

Spontaneous resolution of chiral bis-sulfoxides with asymmetric atropisomerism

Zhiguang Xu,* Haiyang Liu,* Mian HR Mahmood, Yuepeng Cai, Xuan Xu and Youwen Tang

Supporting Information

Contents

1. Experimental:.....	1
2. Crystallography:.....	3
3. ORTEP of 1s and 3s.....	5
4. Spectrum of 1-3s.....	6

1. Experimental:

Preparation of α,α' -di-*tert*-butylthio-*p*-xylene (**1s**) and α,α' -di-*tert*-butylsulfinyl-*p*-xylene (**1**):

Sodium hydroxide (99%, 2.218 g, 0.055 mol) and *tert*-butyl mercaptan (5.000 g, 0.055 mol) were dissolved in anhydrous ethanol (50 ml) at 70°C before α,α' -dichloro-*p*-xylene (4.85 g, 0.027 mol) was added to the above solution, then stirred for 1 h. The solution was extracted with dichloromethane after the addition of 400 ml of water. Evaporating the dichloromethane gave **1s** (6.871 g, 0.024 mol) with a yield of 87%. Hydrogen peroxide (30%, 2.89 ml, 0.028 mol) was added dropwise to a solution of α,α' -di-*tert*-butylthio-*p*-xylene (4.000 g, 0.014 mol) in acetic acid (60 ml) on an ice bath and the solution vigorously stirred for 1 h, then 500 ml of water added. The solution was extracted with dichloromethane, and the product of **1** (3.912 g, 0.012 mol) was obtained after evaporation of CH₂Cl₂ with a yield of 85% and total yield of 74%. The crude product was purified by simple recrystallization from mixtures of *n*-hexane and dichloromethane.

White crystals of the bis-sulfoxides **1** were obtained by slow evaporation of a mixed solution including *n*-hexane and dichloromethane.

Separation of diastereomers *rac*-**1** and *meso*-**1**:

The crystallization of **1** including *rac*-**1** and *meso*-**1** gave two types of crystals, one spiculate shaped and the other block shaped (Figure S1). The spiculate crystal and the block crystal are confirmed as *rac*-**1** and *meso*-**1** by X-ray analysis, respectively. It is easy to separate diastereomers *rac*-**1** and *meso*-**1** by picking out the spiculate crystal or the block crystal from mixed diastereomers crystals by eye or microscope.

The procedure for the preparation of **2** and **3** was the same as for compound **1**. Crystal preparation and separation of diastereomers for **2** and **3** was also the same as for **1**, which gave two types of crystals, one spiculate shaped (*rac*-**2**, *rac*-**3**) and the other block shaped (*meso*-**2**, *meso*-**3**) (see Figure S2 and S3).

By the means of NMR (see Figure S39-S41) approximate diastereomer ratios (*racemate* vs *meso*) for compounds **1**, **2** and **3** are 1:1.09, 1:1.21 and 1:1.24, respectively.



Figure S1. Block shape crystals of *meso-1* (left) and spiculate shape crystals of *rac-1* (right)

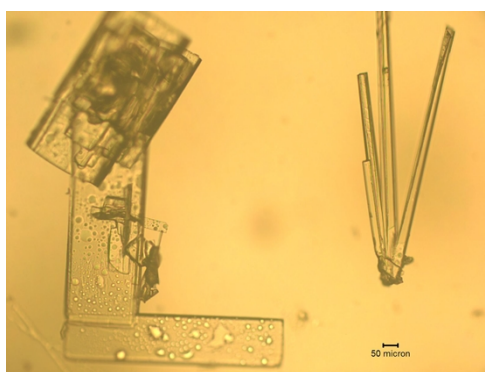


Figure S2. Block shape crystals of *meso-2* (left) and spiculate shape crystals of *rac-2* (right)

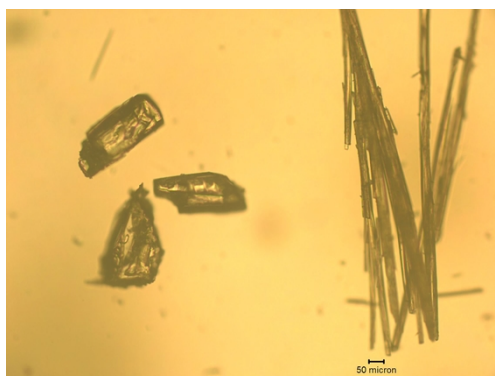


Figure S3. Block shape crystals of *meso-3* (left) and spiculate shape crystals of *rac-3* (right)

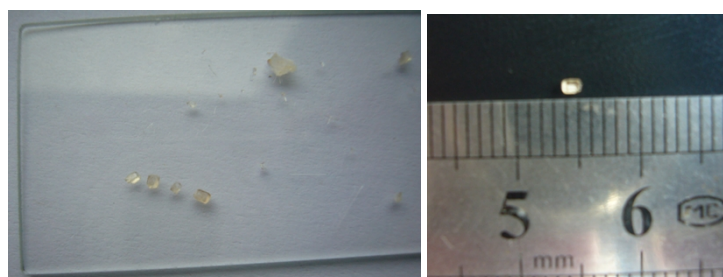


Figure S4. Block shape crystals of *meso-3*

α,α' -di-*tert*-butylthio-*p*-xylene, **1s**:

^1H NMR (400 MHz, CDCl_3) δ : 7.268 (s, 4H, $\text{C}_{\text{AR}}\text{H}$), 3.736 (s, 4H, CH_2), 1.340 (s, 18H, CH_3), ^{13}C NMR δ : 137.041($\text{C}_{\text{AR}}-\text{CH}_2$), 129.044($\text{C}_{\text{AR}}^1-\text{C}_{\text{AR}}^2-\text{CH}_2$), 42.842(CCH_3), 33.100(CH_2), 30.924(CH_3). MS: m/z : 282.12(19%). IR(KBr, cm^{-1}) ν : 3022.60, 2954.52, 1157.43.

(**R,S**)- α,α' -di-*tert*-butylsulfinyl-*p*-xylene, *meso*-1:

^1H NMR (400 MHz, CDCl_3) δ : 7.347 (s, 4H, $\text{C}_{\text{AR}}\text{H}$), 3.819 (d, 2H, $J=13\text{Hz}$, CH_2), 3.624 (d, 2H, $J=13\text{Hz}$, CH_2), 1.328 (s, 18H, CH_3), ^{13}C NMR δ : 131.838, 130.516, 53.790, 52.507, 23.062. MS: m/z : 315.2(100%). IR(KBr, cm^{-1}) ν : 3024.20, 2923.45, 1032.35, 842.44, 673.10.

(**R,R**)/(**S,S**)- α,α' -di-*tert*-butylsulfinyl-*p*-xylene, *rac*-1:

^1H NMR (400 MHz, CDCl_3) δ : 7.347 (s, 4H, $\text{C}_{\text{AR}}\text{H}$), 3.824 (d, 2H, $J=13\text{Hz}$, CH_2), 3.622 (d, 2H, $J=13\text{Hz}$, CH_2), 1.328 (s, 18H, CH_3), ^{13}C NMR δ : 131.843, 130.503, 53.778, 52.505, 23.048. MS: m/z : 315.2(100%). IR(KBr, cm^{-1}) ν : 3024.20, 2923.58, 1031.72, 844.36, 672.24.

(**R,R**)/(**S,S**)- α,α' -di-*tert*-butylsulfinyl-*m*-xylene, *rac*-2:

^1H NMR (400 MHz, CDCl_3) δ : 7.347-7.304 (m, 4H, $\text{C}_{\text{AR}}\text{H}$), 3.813 (d, 2H, $J=13\text{Hz}$, CH_2), 3.641 (d, 2H, $J=13\text{Hz}$, CH_2), 1.328 (s, 18H, CH_3)?, ^{13}C NMR (400 MHz, CDCl_3) δ : 132.188, 131.994, 129.693, 129.397, 53.864, 52.561, 23.122. MS: m/z : 315.2(100%). IR(KBr, cm^{-1}) ν : 3037.71, 2968.86, 1042.97, 816.21, 708.97.

(**R,S**)- α,α' -di-*tert*-butylsulfinyl-*m*-xylene, *meso*-2:

^1H NMR (400 MHz, CDCl_3) δ : 7.383-7.297(m, 4H, $\text{C}_{\text{AR}}\text{H}$), 3.832 (d, 2H, $J=13\text{Hz}$, CH_2), 3.611 (d, 2H, $J=13\text{Hz}$, CH_2), 1.330 (s, 18H, CH_3), ^{13}C NMR δ : 132.705, 131.593, 129.873, 129.409, 53.806, 52.579, 23.080. MS: m/z : 315.2(87.9%). IR(KBr, cm^{-1}) ν : 3049.28, 2970.73, 1036.07, 811.80, 707.09.

α,α' -di-*tert*-butylthio-*o*-xylene, **3s**:

^1H NMR (400 MHz, CDCl_3) δ : 7.338-7.192 (4H, $\text{C}_{\text{AR}}\text{H}$), 3.948 (s, 4H, CH_2), 1.444 (s, 18H, CH_3), ^{13}C NMR δ : 136.271, 130.738, 127.492, 42.982, 30.876, 30.588. MS: m/z : 283.3(14%). IR(KBr, cm^{-1}) ν : 3019.17, 2957.93, 1162.62, 776.51.

(**R,R**)/(**S,S**)- α,α' -di-*tert*-butylsulfinyl-*o*-xylene, *rac*-3:

^1H NMR (400 MHz, CDCl_3) δ : 7.339 (4H, $\text{C}_{\text{AR}}\text{H}$), 4.675 (d, 2H, $J=13\text{Hz}$, CH_2), 3.605 (d, 2H, $J=13\text{Hz}$, CH_2), 1.389(s, 18H, CH_3), ^{13}C NMR δ : 133.26, 131.69, 128.48, 53.91, 48.94, 23.02. MS: m/z : 315.2(58%). IR(KBr, cm^{-1}) ν : 3028.06, 2954.55, 1024.71, 898.81, 764.42.

(**M,R,S**/**P,R,S**)- α,α' -di-*tert*-butylsulfinyl-*o*-xylene, (**M,R,S**)-7/(**P,R,S**)-3:

^1H NMR (400 MHz, CDCl_3) δ : 7.365-7.315 (4H, $\text{C}_{\text{AR}}\text{H}$), 4.284 (d, 2H, $J=13\text{Hz}$, CH_2), 3.769 (d, 2H, $J=13\text{Hz}$, CH_2), 1.386 (s, 18H, CH_3), ^{13}C NMR δ : 132.406, 132.083, 128.746, 54.097, 50.216, 23.019. MS: m/z : 315.2(100%). IR(KBr, cm^{-1}) ν : 3026.13, 2925.42, 1028.87, 922.22, 768.47.

2. Crystallography:

Crystal data for **1s**: $\text{C}_{16}\text{H}_{26}\text{S}_2$, $M = 282.51$, triclinic, $a = 6.171(5) \text{ \AA}$, $b = 12.078(5) \text{ \AA}$, $c = 12.267(5) \text{ \AA}$, $\alpha = 76.243(5)^\circ$, $\beta = 80.572(5)^\circ$, $\gamma = 77.970(5)^\circ$, $V = 862.3(9) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group **PError!**, $Z = 2$, 5111 reflections measured, 3686 independent reflections ($R_{\text{int}} = 0.0127$). The final R_1 values were 0.0732 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2064 ($I > 2\sigma(I)$). The final R_1 values were 0.1041 (all data). The final $wR(F^2)$ values were 0.2324 (all data). The goodness of fit on F^2 was 1.086. The asymmetric unit has two half molecules, each lying about independent inversion centers.

Crystal data for *rac*-1: $\text{C}_{16}\text{H}_{26}\text{O}_2\text{S}_2$, $M = 314.51$, monoclinic, $a = 5.985(4) \text{ \AA}$, $b = 10.346(7) \text{ \AA}$, $c = 27.985(18) \text{ \AA}$, $\alpha =$

90.00°, $\beta = 90.592(9)^\circ$, $\gamma = 90.00^\circ$, $V = 1733(2) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $P21/c$, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.307 \text{ mm}^{-1}$, 9885 reflections measured, 3899 independent reflections ($R_{int} = 0.0632$). The final R_1 values were 0.1103 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2965 ($I > 2\sigma(I)$). The final R_1 values were 0.1749 (all data). The final $wR(F^2)$ values were 0.3307 (all data). The goodness of fit on F^2 was 1.025.

Crystal data for *meso-1*: $\text{C}_{16}\text{H}_{26}\text{O}_2\text{S}_2$, $M = 314.51$, triclinic, $a = 5.927(5) \text{ \AA}$, $b = 6.623(5) \text{ \AA}$, $c = 11.219(5) \text{ \AA}$, $\alpha = 80.046(5)^\circ$, $\beta = 89.205(5)^\circ$, $\gamma = 84.973(5)^\circ$, $V = 432.1(5) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group **PError!**, $Z = 1$, $\mu(\text{MoK}\alpha) = 0.308 \text{ mm}^{-1}$, 2589 reflections measured, 1861 independent reflections ($R_{int} = 0.0109$). The final R_1 values were 0.0562 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1662 ($I > 2\sigma(I)$). The final R_1 values were 0.0638 (all data). The final $wR(F^2)$ values were 0.1758 (all data). The goodness of fit on F^2 was 1.034. The molecule lies about an inversion centre.

Crystal data for *rac-2*: $\text{C}_{16}\text{H}_{26}\text{O}_2\text{S}_2$, $M = 314.51$, triclinic, $a = 6.3438(18) \text{ \AA}$, $b = 10.203(3) \text{ \AA}$, $c = 14.767(4) \text{ \AA}$, $\alpha = 108.771(4)^\circ$, $\beta = 97.042(4)^\circ$, $\gamma = 93.170(4)^\circ$, $V = 893.6(4) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group **PError!**, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.297 \text{ mm}^{-1}$, 5444 reflections measured, 3920 independent reflections ($R_{int} = 0.0223$). The final R_1 values were 0.0576 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1395 ($I > 2\sigma(I)$). The final R_1 values were 0.1101 (all data). The final $wR(F^2)$ values were 0.1667 (all data). The goodness of fit on F^2 was 1.043.

Crystal data for *meso-2*: $\text{C}_{16}\text{H}_{26}\text{O}_2\text{S}_2$, $M = 314.51$, monoclinic, $a = 12.418(5) \text{ \AA}$, $b = 6.541(2) \text{ \AA}$, $c = 21.609(8) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 93.212(6)^\circ$, $\gamma = 90.00^\circ$, $V = 1752.5(11) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $P21/c$, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.303 \text{ mm}^{-1}$, 10160 reflections measured, 4061 independent reflections ($R_{int} = 0.0729$). The final R_1 values were 0.0841 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2220 ($I > 2\sigma(I)$). The final R_1 values were 0.1968 (all data). The final $wR(F^2)$ values were 0.2771 (all data). The goodness of fit on F^2 was 0.963.

Crystal data for *cis-2* (with disorder of sulfinyl): $\text{C}_{16}\text{H}_{26}\text{O}_2\text{S}_2$, $M = 314.49$, monoclinic, $a = 12.443(2) \text{ \AA}$, $b = 6.5577(11) \text{ \AA}$, $c = 21.666(3) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 93.151(2)^\circ$, $\gamma = 90.00^\circ$, $V = 1765.2(5) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $P21/c$, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.301 \text{ mm}^{-1}$, 8800 reflections measured, 3261 independent reflections ($R_{int} = 0.0281$). The final R_1 values were 0.0573 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1502 ($I > 2\sigma(I)$). The final R_1 values were 0.0813 (all data). The final $wR(F^2)$ values were 0.1645 (all data). The goodness of fit on F^2 was 1.062.

Crystal data for *rac-3*: $\text{C}_{16}\text{H}_{26}\text{O}_2\text{S}_2$, $M = 314.51$, monoclinic, $a = 11.940(7) \text{ \AA}$, $b = 19.051(10) \text{ \AA}$, $c = 9.493(5) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 124.504(7)^\circ$, $\gamma = 90.00^\circ$, $V = 1779.5(17) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $C2/c$, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.299 \text{ mm}^{-1}$, 5309 reflections measured, 2060 independent reflections ($R_{int} = 0.0843$). The final R_1 values were 0.0586 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1071 ($I > 2\sigma(I)$). The final R_1 values were 0.1811 (all data). The final $wR(F^2)$ values were 0.1419 (all data). The goodness of fit on F^2 was 0.926. The molecule lies about a twofold axis.

Crystal data for (**P**, **R**, **S**)-**3**: $\text{C}_{16}\text{H}_{26}\text{O}_2\text{S}_2$, $M = 314.51$, orthorhombic, $a = 10.4014(17) \text{ \AA}$, $b = 11.1506(18) \text{ \AA}$, $c = 15.433(3) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$, $V = 1790.0(5) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $P212121$, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.297 \text{ mm}^{-1}$, 10956 reflections measured, 4144 independent reflections ($R_{int} = 0.0731$). The final R_1 values were 0.0547 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0585 ($I > 2\sigma(I)$). The final R_1 values were 0.1443 (all data). The final $wR(F^2)$ values were 0.0721 (all data). The goodness of fit on F^2 was 1.041. Flack parameter = 0.20(8).

Crystal data for (**M**, **R**, **S**)-**3**: $\text{C}_{16}\text{H}_{26}\text{O}_2\text{S}_2$, $M = 314.51$, orthorhombic, $a = 10.4267(16) \text{ \AA}$, $b = 15.449(2) \text{ \AA}$, $c = 11.1546(18) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$, $V = 1796.8(5) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $P212121$, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.296 \text{ mm}^{-1}$, 10429 reflections measured, 4144 independent reflections ($R_{int} = 0.1054$). The final R_1 values were 0.0945 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0813 ($I > 2\sigma(I)$). The final R_1 values were 0.2124 (all data). The final $wR(F^2)$ values were 0.1018 (all data). The goodness of fit on F^2 was 1.003. Flack parameter = 0.11(11).

Crystal data for **3s**: $\text{C}_{16}\text{H}_{26}\text{S}_2$, $M = 282.51$, triclinic, $a = 8.2584(14) \text{ \AA}$, $b = 10.6118(18) \text{ \AA}$, $c = 11.751(2) \text{ \AA}$, $\alpha = 67.631(2)^\circ$, $\beta = 72.609(2)^\circ$, $\gamma = 69.331(2)^\circ$, $V = 874.8(3) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group **PError!**, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.289 \text{ mm}^{-1}$, 5122 reflections measured, 3723 independent reflections ($R_{int} = 0.0148$). The final R_1 values were 0.0453 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1133 ($I > 2\sigma(I)$). The final R_1 values were 0.0745 (all data). The

final $wR(F^2)$ values were 0.1319 (all data). The goodness of fit on F^2 was 1.009.

3. ORTEP of 1s and 3s

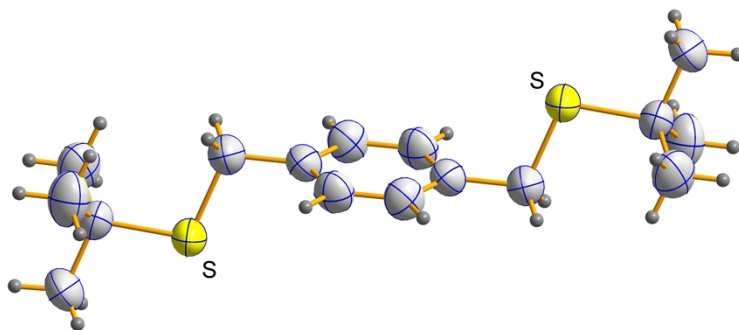


Figure S5. ORTEP of 1s with thermal ellipsoids drawn at the 50% probability level.

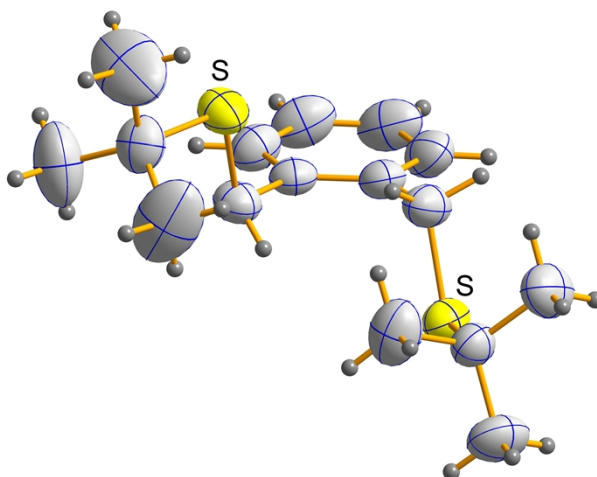


Figure S6. ORTEP of 3s with thermal ellipsoids drawn at the 50% probability level.

4. Spectrum of 1-3s

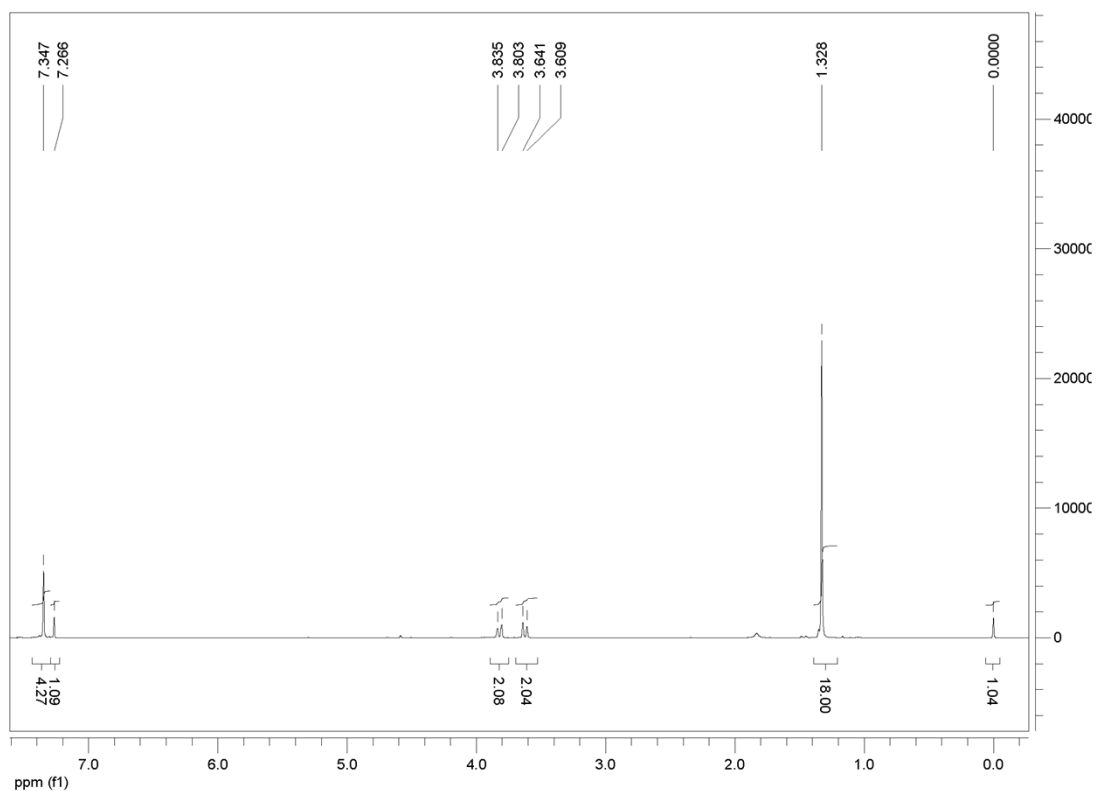


Figure S7. ¹H NMR spectrum of *rac-1*

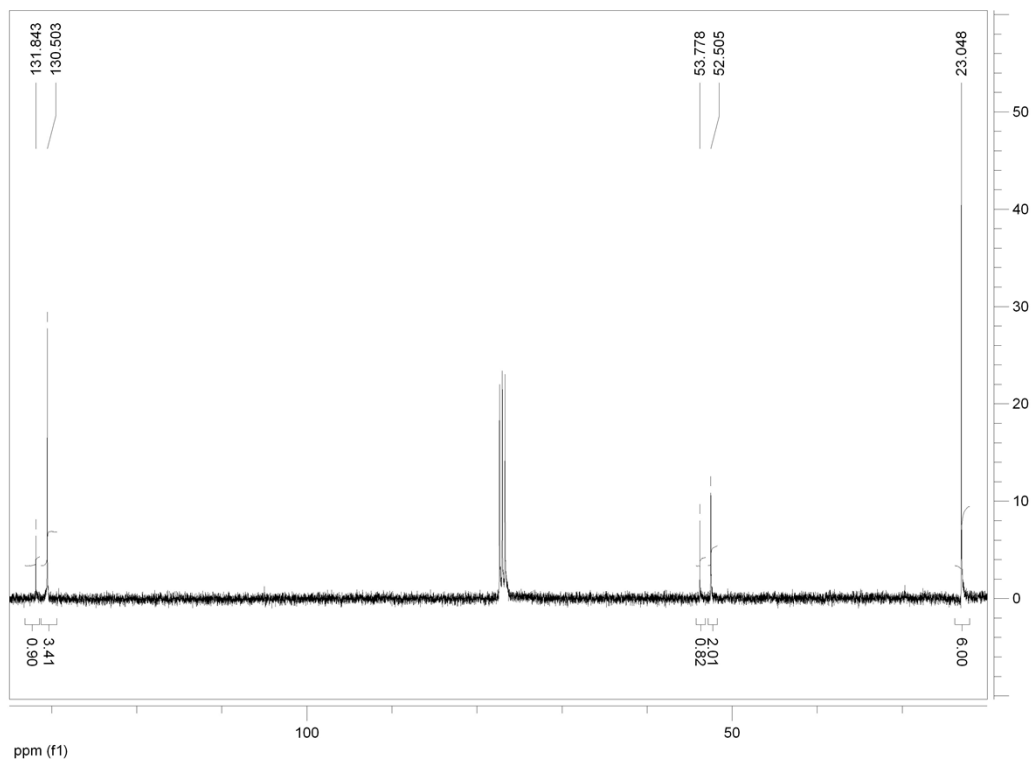
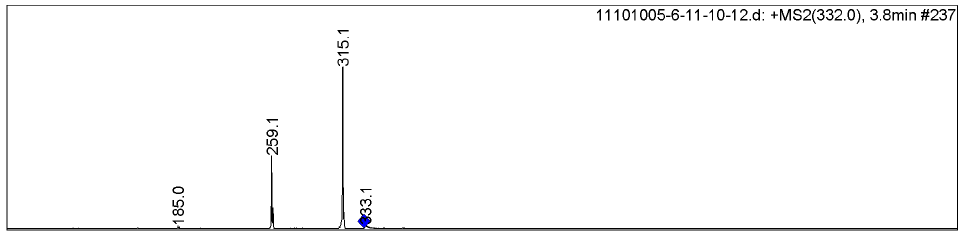


Figure S8. ¹³C NMR spectrum of *rac-1*



#	m/z	I	I%
1	185.0	108746	1.5
2	259.1	3324166	44.9
3	260.1	936272	12.7
4	312.5	64191	0.9
5	315.1	7398854	100.0
6	316.0	730276	9.9
7	333.1	149959	2.0
8	334.1	105991	1.4
9	334.7	87398	1.2
10	336.0	62645	0.8

Figure S9. MS spectrum of *rac-1*

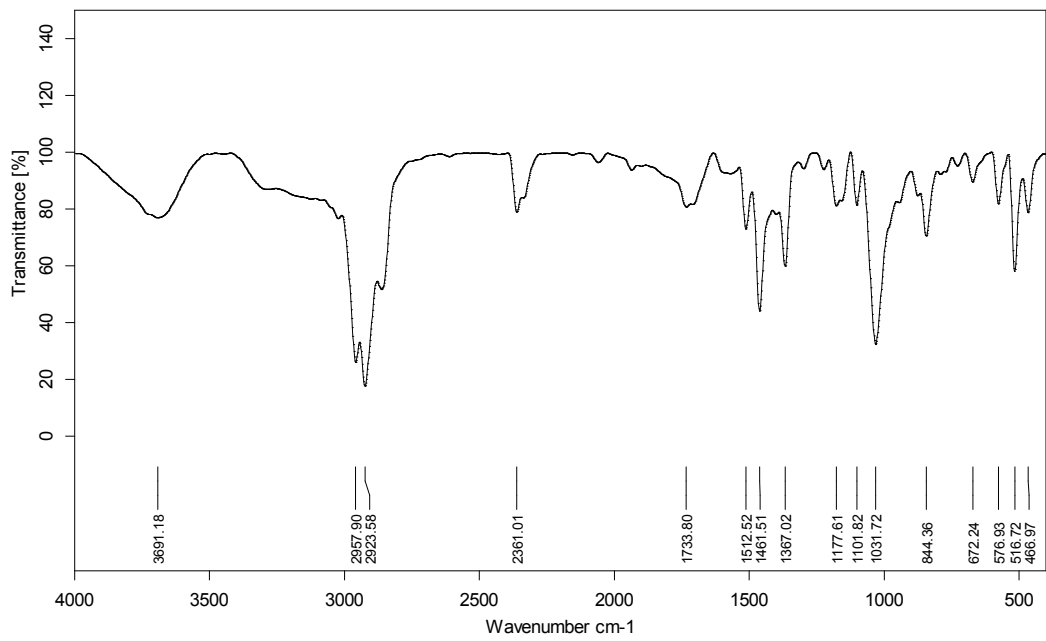


Figure S10. IR spectrum of *rac-1*

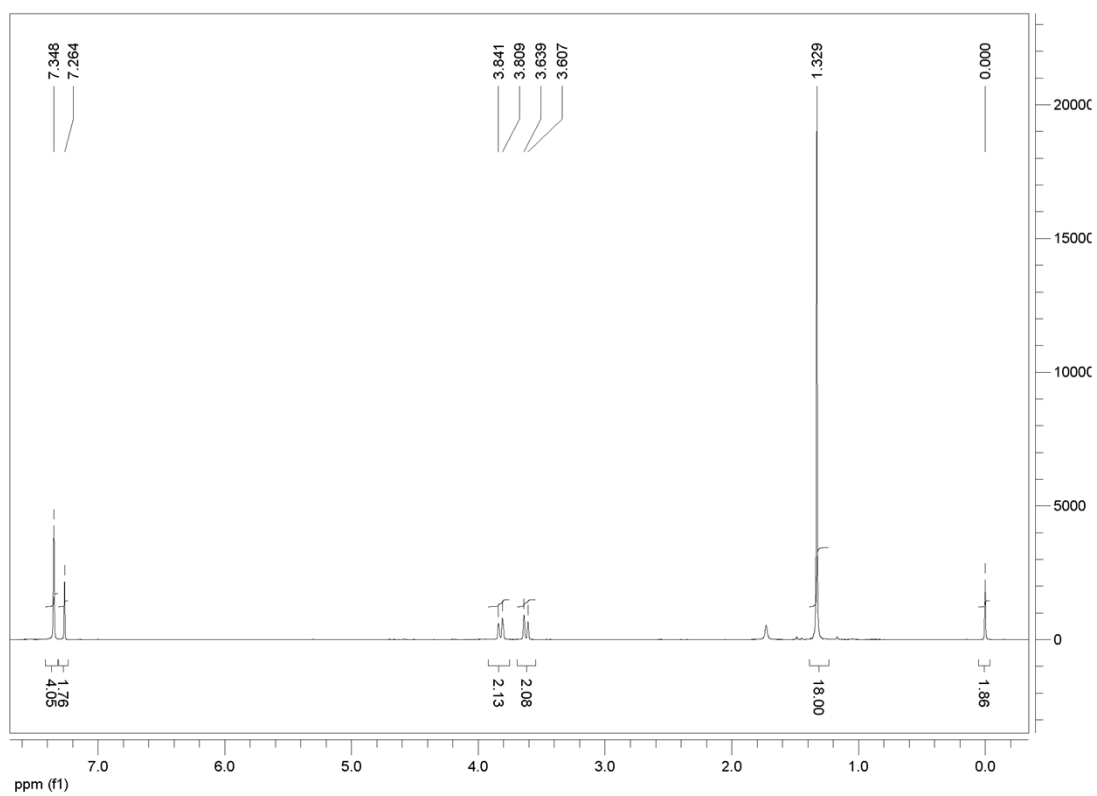


Figure S11. ^1H NMR spectrum of *meso-1*

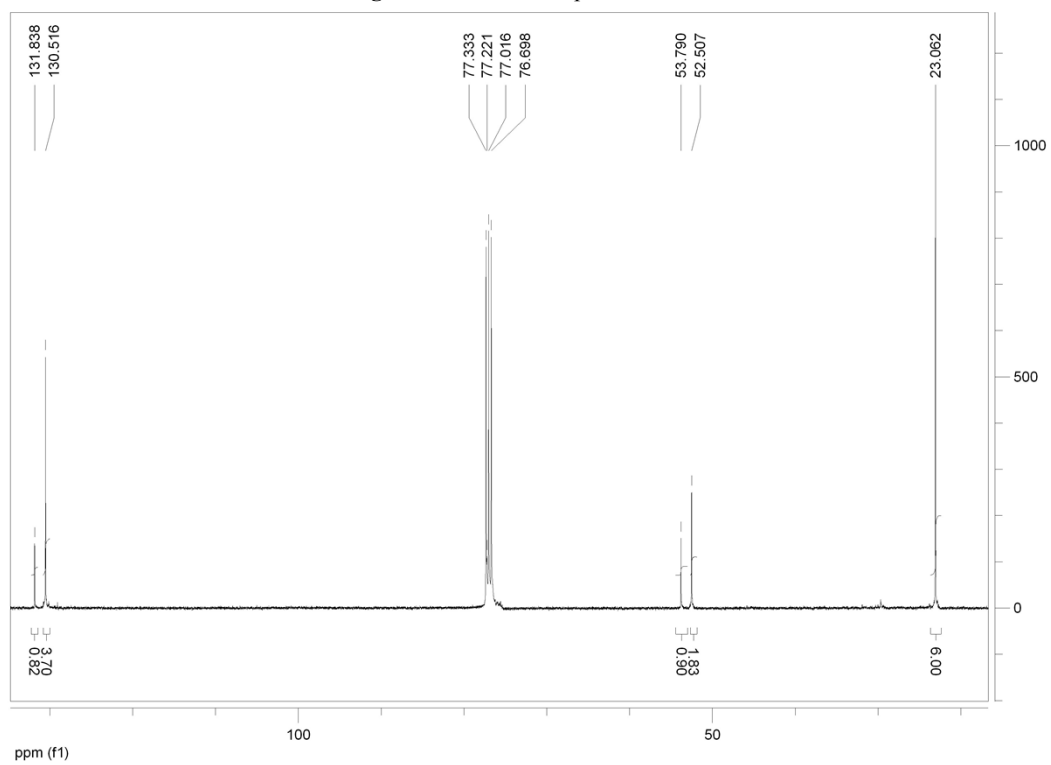


Figure S12. ^{13}C NMR spectrum of *meso-1*

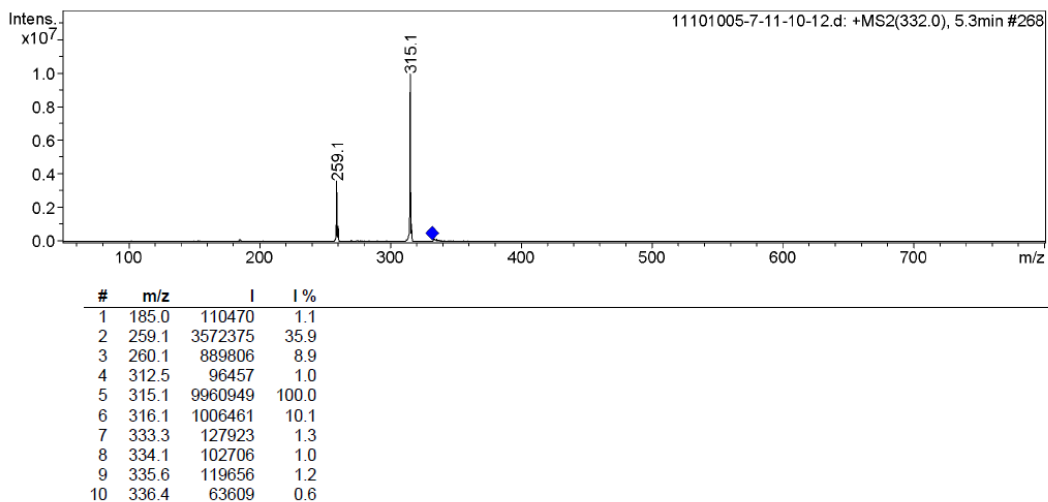


Figure S13. MS spectrum of *meso-1*

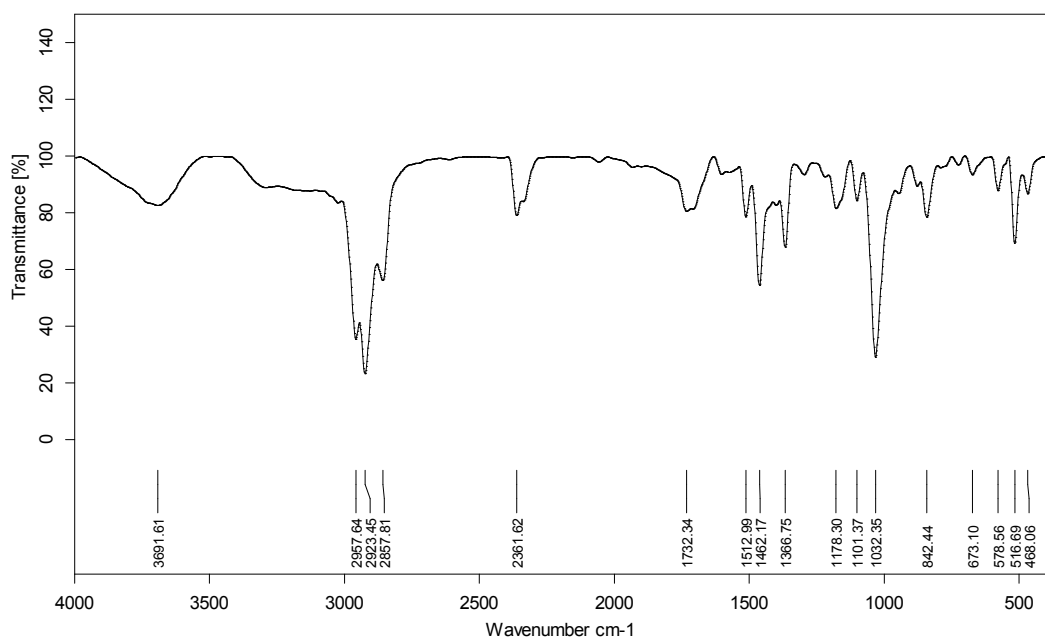


Figure S14. IR spectrum of *meso-1*

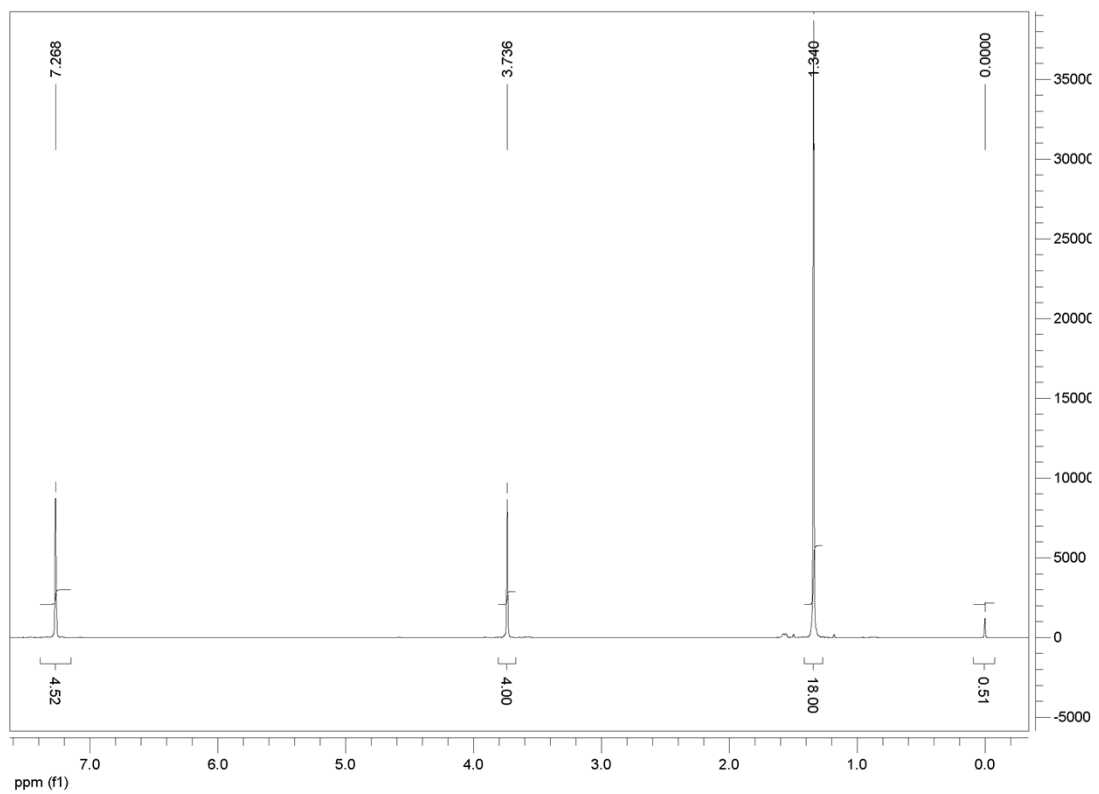


Figure S15. ^1H NMR spectrum of **1s**

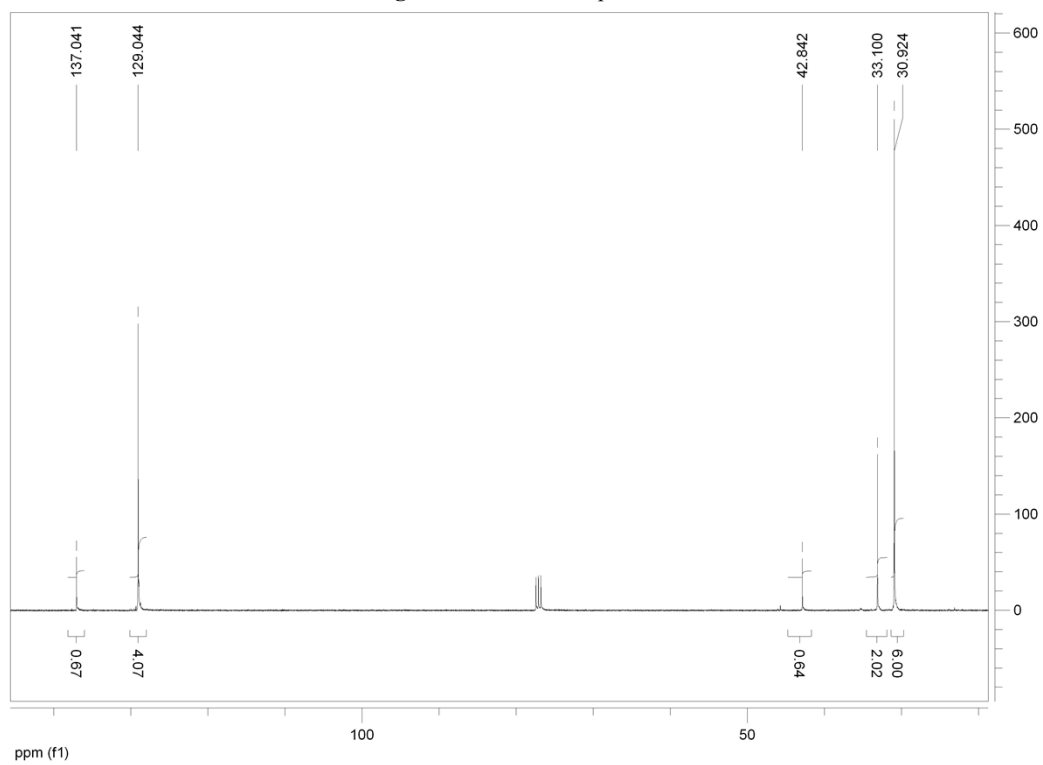


Figure S16. ^{13}C NMR spectrum of **1s**

xzhg-2012-05-22-01 #6379 RT: 39.58 AV: 1 NL: 8.37E6
F: + c Full ms [50.00-470.00]

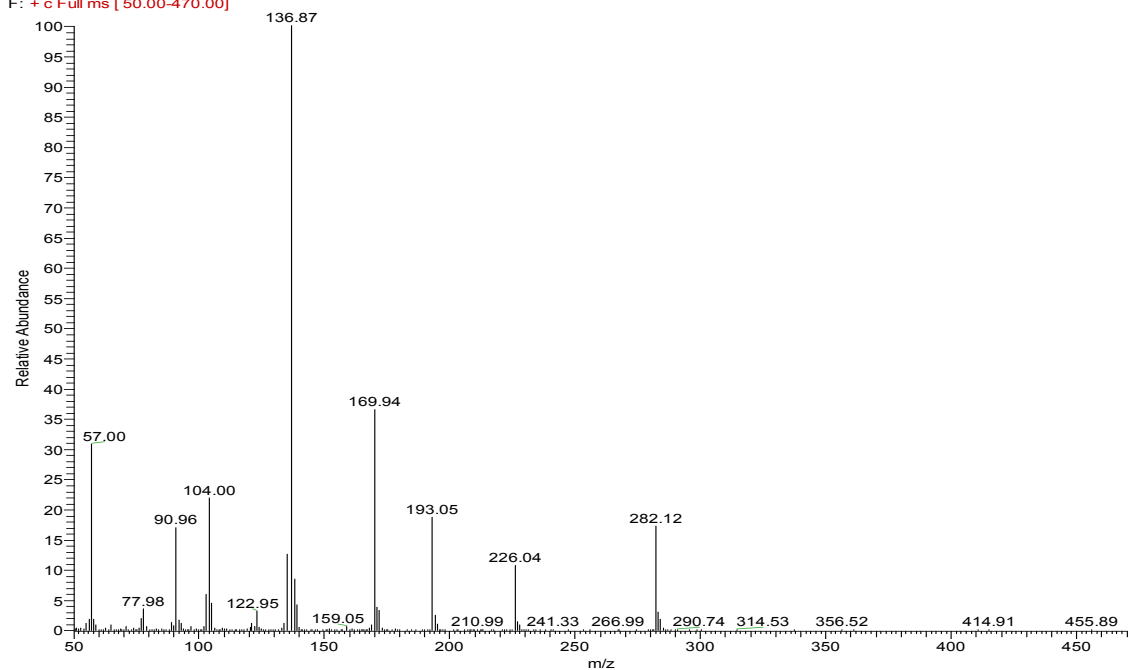


Figure S17. MS spectrum of 1s

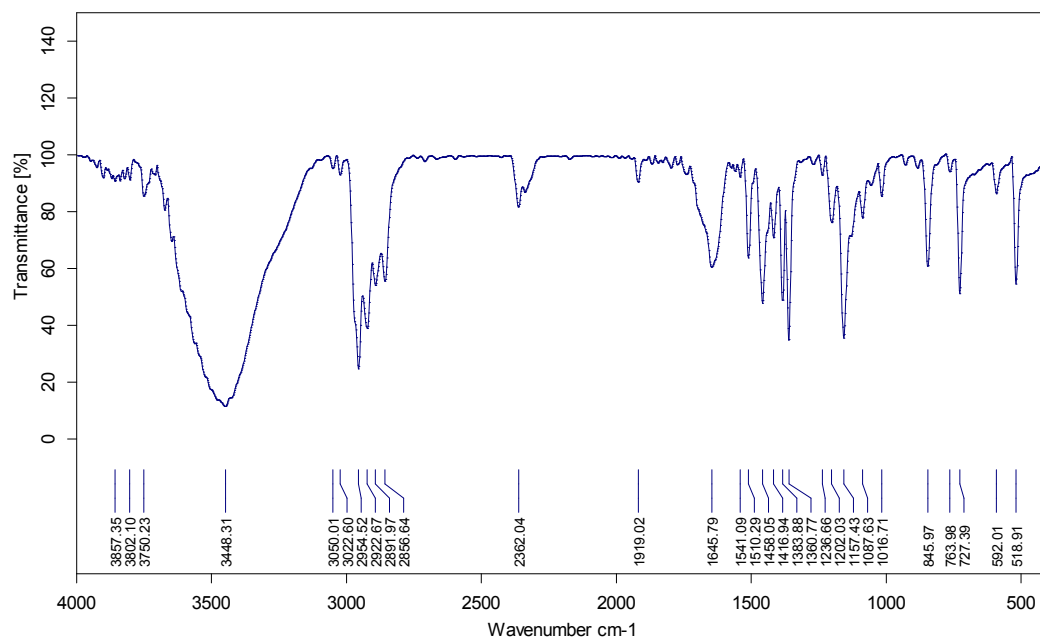


Figure S18. IR spectrum of 1s

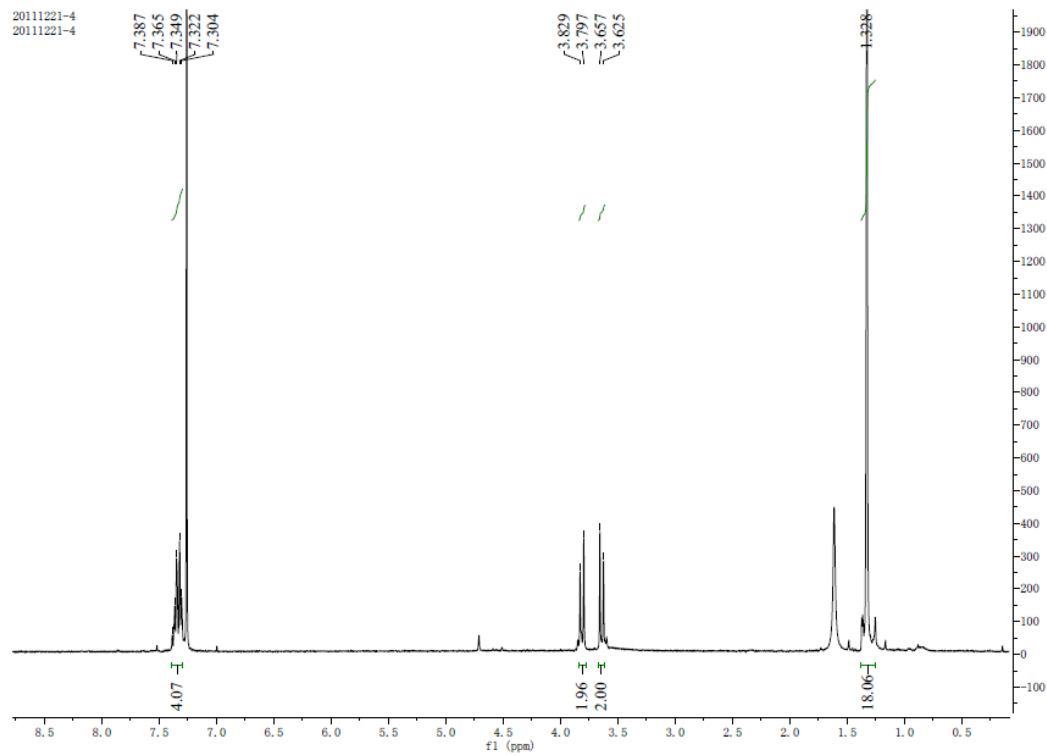


Figure S19. ^1H NMR spectrum of *rac-2*

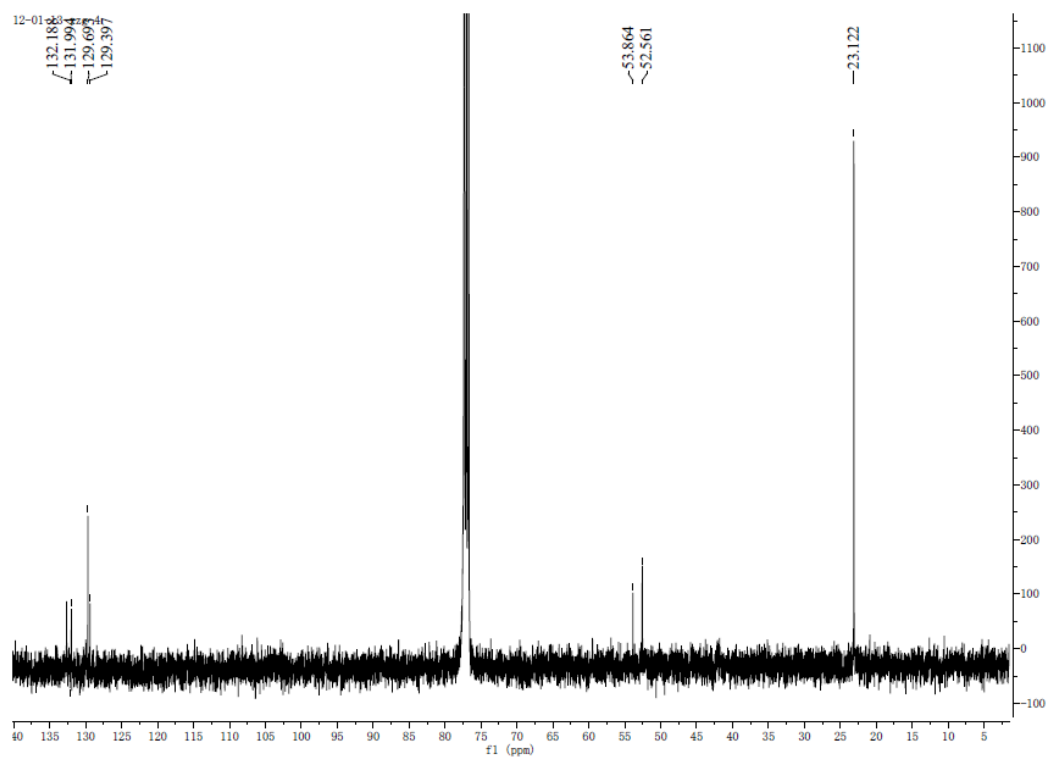
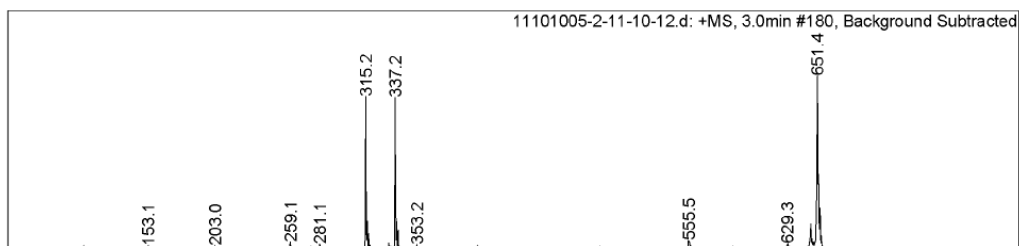


Figure S20. ^{13}C NMR spectrum of *rac-2*



#	m/z	I	I %
1	315.2	25199834	87.9
2	316.2	4497294	15.7
3	317.2	2402572	8.4
4	337.2	25004962	87.3
5	338.2	4401404	15.4
6	339.2	3051993	10.7
7	646.4	4072119	14.2
8	651.4	28652838	100.0
9	652.1	12261394	42.8
10	653.2	6669051	23.3

Figure S21. MS spectrum of *rac-2*

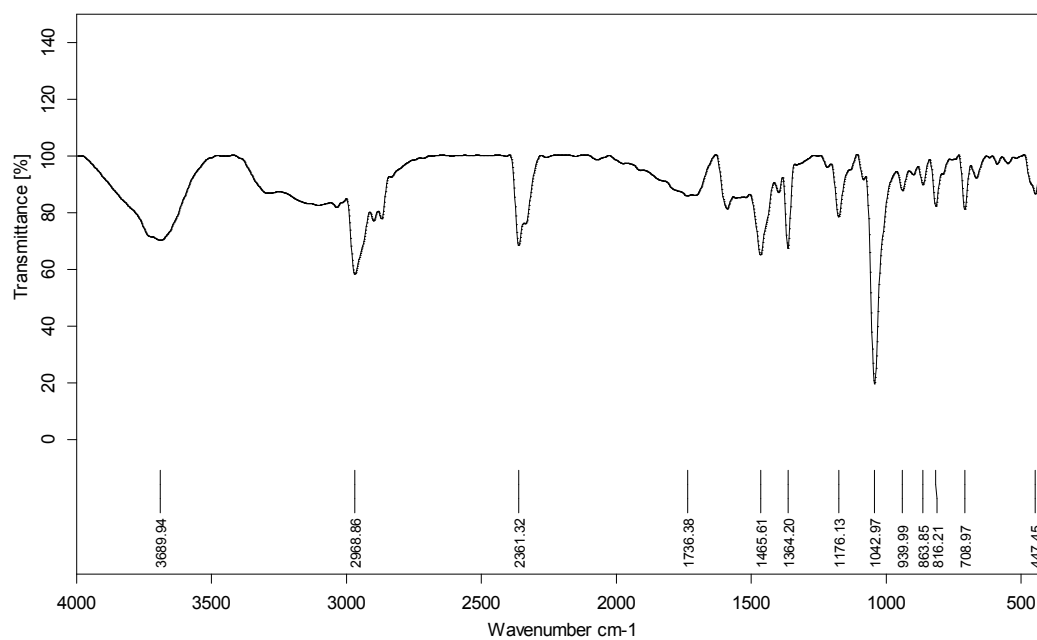


Figure S22. IR spectrum of *rac-2*

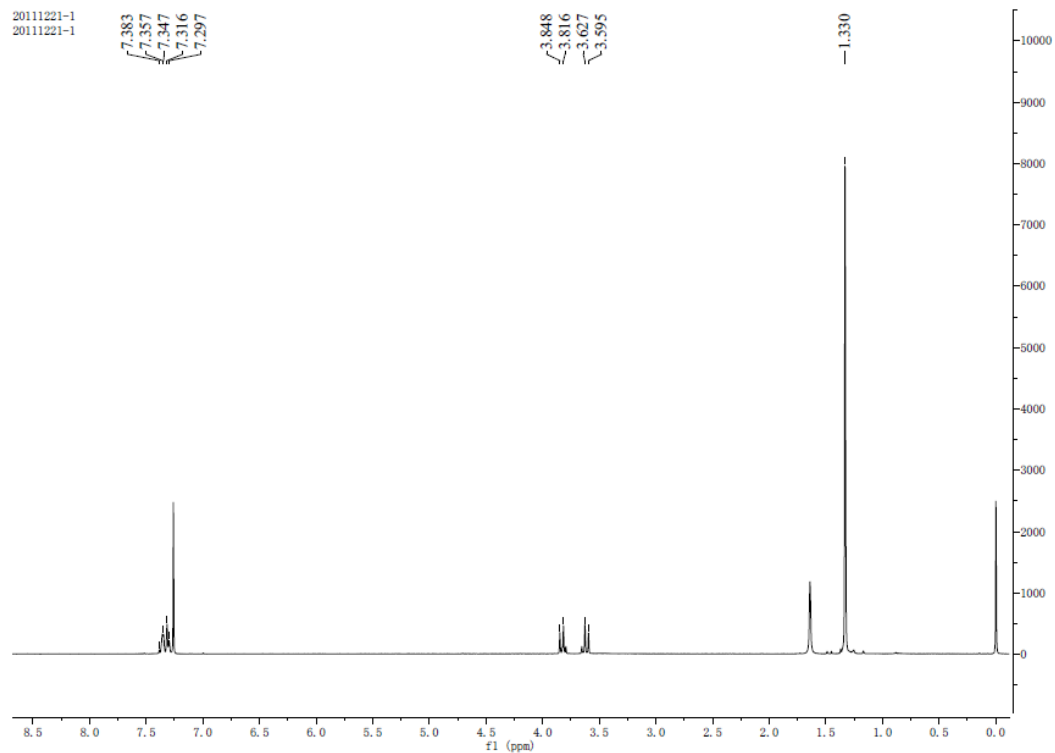


Figure S23. ^1H NMR spectrum of *meso-2*

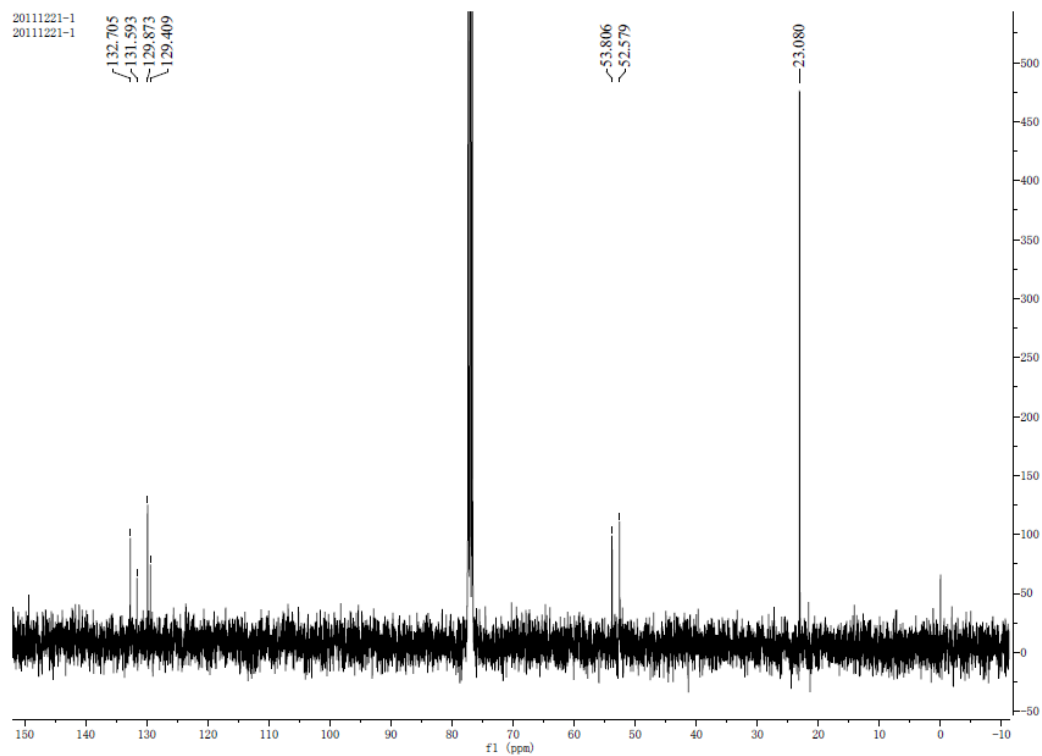
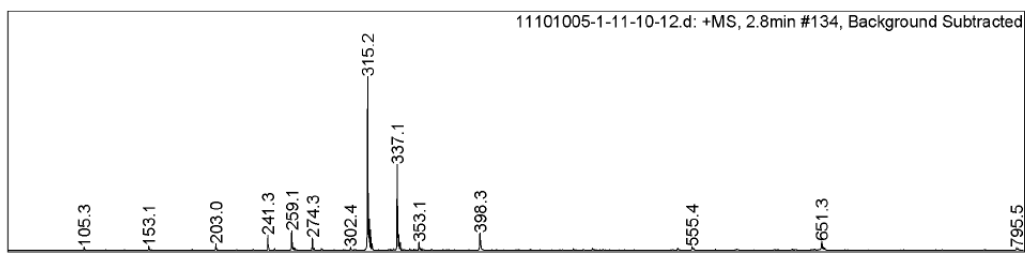


Figure S24. ^{13}C NMR spectrum of *meso-2*



#	m/z	I	I%
1	241.3	2849799	8.6
2	259.1	3678429	11.1
3	274.3	2379591	7.2
4	315.2	33252626	100.0
5	316.1	6019007	18.1
6	317.2	3877498	11.7
7	337.1	16356966	49.2
8	338.1	2935178	8.8
9	398.3	3256804	9.8
10	651.3	1721064	5.2

Figure S25. MS spectrum of *meso-2*

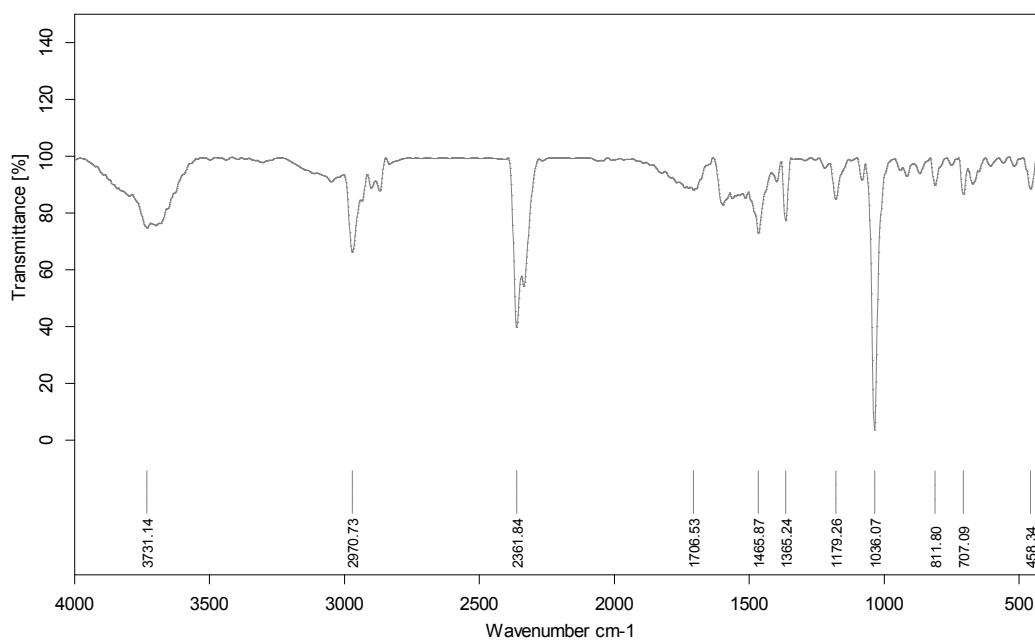


Figure S26. IR spectrum of *meso-2*

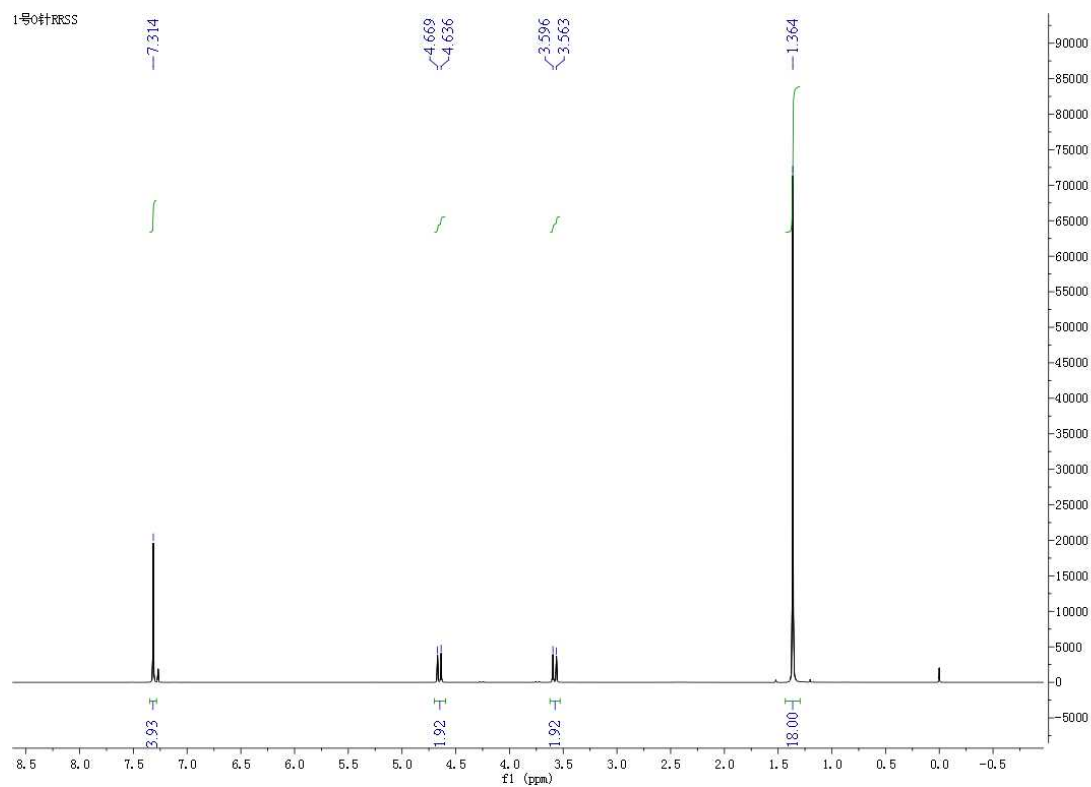


Figure S27. ¹H NMR spectrum of *rac-3*

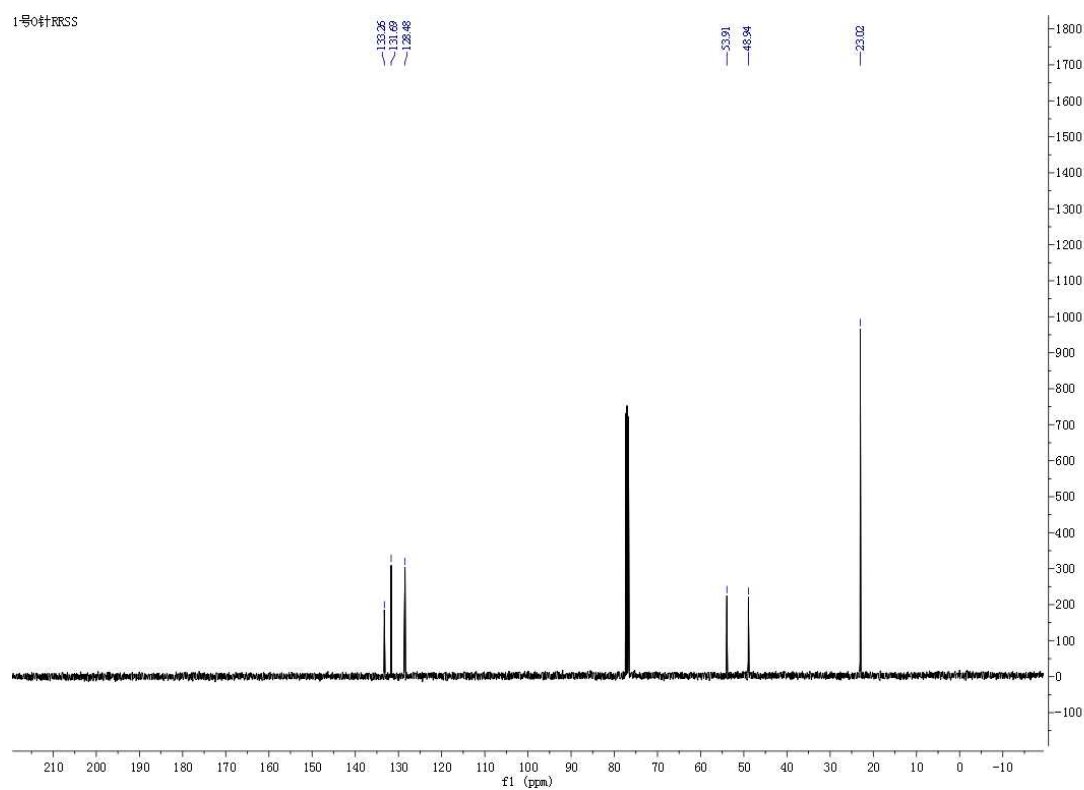
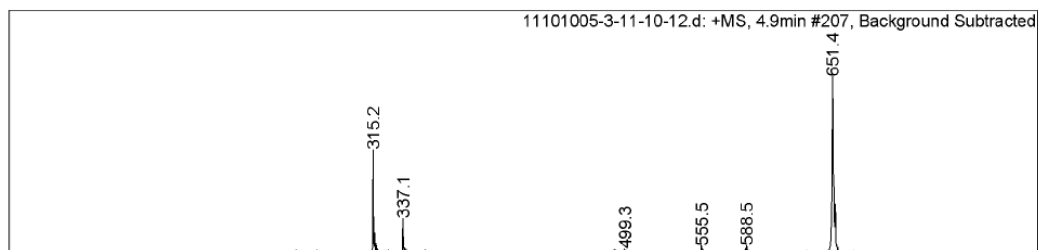


Figure S28. ¹³C NMR spectrum of *rac-3*



#	m/z	I	I%
1	315.2	8986138	58.2
2	316.2	1686158	10.9
3	317.2	789808	5.1
4	337.1	2967648	19.2
5	555.5	553429	3.6
6	588.5	576898	3.7
7	651.4	15432092	100.0
8	653.1	4223690	27.4
9	654.3	688879	4.5
10	655.3	423072	2.7

Figure S29. MS spectrum of *rac-3*

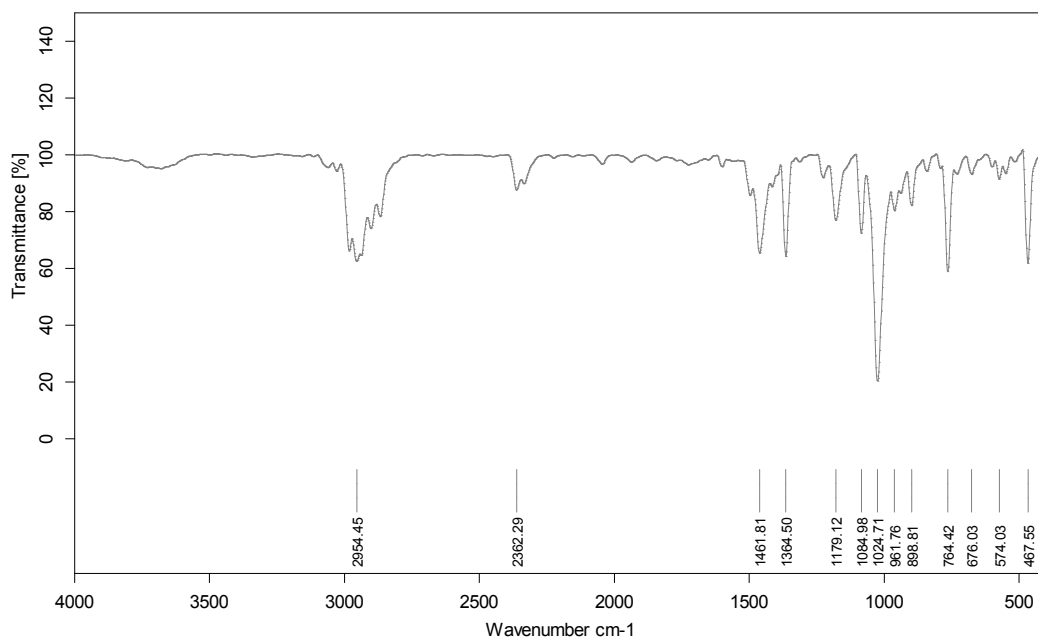


Figure S30. IR spectrum of *rac-3*

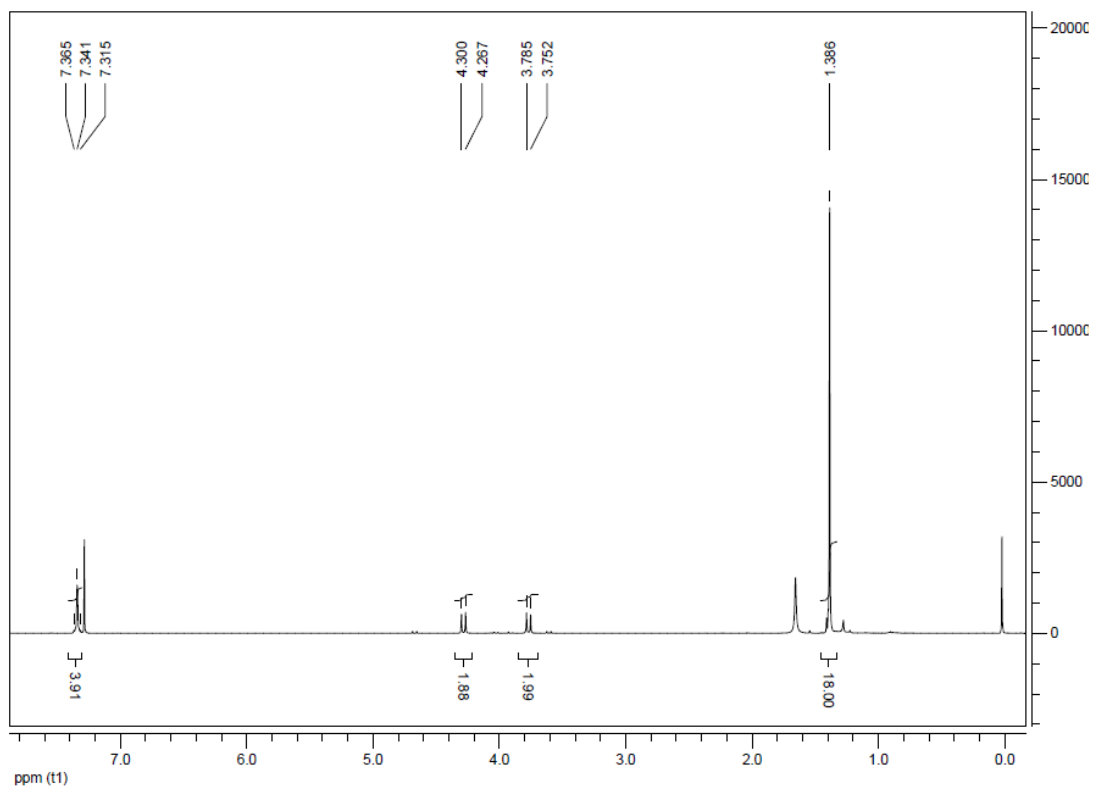


Figure S31. ^1H NMR spectrum of $(M/P,R,S)$ -3

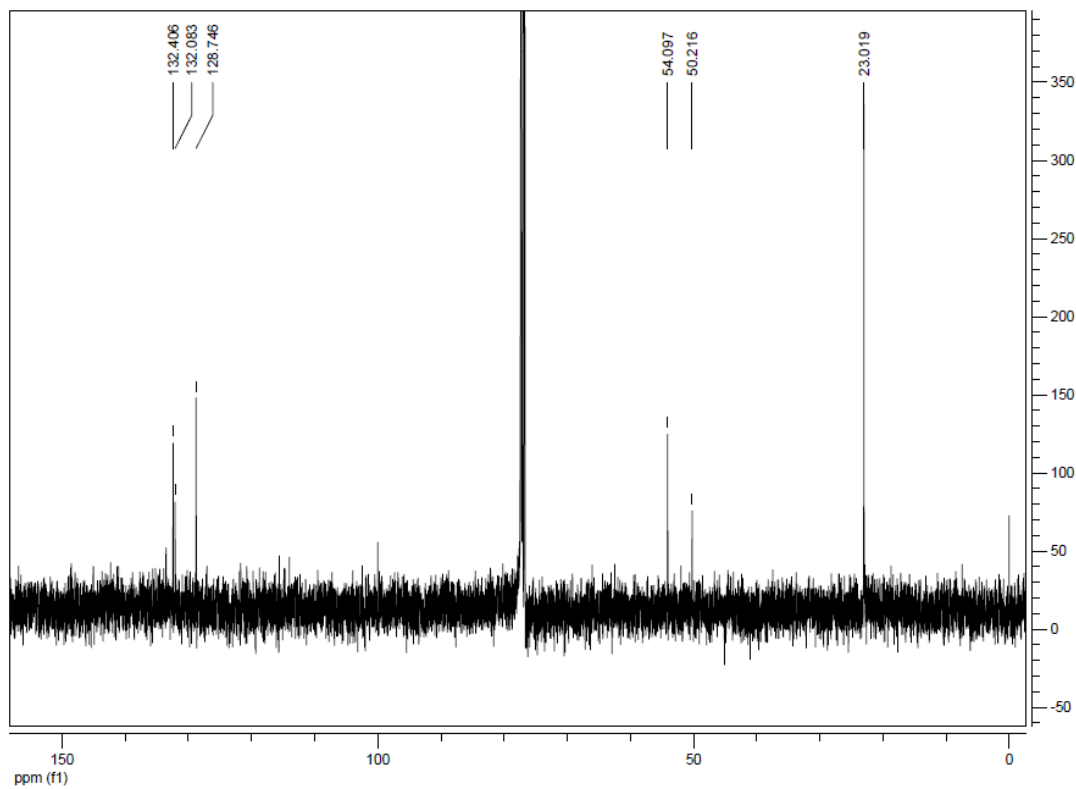
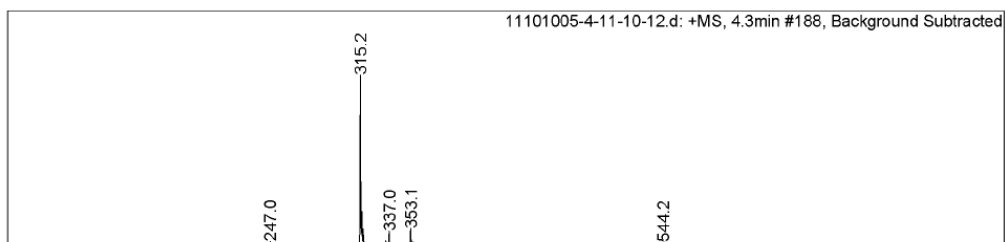


Figure S32. ^{13}C NMR spectrum of $(M/P,R,S)$ -3



#	m/z	I	I%
1	247.0	44190	1.9
2	315.2	2348817	100.0
3	316.1	459867	19.6
4	317.1	217648	9.3
5	334.3	57385	2.4
6	335.0	32243	1.4
7	337.0	186472	7.9
8	353.1	221248	9.4
9	354.2	36090	1.5
10	544.2	33434	1.4

Figure S33. MS spectrum of (M/P,R,S)-3

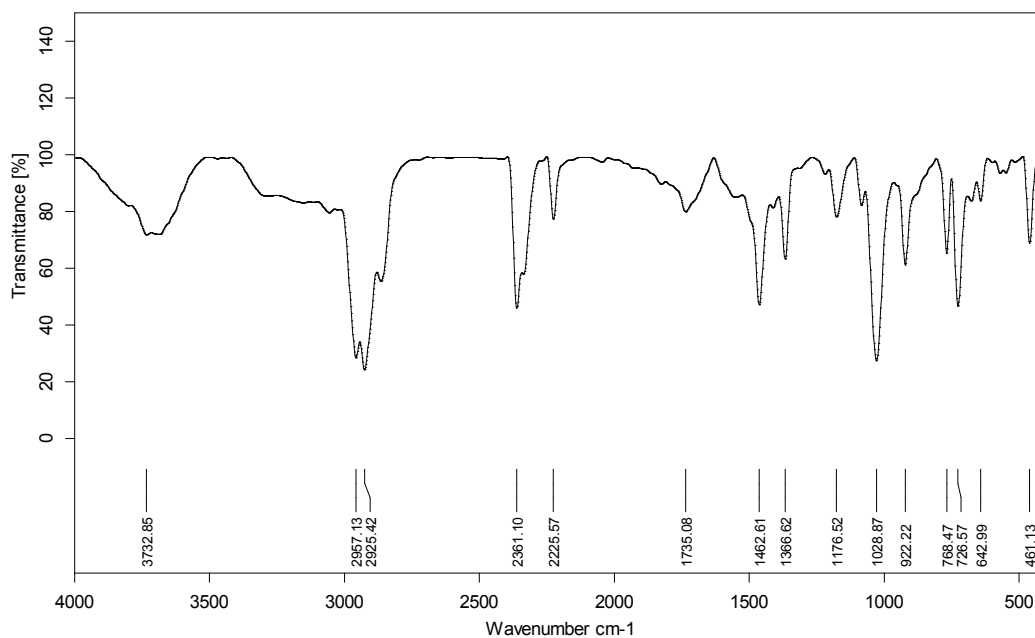


Figure S34. IR spectrum of (M/P,R,S)-3

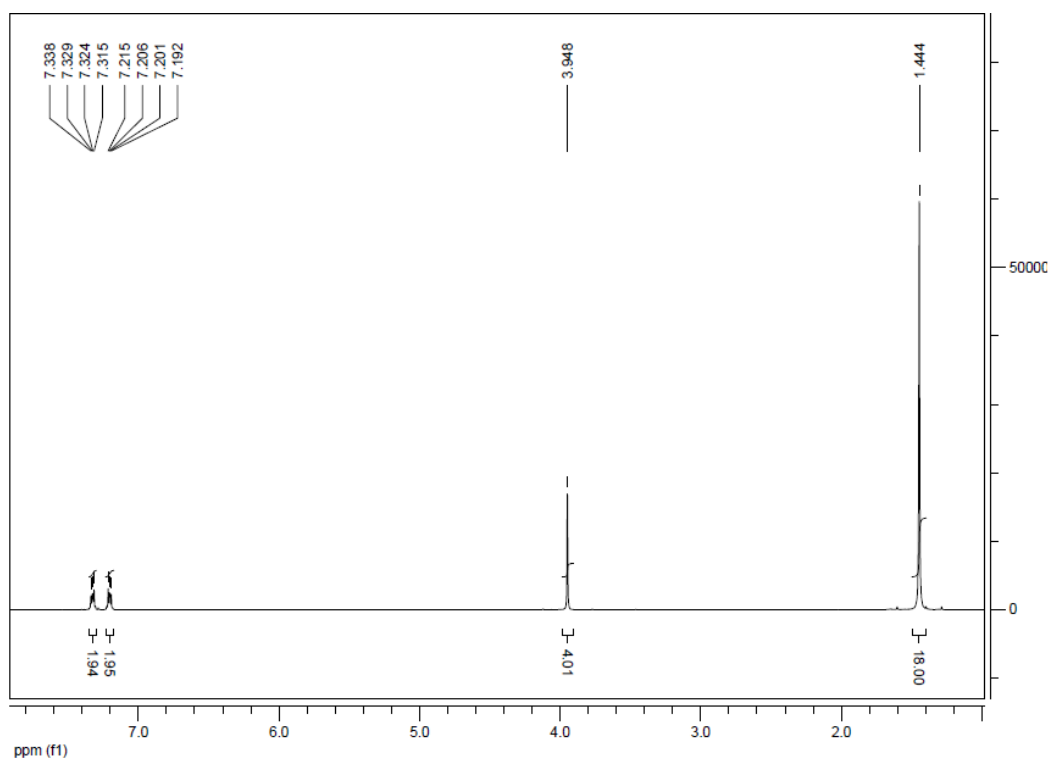


Figure S35. ¹H NMR spectrum of 3s

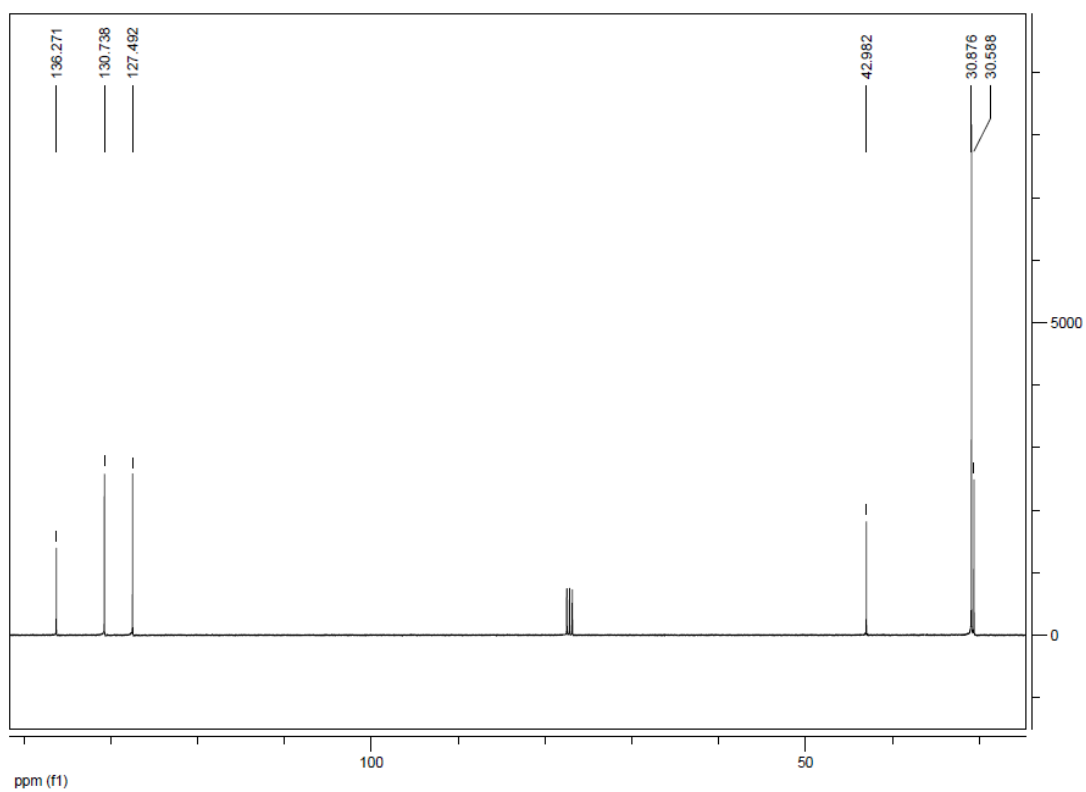
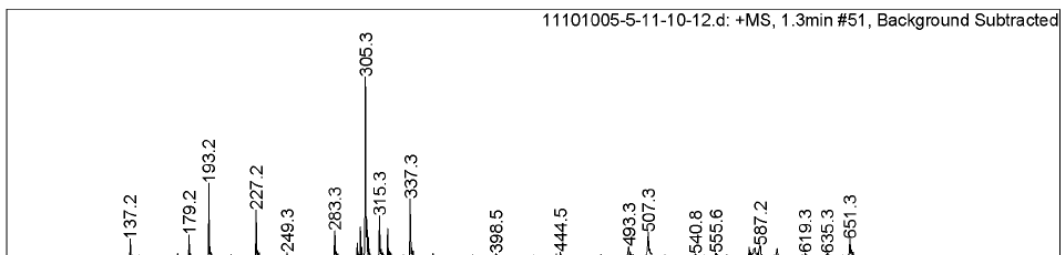


Figure S36. ¹³C NMR spectrum of 3s



#	m/z	I	I%
1	193.2	2751805	40.8
2	227.2	1755851	26.0
3	283.3	972744	14.4
4	301.5	1111028	16.5
5	305.3	6745774	100.0
6	306.2	1404620	20.8
7	315.3	1529572	22.7
8	321.2	1049527	15.6
9	337.3	2169698	32.2
10	507.3	905238	13.4

Figure S37. MS spectrum of 3s

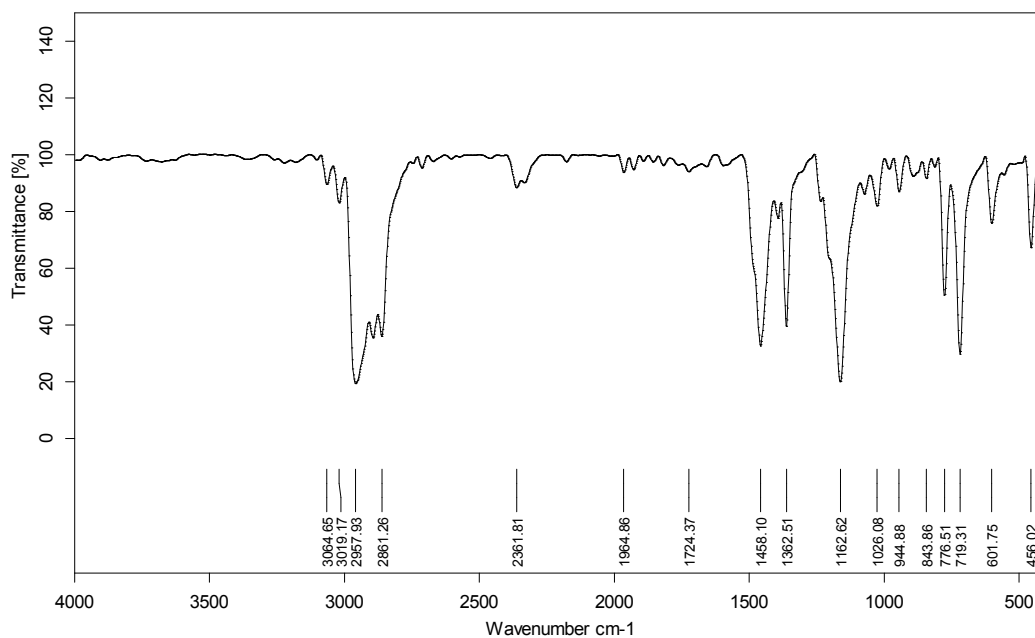


Figure S38. IR spectrum of 3s

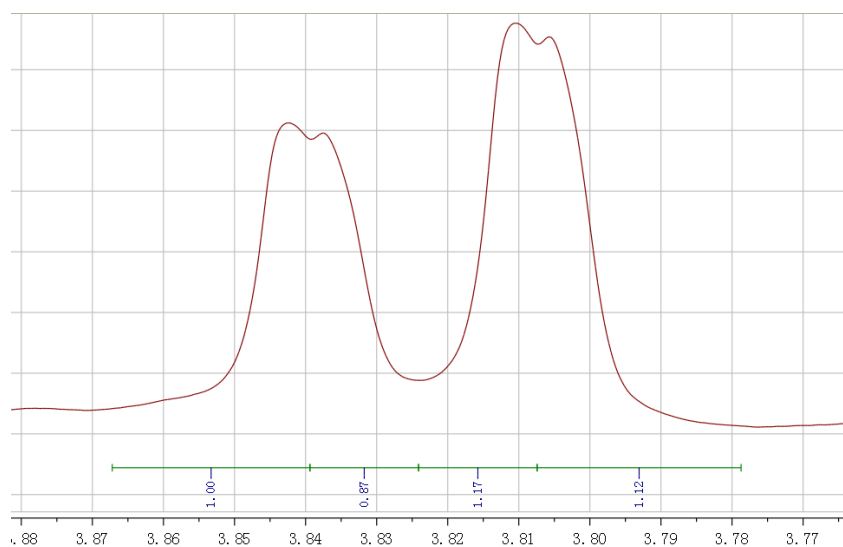


Figure S39. ^1H NMR integral values for CH_2 groups of **1** for calculating diastereomer ratios

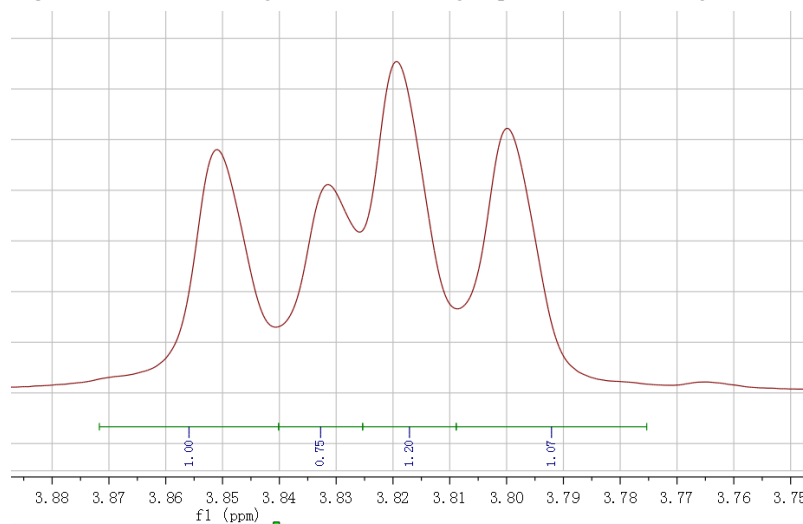


Figure S40. ^1H NMR integral values for CH_2 groups of **2** for calculating diastereomer ratios

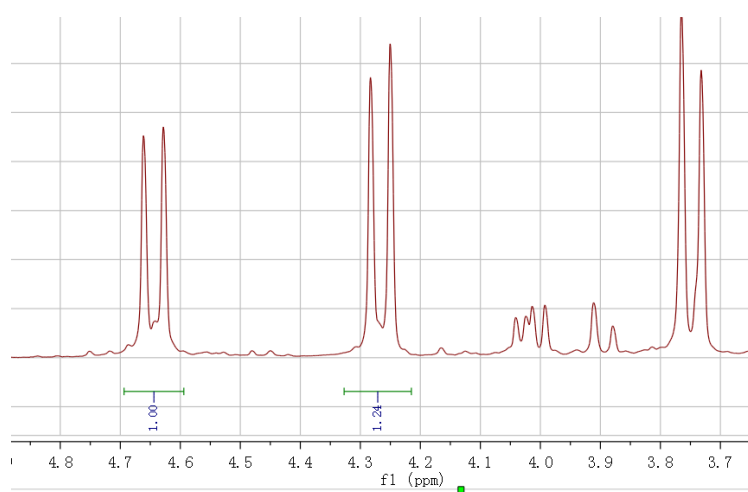


Figure S41. ^1H NMR integral values for CH_2 groups of **3** for calculating diastereomer ratios