Brønsted acid ionic liquid catalyzed facile synthesis of 3-vinylindoles through direct C3 alkenylation of indoles with simple ketones

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1. General remarks:

Indole, benzhydrol, acetophenone, 4-methylacetophenone, 4-*t*-butylacetophenone, 4-fluoroacetophenone, 4-chloroacetophenone, 4-methoxycarbonylacetophenone, divinyl sulfone, trifluoromethanesulfonic acid, 1,3-propane sultone, 2-methylindole, 2-methyl-6-fluoroindole, 1,2-dimethylindole, 2-phenylindole, 1-methyl-2-phenylindole, 1-ethyl-2-phenylindole, 2-hydroxymethylindole, 2-methylcyclohexanone and 2-methylcyclopentanone were purchased from Energy Chemical Company. 1,2-Dimethylindole, phenylacetylene, 2ʾ-bromoacetophenone, 2´-fluoroacetophenone, 1-phenyl-2-buten-1-one, $Sc(OTf)_3$, were purchased from Adamas Reagent Ltd. 4,4-Dimethoxy-2-butanone, 5-bromoindole, 2,6-dimethylcyclohexanone, acetone-d_6, DMSO-d_6, and chloroform-*d* were purchased from Alfa Aesar Chemical Company. 3,3'-(Cyclohexane-1,1-diyl)bis(5-bromo-1H-indole) **5b** was prepared from 5-bromoindole and cyclohexanenone using oxalic acid as catalyst.[1] 2,3´-Diindolylmethan **12a** was synthesized according to a literature method.[2] Acetophenone, methyl isopropyl ketone, *p*-toluenesulfonic acid, ethyl acetate, sodium chloride, acetone and ethanol were all purchased from Sinopharm Chemical Reagents Limited Company (SCRC). ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AV-400. Chemical shifts are expressed in ppm relative to Me_4Si in $CDCl_3$. 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 IL 1a and 1b.

Brønsted acid IL **1a** was synthesized according to our previous report.[3] 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 ^oC 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 ^oC 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 ^oC 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 ^oC under vacuum (10 mmHg) for 4 hours. Finally, IL **1a** was obtained as a viscous brown oil (22.2 g, 96 %). Brønsted acid IL **1b** was synthesized according to a known method reported by us.[4]

3. A typical procedure for the reaction of indoles and ketones

All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, **1a** (34.7 mg, 0.075 mmol) was mixed with 2-methyl-indole **2a** (327.7 mg, 2.5 mmol) and acetophenone **6a** (300.2 mg, 2.5 mmol) under air. The mixture was stirred for 15 minutes at 60 ^oC. After reaction, the temperature was decreased to room temperature and the reaction mixture was extracted with ethyl acetate (3 ml × 3). The organic phase was combined together, and dried with anhydrous Na_2SO_4 then subjected to a flash silica column

chromatography after removing ethyl acetate by a rotary evaporator. A mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is $1/20_{v/v}$) was used as eluting solvent. The desired product **4a** was obtained in 95 % of yield, 553.6 mg. Tests for substrate scope and the reaction of using other indoles and ketones were all performed according to an analogous procedure. The recovered ionic liquid was treated at 100 ^{o}C under vacuum (10 mmHg) for 30 minutes, and then used in the next run.

4. Synthesis of 6a

Reaction was conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, **1a** (34.7 mg, 0.075 mmol) was mixed with 2-methyl-indole **2a** (983.2 mg, 7.5 mmol) and 4,4-dimethoxybutanon (1.98 g, 15.0 mmol) under air. The mixture was stirred for 15 minutes at 60 ^{o}C. After reaction, the temperature was decreased to room temperature and the reaction mixture was extracted with ethyl acetate (5 ml × 3). The organic phase was combined together, and dried with anhydrous Na_2SO_4 then subjected to a flash silica column chromatography after removing ethyl acetate by a rotary evaporator. 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 **5a** was obtained in 90 % of yield, 1.49 g.

5. One-pot step-wise synthesis of 8a

Reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, as first step, **1a** (34.8 mg, 0.075 mmol) was mixed with 2-methyl-indole **2a** (327.7 mg, 2.5 mmol) and acetophenone **6a** (300.2 mg, 2.5 mmol) under air. The mixture was stirred for 15 minutes at 60 ^{o}C. After that, *trans*-1-phenyl-2-buten-1-one **7a** (365.2 mg, 2.5 mmol) was added into the solution. The mixture was stirred for 1 hour at 60 ^{o}C. After reaction, the temperature was decreased to room temperature and the reaction mixture was extracted with ethyl acetate (4 ml × 3). The organic phase was combined together, and dried with anhydrous Na_2SO_4, then subjected to a flash silica column chromatography after removing ethyl acetate by a rotary evaporator. 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 **8a** was obtained in 82 % of overall yield, 777.4 mg.

6. One-pot step-wise synthesis of 10a

Reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, as first step, **1a** (34.7 mg, 0.075 mmol) was mixed with 2-methyl-indole **2a** (327.7 mg, 2.5 mmol) and acetophenone **6a** (300.2 mg, 2.5 mmol) under air. The mixture was stirred for 15 minutes at 60 ^{o}C. After that, benzhydrol **9a** (460.2 mg, 2.5 mmol) was added into the reaction system. The mixture was stirred for 1 hour at 60 ^{o}C. After reaction, the temperature was decreased to room temperature and the reaction mixture was extracted with ethyl acetate (4 ml × 3). The organic phase was combined together, and dried with anhydrous Na_2SO_4 then subjected to a flash silica column chromatography after removing ethyl acetate by a rotary evaporator. 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 **10a** was obtained in 90 % of overall yield, 898.2 mg.

7. Preparation of 5,6,11,12-tetrahydro-6-methyl-6-phenylindolo[3,2-*b*]carbazole 11a

Reaction was conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, **1a** (57.9 mg, 0.125 mmol) was mixed with 2-hydroxymethylindole (367.7 mg, 2.5 mmol) and acetophenone **6a** (172.9 mg, 1.25 mmol) under air. The mixture was stirred for 1 hour at 60 ^{o}C. After reaction, the temperature was decreased to room temperature and the reaction mixture was extracted with ethyl acetate (4 ml × 3). The organic phase was combined together, and dried with anhydrous Na_2SO_4, then subjected to a flash silica column chromatography after removing ethyl acetate by a rotary evaporator. 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 **11a** was obtained in 88 % of yield, 383.0 mg.

8. Spectroscopic data of ionic liquid and products

4-*n*-Butyl-4-(3-sulfopropyl)thiomorpholinium 1,1-dioxide trifluoromethanesulfonate (**1a**):[3] Yellow viscous liquid; ^{1}H NMR (400 MHz, D_2O, 25 ^{o}C): δ = 3.84-3.81 (m, 4H), 3.51 (s, 4H), 3.47-3.43 (m, 2H), 3.30 (t, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 1.97 (t, *J*=8.0 Hz, 2H), 1.51 (t, *J* = 8.0 Hz, 2H), 1.20 (d, *J* = 8.0 Hz, 1H), 1.17 (d, J = 8.0, 1H), 0.74-0.71 (m, 3H) ppm; ^{13}C NMR (100MHz, D_2O, 25 ^{o}C): δ = 124.2, 121.1, 117.9, 57.3, 46.7, 44.9, 22.9, 18.7, 17.3, 12.6 ppm.

2-Methyl-3-(1-phenylethenyl)-1*H*-indole (**4a**):[5] Yellow viscous liquid; ^{1}H NMR (400 MHz, 25 ^{o}C, TMS, $CDCl_3$): δ = 7.91 (s, 1H), 7.48 (dd, J_a = 6.5 Hz, J_b = 3.1 Hz, 2H), 7.37 (dd, J_a = 7.6 Hz, J_b = 3.0 Hz, 3H), 7.32 (dd, J_a = 11.3 Hz, J_b = 8.0 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 5.82 (d, *J* = 1.7 Hz, 1H), 5.41 (d, *J* = 1.7 Hz, 1H), 2.32 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 141.9, 135.2, 133.3, 128.5, 128.3, 127.6, 127.4, 121.3, 119.8, 119.7, 114.9, 114.0, 110.3, 12.9 ppm.

2-Methyl-3-[1-(4-methylphenyl)ethenyl]-1*H*-indole (**4b**):[5] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.94 (s, 1H), 7.33 (dd, J_a = 8.0 Hz, J_b = 2.5 Hz, 3H), 7.28 (d, *J* = 3.2 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 3H), 7.02 (dd, J_a = 7.8 Hz, J_b = 7.3 Hz, 1H), 5.74 (s, 1H), 5.31 (d, *J* = 1.1 Hz, 1H), 2.39 (s, 3H), 2.31 ppm (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ = 142.3, 138.9, 137.3, 136.1, 135.2, 133.1, 128.9, 128.5, 127.2, 121.2, 120.9, 119.6, 114.2, 110.2, 21.2, 12.8 ppm. IR (cm^{-1}): 3400, 3053, 3026, 2923, 2857, 1678, 1613, 1510, 1490, 1458, 1288, 1242, 1184, 1153, 1123, 1075.

2-Methyl-3-[1-(4-*tert*-butylphenyl)ethenyl]-1*H*-indole (**4c**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.94 (s, 1H), 7.35 (q, *J* = 8.7 Hz, 5H), 7.29 (d, *J* = 2.5 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 5.78 (d, *J* = 1.8 Hz, 1H), 5.32 (d, *J* = 1.8 Hz, 1H), 2.31 (s, 3H), 1.35 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ = 150.6, 138.8, 136.1, 135.3, 129.1, 127.0, 125.2, 121.0, 119, 110.5, 100.4， 34.6, 31.5, 13.7 ppm. IR (cm^{-1}): 3403, 3054, 2960, 2866, 1672, 1607, 1555, 1456, 1405, 1342, 1285, 1215, 1149, 1114, 1014. HRMS-ESI (m/z) calcd for $C_{21}H_{24}N$, $[M + H]^+$ 290.1909, found 290.1902.

2-Methyl-3-[1-(4-chlorophenyl)ethenyl]-1*H*-indole (**4d**):[6] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.99 (s, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.32 (t, *J* = 6.5 Hz, 3H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 5.77 (d, *J* = 1.4 Hz, 1H), 5.40 (d, *J* = 1.4 Hz, 1H), 2.32 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ 141.5, 140.4, 135.2, 133.3, 128.7, 128.4, 128.3, 121.4, 119.8, 119.7, 119.6, 115.3,

113.6, 110.3, 12.8 ppm.

2-Methyl-3-[1-(4-fluorophenyl)ethenyl]-1*H*-indole (**4e**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 7.98 (s, 1H), 7.39 (dd, J_a = 8.7 Hz, J_b = 5.5 Hz, 2H), 7.33 (d, J = 8.1 Hz, 1H), 7.21 (d, J = 7.9 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.02 (dd, J_a = 14.4 Hz, J_b = 7.9 Hz, 3H), 5.70 (d, J = 1.5 Hz, 1H), 5.33 (d, J = 1.4 Hz, 1H), 2.32 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 162.5 (d, J = 245.0 Hz), 141.5, 137.9, 135.2, 133.2, 128.9 (d, J = 8.1 Hz), 121.3, 119.7 (d, J = 11.7 Hz), 115.0 (d, J = 21.0 Hz), 114.6, 113.9, 110.2, 12.8 ppm. IR (cm^{-1}): 3398, 3057, 2960, 2926, 2857, 1680, 1600, 1505, 1458, 1295, 1225, 1157, 1132, 1097. HRMS-ESI (m/z) calcd for $C_{17}H_{19}FN$, $[M + H]^+$ 252.1189, found 252.1192.

2-Methyl-3-[1-(4-trifluoromethylphenyl)ethenyl]-1*H*-indole (**4f**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ 8.03 (s, 1H), 7.58 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.1 Hz, 1H), 7.19 (dd, J_a = 18.2 Hz, J_b = 8.0 Hz, 2H), 7.05 (t, J = 7.5 Hz, 1H), 5.84 (s, 1H), 5.48 (s, 1H), 2.31 ppm (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ = 145.5, 141.5, 135.2, 133.3, 129.5 (d, J = 32.0 Hz), 127.6 , 125.2 (q, J = 3.8 Hz), 123.8 (q, J = 272 Hz), 121.5, 119.9, 119.7, 116.8, 113.3, 110.3, 12.8 ppm. IR (cm^{-1}): 3397, 3059, 2926, 1705, 1615, 1526, 1490, 1325, 1224, 1166, 1123, 1068, 1015. HRMS-ESI (m/z) calcd for $C_{18}H_{15}F_3N$, $[M + H]^+$ 302.1157, found 302.1144.

2-Methyl-3-[1-(4-methoxycarbonylphenyl)ethenyl]-1*H*-indole (**4g**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.10 (s, 1H), 8.00 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 5.84 (d, J = 1.4 Hz, 1H), 5.47 (d, J = 1.4 Hz, 1H), 3.94 (s, 3H), 2.29 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$. 25 ^{o}C): δ = 167.2, 146.6, 141.9, 135.2, 133.3, 129.6, 129.1, 128.2, 127.3, 121.4, 119.8, 119.5, 116.8, 113.4, 110.3, 52.1, 12.8 ppm. IR (cm^{-1}): 3383, 3056, 2952, 1935, 1718, 1608, 1491, 1458, 1436, 1362, 1283, 1221, 1112, 1016. HRMS-ESI (m/z) calcd for $C_{19}H_{18}NO_2$, $[M + H]^+$ 292.1338, found 292.1326.

2-Methyl-3-[1-(2-bromophenyl)ethenyl]-1*H*-indole (**4h**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 7.87 (s, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.56 (dd, J_a = 7.3 Hz, J_b = 5.4 Hz, 2H), 7.43 (d, J = 7.4 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.30 (d, J = 1.0 Hz, 2H), 7.22 (t, J = 7.8 Hz, 1H), 5.79 (s, 1H), 5.63 (s, 1H), 2.23 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 144.1, 143.0, 135.3, 133.3, 131.5, 128.9, 128.0, 127.5, 123.0, 121.9, 121.3, 120.0, 119.6, 117.3, 113.5, 110.7, 13.1 ppm. IR (cm^{-1}): IR (cm^{-1}): 3400, 3055, 2924, 2853, 1707, 1613, 1488, 1460, 1431, 1285, 1250, 1217, 1155. HRMS-ESI (m/z) calcd for $C_{17}H_{15}Br^{79}N$, $[M + H]^+$ 312.0388, found 312.0367.

2-Methyl-3-[1-(2-fluorophenyl)ethenyl]-1*H*-indole (**4i**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.86 (s, 1H), 7.32 (dd, J_a = 12.7 Hz, J_b = 7.7 Hz, 4H), 7.18 (t, J = 7.5 Hz, 1H), 7.09 (dd, J_a = 16.8 Hz, J_b = 8.0 Hz, 3H), 5.80 (s, 1H), 5.65 (s, 1H), 2.30 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 160.4 (d, J = 247 Hz), 135.1, 131.1, 130.1 (d, J = 12.5 Hz), 128.9 (d, J = 9.0 Hz), 128.7, 128.4, 128.1, 123.9 (d, J = 3.6 Hz), 121.4 (d, J = 10.1 Hz), 119.8, 119.3, 118.6, 115.9 (d, J = 22.0 Hz), 114.2, 110.3, 12.7 ppm. IR (cm^{-1}): 1399, 3058, 2922, 1704, 1611, 1488, 1457, 1392, 1362, 1288, 1258, 1216, 1094, 1013. HRMS-ESI (m/z) calcd for $C_{17}H_{15}FN$, $[M + H]^+$ 252.1189, found 252.1184.

4-(2-Methylindol-3-yl)-1,2-dihydronaphthalene (**4j**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25

°C): δ = 8.00 (s, 1H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.25 (t, *J* = 6.6 Hz, 2H), 7.14 (t, *J* = 6.4 Hz, 2H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.22 (t, *J* = 4.2 Hz, 1H), 3.02 (dd, J_a = 18.8 Hz, J_b = 6.1 Hz, 2H), 2.60 (dd, J_a = 12.1 Hz, J_b = 7.7 Hz, 2H), 2.39 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 136.4, 135.6, 135.4, 132.7, 132.1, 129.3, 128.9, 127.6, 126.8, 126.4, 125.7, 121.2, 119.6, 119.5, 112.6, 110.4, 28.5, 23.7, 12.6 ppm. IR (cm^{-1}): 3404, 1708, 1485, 1452, 1421, 1363, 1299, 1249, 1226, 1148, 1093, 1073. HRMS-ESI (m/z) calcd for $C_{19}H_{18}N$, $[M + H]^+$ 260.1439, found 260.1441.

2-Methyl-3-[1-(2-naphthyl)ethenyl]-1*H*-indole (**4k**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 8.20 (s, 1H), 7.96 – 7.92 (m, 3H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.36 (dd, J_a = 7.8 Hz, J_b = 5.2 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 5.96 (s, 1H), 5.53 (s, 1H), 2.30 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 142.6, 139.6, 133.6, 133.1, 130.4, 128.6, 128.4, 127.9, 127.7, 126.9, 126.3, 126.1, 125.9, 123.9, 121.3, 119.8, 115.6, 113.9, 110.4, 12.9 ppm. IR (cm^{-1}): 3397, 3055, 2922, 1676, 1624, 1690, 1461, 1430, 1363, 1281, 1228, 1193, 1130, 1070. HRMS-ESI (m/z) calcd for $C_{21}H_{18}N$, $[M + H]^+$ 284.1439, found 284.1438.

3-[Cyclobutylidene(phenyl)methyl]-2-methyl-1*H*-indole (**4l**): Yellow solid, mp. = 62-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 7.83 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 6H), 7.28 – 7.20 (m, 2H), 7.14 (dd, J_a = 11.2 Hz, J_b = 6.9 Hz, 1H), 3.29 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.30 (s, 3H), 2.19 – 2.12 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.4, 140.9, 135.5, 132.3, 128.7, 128.1, 127.7, 125.8, 125.0, 120.9, 119.5, 119.4, 112.5, 110.3, 33.2, 32.5, 17.7, 12.5 ppm. IR (cm^{-1}): 3397, 2948, 2916, 1614, 1598, 1489, 1457, 1301, 1216, 1155, 1106, 1072. HRMS-ESI (m/z) calcd for $C_{20}H_{20}N$, $[M + H]^+$ 274.1596, found 274.1588.

3-(1,2-Diphenylethenyl)-2-methyl-1*H*-indole (*E*, determined by ^{1}H NMR and compared with literature's data) (**4m**):[7] Yellow solid, mp. = 162-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.90 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 6.2 Hz, 4H), 7.19 (dd, J_a = 16.1 Hz, J_b = 7.4 Hz, 8H), 7.05 (t, *J* = 8.3 Hz, 1H), 2.03 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.3, 138.7, 135.8, 135.2, 133.2, 130.4, 129.6, 128.8, 128.6, 128.2, 127.5, 127.4, 126.5, 121.3, 120.0, 119.7, 110.3, 12.5 ppm. IR (cm^{-1}): 3408, 3056, 3022, 2917, 1707, 1598, 1490, 1458, 1430, 1363, 1322, 1297, 1227.

4-(1,2-Dimethylindol-3-yl)-1,2-dihydronaphthalene (**4n**): White solid, mp. = 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 7.41 (t, *J* = 8.3 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.22 (dd, J_a = 7.4 Hz, J_b = 0.8 Hz, 1H), 7.12 (td, J_a = 7.3 Hz, J_b = 2.9 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.20 (t, *J* = 4.6 Hz, 1H), 3.81 (s, 3H), 3.04 (dd, J_a = 18.4 Hz, J_b = 8.0 Hz, 2H), 2.60 (td, J_a = 8.0 Hz, J_b = 4.8 Hz, 2H), 2.41 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 136.4, 135.7, 134.4, 132.4, 129.3, 128.0, 127.5, 126.7, 126.3, 125.6, 120.8, 119.5, 119.2, 112.1, 108.6, 29.7, 28.4, 23.7, 11.4. IR (cm^{-1}): 3011, 2940, 2917, 2881, 2829, 1615, 1544, 1474, 1407, 1372, 1324, 1219, 1040. HRMS-ESI (m/z) calcd for $C_{20}H_{20}N$, $[M + H]^+$ 274.1596, found 274.1591.

1-Methyl-2-phenyl-3-(1-phenylethenyl)-1*H*-indole (**4o**): Yellow solid, mp. = 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.38-7.33 (m, 5H), 7.32-7.25 (m, 4H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.18-7.17 (m, 3H), 7.06-7.03 (m, 1H), 5.57 (s, 1H), 5.13 (s, 1H), 3.67 (s, 1H) ppm;^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 142.3, 141.8, 139.2, 137.3, 131.9, 130.7, 128.1, 128.0, 127.9, 127.2, 121.9, 120.5, 119.8, 116.3, 109.4, 31.1 ppm. IR (cm^{-1}): 3050, 2958, 2923,

2850, 1626, 1486, 1465, 1441, 1371, 1330, 1310, 1238, 1075. HRMS-ESI (m/z) calcd for $C_{23}H_{20}N$, $[M + H]^+$ 310.1596, found 310.1587.

2,5-Dimethyl-3-(1-phenylethenyl)-1*H*-indole (**4p**): colorless viscous liquid;^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.84 (s, 1H), 7.41-7.39 (m, 2H), 7.30-7.28 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.73 (d, *J* = 2.0 Hz, 1H), 5.33 (d, *J* = 1.6 Hz, 1H), 2.34 (s, 3H), 2.22 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 142.5, 141.9, 133.5, 128.9, 128.2, 127.4, 127.3, 122.7, 119.3, 114.9, 113.6, 109.8, 21.5, 12.9 ppm. HRMS-ESI (m/z) calcd for $C_{18}H_{18}N$, $[M + H]^+$ 248.1439, found 248.1435.

3-[(1*E*)-1-Phenyl-1-propen-1-yl]-2-phenyl-1*H*-indole (*Z*/E was determined by liquid chromatography) (**4q**): White solid, mp.= 79-81 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 7.40 (d, J = 8.0 Hz, 1H), 7.38-7.35 (m, 6H), 7.24-7.13 (m, 5H), 7.09 (t, , J = 14.8 Hz, 1H), 6.17 (m, 1H), 3.74 (s, 3H),1.39 ppm (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 143.1, 139.1, 137.7, 134.6, 132.3, 129.9, 128.2, 128.0, 127.7, 126.6, 126.3, 121.8, 120.4, 119.6, 112.3, 109.4, 31.3, 16.0 ppm. IR (cm^{-1}): 3051, 1920, 1600, 1466, 1438, 1382, 1364, 1339, 1311, 1208, 1127, 1072. HRMS-ESI (m/z) calcd for $C_{24}H_{22}N$, $[M + H]^+$ 324.1752, found 324.1745.

1,2-Dimethyl-3-[1-(2-bromophenyl)ethenyl]-1*H*-indole (**4r**): Yellow solid, mp. = 175-176 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 7.63 (dd, J_a = 7.9 Hz, J_b = 0.7 Hz, 1H), 7.48 (dd, J_a = 7.6 Hz, J_b = 1.6 Hz, 1H), 7.37 (dd, J_a = 13.8 Hz, J_b = 7.5 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.21 (dd, J_a = 11.3 Hz, J_b = 7.7 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 5.64 (d, *J* = 1.7 Hz, 1H), 5.56 (d, *J* = 1.7 Hz, 1H), 3.72 (s, 3H), 2.32 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 144.1, 142.9, 136.7, 134.9, 133.2, 131.4, 128.6, 127.2, 122.8, 120.9, 119.6,119.4, 117.8, 113.4, 108.7, 29.6, 11.4 ppm. IR (cm^{-1}): 3051, 2918, 2852, 1725, 1605, 1546, 1472, 1430, 1381, 1290, 1232, 1095. HRMS-ESI (m/z) calcd for $C_{18}H_{17}Br^{79}N$, $[M + H]^+$ 326.0544, found 326.0541.

2-Methyl-3-(3-methyl-2-buten-2-yl)-1H-indole (**4s**): Yellow solid, mp. = 81-83 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.52 (s, 1H), 7.35 (d, J = 4.4 Hz, 1H), 1.16 (d, J = 7.2 Hz, 1H), 7.08-7.04 (m, 2H), 2.16 (s, 3H), 1.96 (s, 3H), 1.86 (s, 3H), 1.51 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 135.4,130.4, 129.7, 128.4, 122.1, 120.8, 119.4, 119.2, 117.1, 110.3, 22.3, 20.3, 20.0, 12.3 ppm. IR (cm^{-1}): 3393, 2980, 2911, 2854, 1457, 1424, 1365, 1305, 1264, 1168, 1129, 1047, 1011. HRMS-ESI (m/z) calcd for $C_{14}H_{18}N$, $[M + H]^+$ 200.1439, found 200.1443.

3-(3-Methyl-2-buten-2-yl)-2-phenyl-1H-indole (**4t**): Yellow solid, mp.= 160-161 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 8.09 (s, 1H), 7.58 (d, J =7.2 Hz, 2H), 7.42-7.32 (m, 4H), 7.26 (t, J = 14.8 Hz, 1H), 7.17 (t, J = 14.0 Hz, 1H), 7.10 (t, J = 14.8 Hz, 1H), 1.92 (s, 3H), 1.88 (s, 3H), 1.49 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 135.9, 133.5, 132.4, 130.6, 128.9, 120.8, 118.9, 117.2, 116.3, 112.3, 122.2, 120.2, 110.7, 22.3, 20.3, 19.8 ppm. IR (cm^{-1}): 3395, 2962, 2918, 2852, 1712, 1670, 1600, 1486, 1449, 1322, 1260, 1129. HRMS-ESI (m/z) calcd for $C_{19}H_{20}N$, $[M + H]^+$ 262.1596, found 262.1583.

1-Ethyl-3-(3-methyl-2-buten-2-yl)-2-phenyl-1H-indole (**4u**): Yellow solid, mp. = 90-92 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 7.44 (d, J =8.0 Hz, 1H), 7.39 (d, J = 6.4 Hz, 2H), 7.35 (d, J =7.3 Hz, 4H), 4.13-4.08 (m, 1H), 1.77 (s, 3H), 1.74 (s, 3H), 1.44 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 136.5, 136.3, 133.2, 130.0, 129.9, 128.2, 127.7, 127.6, 121.9, 121.4, 120.2, 119.2, 118.5, 109.7, 38.8, 22.6, 20.4, 20.4, 15.4 ppm. IR (cm^{-1}): 3057, 2974, 2916, 2853, 1604, 1461, 1408, 1352, 1254, 1213, 1128, 1093, 1021. HRMS-ESI (m/z) calcd for

$C_{21}H_{24}N$, $[M + H]^+$ 290.1909, found 290.1903.

2-Methyl-6-fluoro-3-(1-phenylethenyl)-1*H*-indole (**4v**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 7.90 (s, 1H), 7.38-7.35 (m, 2H), 7.30-7.27 (m, 3H), 7.07 (dd, J_a = 8.4 Hz, J_b = 14.0 Hz, 1H), 6.91 (dd, J_a = 2.4 Hz, J_b = 9.6 Hz, 1H), 6.75-6.70 (m, 1H), 5.71 (d, J = 1.6 Hz, 1H), 5.29 (d, J = 1.6 Hz, 1H), 2.2 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 160.6, 158.3, 142.3, 141.7, 135.0, 133.5, 128.3, 127.7, 127.3, 124.9, 120.4, 120.3, 115.1, 107.9, 96.9, 12.8 ppm. HRMS-ESI (m/z) calcd for $C_{17}H_{15}FN$, $[M + H]^+$ 252.1189, found 252.1186.

1,3-Dimethyl-2-[(1-methyl-2-phenyl)indol-3-yl]cyclohexene (**4w**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 7.40-7.38 (m, 5H), 7.34-7.32 (m, 2H), 7.24-7.20 (m, 1H), 7.13-7.09 (m, 1H), 3.67 (s, 3H), 2.18-2.00 (m, 2H), 1.76-1.65 (m, 2H), 1.58 (s, 3H), 1.52-1.48 (m, 2H), 0.73-0.68 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 137.3, 136.3, 132.7, 132.6, 130.3, 129.8, 128.2, 128.1, 127.5, 121.5, 120.4, 119.3, 116.7, 109.3, 34.2, 32.0, 31.4, 31.2, 21.6, 20.3, 19.7 ppm. IR (cm^{-1}): 3053, 2924, 2865, 1605, 1664, 1465, 1399, 1365, 1323, 1244, 1156, 1130, 1071. HRMS-ESI (m/z) calcd for $C_{22}H_{24}N$, $[M + H]^+$ 302.1909, found 302.1900.

1,3-Dimethyl-2-(1-methylindol-3-yl)cyclohexene (**4x**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 7.64 (s, 1H), 7.37-7.28 (m, 1H), 7.23-7.21 (m, 1H), 7.09-7.02 (m, 2H), 2.22-2.18 (m, 3H), 2.11-2.10 (m, 2H), 1.91-1.76 (m, 2H), 1.71-1.52 (m, 3H), 1.44-1.31 (m, 3H), 0.84-0.76 (m, 3H);^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 135.6, 132.6, 131.5, 129.9, 128.5, 120.7, 120.6, 119.1, 119.0, 110.2, 33.4, 32.0, 31.2, 20.9, 20.3, 19.8, 12.4 ppm. IR (cm^{-1}): 3284, 2920, 2890, 1716, 1696, 1634, 1616, 1458, 1427, 1228, 1160, 1136. HRMS-ESI (m/z) calcd for $C_{17}H_{22}N$, $[M + H]^+$ 240.1752, found 240.1738.

2-Methyl-1-(1,2-dimethylindol-3-yl)cyclopentene (**4y**): Yellow viscous liquid, ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 7.42 (d, J = 7.6 Hz, 1H), 7.23 (d, J =8.0 Hz, 1H), 7.13 (t, J =14.8 Hz, 1H), 7.04 (t, J =14.8 Hz, 1H), 3.63 (s, 3H), 2.70 (s, 3H), 4.49 (t, J =14.0 Hz, 2H), 2.26 (s, 3H), 2.01-1.93 (m, 2H), 1.60 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C) δ = 136.7, 135.5, 133.1, 129.7, 127.5, 120.5, 119.5, 118.8, 110.3, 108.6, 38.5, 37.9, 29.6, 22.7, 15.7, 11.4 ppm. IR (cm^{-1}): 2920, 2842, 1721, 1613, 1472, 1440, 1409, 1374, 1195, 1131, 1091. HRMS-ESI (m/z) calcd for $C_{16}H_{20}N$, $[M + H]^+$ 226.1596, found 226.1581.

2-Methyl-1-(2-methylindol-3-yl)cyclohexene (**4z**): White solid, mp. = 95-96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ = 7.63 (s, 1H), 7.35 (d, J = 4.4 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.10 – 7.03 (m, 2H), 2.37 (t, J = 16.8 Hz, 1H), 2.21 (s, 1H), 2.09-2.04 (m, 3H), 1.79-1.73 (m, 4H), 1.47 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 135.5, 131.8, 130.8, 128.5, 124.7, 120.8, 119.3, 119.2, 116.0, 110.5, 31.8, 31.5, 23.9, 23.7, 21.1, 12.3 ppm. IR (cm^{-1}): 3396, 2932, 2859, 2827, 1459, 1428, 1376, 1341, 1298, 1241, 1141, 1067, 1013. HRMS-ESI (m/z) calcd for $C_{16}H_{20}N$, $[M + H]^+$ 226.1596, found 226.1589.

1-(5-Bromoindol-3-yl)cyclohexene (**4aa**): Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 8.09 (s, 1H), 8.02 (s, 1H), 7.25 (s, 1H), 7.21 (s, 1H), 7.12 (s, 1H), 6.20-6.19 (m, 1H), 2.41-2.39 (m, 2H), 2.24-2.25 (m, 2H), 1.82-1.79 (m, 2H), 1.72-1.69 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 135.3, 130.7, 127.1, 124.9, 123.4, 123.1, 121.8, 113.2, 112.6, 28.6, 25.7, 23.1, 22.4 ppm. IR (cm^{-1}): 2928, 2858, 1708, 1456, 1234, 1107, 884, 797, 732. HRMS-ESI (m/z) calcd for $C_{14}H_{15}Br^{79}N$, $[M + H]^+$ 276.0388, found 276.0382.

3,3'-(Cyclohexane-1,1-diyl)bis(5-bromo-1H-indole) (**5b**), Brown oil, ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C) δ =

8.03 (s, 2H), 7.55 (s, 2H), 7.18 – 7.06 (m, 6H), 2.51 – 2.34 (m, 4H), 1.59 (d, J = 4.3 Hz, 3H); 1.53 ppm (d, J = 4.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C) δ = 135.7, 127.9, 124.2, 123.6, 123.0, 112.6, 111.9, 39.1, 36.8, 26.7, 22.8 ppm. IR (cm^{-1}) v: 3465, 2933, 2853, 1457, 1407, 1333, 1239, 1101, 904, 862, 794, 671, 579, 422. HRMS m/z (ESI) calcd for $C_{22}H_{21}{}^{79}Br_2N_2$ $[M + H]^+$ 471.0071 found 471.0054.

2-Methyl-3-(3-phenyl)indole (**6a**):[8] Yellow solid, mp. = 114-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 7.90 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.37-7.30 (m, 4H), 7.18-7.09 (m, 3H), 2.49 (s, 3H), 2.43 ppm (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$. 25 °C): δ = 138.0, 135.3, 135.2, 131.4, 130.1, 128.4, 127.9, 126.6, 126.5, 121.5, 119.9, 118.9, 114.6, 110.3, 21.6, 12.6 ppm.

3-Methyl-1,5-diphenyl-5-(2-methylindol-3-yl)-4-penten-1-one (E/Z = 1/1, detected by ^{1}H NMR) (**8a**): Colorless viscose liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 6.79 (s, 1H), 6.76 (d, J = 7.2 Hz, 3H), 6.62-6.60 (m, 1H), 6.33-6.30 (m, 2H), 6.20 (t, J = 7.6 Hz, 4H), 6.06-5.98 (m, 5H), 2.68 (dd, J_a = 7.2 Hz, J_b = 14.0, 1H), 2.42 (dd, J_a = 6.4 Hz, J_b = 16.0 Hz, 1H), 2.27 (dd, J_a = 7.6 Hz, J_b = 16.0 Hz, 1H), 1.15 (s, 3H), 0.41 ppm (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 200.6, 137.5, 136.7, 135.8, 133.1, 130.8, 128.7, 128.4, 128.3, 127.3, 126.8, 120.7, 119.2, 119.1, 115.4, 111.0, 110.7, 46.0, 27.7, 21.3, 12.0 ppm. IR (cm^{-1}): 3400, 3057, 2966, 2924, 2872, 1677, 1618, 1597, 1581, 1489, 1457, 1362, 1283, 1211. HRMS-ESI (m/z) calcd for $C_{27}H_{26}NO$, $[M + H]^+$ 380.2014, found 380.2008.

1,1-Diphenyl-3-(2-methylindol-3-yl)-3-propene (**10a**): (E/Z ratio is not measurable with NMR and liquid chromatography) White solid, mp. = 121-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 7.71 (s, 1H), 7.24-7.18 (m, 16H), 7.06-6.99 (m, 3H), 6.89-6.86 (m, 1H), 5.73 (s, 1H), 2.14 ppm (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.9, 135.2, 132.0, 129.2, 128.2, 126.1, 120.8, 119.6, 119.2, 114.1, 110.1, 47.8, 12.4 ppm. 3415, 3049, 3027, 2866, 1598, 1490, 1455, 1304, 1267, 1242, 1155, 1099, 1076. HRMS-ESI (m/z) calcd for $C_{30}H_{26}N$, $[M + H]^+$ 400.2065, found 400.2051.

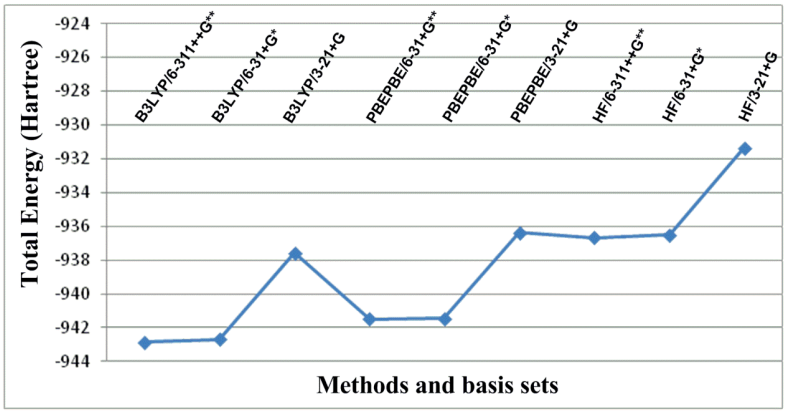
5,6,11,12-Tetrahydro-6-methyl-6-phenylindolo[3,2-*b*]carbazole (**11a**): White solid, mp. = 261-263 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS, 25 °C): δ = 11.07 (s, 1H), 10.67 (s, 1H), 7.54 (d, J=7.6 Hz, 2H), 7.3 (d, J=8.0 Hz, 1H), 7.25 (d, J=7.6 Hz, 1H), 7.20 (t, J=7.6 Hz, 2H), 7.14 (d, J=8 Hz, 1H), 7.10-6.94 (m, 4H), 6.80-6.76 (m, 1H), 4.19 **(d** J = 20.0 Hz, 1H), 4.16 (d, J = 20.0 Hz, 1H), 2.18 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 147.5, 141.9, 137.0, 136.9, 132.3, 128.0, 127.3, 126.4, 125.8, 125.1, 121.0, 120.3, 118.8, 118.5, 118.3, 118.1, 115.70, 111.2, 111.1, 104.2, 41.0, 25.9, 21.1 ppm. IR (cm^{-1}): 3380, 2968, 2925, 2858, 1617, 1461, 1372, 1320, 1216, 1189, 1158, 1026. HRMS-ESI (m/z) calcd for $C_{25}H_{19}N_2$, $[M - 1]^+$ 347.1543, found 347.1532.

9. Molecular calculation of 4o

To investigate the properties of 3-vinylindoles, 1-methyl-2-phenyl-3-(1-phenylvinyl)-1H-indole **4o** is fully determined by X-ray crystallographic analysis. In addition, the structural characteristics were also determined by the analytic techniques employing the hybrid density functional approach (DFT) with B3LYP and PBEPBE and ab inito theory with HF method with 6-311++g**, 6-31+g* and 3-21+g* basis sets. The calculation was implemented in GAUSSIAN 98 suit of the program[9] without any symmetry constraints during the computations. The results

manifested that B3LYP with 6-311++g** basis set enabled a minimum energy during the optimization, **Scheme S1**. The conformation from experimental analysis, X-ray crystallography, is in a good agreement with the results from the calculation, **Figure S1**. The results obtained by comparing the experimental and the theoretical approach convinced us to employ B3LYP/6-311++G** level of the theory to implement the rest of the calculations. Moreover, natural bond orbital, NBO is used to show the atomic electron population and the electronic destabilizing effects of every atom in the structure.

Although every parts of the molecule are supported by electron delocalization of carbon-carbon double bonds in aromatic and non-aromatic systems, there are no conjugated systems that can stabilize C25=C26. This phenomenon is obviously a result of space hindrances of aromatic rings. If the aromatic ring attached to olefin oriented to one surface the distance of H35 to H8 should be much shorter than the summation of two hydrogen van der Waals radius that is naturally impossible. On the other hand, the results of atomic electron population shows that the terminal C26 in the double bond was characterized by a relatively higher electron density, which implies the fact that this carbon can play role of electron donor or act as a nucleophile in a reaction, **Figure S2**. Additionally Structure of **4n** is also fully determined with X-ray crystallography analysis, **Figure S3**.



Scheme S1; Energy surfaces (Hartree) of **4o** optimized at B3LYP, PBEPBE and HF methods of theories, employed 6-311++g**, 6-31+g* and 3-21+g basis sets

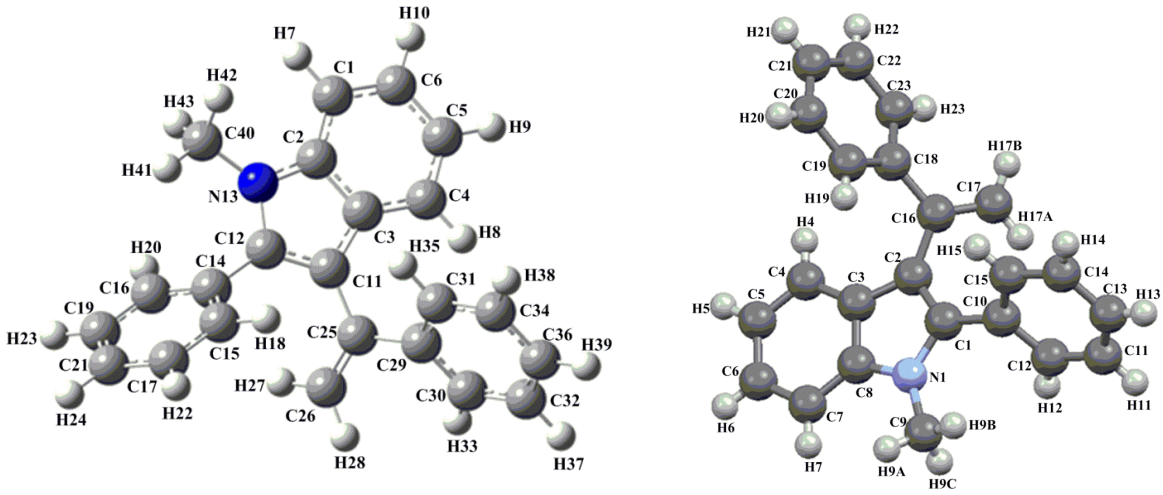


Figure S1. The structure of **4o** from both calculation (left) and X-ray crystallography approaches (right, CCDC number is 1000775).

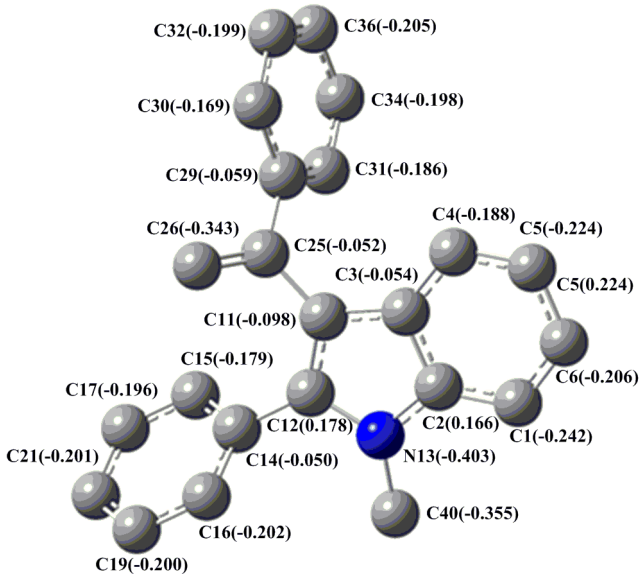


Figure S2. Atomic electron population (in a.u.) and numbering of **4o** by Natural bond orbital approach (hydrogen atoms are omitted for clearness).

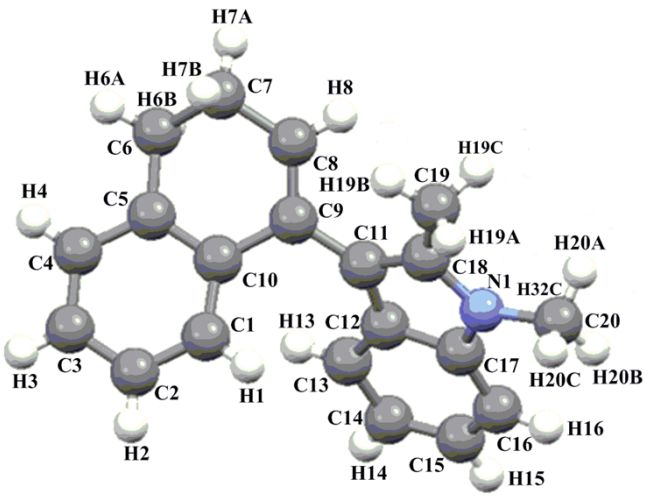


Figure S3. The molecular structure of **4n** fully characterized by X-ray crystallography analysis (CCDC number is 1000776).

10. xyz coordinates calculated according to the methods and basis sets of the DFT and ab inito theories for the structure of 4o studied in this work .

B3LYP/6-311++G**

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4o *(C1)*

Hf= -942.8708751

C	0.01495500	3.84252700	0.28076400
C	-0.26732700	2.48604300	0.09215600
C	0.71737200	1.56236300	-0.33806200
C	2.01295600	2.02830200	-0.61288400
C	2.29630500	3.37470500	-0.43242800
C	1.30862400	4.27262700	0.01391500
H	-0.74479600	4.54072000	0.61235000
H	2.78226600	1.34529500	-0.95250900
H	3.29494900	3.74418300	-0.63623600
H	1.55961500	5.31895900	0.14650600
C	0.07855700	0.27213300	-0.42130900
C	-1.24201700	0.45502100	-0.04090200
N	-1.45318100	1.79966500	0.26748100
C	-2.32928200	-0.54016300	0.05299100
C	-2.17193700	-1.69129500	0.83767300
C	-3.53120500	-0.36973200	-0.65084600
C	-3.18439500	-2.64340200	0.91486500
H	-1.24859600	-1.83666900	1.38532000

C	-4.54551100	-1.32100100	-0.56997600
H	-3.66191800	0.50233000	-1.28223600
C	-4.37566800	-2.46147300	0.21325600
H	-3.04387900	-3.52718400	1.52713700
H	-5.46466200	-1.17529600	-1.12660100
H	-5.16398700	-3.20319100	0.27449100
C	0.70639200	-0.97682400	-0.90516500
C	0.13548700	-1.71611900	-1.87050800
H	-0.77871600	-1.39863800	-2.35583700
H	0.55343300	-2.66698500	-2.17967100
C	1.98948600	-1.40045200	-0.27300900
C	2.97956300	-2.06833500	-1.01086300
C	2.23421100	-1.15406800	1.08622700
C	4.15708300	-2.49822700	-0.40579100
H	2.83219400	-2.23085400	-2.07231200
C	3.41026800	-1.58663300	1.69354100
H	1.49366500	-0.61826900	1.66874400
C	4.37663100	-2.26326500	0.95124500
H	4.91041700	-3.00668400	-0.99768100
H	3.57374100	-1.39061600	2.74763000
H	5.29605500	-2.59341700	1.42160000
C	-2.63567100	2.39168300	0.87036900
H	-3.34628200	1.61041600	1.12883100
H	-2.36051500	2.92824300	1.78252100
H	-3.11997400	3.09351600	0.18403400

B3LYP/6-31+G*

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4o *(C1)*

Hf= -942.6995631

C	0.00884300	3.84797200	0.27920200
C	-0.27042800	2.48765100	0.09160400
C	0.71717400	1.56318000	-0.33786600
C	2.01548400	2.03125900	-0.61121300
C	2.29773200	3.38154900	-0.43098300
C	1.30552600	4.28096500	0.01329300
H	-0.75458900	4.54584300	0.60911500
H	2.78694200	1.34726500	-0.94991900
H	3.29833000	3.75201800	-0.63379100

H	1.55484700	5.32976600	0.14545800
C	0.07902800	0.27112000	-0.42168200
C	-1.24555800	0.45442500	-0.04243800
N	-1.45744000	1.80016100	0.26583500
C	-2.33368800	-0.54193100	0.05302100
C	-2.17441800	-1.69512400	0.84059600
C	-3.53965400	-0.37229500	-0.65079900
C	-3.18888900	-2.64981600	0.92073400
H	-1.24788000	-1.83933100	1.38700500
C	-4.55674000	-1.32542000	-0.56619300
H	-3.67109300	0.50074100	-1.28407800
C	-4.38479600	-2.46818400	0.21969100
H	-3.04612500	-3.53471400	1.53430100
H	-5.47868700	-1.17918400	-1.12186300
H	-5.17449800	-3.21107300	0.28371200
C	0.70840900	-0.97968700	-0.90364300
C	0.13387500	-1.72373100	-1.87001300
H	-0.78244200	-1.40568700	-2.35521500
H	0.54997800	-2.67821800	-2.17698000
C	1.99468500	-1.40133500	-0.27300500
C	2.98307100	-2.07699100	-1.01227400
C	2.24663500	-1.14570100	1.08678900
C	4.16617600	-2.50480300	-0.40849800
H	2.83091400	-2.24609800	-2.07398900
C	3.42801000	-1.57605100	1.69318100
H	1.50718800	-0.60586100	1.67054700
C	4.39316800	-2.26012600	0.94927500
H	4.91725400	-3.01855100	-1.00226100
H	3.59609600	-1.37188900	2.74699000
H	5.31634600	-2.58810500	1.41835300
C	-2.64222100	2.39545300	0.86115700
H	-3.35645100	1.61478900	1.11857300
H	-2.37044600	2.93539800	1.77455300
H	-3.12214400	3.09749800	0.16902800

B3LYP/3-21+G

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4o *(C1)*

Hf= -937.5665902

C	0.23750600	3.81013400	0.23668500
C	-0.13734400	2.47043000	0.07945800
C	0.79232800	1.46546600	-0.31741900
C	2.12837100	1.82719800	-0.56894600
C	2.50040600	3.16236200	-0.42507700
C	1.56764000	4.14328000	-0.01994500
H	-0.47797000	4.56801800	0.53867200
H	2.85374200	1.08115600	-0.87371200
H	3.52711200	3.45705100	-0.61834100
H	1.89020500	5.17417200	0.08720000
C	0.06031500	0.21631000	-0.40266900
C	-1.25450800	0.49010200	-0.04533700
N	-1.38118200	1.86377800	0.24674400
C	-2.39557700	-0.43881800	0.05488900
C	-2.32234300	-1.54496500	0.92063500
C	-3.55423000	-0.25169500	-0.72107900
C	-3.38493900	-2.44734900	1.00609300
H	-1.42795300	-1.69223100	1.51763600
C	-4.61594200	-1.15748500	-0.63375400
H	-3.60898300	0.58688100	-1.40991400
C	-4.53450500	-2.25671500	0.22912000
H	-3.31828300	-3.29844900	1.67690800
H	-5.50225200	-1.01060800	-1.24362800
H	-5.35895900	-2.95976800	0.29413200
C	0.61165700	-1.08082500	-0.84545300
C	-0.02480700	-1.86456600	-1.74002900
H	-0.96011500	-1.55895500	-2.19862500
H	0.36350700	-2.84255700	-2.01156200
C	1.92565700	-1.48092300	-0.25538200
C	2.91542900	-2.10399600	-1.03653800
C	2.18529900	-1.24847500	1.10858900
C	4.13384800	-2.48669400	-0.46644200
H	2.73680000	-2.26190500	-2.09621700
C	3.39892700	-1.63814100	1.67910400
H	1.43194700	-0.75592900	1.71578000
C	4.37992200	-2.25526200	0.89226700
H	4.89455600	-2.95613100	-1.08334800
H	3.58382600	-1.45697900	2.73387200
H	5.32785800	-2.54916700	1.33252000

C	-2.56300900	2.54919900	0.79070900
H	-3.34509000	1.81241200	0.98138100
H	-2.30353500	3.04815000	1.73299600
H	-2.93873600	3.29696500	0.08016400

PBEPBE/6-31+G*

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4o *(C1)*

Hf= -941.4598781

C	0.02993700	3.85329800	0.25141600
C	-0.26028800	2.48914600	0.07391400
C	0.72859000	1.54247700	-0.33245400
C	2.03973400	1.99663600	-0.59626800
C	2.33351100	3.35294700	-0.42601600
C	1.34158800	4.27129300	-0.00303500
H	-0.73834500	4.56831500	0.56438000
H	2.81452600	1.29434900	-0.91992600
H	3.34902500	3.71387900	-0.62135800
H	1.60182700	5.32786700	0.12153500
C	0.07777400	0.25434400	-0.40819600
C	-1.26104300	0.45774800	-0.04560100
N	-1.46037500	1.81416800	0.24088200
C	-2.35596900	-0.52731300	0.05505800
C	-2.18458300	-1.70456000	0.81801500
C	-3.58503400	-0.33376800	-0.61670500
C	-3.20830300	-2.65669300	0.90515900
H	-1.23616200	-1.86588500	1.34075000
C	-4.61152700	-1.28521000	-0.52325700
H	-3.72473500	0.55809900	-1.23828500
C	-4.42706600	-2.45057200	0.23731400
H	-3.05523100	-3.56265500	1.50176300
H	-5.55442200	-1.11945700	-1.05605400
H	-5.22750500	-3.19491200	0.30792800
C	0.69433700	-1.00736300	-0.87344700
C	0.09112300	-1.78559400	-1.80977400
H	-0.84624300	-1.48060100	-2.28425400
H	0.50222200	-2.75898100	-2.09732500
C	1.99638800	-1.41099300	-0.26539300
C	2.97233700	-2.10688900	-1.01494600

C	2.28167000	-1.11857700	1.08765700
C	4.17612800	-2.51813500	-0.42691800
H	2.79136700	-2.30179200	-2.07776800
C	3.48370200	-1.53273200	1.67812500
H	1.54594700	-0.56133700	1.67823100
C	4.43654200	-2.23673800	0.92454100
H	4.92090900	-3.04883900	-1.03070000
H	3.67888400	-1.29954900	2.73086700
H	5.38027300	-2.55248700	1.38254400
C	-2.64340200	2.42786000	0.82281500
H	-3.37062500	1.64856300	1.08884300
H	-2.36809100	2.98223500	1.73753900
H	-3.11785800	3.13034900	0.11308400

PBEPBE/6-31+G**

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4o *(C1)*

Hf= -941.4875693

C	0.03249000	3.85248700	0.25116500
C	-0.25872800	2.48863500	0.07323900
C	0.72956500	1.54106400	-0.33252200
C	2.04125400	1.99391300	-0.59573500
C	2.33588400	3.34991200	-0.42518600
C	1.34466700	4.26902700	-0.00257000
H	-0.73448300	4.56734800	0.56381100
H	2.81469400	1.29135100	-0.91863600
H	3.35071200	3.70993300	-0.61982800
H	1.60585100	5.32424100	0.12221500
C	0.07778200	0.25348600	-0.40867500
C	-1.26112300	0.45820500	-0.04689600
N	-1.45941600	1.81463700	0.23921800
C	-2.35676400	-0.52596400	0.05468200
C	-2.18598600	-1.70196000	0.81967600
C	-3.58550900	-0.33270900	-0.61773900
C	-3.21009600	-2.65335600	0.90786200
H	-1.23855100	-1.86236800	1.34240900
C	-4.61227900	-1.28355500	-0.52288100
H	-3.72447900	0.55713100	-1.24052700
C	-4.42849400	-2.44765900	0.23949400

H	-3.05790800	-3.55755200	1.50543900
H	-5.55410500	-1.11853700	-1.05561600
H	-5.22855200	-3.19076500	0.31104500
C	0.69341000	-1.00875100	-0.87331100
C	0.08983100	-1.78819800	-1.80835600
H	-0.84658200	-1.48256400	-2.28168700
H	0.50240900	-2.76030800	-2.09359900
C	1.99577500	-1.41153400	-0.26539100
C	2.97052600	-2.10944600	-1.01449600
C	2.28210700	-1.11616400	1.08677500
C	4.17425900	-2.52033600	-0.42641100
H	2.78816000	-2.30621400	-2.07570500
C	3.48417800	-1.53006200	1.67701800
H	1.54759300	-0.55731600	1.67557600
C	4.43576700	-2.23629900	0.92416300
H	4.91765400	-3.05226600	-1.02888500
H	3.68033000	-1.29514400	2.72808100
H	5.37866500	-2.55151700	1.38169100
C	-2.64331900	2.42891000	0.81960000
H	-3.36861900	1.65024400	1.08861000
H	-2.36860600	2.98644500	1.73124900
H	-3.11944200	3.12752100	0.10879700

PBEPBE/3-21+G*

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4o *(C1)*

Hf= -936.3638801

C	0.24926000	3.81793500	0.20571100
C	-0.13292800	2.47270900	0.06177000
C	0.80152500	1.44586900	-0.30477800
C	2.15129300	1.79475500	-0.54147800
C	2.53132700	3.13766800	-0.40982100
C	1.59519500	4.13728700	-0.03380000
H	-0.47229100	4.59271700	0.48303300
H	2.88120900	1.03076700	-0.82419000
H	3.57214500	3.42459900	-0.59118900
H	1.92688900	5.17595900	0.06325200
C	0.05846100	0.19943000	-0.38483700
C	-1.27255800	0.49249500	-0.05154000

N	-1.38989800	1.87662000	0.21497900
C	-2.41681600	-0.42966100	0.05473900
C	-2.31463200	-1.57405100	0.88244400
C	-3.61064200	-0.20794400	-0.67285500
C	-3.38428100	-2.47739000	0.97822100
H	-1.38826600	-1.74559900	1.44011600
C	-4.67948600	-1.11611800	-0.57328900
H	-3.68435200	0.65835000	-1.34011200
C	-4.57011100	-2.25174400	0.25106100
H	-3.29686300	-3.35901700	1.62182400
H	-5.59608500	-0.94256400	-1.14693300
H	-5.40326000	-2.95789500	0.32575700
C	0.59835500	-1.10668200	-0.81177800
C	-0.06595600	-1.92095100	-1.67581300
H	-1.02226500	-1.62376200	-2.11879800
H	0.32107500	-2.91489200	-1.92799400
C	1.92960600	-1.48741700	-0.24730300
C	2.90333900	-2.13617100	-1.04196100
C	2.22592600	-1.21024200	1.10957100
C	4.14522000	-2.49851700	-0.49147700
H	2.69109600	-2.32548000	-2.10030400
C	3.46348000	-1.58007000	1.65997500
H	1.47873200	-0.69515800	1.72345900
C	4.42969400	-2.22152200	0.85985900
H	4.89754100	-2.98812100	-1.11936500
H	3.67973400	-1.36424300	2.71190700
H	5.39947500	-2.50009300	1.28528000
C	-2.57371400	2.57756000	0.74012100
H	-3.35562200	1.83589700	0.96588300
H	-2.30651700	3.11690900	1.66840400
H	-2.96243600	3.30192400	-0.00132200

HF/6-311++G**

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***4o** (C1)*

Hf= -936.6822749

C	-0.01682000	3.83206100	-0.34054600
C	0.25675200	2.48173000	-0.12282400
C	-0.71394200	1.59725800	0.35248200

C	-1.99445400	2.07597300	0.64216300
C	-2.27098600	3.40802900	0.43466900
C	-1.28769600	4.27837100	-0.05675400
H	0.73318800	4.50772400	-0.70975300
H	-2.75484400	1.41463200	1.01547100
H	-3.25300300	3.78989200	0.64948700
H	-1.53029700	5.31485900	-0.21142400
C	-0.08026600	0.30104500	0.45604300
C	1.20428600	0.46572800	0.04185800
N	1.42466600	1.78666900	-0.30722200
C	2.29357100	-0.54249100	-0.04175900
C	2.20366900	-1.61175900	-0.92346100
C	3.41741200	-0.43619900	0.77200000
C	3.21483600	-2.55714500	-0.99014100
H	1.33957700	-1.70784800	-1.55490100
C	4.42851200	-1.37918200	0.70586100
H	3.49422100	0.38142600	1.46716800
C	4.32952800	-2.44334400	-0.17696100
H	3.12953800	-3.38046300	-1.67674600
H	5.28813100	-1.28653800	1.34558800
H	5.11359700	-3.17762800	-0.22810000
C	-0.71638200	-0.94196600	0.96455300
C	-0.19026700	-1.62068600	1.97523100
H	0.69017300	-1.27205700	2.48246900
H	-0.61009400	-2.55251600	2.30967000
C	-1.96658000	-1.41049400	0.28679200
C	-2.99413400	-2.01459300	1.00823200
C	-2.12985500	-1.26062500	-1.08754700
C	-4.13299700	-2.47927700	0.37281900
H	-2.91140700	-2.10517400	2.07579300
C	-3.26662500	-1.72813200	-1.72547600
H	-1.36395000	-0.77327500	-1.66227700
C	-4.27270500	-2.34246300	-0.99873100
H	-4.91503400	-2.93866400	0.95137400
H	-3.36717800	-1.60722100	-2.78965500
H	-5.15882800	-2.69975800	-1.49251100
C	2.58964300	2.34698500	-0.95557500
H	3.32384400	1.57487700	-1.12096600
H	2.31725400	2.77415900	-1.91555200

H	3.03546200	3.12393500	-0.34214700

HF/6-31+G*

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4o *(C1)*

Hf= -936.5030893

C	-0.01244000	3.83238100	-0.33696000
C	0.25951900	2.47924500	-0.12361300
C	-0.71326500	1.59294300	0.34875900
C	-1.99582700	2.07250300	0.63684400
C	-2.27155100	3.40698000	0.43219800
C	-1.28516400	4.27956000	-0.05444000
H	0.73975900	4.50878500	-0.70114200
H	-2.75769600	1.41076300	1.00668900
H	-3.25402800	3.78876000	0.64581700
H	-1.52649600	5.31686000	-0.20584600
C	-0.08009000	0.29647300	0.45163200
C	1.20765200	0.46223700	0.03996100
N	1.42729200	1.78353500	-0.30842300
C	2.29926400	-0.54390200	-0.04317300
C	2.21051200	-1.61752900	-0.92271400
C	3.42648900	-0.43260100	0.76835200
C	3.22501200	-2.56198100	-0.98915800
H	1.34506700	-1.71784400	-1.55197000
C	4.44150100	-1.37417000	0.70249500
H	3.50300100	0.38726300	1.46114300
C	4.34297700	-2.44278300	-0.17795600
H	3.14002000	-3.38764000	-1.67304700
H	5.30259000	-1.27705400	1.33967200
H	5.12890900	-3.17514800	-0.22893100
C	-0.71742400	-0.94747500	0.95723200
C	-0.18754000	-1.63383600	1.96415400
H	0.69594500	-1.29162600	2.47031800
H	-0.60592500	-2.56678300	2.29692300
C	-1.97309900	-1.40980200	0.28456800
C	-3.00283600	-2.00634800	1.01237400
C	-2.14178800	-1.26239000	-1.09130900
C	-4.14957200	-2.46522900	0.38255100
H	-2.91645200	-2.09483400	2.08000800

C	-3.28620900	-1.72363900	-1.72397100
H	-1.37503600	-0.78216200	-1.67123300
C	-4.29490900	-2.33007200	-0.99037000
H	-4.93204400	-2.91793600	0.96586500
H	-3.39052000	-1.60430800	-2.78801600
H	-5.18583800	-2.68214500	-1.47939100
C	2.59791900	2.34893000	-0.94113400
H	3.31709300	1.57205000	-1.14325700
H	2.32503100	2.81739500	-1.88047800
H	3.06078100	3.09387400	-0.30209600

HF/3-21+G

****

***4o** (C1)*

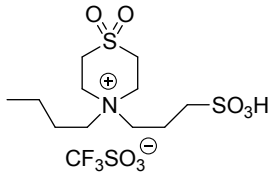
Hf= -931.3633158

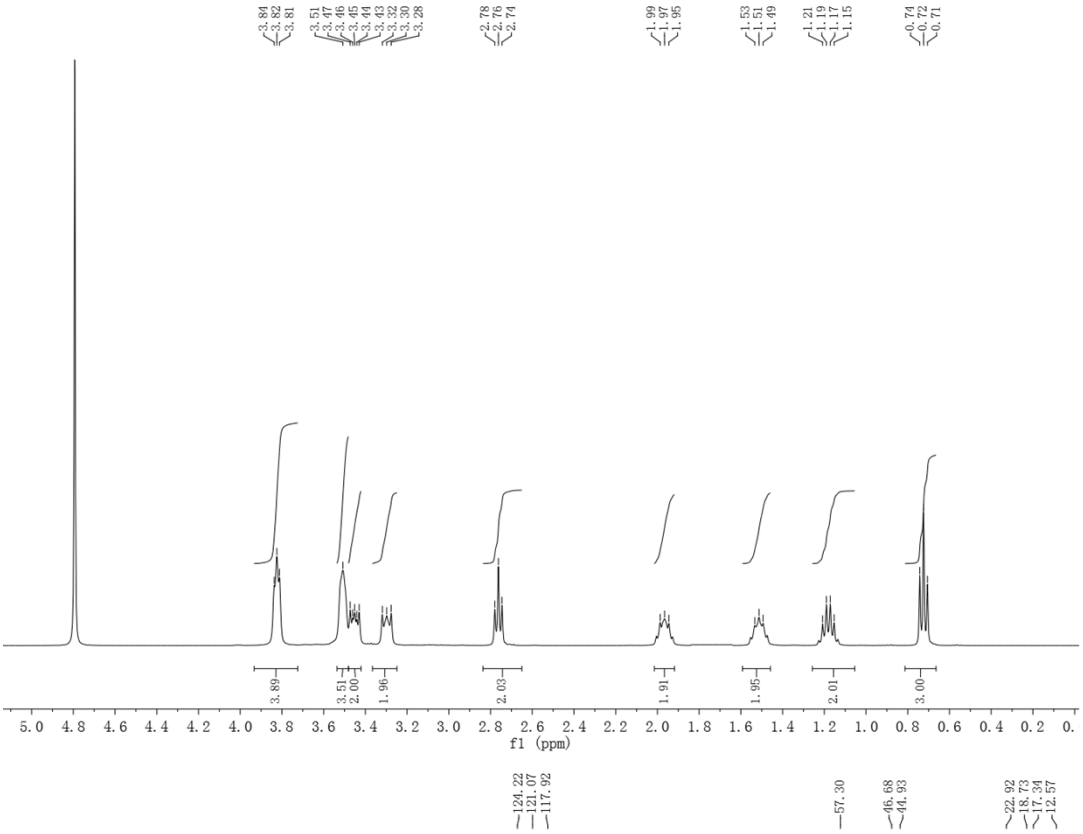
C	0.29855700	3.76988400	0.28734300
C	-0.08936000	2.44553500	0.10142300
C	0.80779300	1.46625100	-0.34909000
C	2.13104100	1.81876800	-0.61853100
C	2.51875900	3.13074600	-0.44331900
C	1.60939800	4.09771000	0.00974200
H	-0.39468800	4.51393200	0.62898700
H	2.83370000	1.08428900	-0.95936800
H	3.53161300	3.41920200	-0.64959000
H	1.93963800	5.11074400	0.13960400
C	0.06161900	0.22627600	-0.45077400
C	-1.21137300	0.49970100	-0.05411100
N	-1.32072700	1.84850000	0.28996900
C	-2.37200100	-0.41367500	0.04662000
C	-2.43242200	-1.35634300	1.06530100
C	-3.40449600	-0.34446000	-0.88344700
C	-3.50783000	-2.22825100	1.14828000
H	-1.63699900	-1.41068300	1.78410500
C	-4.47935100	-1.21519800	-0.79953500
H	-3.35527000	0.37815600	-1.67719300
C	-4.53145800	-2.16012900	0.21575800
H	-3.54439500	-2.95770000	1.93465600
H	-5.26864500	-1.16165900	-1.52503300
H	-5.36178900	-2.83721900	0.27750700

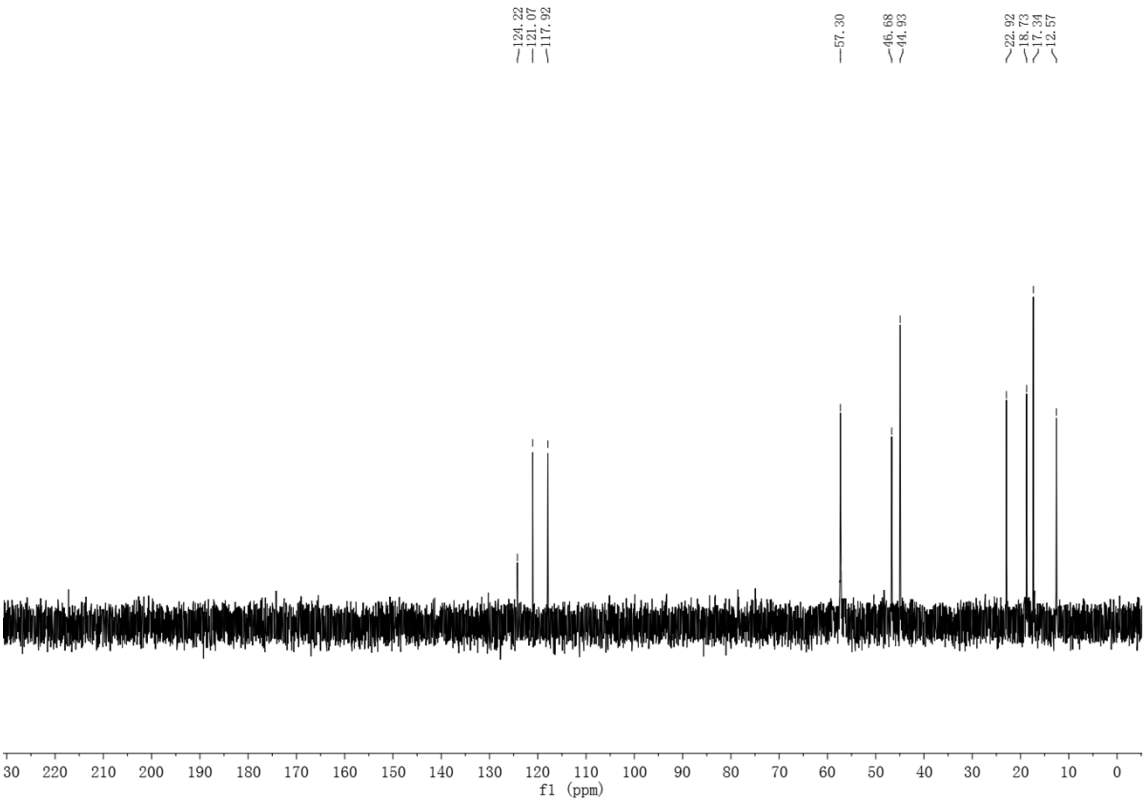
C	0.60622900	-1.07333700	-0.90343500
C	0.00568400	-1.81495800	-1.82875200
H	-0.89325600	-1.48876300	-2.31525200
H	0.38692500	-2.77944900	-2.10974800
C	1.88714400	-1.50615800	-0.26359000
C	2.90477900	-2.08833700	-1.01336500
C	2.07794200	-1.33126600	1.10534900
C	4.08367100	-2.49637600	-0.40604600
H	2.78307100	-2.20153200	-2.07393100
C	3.25026100	-1.74645100	1.71353200
H	1.30830100	-0.86679900	1.69085300
C	4.25973800	-2.32790600	0.95866000
H	4.86362900	-2.93615800	-0.99856800
H	3.38008200	-1.61150300	2.77068600
H	5.17278500	-2.64120400	1.42798400
C	-2.49486800	2.53562900	0.82040500
H	-3.27865500	1.81658000	1.00188200
H	-2.24489600	3.02443900	1.75607400
H	-2.85279600	3.27988900	0.11603800

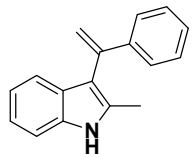
****

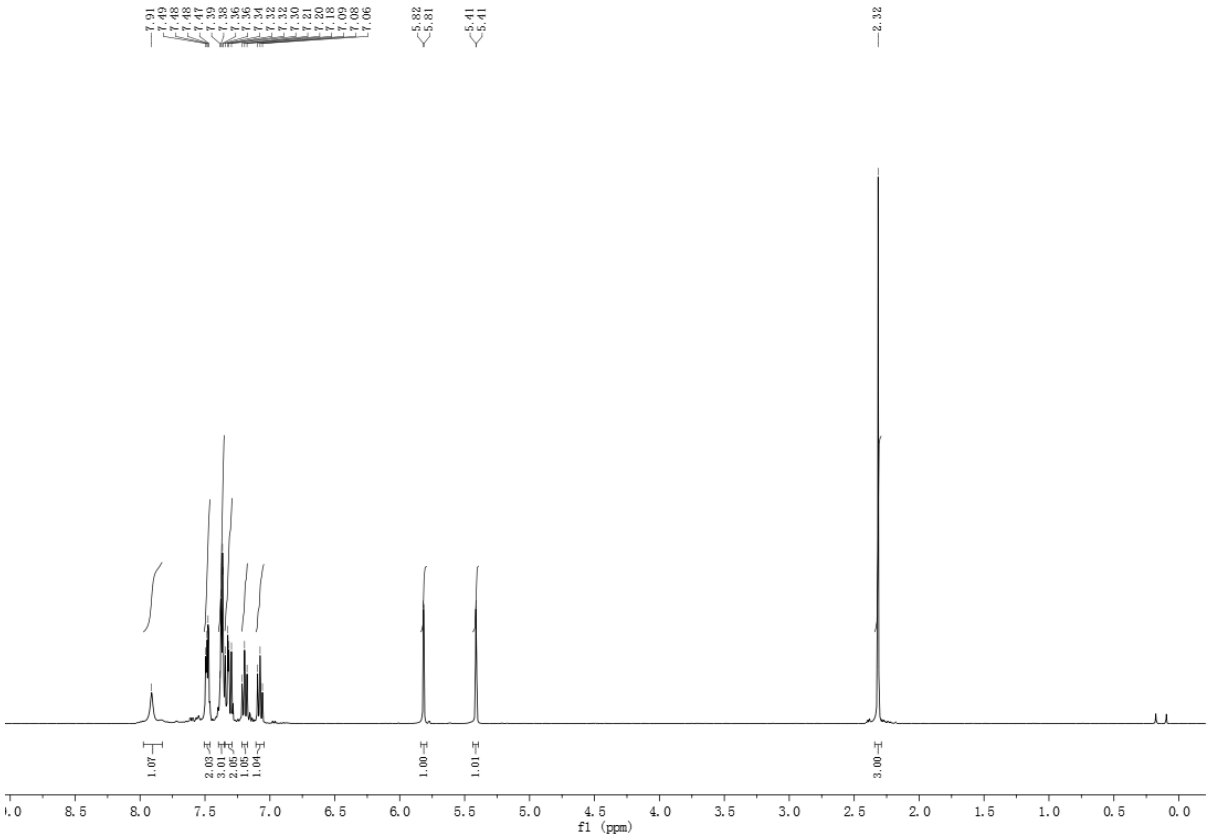
Copy of ^{1}H and ^{13}C NMR Spectra







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7.49
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7.48
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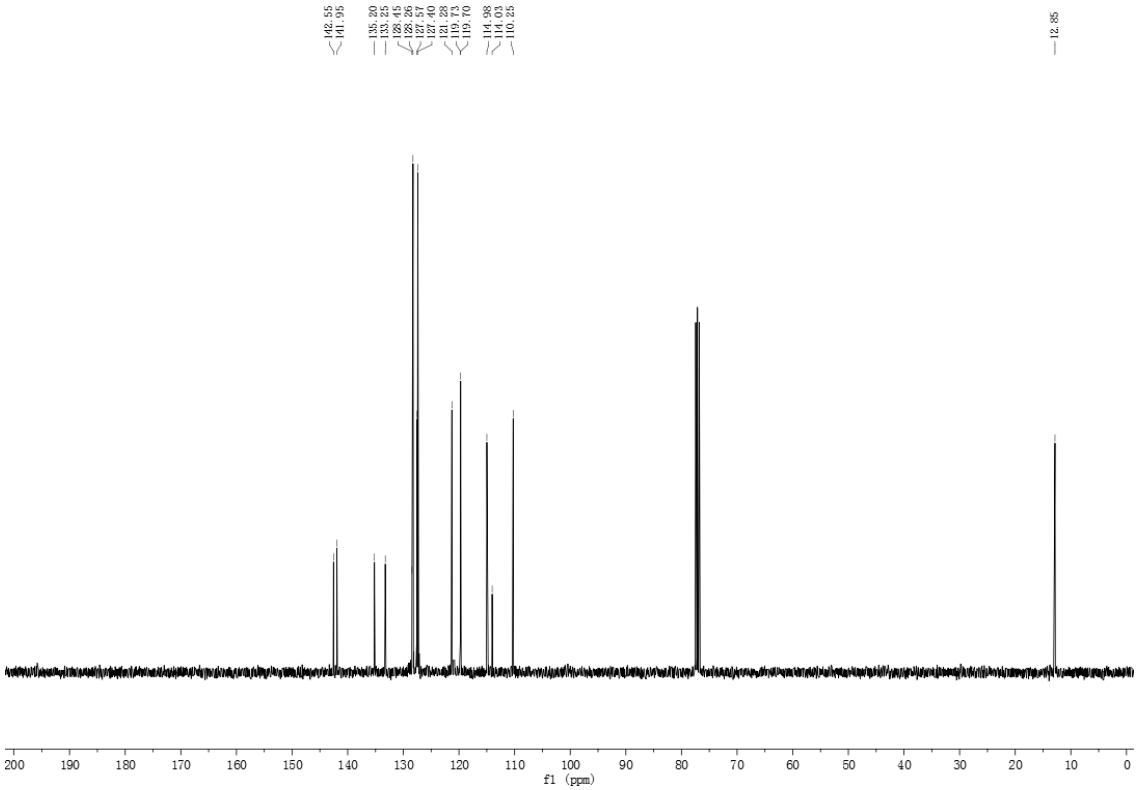
7.38
7.36
7.36
7.34
7.32
7.32
7.30
7.21
7.20
7.18
7.09
7.08
7.06
5.82
5.81
5.41
5.41
2.32
1.07
2.03
3.01
2.05
1.05
1.04
1.00
1.01
3.00
f1 (ppm)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141.95
135.20
133.25
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128.26
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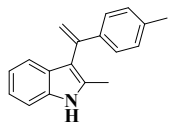
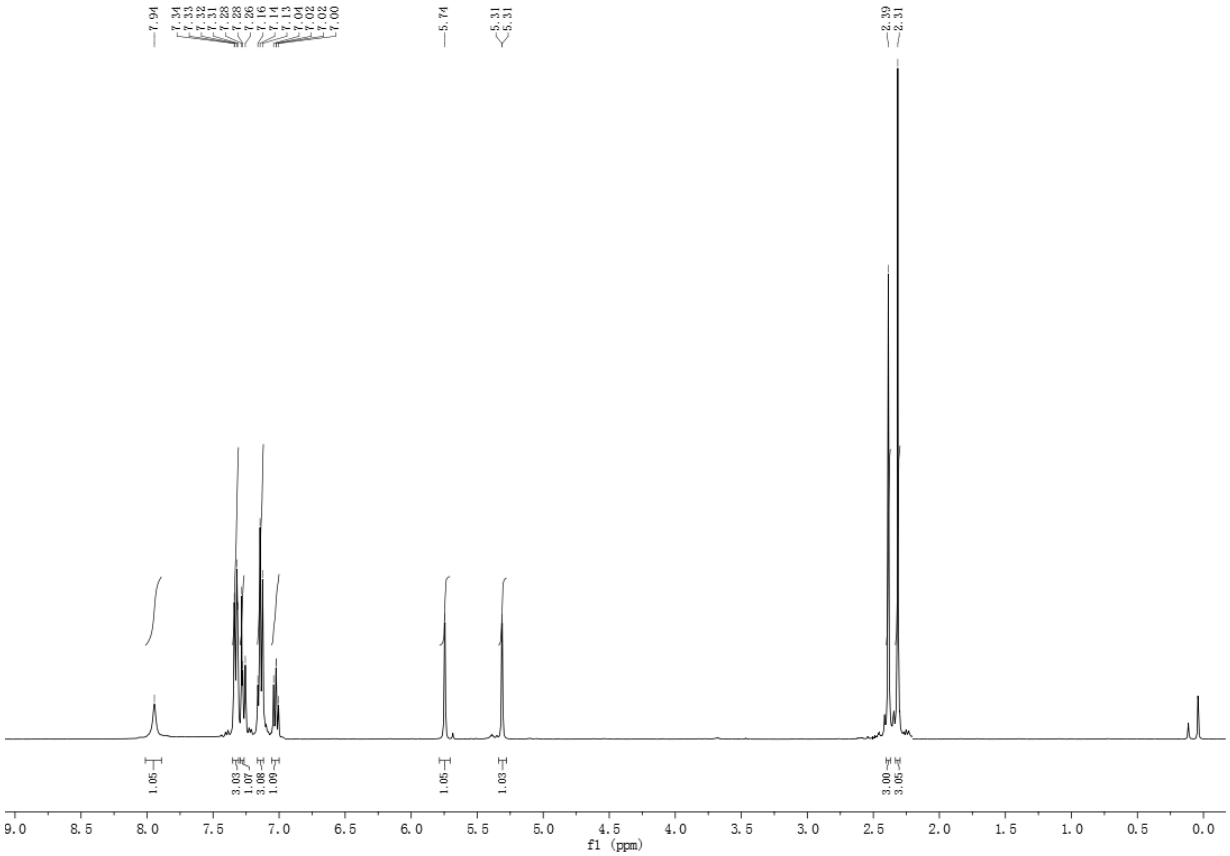
127.40
121.23
119.73
119.70
114.98
114.03
110.25
12.85
f1 (ppm)

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7.32
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7.16
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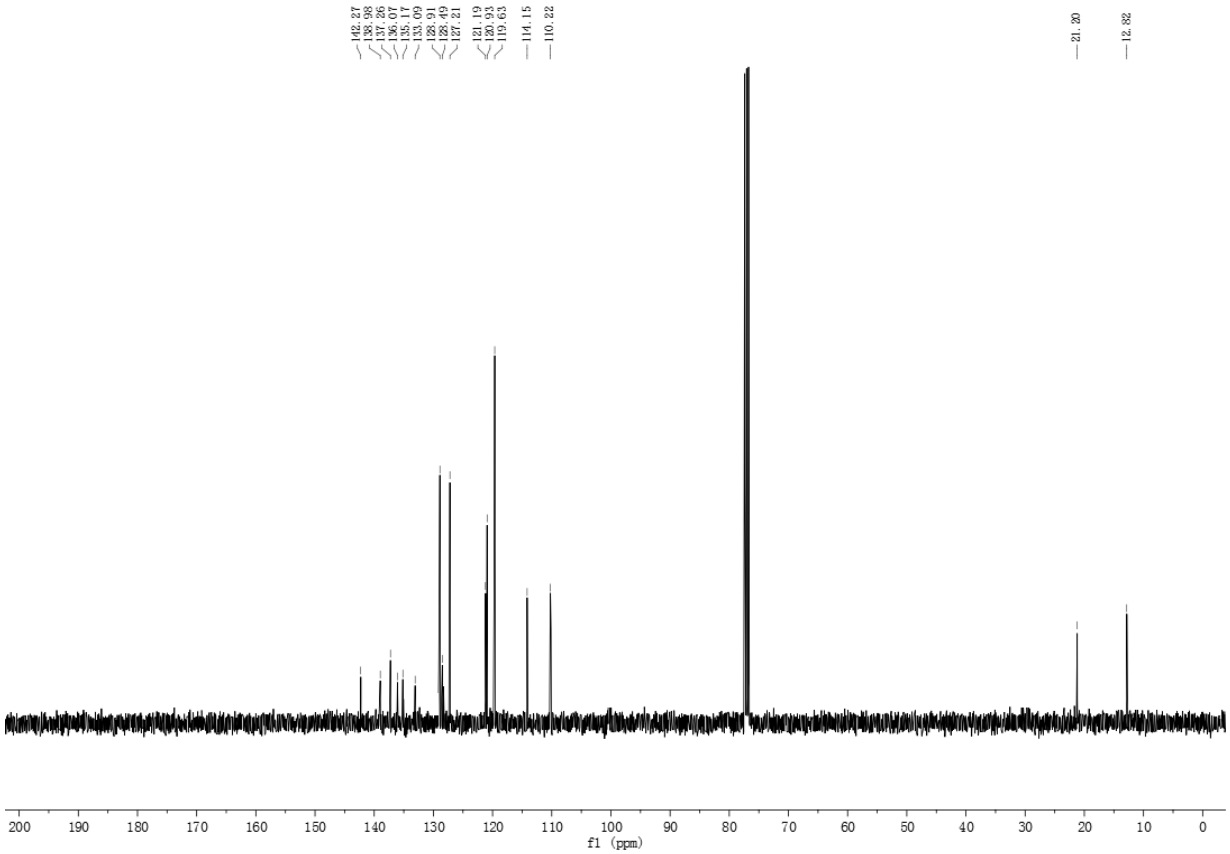
7.13
7.04
7.02
7.00
5.74
5.31
5.31
2.39
2.31
1.05
3.03
1.07
3.08
1.09
1.05
1.03
3.00
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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133.09
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128.49
127.21
121.19
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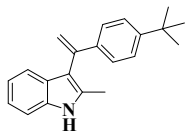
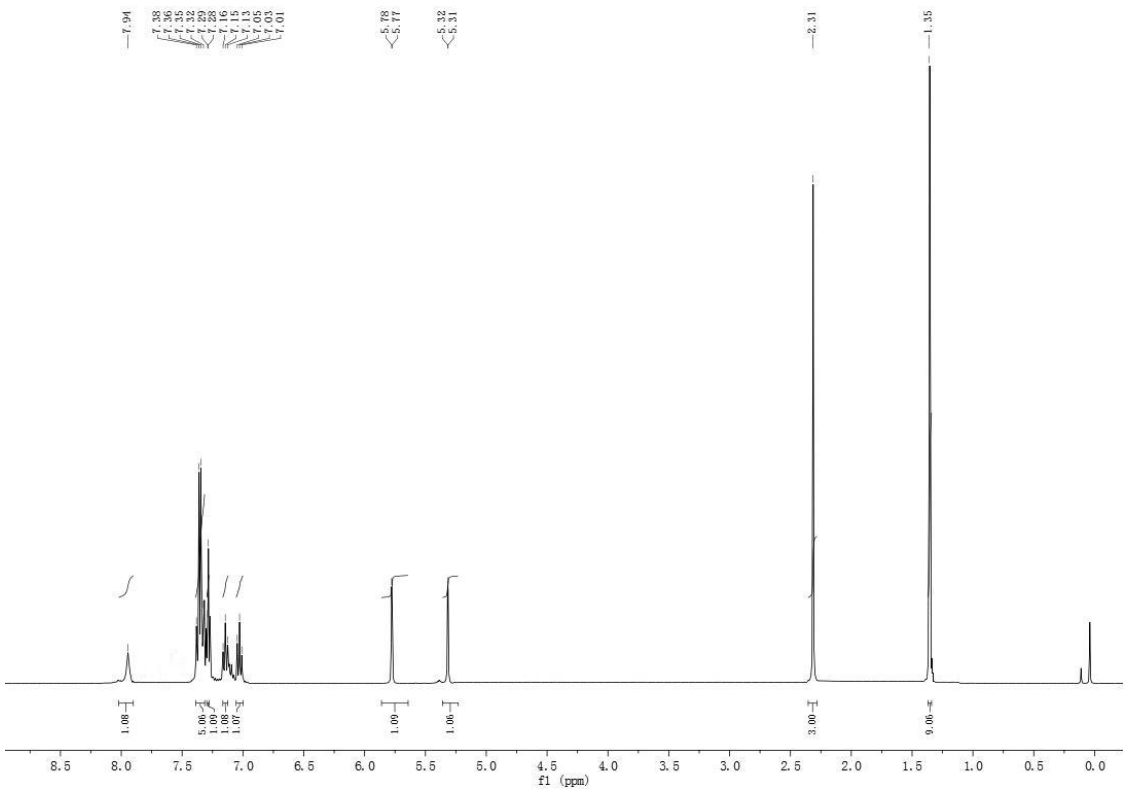
114.15
110.22
21.20
12.82
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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7.13
7.05
7.03
7.01
5.78
5.77
5.32
5.31
2.31
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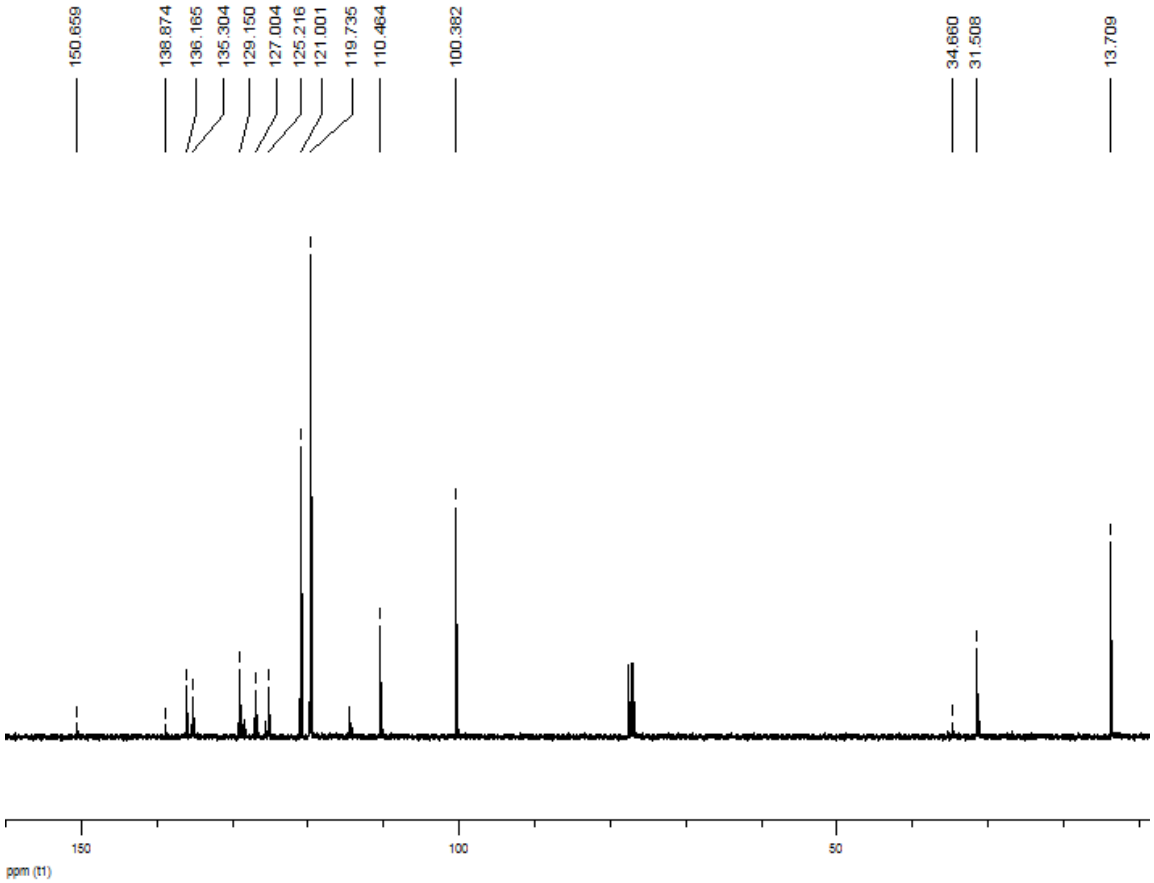
1.07
1.09
1.06
3.00
9.06
f1 (ppm)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125.216
121.001
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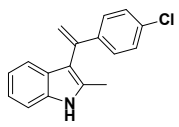
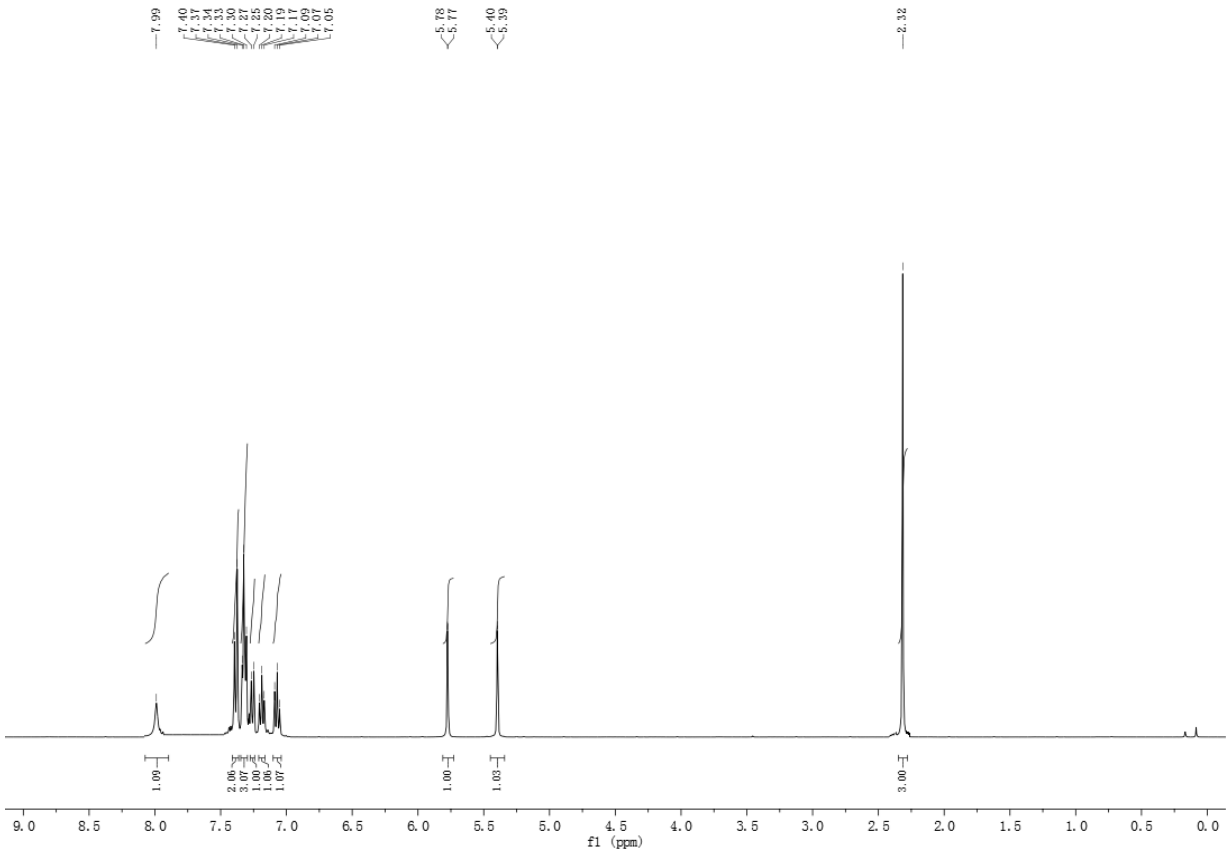
110.464
100.382
34.660
31.508
13.709
ppm (t1)


Cl
N
H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7.25
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7.19
7.17
7.09
7.07
7.05
5.78
5.77
5.40
5.39
2.32
1.09
2.06
3.07
1.00
1.06
1.07
1.00
1.03
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
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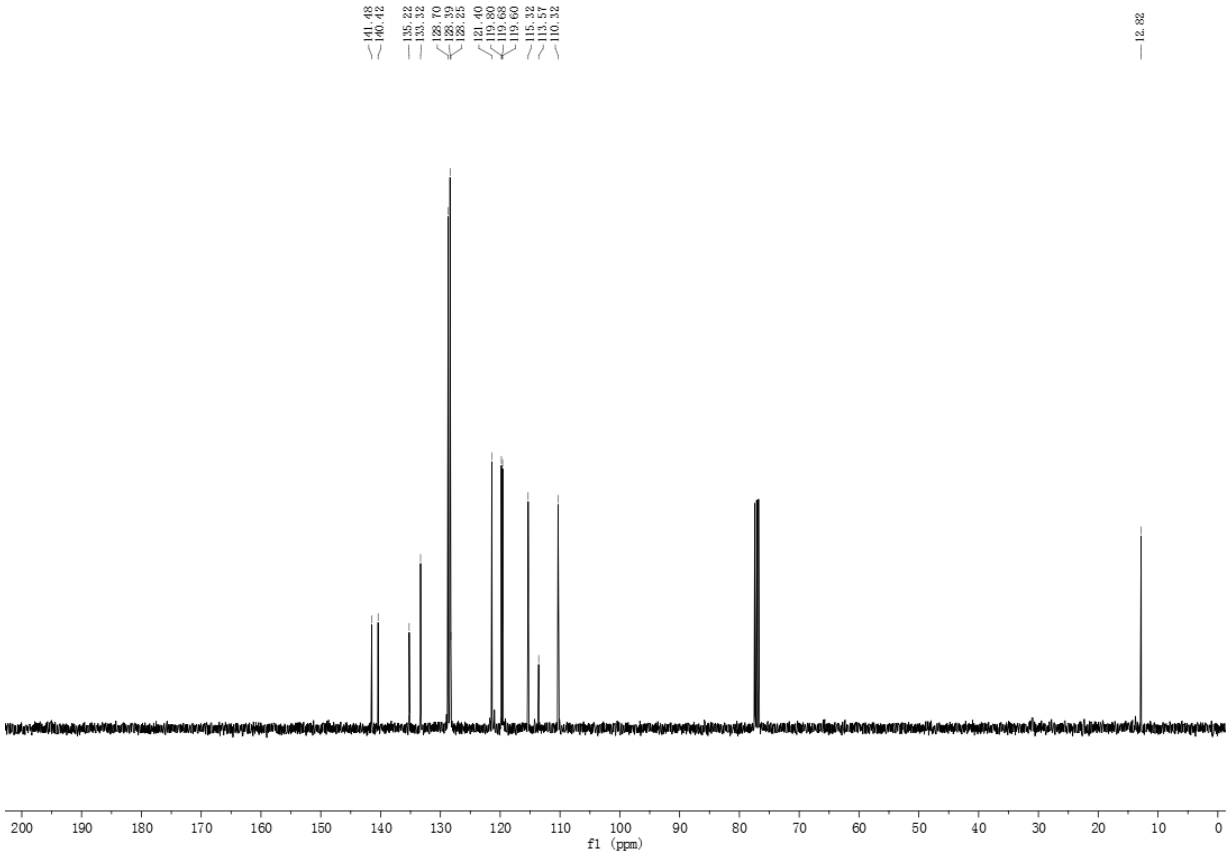
0.0
f1 (ppm)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135.22
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128.70
128.39
128.25
121.40
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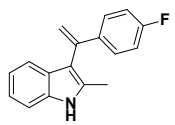
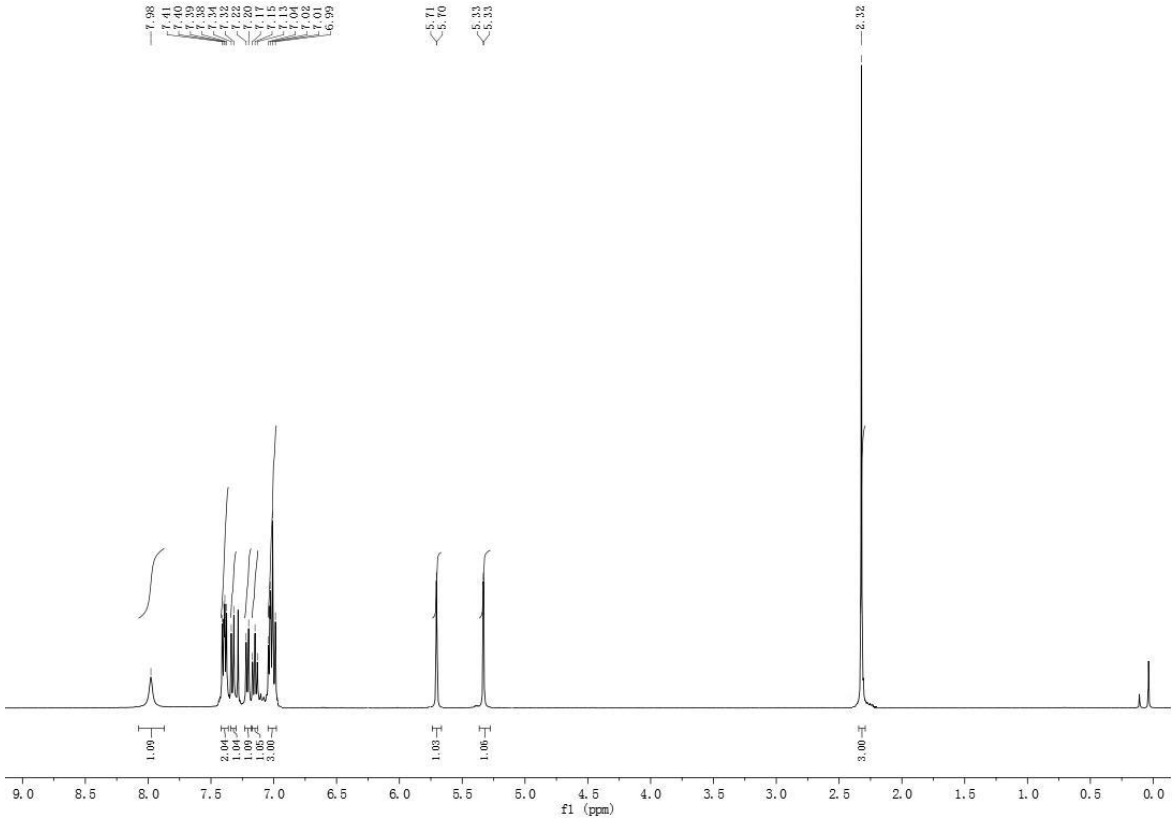
119.68
119.60
115.32
113.57
110.32
12.82
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
N
H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7.38
7.34
7.32
7.22
7.20
7.17
7.15
7.13
7.04
7.02
7.01
6.99
5.71
5.70
5.33
5.33
2.32
1.09
2.04
1.04
1.09
1.05
3.00
1.03
1.06
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
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1.0
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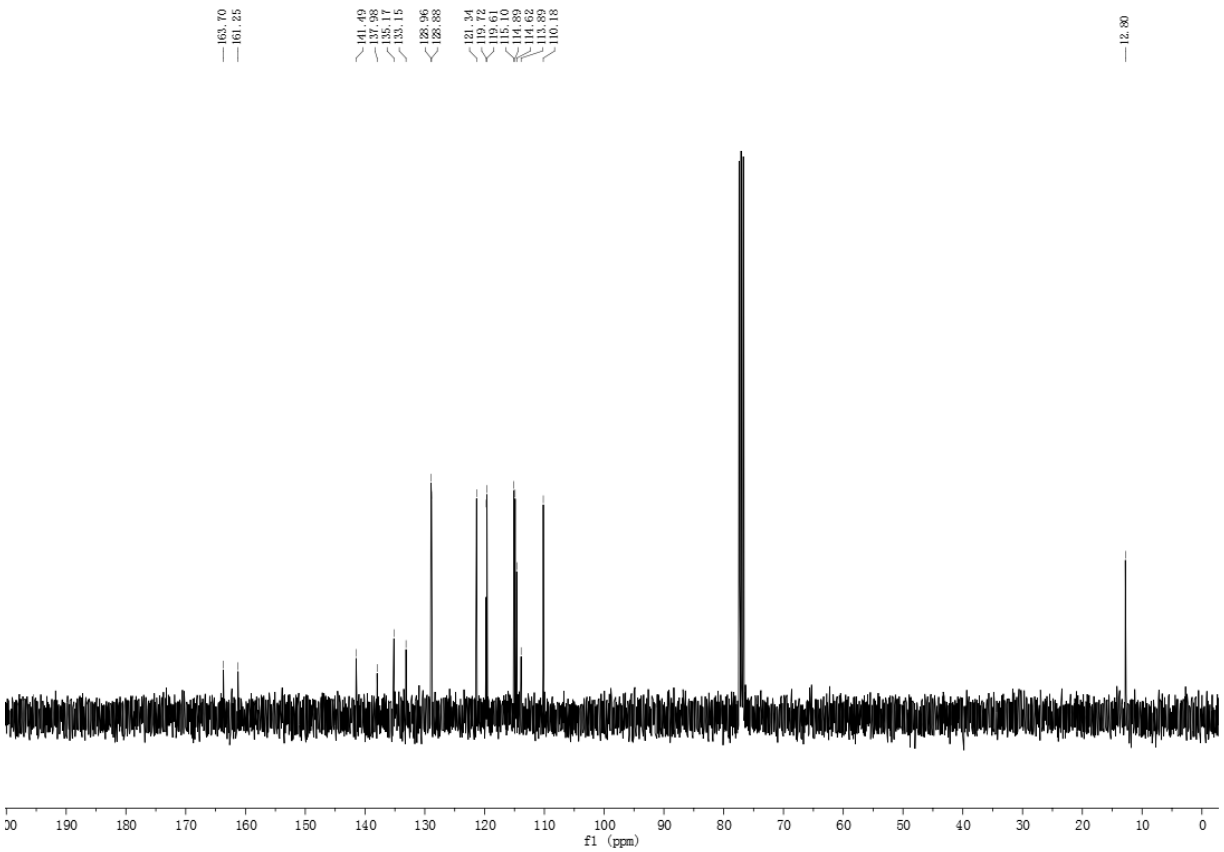
0.0
f1 (ppm)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128.88
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114.89
114.62
113.89
110.18
12.80
190
180
170
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150
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130
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50
40
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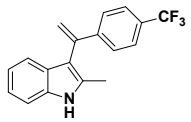
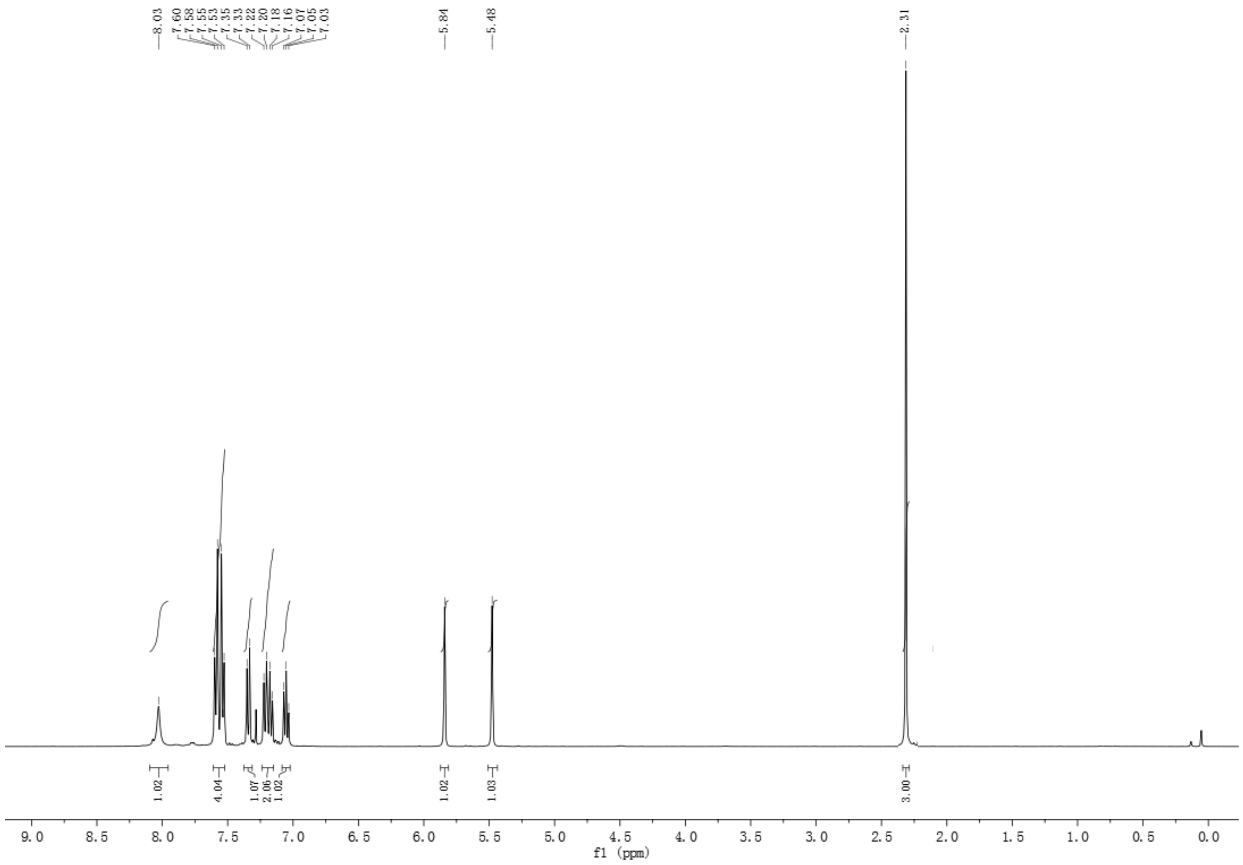
10
0
f1 (ppm)


CF3
N
H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7.07
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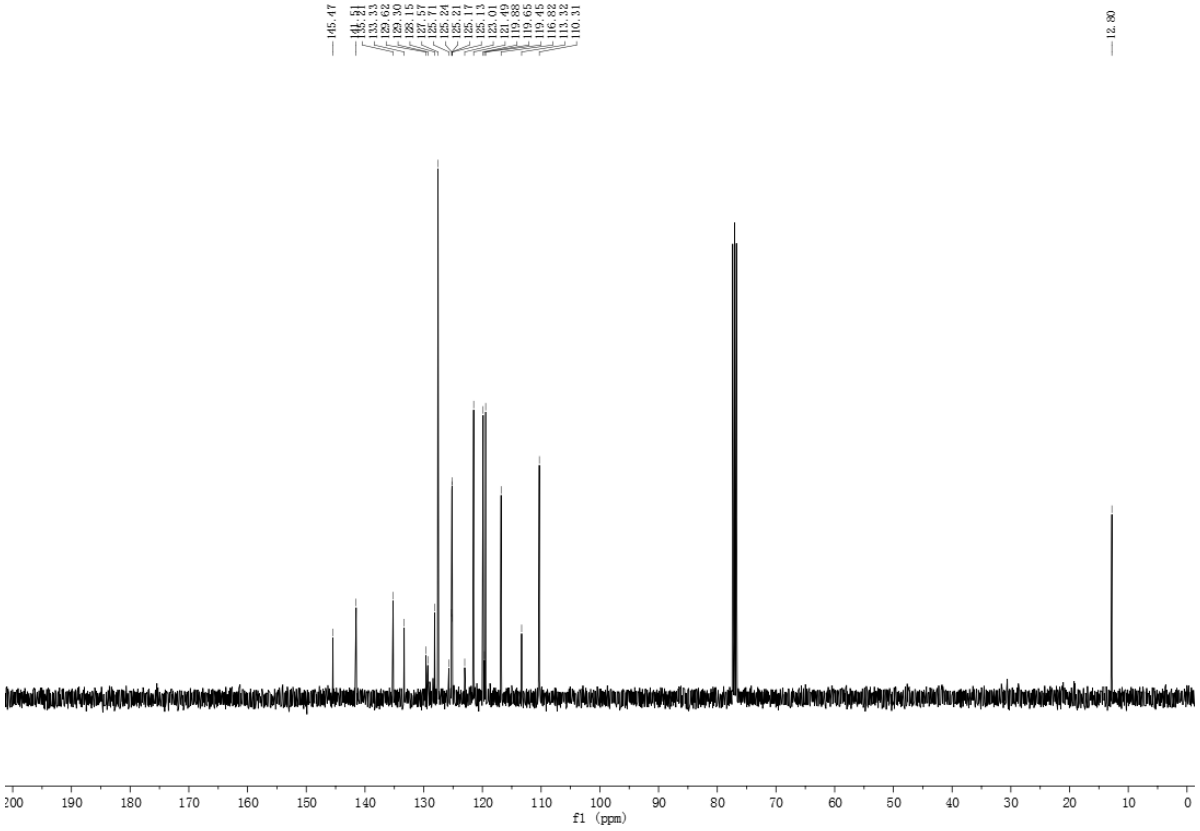
1.02
1.02
1.03
3.00
f1 (ppm)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125.21
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121.49
119.88
119.65
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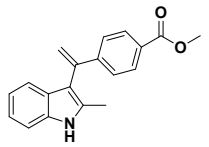
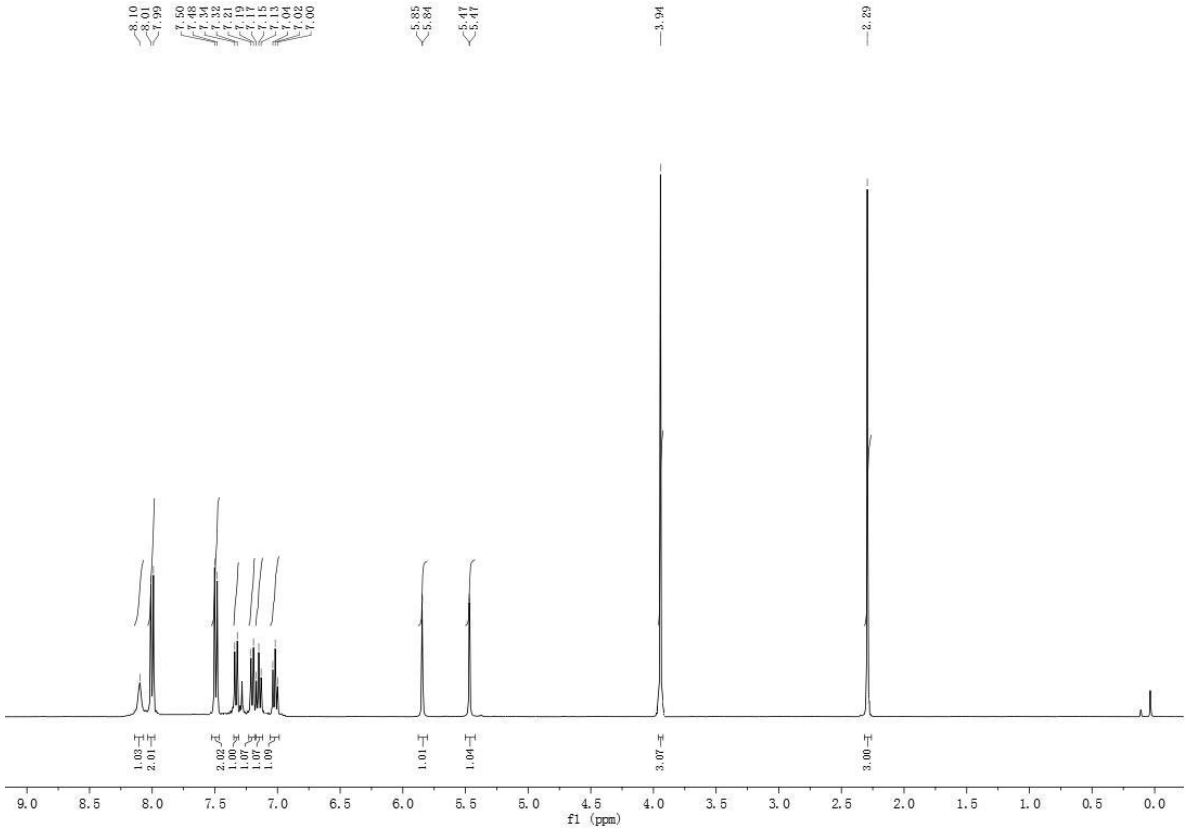
113.32
110.31
12.80
f1 (ppm)


O
O
N
H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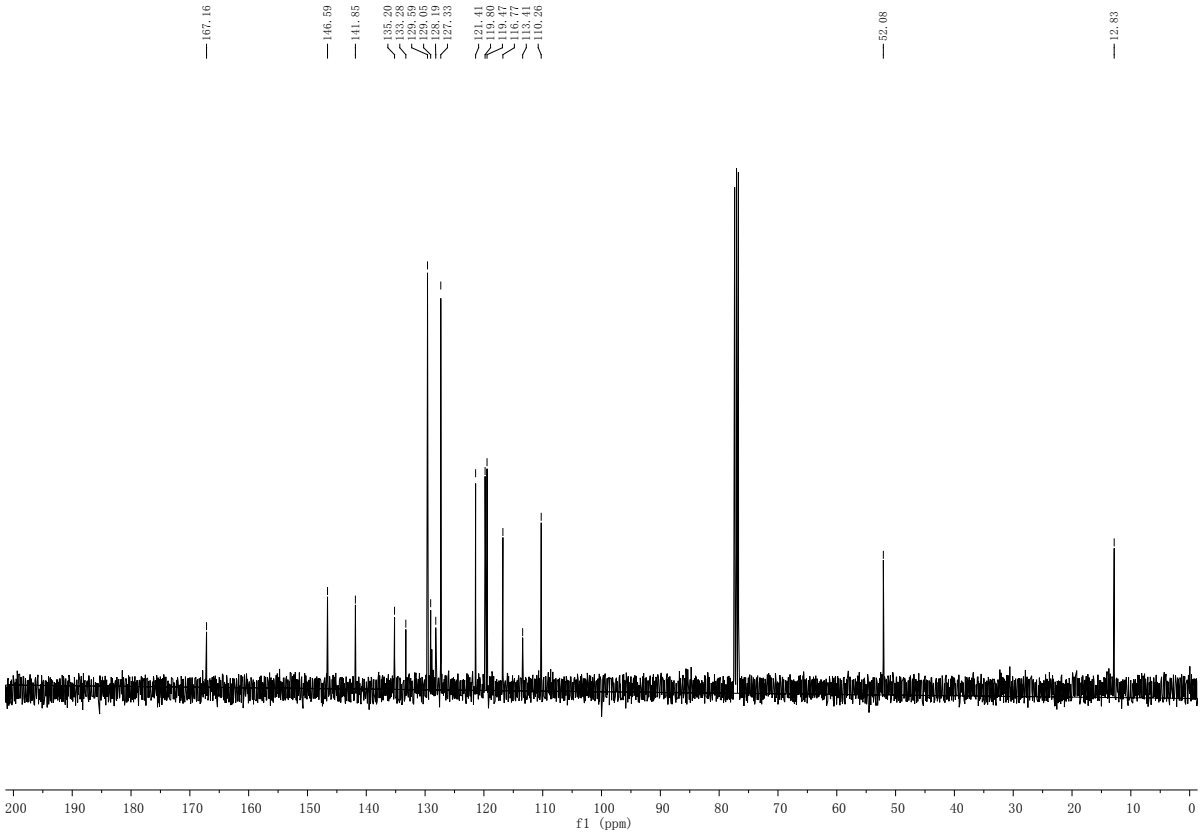
7.34
7.32
7.21
7.19
7.17
7.15
7.13
7.04
7.02
7.00
5.85
5.84
5.47
5.47
3.94
2.29
1.03
2.01
2.02
1.00
1.07
1.07
1.09
1.01
1.04
3.07
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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121.41
119.80
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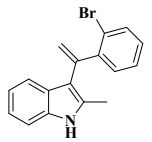
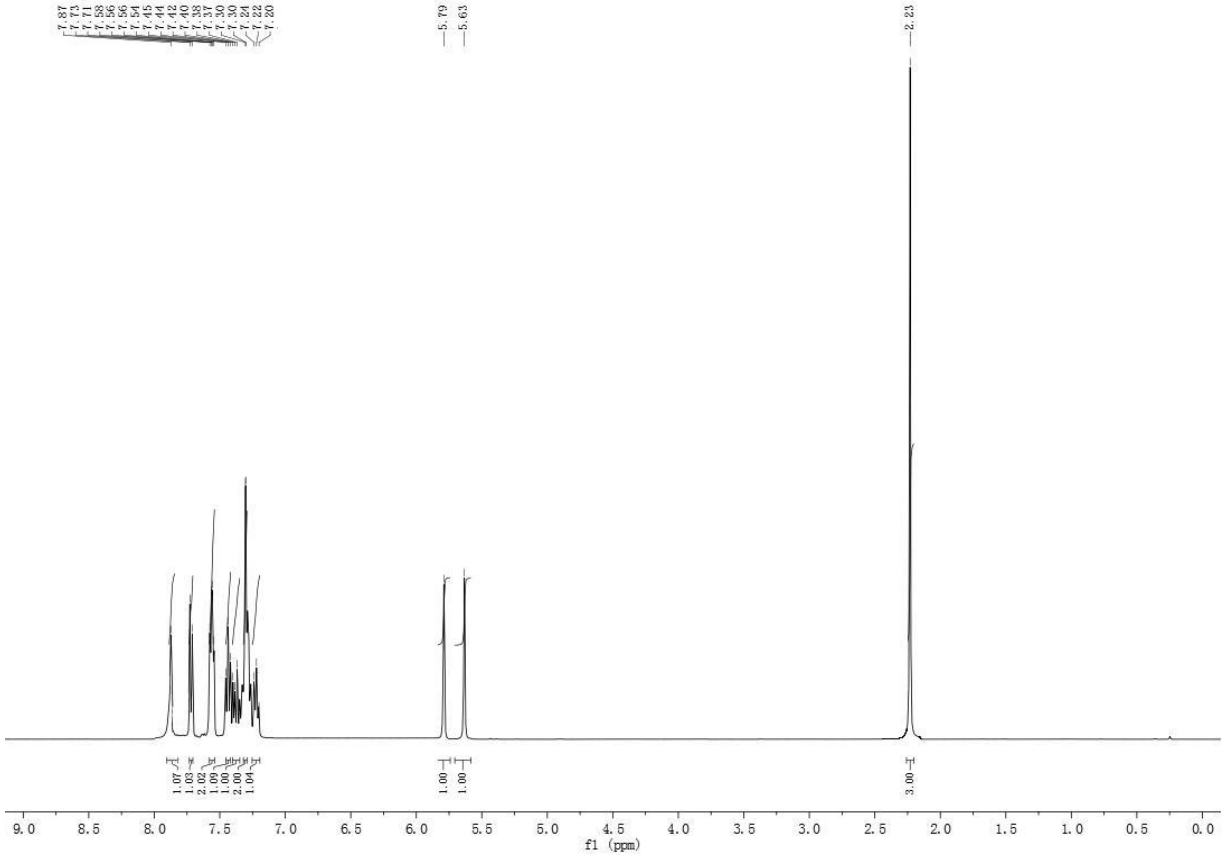
113.41
110.26
52.08
12.83
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
N
H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7.24
7.22
7.20
5.79
5.63
2.23
1.07
1.03
2.02
1.09
1.00
2.00
1.04
1.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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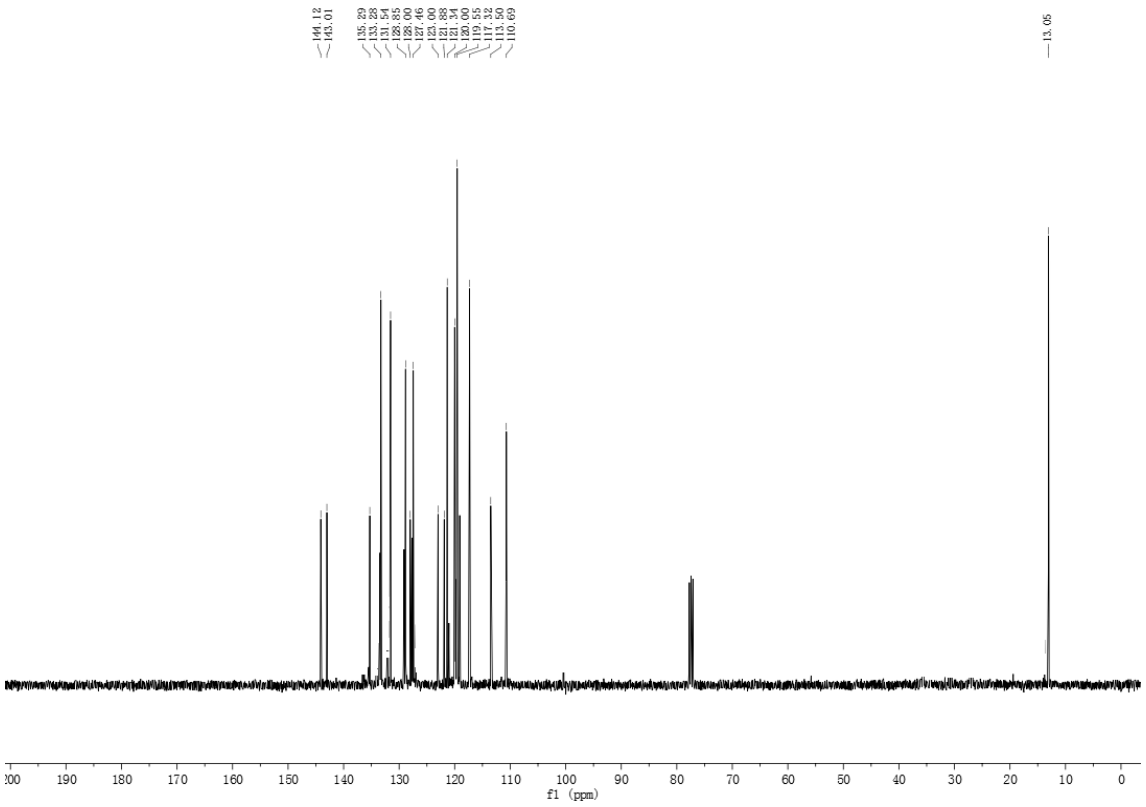
f1 (ppm)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200
190
180
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50
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30
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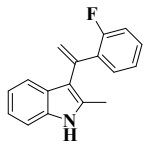
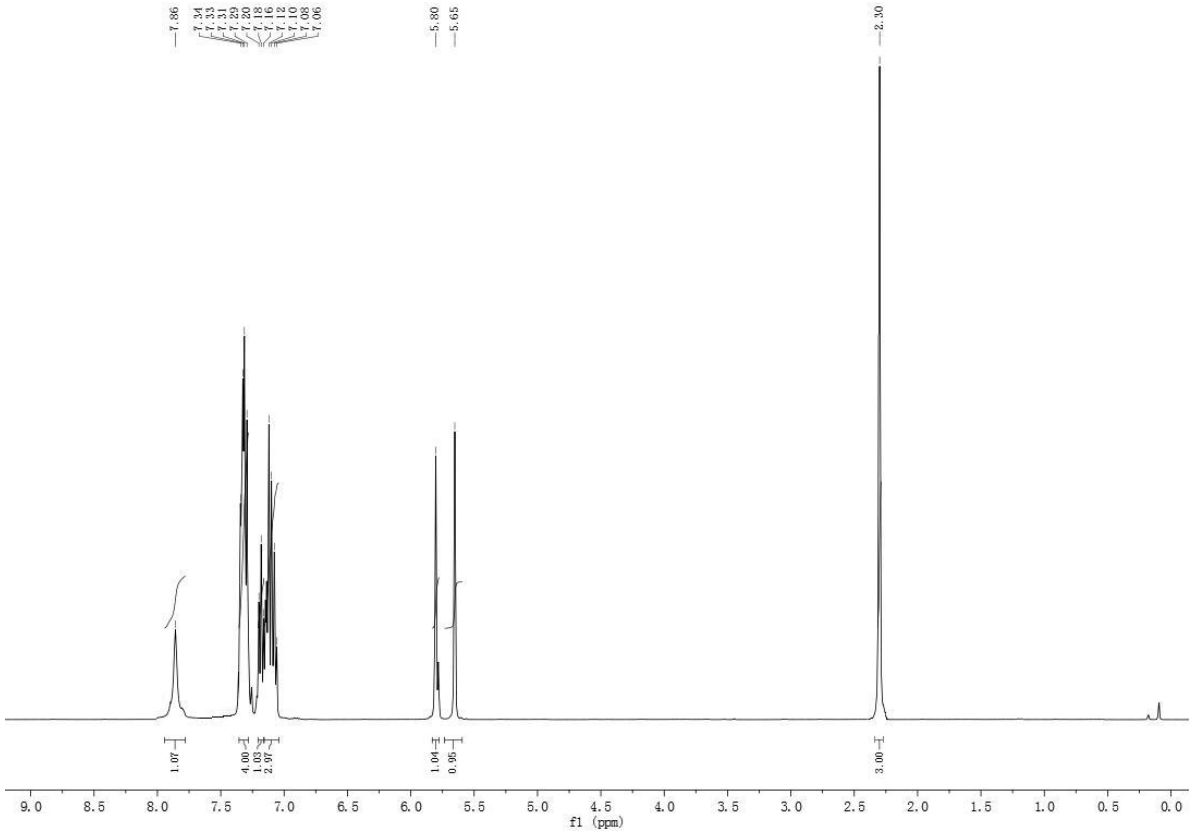
10
0
f1 (ppm)


F
N
H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7.08
7.06
5.80
5.65
2.30
1.07
4.00
1.03
2.97
1.04
0.95
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
2.0
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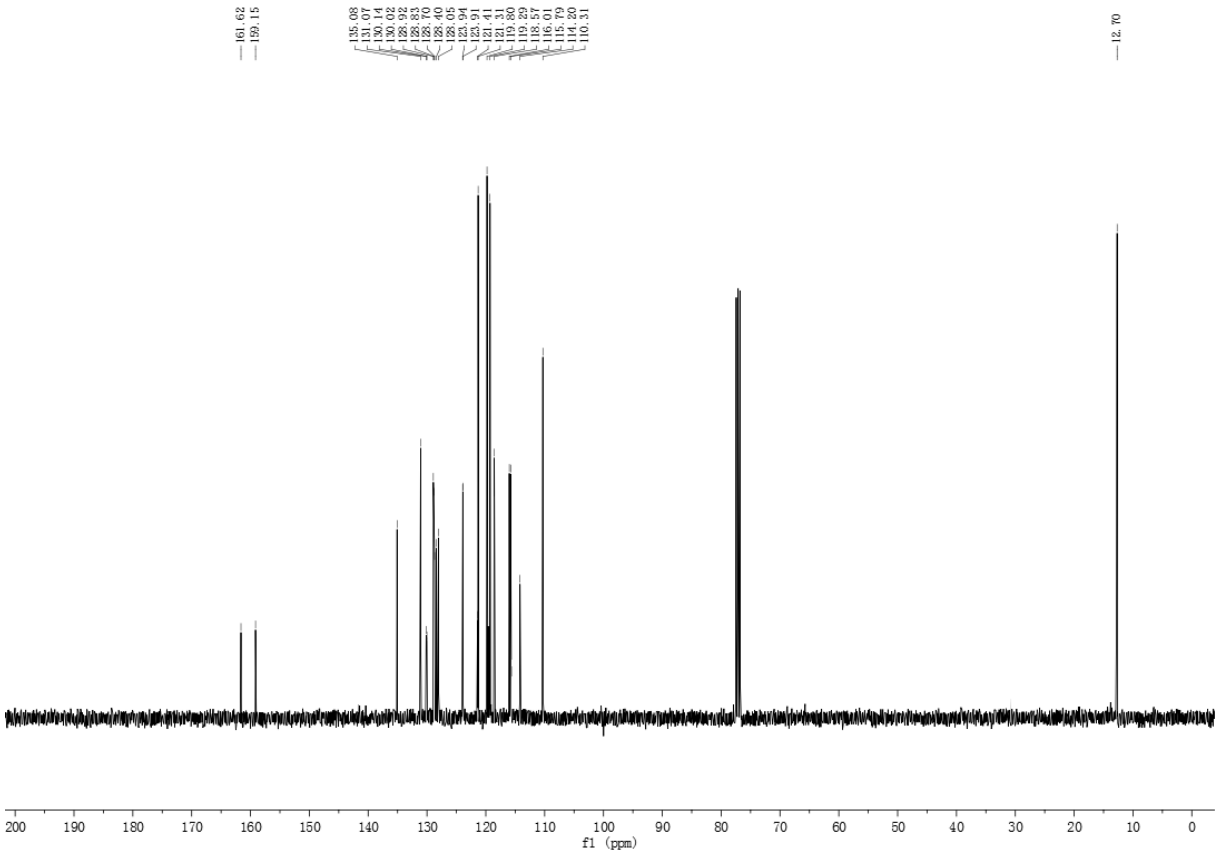
0.0
f1 (ppm)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130.02
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128.83
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128.05
123.94
123.91
121.41
121.31
119.80
119.29
118.57
116.01
115.79
114.20
110.31
12.70
200
190
180
170
160
150
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130
120
110
100
90
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70
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50
40
30
20
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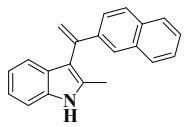
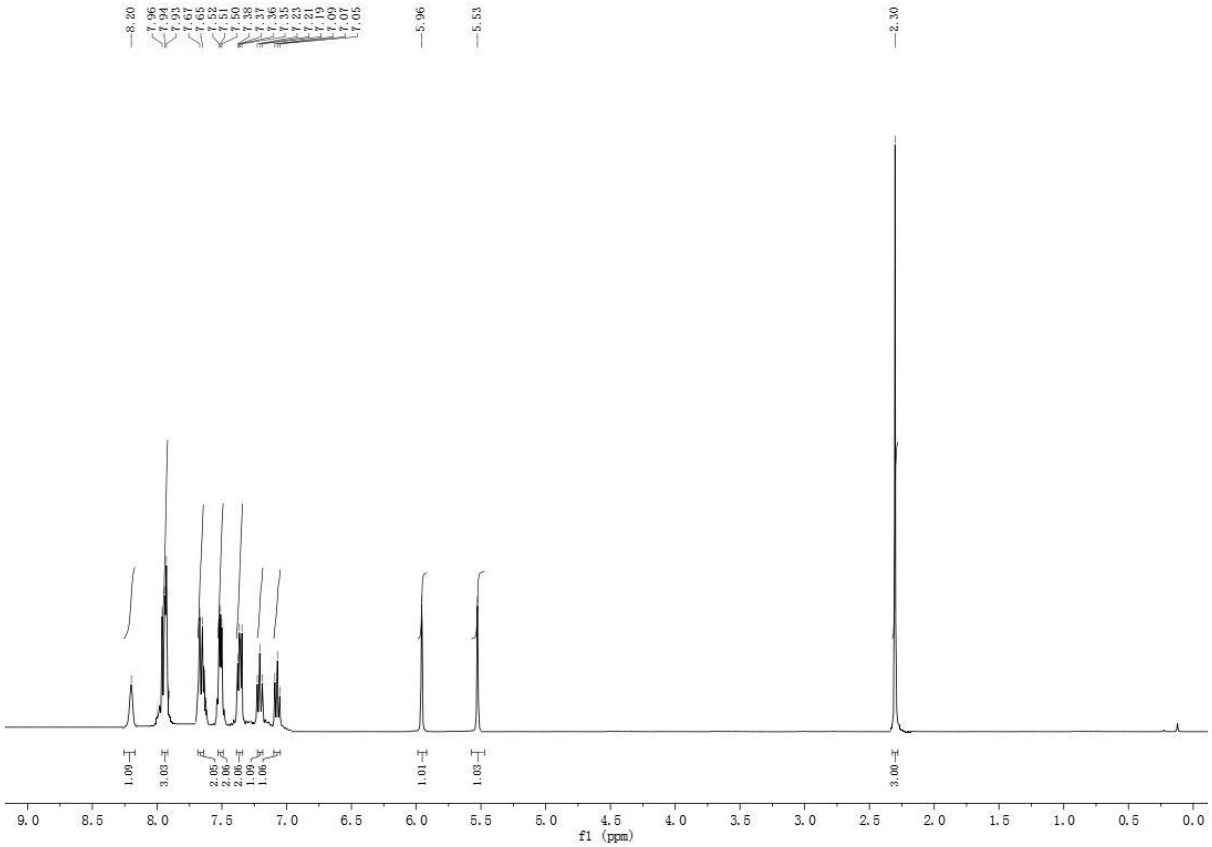
0
f1 (ppm)

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7.51
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7.38
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7.36
7.35
7.23
7.21
7.19
7.09
7.07
7.05
5.96
5.53
2.30
1.09
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2.05
2.06
2.06
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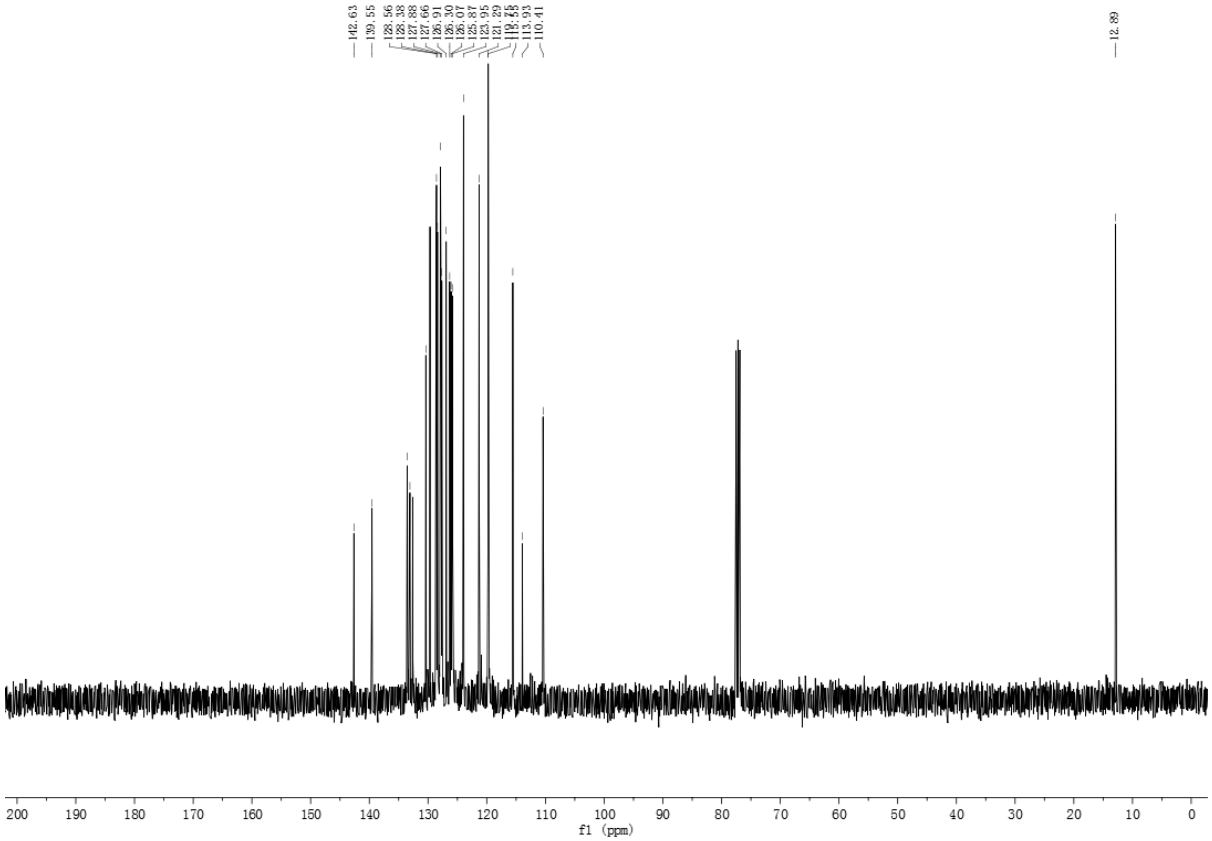
1.06
1.01
1.03
3.00
f1 (ppm)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128.56
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126.70
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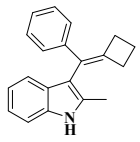
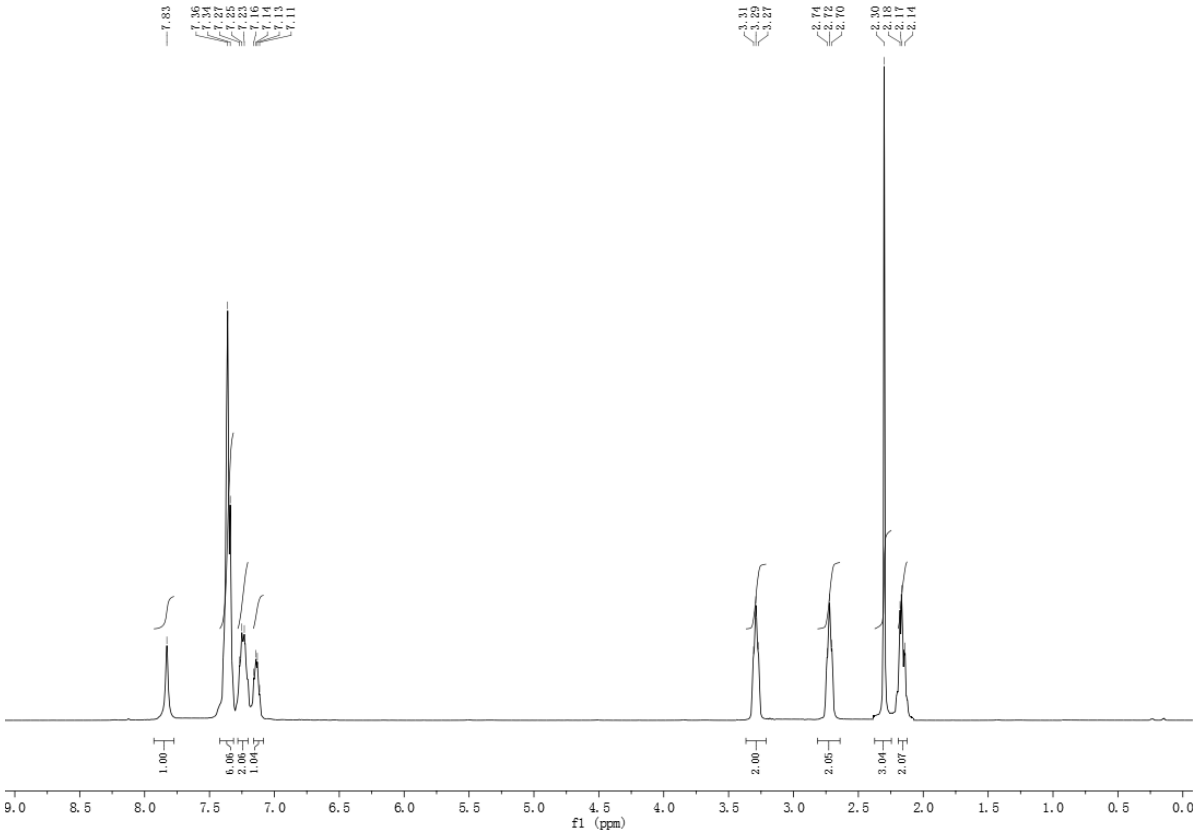
123.95
121.29
113.93
110.41
12.89
f1 (ppm)

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7.23
7.16
7.14
7.13
7.11
3.31
3.29
3.27
2.74
2.72
2.70
2.30
2.18
2.17
2.14
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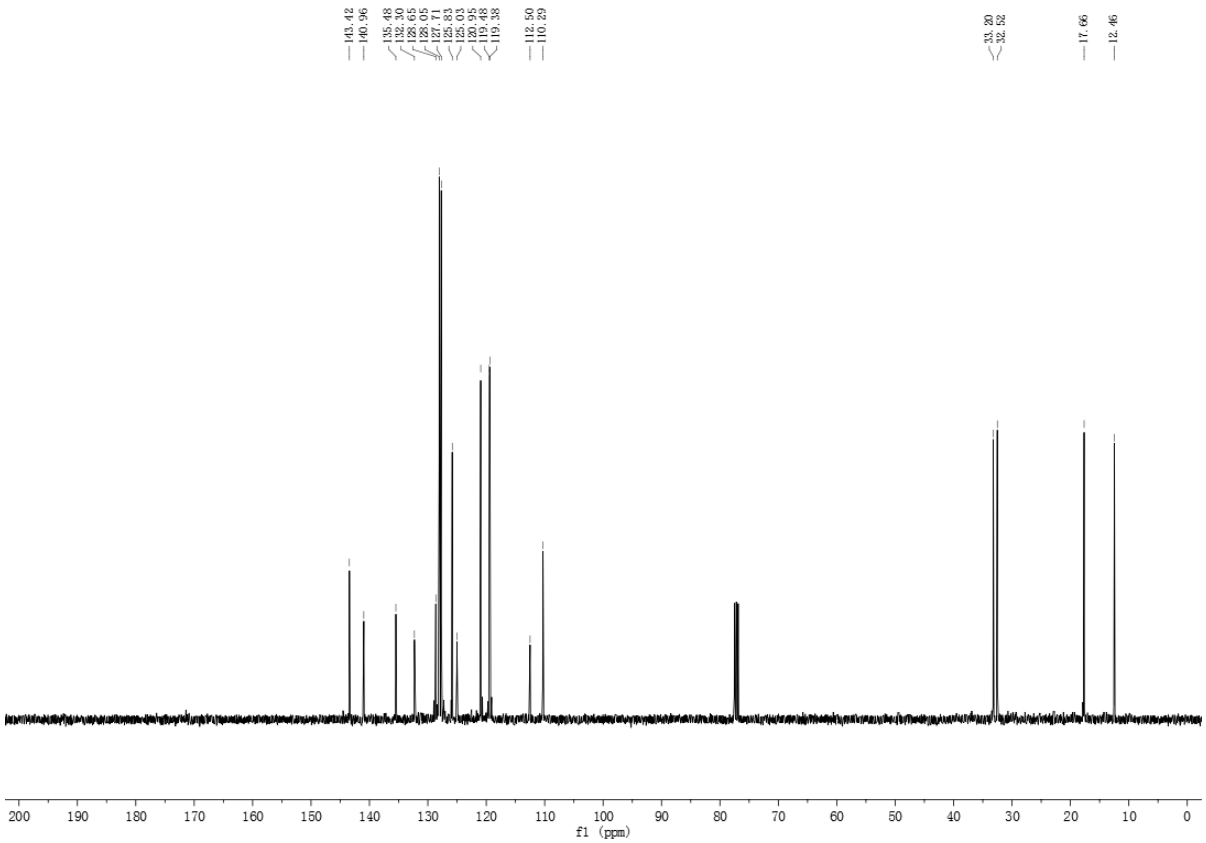
2.06
1.04
2.00
2.05
3.04
2.07
f1 (ppm)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128.05
127.71
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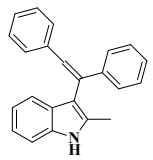
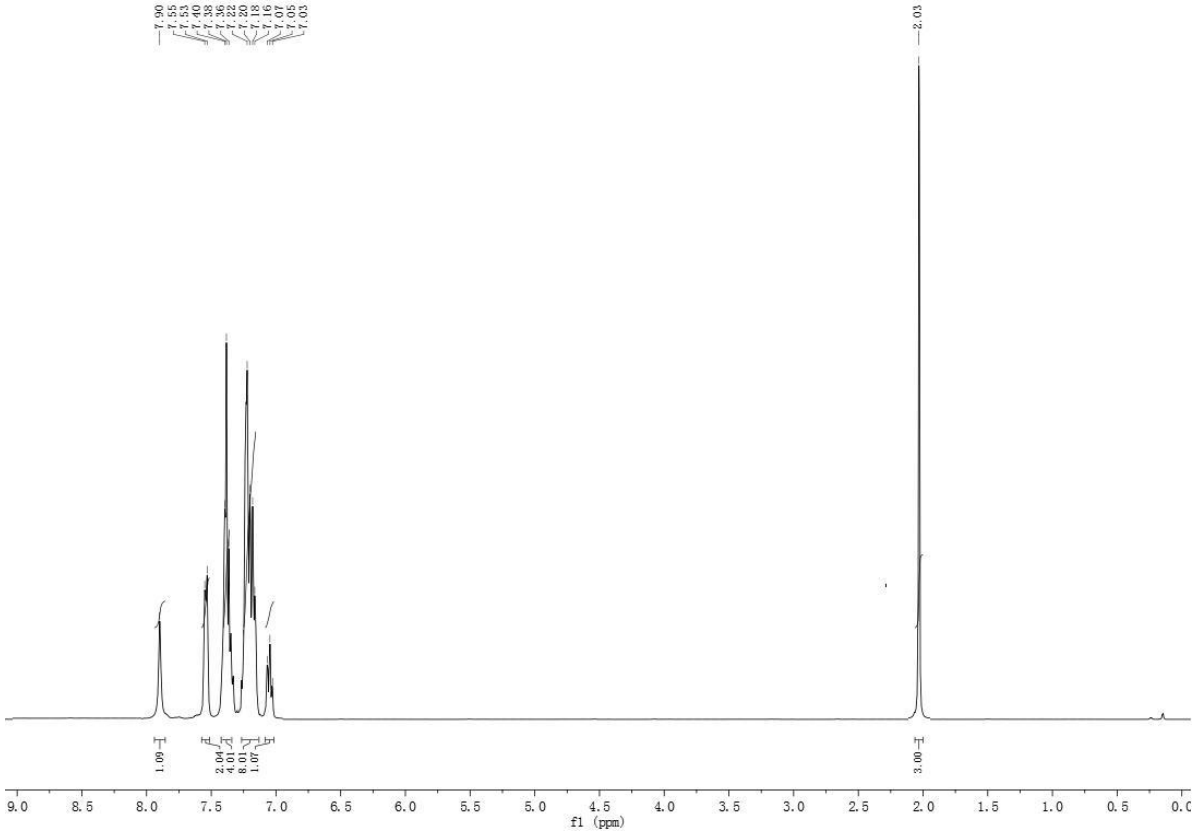
119.48
119.38
112.50
110.29
33.20
32.52
17.66
12.46
f1 (ppm)

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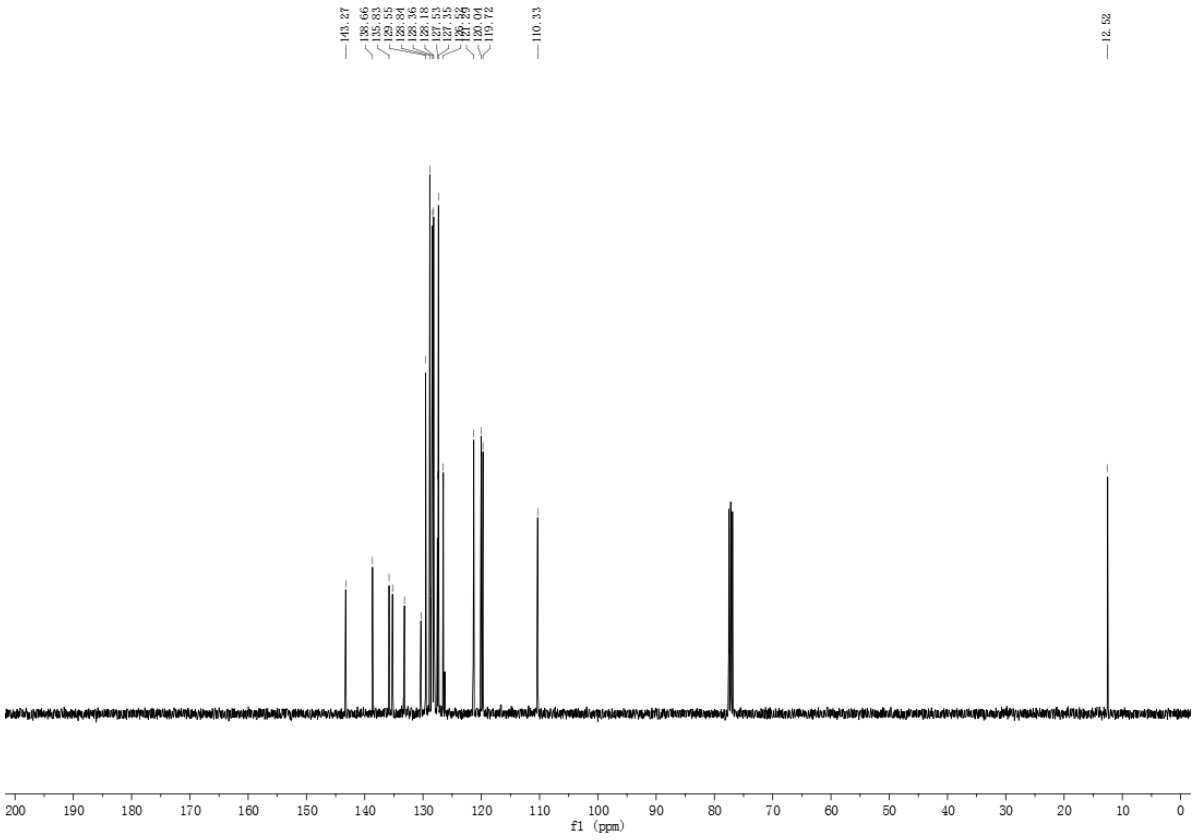
7.22
7.20
7.18
7.16
7.07
7.05
7.03
2.03
1.00
2.04
4.01
8.01
1.07
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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128.84
128.36
128.18
127.53
127.33
120.29
120.04
119.72
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12.52
200
190
180
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150
140
130
120
110
100
90
80
70
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50
40
30
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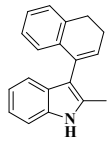
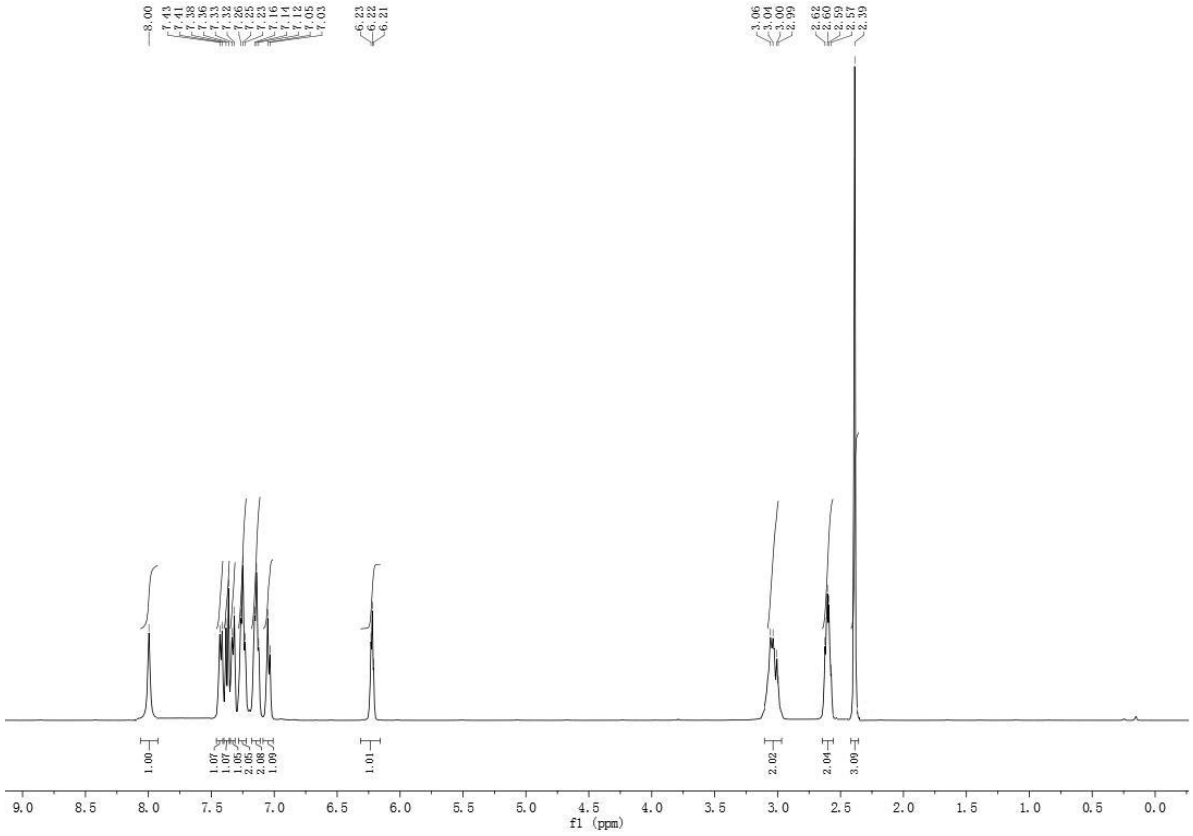
10
0
f1 (ppm)

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7.33
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7.25
7.23
7.16
7.14
7.12
7.05
7.03
6.23
6.22
6.21
3.06
3.04
3.00
2.99
2.62
2.60
2.59
2.57
2.39
1.00
1.07
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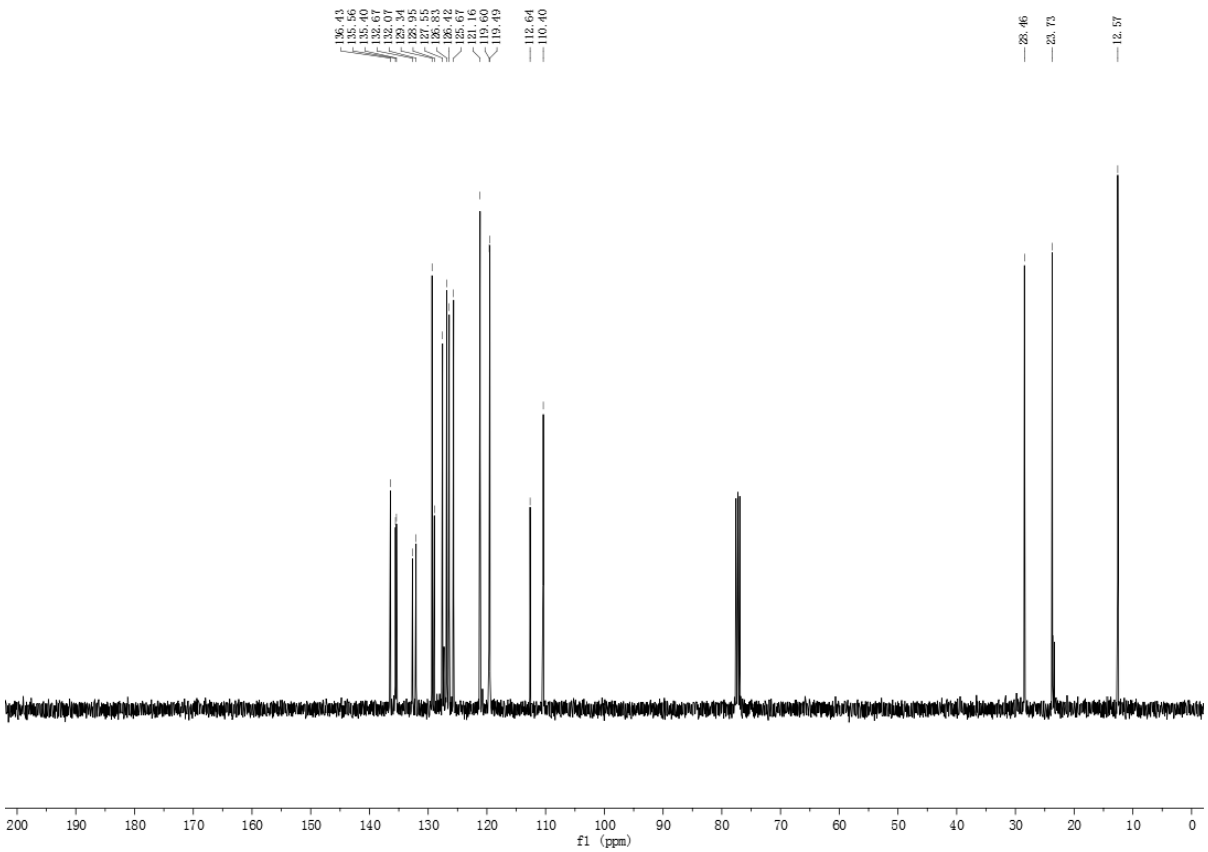
1.01
2.02
2.04
3.09
f1 (ppm)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129.34
128.95
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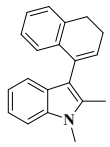
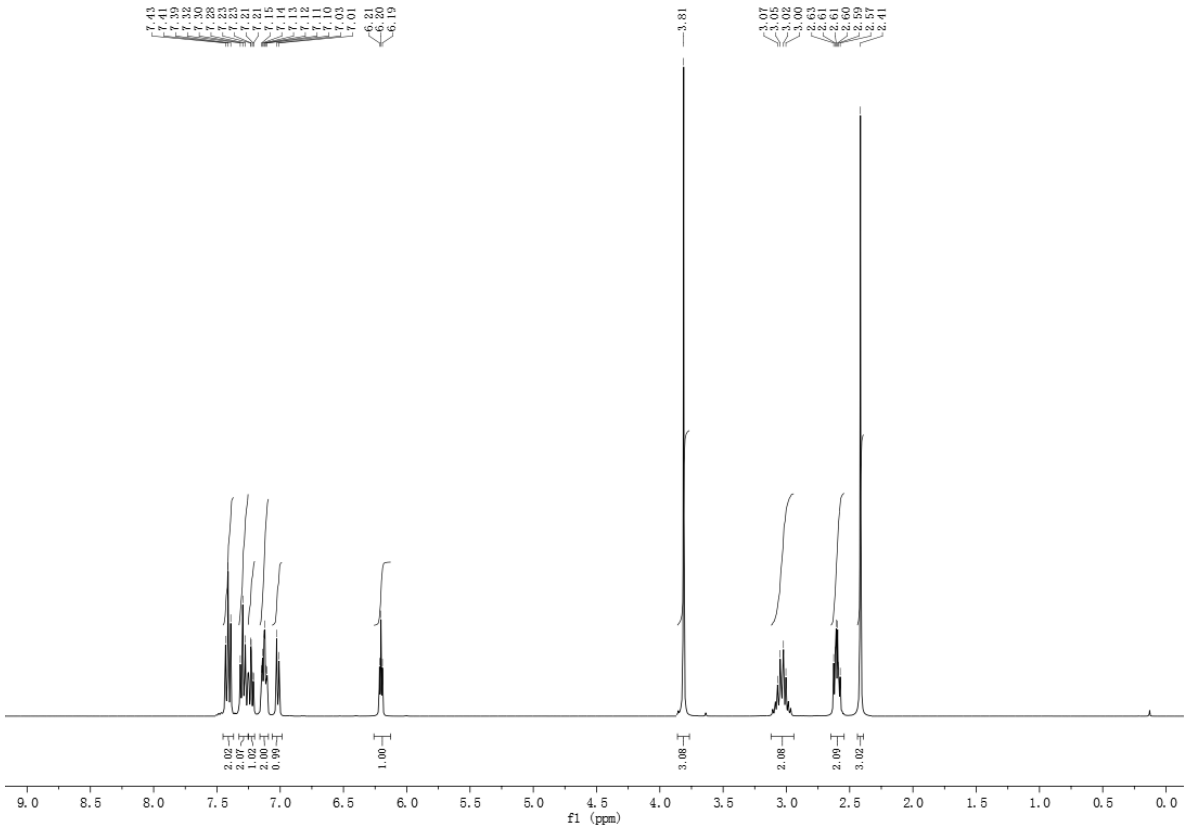
110.40
28.46
23.73
12.57
f1 (ppm)

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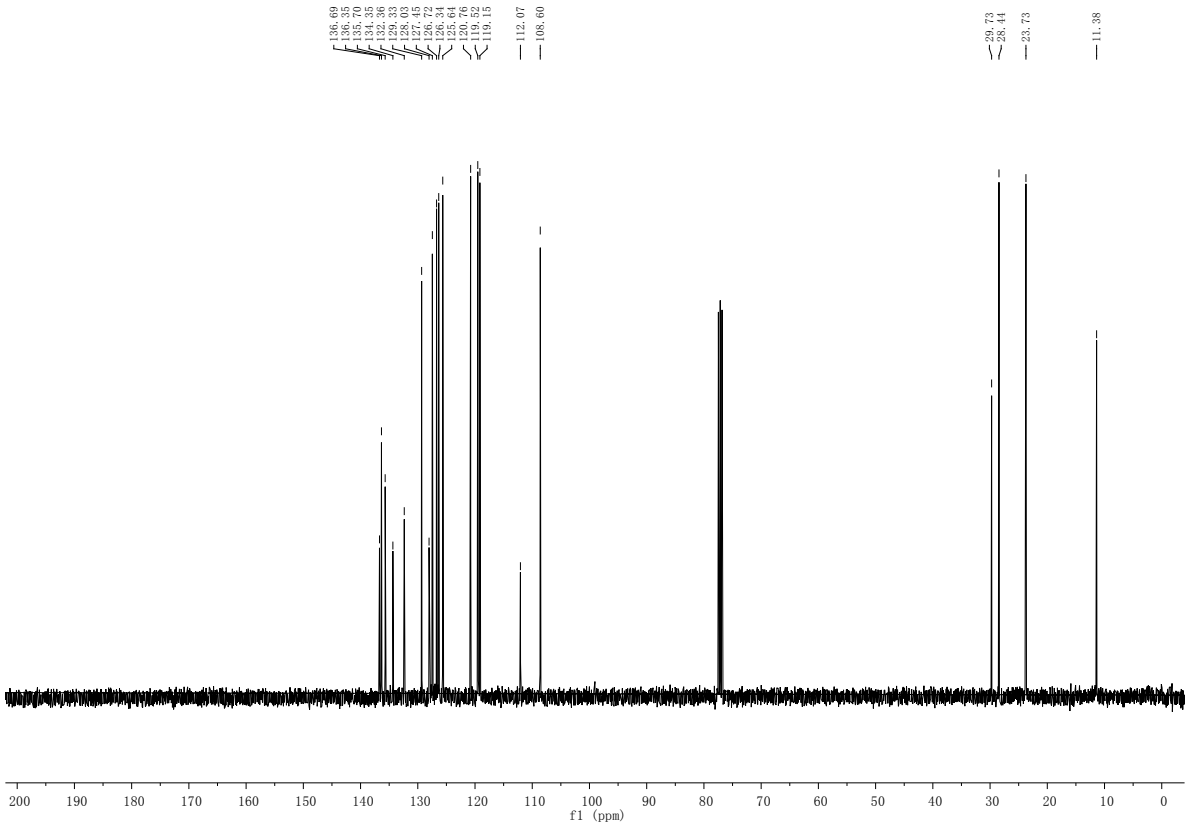
7.14
7.13
7.12
7.11
7.10
7.03
7.01
6.21
6.20
6.19
3.81
3.07
3.05
3.02
3.00
2.63
2.61
2.61
2.60
2.59
2.57
2.41
2.02
2.07
1.02
2.00
0.99
1.00
3.08
2.08
2.09
3.02
f1 (ppm)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132.36
129.33
128.03
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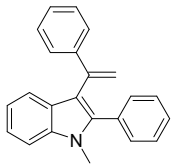
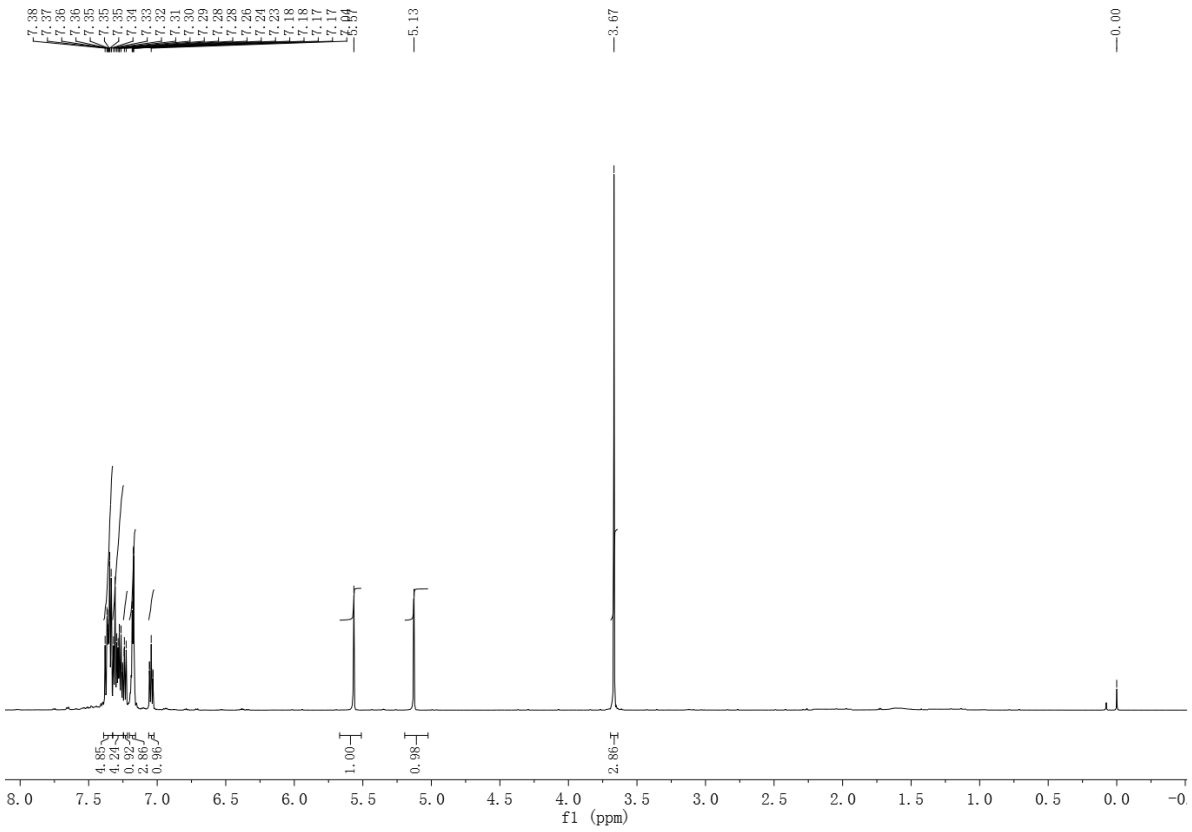
119.15
112.07
108.60
29.73
28.44
23.73
11.38
f1 (ppm)

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7.34
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7.32
7.31
7.30
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7.28
7.28
7.26
7.24
7.23
7.18
7.18
7.17
7.17
7.04
5.67
5.13
3.67
0.00
4.85
4.21
0.92
2.86
0.96
1.00
0.98
2.86
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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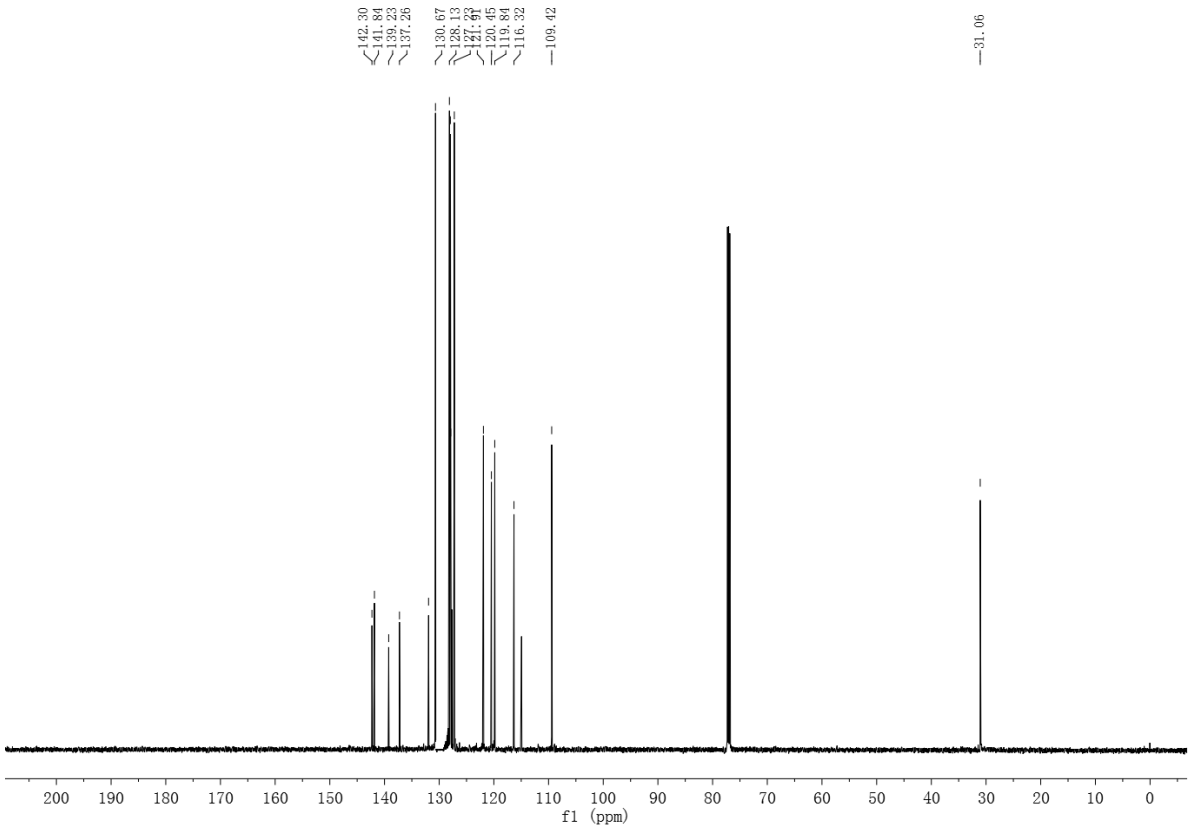
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


142.30
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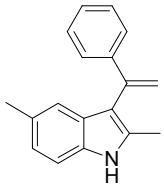
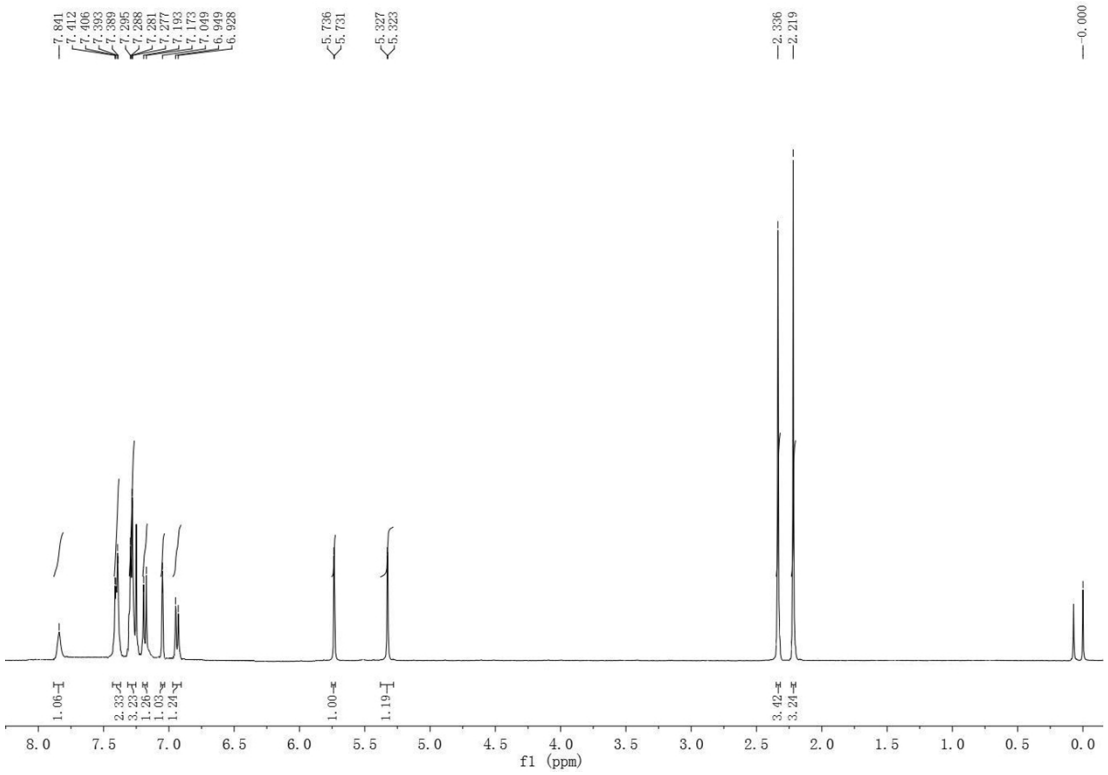
139.23
137.26
130.67
128.13
127.63
127.41
120.45
119.84
116.32
109.42
31.06
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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7.173
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6.949
6.928
5.736
5.731
5.327
5.323
2.336
2.219
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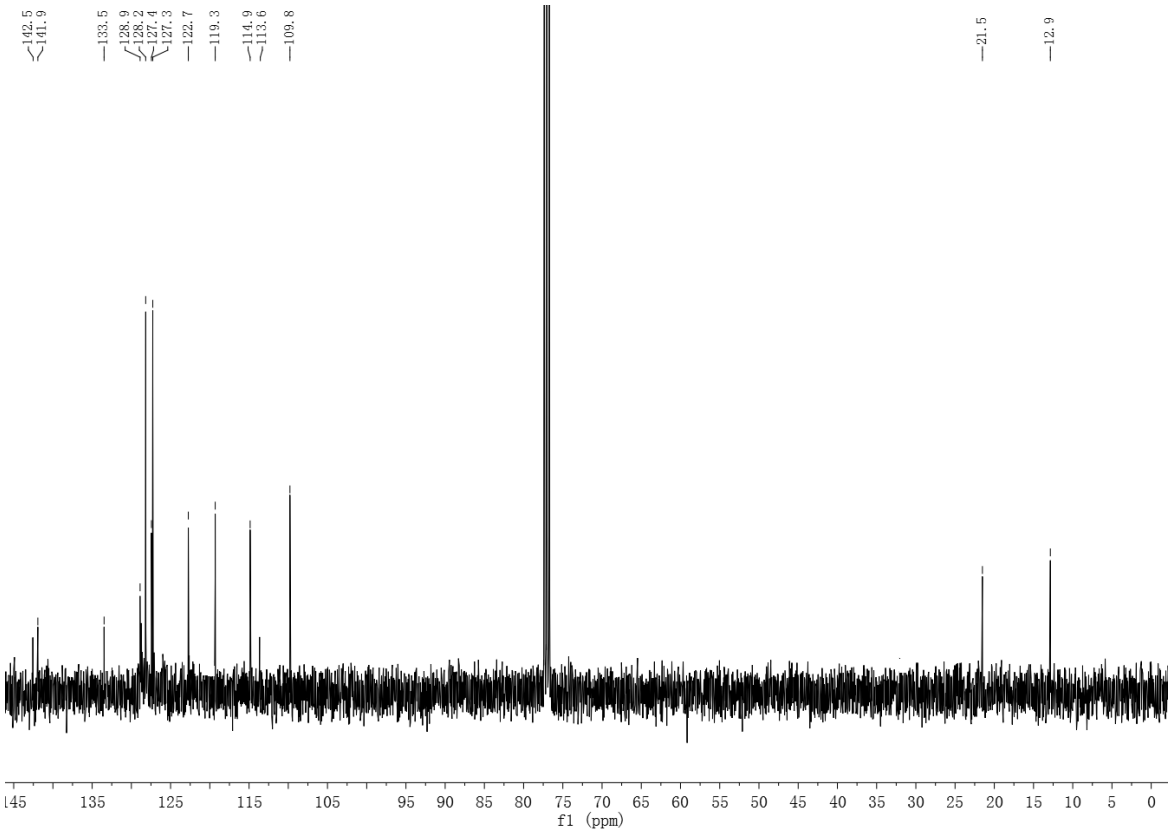
3.23
1.26
1.03
1.24
1.00
1.19
3.42
3.24
f1 (ppm)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122.7
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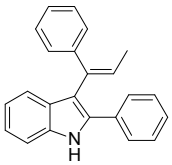
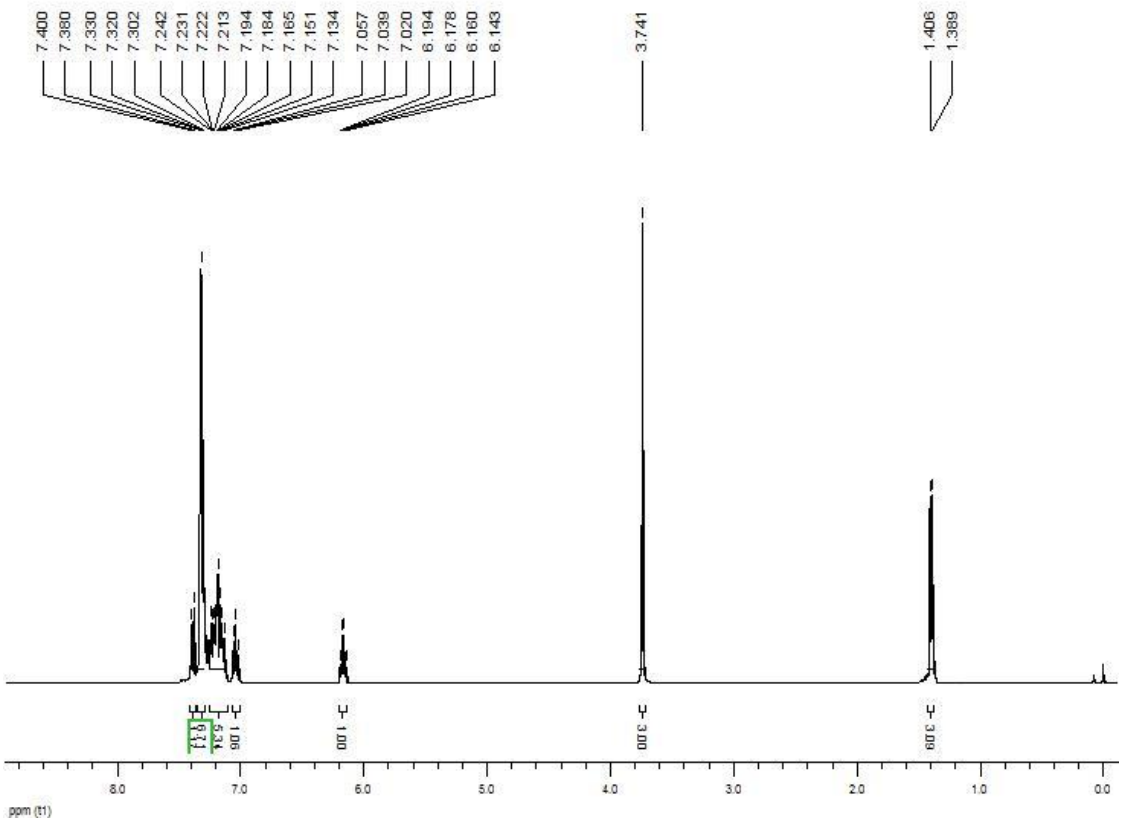
114.9
113.6
109.8
21.5
12.9
f1 (ppm)

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7.222
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7.165
7.151
7.134
7.057
7.039
7.020
6.194
6.178
6.160
6.143
3.741
1.406
1.389
2.13
6.17
5.34
1.06
1.00
3.00
3.09
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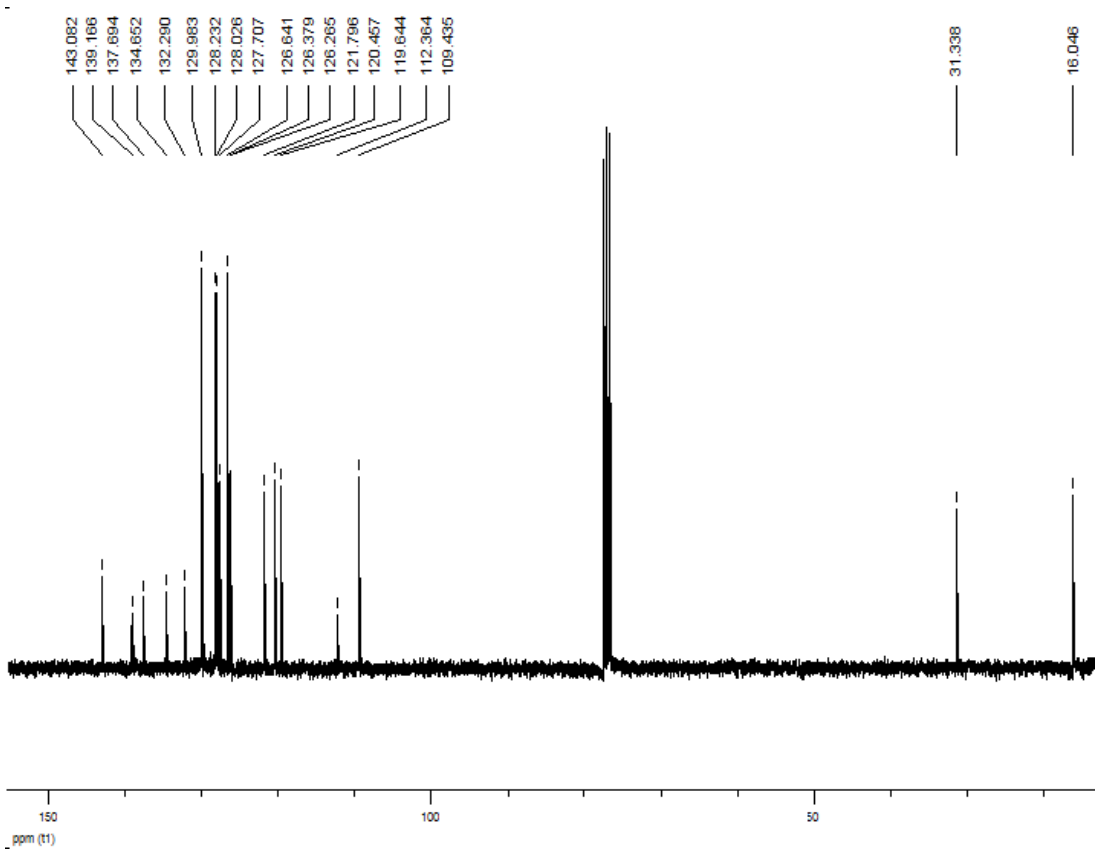
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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128.026
127.707
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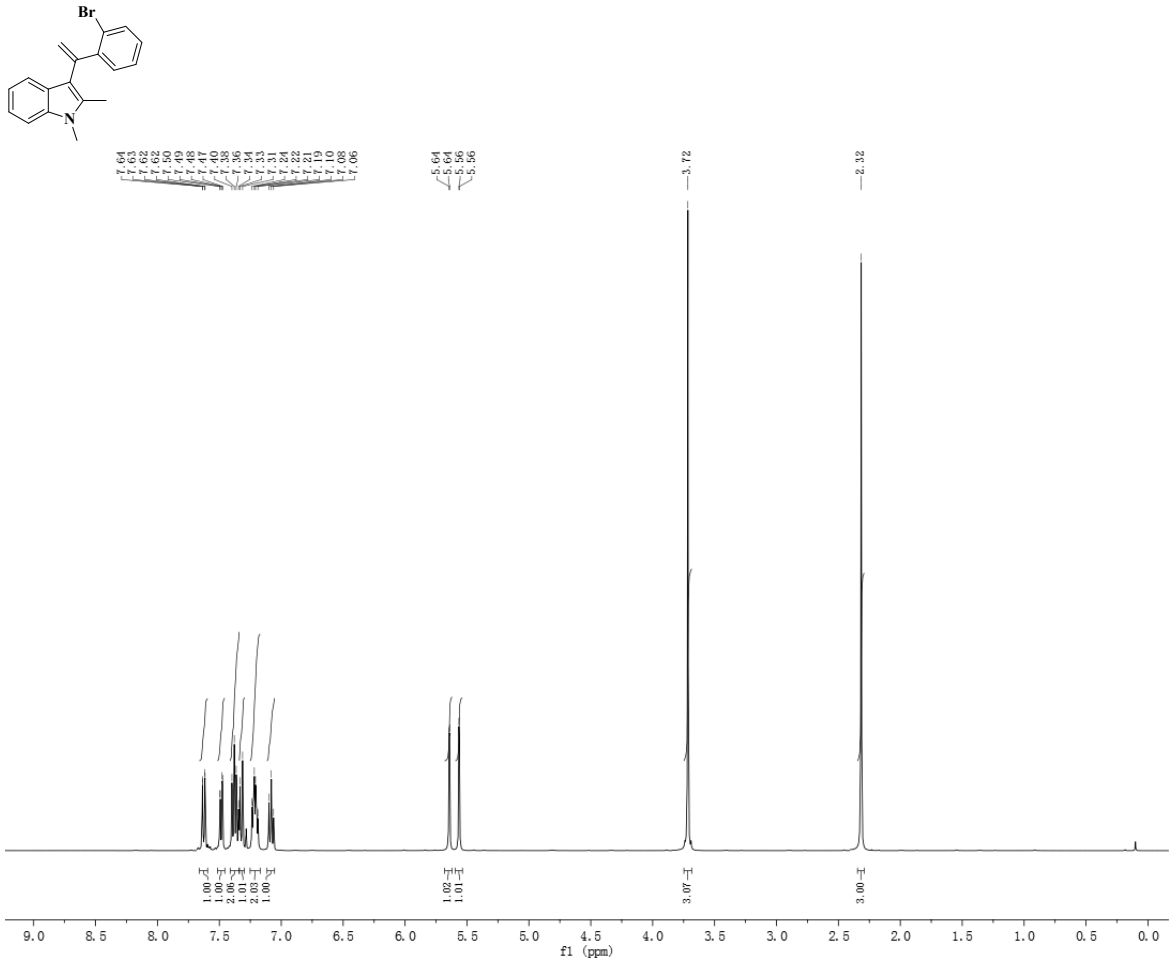
121.796
120.457
119.644
112.364
109.435
31.338
16.046
150
100
50
ppm (t1)


Br
N
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7.48
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7.40
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7.36
7.34
7.33
7.31
7.24
7.22
7.21
7.19
7.10
7.08
7.06
5.64
5.64
5.56
5.56
3.72
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1.00
1.00
2.06
1.01
2.03
1.00
1.02
1.01
3.07
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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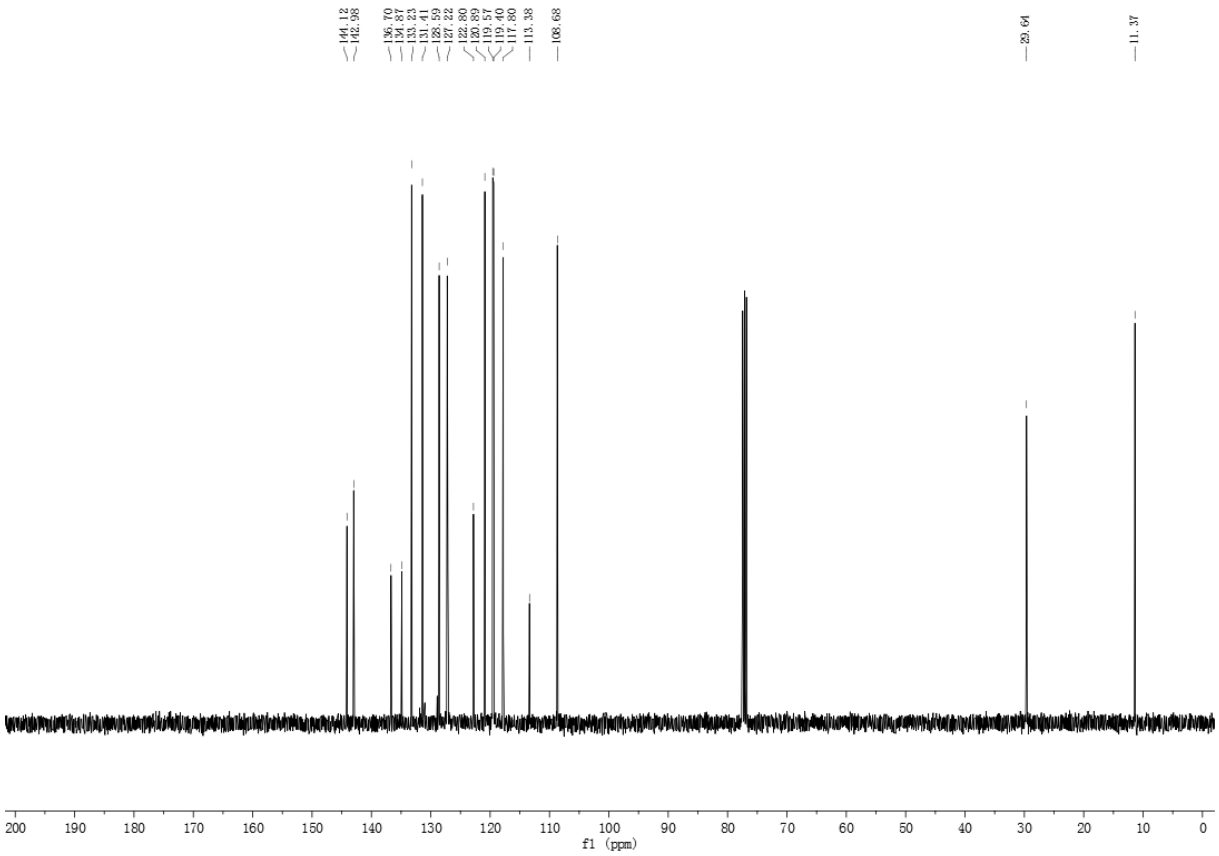
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.41
128.59
127.22
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125.89
119.57
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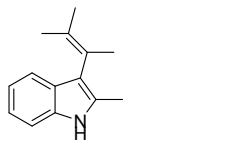
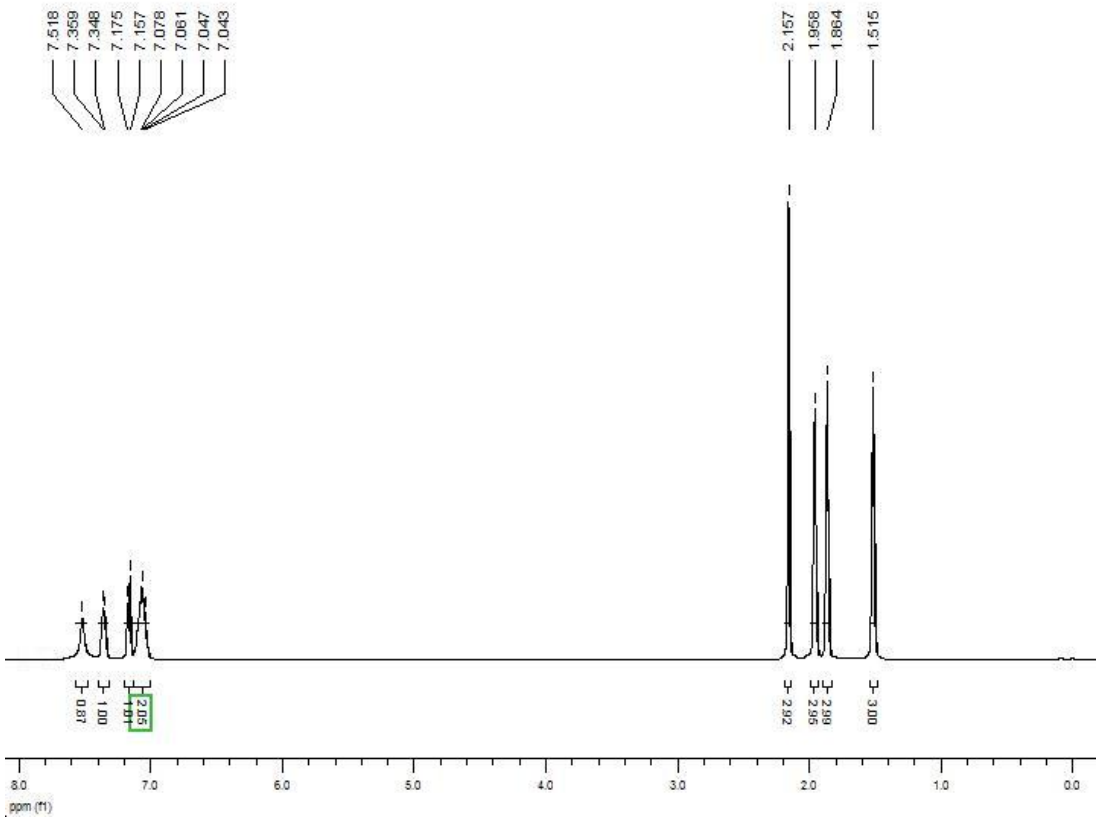
117.80
113.38
108.68
29.64
11.37
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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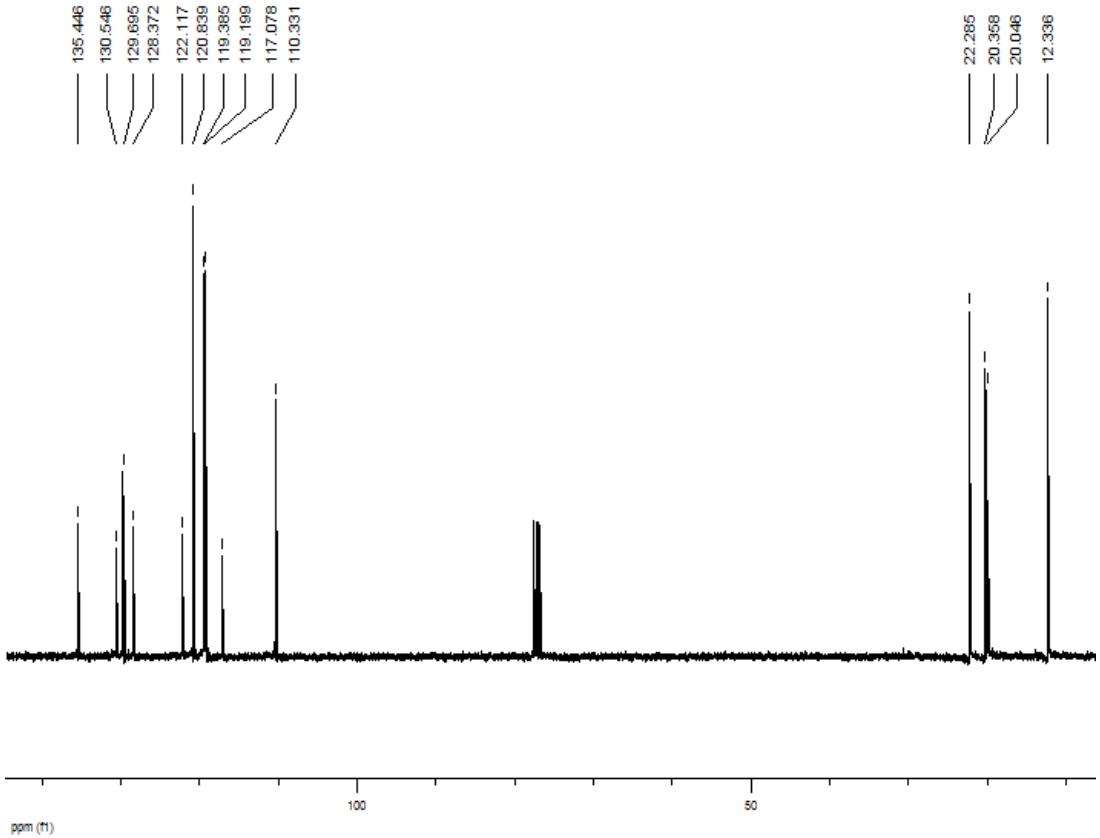
7.078
7.061
7.047
7.043
2.157
1.958
1.864
1.515
0.87
1.00
4.04
2.05
2.92
2.96
2.99
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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128.372
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119.199
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110.331
22.285
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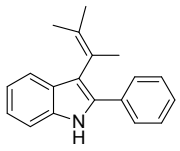
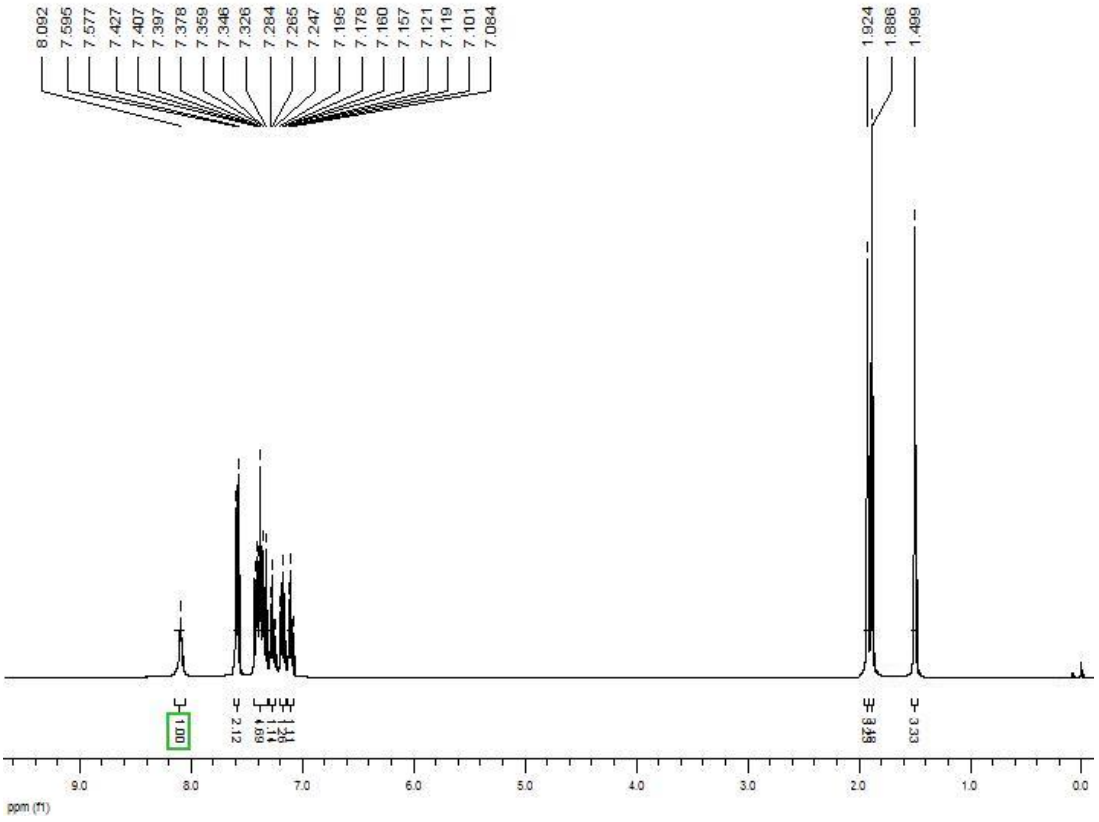
20.046
12.336
100
50
ppm (f1)

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7.247
7.195
7.178
7.160
7.157
7.121
7.119
7.101
7.084
1.924
1.886
1.499
1.00
2.12
6.69
1.14
1.12
1.08
3.48
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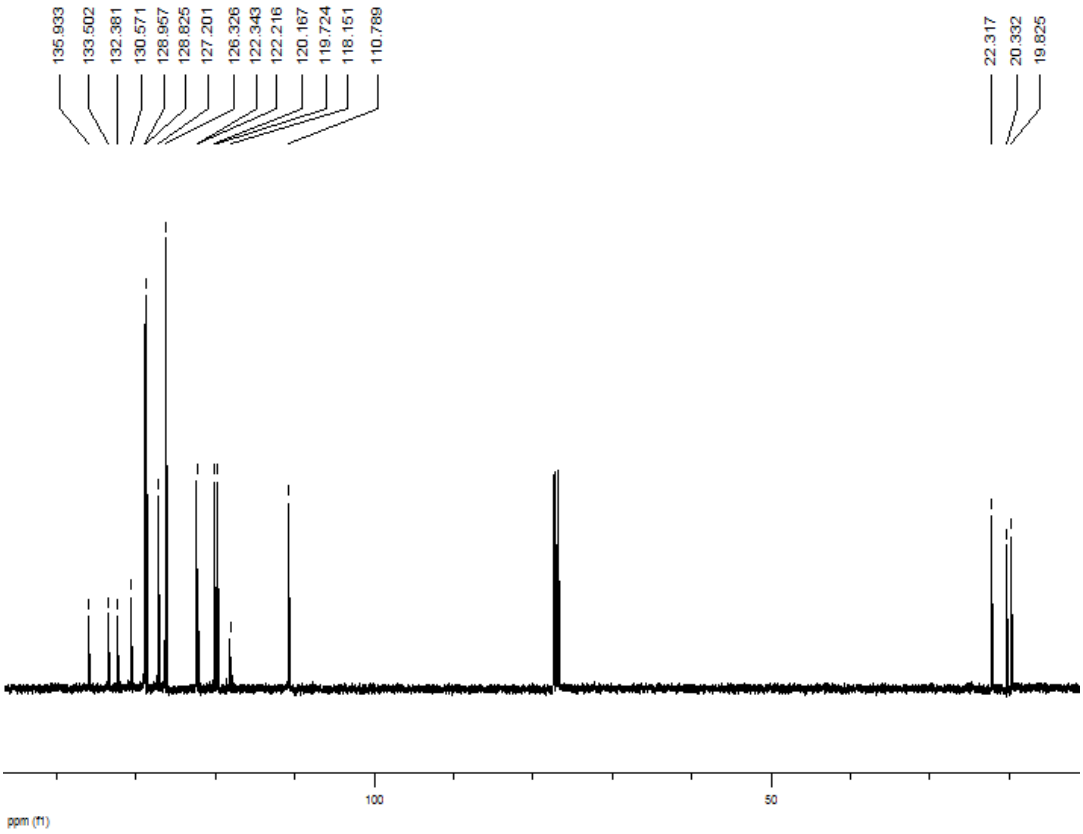
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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128.957
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126.326
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122.216
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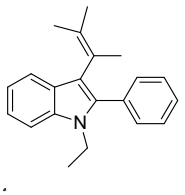
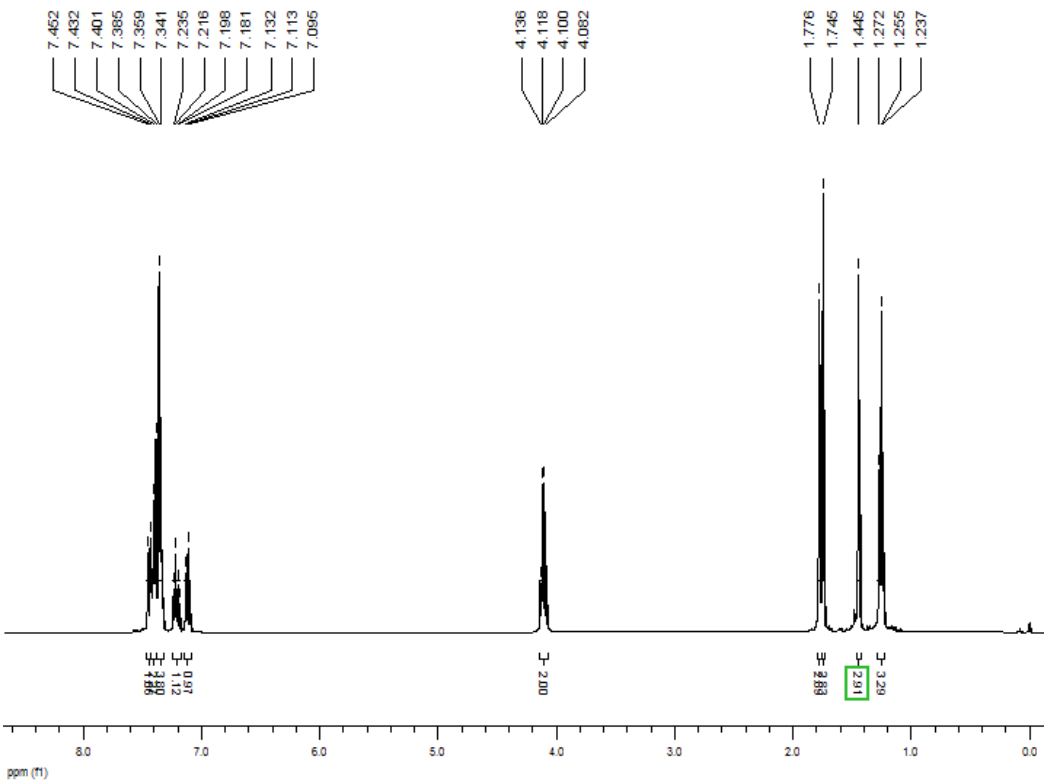
119.724
118.151
110.789
22.317
20.332
19.825
100
50
ppm (f1)

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7.432
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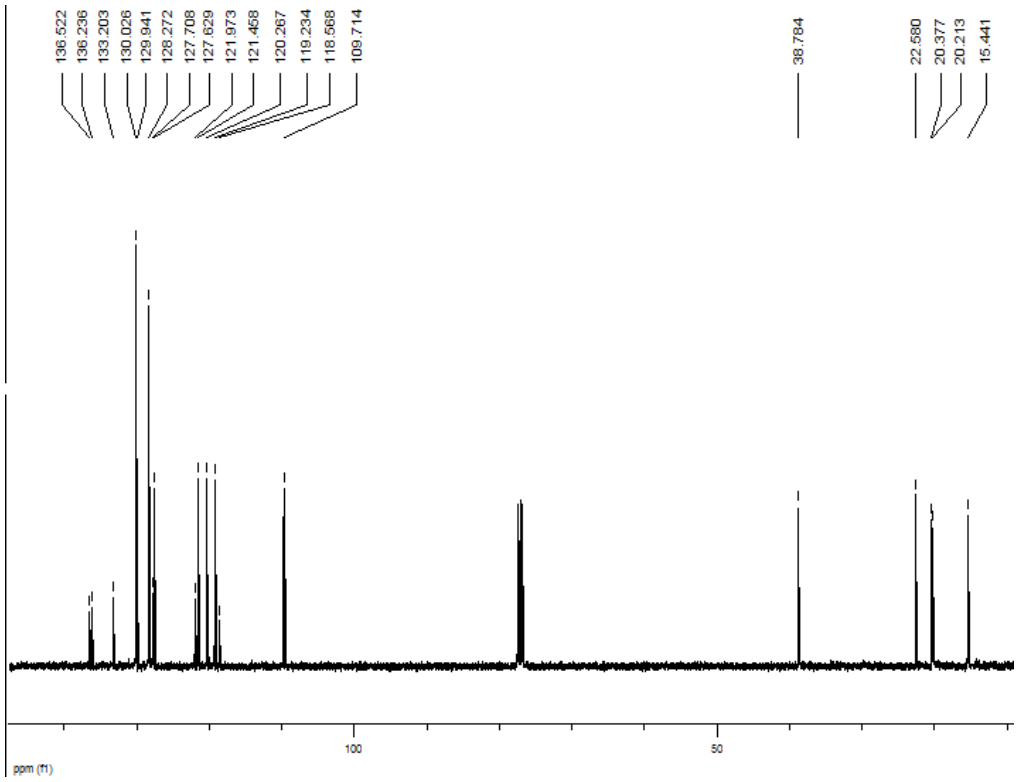
7.341
7.235
7.216
7.198
7.181
7.132
7.113
7.095
4.136
4.118
4.100
4.082
1.776
1.745
1.445
1.272
1.255
1.237
3.00
1.12
0.97
2.00
2.89
2.91
3.29
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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129.941
128.272
127.708
127.629
121.973
121.458
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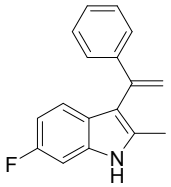
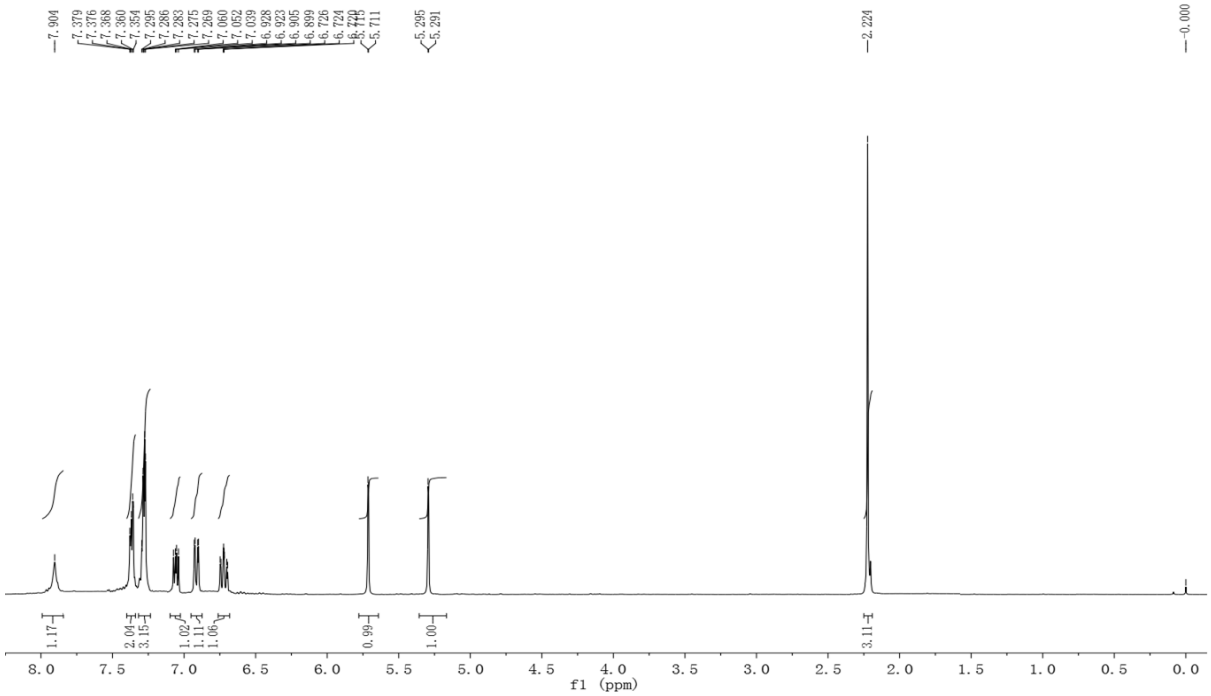
119.234
118.568
109.714
38.784
22.580
20.377
20.213
15.441
100
50
ppm (f1)


F
N
H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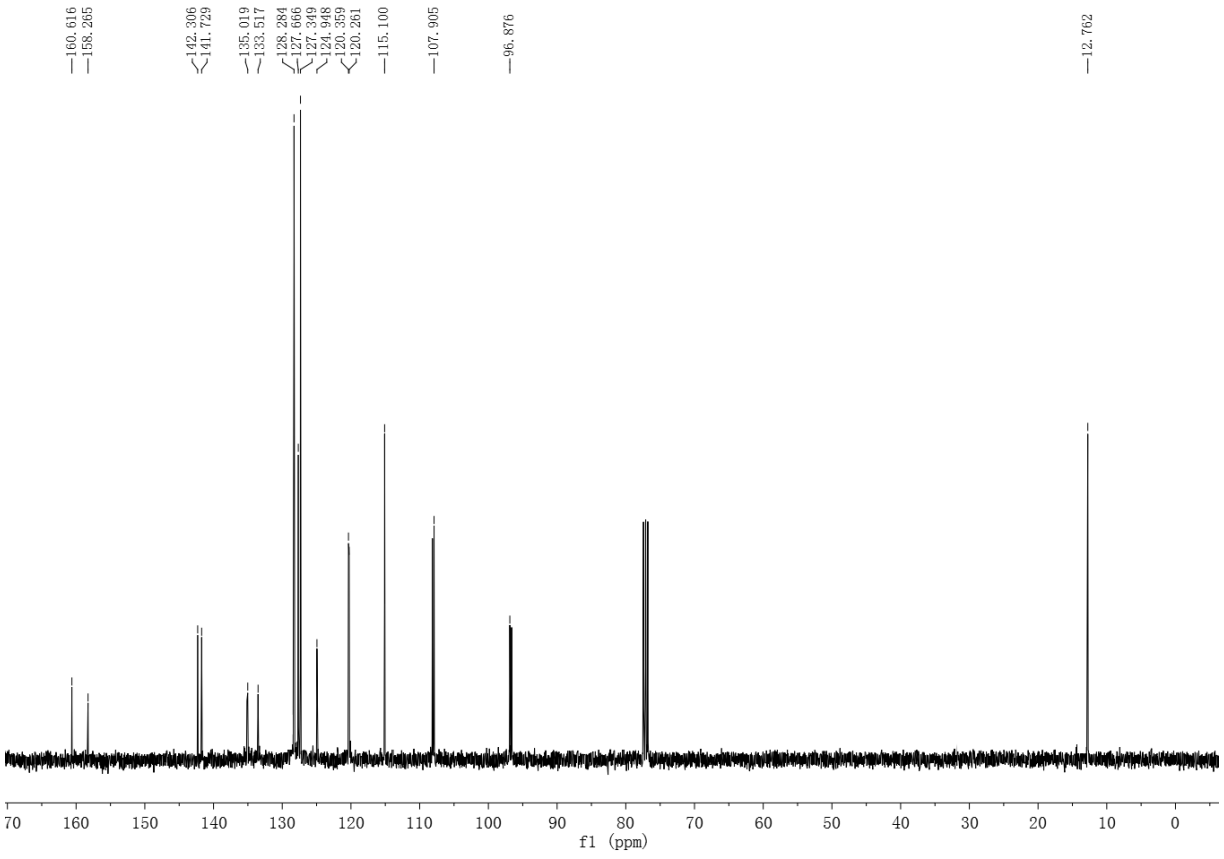
7.376
7.368
7.360
7.354
7.295
7.286
7.283
7.275
7.269
7.060
7.052
7.039
6.928
6.923
6.905
6.899
6.726
6.724
5.711
5.295
5.291
2.224
0.000
1.17
2.04
3.15
1.02
1.11
1.06
0.99
1.00
3.11
f1 (ppm)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141.729
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133.517
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127.349
124.948
120.359
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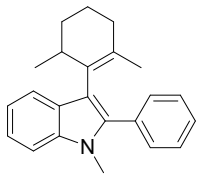
115.100
107.905
96.876
12.762
f1 (ppm)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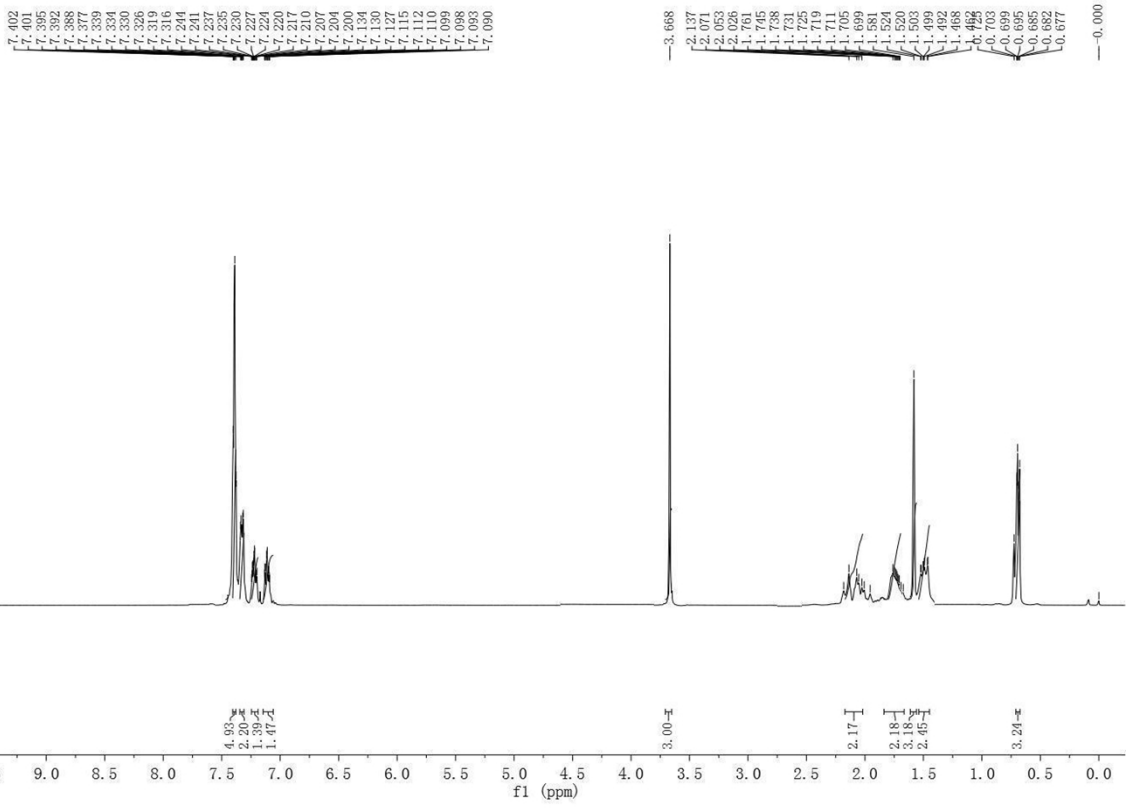
7.402
7.401
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7.392
7.388
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7.334
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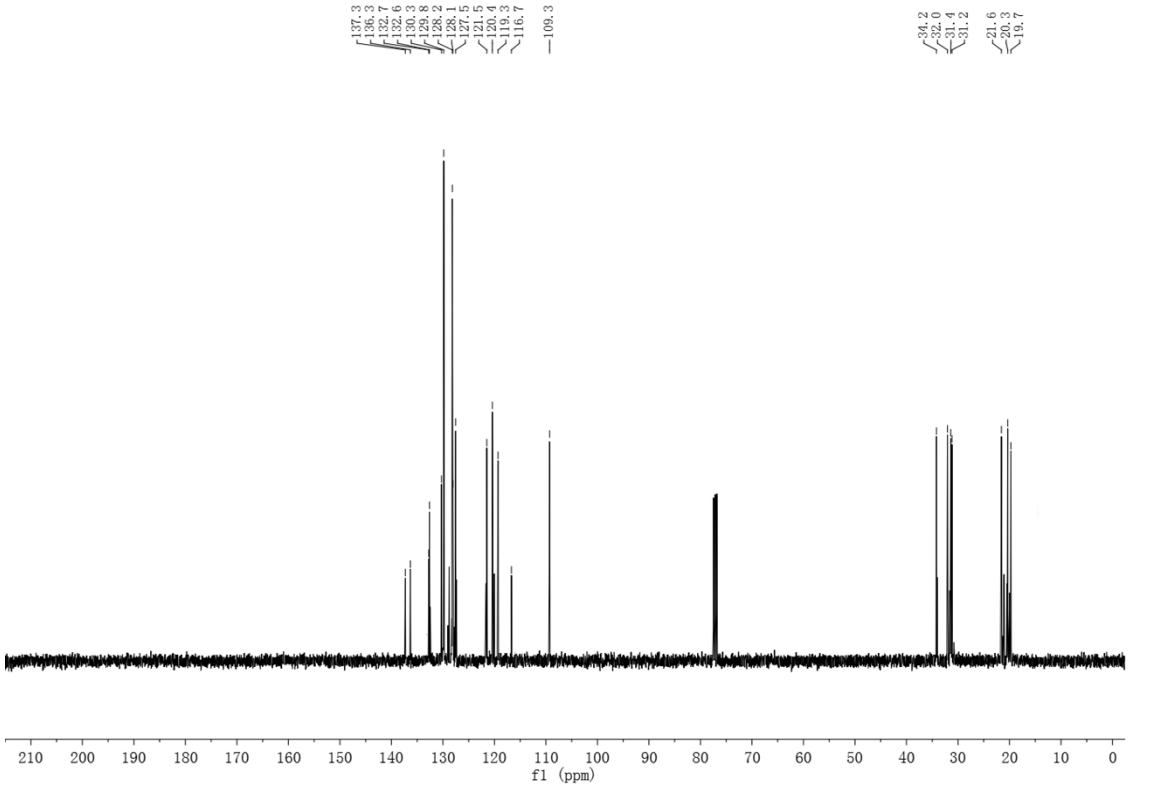
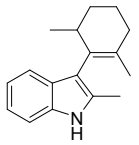
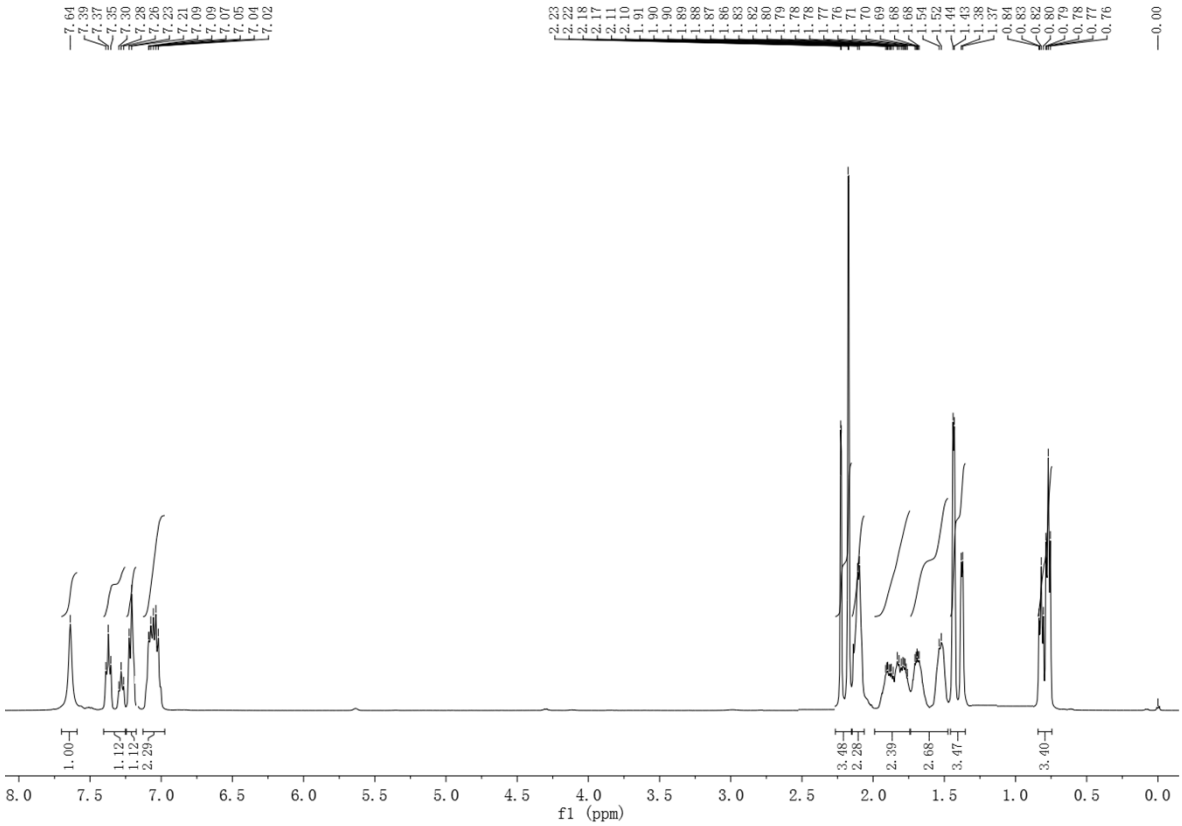
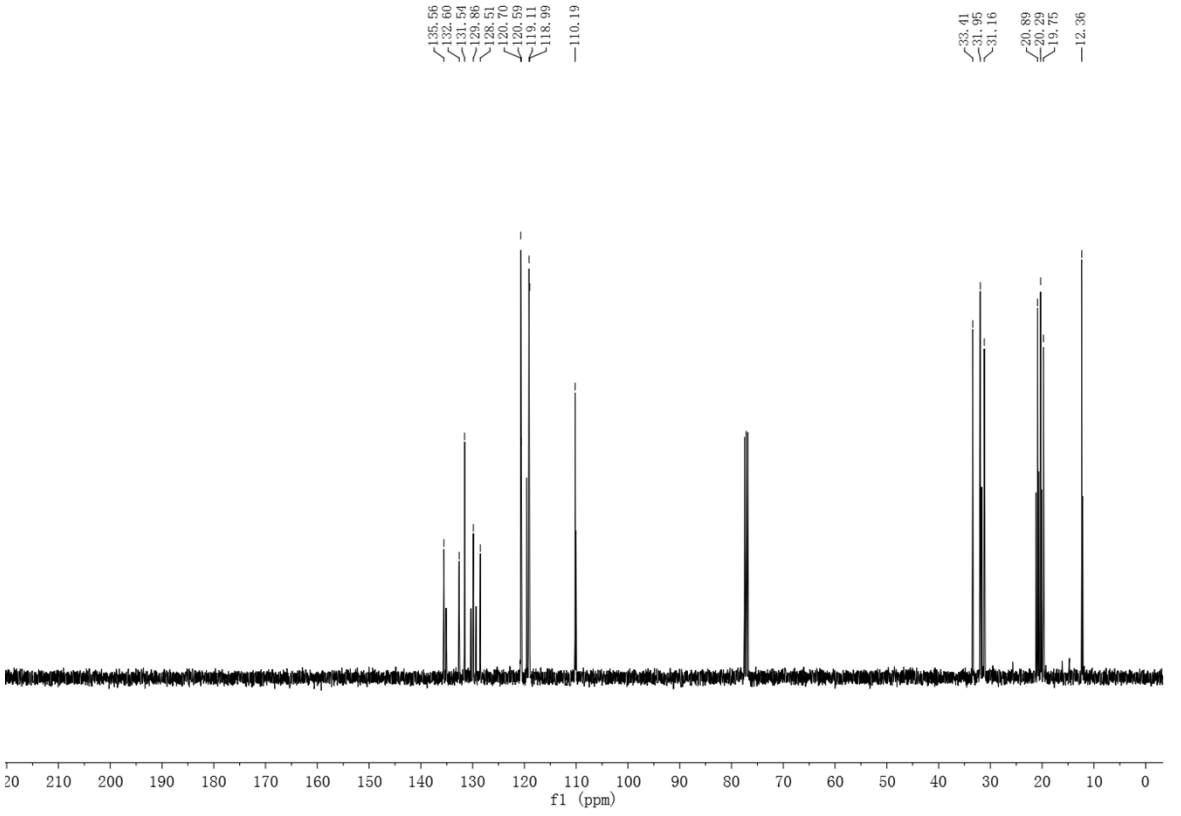
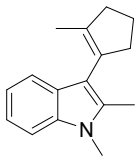
7.326
7.319
7.316
7.244
7.241
7.237
7.235
7.230
7.227
7.224
7.220
7.217
7.210
7.207
7.204
7.200
7.134
7.130
7.127
7.115
7.112
7.110
7.099
7.098
7.093
7.090
3.668
2.137
2.071
2.053
2.026
1.761
1.745
1.738
1.731
1.725
1.719
1.711
1.705
1.699
1.581
1.524
1.520
1.503
1.499
1.492
1.468
0.725
0.703
0.699
0.695
0.685
0.682
0.677
0.000
4.93
2.20
1.39
1.47
3.00
2.17
2.18
3.18
2.45
3.24
f1 (ppm)

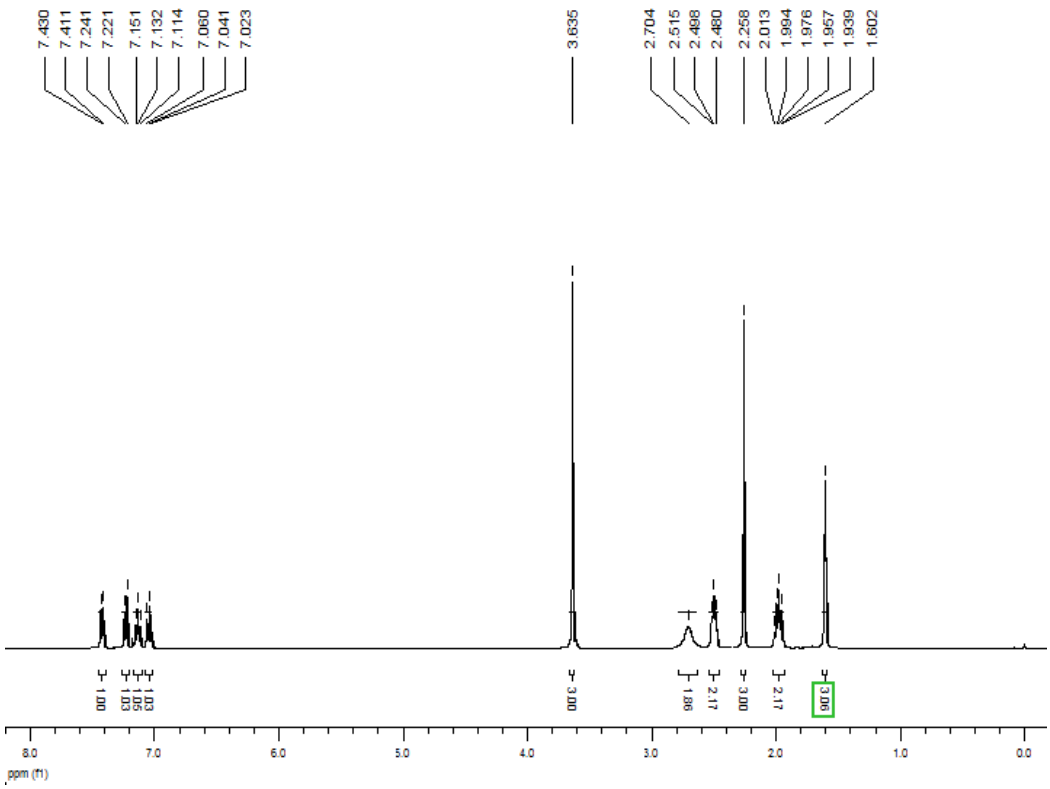

137.3
136.3
132.7
132.6
130.3
129.8
128.2
128.1
127.5
121.5
120.4
119.3
116.7
109.3
34.2
32.0
31.4
31.2
21.6
20.3
19.7
f1 (ppm)




7.64
7.39
7.37
7.35
7.30
7.28
7.26
7.23
7.21
7.09
7.07
7.05
7.04
7.02
2.23
2.22
2.18
2.17
2.11
2.10
1.91
1.90
1.90
1.89
1.88
1.87
1.86
1.83
1.82
1.80
1.79
1.78
1.78
1.77
1.76
1.71
1.70
1.69
1.68
1.68
1.54
1.52
1.44
1.43
1.38
1.37
0.84
0.83
0.82
0.80
0.79
0.78
0.77
0.76
0.00
1.00
1.12
1.12
2.29
3.48
2.28
2.39
2.68
3.47
3.40
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
0.0
f1 (ppm)


135.56
132.60
131.54
129.86
128.51
120.70
120.59
119.11
118.99
110.19
33.41
31.95
31.16
20.89
20.29
19.75
12.36
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)




7.430
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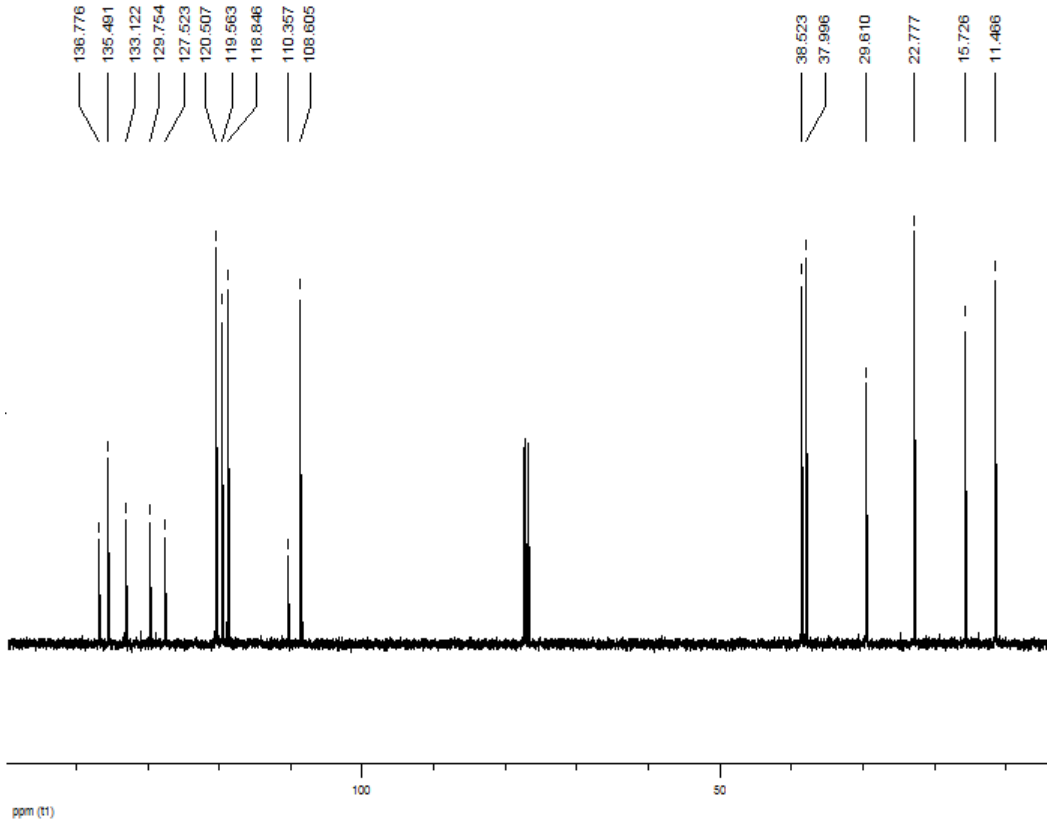
7.241
7.221
7.151
7.132
7.114
7.060
7.041
7.023
3.635
2.704
2.515
2.498
2.480
2.258
2.013
1.994
1.976
1.957
1.939
1.602
1.00
1.05
1.03
1.03
3.00
1.86
2.17
3.00
2.17
3.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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127.523
120.507
119.563
118.846
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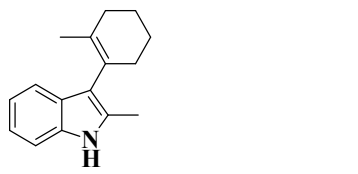
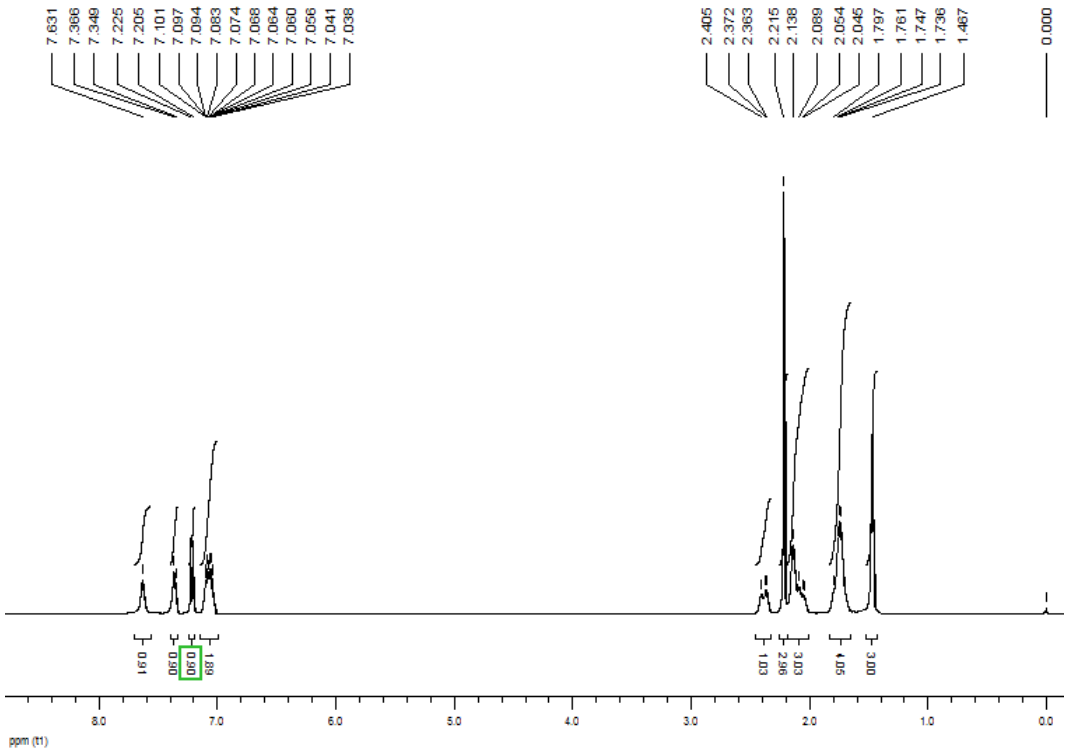
108.605
38.523
37.996
29.610
22.777
15.726
11.466
100
50
ppm (t1)

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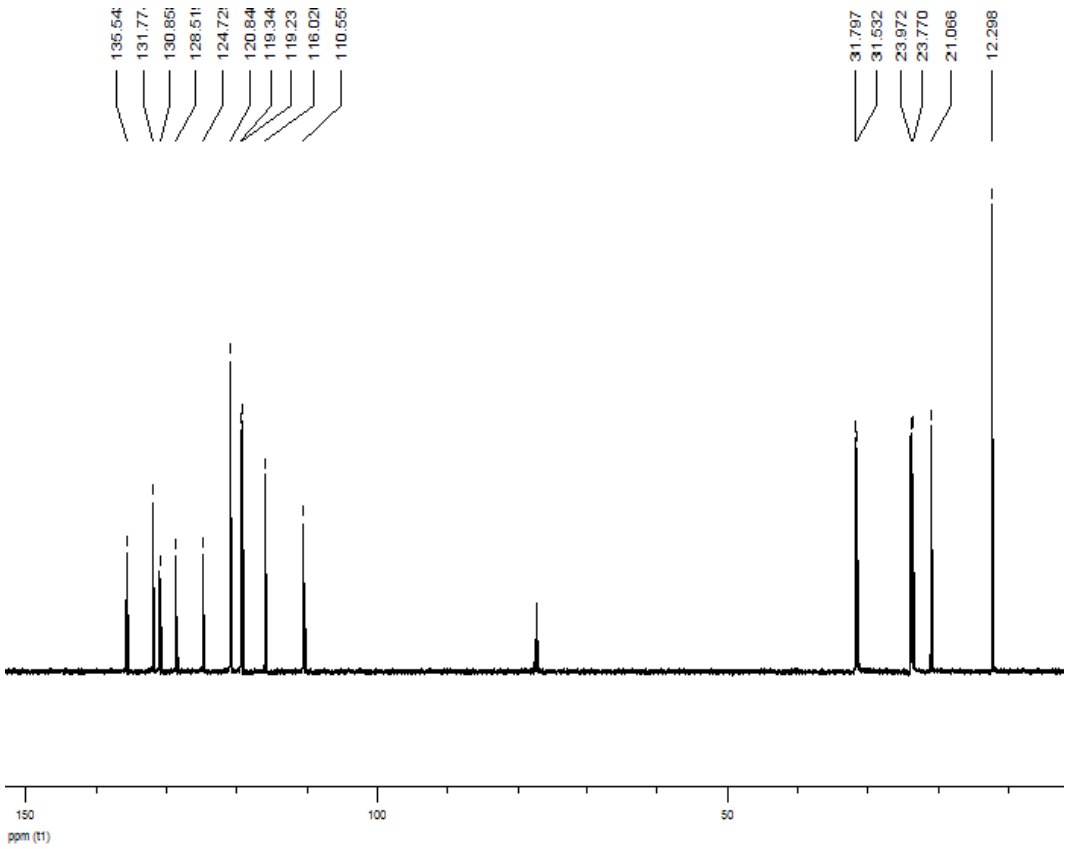
7.349
7.225
7.205
7.101
7.097
7.094
7.083
7.074
7.068
7.064
7.060
7.056
7.041
7.038
2.405
2.372
2.363
2.215
2.138
2.089
2.054
2.045
1.797
1.761
1.747
1.736
1.467
0.000
0.91
0.90
0.90
1.89
1.03
2.96
3.03
4.05
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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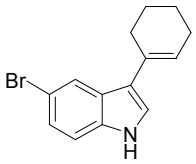
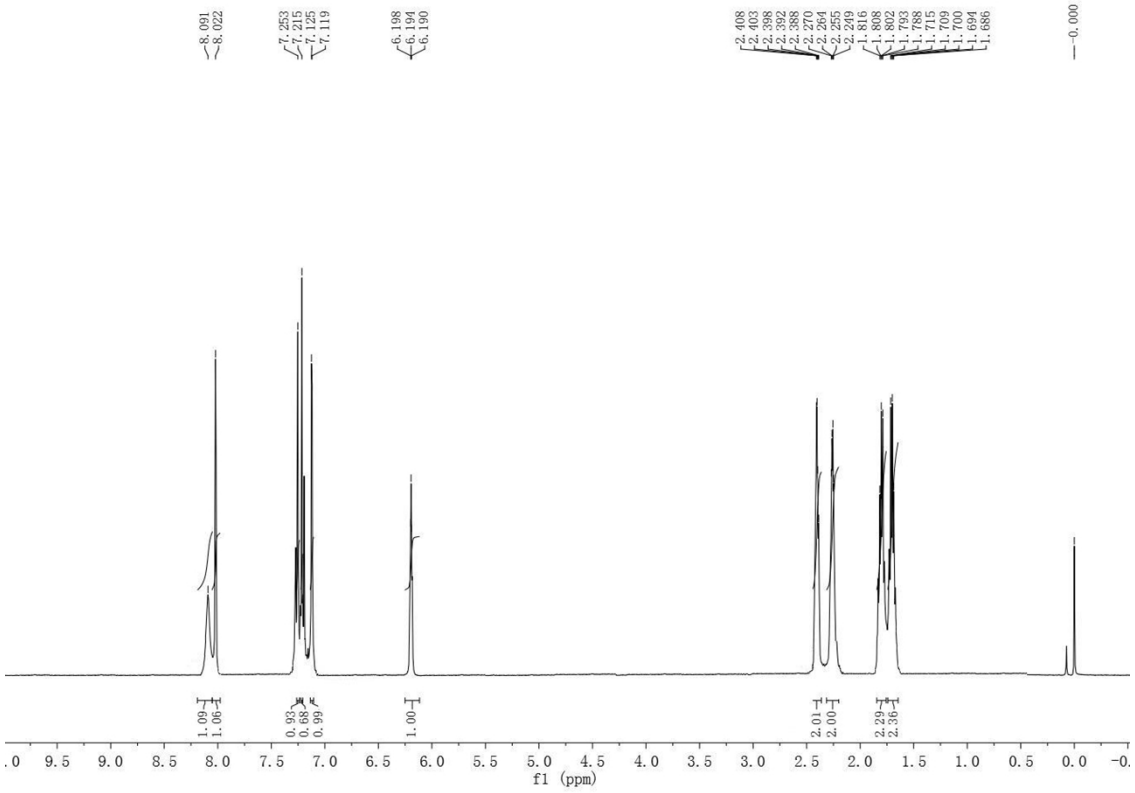
128.51
124.72
120.84
119.34
119.23
116.02
110.55
31.797
31.532
23.972
23.770
21.066
12.298
150
100
50
ppm (t1)


Br
N
H


8.091
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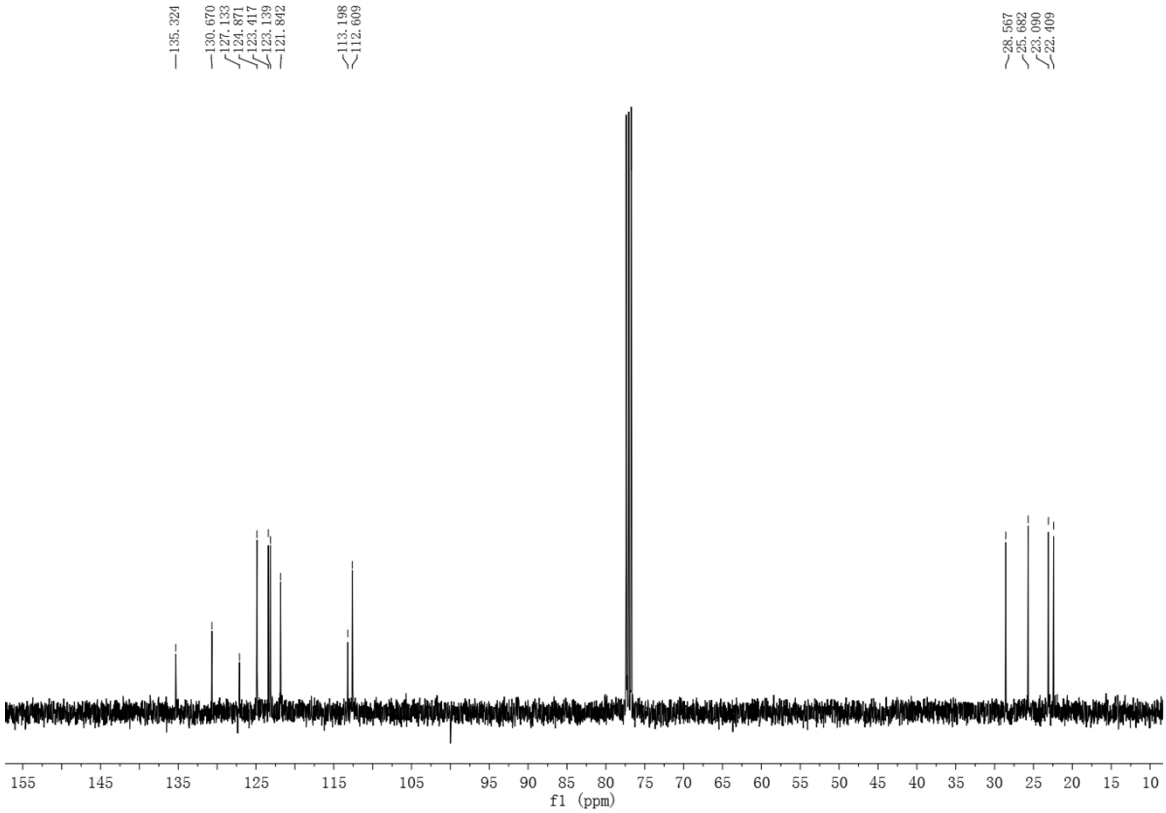
7.253
7.215
7.125
7.119
6.198
6.194
6.190
2.408
2.403
2.398
2.392
2.388
2.270
2.264
2.255
2.249
1.816
1.808
1.802
1.793
1.788
1.715
1.709
1.700
1.694
1.686
0.000
1.09
1.06
0.93
0.68
0.99
1.00
2.01
2.00
2.29
2.36
f1 (ppm)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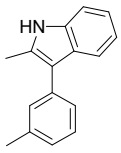
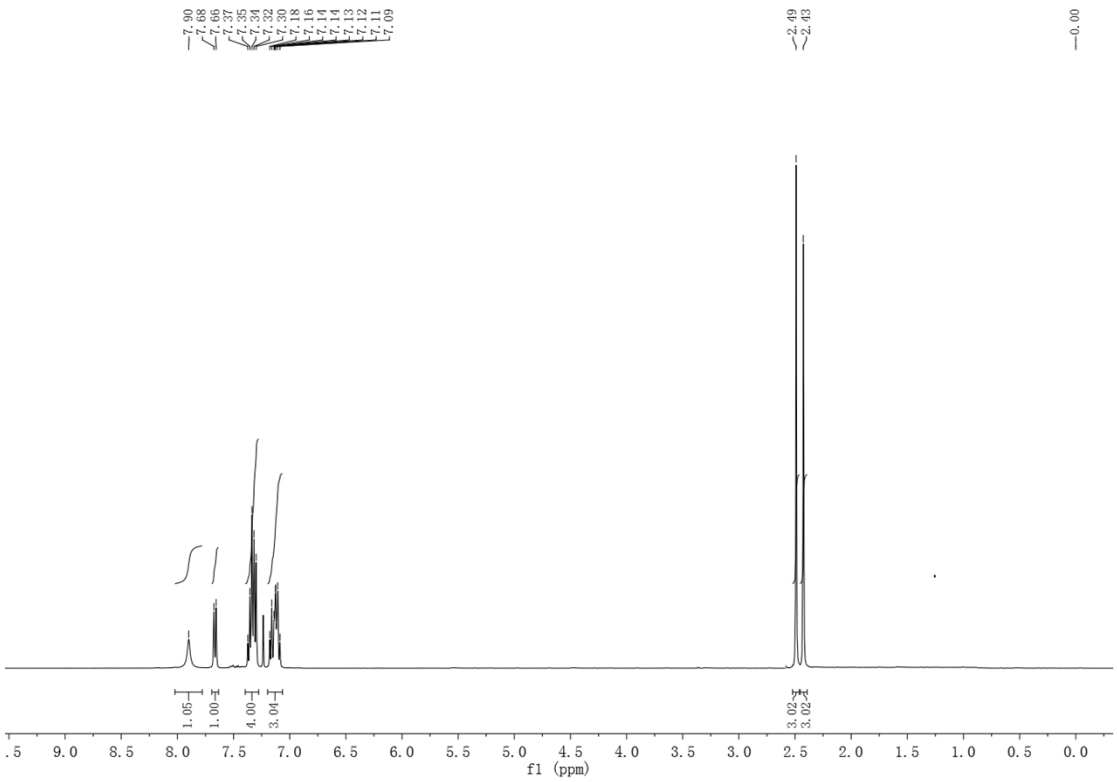
123.139
121.842
113.198
112.609
28.567
25.682
23.090
22.409
f1 (ppm)


HN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7.68
7.66
7.37
7.35
7.34
7.32
7.30
7.18
7.16
7.14
7.13
7.12
7.11
7.09
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2.43
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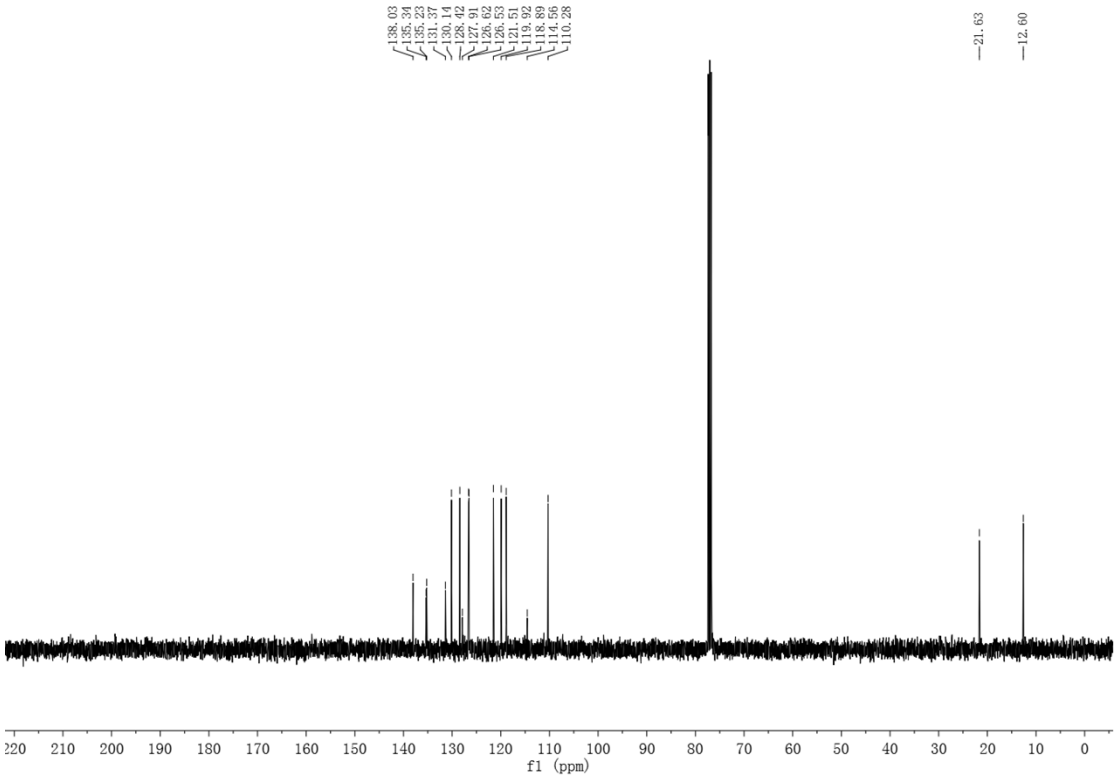
1.05
1.00
4.00
3.04
3.02
3.02
f1 (ppm)


138.03
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131.37
130.14
128.42
127.91
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126.53
121.51
119.92
118.89
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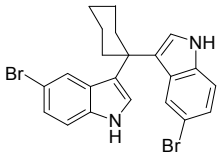
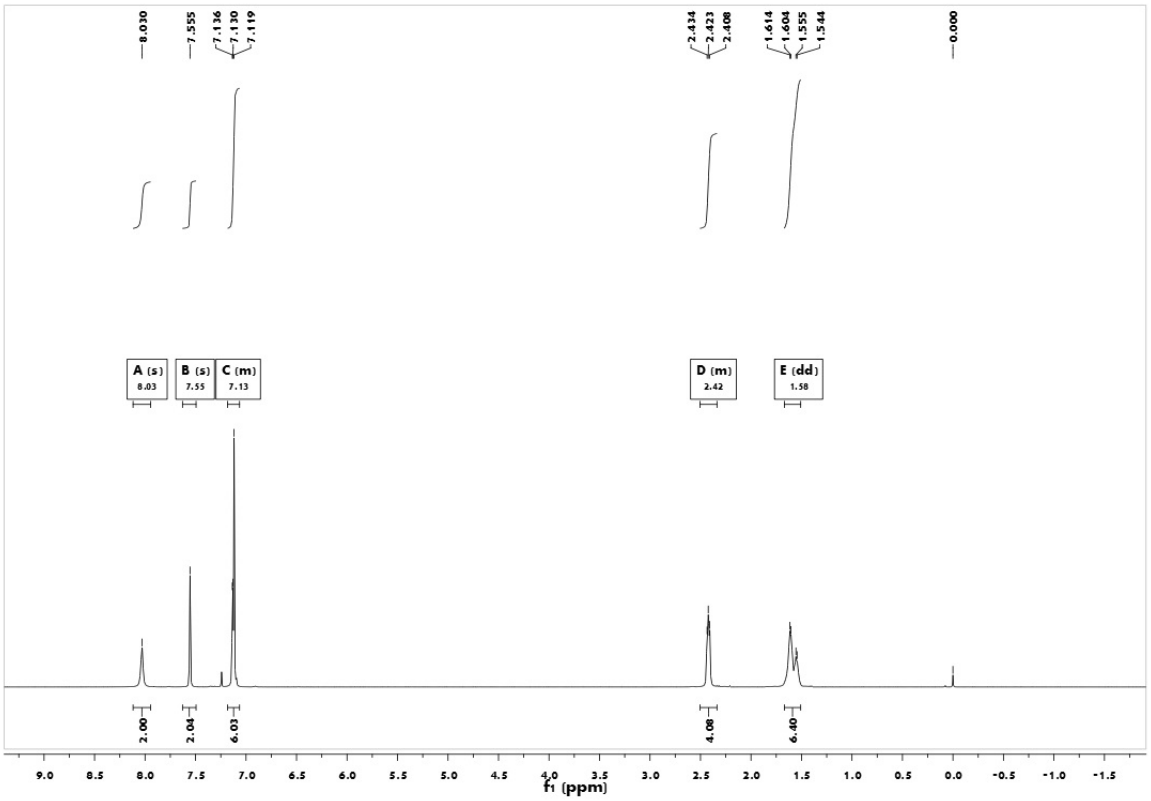
110.28
21.63
12.60
f1 (ppm)


Br
NH
N
H
Br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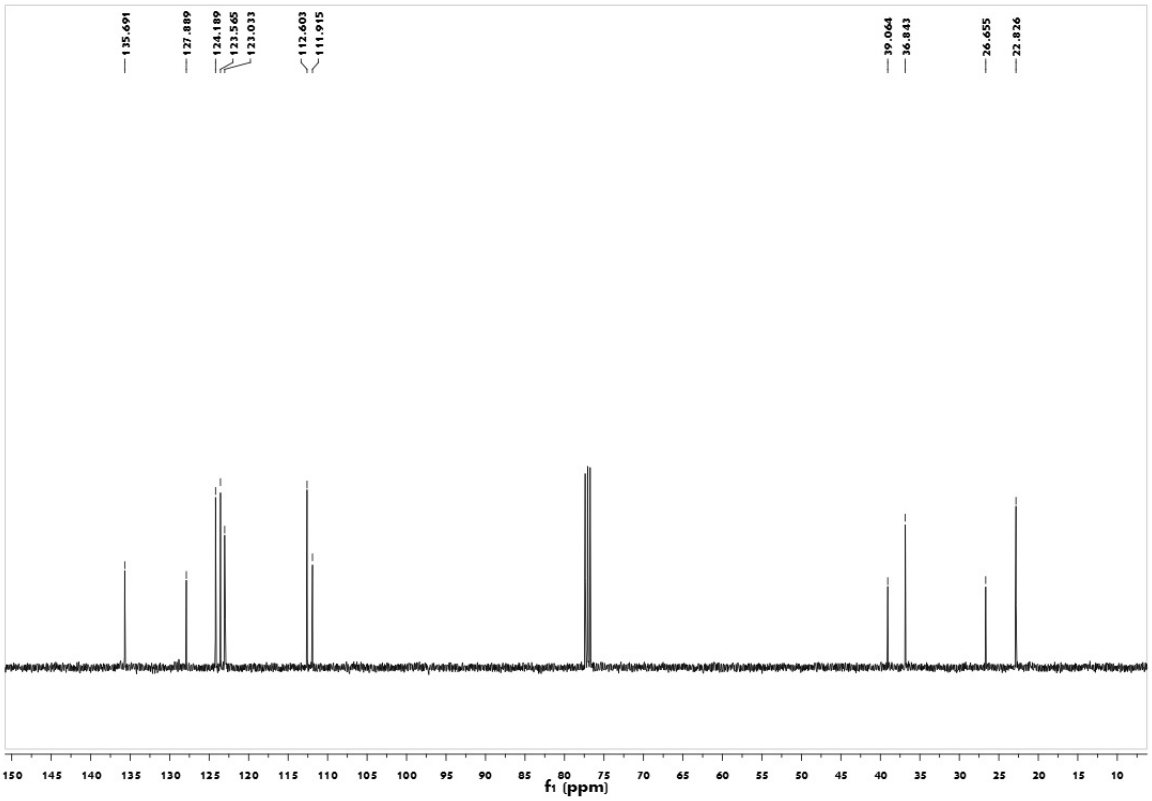
7.555
7.136
7.130
7.119
2.434
2.423
2.408
1.614
1.604
1.555
1.544
0.000
A (s) 8.03
B (s) 7.55
C (m) 7.13
D (m) 2.42
E (dd) 1.58
2.00
2.04
6.03
4.08
6.40
f1 (ppm)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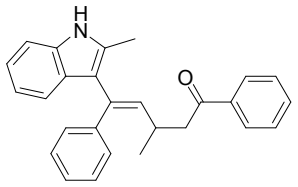
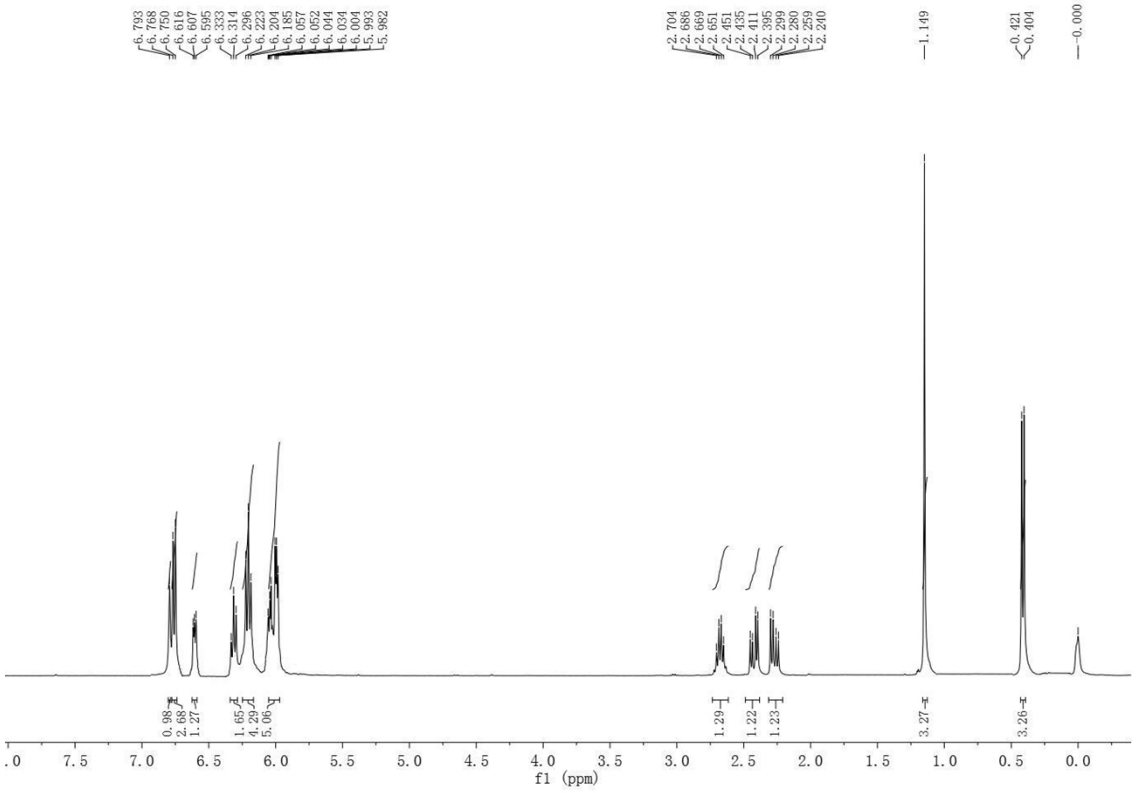
123.565
123.033
112.603
111.915
39.064
36.843
26.655
22.826
f1 (ppm)

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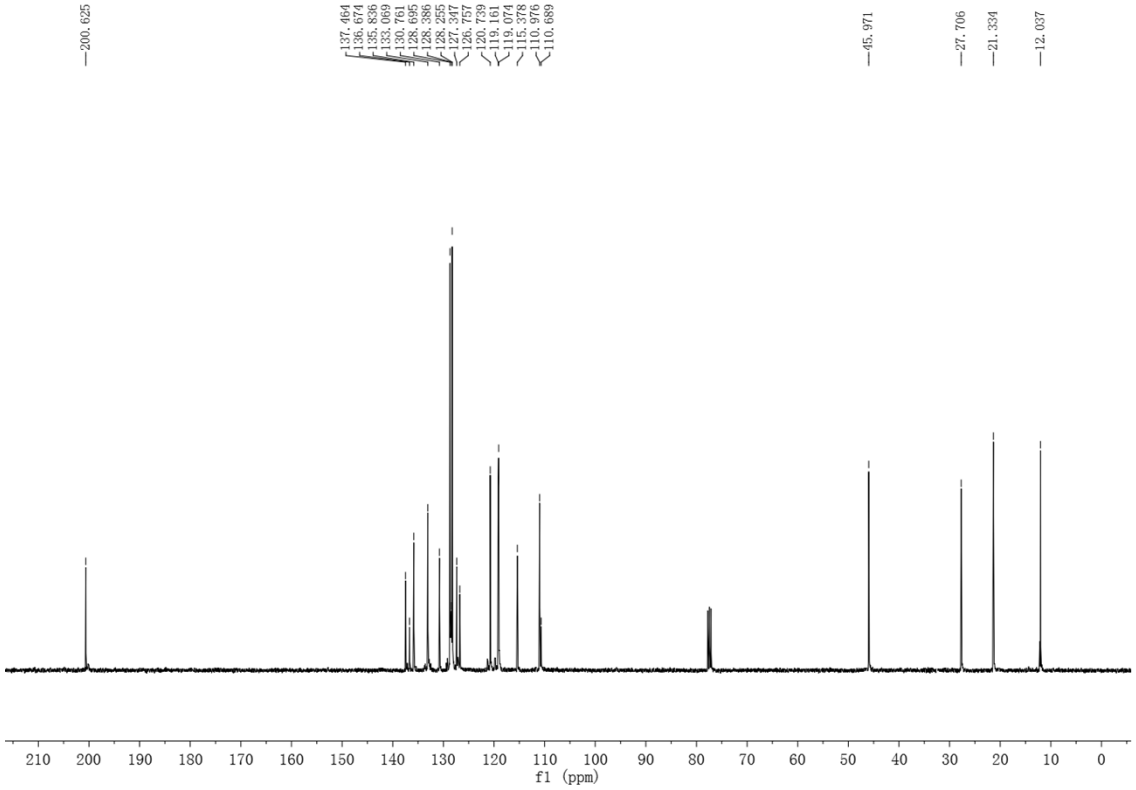
6.616
6.607
6.595
6.333
6.314
6.296
6.223
6.204
6.185
6.057
6.052
6.044
6.034
6.004
5.993
5.982
2.704
2.688
2.669
2.651
2.451
2.435
2.411
2.395
2.299
2.280
2.259
2.240
1.149
0.421
0.404
-0.000
0.98
2.68
1.27
1.65
4.29
5.06
1.29
1.22
1.23
3.27
3.26
f1 (ppm)


200.625
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136.674
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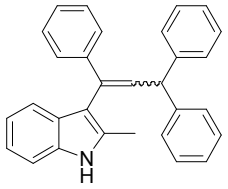
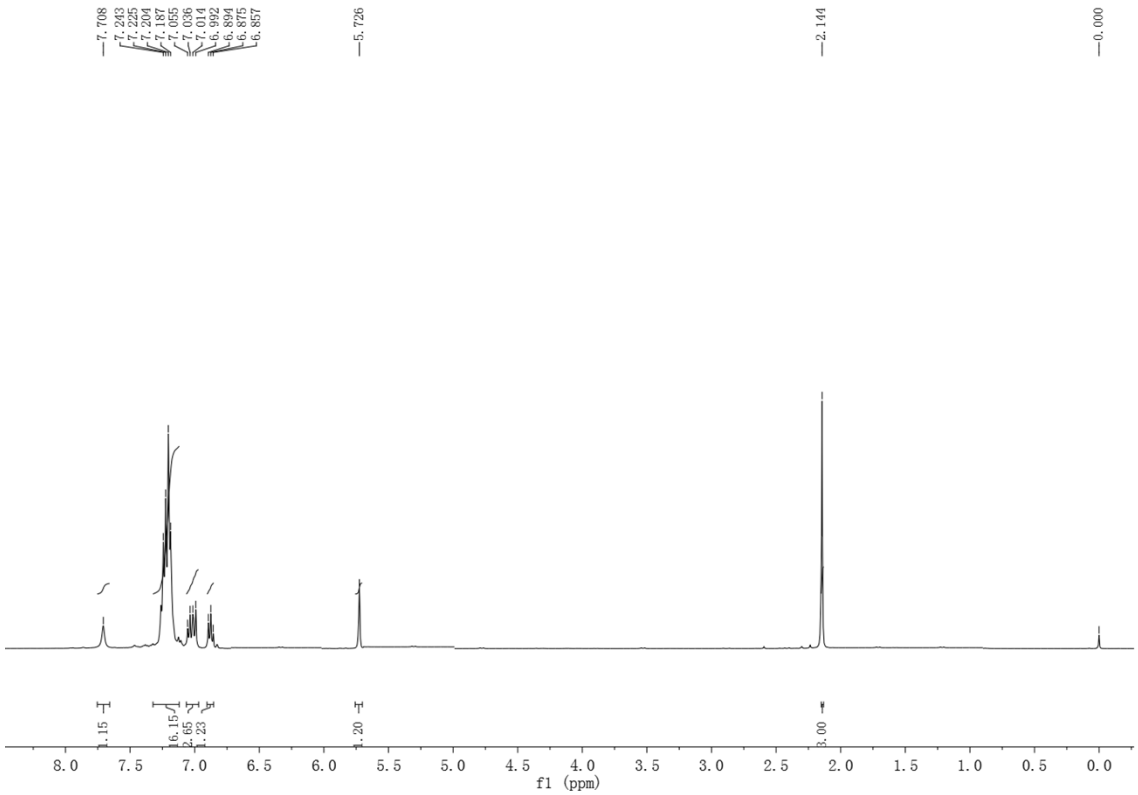
133.069
130.761
128.695
128.386
128.255
127.347
126.757
120.739
119.161
119.074
115.378
110.976
110.689
45.971
27.706
21.334
12.037
f1 (ppm)

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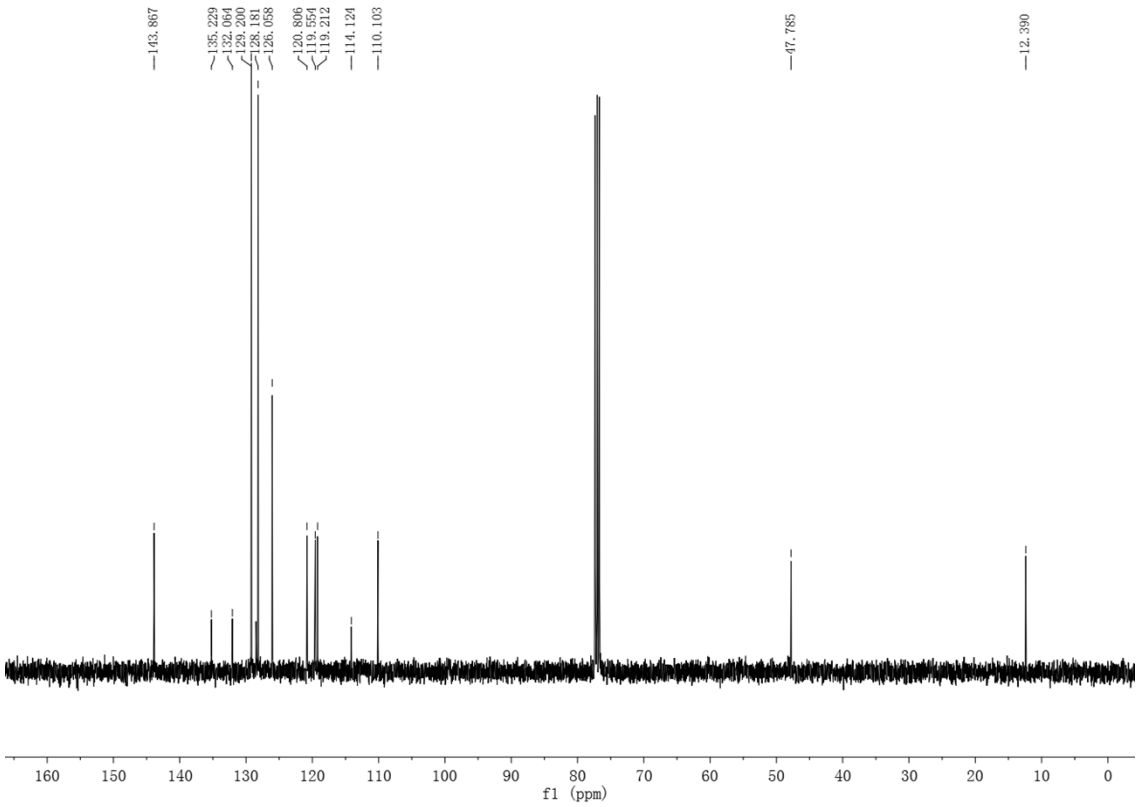
7.243
7.225
7.204
7.187
7.055
7.036
7.014
6.992
6.894
6.875
6.857
5.726
2.144
0.000
1.15
16.15
2.65
1.23
1.20
3.00
f1 (ppm)


143.867
135.229
132.064
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128.181
126.058
120.806
119.554
119.212
114.124
110.103
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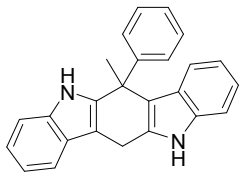
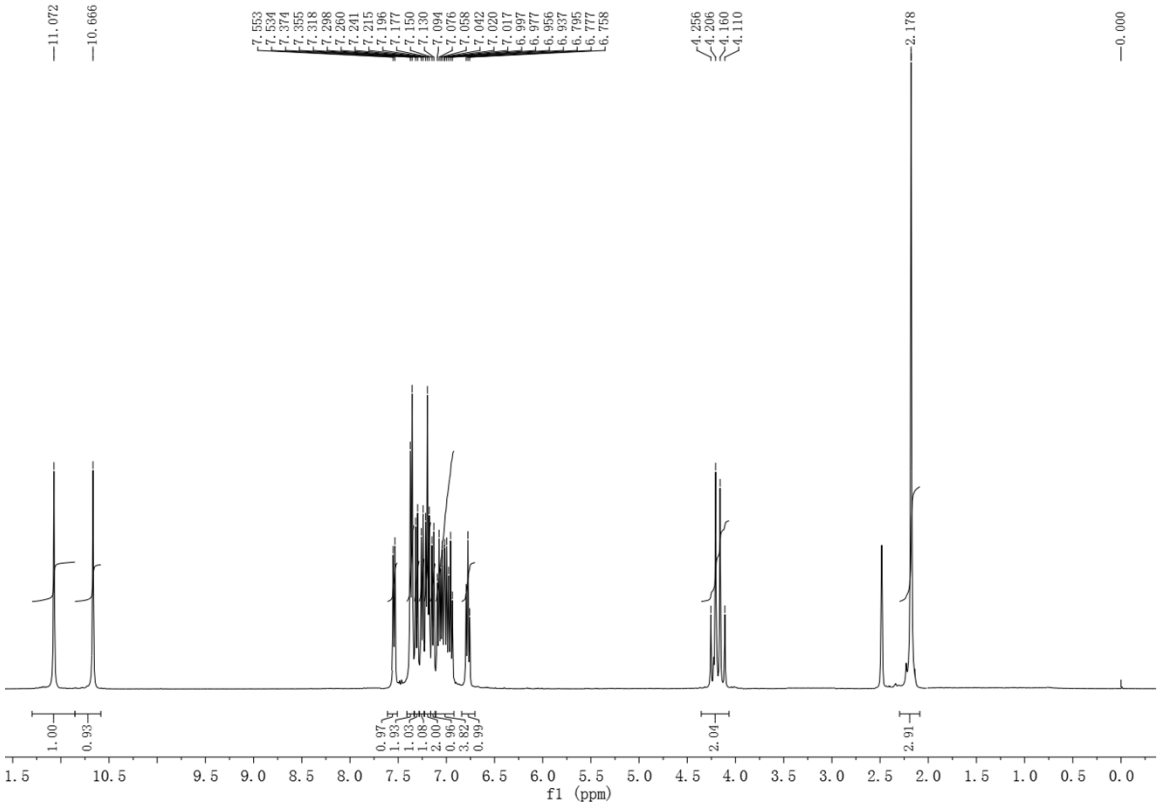
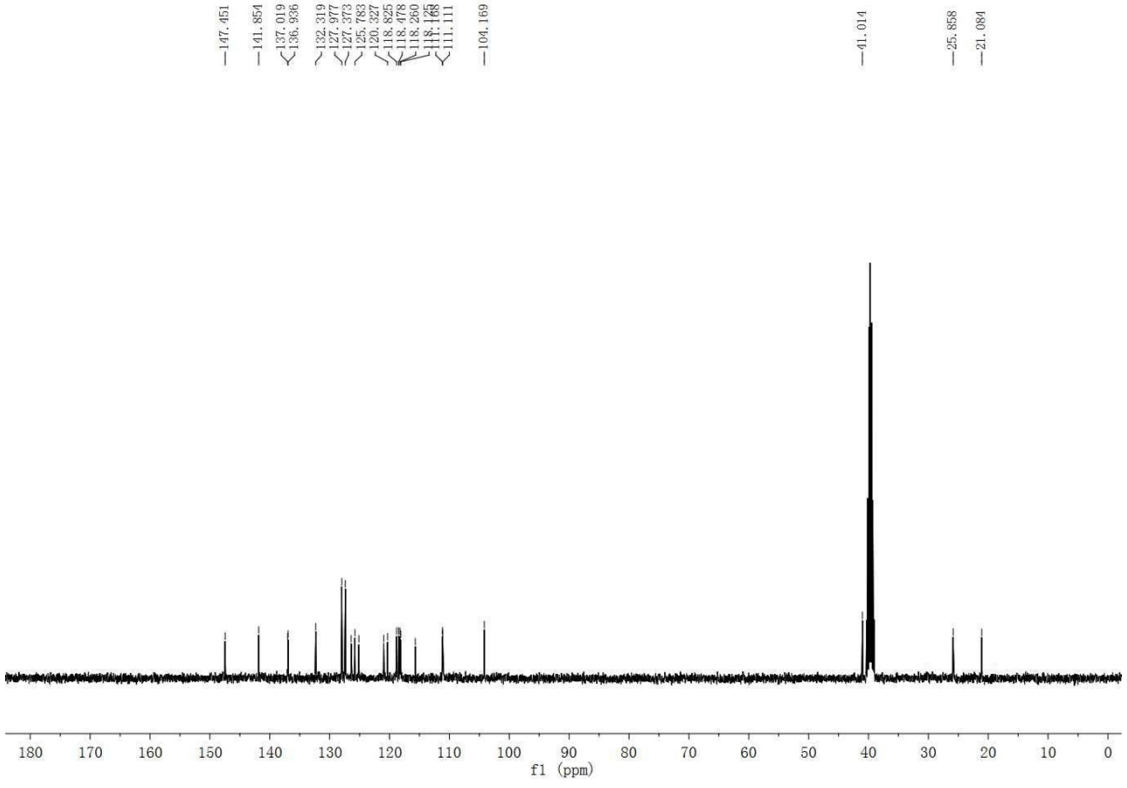
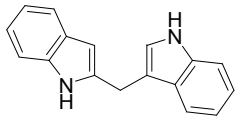
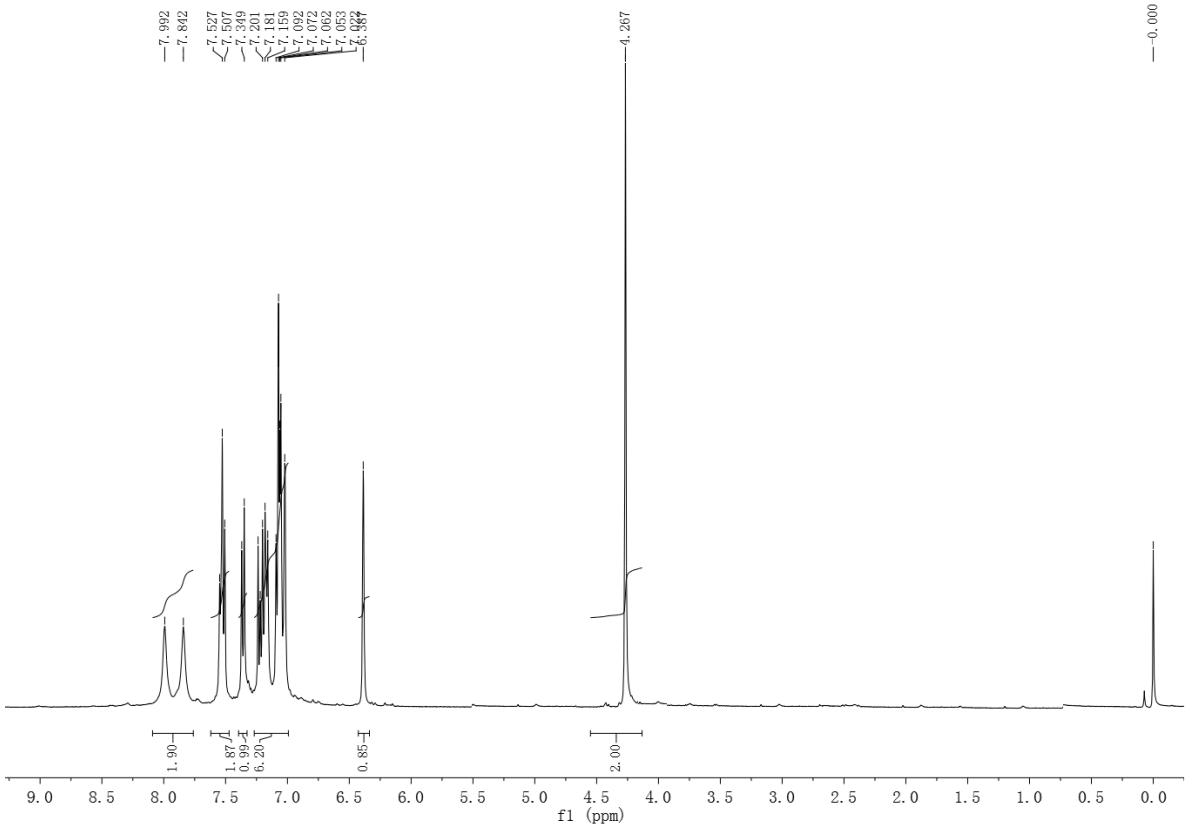
12.390
f1 (ppm)

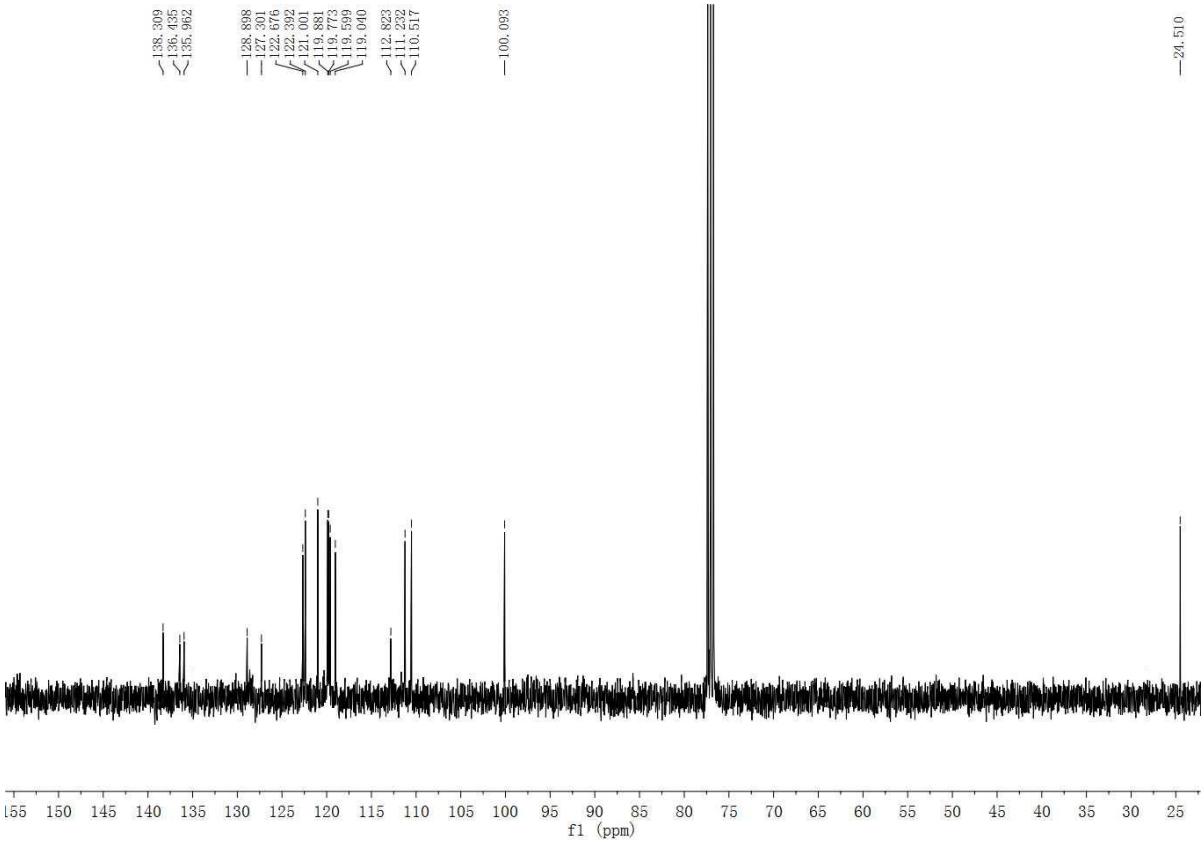



11.072
10.666
7.553
7.534
7.374
7.355
7.318
7.298
7.260
7.241
7.215
7.196
7.177
7.150
7.130
7.094
7.076
7.058
7.042
7.020
7.017
6.997
6.977
6.956
6.937
6.795
6.777
6.758
4.256
4.206
4.160
4.110
2.178
0.000
1.00
0.93
0.97
1.93
1.03
1.08
2.00
0.96
3.82
0.99
2.04
2.91
f1 (ppm)


147.451
141.854
137.019
136.936
132.319
127.977
127.373
125.783
120.327
118.825
118.478
118.260
111.111
104.169
41.014
25.858
21.084
f1 (ppm)




7.992
7.842
7.527
7.507
7.349
7.201
7.181
7.159
7.092
7.072
7.062
7.053
4.267
0.000
1.90
1.87
0.99
6.20
0.85
2.00
f1 (ppm)


138.309
136.435
135.962
128.898
127.301
122.676
122.392
121.001
119.881
119.773
119.599
119.040
112.823
111.232
110.517
100.093
24.510
f1 (ppm)

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