Supporting information：

The facile synthesis of 2-bromoindoles via Cs_2CO_3-promoted intramolecular cyclization of 2-(*gem*-dibromovinyl)anilines under transition-metal-free conditions

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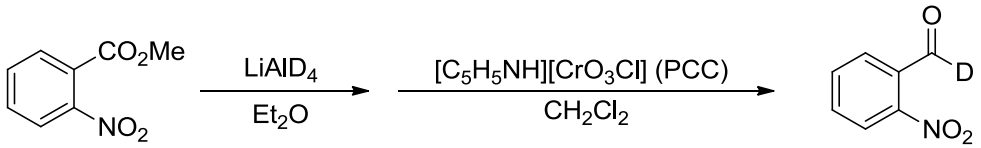
1. General considerations

All reagents were purchased from commercial suppliers and used without further purification. 2-(*gem*-Dibromovinyl)-*N*-methylsulfonylanilines were prepared according to the literature.[1] All Cs_2CO_3-promoted intramolecular cyclization reactions of *gem*-dibromoolefins were carried out under an air atmosphere. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument.

2. General procedures

(1) Typical synthetic procedure of 6a-D

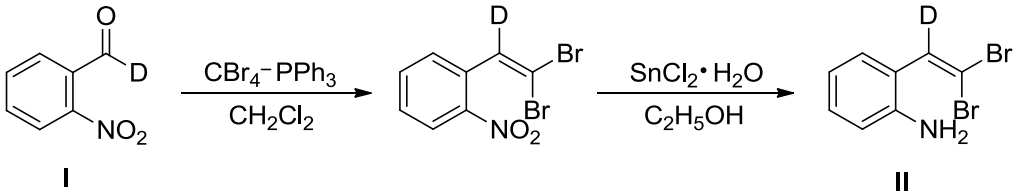


I

To a suspension of methyl 2-nitrobenzoate (5.44 g, 30 mmol) in Et_2O (90 mL) was added $LiAlD_4$ (0.672 g, 16 mmol) in several portions at 0 ºC. After addition, the mixture was stirred at 0 ºC for another 2 h before quenched by pouring into HCl (1.0 mol/L, 100 mL). The resulting mixture was extracted with Et_2O (2×60 mL), washed with $NaHCO_3$ (aq. 20 mL), brine (20 mL), and dried over $MgSO_4$. The crude material was chromatographed with 25% EtOAc in hexanes to afford the benzyl alcohol as a yellow solid (1.52 g, 33%), which was directly used in next step.

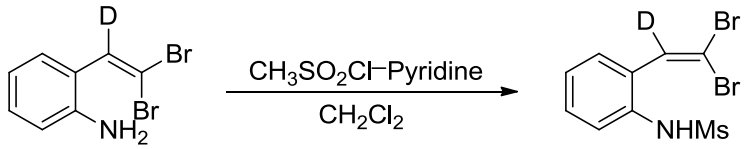
The benzyl alcohol (1.50 g) solution in DCM (30 mL) was added PCC (pyriddinium chlorochromate, 3.2 g), and the mixture was stirred at room temperature overnight. The resulting mixture was filtered through a celite pad. After the celite was washed with DCM (40 mL), the

combined organic solvent was evaporated and chromatographed with 20% EtOAc in hexanes to give the deuterated 2-nitrobenzaldehyde-D (**I**) as a slightly yellow solid (1.19 g, 80%).



I II

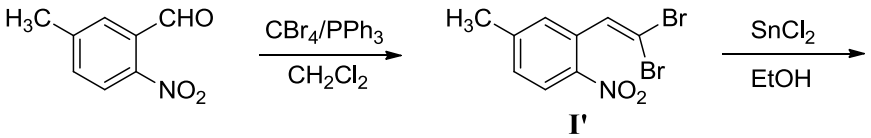
To a solution of 2-nitrobenzaldehyde-D (**I**, 1.19 g, 7.76 mmol) and CBr_4 (3.86 g, 11.64 mmol) in DCM (40 mL) at 0 ºC was added dropwise a solution of PPh_3 (6.10 g, 23.28 mmol) in DCM (20 mL) by an addition funnel. The addition rate was controlled so that the internal temperature was at 1–5 ºC. After addition (about 1 h), the mixture was stirred for another 0.5 h before it was warmed to room temperature, and stirred for an additional 1 h. The reaction mixture was filtered through a short plug of silica gel (12 g) and was washed with a copious amount of DCM until no product was found. Solvent was removed under reduced pressure to give a mixture of the desired intermediate and triphenylphosphine oxide. To the mixture was added EtOH (95%, 20 mL) and $SnCl_2 \cdot H_2O$ (8.76 g, 38.8 mmol). The suspension was heated at 100 ºC (reflux) for 45 min, and then cooled to room temperature. After most of the ethanol was removed under reduced pressure, H_2O (20 mL) and EtOAc (20 mL) were added. To the resulting mixture, solid K_2CO_3 was added carefully until pH > 10. The EtOAc layer was separated from the heterogeneous mixture, and the aqueous phase was extracted with EtOAc until it was free of the product (4×20 mL). The combined organic solution was washed with brine and dried over Na_2SO_4/K_2CO_3. Solvent was removed under reduced pressure and the residue was redissolved in Et_2O. The resulting precipitated $Ph_3P(O)$ was removed by filtration. The product was further purified by flash chromatography using 10% EtOAc in hexanes. The product (**II)** was obtained as a white solid (1.60 g, 74% yield over 2 steps).



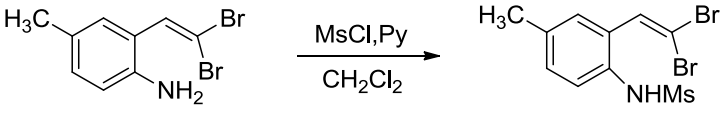
II **1a-D**

To a solution of **II** (1.38g, 5.0 mmol) and pyridine (0.8 mL, 10 mmol) in DCM (10 mL) was added dropwise MsCl (0.58 mL, 7.5 mmol) at 0 ºC. The mixture was warmed slowly to room temperature, stirred for an additional 12 h, and diluted with EtOAc (10 mL). The mixture was washed with $NaHSO_4$ (20%, 2×10 mL), $NaHCO_3$ (aq. 10 mL), brine (10 mL), and dried over anhydrous Na_2SO_4. The crude mixture was purified by column chromatography on silica gel to afford the product **1a**-D as a white solid (1.71 g, 96% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.56–7.54 (m, 1H), 7.46–7.38 (m, 2H), 7.27–7.24 (m, 1H), 6.64 (s, 1H), 3.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 133.76, 130.00, 129.11, 125.79, 122.39, 95.60, 40.15. HRMS (EI) ($[M]^+$) Calcd. for $C_9H_8DBr_2NO_2S$: 353.8784, Found: 353.8788.

(2) Typical procedure for the preparation of 2-(*gem*-dibromovinyl)-*N*-methylsulfonylaniline



I'



II' **6k**

At 0 ºC, to a solution of 4-methyl-2-nitrobenzaldehyde (1.65 g, 10 mmol) and CBr_4 (6.65 g, 20 mmol) in DCM (50 mL) was added dropwise a solution of PPh_3 (10.5 g, 40 mmol) in DCM (50 mL) by an addition funnel. The addition rate was controlled so that the internal temperature was below 5 ºC. After addition (about 1 h), the mixture was stirred for another 2 hrs before

warmed to r. t., and stirred for an additional 3 h. The DCM was removed under vacuum, then EtOAc (200 mL) was added and stirred for 0.5 h, the mixture was filtered and washed with EtOAc until no product was found. Solvent was removed under reduced pressure, the residue was purified by flash chromatography using 10% EtOAc in hexanes. The product (**I'**) was obtained as a light yellow solid (2.60 g, 81%).

I' (1.61 g, 5.0 mmol) and $SnCl_2 \cdot H_2O$ (67.7 g, 25 mmol) were mixed in EtOH (95%, 50 mL). The mixture was refluxed at 100 ºC for 2 h, and then cooled to r. t. After most of the ethanol was removed under vacuum, H_2O (50 mL) and EtOAc (100 mL) were added. To the resulting mixture, solid $NaHCO_3$ was added carefully until pH >10. The EtOAc layer was separated and the aqueous phase was extracted with EtOAc until it was free of the product. The combined organic solution was washed with brine and dried over Na_2SO_4. Solvent was removed under vacuum. The crude product (**II'**) was resolved in DCM (20 mL), and pyridine (1.0 g, 12.5 mmol) was added. After the mixture was cooled to 0 ºC, methylsulfonyl chloride (0.69 g, 6.0 mmol) was added, the mixture was stirred for 4 h before warmed to r. t., and stirred for an additional 5 h. After the reaction was completed, the mixture was washed with HCl (1.0 mol/L, 15 mL), The DCM layer was separated and the aqueous phase was extracted with DCM until it was free of the product. Solvent was removed and the product was further purified by flash chromatography using 25% EtOAc in hexanes. The product **6k** was obtained as a white solid (1.06 g, 58% yield over 2 steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.25 (s, 1H), 7.19 (d, J = 8.4 Hz, 1H), 6.53 (s, 1H), 3.02 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.22, 133.62, 130.97, 130.58, 130.01, 123.66, 94.95, 39.98, 20.89. HRMS (EI) ($[M]^+$) Calcd. for $C_{10}H_{11}NO_2SBr_2$: 366.8877, Found: 366.8875.

(3) Typical procedure for the synthesis of 2-bromoindole (8a) via Cs_2CO_3-promoted intramolecular cyclization of 2-(*gem*-dibromovinyl)-*N*-methylsulfonylaniline (6a)

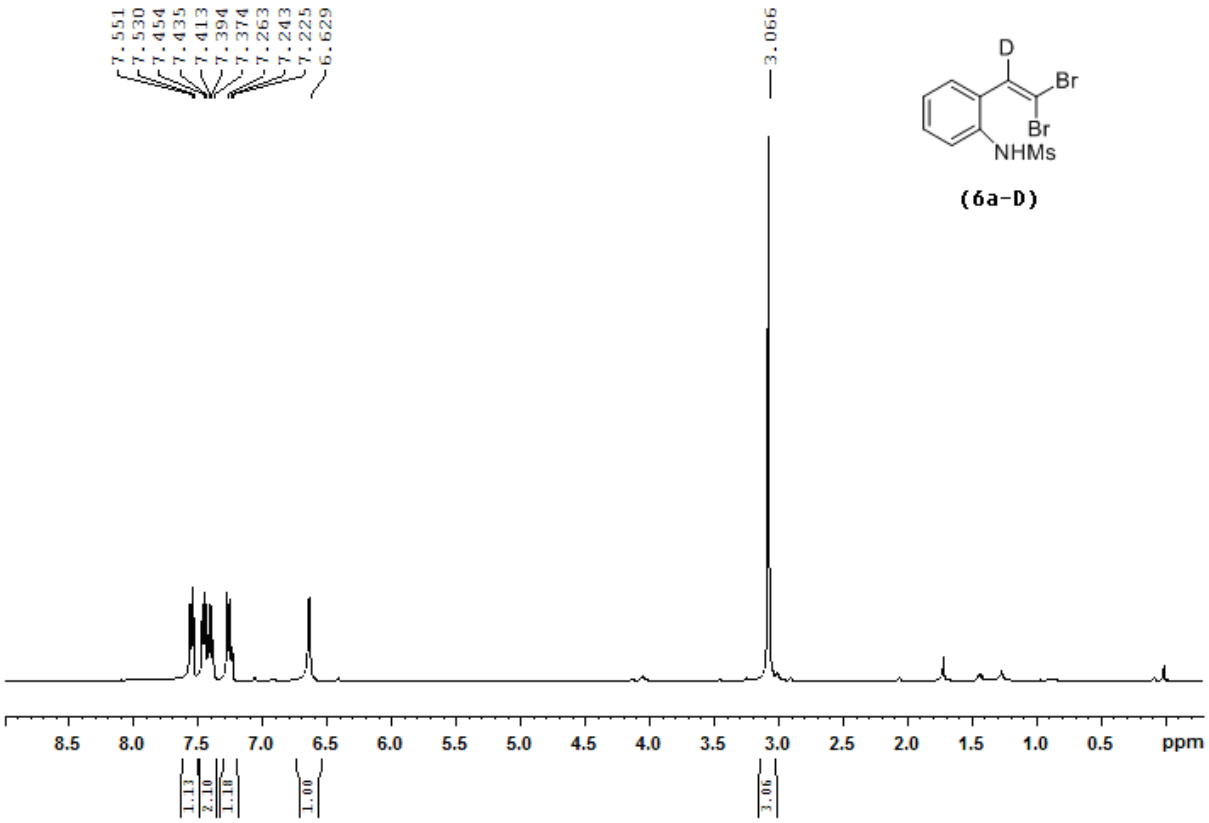
In air atmosphere, a 10 mL of sealable reaction tube with a Teflon-coated screw cap

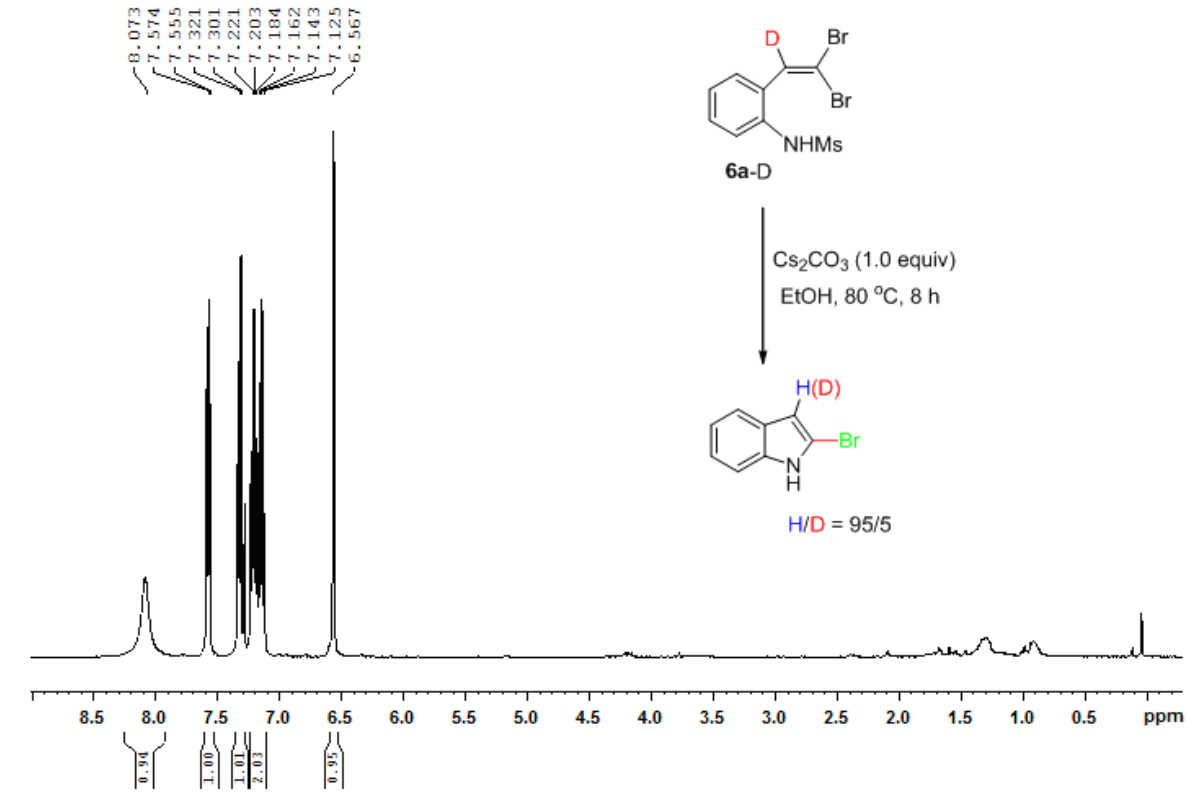
equipped with a magnetic stir bar was charged with 2-(*gem*-dibromovinyl)-*N*-methylsulfonylaniline (**6a**, 0.50 mmol), Cs_2CO_3 (0.50 mmol) and EtOH (2.0 mL). The reaction vessel was placed in an oil bath. After the reaction was carried out at 80 ^oC for 8 h, it was cooled to room temperature, extracted twice with Et_2O. The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography on silica gel (eluant: hexane/ethyl acetate) to give the desired product 2-bromoindole (**8a**).

(4) Typical procedure for the synthesis of 2-bromo-*N*-methylsulfonylindole (9a) via Cs_2CO_3-promoted intramolecular cyclization of 2-(*gem*-dibromovinyl)-*N*-methylsulfonylaniline (6a)

In air atmosphere, a 10 mL of sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with 2-(*gem*-dibromovinyl)-*N*-methylsulfonylaniline (**6a**, 0.50 mmol), Cs_2CO_3 (0.25 mmol) and EtOH (2.0 mL). The reaction vessel was placed in an oil bath. After the reaction was carried out at 80 ^oC for 8 h, it was cooled to room temperature, extracted twice with Et_2O. The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography on silica gel (eluant: hexane/ethyl acetate) to give the desired product 2-bromo-*N*-methylsulfonylindole (**9a**).

3. The ^{1}H NMR spectra of isotope experiment





4. ICP-AES analysis of Cs_2CO_3 sample

Table S1. ICP-MS (Inductively Coupled Plasma Mass Spectroscopy) analysis of metal elements in Cs_2CO_3 sample

Sample	Element (μg/g, ppm)						
	Ni	Co	Fe	Cu	Pd	Ru	Rh
Cs_2CO_3 (99.995%) sample from Aldrich	ND	ND	ND	0.30	0.01	ND	ND

ND: Not detected.

中国科学技术大学理化科学实验中心

检 测 报 告

报告编号：ICP-2012-100 **报告日期：2012.07.20**

样品名称：粉末 **委托单位：淮北师范大学**

送检方式：委托测试 **送检日期：2012.07.16**

样品编号	测定元素含量(μg/g)	
	Cu	Pd
Wang01	0.30	0.01

说明：1．本报告涂改增删无效；

2．本报告只对来样负责；

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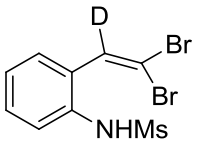
注：采用等离子体质谱仪测定

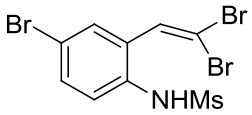
仪器型号：Xseries 2

生产商：Thermo Sciedtific(USA).

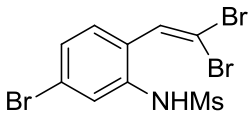
5. Characterization data for starting materials and all the products



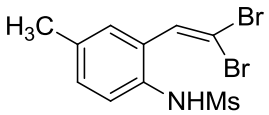
6a-D: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.55–7.53 (m, 1H), 7.45–7.37 (m, 2H), 7.26–7.23 (m, 1H), 6.63 (s, 1H), 3.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 133.76, 130.00, 129.11, 125.79, 122.39, 95.60, 40.15. HRMS (EI) ($[M]^+$) Calcd. for $C_9H_8DBr_2NO_2S$: 353.8784, Found: 353.8788.



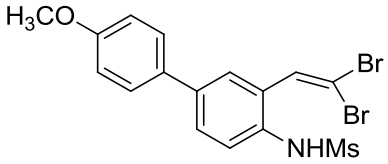
6d: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.57 (d, *J* = 2.0 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.37–7.31 (m, 2H), 6.66 (s, 1H), 3.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 132.89, 132.88, 132.61, 131.80, 130.68, 123.71, 118.78, 97.16, 40.27. HRMS (EI) ($[M]^+$) Calcd. for $C_9H_8NO_2SBr_3$: 430.7826, Found: 430.7829.



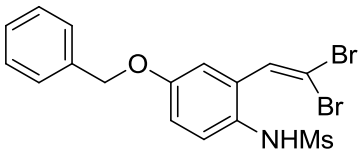
6h: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.74 (s, 1H), 7.36 (d, *J* = 5.2 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 1H), 6.59 (s, 1H), 3.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 135.01, 132.02, 131.16, 128.58, 127.14, 124.18, 123.64, 96.84, 40.45. HRMS (EI) ($[M]^+$) Calcd. for $C_9H_8NO_2SBr_3$: 430.7826, Found: 430.7830.



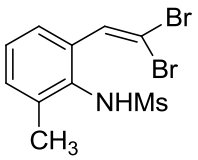
6k: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.50 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.53 (s, 1H), 3.02 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.22, 133.62, 130.97, 130.58, 130.01, 123.66, 94.95, 39.98, 20.89. HRMS (EI) ($[M]^+$) Calcd. for $C_{10}H_{11}NO_2SBr_2$: 366.8877, Found: 366.8875.



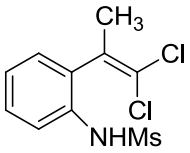
6l: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.62–7.58 (m, 3H), 7.53–7.50 (m, 3H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.42 (s, 1H), 3.87 (s, 3H), 3.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.51, 138.62, 133.19, 132.09, 131.93, 129.57, 128.04, 128.02, 122.97, 114.39, 95.96, 55.39, 40.21. HRMS (EI) ($[M]^+$) Calcd. for $C_{16}H_{15}NO_3SBr_2$: 458.9139, Found: 458.9136.



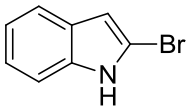
6m: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.53 (s, 1H), 7.44–7.38 (m, 5H), 7.36 (d, *J* = 6.8 Hz, 1H), 7.11 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.19 (s, 1H), 5.09 (s, 2H), 3.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 157.32, 136.31, 133.44, 132.88, 128.71, 128.20, 127.44, 127.35, 126.13, 116.49, 115.71, 94.81, 70.41, 39.98. HRMS (EI) ($[M]^+$) Calcd. for $C_{16}H_{15}NO_3SBr_2$: 458.9139, Found: 458.9142.



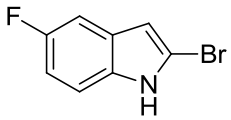
6o: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.58 (s, 1H), 7.33–7.31 (m, 1H), 7.16–7.14 (m, 2H), 6.61 (s, 1H), 2.98 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 138.10, 135.52, 135.23, 131.65, 131.45, 127.87, 127.39, 92.55, 41.64, 18.88. HRMS (EI) ($[M]^+$) Calcd. for $C_{10}H_{11}NO_2SBr_2$: 366.8877, Found: 366.8879.



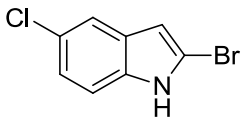
6t: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.63 (d, *J* = 8.4 Hz, 1H), 7.38–7.34 (m, 1H), 7.21–7.18 (m, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.51 (s, 1H), 3.09 (s, 3H), 2.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 133.32, 132.25, 131.22, 129.50, 128.74, 125.13, 120.25, 119.85, 40.15, 22.51. HRMS (EI) ($[M]^+$) Calcd. for $C_{10}H_{11}Cl_2NO_2S$: 278.9888, Found: 278.9885.



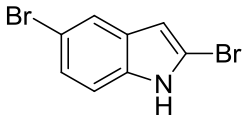
8a[2]**:** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.10 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.21–7.18 (m, 1H), 7.15–7.12 (m, 1H), 6.56 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.36, 128.68, 122.22, 120.47, 119.61, 110.30, 108.65, 104.80.



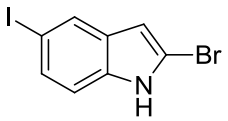
8b: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.11 (s, 1H), 7.18 (m, 2H), 6.94–6.89 (m, 1H), 6.49 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.16 (*J* = 234.2 Hz), 132.96, 129.04 (*J* = 10.4 Hz), 111.02(*J* = 9.4 Hz), 110.60 (*J* = 26.2 Hz), 110.25, 105.01 (*J* = 4.5 Hz), 104.72 (*J* = 23.8 Hz). HRMS (EI) ($[M]^+$) Calcd. for C_8H_5NFBr: 212.9589, Found: 212.9593.



8c: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.18 (s, 1H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.23–7.21 (m, 1H), 7.15–7.13 (m, 1H), 6.49 (br, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 134.71, 129.65, 126.24, 122.56, 119.05, 111.27, 110.09, 104.56. HRMS (EI) ($[M]^+$) Calcd. for C_8H_5NClBr: 228.9294, Found: 228.9297.

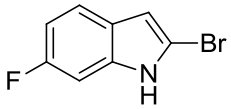


8d[2]**:** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.24 (s, 1H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.28–7.26 (m, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 135.01, 130.30, 125.12, 122.12, 113.77, 111.75, 110.06, 104.43.

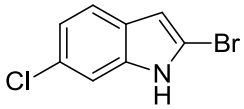


8e[2]**:** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.36 (s, 1H), 7.87 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.47 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 135.46, 131.09, 130.57, 128.33,

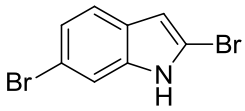
112.20, 109.71, 104.07, 84.01.



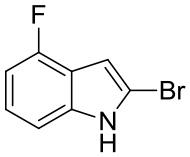
8f[2]**:** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.14 (s, 1H), 7.43 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.90–6.86 (m, 1H), 6.50 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.80 (d, *J* = 237.3 Hz), 136.18 (d, *J* = 12.4 Hz), 125.25 (d, *J* = 1.2 Hz), 120.42 (d, *J* = 9.8 Hz), 109.24 (d, *J* = 24.2 Hz), 108.27 (d, *J* = 3.2 Hz), 104.84, 96.97 (d, *J* = 26.4 Hz).



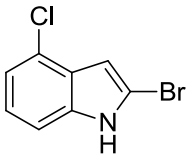
8g: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.07 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.18 (s, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.61, 128.19, 127.26, 121.29, 120.50, 110.34, 109.32, 104.96. HRMS (EI) ($[M]^+$) Calcd. for C_8H_5NClBr: 228.9294, Found: 228.9297.



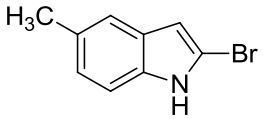
8h: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05 (s, 1H), 7.36 (s, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 137.02, 127.57, 123.87, 120.82, 115.76, 113.23, 109.31, 105.03. HRMS (EI) ($[M]^+$) Calcd. for $C_8H_5NBr_2$: 272.8789, Found: 272.8792.



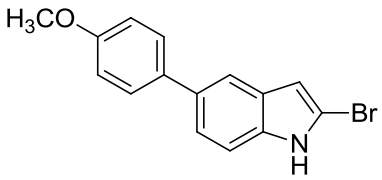
8i: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.19 (s, 1H), 7.09–7.06 (m, 2H), 6.80–6.76 (m, 1H), 6.62 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.80 (d, *J* = 237.3 Hz), 136.18 (d, *J* = 12.4 Hz), 125.25 (d, *J* = 1.2 Hz), 120.42 (d, *J* = 9.9 Hz), 109.24 (d, *J* = 24.2 Hz), 108.27 (d, *J* = 3.2 Hz), 104.84, 96.97 (d, *J* = 26.3 Hz). HRMS (EI) ($[M]^+$) Calcd. for C_8H_5NFBr: 212.9589, Found: 212.9592.



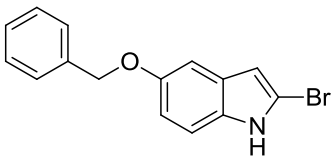
8j: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.31 (s, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.10 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.92, 127.57, 124.77, 122.79, 120.21, 109.44, 108.90, 103.48. HRMS (EI) ($[M]^+$) Calcd. for C_8H_5NClBr: 228.9294, Found: 228.9296.



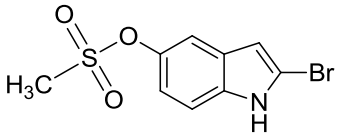
8k: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.91 (s, 1H), 7.30 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.43 (s, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 134.68, 129.73, 128.92, 123.74, 119.27, 109.94, 108.50, 104.35, 21.37. HRMS (EI) ($[M]^+$) Calcd. for C_9H_8NBr: 208.9840, Found: 208.9842.



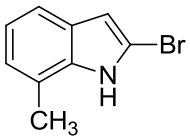
8l: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.09 (s, 1H), 7.68 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.38–7.31 (m, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.56 (s, 1H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.64, 135.61, 134.74, 133.77, 129.25, 128.30, 121.86, 117.62, 114.15, 110.46, 109.07, 105.12, 55.36. HRMS (EI) ($[M]^+$) Calcd. for $C_{15}H_{12}NOBr$: 301.0102, Found: 301.0106.



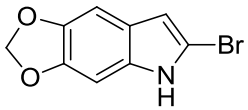
8m: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.86 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.31–7.27 (m, 2H), 7.23 (d, *J* = 6.8 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.97 (s, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.34 (s, 1H), 4.98 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.73, 137.51, 131.79, 129.20, 128.59, 127.89, 127.60, 113.08, 111.17, 109.02, 104.75, 103.25, 70.88. HRMS (EI) ($[M]^+$) Calcd. for $C_{15}H_{12}NOBr$: 301.0102, Found: 301.0103.



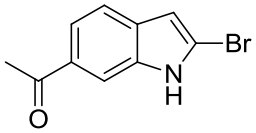
8n: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.41 (s, 1H), 7.45 (s, 1H), 7.30–7.27 (m, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.55 (s, 1H), 3.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 143.46, 134.98, 128.98, 116.49, 112.63, 111.34, 110.84, 105.30, 36.98. HRMS (EI) ($[M]^+$) Calcd. for $C_{16}H_{15}NO_3SBr_2$: 458.9139, Found: 458.9142.



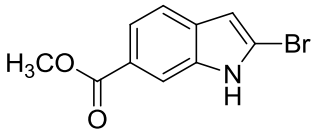
8o: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.99 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.04–7.00 (m, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.52 (s, 1H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.17, 128.36, 122.89, 120.73, 119.61, 117.41, 108.36, 105.40, 16.55. HRMS (EI) ($[M]^+$) Calcd. for C_9H_8NBr: 208.9840, Found: 208.9841.



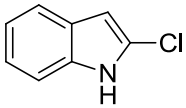
8p: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.99 (s, 1H), 6.93 (s, 1H), 6.78 (s, 1H), 6.40 (d, *J* = 1.6 Hz, 1H), 5.94 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 144.92, 143.32, 131.19, 122.59, 105.32, 105.00, 100.64, 98.48, 91.59. HRMS (EI) ($[M]^+$) Calcd. for $C_9H_6NO_2Br$: 238.9582, Found: 238.9587.



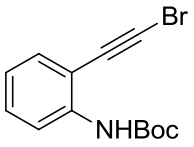
8q: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.09 (s, 1H), 8.03 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 6.58 (s, 1H), 2.66 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 198.53, 136.07, 132.60, 131.40, 120.94, 119.22, 113.31, 111.24, 105.22, 26.79. HRMS (EI) ($[M]^+$) Calcd. for $C_{10}H_8NOBr$: 236.9789, Found: 236.9794.



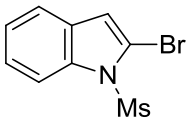
8r[2]**:** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.86 (s, 1H), 8.13 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 6.59 (s, 1H), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.14, 135.78, 132.37, 123.70, 121.51, 119.21, 112.69, 105.23, 52.19.



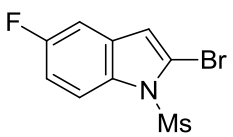
8s[3]**:** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.91 (s, 1H), 7.50 (d, *J* = 0.8 Hz, 1H), 7.23–7.11 (m, 3H), 6.39 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 135.00, 128.16, 123.35, 122.29, 120.63, 119.89, 110.43, 100.79.



A: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.13 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.35–7.30 (m, 1H), 7.13 (s, 1H), 6.98–6.94 (m, 1H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 152.35, 140.27, 132.41, 129.96, 122.09, 117.85, 110.65, 81.01, 75.93, 56.13, 28.29. HRMS (EI) ($[M]^+$) Calcd. for $C_{13}H_{14}NO_2Br$: 295.0208, Found: 295.0206.

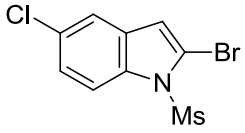


9a:[4] Colorless oil. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.08 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.33–7.28 (m, 2H), 6.83 (d, *J* = 6 .0 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 137.24, 129.40, 124.97, 124.07, 120.13, 114.76, 114.62, 109.45, 41.78.

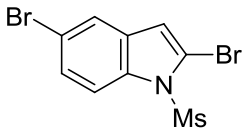


9b:[4] White solid, m.p. 75–77 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.06–8.02 (m, 1H), 7.18–7.16 (m, 1H), 7.07–7.03 (m, 1H), 6.82 (s, 1H), 3.22 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ

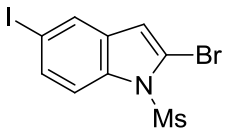
= 159.8 (d, *J* = 240.3 Hz), 133.5 (d, *J* = 1.3 Hz), 130.2 (d, *J* = 10.1 Hz), 116.0 (d, *J* = 9.1 Hz), 114.2 (d, *J* = 3.9 Hz), 112.8 (d, *J* = 25.0 Hz), 111.1, 105.6 (d, *J* = 24.2 Hz), 41.8.



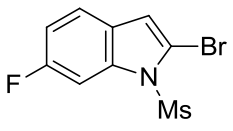
9c:[4] White solid, m.p. 116–118 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.01 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 1.2 Hz, 1H), 7.28–7.26 (m, 1H), 6.80 (s, 1H), 3.23 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 135.48, 130.39, 129.89, 125.10, 119.59, 115.82, 113.67 110.90, 42.04.



9d: White solid, m.p. 132–134 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.95 (d, *J* = 9.2 Hz, 1H), 7.63 (s, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 6.79 (s, 1H), 3.23 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 135.83, 130.86, 127.76, 122.64, 117.51, 116.14, 113.52, 110.79, 42.08. HRMS (EI) ($[M]^+$): calcd for $C_9H_7NO_2Br_2S$, 350.8564; found, 350.8566.

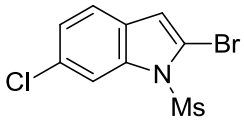


9e: White solid, m.p. 110–112 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.85 (d, *J* = 7.2 Hz, 2H), 7.60–7.58 (m, 1H), 6.78 (s, 1H), 3.23 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 136.45, 133.40, 131.40, 128.79, 116.47, 113.24, 110.46, 88.20, 42.07. HRMS (EI) ($[M]^+$): calcd for $C_9H_7NO_2SBrI$, 398.8426; found, 398.8423.

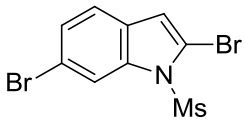


9f:[4] White solid, m.p. 97–99 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.84 (d, *J* = 10.4 Hz, 1H), 7.45–7.42 (m, 1H), 7.07–7.02 (m, 1H), 6.82 (s, 1H), 3.25 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 160.84 (d, *J* = 241.1 Hz), 137.12 (d, *J* = 12.7 Hz), 125.59 (d, *J* = 1.6 Hz), 120.78 (d, *J* = 9.7 Hz), 114.13 (d, *J* = 1.2 Hz), 112.52 (d, *J* = 24.1 Hz), 108.93 (d, *J* = 3.8 Hz), 102.39 (d, *J* = 29.6

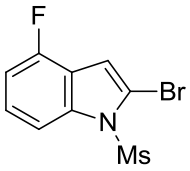
Hz), 42.06.



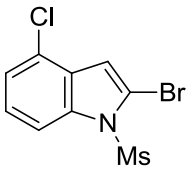
9g:[4] White solid, m.p. 137–139 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.13 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 6.82 (s, 1H), 3.26 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 137.24, 131.08, 127.75, 124.73, 120.78, 114.96, 114.06, 109.88, 42.16.



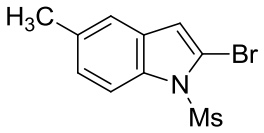
9h: White solid, m.p. 123–125 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.27 (s, 1H), 7.41–7.35 (m, 2H), 6.81 (s, 1H), 3.25 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 137.53, 128.10, 127.40, 121.11, 118.75, 117.74, 114.10, 109.92, 42.20. HRMS (EI) ($[M]^+$): calcd for $C_9H_7NO_2SBr$, 350.8564; found, 350.8561.



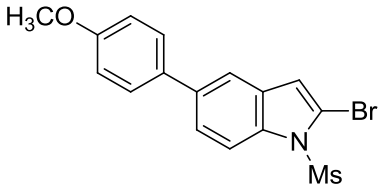
9i: White solid, m.p. 104–106 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.87 (d, *J* = 8.8 Hz, 1H), 7.28–7.22 (m, 1H), 6.99–6.95 (m, 2H), 3.25 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 154.55 (d, *J* = 248.1 Hz), 139.02 (d, *J* = 8.8 Hz), 125.61 (d, *J* = 7.5 Hz), 118.58 (d, *J* = 22.4 Hz), 110.80 (d, *J* = 4.1 Hz), 109.78, 109.31 (d, *J* = 2.3 Hz), 109.16, 42.07. HRMS (EI) ($[M]^+$): calcd for $C_9H_7NO_2SFBr$, 290.9365; found, 290.9359.



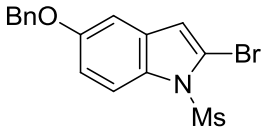
9j:[4] White solid, m.p. 109–111 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.00 (d, *J* = 7.6 Hz, 1H), 7.29–7.22 (m, *2*H), 6.99 (d, *J* = 1.2 Hz, 1H), 3.25 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 137.66, 128.21, 125.56, 125.25, 123.80, 113.20, 112.51, 110.28, 42.16.



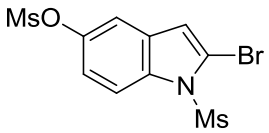
9k: White solid, m.p. 107–109 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.95 (d, *J* = 8.8 Hz, 1H), 7.29 (s, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.77 (s, 1H), 3.16 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 135.51, 133.78, 129.63, 126.32, 119.95, 114.53, 114.47, 109.36, 41.47, 21.17. HRMS (EI) ($[M]^+$): calcd for $C_{10}H_{10}NO_2SBr$: 286.9616, found: 286.9618.



9l: White solid, m.p. 153–155 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.11 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.56–7.50 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 3.87 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 159.19, 137.16, 136.26, 133.29, 129.93, 128.31, 124.10, 117.85, 114.97, 114.81, 114.32, 109.85, 55.39, 41.73. HRMS (EI) ($[M]^+$): calcd for $C_{16}H_{14}NO_3SBr$, 378.9878; found, 378.9879.

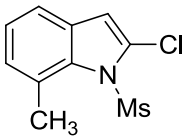


9m: White solid, m.p. 124–126 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.98 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.43–7.39 (t, *J* = 7.2 Hz, 2H), 7.37–7.33 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 9.2 Hz, 2H), 6.77 (s, 1H), 5.11 (s, 2H), 3.15 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 155.88, 136.87, 132.03, 130.31, 128.65, 128.06, 127.49, 115.82, 114.67, 114.48, 109.95, 103.85, 70.52, 41.44. HRMS (EI) ($[M]^+$): calcd for $C_{16}H_{14}NO_3SBr$, 378.9878; found, 378.9883.

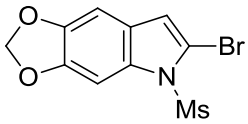


9n: White solid, m.p. 167–168 °C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.14 (d, *J* = 9.2 Hz, 1H), 7.47 (d, *J* = 1.2 Hz, 1H), 7.24–7.21 (dd, J_1 = 9.2 Hz, J_2 = 2.0 Hz, 1H), 6.87 (s, 1H), 3.27 (s, 3H), 3.19 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 145.51, 135.56, 130.10, 118.78, 116.02, 114.06,

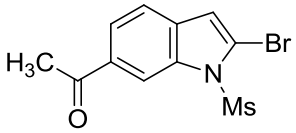
113.35, 111.48, 42.23, 37.43. HRMS (EI) ([M]$^+$): calcd for $C_{10}H_{10}NO_5S_2Br$, 366.9184; found, 366.9188.



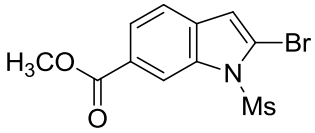
9o: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.93 (s, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.13–7.02 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.49 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.57, 128.41, 122.19, 120.90, 119.31, 117.21, 111.16, 104.42, 41.37, 16.95. HRMS (EI) ([M]$^+$): calcd for $C_{10}H_{10}NO_2SBr$: 286.9616, found: 286.9621.



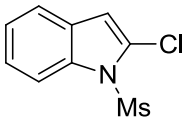
9p:[4] White solid. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.61 (s, 1H), 6.86 (s, 1H), 6.70 (s, 1H), 6.00 (s, 2H), 3.16 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 146.69, 145.41, 132.02, 123.64, 114.78, 106.41, 101.41, 98.79, 96.82, 41.51.



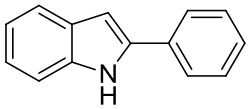
9q: White solid. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.71 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 6.90 (s, 1H), 3.30 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 197.49, 136.78, 133.91, 132.85, 123.85, 119.98, 115.46, 114.20, 113.02, 42.35, 26.72. HRMS (EI) ([M]$^+$): calcd for $C_{11}H_{10}NO_3SBr$, 314.9565; found, 314.9564.



9r:[4] White solid, m.p. 158–160 ^{o}C. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.77 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 6.89 (s, 1H), 3.95 (s, 3H) 3.29 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 167.02, 136.56, 132.79, 126.68, 125.19, 119.79, 116.31, 114.19, 112.77, 52.28, 42.28.

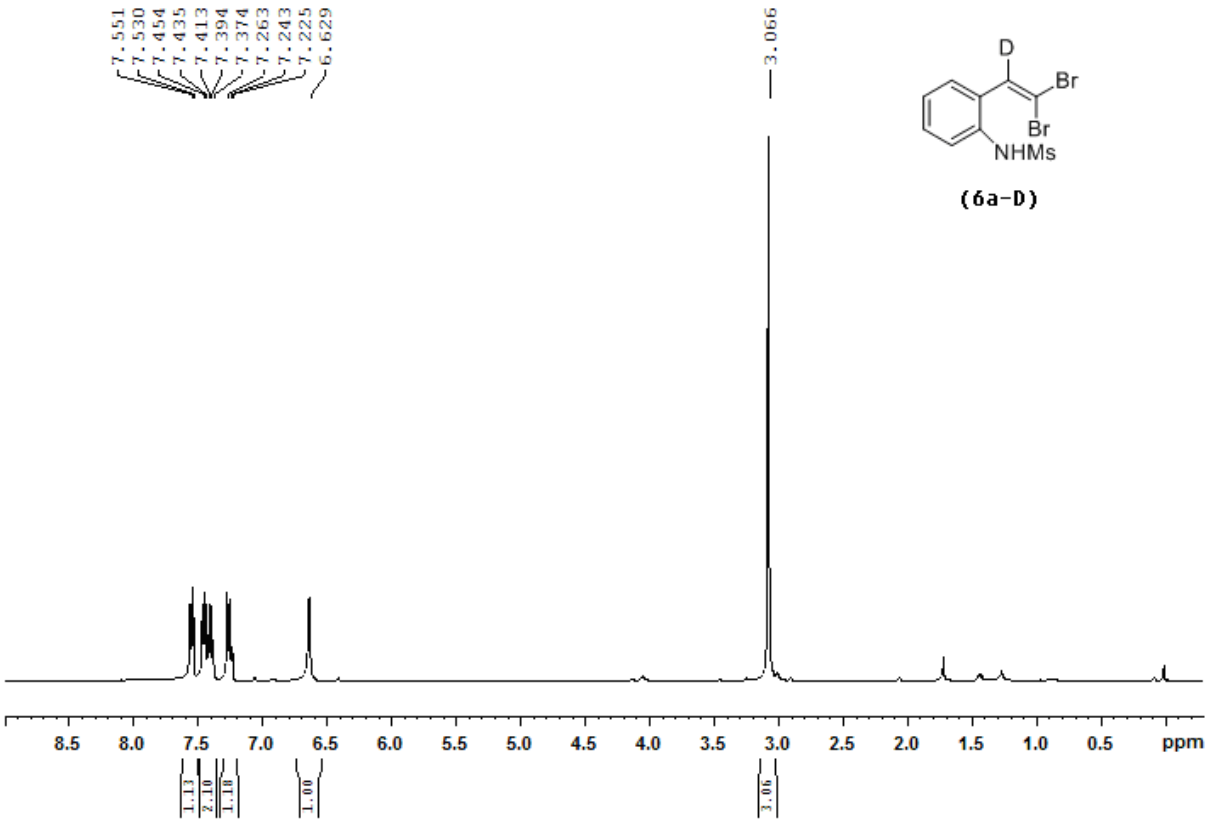


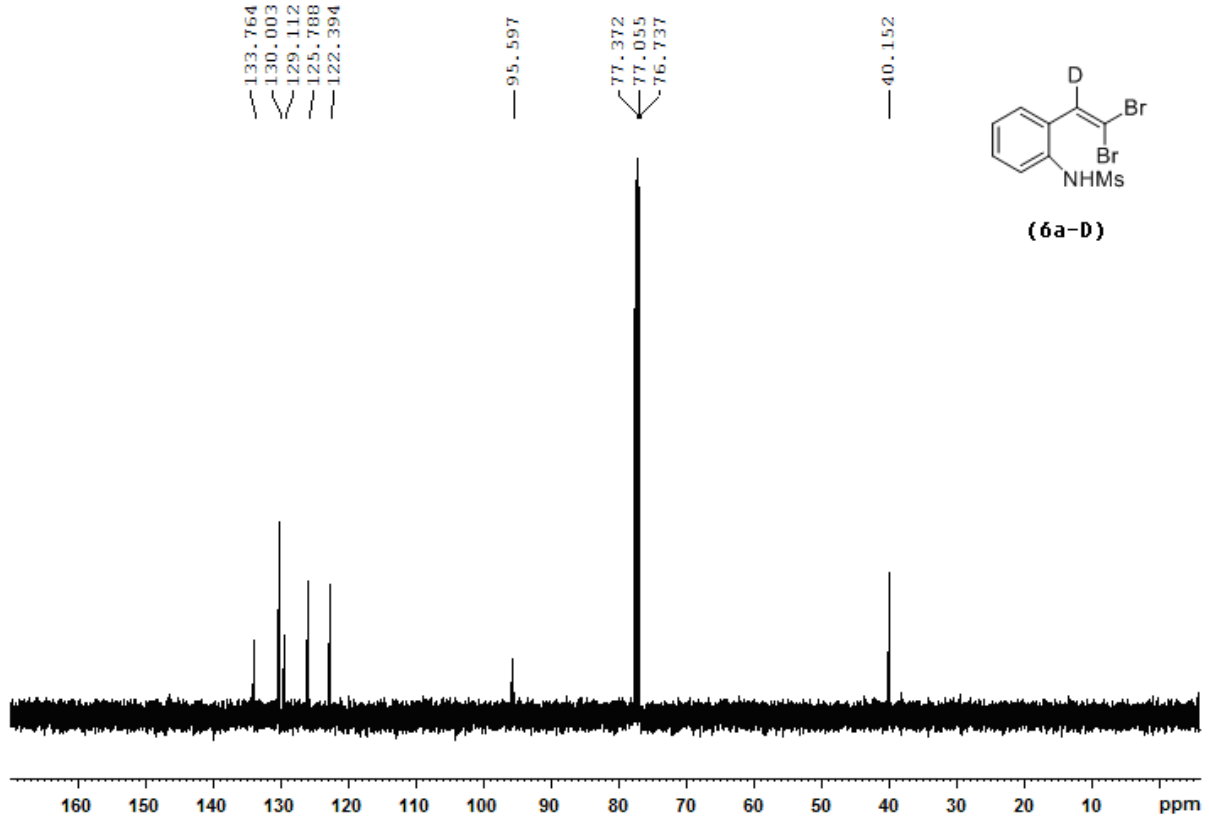
9s: Colorless oil. ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.07 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.36–7.27 (m, 2H), 6.70 (s, 1H), 3.22 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 136.25, 128.20, 124.95, 124.26, 124.13, 120.24, 114.54, 109.75, 41.77. HRMS (EI) ($[M]^+$): calcd for $C_9H_8NO_2SCl$, 228.9964; found, 228.9965.

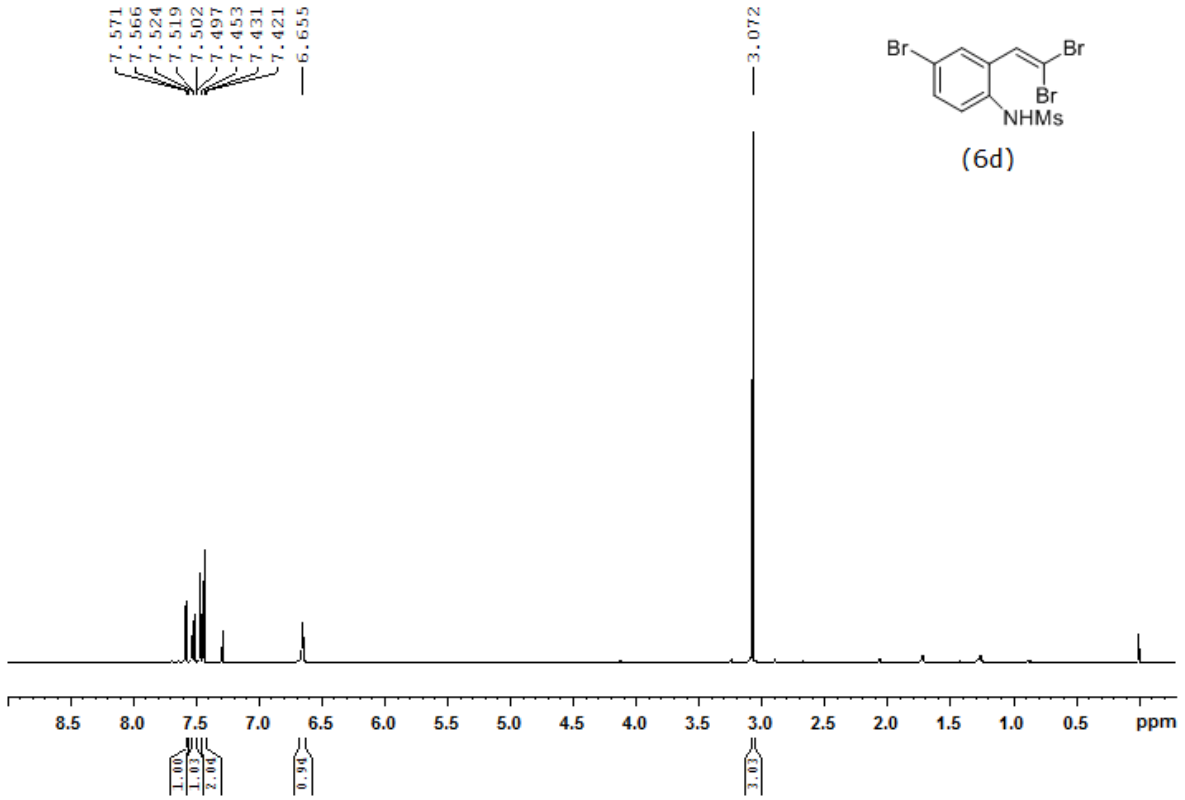


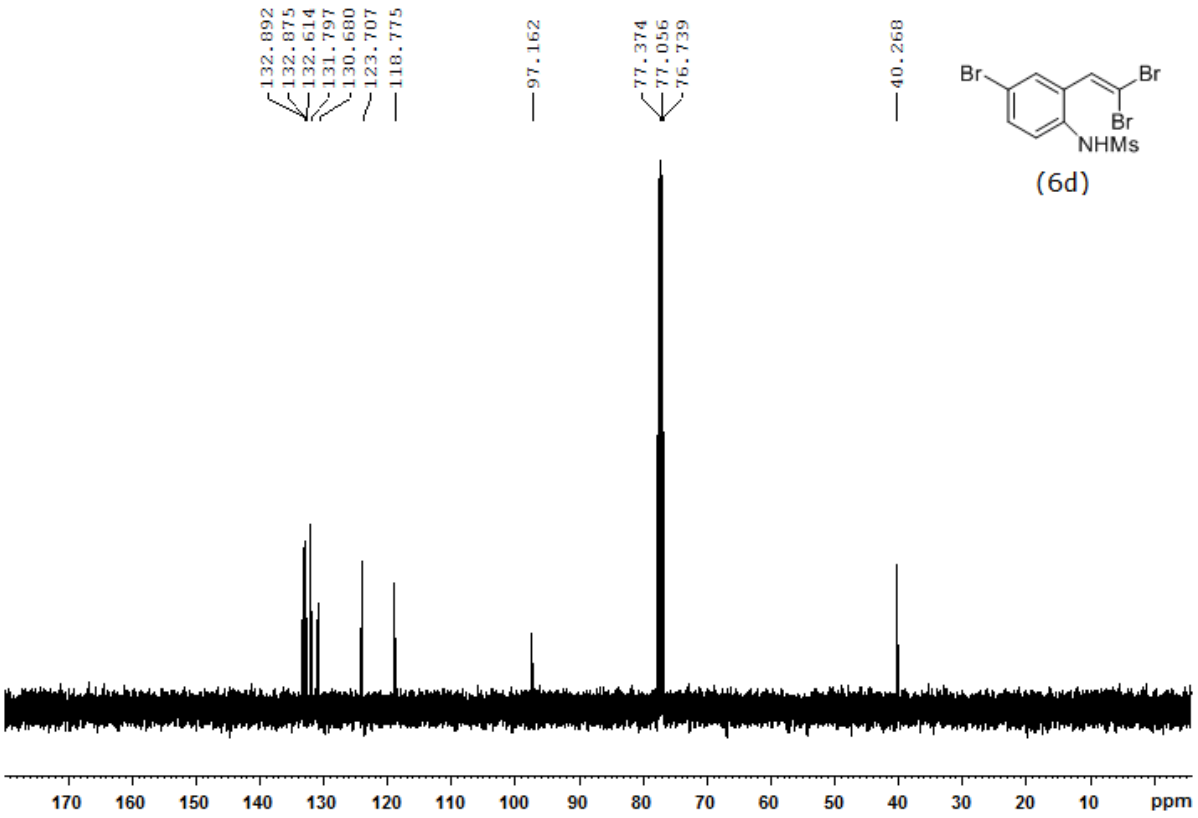
10a[1]**:** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.33 (s, 1H), 7.49–7.46 (m, 3H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.38–7.34 (m, 1H), 7.27–7.23 (m, 2H), 7.19–7.16 (m, 1H), 6.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 137.92, 136.86, 132.41, 129.31, 129.04, 127.73, 125.19, 122.38, 120.70, 120.31, 110.94, 100.03.

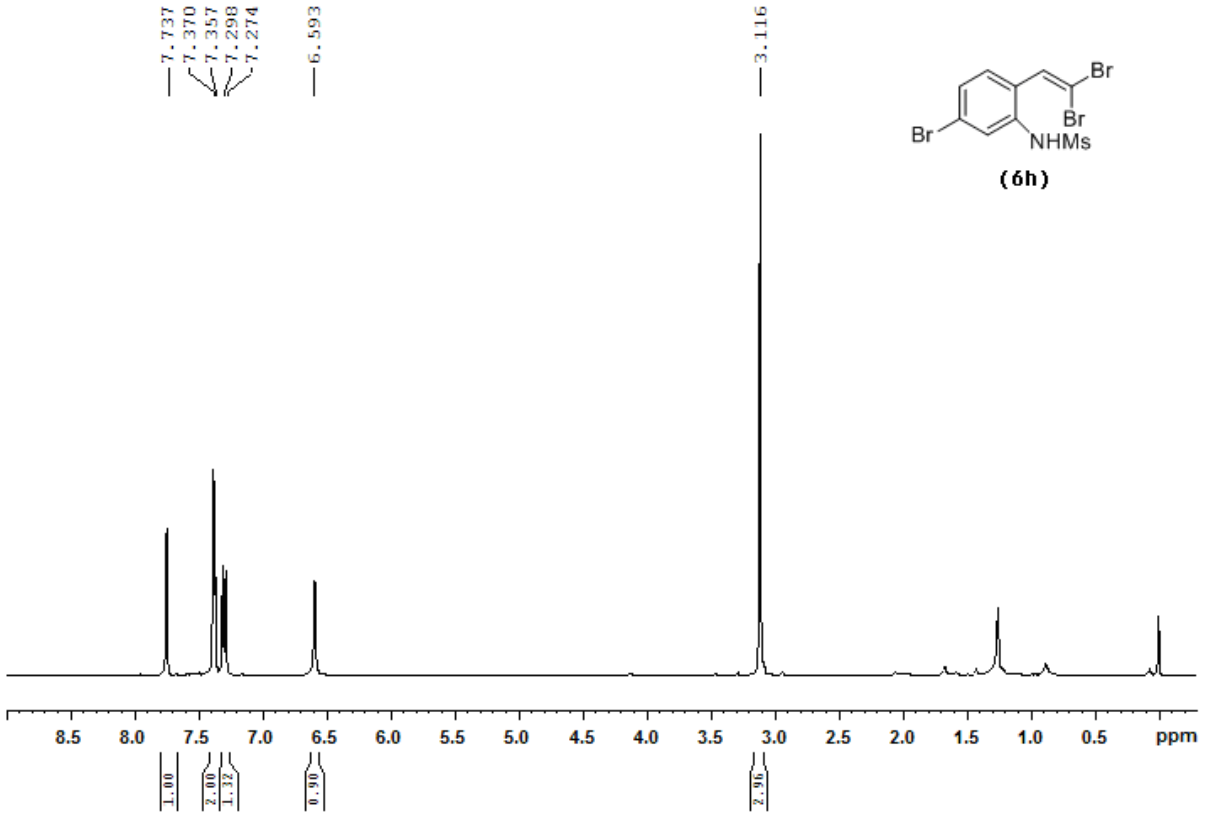
6. ^{1}H and ^{13}C NMR spectra of compounds

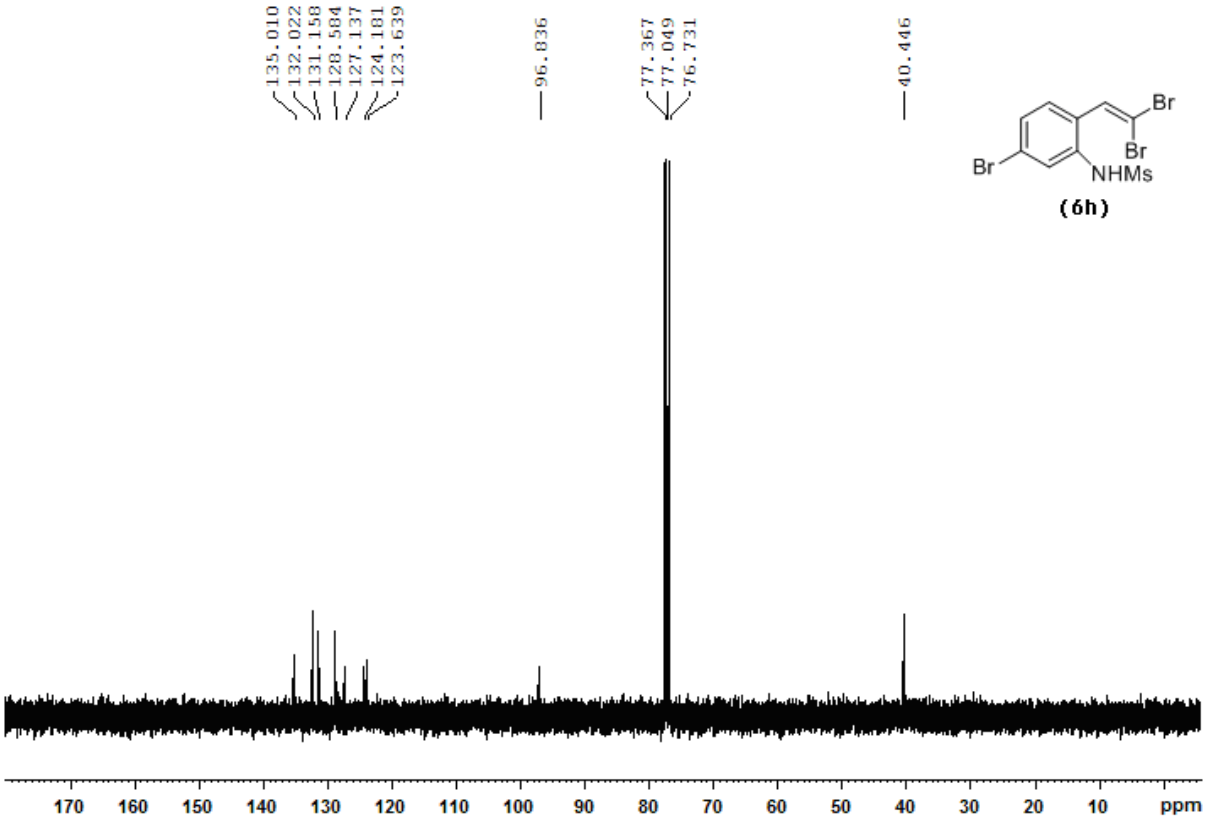


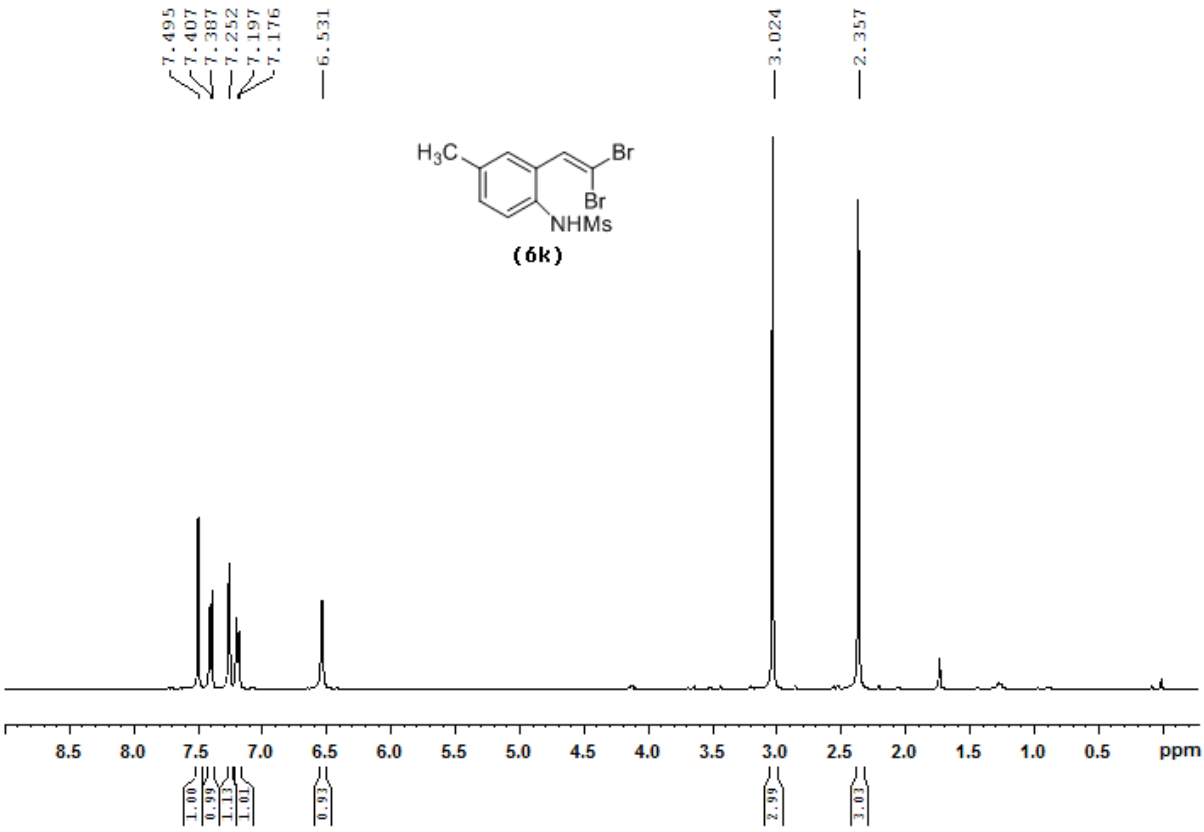


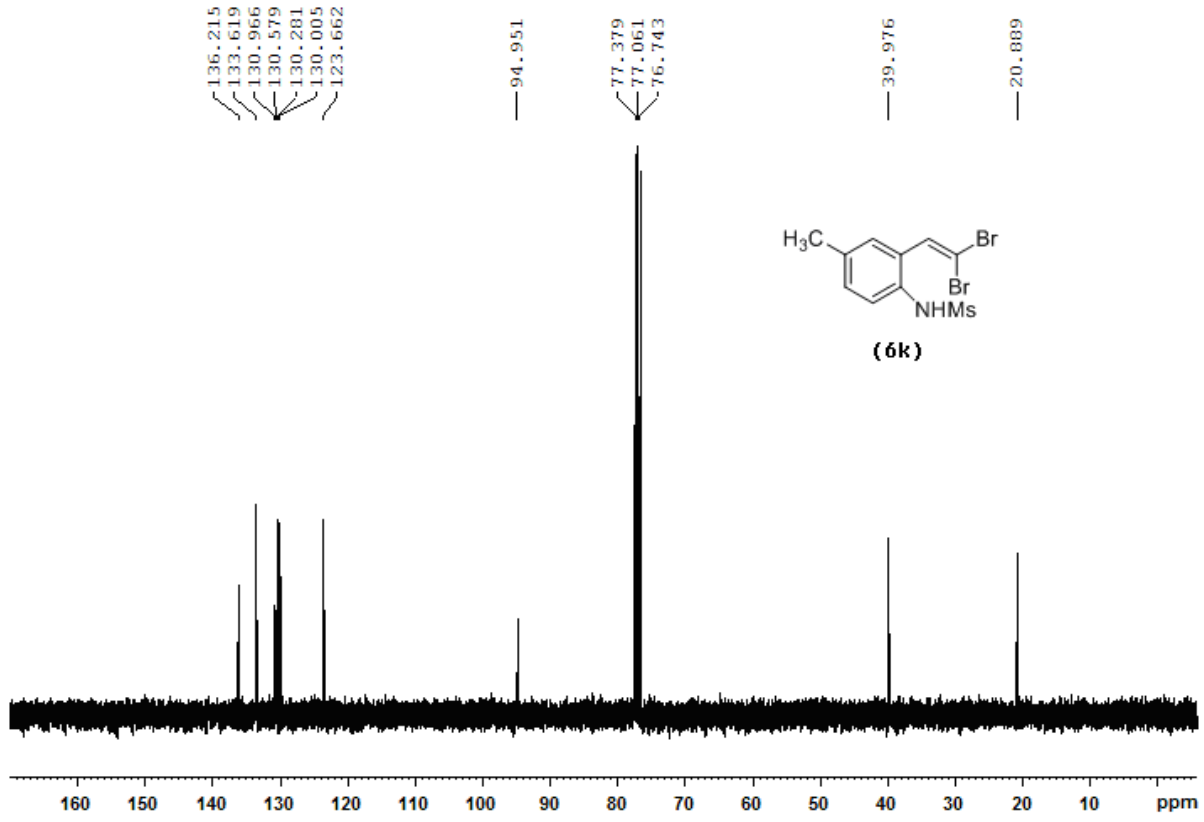


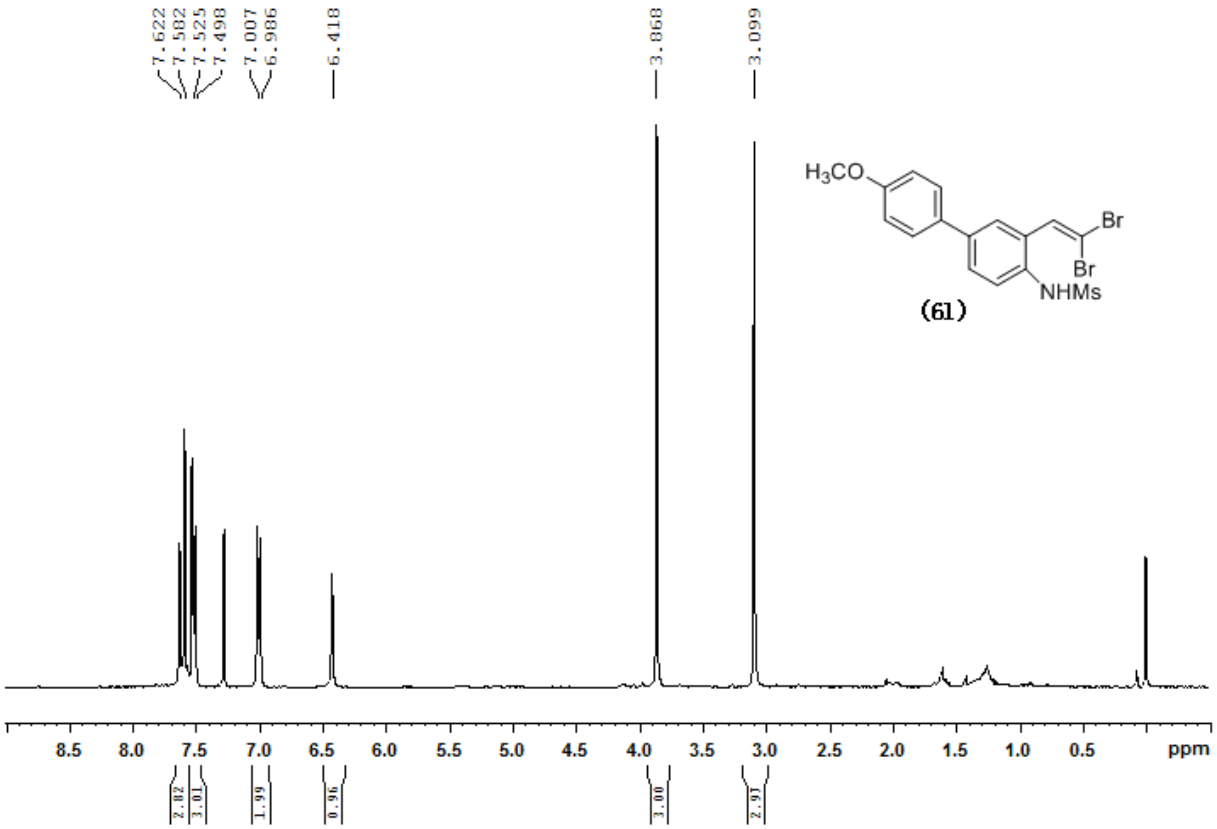


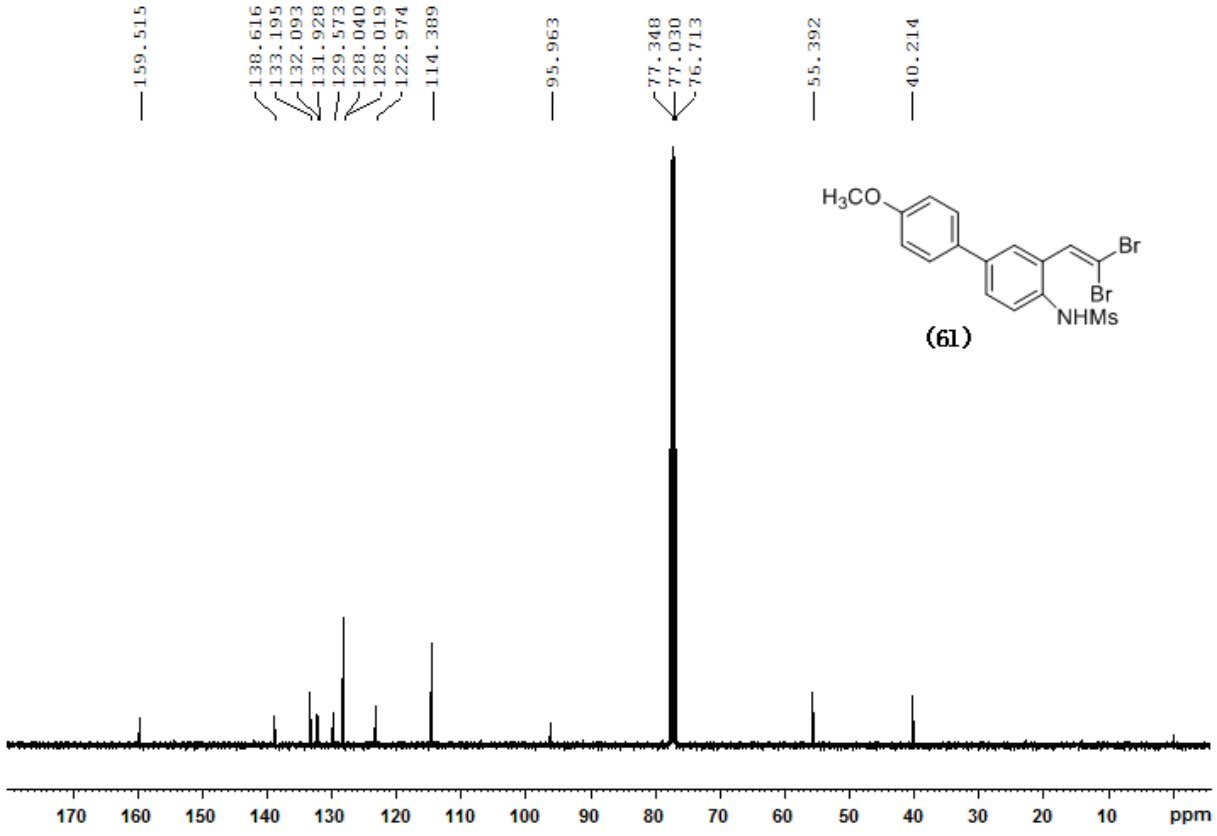


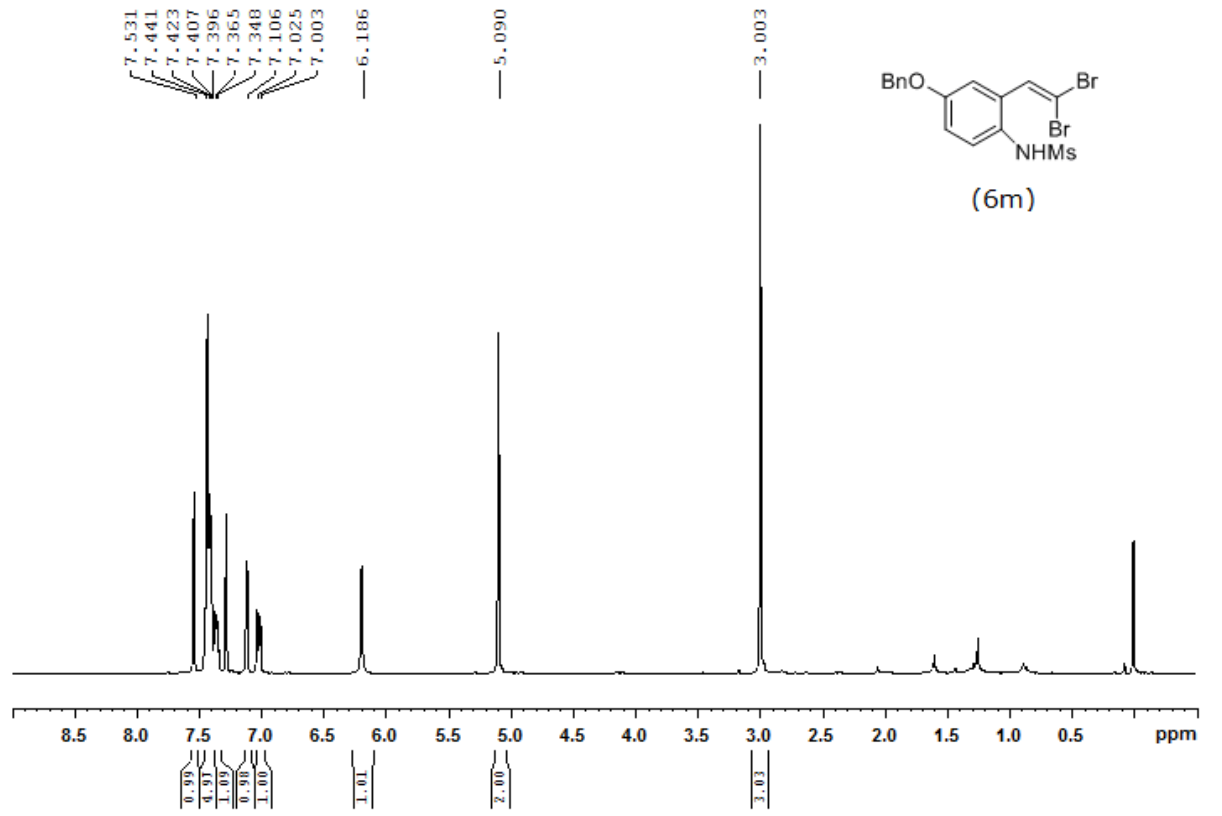


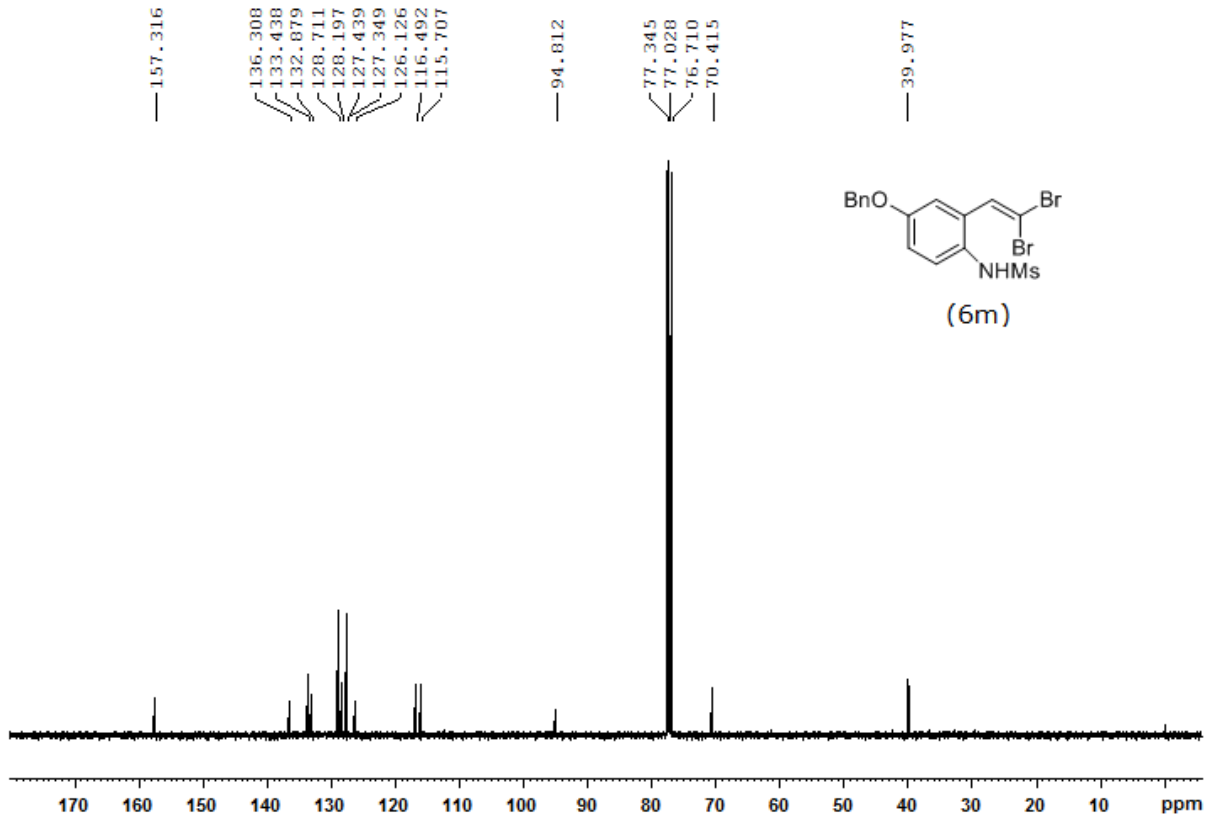


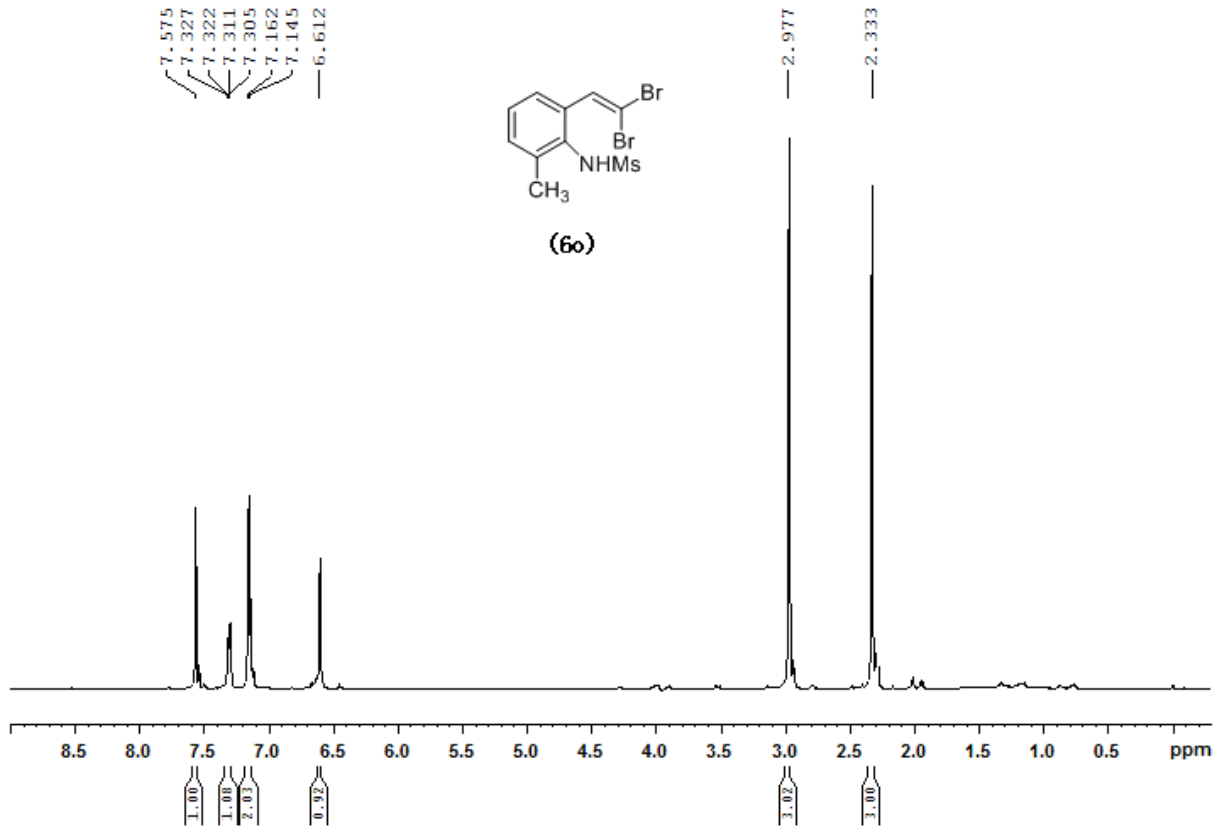



7.622
7.582
7.525
7.498
7.007
6.986
6.418
3.868
3.099
H3CO
Br
Br
NHMs
(61)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.82
3.01
1.99
0.96
3.00
2.97

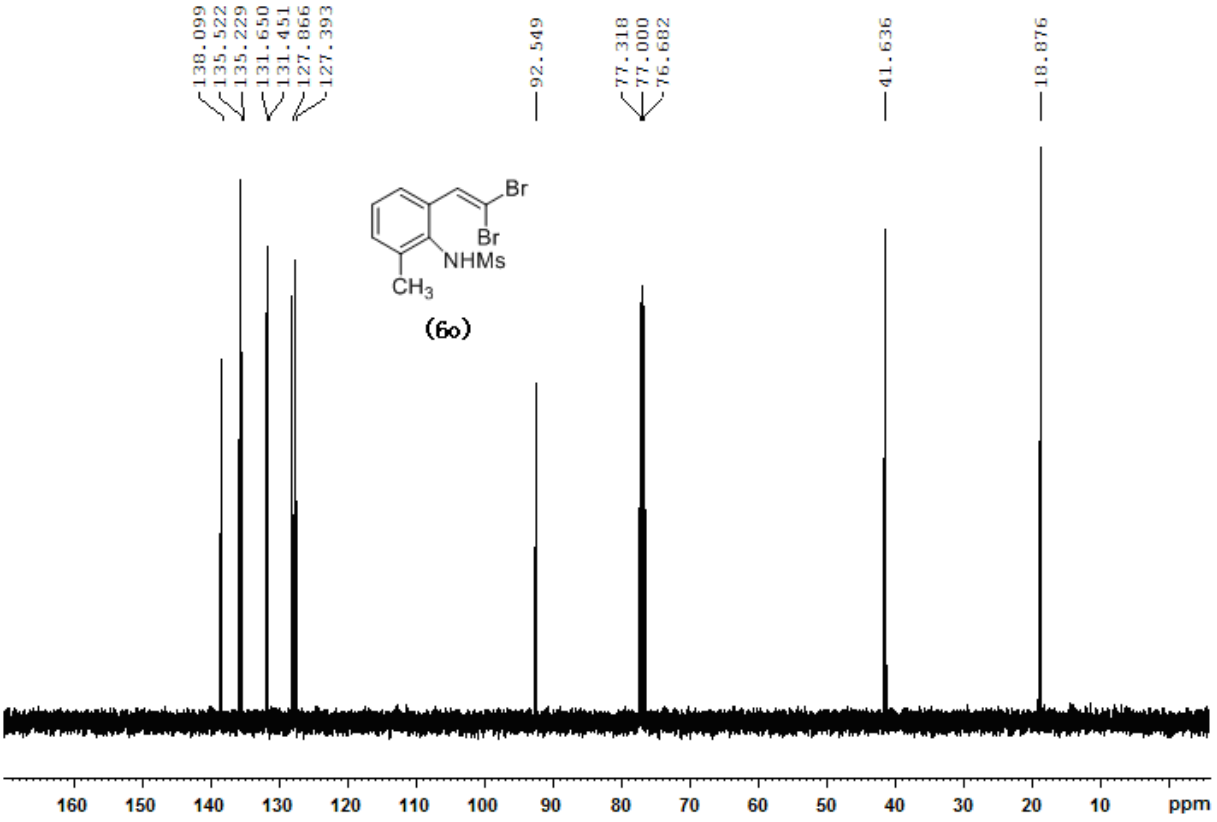

159.515
138.616
133.195
132.093
131.928
129.573
128.040
128.019
122.974
114.389
95.963
77.348
77.030
76.713
55.392
40.214
H3CO
Br
Br
NHMs
(61)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



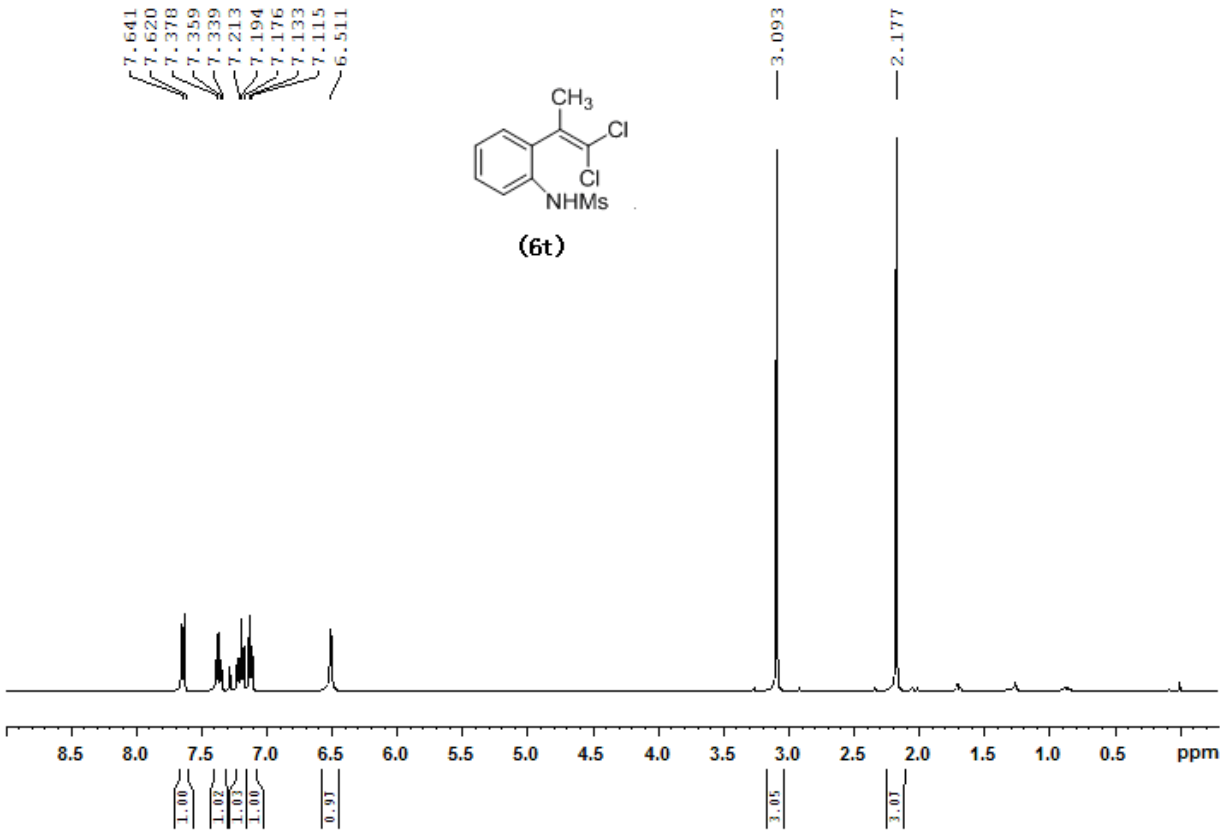


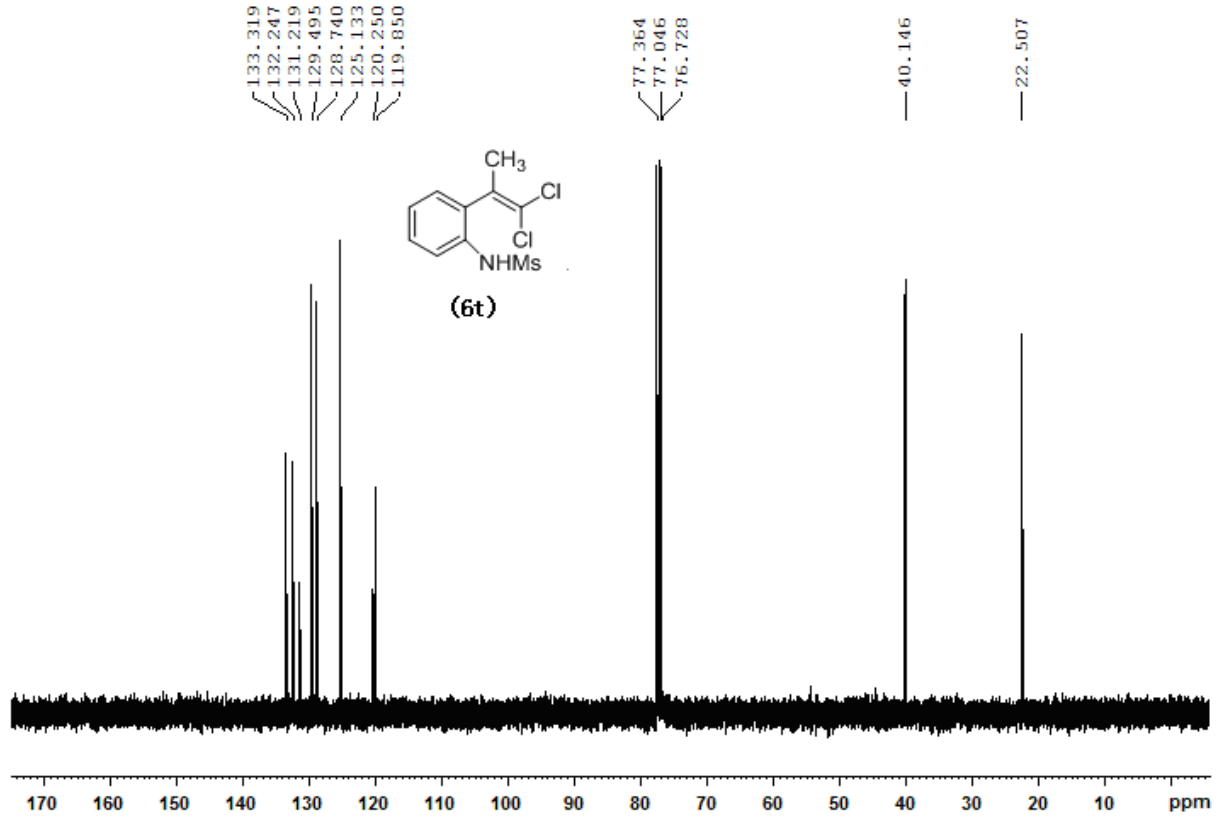


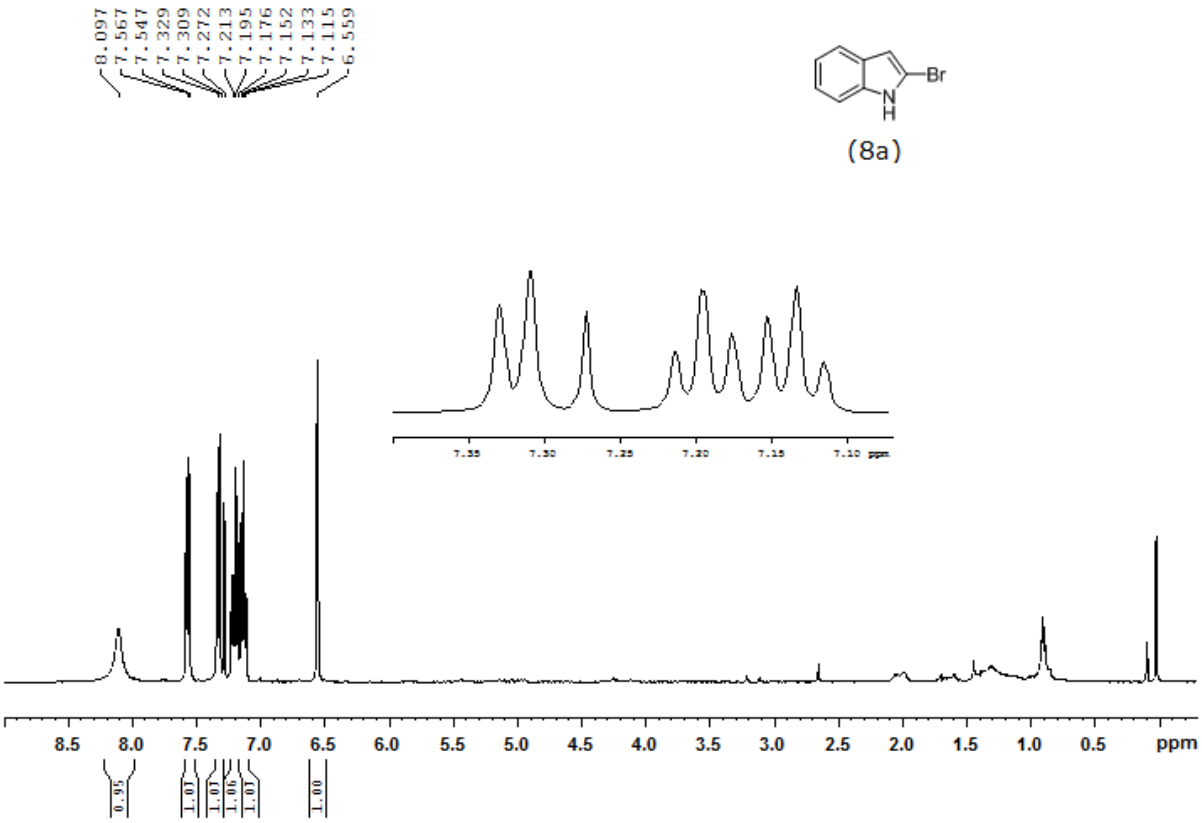
(6o)

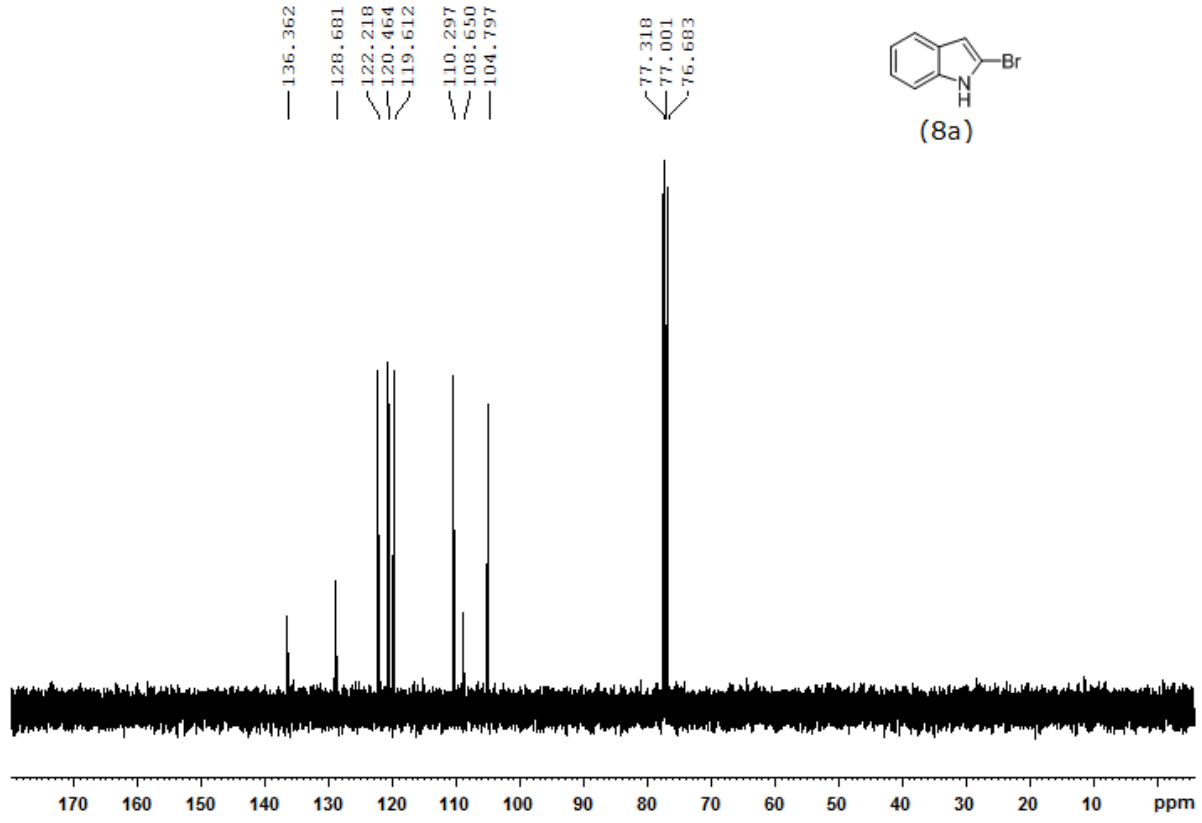


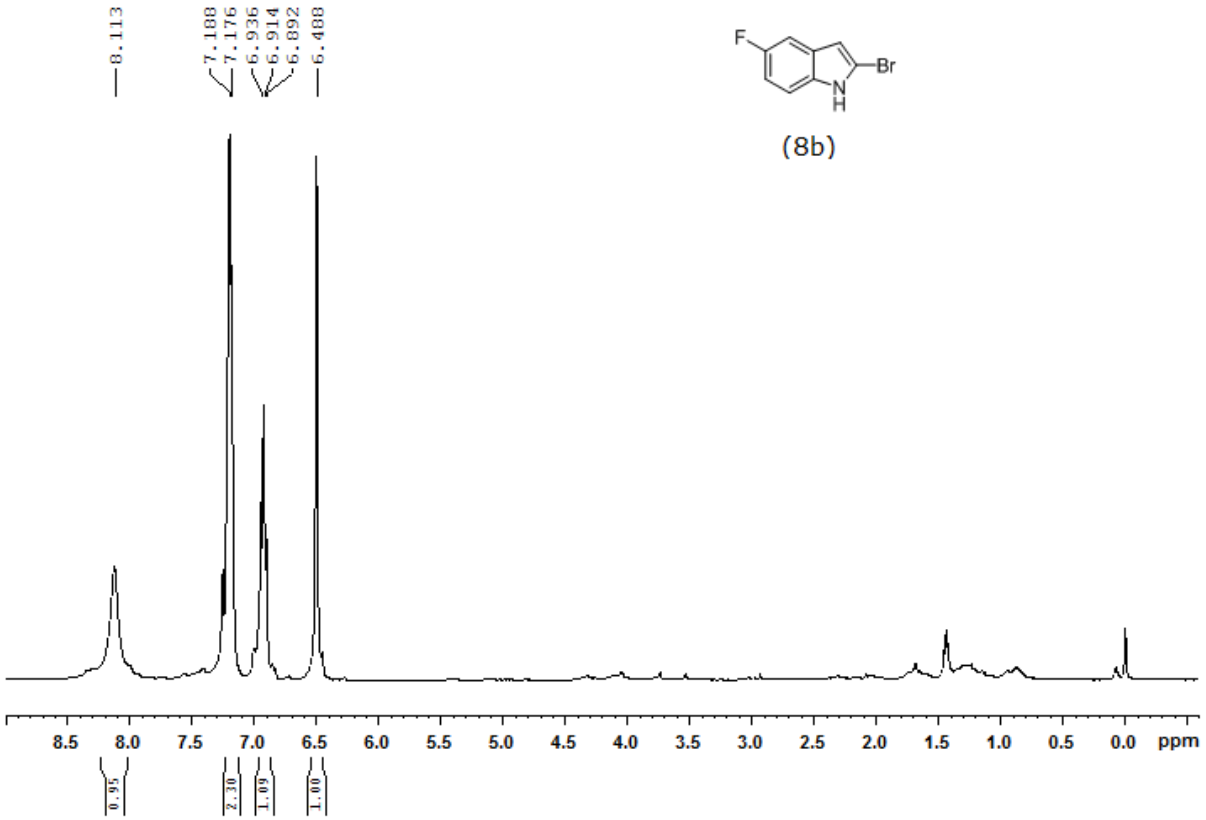
(6o)

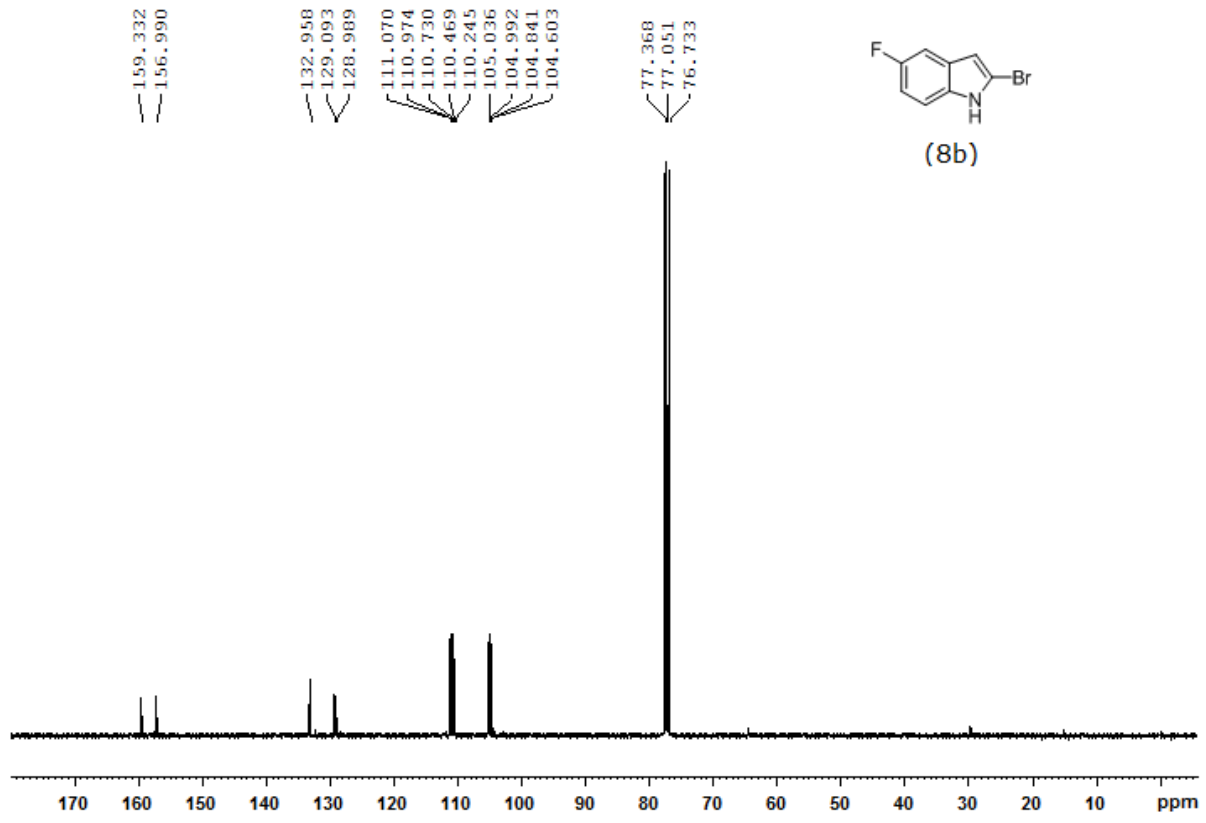


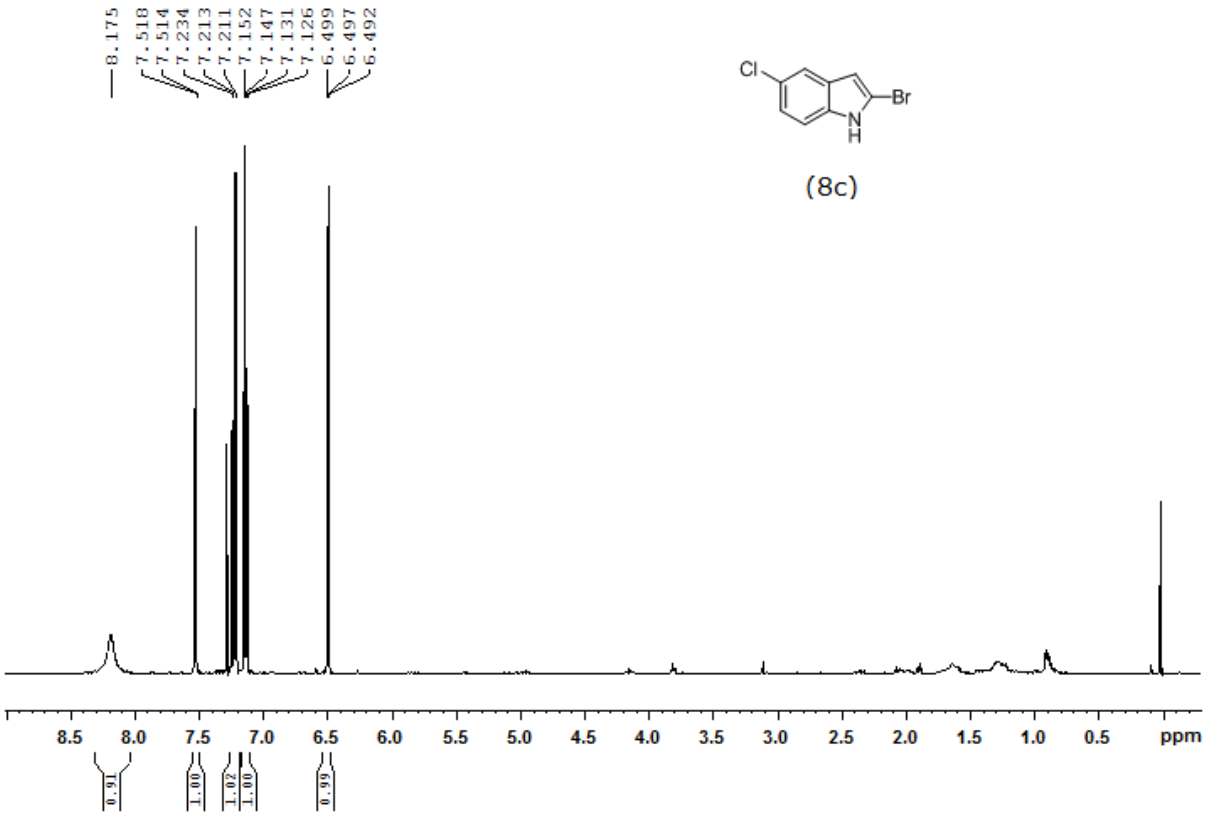


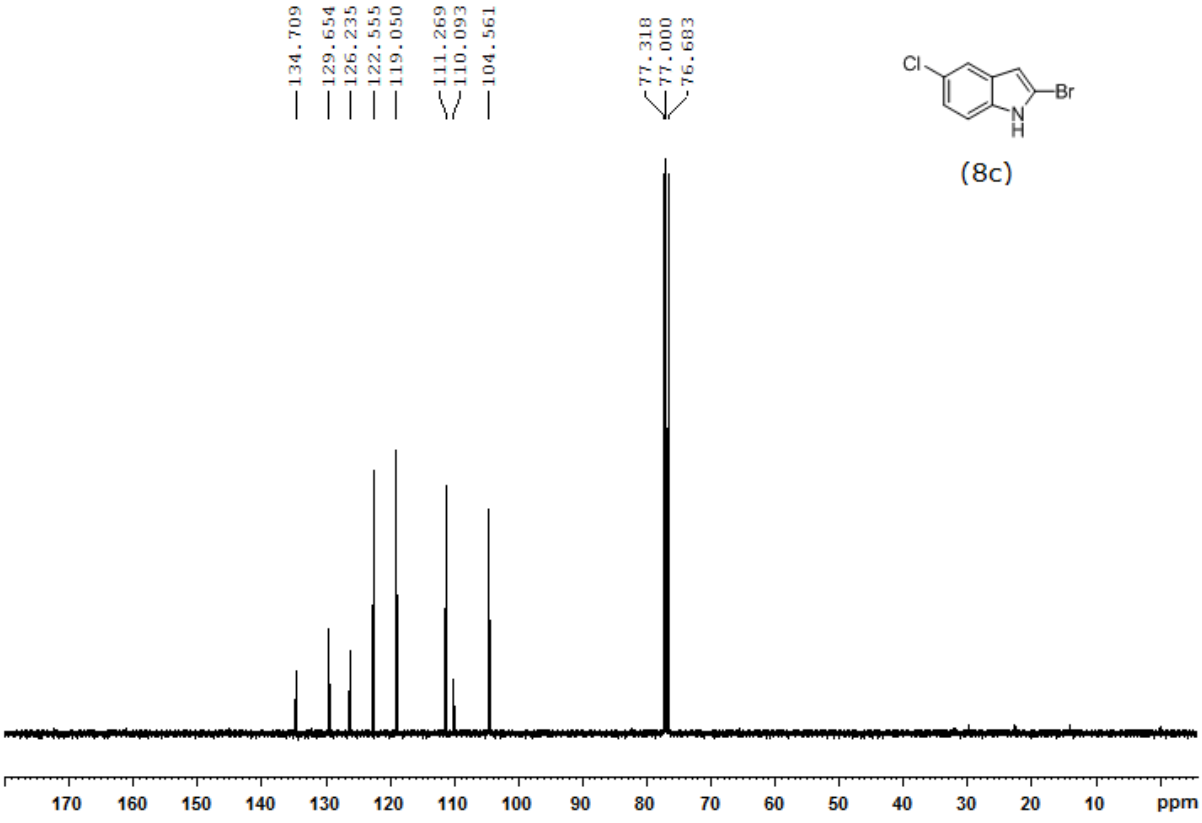


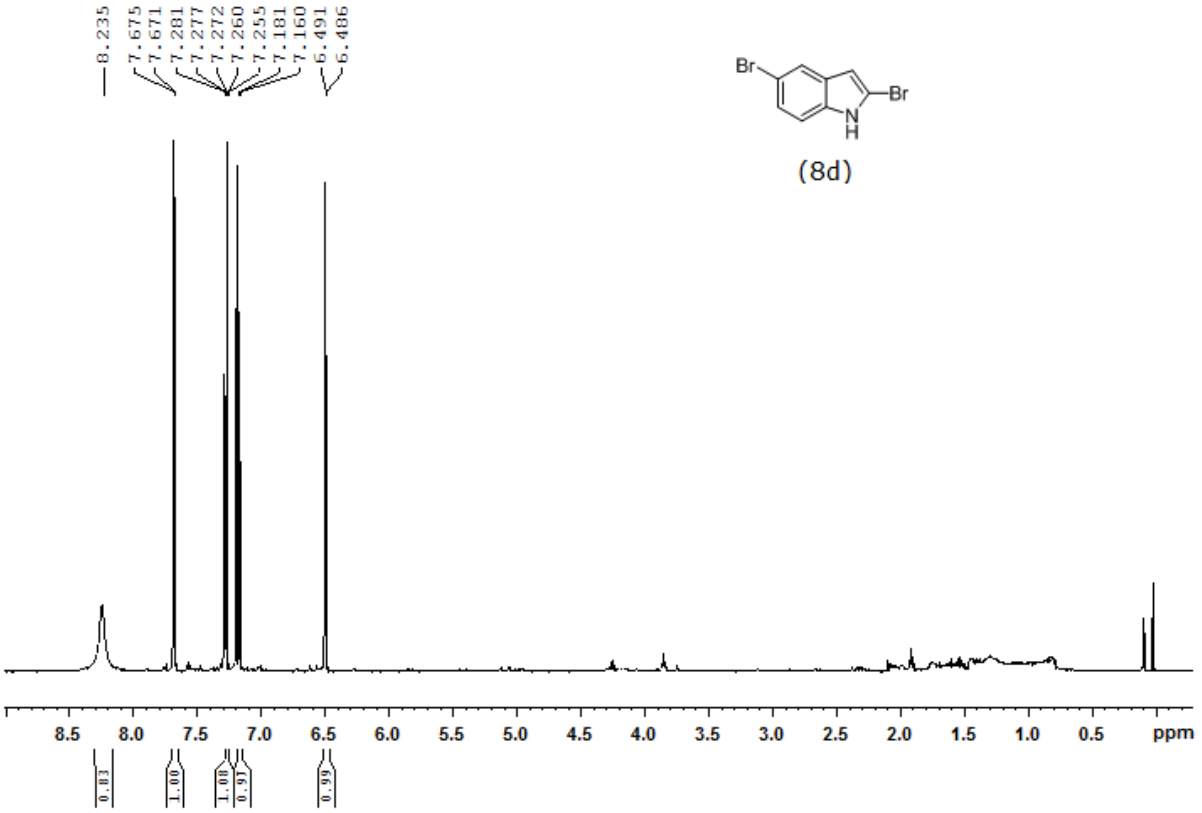


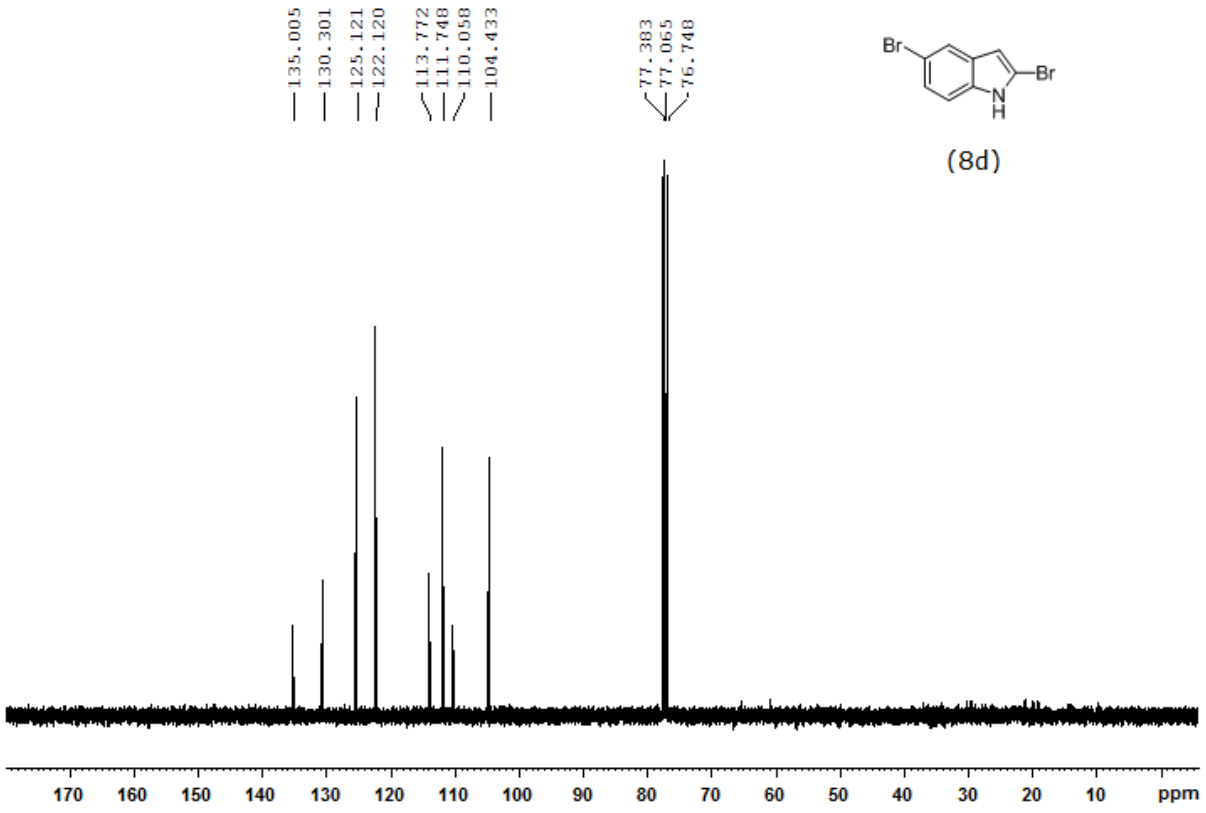


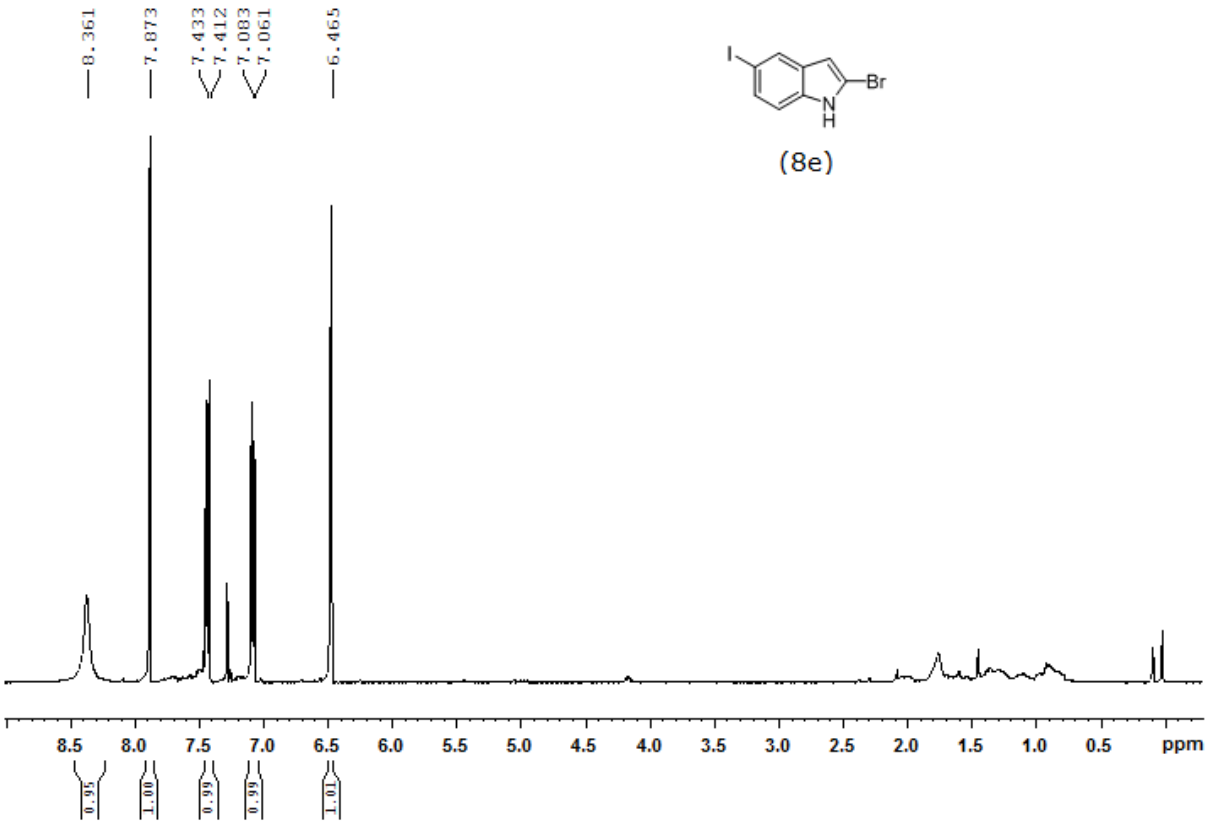


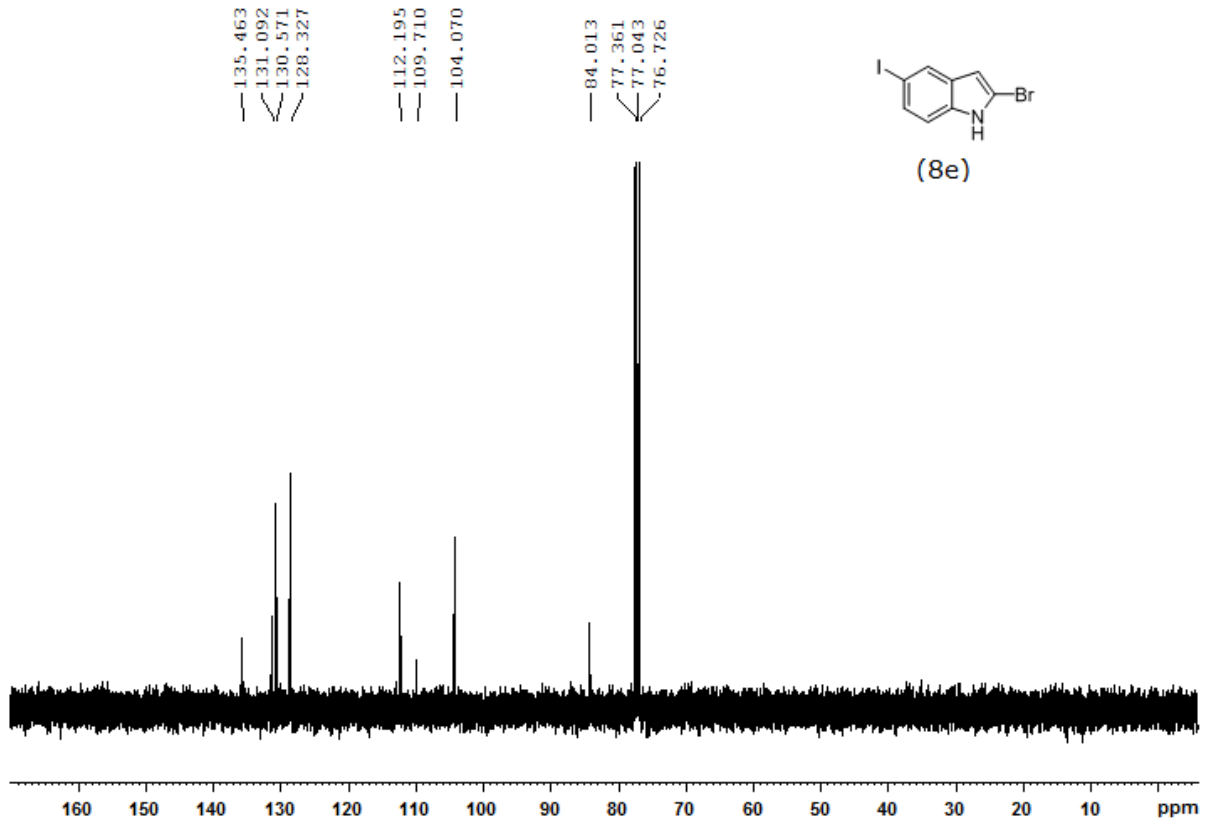


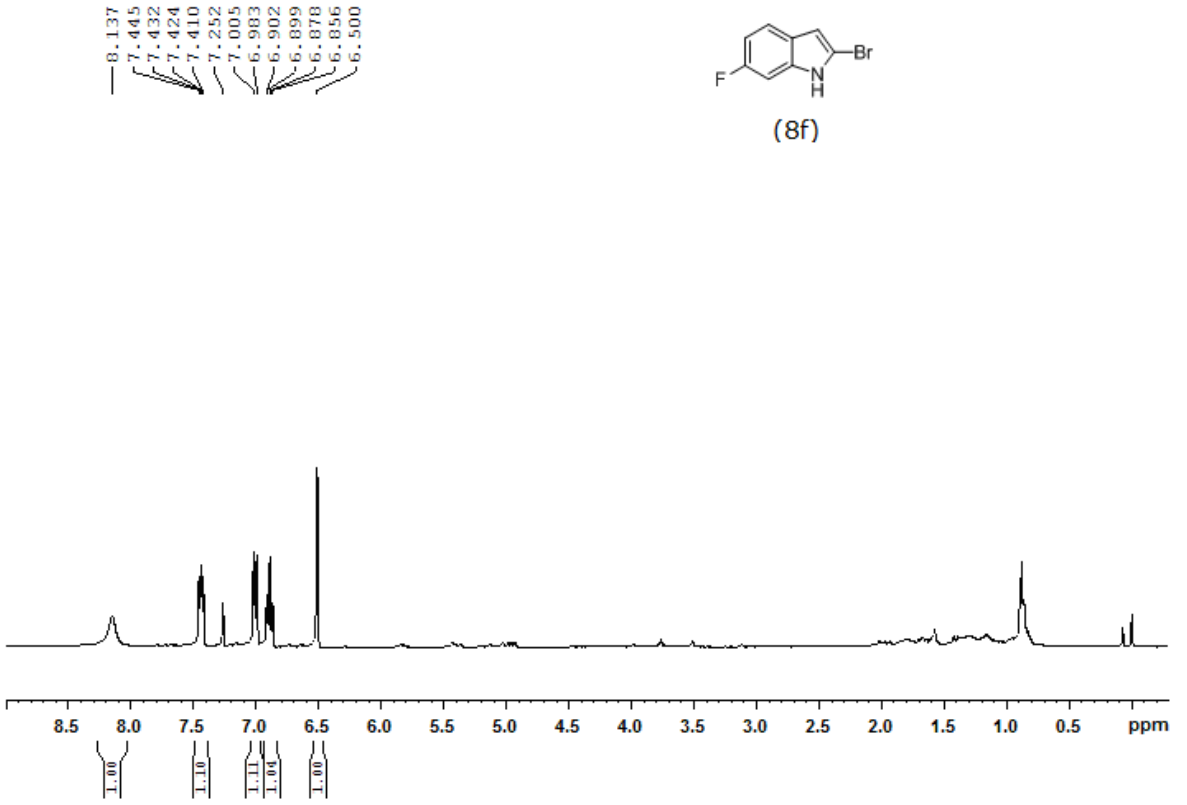


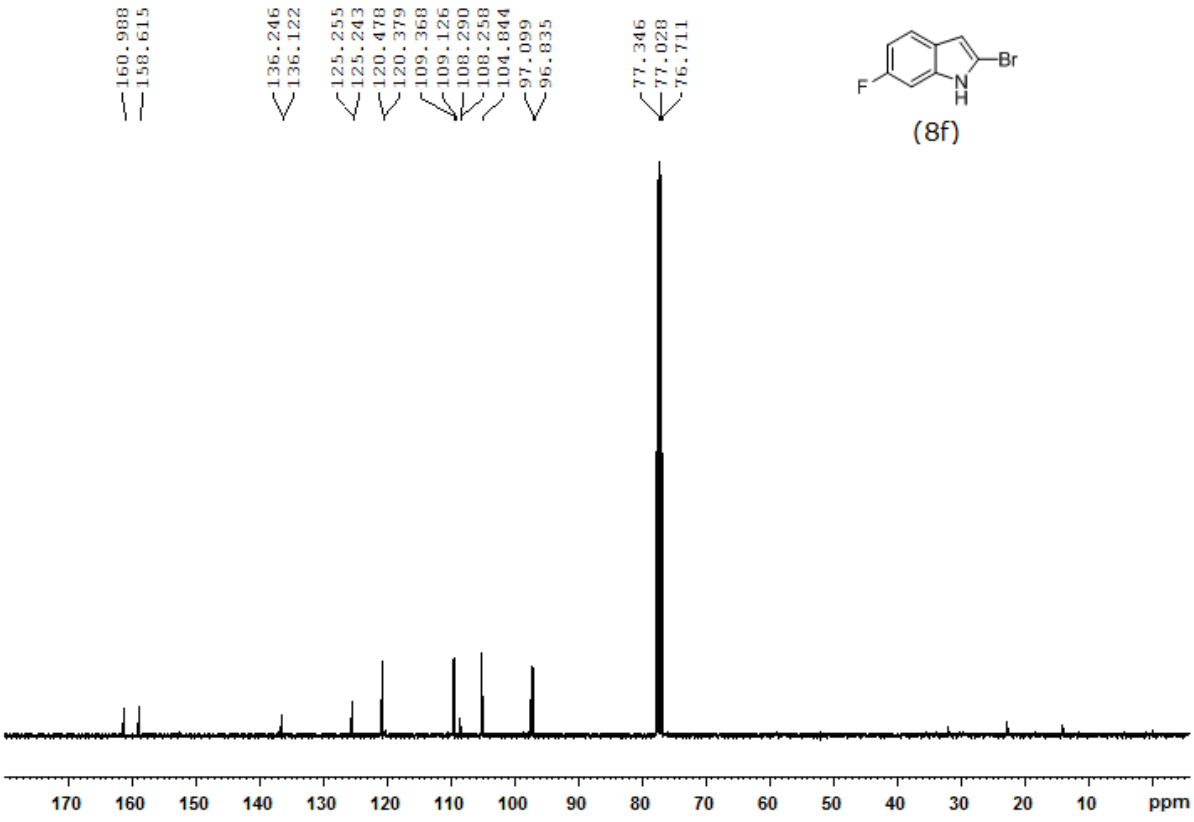


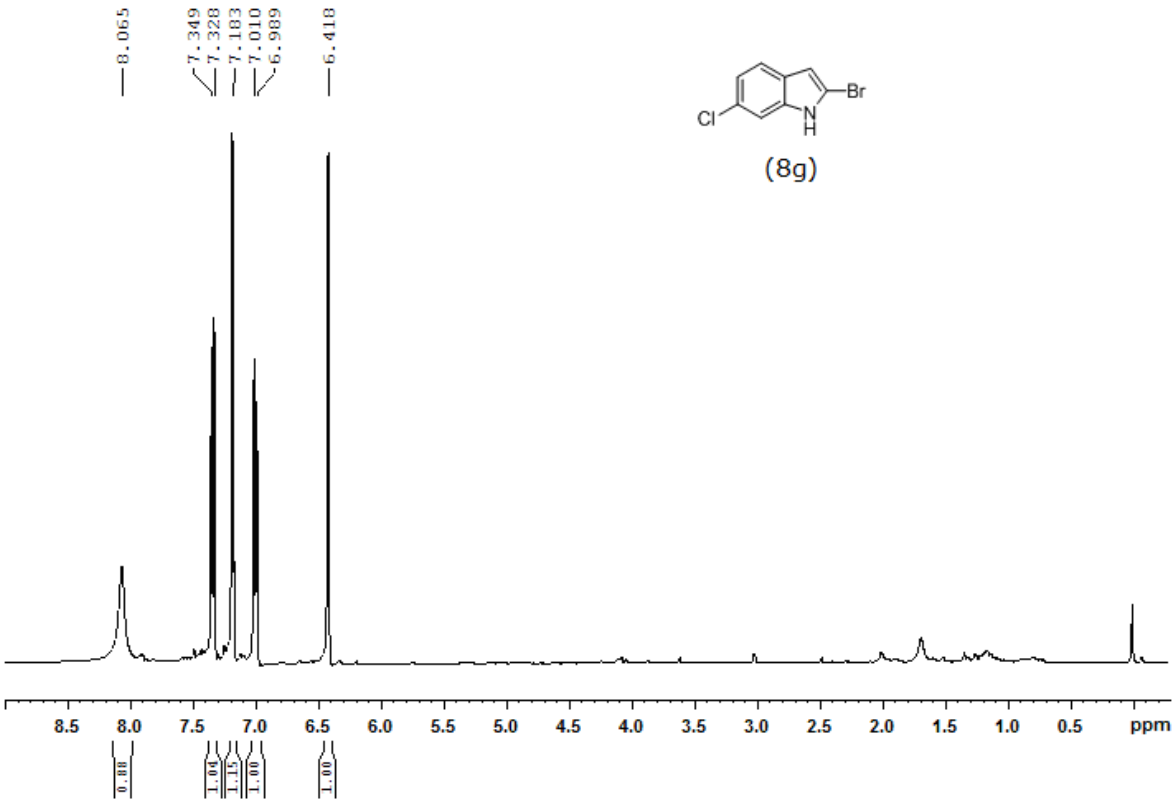


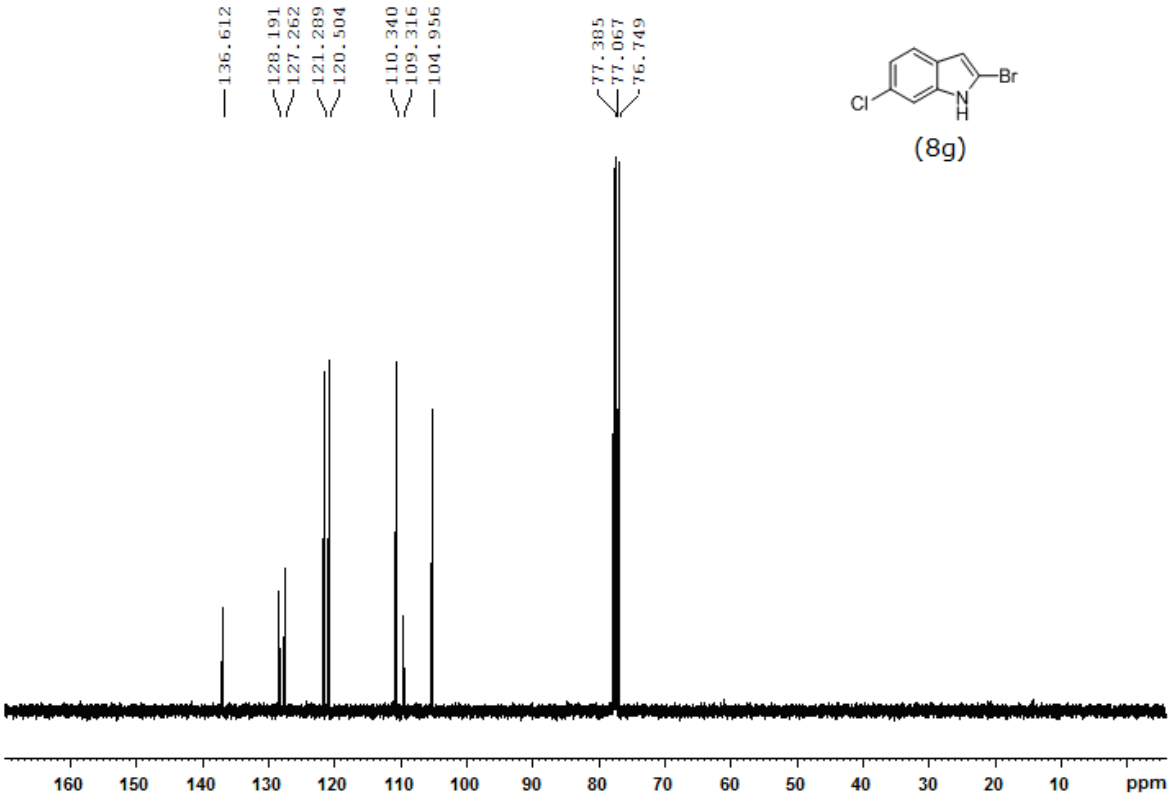


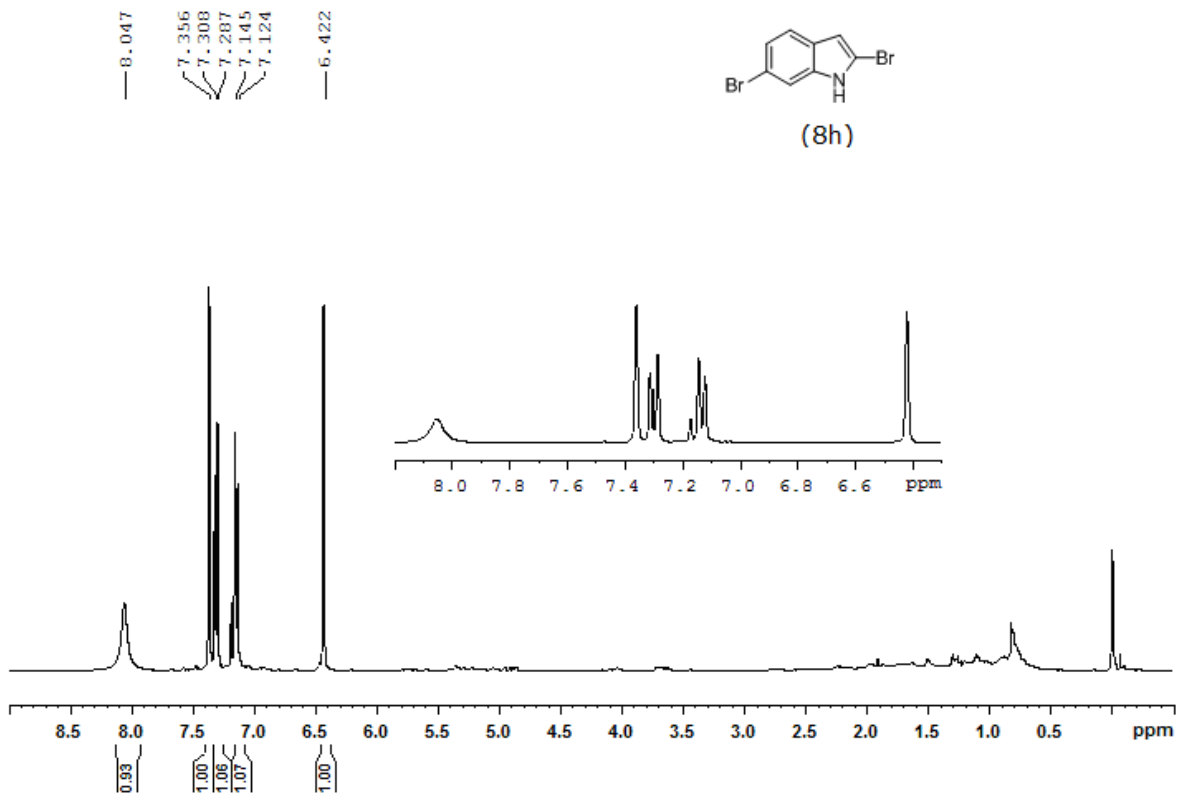


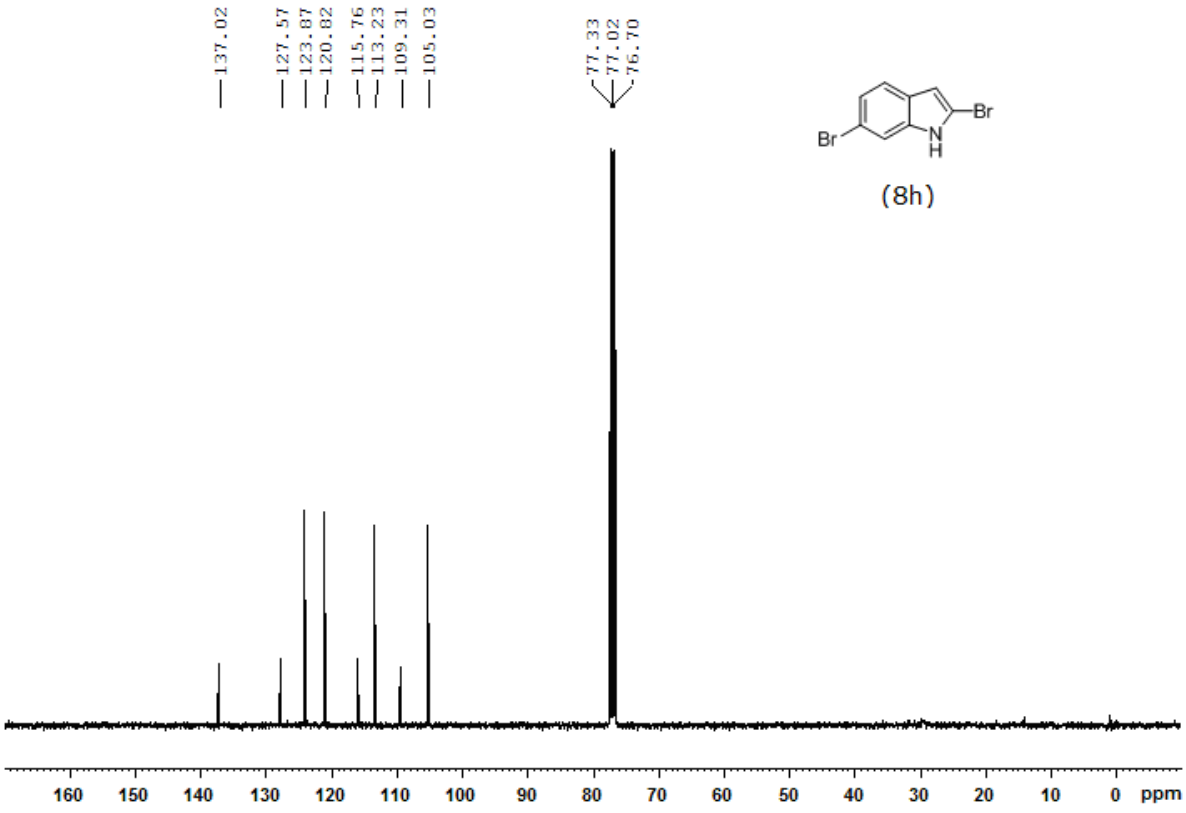


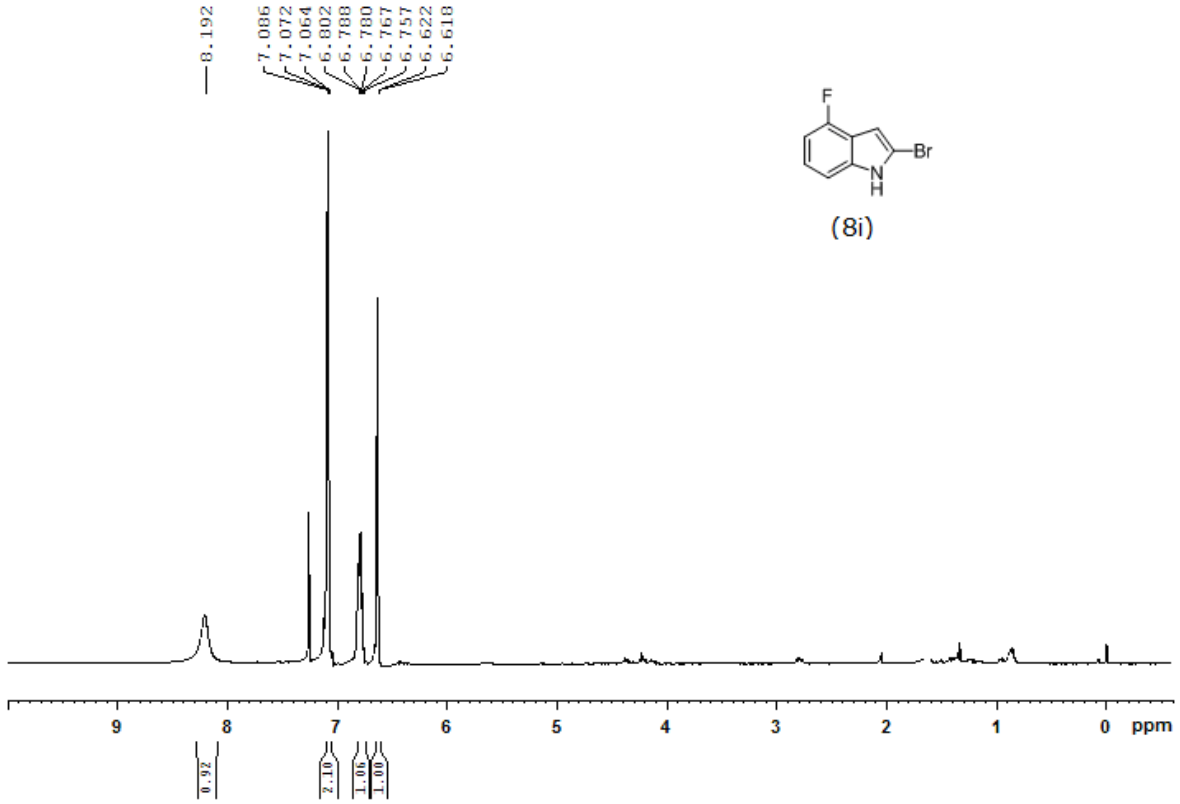


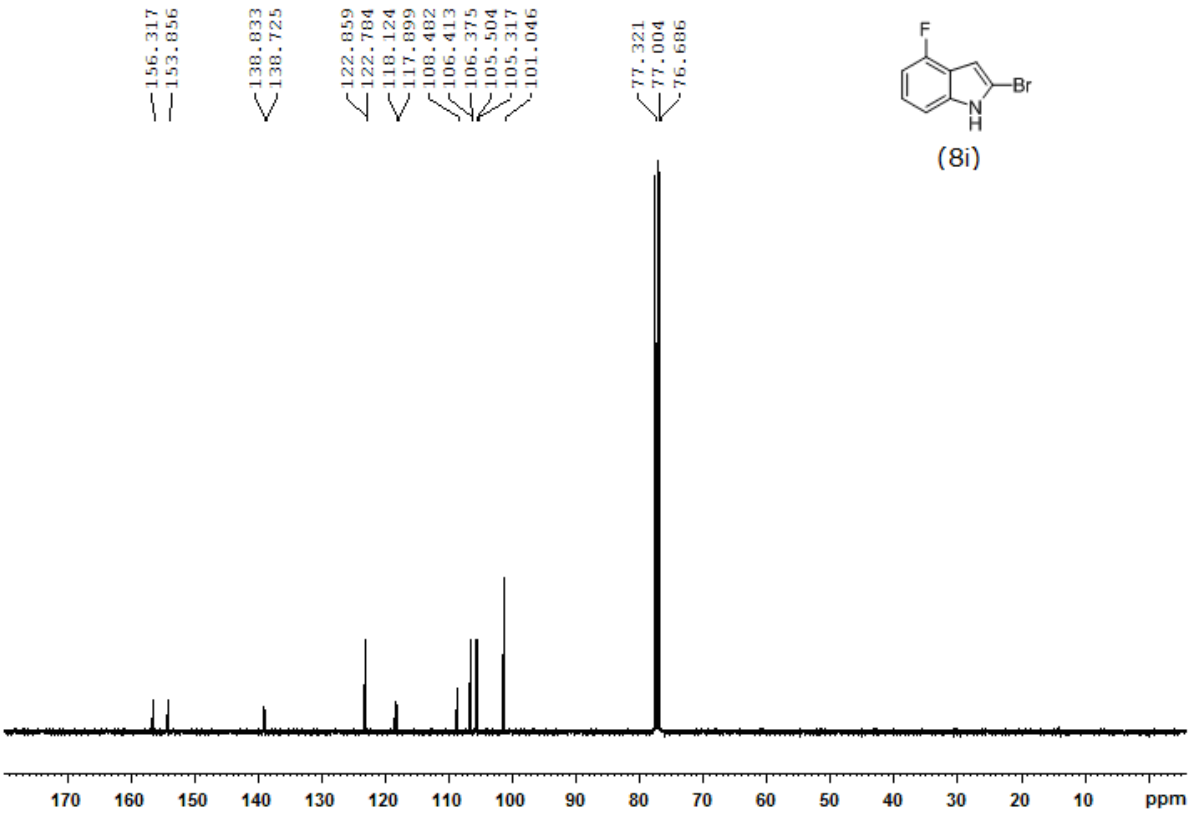


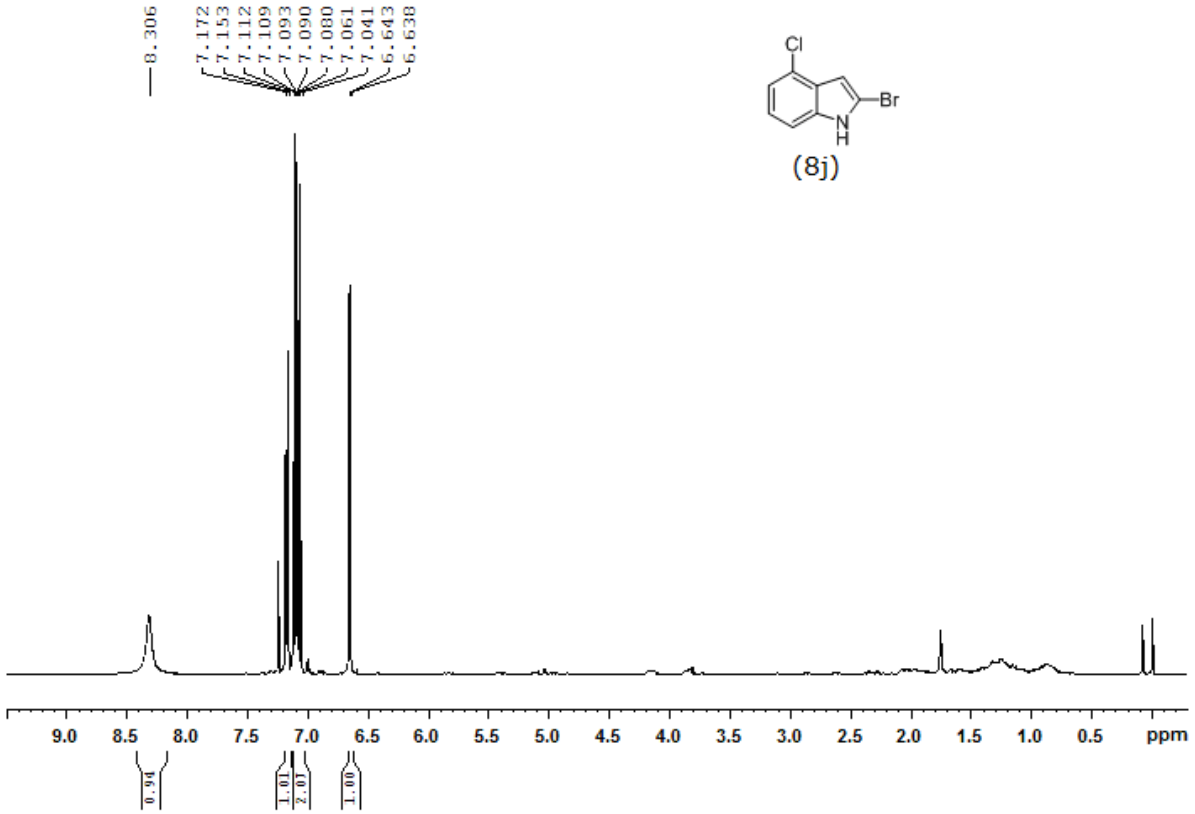


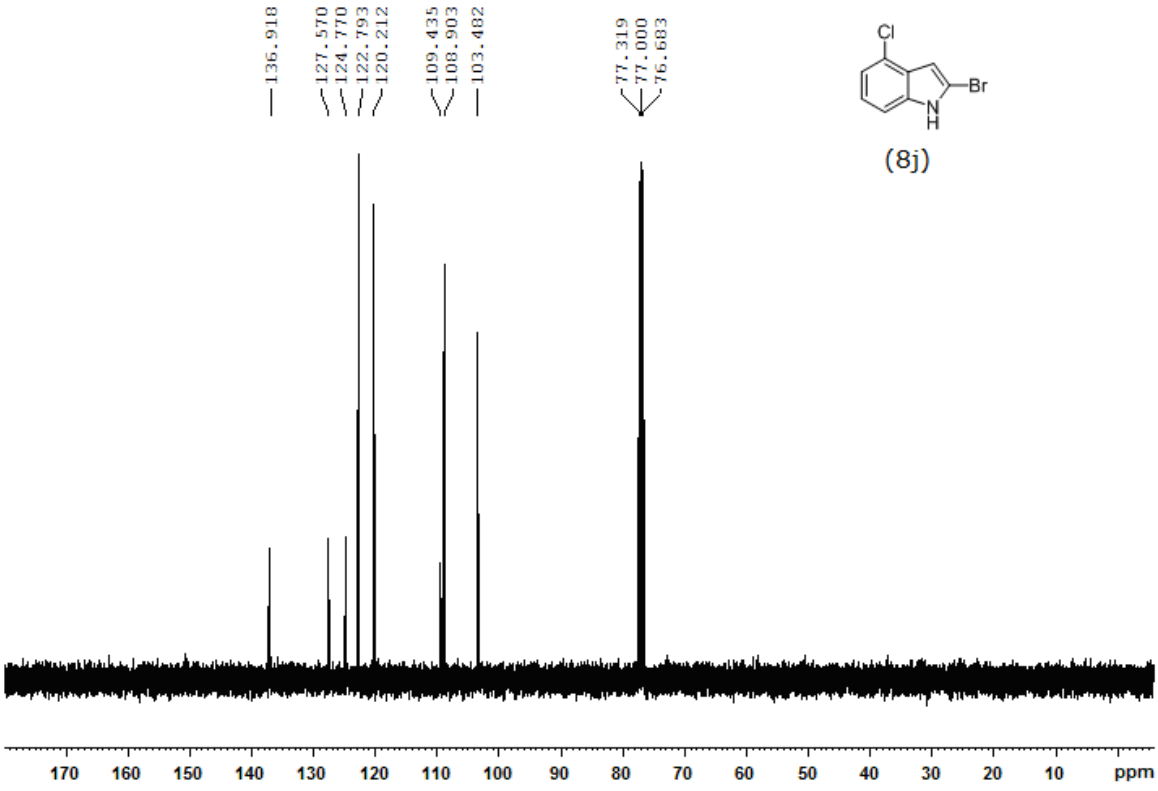


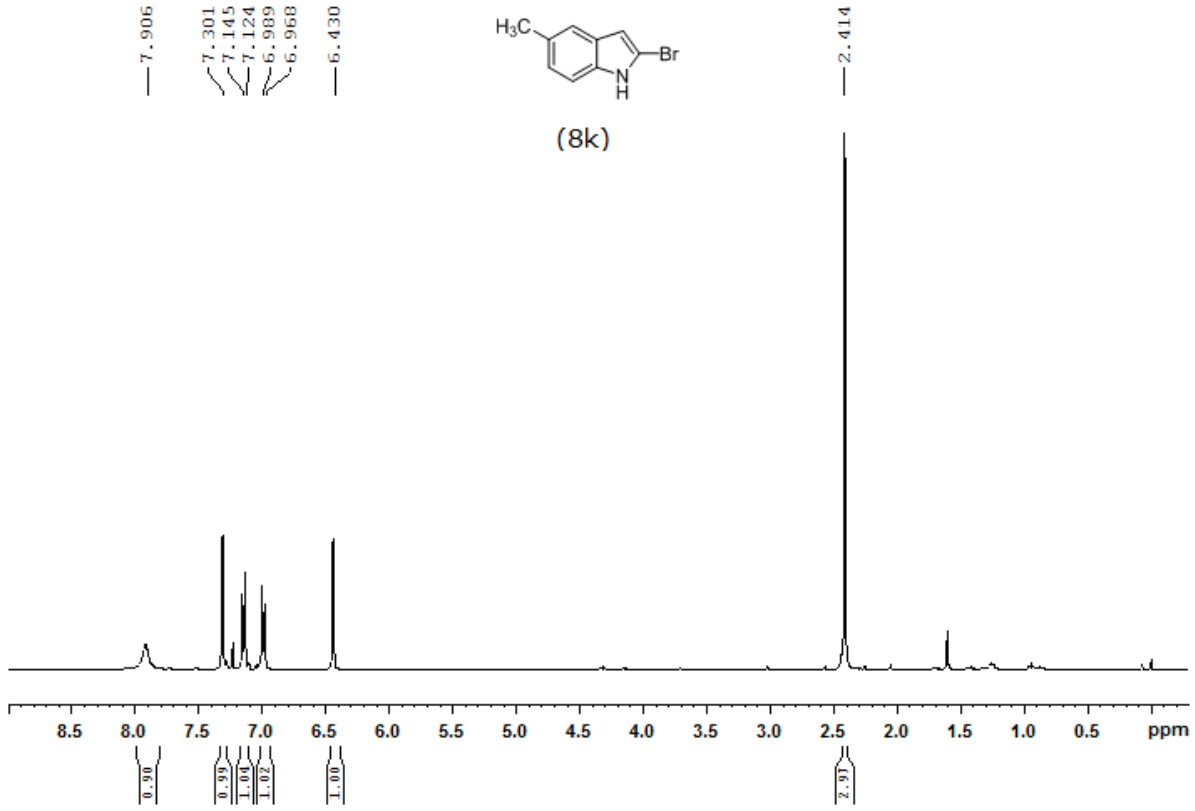


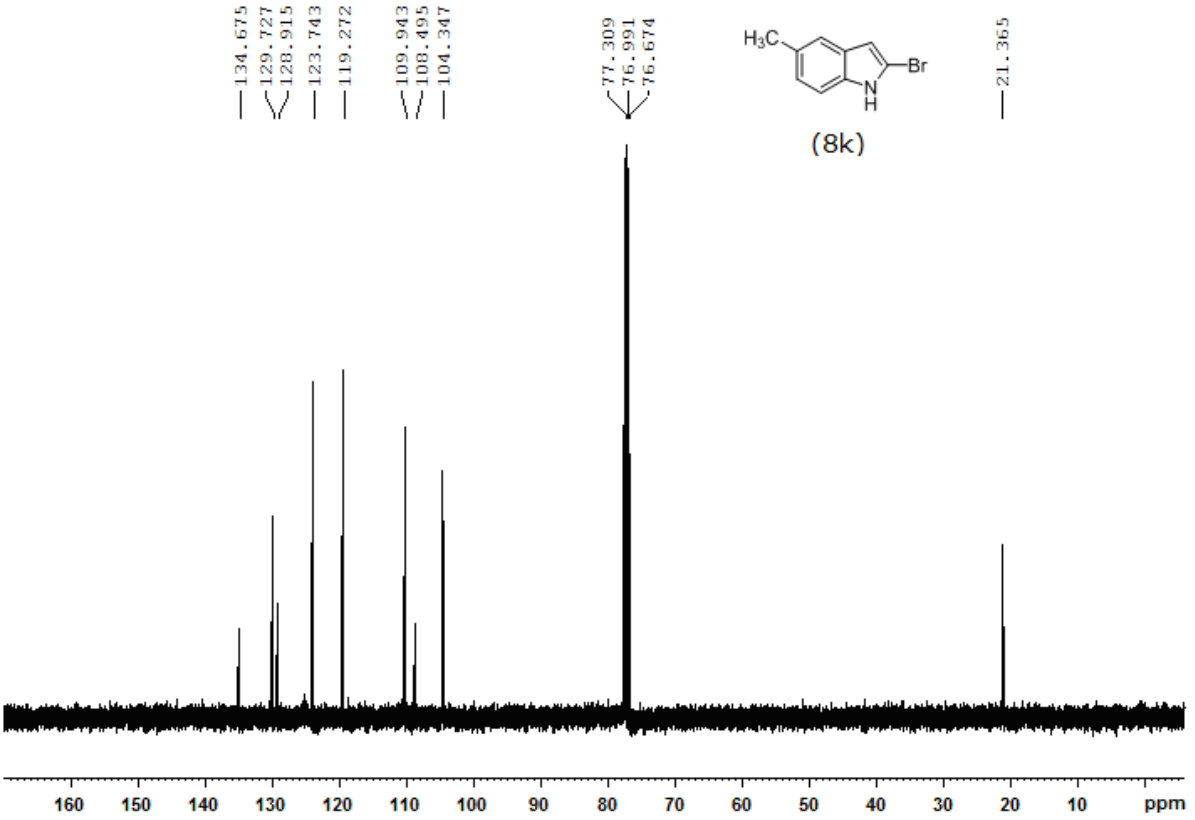


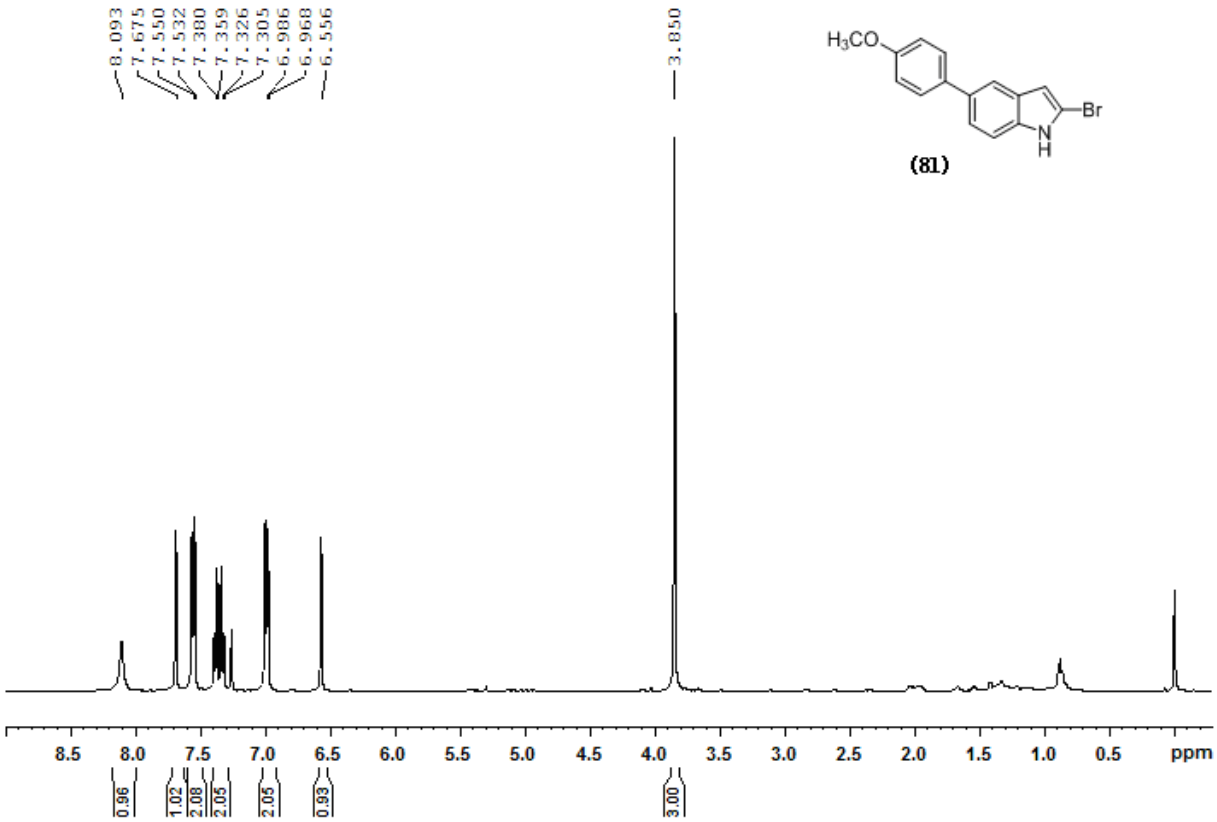


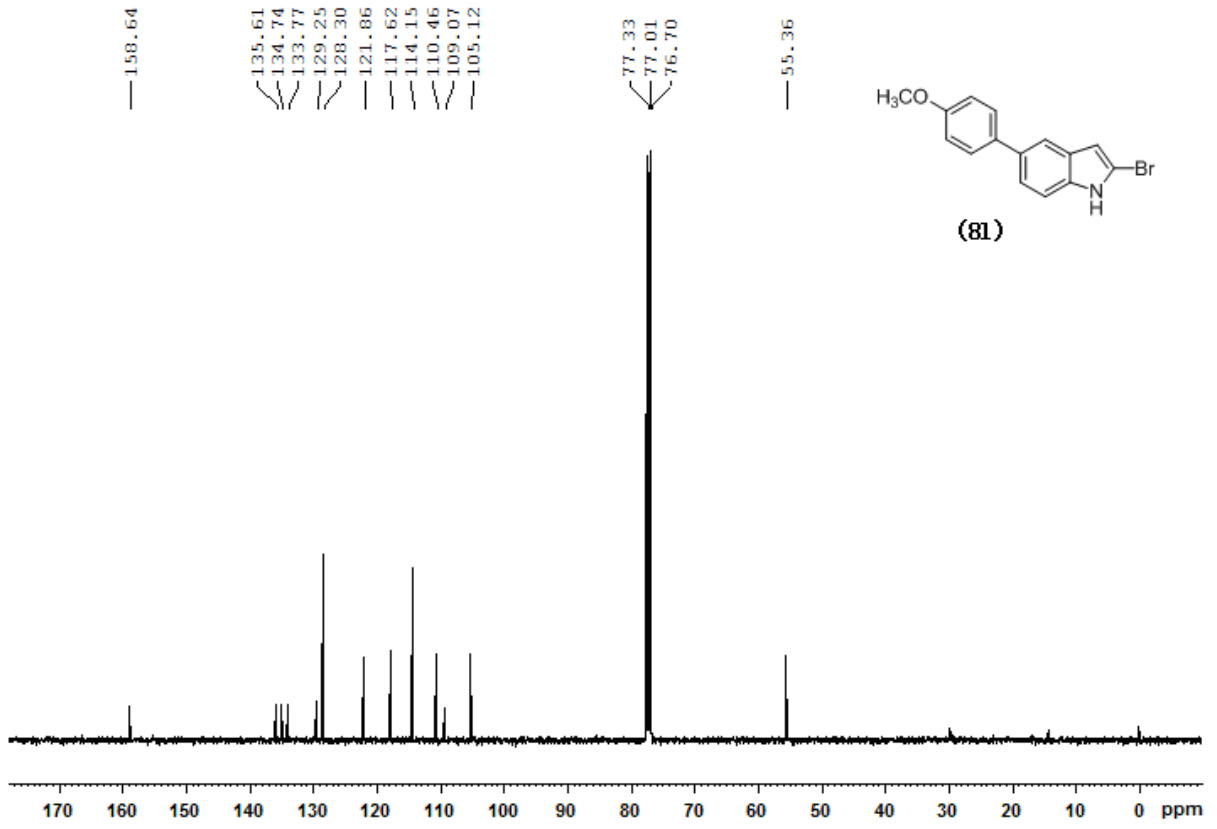


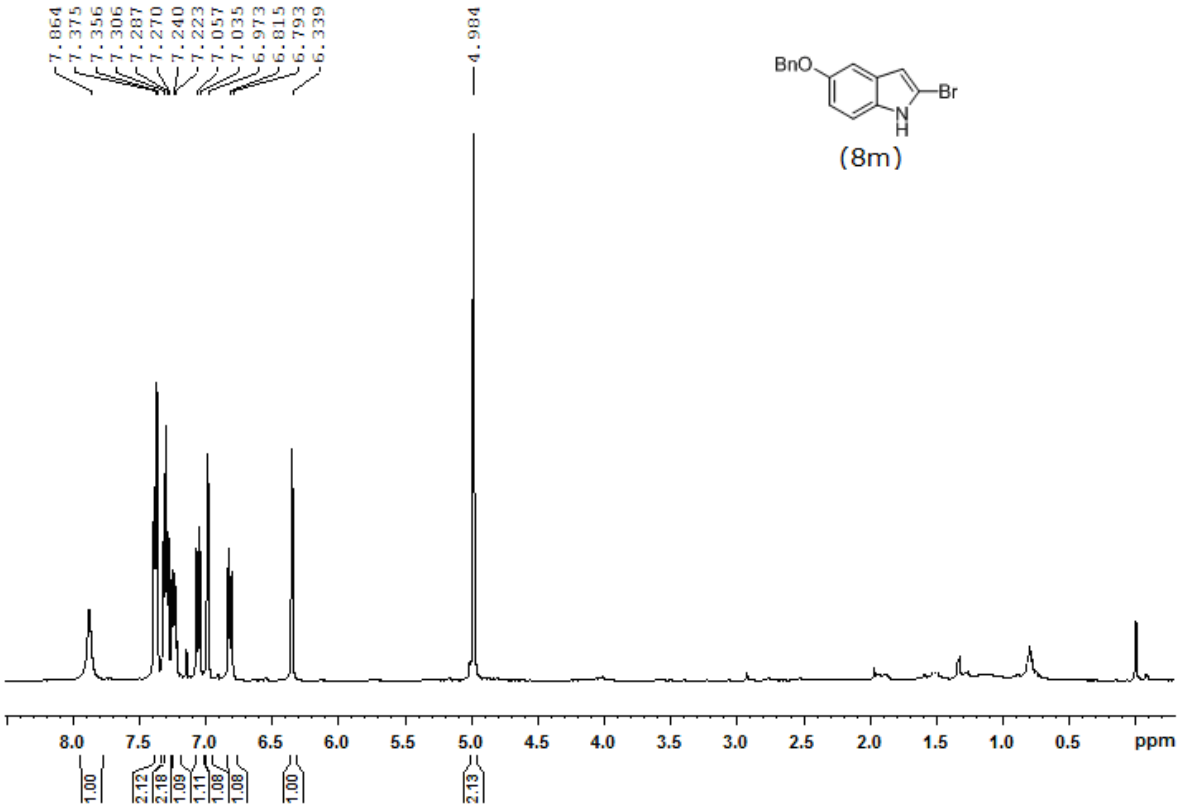


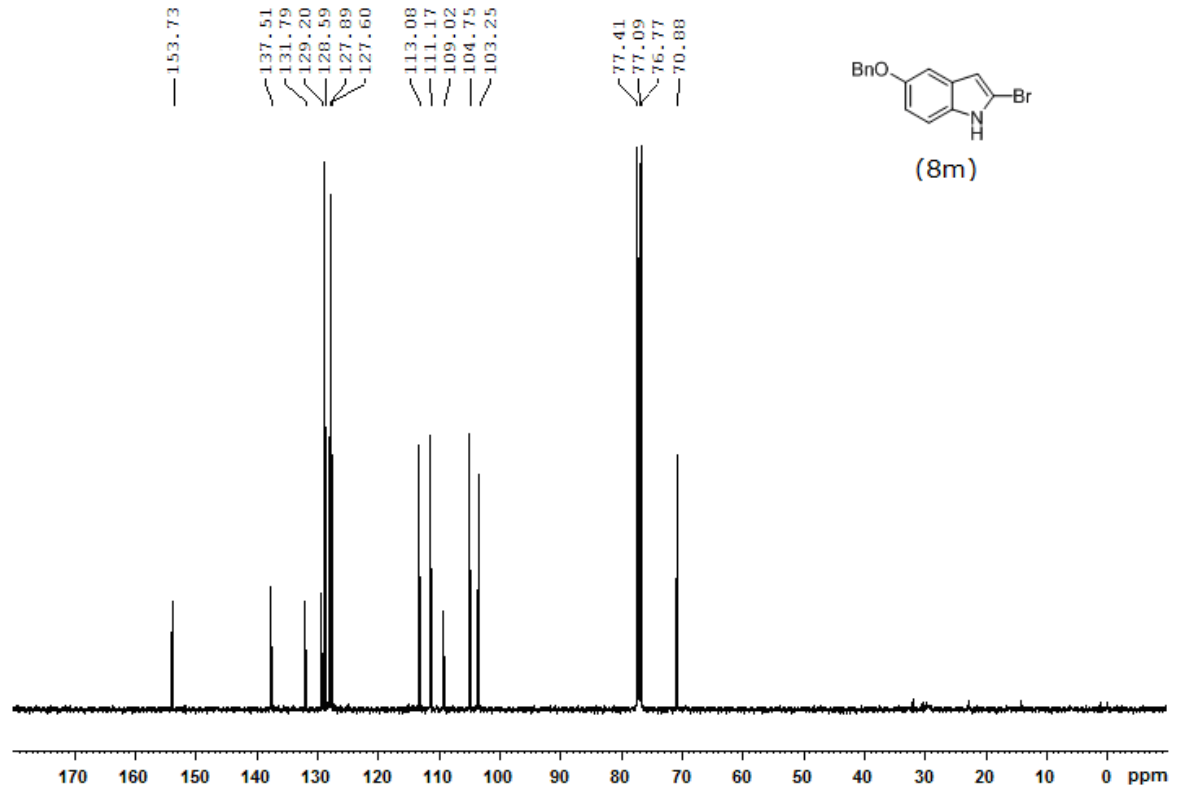


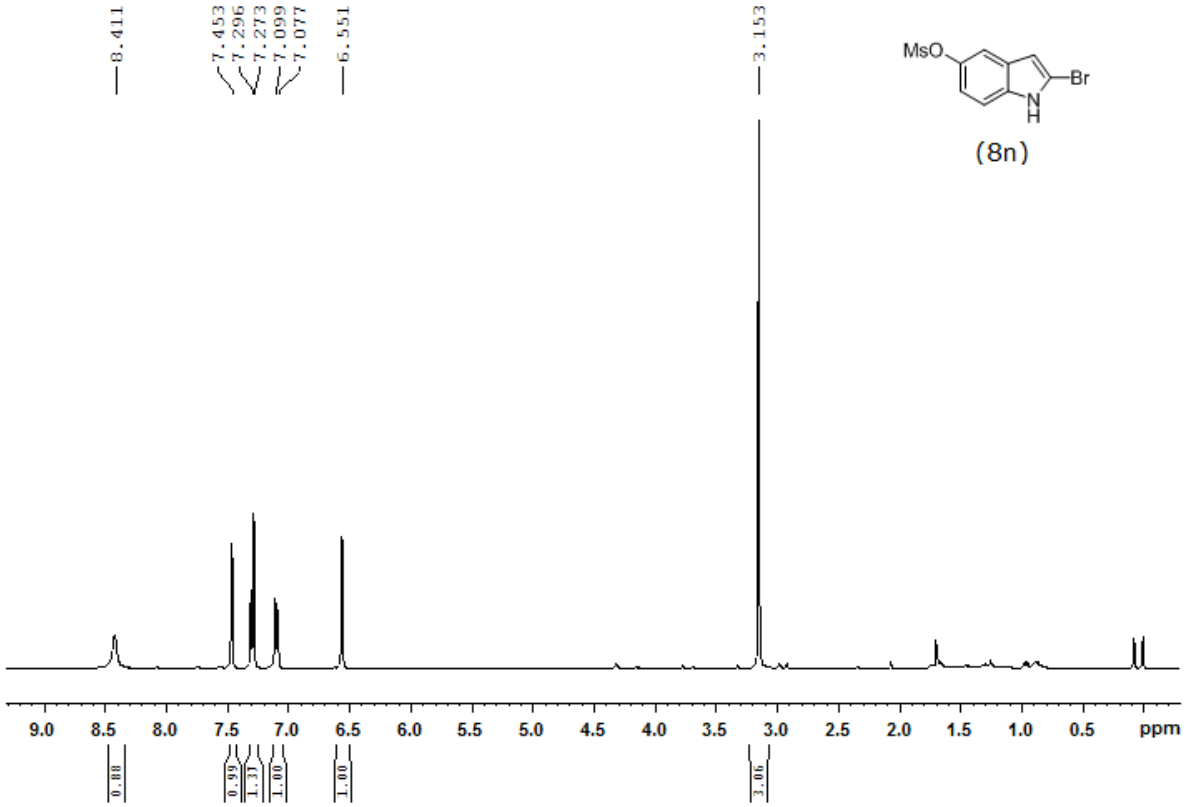


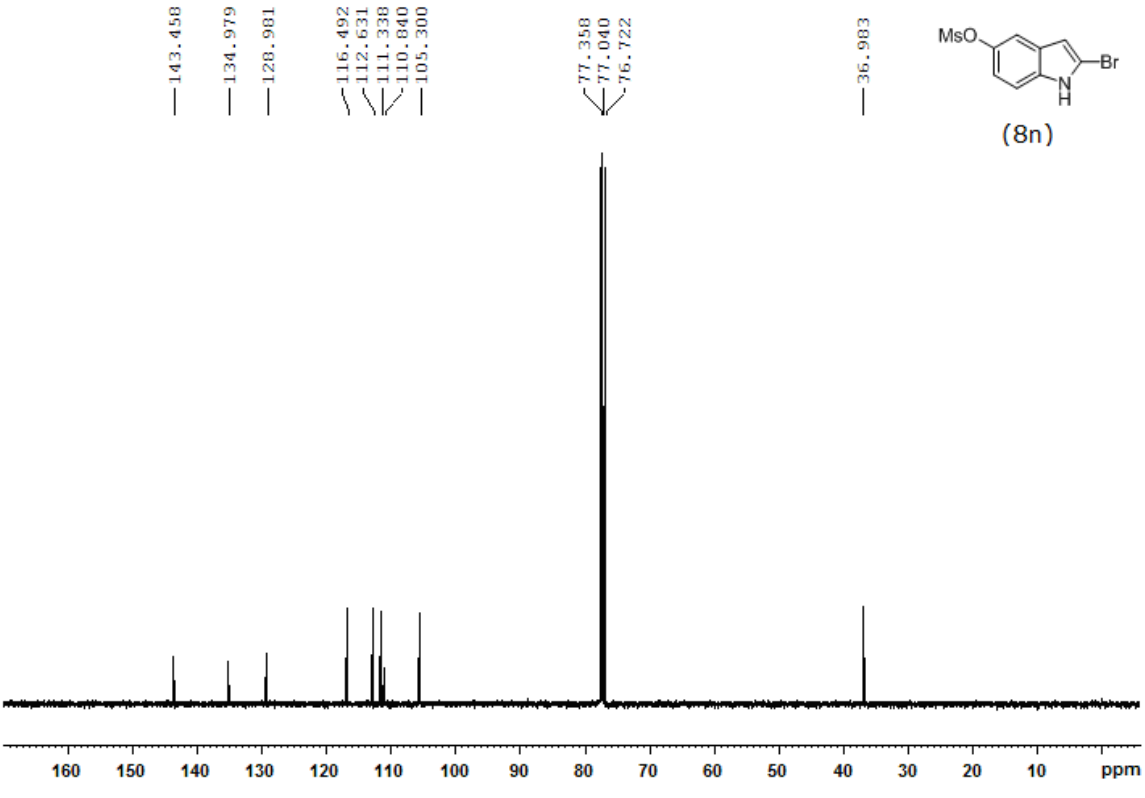


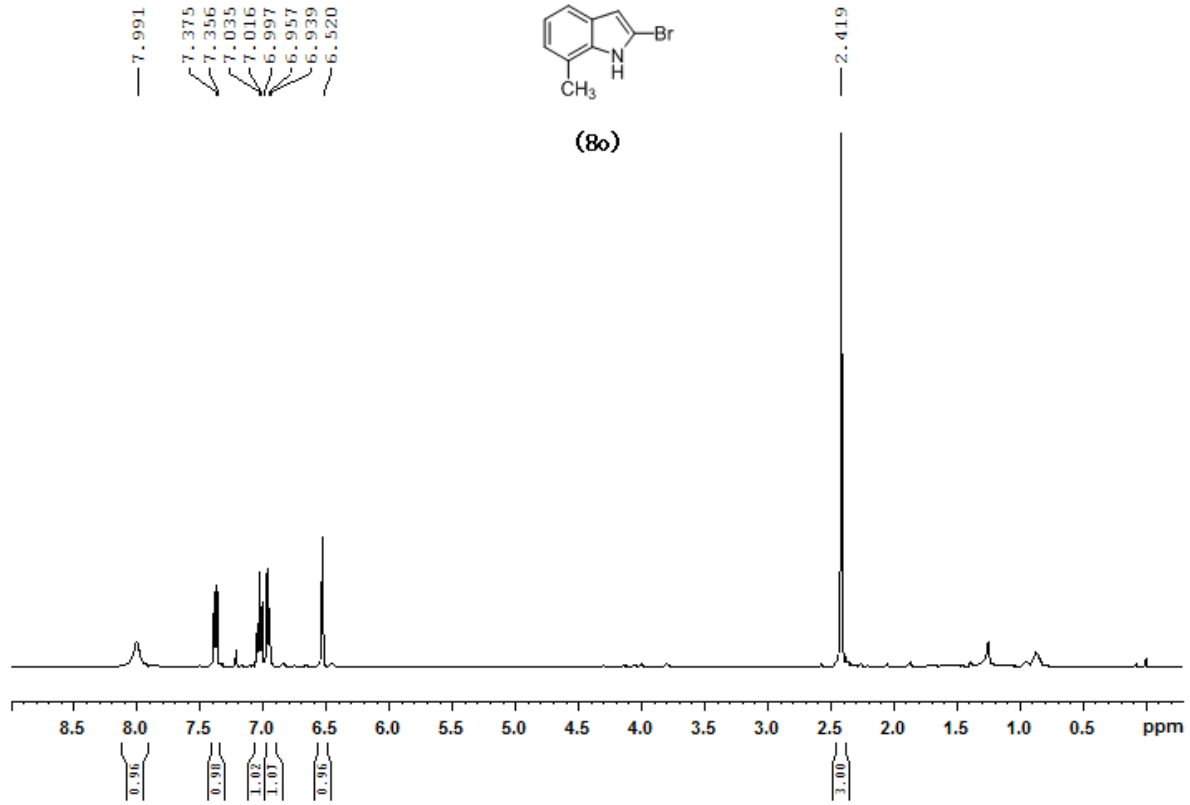


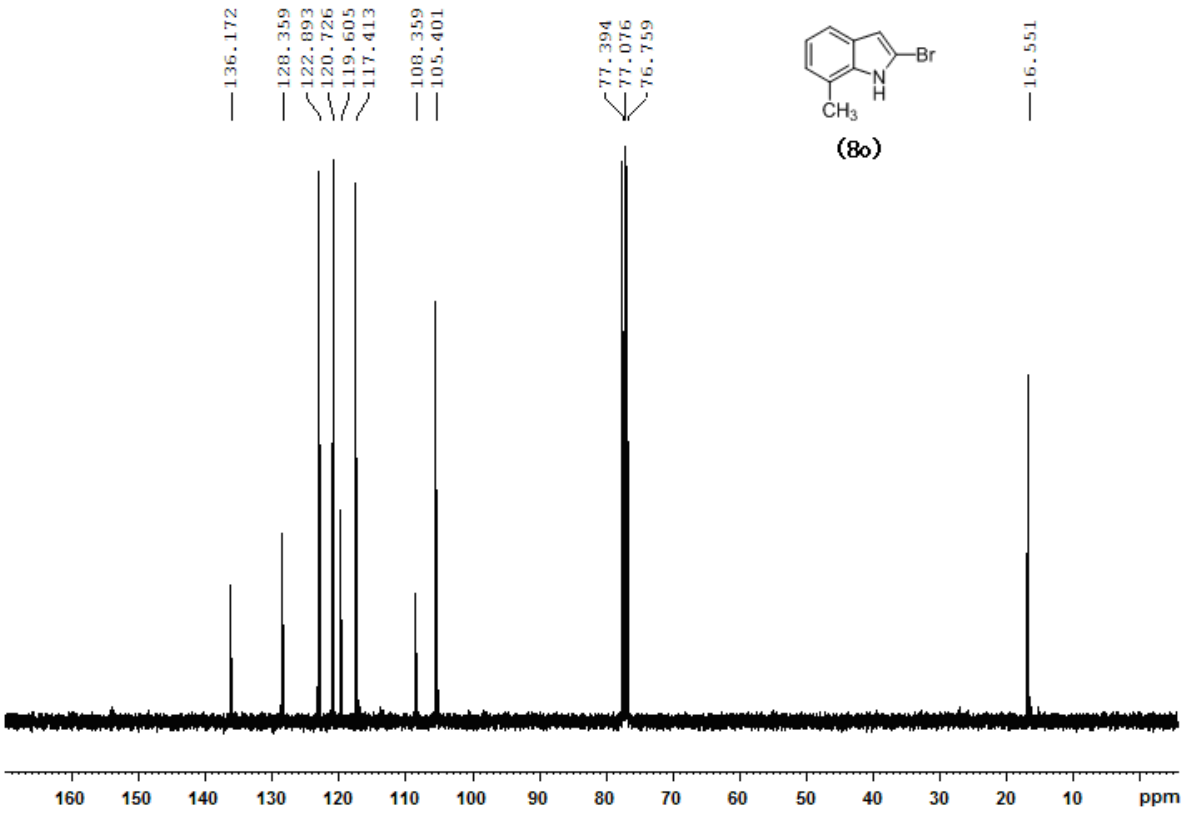


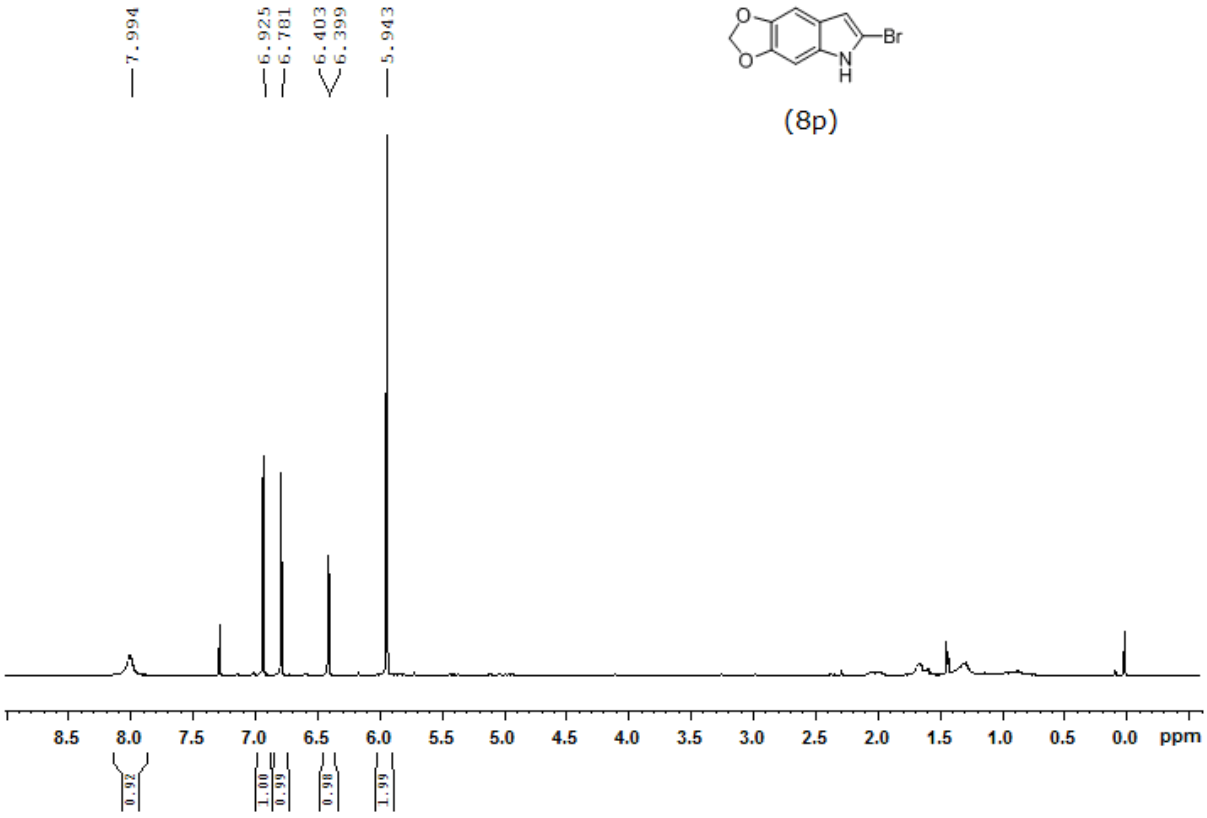


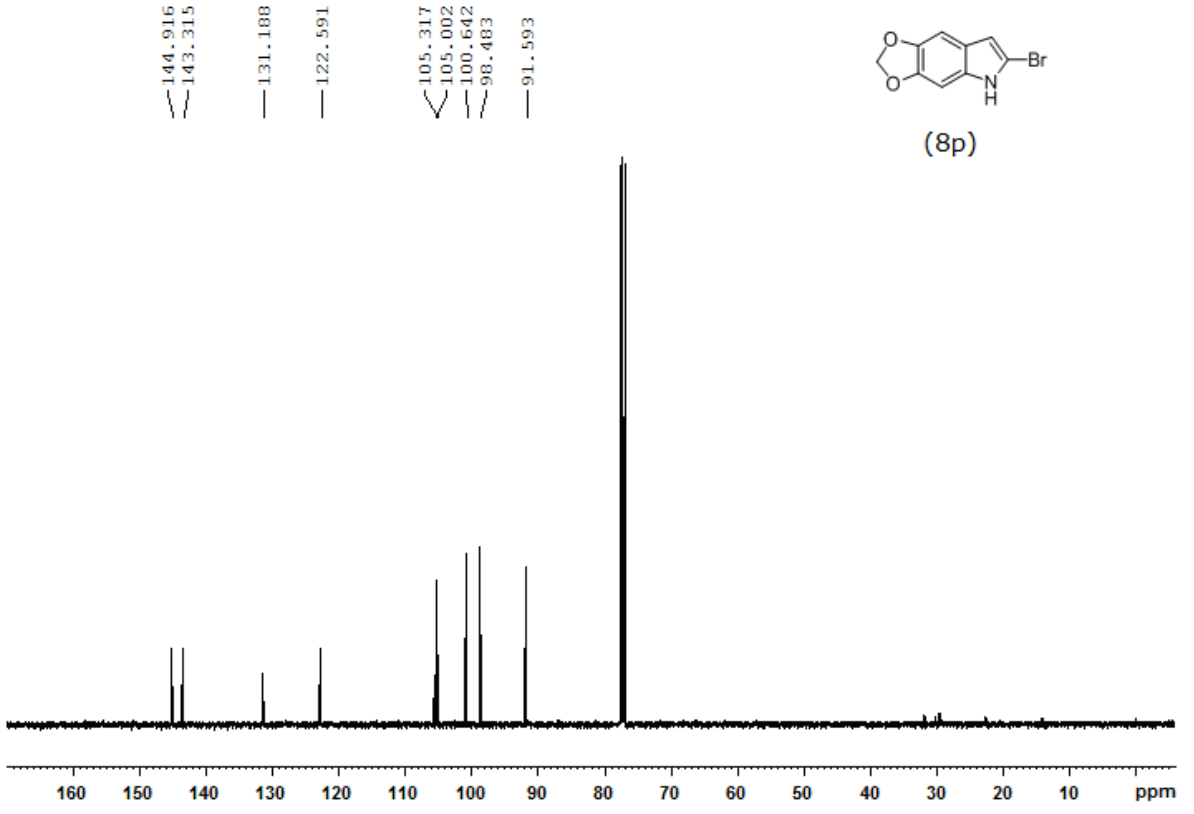


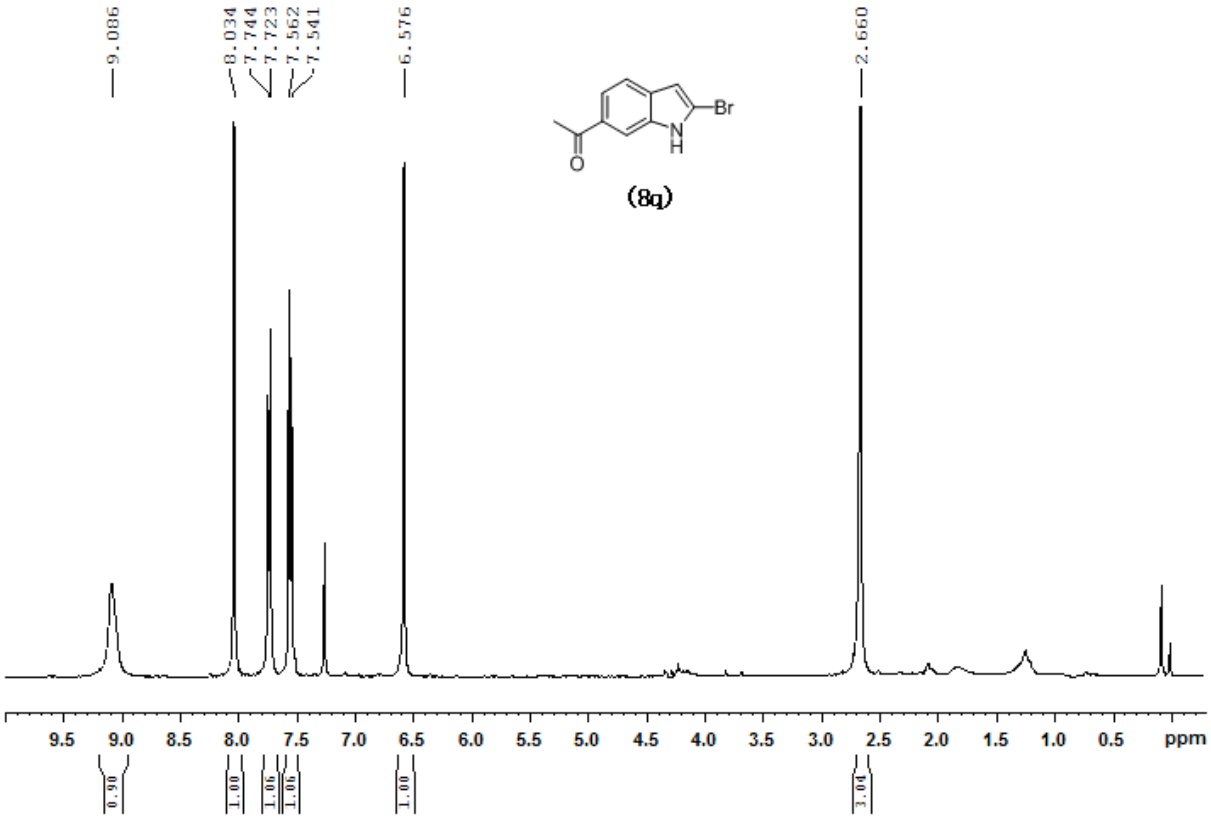


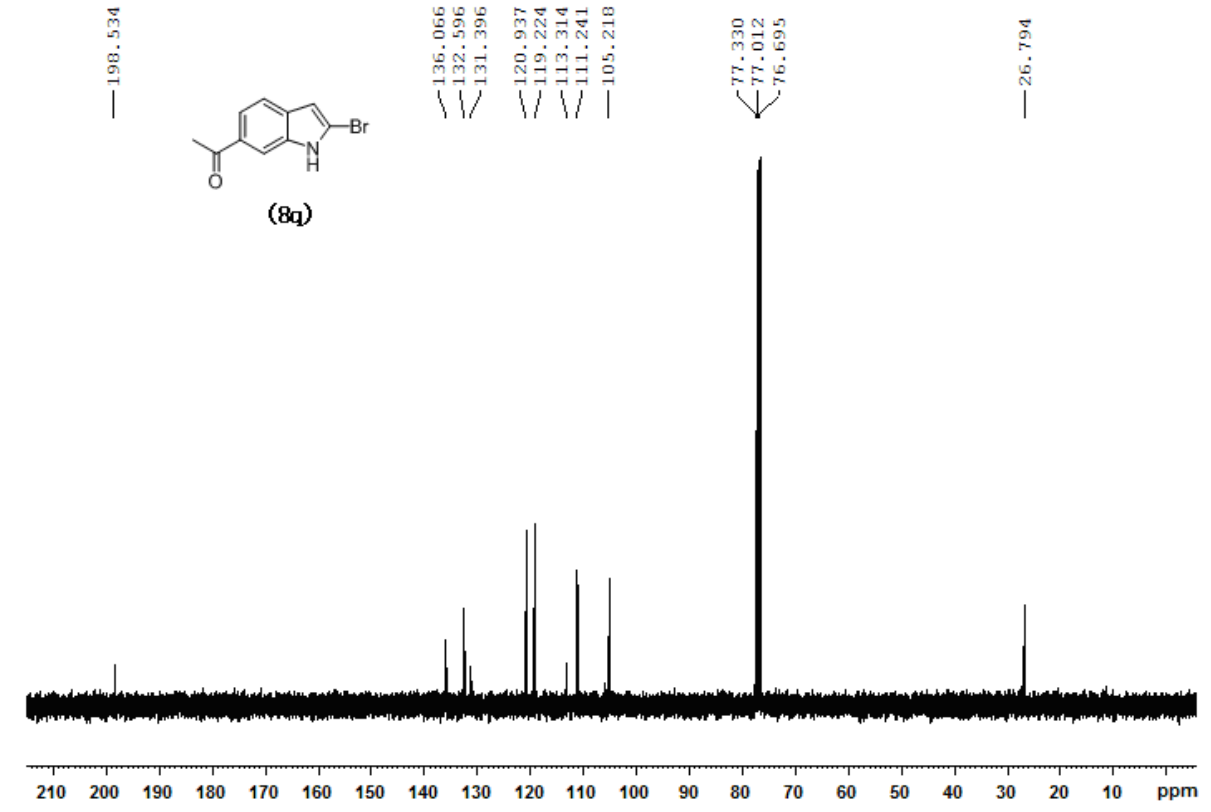


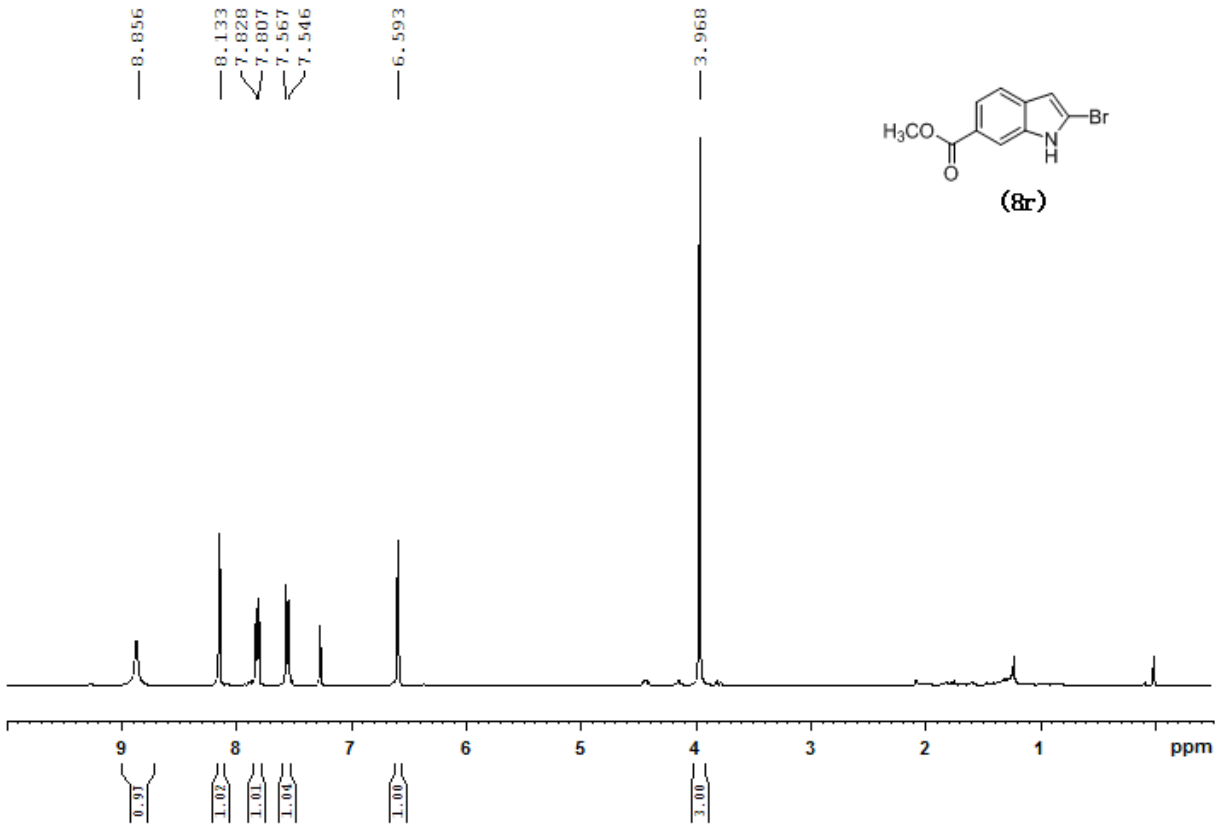


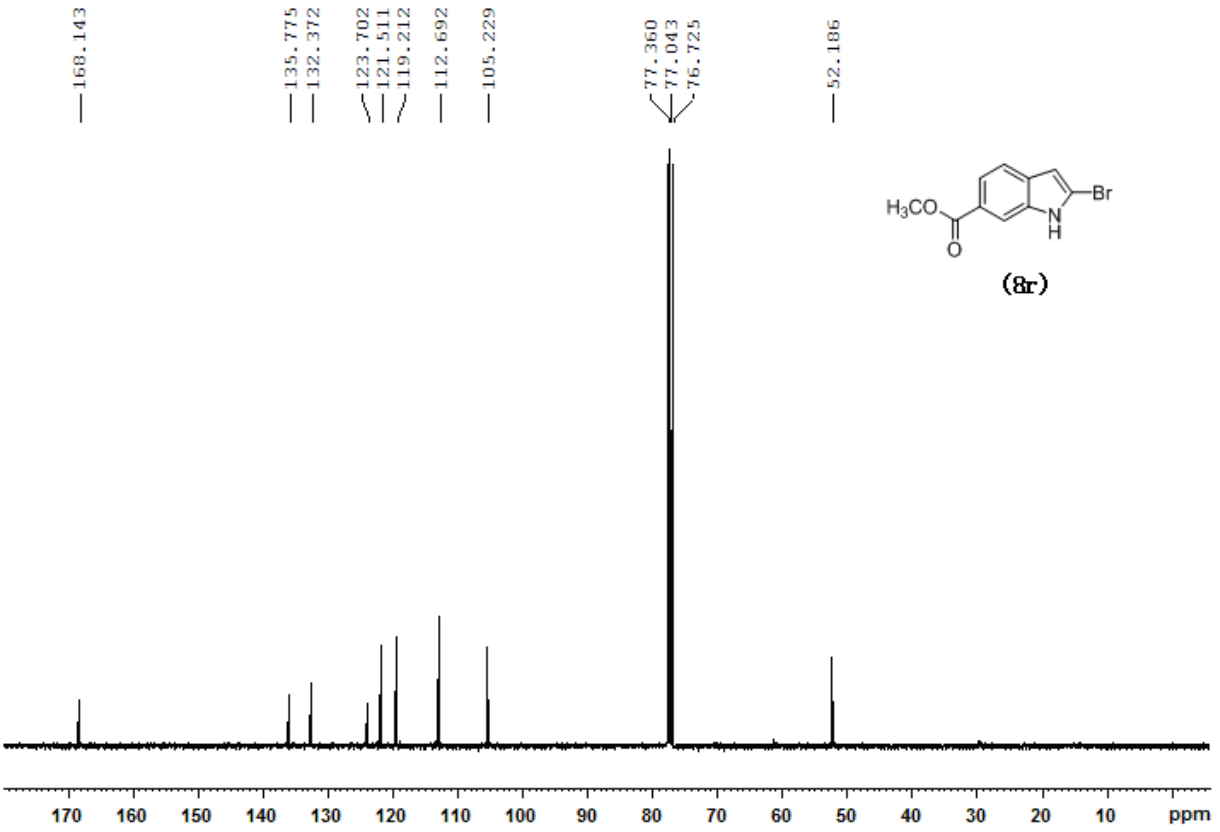


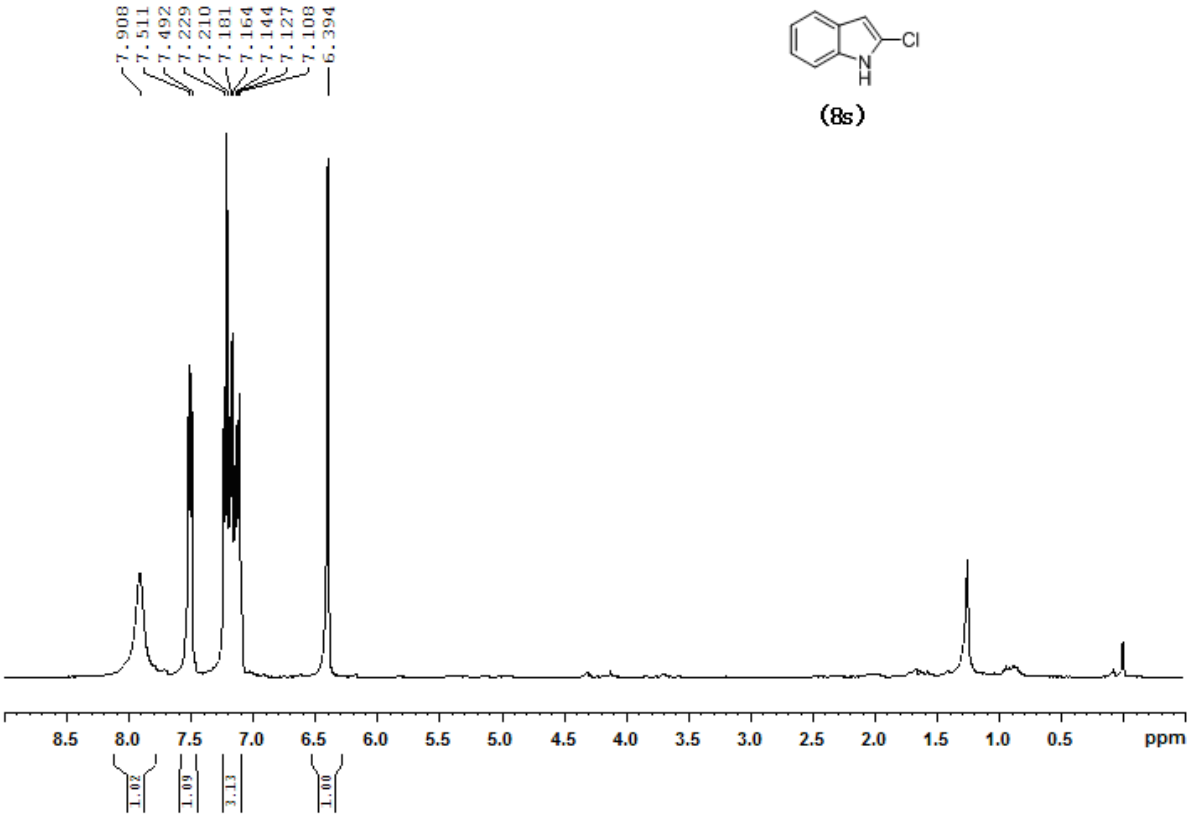


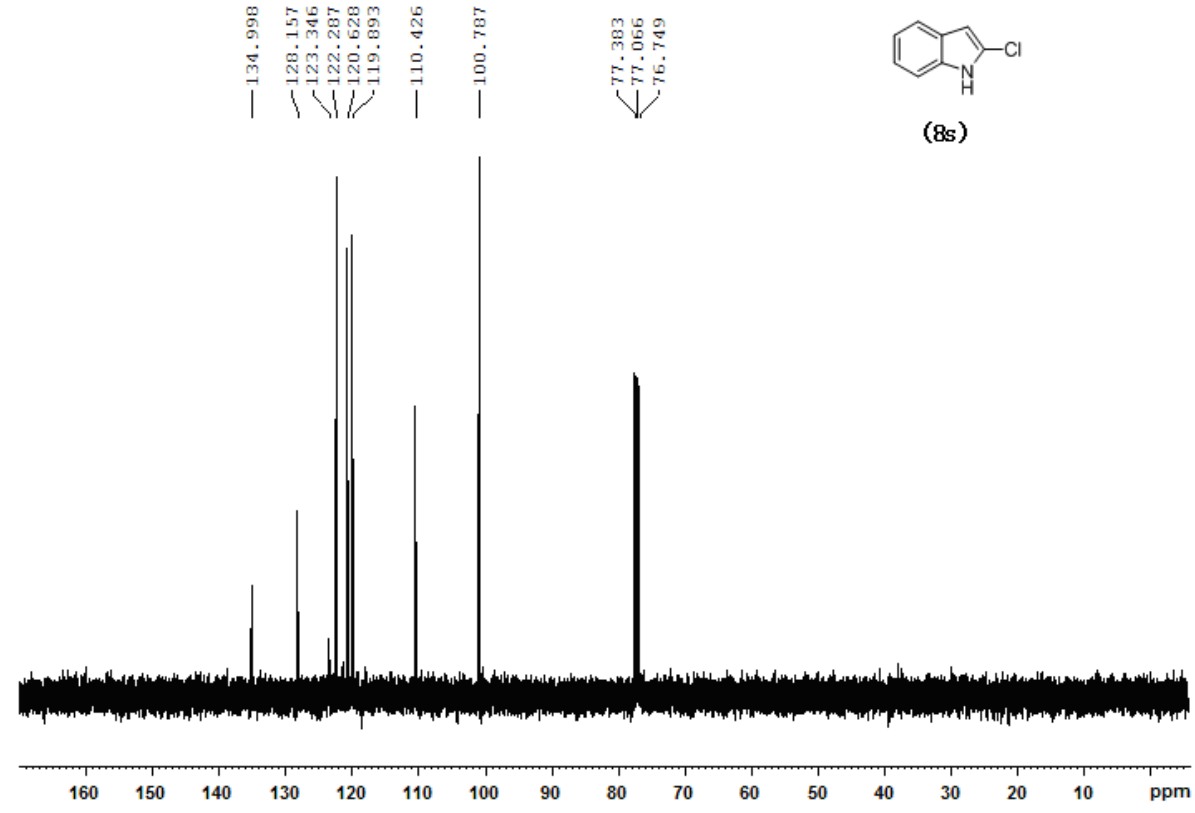


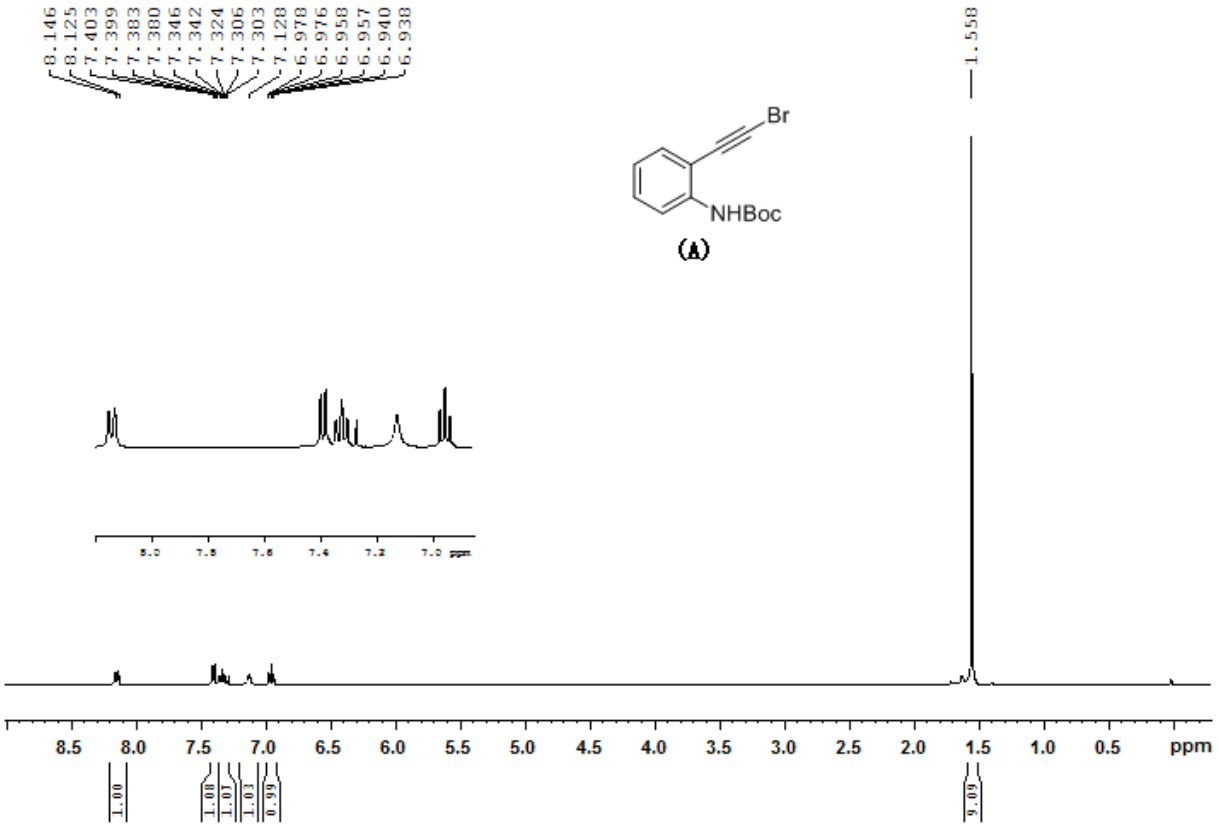








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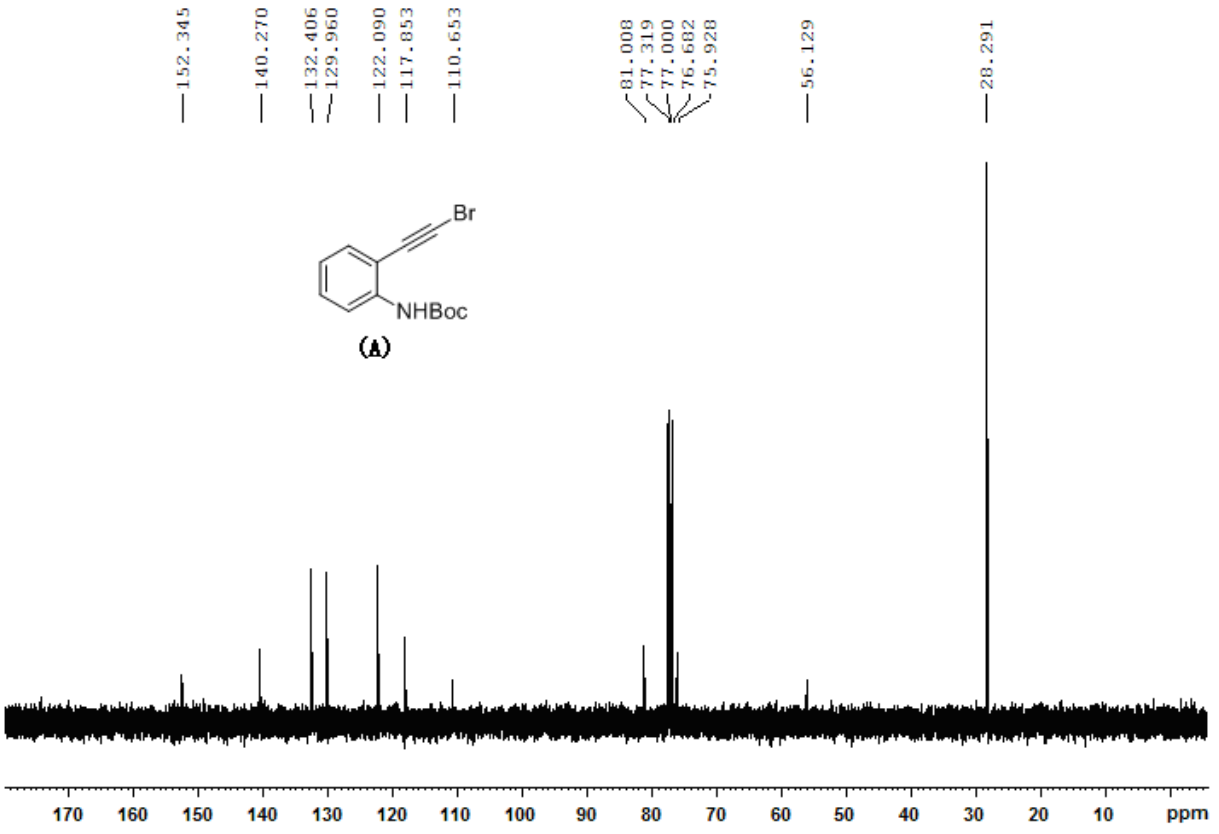
8.125
7.403
7.399
7.383
7.380
7.346
7.342
7.324
7.306
7.303
7.128
6.978
6.976
6.958
6.957
6.940
6.938
1.558
Br
NHBoc
(A)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.08
1.07
1.03
0.99
9.09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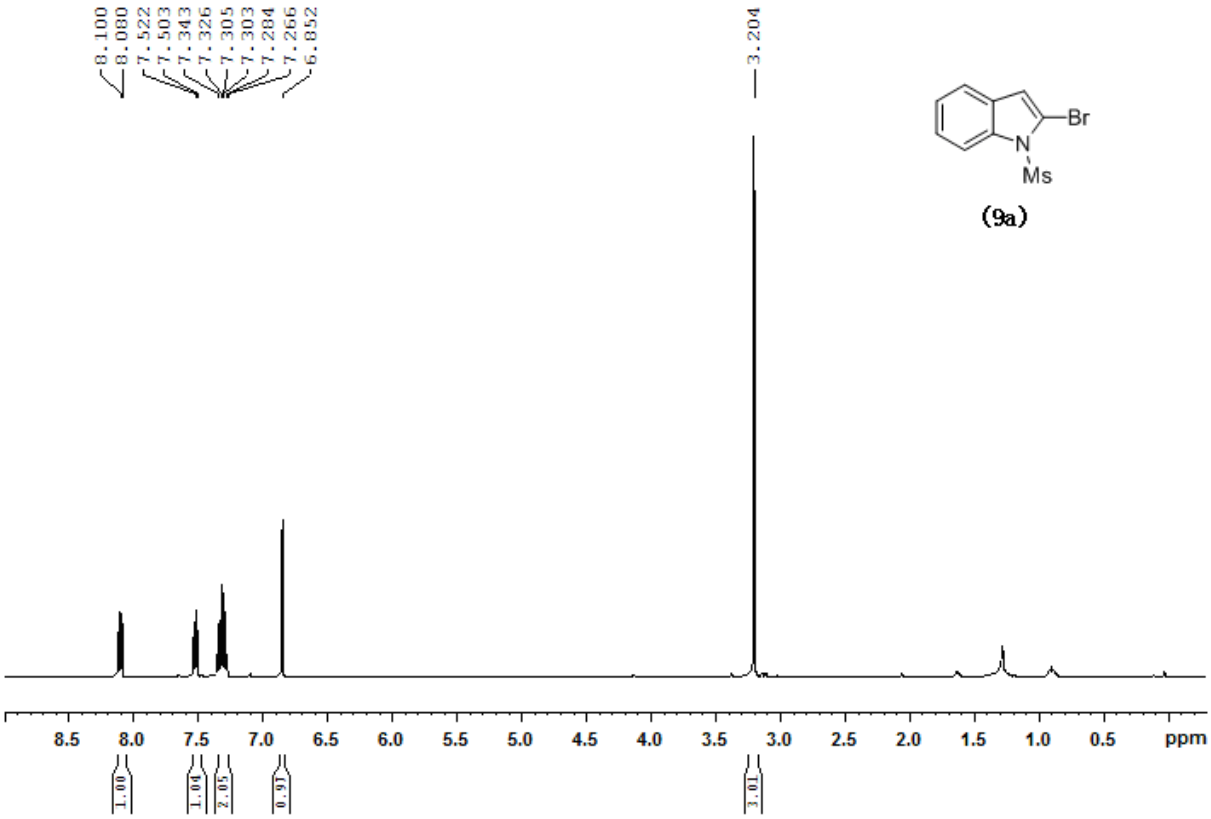
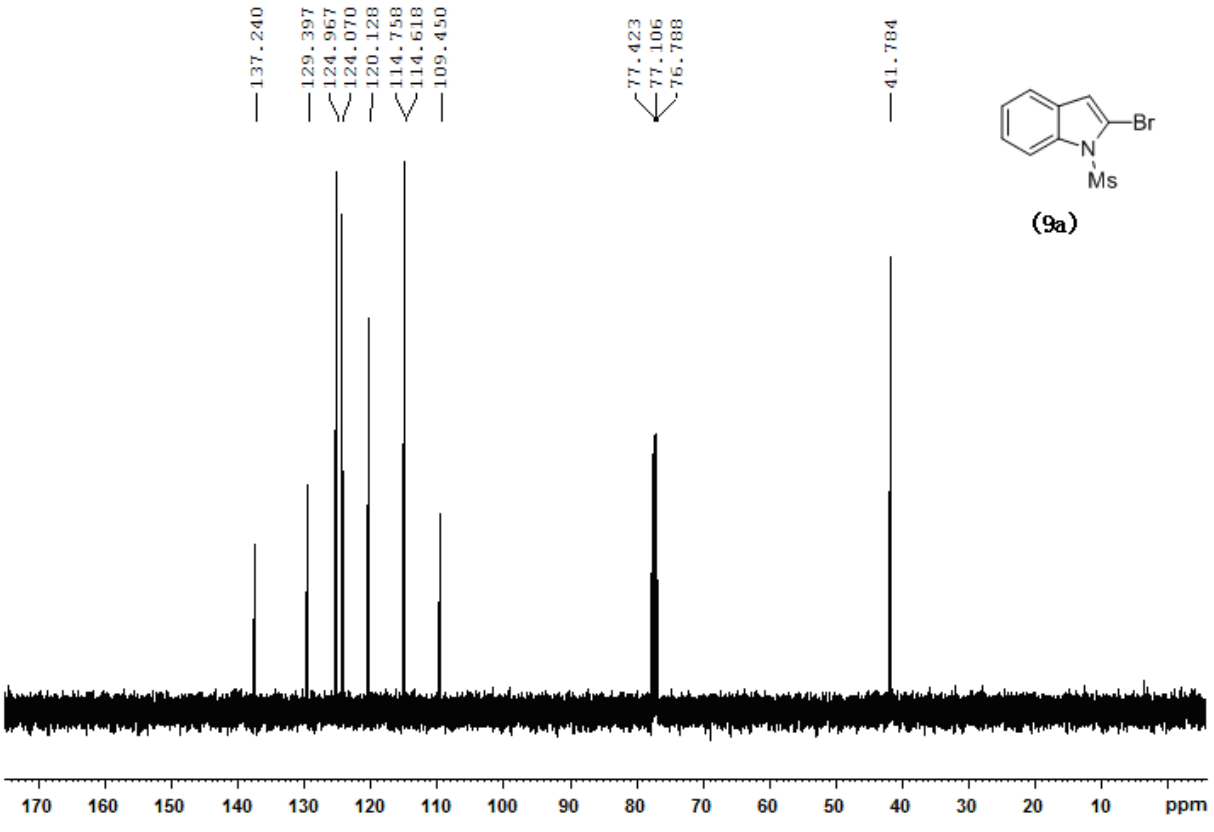
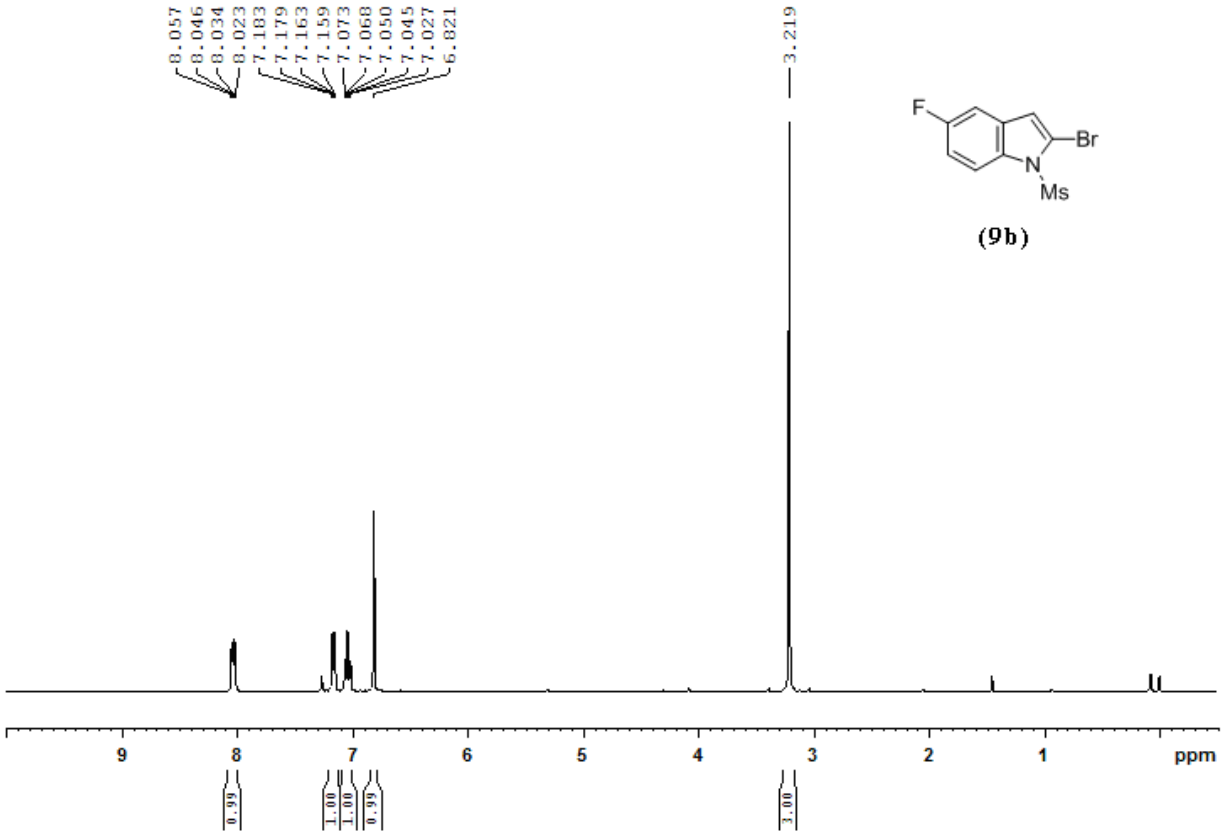
140.270
132.406
129.960
122.090
117.853
110.653
81.008
77.319
77.000
76.682
75.928
56.129
28.291
Br
NHBoc
(A)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



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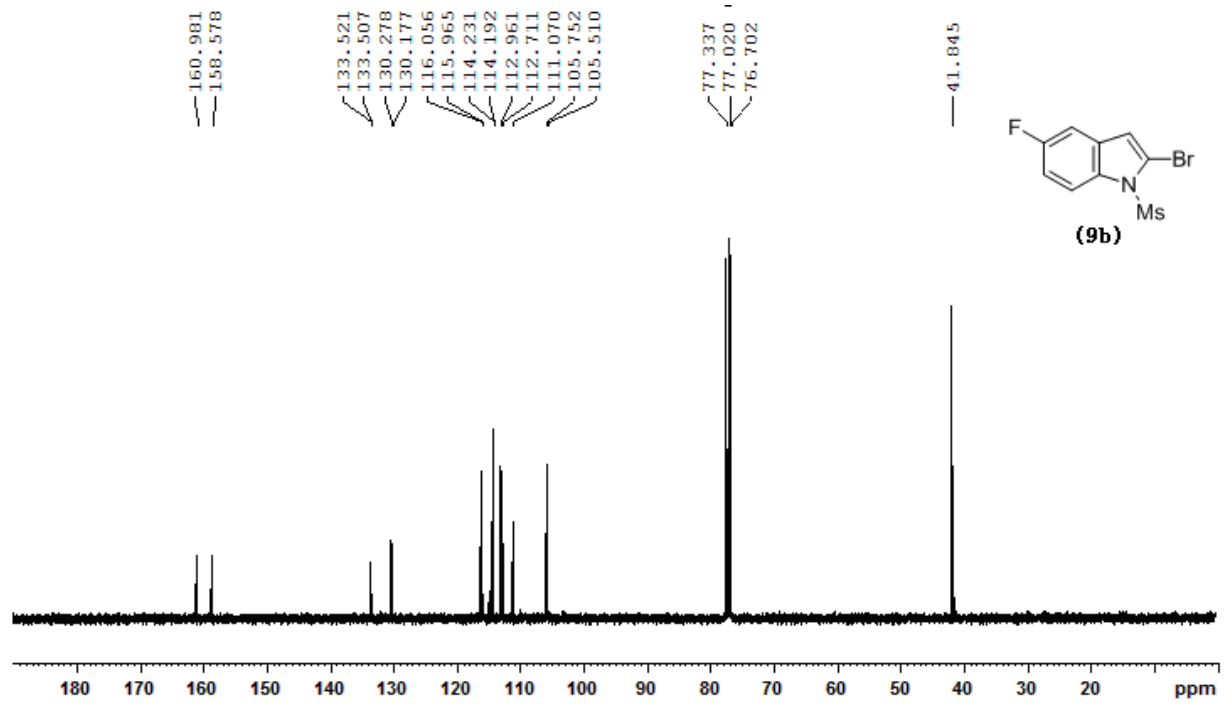
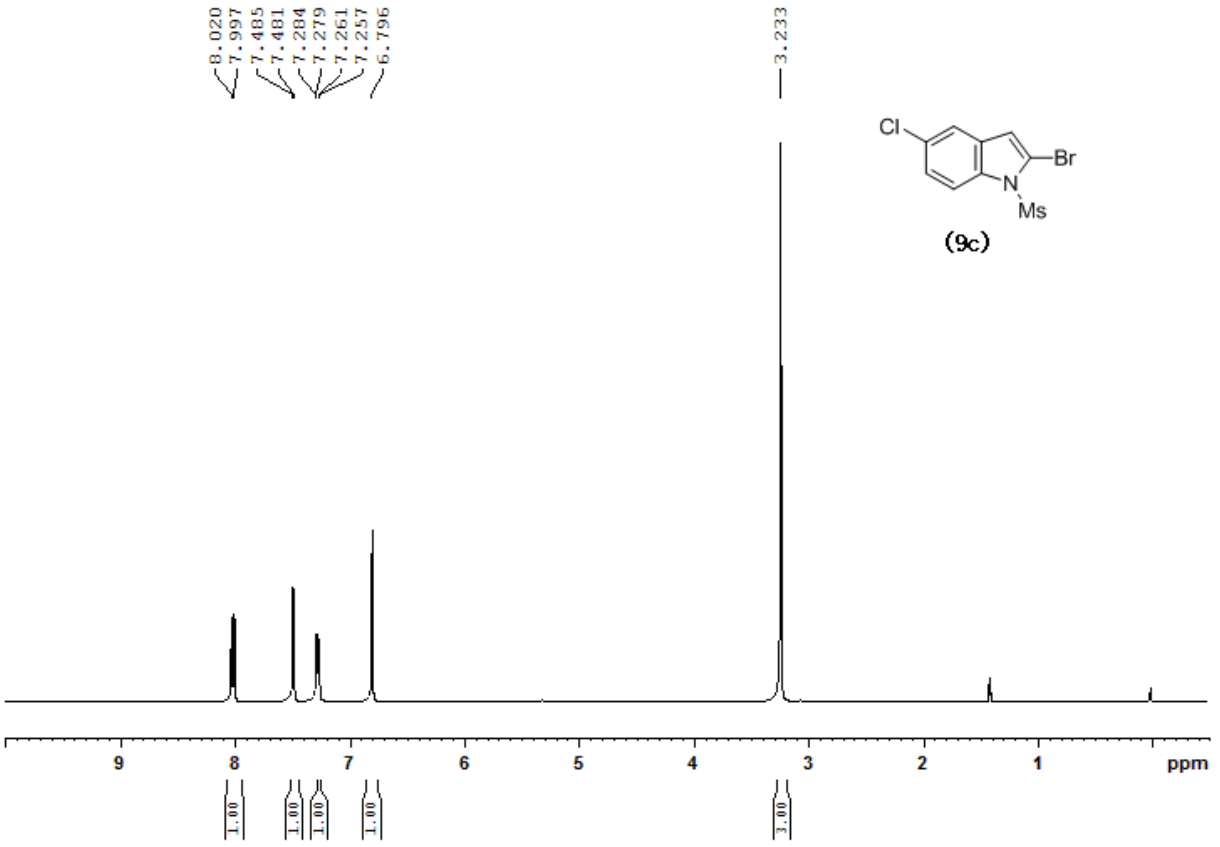
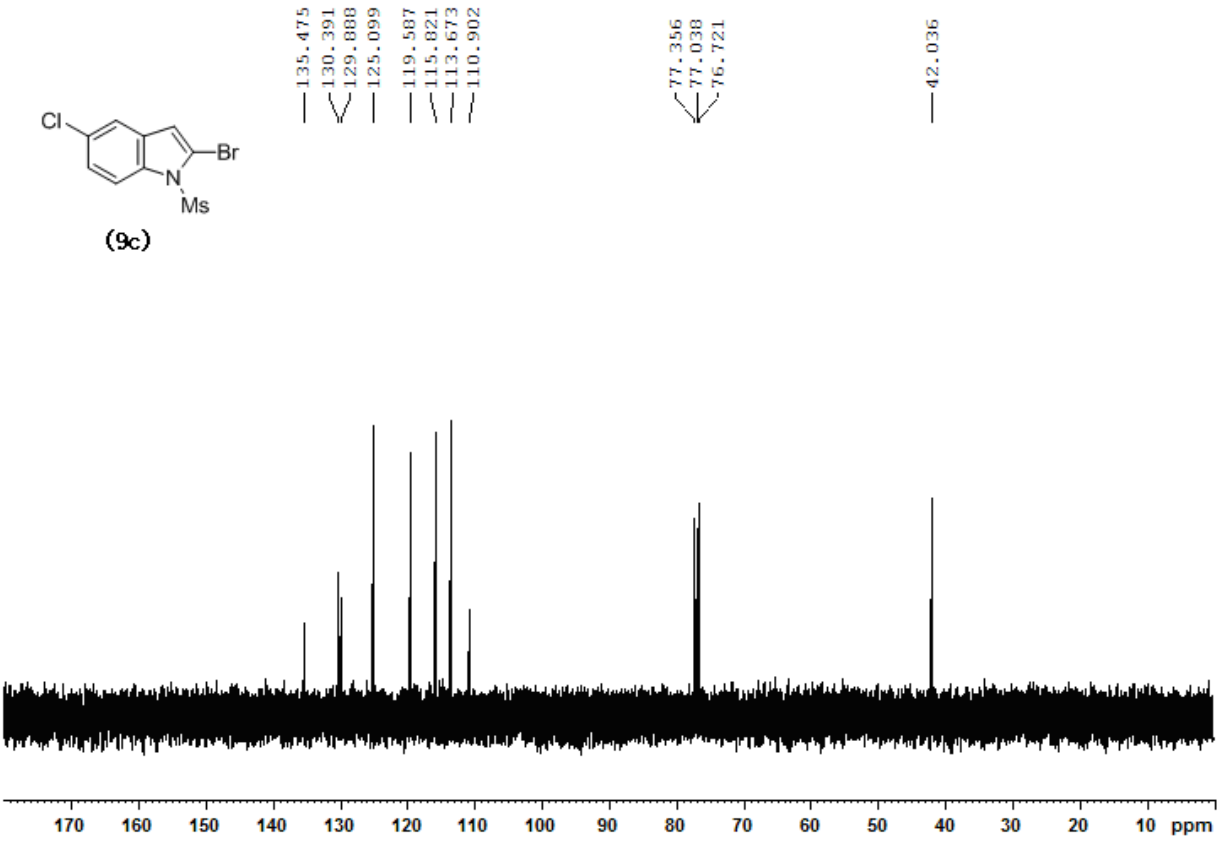
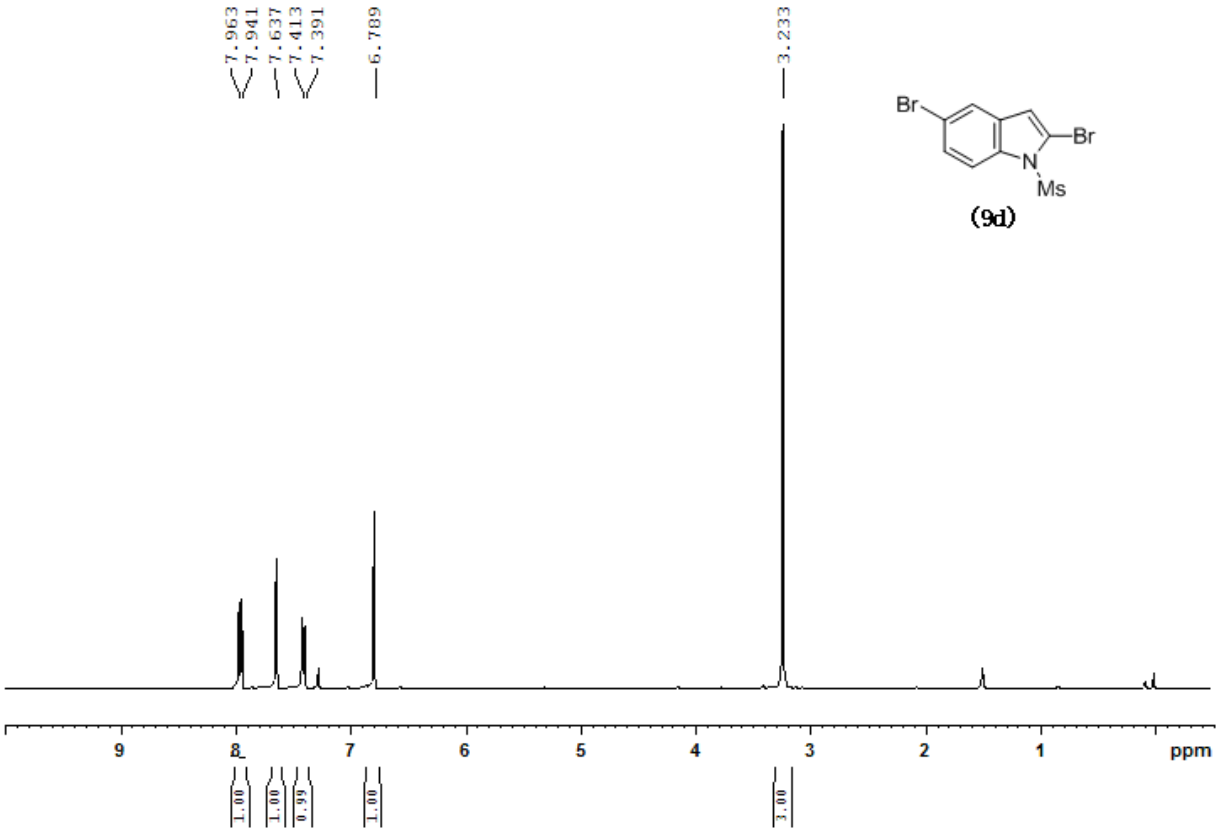
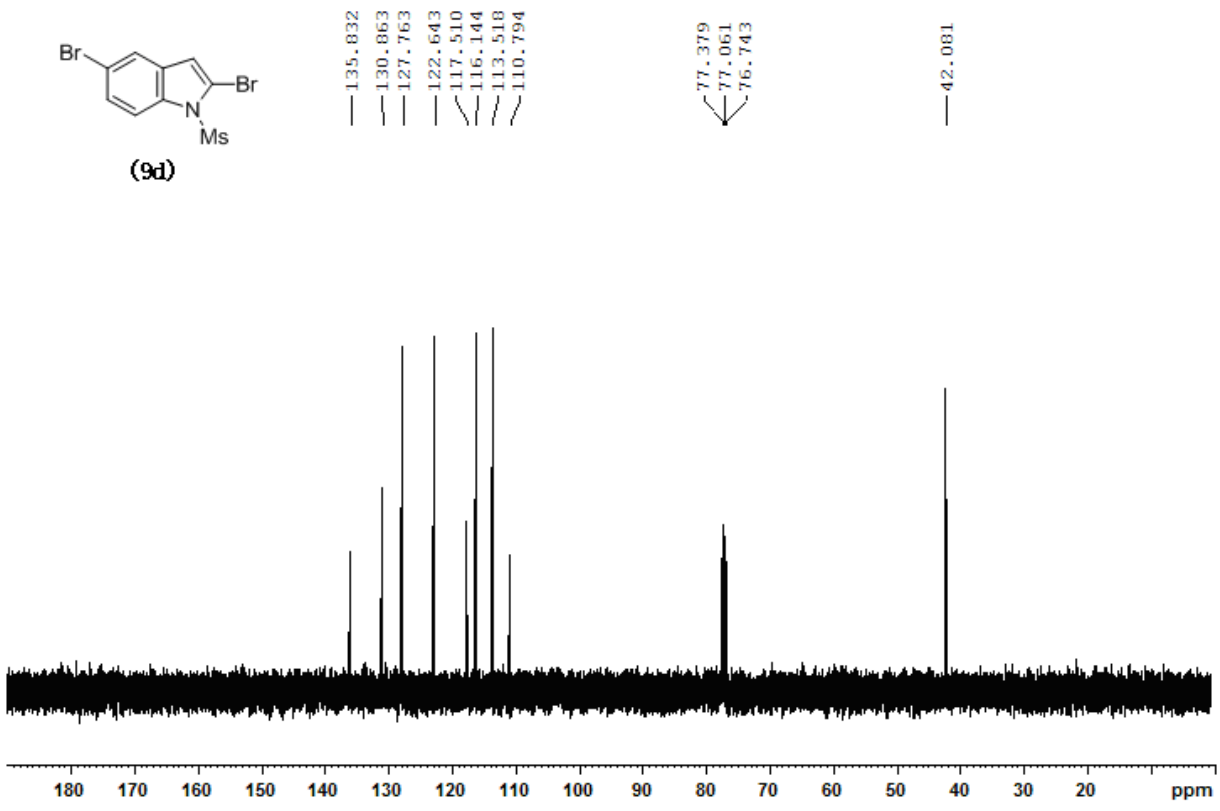
8.046
8.034
8.023
7.183
7.179
7.163
7.159
7.073
7.068
7.050
7.045
7.027
6.821
3.219
F
Br
N
Ms
(9b)
9
8
7
6
5
4
3
2
1
ppm
0.99
1.00
1.00
0.99
3.00

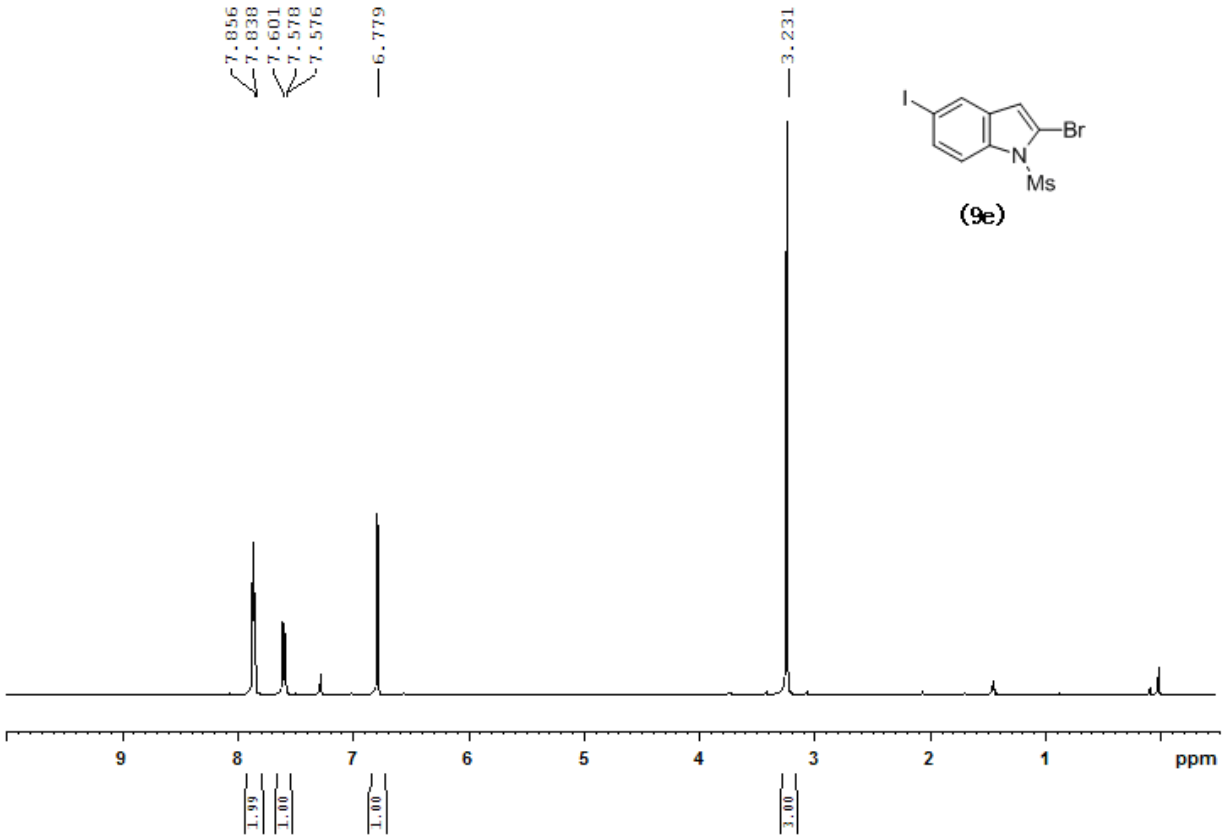

160.981
158.578
133.521
133.507
130.278
130.177
116.056
115.965
114.231
114.192
112.961
112.711
111.070
105.752
105.510
77.337
77.020
76.702
41.845
F
Br
N
Ms
(9b)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

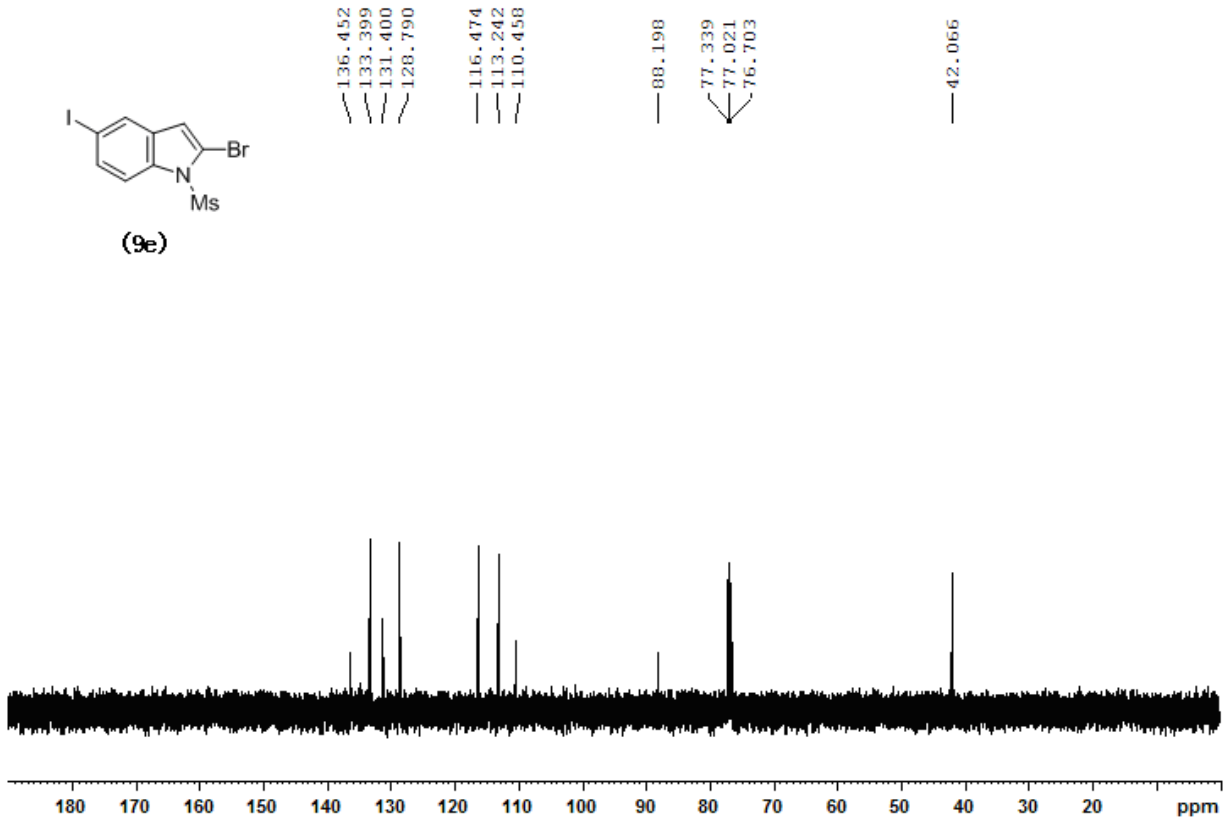


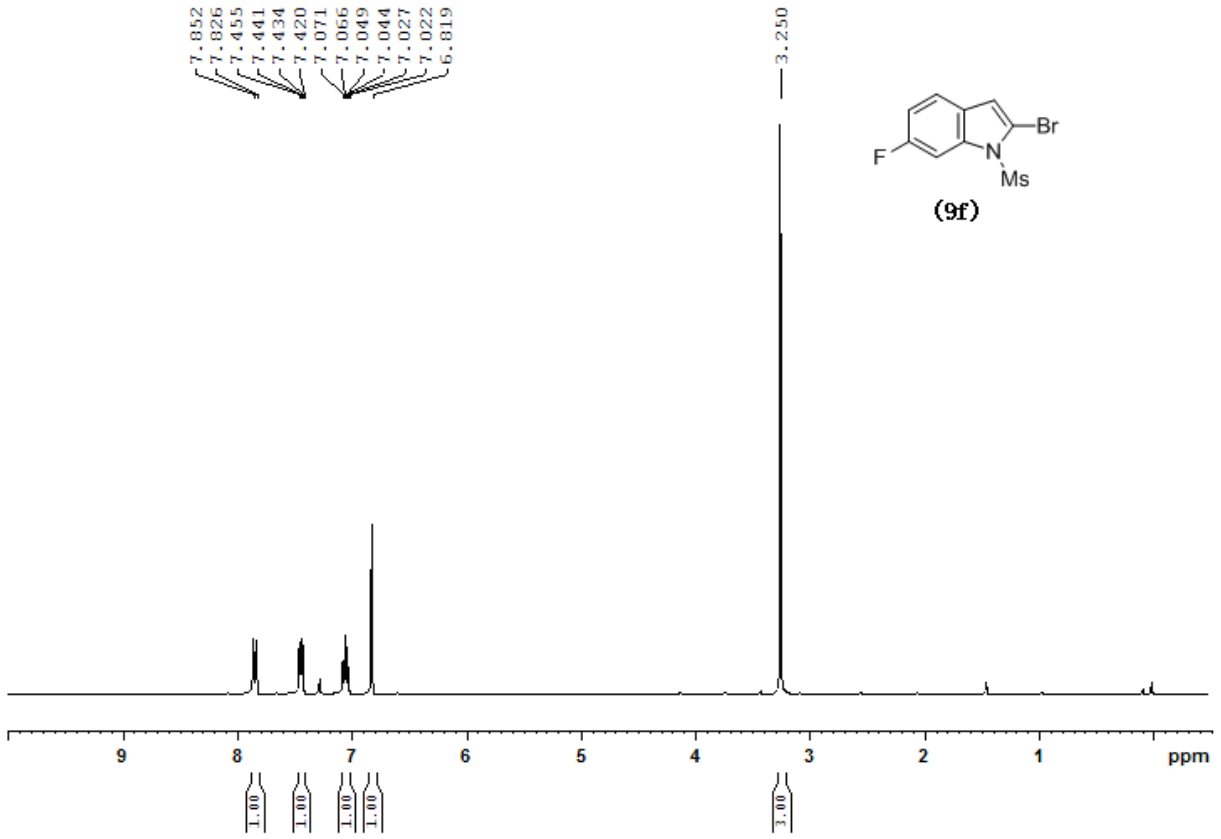


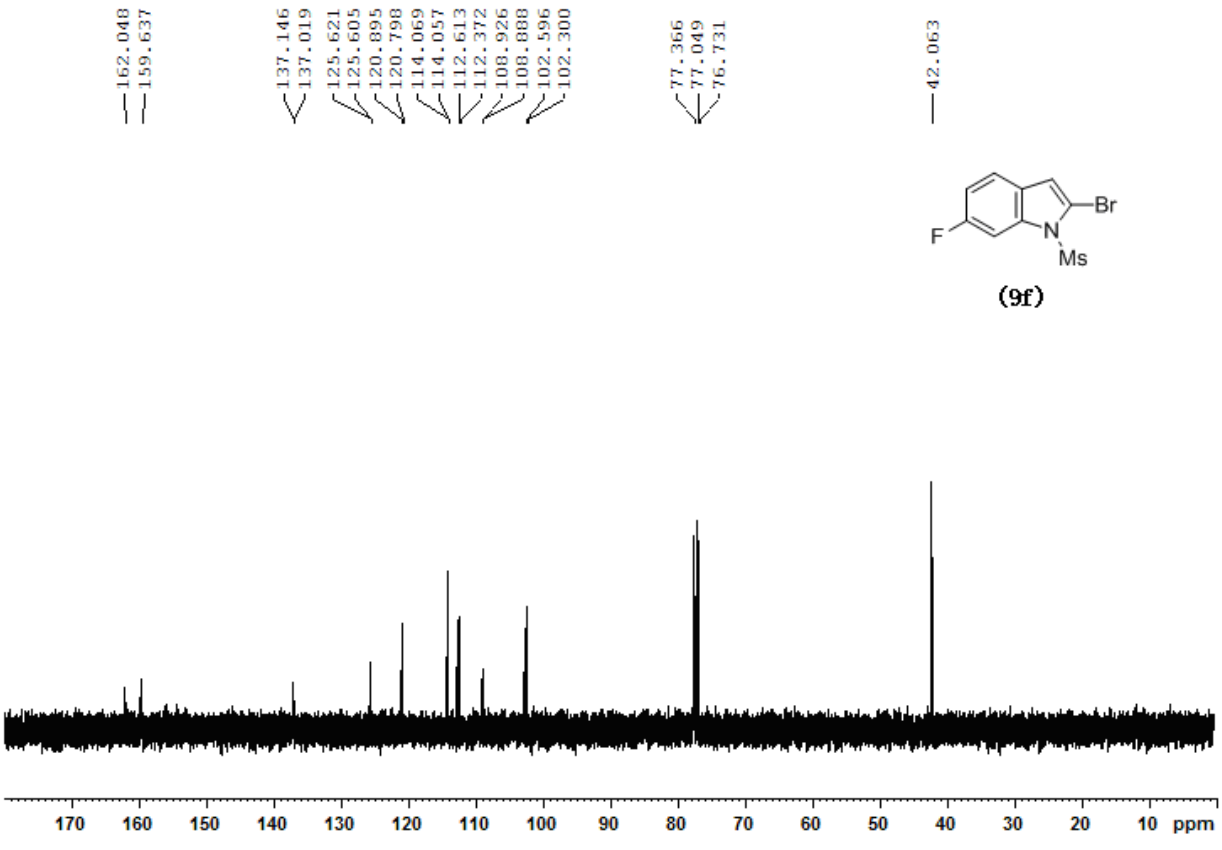

7.963
7.941
7.637
7.413
7.391
6.789
3.233
Br
Br
N
Ms
(9d)
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
0.99
1.00
3.00

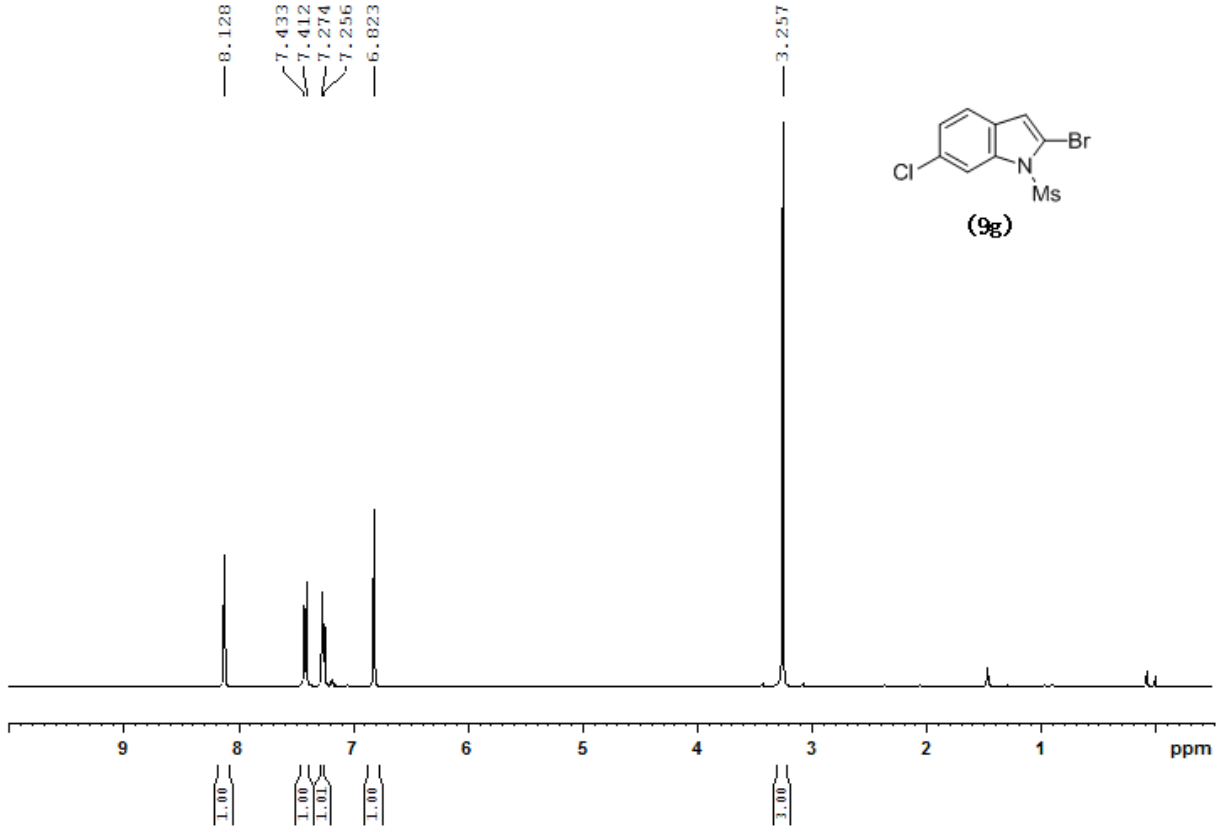

Br
Br
N
Ms
(9d)
135.832
130.863
127.763
122.643
117.510
116.144
113.518
110.794
77.379
77.061
76.743
42.081
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

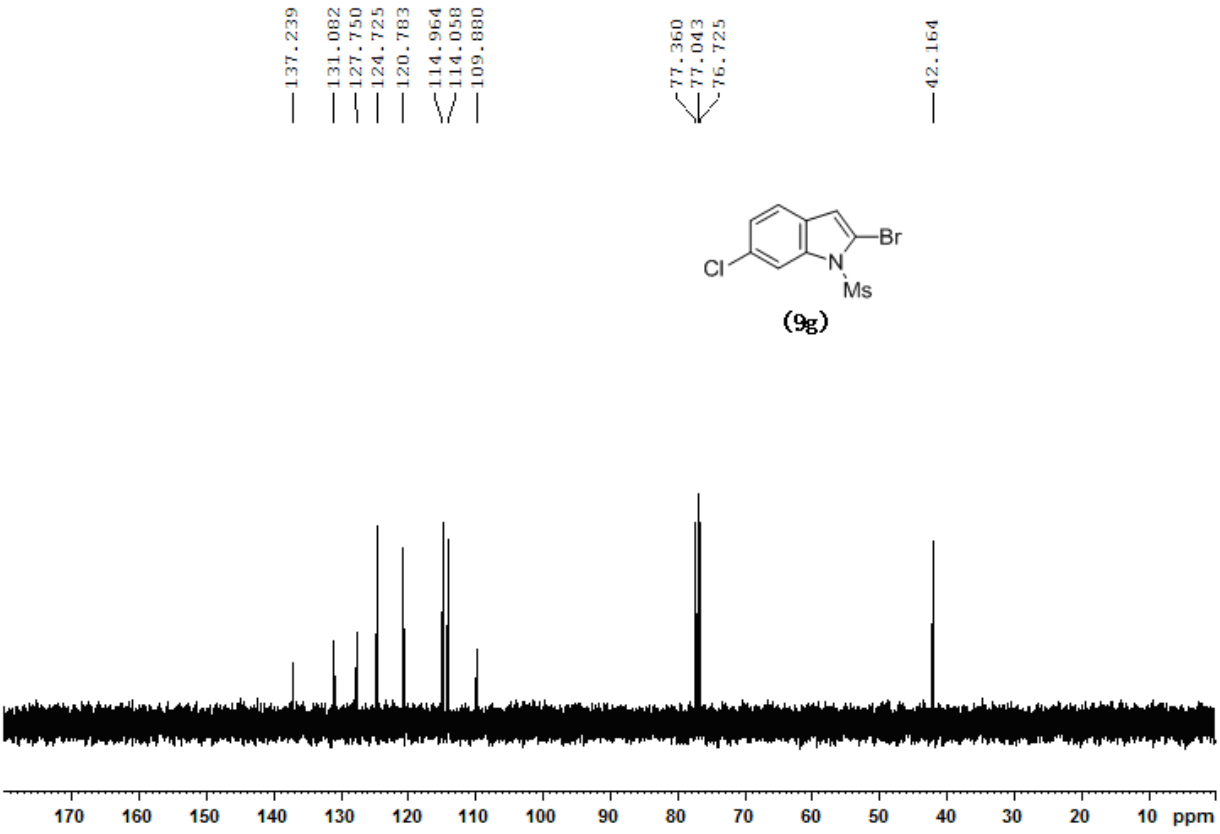


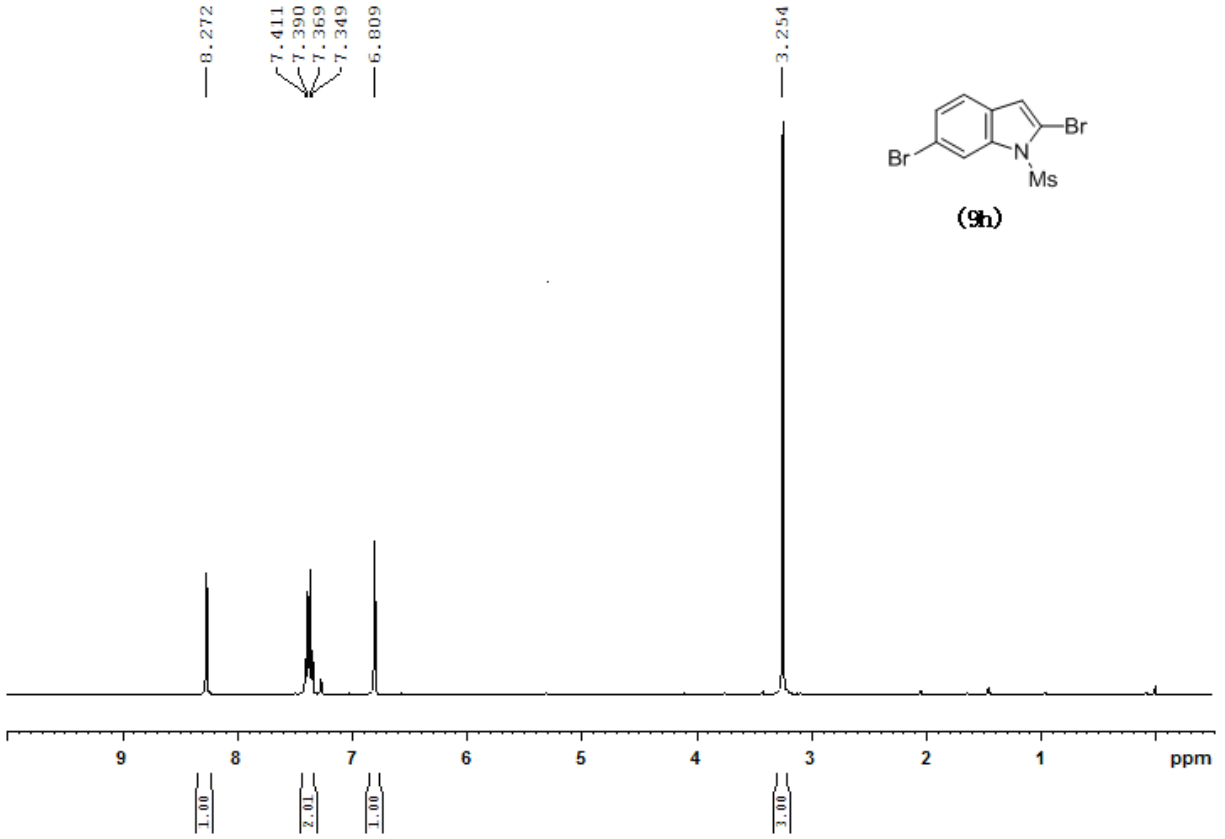


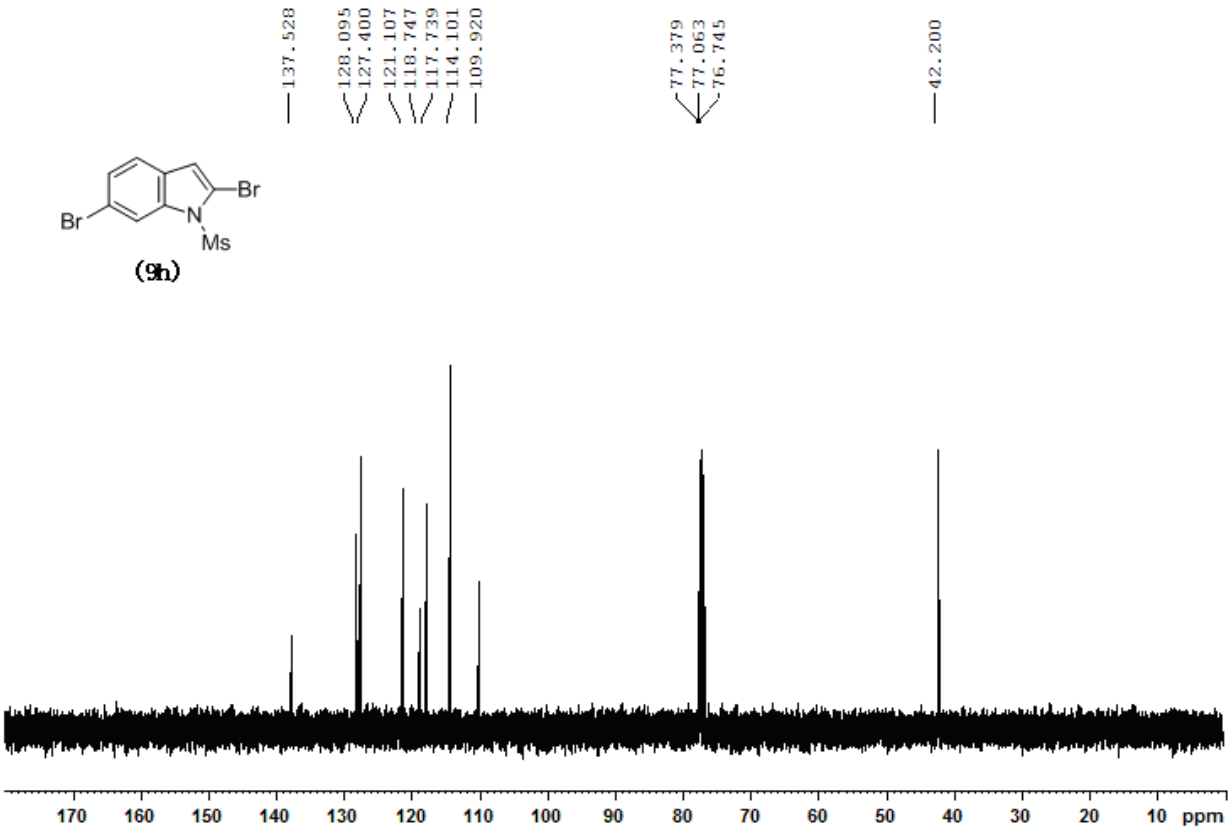


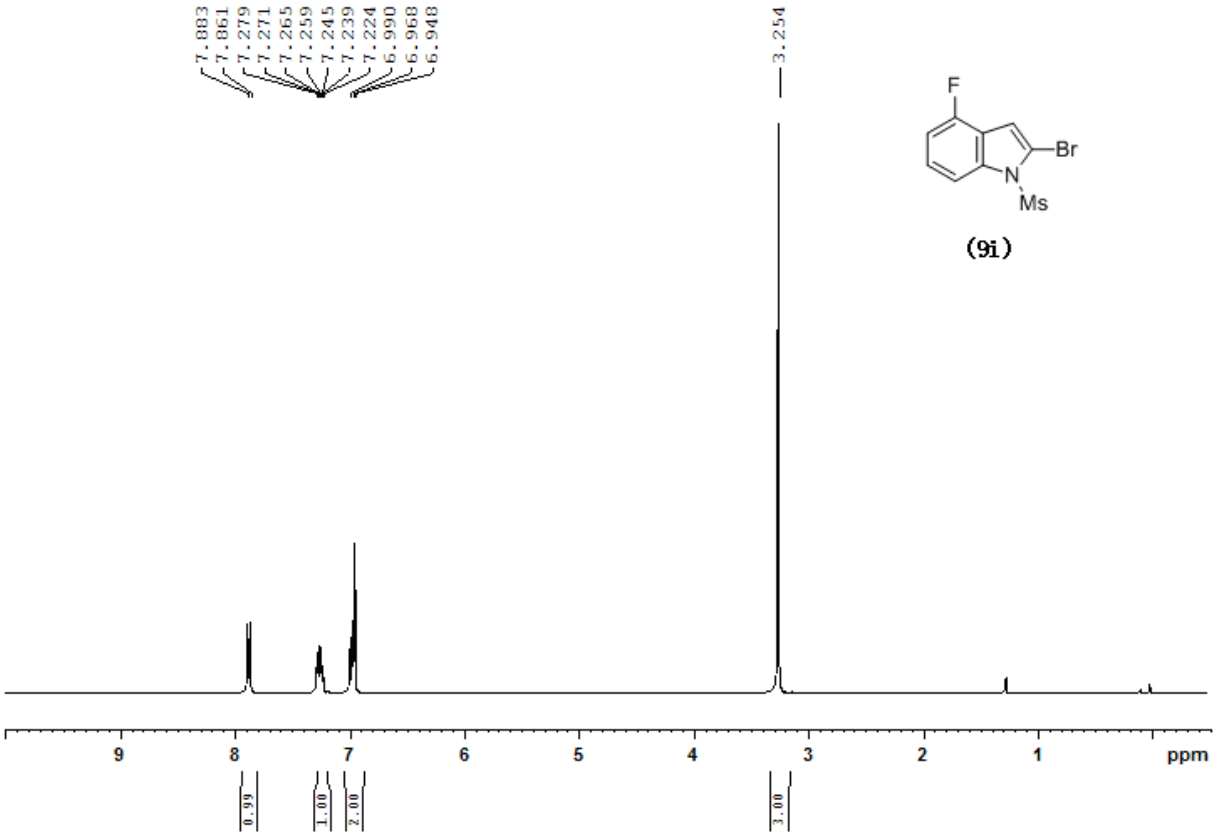


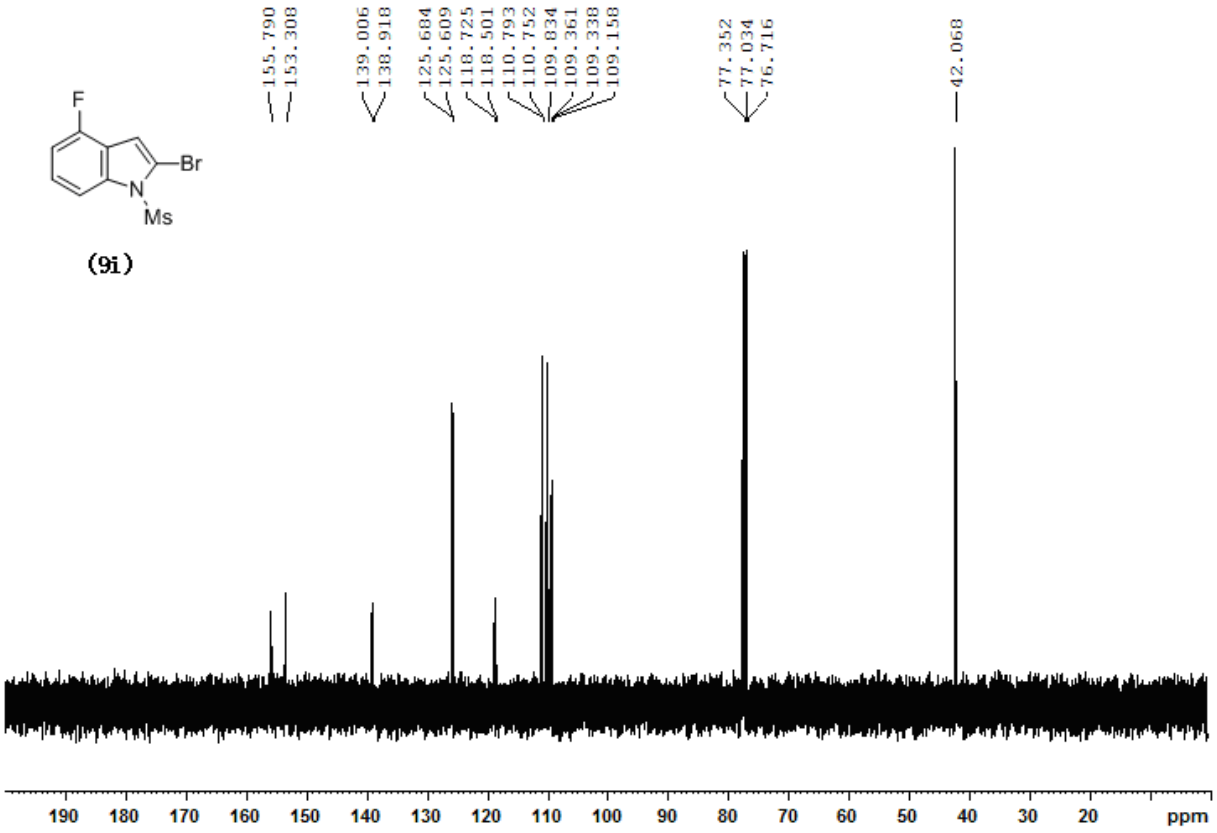


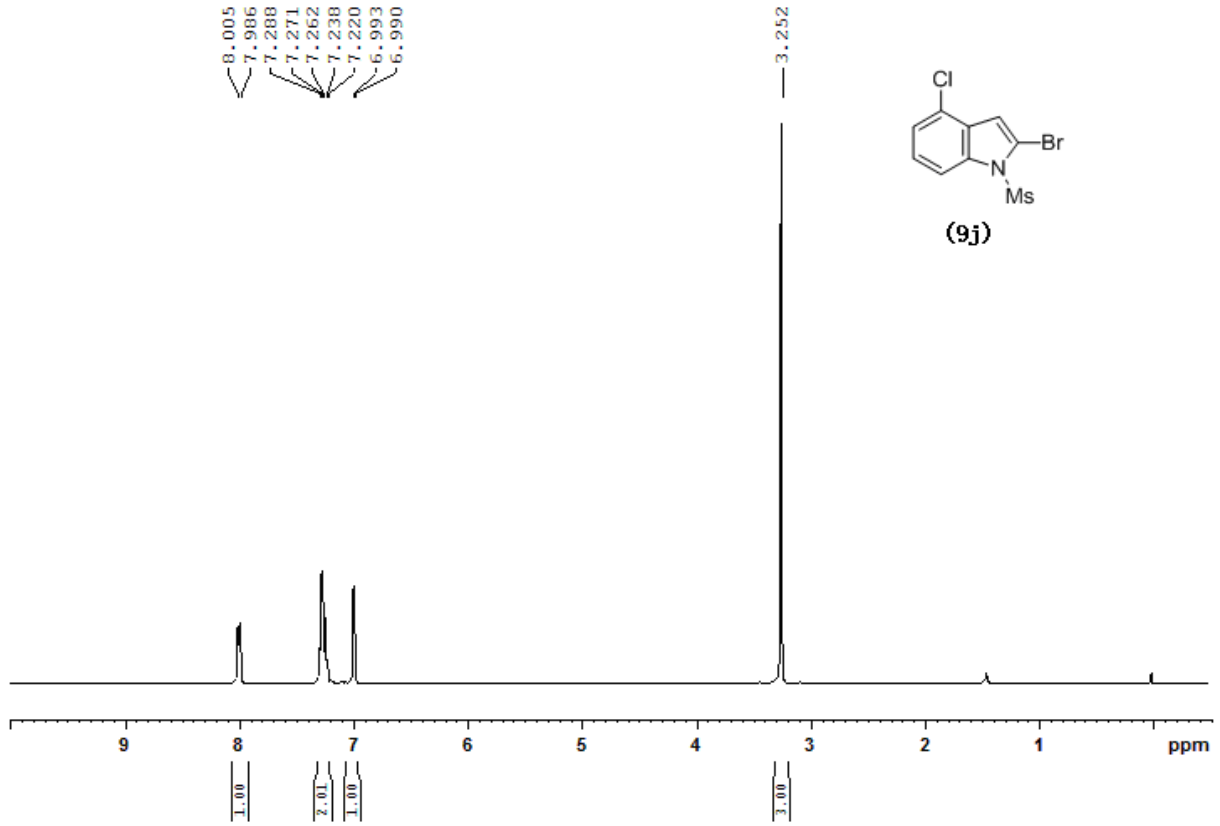


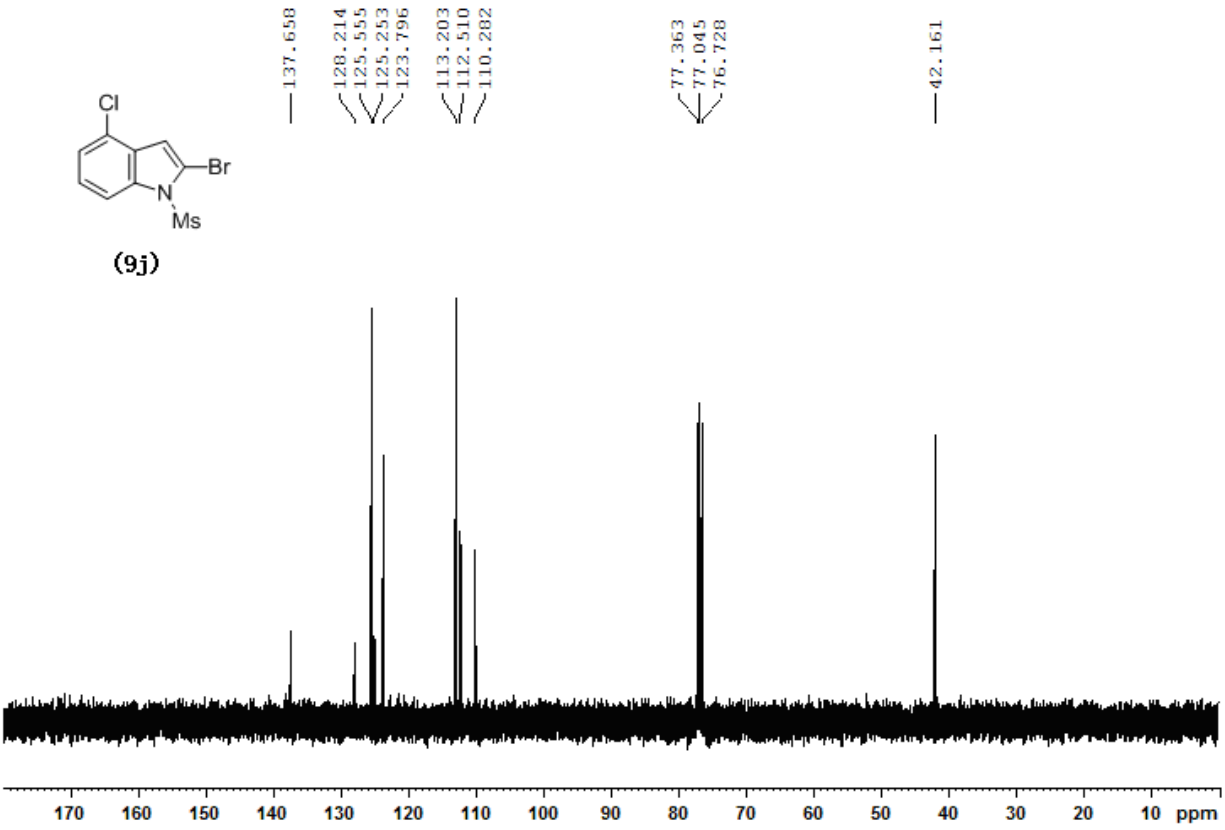

8.272
7.411
7.390
7.369
7.349
6.809
3.254
Br
Br
N
Ms
(9h)
9
8
7
6
5
4
3
2
1
ppm
1.00
2.01
1.00
3.00


137.528
128.095
127.400
121.107
118.747
117.739
114.101
109.920
77.379
77.063
76.745
42.200
Br
Br
N
Ms
(9h)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm






8.005
7.986
7.288
7.271
7.262
7.238
7.220
6.993
6.990
3.252
Cl
Br
N
Ms
(9j)
9
8
7
6
5
4
3
2
1
ppm
1.00
2.01
1.00
3.00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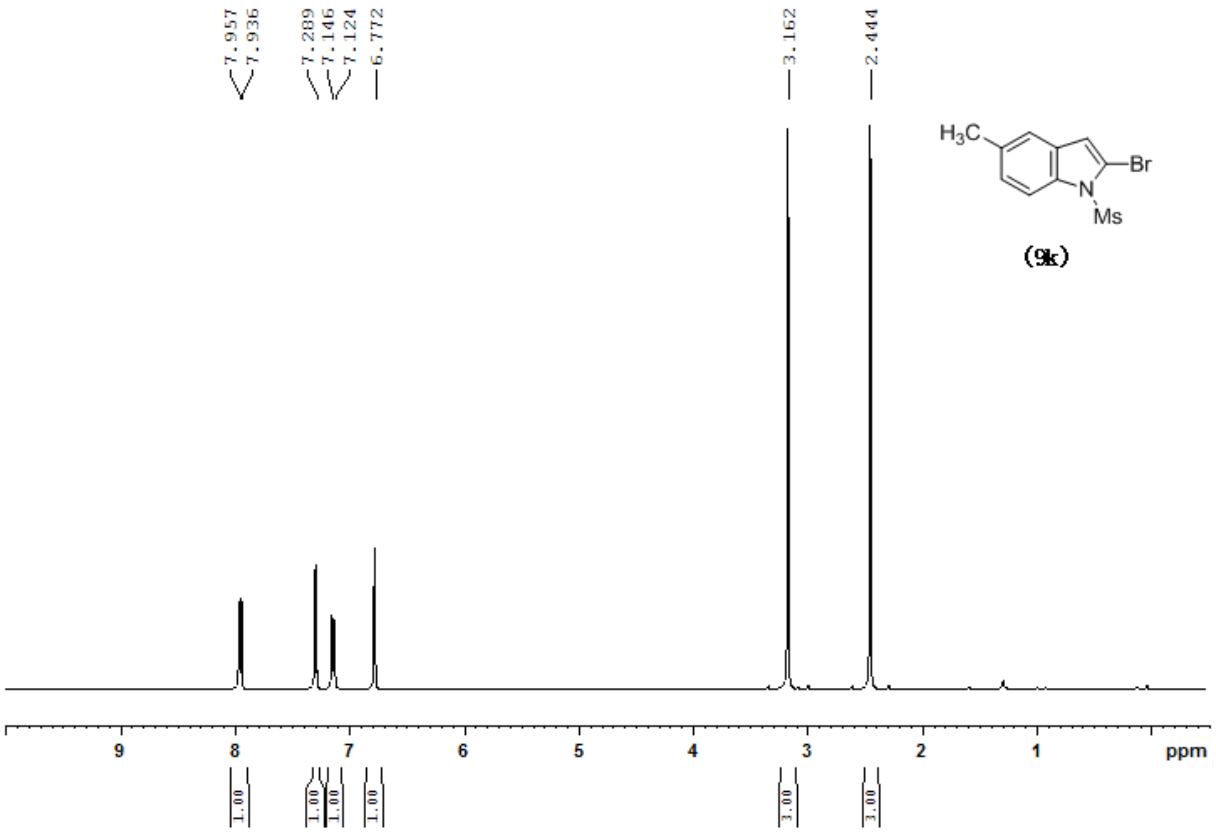
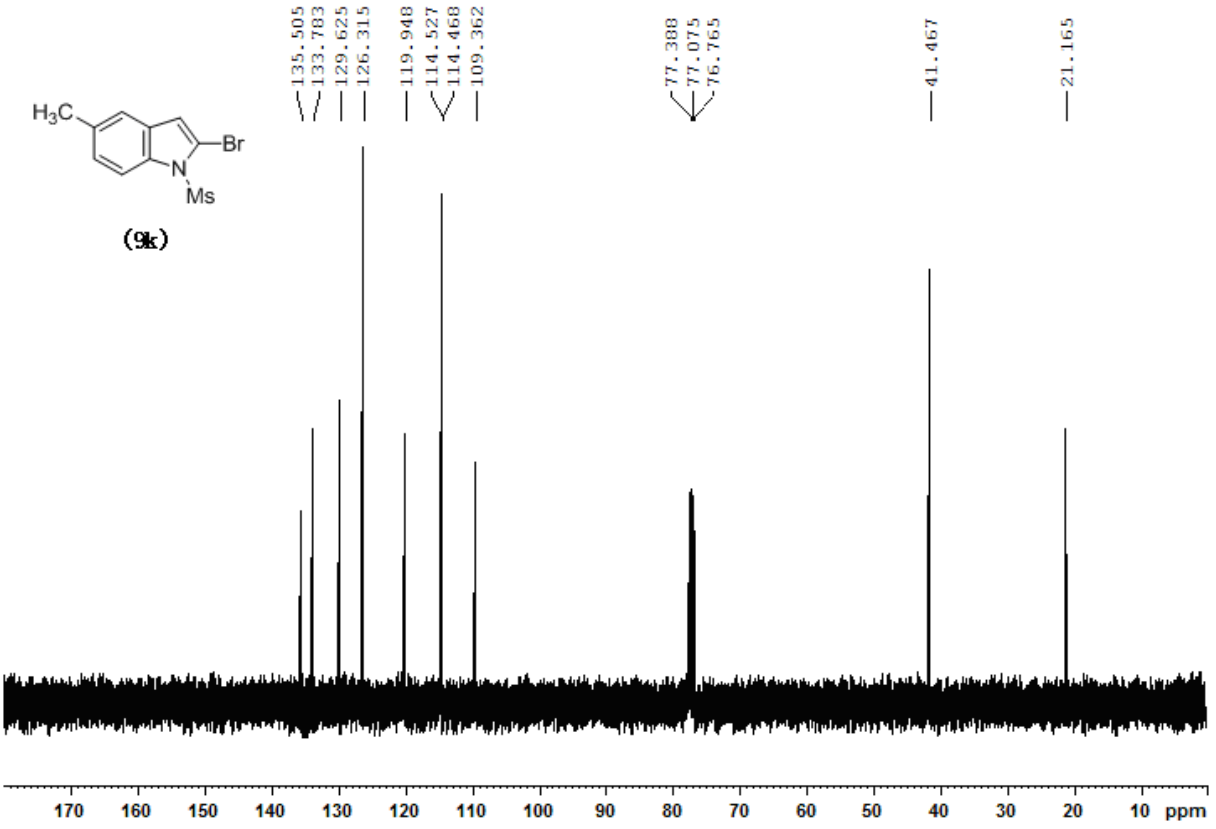
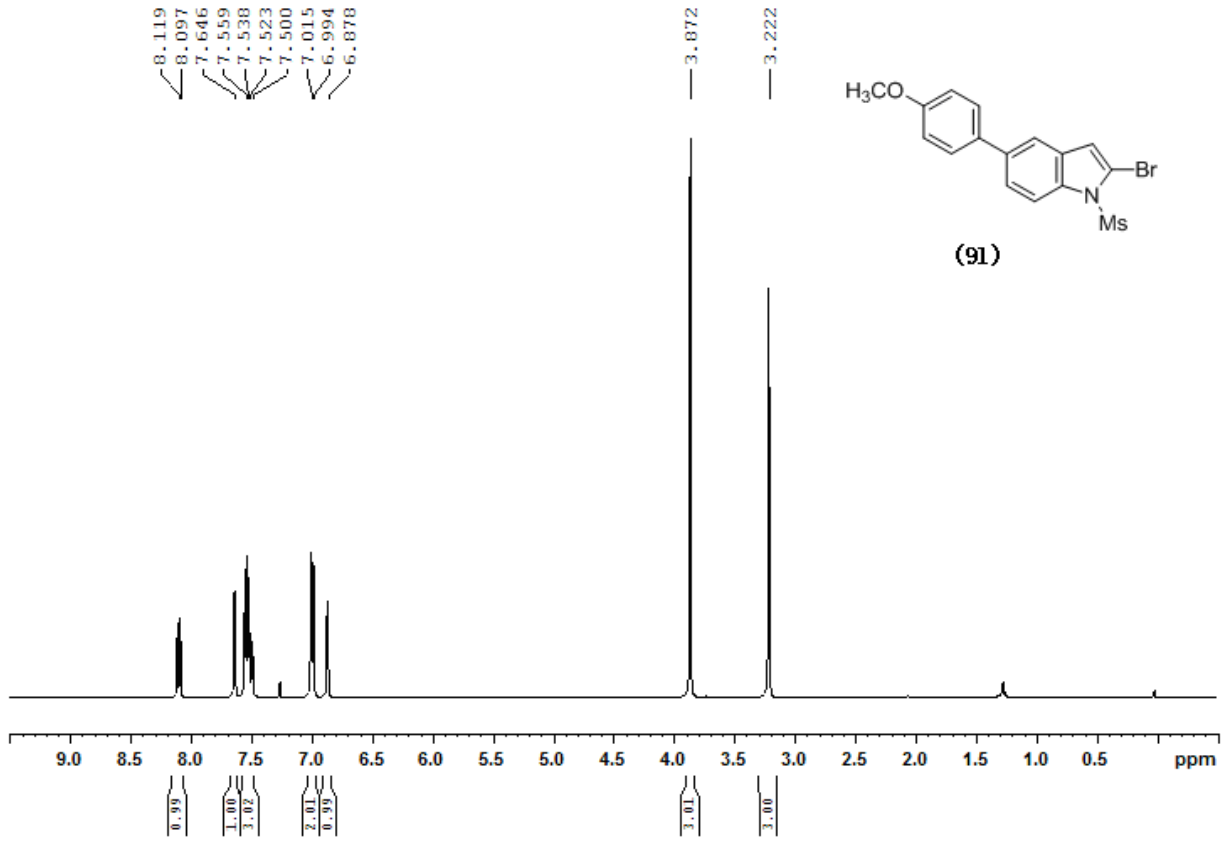
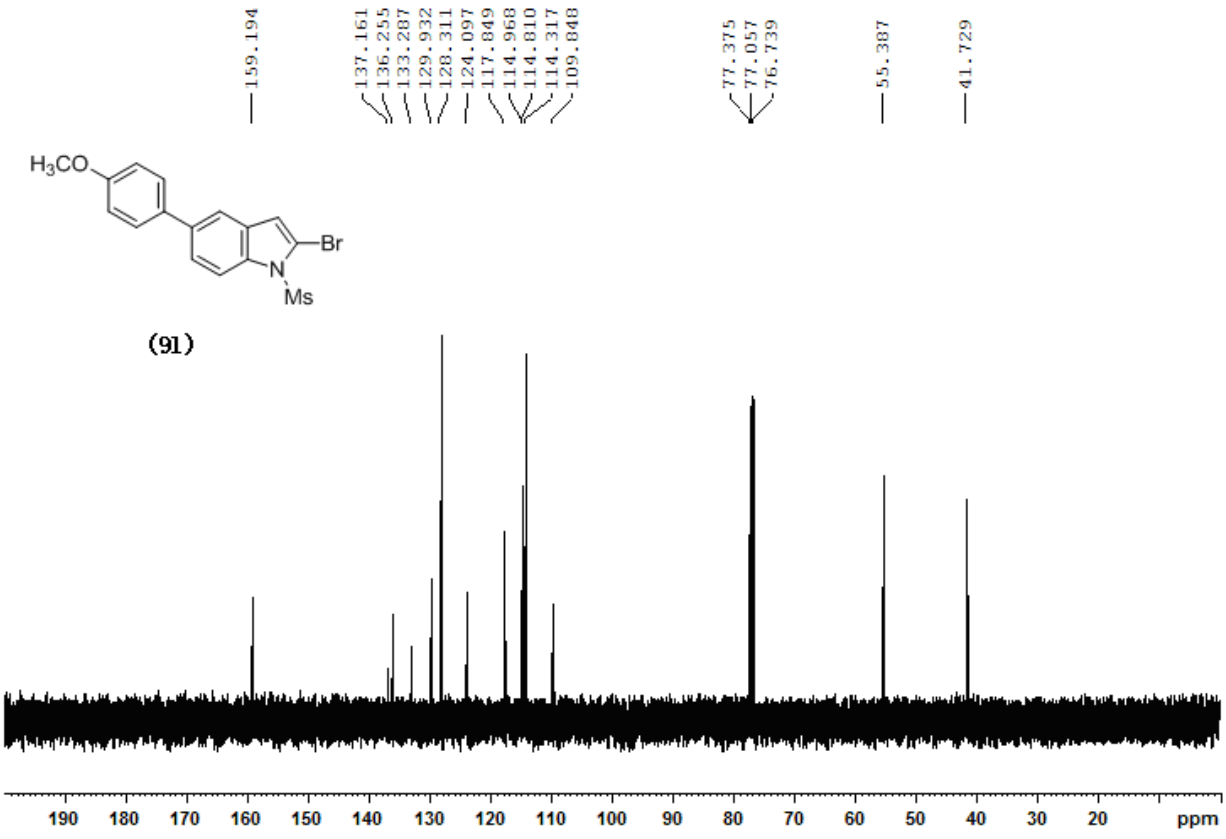
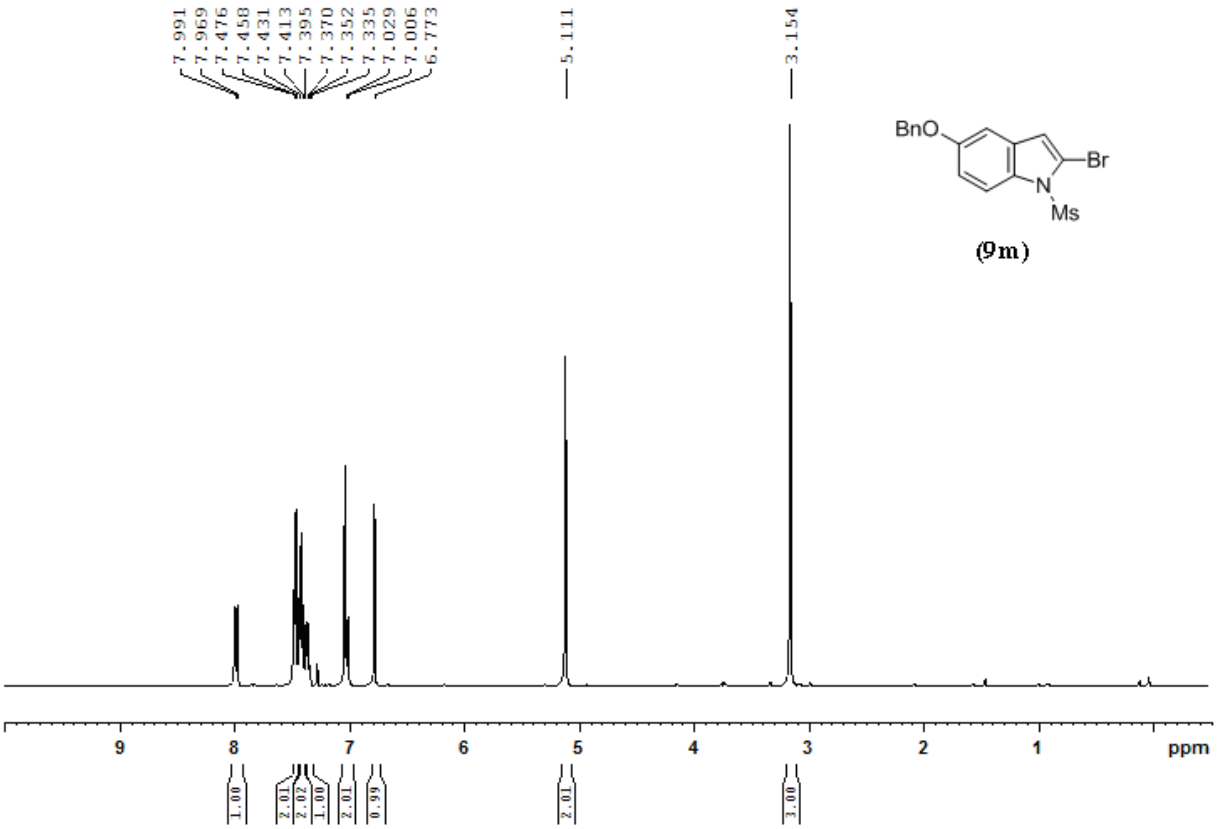
128.214
125.555
125.253
123.796
113.203
112.510
110.282
77.363
77.045
76.728
42.161
Cl
Br
N
Ms
(9j)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

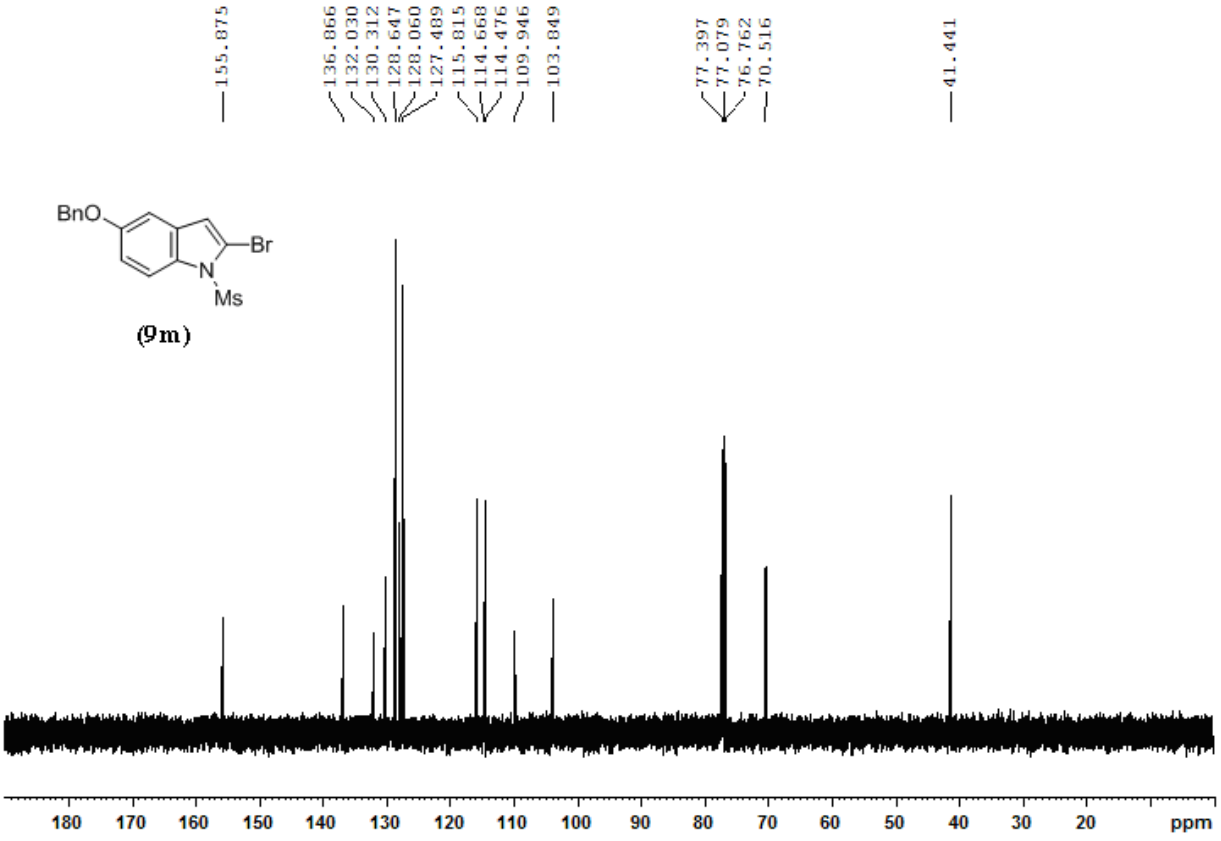

7.957
7.936
7.289
7.146
7.124
6.772
3.162
2.444
H3C
Br
N
Ms
(9k)
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.00
1.00
3.00
3.00

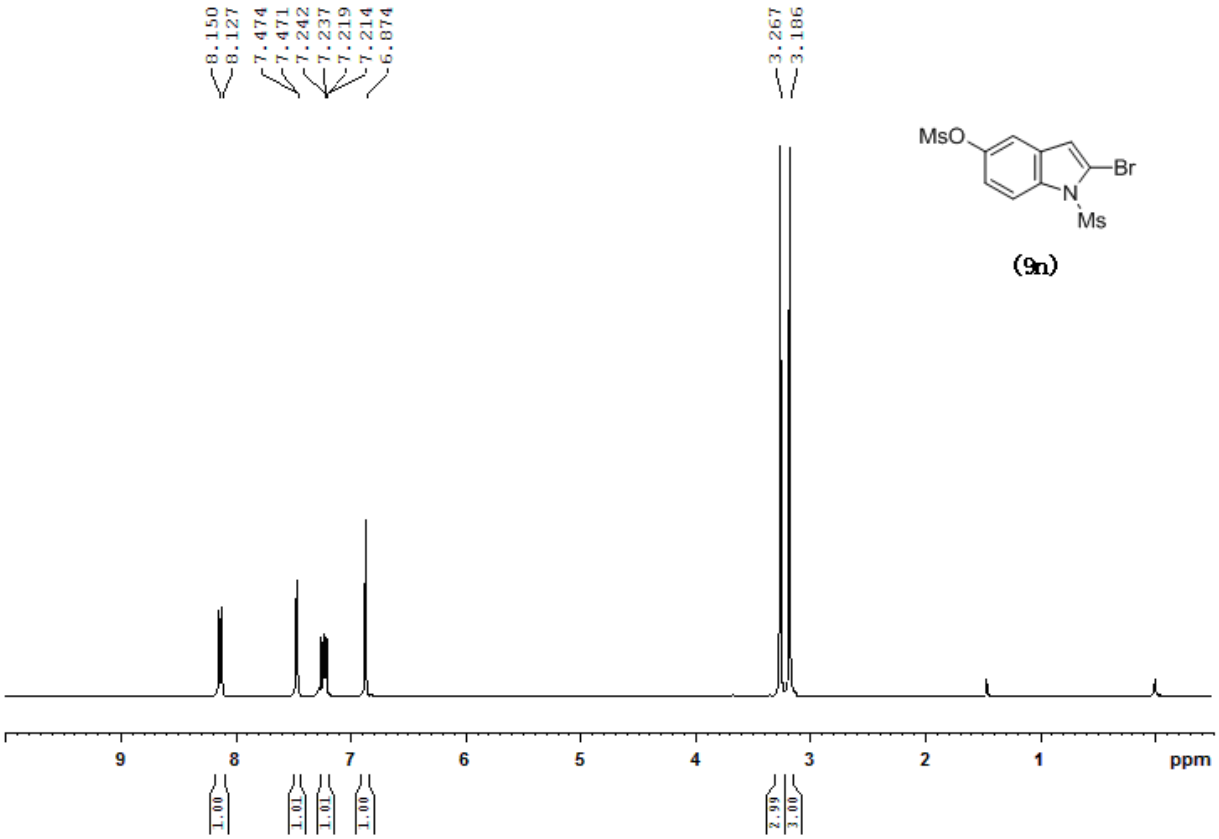

135.505
133.783
129.625
126.315
119.948
114.527
114.468
109.362
77.388
77.075
76.765
41.467
21.165
H3C
Br
N
Ms
(9k)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

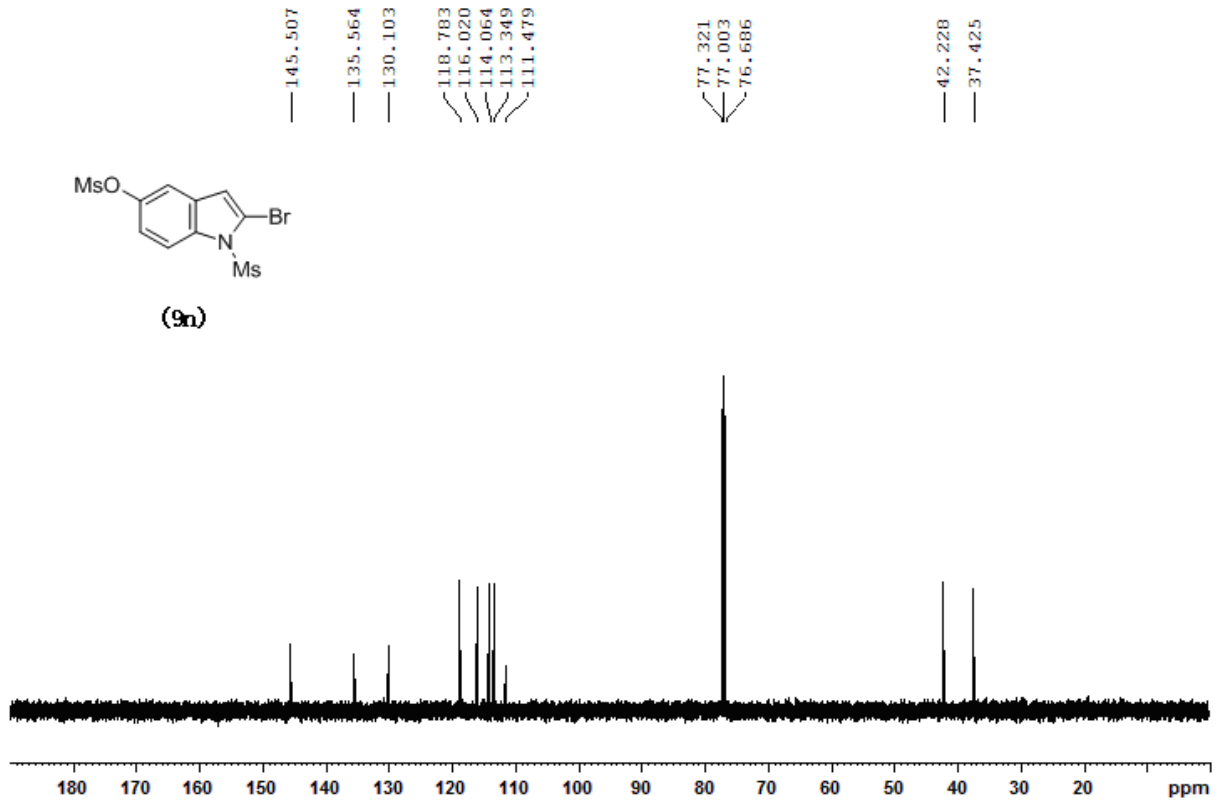


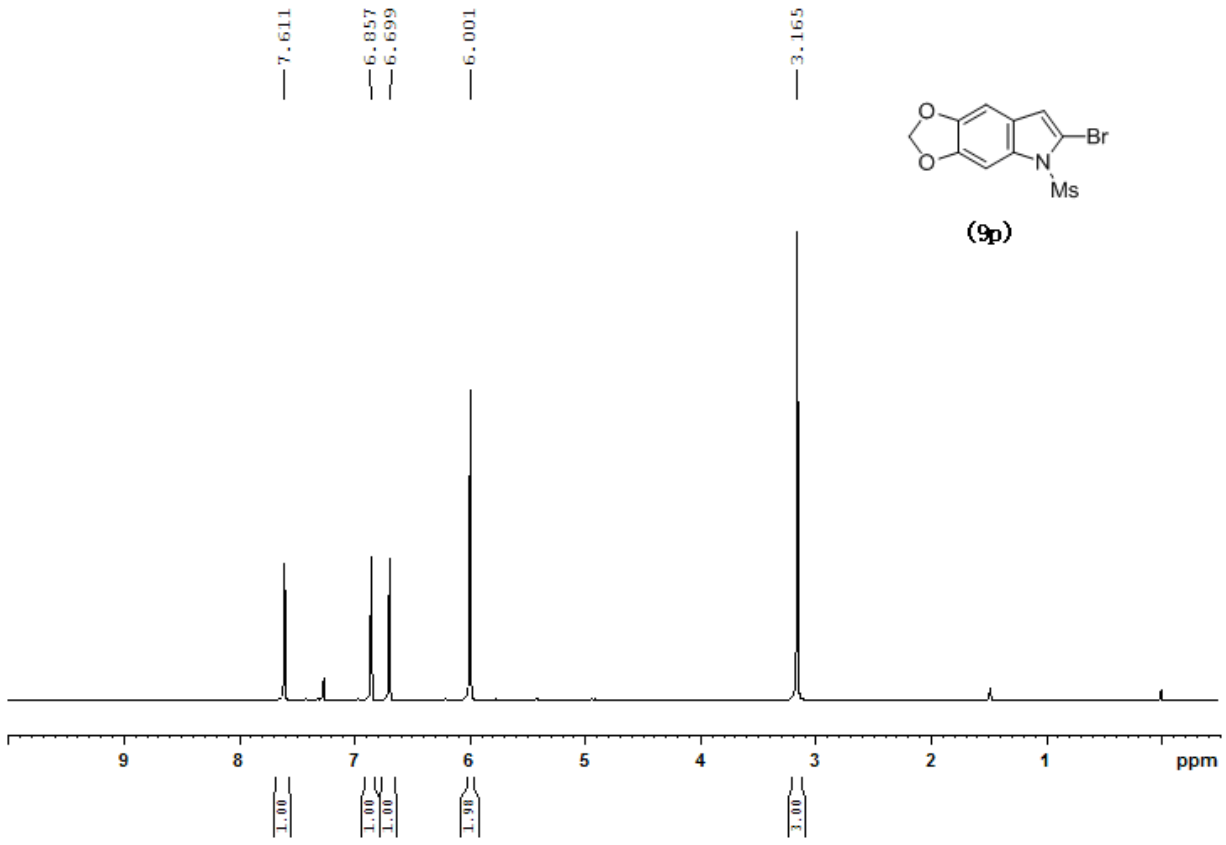


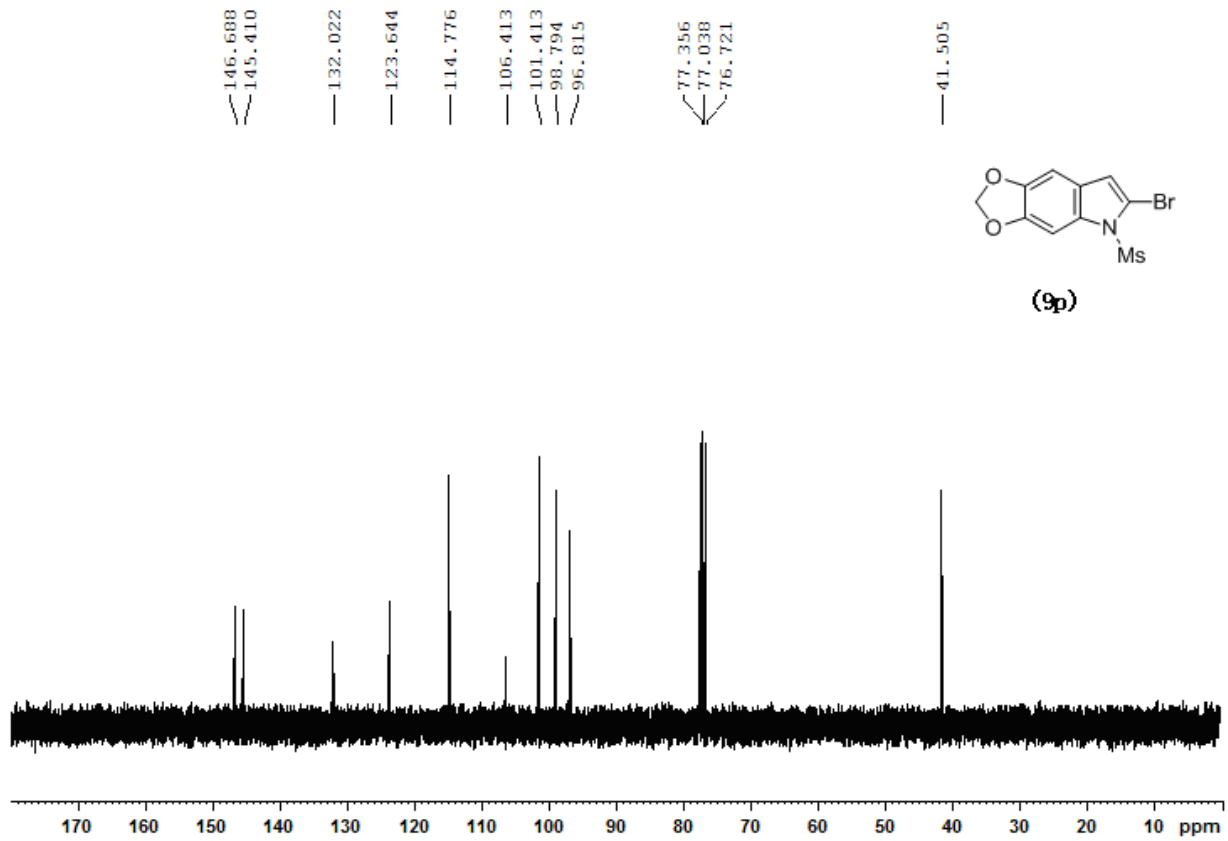

7.991
7.969
7.476
7.458
7.431
7.413
7.395
7.370
7.352
7.335
7.029
7.006
6.773
5.111
3.154
BnO
Br
N
Ms
(9m)
9
8
7
6
5
4
3
2
1
ppm
1.00
2.01
2.02
1.00
2.01
0.99
2.01
3.00

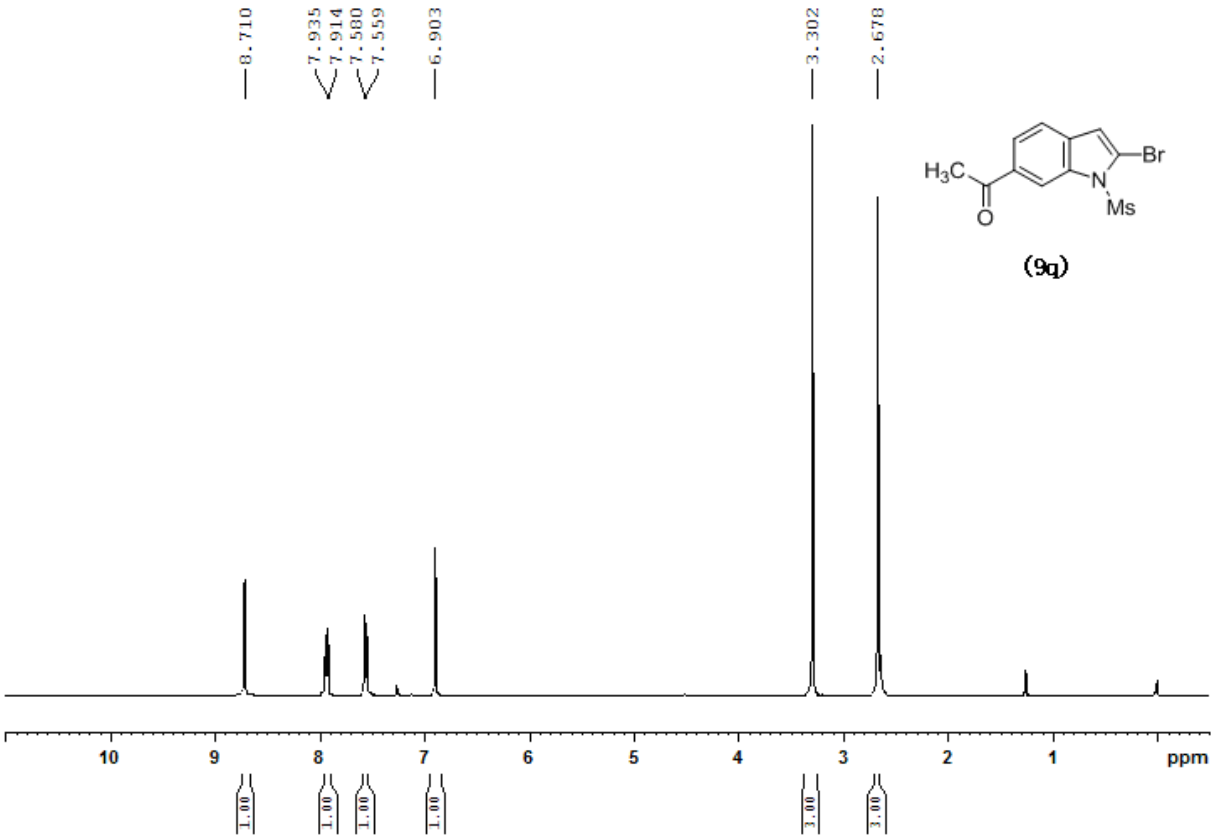

155.875
136.866
132.030
130.312
128.647
128.060
127.489
115.815
114.668
114.476
109.946
103.849
77.397
77.079
76.762
70.516
41.441
BnO
Br
N
Ms
(9m)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

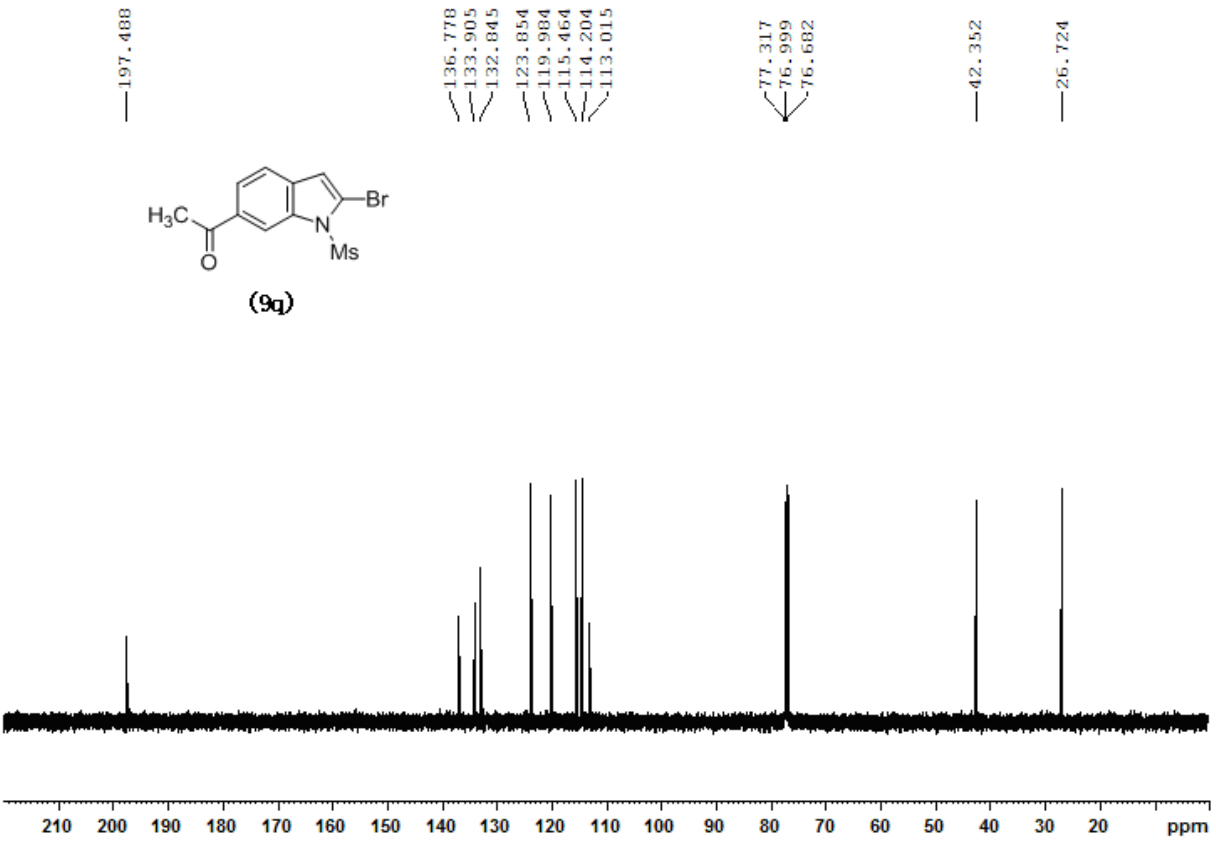


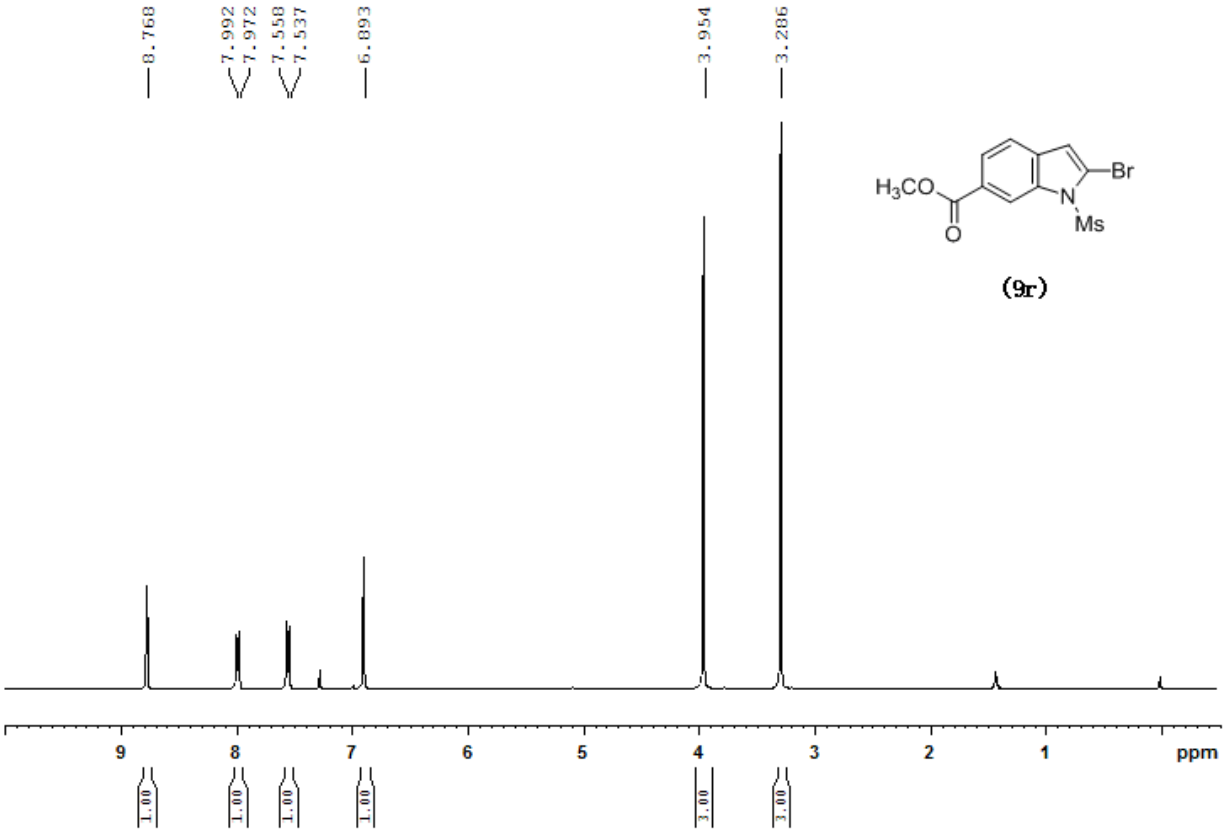


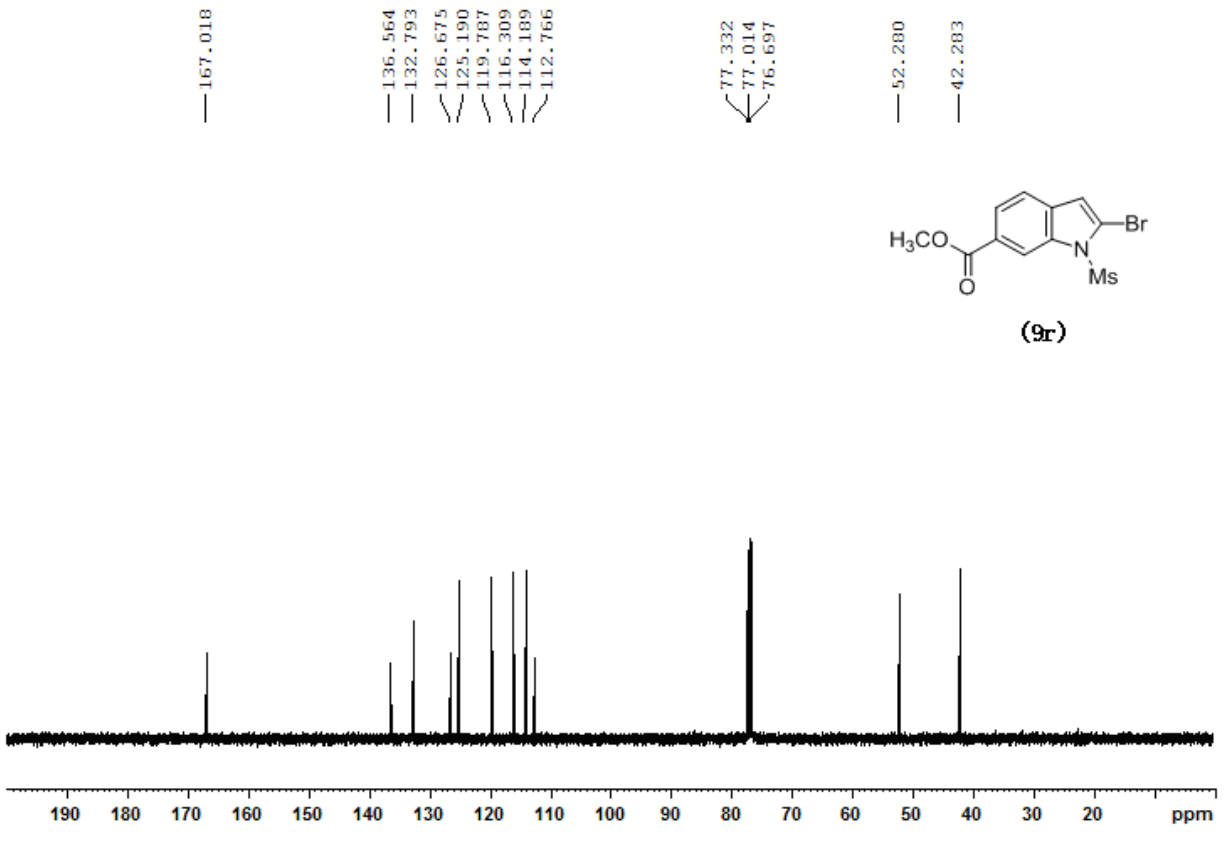


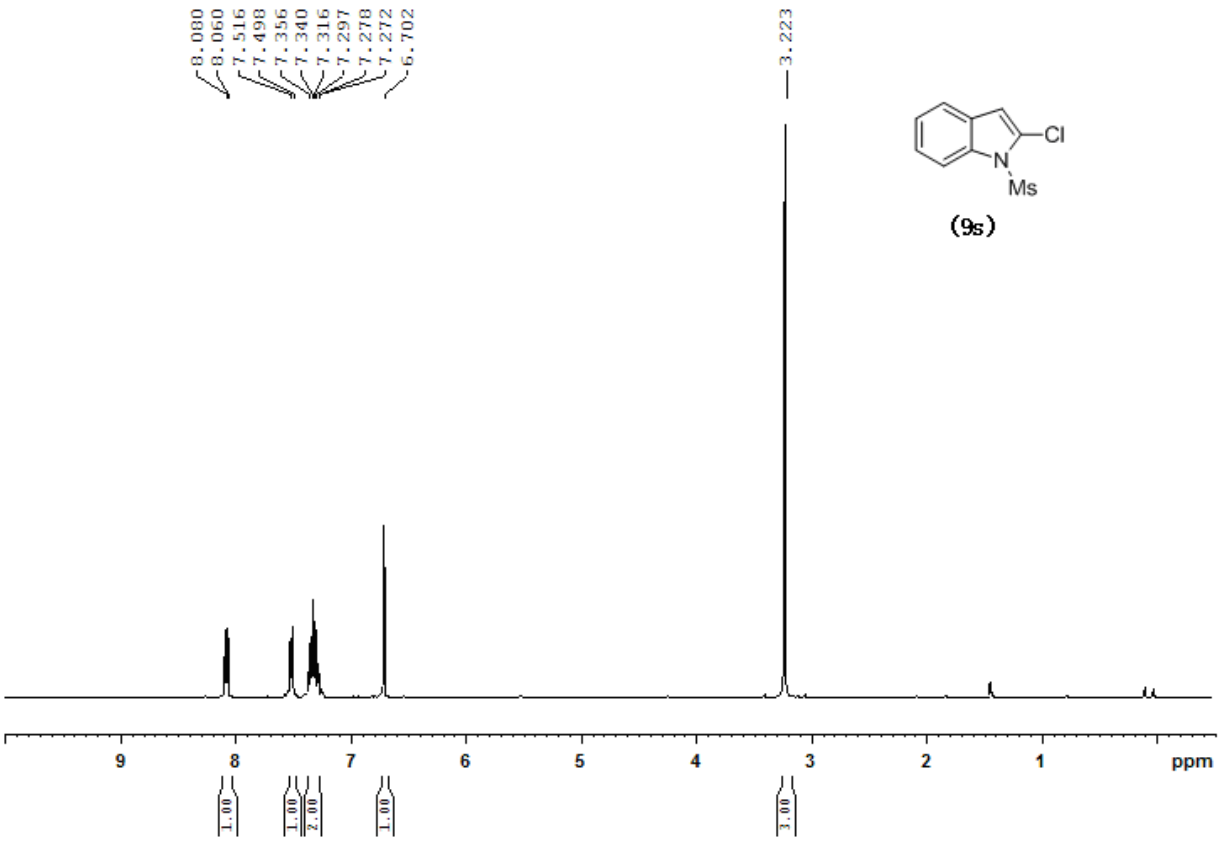


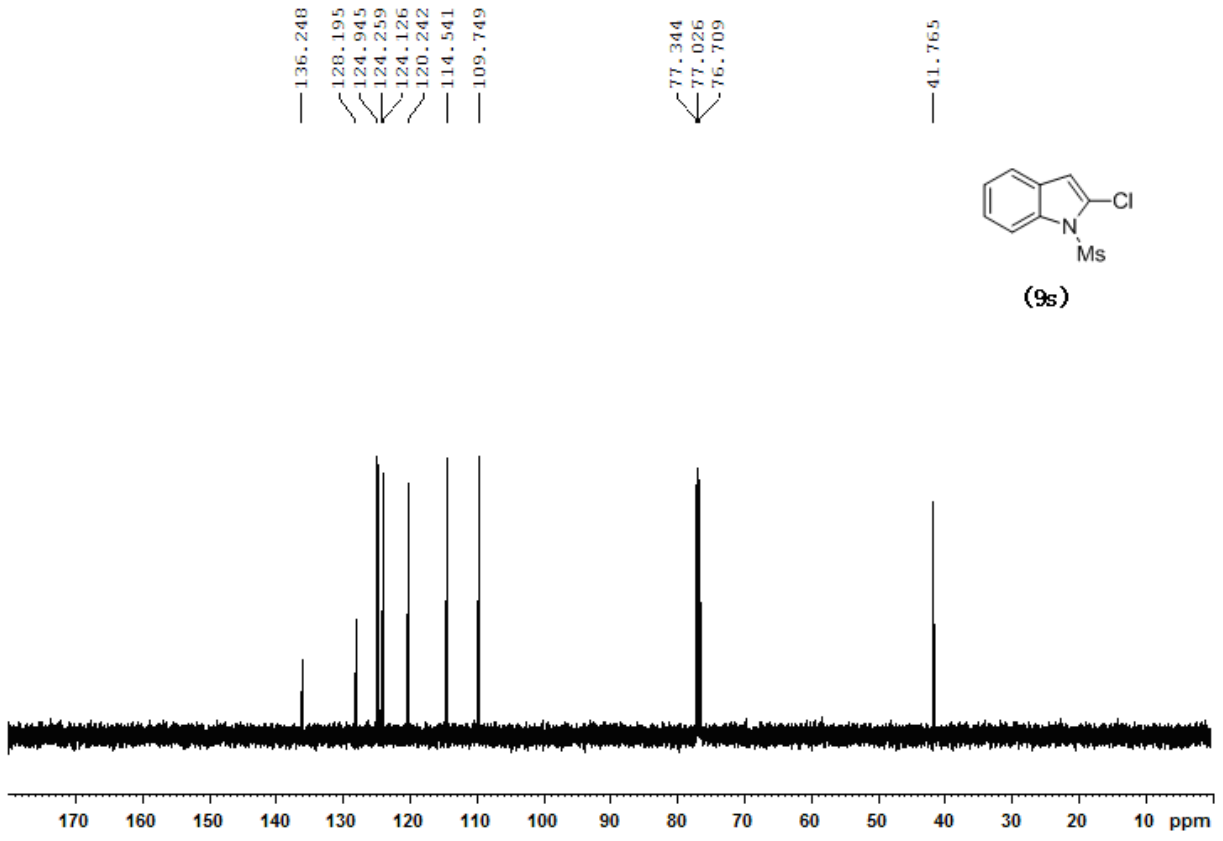

8.710
7.935
7.914
7.580
7.559
6.903
3.302
2.678
H3C
O
N
Br
Ms
(9q)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.00
1.00
3.00
3.00

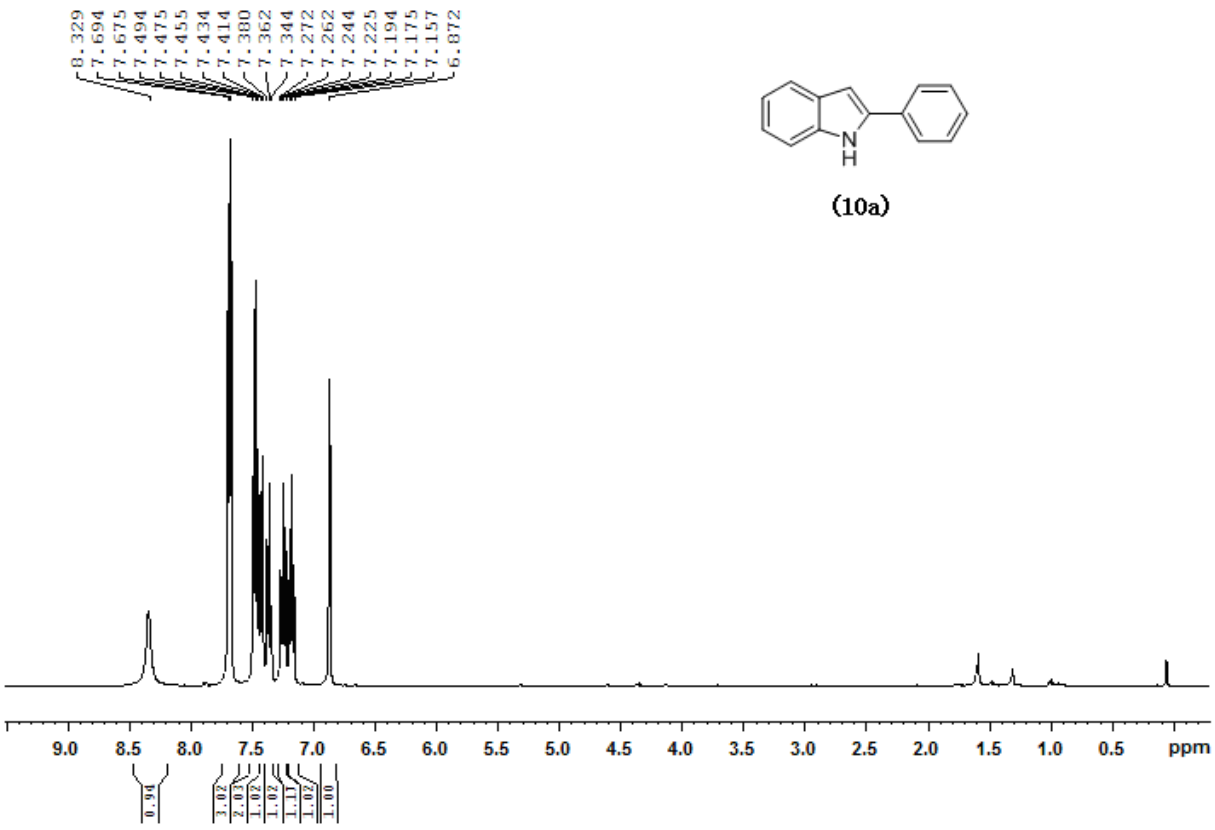

197.488
136.778
133.905
132.845
123.854
119.984
115.464
114.204
113.015
77.317
76.999
76.682
42.352
26.724
H3C
O
N
Br
Ms
(9q)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



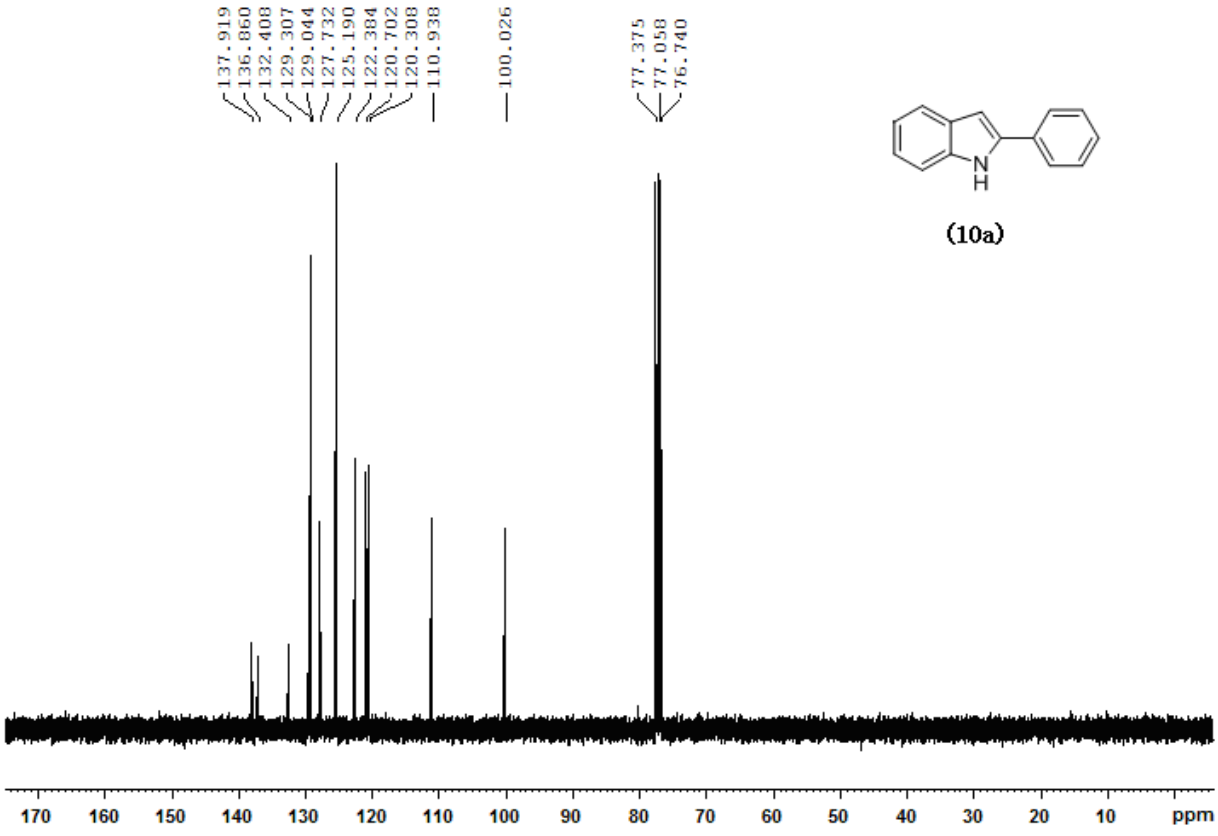








(10a)



(10a)

7. References

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[2] Newman, S. G.; Lautens, M. *J. Am. Chem. Soc.* **2010**, *132*, 11416.

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