Supplementary Material

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

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General

All reactions were carried out under an argon atmosphere. All glassware used was dried in electric oven at 120 ^{o}C. All chemicals were purchased from Aldrich, Alfa Aesar, Adamas, Aladdin, and Chengdu Changzheng Chemical Company and used as received. Petroleumether (PE) refers to the fraction boiling in the 60–90 °C range. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, HR-MS and IR spectroscopy, unless otherwise mentioned. Nuclear magnetic resonance spectra were recorded on a 300MHz instrument or 400 MHz instrument. All ^{1}H 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 ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.2 ppm), DMSO-d_6 (39.5 ppm) or acetone-d_6 (206.7 ppm for C=O) unless otherwise stated, and all were obtained with ^{1}H 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-butanesulfinamide (13.0 mmol), $Pd_2(dba)_3$ (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 ^{o}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 $MgSO_4$. 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-butanesulfinamide.

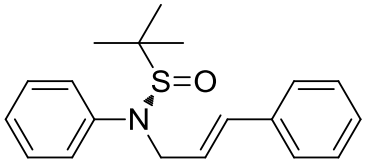
To an oven-dry round-bottom flask with a magnetic stir bar was added N-phenyl (R)-tert-butanesulfinamide (4.0 mmol), 60% NaH (8 mmol), and THF (15 mL). The vessel was evacuated and backfilled with argon for three times. Then the mixture was stirred in an ice water bath for 1 h, and then added cinnamyl bromide (1.2 mmol) by syringe to the flask. The reaction mixture was stirred overnight. Then quenched by saturated NH_4Cl 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 $MgSO_4$. 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-sulfinamide (**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), $[RhCl(C_2H_4)_2]_2$ (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 ^{o}C for 30 min, and then aqueous K_3PO_4 (0.5 mmol) was added by syringe to the flask. After being stirred at 40 ^{o}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 $MgSO_4$. 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.

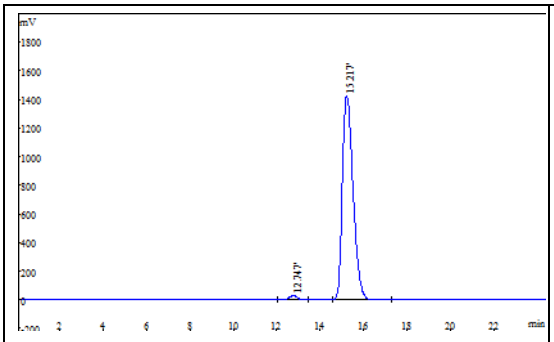
Spectral data of Chiral Ligands



(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°(c 0.21, CH_2Cl_2). **^{1}H NMR** (400 MHz, DMSO-d_6) 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). **^{13}C NMR** (101 MHz, DMSO-d_6) 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 $C_{19}H_{23}NNaOS$ $[M+Na^+]$ 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 %.



Rank	Time	Conc.	Area	Height
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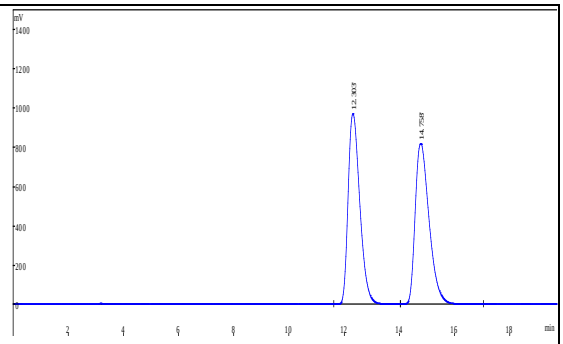
2	15.217	98.2	47299475	1417810
Total		100	48167707	1449275



Rank	Time	Conc.	Area	Height
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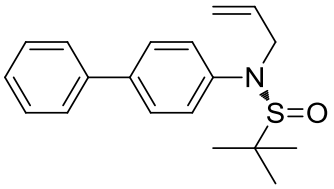
2	14.758	50.13	27860454	817079
Total		100	55572556	1785732

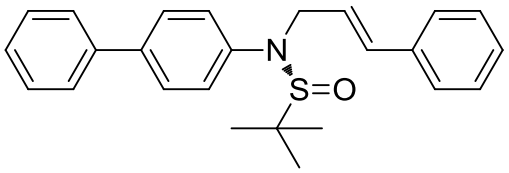


(R)-N-([1,1'-biphenyl]-4-yl)-N-allyl-2-methylpropane-2-sulfinamide (L3)

White solid. Yield: 21.0 mg (80%). Mp. 72-75 °C. $[\alpha]_D^{21.0}$ +88.98° (c 0.12, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (101 MHz, DMSO-d_6) 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 $[M + Na]^+$. HR-MS (ESI-TOF) m/z calcd for $C_{19}H_{23}NOS$ $[M+Na^+]$ 336.1393; found 336.1405.

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: 5.5 min (minor), 10.6 min (major).

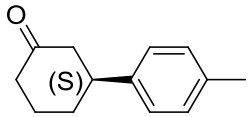


(R)-N-([1,1'-biphenyl]-4-yl)-N-cinnamyl-2-methylpropane-2-sulfinamide (L4)

Yellow solid. Yield: 23.3mg (81%). Mp. 116-119 °C. $[\alpha]_D^{21.2}$ +116.20° (c 0.14, CH_2Cl_2). **^{1}H 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 ($[M + Li]^+$). HR-MS (ESI-TOF) m/z calcd for $C_{25}H_{27}NNaOS$ $[M+Na^+]$ 412.1706; found 412.1715.

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: 15.3 min (minor), 20.3 min (major).

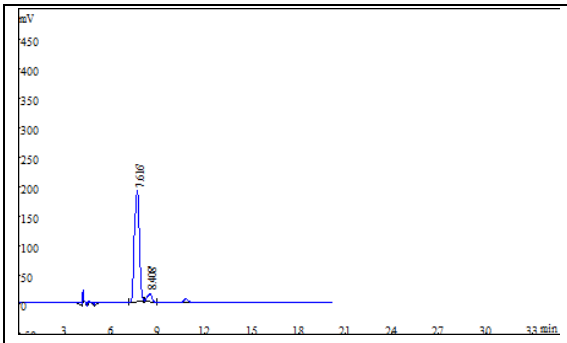
Spectral data and chiral HPLC traces of measured reaction products



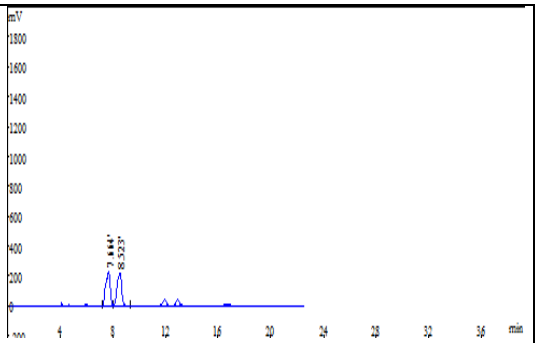
(S)-3-(*p*-Tolyl)cyclohexanone [1]

3a: ^{1}**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}**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).

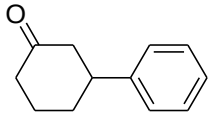
HPLC: Chiralpak AD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 7.6 min (major), 8.4 min (minor). Measured ee value = 89 %.



Rank	Time	Conc.	Area
1	7.616	94.08	3959506
2	8.408	5.916	248941
Total		100	4208447



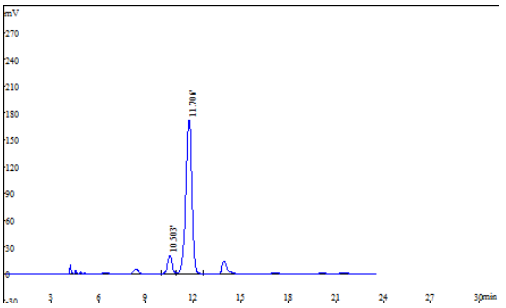
Rank	Time	Conc.	Area
1	7.664	49.36	5027121
2	8.523	50.64	5156672
Total		100	10183793



3-phenylcyclohexanone [4]

3b: ^{1}**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}**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×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 %.



Rank	Time	Conc.	Area
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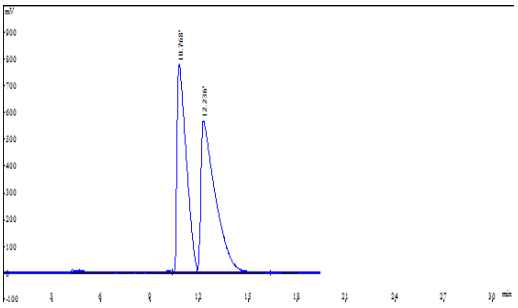
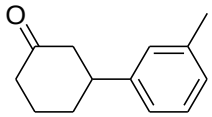
2	11.706	91.31	4709725
Total		100	5157864



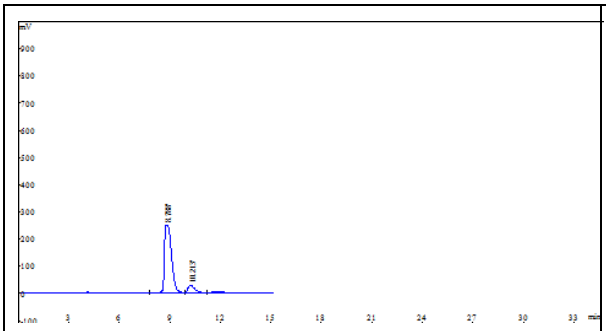
Rank	Time	Conc.	Area
1	10.768	45.87	29576726
2	12.236	54.13	34903440
Total		100	64480166



3-(3-methylphenyl)cyclohexanone [2]

3c: ^{1}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}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×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 %.



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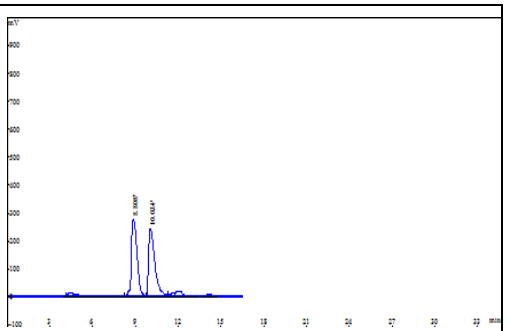
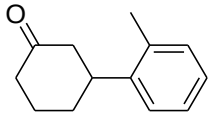
1	8.788	87.6	7102890
2	10.213	12.4	1005173
Total		100	8108063



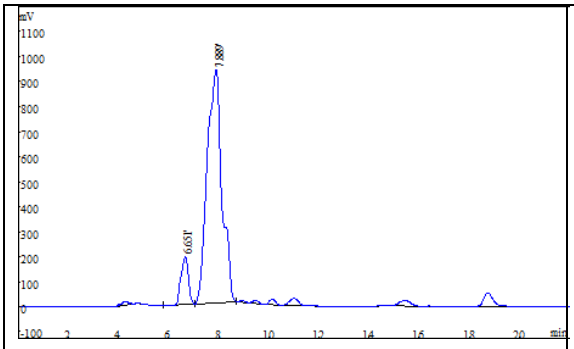
Rank	Time	Conc.	Area
1	8.808	50.23	7427324
2	10.024	49.77	7359170
Total		100	14786494



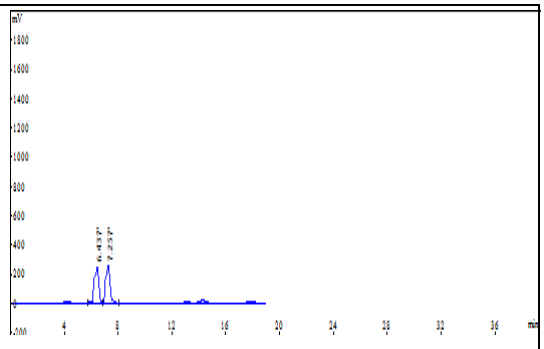
3-(o-Tolyl)cyclohexanone [1]

3d: **^{1}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}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).

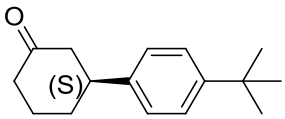
HPLC: Chiralpak AD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 6.7 min (minor), 7.9 min (major). Measured ee value = 81 %.



Rank	Time	Conc.	Area
1	6.651	9.022	3703058
2	7.889	90.98	37342787
Total		100	41045845



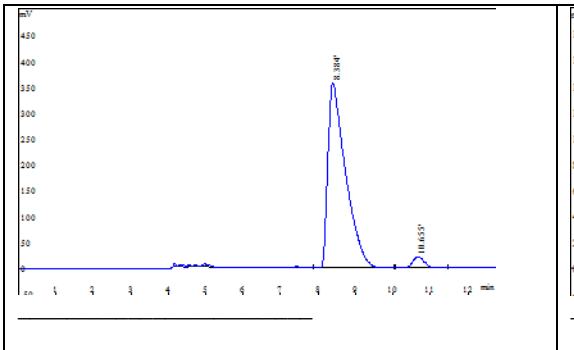
Rank	Time	Conc.	Area
1	6.437	49.16	5299501
2	7.257	50.84	5481229
Total		100	10780730



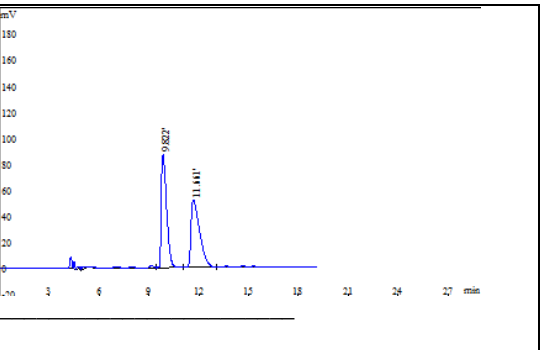
(S)-3-(4-(tert-Butyl)phenyl)cyclohexanone [4]

3e: $[\alpha]_D^{32.5}$ -13.75°(c 0.16, $CHCl_3$). [lit. [9]: $[\alpha]_D^{20}$ = +10.4 (c 0.63, $CHCl_3$), For R-isomer]. **^{1}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}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×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%.



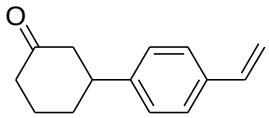
Rank	Time	Conc.	Area



Rank	Time	Conc.	Area

1	8.384	96.28	11554115
2	10.655	3.719	446310
Total		100	12000425

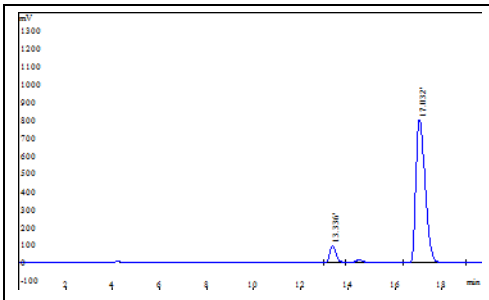
1	9.822	49.73	1788404
2	11.661	50.27	1807588
Total		100	3595992



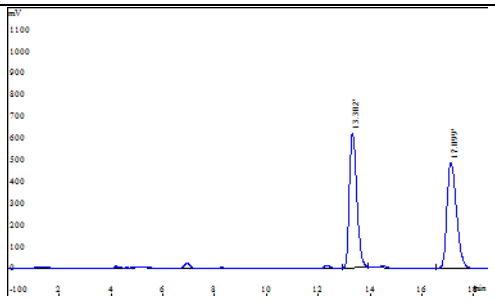
3-(4-vinylphenyl)cyclohexan-1-one

3f: **^{1}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}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).

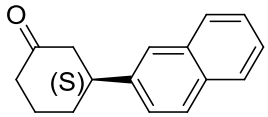
HPLC: Chiralpak AS-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 13.3 min, 17.0 min (major). Measured ee value = 85%.



Rank	Time	Conc.	Area
1	13.336	7.39	1693143
2	17.032	92.61	21219539
Total		100	22912682



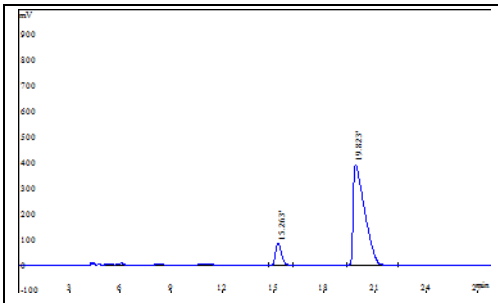
Rank	Time	Conc.	Area
1	13.302	49.57	11786688
2	17.099	50.43	11990669
Total		100	23777357



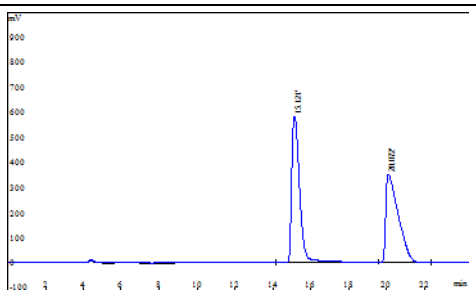
(S)-3-(naphthalen-2-yl)cyclohexan-1-one [4]

3g: $[\alpha]_D^{32.3}$ -6.67°(c 0.15, $CHCl_3$) [lit. [4]: $[\alpha]_D^{20}$ -8.7 (c 0.072, $CHCl_3$)]. **^{1}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}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).

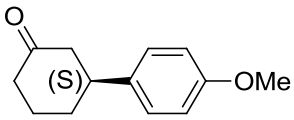
HPLC: Chiralpak AS-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 15.3 min, 19.8 min (major). Measured ee value = 79%.



Rank	Time	Conc.	Area
1	15.263	10.03	1990742
2	19.823	89.97	17865544
Total		100	19856286



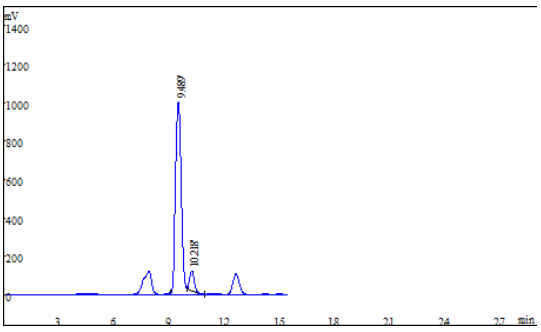
Rank	Time	Conc.	Area
1	15.121	51.54	16608010
2	20.072	48.46	15617286
Total		100	32225296



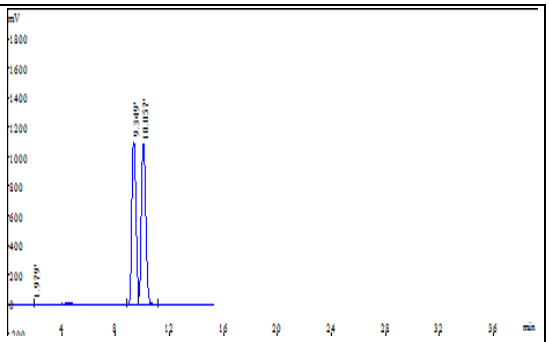
(S)-3-(4-Methoxyphenyl)cyclohexanone [1]

3h: **^{1}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}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).

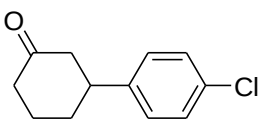
HPLC: Chiralpak AD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 9.5 min (major), 10.2 min (minor). Measured ee value = 85 %.



Rank	Time	Conc.	Area
1	9.489	92.2	21418914
2	10.218	7.804	1813151
Total		100	23232065



Rank	Time	Conc.	Area
1	9.349	50.43	23471046
2	10.057	49.57	23074130
Total		100	46545176

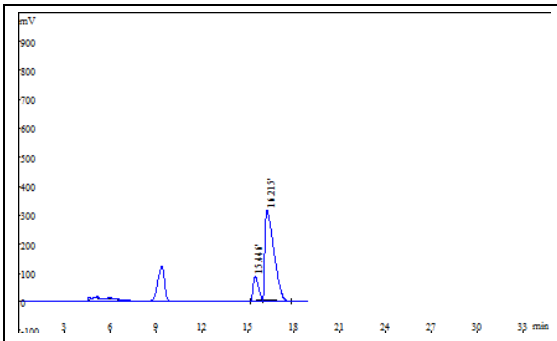


3-(4-Chlorophenyl)cyclohexanone [8]

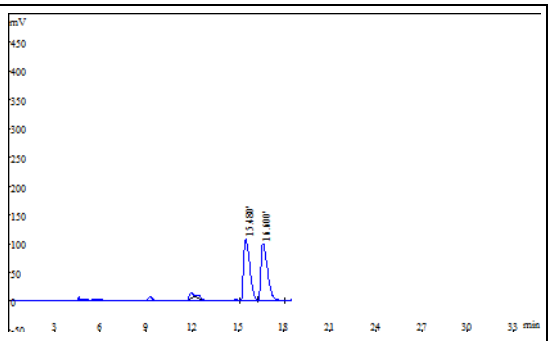
3i: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 2H), 7.11 – 7.05 (m, 2H), 2.92 (tt, *J* = 11.8, 3.9 Hz, 1H), 2.57 – 2.21 (m,

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).

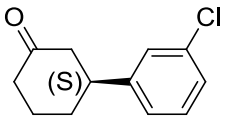
HPLC: Chiralpak AS-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 15.4 min (minor), 16.2 min (major). Measured ee value = 73%.



Rank	Time	Conc.	Area
1	15.446	13.34	1885623
2	16.215	86.66	12250194
Total		100	14135817



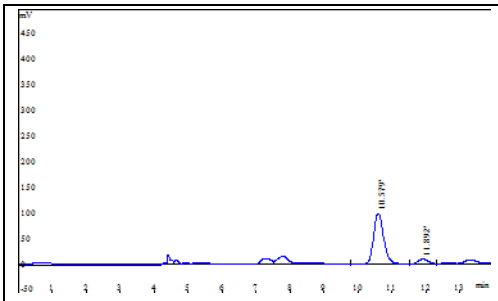
Rank	Time	Conc.	Area
1	15.480	49.3	2776731
2	16.600	50.7	2855229
Total		100	5631960



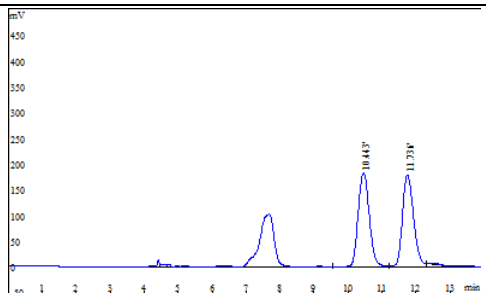
(S)-3-(3-Chlorophenyl)-cyclohexane [5]

3j: ^{1}H 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).

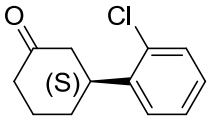
HPLC: Chiralpak AD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 10.6 min (major), 11.9 min (minor). Measured ee value = 83%.



Rank	Time	Conc.	Area
1	10.579	91.11	2015618
2	11.892	8.887	196584
Total		100	2212202



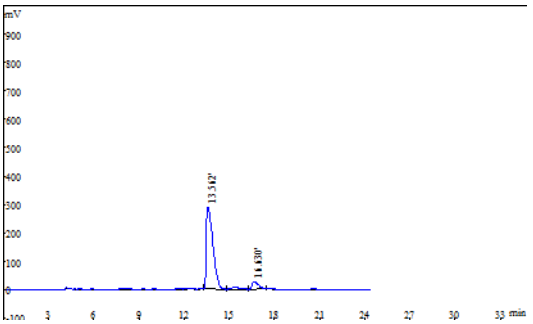
Rank	Time	Conc.	Area
1	10.443	51.82	4074383
2	11.736	48.18	3787748
Total		100	7862131



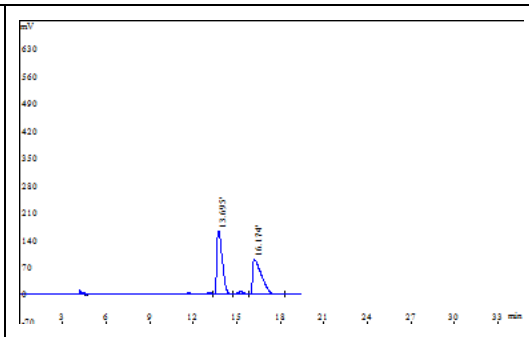
(S)-3-(2-chlorophenyl)cyclohexan-1-one [9]

3k: $[\alpha]_D^{33.1}$ -20.32°(c 0.31, $CHCl_3$) (lit. [9]: $[\alpha]_D^{20}$ = -32.5 (c 0.51, $CHCl_3$)). **^{1}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}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).

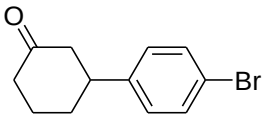
HPLC: Chiralpak AS-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 13.6 min, 16.6 min (major). Measured ee value = 83%.



Rank	Time	Conc.	Area
1	13.562	91.85	8355970
2	16.630	8.151	741591
Total		100	9097561



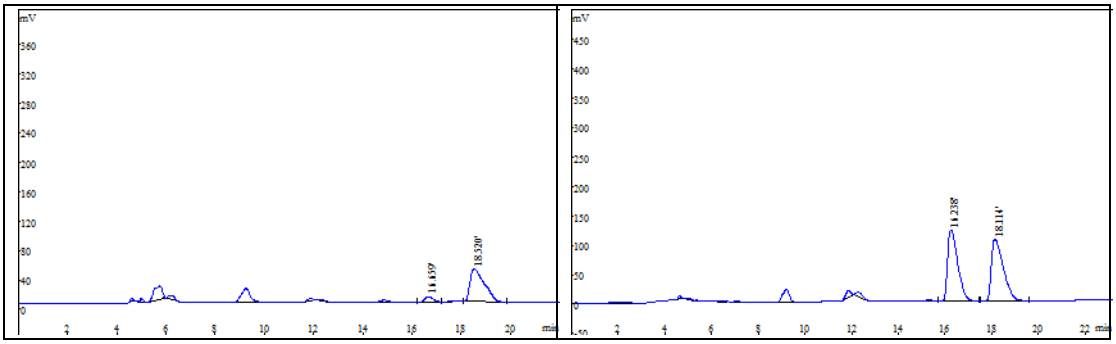
Rank	Time	Conc.	Area
1	13.695	52.06	3928226
2	16.174	47.94	3617375
Total		100	7545601



3-(4-bromophenyl)cyclohexan [10]

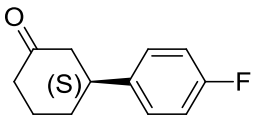
3l: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 2H), 7.09 – 6.98 (m, 2H), 2.90 (tt, *J* = 11.8, 3.9 Hz, 1H), 2.55 – 2.17 (m, 4H), 2.15 – 1.90 (m, 2H), 1.79 – 1.63 (m, 2H). **^{13}C NMR** (101 MHz, CDCl3) δ 210.65 (s), 143.28 (s), 131.77 (s), 128.36 (s), 120.41 (s), 48.72 (s), 44.16 (s), 41.10 (s), 32.63 (s), 25.39 (s).

HPLC: Chiralpak AS-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×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
1	16.613	8.669	189098
2	18.450	91.33	1992353
Total		100	2181451

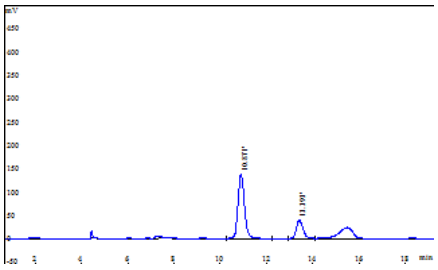
Rank	Time	Conc.	Area
1	16.238	49.65	3459063
2	18.114	50.35	3507152
Total		100	6966215



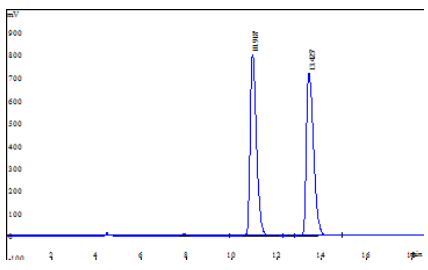
(S)-3-(4-Fluorophenyl)-cyclohexanone [1]

3m: **^{1}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}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).

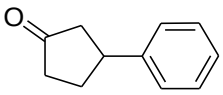
HPLC: Chiralpak AD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 10.9 min (major), 13.4 min (minor). Measured ee value = 55 %.



Rank	Time	Conc.	Area
1	10.871	77.29	2595569
2	13.393	22.71	762530
Total		100	3358099



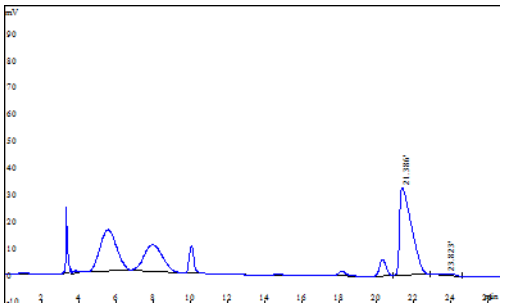
Rank	Time	Conc.	Area
1	10.918	49.82	15473541
2	13.425	50.18	15583955
Total		100	31057496



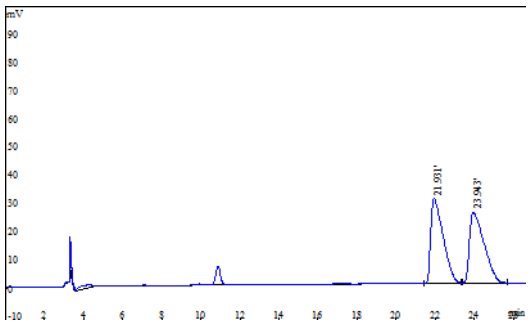
3-Phenylcyclopentanone [3]

3n: **^{1}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}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).

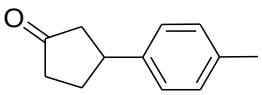
HPLC: Chiralpak AS-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 98:2; flow rate: 1.0 ml/min; retention time: 21.4 min (major), 23.8 min (minor). Measured ee value = 93%.



Rank	Time	Conc.	Area
1	21.386	96.52	1434234
2	23.823	3.48	51704
Total		100	1485938



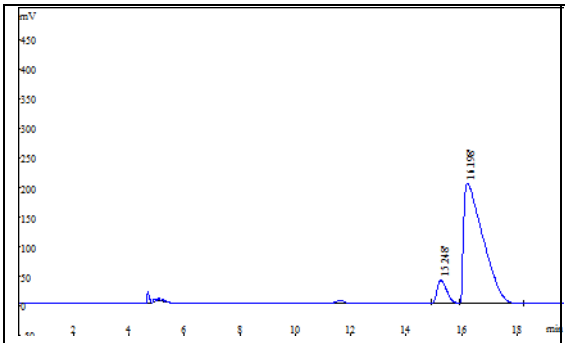
Rank	Time	Conc.	Area
1	21.931	50.33	1277983
2	23.943	49.67	1261332
Total		100	2539315



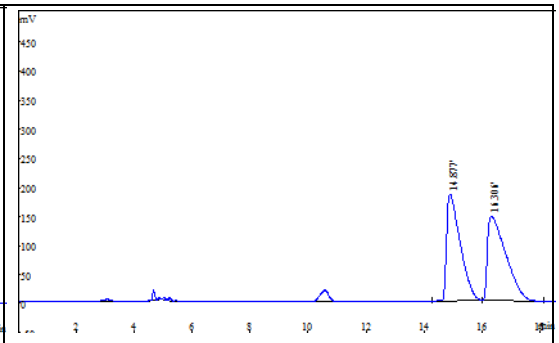
3-(p-tolyl)cyclopentan-1-one [9]

3o: ^{1}**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}**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).

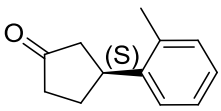
HPLC: Chiralpak AS-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 95:5; flow rate: 0.7 ml/min; retention time: 15.2 min, 16.2 min (major). Measured ee value = 83%.



Rank	Time	Conc.	Area
1	15.248	8.484	895691
2	16.198	91.52	9660918
Total		100	10556609



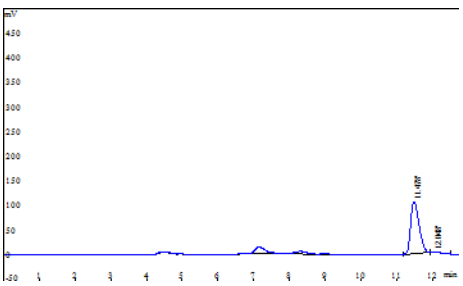
Rank	Time	Conc.	Area
1	14.877	48.47	5904893
2	16.306	51.53	6277469
Total		100	12182362



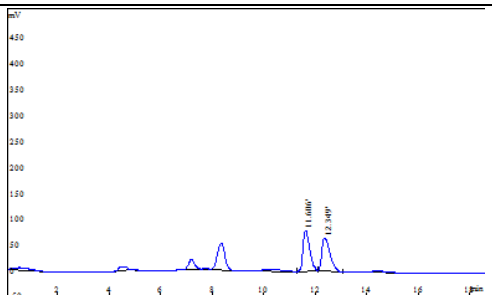
(S)-3-o-tolylcyclopentanone [6]

3p: **^{1}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}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).

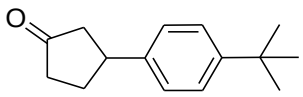
HPLC: Chiralcel OD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate: 0.7 ml/min; retention time: 11.5 min (major), 12.0 min (minor). Measured ee value = 95%.



Rank	Time	Conc.	Area
1	11.478	97.99	1664649
2	12.048	2.009	34131
Total		100	1698780



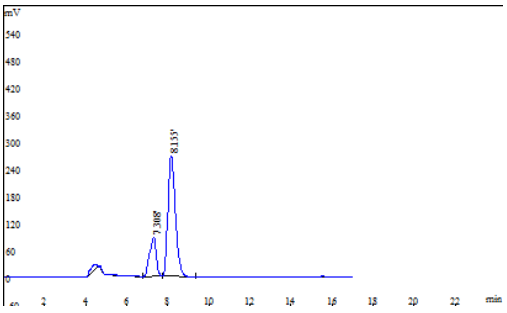
Rank	Time	Conc.	Area
1	11.606	50.02	1404233
2	12.349	49.98	1403028
Total		100	2807261



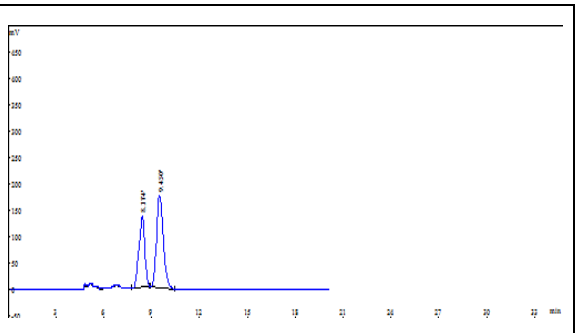
3-(4-(tert-butyl)phenyl)cyclopentan-1-one [4]

3q: **^{1}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}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×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%.



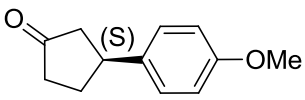
Rank	Time	Conc.	Area
1	7.308	22.12	1826424



Rank	Time	Conc.	Area
1	8.374	40.26	3300145

2	8.155	77.88	6431002
Total		100	8257426

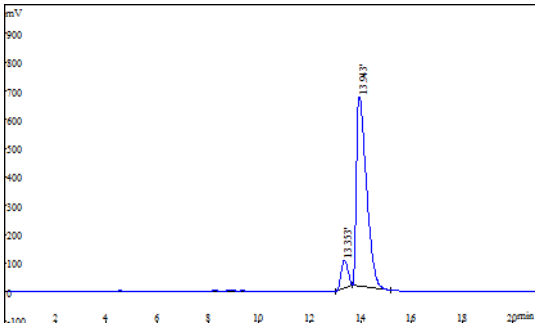
2	9.450	59.74	4897809
Total		100	8197954



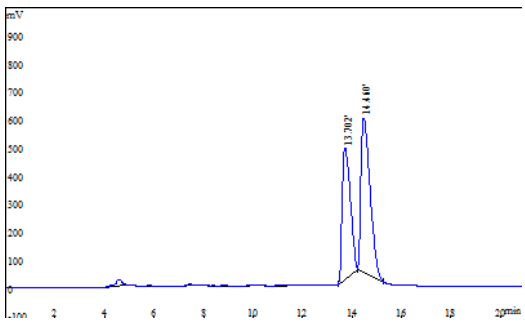
(S)-3-(4-methoxyphenyl)cyclopentan-1-one [4]

3r: ^{1}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}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).

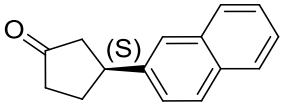
HPLC: Chiralcel OD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol = 90:10; flow rate:0.7 ml/min; retention time: 13.4 min (minor), 13.9 min (major). Measured ee value = 83%.



Rank	Time	Conc.	Area
1	13.353	8.879	1719507
2	13.943	91.12	17645746
Total		100	19365253



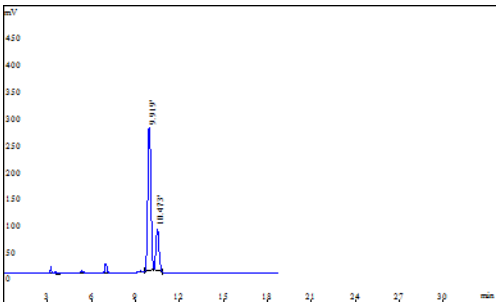
Rank	Time	Conc.	Area
1	13.702	42.67	10279047
2	14.460	57.33	13810458
Total		100	24089505



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

3s: $[\alpha]_D^{32.8}$ -26.67°(c 0.015, $CHCl_3$). [lit. [7]: $[\alpha]_D$ -38° (c 0.14, $CHCl_3$)]. **^{1}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}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×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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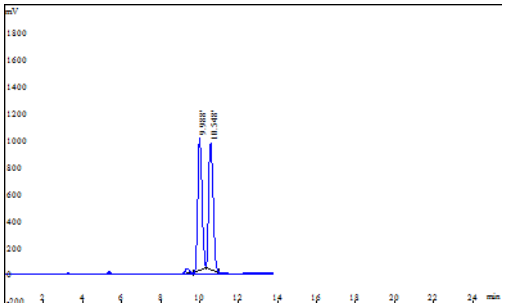
2	10.473	22.58	1032175
Total		100	4570222



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

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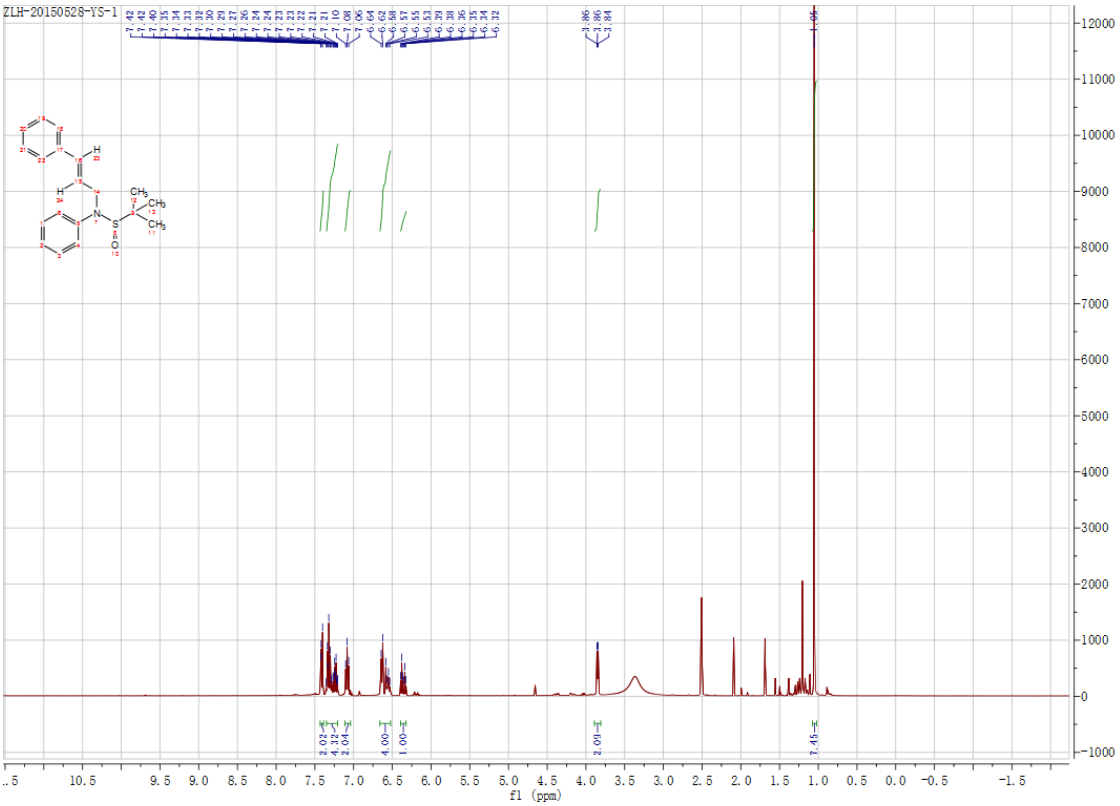
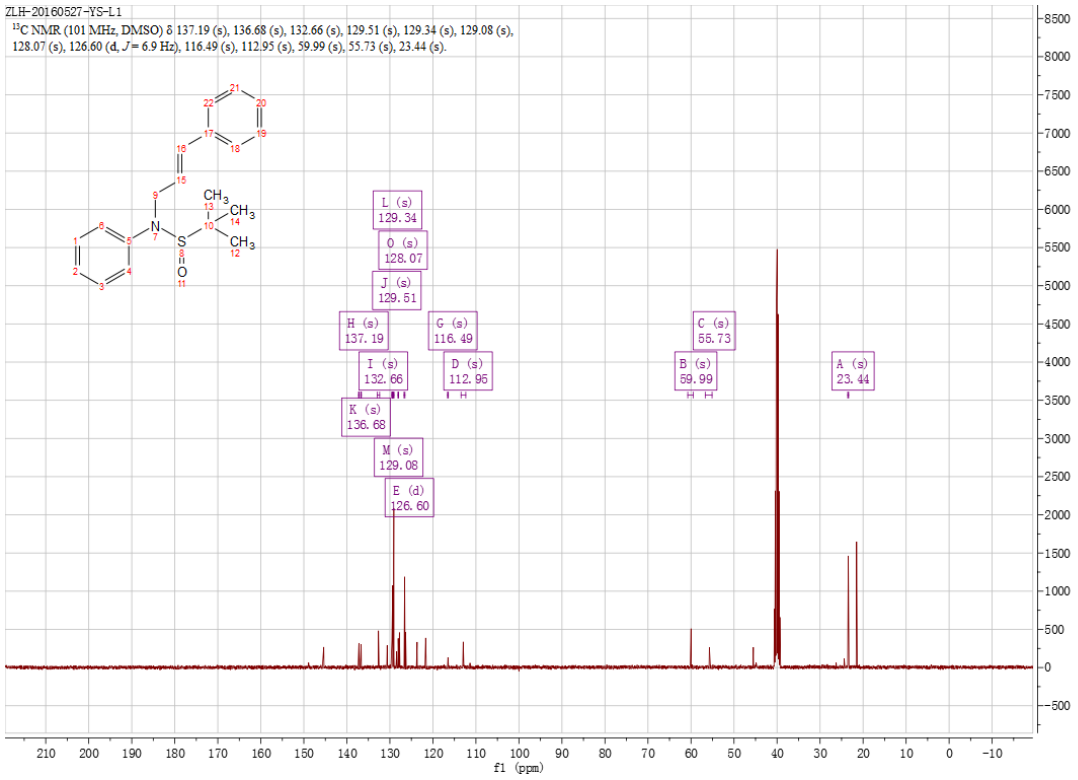
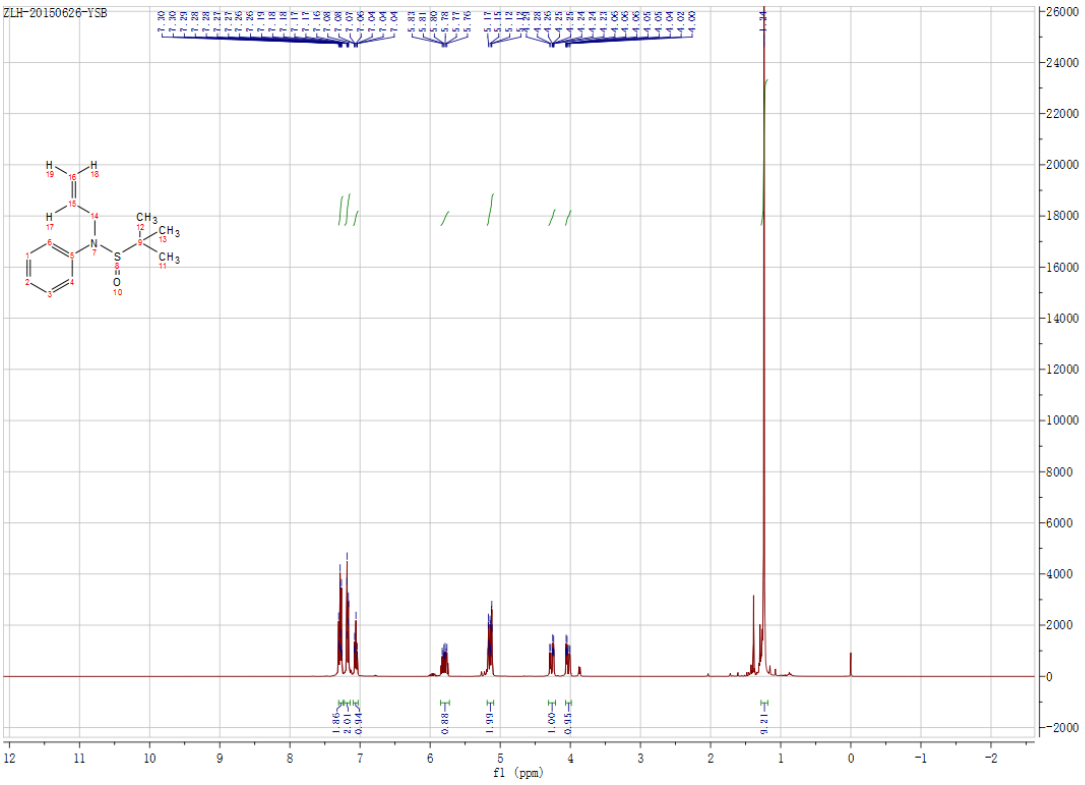
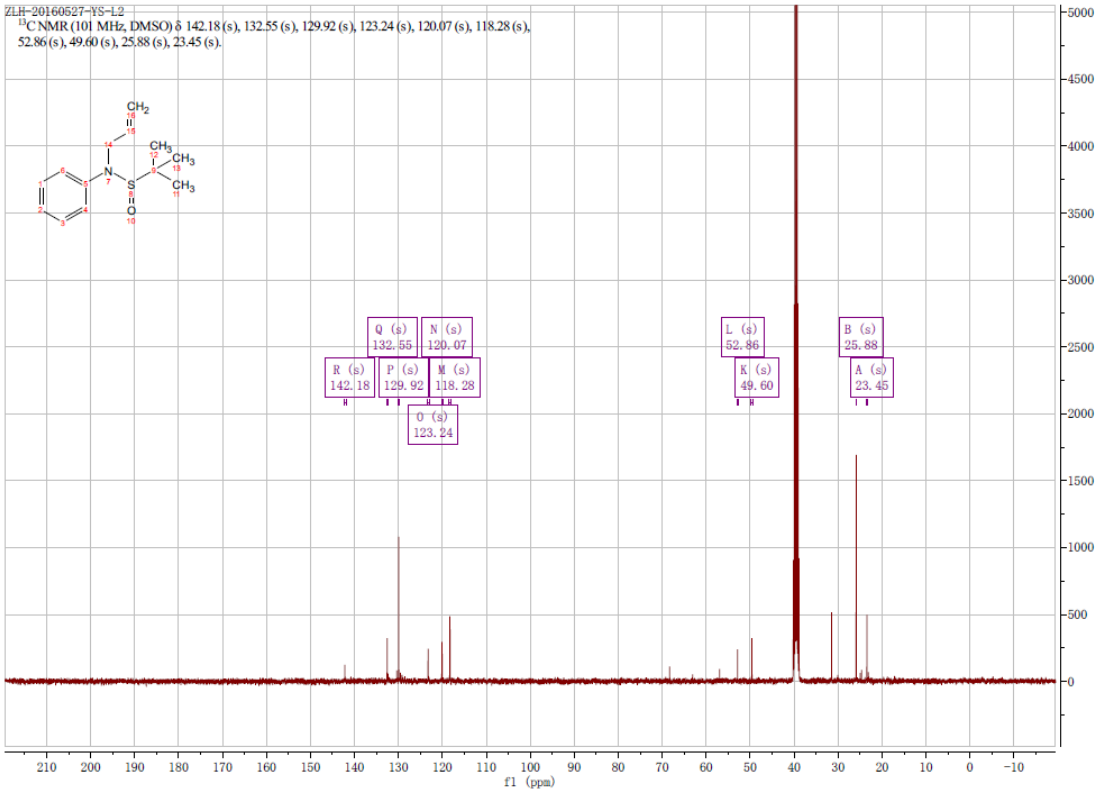
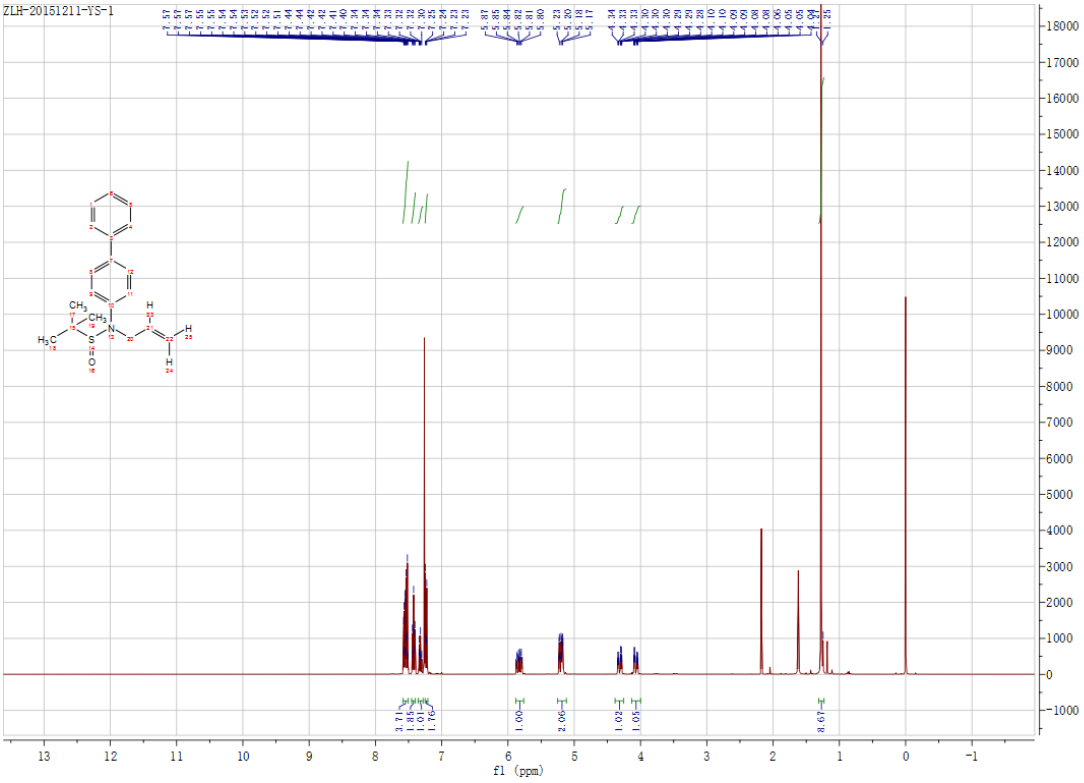
NMR Spectra collection

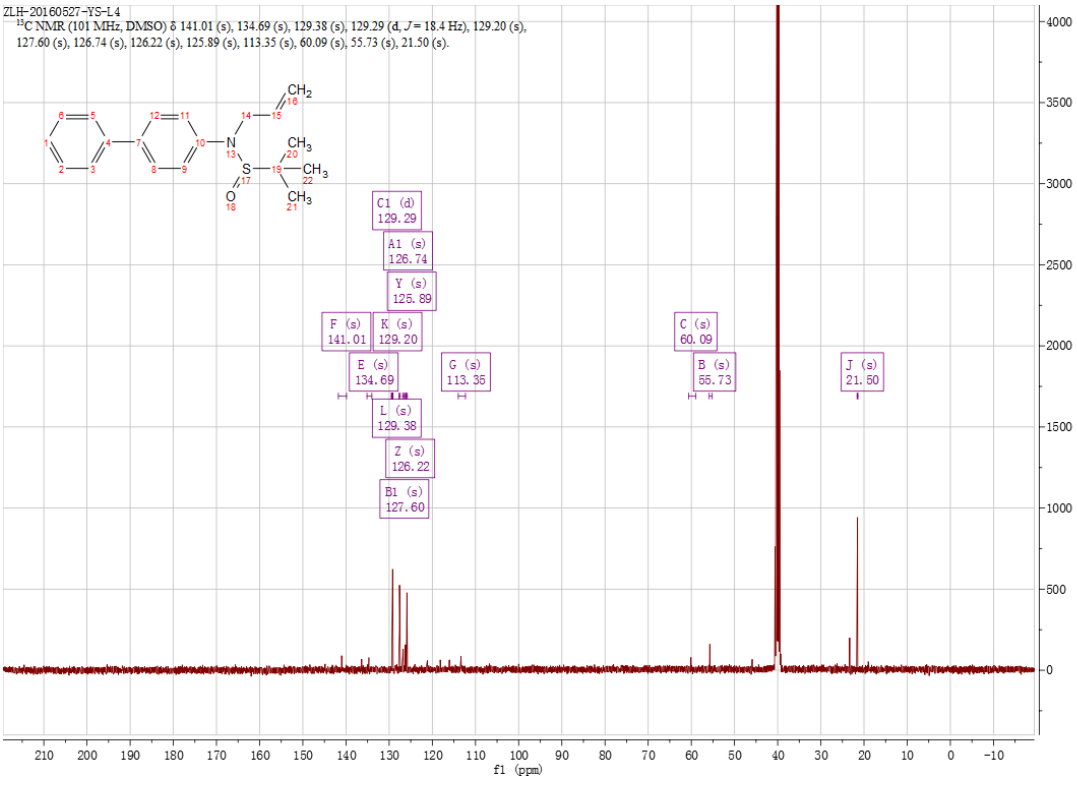


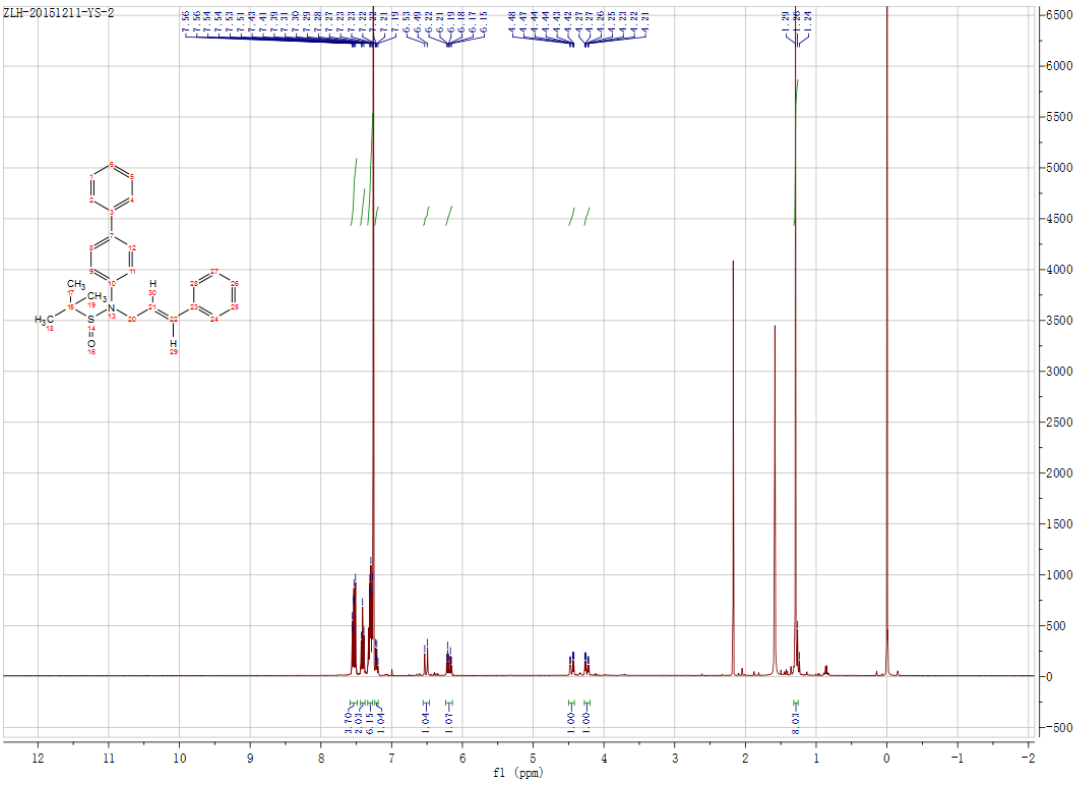


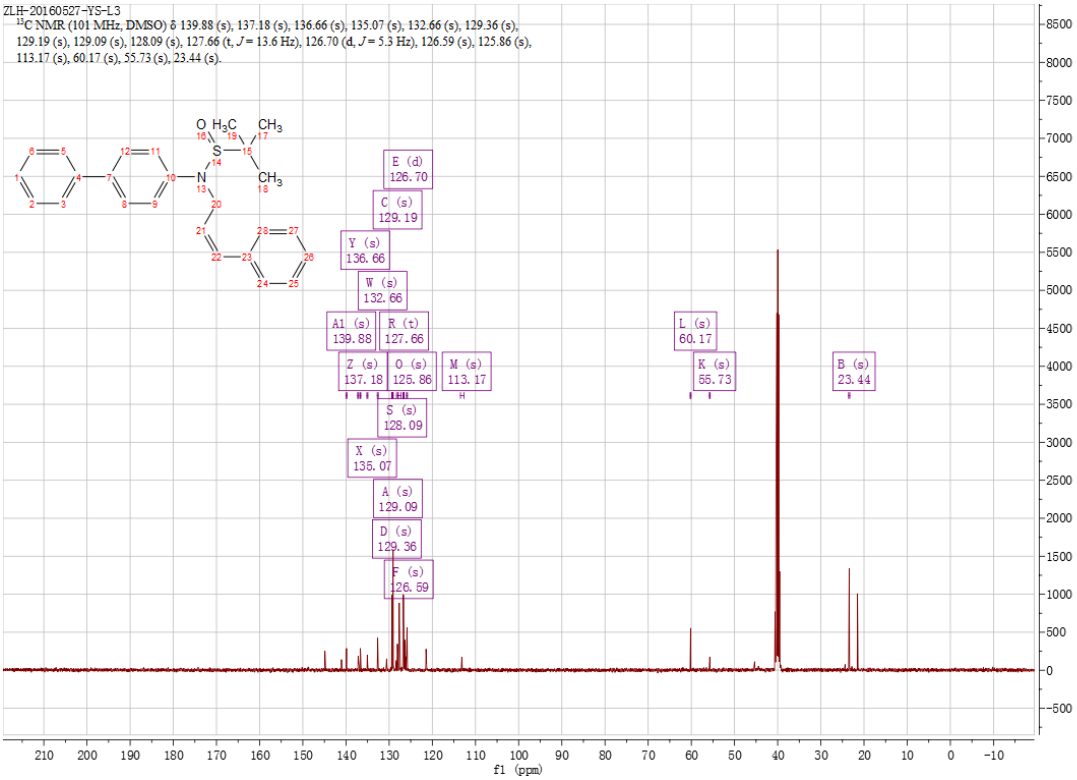


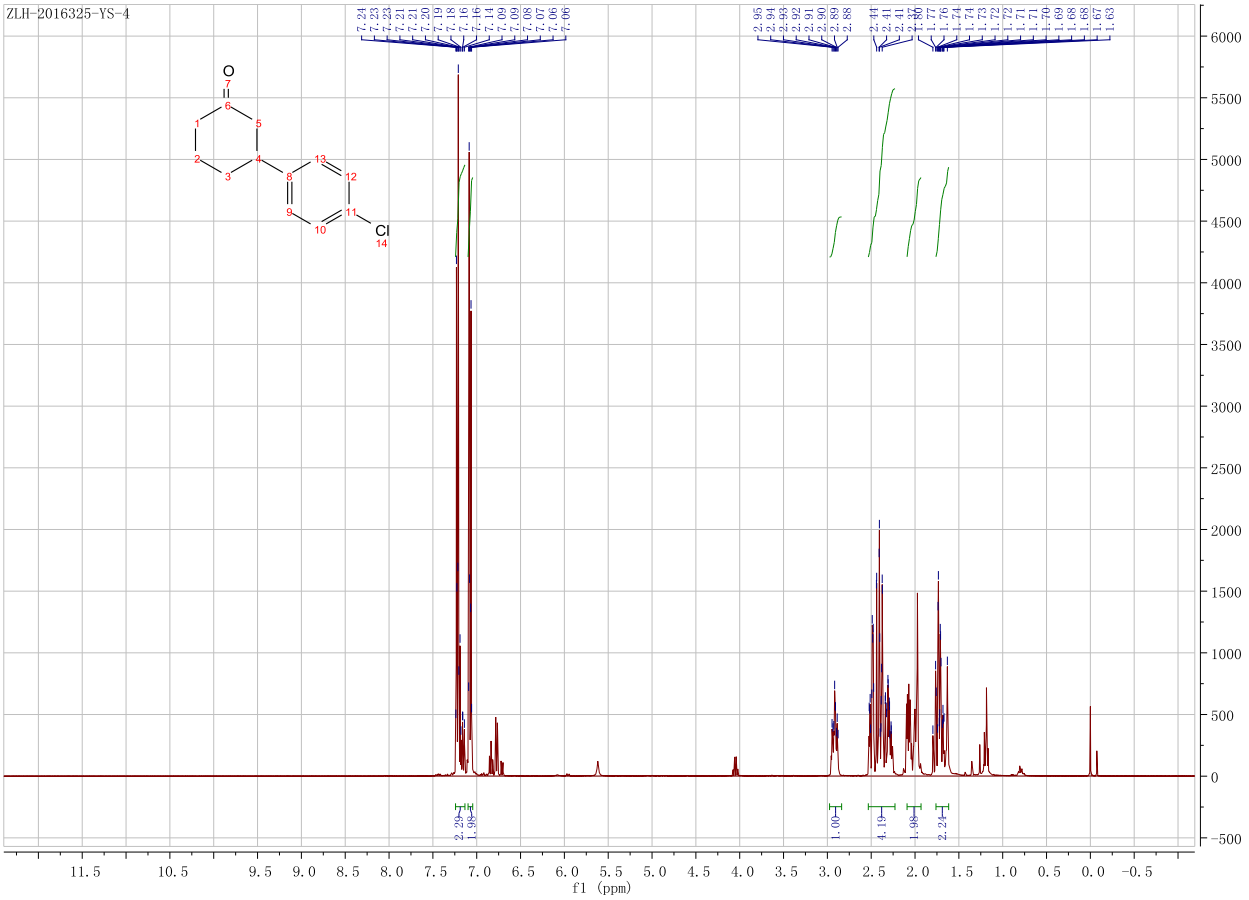


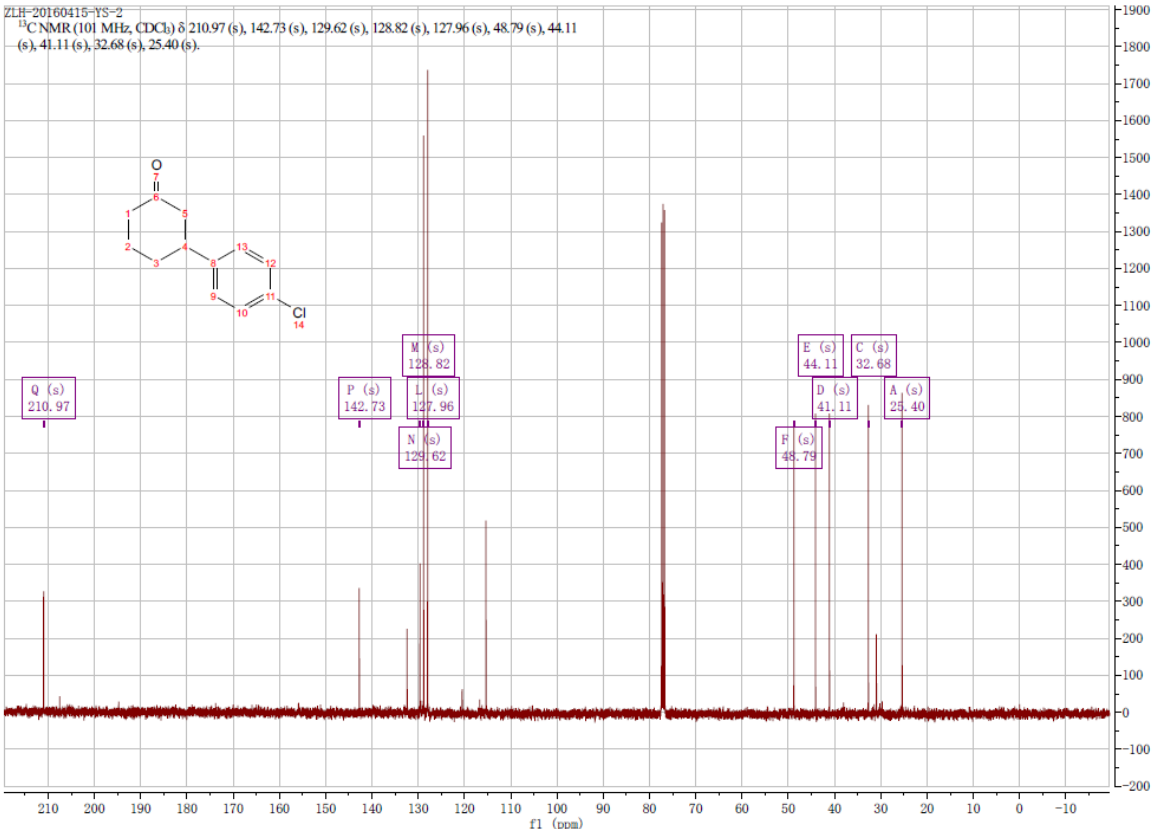


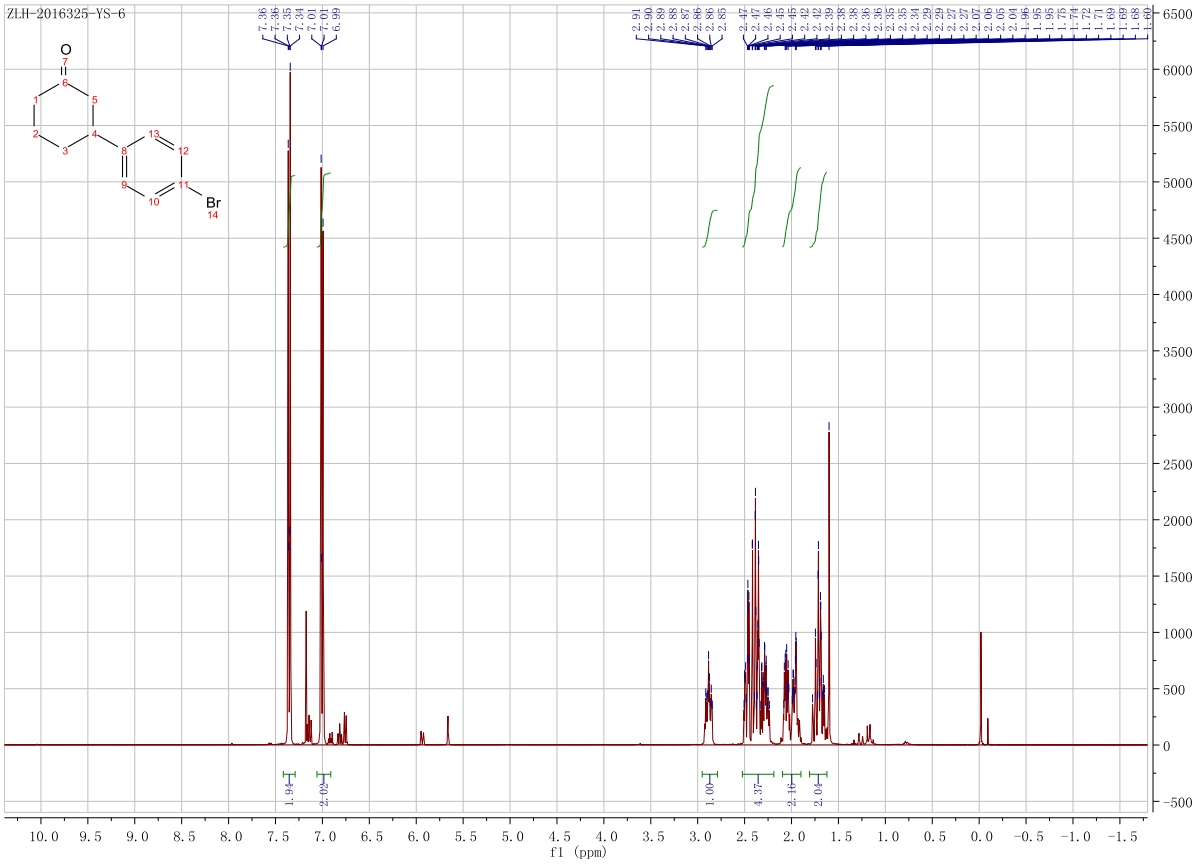


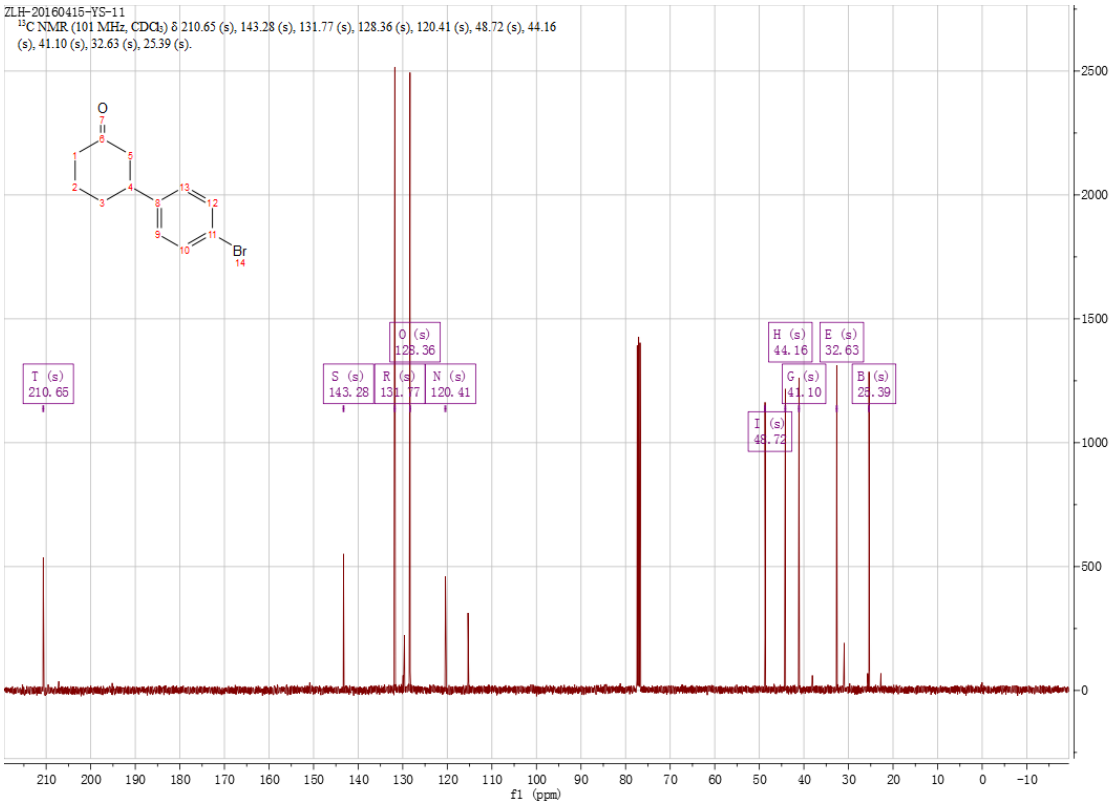


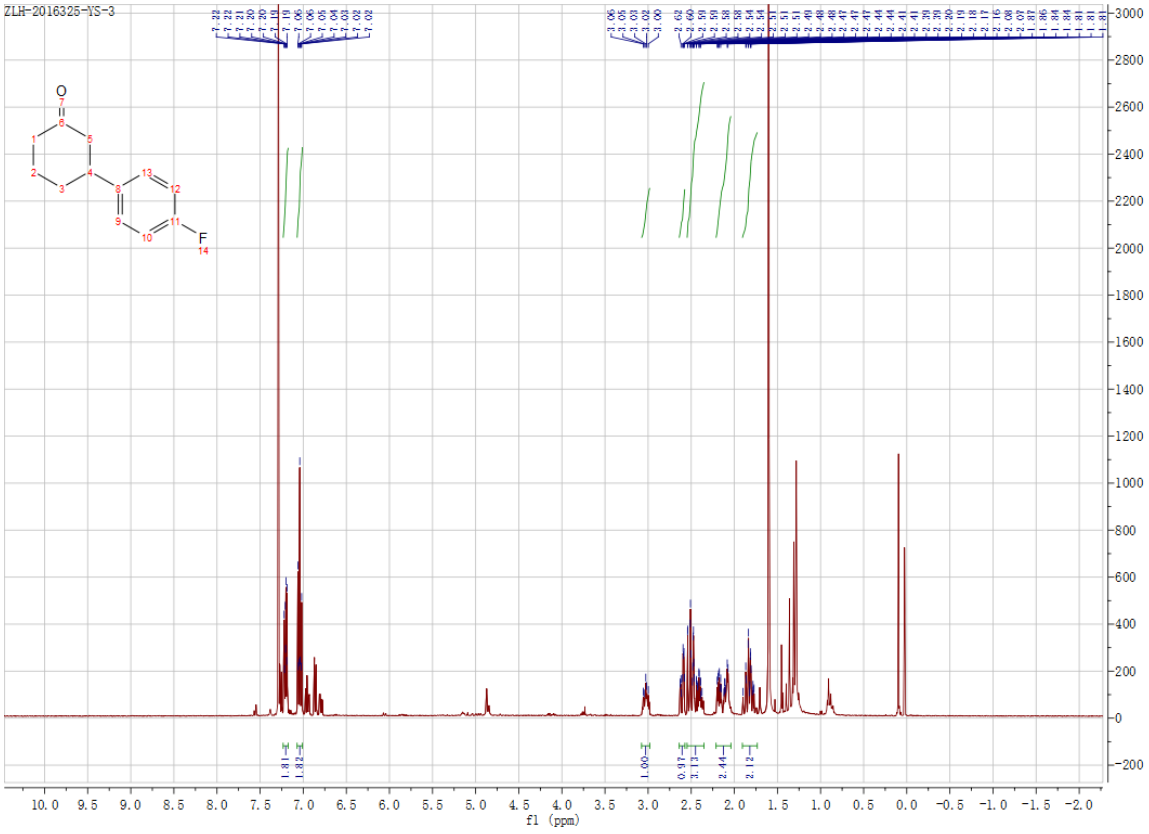


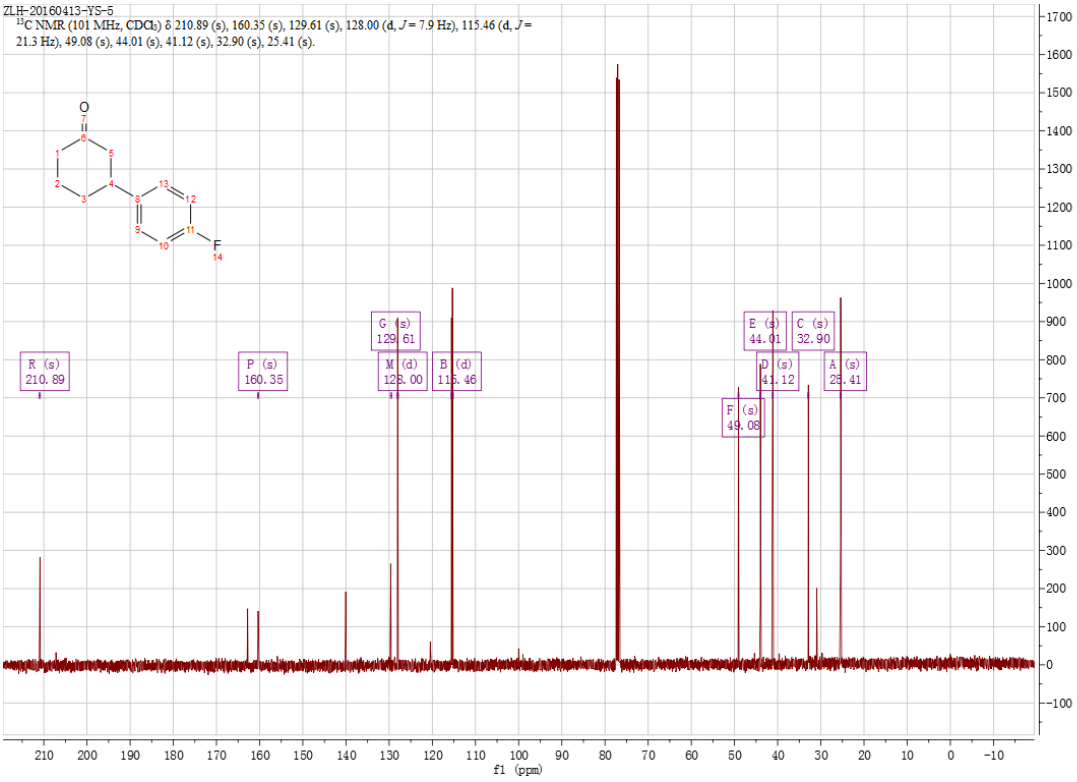


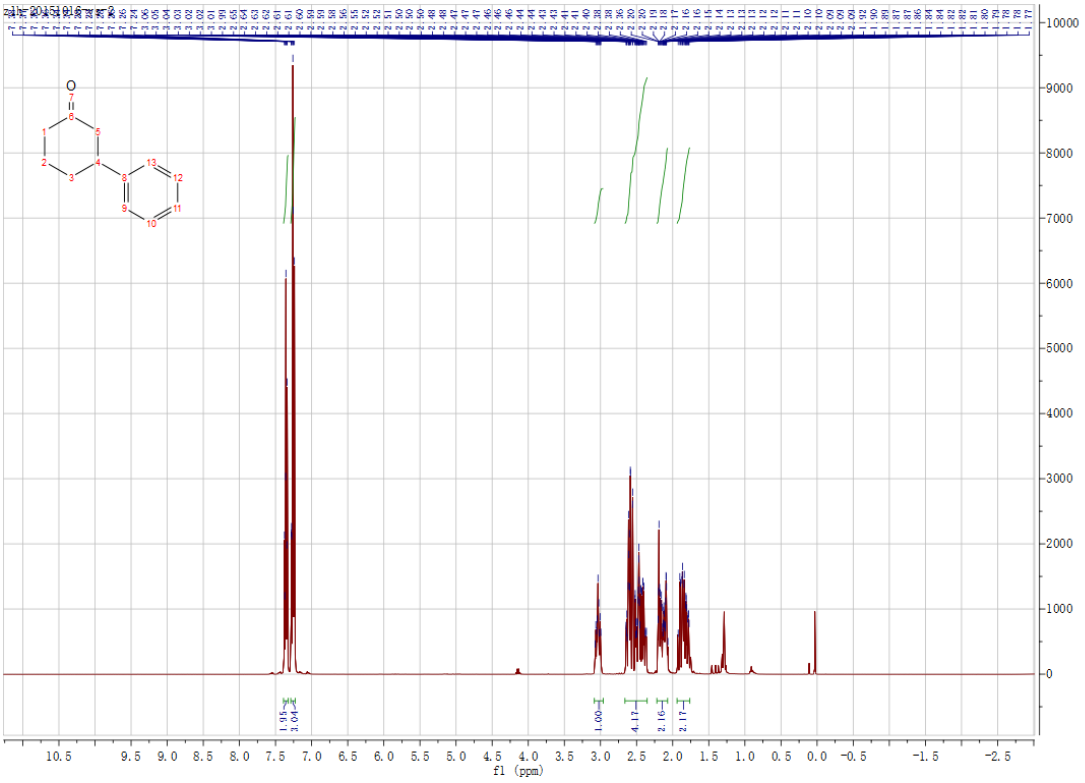


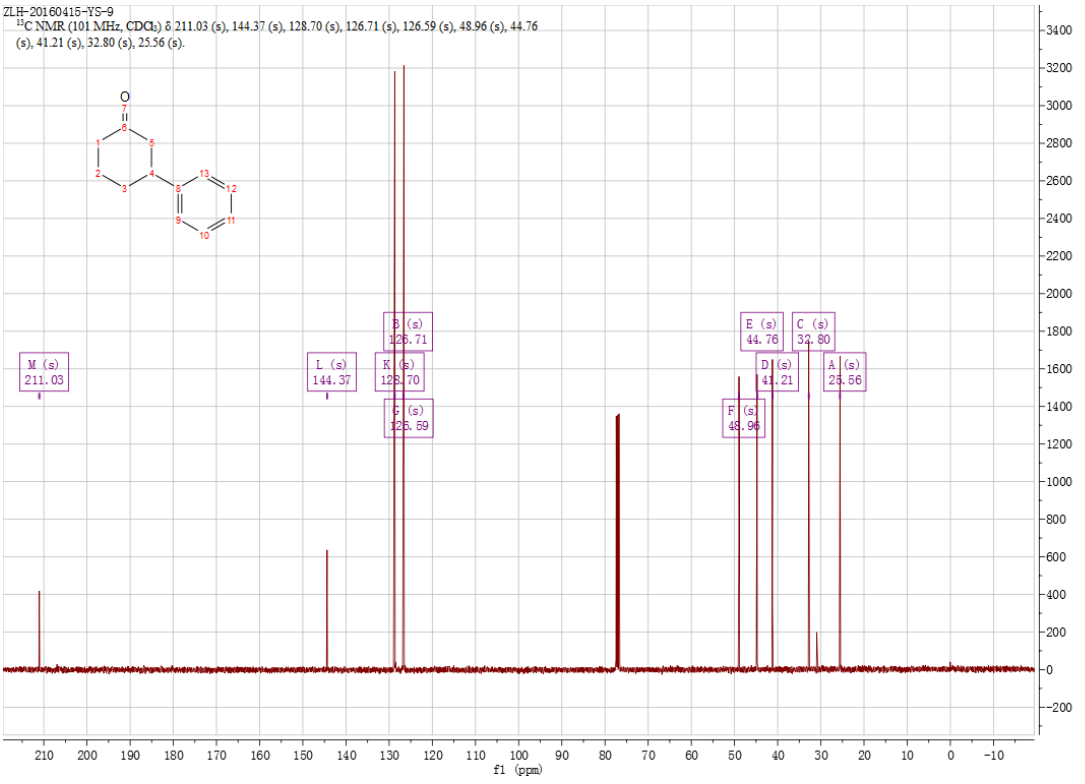


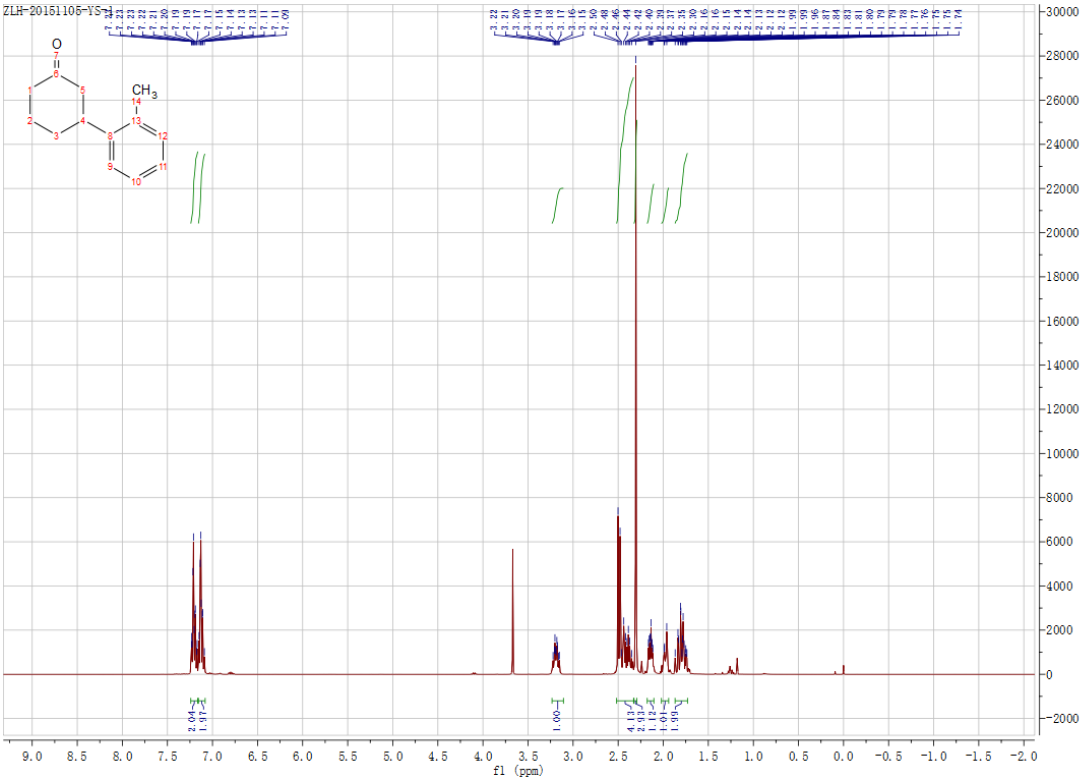


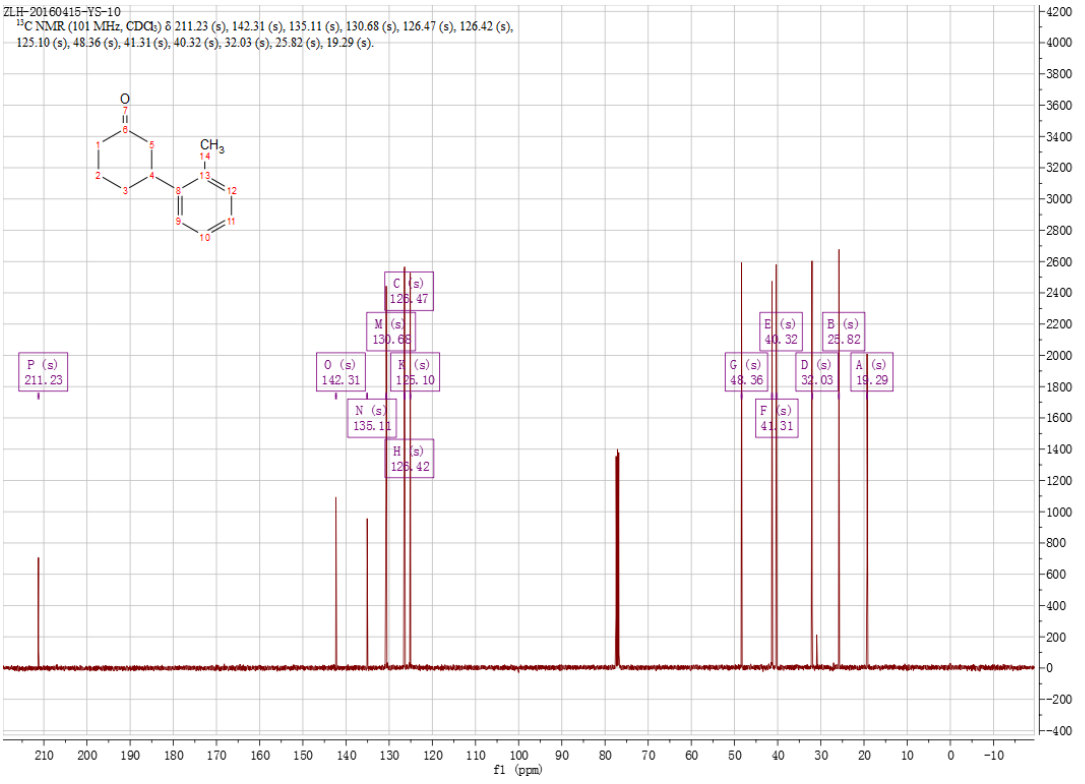


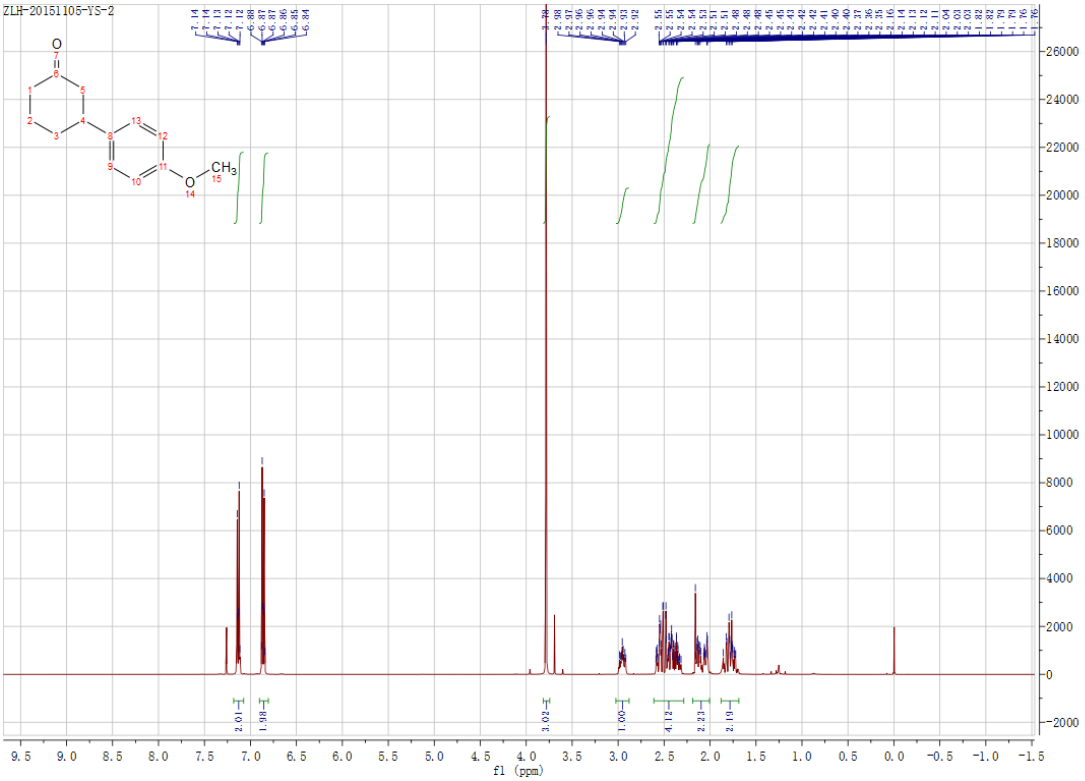


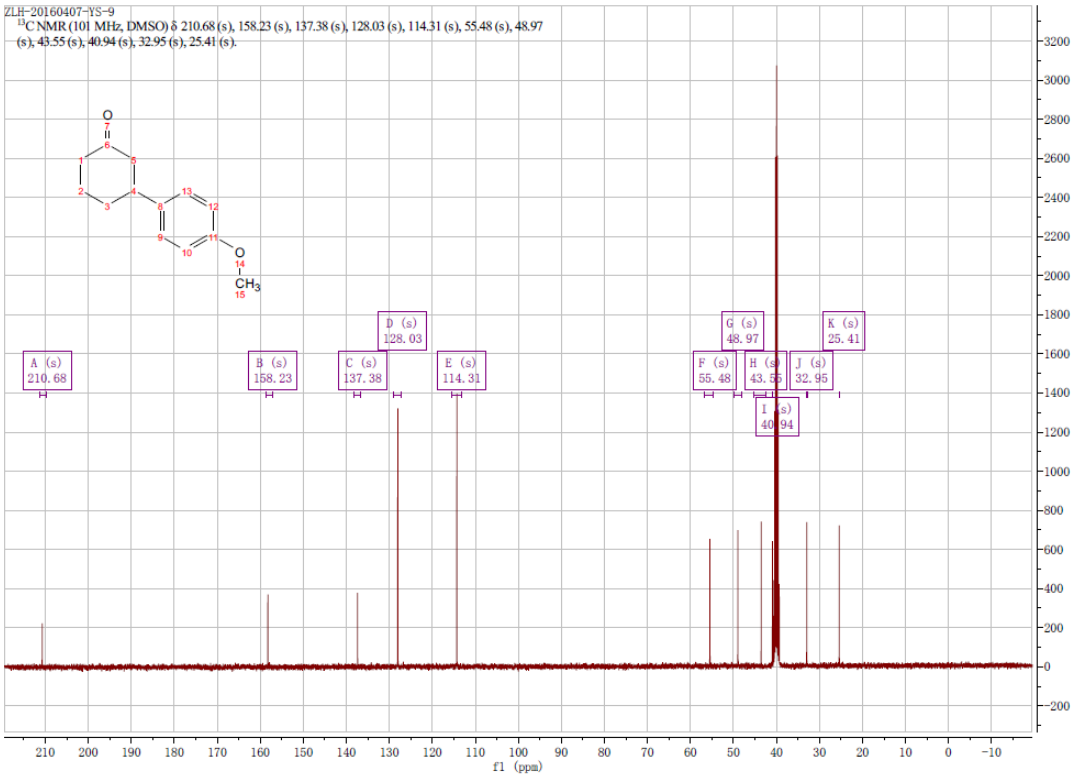


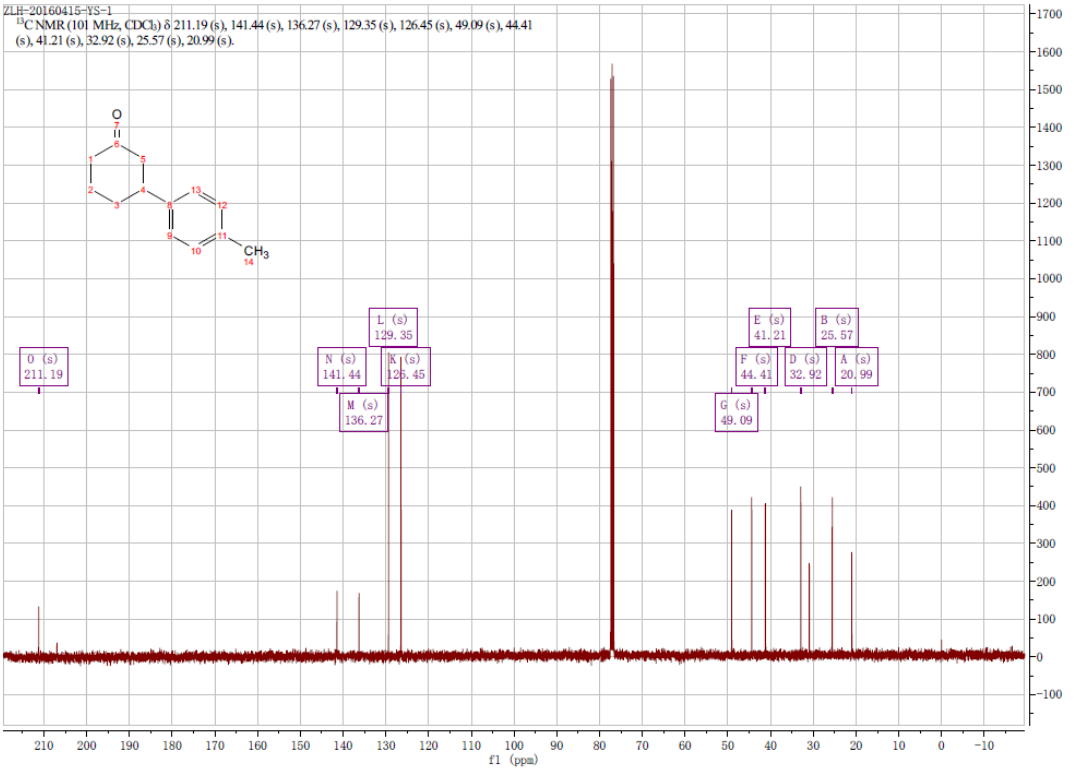


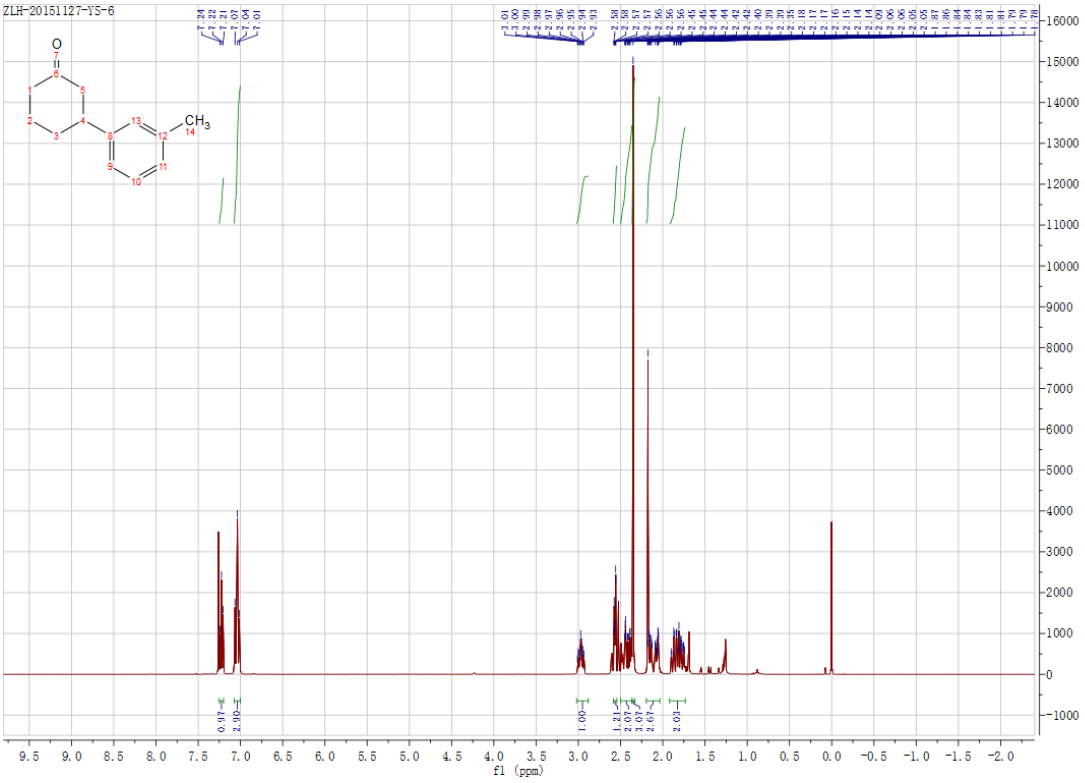


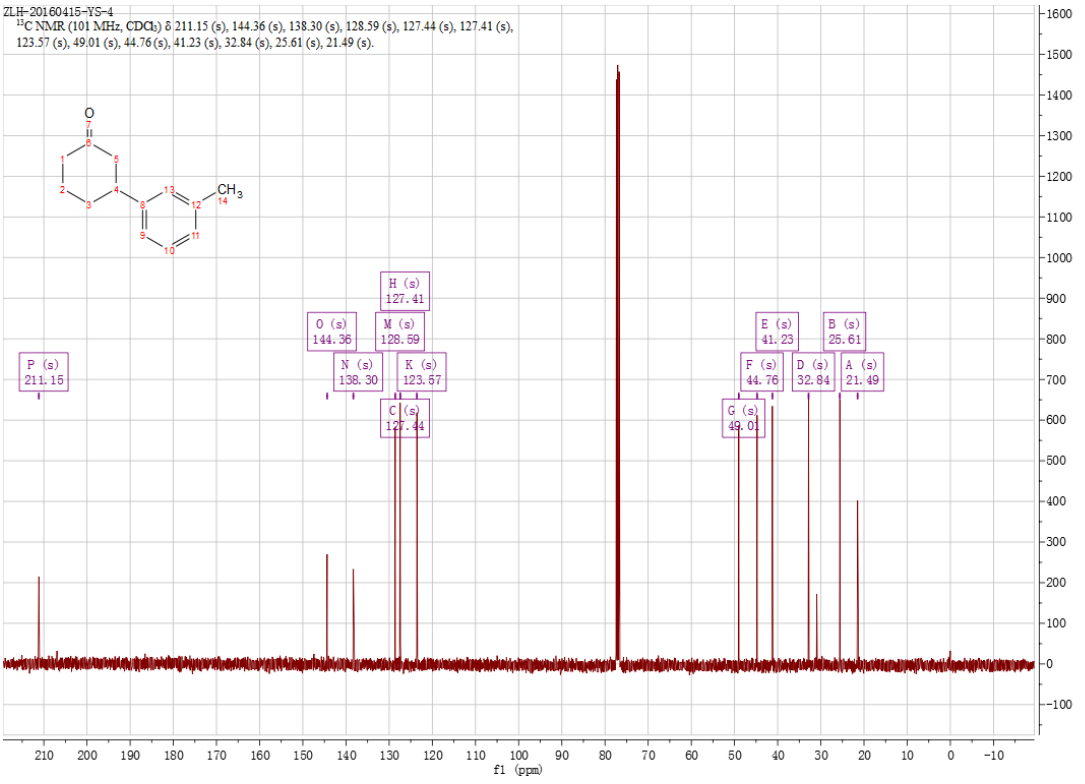


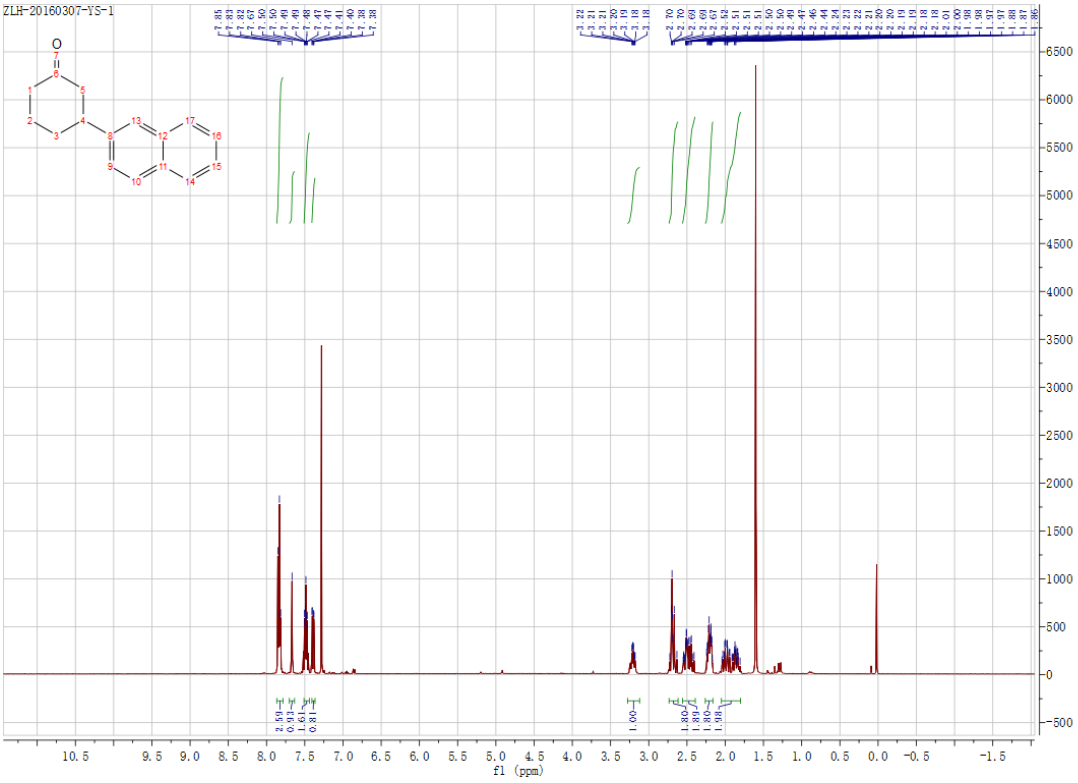


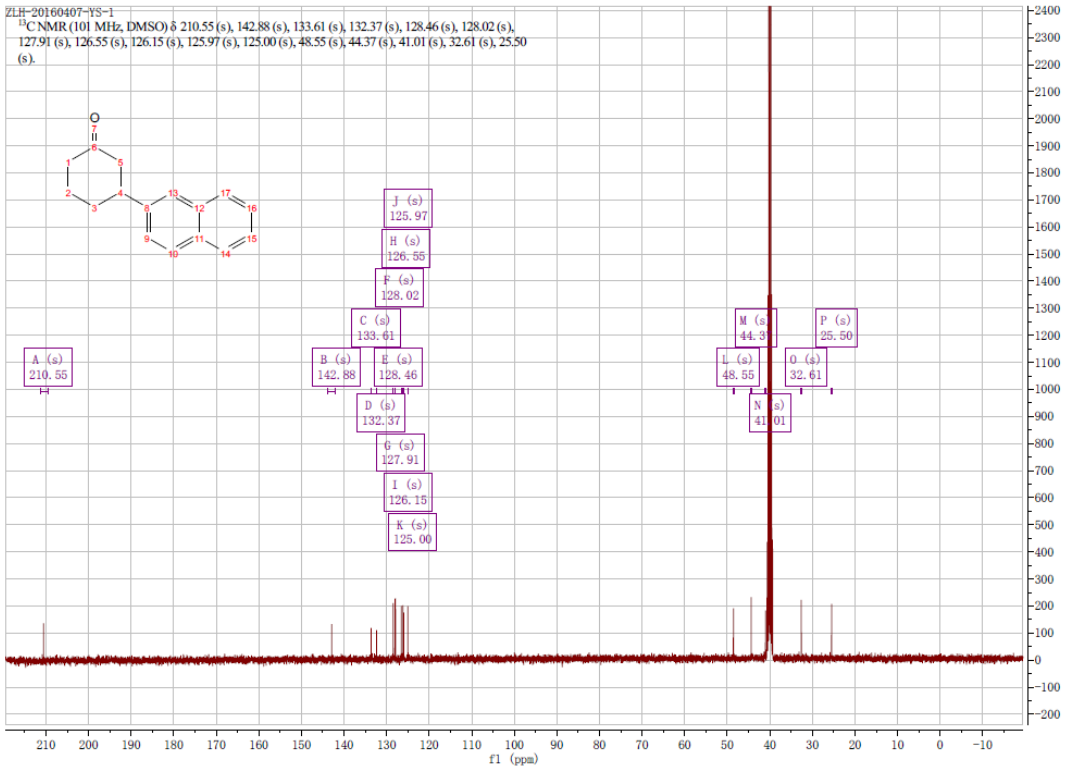


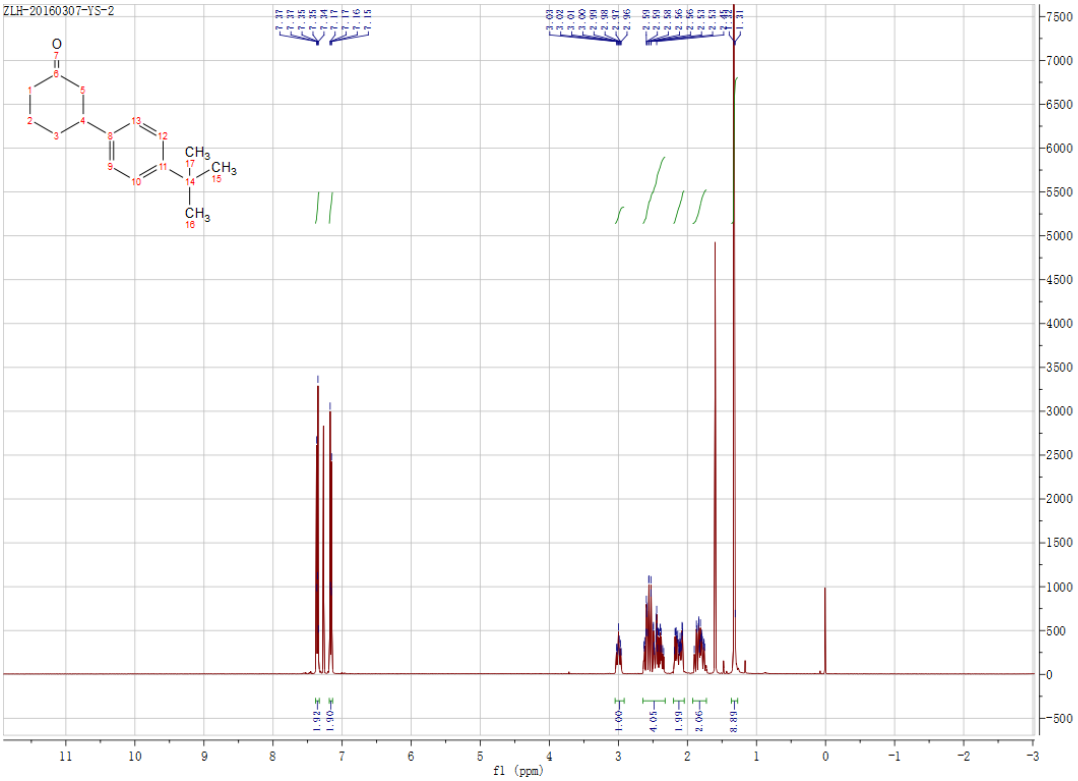


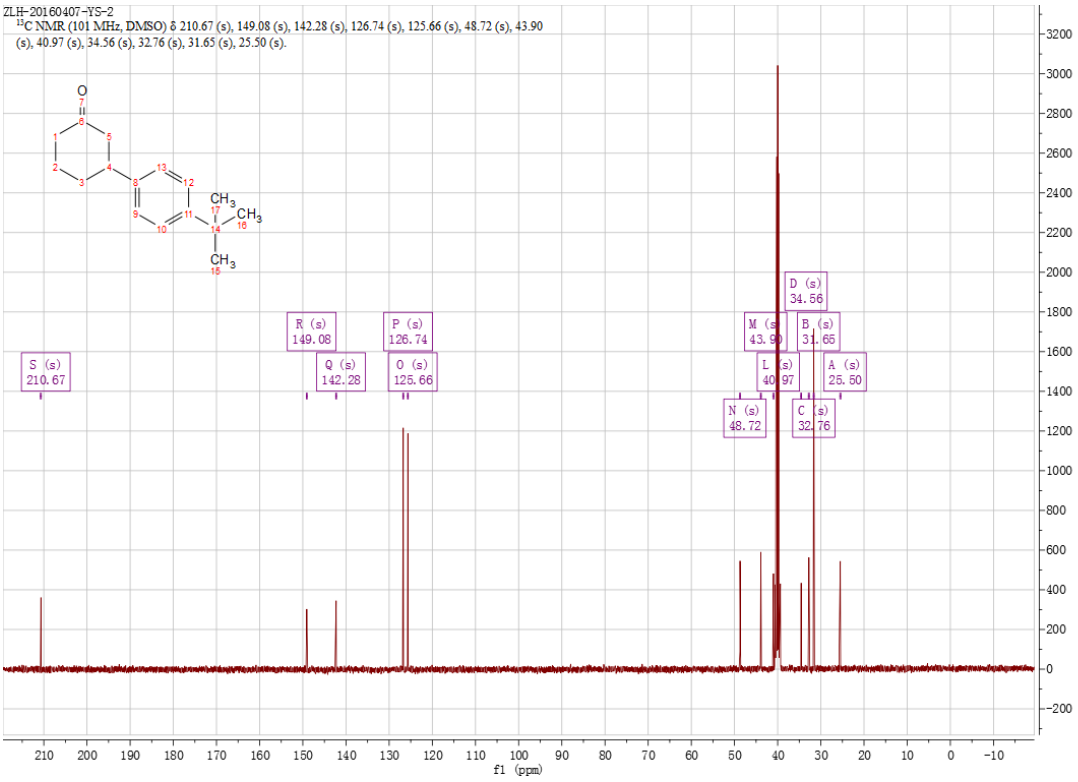


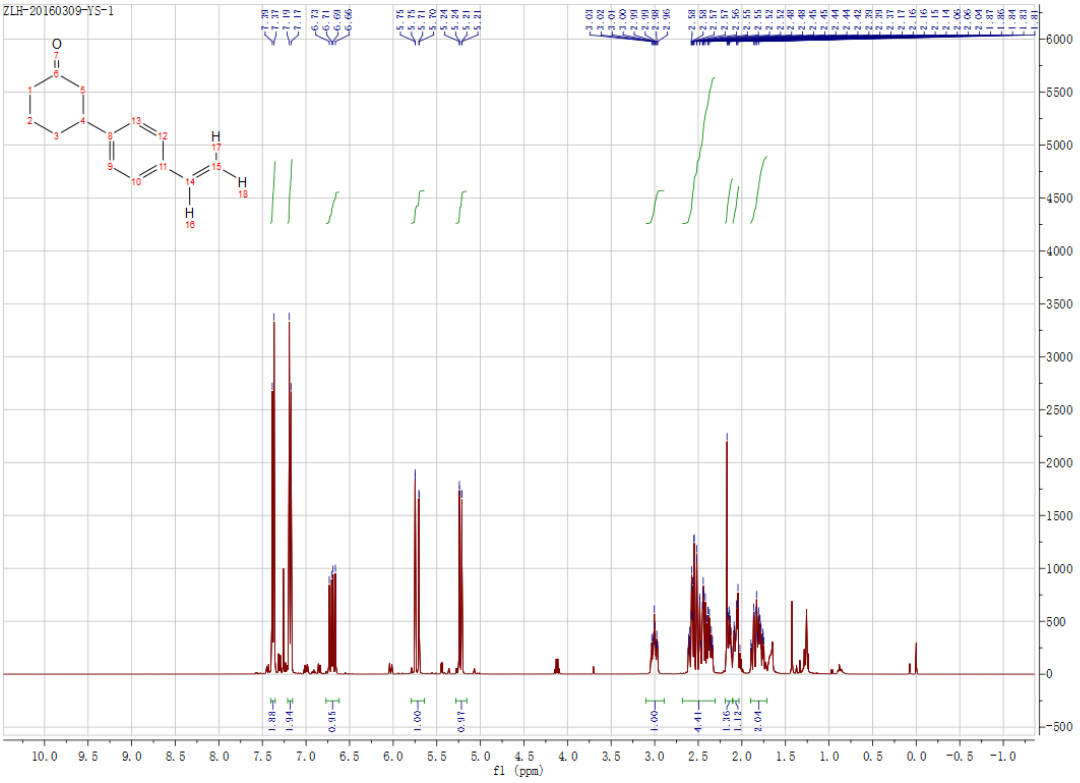


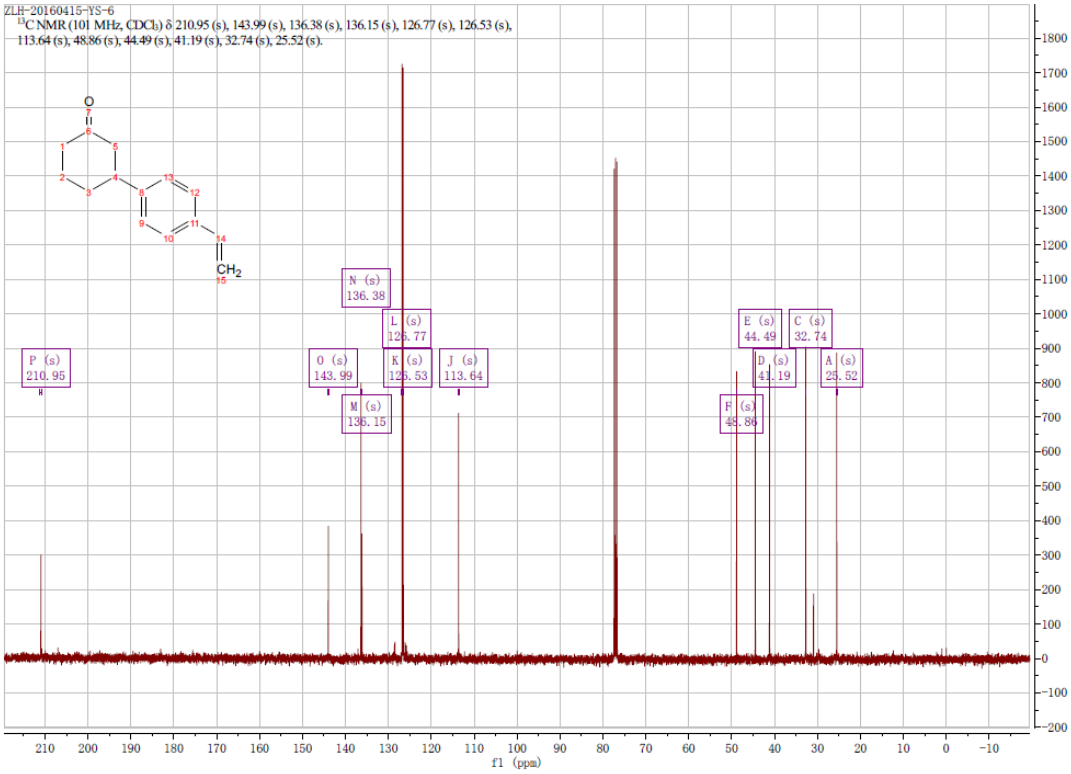


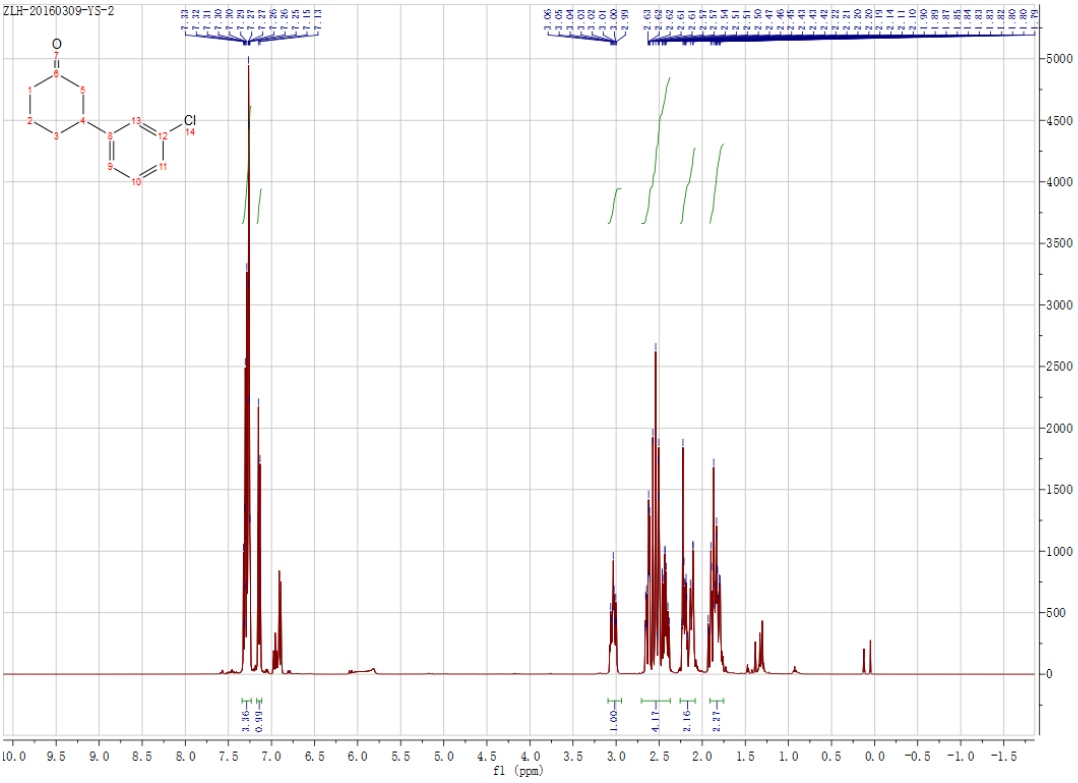


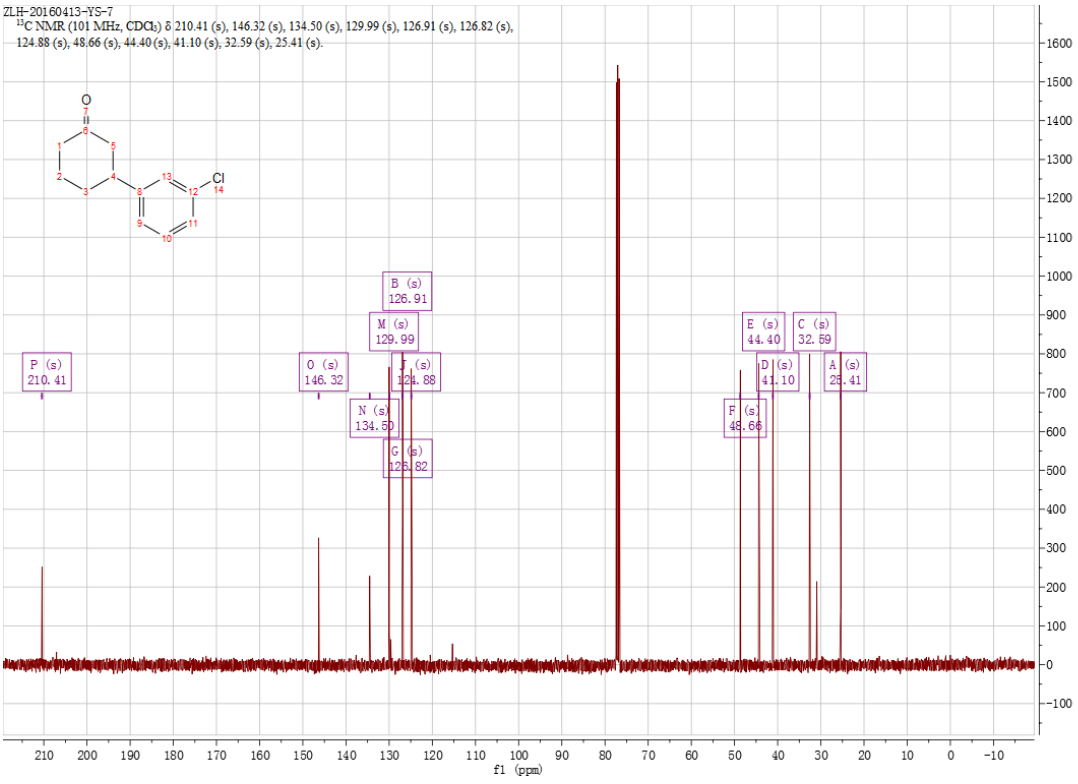


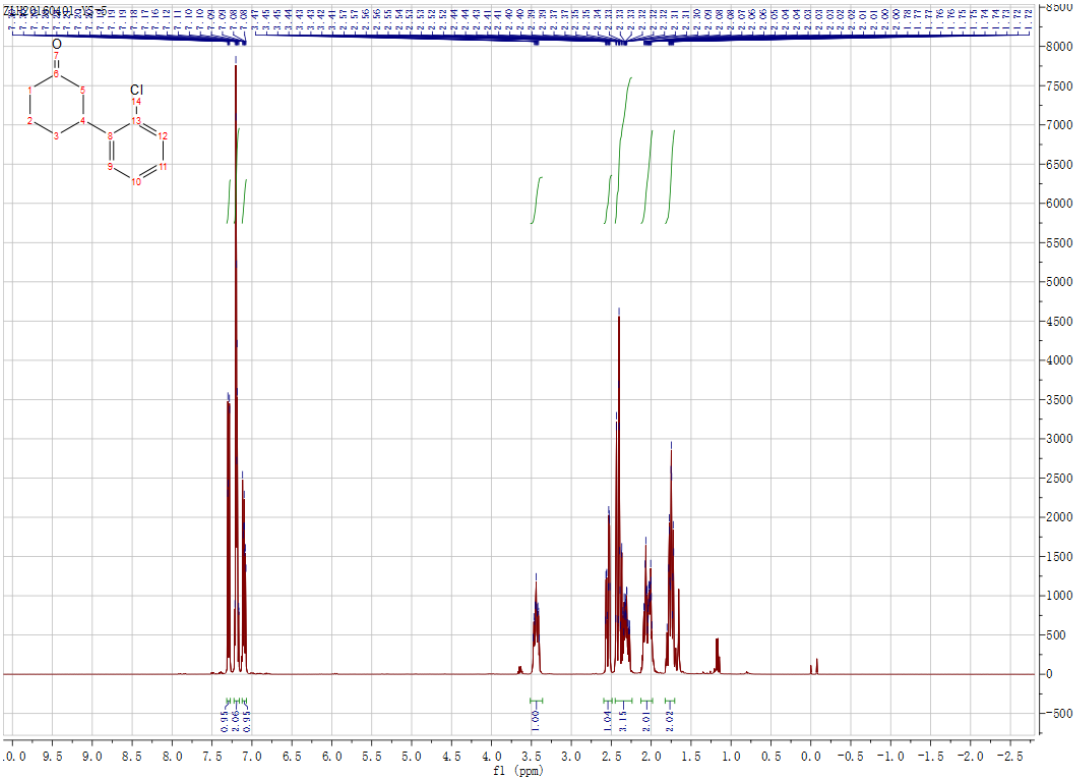


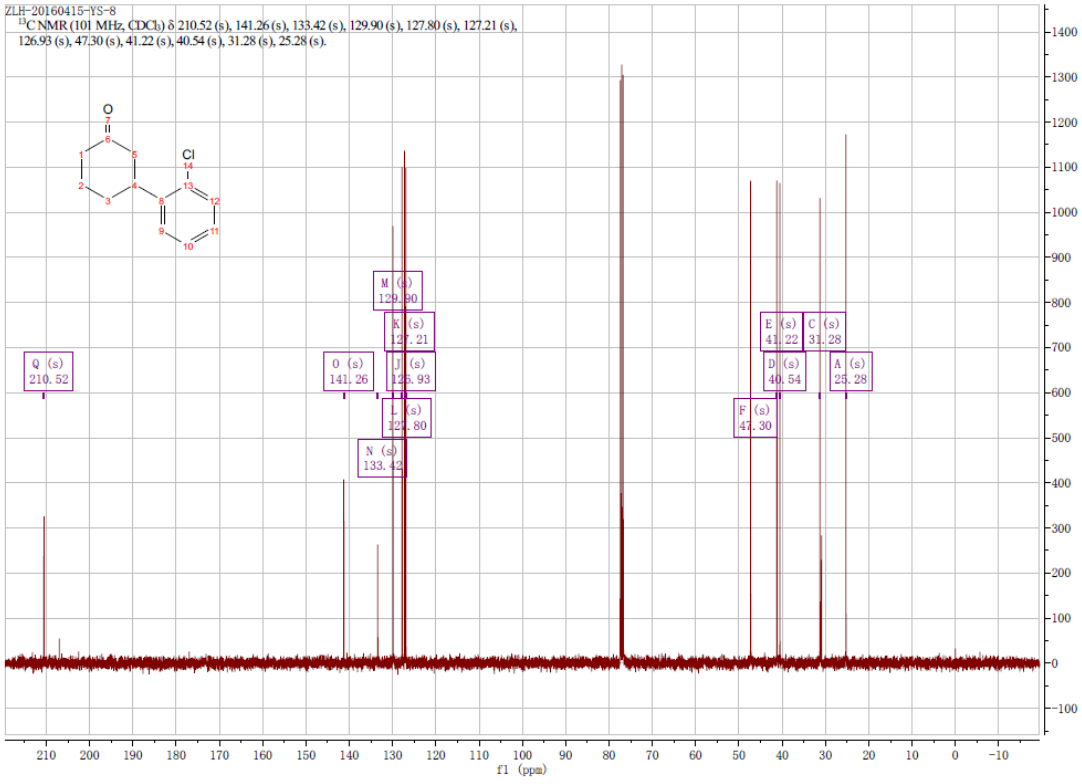


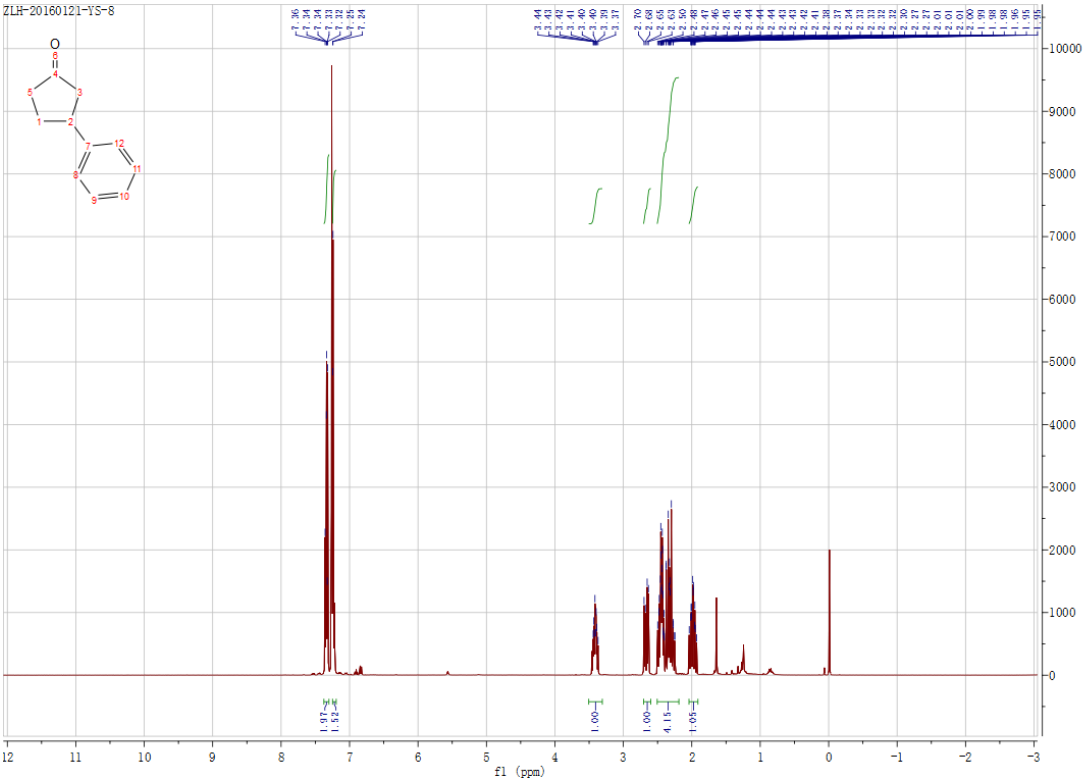


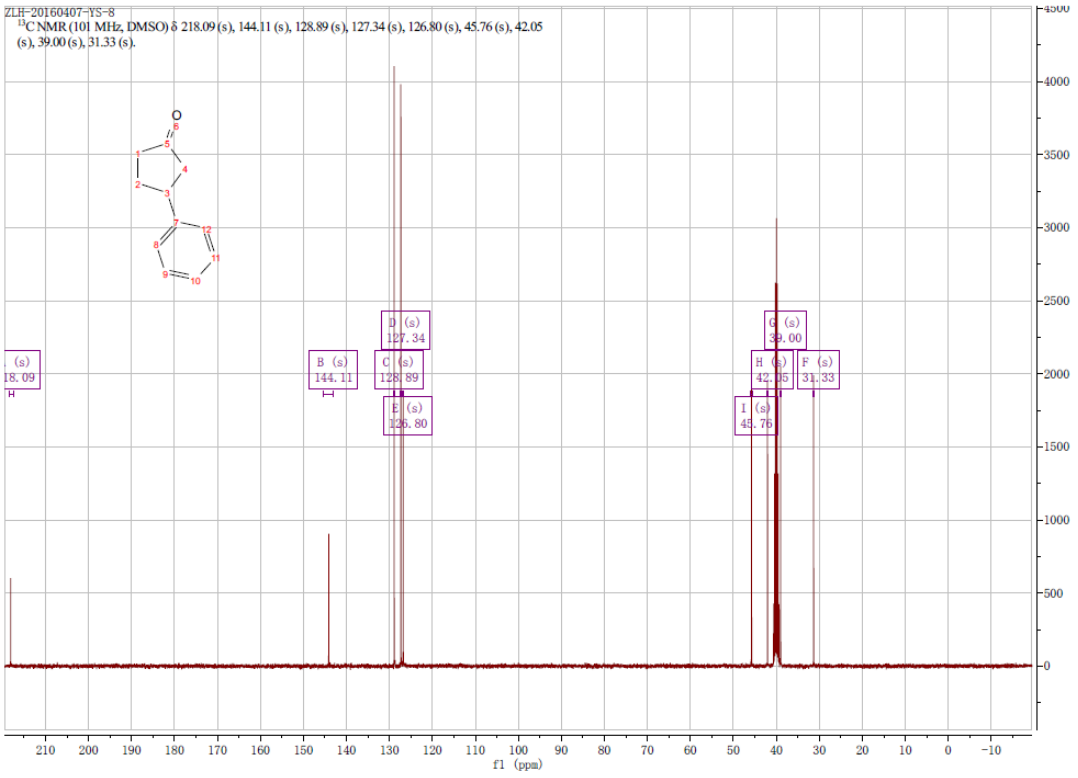


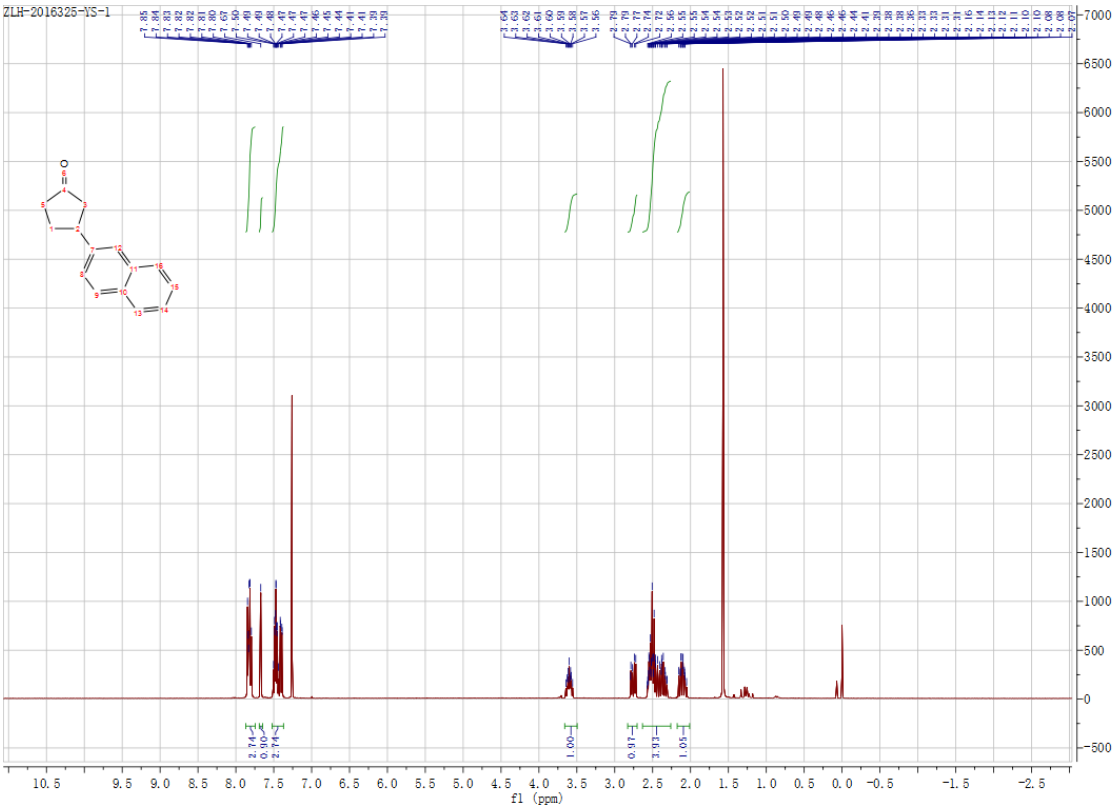


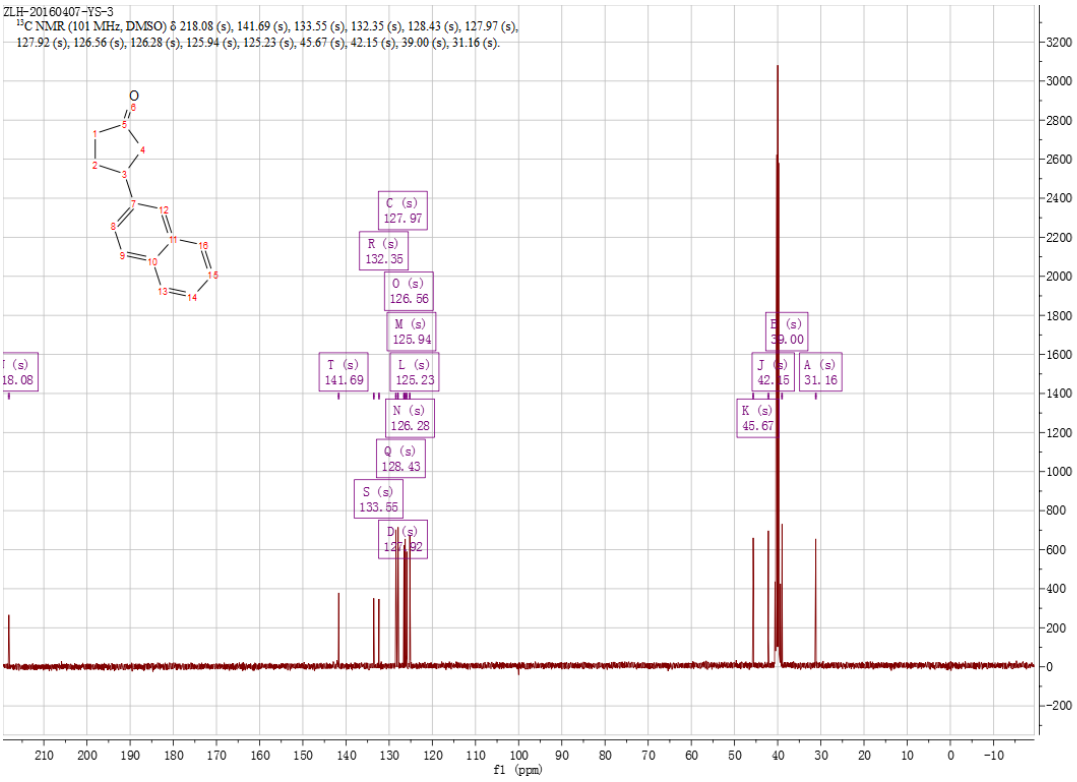


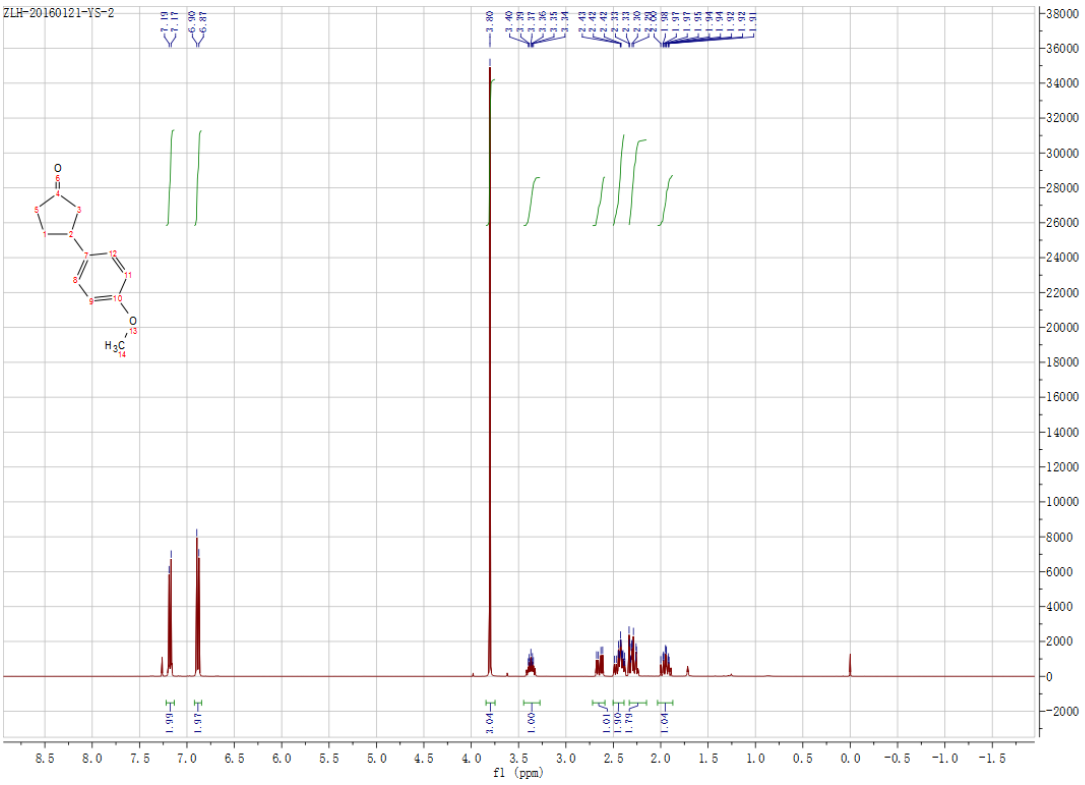


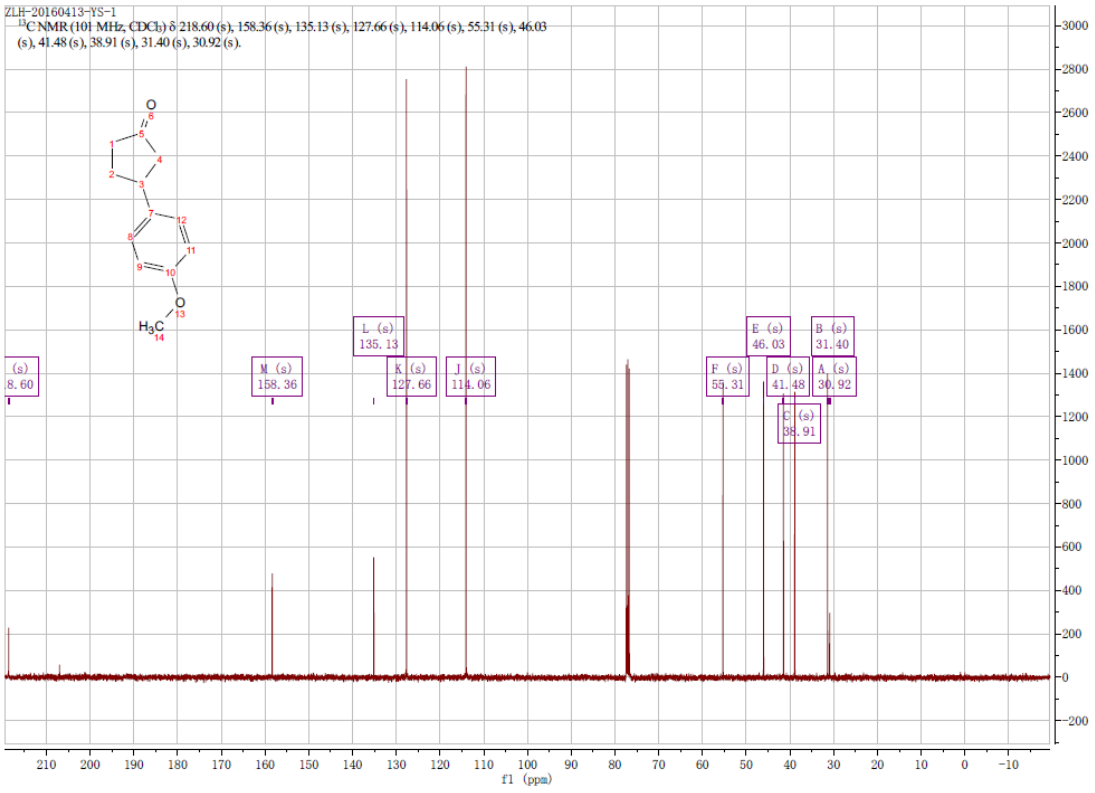


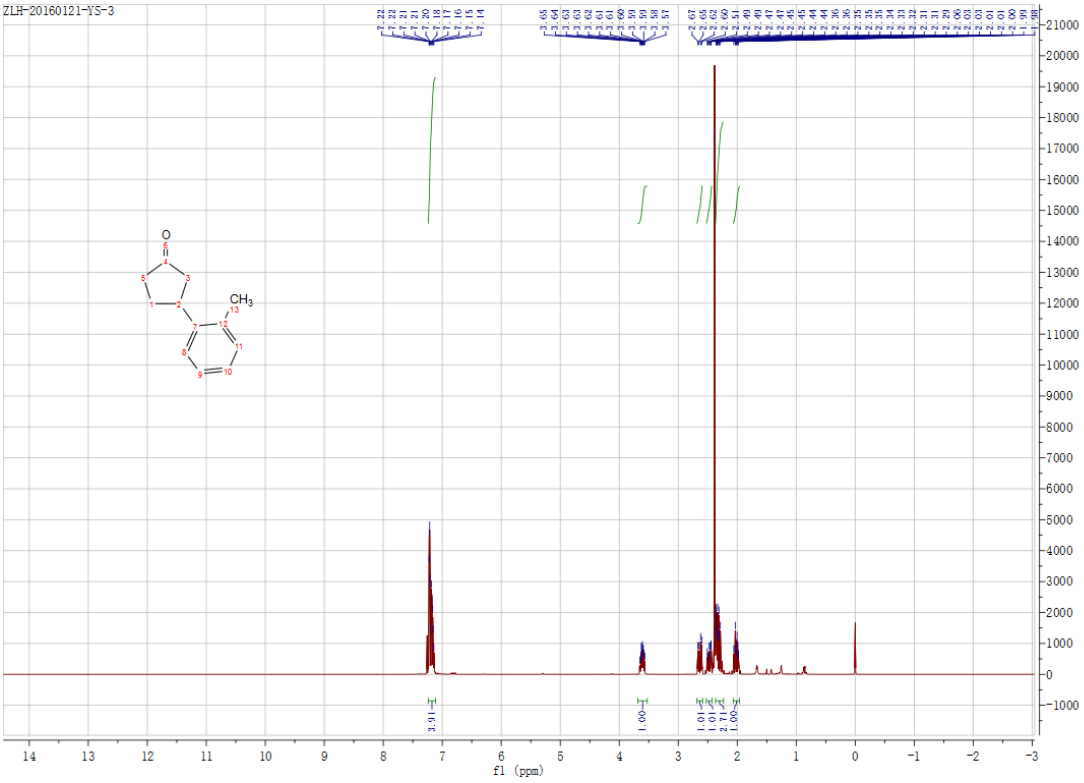


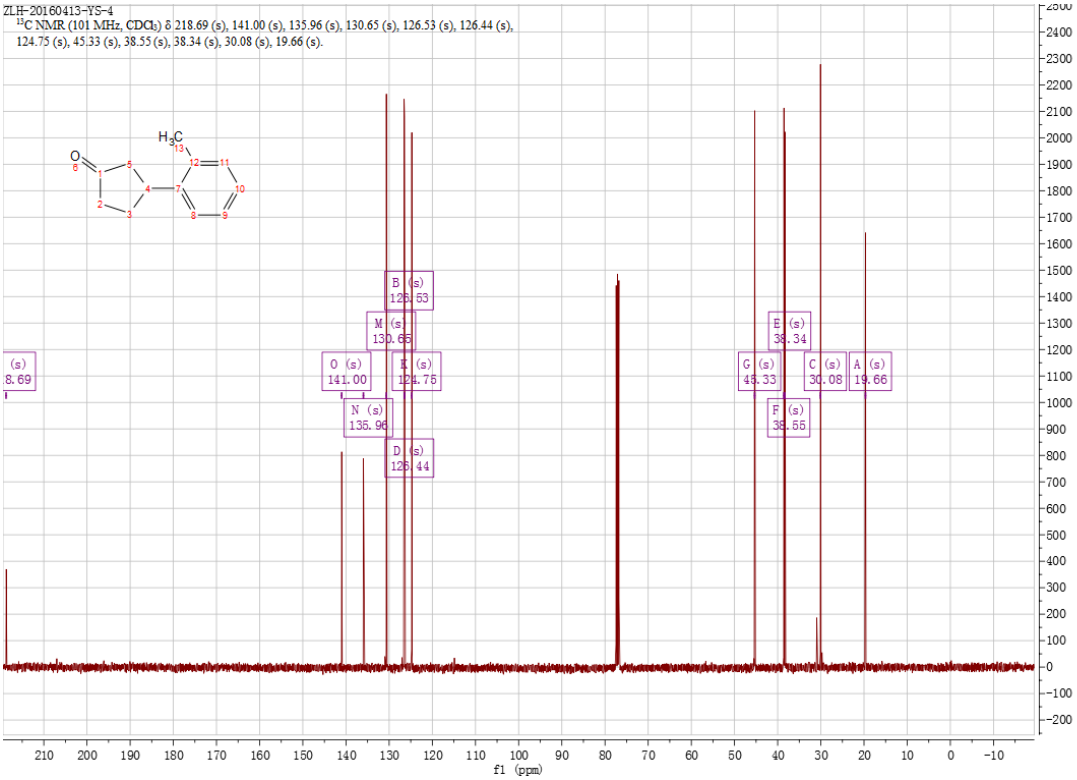


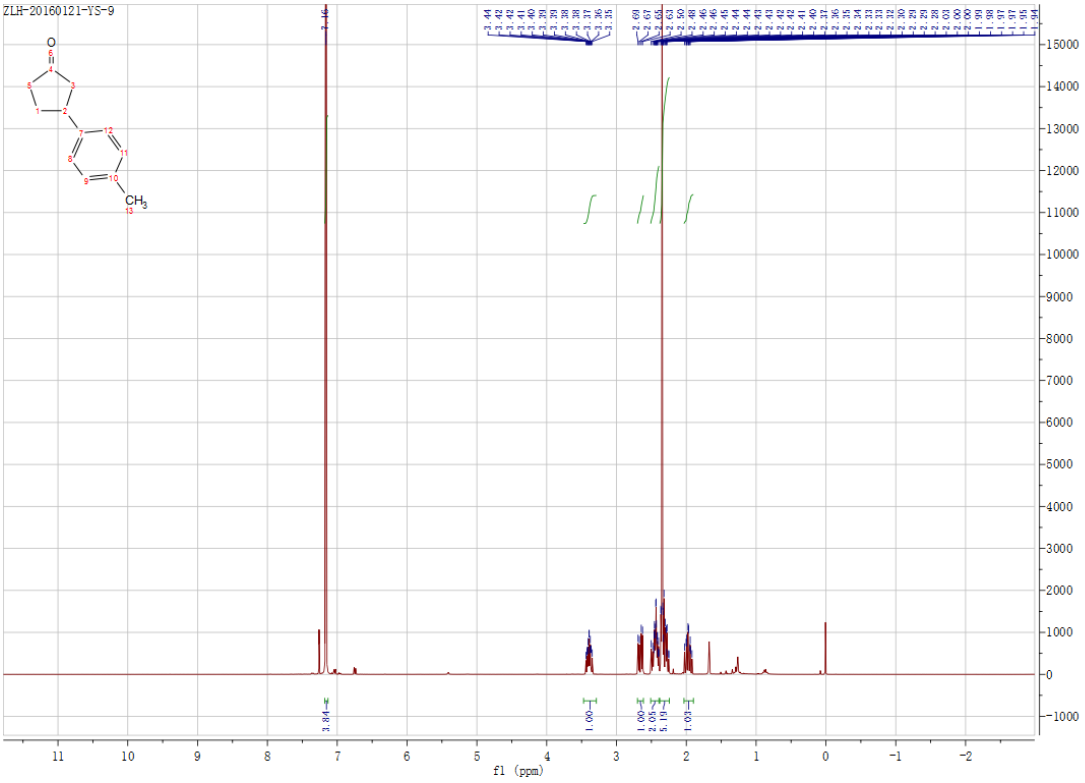


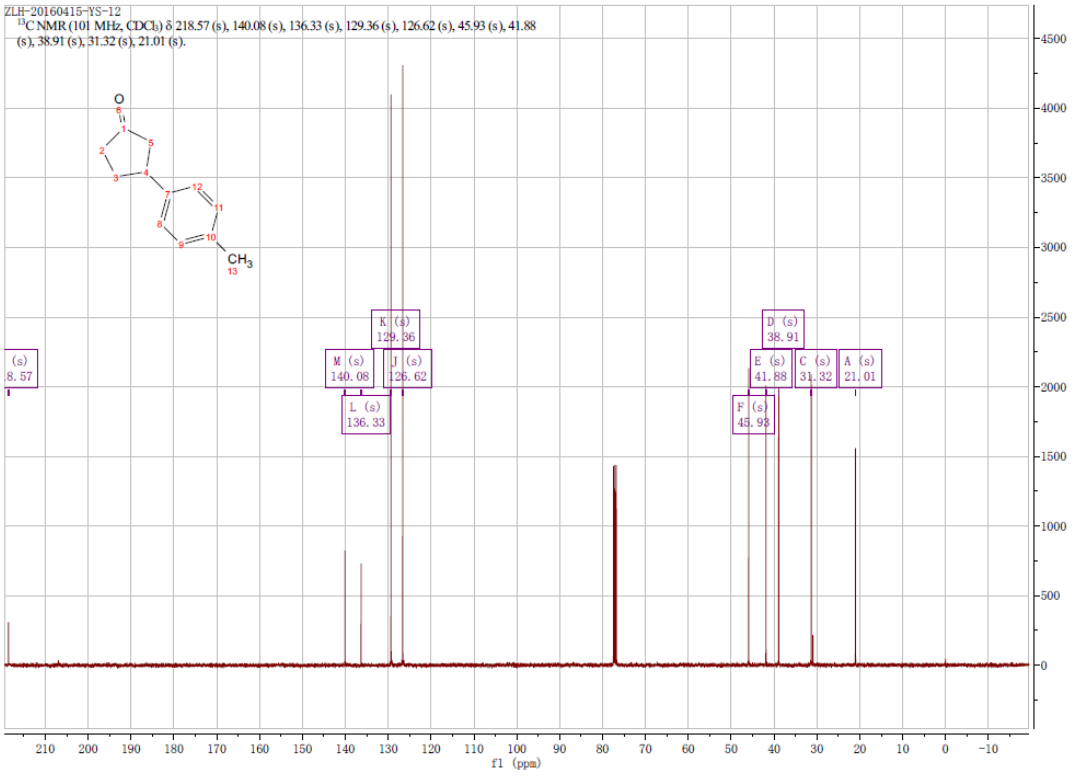


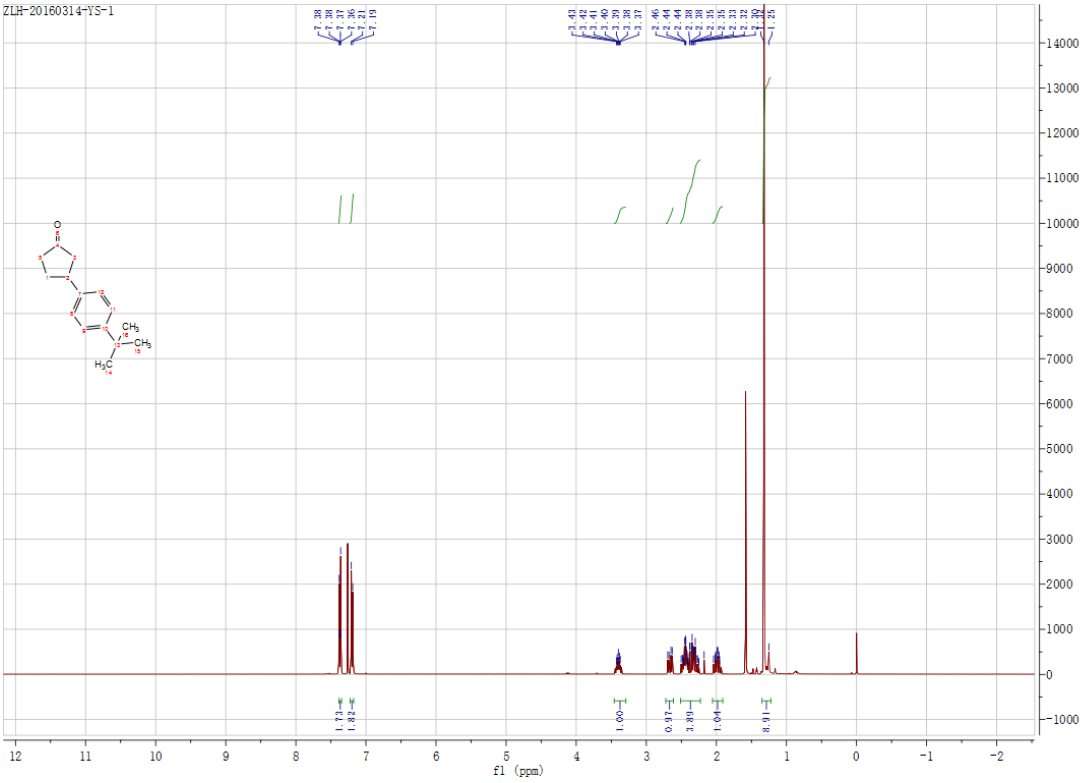


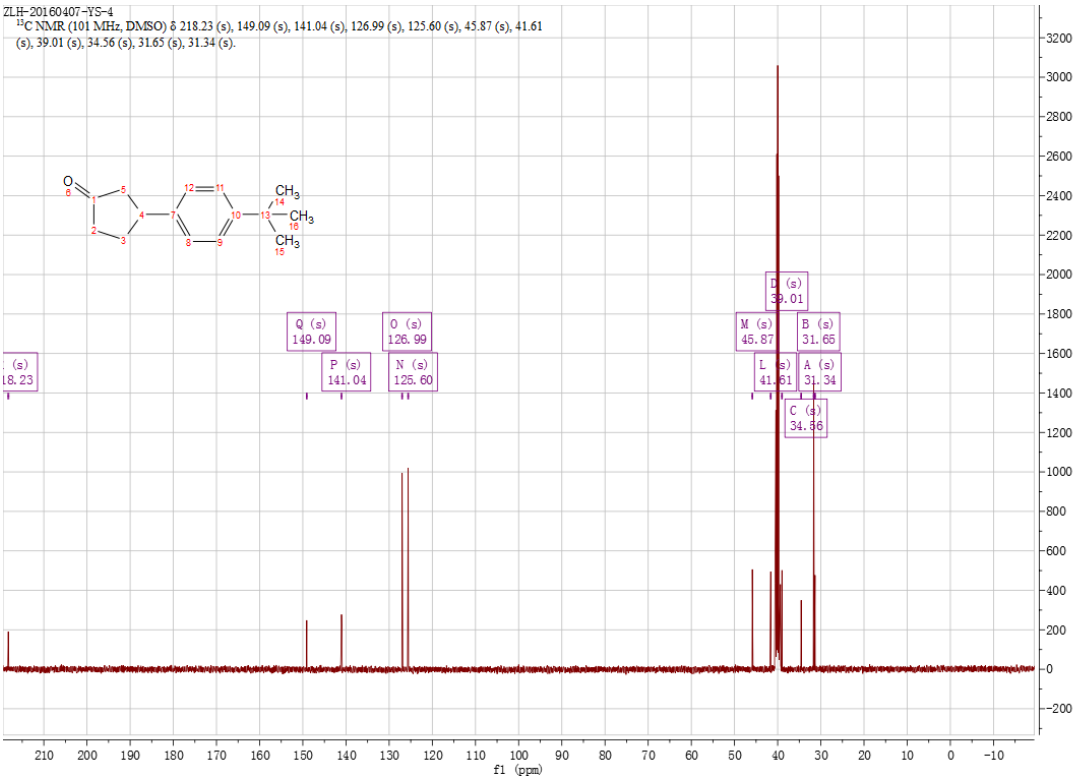


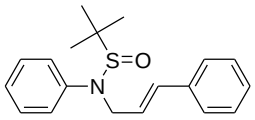




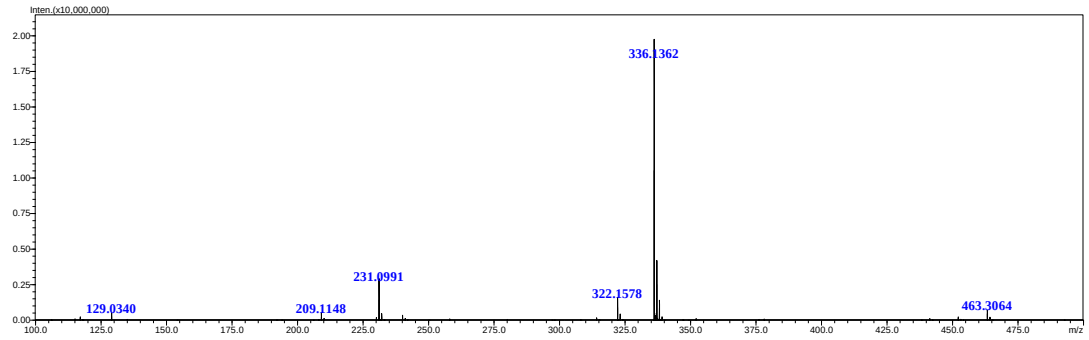


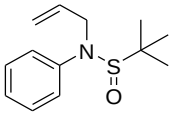




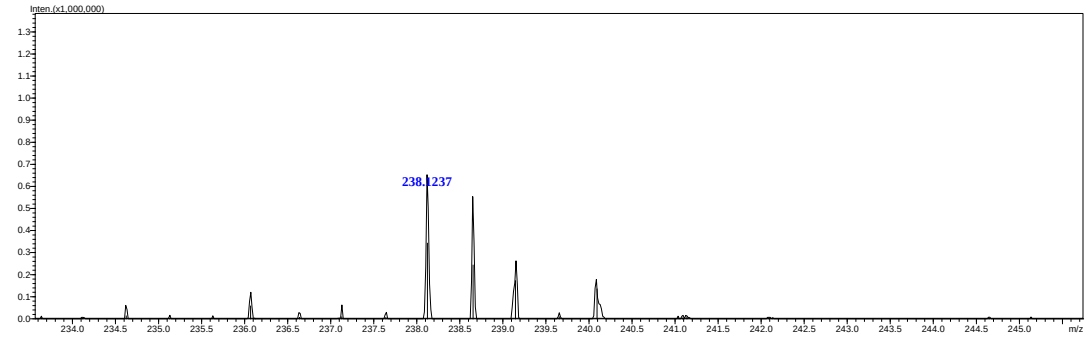


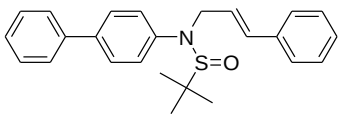
(R)-N-cinnamyl-2-methyl-N-phenylpropane-2-sulfinamide



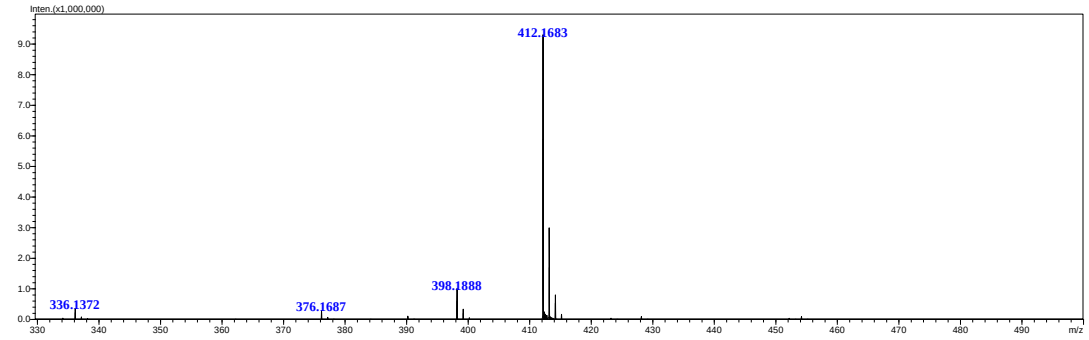


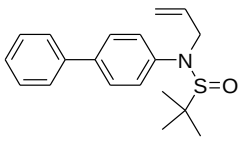
(R)-N-allyl-2-methyl-N-phenylpropane-2-sulfinamide





(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