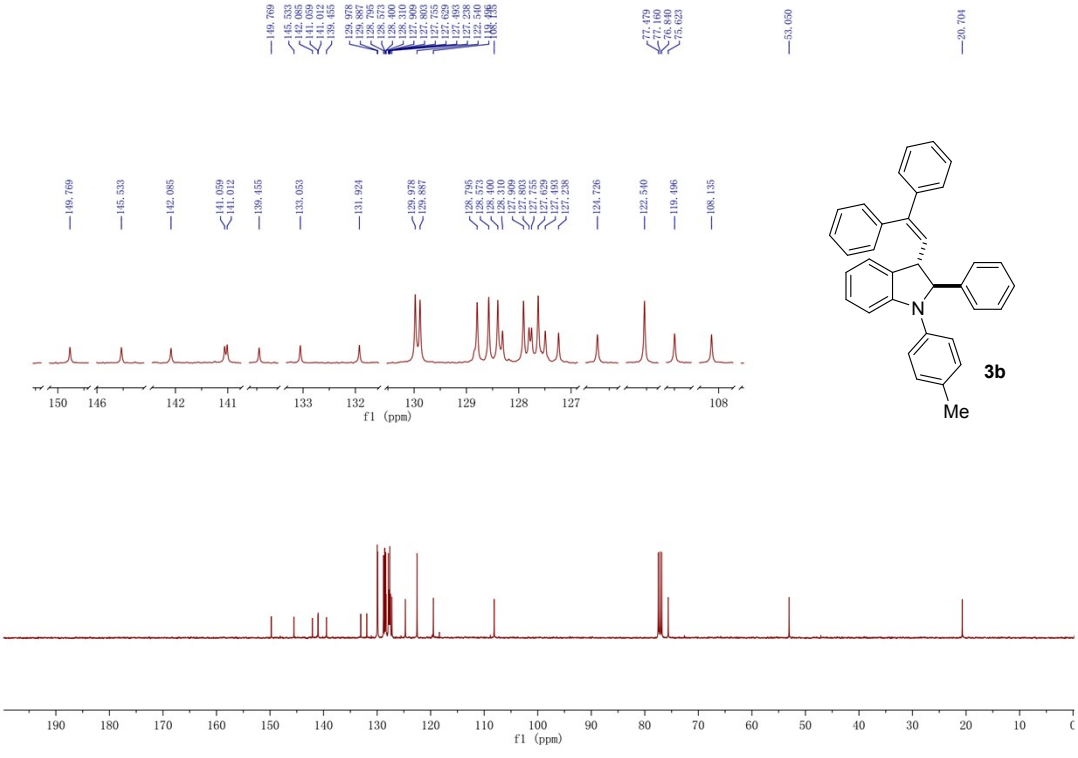

f1 (ppm)

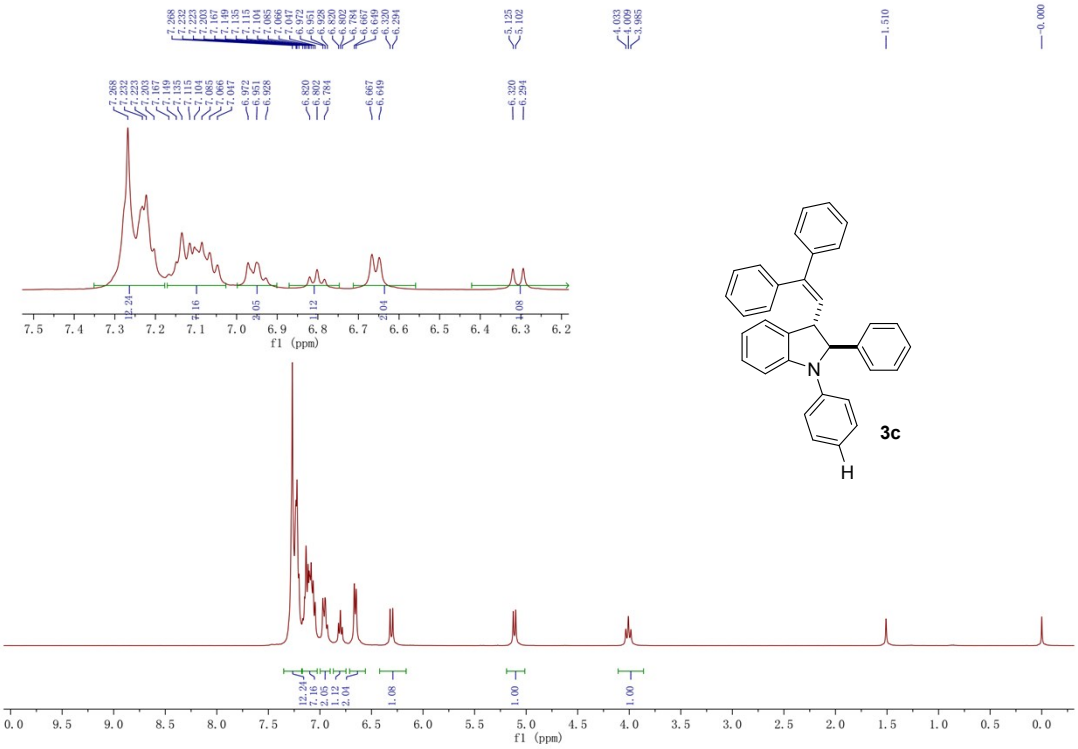
NMR spectra of new compounds (3)

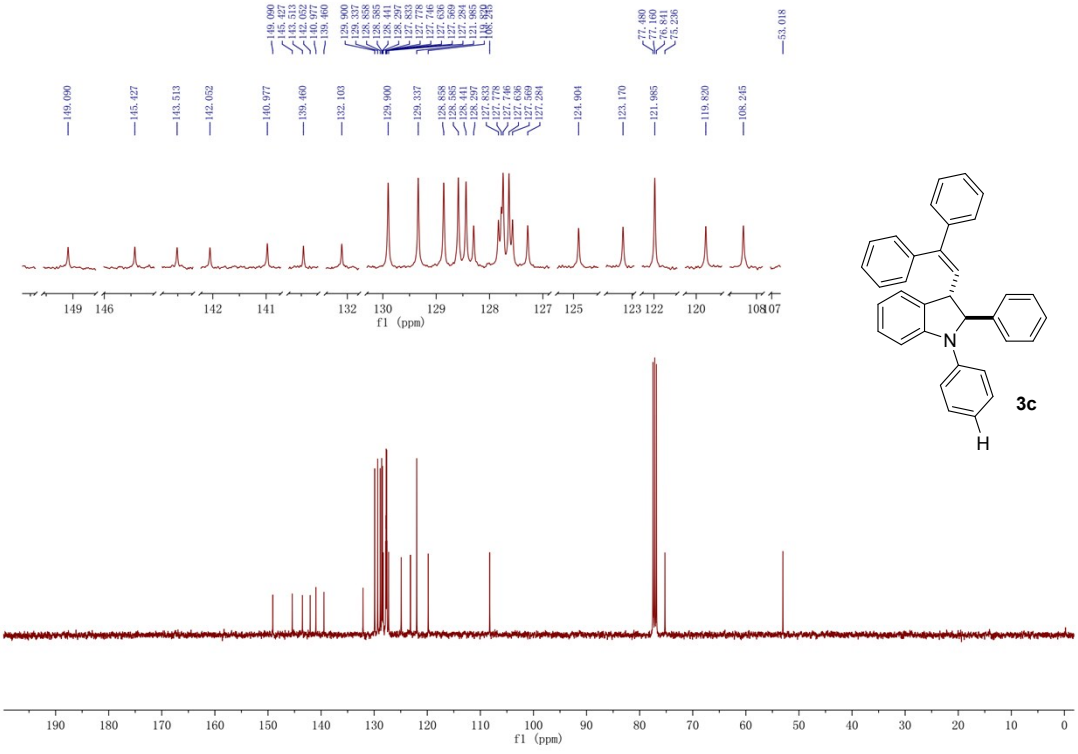


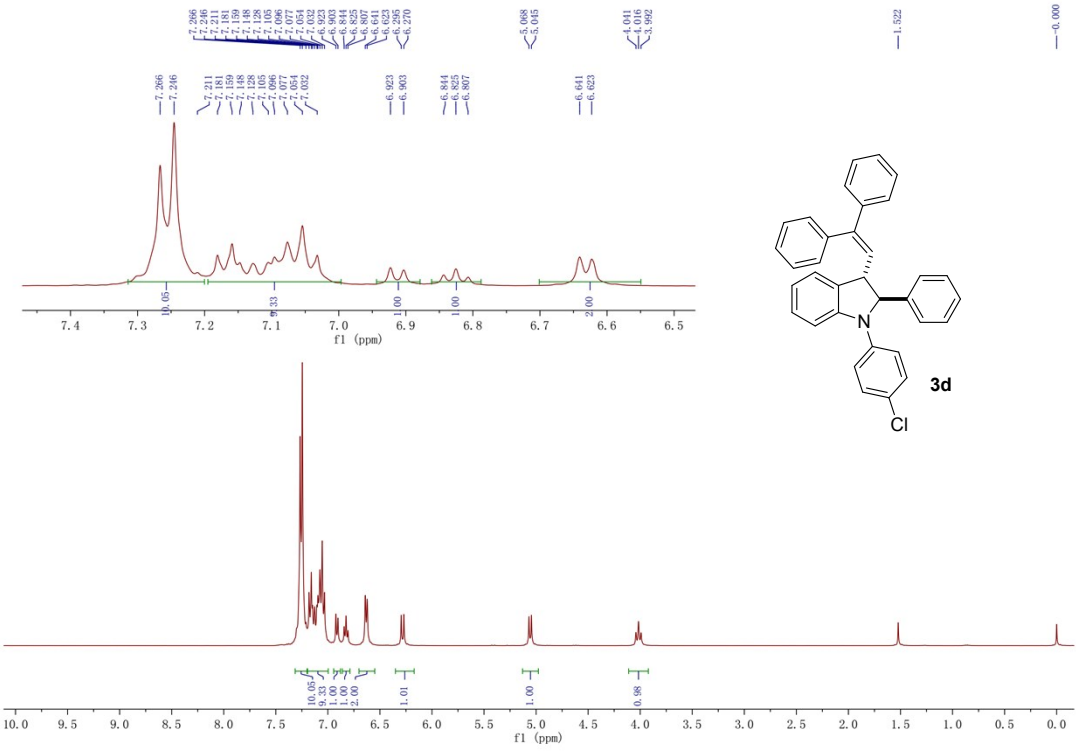



f1 (ppm)
3b
Me


f1 (ppm)
3b
Me

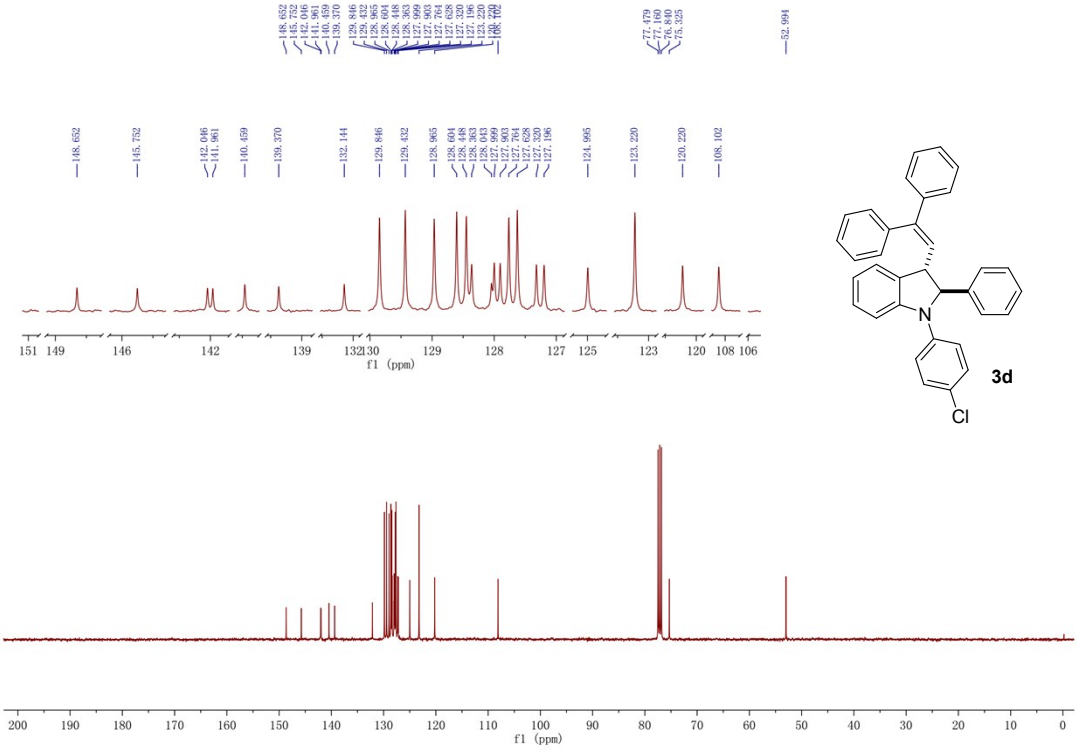

f1 (ppm)
3c
H


f1 (ppm)
3c
H


7.266
7.246
7.211
7.181
7.159
7.148
7.128
7.105
7.096
7.077
7.054
7.032
6.923
6.903
6.844
6.825
6.807
6.641
6.623
5.088
5.045
4.041
4.016
3.992
1.522
0.000
10.05
9.33
1.00
1.00
2.00
1.01
1.00
0.98
f1 (ppm)

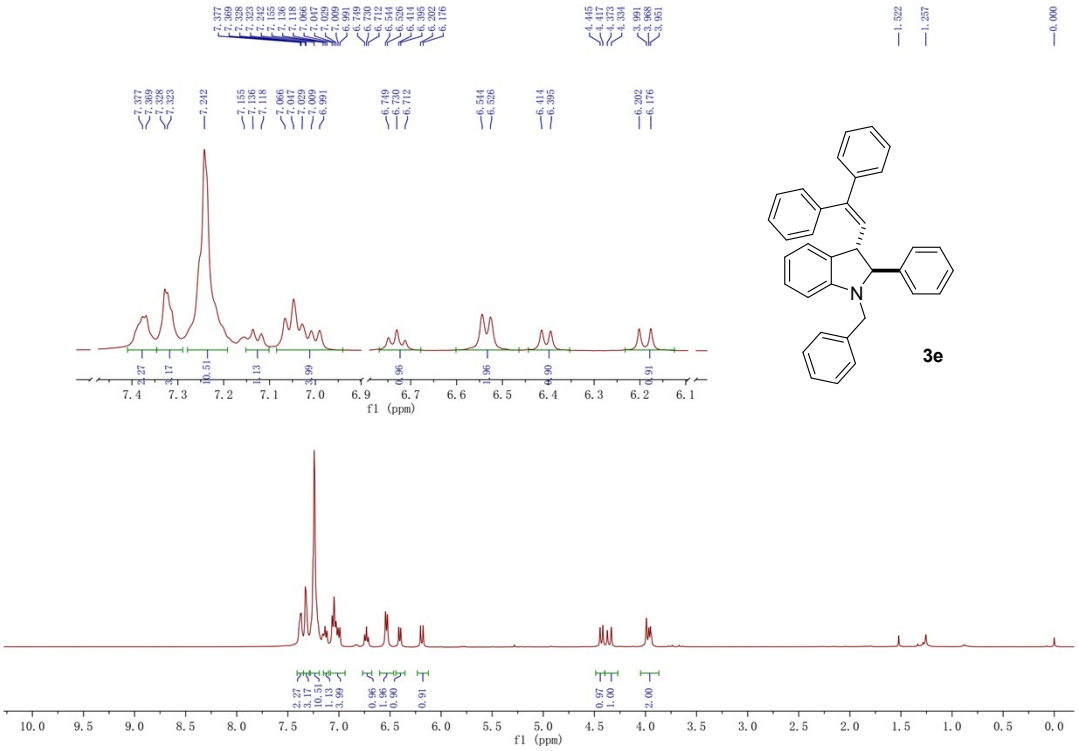
N
Cl

3d


148.652
145.752
142.046
141.961
140.459
139.370
132.144
129.846
129.432
128.985
128.604
128.448
128.363
128.043
127.999
127.903
127.764
127.628
127.320
127.196
124.995
123.220
120.220
108.102
77.479
77.160
76.840
76.325
52.994
f1 (ppm)

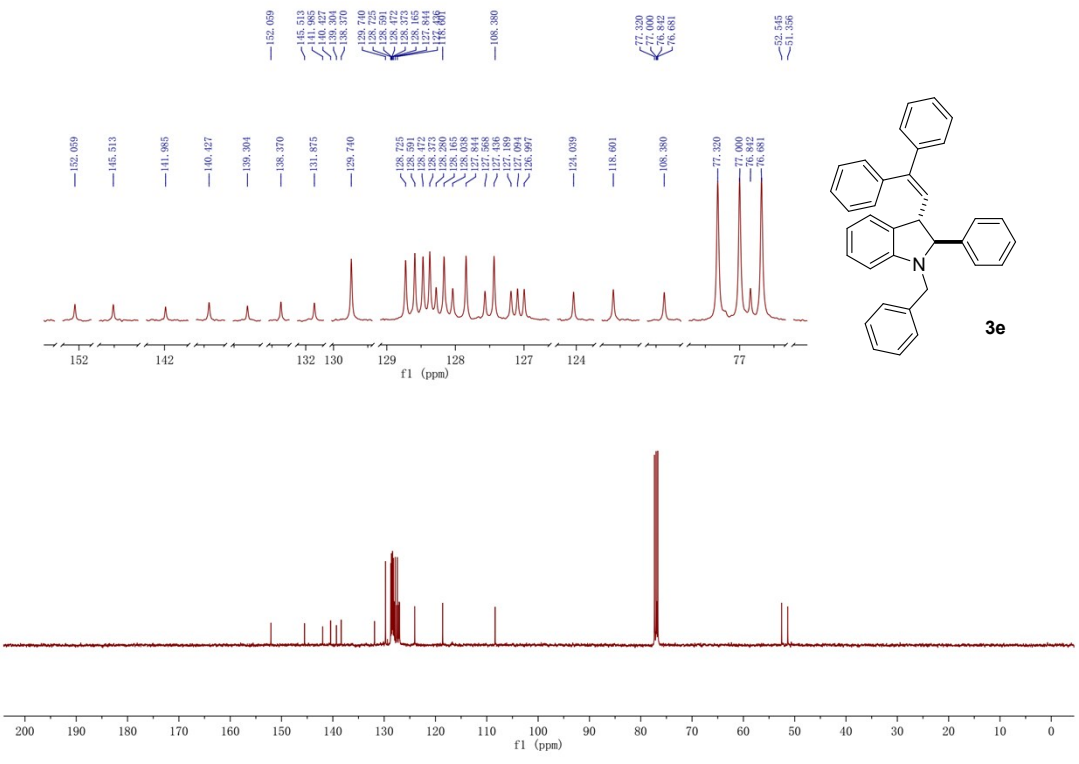
N
Cl

3d


7.377
7.369
7.328
7.323
7.242
7.155
7.136
7.118
7.066
7.047
7.029
7.009
6.991
6.749
6.730
6.712
6.544
6.526
6.414
6.395
6.202
6.176
4.445
4.417
4.353
4.334
3.991
3.968
3.951
1.522
1.257
0.000
2.27
3.17
10.51
1.13
3.99
0.96
1.96
0.90
0.91
1.96
0.90
0.97
1.00
2.00
f1 (ppm)

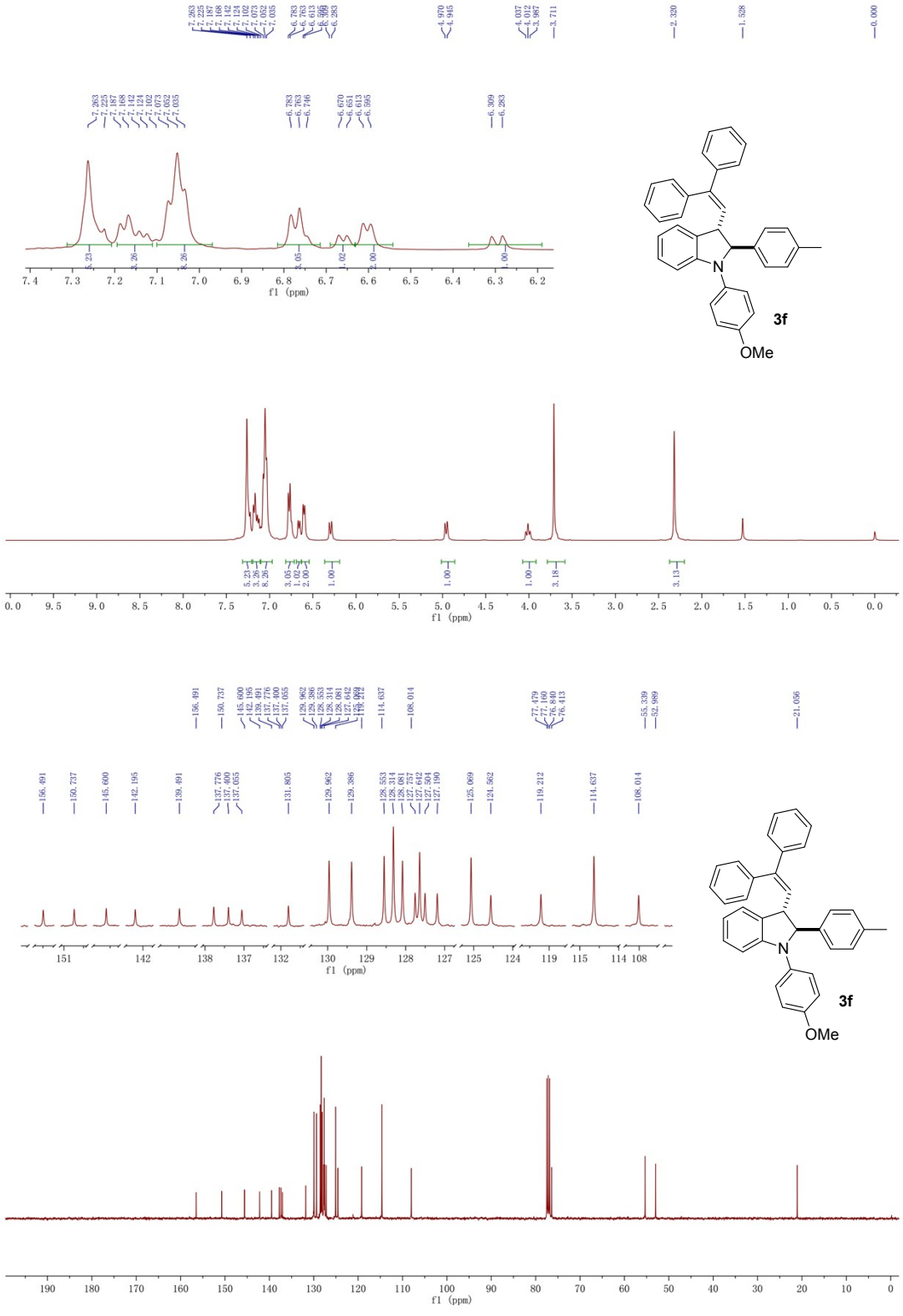
N

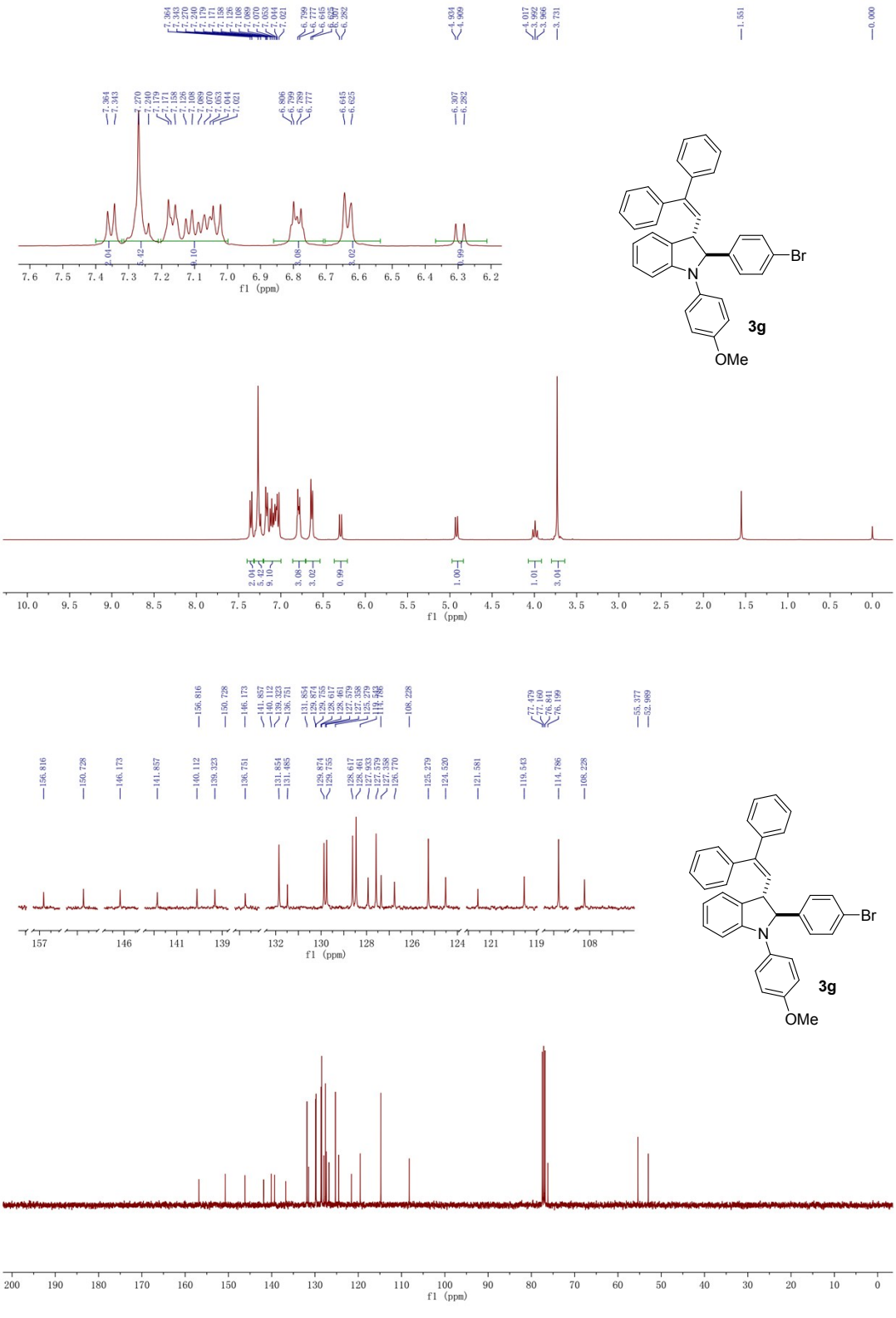
3e

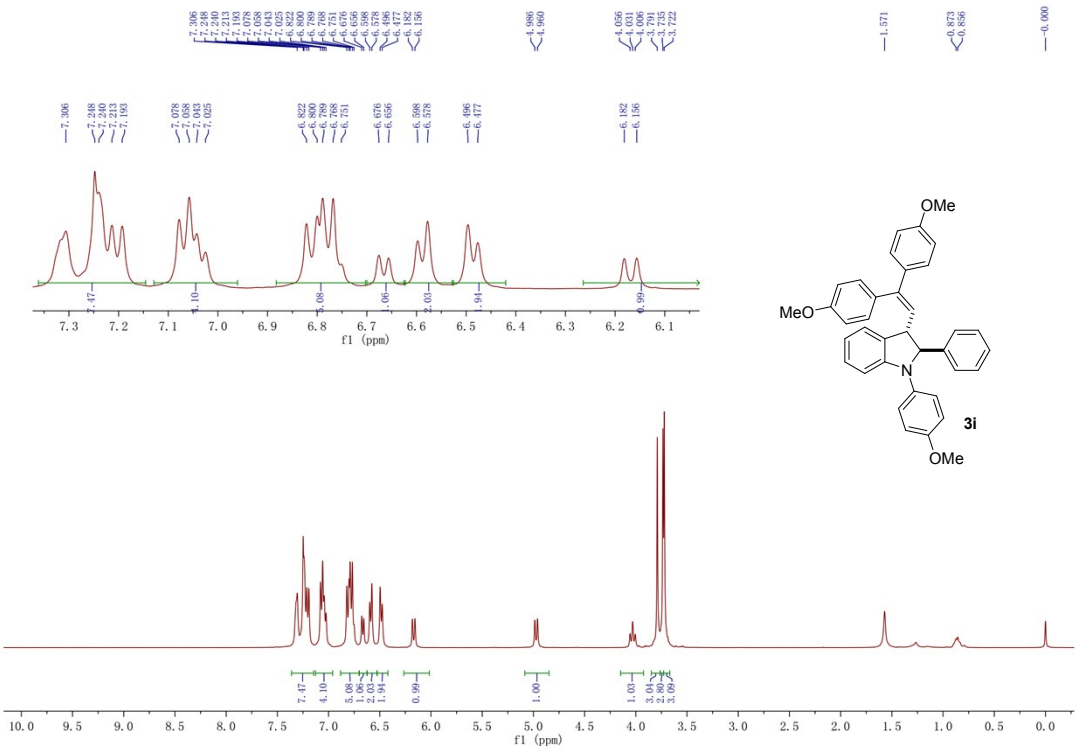

152.059
145.513
141.985
140.427
139.304
138.370
131.875
129.740
128.725
128.591
128.472
128.373
128.259
128.165
128.038
127.844
127.668
127.436
127.189
127.094
126.997
124.039
118.601
108.380
77.320
77.000
76.842
76.681
52.545
51.356
f1 (ppm)

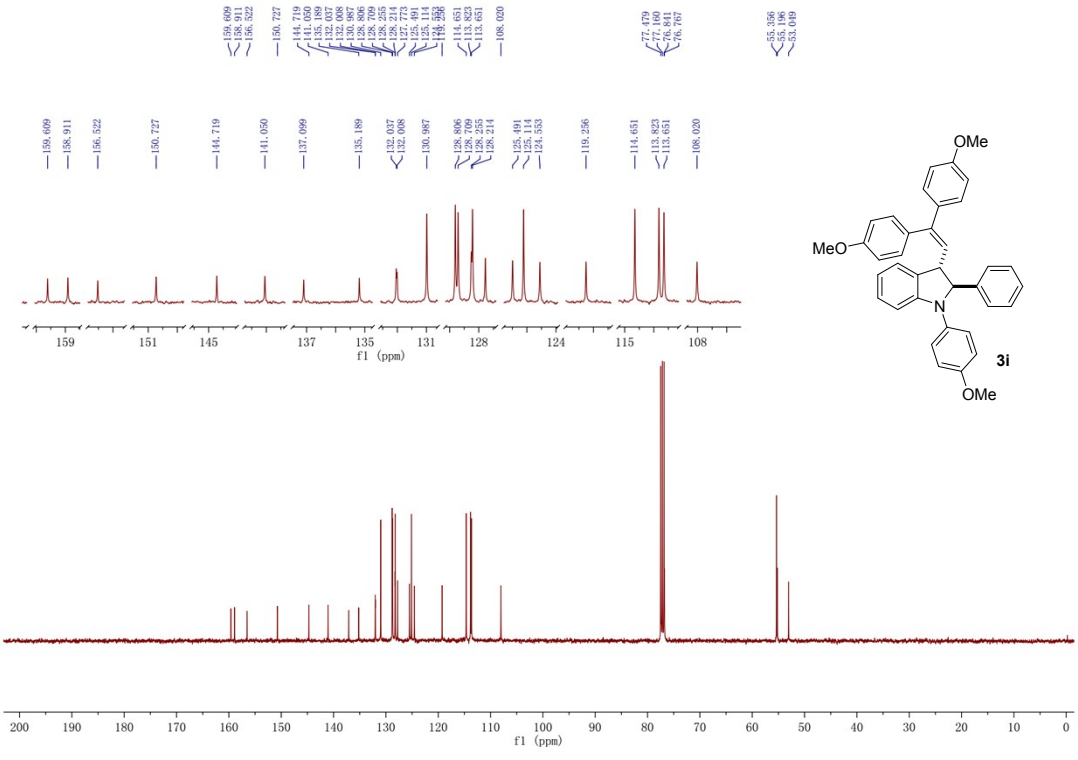
N

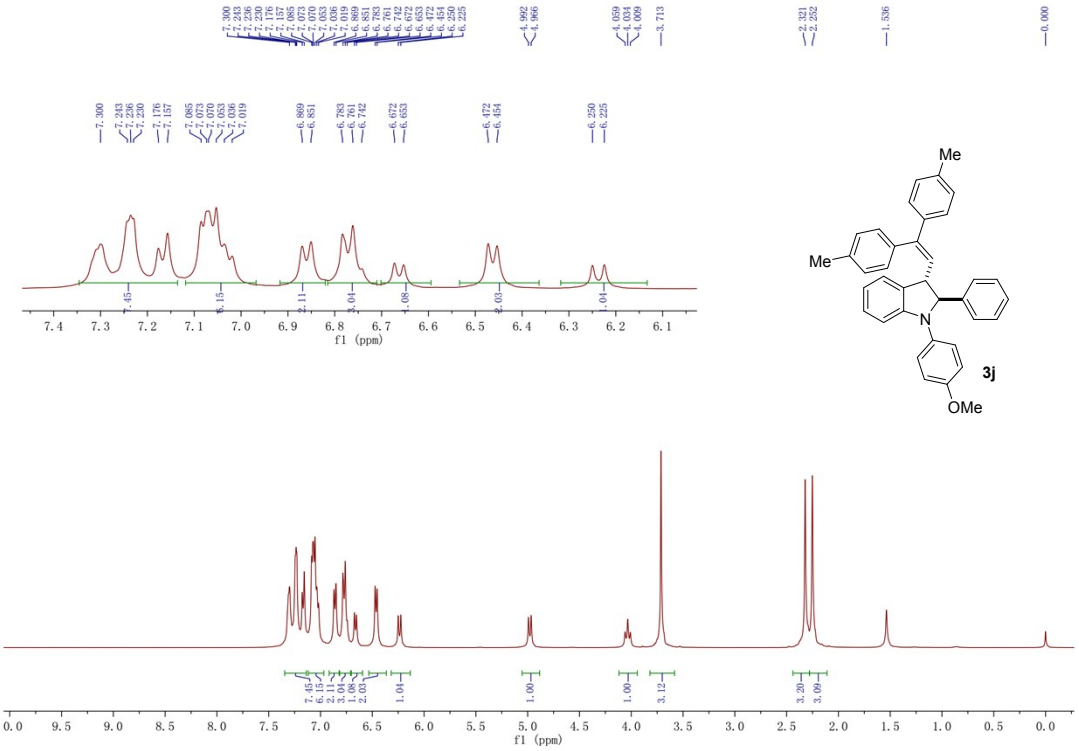
3e

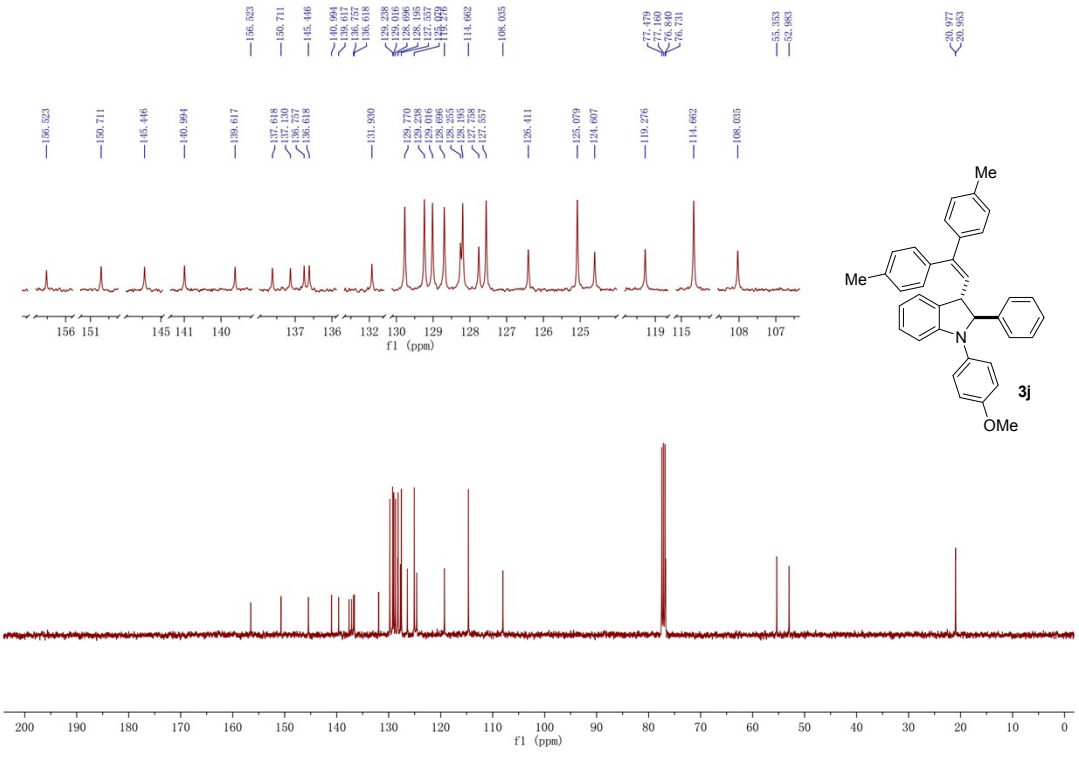

3f
OMe
f1 (ppm)

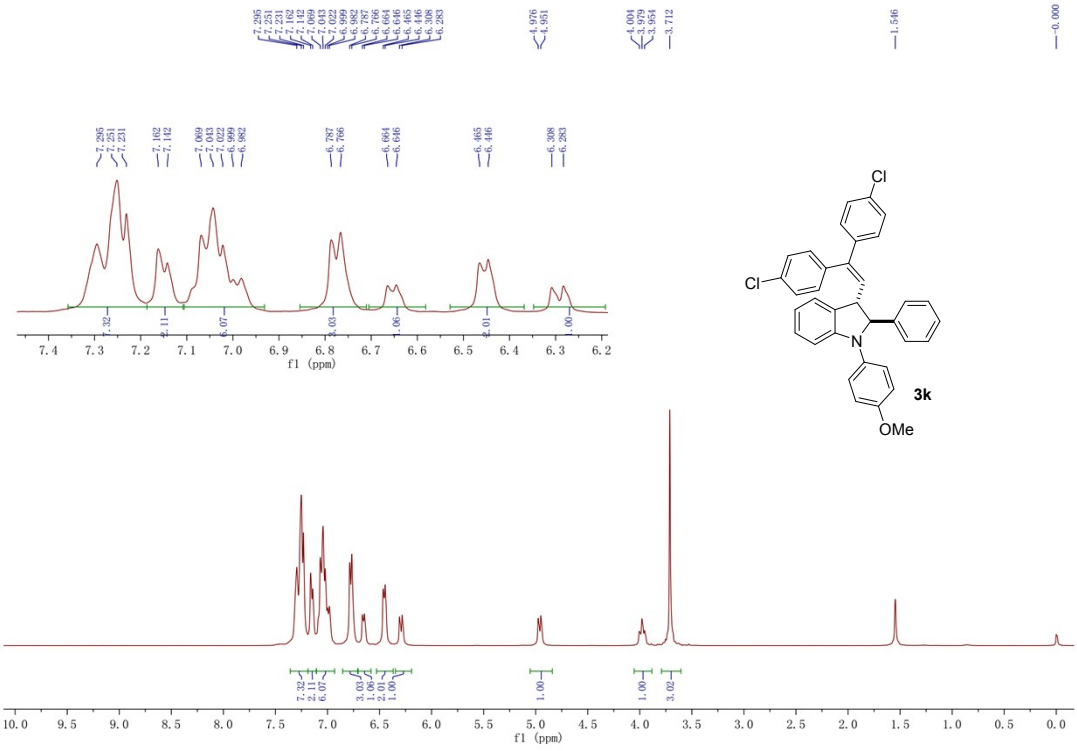

7.364
7.343
7.270
7.240
7.179
7.171
7.158
7.108
7.089
7.070
7.055
7.044
7.021
6.806
6.799
6.789
6.777
6.645
6.625
6.307
6.282
4.934
4.909
4.017
3.992
3.966
3.731
1.551
0.000
2.04
5.42
4.10
3.08
3.02
0.99
1.00
1.01
3.04
f1 (ppm)
Br
N
OMe
3g
156.816
150.728
146.173
141.857
140.112
139.323
136.751
131.854
131.485
129.874
129.755
128.617
128.461
127.579
127.398
125.279
124.520
121.581
119.543
114.786
108.228
77.479
77.160
76.841
76.199
55.377
52.989


OMe
MeO
N
OMe
3i
f1 (ppm)


OMe
MeO
N
OMe
3i
f1 (ppm)


Me
Me
N
3j
OMe


Me
Me
N
3j
OMe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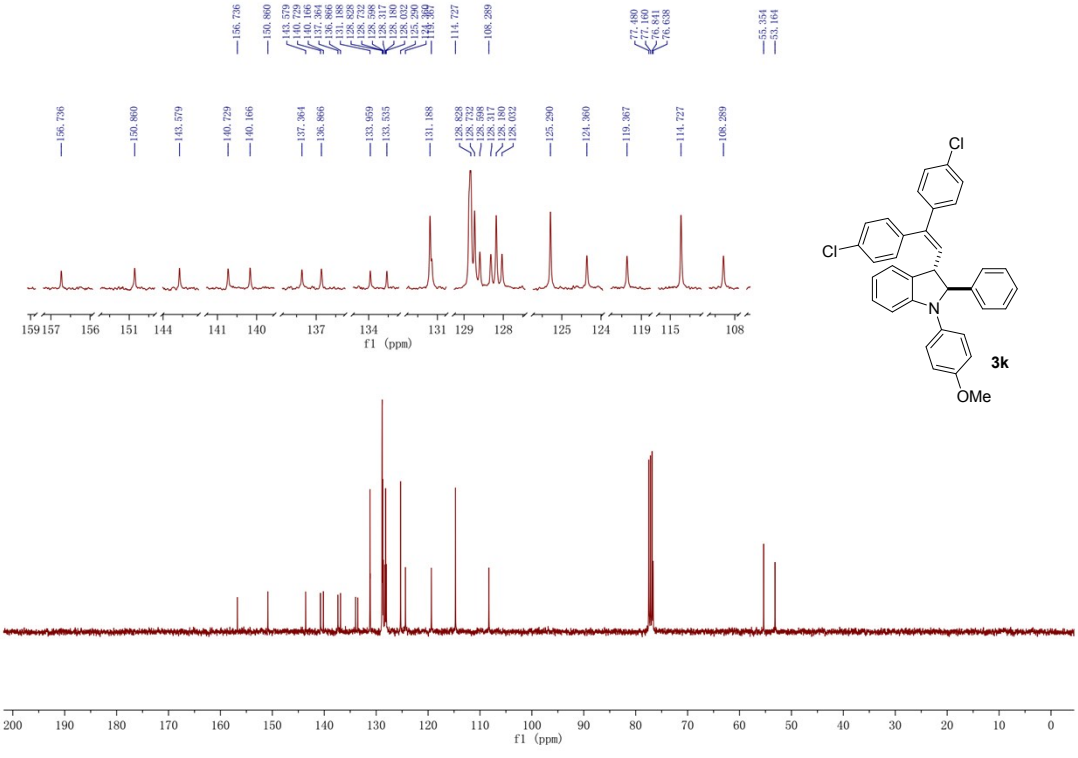
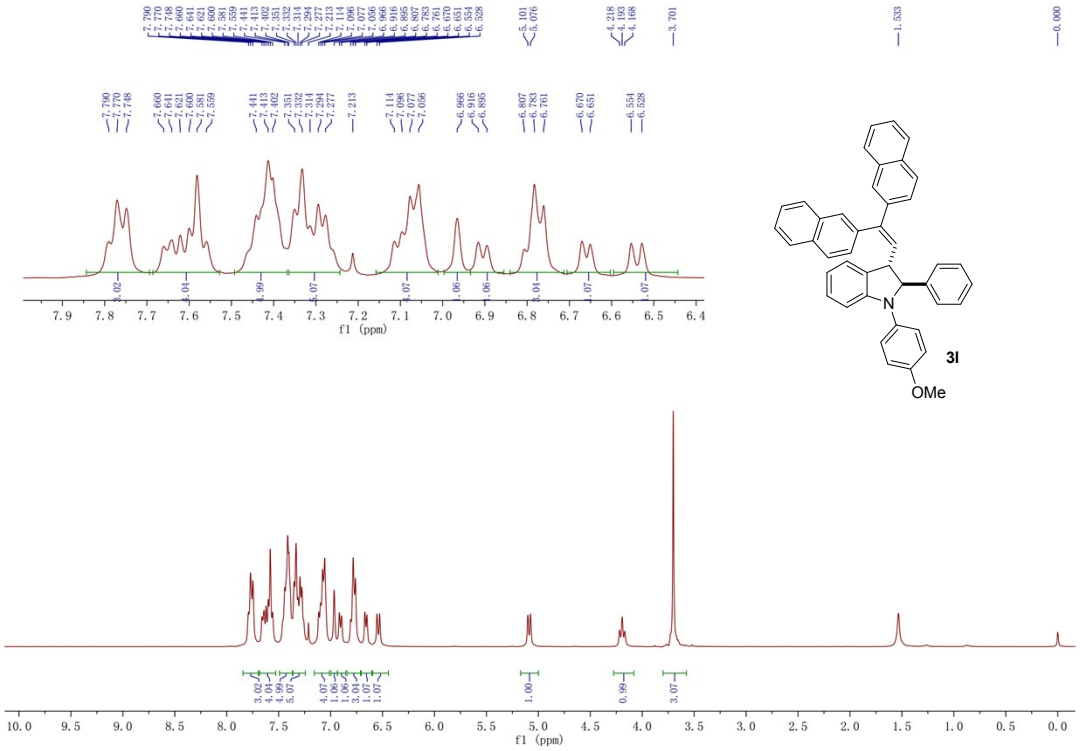
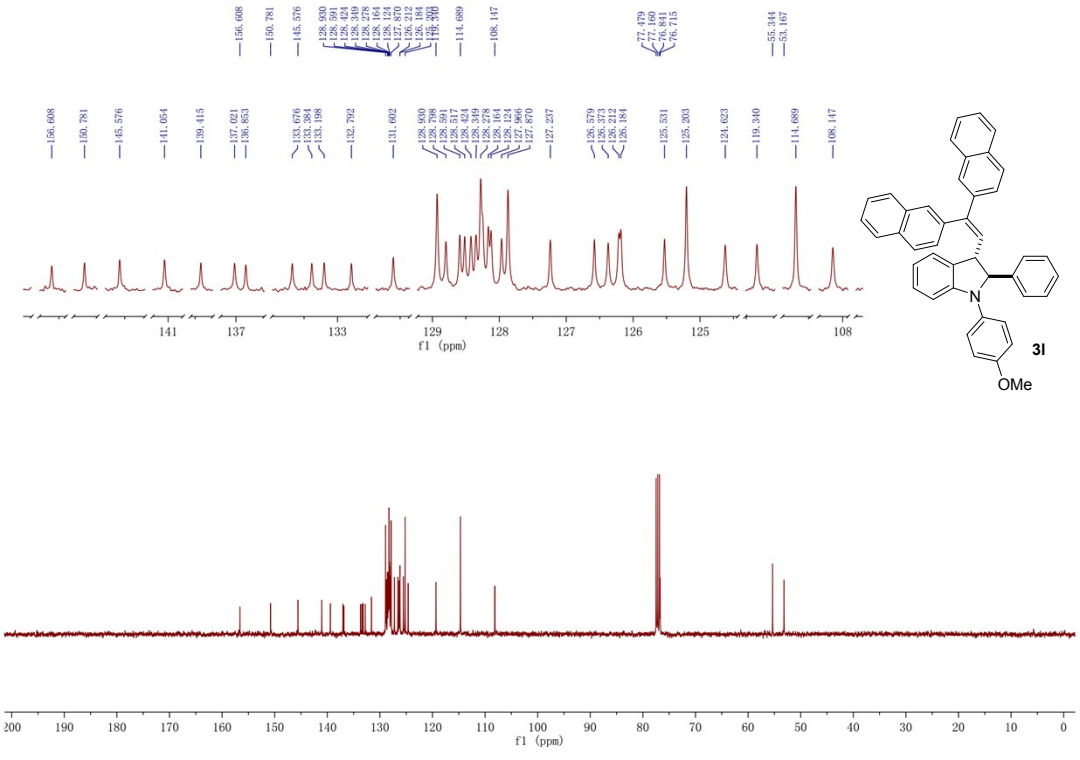
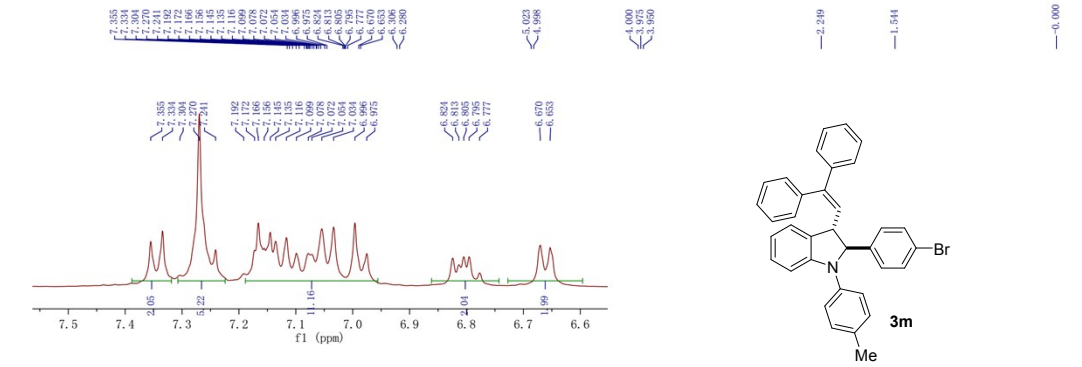
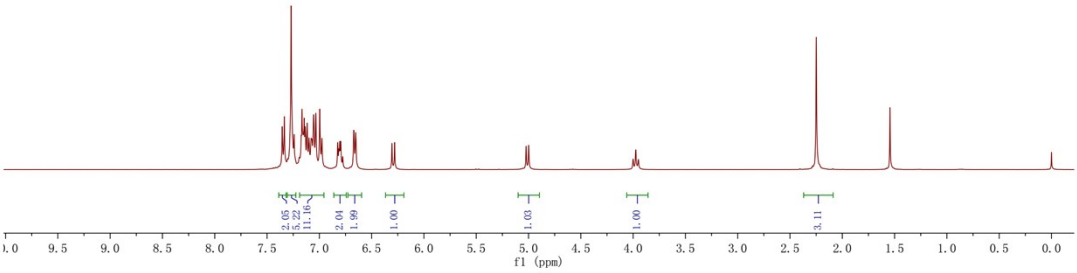
7.251
7.231
7.162
7.142
7.069
7.043
7.022
6.999
6.982
6.787
6.766
6.664
6.646
6.465
6.446
6.308
6.283
4.976
4.951
4.004
3.979
3.954
3.712
1.546
0.000
Cl
Cl
N
3k
OMe
f1 (ppm)

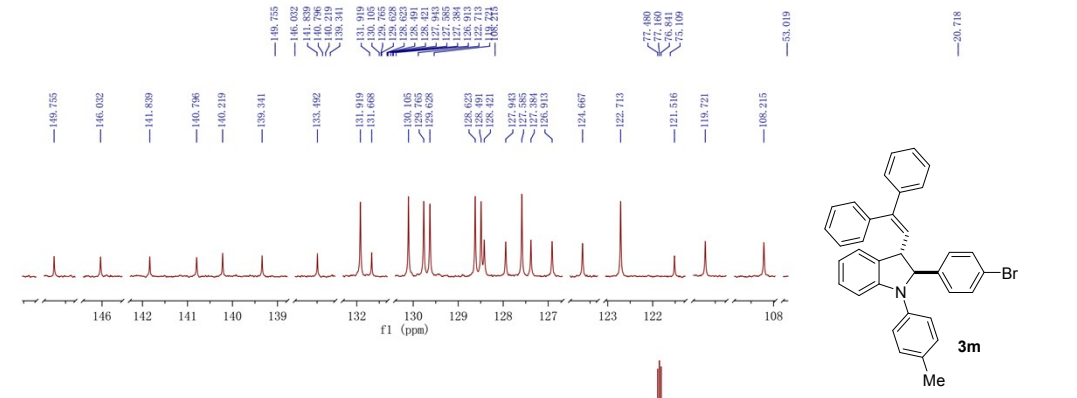

156.736
150.860
143.579
140.729
140.166
137.964
136.866
131.188
128.828
128.732
128.598
128.317
128.180
128.032
125.290
124.360
119.367
114.727
108.289
77.480
77.160
76.841
76.638
55.354
53.164
Cl
Cl
N
3k
OMe
f1 (ppm)

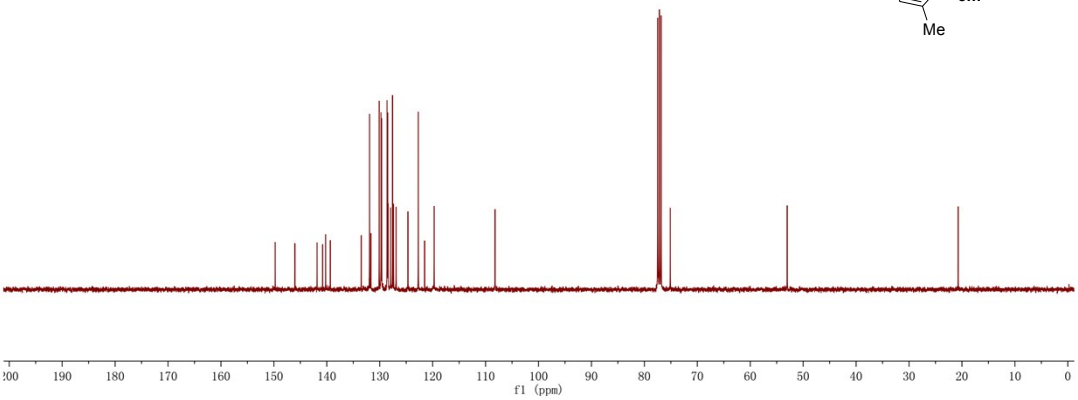

3I
OMe
f1 (ppm)

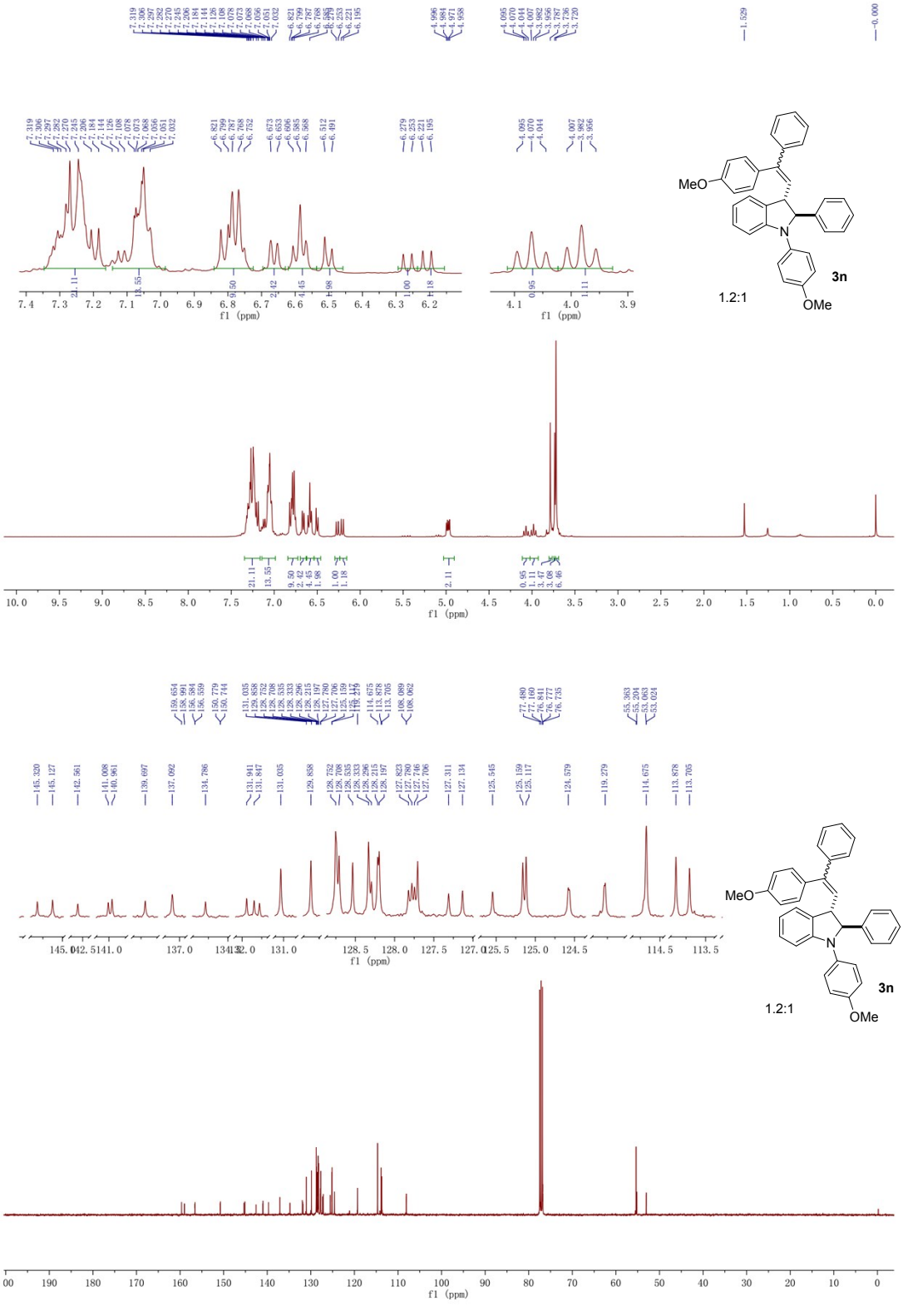

3I
OMe
f1 (ppm)

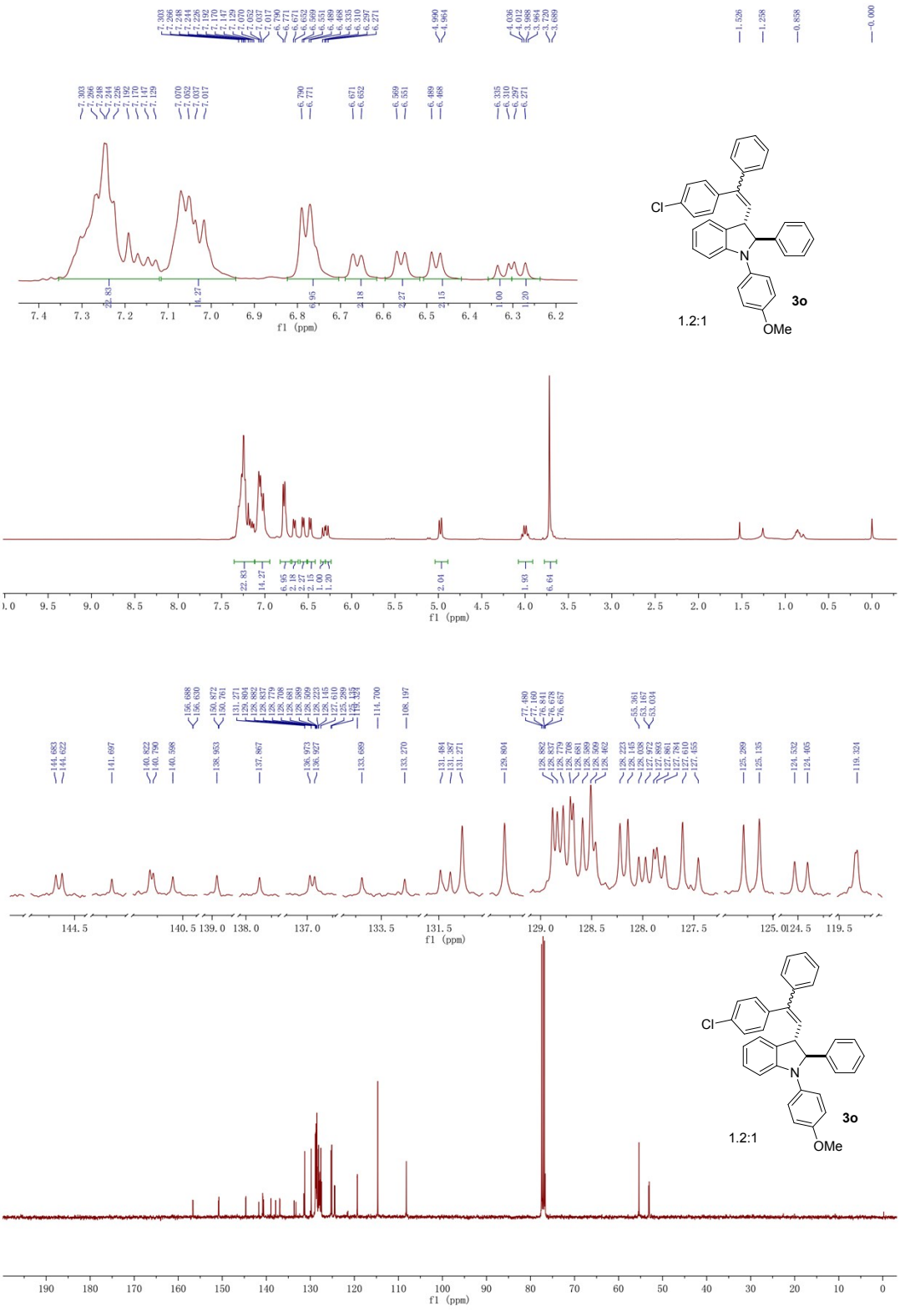

Br
N
Me
3m
f1 (ppm)

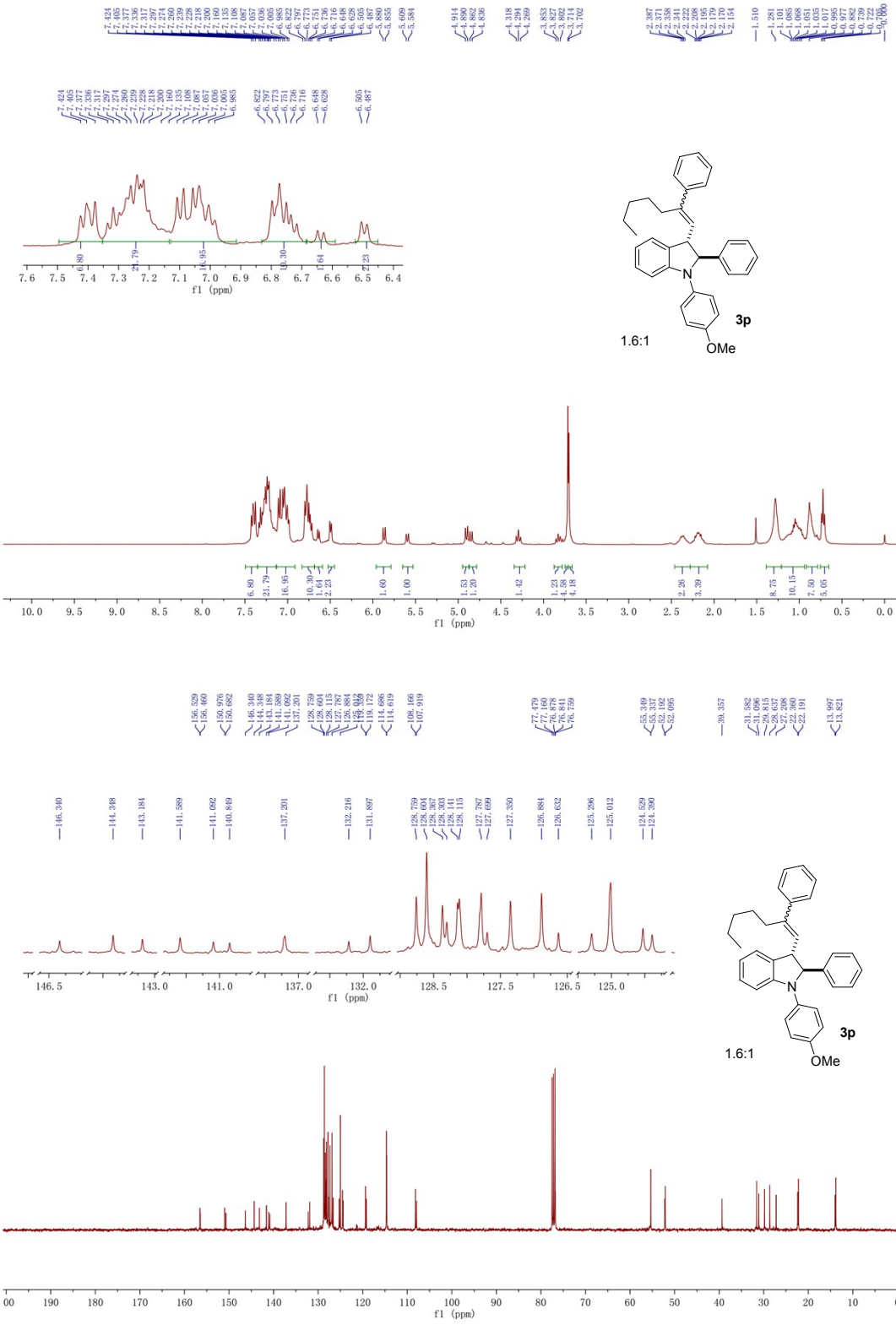

f1 (ppm)

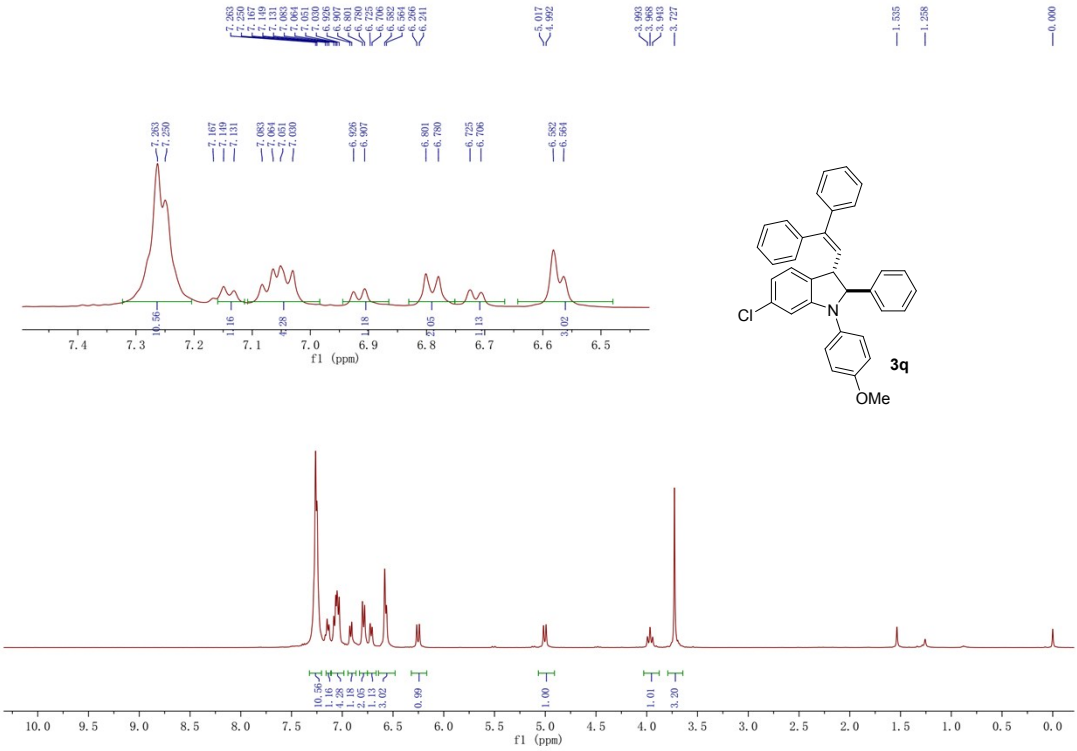

Br
N
Me
3m
f1 (ppm)


f1 (ppm)


MeO
N
OMe
3n
1.2:1
f1 (ppm)


Cl
N
OMe
3o
1.2:1
f1 (ppm)


3p
1.6:1
OMe
f1 (ppm)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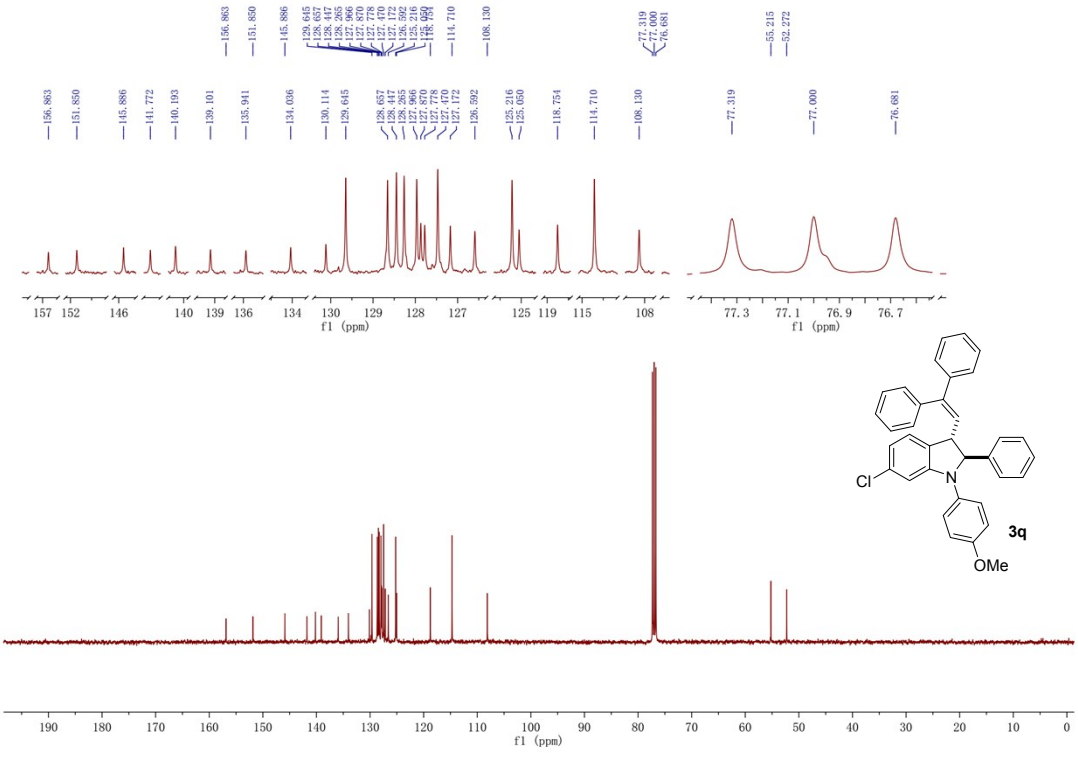
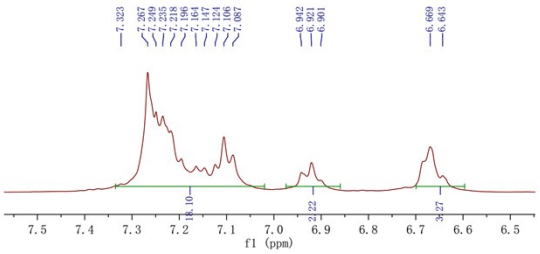
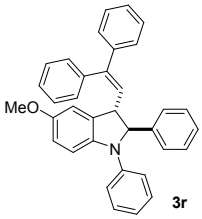
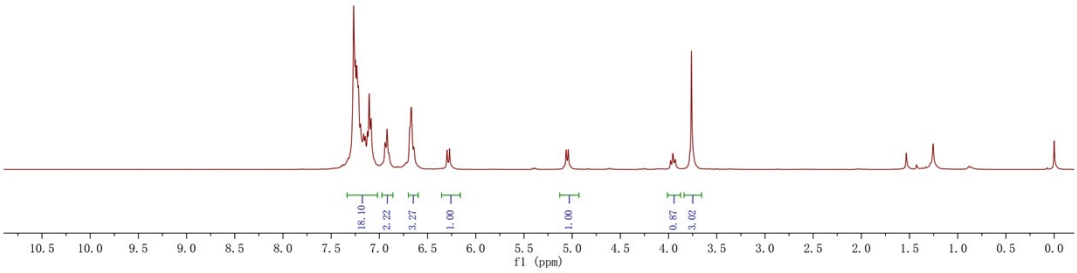
7.167
7.149
7.131
7.083
7.064
7.051
7.030
6.926
6.907
6.801
6.780
6.725
6.706
6.582
6.564
6.266
6.241
5.017
4.992
3.993
3.968
3.943
3.727
1.535
1.258
0.000
10.56
1.16
4.28
1.18
2.13
3.02
0.89
1.00
1.01
3.20
f1 (ppm)
Cl
N
OMe
3q

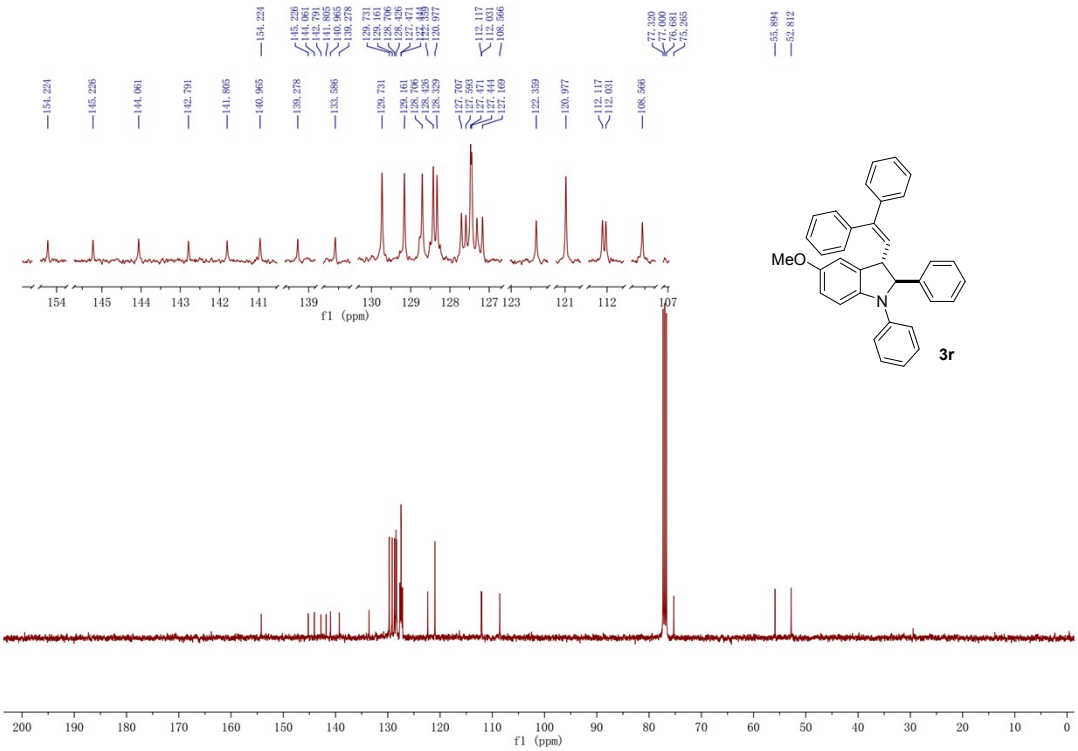

156.863
151.850
145.886
129.645
128.657
128.447
128.265
127.966
127.870
127.778
127.470
127.172
126.592
125.216
125.050
118.754
114.710
108.130
77.319
77.000
76.681
55.215
52.272
f1 (ppm)
Cl
N
OMe
3q





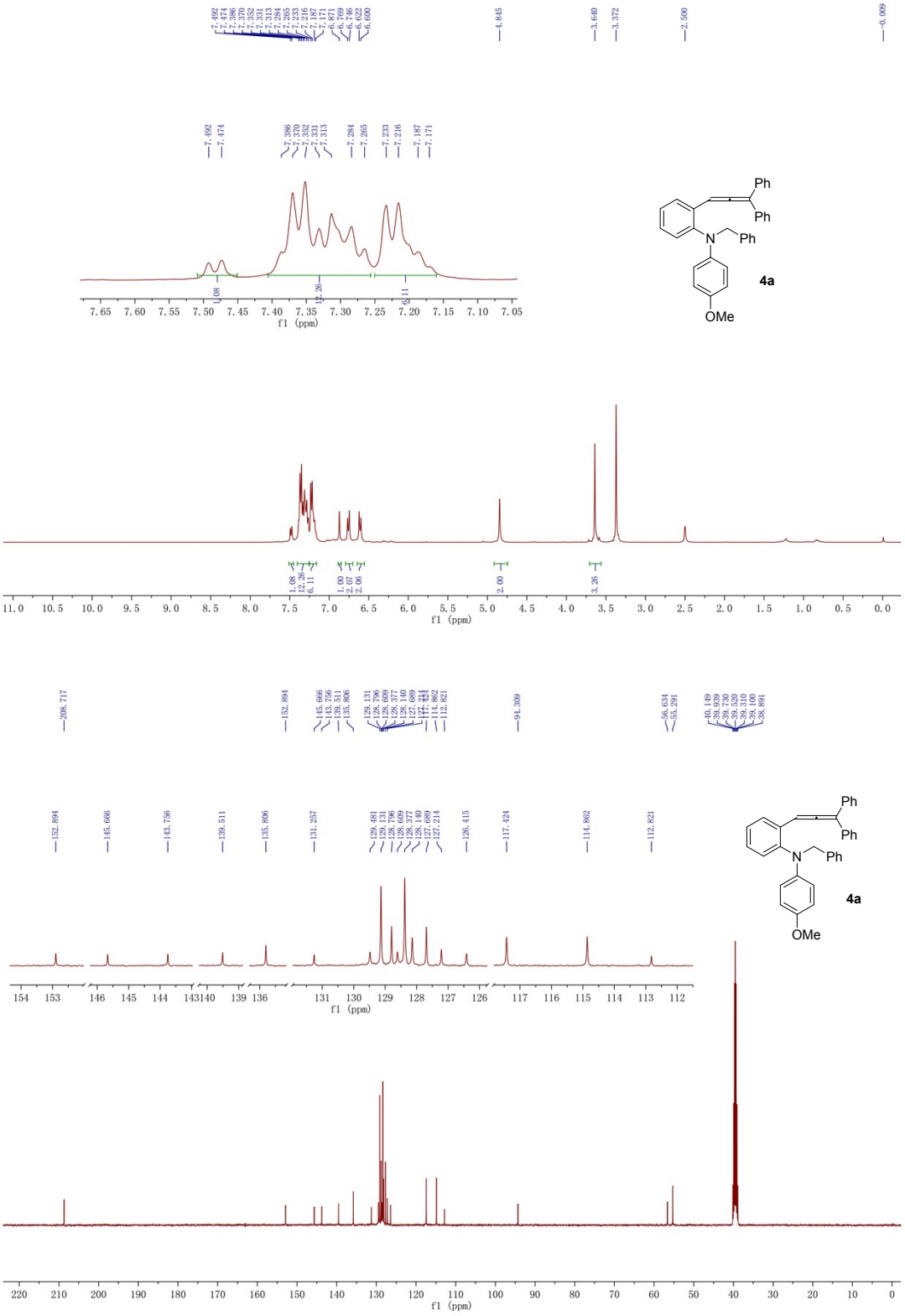
3r



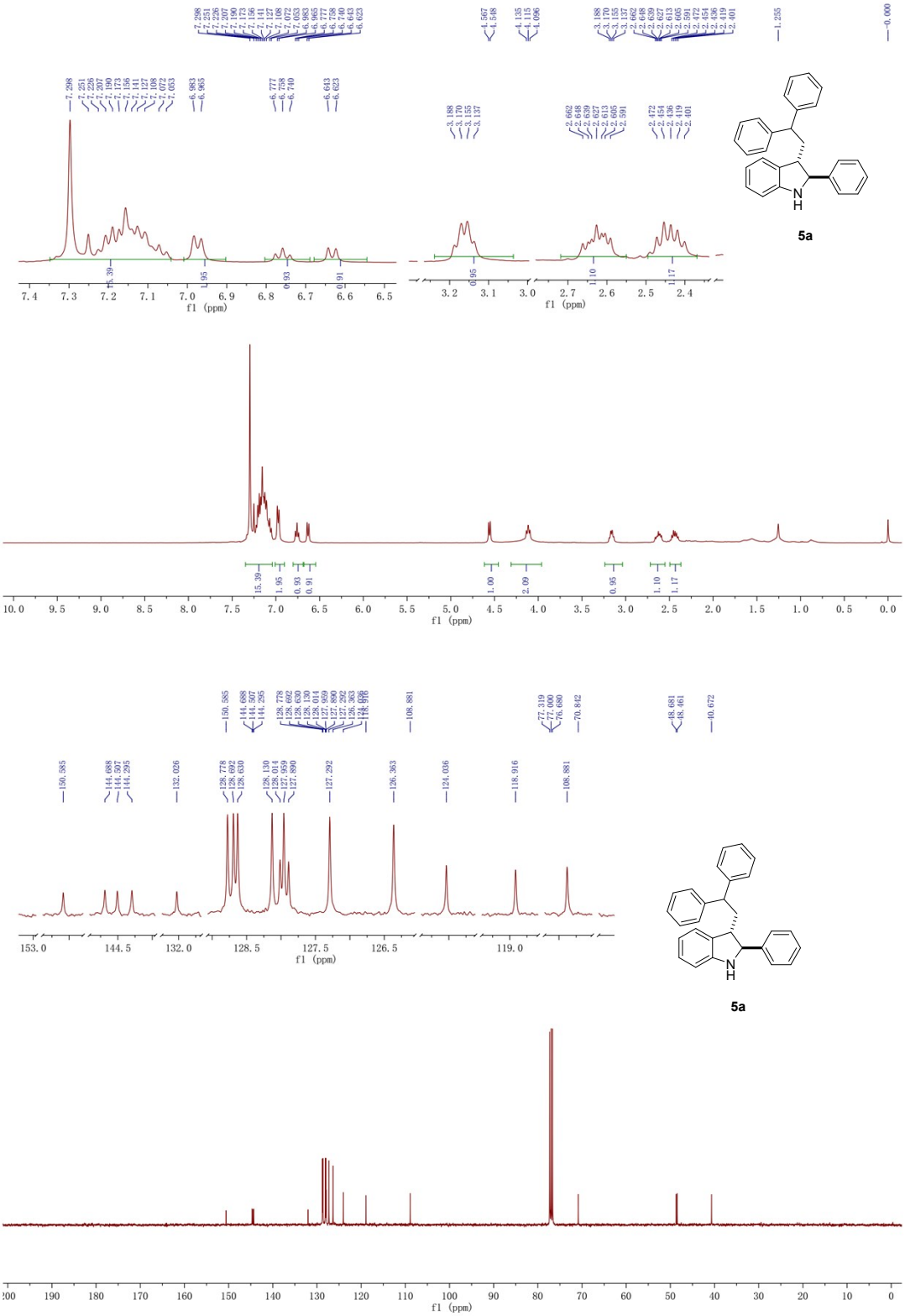


3r

NMR spectra of new compounds (4a)

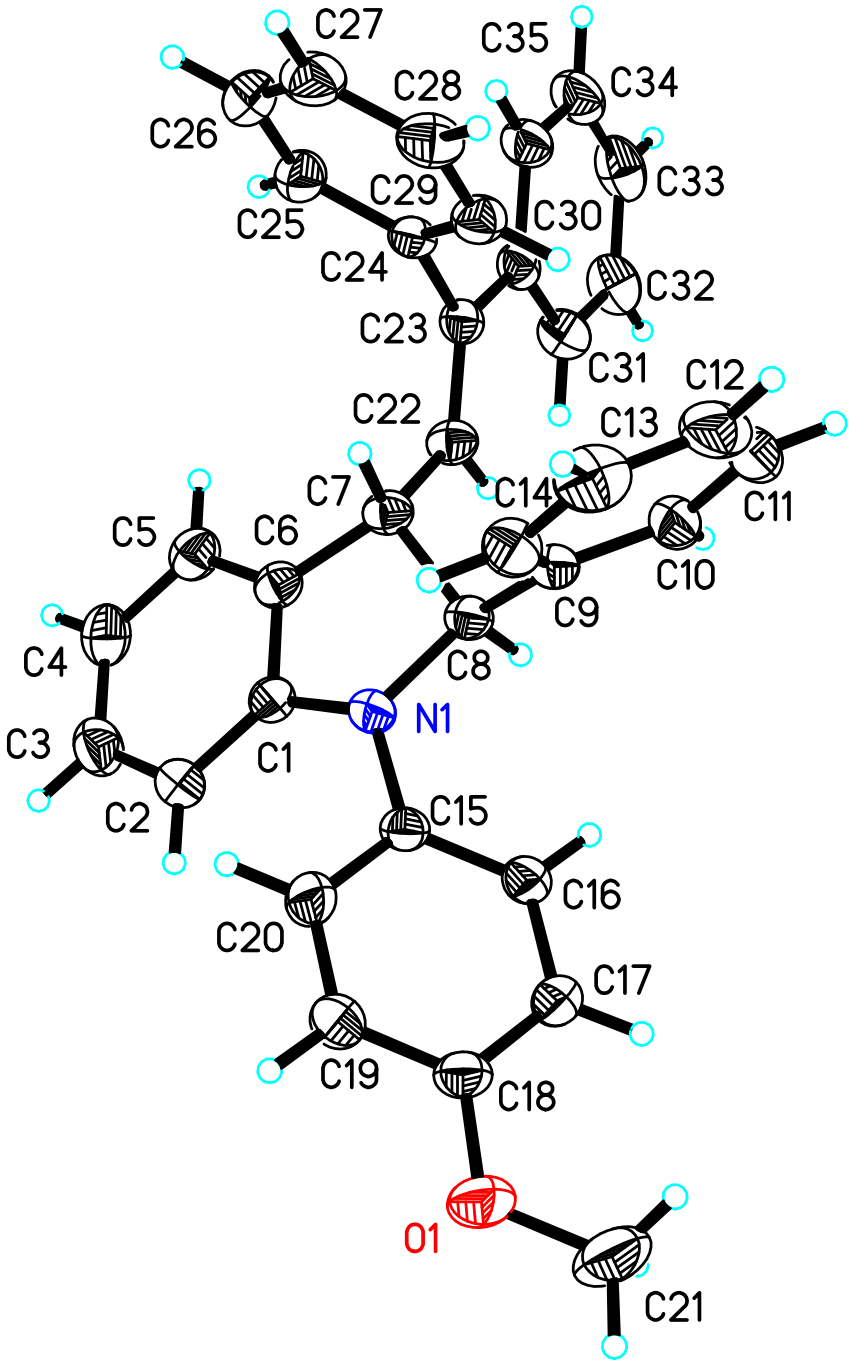


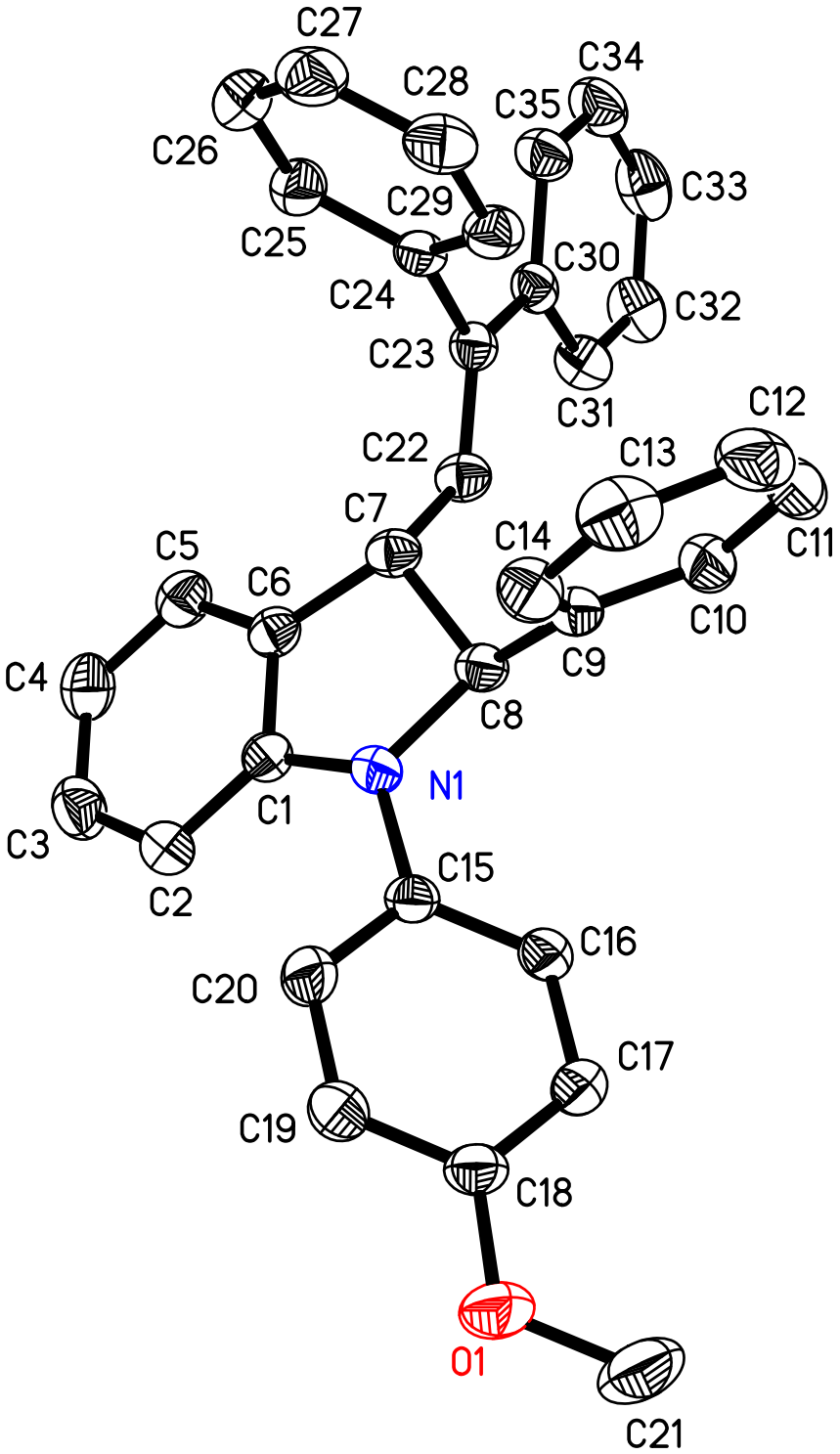
NMR spectra of new compounds (5a)



X-ray crystal structure of 3a

X-ray ORTEP illustration of 5-chloro-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (**3a**) (50% probability ellipsoids)




C27
C28
C34
C35
C26
C33
C29
C25
C30
C24
C32
C23
C31
C12
C22
C13
C7
C14
C11
C5
C6
C10
C9
C4
C8
N1
C1
C3
C15
C2
C16
C20
C17
C19
C18
O1
C21

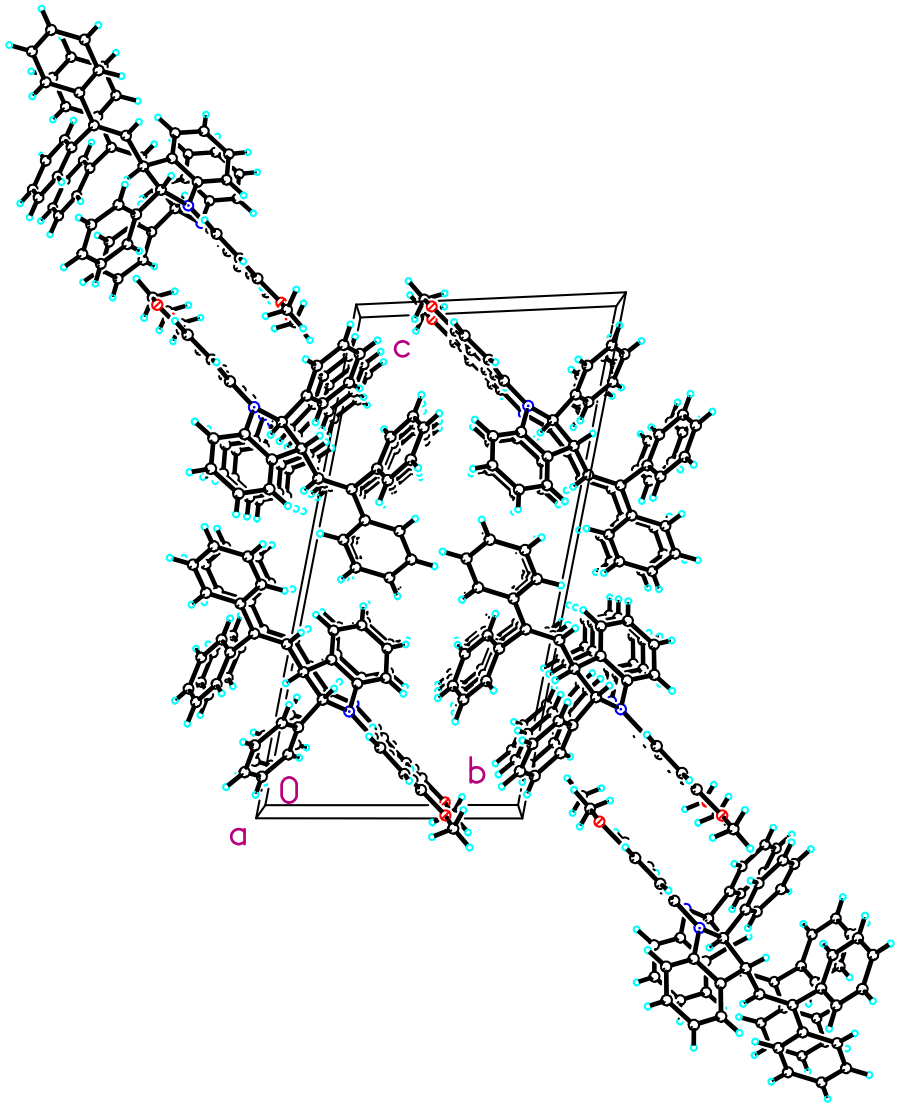

c
b
0
a

Table 1. Crystal data and structure refinement for cd16159 (**3a**).

Identification code	cd16159	
Empirical formula	C35 H29 N O	
Formula weight	479.59	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.3044(9) Å	α= 77.669(4)°.
	b = 10.7952(15) Å	β= 88.541(3)°.
	c = 20.613(3) Å	γ = 75.011(3)°.
Volume	1323.2(3) $Å^3$	
Z	2	
Density (calculated)	1.204 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	508	
Crystal size	0.220 x 0.170 x 0.120 mm^3	
Theta range for data collection	1.012 to 25.500°.	
Index ranges	-7<=h<=7, -13<=k<=12, -18<=l<=24	
Reflections collected	7650	
Independent reflections	4912 [R(int) = 0.0220]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6383	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4912 / 0 / 335	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1170	
R indices (all data)	R1 = 0.0717, wR2 = 0.1316	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.178 and -0.166 $e.Å^{-3}$	