# **Supporting Information**

# Pt-Catalyzed Tandem 1,2-Acyloxy Migration/Intramolecular [3+2] Cycloaddition of Enynyl Esters

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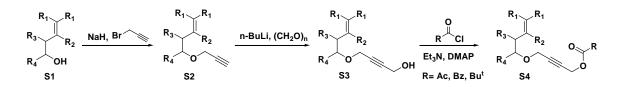
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Та	ble of Contents	
1.	General Information	S-2
2.	Preparation of starting materials 1a-m, and 1s	S-2
3.	Preparation of starting materials <b>1n-r</b>	S-3
4.	Preparation of starting materials 1t, and 1u	S-4
5.	<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra data of compounds <b>1a-u</b>	S-4
6.	General Procedure for the preparation of the [3+2] cycloaddition products	S-9
7.	Characterization data of the [3+2] cycloaddition products	S-9
8.	Spectra	S-15

#### **General Information**

All chemicals were used as received. Solvent THF and toluene was refluxed with Na , CH<sub>2</sub>Cl<sub>2</sub> was refluxed with CaH<sub>2</sub> and freshly distilled prior to use. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petroleum was 60-90 °C. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AM-400 MHz instrument, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a Nicolet FT-170SX spectrometer. HRMS data were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer.

#### General ProcedureA: Synthesis of 1a-m, and 1s.

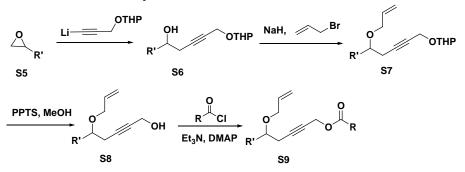


To a suspension 60% NaH (7.5 mmol, freshly pre-washed with dry hexane) in THF (10 mL) was added the alcohol **S1** (5 mmol) under Ar at 0 °C. The white suspension was slowly warmed to room temperature and stirred for 1 hour. The reaction mixture was then recooled to 0°C and 3-bromoprop-1-yne (10 mmol) was added dropwise, followed by tetrabutylammonium iodide (0.5 mmol). After the reaction mixture was stirred at room temperature for 12 hours. The mixture was quenched by addition of saturated aqueous ammonium chloride and extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with brine, dried over sodium sulfate and concentrated. The residue was purified by silica gel flash chromatography (PE:EtOAc = 50:1) to give propargyl ether **S2**.

To a stirred solution of the propargyl ether **S2** (2 mmol) in THF (40 ml) was added n-BuLi (3 mmol) under Ar at -78 °C. An hour later, paraformaldehyde (10 mmol)<sup>1</sup> was added in one portion and the mixture was slowly warmed to room temperature and stirred overnight. After addition of saturated aqueous ammonium chloride (1 ml), the solvent was removed under reduced pressure and the residue was dissolved in diethyl ether, washed with brine, dried over sodium sulfate and concentrated. The residue was purified by column chromatography (PE:EtOAc = 10:1) to afford the propargyl alcohol **S3**.

To a stirred solution of the propargylic alcohol **S3** (1 mmol) in dichloromethane (10 ml) was added triethylamine (3 mmol), acyl chloride (1.2 equivs.), and DMAP (0.1 mmol) at 0°C. The resultant mixture was stirred for 1 h at RT, then quenched by addition of water, washed with brine, dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (PE:EtOAc = 20:1) to afford the corresponding product **S4**.

#### General Procedure B: the Synthesis of 1n-r.



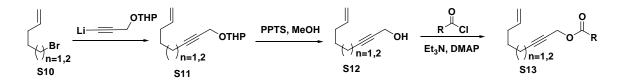
To a stirred solution of the tetrahydro-2-(prop-2-ynyloxy)-2H-pyran (8 mmol) in THF (20 ml) was added n-BuLi (7.5 mmol) under Ar at -78 °C. 30 min later, the mixture was added the epoxide **S5** (5 mmol) in THF (5 ml) slowly, followed by BF<sub>3</sub>:Et<sub>2</sub>O (7.5 mmol). The mixture was slowly warmed to room temperature and then quenched by addition of saturated aqueous ammonium chloride (10 ml), extracted with diethyl ether, washed with brine, dried over sodium sulfate and concentrated. The residue was purified by column chromatography (PE:EtOAc = 10:1) to afford the alcohol **S6**.

To a suspension 60% NaH (4.5 mmol, freshly pre-washed with dry hexane) in THF (10 mL) was added the alcohol **S6** (3 mmol) under Ar at 0 °C. The white suspension was slowly warmed to room temperature and stirred for 1 hour. The reaction mixture was then recooled to 0°C and allyl bromide (6 mmol) was added dropwise, followed by tetrabutylammonium iodide (0.3 mmol). After the reaction mixture was stirred at room temperature for 6 hours. The mixture was quenched by addition of saturated aqueous ammonium chloride and extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with brine, dried over sodium sulfate and concentrated. The residue was purified by silica gel flash chromatography (PE:EtOAc = 50:1) to give allyl ether **S7**.

To a stirred solution of the allyl ether **S7** (2 mmol) in MeOH (10 ml) was added PPTS (0.4 mmol) at RT. 3 hours later, the mixture was quenched by addition of saturated aqueous sodium bicarbonate, the solvent was removed under reduced pressure and the residue was dissolved in diethyl ether, washed with brine, dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (PE:EtOAc = 10:1) to afford the propargyl alcohol **S8**.

To a stirred solution of the propargylic alcohol **S8** (1 mmol) in dichloromethane (10 ml) was added triethylamine (3 mmol), acyl chloride (1.2 equivs.), and DMAP (0.1 mmol) at 0°C. The resultant mixture was stirred for 1 h at RT, then quenched by addition of water, washed with brine, dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (PE:EtOAc = 20:1) to afford the corresponding product **S9**.

#### General Procedure C: the Synthesis of 1t, and 1u.

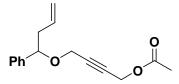


To a stirred solution of the tetrahydro-2-(prop-2-ynyloxy)-2H-pyran (5 mmol) in THF (2.5 ml) was added n-BuLi (5 mmol) under Ar at -50 °C. An hour later, the mixture was added the bromide **S10** (6 mmol) in HMPA (2.5 ml). The mixture was slowly warmed to room temperature and stirred overnight. Then the reaction was quenched by addition of saturated aqueous ammonium chloride (10 ml), extracted with diethyl ether, washed with brine, dried over sodium sulfate and concentrated. The residue was purified by column chromatography (PE:EtOAc = 20:1) to afford the THP ether **S11**.

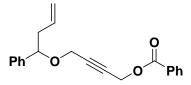
To a stirred solution of the THP ether **S11** (2 mmol) in MeOH (10 ml) was added PPTS (0.4 mmol) at RT. 3 hours later, the mixture was quenched by addition of saturated aqueous sodium bicarbonate, the solvent was removed under reduced pressure and the residue was dissolved in diethyl ether, washed with brine, dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (PE:EtOAc = 10:1) to afford the propargyl alcohol **S12**.

To a stirred solution of the propargylic alcohol **S12** (1 mmol) in dichloromethane (10 ml) was added triethylamine (3 mmol), acyl chloride (1.2 mmol), and DMAP (0.1 mmol) at 0°C. The resultant mixture was stirred for 1 h at RT, then quenched by addition of water, washed with brine, dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (PE:EtOAc = 20:1) to afford the corresponding product **S13**.

## <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra data of compounds 1a-u.

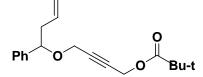


**4-(1-phenylbut-3-enyloxy)but-2-ynyl acetate (1a):** <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.35-7.28 (m, 5H), 5.82-5.72 (m, 1H), 5.67 (d, *J* =17.6 Hz, 1H), 5.32 (d, *J* = 10.8 Hz, 1H), 4.71 (s, 2H), 4.50 (t, *J* = 6.8 Hz, 1H), 4.15 (d, *J* = 16 Hz, 1H), 3.92 (d, *J* = 16 Hz, 1H), 2.66-2.59 (m, 1H), 2.48-2.42 (m, 1H), 2.10 (s, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 170.1, 140.6, 134.4, 128.4, 127.9, 127.0, 117.0, 82.9, 80.7, 80.0, 55.8, 52.3, 42.1, 20.7.

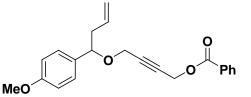


**4-(1-phenylbut-3-enyloxy)but-2-ynyl benzoate (1b):** <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.06 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.34-7.24 (m, 5H), 5.79-5.73 (m, 1H), 5.07-4.99 (m, 2H), 4.95 (s, 2H), 5.20 (t, *J* = 6.8 Hz, 1H), 4.16 (d, *J* = 16 Hz, 1H), 3.93 (d,

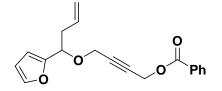
*J* = 16 Hz, 1H), 2.66-2.59 (m, 1H), 2.47-2.42 (m, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 165.7, 140.5, 134.3, 133.1, 129.7, 129.4, 128.3, 128.3, 127.8, 126.9, 117.0, 83.0, 80.5, 80.1, 55.8, 52.7, 42.0.



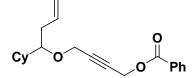
**4-(1-phenylbut-3-enyloxy)but-2-ynyl pivalate (1c):** <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 7.37-7.26 (m, 5H), 5.81-5.71(m, 1H), 5.06 (d, *J* = 18 Hz, 1H), 5.02 (d, *J* = 11.2 Hz, 1H), 4.69 (s, 2H), 4.51 (t, *J* = 6.8 Hz, 1H), 4.14 (d, *J* = 16 Hz, 1H), 3.90 (d, *J* = 16 Hz, 1H) 2.66-2.58 (m, 1H), 2.48-2.41 (m, 1H), 1.23 (s, 9H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 177.7, 140.6, 134.4, 128.4, 127.9, 127.0, 117.0, 82.5, 80.5, 55.8, 52.3, 42.1, 38.7, 27.1.



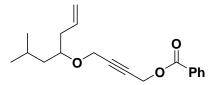
**4-(1-(4-methoxyphenyl)but-3-enyloxy)but-2-ynyl benzoate** (**1d**): <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.08 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.81-5.71 (m, 1H), 5.09-5.00 (m, 2H), 4.98 (s, 2H), 4.49 (t, *J* = 6.8 Hz, 1H), 4.15 (d, *J* = 16 Hz, 1H), 3.92 (d, *J* = 16 Hz, 1H), 3.80 (s, 3H), 2.68-2.60 (m, 1H), 2.48-2.41 (m, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 165.7, 159.3, 134.5, 133.2, 132.4, 129.7, 129.5, 128.3, 128.2, 116.9, 113.8, 83.2, 80.1, 80.0, 55.5, 55.1, 52.7, 42.0.



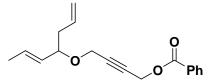
**4-(1-(furan-2-yl)but-3-enyloxy)but-2-ynyl benzoate** (**1e**): <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.08 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 1.2 Hz, 1H), 6.33 (d, *J* = 1.2 Hz, 2H), 5.81-5.71 (m, 1H), 5.13-5.02 (m, 2H), 4.97 (s, 2H), 4.58 (t, *J* = 6.8 Hz, 1H), 4.21 (d, *J* = 16 Hz, 1H), 4.05 (d, *J* = 16 Hz, 1H), 2.75-2.59 (m, 2H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 165.8, 152.7, 142.6, 133.7, 133.2, 129.7, 129.5, 128.4, 117.3, 110.0, 109.0, 82.8, 80.3, 73.1, 55.8, 52.7, 38.2.



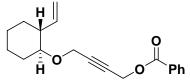
**4-(1-cyclohexylbut-3-enyloxy)but-2-ynyl benzoate** (**1f**): <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.08 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.90-5.81 (m, 1H), 5.11-5.03 (m, 2H), 4.23 (dd, *J* = 15.6, 10.4 Hz, 2H), 3.27-3.24 (m, 1H), 2.32-2.26 (m, 2H), 1.85-0.99 (m, 11H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 165.8, 135.2, 133.2, 129.7, 128.4, 116.7, 83.8, 82.9, 79.5, 55.8, 57.3, 52.8, 40.8, 35.1, 28.8, 28.4, 26.5, 26.3, 26.2.



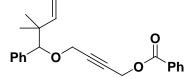
**4-(6-methylhept-1-en-4-yloxy)but-2-ynyl benzoate (1g):** <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.07 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.88-5.77 (m, 1H), 5.11-5.04 (m, 2H), 4.97 (s, 2H), 4.24 (dd, *J* = 24, 16 Hz, 2H), 3.62-3.59 (m, 1H), 2.30-2.27 (m, 2H), 1.83-1.72 (m, 1H), 1.50-1.43 (m, 1H), 1.27-1.21 (m, 1H), 0.91 (d, *J* = 6.8 Hz, 6H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 165.8, 134.5, 133.2, 129.7, 128.3, 117.1, 83.7, 79.7, 76.3, 56.2, 52.7, 43.2, 38.2, 24.4, 23.2, 22.3.



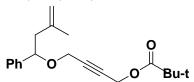
**4**-((**E**)-hepta-1,5-dien-4-yloxy)but-2-ynyl benzoate (1h): <sup>1</sup>H NMR (400 MHz , CDCl<sub>3</sub>) δ ppm 8.07 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.85-5.75 (m, 1H), 5.74-5.65 (m, 1H), 5.33-5.26 (dq, *J* = 6.4, 1.6 Hz,, 1H), 5.11-5.03 (m, 2H), 4.97 (s, 2H), 4.12 (dd, *J* = 20, 16 Hz, 2H), 3.92-3.86 (m, 1H), 2.43-2.36 (m, 1H), 2.31-2.24 (m, 1H), 1.72 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm 165.8, 134.5, 133.2, 130.5, 130.2, 129.7, 128.8, 128.4, 116.8, 83.5, 79.7, 79.2, 55.1, 52.8, 39.9, 17.6.



**4-(trans-2-vinylcyclohexyloxy)but-2-ynyl benzoate** (**1i**): <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.07 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.93-5.85 (m, 1H), 5.09-5.00 (m, 2H), 4.97 (s, 2H), 4.24 (dd, *J* = 18, 16 Hz, 2H), 3.23-3.17 (m, 1H), 2.12-2.06 (m, 2H), 1.76-1.21 (m, 7H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 165.8, 141.2, 133.2, 129.7, 128.3, 114.3, 83.8, 80.7, 79.5, 56.2, 52.8, 47.5, 31.2, 30.9, 24.9, 24.4.

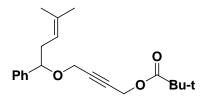


**4-(2,2-dimethyl-1-phenylbut-3-enyloxy)but-2-ynyl benzoate** (**1j**): <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.06 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8Hz, 2H), 7.30-7.22 (m, 5H), 5.94 (dd, *J* = 17.6, 10.8 Hz, 1H), 4.98-4.86 (m, 2H), 4.95 (s, 2H), 4.24 (s, 1H), 4.18 (d, *J* = 16 Hz, 1H), 3.86 (d, *J* = 16 Hz, 1H), 1.03 (s, 3H), 0.98 (s, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 165.8, 144.9, 138.1, 133.2, 129.8, 129.6, 128.7, 128.4, 127.5, 127.4, 112.1, 87.7, 83.4, 80.0, 56.3, 52.8, 41.4, 24.1, 23.1.

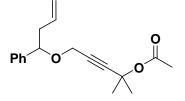


4-(3-methyl-1-phenylbut-3-enyloxy)but-2-ynyl pivalate (1k): <sup>1</sup>H NMR (400 MHz , CDCl<sub>3</sub>) δ

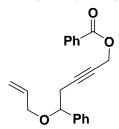
ppm 7.30-7.26 (m, 5H), 4.76 (d, J = 16.0 Hz, 2H), 4.69 (s, 2H),4.69-4.65 (m, 1H), 4.15 (d, J = 16.0 Hz, 1H), 3.88 (d, J = 16 Hz, 1H), 2.60 (dd, J = 14.4, 8.4 Hz, 1H), 2.34 (dd, J = 14.4, 5.6 Hz, 1H), 1.75 (s, 3H), 1.23 (s, 9H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 177.6, 142.0, 141.0, 128.4, 127.8, 126.9, 112.7, 82.5, 80.5, 79.0, 55.6, 52.2, 46.1, 38.7, 27.0, 22.6.



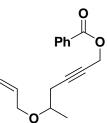
**4-(4-methyl-1-phenylpent-3-enyloxy)but-2-ynyl pivalate** (**11):** <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 7.34-7.29 (m, 5H), 5.13-5.09 (m, 1H), 4.71 (s, 2H), 4.44 (t, *J* = 6.8 Hz, 1H), 4.15 (d, *J* = 16 Hz, 1H), 3.92 (d, *J* = 16 Hz, 1H), 2.60-2.53 (m, 1H), 2.43-2.36 (m, 1H), 1.67 (s, 3H), 1.50 (s, 3H), 1.24 (s, 9H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 177.7, 141.0, 133.8, 128.3, 127.7, 127.0, 119.8, 82.7, 81.0, 80.3, 55.9, 52.3, 38.7, 36.5, 27.1, 25.7, 17.8.



**5-(1-phenylbut-3-enyloxy)-2-methylpent-3-yn-2-yl benzoate (1m):** <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 7.32-7.26 (m, 5H), 5.84-5.74 (m, 1H), 5.09-5.01 (m, 2H), 4.58 (dd, *J* = 7.2, 6.0 Hz, 1H), 4.15 (d, *J* = 16 Hz, 1H), 3.91 (d, *J* = 16 Hz, 1H), 2.64-2.57 (m, 1H), 2.46-2.40 (m, 1H), 2.02 (s, 3H), 1.65 (s, 3H), 1.64 (s, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 169.2, 140.9, 134.7, 128.3, 127.7, 127.0, 116.8, 87.2, 80.2, 79.9, 71.9, 55.9, 42.0, 28.9, 28.8, 21.9.

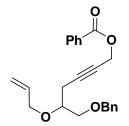


**5-(allyloxy)-5-phenylpent-2-ynyl benzoate (1n):** <sup>1</sup>H NMR (400 MHz , CDCl<sub>3</sub>) δ ppm 8.05 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35-7.25 (m, 5H), 5.91-5.85 (m, 1H), 5.26 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.15 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.87 (s, 2H), 4.49 (t, *J* = 6.8 Hz, 1H), 3.99-3.95 (m, 1H), 3.85-3.80 (m, 1H), 2.80-2.74 (m, 1H), 2.63-2.57 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm 165.9, 140.7, 134.5, 133.1, 129.7, 128.3, 127.9, 126.7, 117.0, 84.0, 79.3, 75.9, 69.7, 53.1, 28.5.

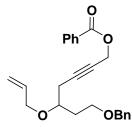


**5-(allyloxy)hex-2-ynyl benzoate** (**1o):** <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.06 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 5.95-5.85 (m, 1H), 5.27 (d, *J* = 17.2 Hz, 1H),

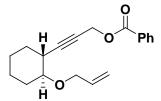
5.14 (d, J = 10.4 Hz, 1H), 4.92 (s, 2H), 4.02 (d, J = 5.6 Hz, 2H), 3.67-3.59 (m, 1H), 2.55-2.50 (m, 1H), 2.39-2.33 (m, 1H), 1.26 (d, J = 6.0, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 165.8, 134.9, 133.0, 129.6, 128.3, 116.6, 84.2, 75.7, 73.1, 69.7, 53.1, 26.3, 19.6.



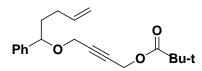
**5-(allyloxy)-6-(benzyloxy)hex-2-ynyl benzoate** (**1p**): <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.06 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.35-7.27 (m, 5H), 5.98-5.88 (m, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.91 (s, 2H), 4.58 (s, 2H), 4.14 (d, *J* = 5.6 Hz, 1H), 3.75-3.70 (m, 1H), 3.66-3.59 (m, 2H), 2.64-2.52 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm 165.9, 138.1, 134.8, 133.1, 129.7, 128.3, 128.3, 127.6, 127.5, 117.1, 83.9, 76.1, 75.7, 73.4, 71.1, 71.0, 53.1, 21.9.



**5-(allyloxy)-7-(benzyloxy)hept-2-ynyl benzoate** (**1q**): **<sup>1</sup>H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.06 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.36-7.27 (m, 5H), 5.92-5.84 (m, 1H), 5.27 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.18 (d, *J* = 10.4, 1.6 Hz, 1H), 4.93 (s, 2H), 4.52 (dd, *J* = 17.6, 12 Hz, 2H), 4.12-4.11 (m, 1H), 4.01-3.96 (m, 1H), 3.66-3.58 (m, 3H), 2.52-2.49 (m, 2H), 2.01-1.85 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm 165.9, 138.4, 134.9, 133.1, 129.7, 128.3, 127.6, 127.5, 116.9, 84.1, 75.8, 74.2, 72.9, 70.7, 66.5, 53.2, 34.5, 24.5.

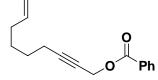


**3-(trans-2-(allyloxy)cyclohexyl)prop-2-ynyl benzoate** (**1r**): <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.05 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 5.96-5.86 (m, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.4 Hz, 1H), 4.93 (s, 2H), 4.10 (d, *J* = 5.6 Hz, 2H), 3.31-3.27 (m, 1H), 2.48 (br s, 1H), 1.97-1.95 (m, 2H), 1.69-1.60 (m, 2H), 1.48-1.23 (m, 4H); <sup>13</sup>C **NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 165.7, 135.3, 132.9, 129.6, 128.2, 116.3, 89.5, 78.9, 75.1, 70.2, 53.2, 35.2, 30.3, 30.0, 23.8, 23.1.

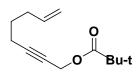


**4-(1-phenylpent-4-enyloxy)but-2-ynyl pivalate** (1s): <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 7.36-7.26 (m, 5H), 5.86-5.76 (m, 1H), 5.04-4.95 (m, 2H), 4.69 (s, 2H), 4.45 (dd, *J* = 7.2, 5.6 Hz,

2H), 4.12 (d, *J* = 15.6 Hz, 1H), 3.88 (d, *J* = 15.6 Hz, 1H), 2.17-2.05 (m, 2H), 1.99-1.90 (m, 1H), 1.78-1.69 (m, 1H), 1.23 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm 177.7, 141.2, 138.0, 128.4, 127.8, 126.9, 114.8, 82.7, 80.3, 80.2, 55.8, 52.3, 38.7, 36.9, 29.9, 27.1.

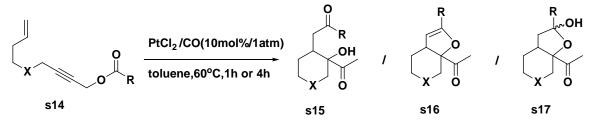


**non-8-en-2-ynyl benzoate** (**1t**): <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 8.08 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.86-5.76 (m, 1H), 5.05-4.94 (m, 2H), 4.93 (s, 2H), 2.28-2.24 (m, 2H), 2.10-2.05 (m, 2H), 1.58-1.49 (m, 4H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 166.0, 138.5, 133.1, 129.7, 128.3, 114.6, 87.5, 74.2, 53.3, 33.2, 28.0, 27.8, 18.6.



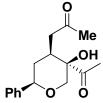
**oct-7-en-2-ynyl pivalate** (**1u**): <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>) δ ppm 5.82-5.72 (m, 1H), 5.05-4.95 (m, 2H), 4.64 (s, 2H), 2.24-2.20 (m, 2H), 2.17-2.11 (m, 2H), 1.63-1.56 (m, 2H), 1.21 (s, 9H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ ppm 177.8, 137.7, 115.2, 86.7, 74.6, 52.7, 38.7, 32.6, 27.4, 27.0, 18.1.

#### General Procedure for the preparation of the [3+2] cycloaddition products.



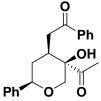
A suspension of the propargylic esters 1a-u (0.15 mmol) and PtCl<sub>2</sub> (0.015 mmol) in toluene (1.5 ml) under CO (1 atm) at 60°C was stirred until the starting material disappeared (1h for 1a-k and 1s-u, 4h for 1n-1r). After the mixture was stirred at RT under Air for another one hour, the suspension was directly loaded onto a silica gel column, elution with a 10:1 mixture of PE/EtOAc yielded the desired products.

#### Characterization data of the [3+2] cycloaddition products.

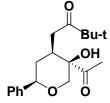


**Compound 3a:** solid, mp: 131°C; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.34-7.25 (m, 5H), 4.52 (dd, J = 11.6, 2.0 Hz, 1H), 3.92 (d, J = 11.6 Hz, 1H), 3.82 (d, J = 11.6 Hz, 1H), 3.73 (s, 1H), 2.91-2.84 (m, 1H), 2.40-2.27 (m, 2H), 2.31 (s, 3H), 2.08 (s, 3H), 1.94-1.89 (m, 1H), 1.64 (dd, J = 25.6, 12.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 210.9, 207.0, 141.4, 128.4, 127.8, 125.7, 79.6, 79.1, 73.5, 44.1, 36.0, 35.0, 30.5, 26.0; **IR** v (cm<sup>-1</sup>): 3464, 2984, 2938, 1740, 1708, 1373,

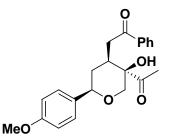
1242, 1046; **HRMS** (EIS) calcd. for  $C_{16}H_{20}NaO_4$  [M+Na]<sup>+</sup>: 299.1254, found 299.1251.



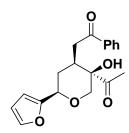
**Compound 3b:** solid, mp: 138-140°C; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.55 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.35-7.24 (m, 5H), 4.56 (dd, J = 11.6, 2.0 Hz, 1H), 3.96 (d, J = 11.6 Hz, 1H), 3.86 (d, J = 11.6 Hz, 1H), 3.82 (s, 1H), 3.14-3.07 (m, 1H), 2.97 (dd, J = 17.6, 8.4 Hz, 1H), 2.77 (dd, J = 17.6, 4.0 Hz, 1H), 2.37 (s, 3H), 2.01-1.97 (m, 1H), 1.73 (dd, J = 25.2, 12.0 Hz, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 210.9, 198.4, 141.3, 136.7, 133.4, 128.6, 128.4, 128.0, 127.8, 125.7, 79.7, 79.5, 73.6, 39.1, 36.5, 35.1, 26.1; **IR**  $\nu$  (cm<sup>-1</sup>): 3454, 2922, 2854, 1705, 1683, 1448, 1365, 1094, 756, 697; **HRMS** (EIS) calcd. for C<sub>21</sub>H<sub>22</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 361.1410, found 361.1414.



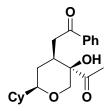
**Compound 3c:** solid, mp: 139-141°C; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 7.37-7.25 (m, 5H), 4.52 (dd, J = 11.6, 2.0 Hz, 1H), 3.94 (d, J = 11.6 Hz, 1H), 3.85 (d, J = 11.6 Hz, 1H), 3.80 (s, 1H), 2.95-2.88 (m, 1H), 2.50 (dd, J = 18.0, 8.0 Hz, 1H), 2.32 (s, 3H), 2.22 (dd, J = 18.0, 4.0 Hz, 1H), 1.85-1.80 (m, 1H), 1.63 (dd, J = 25.2, 12.0 Hz, 1H), 1.07 (s, 9H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 214.3, 210.7, 141.5, 128.3, 127.7, 125.7, 79.7, 79.3, 73.5, 44.2, 37.3, 36.0, 35.0, 26.1, 25.8; **IR**  $\nu$  (cm<sup>-1</sup>): 3458, 2963, 2927, 2867, 1703, 1364, 1095, 757, 700; **HRMS** (EIS) calcd. for C<sub>19</sub>H<sub>26</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 341.1723, found 361.1420.



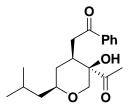
**Compound 3d:** solid, mp: 124-127°C; <sup>1</sup>**H** NMR (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.91 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 7.31 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.51 (dd, J = 11.6, 2.0 Hz, 1H), 3.95 (d, J = 11.6 Hz, 1H), 3.85 (d, J = 11.6 Hz, 1H), 3.86-3.78 (m, 1H), 3.78 (s, 3H), 3.12-3.05 (m, 1H), 2.97 (dd, J = 17.2, 8.4 Hz, 1H), 2.78 (dd, J = 17.2, 4.0 Hz, 1H), 2.37 (s, 3H), 1.98-1.93 (m, 1H), 1.75 (dd, J = 25.2, 12.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 211.0, 198.5, 159.2, 136.7, 133.5, 133.3, 128.6, 128.0, 127.1, 113.7, 79.5, 79.4, 73.6, 55.2, 39.1, 36.6, 34.9, 26.1; **IR** v (cm<sup>-1</sup>): 3460, 2935, 1704, 1683, 1514, 1247; **HRMS** (EIS) calcd. for C<sub>22</sub>H<sub>24</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 391.1516, found 391.1512.



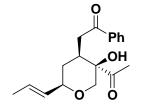
**Compound 3e:** solid, mp: 90-93°C; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.91 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 1.2 Hz, 1H), 6.31 (m, 2H), 4.60 (dd, J = 11.2, 2.8 Hz, 1H), 3.90 (d, J = 11.6 Hz, 1H), 3.83 (s, 1H), 3.79 (d, J = 11.6 Hz, 1H), 3.04-3.01 (m, 1H), 2.97 (d, J = 8.4 Hz, 1H), 2.80 (d, J = 13.6 Hz, 1H), 2.33 (s, 3H), 2.04-1.94 (m, 2H); <sup>13</sup>C **NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 210.9, 198.2, 153.2, 142.3, 136.6, 133.3, 128.6, 128.0, 110.1, 107.1, 79.4, 73.3, 72.7, 39.1, 36.1, 30.5, 26.2; **IR**  $\nu$  (cm<sup>-1</sup>): 3459, 2924, 2858, 2252, 1707, 1680, 1358, 1081, 1014, 989, 913, 752, 734, 692, 600; **HRMS** (EIS) calcd. for C<sub>19</sub>H<sub>20</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 351.1203, found 351.1206.



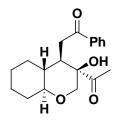
**Compound 3f:** oil; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.90 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.68 (d, *J* = 1.6 Hz, 2H), 3.66 (s, 1H), 3.22-3.17 (m, 1H), 2.93-2.71 (m, 3H), 2.29 (s, 3H), 1.94-1.91 (m, 1H), 1.74-1.63 (m, 5H), 1.42-1.32 (m, 2H), 1.20-1.15 (m, 3H), 0.98 (m, 2H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 211.1, 198.6, 136.7, 133.2, 128.6, 128.0, 82.0, 79.9, 73.4, 42.6, 39.4, 36.1, 30.1, 28.8, 28.5, 26.4, 26.0, 25.9; **IR** *v* (cm<sup>-1</sup>): 3464, 2925, 2852, 1706, 1685, 1448, 1357, 1288, 1217, 1099, 988, 755, 692; **HRMS** (EIS) calcd. for C<sub>21</sub>H<sub>28</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 367.1880, found 367.1884.



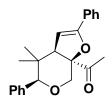
**Compound 3g:** oil; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.91 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 3.75 (d, J = 11.6 Hz, 1H), 3.69 (s, 1H), 3.68 (d, J = 11.6 Hz, 1H), 3.57-3.51 (m, 1H), 2.95-2.71 (m, 3H), 2.32 (s, 3H), 1.84-1.77 (m, 1H), 1.73-1.68 (m, 1H), 1.58-1.50 (m, 1H), 1.37 (dd, J = 24.0, 11.2 Hz, 1H), 1.23-1.16 (m, 1H), 0.89 (d, J = 6.8 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 211.1, 198.6, 136.8, 133.3, 128.6, 128.1, 79.8, 76.0, 73.3, 44.9, 39.3, 36.2, 33.7, 26.0, 24.2, 23.2, 22.2; **IR** v (cm<sup>-1</sup>): 3463, 2954, 1704, 1684, 1448, 1362, 1094, 986, 754, 691; **HRMS** (EIS) calcd. for C<sub>19</sub>H<sub>26</sub>NO<sub>4</sub> [M+Na]<sup>+</sup>: 341.1723, found 341.1729.



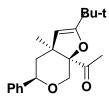
**Compound 3h:** oil; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.91 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 5.79-5.71 (m, 1H), 5.50 (dq, J = 15.6, 6.4 Hz, 1H), 3.98-3.93 (m, 1H), 3.79 (d, J = 11.6 Hz, 1H), 3.73 (s, 1H), 3.71 (d, J = 11.6 Hz, 1H), 2.97-2.89 (m, 2H), 2.74 (dd, J = 20.8, 7.6 Hz, 1H), 2.32 (s, 3H), 1.79-1.74 (m, 1H), 1.68 (d, J = 6.4 Hz, 3H), 1.49 (dd, J = 24.8, 11.6 Hz, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 211.1, 198.5, 136.7, 133.3, 130.7, 128.6, 128.2, 128.1, 79.5, 78.2, 73.1, 39.2, 36.1, 33.2, 26.1, 17.7; **IR**  $\nu$  (cm<sup>-1</sup>): 3457, 2940, 2918, 2855, 1705, 1683, 1597, 1448, 1359, 1280, 1220, 1088, 971, 915, 754, 692; **HRMS** (EIS) calcd. for C<sub>18</sub>H<sub>22</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 325.1410, found 325.1412.



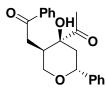
**Compound 3i:** semi-solid, mp: ~ 80°C; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.91 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.12 (br s, 1H), 3.88 (d, *J* = 11.6 Hz, 1H), 3.66 (d, *J* = 11.6 Hz, 1H), 3.22-3.16 (m, 1H), 3.01 (d, *J* = 11.6 Hz, 1H), 2.84-2.79 (m, 1H), 2.64 (dd, *J* = 18.8, 4.0 Hz, 1H), 2.28 (s, 3H), 1.98-1.94 (m, 1H), 1.79-1.76 (m, 1H), 1.65-1.62 (m, 1H), 1.50-0.89 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 210.5, 198.6, 136.3, 133.2, 128.5, 81.8, 80.9, 72.9, 42.7, 39.7, 37.4, 32.0, 28.3, 25.8, 25.5, 24.6; **IR** *v* (cm<sup>-1</sup>): 3459, 2931, 2858, 2249, 1707, 1687, 1597, 1448, 1359, 1096, 914, 773, 692; **HRMS** (EIS) calcd. for C<sub>19</sub>H<sub>25</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 317.1747, found 317.1745.



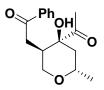
**Compound 3j:** solid, mp: 152-154°C; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.70 (d, J = 6.8 Hz, 2H), 7.42-7.23 (m, 8H), 5.50 (d, J = 3.2 Hz, 1H), 4.56 (d, J = 13.2 Hz, 1H), 4.15 (s, 1H), 3.85 (d, J = 13.2 Hz, 1H), 3.14 (d, J = 3.2 Hz, 1H), 2.21 (s, 3H), 0.85 (s, 3H), 0.74 (s, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 214.3, 156.8, 138.0, 130.0, 129.0, 128.5, 127.7, 127.4, 127.2, 125.1, 99.6, 92.7, 85.5, 70.4, 53.7, 36.8, 26.5, 26.0, 16.7; **IR**  $\nu$  (cm<sup>-1</sup>): 2969, 1711, 1447, 1356, 1125, 1092, 755, 697; **HRMS** (EIS) calcd. for C<sub>23</sub>H<sub>25</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 349.1798, found 349.1803.



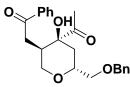
**Compound 3k:** oil; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.34-7.22 (m, 5H), 4.58 (dd, J = 8.8, 4.4 Hz, 1H), 4.43 (s, 1H), 4.09 (dd, J = 24.0, 12.8 Hz, 2H), 2.30 (s, 3H), 1.96 (dd, J = 14.0, 4.4 Hz, 1H), 1.78 (dd, J = 14.0, 8.8 Hz, 1H), 1.16 (s, 9H), 1.11 (s, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 211.9, 164.3, 143.0, 128.1, 127.1, 125.7, 104.7, 91.7, 74.0, 68.5, 46.3, 44.6, 31.9, 28.9, 27.7, 23.2; **IR** v (cm<sup>-1</sup>): 2963, 2930, 2868, 1708, 1656, 1455, 1356, 1129, 1071, 755, 702; **HRMS** (EIS) calcd. for C<sub>20</sub>H<sub>27</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 315.1955, found 315.1960.



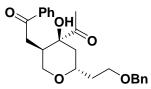
**Compound 3n:** oil; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.55 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.37-7.25 (m, 5H), 4.83 (dd, J = 11.2, 2.0 Hz, 1H), 4.28 (s, 1H), 4.06 (dd, J = 11.2, 5.2 Hz, 1H), 3.76 (dd, J = 7.2 Hz, 1H), 3.11-3.04 (m, 1H), 2.72 (d, J = 5.6 Hz, 1H), 2.33 (s, 3H), 2.13 (dd, J = 12.8, 11.2 Hz, 1H), 1.70 (dd, J = 12.8, 2.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 210.6, 197.8, 141.8, 136.5, 133.4, 128.6, 128.4, 128.0, 127.6, 125.7, 78.7, 74.6, 68.2, 42.7, 35.6, 34.8, 23.9; **IR**  $\nu$  (cm<sup>-1</sup>): 3457, 2952, 2922, 2861, 1701, 1686, 1450, 1360, 1214, 1081, 756, 696; **HRMS** (EIS) calcd. for C<sub>21</sub>H<sub>22</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 361.1410, found 361.1416.



**Compound 30:** oil; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.88 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 4.16 (br s, 1H), 3.92-3.85 (m, 2H), 3.58 (dd, J = 11.2 Hz, 1H), 2.96-2.89 (m, 1H), 2.72-2.60 (m, 2H), 2.72 (d, J = 5.6 Hz, 1H), 2.34 (s, 3H), 1.84 (dd, J = 12.8, 11.2 Hz, 1H), 1.49 (dd, J = 12.8, 2.0 Hz, 1H), 1.23 (d, J = 6.4 Hz, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 210.0, 197.9, 141.8, 136.6, 133.3, 128.6, 128.0, 78.6, 68.7, 67.8, 41.9, 35.6, 34.7, 23.9, 21.4; **IR**  $\nu$  (cm<sup>-1</sup>): 3455, 2970, 2932, 2869, 1702, 1687, 1597, 1358, 1124, 1058, 755, 691; **HRMS** (EIS) calcd. for C<sub>16</sub>H<sub>20</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 299.1254, found 299.1250.

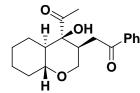


**Compound 3p:** oil; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.88 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.36-7.28 (m, 5H), 4.60 (s, 2H), 4.16 (s, 1H), 4.04-3.98 (m, 1H), 3.94 (dd, J = 11.2, 5.2 Hz, 1H), 3.61 (dd, J = 11.2 Hz, 1H), 3.52 (d, J = 5.2 Hz, 1H), 3.00-2.93 (m, 1H), 2.73-2.61 (m, 2H), 2.34 (s, 3H), 2.02 (dd, J = 12.4, 11.6 Hz, 1H), 1.46 (dd, J = 12.8, 2.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 210.9, 197.8, 138.0, 136.5, 133.4, 128.6, 128.4, 128.0, 127.8, 127.7, 78.3, 73.5, 72.6, 71.8, 67.9, 36.8, 35.7, 34.8, 23.9; **IR**  $\nu$  (cm<sup>-1</sup>): 3454, 2921, 2862, 1703, 1686, 1597, 1451, 1359, 1103, 987, 752, 695; **HRMS** (EIS) calcd. for C<sub>23</sub>H<sub>30</sub>NO<sub>5</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 400.2118, found 400.2122.

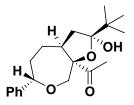


**Compound 3q:** oil; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 7.88 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6

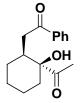
Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.34-7.26 (m, 5H), 4.51 (s, 2H), 4.13 (br s, 1H), 3.95-3.83 (m, 2H), 3.61-3.52 (m, 3H), 2.95-2.88 (m, 1H), 2.65 (m, 2H), 2.31 (s, 3H), 1.90-1.73 (m, 3H), 1.49 (dd, J = 13.2, 2.0 Hz, 1H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 210.9, 197.9, 138.4, 136.6, 133.3, 128.6, 128.3, 128.0, 127.6, 127.5, 78.5, 72.9, 70.0, 67.7, 66.6, 40.4, 36.0, 35.8, 34.7, 23.9; **IR**  $\nu$  (cm<sup>-1</sup>): 3457, 2922, 2860, 1699, 1687, 1598, 1451, 1359, 1118, 751, 694; **HRMS** (EIS) calcd. for C<sub>24</sub>H<sub>28</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 419.1829, found 419.1825.



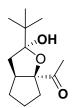
**Compound 3r:** solid, mp: 98-100°C; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.85 (d, J = 7.6 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 4.01 (s, 1H), 3.82 (dd, J = 10.8, 4.8 Hz, 1H), 3.54 (dd, J = 10.8 Hz, 1H), 3.43-3.37 (m, 1H), 3.01-2.94 (m, 1H), 2.66-2.55 (m, 2H), 2.26 (s, 3H), 2.00-1.98 (m, 1H), 1.77-1.65 (m, 3H), 1.40-1.16 (m, 5H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 211.1, 197.6, 136.5, 133.2, 128.5, 127.9, 80.6, 75.1, 67.4, 46.9, 37.3, 34.8, 32.5, 25.2, 24.3, 23.9, 23.8; **IR** v (cm<sup>-1</sup>): 3459, 2933, 2859, 1689, 1597, 1449, 1358, 1260, 1113, 755, 691, 602; **HRMS** (EIS) calcd. for C<sub>19</sub>H<sub>28</sub>NO<sub>4</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 334.2013, found 334.2015.



**Compound 3s:** oil; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 7.37-7.24 (m, 5H), 4.42 (dd, J = 10.8, 3.2 Hz, 1H), 4.09 (d, J = 13.6 Hz, 1H), 3.90 (d, J = 13.6 Hz, 1H), 3.03-2.96 (m, 1H), 2.48 (t, J = 12.0 Hz, 1H), 2.38 (br s, 1H), 2.31 (s, 3H), 2.06 (dd, J = 8.8, 2.8 Hz, 1H), 2.08-1.90 (m, 3H), 1.70 (dd, J = 12.0, 7.6 Hz, 1H), 1.16 (s, 9H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 213.6, 143.4, 128.3, 127.2, 125.4, 110.3, 95.4, 87.4, 76.4, 41.8, 38.0, 35.4, 34.9, 26.4, 25.7, 25.3; **IR**  $\nu$  (cm<sup>-1</sup>): 3502, 2959, 2930, 2870, 1704, 1358, 1138, 1097, 1061, 937, 756, 700; **HRMS** (EIS) calcd. for C<sub>20</sub>H<sub>32</sub>NO<sub>4</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 350.2326, found 350.2331.

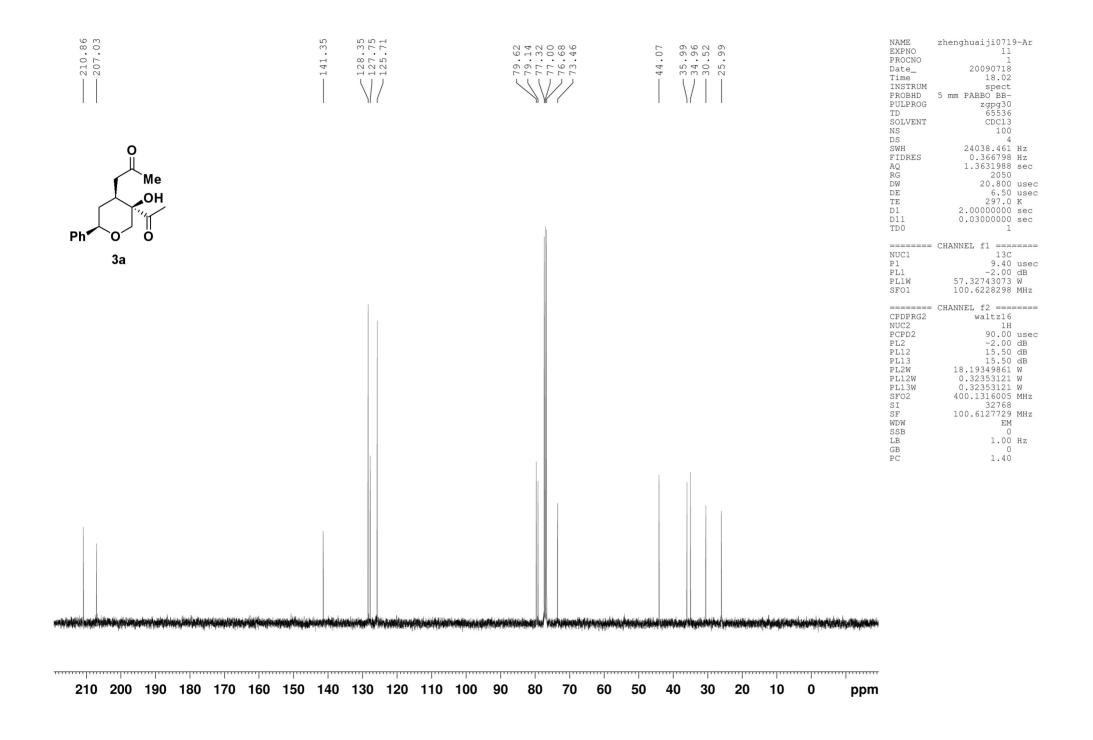


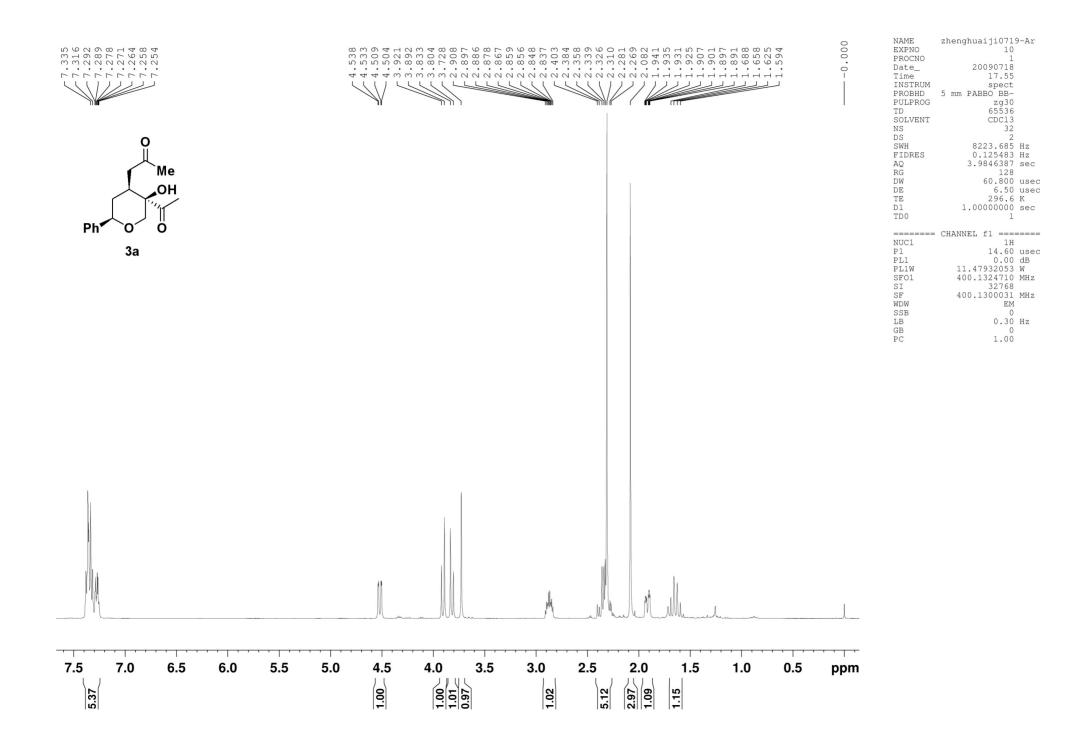
**Compound 3t:** oil; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 7.90 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 3.96 (s, 1H), 2.92 (dd, J = 17.6, 8.0 Hz, 1H), 2.65-2.58 (m, 1H), 2.49 (dd, J = 17.6, 3.6 Hz, 1H), 2.28 (s, 3H), 1.83-1.43 (m, 8H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 213.0, 199.2, 137.1, 133.2, 128.5, 128.0, 80.4, 39.7, 37.4, 35.3, 28.2, 25.4, 23.9, 20.7; **IR**  $\nu$  (cm<sup>-1</sup>): 3468, 2934, 2858, 1699, 1686, 1597, 1447, 1361, 1211, 1119, 1008, 753, 691, 602; **HRMS** (EIS) calcd. for C<sub>16</sub>H<sub>21</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 261.1485, found 261.1488.



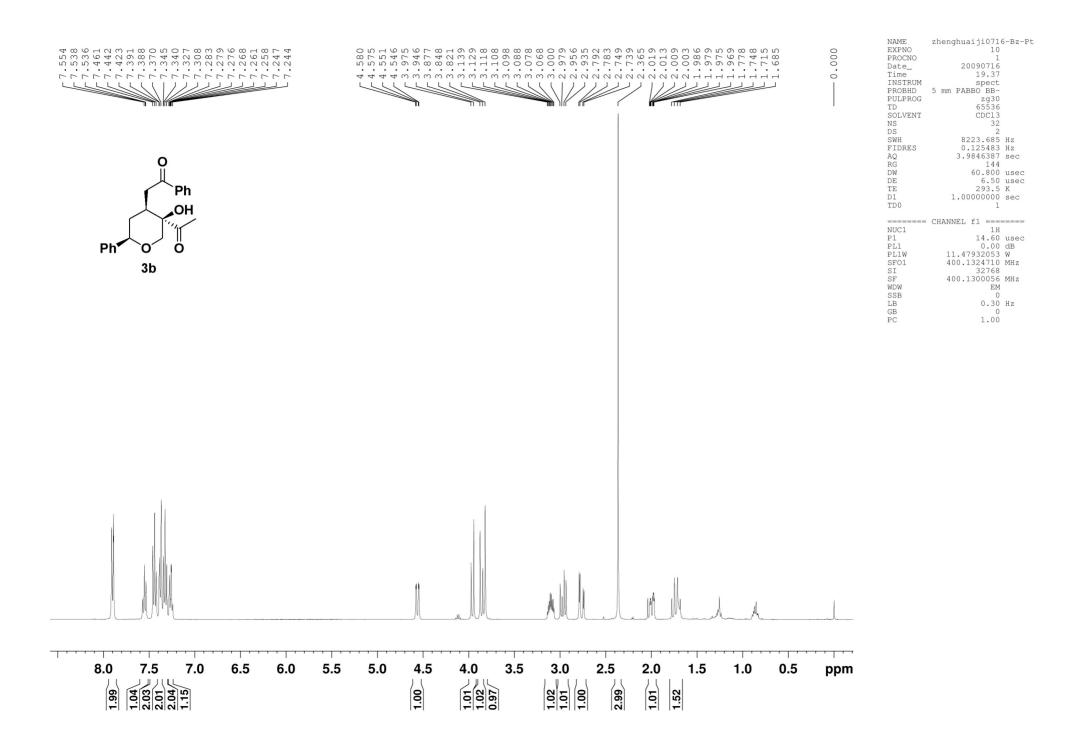
**Compound 3u:** solid, mp: 67-70°C; <sup>1</sup>**H NMR** (400 MHz , CDCl<sub>3</sub>)  $\delta$  ppm 3.14 (m, 1H), 2.22 (s, 3H), 2.06-1.57 (m, 8H), 1.02 (s, 9H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 213.2, 112.0, 99.6, 44.8, 40.2, 38.1, 37.4, 34.0, 25.8, 25.0, 24.7; **IR**  $\nu$  (cm<sup>-1</sup>): 3442, 2957, 1704, 1356, 1045; **HRMS** (EIS) calcd. for C<sub>14</sub>H<sub>25</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 225.1849, found 225.1853.

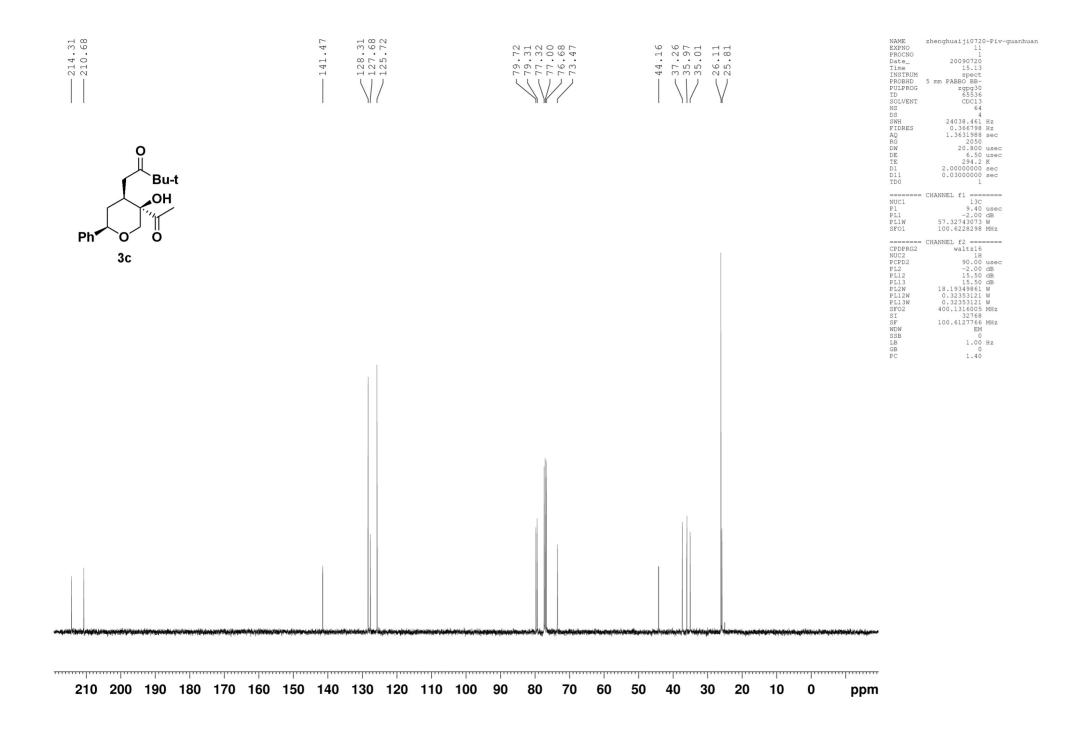
Spectra.

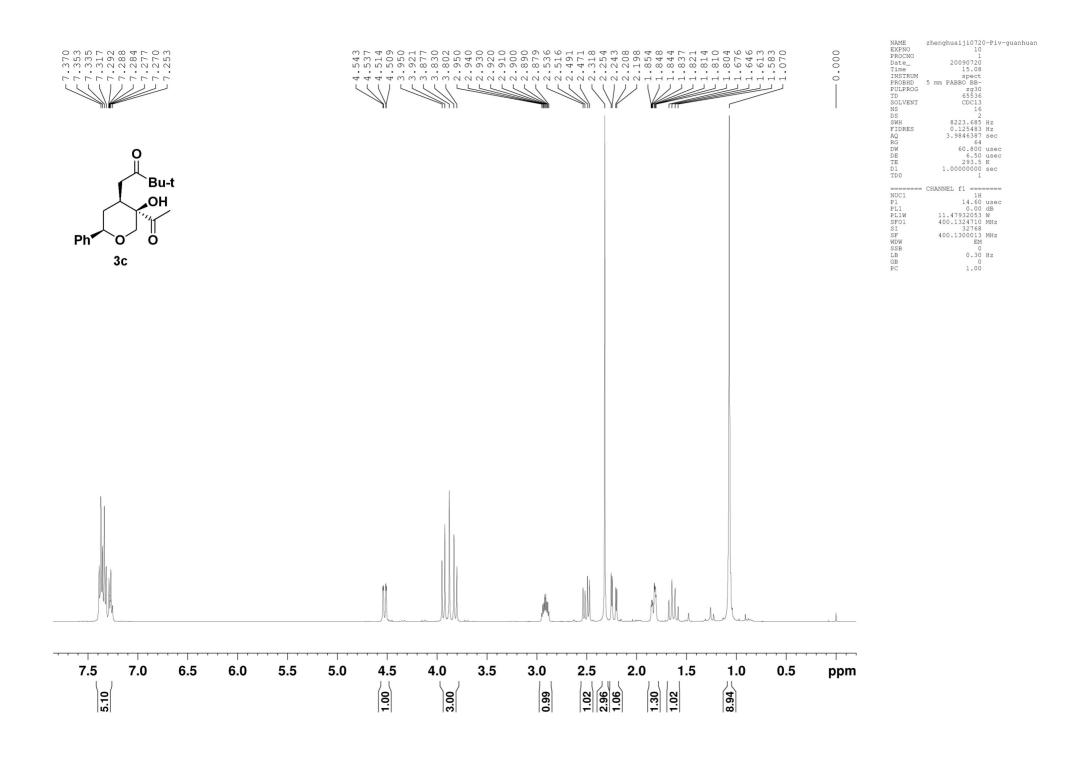


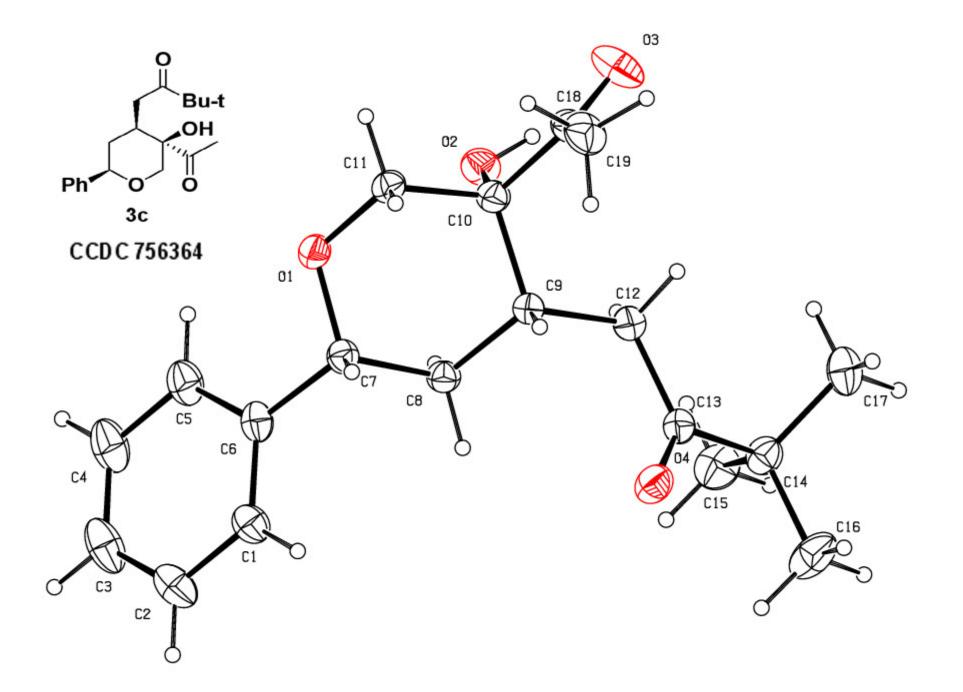


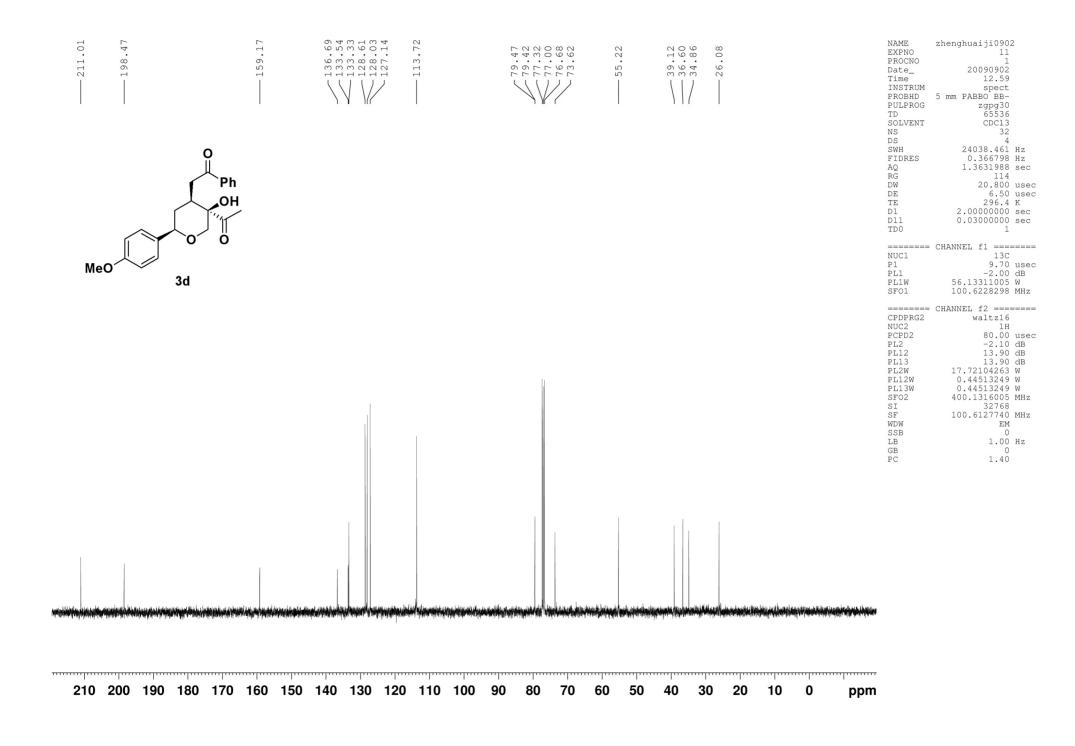
<b>Bu</b> <b>OH</b> <b>OH</b> <b>OH</b> <b>OH</b> <b>OH</b> <b>OH</b> <b>OH</b> <b>OH</b>	141.32 136.66 133.36 128.63 128.63 128.35 128.75 125.74	79.72	7 35.09 35.06 35.06	NAME zhenghuaiji0716-Bz-Pt   EXPNO 11   PROCNO 1   Date_ 20090716   Time 19.46   INSTRUM spect   PROBHD 5 mm PABBO BB-   PULPROG zgpq30   TD 65536   SOLVENT CDC13   NS 128   DS 4   SWH 24038.461   FIDRES 0.366798   AQ 1.3631988 sec   RG 20.800   DW 20.0000   DE 6.50   DI 2.00000000 sec   DI 0.03000000 sec   DI 13C   P1 9.40 usec   P1 9.40 usec
				CHANNEL f2 CPDPRG2 waltz16 NUC2 1H PCPD2 90.00 usec PL2 -2.00 dB PL13 15.50 dB PL13 15.50 dB PL2W 18.19349861 W PL12W 0.32353121 W SF02 400.1316005 MHz SI 32768 SF 100.6127736 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40
	160 150 140 130 120 110		50 40 30 20 10	0 ppm

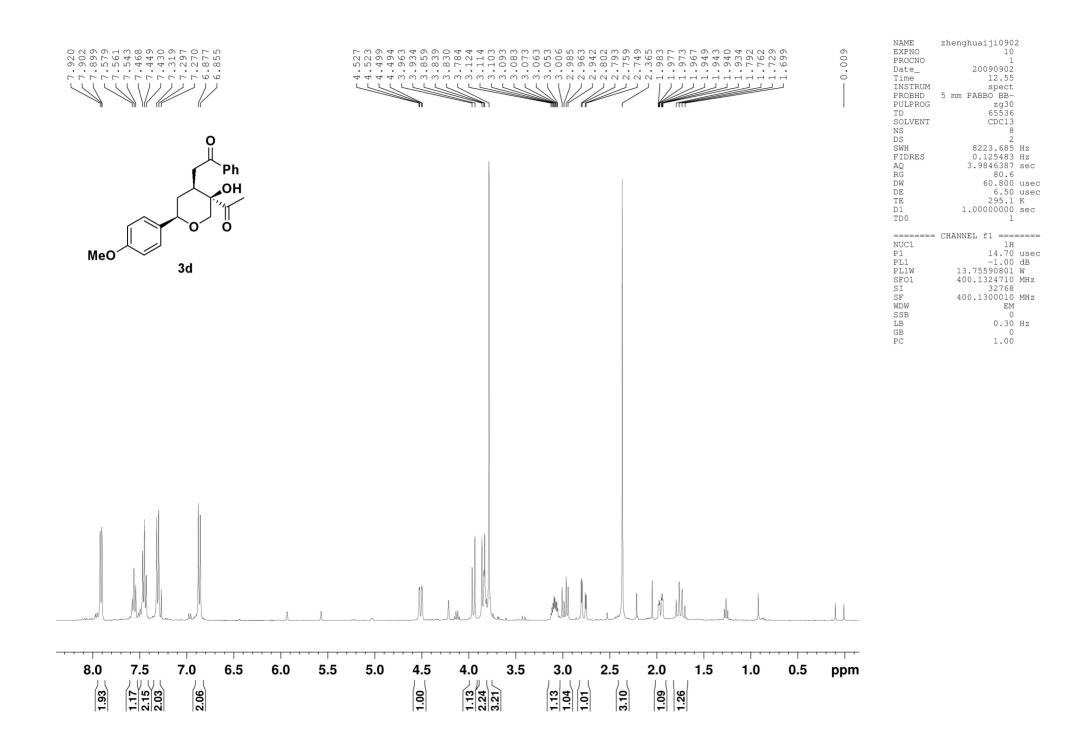


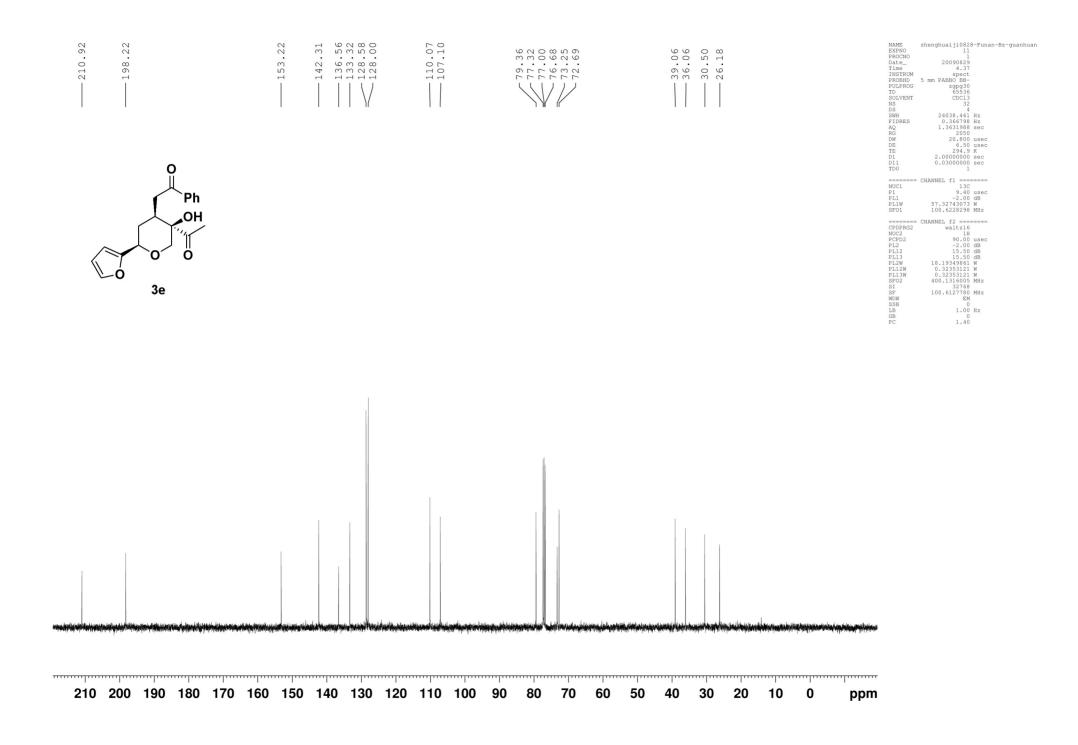


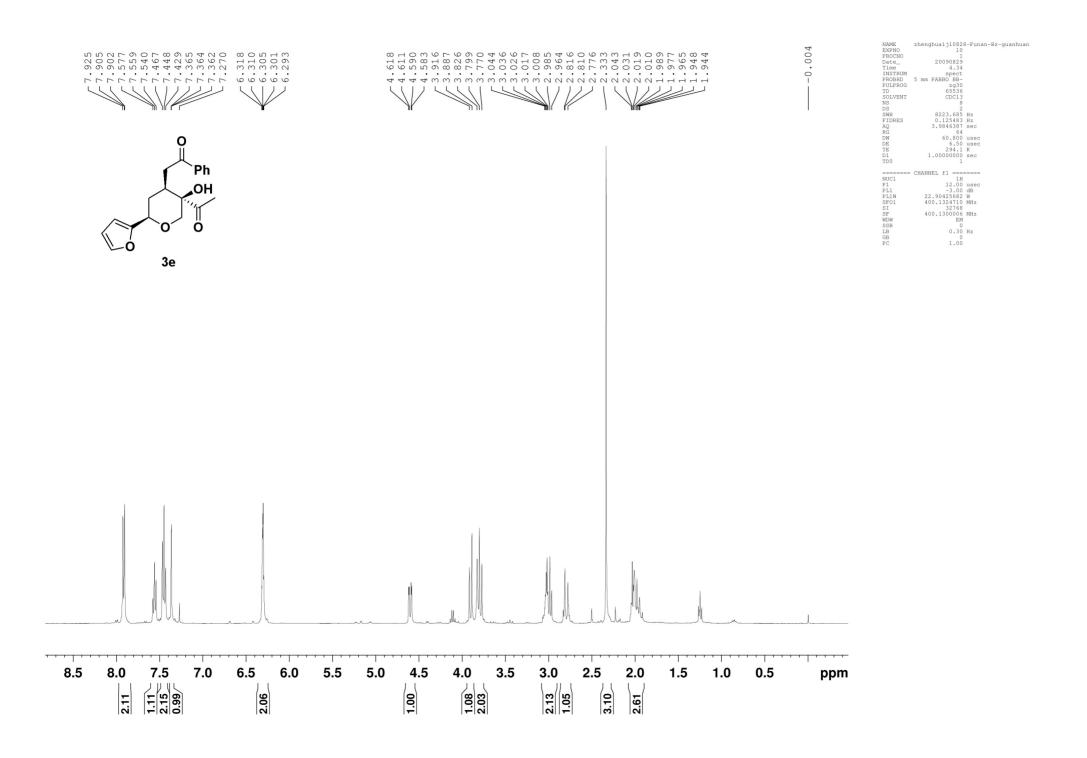


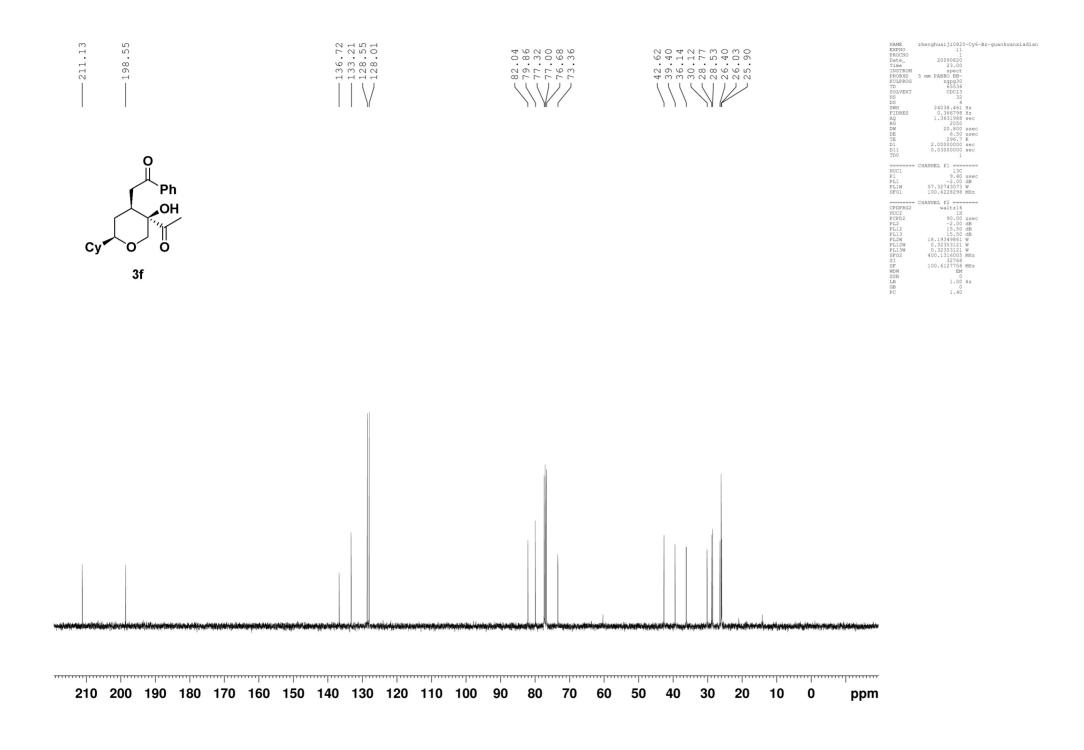


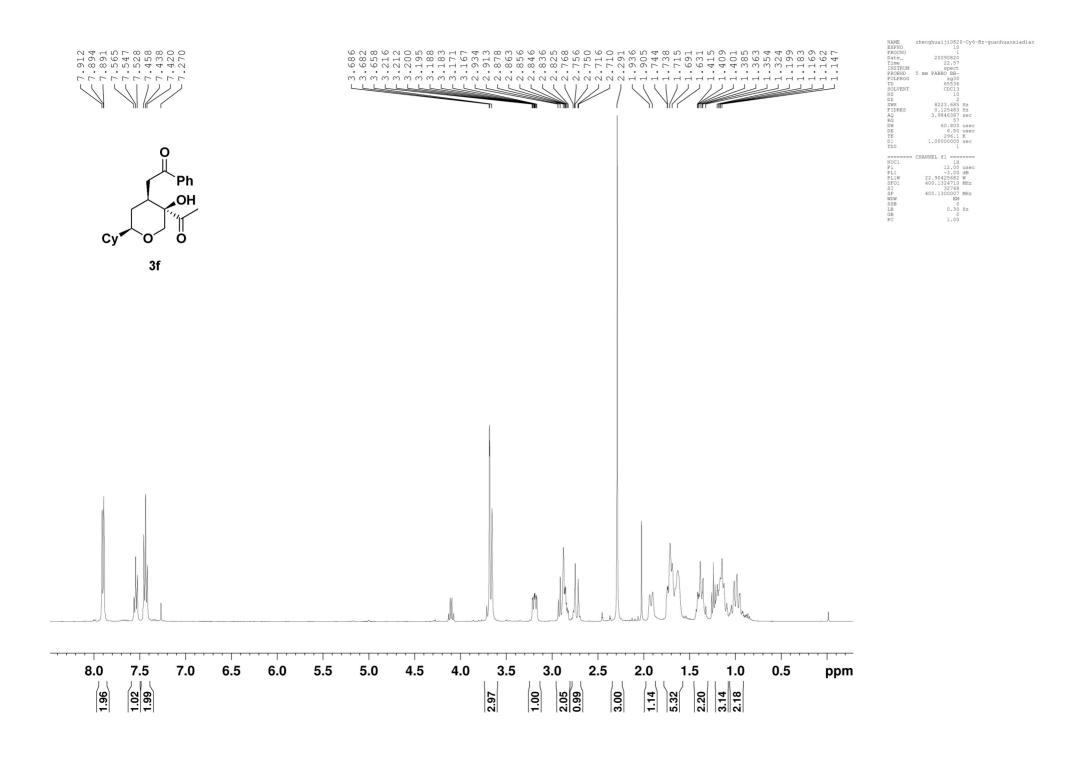


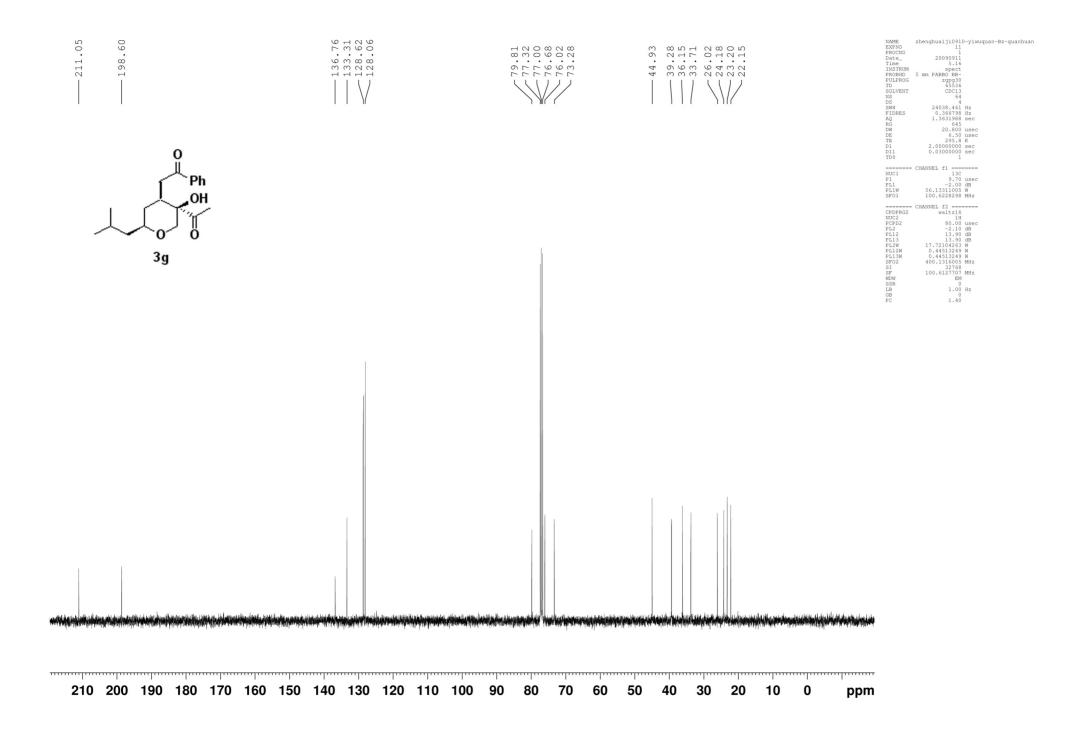


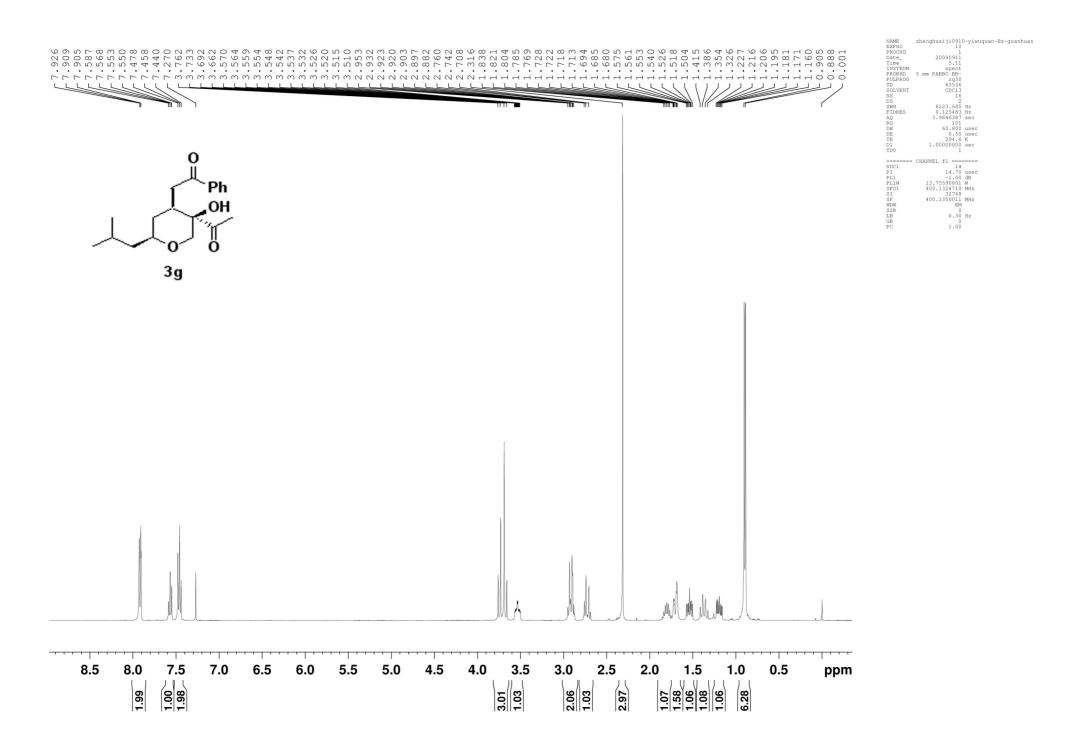


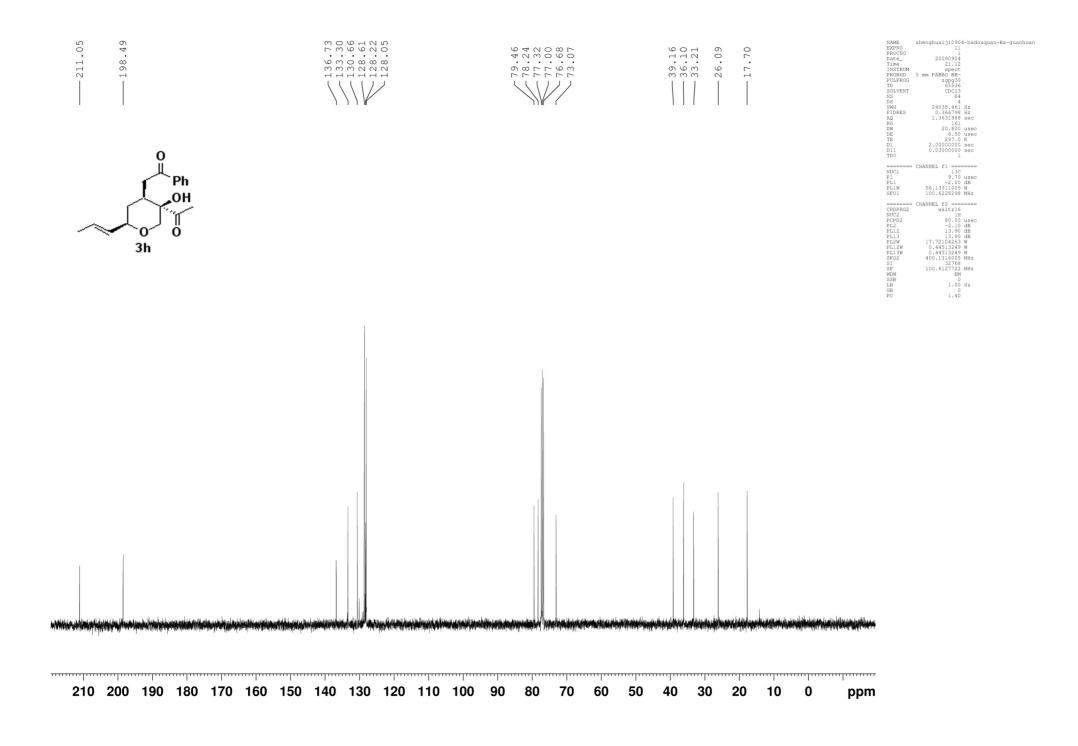


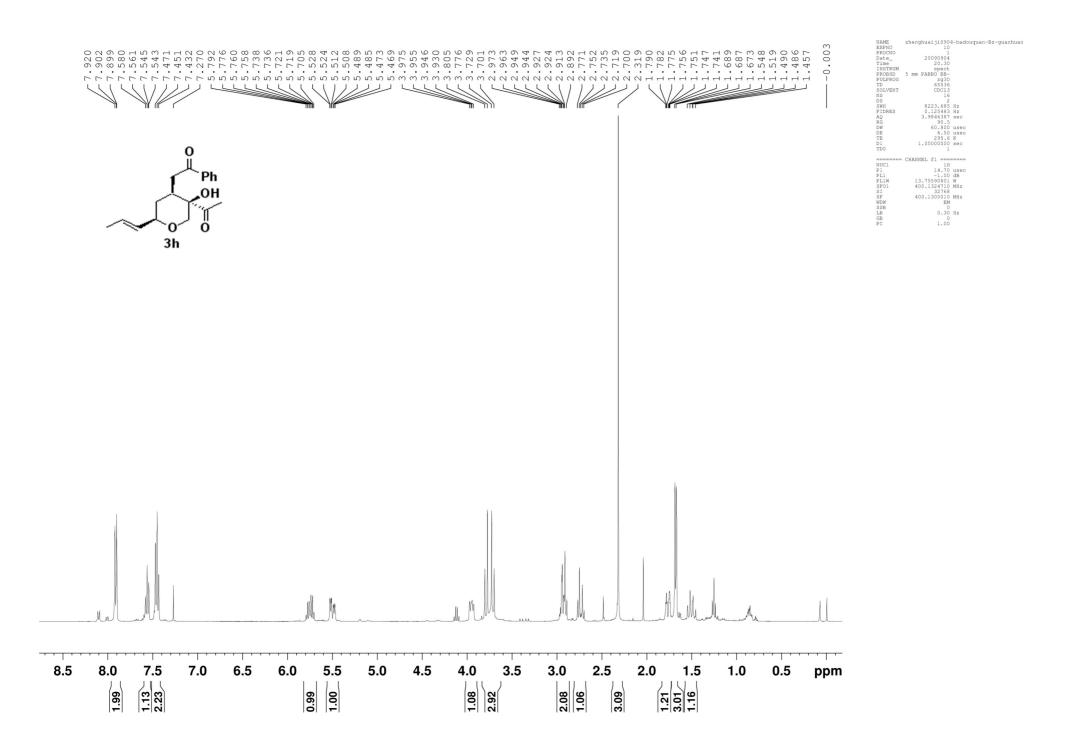


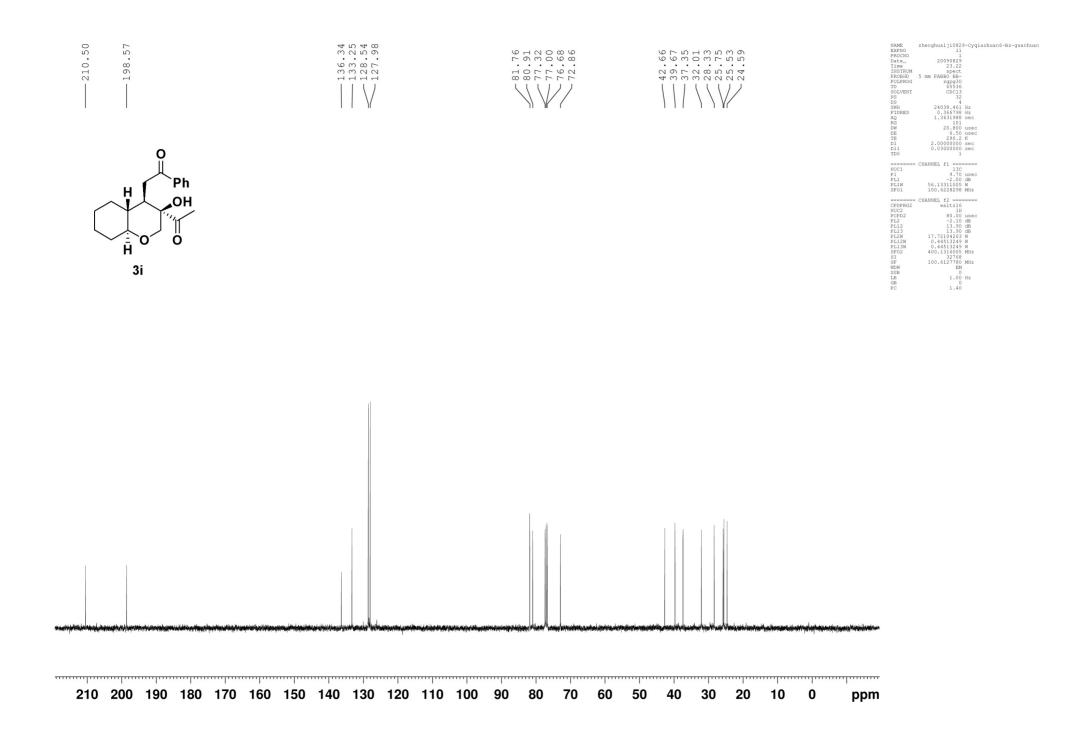


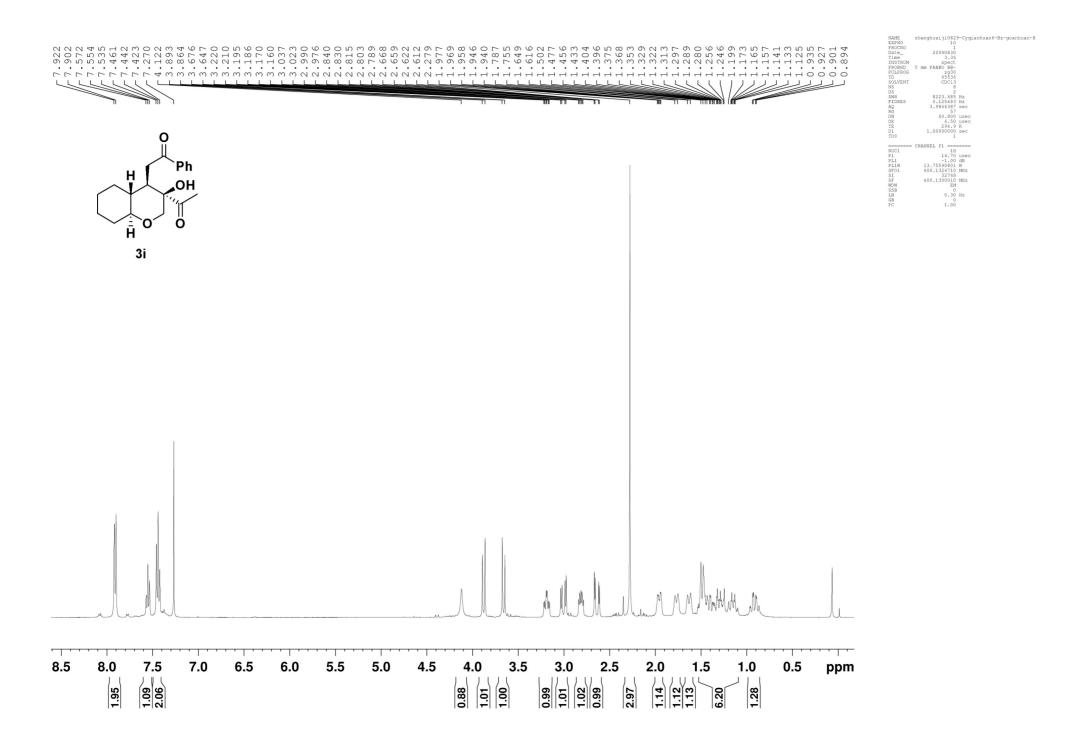


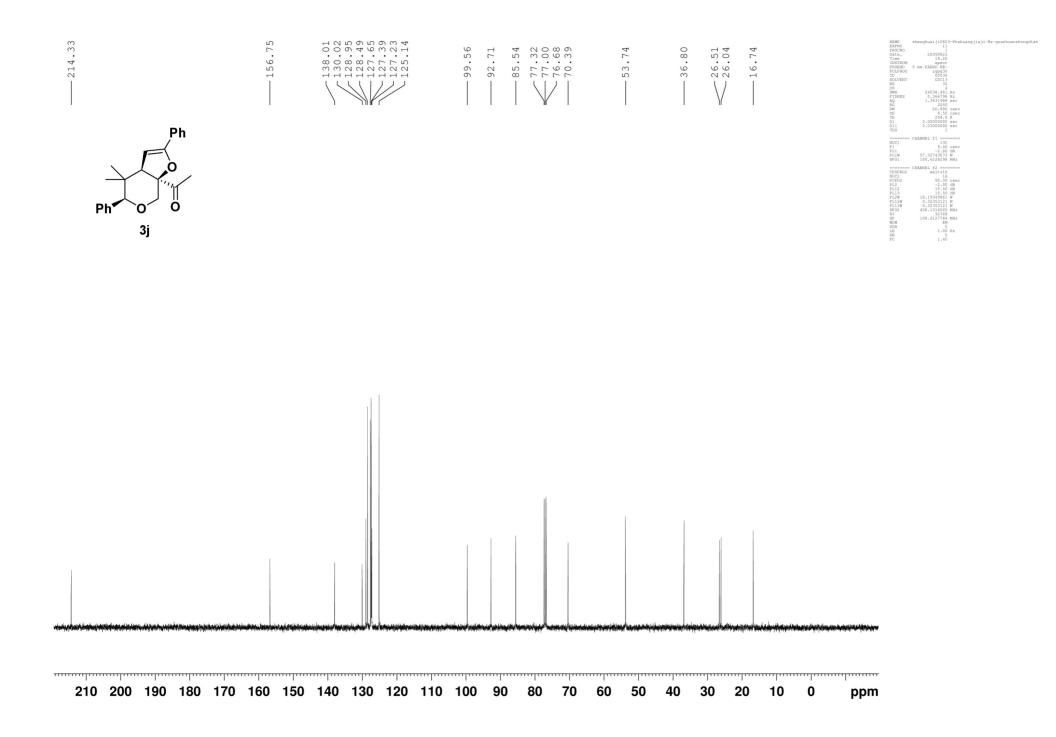


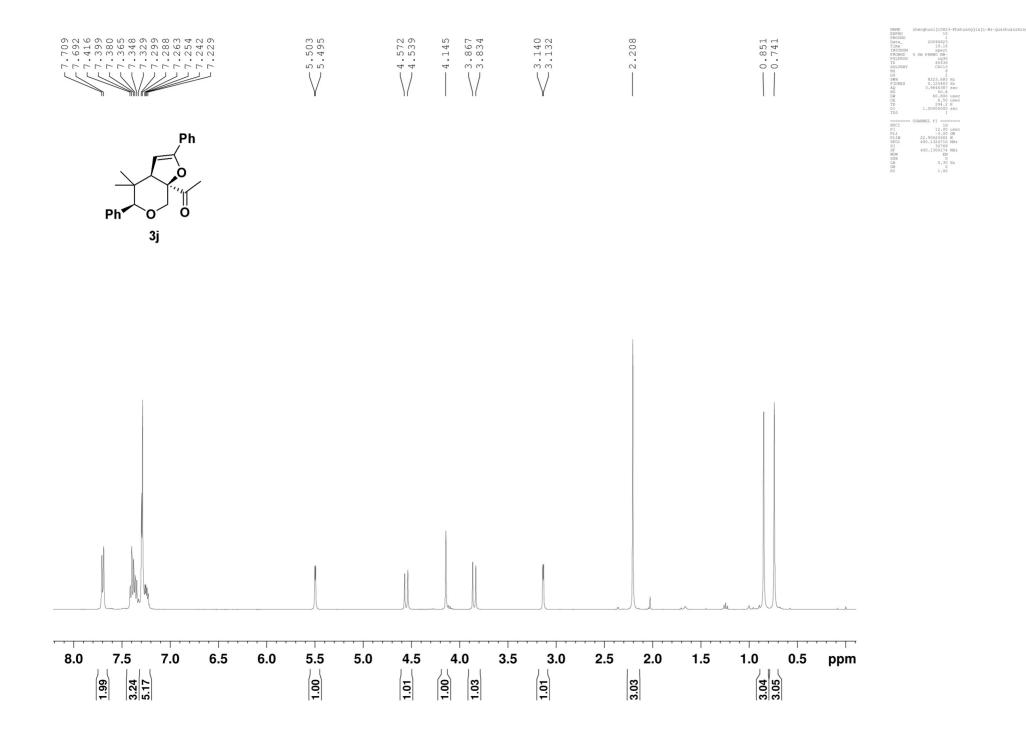


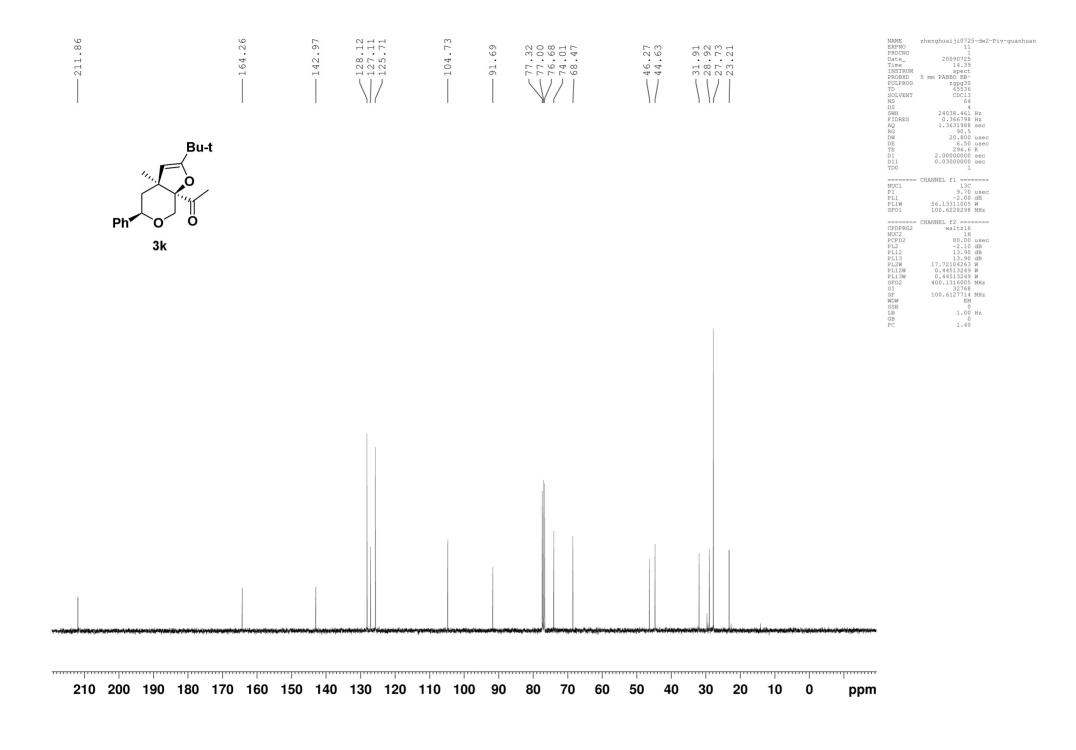


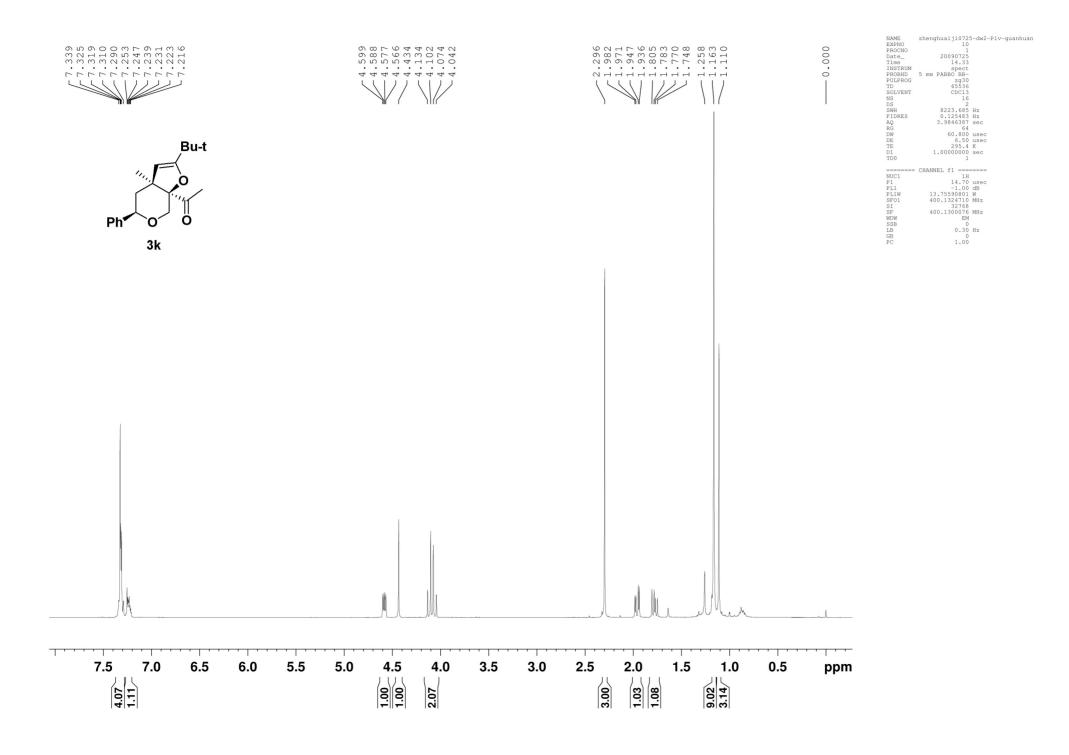


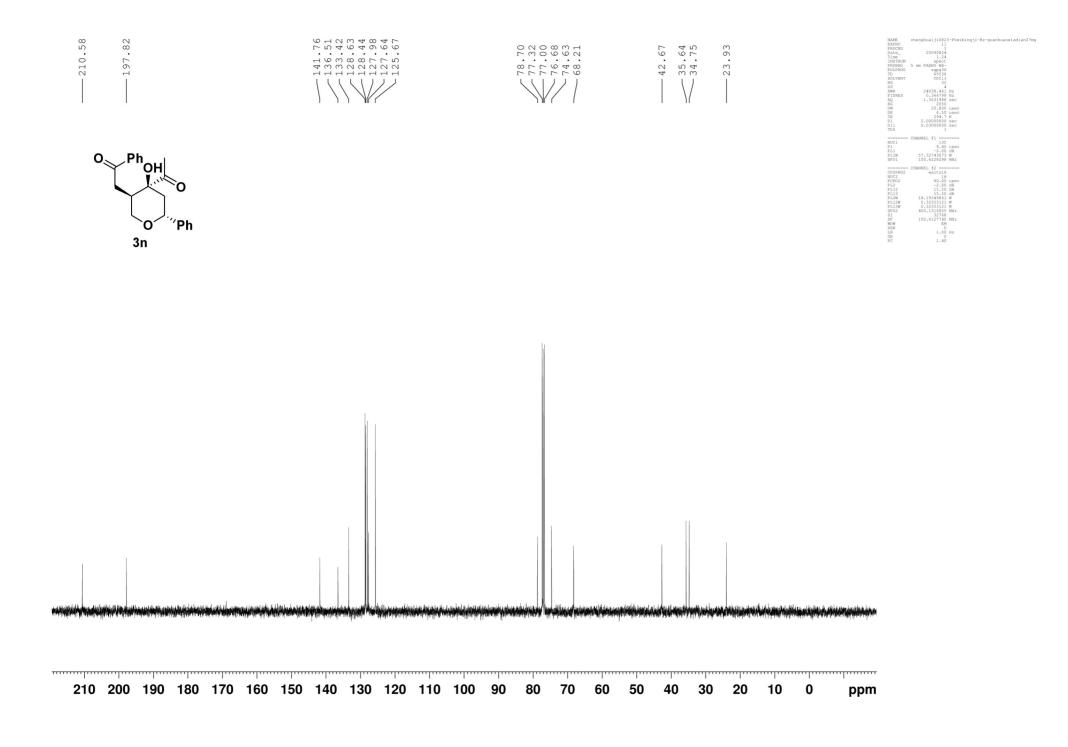


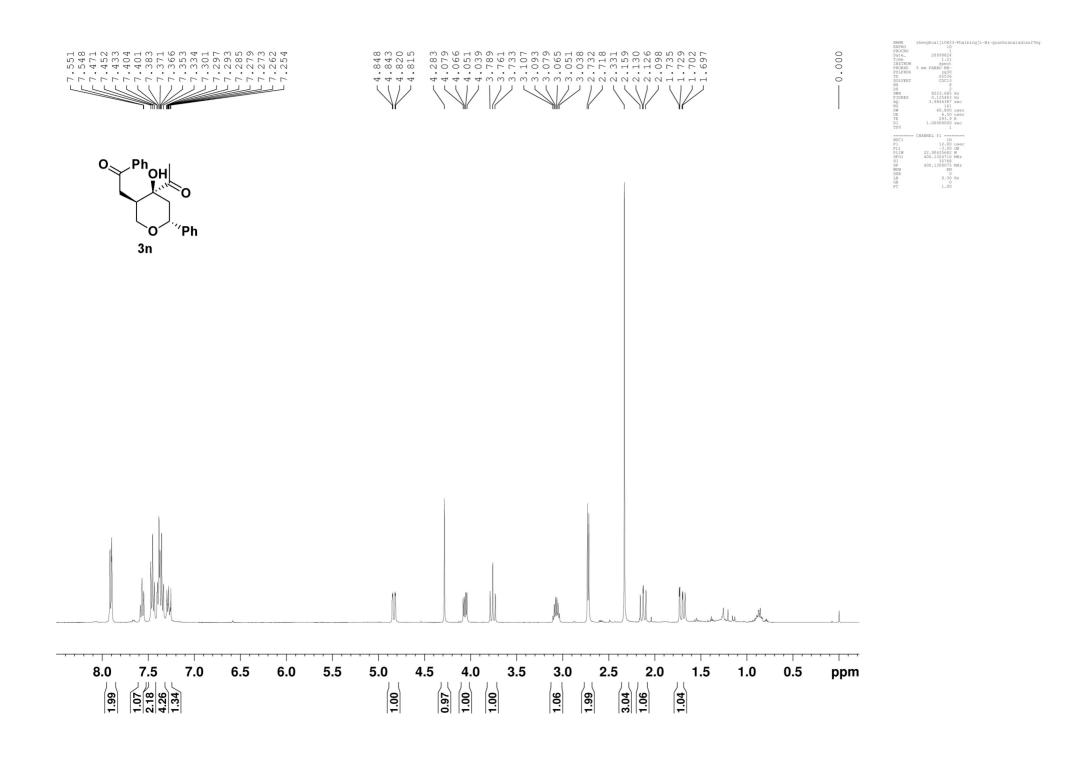


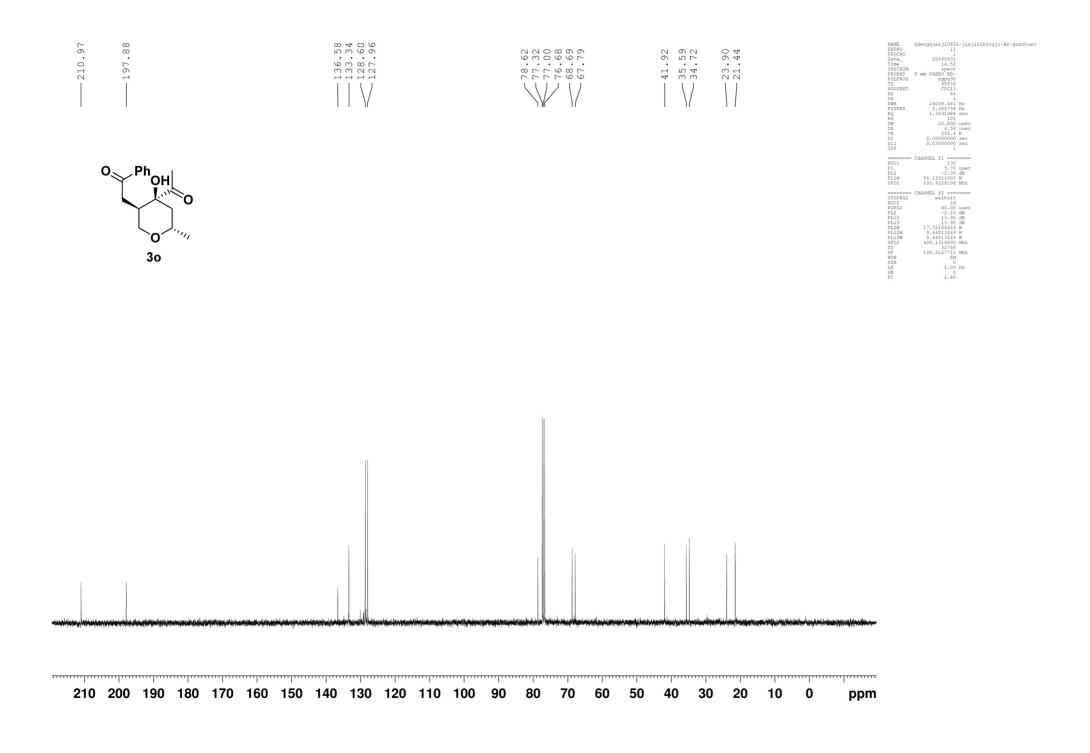


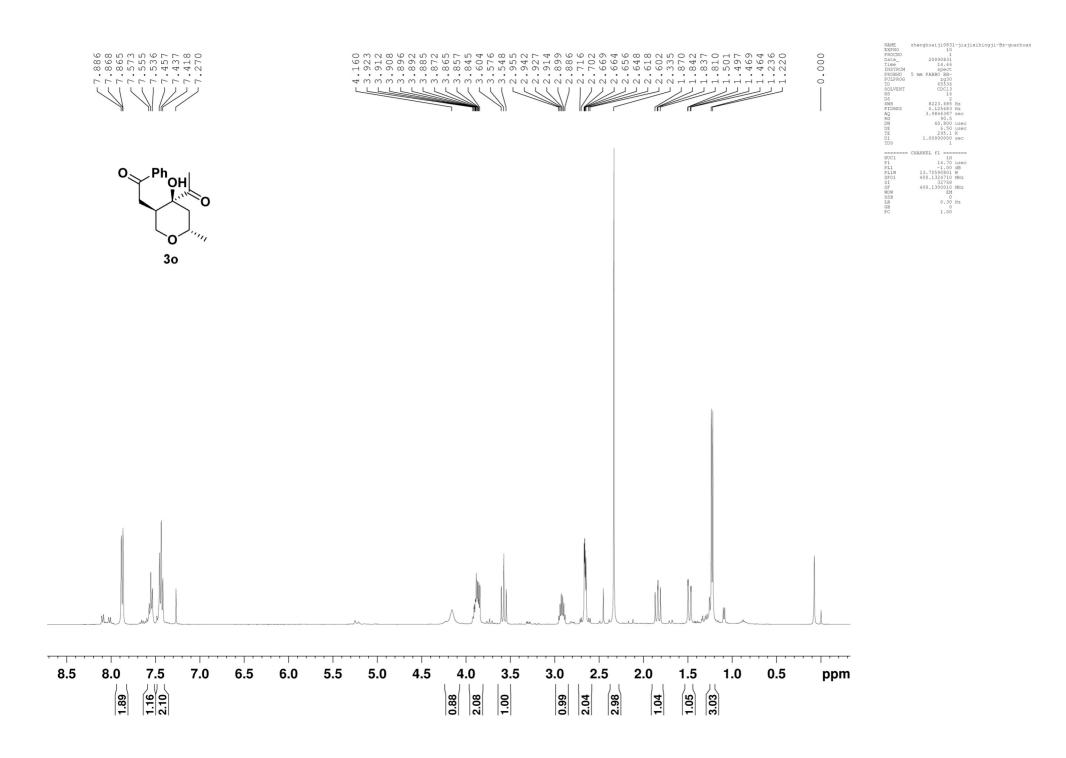


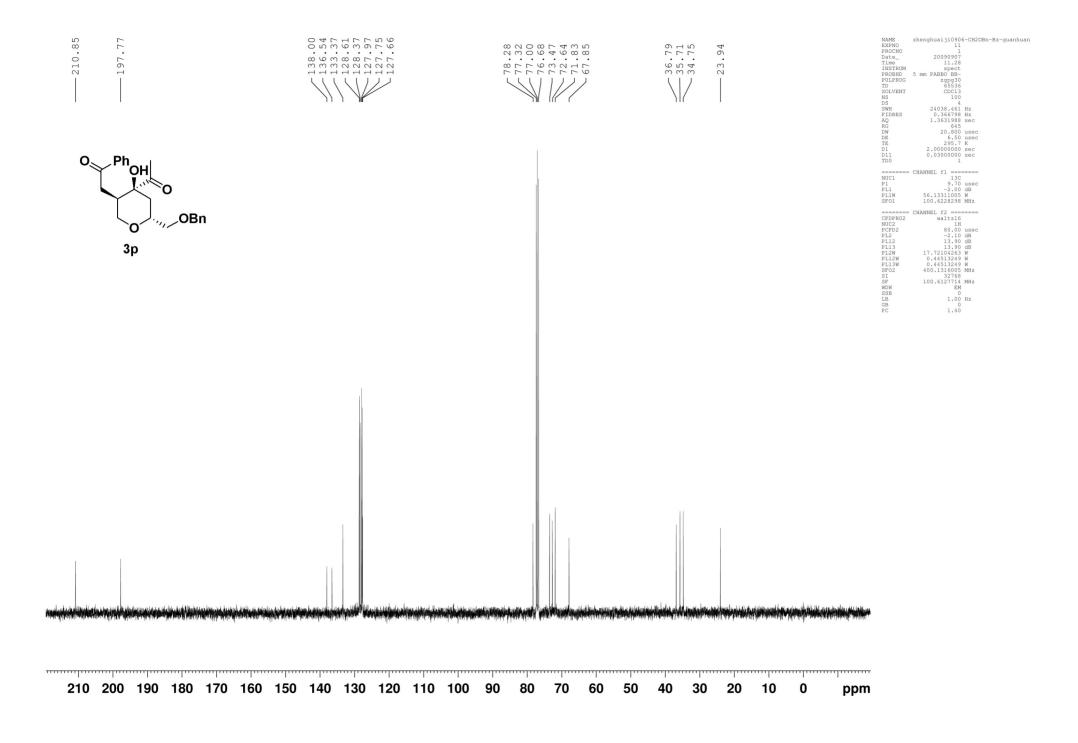


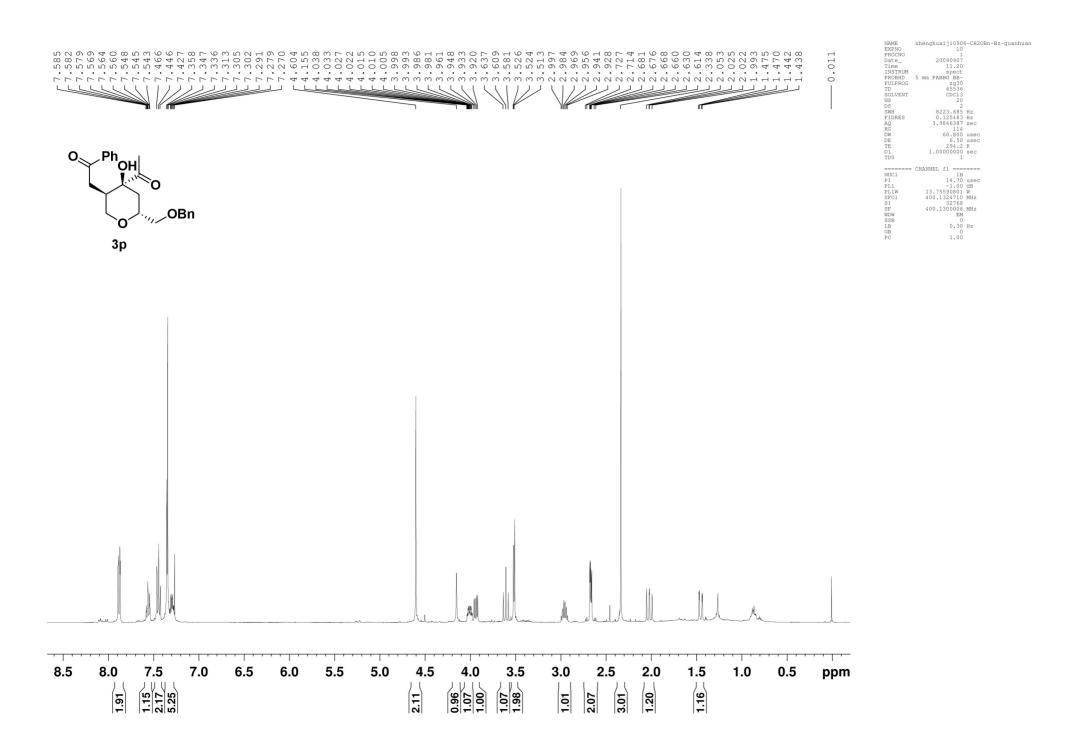


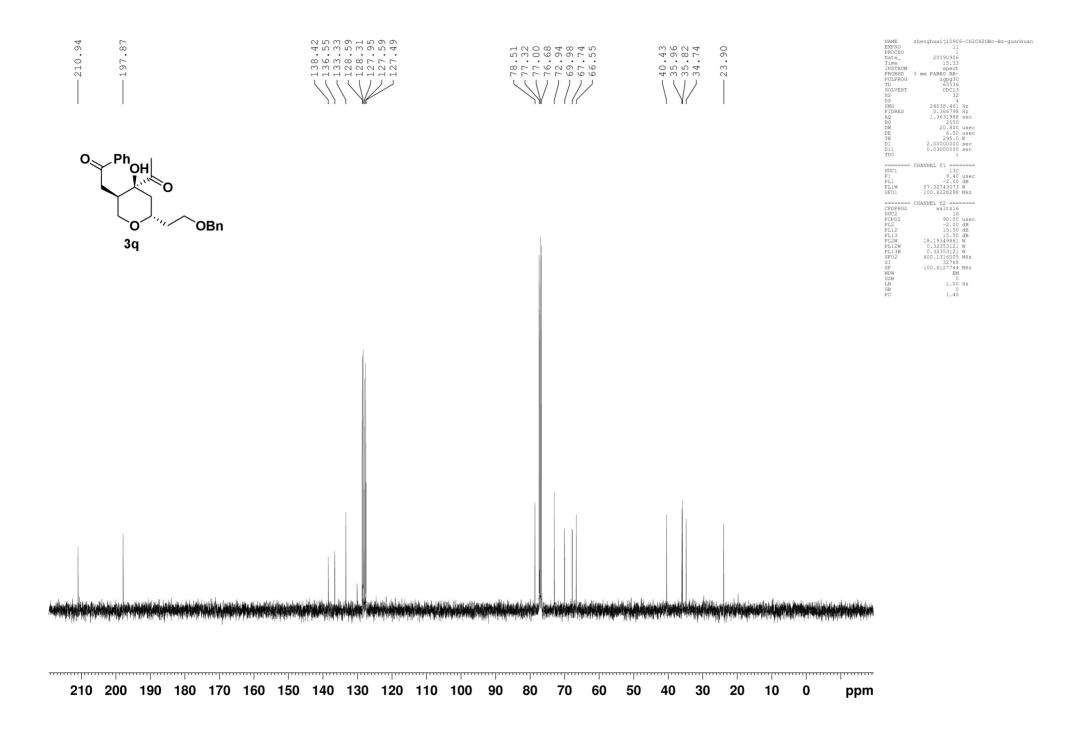


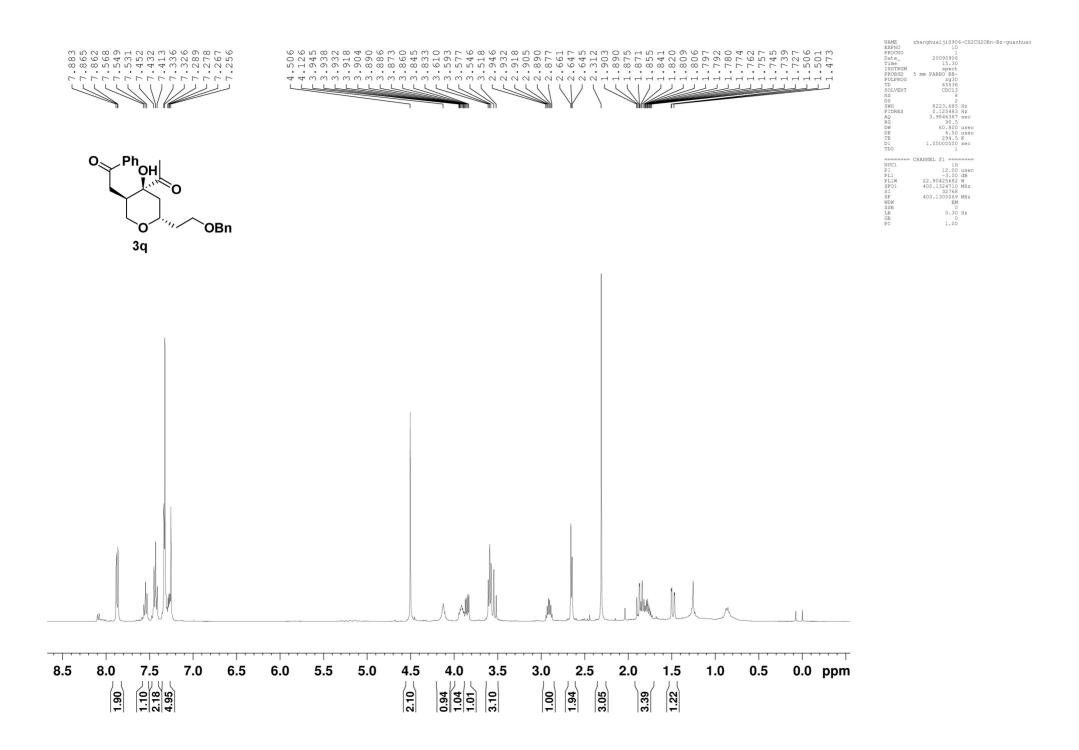


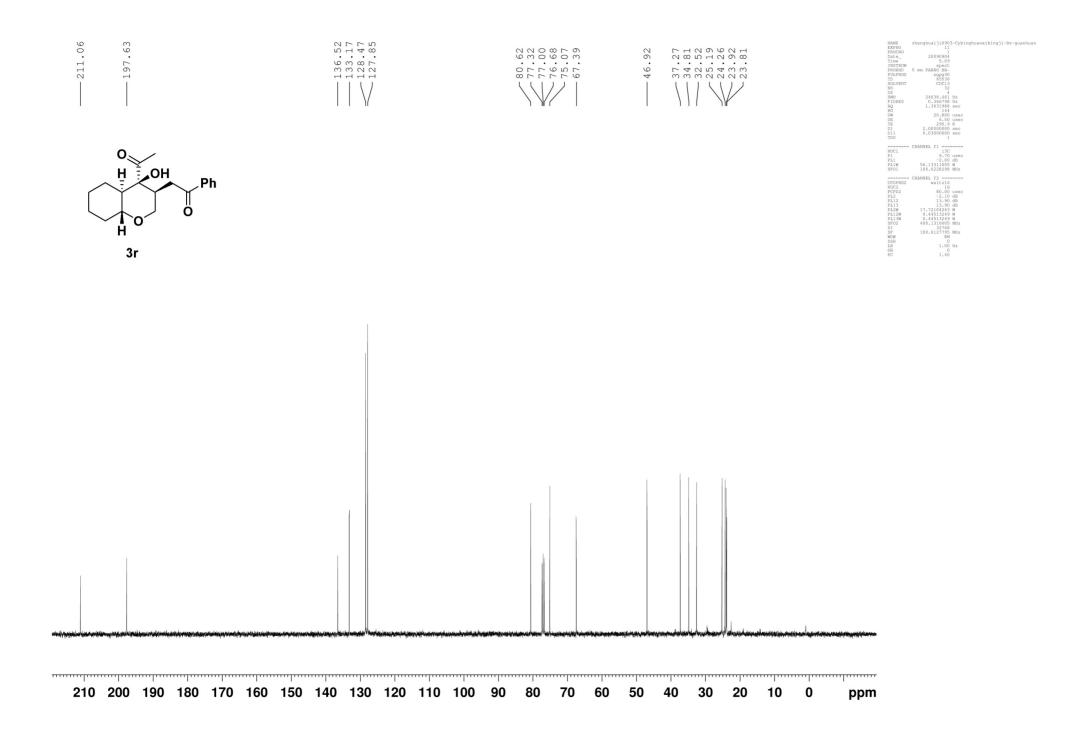


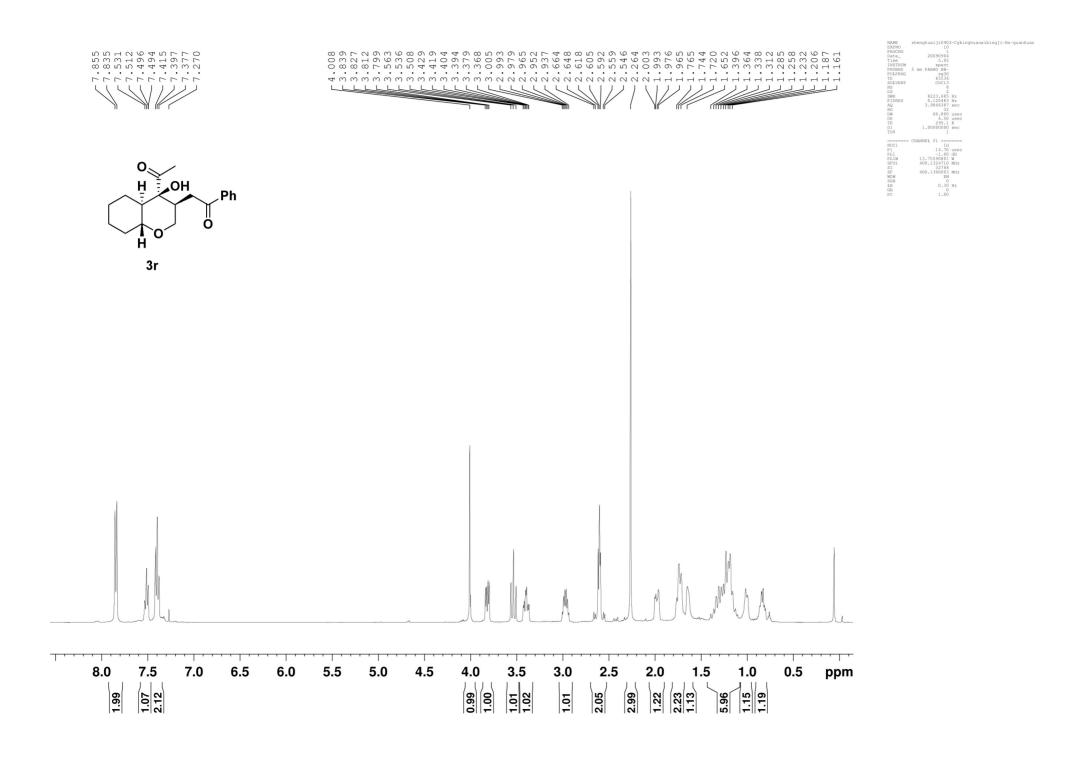


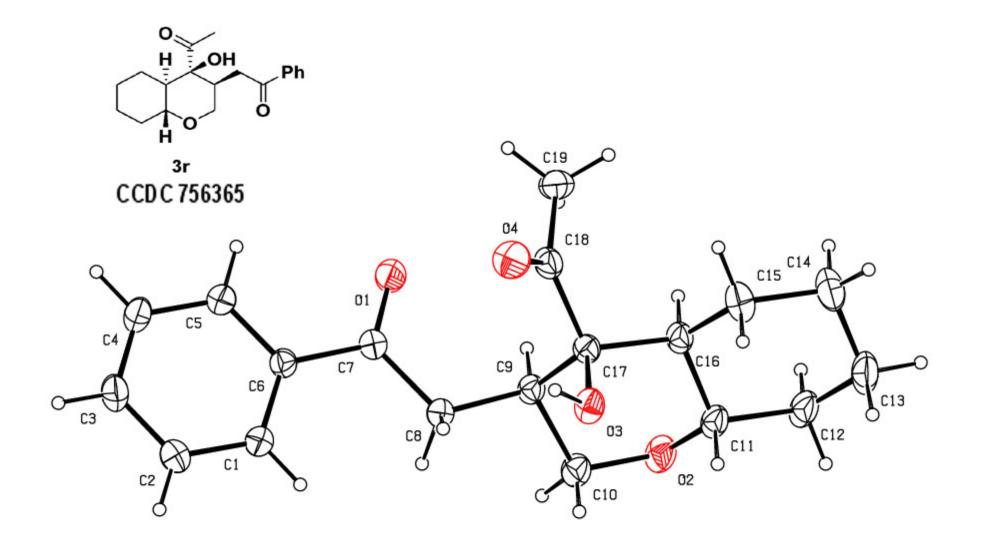


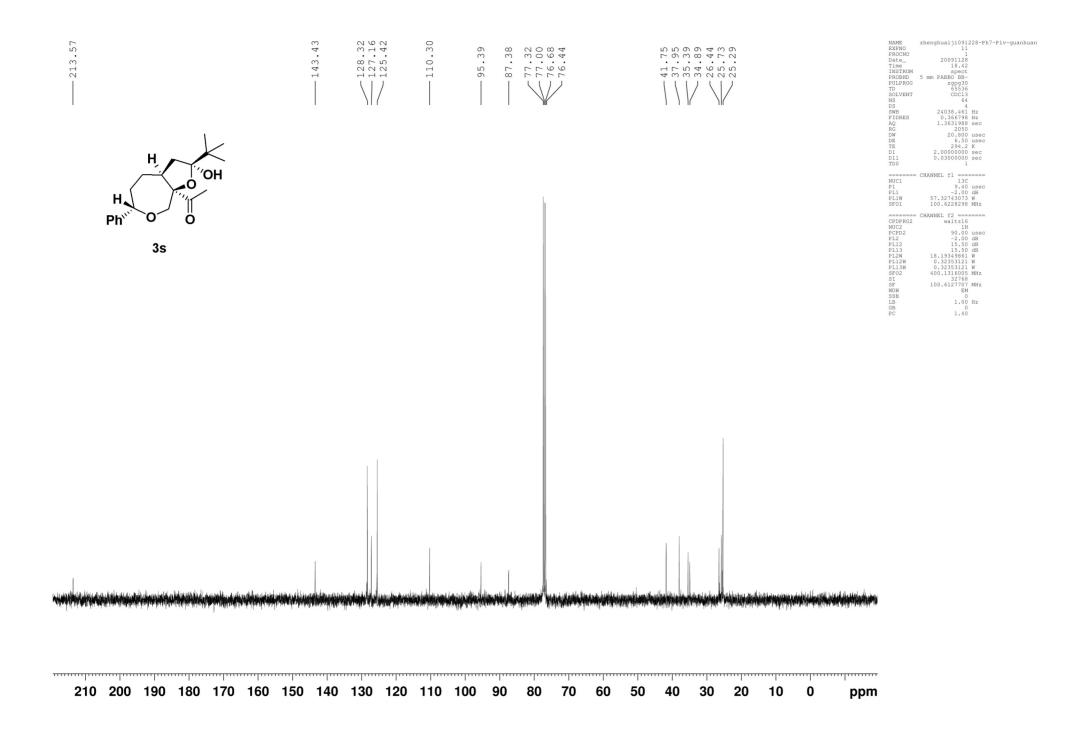


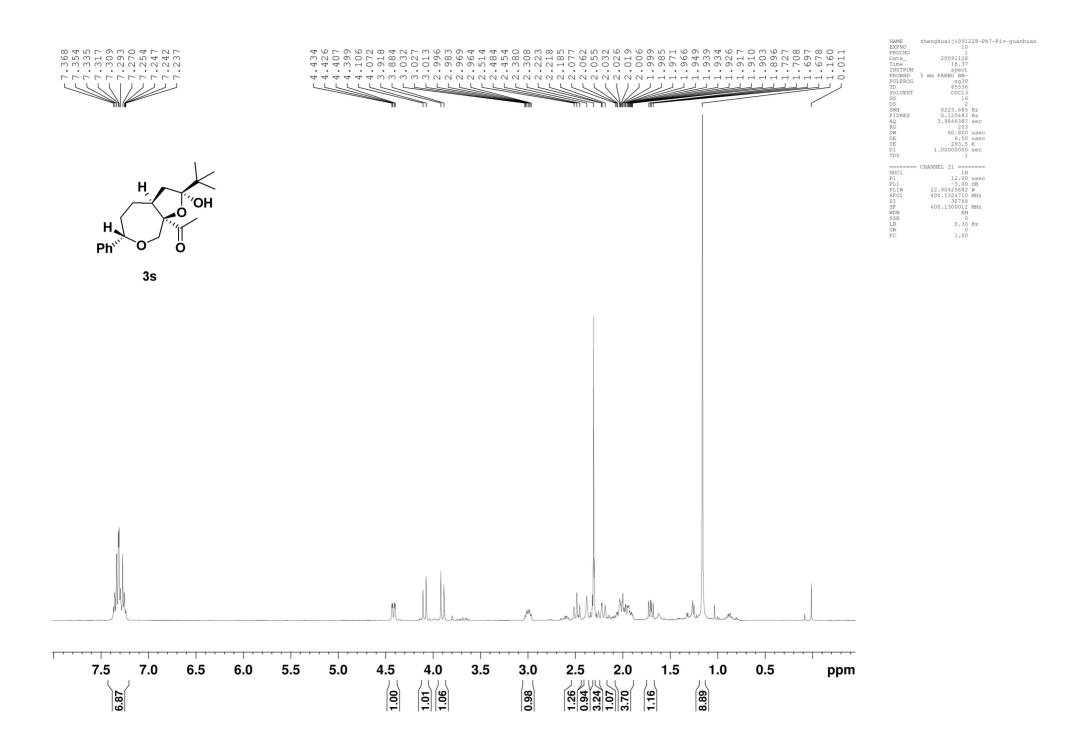


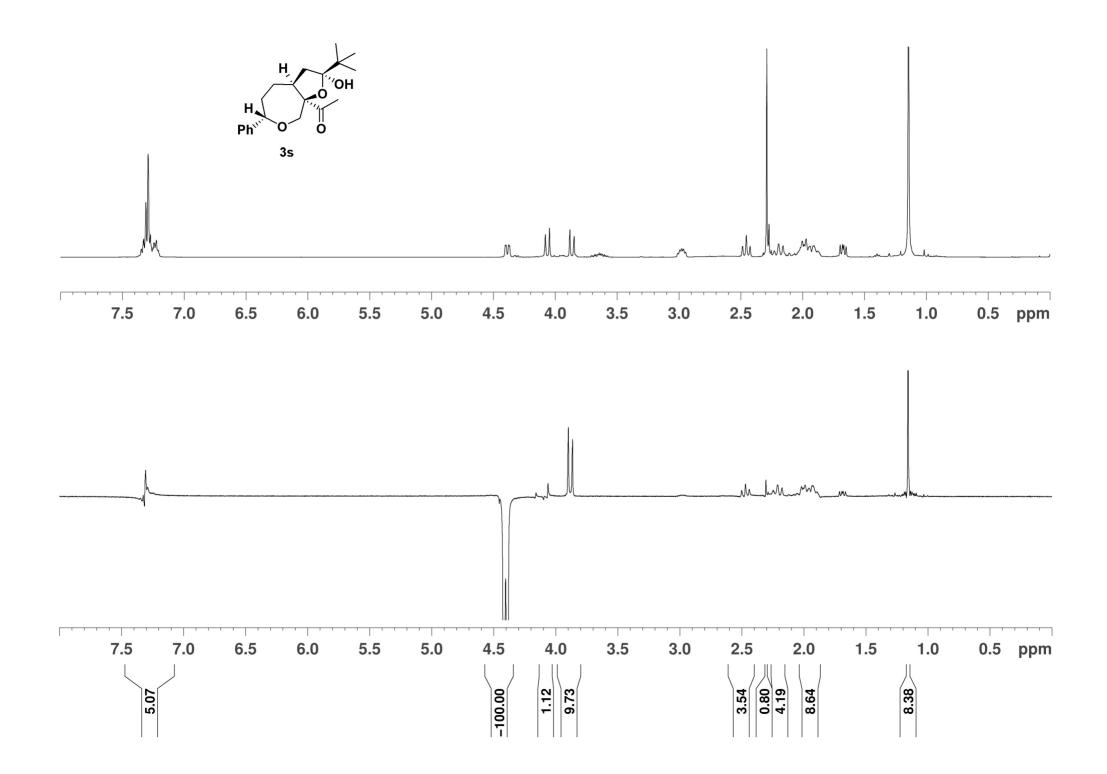


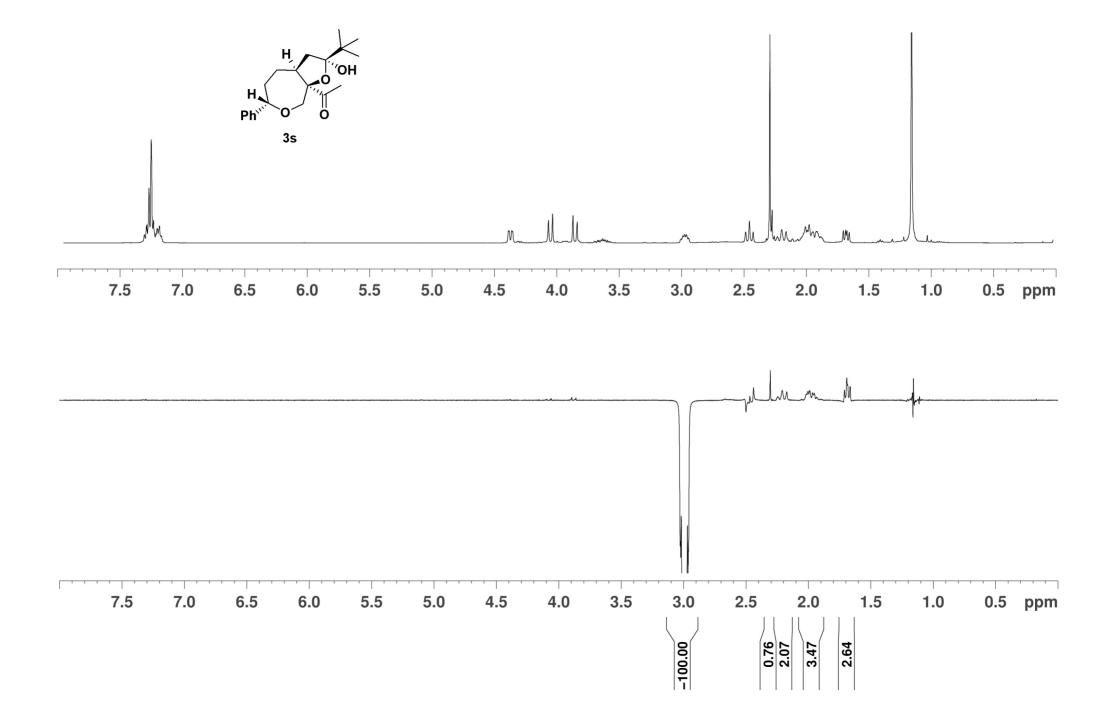


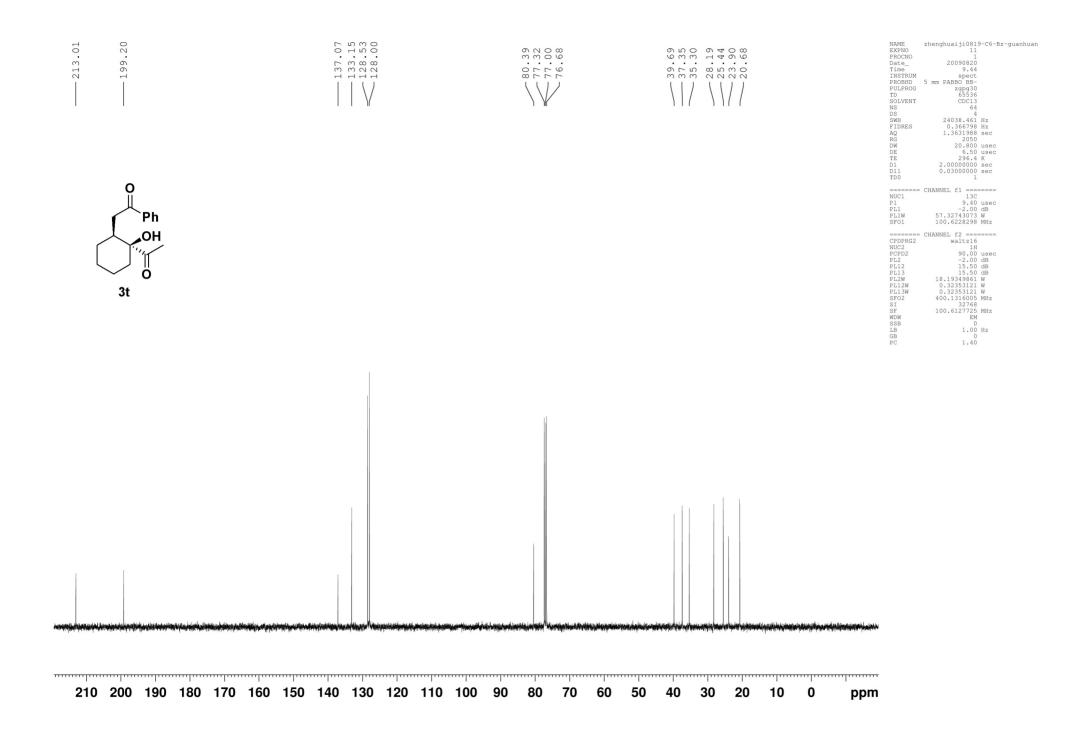


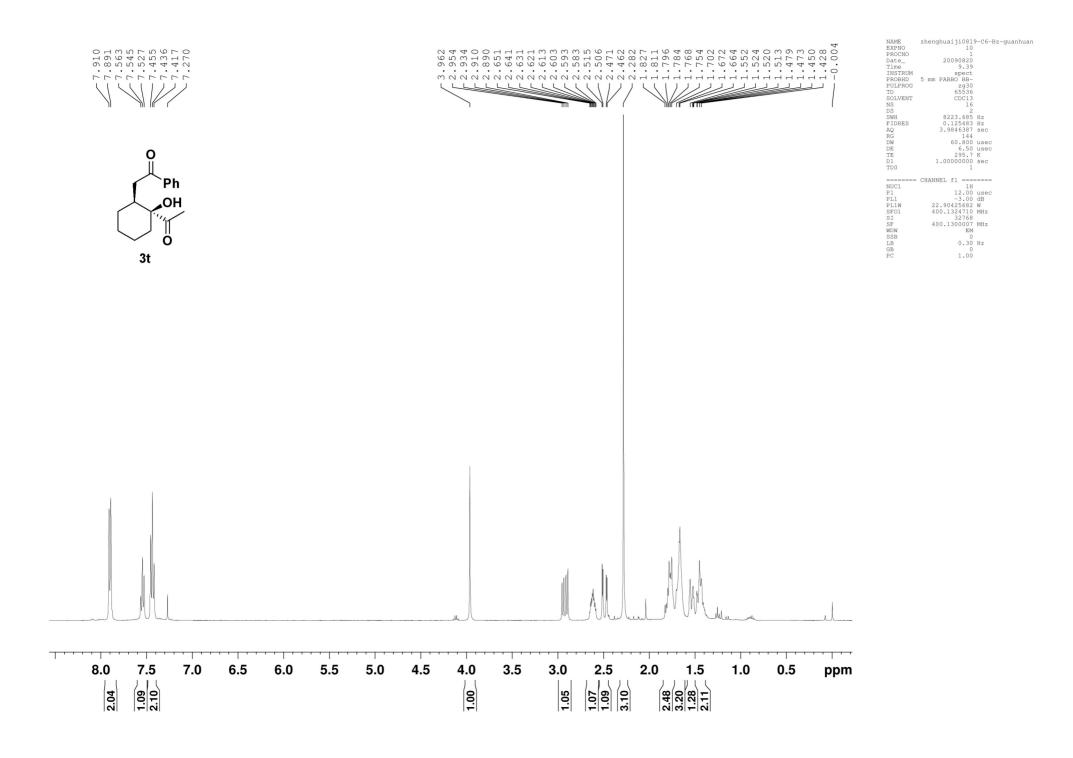












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