Rh(III)-Catalyzed Dienylation and Cyclopropylation of Indoles at C4 Position with Alkylidenecyclopropanes

Yan-Zhi Liu,[a] Yao-Fu Zeng,[*b] Bing Shu,[c] Yi-Chuan Zheng,[a] Lin Xiao,[a] Shao-Yong Chen,[a] Jia-Lin Song,[a] Xuanxuan Zhang,[*a] Shang-Shi Zhang[*a]

[a]*Center for Drug Research and Development, Guangdong Pharmaceutical University, Guangzhou, 510006, China.*

[b]*School of Pharmaceutical Science, Hunan Provincial Key Laboratory of Tumor Microenvironment Responsive Drug Research, Hengyang Medical School, University of South China, Hengyang, Hunan, 421001, China.*

[c]*School of Pharmacy, Guangdong Pharmaceutical University, Guangzhou, 510006, PR China.*

**E-mail: zhangshangshi@gdpu.edu.cn*

**E-mail: phil2424123@163.com*

**E-mail: zengyf@usc.edu.cn*.

Supporting Information

1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous DCM, MeOH, DMF and 1,4-dioxane etc. were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR (^{1}H) were recorded at 400 MHz, and Carbon NMR (^{13}C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

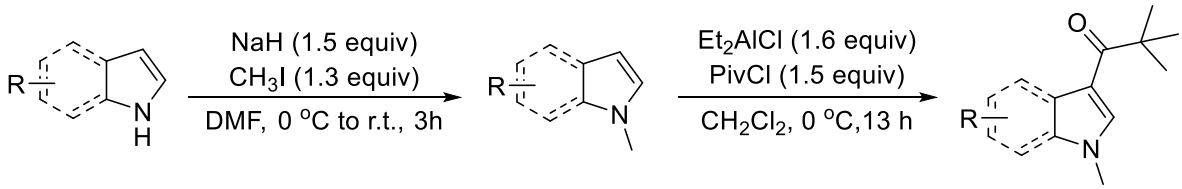
High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light, or KMnO4 staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.

2. Preparation of starting materials

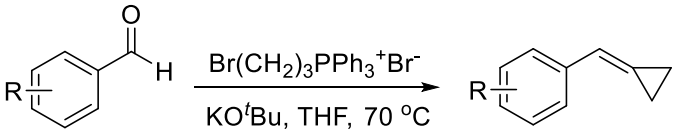
(1) The synthesis of indole substrates[1]



1-methyl-1*H*-indole: NaH (1.1 g, 65% dispersion in mineral oil, 30.0 mmol) was slowly added into the solution of indole (2.34 g, 20.0 mmol) in DMF (10.0 mL) at 0 °C. The heterogeneous mixture was stirred at 0 °C for 10.0 min and 1 h at room temperature. The mixture was then cooled to 0 °C and then iodomethane (1.60 mL, 23.0 mmol) was added. After 3 h, the reaction mixture was cooled to 0 °C, quenched with saturated NH_4Cl (40.0 mL) and water (100.0 mL). The organic phase was extracted by EtOAc and dried over anhydrous Na_2SO_4. The product was obtained by column chromatography on silica gel (PE : EA 100:1, yellow oil, 2.57 g, 98 %).

2,2-dimethyl-1-(1-methyl-1*H*-indole-3-yl) propan-1-one: To a CH_2Cl_2 solution of indole derivative was added Et_2AlCl (1.6 equiv, 2.0 M in hexane) at 0 °C. The mixture was stirred at 0 °C for 1 h. To this solution was added dropwise a CH_2Cl_2 solution of PivCl (1.5 equiv) at 0 °C. The resulting solution was stirred at 0 °C for 12 h, and pH 7.0 aqueous buffer solution was added to quench the reaction, Then the mixture was extracted with CH_2Cl_2 or ethyl acetate and dried over Na_2SO_4. The crude product was purified by chromatography on silica gel (PE : EA 16:1).

(2) (cyclopropylidenemethyl)benzene was prepared according to the reported procedure as following depicted.[2]

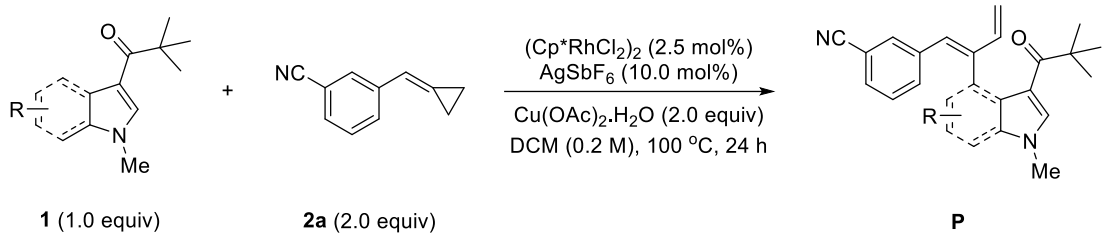


(cyclopropylidenemethyl)benzene: A solution of KO^{t}Bu (3.36 g, 30 mmol, 3.0 equiv) in THF (20.0 ml, 1.5 M) was slowly added to a solution of (3-bromopropyl)triphenylphosphonium bromide (6.96 g, 15 mmol, 1.5 equiv) in dry THF (30.0 ml, 0.5 M) and stirred at 70 °C for 1.0 h. Then a THF solution of 4-(tert-butyl)benzaldehyde (1.62 g, 10 mmol, 2.0 M in THF, 1.0 equiv) was added dropwise and the mixture was refluxed for 3.0 h. After cooling, the suspension was filtered and the

solvent of the filtrate was remove under vacuum, the products were purified by column chromatography on silica gel, eluting with petroleum to afford 1-(tert-butyl)-4-(cyclopropylidenemethyl)benzene (783 mg, 42 %).

3. General procedure for the product

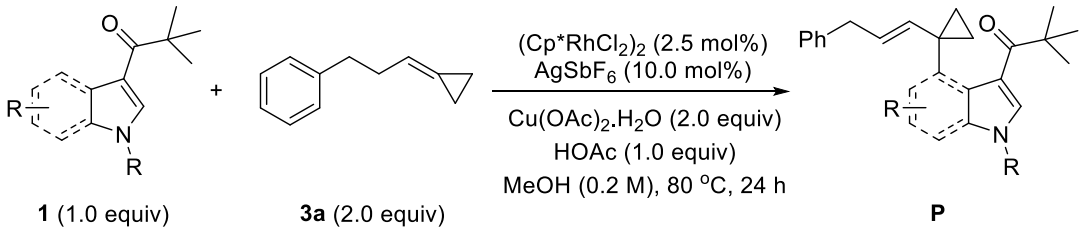
(1) General procedure A



1 (1.0 equiv) **2a** (2.0 equiv) **P**

To a Schlenk tube, 2,2-dimethyl-1-(1-methyl-1*H*-indole-3-yl) propan-1-one **1** (0.2 mmol, 1.0 equiv), 3-(cyclopropylidenemethyl)benzonitrile **2** (31.0 mg, 0.4 mmol, 2.0 equiv), $(Cp^*RhCl_2)_2$ (3.2 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (7.0 mg, 0.02 mmol, 10.0 mmol%), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.4 mmol, 2.0 equiv), and DCM (1.0 ml) were added. The resulting mixture was stirred at 100 °C for 24 h. After that, the resulting mixture was purified by silica gel chromatography using a mixture of petroleum ether/ethyl acetate as an eluent to get **4a-4p.** Fine-tuned temperature and reaction time of the condition above to get **5a-5o**.

(2) General procedure B

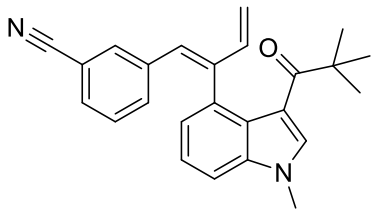


1 (1.0 equiv) **3a** (2.0 equiv) **P**

To a Schlenk tube, 2,2-dimethyl-1-(1-methyl-1*H*-indole-3-yl) propan-1-one **1** (0.1 mmol, 1.0 equiv), (3-cyclopropylidenepropyl)benzene **3** (31.6 mg, 0.2 mmol, 2.0 equiv), $(Cp^*RhCl_2)_2$ (1.6 mg, 0.0025 mmol, 2.5 mmol%), $AgSbF_6$ (3.5 mg, 0.01 mmol, 10.0 mmol%), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.4 mmol, 2.0 equiv), HOAc (6.0 mg, 0.1 mmol, 1.0 equiv), and MeOH (1.0 ml) were added. The resulting mixture was stirred at 80 °C for 24 h. After that, the resulting mixture was purified by silica gel chromatography using a mixture of petroleum ether/ethyl acetate as an eluent to get **6a-6j**.

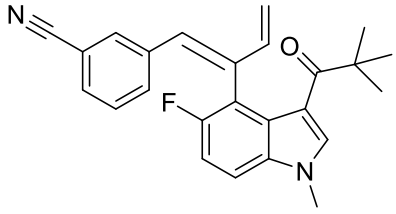
4. Product characterization

(*Z*)-3-(2-(1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4a)



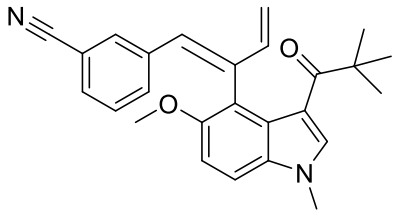
The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.4 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.22), the desired product **4a** was obtained as a yellow solid (59.7 mg, 81 % yield, Z/E = 16.6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.09 (s, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.71 (dd, *J* = 17.2, 10.4 Hz, 1H), 6.58 (s, 1H), 5.10 (d, *J* = 10.5 Hz, 1H), 4.64 (d, *J* = 17.2 Hz, 1H), 3.87 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.33, 144.48, 141.09, 138.84, 137.46, 133.75, 132.68, 131.99, 130.81, 129.47, 128.51, 127.28, 125.61, 123.97, 123.49, 119.12, 116.76, 115.76, 111.72, 109.28, 43.83, 33.55, 28.79. ESI-MS: Calcd. for $C_{25}H_{25}N_2O^+$ $[M+H]^+$: 369.1967, found: 369.1967.

(*Z*)-3-(2-(5-fluoro-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4b)



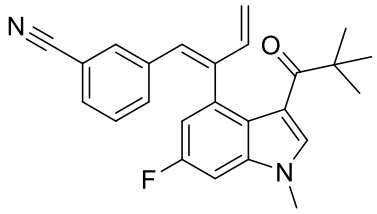
The reaction was performed according to general procedure A with 1-(5-fluoro-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1b** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.18), the desired product **4b** was obtained as a white solid (34.8 mg, 90 % yield, Z/E = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.24 (dd, *J* = 9.1, 4.3 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 5.8 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 9.2 Hz, 1H), 6.73 – 6.59 (m, 1H), 5.05 (d, *J* = 10.5 Hz, 1H), 4.57 (d, *J* = 17.2 Hz, 1H), 3.81 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 155.2 (d, *J* = 236.7 Hz), 139.9, 138.80, 136.9, 133.8, 133.3, 133.0, 132.1, 130.0, 129.6, 128.8, 126.4 (d, *J* = 5.2 Hz), 119.1, 116.5 (d, *J* = 19.9 Hz), 116.2, 112.2, 111.9 (d, *J* = 6.2 Hz), 110.5 (d, *J* = 10.2 Hz). 43.9, 33.8, 28.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.5. ESI-MS: Calcd. for $C_{25}H_{24}FN_2O^+$ $[M+H]^+$: 387.1873, found: 387.1876.

(*Z*)-3-(2-(5-methoxy-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4c)



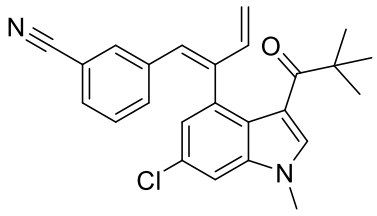
The reaction was performed according to general procedure A with 1-(5-methoxy-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1c** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.17), the desired product **4c** was obtained as a yellow oil (44.4 mg, 79 % yield, Z/E = 7.7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 8.9, 6.4 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 1H), 6.74 (dd, *J* = 17.1, 10.4 Hz, 1H), 6.67 (s, 1H), 5.09 (d, *J* = 10.3 Hz, 1H), 4.65 (d, *J* = 17.1 Hz, 1H), 3.84 (s, 3H), 3.62 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 152.0, 140.5, 139.6, 139.3, 133.3, 133.1, 132.5, 132.0, 129.6, 128.8, 128.6, 126.4, 119.3, 118.3, 115.8, 115.7, 111.8, 110.5, 110.0, 57.7, 43.9, 33.4, 28.8. ESI-MS: Calcd. for $C_{26}H_{27}N_2O_2^+$ $[M+H]^+$: 399.2073, found: 399.2078.

(*Z*)-3-(2-(6-fluoro-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4d)



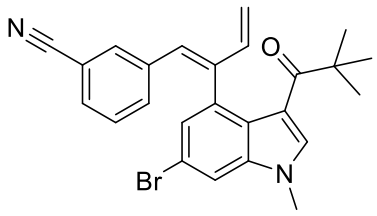
The reaction was performed according to general procedure A with 1-(6-fluoro-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1d** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.21), the desired product **4d** was obtained as a white solid (39.7 mg, 81 % yield, Z/E = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.16 (d, *J* = 12.8 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.75 – 6.62 (m, 2H), 6.59 (s, 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 4.63 (d, *J* = 17.2 Hz, 1H), 3.83 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 160.1 (d, *J* = 241.2 Hz), 143.2, 140.5, 138.4, 137.7 (d, *J* = 12.1 Hz), 133.2 (d, *J* = 103.0 Hz), 132.4, 132.4, 132.4, 129.8, 128.7, 127.7, 122.2, 119.0, 116.9, 116.0, 112.3 (d, *J* = 24.1 Hz), 111.9, 95.8 (d, *J* = 25.7 Hz). 43.9, 33.6, 28.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.66. ESI-MS: Calcd. for $C_{25}H_{24}FN_2O^+$ $[M+H]^+$: 387.1873, found: 387.1878.

(*Z*)-3-(2-(6-chloro-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4e)



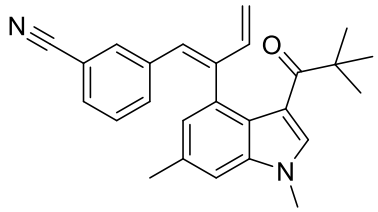
The reaction was performed according to general procedure A with 1-(6-chloro-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1e** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile 2a (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.22), the desired product **4e** was obtained as a white solid (32.6 mg, 81 % yield, Z/E = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.34 (d, *J* = 6.9 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.15 (d, *J* = 9.1 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 6.67 (dd, *J* = 17.2, 10.5 Hz, 1H), 6.59 (s, 1H), 5.11 (d, *J* = 10.4 Hz, 1H), 4.60 (d, *J* = 17.2 Hz, 1H), 3.85 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 143.0, 140.7, 138.4, 137.9, 133.7, 132.8, 132.5, 132.3, 129.9, 129.3, 128.7, 127.9, 124.5, 124.2, 119.1, 117.0, 116.0, 112.0, 109.4, 43.9, 33.7, 28.7. ESI-MS: Calcd. for $C_{25}H_{24}ClN_2O^+$ $[M+H]^+$: 403.1577, found: 403.1577.

(*Z*)-3-(2-(6-bromo-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4f)



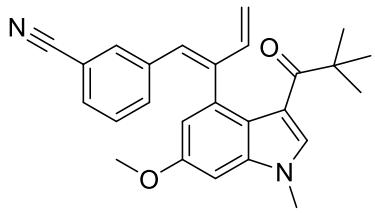
The reaction was performed according to general procedure A with 1-(6-bromo-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1f** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.22), the desired product **4f** was obtained as a white solid (28.5 mg, 64 % yield, Z/E = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.53 – 7.50 (m, 1H), 7.49 (s, 1H), 7.28 (d, *J* = 6.1 Hz, 1H), 7.13 (s, 2H), 7.00 (d, *J* = 1.2 Hz, 1H), 6.67 (dd, *J* = 17.2, 10.5 Hz, 1H), 6.59 (s, 1H), 5.11 (d, *J* = 10.5 Hz, 1H), 4.60 (d, *J* = 17.2 Hz, 1H), 3.85 (s, 3H), 1.18 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 142.9, 140.7, 138.4, 138.2, 133.7, 132.8, 132.6, 132.4, 129.9, 128.7, 128.0, 126.7, 124.8, 119.1, 117.0, 116.8, 116.1, 112.4, 112.0, 44.00, 33.7, 28.7. ESI-MS: Calcd. for $C_{25}H_{24}BrN_2O^+$ $[M+H]^+$: 447.1072, found: 447.1071.

(*Z*)-3-(2-(1,6-dimethyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4g)



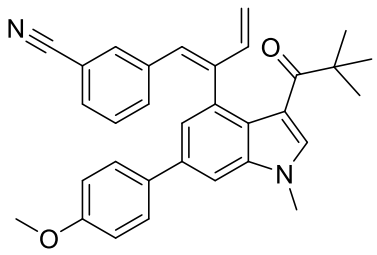
The reaction was performed according to general procedure A with 1-(1,6-dimethyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1g** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.15), the desired product **4g** was obtained as a yellow solid (32.6 mg, 85 % yield, Z/E = 7.1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 5.9 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.07 (s, 1H), 6.72 (q, *J* = 10.3 Hz, 1H), 6.55 (s, 1H), 5.12 (d, *J* = 10.5 Hz, 1H), 4.67 (d, *J* = 17.1 Hz, 1H), 3.83 (s, 3H), 2.42 (s, 3H), 1.17 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 144.5, 141.3, 138.9, 138.0, 133.8, 133.5, 132.7, 131.7, 130.5, 129.5, 128.5, 127.3, 125.5, 123.5, 119.2, 116.8, 115.6, 111.8, 109.3, 43.8, 33.5, 28.8, 21.7. ESI-MS: Calcd. for $C_{26}H_{27}N_2O^+$ $[M+H]^+$: 383.2123, found: 383.2125.

(*Z*)-3-(2-(6-methoxy-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4h)



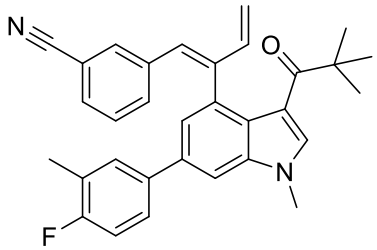
The reaction was performed according to general procedure A with 1-(6-methoxy-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1h** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.15), the desired product **4h** was obtained as a yellow solid (37.9 mg, 95 % yield, Z/E = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.77 (s, 1H), 6.69 (dd, *J* = 17.1, 10.4 Hz, 1H), 6.55 (s, 2H), 5.12 (d, *J* = 10.4 Hz, 1H), 4.69 (d, *J* = 17.1 Hz, 1H), 3.82 (s, 6H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 157.2, 144.1, 141.0, 138.7, 138.5, 133.8, 132.7, 131.8, 131.3, 129.6, 128.6, 127.4, 119.9, 119.2, 116.9, 115.8, 113.3, 111.8, 92.7, 55.8, 43.9, 33.6, 28.8. ESI-MS: Calcd. for $C_{26}H_{27}N_2O_2^+$ $[M+H]^+$: 399.2073, found: 399.2069.

(*Z*)-3-(2-(6-(4-methoxyphenyl)-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4i)



The reaction was performed according to general procedure A with 1-(6-(4-methoxyphenyl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1i** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.13), the desired product **4i** was obtained as a yellow solid (34.5 mg, 73 % yield, Z/E = 7.1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.49 (d, *J* = 8.7 Hz, 3H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 9.0 Hz, 2H), 7.12 (s, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.74 (dd, *J* = 17.2, 10.4 Hz, 1H), 6.61 (s, 1H), 5.14 (d, *J* = 10.5 Hz, 1H), 4.73 (d, *J* = 17.1 Hz, 1H), 3.91 (s, 3H), 3.83 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 159.1, 144.5, 141.2, 138.8, 138.2, 136.6, 133.8, 133.8, 132.8, 132.4, 131.1, 129.6, 128.6, 128.4, 127.5, 124.6, 123.4, 119.2, 116.9, 115.8, 114.3, 111.8, 107.1, 55.5, 43.9, 33.6, 28.8. ESI-MS: Calcd. for $C_{32}H_{31}N_2O_2^+$ $[M+H]^+$: 475.2386, found: 475.2379.

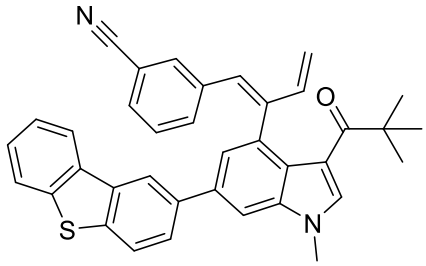
(*Z*)-3-(2-(6-(4-fluoro-3-methylphenyl)-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4j)



The reaction was performed according to general procedure A with 1-(6-(4-fluoro-3-methylphenyl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1j** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.24), the desired product **4j** was obtained as a yellow solid (30.2 mg, 63 % yield, Z/E = 5.6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.46 (d, *J* = 4.1 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.13 (s, 1H), 7.12 – 7.07 (m, 2H), 7.03 (t, *J* = 8.9 Hz, 1H), 6.75 (dd, *J* = 17.2, 10.3 Hz, 1H), 6.62 (s, 1H), 5.14 (d, *J* = 10.5 Hz, 1H), 4.72 (d, *J* = 17.2 Hz, 1H), 3.92 (s, 3H), 2.32 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 161.0 (d, *J* = 245.1 Hz), 144.3, 141.2, 138.8, 138.1, 137.1 (d, *J* = 3.5 Hz), 136.2, 133.8, 132.8, 132.6, 131.2, 130.4 (d, *J* = 5.1 Hz), 129.6, 128.6, 127.6, 126.2 (d, *J* = 8.0 Hz), 125.1 (d, *J* = 17.4 Hz), 124.9, 123.6,

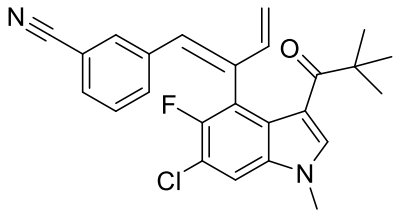
119.1, 117.0, 115.3 (d, J = 22.4 Hz). 115.2, 111.84 107.4, 43.9, 33.7, 28.8, 14.8 (d, J = 3.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.22. ESI-MS: Calcd. for $C_{32}H_{30}FN_2O^+$ $[M+H]^+$: 477.2342, found: 477.2341.

(*Z*)-3-(2-(6-(dibenzo[b,d]thiophen-2-yl)-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4k)



The reaction was performed according to general procedure A with 1-(6-(dibenzo[b,d]thiophen-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1k** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.16), the desired product **4k** was obtained as a yellow oil (34.5 mg, 63 % yield, Z/E = 6.3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.23 – 8.17 (m, 1H), 7.86 (dd, J = 9.5, 6.1 Hz, 2H), 7.68 – 7.60 (m, 3H), 7.51 – 7.42 (m, 2H), 7.26 – 7.19 (m, 2H), 7.11 (t, J = 7.7 Hz, 1H), 6.78 (dd, J = 17.2, 10.5 Hz, 1H), 6.66 (s, 1H), 5.17 (d, J = 10.5 Hz, 1H), 4.78 (d, J = 17.2 Hz, 1H), 3.97 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 144.4, 141.1, 140.0, 138.9, 138.4, 138.2, 138.0, 136.9, 136.2, 135.5, 133.8, 132.8, 132.6, 131.3, 129.7, 128.6, 127.6, 127.0, 126.4, 125.1, 124.5, 124.0, 123.1, 123.0, 121.8, 120.2, 119.1, 117.0, 115.9, 111.9, 107.8, 43.9, 33.7, 28.8. ESI-MS: Calcd. for $C_{37}H_{31}N_2OS^+$ $[M+H]^+$: 551.2157, found: 551.2158

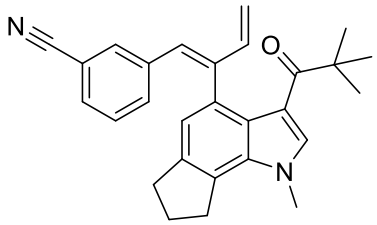
(*Z*)-3-(2-(6-chloro-5-fluoro-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4l)



The reaction was performed according to general procedure A with 1-(6-chloro-5-fluoro-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1l** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.13), the desired product **4l** was obtained as a white solid (26.5 mg, 63 % yield, Z/E = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.41 (d, J = 5.8 Hz, 1H), 7.30 (d, J = 7.4 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 7.7 Hz, 1H), 6.76 (s, 1H), 6.68 (dd, J = 17.2, 10.5 Hz, 1H), 5.10 (d, J = 10.4 Hz, 1H), 4.56 (d, J = 17.2 Hz, 1H), 3.85 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 150.4 (d, J = 239.4 Hz), 139.6, 138.5, 136.0, 133.2 (d, J = 3.1 Hz), 132.1, 130.3, 130.1, 128.9, 125.1 (d, J = 3.9 Hz), 119.0,

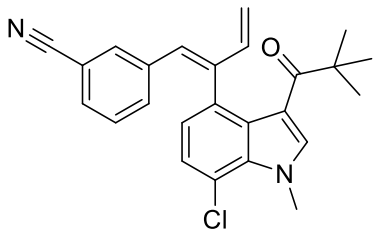
118.0 (d, J = 20.1 Hz), 117.7 (d, J = 23.1 Hz), 116.4 (d, J = 4.4 Hz). 116.3, 112.1, 111.0, 44.0, 33.9, 28.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.64. ESI-MS: Calcd. for $C_{25}H_{23}ClFN_2O^+$ $[M+H]^+$: 421.1483, found: 421.1484.

(*Z*)-3-(2-(1-methyl-3-pivaloyl-1,6,7,8-tetrahydrocyclopenta[*g*]indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4m)



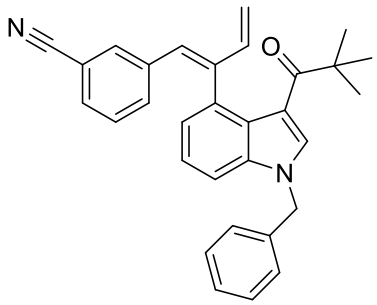
The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1,6,7,8-tetrahydrocyclopenta[*g*]indol-3-yl)propan-1-one **1m** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.15), the desired product **4m** was obtained as a yellow solid (31.3 mg, 78 % yield, Z/E = 7.7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.73 (s, 1H), 6.66 (dd, J = 17.2, 10.4 Hz, 1H), 6.53 (s, 1H), 5.09 (d, J = 10.6 Hz, 1H), 4.66 (d, J = 17.0 Hz, 1H), 4.03 (s, 3H), 3.54 – 3.32 (m, 2H), 2.93 (t, J = 7.5 Hz, 2H), 2.21 (ddd, J = 11.9, 7.3, 4.1 Hz, 2H), 1.18 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 145.0, 141.3, 140.9, 139.0, 134.9, 133.9, 132.83, 131., 129.4, 128.9, 128.5, 127.1, 125.3, 124.8, 120.8, 119.30, 116., 116.10, 111.1, 43., 36.0, 32.6, 31.6, 28.9, 25.4. ESI-MS: Calcd. for $C_{28}H_{28}N_2O^+$ $[M+H]^+$: 409.2280, found: 409.2284.

(*Z*)-3-(2-(7-chloro-1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4n)



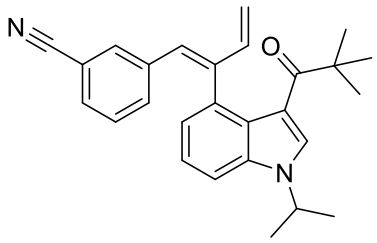
The reaction was performed according to general procedure A with 1-(7-chloro-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1n** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.20), the desired product **4n** was obtained as a yellow solid (34.8 mg, 86 % yield, Z/E = 4.3:1). ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.32 – 7.26 (m, 1H), 7.24 (s, 1H), 7.18 (dd, J = 7.8, 3.5 Hz, 1H), 7.13 (t, J = 7.7 Hz, 1H), 6.71 (d, J = 7.9 Hz, 1H), 6.67 – 6.56 (m, 1H), 5.08 (d, J = 10.5 Hz, 1H), 4.57 (d, J = 17.2 Hz, 1H), 4.25 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 143.5, 140.7, 138.7, 134.2, 133.8, 132.9, 129.8, 129.8, 128.7, 127.7, 125.2, 124.8, 116.9, 44.0, 38.0, 28.8. ESI-MS: Calcd. for $C_{25}H_{24}ClN_2O^+$ $[M+H]^+$: 403.1577, found: 403.1579.

(*Z*)-3-(2-(1-benzyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4o)



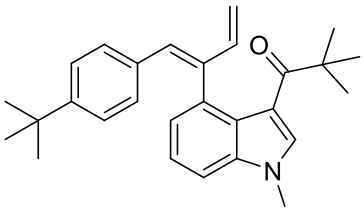
The reaction was performed according to general procedure A with 1-(1-benzyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1o** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.24), the desired product **4o** was obtained as a yellow oil (28.4 mg, 64 % yield, Z/E = 6.3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 4.5 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.03 (dd, *J* = 12.3, 6.9 Hz, 4H), 6.95 (s, 1H), 6.83 (d, *J* = 7.1 Hz, 1H), 6.68 (dd, *J* = 17.2, 10.4 Hz, 1H), 6.50 (s, 1H), 5.33 (s, 2H), 5.10 (d, *J* = 10.5 Hz, 1H), 4.68 (d, *J* = 17.1 Hz, 1H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 144.3, 141.3, 138.8, 137.1, 136.2, 133.7, 132.6, 131.5, 130.9, 129.6, 129.2, 128.6, 128.2, 127.5, 126.7, 125.6, 124.2, 123.7, 119.1, 117.1, 116.2, 111.9, 109.9, 50.7, 43.9, 28.8. ESI-MS: Calcd. for $C_{31}H_{29}N_2O^+$ $[M+H]^+$: 445.2280, found: 445.2279.

(*Z*)-3-(2-(1-isopropyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (4p)



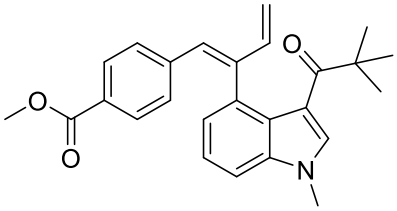
The reaction was performed according to general procedure A with 1-(1-isopropyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1p** (0.1 mmol) and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.19), the desired product **4p** was obtained as a white solid (24.7 mg, 62 % yield, Z/E = 8.3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.97 (s, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.73 (dd, *J* = 17.2, 10.4 Hz, 1H), 6.55 (s, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 4.82 – 4.69 (m, 2H), 1.60 (dd, *J* = 6.5, 3.7 Hz, 6H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 144.5, 141.2, 138.8, 136.5, 133.8, 132.6, 130.9, 129.5, 128.5, 127.3, 127.0, 125.6, 124.0, 123.3, 119.1, 117.0, 116.0, 111.8, 109.5, 47.7, 43.8, 28.9, 22.8, 22.8. ESI-MS: Calcd. for $C_{27}H_{29}N_2O^+$ $[M+H]^+$: 397.2280, found: 397.2285.

(*Z*)-1-(4-(1-(4-(tert-butyl)phenyl)buta-1,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (5a)



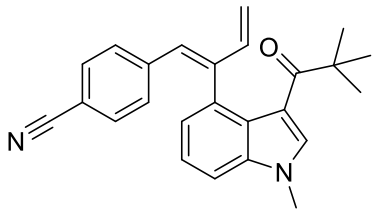
The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.1 mmol) and 1-(*tert*-butyl)-4-(cyclopropylidenemethyl)benzene **2** (0.2 mmol) at 80°C for 20 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate =16:1, R_f = 0.18), the desired product **5a** was obtained as a yellow solid (26.5 mg, 66 % yield, Z/E = 4.3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.36 – 7.29 (m, 2H), 7.03 (dd, *J* = 5.8, 2.5 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.80 (dd, *J* = 17.2, 10.5 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 2H), 6.60 (s, 1H), 5.07 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 17.1 Hz, 1H), 3.85 (s, 3H), 1.18 (s, 9H), 1.12 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.6, 149.3, 142.5, 140.5, 137.5, 134.4, 132.2, 131.2, 130.5, 129.2, 125.4, 124.8, 124.1, 123.3, 116.1, 114.6, 108.6, 43.8, 34.4, 33.5, 31.2, 28.7. ESI-MS: Calcd. for $C_{28}H_{34}NO^+$ $[M+H]^+$: 400.2640, found: 400.2638.

methyl (*Z*)-4-(2-(1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzoate (5b)



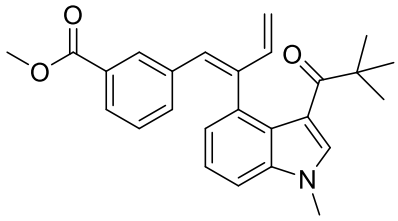
The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and methyl 4-(cyclopropylidenemethyl)benzoate **2b** (0.4 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate =8:1, R_f = 0.18), the desired product **5b** was obtained as a yellow solid (48.1 mg, 60 % yield, Z/E = 6.6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.52 (s, 1H), 7.31 (dd, *J* = 16.5, 7.5 Hz, 2H), 6.94 (d, *J* = 6.9 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.79 (dd, *J* = 17.2, 10.4 Hz, 1H), 6.64 (s, 1H), 5.15 (d, *J* = 10.5 Hz, 1H), 4.72 (d, *J* = 17.1 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 167.1, 144.2, 142.3, 141.8, 137.5, 131.8, 131.4, 129.2, 129.1, 129.1, 127.4, 125.5, 124.1, 123.4, 116.6, 115.8, 109.0, 51.9, 43.9, 33.5, 28.8. ESI-MS: Calcd. for $C_{26}H_{28}NO_3^+$ $[M+H]^+$: 402.2069, found: 402.2061.

(*Z*)-4-(2-(1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzonitrile (5c)



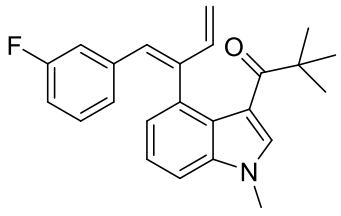
The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 4-(cyclopropylidenemethyl)benzonitrile **2c** (0.4 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate =8:1, R_f = 0.19), the desired product **5c** was obtained as a yellow solid (37.9 mg, 51 % yield, Z/E = 14.3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.25 (s, 1H), 7.23 (s, 1H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 7.1 Hz, 1H), 6.73 (dd, *J* = 17.2, 10.4 Hz, 1H), 6.61 (s, 1H), 5.14 (d, *J* = 10.5 Hz, 1H), 4.67 (d, *J* = 17.2 Hz, 1H), 3.87 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 145.4, 142.4, 141.3, 137.5, 132.0, 131.5, 131.0, 129.8, 128.1, 125.6, 124.0, 123.5, 119.4, 117.3, 115.8, 109.3, 109.0, 43.9, 33.6, 28.8. ESI-MS: Calcd. for $C_{25}H_{25}N_2O^+$ $[M+H]^+$: 369.1967, found: 369.1966

methyl (*Z*)-3-(2-(1-methyl-3-pivaloyl-1*H*-indol-4-yl)buta-1,3-dien-1-yl)benzoate (5d)



The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and methyl 3-(cyclopropylidenemethyl)benzoate **2d** (0.4 mmol) for 23 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate =8:1, R_f = 0.19), the desired product **5d** was obtained as a colorless oil (50.9 mg, 63 % yield, Z/E = 8.3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.3 Hz, 1H), 7.57 (s, 1H), 7.51 (s, 1H), 7.37 – 7.23 (m, 2H), 7.02 – 6.88 (m, 3H), 6.78 (dd, *J* = 17.2, 10.4 Hz, 1H), 6.64 (s, 1H), 5.12 (d, *J* = 10.5 Hz, 1H), 4.71 (d, *J* = 17.2 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 167.1, 142.9, 141.8, 137.7, 137.6, 133.5, 131.7, 131.4, 130.7, 129.6, 129.0, 127.8, 127.3, 125.5, 124.10, 123.4, 115.9, 108.8, 51.9, 43.8, 33.5, 28.7. ESI-MS: Calcd. for $C_{26}H_{28}NO_3^+$ $[M+H]^+$: 402.2069, found: 402.2072.

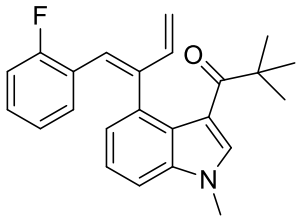
(*Z*)-1-(4-(1-(3-fluorophenyl)buta-1,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (5e)



The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 1-(cyclopropylidenemethyl)-3-fluorobenzene **2e**

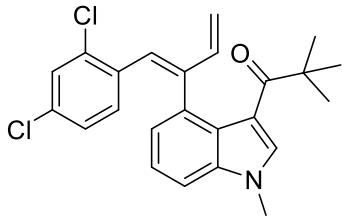
(0.4 mmol) at 80ºC for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate =16:1, R_f = 0.17), the desired product **5e** was obtained as a yellow solid (49.4 mg, 68 % yield, Z/E = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.32 (dd, *J* = 11.7, 7.5 Hz, 2H), 6.96 (q, *J* = 7.5 Hz, 2H), 6.76 (dd, *J* = 17.1, 10.4 Hz, 1H), 6.67 (dd, *J* = 18.1, 7.9 Hz, 2H), 6.58 (s, 1H), 6.43 (d, *J* = 11.2 Hz, 1H), 5.10 (d, *J* = 10.4 Hz, 1H), 4.67 (d, *J* = 17.2 Hz, 1H), 3.85 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 162.5 (d, *J* = 243.2 Hz), 143.0, 141.8, 139.7 (d, *J* = 8.1 Hz), 137.5, 131.7, 131.4, 129.1 (d, *J* = 8.5 Hz), 129.0 (d, *J* = 2.6 Hz), 125.5, 124.1, 123.4, 116.0, 115.9, 115.6 (d, *J* = 22.3 Hz), 113.1 (d, *J* = 21.6 Hz), 109.0, 43.9, 33.6, 28.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.49. ESI-MS: Calcd. for $C_{24}H_{25}FNO^+$ $[M+H]^+$: 362.1920, found: 362.1923.

(*Z*)-1-(4-(1-(2-fluorophenyl)buta-1,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (5f)



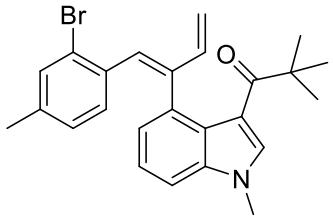
The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 1-(cyclopropylidenemethyl)-2-fluorobenzene **2f** (0.4 mmol) at 80ºC for 23 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate =16:1, R_f = 0.15), the desired product **5f** was obtained as a yellow solid (53.0 mg, 73 % yield, Z/E = 14.3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 6.92 (dd, *J* = 17.4, 7.8 Hz, 3H), 6.84 (s, 1H), 6.77 (dd, *J* = 17.2, 10.4 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.52 (dd, *J* = 11.0, 4.7 Hz, 1H), 5.07 (d, *J* = 10.5 Hz, 1H), 4.62 (d, *J* = 17.2 Hz, 1H), 3.85 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 160.8 (d, *J* = 248.1 Hz), 143.3, 141.7, 137.4, 131.7, 131.5, 130.4 (d, *J* = 2.9 Hz), 127.7 (d, *J* = 8.4 Hz), 125.8, 125.4 (d, *J* = 11.6 Hz), 124.2, 123.4, 123.3 (d, *J* = 3.5 Hz), 121.3, 121.2, 116.1, 115.6, 114.7 (d, *J* = 22.3 Hz), 108.8, 43.9, 33.5, 28.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.01. ESI-MS: Calcd. for $C_{24}H_{25}FNO^+$ $[M+H]^+$: 362.1920, found: 362.1922

(*Z*)-1-(4-(1-(2,4-dichlorophenyl)buta-1,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (5g)



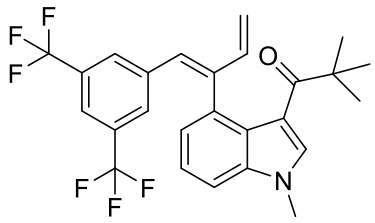
The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 2,4-dichloro-1-(cyclopropylidenemethyl)benzene **2g** (0.4 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate =16:1, R_f = 0.17), the desired product **5g** was obtained as a yellow oil (44.5 mg, 54 % yield, Z/E > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.26 (s, 2H), 7.16 (s, 1H), 6.81 (d, *J* = 12.0 Hz, 3H), 6.75 – 6.59 (m, 2H), 5.02 (d, *J* = 6.4 Hz, 1H), 4.53 (d, *J* = 17.2 Hz, 1H), 3.83 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 144.6, 140.8, 137.3, 134.7, 134.5, 132.3, 132.1, 131.7, 131.4, 128.6, 126.3, 124.9, 124.5, 123.5, 116.2, 116.1, 108.9, 43.9, 33.5, 28.9. ESI-MS: Calcd. for $C_{24}H_{24}Cl_2NO^+$ $[M+H]^+$: 412.1235, found: 412.1237.

(*Z*)-1-(4-(1-(2-bromo-4-methylphenyl)buta-1,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (5h)



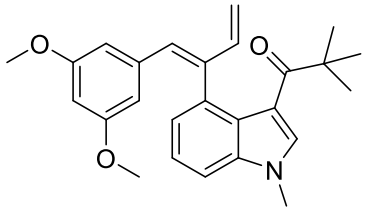
The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 2-bromo-1-(cyclopropylidenemethyl)-4-methylbenzene **2h** (0.4 mmol) at 80^{o}C for 23 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate =16:1, R_f = 0.15), the desired product **5h** was obtained as a yellow solid (69.6 mg, 80 % yield, Z/E = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.23 (s, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 3.0 Hz, 1H), 6.75 (dd, *J* = 13.2, 7.7 Hz, 2H), 6.65 (dd, *J* = 17.2, 10.5 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 10.5 Hz, 1H), 4.45 (d, *J* = 17.2 Hz, 1H), 3.77 (s, 3H), 2.07 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 143.2, 141.1, 137.6, 137.2, 134.6, 132.4, 131.8, 131.4, 131.4, 128.6, 127.5, 126.3, 124.6, 124.5, 123.4, 116.2, 115.2, 108.6, 43.9, 33.5, 28.9, 20.8. ESI-MS: Calcd. for $C_{25}H_{27}BrNO^+$ $[M+H]^+$: 436.1276, found: 436.1278.

(*Z*)-1-(4-(1-(3,5-bis(trifluoromethyl)phenyl)buta-1,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (5i)



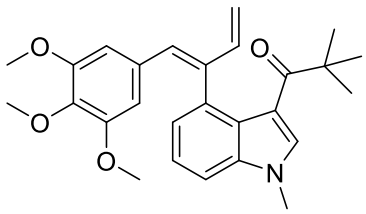
The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 1-(cyclopropylidenemethyl)-3,5-bis(trifluoromethyl)benzene **2i** (0.4 mmol) at 80°C for 29 h. However, The solvent of this reaction needs to be changed to methanol. After purification by silica gel chromatography (petroleum ether/ethyl acetate =16:1, R_f = 0.19), the desired product **5i** was obtained as a white solid (66.2 mg, 69 % yield, Z/E > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.40 (s, 1H), 7.37 (d, *J* = 4.4 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.08 (s, 2H), 6.99 (d, *J* = 6.8 Hz, 1H), 6.84 (dd, *J* = 17.1, 10.4 Hz, 1H), 6.60 (s, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.94 (d, *J* = 17.1 Hz, 1H), 3.86 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 145.6, 141.2, 139.4, 137.7, 132.6, 130.8 (q, *J* = 32.9 Hz), 130.4, 128.9 (d, *J* = 2.9 Hz), 126.6, 125.2, 124.0, 123.7, 123.3 (q, *J* = 545.4, 272.8 Hz), 119.3 (dt, *J* = 7.0, 3.5 Hz), 118.1, 115.5, 109.4, 43.7, 33.6, 28.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.39. ESI-MS: Calcd. for $C_{26}H_{24}F_6NO^+$ $[M+H]^+$: 480.1762, found: 480.1769.

(*Z*)-1-(4-(1-(3,5-dimethoxyphenyl)buta-1,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (5j)



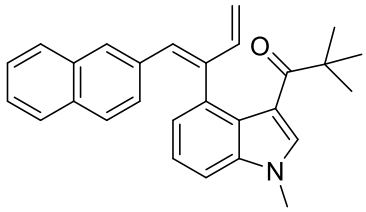
The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 1-(cyclopropylidenemethyl)-3,5-dimethoxybenzene **2j** (0.4 mmol) at 120°C for 35 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.13), the desired product **5j** was obtained as a yellow solid (48.1 mg, 60 % yield, Z/E = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.28 – 7.22 (m, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 6.8 Hz, 1H), 6.73 (dd, *J* = 17.1, 10.4 Hz, 1H), 6.43 (s, 1H), 6.01 (s, 1H), 5.88 (d, *J* = 1.9 Hz, 2H), 5.06 (d, *J* = 10.3 Hz, 1H), 4.70 (d, *J* = 17.1 Hz, 1H), 3.73 (s, 3H), 3.25 (s, 6H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 159.9, 142.3, 141.9, 139.0, 137.5, 132.0, 131.6, 130.3, 125.5, 124.3, 123.4, 116.0, 115.6, 108.6, 107.0, 100.0, 54.8, 43.8, 33.5, 28.7. ESI-MS: Calcd. for $C_{26}H_{30}NO_3^+$ $[M+H]^+$: 404.2226, found: 404.2229.

(*Z*)-2,2-dimethyl-1-(1-methyl-4-(1-(3,4,5-trimethoxyphenyl)buta-1,3-dien-2-yl)-1*H*-indol-3-yl)propan-1-one (5k)



The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 5-(cyclopropylidenemethyl)-1,2,3-trimethoxybenzene **2k** (0.4 mmol) at 120°C for 31.5 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.12), the desired product **5k** was obtained as a white solid (28.4 mg, 33 % yield, Z/E > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 7.1 Hz, 1H), 6.83 (dd, *J* = 17.1, 10.4 Hz, 1H), 6.47 (s, 1H), 5.99 (s, 2H), 5.15 (d, *J* = 10.4 Hz, 1H), 4.80 (d, *J* = 17.1 Hz, 1H), 3.83 (s, 3H), 3.68 (s, 3H), 3.33 (s, 6H), 1.09 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 152.4, 142.3, 140.9, 137.6, 136.7, 132.7, 132.0, 131.6, 130.1, 125.4, 124.4, 123.5, 116.0, 115.3, 108.6, 106.4, 60.8, 55.4, 43.8, 33.5, 28.7. ESI-MS: Calcd. for $C_{27}H_{32}NO_4^+$ $[M+H]^+$: 434.2331, found: 434.2330.

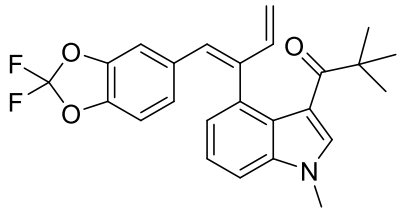
(*Z*)-2,2-dimethyl-1-(1-methyl-4-(1-(naphthalen-2-yl)buta-1,3-dien-2-yl)-1*H*-indol-3-yl)propan-1-one (5l)



The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 2-(cyclopropylidenemethyl)naphthalene **2l** (0.4 mmol) at 80°C for 22 h. However, the solvent of this reaction needs to be changed to methanol. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.19), the desired product **5l** was obtained as a yellow oil (54.8 mg, 70 % yield, Z/E = 2.3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.58 (t, *J* = 8.7 Hz, 2H), 7.52 – 7.40 (m, 4H), 7.39 – 7.24 (m, 5H), 7.24 – 7.08 (m, 2H), 7.01 (d, *J* = 6.9 Hz, 1H), 6.90 – 6.73 (m, 1H), 6.63 (s, 1H), 5.22 (d, *J* = 10.7 Hz, 1H), 5.10 (d, *J* = 10.4 Hz, 1H), 5.02 (d, *J* = 17.3 Hz, 1H), 4.70 (d, *J* = 17.1 Hz, 1H), 3.80 (s, 1H), 3.79 (s, 3H), 1.23 (s, 9H), 1.11 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 202.5, 142.3, 142.1, 137.5, 137.5, 135.8, 135.4, 135.4, 135.2, 133.4, 133.3, 132.4, 132.2, 131.9, 131.5, 131.1, 130.4, 129.7, 128.9, 128.6, 128.2, 128.2, 128.0, 127.7, 127.5, 127.4, 127.3, 127.0, 126.2, 126.0, 125.7, 125.6, 125.5, 124.4, 123.8, 123.4, 122.8, 118.1,

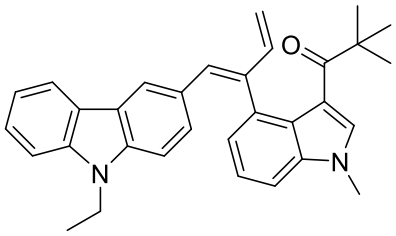
116.1, 115.9, 115.2, 108.7, 108.6, 44.2, 43.8, 33.5, 33.4, 28.7, 28.5. ESI-MS: Calcd. for $C_{28}H_{28}NO^+$ $[M+H]^+$: 394.2171, found: 394.2175.

(*Z*)-1-(4-(1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)buta-1,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (5m)



The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 5-(cyclopropylidenemethyl)-2,2-difluorobenzo[*d*][1,3]dioxole **2m** (0.4 mmol) for 29.5 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 16:1, R_f = 0.13), the desired product **5m** was obtained as a white solid (36.4 mg, 43 % yield, Z/E = 13.6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 6.9 Hz, 1H), 6.77 (q, *J* = 8.4 Hz, 2H), 6.69 (dd, *J* = 17.1, 10.4 Hz, 1H), 6.58 (s, 1H), 6.44 (s, 1H), 5.04 (d, *J* = 10.4 Hz, 1H), 4.55 (d, *J* = 17.2 Hz, 1H), 3.92 – 3.84 (m, 3H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 143.5, 142.3, 142.0, 141.5, 137.5, 134.1, 131.6, 131.3, 128.6, 125.8, 125.7, 124.0, 123.6, 116.0, 115.7, 109.9, 109.1, 108.7, 44.0, 33.6, 28.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.31. ESI-MS: Calcd. for $C_{25}H_{24}F_2NO_3^+$ $[M+H]^+$: 424.1724, found: 424.1718.

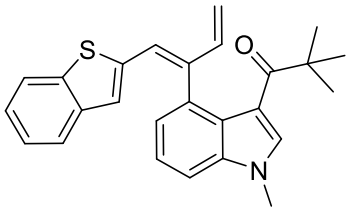
(*Z*)-1-(4-(1-(9-ethyl-9H-carbazol-3-yl)buta-1,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (5n)



The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 3-(cyclopropylidenemethyl)-9-ethyl-9*H*-carbazole **2n** (0.4 mmol) for 27.5 h. However, the solvent of this reaction needs to be changed to methanol. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.22), the desired product **5n** was obtained as a yellow solid (27.8 mg, 30 % yield, Z/E = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 7.64 (dd, *J* = 21.1, 8.0 Hz, 2H), 7.55 – 7.07 (m, 18H), 7.04 – 6.95 (m, 1H), 6.89 (dd, *J* = 17.1, 10.4 Hz, 1H), 6.81 (s, 1H), 6.72 (s, 1H), 5.22 (d, *J* = 10.7 Hz, 1H), 5.10 (d, *J* = 10.4 Hz, 1H), 5.02 (d, *J* = 17.3 Hz, 1H), 4.74 (d, *J* = 17.1 Hz, 1H), 4.39 (dd, *J* = 14.3, 7.1 Hz, 3H), 3.85 (s, 4H), 1.47 (t, *J* = 7.1 Hz, 6H), 1.27 (s, 12H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 142.6, 140.3, 140.3, 139.1, 137.5,

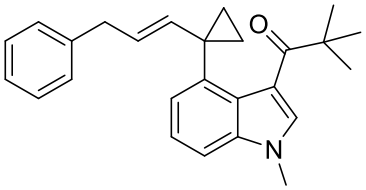
136.3, 135.8, 130.9, 130.8, 128.8, 128.1, 128.0, 126.3, 125.6, 125.3, 124.4, 123.9, 123.5, 123.2, 122.9, 122.8, 121.8, 121.3, 120.7, 120.2, 118.9, 117.0, 116.1, 113.7, 108.6, 108.4, 108.4, 108.0, 107.8, 44.3, 37.7, 33.5, 28.7, 28.5, 14.0. ESI-MS: Calcd. for $C_{32}H_{33}N_2O^+$ $[M+H]^+$: 461.2593, found: 461.2587.

(*Z*)-1-(4-(1-(benzo[b]thiophen-2-yl)buta-1,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (5o)



The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and 2-(cyclopropylidenemethyl)benzo[*b*]thiophene **2o** (0.4 mmol) for 27.5 h. However, the solvent of this reaction needs to be changed to methanol. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.18), the desired product **5o** was obtained as a yellow oil (53.6 mg, 67 % yield, Z/E = 1.8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.04 (m, 14H), 6.97 – 6.76 (m, 1H), 6.64 (s, 1H), 5.34 (d, *J* = 10.7 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 5.08 (t, *J* = 14.9 Hz, 1H), 4.78 (t, *J* = 16.2 Hz, 1H), 3.88 (d, *J* = 10.7 Hz, 2H), 3.82 (s, 3H), 1.26 (s, 9H), 1.14 (s, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 202.9, 142.6, 142.0, 141.5, 141.4, 141.1, 140.7, 140.5, 139.8, 138.8, 137.7, 137.4, 135.2, 135.0, 131.5, 131.2, 130.0, 126.1, 125.8, 125.0, 124.9, 124.9, 124.6, 124.4, 124.2, 123.9, 123.8, 123.8, 123.4, 123.3, 123.0, 122.7, 122.4, 122.0 121.8, 119.2, 116.2, 115.8, 115.8, 109.6, 108.9, 44.2, 44.1, 33.5, 33.4, 28.6, 28.5. ESI-MS: Calcd. for $C_{26}H_{26}NOS^+$ $[M+H]^+$: 400.1735, found: 400.1737.

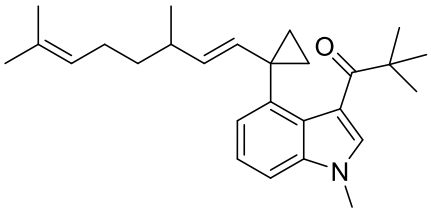
(*E*)-2,2-dimethyl-1-(1-methyl-4-(1-(3-phenylprop-1-en-1-yl)cyclopropyl)-1*H*-indol-3-yl)propan-1-one (6a)



The reaction was performed according to general procedure B with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and (3-cyclopropylidenepropyl)benzene **3a** (0.4 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 16:1, R_f = 0.15), the desired product **6a** was obtained as a colorless oil (58.1 mg, 78 % yield, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.21 (ddd, *J* = 11.4, 5.9, 2.6 Hz, 5H), 7.14 (dd, *J* = 12.3, 7.1 Hz, 3H), 5.68 (d, *J* = 15.3 Hz, 1H), 5.24 – 5.10 (m, 1H), 3.77 (s, 3H), 3.33 (d, *J* = 6.9 Hz, 2H), 1.39 (s, 9H), 1.09 (d, *J* = 6.7 Hz, 2H), 0.99 (t, *J* = 5.2 Hz, 2H). ^{13}C NMR

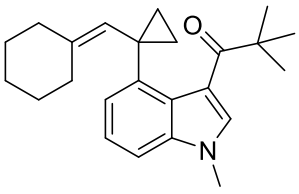
(101 MHz, $CDCl_3$) δ 204.5, 141.6, 139.8, 137.8, 137.5, 130.6, 128.7, 128.2, 126.3, 125.7, 125.3, 125.2, 122.8, 116.1, 108.1, 44.3, 39.0, 33.4, 29.1, 27.6. ESI-MS: Calcd. for $C_{26}H_{30}NO^+$ $[M+H]^+$: 372.2327, found: 372.2328.

(*E*)-1-(4-(1-(3,7-dimethylocta-1,6-dien-1-yl)cyclopropyl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (6b)



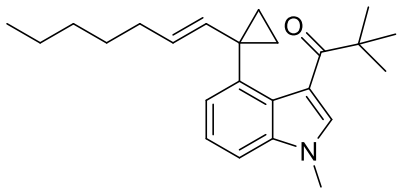
The reaction was performed according to general procedure B with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and (3,7-dimethyloct-6-en-1-ylidene)cyclopropane **3b** (0.4 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 16:1, R_f = 0.21), the desired product **6b** was obtained as a yellow oil (56.2 mg, 72 % yield, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.24 (dd, *J* = 9.0, 7.4 Hz, 2H), 7.19 (t, *J* = 6.7 Hz, 1H), 5.62 (d, *J* = 15.4 Hz, 1H), 5.06 (t, *J* = 7.0 Hz, 1H), 4.98 (dd, *J* = 15.4, 7.3 Hz, 1H), 3.78 (s, 3H), 1.91 (dd, *J* = 15.0, 7.2 Hz, 2H), 1.64 (s, 3H), 1.53 (s, 3H), 1.37 (s, 9H), 1.22 (ddd, *J* = 13.3, 7.1, 3.5 Hz, 2H), 1.01 (s, 2H), 0.93 (s, 2H), 0.91 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5, 138.6, 137.5, 135.6, 132.9, 131.0, 130.4, 126.2, 125.3, 125.3, 122.8, 116.1, 107.8, 44.3, 37.6, 35.8, 33.4, 29.1, 27.6, 25.9, 25.8, 20.5, 17.7. ESI-MS: Calcd. for $C_{27}H_{38}NO^+$ $[M+H]^+$: 392.2953, found: 392.2945.

1-(4-(1-(cyclohexylidenemethyl)cyclopropyl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (6c)



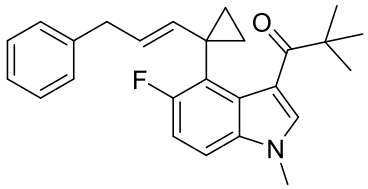
The reaction was performed according to general procedure B with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and (cyclopropylidenemethyl)cyclohexane **3c** (0.4 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 16:1, R_f = 0.17), the desired product **6c** was obtained as a white solid (35.4 mg, 51 % yield, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.17 – 7.11 (m, 1H), 5.84 (s, 1H), 3.76 (s, 3H), 2.34 – 2.20 (m, 2H), 2.03 (d, *J* = 23.5 Hz, 2H), 1.43 (s, 9H), 1.40 (d, *J* = 2.4 Hz, 6H), 1.12 (s, 2H), 0.92 (d, *J* = 1.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 142.3, 140.5, 137.6, 130.3, 126.6, 125.8, 122.8, 116.4, 107.6, 44.3, 37.1, 33.4, 29.8, 29.1, 28.6, 27.3, 26.8, 23.9, 16.4. ESI-MS: Calcd. for $C_{24}H_{32}NO^+$ $[M+H]^+$: 350.2484, found: 350.2488.

(*E*)-1-(4-(1-(hept-1-en-1-yl)cyclopropyl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (6d)



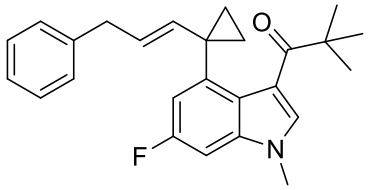
The reaction was performed according to general procedure B with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.2 mmol) and heptylidenecyclopropane **4d** (0.4 mmol) at 100 °C for 31.5 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 16:1, R_f = 0.19), the desired product **6d** was obtained as a white solid (38.6 mg, 53 % yield, E/Z = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.20 (dd, *J* = 14.8, 2.7 Hz, 3H), 5.49 (d, *J* = 15.3 Hz, 1H), 5.07 – 4.91 (m, 1H), 3.76 (s, 3H), 1.94 (d, *J* = 5.2 Hz, 2H), 1.36 (s, 9H), 1.29 (d, *J* = 3.8 Hz, 2H), 1.25 (s, 2H), 1.21 (s, 2H), 1.06 (s, 2H), 0.95 (s, 2H), 0.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 138.1, 137.5, 130.3, 127.2, 126.2, 124.9, 122.7, 116.2, 108.0, 44.2, 33.4, 32.6, 31.7, 29.4, 29.0, 27.4, 22.6, 14.2. ESI-MS: Calcd. for $C_{24}H_{34}NO^+$ $[M+H]^+$: 352.2640, found: 352.2637.

(*E*)-1-(5-fluoro-1-methyl-4-(1-(3-phenylprop-1-en-1-yl)cyclopropyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (6e)



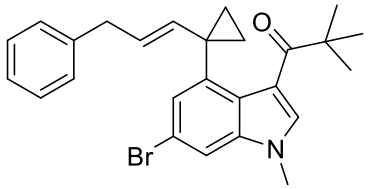
The reaction was performed according to general procedure B with 1-(5-fluoro-1-methyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one **1b** (0.1 mmol) and (3-cyclopropylidenepropyl)benzene **3a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.32), the desired product **6e** was obtained as a white solid (36.2 mg, 93 % yield, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.25 (d, *J* = 4.4 Hz, 4H), 7.18 – 7.13 (m, 1H), 7.13 – 7.09 (m, 1H), 7.05 – 6.98 (m, 1H), 5.75 (d, *J* = 15.2 Hz, 1H), 5.43 (dt, *J* = 14.2, 7.0 Hz, 1H), 3.77 (s, 3H), 3.43 (d, *J* = 7.0 Hz, 2H), 1.41 (s, 9H), 1.27 (dd, *J* = 14.6, 7.5 Hz, 2H), 0.86 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 159.1 (d, *J* = 238.5 Hz), 141.8, 137.4, 134.0, 131.9, 128.5 (d, *J* = 52.8 Hz), 127.1 (d, *J* = 5.6 Hz), 125.7, 125.5, 123.4 (d, *J* = 16.3 Hz), 116.2 (d, *J* = 4.9 Hz), 112.1, 111.8, 108.8 (d, *J* = 10.6 Hz), 44.2, 38.8, 33.6, 29.1, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.26. ESI-MS: Calcd. for $C_{26}H_{29}FNO^+$ $[M+H]^+$: 390.2233, found: 390.2240.

(*E*)-1-(6-fluoro-1-methyl-4-(1-(3-phenylprop-1-en-1-yl)cyclopropyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (6f)



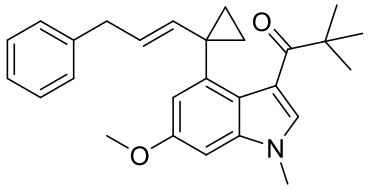
The reaction was performed according to general procedure B with 1-(6-fluoro-1-methyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one **1d** (0.1 mmol) and (3-cyclopropylidenepropyl)benzene **3a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.40), the desired product **6f** was obtained as a colorless oil (22.9 mg, 59 % yield, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.18 – 7.11 (m, 3H), 7.01 (dd, *J* = 10.7, 2.2 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.2 Hz, 1H), 5.61 (d, *J* = 15.3 Hz, 1H), 5.24 – 5.10 (m, 1H), 3.73 (s, 3H), 3.33 (d, *J* = 6.9 Hz, 2H), 1.38 (s, 9H), 1.07 (s, 2H), 1.00 (t, *J* = 5.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 159.9 (d, *J* = 239.7 Hz), 141.4, 139.7 (d, *J* = 8.9 Hz), 139.0, 137.7 (d, *J* = 12.3 Hz), 130.8, 128.5 (d, *J* = 37.1 Hz), 125.8 (d, *J* = 13.3 Hz), 122.7, 116.3, 113.6, 113.3, 94.5 (d, *J* = 25.7 Hz). 44.3, 39.0, 33.5, 29.0, 27.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.84. ESI-MS: Calcd. for $C_{26}H_{29}FNO^+$ $[M+H]^+$: 390.2233, found: 390.2232.

(*E*)-1-(6-bromo-1-methyl-4-(1-(3-phenylprop-1-en-1-yl)cyclopropyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (6g)



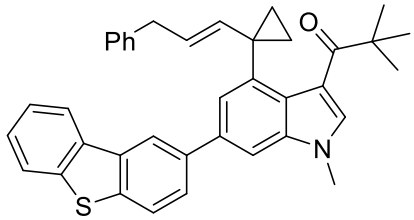
The reaction was performed according to general procedure B with 1-(6-bromo-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1f** (0.1 mmol) and (3-cyclopropylidenepropyl)benzene **3a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.42), the desired product **6g** was obtained as a colorless oil (24.6 mg, 55 % yield, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.35 (d, *J* = 2.6 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 6.4 Hz, 3H), 5.60 (d, *J* = 15.3 Hz, 1H), 5.22 – 5.08 (m, 1H), 3.74 (s, 3H), 3.32 (d, *J* = 6.9 Hz, 2H), 1.37 (s, 9H), 1.08 (s, 2H), 1.00 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 141.3, 139.63 139.0, 138.3, 130.83, 128.1, 128.1, 128., 126.2, 125.8, 125.7, 125.32 116.3, 116.3, 111.2, 44.3, 39.0, 33.5, 29.0, 27.5. ESI-MS: Calcd. for $C_{26}H_{29}BrNO^+$ $[M+H]^+$: 450.1433, found: 450.1436.

(*E*)-1-(6-methoxy-1-methyl-4-(1-(3-phenylprop-1-en-1-yl)cyclopropyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (6h)



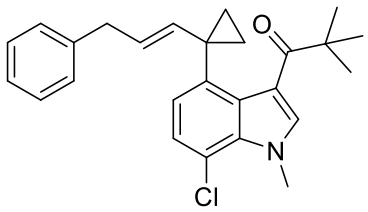
The reaction was performed according to general procedure B with 1-(6-methoxy-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1h** (0.1 mmol) and (3-cyclopropylidenepropyl)benzene **3a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.32), the desired product **6h** was obtained as a white solid (17.4 mg, 43 % yield, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.23 (d, *J* = 6.3 Hz, 2H), 7.17 (s, 3H), 6.93 (s, 1H), 6.63 (s, 1H), 5.66 (d, *J* = 15.2 Hz, 1H), 5.33 – 5.08 (m, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 3.34 (d, *J* = 5.8 Hz, 2H), 1.39 (s, 9H), 1.10 (s, 2H), 1.00 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 156.6, 141.5, 139.4, 139.0, 138.4, 131.1, 129.8, 128.7, 128.3, 125.7, 125.4, 120.5, 116.1, 114.6, 91.4, 55.7, 44.2, 39.0, 33.4, 29.1, 27.7. ESI-MS: Calcd. for $C_{27}H_{31}NO_2^+$ $[M+H]^+$: 402.2433, found: 402.2433.

(*E*)-1-(6-(dibenzo[b,d]thiophen-2-yl)-1-methyl-4-(1-(3-phenylprop-1-en-1-yl)cyclopropyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (6i)



The reaction was performed according to general procedure B with 1-(6-(dibenzo[b,d]thiophen-2-yl)-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1k** (0.1 mmol) and (3-cyclopropylidenepropyl)benzene **3a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.33), the desired product **6i** was obtained as a colorless oil (25.8 mg, 47 % yield, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.2 Hz, 1H), 8.23 (dd, *J* = 6.1, 3.0 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 5.9, 3.0 Hz, 1H), 7.75 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.63 (d, *J* = 1.3 Hz, 1H), 7.52 (s, 1H), 7.49 (dd, *J* = 5.5, 2.4 Hz, 3H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 6.9 Hz, 2H), 7.16 (d, *J* = 7.0 Hz, 1H), 5.76 (d, *J* = 15.3 Hz, 1H), 5.31 (dt, *J* = 9.2, 7.0 Hz, 1H), 3.88 (s, 3H), 3.38 (d, *J* = 6.9 Hz, 2H), 1.42 (s, 9H), 1.17 (t, *J* = 5.3 Hz, 2H), 1.06 (t, *J* = 5.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 141.6, 140.0, 139.6, 138.4, 138.4, 138.3, 136.2, 135.7, 131.3, 128.7, 128.3, 127.0, 126.7, 125.8, 125.7, 125.6, 125.2, 124.5, 123.1, 123.0, 121.9, 120.3, 116.1, 106.7, 44.4, 39.0, 33.6, 29.1, 27.9. ESI-MS: Calcd. for $C_{38}H_{36}NOS^+$ $[M+H]^+$: 554.2518, found: 554.2510.

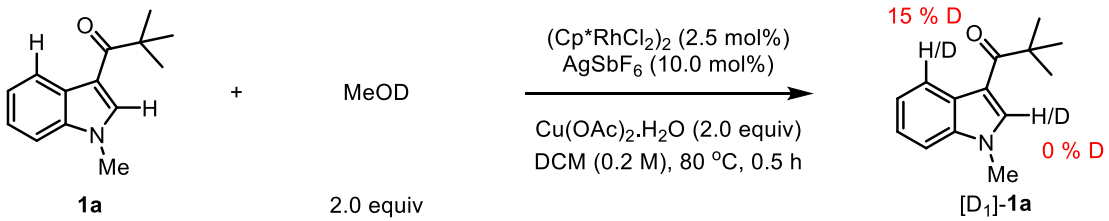
(*E*)-1-(7-chloro-1-methyl-4-(1-(3-phenylprop-1-en-1-yl)cyclopropyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (6j)



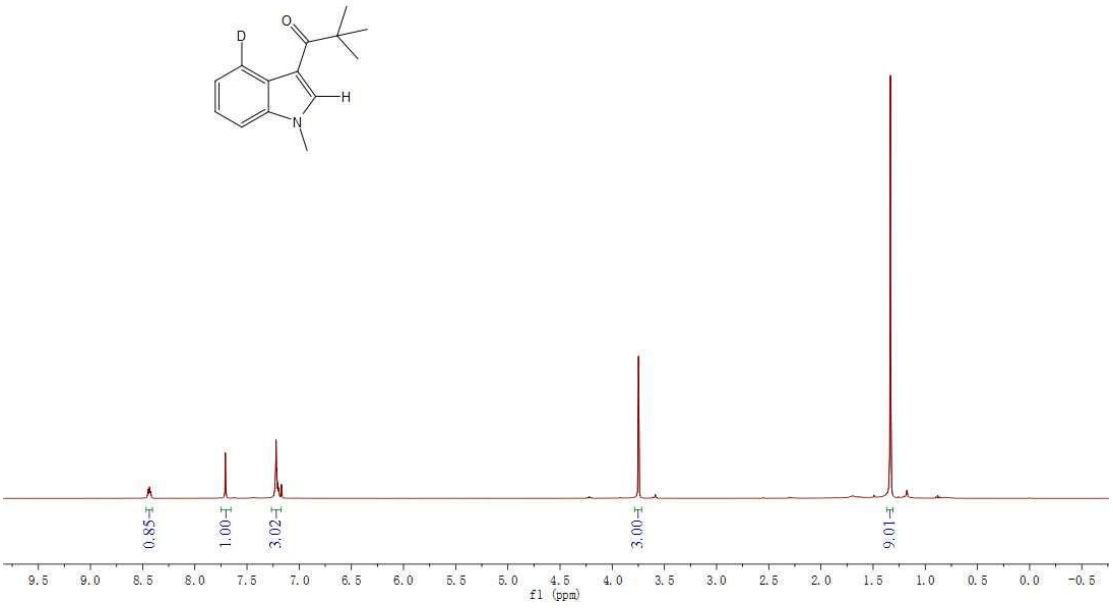
The reaction was performed according to general procedure B with 1-(7-chloro-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1n** (0.1 mmol) and (3-cyclopropylidenepropyl)benzene **3a** (0.2 mmol) for 24 h. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 16:1, R_f = 0.19), the desired product **6j** was obtained as a colorless oil (31.1 mg, 77 % yield, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.22 (d, *J* = 7.0 Hz, 2H), 7.15 (d, *J* = 7.0 Hz, 3H), 7.11 (d, *J* = 4.2 Hz, 2H), 5.59 (d, *J* = 15.3 Hz, 1H), 5.24 – 5.07 (m, 1H), 4.15 (s, 3H), 3.33 (d, *J* = 6.9 Hz, 2H), 1.37 (s, 9H), 1.03 (t, *J* = 5.2 Hz, 2H), 0.96 (t, *J* = 5.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6, 141.4, 139.3, 136.5, 132.9, 132.7, 129.2, 128.7, 128.3, 126.0, 125.8, 125.6, 124.4, 116.2, 115.7, 44.4, 39.0, 37.9, 29.0, 27.2. ESI-MS: Calcd. for $C_{26}H_{29}ClNO^+$ $[M+H]^+$: 406.1938, found: 406.1940.

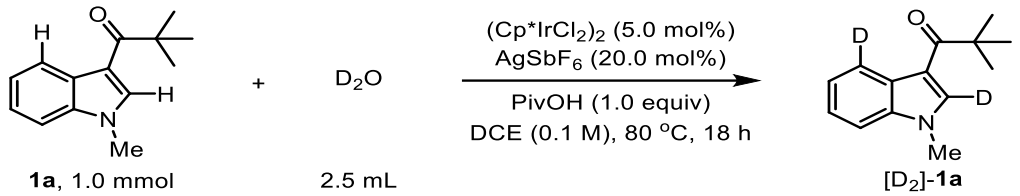
5. Mechanistic studies

(1) H/D Exchange experiment

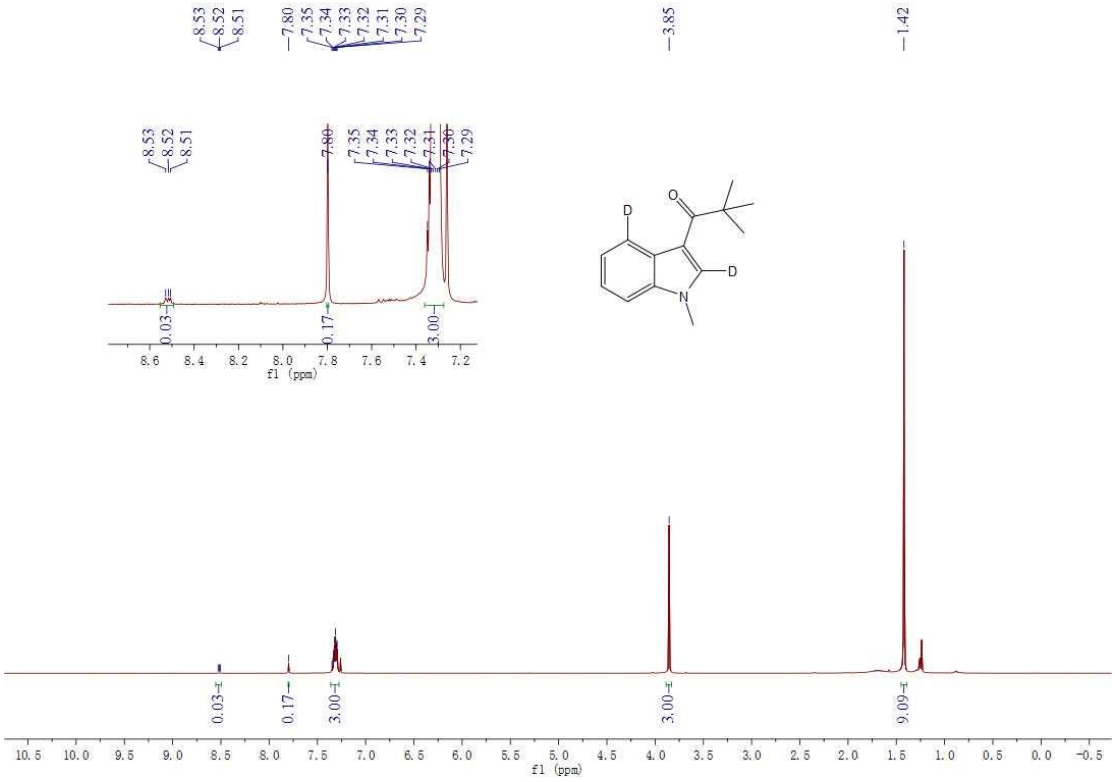


The reaction was performed according to general procedure A with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.1 mmol, 1.0 equiv), and MeOD (0.2 mmol, 2.0 equiv) instead of (cyclopropylidenemethyl)benzene **2** After 0.5 h, the reaction was cooled to room temperature, diluted with 5 ml CH_2Cl_2, filtered through a celite pad and washed with 10-20 ml CH_2Cl_2, The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to provide the product [D_1]-**1a** as a white solid (20.4 mg, 92%).

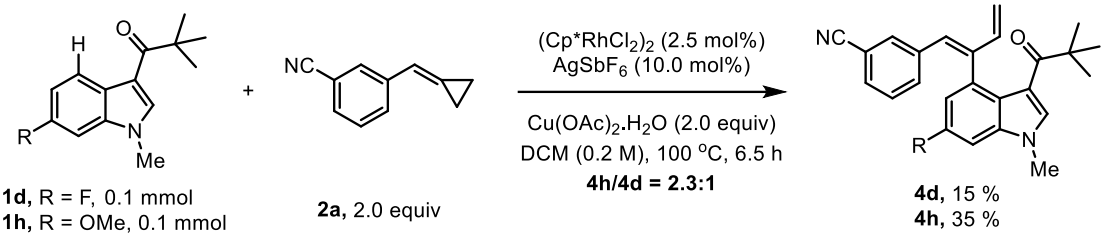




Under N_2 atmosphere, a 50 mL round bottom flask was charged with 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (215.3 mg, 1.0 mmol), $(Cp^*IrCl_2)_2$ (39.8 mg, 5.0 mol%), $AgSbF_6$ (68.7 mg, 20.0 mol%), PivOH (102.1 mg, 1.0 equiv), D_2O (2.5 ml), and DCE (12.5 mL). Then the tube was sealed and the minture was stirred at 80 °C for 18 h. Subsequently, the reaction solution was cooled to room temperature, diluted with 15 ml CH_2Cl_2, filtered through a celite pad and washed with 20-30 ml CH_2Cl_2, the filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to provide the product $[D_2]$-**1a** as a white solid (211.5 mg, 97%).



(2) Competitive experiment



The reaction was performed according to general procedure A with 1-(6-fluoro-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1d** (0.1 mmol, 0.5 equiv), 1-(6-methoxy-1-methyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1h** (0.1 mmol, 0.5 equiv), and 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.4 mmol, 2.0 equiv) for 6.5 h**.** After that, the resulting mixture was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1) to get the pure product of **4d** (11.6 mg, 15%) and **4h** (27.5 mg, 35 %). The **4h/4d** value was determined to be **2.3:1**.

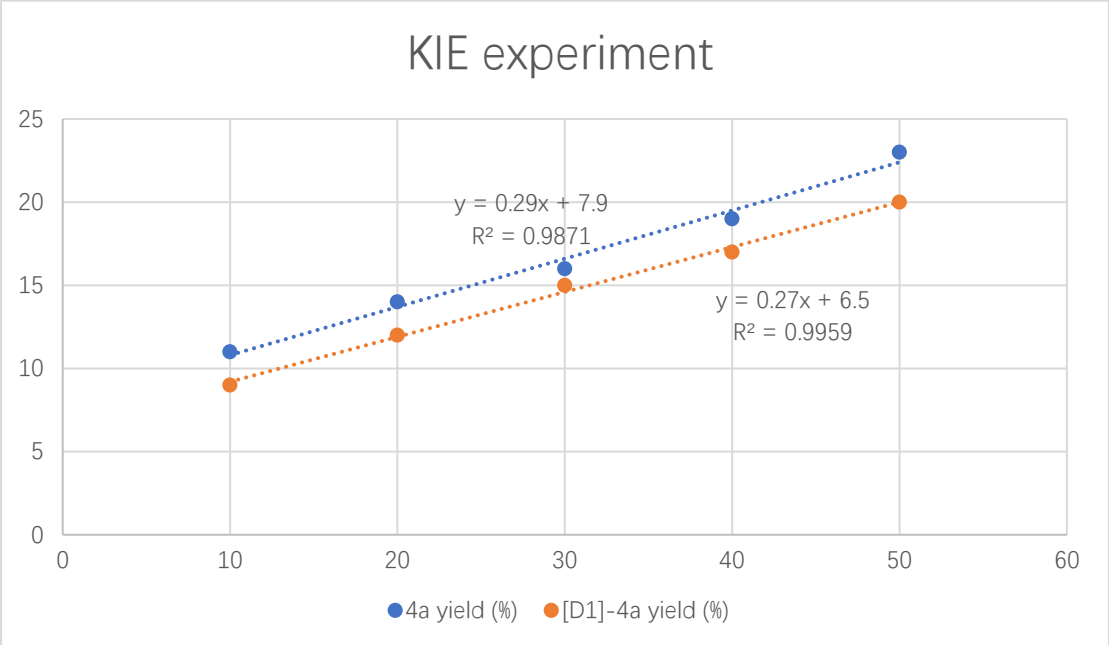
(3) Kinetic isotope effect experiment

Procedure for kinetic isotopic effect experiments: To five identical Schlenk tube, 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (0.1 mmol, 1.0 equiv), 3-(cyclopropylidenemethyl) benzonitrile **2a** (0.2 mmol, 2 equiv), 1-iodo-4-methoxybenzene (0.5 equiv), $(Cp^*RhCl_2)_2$ (1.6 mg, 0.0025 mmol, 2.5 mmol%), $AgSbF_6$ (3.4 mg, 0.01 mmol, 10.0 mmol%), $Cu(OAc)_2{\cdot}H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv), and DCM (0.5 mL) were added. The resulting mixture was stirred at 100 °C with same speed. Those five reaction will stop (rapid cooling and quenching with water) after 10 min, 20 min, 30 min, 40 min, 50 min respectively， and diluted with 6.0 ml DCM. Then an aliquot (1000 μL) was taken in five reactions. The yield of product **4a** was determined by NMR using 1-iodo-4-methoxybenzene as the internal standard.

To five identical Schlenk tube, 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl-2,4-d_2)propan-1-one **[D_2]-1a** (0.1 mmol, 1.0 equiv), 3-(cyclopropylidenemethyl)benzonitrile **2a** (0.2 mmol, 2 equiv), 1-iodo-4-methoxybenzene (0.5 equiv), $(Cp^*RhCl_2)_2$ (1.6 mg, 0.0025 mmol, 2.5 mmol%), $AgSbF_6$ (3.4 mg, 0.01 mmol, 10.0 mmol%), $Cu(OAc)_2{\cdot}H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv), and DCM (0.5 mL) were added. The resulting mixture was stirred at 100 °C with same speed. Those five reaction will stop (rapid cooling and quenching with water) after 10 min, 20 min, 30 min, 40 min, 50 min respectively， and diluted with 6.0 ml DCM. Then an aliquot (1000 μL) was taken in five reactions.

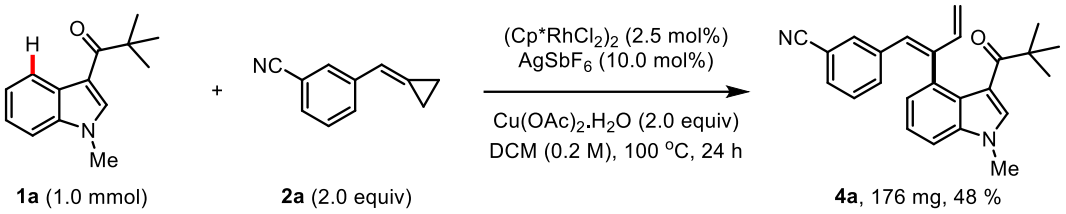
The yield of product [D_1]-**4a** was determined by NMR using 1-iodo-4-methoxybenzene as the internal standard. The K_H/K_D value was determined to be 0.29/0.27 = **1.1**.

Time (min)	**4a** yield (%)	[D_1]-**4a** yield (%)
10	11%	9%
20	14%	12%
30	16%	15%
40	19%	17%
50	23%	20%



6. Synthetic application of the product

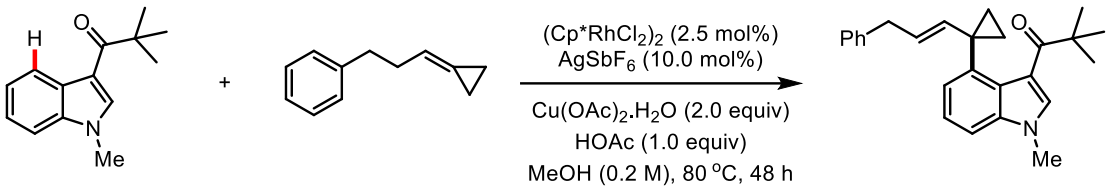
Scale-up Synthesis



1a (1.0 mmol) **2a** (2.0 equiv) **4a**, 176 mg, 48 %

According to the general procedure A, to a Schlenk tube, 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (215.3 mg, 1.0 mmol, 1.0 equiv), 3-(cyclopropylidenemethyl)benzonitrile **2a** (310.4 mg, 2.0 mmol, 2.0 equiv), $(Cp^*RhCl_2)_2$ (15.5 mg, 0.025 mmol, 2.5 mmol%), $AgSbF_6$ (34.4 mg, 0.10 mmol, 10.0 mmol%), $Cu(OAc)_2 \cdot H_2O$ (399.3 mg, 2.0 mmol, 2.0 equiv), and DCM (5.0 mL) were added. The resulting mixture was stirred at 100 °C for 24 h. After that, the resulting mixture was purified by silica gel chromatography (petroleum ether/ethyl acetate = 8:1) to get the product **4a** as a yellow solid (175.7 mg, 48 % yield).

Gram-s Synthesis

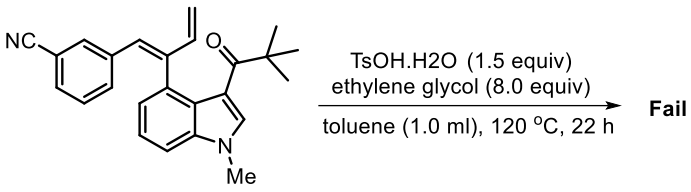


1a (5.0 mmol) **3a** (2.0 equiv) **6a**, 1.02 g, 55 %

According to the general procedure B, to a 100 ml Schlenk tube, 2,2-dimethyl-1-(1-methyl-1*H*-indol-3-yl)propan-1-one **1a** (1.08 g, 5.0 mmol, 1.0 equiv), (3-cyclopropylidenepropyl)benzene **3a** (1.58 g, 10.0 mmol, 2.0 equiv), $(Cp^*RhCl_2)_2$ (77.3 mg, 0.125 mmol, 2.5 mmol%), $AgSbF_6$ (171.8 mg, 0.50 mmol, 10.0 mmol%), $Cu(OAc)_2 \cdot H_2O$ (2.00 g, 10.0 mmol, 2.0 equiv), HOAc (286 μL, 5.0 mmol, 1.0 equiv) and DCM (25.0 mL) were added. The resulting mixture was stirred at 80 °C for 24 h. After that, the resulting mixture was purified by silica gel chromatography (petroleum ether/ethyl acetate = 8:1) to get the product **6a** as a yellow oil (1.02 g, 55 % yield).

Additional Experiments：

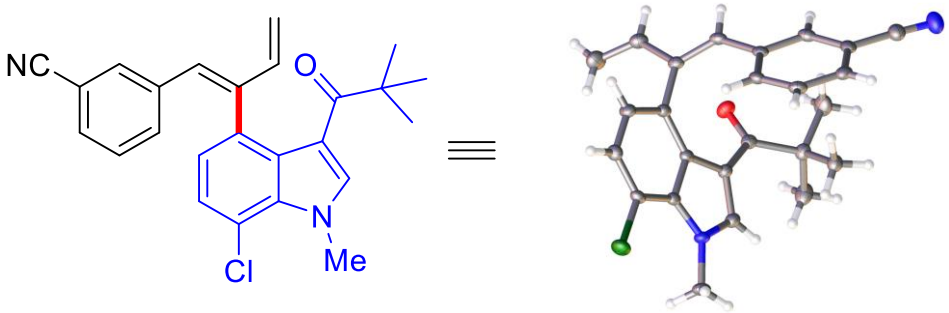
Removal of the pivaloyl directing group experiment:



4a

The pivaloyl directing group in **4a** could not be removed according to the existing literature method (*ACS Catal*. **2019**, *9*, 6372-6379, **most used method**). We also tried other methods, but they all failed, it may be because the allyl alcohol moiety and isopentenyl fragment in the product are unstable under acidic conditions or high temperature conditions.

7. X-Ray crystal data for compound 4n



4n **CCDC: 2167244**

X-ray-quality crystal was obtained by slow diffusion of Petroleum ether into a dilute dichloromethane solution of **4n** at room temperature under air. Thermal ellipsoids drawn at the 50 % probability level. Crystal data were obtained on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer using Mo Kα radiation (λ = 0.71073 Å). The crystal was kept at 200.00(10) K during data collection.

Table 1 Crystal data and structure refinement for 4n.

Identification code	1230-2
Empirical formula	$C_{25}H_{23}ClN_2O$
Formula weight	402.90
Temperature/K	169.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.9471(18)
b/Å	10.8316(16)
c/Å	11.5440(19)
α/°	70.149(14)
β/°	68.430(16)
γ/°	80.750(13)
Volume/Å^3	1087.0(3)
Z	2
ρ_{calc}g/cm^3	1.231
μ/mm^{-1}	0.193
F(000)	424.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.984 to 50

Index ranges	$-11 \le h \le 11, -12 \le k \le 8, -13 \le l \le 10$
Reflections collected	6966
Independent reflections	3822 [R_{int} = 0.0274, R_{sigma} = 0.0499]
Data/restraints/parameters	3822/0/266
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0446, wR_2 = 0.1039
Final R indexes [all data]	R_1 = 0.0616, wR_2 = 0.1128
Largest diff. peak/hole / e $Å^{-3}$	0.19/-0.23

Crystal structure determination of 4n

Crystal Data for $C_{25}H_{23}ClN_2O$ (*M* =402.90 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.9471(18) Å, *b* = 10.8316(16) Å, *c* = 11.5440(19) Å, *α* = 70.149(14)°, *β* = 68.430(16)°, *γ* = 80.750(13)°, *V* = 1087.0(3) $Å^3$, *Z* = 2, *T* = 169.99(10) K, μ(MoKα) = 0.193 mm^{-1}, *Dcalc* = 1.231 g/cm^3, 6966 reflections measured ($3.984° \le 2\Theta \le 50°$), 3822 unique ($R_{int}$ = 0.0274, R_{sigma} = 0.0499) which were used in all calculations. The final R_1 was 0.0446 ($I > 2\sigma(I)$) and wR_2 was 0.1128 (all data).

Refinement model description

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4n. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	6206.2(6)	5075.7(5)	2809.3(5)	44.42(18)
O1	9578.7(14)	7261.9(13)	6142.3(12)	40.6(4)
N1	7372.6(17)	4479.4(14)	5273.8(14)	31.8(4)
N2	3912(2)	8480(2)	11181.4(18)	59.3(6)
C1	7733.6(19)	8012.1(17)	4106.4(16)	28.1(4)
C2	7292(2)	8375.0(18)	3020.7(17)	34.3(5)
C3	6836(2)	7474.2(18)	2630.1(17)	34.7(5)
C4	6820(2)	6150.4(18)	3328.2(17)	30.3(4)
C5	7285.7(19)	5730.1(17)	4410.9(16)	27.3(4)
C6	7757.4(19)	6649.5(17)	4813.9(16)	26.6(4)
C7	8111.8(19)	5884.5(17)	5973.1(16)	29.4(4)
C8	7847(2)	4598.2(18)	6190.2(17)	33.8(5)
C9	8759(2)	6348.2(18)	6714.1(17)	30.0(4)
C10	8404(2)	5677.5(18)	8207.2(17)	34.2(5)
C11	6815(2)	5325(2)	8897.9(17)	38.0(5)
C12	8718(3)	6653(2)	8777.9(19)	54.2(6)
C13	9412(2)	4443(2)	8428(2)	51.1(6)
C14	7059(2)	3201.9(18)	5264.0(19)	39.9(5)
C15	8123(2)	9079.0(17)	4469.0(17)	30.1(4)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 4n. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C16	9457(2)	9775.5(19)	3575.8(19)	39.7(5)
C17	10374(2)	9517(2)	2513(2)	53.4(6)
C18	7317(2)	9451.6(17)	5523.7(17)	32.2(5)
C19	5943(2)	8950.1(17)	6536.1(17)	29.8(4)
C20	5641(2)	9014.7(17)	7799.9(17)	34.0(5)
C21	4364(2)	8539.4(18)	8803.6(17)	35.1(5)
C22	3321(2)	8050.0(18)	8552.5(18)	37.4(5)
C23	3584(2)	8028.3(18)	7298.0(18)	37.3(5)
C24	4873(2)	8451.9(17)	6309.6(17)	33.3(5)
C25	4110(2)	8533(2)	10127(2)	43.7(5)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 4n. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	53.4(4)	43.1(3)	50.7(3)	-22.7(2)	-23.0(3)	-8.0(3)
O1	40.7(9)	39.0(8)	43.9(8)	-4.4(6)	-18.7(6)	-13.8(7)
N1	39.7(10)	21.5(9)	35.1(8)	-9.0(6)	-12.0(7)	-4.5(7)
N2	68.5(15)	69.3(15)	41.6(11)	-21.8(9)	-17.7(10)	2.0(11)
C1	28.6(11)	25.0(10)	31.5(10)	-9.8(8)	-9.0(8)	-3.1(8)
C2	43.0(13)	24.8(11)	37.2(10)	-7.1(8)	-18.7(9)	0.4(9)
C3	40.0(12)	35.9(12)	33.1(10)	-10.9(8)	-18.4(9)	0.9(9)
C4	29.7(11)	31.9(11)	34.6(10)	-17.5(8)	-8.7(8)	-4.5(8)
C5	26.8(11)	24.9(10)	29.8(9)	-10.5(7)	-7.2(8)	-0.8(8)
C6	25.0(10)	25.8(10)	29.2(9)	-10.7(7)	-6.9(8)	-1.8(8)
C7	31.2(11)	26.7(11)	28.7(9)	-5.7(7)	-9.8(8)	-3.2(8)
C8	38.9(12)	27.9(11)	32.5(10)	-5.0(8)	-12.8(9)	-2.4(9)
C9	26.4(11)	28.6(11)	35.6(10)	-9.3(8)	-12.6(8)	1.6(9)
C10	32.5(11)	37.7(12)	33.9(10)	-7.3(8)	-15.7(8)	-2.3(9)
C11	37.4(12)	39.8(12)	33.8(10)	-8.2(8)	-11.7(9)	-1.0(9)
C12	66.2(16)	65.9(16)	41.2(12)	-14.0(11)	-26.5(11)	-16.7(13)
C13	41.2(14)	57.8(16)	43.9(12)	-3.0(10)	-18.0(10)	7.1(11)
C14	46.7(13)	25.2(11)	48.7(12)	-13.5(9)	-12.7(10)	-6.9(9)
C15	35.8(12)	22.4(10)	35.6(10)	-7.3(8)	-17.4(9)	-1.1(8)
C16	41.0(13)	33.1(12)	48.6(12)	-12.0(9)	-17.4(10)	-6.9(10)
C17	43.5(14)	55.1(16)	57.8(14)	-18.5(11)	-5.0(11)	-17.6(12)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 4n. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C18	40.6(12)	23.2(10)	40.8(11)	-11.5(8)	-21.0(9)	-1.8(9)
C19	38.4(12)	18.6(10)	37.3(10)	-10.4(7)	-18.0(9)	2.4(8)
C20	40.0(12)	26.7(11)	44.8(11)	-16.5(8)	-22.1(10)	4.3(9)
C21	47.2(13)	24.1(11)	35.8(10)	-11.8(8)	-17.1(9)	6.9(9)
C22	41.4(13)	23.9(11)	41.4(11)	-6.8(8)	-10.9(9)	-0.7(9)
C23	41.1(13)	27.4(11)	49.8(12)	-14.7(9)	-19.1(10)	-3.5(9)
C24	44.1(13)	24.8(11)	36.1(10)	-13.1(8)	-16.2(9)	-0.7(9)
C25	50.2(14)	38.8(13)	42.0(13)	-12.8(9)	-17.2(10)	3.8(10)

Table 4 Bond Lengths for 4n.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C4	1.7486(18)	C9	C10	1.552(2)
O1	C9	1.225(2)	C10	C11	1.529(3)
N1	C5	1.394(2)	C10	C12	1.543(3)
N1	C8	1.355(2)	C10	C13	1.544(3)
N1	C14	1.471(2)	C15	C16	1.477(3)
N2	C25	1.142(2)	C15	C18	1.342(3)
C1	C2	1.391(2)	C16	C17	1.320(3)
C1	C6	1.425(2)	C18	C19	1.471(3)
C1	C15	1.501(2)	C19	C20	1.402(2)
C2	C3	1.397(3)	C19	C24	1.406(2)
C3	C4	1.385(3)	C20	C21	1.394(3)
C4	C5	1.398(2)	C21	C22	1.394(3)
C5	C6	1.433(2)	C21	C25	1.451(3)
C6	C7	1.450(2)	C22	C23	1.382(3)
C7	C8	1.381(2)	C23	C24	1.383(3)
C7	C9	1.483(2)			

Table 5 Bond Angles for 4n.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	N1	C14	129.60(15)	C7	C9	C10	120.21(15)
C8	N1	C5	107.96(14)	C11	C10	C9	112.06(14)
C8	N1	C14	122.44(14)	C11	C10	C12	108.56(17)
C2	C1	C6	117.48(16)	C11	C10	C13	110.87(16)

Table 5 Bond Angles for 4n.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C15	118.01(15)	C12	C10	C9	107.74(15)
C6	C1	C15	124.50(15)	C12	C10	C13	108.70(17)
C1	C2	C3	122.99(17)	C13	C10	C9	108.80(17)
C4	C3	C2	120.13(17)	C16	C15	C1	117.04(17)
C3	C4	Cl1	117.97(14)	C18	C15	C1	124.03(16)
C3	C4	C5	119.14(16)	C18	C15	C16	118.90(17)
C5	C4	Cl1	122.88(14)	C17	C16	C15	126.29(19)
N1	C5	C4	130.84(16)	C15	C18	C19	129.70(17)
N1	C5	C6	108.20(14)	C20	C19	C18	118.54(16)
C4	C5	C6	120.96(16)	C20	C19	C24	117.21(17)
C1	C6	C5	119.27(15)	C24	C19	C18	124.20(16)
C1	C6	C7	134.76(16)	C21	C20	C19	121.10(17)
C5	C6	C7	105.91(15)	C20	C21	C25	120.46(18)
C6	C7	C9	127.66(16)	C22	C21	C20	120.43(17)
C8	C7	C6	106.02(15)	C22	C21	C25	119.10(18)
C8	C7	C9	126.10(15)	C23	C22	C21	118.86(18)
N1	C8	C7	111.91(15)	C22	C23	C24	120.94(18)
O1	C9	C7	119.73(15)	C23	C24	C19	121.34(17)
O1	C9	C10	120.06(15)	N2	C25	C21	177.6(2)

Table 6 Torsion Angles for 4n.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C4	C5	N1	-0.2(3)	C6	C7	C9	C10	149.99(18)
Cl1	C4	C5	C6	-178.95(14)	C7	C9	C10	C11	-39.3(2)
O1	C9	C10	C11	140.88(19)	C7	C9	C10	C12	-158.63(18)
O1	C9	C10	C12	21.5(3)	C7	C9	C10	C13	83.7(2)
O1	C9	C10	C13	-96.2(2)	C8	N1	C5	C4	-177.80(19)
N1	C5	C6	C1	-178.31(15)	C8	N1	C5	C6	1.1(2)
N1	C5	C6	C7	-0.8(2)	C8	C7	C9	O1	143.5(2)
C1	C2	C3	C4	-0.4(3)	C8	C7	C9	C10	-36.3(3)
C1	C6	C7	C8	177.1(2)	C9	C7	C8	N1	-174.28(17)
C1	C6	C7	C9	-8.1(3)	C14	N1	C5	C4	3.3(3)
C1	C15	C16	C17	-2.8(3)	C14	N1	C5	C6	-177.85(18)
C1	C15	C18	C19	0.3(3)	C14	N1	C8	C7	178.00(17)
C2	C1	C6	C5	-2.1(3)	C15	C1	C2	C3	-176.79(18)
C2	C1	C6	C7	-178.78(19)	C15	C1	C6	C5	176.62(17)
C2	C1	C15	C16	-69.3(2)	C15	C1	C6	C7	-0.1(3)

Table 6 Torsion Angles for 4n.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C1	C15	C18	108.8(2)	C15	C18	C19	C20	150.62(19)
C2	C3	C4	Cl1	178.80(15)	C15	C18	C19	C24	-32.0(3)
C2	C3	C4	C5	-1.0(3)	C16	C15	C18	C19	178.39(16)
C3	C4	C5	N1	179.65(18)	C18	C15	C16	C17	178.9(2)
C3	C4	C5	C6	0.9(3)	C18	C19	C20	C21	-179.18(17)
C4	C5	C6	C1	0.7(3)	C18	C19	C24	C23	-178.17(17)
C4	C5	C6	C7	178.27(16)	C19	C20	C21	C22	-3.4(3)
C5	N1	C8	C7	-1.0(2)	C19	C20	C21	C25	175.87(17)
C5	C6	C7	C8	0.1(2)	C20	C19	C24	C23	-0.8(3)
C5	C6	C7	C9	174.86(18)	C20	C21	C22	C23	0.9(3)
C6	C1	C2	C3	2.0(3)	C21	C22	C23	C24	1.6(3)
C6	C1	C15	C16	112.0(2)	C22	C23	C24	C19	-1.7(3)
C6	C1	C15	C18	-69.9(3)	C24	C19	C20	C21	3.3(3)
C6	C7	C8	N1	0.5(2)	C25	C21	C22	C23	-178.40(18)
C6	C7	C9	O1	-30.2(3)					

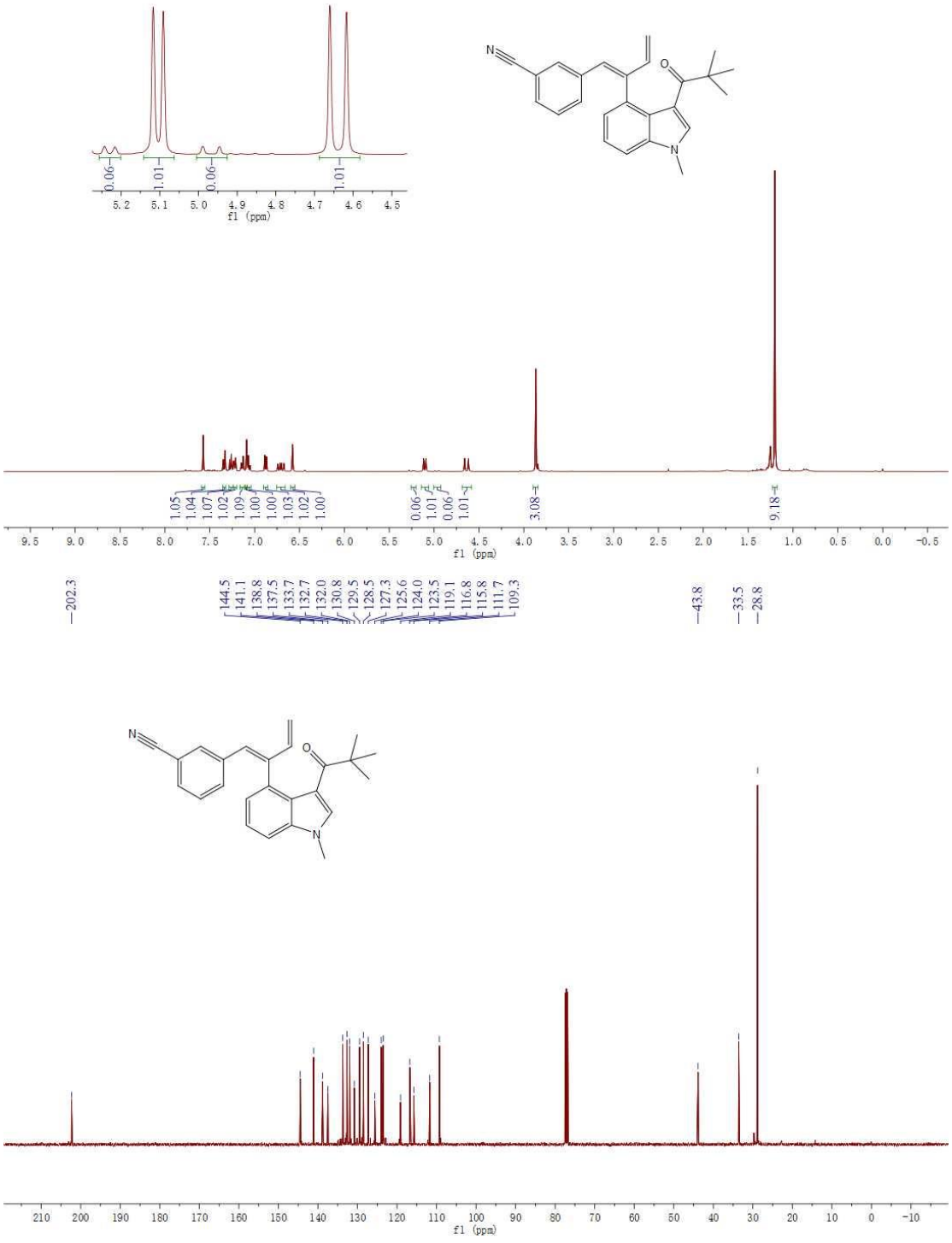
Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4n.

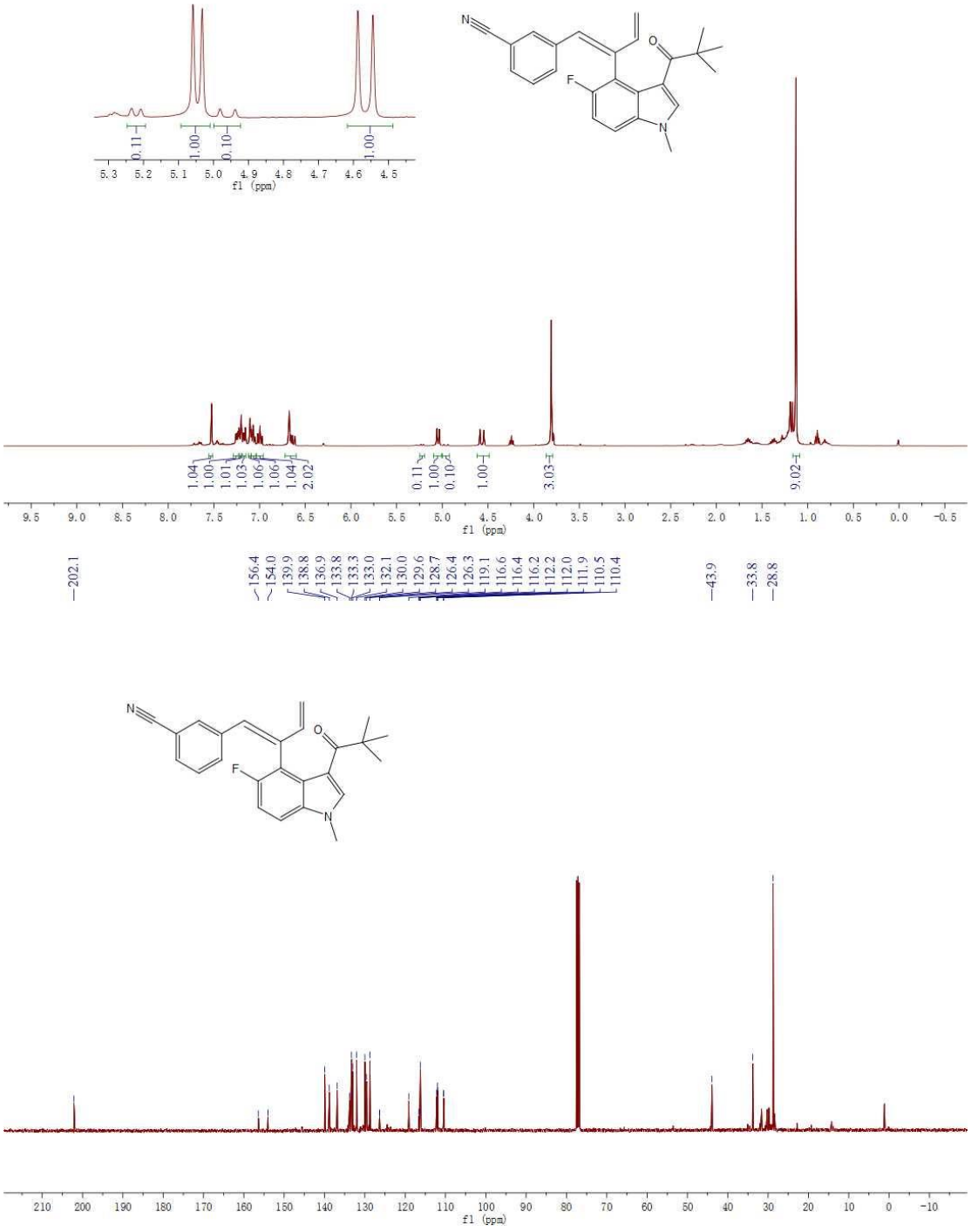
Atom	*x*	*y*	*z*	U(eq)
H2	7299.3	9257.61	2532.47	41
H3	6543.84	7763.82	1900.01	42
H8	7977.58	3897.16	6882.51	41
H11A	6209.01	6084.02	8665.6	57
H11B	6605.54	5033.85	9827.69	57
H11C	6634.09	4635.01	8634.09	57
H12A	9719.69	6864.82	8369.86	81
H12B	8506.64	6261.83	9703.63	81
H12C	8124.57	7440.1	8615.44	81
H13A	9205.38	3816.77	8100.36	77
H13B	9255.29	4060.64	9346.83	77
H13C	10400.87	4684.2	7974.6	77
H14A	6103.55	3245.02	5226.14	60
H14B	7115.39	2534.61	6045.95	60
H14C	7752.19	2992.35	4513.62	60
H16	9672.7	10462.51	3781.6	48
H17A	10204.3	8838.73	2267.69	64
H17B	11188.65	10012.84	2010.81	64

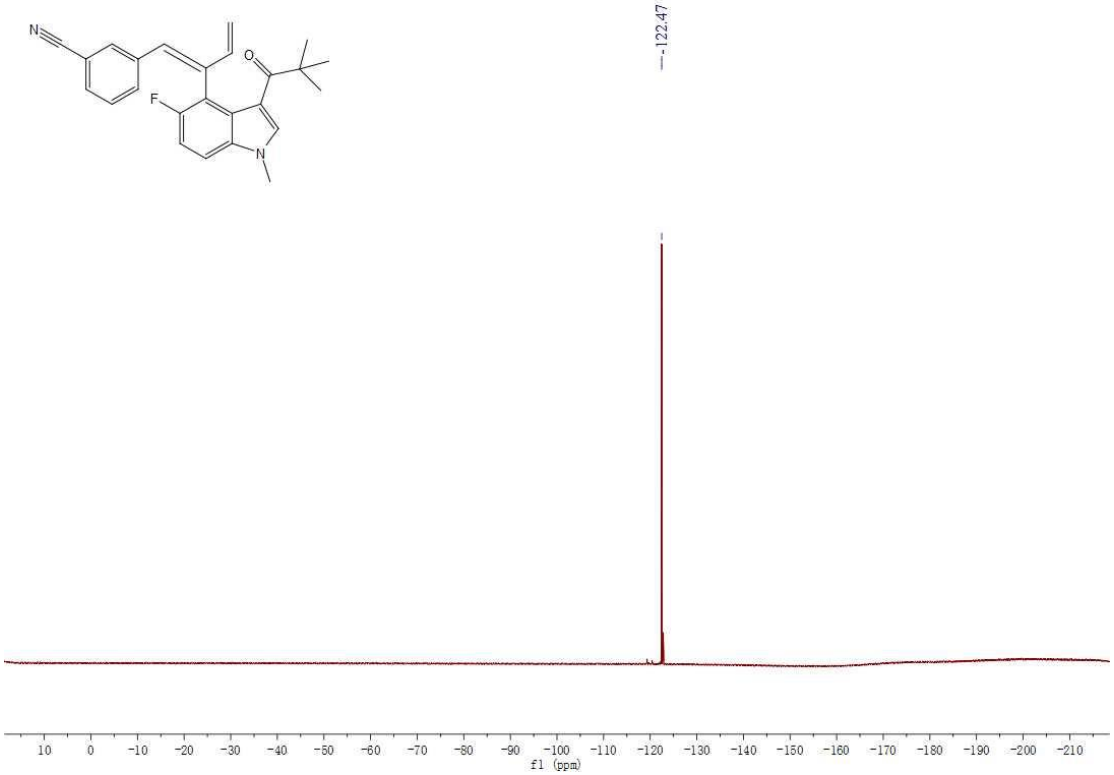
Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4n.

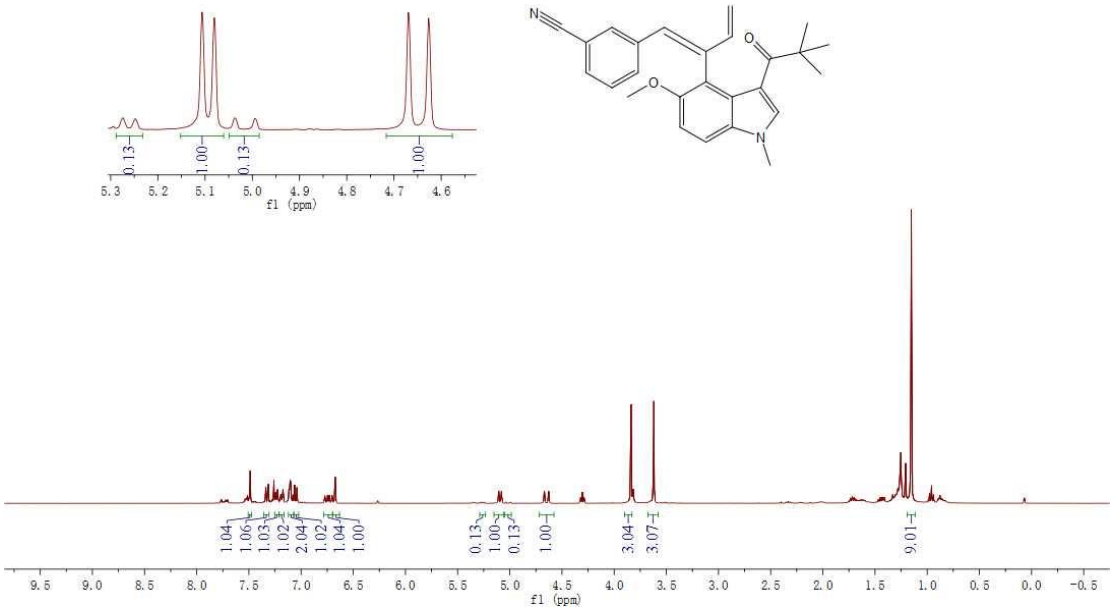
Atom	*x*	*y*	*z*	U(eq)
H18	7682.4	10128.5	5630.67	39
H20	6303.48	9380.71	7972.09	41
H22	2462.69	7743.28	9218.08	45
H23	2884.81	7724.64	7115.29	45
H24	5034.85	8406.19	5478.53	40

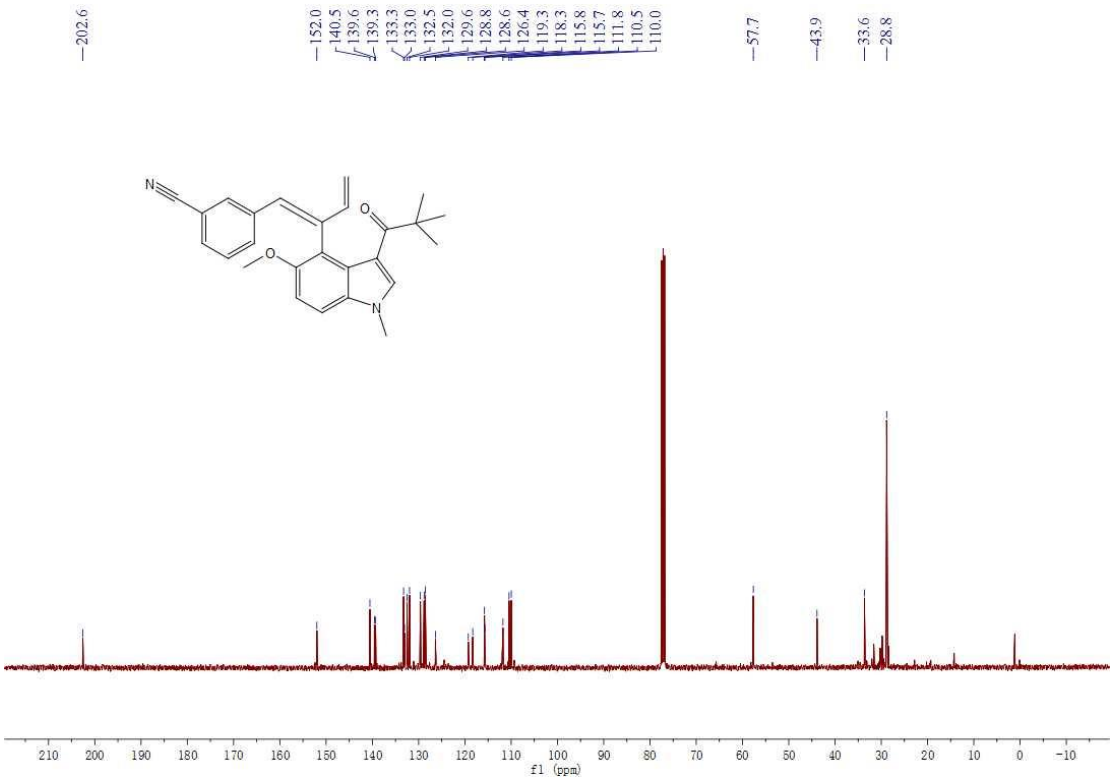
8. Copies of product NMR spectra

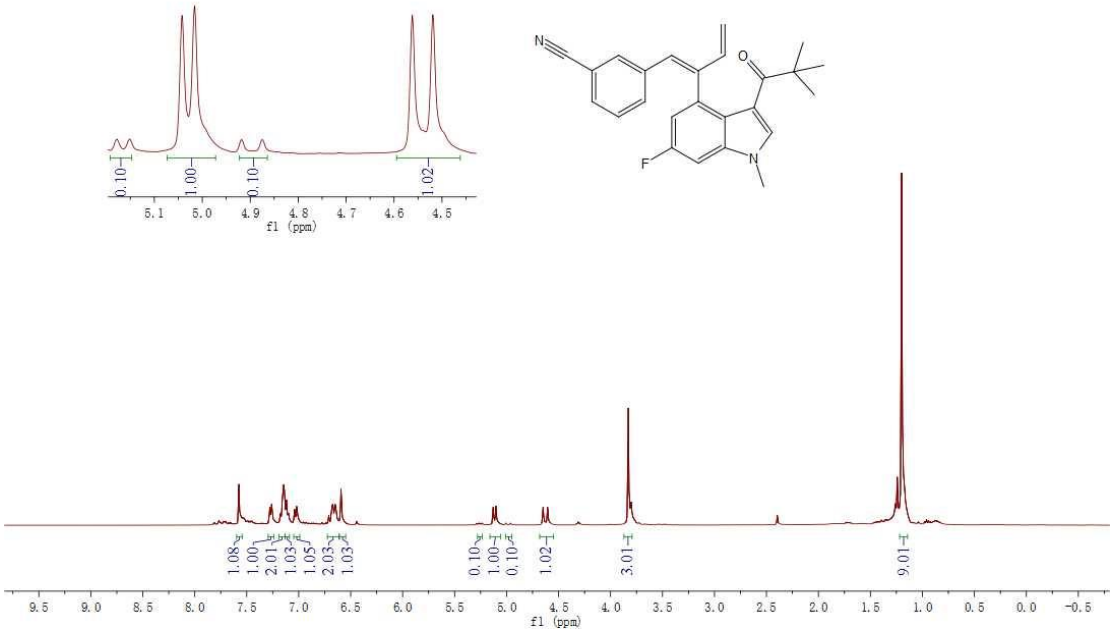


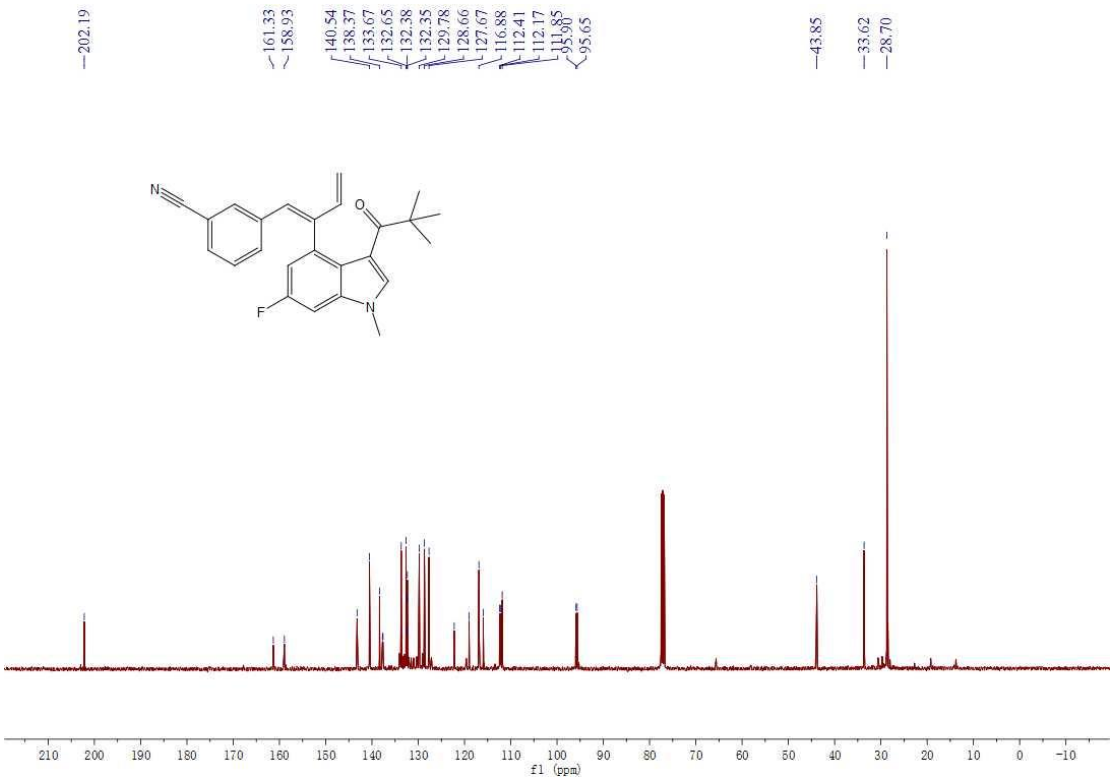

N
O
F
N
0.11
1.00
0.10
1.00
5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5
f1 (ppm)
1.04
1.00
1.01
1.03
1.06
1.06
1.04
2.02
0.11
1.00
0.10
1.00
3.03
9.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
202.1
156.4
154.0
139.9
138.8
136.9
133.8
133.3
133.0
132.1
130.0
129.6
128.7
126.4
126.3
119.1
116.6
116.4
116.2
112.2
112.0
111.9
110.5
110.4
43.9
33.8
28.8
N
O
F
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

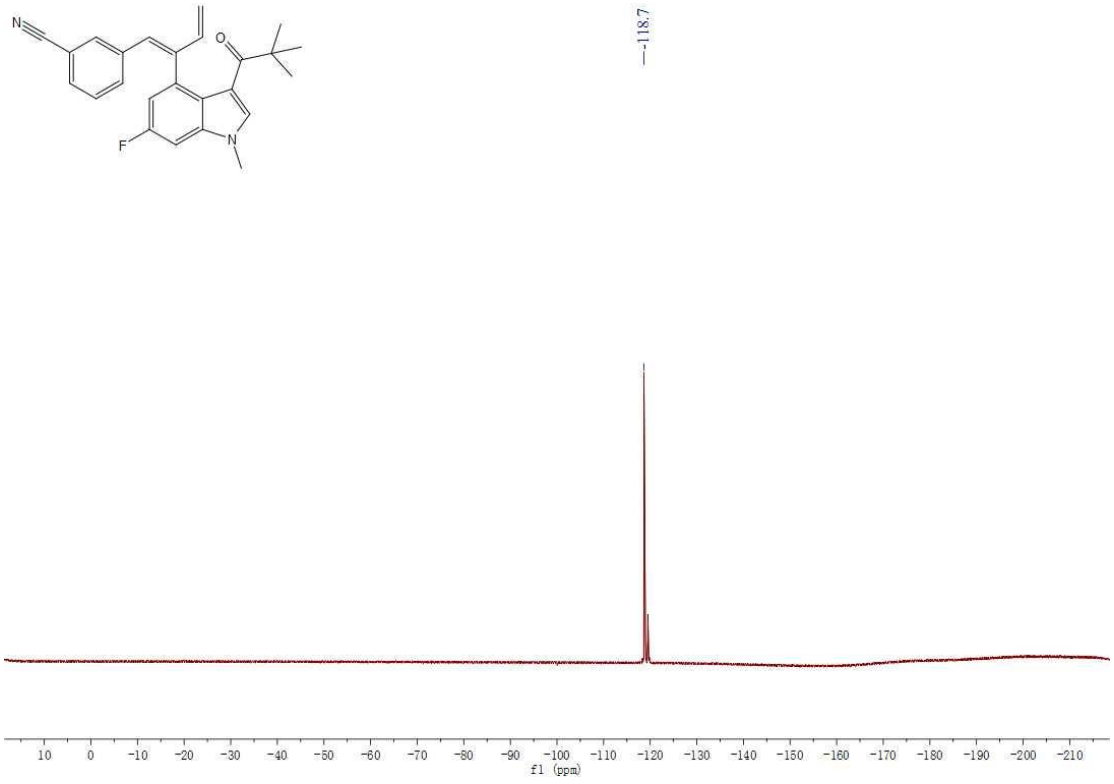

N
O
F
N
-122.47
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

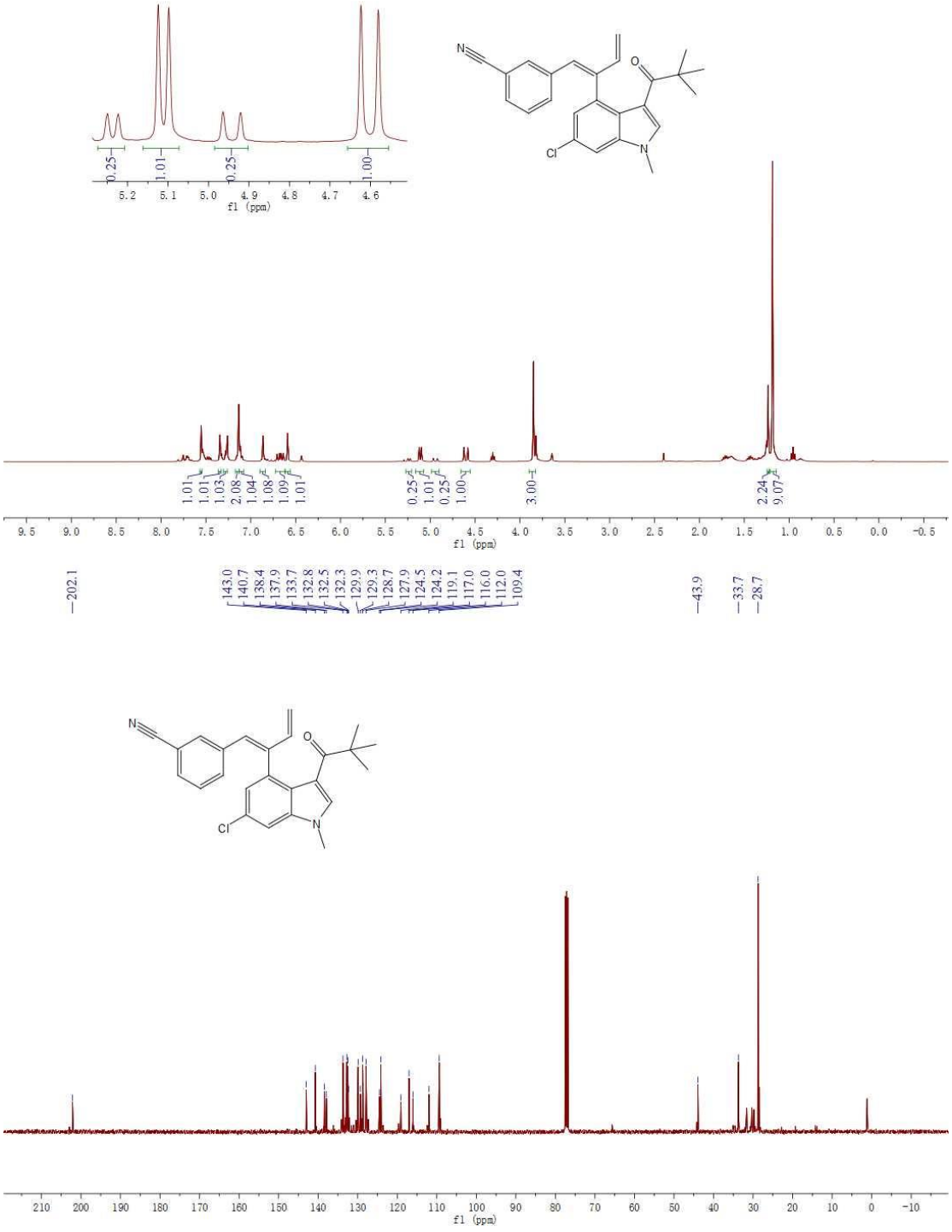

N
O
O
N
0.13
1.00
0.13
1.00
5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6
f1 (ppm)
1.04
1.06
1.03
1.02
2.04
1.02
1.04
1.00
0.13
1.00
0.13
1.00
3.04
3.07
9.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

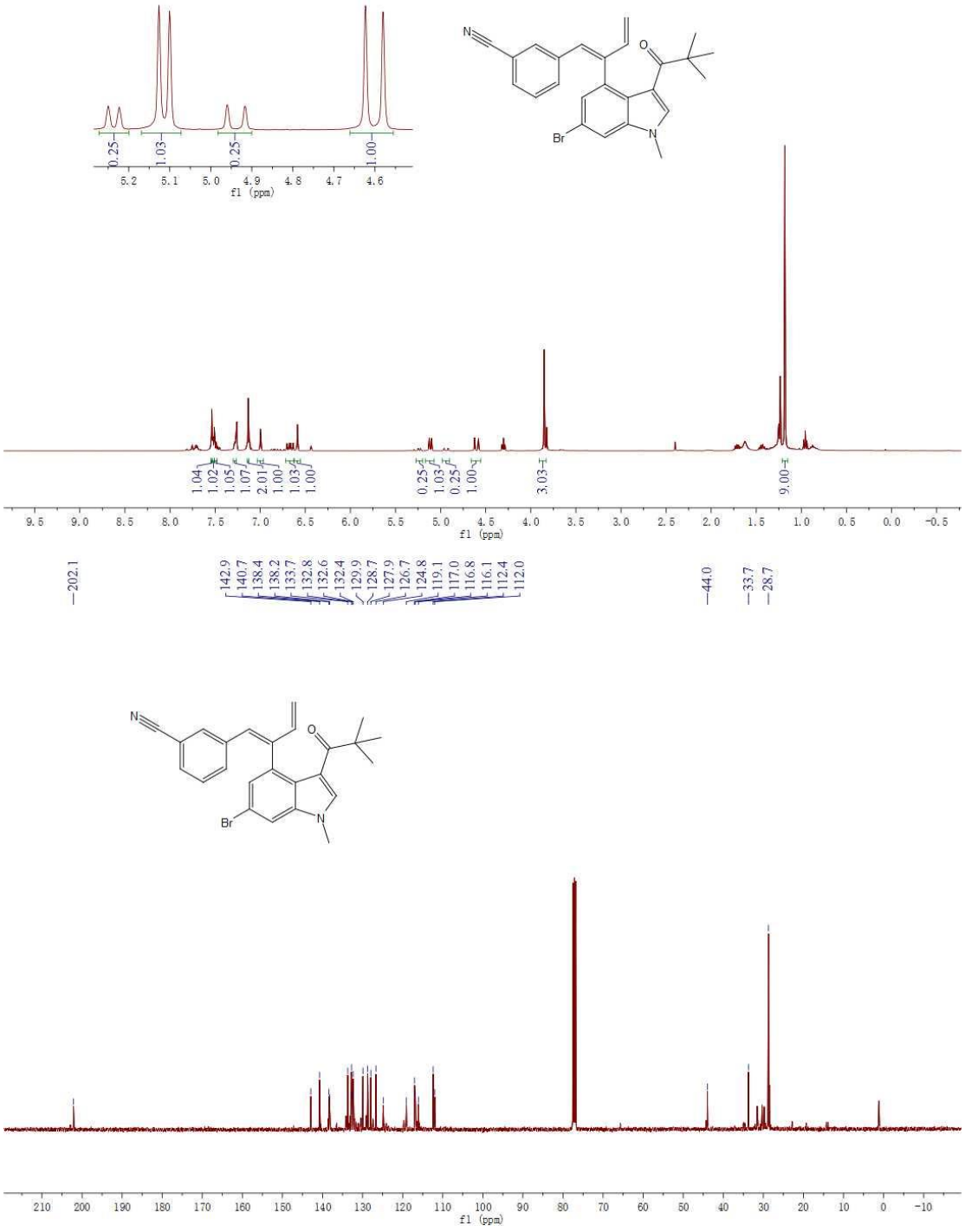

202.6
152.0
140.5
139.6
139.3
133.3
133.0
132.5
132.0
129.6
128.8
128.6
126.4
119.3
118.3
115.8
115.7
111.8
110.5
110.0
57.7
43.9
33.6
28.8
N
O
O
N
f1 (ppm)

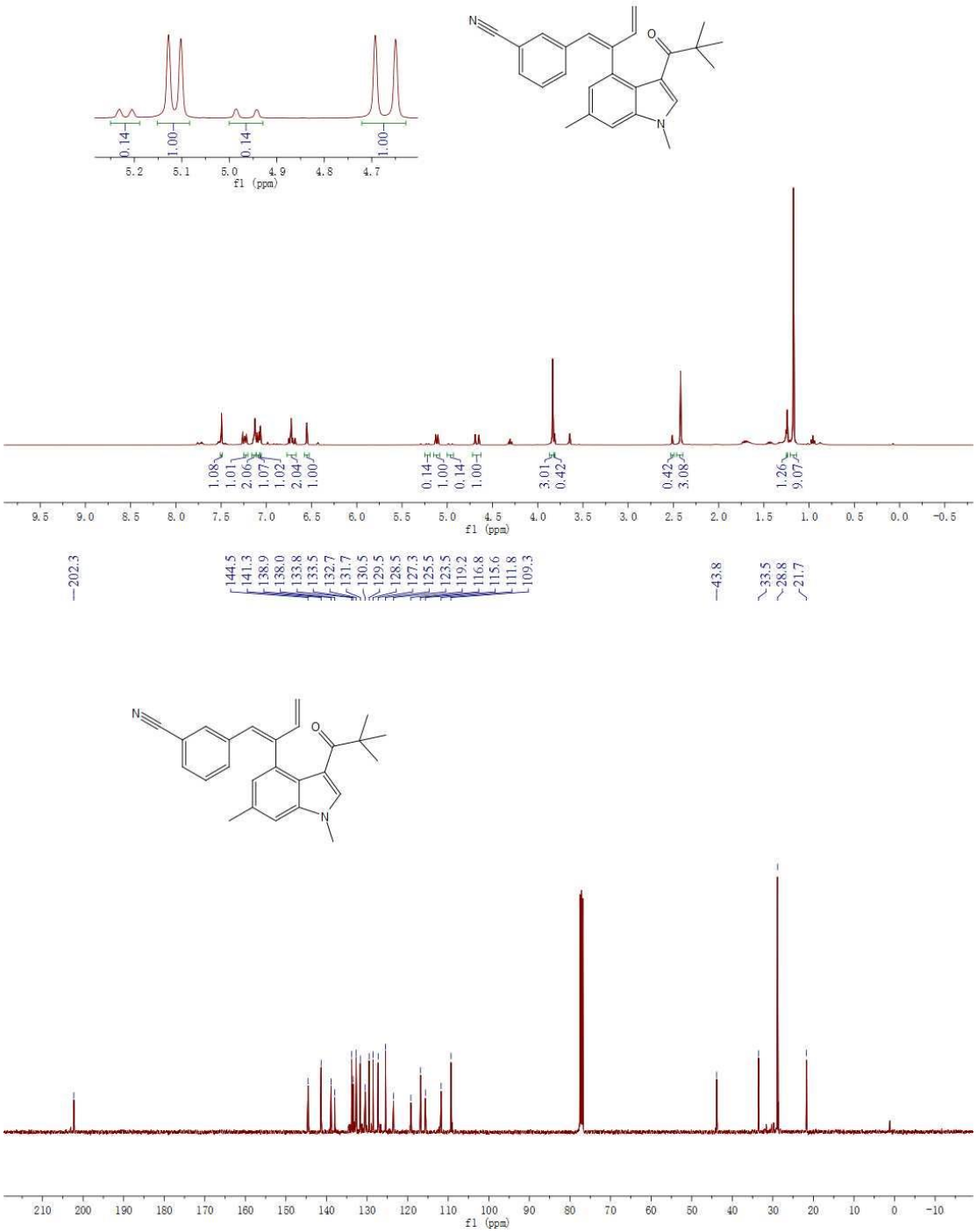

0.10
1.00
0.10
1.02
f1 (ppm)
N
O
F
N
1.08
1.00
2.01
1.03
1.05
2.03
1.03
0.10
1.00
0.10
1.02
3.01
9.01
f1 (ppm)

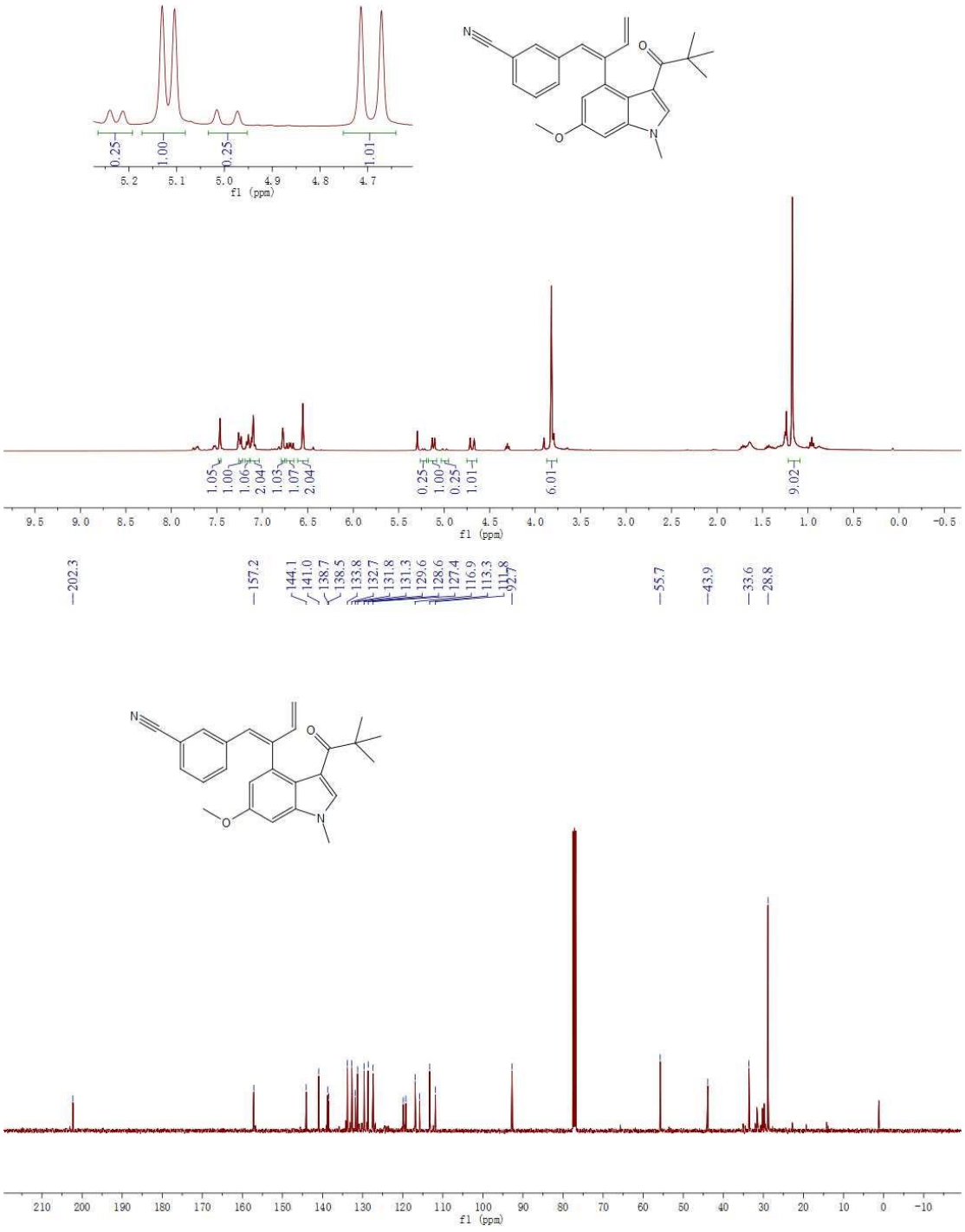

202.19
161.33
158.93
140.54
138.37
133.67
132.65
132.38
132.35
129.78
128.66
127.67
116.88
112.41
112.17
111.85
95.90
95.65
43.85
33.62
28.70
N
O
F
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

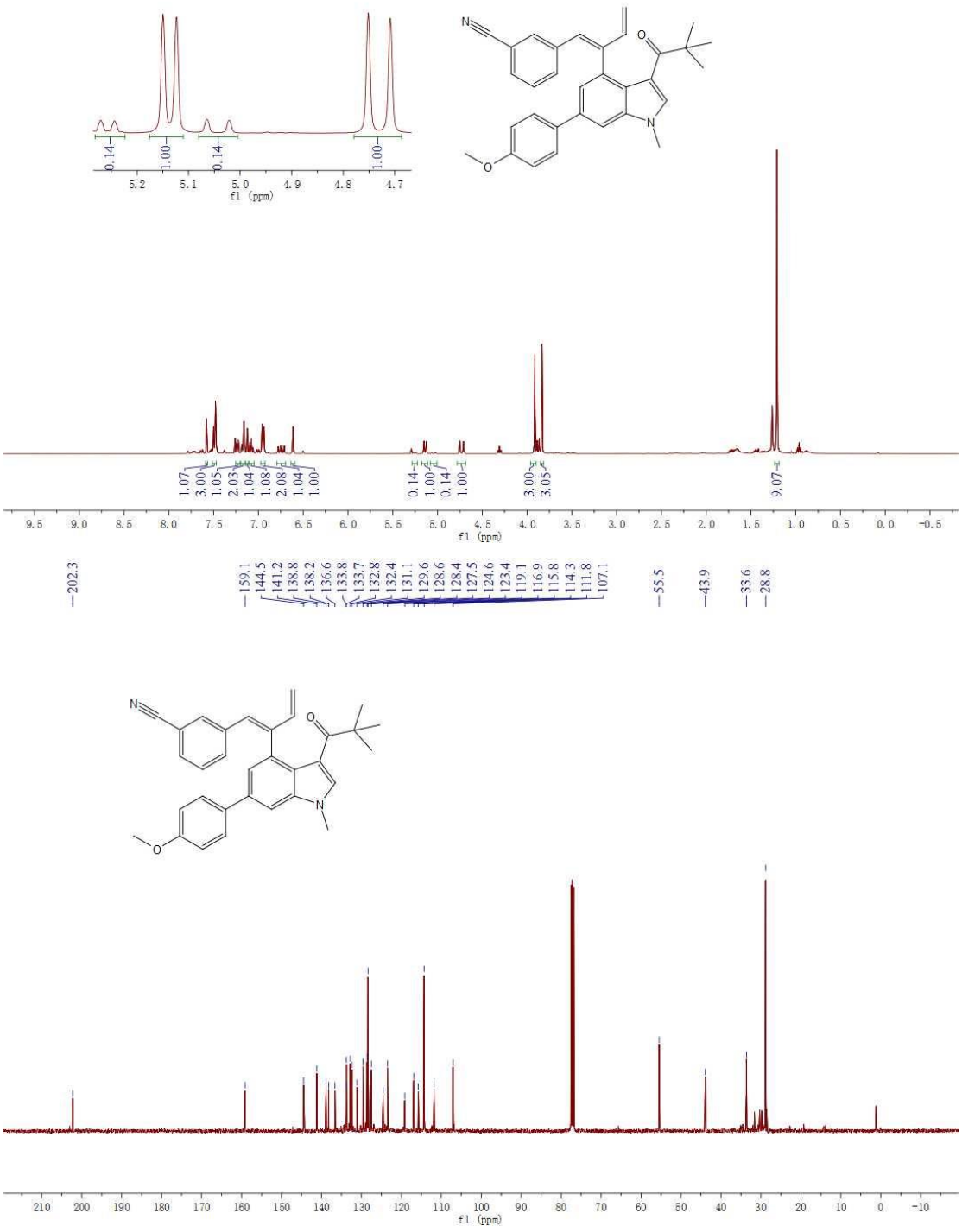

-118.7
N
O
F
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

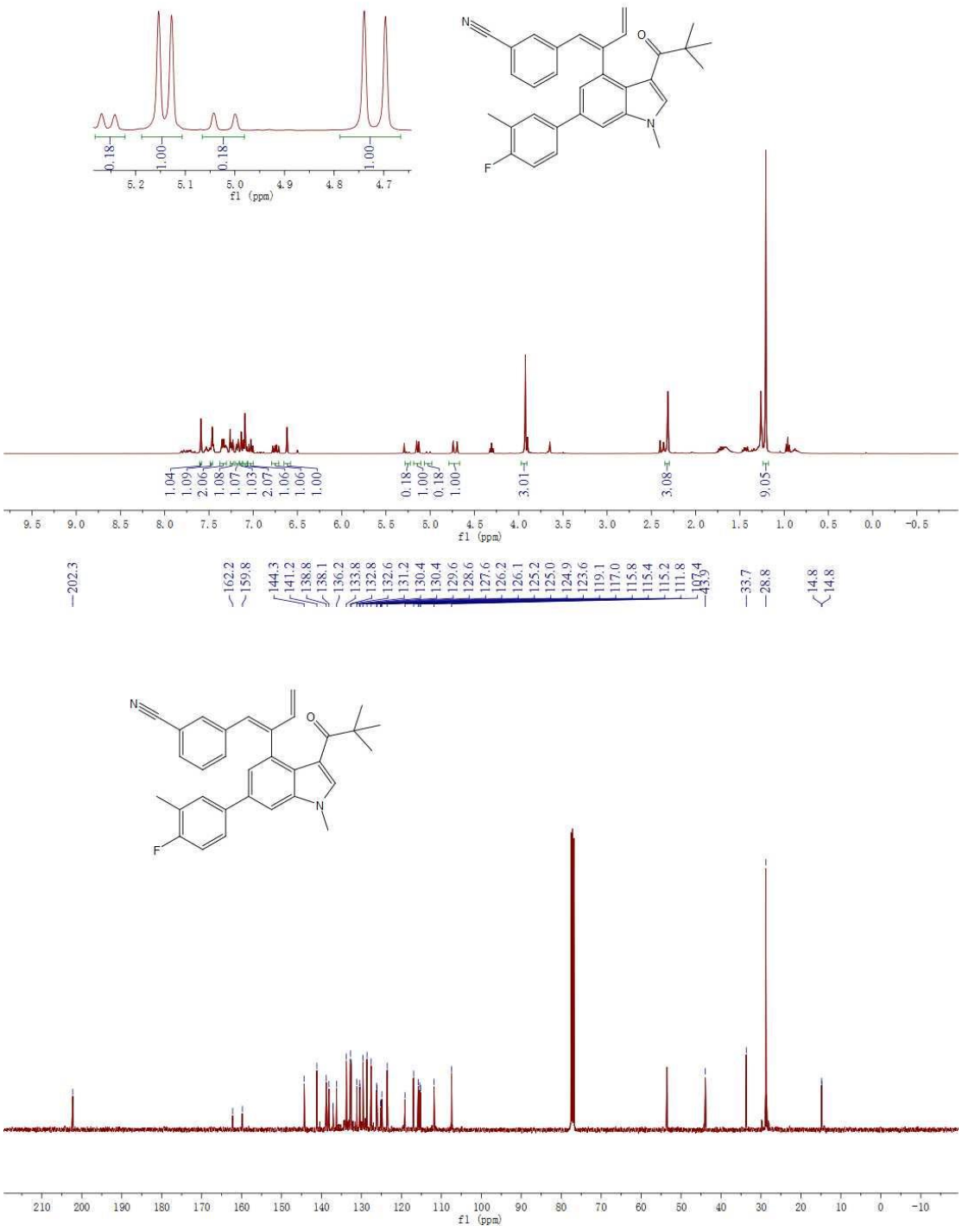

N
O
Cl
N
0.25
1.01
0.25
1.00
5.2
5.1
5.0
4.9
4.8
4.7
4.6
f1 (ppm)
1.01
1.01
1.03
2.08
1.04
1.08
1.09
1.01
0.25
1.01
0.25
1.00
3.00
2.24
9.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
202.1
143.0
140.7
138.4
137.9
133.7
132.8
132.5
132.3
129.9
129.3
128.7
127.9
124.5
124.2
119.1
117.0
116.0
112.0
109.4
43.9
33.7
28.7
N
O
Cl
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

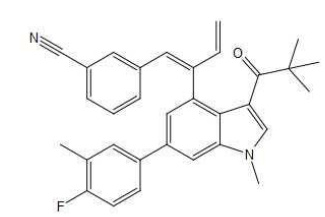

N
O
Br
N
0.25
1.03
0.25
1.00
5.2
5.1
5.0
4.9
4.8
4.7
4.6
f1 (ppm)
1.04
1.02
1.05
1.07
2.01
1.00
1.03
1.00
0.25
1.03
0.25
1.00
3.03
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
202.1
142.9
140.7
138.4
138.2
133.7
132.8
132.6
132.4
129.9
128.7
127.9
126.7
124.8
119.1
117.0
116.8
116.1
112.4
112.0
44.0
33.7
28.7
N
O
Br
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
O
N
0.14
1.00
0.14
1.00
5.2
5.1
5.0
4.9
4.8
4.7
f1 (ppm)
1.08
1.01
2.06
1.07
1.02
2.04
1.00
0.14
1.00
0.14
1.00
3.01
0.42
0.42
3.08
1.26
9.07
9.5
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
-0.5
f1 (ppm)
202.3
144.5
141.3
138.9
138.0
133.8
133.5
132.7
131.7
130.5
129.5
128.5
127.3
125.5
123.5
119.2
116.8
115.6
111.8
109.3
43.8
33.5
28.8
21.7
N
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

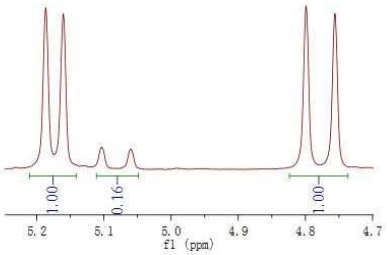

0.25
1.00
0.25
1.01
5.2
5.1
5.0
4.9
4.8
4.7
f1 (ppm)
N
O
O
N
1.05
1.00
1.06
2.04
1.03
1.07
2.04
0.25
1.00
0.25
1.01
6.01
9.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
202.3
157.2
144.1
141.0
138.7
138.5
133.8
132.7
131.8
131.3
129.6
128.6
127.4
116.9
113.3
111.8
92.7
55.7
43.9
33.6
28.8
N
O
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

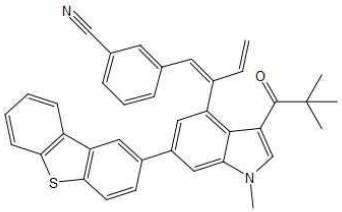

N
O
N
O
0.14
1.00
0.14
1.00
5.2
5.1
5.0
4.9
4.8
4.7
f1 (ppm)
1.07
3.00
1.05
2.03
1.04
1.08
2.08
1.04
1.00
0.14
1.00
0.14
1.00
3.00
3.05
9.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
202.3
159.1
144.5
141.2
138.8
138.2
136.6
133.8
133.7
132.8
132.4
131.1
129.6
128.6
128.4
127.5
124.6
123.4
119.1
116.9
115.8
114.3
111.8
107.1
55.5
43.9
33.6
28.8
N
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

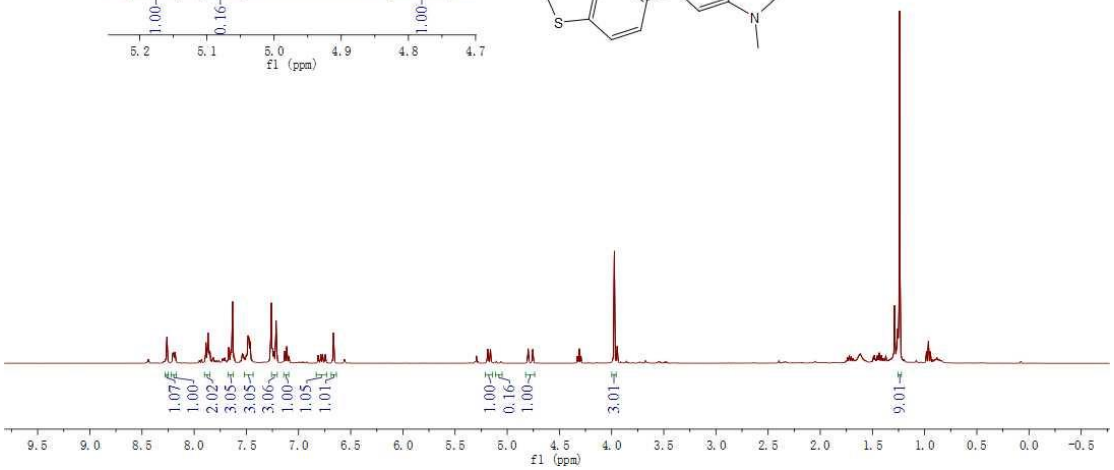

N
O
N
F
0.18
1.00
0.18
1.00
5.2
5.1
5.0
4.9
4.8
4.7
f1 (ppm)
1.04
1.09
2.06
1.08
1.07
1.03
2.07
1.06
1.06
1.00
0.18
1.00
0.18
1.00
3.01
3.08
9.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
202.3
162.2
159.8
144.3
141.2
138.8
138.1
136.2
133.8
132.8
132.6
131.2
130.4
130.4
129.6
128.6
127.6
126.2
126.1
125.2
125.0
124.9
123.6
119.1
117.0
115.8
115.4
115.2
111.8
107.4
43.9
33.7
28.8
14.8
14.8
N
O
N
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

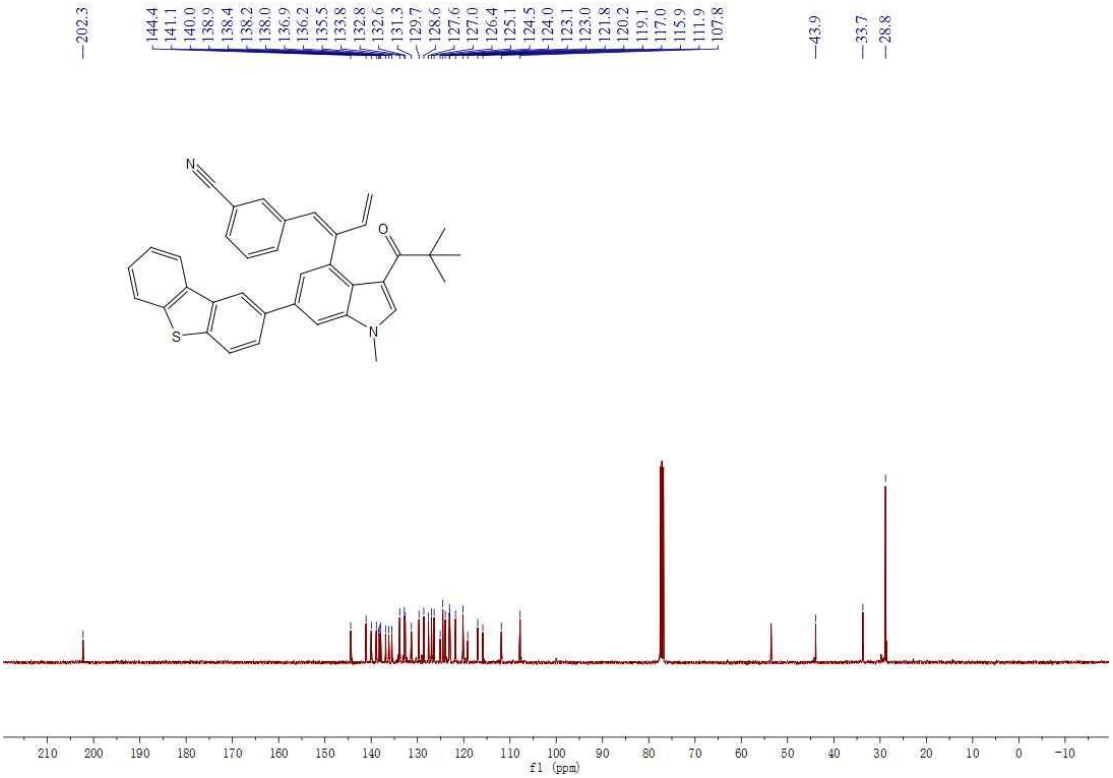

N
O
N
F

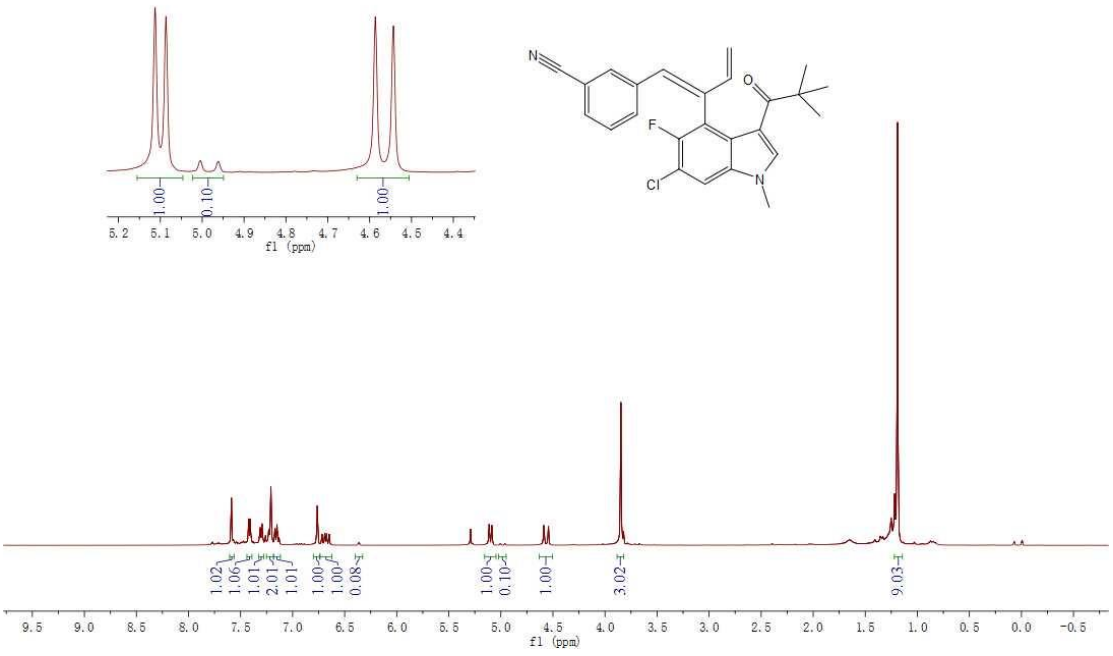
-120.22
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

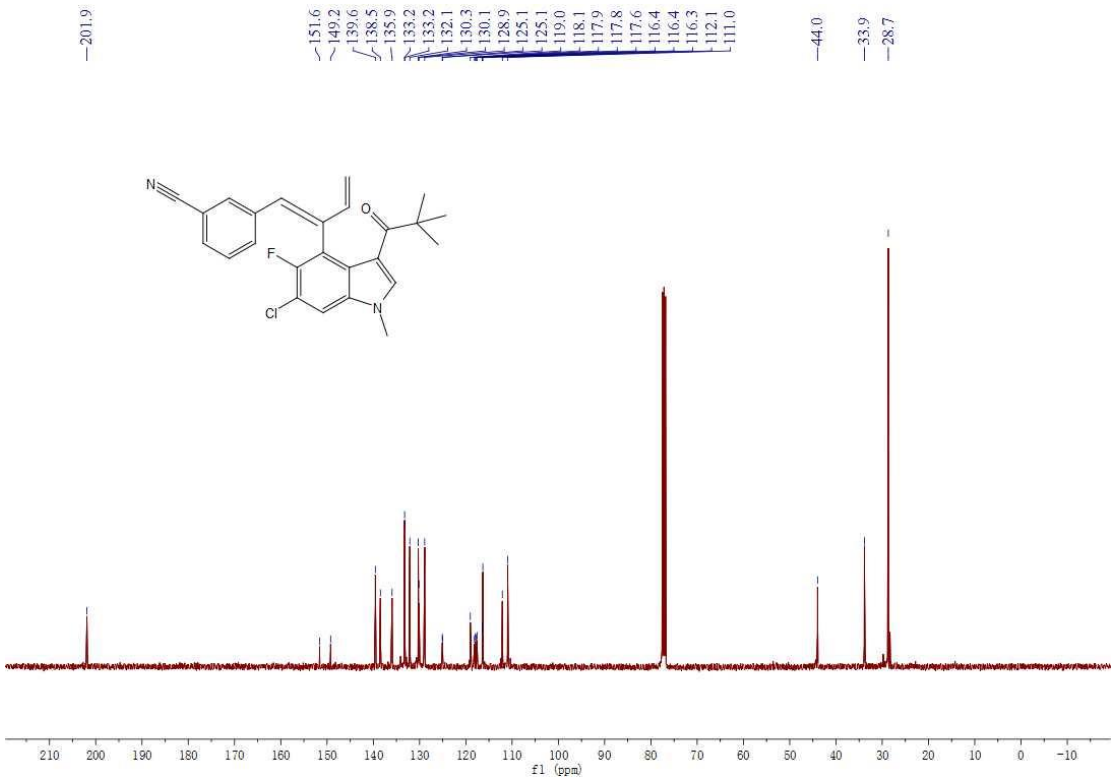

1.00
0.16
1.00
5.2 5.1 5.0 4.9 4.8 4.7
f1 (ppm)

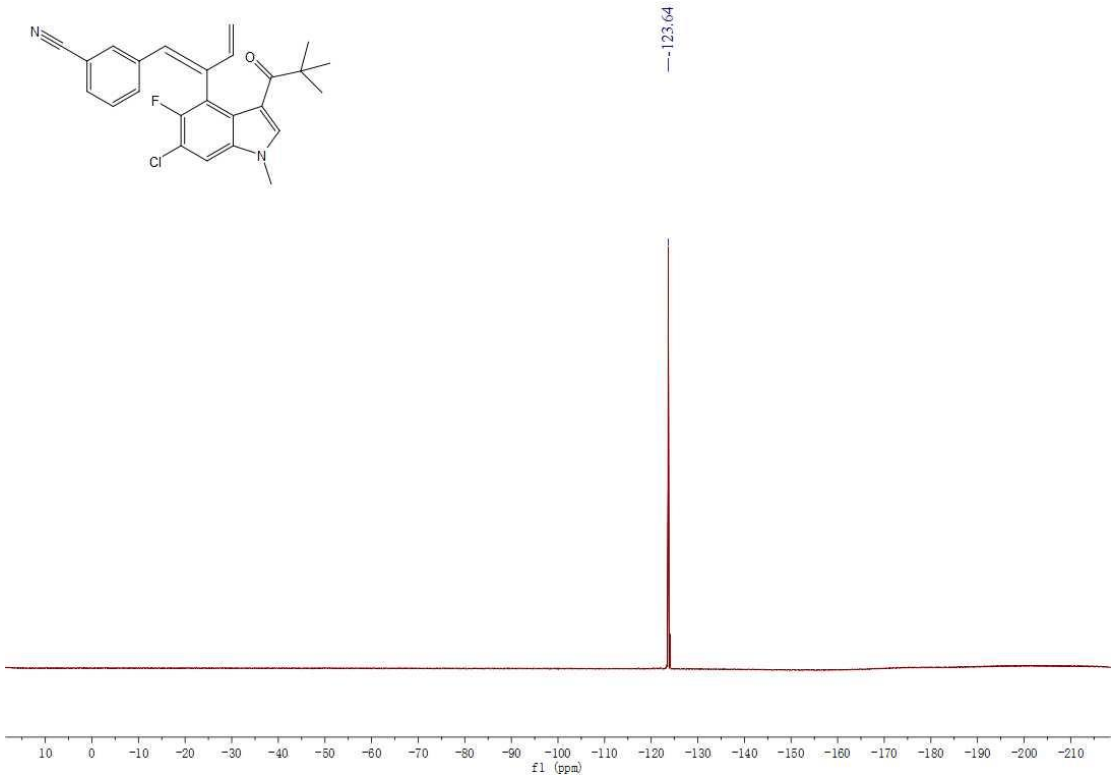

N
O
S
N

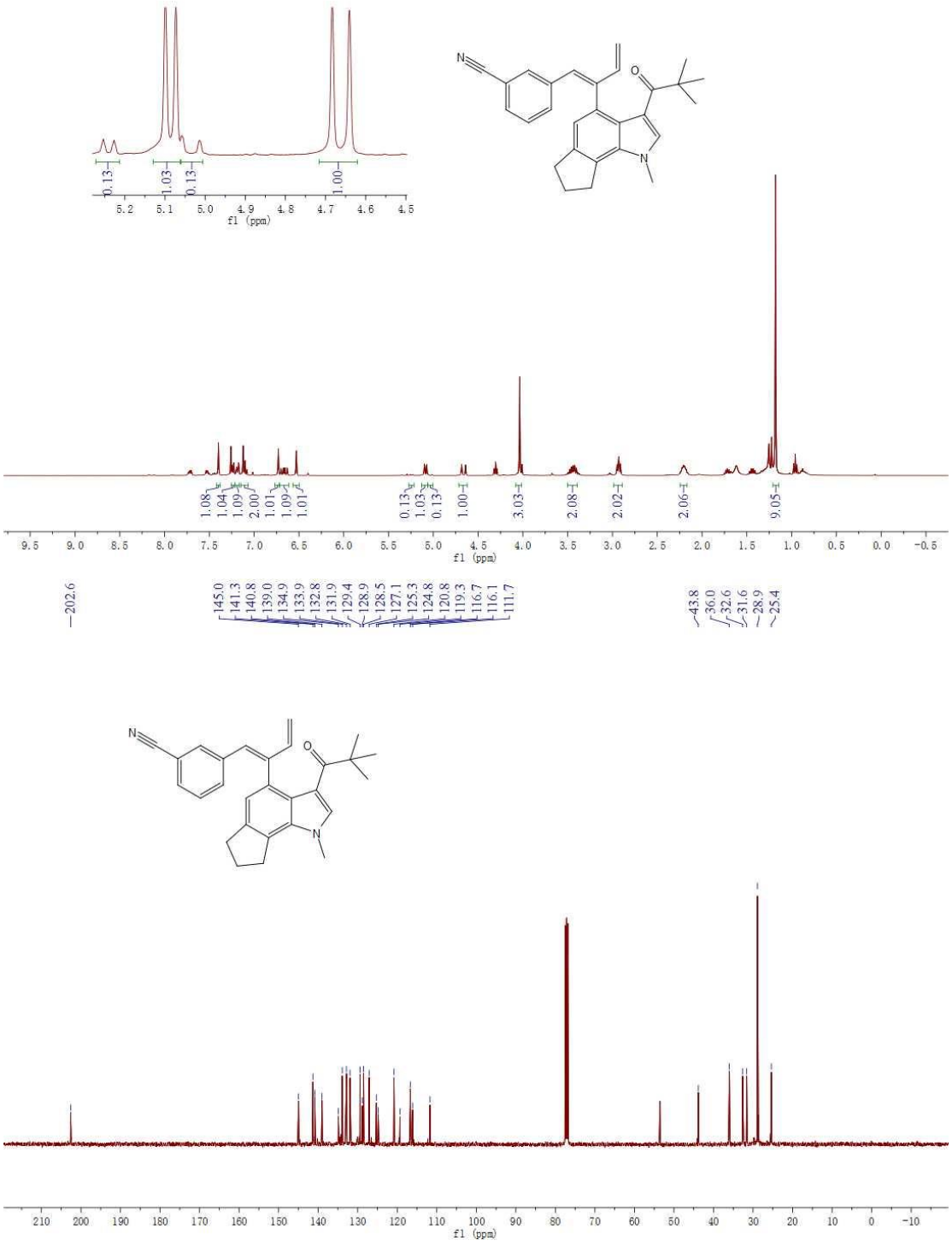

1.07
1.00
2.02
3.05
3.05
3.06
1.00
1.05
1.01
1.00
0.16
1.00
3.01
9.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

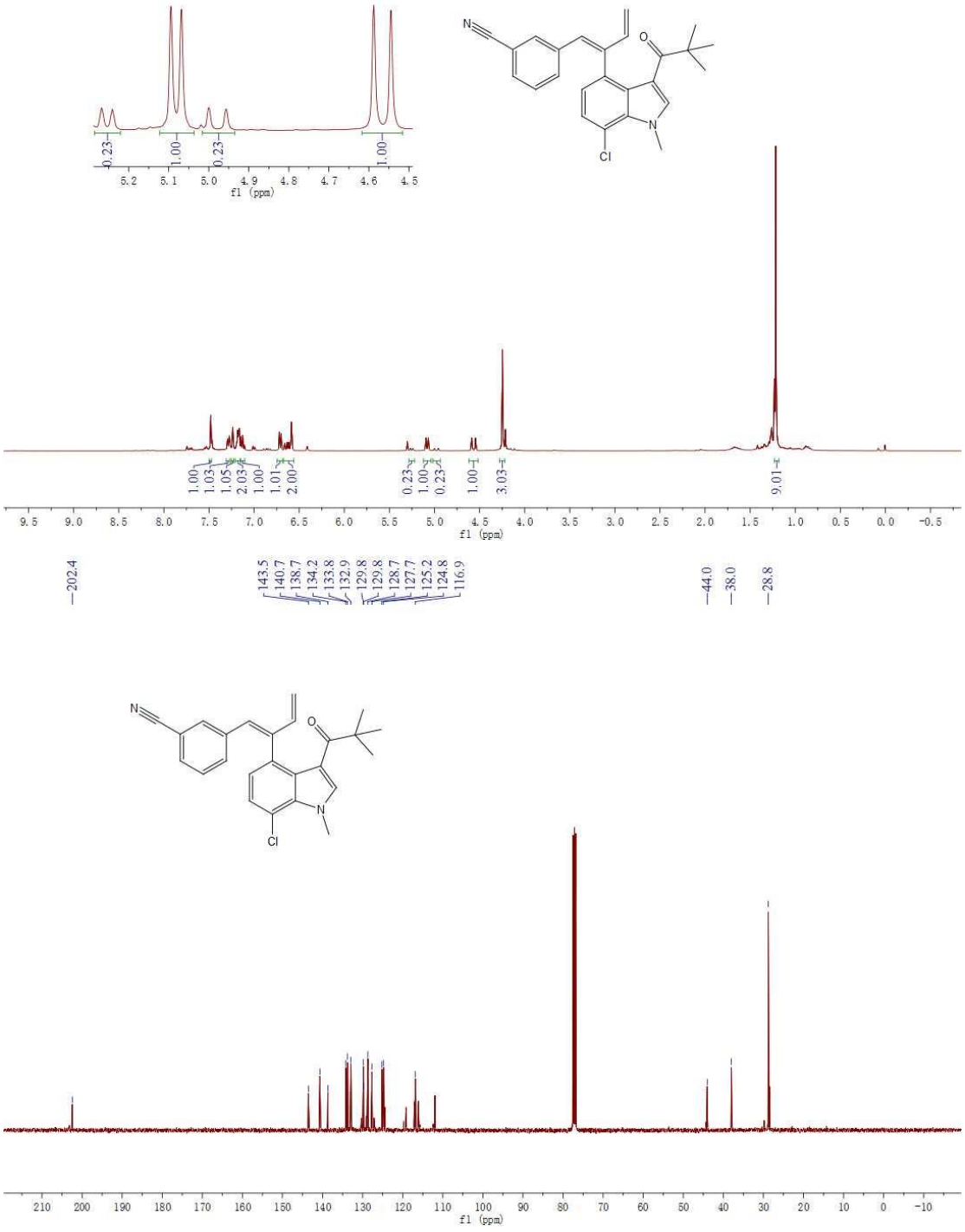

202.3
144.4
141.1
140.0
138.9
138.4
138.2
138.0
136.9
136.2
135.5
133.8
132.8
132.6
131.3
129.7
128.6
127.6
127.0
126.4
125.1
124.5
124.0
123.1
123.0
121.8
120.2
119.1
117.0
115.9
111.9
107.8
43.9
33.7
28.8
N
O
S
N
f1 (ppm)

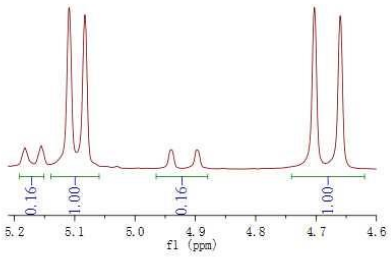

1.00
0.10
1.00
f1 (ppm)
N
O
F
Cl
N
1.02
1.06
1.01
2.01
1.01
1.00
1.00
0.08
1.00
0.10
1.00
3.02
9.03
f1 (ppm)

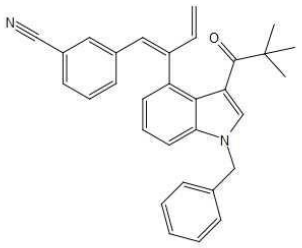

201.9
151.6
149.2
139.6
138.5
135.9
133.2
133.2
132.1
130.3
130.1
128.9
125.1
125.1
119.0
118.1
117.9
117.8
117.6
116.4
116.4
116.3
112.1
111.0
44.0
33.9
28.7
N
O
F
Cl
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

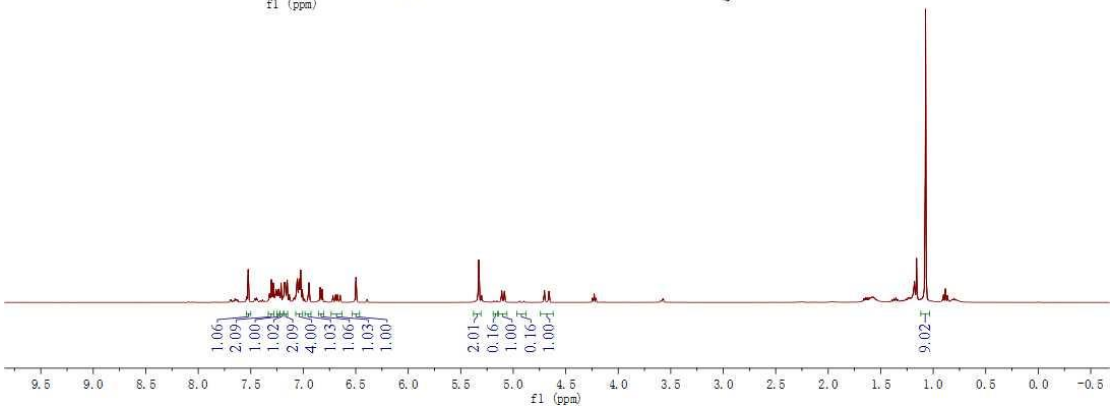

-123.64
N
O
F
Cl
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


0.13
1.03
0.13
1.00
f1 (ppm)
N
O
1.08
1.04
1.09
2.00
1.01
1.09
1.01
0.13
1.03
0.13
1.00
3.03
2.08
2.02
2.06
9.05
f1 (ppm)
202.6
145.0
141.3
140.8
139.0
134.9
133.9
132.8
131.9
129.4
128.9
128.5
127.1
125.3
124.8
120.8
119.3
116.7
116.1
111.7
43.8
36.0
32.6
31.6
28.9
25.4
N
O
f1 (ppm)

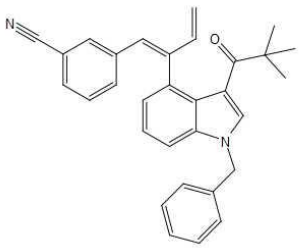

N
O
N
Cl
0.23
1.00
0.23
1.00
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
f1 (ppm)
1.00
1.03
1.05
2.03
1.00
1.01
2.00
0.23
1.00
0.23
1.00
3.03
9.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
202.4
143.5
140.7
138.7
134.2
133.8
132.9
129.8
129.8
128.7
127.7
125.2
124.8
116.9
44.0
38.0
28.8
N
O
N
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

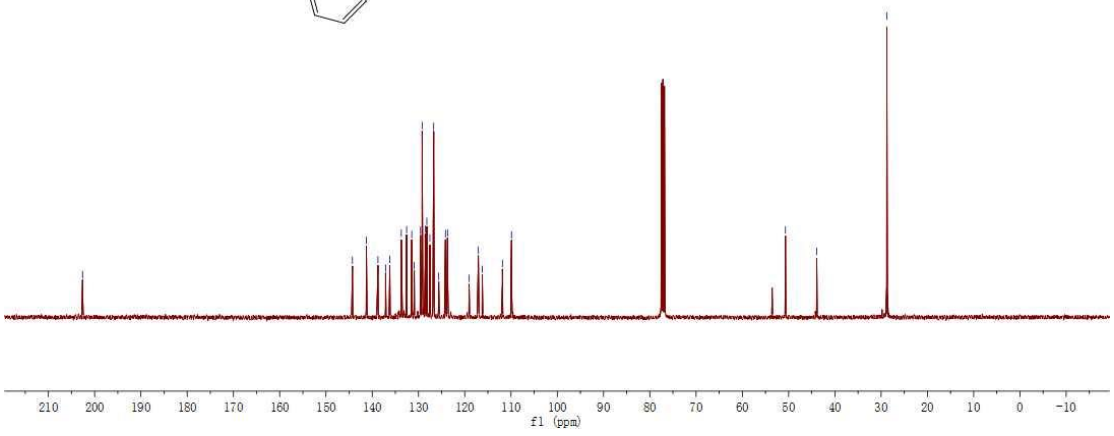

0.16
1.00
0.16
1.00
5.2
5.1
5.0
4.9
4.8
4.7
4.6
f1 (ppm)

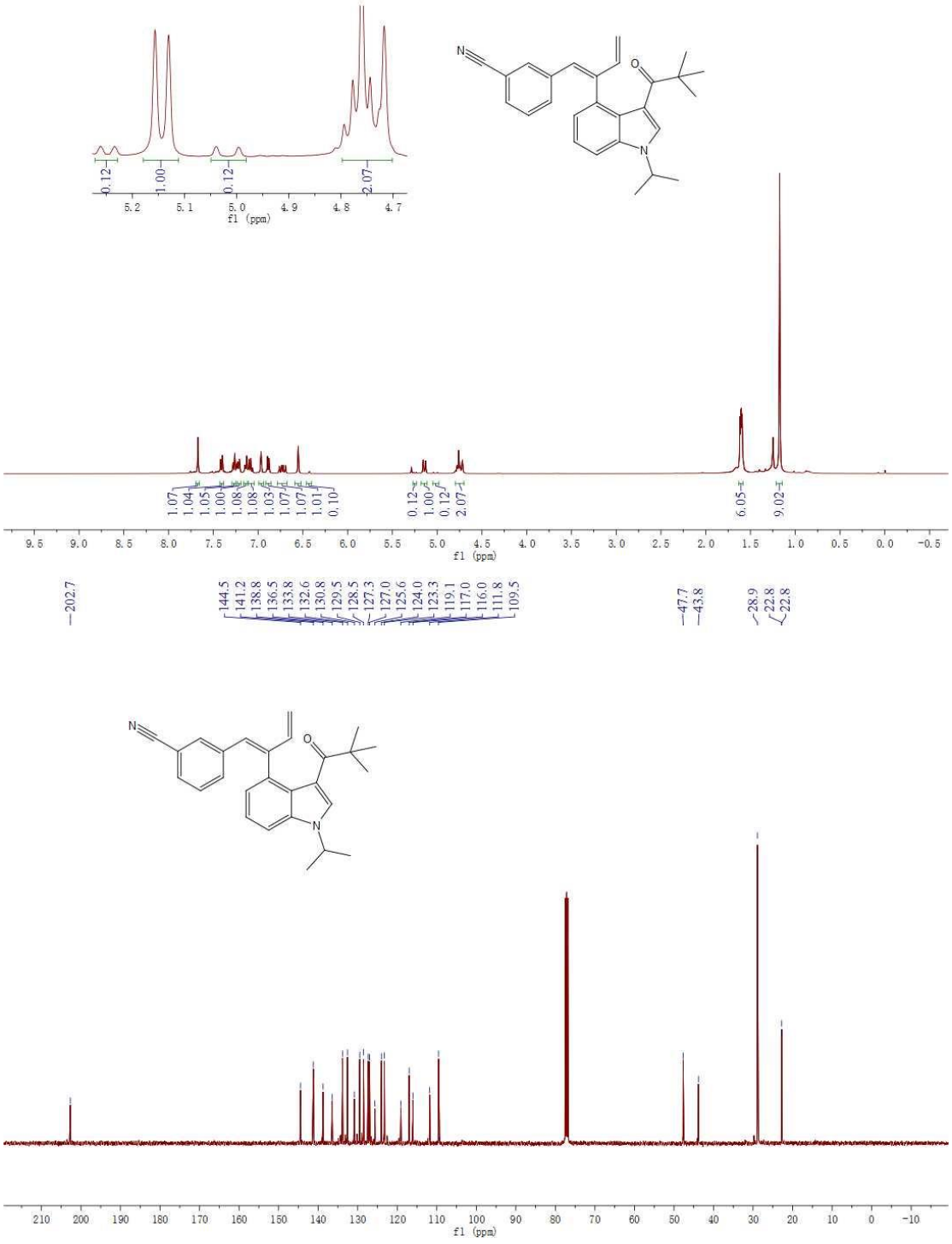

N
O
N

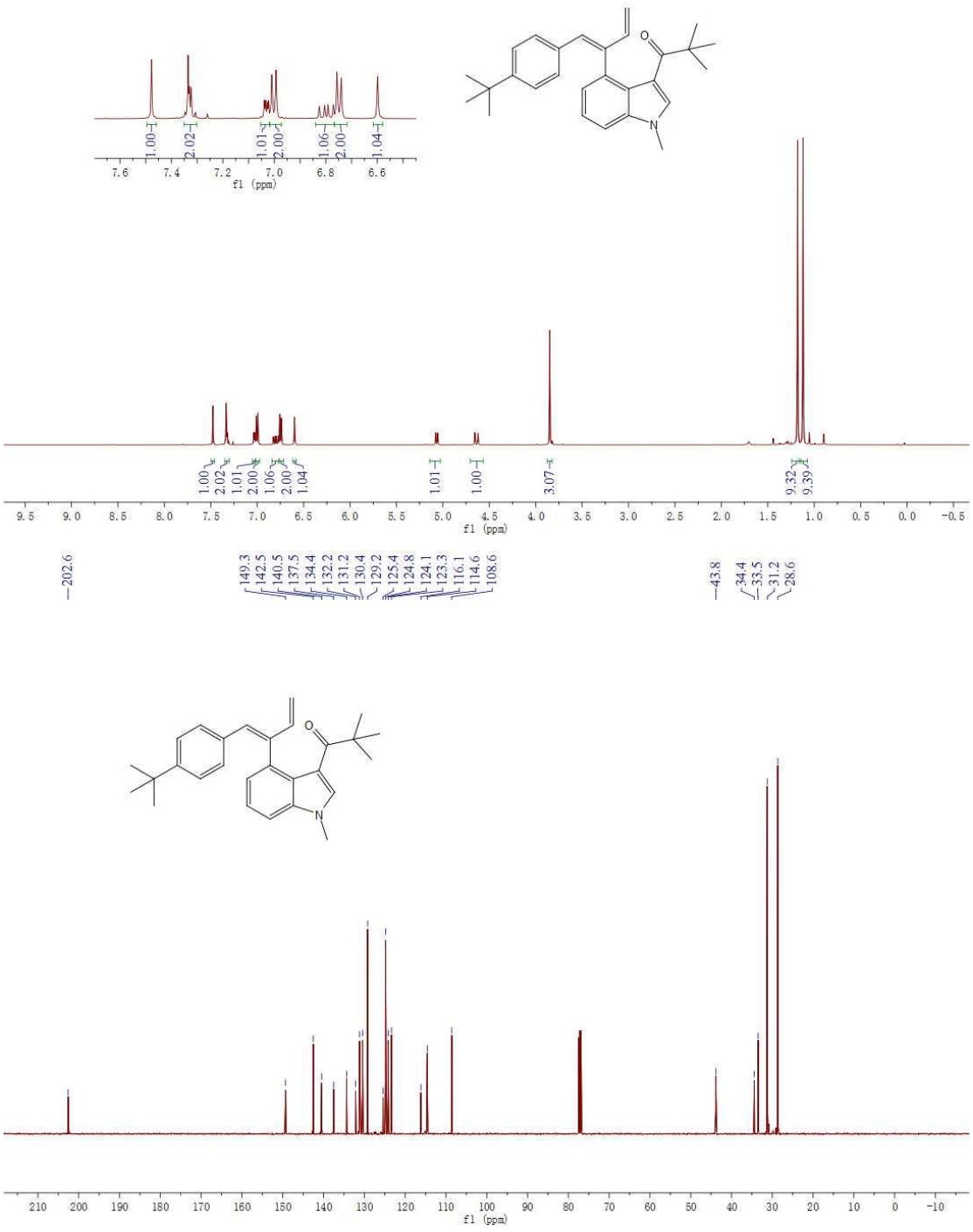

1.06
2.09
1.00
1.02
2.09
4.00
1.03
1.06
1.03
1.00
2.01
0.16
1.00
0.16
1.00
9.02
f1 (ppm)

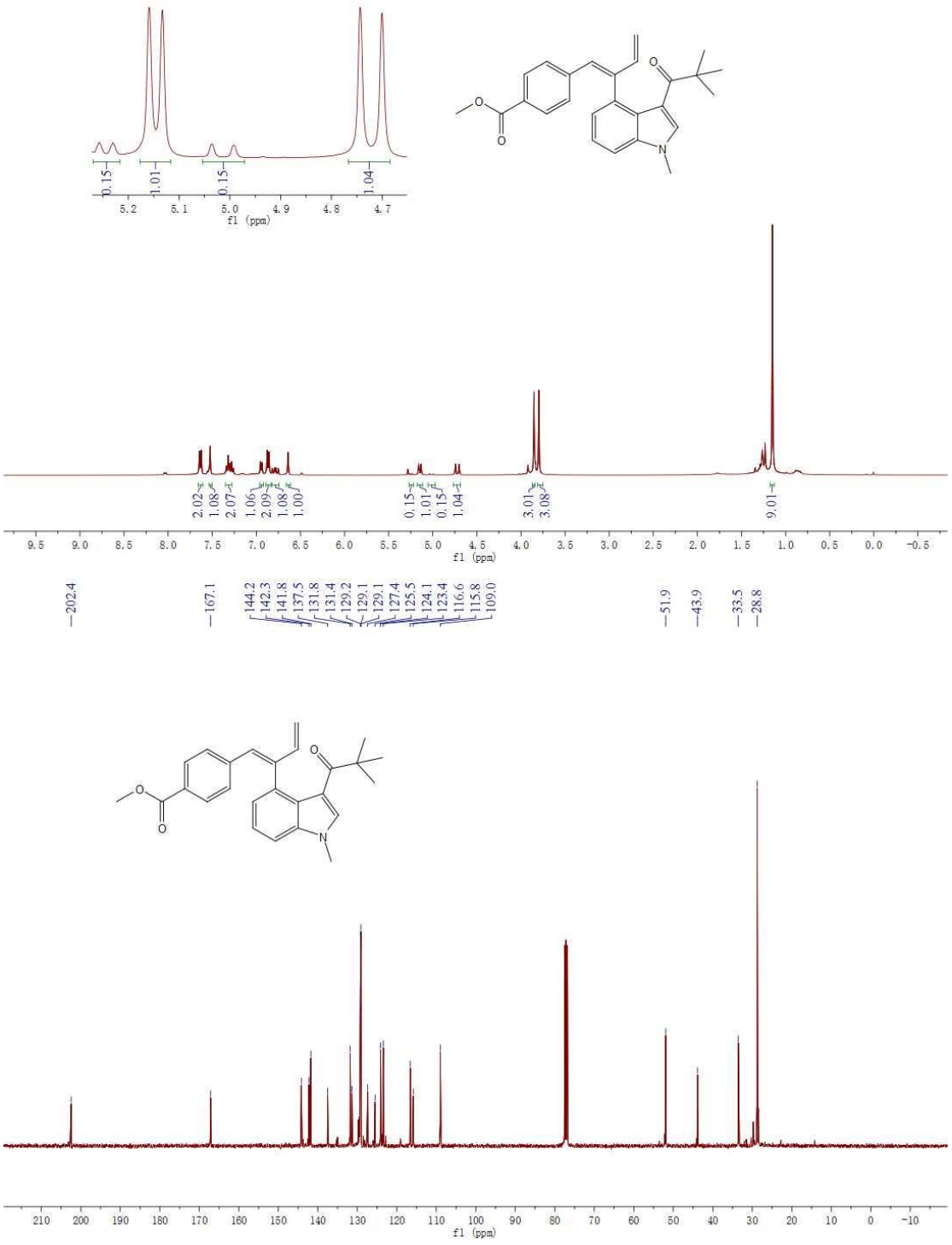

202.6
144.3
141.3
138.8
137.1
136.2
133.7
132.6
131.5
130.9
129.6
129.2
128.6
128.2
127.5
126.7
125.6
124.2
123.7
119.1
117.1
116.2
111.9
109.9
50.7
43.9
28.8

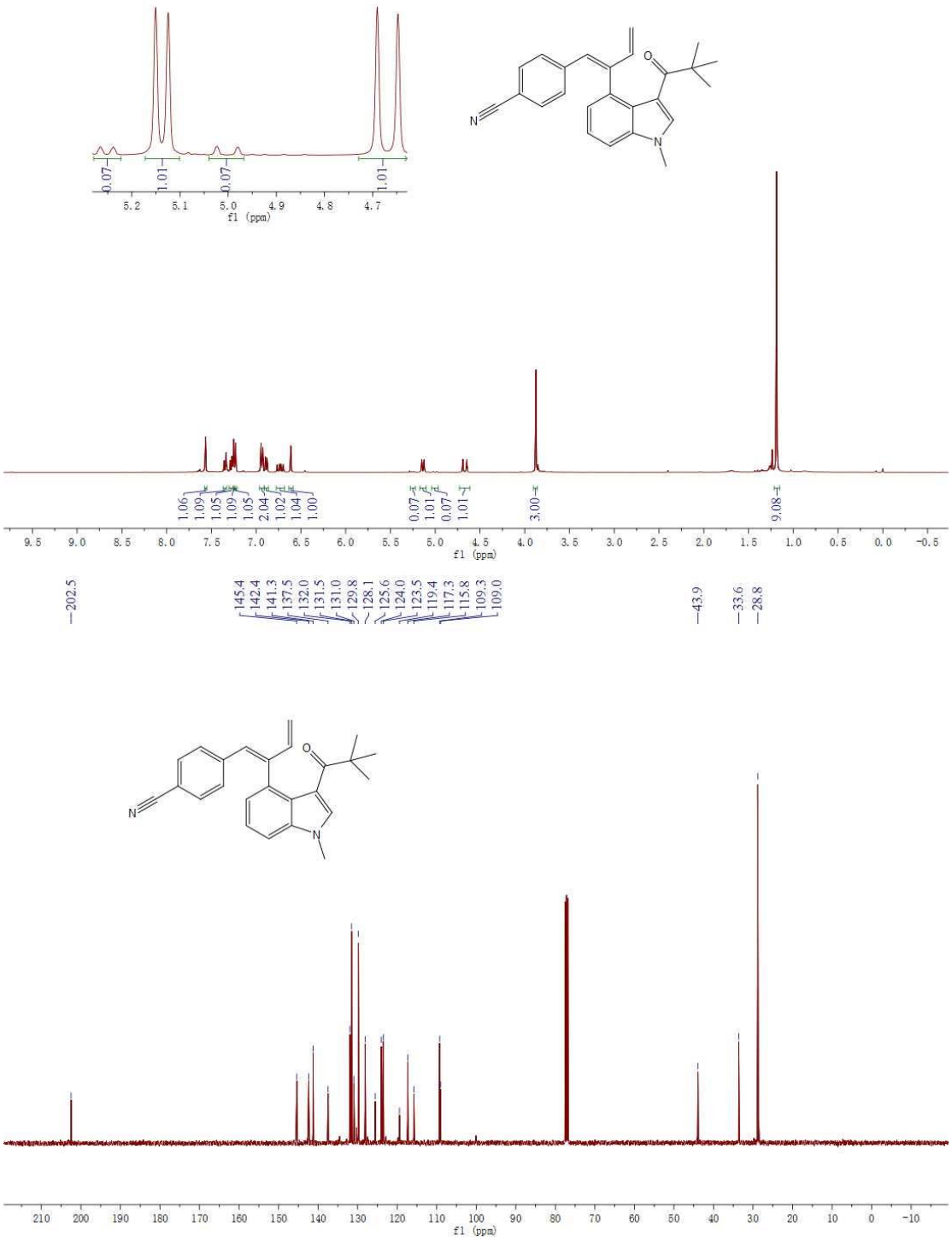

N
O
N

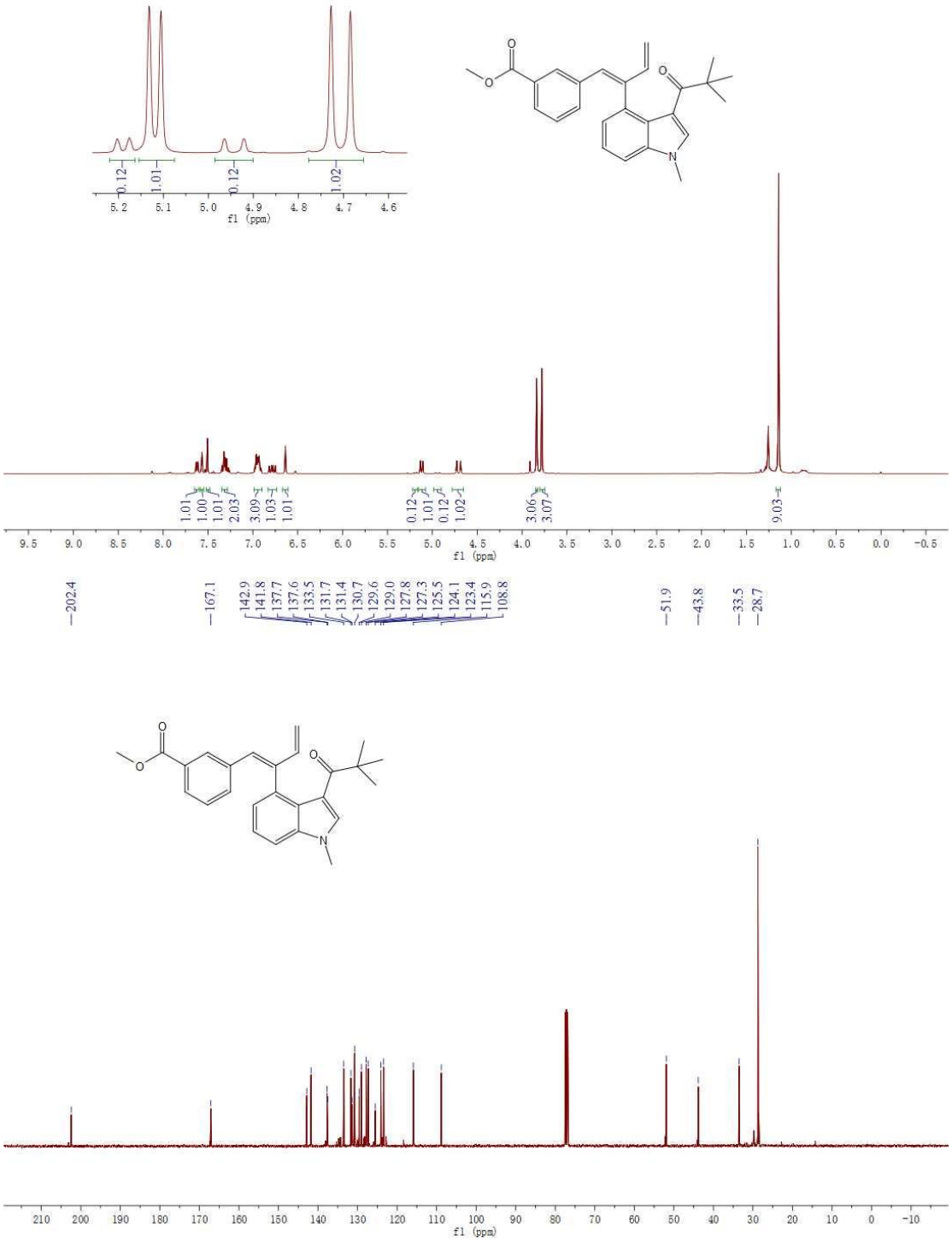

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

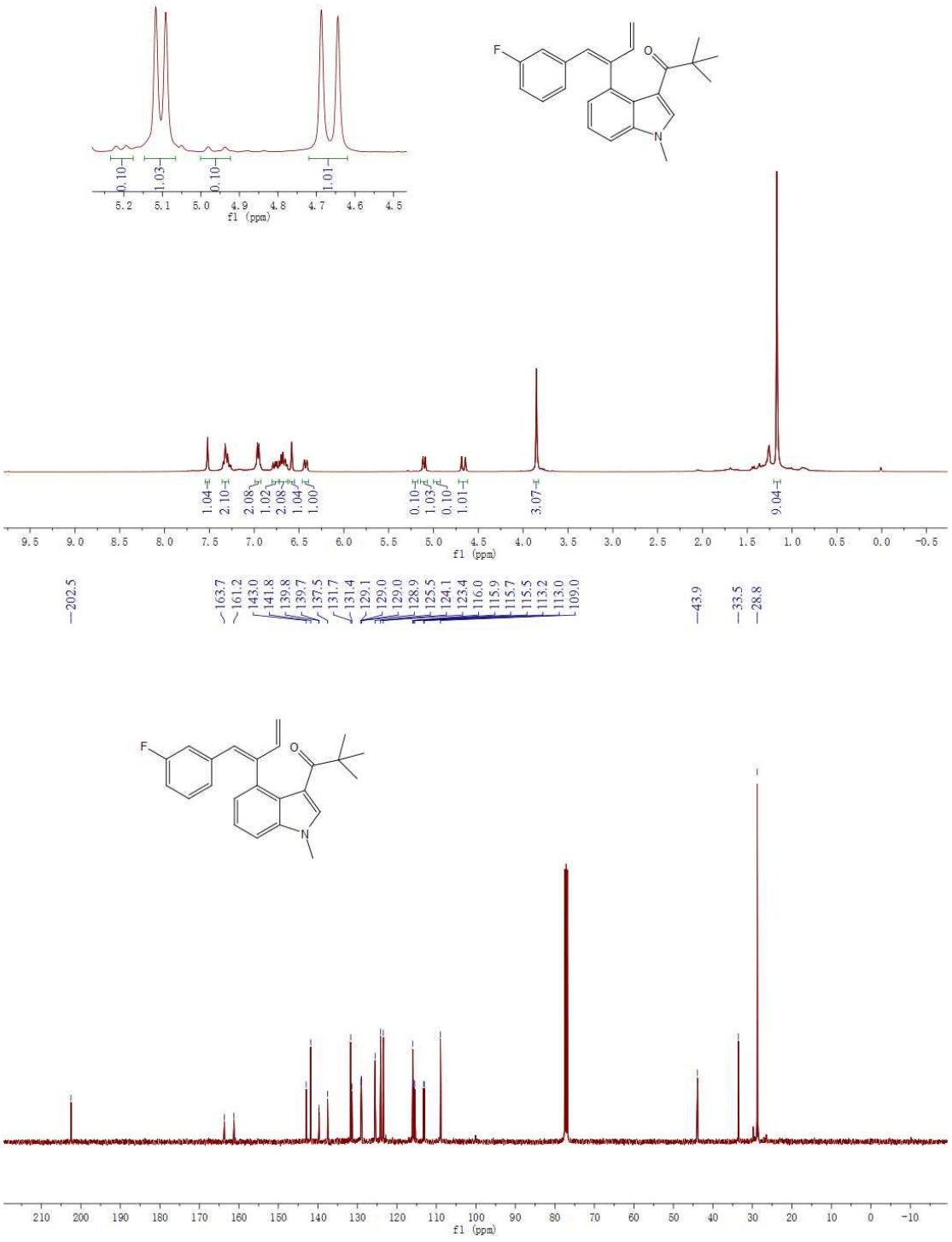

N
O
N
0.12
1.00
0.12
2.07
5.2
5.1
5.0
4.9
4.8
4.7
f1 (ppm)
1.07
1.04
1.05
1.00
1.08
1.08
1.03
1.07
1.07
1.01
0.10
0.12
1.00
0.12
2.07
6.05
9.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
202.7
144.5
141.2
138.8
136.5
133.8
132.6
130.8
129.5
128.5
127.3
127.0
125.6
124.0
123.3
119.1
117.0
116.0
111.8
109.5
47.7
43.8
28.9
22.8
22.8
N
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

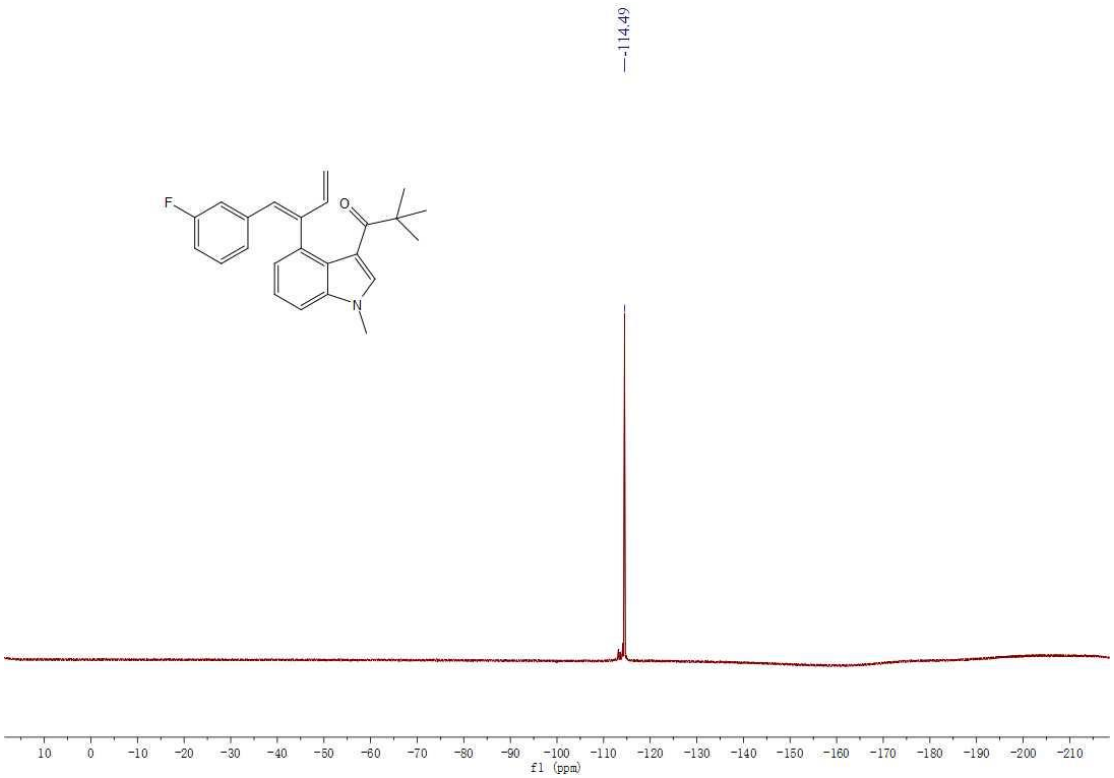

O
N
1.00
2.02
1.01
2.00
1.06
2.00
1.04
1.01
1.00
3.07
9.32
9.39
f1 (ppm)
202.6
149.3
142.5
140.5
137.5
134.4
132.2
131.2
130.4
129.2
125.4
124.8
124.1
123.3
116.1
114.6
108.6
43.8
34.4
33.5
31.2
28.6

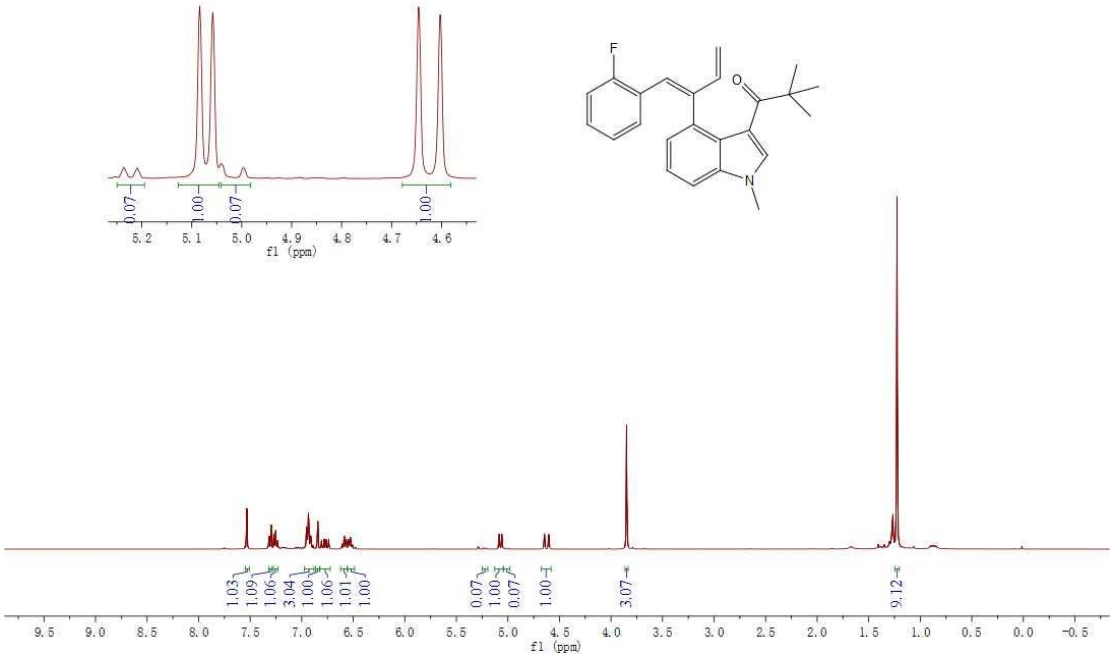

0.15
1.01
0.15
1.04
5.2
5.1
5.0
4.9
4.8
4.7
f1 (ppm)
O
O
O
N
2.02
1.08
2.07
1.06
2.09
1.08
1.00
0.15
1.01
0.15
1.04
3.01
3.08
9.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
202.4
167.1
144.2
142.3
141.8
137.5
131.8
131.4
129.2
129.1
129.1
127.4
125.5
124.1
123.4
116.6
115.8
109.0
51.9
43.9
33.5
28.8
O
O
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

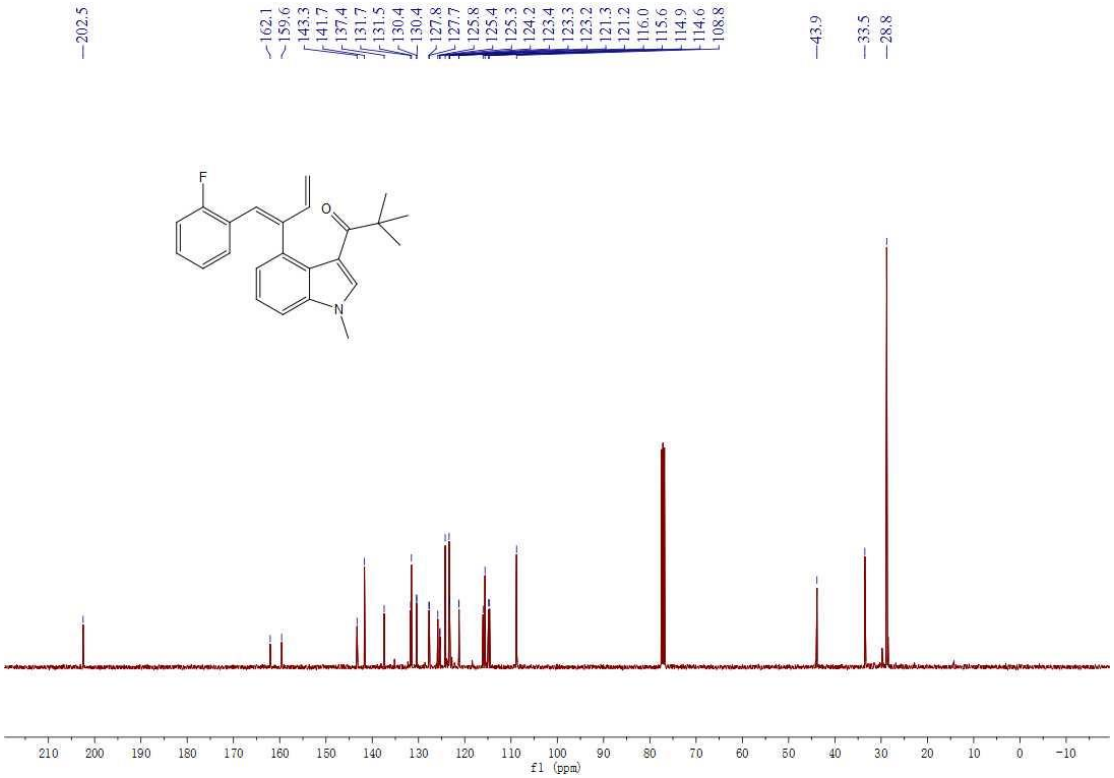

0.07
1.01
0.07
1.01
5.2
5.1
5.0
4.9
4.8
4.7
f1 (ppm)
O
N
N
1.06
1.09
1.05
1.09
1.05
2.04
1.02
1.04
1.00
0.07
1.01
0.07
1.01
3.00
9.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
202.5
145.4
142.4
141.3
137.5
132.0
131.5
131.0
129.8
128.1
125.6
124.0
123.5
119.4
117.3
115.8
109.3
109.0
43.9
33.6
28.8
O
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

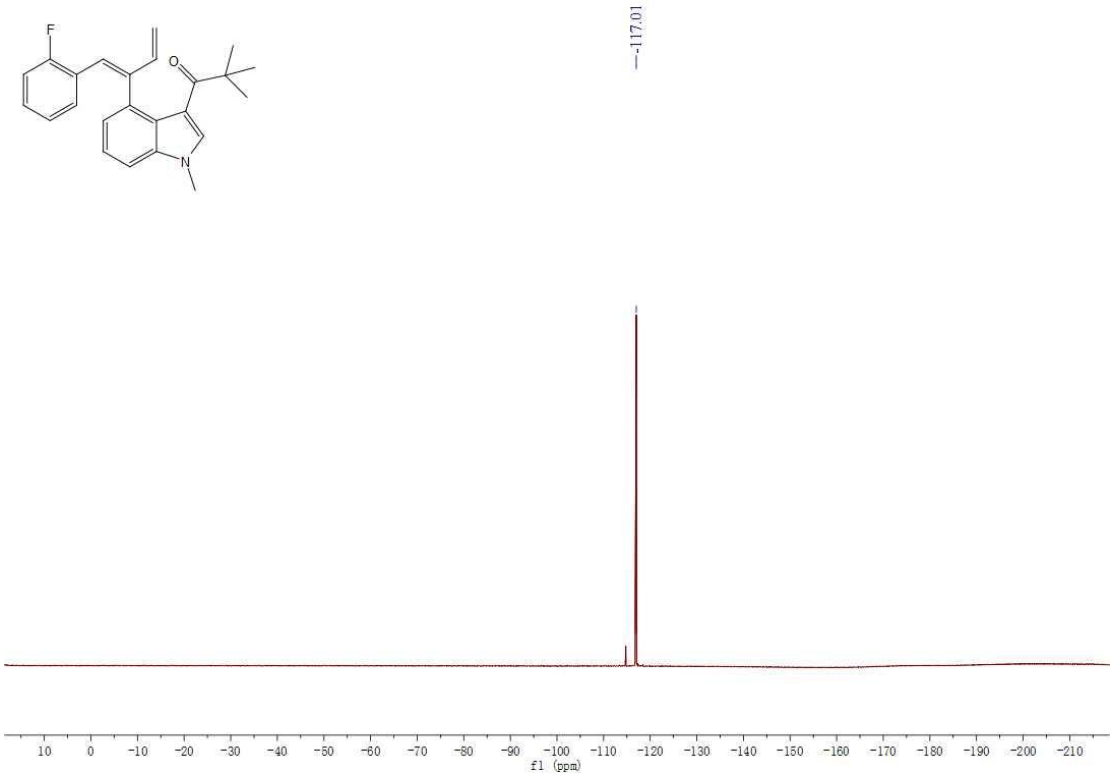

0.12
1.01
0.12
1.02
5.2
5.1
5.0
4.9
4.8
4.7
4.6
f1 (ppm)
O
O
O
N
1.01
1.00
1.01
2.03
3.09
1.03
1.01
0.12
1.01
0.12
1.02
3.06
3.07
9.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
202.4
167.1
142.9
141.8
137.7
137.6
133.5
131.7
131.4
130.7
129.6
129.0
127.8
127.3
125.5
124.1
123.4
115.9
108.8
51.9
43.8
33.5
28.7
O
O
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

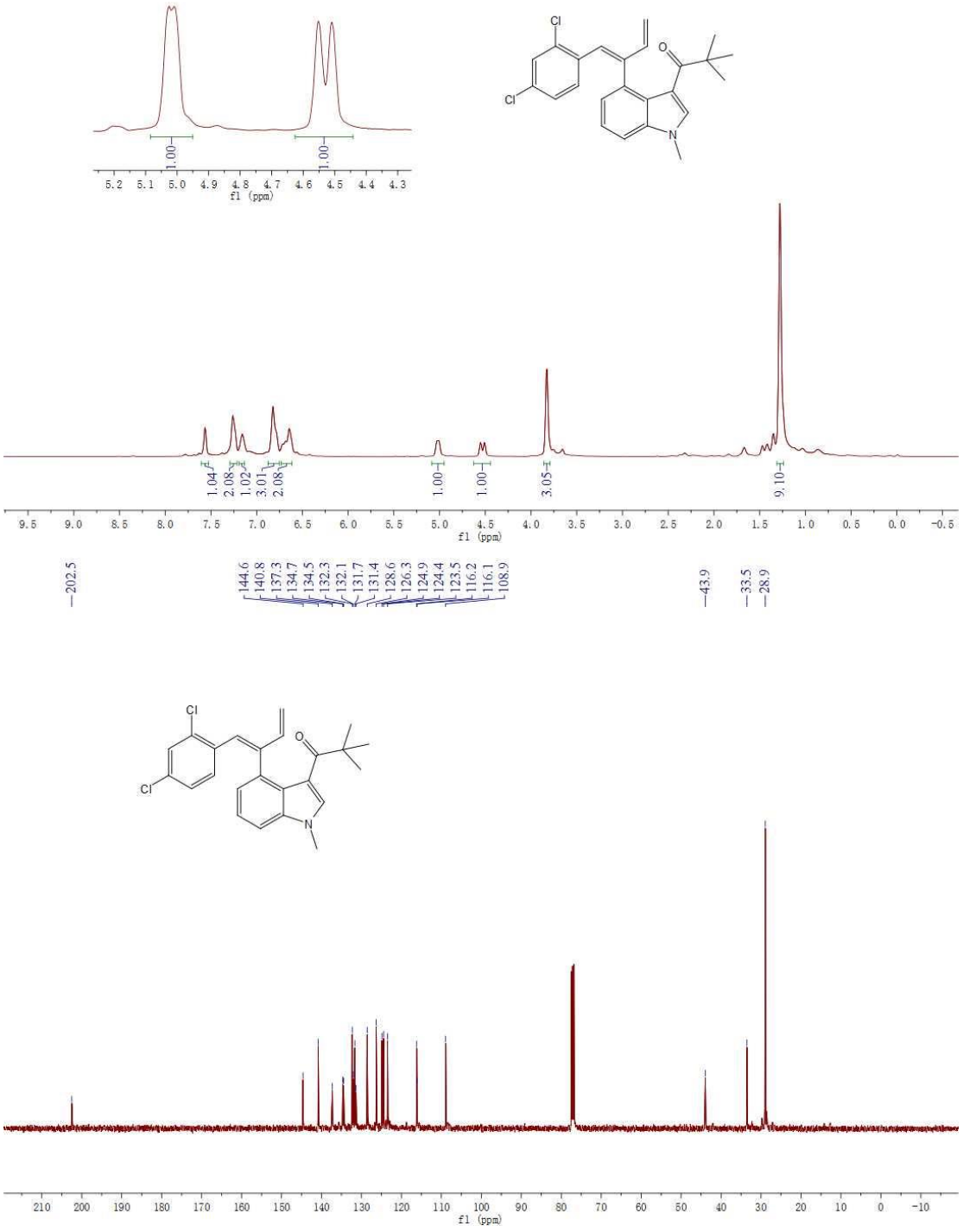

F
O
N
0.10
1.03
0.10
1.01
5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5
f1 (ppm)
1.04
2.10
2.08
1.02
2.08
1.04
1.00
0.10
1.03
0.10
1.01
3.07
9.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
202.5
163.7
161.2
143.0
141.8
139.8
139.7
137.5
131.7
131.4
129.1
129.0
129.0
128.9
125.5
124.1
123.4
116.0
115.9
115.7
115.5
113.2
113.0
109.0
43.9
33.5
28.8
F
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

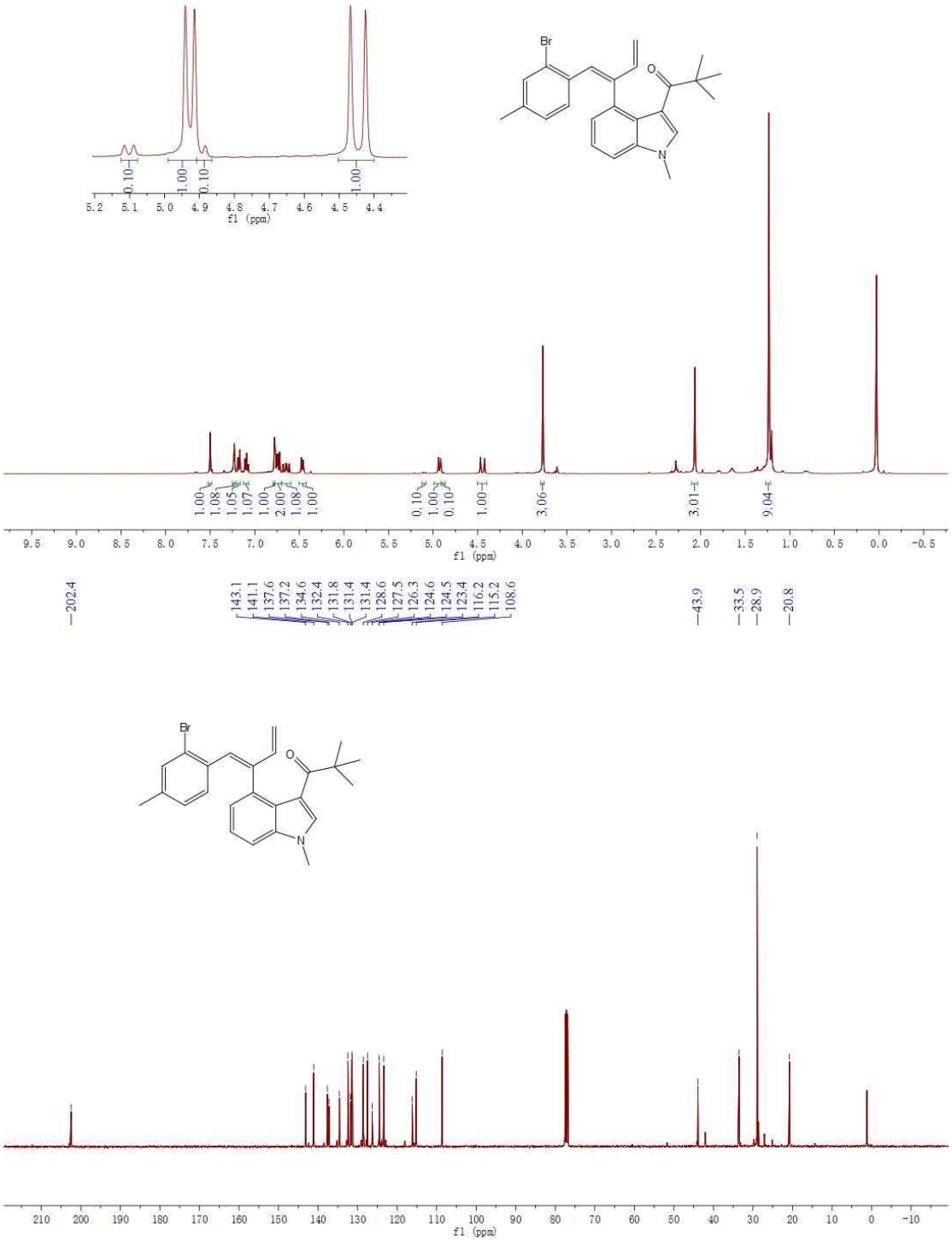

-114.49
F
O
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

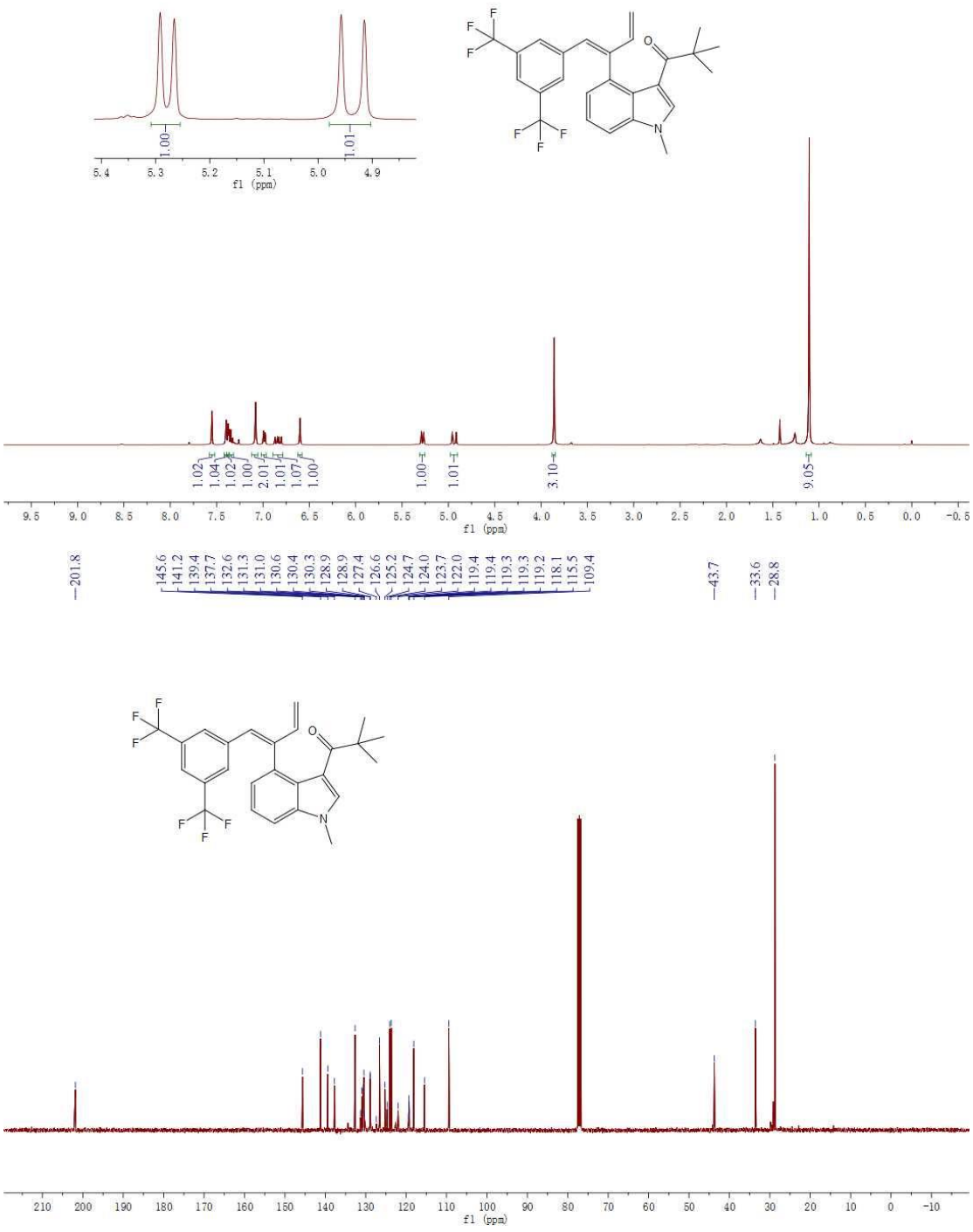

F
O
N
0.07
1.00
0.07
1.00
5.2 5.1 5.0 4.9 4.8 4.7 4.6
f1 (ppm)
1.03
1.09
1.06
3.04
1.00
1.06
1.01
1.00
0.07
1.00
0.07
1.00
3.07
9.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

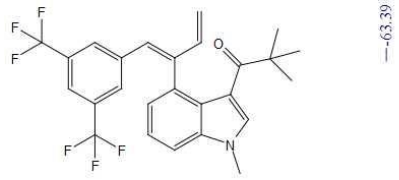

202.5
162.1
159.6
143.3
141.7
137.4
131.7
131.5
130.4
130.4
127.8
127.7
125.8
125.4
125.3
124.2
123.4
123.3
123.2
121.3
121.2
116.0
115.6
114.9
114.6
108.8
43.9
33.5
28.8
F
O
N
f1 (ppm)


-117.01
F
O
N
f1 (ppm)

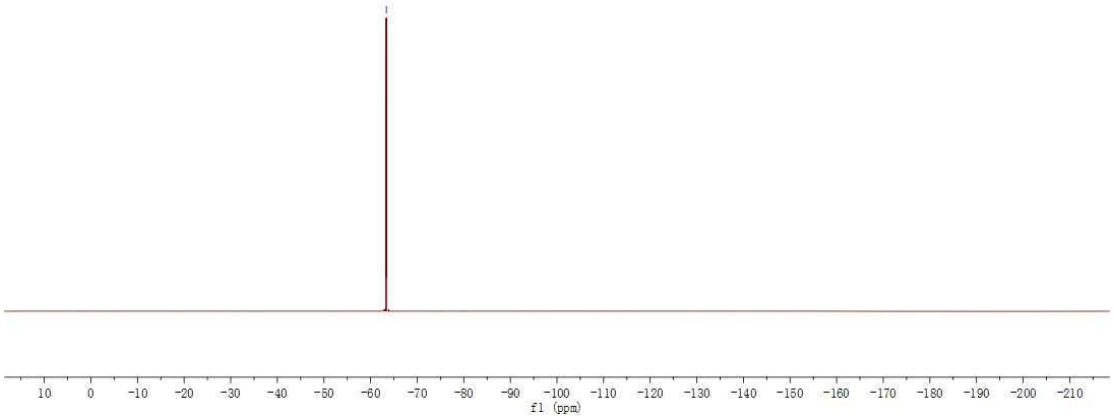

Cl
Cl
O
N
1.00
1.00
5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3
f1 (ppm)
1.04
2.08
1.02
3.01
2.08
1.00
1.00
3.05
9.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
202.5
144.6
140.8
137.3
134.7
134.5
132.3
132.1
131.7
131.4
128.6
126.3
124.9
124.4
123.5
116.2
116.1
108.9
43.9
33.5
28.9
Cl
Cl
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

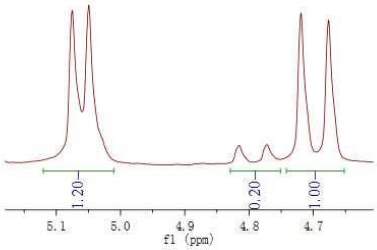

Br
O
N
0.10
1.00
0.10
1.00
f1 (ppm)
1.00
1.08
1.05
1.07
1.00
2.00
1.08
1.00
0.10
1.00
0.10
1.00
3.06
3.01
9.04
f1 (ppm)
202.4
143.1
141.1
137.6
137.2
134.6
132.4
131.8
131.4
131.4
128.6
127.5
126.3
124.6
124.5
123.4
116.2
115.2
108.6
43.9
33.5
28.9
20.8
Br
O
N
f1 (ppm)

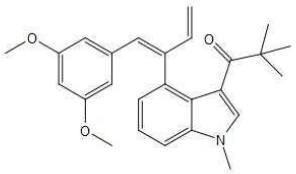

1.00
1.01
5.4 5.3 5.2 5.1 5.0 4.9
f1 (ppm)
F
F
F
F
F
O
N
1.02 1.04 1.02 1.00 2.01 1.01 1.07 1.00 1.00 1.01 3.10 9.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
201.8
145.6 141.2 139.4 137.7 132.6 131.3 131.0 130.6 130.4 130.3 128.9 128.9 127.4 126.6 125.2 124.7 124.0 123.7 122.0 119.4 119.4 119.3 119.3 119.2 118.1 115.5 109.4
43.7
33.6
28.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
F
F
F
F
O
N

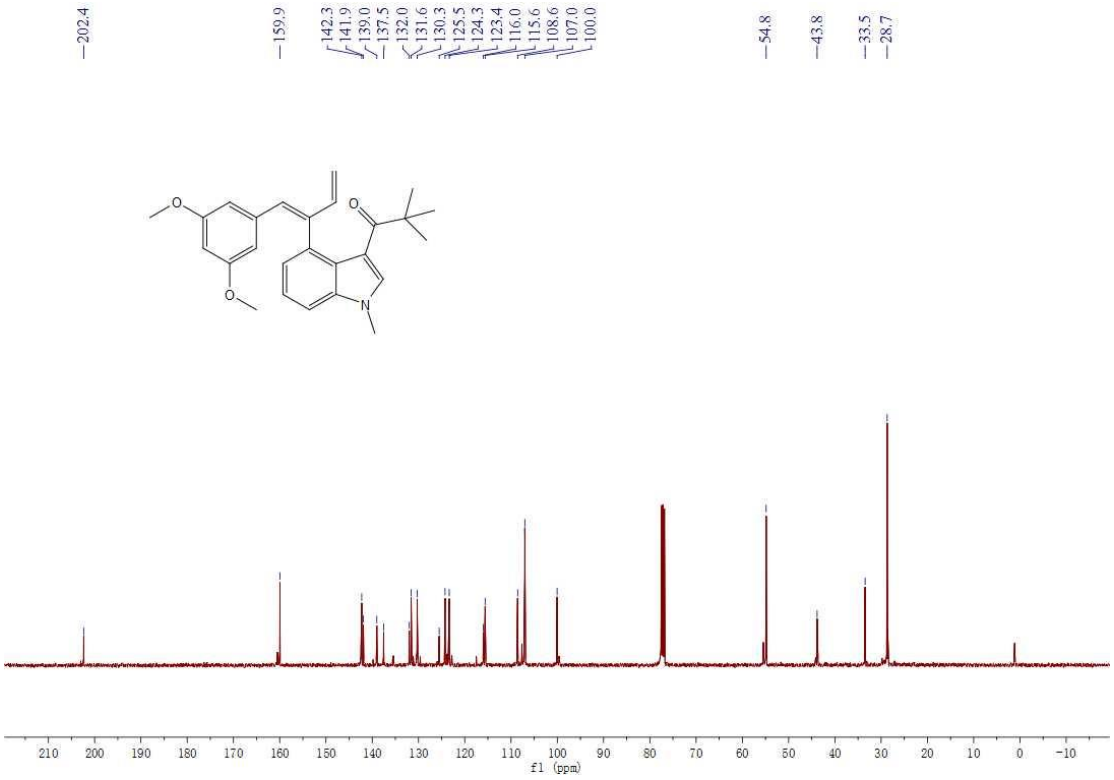
-63.39

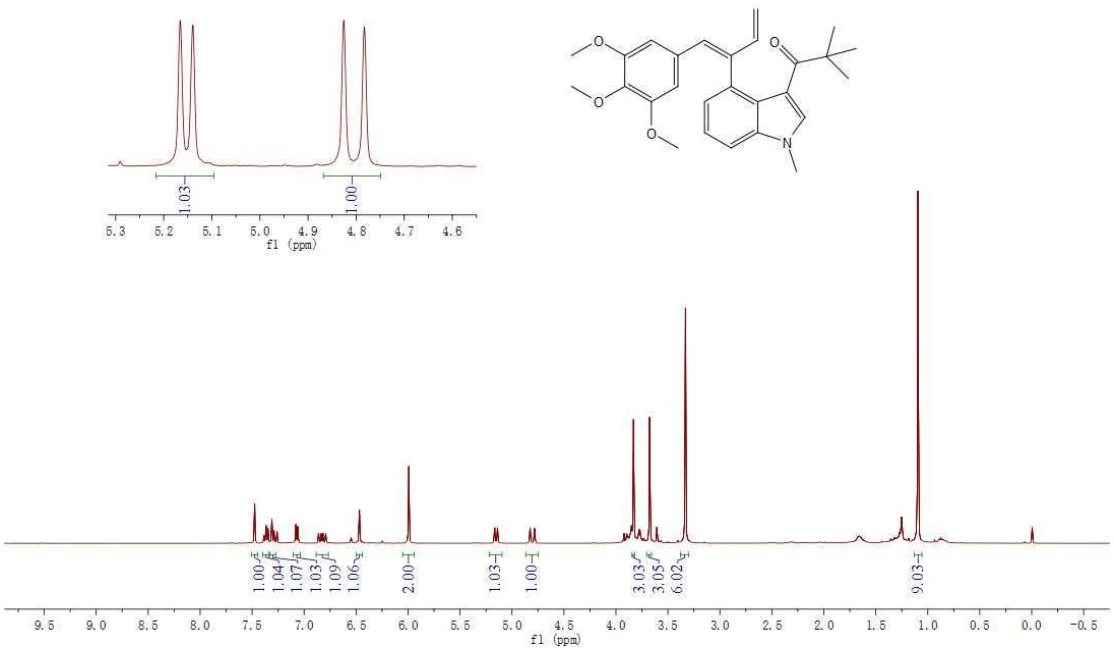

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

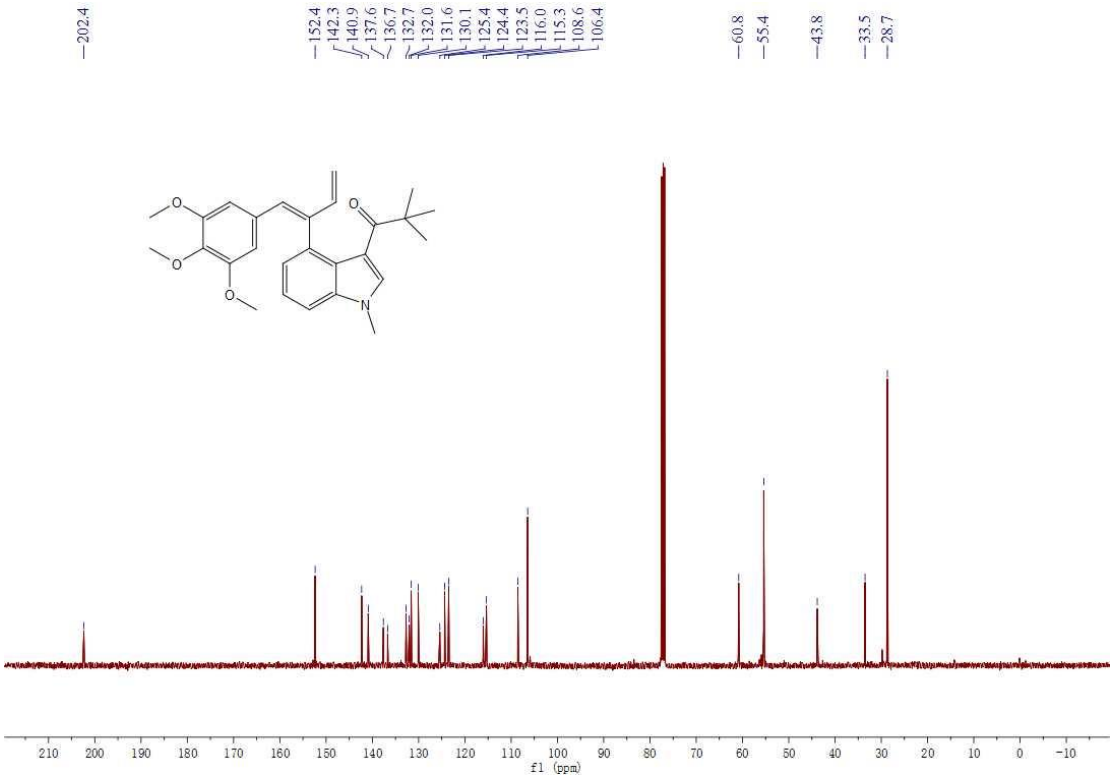

1.20
0.20
1.00
5.1 5.0 4.9 4.8 4.7
f1 (ppm)

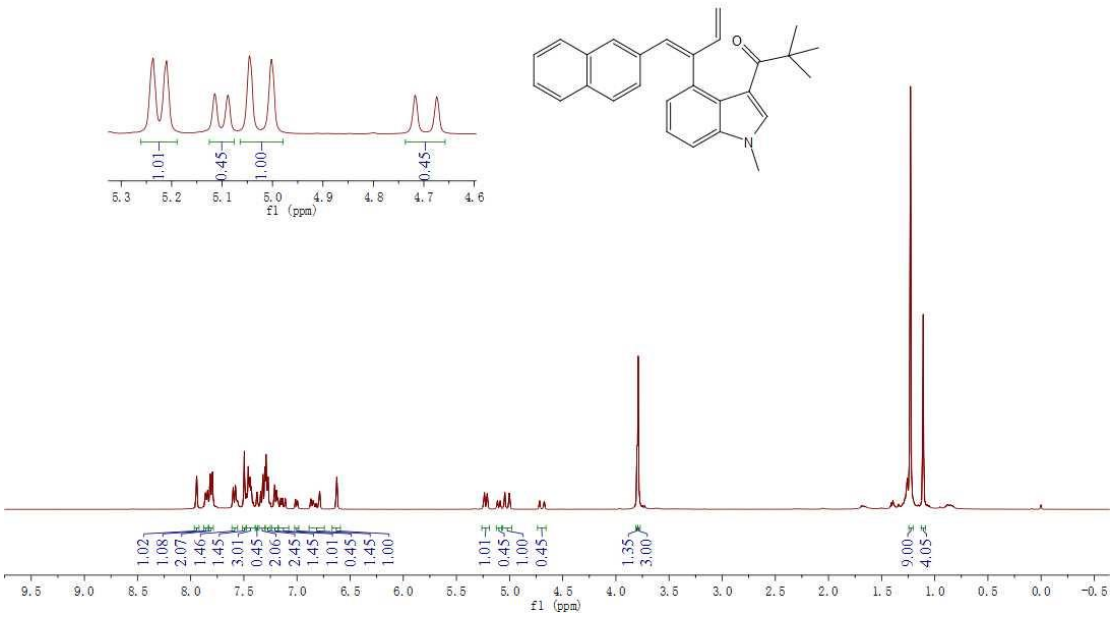

O
O
O
N

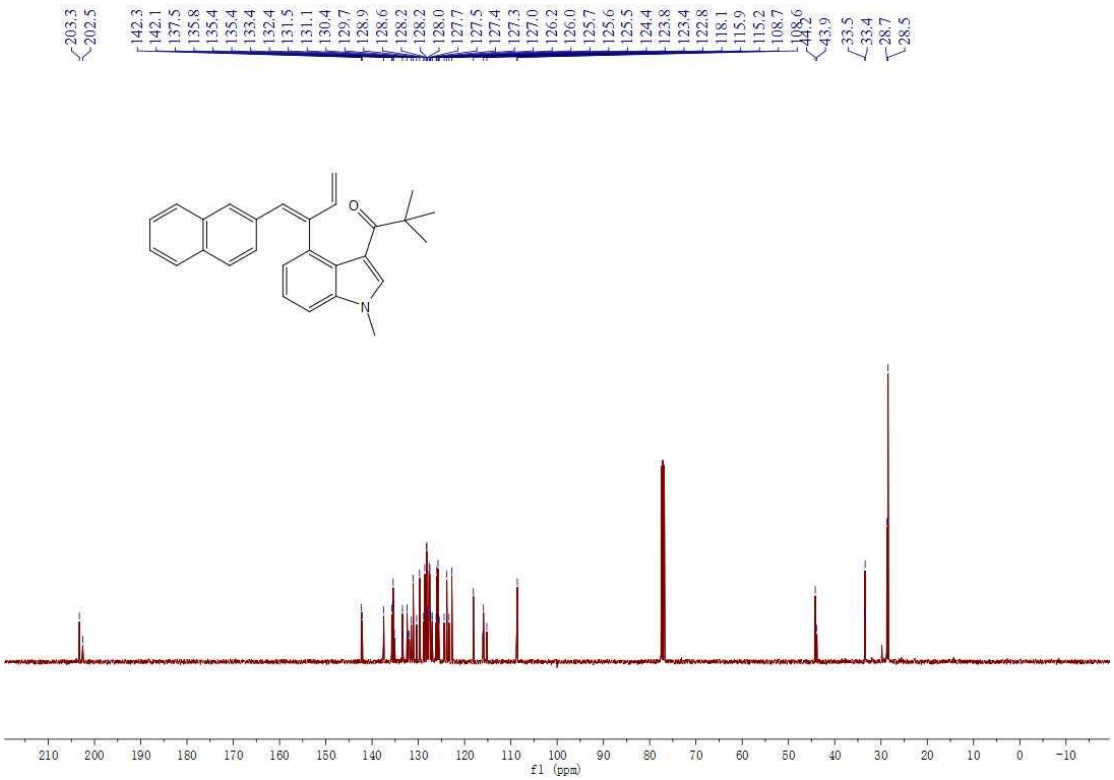
0.21 1.00 1.21 1.05 0.20 0.21 1.06 1.20 0.40 1.03 0.20 0.20 1.01 2.01
1.20 0.20 1.00
3.63
7.20
1.81
9.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

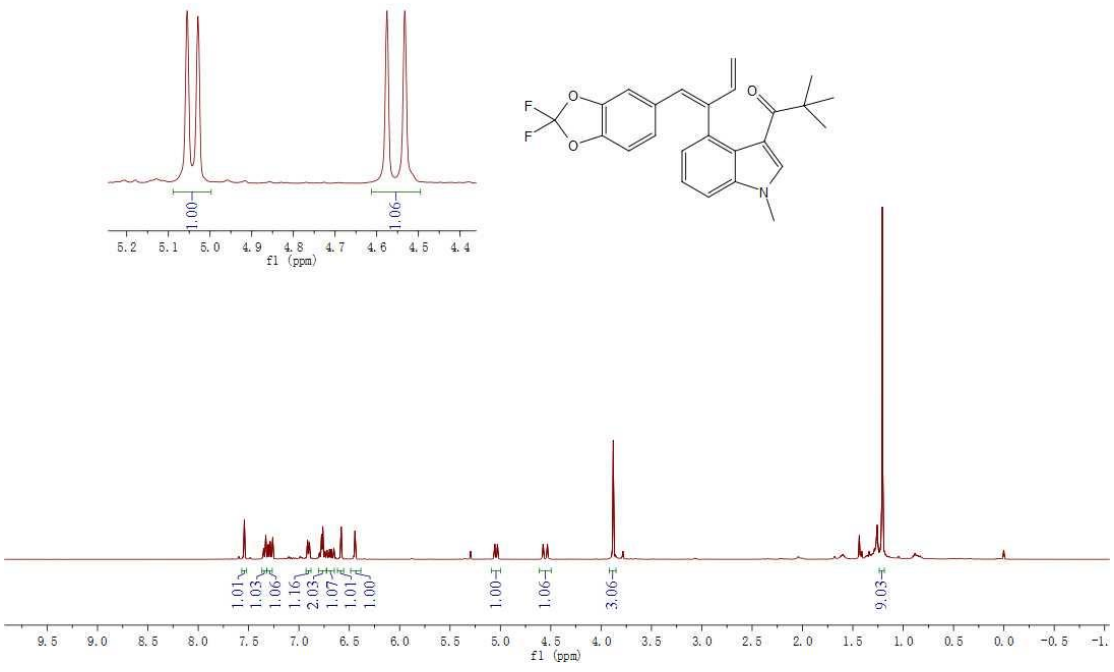

202.4
159.9
142.3
141.9
139.0
137.5
132.0
131.6
130.3
125.5
124.3
123.4
116.0
115.6
108.6
107.0
100.0
54.8
43.8
33.5
28.7
f1 (ppm)

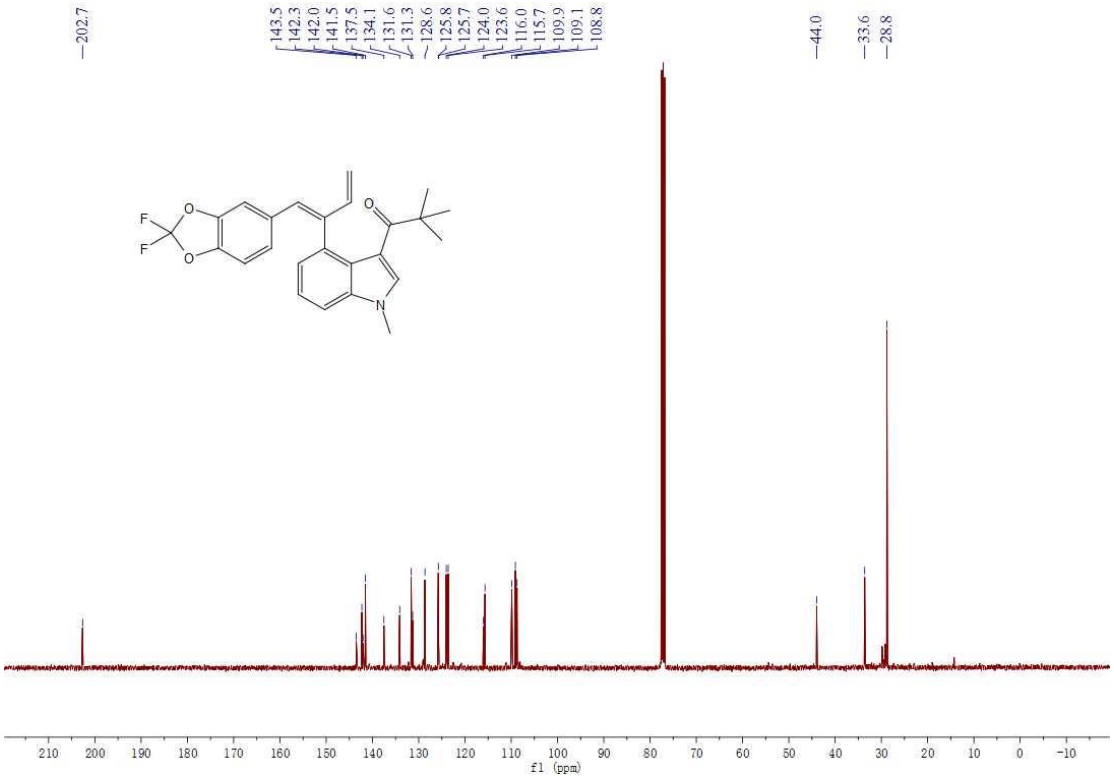

1.03
1.00
f1 (ppm)
1.00
1.04
1.07
1.03
1.09
1.06
2.00
1.03
1.00
3.03
3.05
6.02
9.03
f1 (ppm)

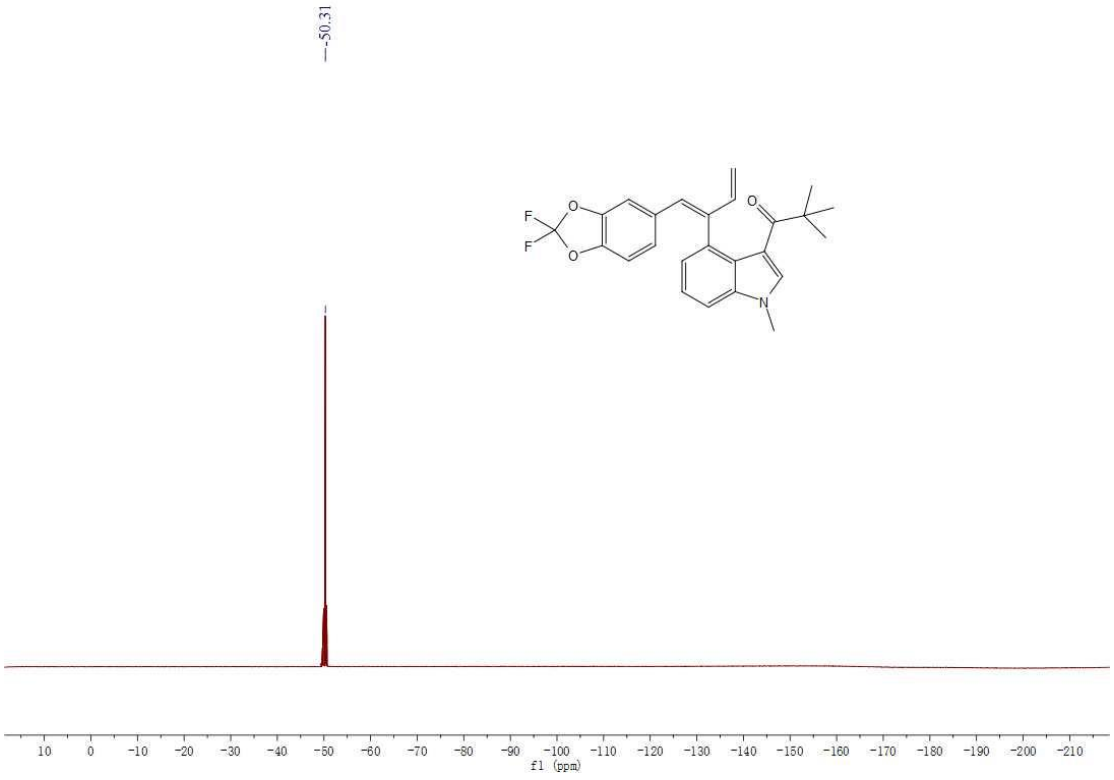

202.4
152.4
142.3
140.9
137.6
136.7
132.7
132.0
131.6
130.1
125.4
124.4
123.5
116.0
115.3
108.6
106.4
60.8
55.4
43.8
33.5
28.7
O
O
O
O
N
f1 (ppm)

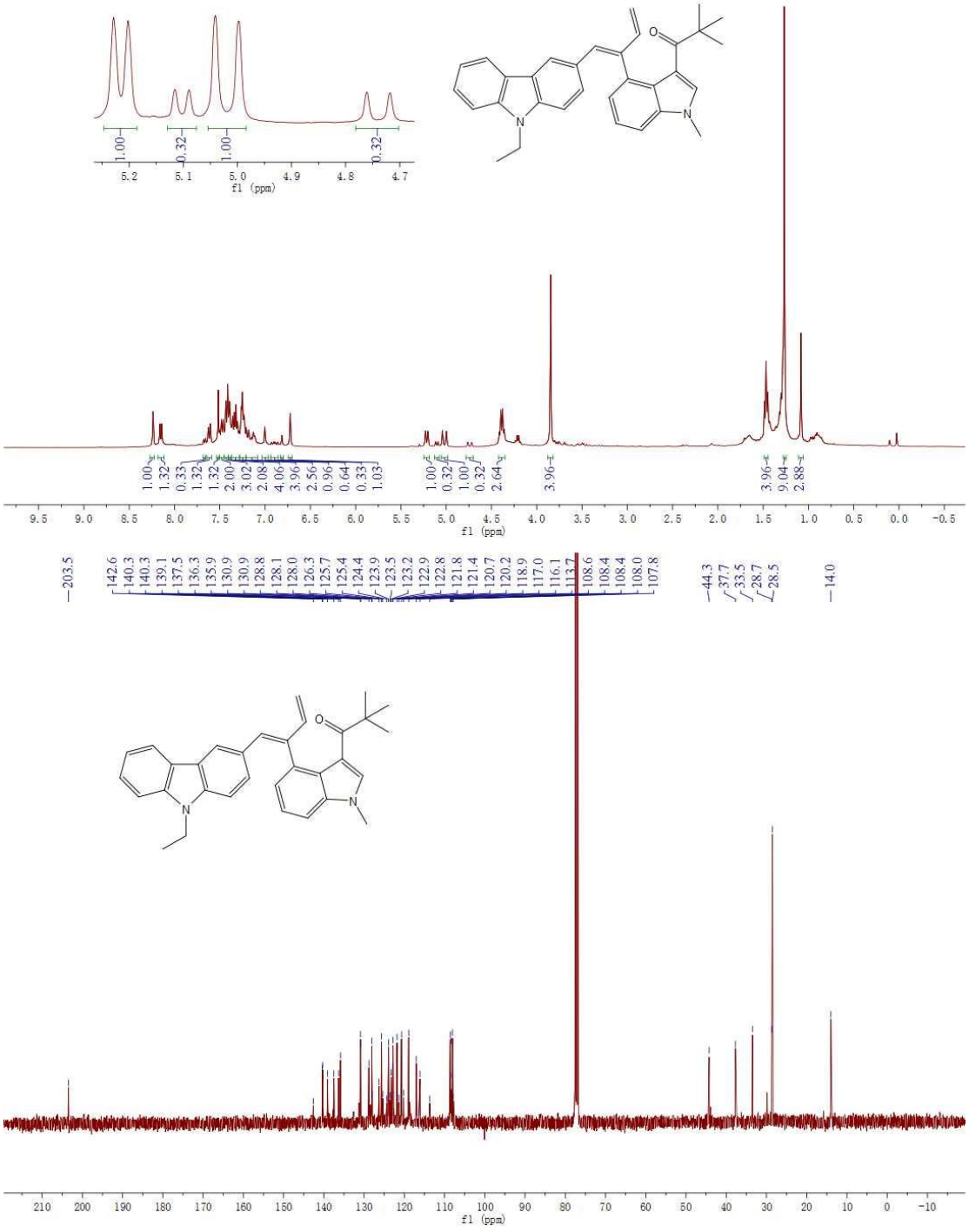

1.01
0.45
1.00
0.45
f1 (ppm)
O
N
1.02
1.08
2.07
1.46
1.45
3.01
0.45
2.06
2.45
1.45
1.01
0.45
1.45
1.00
1.01
0.45
1.00
0.45
1.35
3.00
9.00
4.05
f1 (ppm)

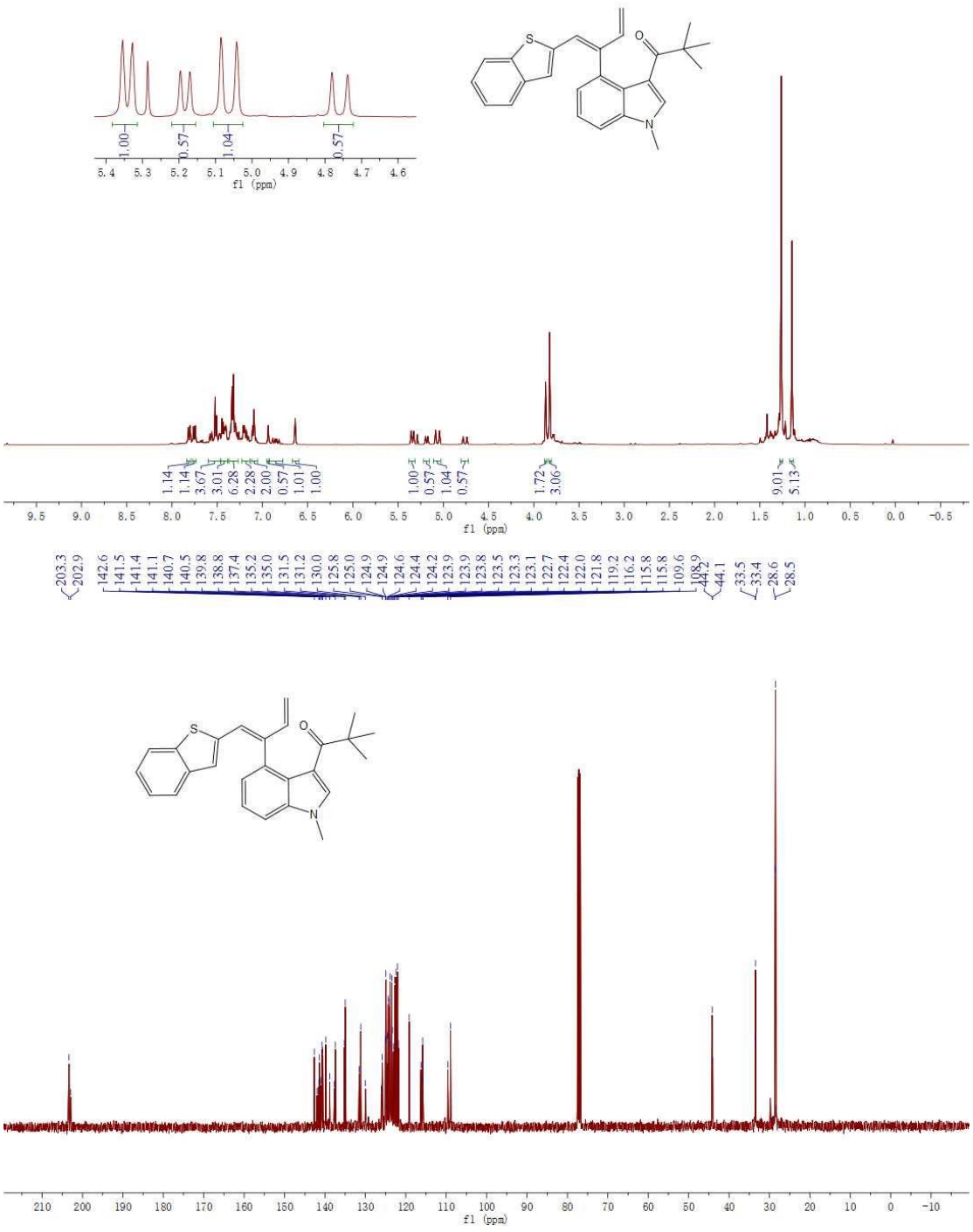

203.3
202.5
142.3
142.1
137.5
135.8
135.4
135.4
133.4
132.4
131.5
131.1
130.4
129.7
128.9
128.6
128.2
128.2
128.0
127.7
127.5
127.4
127.3
127.0
126.2
126.0
125.7
125.6
125.5
124.4
123.8
123.4
122.8
118.1
115.9
115.2
108.7
108.6
44.2
43.9
33.5
33.4
28.7
28.5
O
N
f1 (ppm)

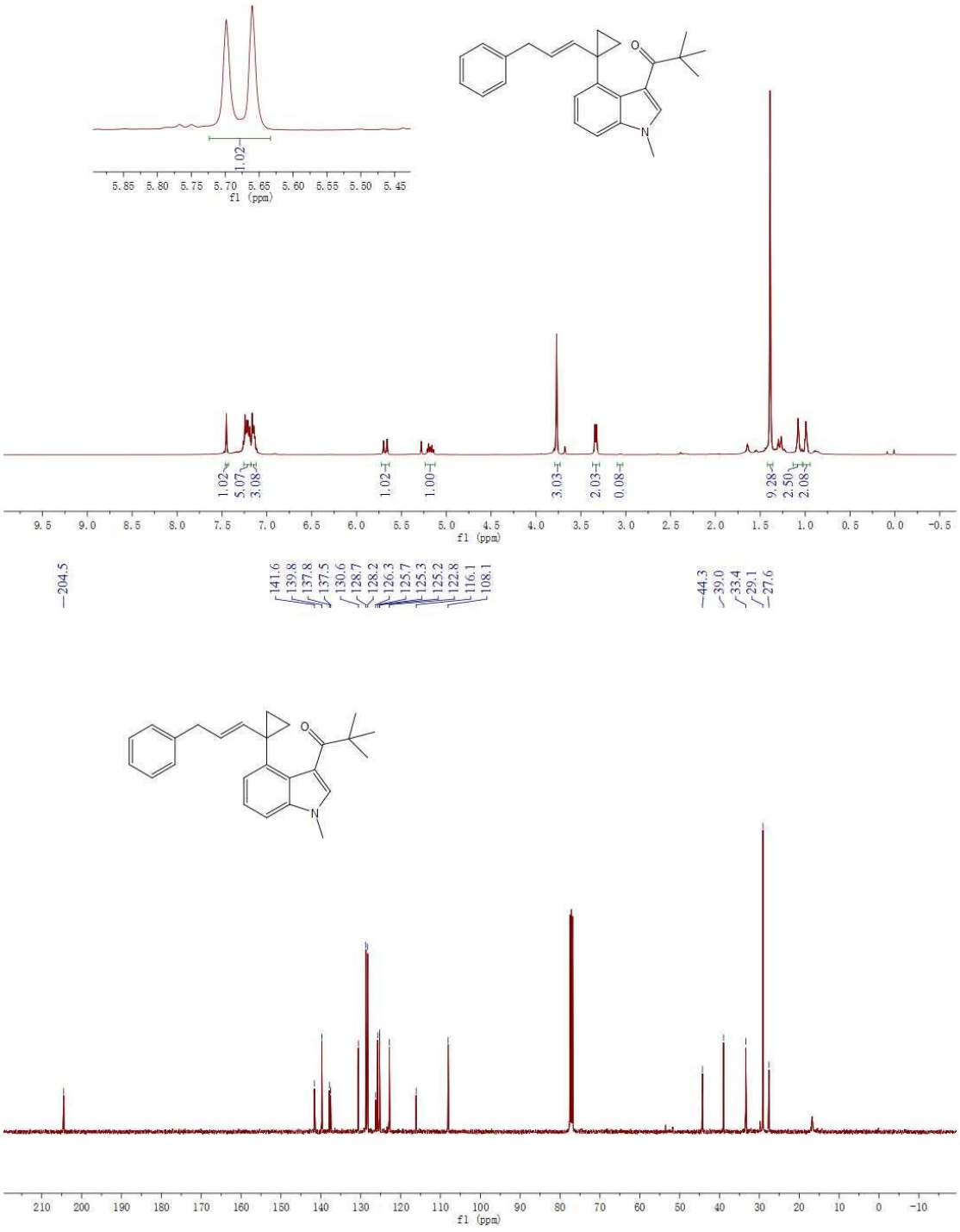

1.00
1.06
f1 (ppm)
F
F
O
O
O
N
1.01
1.03
1.06
1.16
2.03
1.07
1.01
1.00
1.00
1.06
3.06
9.03
f1 (ppm)

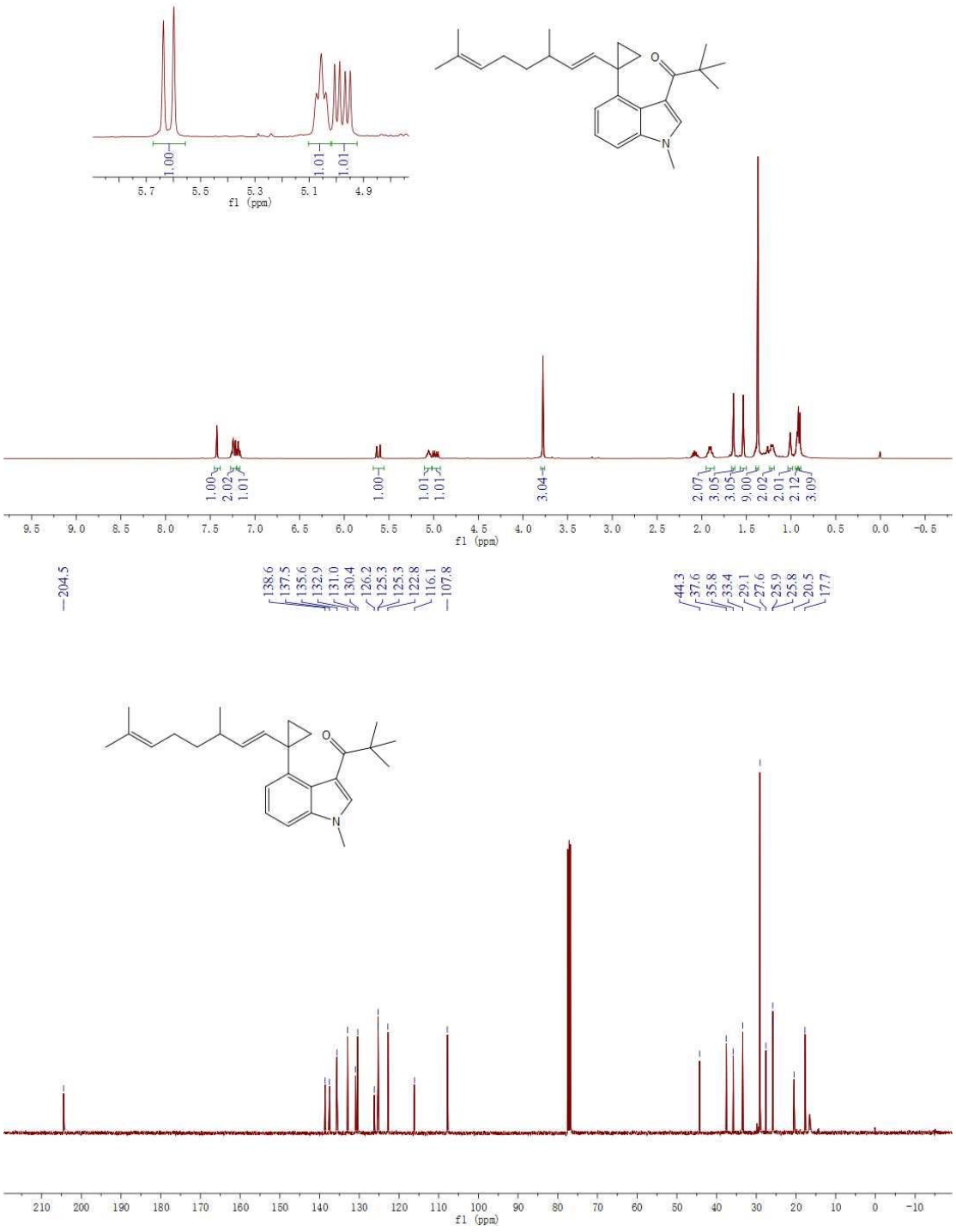

202.7
143.5
142.3
142.0
141.5
137.5
134.1
131.6
131.3
128.6
125.8
125.7
124.0
123.6
116.0
115.7
109.9
109.1
108.8
44.0
33.6
28.8
F
F
O
O
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

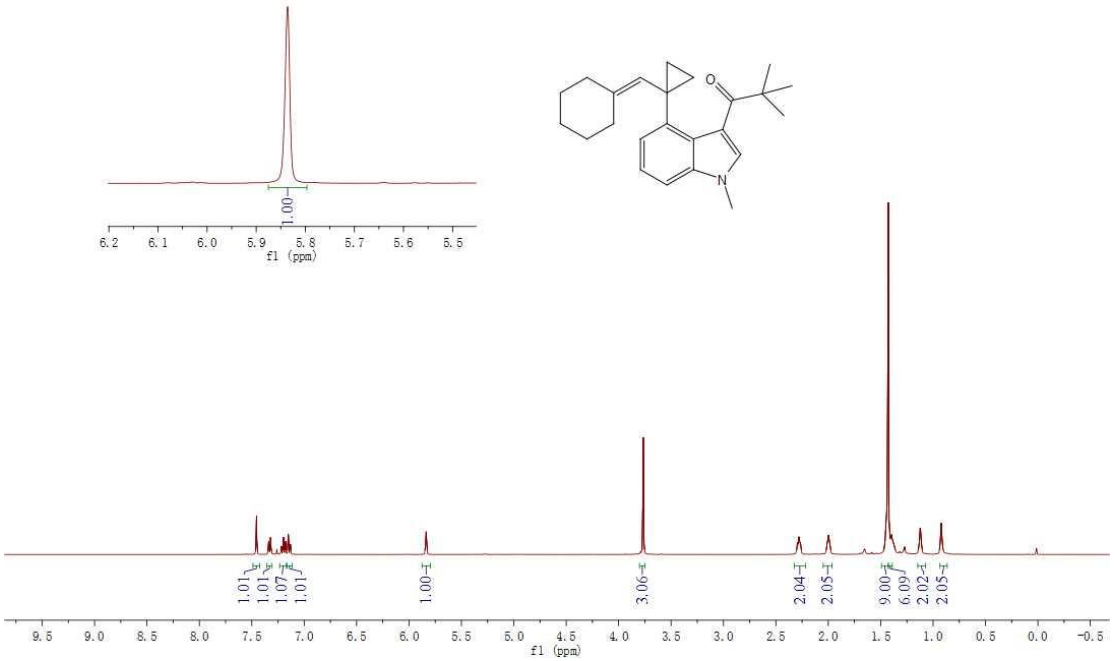

-50.31
F
F
O
O
O
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

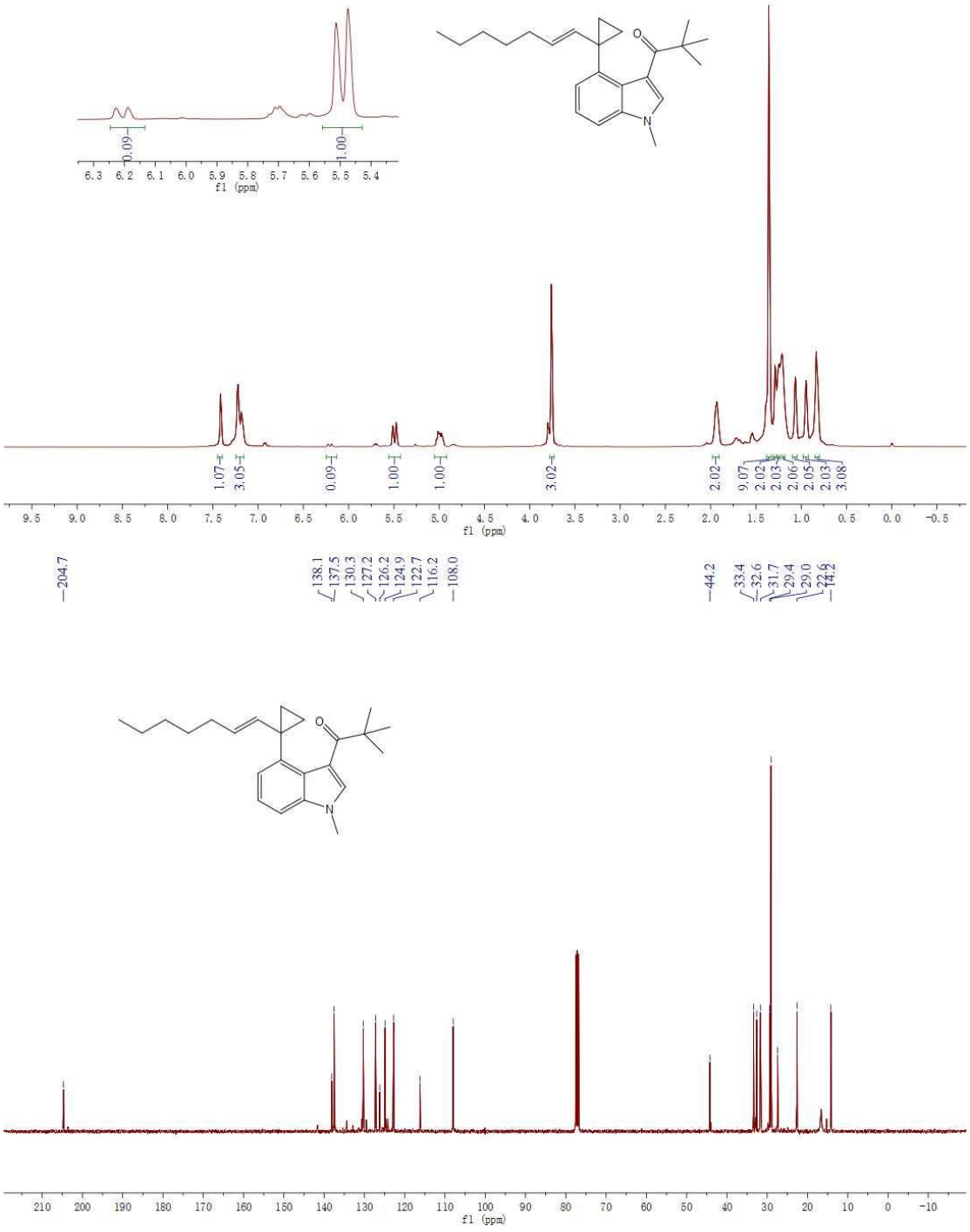

1.00
0.32
1.00
0.32
5.2
5.1
5.0
4.9
4.8
4.7
f1 (ppm)
O
N
N
1.00
1.32
0.33
1.32
2.00
3.02
2.08
4.06
3.96
2.56
0.96
0.64
0.33
1.03
1.00
0.32
1.00
0.32
2.64
3.96
3.96
9.04
2.88
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
203.5
142.6
140.3
140.3
139.1
137.5
136.3
135.9
130.9
130.9
128.8
128.1
128.0
126.3
125.7
125.4
124.4
123.9
123.5
123.2
122.9
122.8
121.8
121.4
120.7
120.2
118.9
117.0
116.1
113.7
108.6
108.4
108.4
108.0
107.8
44.3
37.7
33.5
28.7
28.5
14.0
O
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

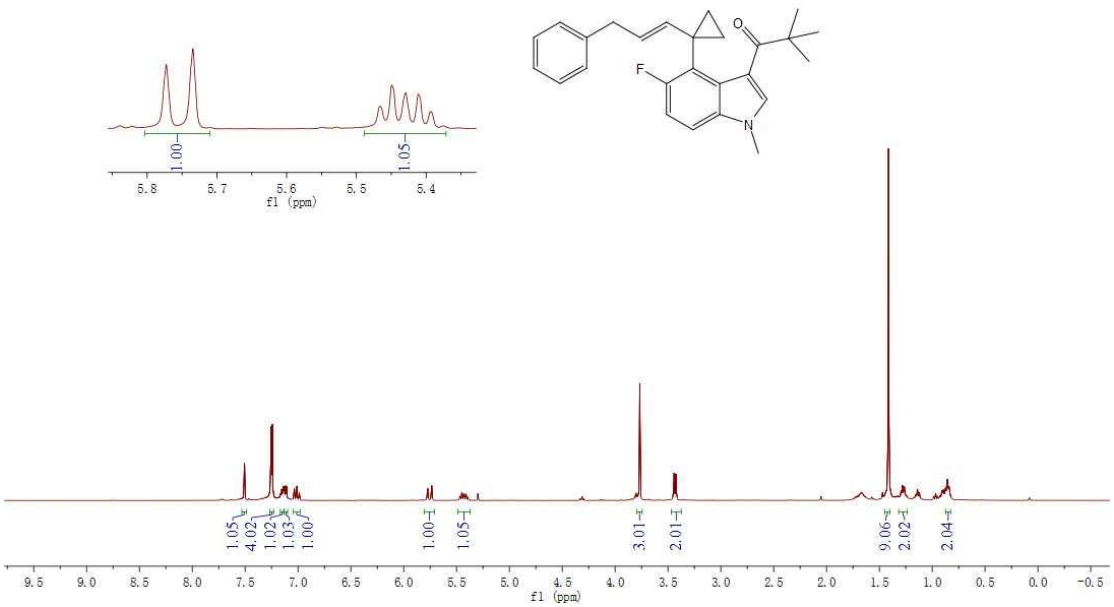

1.00
0.57
1.04
0.57
f1 (ppm)
S
O
N
1.14
1.14
3.67
3.01
6.28
2.28
2.00
0.57
1.01
1.00
1.00
0.57
1.04
0.57
1.72
3.06
9.01
5.13
f1 (ppm)
203.3
202.9
142.6
141.5
141.4
141.1
140.7
140.5
139.8
138.8
137.4
135.2
135.0
131.5
131.2
130.0
125.8
125.0
124.9
124.9
124.6
124.4
124.2
123.9
123.9
123.8
123.5
123.3
123.1
122.7
122.4
122.0
121.8
119.2
116.2
115.8
115.8
109.6
108.9
44.2
44.1
33.5
33.4
28.6
28.5
S
O
N
f1 (ppm)

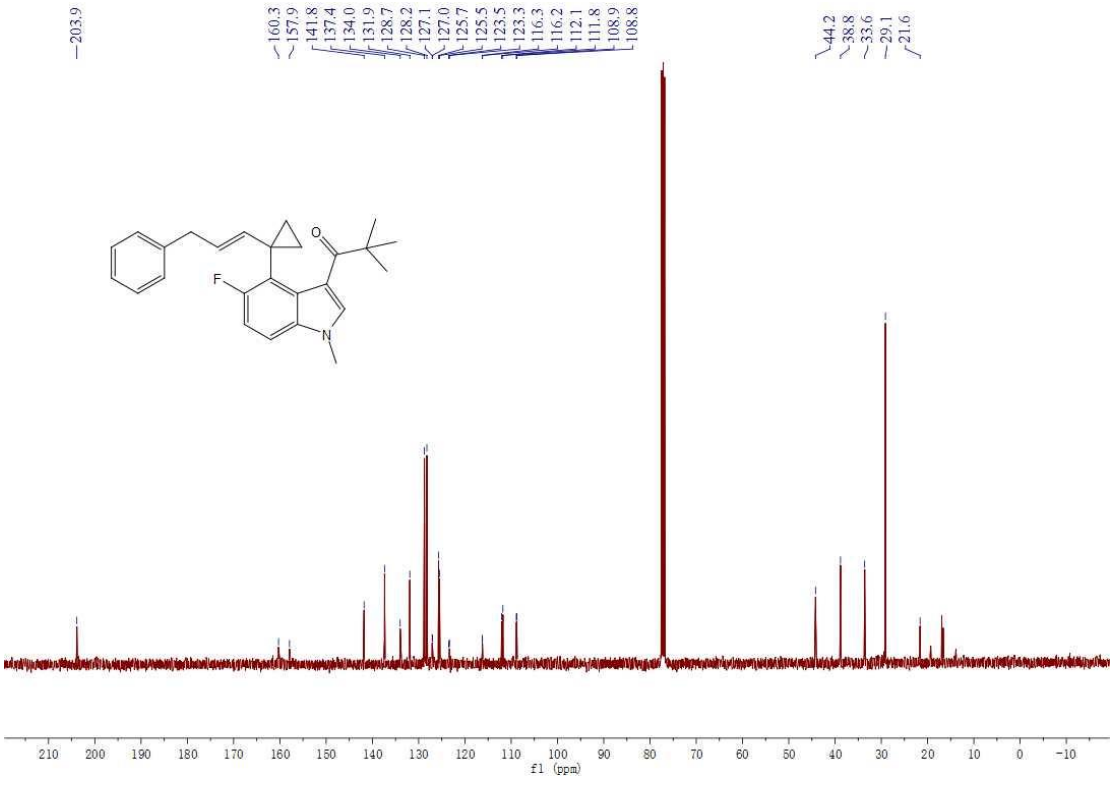

1.02
5.85 5.80 5.75 5.70 5.65 5.60 5.55 5.50 5.45
f1 (ppm)
O
N
1.02
5.07
3.08
1.02
1.00
3.03
2.03
0.08
9.28
2.50
2.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
204.5
141.6
139.8
137.8
137.5
130.6
128.7
128.2
126.3
125.7
125.3
125.2
122.8
116.1
108.1
44.3
39.0
33.4
29.1
27.6
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

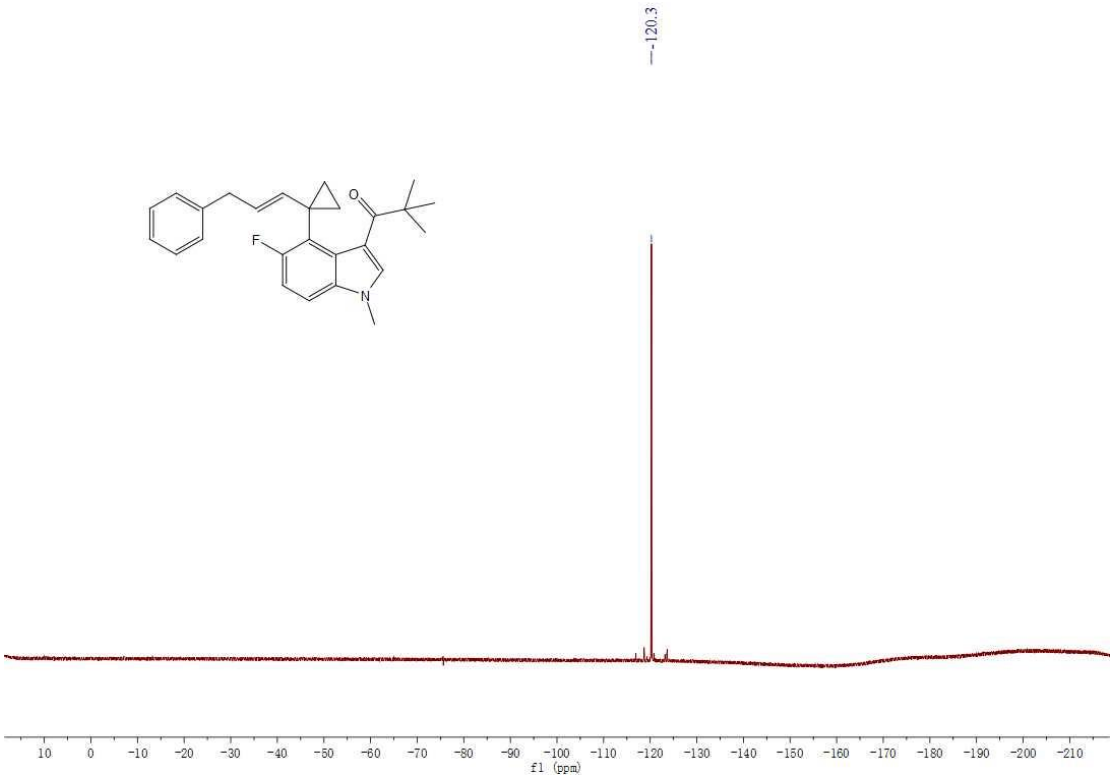

1.00
1.01
1.01
5.7
5.5
5.3
5.1
4.9
f1 (ppm)
O
N
1.00
2.02
1.01
1.00
1.01
1.01
3.04
2.07
3.05
3.05
9.00
2.02
2.01
2.12
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
204.5
138.6
137.5
135.6
132.9
131.0
130.4
126.2
125.3
125.3
122.8
116.1
107.8
44.3
37.6
35.8
33.4
29.1
27.6
25.9
25.8
20.5
17.7
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

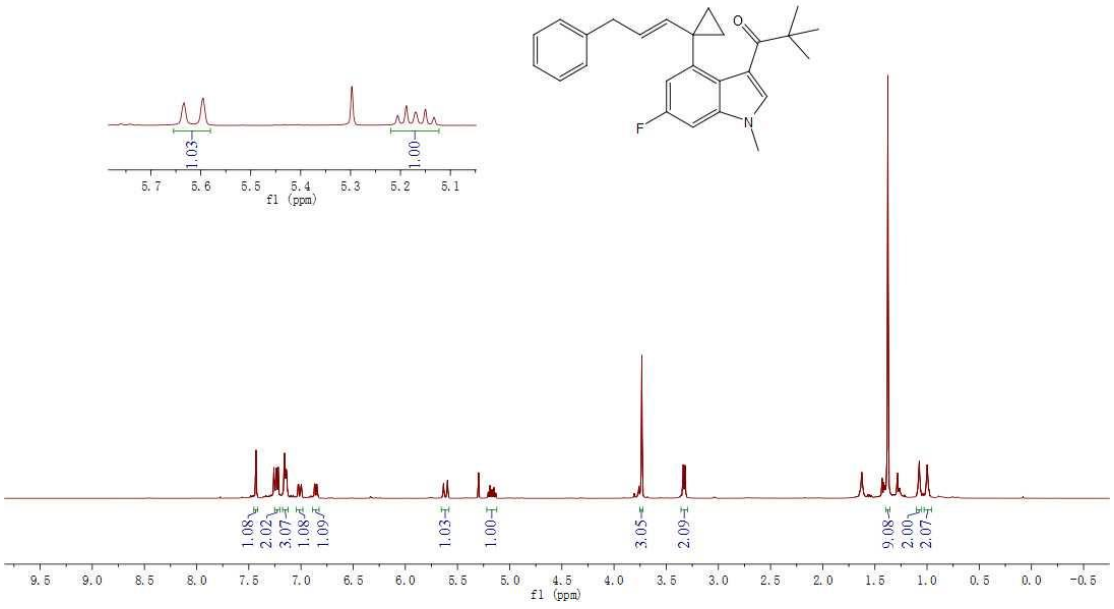

1.00
6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5
f1 (ppm)
O
N
1.01 1.01 1.07 1.01 1.00 3.06 2.04 2.05 9.00 6.09 2.02 2.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
205.0
142.3 140.5 137.6 130.3 126.6 125.8 122.8 116.4
107.6
44.3 37.1 33.4 29.8 29.1 28.6 27.3 26.8 23.9 16.4
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

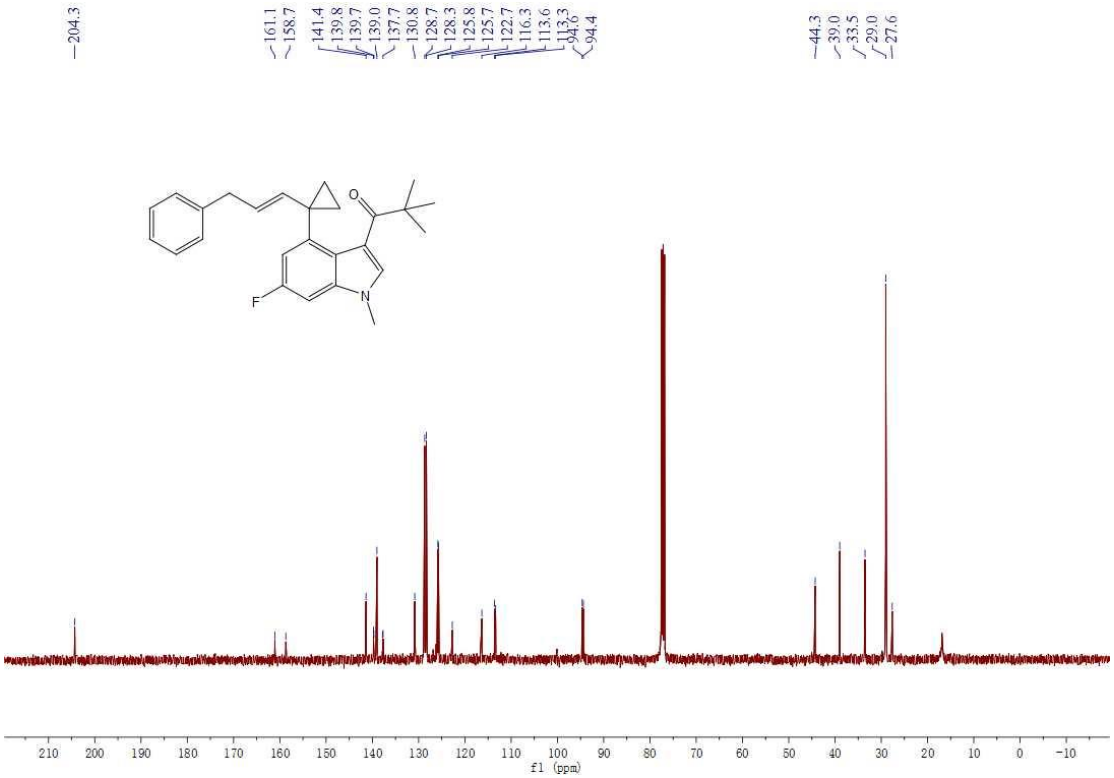

O
N
0.09
1.00
6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4
f1 (ppm)
1.07
3.05
0.09
1.00
1.00
3.02
2.02
9.07
2.02
2.03
2.06
2.05
2.03
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
204.7
138.1
137.5
130.3
127.2
126.2
124.9
122.7
116.2
108.0
44.2
33.4
32.6
31.7
29.4
29.0
24.6
14.2
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

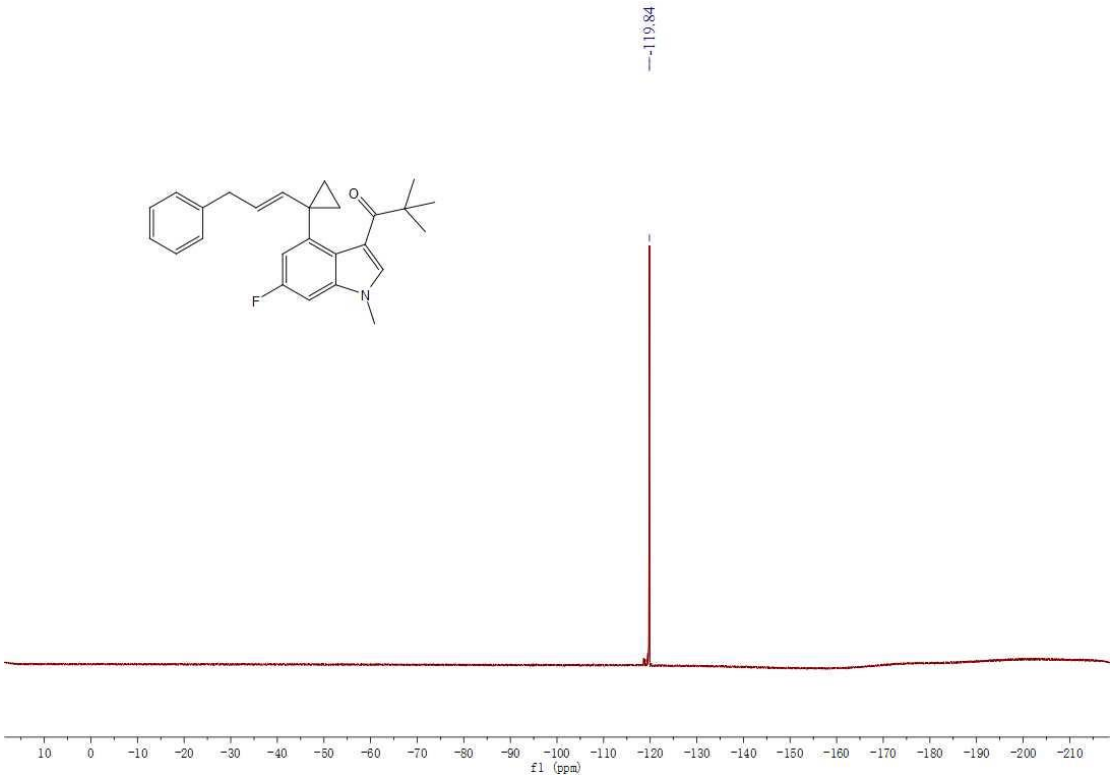

1.00
1.05
5.8
5.7
5.6
5.5
5.4
f1 (ppm)
O
F
N
1.05
4.02
1.02
1.03
1.00
1.00
1.05
3.01
2.01
9.06
2.02
2.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

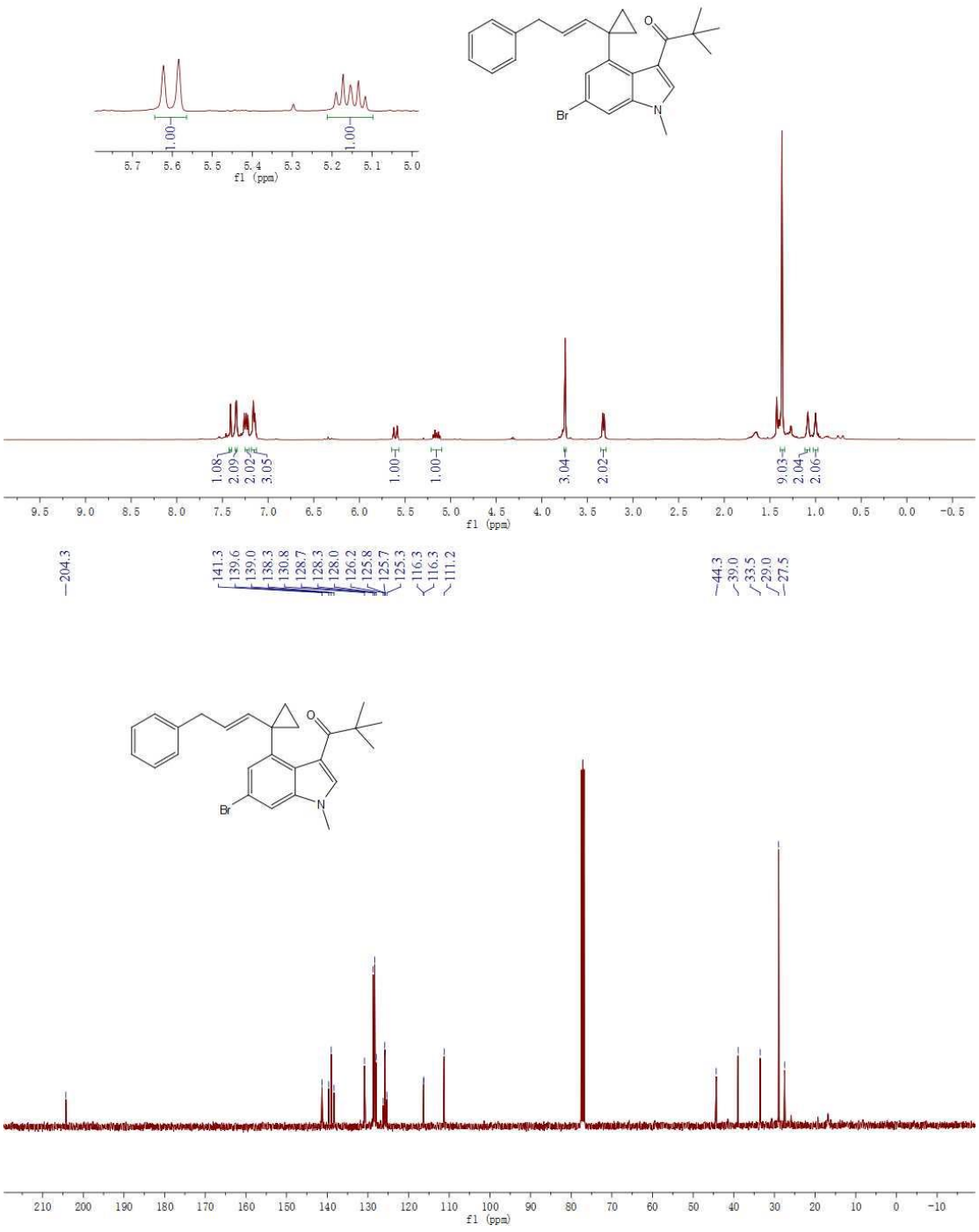

203.9
160.3
157.9
141.8
137.4
134.0
131.9
128.7
128.2
127.1
127.0
125.7
125.5
123.5
123.3
116.3
116.2
112.1
111.8
108.9
108.8
44.2
38.8
33.6
29.1
21.6
O
F
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

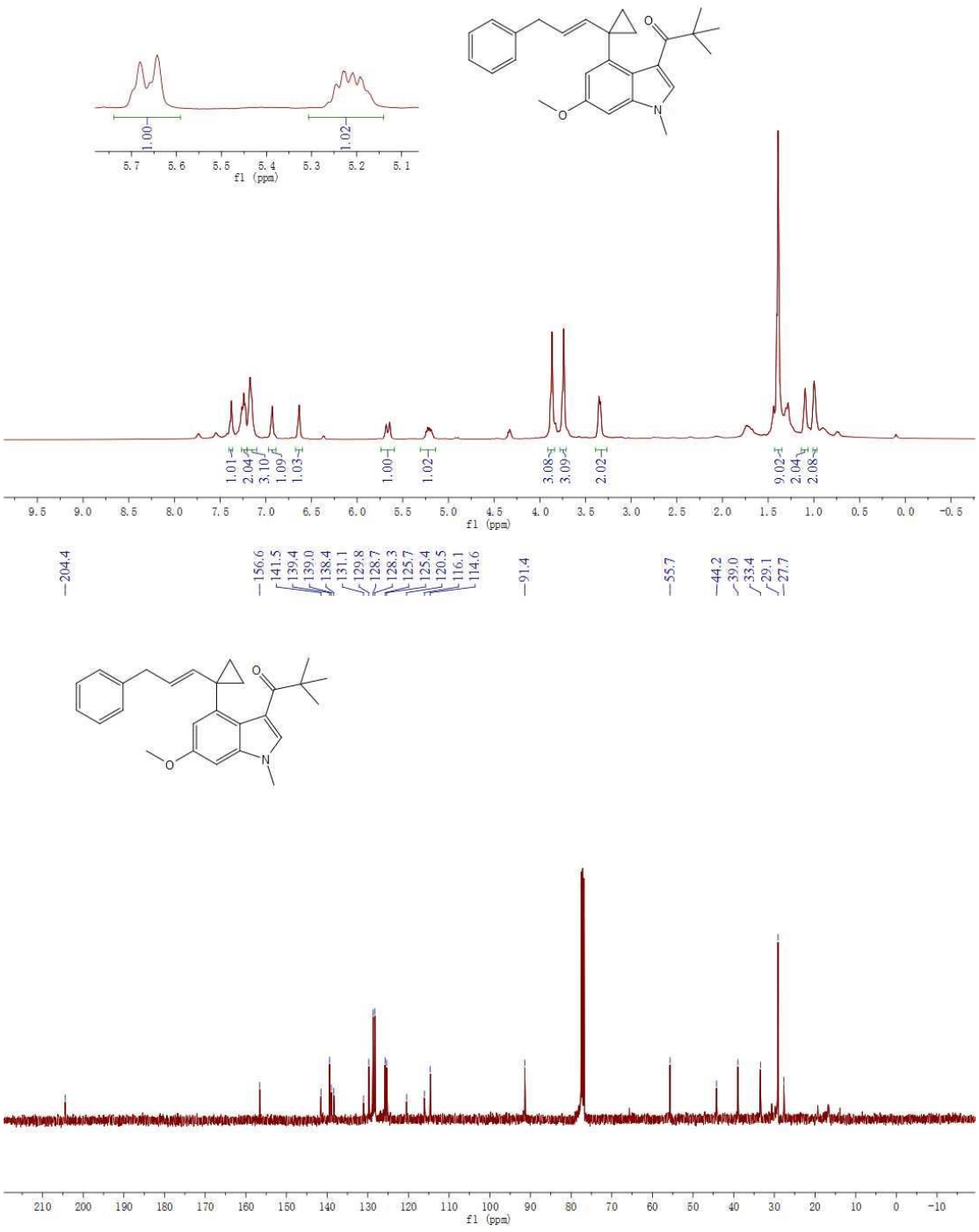

-120.3
O
F
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

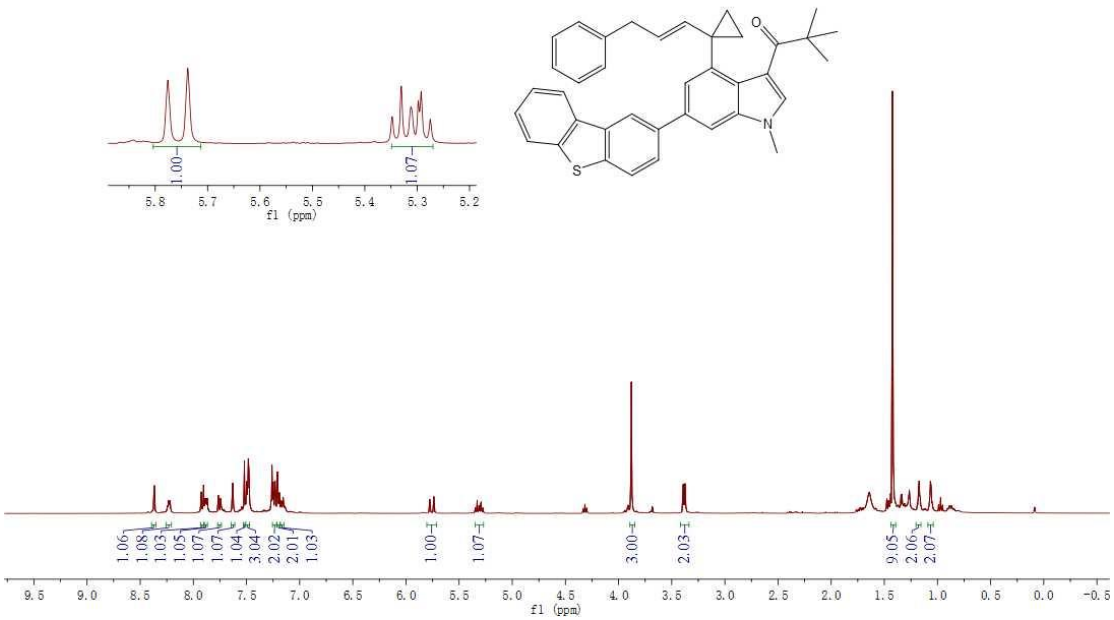

O
F
N
1.03
1.00
5.7 5.6 5.5 5.4 5.3 5.2 5.1
f1 (ppm)
1.08
2.02
3.07
1.08
1.09
1.03
1.00
3.05
2.09
9.08
2.00
2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

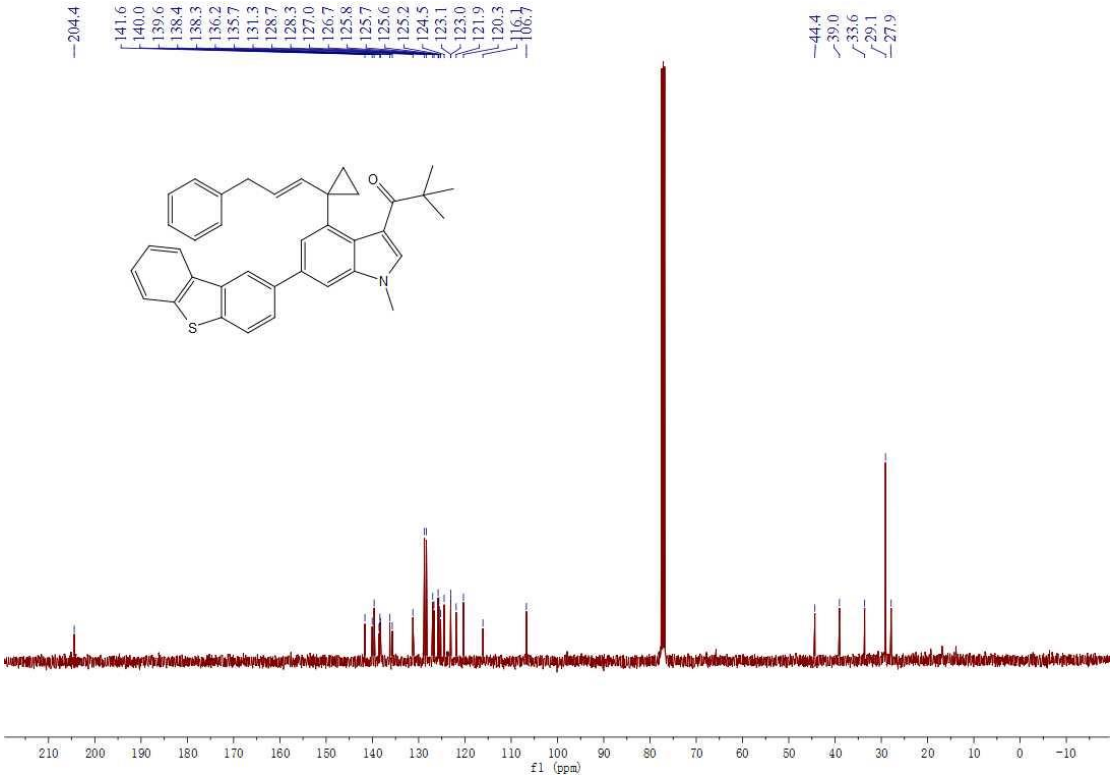

204.3
161.1
158.7
141.4
139.8
139.7
139.0
137.7
130.8
128.7
128.3
125.8
125.7
122.7
116.3
113.6
113.3
94.6
94.4
44.3
39.0
33.5
29.0
27.6
O
F
N
f1 (ppm)

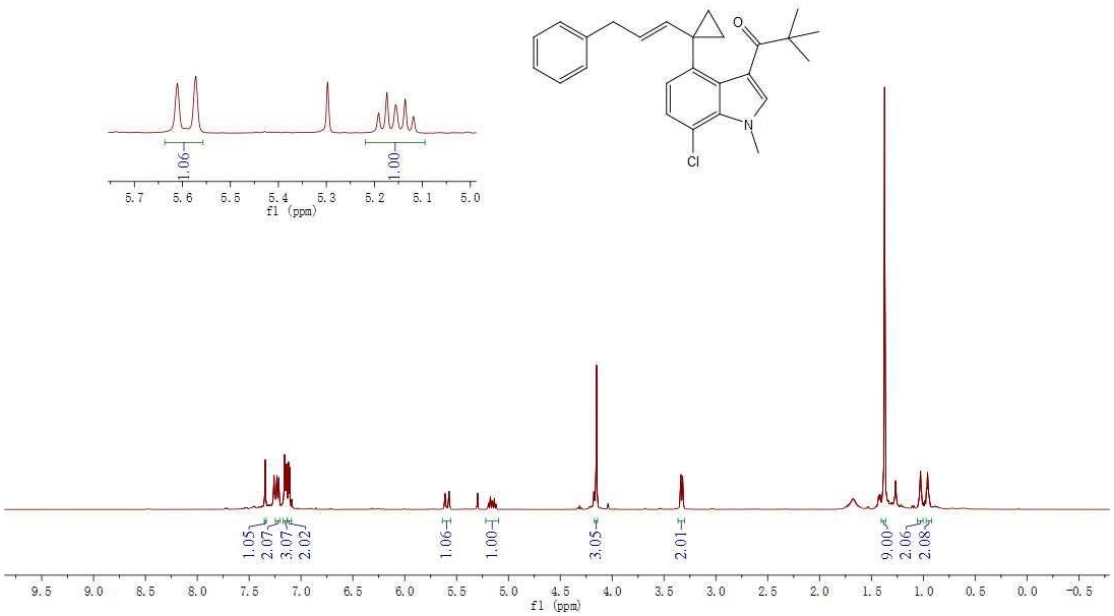

-119.84
O
F
N
f1 (ppm)

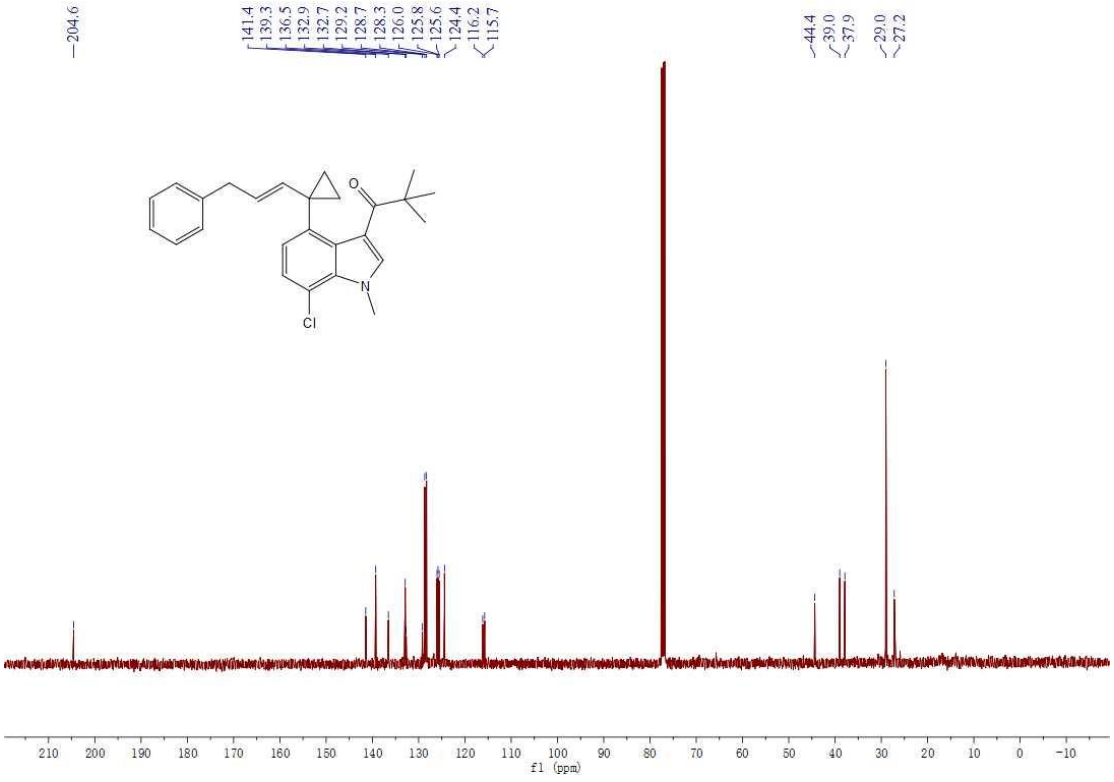

O
Br
N
1.00
1.00
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0
f1 (ppm)
1.08
2.09
2.02
3.05
1.00
1.00
3.04
2.02
9.03
2.04
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
204.3
141.3
139.6
139.0
138.3
130.8
128.7
128.3
128.0
126.2
125.8
125.7
125.3
116.3
116.3
111.2
44.3
39.0
33.5
29.0
27.5
O
Br
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1.00
1.02
5.7 5.6 5.5 5.4 5.3 5.2 5.1
f1 (ppm)
O
O
N
1.01
2.04
3.10
1.09
1.03
1.00
1.02
3.08
3.09
2.02
9.02
2.04
2.08
9.5 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 -0.5
f1 (ppm)
204.4
156.6
141.5
139.4
139.0
138.4
131.1
129.8
128.7
128.3
125.7
125.4
120.5
116.1
114.6
91.4
55.7
44.2
39.0
33.4
29.1
27.7
O
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1.00
1.07
5.8 5.7 5.6 5.5 5.4 5.3 5.2
f1 (ppm)
O
N
S
1.06 1.08 1.03 1.05 1.07 1.07 1.04 3.04 2.02 2.01 1.03 1.00 1.07 3.00 2.03 9.05 2.06 2.07
9.5 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 -0.5
f1 (ppm)


204.4
141.6 140.0 139.6 138.4 138.3 136.2 135.7 131.3 128.7 128.3 127.0 126.7 125.8 125.7 125.6 125.2 124.5 123.1 123.0 121.9 120.3 116.1 106.7
44.4 39.0 33.6 29.1 27.9
O
N
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1.06
1.00
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0
f1 (ppm)
O
N
Cl
1.05
2.07
3.07
2.02
1.06
1.00
3.05
2.01
9.00
2.06
2.08
9.5 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 -0.5
f1 (ppm)


204.6
141.4
139.3
136.5
132.9
132.7
129.2
128.7
128.3
126.0
125.8
125.6
124.4
116.2
115.7
44.4
39.0
37.9
29.0
27.2
O
N
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

9. Reference

[1] J. Lv, X. Chen, X.-S. Xue, B. Zhao, Y. Liang, M. Wang, L. Jin, Y. Yuan, Y. Han, Y. Zhao, Y. Lu, J. Zhao, W.-Y. Sun, K. N. Houk and Z. Shi, Metal-free directed sp^2-C-H borylation, *Nature*, 2019, **575**, 336-341.

[2] W. Ai, Y. Liu, Q. Wang, Z. Lu, Q, Liu, Cu-Catalyzed Redox-Neutral Ring Cleavage of Cycloketone O-Acyl Oximes: Chemodivergent Access to Distal Oxygenated Nitriles. *Org. Lett.* 2018, **20**, 409-412.