Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Diastereoselective Rh-Catalyzed Decarboxylative Allylation to Form the Quaternary Stereocenters Using Sulfinimine as Chiral Directing Group

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Contents of supporting information

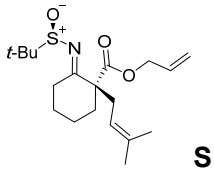
1. General Information S3
2. Preparation of compounds **1**, **S3**-**S26** S3
3. Decarboxylative Allylation of β-sulfinimine ester S5
4. Application of Rh-catalyzed Decarboxylative Allylation in Forge Polycyclic Scaffolds S15
5. Preparation of compound **27** and **rac-27** S20
6. HPLC analysis for determination of the *ee* value of compound **27** S22
7. NMR Spectrums of Compounds S24
8. Crystal data of Compound **29** S66

1. General Information

All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. The used solvents were purified and dried according to common procedures. Other chemicals and solvents were commercially available. High-resolution mass spectra (HRMS) were obtained with a FTICR-MS (Ion spec 7.0T) spectrometer. ^{1}H NMR spectra were obtained by using a Bruker AV 400 or AV 600. Chemical shifts are reported in parts per million (ppm) relative to either a tetramethylsilane internal standard or solvent signals. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants and integration. ^{13}C NMR spectra were recorded using a Bruker AV 400 spectrometer (100 MHz) using $CDCl_3$ as the solvent. Chemical shifts (δ) are reported in parts per million measured relative to the solvent peak. Melting points (m.p.) were obtained on a Mel-Temp capillary melting point apparatus. Enantiomeric excess(ee) was determined using Agilent HPLC 1260. IR spectra were recorded with a Bio-Rad FTS 6000 Fourier infrared spectrometer.

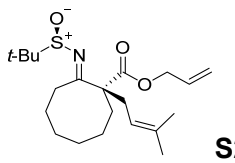
2. Preparation of compounds 1, S2-S25

The synthesis of Sulfinimines **1, S3-S26**, as the starting marterials of **2a**，**3-26**, was based on the reported procedure.[1] Only the corresponding analysis date of **S11**, **S24**, **S25** and **S26**, which were not reported before, were presentted in this supporting information.



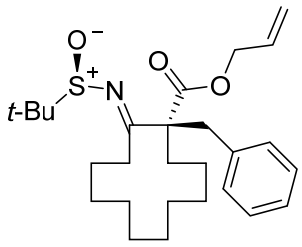
S11

Allyl-(*S*, *E*)-2-(((*R*)-*tert*-butylsulfinyl) imino)-1-(3-methylbut-2-en-1-yl) cyclohexane-1-carboxylate **S11**: $[\alpha]_D^{23}$= - 117.60 (c 0.84, $CHCl_3$) .IR (KBr) ν_{max}: 2930, 2866, 1734, 1629, 1511, 1452, 1213, 1179, 1081, 987 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 16.5, 10.6, 5.3 Hz, 1H), 5.31 (d, *J* = 16.8 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 5.08 (d, *J* = 7.8 Hz, 1H), 4.58 (t, *J* = 5.1 Hz, 2H), 3.66 – 3.55 (m, 1H), 2.62 (dd, *J* = 14.4, 7.3 Hz, 1H), 2.38 (m, 3H), 1.95 – 1.77 (m, 2H), 1.74 – 1.62 (m, 6H), 1.46 (m, 3H), 1.27 (s, 9H).^{13}C NMR (400 MHz, $CDCl_3$) δ 184.1 , 172.3 , 134.8 , 131.8 , 119.0 , 65.9 , 59.6 , 58.0 , 35.6 , 34.5 , 32.3 , 27.4 , 26.2 , 22.8 , 22.4 , 18.1. HRMS (ESI) calculated for $C_{19}H_{31}NNaO_3S^+$[M+Na]$^+$: 376.1917, found 376.1915.



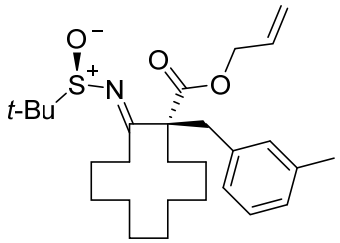
S24

Allyl-(*S*,*E*)-2-(((*R*)-*tert*-butylsulfinyl)imino)-1-(3-methylbut-2-en-1-yl)cyclooctane-1-carboxylate **S24**: $[\alpha]_D^{26}$= - 252.88 (c 2.9, $CHCl_3$) . IR (KBr) ν_{max}: 2961, 2927, 2858, 1734, 1649, 1617, 1466, 1260, 1190, 1081, 1019, 801 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 5.91 – 5.73 (m, 1H), 5.23 (dd, *J* = 29.6, 13.7 Hz, 2H), 4.99 (s, 1H), 4.52 (dd, *J* = 33.4, 12.8 Hz, 2H), 3.37 (d, *J* = 9.7 Hz, 1H), 2.77 (d, *J* = 14.4 Hz, 1H), 2.43 – 2.16 (m, 3H), 2.09 – 1.91 (m, 2H), 1.81 – 1.62 (m, 6H), 1.58 (s, 3H), 1.49 (d, *J* = 5.1 Hz, 2H), 1.30 (s, 9H), 1.24 (s, 1H), 1.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 172.5, 134.6, 131.8, 119.4, 119.0, 66.0, 61.7, 58.5, 31.2, 30.6, 27.2, 27.2, 26.1, 25.3, 25.2, 23.3, 23.1, 18.1. HRMS (ESI) calculated for $C_{21}H_{35}NNaO_3S^+$ $[M+Na]^+$:404.2230, found 404.2233.



S25

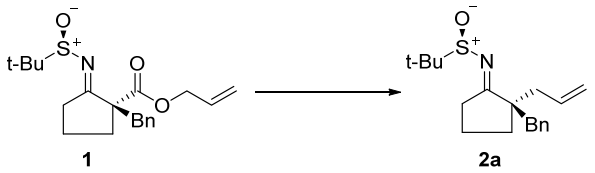
Allyl-(*S*,*E*)-1-benzyl-2-(((*R*)-*tert*-butylsulfinyl)imino)cyclododecane-1-carboxylate **S25**: $[\alpha]_D^{20}$= - 98.11 (c 0.4, $CHCl_3$). IR (KBr) ν_{max}: 2960, 2926, 2858, 1738, 1619, 1465, 1452, 1360, 1261, 1173, 1089, 1078, 1017, 802, 701 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.19 (m, 3H), 7.11 – 6.99 (m, 2H), 5.89 (ddt, *J* = 16.6, 10.4, 5.9 Hz, 1H), 5.39 – 5.24 (m, 2H), 4.67 – 4.52 (m, 2H), 3.34 – 3.21 (m, 2H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.17 (dt, *J* = 13.8, 5.8 Hz, 1H), 2.08 – 1.82 (m, 3H), 1.71 (td, *J* = 13.9, 5.1 Hz, 3H), 1.57 – 1.39 (m, 12H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.4, 172.5, 137.4, 131.5, 129.9, 128.5, 126.9, 119.5, 66.1, 64.7, 58.5, 38.9, 31.2, 29.5, 26.8, 26.0, 25.2, 25.0, 24.1, 24.0, 23.6, 23.1, 20.8. HRMS (ESI) calculated for $C_{27}H_{41}NNaO_3S^+$ $[M+Na]^+$: 482.2699, found 482.2693.



S26

Allyl-(*S*,*E*)-2-(((*R*)-*tert*-butylsulfinyl)-imino)-1-(3-methylbenzyl)-cyclododecane-1-carboxylate **S26**: $[\alpha]_D^{20}$ = - 234.49 (c 0.8, $CHCl_3$). IR (KBr) ν_{max}:2930, 2863, 1737, 1620, 1453, 1393, 1261, 1231, 1195, 1175, 1143, 1081, 1037, 991, 931, 801, 703 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.13 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 4.7 Hz, 2H), 5.90 (ddt, *J* = 16.6, 11.2, 6.0 Hz, 1H), 5.31 (dd, *J* = 34.1, 13.8 Hz, 2H), 4.64 – 4.53 (m, 2H), 3.35 – 3.24 (m, 1H), 3.23 – 3.03 (m, 2H), 2.29 (s, 3H), 2.16 (dt, *J* = 13.0, 5.7 Hz, 1H), 2.05 – 1.89 (m, 2H), 1.72 (td, *J* = 14.4, 4.1 Hz, 2H), 1.62 – 1.34 (m, 14H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.3, 172.4, 137.7, 137.1, 131.4, 130.5, 128.1, 127.5, 126.7, 119.3, 65.9, 64.5, 58.3, 38.6, 31.0, 29.3, 26.6, 25.8, 24.9, 24.8, 23.9, 23.8, 23.4, 22.9, 21.4, 20.6. HRMS (ESI) calculated for $C_{28}H_{43}NNaO_3S^+$ $[M+Na]^+$: 496.2856, found 496.2852.

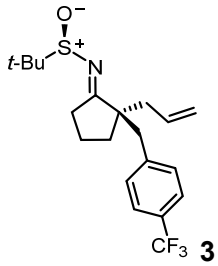
3. Decarboxylative Allylation of β-sulfinimine ester



1 **2a**

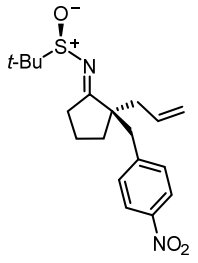
Representative Procedure:

In a round bottom flask, a solution of compound **1** (0.5 g, 1.36 mmol) in fresh distillated THF (13 mL) was added NaHMDS (0.75 mL, 2M in THF) and $RhCl(PPh_3)_3$ (0.06 g, 0.06 mmol) in a nitrogen atmosphere at room temperature. The mixture was kept stirring at room temperature 1.5 hours. After the substrate was completely consumed (monitored by TLC analysis), the reaction mixture was quenched with saturated NH_4Cl (50 mL), and extracted by ethyl acetate (3 x 50 mL). The combined organic phase was dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate=5:1) to furnish the desired compound **2a** (379 mg, 88% yield) as a colorless oil: $[\alpha]_D^{22}$= - 92.56 (c 0.14, $CHCl_3$) . IR (KBr) ν_{max}: 2959, 2924, 2854, 1633, 1456, 1261, 1088, 1022, 802, 702 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 3H), 7.16 – 7.04 (m, 2H), 5.83 – 5.72 (m, 1H), 5.14 – 5.03 (m, 2H), 2.97 – 2.83 (m, 2H), 2.70 (d, *J* = 13.2 Hz, 1H), 2.49 – 2.32 (m, 2H), 2.22 (dd, *J* = 13.8, 8.2 Hz, 1H), 1.78 – 1.64 (m, 3H), 1.39 – 1.32 (m, 1H), 1.29 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 138.3, 134.3, 130.5, 128.2, 126.6, 118.7, 57.0, 54.7, 43.7, 43.3, 34.5, 31.7, 22.6, 21.7. HRMS (ESI) calculated for: $C_{19}H_{27}NNaOS^+$ $[M+Na]^+$: 340.1706, found 340.1705.



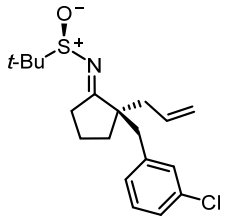
3

(*R*)-N-((*S*,*E*)-2-allyl-2-(4-(trifluoromethyl)benzyl)cyclopentylidene)-2-methylpropane-2-sulfinamide **3**：Prepared by using the representative procedure above from compound **S3** (0.10 g, 0.23 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **3** (73 mg, 82% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 71.69 (c 0.2, $CHCl_3$) . IR (KBr) ν_{max}: 2960, 2925, 2855, 1634, 1457, 1417, 1325, 1261, 1165, 1126, 1108, 1084, 1020, 855, 802 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.83 – 5.72 (m, 1H), 5.17 – 5.06 (m, 2H), 3.05 – 2.91 (m, 2H), 2.78 (d, *J* = 13.2 Hz, 1H), 2.45 (ddd, *J* = 19.6, 8.7, 5.1 Hz, 1H), 2.37 – 2.30 (m, 1H), 2.21 (dd, *J* = 13.8, 8.1 Hz, 1H), 1.81 – 1.64 (m, 3H), 1.45 – 1.37 (m, 1H), 1.27 (s, 9H).^{13}C NMR (400 MHz, $CDCl_3$) δ 196.0, 142.4 , 133.8, 130.8, 125.1, 119.0, 57.1, 54.6, 43.0, 34.2, 31.8, 22.6, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4. HRMS (ESI) calculated for $C_{20}H_{26}F_3NNaOS^+$ $[M+Na]^+$: 408.1579, found 408.1577.



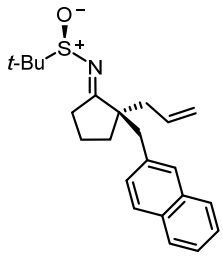
4

(*R*)-N-((*S*,*E*)-2-allyl-2-(4-nitrobenzyl)cyclopentylidene)-2-methylpropane-2-sulfinamide **4**: Prepared by using the representative procedure above from compound **S4** (0.10 g, 0.25 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **4** (71 mg, 78% yield) as a pale yellow oil: $[\alpha]_D^{22}$= -31.48 (c 0.5, $CHCl_3$) . IR (KBr) ν_{max}: 2961, 2925, 2856, 1635, 1602, 1520, 1491, 1457, 1346, 1261, 1081, 1019, 867, 855, 804, 705 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 5.83 – 5.72 (m, 1H), 5.18 – 5.08 (m, 2H), 3.06 – 2.94 (m, 2H), 2.84 (d, J = 13.1 Hz, 1H), 2.45 (ddd, J = 14.0, 8.8, 5.6 Hz, 1H), 2.33 (dd, J = 13.9, 6.5 Hz, 1H), 2.21 (dd, J = 13.9, 8.0 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.69 – 1.61 (m, 1H), 1.45 (m, 1H), 1.28 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 146.9, 146.3, 133.5, 131.4, 123.4, 119.4, 57.2, 54.7, 43.0, 42.9, 34.0, 31.9, 22.7, 21.6. HRMS (ESI) calculated for $C_{19}H_{26}N_2NaO_3S^+$ $[M+Na]^+$: 385.1556, found 385.1557.



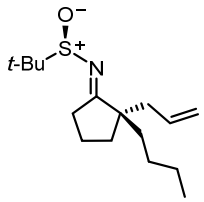
5

(*R*)-N-((*S*,*E*)-2-allyl-2-(3-chlorobenzyl)cyclopentylidene)-2-methylpropane-2-sulfinamide **5**: Prepared by using the representative procedure above from compound **S5** (0.10 g, 0.25 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **5** (69 mg, 78% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 105.28 (c 0.3, $CHCl_3$) . IR (KBr) ν_{max}: 2958, 2925, 2857, 1633, 1597, 1572, 1472, 1454, 1361, 1261, 1165, 1081, 1019, 802, 714 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 4.7, 1.2 Hz, 2H), 7.10 (s, 1H), 7.01 – 6.95 (m, 1H), 5.82 – 5.71 (m, 1H), 5.11 (t, J = 12.5 Hz, 2H), 3.01 – 2.85 (m, 2H), 2.69 (d, J = 13.3 Hz, 1H), 2.51 – 2.39 (m, 1H), 2.33 (dd, J = 13.8, 6.4 Hz, 1H), 2.20 (dd, J = 13.9, 8.1 Hz, 1H), 1.79 – 1.65 (m, 3H), 1.44 (m, 1H), 1.28 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 140.3, 134.0, 130.7, 129.5, 128.7, 126.8, 119.0, 57.0, 54.6, 43.0, 42.9, 34.3, 31.8, 22.6, 21.6. HRMS (ESI) calculated for $C_{19}H_{26}ClNNaOS^+$ $[M+Na]^+$: 374.1316, found 374.1313.



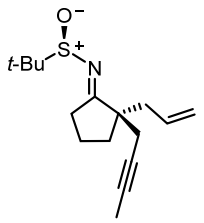
6

(*R*)-N-((*S*,*E*)-2-allyl-2-(naphthalen-2-ylmethyl)cyclopentylidene)-2-methylpropane-2-sulfinamide **6**：Prepared by using the representative procedure above from compound **S6** (0.10 g, 0.24 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **6** (75 mg, 85% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 39.12 (c 0.2, $CHCl_3$) . IR (KBr) ν_{max}: 2960, 2924, 2854, 1632, 1458, 1261, 1085, 1021, 858, 802, 752 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 3H), 7.57 (s, 1H), 7.45 (ddd, *J* = 6.9, 4.3, 1.8 Hz, 2H), 7.23 (d, *J* = 1.7 Hz, 1H), 5.81 (td, *J* = 16.8, 7.9 Hz, 1H), 5.11 (dd, *J* = 13.5, 11.3 Hz, 2H), 3.11 (d, *J* = 13.2 Hz, 1H), 2.97 – 2.86 (m, 2H), 2.48 – 2.38 (m, 2H), 2.26 (dd, *J* = 13.8, 8.1 Hz, 1H), 1.81 – 1.68 (m, 3H), 1.40 – 1.35 (m, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 197.1, 135.9, 134.3, 133.4, 132.3, 129.1, 129.0, 127.7, 127.7, 126.1, 125.6, 118.8, 100.1, 57.0, 55.0, 43.7, 43.3, 34.4, 31.7, 22.7, 21.7. HRMS (ESI) calculated for $C_{23}H_{29}NNaOS^+$ $[M+Na]^+$: 390.1862, found 390.1858.



7

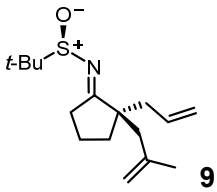
(*R*)-N-((*S*,*E*)-2-allyl-2-butylcyclopentylidene)-2-methylpropane-2-sulfinamide **7**：Prepared by using the representative procedure above from compound **S7** (0.10 g, 0.31 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **7** (76 mg, 87% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 132.18 (c 0.8, $CHCl_3$) . IR (KBr) ν_{max}: 2957, 2928, 2860, 1633, 1457, 1410, 1361, 1261, 1172, 1082, 914, 802, 761, 697 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.81 – 5.68 (m, 1H), 5.04 (dd, *J* = 13.6, 1.7 Hz, 2H), 3.03 – 2.91 (m, 1H), 2.63 – 2.53 (m, 1H), 2.22 (d, *J* = 7.4 Hz, 2H), 1.86 – 1.62 (m, 5H), 1.46 (m, 2H), 1.40 – 1.34 (m, 1H), 1.24 (s, 9H), 1.21 – 1.07 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) *δ* 197.8, 134.6, 118.0, 56.7, 53.2, 42.1, 36.9, 34.1, 33.1, 26.5, 23.5, 22.5, 21.6, 14.2. HRMS (ESI) calculated for $C_{16}H_{29}NNaOS^+$ $[M+Na]^+$: 306.1862, found 306.1861.



8

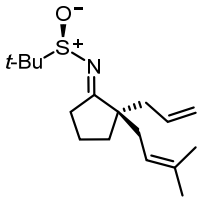
(*R*)-N-((*S*,*E*)-2-allyl-2-(but-2-yn-1-yl)cyclopentylidene)-2-methylpropane-2-sulfinamide **8**：

Prepared by using the representative procedure above from compound **S8** (0.10 g, 0.31 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **8** (74 mg, 85% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 19.34 (c 0.1, $CHCl_3$) . IR (KBr) ν_{max}: 2960, 2924, 2857, 1634, 1457, 1261, 1085, 1020, 803 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 (dt, *J* = 16.3, 7.5 Hz, 1H), 5.13 – 5.03 (m, 2H), 2.97 (dt, *J* = 14.3, 8.5 Hz, 1H), 2.60 – 2.52 (m, 1H), 2.35 (dd, *J* = 16.4, 2.4 Hz, 1H), 2.30 – 2.27 (m, 2H), 1.91 – 1.80 (m, 3H), 1.75 (t, *J* = 2.4 Hz, 3H), 1.39 – 1.27 (m, 2H), 1.26 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 133.8, 118.8, 77.6, 76.2, 56.9, 53.0, 41.9, 34.5, 32.5, 27.6, 22.4, 21.7, 3.6. HRMS (ESI) calculated for $C_{16}H_{25}NNaOS^+$ $[M+Na]^+$: 302.1549, found 302.1543.



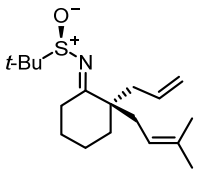
9

(*R*)-N-((*S*,*E*)-2-allyl-2-(2-methylallyl)cyclopentylidene)-2-methylpropane-2-sulfinamide **9**：Prepared by using the representative procedure above from compound **S9** (0.10 g, 0.31 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **9** (79 mg, 90% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 261.42 (c 0.2, $CHCl_3$) . IR (KBr) ν_{max}: 2959, 2925, 2854, 1635, 1559, 1507, 1457, 1361, 1262, 1084, 915, 812 cm^{-1}.^1H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddd, *J* = 17.0, 10.3, 7.3 Hz, 1H), 5.07 (dd, *J* = 13.3, 6.6 Hz, 2H), 4.82 (s, 1H), 4.69 (s, 1H), 3.01 (dt, *J* = 19.8, 7.5 Hz, 1H), 2.59 (m, 1H), 2.37 (d, *J* = 13.4 Hz, 1H), 2.30 – 2.15 (m, 3H), 1.85 – 1.71 (m, 4H), 1.66 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 142.9, 134.3, 118.6, 115.4, 56.8, 53.6, 45.5, 43.6, 34.0, 32.0, 24.8, 22.6, 21.7. HRMS (ESI) calculated for $C_{16}H_{27}NNaOS^+$ $[M+Na]^+$: 304.1706, found 304.1702.



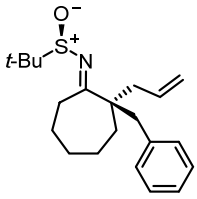
10

(*R*)-N-((*S*,*E*)-2-allyl-2-(3-methylbut-2-en-1-yl)cyclopentylidene)-2-methylpropane-2-sulfinamide **10**：Prepared by using the representative procedure above from compound **S10** (0.10 g, 0.29 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **10** (70 mg, 82% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 110.48 (c 0.3, $CHCl_3$) . IR (KBr) ν_{max}: 2959, 2925, 2856, 1635, 1457, 1261, 1085, 1019, 805 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 5.80 – 5.69 (m, 1H), 5.14 – 4.98 (m, 3H), 2.94 (dt, *J* = 15.7, 8.1 Hz, 1H), 2.62 – 2.53 (m, 1H), 2.24 (ddd, *J* = 24.7, 16.3, 7.2 Hz, 4H), 1.86 – 1.70 (m, 3H), 1.69 (s, 3H), 1.68 – 1.63 (m, 1H), 1.58 (s, 3H), 1.25 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 134.6, 134.3, 119.9, 118.2, 56.8, 54.0, 42.3, 35.8, 34.3, 32.4, 26.2, 22.5, 21.8, 18.2. HRMS (ESI) calculated for $C_{17}H_{29}NNaOS^+$ $[M+Na]^+$: 318.1862, found 318.1859.



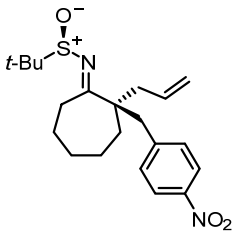
11

(*R*)-N-((*S*,*E*)-2-allyl-2-(3-methylbut-2-en-1-yl)cyclohexylidene)-2-methylpropane-2-sulfinamide **11**：Prepared by using the representative procedure above from compound **S11** (0.10 g, 0.28 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **11** (69 mg, 80% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 45.66 (c 0.27, $CHCl_3$) . IR (KBr) ν_{max}: 2958, 2925, 2855, 1618, 1454, 1378, 1361, 1261, 1080, 1021, 803 cm^{-1}.^{1}H NMR (400 MHz, $CHCl_3$) δ 5.72 (dt, *J* = 16.2, 7.5 Hz, 1H), 5.11 – 4.98 (m, 3H), 2.98 – 2.80 (m, 2H), 2.44 (dd, *J* = 14.8, 7.1 Hz, 1H), 2.33 (d, *J* = 7.1 Hz, 2H), 2.16 (dd, *J* = 14.9, 7.6 Hz, 1H), 1.80 – 1.65 (m, 9H), 1.60 (s, 3H), 1.25 (s, 9H).^{13}C NMR (100 MHz, CHCl3) δ 191.2 , 134.8 , 134.1 , 119.6 , 117.6 , 56.5 , 49.8 , 40.3 , 36.7 , 34.8 , 31.4 , 27.2 , 26.2 , 22.5 , 20.9 , 18.2 .HRMS (ESI) calculated for $C_{18}H_{31}NNaOS^+$ $[M+Na]^+$: 332.2019, found 332.2017.



12

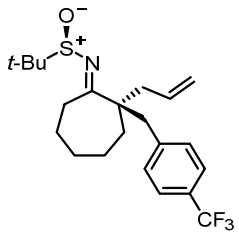
(*R*)-N-((*S*,*E*)-2-allyl-2-benzylcycloheptylidene)-2-methylpropane-2-sulfinamide **12**：Prepared by using the representative procedure above from compound **S12** (0.10 g, 0.26 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **12** (77 mg, 85% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 14.60 (c 0.8, $CHCl_3$) . IR (KBr) ν_{max}: 2958, 2927, 2857, 1606, 1493, 1474, 1452, 1359, 1070, 912, 794, 708, 622 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 3H), 7.03 (d, *J* = 7.5 Hz, 2H), 5.92 (td, *J* = 17.0, 7.6 Hz, 1H), 5.07 (m, 2H), 2.95 – 2.75 (m, 3H), 2.62 – 2.17 (m, 3H), 1.66 (m, 5H), 1.43 – 1.27 (m, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 137.9, 135.1, 130.6, 128.1, 126.5, 118.4, 56.6, 53.6, 44.7, 41.3, 34.3, 33.3, 30.2, 28.0, 23.9, 22.6. HRMS (ESI) calculated for $C_{21}H_{31}NNaOS^+$ $[M+Na]^+$: 368.2019, found 368.2015.



13

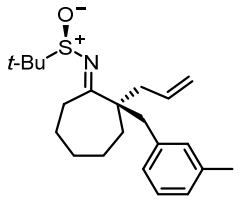
(*R*)-N-((*S*,*E*)-2-allyl-2-(4-nitrobenzyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **13**：Prepared by using the representative procedure above from compound **S13** (0.10 g, 0.23 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **13** (76 mg, 85% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 45.65 (c 0.45, $CHCl_3$) . IR (KBr) ν_{max}: 2926, 2857, 1637, 1601, 1495, 1454, 1387, 1360, 1261, 1074, 913, 805, 702

cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 5.88 (dq, J = 10.1, 7.3 Hz, 1H), 5.15 (dd, J = 20.6, 13.5 Hz, 2H), 2.98 – 2.83 (m, 3H), 2.69 – 2.61 (m, 1H), 2.31 (m, 2H), 1.90 – 1.66 (m, 4H), 1.53 – 1.30 (m, 4H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 146.8, 146.2, 134.1, 131.5, 123.3, 119.2, 56.9, 53.6, 43.6, 41.2, 33.8, 33.6, 30.1, 27.8, 23.8, 22.7. HRMS (ESI) calculated for $C_{21}H_{30}N_2NaO_3S^+$ [M+Na]$^+$: 413.1869, found 413.1867.



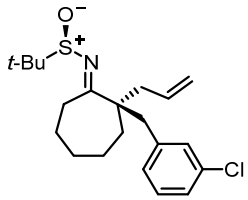
14

(*R*)-N-((*S*,*E*)-2-allyl-2-(4-(trifluoromethyl)benzyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **14**：Prepared by using the representative procedure above from compound **S14** (0.10 g, 0.22 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **14** (78 mg, 85% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 17.68 (c 0.46, $CHCl_3$) . IR (KBr) ν_{max}: 2927, 2857, 1609, 1458, 1388, 1326, 1164, 1125, 1068, 1019, 916, 797 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 5.90 (dq, J = 10.0, 7.3 Hz, 1H), 5.22 – 5.02 (m, 2H), 2.87 (q, J = 13.6 Hz, 3H), 2.59 (dd, J = 15.8, 6.1 Hz, 1H), 2.32 (ddd, J = 32.7, 14.4, 7.2 Hz, 2H), 1.89 – 1.62 (m, 4H), 1.57 – 1.23 (m, 4H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 142.2, 134.5, 130.9, 125.0, 125.0, 118.9, 56.7, 53.5, 44.0, 41.0, 34.1, 33.6, 30.2, 27.9, 23.8, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4. HRMS (ESI) calculated for $C_{22}H_{30}F_3NNaOS^+$ [M+Na]$^+$: 436.1892, found 436.1893.



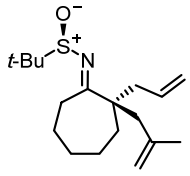
15

(*R*)-N-((*S*,*E*)-2-allyl-2-(3-methylbenzyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **15**：Prepared by using the representative procedure above from compound **S15** (0.10 g, 0.25 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **15** (81 mg, 90% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 11.34 (c 0.5, $CHCl_3$) . IR (KBr) ν_{max}: 2925, 2855, 1736, 1606, 1456, 1360, 1260, 1176, 1077, 913, 801, 742, 700, 585 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, J = 7.7 Hz, 1H), 7.00 (d, J = 7.3 Hz, 1H), 6.83 (s, 2H), 5.92 (td, J = 17.1, 7.4 Hz, 1H), 5.11 (t, J = 12.8 Hz, 2H), 2.96 – 2.84 (m, 1H), 2.77 (q, J = 13.5 Hz, 2H), 2.40 (ddd, J = 27.1, 22.1, 9.4 Hz, 3H), 2.30 (s, 3H), 1.82 – 1.57 (m, 6H), 1.41 (m, 2H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CHCl_3$) δ 194.2, 137.8, 137.6, 135.2, 131.5, 128.0, 127.6, 127.2, 118.4, 56.6, 53.5, 44.7, 41.3, 34.4, 33.4, 30.2, 28.0, 23.9, 22.6, 21.6. HRMS (ESI) calculated for $C_{22}H_{33}NNaOS^+$ [M+Na]$^+$: 382.2175, found 382.2173.



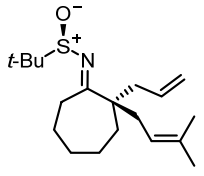
16

(*R*)-N-((*S*,*E*)-2-allyl-2-(3-chlorobenzyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **16**：Prepared by using the representative procedure above from compound **S16** (0.10 g, 0.24 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **16** (82 mg, 90% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 12.93 (c 0.5, $CHCl_3$) . IR (KBr) ν_{max}: 2926, 2859, 1608, 1458, 1388, 1327, 1163, 1125, 1068, 1019, 910, 801 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 4.8 Hz, 2H), 7.02 (s, 1H), 6.97 – 6.86 (m, 1H), 5.88 (td, *J* = 17.3, 7.4 Hz, 1H), 5.12 (t, *J* = 14.1 Hz, 2H), 2.87 (dd, *J* = 15.0, 5.7 Hz, 1H), 2.78 (dd, *J* = 28.9, 13.6 Hz, 2H), 2.57 (dd, *J* = 15.8, 6.0 Hz, 1H), 2.32 (qd, *J* = 14.4, 7.4 Hz, 2H), 1.73 (m, 5H), 1.46 (m, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 140.0, 134.7, 133.9, 130.7, 129.3, 128.8, 126.7, 118.7, 56.7, 53.5, 43.9, 41.2, 34.1, 33.5, 30.2, 27.9, 23.8, 22.6. HRMS (ESI) calculated for $C_{21}H_{30}ClNNaOS^+$ $[M+Na]^+$: 402.1629, found 402.1626.



17

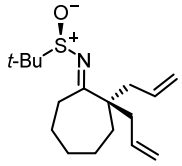
(*R*)-N-((*S*,*E*)-2-allyl-2-(2-methylallyl)cycloheptylidene)-2-methylpropane-2-sulfinamide **17**：Prepared by using the representative procedure above from compound **S17** (0.10 g, 0.28 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **17** (82 mg, 91% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 48.35 (c 0.2, $CHCl_3$) . IR (KBr) ν_{max}: 2925, 2855, 1608, 1457, 1360, 1261, 1182, 1150, 1079, 1020, 913, 894, 801, 590 cm^{-1}.^1H NMR (400 MHz, $CHCl_3$) δ 5.83 (ddt, *J* = 17.4, 10.3, 7.4 Hz, 1H), 5.11 – 5.00 (m, 2H), 4.89 – 4.82 (m, 1H), 4.70 – 4.62 (m, 1H), 3.02 (ddd, *J* = 11.0, 7.9, 2.3 Hz, 1H), 2.66 (td, *J* = 11.4, 2.8 Hz, 1H), 2.49 (dd, *J* = 14.4, 7.1 Hz, 1H), 2.32 (dd, *J* = 14.4, 7.7 Hz, 1H), 2.23 (s, 2H), 1.94 – 1.72 (m, 3H), 1.66 (s, 3H), 1.62 – 1.30 (m, 5H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CHCl_3$) δ 193.9, 142.2, 135.3, 118.2, 115.6, 56.7, 52.9, 46.8, 41.2, 34.4, 34.2, 30.3, 28.5, 25.1, 23.9, 22.7. HRMS (ESI) calculated for $C_{18}H_{31}NNaOS^+$ $[M+Na]^+$: 332.2019, found 332.2017.



18

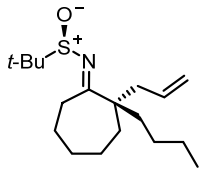
(*R*)-N-((*S*,*E*)-2-allyl-2-(3-methylbut-2-en-1-yl)cycloheptylidene)-2-methylpropane-2-sulfinamide **18**：Prepared by using the representative procedure above from compound **S18** (0.10 g, 0.27 mmol). Purified by columnchromatographyon silica gel (petroleum

ether:ethyl acetate = 5:1) to afford **18** (81 mg, 92% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 18.28 (c 0.9, $CHCl_3$) . IR (KBr) ν_{max}: 2926, 2858, 1658, 1640, 1608, 1546, 1510, 1455, 1361, 1077, 910 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 – 5.71 (m, 1H), 5.09 – 5.01 (m, 3H), 2.93 – 2.73 (m, 2H), 2.45 (dd, *J* = 14.2, 6.9 Hz, 1H), 2.22 (dd, *J* = 14.3, 8.0 Hz, 2H), 2.10 (dd, *J* = 14.8, 7.8 Hz, 1H), 1.86 – 1.70 (m, 3H), 1.68 (s, 3H), 1.63 – 1.60 (m, 1H), 1.59 (s, 3H), 1.53 – 1.34 (m, 4H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 135.1, 134.1, 119.8, 118.0, 56.5, 53.1, 40.5, 35.8, 34.4, 33.1, 30.4, 27.8, 26.2, 23.9, 22.6, 18.1. HRMS (ESI) calculated for $C_{19}H_{33}NNaOS^+$ $[M+Na]^+$: 346.2175, found 346.2173.



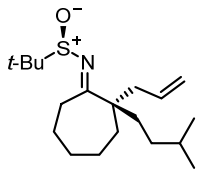
19

(*R*,*E*)-N-(2,2-diallylcycloheptylidene)-2-methylpropane-2-sulfinamide **19**:
Prepared by using the representative procedure above from compound **S19** (0.10 g, 0.29 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **19** (77 mg, 89% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 67.10 (c 0.35, $CHCl_3$) . IR (KBr) ν_{max}: 2977, 2926, 2858, 1638, 1610, 1445, 1360, 1183, 1077, 995, 913 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 – 5.68 (m, 2H), 5.08 – 4.98 (m, 4H), 2.93 (ddd, *J* = 12.1, 8.4, 3.9 Hz, 1H), 2.80 (ddd, *J* = 12.0, 8.1, 3.8 Hz, 1H), 2.43 (dd, *J* = 14.3, 7.0 Hz, 1H), 2.26 (dtd, *J* = 21.5, 14.2, 6.9 Hz, 3H), 1.81 – 1.71 (m, 2H), 1.67 – 1.62 (m, 2H), 1.55 (dd, *J* = 11.7, 5.9 Hz, 2H), 1.43 (dt, *J* = 10.6, 5.4 Hz, 2H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 134.6, 134.6, 118.2, 118.0, 56.7, 52.5, 41.7, 41.2, 34.4, 32.7, 30.3, 27.5, 23.9, 22.7. HRMS (ESI) calculated for $C_{17}H_{29}NNaOS^+$ $[M+Na]^+$: 318.1862, found 318.1861.



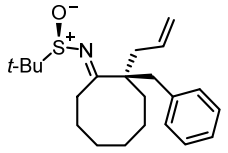
20

(*R*)-N-((*S*,*E*)-2-allyl-2-butylcycloheptylidene)-2-methylpropane-2-sulfinamide **20**: Prepared by using the representative procedure above from compound **S20** (0.10 g, 0.28 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **20** (87 mg, 95% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 29.55 (c 1.0, $CHCl_3$) . IR (KBr) ν_{max}: 2955, 2928, 2856, 1607, 1469, 1396, 1361, 1261, 1167, 1077, 1019, 912, 801, 702 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (td, *J* = 17.3, 7.4 Hz, 1H), 5.08 – 4.99 (m, 2H), 3.00 – 2.90 (m, 1H), 2.68 (t, *J* = 11.0 Hz, 1H), 2.53 (dd, *J* = 14.2, 6.9 Hz, 1H), 2.16 (dd, *J* = 14.2, 8.0 Hz, 1H), 1.91 – 1.83 (m, 1H), 1.79 – 1.64 (m, 3H), 1.58 – 1.28 (m, 7H), 1.25 (s, 9H), 1.21 – 1.04 (m, 3H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 135.3, 117.9, 56.6, 52.2, 39.7, 37.9, 35.2, 33.0, 30.4, 28.3, 26.1, 23.9, 23.4, 22.7, 14.2. HRMS (ESI) calculated for $C_{18}H_{33}NNaOS^+$ $[M+Na]^+$: 334.2175, found 334.2171.



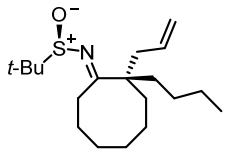
21

(*R*)-N-((*R*,*E*)-2-allyl-2-isopentylcycloheptylidene)-2-methylpropane-2-sulfinamide **21**：Prepared by using the representative procedure above from compound **S21** (0.10 g, 0.27 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **21** (83 mg, 94% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 45.23 (c 0.05, $CHCl_3$) . IR (KBr) ν_{max}: 2954, 2927, 2858, 1609, 1466, 1385, 1361, 1261, 1168, 1079, 1020, 912, 803, 703, 588 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 – 5.67 (m, 1H), 5.08 – 4.98 (m, 2H), 3.01 – 2.89 (m, 1H), 2.66 (t, *J* = 11.1 Hz, 1H), 2.51 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.15 (dd, *J* = 13.8, 8.1 Hz, 1H), 1.88 – 1.64 (m, 4H), 1.57 – 1.33 (m, 7H), 1.25 (s, 9H), 1.10 – 0.97 (m, 2H), 0.85 – 0.80 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 135.2, 117.9, 56.6, 52.1, 39.5, 35.9, 35.2, 33.0, 32.9, 30.4, 28.7, 28.3, 23.9, 22.8, 22.7. HRMS (ESI) calculated for $C_{19}H_{35}NNaOS^+$ $[M+Na]^+$: 348.2332, found 348.2330.



22

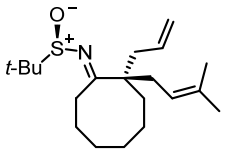
(*R*)-N-((*S*,*E*)-2-allyl-2-benzylcyclooctylidene)-2-methylpropane-2-sulfinamide **22**：Prepared by using the representative procedure above from compound **S22** (0.10 g, 0.25 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **22** (81 mg, 90% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 31.76 (c 0.2, $CHCl_3$) . IR (KBr) ν_{max}: 2956, 2924, 2855, 1601, 1464, 1455, 1261, 1085, 1075, 1056, 795, 699 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dq, *J* = 14.3, 7.1 Hz, 3H), 7.05 (d, *J* = 7.2 Hz, 2H), 5.99 – 5.86 (m, 1H), 5.17 (m, 2H), 2.81 (d, *J* = 5.5 Hz, 2H), 2.70 – 2.62 (m, 1H), 2.40 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.21 (dd, *J* = 15.1, 7.3 Hz, 1H), 2.09 – 1.83 (m, 3H), 1.76 – 1.41 (m, 7H), 1.33 – 1.27 (m, 1H), 1.12 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 138.0, 134.7, 130.5, 128.2, 126.5, 118.5, 56.8, 53.1, 37.9, 32.4, 31.0, 30.7, 25.9, 25.1, 25.0, 22.7. HRMS (ESI) calculated for $C_{22}H_{33}NNaOS^+$ $[M+Na]^+$: 382.2175, found 382.2172.



23

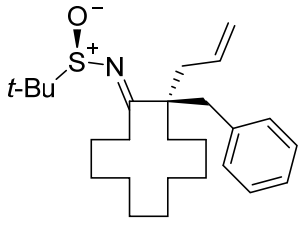
(*R*)-N-((*S*,*E*)-2-allyl-2-butylcyclooctylidene)-2-methylpropane-2-sulfinamide **23**：Prepared by using the representative procedure above from compound **S23** (0.10 g, 0.27 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **23** (75 mg, 85% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 78.48 (c 2.0, $CHCl_3$) . IR (KBr) ν_{max}: 2955, 2928, 2859, 1601, 1467, 1360, 1261, 1180, 1075, 913, 797 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 – 5.60 (m, 1H), 5.05 – 4.99 (m, 2H), 2.98 – 2.81 (m, 1H), 2.62 (ddd, *J* = 12.4, 8.5, 3.9 Hz, 1H), 2.42 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.19 (dd, *J* = 14.5, 7.9 Hz, 1H),

2.04 – 1.93 (m, 2H), 1.73 (m, 2H), 1.39 (m, 9H), 1.25 (s, 9H), 1.20 – 0.96 (m, 3H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 194.9, 134.7, 117.8, 56.9, 51.4, 38.1, 31.1, 30.8, 30.2, 25.9, 25.8, 24.8, 24.8, 23.4, 22.9, 22.4, 14.2. HRMS (ESI) calculated for $C_{19}H_{35}NNaOS^+$ $[M+Na]^+$: 348.2332, found 348.2331.



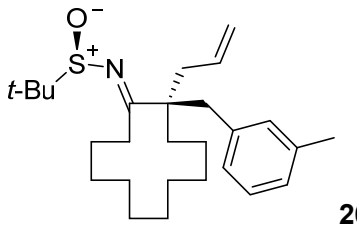
24

(*R)*-N-((*S*,*E*)-2-allyl-2-(3-methylbut-2-en-1-yl)cyclooctylidene)-2-methylpropane-2-sulfinamide **24**：Prepared by using the representative procedure above from compound **S24** (0.10 g, 0.26 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **24** (81 mg, 92% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 59.80 (c 0.9, $CHCl_3$) . IR (KBr) ν_{max}: 2956, 2928, 2858, 1603, 1466, 1454，1360, 1261, 1181, 1075, 912 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 – 5.65 (m, 1H), 5.03 (m, 3H), 2.90 (t, *J* = 11.3 Hz, 1H), 2.64 – 2.55 (m, 1H), 2.41 – 2.19 (m, 3H), 2.14 – 1.90 (m, 4H), 1.78 (d, *J* = 5.6 Hz, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.52 – 1.32 (m, 5H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 134.6, 133.7, 119.9, 117.9, 56.8, 52.2, 39.0, 33.1, 31.0, 29.8, 26.3, 25.9, 25.0, 24.9, 22.8, 18.2. HRMS (ESI) calculated for $C_{20}H_{35}NNaOS^+$ $[M+Na]^+$: 360.2332, found 360.2330.



25

(*R*)-N-((*S*,*E*)-2-allyl-2-benzylcyclododecylidene)-2-methylpropane-2-sulfinamide **25**: Prepared by using the representative procedure above from compound **S25** (0.10 g, 0.22 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **25** (81 mg, 89% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 82.33 (c 0.5, $CHCl_3$) . IR (KBr) ν_{max}: 2957, 2926, 2856, 1601, 1464, 1456, 1261, 1085, 1075, 1056, 799, 697 cm^{-1}.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (dd, *J* = 16.7, 7.1 Hz, 3H), 7.10 (d, *J* = 7.4 Hz, 2H), 5.90 – 5.79 (m, 1H), 5.18 – 5.09 (m, 2H), 2.88 (s, 3H), 2.58 (ddd, *J* = 14.1, 9.1, 5.6 Hz, 1H), 2.27 (tt, *J* = 15.0, 7.7 Hz, 2H), 2.04 – 1.98 (m, 1H), 1.84 – 1.76 (m, 1H), 1.55 – 1.31 (m, 16H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.8, 138.5, 134.4, 130.5, 128.2, 126.4, 118.4, 56.8, 54.9, 40.1, 39.0, 34.8, 31.0, 27.7, 27.6, 26.5, 25.8, 25.2, 24.3, 23.5, 22.7, 22.5. HRMS (ESI) calculated for $C_{26}H_{41}NNaOS^+$ $[M+Na]^+$: 438.2801, found 438.2800.



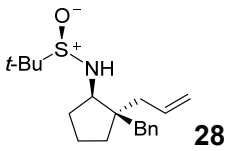
26

Prepared by using the representative procedure above from compound **S26** (0.10 g, 0.21 mmol). Purified by columnchromatographyon silica gel (petroleum ether:ethyl acetate = 5:1) to afford **26** (75 mg, 83% yield) as a pale yellow oil: $[\alpha]_D^{22}$= - 96.24 (c 0.5, $CHCl_3$) . IR (KBr) ν_{max}: 2956, 2926, 2858, 1600, 1466, 1452, 1261, 1086, 1075, 1056, 798, 696 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.11 (m, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 2H), 5.89 – 5.79 (m, 1H), 5.16 – 5.10 (m, 2H), 2.84 (s, 3H), 2.58 (ddd, *J* = 13.5, 9.2, 5.6 Hz, 1H), 2.36 – 2.32 (m, 1H), 2.30 (s, 3H), 2.27 – 2.21 (m, 1H), 2.05 – 1.96 (m, 1H), 1.80 (dt, *J* = 14.1, 6.6 Hz, 1H), 1.68 – 1.44 (m, 10H), 1.41 – 1.28 (m, 6H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.9, 138.4, 137.6, 134.5, 131.4, 128.1, 127.5, 127.1, 118.3, 56.7, 54.8, 40.1, 39.0, 34.8, 31.0, 27.7, 27.6, 26.6, 25.7, 25.1, 24.3, 23.5, 22.6, 22.5, 21.6. HRMS (ESI) calculated for $C_{27}H_{43}NNaOS^+$ $[M+Na]^+$: 452.2958, found 452.2955.

References:

[1] Qin, S. L.; Liu, S. W.; Cao, Y. T.; Li, J. N.; Chong, C. K.; Liu, T. T.; Luo, Y. H.; Hu, J. Y.; Jiang, S. D.; Zhou, H. G.; Yang, G.; Yang, C. *Org. Lett*. **2018**, *20*, 1350.

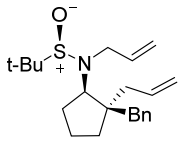
4. Application of Rh-catalyzed Decarboxylative Allylation in Forge Polycyclic Scaffolds



28

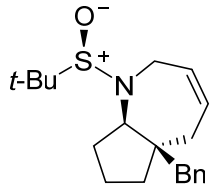
(*R*)-N-((*1R*,*2S*)-2-allyl-2-benzylcyclopentyl)-2-methylpropane-2-sulfinamide **28**：In a round bottom flask, a solution of compound **2a** (0.2 g, 0.63 mmol) in THF : MeOH (10 : 1) (7 mL) was added $NaBH_4$ (0.05 g, 1.26 mmol) in a nitrogen atmosphere at 0 ℃. The mixture was kept stirring at room temperature 0.5 hours. After the substrate was completely consumed (monitored by TLC analysis), the reaction mixture was quenched with saturated NH_4Cl (50 mL), and extracted by ethyl acetate (3 x 50 mL). The combined organic phase was dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 2 : 1) to furnish the desired compound **28** (180 mg, 89% yield) as a colorless oil: $[\alpha]_D^{22}$= - 132.61 (c 1.0, $CHCl_3$) . IR (KBr) ν_{max}: 2957, 2925, 2854, 1600, 1571, 1458, 1363, 1261, 1057, 866, 800, 710, 687 cm^{-1}.^1H NMR (400 MHz, $CDCl_3$) *δ* 7.30 – 7.26 (m, 2H), 7.21 (m, 1H), 7.15 – 7.11 (m, 2H), 5.94 (ddt, *J* = 12.1, 9.2, 7.3 Hz, 1H), 5.16 – 5.09 (m, 2H), 3.37 (dd, *J* = 18.9, 8.9 Hz, 1H), 3.09 (d, *J* = 10.4 Hz, 1H), 2.73 (d, *J* = 13.4 Hz, 1H), 2.63 (d, *J* = 13.4 Hz, 1H), 2.18 (ddd, *J* = 11.8, 8.6, 4.4 Hz, 1H), 2.08 (d, *J* = 7.3 Hz, 2H), 1.65 – 1.57 (m, 2H), 1.52 (m, 1H), 1.45 –

1.35 (m, 2H), 1.26 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.9, 131.0, 128.1, 126.3, 117.7, 63.6, 56.2, 48.3, 41.9, 38.3, 32.9, 31.7, 23.1, 19.5. HRMS (ESI) calculated for $C_{19}H_{29}NNaOS^+$ [M+Na]$^+$: 342.1862, found 342.1863.



28a

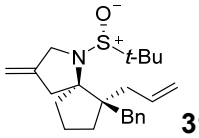
(*R*)-N-allyl-N-((*1R,2S*)-2-allyl-2-benzylcyclopentyl)-2-methylpropane-2-sulfinamide **28a**：In a round bottom flask, a solution of compound **28** (0.18 g, 0.56 mmol) in DMF (2 mL) at -20 °C was added LiHMDS (1.0 M in THF, 0.6 mL, 1.2 mmol) dropwise. The mixture was stirred at -20° C. for 20 min followed by addition of allyl bromide (0.19 mL, 2.24 mmol). After 0.5 h stirring at -20° C., the reaction was quenched with sat. NH_4Cl and warmed to rt. It was extracted with EtOAc (3 x 10 mL), the organic layer was washed with brine and dried over Na_2SO_4. After removal of solvent, the crude was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 4:1) to furnish the desired compound **28a** (152 mg, 75% yield) as a colorless oil: $[\alpha]_D^{22}$= - 28.03 (c 1.4, $CHCl_3$). IR (KBr) ν_{max}: 2958, 2926, 2873, 1637, 1454, 1070, 916, 704 cm^{-1}.^{1}H NMR (400 MHz, $CHCl_3$) δ 7.28 (t, *J* = 6.2 Hz, 2H), 7.25 – 7.15 (m, 3H), 5.97 (ddt, *J* = 16.8, 11.5, 6.4 Hz, 1H), 5.82 (dq, *J* = 17.0, 7.8 Hz, 1H), 5.20 (dd, *J* = 13.7, 9.0 Hz, 2H), 5.03 (dd, *J* = 24.4, 13.5 Hz, 2H), 3.96 (dd, *J* = 16.1, 6.1 Hz, 1H), 3.52 (dt, *J* = 15.8, 7.5 Hz, 2H), 2.86 – 2.70 (m, 2H), 2.17 (dq, *J* = 21.4, 7.1 Hz, 3H), 1.96 (dd, *J* = 14.5, 7.8 Hz, 1H), 1.85 (dq, *J* = 14.0, 4.6 Hz, 1H), 1.78 – 1.54 (m, 3H), 1.32 (s, 9H).^{13}C NMR (100 MHz, $CHCl_3$) δ 139.4， 137.1 , 135.1 , 130.7 , 128.0 , 126.1 , 118.2 , 117.7 , 68.8 , 58.9 , 49.6 , 49.4 , 40.3 , 40.2 , 33.7 , 28.7 , 24.9, 20.6 . HRMS (ESI) calculated for $C_{22}H_{33}NNaOS^+$ [M+Na]$^+$: 382.2175, found 382.2171.



29

(*5aS,8aR*)-5a-benzyl-1-((*R*)-*tert*-butylsulfinyl)-1,2,5,5a,6,7,8,8a-octahydrocyclopenta[b]azepine **29**： To a solution of **28a** (0.15g, 0.42 mmol) in dichloromethane (10 mL) was added Grubb's second generation catalyst (15 mg, 0.13 mmol). The reaction mixture was stirred at room temperature for 7 h and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 4:1) to give the compound **29** as a white solid (137 mg, 99%). $[\alpha]_D^{22}$= - 84.79 (c 0.35, $CHCl_3$), m.p. = 103.6-104.4 ℃. IR (KBr) ν_{max}: 2962, 2924, 2855, 1632, 1453, 1261, 1092, 1024, 802, 703, 678, 595 cm^{-1}.^{1}H NMR (400 MHz, $CHCl_3$) δ 7.27 (d, *J* = 7.0 Hz, 2H), 7.17 (dd, *J* = 38.6, 7.8 Hz, 3H), 6.11 – 5.98 (m, 2H), 4.24 – 4.15 (m, 1H), 3.31 (dd, *J* = 11.3, 8.2 Hz, 1H), 2.93 (dd, *J* = 24.4, 14.3 Hz, 2H), 2.31 (q, *J* = 10.2, 9.4 Hz, 1H), 2.24 – 2.11 (m, 2H), 2.02 (dt, *J* = 12.6, 6.5 Hz, 1H), 1.88 (t, *J* = 14.9 Hz, 2H), 1.78 – 1.65 (m, 2H), 1.23 (s, 9H), 1.05 (d, *J* = 11.7 Hz, 1H). ^{13}C NMR (100 MHz, $CHCl_3$) δ 139.3, 134.1 , 130.5 , 128.1 , 127.9 , 126.1 , 79.0 , 58.5 , 47.9 , 44.4 , 36.7 , 34.0 , 33.3 , 29.1 ,

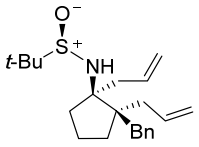
24.0 , 18.7 .HRMS (ESI) calculated for $C_{20}H_{29}NNaOS^+$ [M+Na]$^+$: 354.1862, found 354.1860.



31

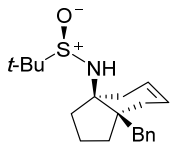
((*5R*,*6S*)-6-allyl-6-benzyl-3-methylene-1-azaspiro[4.4]nonan-1-yl)(*tert*-butyl)-l3-sulfanolate

31： A Solution of **2a** (0.2 g, 0.63 mmol) in THF was charged to $Pd(PPh_3)_4$ (70 mg, 0.06 mmol), to which 2-(trimethylsilylMethyl) allyl acetate (0.27 mL, 1.26 mmol) was added and stirred overnight in a nitrogen atmosphere at 60 °C. After the substrate was completely consumed (monitored by TLC analysis), the solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether :ethyl acetate=4:1) to furnish the desired compound **31** (194 mg, 83% yield) as a colorless oil:^{1}H NMR indicated **31** is a mixture of two diastereoisomers in a ratio of 10:1. Major isomer: $[\alpha]_D^{22}$= - 24.32 (c 0.89, $CHCl_3$) . IR (KBr) ν_{max}: 2959, 2924, 2855, 1628, 1494, 1455, 1377, 1361, 1261, 1085, 1021, 916, 888, 802, 744, 703 cm^{-1}. ^{1}H NMR (400 MHz, $CHCl_3$) δ 7.22 (dd, *J* = 18.6, 8.1 Hz, 3H), 7.12 (d, *J* = 7.1 Hz, 2H), 5.79 (td, *J* = 16.6, 9.0 Hz, 1H), 5.16 – 5.06 (m, 2H), 4.72 (s, 1H), 4.61 (s, 1H), 3.15 – 3.04 (m, 1H), 2.92 (d, *J* = 12.8 Hz, 1H), 2.66 (d, *J* = 12.9 Hz, 1H), 2.54 (d, *J* = 13.1 Hz, 1H), 2.42 (d, *J* = 8.1 Hz, 1H), 2.25 (dd, *J* = 13.5, 8.7 Hz, 1H), 2.02 (t, *J* = 12.8 Hz, 1H), 1.79 – 1.67 (m, 5H), 1.62(s, 1H), 1.49 (dd, *J* = 12.7, 6.4 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CHCl_3$) δ198.1 , 143.6 , 138.4 , 134.7, 130.4 , 128.3 , 126.6 , 118.7 , 112.5 , 57.4 , 54.6 , 45.5 , 44.7 , 43.5 , 42.2 , 28.5 , 25.3 , 23.1 , 21.5 . HRMS (ESI) calculated for $C_{23}H_{33}NNaOS^+$ [M+Na]$^+$: 394.2175, found 394.2173.



32

(*R*)-N-((*1S*,*2S*)-1,2-diallyl-2-benzylcyclopentyl)-2-methylpropane-2-sulfinamide **32**： In a round bottom flask, a solution of compound **2a** (0.2 g, 0.63 mmol) in THF (10 mL) was added allylmagnesium chloride (2M in THF, 1.26 mL, 2.52 mmol) in a nitrogen atmosphere at 0 ℃. The mixture was kept stirring at 0 ℃ 3.0 hours. After the substrate was completely consumed (monitored by TLC analysis), the reaction mixture was quenched with saturated NH_4Cl (50 mL), and extracted by ethyl acetate (3 x 50 mL). The combined organic phase was dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether :ethyl acetate = 3 : 1) to furnish the desired compound **32** (170 mg, 75% yield) as a colorless oil: $[\alpha]_D^{22}$= - 46.05 (c 0.55, $CHCl_3$) . IR (KBr) ν_{max}: 2960, 2925, 2855, 1635, 1455, 1261, 1071, 1022, 912, 803, 703 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.23 (m, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 6.29 – 6.12 (m, 1H), 5.96 (td, *J* = 16.8, 7.3 Hz, 1H), 5.16 (dd, *J* = 18.9, 10.0 Hz, 4H), 3.53 (s, 1H), 2.94 (d, *J* = 13.5 Hz, 1H), 2.59 (d, *J* = 13.6 Hz, 1H), 2.50 – 2.39 (m, 2H), 2.18 (d, *J* = 7.1 Hz, 2H), 2.02 (t, *J* = 11.0 Hz, 1H), 1.80 – 1.68 (m, 2H), 1.36 (t, *J* = 11.8 Hz, 2H), 1.28 (s, 1H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 135.9, 135.0, 130.8, 128.3, 126.4, 118.6, 118.0, 70.6, 56.6, 53.6, 42.4, 39.1, 38.0, 33.5, 33.0, 23.2, 19.0. HRMS (ESI) calculated for $C_{22}H_{33}NNaOS^+$ [M+Na]$^+$: 382.2175, found 382.2177.

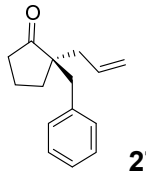


33

(*R*)-N-((*3aS*,*7aS*)-7a-benzyl-1,2,3,4,7,7a-hexahydro-3aH-inden-3a-yl)-2-methylpropane-2-sulfinamide **33**：To a solution of **32** (0.17 g, 0.47 mmol) in dichloromethane (10 mL) was added Grubb's second generation catalyst (120 mg, 0.14 mmol). The reaction mixture was stirred at room temperature for 2 h and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc : PE = 1 : 4) to give the compound **33** as a colorless oil (140 mg, 90%). $[\alpha]_D^{22}$= 4.61 (c 0.72, $CHCl_3$). IR (KBr) ν_{max}: 2959, 2925, 2869, 1494, 1456, 1436, 1261, 1096, 1048, 802, 703, 669, 655 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.24 – 7.18 (m, 1H), 7.12 (d, *J* = 7.4 Hz, 2H), 5.57 (dd, *J* = 29.6, 10.3 Hz, 2H), 3.23 (s, 1H), 2.60 (d, *J* = 21.1 Hz, 3H), 2.40 (d, *J* = 18.6 Hz, 1H), 2.26 – 2.16 (m, 1H), 1.93 (dd, *J* = 20.1, 11.2 Hz, 2H), 1.87 – 1.79 (m, 1H), 1.73 (dd, *J* = 14.0, 3.9 Hz, 3H), 1.35 (dd, *J* = 11.1, 5.0 Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 130.5, 128.2, 126.3, 124.4, 124.1, 66.4, 56.0, 47.7, 38.4, 36.3, 33.9, 33.2, 31.7, 22.9, 18.5. HRMS (ESI) calculated for $C_{20}H_{29}NNaOS^+$ $[M+Na]^+$: 354.1862, found 354.1861.

5. Preparation of compound 27 and rac-27

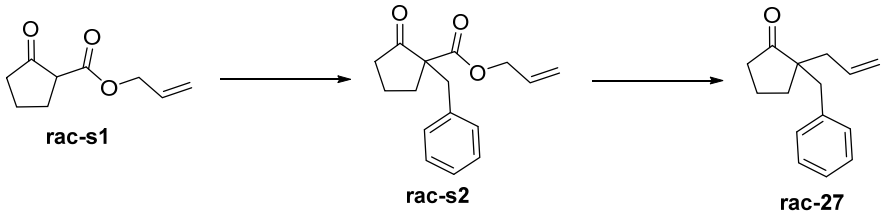
1) The preparation of compound **27**

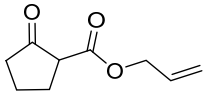


27

(*S*)-2-allyl-2-benzylcyclopentan-1-one **27**：The sulfinimine **2a** (0.12 g, 0.38mmol) was dissolved in methanol (2 mL). The resulting solution was treated with aqueous solution of HCl (4.0 M in water, 1 mL). The mixture was stirred at room temperature overnight. TLC indicated the starting material was fully consumed. The reaction was concentrated in high vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 30 : 1) to give the ketone **27** (0.073 g, 90%) as colorless oil. $[\alpha]_D^{25}$= +10.27 (c 1.95, $CHCl_3$) . ^1H NMR (400 MHz, $CHCl_3$) δ 7.26 – 7.18 (m, 3H), 7.10 (d, *J* = 7.3 Hz, 2H), 5.73 (m, 1H), 5.09 (t, *J* = 13.7 Hz, 2H), 2.92 (d, *J* = 13.3 Hz, 1H), 2.60 (d, *J* = 13.3 Hz, 1H), 2.28 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.14 (dd, *J* = 14.9, 8.2 Hz, 2H), 2.01 – 1.84 (m, 3H), 1.77 – 1.69 (m, 1H), 1.51 – 1.43 (m, 1H). ^{13}C NMR (100 MHz, $CHCl_3$) δ 223.0 , 137.9 , 133.8 , 130.4 , 128.3 , 126.6 , 118.8 , 53.4 , 41.9 , 41.1 , 39.0 , 31.2 , 18.8 . HRMS (ESI) calculated for $C_{15}H_{18}NaO^+$ $[M+Na]^+$: 237.1250, found 237.1251.

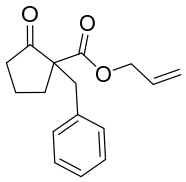
2）The preparation of **rac-27**





rac-s1

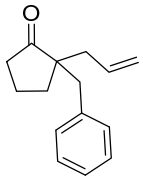
Allyl-2-oxocyclopentane-1-carboxylate **rac-s1**: In a round bottom flask, a solution of compound **2a** (3.0 g, 13.25 mmol) in THF (65 mL) was added LiHMDS (1 M in THF, 27 mL, 27.00 mmol) in a nitrogen atmosphere at 0 ℃. The mixture was kept stirring at room teperature for 4.0 hours. After the substrate was completely consumed (monitored by TLC analysis), the reaction mixture was quenched with saturated NH_4Cl (30 mL), and extracted by ethyl acetate (3 x 50 mL). The combined organic phase was dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether :ethyl acetate = 10 : 1) to furnish the desired compound **rac-s1** (2.0 g, 83% yield) as a colorless oil:^{1}H NMR (400 MHz, $CHCl_3$) δ 5.97 – 5.87 (m, 1H), 5.38 – 5.24 (m, 2H), 4.68 – 4.63 (m, 2H), 3.20 (t, J = 9.1 Hz, 1H), 2.36 – 2.28 (m, 4H), 2.20 – 2.12 (m, 1H), 1.92 – 1.84 (m, 1H).^{13}C NMR (100 MHz, $CHCl_3$) δ 212.3 , 169.2 , 131.8 , 118.6 , 66.0 , 54.8 , 38.2 , 27.5 , 21.1 .



rac-s2

Allyl-1-benzyl-2-oxocyclopentane-1-carboxylate **rac-s2**: β-ketoester **rac-s1** (2.0 g, 11.9 mmol) was added to a suspension of anhydrous K_2CO_3 (4.90 g, 35.7 mmol) in acetone (12 mL). To the reaction mixture was added Benzyl bromide (0.28 mL, 23.8 mmol). The resultant solution was placed in a preheated 50 °C oil bath. After 5 h, the reaction was removed from the heating bath and allowed to cool to ambient temperature. After cooling, the solution was filtered and concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether:ethyl acetate = 10:1) to furnish β-ketoester **rac-s2** (2.3 g, 76% yield) as a clear colorless oil:

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.23 (dd, J = 15.7, 7.6 Hz, 3H), 7.14 (d, J = 7.0 Hz, 2H), 5.89 (ddt, J = 17.0, 11.2, 5.6 Hz, 1H), 5.28 (dd, J = 26.3, 13.8 Hz, 2H), 4.65 – 4.59 (m, 2H), 3.18 (q, J = 13.7 Hz, 2H), 2.46 – 2.34 (m, 2H), 2.08 – 1.88 (m, 3H), 1.60 (dd, J = 12.9, 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CHCl_3$) δ 214.9, 170.8, 136.6, 131.7, 130.3, 128.5, 127.0, 118.7, 66.2, 61. 6, 39.1, 38.5, 31.8, 19.6.

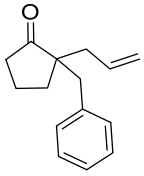


rac-27

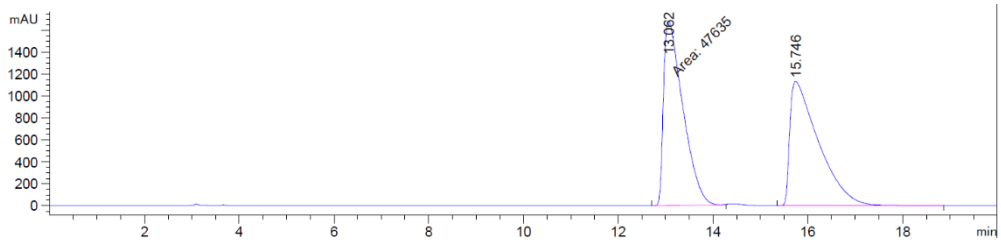
2-Allyl-2-benzylcyclopentan-1-one **rac-27**: In a round bottom flask, a solution of compound **rac-s2** (0.2 g, 0.77 mmol) in THF (2 mL) was added $Pd(OAc)_2$ (18 mg, 0.077 mmol) and PPh_3 (79 mg, 0.3 mmol) in a nitrogen atmosphere at room temperature. The mixture was kept stirring at 60 ℃ for 1.0 hours. After the substrate was completely consumed (monitored by TLC analysis), the reaction mixture was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether :ethyl acetate = 10 : 1) to furnish the desired compound **rac-27** (150 mg, 91% yield) as a colorless oil: ^{1}H NMR (400 MHz, $CHCl_3$) δ 7.29 – 7.25 (m, 1H), 7.25 – 7.18 (m, 2H), 7.12 – 7.06 (m, 2H), 5.78 – 5.67 (m, 1H), 5.13 – 5.05 (m, 2H), 2.92 (d, *J* = 13.3 Hz, 1H), 2.59 (d, *J* = 13.3 Hz, 1H), 2.28 (dd, *J* = 13.7, 6.9 Hz, 1H), 2.15 (ddd, *J* = 14.8, 6.8, 4.5 Hz, 2H), 1.97 (ddd, *J* = 15.0, 7.0, 5.0 Hz, 1H), 1.89 (dt, *J* = 14.2, 5.2 Hz, 2H), 1.78 – 1.69 (m, 1H), 1.47 (tdd, *J* = 8.8, 7.9, 4.3 Hz, 1H).^{13}C NMR (100 MHz, $CHCl_3$) δ 223.1 , 137.9 , 133.8 , 130.4 , 128.3 , 126.6 , 118.8 , 53.3 , 41.8 , 41.0 , 39.0 , 31.1 , 18.8 . HRMS (ESI) calculated for $C_{15}H_{18}NaO^+$ $[M+Na]^+$: 237.1250, found 237.1253.

6. HPLC analysis for determination of the *ee* value of compound 27

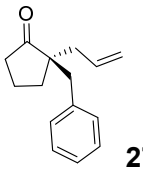
The crude product **27** was analyzed directly by Chiral HPLC using OJ-H (Agilent HPLC 1260) column. Eluted by 0.1% EtOH in hexanes.



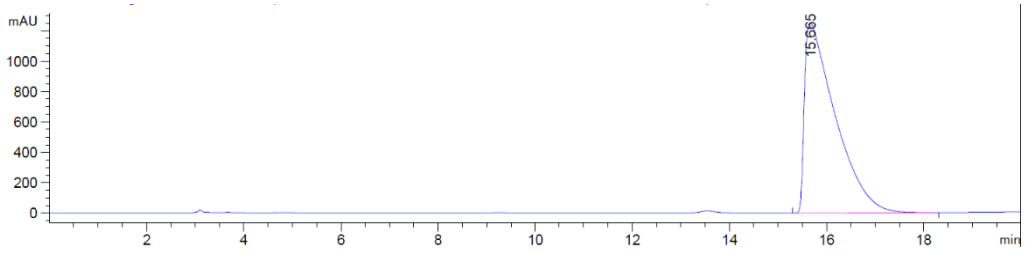
rac-27



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.062	MM	0.4710	4.76350e4	1685.65491	49.9091
2	15.746	VB	0.6086	4.78085e4	1132.28076	50.0909

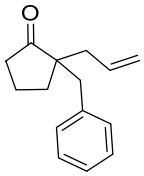


27

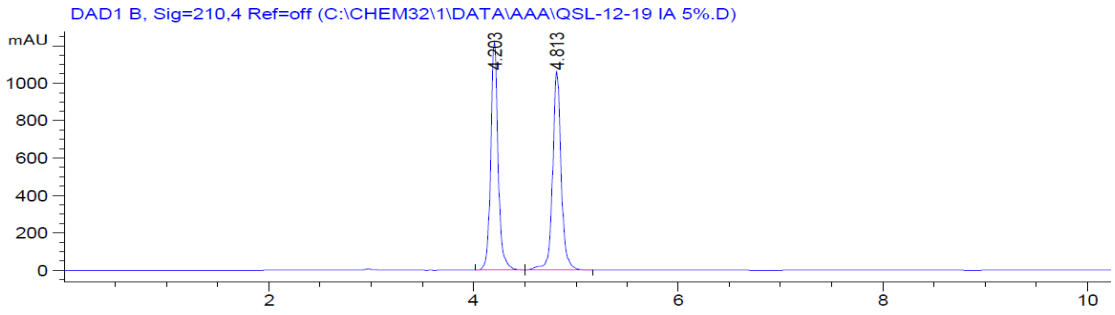


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.665	BB	0.6251	5.50327e4	1251.25659	100.0000

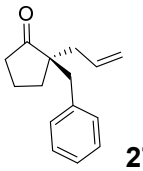
The crude product **27** was also analyzed directly by Chiral HPLC using IA (Agilent HPLC 1260) column. Eluted by 5% i-PrOH in hexanes.



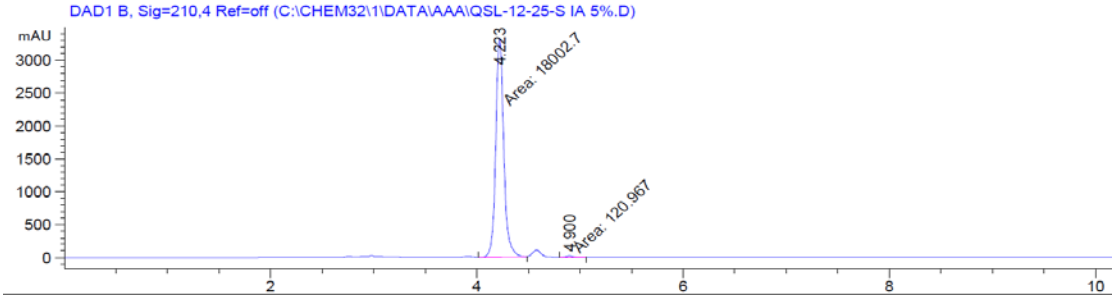
rac-27



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.203	BB	0.0758	95.44016	19.28055	49.6280
2	4.813	BB	0.0871	96.87086	16.83857	50.3720

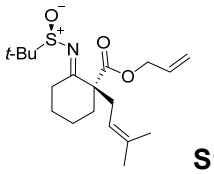


27

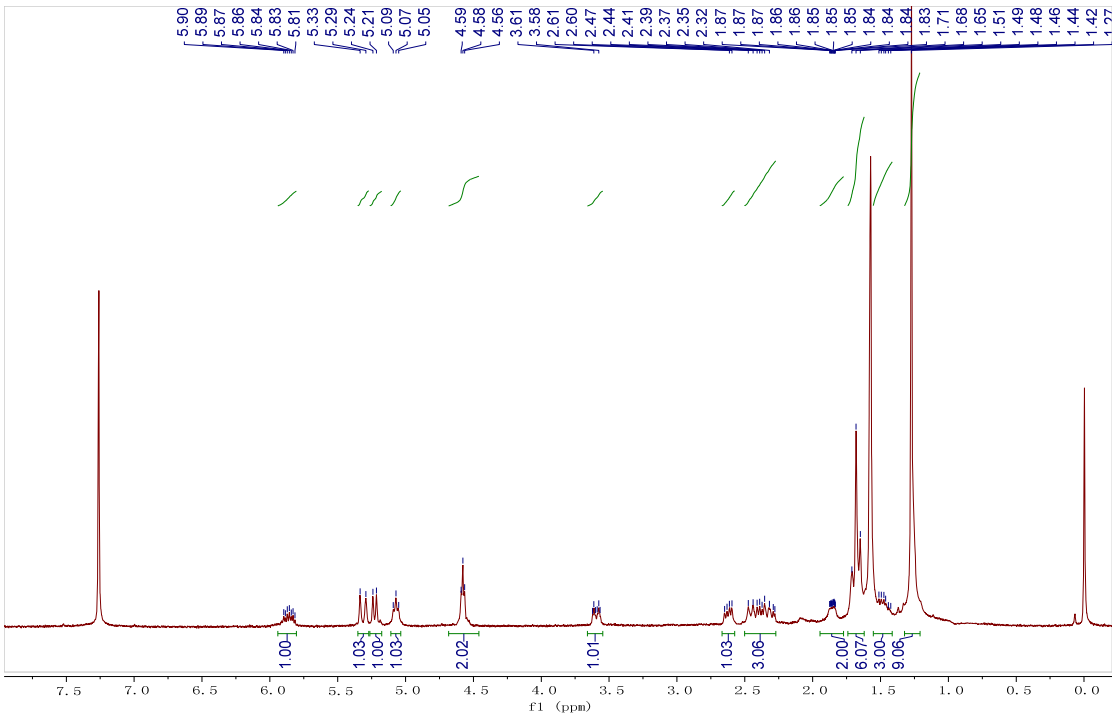


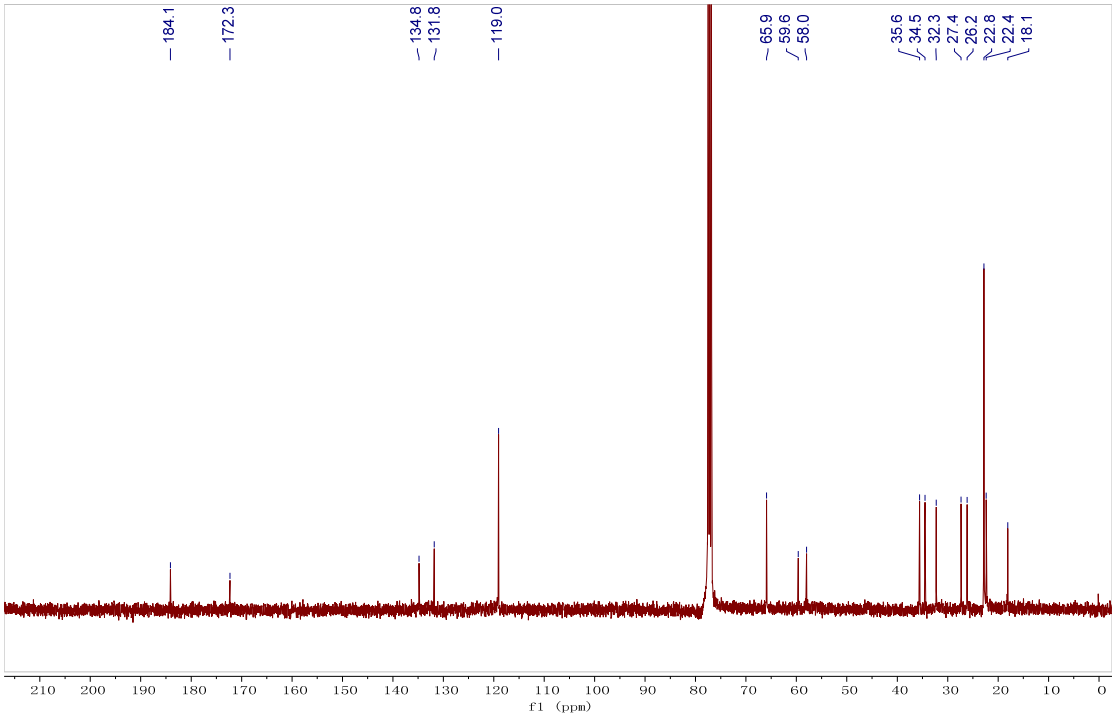
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.223	MM	0.0898	1.80027e4	3341.02881	99.3325
2	4.900	PM	0.0986	120.96748	20.44569	0.6675

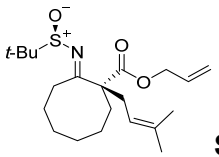
7. NMR Spectrums of Compounds



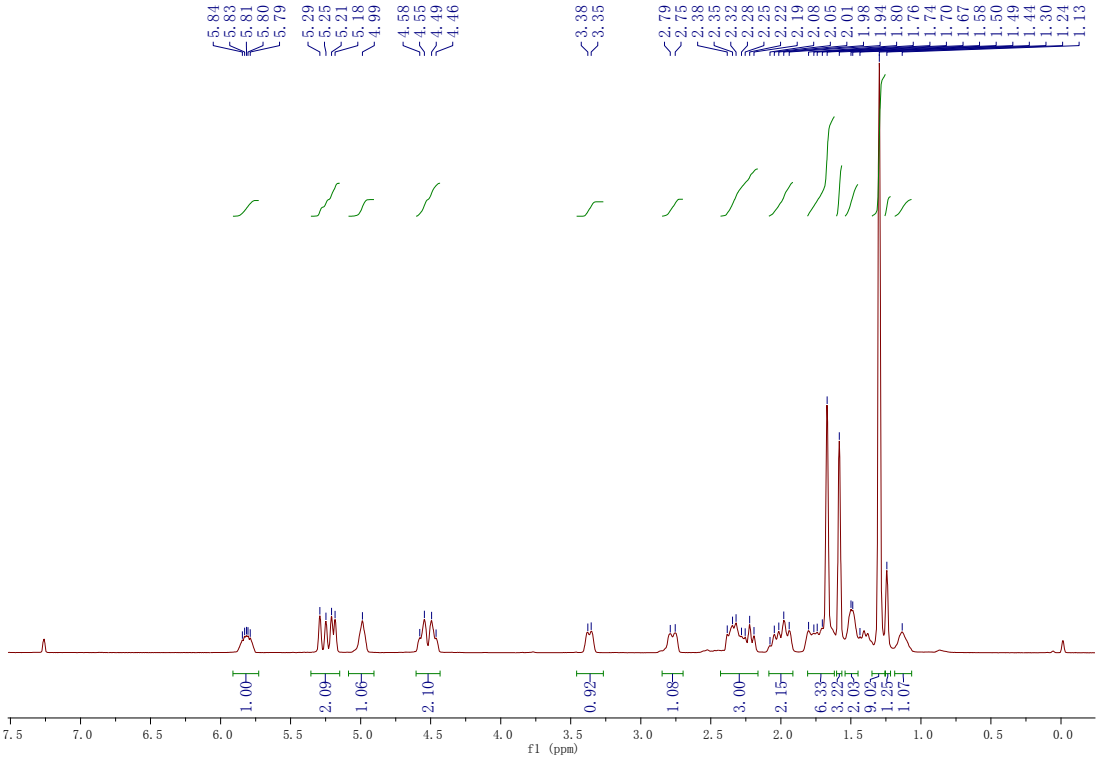
S11







S24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1.30
1.24
1.13
1.00
2.09
1.06
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3.22
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9.02
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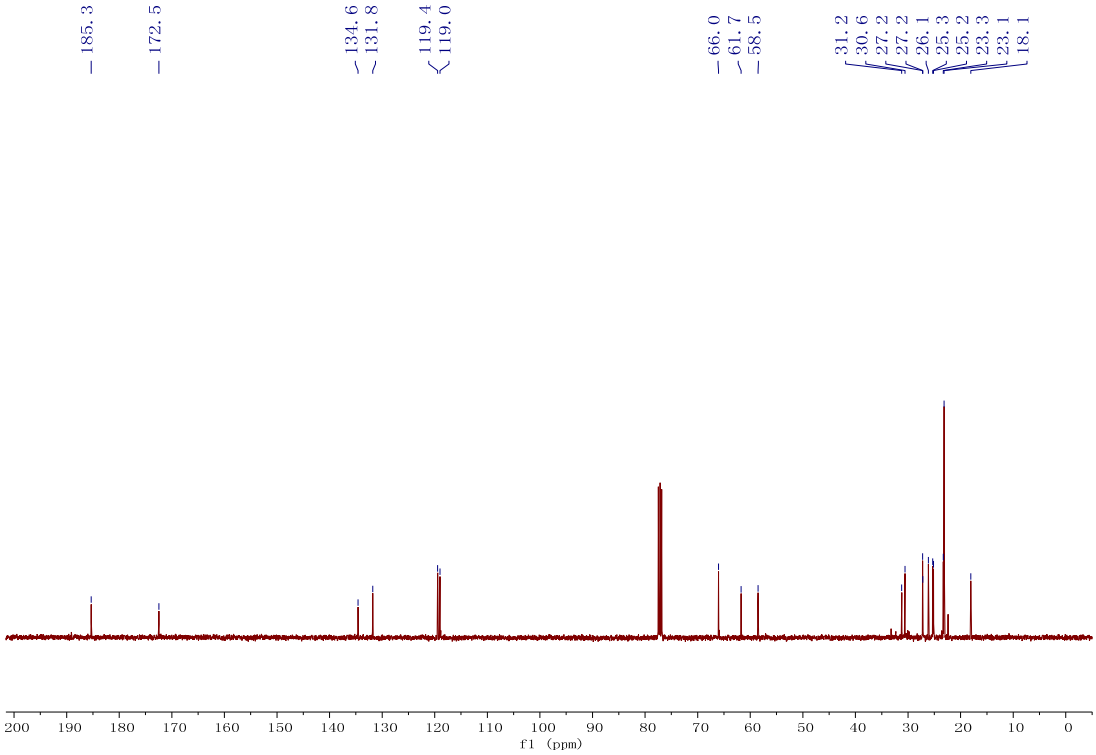
1.07
f1 (ppm)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66.0
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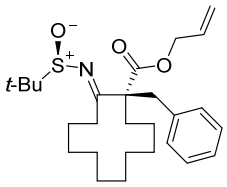
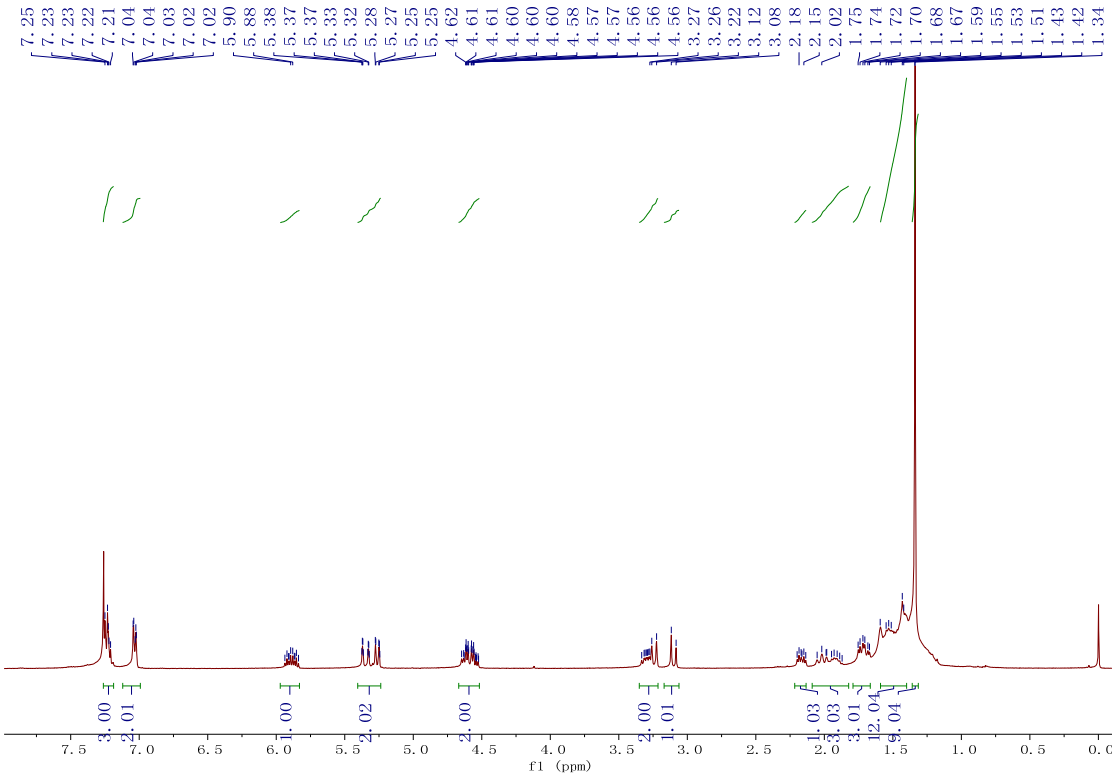
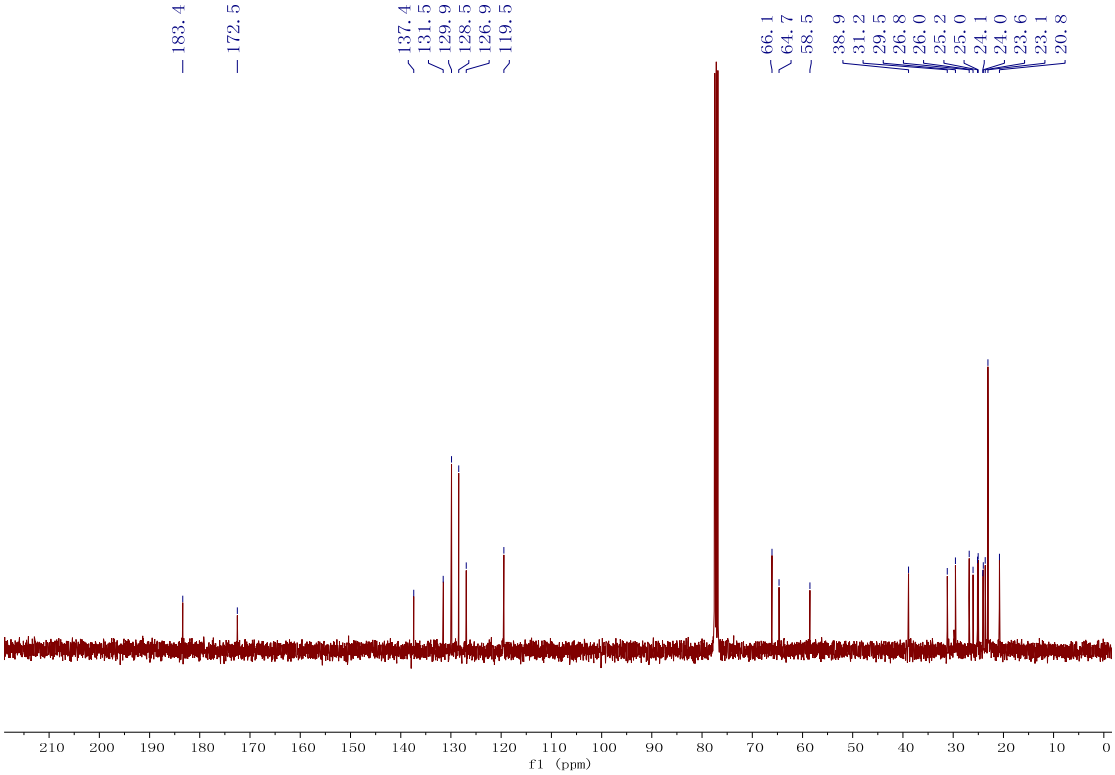
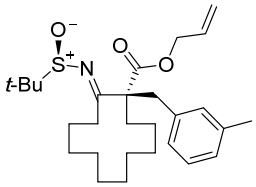
25.2
23.3
23.1
18.1
f1 (ppm)


O
S
N
t-Bu
O
O

S25


7.25 7.23 7.23 7.22 7.21 7.04 7.04 7.03 7.02 7.02 5.90 5.88 5.38 5.37 5.37 5.33 5.32 5.28 5.27 5.25 5.25 4.62 4.61 4.61 4.60 4.60 4.60 4.58 4.57 4.56 4.56 4.56 4.56 3.27 3.26 3.22 3.12 3.08 2.18 2.15 2.02 1.75 1.74 1.72 1.70 1.68 1.67 1.59 1.55 1.53 1.51 1.43 1.42 1.34
3.00 2.01 1.00 2.02 2.00 2.00 1.01 1.03 3.03 3.01 12.04 9.04
f1 (ppm)


183.4 172.5 137.4 131.5 129.9 128.5 126.9 119.5 66.1 64.7 58.5 38.9 31.2 29.5 26.8 26.0 25.2 25.0 24.1 24.0 23.6 23.1 20.8
f1 (ppm)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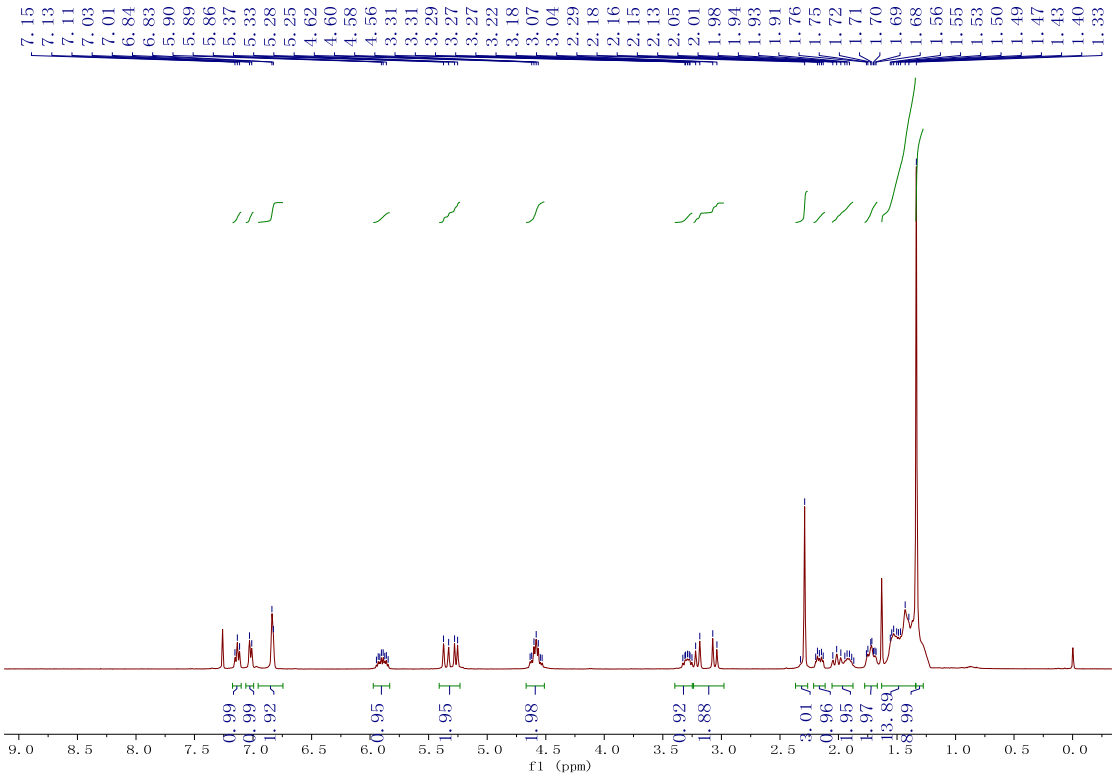
S⁺
N
t-Bu
O
O

S26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1.93
1.91
1.76
1.75
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1.69
1.68
1.56
1.55
1.53
1.50
1.49
1.47
1.43
1.40
1.33
0.99
0.99
1.92
0.95
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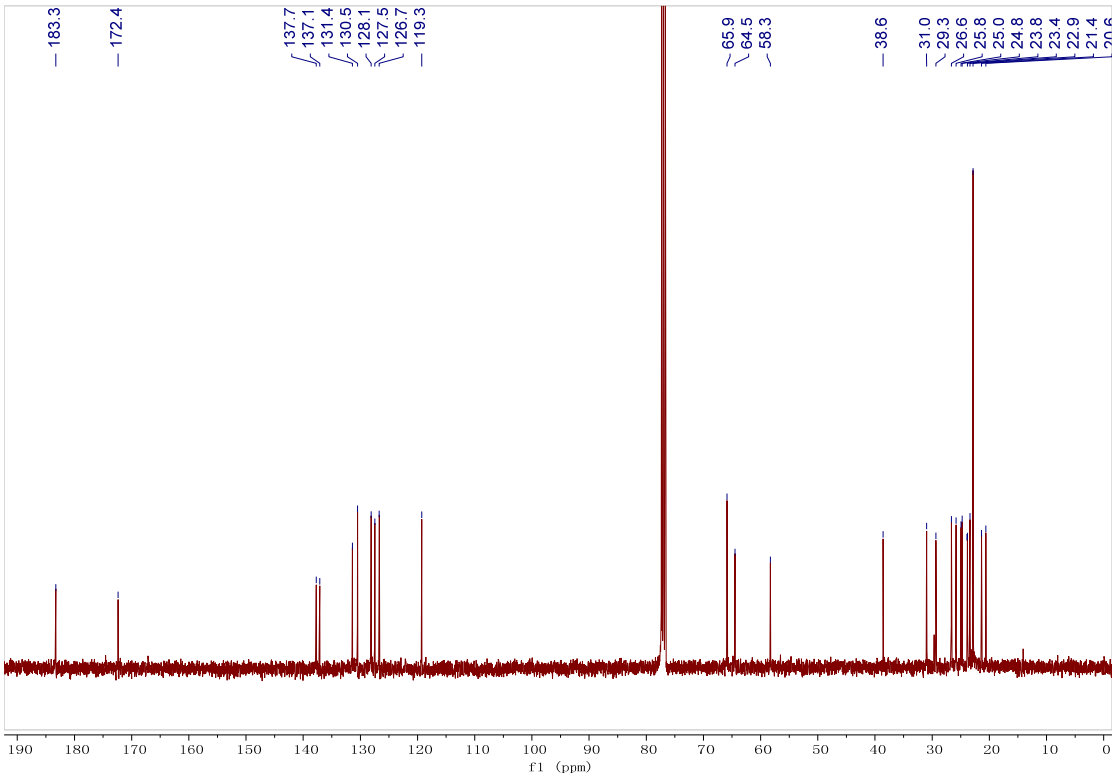
3.01
0.96
1.95
1.97
3.89
8.99
f1 (ppm)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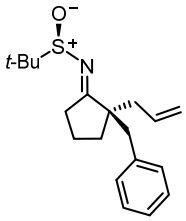
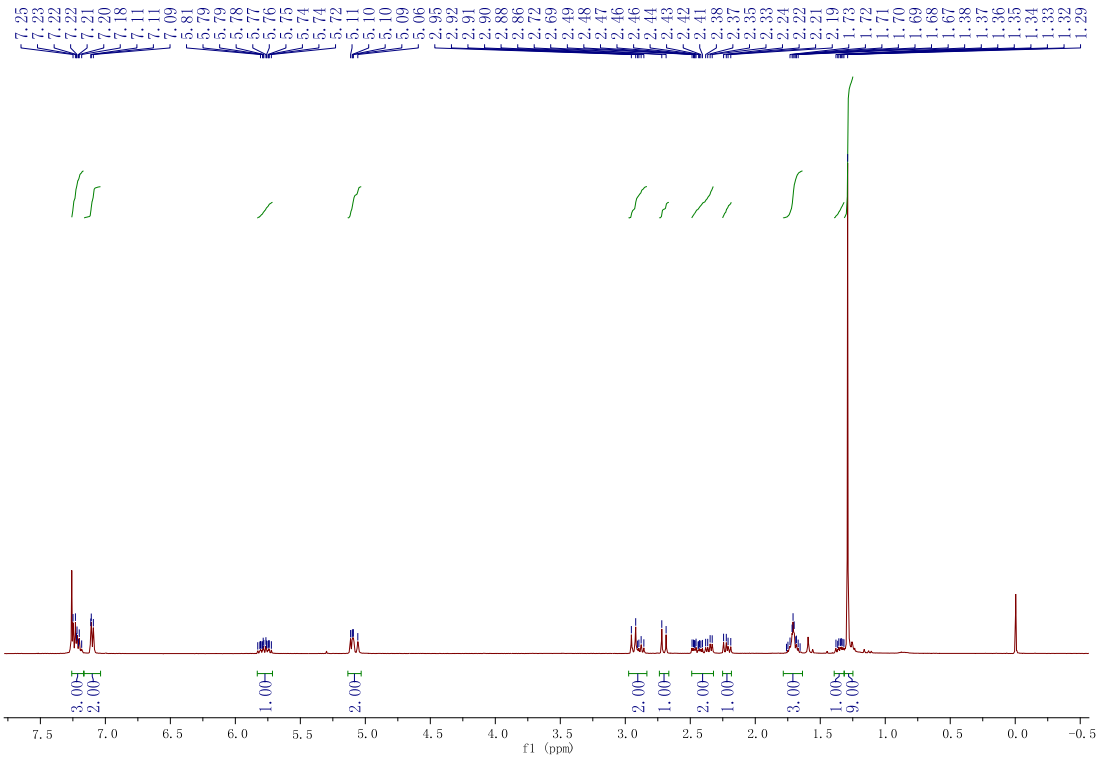
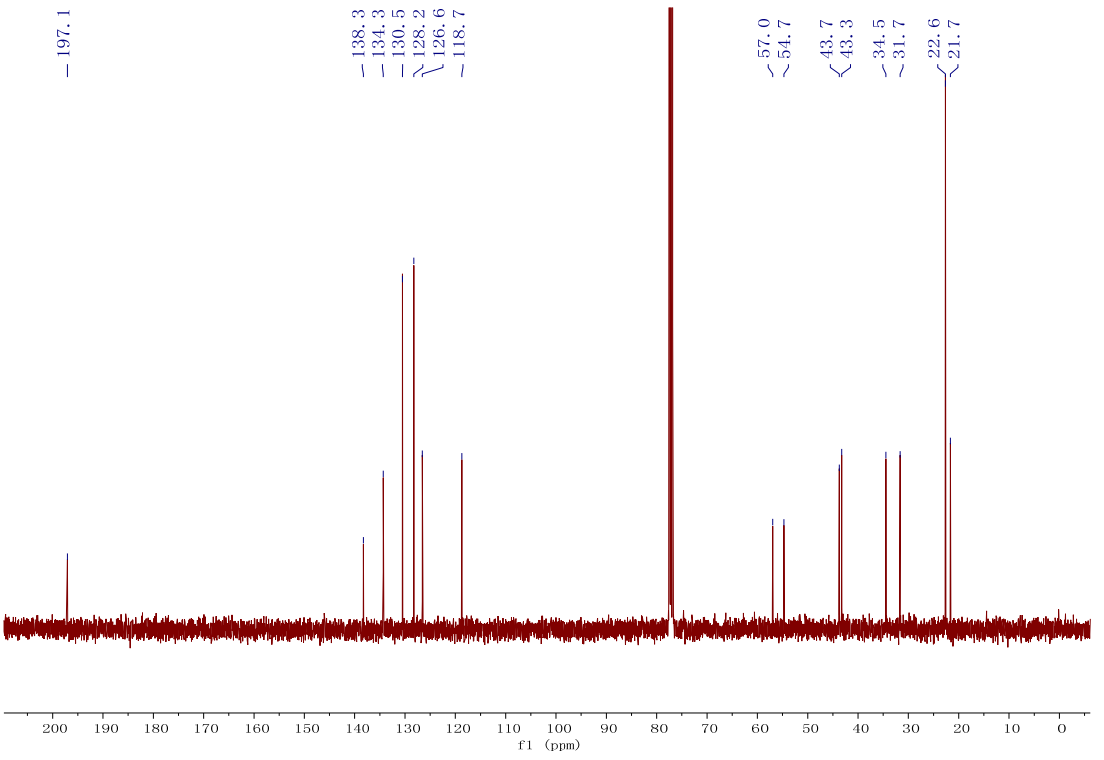
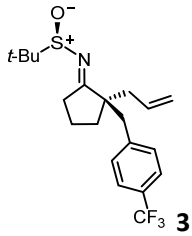
131.4
130.5
128.1
127.5
126.7
119.3
65.9
64.5
58.3
38.6
31.0
29.3
26.6
25.8
25.0
24.8
23.8
23.4
22.9
21.4
f1 (ppm)


O
S
N
t-Bu

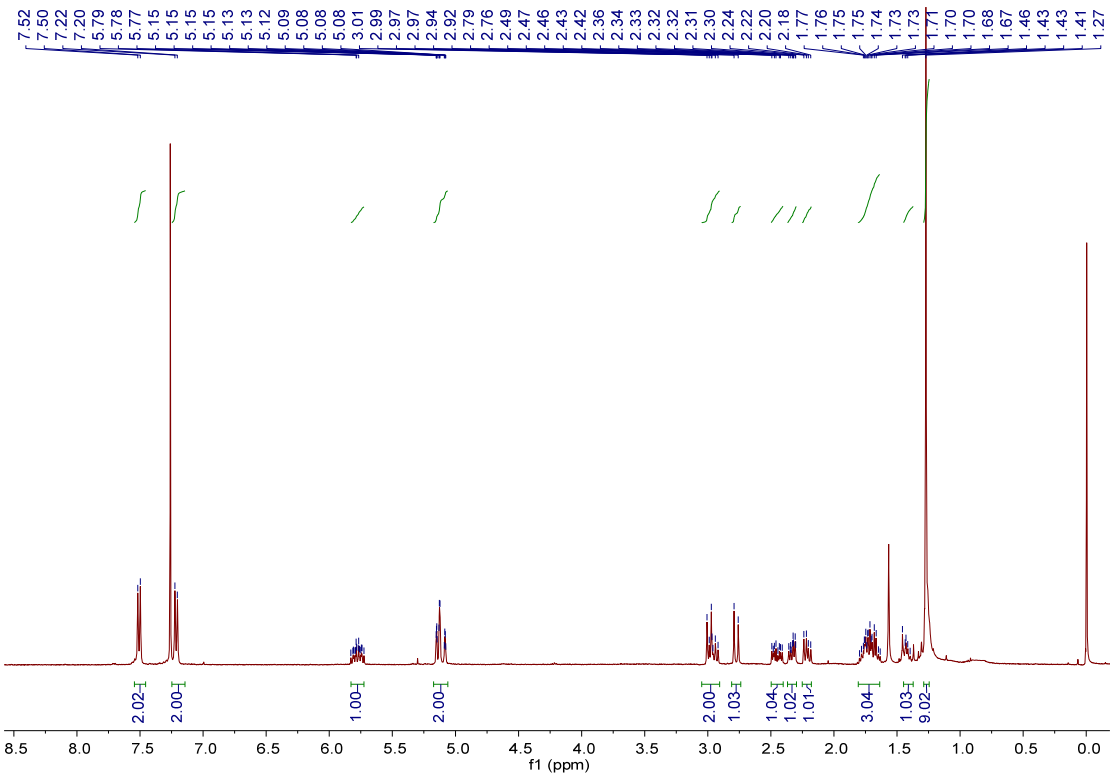
2a

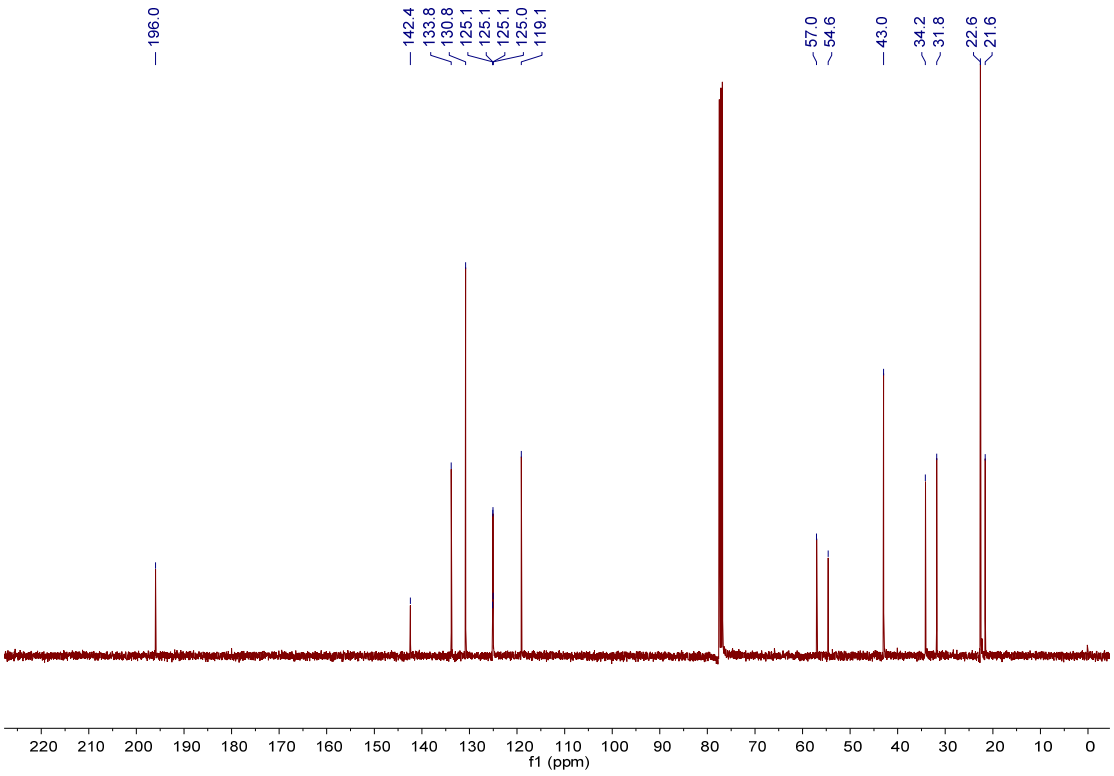

7.25 7.23 7.22 7.22 7.21 7.20 7.18 7.11 7.11 7.09 5.81 5.79 5.79 5.78 5.77 5.76 5.75 5.74 5.74 5.72 5.11 5.10 5.10 5.09 5.06 2.95 2.92 2.91 2.90 2.88 2.86 2.72 2.69 2.49 2.48 2.47 2.46 2.46 2.44 2.43 2.42 2.41 2.38 2.37 2.35 2.33 2.24 2.22 2.21 2.19 1.73 1.72 1.71 1.70 1.69 1.68 1.67 1.38 1.37 1.36 1.35 1.34 1.33 1.32 1.29
3.00 2.00 1.00 2.00 2.00 1.00 2.00 1.00 3.00 1.00 9.00
f1 (ppm)

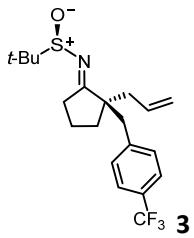

197.1
138.3 134.3 130.5 128.2 126.6 118.7
57.0 54.7 43.7 43.3 34.5 31.7 22.6 21.7
f1 (ppm)


O
S
N
t-Bu
CF3

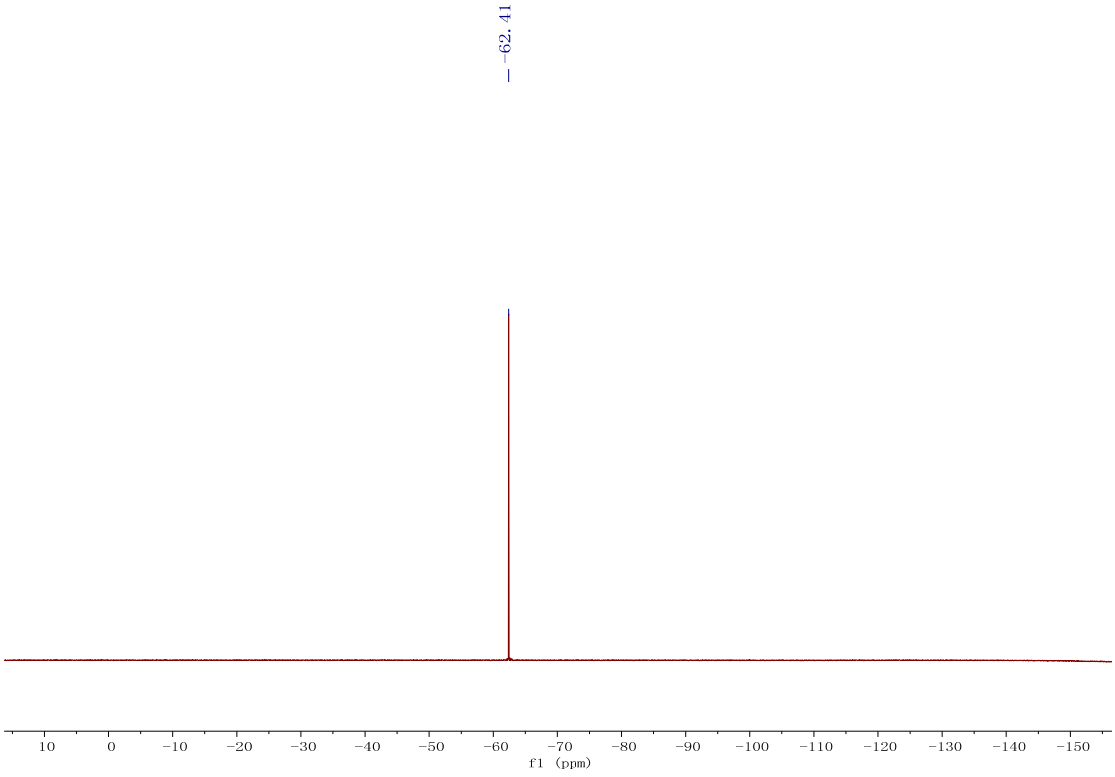
3


7.52 7.50 7.22 7.20 5.79 5.78 5.77 5.15 5.15 5.15 5.13 5.13 5.12 5.09 5.08 5.08 5.08 3.01 2.99 2.97 2.97 2.94 2.92 2.79 2.76 2.49 2.47 2.46 2.43 2.42 2.36 2.34 2.33 2.32 2.32 2.31 2.30 2.24 2.22 2.20 2.18 1.77 1.76 1.75 1.75 1.74 1.73 1.73 1.71 1.70 1.70 1.68 1.67 1.46 1.43 1.43 1.41 1.27
2.02 2.00 1.00 2.00 2.00 1.03 1.04 1.02 1.01 3.04 1.03 9.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.0
142.4 133.8 130.8 125.1 125.1 125.1 125.0 119.1
57.0 54.6
43.0
34.2 31.8
22.6 21.6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
S
N
t-Bu
CF3

3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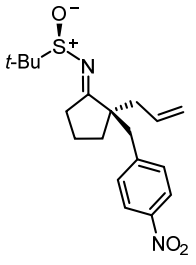
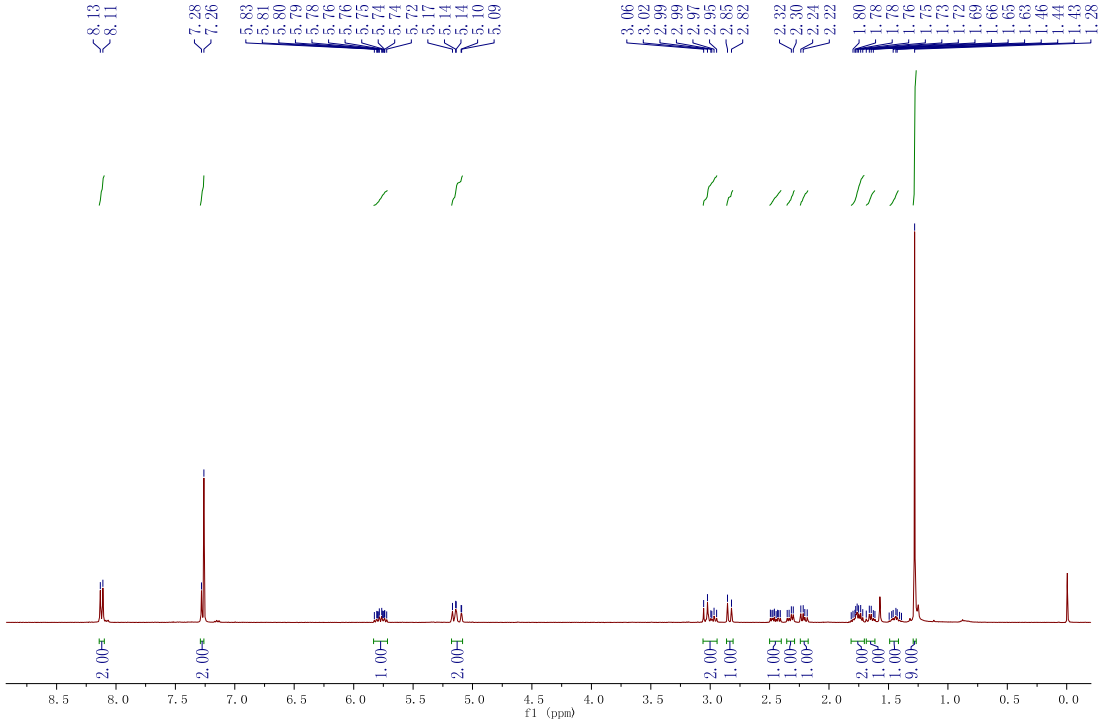
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
f1 (ppm)


O
S
N
t-Bu
NO2

4


8.13
8.11
7.28
7.26
5.83
5.81
5.80
5.79
5.78
5.76
5.76
5.75
5.74
5.74
5.72
5.17
5.14
5.14
5.10
5.09
3.06
3.02
2.99
2.99
2.97
2.95
2.85
2.82
2.32
2.30
2.24
2.22
1.80
1.78
1.78
1.76
1.75
1.73
1.72
1.69
1.66
1.65
1.63
1.46
1.44
1.43
1.28
2.00
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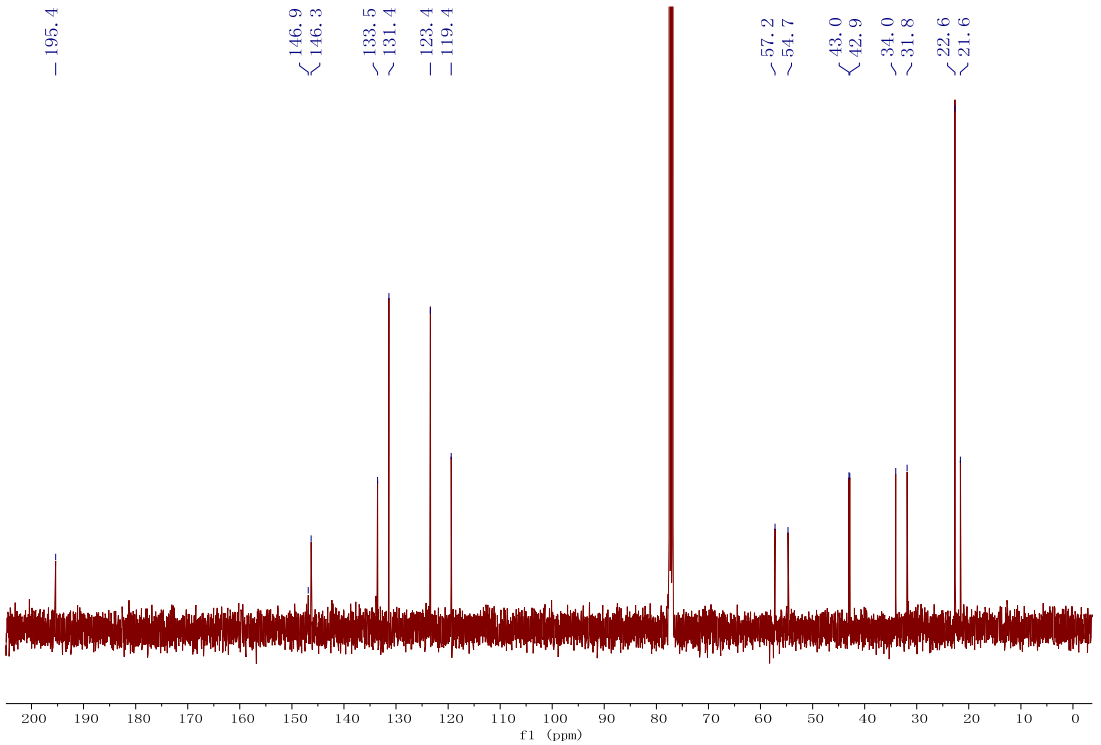
2.00
1.00
1.00
9.00
f1 (ppm)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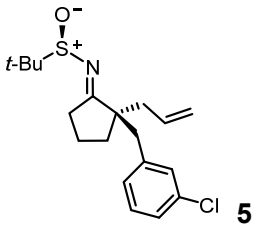
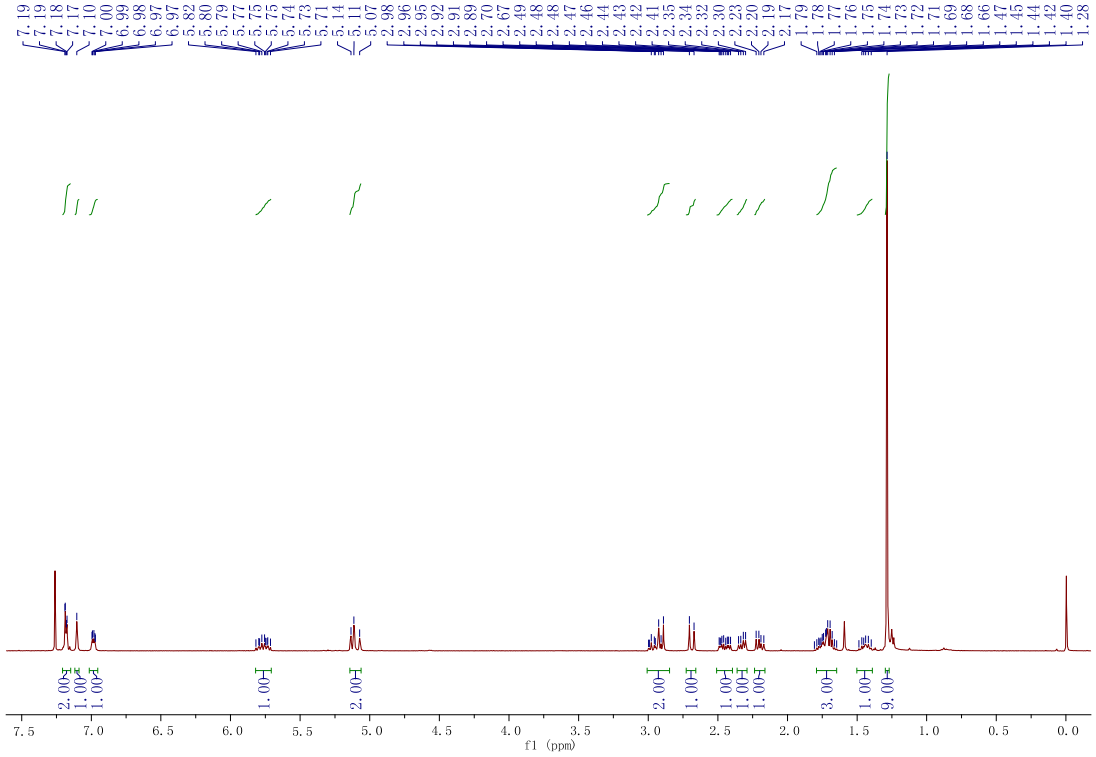
146.9
146.3
133.5
131.4
123.4
119.4
57.2
54.7
43.0
42.9
34.0
31.8
22.6
21.6
f1 (ppm)


O
S
N
t-Bu
Cl

5


7.19
7.19
7.18
7.17
7.10
7.00
6.99
6.98
6.97
6.97
5.82
5.80
5.79
5.77
5.75
5.75
5.74
5.73
5.71
5.14
5.11
3.07
2.98
2.96
2.95
2.92
2.91
2.89
2.70
2.67
2.49
2.48
2.48
2.47
2.46
2.44
2.43
2.42
2.41
2.35
2.34
2.32
2.30
2.23
2.20
2.19
2.17
1.79
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.69
1.68
1.66
1.47
1.45
1.44
1.42
1.40
1.28
2.00
1.00
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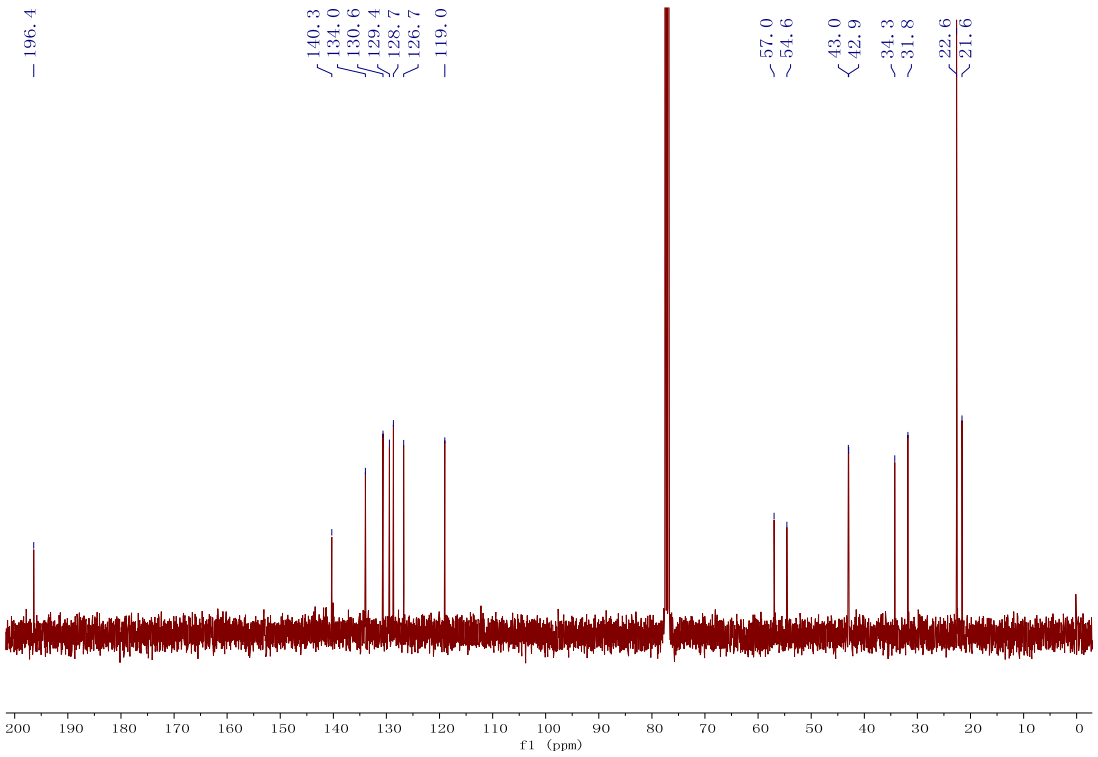
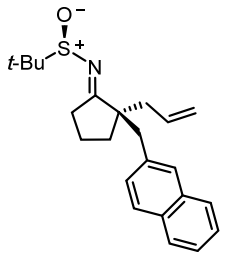
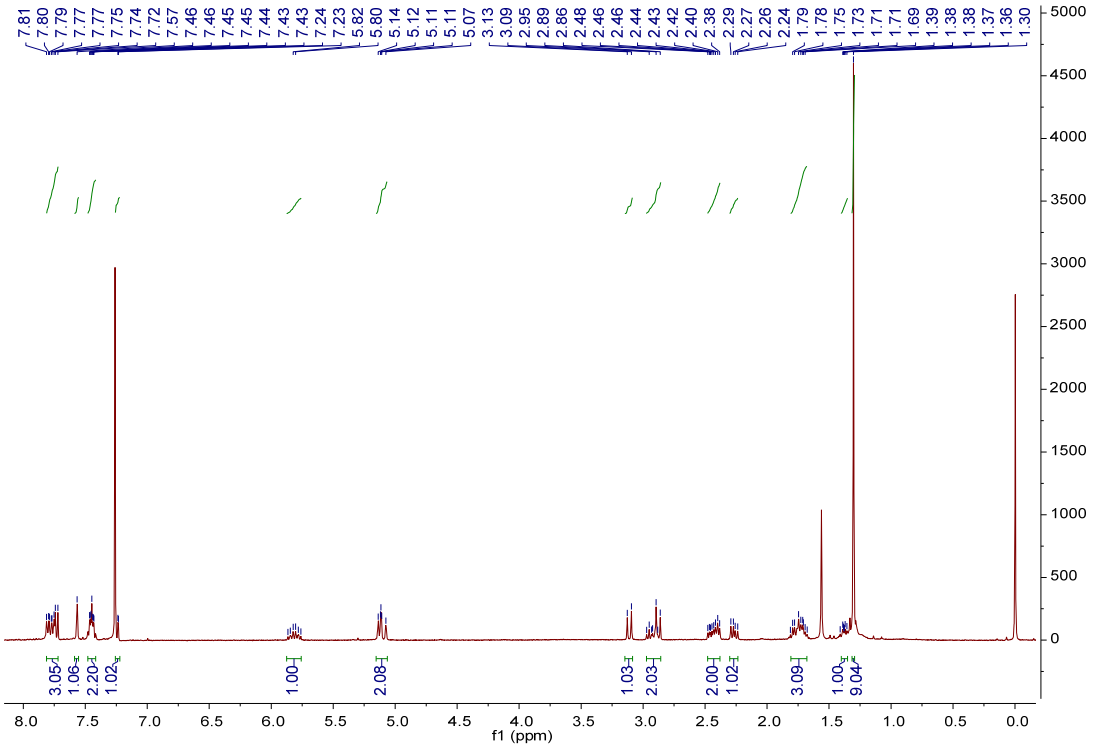
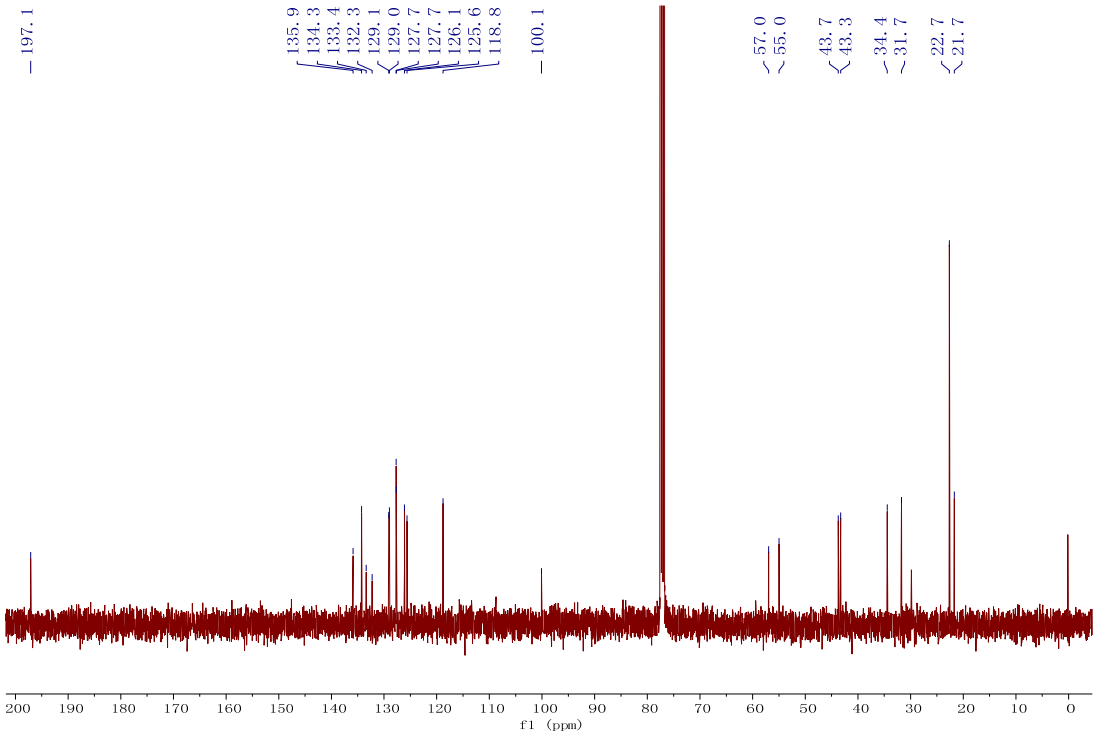
1.00
3.00
1.00
9.00
f1 (ppm)

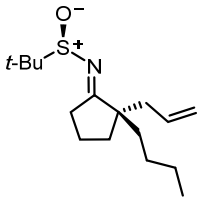

196.4
140.3
134.0
130.6
129.4
128.7
126.7
119.0
57.0
54.6
43.0
42.9
34.3
31.8
22.6
21.6
f1 (ppm)


O
S
N
t-Bu

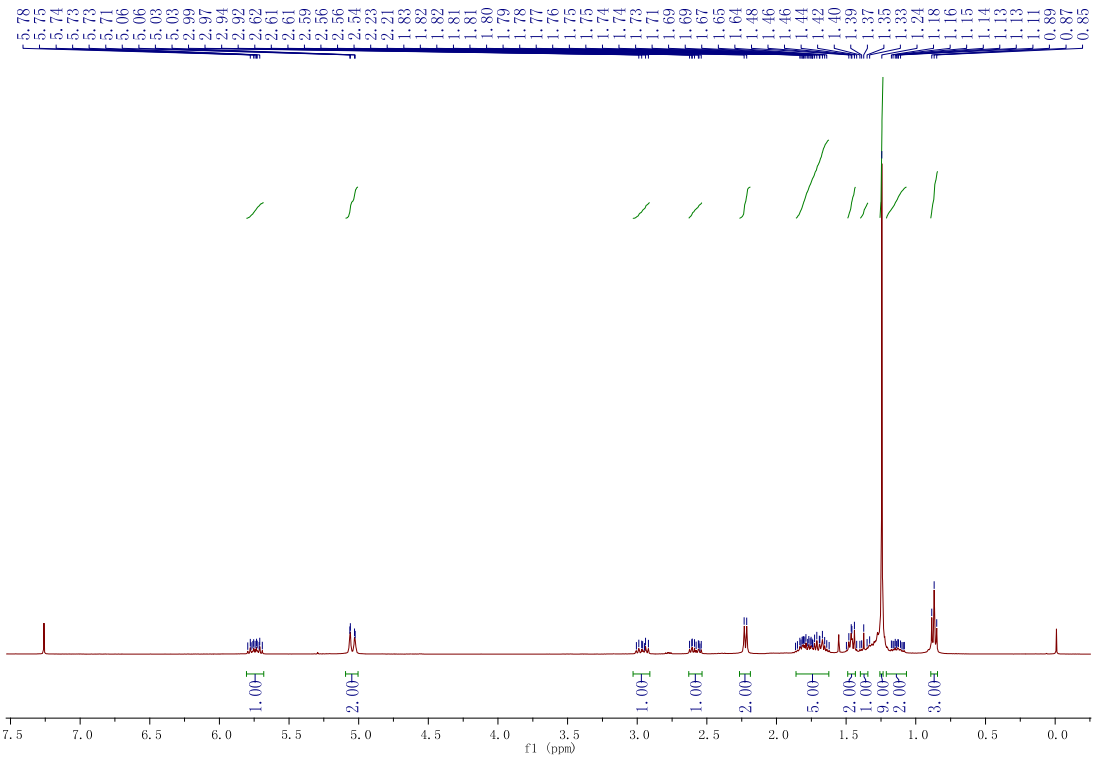
6

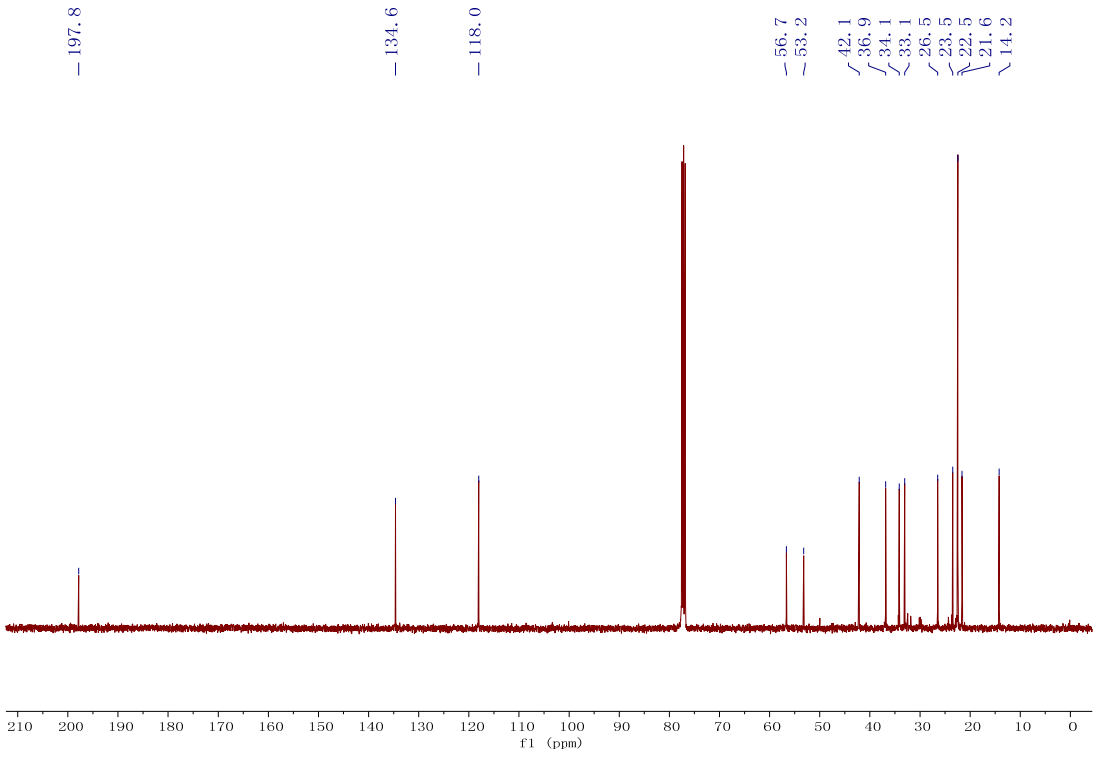

7.81 7.80 7.79 7.77 7.77 7.75 7.74 7.72 7.57 7.46 7.46 7.45 7.45 7.44 7.43 7.43 7.24 7.23 5.82 5.80 5.14 5.12 5.11 5.11 5.07 3.13 3.09 2.95 2.89 2.86 2.48 2.46 2.46 2.44 2.43 2.42 2.40 2.38 2.29 2.27 2.26 2.24 1.79 1.78 1.75 1.73 1.71 1.71 1.69 1.39 1.38 1.38 1.37 1.36 1.30
3.05 1.06 2.20 1.02 1.00 2.08 1.03 2.03 2.00 1.02 3.09 1.00 9.04
f1 (ppm)

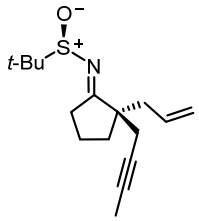

197.1
135.9 134.3 133.4 132.3 129.1 129.0 127.7 127.7 126.1 125.6 118.8
100.1
57.0 55.0 43.7 43.3 34.4 31.7 22.7 21.7
f1 (ppm)


O⁻
S⁺
t-Bu
N

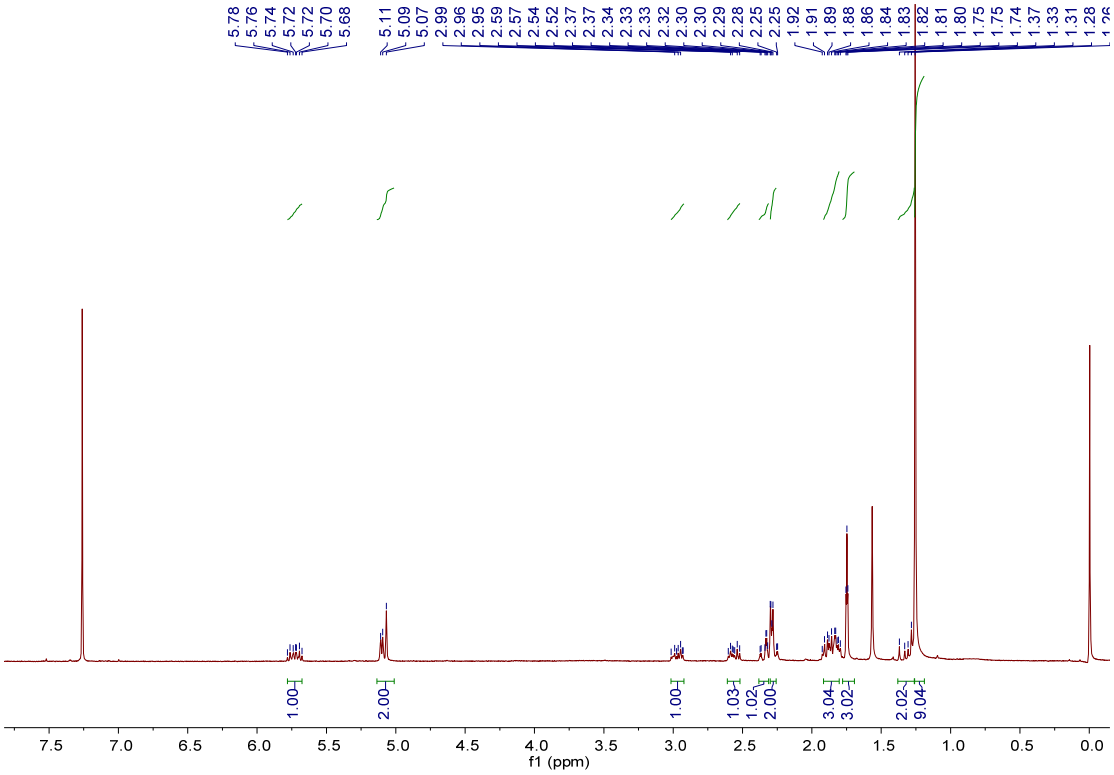
7

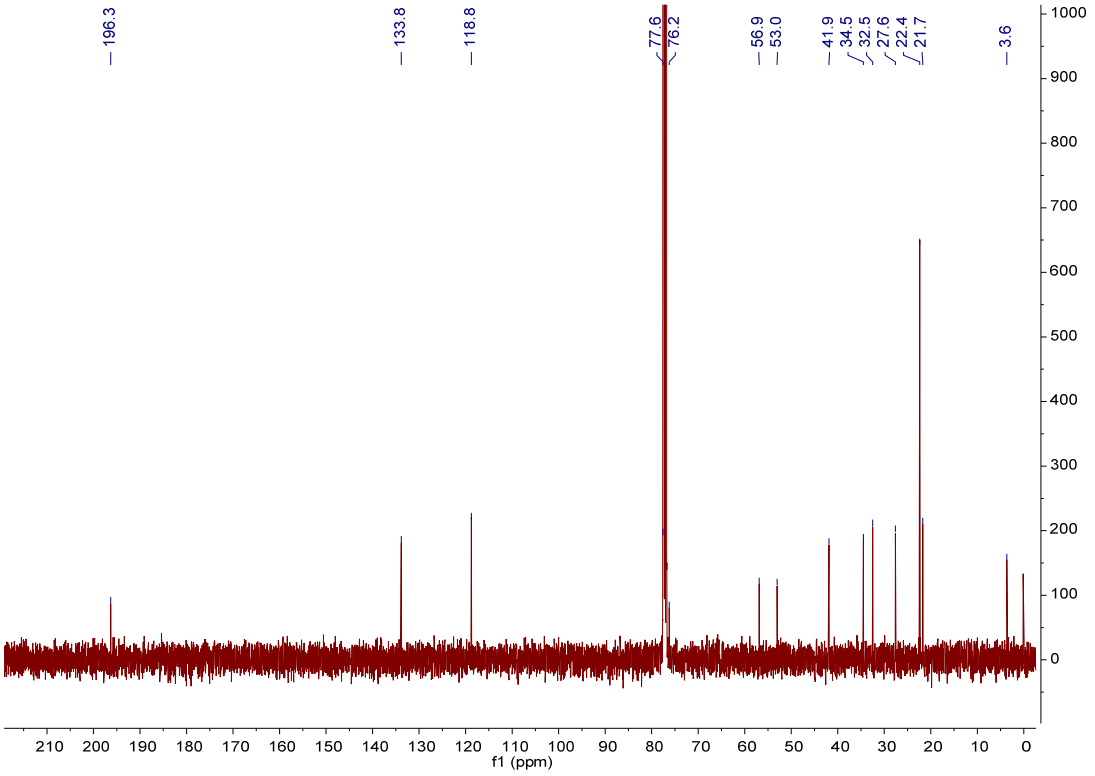

5.78 5.75 5.74 5.73 5.73 5.71 5.06 5.03 2.99 2.97 2.94 2.92 2.62 2.61 2.61 2.59 2.56 2.54 2.23 2.21 1.83 1.82 1.81 1.81 1.80 1.79 1.78 1.77 1.76 1.75 1.74 1.74 1.73 1.71 1.69 1.69 1.67 1.65 1.64 1.48 1.46 1.46 1.44 1.42 1.40 1.39 1.37 1.35 1.33 1.24 1.18 1.16 1.15 1.14 1.13 1.11 0.89 0.87 0.85
1.00 2.00 1.00 1.00 2.00 5.00 2.00 1.00 9.00 2.00 3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

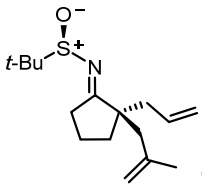

197.8
134.6
118.0
56.7
53.2
42.1
36.9
34.1
33.1
26.5
23.5
22.5
21.6
14.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O⁻
S⁺
t-Bu
N

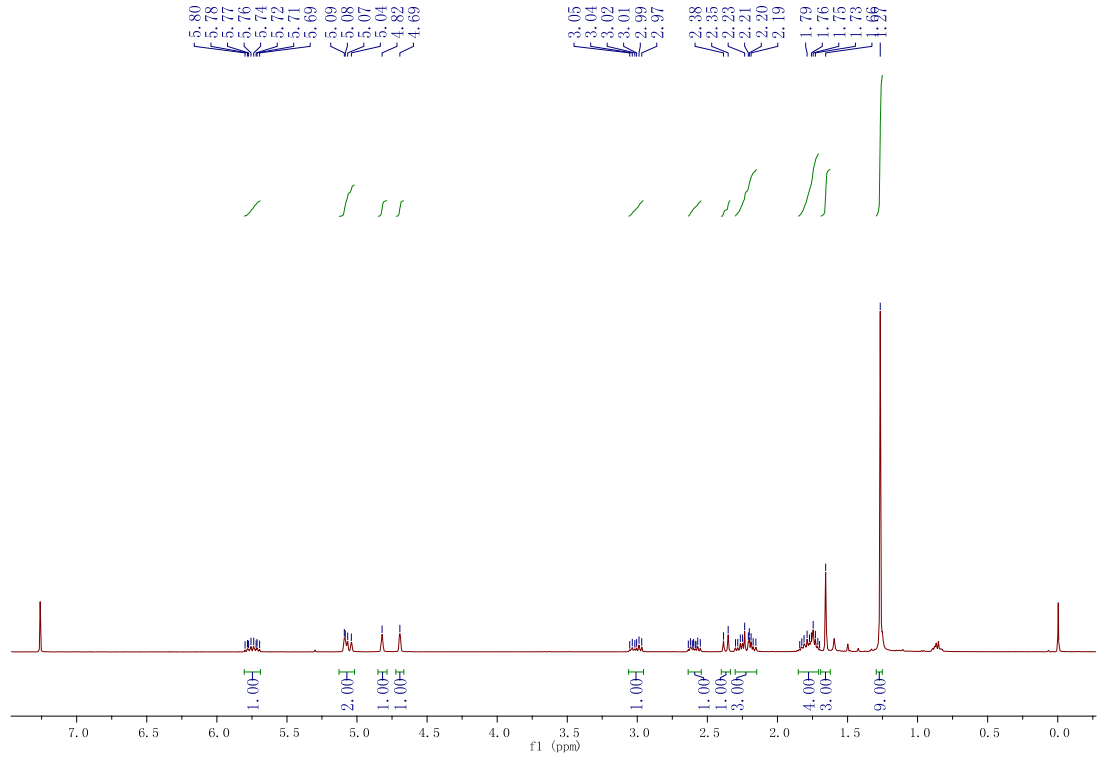
8


5.78 5.76 5.74 5.72 5.72 5.70 5.68
5.11 5.09 5.07 2.99 2.96 2.95 2.59 2.57 2.54 2.52 2.37 2.37 2.34 2.33 2.33 2.32 2.30 2.30 2.29 2.28 2.25 2.25
1.92 1.91 1.89 1.88 1.86 1.84 1.83 1.82 1.81 1.80 1.75 1.75 1.74 1.37 1.33 1.31 1.28
1.00 2.00 1.00 1.03 1.02 2.00 3.04 3.02 2.02 9.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.3
133.8
118.8
77.6
76.2
56.9
53.0
41.9
34.5
32.5
27.6
22.4
21.7
3.6
1000 900 800 700 600 500 400 300 200 100 0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O⁻
S⁺
t-Bu
N

9


5.80
5.78
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5.76
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5.72
5.71
5.69
5.09
5.08
5.07
5.04
4.82
4.69
3.05
3.04
3.02
3.01
2.99
2.97
2.38
2.35
2.23
2.21
2.20
2.19
1.79
1.76
1.75
1.73
1.66
1.27
1.00
2.00
1.00
1.00
1.00
1.00
3.00
4.00
3.00
9.00
7.0
6.5
6.0
5.5
5.0
4.5
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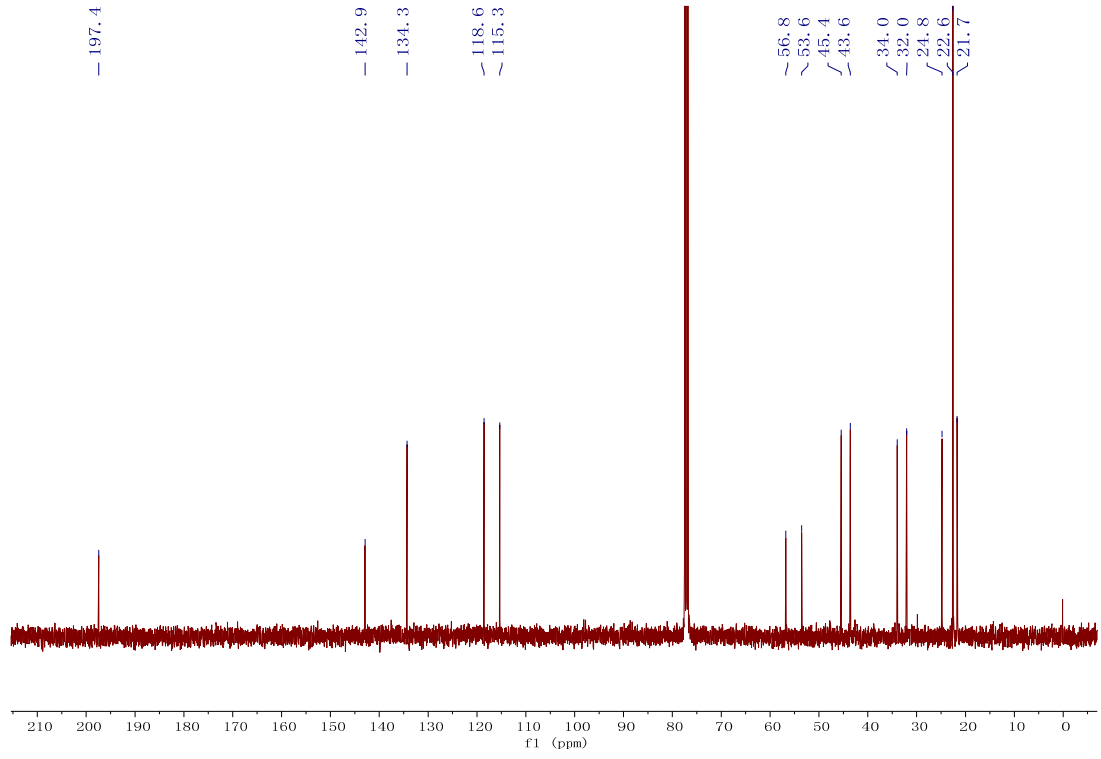
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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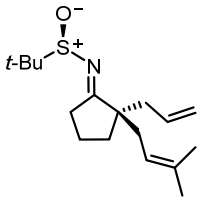
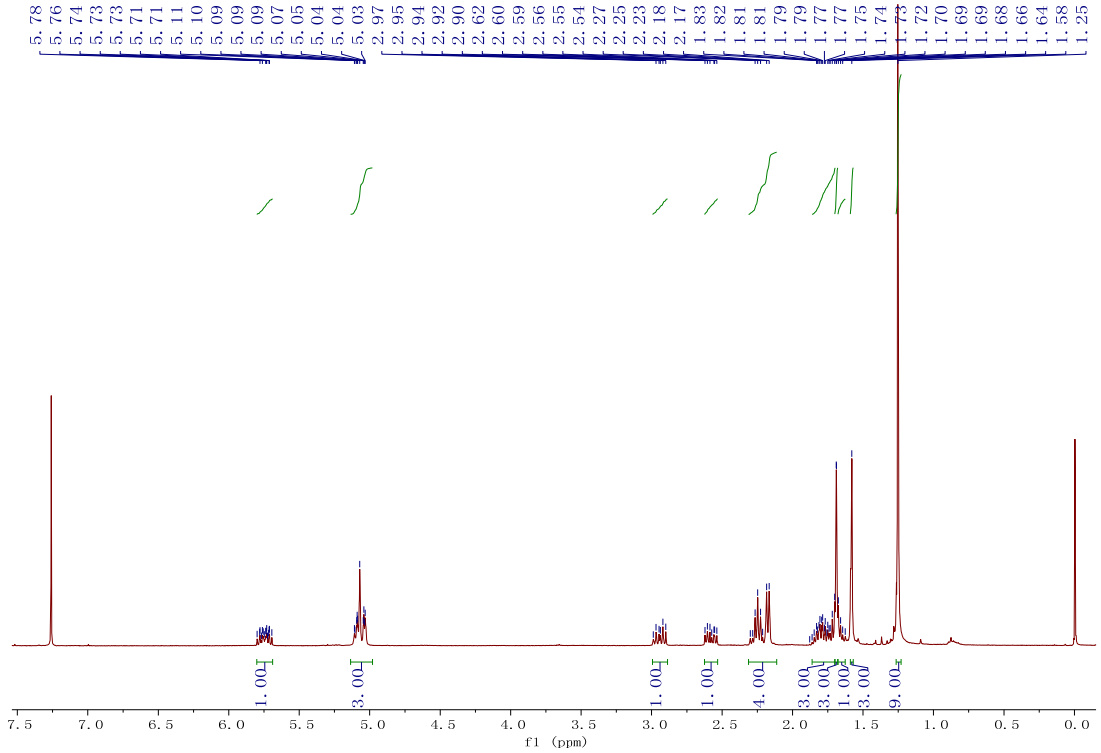
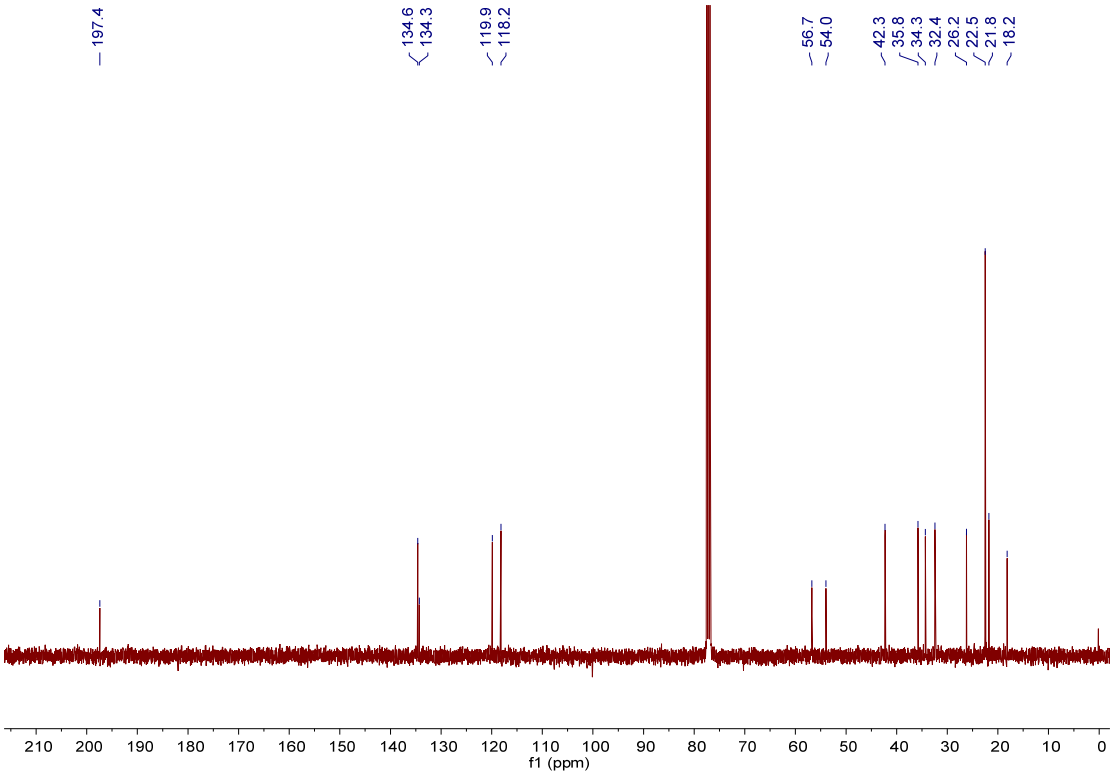
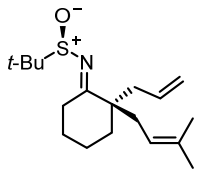
142.9
134.3
118.6
115.3
56.8
53.6
45.4
43.6
34.0
32.0
24.8
22.6
21.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O⁻
S⁺
N
t-Bu

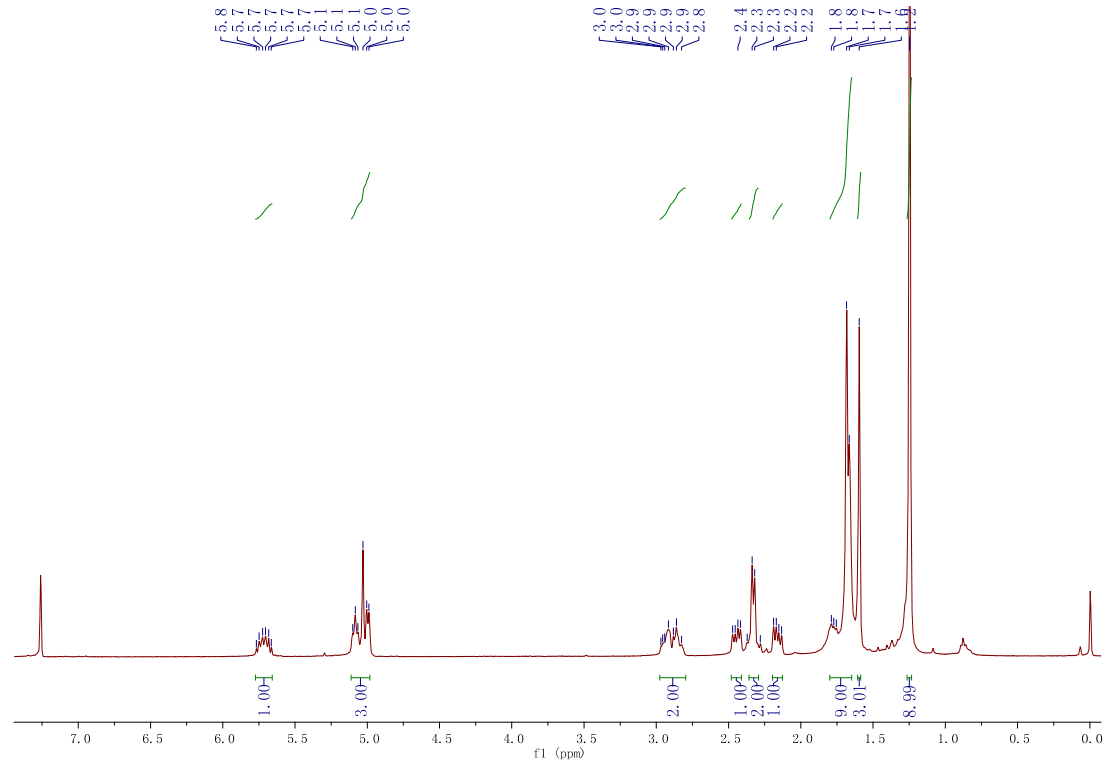
10


5.78 5.76 5.74 5.73 5.73 5.71 5.71 5.11 5.10 5.09 5.09 5.09 5.07 5.05 5.04 5.04 5.03 2.97 2.95 2.94 2.92 2.90 2.62 2.60 2.59 2.56 2.55 2.54 2.27 2.25 2.23 2.18 2.17 1.83 1.82 1.81 1.81 1.79 1.79 1.77 1.77 1.75 1.74 1.73 1.72 1.70 1.69 1.69 1.68 1.66 1.64 1.58 1.25
1.00 3.00 1.00 1.00 4.00 3.00 3.00 1.00 3.00 9.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.4
134.6
134.3
119.9
118.2
56.7
54.0
42.3
35.8
34.3
32.4
26.2
22.5
21.8
18.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
S
N
t-Bu

11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5.0
5.0
3.0
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2.9
2.9
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2.3
2.2
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1.8
1.7
1.7
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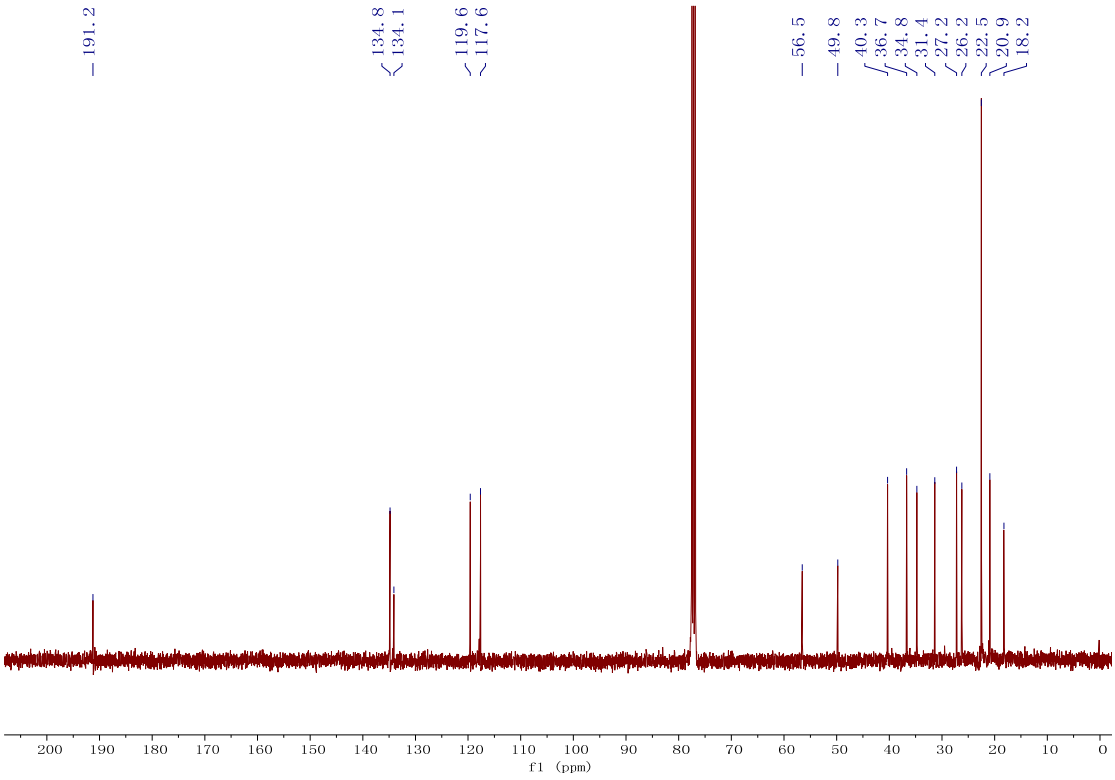
3.00
2.00
1.00
2.00
1.00
9.00
3.01
8.99
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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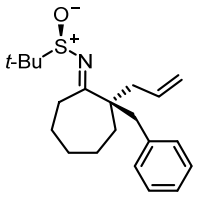
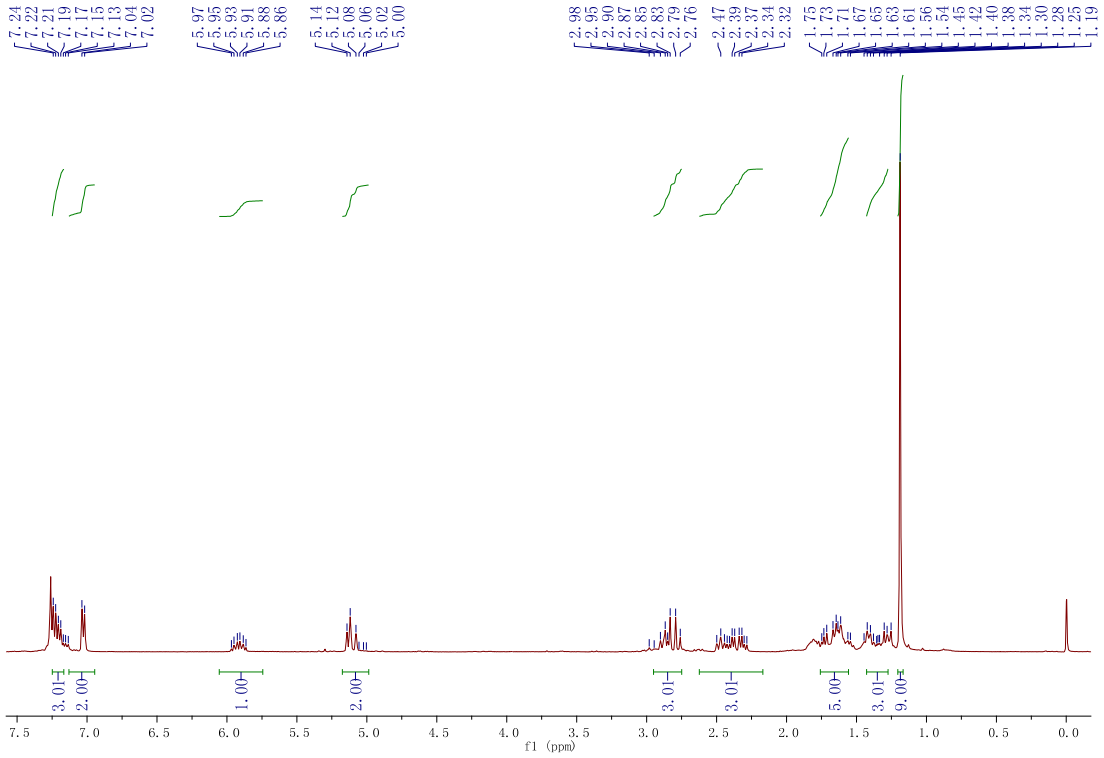
134.1
119.6
117.6
56.5
49.8
40.3
36.7
34.8
31.4
27.2
26.2
22.5
20.9
18.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
S
N
t-Bu

12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7.04
7.02
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5.95
5.93
5.91
5.88
5.86
5.14
5.12
5.08
5.06
5.02
5.00
2.98
2.95
2.90
2.87
2.85
2.83
2.79
2.76
2.47
2.39
2.37
2.34
2.32
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1.73
1.71
1.67
1.65
1.63
1.61
1.56
1.54
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1.42
1.40
1.38
1.34
1.30
1.28
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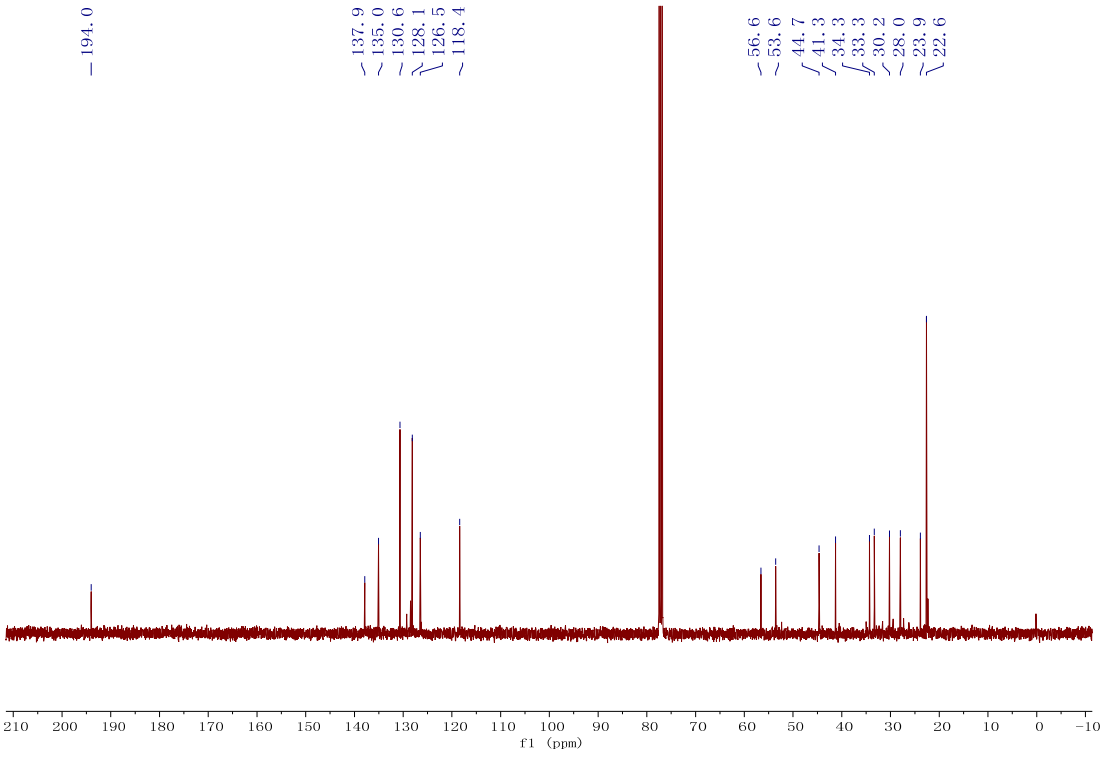
f1 (ppm)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126.5
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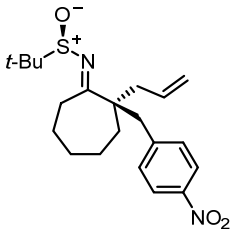
56.6
53.6
44.7
41.3
34.3
33.3
30.2
28.0
23.9
22.6
f1 (ppm)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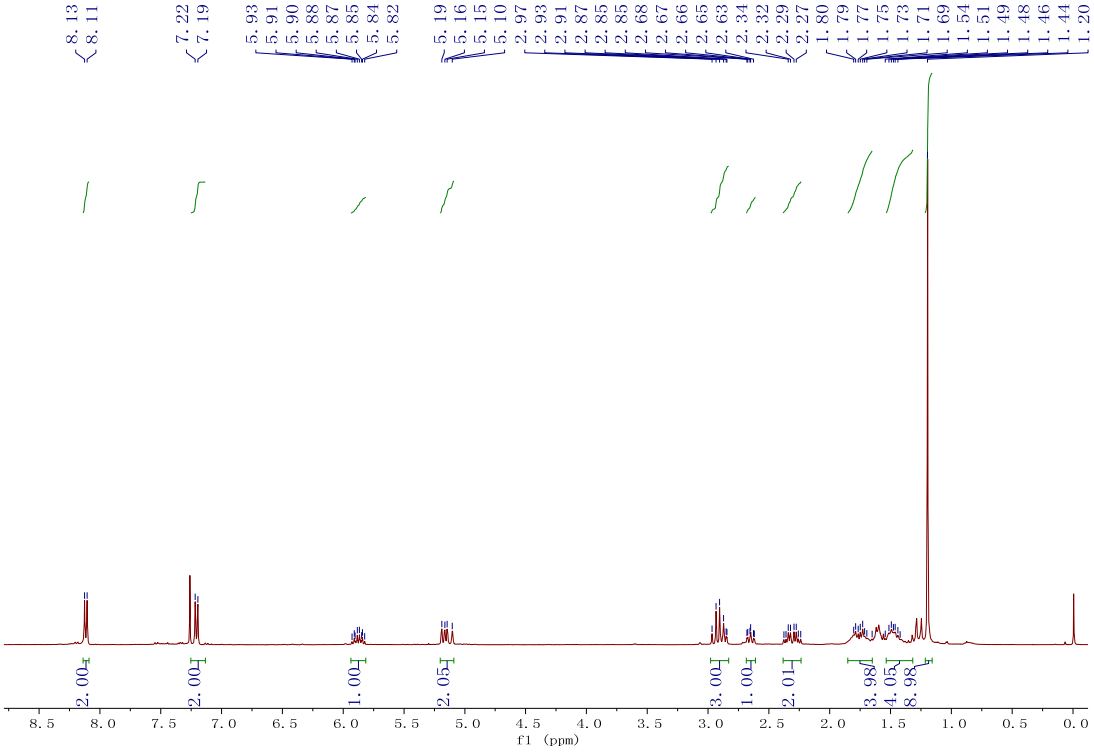
S
N
t-Bu
NO2

13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7.22
7.19
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5.91
5.90
5.88
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5.82
5.19
5.16
5.15
5.10
2.97
2.93
2.91
2.87
2.85
2.85
2.68
2.67
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2.65
2.63
2.34
2.32
2.29
2.27
1.80
1.79
1.77
1.75
1.73
1.71
1.69
1.54
1.51
1.49
1.48
1.46
1.44
1.20
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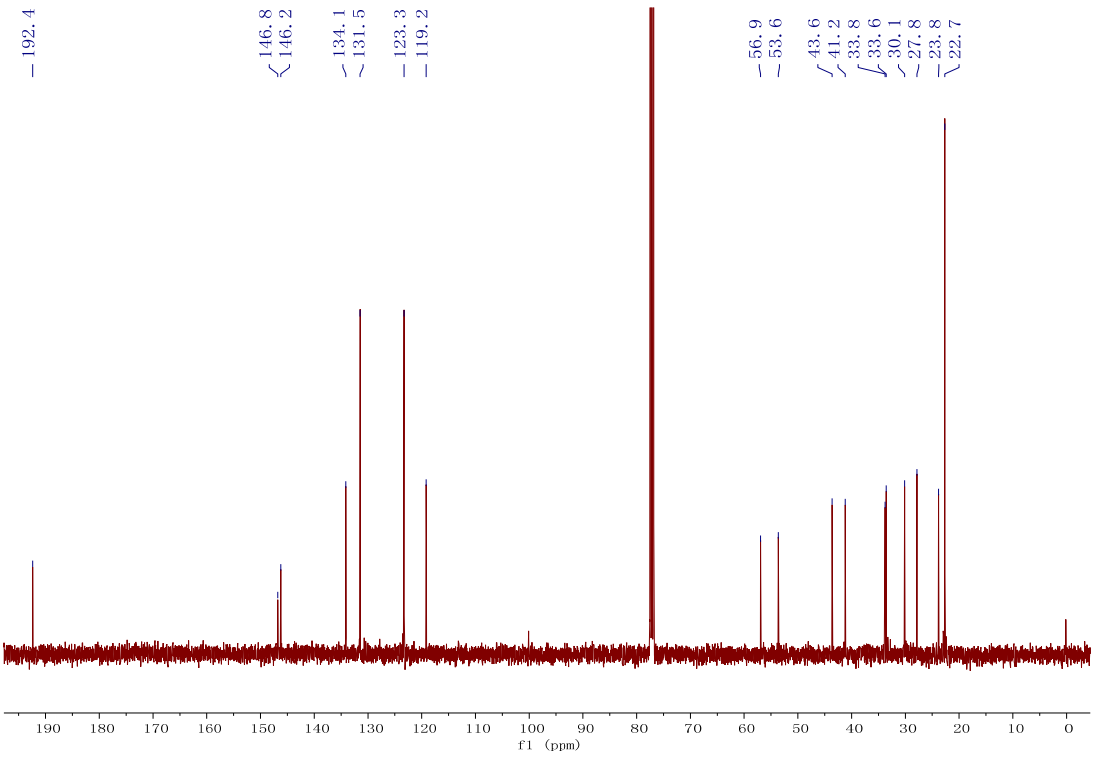
1.00
2.05
3.00
1.00
2.01
3.98
4.05
8.98
f1 (ppm)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146.8
146.2
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123.3
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56.9
53.6
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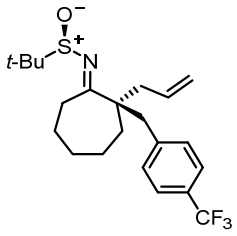
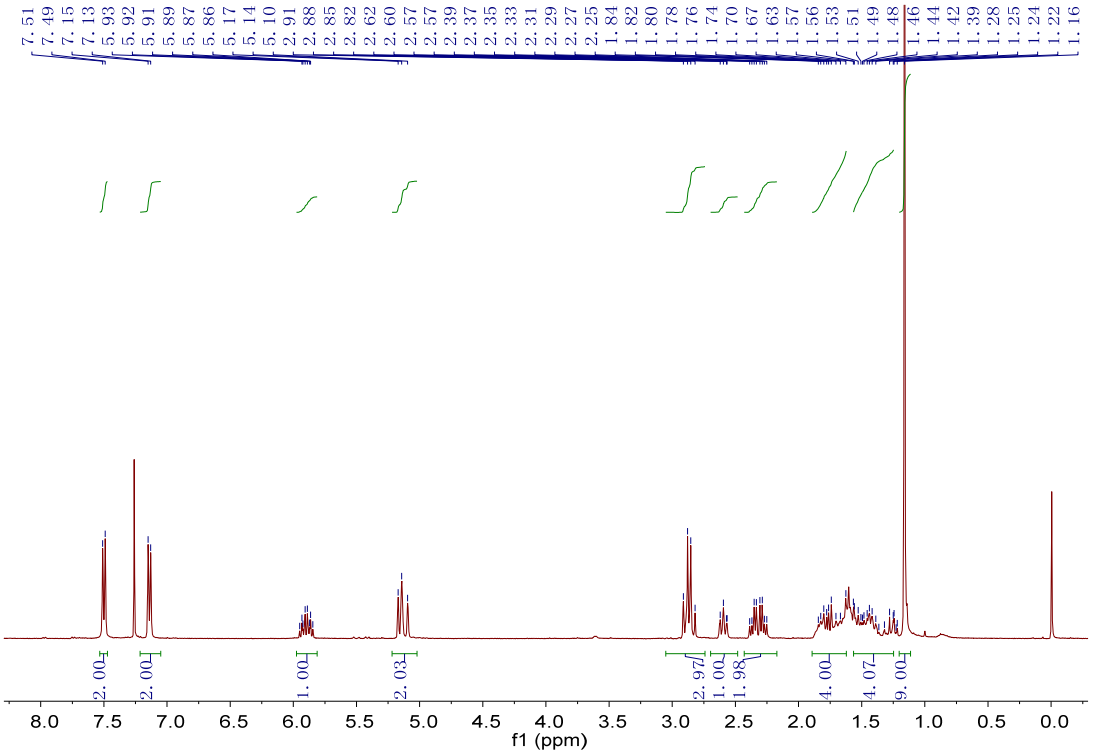
41.2
33.8
33.6
30.1
27.8
23.8
22.7
f1 (ppm)


O
S
N
t-Bu
CF3

14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5.92
5.91
5.89
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5.86
5.17
5.14
5.10
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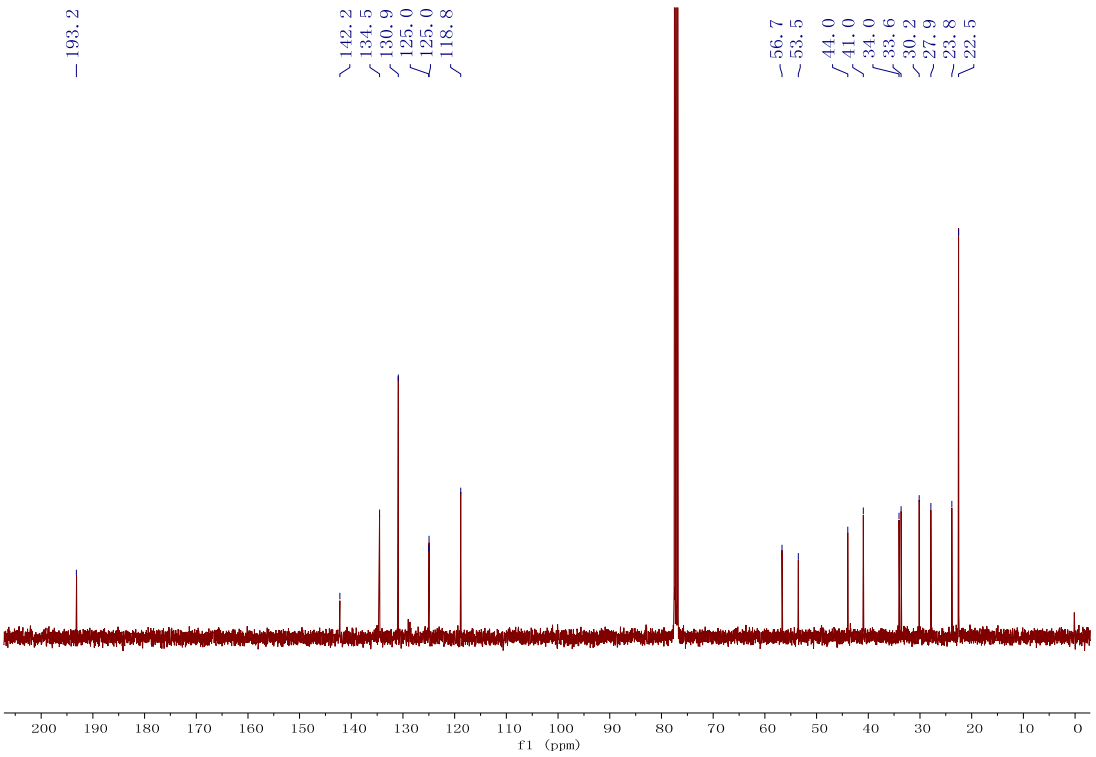
2.88
2.85
2.82
2.62
2.60
2.57
2.57
2.39
2.37
2.35
2.33
2.31
2.29
2.27
2.25
1.84
1.82
1.80
1.78
1.76
1.74
1.70
1.67
1.63
1.57
1.56
1.53
1.51
1.49
1.48
1.46
1.44
1.42
1.39
1.28
1.25
1.24
1.22
1.16
2.00
2.00
1.00
2.03
2.97
1.00
1.98
4.00
4.07
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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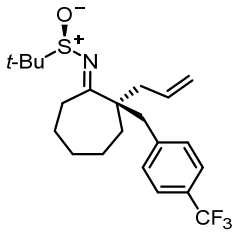
125.0
118.8
56.7
53.5
44.0
41.0
34.0
33.6
30.2
27.9
23.8
22.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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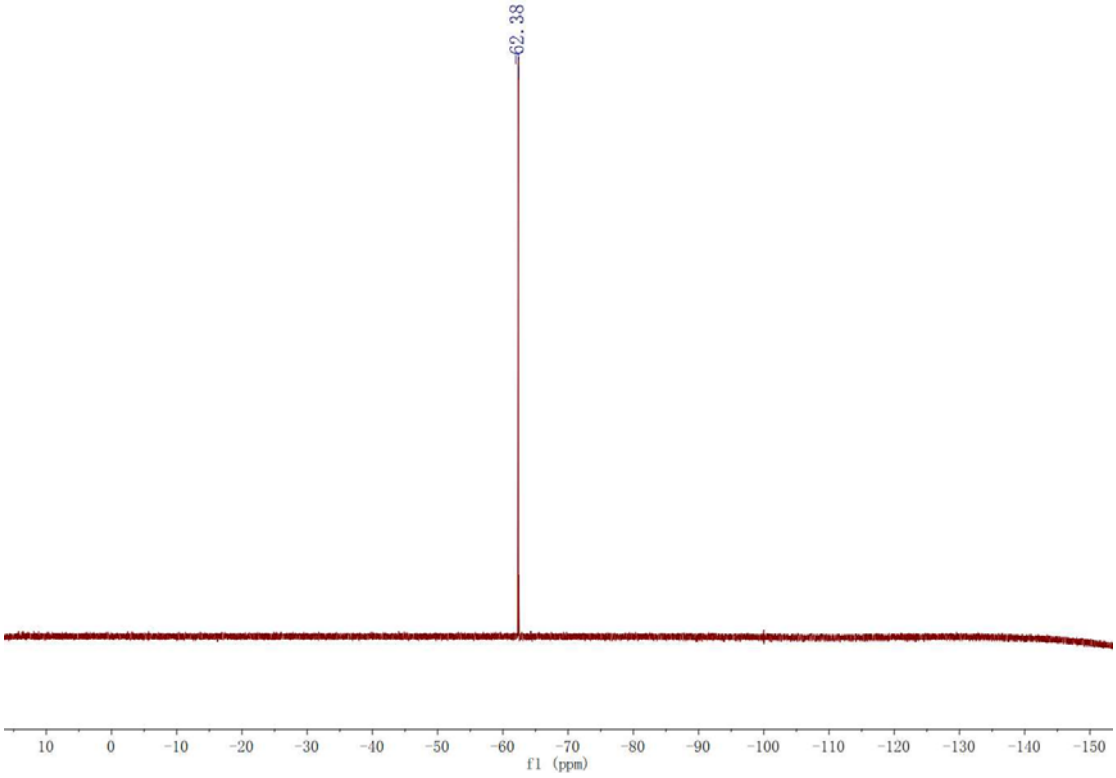
S
N
t-Bu
CF3

14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-10
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-50
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-70
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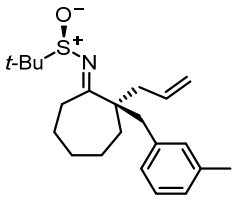
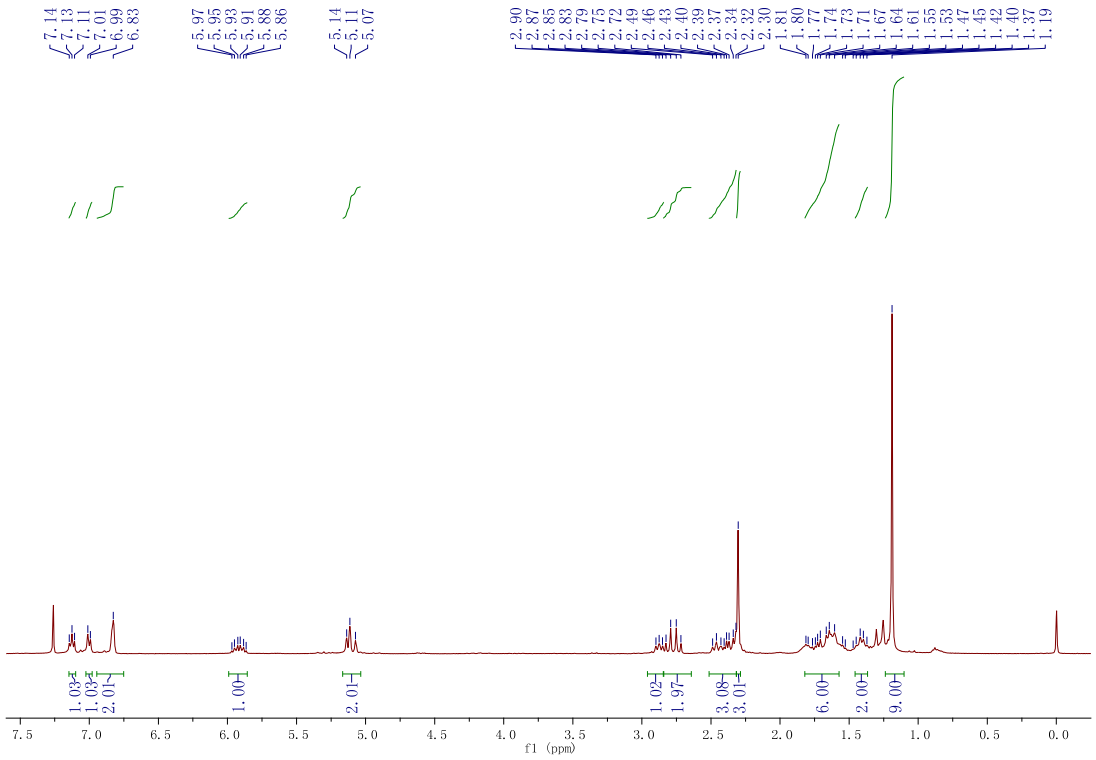
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


O
S
N
t-Bu

15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5.97
5.95
5.93
5.91
5.88
5.86
5.14
5.11
5.07
2.90
2.87
2.85
2.83
2.79
2.75
2.72
2.49
2.46
2.43
2.40
2.39
2.37
2.34
2.32
2.30
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1.80
1.77
1.74
1.73
1.71
1.67
1.64
1.61
1.55
1.53
1.47
1.45
1.42
1.40
1.37
1.19
1.03
1.03
2.01
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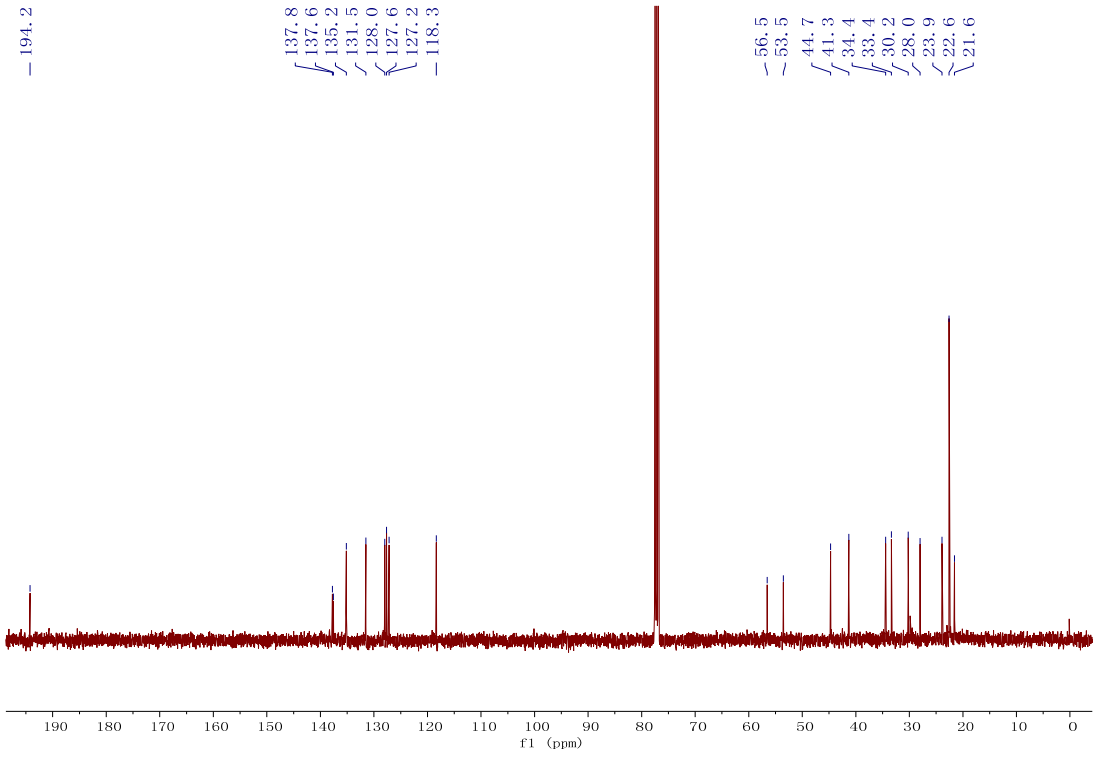
2.01
1.02
1.97
3.08
3.01
6.00
2.00
9.00
f1 (ppm)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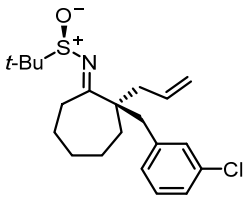
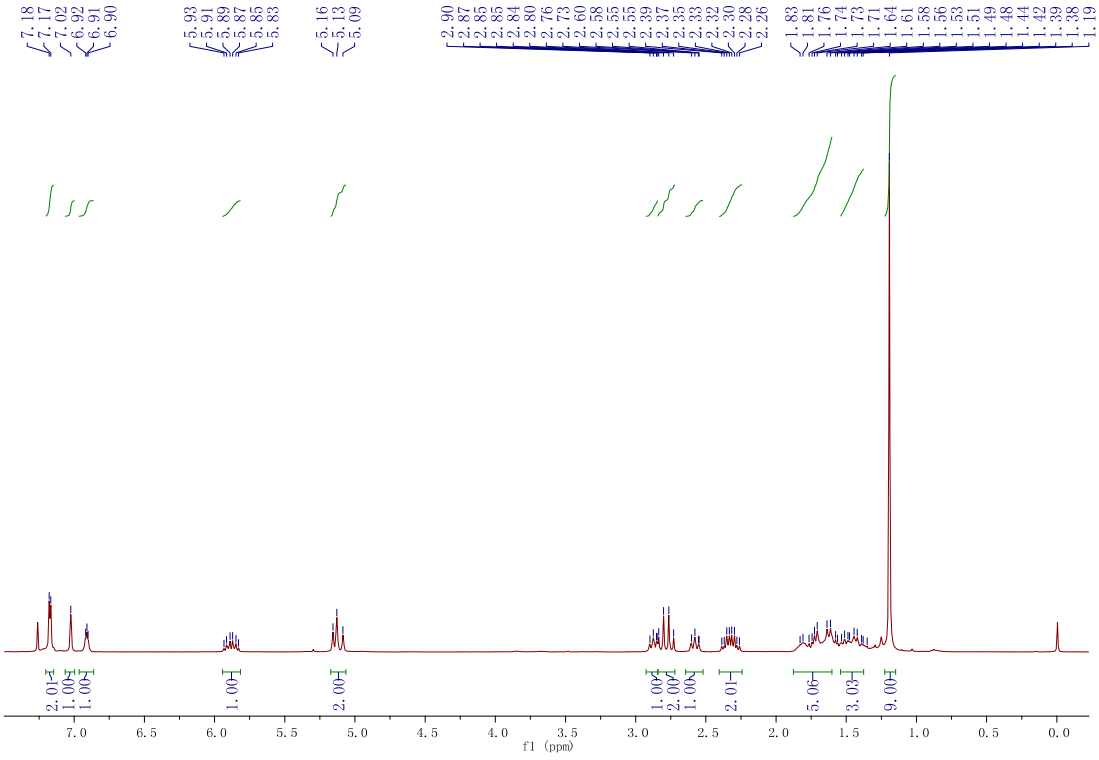
137.6
135.2
131.5
128.0
127.6
127.2
118.3
56.5
53.5
44.7
41.3
34.4
33.4
30.2
28.0
23.9
22.6
21.6
f1 (ppm)


O
S
N
t-Bu
Cl

16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6.90
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5.91
5.89
5.87
5.85
5.83
5.16
5.13
5.09
2.90
2.87
2.85
2.85
2.84
2.80
2.76
2.73
2.60
2.58
2.55
2.55
2.39
2.37
2.35
2.33
2.32
2.30
2.28
2.26
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1.81
1.76
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1.73
1.71
1.64
1.61
1.58
1.56
1.53
1.51
1.49
1.48
1.44
1.42
1.39
1.38
1.19
2.01
1.00
1.00
1.00
2.00
1.00
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3.03
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6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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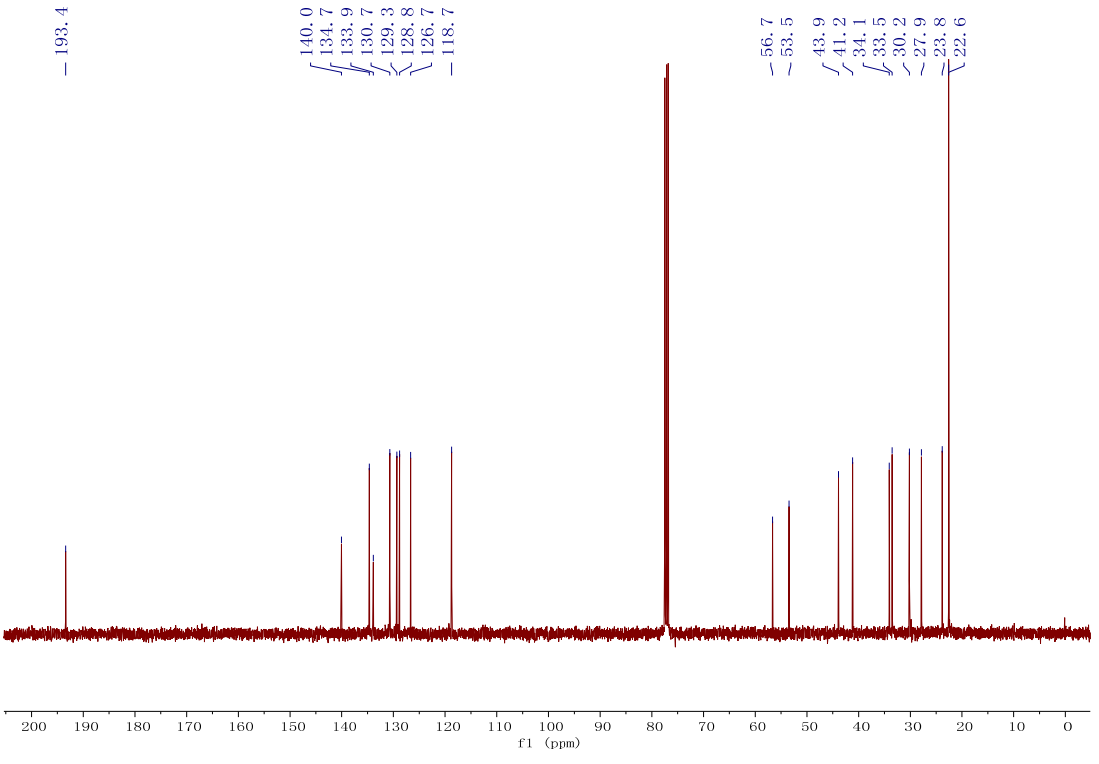
0.0
f1 (ppm)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133.9
130.7
129.3
128.8
126.7
118.7
56.7
53.5
43.9
41.2
34.1
33.5
30.2
27.9
23.8
22.6
200
190
180
170
160
150
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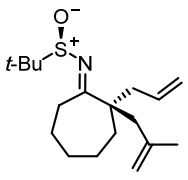
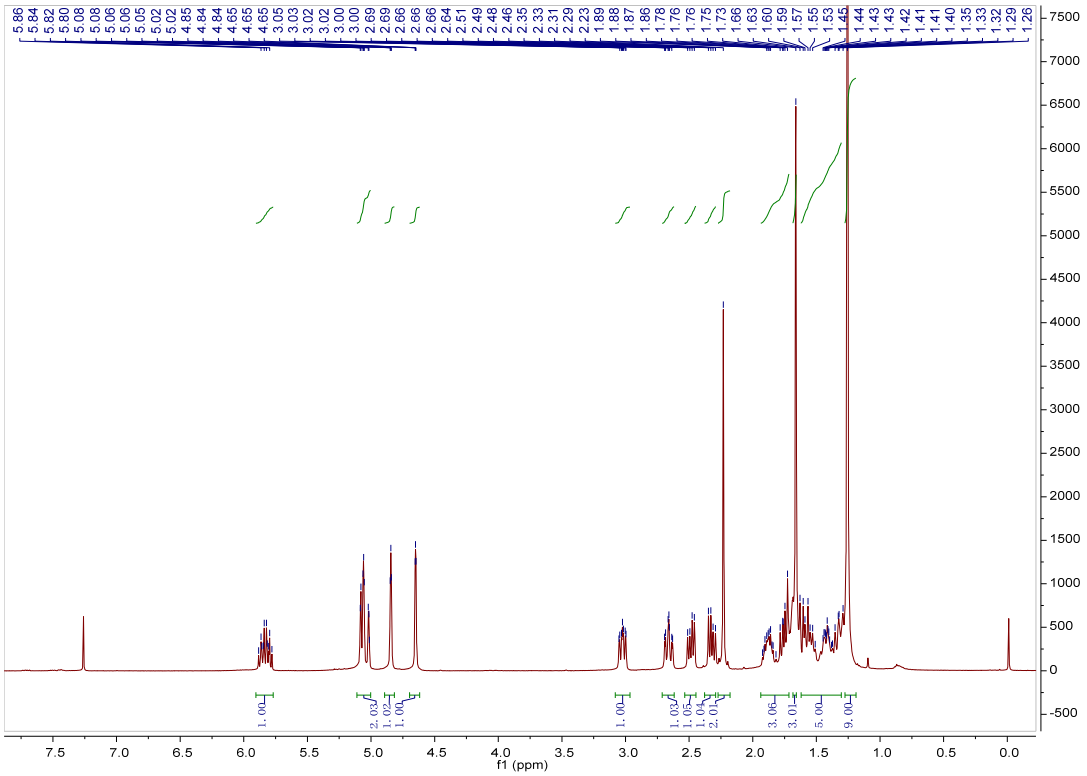
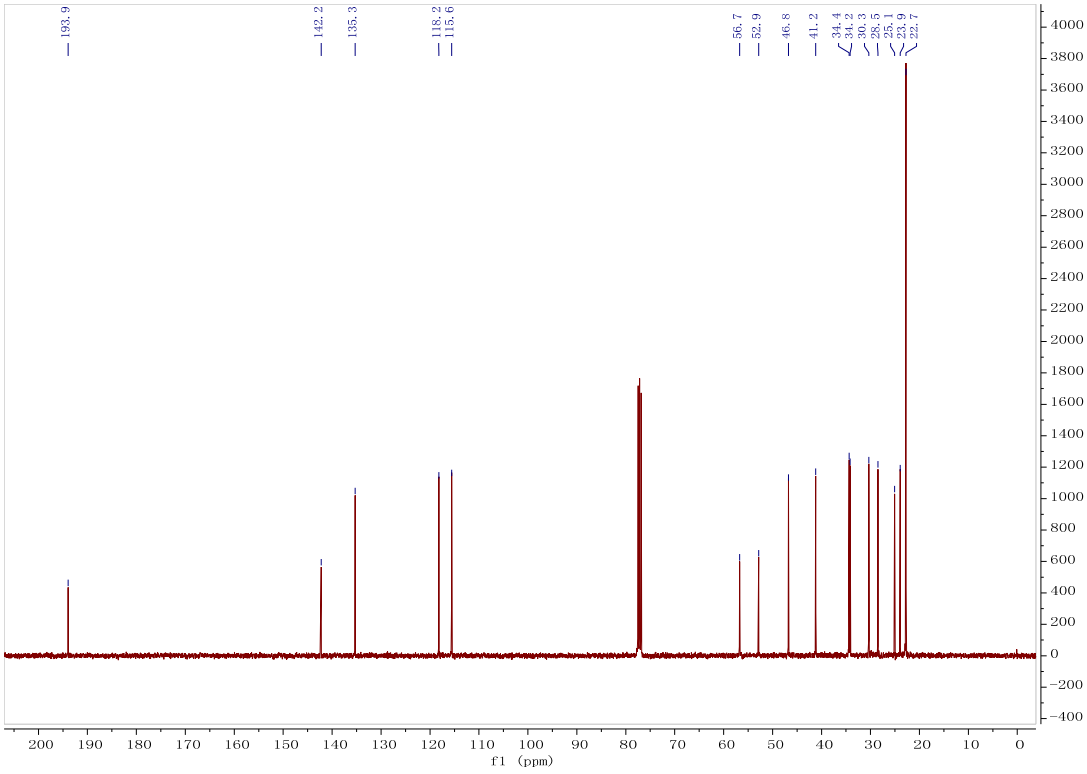
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
S
N
t-Bu

17


f1 (ppm)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118.2
115.6
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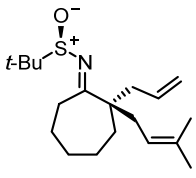
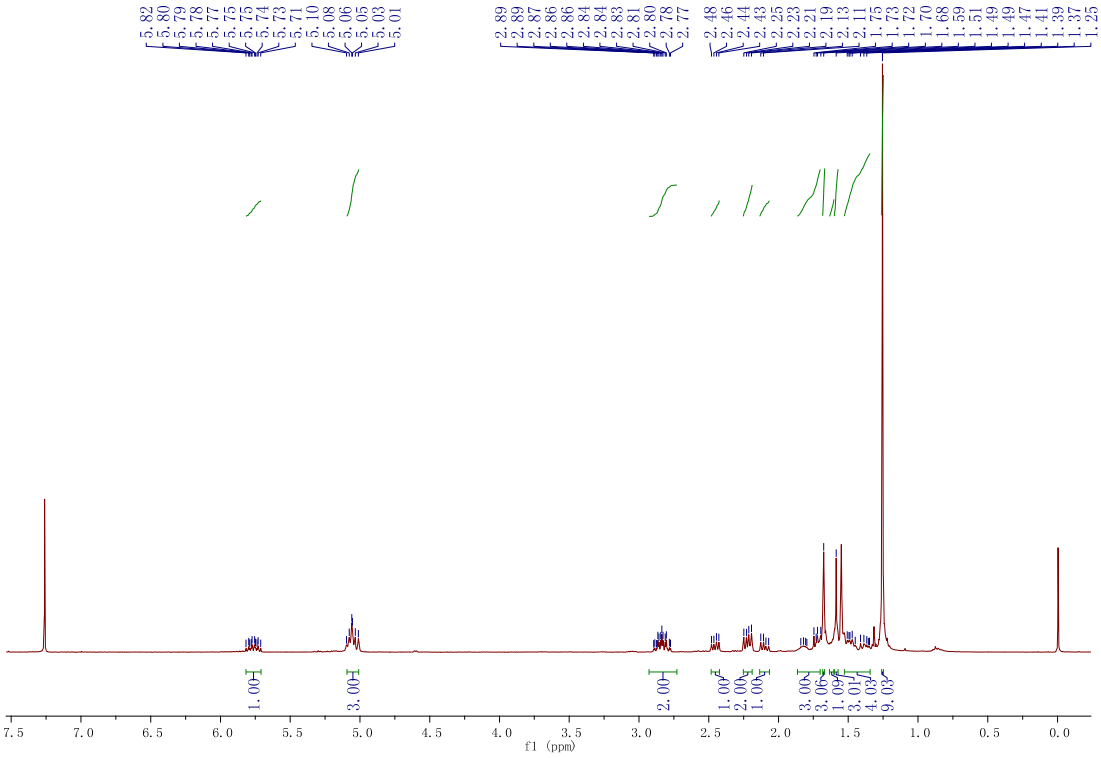
52.9
46.8
41.2
34.4
34.2
30.3
28.5
25.1
23.9
22.7
f1 (ppm)


O
S
N
t-Bu

18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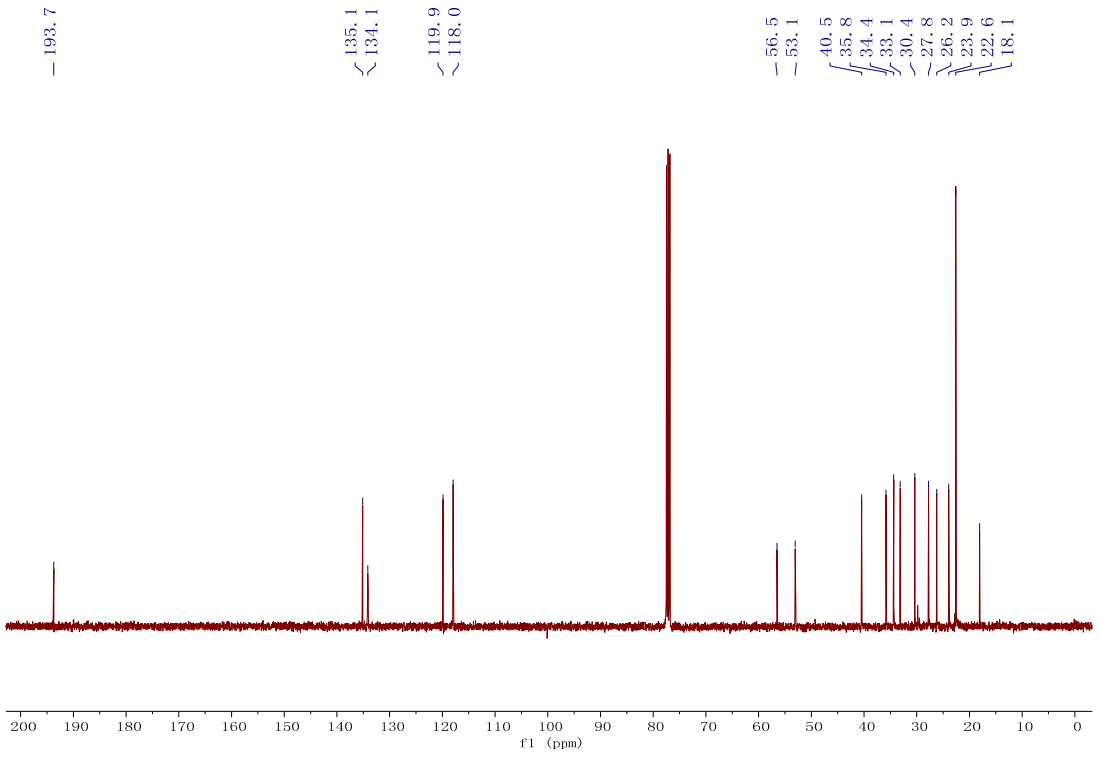
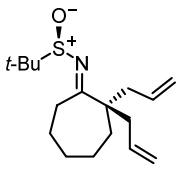
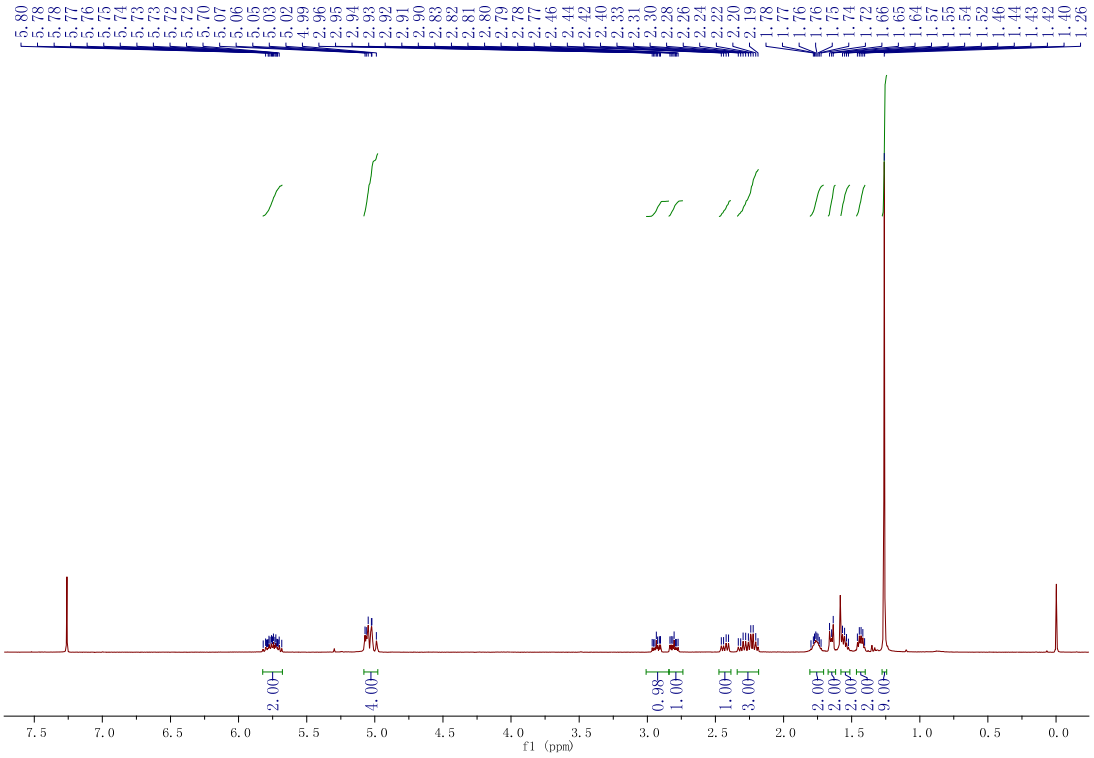
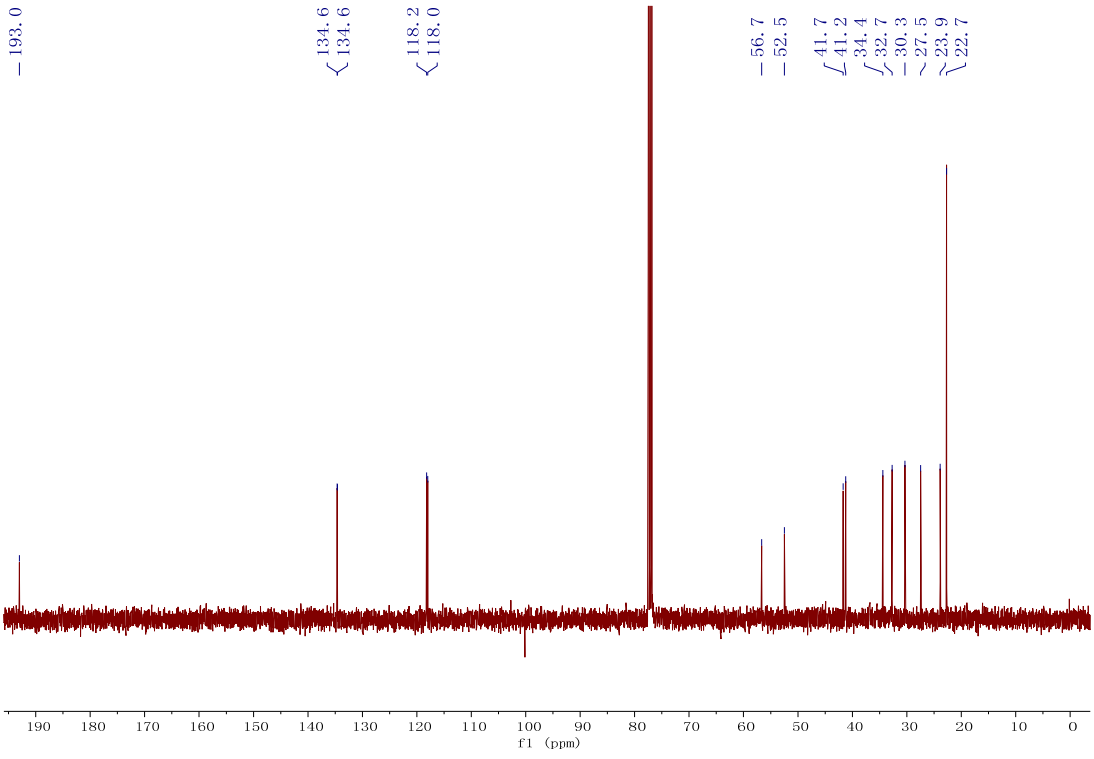
2.89 2.89 2.87 2.86 2.86 2.84 2.84 2.83 2.81 2.80 2.78 2.77 2.48 2.46 2.44 2.43 2.25 2.23 2.21 2.19 2.13 2.11 1.75 1.73 1.72 1.70 1.68 1.59 1.51 1.49 1.49 1.47 1.41 1.39 1.37 1.25
1.00 3.00 2.00 1.00 2.00 1.00 3.06 3.06 1.09 3.01 4.03 9.03
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

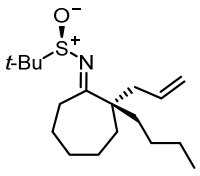

193.7
135.1 134.1 119.9 118.0
56.5 53.1 40.5 35.8 34.4 33.1 30.4 27.8 26.2 23.9 22.6 18.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
S
N
t-Bu

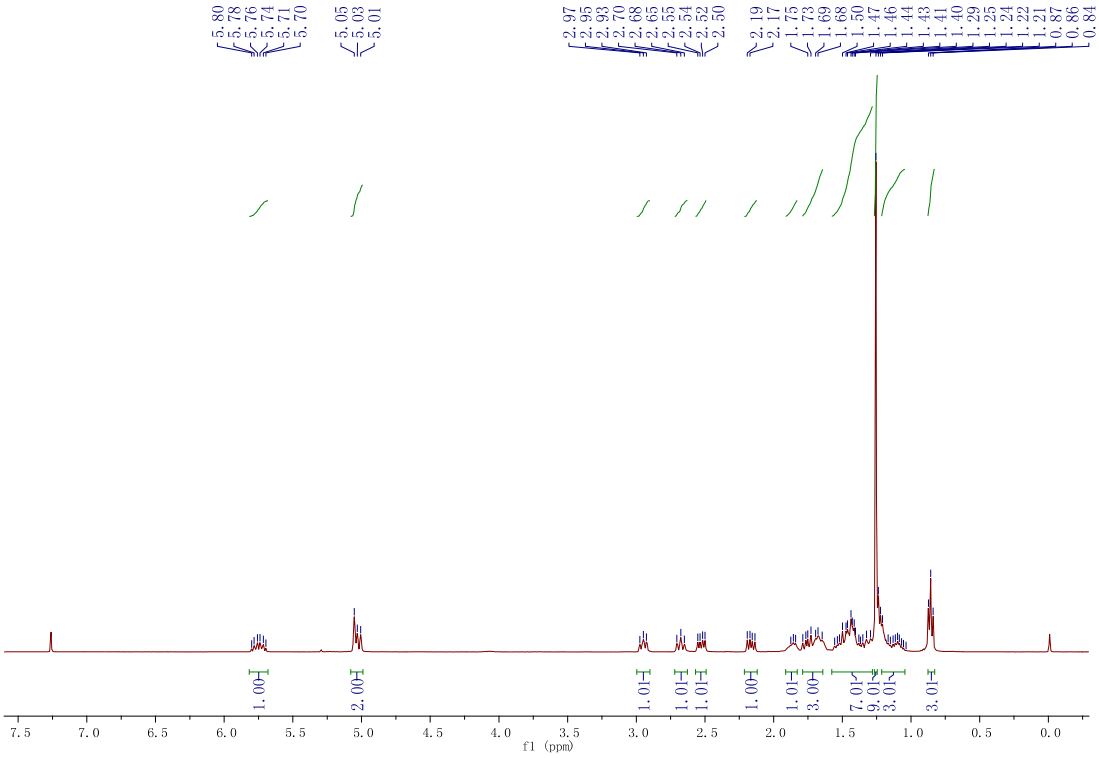
19


5.80 5.78 5.78 5.77 5.76 5.75 5.74 5.73 5.73 5.72 5.72 5.70 5.07 5.06 5.05 5.03 5.02 4.99 2.96 2.95 2.94 2.93 2.92 2.91 2.90 2.83 2.82 2.81 2.80 2.79 2.78 2.77 2.46 2.44 2.42 2.40 2.33 2.31 2.30 2.28 2.26 2.24 2.22 2.20 2.19 1.78 1.77 1.76 1.76 1.75 1.74 1.72 1.66 1.65 1.64 1.57 1.55 1.54 1.52 1.46 1.44 1.43 1.42 1.40 1.26
2.00 4.00 0.98 1.00 1.00 3.00 2.00 2.00 2.00 2.00 9.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


193.0
134.6 134.6
118.2 118.0
56.7 52.5
41.7 41.2 34.4 32.7 30.3 27.5 23.9 22.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
S
N
t-Bu

20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5.05
5.03
5.01
2.97
2.95
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1.50
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1.44
1.43
1.41
1.40
1.29
1.25
1.24
1.22
1.21
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0.86
0.84
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2.00
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1.01
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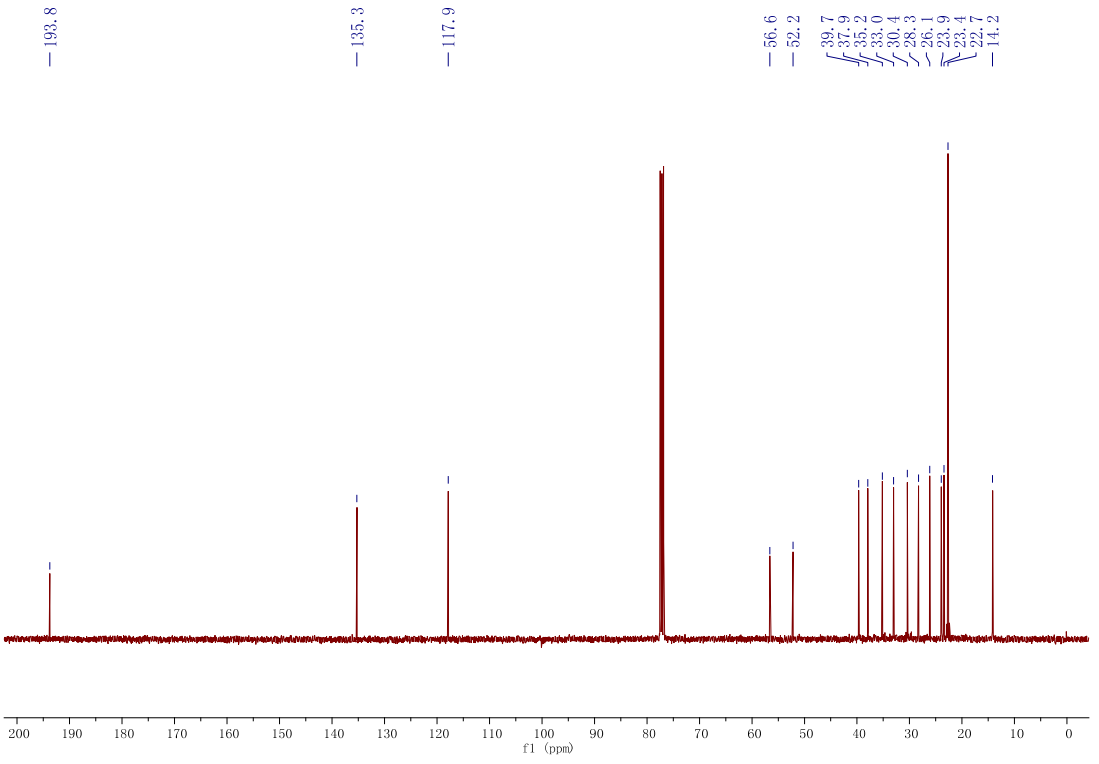
3.00
7.01
9.01
3.01
3.01
f1 (ppm)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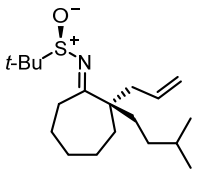
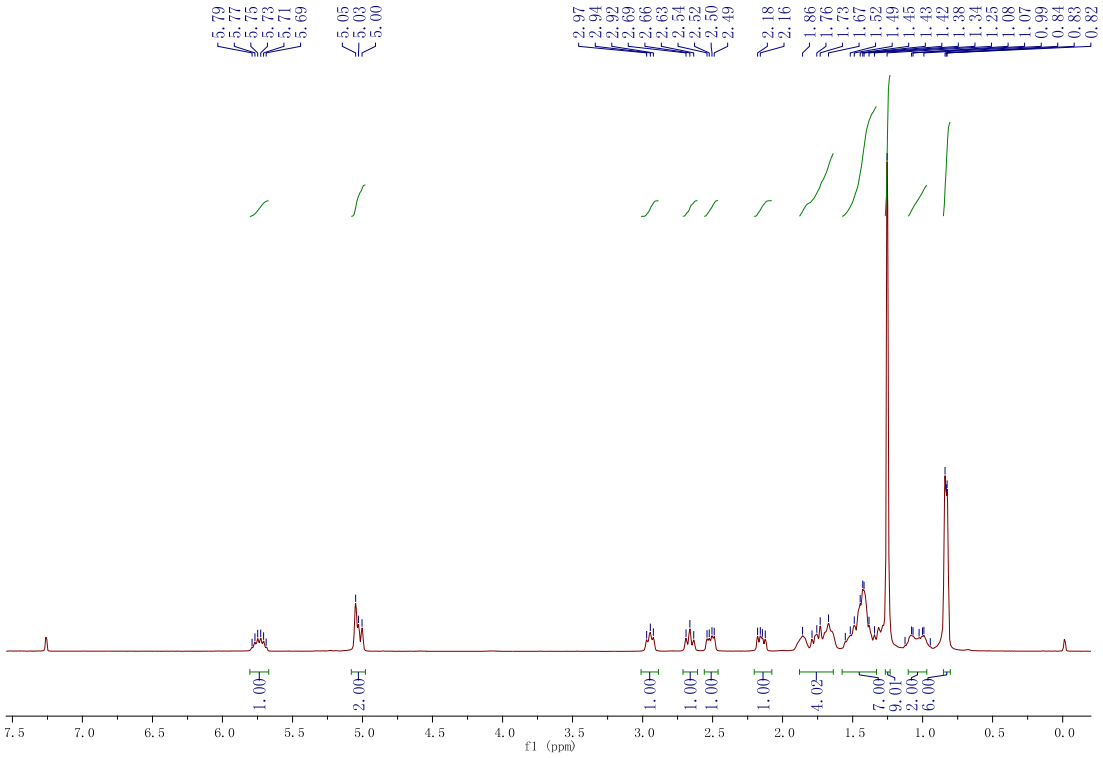
117.9
56.6
52.2
39.7
37.9
35.2
33.0
30.4
28.3
26.1
23.9
23.4
22.7
14.2
f1 (ppm)


O
S
N
t-Bu

21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5.73
5.71
5.69
5.05
5.03
5.00
2.97
2.94
2.92
2.69
2.66
2.63
2.54
2.52
2.50
2.49
2.18
2.16
1.86
1.76
1.73
1.67
1.52
1.49
1.45
1.43
1.42
1.38
1.34
1.25
1.08
1.07
0.99
0.84
0.83
0.82
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1.00
1.00
1.00
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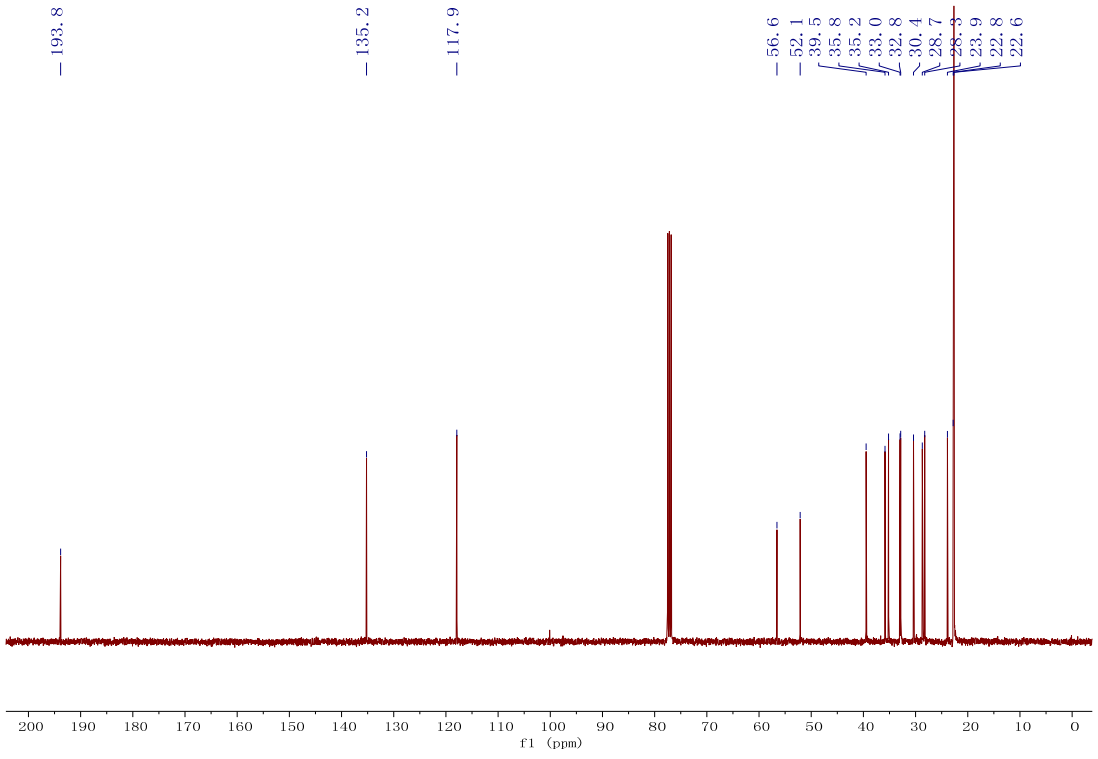
9.01
2.00
6.00
f1 (ppm)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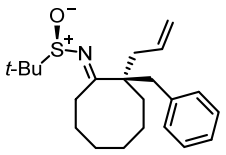
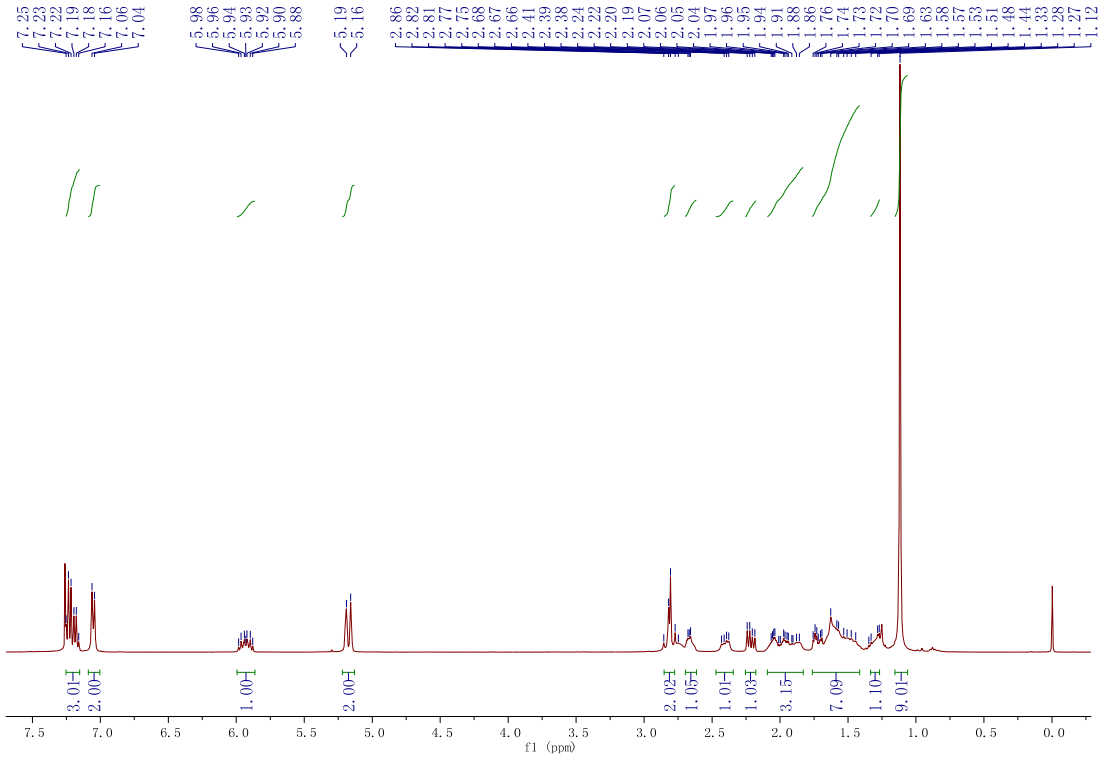
f1 (ppm)


O
S
N
t-Bu

22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5.19
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2.82
2.81
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2.66
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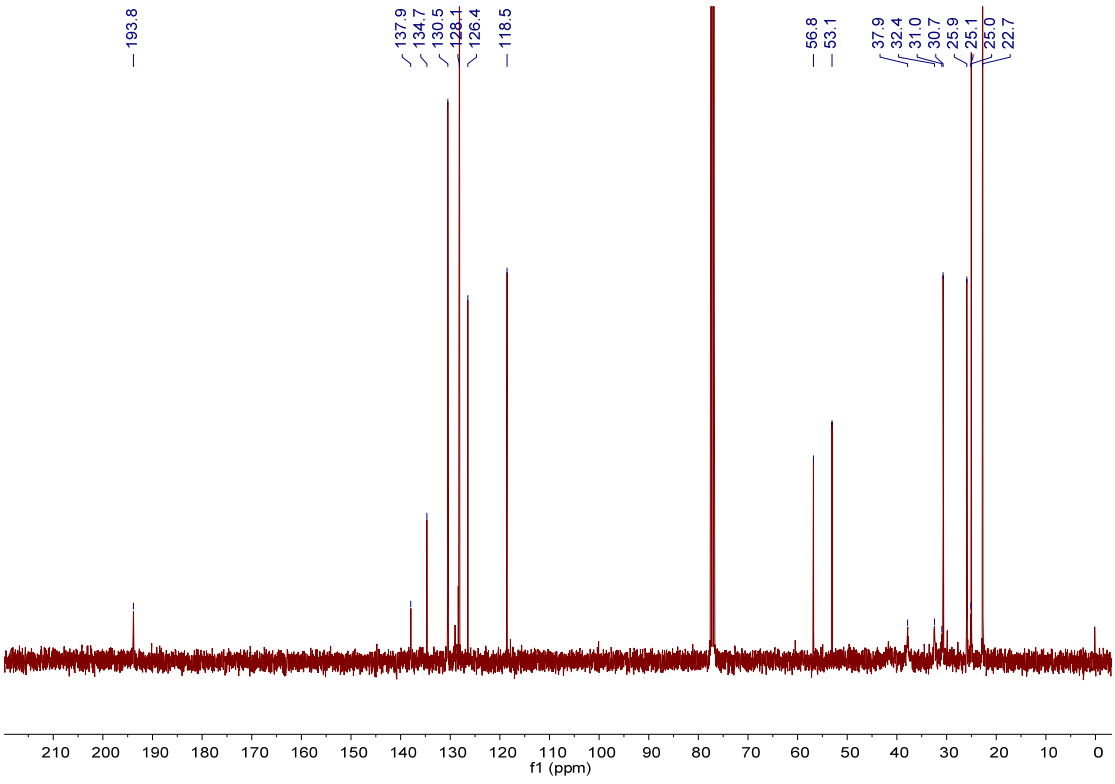
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25.0
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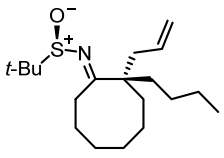
f1 (ppm)


O
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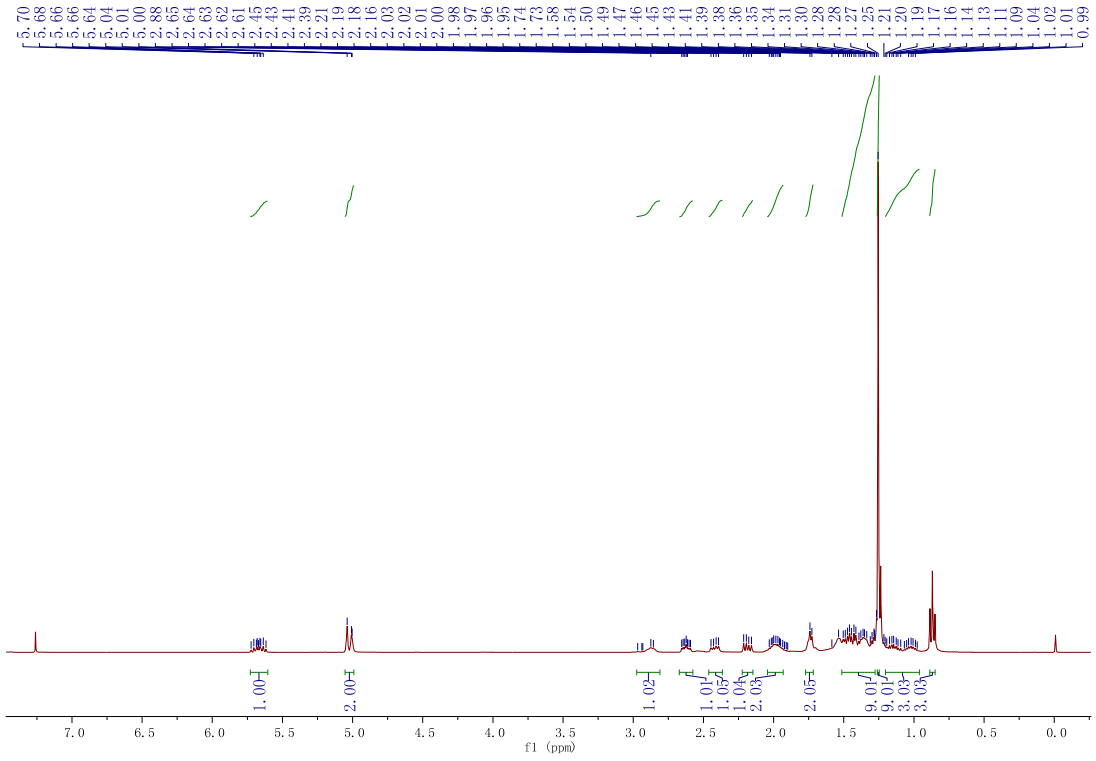
23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1.00 2.00 1.02 1.01 1.05 1.04 2.03 2.05 9.01 9.01 3.03 3.03
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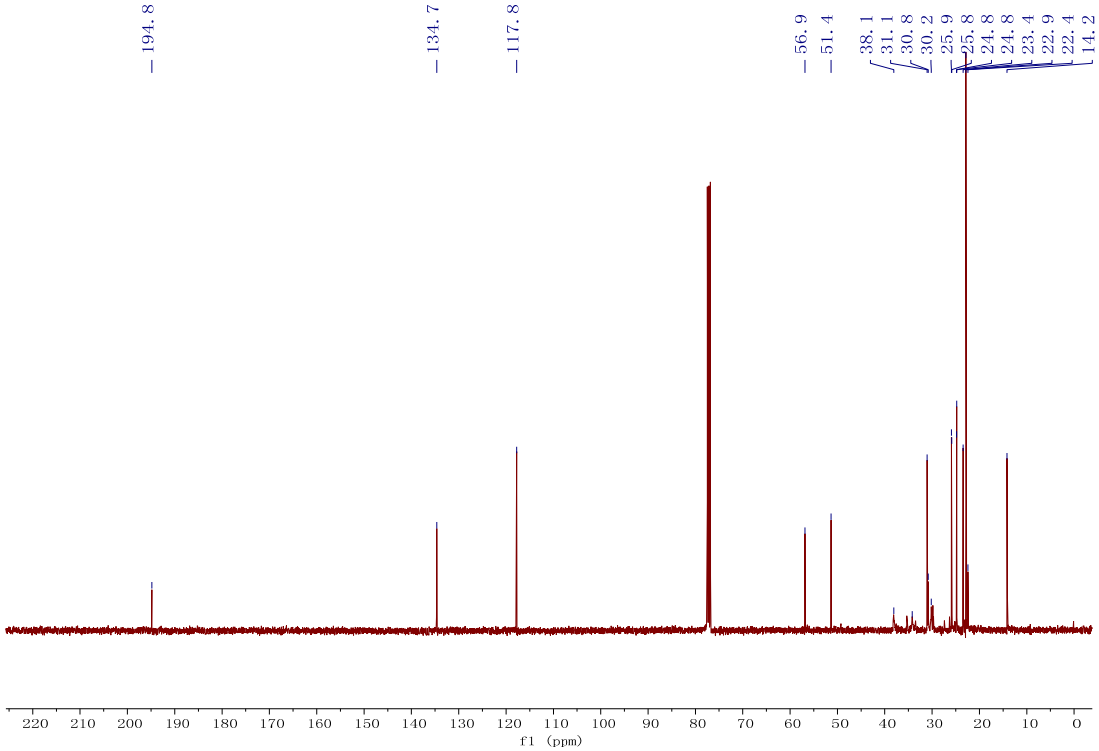
f1 (ppm)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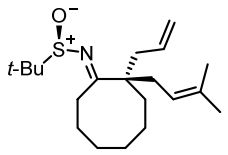
f1 (ppm)


O
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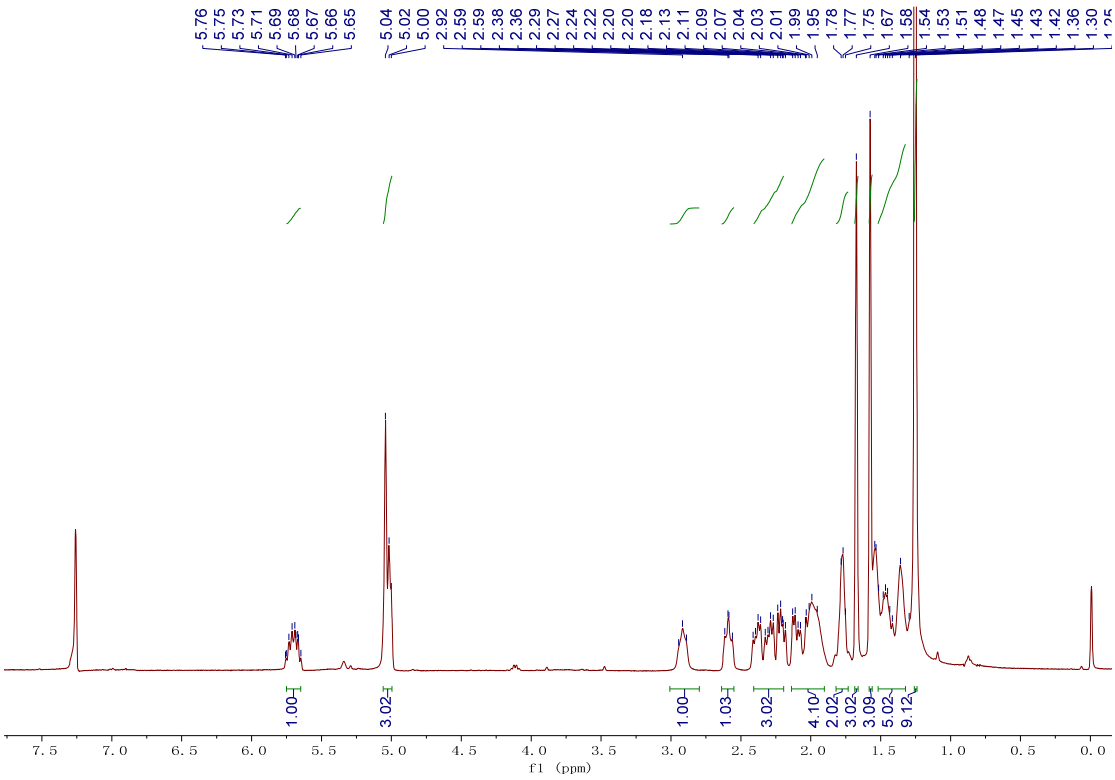
24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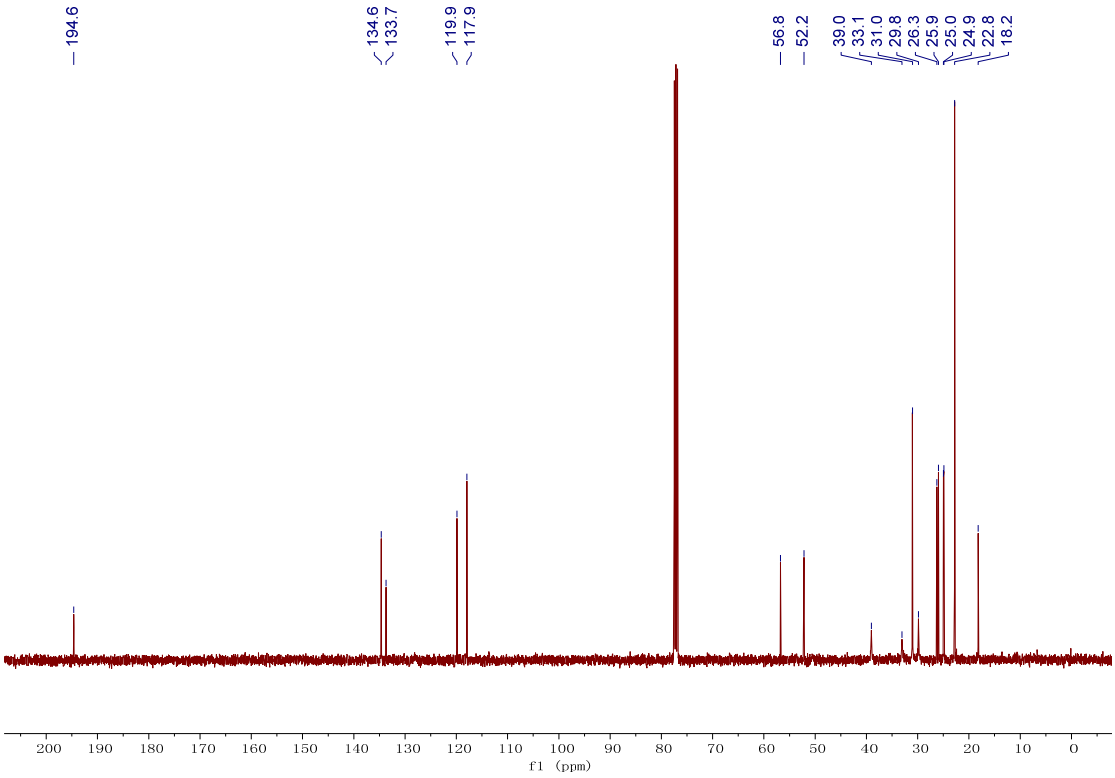
5.04 5.02 5.00 2.92 2.59 2.59 2.38 2.36 2.29 2.27 2.24 2.22 2.20 2.20 2.18 2.13 2.11 2.09 2.07 2.04 2.03 2.01 1.99 1.95 1.78 1.77 1.75 1.67 1.58 1.54 1.53 1.51 1.48 1.47 1.45 1.43 1.42 1.36 1.30
1.00 3.02 1.00 1.03 3.02 4.10 2.02 3.02 3.09 5.02 9.12
f1 (ppm)


194.6
134.6 133.7 119.9 117.9
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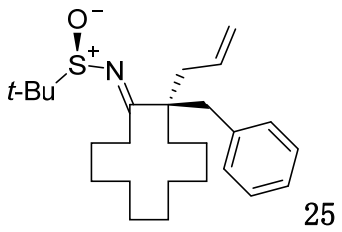
f1 (ppm)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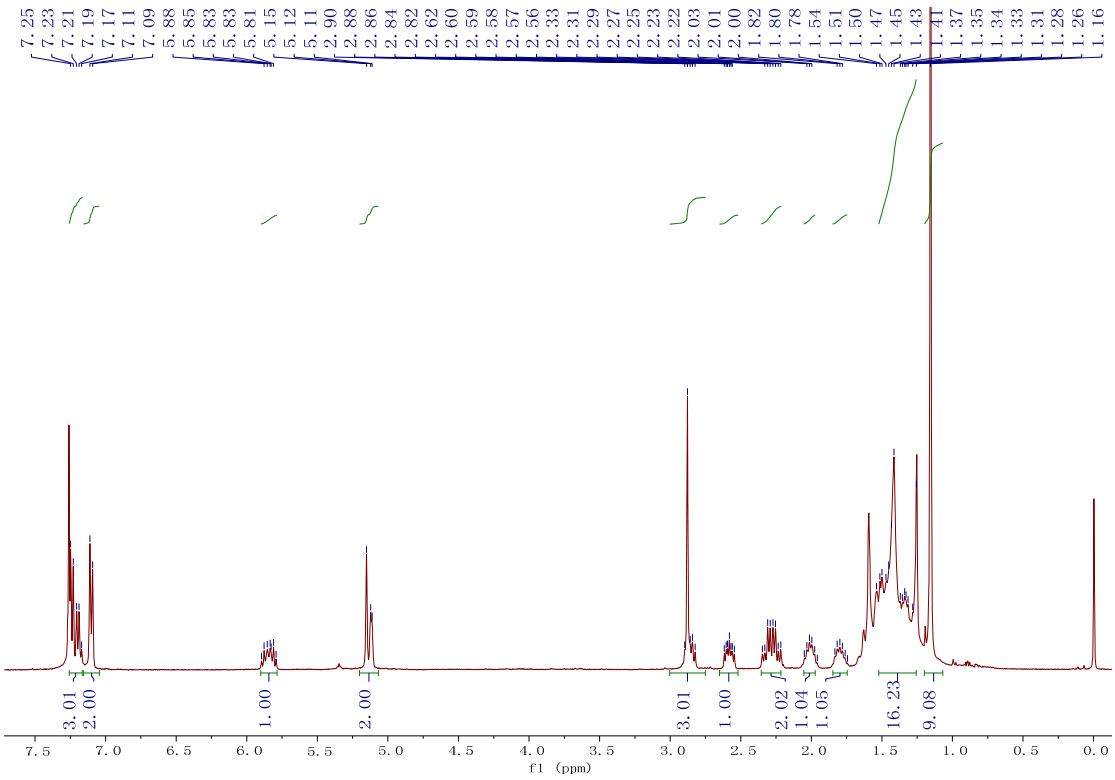
t-Bu

25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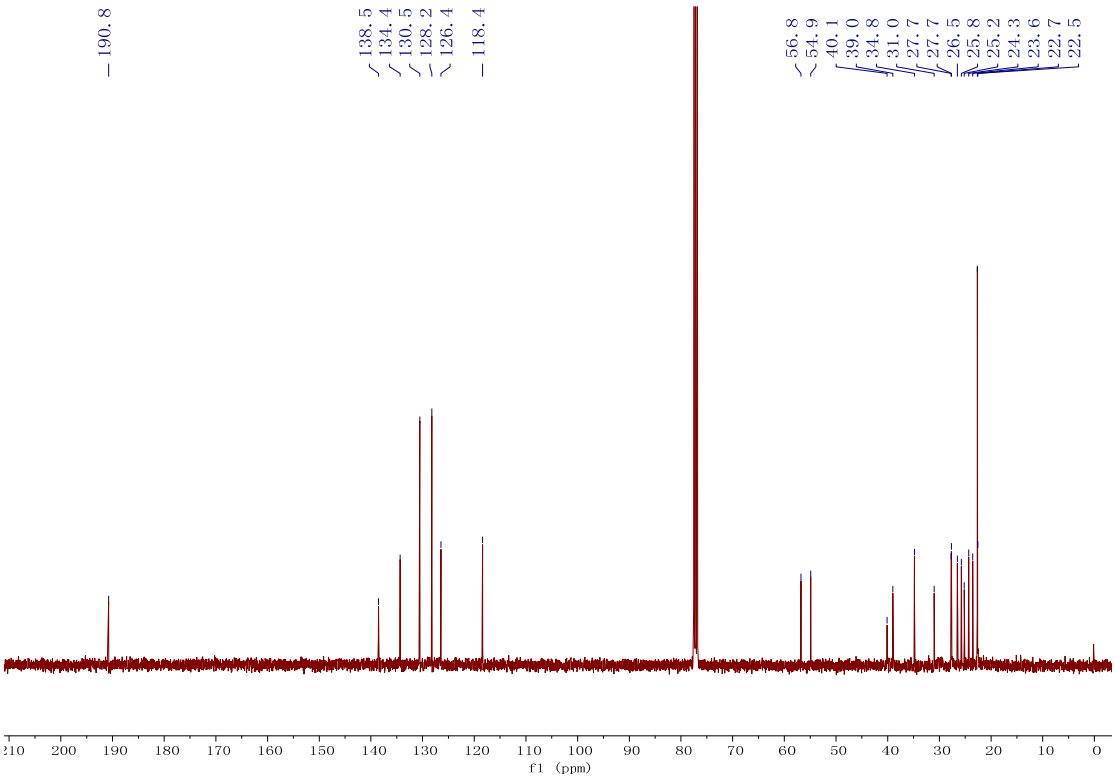
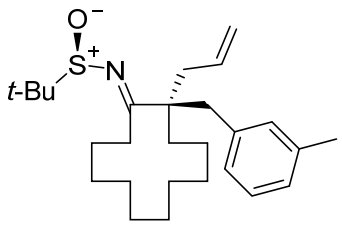

190.8
138.5 134.4 130.5 128.2 126.4 118.4
56.8 54.9 40.1 39.0 34.8 31.0 27.7 27.7 26.5 25.8 25.2 24.3 23.6 22.7 22.5
f1 (ppm)


O
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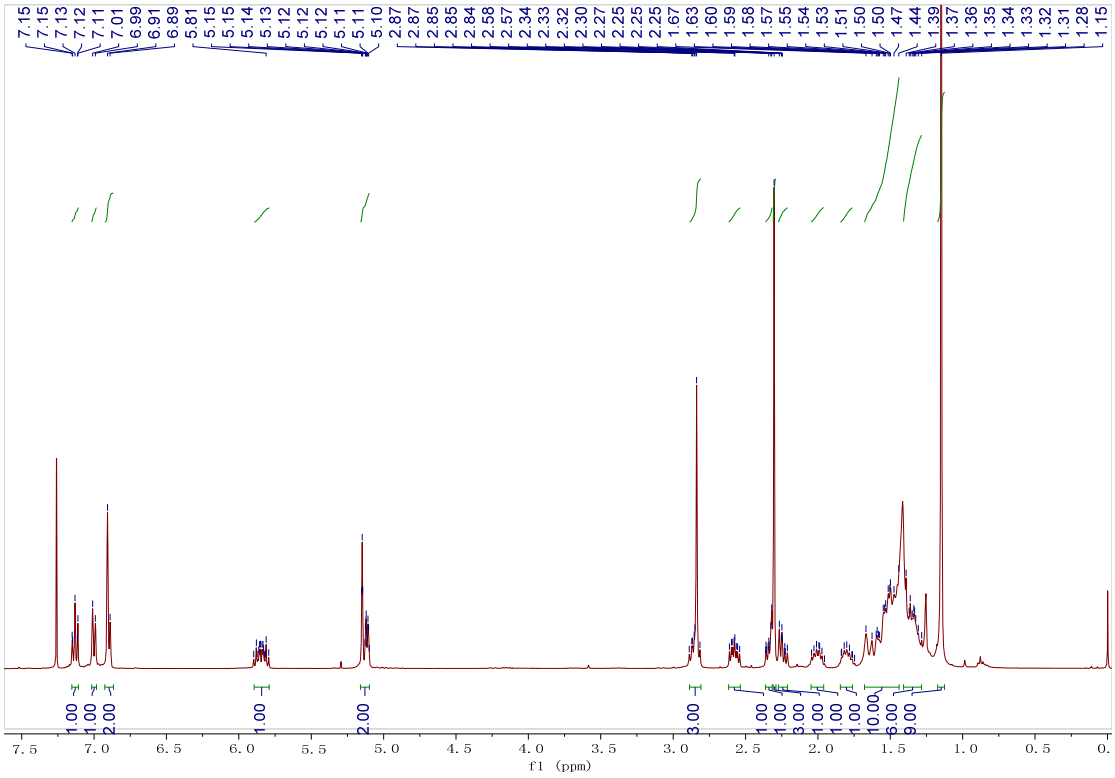
N
t-Bu

26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1.00 1.00 2.00 1.00 2.00 3.00 1.00 1.00 3.00 1.00 1.00 10.00 6.00 9.00
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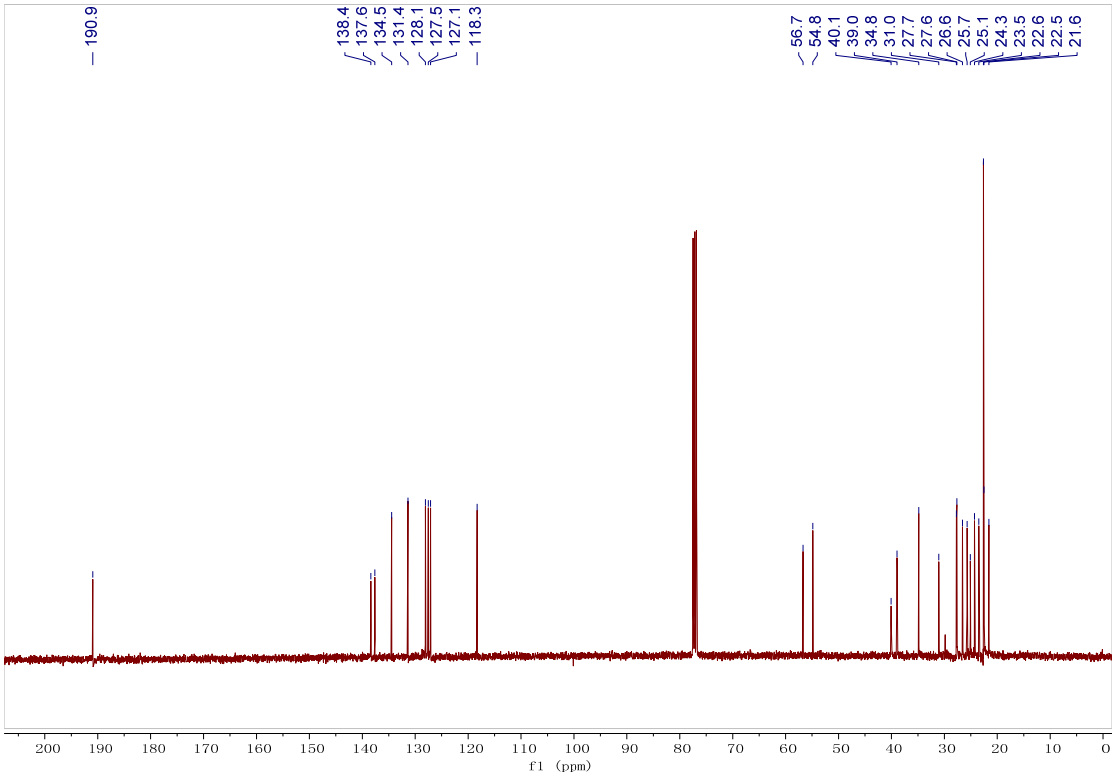
f1 (ppm)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56.7 54.8 40.1 39.0 34.8 31.0 27.7 27.6 26.6 25.7 25.1 24.3 23.5 22.6 22.5 21.6
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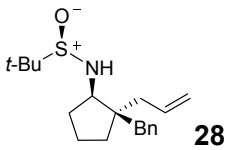
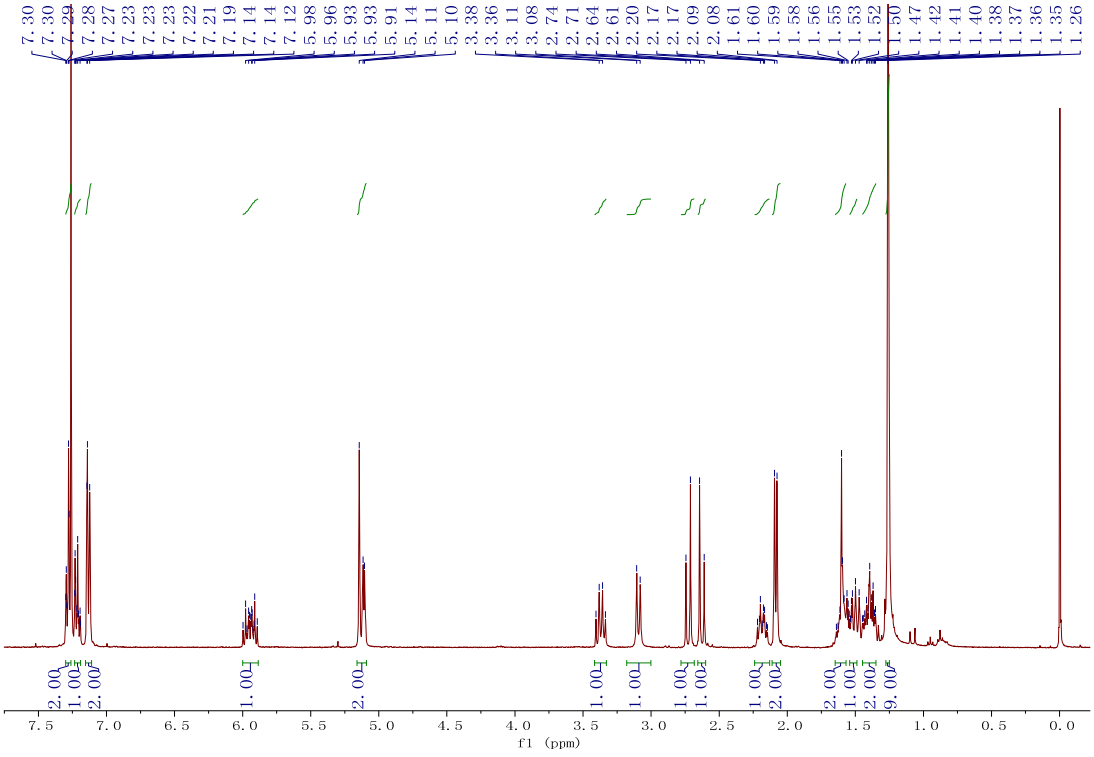
f1 (ppm)


O
S
NH
t-Bu
Bn

28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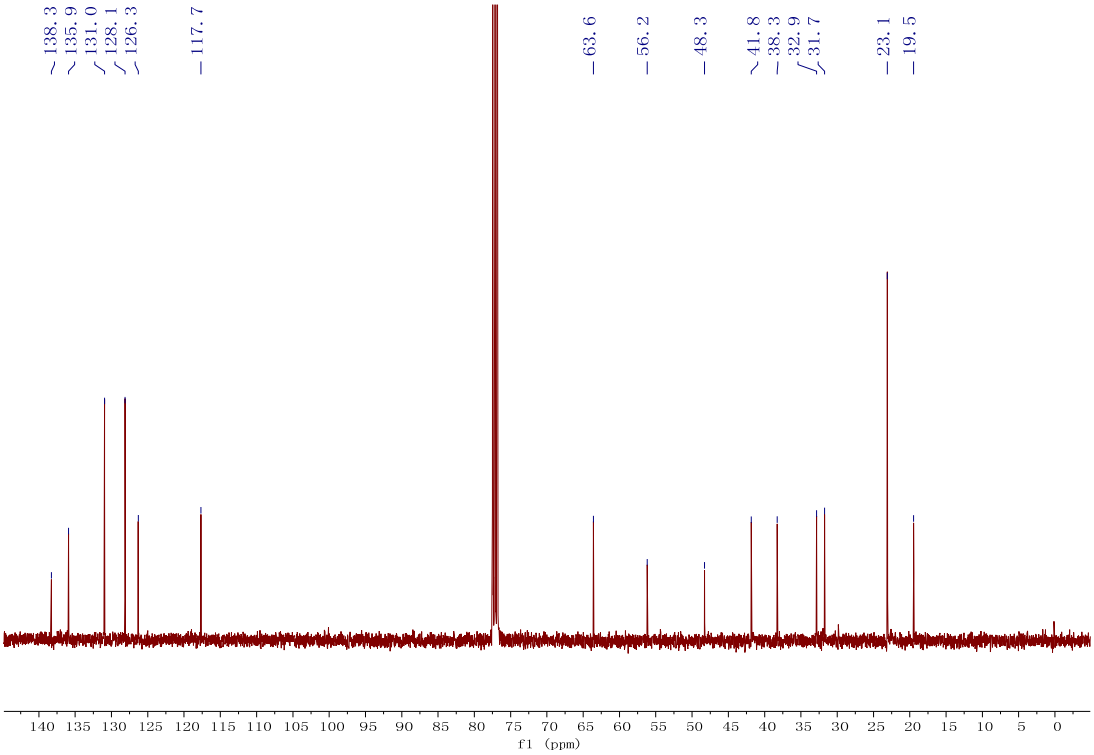
f1 (ppm)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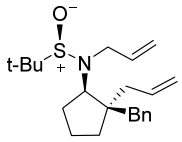
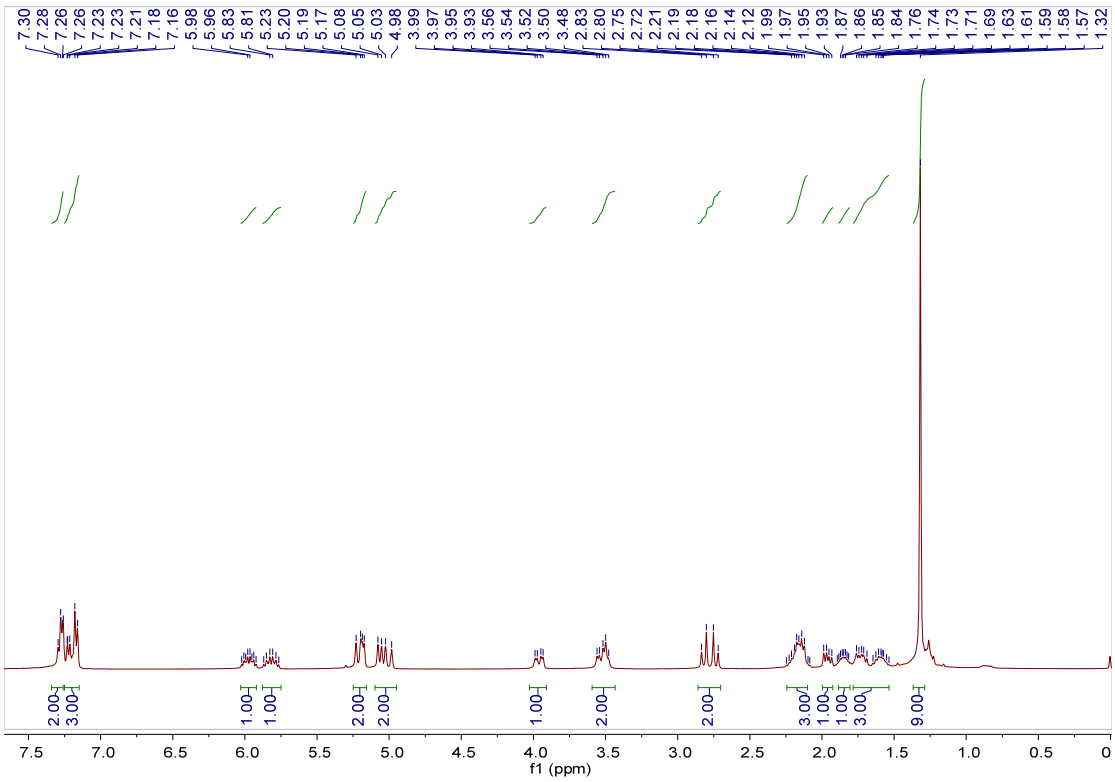
f1 (ppm)


O
S
t-Bu
+
N
Bn

28a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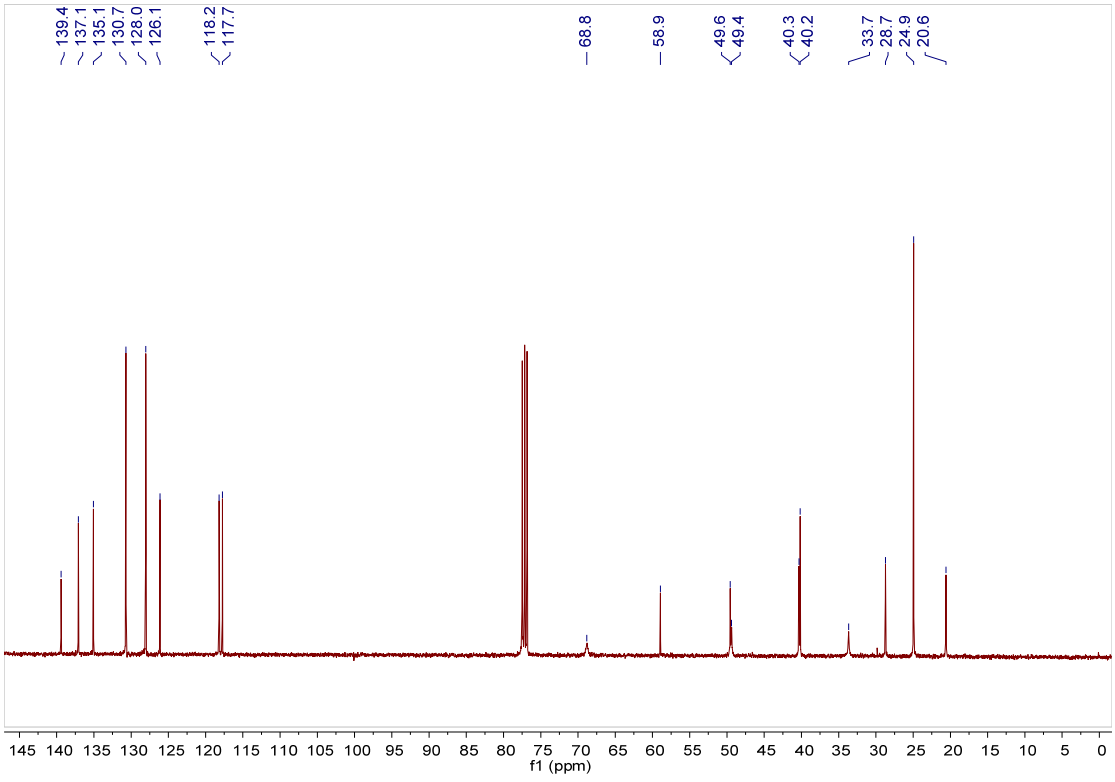
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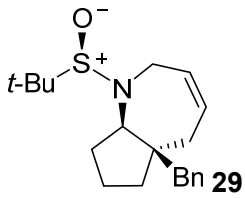
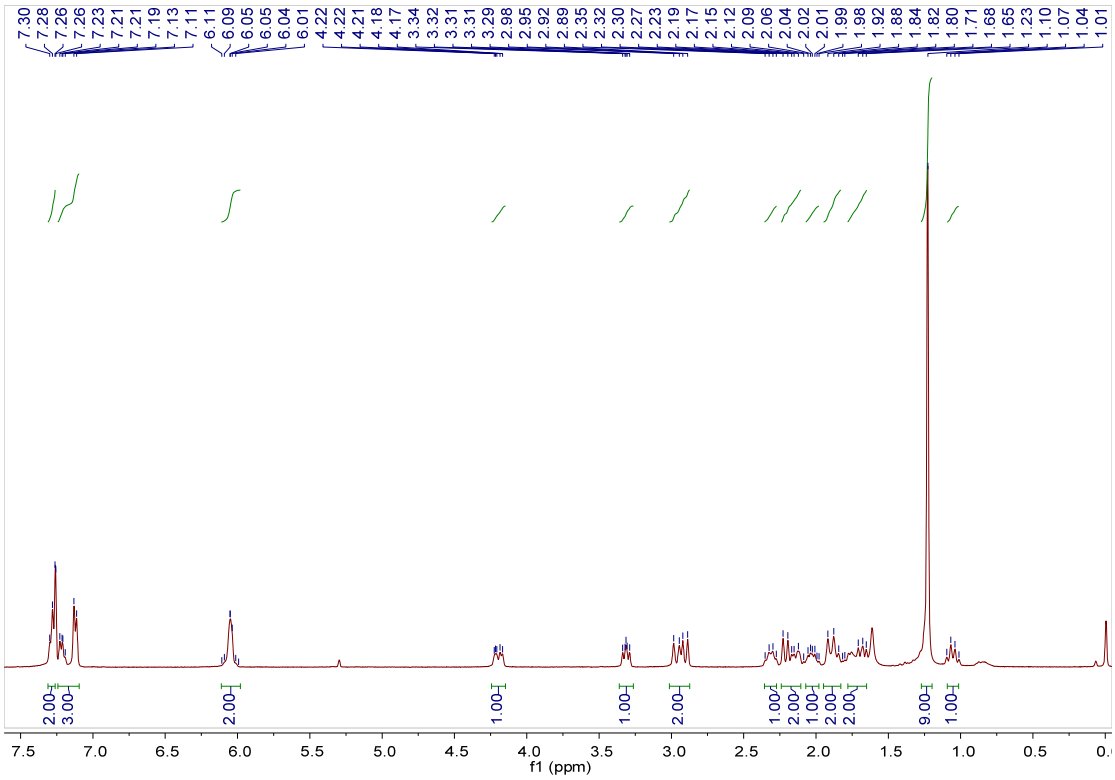
f1 (ppm)


O
S
t-Bu
N
Bn

29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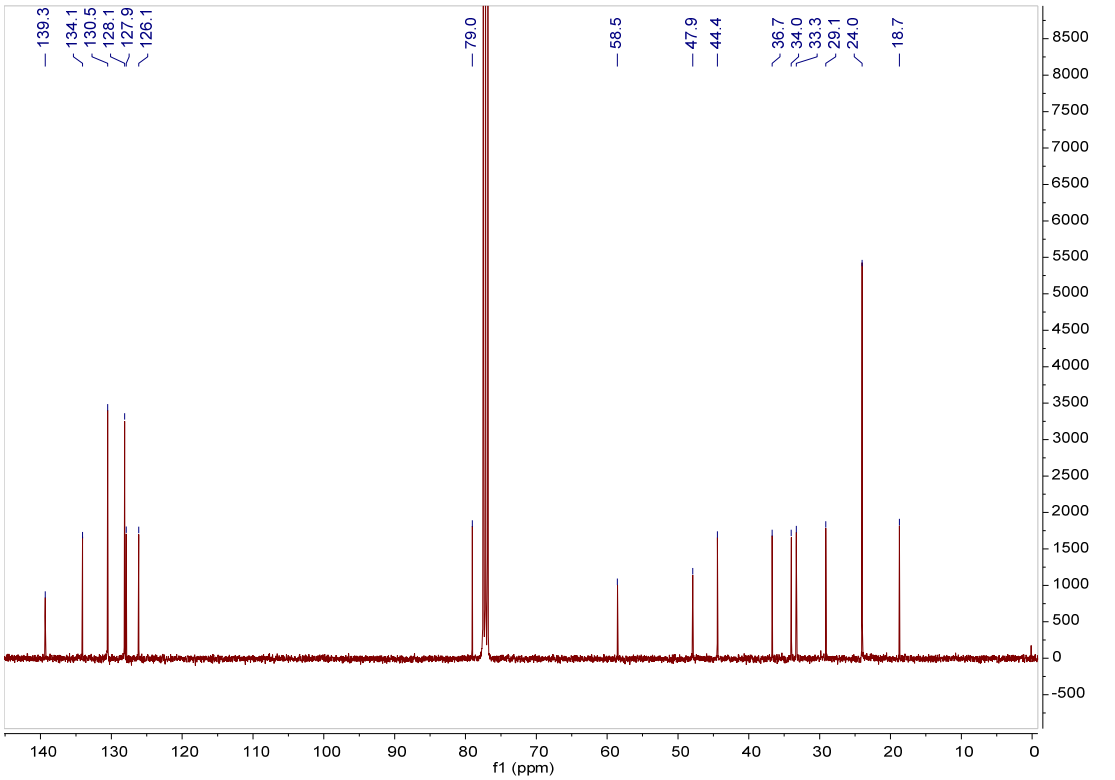
f1 (ppm)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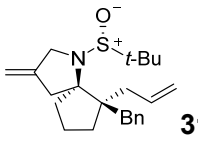
f1 (ppm)


O
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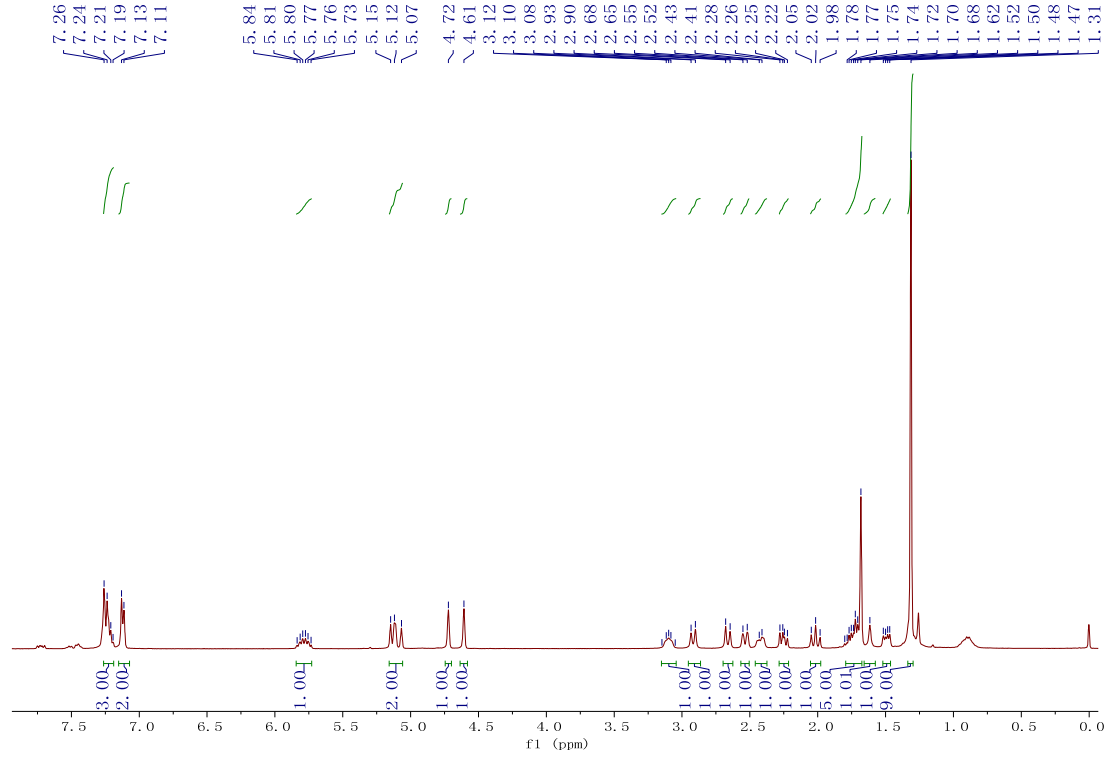
t-Bu
Bn

31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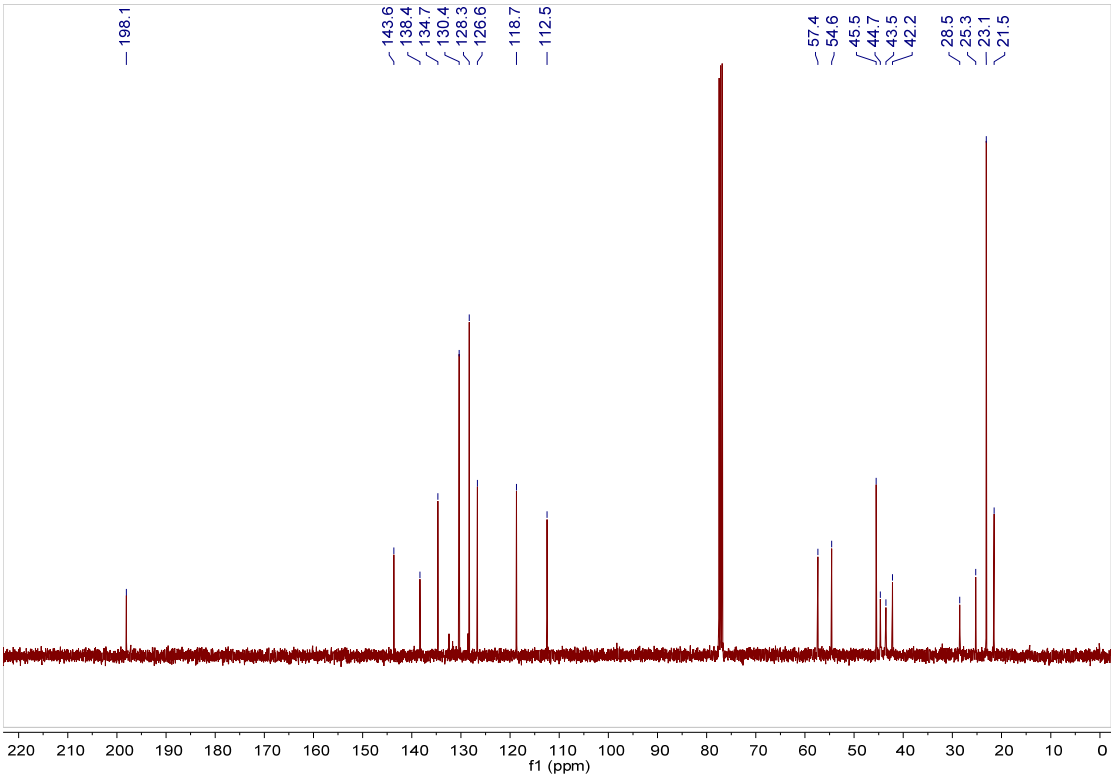
f1 (ppm)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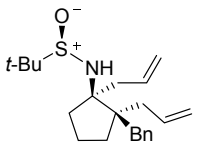
25.3
23.1
21.5
f1 (ppm)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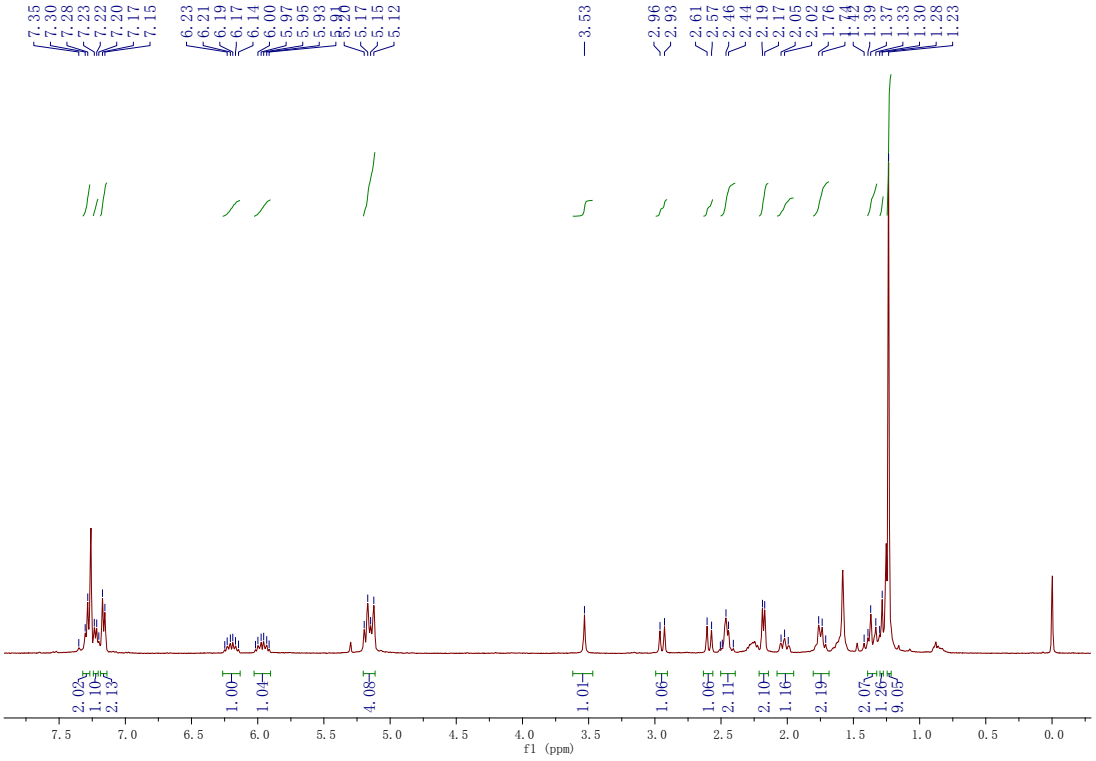
t-Bu
NH
Bn

32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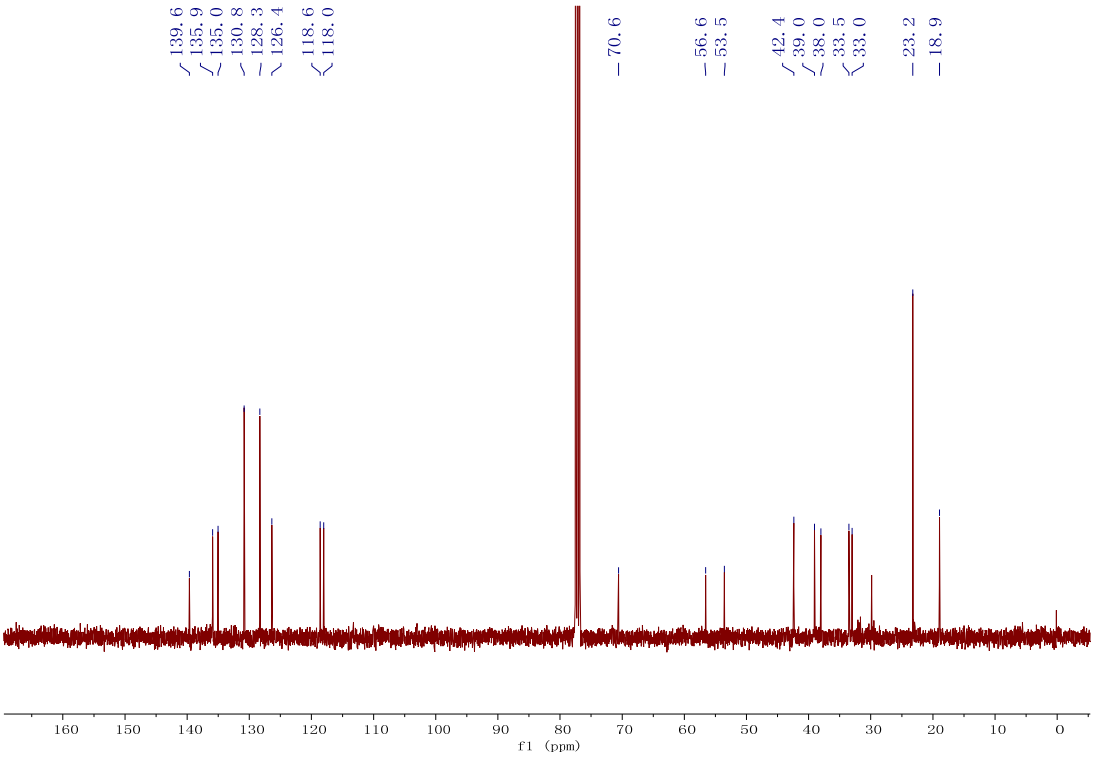
9.05
f1 (ppm)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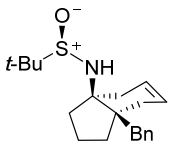
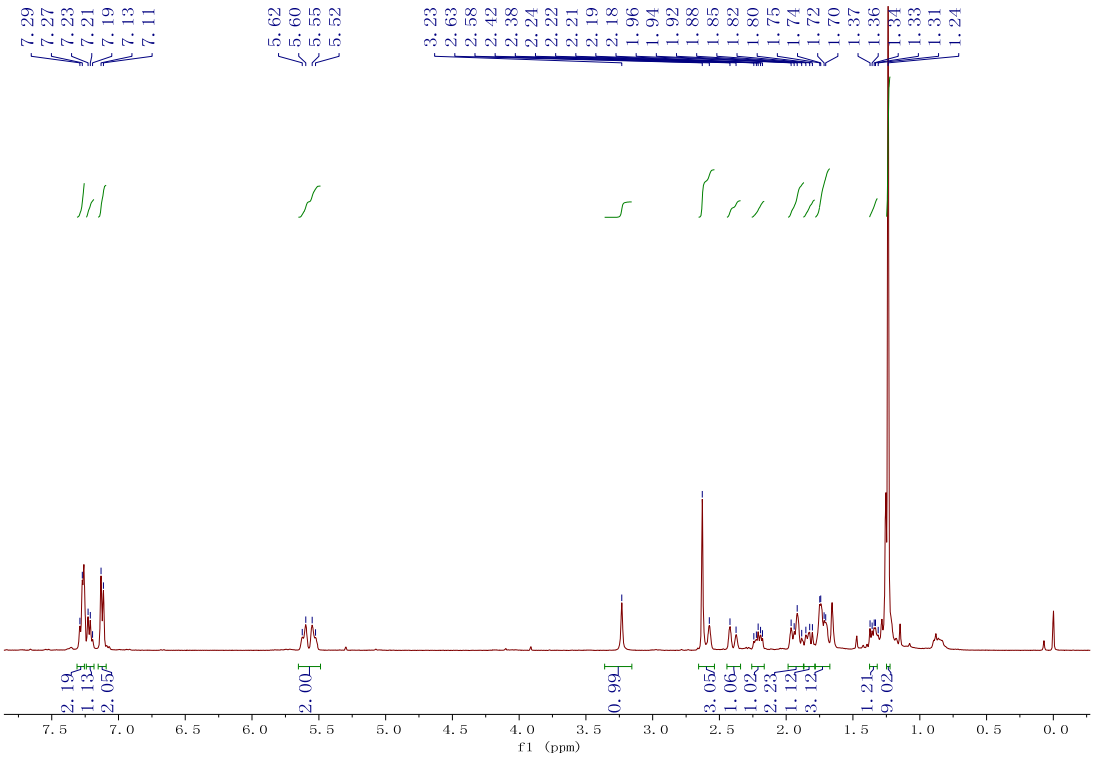
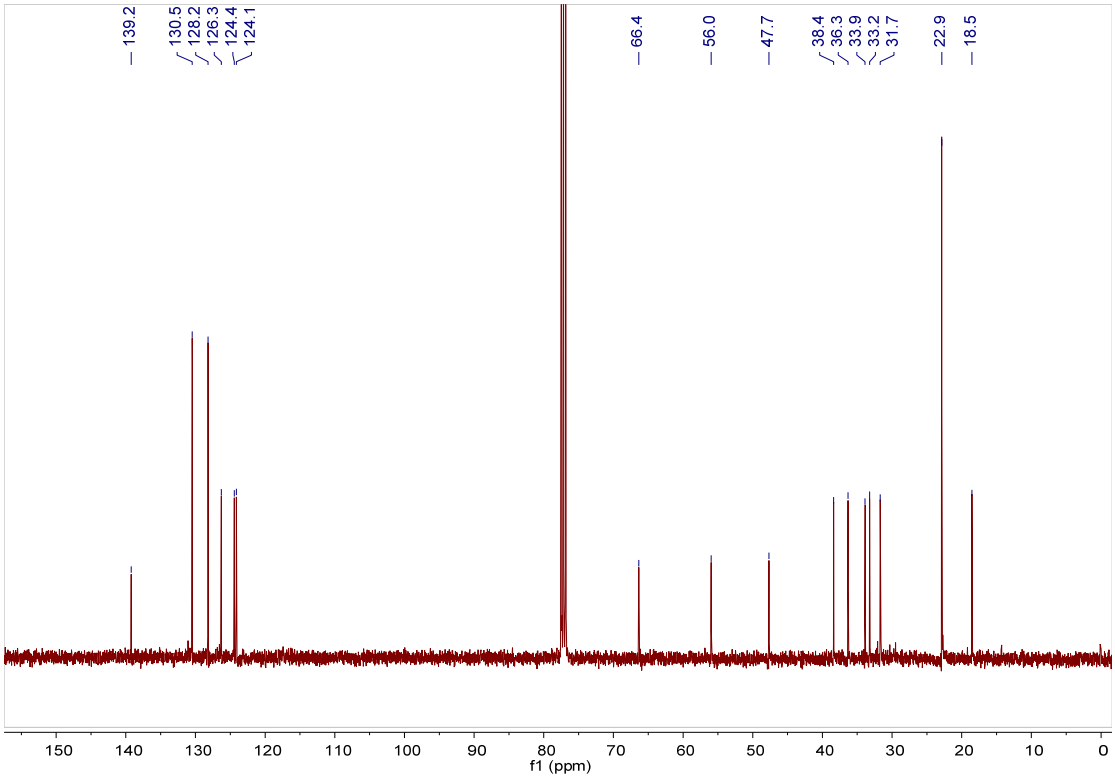
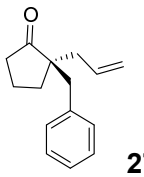
39.0
38.0
33.5
33.0
23.2
18.9
f1 (ppm)


O
S
t-Bu
NH
Bn

33

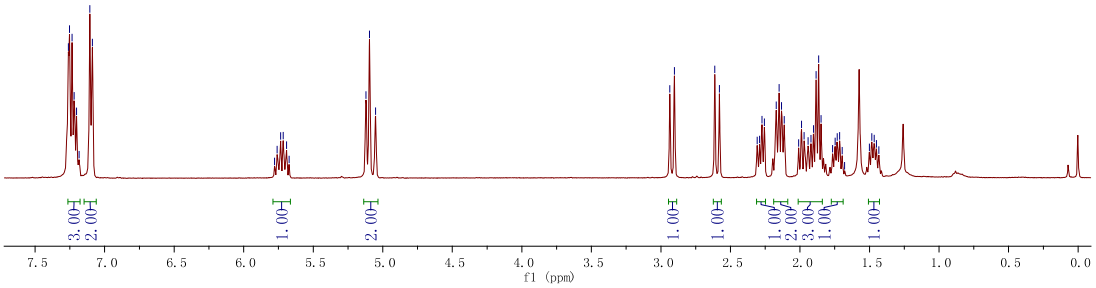

7.29
7.27
7.23
7.21
7.19
7.13
7.11
5.62
5.60
5.55
5.52
3.23
2.63
2.58
2.42
2.38
2.24
2.22
2.21
2.19
2.18
1.96
1.94
1.92
1.88
1.85
1.82
1.80
1.75
1.74
1.72
1.70
1.37
1.36
1.34
1.33
1.31
1.24
2.19
1.13
2.05
2.00
0.99
3.05
1.06
1.02
2.23
1.12
3.12
1.21
9.02
f1 (ppm)

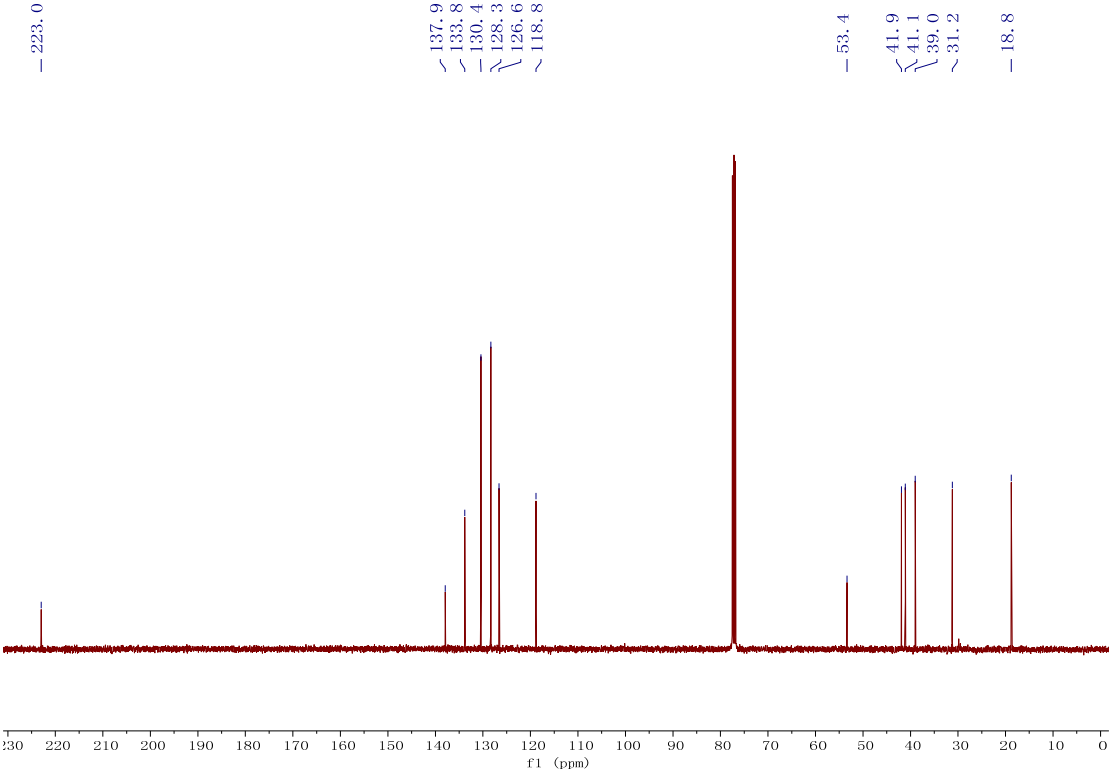

139.2
130.5
128.2
126.3
124.4
124.1
66.4
56.0
47.7
38.4
36.3
33.9
33.2
31.7
22.9
18.5
f1 (ppm)

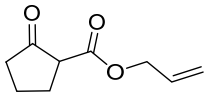


27

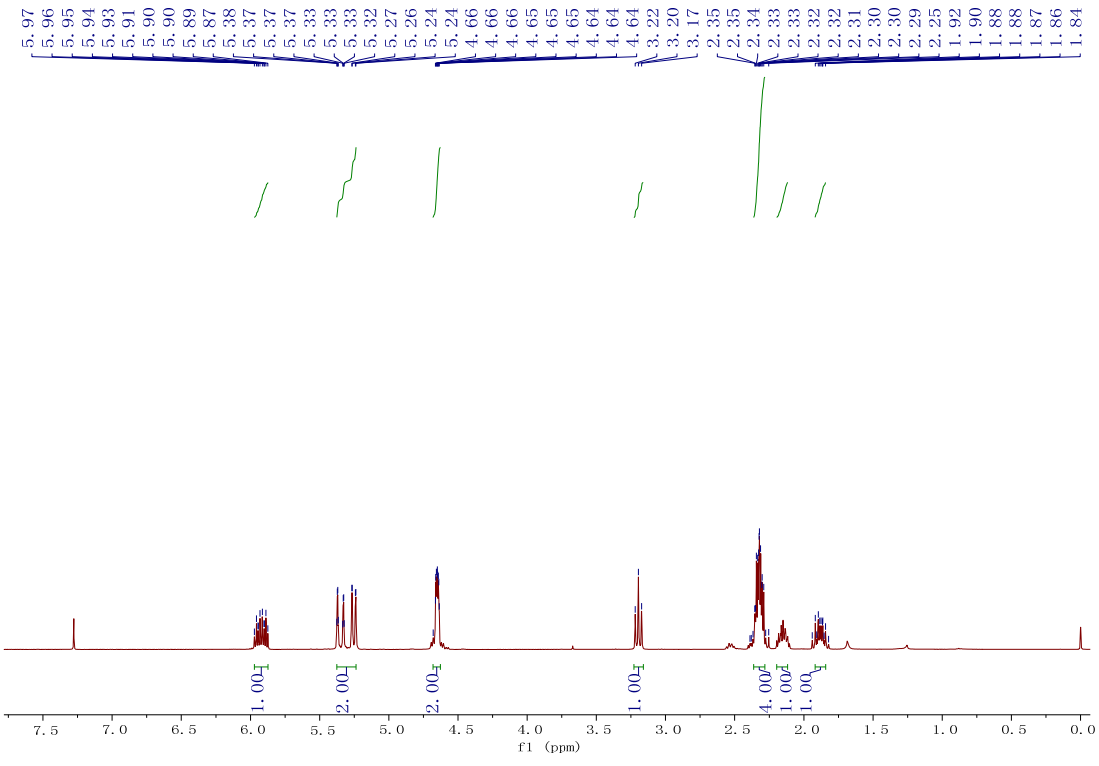

7.3
7.3
7.2
7.2
7.2
7.2
7.1
7.1
5.8
5.8
5.7
5.7
5.7
5.7
5.1
5.1
5.1
2.9
2.9
2.6
2.6
2.3
2.3
2.3
2.3
2.2
2.1
2.1
2.1
2.0
2.0
1.9
1.9
1.9
1.9
1.8
1.7
1.7
1.7
1.5
1.5

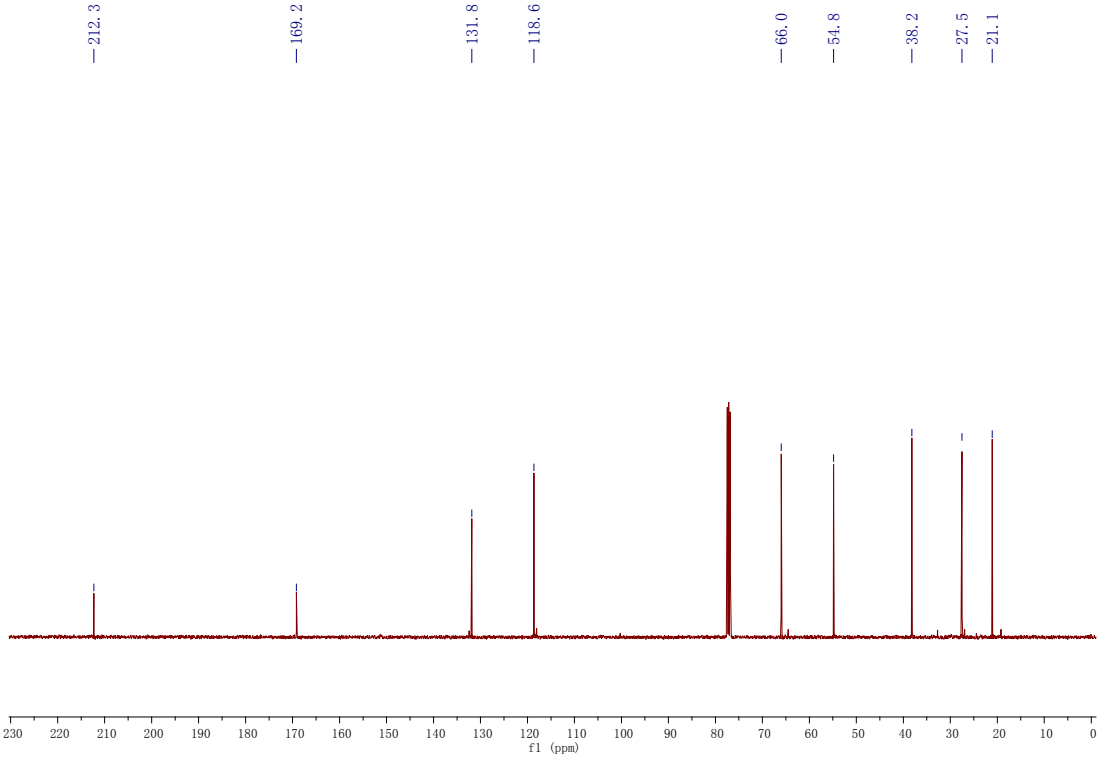

3.00
2.00
1.00
2.00
1.00
1.00
1.00
2.00
3.00
1.00
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

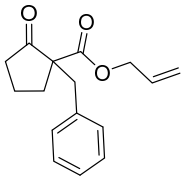

223.0
137.9
133.8
130.4
128.3
126.6
118.8
53.4
41.9
41.1
39.0
31.2
18.8
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



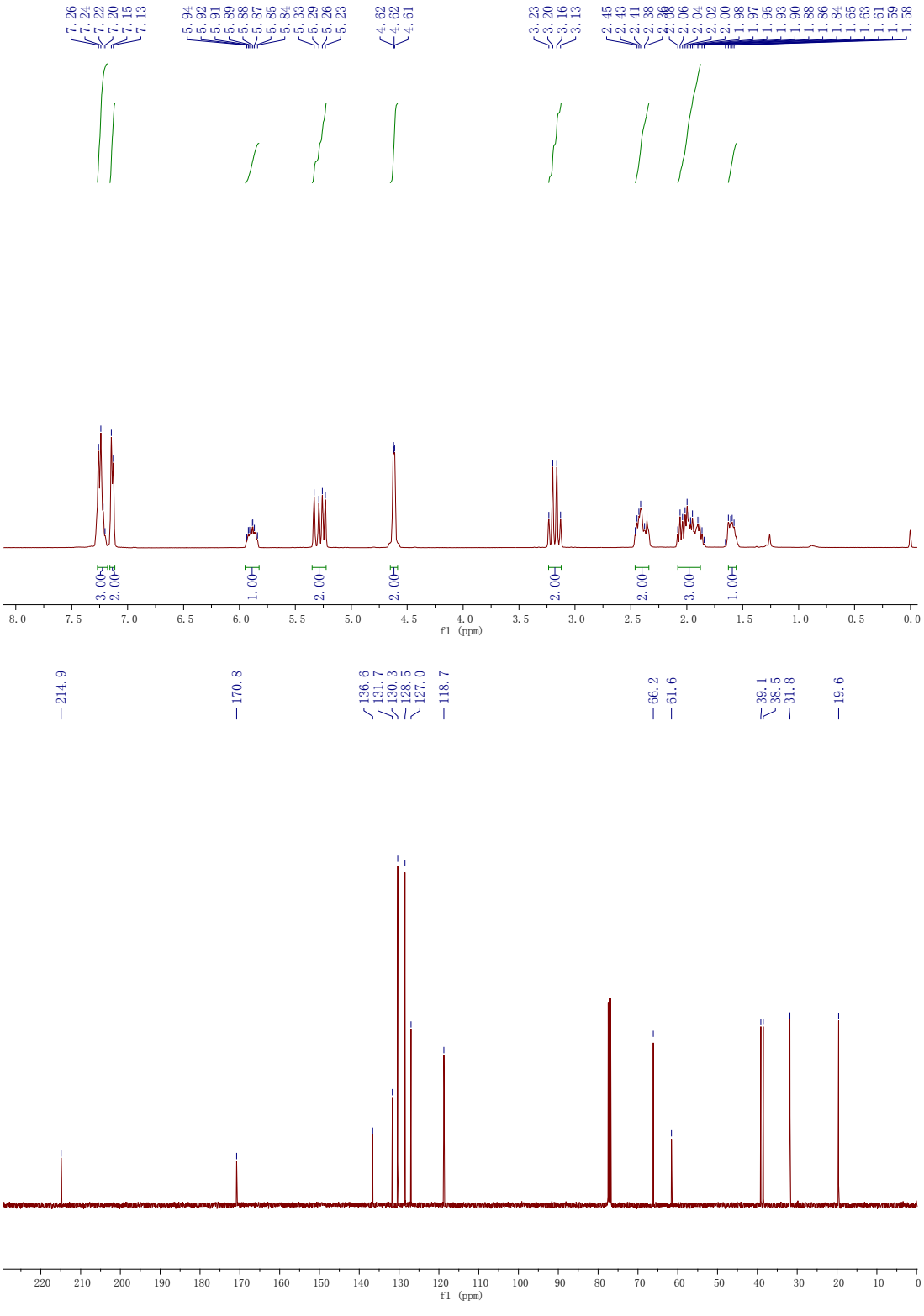
rac-s1

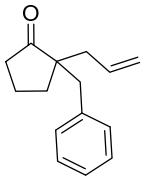

5.97 5.96 5.95 5.94 5.93 5.91 5.90 5.90 5.89 5.87 5.38 5.37 5.37 5.37 5.33 5.33 5.33 5.32 5.27 5.26 5.24 5.24 4.66 4.66 4.66 4.65 4.65 4.65 4.64 4.64 4.64 4.64 3.22 3.20 3.17 2.35 2.35 2.34 2.33 2.33 2.32 2.32 2.31 2.30 2.30 2.29 2.25 1.92 1.90 1.88 1.88 1.87 1.86 1.84
1.00 2.00 2.00 1.00 4.00 1.00 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


212.3 169.2 131.8 118.6 66.0 54.8 38.2 27.5 21.1
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

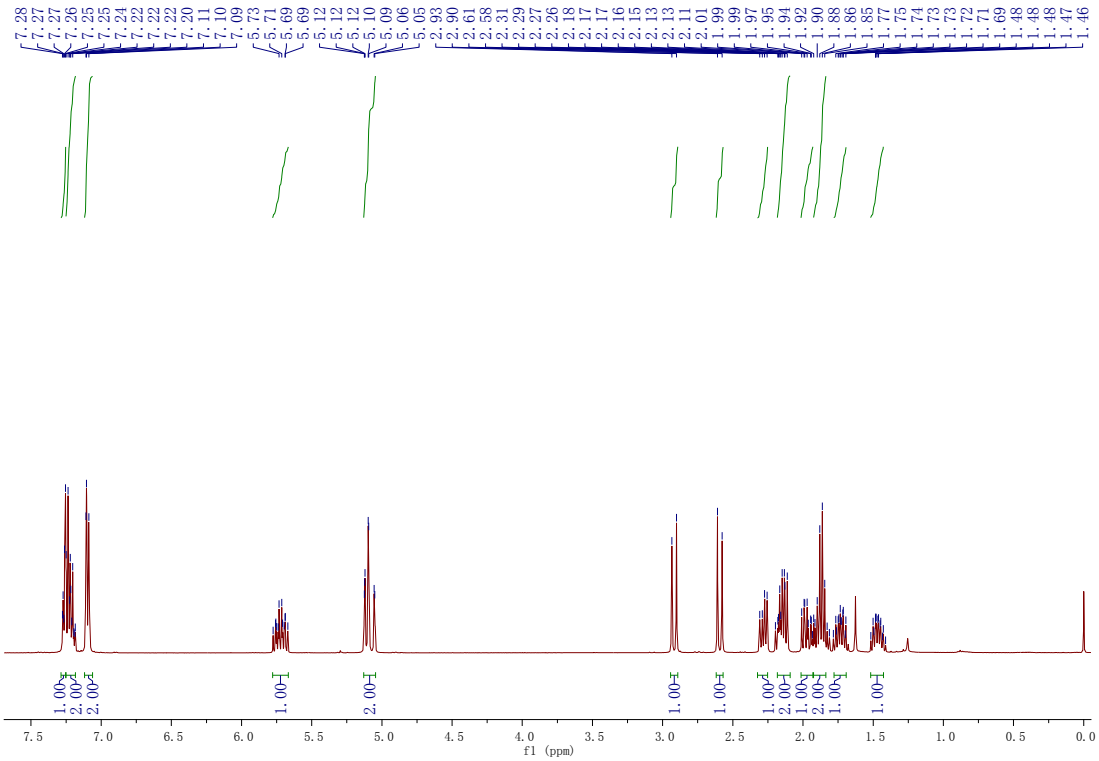


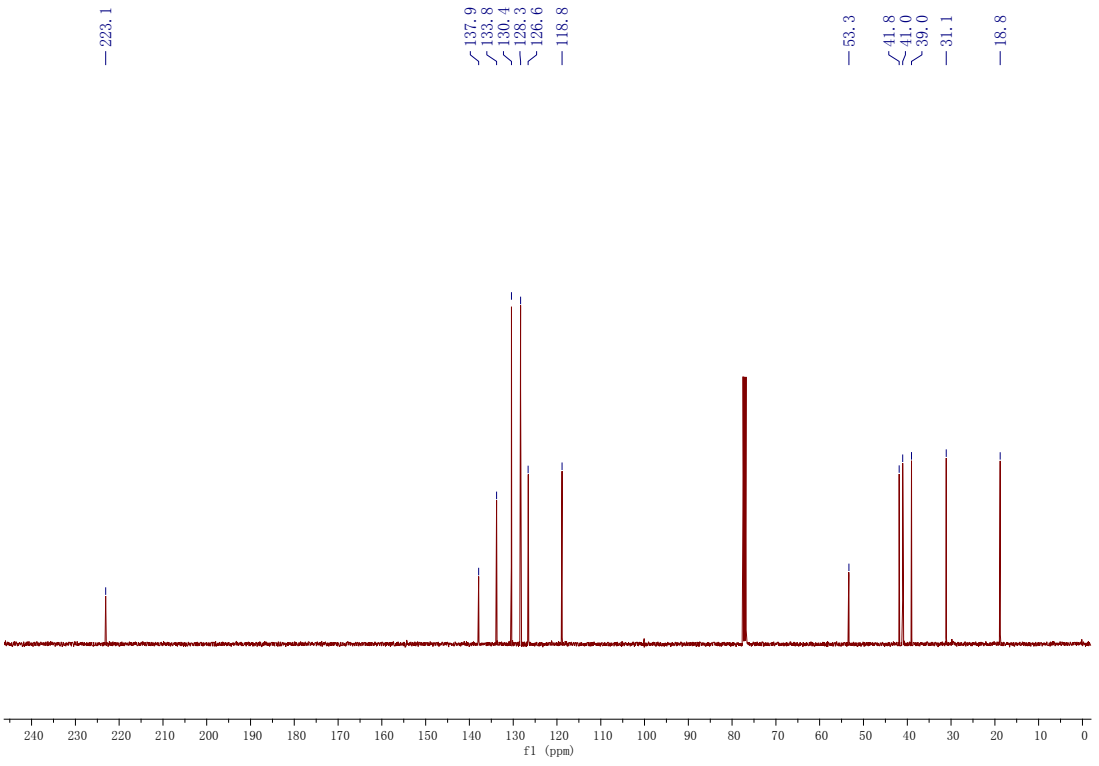
rac-s2


7.26 7.24 7.22 7.20 7.15 7.13
5.94 5.92 5.91 5.89 5.88 5.87 5.85 5.84 5.33 5.29 5.26 5.23
4.62 4.62 4.61
3.23 3.20 3.16 3.13
2.45 2.43 2.41 2.38 2.06 2.04 2.02 2.00 1.98 1.97 1.95 1.93 1.90 1.88 1.86 1.84 1.65 1.63 1.61 1.59 1.58
3.00 2.00 1.00 2.00 2.00 2.00 2.00 3.00 1.00
f1 (ppm)
214.9 170.8 136.6 131.7 130.3 128.5 127.0 118.7 66.2 61.6 39.1 38.5 31.8 19.6
f1 (ppm)



rac-27





8. Crystal data of Compound 29

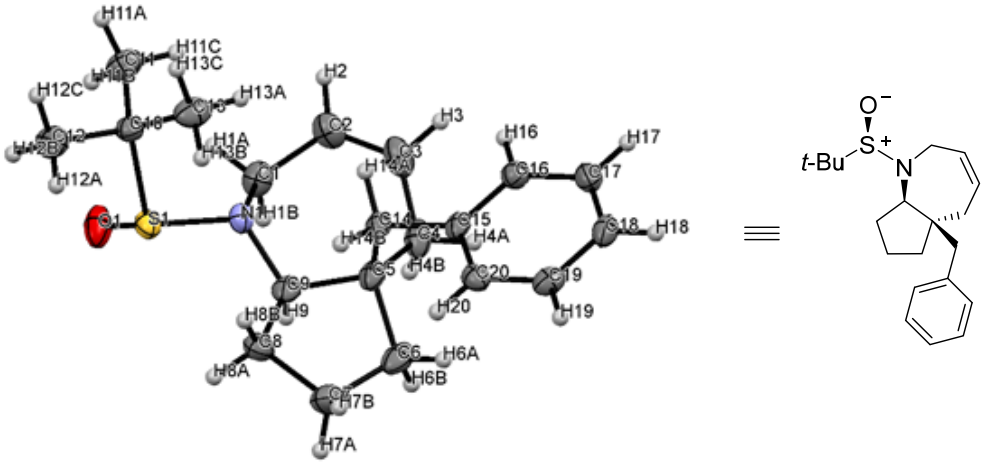


Figure 1. ORTEP representation of the compound with thermal ellipsoids at 50% probability

Identification code	**29**
Empirical formula	$C_{20}H_{29}NOS$
Formula weight	331.50
Temperature/K	113(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.5315(8)
b/Å	7.0899(4)
c/Å	12.4878(12)
α/°	90
β/°	105.290(8)
γ/°	90
Volume/Å^3	899.42(13)
Z	2
ρ_{calc}g/cm^3	1.224
μ/mm^{-1}	0.185
F(000)	360.0
Crystal size/mm^3	0.200 × 0.180 × 0.120
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.382 to 51.992
Index ranges	$-12 \le h \le 12$, $-8 \le k \le 8$, $-15 \le l \le 15$
Reflections collected	7945
Independent reflections	3484 [R_{int} = 0.0374, R_{sigma} = 0.0496]
Data/restraints/parameters	3484/1/211
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0778

Final R indexes [all data]	$R_1 = 0.0438$, $wR_2 = 0.0809$
Largest diff. peak/hole / e Å^{-3}	0.16/-0.22
Flack parameter	-0.01(5)