Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-catalyzed tandem hydrocarbonylative cycloaddition for expedite construction of bridged lactones

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1. General information

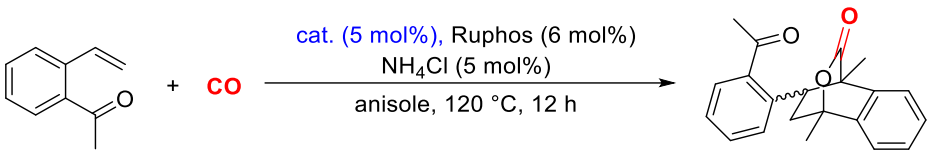
All non-aqueous reactions and manipulations were performed in a N_2 atmosphere glove box. All solvents before used were dried and degassed by standard methods and stored under nitrogen atmosphere. Purification of products was performed by flash chromatography (FC) using silica gel. NMR spectra were recorded on BRUKER Avence III 400 MHz or 500 MHz NMR spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) were reported in Hz and referred to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass (ESI). Gas chromatography (GC) analyses were performed on Agilent 7890B instrument with Hp-5 column. GC-MS analyses were performed on Agilent 7890B/5975B GC-MS system. All commercially available compounds were purchased from Alfa Aesar, J&K, Adamas and Energy Chemical.

2. Optimization of the reaction conditions

2.1 Screening of catalyst

In a N_2 atmosphere glove box, Pd catalyst (0.025 mmol), NH_4Cl (1.3 mg, 0.025 mmol), acetophenone **1a** (146.2 mg, 1 mmol), Ruphos (14.0 mg, 0.03 mmol) and anisole (1 mL) were added into a glass tube which was placed in an autoclave. Then the autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at the designed reaction temperature for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the hood. The d.r. values were measured by GC and GC-MS analysis of the crude reaction mixture. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 50/1 - 10/1) to give the desired product **3aa**.

Table 1 Screening of catalyst [a]



1a **3aa**

entry	catalyst	yield	endo/exo
1	$Pd(OAc)_2$	trace	/
2	$PdCl_2$	trace	/
3	$PdBr_2$	15%	86/14
4	PdI_2	n.r.	/
5	$[Pd(allyl)Cl]_2$[b]	49%	87/13
6	$Pd(CH_3CN)_2Cl_2$	40%	87/13
7	$Pd(COD)Br_2$	n.r.	/
8	$Pd(PPh_3)_2Cl_2$	45%	87/13
9	$Pd(xantphos)Cl_2$	10%	85/15
10	$Pd(acac)_2$	n.d.	/
11	$Pd_2(dba)_3$[b]	trace	/

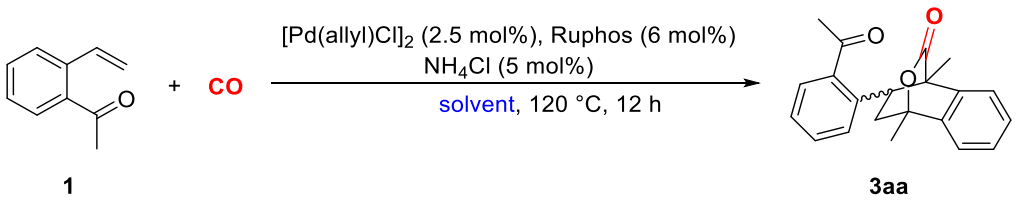
[a]Reaction conditions: **1a** (1 mmol), catalyst (0.025 mmol, 5 mol%), Ruphos (0.03 mmol, 6 mol%), NH_4Cl (0.025 mmol, 5 mol%), CO (20 atm), anisole (1.0 mL), 120 °C, 12 hours. The ratio of the products was determined by GC and GC−MS analysis of the crude reaction mixtures. [b](0.0125 mmol, 2.5 mol%).

2.2 Screening of solvent

In a N_2 atmosphere glove box, $[Pd(allyl)Cl]_2$ (4.6 mg, 0.0125 mmol), NH_4Cl (1.3 mg, 0.025 mmol), acetophenone **1a** (146.2 mg, 1 mmol), Ruphos (14.0 mg, 0.03 mmol) and solvent (1 mL) were added into a glass tube which was placed in an autoclave. Then the autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at the designed reaction temperature for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the hood. The d.r. values were measured by GC and GC-MS analysis of the crude reaction mixture. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 50/1 -

10/1) to give the desired product **3aa**.

Table 2 Screening of solvent[a]



1 **3aa**

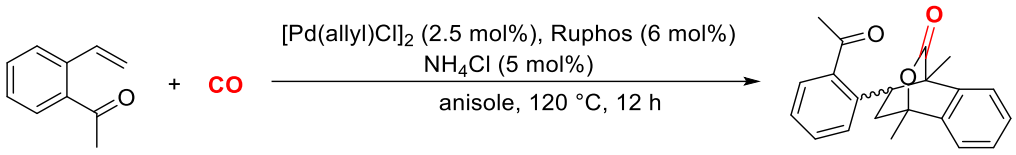
entry	solvent	yield	endo/exo
1	NMP	trace	/
2	Dioxane	30%	85/15
3	CH_3CN	n.d.	/
4	DME	37%	87/13
5	DMF	n.d.	/

[a]Reaction conditions: **1a** (1 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol, 2.5 mol%), Ruphos (0.03 mmol, 6 mol%), NH_4Cl (0.025 mmol, 5 mol%), CO (20 atm), solvent (1.0 mL), 120 °C, 12 hours. The ratio of the products was determined by GC and GC−MS analysis of the crude reaction mixtures.

2.3 Screening of pressure of CO

In a N_2 atmosphere glove box, $[Pd(allyl)Cl]_2$ (4.6 mg, 0.0125 mmol), NH_4Cl (1.3 mg, 0.025 mmol), acetophenone **1a** (146.2 mg, 1 mmol), Ruphos (14.0 mg, 0.03 mmol) and anisole (1 mL) were added into a glass tube which was placed in an autoclave. Then the autoclave was purged and charged with CO at the designed pressure. The reaction mixture was stirred at the designed reaction temperature for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the hood. The d.r. values were measured by GC and GC-MS analysis of the crude reaction mixture. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 50/1 - 10/1) to give the desired product **3aa**.

Table 3 Screening of pressure of CO[a]

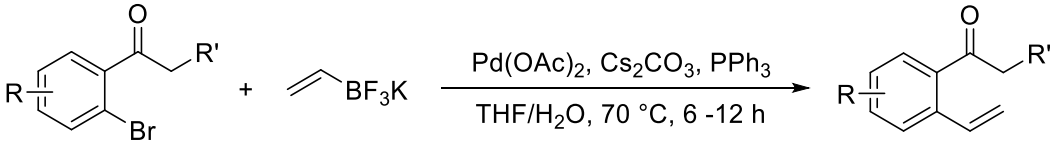


1 3aa

entry	Pressue of CO	yield	endo/exo
1	20	49%	87/13
2	30	60%	87/13
3	40	87%	87/13

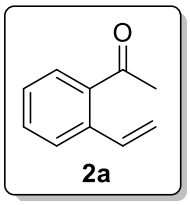
[a]Reaction conditions: **1a** (1 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol, 2.5 mol%), Ruphos (0.03 mmol, 6 mol%), NH_4Cl (0.025 mmol, 5 mol%), CO, anisole (1.0 mL), 120 °C, 12 hours. The ratio of the products was determined by GC and GC−MS analysis of the crude reaction mixtures.

3. General procedure for the synthesis of substrates.



2-Br acetophenone derivatives (4 mmol), potassium vinyltrifluoroborate (804 mg, 6 mmol), $Pd(OAc)_2$ (44.8 mg, 0.2 mmol), Cs_2CO_3 (3.9 g, 12 mmol), PPh_3 (104.8 mg, 0.4 mmol), THF (40 mL) and H_2O (4 mL) were added to a 100 mL Schlenk tube under N_2, the mixture was degassed for 3 times. Then the mixture was stirred at 70 °C for 6 – 12 hours. After the reaction finished, the mixture was washed with H_2O and extracted with ethyl acetate for 3 times. The organic layer was dried with anhydrous Na_2SO_4. The solvent was then removed under reduced pressure after filtration. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 50/1 - 10/1) to give the desired product.

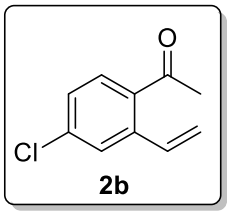
1-(2-vinylphenyl)ethan-1-one (2a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.49 – 7.43 (m, 1H), 7.37 – 7.27 (m, 1H), 7.20 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.64 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.35 (dd, *J* = 11.0, 1.3 Hz, 1H), 2.59 (s, 3H). **^{13}C NMR** (101 MHz,



2a

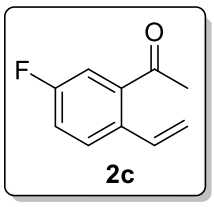
$CDCl_3$) δ 202.2, 137.8, 137.6, 136.0, 131.7, 128.8, 127.7, 127.6, 116.8, 30.0.

1-(4-chloro-2-vinylphenyl)ethan-1-one (2b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 2.1 Hz, 1H), 7.31 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.18 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.65 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.40 (dd, *J* = 10.9, 1.0 Hz, 1H), 2.57 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.8, 139.9, 138.0, 135.5, 135.1, 130.4, 127.8, 127.6, 118.0, 29.8.



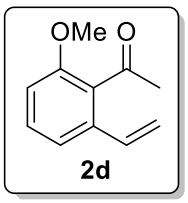
2b

1-(5-fluoro-2-vinylphenyl)ethan-1-one (2c): ^{1}H NMR (400 MHz, CDCl3) δ 7.56 – 7.52 (m, 1H), 7.31 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.14 – 7.06 (m, 1H), 5.58 (ddd, *J* = 17.5, 1.2, 0.5 Hz, 1H), 5.34 (ddd, *J* = 11.0, 1.1, 0.6 Hz, 1H), 2.57 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.9, 161.8 (d, *J* = 248.7 Hz), 139.0 (d, *J* = 5.8 Hz), 134.9, 133.9, 129.6 (d, *J* = 7.5 Hz), 118.7 (d, *J* = 21.2 Hz), 116.9, 115.4 (d, *J* = 22.6 Hz), 29.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.7.



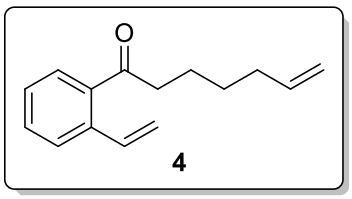
2c

1-(2-methoxy-6-vinylphenyl)ethan-1-one (2d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 1H), 7.17 (dt, *J* = 7.9, 0.8 Hz, 1H), 6.83 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.66 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.70 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.31 (dd, *J* = 11.0, 1.0 Hz, 1H), 3.83 (s, 3H), 2.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.4, 156.2, 135.6, 133.5, 130.7, 130.1, 118.2, 117.3, 110.1, 55.9, 32.7.



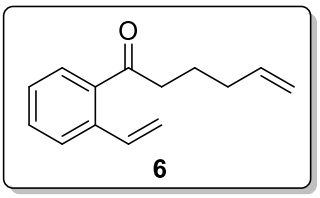
2d

1-(2-vinylphenyl)hept-6-en-1-one (4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.46 – 7.42 (m, 1H), 7.37 – 7.29 (m, 1H), 7.08 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.80 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.64 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.33 (dd, *J* = 11.0, 1.2 Hz, 1H), 5.05 – 4.92 (m, 2H), 2.94 – 2.83 (m, 2H), 2.12 – 2.05 (m, 2H), 1.78 – 1.68 (m, 2H), 1.52 – 1.42 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.3, 138.6, 138.3, 137.3, 135.7, 131.2, 127.9, 127.6, 127.5, 116.8, 114.8, 42.1, 33.7, 28.6, 24.0.



4

1-(2-vinylphenyl)hex-5-en-1-one (6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.46 – 7.42 (m, 1H), 7.36 – 7.29 (m, 1H), 7.09 (ddd, *J* = 17.4, 10.9, 0.6 Hz, 1H), 5.80 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.64 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.33 (dd, *J* = 10.9, 1.2 Hz, 1H), 5.06 – 4.97 (m, 2H), 2.91 – 2.87 (m, 2H), 2.16 – 2.10 (m, 2H), 1.85 – 1.78 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 205.2, 138.2, 138.1, 137.3, 135.7, 131.3, 127.9, 127.6, 127.4, 116.8, 115.5, 41.4, 33.3, 23.5.

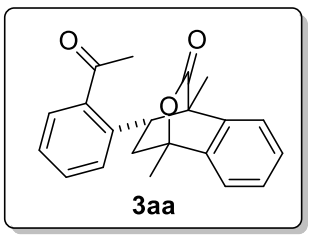


4. General procedure for the synthesis of bridged lactone.

In a N_2 atmosphere glove box, $[Pd(allyl)Cl]_2$ (4.6 mg, 0.0125 mmol), NH_4Cl (1.3 mg, 0.025 mmol), acetophenones (0.5 mmol), alkenes (0.6 mmol), Ruphos (14.0 mg, 0.03 mmol) and anisole (1 mL) were added into a glass tube which was placed in an autoclave. Then the autoclave was purged and charged with CO (40 atm). The reaction mixture was stirred at the designed reaction temperature for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the hood. The d.r. values were measured by GC and GC-MS analysis of the crude reaction mixture. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 50/1 - 10/1) to give the desired product **3**.

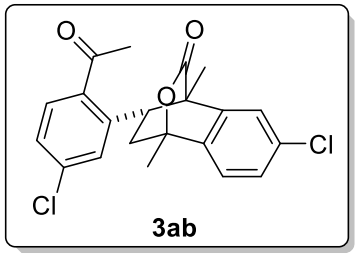
5. Experimental characterization data for products.

3-(2-acetylphenyl)-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (3aa): (white solid, 139.4 mg, yield: 87%; endo/exo = 87/13). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.32 (m, 4H), 7.23 – 7.08 (m, 1H), 7.06 – 6.94 (m, 2H), 5.70 (d, *J* = 8.0 Hz, 0.12H), 5.60 (d, *J* = 8.0 Hz, 0.88H), 4.39 (dd, *J* = 10.0, 6.8 Hz, 0.12H), 4.22 (dd, *J* = 10.3, 5.2 Hz, 0.88H), 2.89 (dd, *J* = 14.0, 10.3 Hz, 1H), 2.61 (s, 0.40H), 2.60 (s, 2.67H), 1.97 (s, 2.85H), 1.75 (dd, *J* = 14.0, 5.2 Hz, 1H), 1.74 (s, 0.37H), 1.59 (s, 0.4H), 1.31 (s, 2.72H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.2, 203.2, 176.0, 175.5, 141.0, 140.9,



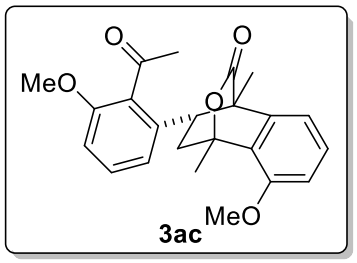
140.6, 140.2, 139.1, 138.9, 138.0, 136.7, 130.8, 130.7, 129.2, 128.8, 127.9, 127.8, 127.7, 127.7, 127.6, 127.1, 126.8, 126.6, 124.9, 123.7, 121.7, 120.5, 84.7, 81.1, 49.4, 45.1, 44.2, 43.8, 41.9, 37.8, 30.8, 30.7, 20.5, 18.8, 16.1, 14.0. **HRMS** (ESI) calcd. for $C_{21}H_{20}NaO_3$ $[M+Na]^+$: 343.1305, found: 343.1302.

3-(2-acetyl-5-chlorophenyl)-6-chloro-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (3ab): (colorless oil, 118.9 mg, yield: 61%; endo/exo = 82/18) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.35 (m, 3H), 7.20 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.10 – 7.02 (m, 1H), 5.67 (d, *J* = 2.1 Hz, 0.2H), 5.50 (d, *J* = 2.1 Hz, 0.8H), 4.47 (dd, *J* = 10.1, 6.7 Hz, 0.2H), 4.34 (dd, *J* = 10.3, 5.0 Hz, 0.81H), 2.89 (dd, *J* = 14.2, 10.4 Hz, 1H), 2.60 (s, 0.48H), 2.59 (s, 2.62H), 1.97 (s, 2.6H), 1.73 (s, 0.38H), 1.70 (dd, *J* = 14.2, 5.1 Hz, 1H), 1.58 (s, 0.6H), 1.29 (s, 2.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.6, 201.6, 174.8, 174.3, 142.0, 141.3, 141.2, 138.9, 138.8, 138.5, 137.2, 137.1, 136.2, 135.7, 135.4, 129.7, 129.5, 129.3, 128.3, 128.1, 128.1, 127.4, 127.2, 127.1, 125.3, 125.1, 122.6, 122.3, 84.1, 80.7, 49.5, 45.2, 43.9, 43.4, 41.6, 37.6, 30.6, 30.5, 20.5, 18.7, 15.9, 13.9. **HRMS** (ESI) calcd. for $C_{21}H_{18}Cl_2NaO_3$ $[M+Na]^+$: 411.0525, found: 411.0531.



3ab

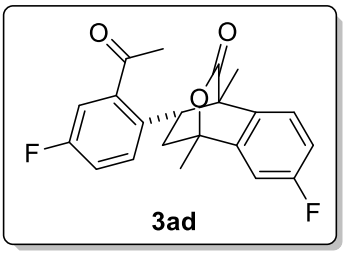
3-(2-acetyl-3-methoxyphenyl)-8-methoxy-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (3ac): (colorless oil, 120.4 mg, yield: 63%; endo/exo = 67/33). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 1H), 7.01 – 6.89 (m, 2H), 6.74 – 6.69 (m, 2H), 5.51 (dd, *J* = 8.1, 0.8 Hz, 0.32H), 5.27 (dd, *J* = 8.1, 0.9 Hz, 0.68H), 3.88 (s, 2.10H), 3.79 (s, 1.03H), 3.77 (s, 1.97H), 3.67 (s, 1.08H), 3.37 (dd, *J* = 10.0, 7.1 Hz, 0.39H), 3.26 (dd, *J* = 10.3, 5.4 Hz, 0.72H), 2.70 (dd, *J* = 14.0, 10.4 Hz, 0.8H), 2.54 (s, 1.04H), 2.51 (s, 1.93H), 2.49 – 2.46 (m, 0.38H), 2.06 (s, 2.11H), 1.86 (dd, *J* = 13.9, 5.4 Hz, 0.84H), 1.79 (s, 1.06H), 1.67 (s, 1.18H), 1.51 (dd, *J* = 13.1, 7.1 Hz, 0.40H), 1.37 (s, 2.10H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.5, 204.4, 174.9, 174.5, 155.8, 154.6, 154.5, 153.3, 141.8, 138.2, 137.3, 137.2, 132.1, 132.0, 129.2, 128.9, 128.8, 128.5, 126.0, 123.7, 117.9, 117.3, 116.5, 113.2, 110.3, 110.1, 108.3, 108.2, 84.6, 81.4, 54.6, 54.6, 54.6, 54.5, 47.8,



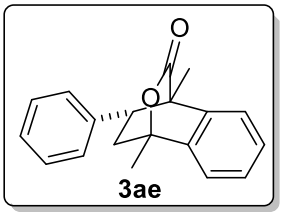
3ac

46.1, 44.7, 44.0, 41.1, 38.6, 32.0, 32.0, 23.1, 22.1, 15.5, 14.0. **HRMS** (ESI) calcd. for $C_{23}H_{24}NaO_5$ $[M+Na]^+$: 403.1516, found: 403.1518.

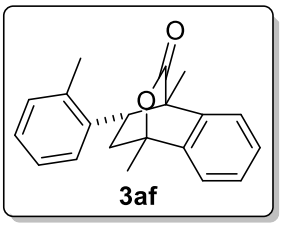
3-(2-acetyl-4-fluorophenyl)-7-fluoro-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (3ad): (colorless oil, 131.9 mg, yield: 74%; endo/exo = 85/15) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 2H), 7.13 – 7.07 (m, 1H), 7.02 – 6.98 (m, 1H), 6.87 – 6.70 (m, 1H), 5.73 (dd, *J* = 8.9, 5.3 Hz, 0.13H), 5.60 (dd, *J* = 8.9, 5.3 Hz, 0.87H), 4.36 (dd, *J* = 10.1, 6.7 Hz, 0.13H), 4.16 (dd, *J* = 10.4, 5.2 Hz, 0.88H), 2.89 (dd, *J* = 14.2, 10.4 Hz, 1H), 2.61 (s, 0.42H), 2.59 (s, 2.55H), 1.95 (s, 2.64H), 1.73 (s, 0.42H), 1.70 (dd, *J* = 14.1, 5.2 Hz, 1H), 1.56 (s, 0.44H), 1.29 (s, 2.65H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.6, 201.5, 175.2, 174.7, 162.5 (d, *J* = 249.5 Hz), 160.8 (d, *J* = 250.5 Hz), 142.6 (d, *J* = 7.3 Hz), 142.5 (d, *J* = 5.5 Hz), 134.6 (d, *J* = 3.6 Hz), 134.3 (d, *J* = 3.3 Hz), 132.1 (d, *J* = 2.9 Hz), 129.6 (d, *J* = 7.6 Hz), 129.4 (d, *J* = 7.6 Hz), 126.5 (d, *J* = 8.4 Hz), 123.5 (d, *J* = 8.5 Hz), 117.8 (d, *J* = 21.0 Hz), 115.9 (d, *J* = 21.7 Hz), 115.5 (d, *J* = 21.7 Hz), 114.8 (d, *J* = 22.4 Hz), 114.6 (d, *J* = 22.2 Hz), 111.5 (d, *J* = 23.2 Hz), 108.8 (d, *J* = 23.4 Hz), 80.5, 80.5, 48.9, 44.7, 43.9, 43.1, 41.8, 37.2, 30.6, 30.5, 20.4, 18.7, 16.1, 14.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.74, -113.62, -113.77, -113.95. **HRMS** (ESI) calcd. for $C_{21}H_{18}F_2NaO_3$ $[M+Na]^+$: 379.1116, found: 379.1117.



1,4-dimethyl-3-phenyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (3ae): (colorless oil, 100.3 mg, yield: 72%; endo/exo > 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 3H), 7.17 – 6.98 (m, 4H), 6.29 (d, *J* = 7.5 Hz, 2H), 3.29 (dd, *J* = 10.3, 4.7 Hz, 1H), 2.82 (dd, *J* = 14.1, 10.3 Hz, 1H), 1.99 (s, 3H), 1.85 (dd, *J* = 14.1, 4.7 Hz, 1H), 1.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.1, 140.4, 140.2, 136.5, 128.8, 128.5, 128.1, 127.7, 127.3, 124.9, 120.5, 81.2, 49.4, 45.6, 43.7, 20.7, 14.7. **HRMS** (ESI) calcd. for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1380, found: 279.1384.

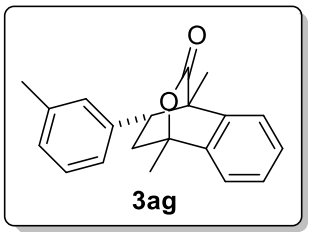


1,4-dimethyl-3-(o-tolyl)-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one



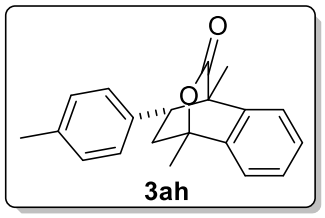
(**3af):** (colorless oil, 111.4 mg**,** yield: 76%; endo/exo = 94/6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.34 (m, 3H), 7.15 – 6.99 (m, 3H), 6.79 – 6.71 (m, 1H), 5.51 (d, *J* = 8.8 Hz 0.05H), 5.36 (d, *J* = 7.9 Hz, 0.95H), 3.95 (dd, *J* = 10.0, 6.8 Hz, 0.05H), 3.73 (dd, *J* = 10.3, 5.1 Hz, 0.94H), 2.81 (dd, *J* = 13.9, 10.4 Hz, 0.95H), 2.54 (dd, *J* = 13.2, 10.1 Hz, 0.09H), 2.46 (s, 0.18H), 2.40 (s, 2.80H), 1.98 (s, 3H), 1.75 (dd, *J* = 13.8, 5.1 Hz, 1H), 1.65 (s, 0.16H), 1.40 (s, 2.87H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.3, 140.5, 139.0, 137.0, 136.7, 130.3, 128.8, 127.7, 126.8, 126.4, 126.0, 125.2, 120.4, 81.3, 49.9, 44.3, 38.8, 20.7, 20.7, 13.7. **HRMS** (ESI) calcd. for $C_{20}H_{20}NaO_2$ $[M+Na]^+$: 315.1356, found: 315.1361.

1,4-dimethyl-3-(m-tolyl)-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one



(3ag): (white solid, 111.1 mg, yield: 76%; endo/exo = 93/7). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.37 (m, 2H), 7.39 – 7.25 (m, 1H), 7.07 – 6.89 (m, 3H), 6.20 – 6.06 (m, 2H), 3.47 (dd, *J* = 10.1, 6.3 Hz, 0.08H), 3.24 (dd, *J* = 10.3, 4.7 Hz, 0.92H), 2.78 (dd, *J* = 14.0, 10.3 Hz, 0.97H), 2.52 (dd, *J* = 13.3, 10.1 Hz, 0.12H), 2.15 (s, 0.44H), 2.12 (s, 2.57H), 1.98 (s, 2.89H), 1.82 (dd, *J* = 14.0, 4.7 Hz, 1H), 1.75 (s, 0.26H), 1.61 (s, 0.27H), 1.36 (s, 2.85H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.2, 176.1, 140.3, 140.1, 140.0, 139.9, 137.7, 137.5, 136.6, 136.5, 129.5, 129.3, 129.1, 128.5, 128.0, 128.0, 127.9, 127.9, 127.5, 126.9, 125.4, 125.4, 124.9, 123.7, 121.6, 120.4, 84.7, 81.1, 50.7, 49.3, 45.4, 45.0, 43.6, 40.9, 21.3, 20.6, 20.5, 19.4, 16.1, 14.6. **HRMS** (ESI) calcd. for $C_{20}H_{20}NaO_2$ $[M+Na]^+$: 315.1356, found: 315.1362.

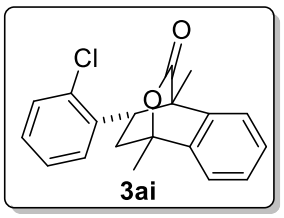
1,4-dimethyl-3-(p-tolyl)-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one



(3ah): (colorless oil, 107.1 mg, yield: 73%; endo/exo > 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 3H), 7.00 – 6.86 (m, 3H), 6.17 (d, *J* = 7.6 Hz, 2H), 3.25 (dd, *J* = 10.3, 4.7 Hz, 1H), 2.79 (dd, *J* = 14.0, 10.3 Hz, 1H), 2.23 (s, 3H), 1.98 (s, 3H), 1.81 (dd, *J* = 14.0, 4.7 Hz, 1H), 1.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.2, 140.3, 137.0, 136.9, 136.5, 128.8, 128.7,

128.3, 127.6, 124.9, 120.4, 81.1, 49.3, 45.2, 43.6, 21.0, 20.6, 14.6. **HRMS** (ESI) calcd. for $C_{20}H_{20}NaO_2$ $[M+Na]^+$: 315.1356, found: 315.1363.

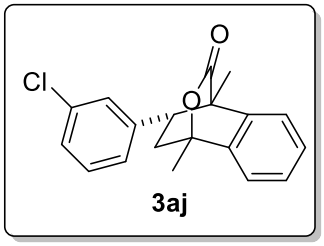
3-(2-chlorophenyl)-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-



3ai

(epoxymethano)naphthalen-9-one (3ai): (colorless oil, 119.3 mg, yield: 76%; endo/exo = 86/14). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.32 (m, 4H), 7.08 – 7.03 (m, 2H), 6.81 – 6.77 (m, 1H), 5.55 (dd, *J* = 8.0, 1.6 Hz, 0.11H), 5.42 (dd, *J* = 8.0, 1.7 Hz, 0.89H), 4.40 (dd, *J* =10.2, 6.4 Hz, 0.12H), 4.18 (dd, *J* =10.4, 4.9 Hz, 0.88H), 2.85 (dd, *J* = 14.0, 10.4 Hz, 0.91H), 2.59 (dd, *J* = 13.3, 10.2 Hz, 0.13H), 1.99 (s, 2.80H), 1.74 (s, 0.34H), 1.72 (dd, *J* =14.3, 4.9Hz, 1H), 1.70 (s, 0.30H), 1.46 (s, 2.69H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.6, 140.4, 138.1, 136.4, 135.3, 129.5, 128.9, 128.2, 128.0, 127.8, 126.7, 125.1, 120.6, 81.0, 49.8, 43.7, 39.2, 20.6, 13.5. **HRMS** (ESI) calcd. for $C_{19}H_{17}ClNaO_2$ $[M+Na]^+$: 335.0809, found: 335.0811.

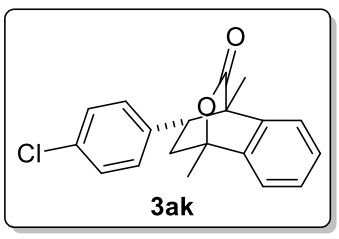
3-(3-chlorophenyl)-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-



3aj

(epoxymethano)naphthalen-9-one (3aj): (colorless oil, 112.8 mg, yield: 72%; endo/exo = 90/10). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 3H), 7.13 – 6.99 (m, 3H), 6.34 – 6.18 (m, 2H), 3.50 (dd, *J* = 10.1, 6.2 Hz, 0.09H), 3.26 (dd, *J* = 10.3, 4.6 Hz, 0.91H), 2.82 (dd, *J* = 14.2, 10.3 Hz, 0.92H), 2.56 (dd, *J* = 13.4, 10.1 Hz, 0.11H), 1.99 (s, 2.78H), 1.79 (dd, *J* = 14.1, 4.6 Hz, 1H), 1.77 (s, 0.25H), 1.63 (s, 0.30H), 1.38 (s, 2.70H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.7, 175.6, 142.4, 142.3, 140.2, 139.8, 136.1, 134.1, 134.0, 129.3, 128.9, 128.7, 128.5, 127.9, 127.6, 127.5, 127.3, 126.7, 125.0, 123.8, 121.8, 120.6, 84.3, 81.1, 50.6, 49.2, 45.4, 45.0, 43.6, 40.9, 20.6, 19.4, 16.1, 14.7. **HRMS** (ESI) calcd. for $C_{19}H_{17}ClNaO_2$ $[M+H]^+$: 335.0809, found: 335.0811.

3-(4-chlorophenyl)-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-

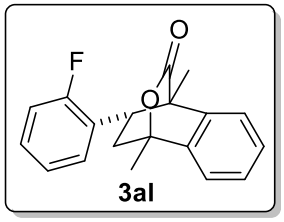


3ak

(epoxymethano)naphthalen-9-one (3ak): (colorless oil, 109.5 mg, yield: 70%; endo/exo = 93/7): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 3H), 7.05 – 6.98 (m, 3H), 6.20 (d, *J* = 8.0 Hz, 2H), 3.27 (dd, *J* = 10.3, 4.6 Hz, 1H), 2.82 (dd, *J* = 14.1, 10.3 Hz, 1H), 1.99 (s, 3H), 1.78 (dd, *J*

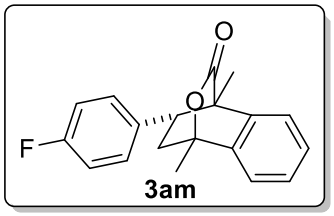
= 14.1, 4.6 Hz, 1H), 1.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.7, 140.2, 138.6, 136.2, 133.2, 129.7, 128.9, 128.3, 127.9, 124.9, 120.6, 81.0, 49.2, 45.0, 43.6, 20.6, 14.6. **HRMS** (ESI) calcd. for $C_{19}H_{18}ClO_2$ $[M+H]^+$: 313.0990, found: 313.1004.

3-(2-fluorophenyl)-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-



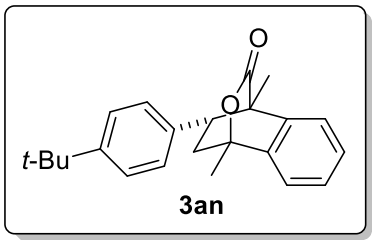
(epoxymethano)naphthalen-9-one (3al): (colorless oil, 114.9 mg, yield: 78%; endo/exo = 83/17). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 3H), 7.00 – 6.98 (m, 1H), 6.79 – 6.74 (m, 2H), 6.24 (t, *J* = 4.2 Hz, 2H), 3.52 (dd, *J* = 10.1, 6.1 Hz, 0.12H), 3.29 (dd, *J* = 10.3, 4.6 Hz, 0.88H), 2.82 (dd, *J* = 14.1, 10.3 Hz, 0.89H), 2.56 (dd, *J* = 13.4, 10.1 Hz, 0.12H), 1.99 (s, 2.76H), 1.79 (dd, *J* = 14.1, 4.6 Hz, 1H),1.76 (s, 0.20H), 1.61 (s, 0.37H), 1.36 (s, 2.63H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.0, 175.9, 162.1 (*J* = 242.4 Hz), 140.3, 140.0, 137.3, 136.3, 136.0 (*J* = 2.1 Hz), 135.9 (*J* = 2.3 Hz), 130.0 (*J* = 1.9 Hz), 129.9 (*J* = 2.3 Hz), 129.4, 128.8, 127.8, 127.2, 124.9, 123.8, 121.7, 120.5, 115.2 (*J* = 20.3 Hz), 115.0 (*J* = 20.2 Hz), 84.5, 81.0, 50.1, 49.3, 45.0, 44.9, 43.7, 41.1, 20.6, 19.4, 16.1, 14.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.2, -115.4. **HRMS** (ESI) calcd. for $C_{19}H_{17}FNaO_2$ $[M+Na]^+$: 319.1105, found: 319.1109.

3-(4-fluorophenyl)-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-



(epoxymethano)naphthalen-9-one (3am): (colorless oil, 111.4 mg, yield: 75%; endo/exo = 83/17) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 3H), 7.00 – 6.97 (m, 1H), 6.79 – 6.74 (m, 2H), 6.26 – 6.22 (m, 2H), 3.52 (dd, *J* = 10.2, 6.2 Hz, 0.11H), 3.29 (dd, *J* = 10.3, 4.6 Hz, 0.89H), 2.82 (dd, *J* = 14.1, 10.3 Hz, 0.90H), 2.57 (dd, *J* = 13.4, 10.2 Hz, 0.11H), 1.99 (s, 2.73H), 1.79 (dd, *J* = 14.1, 4.6 Hz, 1H), 1.76 (s, 0.21H), 1.61 (s, 0.24H), 1.36 (s, 2.72H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.9, 175.8, 162.5 (*J* = 252.5Hz), 162.1 (*J* = 247.1Hz), 140.3, 136.3, 135.9 (*J* = 10.1 Hz), 130.1 (*J* = 9.1 Hz), 129.9 (*J* = 8.1 Hz), 129.4, 128.8, 127.8, 127.2, 124.9, 123.7, 121.7, 120.5, 115.3 (*J* = 20.2Hz), 115.0 (*J* = 21.3Hz), 84.5, 81.0, 50.1, 49.3, 45.0, 44.9, 43.7, 41.1, 20.6, 19.4, 16.1, 14.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.2, -115.4. **HRMS** (ESI) calcd. for $C_{19}H_{17}FNaO_2$ $[M+Na]^+$: 319.1105, found: 319.1112.

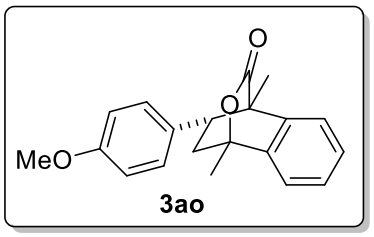
3-(4-(tert-butyl)phenyl)-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-



3an

(epoxymethano)naphthalen-9-one (3an): (colorless oil, 107.5 mg, yield: 64%; endo/exo > 95/5) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 3H), 7.09 – 7.02 (m, 3H), 6.23 (d, *J* = 7.9 Hz, 2H), 3.26 (dd, *J* = 10.3, 4.8 Hz, 1H), 2.79 (dd, *J* = 14.0, 10.3 Hz, 1H), 1.98 (s, 3H), 1.82 (dd, *J* = 14.0, 4.7 Hz, 1H), 1.38 (s, 3H), 1.23 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.3, 150.2, 140.4, 137.1, 136.6, 128.7, 128.1, 127.6, 125.0, 120.4, 81.2, 49.4, 45.1, 43.8, 34.5, 31.4, 20.7, 14.7. **HRMS** (ESI) calcd. for $C_{23}H_{27}NaO_2$ $[M+Na]^+$: 335.2006, found: 335.2009.

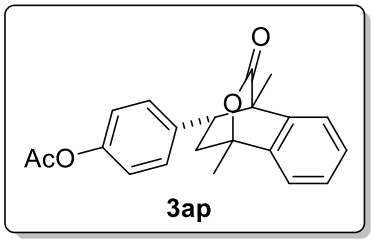
3-(4-methoxyphenyl)-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-



3ao

(epoxymethano)naphthalen-9-one (3ao): (colorless oil, 107.9 mg, yield: 70%; endo/exo = 91/9). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.34 (ddt, *J* = 7.5, 5.7, 3.6 Hz, 1H), 7.05 – 6.97 (m, 1H), 6.94 – 6.59 (m, 2H), 6.31 (d, *J* = 10.7 Hz, 0.15H), 6.19 (d, *J* = 10.3 Hz, 1.81H), 3.78 (s, 0.13H), 3.70 (s, 2.90H), 3.46 (dd, *J* = 10.1, 6.3 Hz, 0.06H), 3.23 (dd, *J* = 10.3, 4.7 Hz, 0.94H), 2.78 (dd, *J* = 14.1, 10.4 Hz, 1H), 1.97 (s, 2.90H), 1.79 (dd, *J* = 14.0, 4.7 Hz, 1H), 1.74 (s, 0.18H), 1.61 (s, 0.19H), 1.36 (s, 2.74H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.1, 175.3, 158.7, 157.9, 140.3, 140.0, 137.5, 136.5, 132.8, 132.0, 129.5, 129.3, 129.1, 128.6, 127.5, 127.0, 124.8, 123.7, 121.5, 120.4, 114.2, 113.4, 84.7, 81.0, 55.2, 49.9, 49.4, 47.7, 45.0, 44.8, 43.7, 41.0, 20.5, 19.3, 16.1, 14.6. **HRMS** (ESI) calcd. for $C_{20}H_{20}NaO_3$ $[M+Na]^+$: 331.1305, found: 331.1301.

1,4-dimethyl-9-oxo-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-3-

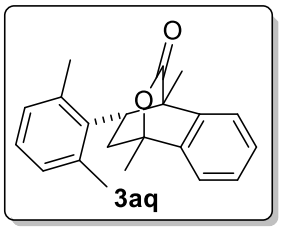


3ap

yl)phenyl acetate (3ap): (colorless oil, 87.8 mg, yield: 52%; endo/exo = 84/16). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 2H), 7.37 – 7.30 (m, 1H), 7.07 – 6.96 (m, 1H), 6.84 – 6.79 (m, 2H), 6.40 (d, *J* = 8.5 Hz, 0.24H), 6.28 (d, *J* = 8.1 Hz, 1.73H), 3.53 (dd, *J* = 10.1, 6.3 Hz, 0.11H), 3.30 (dd, *J* = 10.3, 4.6 Hz, 0.89H), 2.81 (dd, *J* = 14.1, 10.3 Hz, 0.93H), 2.55 (dd, *J* = 13.4, 10.1 Hz, 0.16H), 2.29 (s, 0.23H), 2.23 (s, 2.81H), 1.98 (s, 2.85H),

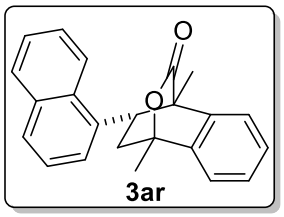
1.80 (dd, *J* = 14.1, 4.7 Hz, 1H), 1.75 (s, 0.3H), 1.63 (s, 0.35H), 1.38 (s, 2.60H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.8, 169.4, 150.9, 149.9, 140.3, 137.8, 137.6, 136.8, 136.3, 135.3, 130.7, 129.4, 129.3, 128.8, 127.7, 127.2, 124.9, 123.8, 121.6, 121.3, 121.2, 120.5, 84.5, 81.1, 50.3, 49.3, 45.0, 44.3, 43.7, 37.9, 21.2, 20.6, 19.4, 16.1, 14.7, 14.1. **HRMS** (ESI) calcd. for $C_{21}H_{20}NaO_4$ $[M+Na]^+$: 359.1254, found: 359.1258.

3-(2,6-dimethylphenyl)-1,4-dimethyl-1,2,3,4-tetrahydro-1,4-



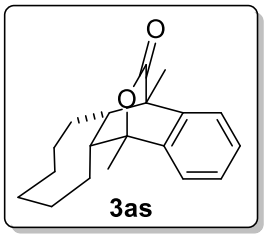
(epoxymethano)naphthalen-9-one (**3aq):** (colorless oil, 110.7 mg, yield: 72%; endo/exo = 94/6). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 3H), 7.00 (dd, *J* = 32.0, 7.6 Hz, 2H), 6.82 (d, *J* = 1.8 Hz, 1H), 5.03 (s, 1H), 3.69 (dd, *J* = 10.4, 4.9 Hz, 1H), 2.79 (dd, *J* = 13.9, 10.4 Hz, 1H), 2.34 (s, 3H), 1.99 (s, 3H), 1.86 (s, 3H), 1.73 (dd, *J* = 13.9, 4.9 Hz, 1H), 1.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.3, 140.4, 138.6, 136.9, 135.2, 133.7, 130.0, 128.6, 127.6, 127.4, 127.3, 125.2, 120.5, 81.3, 50.0, 44.2, 38.8, 21.0, 20.6, 20.2, 13.6. **HRMS** (ESI) calcd. for $C_{21}H_{23}O_2$ $[M+H]^+$: 307.1693, found: 307.1698.

1,4-dimethyl-3-(naphthalen-1-yl)-1,2,3,4-tetrahydro-1,4-



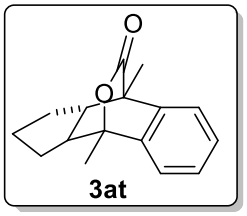
(epoxymethano)naphthalen-9-one (3ar): (colorless oil, 90.8 mg, yield: 55%; endo/exo = 90/10). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 – 7.35 (m, 8H), 6.96 – 6.94 (m, 2H), 6.37 – 6.26 (m, 1H), 3.70 (dd, *J* = 10.1, 6.2 Hz, 0.10H), 3.46 (dd, *J* = 10.3, 4.7 Hz, 0.86H), 2.88 (dd, *J* = 14.1, 10.3 Hz, 0.89H), 2.62 (dd, *J* = 13.5, 10.1 Hz, 0.11H), 2.03 (s, 2.68H), 1.96 (dd, *J* = 14.2, 4.7 Hz, 1H), 1.80 (s, 0.32H), 1.65 (s, 0.34H), 1.39 (s, 2.63H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.2, 176.0, 140.4, 140.0, 137.7, 137.6, 136.6, 133.1, 133.0, 132.6, 132.6, 129.3, 128.8, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 126.3, 126.2, 126.1, 126.0, 125.0, 123.8, 121.8, 120.6, 115.4, 84.8, 81.2, 51.0, 49.5, 45.8, 45.1, 43.7, 41.0, 20.7, 19.5, 16.2, 14.8. **HRMS** (ESI) calcd. for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1536, found: 329.1546.

5,12-dimethyl-5,5a,6,7,8,9,10,11,11a,12-decahydro-5,12-



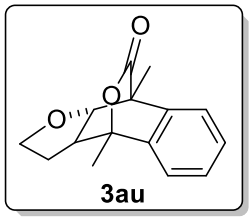
(epoxymethano)cycloocta[b]naphthalen-13-one (3as): (colorless oil, 91.0 mg**,** yield: 64%; endo/exo = 93/7). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 4H), 2.29 (t, *J* = 10.0 Hz, 1H), 2.05 (t, *J* = 9.5 Hz, 1H), 1.89 (s, 3H), 1.69 (s, 3H), 1.60 – 1.57 (m, 2H), 1.46 – 1.16 (m, 8H), 0.78 – 0.62 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.6, 137.9, 137.5, 128.4, 126.8, 123.4, 122.3, 84.6, 49.6, 49.5, 45.0, 31.0, 31.0, 26.2, 26.1, 25.0, 23.6, 19.8, 15.0. **HRMS** (ESI) calcd. for $C_{19}H_{24}NaO_2$ $[M+Na]^+$: 307.1669, found: 307.1671.

4,9-dimethyl-2,3,3a,4,9,9a-hexahydro-1H-4,9-



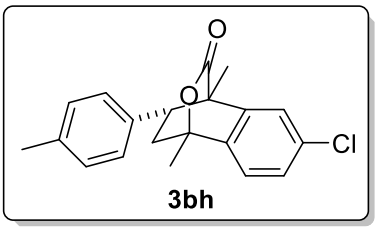
(epoxymethano)cyclopenta[b]naphthalen-10-one (3at): (colorless oil, 87.3 mg, yield: 72%; endo/exo = 92/8). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.21 (m, 4H), 2.76 (dd, *J* = 19.1, 10.4 Hz, 1H), 2.50 (dd, *J* = 19.4, 8.8 Hz, 1H), 1.81 (s, 3H), 1.77 – 1.66 (m, 2H), 1.62 (s, 3H), 1.37 – 1.15 (m, 2H), 0.67 – 0.50 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 138.4, 137.6, 128.5, 127.0, 124.3, 123.0, 84.2, 50.2, 48.4, 46.2, 29.2, 28.2, 26.9, 19.6, 14.8. **HRMS** (ESI) calcd. for $C_{16}H_{18}NaO_2$ $[M+Na]^+$: 265.1199, found: 265.1207.

4,9-dimethyl-2,3,3a,4,9,9a-hexahydro-4,9-(epoxymethano)naphtho[2,3-b]furan-



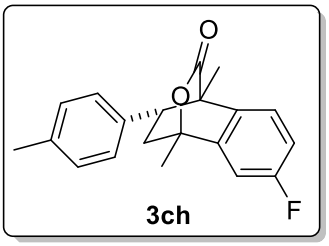
10-one (3au): (colorless oil, 49.1 mg, yield: 40%; endo/exo = 84/16). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 4H), 5.60 (d, *J* = 8.0 Hz, 0.14H), 4.29 (d, *J* = 8.1 Hz, 0.85H), 4.20 (dd, *J* = 10.4, 5.1 Hz, 0.13H), 3.47 (dd, *J* = 15.5, 7.3 Hz, 0.88H), 3.06 – 3.01 (m, 0.85H), 2.91 (dd, *J* = 14.0, 10.3 Hz, 0.13H). 2.80 – 2.75 (m, 0.85H), 2.60 (s, 33H), 2.23 (t, *J* = 7.6 Hz, 0.15H), 2.02 – 1.89 (m, 1.55H), 1.89 (s, 2.58H), 1.79 (s, 2.57H), 1.16 – 1.09 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.3, 137.2, 136.2, 129.4, 127.4, 124.6, 122.5, 83.5, 82.4, 69.3, 51.2, 50.1, 28.7, 19.5, 13.7. **HRMS** (ESI) calcd. for $C_{15}H_{16}NaO_3$ $[M+Na]^+$: 267.0992, found: 267.0993.

6-chloro-1,4-dimethyl-3-(p-tolyl)-1,2,3,4-tetrahydro-1,4-



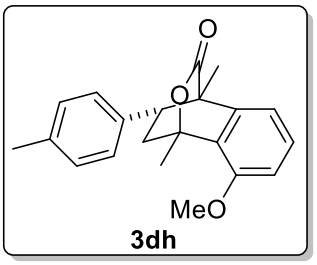
(epoxymethano)naphthalen-9-one (3bh): (colorless oil, 66.3 mg, yield: 41%; endo/exo > 95/5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 2H), 6.97 (d, *J* = 1.9 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 2H), 6.22 (d, *J* = 7.7 Hz, 2H), 3.26 (dd, *J* = 10.3, 4.7 Hz, 1H), 2.80 (dd, *J* = 14.1, 10.3 Hz, 1H), 2.25 (s, 3H), 1.96 (s, 3H), 1.83 (dd, *J* = 14.1, 4.7 Hz, 1H), 1.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.4, 138.9, 138.7, 137.3, 136.5, 134.9, 129.0, 128.2, 127.7, 125.3, 121.9, 80.8, 49.6, 45.1, 43.4, 21.1, 20.6, 14.6. **HRMS** (ESI) calcd. for $C_{20}H_{20}ClO_2$ $[M+H]^+$: 327.1146, found: 327.1148.

7-fluoro-1,4-dimethyl-3-(p-tolyl)-1,2,3,4-tetrahydro-1,4-



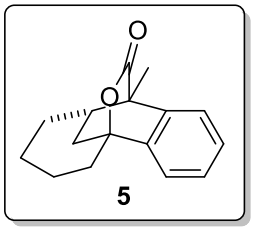
(epoxymethano)naphthalen-9-one (3ch): (colorless oil, 71.6 mg, yield: 46%; endo/exo = 90/10) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.4, 5.0 Hz, 0.13H), 7.17 (dd, *J* = 8.5, 2.6 Hz, 0.91H), 7.03 (td, *J* = 8.7, 2.6 Hz, 1H), 7.01 – 6.72 (m, 3H), 6.32 (d, *J* = 7.8 Hz, 0.33H), 6.20 (d, *J* = 7.6 Hz, 1.67H), 3.48 (dd, *J* = 10.1, 6.2 Hz, 0.12H), 3.24 (dd, *J* = 10.3, 4.7 Hz, 0.88H), 2.79 (dd, *J* = 14.2, 10.3 Hz, 0.92H), 2.52 (dd, *J* = 13.3, 10.1 Hz, 0.19H), 2.28 (s, 0.21H), 2.24 (s, 2.74H), 1.95 (s, 2.68H), 1.81 (dd, *J* = 14.1, 4.7 Hz, 1H), 1.74 (s, 0.34H), 1.58 (s, 0.34H), 1.35 (s, 2.69H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.7, 175.6, 162.4 (d, *J* = 247.1 Hz), 162.0 (d, *J* = 247.5 Hz), 142.3 (d, *J* = 7.3 Hz), 139.8 (d, *J* = 7.1 Hz), 137.2, 137.0, 136.7, 136.6, 135.6 (d, *J* = 3.0 Hz), 132.2 (d, *J* = 2.9 Hz), 129.0, 128.8, 128.3, 128.2, 126.5 (d, *J* = 8.4 Hz), 123.3 (d, *J* = 8.3 Hz), 115.7 (d, *J* = 21.8 Hz), 115.2 (d, *J* = 21.7 Hz), 111.6 (d, *J* = 23.3 Hz), 108.5 (d, *J* = 23.5 Hz), 84.2, 80.7, 50.2, 48.9, 45.0, 44.7, 43.2, 40.7, 28.4, 21.0, 20.5, 19.3, 16.1, 14.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.5, -114.4. **HRMS** (ESI) calcd. for $C_{20}H_{20}FO_2$ $[M+H]^+$: 311.1442, found: 311.1447.

8-methoxy-1,4-dimethyl-3-(p-tolyl)-1,2,3,4-tetrahydro-1,4-



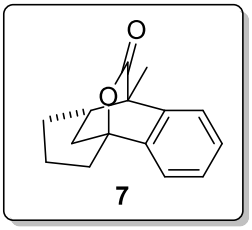
(epoxymethano)naphthalen-9-one (3dh): (colorless oil, 89.2 mg, yield: 55%; endo/exo = 76/24). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (dt, *J* = 7.8 Hz, 0.23H), 7.25 (dt, *J* = 8.0 Hz, 0.84H), 7.16 – 6.51 (m, 4H), 6.38 (d, *J* = 7.8 Hz, 0.39H), 6.23 (d, *J* = 7.7 Hz, 1.54H), 3.89 (s, 2.22H), 3.56 (s, 0.61H), 3.35 (dd, *J* = 10.1, 6.4 Hz, 0.24H), 3.20 (dd, *J* = 10.4, 4.7 Hz, 0.76H), 2.68 (dd, *J* = 14.1, 10.3 Hz, 0.76H), 2.48 (dd, *J* = 13.4, 10.2 Hz, 0.34H), 2.25 (s, 0.83H), 2.23 (s, 1.96H), 2.10 (s, 2.27H), 1.96 (dd, *J* = 14.1, 4.7 Hz, 0.88H), 1.78 (s, 0.64H), 1.71 (s, 0.63H), 1.63 – 1.56 (m, 0.32H), 1.33 (s, 2.3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.4, 176.3, 157.0, 154.4, 142.7, 139.2, 86.1, 82.6, 77.5, 55.8, 55.6, 51.6, 49.1, 45.0, 45.0, 44.8, 41.1, 24.3, 23.1, 21.0, 21.0, 16.7, 15.3. **HRMS** (ESI) calcd. for $C_{21}H_{23}O_3$ $[M+H]^+$: 323.1642, found: 323.1641.

11-methyl-6,7,8,9,10,11-hexahydro-5,11-(epoxymethano)-5,10-



methanobenzo[9]annulen-12-one (5): (colorless oil, 61.9 mg, yield: 51%; endo/exo = 71/29). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.22 (m, 4H), 2.52 – 2.39 (m, 1H), 2.36 – 2.03 (m, 2H), 1.93 – 1.79 (m, 3H), 1.77 – 1.67 (m, 1H), 1.65 (s, 2.11H), 1.62 (s, 0.89H), 1.56 – 1.03 (m, 3H), 0.88 – 0.69 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.9, 176.4, 140.8, 139.9, 139.2, 136.3, 128.5, 128.4, 127.1, 127.0, 124.7, 121.8, 120.8, 120.1, 91.5, 81.8, 54.6, 49.2, 44.3, 39.2, 38.7, 38.4, 30.1, 29.5, 29.2, 28.1, 25.2, 22.6, 20.8, 16.9, 16.2, 13.9. **HRMS** (ESI) calcd. for $C_{16}H_{18}NaO_2$ $[M+Na]^+$: 265.1199, found: 265.1199.

10-methyl-7,8,9,10-tetrahydro-6H-5,10-(epoxymethano)-5,9-

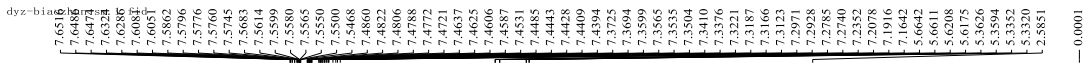


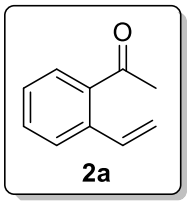
methanobenzo[8]annulen-11-one (7): (colorless oil, 48.2 mg, yield: 42%; endo/exo > 95/5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 4H), 2.50 – 2.41 (m, 1H), 2.38 – 2.33 (m, 1H), 2.19 – 2.08 (m, 2H), 2.01 – 1.92 (m, 2H), 1.82 – 1.72 (m, 2H), 1.70 – 1.62 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.6, 139.5,

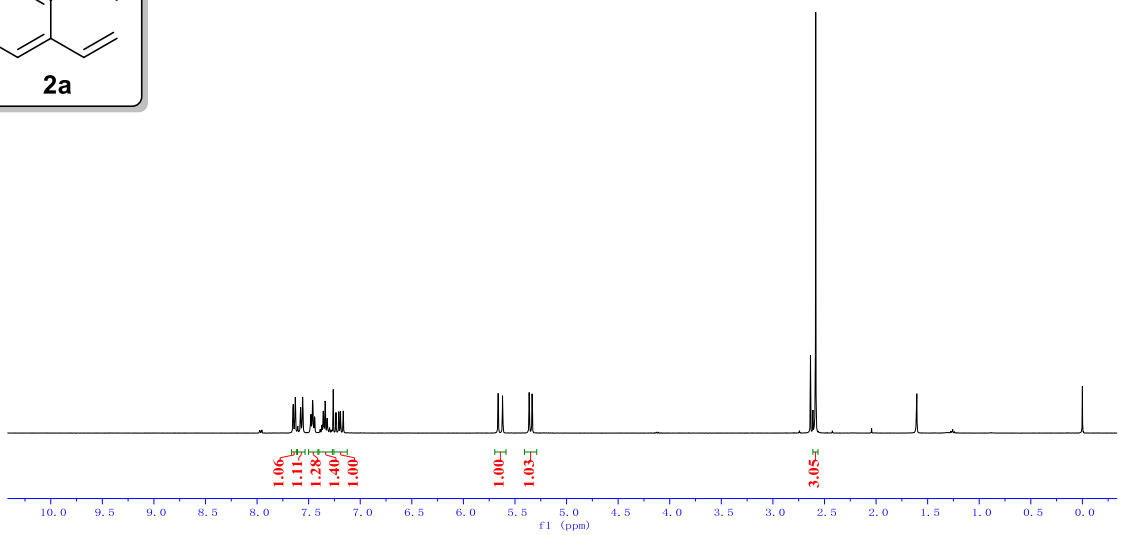
138.7, 128.6, 127.0, 122.9, 120.3, 92.9, 45.5, 45.1, 34.8, 30.0, 28.2, 22.7, 16.3. **HRMS** (ESI) calcd. for $C_{15}H_{17}O_2$ $[M+H]^+$: 229.1223, found: 229.1228.

6. Spectra of the substrates and products.

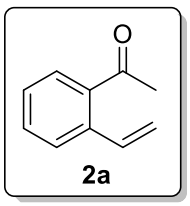
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2a

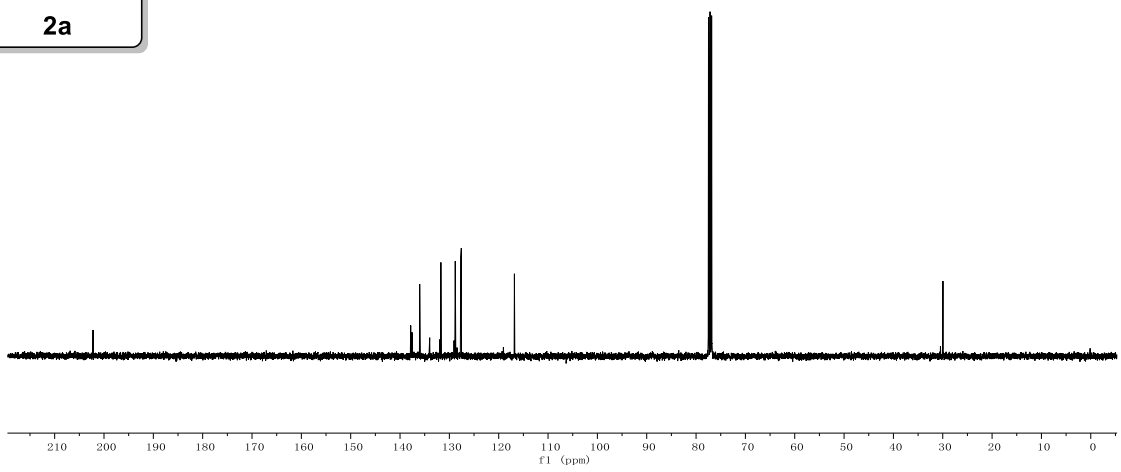




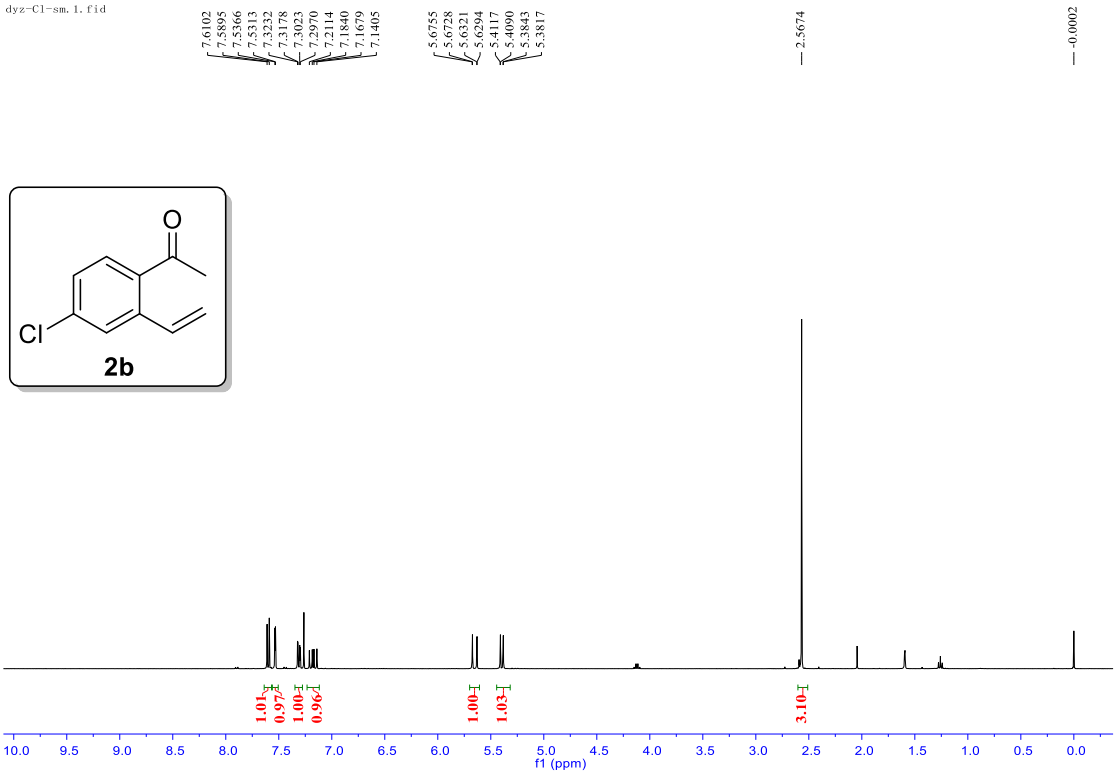


^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 2a

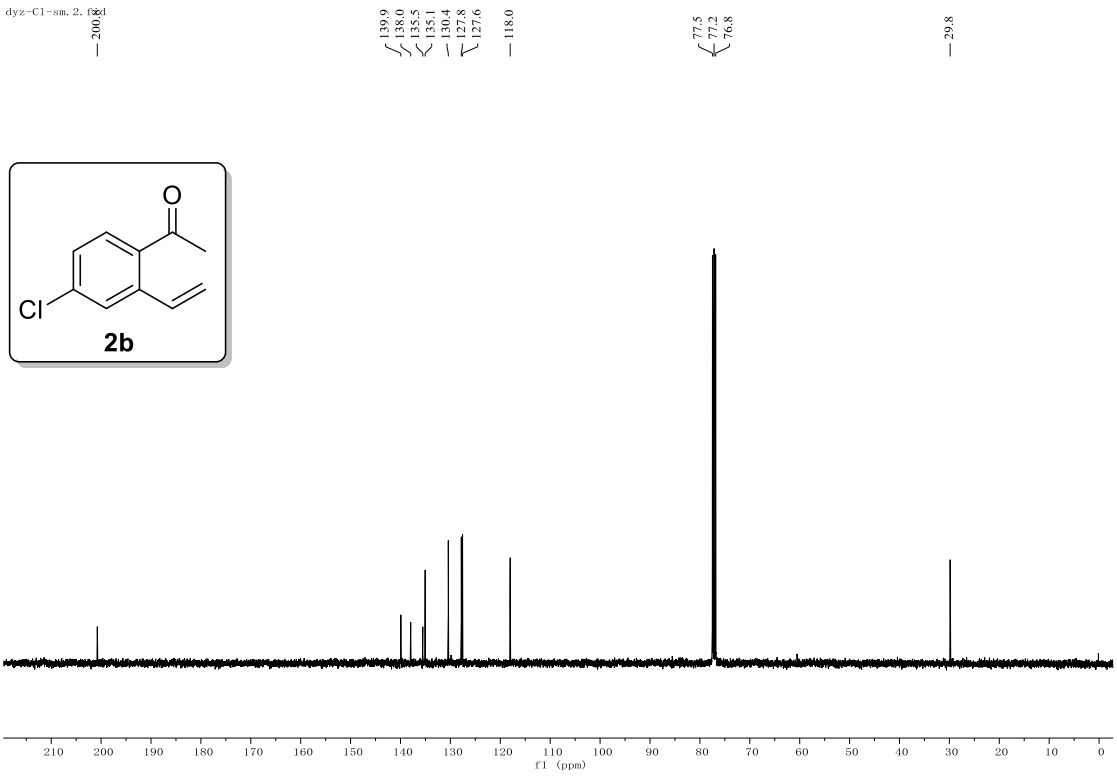




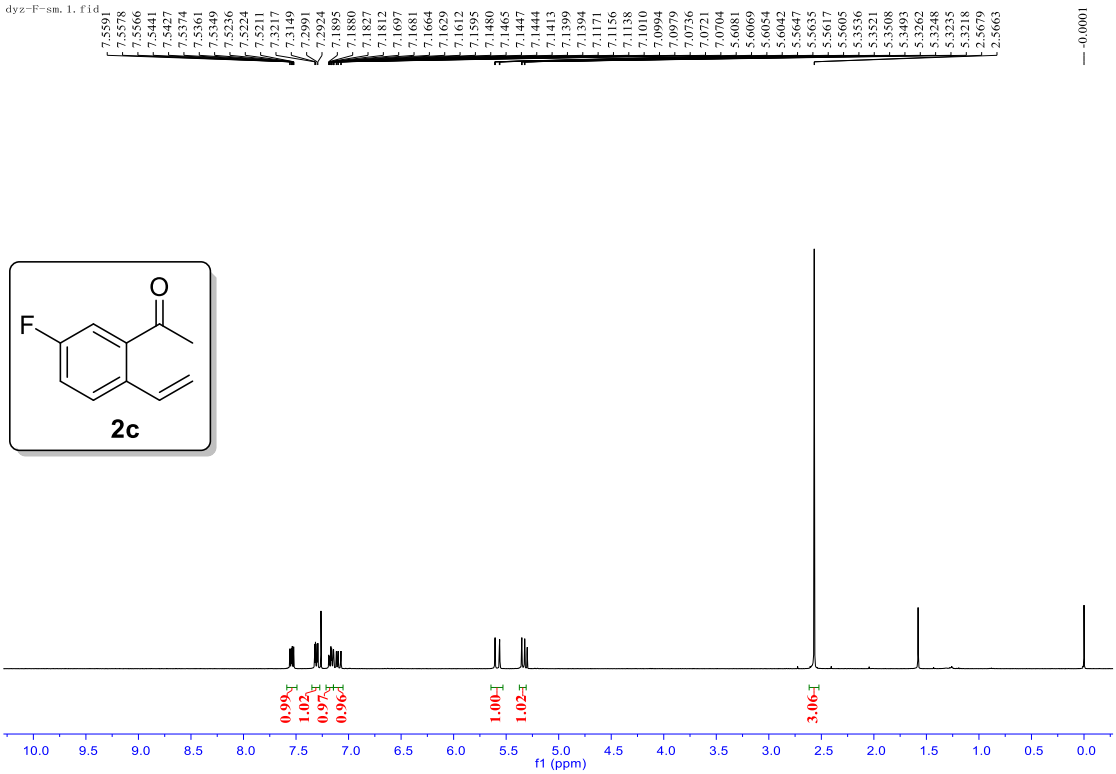
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2b



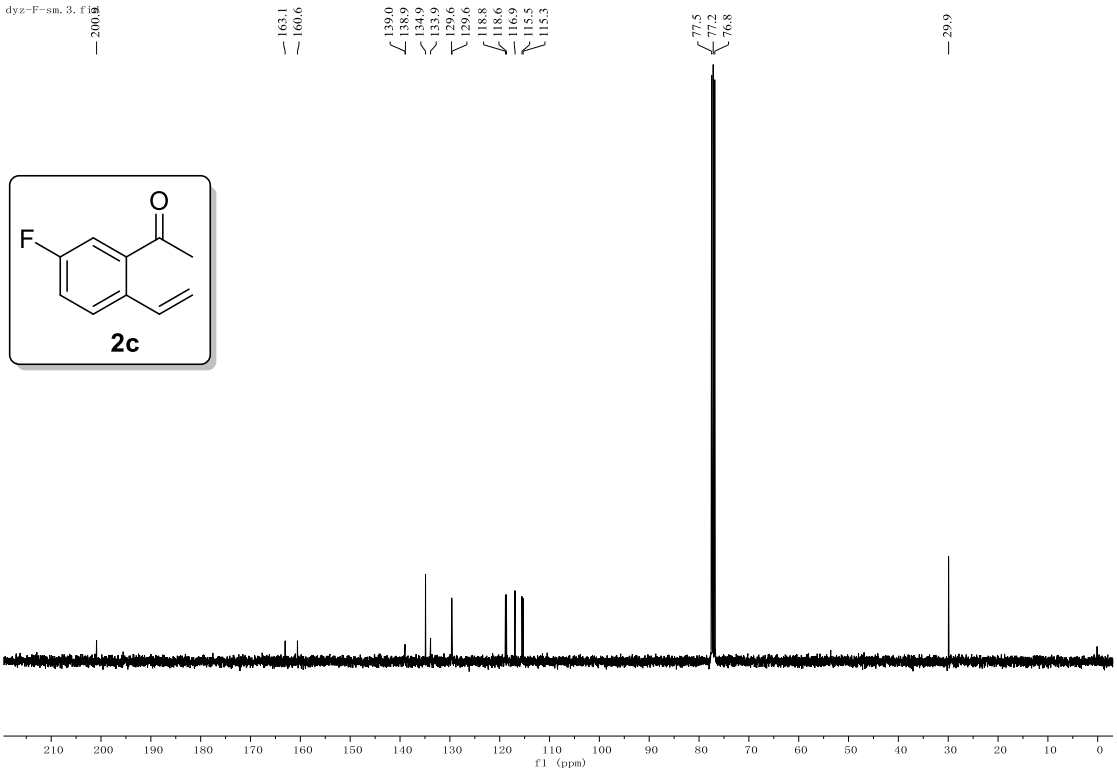
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 2b



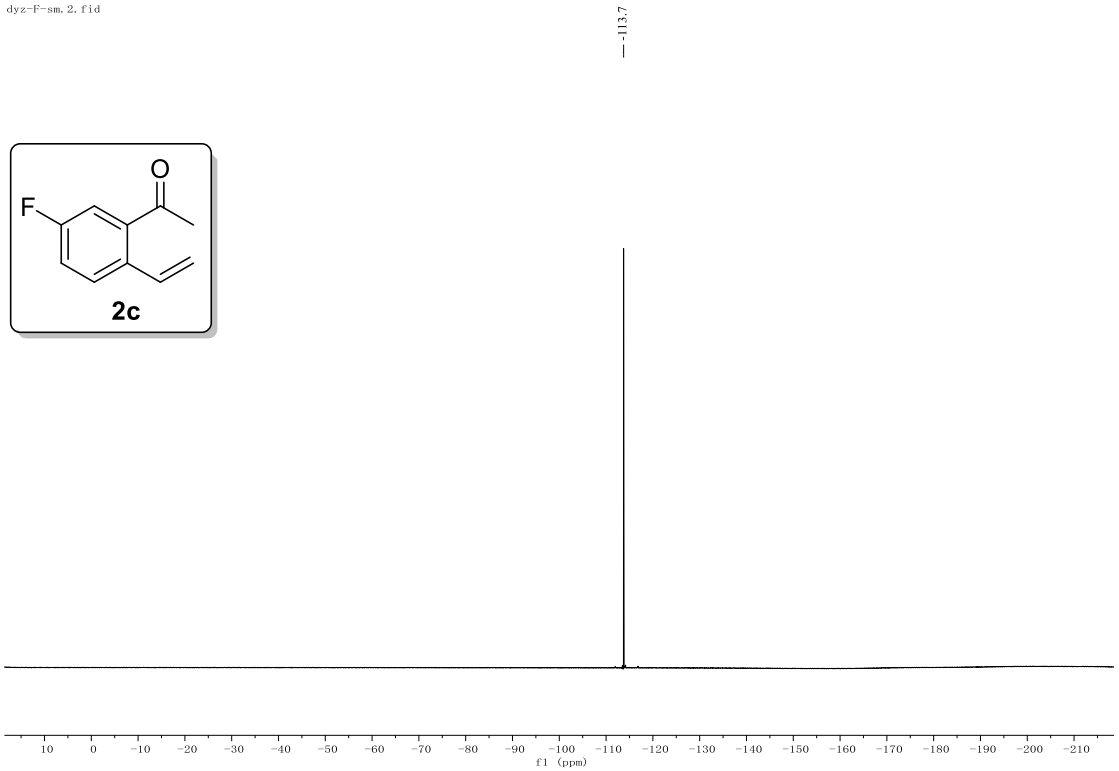
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2c



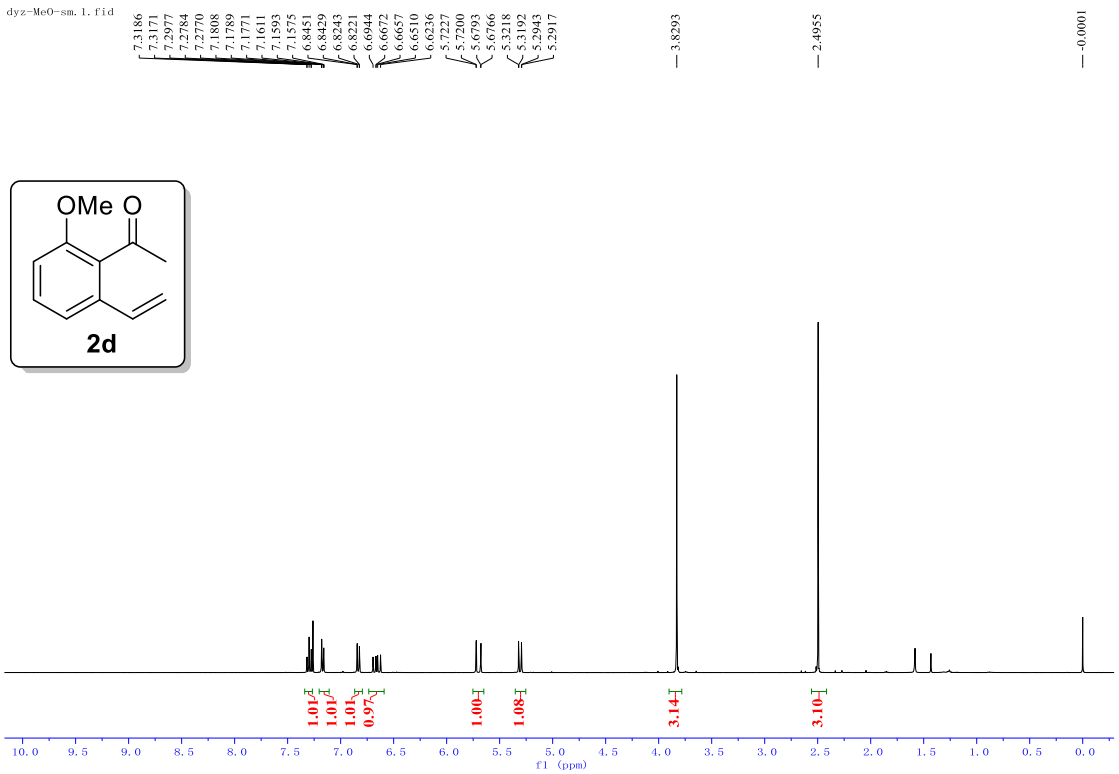
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 2c



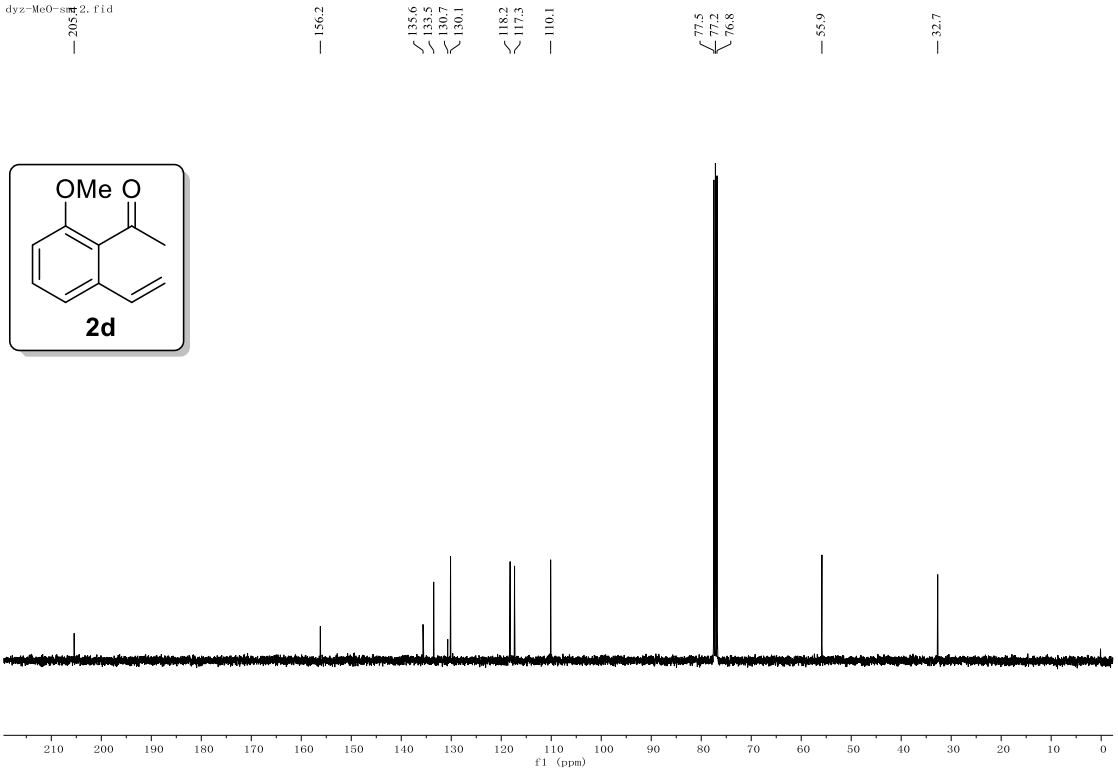
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 2c



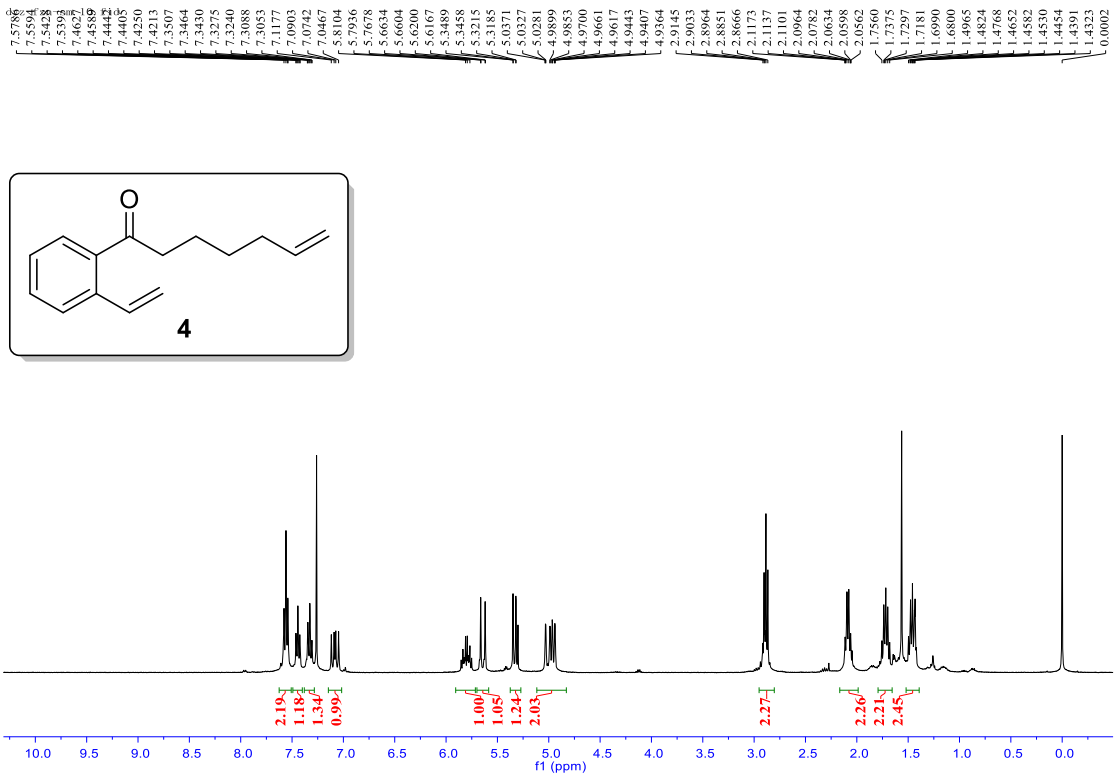
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2d



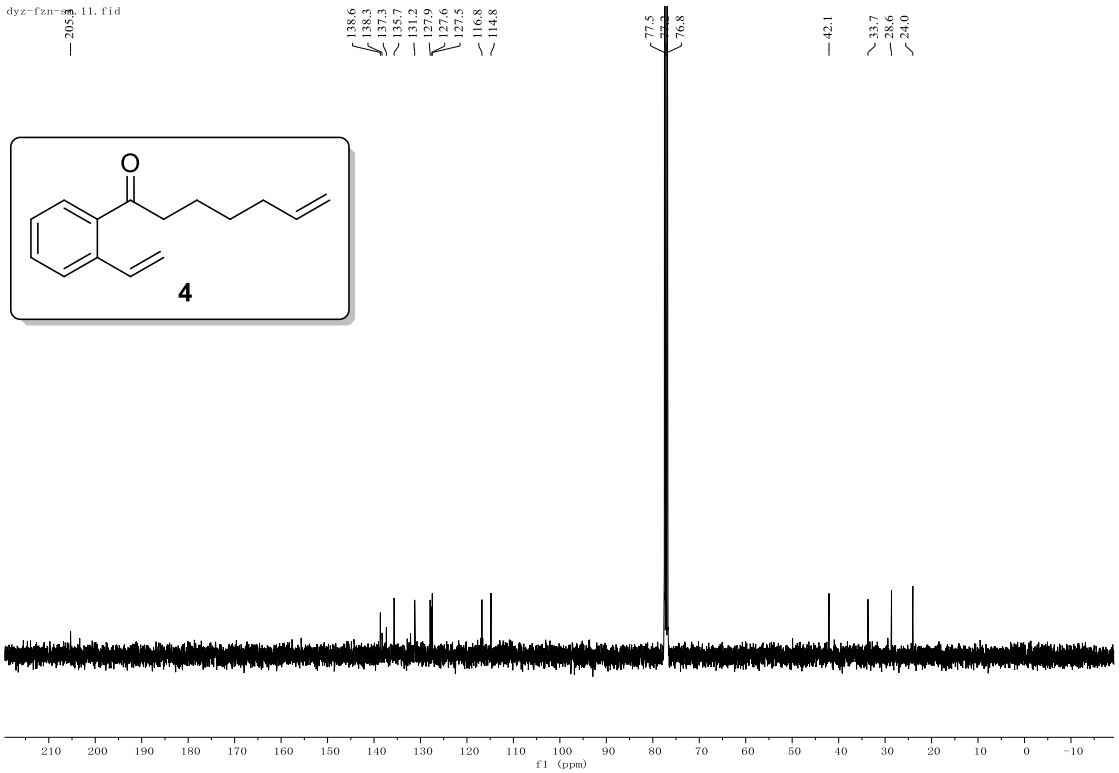
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 2d



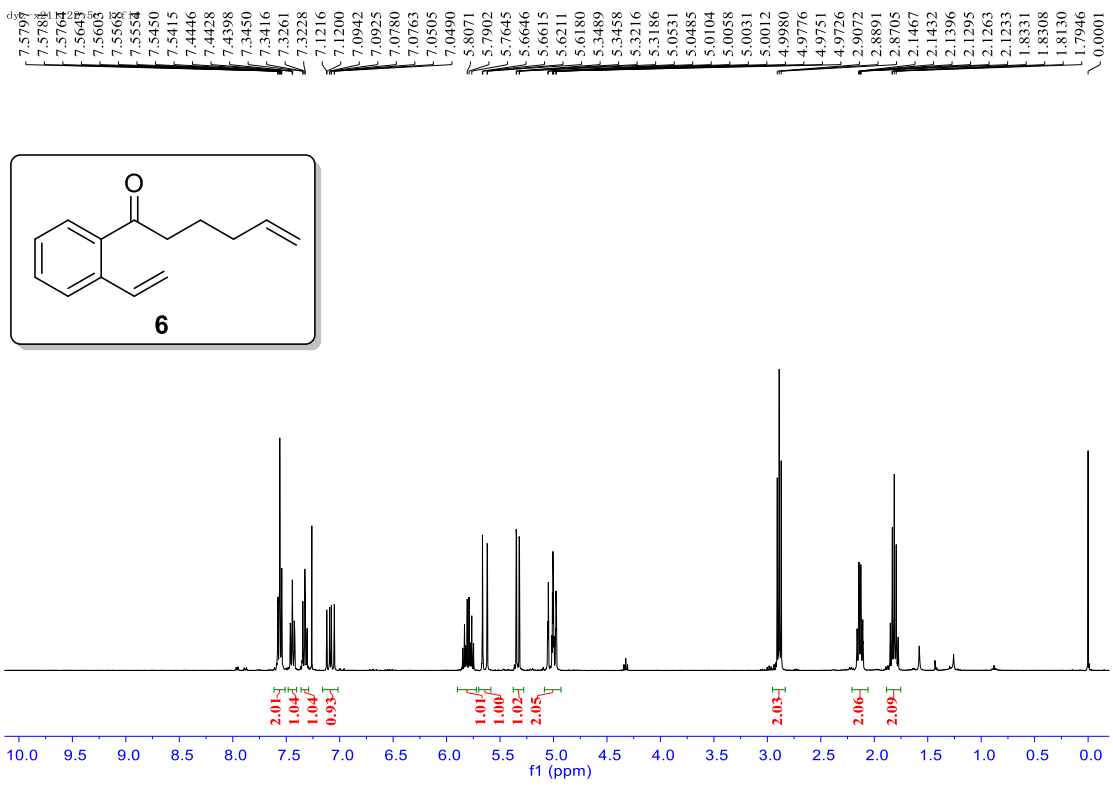
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4



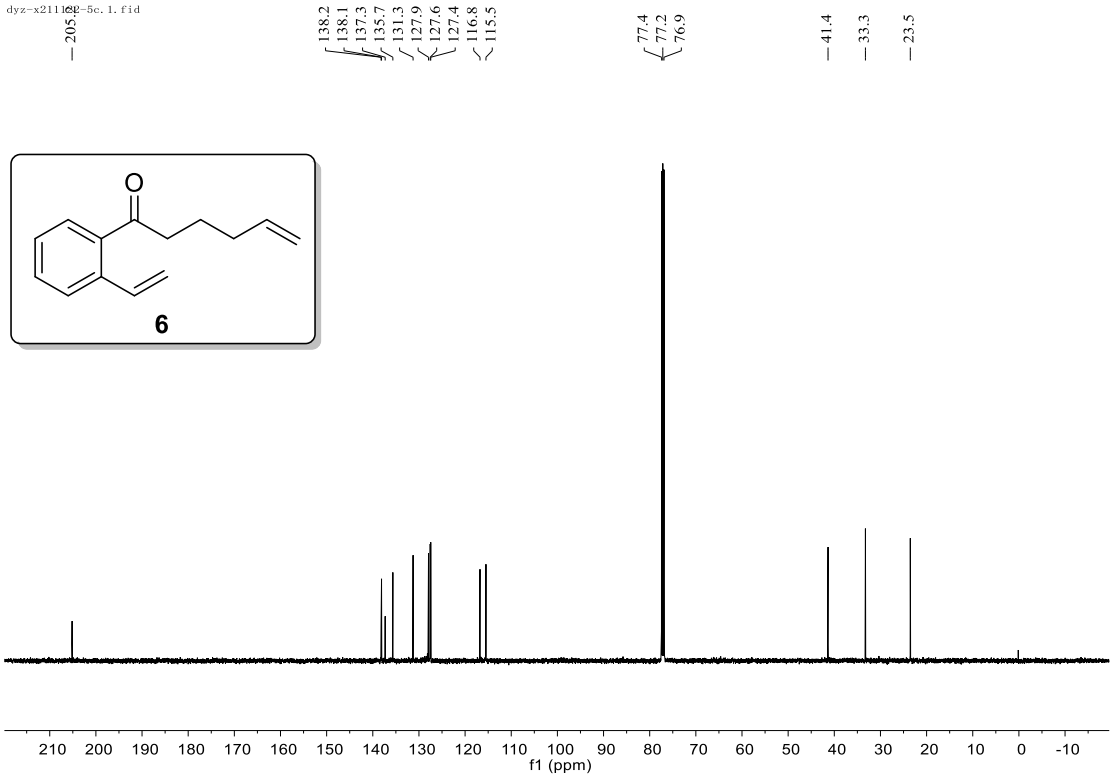
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4



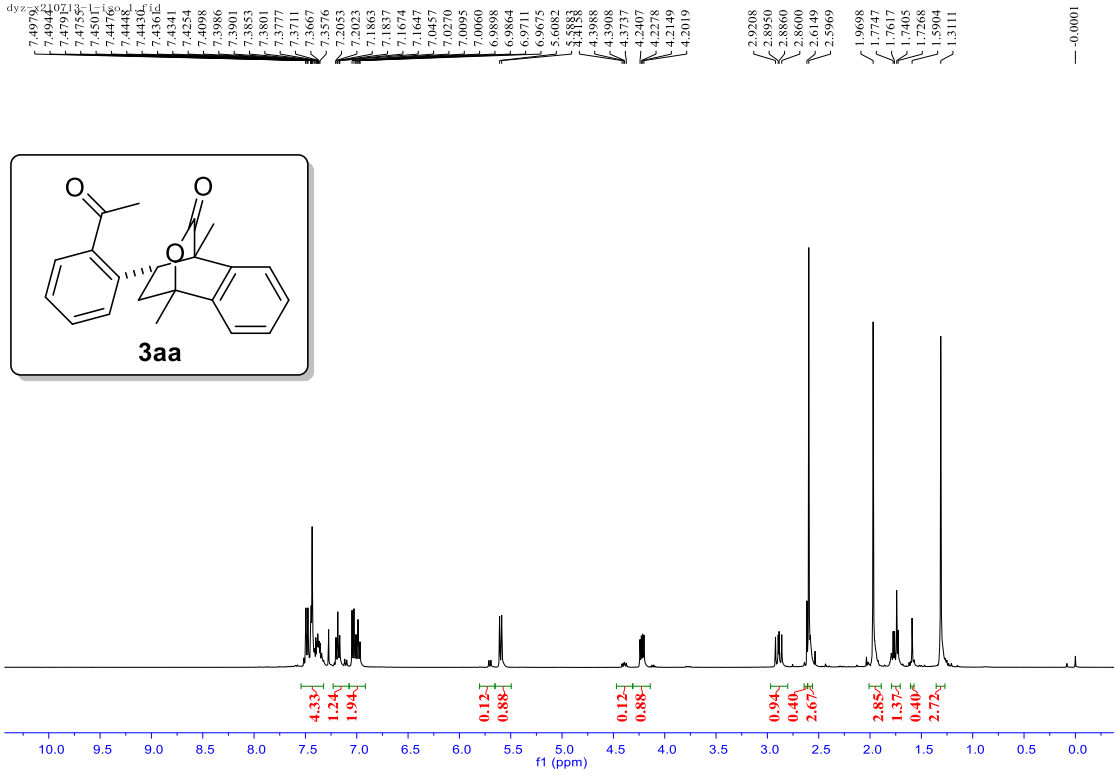
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 6



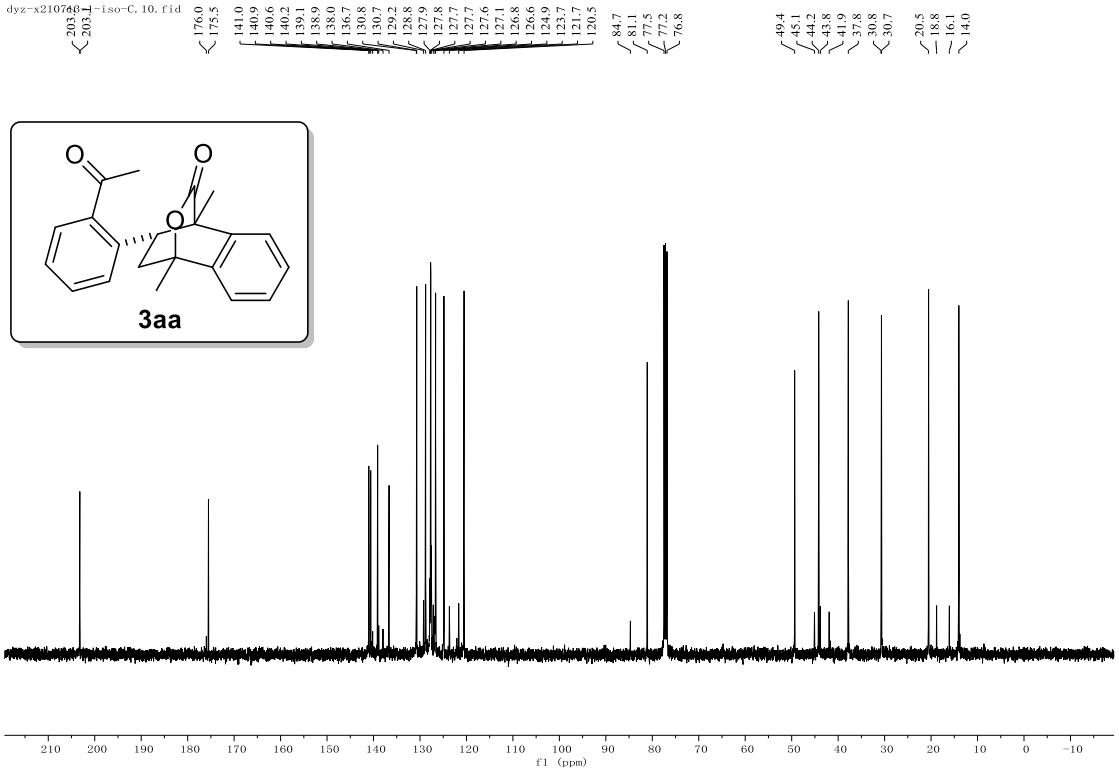
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 6



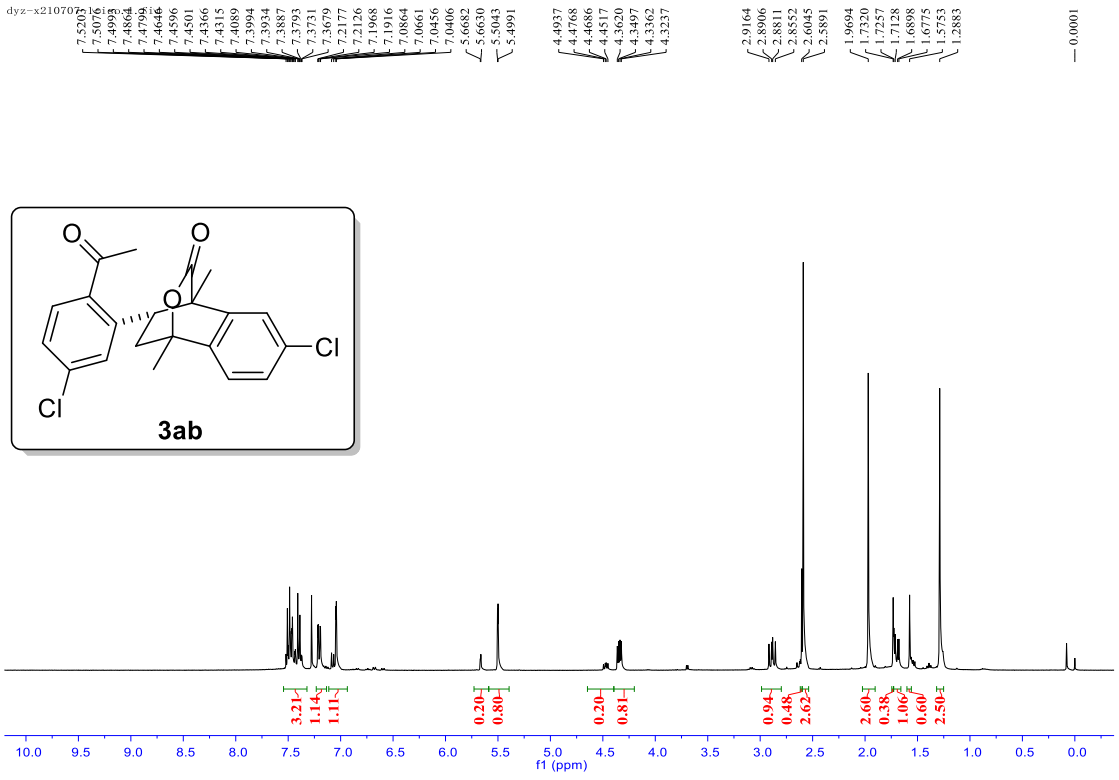
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3aa



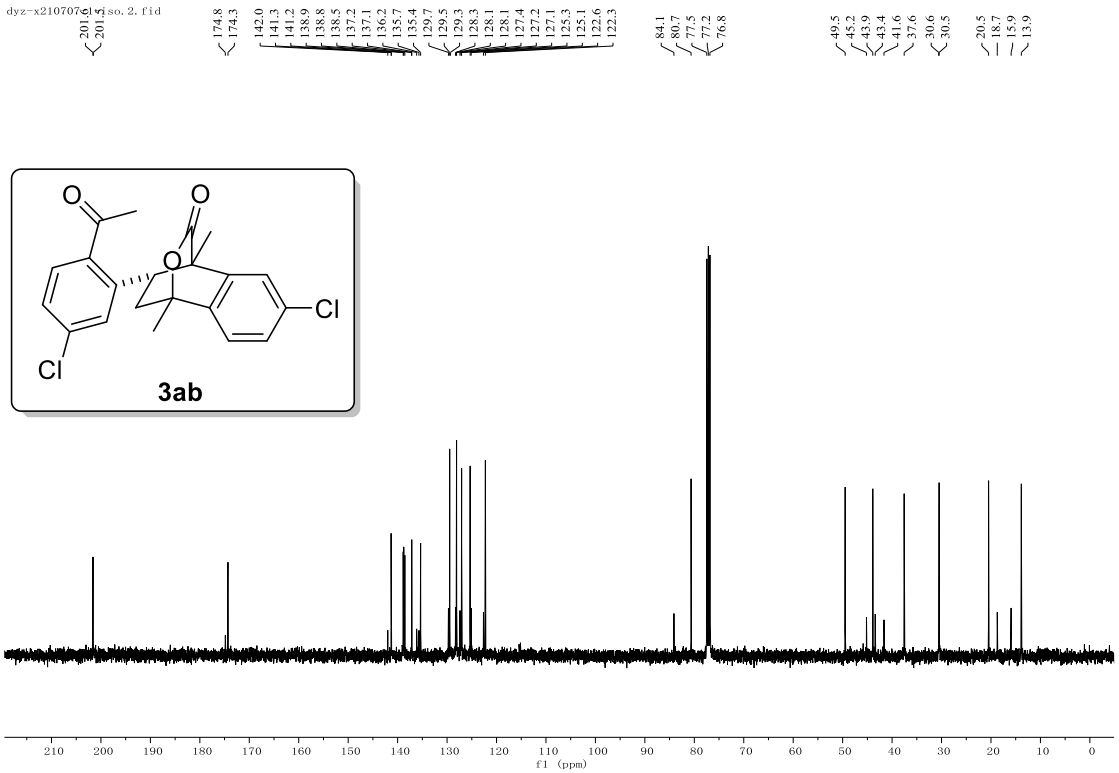
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3aa



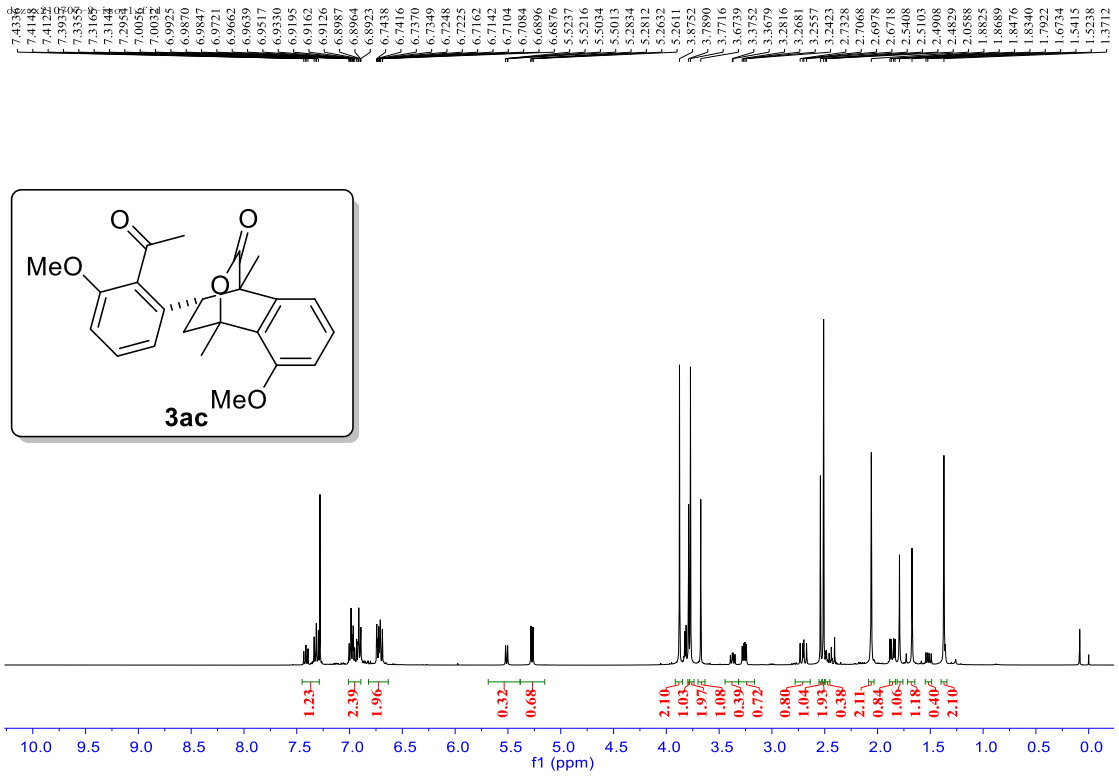
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ab



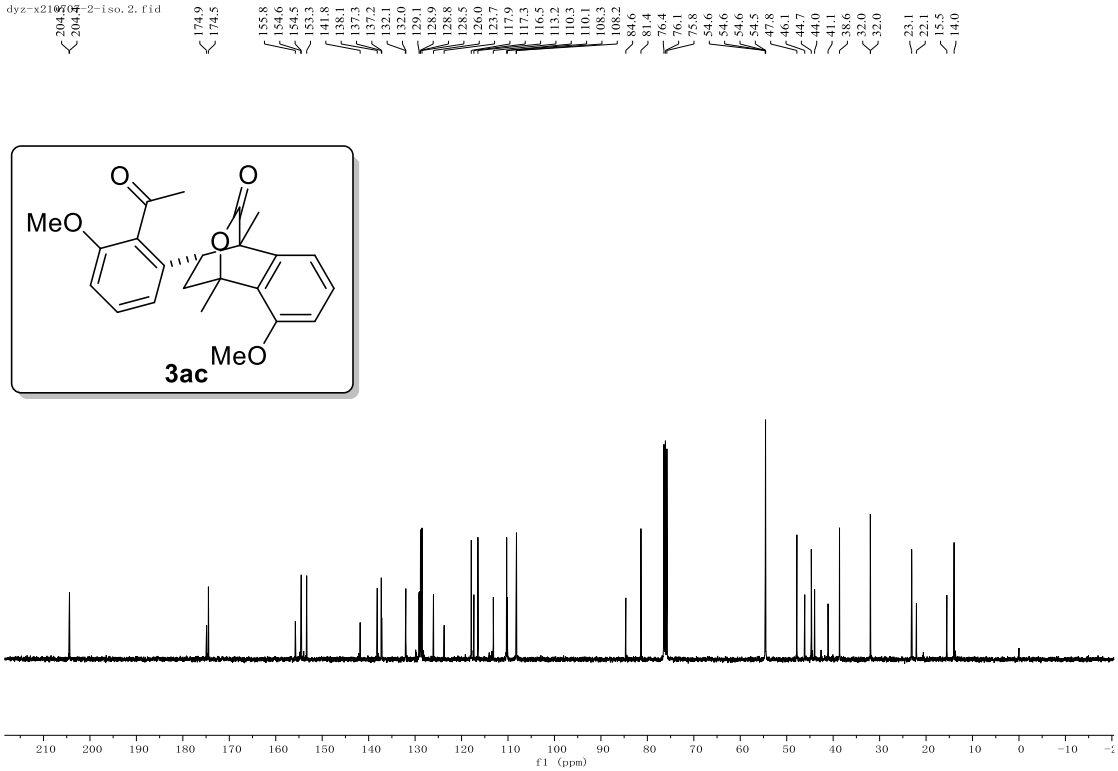
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ab



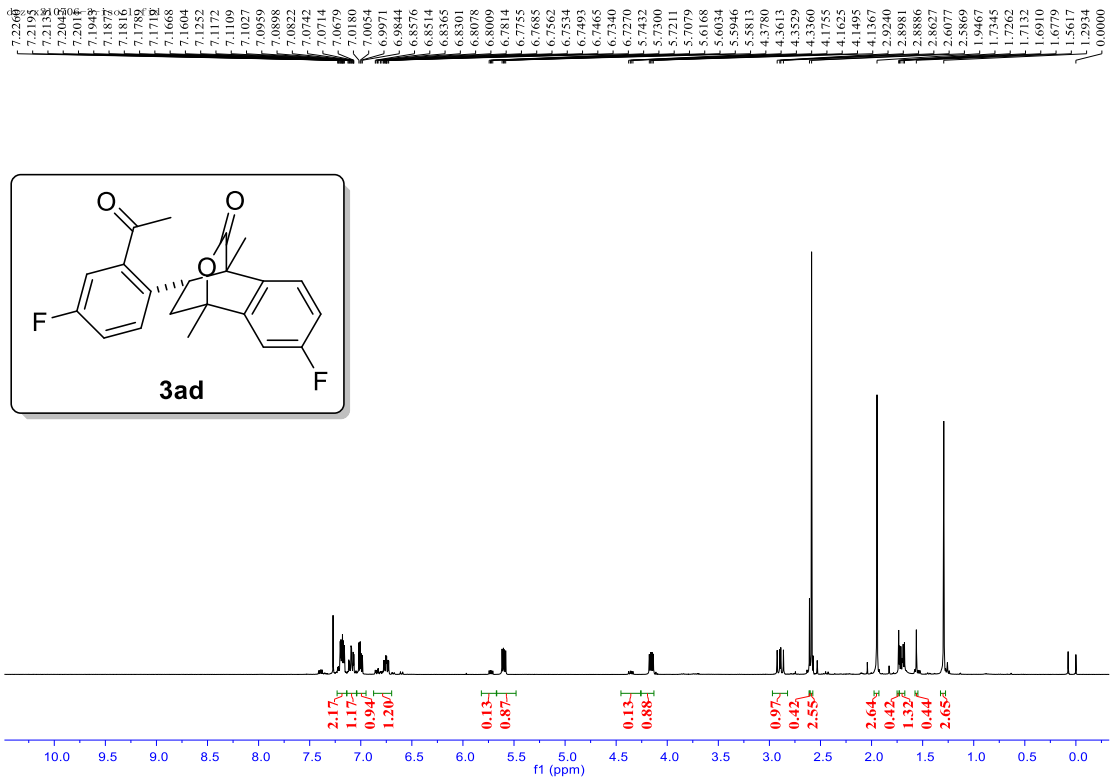
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ac



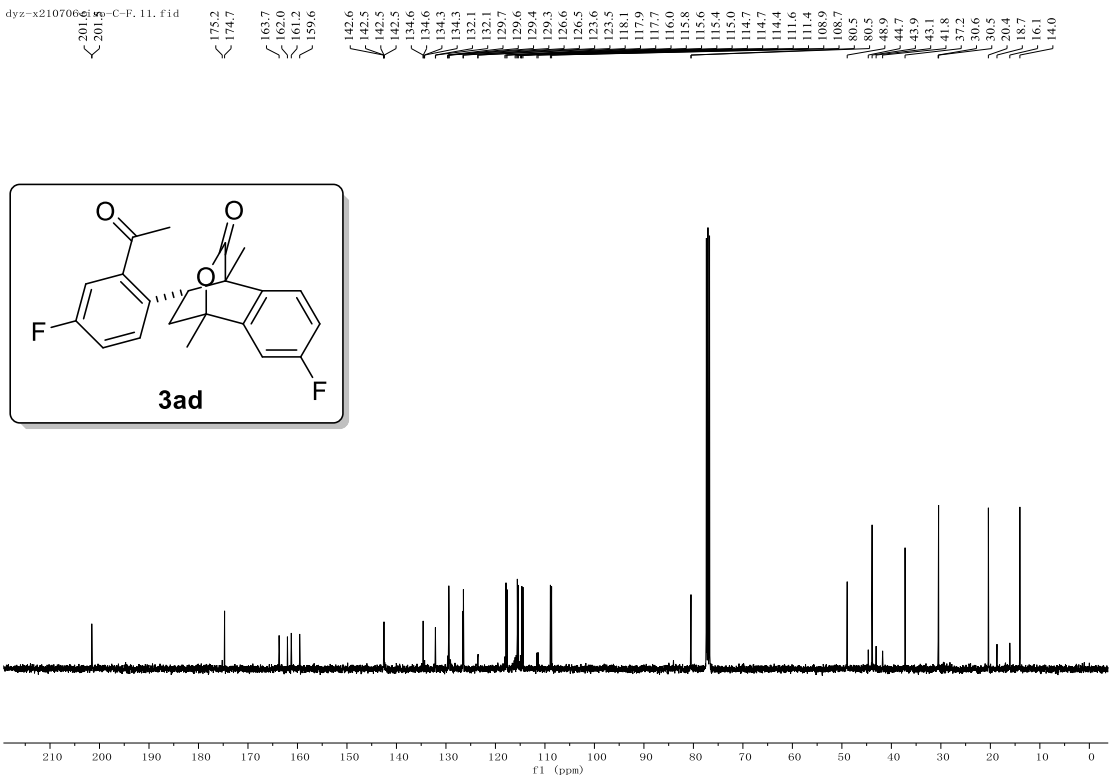
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ac



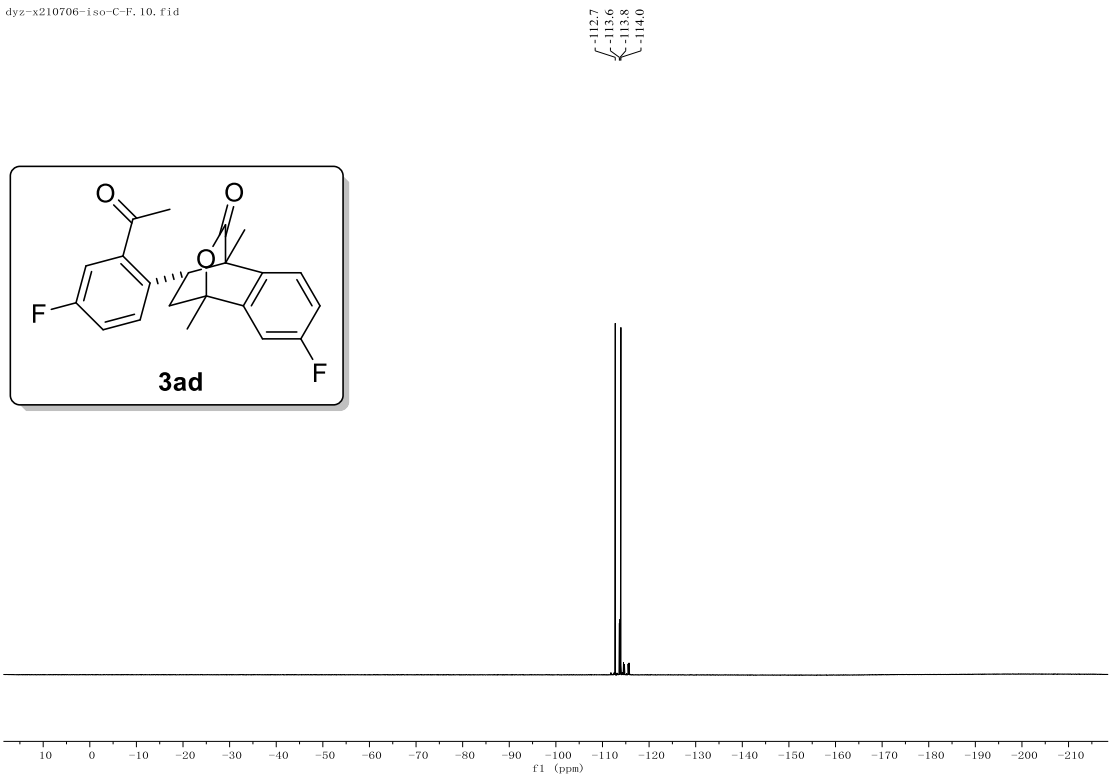
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ad



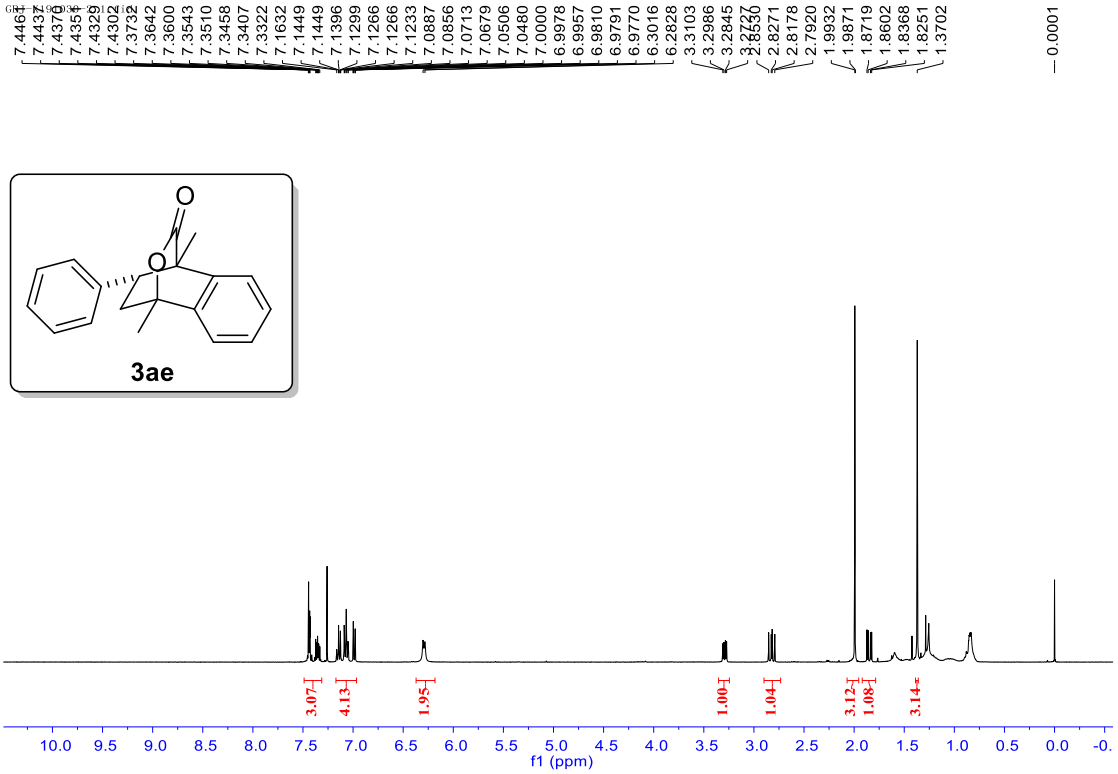
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ad



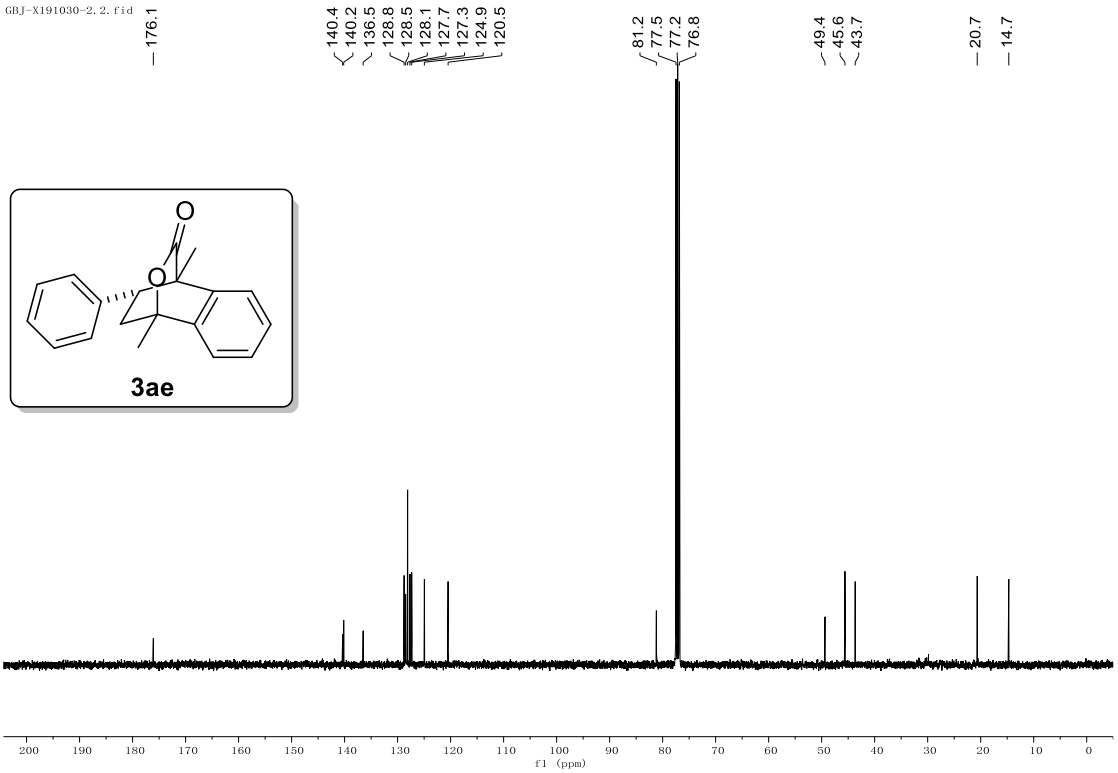
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3ad



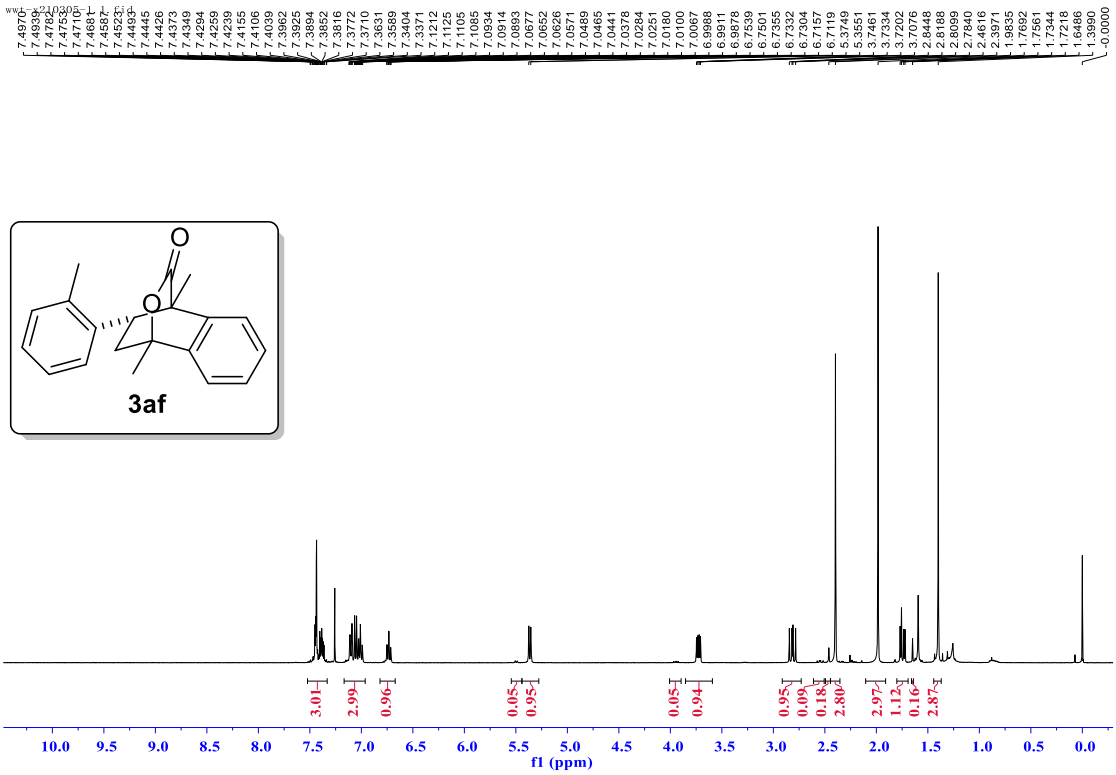
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ae



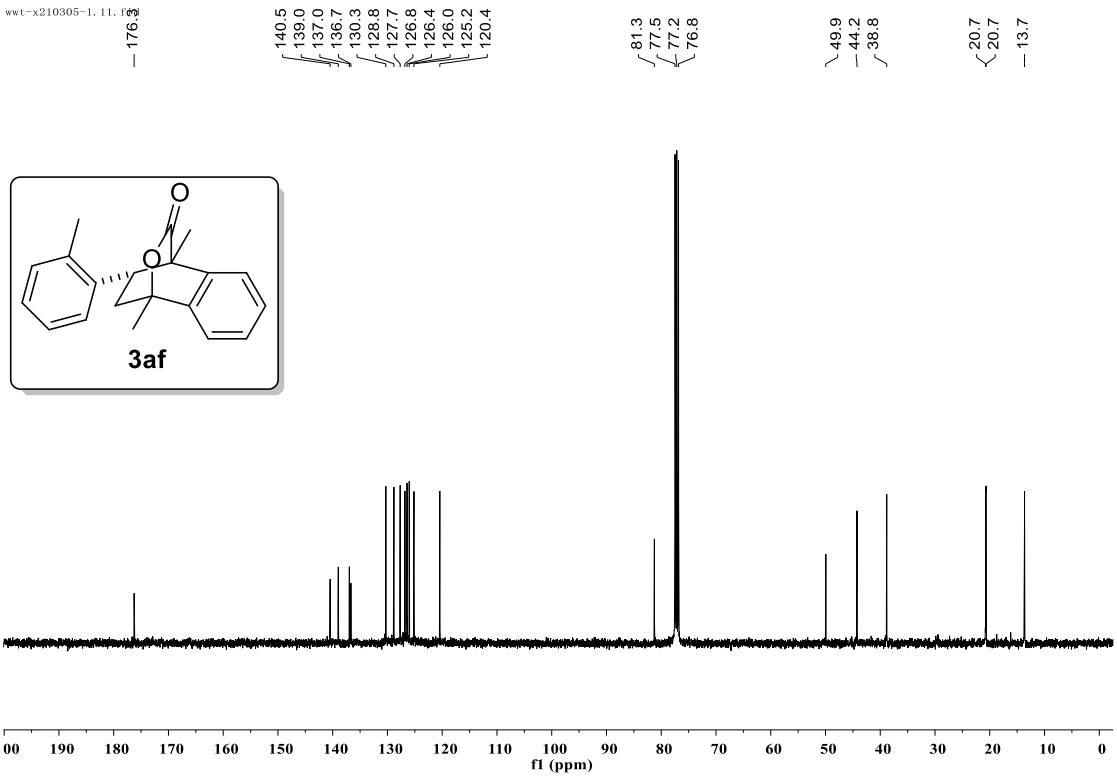
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ae



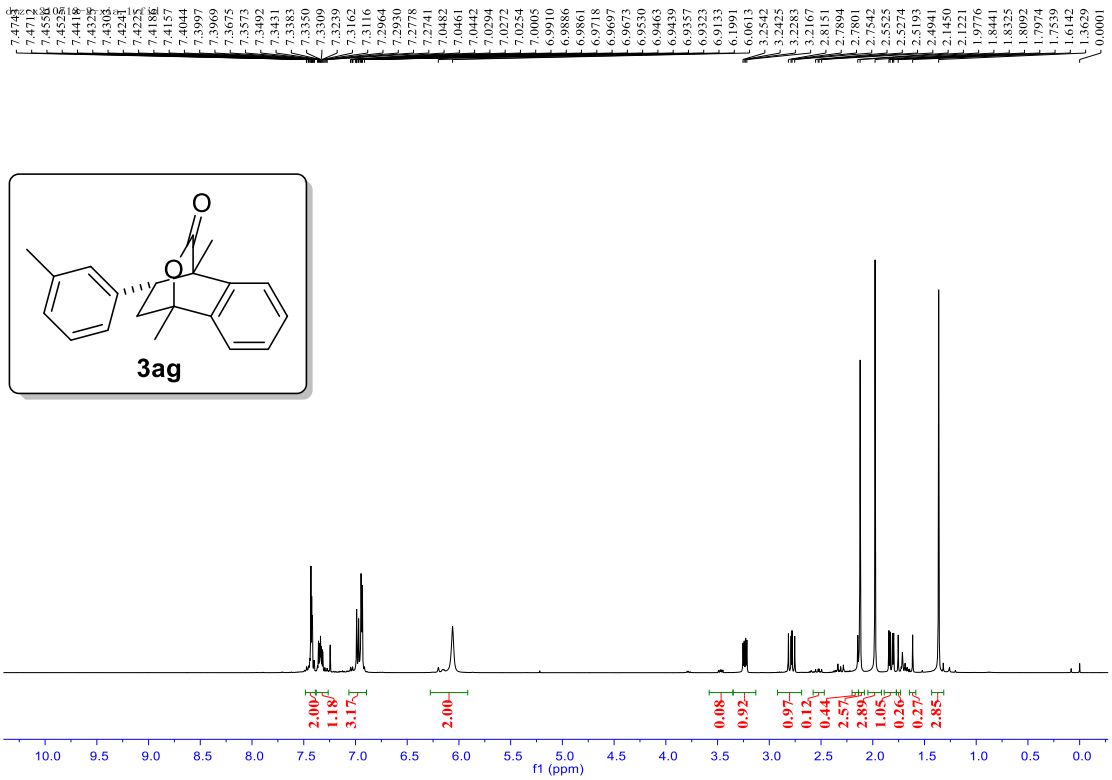
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3af



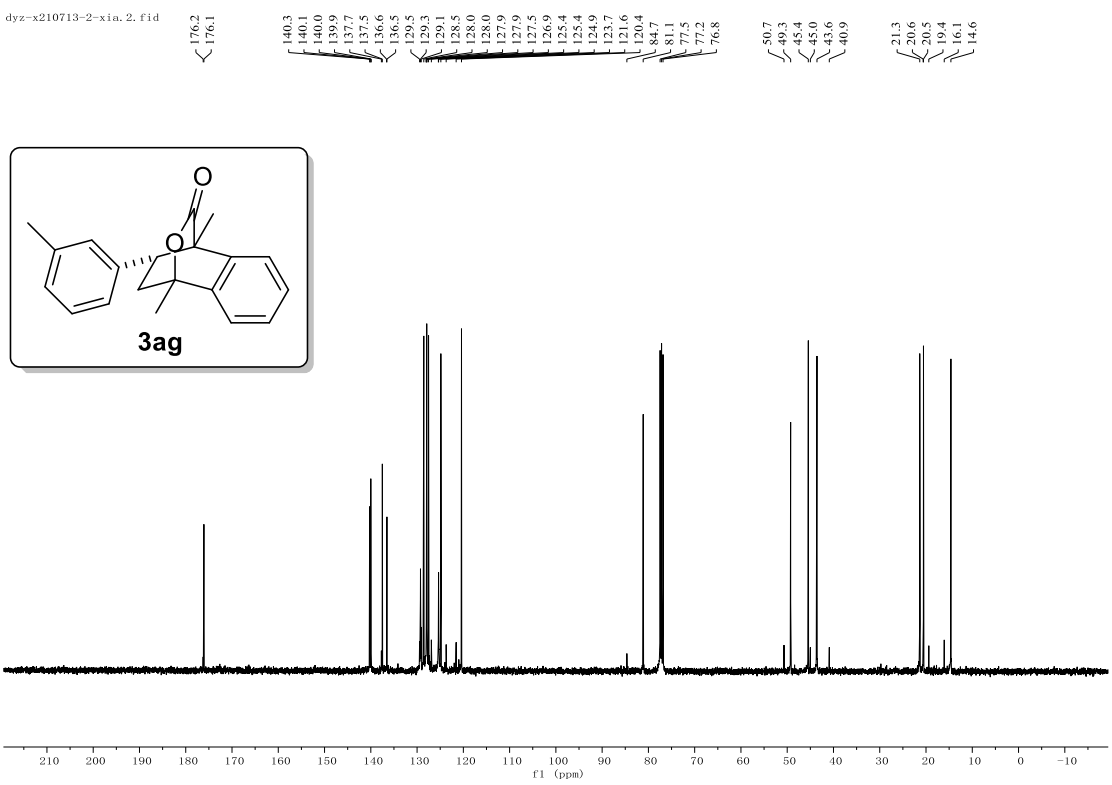
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3af



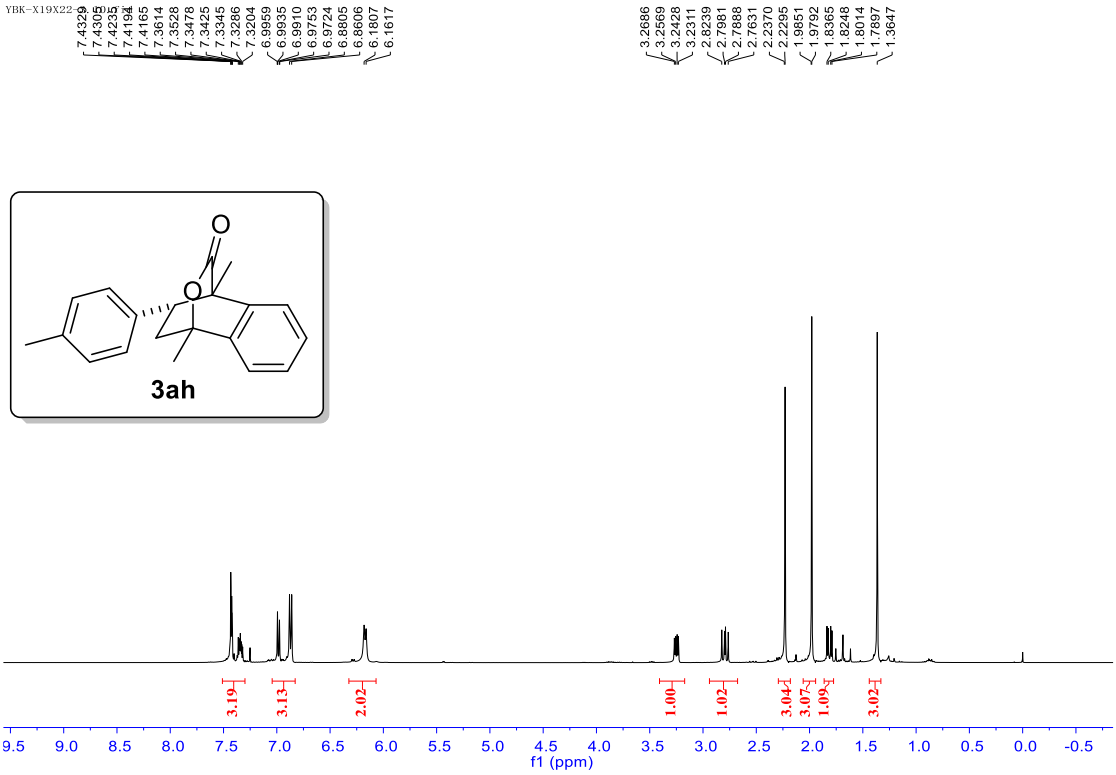
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ag



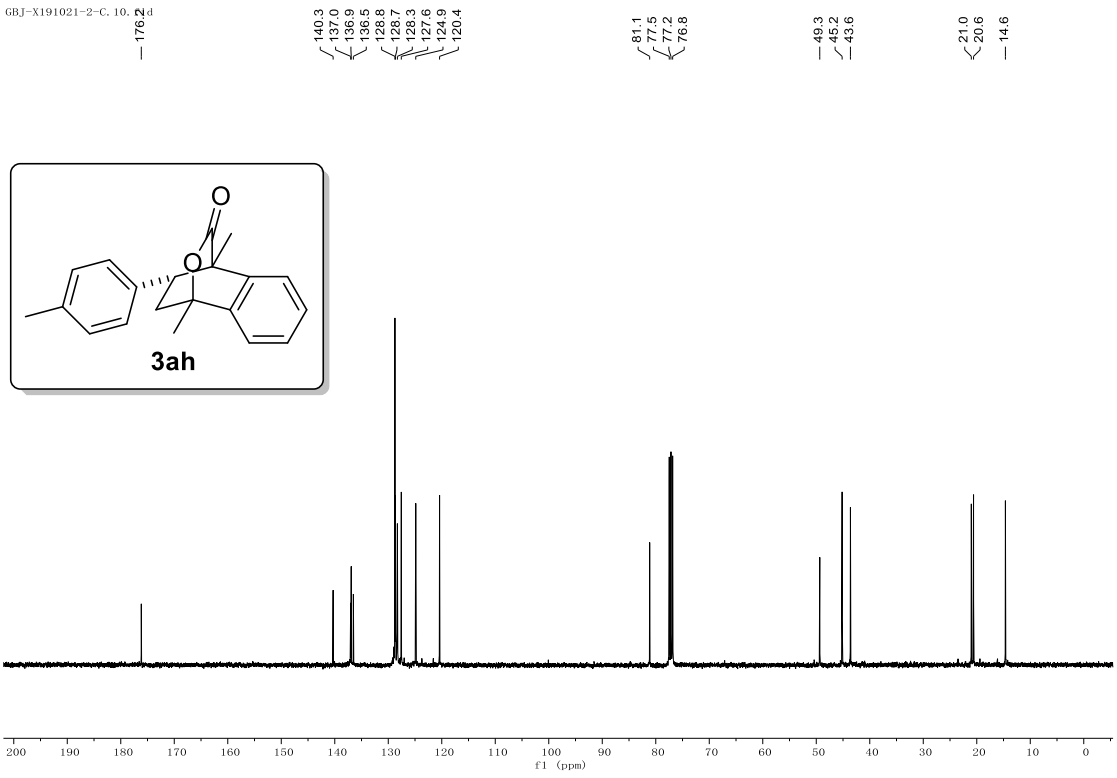
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ag



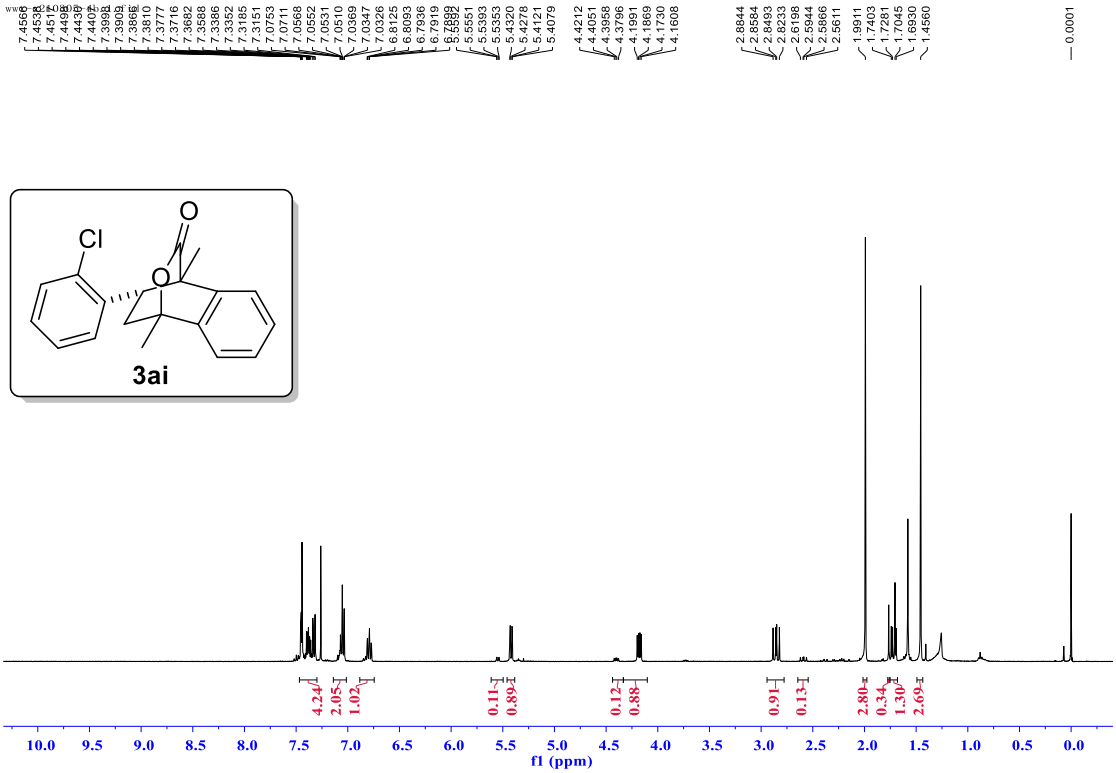
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ah



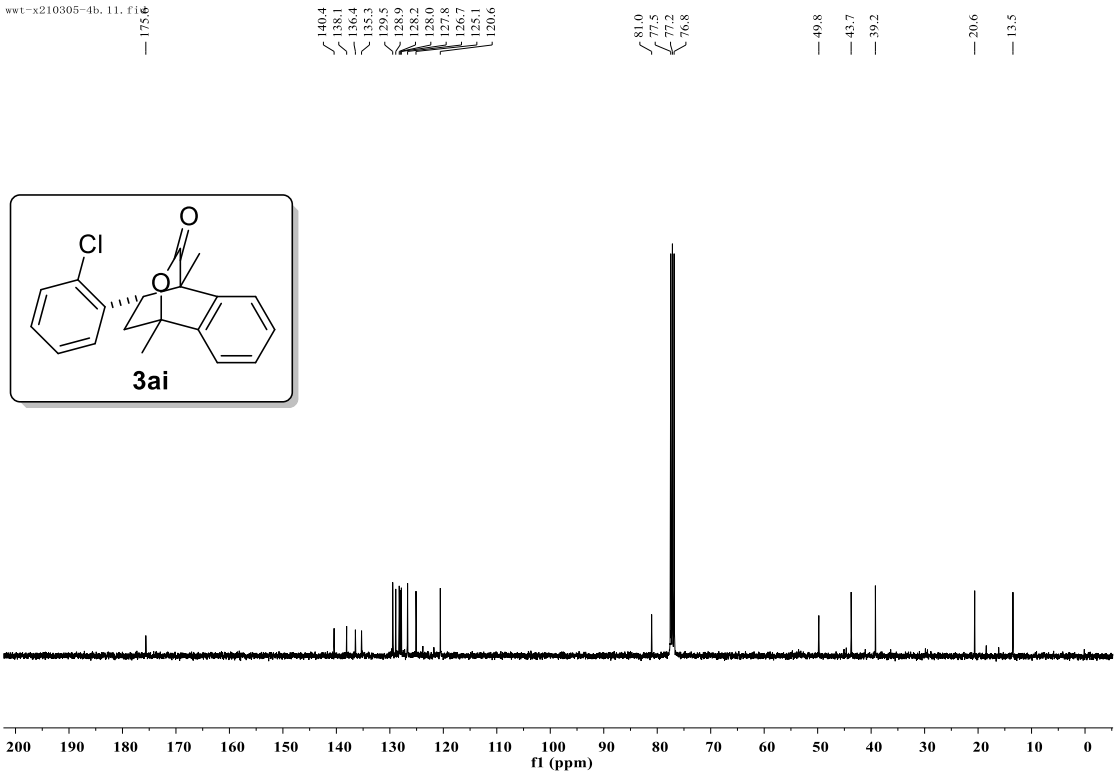
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ah



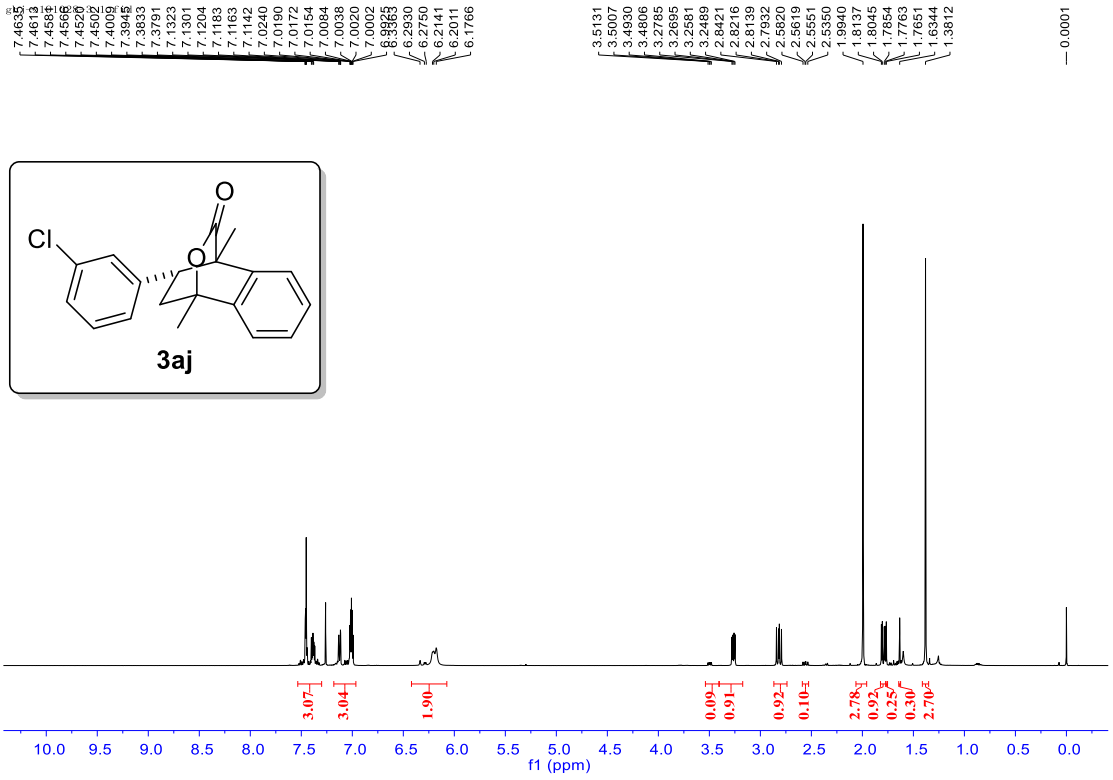
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ai



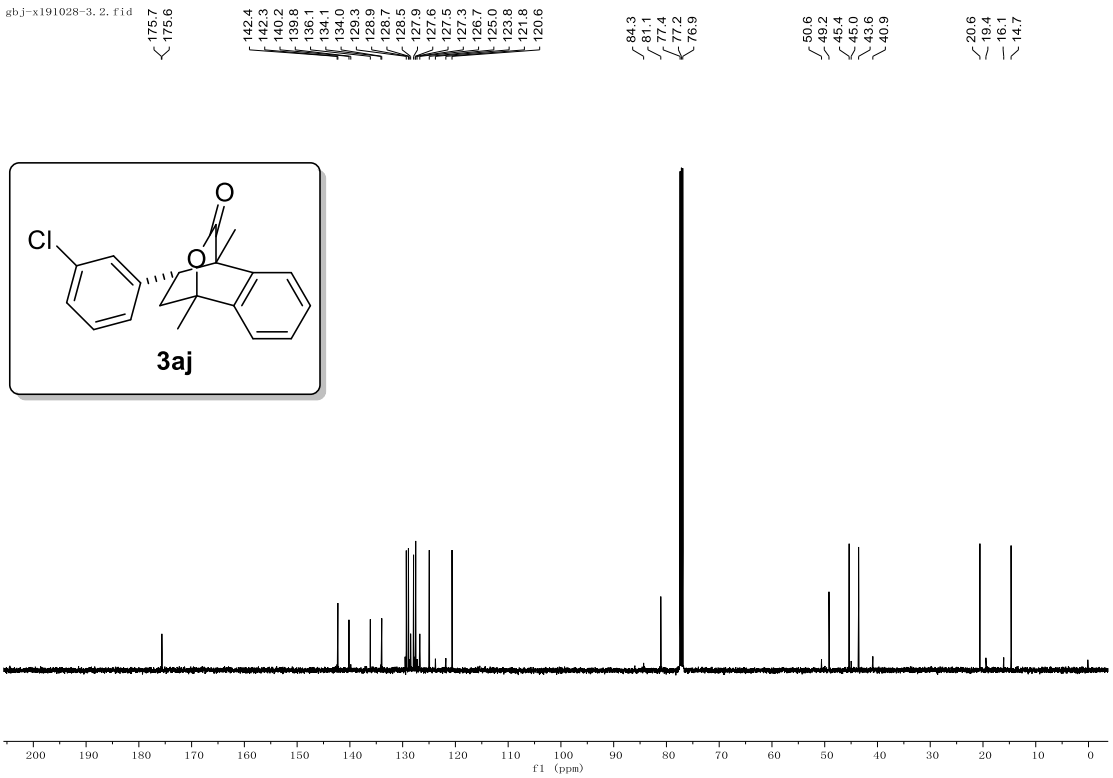
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ai



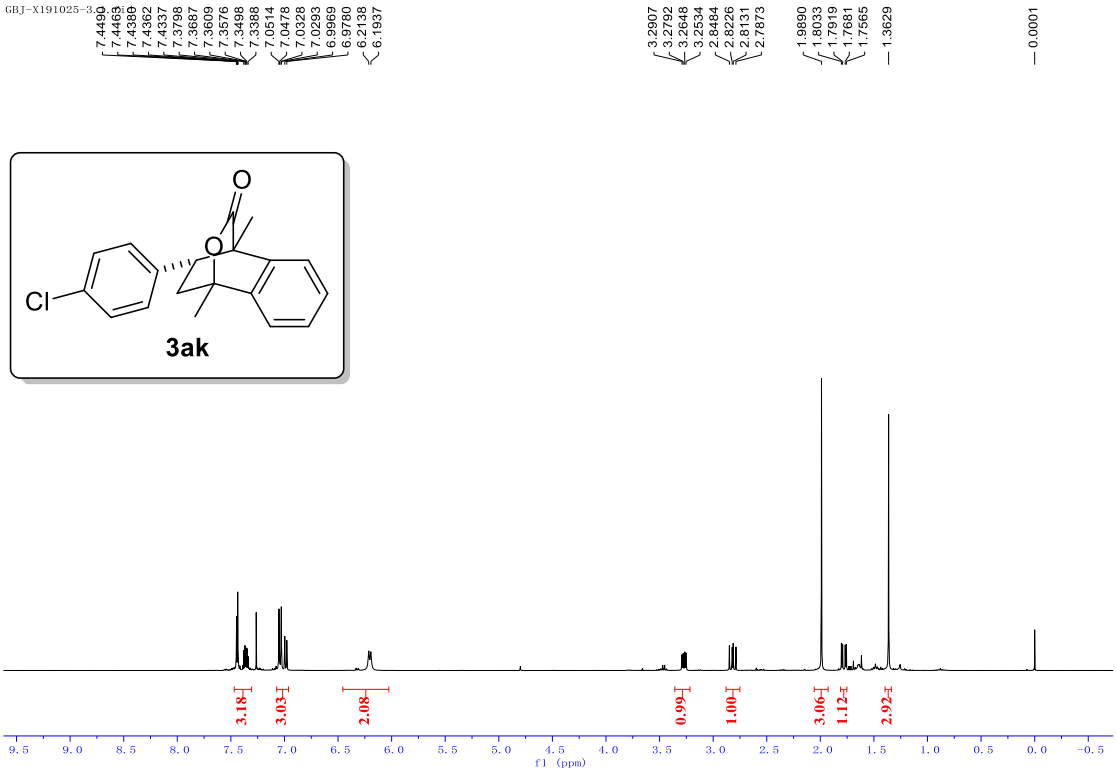
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 3aj



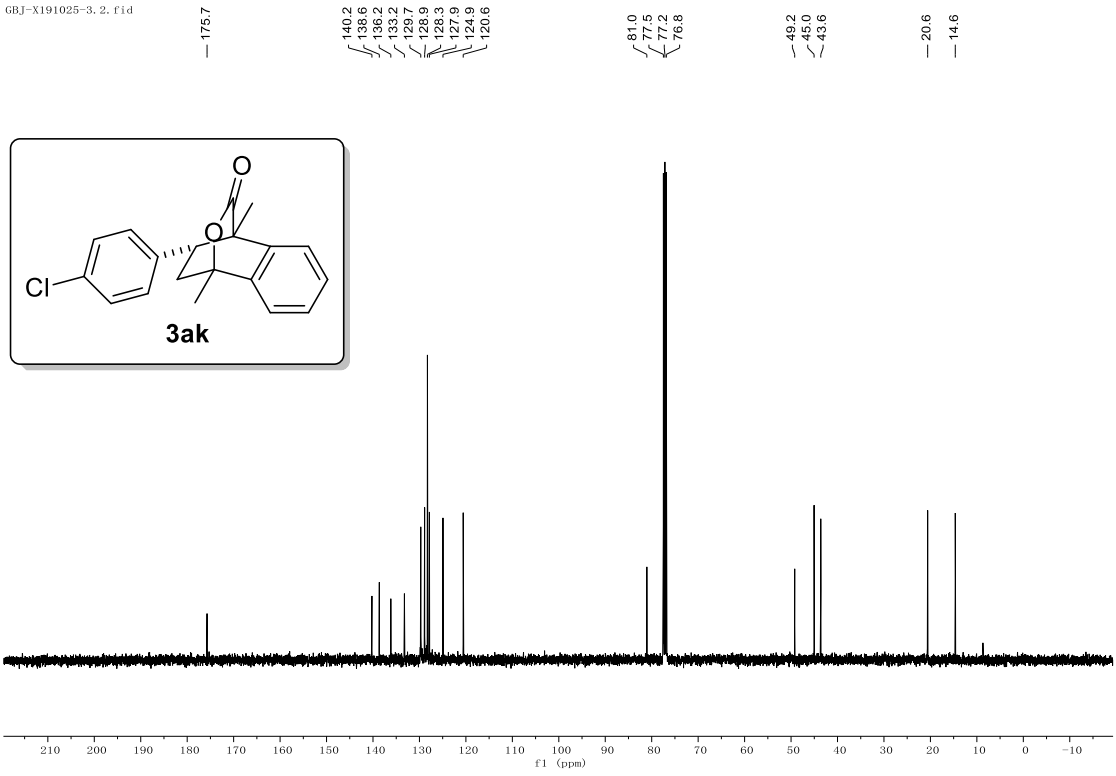
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 3aj



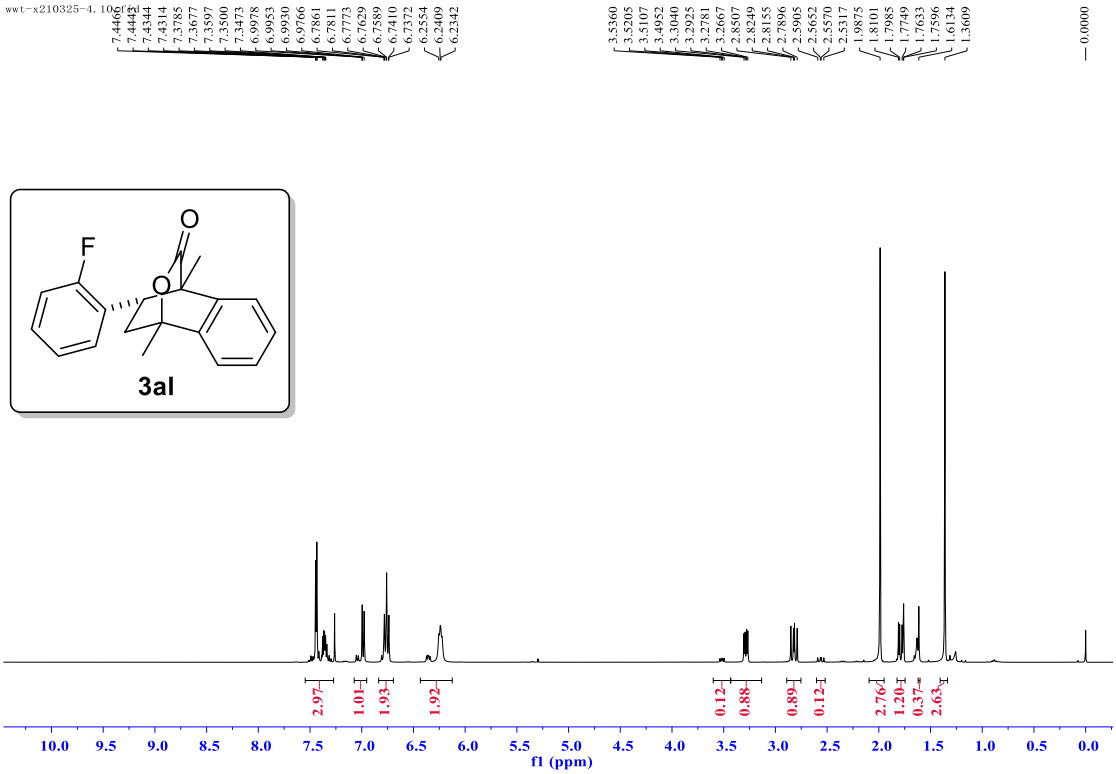
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ak



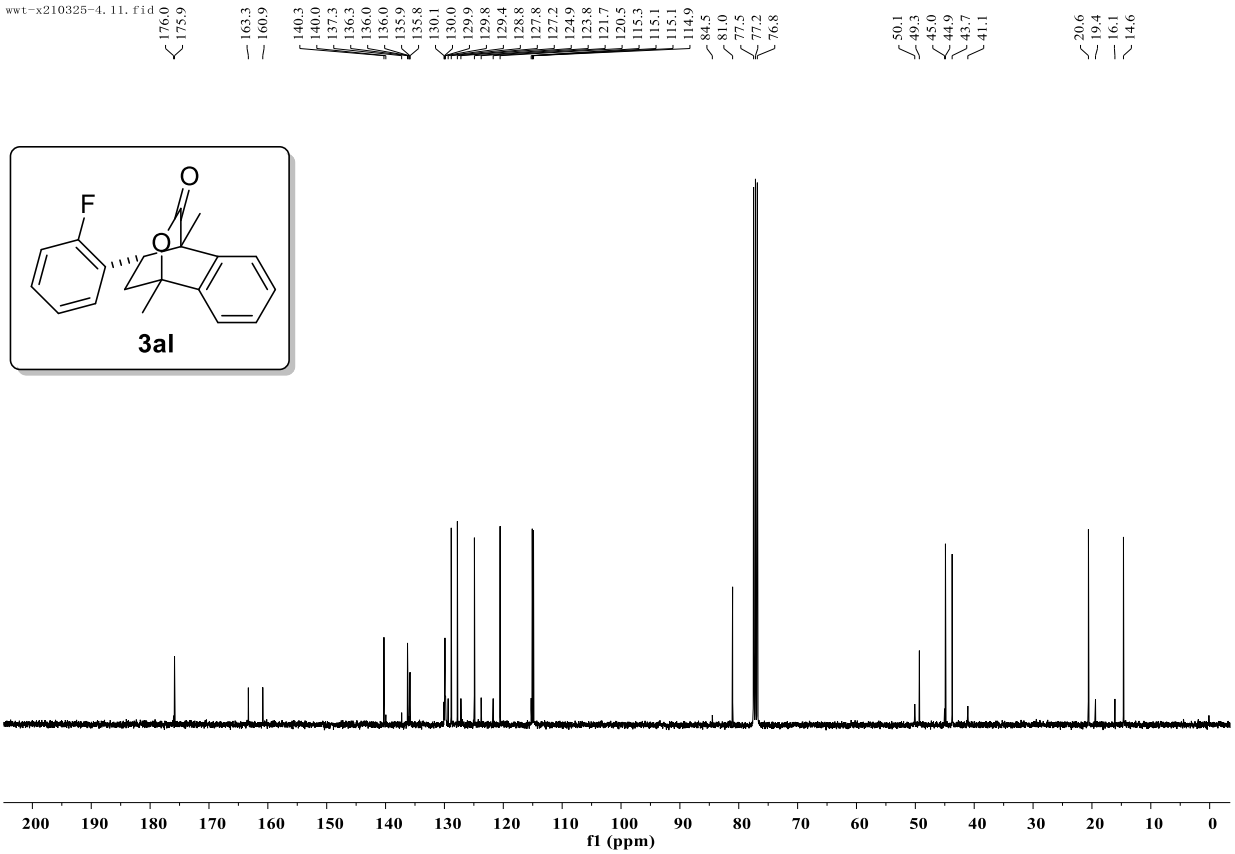
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ak



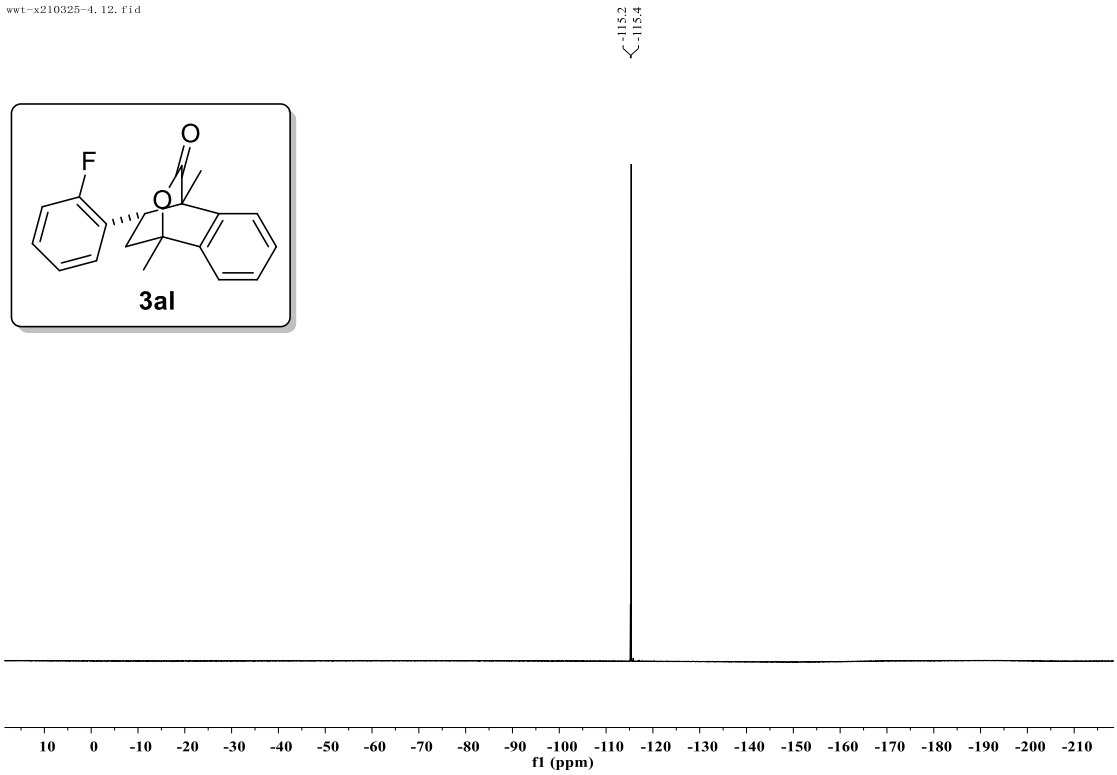
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 3al



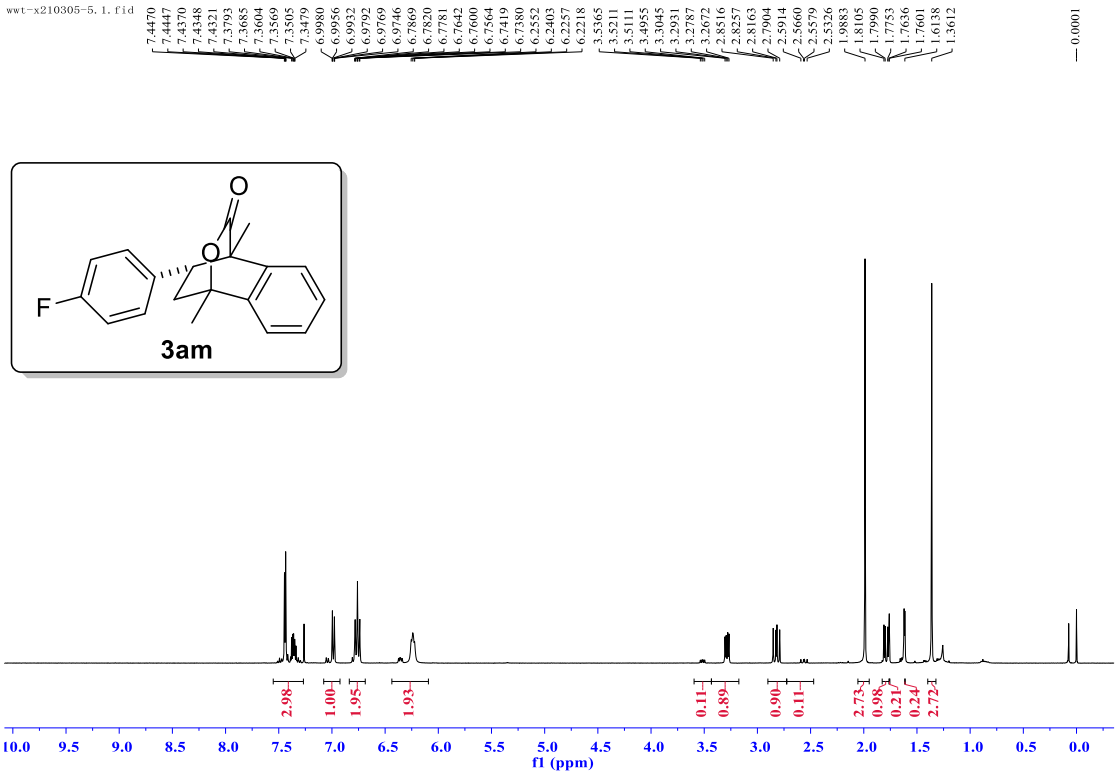
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 3al



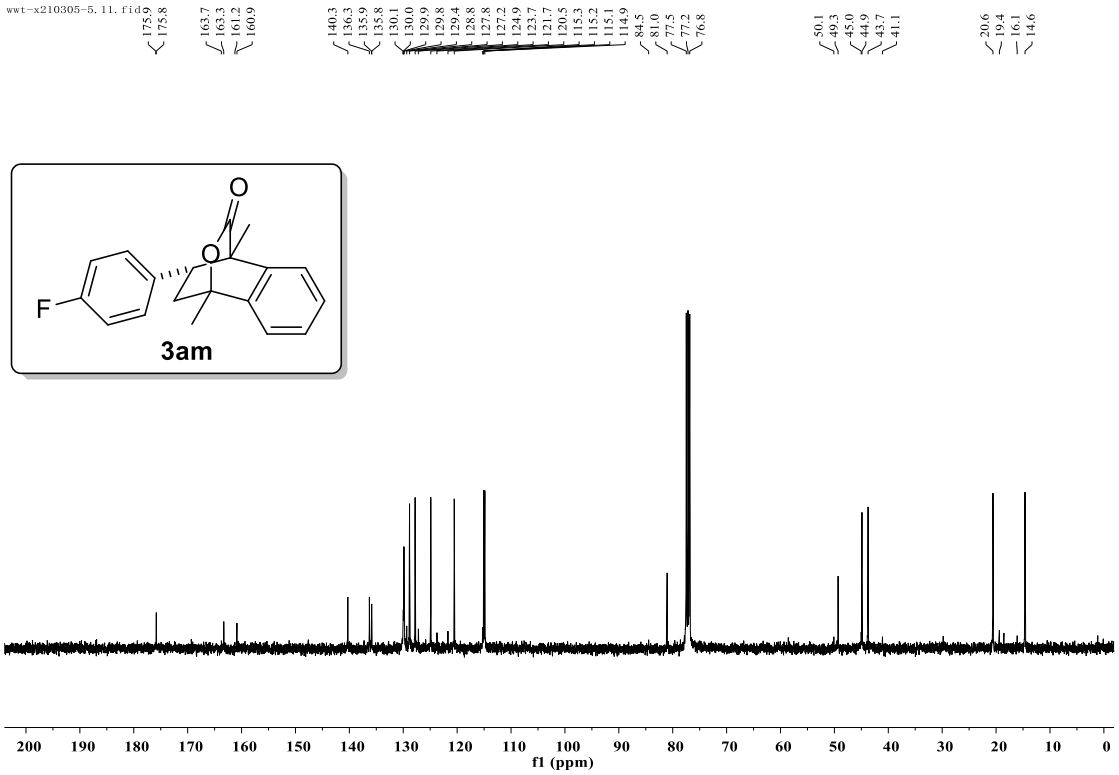
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3al



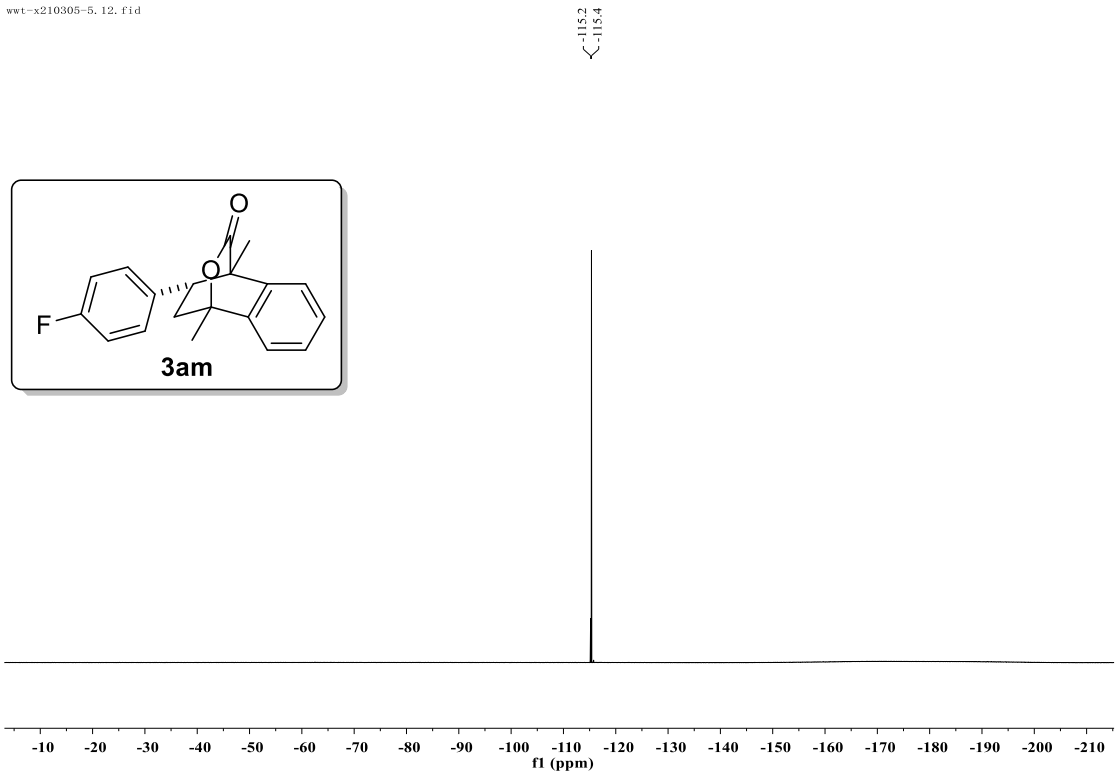
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3am



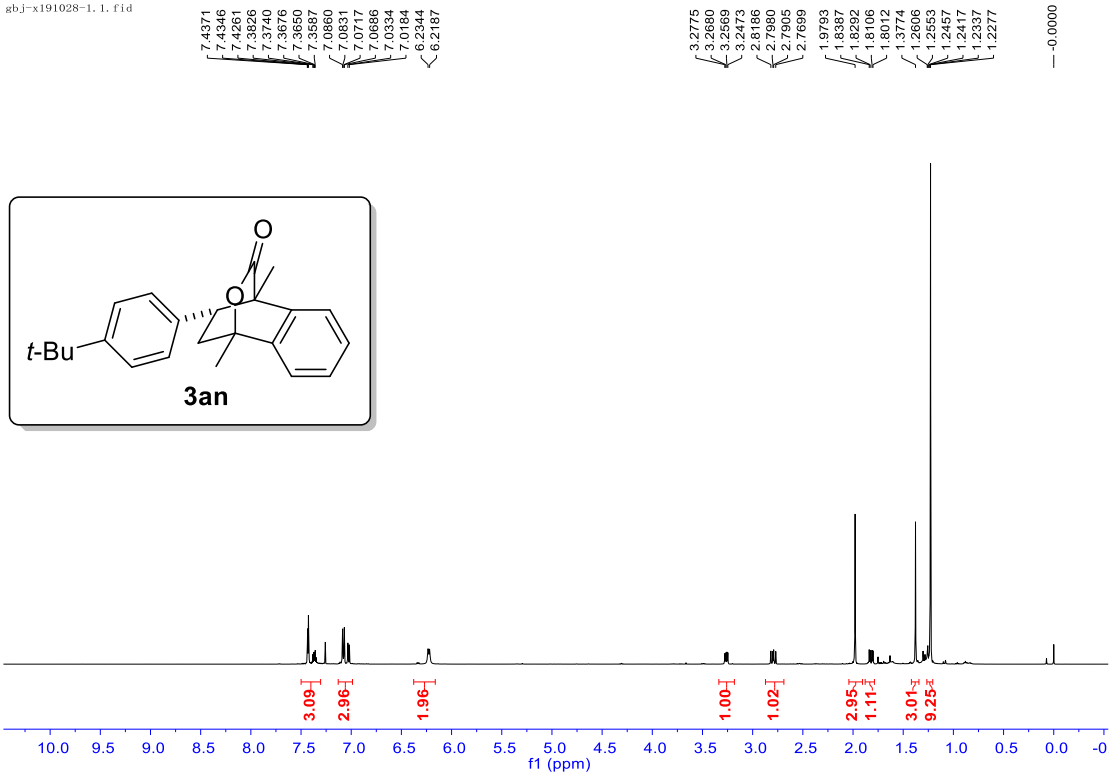
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3am



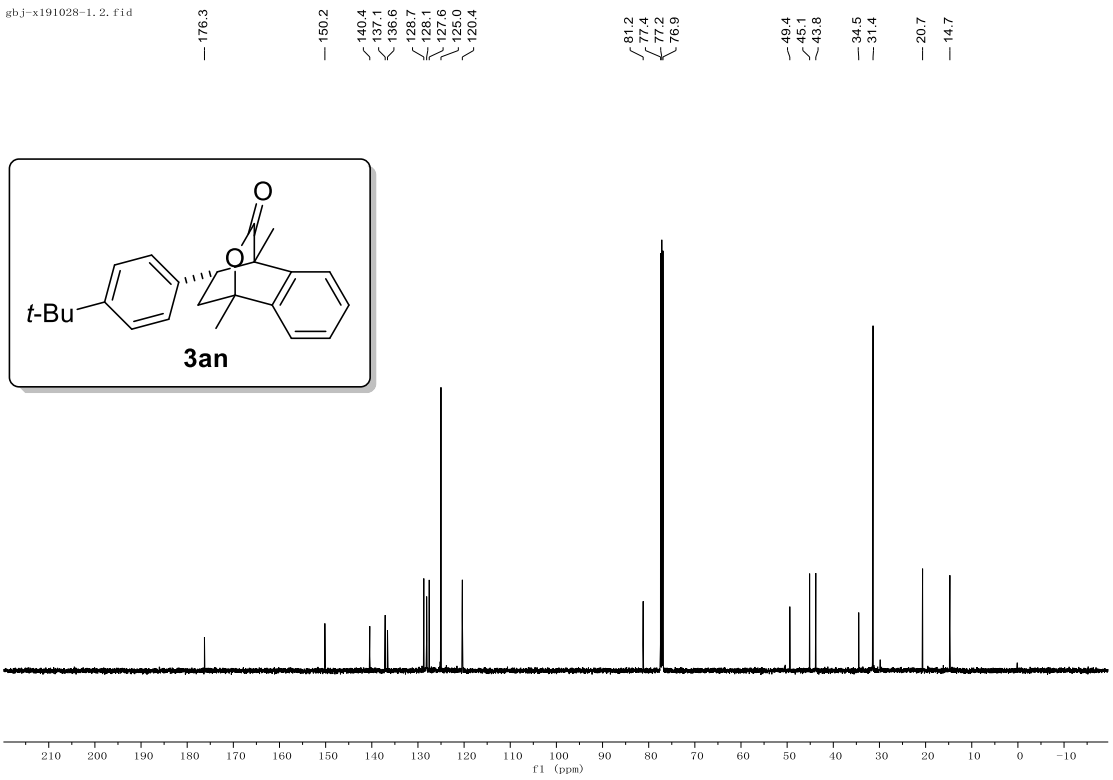
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3am



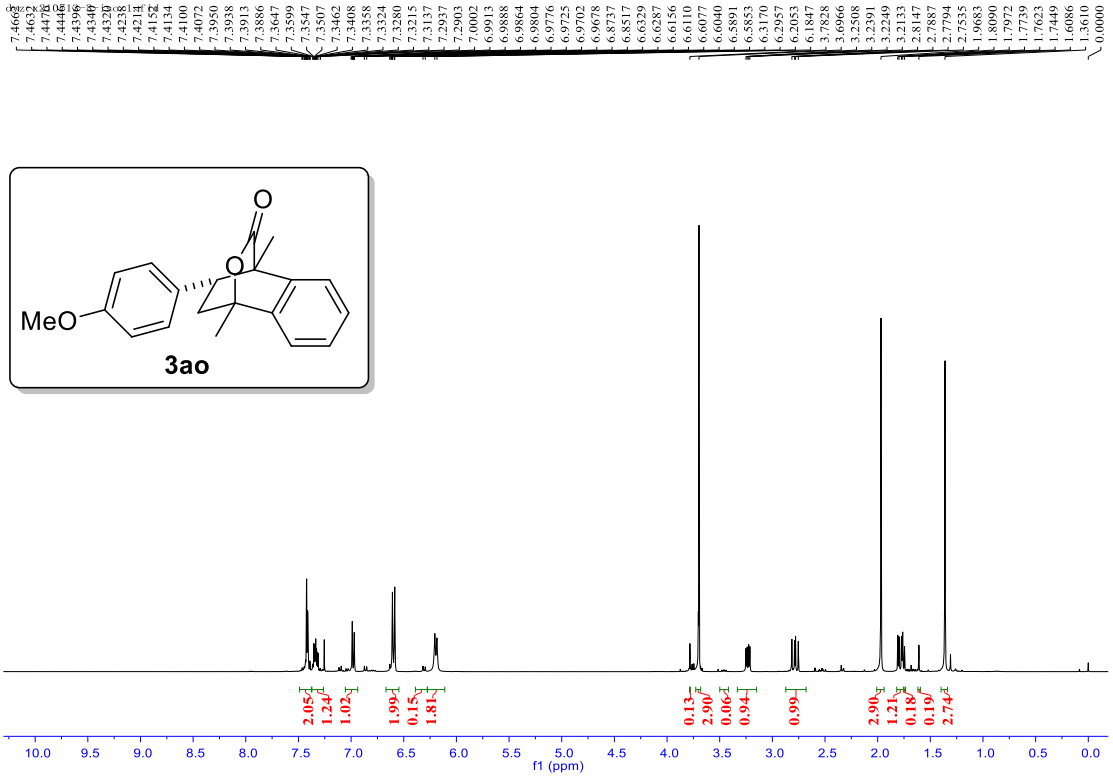
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 3an



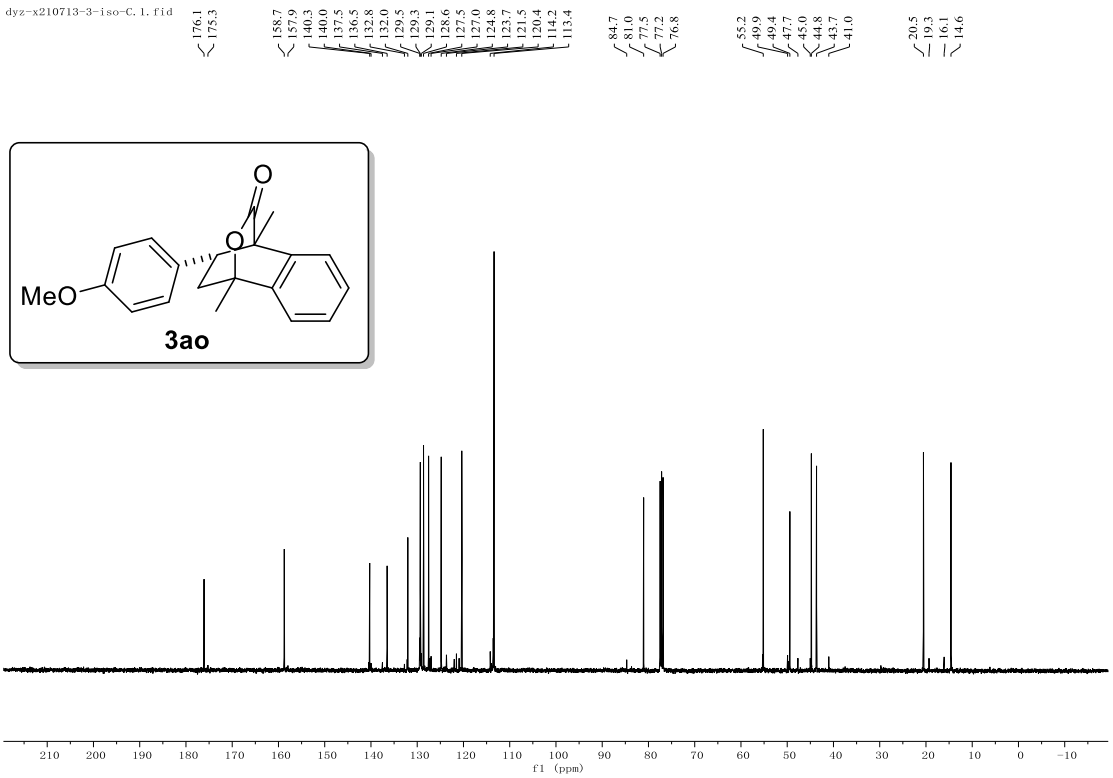
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 3an



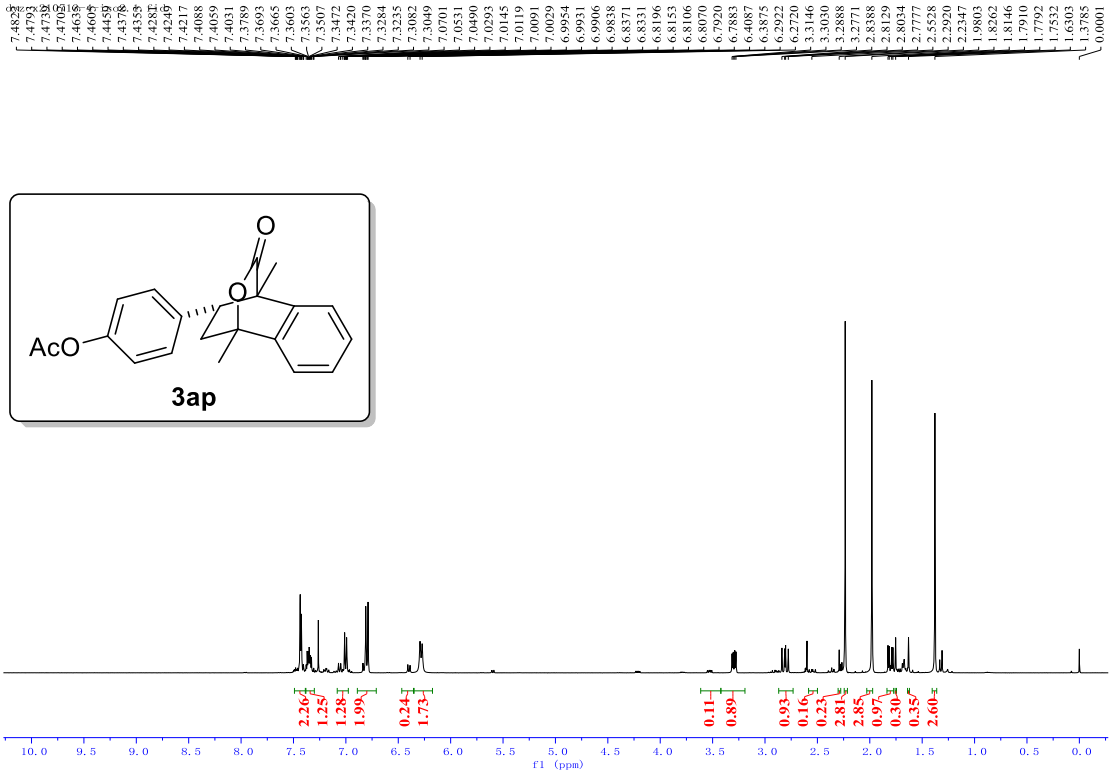
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ao



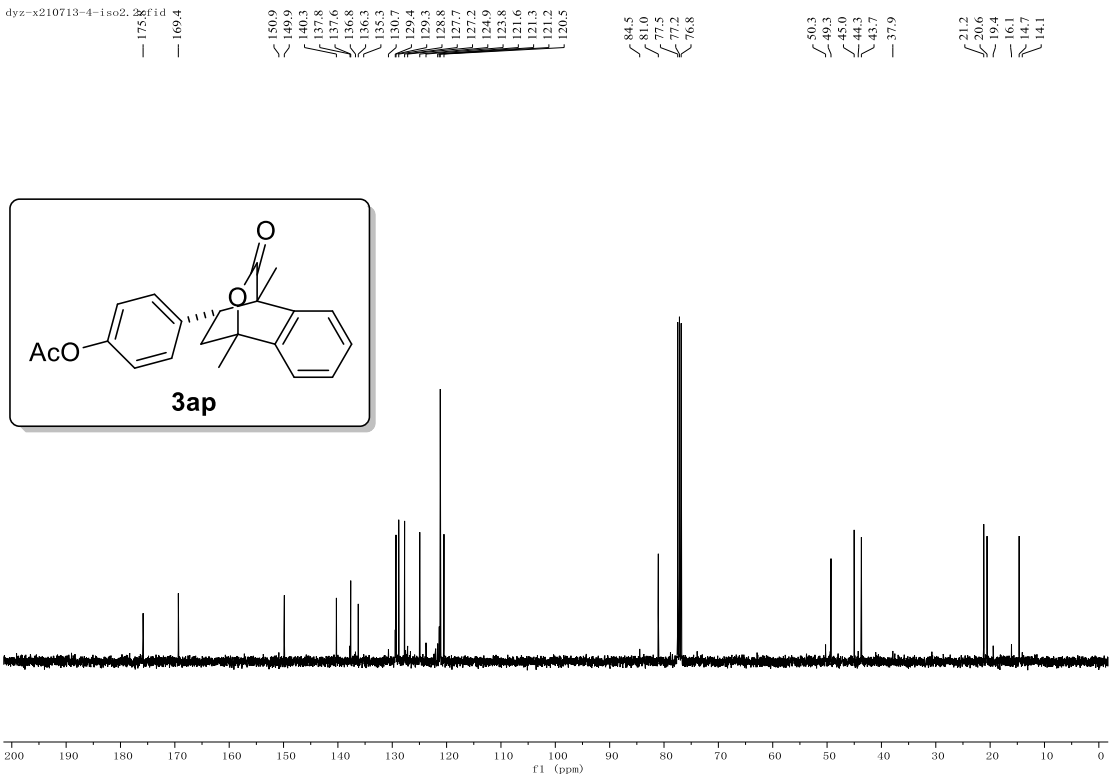
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ao



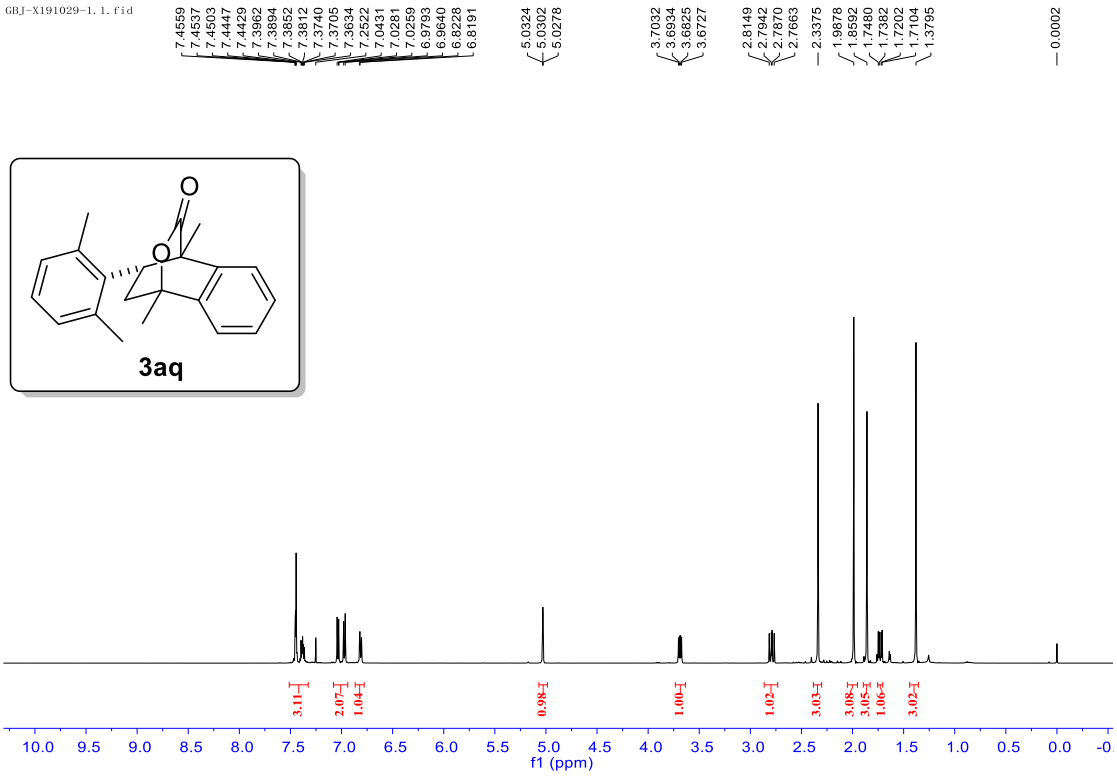
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ap



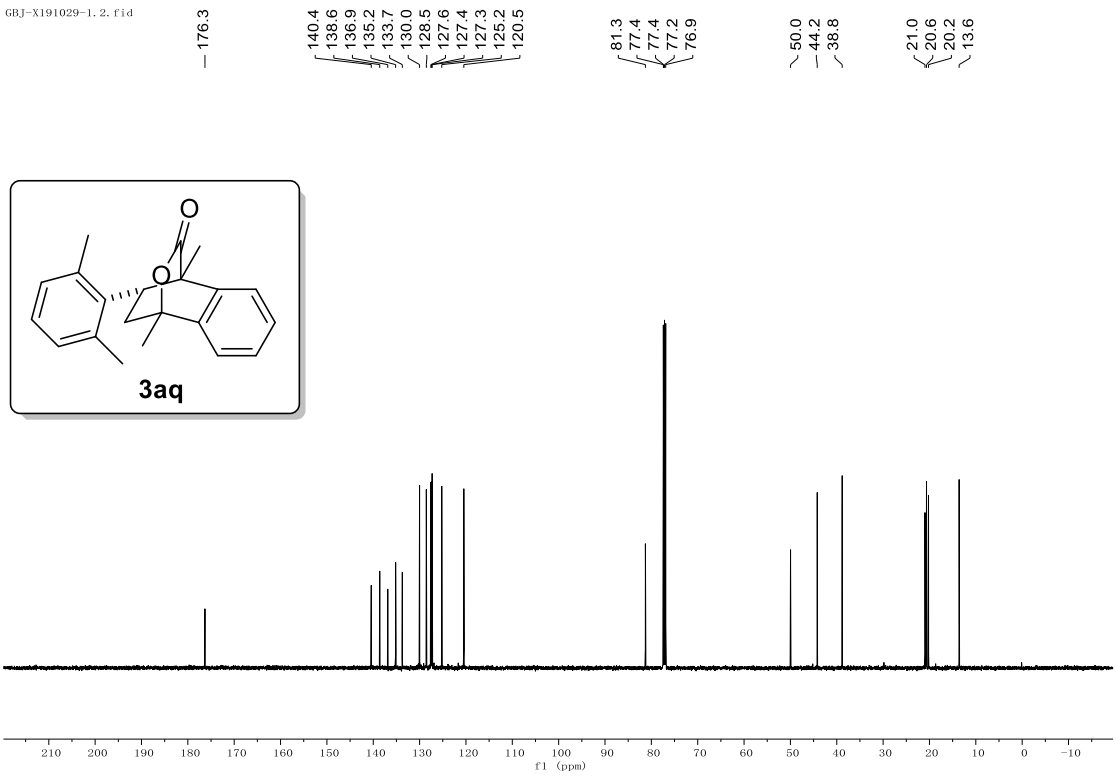
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ap



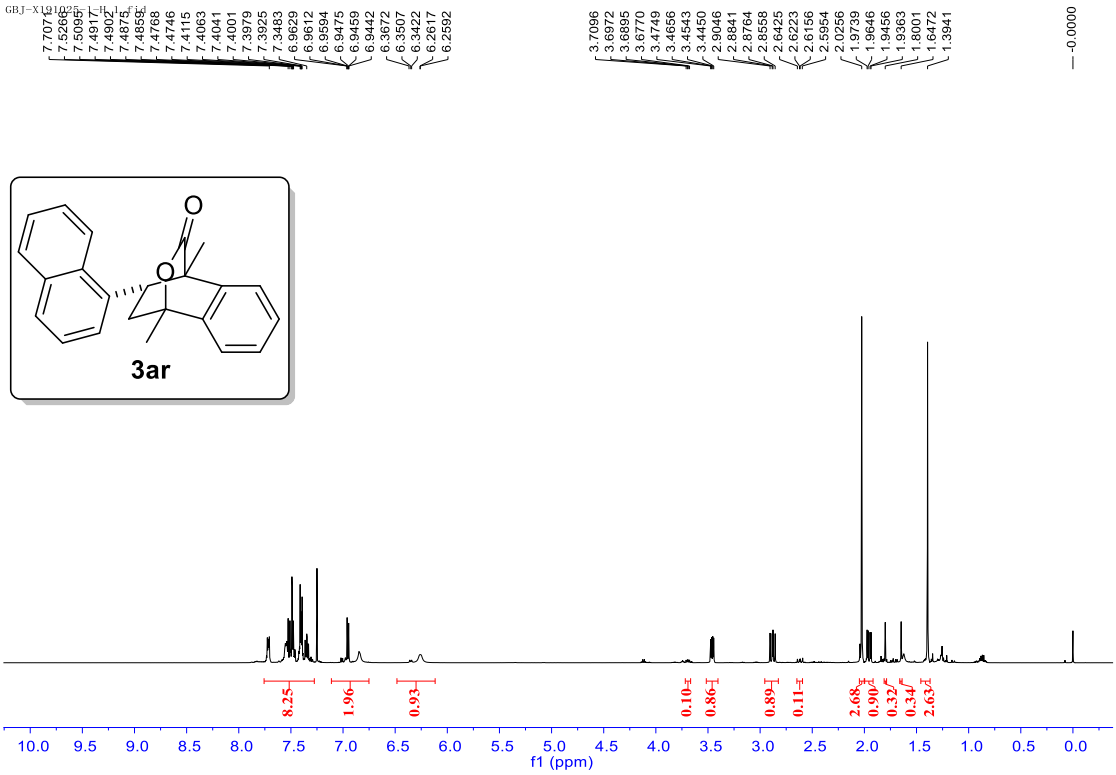
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 3aq



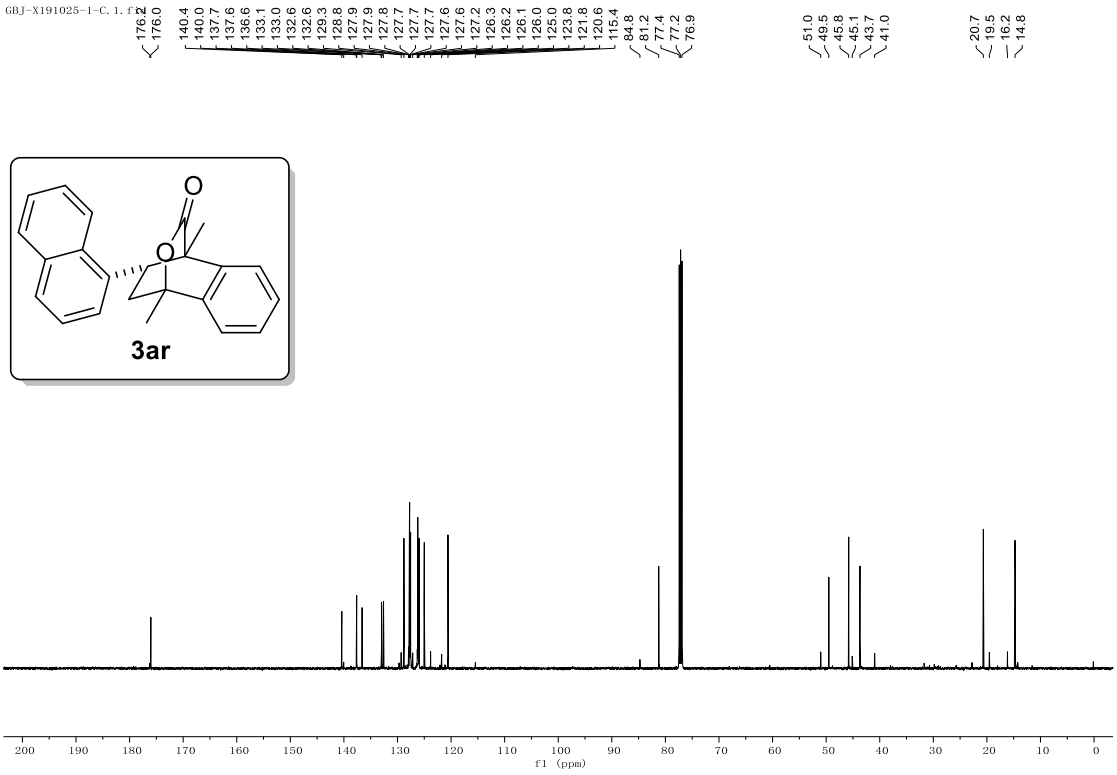
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 3aq



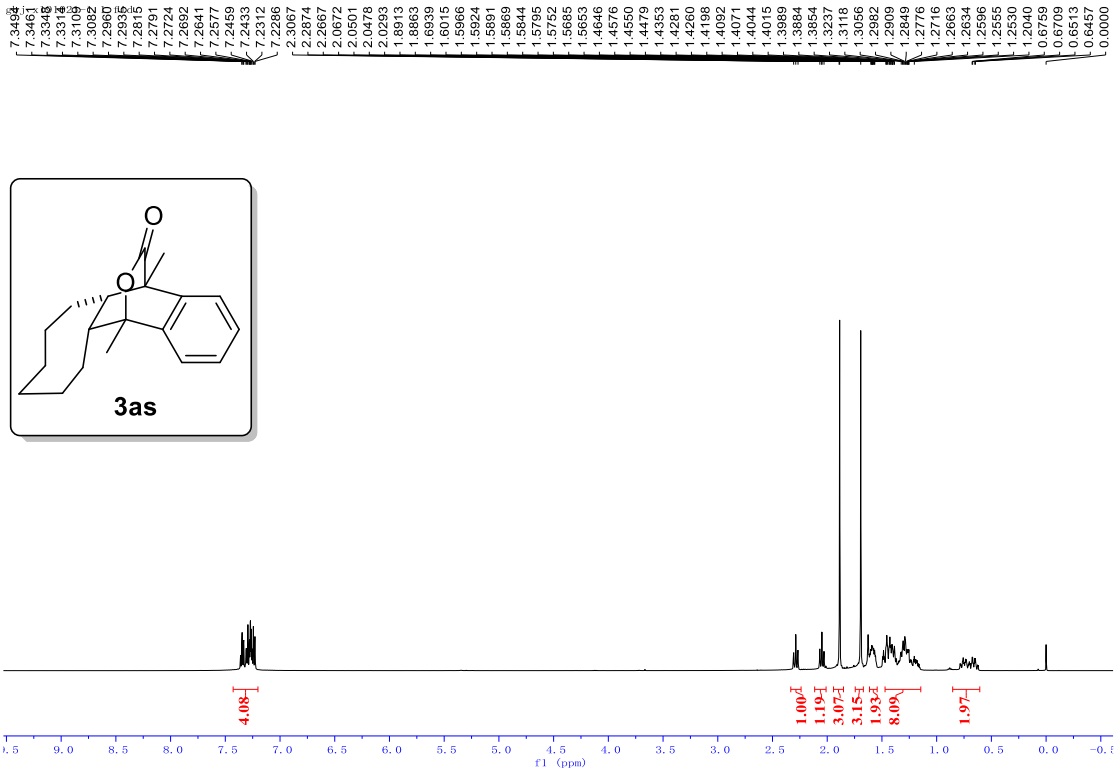
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 3ar



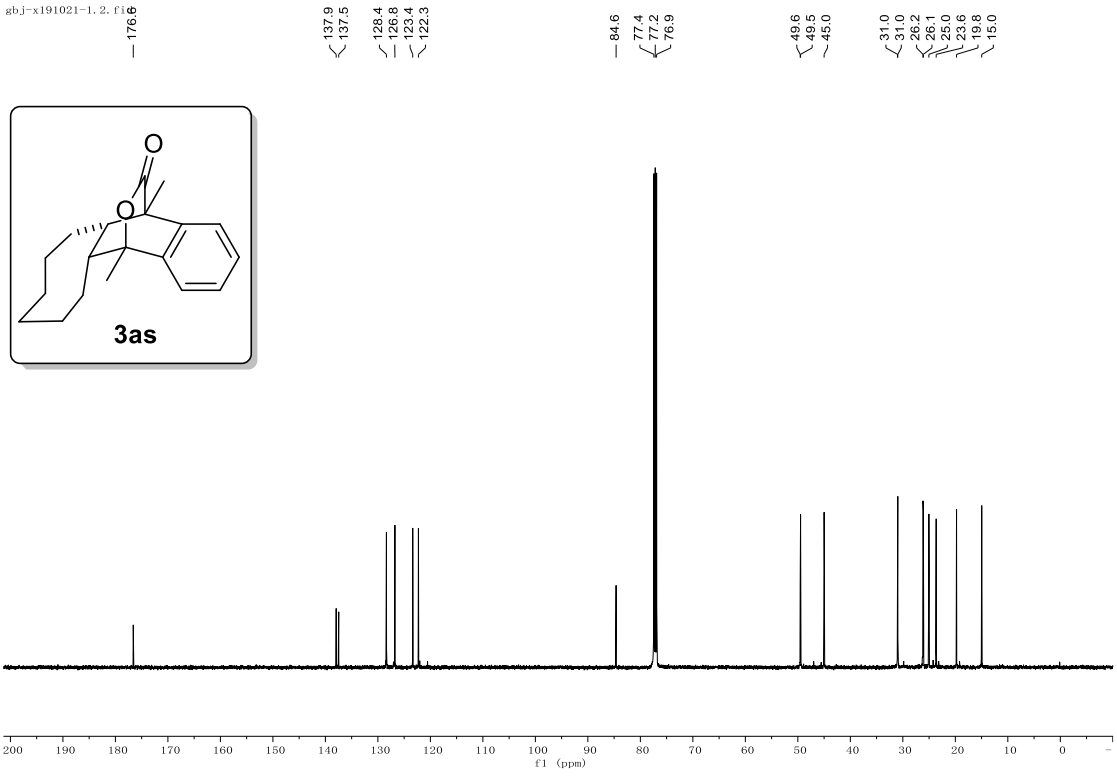
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 3ar



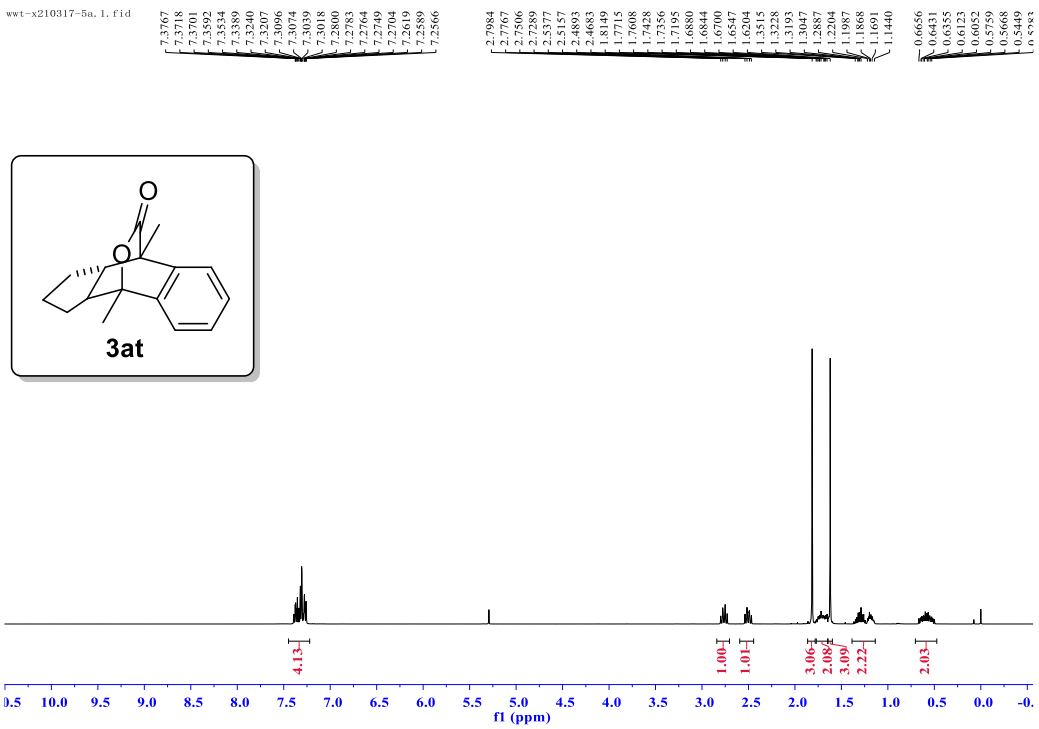
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 3as



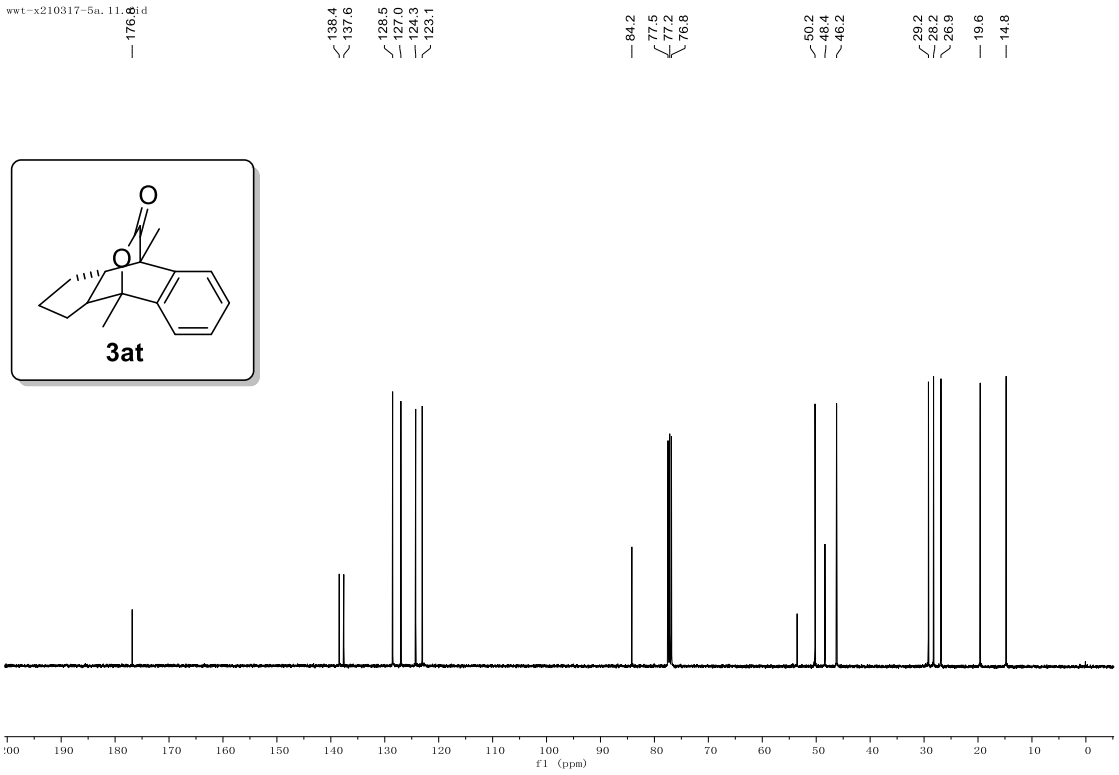
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 3as



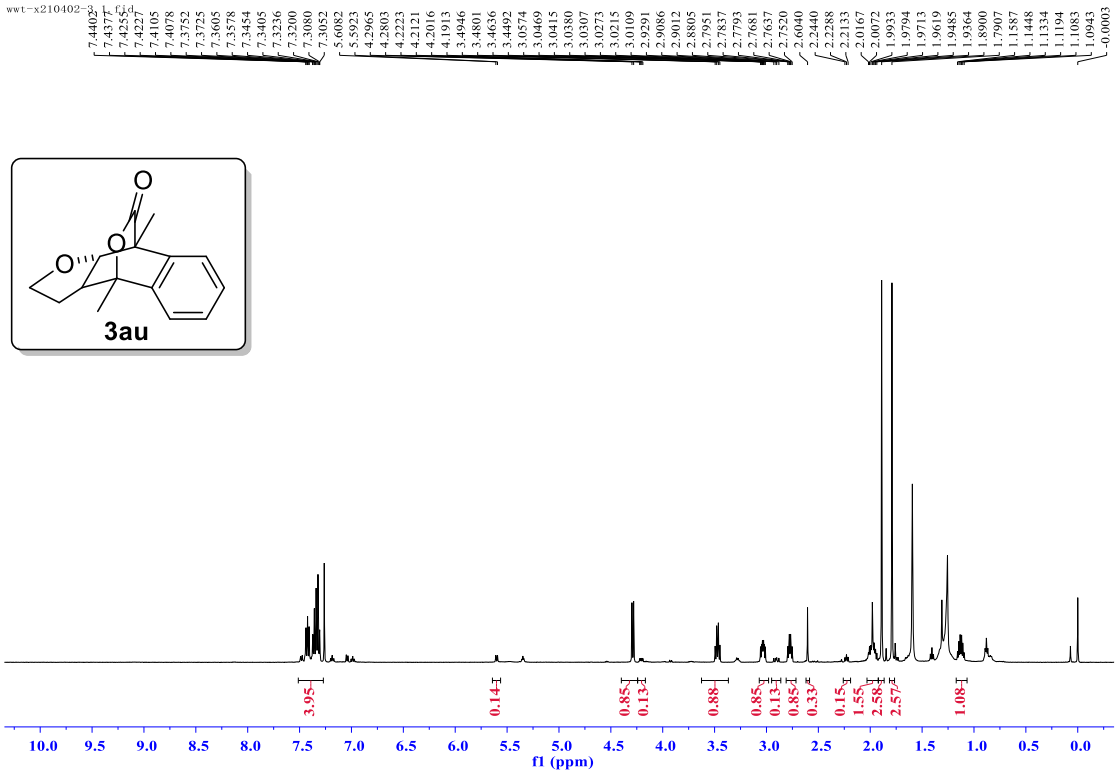
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3at



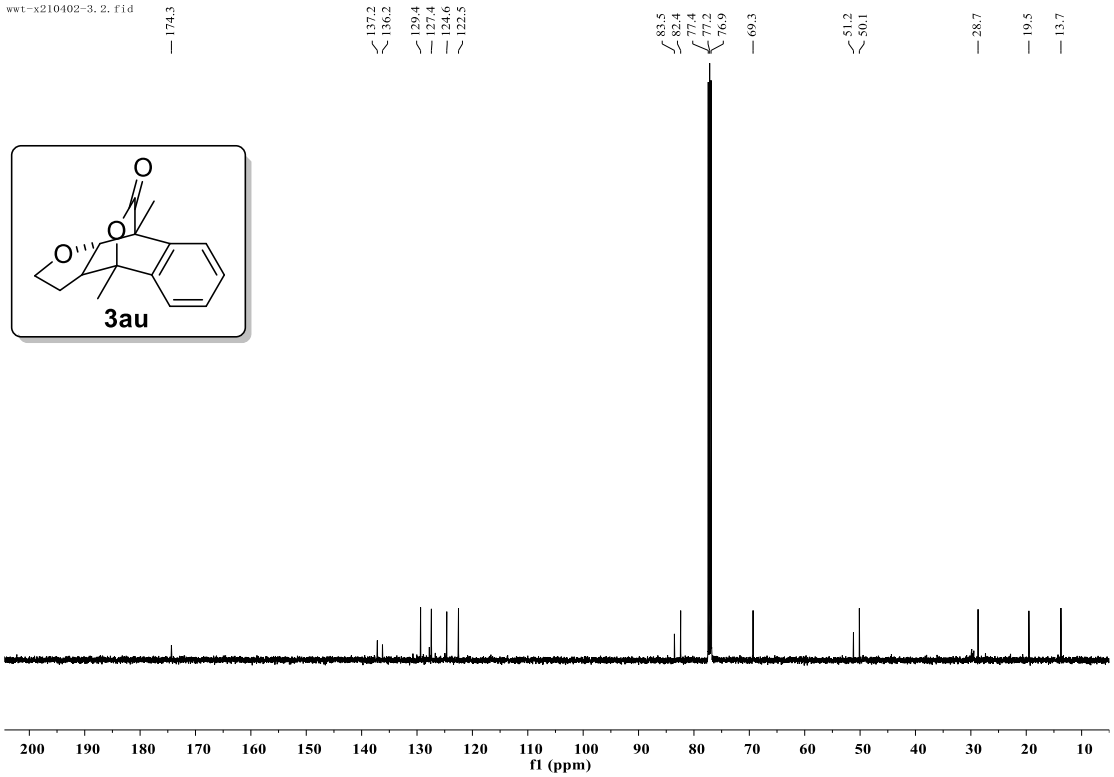
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3at



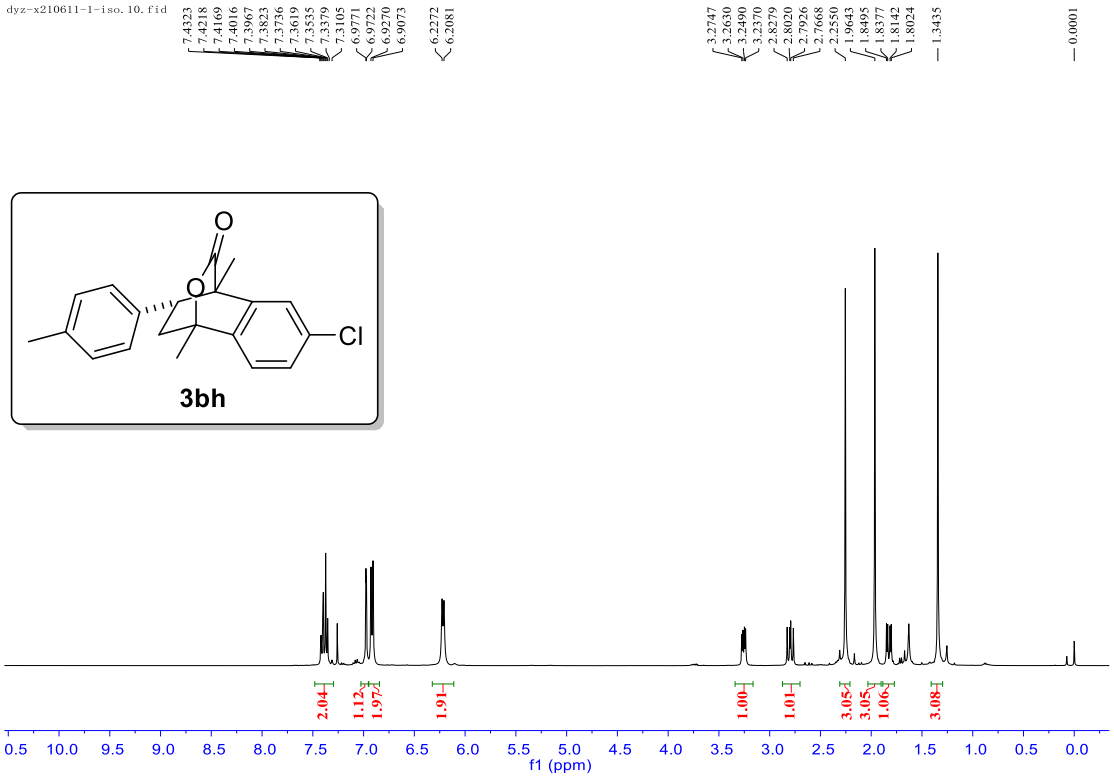
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 3au



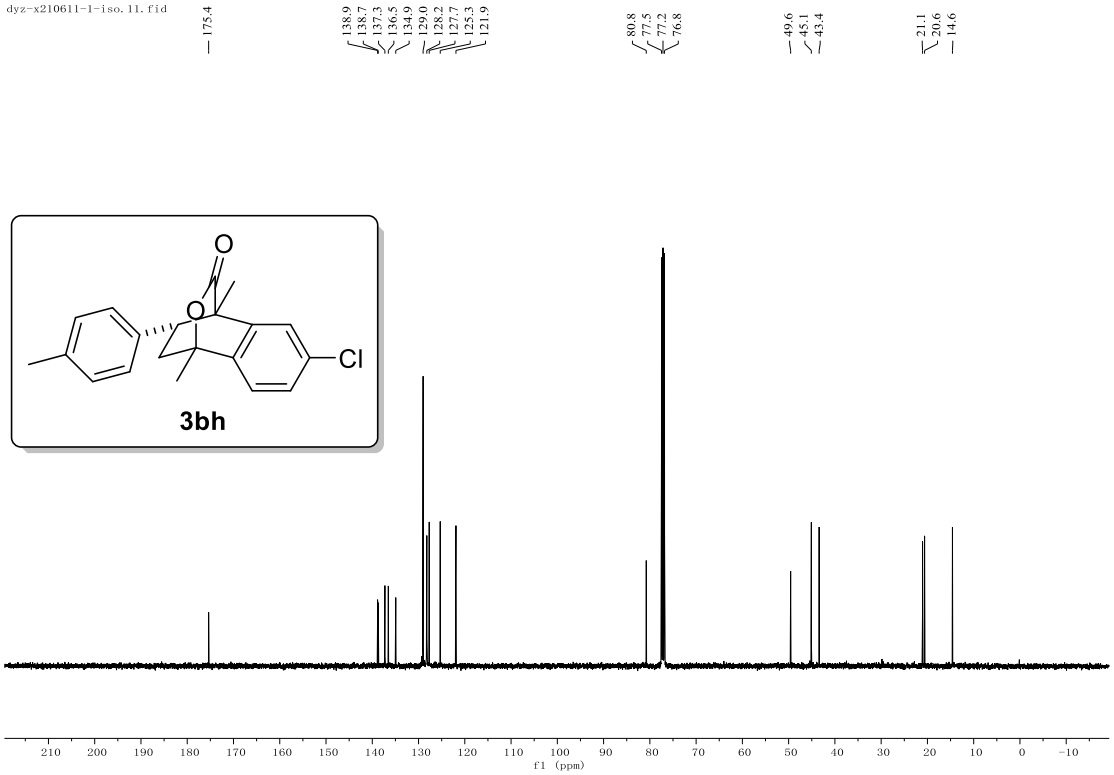
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 3au



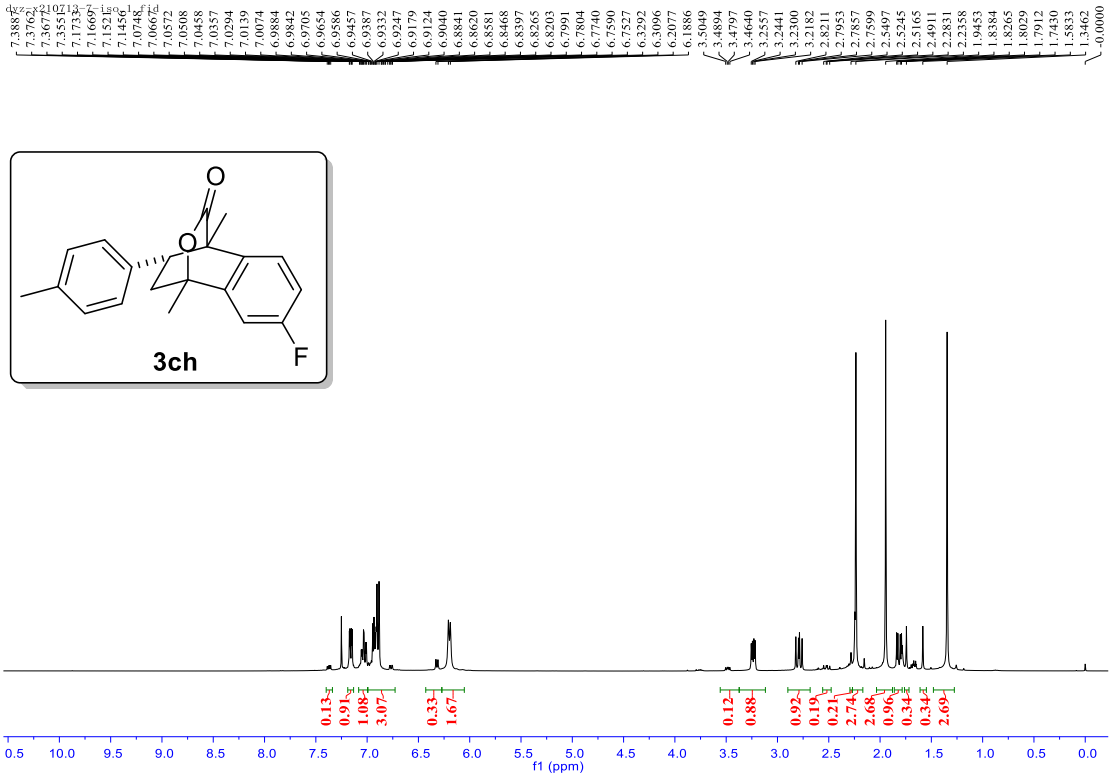
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3bh



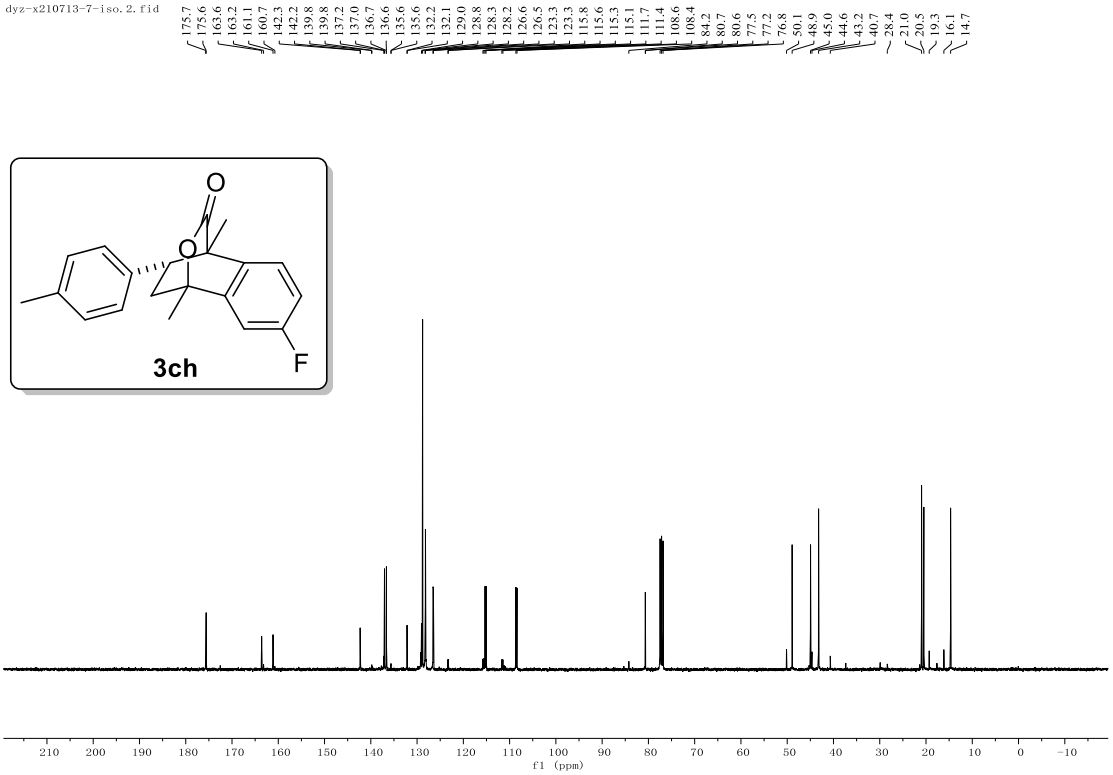
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3bh



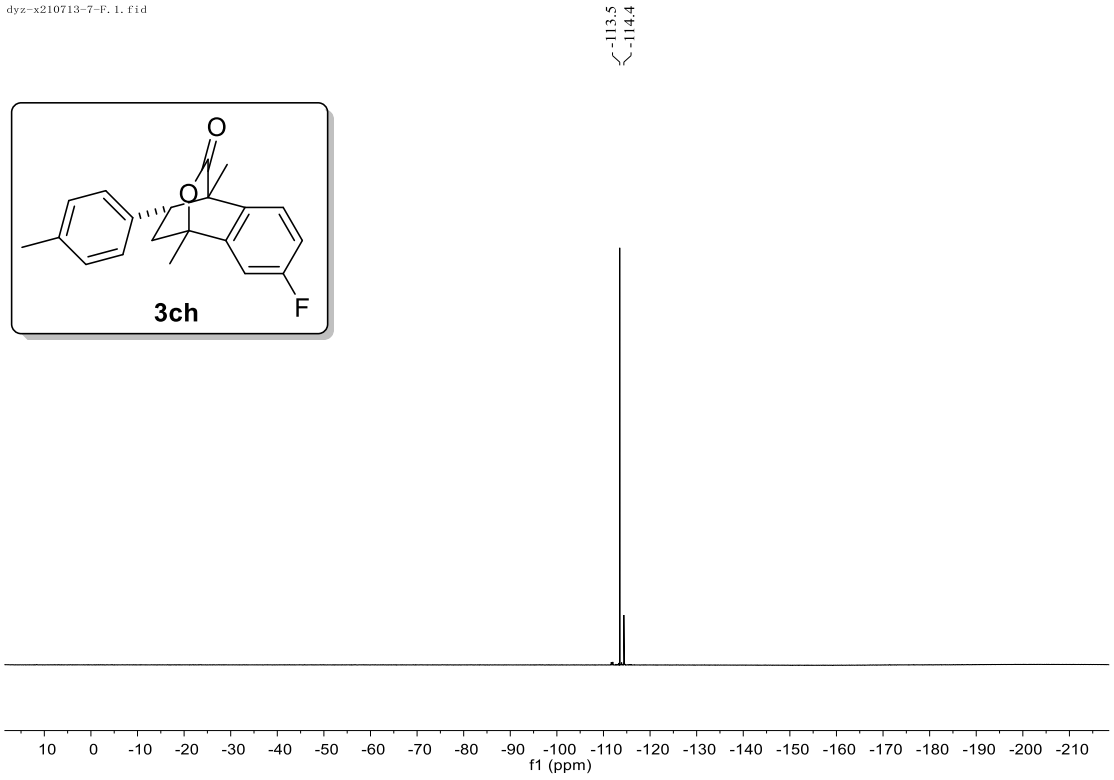
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3ch



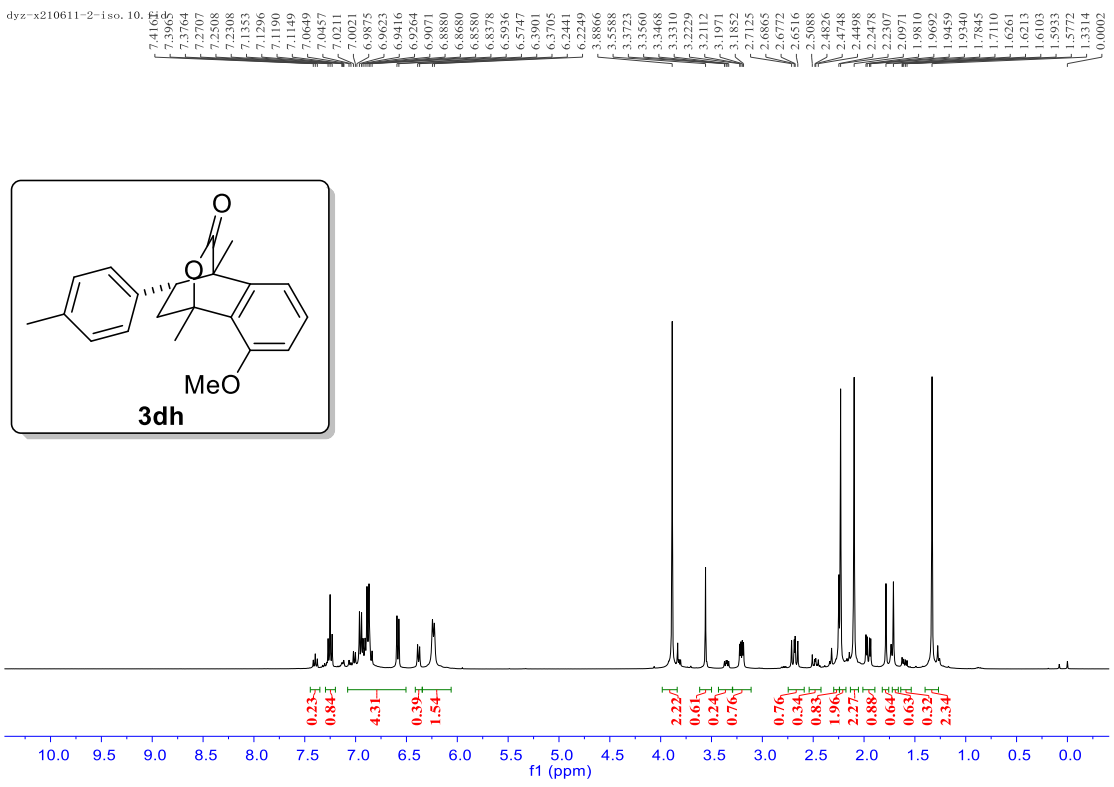
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3ch



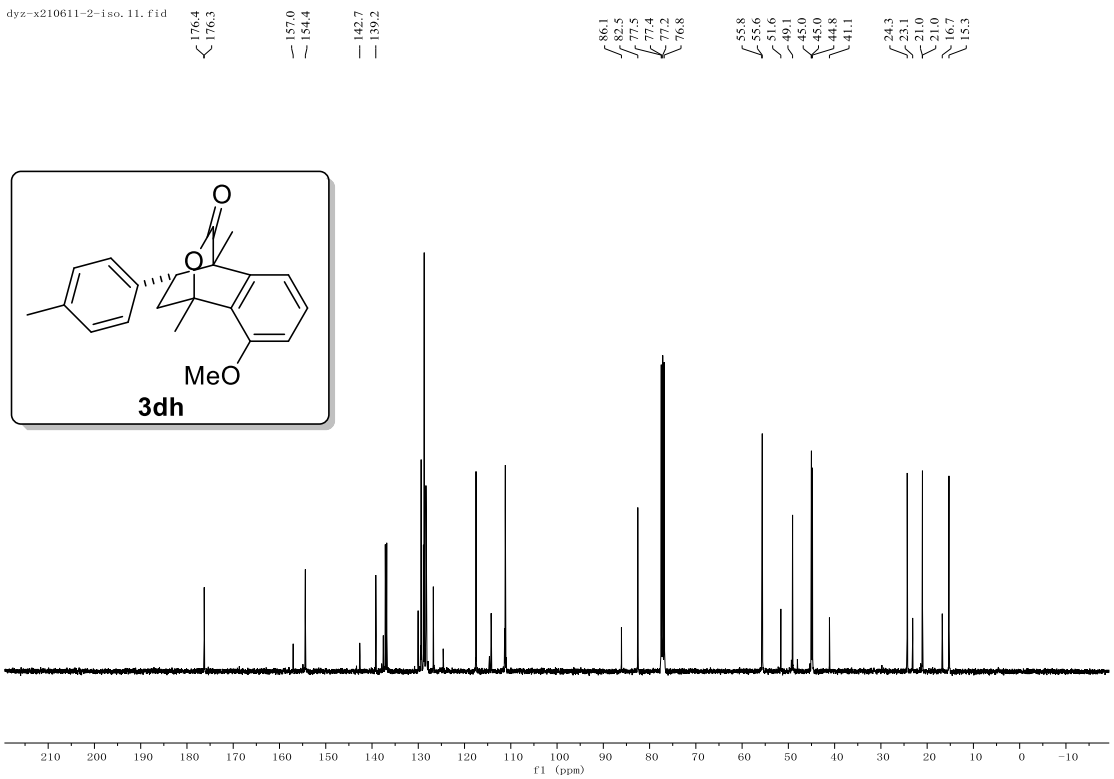
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3ch



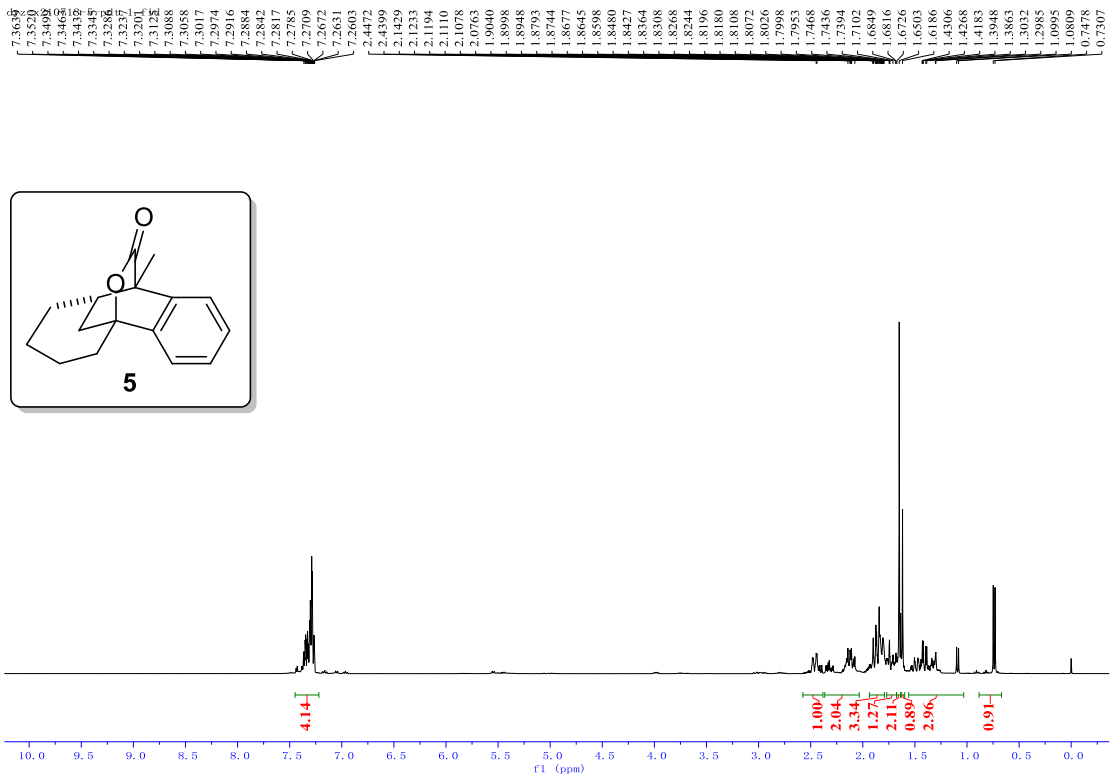
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3dh



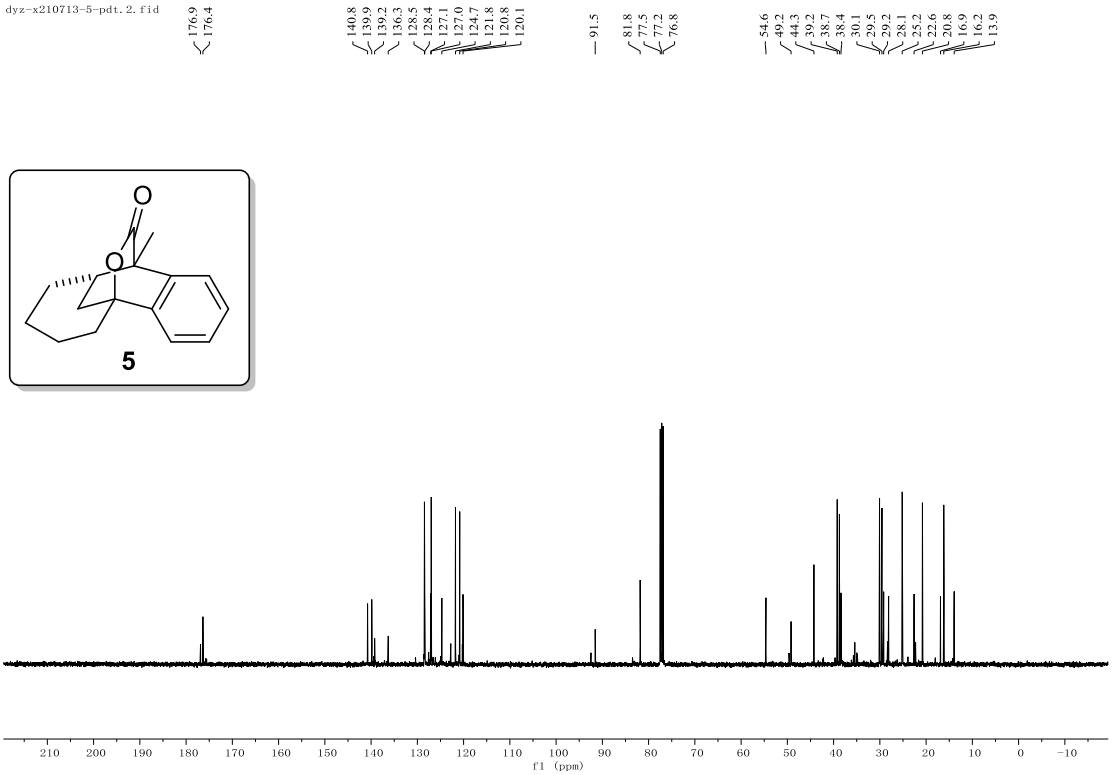
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3dh



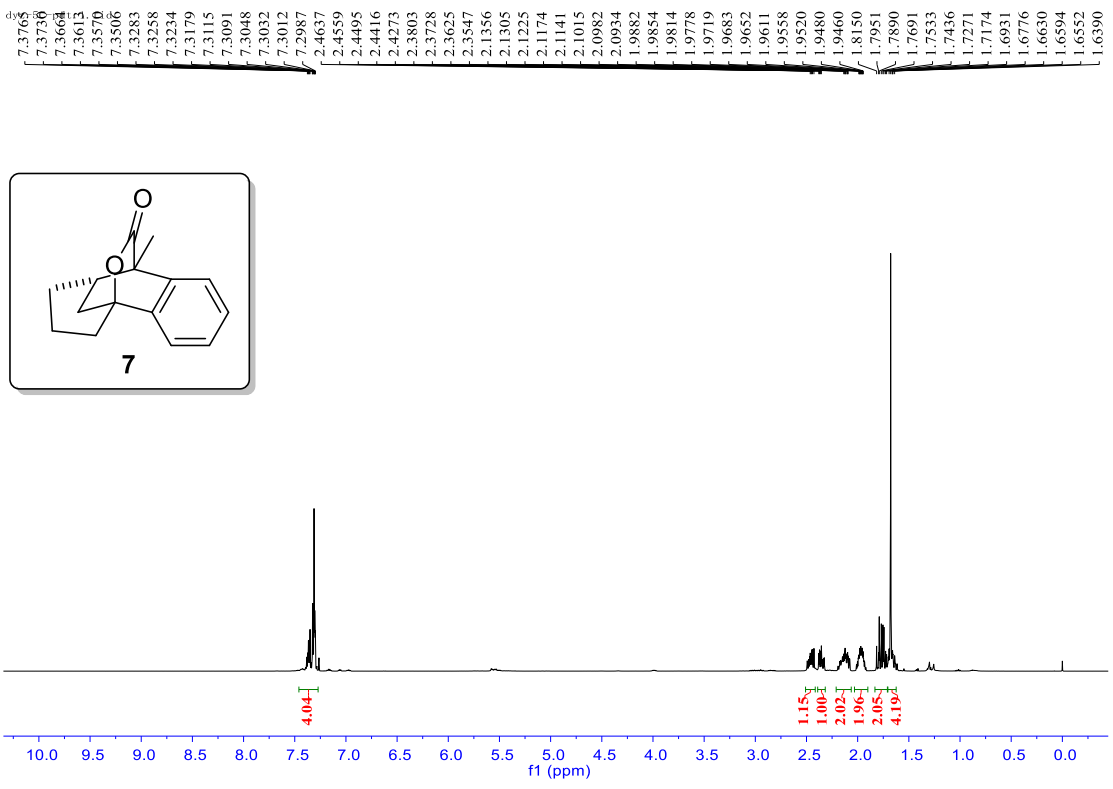
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5



^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5



^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 7



^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 7