

Palladium-Catalyzed Heck Cyclization/Allylation with Homoallyl Alcohols via Retro-Allylation

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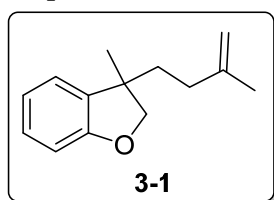
1. General remarks

The desired product was purified by flash column chromatography, silica gel (200~300 mesh). ^1H NMR spectra and ^{13}C NMR spectra were recorded on 400 MHz in CDCl_3 and TMS as internal standard. All products were further characterized by HRMS (high resolution mass spectra). Copies of their ^1H NMR and ^{13}C NMR spectra are provided. All solvents were dried and distilled according to standard procedures. Commercially available reagents and solvents were used without further purification. Compound **1** was synthesized according to the literature procedure.¹ For homoallyl alcohol **2** was prepared based on reported procedures and NMR data have matched to literatures.² All reactions were heated by oil bath. HRMS analysis of compounds was performed with a time-of-flight mass spectrometer (micrOTOF-Q, Bruker Daltonik, Germany).

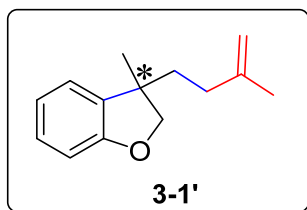
2. General procedure for the preparation of the products **3**

An oven-dried Schlenk tube under a nitrogen atmosphere was charged aryl iodide-tethered alkene **1** (0.3 mmol, 1.0 equiv) and homoallyl alcohol **2** (0.6 mmol, 2.0 equiv), $\text{Pd}_2(\text{dba})_3$ (5 mol %), $\text{P}(p\text{-Me-C}_6\text{H}_4)_3$ (20 mol%), Cs_2CO_3 (0.30 mmol, 1.5 equiv), toluene (1.5 mL). The mixture was stirred at 35 °C for 30 mins and then stirred at 110 °C for 24 h. The resulting mixture was cooled to room temperature and filtered through Celite eluting with EtOAc. The volatiles were evaporated under reduced pressure and the residue was purified by silica gel flash chromatography to afford the desired products **3**.

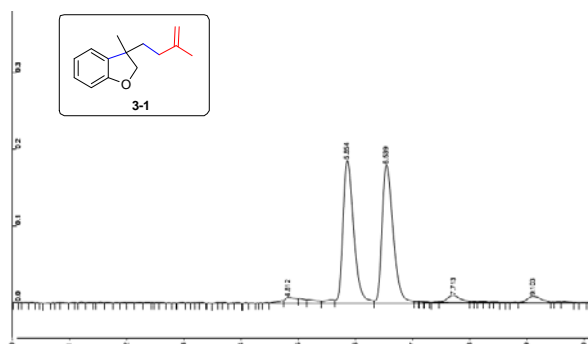
3. Spectral data of compound **3**



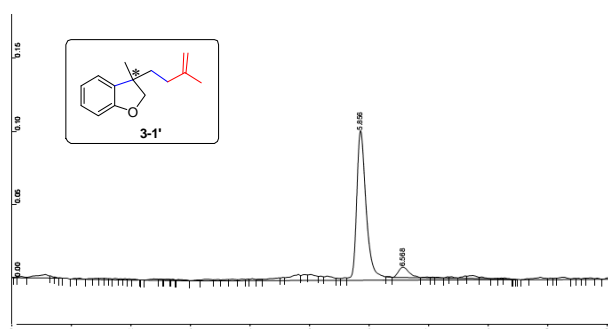
3-methyl-3-(3-methylbut-3-en-1-yl)-2,3-dihydrobenzofuran: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.08-7.00(m, 2H), 6.83-6.79(m, 1H), 6.71(d, $J=8.0\text{Hz}$, 1H), 4.59(d, $J=11.2\text{Hz}$, 2H), 4.30(d, $J=8.4\text{Hz}$, 1H), 4.10(d, $J=8.4\text{Hz}$, 1H), 2.01-1.92(m, 1H), 1.74-1.65(m, 3H), 1.61(s, 3H), 1.29(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 159.5, 145.7, 134.9, 128.0, 122.8, 120.5, 109.7, 109.6, 82.3, 45.1, 38.9, 32.7, 25.7, 22.7; MS (EI): m/z (%) 202 (75) $[\text{M}]^+$, 133(100), 105(100), 77(36).



The ee value (87% ee) of **3-1'** was determined by chiral HPLC analysis: OJ-H Column Column (254 mm); detected at 254 nm; n-hexane/i-propanol = 95/5; flow = 1 ml/min; Retention time: 5.8 min (major), 6.5 min (minor).

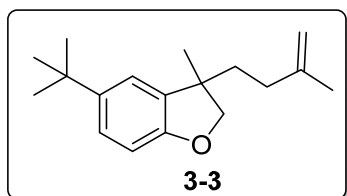


Peak No	Peak Name	Result (ug/ml)	Ret. Time (min)	Time Offset (min)	Width 1/2 (sec)	Area (counts)
1		1.8474	4.812	0.000	6.7	1012637
2		44.5376	5.854	0.000	11.7	24413510
3		48.2684	6.539	0.000	12.2	26458618
4		2.6898	7.713	0.000	0.0	1474435
5		2.6568	9.103	0.000	0.0	1456345
Totals		100.0000		0.000		54815564



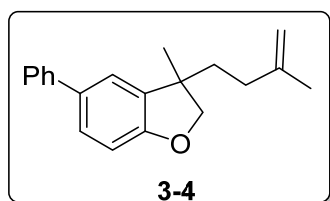
Peak No	Peak Name	Result (ug/ml)	Ret. Time (min)	Time Offset (min)	Width 1/2 (sec)	Area (counts)
1		93.6601	5.836	0.000	9.6	12793603
2		6.3399	6.568	0.000	0.0	866003
Totals		100.0000		0.000		13659606

3,5-dimethyl-3-(3-methylbut-3-en-1-yl)-2,3-dihydrobenzofuran: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 6.84(d, $J=8.0\text{Hz}$, 1H), 6.80(s, 1H), 6.60(d, $J=8.0\text{Hz}$, 1H), 4.59(d, $J=10.0\text{Hz}$, 2H), 4.27(d, $J=8.8\text{Hz}$, 1H), 4.07(d, $J=8.8\text{Hz}$, 1H), 2.22(s, 3H), 2.01-1.93(m, 1H), 1.76-1.64(m, 3H), 1.62(s, 3H), 1.27(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 157.4, 145.7, 135.0, 129.7, 128.4, 123.3, 109.6, 109.1, 82.4, 45.1, 38.8, 32.7, 25.5, 22.7, 20.9; MS (EI): m/z (%) 216 (87) $[\text{M}]^+$, 147(100), 119(100), 91(42).

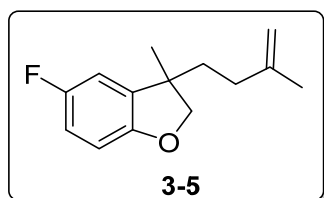


5-(tert-butyl)-3-methyl-3-(3-methylbut-3-en-1-yl)-2,3-dihydrobenzofuran: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.09-7.06(m, 1H), 7.01(d, $J=2.0\text{Hz}$, 1H), 6.63(d, $J=8.4\text{Hz}$, 1H), 4.58(d, $J=9.6\text{Hz}$, 2H), 4.28(d, $J=8.8\text{Hz}$, 1H), 4.08(d, $J=8.8\text{Hz}$, 1H), 2.02-1.95(m, 1H), 1.75-1.65(m, 3H),

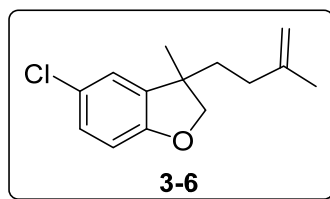
1.61(s, 3H), 1.28(s, 3H), 1.23(s, 9H); ^{13}C NMR(100MHz, CDCl_3) δ : 157.2, 145.8, 143.5, 134.6, 124.7, 119.6, 109.7, 108.6, 82.5, 45.3, 38.9, 34.3, 32.8, 31.7, 25.4, 22.6; HRMS(APCI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{27}\text{O}$ 259.2056; found 259.2057.



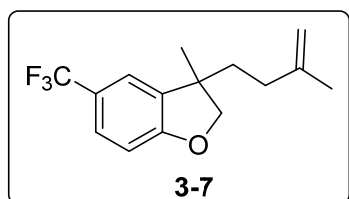
3-methyl-3-(3-methylbut-3-en-1-yl)-5-phenyl-2,3-dihydrobenzofuran: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.47-7.45(m, 2H), 7.33-7.27(m, 3H), 7.22-7.18(m, 2H), 6.76(d, $J=8.4\text{Hz}$, 1H), 4.58(d, $J=8.8\text{Hz}$, 2H), 4.34(d, $J=8.4\text{Hz}$, 1H), 4.13(d, $J=8.8\text{Hz}$, 1H), 2.03-1.93(m, 1H), 1.77-1.69(m, 3H), 1.61(s, 3H), 1.32(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 159.2, 145.6, 141.4, 135.6, 134.1, 128.7, 127.1, 126.8, 126.5, 121.6, 109.8, 109.7, 82.7, 45.2, 38.9, 32.7, 25.6, 22.7; HRMS(APCI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{O}$ 279.1743; found 279.1742.



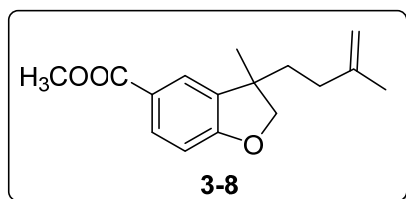
5-fluoro-3-methyl-3-(3-methylbut-3-en-1-yl)-2,3-dihydrobenzofuran: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 6.75-6.69(m, 2H), 6.63-6.59(m, 1H), 4.59(d, $J=14.8\text{Hz}$, 2H), 4.31(d, $J=8.8\text{Hz}$, 1H), 4.11(d, $J=8.8\text{Hz}$, 1H), 2.01-1.94(m, 1H), 1.73-1.65(m, 3H), 1.62(s, 3H), 1.28(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 158.8, 156.4(d, $J=109\text{Hz}$), 145.4, 136.5(d, $J=7\text{Hz}$), 114.1(d, $J=24\text{Hz}$), 110.0(d, $J=24\text{Hz}$), 109.8, 109.7(d, $J=9\text{Hz}$), 82.8, 45.5, 38.7, 32.6, 25.5, 22.7; HRMS(APCI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{FO}$ 221.1336; found 221.1334.



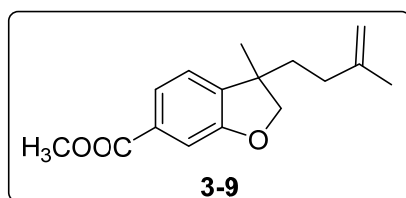
5-chloro-3-methyl-3-(3-methylbut-3-en-1-yl)-2,3-dihydrobenzofuran: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.00(dd, $J=2.4\text{Hz}$, 8.4Hz, 1H), 6.95(d, $J=2.0\text{Hz}$, 1H), 6.62(d, $J=8.4\text{Hz}$, 1H), 4.60(d, $J=15.2\text{Hz}$, 2H), 4.32(d, $J=8.2\text{Hz}$, 1H), 4.11(d, $J=8.8\text{Hz}$, 1H), 1.99-1.93(m, 1H), 1.72-1.63(m, 3H), 1.62(s, 3H), 1.28(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 158.2, 145.3, 136.9, 127.9, 125.1, 123.1, 110.6, 109.9, 82.8, 45.4, 38.7, 32.5, 25.6, 22.7; HRMS(APCI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{ClO}$ 237.1041; found 237.1045.



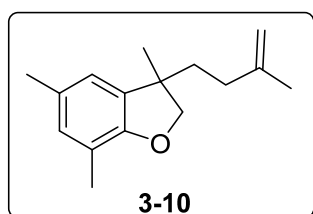
3-methyl-3-(3-methylbut-3-en-1-yl)-5-(trifluoromethyl)-2,3-dihydrobenzofuran: NMR yield;
HRMS(APCI) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}F_3O$ 271.1304; found 271.1300.



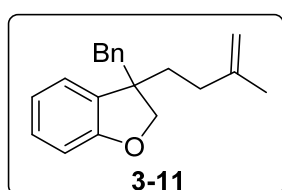
methyl 3-methyl-3-(3-methylbut-3-en-1-yl)-2,3-dihydrobenzofuran-5-carboxylate: Colorless oil; 1H NMR(400MHz, $CDCl_3$) δ : 7.83-7.80(m, 1H), 7.70(d, $J=1.6$ Hz, 1H), 6.71(d, $J=8.4$ Hz, 1H), 4.58(d, $J=14.4$ Hz, 2H), 4.38(d, $J=8.8$ Hz, 1H), 4.17(d, $J=8.8$ Hz, 1H), 3.80(s, 3H), 1.99-1.89(m, 1H), 1.72-1.65(m, 3H), 1.60(s, 3H), 1.31(s, 3H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 166.9, 163.7, 145.2, 135.4, 131.1, 124.8, 122.7, 109.8, 109.3, 83.2, 51.8, 44.7, 38.8, 32.5, 25.7, 22.6; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}O_3Na$ 283.1305; found 283.1299.



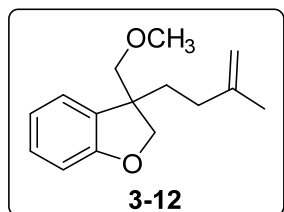
methyl 3-methyl-3-(3-methylbut-3-en-1-yl)-2,3-dihydrobenzofuran-6-carboxylate: Colorless oil; 1H NMR(400MHz, $CDCl_3$) δ : 7.55-7.53(m, 1H), 7.34(d, $J=1.2$ Hz, 1H), 7.04(d, $J=8.0$ Hz, 1H), 4.58(d, $J=16.0$ Hz, 2H), 4.35(d, $J=8.4$ Hz, 1H), 4.14(d, $J=8.8$ Hz, 1H), 3.81(s, 3H), 1.97-1.93(m, 1H), 1.71-1.65(m, 3H), 1.60(s, 3H), 1.29(s, 3H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 166.9, 159.7, 145.3, 140.5, 130.4, 122.6, 122.5, 110.4, 109.8, 82.5, 52.1, 45.2, 38.7, 32.5, 25.5, 22.6; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}O_3Na$ 283.1305; found 283.1297.



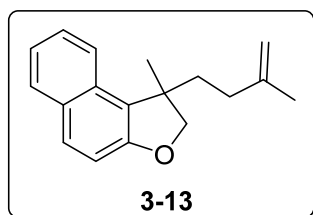
3,5,7-trimethyl-3-(3-methylbut-3-en-1-yl)-2,3-dihydrobenzofuran: Colorless oil; 1H NMR(400MHz, $CDCl_3$) δ : 6.68(s, 1H), 6.63(s, 1H), 4.58(d, $J=7.6$ Hz, 2H), 4.27(d, $J=8.4$ Hz, 1H), 4.06(d, $J=8.4$ Hz, 1H), 2.19(s, 3H), 2.10(s, 3H), 2.00-1.93(m, 1H), 1.78-1.64(m, 3H), 1.61(s, 3H), 1.25(s, 3H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 155.6, 145.8, 134.3, 129.8, 129.6, 120.6, 119.1, 109.6, 82.1, 45.3, 38.8, 32.7, 25.6, 22.7, 20.8, 15.0; MS (EI): m/z(%) 230 (95) $[M]^+$, 161(100), 133(92), 91(30).



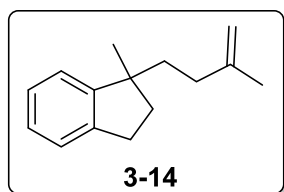
3-benzyl-3-(3-methylbut-3-en-1-yl)-2,3-dihydrobenzofuran: Yellow oil; ^1H NMR(400MHz, CDCl_3) δ : 7.16-7.12(m, 3H), 7.07-7.03(m, 1H), 6.89-6.84(m, 3H), 6.81-6.77(m, 1H), 6.65(d, $J=8.0\text{Hz}$, 1H), 4.58(d, $J=13.6\text{Hz}$, 2H), 4.38(d, $J=8.8\text{Hz}$, 1H), 4.15(d, $J=8.8\text{Hz}$, 1H), 2.94-2.85(m, 2H), 2.01-1.95(m, 1H), 1.78-1.71(m, 3H), 1.60(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 160.0, 145.6, 137.2, 132.6, 130.3, 128.3, 127.9, 126.5, 123.9, 120.1, 109.8, 109.6, 79.6, 49.7, 45.1, 35.9, 32.5, 22.7; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{O}$ 279.1743; found 279.1739.



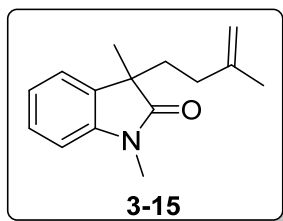
3-(methoxymethyl)-3-(3-methylbut-3-en-1-yl)-2,3-dihydrobenzofuran: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.10-7.04(m, 2H), 6.82-6.78(m, 1H), 6.72(d, $J=8.0\text{Hz}$, 1H), 4.59(d, $J=10.0\text{Hz}$, 2H), 4.37(d, $J=9.2\text{Hz}$, 1H), 4.26(d, $J=9.2\text{Hz}$, 1H), 3.44-3.38(m, 2H), 3.27(s, 3H), 1.98-1.66(m, 4H), 1.62(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 160.2, 145.7, 130.9, 128.6, 123.7, 120.3, 109.7, 109.6, 78.6, 78.3, 59.4, 50.0, 33.9, 32.3, 22.7; HRMS(APCI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2$ 233.1536; found 233.1531.



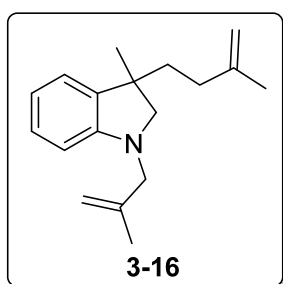
1-methyl-1-(3-methylbut-3-en-1-yl)-1,2-dihydronaphtho[2,1-b]furan: Yellow oil; ^1H NMR(400MHz, CDCl_3) δ : 7.79(d, $J=8.4\text{Hz}$, 1H), 7.71(d, $J=8.4\text{Hz}$, 1H), 7.57(d, $J=8.8\text{Hz}$, 1H), 7.35-7.32(m, 1H), 7.18(t, $J=7.6\text{Hz}$, 1H), 6.99(d, $J=8.4\text{Hz}$, 1H), 4.54(d, $J=12.4\text{Hz}$, 2H), 4.43(d, $J=8.8\text{Hz}$, 1H), 4.20(d, $J=8.8\text{Hz}$, 1H), 2.18-2.11(m, 1H), 2.03-1.95(m, 1H), 1.88-1.80(m, 1H), 1.66-1.61(m, 1H), 1.56(s, 3H), 1.55(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 157.6, 145.7, 130.6, 129.9, 129.7, 129.4, 126.5, 123.8, 122.5, 121.6, 112.3, 109.6, 82.5, 47.0, 37.8, 32.9, 26.6, 22.7; HRMS(APCI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{O}$ 253.1587; found 253.1586.



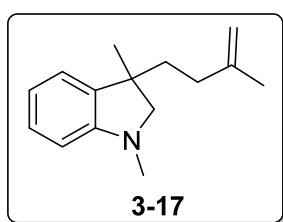
1-methyl-1-(3-methylbut-3-en-1-yl)-2,3-dihydro-1H-indene: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.21-7.10(m, 4H), 4.65(s, 2H), 2.88(t, $J=7.2\text{Hz}$, 2H), 2.07-1.97(m, 2H), 1.92-1.81(m, 2H), 1.77-1.62(m, 5H), 1.25(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 151.3, 146.6, 143.1, 126.2, 126.1, 124.5, 122.6, 109.2, 47.2, 39.3, 38.3, 33.1, 30.2, 26.8, 22.8; MS (EI): m/z (%) 200 (50) $[\text{M}]^+$, 131(100), 115(34), 91(68).



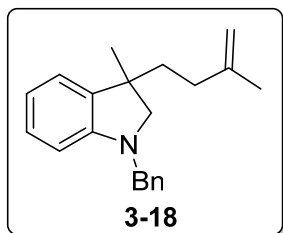
1,3-dimethyl-3-(3-methylbut-3-en-1-yl)indolin-2-one: Yellow oil; ^1H NMR(400MHz, CDCl_3) δ : 7.23-7.18(m, 1H), 7.11(dd, $J=0.8\text{Hz}$, 7.2Hz, 1H), 7.02-6.98(m, 1H), 6.77(d, $J=7.6\text{Hz}$, 1H), 4.53-4.44(m, 2H), 3.14(s, 3H), 2.05-1.97(m, 1H), 1.83-1.75(m, 1H), 1.65-1.58(m, 1H), 1.55(s, 3H), 1.49-1.42(m, 1H), 1.30(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 180.5, 145.0, 143.3, 133.8, 127.7, 122.5, 122.4, 109.8, 107.9, 48.1, 36.4, 32.5, 26.1, 23.9, 22.4; HRMS(ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{NONa}$ 252.1359; found 252.1361.



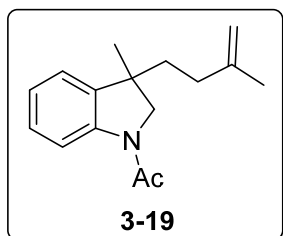
3-methyl-1-(2-methylallyl)-3-(3-methylbut-3-en-1-yl)indoline: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 6.99-6.96(m, 1H), 6.90(d, $J=7.2\text{Hz}$, 1H), 6.60-6.57(m, 1H), 6.37(d, $J=8.0\text{Hz}$, 1H), 4.87(d, $J=29.2\text{Hz}$, 2H), 4.58(s, 2H), 3.56-3.43(m, 2H), 3.14(d, $J=8.8\text{Hz}$, 1H), 2.93(d, $J=8.8\text{Hz}$, 1H), 2.03-1.95(m, 1H), 1.82-1.75(m, 1H), 1.72-1.62(m, 8H), 1.23(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 151.5, 146.2, 142.3, 137.3, 127.4, 122.2, 117.2, 112.0, 109.3, 106.5, 65.4, 55.3, 43.2, 38.7, 32.9, 26.0, 22.7, 20.3; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{26}\text{N}$ 256.2060; found 256.2054.



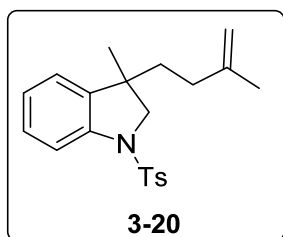
1,3-dimethyl-3-(3-methylbut-3-en-1-yl)indoline: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.02(td, $J=1.2\text{Hz}$, 7.6Hz, 1H), 6.91(dd, $J=0.8\text{Hz}$, 7.2Hz, 1H), 6.64-6.61(m, 1H), 6.41(d, $J=8.0\text{Hz}$, 1H), 4.59(s, 2H), 3.13(d, $J=8.8\text{Hz}$, 1H), 2.93(d, $J=8.8\text{Hz}$, 1H), 2.68(s, 3H), 2.03-1.96(m, 1H), 1.86-1.79(m, 1H), 1.74-1.64(m, 2H), 1.63(s, 3H), 1.23(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 152.3, 146.3, 137.9, 127.5, 122.2, 117.6, 109.4, 107.2, 68.1, 43.5, 38.4, 35.9, 32.9, 25.5, 22.8; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{22}\text{N}$ 216.1747; found 216.1744.



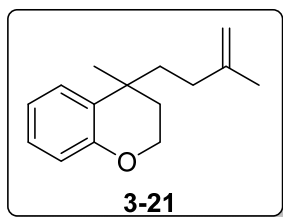
1-benzyl-3-methyl-3-(3-methylbut-3-en-1-yl)indoline: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.27-7.21(m, 4H), 7.19-7.15(m, 1H), 6.97(td, $J=1.2\text{Hz}$, 7.6Hz, 1H), 6.93-6.91(m, 1H), 6.62-6.59(m, 1H), 6.39(d, $J=8.0\text{Hz}$, 1H), 4.56(d, $J=7.2\text{Hz}$, 2H), 4.21(d, $J=15.2\text{Hz}$, 1H), 4.11(d, $J=14.8\text{Hz}$, 1H), 3.11(d, $J=8.8\text{Hz}$, 1H), 2.92(d, $J=8.8\text{Hz}$, 1H), 1.99-1.92(m, 1H), 1.79-1.62(m, 3H), 1.59(s, 3H), 1.21(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 151.4, 146.2, 138.5, 137.4, 128.4, 127.7, 127.5, 127.0, 122.3, 117.5, 109.3, 106.8, 65.4, 52.9, 43.3, 38.7, 32.9, 25.9, 22.7; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{26}\text{N}$ 292.2060; found 292.2064.



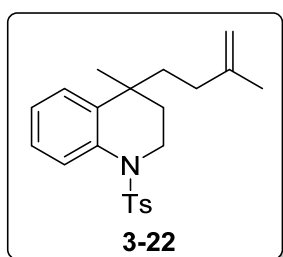
1-(3-methyl-3-(3-methylbut-3-en-1-yl)indolin-1-yl)ethan-1-one: Yellow oil; ^1H NMR(400MHz, CDCl_3) δ : 8.19(d, $J=8.0\text{Hz}$, 1H), 7.33-7.16(m, 1H), 7.13-7.03(m, 2H), 4.66(d, $J=18.0\text{Hz}$, 2H), 3.89(d, $J=10.4\text{Hz}$, 1H), 3.70(d, $J=10.0\text{Hz}$, 1H), 2.23(s, 3H), 2.02-1.93(m, 1H), 1.79-1.74(m, 3H), 1.68(s, 3H), 1.37(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 168.5, 145.2, 142.0, 138.7, 127.7, 123.7, 122.2, 116.8, 109.8, 61.1, 43.3, 39.4, 32.5, 27.1, 24.2, 22.6; HRMS(ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{21}\text{NONa}$ 266.1515; found 266.1517.



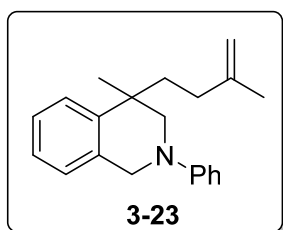
3-methyl-3-(3-methylbut-3-en-1-yl)-1-tosylindoline: Yellow oil; ^1H NMR(400MHz, CDCl_3) δ : 7.64-7.57(m, 3H), 7.15-7.09(m, 3H), 6.91(d, $J=4.0\text{Hz}$, 2H), 4.47(d, $J=43.2\text{Hz}$, 2H), 3.68(d, $J=10.4\text{Hz}$, 1H), 3.46(d, $J=10.4\text{Hz}$, 1H), 2.25(s, 3H), 1.69-1.62(m, 1H), 1.54-1.39(m, 6H), 1.06(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 145.1, 144.0, 141.0, 139.0, 133.8, 129.6, 127.9, 127.1, 123.5, 122.9, 114.2, 109.6, 61.0, 43.2, 38.8, 32.3, 26.5, 22.5, 21.4; HRMS(ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_2\text{SNa}$ 378.1498; found 378.1501.



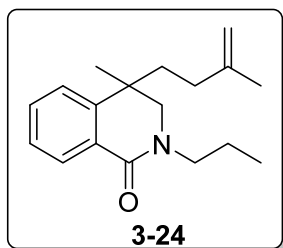
4-methyl-4-(3-methylbut-3-en-1-yl)chromane: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.20(dd, $J=1.6\text{Hz}$, 8.0Hz, 1H), 7.09-7.05(m, 1H), 6.90-6.86(m, 1H), 6.79(dd, $J=1.2\text{Hz}$, 8.4Hz, 1H), 4.66(d, $J=7.6\text{Hz}$, 2H), 4.25-4.20(m, 1H), 4.17-4.12(m, 1H), 2.04-1.97(m, 2H), 1.87-1.75(m, 3H), 1.71-1.66(m, 4H), 1.33(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 154.1, 146.1, 130.6, 127.1, 127.0, 120.4, 117.0, 109.5, 62.9, 40.5, 34.0, 33.4, 32.3, 29.5, 22.7; MS (EI): $m/z(\%)$ 216 (28) $[\text{M}]^+$, 147(100), 91(80).



4-methyl-4-(3-methylbut-3-en-1-yl)-1-tosyl-1,2,3,4-tetrahydroquinoline; white solid; ^1H NMR(400MHz, CDCl_3) δ : 7.92-7.89(m, 1H), 7.47(d, $J=8.0\text{Hz}$, 2H), 7.19-7.13(m, 5H), 4.51(d, $J=58.4\text{Hz}$, 2H), 4.20-4.14(m, 1H), 3.61-3.54(m, 1H), 2.32(s, 3H), 1.56-1.39(m, 6H), 1.27-1.16(m, 3H), 1.09(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 145.6, 143.6, 137.4, 137.0, 136.1, 129.5, 127.2, 127.1, 126.2, 125.3, 125.0, 109.4, 43.7, 40.4, 35.5, 31.9, 30.9, 22.4, 21.4; HRMS(ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_2\text{SNa}$ 392.1655; found 392.1653.

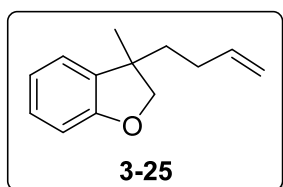


4-methyl-4-(3-methylbut-3-en-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Yellow oil; ^1H NMR(400MHz, CDCl_3) δ : 7.27-7.22(m, 3H), 7.16-7.08(m, 3H), 6.91(d, $J=8.0\text{Hz}$, 2H), 6.78-6.74(m, 1H), 4.57(d, $J=5.2\text{Hz}$, 2H), 4.36(d, $J=15.2\text{Hz}$, 1H), 4.24(d, $J=15.2\text{Hz}$, 1H), 3.42(d, $J=12.4\text{Hz}$, 1H), 3.09(d, $J=12.0\text{Hz}$, 1H), 1.94-1.71(m, 4H), 1.59(s, 3H), 1.30(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 150.8, 146.2, 142.7, 133.6, 129.2, 126.5, 126.4, 126.0, 125.8, 118.4, 114.6, 109.5, 57.5, 51.0, 38.9, 38.3, 32.8, 25.7, 22.7; MS (EI): $m/z(\%)$ 291(24) $[\text{M}]^+$, 145(50), 129(100).



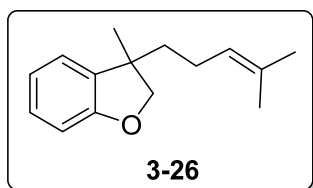
4-methyl-4-(3-methylbut-3-en-1-yl)-2-propyl-3,4-dihydroisoquinolin-1(2H)-one: Yellow oil;

^1H NMR(400MHz, CDCl_3) δ : 8.13-8.10(m, 1H), 7.48(td, $J=1.6\text{Hz}$, 7.6Hz, 1H), 7.35-7.31(m, 1H), 7.25-7.23(m, 1H), 4.64(d, $J=20.0\text{Hz}$, 2H), 3.61-3.47(m, 2H), 3.44(d, $J=12.8\text{Hz}$, 1H), 3.27(d, $J=12.4\text{Hz}$, 1H), 2.01-1.96(m, 1H), 1.83-1.66(m, 8H), 1.34(s, 3H), 0.99-0.96(t, $J=7.2\text{Hz}$, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 164.0, 145.3, 145.2, 131.5, 128.6, 128.5, 126.7, 124.1, 109.9, 56.4, 49.1, 37.2, 36.8, 32.4, 23.1, 22.6, 20.7, 11.4; HRMS(ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{25}\text{NO}$ 294.1828; found 294.1834.

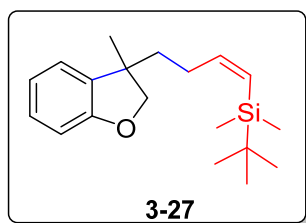


3-(but-3-en-1-yl)-3-methyl-2,3-dihydrobenzofuran: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ :

7.07-6.99(m, 2H), 6.82-6.78(m, 1H), 6.70(d, $J=8.0\text{Hz}$, 1H), 5.72-5.65(m, 1H), 4.93-4.83(m, 2H), 4.29(d, $J=8.8\text{Hz}$, 1H), 4.08(d, $J=8.8\text{Hz}$, 1H), 2.07-1.98(m, 1H), 1.83-1.74(m, 1H), 1.65-1.60(m, 2H), 1.27(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 159.5, 138.3, 134.8, 128.0, 122.8, 120.4, 114.5, 109.6, 82.4, 45.1, 40.0, 29.0, 25.5; MS (EI): m/z (%) 188 (77) $[\text{M}]^+$, 133(100), 105(100), 77(40).

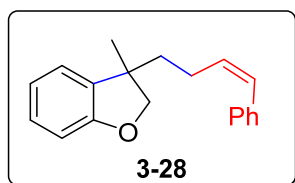


3-methyl-3-(4-methylpent-3-en-1-yl)-2,3-dihydrobenzofuran: Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.06-6.99(m, 2H), 6.82-6.78(m, 1H), 6.71(d, $J=8.0\text{Hz}$, 1H), 4.99-4.95(m, 1H), 4.31(d, $J=8.4\text{Hz}$, 1H), 4.09(d, $J=8.4\text{Hz}$, 1H), 1.99-1.90(m, 1H), 1.76-1.67(m, 1H), 1.62-1.53(m, 5H), 1.46(s, 3H), 1.27(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 159.5, 135.1, 131.8, 127.9, 123.9, 122.8, 120.4, 109.5, 82.4, 45.2, 40.8, 25.7, 25.6, 23.3, 17.6; HRMS(APCI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{21}\text{O}$ 217.1587; found 217.1585.

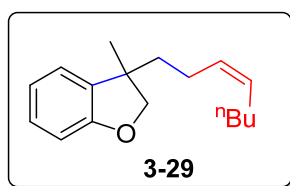


(Z)-tert-butyl dimethyl(4-(3-methyl-2,3-dihydrobenzofuran-3-yl)but-1-en-1-yl)silane,

Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.16-7.09(m, 2H), 6.92-6.88(m, 1H), 6.81(d, $J=8.0\text{Hz}$, 1H), 6.04-5.96(m, 1H), 5.66-5.60(m, 1H), 4.40(d, $J=8.8\text{Hz}$, 1H), 4.18(d, $J=8.8\text{Hz}$, 1H), 2.23-2.17(m, 1H), 2.01-1.94(m, 1H), 1.76-1.71(m, 2H), 1.38(s, 3H), 0.87(s, 9H), 0.01(s, 6H); ^{13}C NMR(100MHz, CDCl_3) δ : 159.5, 147.7, 134.9, 128.1, 127.1, 122.8, 120.4, 109.5, 82.4, 45.1, 39.9, 32.1, 26.4, 25.5, 16.4, -6.1; MS (EI): m/z (%) 302 (10) $[\text{M}]^+$, 245(80), 163(100).



(Z)-3-methyl-3-(4-phenylbut-3-en-1-yl)-2,3-dihydrobenzofuran, Colorless oil; ^1H NMR(400MHz, CDCl_3) δ : 7.22-7.16(m, 4H), 7.09-7.01(m, 3H), 6.82-6.78(m, 1H), 6.72(d, $J=8.0\text{Hz}$, 1H), 6.25(d, $J=15.6\text{Hz}$, 1H), 6.08-6.01(m, 1H), 4.32(d, $J=8.4\text{Hz}$, 1H), 4.09(d, $J=8.8\text{Hz}$, 1H), 2.17-2.14(m, 1H), 1.97-1.91(m, 1H), 1.72-1.67(m, 2H), 1.29(s, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 159.5, 137.6, 134.7, 130.1, 129.9, 128.4, 128.1, 126.8, 125.8, 122.8, 120.5, 109.6, 82.3, 45.1, 40.4, 28.3, 25.6; MS (EI): m/z (%) 264 (40) $[\text{M}]^+$, 249(30), 133(100), 105(65).

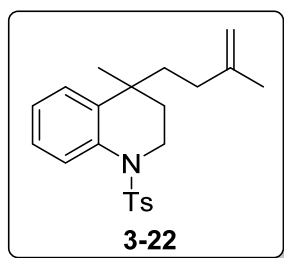


(Z)-3-methyl-3-(oct-3-en-1-yl)-2,3-dihydrobenzofuran, Colorless oil; ^1H NMR (400MHz, CDCl_3) δ : 7.07-6.99(m, 2H), 6.82-6.78(m, 1H), 6.71(d, $J=7.6\text{Hz}$, 1H), 5.33-5.23(m, 2H), 4.29(d, $J=8.8\text{Hz}$, 1H), 4.08(d, $J=8.8\text{Hz}$, 1H), 1.97-1.92(m, 1H), 1.89-1.84(m, 2H), 1.77-1.69(m, 1H), 1.62-1.57(m, 2H), 1.27(s, 3H), 1.22-1.19(m, 4H), 0.81-0.78(m, 3H); ^{13}C NMR(100MHz, CDCl_3) δ : 159.5, 135.1, 130.7, 129.5, 127.9, 122.8, 120.4, 109.5, 82.4, 45.1, 40.7, 32.2, 31.6, 27.8, 25.5, 22.1, 13.9; MS (EI): m/z (%) 244 (30) $[\text{M}]^+$, 133(100), 105(45).

4. References

1. (a) Y. Gao, W. Xiong, H. Chen, W. Wu, J. Peng, Y. Gao and H. Jiang, Pd-Catalyzed Highly Regio- and Stereoselective Formation of C-C Double Bonds: An Efficient Method for the Synthesis of Benzofuran-, Dihydrobenzofuran-, and Indoline-Containing Alkenes, *J. Org. Chem.*, 2015, **80**, 7456; (b) J. He, Y. Xue, B. Han, C. Zhang, Y. Wang and S. Zhu, Nickel-Catalyzed Asymmetric Reductive 1,2-Carboamination of Unactivated Alkenes, *Angew. Chem. Int. Ed.*, 2020, **59**, 2328.
2. (a) W. H. Bunnelle, M. A. Rafferty and S. L. Hodges, Aldol-equivalent elaboration of sterically hindered ketones: methallylmagnesium chloride as a synthon for acetone enolate, *J. Org. Chem.*, 1987, **52**, 1603; (b) M. Iwasaki, S. Hayashi, K. Hirano, H. Yorimitsu and K. Oshima, Pd(OAc)₂/P(C₆H₁₁)₃-Catalyzed Allylation of Aryl Halides with Homoallyl Alcohols via Retro-Allylation, *J. Am. Chem. Soc.*, 2007, **129**, 4463.

5. The crystal structure of product 3-22



Bond precision: C-C = 0.0027 Å Wavelength=1.54184

Cell: a=14.0561 (3) b=8.6104 (1) c=17.7562 (3)
 alpha=90 beta=111.764 (2) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1995.83 (7)	1995.82 (6)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C22 H27 N O2 S	C22 H27 N O2 S
Sum formula	C22 H27 N O2 S	C22 H27 N O2 S
Mr	369.51	369.50
Dx, g cm ⁻³	1.230	1.230
Z	4	4
Mu (mm ⁻¹)	1.553	1.553
F000	792.0	792.0
F000'	795.35	
h, k, lmax	17, 10, 21	17, 10, 21
Nref	3900	3822
Tmin, Tmax	0.985, 0.985	0.756, 1.000
Tmin'	0.985	

Correction method= # Reported T Limits: Tmin=0.756 Tmax=1.000
 AbsCorr = MULTI-SCAN

Data completeness= 0.980

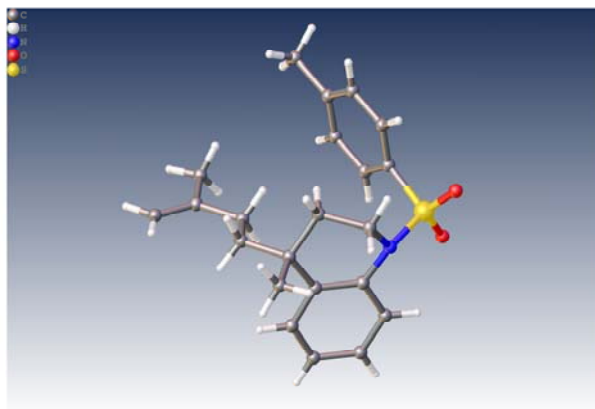
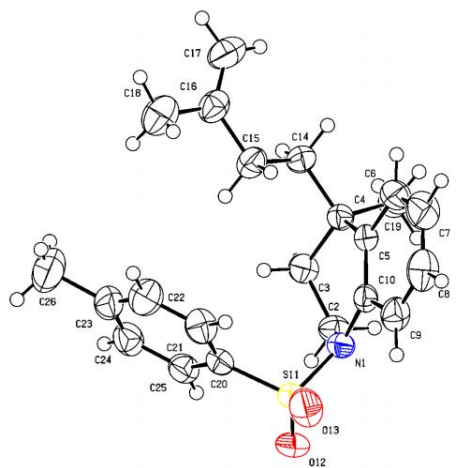
Theta(max)= 71.544

R(reflections)= 0.0401(3329)

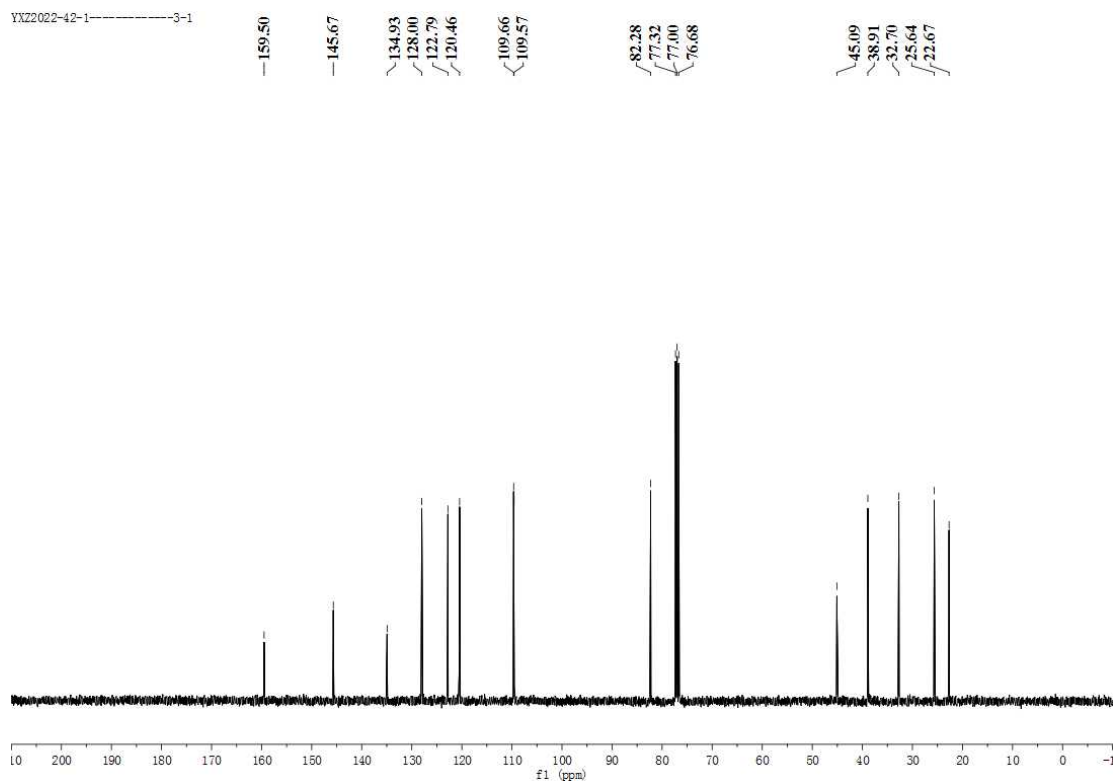
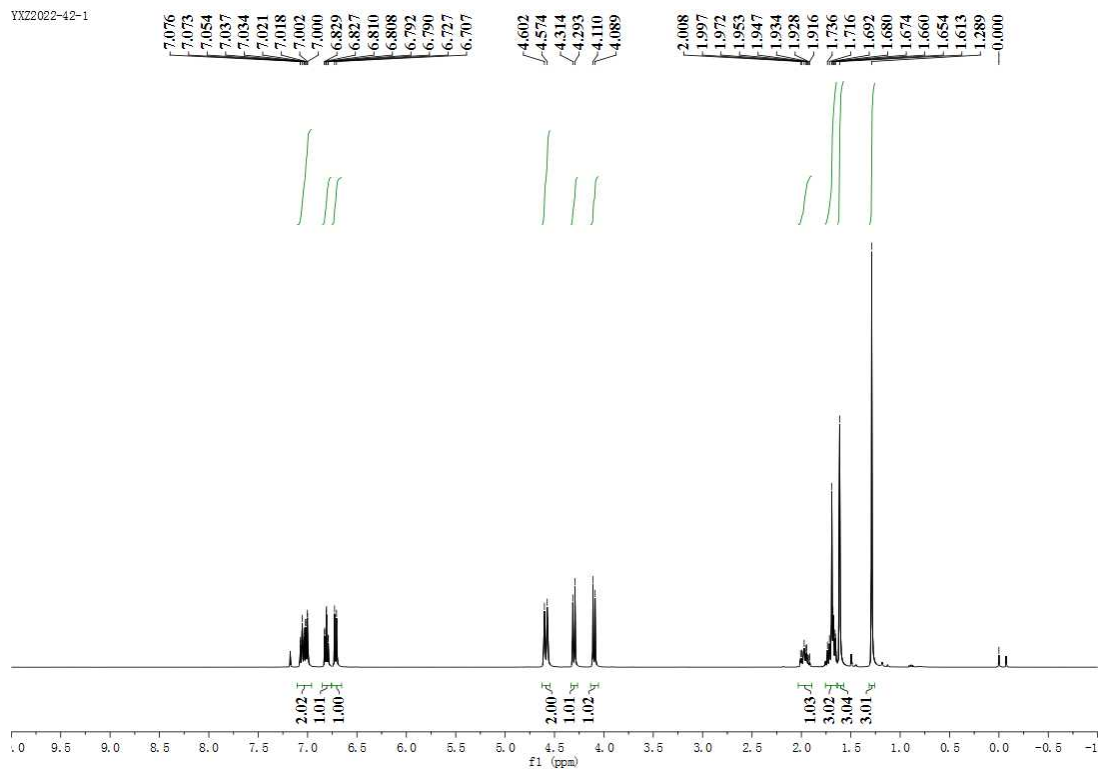
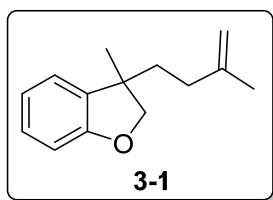
wR2(reflections)=
0.1117(3822)

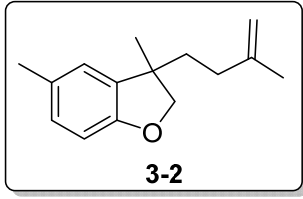
S = 1.021

Npar= 246

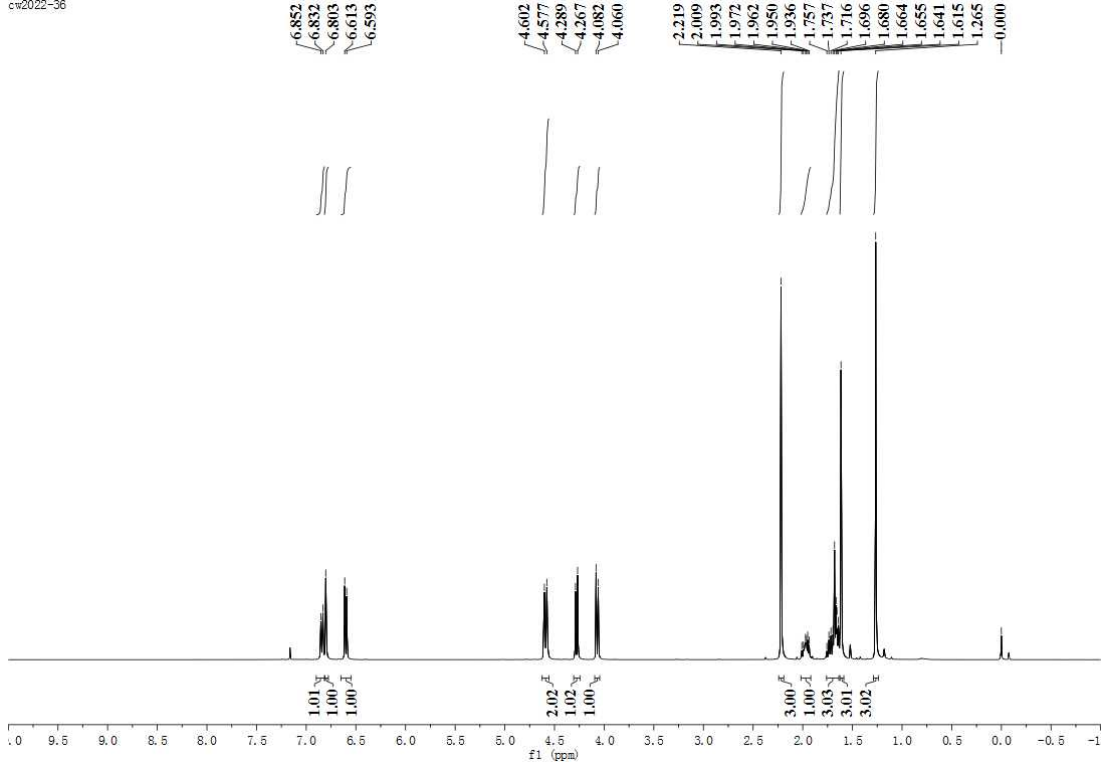


6. ^1H , ^{13}C spectra for compound 3

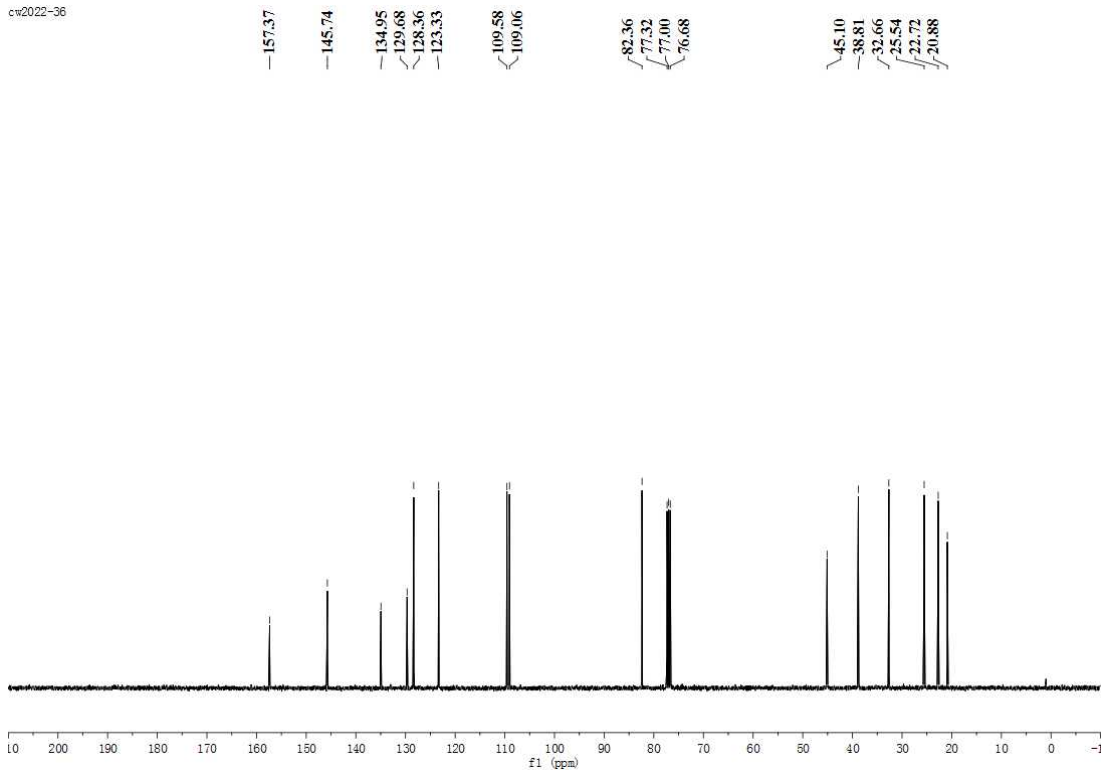


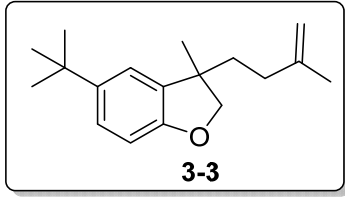


cv2022-36

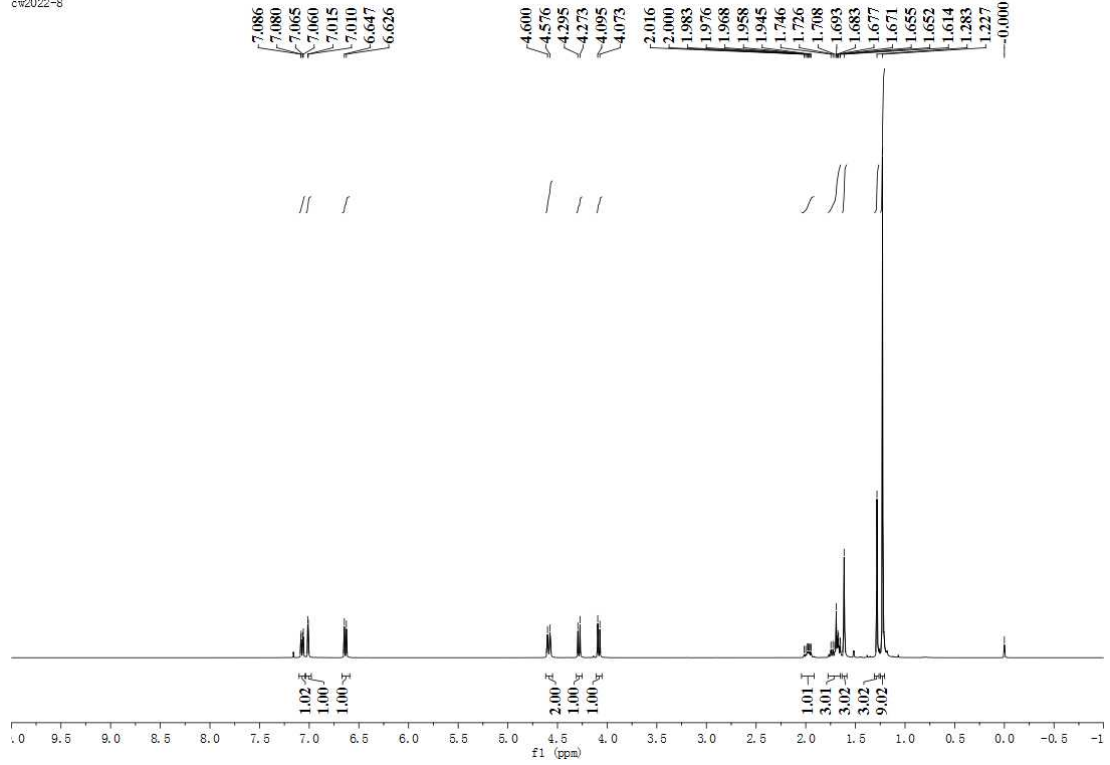


cv2022-36

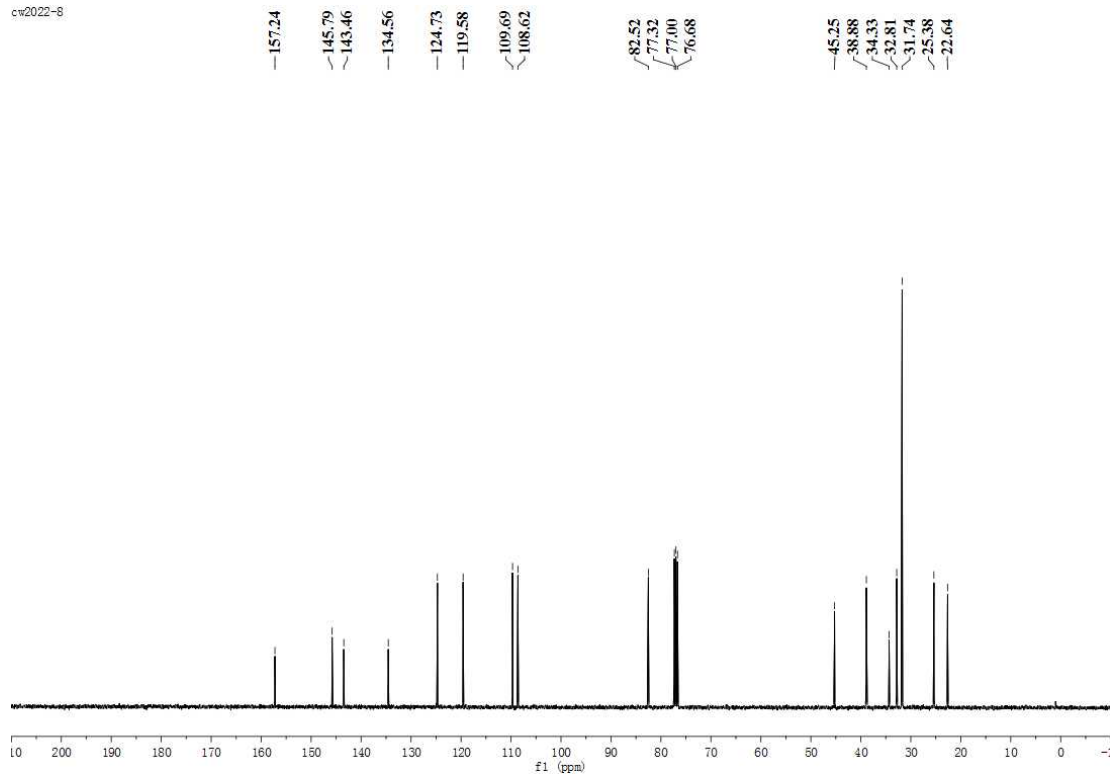


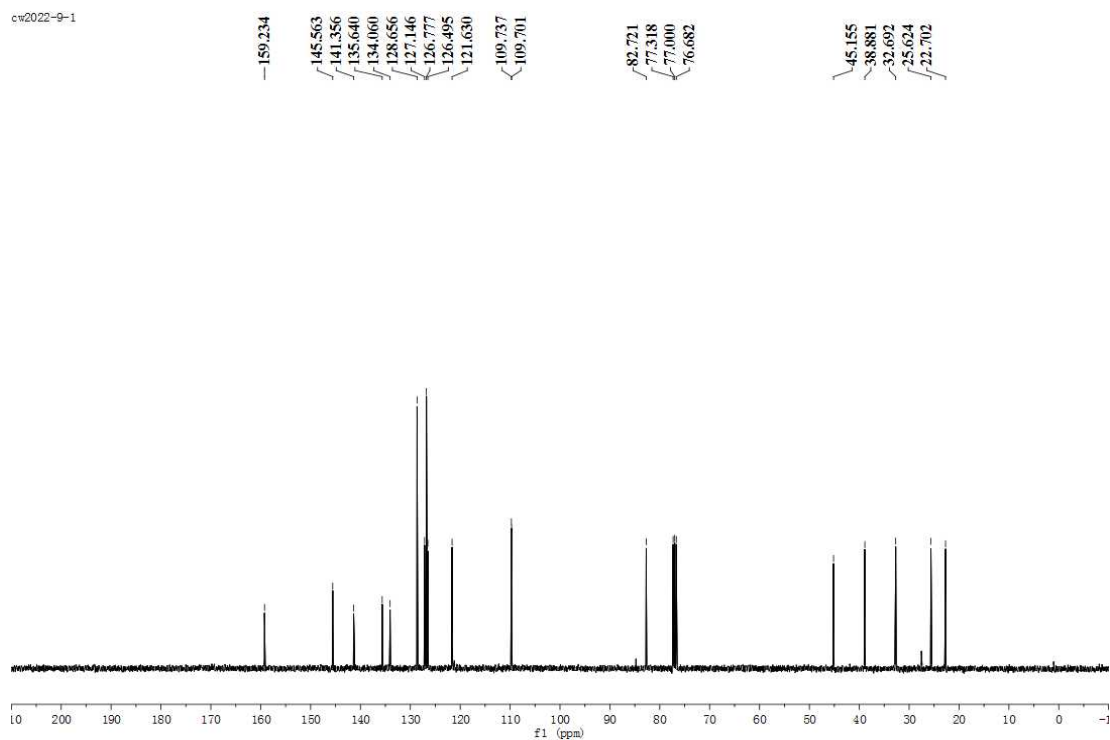
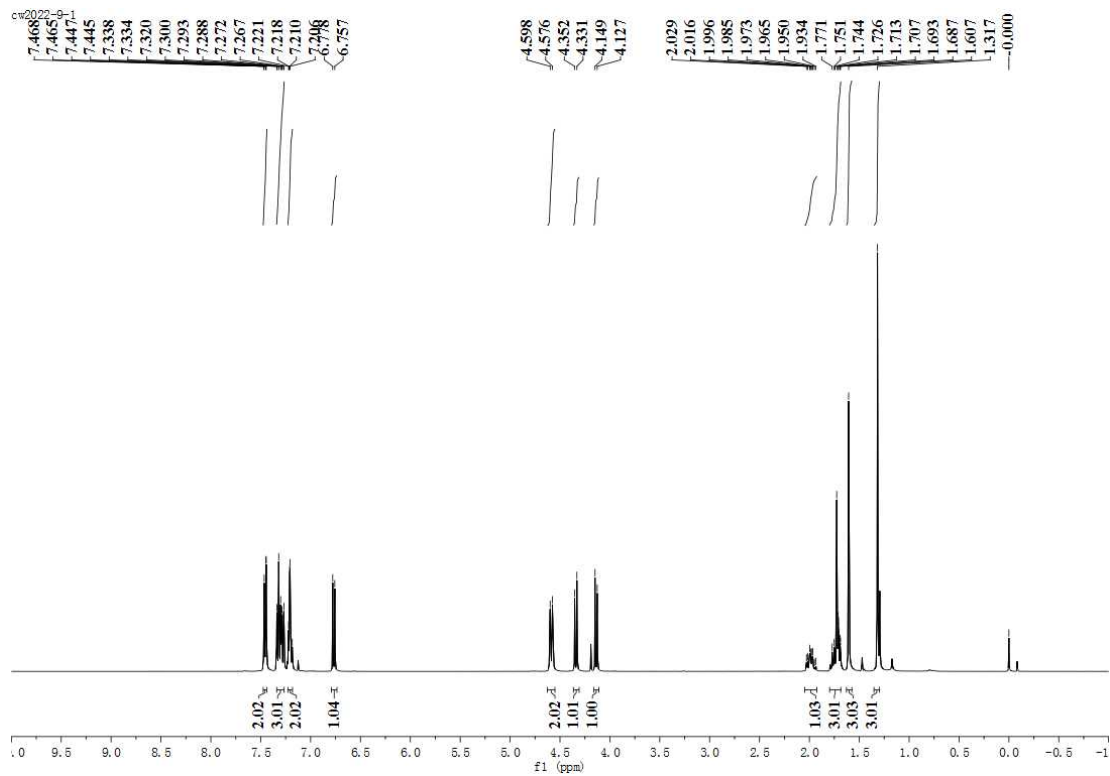
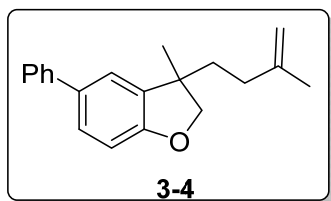


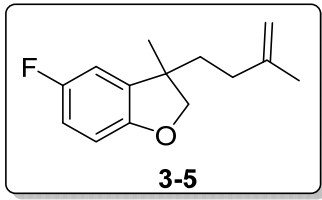
cw2022-8



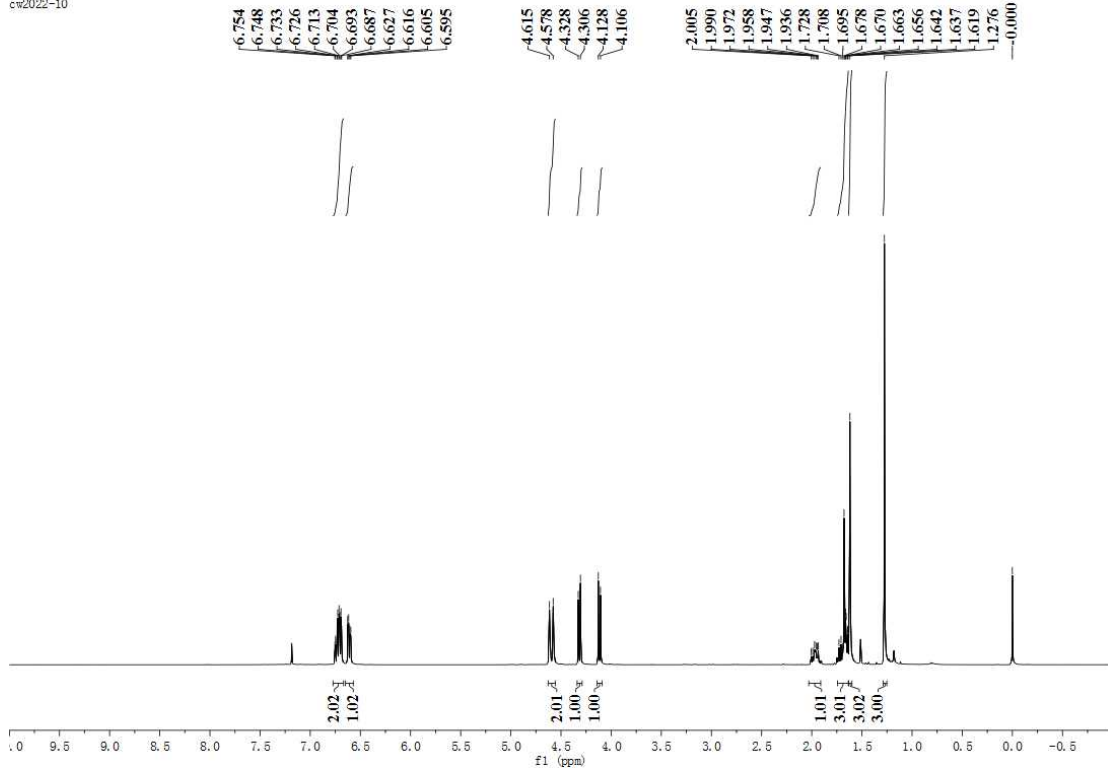
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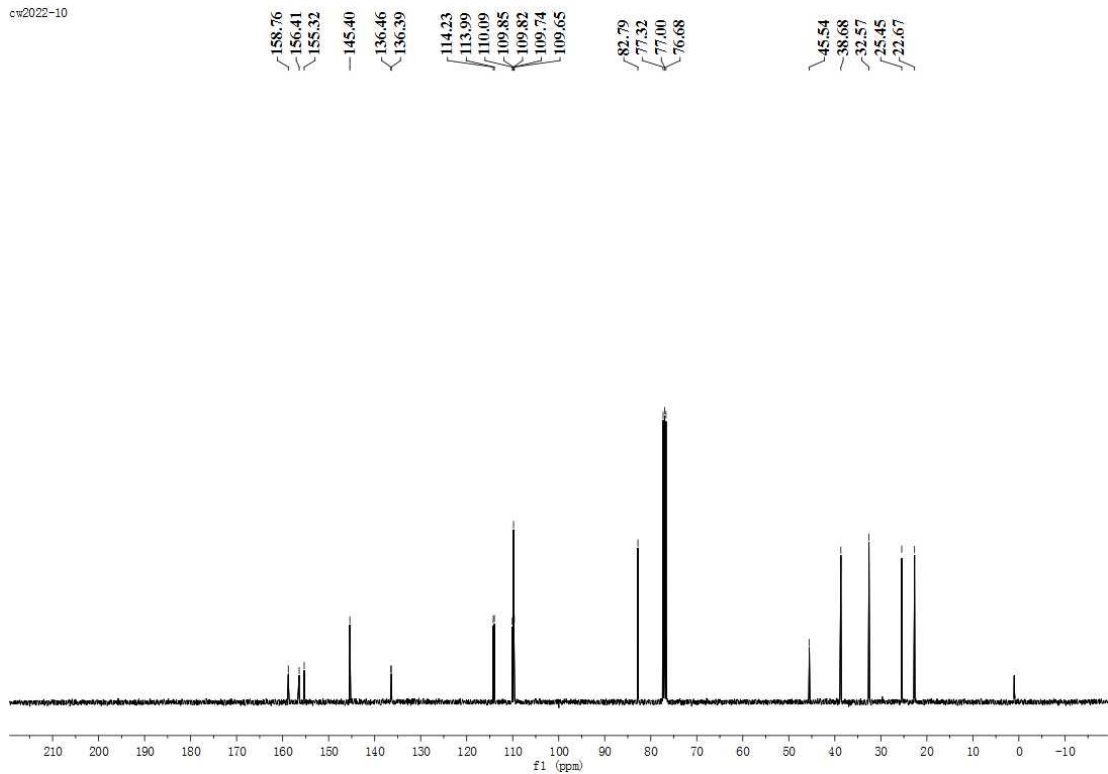


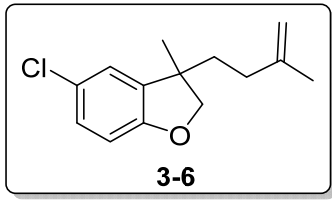


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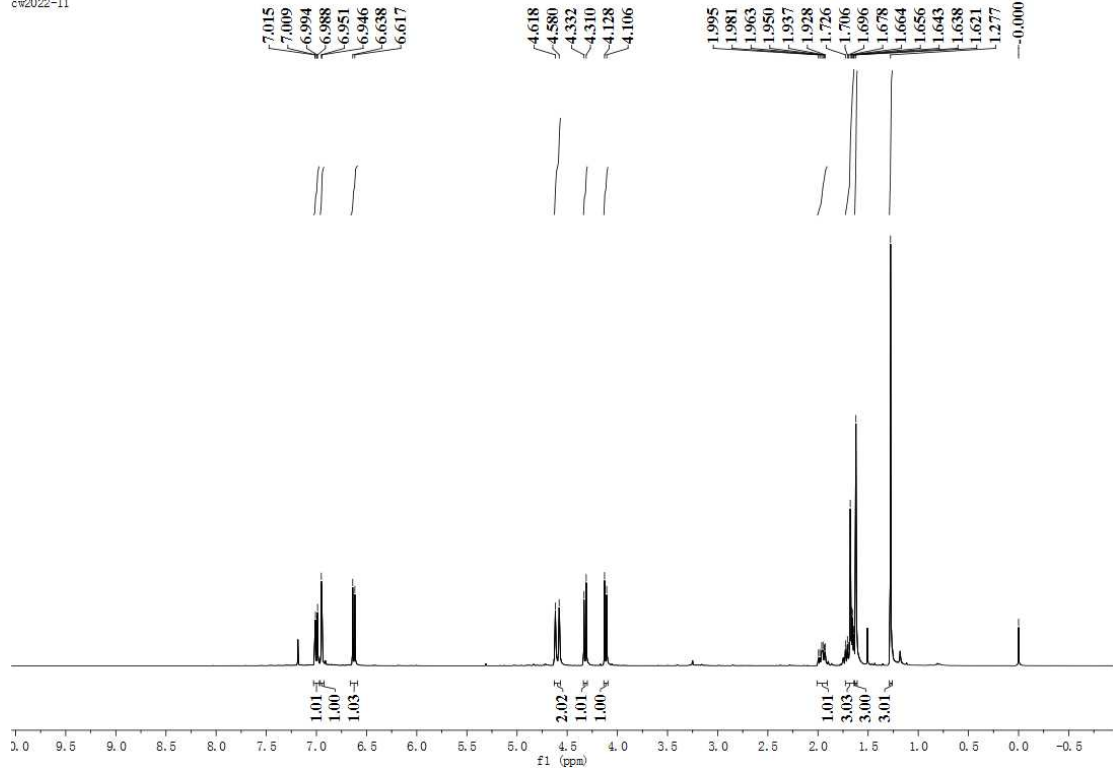


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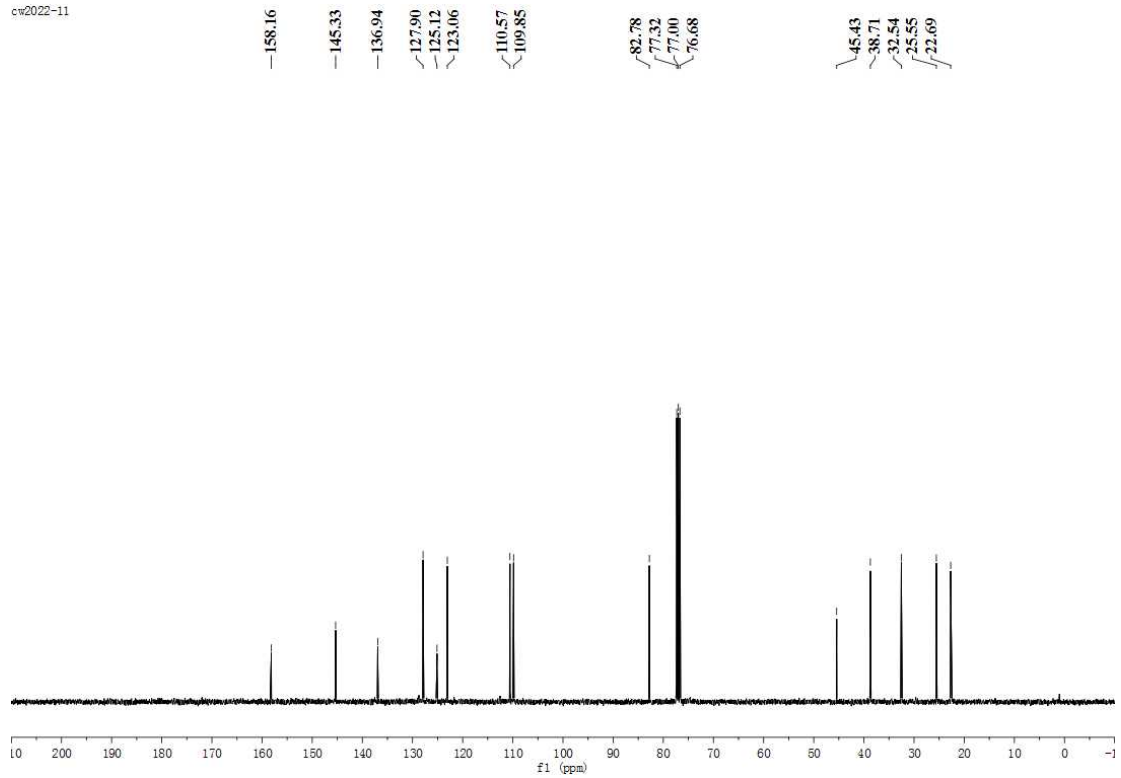


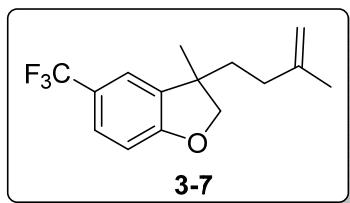


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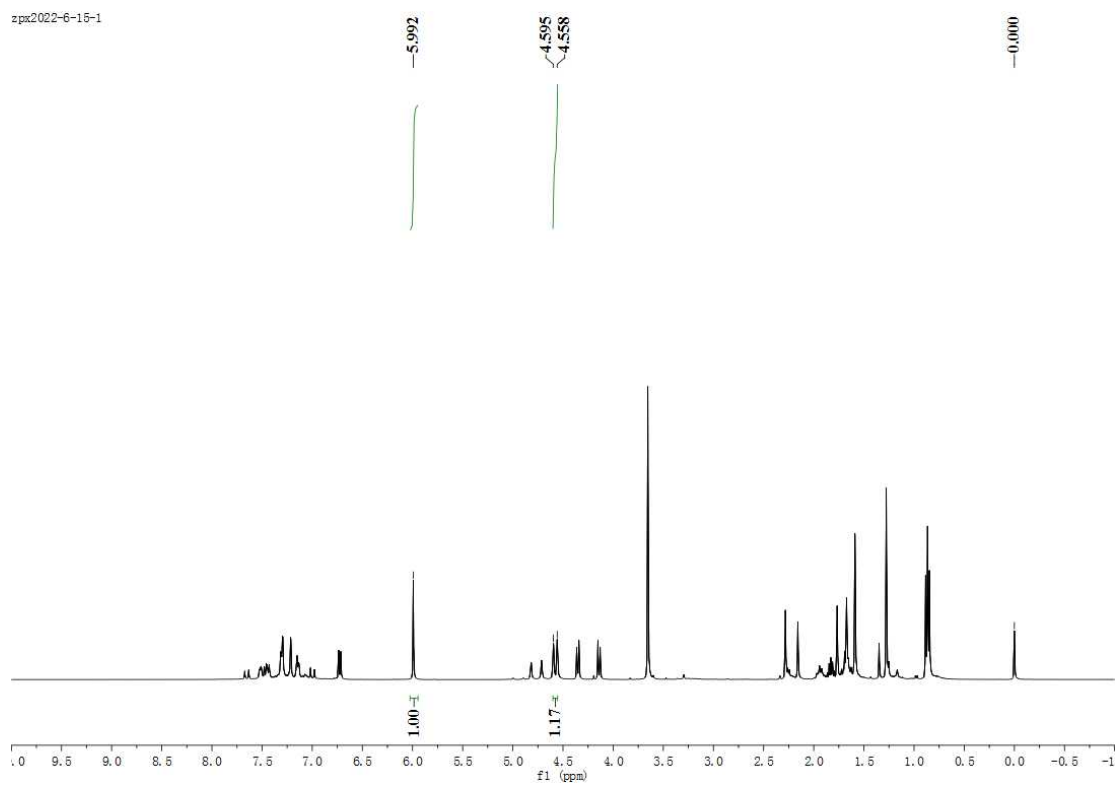


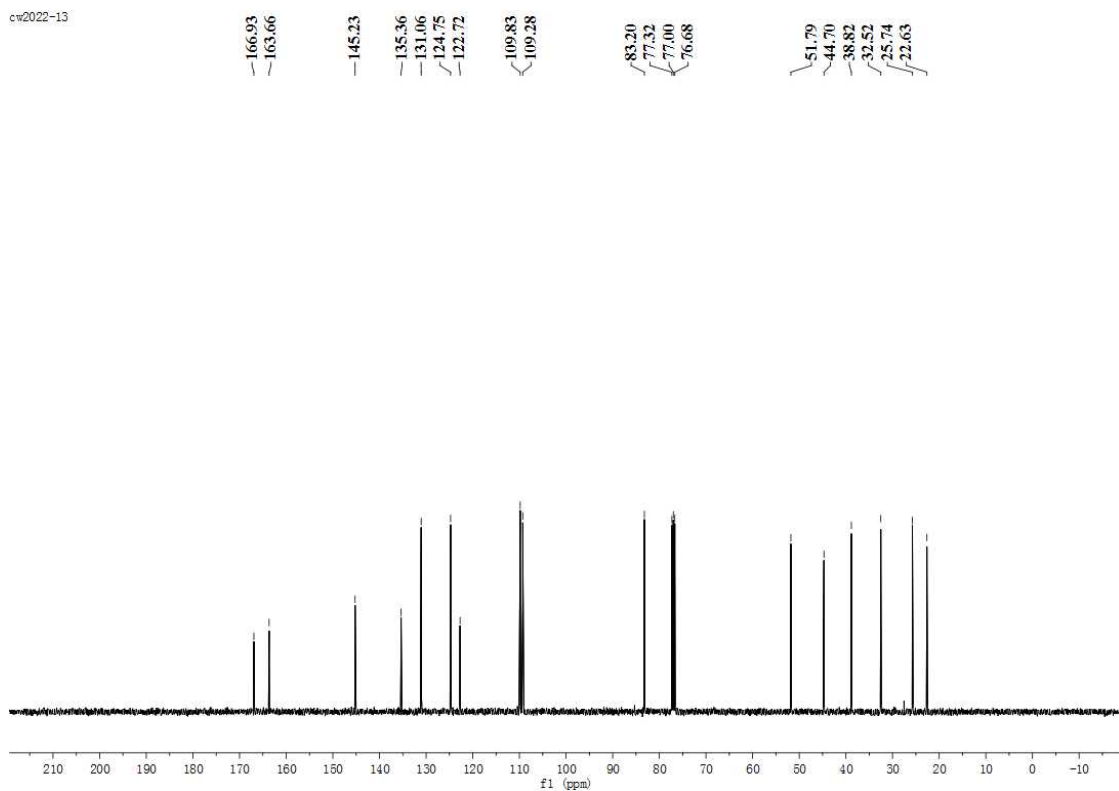
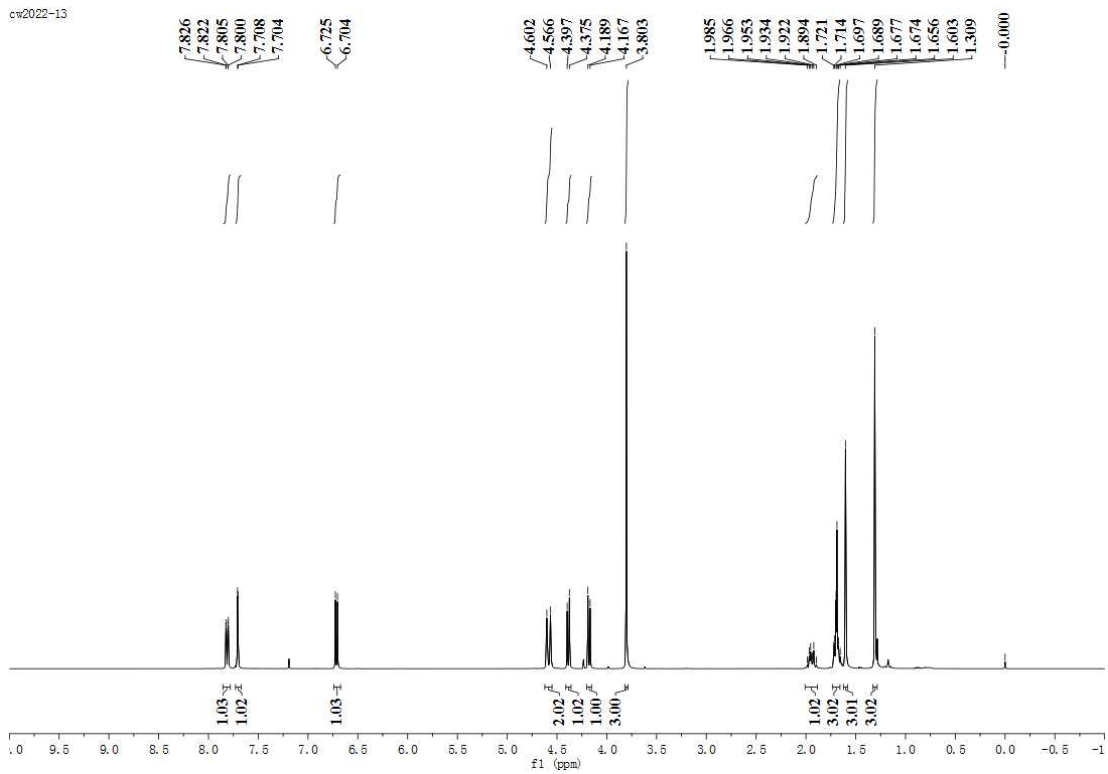
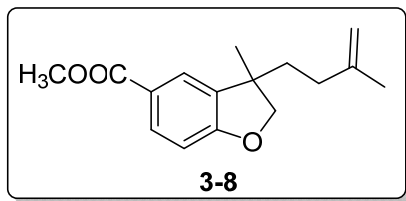
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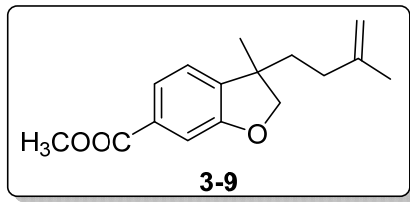




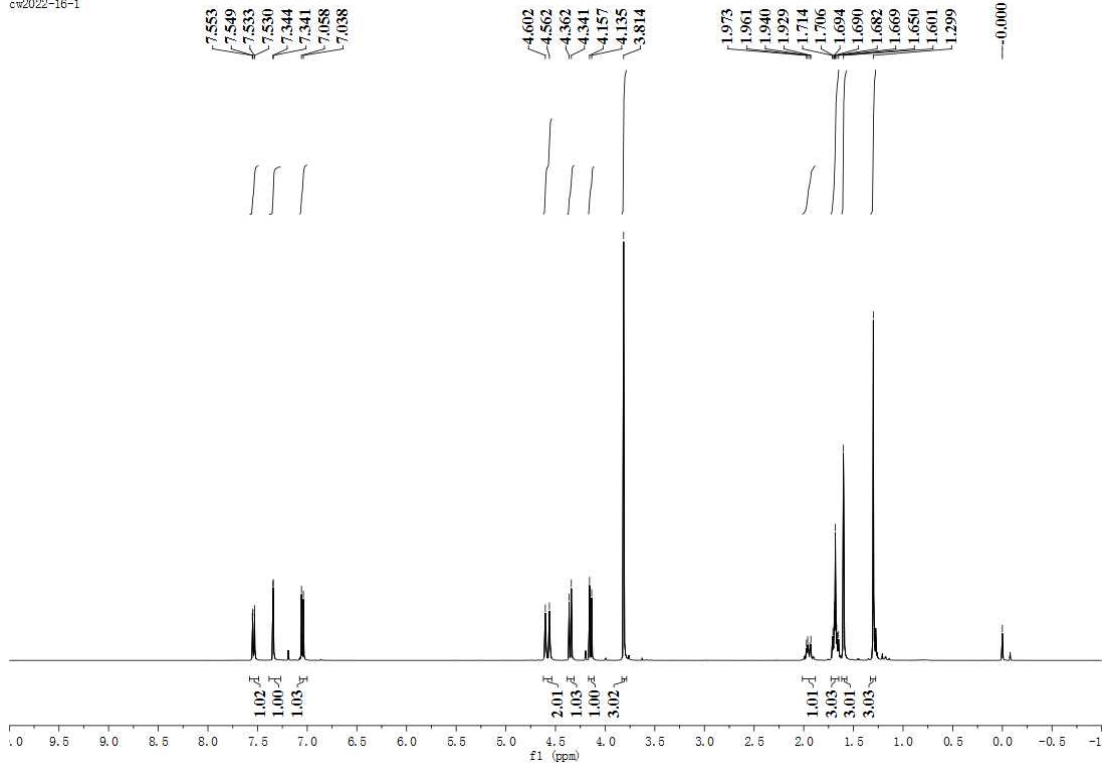
NMR yield: The yield was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.



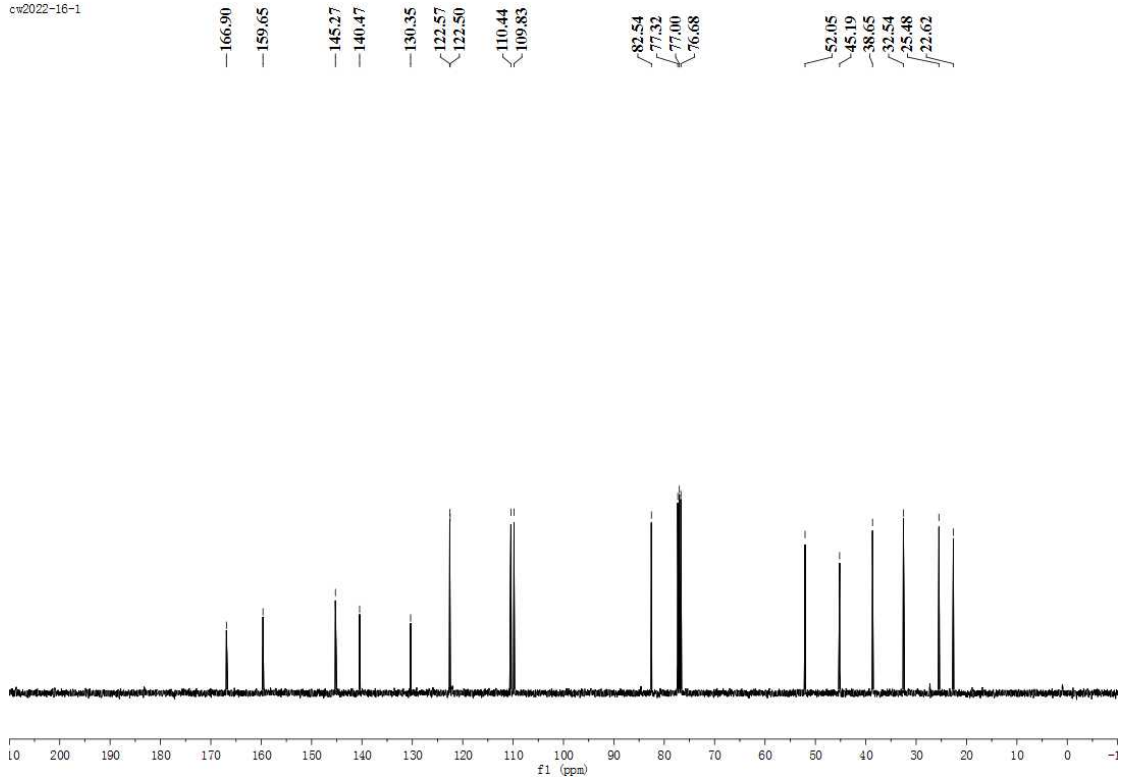


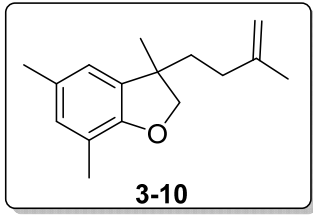


cw2022-16-1

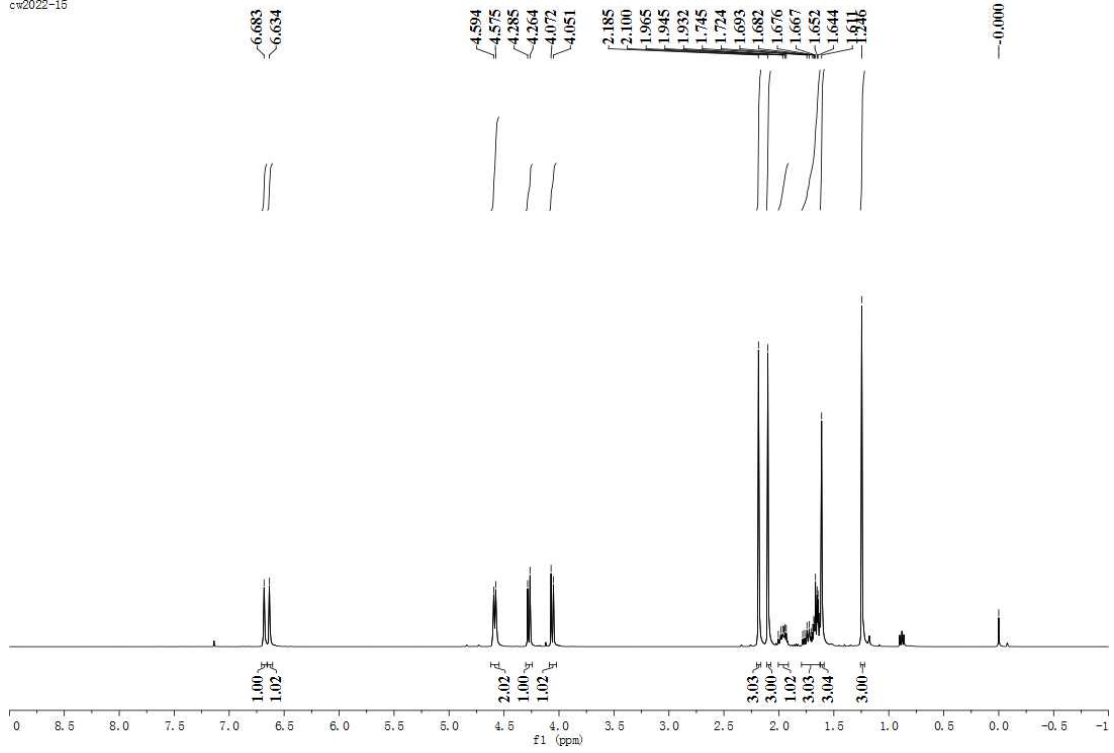


cw2022-16-1

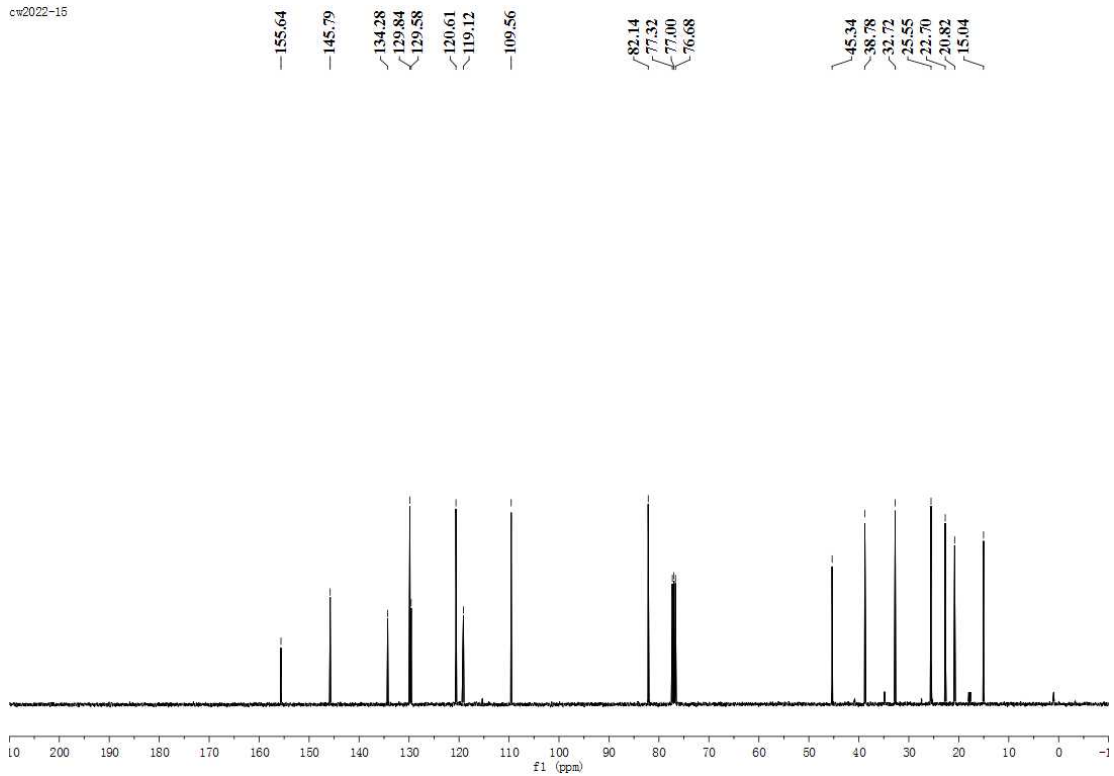


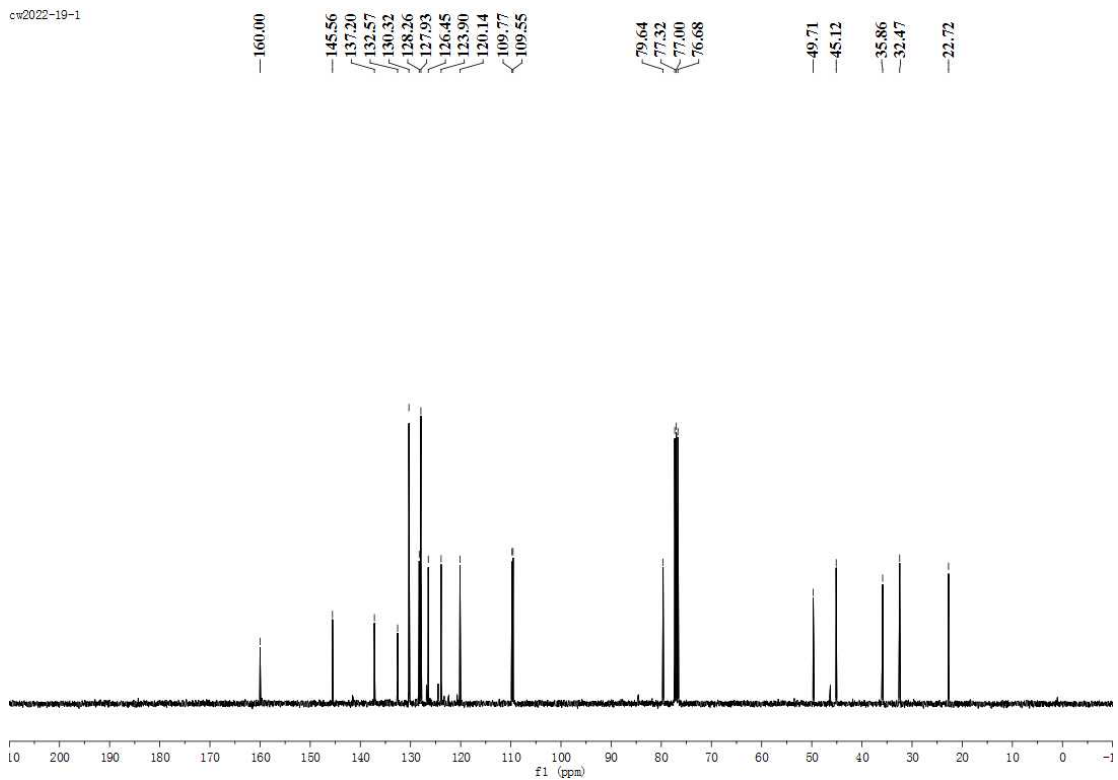
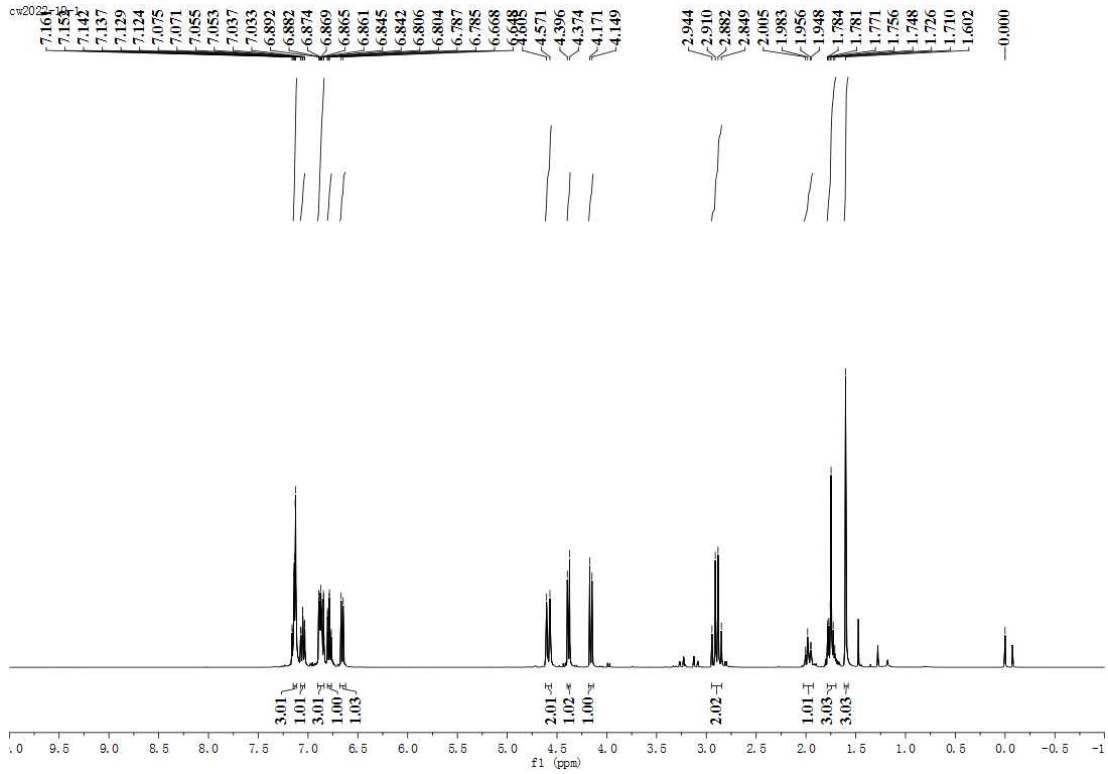
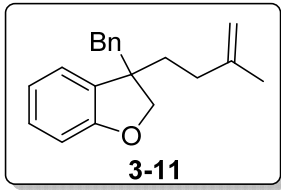


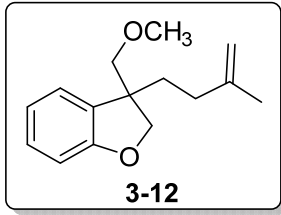
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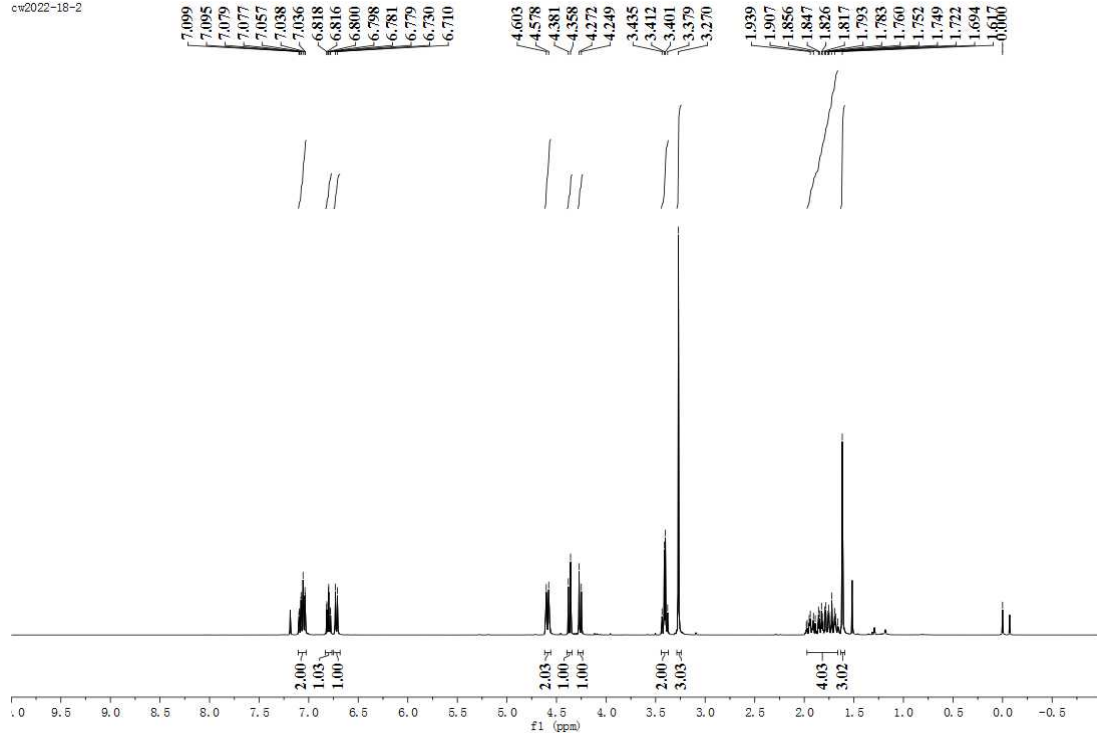
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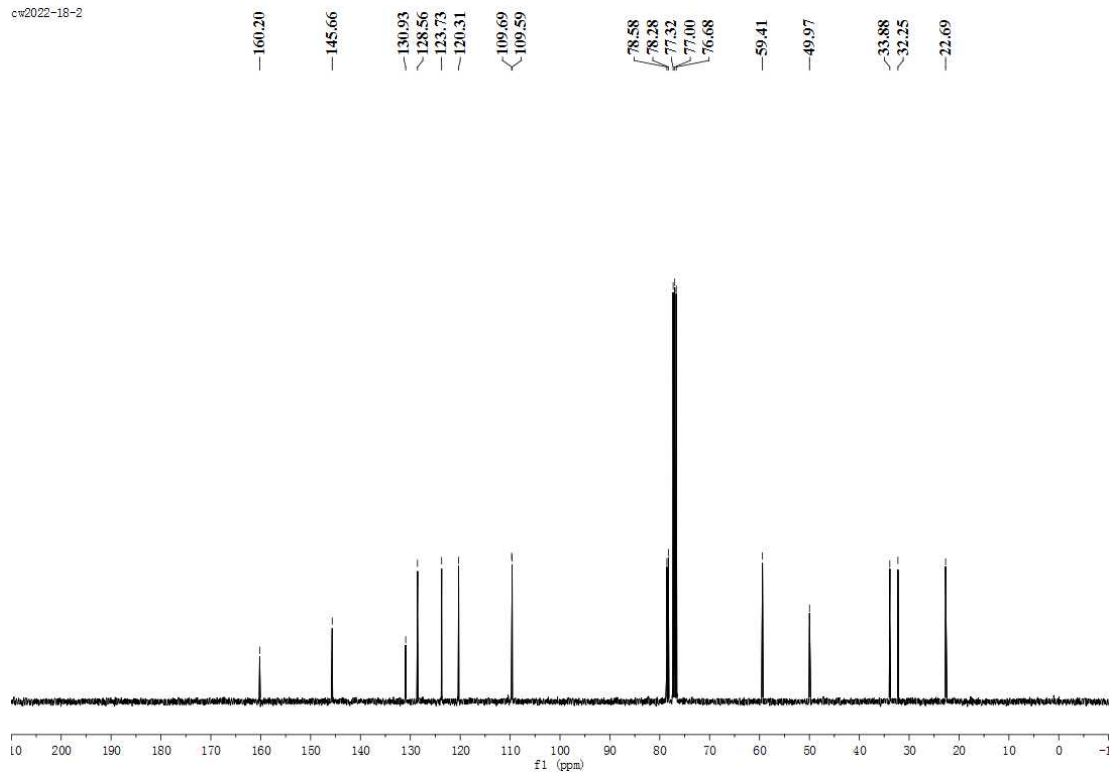


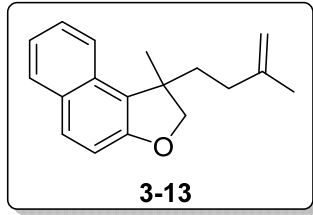


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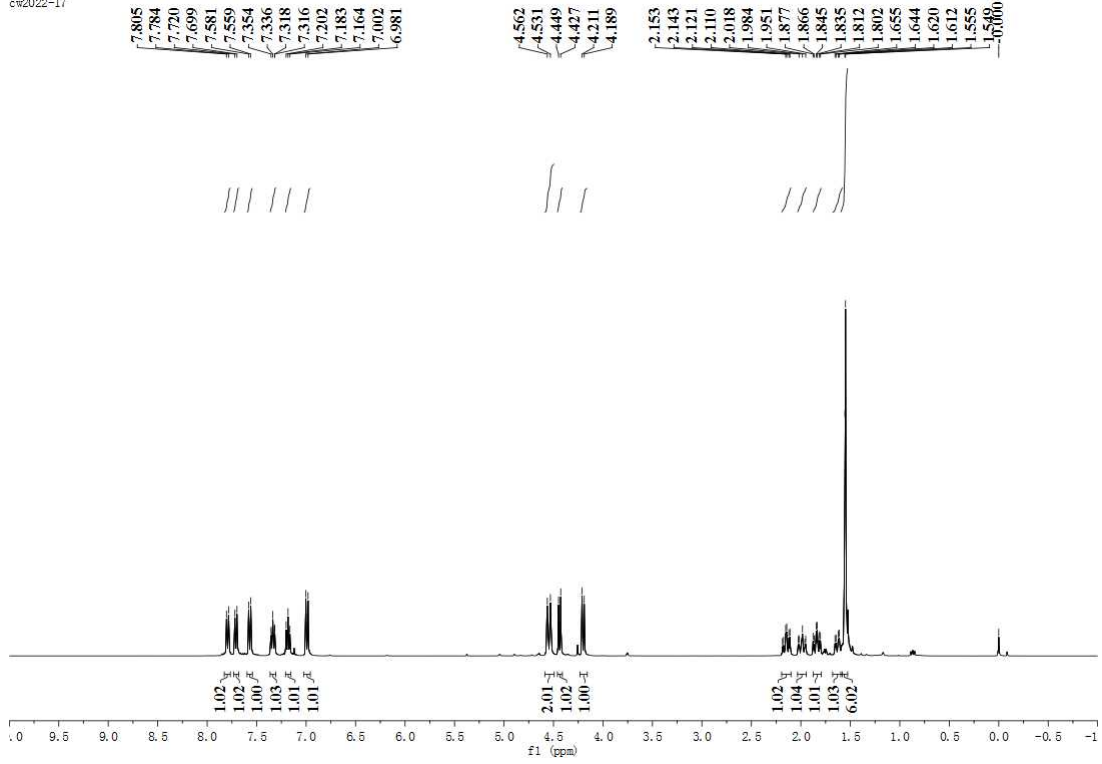


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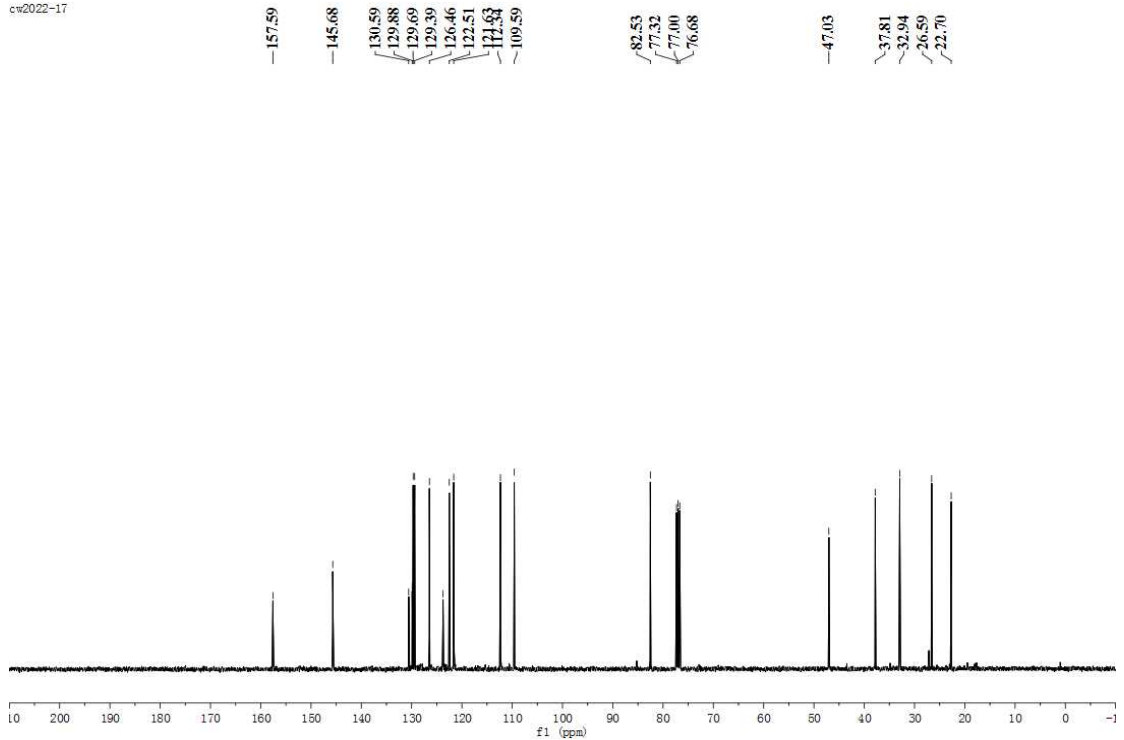


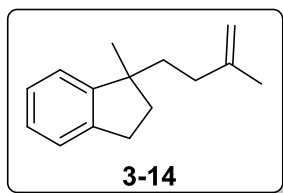


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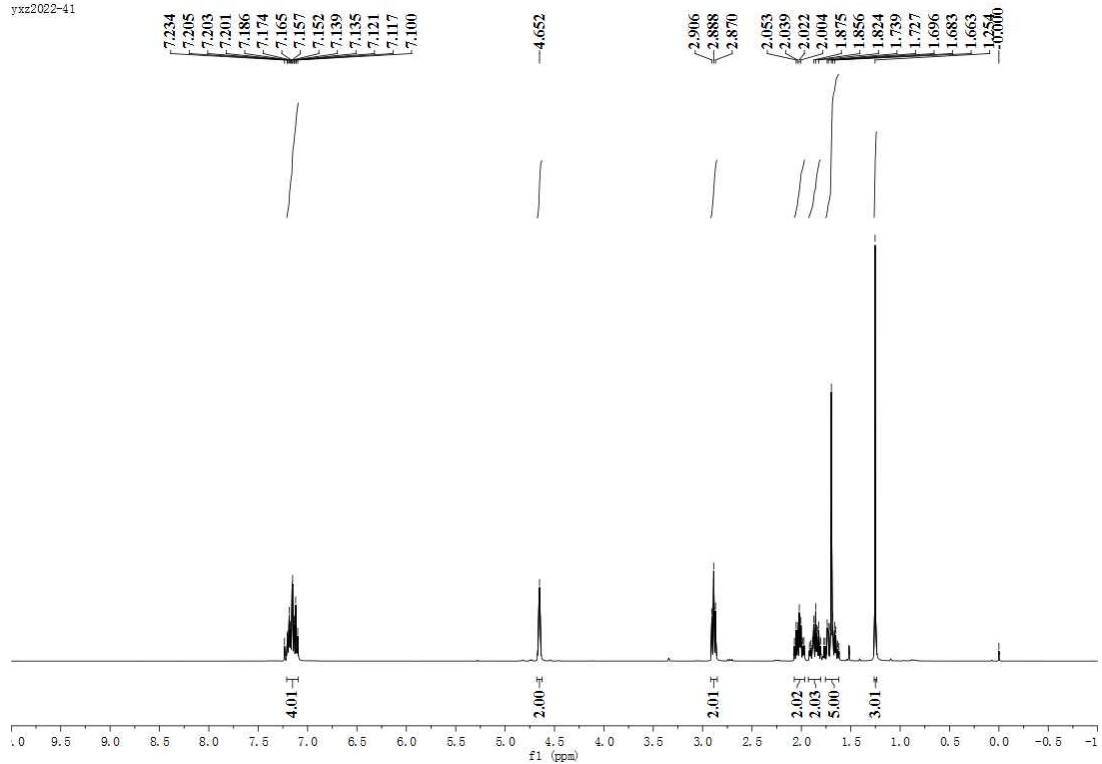


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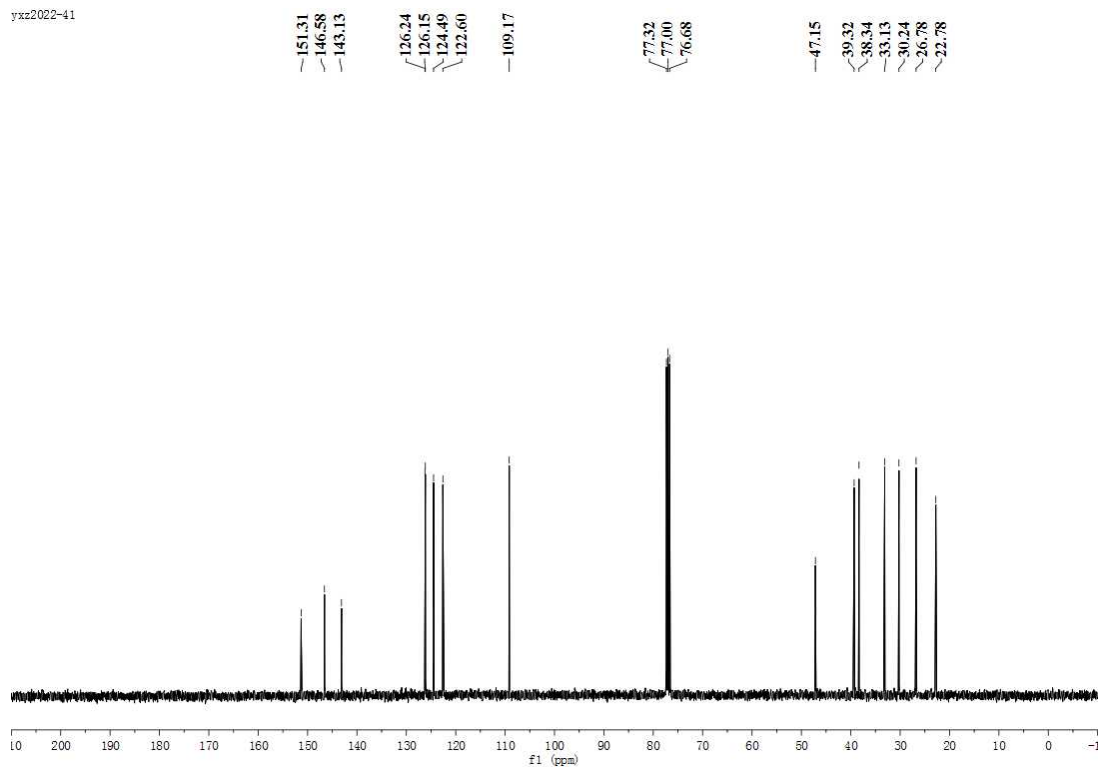


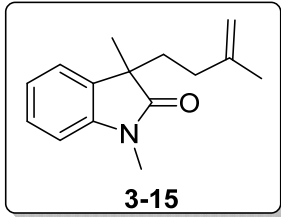


yxz2022-41

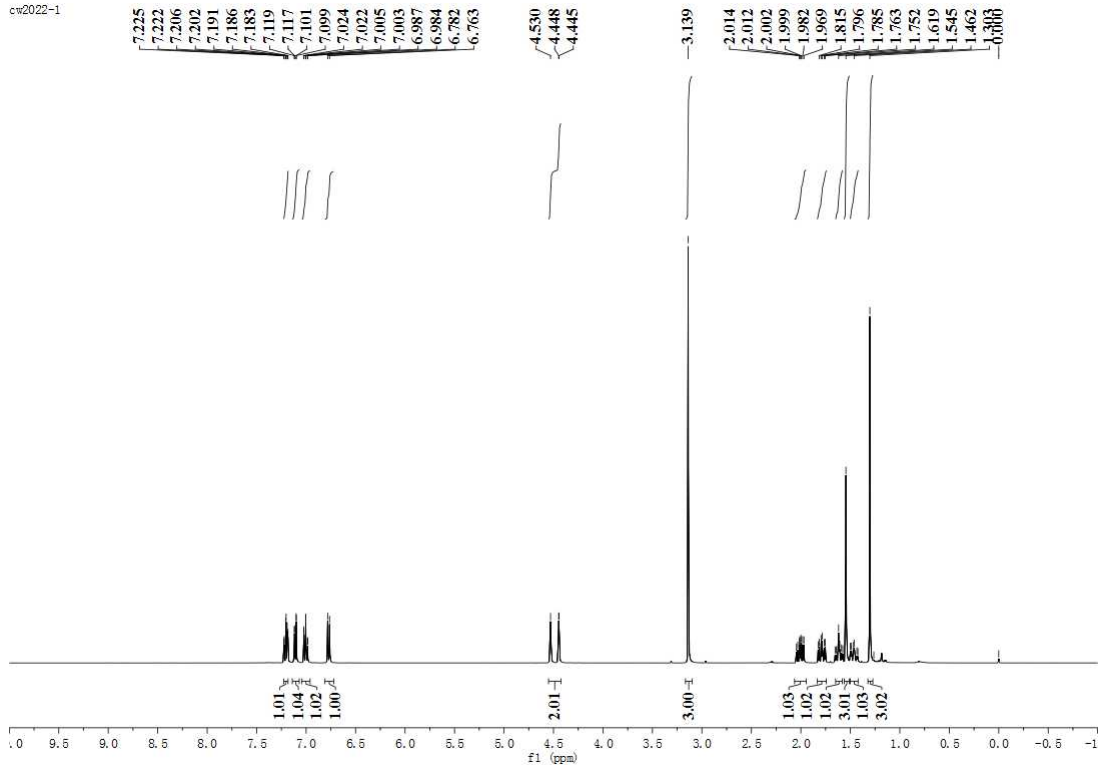


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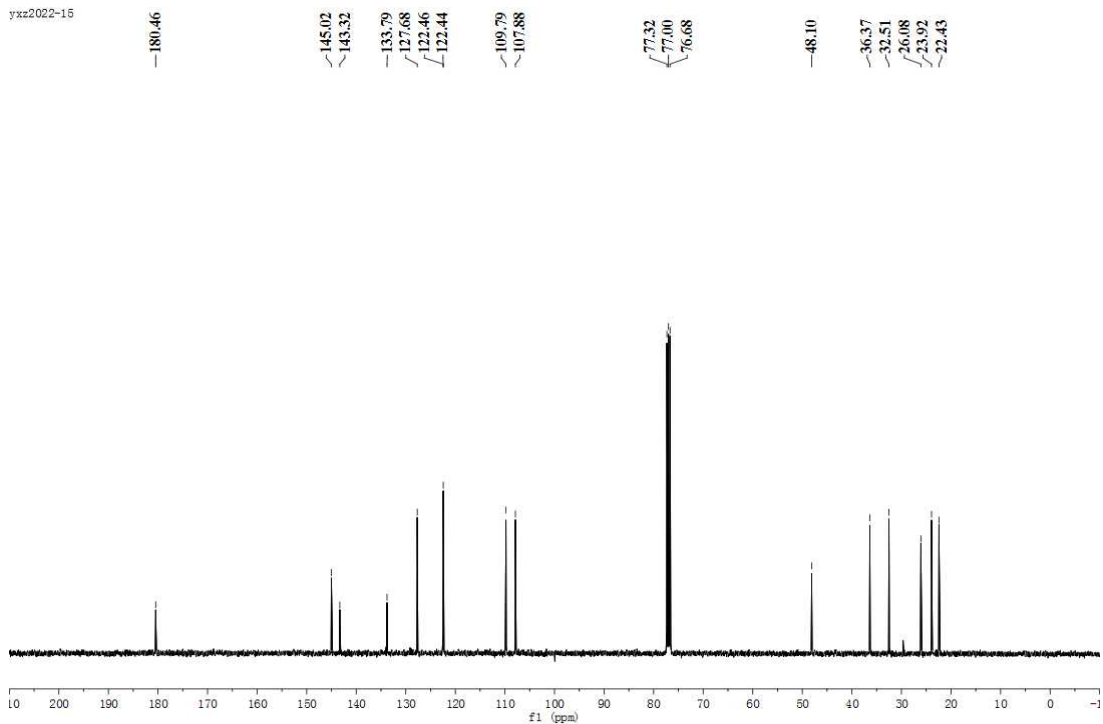


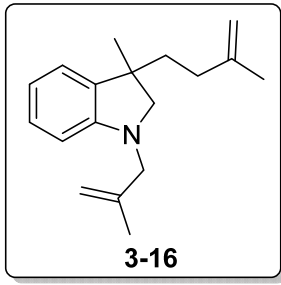


cw2022-1

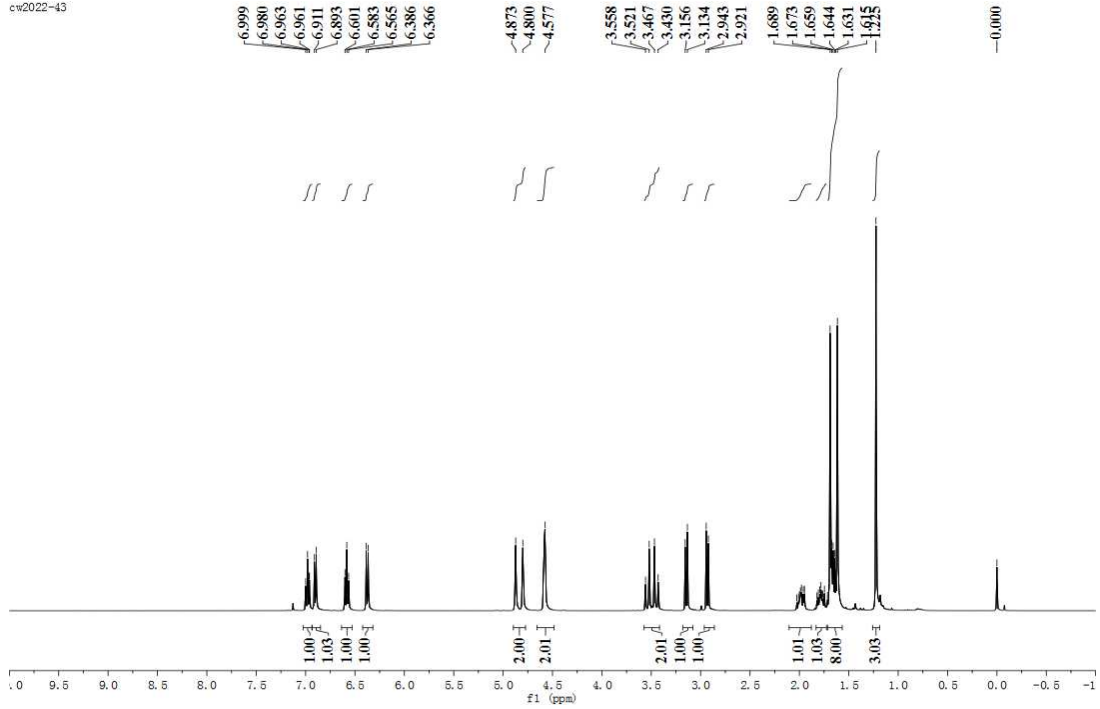


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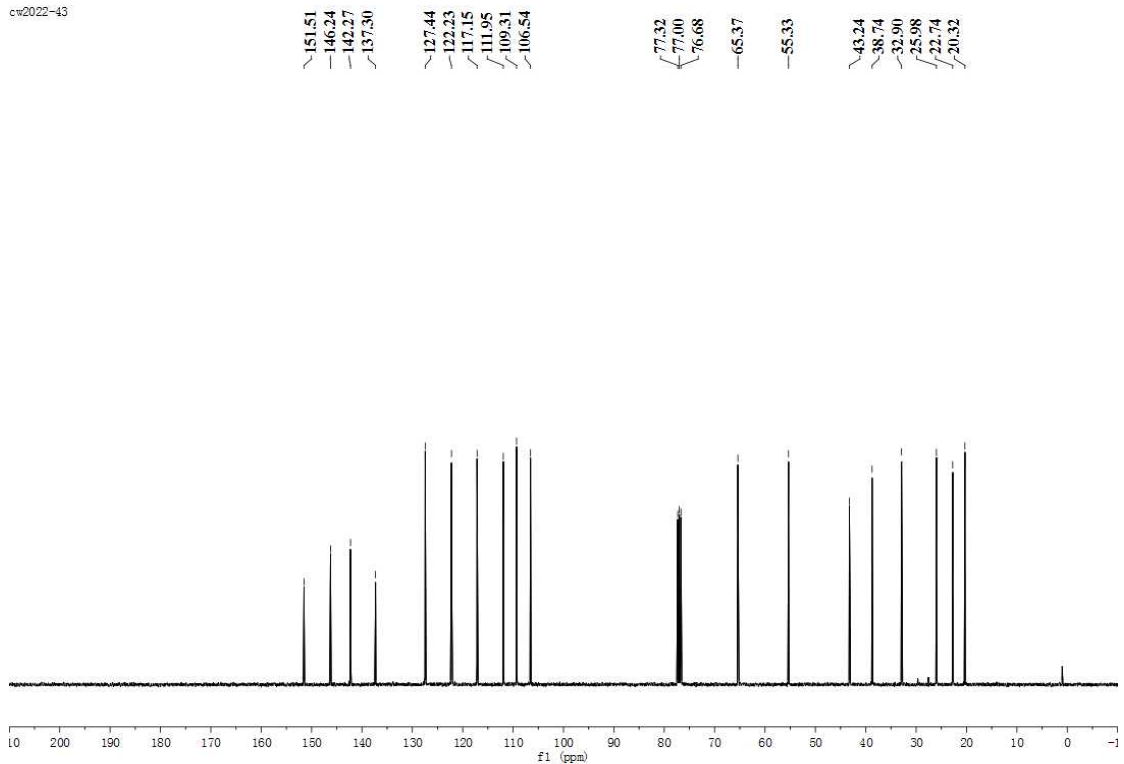


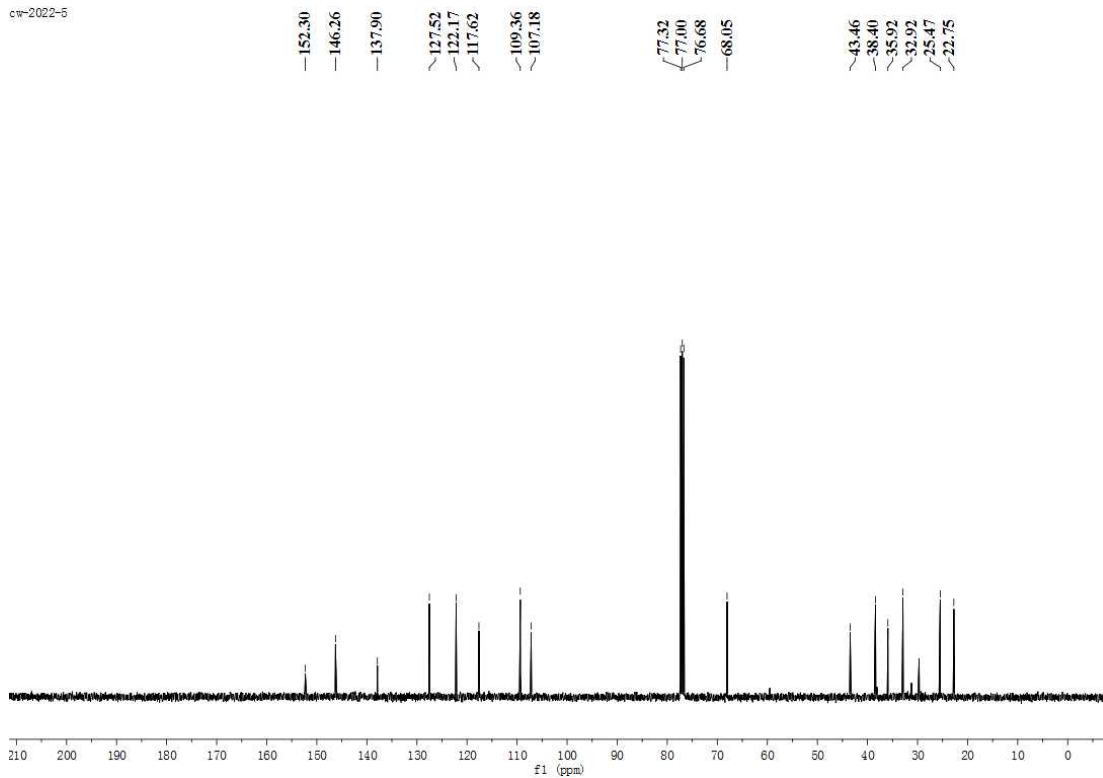
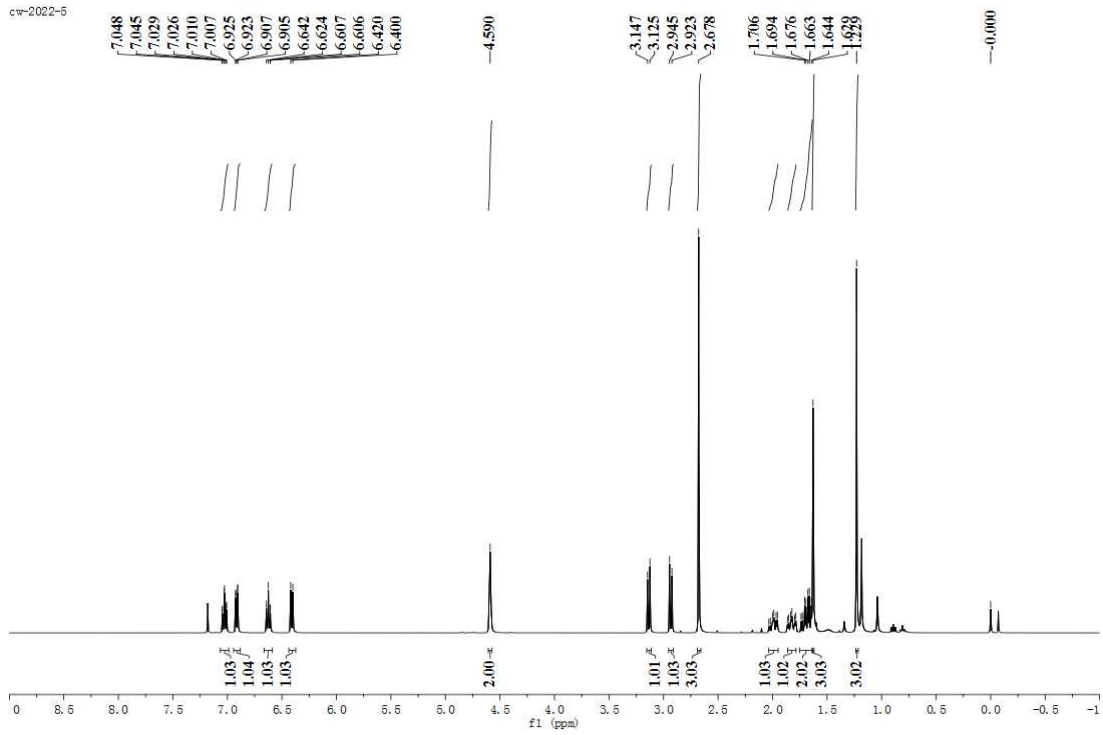
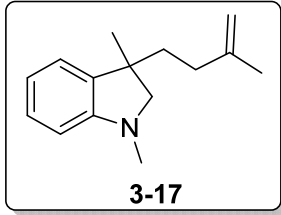


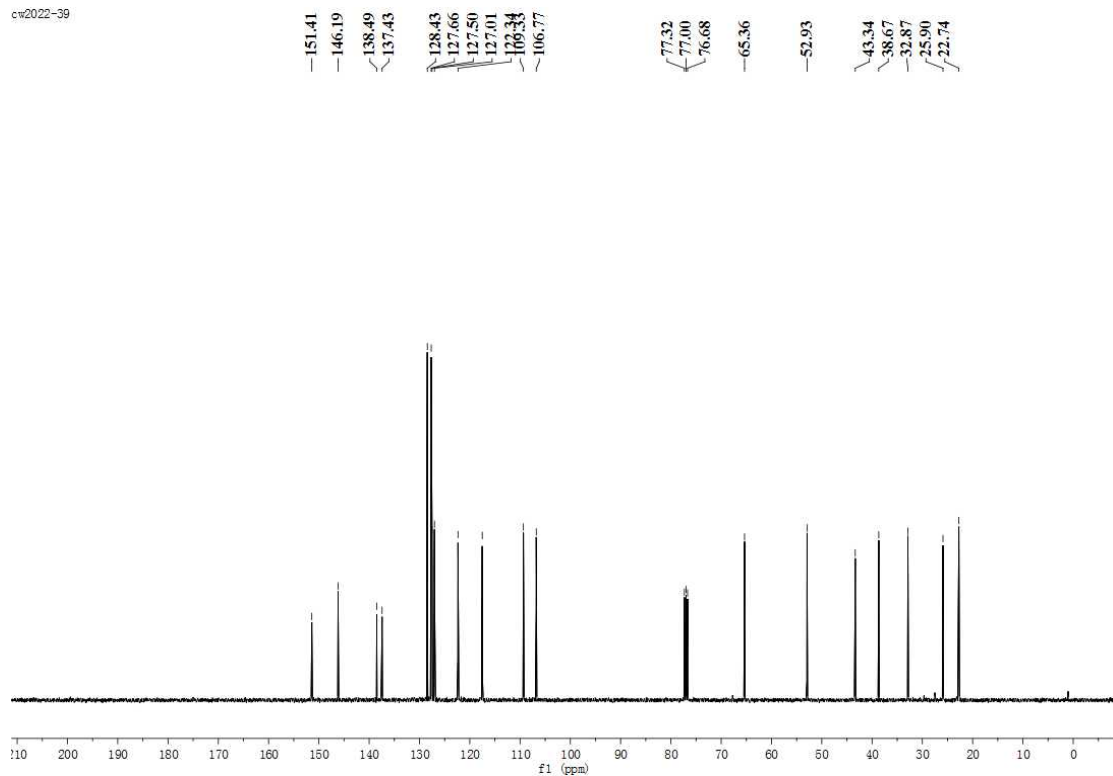
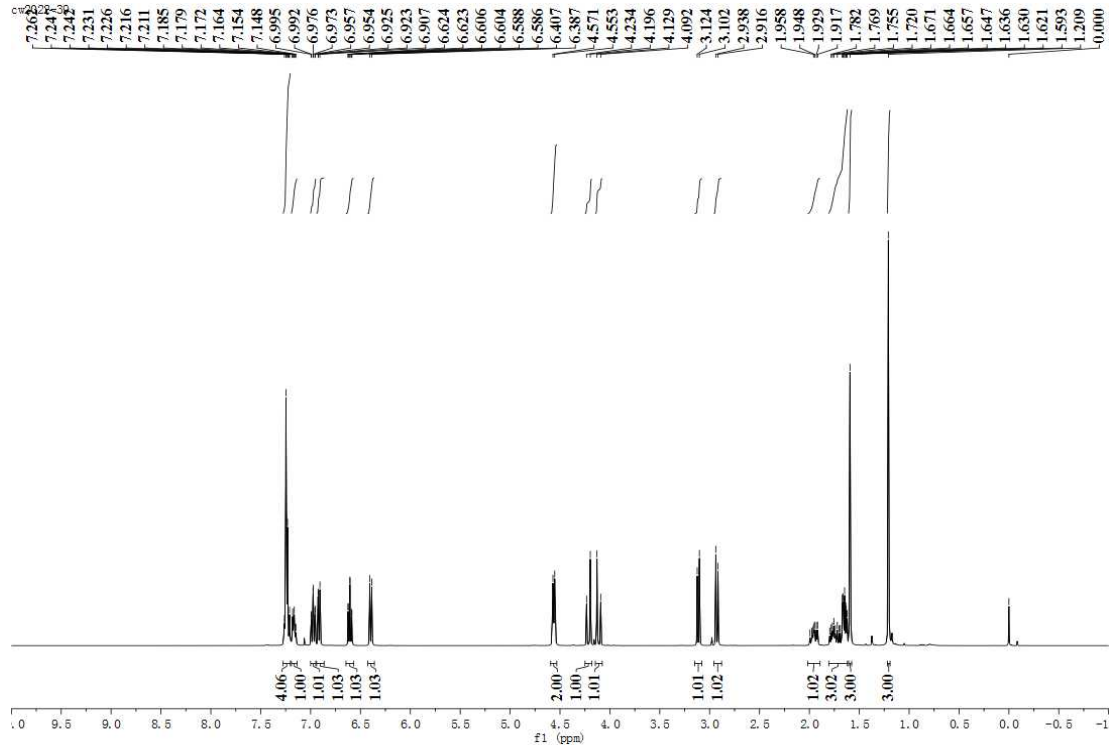
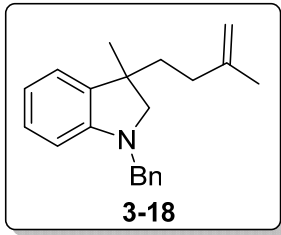
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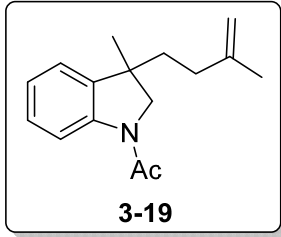


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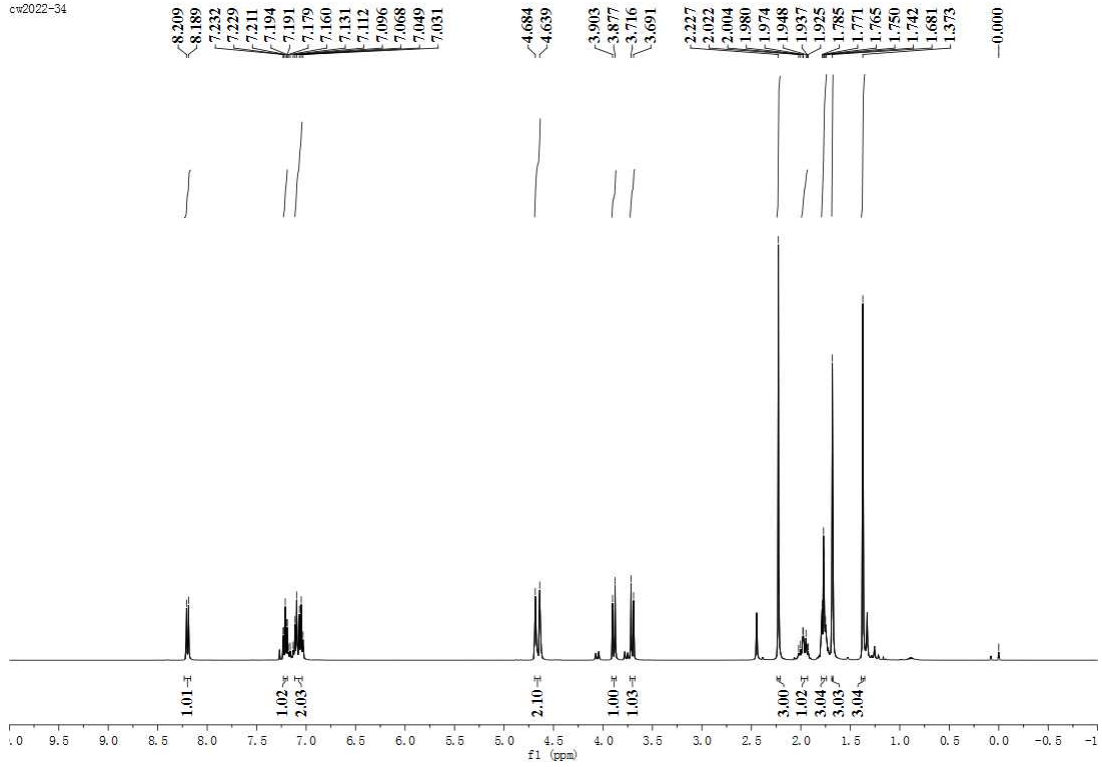




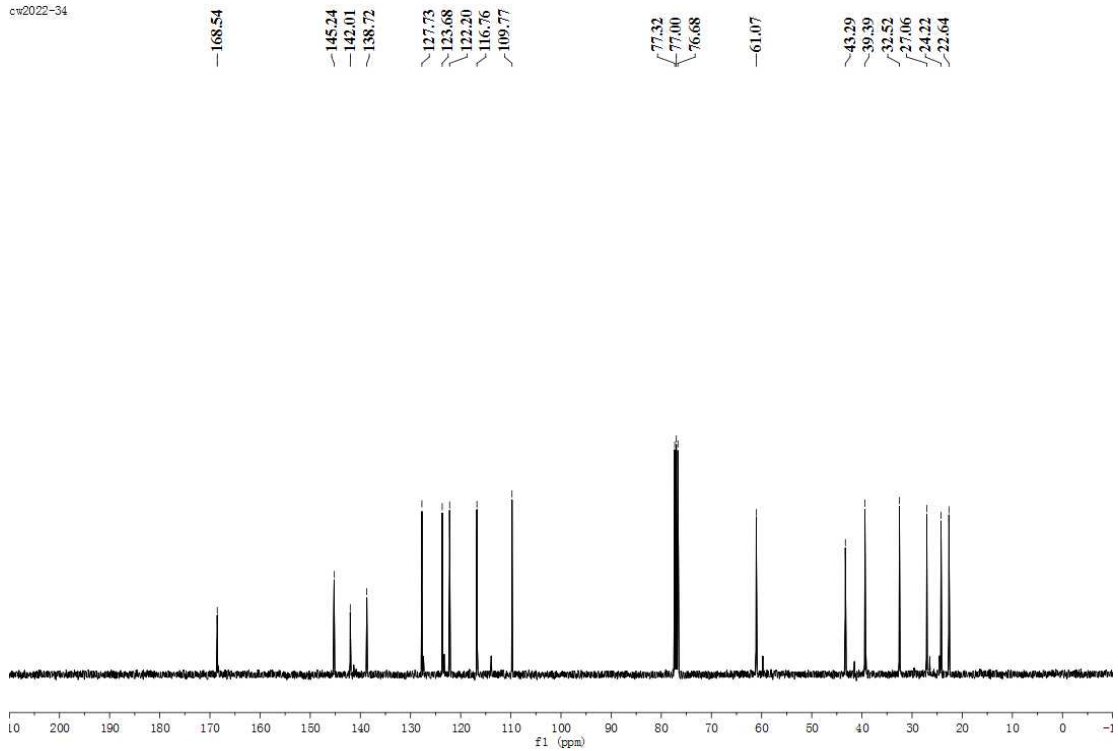


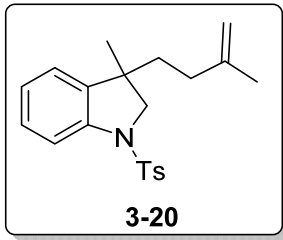


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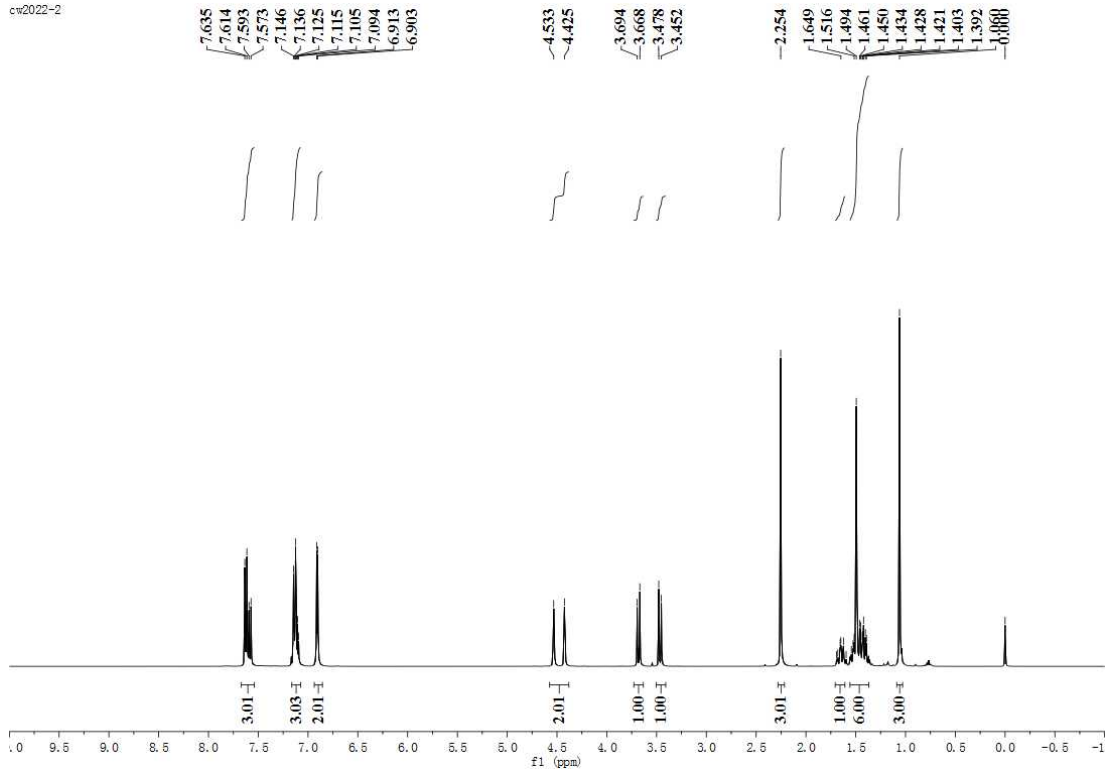


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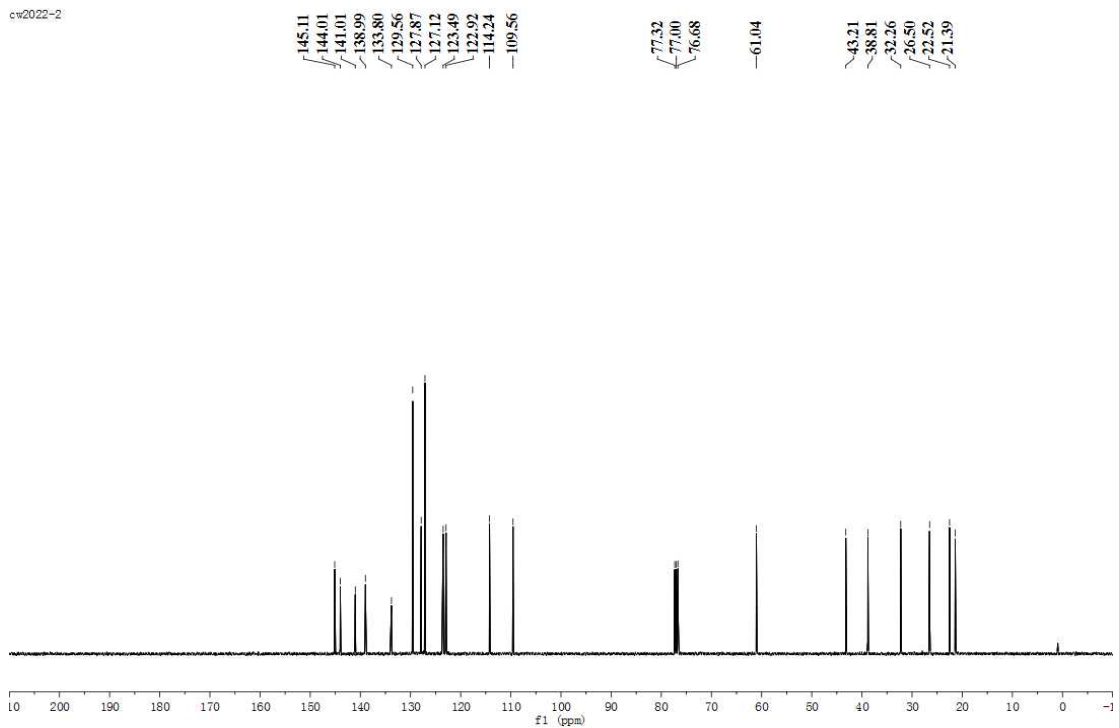


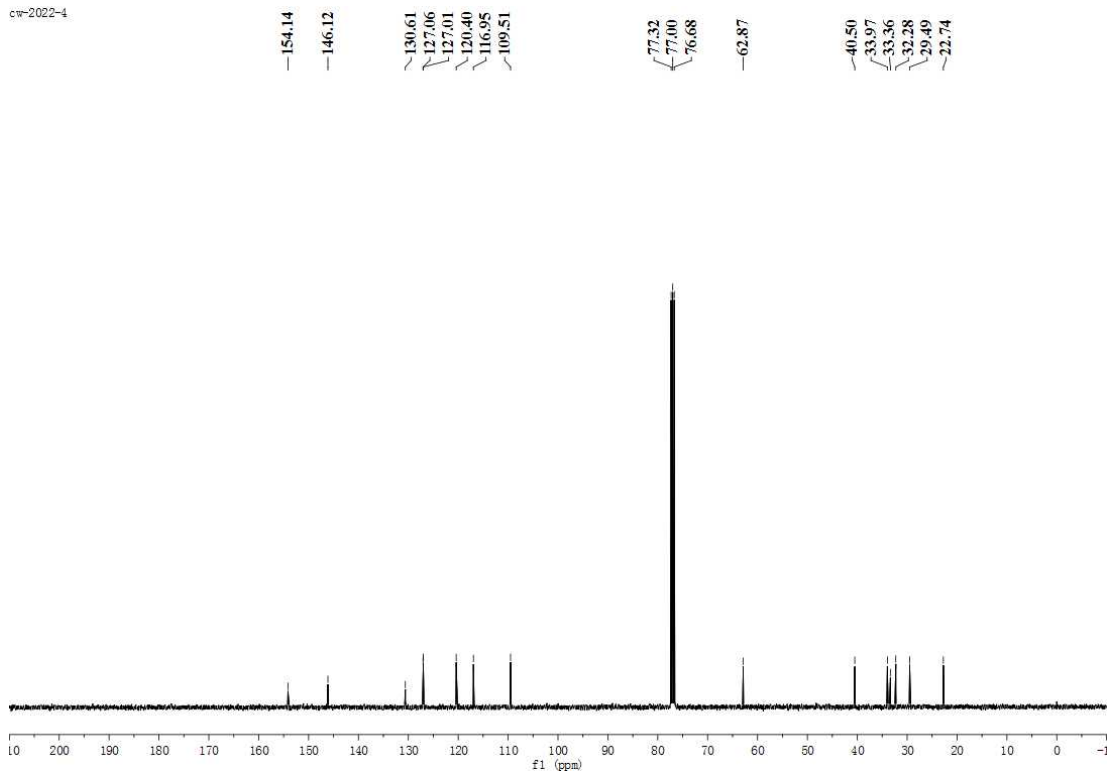
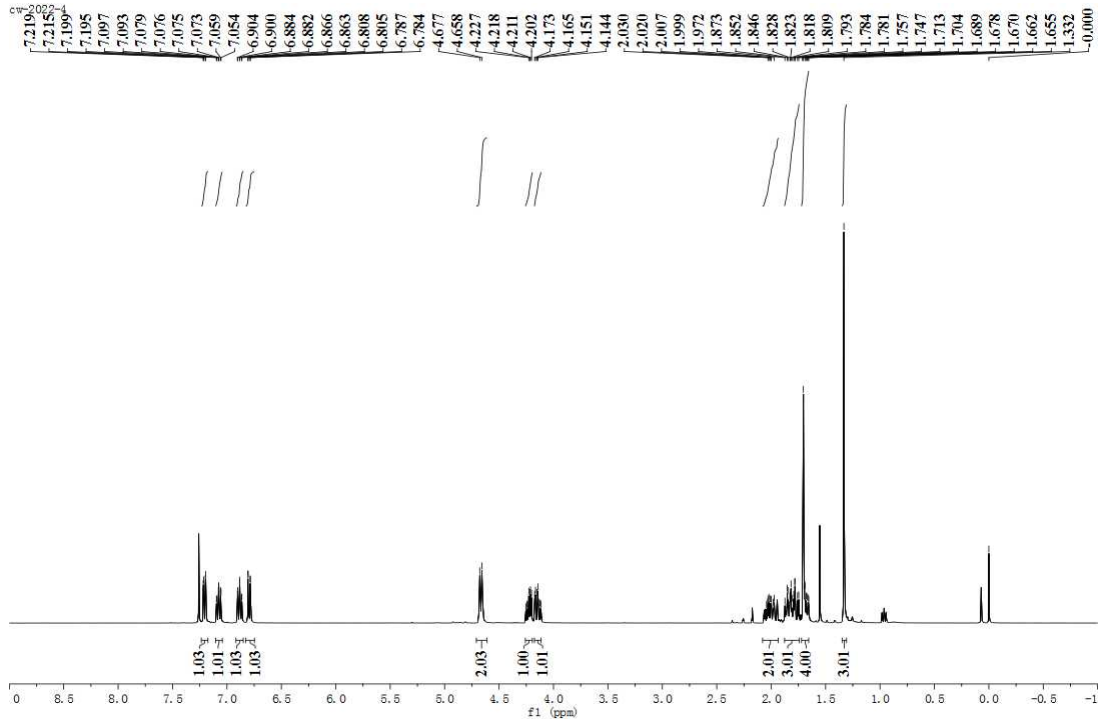
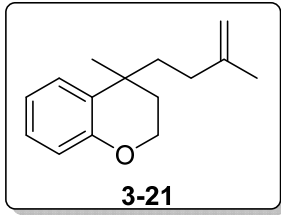


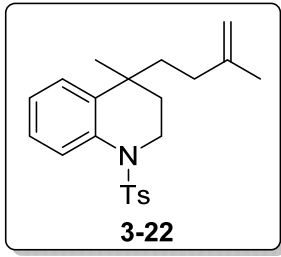
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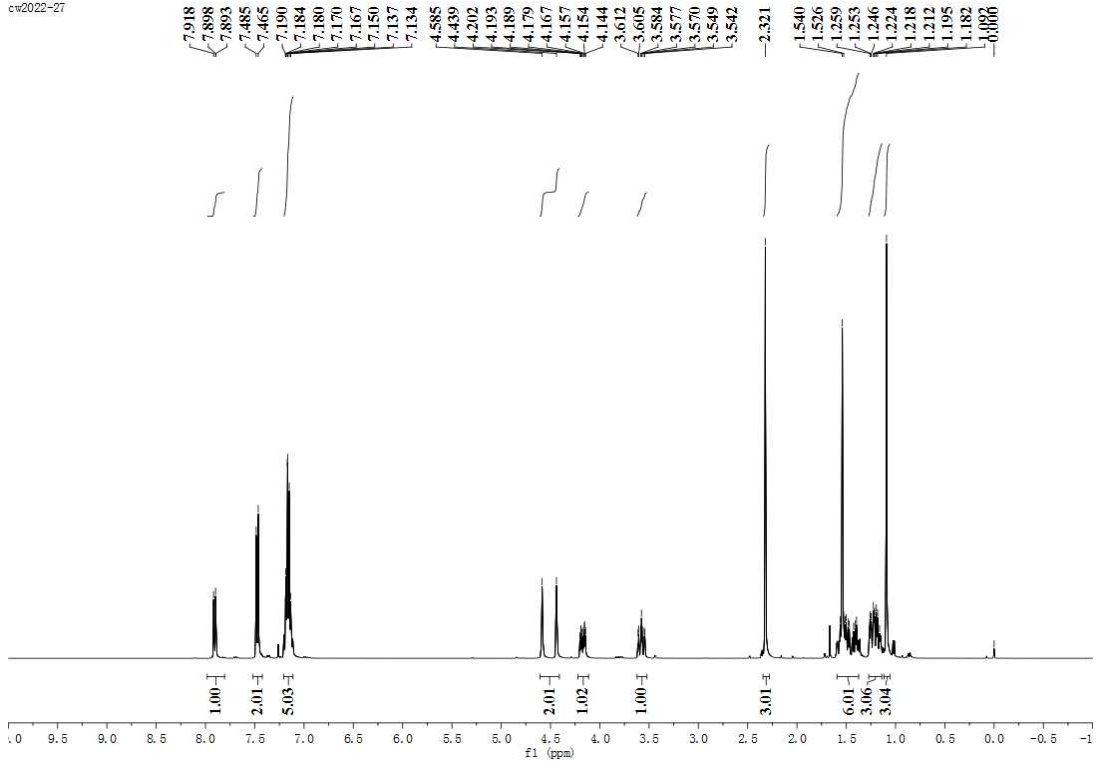
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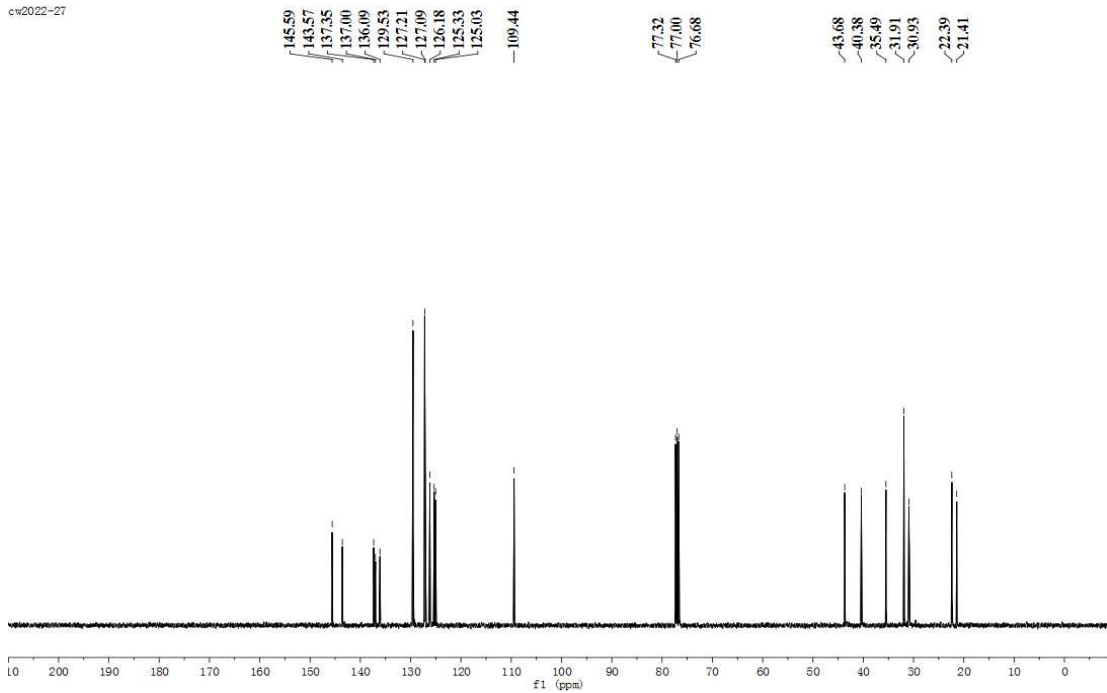


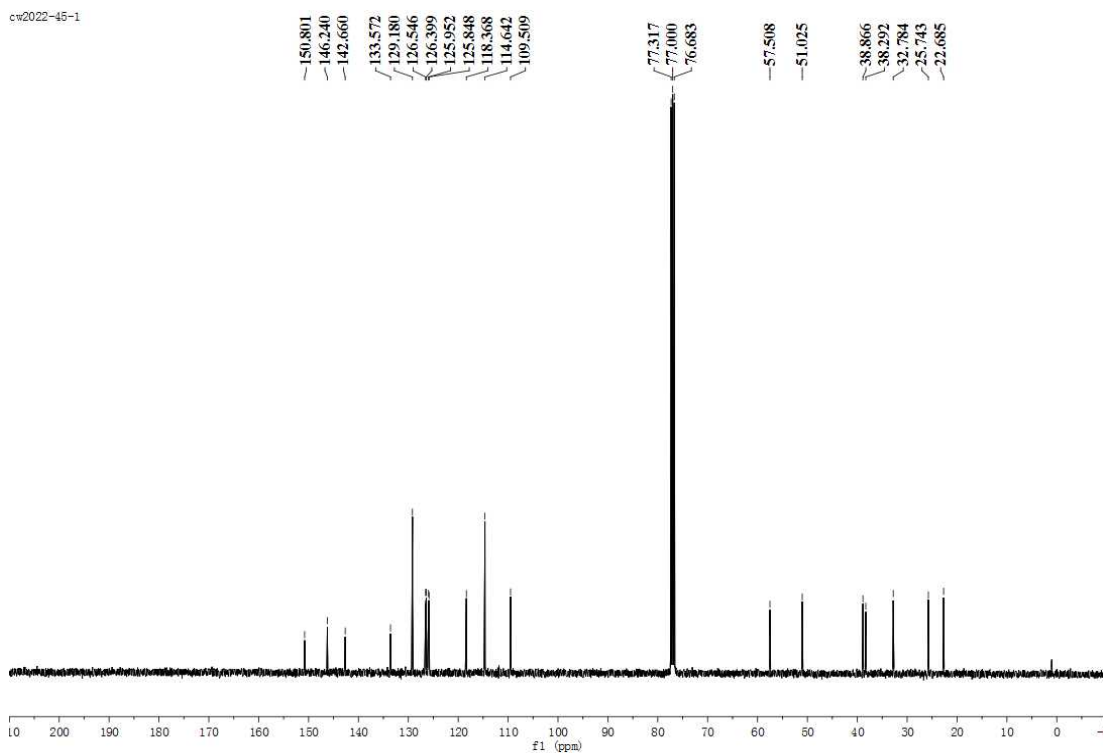
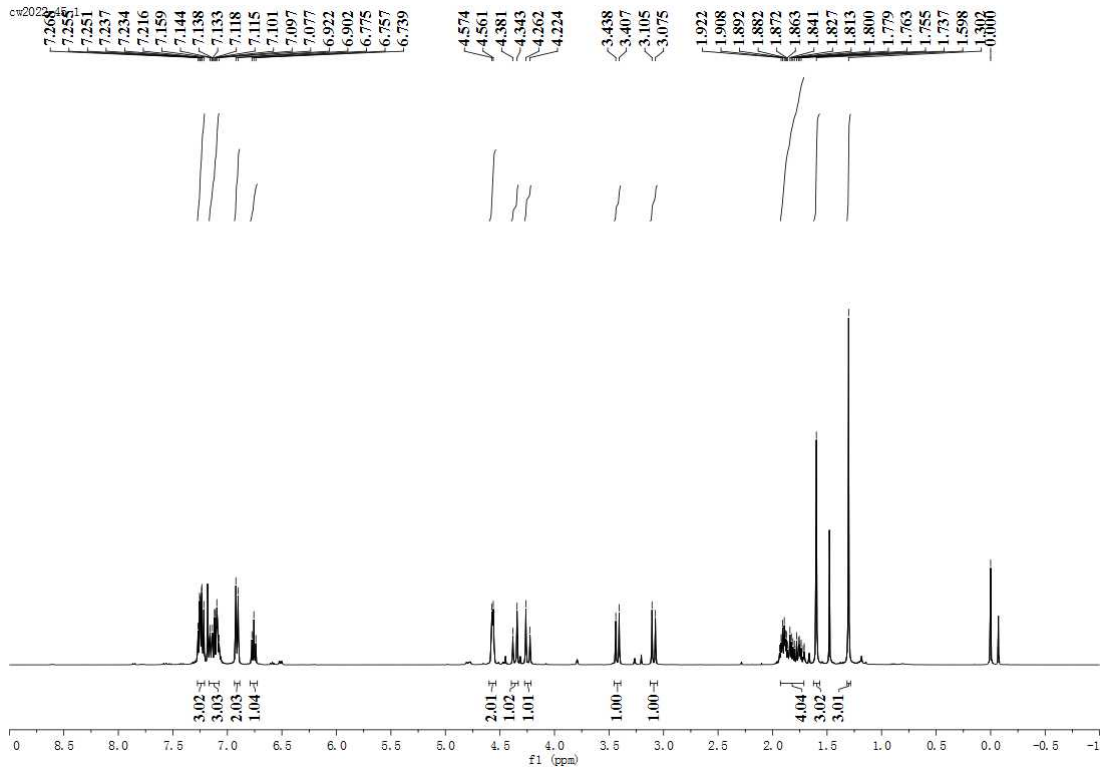
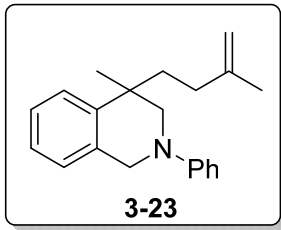


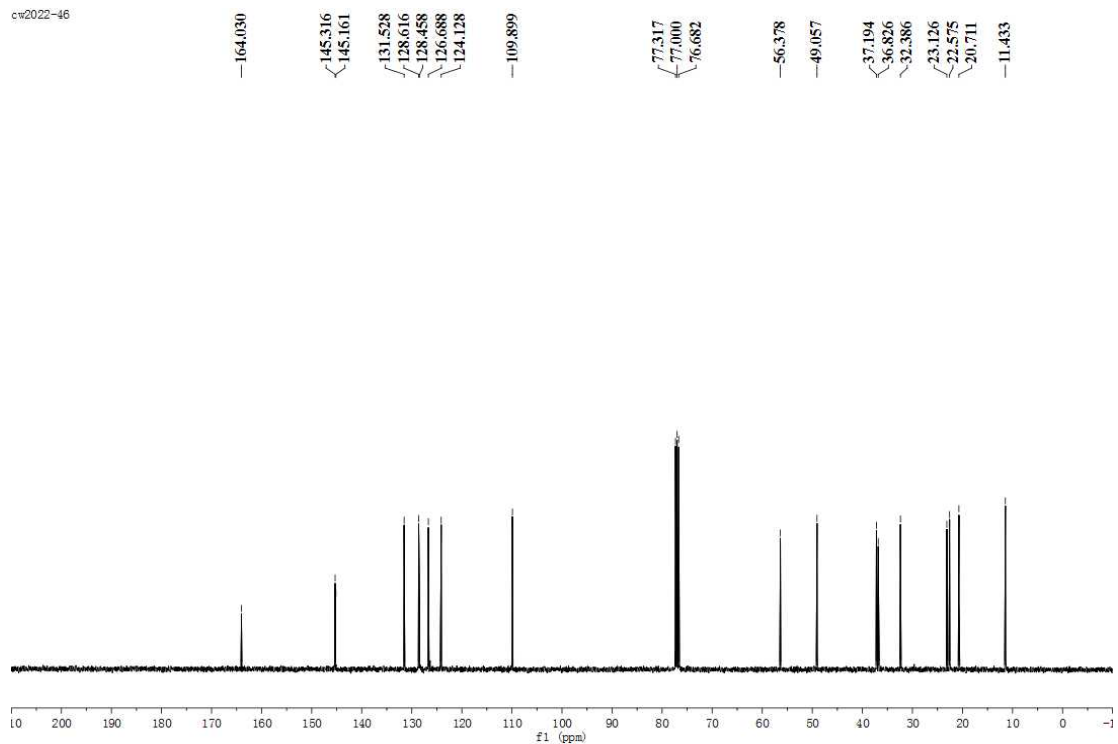
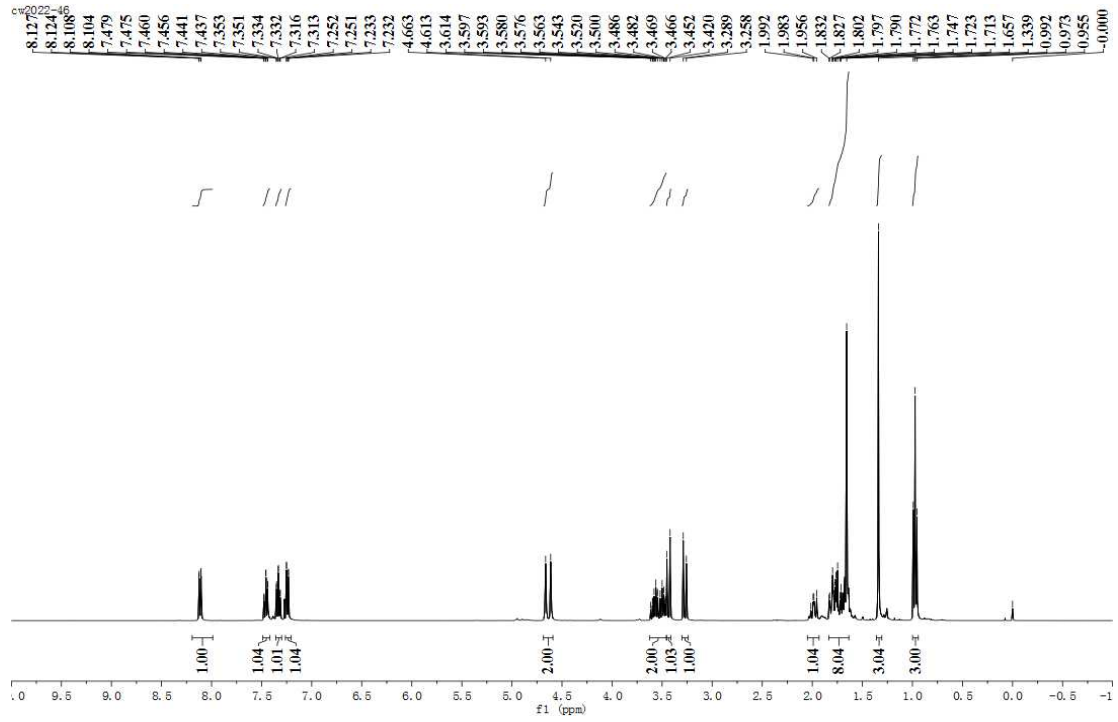
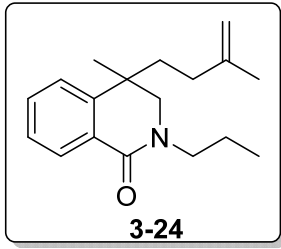
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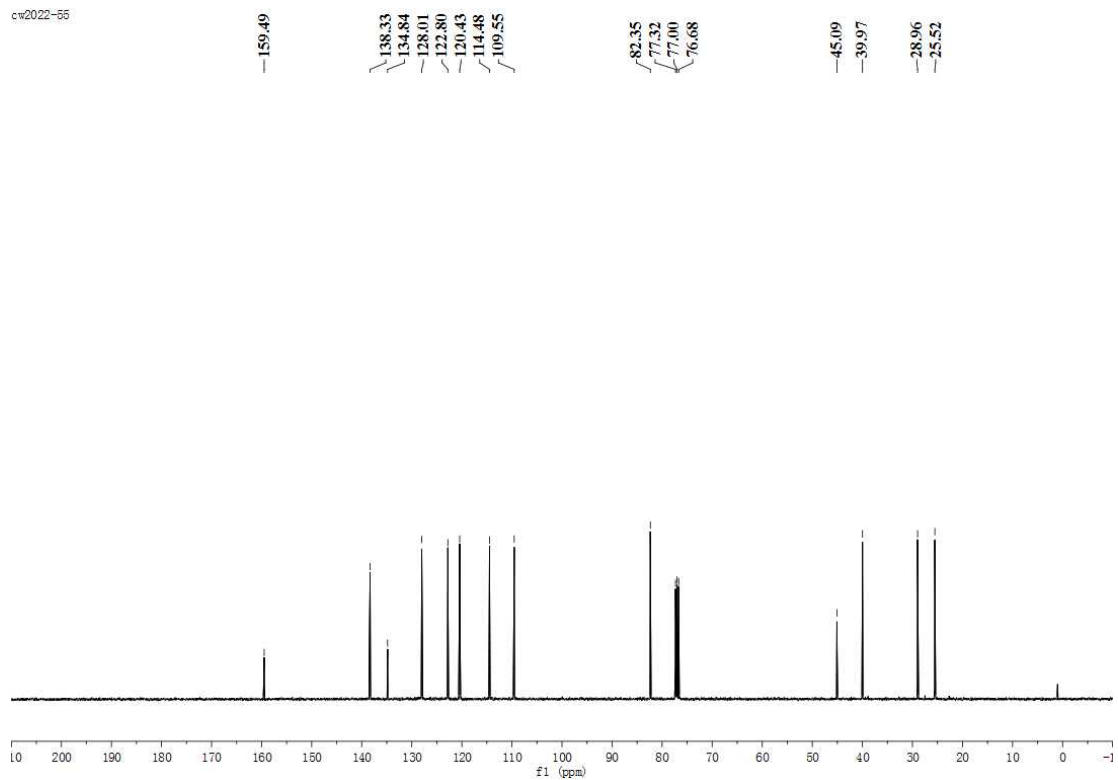
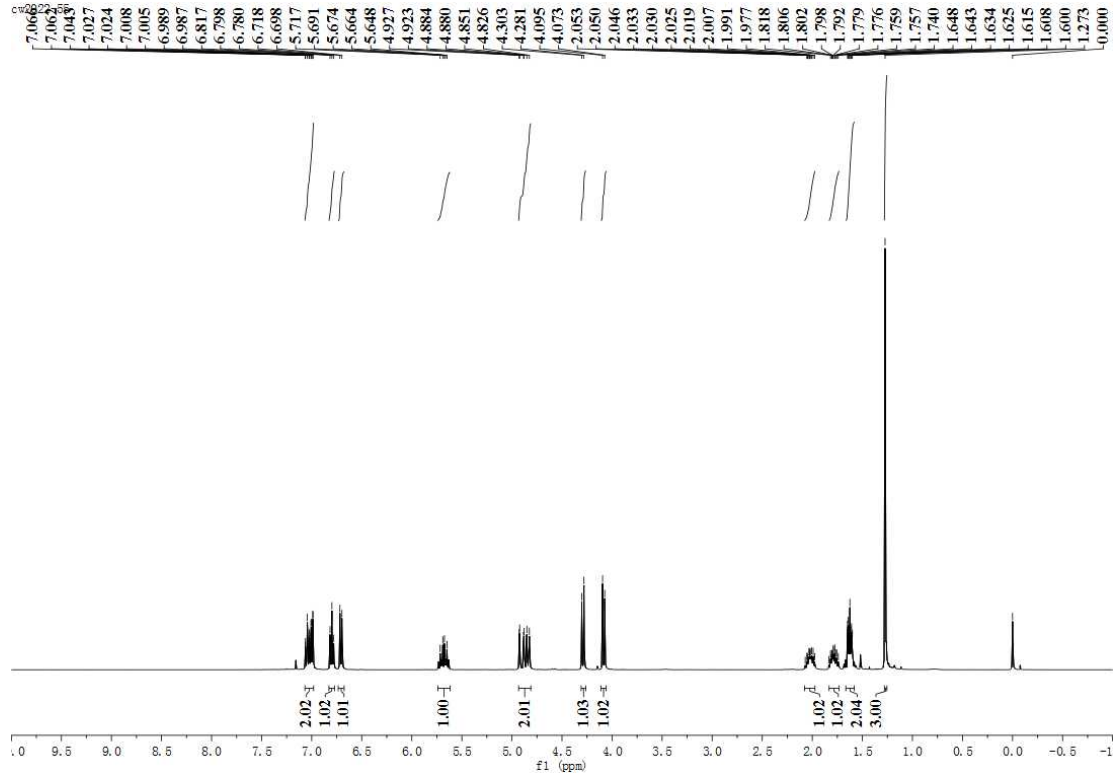
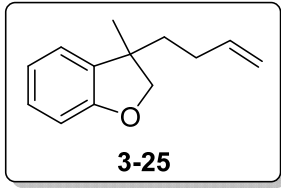


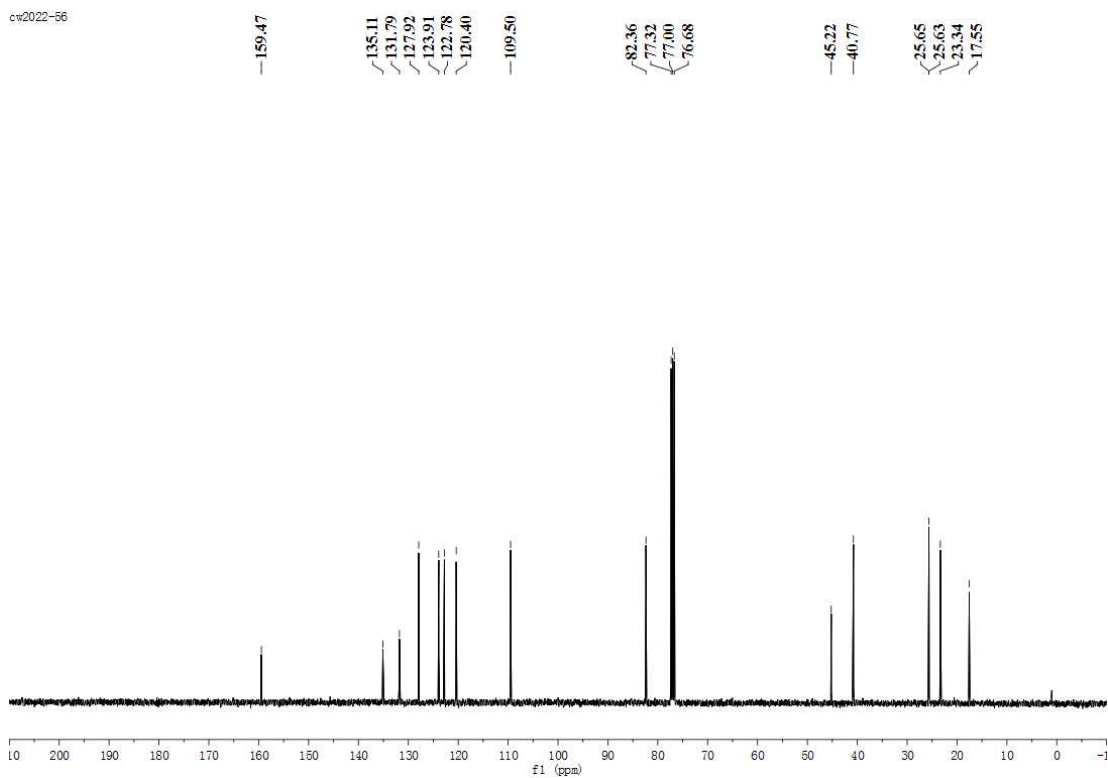
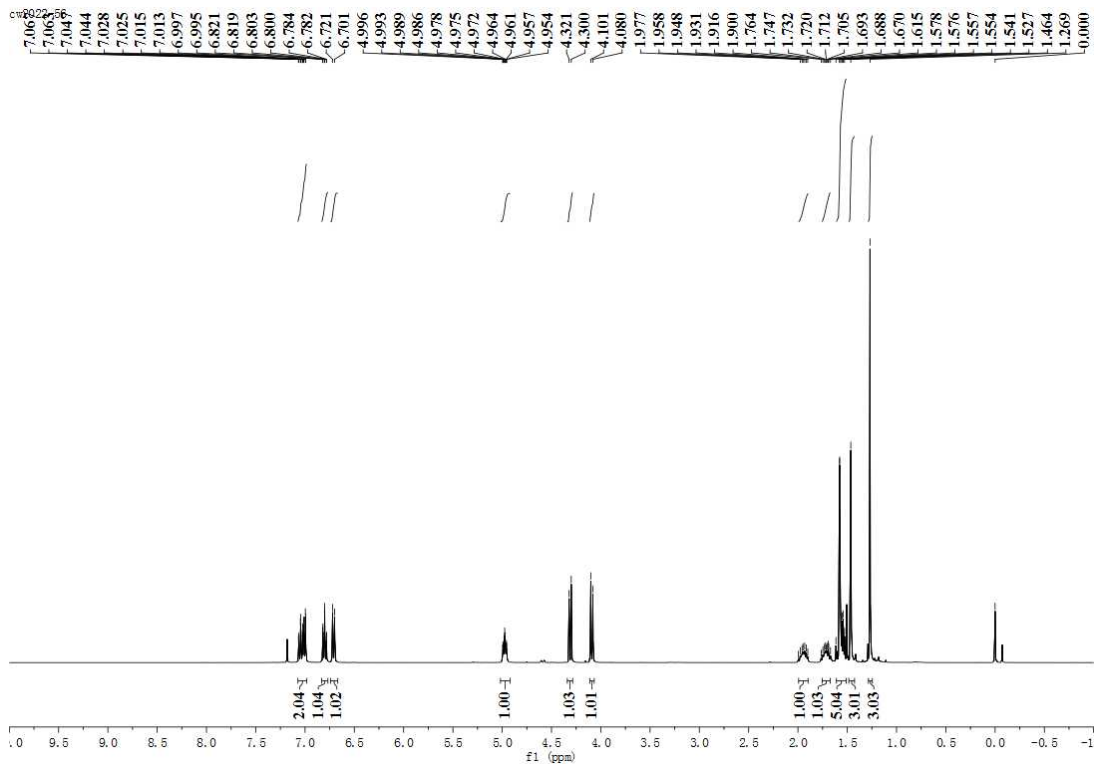
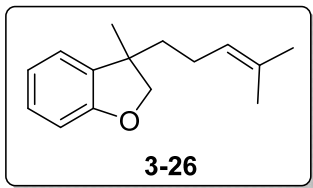
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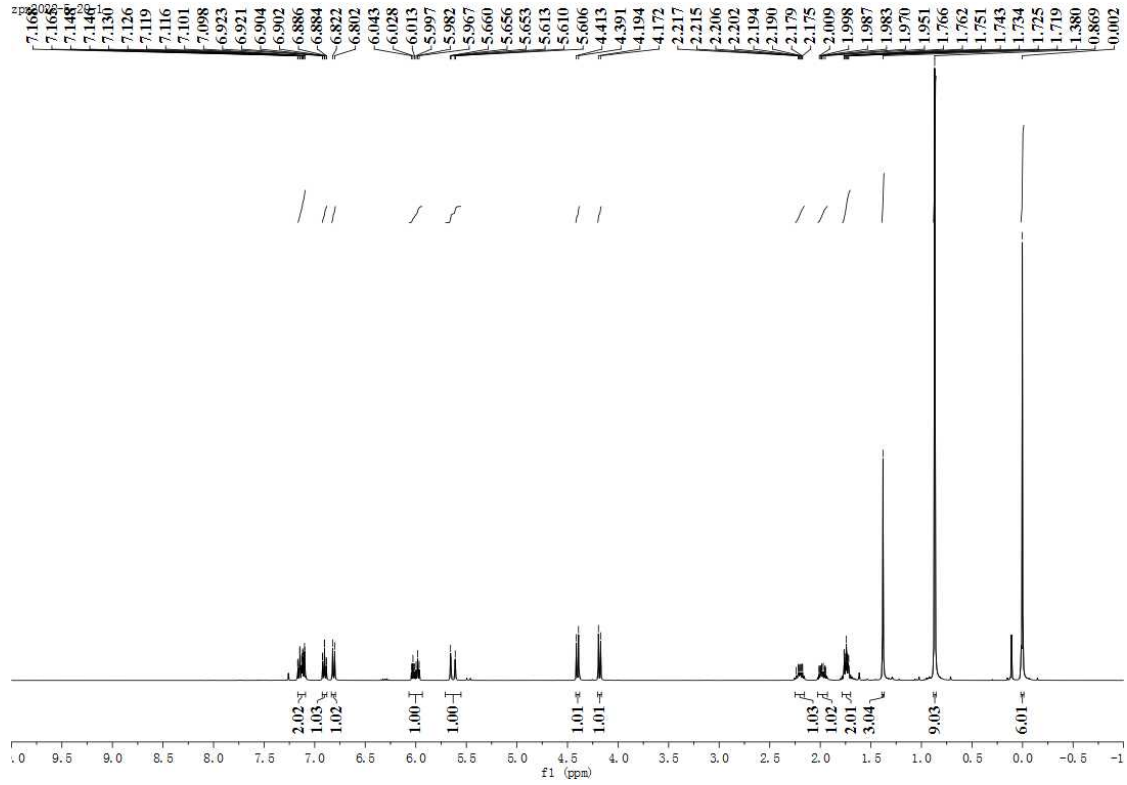
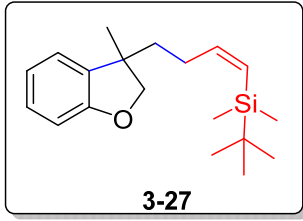






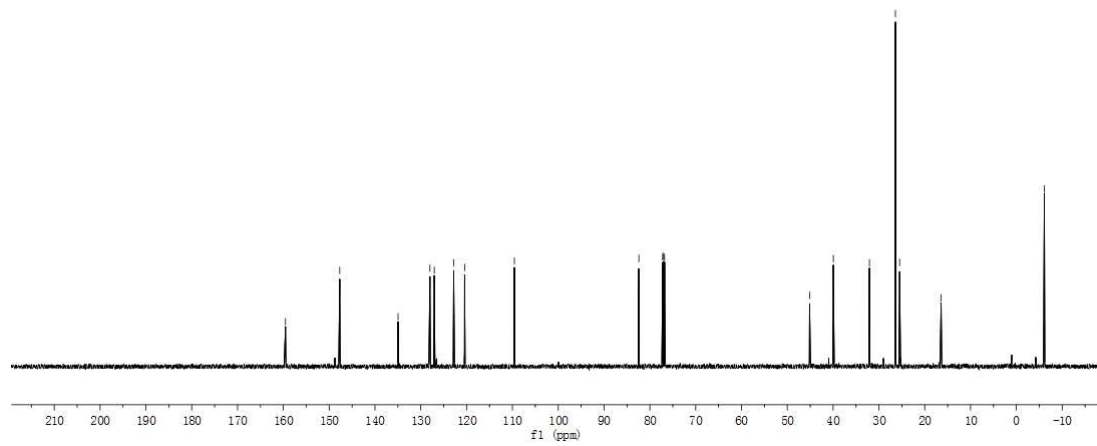


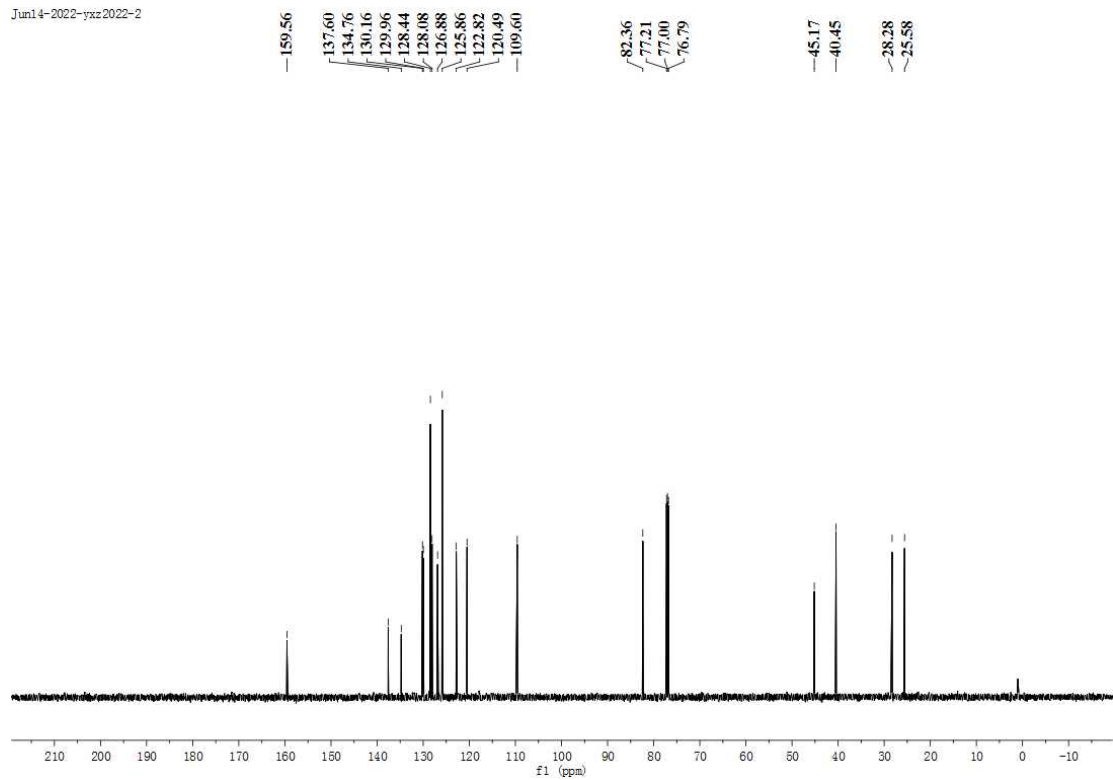
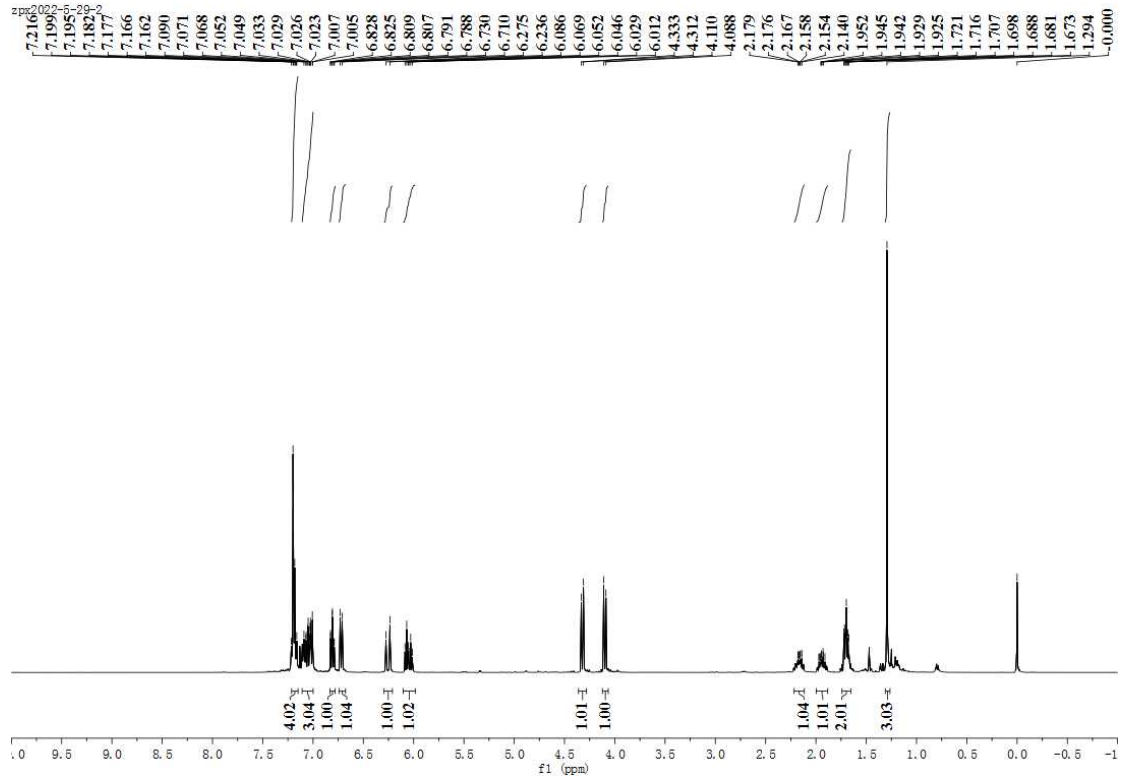
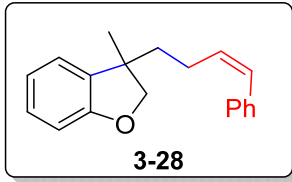


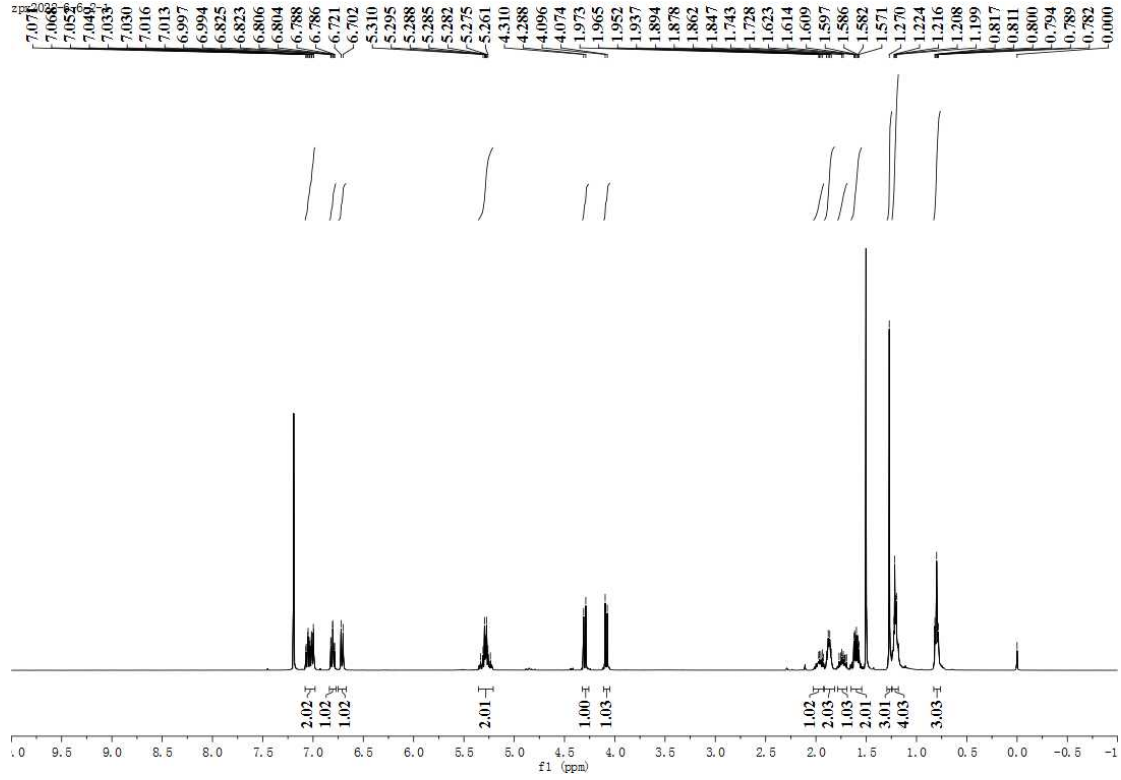
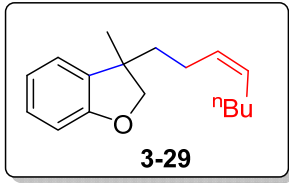


Jun14-2022-yxz2022-1

Chemical shift labels (ppm): -159.54, -147.70, -134.95, -128.01, -127.05, -122.82, -120.44, -109.57, 82.40, 77.21, 77.00, 76.79, 45.13, 39.95, 32.07, 26.41, 25.48, -16.43, -6.11.







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