

Pd-catalyzed Alkynyl Aryl Iodide Cyclization/Alkylation with Cyclobutanols

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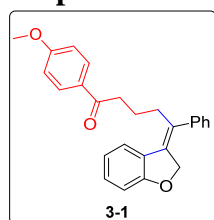
1. General remarks

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 cyclobutanols **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).

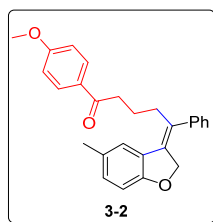
2. General procedure for the preparation of the products **3**

An oven-dried Schlenk tube under a nitrogen atmosphere was charged with alkyne **1** (0.4 mmol, 2.0 equiv), cyclobutanols **2** (0.2 mmol, 1.0 equiv), $\text{Pd}(\text{PPh}_3)_4$ (10 mol%), Cs_3CO_3 (0.40 mmol, 2.0 equiv.), toluene (1.0 mL). The mixture was stirred at 35°C for 30mins and then stirred at 90°C for 24h. 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**

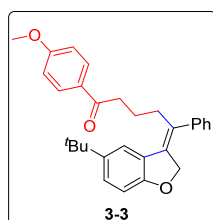


(Z)-5-(benzofuran-3(2H)-ylidene)-1-(4-methoxyphenyl)-5-phenylpentan-1-one: white solid; $R_f=0.28$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); ^1H NMR(400MHz, CDCl_3) δ : 7.90-7.88(m, 2H), 7.65(d, $J=7.6\text{Hz}$, 1H), 7.39-7.36(m, 2H), 7.29-7.27(m, 1H), 7.23-7.16(m, 3H), 6.95-6.89(m, 3H), 6.84(d, $J=8.0\text{Hz}$, 1H), 4.91(s, 2H), 3.86(s, 3H), 3.00(t, $J=7.2\text{Hz}$, 2H), 2.86(t, $J=8.0\text{Hz}$, 2H), 2.01-1.93(m, 2H); ^{13}C NMR(100MHz, CDCl_3) δ : 198.5, 164.1, 163.3, 143.0, 133.4, 132.4, 130.3, 130.0, 129.5, 128.8, 127.4, 127.2, 125.6, 124.1, 120.7, 113.7, 110.4, 75.2, 55.4, 37.8, 33.7, 22.7; HRMS(ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{O}_3\text{Na}$ 407.1618; found 407.1616.



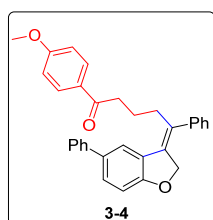
(Z)-1-(4-methoxyphenyl)-5-(5-methylbenzofuran-3(2H)-ylidene)-5-phenylpentan-1-one:

white solid; Rf=0.30(petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); ¹H NMR(400MHz, CDCl₃) δ: 7.92-7.89(m, 2H), 7.49(s, 1H), 7.39-7.35(m, 2H), 7.29-7.25(m, 1H), 7.22-7.20(m, 2H), 6.98(d, *J*=7.6Hz, 1H), 6.90(d, *J*=8.8Hz, 2H), 6.72(d, *J*=8.4 Hz, 1H), 4.89(s, 2H), 3.85(s, 3H), 2.99-2.96(m, 2H), 2.88-2.84(m, 2H), 2.34(s, 3H), 2.00-1.93(m, 2H); ¹³C NMR(100MHz, CDCl₃) δ: 198.5, 163.3, 162.2, 143.0, 133.0, 132.7, 130.2, 130.1, 130.0, 129.8, 128.7, 127.4, 127.1, 125.5, 124.6, 113.6, 109.8, 75.3, 55.4, 37.6, 33.7, 22.7, 21.1; HRMS(ESI) m/z: [M+Na]⁺ calcd for C₂₇H₂₆O₃Na 421.1774; found 421.1777



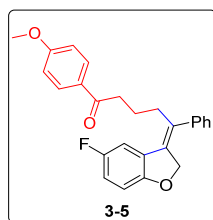
(Z)-5-(5-(tert-butyl)benzofuran-3(2H)-ylidene)-1-(4-methoxyphenyl)-5-phenylpentan-1-one:

yellow oil; Rf=0.30(petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); ¹H NMR(400MHz, CDCl₃) δ: 7.90-7.87(m, 2H), 7.72(d, *J*=2.0Hz, 1H), 7.39-7.35(m, 2H), 7.29-7.20(m, 4H), 6.92-6.88(m, 2H), 6.78(d, *J*=8.8Hz, 1H), 4.90(s, 2H), 3.85(s, 3H), 2.99(t, *J*=7.2Hz, 2H), 2.92-2.88(m, 2H), 2.03-1.96(m, 2H), 1.36(s, 9H); ¹³C NMR(100MHz, CDCl₃) δ: 198.2, 163.3, 162.1, 143.5, 143.1, 132.9, 132.9, 130.2, 130.0, 128.8, 127.4, 127.1, 126.7, 125.1, 120.9, 113.6, 109.6, 75.5, 55.4, 37.6, 34.4, 33.8, 31.7, 22.8; HRMS(ESI) m/z: [M+Na]⁺ calcd for C₃₀H₃₂O₃Na 463.2244; found 463.2239.



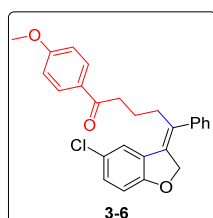
(Z)-1-(4-methoxyphenyl)-5-phenyl-5-(5-phenylbenzofuran-3(2H)-ylidene)pentan-1-one:

white solid; Rf=0.27(petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); ¹H NMR(400MHz, CDCl₃) δ: 7.93(d, *J*=1.6Hz, 1H), 7.84(d, *J*=8.8Hz, 2H), 7.64(d, *J*=7.2Hz, 2H), 7.47-7.22(m, 9H), 6.90(d, *J*=8.4Hz, 1H), 6.82(d, *J*=8.8Hz, 2H), 4.96(s, 2H), 3.82(s, 3H), 3.01-2.97(m, 2H), 2.93(t, *J*=8.0Hz, 2H), 2.03-1.96(m, 2H); ¹³C NMR(100MHz, CDCl₃) δ: 198.3, 163.9, 163.3, 142.9, 141.4, 134.2, 133.9, 132.2, 130.2, 129.9, 128.8, 128.7, 127.4, 127.3, 127.0, 126.7, 126.1, 122.9, 113.6, 110.5, 75.7, 55.4, 37.5, 33.9, 22.8; HRMS(ESI) m/z: [M+Na]⁺ calcd for C₃₂H₂₈O₃Na 483.1931; found 483.1933.



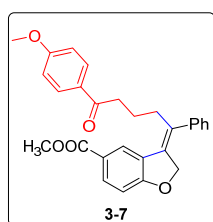
(Z)-5-(5-fluorobenzofuran-3(2H)-ylidene)-1-(4-methoxyphenyl)-5-phenylpentan-1-one:

yellow oil; Rf=0.32(petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); ¹H NMR(400MHz, CDCl₃) δ: 7.90(dd, J=2Hz, 6.8Hz, 2H), 7.43-7.36(m, 3H), 7.31-7.25(m, 1H), 7.21-7.20(m, 2H), 6.93-6.85(m, 3H), 6.73(dd, J=4.4Hz, 8.8Hz, 1H), 4.92(s, 2H), 3.68(s, 3H), 3.01-2.97(m, 2H), 2.83-2.79(m, 2H), 1.99-1.91(m, 2H); ¹³C NMR(100MHz, CDCl₃) δ: 198.3, 163.4, 160.1, 156.2, 142.6, 134.8, 132.1, 130.3, 129.9, 128.8, 127.4, 127.3, 126.5, 115.8, 113.7, 111.0, 110.3, 75.8, 55.4, 37.6, 33.7, 22.5; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₆H₂₄FO₃ 403.1704; found 403.1700.



(Z)-5-(5-chlorobenzofuran-3(2H)-ylidene)-1-(4-methoxyphenyl)-5-phenylpentan-1-one:

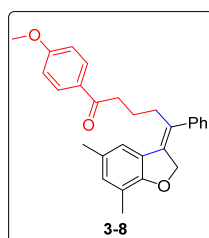
white solid; Rf=0.32(petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); ¹H NMR(400MHz, CDCl₃) δ: 7.91(d, J=8.8Hz, 2H), 7.65(d, J=2.0Hz, 1H), 7.39-7.36(m, 2H), 7.28(t, J=7.2Hz, 1H), 7.19(d, J=7.4Hz, 2H), 7.12(dd, J=2.0Hz, 8.8Hz, 1H), 6.90(d, J=8.8Hz, 2H), 6.74(d, J=8.4Hz, 1H), 4.92(s, 2H), 3.85(s, 3H), 3.00-2.97(m, 2H), 2.81(t, J=8.0Hz, 2H), 1.98-1.91(m, 2H); ¹³C NMR(100MHz, CDCl₃) δ: 198.3, 163.4, 162.7, 142.5, 135.1, 131.4, 130.3, 129.9, 129.1, 128.8, 127.4, 127.2, 125.5, 124.0, 113.7, 111.1, 75.8, 55.4, 37.5, 33.7, 22.6; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₆H₂₄ClO₃ 419.1408; found 419.1409.



Methyl(Z)-3-(5-(4-methoxyphenyl)-5-oxo-1-phenylpentylidene)-2,3-dihydrobenzofuran-5-carboxylate:

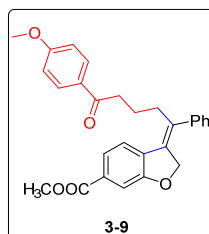
white solid; Rf=0.22(petroleum ether/ethyl acetate, 10:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 20:1); ¹H NMR(400MHz, CDCl₃) δ: 8.33(d, J=1.6Hz, 1H), 7.95-7.90(m, 3H), 7.40-7.36(m, 2H), 7.30(d, J=7.6Hz, 1H), 7.23-7.21(m, 2H), 6.91-6.89(m, 2H), 6.84(d, J=8.4Hz, 1H), 4.99(s, 2H), 3.92(s, 3H), 3.85(s, 3H), 3.06-3.02(m, 2H), 2.90(t, J=8.0Hz, 2H), 2.03-1.95(m, 2H); ¹³C NMR(100MHz, CDCl₃) δ: 198.3, 167.9, 166.9, 163.3, 142.5, 135.4, 132.0, 130.8, 130.3, 129.9, 128.8, 127.5, 127.2, 125.9, 125.8, 122.7, 113.6, 110.1, 76.2, 55.4, 52.0, 37.7, 33.8, 22.8; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₈H₂₇O₅ 443.1853;

found 443.1845

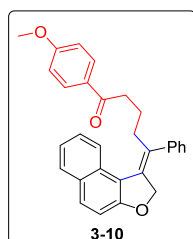


(Z)-5-(5,7-dimethylbenzofuran-3(2H)-ylidene)-1-(4-methoxyphenyl)-5-phenylpentan-1-one:

white solid; Rf=0.30(peterolium ether/ethyl acetate, 20:1); Column chromatography(silica gel; peterolium ether/ethyl acetate, 40:1); ^1H NMR(400MHz, CDCl_3) δ : 7.89(d, $J=8.4\text{Hz}$, 2H), 7.39-7.35(m, 2H), 7.31(s, 1H), 7.26(t, $J=7.2\text{Hz}$, 1H), 7.20(d, $J=7.6\text{Hz}$, 2H), 6.89(d, $J=8.8\text{Hz}$, 2H), 6.83(s, 1H), 4.89(s, 2H), 3.85(s, 3H), 2.98(t, $J=7.2\text{Hz}$, 2H), 2.87-2.83(m, 2H), 2.31(s, 3H), 2.16(s, 3H), 2.00-1.92(m, 2H); ^{13}C NMR(100MHz, CDCl_3) δ : 198.7, 163.4, 160.6, 143.2, 133.3, 132.6, 131.5, 130.3, 130.1, 129.6, 128.8, 127.5, 127.1, 124.8, 122.0, 119.9, 113.7, 75.1, 55.5, 37.7, 33.7, 22.9, 21.1, 15.0; HRMS(ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{28}\text{O}_3\text{Na}$ 435.1931; found 435.1929.

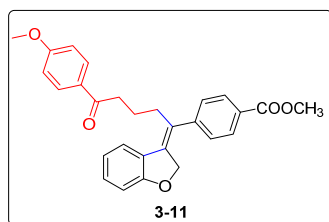


Methyl (Z)-3-(5-(4-methoxyphenyl)-5-oxo-1-phenylpentylidene)-2,3-dihydrobenzofuran-6-carboxylate: NMR yield; HRMS(ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{O}_5\text{Na}$ 465.1672; found 465.1665.

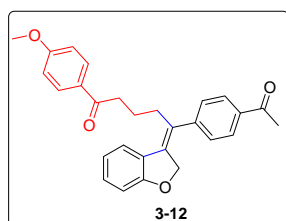


(Z)-1-(4-methoxyphenyl)-5-(naphtho[2,1-b]furan-1(2H)-ylidene)-5-phenylpentan-1-one:

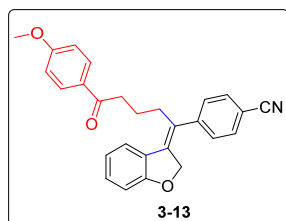
white solid; Rf=0.29 (peterolium ether/ethyl acetate, 20:1); Column chromatography(silica gel; peterolium ether/ethyl acetate, 40:1); ^1H NMR(400MHz, CDCl_3) δ : 7.86(d, $J=8.8\text{Hz}$, 1H), 7.81-7.78(m, 2H), 7.73(d, $J=8.0\text{Hz}$, 1H), 7.66(d, $J=8.8\text{Hz}$, 1H), 7.42-7.38(m, 1H), 7.34-7.27(m, 2H), 7.26-7.20(m, 4H), 7.02(d, $J=8.8\text{Hz}$, 1H), 6.82(d, $J=8.8\text{Hz}$, 2H), 4.87(s, 2H), 3.78(s, 3H), 2.89-2.86(m, 2H), 2.80(t, $J=8.4\text{Hz}$, 2H), 1.97-1.89(m, 2H); ^{13}C NMR(100MHz, CDCl_3) δ : 198.5, 163.3, 153.6, 143.1, 141.8, 130.7, 130.2, 130.0, 128.9, 128.6, 128.3, 128.1, 126.6, 126.0, 125.7, 125.6, 123.9, 123.7, 120.9, 113.6, 112.7, 55.4, 43.2, 38.0, 36.5, 23.0; HRMS(ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{27}\text{O}_3$ 435.1955; found 435.1955.



Methyl (Z)-4-(1-(benzofuran-3(2H)-ylidene)-5-(4-methoxyphenyl)-5-oxopentyl)benzoate: yellow oil; Rf=0.28 (petroleum ether/ethyl acetate, 10:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 20:1); ^1H NMR(400MHz, CDCl_3) δ : 8.04(d, $J=8.4\text{Hz}$, 2H), 7.89-7.86(m, 2H), 7.66(d, $J=7.6\text{Hz}$, 1H), 7.29(d, $J=8.4\text{Hz}$, 2H), 7.22-7.18(m, 1H), 6.97-6.93(m, 1H), 6.90(d, $J=8.8\text{Hz}$, 2H), 6.85(d, $J=8.0\text{Hz}$, 1H), 4.89(s, 2H), 3.93(s, 3H), 3.86(s, 3H), 3.01-2.97(m, 2H), 2.89-2.85(m, 2H), 2.00-1.93(m, 2H); ^{13}C NMR(100MHz, CDCl_3) δ : 198.2, 166.7, 164.2, 163.4, 147.8, 133.5, 132.2, 130.2, 130.1, 129.9, 128.9, 127.5, 125.2, 124.3, 120.8, 113.6, 110.5, 74.9, 55.4, 52.1, 37.5, 33.5, 22.6; HRMS(ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{O}_5\text{Na}$ 465.1672; found 465.1670.

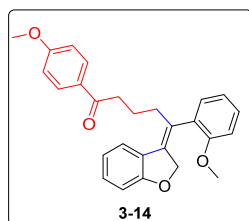


(Z)-5-(4-acetylphenyl)-5-(benzofuran-3(2H)-ylidene)-1-(4-methoxyphenyl)pentan-1-one: yellow oil; Rf=0.20(petroleum ether/ethyl acetate, 10:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 15:1); ^1H NMR(400MHz, CDCl_3) δ : 7.98-7.96(m, 2H), 7.88(dd, $J=2.0\text{Hz}$, 6.8Hz, 2H), 7.67(d, $J=7.2\text{Hz}$, 1H), 7.32(d, $J=8.4\text{Hz}$, 2H), 7.23-7.19(m, 1H), 6.95(td, $J=0.8\text{Hz}$, 7.6Hz, 1H), 6.90(dd, $J=2.0\text{Hz}$, 6.8Hz, 2H), 6.85(d, $J=8.0\text{Hz}$, 1H), 4.91(s, 2H), 3.86(s, 3H), 3.01-2.98(m, 2H), 2.90-2.86(m, 2H), 2.62(s, 3H), 2.01-1.93(m, 2H); ^{13}C NMR(100MHz, CDCl_3) δ : 198.2, 197.5, 164.3, 163.4, 148.0, 135.8, 133.7, 132.1, 130.2, 130.0, 129.9, 128.9, 127.7, 125.2, 124.3, 120.9, 113.7, 110.5, 74.9, 55.4, 37.5, 33.4, 26.6, 22.7; HRMS(ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{O}_4\text{Na}$ 449.1723; found 449.1728.



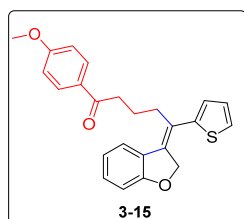
(Z)-4-(1-(benzofuran-3(2H)-ylidene)-5-(4-methoxyphenyl)-5-oxopentyl)benzotrile: yellow solid; Rf=0.24(petroleum ether/ethyl acetate, 10:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 20:1); ^1H NMR(400MHz, CDCl_3) δ : 7.88(d, $J=8.8\text{Hz}$, 2H), 7.68-7.66(m, 3H), 7.34(d, $J=8.0\text{Hz}$, 2H), 7.25-7.21(m, 1H), 6.96(t, $J=7.6\text{Hz}$, 1H), 6.92(d, $J=8.8\text{Hz}$, 2H), 6.86(d, $J=8.0\text{Hz}$, 1H), 4.88(s, 2H), 3.87(s, 3H), 3.00(t, $J=6.8\text{Hz}$, 2H), 2.88-2.84(m, 2H), 1.99-1.92(m, 2H); ^{13}C NMR(100MHz, CDCl_3) δ : 198.0, 164.3, 163.5, 147.8, 134.3, 132.7, 131.2,

130.3, 130.2, 129.9, 128.3, 124.9, 124.4, 121.0, 118.7, 113.7, 110.9, 110.6, 74.7, 55.5, 37.4, 33.4, 22.5; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{24}NO_3$ 410.1751; found 410.1749.



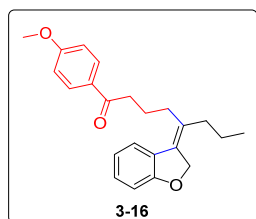
(Z)-5-(benzofuran-3(2H)-ylidene)-5-(2-methoxyphenyl)-1-(4-methoxyphenyl)pentan-1-one:

white solid; Rf=0.25(petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 35:1); 1H NMR(400MHz, $CDCl_3$) δ : 7.90-7.88(m, 2H), 7.67-7.65(m, 1H), 7.30-7.26(m, 1H), 7.18-7.14(m, 1H), 7.11-7.09(m, 1H), 6.98-6.88(m, 5H), 6.82(d, $J=8.0$ Hz, 1H), 4.76(s, 2H), 3.85(s, 3H), 3.78(s, 3H), 2.99(t, $J=3.2$ Hz, 2H), 2.84-2.80(m, 2H), 1.95-1.91(m, 2H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 198.8, 164.5, 163.3, 155.9, 132.9, 131.2, 130.3, 130.1, 129.6, 129.4, 129.2, 128.6, 125.5, 124.2, 120.9, 120.6, 113.6, 111.1, 110.3, 75.2, 55.4, 55.3, 37.8, 33.3, 22.5; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{26}O_4Na$ 437.1723; found 437.1720.



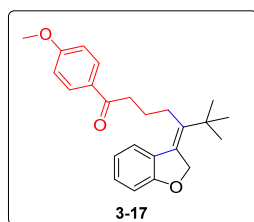
(Z)-5-(benzofuran-3(2H)-ylidene)-1-(4-methoxyphenyl)-5-(thiophen-2-yl)pentan-1-one:

white solid; Rf=0.33(petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); 1H NMR(400MHz, $CDCl_3$) δ : 7.96-7.92(m, 2H), 7.64(d, $J=7.6$ Hz, 1H), 7.31(dd, $J=0.8$ Hz, 5.2Hz, 1H), 7.22-7.19(m, 1H), 7.09(dd, $J=3.6$ Hz, 5.2Hz, 1H), 7.02(d, $J=2.8$ Hz, 1H), 6.98-6.89(m, 4H), 5.28(s, 2H), 3.87(s, 3H), 3.11-3.07(m, 2H), 3.00-2.96(m, 2H), 2.14-2.06(m, 2H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 198.4, 164.0, 163.4, 145.2, 132.9, 130.3, 130.0, 129.7, 127.5, 125.6, 125.5, 125.4, 124.6, 124.4, 120.9, 113.7, 110.4, 75.9, 55.5, 37.7, 33.7, 23.0; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{23}O_3S$ 391.1362; found 391.1359

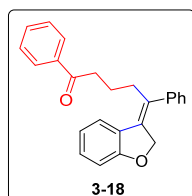


(E)-5-(benzofuran-3(2H)-ylidene)-1-(4-methoxyphenyl)octan-1-one: white solid; Rf=0.31 (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); 1H NMR(400MHz, $CDCl_3$) δ : 7.94(d, $J=8.8$ Hz, 2H), 7.47(d, $J=8.0$ Hz, 1H), 7.10(t, $J=7.6$ Hz, 1H), 6.92(d, $J=8.8$ Hz, 2H), 6.87-6.80(m, 2H), 5.08(s, 2H), 3.86(s, 3H), 3.02(t, $J=7.2$ Hz, 2H), 2.50-2.46(m, 2H), 2.02-1.92(m, 4H), 1.55-1.46(m, 2H), 0.97-0.93(m, 3H); ^{13}C

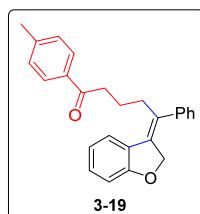
NMR(100MHz, CDCl₃) δ : 198.5, 164.1, 163.4, 132.3, 130.3, 130.1, 130.0, 128.4, 125.8, 123.7, 120.5, 113.7, 110.0, 74.3, 55.4, 38.0, 37.5, 31.5, 22.3, 20.5, 14.2; HRMS(ESI) m/z : [M+Na]⁺ calcd for C₂₃H₂₆O₃Na 373.1774; found 373.1773.



(Z)-5-(benzofuran-3(2H)-ylidene)-1-(4-methoxyphenyl)-6,6-dimethylheptan-1-one: yellow oil; R_f=0.30(peterolium ether/ethyl acetate, 20:1); Column chromatography(silica gel; peterolium ether/ethyl acetate, 40:1); ¹H NMR(400MHz, CDCl₃) δ : 8.00-7.98(m, 2H), 7.41(d, *J*=8.0Hz, 1H), 7.15-7.11(m, 1H), 6.96-6.93(m, 2H), 6.88-6.81(m, 2H), 5.23(s, 2H), 3.88(s, 3H), 3.09-3.06(m, 2H), 2.52-2.47(m, 2H), 2.01-1.94(m, 2H), 1.22(s, 9H); ¹³C NMR(100MHz, CDCl₃) δ : 198.4, 163.4, 162.9, 141.2, 130.3, 130.0, 129.9, 128.6, 127.0, 124.7, 120.4, 113.7, 109.9, 74.0, 55.5, 38.2, 37.8, 31.1, 29.6, 23.5; HRMS(ESI) m/z : [M+Na]⁺ calcd for C₂₄H₂₈O₃Na 387.1931; found 387.1929.

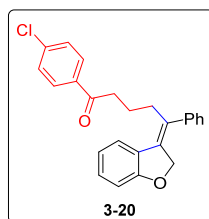


(Z)-5-(benzofuran-3(2H)-ylidene)-1,5-diphenylpentan-1-one: yellow solid; R_f=0.30(peterolium ether/ethyl acetate, 20:1); Column chromatography(silica gel; peterolium ether/ethyl acetate, 40:1); ¹H NMR(400MHz, CDCl₃) δ : 7.91-7.89(m, 2H), 7.65(d, *J*=7.6Hz, 1H), 7.56-7.52(m, 1H), 7.45-7.42(m, 2H), 7.39-7.36(m, 2H), 7.29-7.26(m, 1H), 7.23-7.16(m, 3H), 6.93(td, *J*=0.8Hz, 7.6Hz, 1H), 6.83(d, *J*=8.0Hz, 1H), 4.91(s, 2H), 3.04(t, *J*=7.2Hz, 2H), 2.89-2.85(m, 2H), 2.02-1.95(m, 2H); ¹³C NMR(100MHz, CDCl₃) δ : 199.9, 164.2, 143.0, 136.9, 133.3, 133.0, 132.5, 129.5, 128.8, 128.5, 128.0, 127.4, 127.2, 125.5, 124.1, 120.7, 110.4, 75.2, 38.1, 33.7, 22.5; HRMS(ESI) m/z : [M+Na]⁺ calcd for C₂₅H₂₂O₂Na 377.1512; found 377.1519.

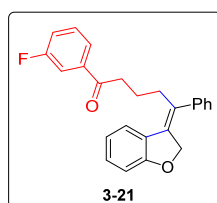


(Z)-5-(benzofuran-3(2H)-ylidene)-5-phenyl-1-(p-tolyl)pentan-1-one: yellow oil; R_f=0.32 (peterolium ether/ethyl acetate, 20:1); Column chromatography(silica gel; peterolium ether/ethyl acetate, 40:1); ¹H NMR(400MHz, CDCl₃) δ : 7.72(d, *J*=8.4Hz, 2H), 7.56(d, *J*=7.6Hz, 1H), 7.31-7.27(m, 2H), 7.21-7.17(m, 1H), 7.15-7.07(m, 5H), 6.86-6.82(m, 1H), 6.75(d, *J*=7.6Hz, 1H), 4.82(s, 2H), 2.92(t, *J*=7.2Hz, 2H), 2.77(t, *J*=8.0Hz, 2H), 2.31(s, 3H), 1.92-1.85(m, 2H); ¹³C NMR(100MHz, CDCl₃) δ : 199.5, 164.1, 143.7, 143.0, 134.4, 133.3, 132.5, 129.5, 129.2, 128.8,

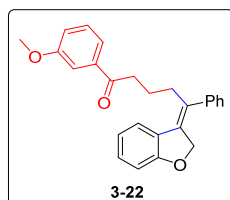
128.1, 127.4, 127.2, 125.5, 124.1, 120.7, 110.3, 75.1, 38.0, 33.7, 22.6, 21.6; HRMS(ESI) m/z : $[M+NH_4]^+$ calcd for $C_{26}H_{28}NO_2$ 386.2115; found 386.2109.



(Z)-5-(benzofuran-3(2H)-ylidene)-1-(4-chlorophenyl)-5-phenylpentan-1-one: yellow oil; $R_f=0.32$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); 1H NMR(400MHz, $CDCl_3$) δ : 7.75-7.71(m, 2H), 7.55(d, $J=7.6$ Hz, 1H), 7.31-7.26(m, 4H), 7.21-7.17(m, 1H), 7.13-7.07(m, 3H), 6.84(td, $J=0.8$ Hz, 7.6Hz, 1H), 6.75(d, $J=7.6$ Hz, 1H), 4.82(s, 2H), 2.90(t, $J=7.2$ Hz, 2H), 2.77(t, $J=8.0$ Hz, 2H), 1.92-1.85(m, 2H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 198.6, 164.2, 142.9, 139.3, 135.2, 133.1, 132.6, 129.6, 129.4, 128.8, 128.7, 127.3, 127.2, 125.5, 124.0, 120.6, 110.4, 75.1, 37.9, 33.5, 22.3; HRMS(ESI) m/z : $[M+Na]^+$ calcd for $C_{25}H_{21}ClO_2Na$ 411.1122; found 411.1125.

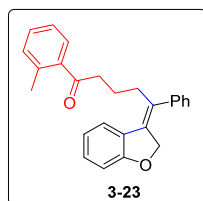


(Z)-5-(benzofuran-3(2H)-ylidene)-1-(3-fluorophenyl)-5-phenylpentan-1-one: yellow oil; $R_f=0.31$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); 1H NMR(400MHz, $CDCl_3$) δ : 7.66(t, $J=6.8$ Hz, 2H), 7.59-7.56(m, 1H), 7.43-7.36(m, 3H), 7.29-7.17(m, 5H), 6.96-6.92(m, 1H), 6.84(d, $J=8.0$ Hz, 1H), 4.91(s, 2H), 3.03-2.99(m, 2H), 2.89-2.85(m, 2H), 2.02-1.95(m, 2H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 198.6, 164.2, 161.6, 142.9, 139.0, 133.1, 132.7, 130.2, 129.6, 128.8, 127.4, 127.3, 125.5, 124.0, 123.7, 120.7, 120.1, 114.8, 110.4, 75.1, 38.2, 33.5, 22.3; HRMS(ESI) m/z : $[M+Na]^+$ calcd for $C_{25}H_{21}FO_2Na$ 395.1418; found 395.1415.

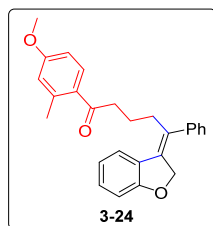


(Z)-5-(benzofuran-3(2H)-ylidene)-1-(3-methoxyphenyl)-5-phenylpentan-1-one: yellow solid; $R_f=0.26$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); 1H NMR(400MHz, $CDCl_3$) δ : 7.57(d, $J=7.6$ Hz, 1H), 7.39-7.36(m, 2H), 7.31-7.22(m, 3H), 7.21-7.16(m, 1H), 7.14-7.11(m, 2H), 7.09-7.07(m, 1H), 7.01-6.98(m, 1H), 6.87-6.83(m, 1H), 6.75(d, $J=8.0$ Hz, 1H), 4.82(s, 2H), 3.74(s, 3H), 2.95-2.92(m, 2H), 2.77(t, $J=8.0$ Hz, 2H), 1.93-1.85(m, 2H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 199.7, 164.1, 159.7, 142.9, 138.2,

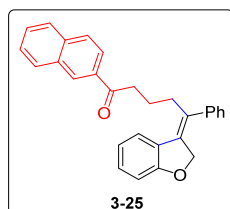
133.2, 132.5, 129.5, 129.4, 128.8, 127.3, 127.2, 125.5, 124.1, 120.7, 120.6, 119.4, 112.1, 110.3, 75.1, 55.4, 38.2, 33.7, 22.5; HRMS(ESI) m/z: $[M+NH_4]^+$ calcd for $C_{26}H_{28}NO_3$ 402.2064; found 402.2062.



(Z)-5-(benzofuran-3(2H)-ylidene)-5-phenyl-1-(o-tolyl)pentan-1-one: yellow solid; $R_f=0.34$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); 1H NMR(400MHz, $CDCl_3$) δ : 7.62(d, $J=7.6$ Hz, 1H), 7.52(d, $J=8.0$ Hz, 1H), 7.39-7.33(m, 3H), 7.29-7.23(m, 1H), 7.21-7.16(m, 5H), 6.93(td, $J=0.8$ Hz, 7.6Hz, 1H), 6.84(d, $J=8.0$ Hz, 1H), 4.91(s, 2H), 2.96(t, $J=7.2$ Hz, 2H), 2.84(t, $J=8.0$ Hz, 2H), 2.47(s, 3H), 1.98-1.91(m, 2H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 204.1, 164.1, 142.9, 137.9, 133.3, 132.5, 131.9, 131.2, 129.6, 128.8, 128.3, 127.4, 127.2, 125.6, 125.5, 124.1, 120.7, 110.4, 75.1, 41.0, 33.6, 22.6, 21.3; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{24}O_2Na$ 391.1669; found 391.1668.

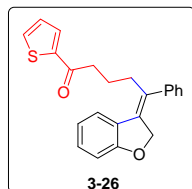


(Z)-5-(benzofuran-3(2H)-ylidene)-1-(4-methoxy-2-methylphenyl)-5-phenylpentan-1-one: yellow oil; $R_f=0.24$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); 1H NMR(400MHz, $CDCl_3$) δ : 7.63-7.60(m, 2H), 7.38-7.35(m, 2H), 7.29-7.24(m, 1H), 7.21-7.15(m, 3H), 6.93-6.89(m, 1H), 6.83(d, $J=8.0$ Hz, 1H), 6.74-6.70(m, 2H), 4.90(s, 2H), 3.82(s, 3H), 2.94(t, $J=7.2$ Hz, 2H), 2.85-2.81(m, 2H), 2.53(s, 3H), 1.97-1.90(m, 2H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 201.6, 164.1, 161.7, 143.0, 141.9, 133.4, 132.4, 131.5, 130.0, 129.5, 128.8, 127.4, 127.2, 125.6, 124.1, 120.6, 117.4, 110.5, 110.3, 75.1, 55.2, 40.3, 33.7, 23.0, 22.4; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{27}O_3$ 399.1955; found 399.1954.

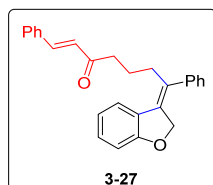


(Z)-5-(benzofuran-3(2H)-ylidene)-1-(naphthalen-2-yl)-5-phenylpentan-1-one: white solid; $R_f=0.28$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); 1H NMR(400MHz, $CDCl_3$) δ : 8.39(s, 1H), 7.99(dd, $J=1.6$ Hz, 8.8Hz, 1H), 7.92(d, $J=8.0$ Hz, 1H), 7.88-7.85(m, 2H), 7.68(d, $J=7.6$ Hz, 1H), 7.61-7.52(m, 2H), 7.39-7.36(m, 2H), 7.29-7.26(m, 1H), 7.25-7.22(m, 2H), 7.19-7.15(m, 1H), 6.94-6.90(m, 1H),

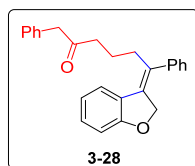
6.83(d, $J=8.0\text{Hz}$, 1H), 4.92(s, 2H), 3.19-3.14(m, 2H), 2.93-2.89(m, 2H), 2.08-2.01(m, 2H); ^{13}C NMR(100MHz, CDCl_3) δ : 199.9, 164.1, 143.0, 135.5, 134.2, 133.3, 132.5, 132.4, 129.7, 129.6, 129.5, 128.8, 128.4, 128.3, 127.7, 127.4, 127.2, 126.7, 125.6, 124.1, 123.8, 120.7, 110.4, 75.2, 38.2, 33.7, 22.7; HRMS(ESI) m/z : $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{29}\text{H}_{28}\text{NO}_2$ 422.2115; found 422.2108.



(Z)-5-(benzofuran-3(2H)-ylidene)-5-phenyl-1-(thiophen-2-yl)pentan-1-one: yellow solid; $R_f=0.31$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); ^1H NMR(400MHz, CDCl_3) δ : 7.65-7.60(m, 3H), 7.40-7.36(m, 2H), 7.29-7.26(m, 1H), 7.22-7.20(m, 2H), 7.18-7.16(m, 1H), 7.10-7.08(m, 1H), 6.96-6.92(m, 1H), 6.83(d, $J=8.0\text{Hz}$, 1H), 4.91(s, 2H), 2.97(t, $J=7.2\text{Hz}$, 2H), 2.86(t, $J=8.0\text{Hz}$, 2H), 2.03-1.95(m, 2H); ^{13}C NMR(100MHz, CDCl_3) δ : 192.8, 164.2, 144.2, 142.9, 133.5, 133.1, 132.6, 131.7, 129.6, 128.8, 128.0, 127.4, 127.2, 125.5, 124.1, 120.7, 110.4, 75.1, 38.8, 33.6, 22.8; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{O}_2\text{S}$ 361.1257; found 361.1256.

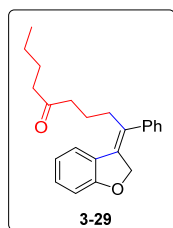


(E)-7-((Z)-benzofuran-3(2H)-ylidene)-1,7-diphenylhept-1-en-3-one: yellow oil; $R_f=0.30$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); ^1H NMR(400MHz, CDCl_3) δ : 7.68(d, $J=7.6\text{Hz}$, 1H), 7.53-7.49(m, 3H), 7.39-7.36(m, 5H), 7.29-7.26(m, 1H), 7.23-7.16(m, 3H), 6.95(t, $J=7.6\text{Hz}$, 1H), 6.84(d, $J=8.0\text{Hz}$, 1H), 6.96(d, $J=16.4\text{Hz}$, 1H), 4.91(s, 2H), 2.83(t, $J=8.0\text{Hz}$, 2H), 2.74(t, $J=7.2\text{Hz}$, 2H), 1.96-1.89(m, 2H); ^{13}C NMR(100MHz, CDCl_3) δ : 199.9, 164.1, 142.9, 142.5, 134.4, 133.3, 132.5, 130.4, 129.6, 128.9, 128.8, 128.2, 127.4, 127.2, 126.0, 125.5, 124.1, 120.7, 110.4, 75.1, 40.3, 33.6, 22.4; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{O}_2$ 381.1849; found 381.1846.

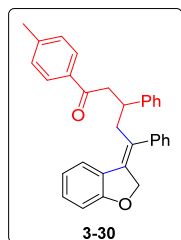


(Z)-6-(benzofuran-3(2H)-ylidene)-1,6-diphenylhexan-2-one: yellow oil; $R_f=0.33$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); ^1H NMR(400MHz, CDCl_3) δ : 7.58(d, $J=7.6\text{Hz}$, 1H), 7.38-7.34(m, 2H), 7.30-7.24(m, 4H), 7.20-7.16(m, 1H), 7.14-7.12(m, 4H), 6.96-6.92(m, 1H), 6.83(d, $J=7.6\text{Hz}$, 1H), 4.87(s, 2H), 3.59(s, 2H), 2.73-2.69(m, 2H), 2.52-2.49(m, 2H), 1.81-1.73(m, 2H); ^{13}C NMR(100MHz, CDCl_3) δ : 208.0, 164.1, 142.9, 134.2, 133.1, 132.5, 129.6, 129.4, 128.8, 128.7, 127.3, 127.2, 127.0, 125.5, 124.1,

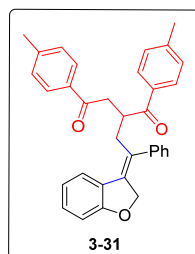
120.7, 110.4, 75.1, 50.2, 41.1, 33.2, 21.8; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{24}O_2Na$ 391.1669; found 391.1666.



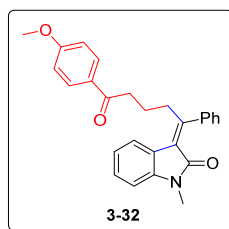
(Z)-1-(benzofuran-3(2H)-ylidene)-1-phenylnonan-5-one: yellow oil; $R_f=0.35$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); 1H NMR(400MHz, $CDCl_3$) δ : 7.63(d, $J=7.6$ Hz, 1H), 7.39-7.36(m, 2H), 7.30-7.26(m, 1H), 7.19-7.17(m, 3H), 6.96(t, $J=7.6$ Hz, 1H), 6.84(d, $J=8.4$ Hz, 1H), 4.89(s, 2H), 2.79-2.75(m, 2H), 2.49-2.45(m, 2H), 2.33-2.29(m, 2H), 1.84-1.76(m, 2H), 1.55-1.47(m, 2H), 1.31-1.22(m, 2H), 0.89-0.86(m, 3H); ^{13}C NMR(100MHz, $CDCl_3$) δ : 210.9, 164.2, 143.0, 133.3, 132.5, 129.6, 128.8, 127.4, 127.2, 125.5, 124.0, 120.7, 110.4, 75.1, 42.6, 41.9, 33.5, 25.9, 22.3, 21.9, 13.8; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{26}O_2Na$ 357.1825; found 357.1828.



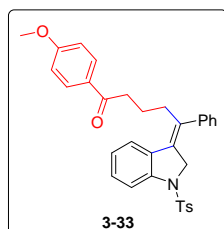
(Z)-5-(benzofuran-3(2H)-ylidene)-3,5-diphenyl-1-(p-tolyl)pentan-1-one: yellow oil; $R_f=0.30$ (petroleum ether/ethyl acetate, 20:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 40:1); 1H NMR(400MHz, $CDCl_3$) δ : 7.72(d, $J=7.6$ Hz, 1H), 7.69(d, $J=8.0$ Hz, 2H), 7.29-7.26(m, 2H), 7.25-7.12(m, 9H), 6.99-6.97(m, 2H), 6.95-6.91(m, 1H), 6.82(d, $J=8.0$ Hz, 1H), 4.91-4.78(m, 2H), 3.64-3.57(m, 1H), 3.82-3.32(m, 3H), 3.06(dd, $J=7.6$ Hz, 14.0Hz, 1H), 2.36(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ : 198.4, 164.3, 143.9, 143.7, 142.9, 134.5, 133.8, 131.8, 129.7, 129.1, 128.5, 128.3, 128.1, 127.6, 127.3, 126.9, 126.4, 125.4, 124.1, 120.6, 110.5, 75.2, 44.6, 40.4, 21.6; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{28}O_2Na$ 467.1982; found 467.1981.



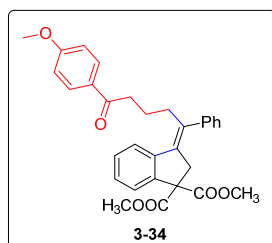
(Z)-2-(2-(benzofuran-3(2H)-ylidene)-2-phenylethyl)-1,4-di-p-tolylbutane-1,4-dione: NMR yield; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{34}H_{31}O_3$ 487.2268; found 487.2270.



(Z)-3-(5-(4-methoxyphenyl)-5-oxo-1-phenylpentylidene)-1-methylindolin-2-one: yellow oil; $R_f=0.32$ (petroleum ether/ethyl acetate, 3:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 6:1); $^1\text{H NMR}$ (400MHz, CDCl_3) δ : 7.83(d, $J=8.8\text{Hz}$, 2H), 7.41-7.33(m, 3H), 7.19(d, $J=6.4\text{Hz}$, 2H), 7.04(t, $J=7.6\text{Hz}$, 1H), 6.81(d, $J=8.4\text{Hz}$, 2H), 6.65(d, $J=8.0\text{Hz}$, 1H), 6.54(t, $J=7.6\text{Hz}$, 1H), 5.98(d, $J=8.0\text{Hz}$, 1H), 3.76(s, 3H), 3.34(t, $J=7.6\text{Hz}$, 2H), 3.17(s, 3H), 2.98(t, $J=7.6\text{Hz}$, 2H), 1.89-1.82(m, 2H); $^{13}\text{C NMR}$ (100MHz, CDCl_3) δ : 198.5, 167.7, 163.2, 158.4, 142.3, 141.1, 130.3, 130.0, 129.1, 128.4, 128.2, 126.9, 123.7, 122.9, 122.5, 121.4, 113.5, 107.4, 55.4, 38.0, 34.2, 25.7, 22.7; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_3$ 412.1907; found 412.1914.



(Z)-1-(4-methoxyphenyl)-5-phenyl-5-(1-tosylindolin-3-ylidene)pentan-1-one: white solid; $R_f=0.30$ (petroleum ether/ethyl acetate, 3:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 6:1); $^1\text{H NMR}$ (400MHz, CDCl_3) δ : 7.86-7.84(m, 2H), 7.71(d, $J=8.0\text{Hz}$, 1H), 7.60(d, $J=7.6\text{Hz}$, 1H), 7.56(d, $J=8.4\text{Hz}$, 2H), 7.39-7.36(m, 2H), 7.30(d, $J=7.2\text{Hz}$, 1H), 7.24(d, $J=7.6\text{Hz}$, 1H), 7.21-7.19(m, 2H), 7.09-7.04(m, 3H), 6.88(d, $J=8.8\text{Hz}$, 2H), 4.29(s, 2H), 3.84(s, 3H), 2.90(t, $J=6.8\text{Hz}$, 2H), 2.69(t, $J=8.0\text{Hz}$, 2H), 2.36(s, 3H), 1.89-1.81(m, 2H); $^{13}\text{C NMR}$ (100MHz, CDCl_3) δ : 198.3, 163.5, 144.8, 144.1, 142.9, 136.2, 133.7, 130.2, 129.9, 129.8, 129.6, 128.9, 128.7, 127.4, 127.3, 127.2, 124.4, 123.9, 115.2, 113.6, 55.5, 55.4, 37.7, 33.9, 22.4, 21.5; HRMS(ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{33}\text{H}_{31}\text{NO}_4\text{SNa}$ 560.1866; found 560.1870.



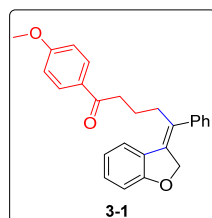
Dimethyl(E)-3-(5-(4-methoxyphenyl)-5-oxo-1-phenylpentylidene)-2,3-dihydro-1H-indene-1,1-dicarboxylate: yellow oil; $R_f=0.30$ (petroleum ether/ethyl acetate, 5:1); Column chromatography(silica gel; petroleum ether/ethyl acetate, 10:1); $^1\text{H NMR}$ (400MHz, CDCl_3) δ : 7.89-7.87(m, 2H), 7.73(d, $J=7.6\text{Hz}$, 1H), 7.61(d, $J=7.2\text{Hz}$, 1H), 7.39-7.35(m, 3H), 7.29-7.25(m, 4H), 6.89(d, $J=8.8\text{Hz}$, 2H), 3.84(s, 3H), 3.69(s, 6H), 3.19(s, 2H), 2.95(t, $J=7.2\text{Hz}$, 2H), 2.85(t, $J=8.0\text{Hz}$, 2H), 1.98-1.91(m, 2H); $^{13}\text{C NMR}$ (100MHz, CDCl_3) δ : 191.5, 163.7, 156.3, 136.8, 134.7,

133.8, 130.1, 126.9, 123.2, 123.0, 121.9, 121.4, 121.1, 120.6, 120.1, 119.8, 117.3, 106.6, 55.6, 48.4, 45.9, 34.9, 30.8, 27.1, 15.8; HRMS(ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{30}O_6Na$ 521.1935; found 521.1929.

4. References

- (1) (a) Paul, K.; Jalal, S.; Kundal, S.; Jana, U., Synthesis of Fused Dibenzofuran Derivatives via Palladium-Catalyzed Domino C-C Bond Formation and Iron-Catalyzed Cycloisomerization/Aromatization, *J. Org. Chem.* **2016**, *81*, 1164. (b) Pertschi, R.; Wagner, P.; Ghosh, N.; Gandon, V.; Blond, G. Gold(I)-Catalyzed Synthesis of Furofurans: Insight into Hetero-Diels-Alder Reactions, *Org. Lett.* **2019**, *21*, 6084. (c) Zuo, Y.; He, X.; Tang, Q.; Hu, W.; Zhou, T.; Hu, W.; Shang, Y. Palladium-Catalyzed 5-exo-dig Cyclization Cascade, Sequential Amination/Etherification for Stereoselective Construction of 3-Methyleneindolinones. *Adv. Synth. Catal.* **2021**, *363*, 2117.
- (2) (a) Ishida, N.; Sawano, S.; Murakami, M., Synthesis of 3,3-disubstituted α -tetralones by rhodium-catalysed reaction of 1-(2-haloaryl)cyclobutanols. *Chem. Commun.* **2012**, *48*, 1973. (b) Ishida, N.; Nakanishi, Y.; Murakami, M., Reactivity Change of Cyclobutanols towards Isocyanates: Rhodium Favors C-Carbamoylation over O-Carbamoylation. *Angew. Chem. Int. Ed.* **2013**, *52*, 11875. (c) Wang, Z.; Chen, Z.; Sun, J., Catalytic Enantioselective Intermolecular Desymmetrization of 3-Substituted Oxetanes. *Angew. Chem. Int. Ed.* **2013**, *52*, 6685. (d) Yada, A.; Fujita, S.; Murakami, M., Enantioselective Insertion of a Carbenoid Carbon into a C-C Bond To Expand Cyclobutanols to Cyclopentanols. *J. Am. Chem. Soc.* **2014**, *136*, 7217.

5. The crystal structure of product 3-1



Bond precision:	C-C = 0.0066 Å	Wavelength=1.54184
Cell:	a=14.0101(3) alpha=90	b=24.6150(6) beta=90
		c=5.6930(1) gamma=90
Temperature: 150 K		
	Calculated	Reported
Volume	1963.28(7)	1963.28(7)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
Moiety formula	C ₂₆ H ₂₄ O ₃	C ₂₆ H ₂₄ O ₃
Sum formula	C ₂₆ H ₂₄ O ₃	C ₂₆ H ₂₄ O ₃
Mr	384.45	384.45
Dx, g cm ⁻³	1.301	1.301
Z	4	4

Mu (mm-1)	0.665	0.665
F000	816.0	816.0
F000'	818.38	
h,k,lmax	17,30,6	17,29,6
Nref	3802[2105]	2628
Tmin,Tmax	0.993,0.993	0.470,1.000
Tmin'	0.993	

Correction method= # Reported T Limits: Tmin=0.470 Tmax=1.000 AbsCorr =

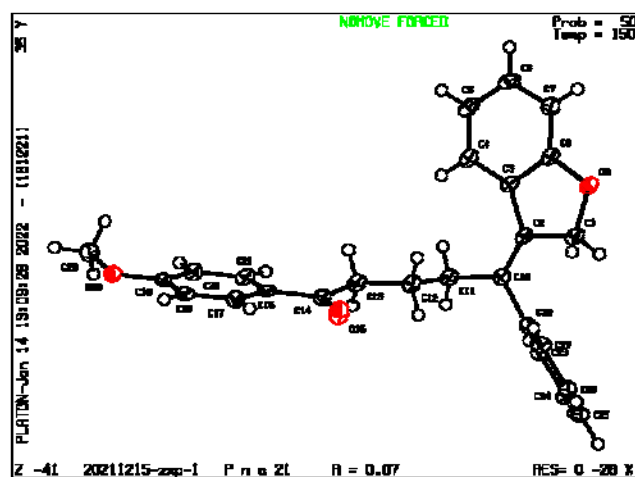
Data completeness= 1.25/0.69 Theta(max)= 71.310

R(reflections)= 0.0651(2446)

wR2(reflections)= 0.1976(2628)

S = 1.127

Npar= 263

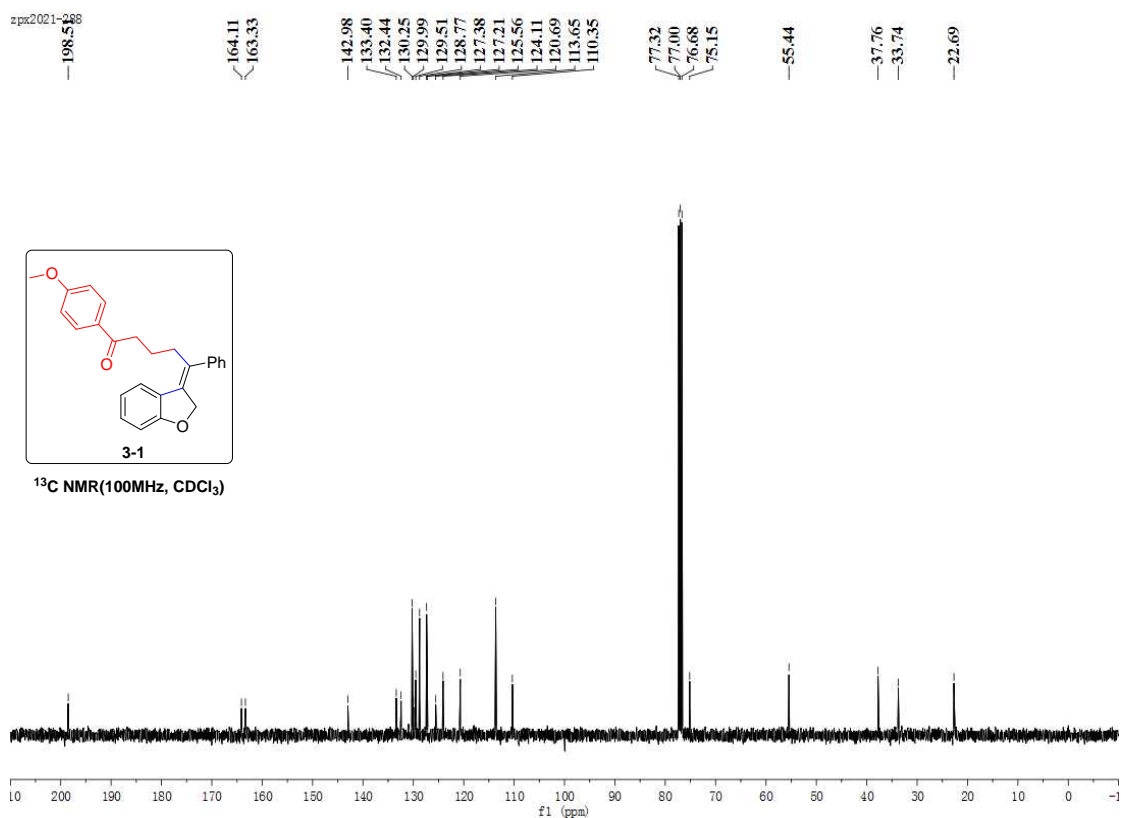
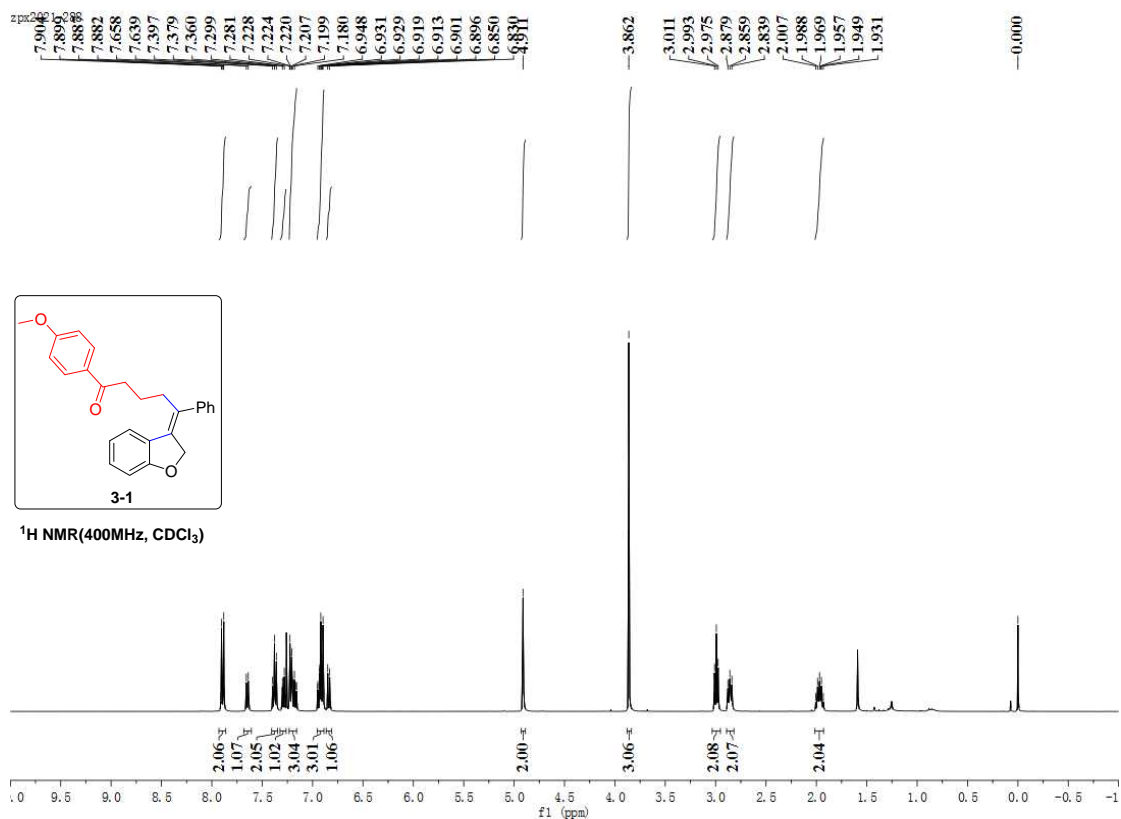


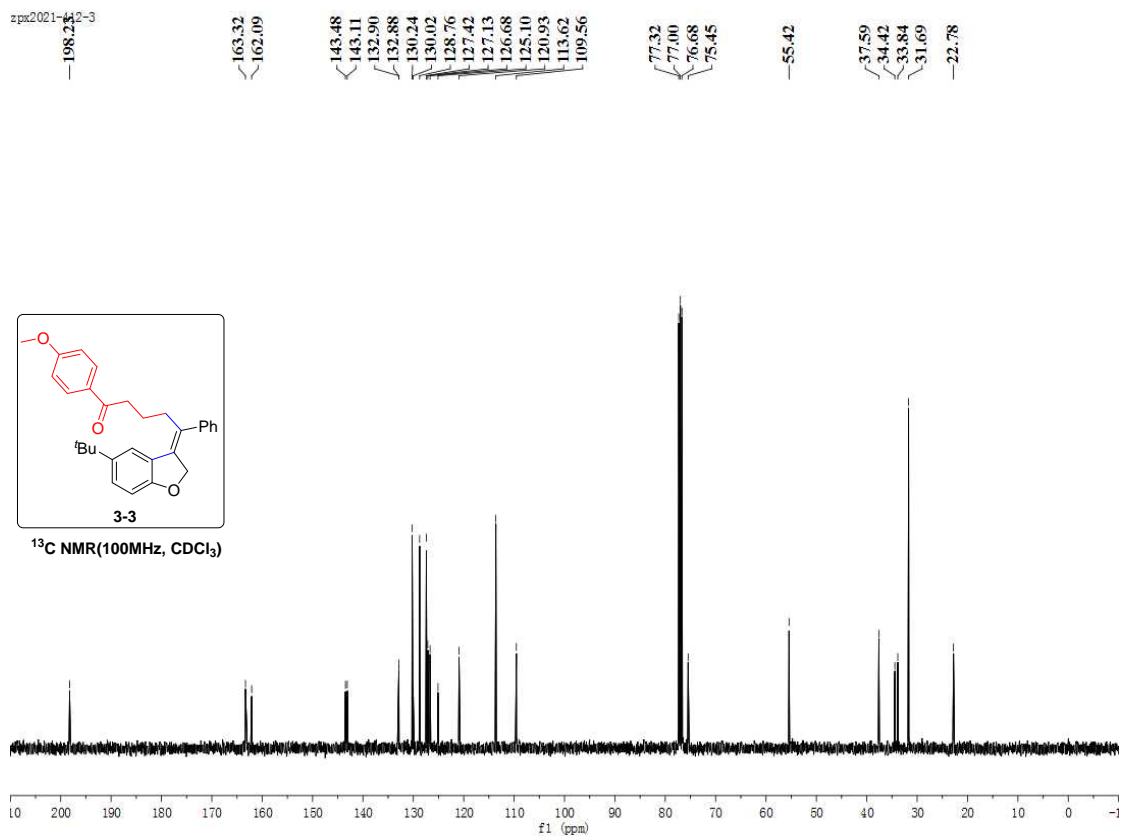
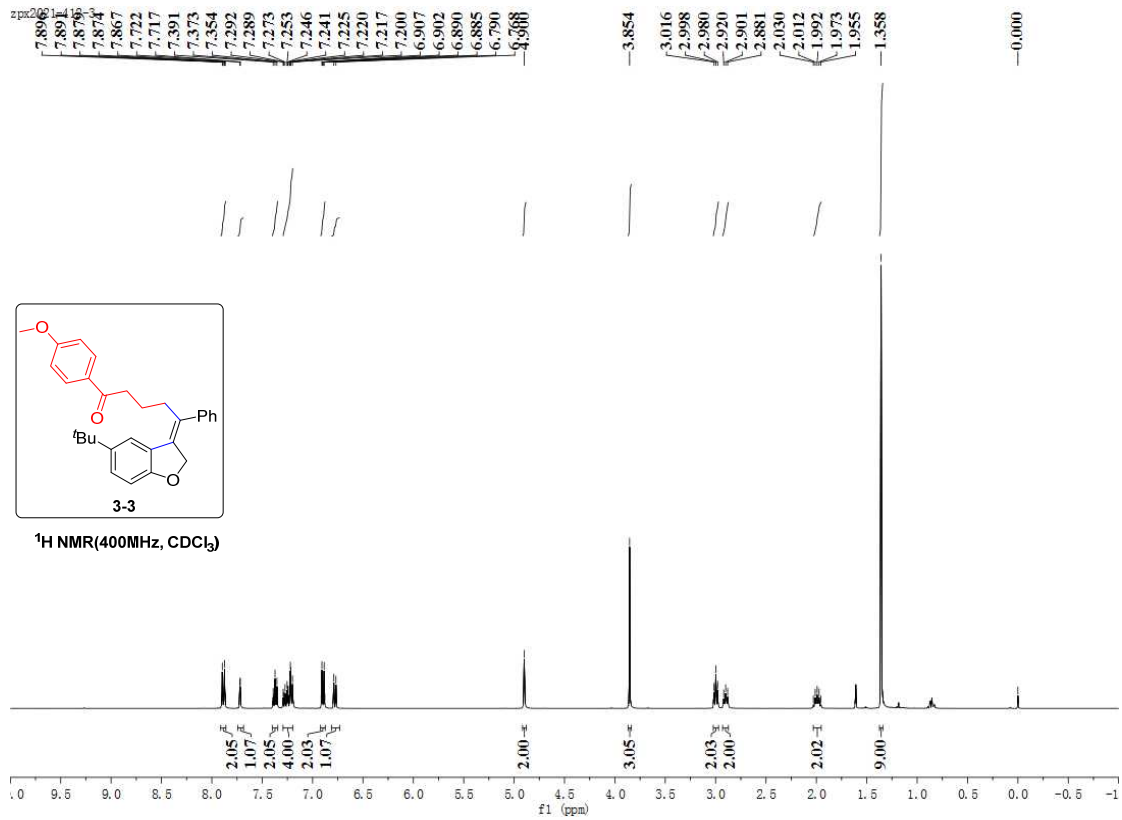
Thermal ellipsoids are drawn at 30% probability level.

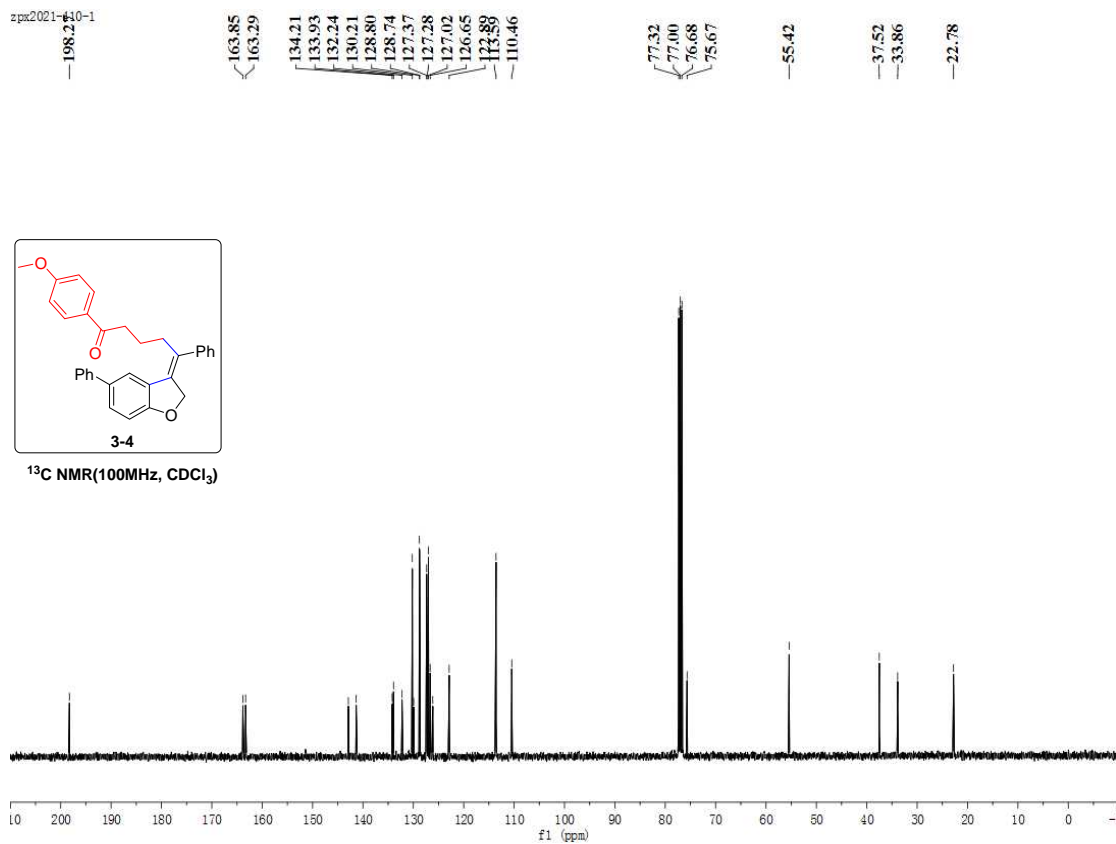
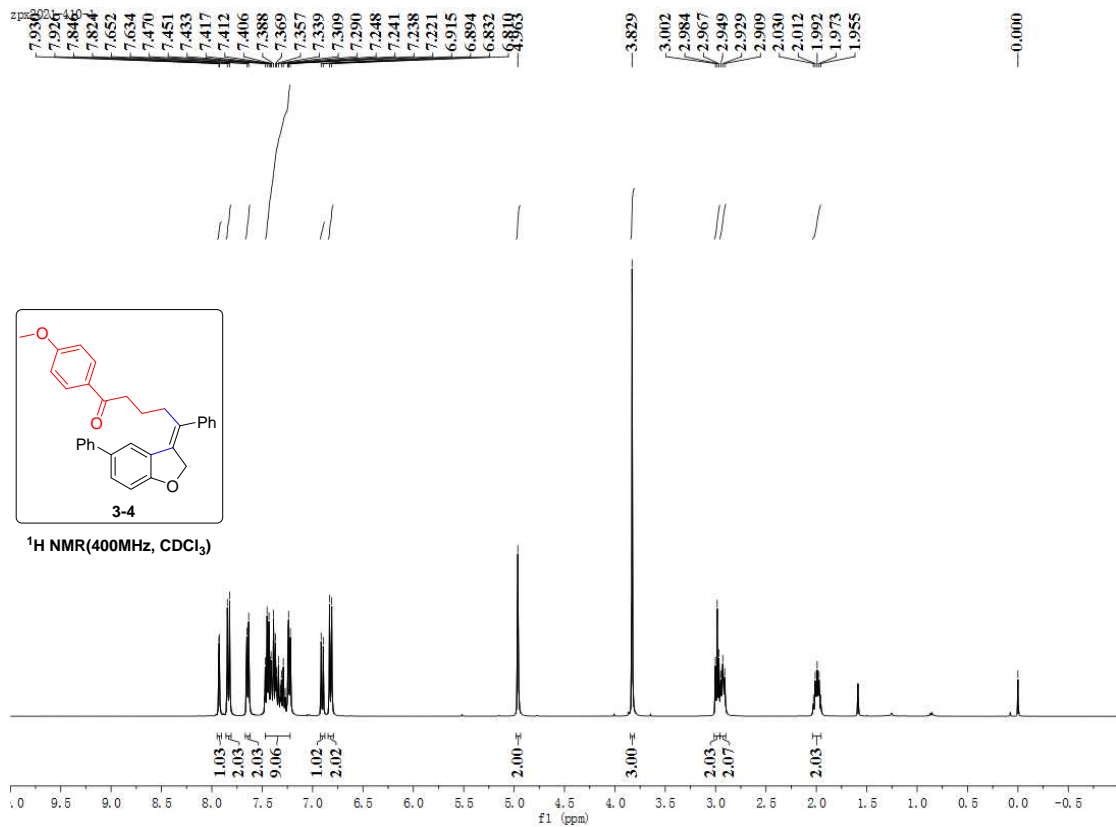
Sample preparation: A solution of compound **3-1** (100 mg) in ethyl acetate was placed in a vial (5 mL). Petroleum ether was added to the vial with a dropper until a small amount of solid precipitation, then, added the ethyl acetate until the solution clarification. The single crystal **3-1** was obtained by slowly evaporating mixed solvent at room temperature under the air conditions.

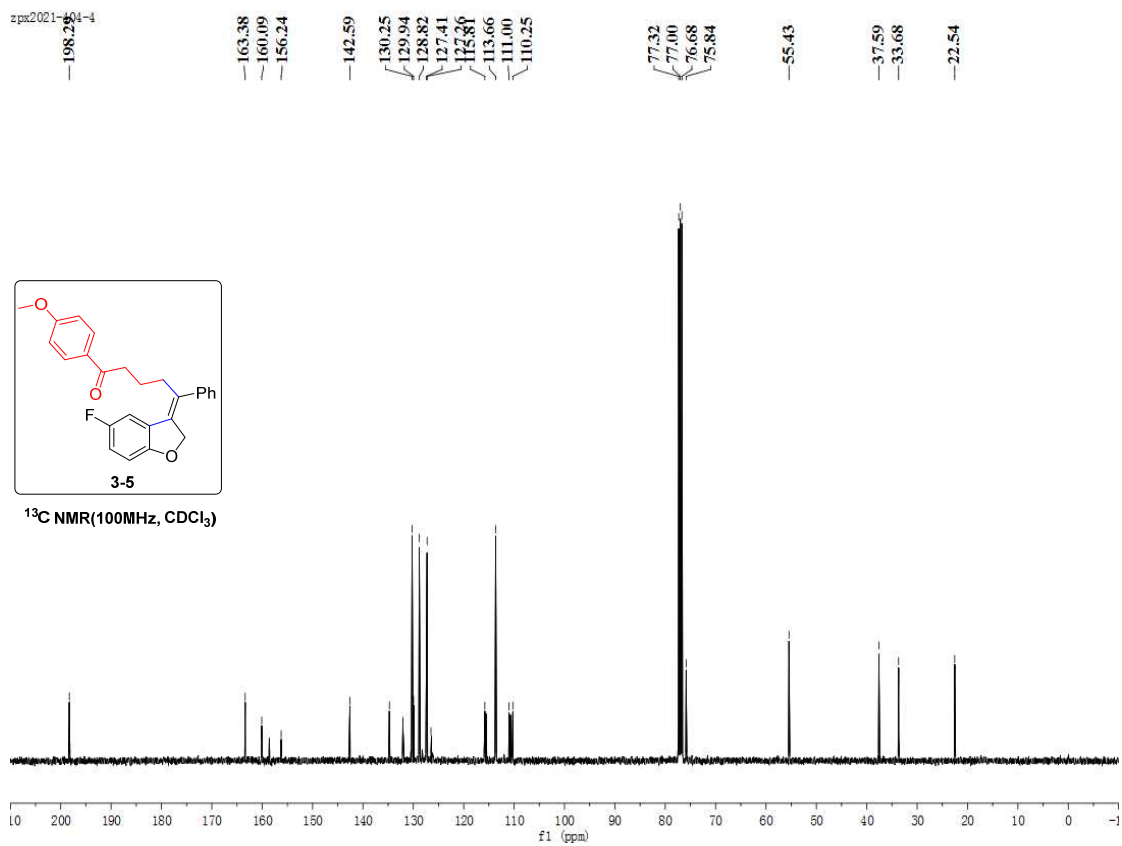
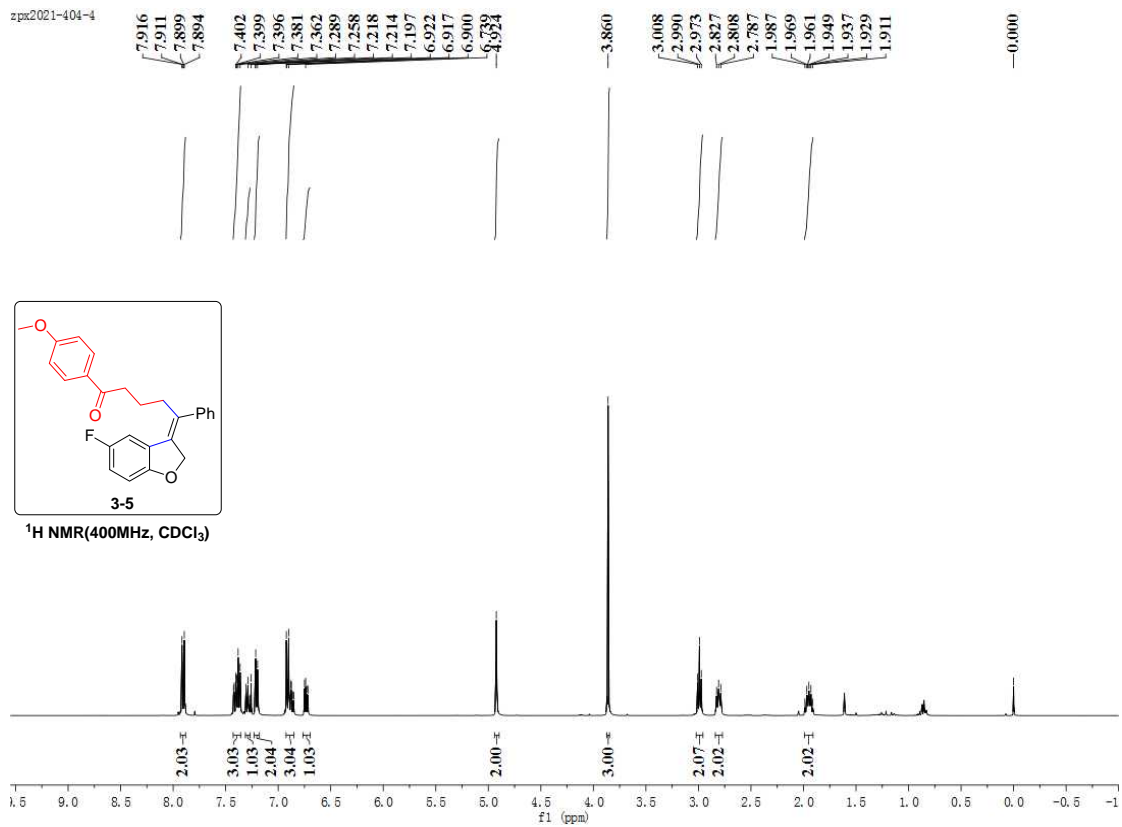
Crystal measurement: X-ray crystal structures were determined at 150 K. The crystal was measured on a SuperNova, Dual, Cu at zero, Eos diffractometer.

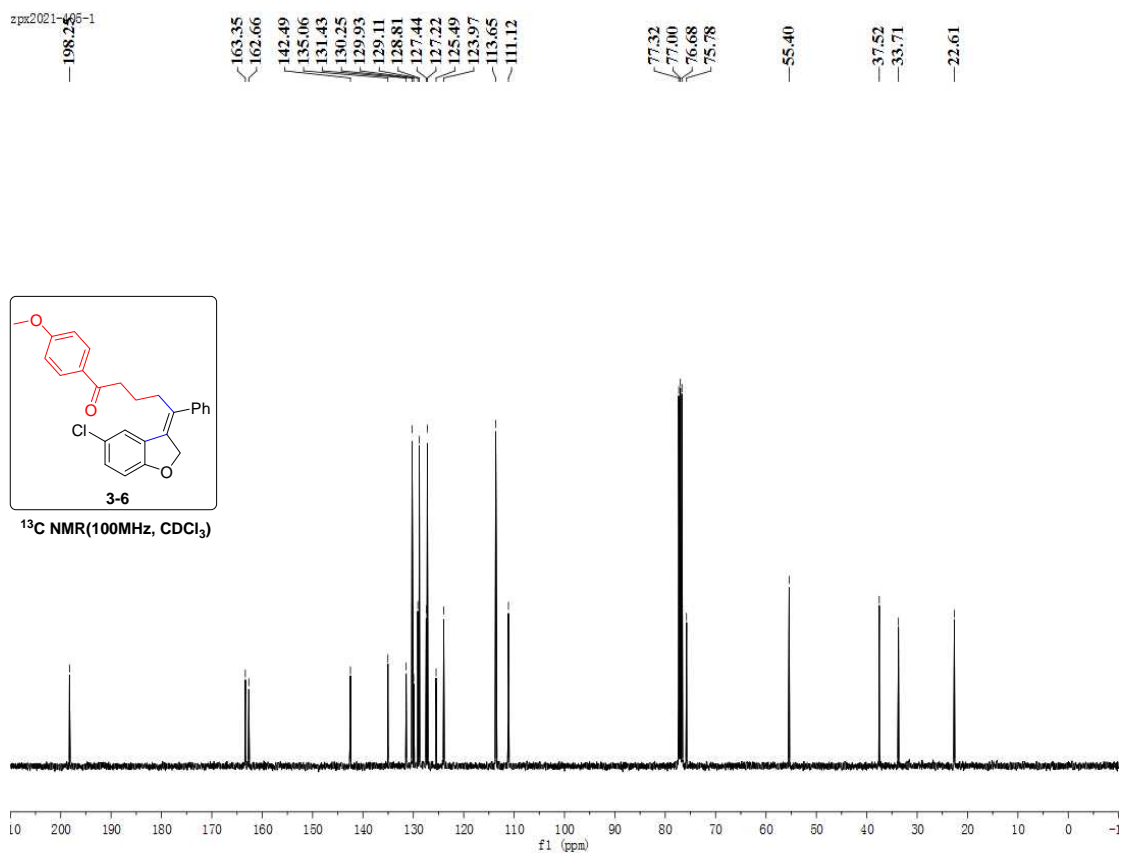
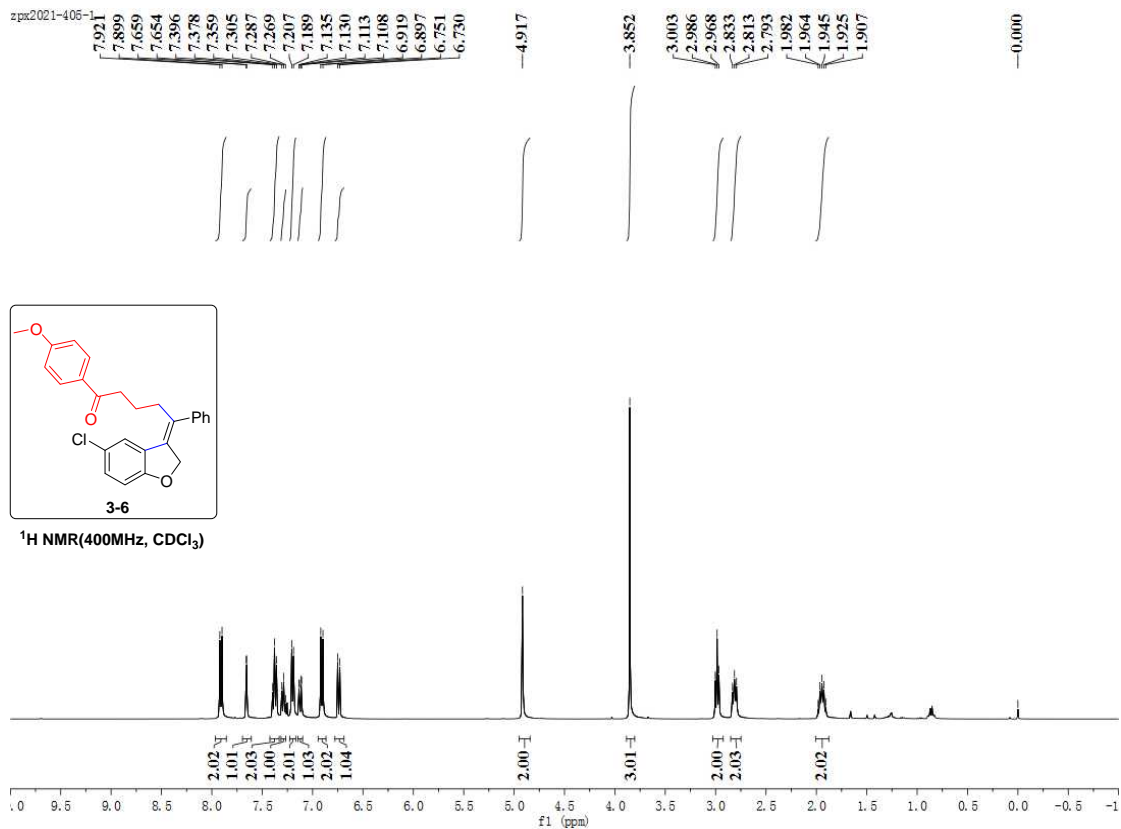
6. ^1H , ^{13}C spectra for compound 3



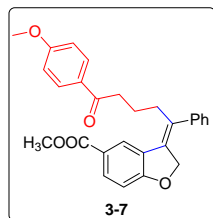
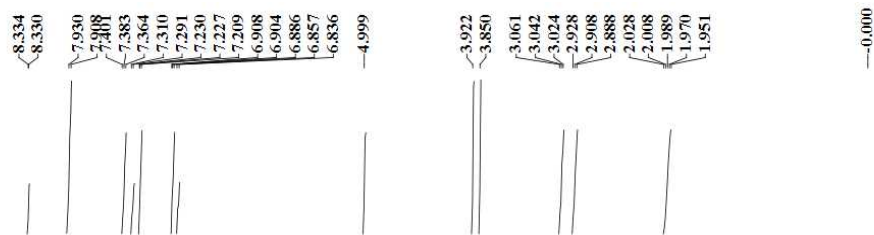




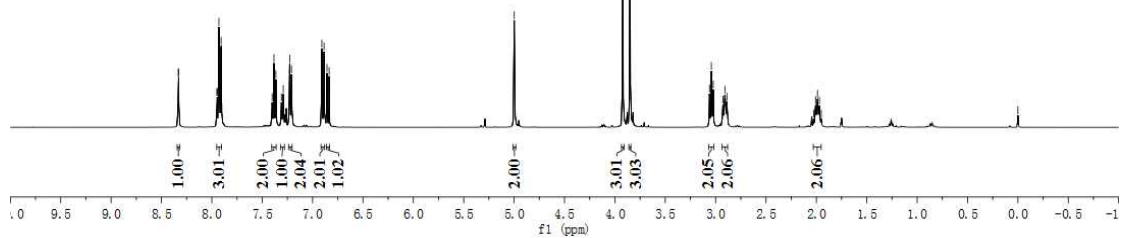




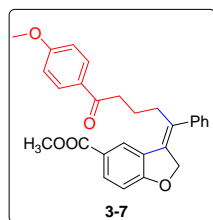
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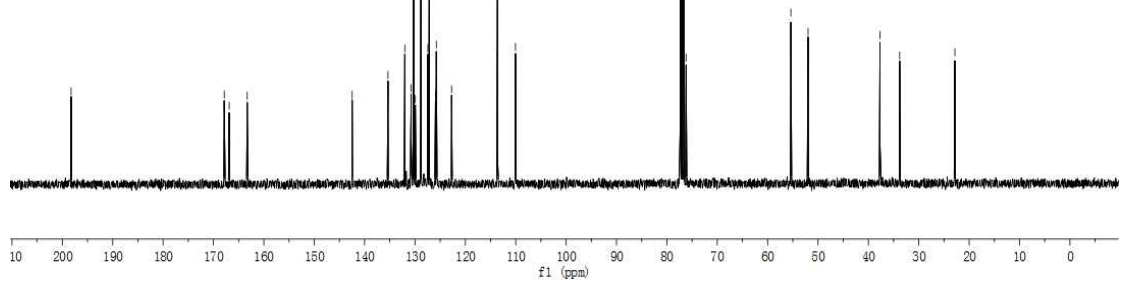
¹H NMR(400MHz, CDCl₃)



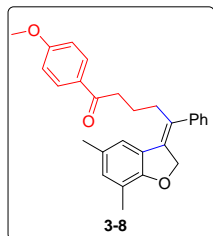
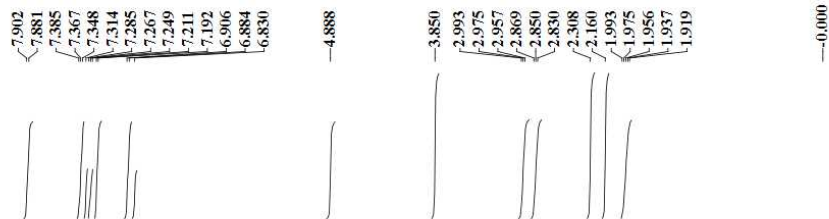
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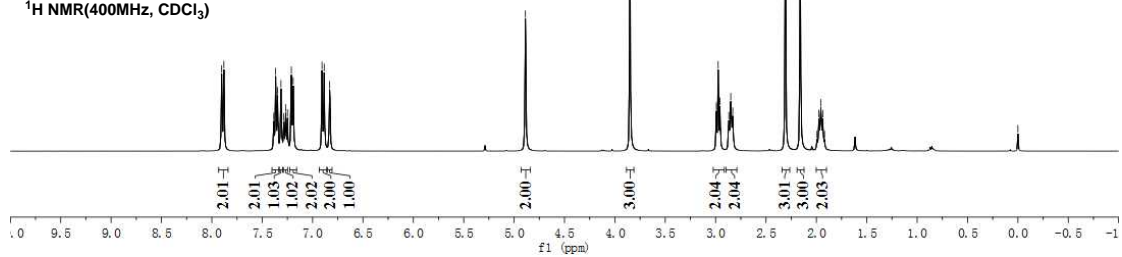
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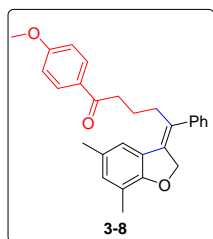
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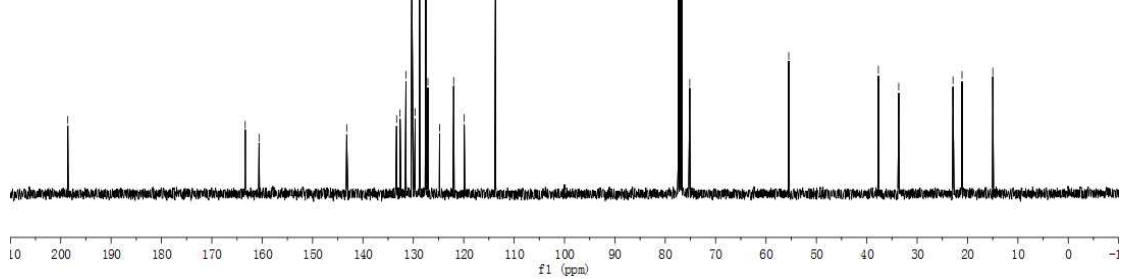
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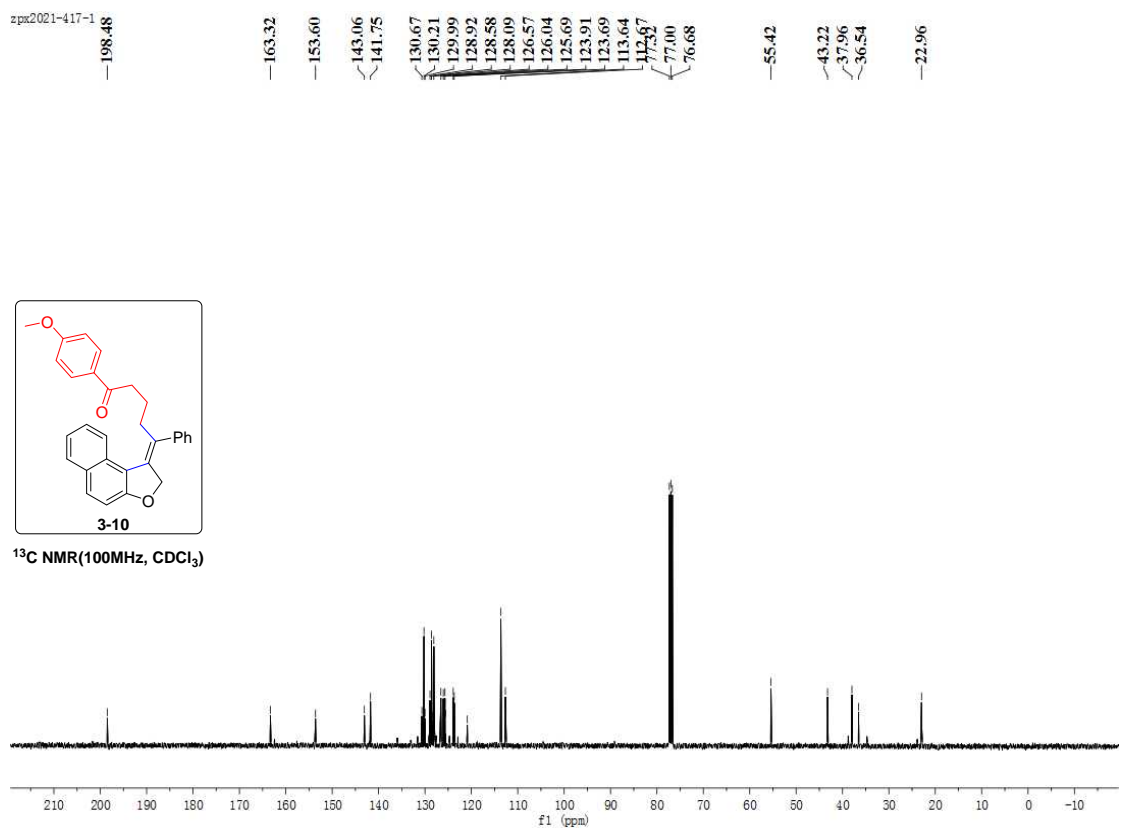
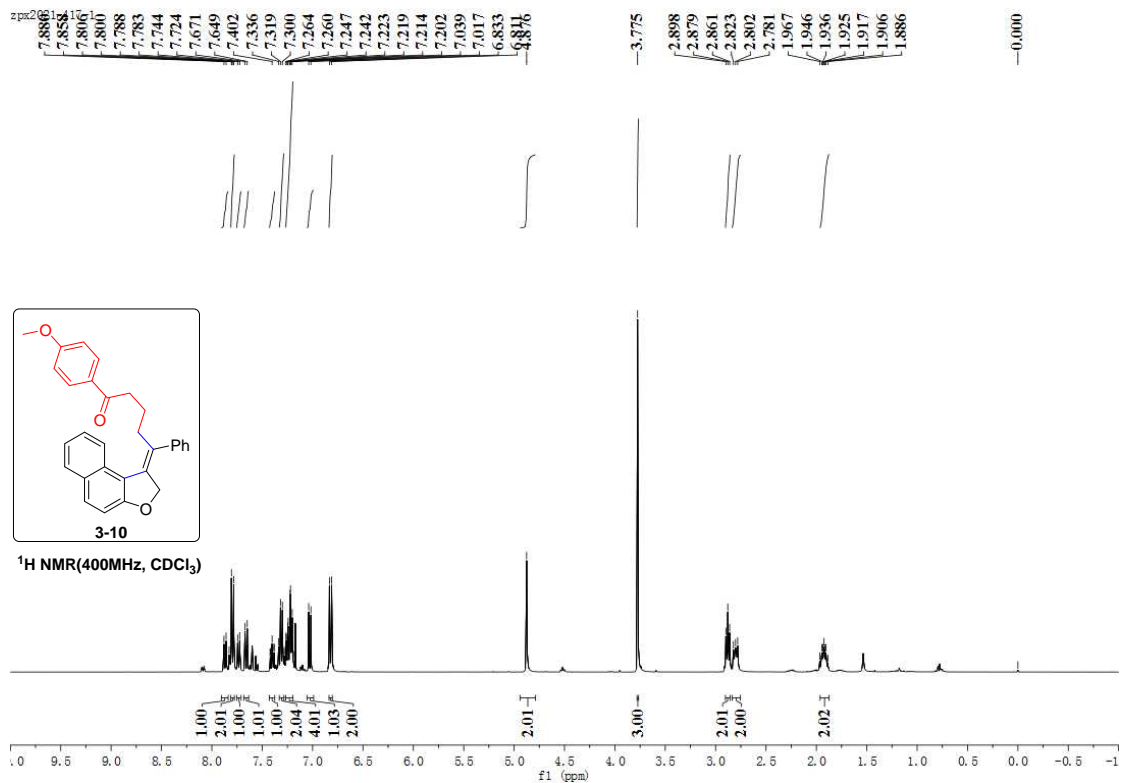


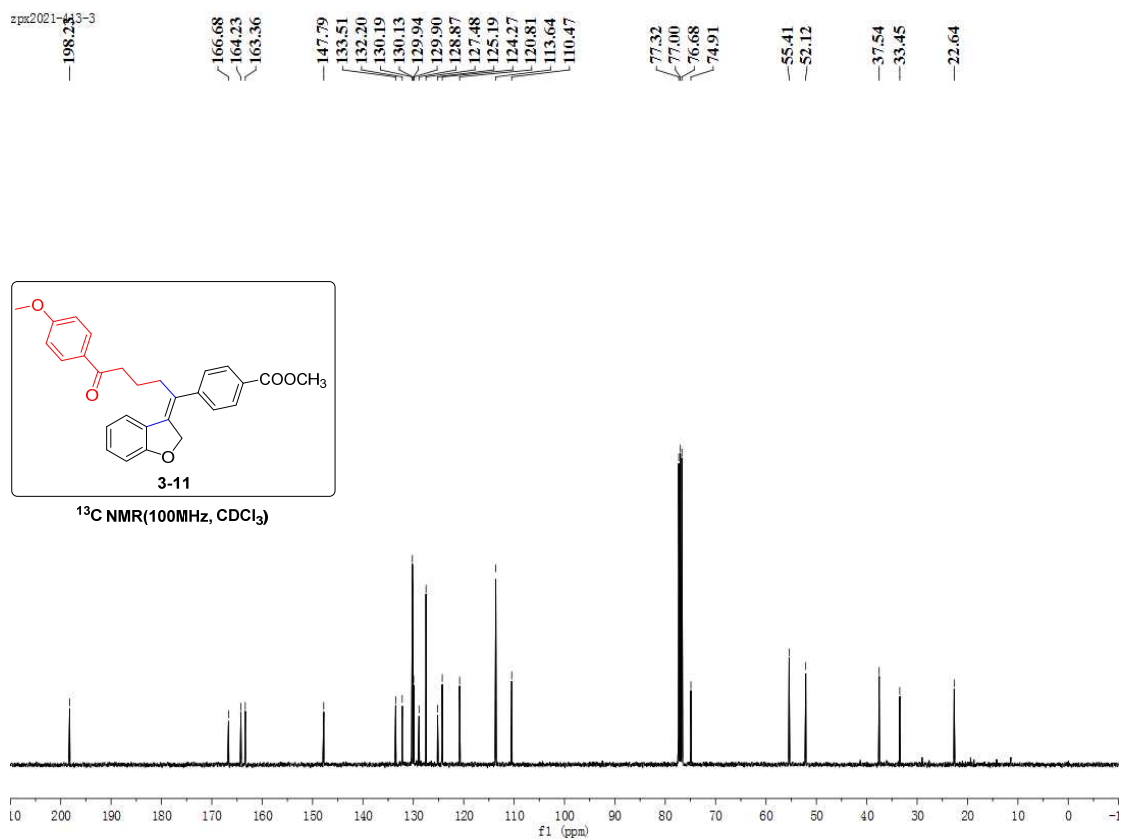
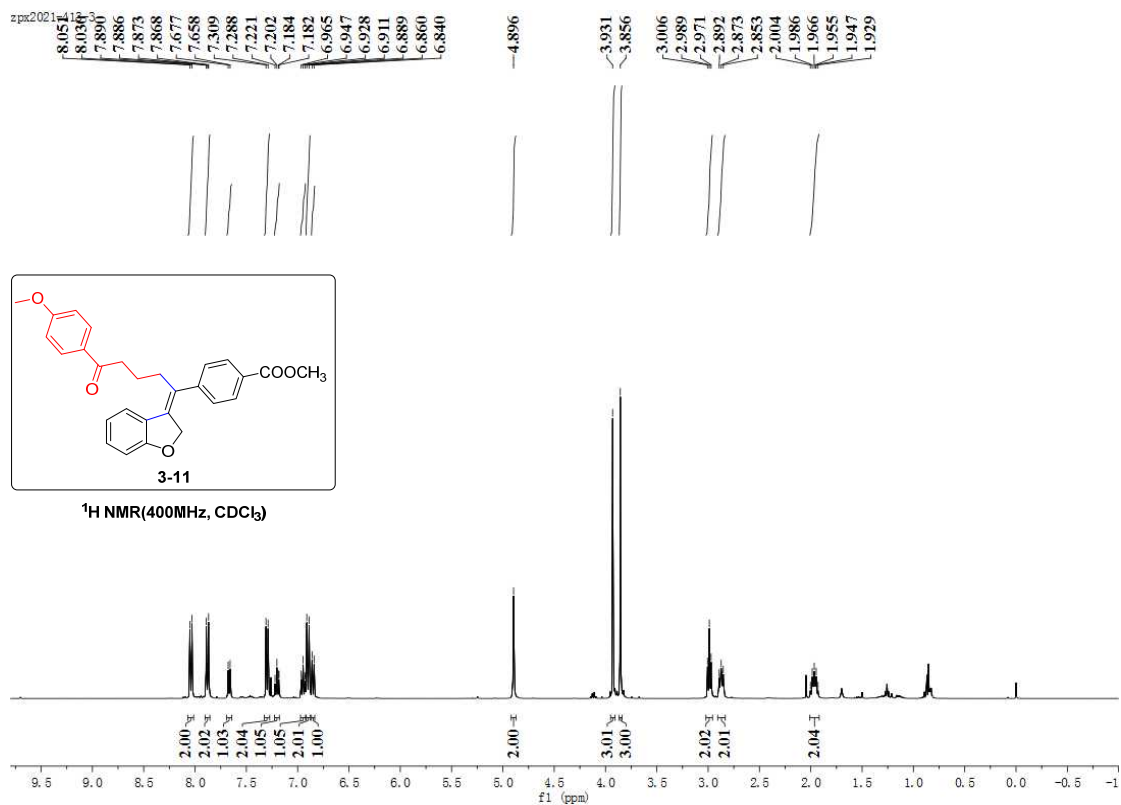
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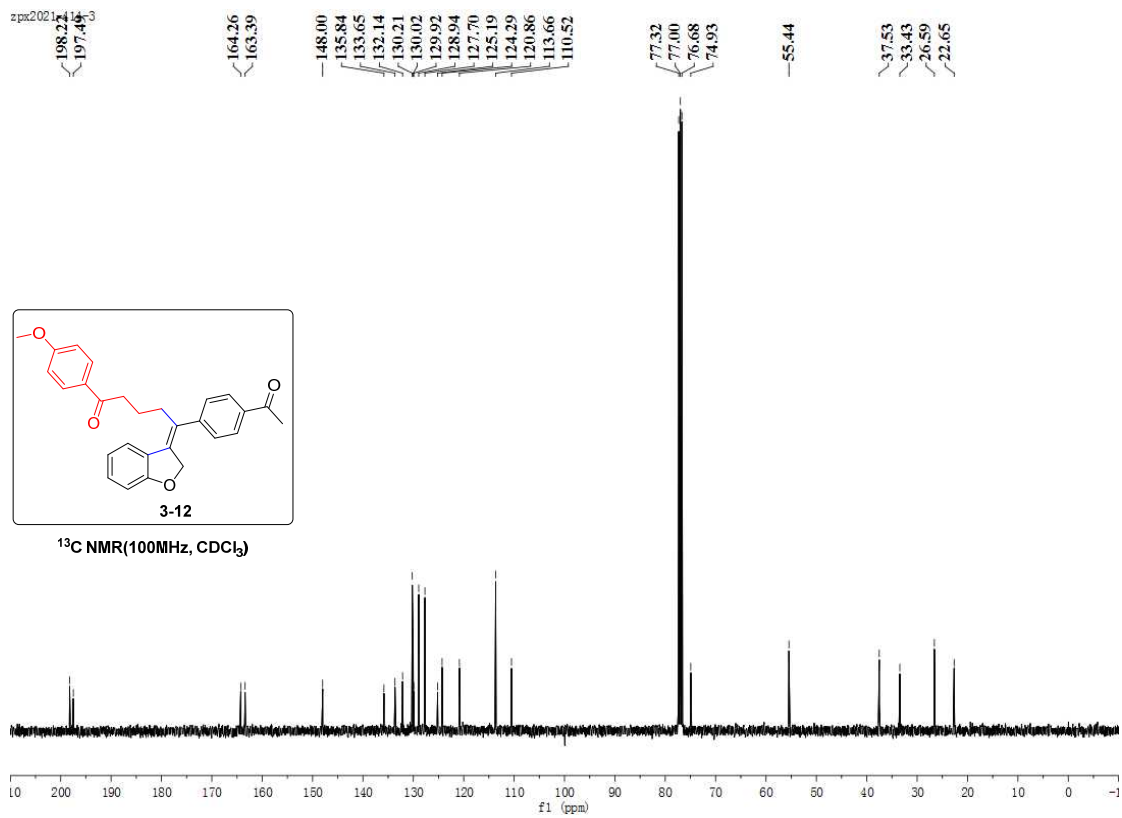
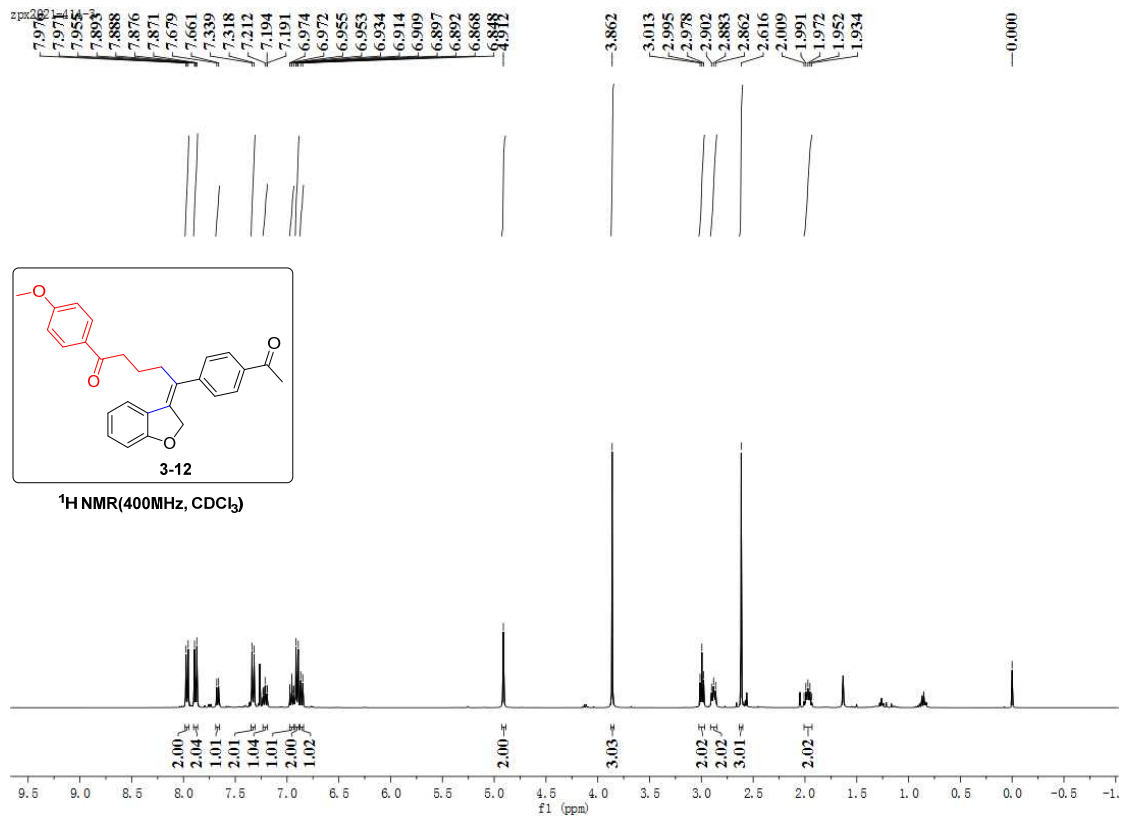


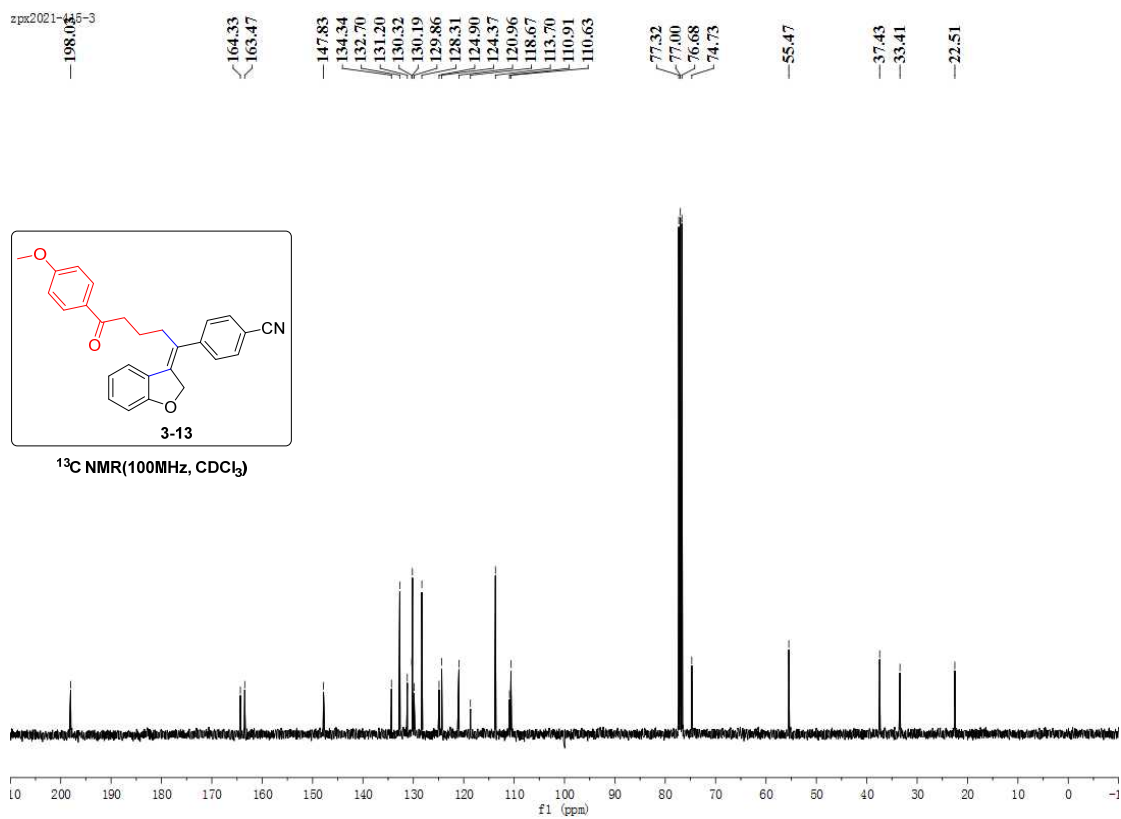
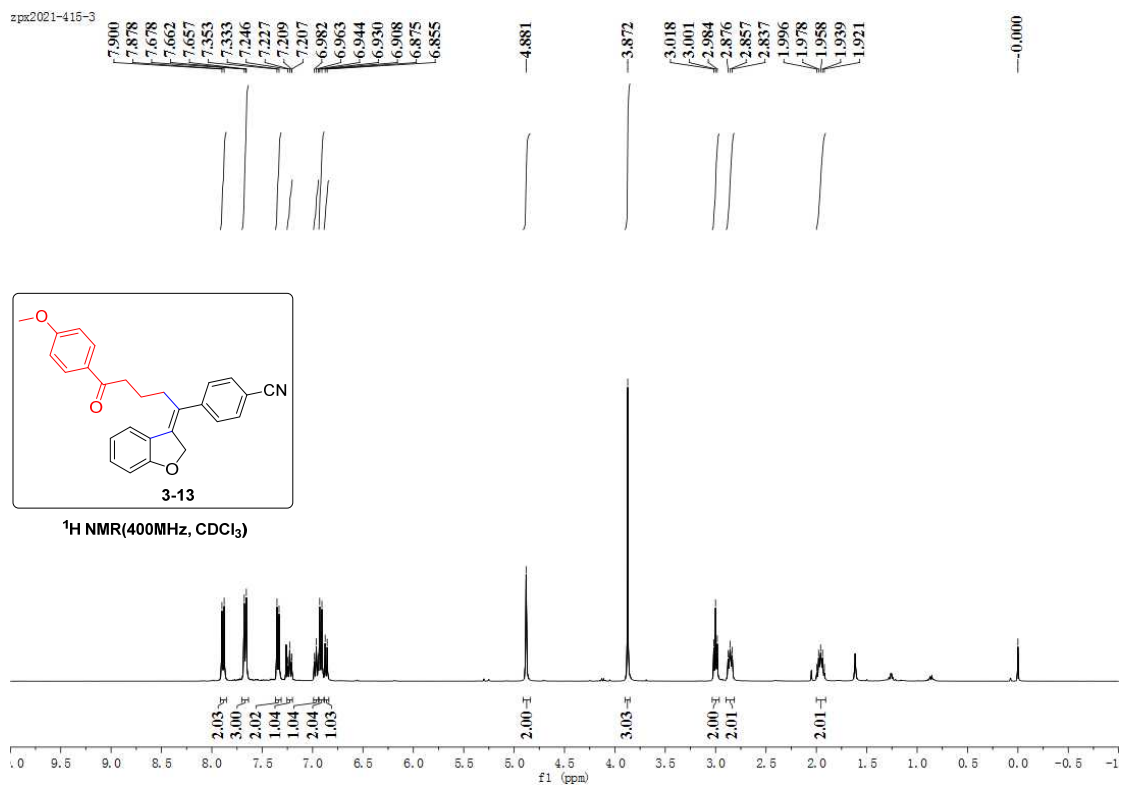
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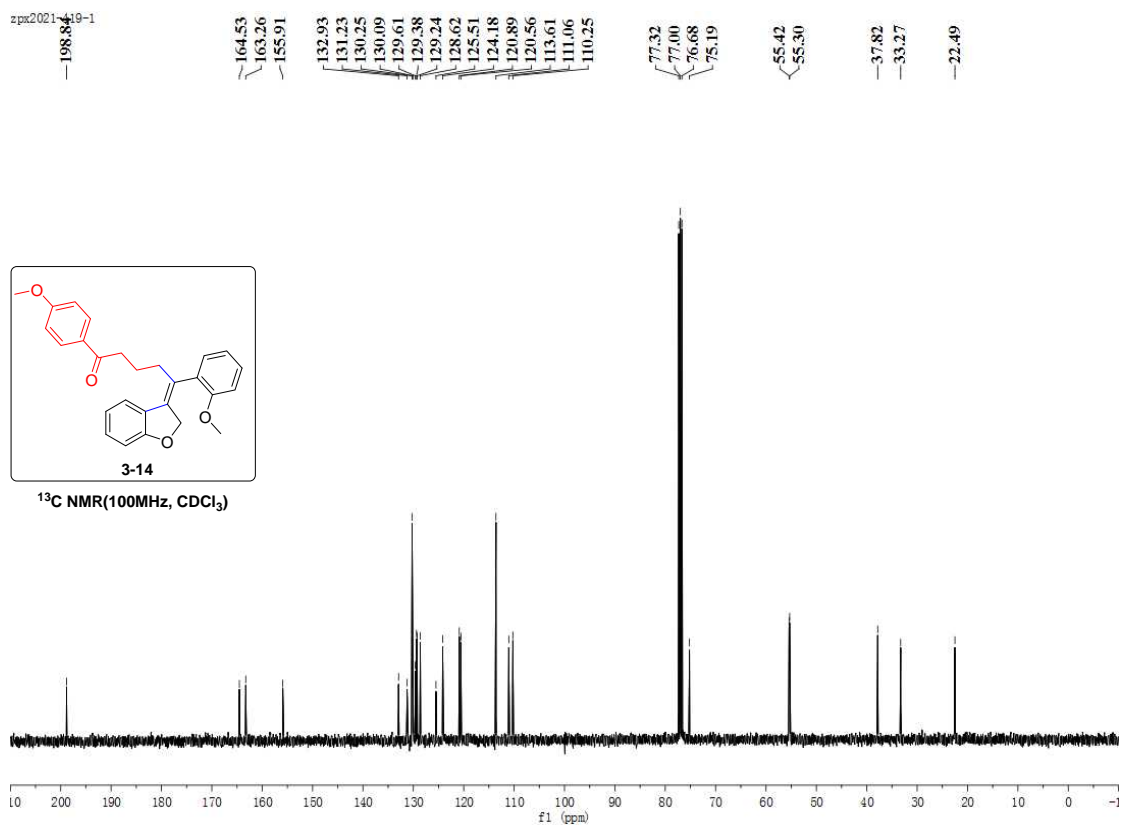
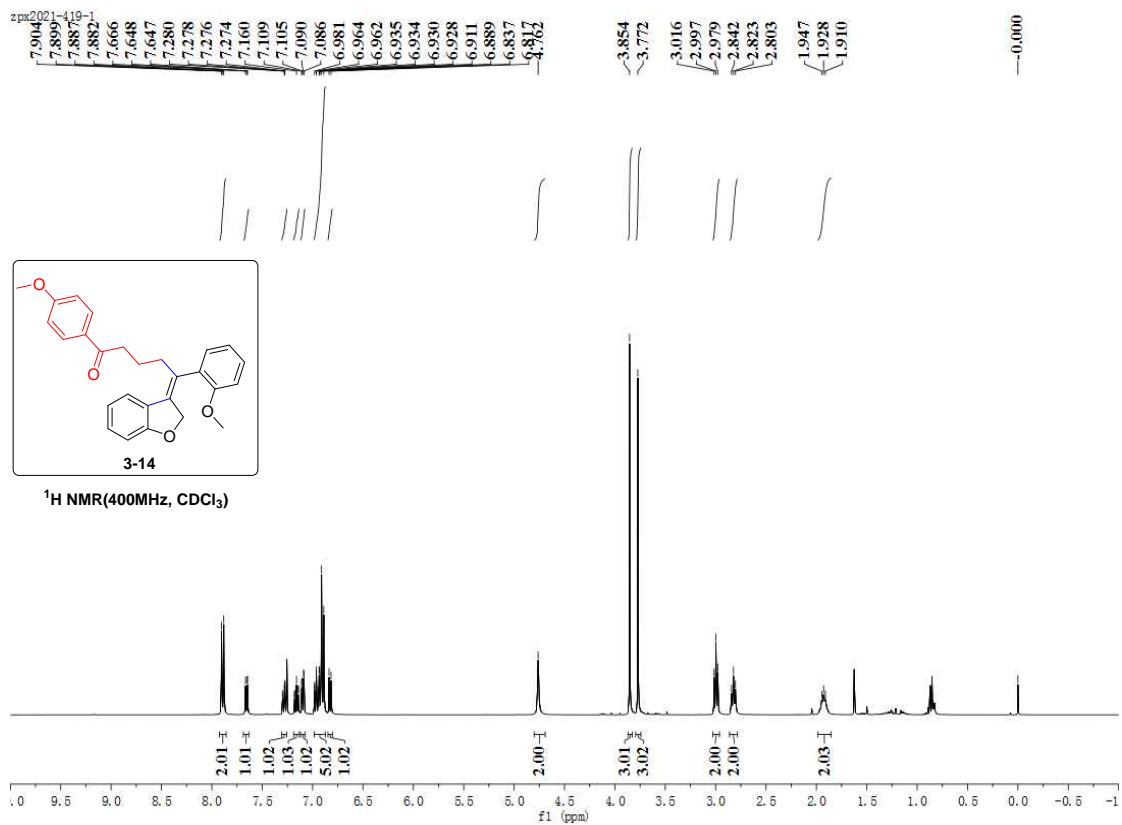


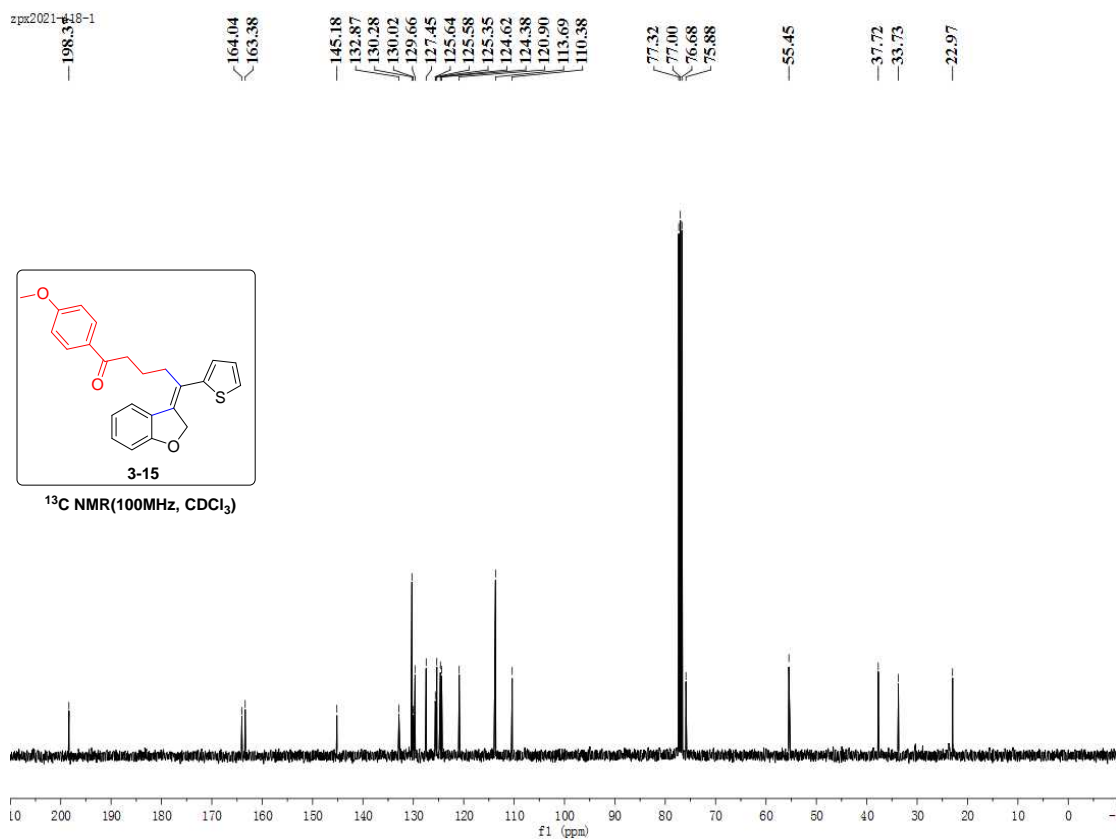
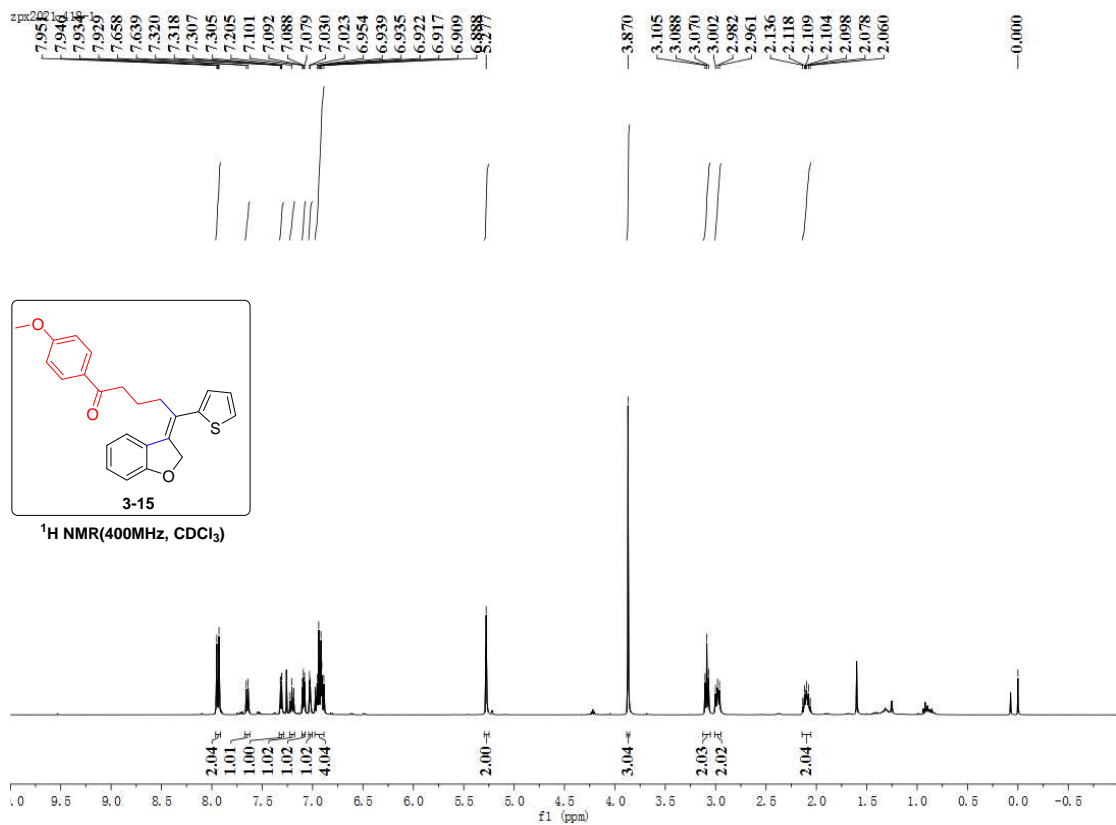




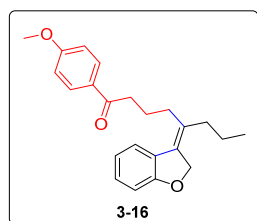
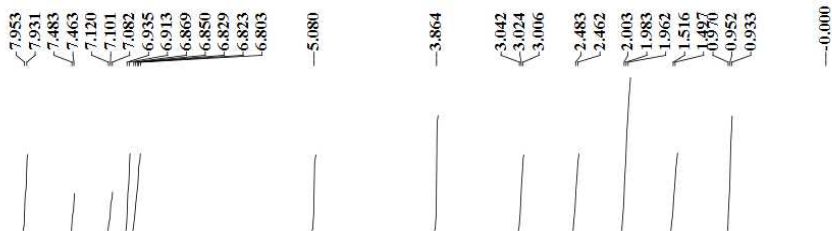






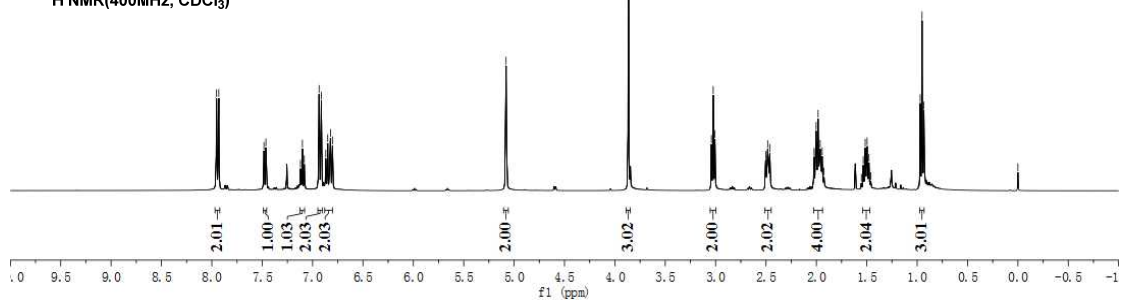


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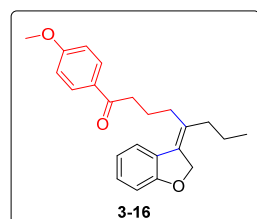
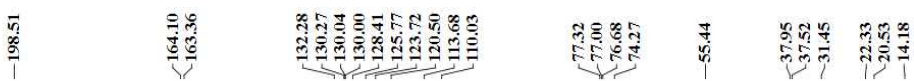


3-16

¹H NMR(400MHz, CDCl₃)

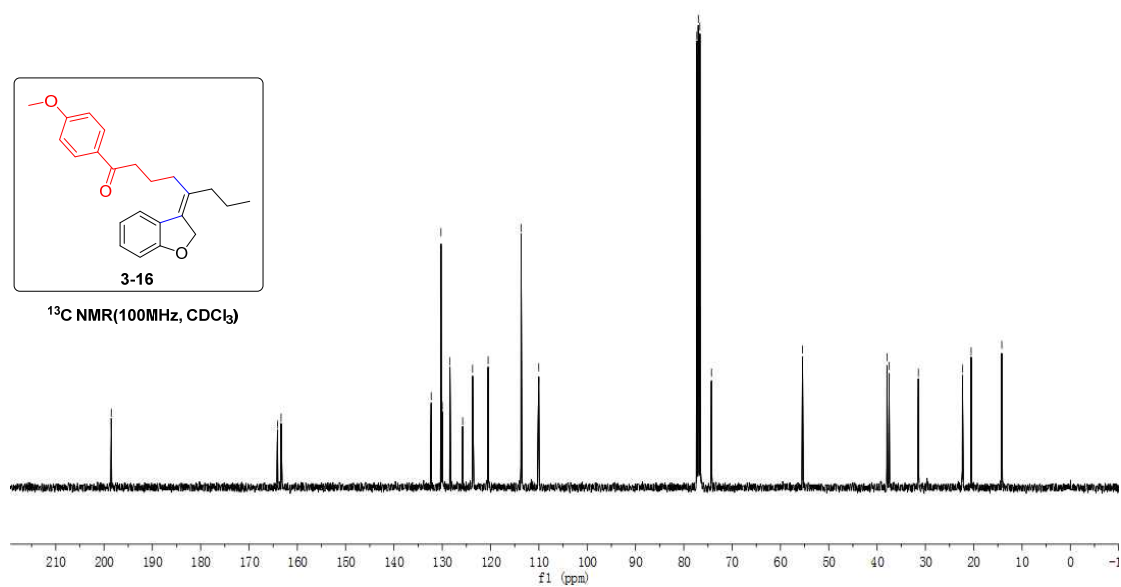


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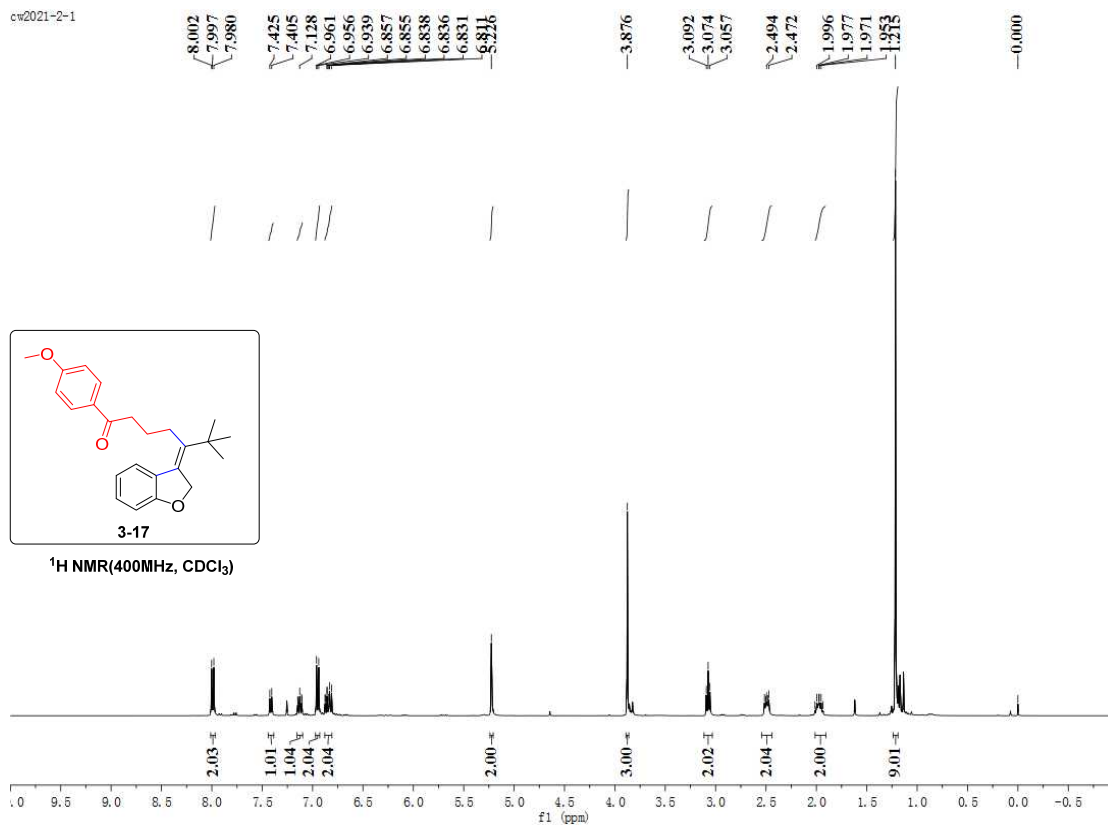


3-16

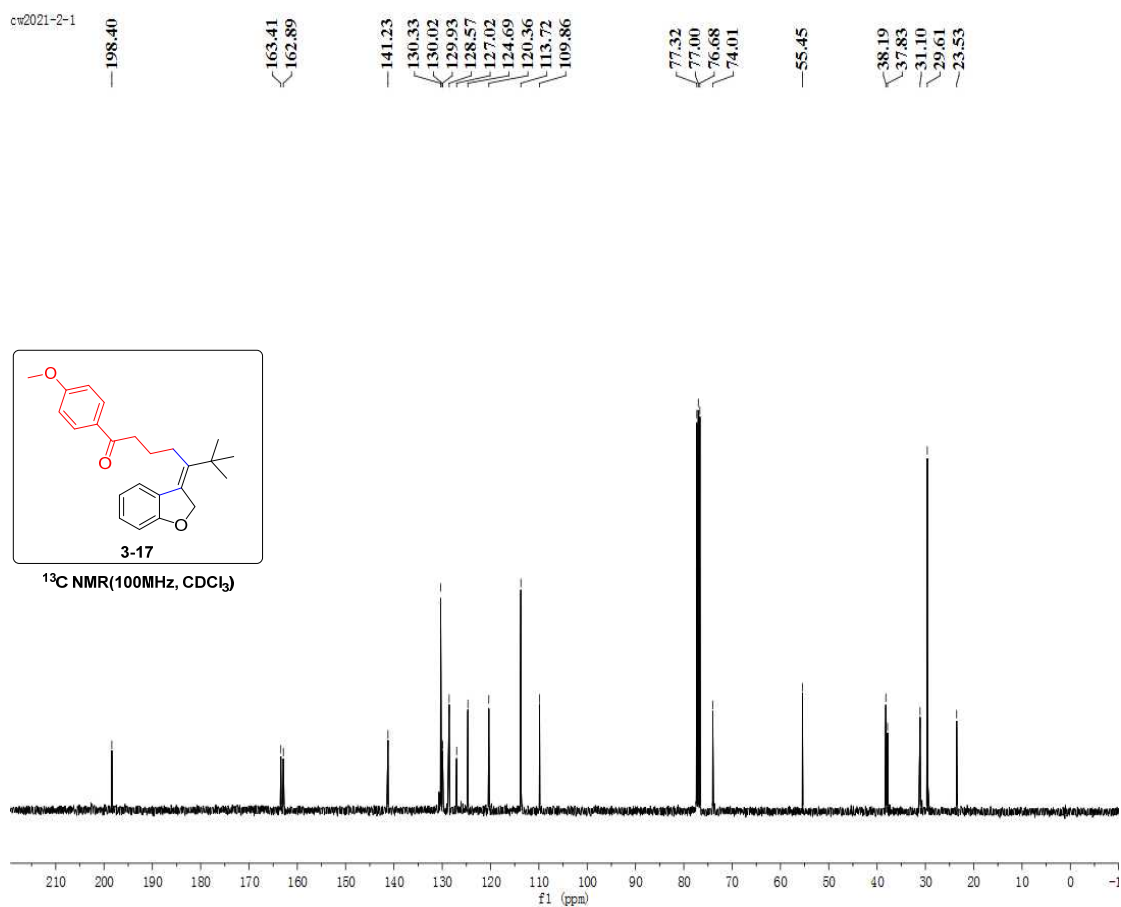
¹³C NMR(100MHz, CDCl₃)

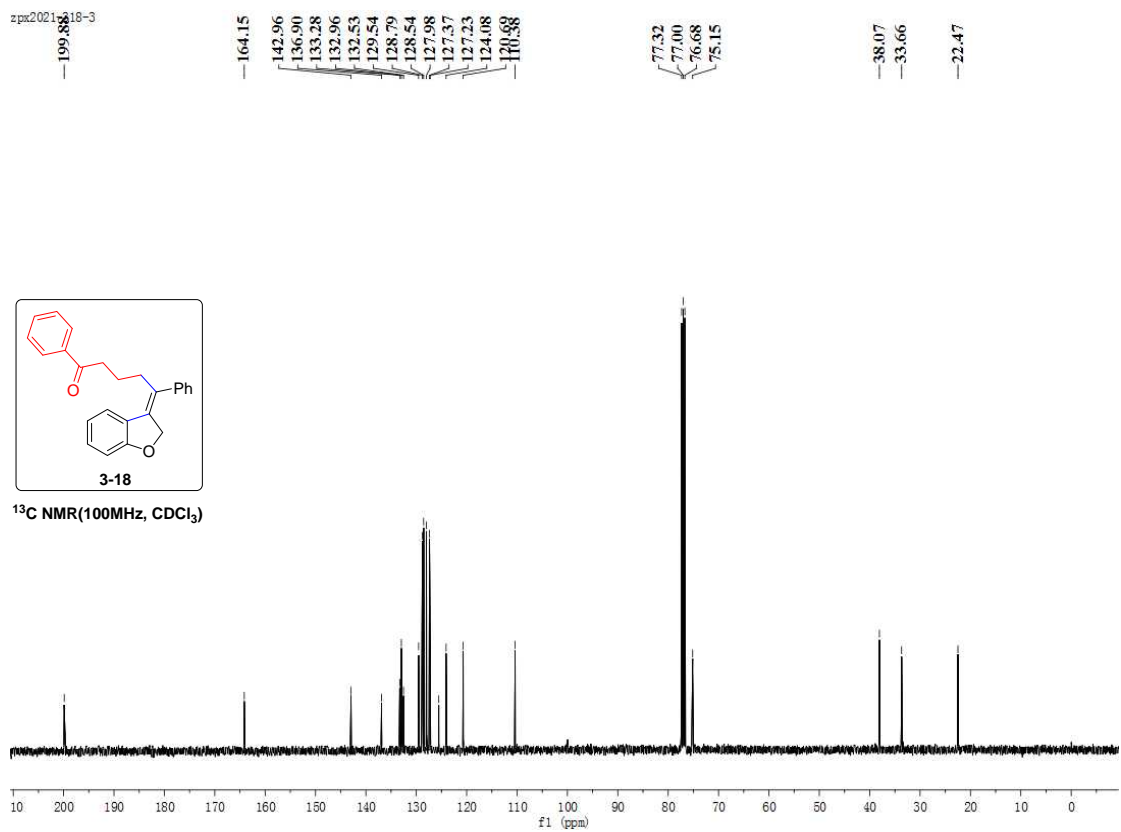
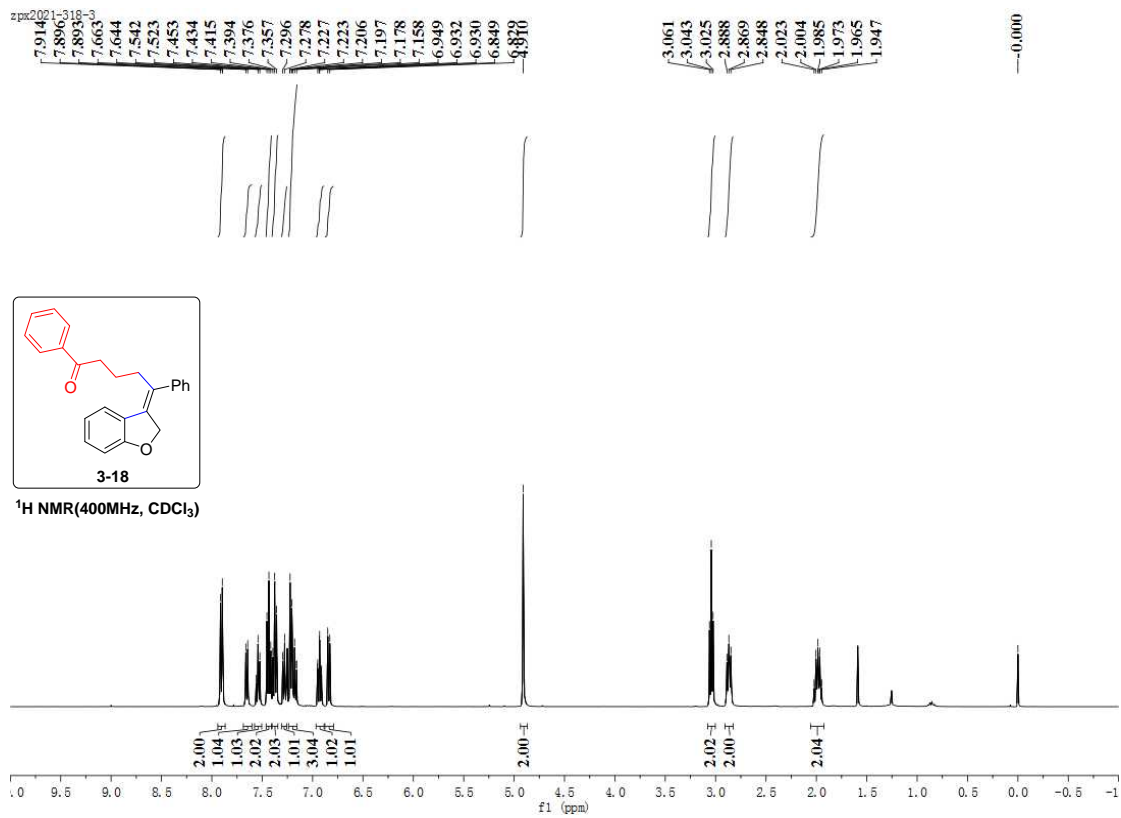


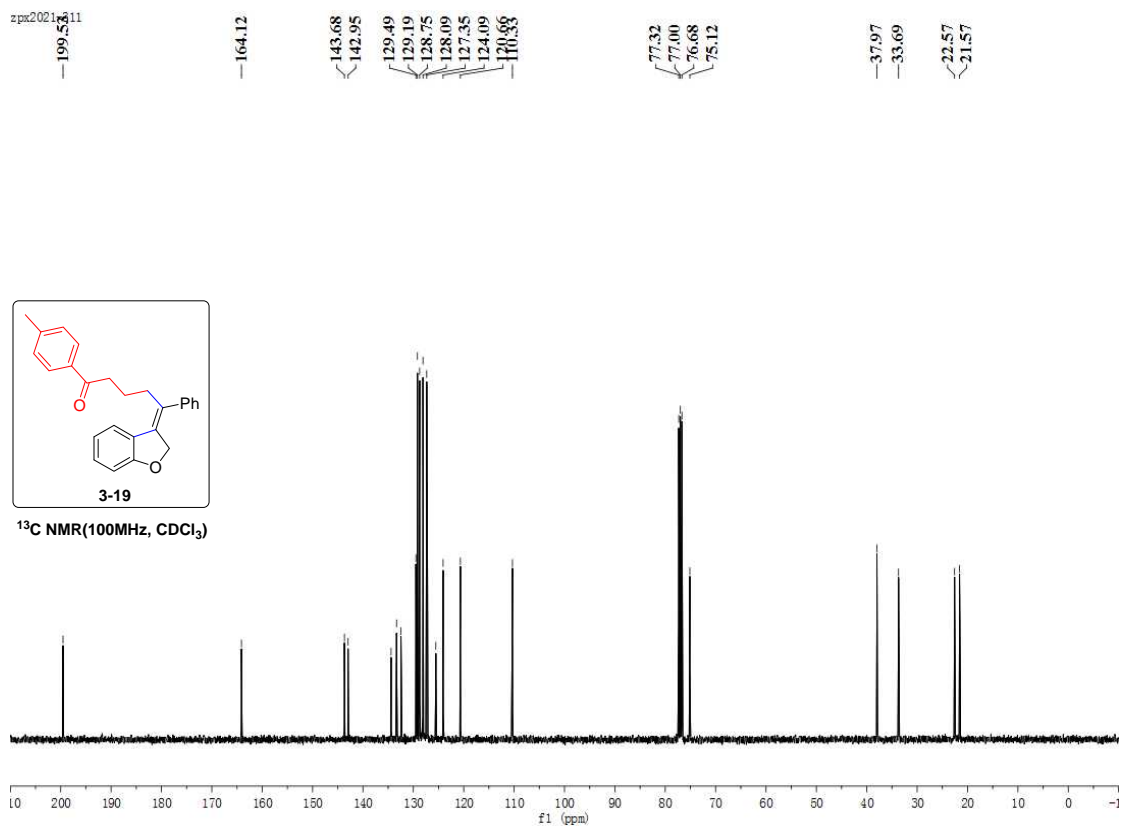
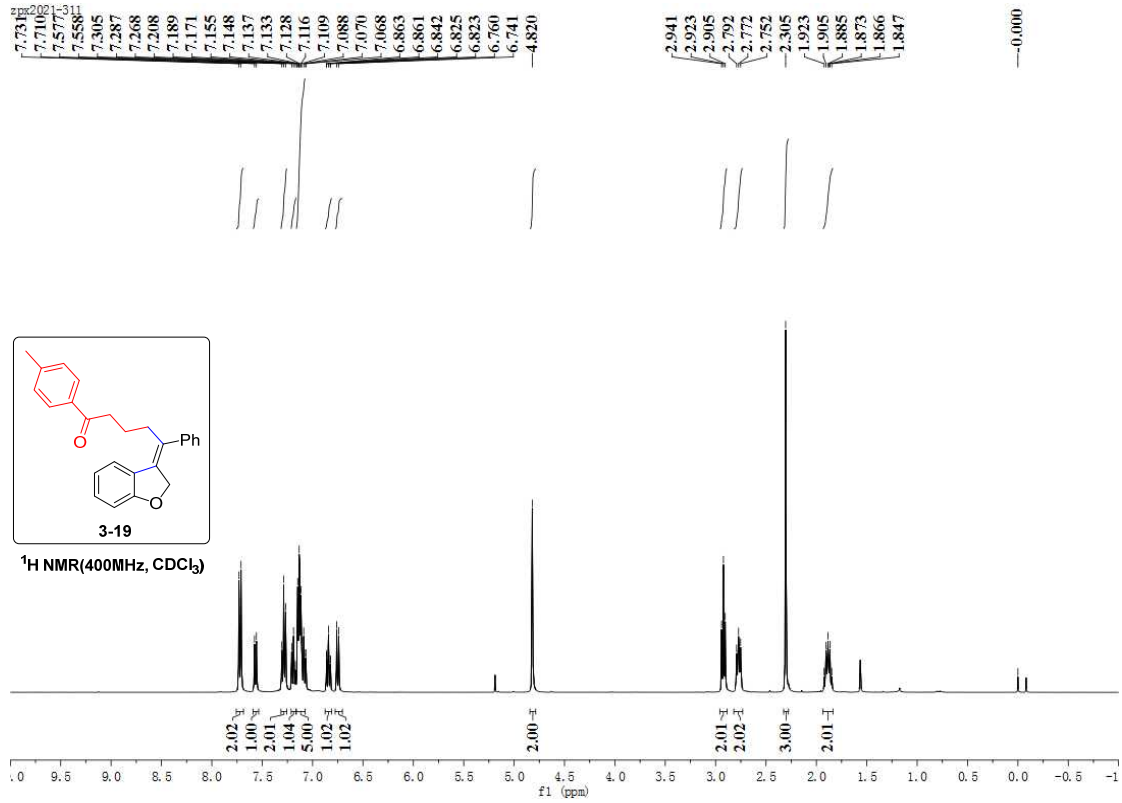
cw2021-2-1

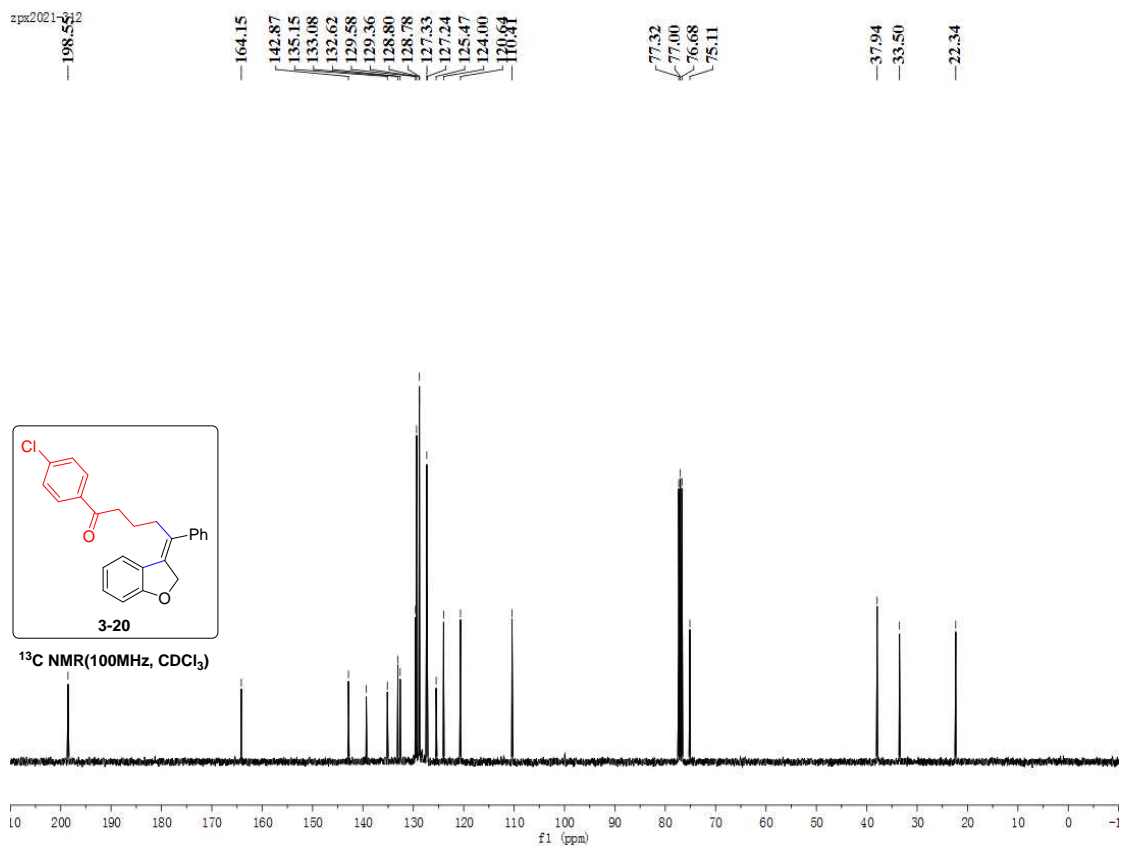
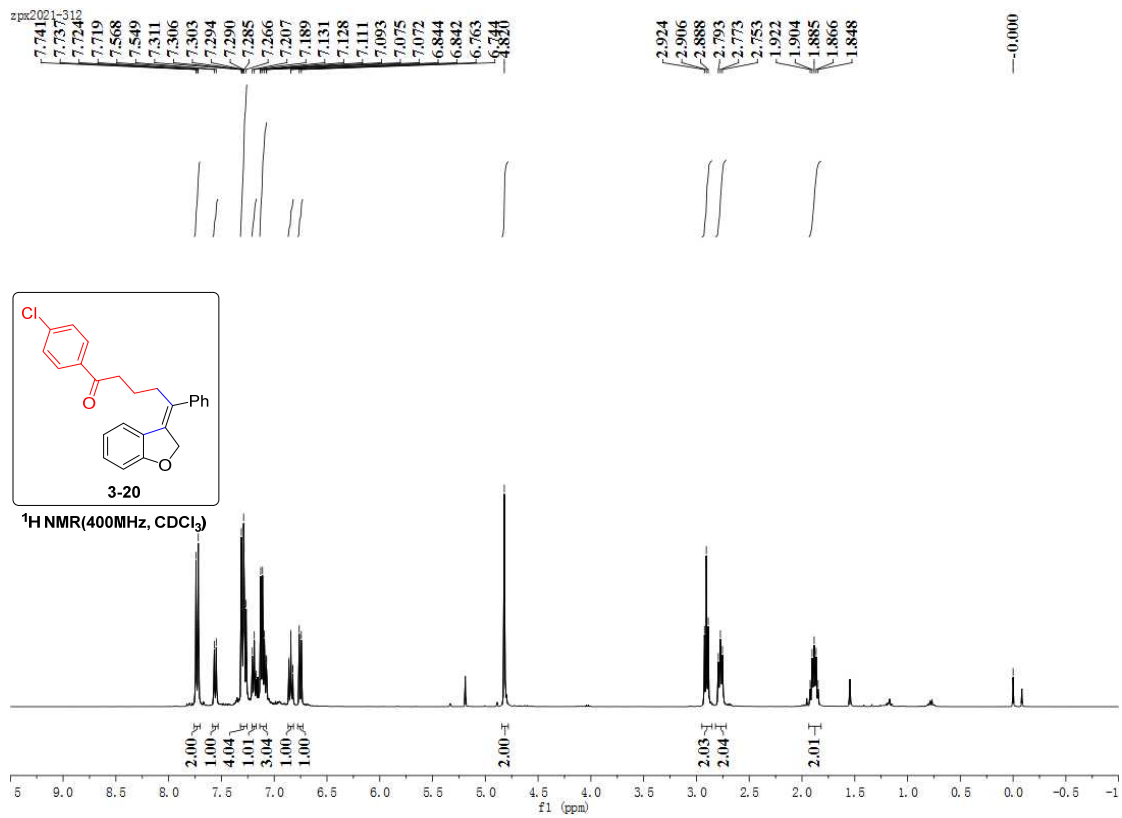


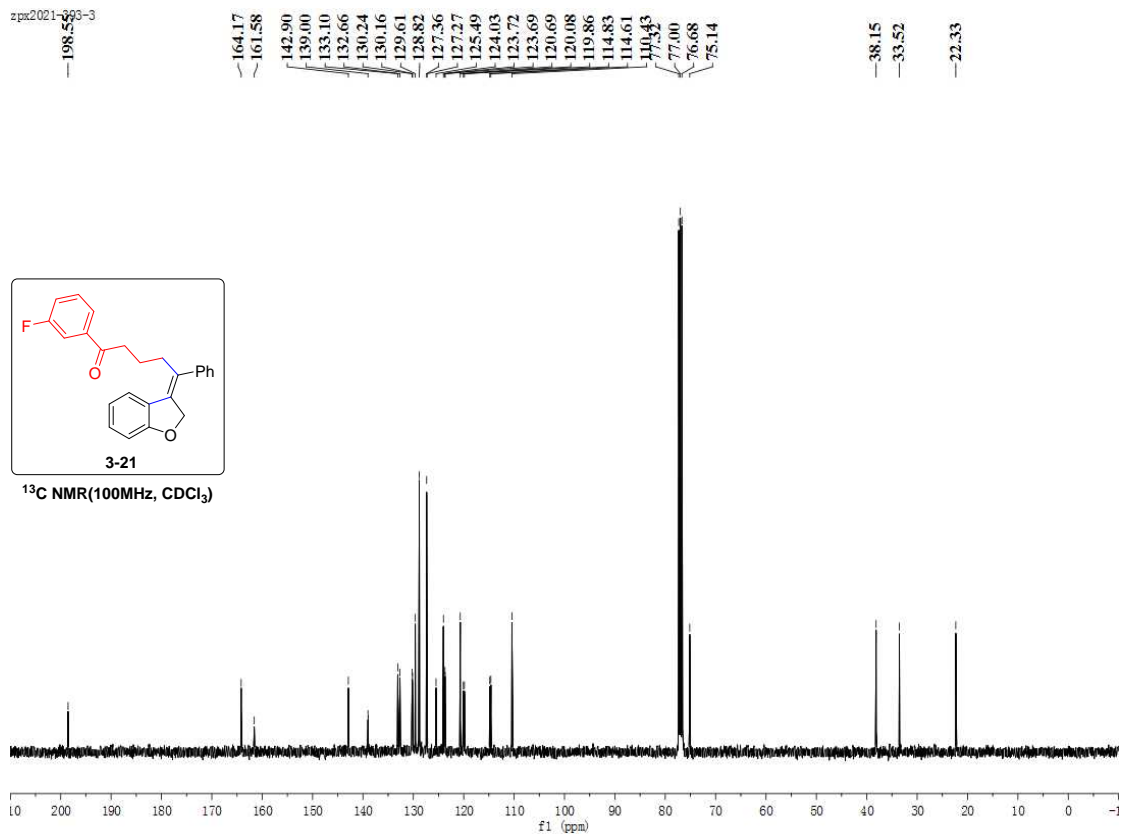
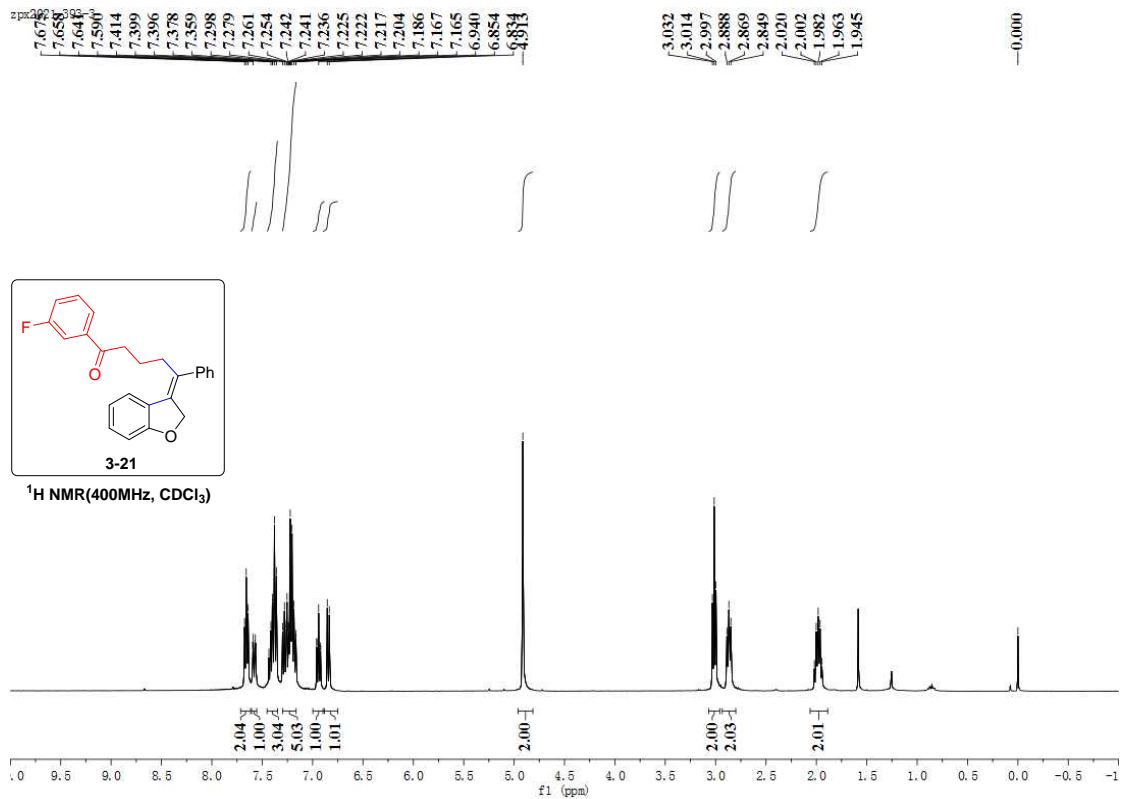
cw2021-2-1

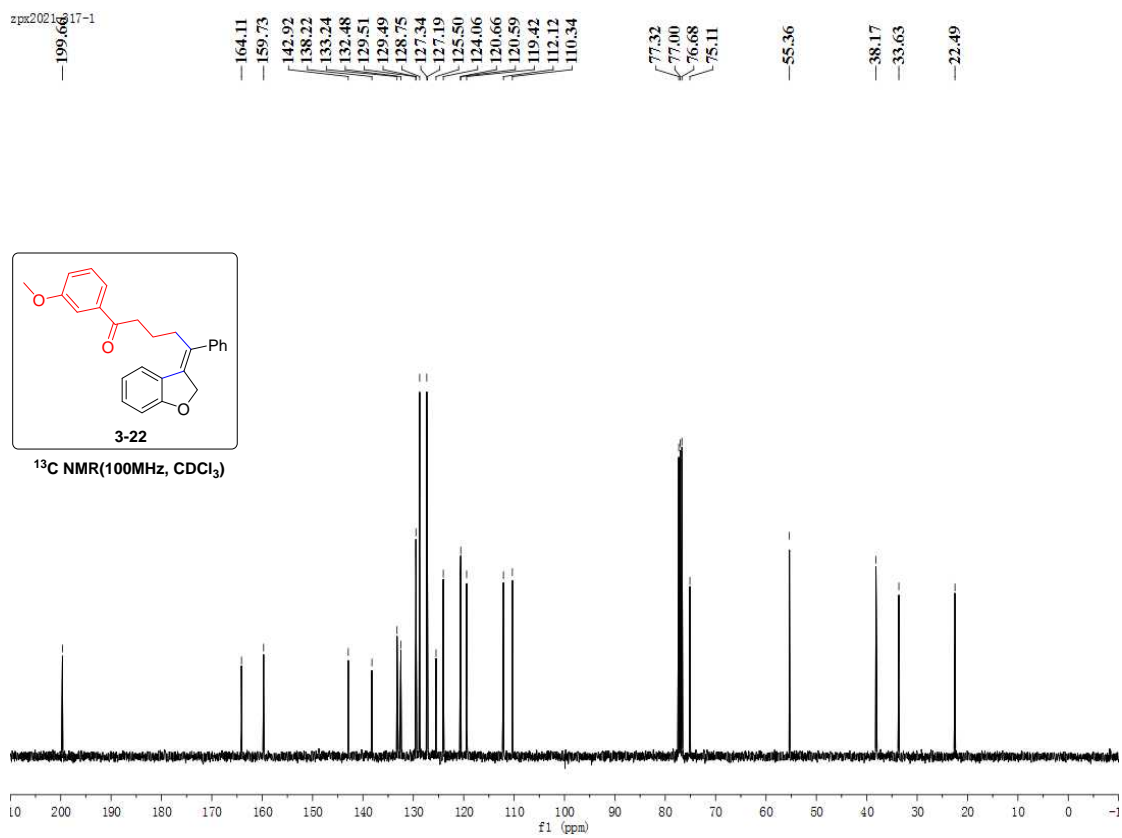
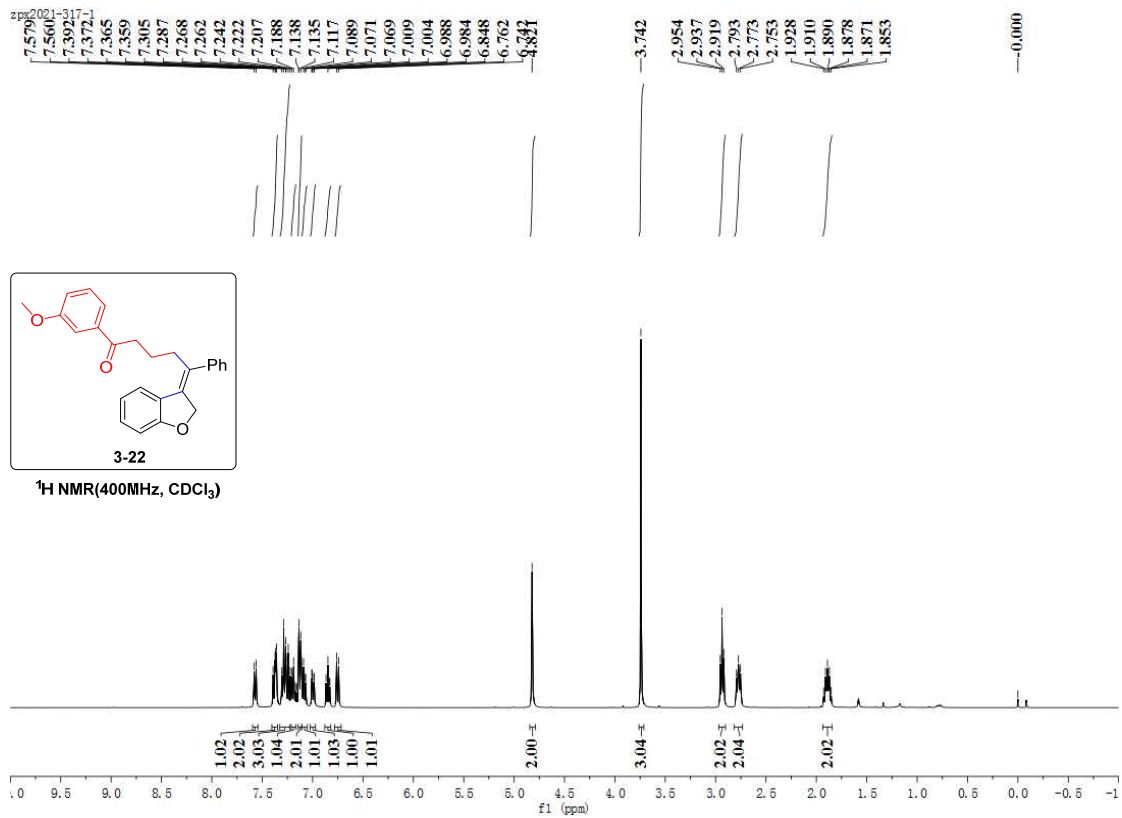


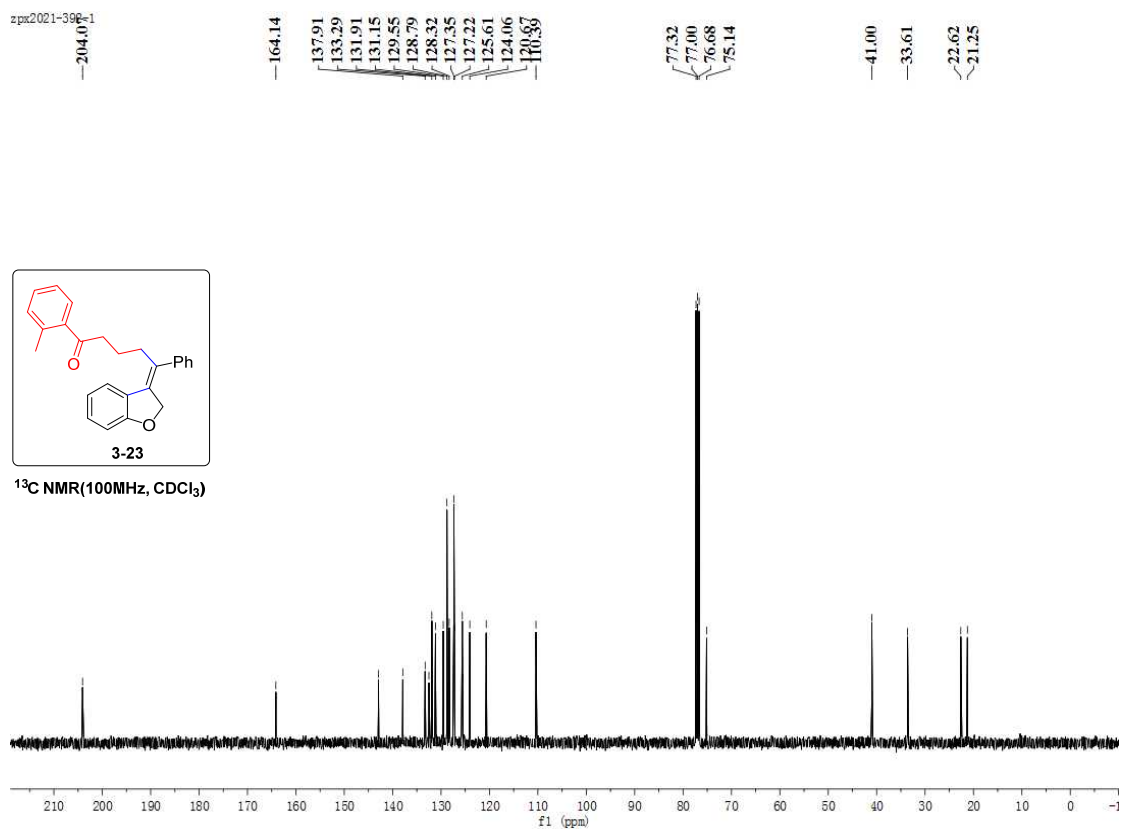
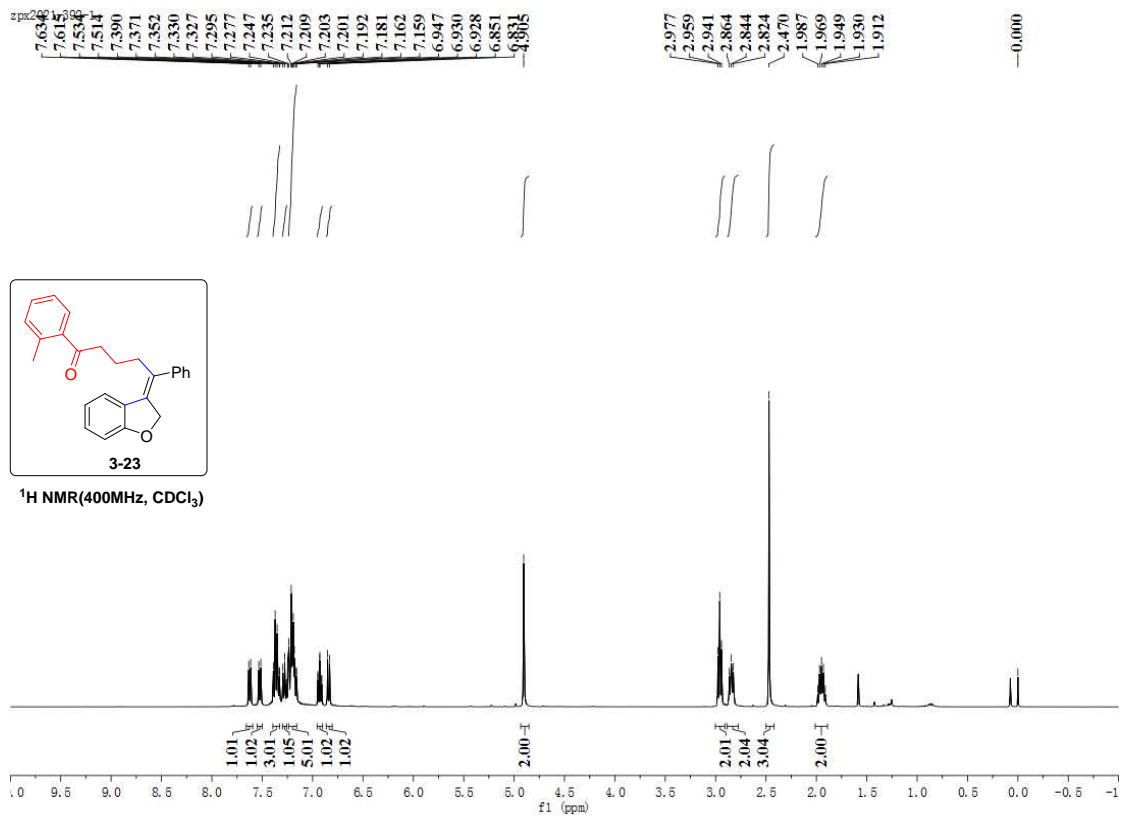


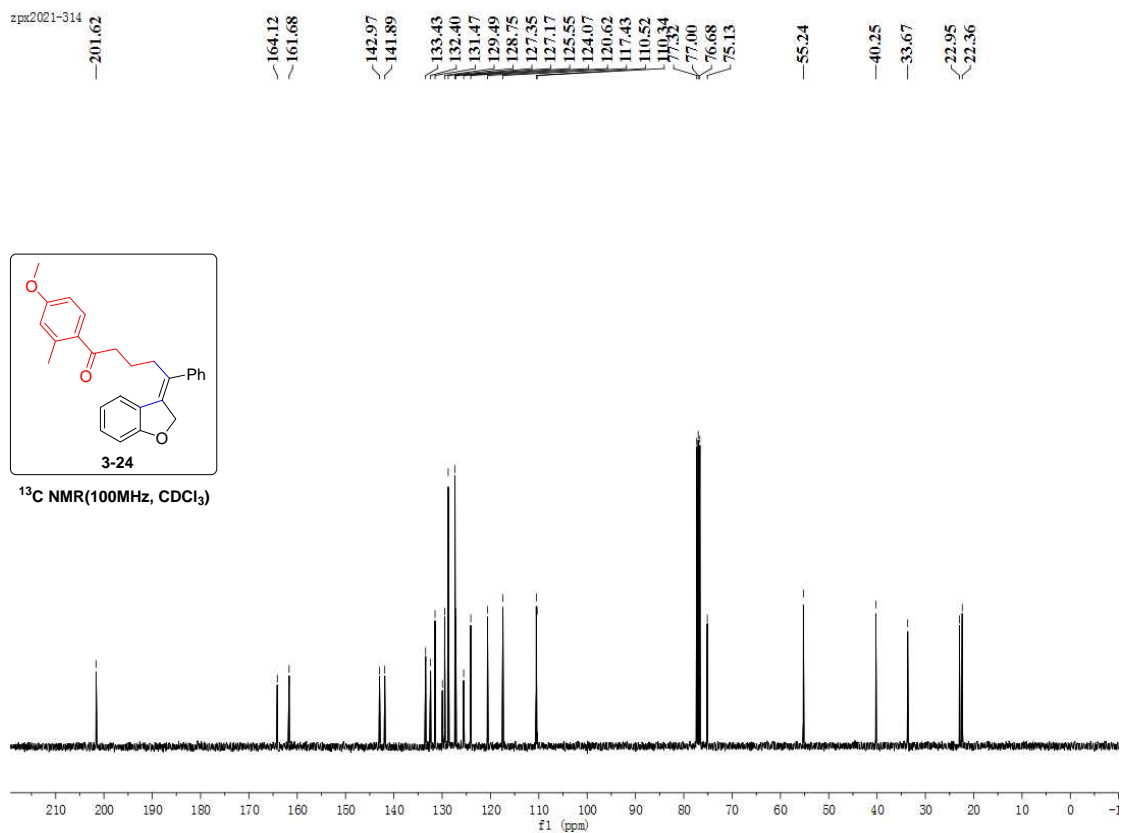
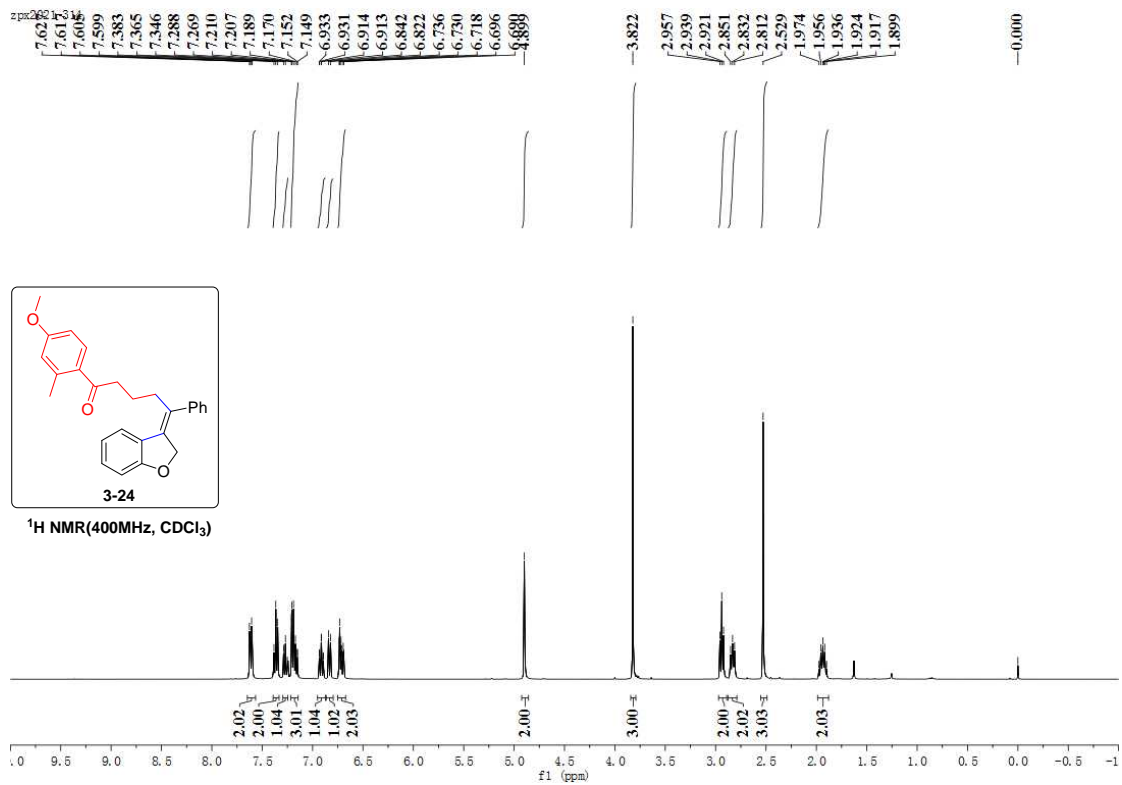


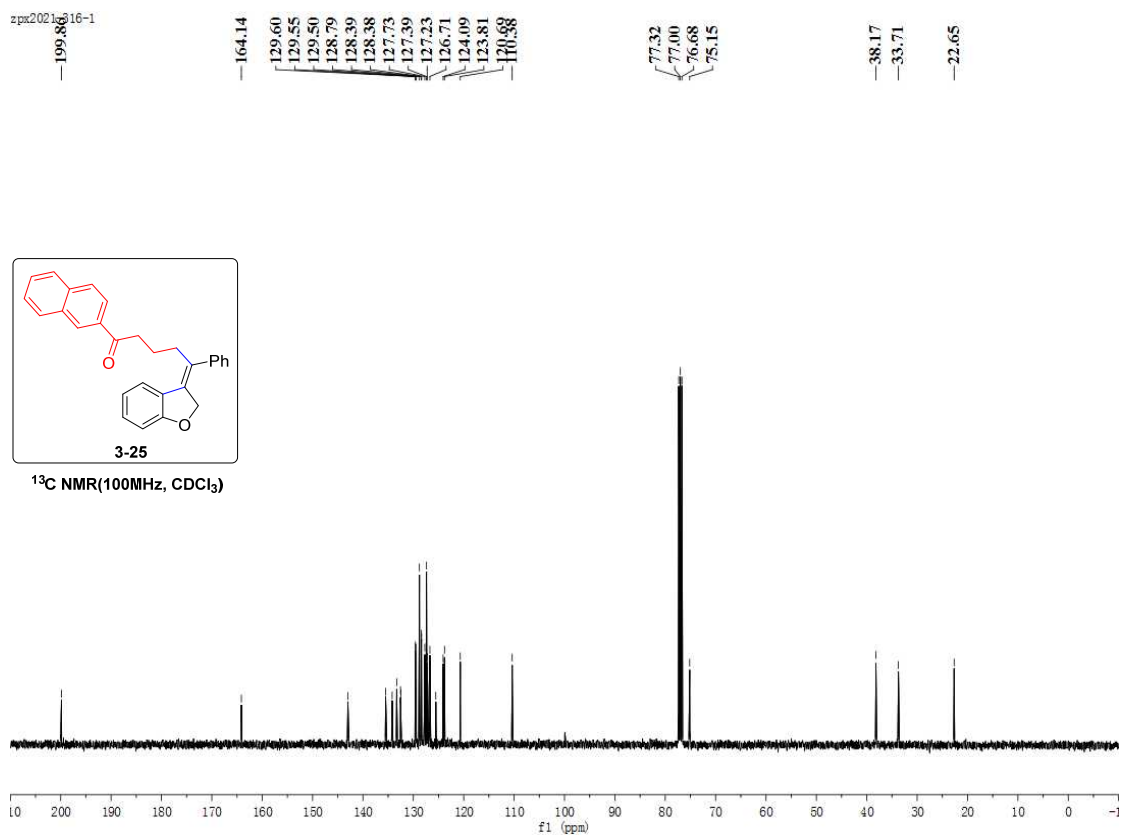
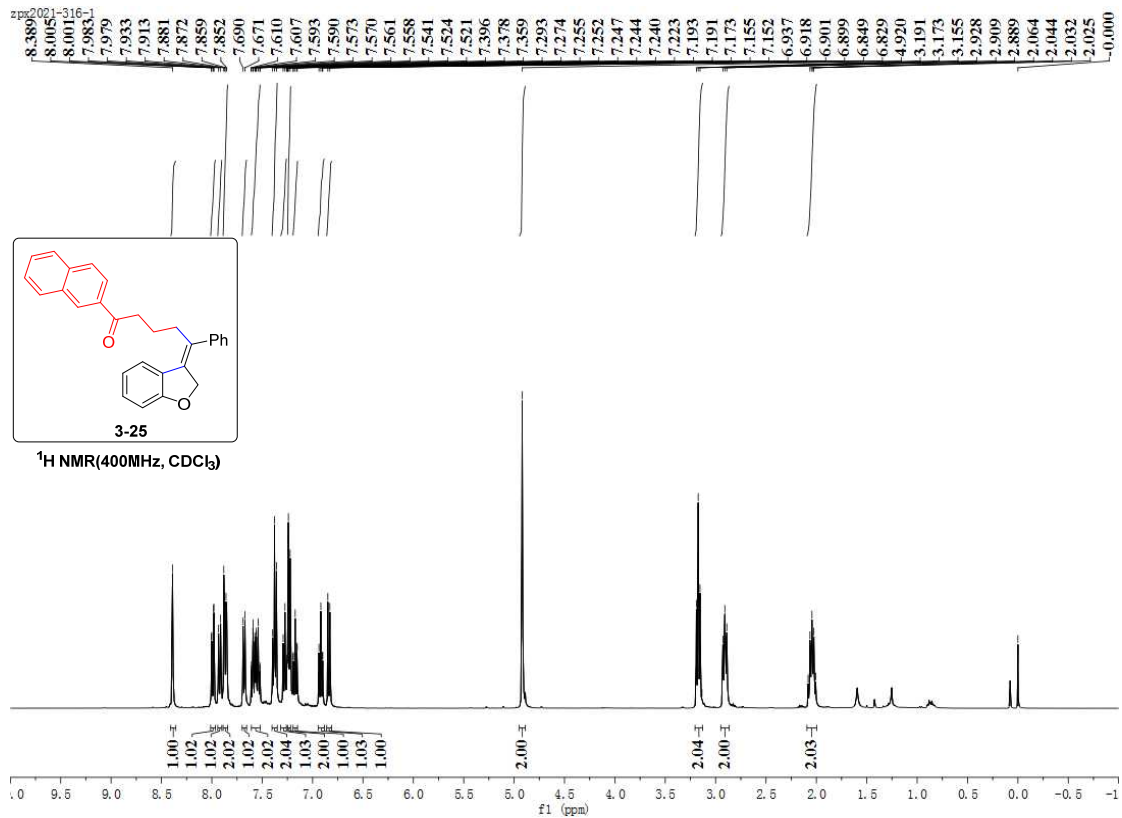


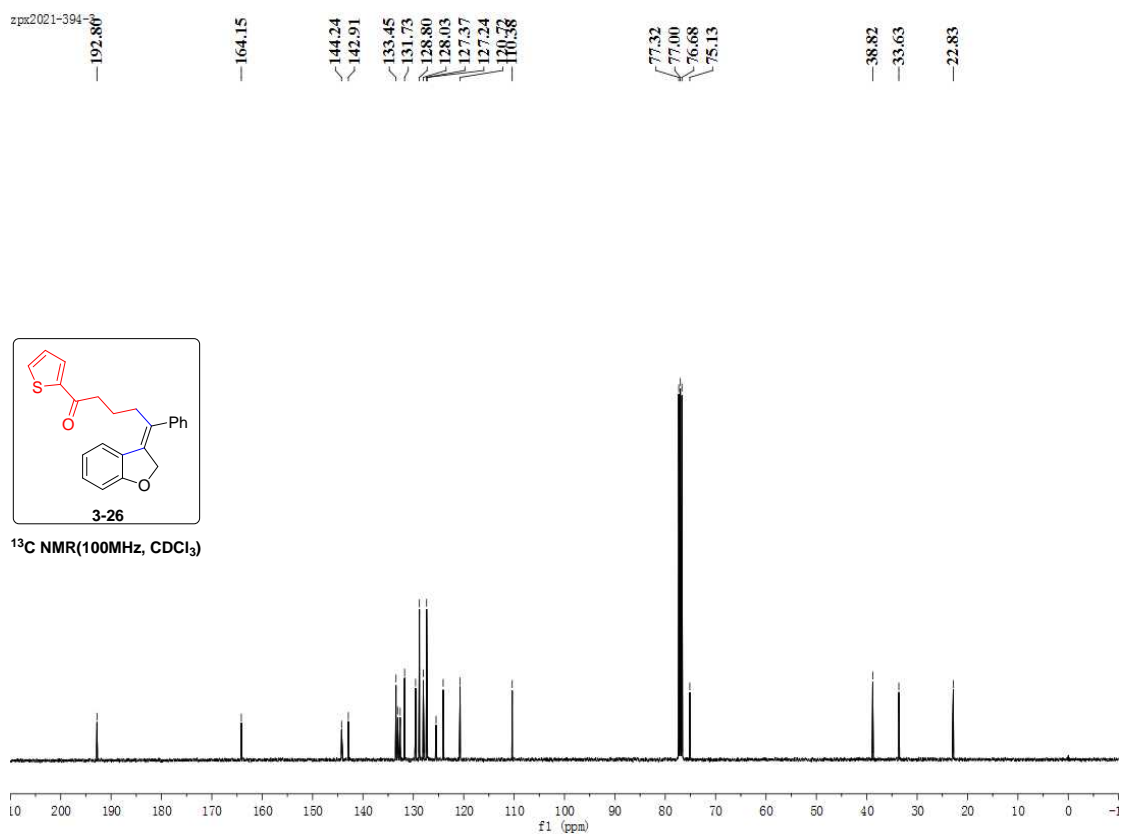
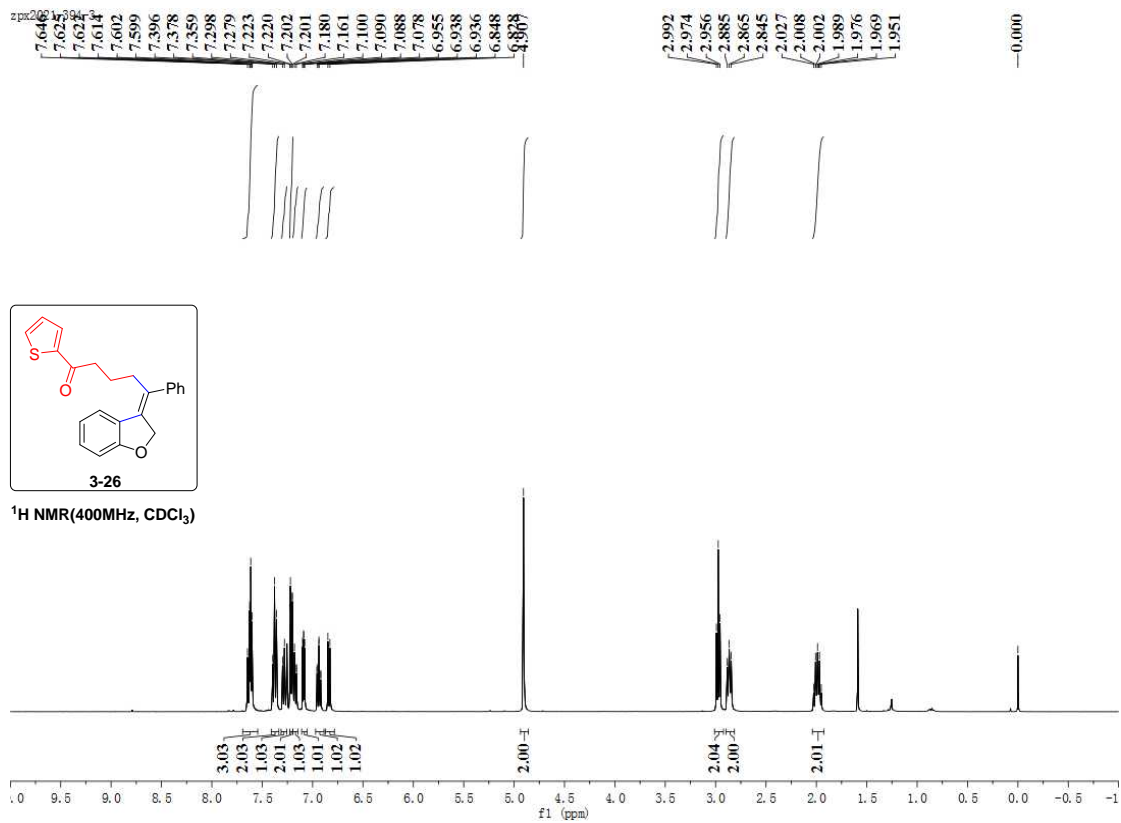


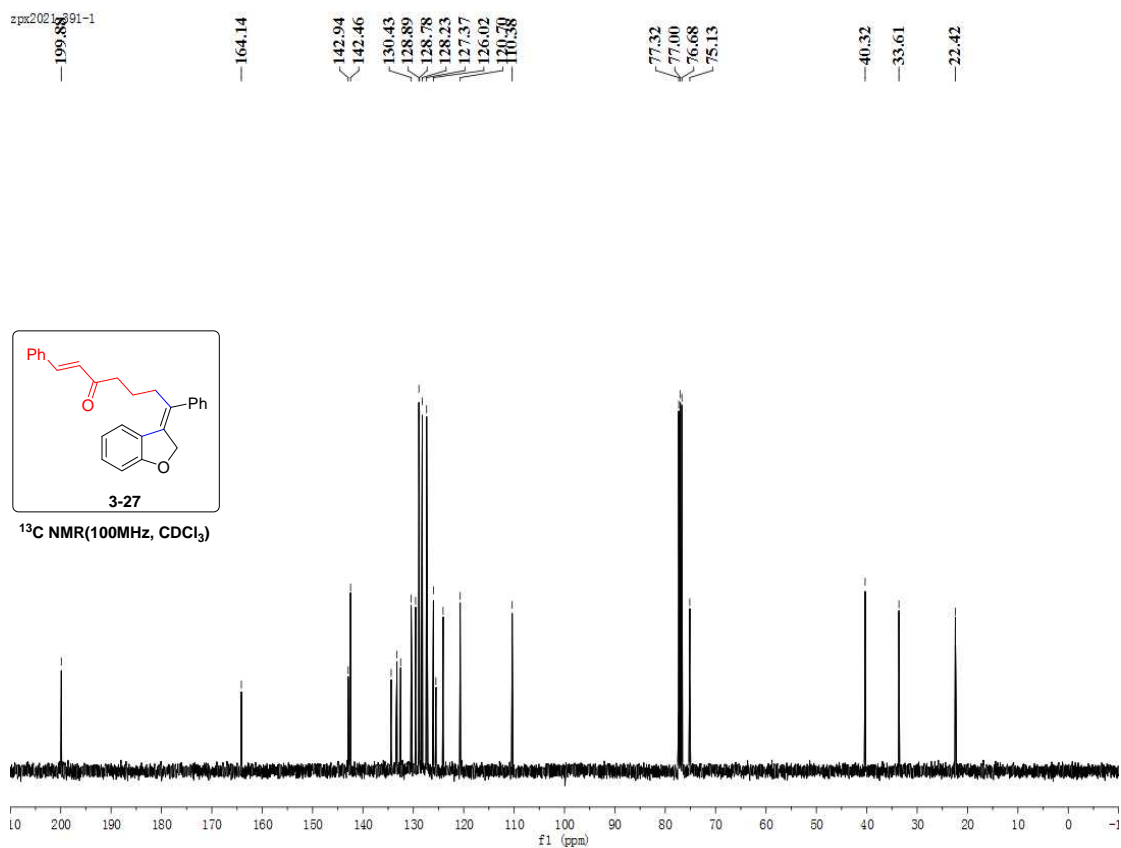
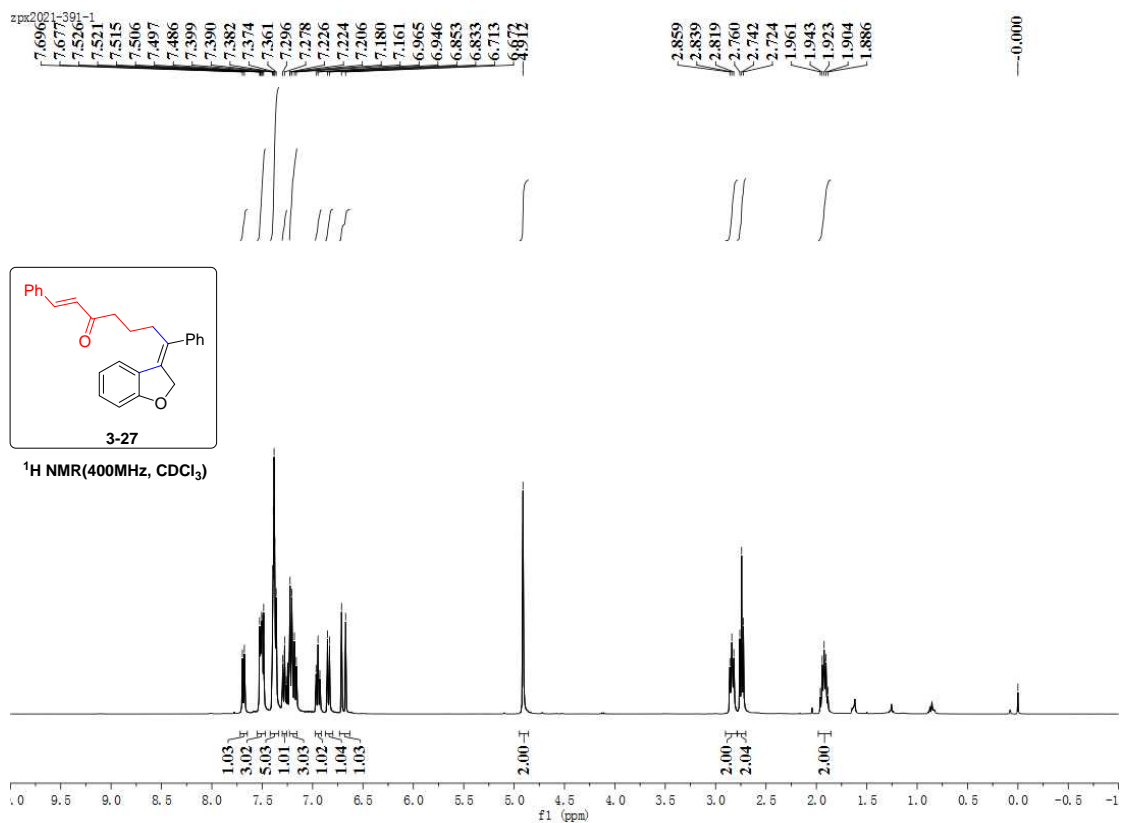


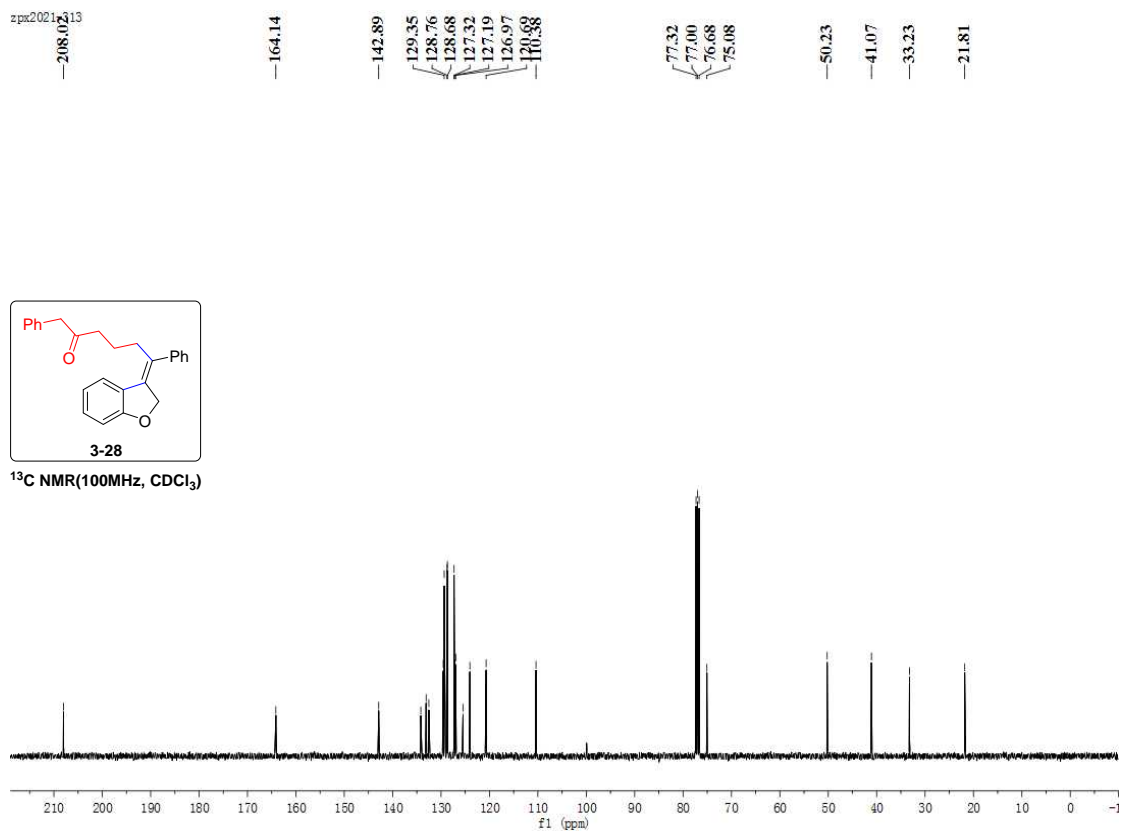
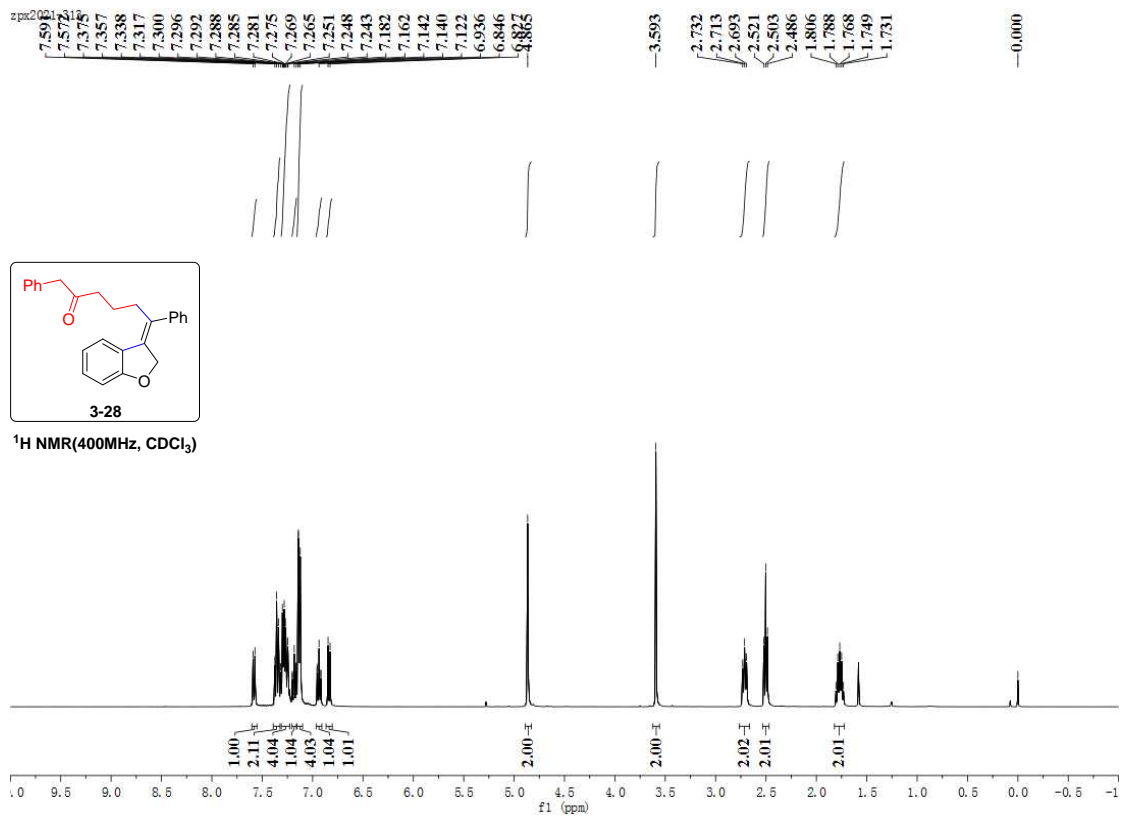


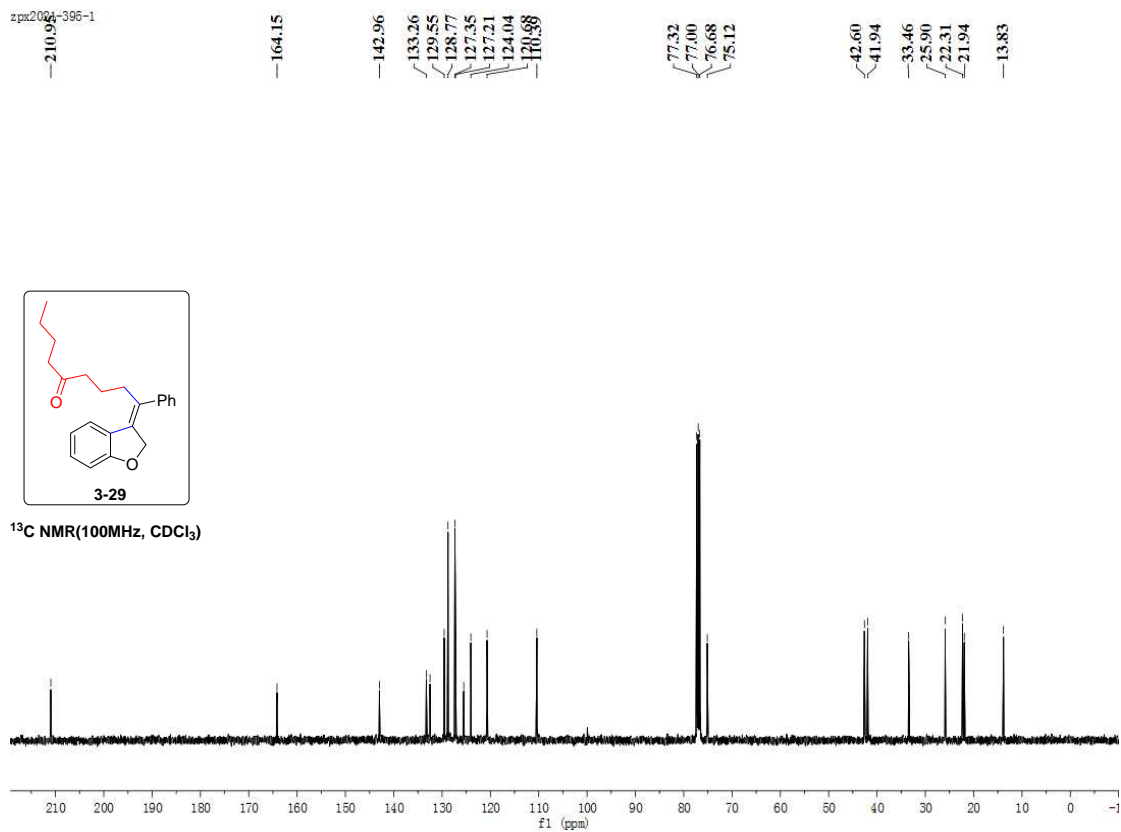
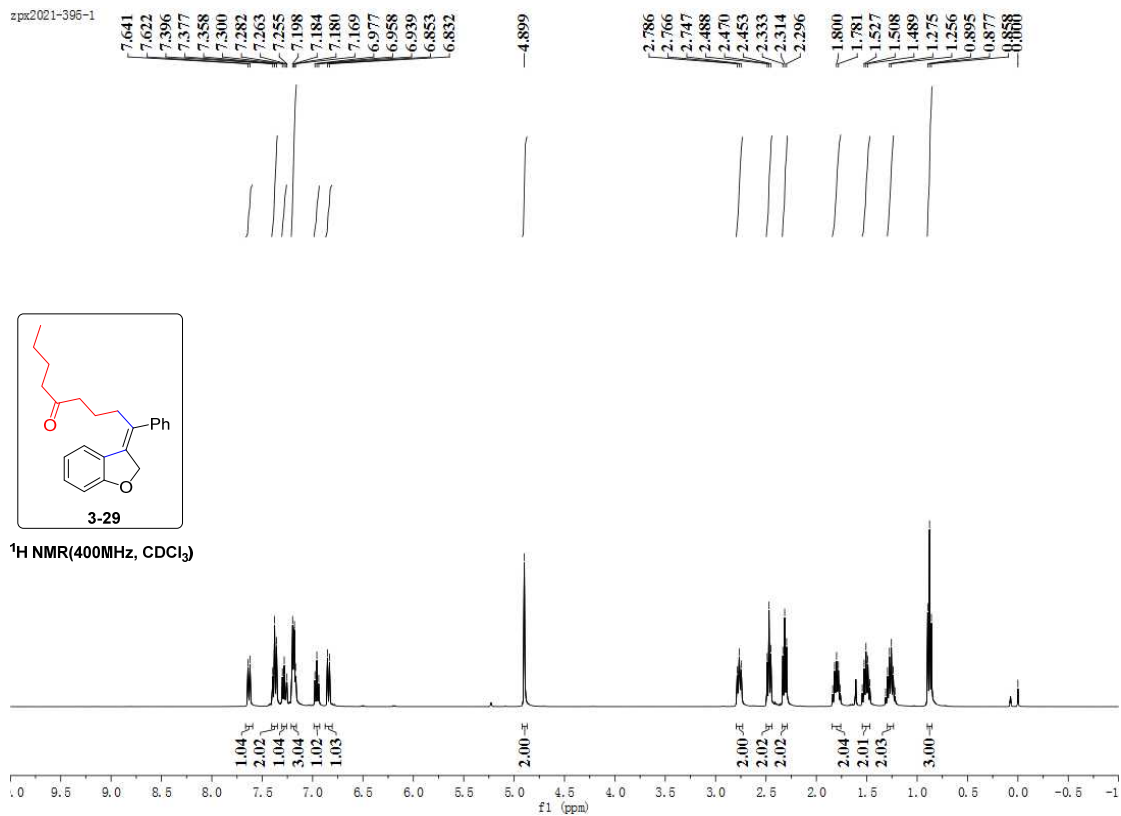




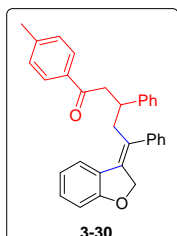
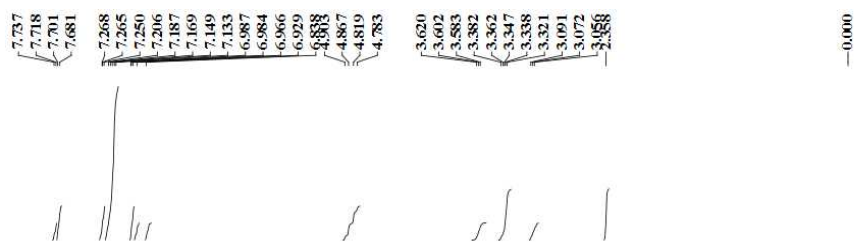




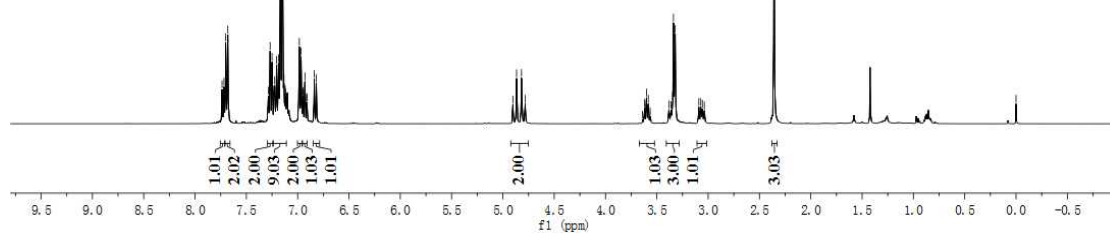




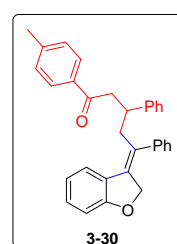
zpk2021-401-1



¹H NMR(400MHz, CDCl₃)



zpk-2021-400-3



¹³C NMR(100MHz, CDCl₃)

