

Supplementary Material

Chiral N-aryl tert-butanefulfonamide-olefin ligands for rhodium-catalyzed asymmetric 1,4-addition

Shuai Yuan, Qingle Zeng,* Jiajun Wang, Lihong Zhou

State Key Laboratory of Geohazard Prevention and Geoenvironment Protection (Chengdu University of Technology), College of Materials, Chemistry & Chemical Engineering, Chengdu University of Technology, 1#, Dongsanlu, Erxianqiao, Chengdu 610059, Sichuan, P. R. China

E-mail: qinglezeng@hotmail.com; qlzeng@cdut.edu.cn

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General

All reactions were carried out under an argon atmosphere. All glassware used was dried in electric oven at 120 °C. All chemicals were purchased from Aldrich, Alfa Aesar, Adamas, Aladdin, and Chengdu Changzheng Chemical Company and used as received. Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. All compounds were characterized by ¹H NMR, ¹³C NMR, HR-MS and IR spectroscopy, unless otherwise mentioned. Nuclear magnetic resonance spectra were recorded on a 300MHz instrument or 400 MHz instrument. All ¹H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), DMSO (2.50 ppm) or acetone (2.05 ppm) in the deuterated solvent, unless otherwise stated. All ¹³C NMR spectra are reported in ppm relative to deuteriochloroform (77.2 ppm), DMSO-d₆ (39.5 ppm) or acetone-d₆ (206.7 ppm for C=O) unless otherwise stated, and all were obtained with ¹H decoupling. All IR spectra were taken on an infrared spectrometer. High-resolution mass spectra are recorded on an LCMS-IT-TOF instrument. Chiral HPLC analyses were performed on a Shimadzu liquid chromatography with a Chiralcel OD-H, AD-H, AS-H chiral column (4.6 mm × 250 mm × 5 μm). All rotation data are recorded on an auto rotation (Na D line, cell long 10 cm, λ = 589 nm).

Procedure of synthesis of chiral ligands L1 to L4

An oven-dried round-bottom flask with a magnetic stir bar and fitted with a rubber septum, was charged with (R)-tert-butanesulfonamide (13.0 mmol), Pd₂(dba)₃ (0.26 mmol), tBu-XPhos (0.45 mmol), NaOH (26 mmol), bromobenzene (10.0 mmol), toluene (20 mL), and degassed water (3.0 mL). The vessel was evacuated and backfilled with argon for three times. The solution was stirred at 90 °C for 20 h. when cooled to room temperature, quenched by water, and extracted with ethyl acetate (35 mL) for three times. The combined organic layer was dried over anhydrous MgSO₄. The filtrate was condensed under vacuum. The resulting residual was purified with silica gel column chromatography with a solution of petroleum ether and ethyl acetate (5:1 (v:v)) as an eluent to afford N-aryl tert-butanesulfonamide.

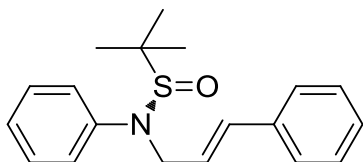
To an oven-dry round-bottom flask with a magnetic stir bar was added N-phenyl (R)-tert-butanesulfonamide (4.0 mmol), 60% NaH (8 mmol), and THF (15 mL). The vessel was evacuated and backfilled with argon for three times. Then the mixture was stirred in an ice water bath for 1 h, and then added cinnamyl bromide (1.2 mmol) by syringe to the flask. The reaction mixture was stirred overnight. Then quenched by saturated NH₄Cl solution, the reaction mixture was extracted with ethyl acetate (20 mL) three times. The combined organic layer was washed with saturated NaCl solution and then dried over anhydrous MgSO₄. The filtrate was condensed under vacuum. The residual was purified with a silica gel column chromatography with a mixed solution of petroleum ether and ethyl acetate (5:1(v:v)) as an eluent to afford (R)-N-cinnamyl-2-methyl-N-phenylpropane-2-sulfonamide (**L2**).

Chiral ligands **L1**, **L3**, **L4** adopted the same synthetic methods as **L2**.

Procedure of rhodium-catalyzed 1,4-addition reaction

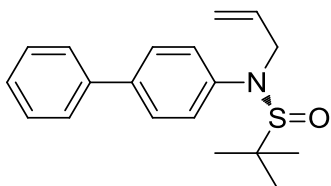
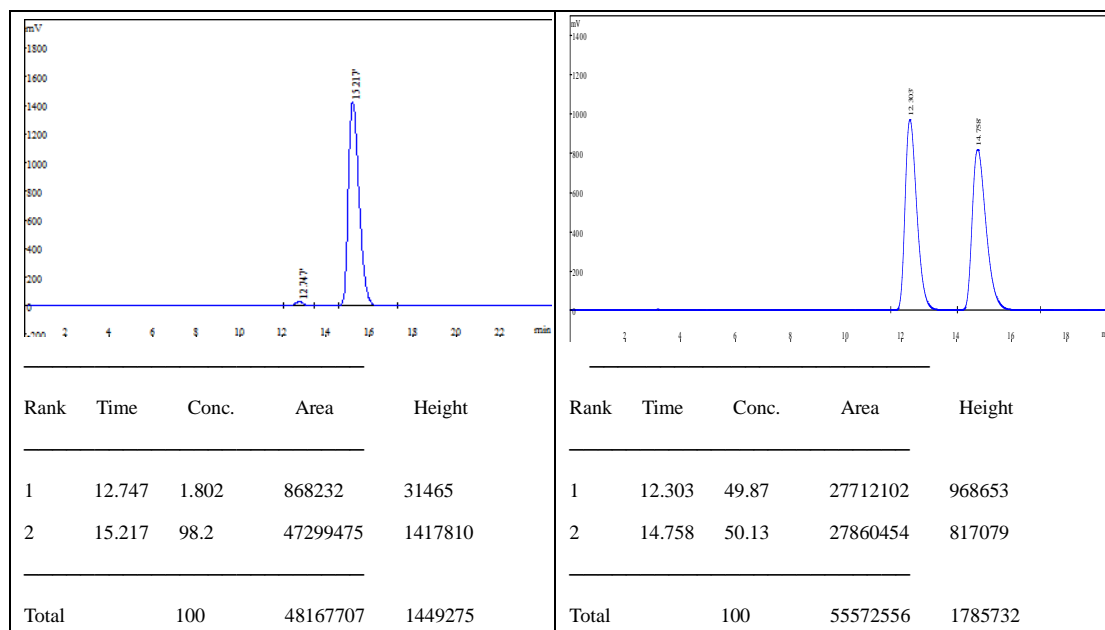
To an oven-dry test tube with a ground joint neck with a magnetic stir bar were added enone (1.00 mmol), arylboronic acid (1.5 mmol), [RhCl(C₂H₄)₂]₂ (0.015 mmol), Ligand (0.035 mmol) in 1,4-dioxane (3.0 mL). The vessel was evacuated and backfilled with argon for three times. The solution was stirred at 40 °C for 30 min, and then aqueous K₃PO₄ (0.5 mmol) was added by syringe to the flask. After being stirred at 40 °C for 3 h, the reaction mixture was then cooled to room temperature, quenched by water, and extracted with ethyl acetate (15 mL) for three times. The combined organic layer was dried over anhydrous MgSO₄. The filtrate was condensed in vacuum. The residual was purified with silica gel column chromatography with a solution of petroleum ether and ethyl acetate as an eluent to afford the product. The ee was determined by chiral HPLC.

Spectral data of Chiral Ligands

**(R)-N-cinnamyl-2-methyl-N-phenylpropane-2-sulfinamide (L2)**

White solid. Yield: 25.3 mg (81%). Mp. 94-97 °C. $[\alpha]_D^{20.5} +105^\circ$ (c 0.21, CH₂Cl₂). **¹H NMR** (400 MHz, DMSO-d₆) δ 7.43 – 7.39 (m, 2H), 7.35 – 7.21 (m, 4H), 7.07 (dd, J = 16.2, 8.0 Hz, 2H), 6.58 (dt, J = 14.4, 7.6 Hz, 4H), 6.36 (dt, J = 16.0, 5.6 Hz, 1H), 3.89 – 3.81 (m, 2H), 1.05 (s, 7H). **¹³C NMR** (101 MHz, DMSO-d₆) δ 137.19 (s), 136.68 (s), 132.66 (s), 129.51 (s), 129.34 (s), 129.08 (s), 128.07 (s), 126.60 (d, J = 6.9 Hz), 116.49 (s), 112.95 (s), 59.99 (s), 55.73 (s), 23.44 (s). **IR** (KBr), ν (cm⁻¹): 3056, 3025, 2936, 1655, 1592, 1472, 1363, 1298, 1246, 1176, 1075, 968, 852, 781. **ESI-MS** (positive mode), m/z = 336 [M + Na]⁺. **HR-MS** (ESI-TOF) m/z calcd for C₁₉H₂₃NNaOS [M+Na⁺] 336.1393; found 336.1379.

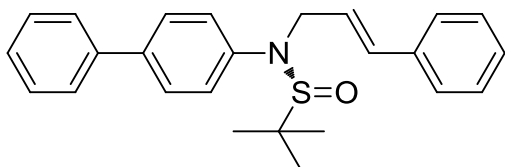
HPLC: Chiralcel OD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 12.7 min (minor), 15.2 min (major). Measured ee value = 97 %.

**(R)-N-([1,1'-biphenyl]-4-yl)-N-allyl-2-methylpropane-2-sulfinamide (L3)**

White solid. Yield: 21.0 mg (80%). Mp. 72-75 °C. $[\alpha]_D^{21.0} +88.98^\circ$ (c 0.12, CH₂Cl₂). **¹H NMR** (400 MHz, CDCl₃) δ 7.59 – 7.51 (m, 4H), 7.45 – 7.40 (m, 2H), 7.32 (ddt, J = 9.5, 8.2, 4.1 Hz, 1H), 7.25 – 7.21 (m, 2H), 5.88 – 5.76 (m, 1H), 5.25 – 5.12 (m, 2H), 4.38 – 4.25 (m, 1H), 4.14 – 4.00 (m, 1H), 1.26 (d, J = 11.7 Hz, 9H). **¹³C NMR** (101 MHz, DMSO-d₆) δ 141.01 (s),

134.69 (s), 129.38 (s), 129.29 (d, $J = 18.4$ Hz), 129.20 (s), 127.60 (s), 126.74 (s), 126.22 (s), 125.89 (s), 113.35 (s), 60.09 (s), 55.73 (s), 21.50 (s). **IR** (KBr), ν (cm^{-1}): 3050, 2959, 1601, 1519, 1484, 1450, 1364, 1295, 1251, 1204, 1142, 1091, 1055, 995, 918, 827, 757, 692. **ESI-MS** (positive mode), $m/z = 336$ $[\text{M} + \text{Na}]^+$. **HR-MS** (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{23}\text{NOS}$ $[\text{M} + \text{Na}]^+$ 336.1393; found 336.1405.

HPLC: Chiralcel OD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 5.5 min (minor), 10.6 min (major).

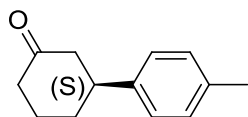


(R)-N-([1,1'-biphenyl]-4-yl)-N-cinnamyl-2-methylpropane-2-sulfinamide (L4)

Yellow solid. Yield: 23.3mg (81%). Mp. 116-119 $^{\circ}\text{C}$. $[\alpha]_{\text{D}}^{21.2} +116.20^{\circ}$ (c 0.14, CH_2Cl_2). **^1H NMR** (400 MHz, CDCl_3) δ 7.59 – 7.49 (m, 4H), 7.44 – 7.38 (m, 2H), 7.30 (ddd, $J = 8.8, 7.4, 2.0$ Hz, 6H), 7.21 (ddd, $J = 6.8, 3.8, 1.6$ Hz, 1H), 6.51 (d, $J = 16.0$ Hz, 1H), 6.19 (dt, $J = 16.0, 5.9$ Hz, 1H), 4.45 (ddd, $J = 16.8, 6.2, 1.5$ Hz, 1H), 4.24 (ddd, $J = 16.8, 5.6, 1.5$ Hz, 1H), 1.28 (d, $J = 11.9$ Hz, 8H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 139.88 (s), 137.18 (s), 136.66 (s), 135.07 (s), 132.66 (s), 129.36 (s), 129.19 (s), 129.09 (s), 128.09 (s), 127.66 (t, $J = 13.6$ Hz), 126.70 (d, $J = 5.3$ Hz), 126.59 (s), 125.86 (s), 113.17 (s), 60.17 (s), 55.73 (s), 23.44 (s). **IR** (KBr), ν (cm^{-1}): 3041, 2938, 1602, 1519, 1486, 1364, 1305, 1254, 1203, 1083, 1050, 962, 845, 733, 694. **ESI-MS** (positive mode), $m/z = 412$ $[\text{M} + \text{Li}]^+$. **HR-MS** (ESI-TOF) m/z calcd for $\text{C}_{25}\text{H}_{27}\text{NNaOS}$ $[\text{M} + \text{Na}]^+$ 412.1706; found 412.1715.

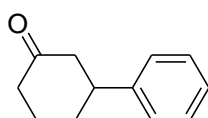
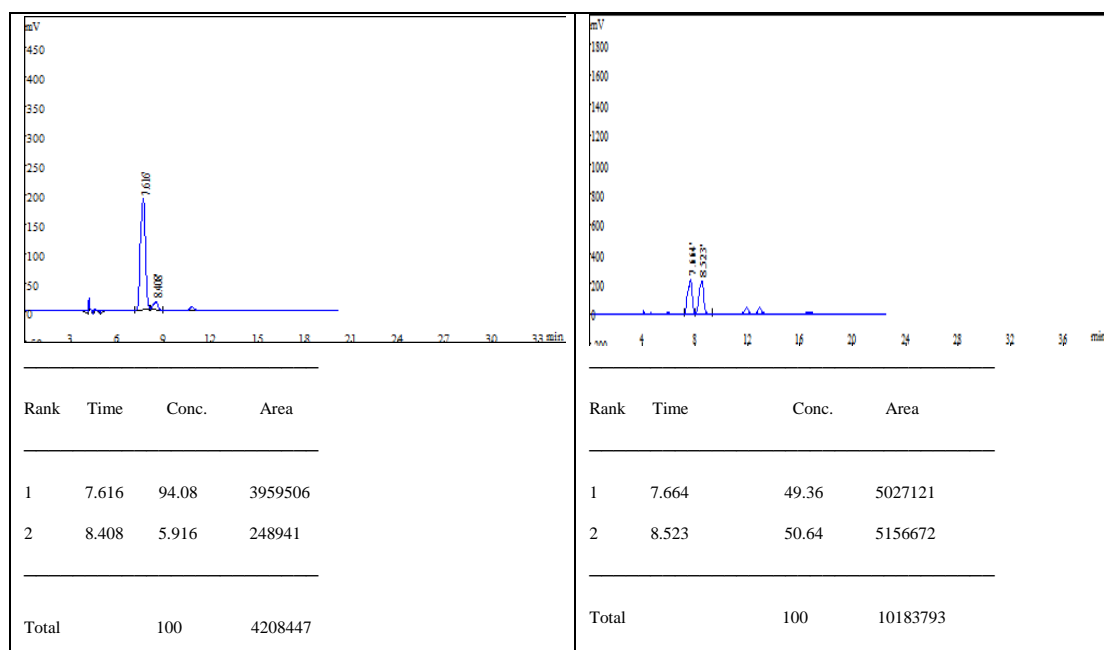
HPLC: Chiralcel OD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 15.3 min (minor), 20.3 min (major).

Spectral data and chiral HPLC traces of measured reaction products

**(S)-3-(p-Tolyl)cyclohexanone** [1]

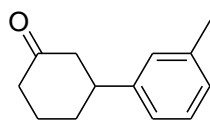
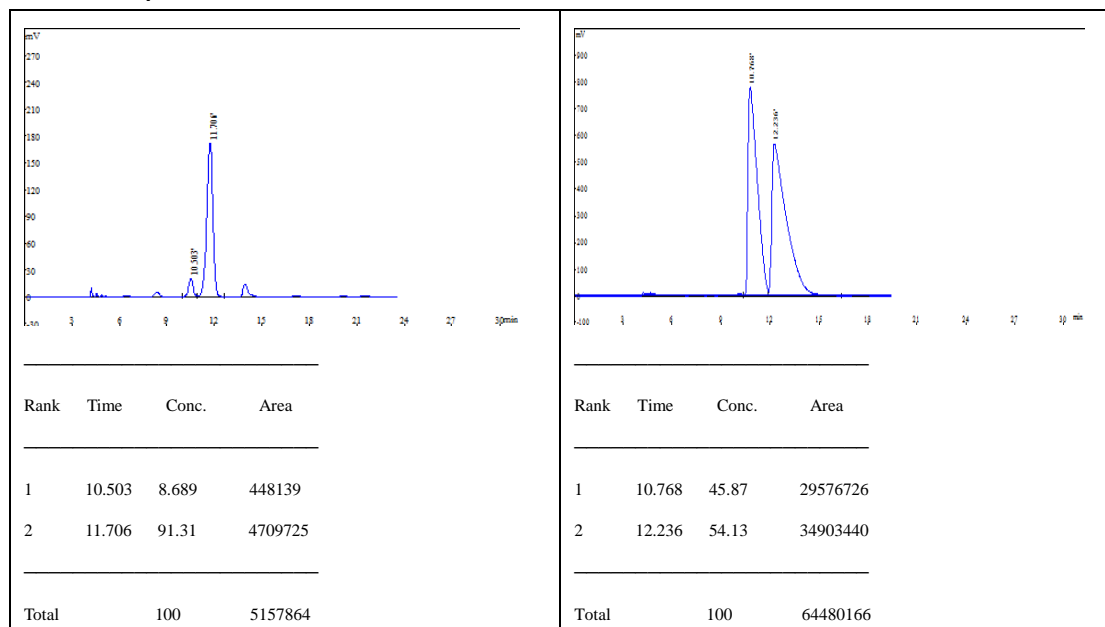
3a: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31 – 7.22 (m, 4H), 3.11 (tt, $J = 11.6, 4.0$ Hz, 1H), 2.75 – 2.66 (m, 1H), 2.66 – 2.49 (m, 3H), 2.46 (d, $J = 8.5$ Hz, 3H), 2.32 – 2.16 (m, 2H), 2.03 – 1.85 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 211.19 (s), 141.44 (s), 136.27 (s), 129.35 (s), 126.45 (s), 49.09 (s), 44.41 (s), 41.21 (s), 32.92 (s), 25.57 (s), 20.99 (s).

HPLC: Chiralpak AD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 7.6 min (major), 8.4 min (minor). Measured ee value = 89 %.

**3-phenylcyclohexanone** [4]

3b: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.29 (m, 2H), 7.26 – 7.19 (m, 3H), 3.00 (tt, $J = 11.7, 4.0$ Hz, 1H), 2.65 – 2.28 (m, 4H), 2.21 – 2.02 (m, 2H), 1.95 – 1.70 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 211.03 (s), 144.37 (s), 128.70 (s), 126.71 (s), 126.59 (s), 48.96 (s), 44.76 (s), 41.21 (s), 32.80 (s), 25.56 (s).

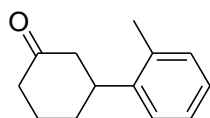
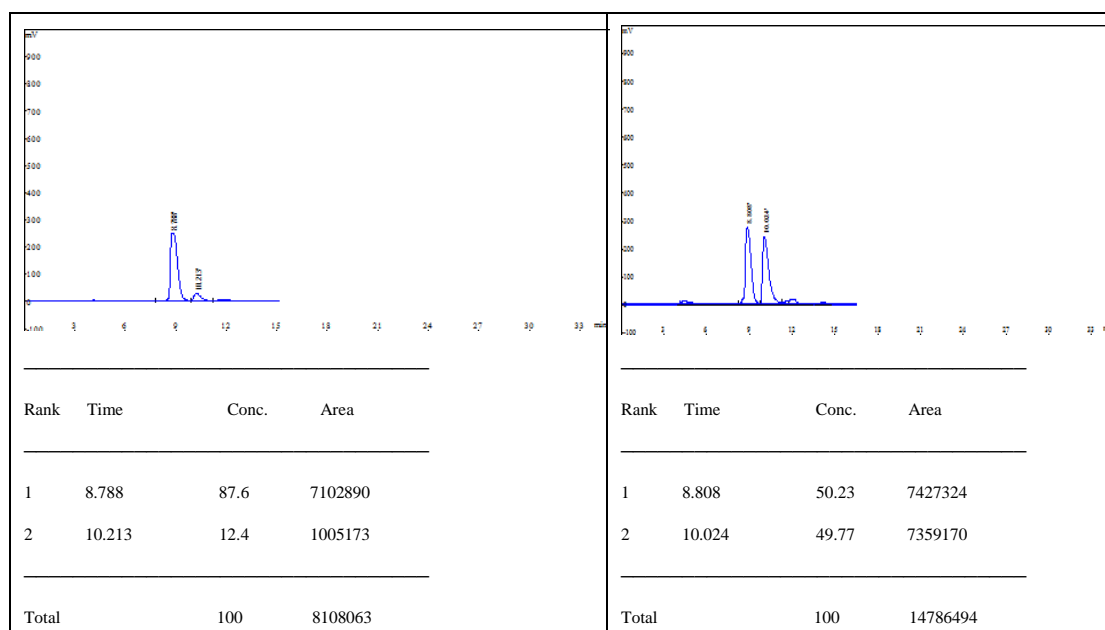
HPLC: Chiralpak AD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 10.5 min (minor), 11.7 min (major). Measured ee value = 83 %.



3-(3-methylphenyl)cyclohexanone [2]

3c: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.23 (dd, $J = 14.7, 7.1$ Hz, 1H), 7.04 (t, $J = 10.2$ Hz, 3H), 3.04 – 2.89 (m, 1H), 2.62 – 2.54 (m, 1H), 2.53 – 2.31 (m, 6H), 2.20 – 2.02 (m, 3H), 1.92 – 1.66 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 211.15 (s), 144.36 (s), 138.30 (s), 128.59 (s), 127.44 (s), 127.41 (s), 123.57 (s), 49.01 (s), 44.76 (s), 41.23 (s), 32.84 (s), 25.61 (s), 21.49 (s).

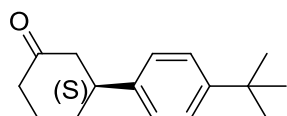
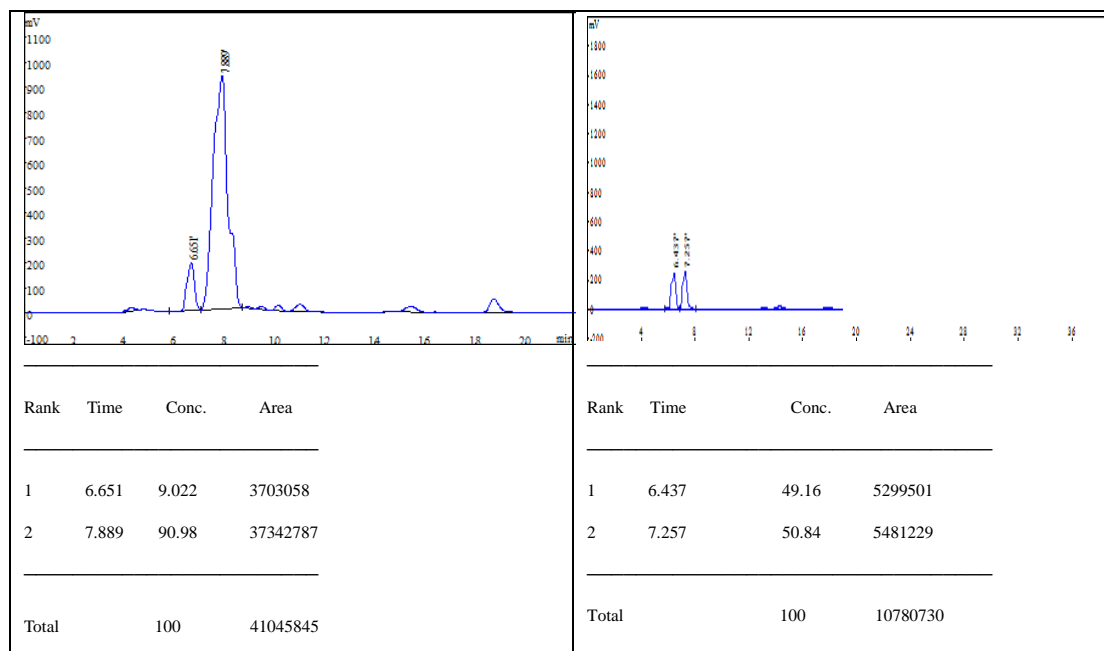
HPLC: Chiralcel OD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 8.8 min (major), 10.2 min (minor). Measured ee value = 75 %.



3-(o-Tolyl)cyclohexanone [1]

3d: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.24 – 7.16 (m, 2H), 7.12 (qd, $J = 7.8, 3.3$ Hz, 2H), 3.27 – 3.11 (m, 1H), 2.53 – 2.33 (m, 4H), 2.30 (s, 3H), 2.20 – 2.07 (m, 1H), 2.04 – 1.91 (m, 1H), 1.88 – 1.70 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 211.23 (s), 142.31 (s), 135.11 (s), 130.68 (s), 126.47 (s), 126.42 (s), 125.10 (s), 48.36 (s), 41.31 (s), 40.32 (s), 32.03 (s), 25.82 (s), 19.29 (s).

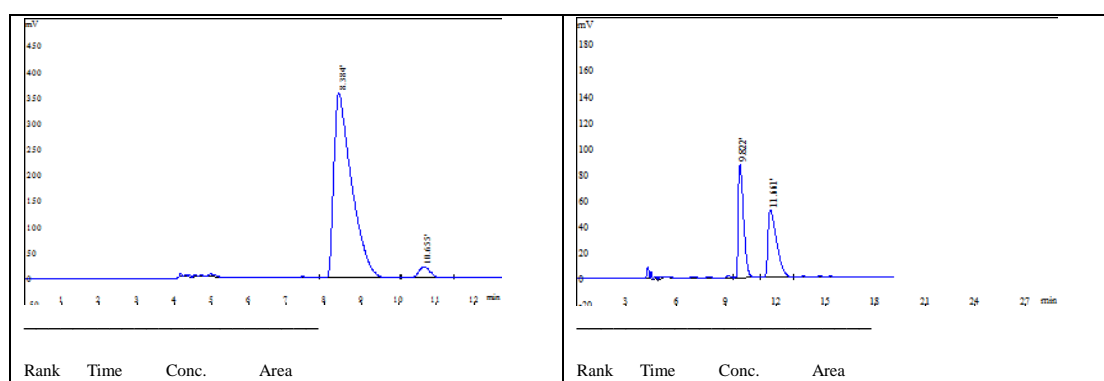
HPLC: Chiralpak AD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 6.7 min (minor), 7.9 min (major). Measured ee value = 81 %.



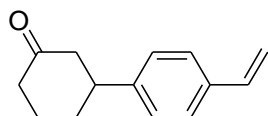
(S)-3-(4-(tert-Butyl)phenyl)cyclohexanone [4]

3e: $[\alpha]_{\text{D}}^{32.5} -13.75^\circ$ (c 0.16, CHCl_3). [lit. [9]: $[\alpha]_{\text{D}}^{20} = +10.4$ (c 0.63, CHCl_3), For R-isomer]. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 – 7.30 (m, 2H), 7.21 – 7.11 (m, 2H), 3.00 (tt, $J = 11.7, 3.9$ Hz, 1H), 2.66 – 2.33 (m, 4H), 2.22 – 2.05 (m, 2H), 1.94 – 1.72 (m, 2H), 1.32 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 210.67 (s), 149.08 (s), 142.28 (s), 126.74 (s), 125.66 (s), 48.72 (s), 43.90 (s), 40.97 (s), 34.56 (s), 32.76 (s), 31.65 (s), 25.50 (s).

HPLC: Chiralpak AS-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 8.4 min (major), 10.7 min (minor). Measured ee value = 93%.



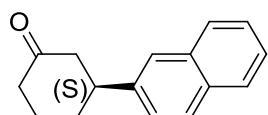
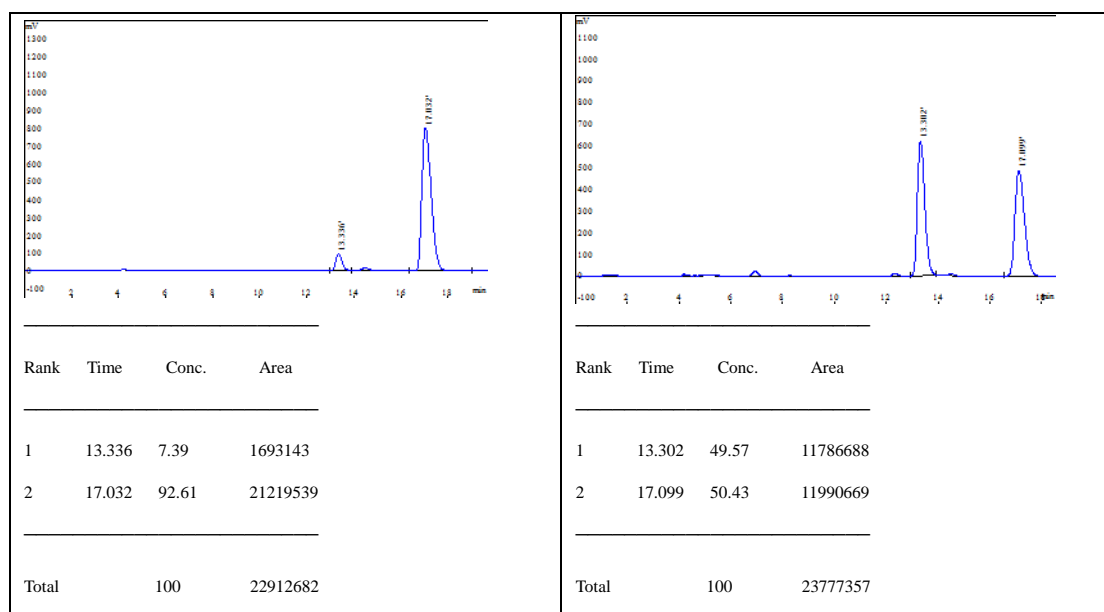
1	8.384	96.28	11554115	1	9.822	49.73	1788404
2	10.655	3.719	446310	2	11.661	50.27	1807588
Total	100		12000425	Total	100		3595992



3-(4-vinylphenyl)cyclohexan-1-one

3f: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 (d, $J = 8.2$ Hz, 2H), 7.18 (d, $J = 8.2$ Hz, 2H), 6.70 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.73 (dd, $J = 17.6, 0.8$ Hz, 1H), 5.25 – 5.18 (m, 1H), 3.00 (tt, $J = 11.6, 4.0$ Hz, 1H), 2.67 – 2.29 (m, 4H), 2.19 – 2.11 (m, 1H), 2.05 (ddd, $J = 20.0, 11.7, 4.0$ Hz, 1H), 1.91 – 1.72 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 210.95 (s), 143.99 (s), 136.38 (s), 136.15 (s), 126.77 (s), 126.53 (s), 113.64 (s), 48.86 (s), 44.49 (s), 41.19 (s), 32.74 (s), 25.52 (s).

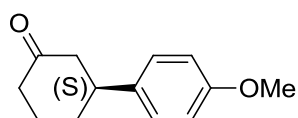
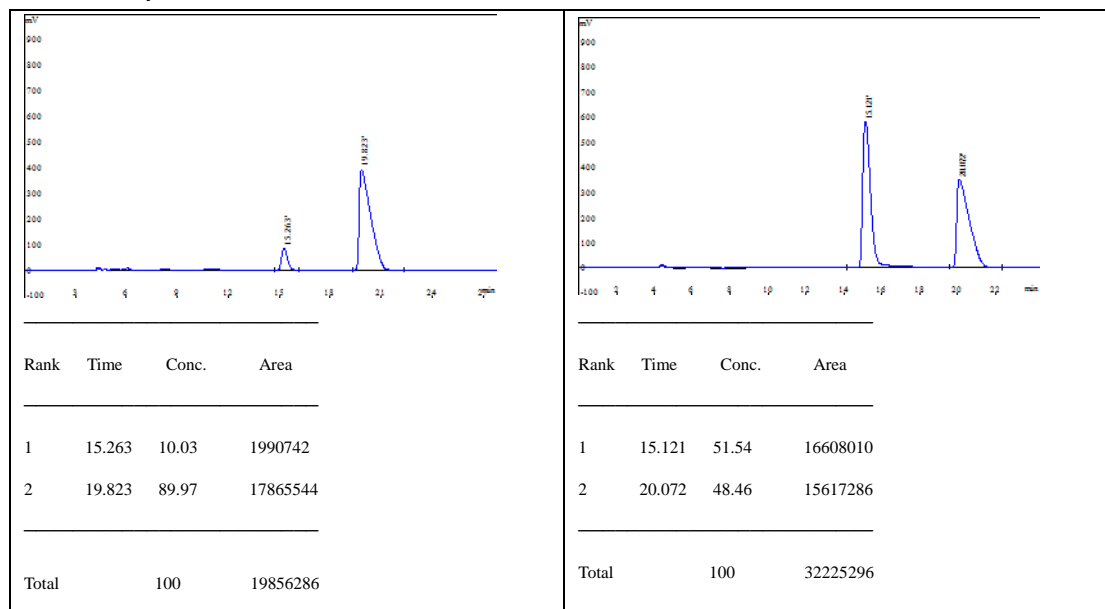
HPLC: Chiralpak AS-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 13.3 min, 17.0 min (major). Measured ee value = 85%.



(S)-3-(naphthalen-2-yl)cyclohexan-1-one [4]

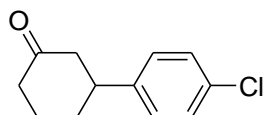
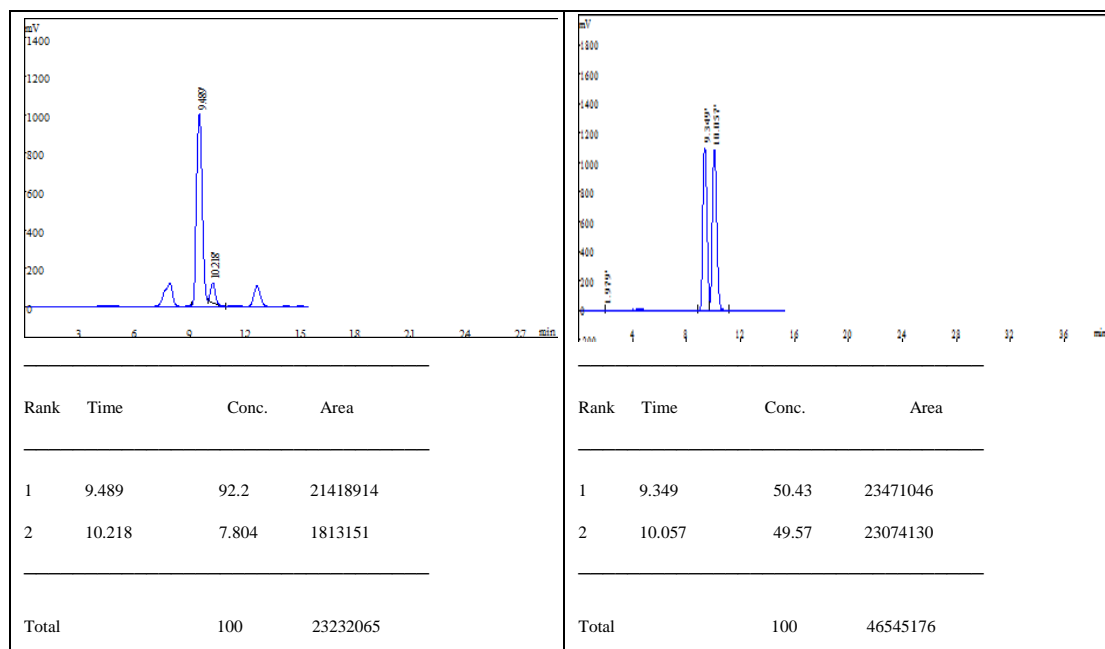
3g: $[\alpha]_{\text{D}}^{32.3} -6.67^\circ$ (c 0.15, CHCl_3) [lit. [4]: $[\alpha]_{\text{D}}^{20} -8.7$ (c 0.072, CHCl_3)]. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (t, $J = 7.4$ Hz, 3H), 7.65 (s, 1H), 7.51 – 7.42 (m, 2H), 7.37 (dd, $J = 8.5, 1.8$ Hz, 1H), 3.19 (tdd, $J = 11.3, 5.3, 3.3$ Hz, 1H), 2.75 – 2.59 (m, 2H), 2.57 – 2.35 (m, 2H), 2.26 – 2.12 (m, 2H), 2.05 – 1.78 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 210.55 (s), 142.88 (s), 133.61 (s), 132.37 (s), 128.46 (s), 128.02 (s), 127.91 (s), 126.55 (s), 126.15 (s), 125.97 (s), 125.00 (s), 48.55 (s), 44.37 (s), 41.01 (s), 32.61 (s), 25.50 (s).

HPLC: Chiralpak AS-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 15.3 min, 19.8 min (major). Measured ee value = 79%.

**(S)-3-(4-Methoxyphenyl)cyclohexanone** [1]

3h: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.20 – 7.09 (m, 2H), 6.91 – 6.82 (m, 2H), 3.79 (s, 3H), 2.96 (tt, $J = 11.7, 3.9$ Hz, 1H), 2.64 – 2.31 (m, 4H), 2.23 – 1.98 (m, 2H), 1.89 – 1.71 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 210.68 (s), 158.23 (s), 137.38 (s), 128.03 (s), 114.31 (s), 55.48 (s), 48.97 (s), 43.55 (s), 40.94 (s), 32.95 (s), 25.41 (s).

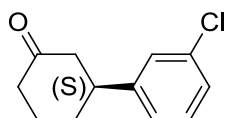
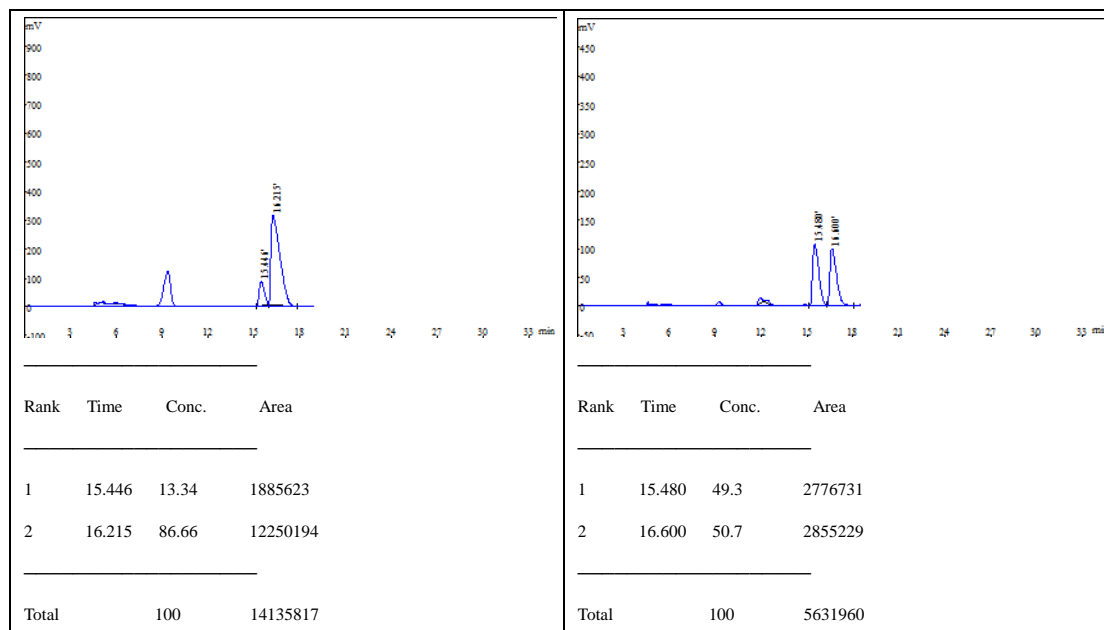
HPLC: Chiralpak AD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 9.5 min (major), 10.2 min (minor). Measured ee value = 85 %.

**3-(4-Chlorophenyl)cyclohexanone** [8]

3i: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.25 – 7.14 (m, 2H), 7.11 – 7.05 (m, 2H), 2.92 (tt, $J = 11.8, 3.9$ Hz, 1H), 2.57 – 2.21 (m,

4H), 2.16 – 1.92 (m, 2H), 1.80 – 1.60 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 210.97 (s), 142.73 (s), 129.62 (s), 128.82 (s), 127.96 (s), 48.79 (s), 44.11 (s), 41.11 (s), 32.68 (s), 25.40 (s).

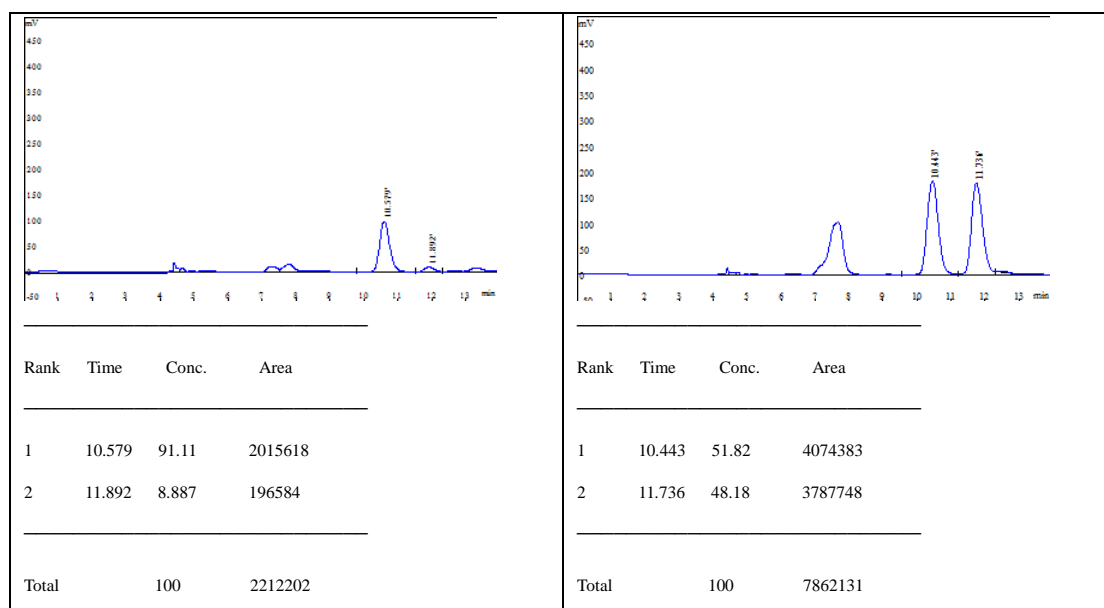
HPLC: Chiralpak AS-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 15.4 min (minor), 16.2 min (major). Measured ee value = 73%.

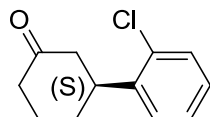


(S)-3-(3-Chlorophenyl)cyclohexane [5]

3j: ^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.20 (m, 2H), 7.10 (t, J = 6.3 Hz, 1H), 6.94 – 6.81 (m, 1H), 2.99 (tt, J = 11.9, 3.9 Hz, 1H), 2.62 – 2.32 (m, 4H), 2.20 – 2.02 (m, 2H), 1.89 – 1.70 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 210.41 (s), 146.32 (s), 134.50 (s), 129.99 (s), 126.91 (s), 126.82 (s), 124.88 (s), 48.66 (s), 44.40 (s), 41.10 (s), 32.59 (s), 25.41 (s).

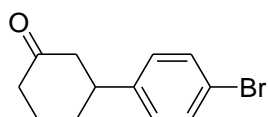
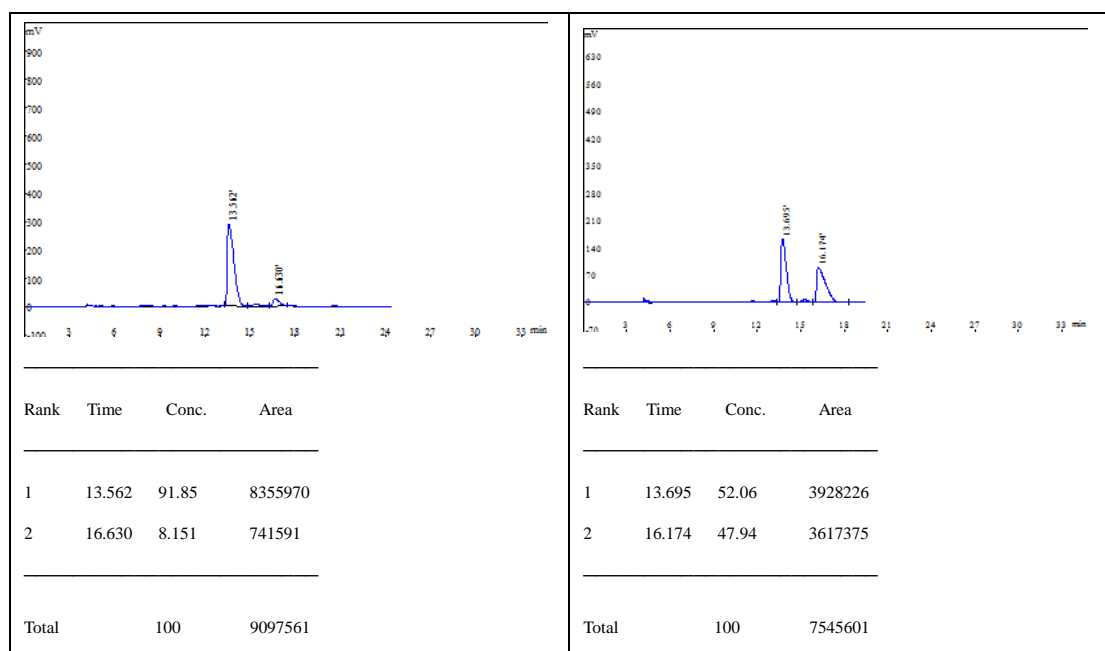
HPLC: Chiralpak AD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 10.6 min (major), 11.9 min (minor). Measured ee value = 83%.



**(S)-3-(2-chlorophenyl)cyclohexan-1-one** [9]

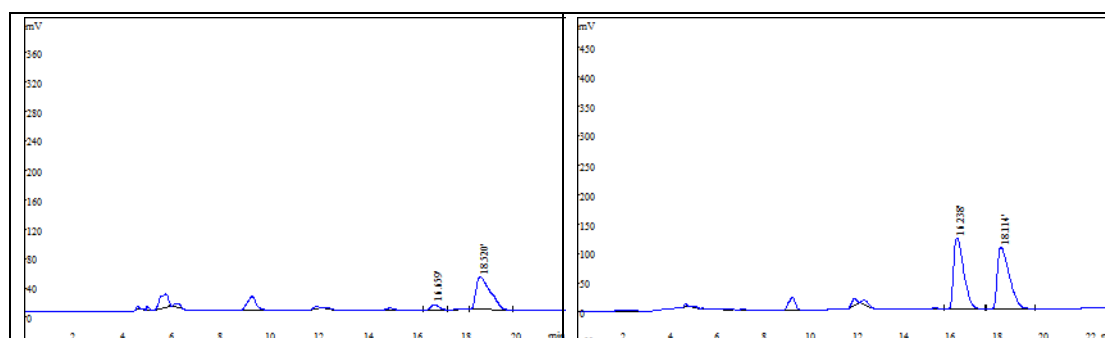
3k: $[\alpha]_D^{33.1} -20.32^\circ$ (c 0.31, CHCl_3) (lit. [9]: $[\alpha]_D^{20} = -32.5$ (c 0.51, CHCl_3)). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.33 (m, 1H), 7.28 – 7.22 (m, 2H), 7.16 (tt, $J = 6.3, 3.6$ Hz, 1H), 3.56 – 3.41 (m, 1H), 2.60 (ddt, $J = 14.0, 4.1, 2.0$ Hz, 1H), 2.53 – 2.30 (m, 3H), 2.20 – 2.01 (m, 2H), 1.91 – 1.72 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 210.52 (s), 141.26 (s), 133.42 (s), 129.90 (s), 127.80 (s), 127.21 (s), 126.93 (s), 47.30 (s), 41.22 (s), 40.54 (s), 31.28 (s), 25.28 (s).

HPLC: Chiralpak AS-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 13.6 min, 16.6 min (major). Measured ee value = 83%.

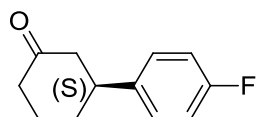
**3-(4-bromophenyl)cyclohexan** [10]

3l: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 – 7.33 (m, 2H), 7.09 – 6.98 (m, 2H), 2.90 (tt, $J = 11.8, 3.9$ Hz, 1H), 2.55 – 2.17 (m, 4H), 2.15 – 1.90 (m, 2H), 1.79 – 1.63 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 210.65 (s), 143.28 (s), 131.77 (s), 128.36 (s), 120.41 (s), 48.72 (s), 44.16 (s), 41.10 (s), 32.63 (s), 25.39 (s).

HPLC: Chiralpak AS-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 16.6 min, 18.5 min (major). Measured ee value = 83%.

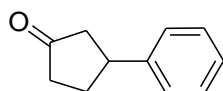
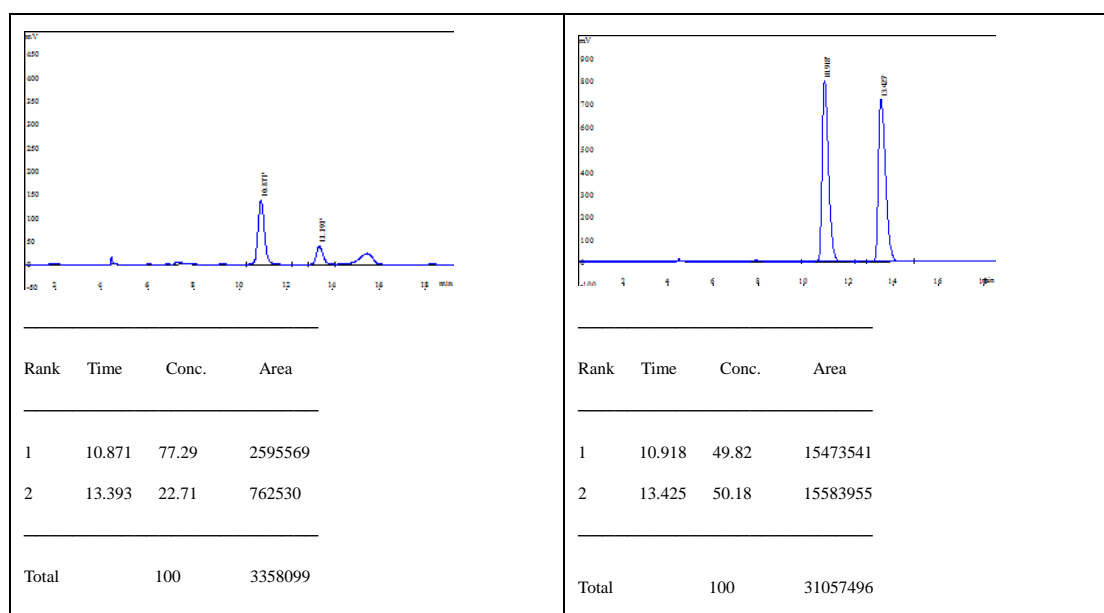


Rank	Time	Conc.	Area	Rank	Time	Conc.	Area
1	16.613	8.669	189098	1	16.238	49.65	3459063
2	18.450	91.33	1992353	2	18.114	50.35	3507152
Total		100	2181451	Total		100	6966215

**(S)-3-(4-Fluorophenyl)-cyclohexanone [1]**

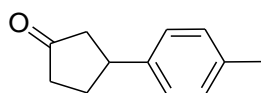
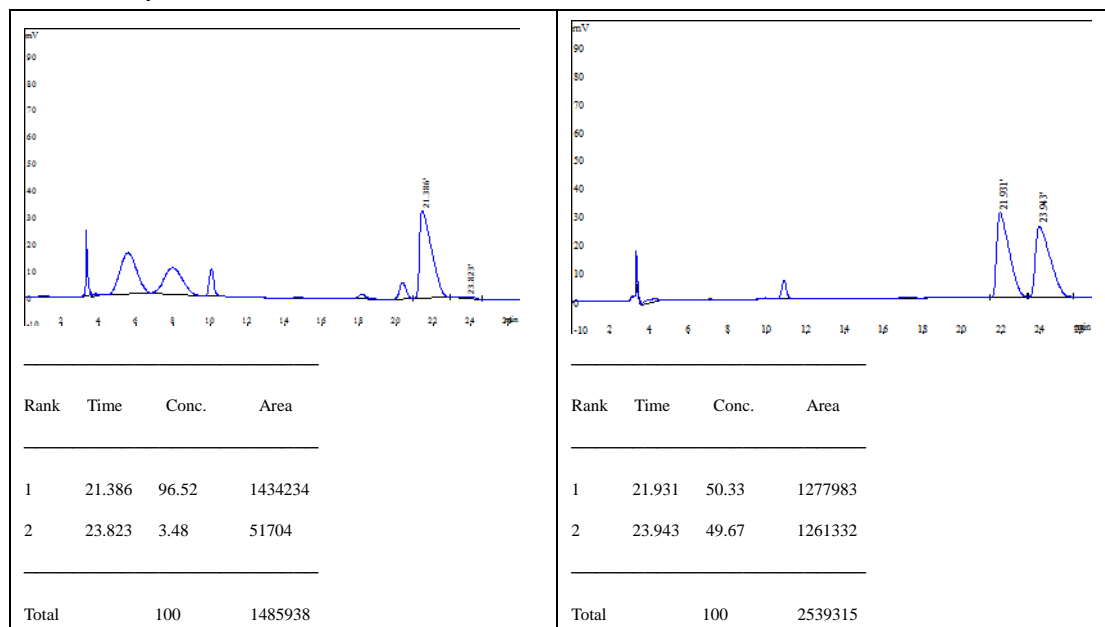
3m: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.18 (ddd, $J = 7.0, 5.1, 2.5$ Hz, 2H), 7.02 (ddd, $J = 10.7, 5.9, 2.6$ Hz, 2H), 3.00 (ddd, $J = 15.7, 7.8, 3.9$ Hz, 1H), 2.65 – 2.31 (m, 4H), 2.22 – 2.01 (m, 2H), 1.89 – 1.63 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 210.89 (s), 160.35 (s), 129.61 (s), 128.00 (d, $J = 7.9$ Hz), 115.46 (d, $J = 21.3$ Hz), 49.08 (s), 44.01 (s), 41.12 (s), 32.90 (s), 25.41 (s).

HPLC: Chiralpak AD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 10.9 min (major), 13.4 min (minor). Measured ee value = 55 %.

**3-Phenylcyclopentanone [3]**

3n: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34 (ddd, $J = 7.6, 5.9, 3.0$ Hz, 2H), 7.27 – 7.19 (m, 3H), 3.51 – 3.31 (m, 1H), 2.67 (dd, $J = 18.2, 7.4$ Hz, 1H), 2.54 – 2.23 (m, 4H), 2.08 – 1.91 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 218.09 (s), 144.11 (s), 128.89 (s), 127.34 (s), 126.80 (s), 45.76 (s), 42.05 (s), 39.00 (s), 31.33 (s).

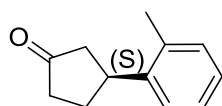
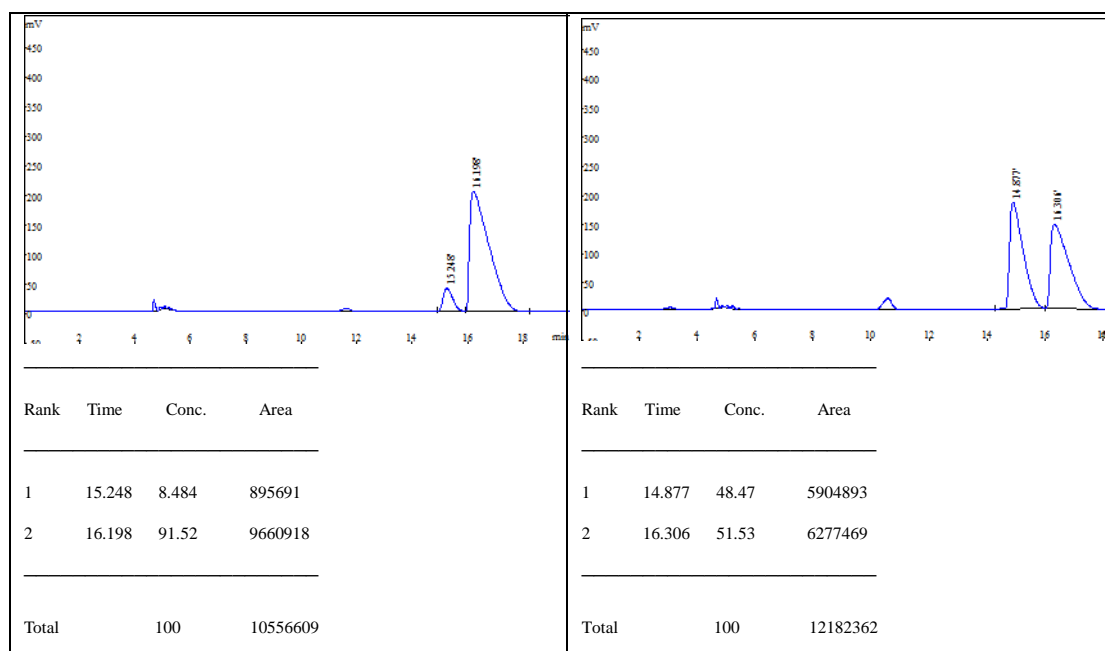
HPLC: Chiralpak AS-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 98:2; flow rate: 1.0 ml/min; retention time: 21.4 min (major), 23.8 min (minor). Measured ee value = 93%.



3-(p-tolyl)cyclopentan-1-one [9]

3o: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.16 (s, 4H), 3.39 (tdd, $J = 11.1, 7.4, 6.3$ Hz, 1H), 2.66 (dd, $J = 18.2, 7.5$ Hz, 1H), 2.51 – 2.38 (m, 2H), 2.38 – 2.25 (m, 5H), 2.04 – 1.91 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 218.57 (s), 140.08 (s), 136.33 (s), 129.36 (s), 126.62 (s), 45.93 (s), 41.88 (s), 38.91 (s), 31.32 (s), 21.01 (s).

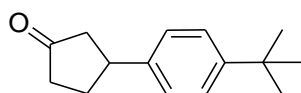
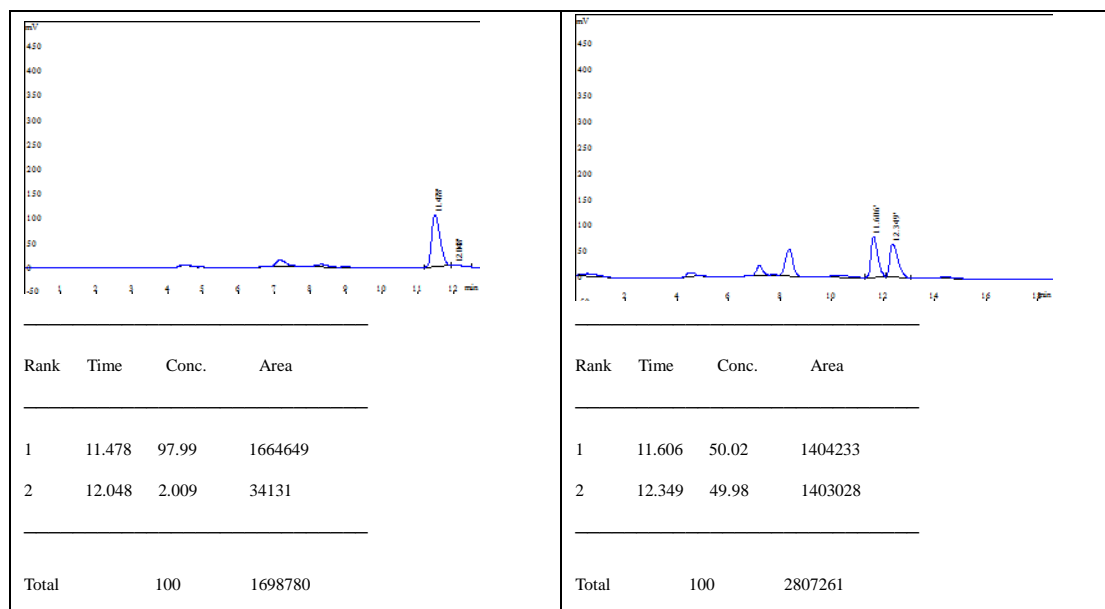
HPLC: Chiralpak AS-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 15.2 min, 16.2 min (major). Measured ee value = 83%.



(S)-3-o-tolylcyclopentanone [6]

3p: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.21 (dt, $J = 4.1, 1.9$ Hz, 2H), 7.19 – 7.13 (m, 2H), 3.67 – 3.53 (m, 1H), 2.63 (dd, $J = 18.1, 7.5$ Hz, 1H), 2.53 – 2.43 (m, 1H), 2.39 (d, $J = 5.0$ Hz, 3H), 2.37 – 2.25 (m, 3H), 2.07 – 1.96 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 218.69 (s), 141.00 (s), 135.96 (s), 130.65 (s), 126.53 (s), 126.44 (s), 124.75 (s), 45.33 (s), 38.55 (s), 38.34 (s), 30.08 (s), 19.66 (s).

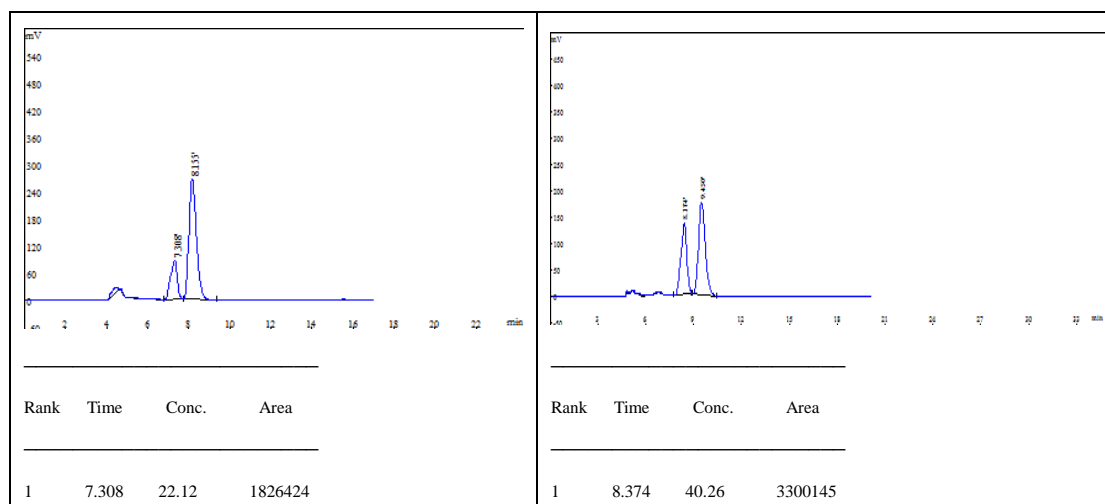
HPLC: Chiralcel OD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 11.5 min (major), 12.0 min (minor). Measured ee value = 95%.



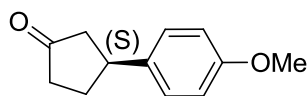
3-(4-(tert-butyl)phenyl)cyclopentan-1-one [4]

3q: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.34 (m, 2H), 7.20 (d, $J = 8.2$ Hz, 2H), 3.45 – 3.30 (m, 1H), 2.66 (dd, $J = 18.2, 7.4$ Hz, 1H), 2.52 – 2.24 (m, 4H), 2.06 – 1.92 (m, 1H), 1.32 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 218.23 (s), 149.09 (s), 141.04 (s), 126.99 (s), 125.60 (s), 45.87 (s), 41.61 (s), 39.01 (s), 34.56 (s), 31.65 (s), 31.34 (s).

HPLC: Chiralpak AS-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 7.3 min, 8.2 min (major). Measured ee value = 55%.

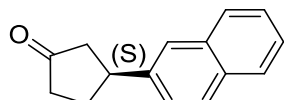
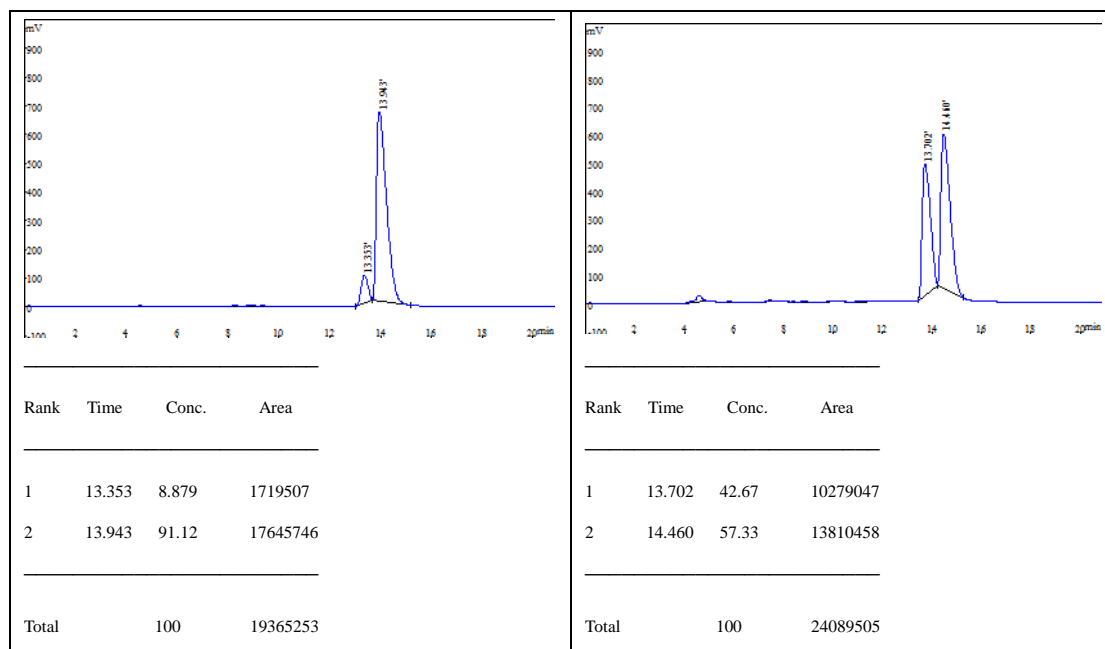


2	8.155	77.88	6431002	2	9.450	59.74	4897809
<hr/>				<hr/>			
Total		100	8257426	Total		100	8197954

**(S)-3-(4-methoxyphenyl)cyclopentan-1-one** [4]

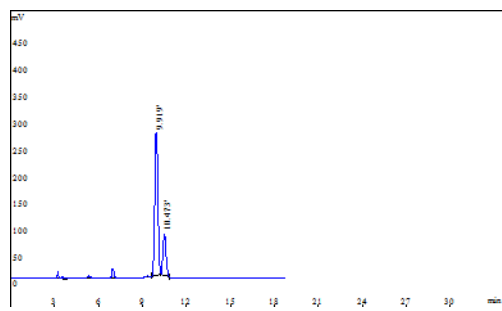
3r: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22 – 7.13 (m, 2H), 6.93 – 6.83 (m, 2H), 3.80 (s, 3H), 3.43 – 3.31 (m, 1H), 2.64 (dd, $J = 18.1, 7.5$ Hz, 1H), 2.42 (dddd, $J = 8.9, 8.2, 6.2, 5.0$ Hz, 2H), 2.36 – 2.22 (m, 2H), 2.05 – 1.87 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 218.60 (s), 158.36 (s), 135.13 (s), 127.66 (s), 114.06 (s), 55.31 (s), 46.03 (s), 41.48 (s), 38.91 (s), 31.40 (s), 30.92 (s).

HPLC: Chiralcel OD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 13.4 min (minor), 13.9 min (major). Measured ee value = 83%.

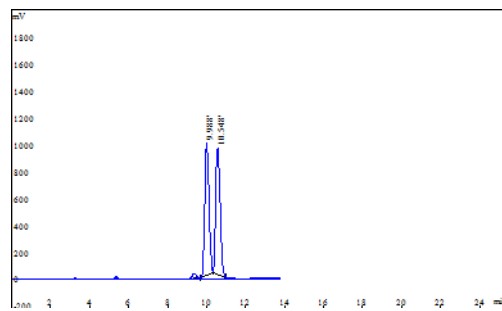
**(S)-3-(naphthalen-2-yl)cyclopentan-1-one** [7]

3s: $[\alpha]_{\text{D}}^{32.8} -26.67^\circ$ (c 0.015, CHCl_3). [lit. [7]: $[\alpha]_{\text{D}} -38^\circ$ (c 0.14, CHCl_3)]. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90 – 7.77 (m, 3H), 7.70 (s, 1H), 7.57 – 7.39 (m, 3H), 3.63 (tt, $J = 10.7, 6.9$ Hz, 1H), 2.83 – 2.72 (m, 1H), 2.62 – 2.33 (m, 4H), 2.21 – 2.06 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 218.08 (s), 141.69 (s), 133.55 (s), 132.35 (s), 128.43 (s), 127.97 (s), 127.92 (s), 126.56 (s), 126.28 (s), 125.94 (s), 125.23 (s), 45.67 (s), 42.15 (s), 39.00 (s), 31.16 (s).

HPLC: Chiralpak AD-H Column (Particle Size: 5 μm , dimensions: 4.6 mm \times 250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 1.0 ml/min; retention time: 9.9 min (major), 10.5 min. Measured ee value = 55%.



Rank	Time	Conc.	Area
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2	10.473	22.58	1032175
Total		100	4570222

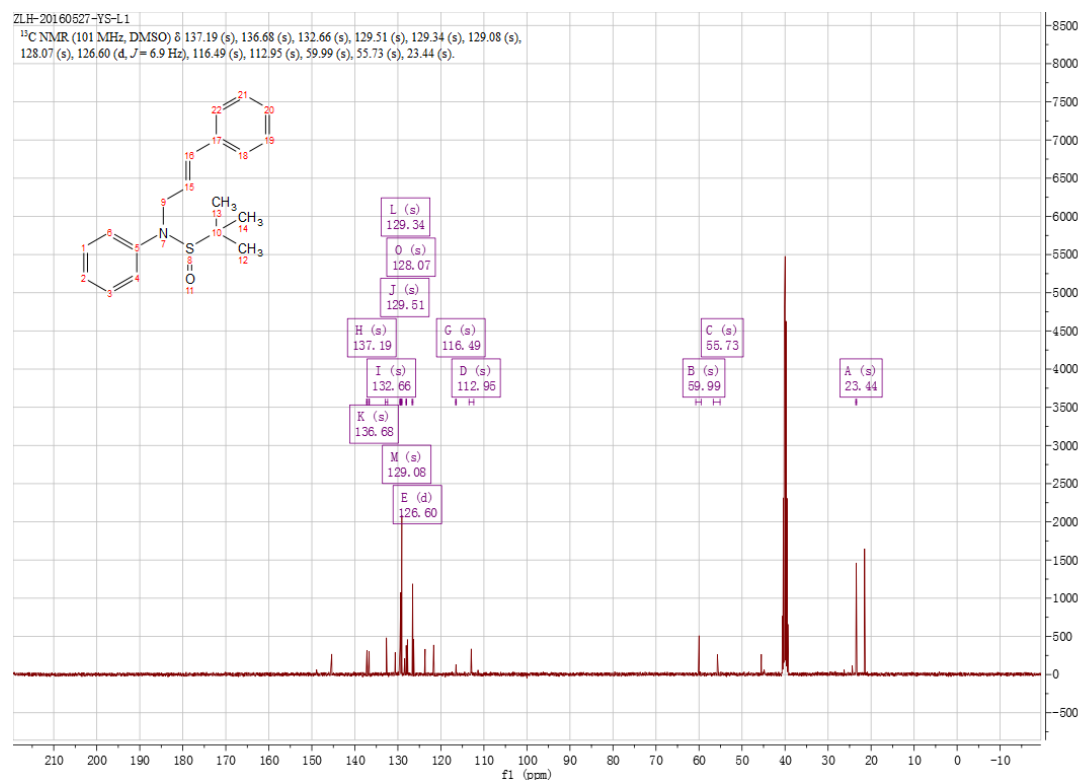
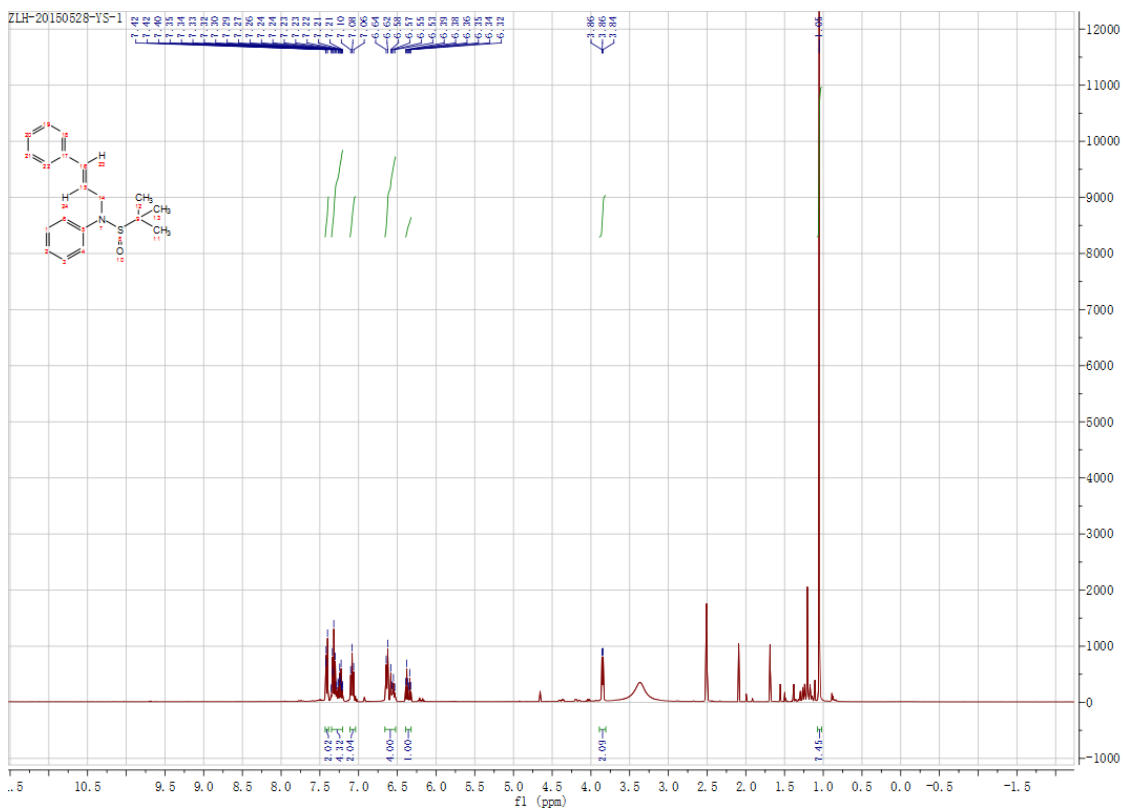


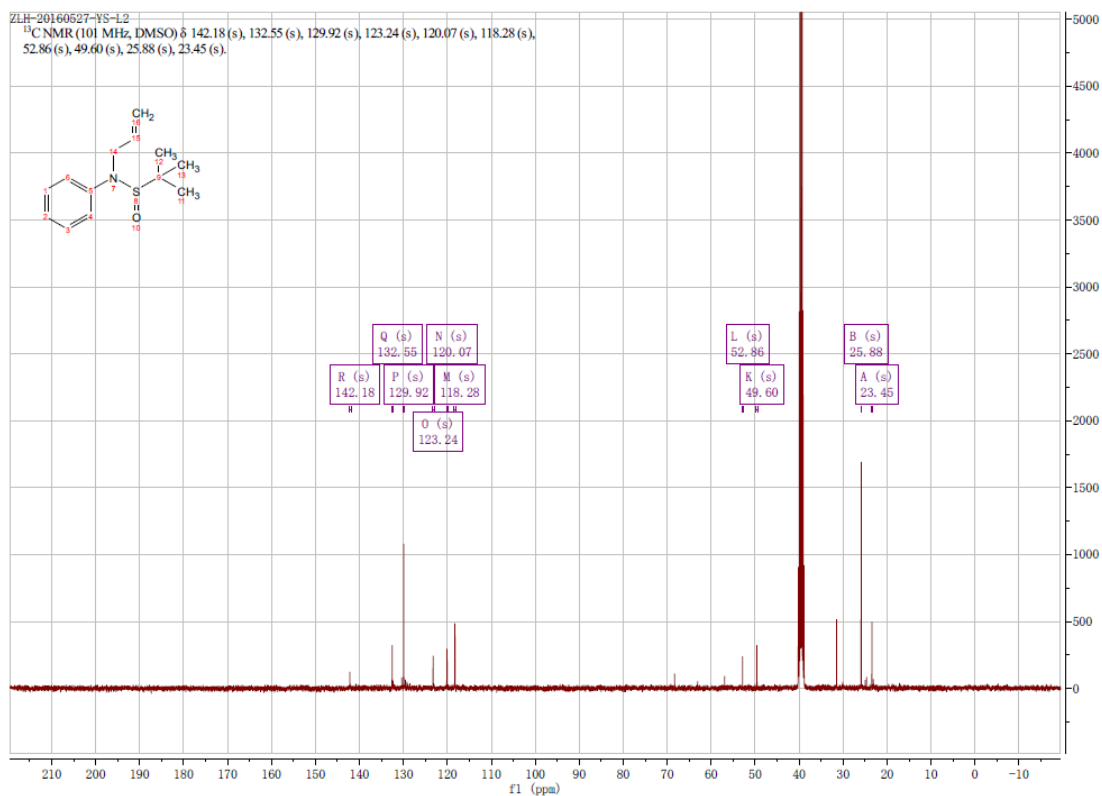
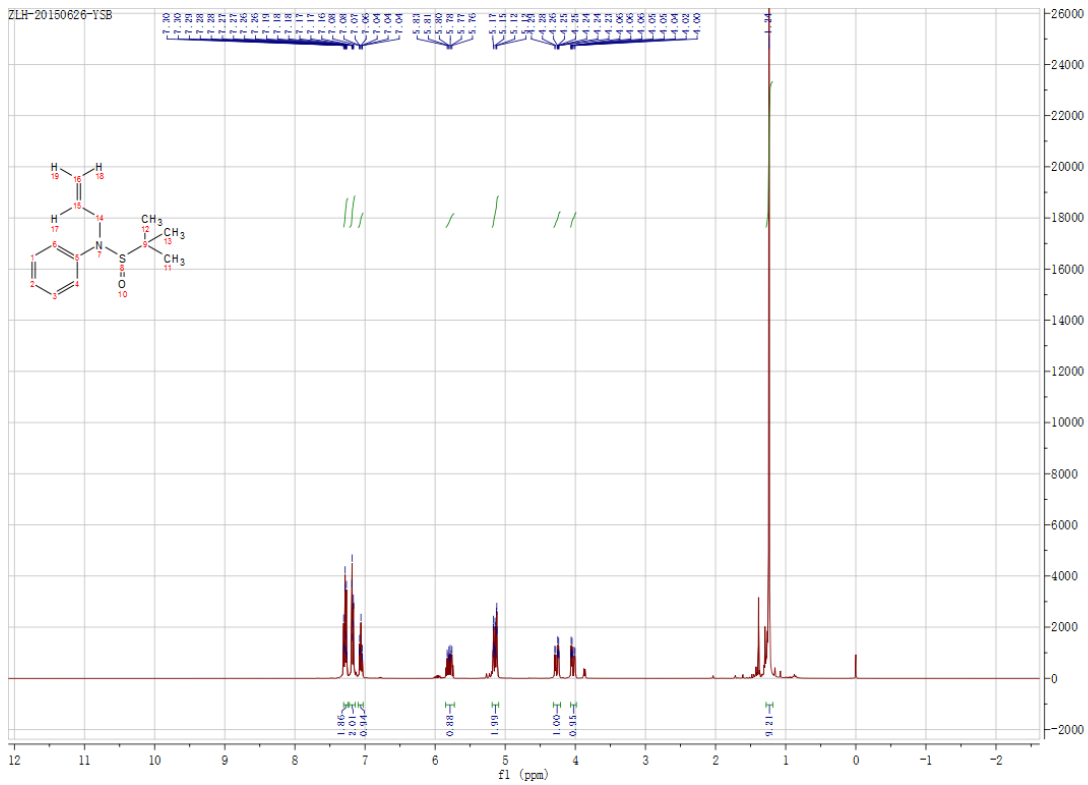
Rank	Time	Conc.	Area
1	9.988	49.95	13794061
2	10.548	50.05	13821123
Total		100	27615184

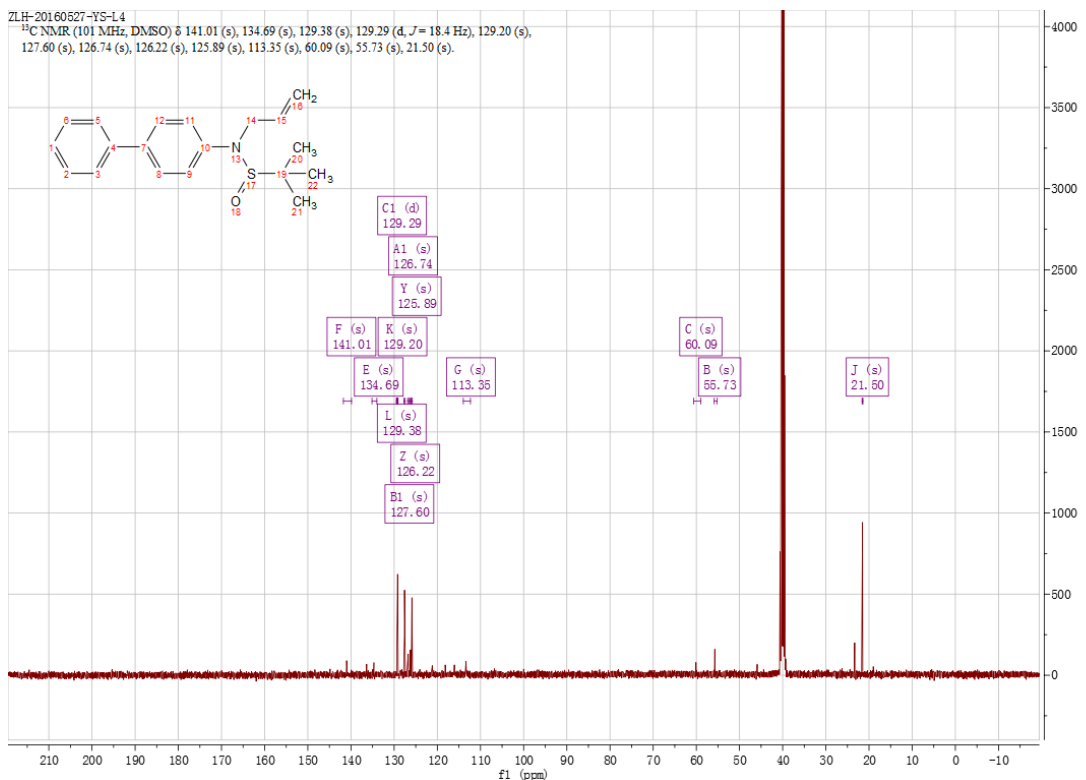
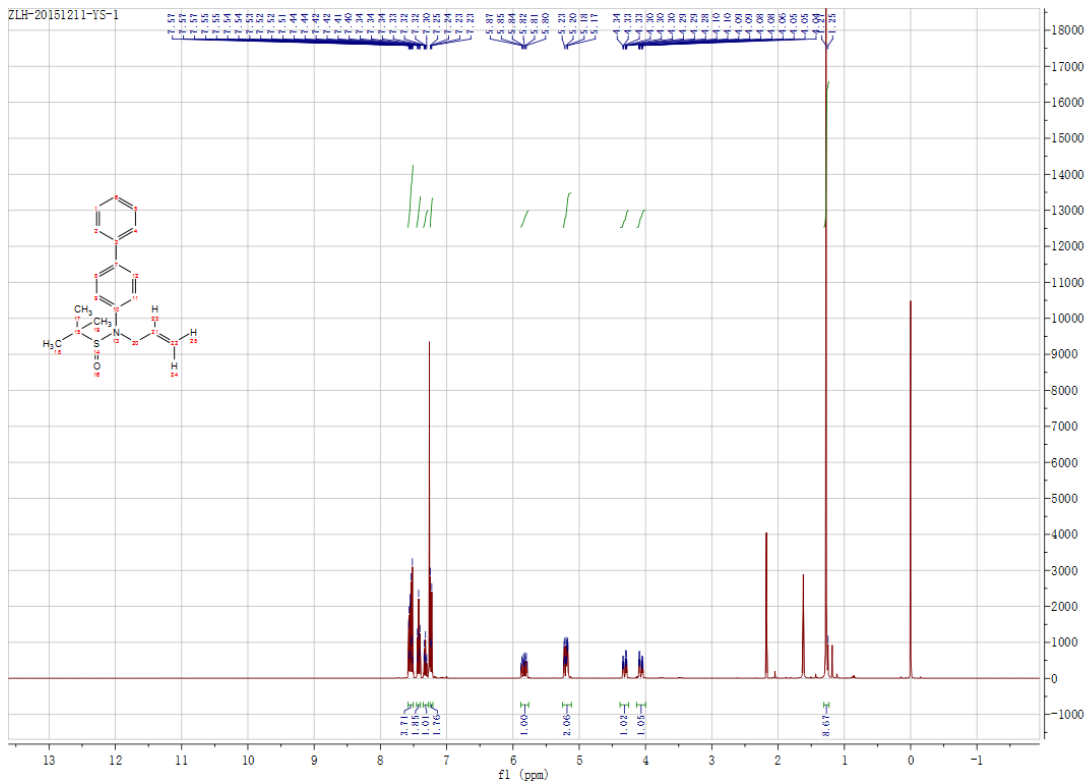
References

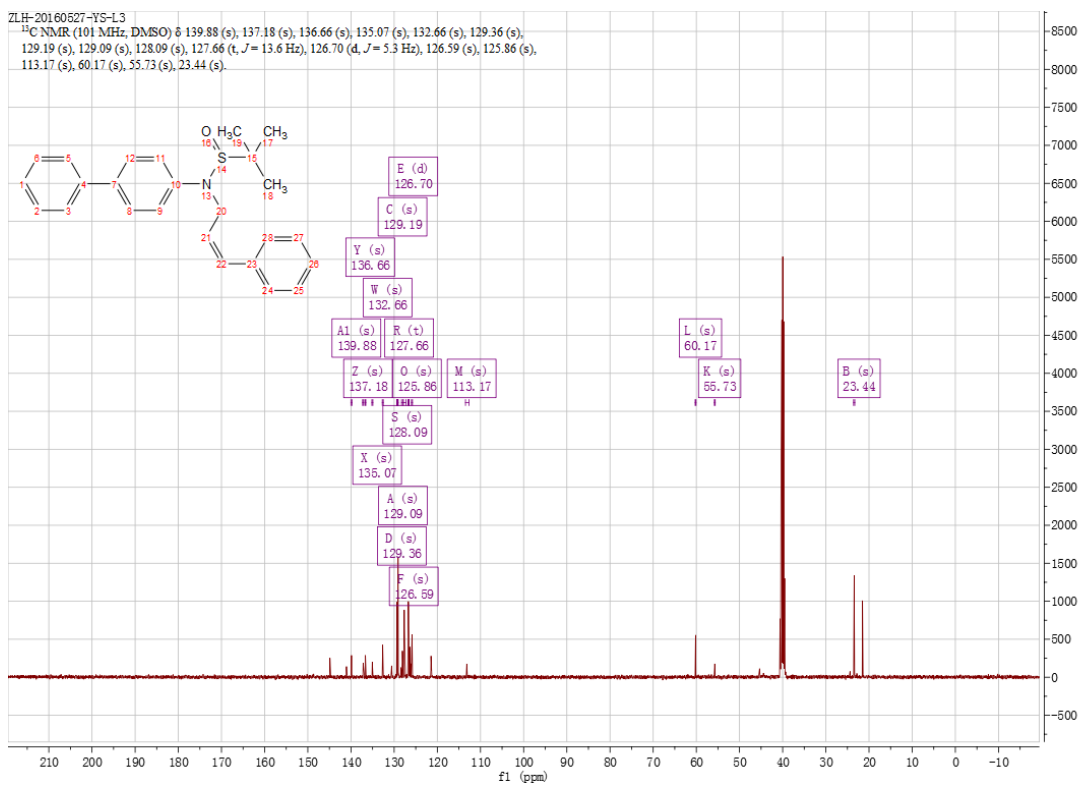
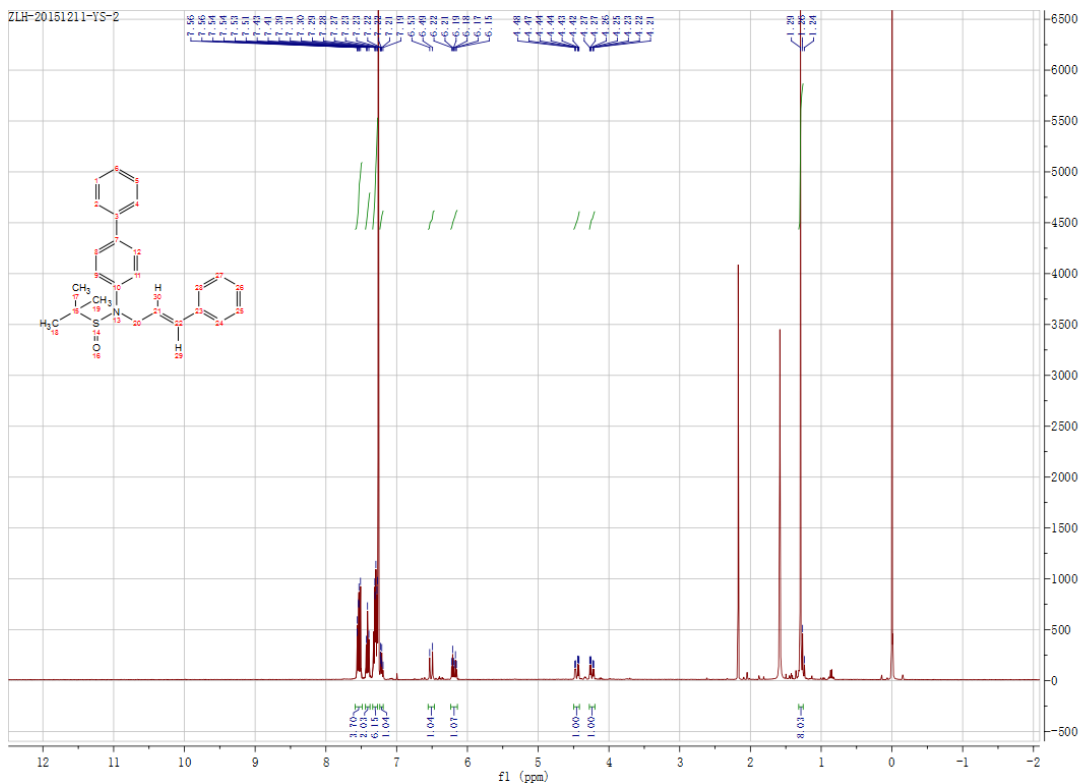
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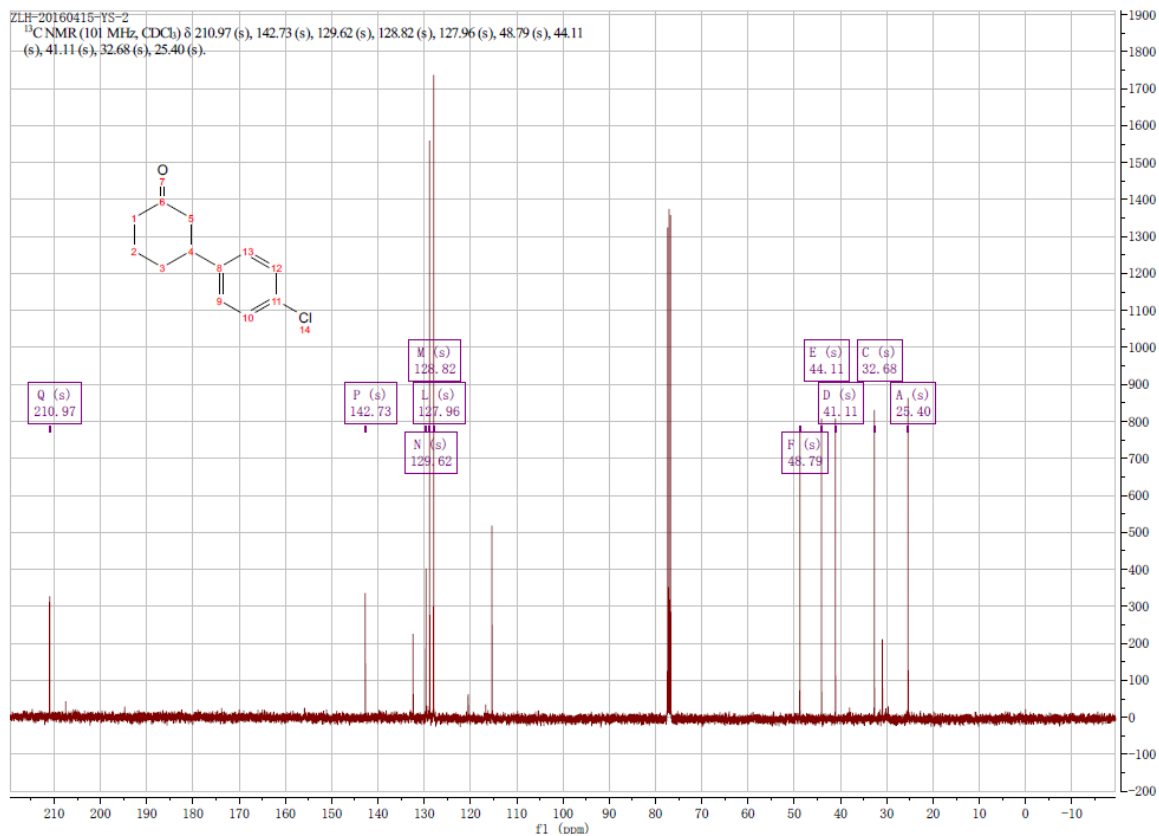
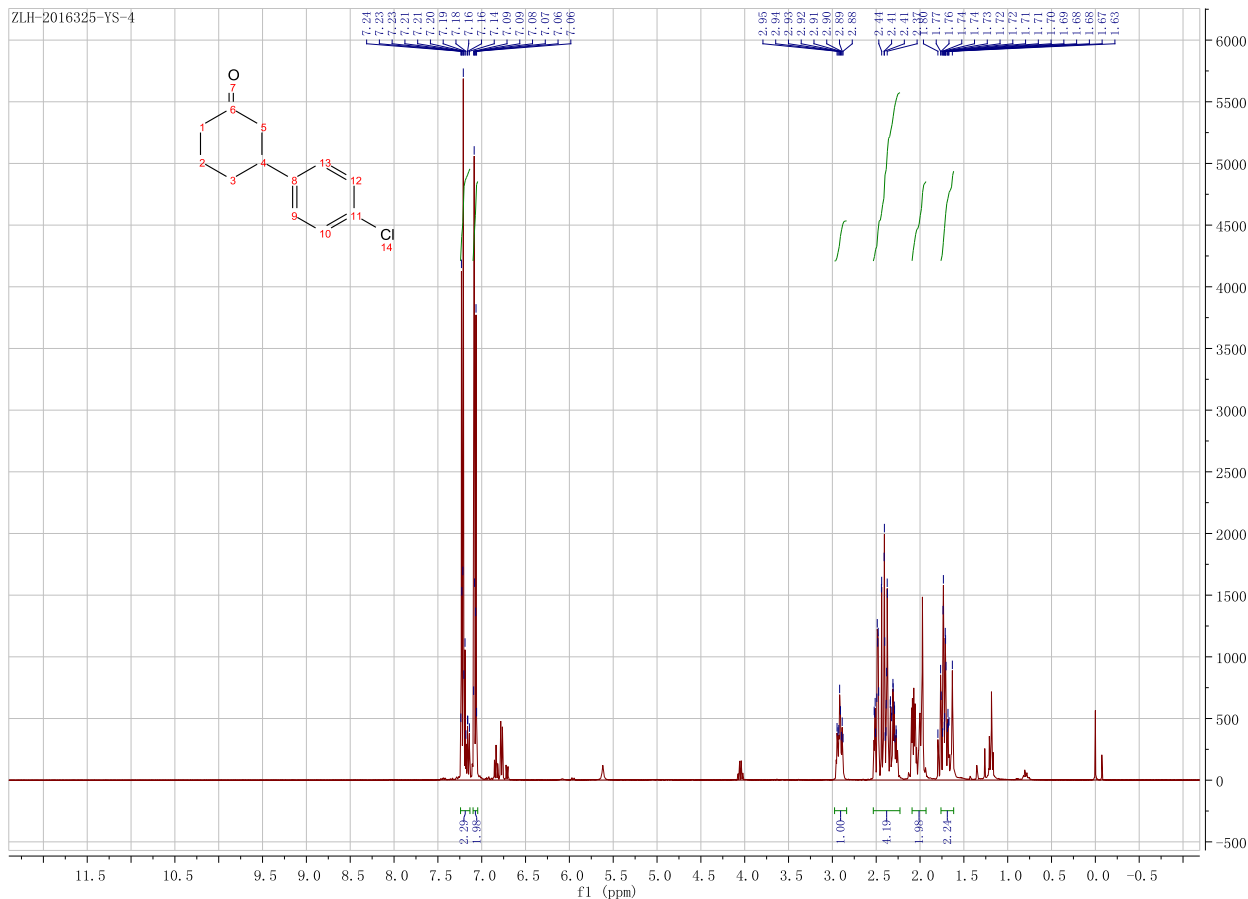
NMR Spectra collection

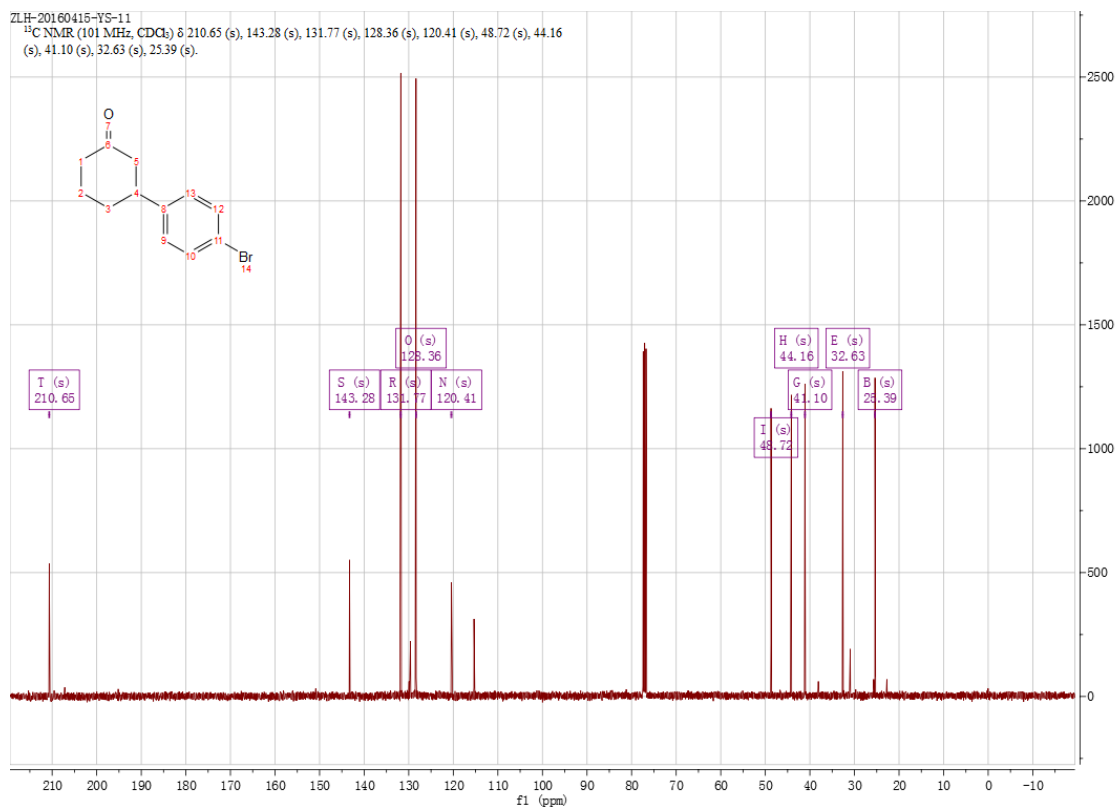
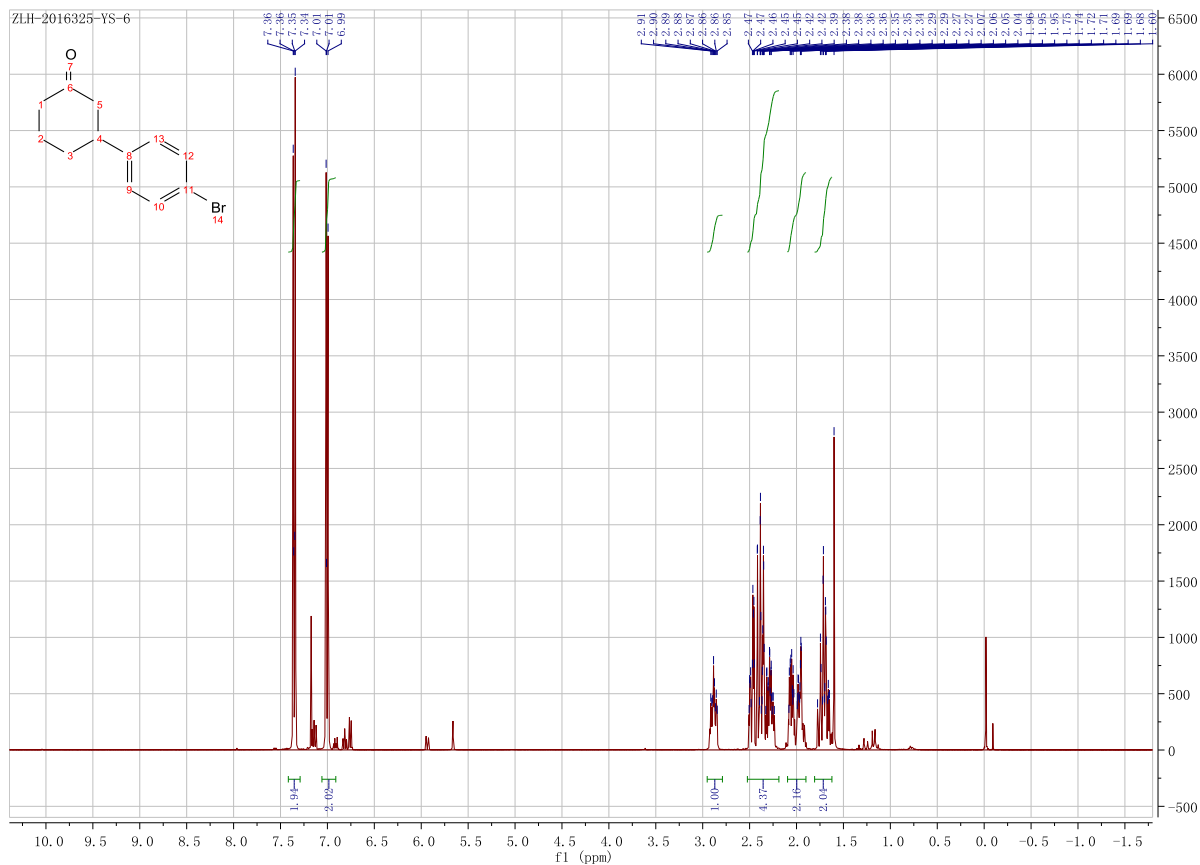


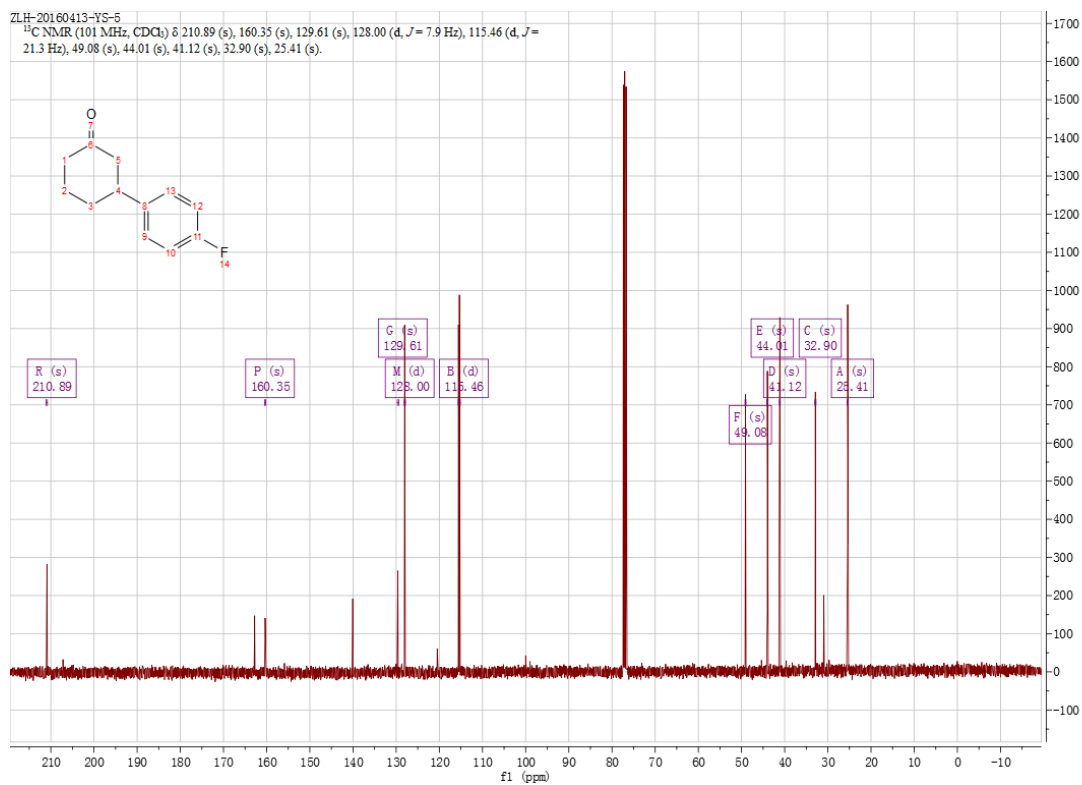
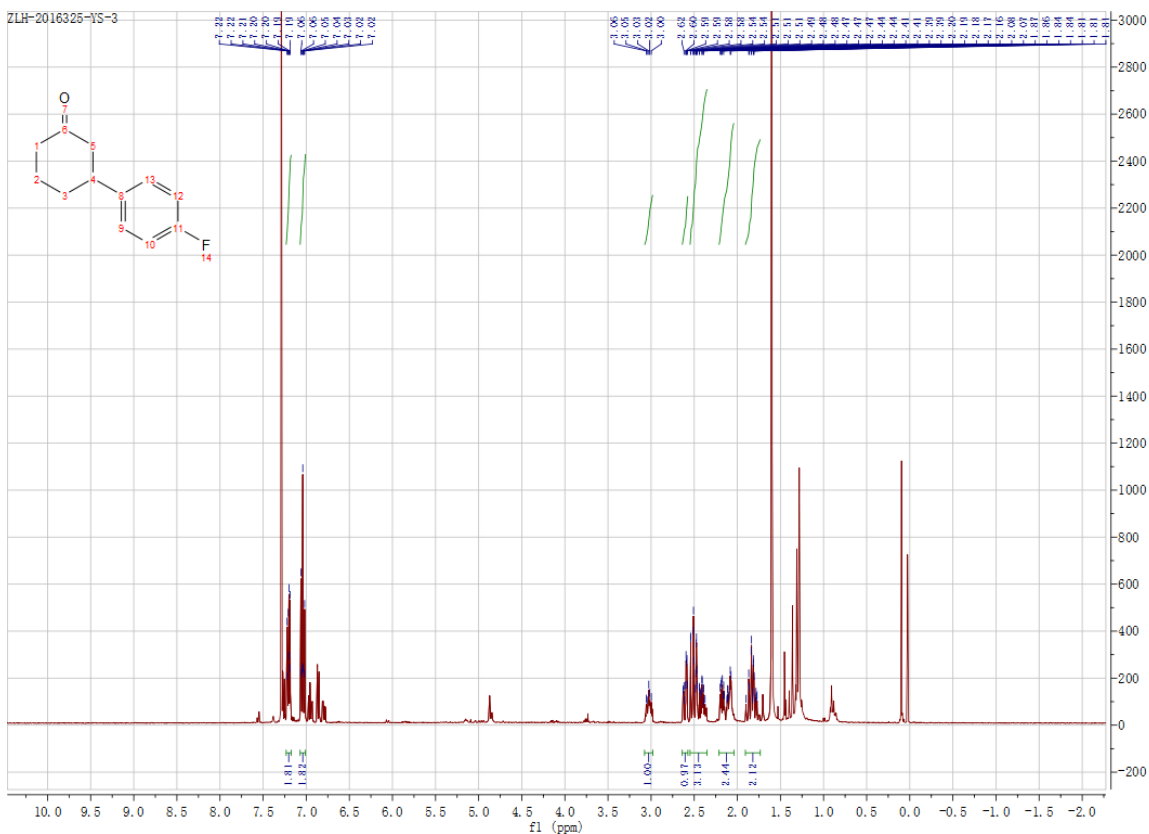


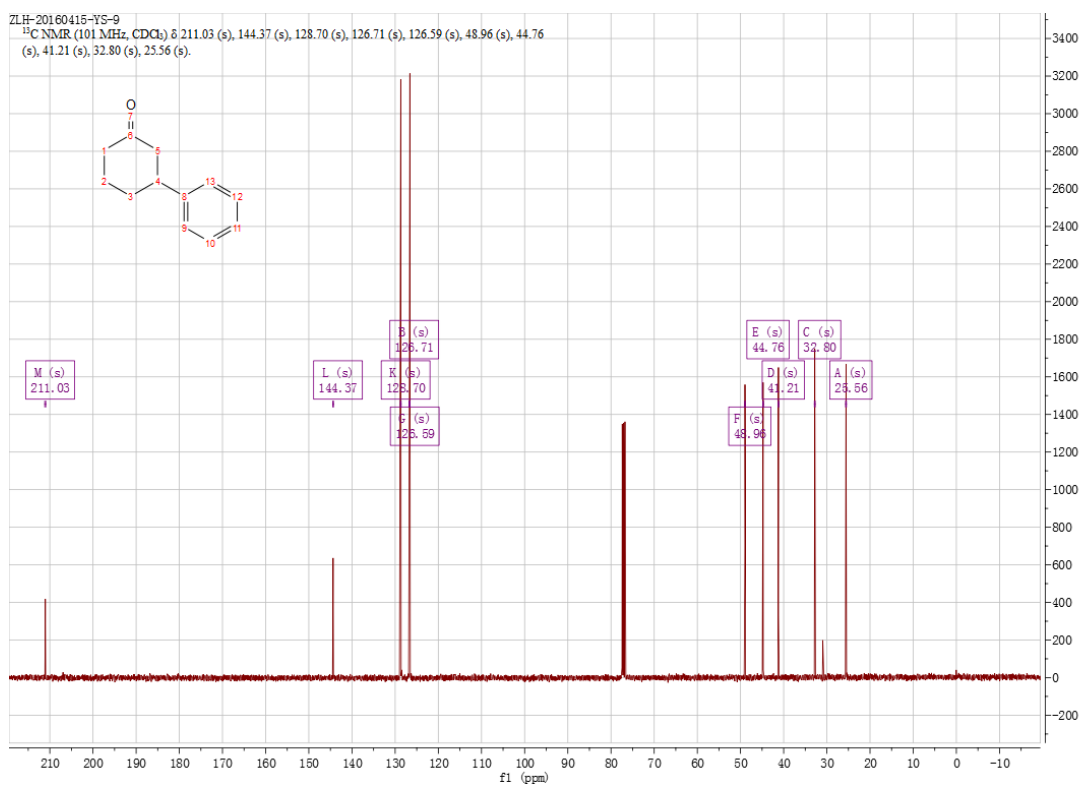
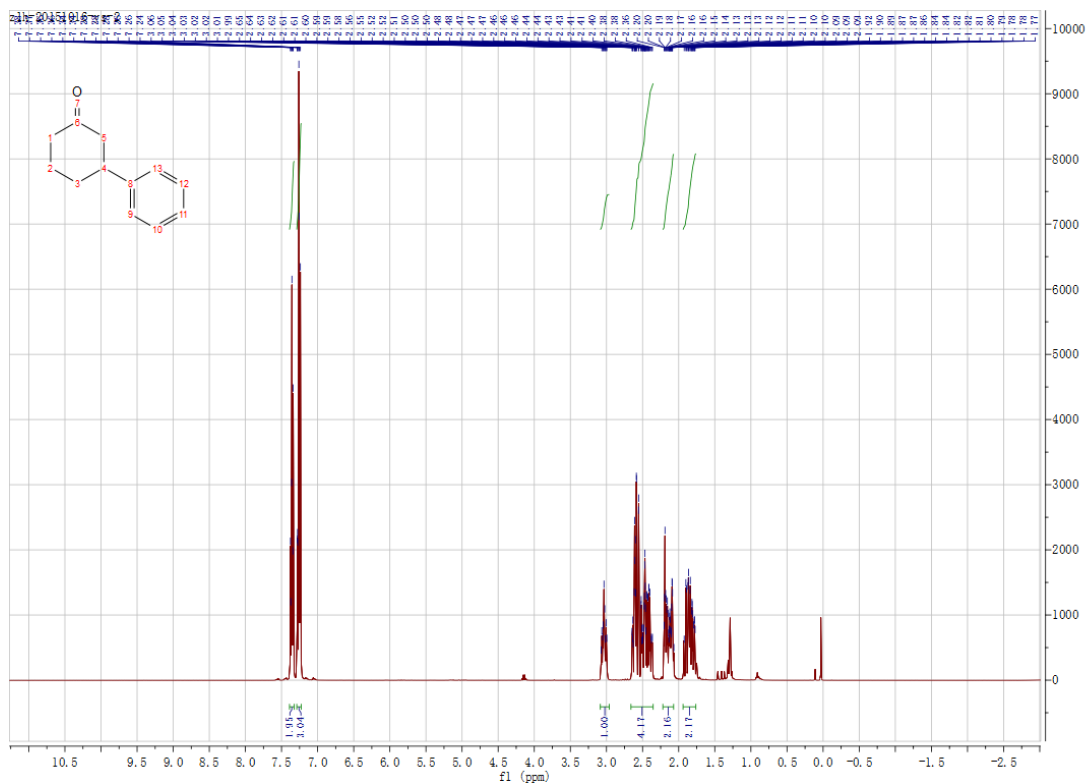


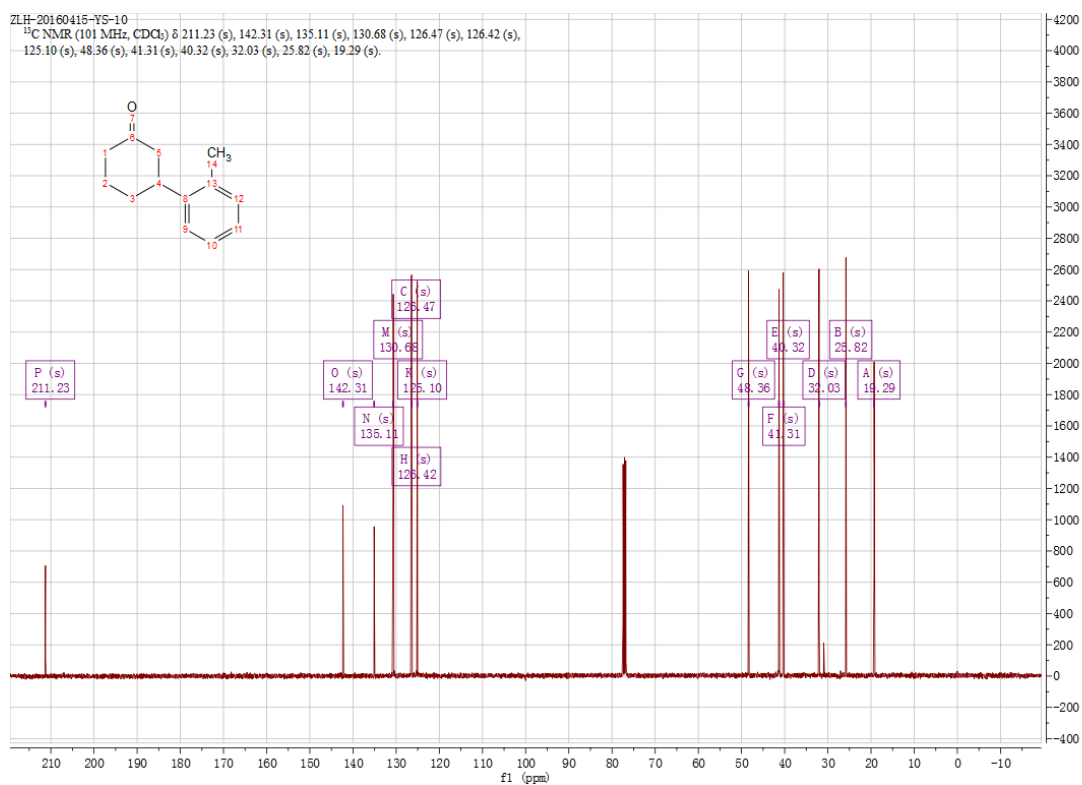
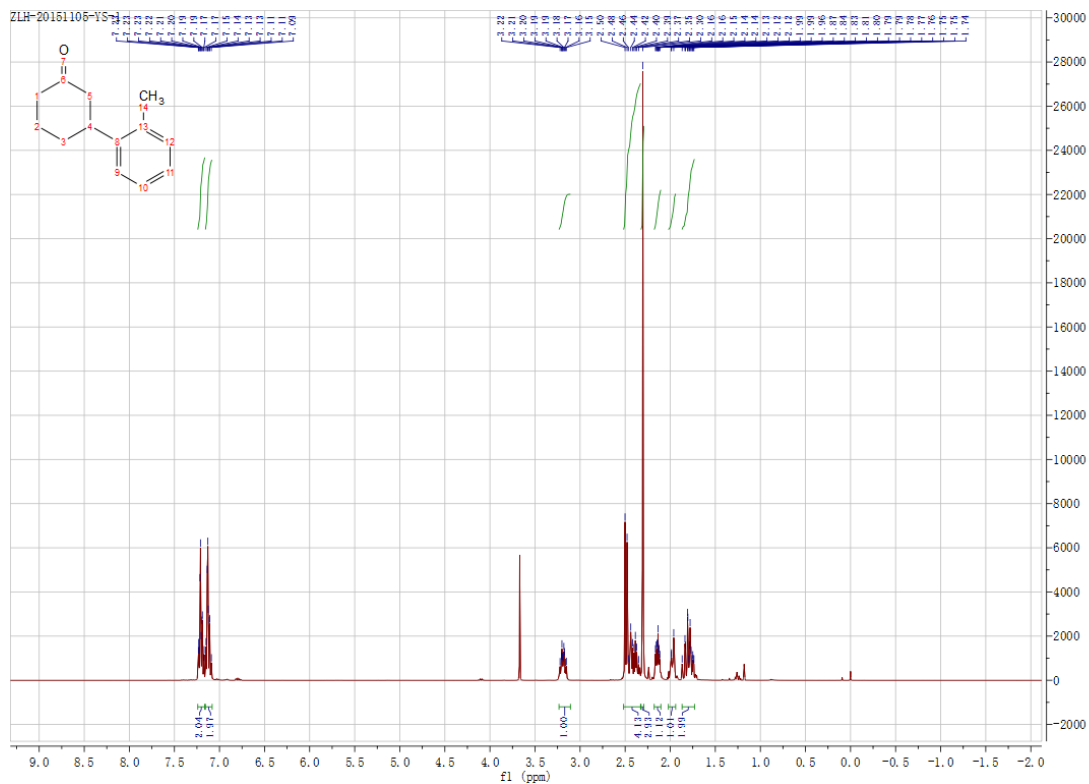


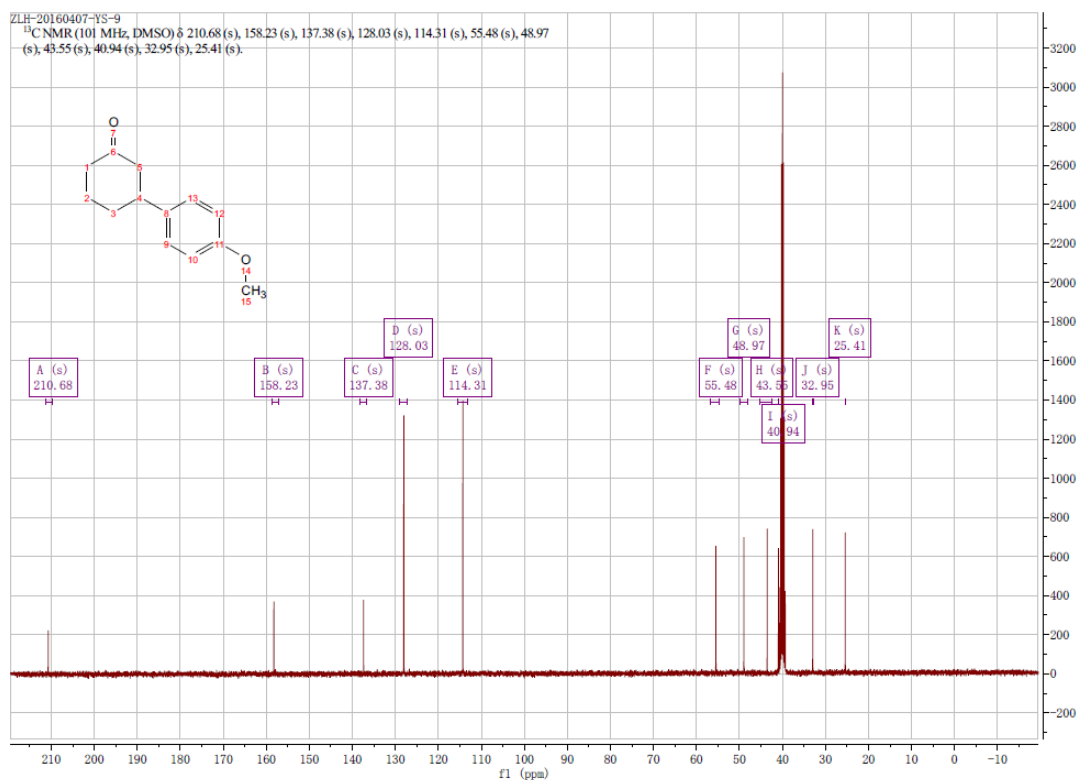
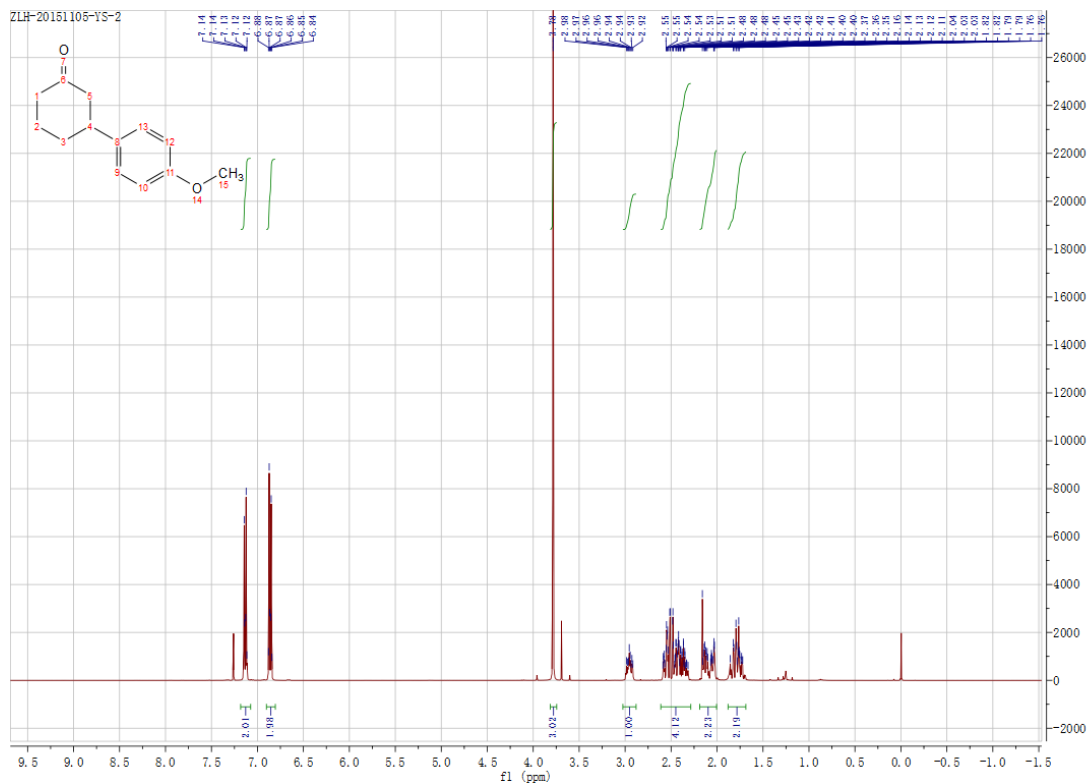


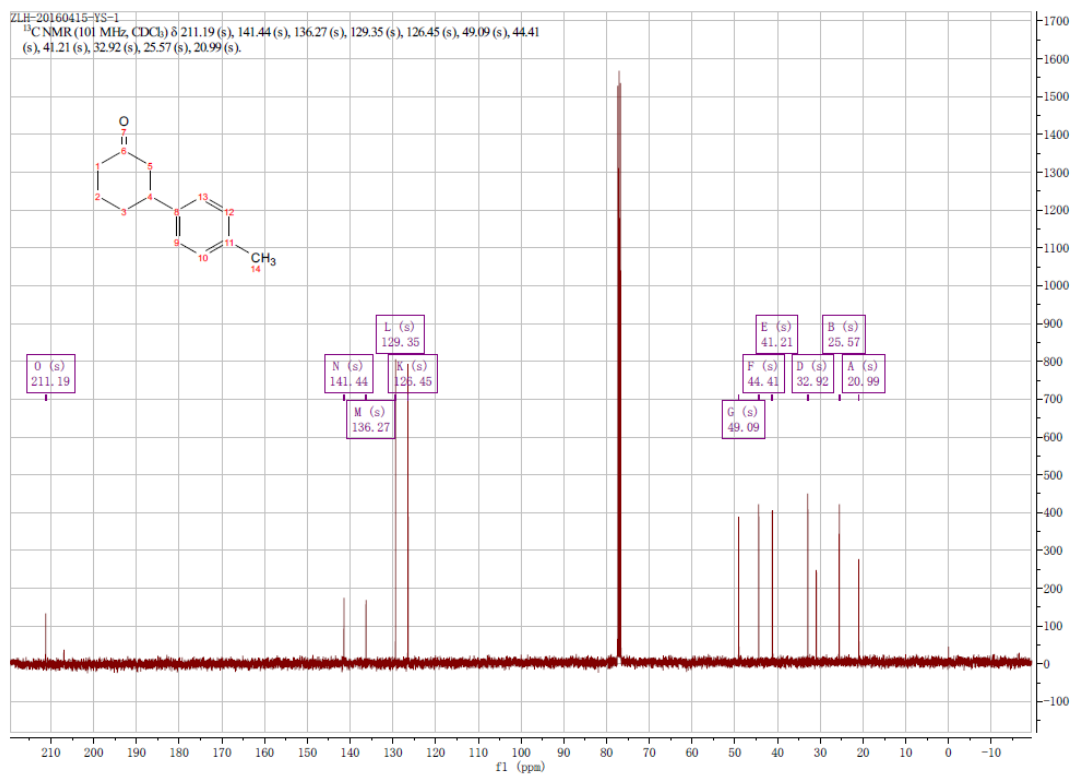
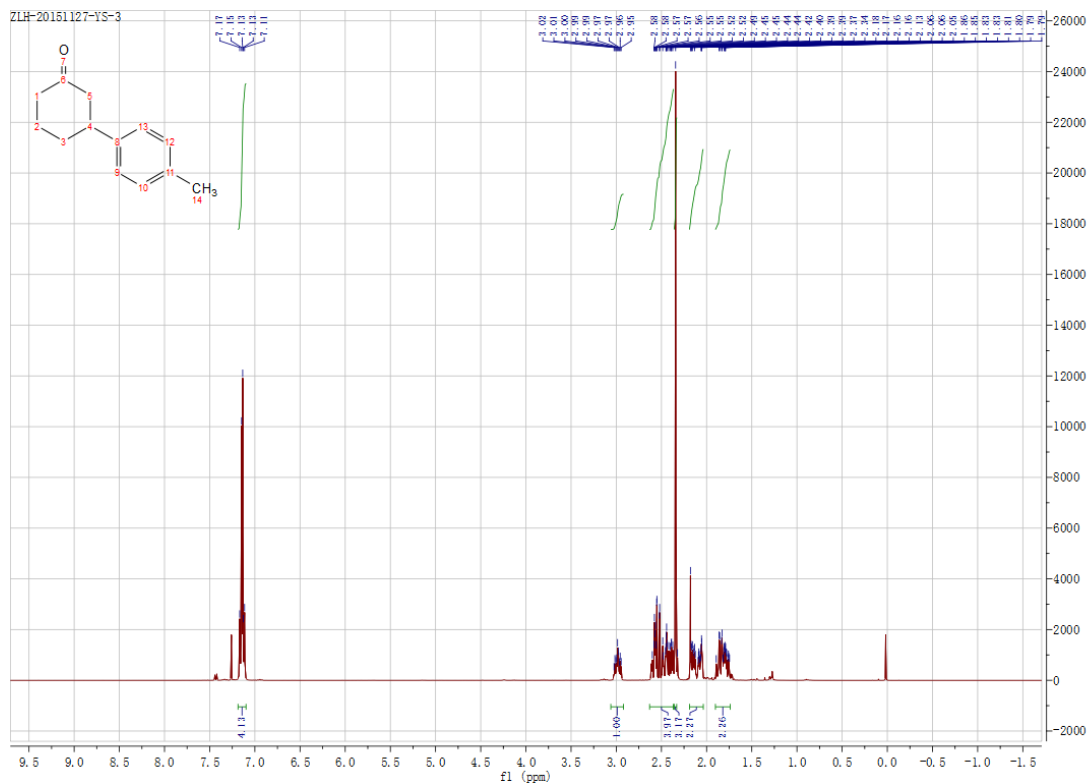


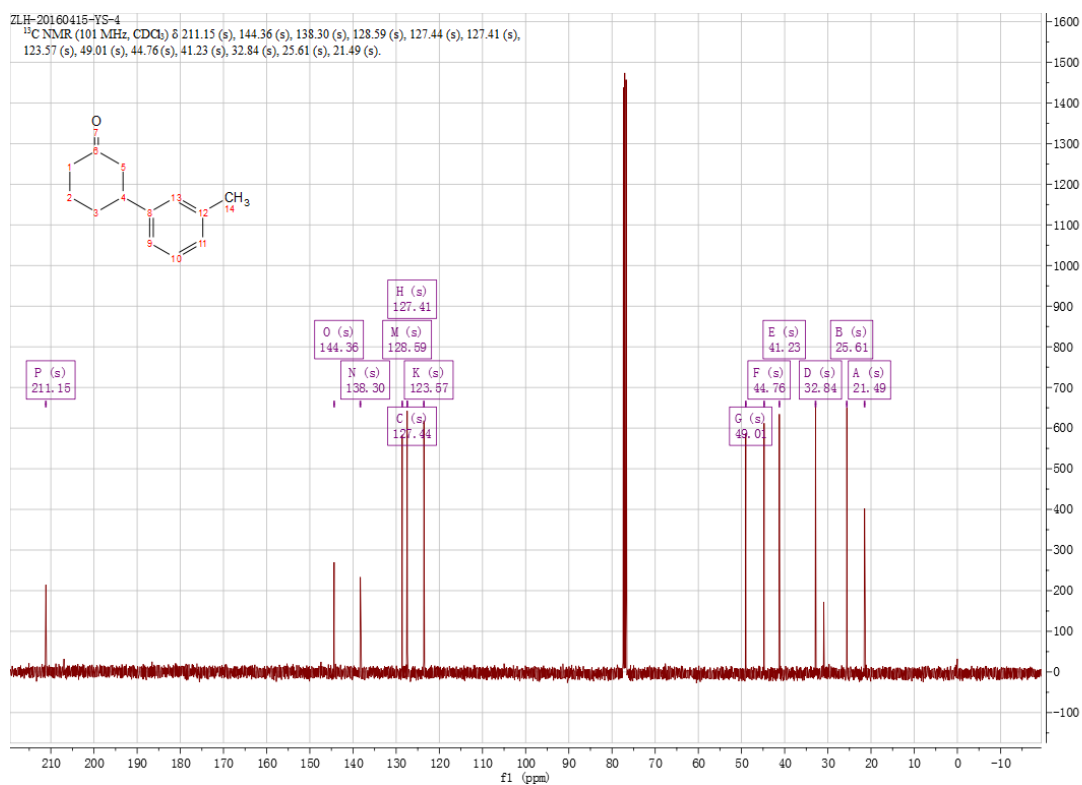
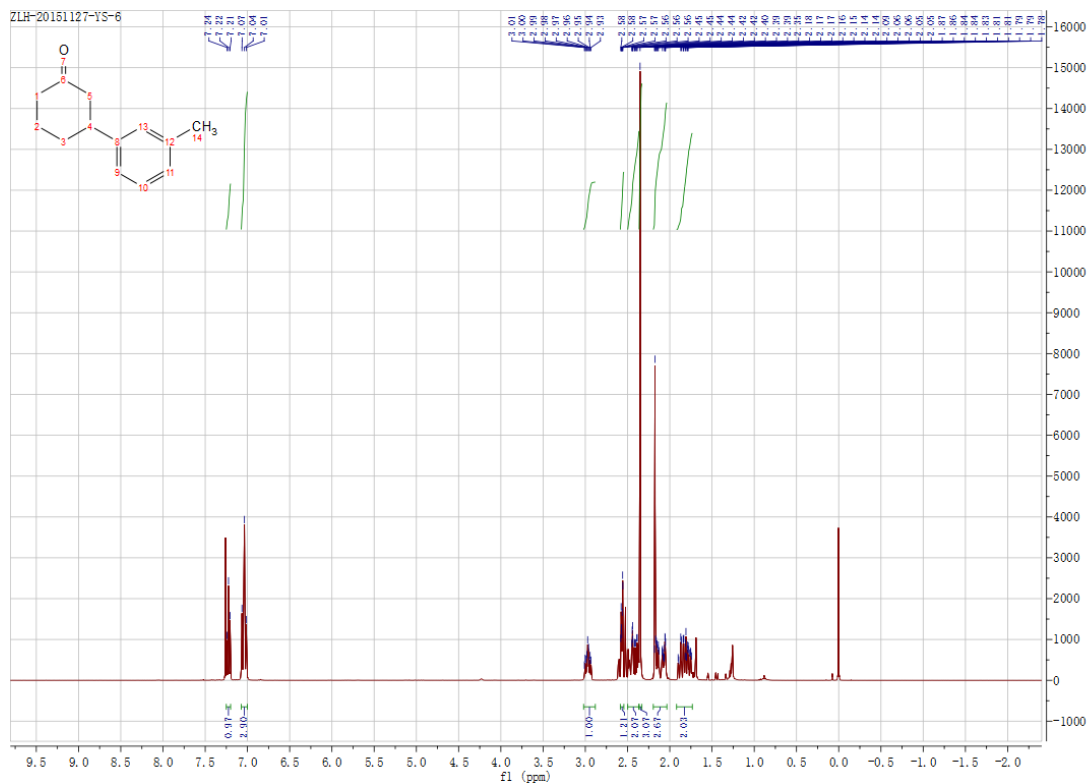


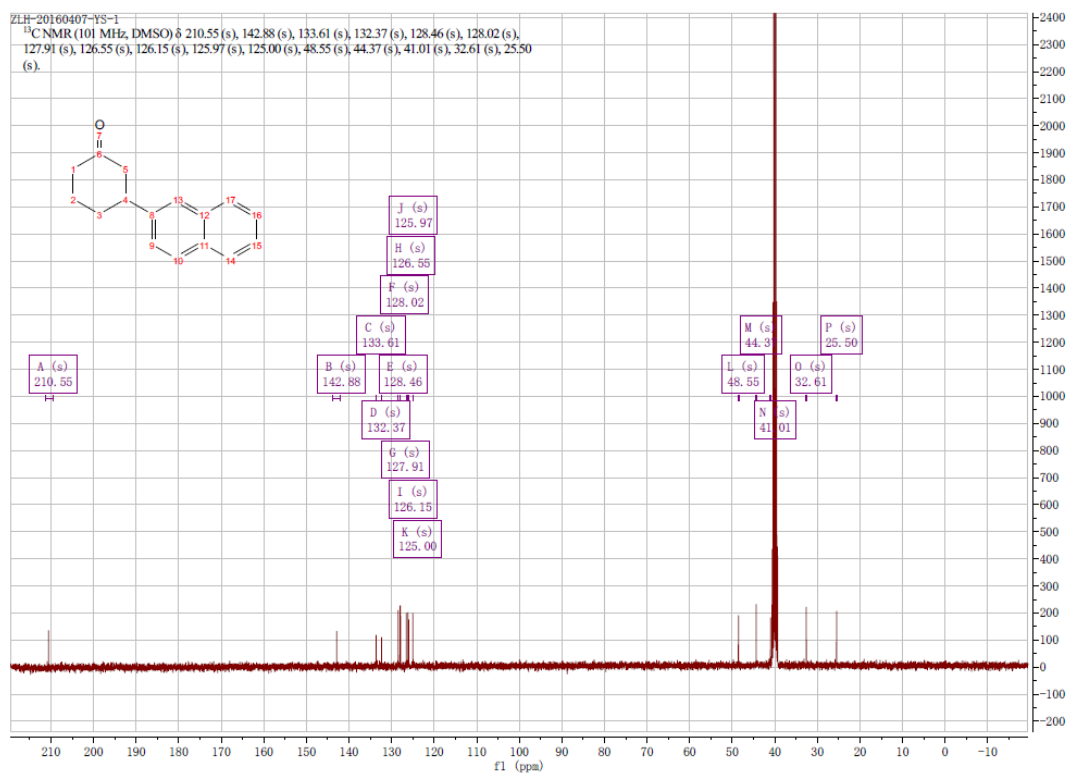
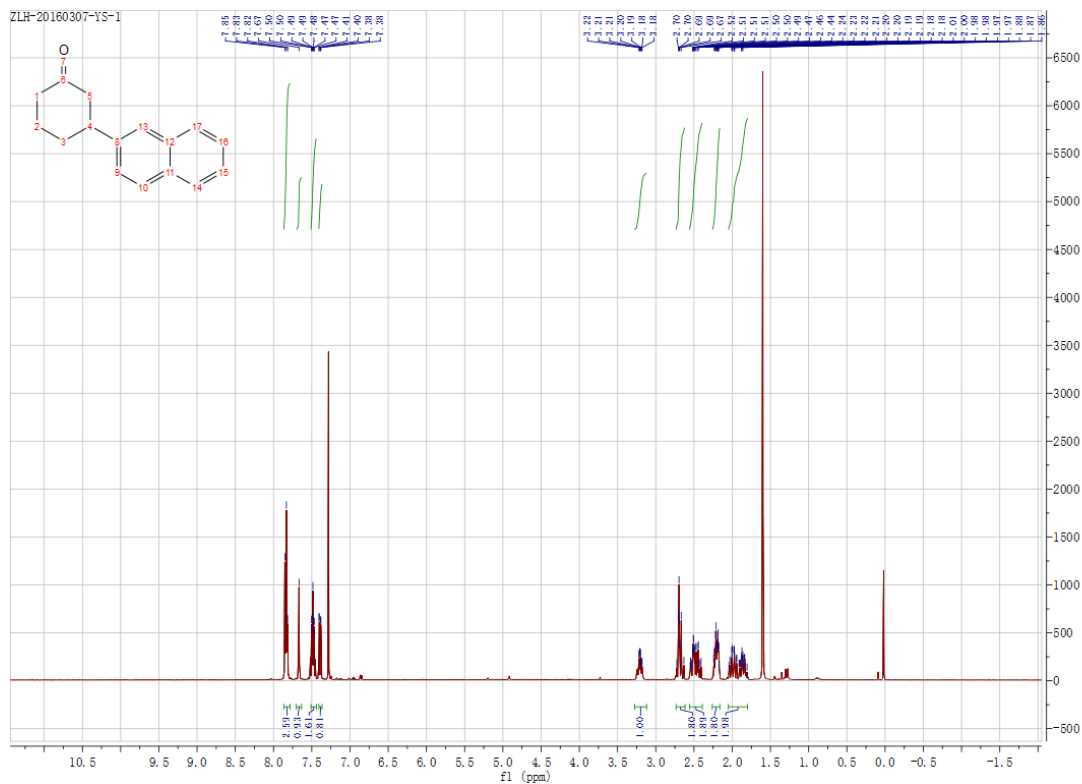


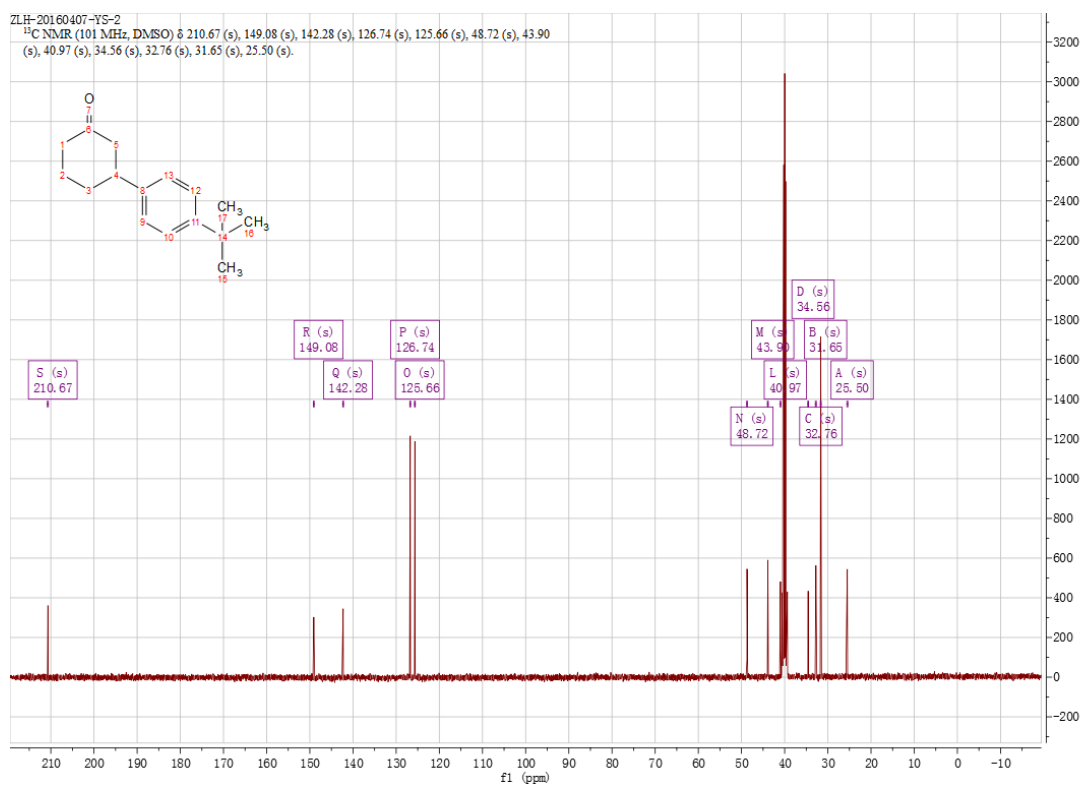
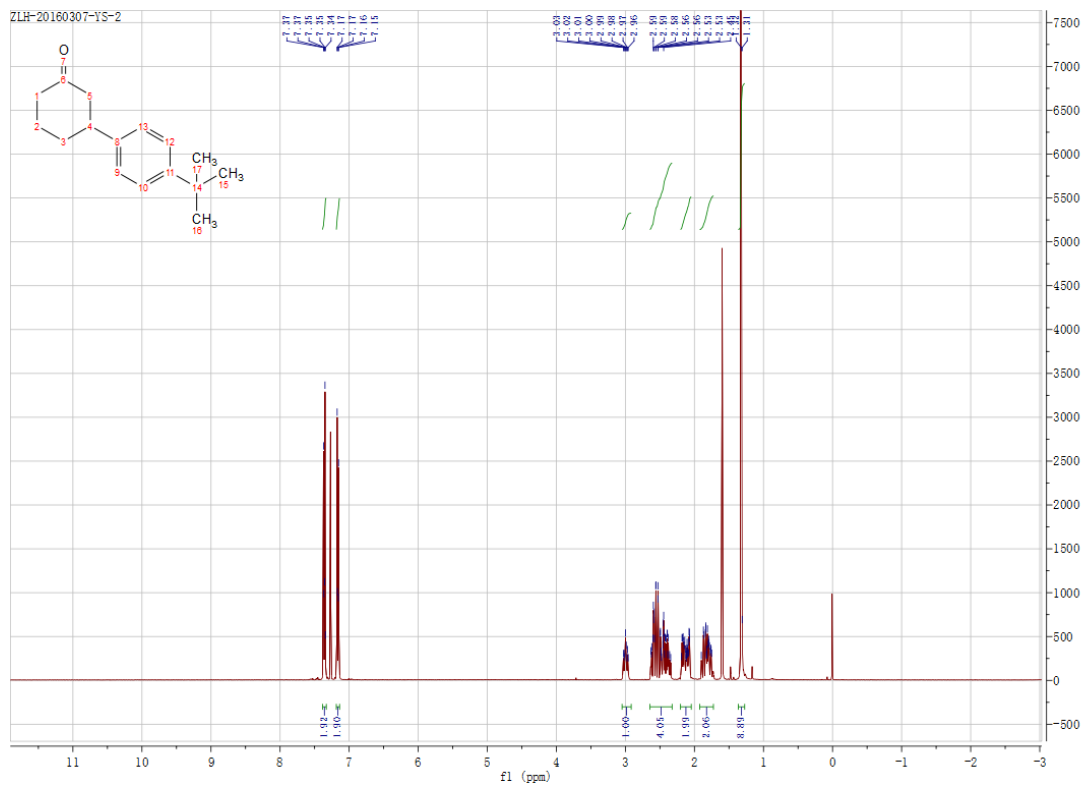


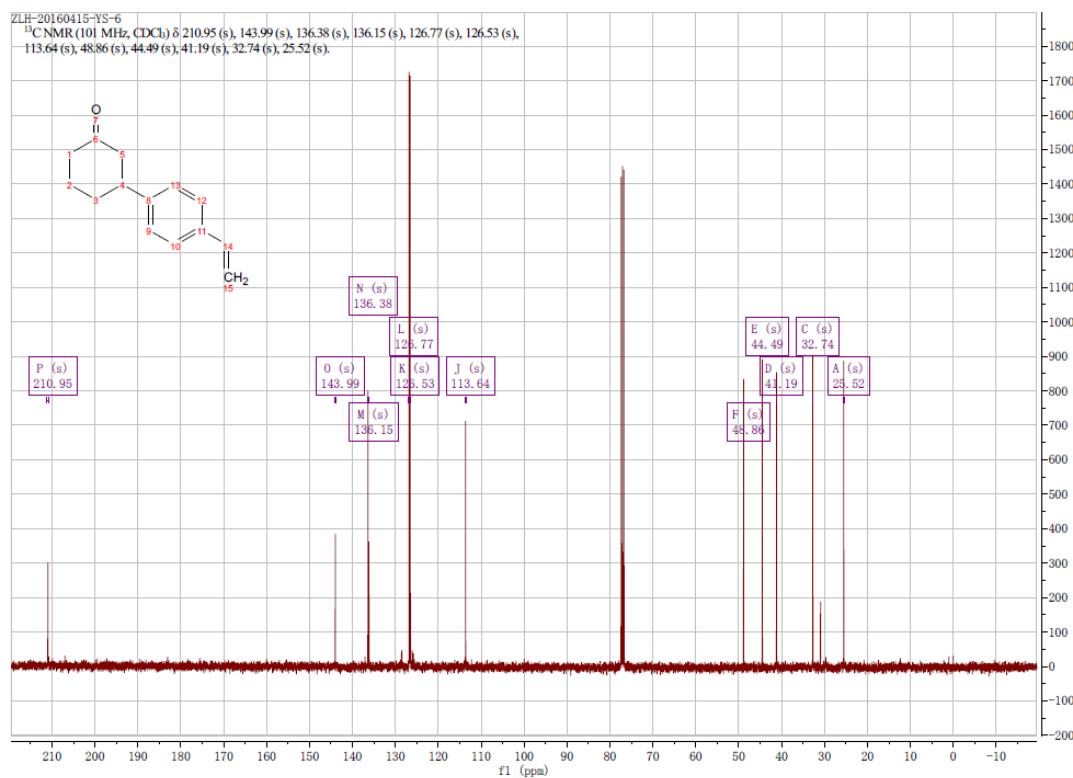
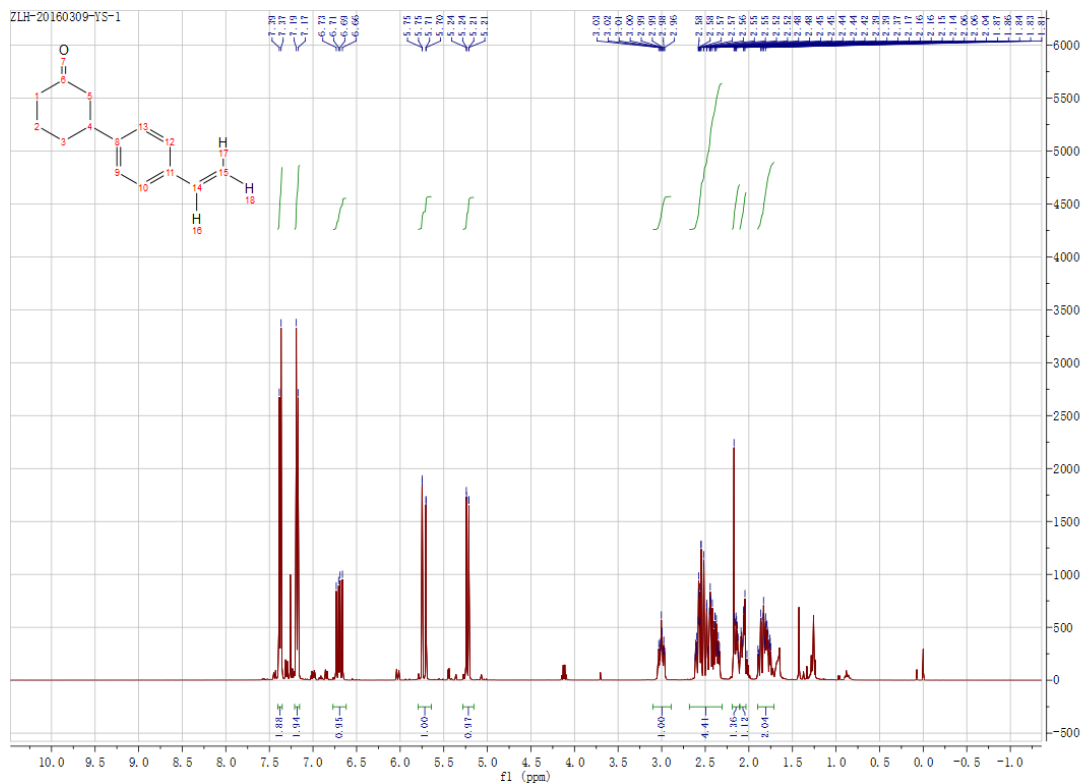


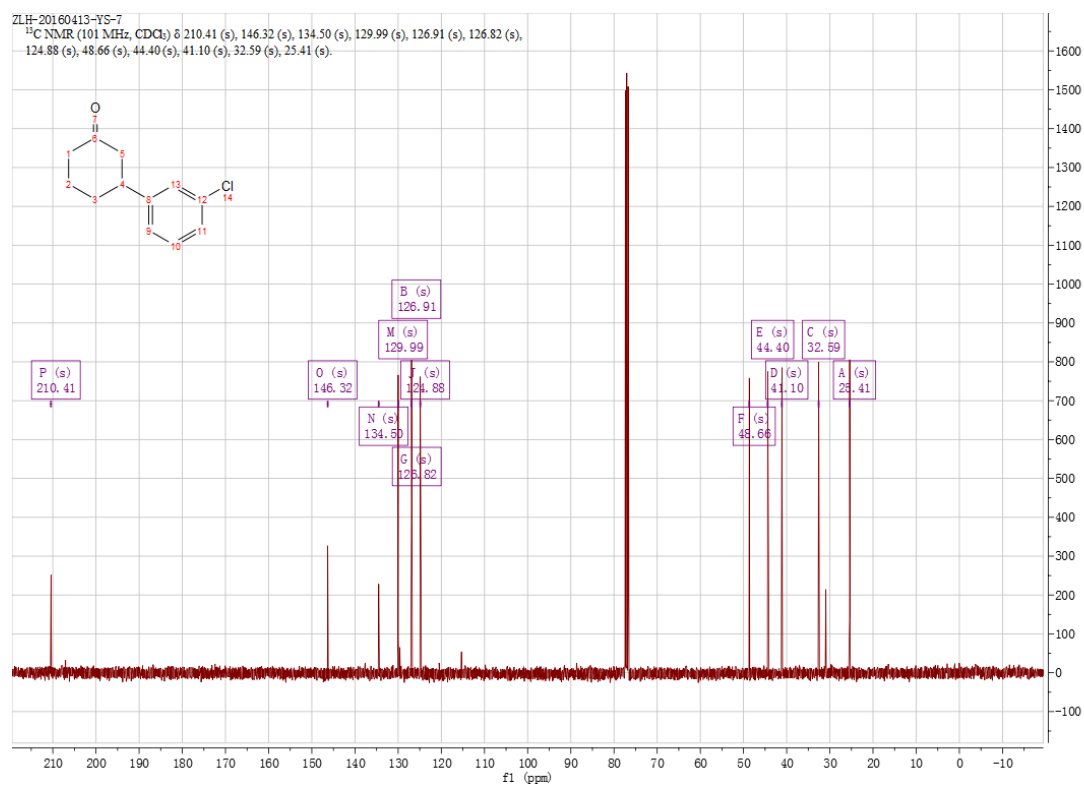
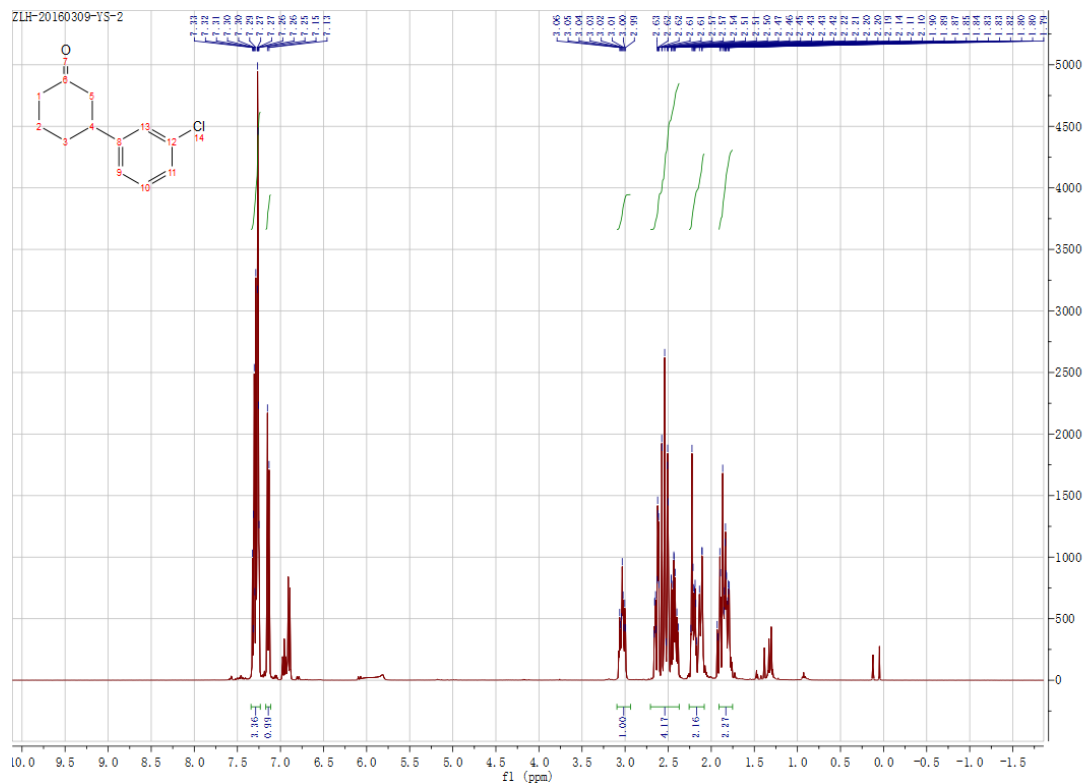


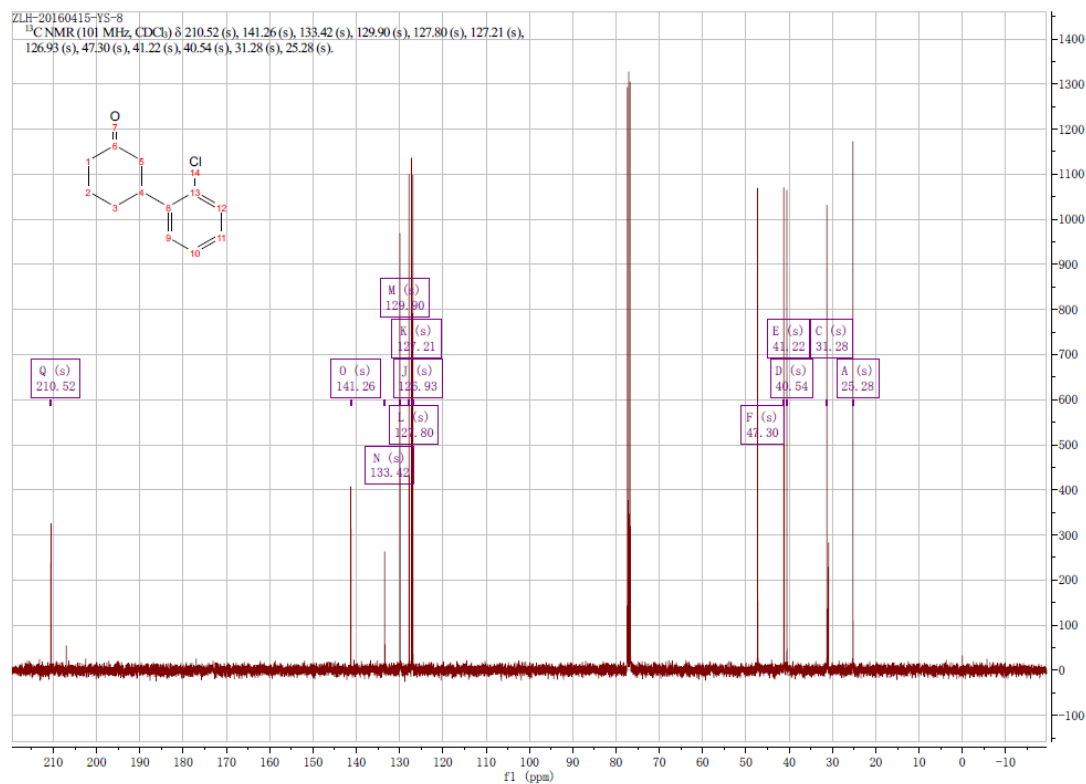
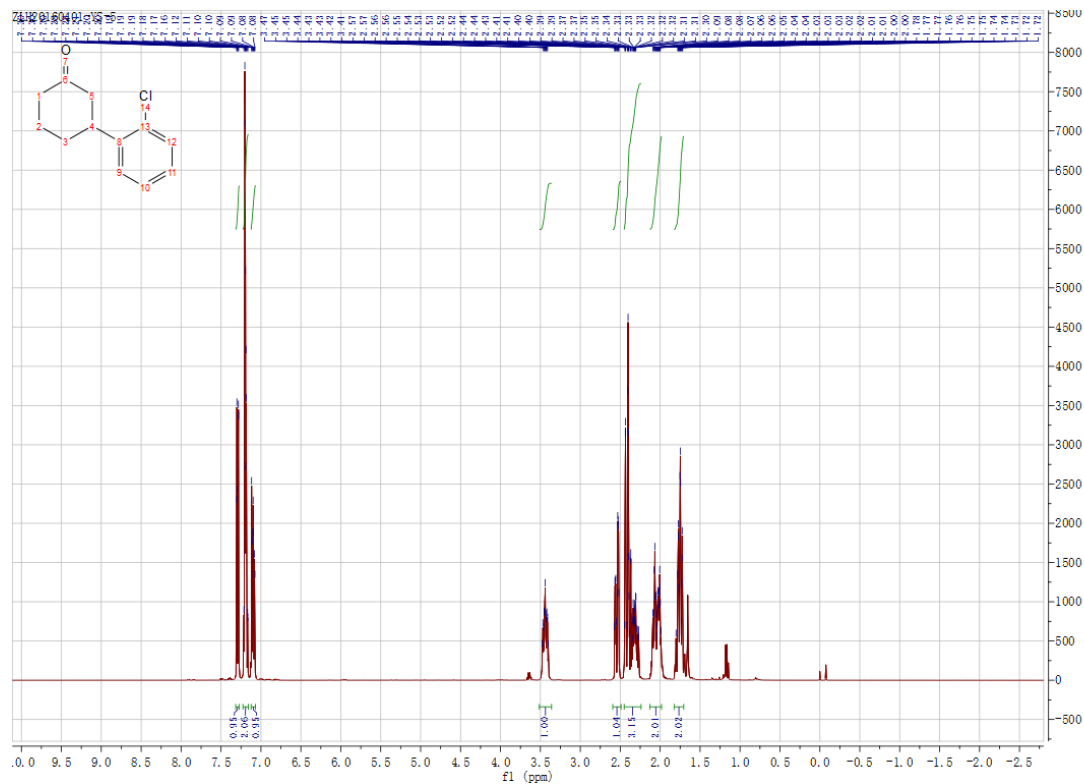


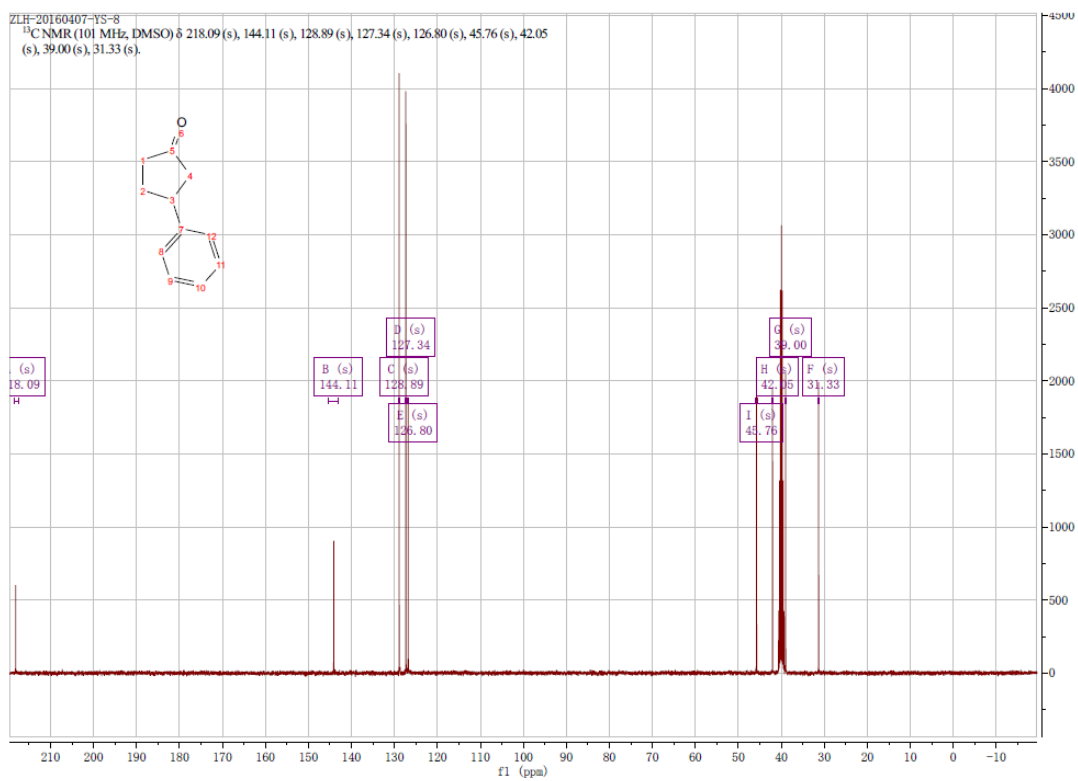
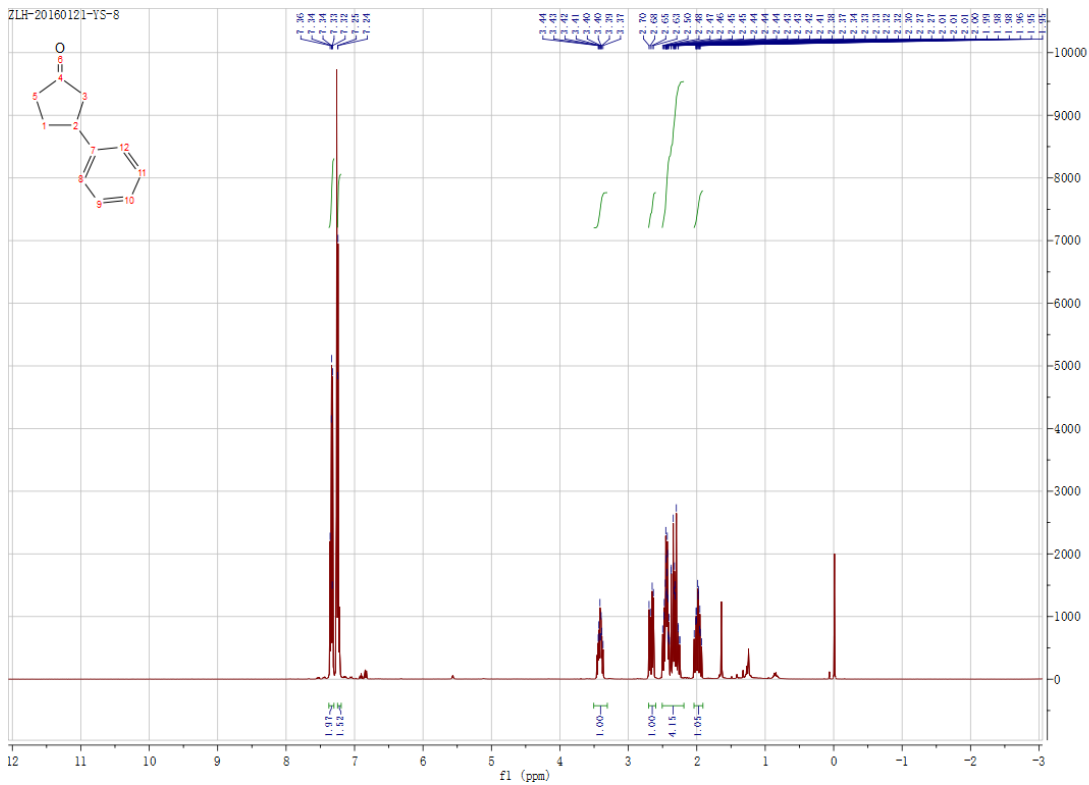


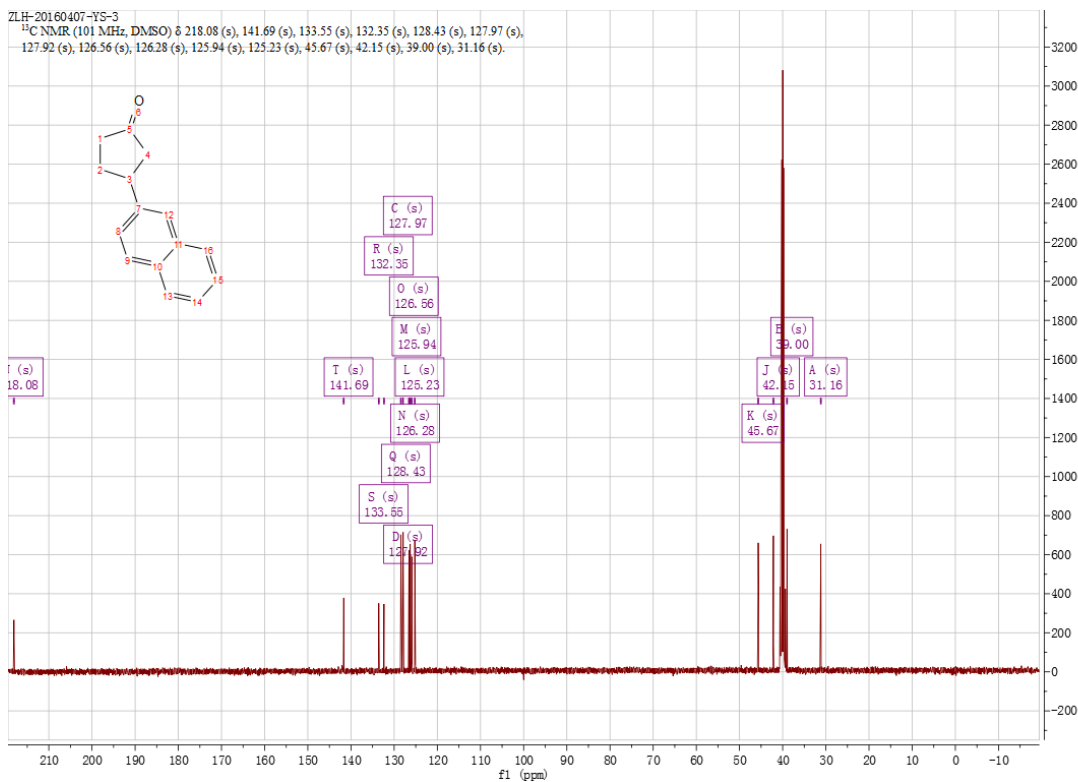
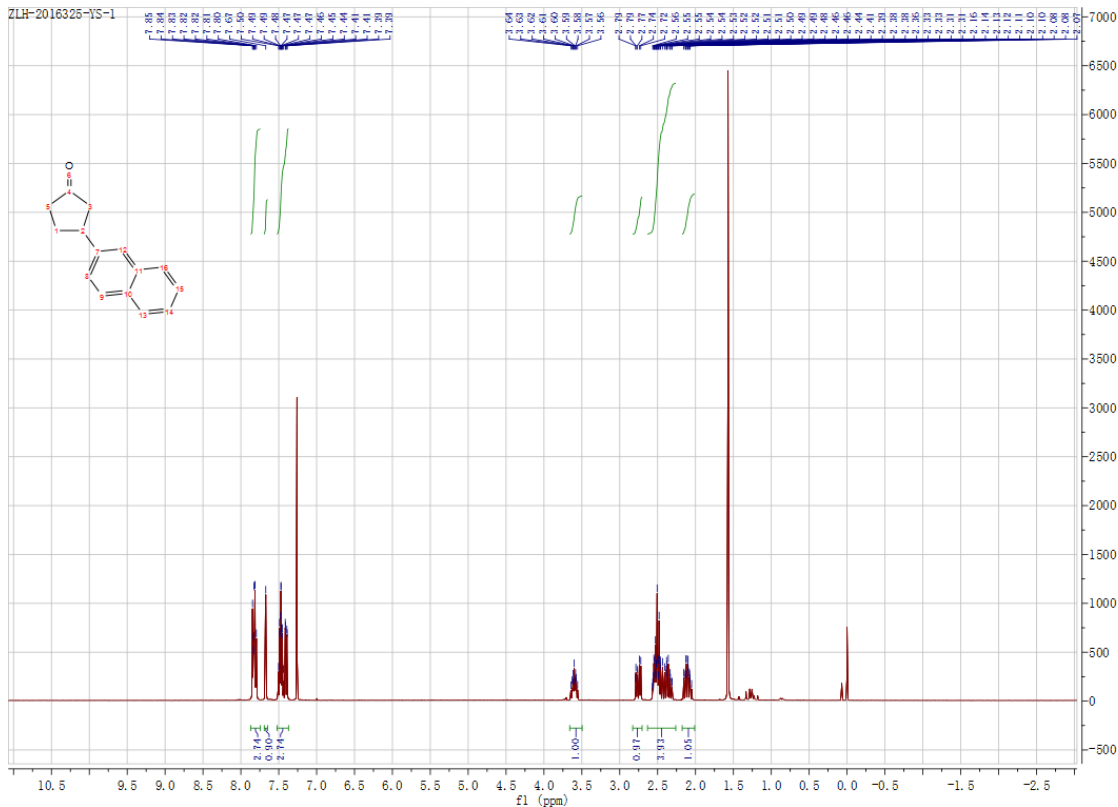


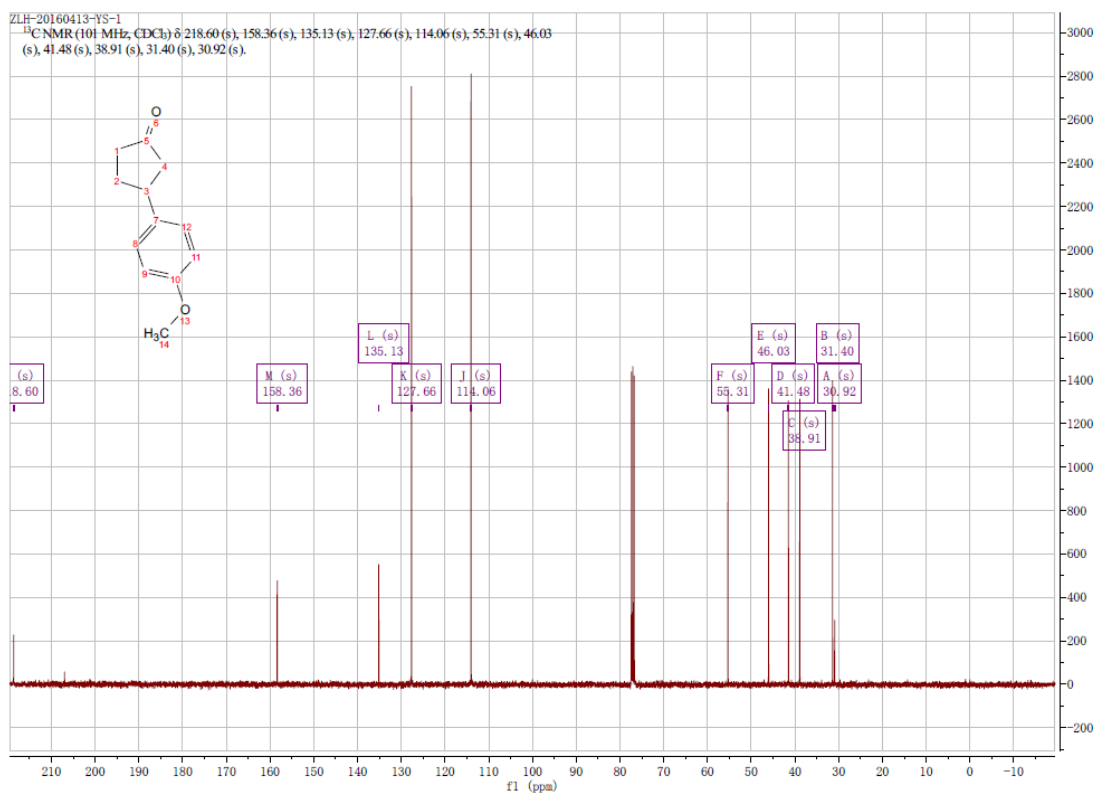
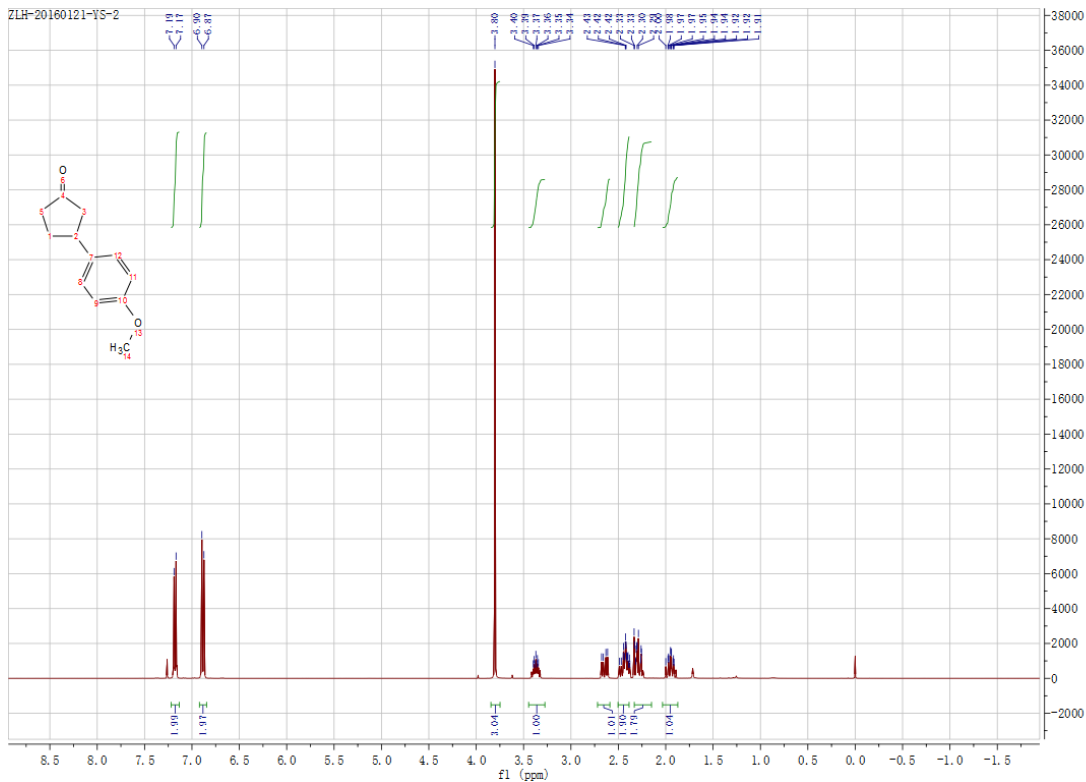


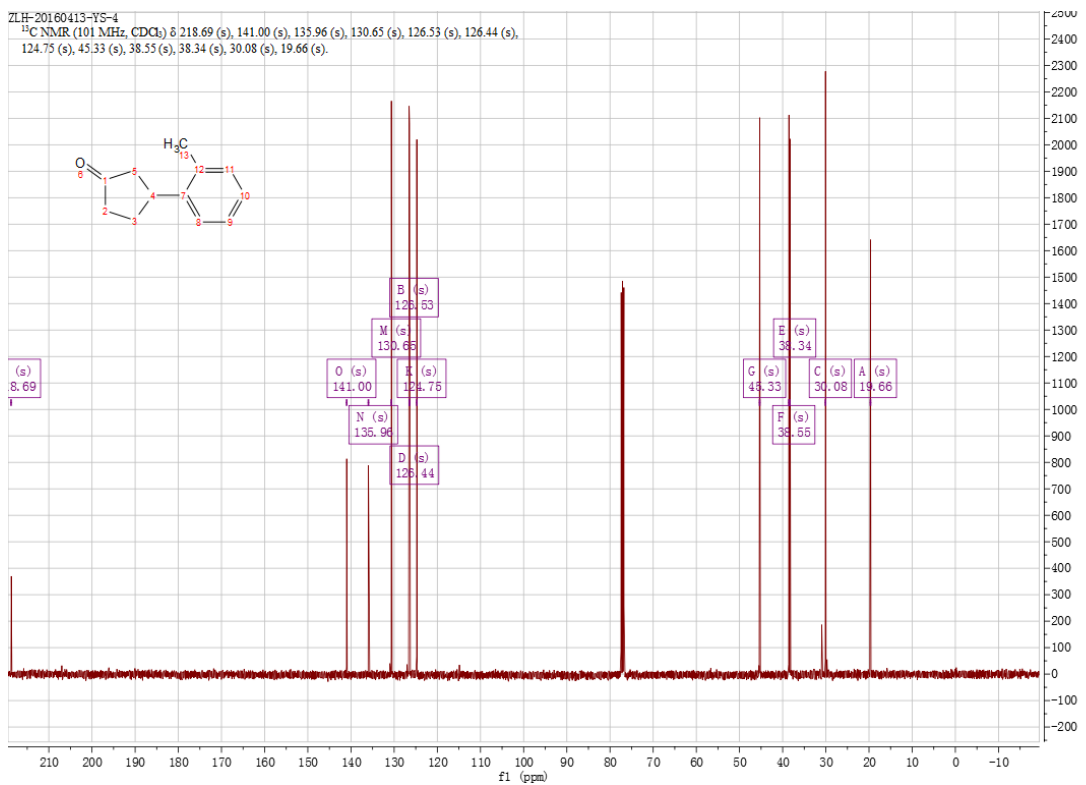
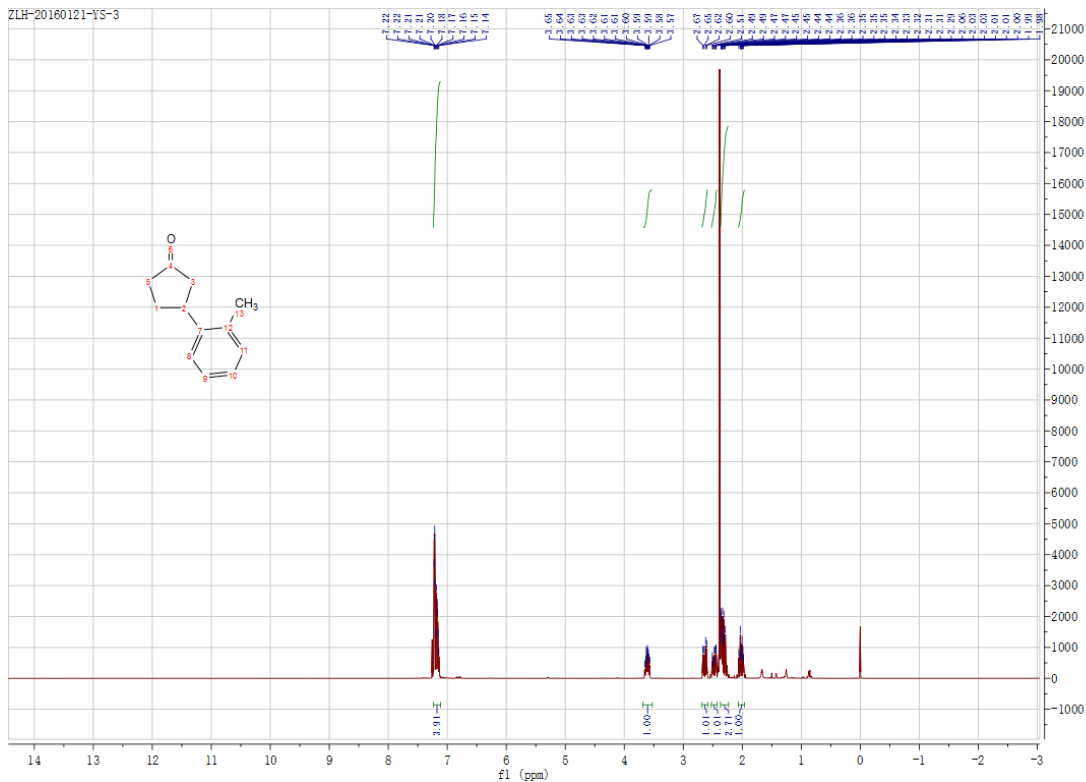


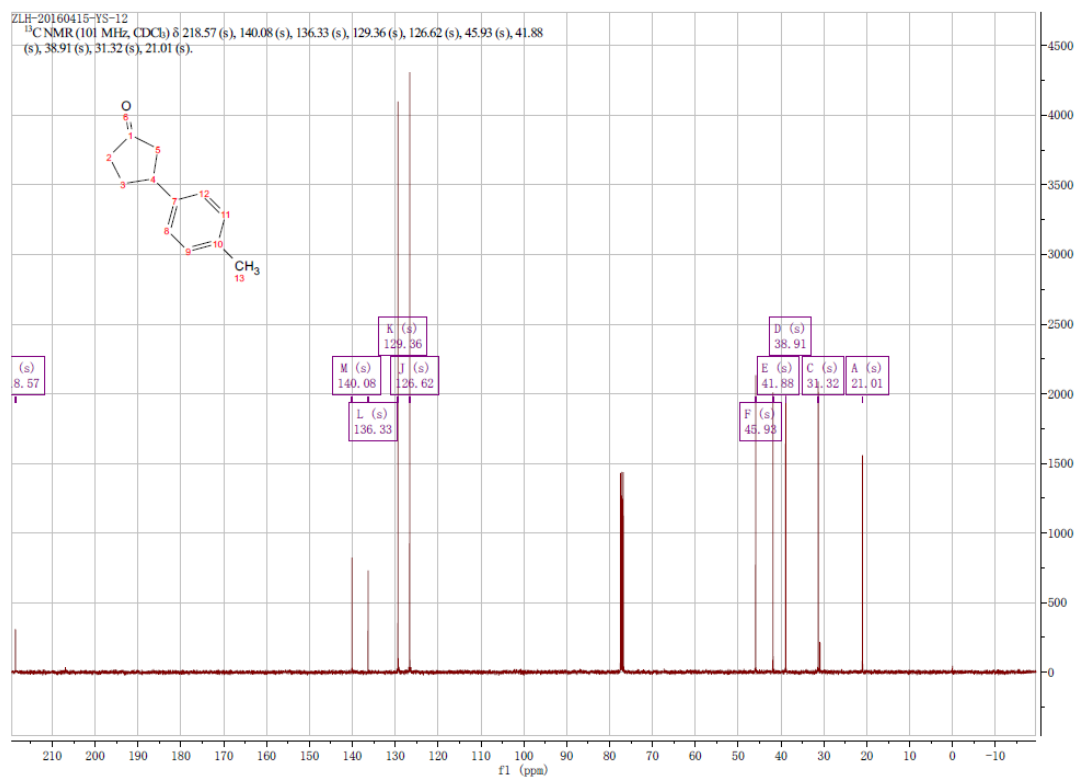
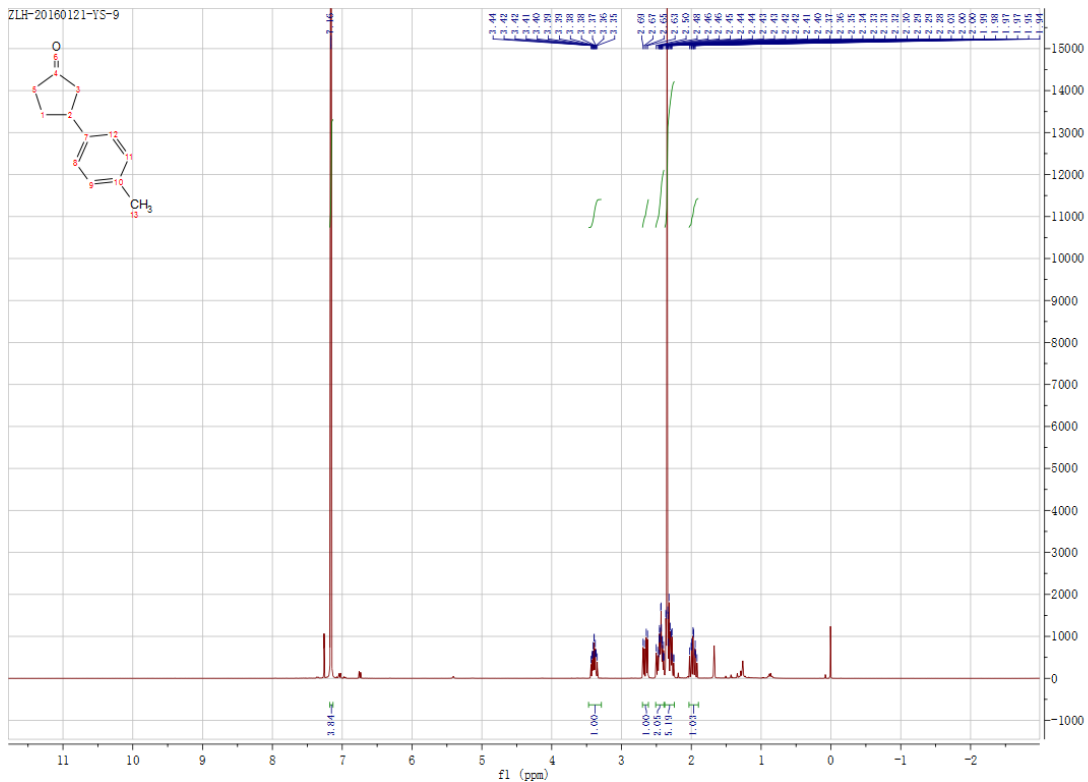




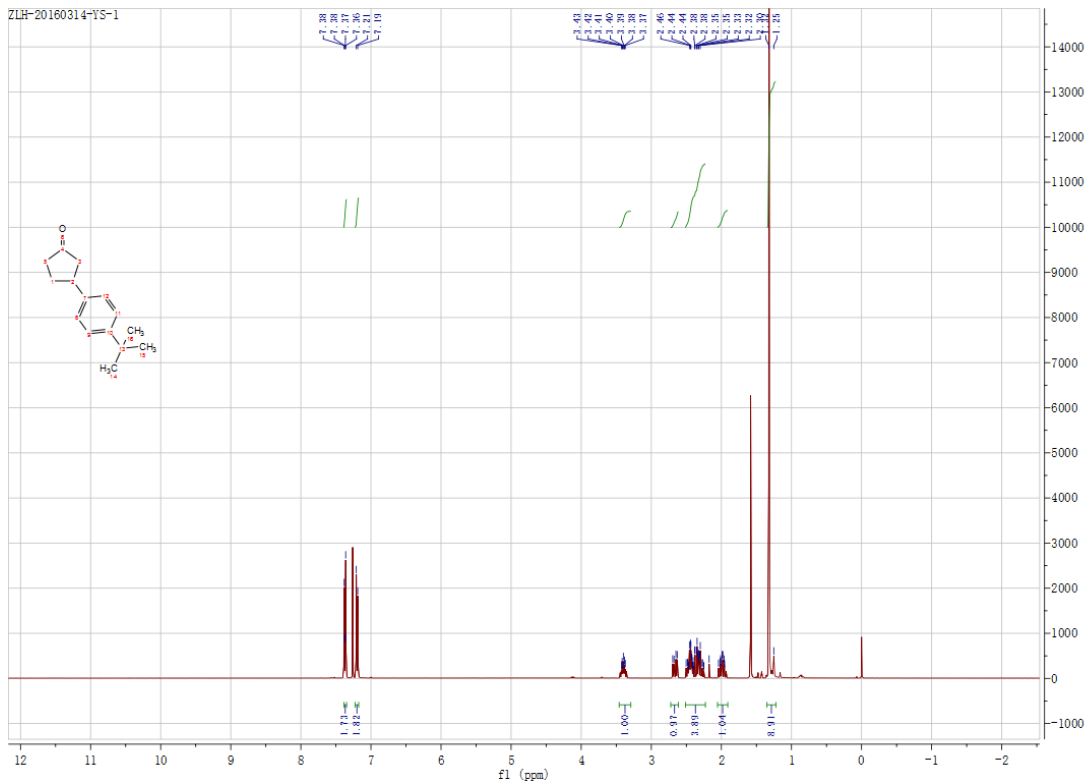




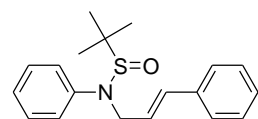
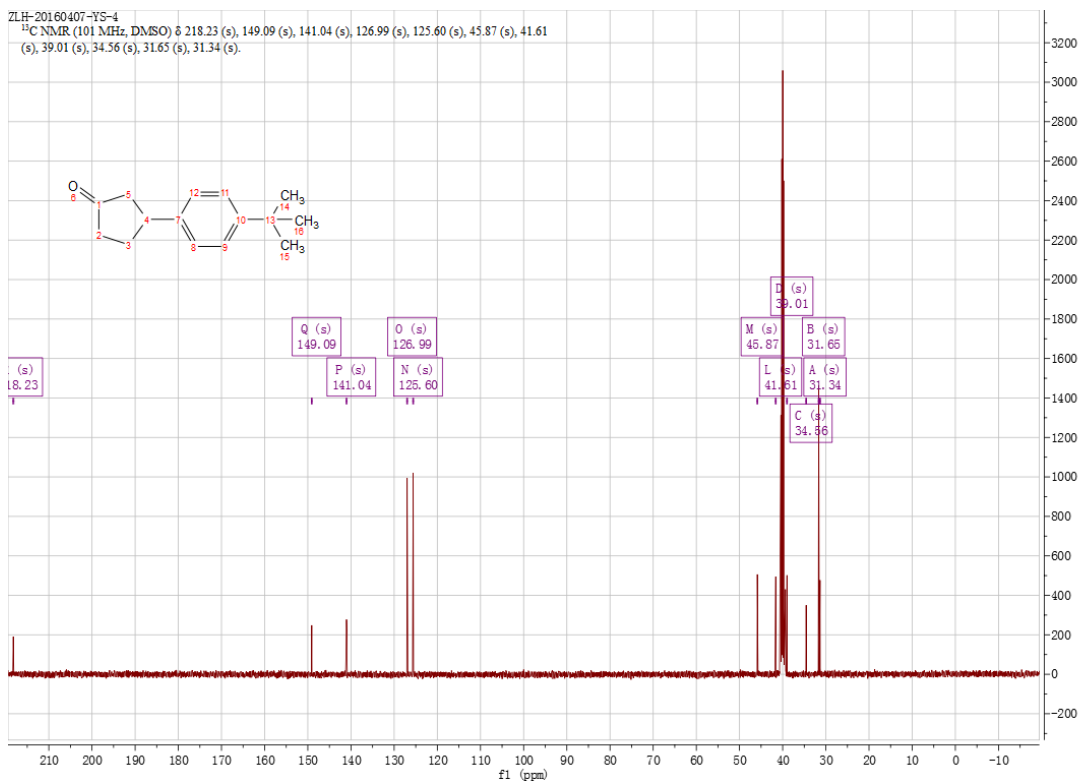




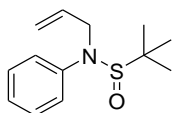
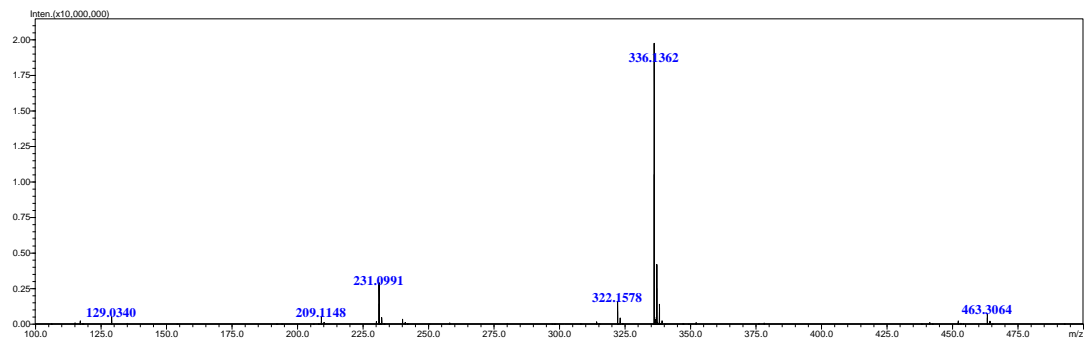
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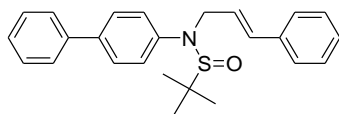
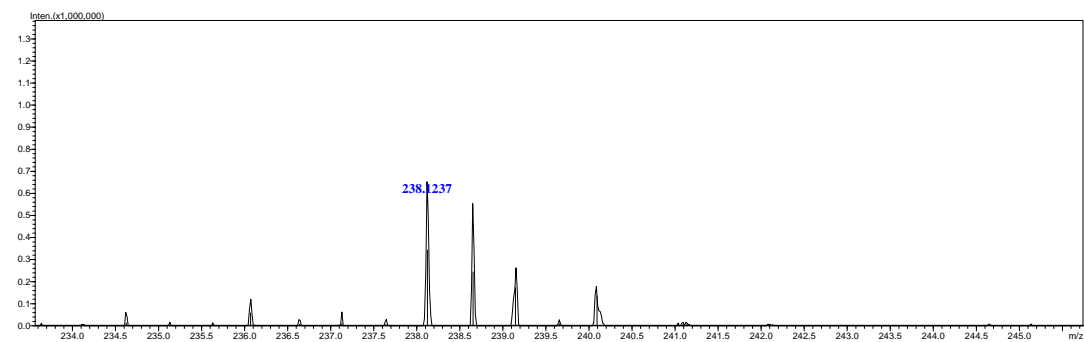
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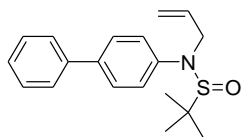
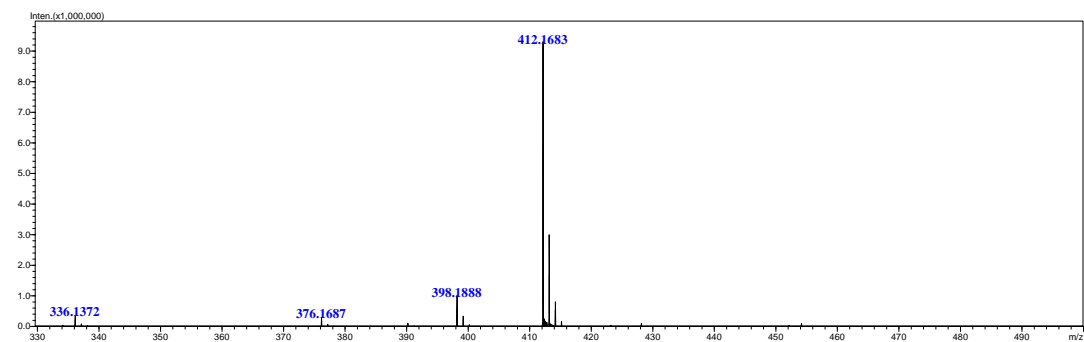
(R)-N-cinnamyl-2-methyl-N-phenylpropane-2-sulfonamide



(R)-N-allyl-2-methyl-N-phenylpropane-2-sulfinamide



(R)-N-([1,1'-biphenyl]-4-yl)-N-cinnamyl-2-methylpropane-2-sulfinamide



(R)-N-([1,1'-biphenyl]-4-yl)-N-allyl-2-methylpropane-2-sulfinamide

