

Supporting information

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1. General remarks:

Indole, 3,3,5-trimethylcyclohexanone, 4-methylcyclohexanone, 4-(tert-butyl)cyclohexanone, 4-phenylcyclohexanone, ethyl 4-oxocyclohexanecarboxylate, cyclopentanone, cycloheptanone, cyclooctanone, adamantan-2-one, 1-methyl-1H-indole, 5-bromo-1H-indole, 5-methoxy-1H-indole, 6-methyl-1H-indole, 6-fluoro-1H-indole, 7-ethyl-1H-indole, 5-methoxy-7-methyl-1H-indole, methyl 1H-indole-5-carboxylate, 6-methyl-1H-indole, 1-methyl-2-phenyl-1H-indole, 1H-indole-5-carboxylic acid, 1H-indole-6-carboxylic acid. N-buthylamine, divinyl sulfone, trifluoromethanesulfonic acid, 1,3-propane sultone, deuterium oxide, acetone were purchased from Energy Chemical Company., Sc(OTf)₃, Fe(OTf)₃ were purchased from Adamas Reagent Ltd. Acetone-*d*₆, DMSO-*d*₆, and chloroform-*d* were purchased from Alfa Aesar Chemical Company. *p*-Toluenesulfonic acid, ethyl acetate, 1,2-dichloroethane, DCE, sodium chloride, acetone, methanol and ethanol were all purchased from Sinopharm Chemical Reagents Limited Company (SCRC). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV-400. Chemical shifts are expressed in ppm relative to Me₄Si in CDCl₃. HRMS was recorded on a Bruker micrOTOF-Q II instrument. IR spectra were recorded on a FT-IR Bruker (VERTEX 70) using liquid film technology.

2. Synthesis of Brønsted acid ILs **1a** and **1b**

Brønsted acid IL **1a** was synthesized according to our previous report.¹ In 250 ml of round bottomed flask equipped with mechanical stirring, divinyl sulfone (11.8 g, 0.10 mol) was mixed with *n*-butylamine (7.3 g, 0.10 mol) in methanol (150 ml). The mixture was then stirred at 60 °C for 5 hours. Methanol was removed by a rotary evaporator under vacuum, and 4-*n*-butylthiomorpholine 1,1-dioxide was obtained as a color-less oil quantitatively. The obtained 4-*n*-butylthiomorpholine 1,1-dioxide was then mixed with 1,3-propane sultone (13.4 g, 0.11 mol) in acetonitrile (150 ml). The solution was refluxed for 5 hours. Then, the generated white solid was filtrated, and washed with acetone (10 ml × 3). After 6 hours of drying at 60 °C under vacuum (20 mmHg), 4-*n*-butyl-4-(3-sulfopropyl)thiomorpholinium 1,1-dioxide inner salt was obtained as a white powder (23.1 g, 74 %). In a 100 ml of round bottomed flask, 4-*n*-butyl-4-(3-sulfopropyl)thiomorpholinium 1,1-dioxide inner salt (15.6 g, 50 mmol) was mixed with trifluoromethanesulfonic acid (7.5 g, 50 mmol). Then, the mixture was stirred at 80 °C for 8 hours. In order to facilitate the stirring, water (1.0 ml) was added into the system. The formed liquid was washed with ethyl acetate (15 ml × 3) and diethyl ether (15 ml × 3). After that, it was dried at 80 °C under vacuum (10 mmHg) for 4 hours. Finally, IL **1a** was obtained as viscous brown oil (22.2 g, 96 %). Ionic liquid **1b** was synthesized according to a literature method.²

3. A typical procedure for the reaction of indole and cycloalkanone

All reactions were performed in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, ionic liquid **1a** (46.4 mg, 0.1 mmol) was mixed with indole **2a** (117.1 mg, 1.0 mmol) and cyclohexanone **3a** (117.7 mg, 1.2 mmol) under air. The mixture was stirred for 1 hour at 100 °C. After reaction, the mixture was cooled to room temperature and then extracted with ethyl acetate (1.5 ml × 3). The organic phase was combined together, and then subjected to isolation with preparative TLC. A mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is 1/15_{v/v}) was used as eluting solvent. The desired product **4a** was obtained in 92 %

of yield, 183.2 mg. The reaction of using other indoles and cycloalkanones were all performed according to an analogous procedure. The recovered ionic liquid was treated at 100 °C under vacuum (10 mmHg) for 30 minutes, and then reused in the next run.

4. Synthesis of **6a**

Ionic liquid **1a** (46.4 mg, 0.1 mmol) was mixed together with indole **2a** (234.2 mg, 2.0 mmol) and cyclohex-2-enone **5a** (96.1 mg, 1.0 mmol). The mixture was stirred for 1 hour at 100 °C. After reaction, the mixture was cooled to room temperature and then extracted with ethyl acetate (1.5 ml × 3). The organic phase was combined together, and then subjected to isolation with preparative TLC. A mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is 1/15_{v/v}) was used as eluting solvent. The desired product **6a** was obtained in 85 % of yield, 267.2 mg.

5. Control experiments for understanding the mechanism

Compound **8a** was synthesized according to a reported method.³ The reaction of **8a** with water was performed in a 10 mL of V-type flask equipped with triangle magnetic stirring. **1a** (46.4 mg, 0.1 mmol) was mixed with **8a** (472.1 mg, 1.0 mmol) and water (18.1 mg, 1.0 mmol). The mixture was stirred at 100 °C for 1 hour. After reaction, the mixture was cooled to room temperature and then extracted with ethyl acetate (1.5 ml × 3). The organic phase was combined together, and then subjected to isolation with preparative TLC. A mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is 1/15_{v/v}) was used as eluting solvent. Two products were finally obtained. The first one is **4c** that was obtained in 88 % yield, 244.6 mg. The second one is **2b** that was obtained in 91 % yield, 178.4 mg. The reaction without addition of water was also performed in an analogous procedure. The reaction of **2b** and **3a** was performed at 60 °C in the presence of 3 mol % of ionic liquid **1a**. The procedure is quite similar to that of synthesizing **4a**. After 15 minutes of reaction, a compound **9a** was obtained in 96 % yield (265.1 mg) by preparative TLC isolation using a mixture of ethyl acetate and petroether as an eluting solvent (E/P = 1/15_{v/v}). The reaction of **9a** and water catalyzed by ionic liquid **1a** was performed at 100 °C. After one hour of reaction, compound **4c** was obtained in 93 % yield (258.5 mg) by preparative TLC isolation using a mixture of ethyl acetate and petroether as an eluting solvent (E/P = 1/15_{v/v}). When D₂O was used instead of H₂O, compound **4c-D** was obtained in 89 % yield (248.4 mg).

6. Synthesis of **10a**

In a 10 mL of V-type flask equipped with triangle magnetic stirring, **1a** (46.4 mg, 0.1 mmol) was mixed with 1H-indole-5-carboxylic acid **2c** (161.1 mg, 1.0 mmol), and cyclohexanone **3a** (117.7 mg, 1.2 mmol). The mixture was stirred for 1 hour at 100 °C. After reaction, the mixture was cooled to room temperature and then extracted with ethyl acetate (1.5 ml × 3). The organic phase was combined together, and then subjected to isolation with preparative TLC. A mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is 1/6_{v/v}) was used as eluting solvent. The desired product **10a** was obtained in 46 % yield, 119.2 mg.

7. Synthesis of 4af

In a 10 mL of V-type flask equipped with triangle magnetic stirring, **1a** (46.4 mg, 0.1 mmol) was mixed with 1H-indole-6-carboxylic acid **2d** (161.1 mg, 1.0 mmol), cyclohexanone **3a** (117.7 mg, 1.2 mmol) and methanol (64.0 mg, 2.0 mmol). The mixture was stirred for 1 hour at 100 °C. After reaction, the mixture was cooled to room temperature and the extracted with ethyl acetate (1.5 ml × 3). The organic phase was combined together, and then subjected to isolation with preparative TLC. A mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is 1/15_{v/v}) was used as eluting solvent. The desired product **4af** was obtained in 86 % of yield, 221.2 mg.

8. Spectroscopic data of ionic liquid and organic products

4-*n*-Butyl-4-(3-sulfopropyl)thiomorpholinium 1,1-dioxide trifluoromethanesulfonate (**1a**):¹ Yellow viscous liquid; ¹H NMR (400 MHz, D₂O, 25 °C): δ = 3.82-3.79 (m, 4H), 3.49 (s, 4H), 3.46-3.41 (m, 2H), 3.28 (t, *J* = 8.0 Hz, 2H), 2.75 (t, *J* = 4.0 Hz, 2H), 1.99-1.91 (m, 2H), 1.50 (q, *J* = 8.0 Hz, 2H), 1.17 (sextet, *J* = 8.0 Hz, 2H), 0.71 ppm (t, *J* = 8.0 Hz, 3H); ¹³C NMR (100MHz, D₂O, 25 °C): δ = 123.6, 120.5, 61.4, 59.9, 59.1, 49.3, 47.5, 25.5, 21.3, 19.9, 15.1 ppm.

3-Cyclohexyl-1H-indole (**4a**):⁴ Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.75 (s, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.19-7.14 (m, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 2.82 (s, 1H), 2.10 (d, *J* = 8.0 Hz, 2H), 1.84-1.76 (m, 3H), 1.48-1.43 (m, 4H), 1.32-1.27 ppm (m, 1H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 136.4, 126.8, 123.2, 121.8, 119.5, 119.4, 119.0, 111.2, 35.5, 34.1, 27.0, 26.6 ppm.

3-Cyclohexyl-5-methoxy-1H-indole (**4b**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.77 (s, 1H), 7.22-7.19 (m, 1H), 7.08 (s, 1H), 6.89 (s, 1H), 6.85-6.82 (m, 1H), 3.87 (d, *J* = 4.0 Hz, 3H), 2.77-7.75 (m, 1H), 2.10-2.08 (m, 2H), 1.83-1.76 (m, 3H), 1.48-1.41 (m, 4H), 1.32-1.23 ppm (m, 1H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 153.7, 131.7, 127.2, 122.9, 120.4, 111.8, 101.5, 56.1, 35.4, 34.0, 27.0, 26.6 ppm. IR (cm⁻¹): 3416, 2925, 2850, 1582, 1483, 1448, 1282, 1243, 1211, 1170, 1097, 1057. HRMS-ESI (m/z) calcd for C₁₅H₂₀NO, [M + H]⁺ 230.1545, found 230.1542.

5-Bromo-3-cyclohexyl-1H-indole (**4c**):² Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.97 (s, 1H), 7.76 (d, *J* = 1.6 Hz, 1H), 7.27-7.21 (m, 1H), 7.18-7.16 (m, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 2.77-2.72 (m, 1H), 2.05 (d, *J* = 7.2 Hz, 3H), 1.85-1.75 (m, 3H), 1.50-1.36 ppm (m, 4H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 135.0, 128.6, 124.5, 122.9, 121.9, 120.8, 112.6, 112.2, 35.3, 34.0, 26.9, 26.5 ppm.

3-Cyclohexyl-6-methyl-1H-indole (**4d**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.67 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 0.4 Hz, 1H), 6.92 (dd, *J*_a = 0.9 Hz, *J*_b = 8.1 Hz, 1H), 6.79 (d, *J* = 1.8 Hz, 1H), 2.81-2.76 (m, 1H), 2.44 (s, 3H), 2.09-2.07 (m, 2H), 1.82-1.78 (m, 4H), 1.47-1.25 ppm (m, 4H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 136.9, 131.5, 124.7, 123.0, 120.7, 119.0, 118.8, 111.2, 35.6, 34.1, 27.0, 26.6, 21.7 ppm. IR (cm⁻¹): 3412, 2924, 2852, 1704, 1621, 1452, 1402, 1337, 1222, 1156, 1094, 1036, 986. HRMS-ESI (m/z) calcd for C₁₅H₂₀N, [M + H]⁺ 214.1596, found 214.1591.

3-Cyclohexyl-6-fluoro-1H-indole (**4e**): Yellow solid, mp. = 94 - 96 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.84 (s, 1H), 7.55 (dd, *J*_a = 4.0, Hz, *J*_b = 8.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.90-6.84 (m, 2H), 2.79-2.77 (m, 1H), 2.09-2.07 (m, 2H), 1.85-1.76 (m, 3H), 1.44-1.41 (m, 4H), 1.32-1.26 ppm (m, 1H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 161.1, 158.7, 136.2, 123.4, 123.3, 120.0, 119.9, 119.6, 119.6, 107.8, 107.6, 97.5, 97.2, 35.4, 34.0, 26.9, 26.5 ppm. IR (cm⁻¹): 3425, 2926, 2852, 1703, 1624, 1592, 1552, 1496, 1454, 1342, 1305, 1248, 1217, 1137. HRMS-ESI (m/z) calcd for C₁₄H₁₇FN, [M + H]⁺ 218.1345, found 218.1338.

3-Cyclohexyl-7-ethyl-1H-indole (**4f**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.90 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 4.0 Hz, 1H), 2.90 (q, *J* = 8.0 Hz, 3H), 2.19 (d, *J* = 4.0 Hz, 1H), 1.94-1.92 (m, 2H), 1.88-1.84 (m, 1H), 1.55 (t, *J* = 8.0 Hz, 4H), 1.43 ppm (t, *J* = 8.0 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 135.3, 126.6, 126.5, 123.7, 120.3, 119.3, 117.2, 35.6, 34.1, 27.0, 26.6, 24.1, 13.9 ppm. IR (cm⁻¹): 3424, 2925, 2851, 1699, 1611, 1442, 1373, 1349, 1321, 1222, 1168, 1118, 1074. HRMS-ESI (*m/z*) calcd for C₁₆H₂₂N, [*M* + *H*]⁺ 228.1752, found 228.1751.

3-Cyclohexyl-5-methoxy-7-methyl-1H-indole (**4g**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.77 (s, 1H), 6.93 (d, *J* = 4.0 Hz, 1H), 6.88 (d, *J* = 4 Hz, 1H), 6.67 (d, *J* = 0.4 Hz, 1H), 3.86 (s, 3H), 2.79-2.74 (m, 1H), 2.40 (s, 3H), 2.10 (d, *J* = 12.0 Hz, 2H), 1.84-1.76 (m, 4H), 1.49-1.41 ppm (m, 2H). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 153.9, 131.3, 126.5, 123.4, 121.4, 120.0, 112.6, 98.9, 56.1, 35.5, 34.0, 27.0, 26.6, 16.7 ppm. IR (cm⁻¹): 3421, 2925, 2851, 1700, 1599, 1486, 1446, 1376, 1322, 1238, 1204, 1167, 1135. 1053. HRMS-ESI (*m/z*) calcd for C₁₆H₂₂NO, [*M* + *H*]⁺ 244.3520, found 244.3512.

Methyl 3-cyclohexyl-1H-indole-5-carboxylate (**4h**): White solid, mp. = 132-133 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 8.42-8.39 (m, 2H), 7.87 (dd, *J*_a = 4.0 Hz, *J*_b = 12.0 Hz, 1H), 7.32 (d, *J* = 12.0 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 3.94 (s, 3H), 2.89-2.83 (m, 1H), 2.09 (d, *J* = 8.0 Hz, 2H), 1.85-1.75 (m, 4H), 1.51-1.38 ppm (m, 4H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 168.6, 139.1, 126.5, 124.7, 123.1, 122.4, 120.9, 120.8, 110.8, 51.9, 35.2, 34.1, 26.9, 26.4 ppm. IR (cm⁻¹): 3346, 2925, 2851, 1692, 1617, 1580, 1439, 1356, 1317, 1293, 1262, 1216, 1191, 1107. HRMS-ESI (*m/z*) calcd for C₁₆H₂₀NO₂, [*M* + *H*]⁺ 258.1494, found 258.1485.

3-(4-Methylcyclohexyl)-1H-indole (**4i**):⁵ Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.93 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 4.0 Hz, 1H), 2.81 (tt, *J*_a = 4.0 Hz, *J*_b = 12.0 Hz, 1H), 2.16 (d, *J* = 12.0 Hz, 2H), 1.86 (d, *J* = 12.0 Hz, 2H), 1.56-1.49 (m, 3H), 1.25-1.18 (m, 2H), 1.00 ppm (d, *J* = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 136.4, 126.9, 122.9, 121.8, 118.9, 111.1, 35.7, 35.1, 33.9, 32.8, 31.9, 31.0, 28.8, 22.7 ppm.

1-Methyl-3-(4-Methylcyclohexyl)-1H-indole (**4j**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.62 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.20-7.15 (m, 1H), 7.08-7.04 (m, 1H), 6.75 (s, 1H), 3.67 (s, 3H), 2.76 (td, *J*_a = 4.0 Hz, *J*_b = 12.0 Hz, 1H), 2.09 (d, *J* = 12.0 Hz, 2H), 1.81 (d, *J* = 12.0 Hz, 2H), 1.48 (dd, *J*_a = 12.0 Hz, *J*_b = 24.0 Hz, 3H), 1.14 (dd, *J*_a = 12.0 Hz, *J*_b = 24.0 Hz, 2H), 0.95 ppm (dd, *J*_a = 4.0 Hz, *J*_b = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 137.2, 127.3, 124.4, 121.5, 121.5, 119.5, 118.5, 109.3, 35.9, 35.2, 34.3, 32.9, 32.6, 23.0 ppm. IR (cm⁻¹): 2918, 2849, 1614, 1473, 1450, 1374, 1346, 1326, 1249, 1226, 1157, 1081, 1013. HRMS-ESI (*m/z*) calcd for C₁₆H₂₂N, [*M* + *H*]⁺ 228.1752, found 228.1747.

3-(4-(Tert-butyl)cyclohexyl)-1H-indole (**4k**): Yellow solid, mp. = 95-97 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.89 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 2.80-2.73 (m, 1H), 1.48 (dd, *J*_a = 4.0 Hz, *J*_b = 12.0 Hz, 2H), 1.26-1.05 (m, 7H), 0.09 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 136.5, 126.9, 123.0, 121.8, 119.4, 119.3, 118.9, 111.1, 48.1, 35.5, 34.4, 32.5, 27.8, 27.7 ppm. IR (cm⁻¹): 3422, 2926, 2854, 1714, 1664, 1617, 1456, 1420, 1364, 1338, 1223, 1183, 1152, 1095, 1012. HRMS-ESI (*m/z*) calcd for C₁₈H₂₆N, [*M* + *H*]⁺ 256.2065, found 256.2053.

3-(4-(Tert-butyl)cyclohexyl)-1-methyl-1H-indole (**4l**): White solid, mp. = 68 - 70 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.64 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.21-7.17 (m, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 3.70 (s, 3H), 2.75 (o, *J* = 4.0 Hz, 1H), 2.18 (s, 1H), 1.90 (d, *J* = 12.0 Hz, 2H), 1.51-1.39 (m, 2H), 1.26-1.10 (m, 4H), 0.90 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 137.1, 127.3, 124.3, 121.5, 121.4, 119.5, 118.4, 109.2, 48.2, 35.5, 34.6, 32.6, 27.8, 27.7 ppm.

IR (cm⁻¹): 2935, 2855, 1614, 1550, 1473, 1448, 1367, 1326, 1247, 1228, 1204, 1156, 1130. HRMS-ESI (m/z) calcd for C₁₉H₂₈N, [M + H]⁺ 270.2222, found 270.2210.

3-(4-Phenylcyclohexyl)-1H-indole (**4m**): White solid, mp. = 97 - 99 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.92 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.42-7.35 (m, 5H), 7.35-7.25 (m, 2H), 7.19 (t, *J* = 4.0 Hz, 1H), 7.03 (s, 1H), 3.00(t, *J* = 8.0 Hz, 1H), 2.71 (d, *J* = 12.0 Hz, 2H), 2.12 (d, *J* = 12.0 Hz, 2H), 1.84-1.69 ppm (sextet, *J* = 12.0 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 147.8, 136.5, 128.5, 127.0, 126.9, 126.0, 122.6, 121.5, 119.5, 119.4, 119.1, 111.2, 44.5, 35.1, 34.7, 34.2 ppm. IR (cm⁻¹): 3421, 2922, 2851, 1600, 1549, 1452, 1419, 1373, 1337, 1218, 1188, 1095, 1010. HRMS-ESI (m/z) calcd for C₂₀H₂₂N, [M + H]⁺ 276.1752, found 276.1746.

1-Methyl-3-(4-phenylcyclohexyl)-1H-indole (**4n**): White solid, mp. = 72-74 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.67-7.65 (m, 1H), 7.29-7.17 (m, 7H), 7.10-7.06 (m, 1H), 6.77 (s, 1H), 3.65 (s, 3H), 2.90 (s, 1H), 2.60 (s, 1H), 2.23 (d, *J* = 8.0 Hz, 2H), 2.00 (s, 2H), 14.69-1.61 ppm (m, 4H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 147.9, 137.4, 128.6, 127.4, 127.2, 126.2, 124.6, 121.7, 121.3, 119.7, 118.7, 109.5, 44.7, 35.3, 34.9, 34.6, 32.8 ppm. IR (cm⁻¹): 2923, 2852, 1472, 1448, 1374, 1326, 1227, 1156, 1131, 1065, 1014, 979. HRMS-ESI (m/z) calcd for C₂₁H₂₄N, [M + H]⁺ 290.1909, found 290.1904.

5-Methoxy-3-(4-methylcyclohexyl)-1H-indole (**4o**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.88 (s, 1H), 7.25-7.20 (m, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.91 (d, *J* = 4.0 Hz, 1H), 6.84 (dd, *J*_a = 4.0 Hz, *J*_b = 8.0 Hz, 1H), 3.87 (s, 3H), 2.93 (dd, *J*_a = 8.0 Hz, *J*_b = 12.0 Hz, 0.34H), 2.75-2.68 (m, 0.83H), 2.10 (d, *J* = 12.0 Hz, 2H), 1.84-1.80 (m, 4H), 1.47 (dd, *J*_a = 4.0 Hz, *J*_b = 12.0 Hz, 2H), 1.15 (dd, *J*_a = 4.0 Hz, *J*_b = 12.0 Hz, 1H), 0.96 ppm (d, *J* = 4.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 153.6, 131.7, 127.2, 122.6, 120.3, 111.8, 101.5, 56.1, 35.7, 35.1, 33.8, 32.8, 31.9, 28.7, 22.9 ppm. IR (cm⁻¹): 3414, 2921, 2852, 1624, 1582, 1485, 1454, 1374, 1344, 1282, 1210, 1173, 1135, 1031. HRMS-ESI (m/z) calcd for C₁₆H₂₂NO, [M + H]⁺ 244.1707, found 244.1703.

5-Methoxy-1-methyl-3-(4-phenylcyclohexyl)-1H-indole (**4p**): White solid, mp. = 90-91 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.85 (s, 1H), 7.34-7.29 (m, 4H), 7.24-7.19 (m, 2H), 7.12 (d, *J* = 4.0 Hz, 1H), 6.95 (d, *J* = 4.0 Hz, 1H), 6.87-6.84 (m, 1H), 3.88 (s, 3H), 2.91-2.84 (m, 1H), 2.63 (o, *J* = 4.0 Hz, 1H), 2.26 (d, *J* = 12.0 Hz, 2H), 2.06-2.03 (m, 2H), 1.77-1.59 ppm (m, 4H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 153.7, 147.7, 131.7, 128.4, 127.2, 126.9, 126.0, 122.3, 120.4, 111.9, 101.5, 56.2, 44.5, 35.0, 34.7, 34.1 ppm. IR (cm⁻¹): 3423, 2923, 2852, 1582, 1484, 1449, 1283, 1211, 1171, 1058, 1029, 1100, 1029. HRMS-ESI (m/z) calcd for C₂₁H₂₄NO, [M + H]⁺ 306.1858, found 306.1859.

Ethyl 4-(1-methyl-1H-indol-3-yl)cyclohexanecarboxylate (**4q**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.61(d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.23-7.18 (m, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 4.17-4.12 (m, 2H), 3.72 (d, *J* = 4.0 Hz, 3H), 2.86-2.80 (m, 1H), 2.39-2.33 (m, 1H), 2.20-2.17 (m, 2H), 2.13-2.07 (m, 2H), 1.73-1.61 (m, 2H), 1.52 (td, *J*_a = 4.0 Hz, *J*_b = 12.0 Hz, 2H), 1.29-1.25 ppm (m, 3H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 176.2, 137.1, 127.0, 124.9, 124.4, 121.5, 121.4, 120.6, 119.3, 118.5, 118.4, 109.3, 109.2, 60.2, 43.5, 34.7, 33.1, 32.6, 30.3, 29.5, 27.3, 14.3 ppm. IR (cm⁻¹): 2932, 2858, 1729, 1471, 1450, 1374, 1325, 1295, 1244, 1226, 1178, 1139, 1099. HRMS-ESI (m/z) calcd for C₁₈H₂₄NO₂, [M + H]⁺ 286.1807, found 286.1800.

3-Cyclopentyl-1-methyl-2-phenyl-1H-indole (**4r**): White solid, mp. = 55-56 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.72 (d, *J* = 8.0 Hz, 1H), 7.47-7.44 (m, 2H), 7.40 (t, *J* = 4.0 Hz, 1H), 7.37 (d, *J* = 4.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 4.0 Hz, 1H), 7.11-7.08 (m, 1H), 3.51 (s, 3H), 3.11-3.05 (m, 1H), 2.07-2.01 (m, 2H), 1.89-1.85 (m, 4H), 1.64-1.62 ppm (m, 2H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 137.7, 137.7, 132.6, 131.0, 128.4, 128.0, 126.0, 121.5, 120.3, 118.8, 116.5, 109.7, 37.6, 33.4, 30.8, 26.6 ppm. IR (cm⁻¹): 3053, 2949, 2867, 1713, 1605, 1467, 1401, 1366, 1339, 1248, 1219, 1149, 1168. HRMS-ESI (m/z) calcd for C₂₀H₂₂N, [M + H]⁺ 276.1752, found 276.1750.

3-Cyclopentyl-1H-indole (**4s**):¹ Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.70 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.18-7.14 (m, 1H), 7.11-7.07 (m, 1H), 3.25 (d, *J* = 8.0 Hz, 1H), 2.15-2.13 (m, 3H), 1.79 (t, *J* = 4.0 Hz, 2H), 1.72-1.68 (m, 5H), 1.24 ppm (t, *J* = 8.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 136.7, 127.4, 121.9, 121.3, 119.7, 119.7, 119.0, 111.2, 37.1, 33.3, 25.3 ppm.

3-Cycloheptyl-1H-indole (**4t**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.84 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 4.0 Hz, 1H), 3.15-3.08 (m, 1H), 2.20-2.15 (m, 2H), 1.88-1.79 (m, 6H), 1.76-1.68 ppm (m, 4H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 136.5, 126.7, 124.4, 121.8, 119.4, 119.0, 111.1, 37.3, 35.7, 28.4, 27.0 ppm. IR (cm⁻¹): 3417, 2922, 2853, 1705, 1616, 1457, 1419, 1339, 1285, 1225, 1150, 1122, 1095. 1012. HRMS-ESI (*m/z*) calcd for C₁₅H₂₀N, [M + H]⁺ 214.1596, found 214.1591.

3-Cycloheptyl-1-methyl-1H-indole (**4u**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.60 (d, *J* = 8.0 Hz, 1H), 7.20 (q, *J*_a = 8.0 Hz, *J*_b = 16.0 Hz, 2H), 7.08-7.05 (m, 1H), 6.76 (s, 1H), 3.66 (s, 3H), 3.05-3.00 (m, 1H), 2.11-2.08 (m, 2H), 1.79-1.67 (m, 6H), 1.60 ppm (t, *J* = 4.0 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 137.3, 127.2, 124.5, 123.1, 121.6, 119.6, 118.5, 109.3, 37.5, 36.1, 32.6, 28.6, 27.2 ppm. IR (cm⁻¹): 2923, 2853, 1613, 1467, 1423, 1374, 1326, 1234, 1153, 1130, 1061, 1014. HRMS-ESI (*m/z*) calcd for C₁₆H₂₂NO, [M + H]⁺ 228.1752, found 228.1745.

5-Bromo-3-cycloheptyl-1H-indole (**4v**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.91 (s, 1H), 7.73 (d, *J* = 4.0 Hz, 1H), 7.25-7.22 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 2.99-2.92 (m, 1H), 1.80-1.56 ppm (m, 12H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 135.0, 128.5, 124.6, 124.2, 121.9, 120.7, 112.5, 112.2, 37.2, 35.7, 28.2, 27.0 ppm. IR (cm⁻¹): 3431, 2923, 2854, 1688, 1565, 1458, 1417, 1338, 1318, 1221, 1097, 1047. HRMS-ESI (*m/z*) calcd for C₁₅H₁₉BrNO, [M + H]⁺ 292.0701, found 292.0694.

3-Cycloheptyl-5-methoxy-1H-indole (**4w**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.93 (s, 1H), 7.22 (d, *J* = 12.0 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.93 (d, *J* = 4.0 Hz, 1H), 6.84 (dd, *J*_a = 4.0 Hz, *J*_b = 8.0 Hz, 1H), 3.87 (s, 3H), 2.99 (h, *J* = 4.0 Hz, 1H), 1.73-1.60 ppm (m, 12H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 153.6, 131.7, 127.1, 124.0, 120.4, 111.8, 111.6, 101.5, 56.1, 43.9, 37.2, 35.6, 28.4, 27.0, 24.4 ppm. IR (cm⁻¹): 3416, 2924, 2854, 1692, 1624, 1582, 1483, 1456, 1348, 1284, 1266, 1212, 1167, 1058, 1029. HRMS-ESI (*m/z*) calcd for C₁₆H₂₂NO, [M + H]⁺ 244.1701, found 244.1702.

3-Cycloheptyl-6-methyl-1H-indole (**4x**): Yellow solid, mp. = 62-63 °C. ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.75 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.16 (s, 1H), 6.90 (d, *J* = 0.4 Hz, 1H), 6.88 (dd, *J*_a = 0.9 Hz, *J*_b = 8.1 Hz, 1H), 3.09-3.03 (m, 1H), 2.50 (s, 3H), 2.17-2.12 (m, 2H), 1.85-1.72 (m, 8H), 1.67-1.65 ppm (m, 4H). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 136.9, 131.6, 124.6, 124.2, 120.7, 119.1, 118.7, 111.1, 43.9, 37.4, 35.7, 30.5, 28.4, 27.0, 24.4, 21.7 ppm. IR (cm⁻¹): 3412, 2922, 2853, 1691, 1625, 1547, 1456, 1400, 1338, 1225, 1154, 1094, 1067, 1033. HRMS-ESI (*m/z*) calcd for C₁₆H₂₂N, [M + H]⁺ 228.1752, found 228.1747.

3-Cyclooctyl-1H-indole (**4y**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.86 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.10 (td, *J*_a = 4.0 Hz, *J*_b = 8.0 Hz, 1H), 6.96 (d, *J* = 4.0 Hz, 1H), 3.18-3.11 (m, 1H), 2.05-1.98 (m, 2H), 1.87-1.84 (m, 2H), 1.78-1.74 (m, 2H), 1.70-1.62 ppm (m, 8H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 136.5, 126.7, 124.4, 121.8, 119.6, 119.3, 118.9, 111.1, 100.0, 35.1, 32.8, 27.3, 26.3, 25.8 ppm. IR (cm⁻¹): 3418, 2921, 2851, 1711, 1664, 1617, 1457, 1418, 1339, 1221, 1095, 1013. HRMS-ESI (*m/z*) calcd for C₁₆H₂₂N, [M + H]⁺ 228.1752, found 228.1745.

3-Cyclooctyl-1-methyl-1H-indole (**4z**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.60 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.21-7.17 (m, 1H), 7.07 (td, *J*_a = 0.8 Hz, *J*_b = 8.0 Hz, 1H), 6.78 (s, 1H), 3.69 (s, 3H), 3.16-3.10 (m, 1H), 2.02-1.97 (m, 2H), 1.87-1.73 (m, 4H), 1.69-1.61 ppm (m, 8H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 137.2, 127.1, 124.7, 123.0, 121.4, 119.5, 118.4, 109.2, 35.1, 33.1, 32.6, 27.5, 26.4, 25.9 ppm. IR (cm⁻¹): 2919, 2871, 1721, 1674, 1647,

1437, 1428, 1341, 1231, 1098, 1015. HRMS-ESI (m/z) calcd for C₁₇H₂₄N, [M + H]⁺ 242.1909, found 242.1905.

3-(3,3,5-Trimethylcyclohexyl)-1H-indole (**4aa**): Yellow solid, mp. = 110-112 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.83 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.19-7.14 (m, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 4.0 Hz, 1H), 3.08 (tt, *J*_a = 4.0 Hz, *J*_b = 12.0 Hz, 1H), 2.06 (dt, *J*_a = 4.0 Hz, *J*_b = 12.0 Hz, 1H), 1.85-1.75 (m, 2H), 1.45 (dt, *J*_a = 4.0 Hz, *J*_b = 12.0 Hz, 1H), 1.26 (t, *J* = 12.0 Hz, 2H), 1.06 (s, 3H), 0.96 (s, 3H), 0.92 ppm (d, *J* = 4.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 136.5, 126.9, 122.7, 121.8, 119.5, 119.3, 119.0, 111.3, 48.5, 46.7, 42.6, 33.5, 31.8, 31.0, 28.8, 25.5, 23.0 ppm. IR (cm⁻¹): 3419, 2949, 2868, 2839, 1704, 1457, 1421, 1363, 1338, 1262, 1225, 1149, 1095, 1011. HRMS-ESI (m/z) calcd for C₁₇H₂₄N, [M + H]⁺ 242.1909, found 242.1901.

1-Methyl-3-(3,3,5-trimethylcyclohexyl)-1H-indole (**4ab**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.65-7.62 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.21-7.17 (m, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.71 (d, *J* = 4.0 Hz, 3H), 3.32-3.27 (m, 0.45 H), 3.11-3.04 (m, 0.55H), 1.86-1.58 (m, 3H), 1.46-1.41 (m, 1H), 1.29-1.19 (m, 1H), 1.13 (d, *J* = 8.0 Hz, 1H), 1.06 (d, *J* = 4.0 Hz, 3H), 0.97-0.81 ppm (m, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 137.2, 137.1, 127.5, 127.2, 124.8, 124.3, 121.4, 121.4, 121.2, 119.6, 119.3, 118.4, 118.4, 109.3, 109.2, 48.5, 46.9, 46.2, 45.4, 42.8, 39.1, 33.5, 32.6, 32.6, 32.0, 31.8, 31.5, 31.0, 30.9, 30.6, 28.8, 27.6, 27.2, 25.5, 22.9, 22.1 ppm. IR (cm⁻¹): 2948, 2841, 1614, 1547, 1550, 1468, 1425, 1377, 1325, 1234, 1208, 1156, 1128, 1014. HRMS-ESI (m/z) calcd for C₁₈H₂₆N, [M + H]⁺ 256.2065, found 256.2053.

5-Methoxy-3-(3,3,5-trimethylcyclohexyl)-1H-indole (**4ac**): Yellow viscous liquid; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.80 (s, 1H), 7.23-7.20 (m, 1H), 7.10-7.08 (m, 1H), 6.92-6.89 (m, 1H), 6.85 (dd, *J*_a = 4.0 Hz, *J*_b = 8.0 Hz, 1H), 3.87 (s, 3H), 3.25 (h, *J* = 4.0 Hz, 0.65H), 3.06-2.99 (m, 0.35H), 1.87-1.60 (m, 4H), 1.46-1.41 (m, 1H), 1.29-1.25 (d, *J* = 16.0 Hz, 1H), 1.20 (dd, *J*_a = 8.0 Hz, *J*_b = 12.0 Hz, 1H), 1.12 (d, *J* = 8.0 Hz, 2H), 1.06 (d, *J* = 12.0 Hz, 3H), 0.96 (s, 1H), 0.92 (d, *J* = 8.0 Hz, 1H), 0.80 ppm (s, 2H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 153.6, 153.6, 131.8, 127.5, 122.5, 122.2, 120.8, 120.4, 111.8, 111.8, 111.6, 111.5, 101.9, 101.7, 56.2, 56.1, 48.5, 46.5, 46.3, 44.8, 42.5, 38.8, 33.5, 31.8, 31.5, 31.5, 31.0, 30.9, 30.8, 28.7, 27.7, 27.0, 25.5, 22.9, 22.2 ppm. IR (cm⁻¹): 3419, 2948, 2839, 1582, 1482, 1457, 1364, 1289, 1263, 1211, 1169, 1096, 1046. HRMS-ESI (m/z) calcd for C₁₈H₂₆NO, [M + H]⁺ 272.2014, found 272.2018.

3-((2R)-Adamantan-2-yl)-6-methyl-1H-indole (**4ad**): White solid, mp. = 87 – 89 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.77 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 7.00 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 3.33 (s, 1H), 2.44 (s, 3H), 2.34 (s, 2H), 2.06-1.95 ppm (m, 12H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 136.7, 131.5, 125.4, 120.7, 120.6, 120.1, 119.4, 111.0, 47.0, 42.5, 39.5, 39.3, 38.3, 32.7, 32.3, 28.4, 28.2, 27.5, 21.7 ppm. IR (cm⁻¹): 3412, 2904, 2851, 1716, 1623, 1452, 1396, 1340, 1312, 1226, 1156, 1116, 1096, 1062. HRMS-ESI (m/z) calcd for C₁₉H₂₄NO, [M + H]⁺ 282.1858, found 282.1856.

3-((2R)-Adamantan-2-yl)-5-methoxy-1H-indole (**4ae**): White solid, mp. = 125- 127 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 7.89 (s, 1H), 7.25-7.22 (m, 1H), 7.11 (s, 1H), 7.05 (d, *J* = 4.0 Hz, 1H), 6.85 (dd, *J*_a = 4.0 Hz, *J*_b = 8.0 Hz, 1H), 3.86 (s, 3H), 3.30 (s, 1H), 2.33 (s, 2H), 2.09-1.97 ppm (m, 12H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 153.6, 131.5, 127.9, 122.2, 120.0, 111.6, 111.5, 102.2, 56.2, 47.0, 42.5, 39.5, 39.3, 38.2, 36.3, 32.7, 32.2, 28.3, 28.1, 27.5 ppm. IR (cm⁻¹): 3415, 2903, 2850, 1716, 1704, 1676, 1624, 1582, 1482, 1450, 1349, 1314, 1287, 1209, 1034. HRMS-ESI (m/z) calcd for C₁₉H₂₄N, [M + H]⁺ 266.1909, found 266.1902.

Methyl 3-cyclohexyl-1H-indole-6-carboxylate (**4af**):⁶ White solid, mp. = 128-130 °C; ¹H NMR (400 MHz, 25 °C, TMS, CDCl₃): δ = 8.44 (s, 1H), 8.11 (d, *J* = 0.8 Hz, 1H), 7.78 (dd, *J*_a = 1.6 Hz, *J*_b = 8.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 4.0 Hz, 1H), 3.92 (s, 3H), 2.86-2.80 (m, 1H), 2.09-2.06 (m, 2H), 1.85-1.75 (m, 4H), 1.47-1.42 ppm (m, 4H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 168.4, 135.7, 130.4, 123.6, 123.3, 123.1, 120.0, 118.9, 113.6, 51.9, 35.3, 34.0, 26.9, 26.4 ppm.

5-bromo-3-(1-deuteriumcyclohexyl)-1H-indole (**4c-D**): Yellow viscous liquid; ^1H NMR (400 MHz, CDCl_3): δ = 8.53 (s, 1H), 8.16 (s, 1H), 7.97 (dd, J_a = 4.0 Hz, J_b = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 4.0 Hz, 1H), 2.92-2.87 (m, 1H), 2.13-2.11 (m, 2H), 1.87-1.78 (m, 3H), 1.51-1.44 (m, 4H), 1.35-1.24 ppm (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 173.3, 139.5, 126.6, 125.0, 123.8, 123.4, 120.8, 120.1, 110.8, 35.2, 34.1, 26.9, 26.4 ppm. IR (cm^{-1}): 3421, 2930, 2858, 1698, 1631, 1620, 1563, 1522, 1454, 1333, 1280, 1237, 1175, 1106, 1012. HRMS-ESI (m/z) calcd for $\text{C}_{14}\text{H}_{16}\text{DBrN}$, $[\text{M} + \text{H}]^+$ 279.0606, found 279.0603.

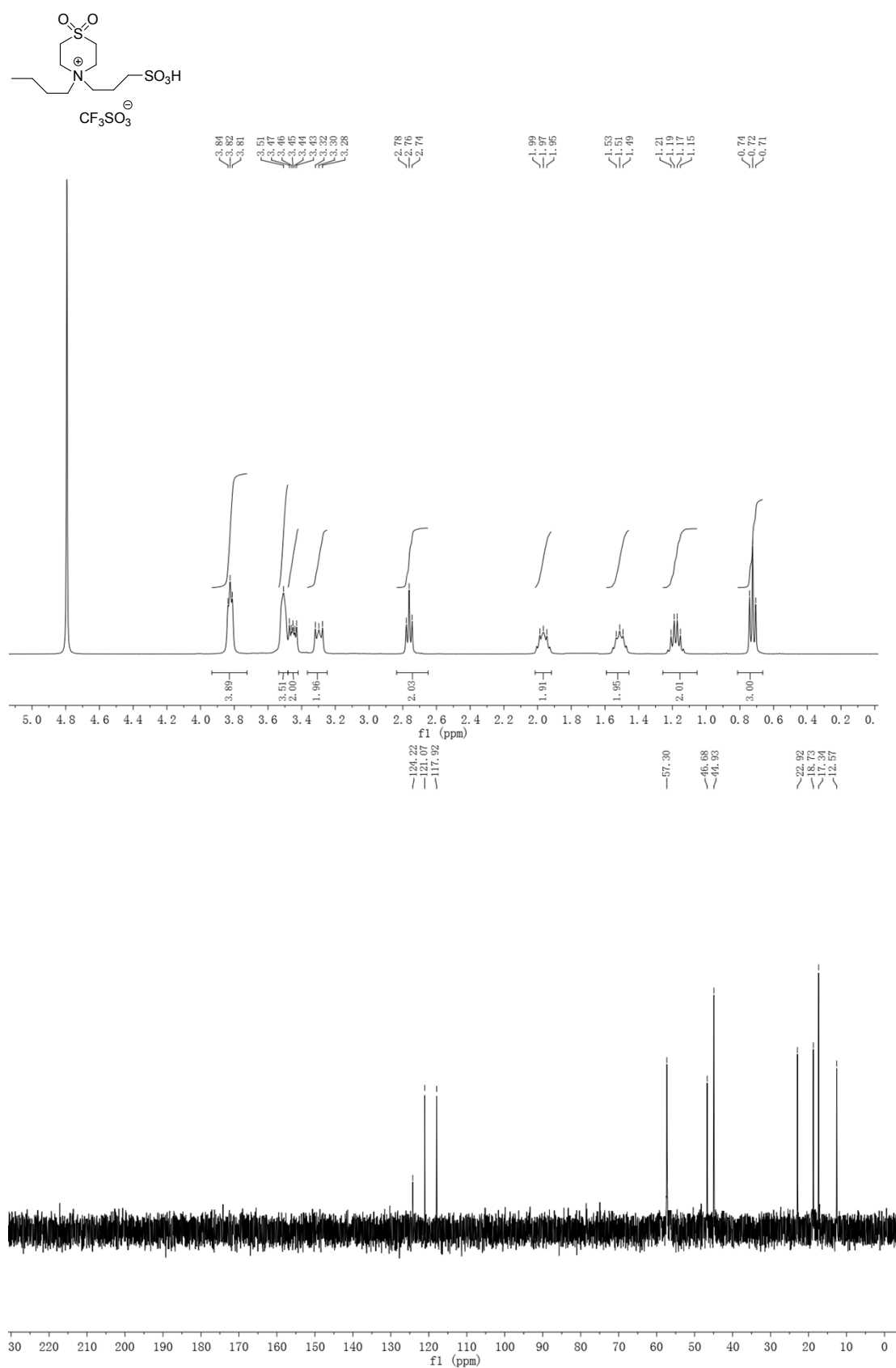
1,3-Di(1H-indol-3-yl)cyclohexane (**6a**): Yellow viscous liquid; ^1H NMR (400 MHz, CDCl_3): δ = 7.75 (s, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 8.0 Hz, 2H), 7.06 (t, J = 8.0 Hz, 2H), 6.99 (s, 2H), 3.38 (t, J = 4.0 Hz, 2H), 2.32-2.29 (m, 2H), 2.03-1.98 (m, 2H), 1.93-1.88 (m, 2H), 1.77-1.73 ppm (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 136.5, 127.2, 121.9, 121.5, 120.7, 119.6, 119.1, 111.3, 37.8, 32.3, 30.9, 22.8 ppm. IR (cm^{-1}): 3414, 3054, 2926, 2854, 1618, 1548, 1485, 1455, 1418, 1337, 1293, 1228, 1097, 1040, 1013. HRMS-ESI (m/z) calcd for $\text{C}_{22}\text{H}_{23}\text{N}_2$, $[\text{M} + \text{H}]^+$ 315.1861, found 315.1850.

3,3'-(Cyclohexane-1,1-diyl)bis(5-bromo-1H-indole) (**8a**):⁷ Brown oil, ^1H NMR (400 MHz, 25 °C, TMS, CDCl_3): δ = 8.00 (s, 2H), 7.55(s, 2H), 7.15-7.13 (m, 6H), 2.43 (t, J = 4.0 Hz, 4H), 1.62-1.55 ppm (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ 135.7, 127.9, 124.2, 123.6, 123.0, 112.6, 112.0, 39.1, 36.9, 26.7, 22.8 ppm.

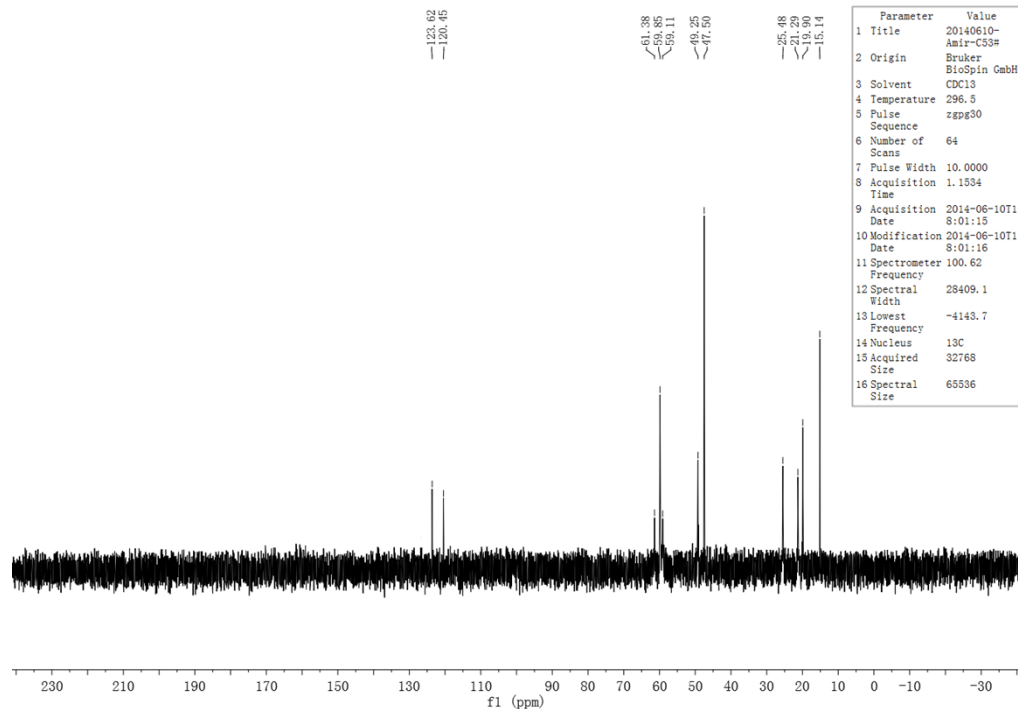
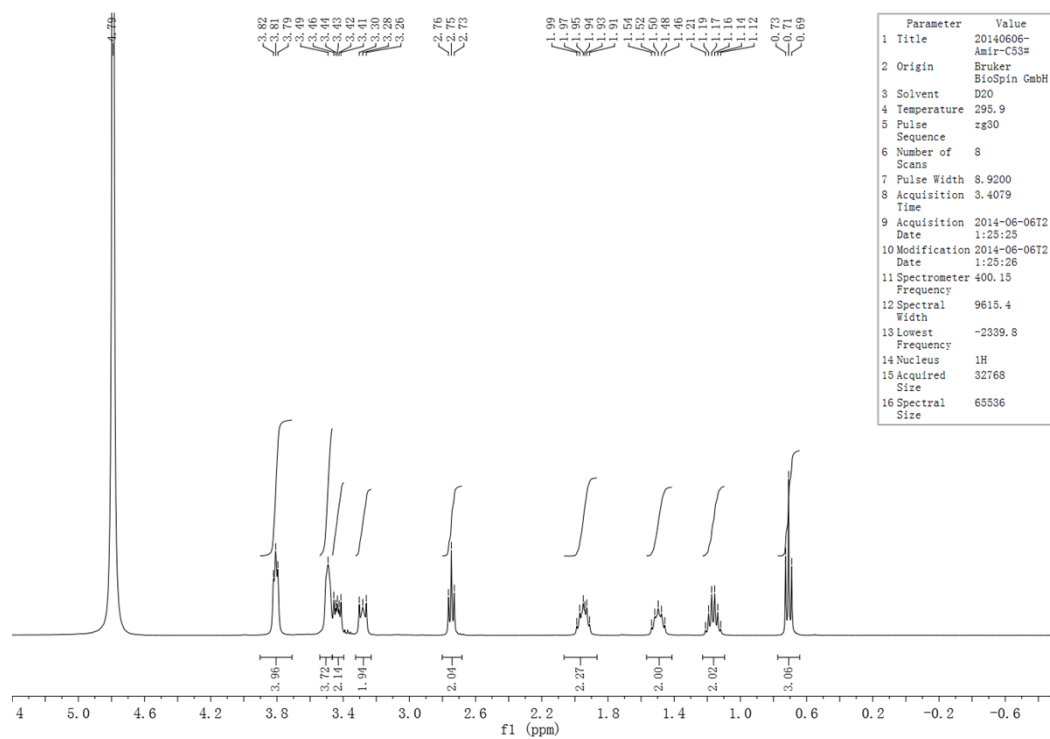
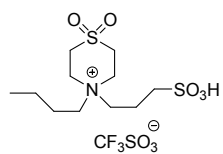
5-Bromo-3-(cyclohex-1-en-1-yl)-1H-indole (**9a**):⁷ Yellow viscous liquid; ^1H NMR (400 MHz, 25 °C, TMS, CDCl_3): δ = 8.08 (s, 1H), 8.02 (d, J = 4.0 Hz, 1H), 7.26 (dd, J_a = 4.0 Hz, J_b = 8.0 Hz, 1H), 7.20-7.18 (m, 1H), 7.11 (d, J = 4.0 Hz, 1H), 6.20-6.18 (m, 1H), 2.40-2.39 (m, 2H), 2.27-2.24 (m, 2H), 1.81-1.77 (m, 2H), 1.73-1.68 ppm (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 135.3, 130.7, 127.1, 124.9, 123.4, 123.2, 121.8, 113.2, 112.6, 28.6, 25.7, 23.1 ppm .

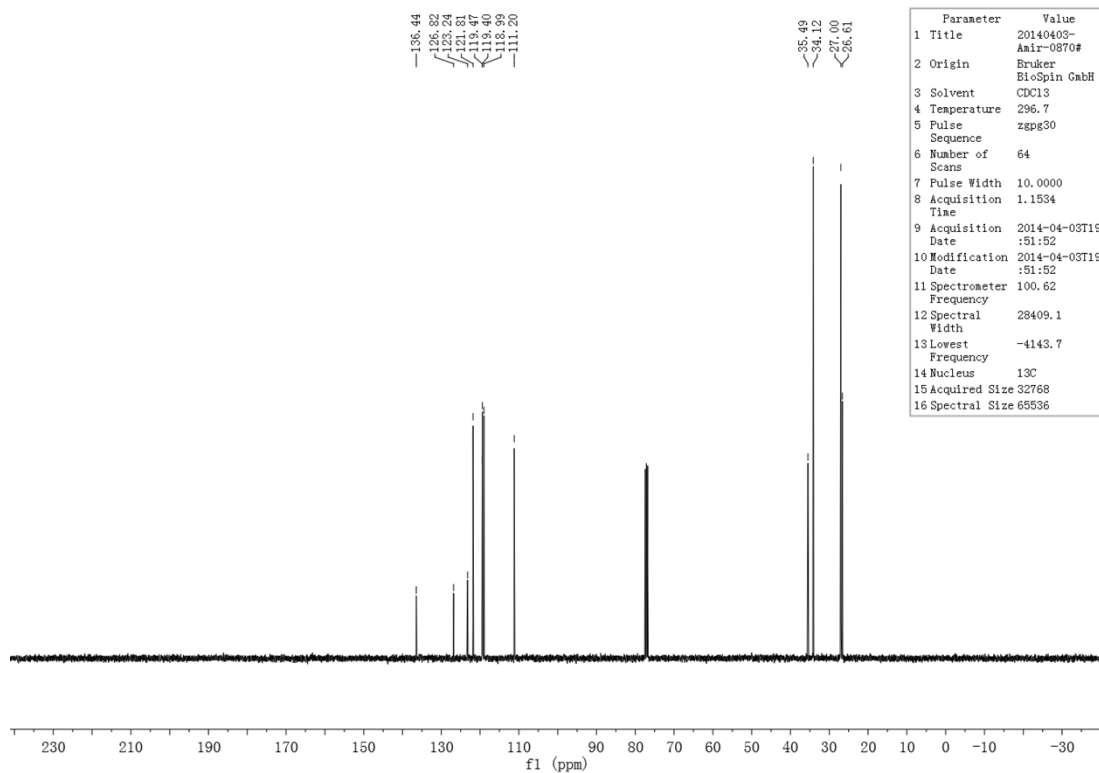
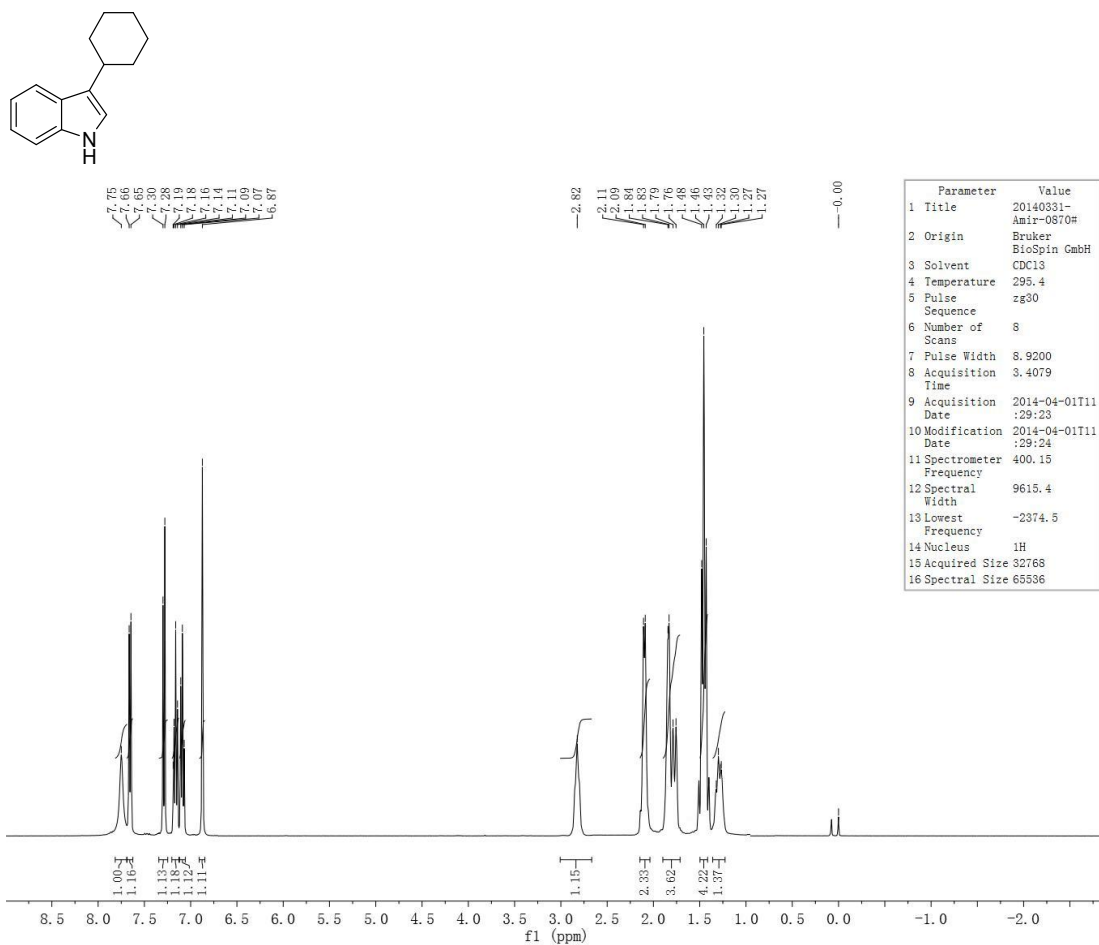
3-Cyclohexyl-1H-indole-5-carboxylic acid (**10a**): White solid, mp. = 145-147 °C; ^1H NMR (400 MHz, CDCl_3) δ = 8.53 (s, 1H), 8.16 (s, 1H), 7.97 (dd, J_a = 4.0 Hz, J_b = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 4.0 Hz, 1H), 2.92-2.87 (m, 1H), 2.13-2.11 (m, 2H), 1.87-1.78 (m, 3H), 1.51-1.44 (m, 4H), 1.35-1.24 ppm (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ = 173.3, 139.5, 126.6, 125.0, 123.8, 123.4, 120.8, 120.1, 110.8, 35.2, 34.1, 26.9, 26.4 ppm. IR (cm^{-1}): 3440, 2925, 2853, 2538, 1674, 1612, 1432, 1262, 908. HRMS-ESI (m/z) calcd for $\text{C}_{17}\text{H}_{24}\text{N}$, $[\text{M} + \text{H}]^+$ 242.1909, found 242.1901. HRMS-ESI (m/z) calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_3$, $[\text{M} + \text{H}]^+$ 260.1287, found 260.1279.

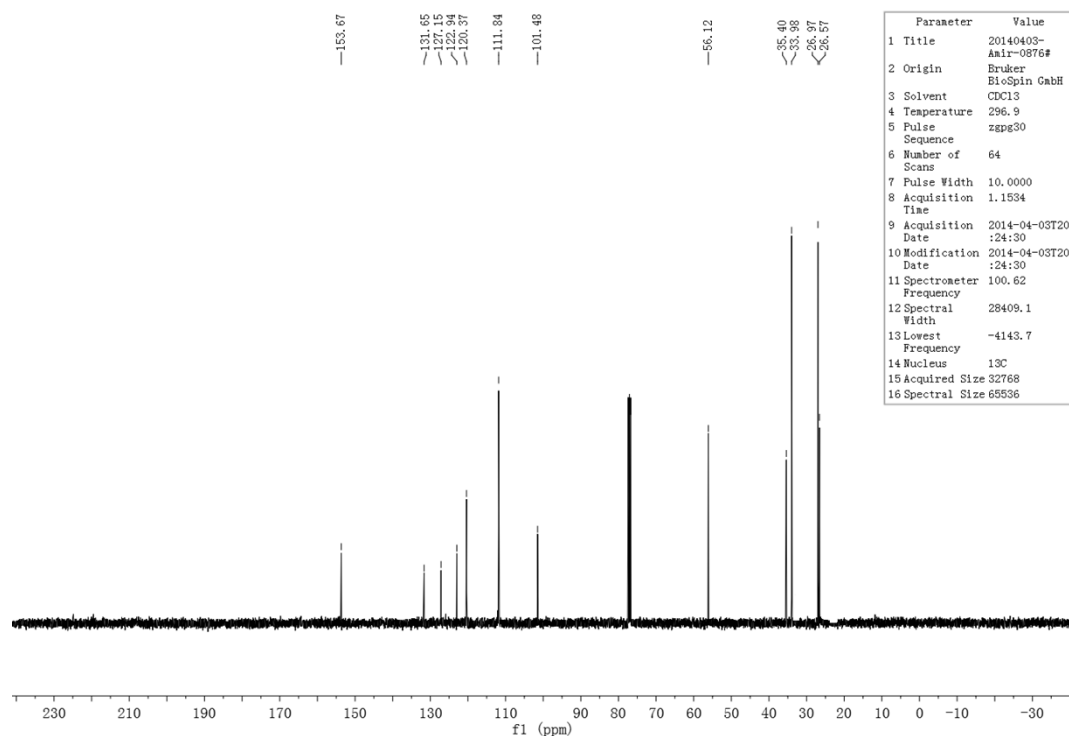
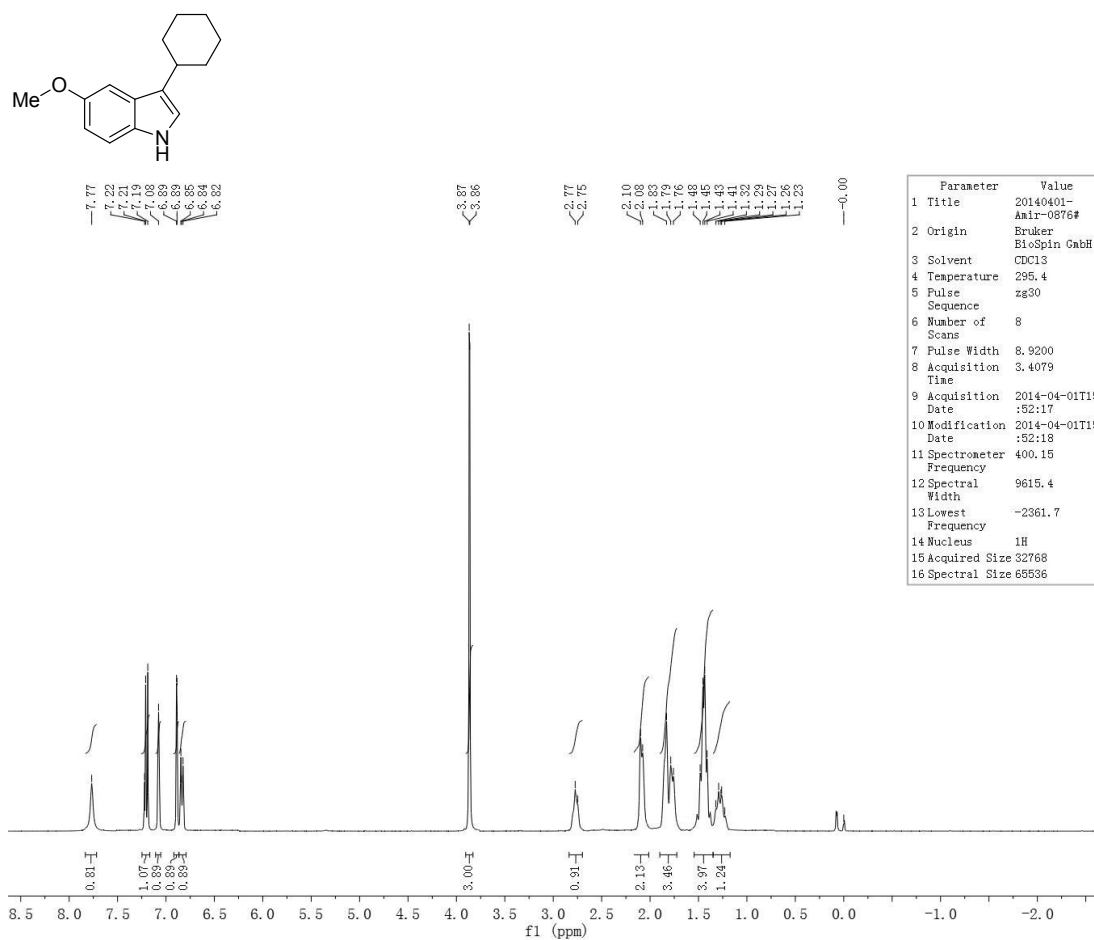
9. Copy of ^1H and ^{13}C NMR Spectra

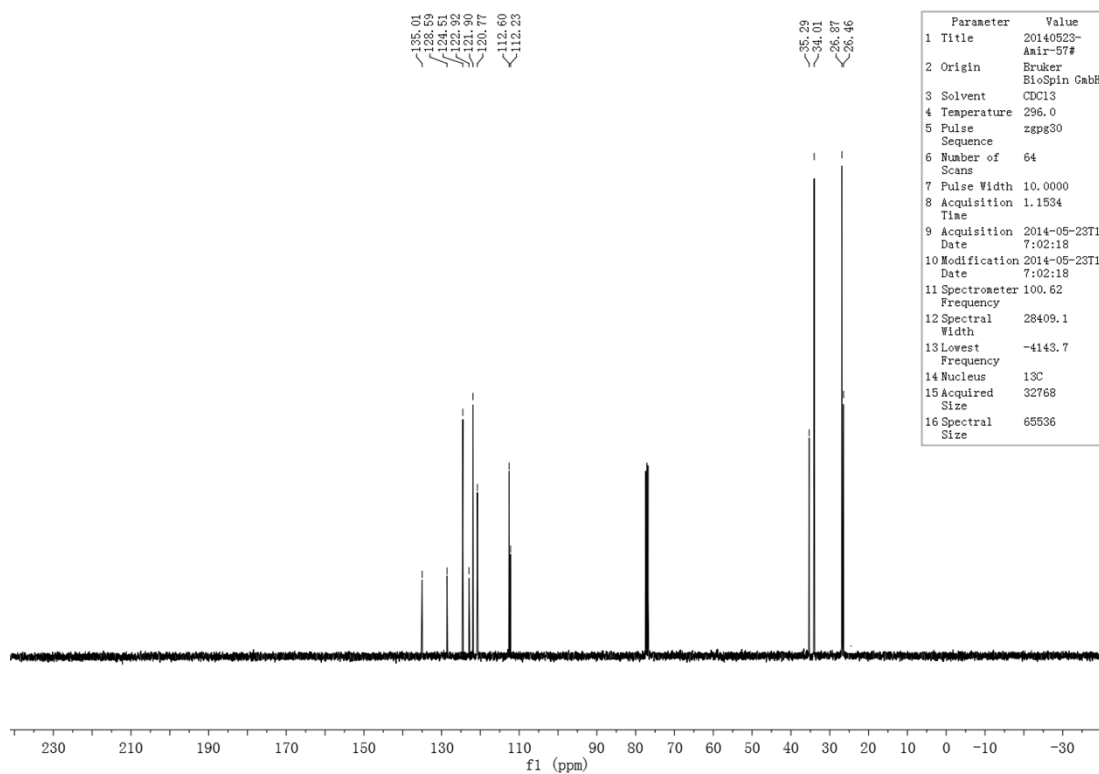
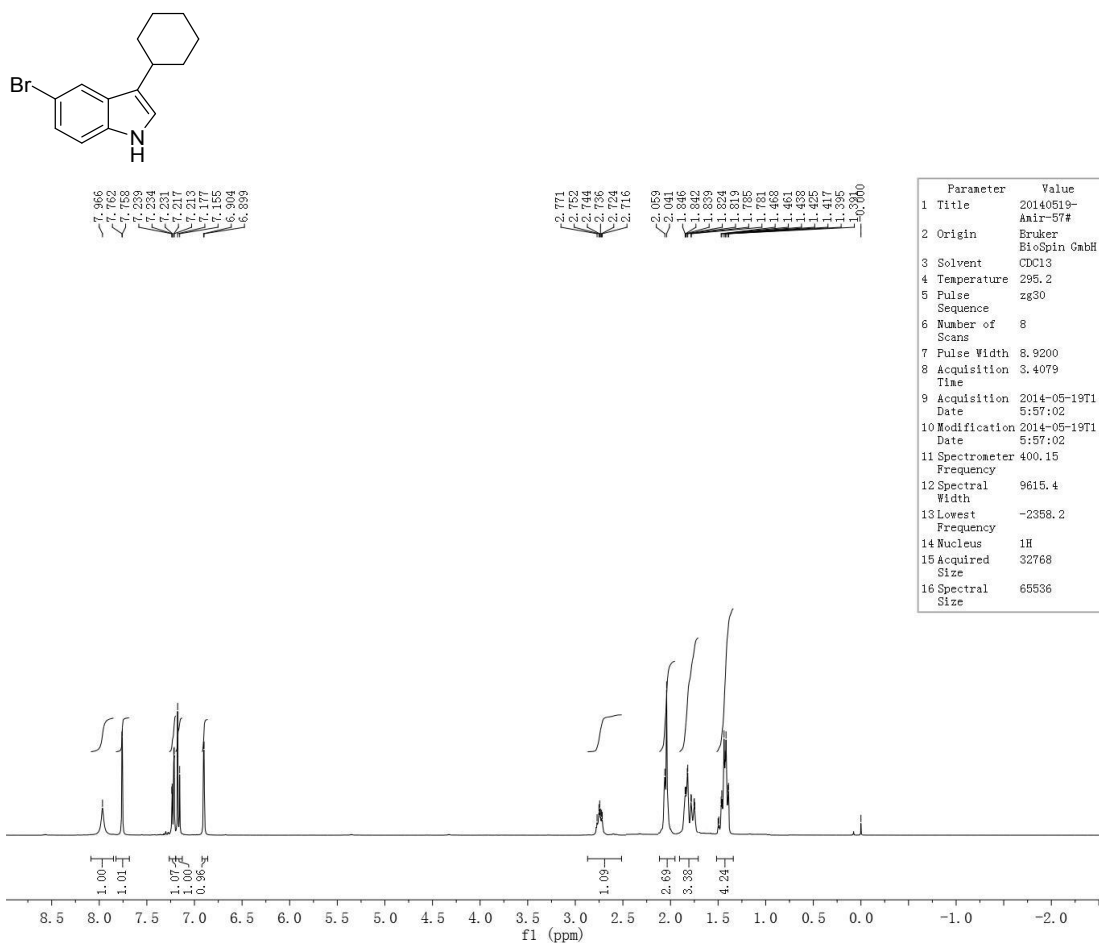


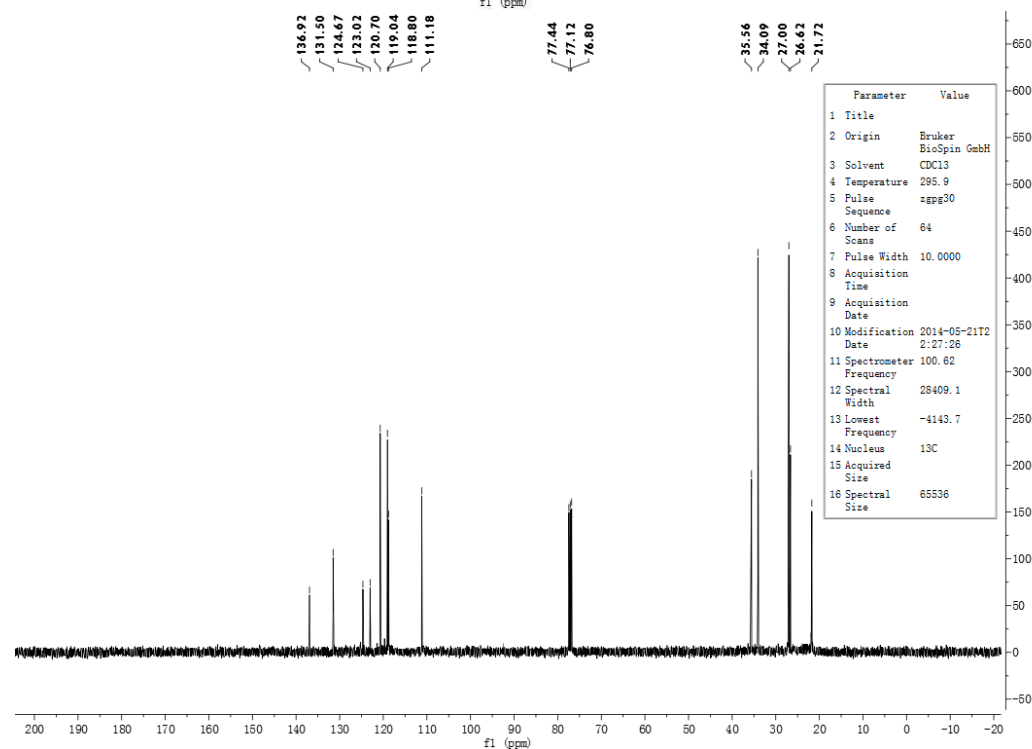
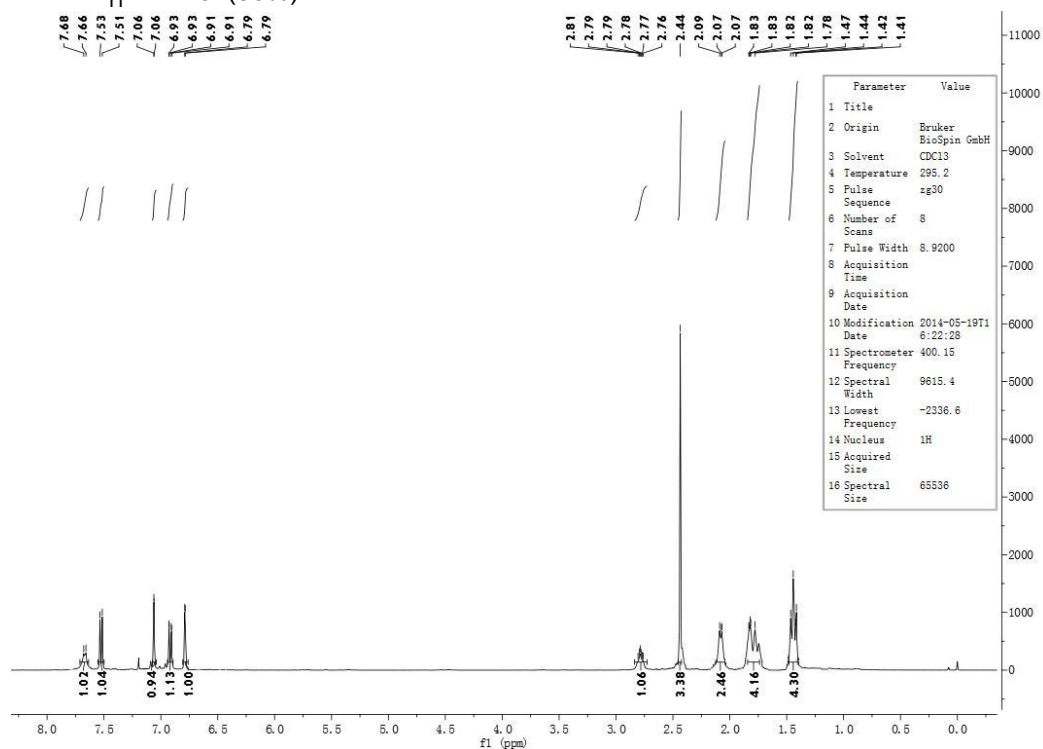
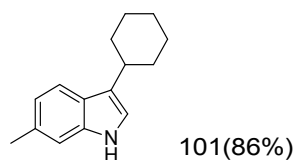
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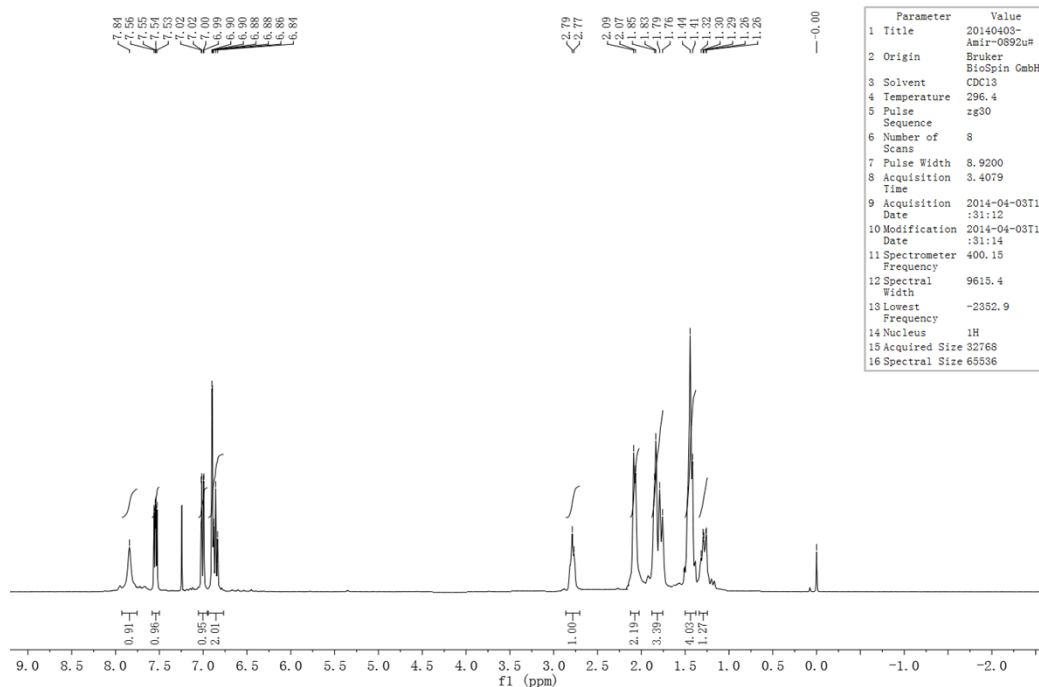
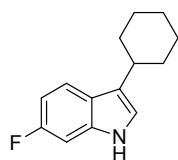




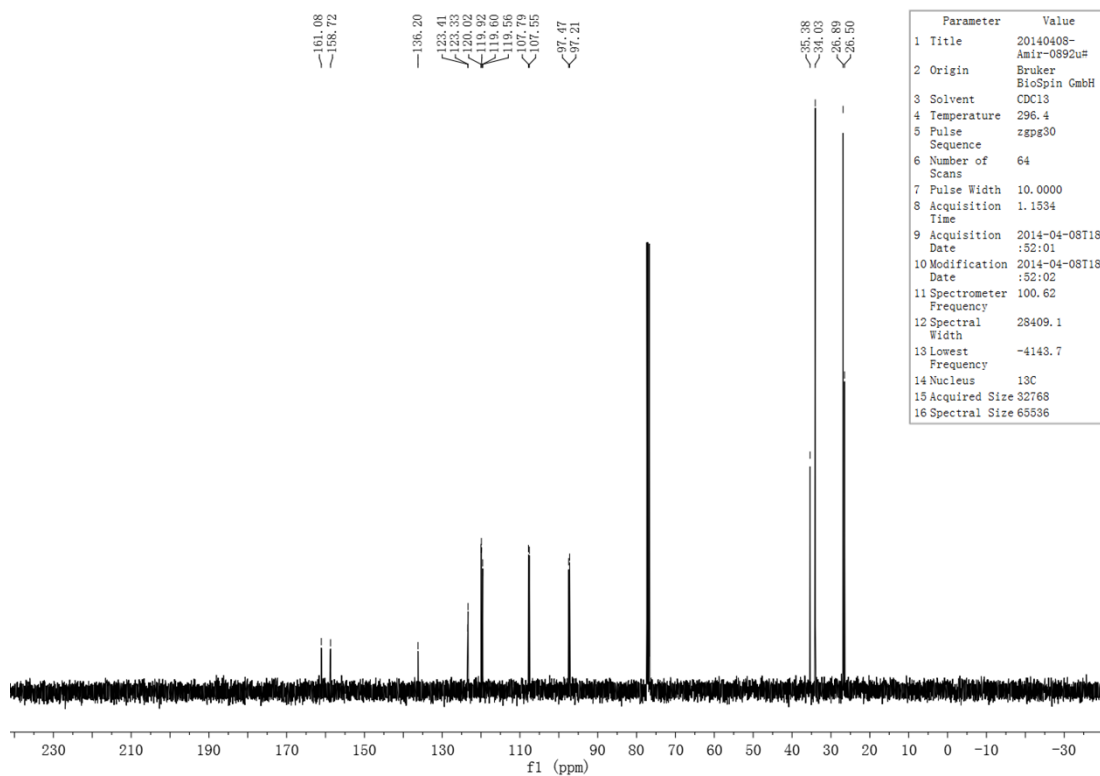




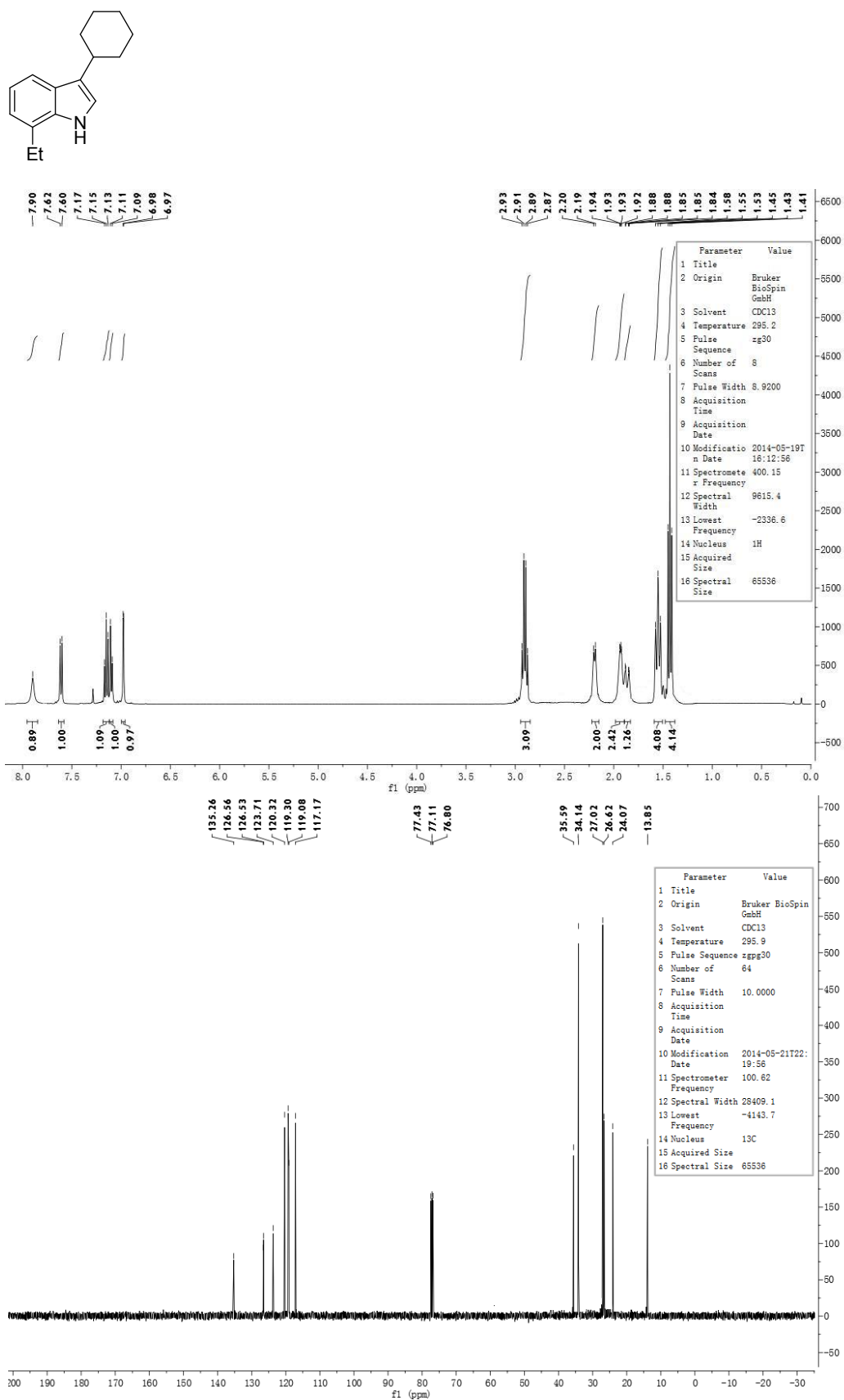


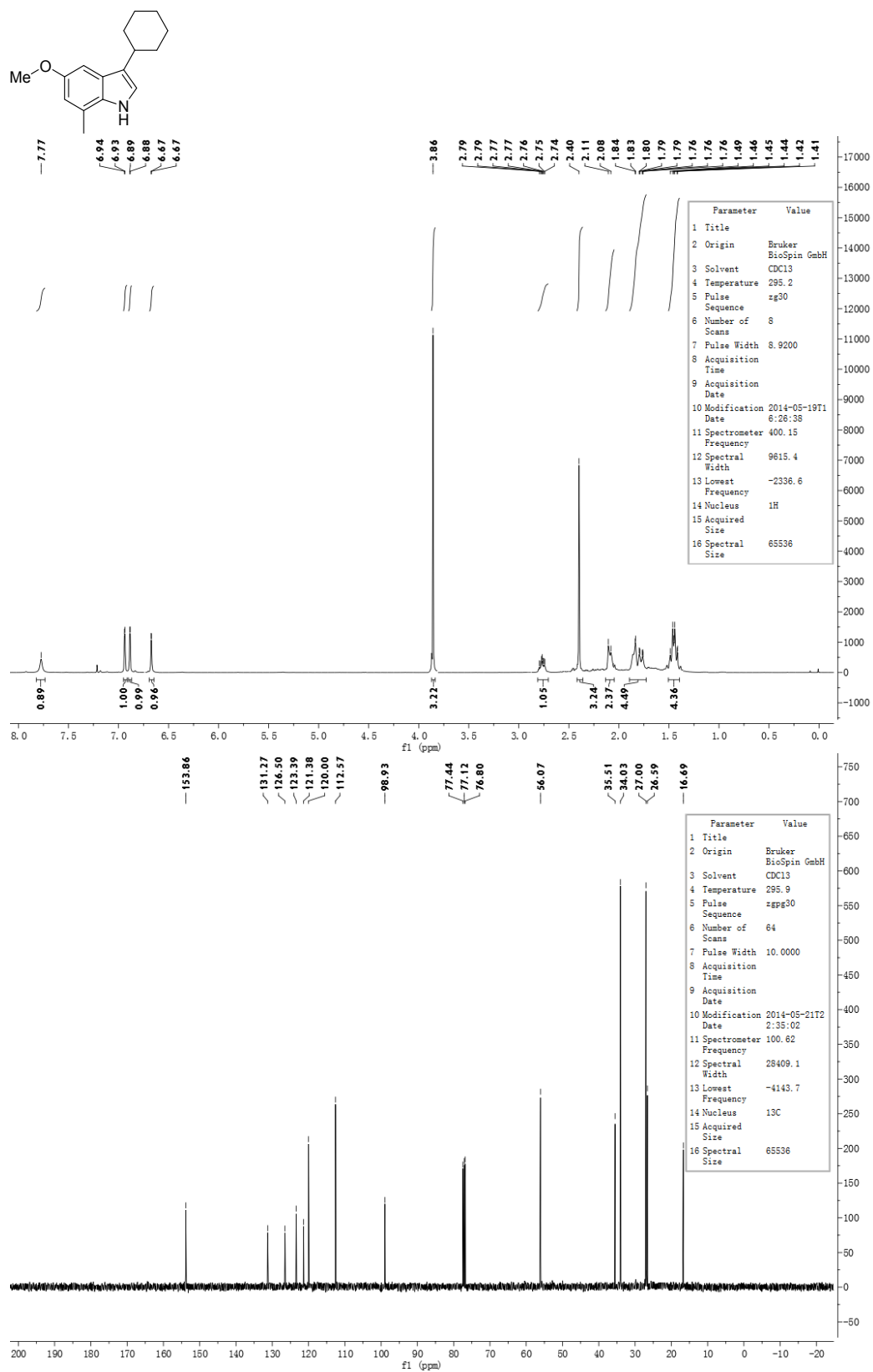


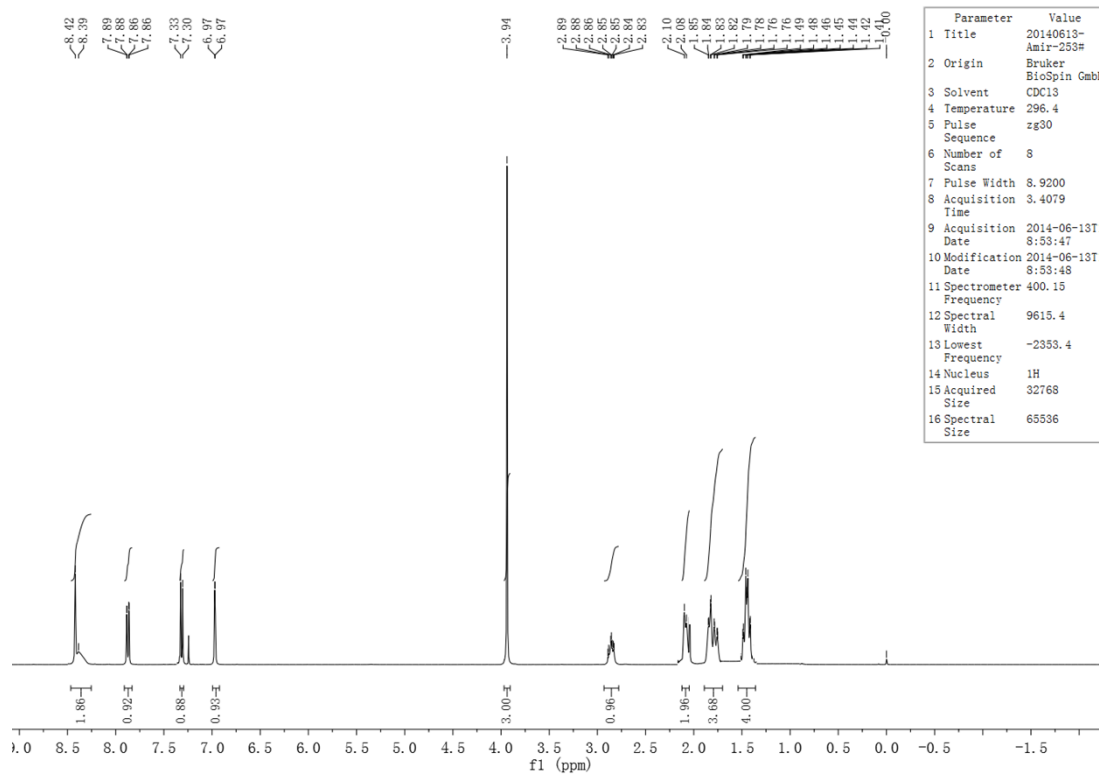
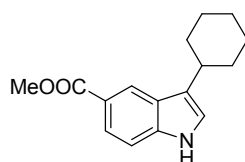
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6 Number of Scans	8
7 Pulse Width	8.9200
8 Acquisition Time	3.4079
9 Acquisition Date	2014-04-03T19:31:12
10 Modification Date	2014-04-03T19:31:14
11 Spectrometer	400.15
12 Spectral Frequency	9615.4
13 Width	-2352.9
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536



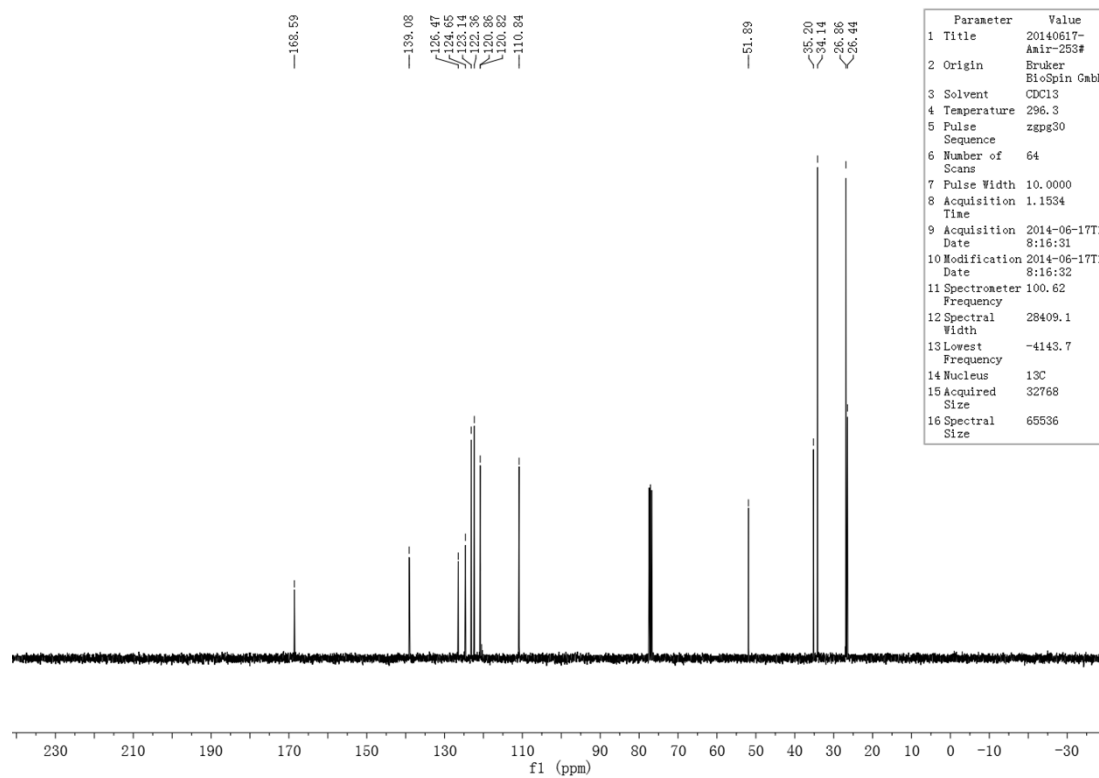
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1 Title	20140408-Amir-0892u#
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.4
5 Pulse Sequence	zgpg30
6 Number of Scans	64
7 Pulse Width	10.0000
8 Acquisition Time	1.1534
9 Acquisition Date	2014-04-08T18:52:01
10 Modification Date	2014-04-08T18:52:02
11 Spectrometer	100.62
12 Spectral Frequency	28409.1
13 Width	-4143.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536



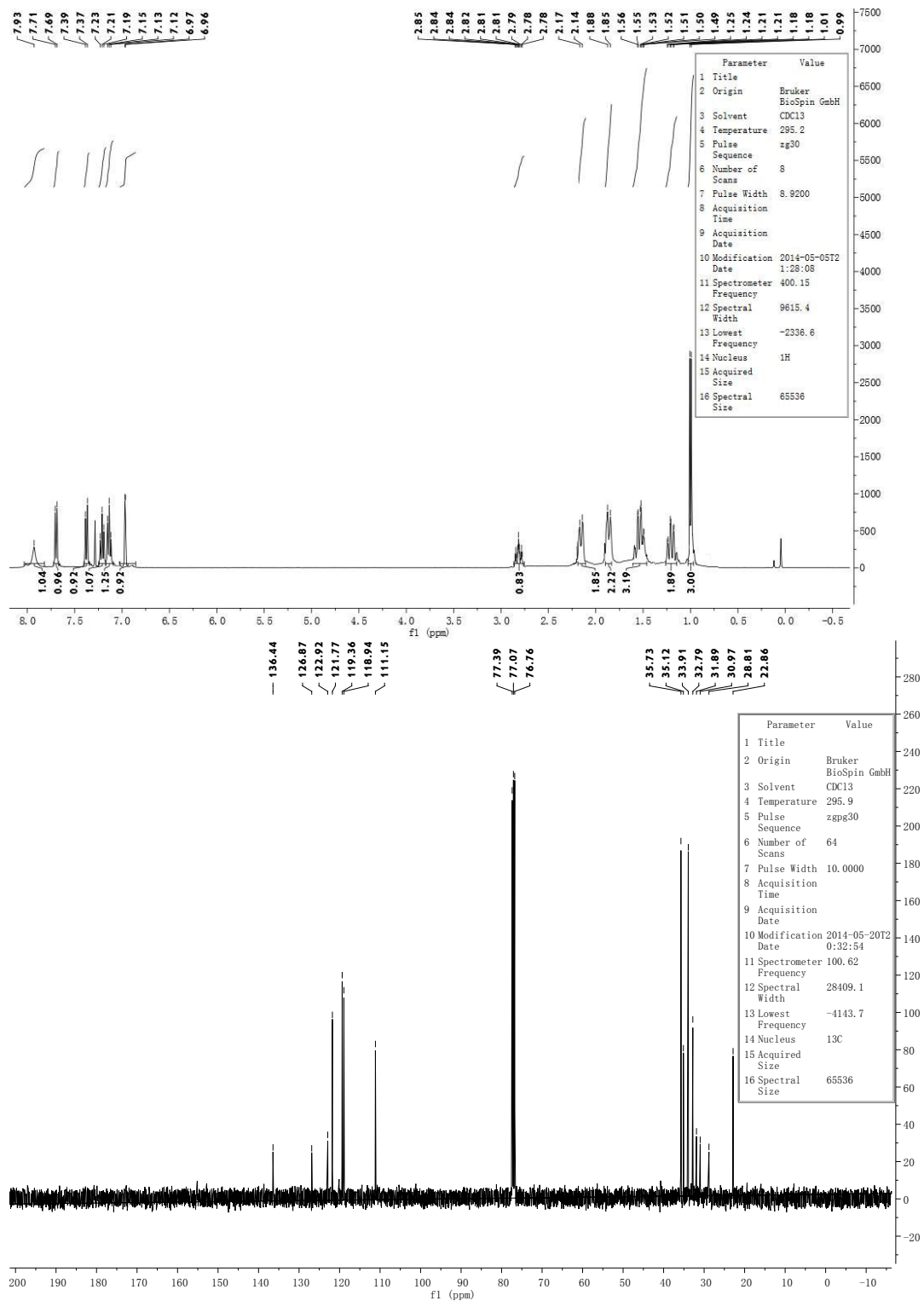
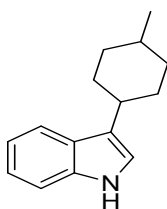


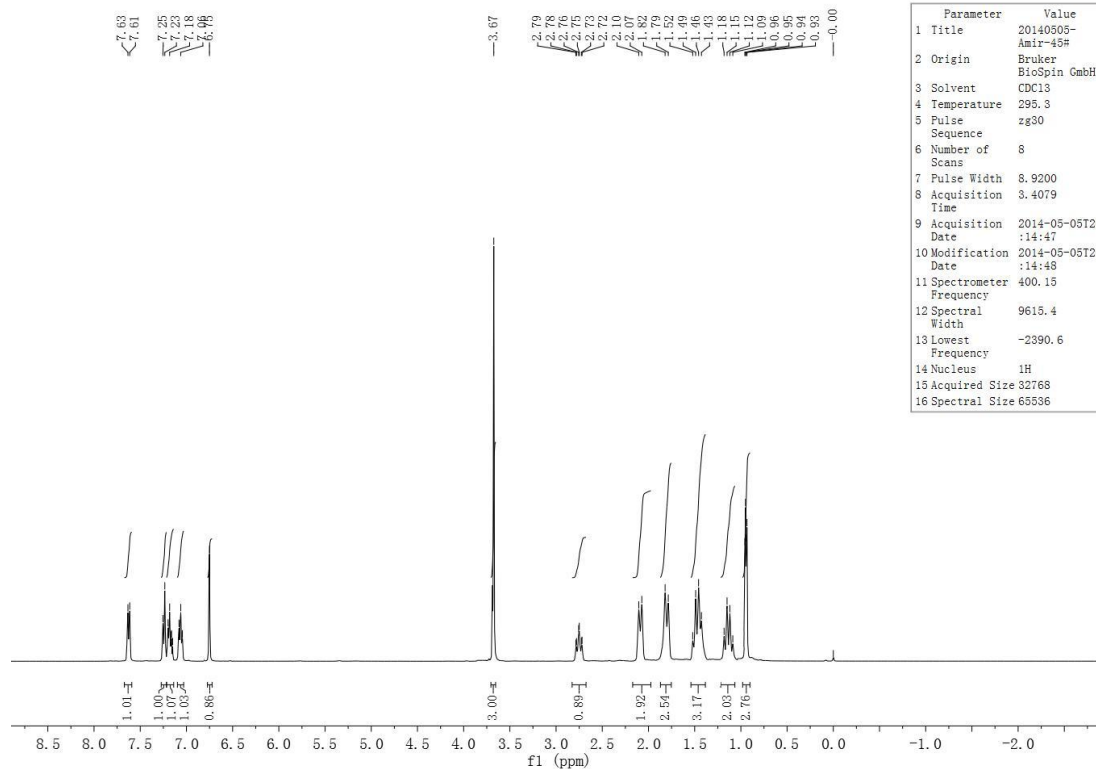
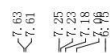


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3 Solvent	BioSpin GmbH
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5 Pulse	zg30
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7 Pulse Width	8.9200
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13 Lowest Frequency	-2353.4
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

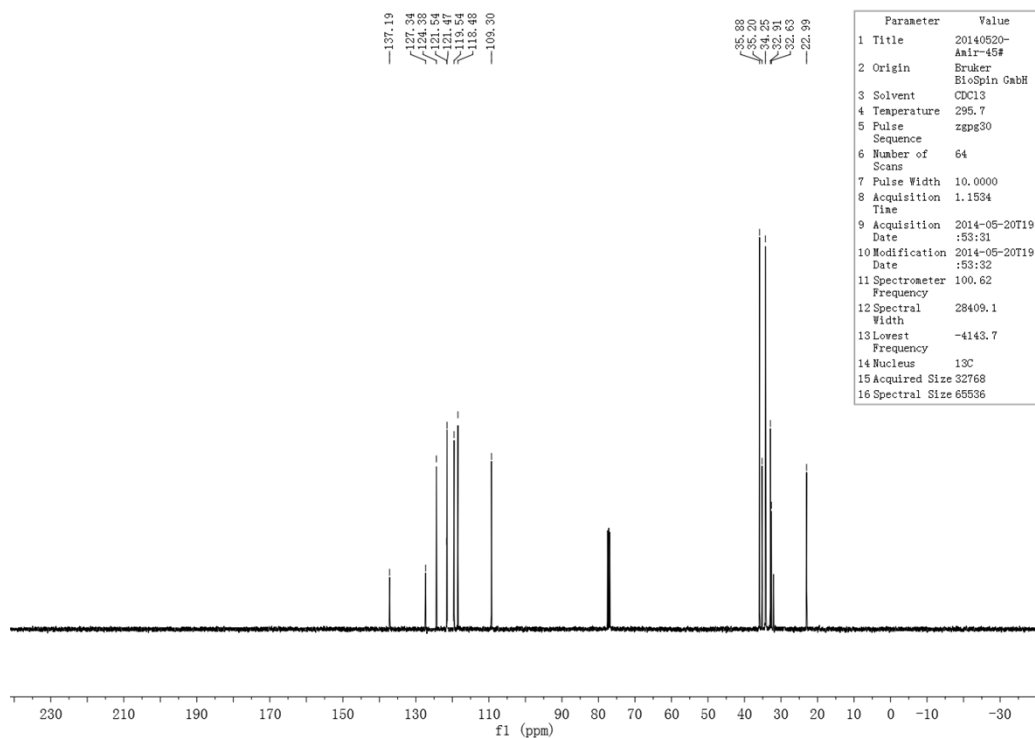


Parameter	Value
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3 Solvent	BioSpin GmbH
4 Temperature	296.3
5 Pulse	zgpg30
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7 Pulse Width	10.0000
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14 Nucleus	13C
15 Acquired Size	32768
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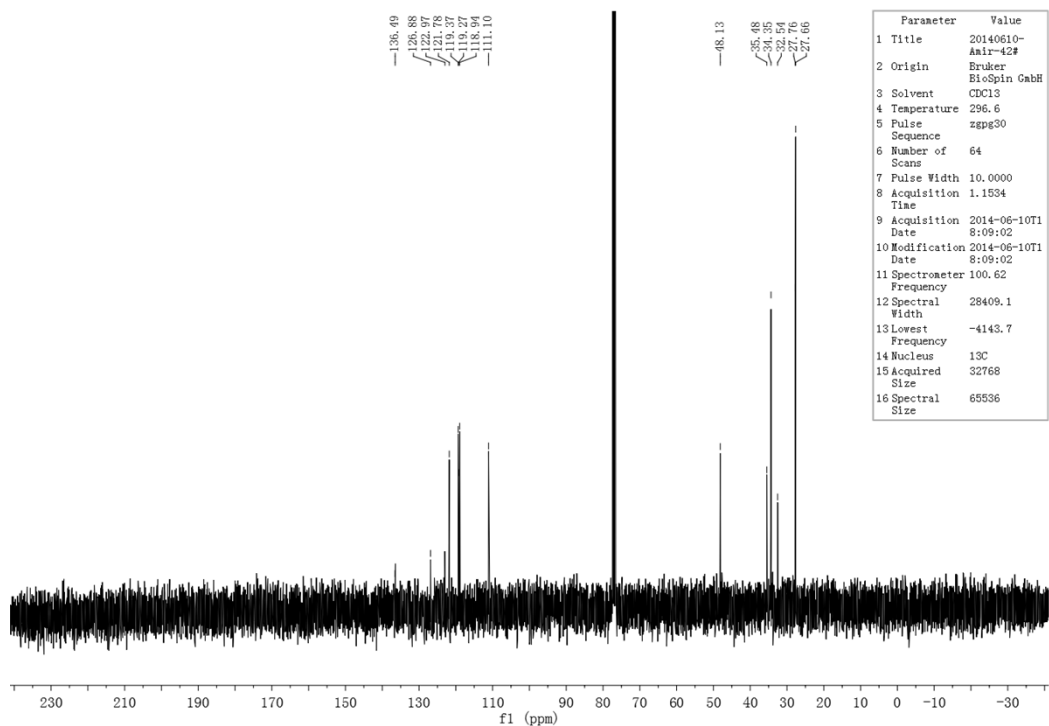
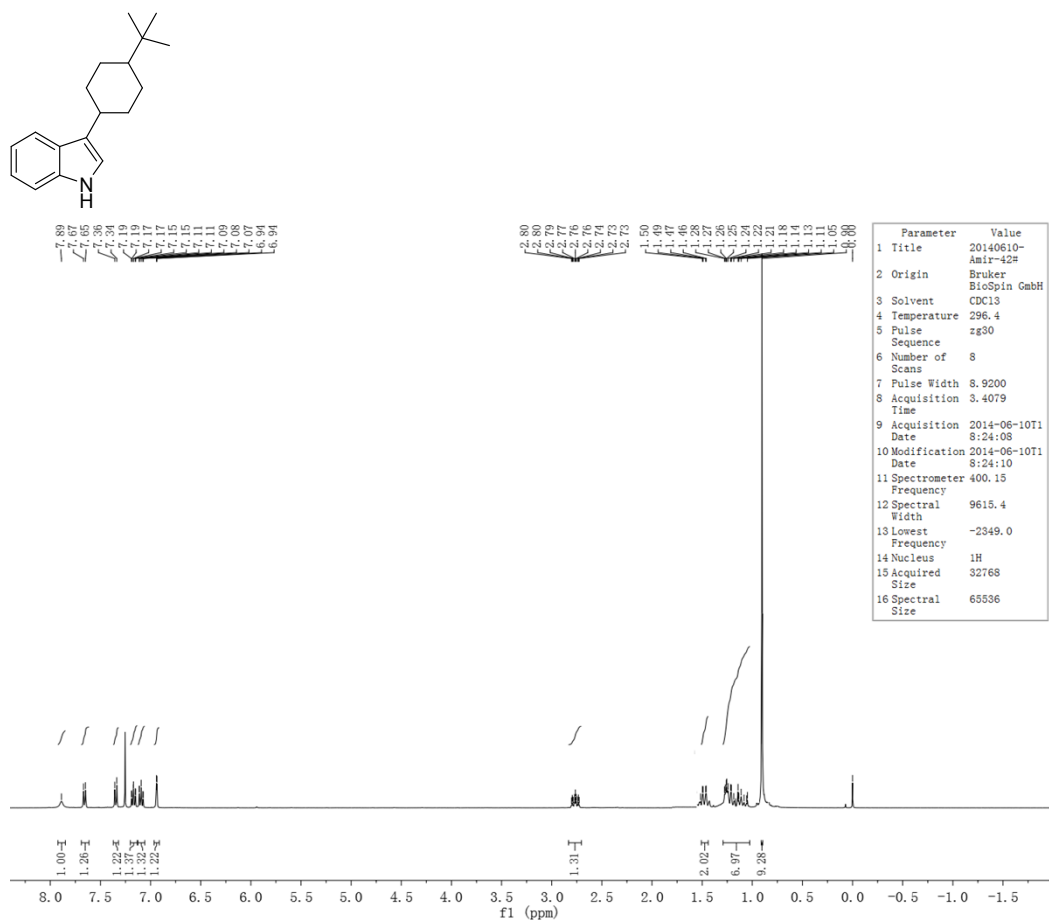


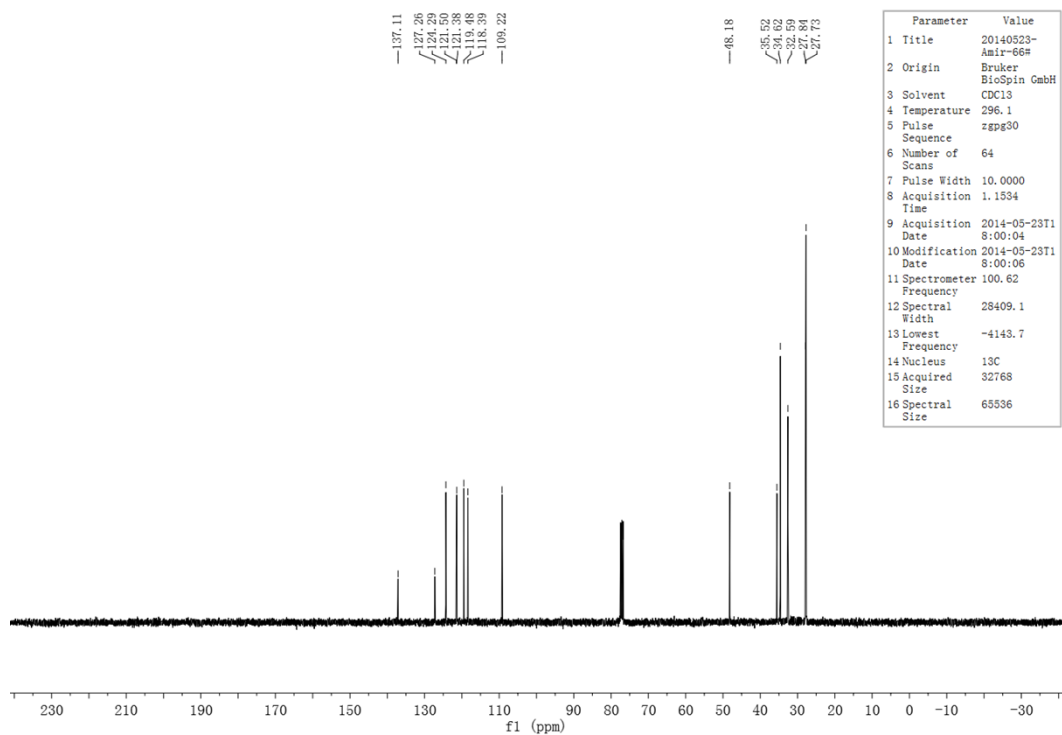
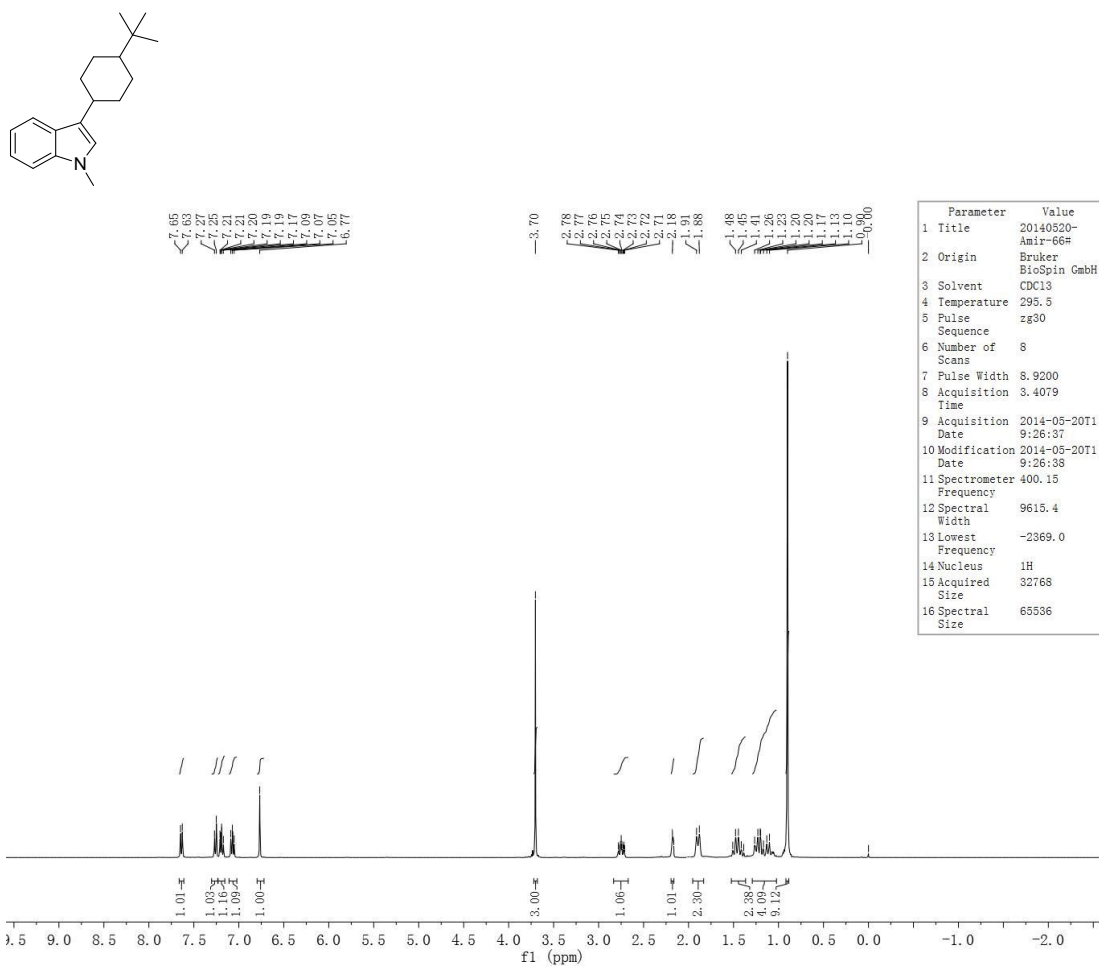


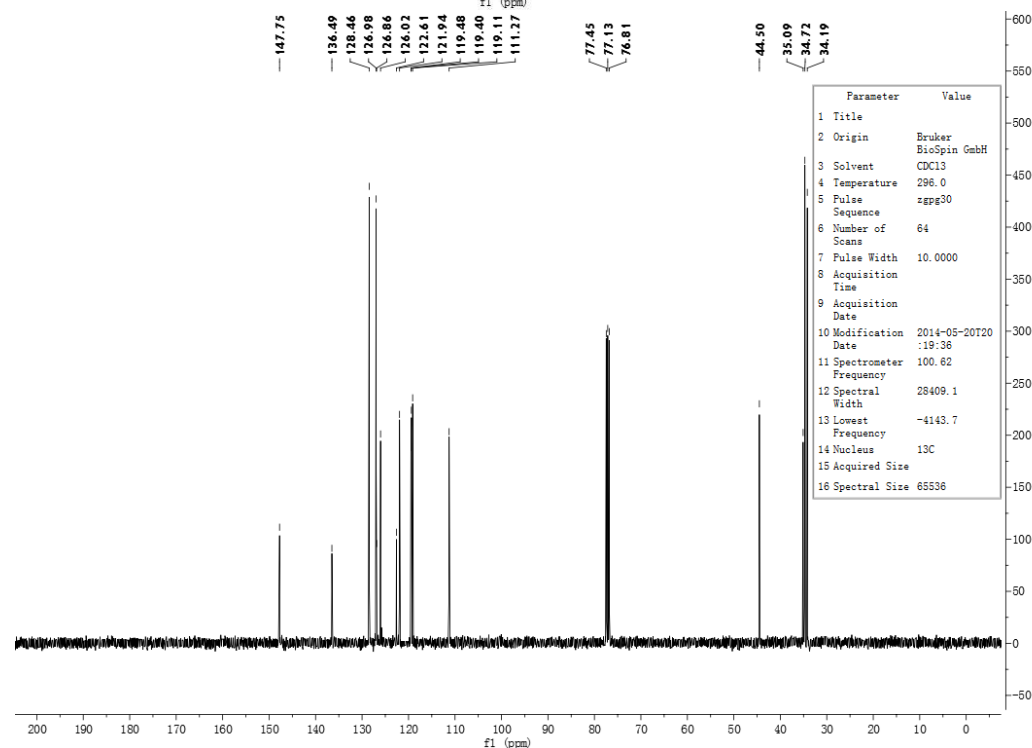
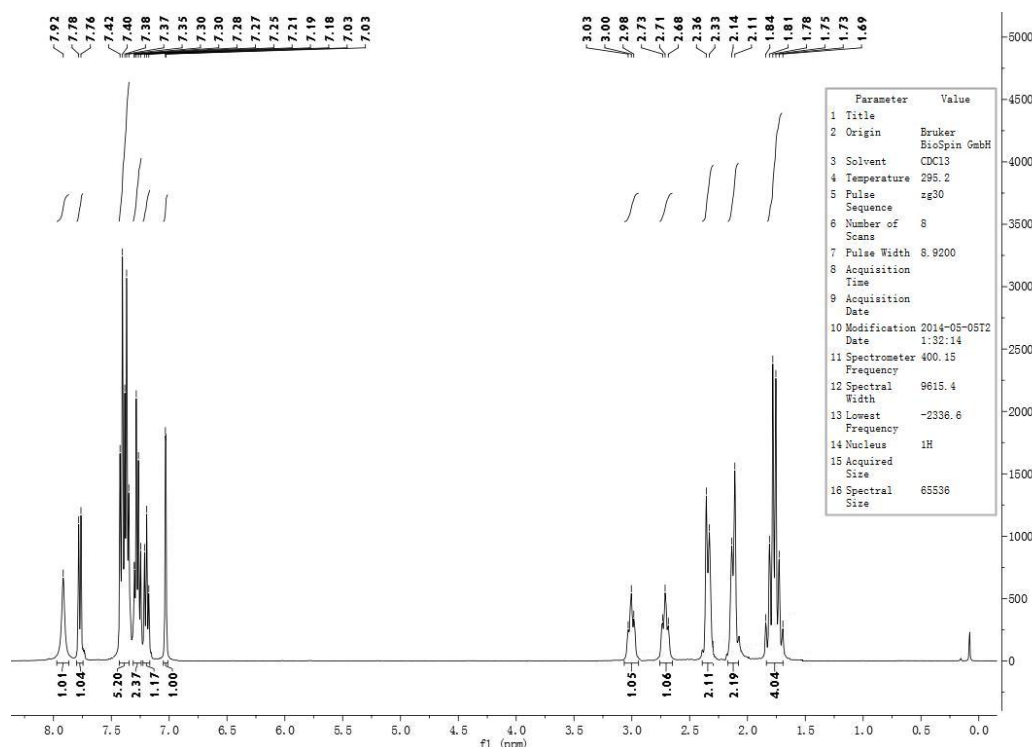
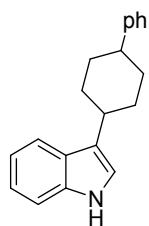
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4	Temperature	295.3
5	Pulse Sequence	zg30
6	Number of Scans	8
7	Pulse Width	8.9200
8	Acquisition Time	3.4079
9	Acquisition Date	2014-05-05T20 :14:47
10	Modification Date	2014-05-05T20 :14:48
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15	Acquired Size	32768
16	Spectral Size	65536

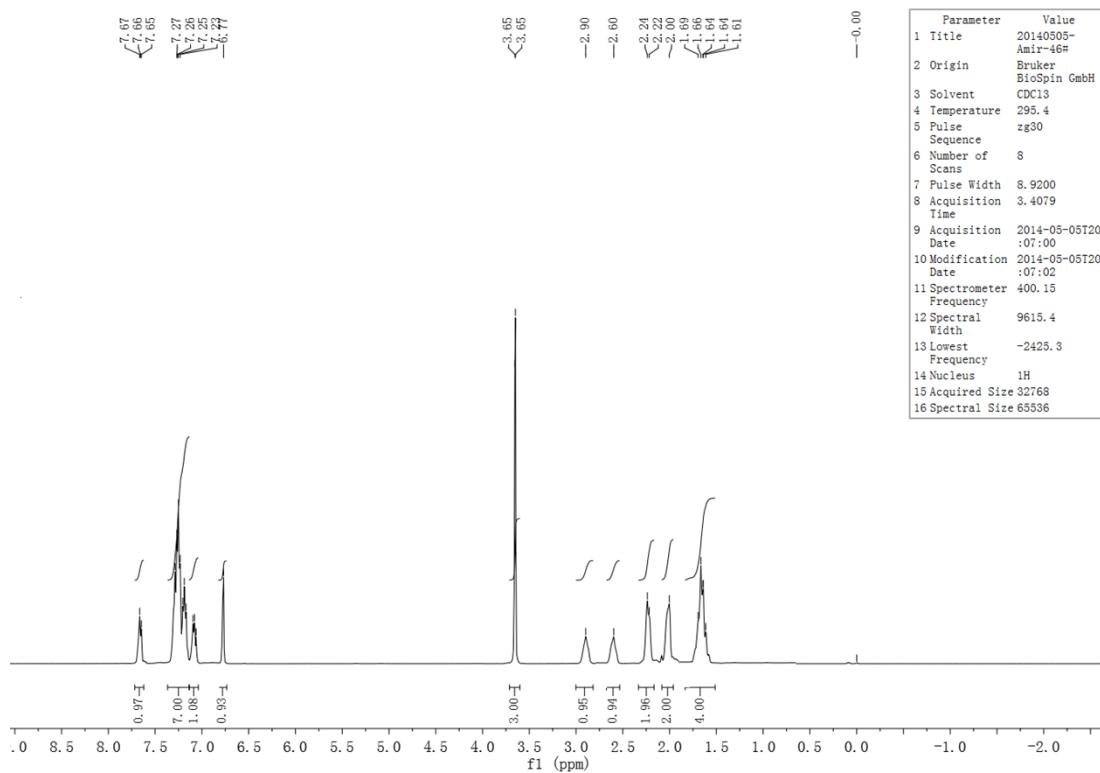
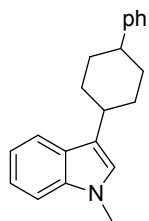


Parameter	Value
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11 Date	2014-05-20T19
12 Time	153132
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16 Nucleus	13C
17 Acquired Size	32768
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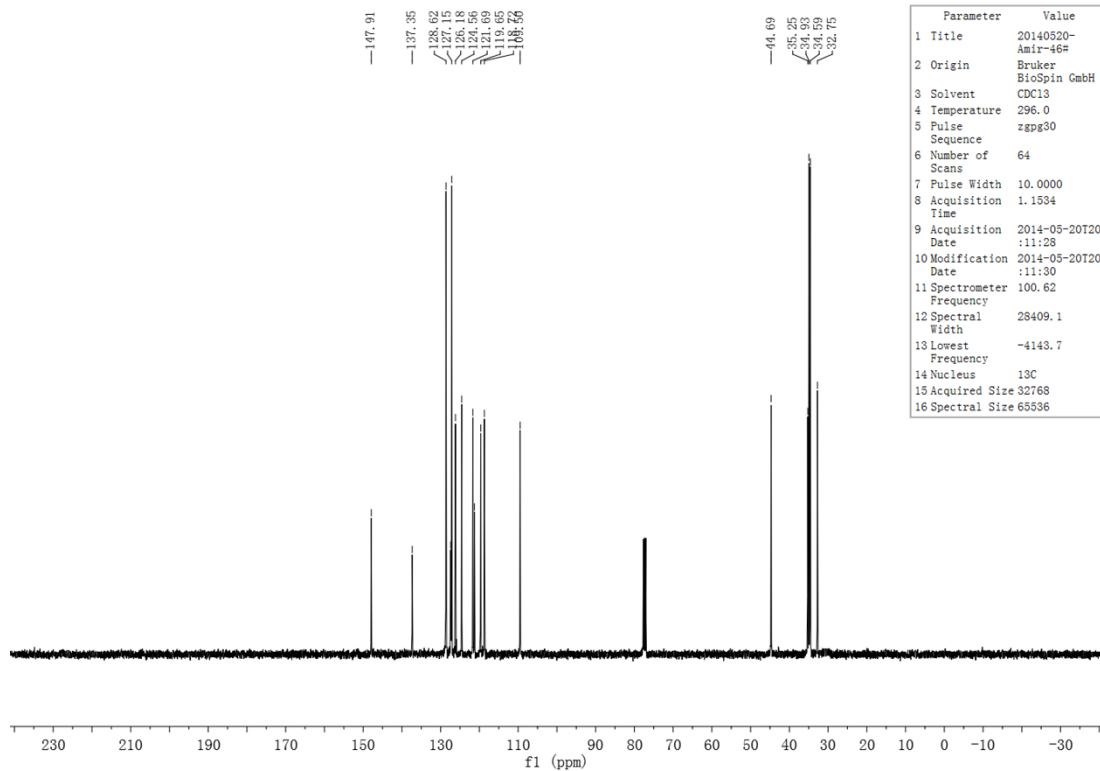




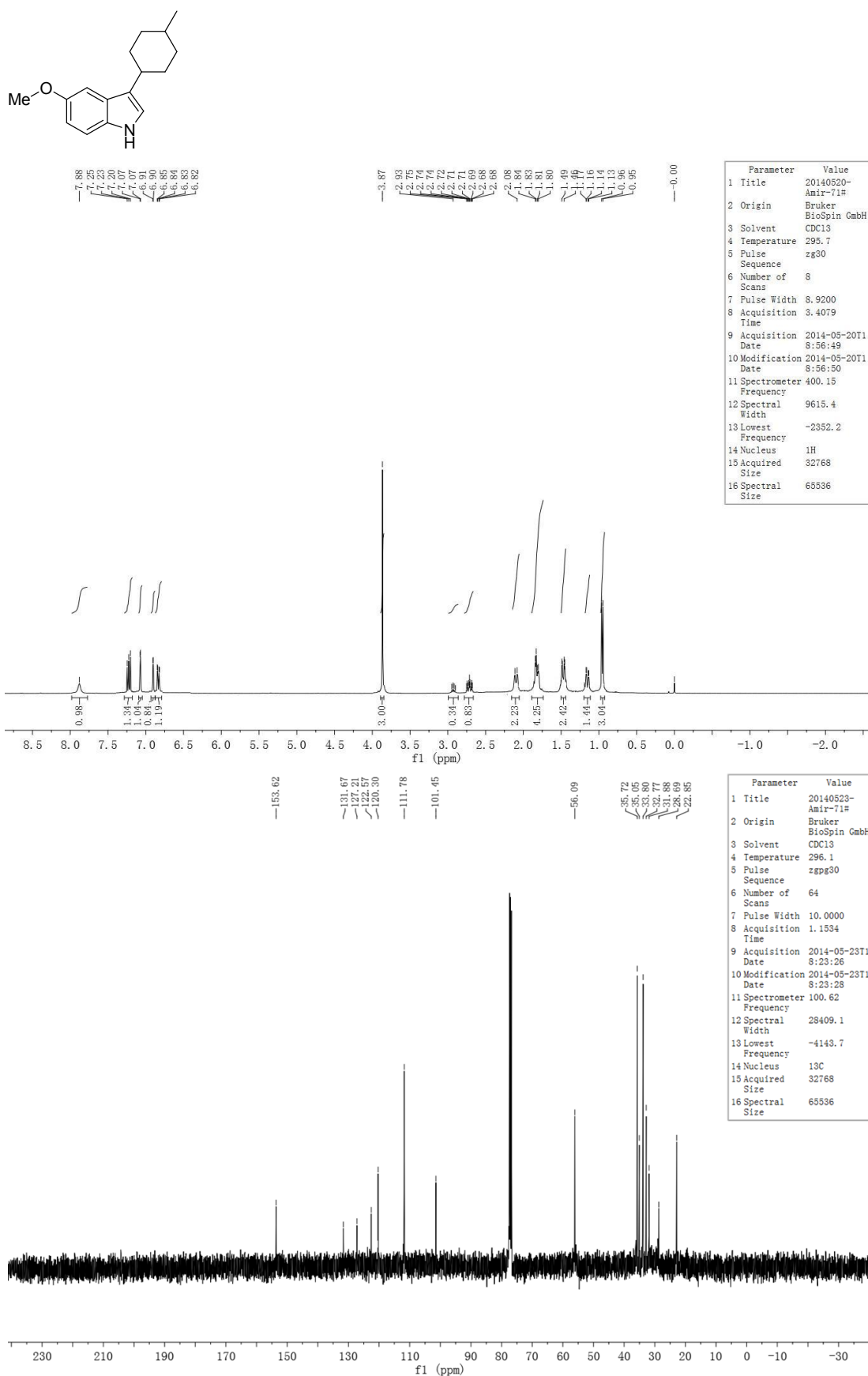


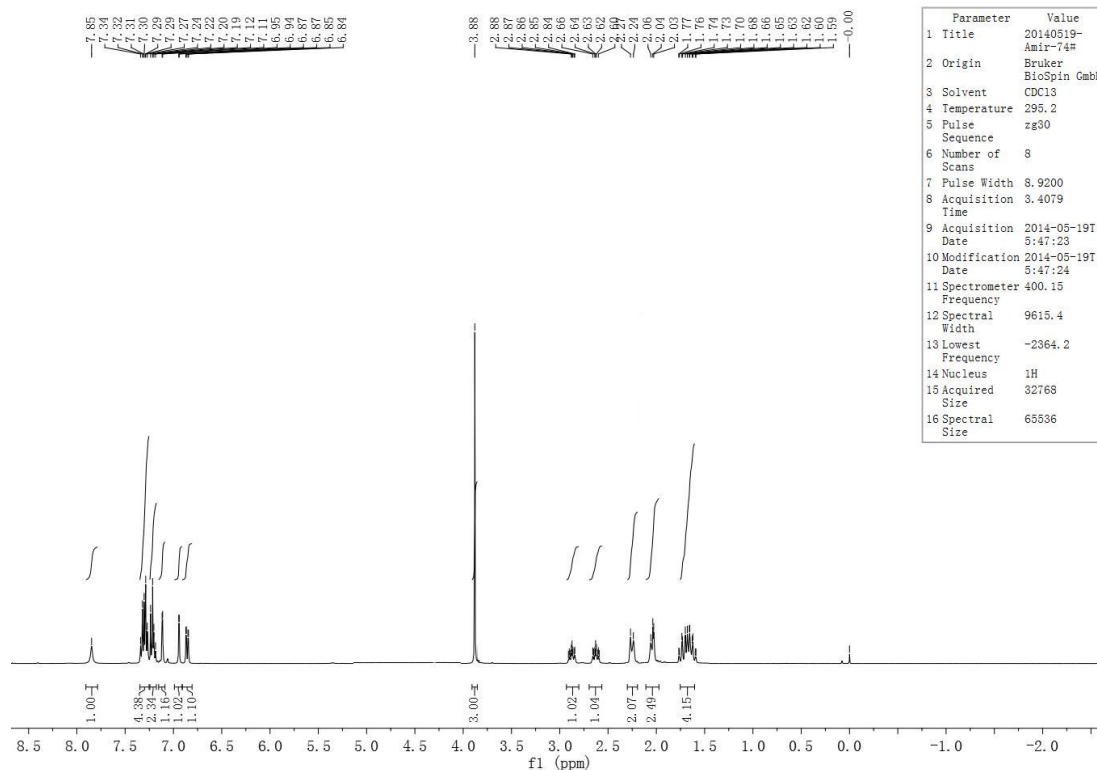
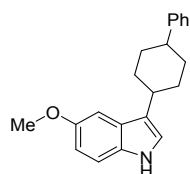


Parameter	Value
1 Title	20140505-Amir-46s
2 Origin	Bruker BioSpin GmbH
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4 Temperature	295.4
5 Pulse Sequence	zg30
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9 Acquisition Date	2014-05-05T20:07:00
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15 Acquired Size	32768
16 Spectral Size	65536

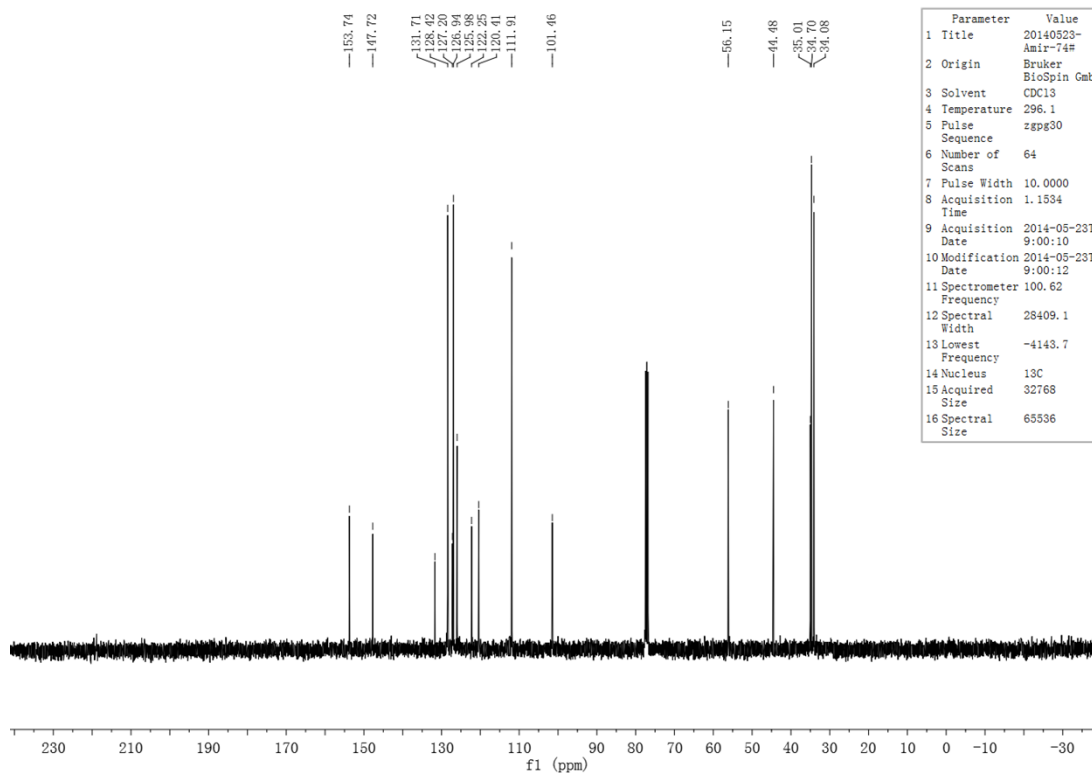


Parameter	Value
1 Title	20140520-Amir-46s
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3 Solvent	CDCl3
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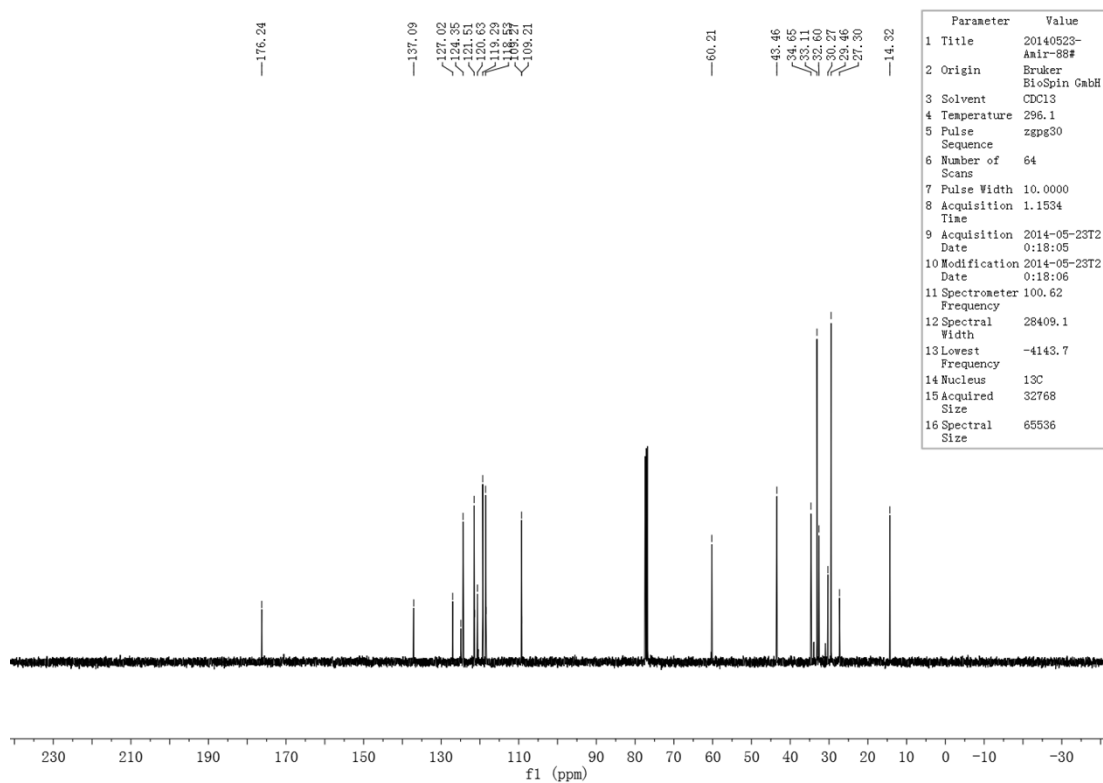
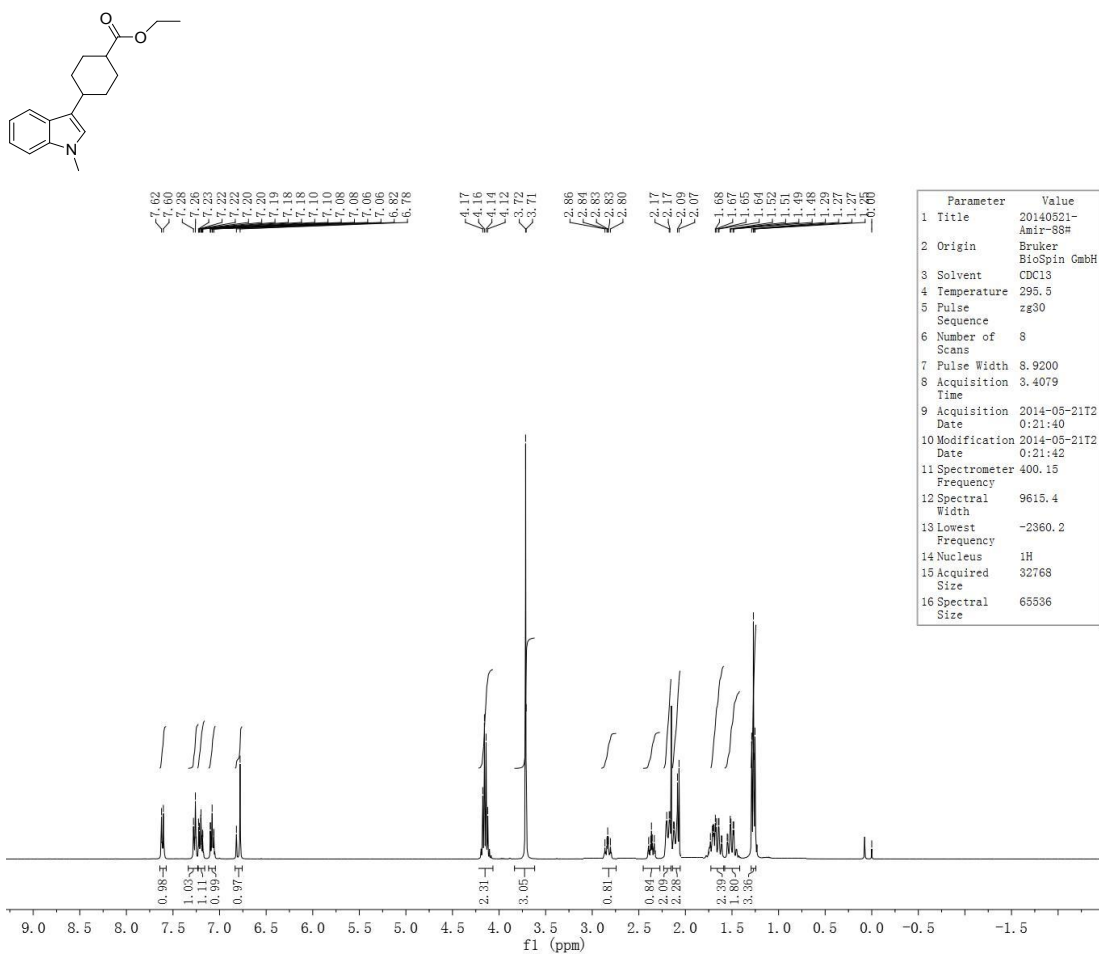


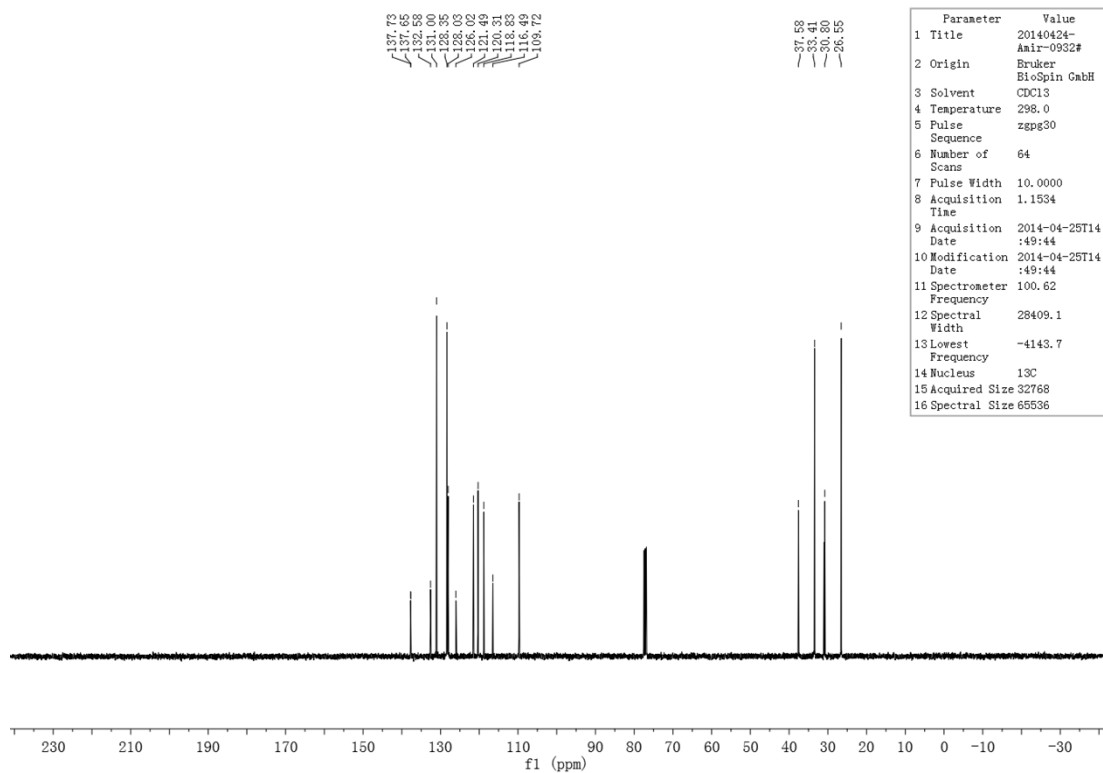
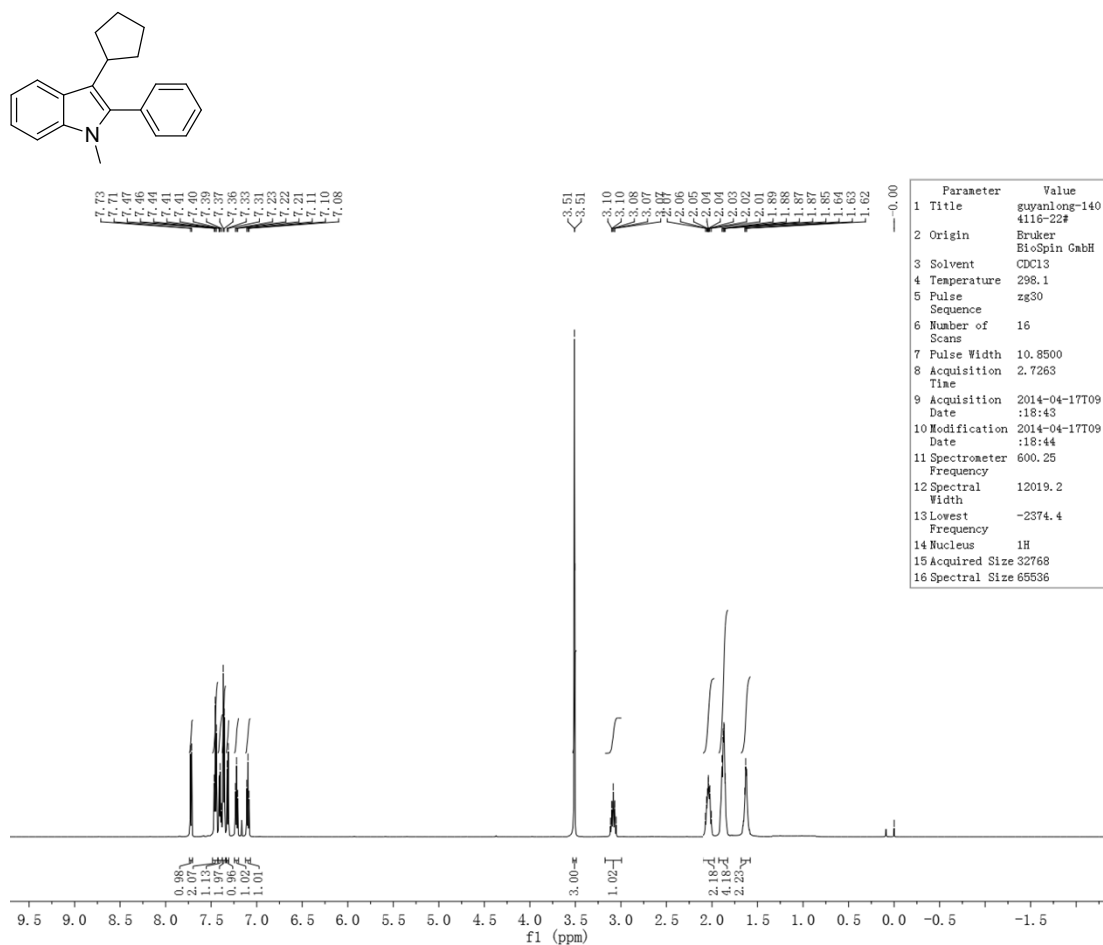


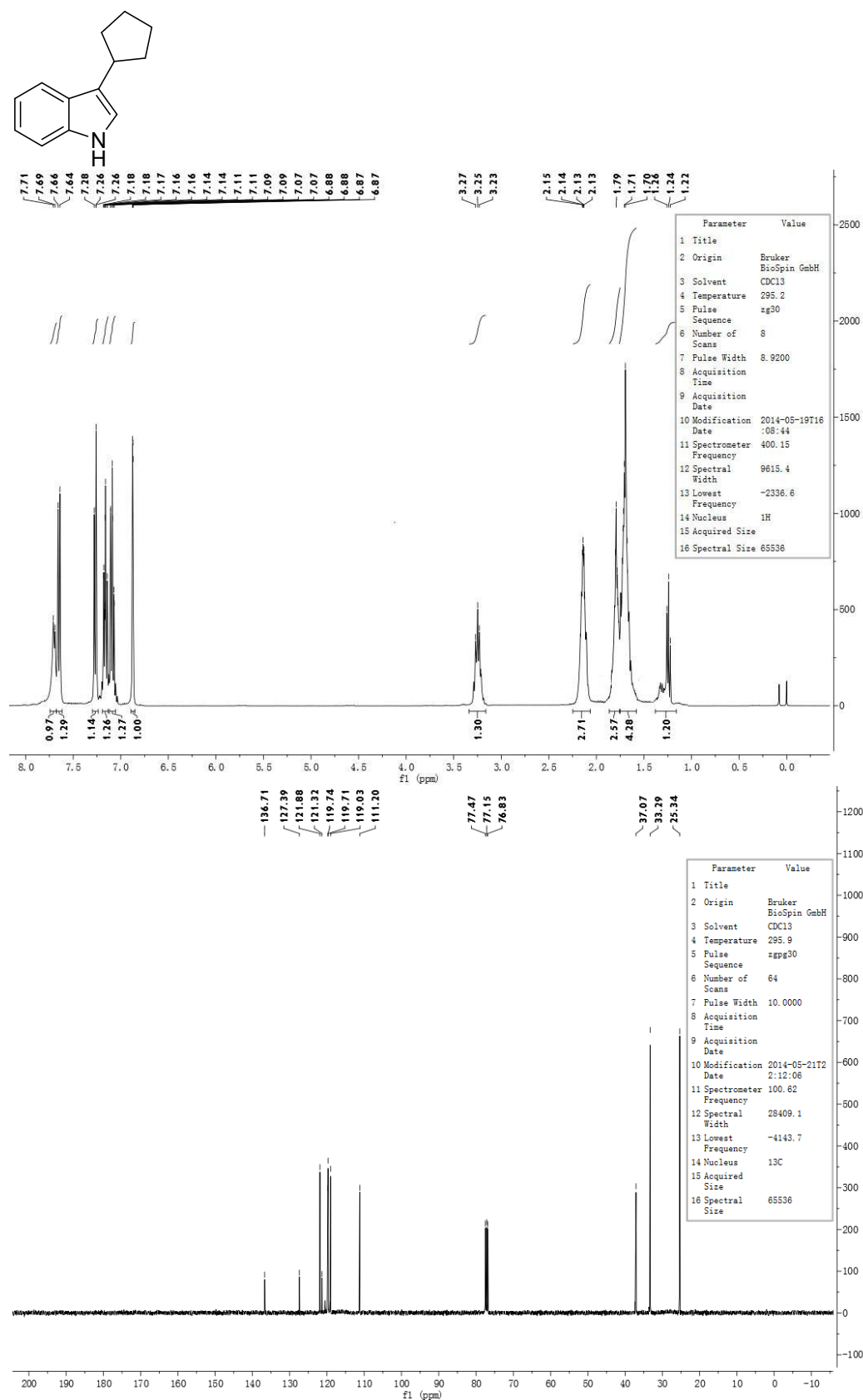
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10 Modification Date	2014-05-19T15:47:24
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15 Acquired Size	32768
16 Spectral Size	65536

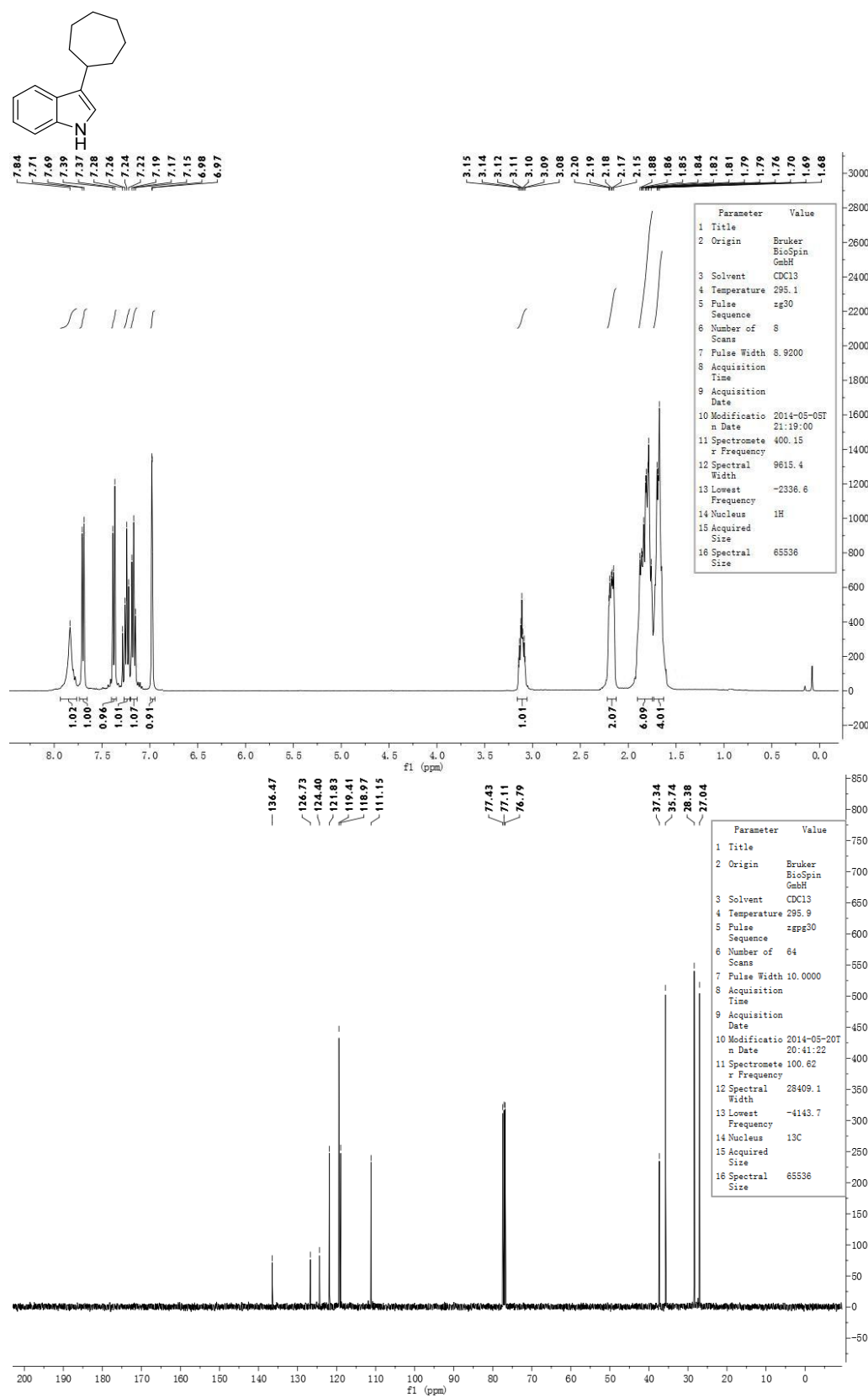


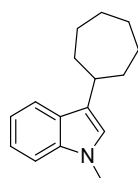
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9 Acquisition Date	2014-05-23T19:00:10
10 Modification Date	2014-05-23T19:00:12
11 Spectrometer Frequency	100.62
12 Spectral Width	28409.1
13 Lowest Frequency	-4143.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536



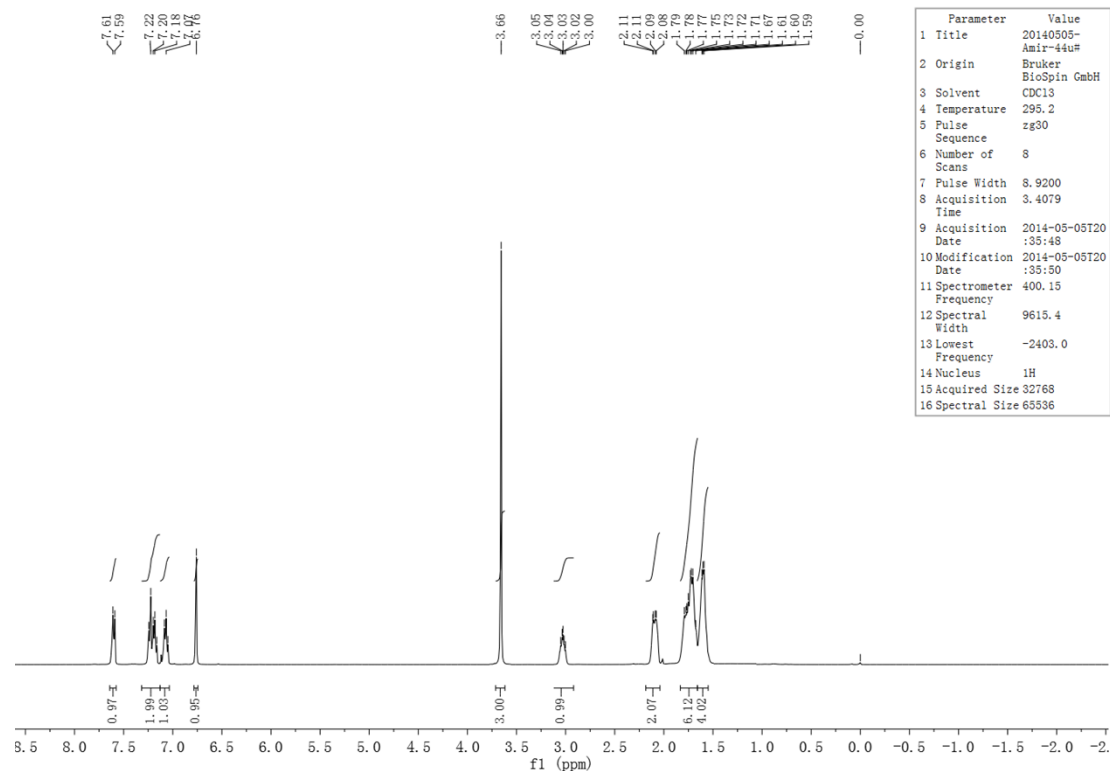




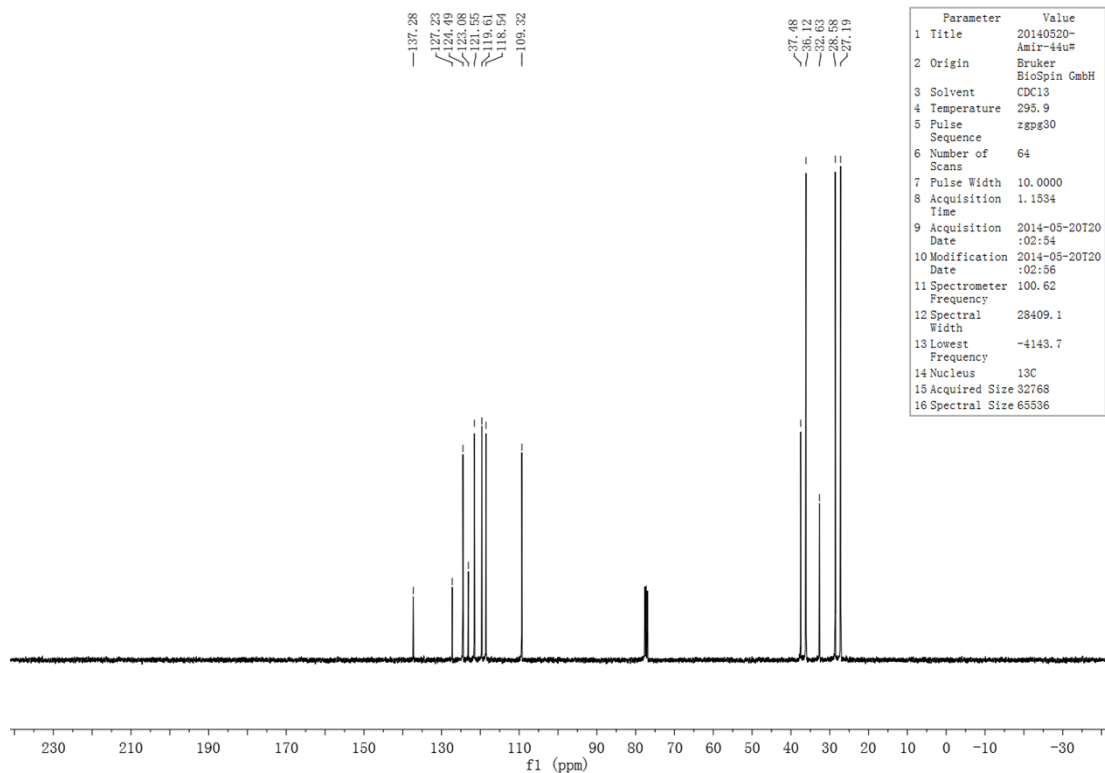




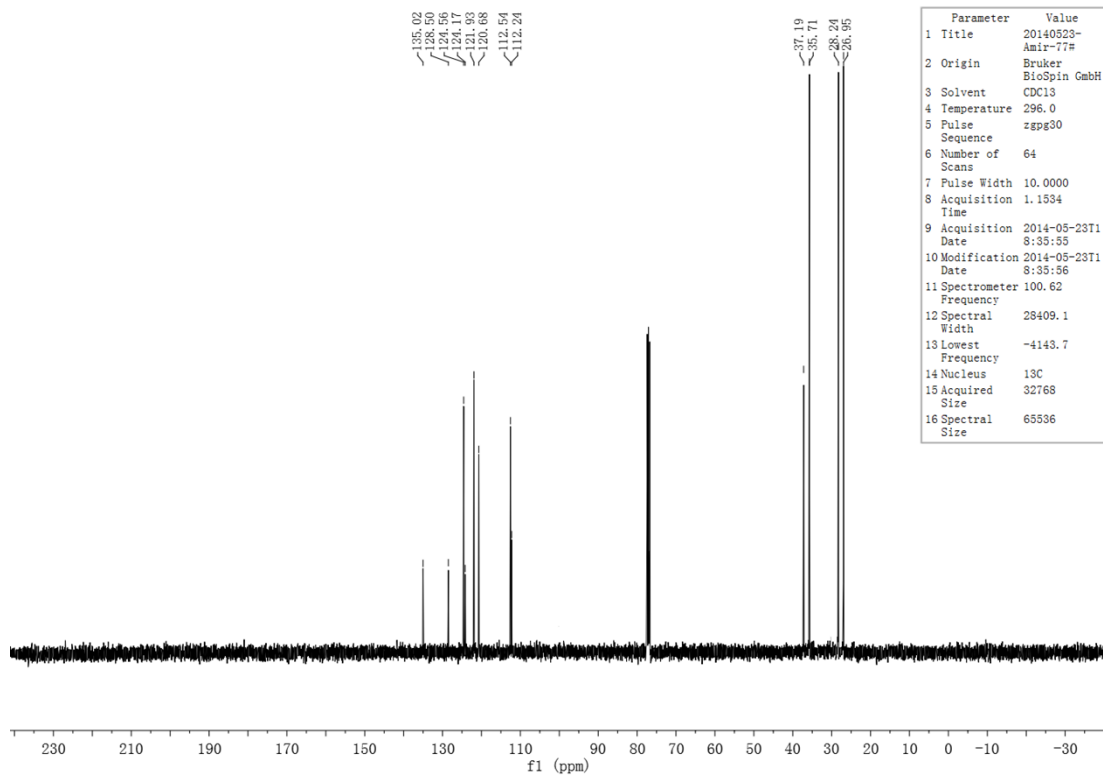
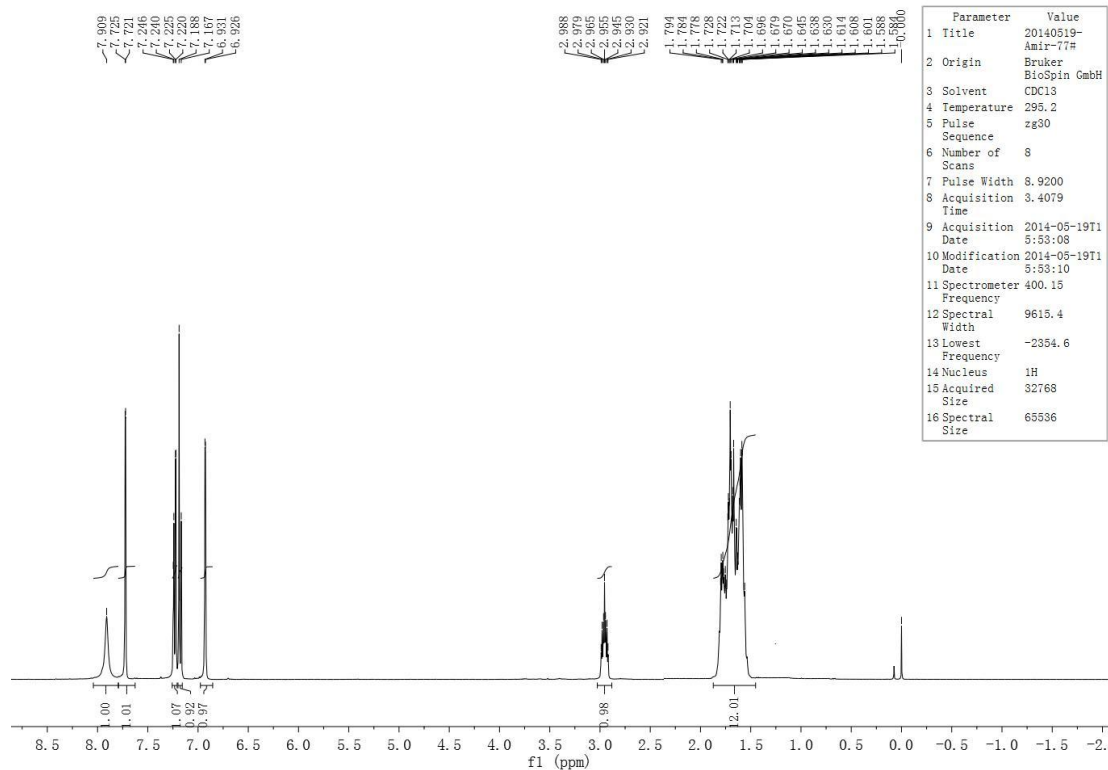
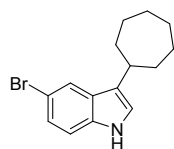
44U

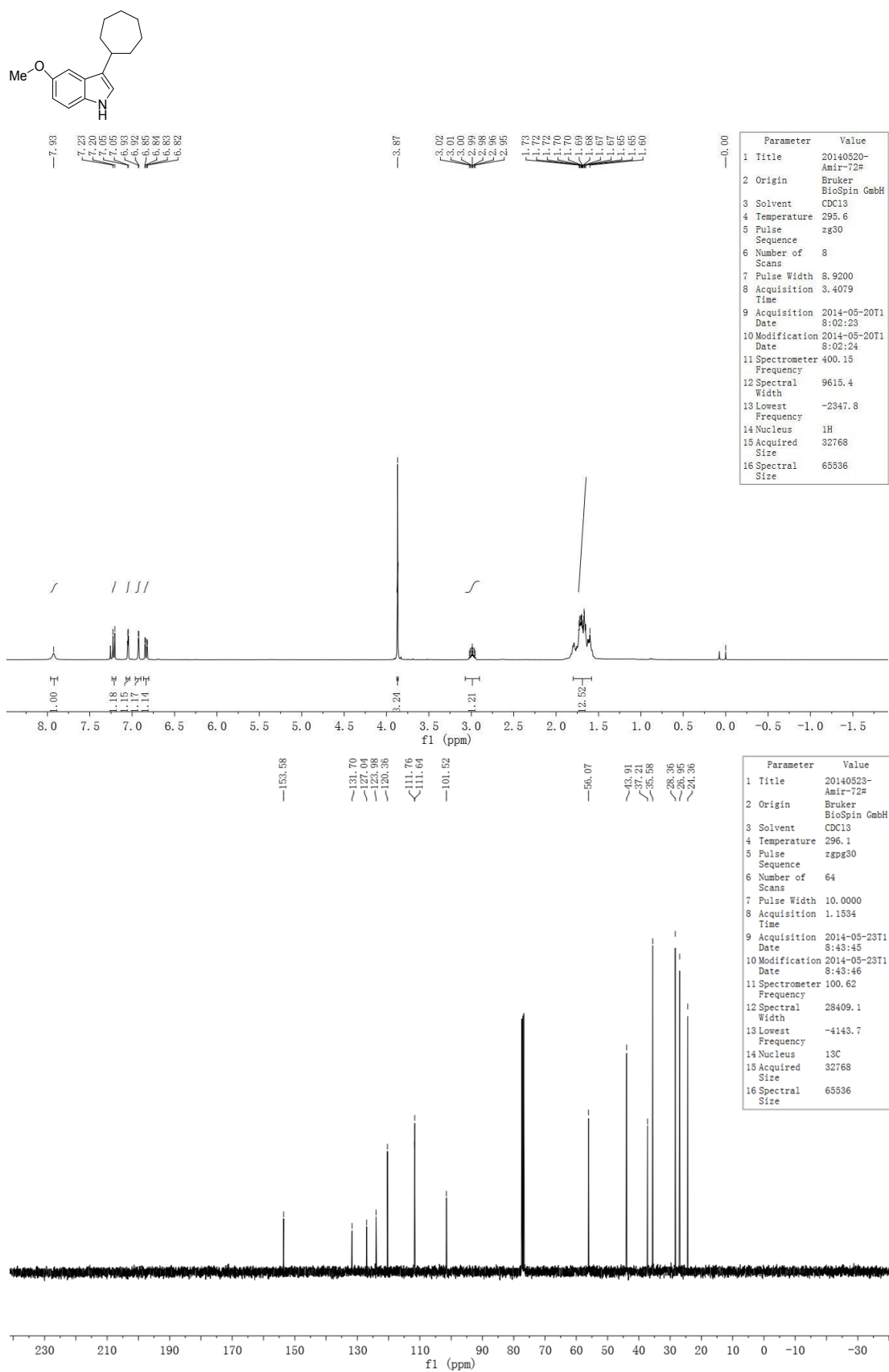


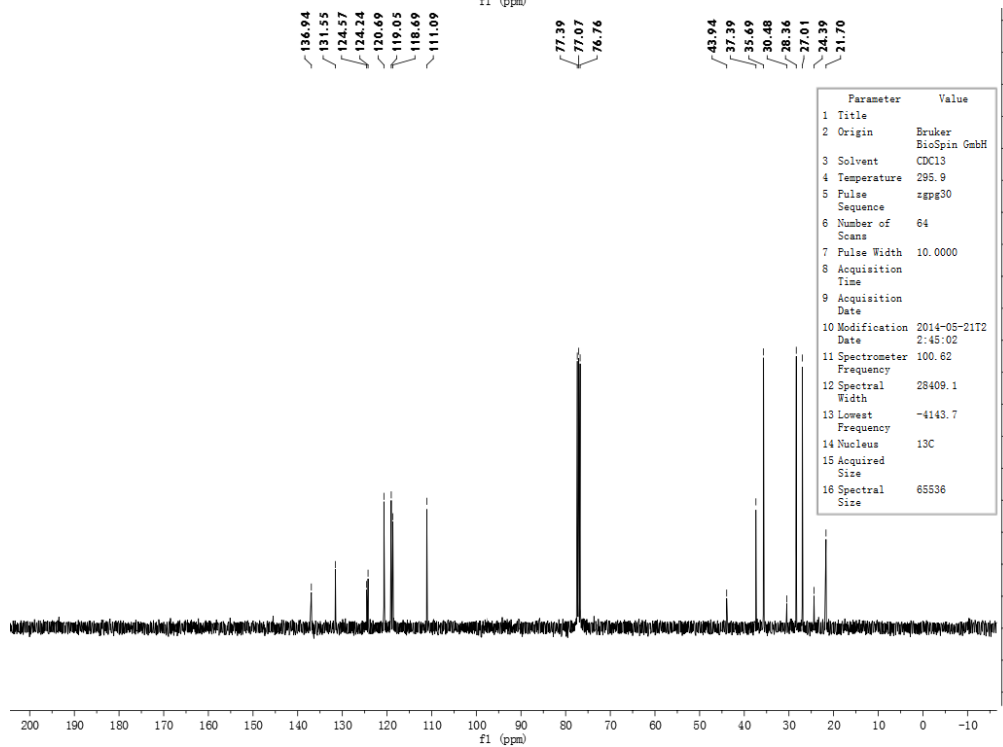
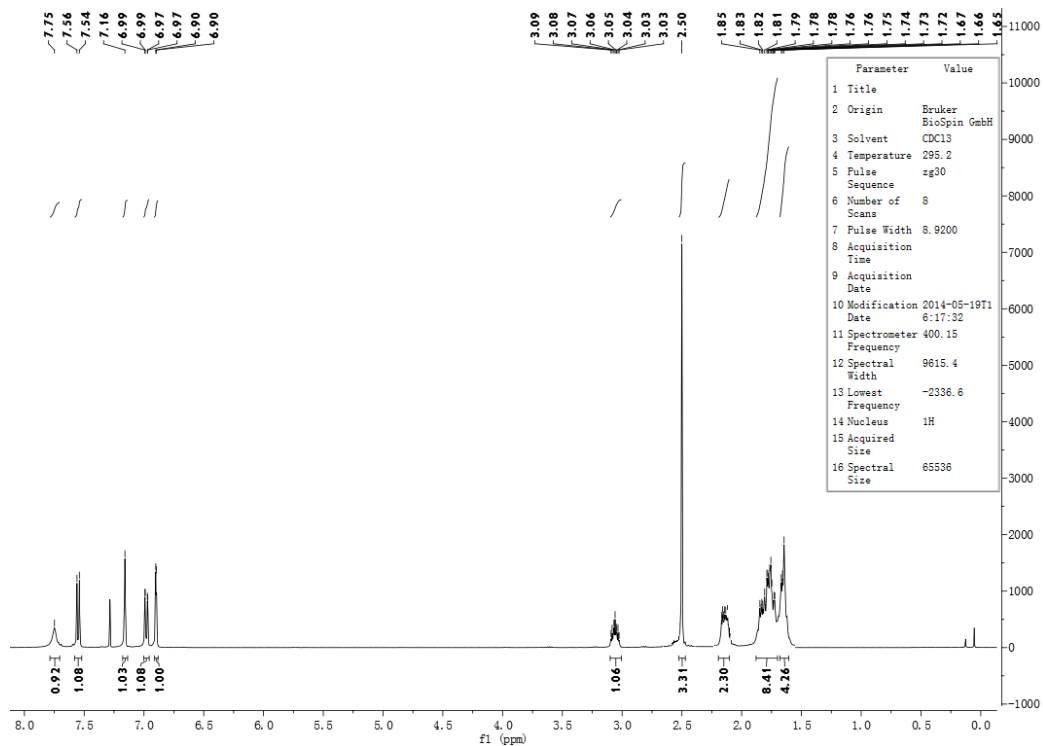
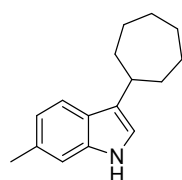
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1 Title	20140505- Amir-44u#
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.2
5 Pulse Sequence	zg30
6 Number of Scans	8
7 Pulse Width	8.9200
8 Acquisition Time	3.4079
9 Acquisition Date	2014-05-05T20 :35:48
10 Modification Date	2014-05-05T20 :35:50
11 Spectrometer Frequency	400.15
12 Spectral Width	9615.4
13 Lowest Frequency	-2403.0
14 Nucleus	¹ H
15 Acquired Size	32768
16 Spectral Size	65536

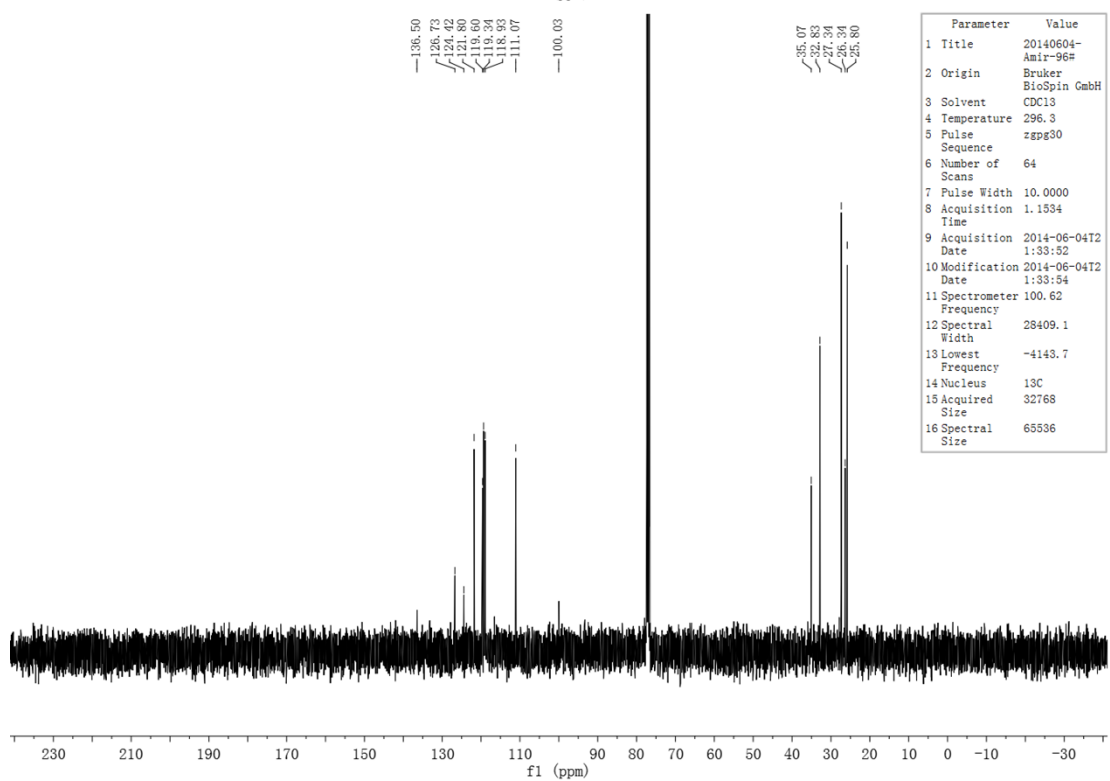
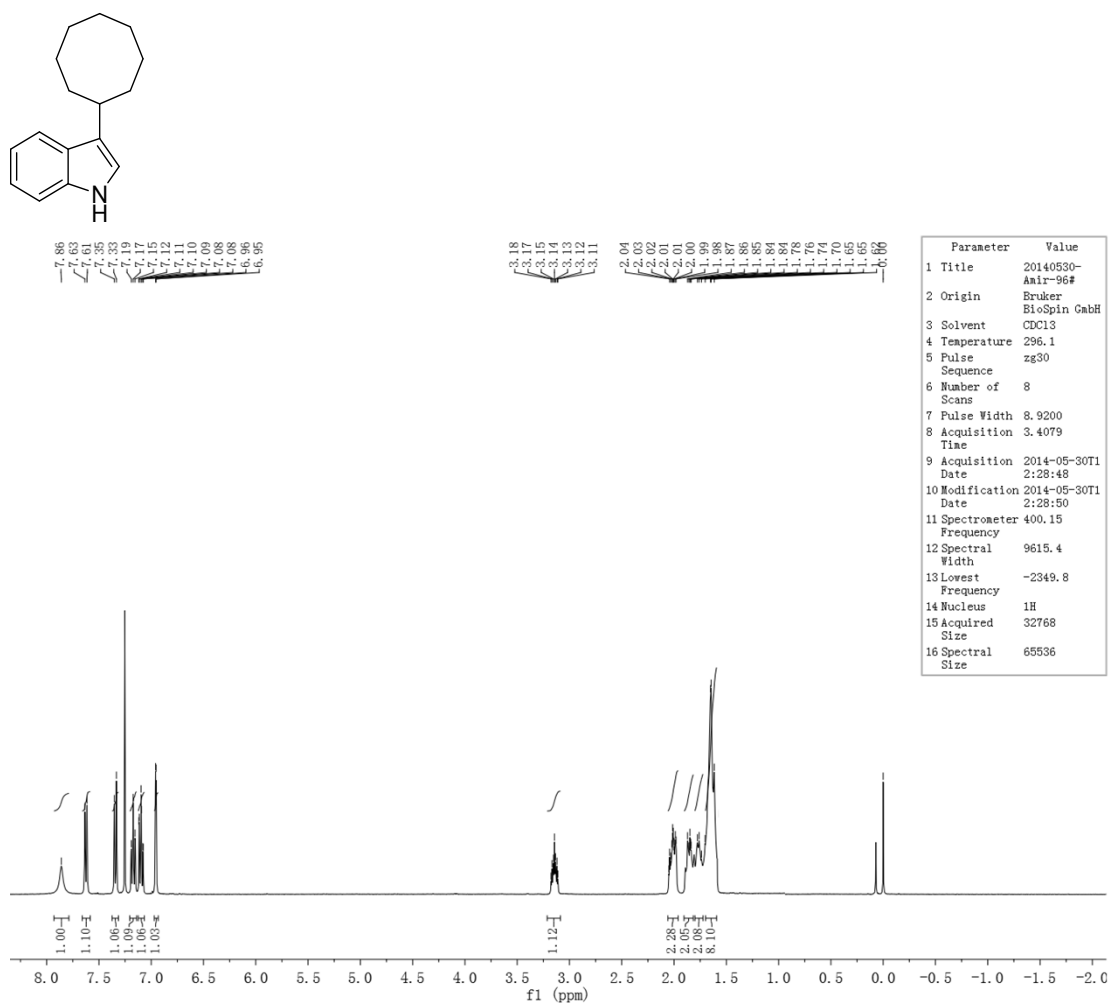


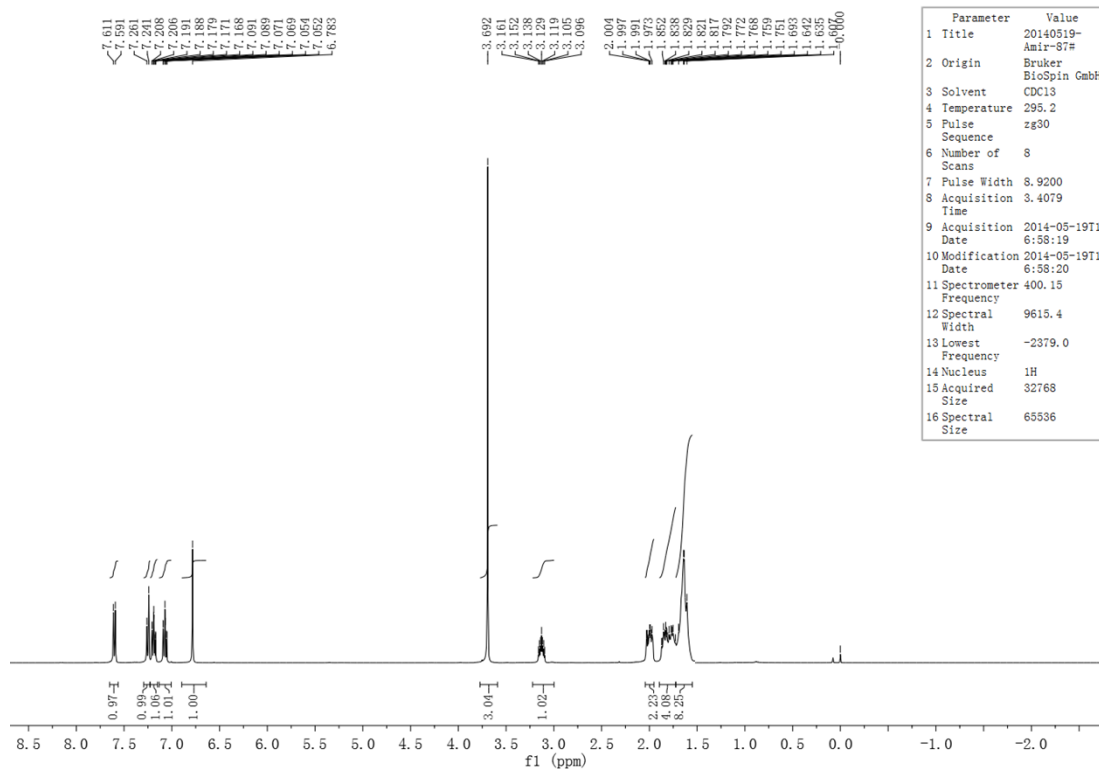
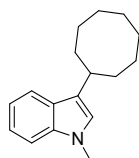
Parameter	Value
1 Title	20140520- Amir-44u#
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.9
5 Pulse Sequence	zgpg30
6 Number of Scans	64
7 Pulse Width	10.0000
8 Acquisition Time	1.1534
9 Acquisition Date	2014-05-20T20 :02:54
10 Modification Date	2014-05-20T20 :02:56
11 Spectrometer Frequency	100.62
12 Spectral Width	28409.1
13 Lowest Frequency	-4143.7
14 Nucleus	¹³ C
15 Acquired Size	32768
16 Spectral Size	65536



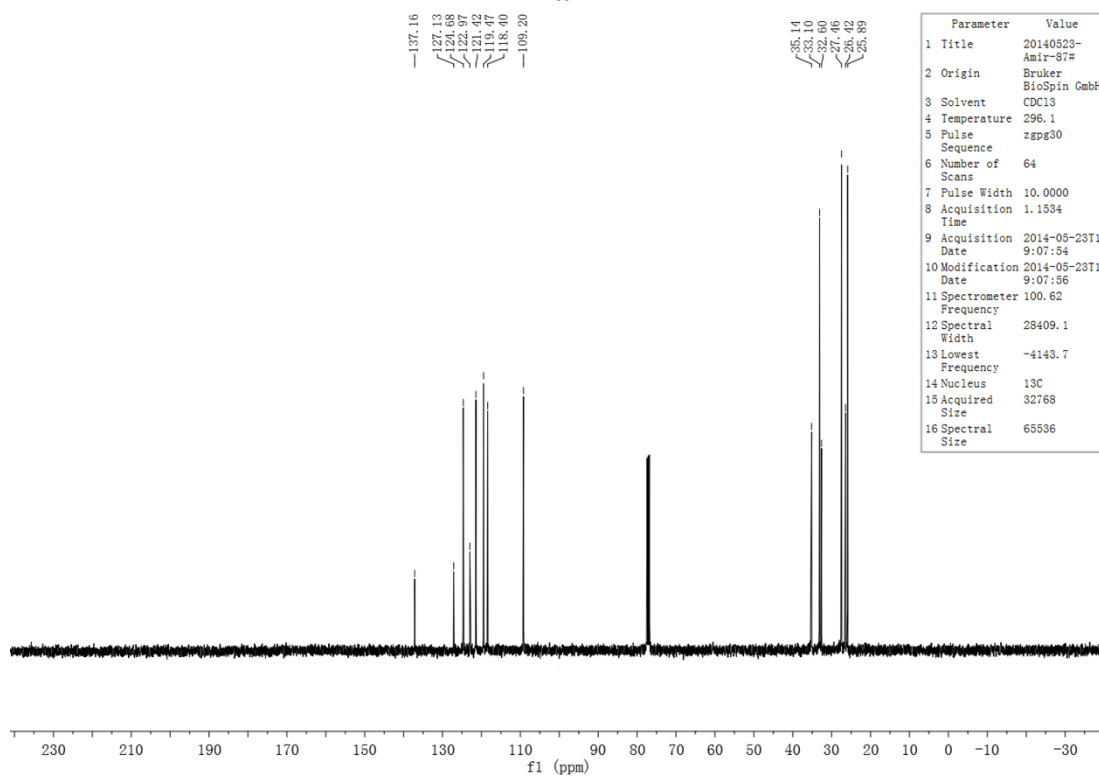




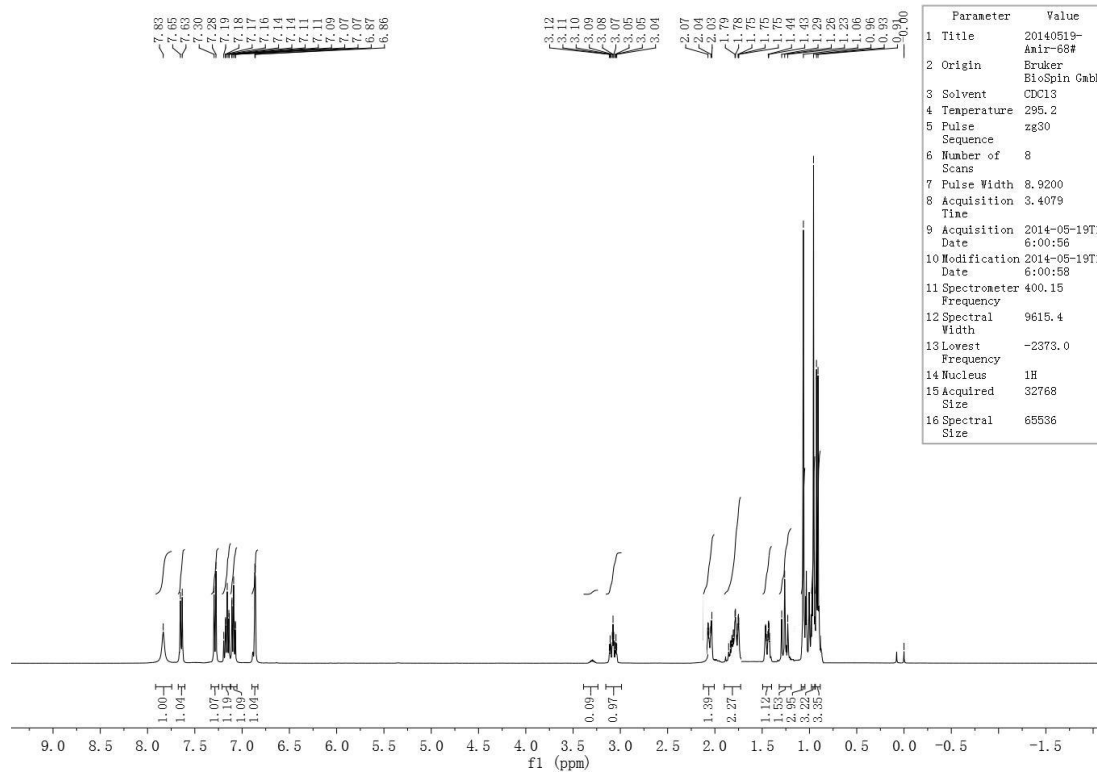
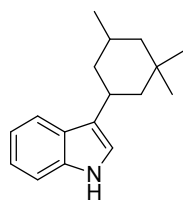




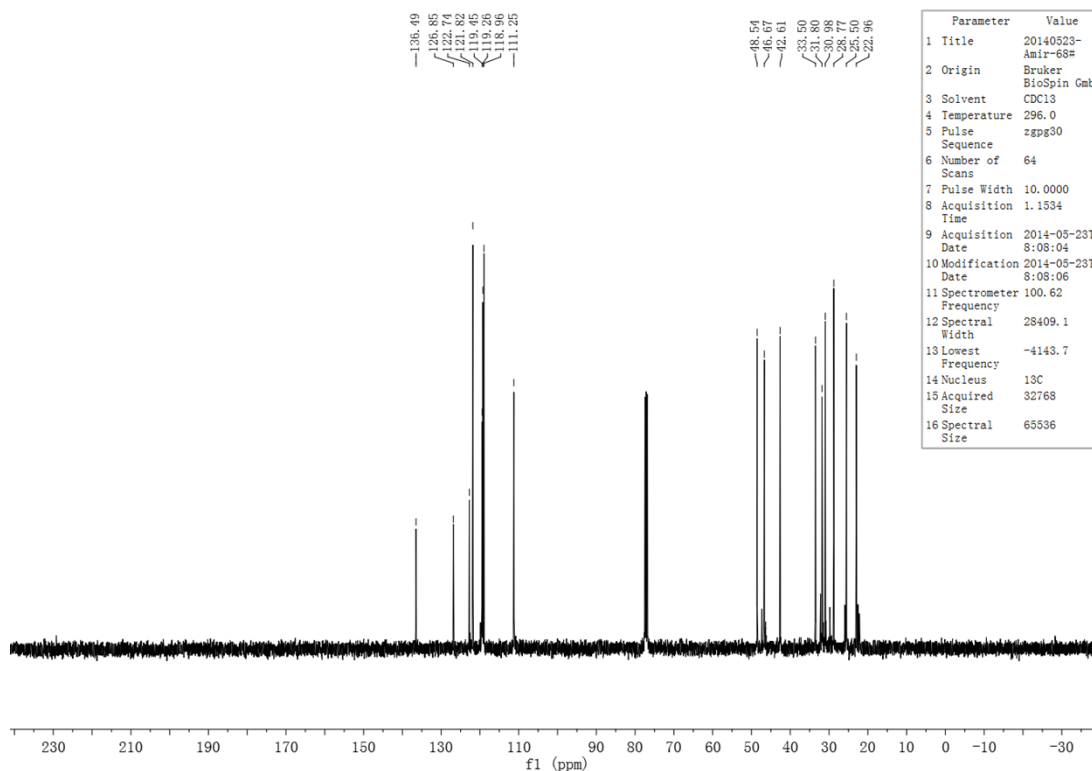
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1 Title	20140519-Amir-87#
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	295.2
5 Pulse Sequence	zg30
6 Number of Scans	8
7 Pulse Width	8.9200
8 Acquisition Time	3.4079
9 Acquisition Date	2014-05-19T16:58:19
10 Modification Date	2014-05-19T16:58:20
11 Spectrometer	400.15
12 Spectral Width	9615.4
13 Lowest Frequency	-2379.0
14 Nucleus	¹ H
15 Acquired Size	32768
16 Spectral Size	65536



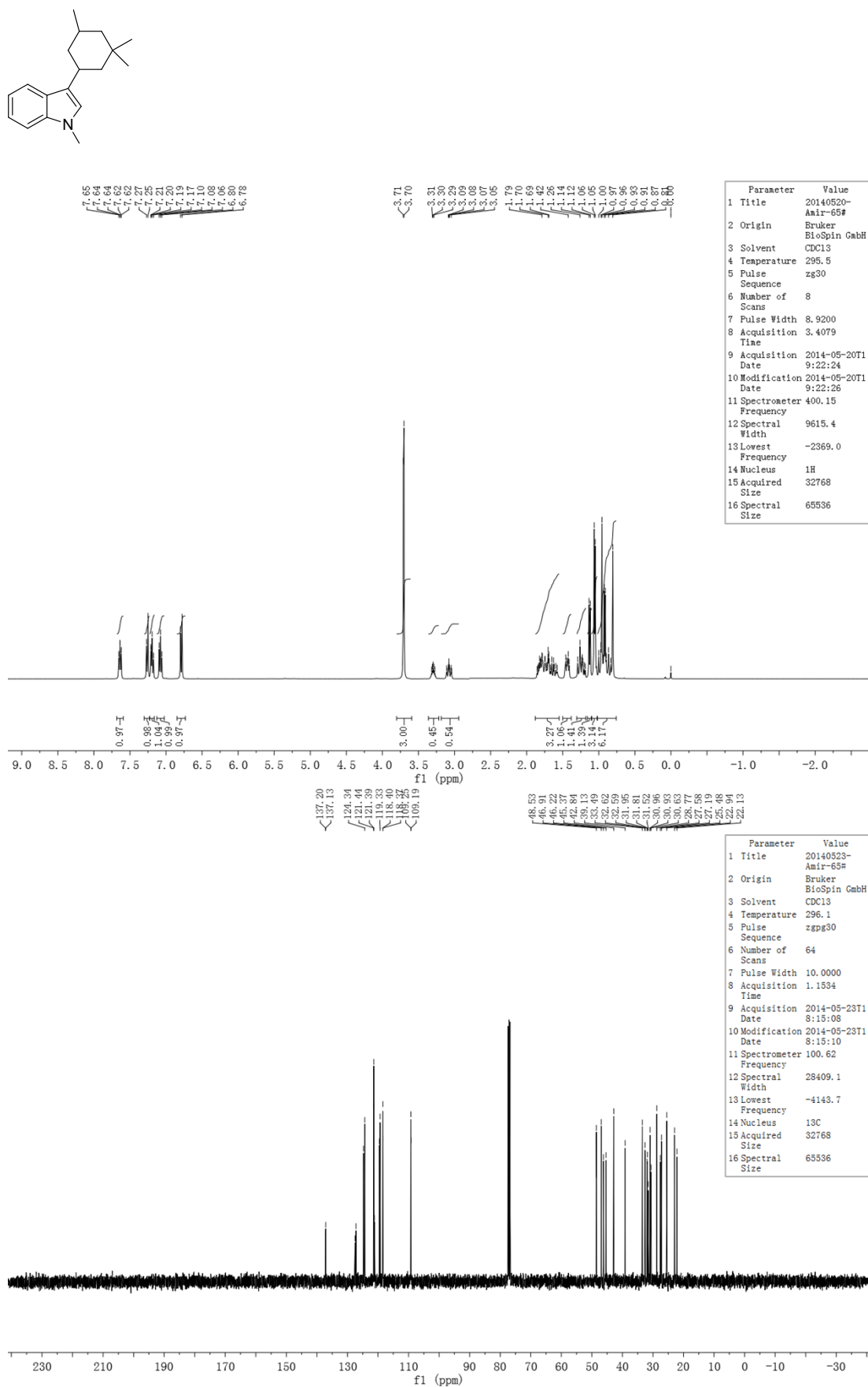
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1 Title	20140523-Amir-87#
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Number of Scans	64
7 Pulse Width	10.0000
8 Acquisition Time	1.1534
9 Acquisition Date	2014-05-23T19:07:54
10 Modification Date	2014-05-23T19:07:56
11 Spectrometer	100.62
12 Spectral Width	28409.1
13 Lowest Frequency	-4143.7
14 Nucleus	¹³ C
15 Acquired Size	32768
16 Spectral Size	65536

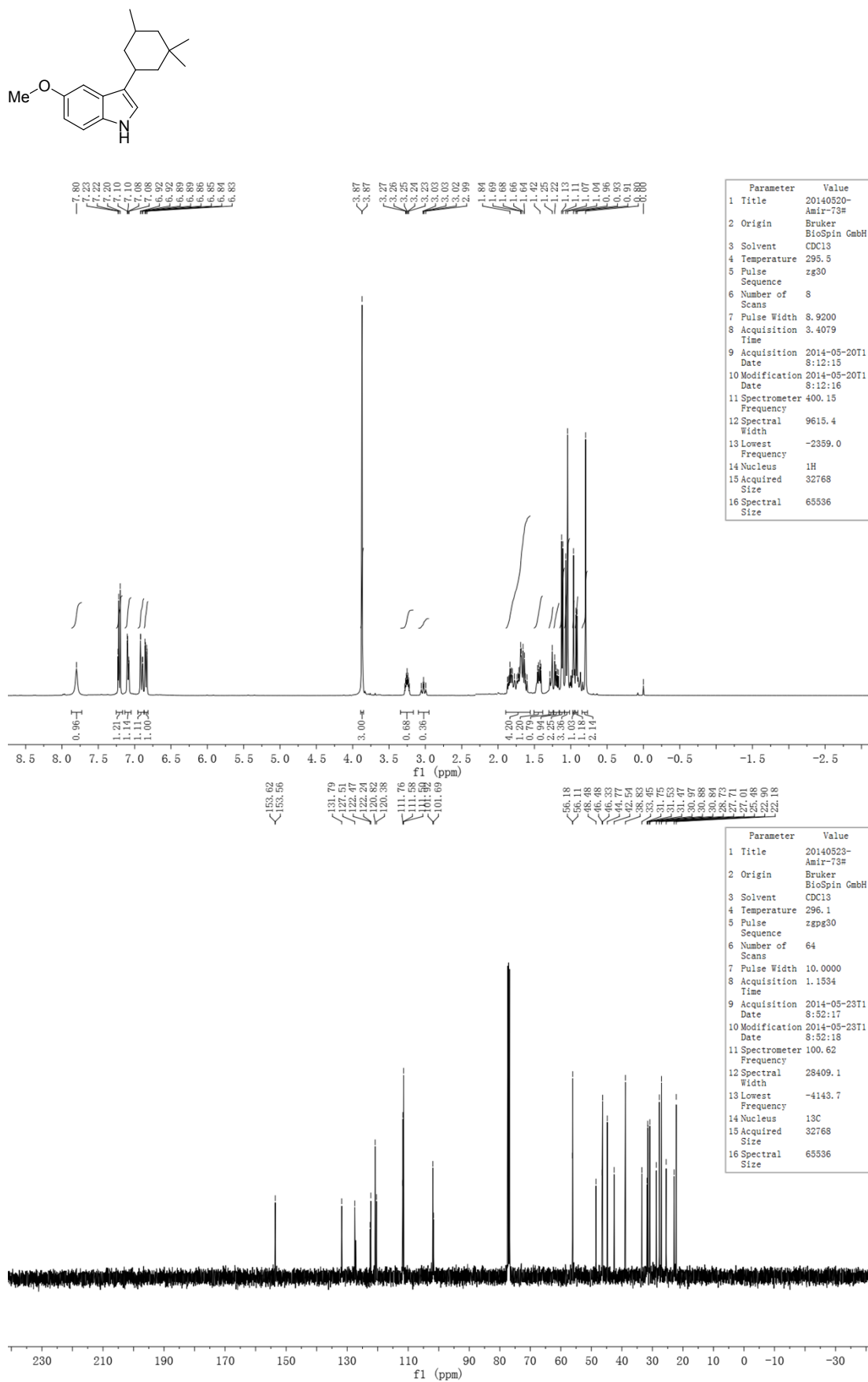


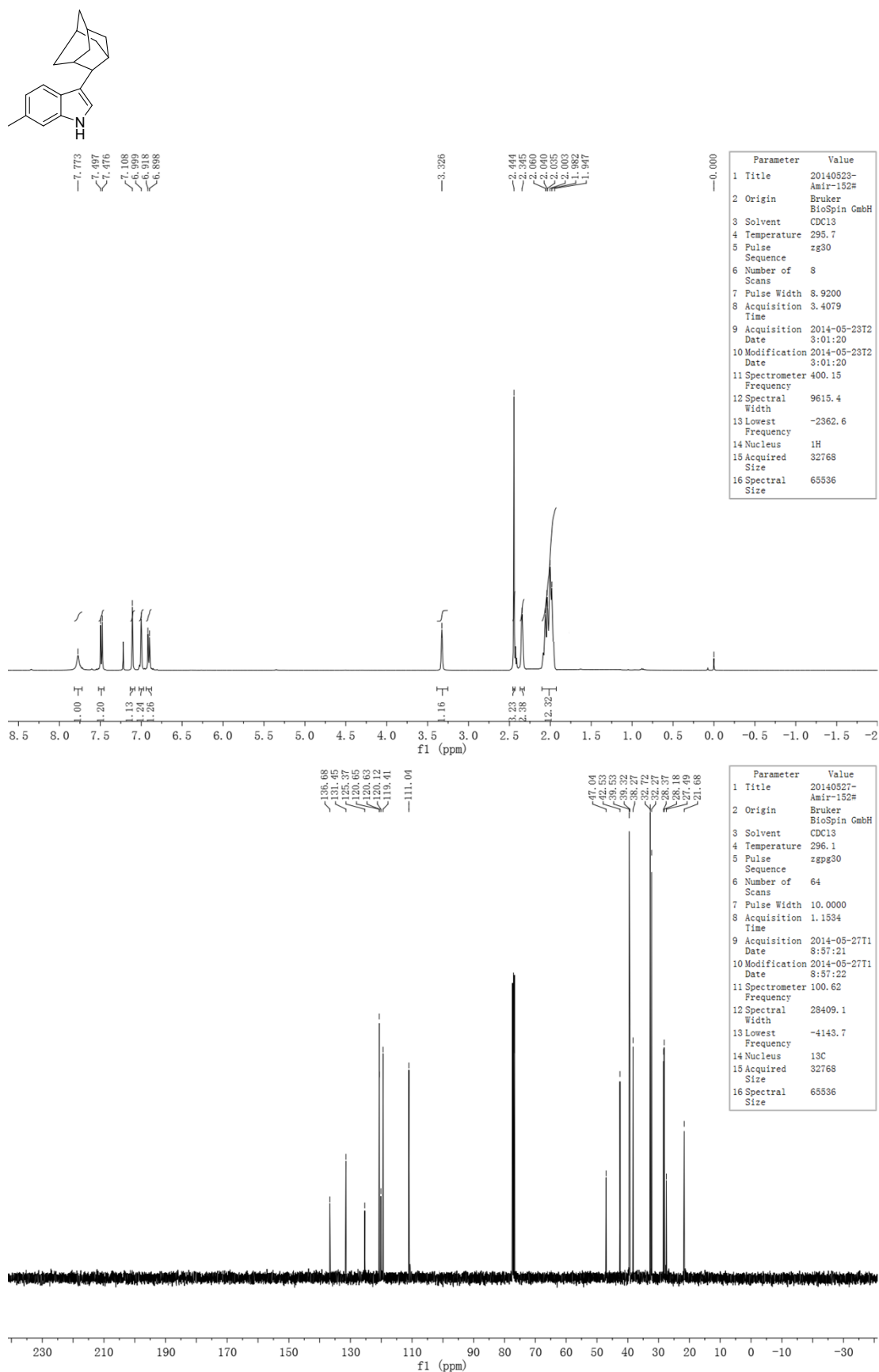
Parameter	Value
1 Title	20140519-Amir-68#
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.2
5 Pulse Sequence	zg30
6 Number of Scans	8
7 Pulse Width	8.9200
8 Acquisition Time	3.4079
9 Acquisition Date	2014-05-19T16:00:56
10 Modification Date	2014-05-19T16:00:58
11 Spectrometer Frequency	400.15
12 Spectral Width	9615.4
13 Lowest Frequency	-2373.0
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

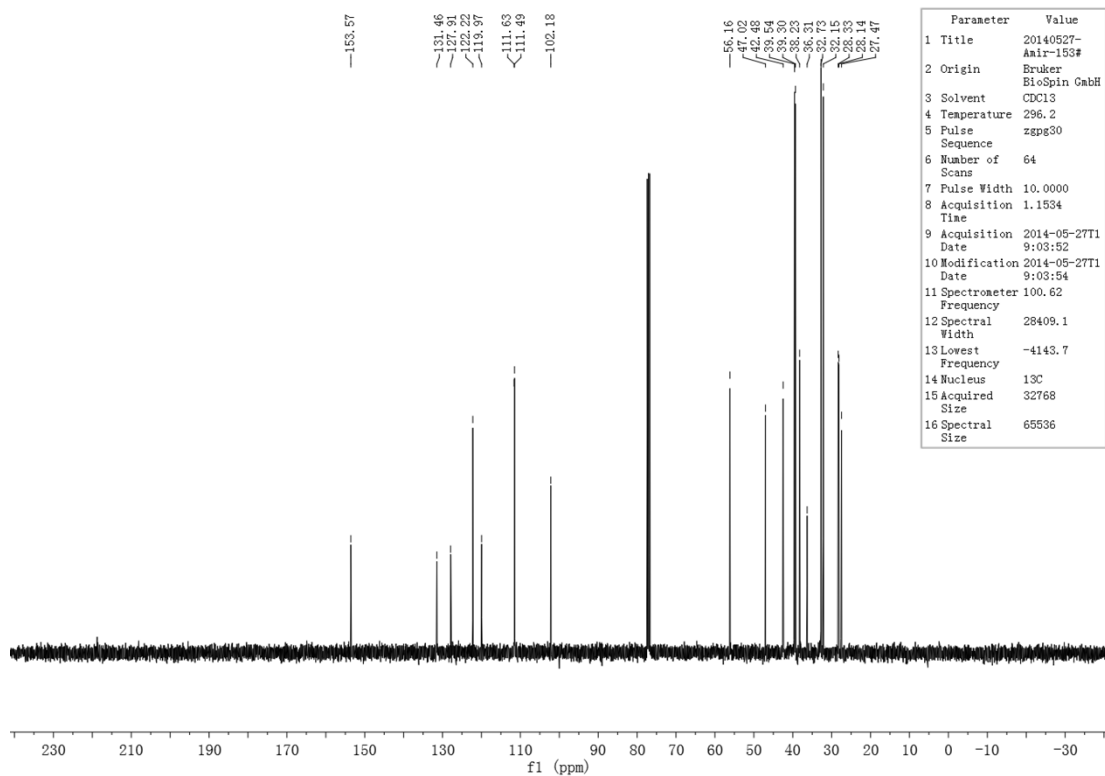
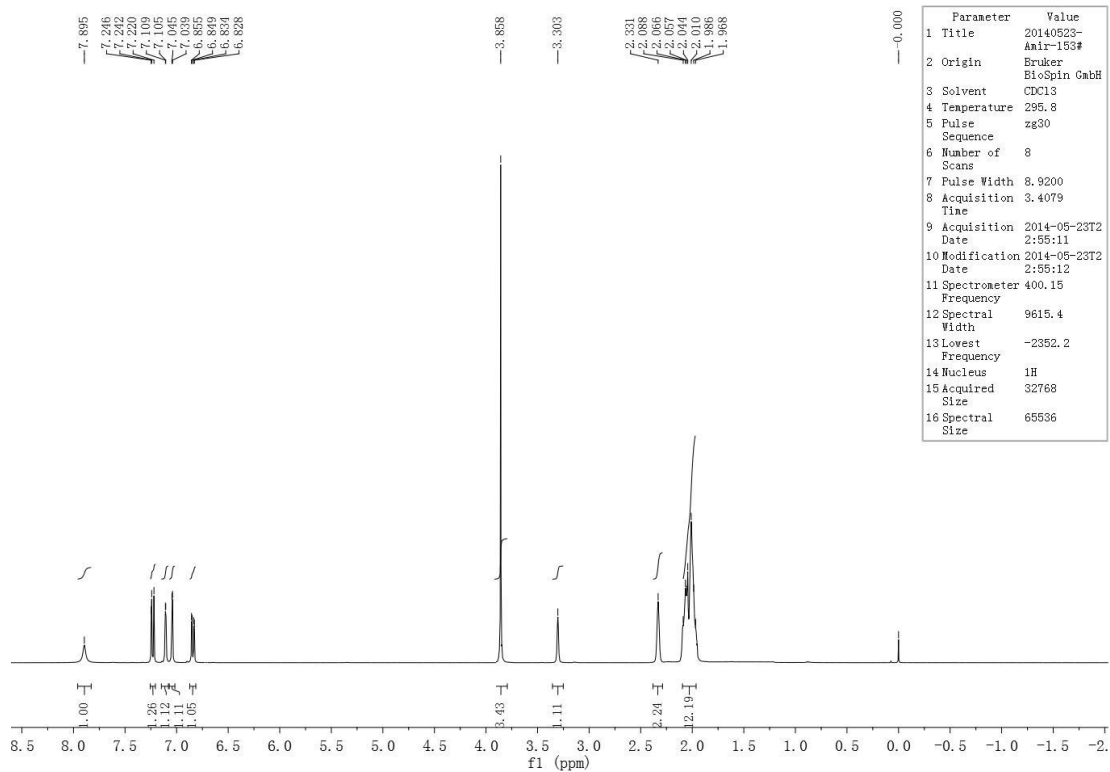


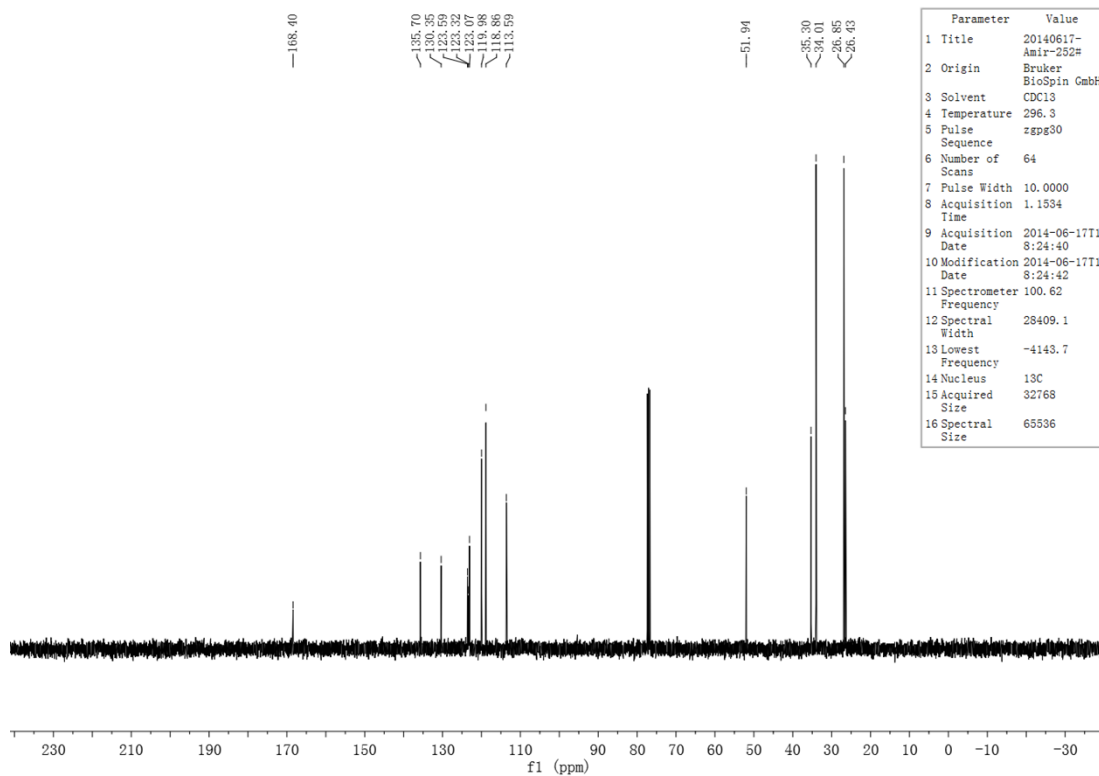
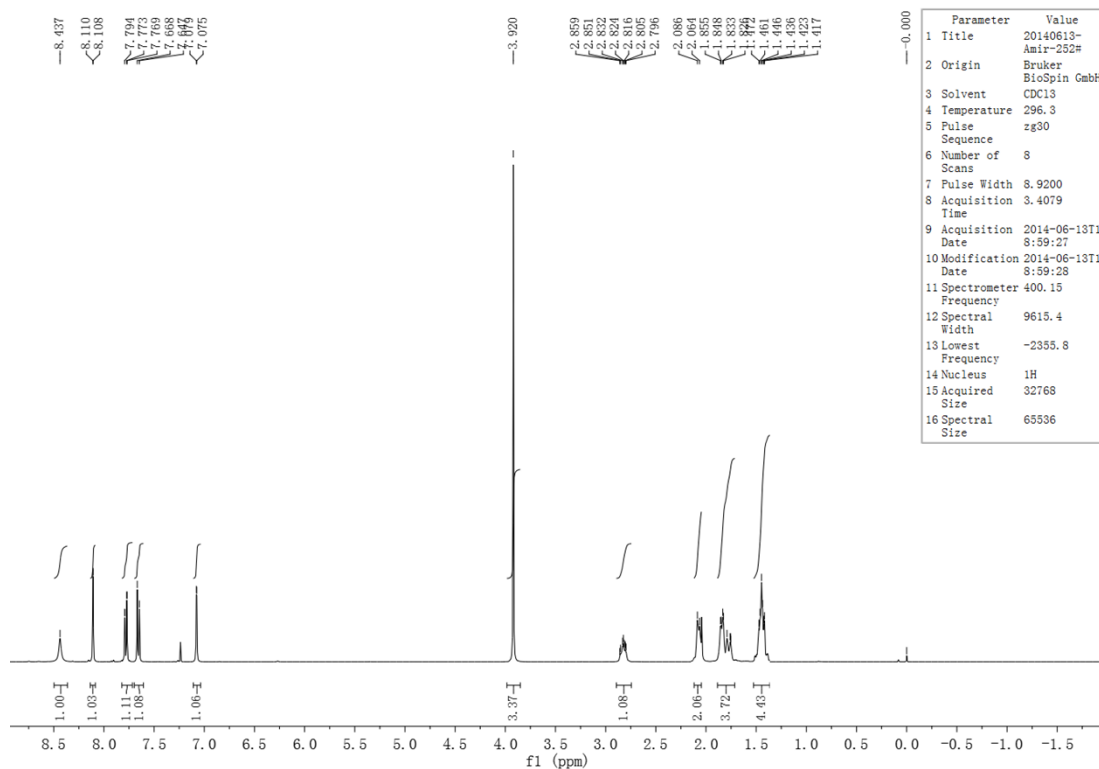
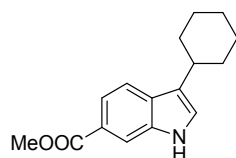
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1 Title	20140523-Amir-68#
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.0
5 Pulse Sequence	zgpg30
6 Number of Scans	64
7 Pulse Width	10.0000
8 Acquisition Time	1.1534
9 Acquisition Date	2014-05-23T18:08:04
10 Modification Date	2014-05-23T18:08:06
11 Spectrometer Frequency	100.62
12 Spectral Width	28409.1
13 Lowest Frequency	-4143.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

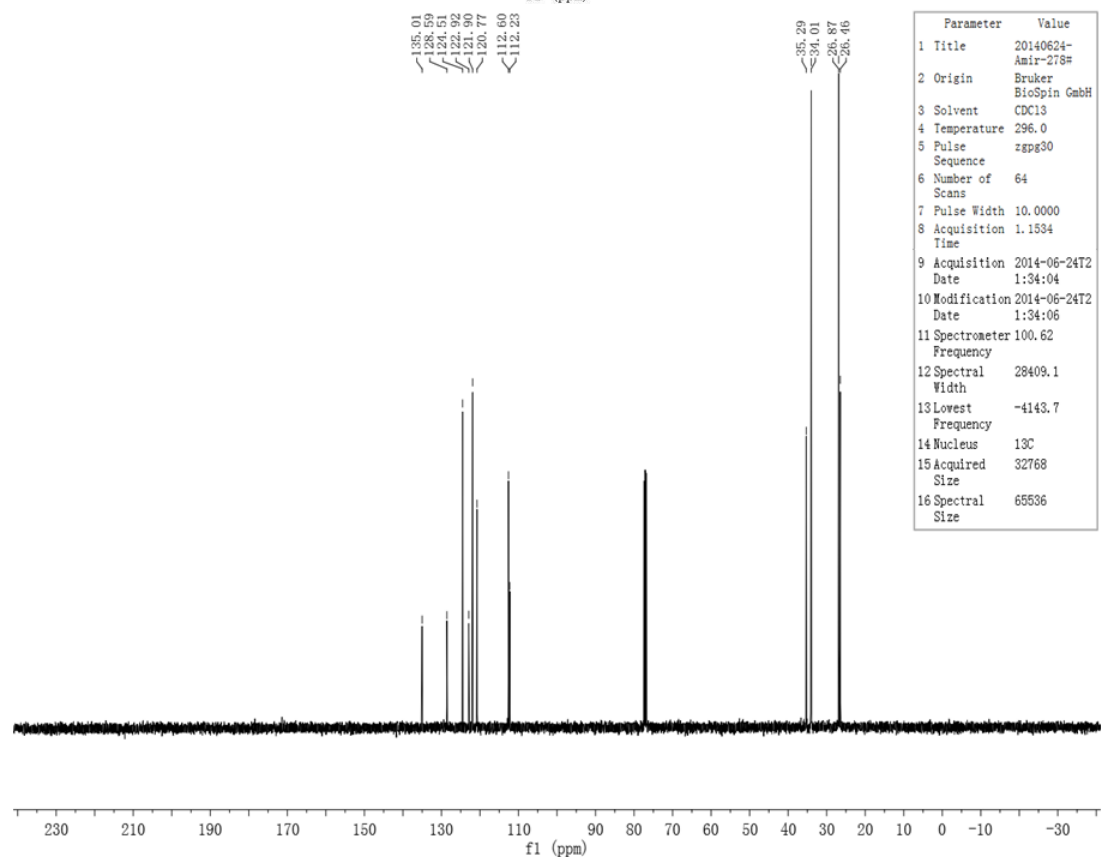
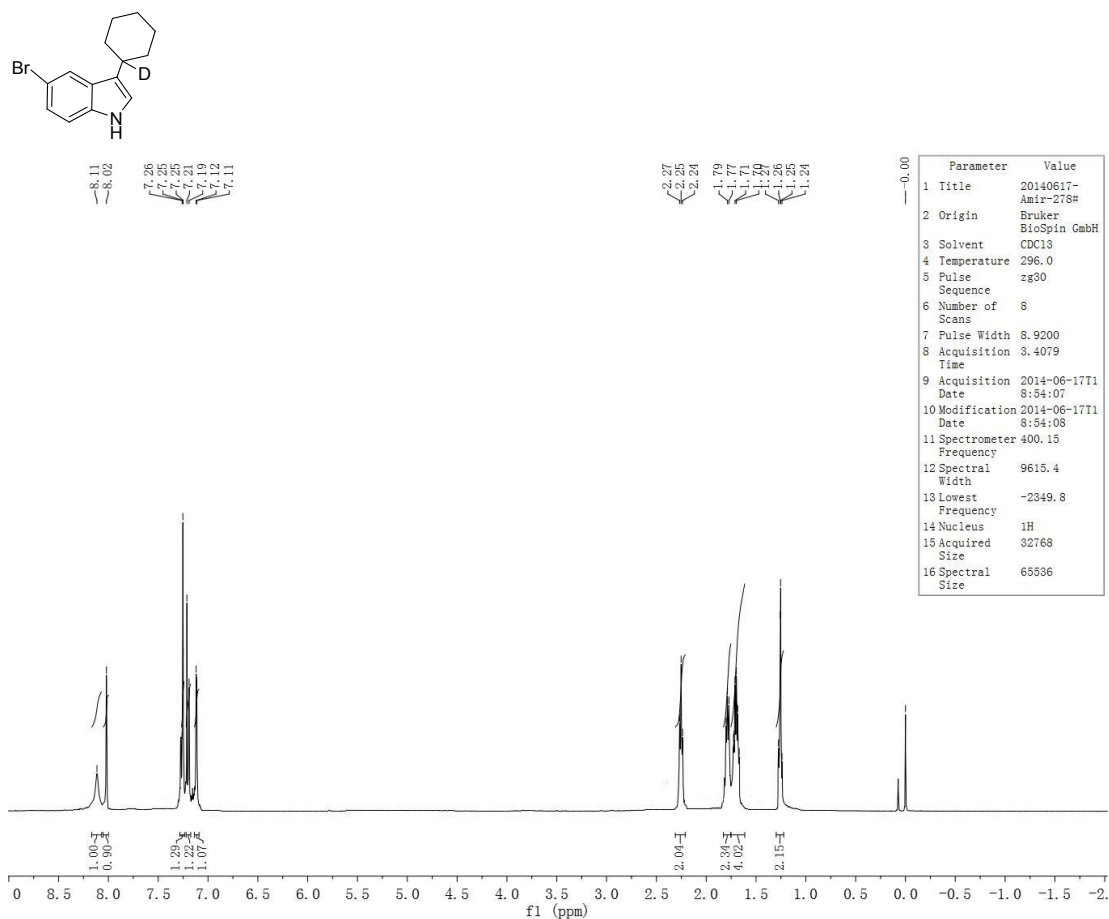


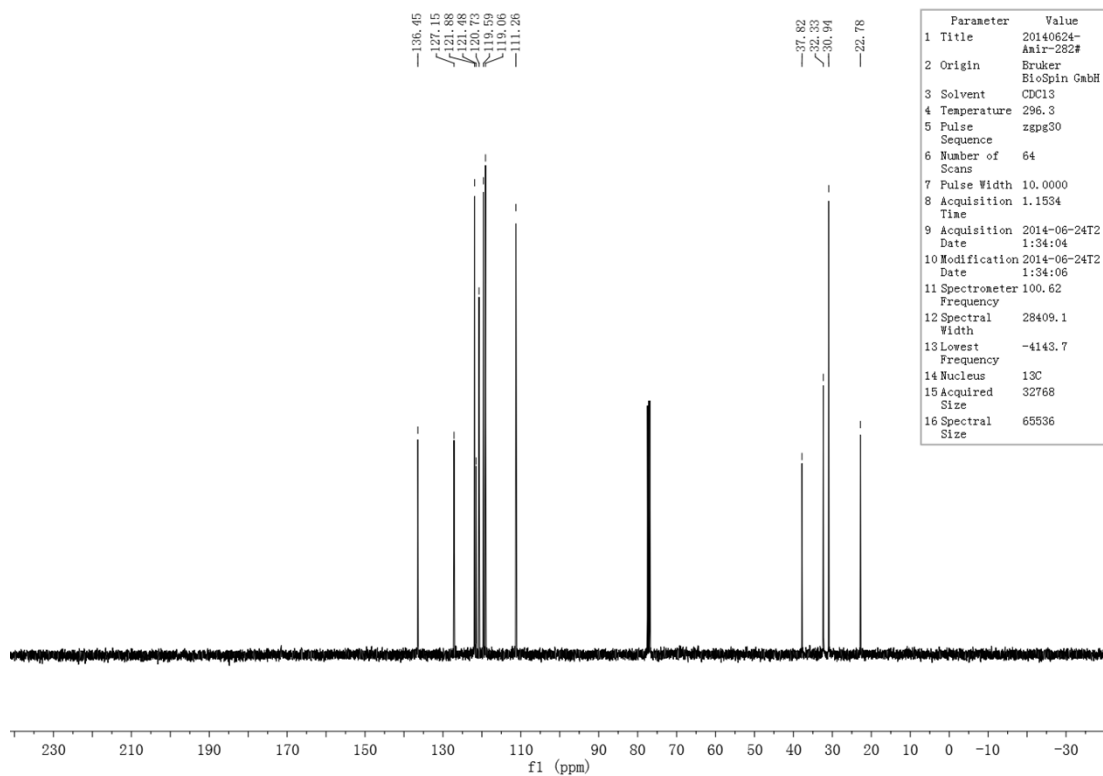
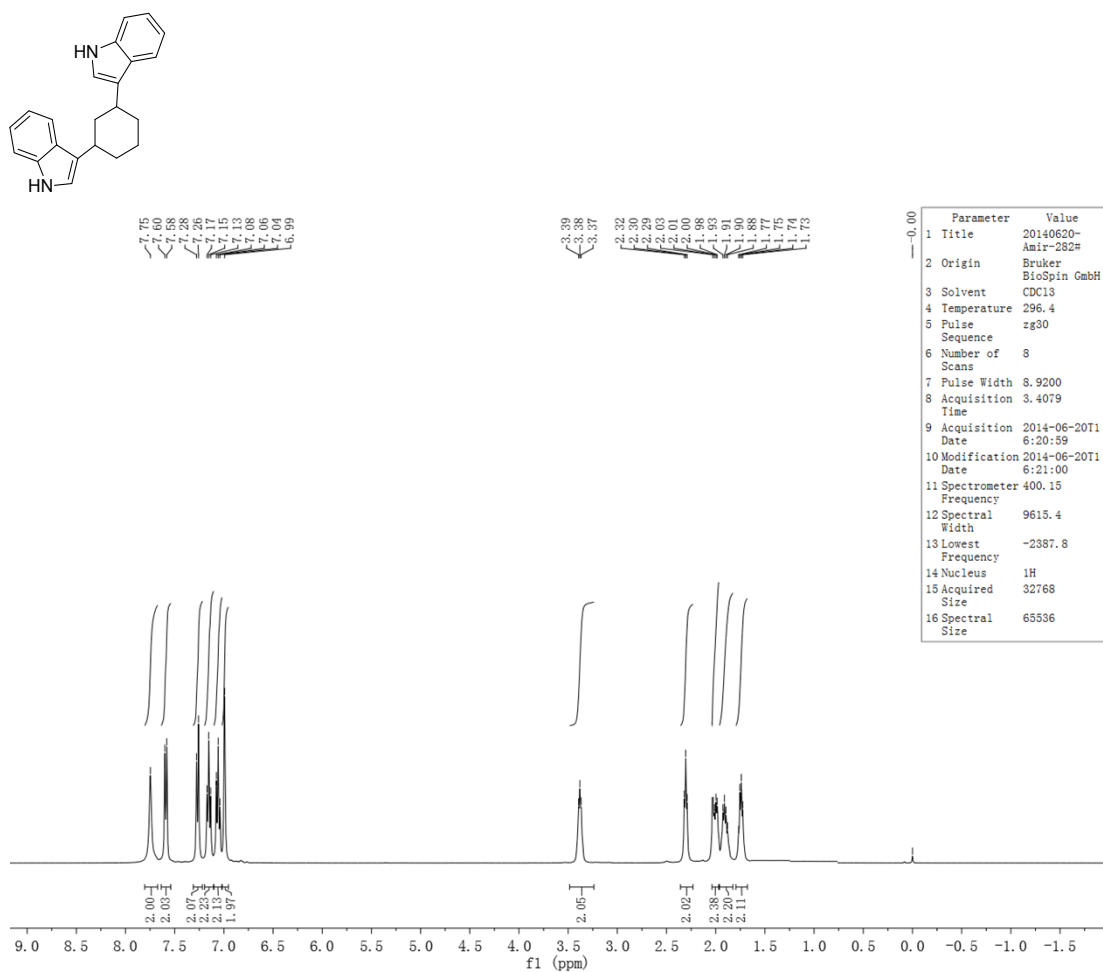


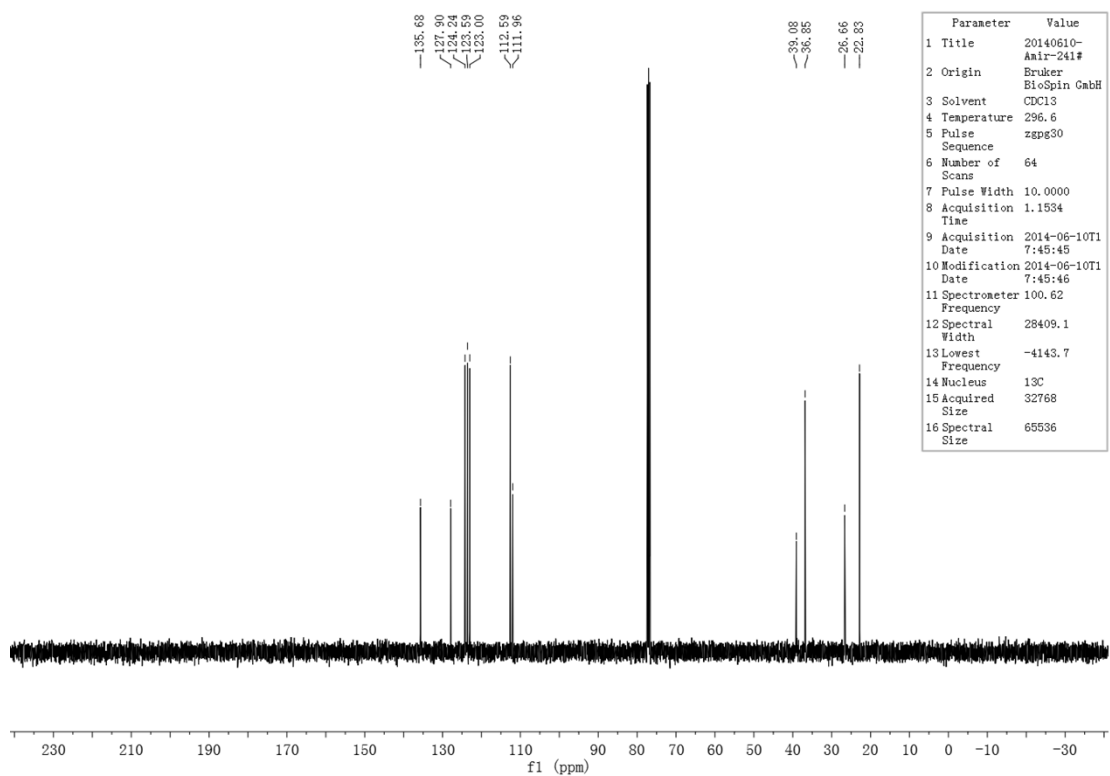
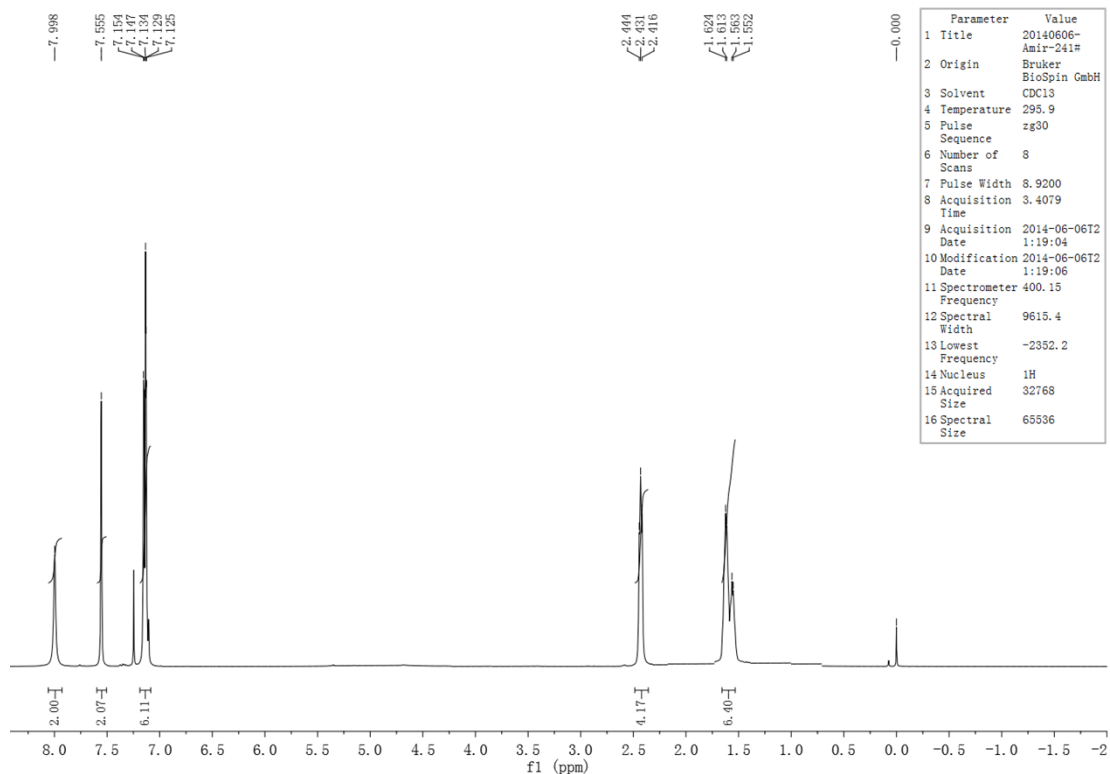
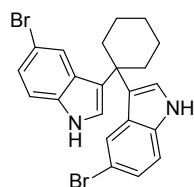


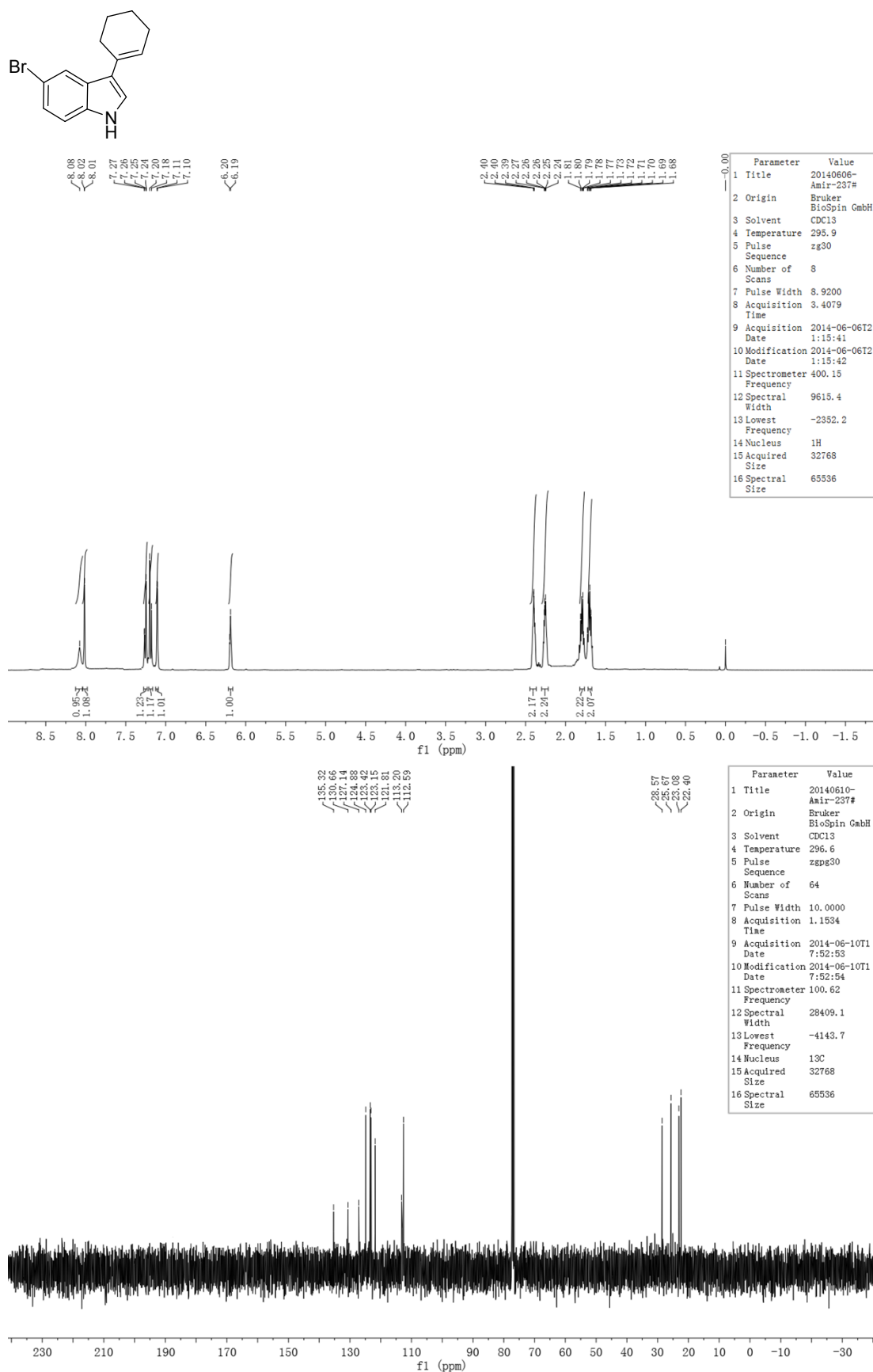


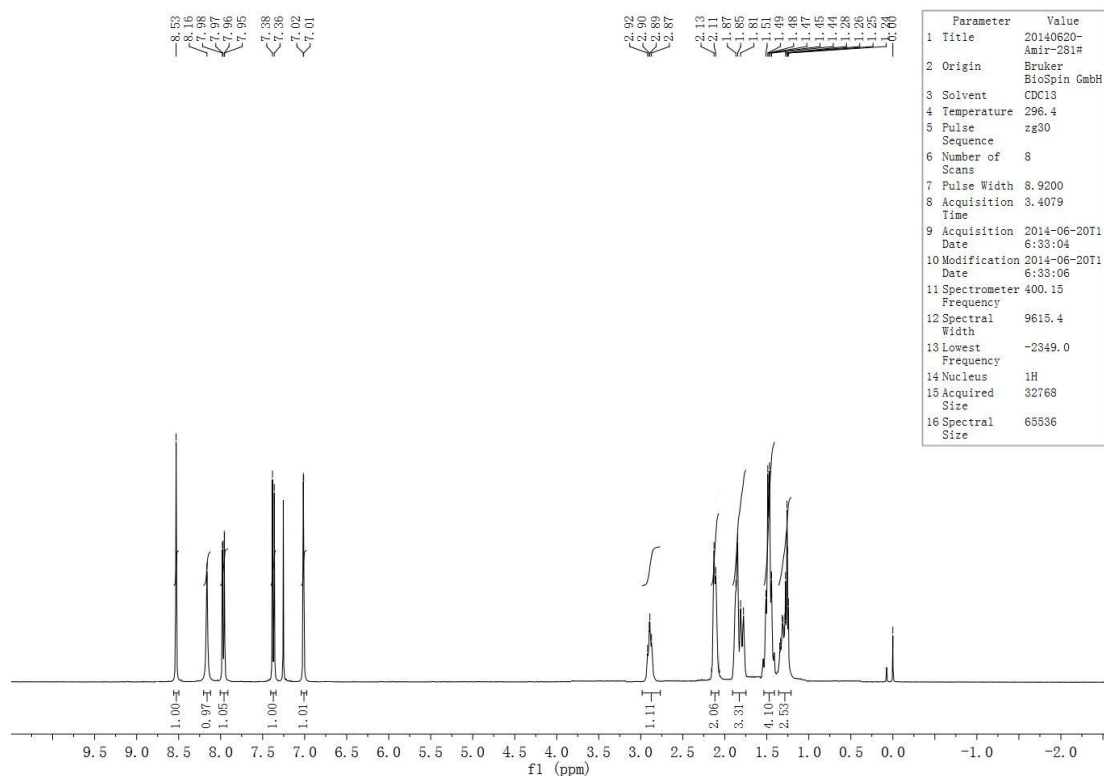
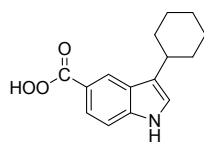




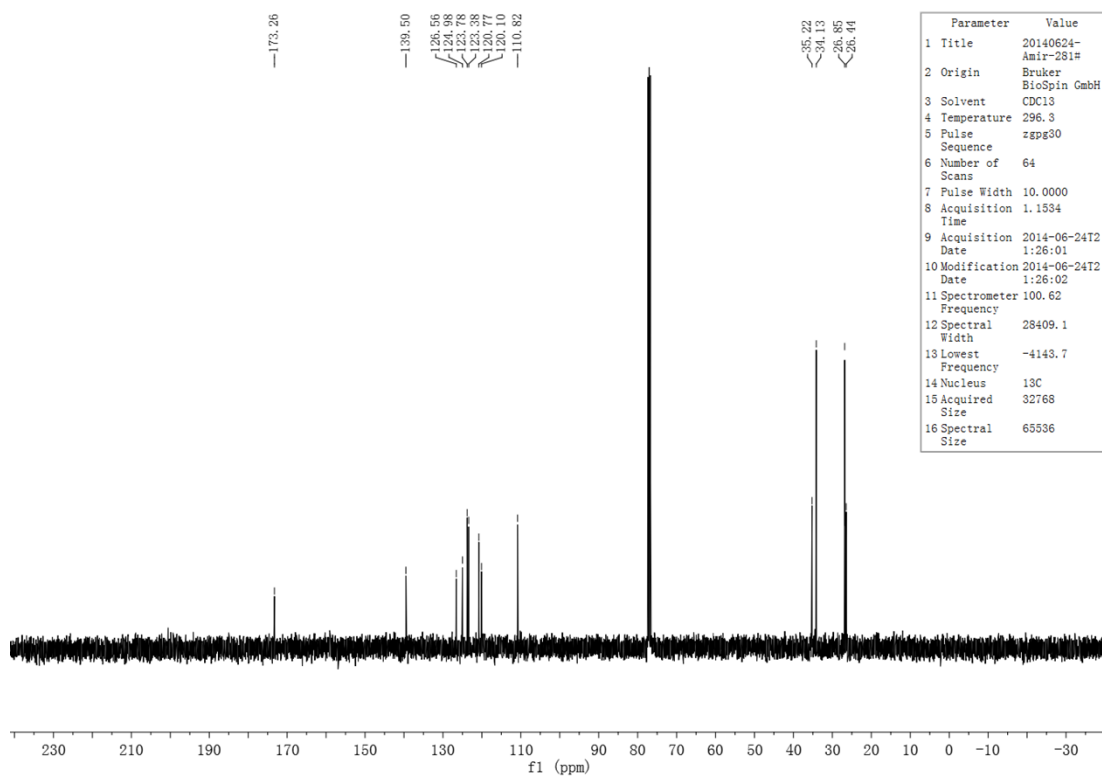






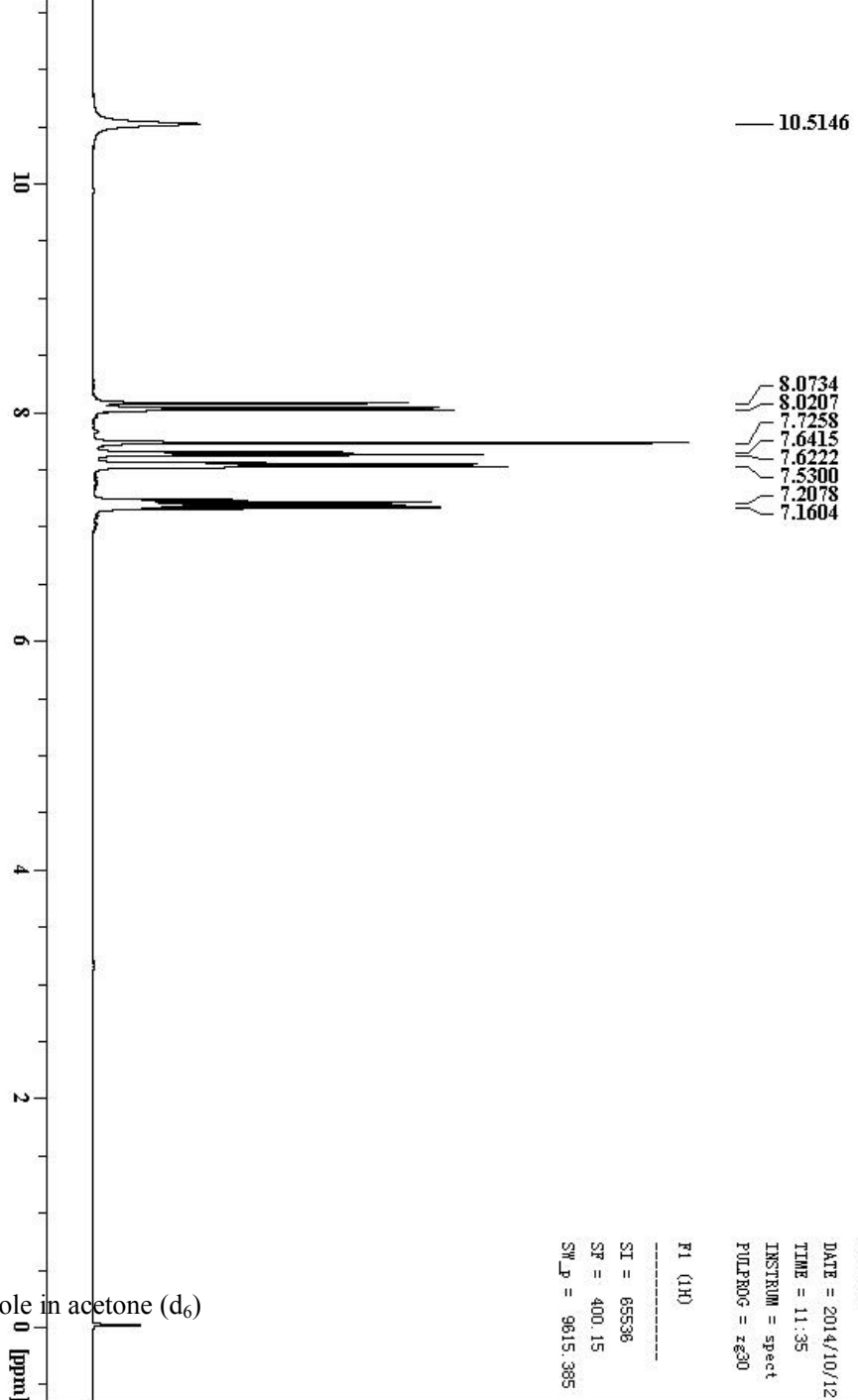


Parameter	Value
1 Title	20140620-Amir-281#
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.4
5 Pulse Sequence	zg30
6 Number of Scans	8
7 Pulse Width	8.9200
8 Acquisition Time	3.4079
9 Acquisition Date	2014-06-20T16:33:04
10 Modification Date	2014-06-20T16:33:06
11 Spectrometer Frequency	400.15
12 Spectral Width	9615.4
13 Lowest Frequency	-2349.0
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

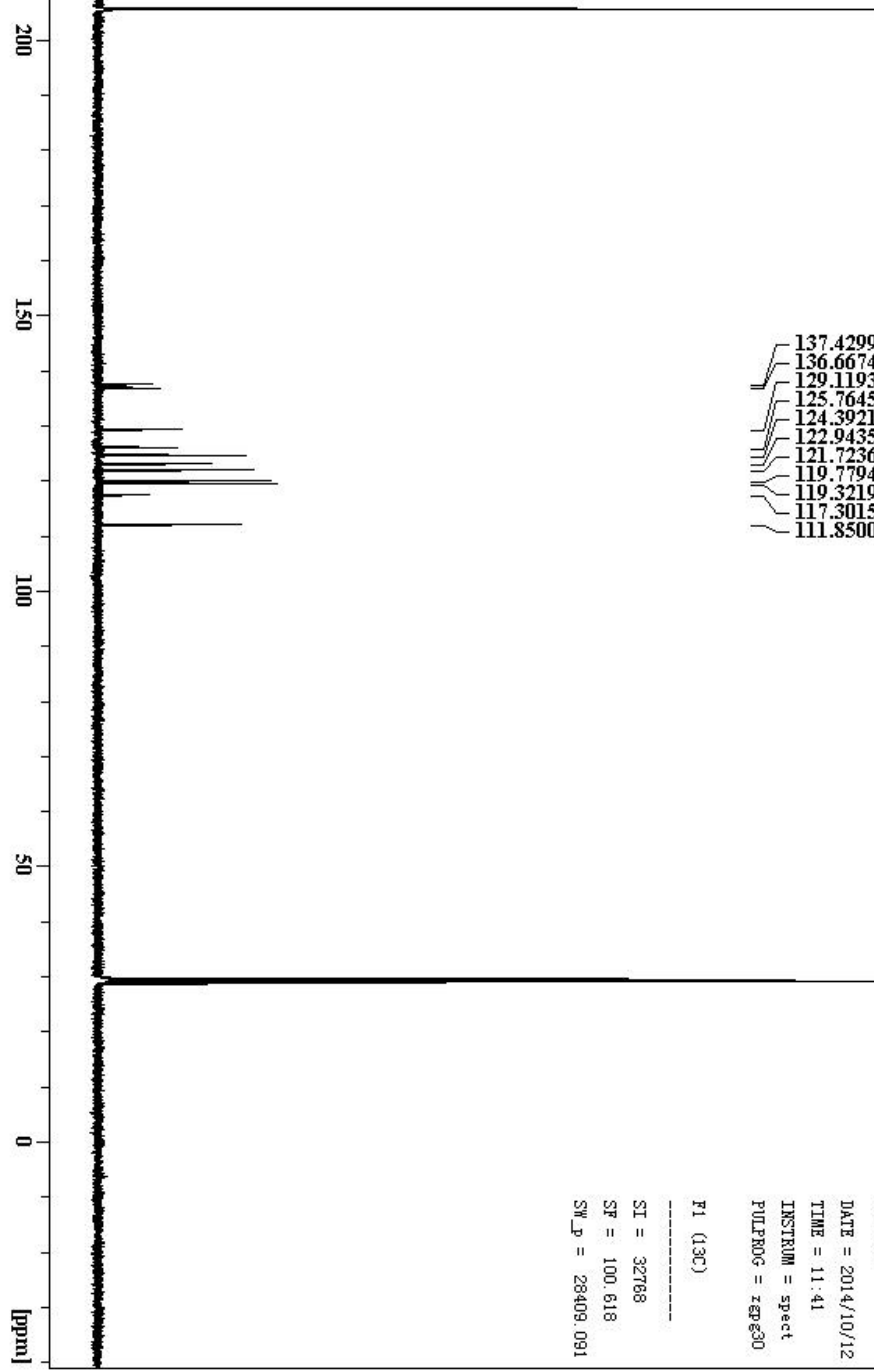


Parameter	Value
1 Title	20140624-Amir-281#
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.3
5 Pulse Sequence	zgpg30
6 Number of Scans	64
7 Pulse Width	10.0000
8 Acquisition Time	1.1534
9 Acquisition Date	2014-06-24T21:26:01
10 Modification Date	2014-06-24T21:26:02
11 Spectrometer Frequency	100.62
12 Spectral Width	28409.1
13 Lowest Frequency	-4143.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

The ^1H NMR chart of the oligome



The ^{13}C NMR chart of the oligomer of indole in acetone (d_6)



10. References

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