Supporting Information

Dearomatization of Aryl Sulfoxides:

A Switch between Mono- and Dual-Difluoroalkylation

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1 General information

Unless otherwise indicated, all glassware was oven dried before use and all reactions were performed under an atmosphere of Nitrogen. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers. Reaction progress was monitored by thin layer chromatography (TLC) performed on plastic plates coated with silica gel GF254 with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Compound isolation was performed on chromatography column using silica gel 60 (160-200 mesh) or Biotage Isolera Prime flash column system. Neat infrared spectra were recorded using a NEXUS670 FT-IR spectrometer. Wavelengths (ν) are reported in cm^{-1}. MS (EI) analysis was performed on Agilent GC-MS instrument. High-resolution mass spectrometry (HRMS) analysis was carried out using a TOF MS instrument with ESI or APCI source. All ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV-400 or AV-600. ^{1}H-NMR and ^{13}C-NMR chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26, methanol δ 3.31), carbon (chloroform δ 77.16, methanol δ 49.00). ^{19}F-NMR chemical shift were determined relative to $CFCl_3$ as inter standard. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). Coupling constants were reported in Hertz (Hz).

2 Preparation of starting materials

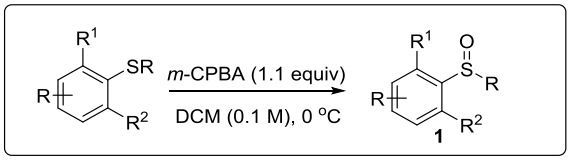
Difluoroenol silyl ether **2a**[1], **2b**[2], **2c**[3] **and 2d**[4] are known compounds.

1. Wu, Y.-B., Lu, G.-P., Zhou, B.-J., Bu, M.-J., Wan, L., Cai, C. *Chem. Commun*. 2016, **52**, 5965.

2. Yamana, M.; Ishihara, T.; Ando, T. *Tetrahedron Lett.* 1983, **24**, 507.

3. Fedorov, O. V.; Struchkova, M. I.; Dilman, A. D. *J. Org. Chem.* 2016, **81**, 9455.

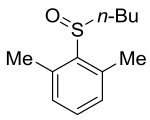
4. Zhang, Y.; Yan, W.; Wang, Y.; Weng, Z. *Org. Lett*. 2017, **19**, 5478.



General procedure: To a solution of sulfide (3.0-10 mmol) in DCM (0.1 M) was added a solution

of *m*-CPBA (1.1 equiv.) in DCM (0.5 M) at -5 ^{o}C. After the starting sulfide completely consumed, the reaction was quenched with sat. aq. $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated and concentrated in vacuum. The obtained residue was purified by column chromatography on silica gel to afford the corresponding sulfoxides **1**.

2-(butylsulfinyl)-1,3-dimethylbenzene (1a):



1a

Following general procedure, the title compound was prepared from 20 mmol of corresponding aryl sulfide and was obtained as colorless oil, 3.1 g, 73% yield.

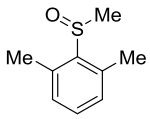
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22 – 7.18 (m, 1H), 7.02 (d, *J* = 7.6 Hz, 2H), 3.28 – 3.23 (m, 1H), 2.85 – 2.78 (m, 1H), 2.56 (s, 6H), 1.81 – 1.62 (m, 2H), 1.56 – 1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.4, 138.3, 130.8, 130.3, 52.1, 25.8, 22.0, 19.4, 13.8.

IR (neat): 2957, 2928, 2871, 1580, 1458, 1380, 913, 773.

HRMS (APCI-TOF): calculated for [$C_{12}H_{18}OSNa$ ($M + Na^+$)]: 233.0971, found: 233.1006.

1,3-dimethyl-2-(methylsulfinyl)benzene (1b):



1b

Following general procedure, the title compound was prepared from 10 mmol of corresponding aryl sulfide and was obtained as white solid, m.p. 51 – 52 ℃, 1.3 g, 80% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26 – 7.22 (m, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 2.88 (s, 3H), 2.61 (s, 6H).

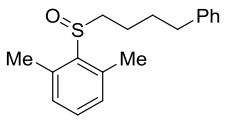
^{13}C NMR (151 MHz, $CDCl_3$): δ 139.1, 137.9, 130.9, 130.3, 38.3, 19.1.

IR (neat): 3057, 2919, 1579, 1459, 1381, 774.

The expected MS of title compound was not detected by LC/TOF-MS with ESI and APCI sources under both positive and negative models.

EI-MS: found 168.0.

1,3-dimethyl-2-((4-phenylbutyl)sulfinyl)benzene (1c):



1c

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 1.1 g, 75% yield.

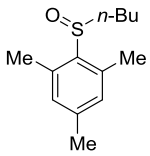
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.28 (m, 2H), 7.26 – 7.19 (m, 2H), 7.18 (d, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 3.35 – 3.29 (m, 1H), 2.91 – 2.81 (m, 1H), 2.68 (t, *J* = 6.5 Hz, 2H), 2.59 (s, 6H), 1.93 – 1.73 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 141.6, 138.4, 138.3, 130.8, 130.3, 128.5, 128.4, 126.0, 52.3, 35.6, 30.6, 23.5, 19.3.

IR (neat): 3057, 3024, 2927, 2857, 1602, 1581, 1458, 1380, 910, 773.

HRMS (APCI -TOF): calculated for [$C_{18}H_{22}OSNa$ ($M + Na^+$)]: 309.1284, found: 309.1308.

2-(butylsulfinyl)-1,3,5-trimethylbenzene (1d):



1d

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 1.8 g, 82% yield.

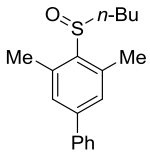
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.84 (s, 2H), 3.27 – 3.22 (m, 1H), 2.86 – 2.78 (m, 1H), 2.52 (s, 6H), 2.27 (s, 3H), 1.81 – 1.70 (m, 1H), 1.66 – 1.57 (m, 1H), 1.56 – 1.37 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 141.0, 138.4, 135.1, 131.0, 52.3, 25.9, 22.1, 21.1, 19.3, 13.8.

IR (neat): 2957, 2927, 2870, 1600, 1567, 1456, 1378, 1291, 1075, 1023, 850, 615.

HRMS (APCI -TOF): calculated for [$C_{13}H_{20}OSNa$ ($M + Na^+$)]: 247.1127, found: 247.1164.

4-(butylsulfinyl)-3,5-dimethyl-1,1'-biphenyl (1e):



1e

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as white solid, m.p. 93 – 94 ℃, 958 mg, 67% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 – 7.55 (m, 2H), 7.46 – 7.42 (m, 2H), 7.39 – 7.35 (m, 1H), 3.33 – 3.27 (m, 1H), 2.91 – 2.85 (m, 1H), 2.64 (s, 6H), 1.87 – 1.77 (m, 1H), 1.74 – 1.66 (m, 1H), 1.59 – 1.42 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

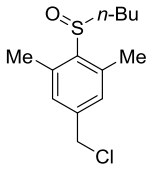
^{13}C NMR (151 MHz, $CDCl_3$): δ 143.5, 139.8, 138.9, 137.2, 128.92, 128.89, 129.1, 127.2, 52.4,

25.9, 22.1, 19.6, 13.8.

IR (neat): 3061, 2956, 2926, 2868, 1594, 1560, 1071, 1022, 766, 697.

HRMS (APCI -TOF): calculated for [$C_{18}H_{22}OSNa$ ($M + Na^+$)]: 309.1284, found: 309.1300.

2-(butylsulfinyl)-5-(chloromethyl)-1,3-dimethylbenzene (1f):



1f

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 929 mg, 72% yield.

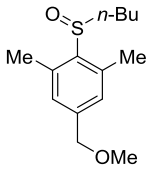
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.04 (s, 2H), 4.47 (s, 2H), 3.26 – 3.21 (m, 1H), 2.83 – 2.77 (m, 1H), 2.55 (s, 6H), 1.84 – 1.60 (m, 2H), 1.58 – 1.38 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 139.9, 139.0, 138.4, 130.2, 52.2, 45.2, 25.8, 22.0, 19.3, 13.7.

IR (neat): 2957, 2928, 2870, 1600, 1571, 1445, 1380, 1075, 1027, 728, 699.

HRMS (APCI -TOF): calculated for [$C_{13}H_{19}ClOSNa$ ($M + Na^+$)]: 281.0737, found: 281.0783.

2-(butylsulfinyl)-5-(methoxymethyl)-1,3-dimethylbenzene (1g):



1g

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 660 mg, 52% yield.

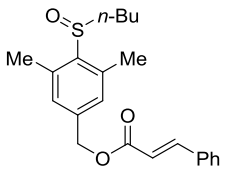
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.98 (s, 2H), 4.35 (s, 2H), 3.36 (s, 3H), 3.26 – 3.18 (m, 1H), 2.82 – 2.75 (m, 1H), 2.54 (s, 6H), 1.76 – 1.56 (m, 2H), 1.54 – 1.39 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 141.0, 138.6, 137.3, 129.1, 73.9, 58.5, 52.2, 25.7, 22.0, 19.3, 13.7.

IR (neat): 2957, 2927, 2871, 1601, 1567, 1449, 1419, 1379, 1100, 1074, 1023, 859.

HRMS (APCI -TOF): calculated for [$C_{14}H_{22}O_2SNa$ ($M + Na^+$)]: 277.1233, found: 277.1276.

4-(butylsulfinyl)-3,5-dimethylbenzyl cinnamate (1h):



1h

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 1.2 g, 63% yield.

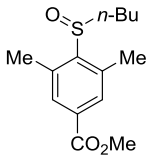
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, J = 16.0 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.42 – 7.35 (m, 3H), 7.07 (s, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 5.18 (s, 2H), 3.29 – 3.23 (m, 1H), 2.85 – 2.79 (m, 1H), 2.58 (s, 6H), 1.78 – 1.42 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.8, 145.6, 138.9, 138.8, 138.3, 134.3, 130.6, 129.7, 129.0, 128.3, 117.6, 65.5, 52.3, 25.8, 22.1, 19.4, 13.8.

IR (neat): 2957, 2928, 2871, 1708, 1634, 1156, 1028, 980, 863, 767.

HRMS (APCI -TOF): calculated for [$C_{22}H_{26}O_3SNa$ ($M + Na^+$)]: 393.1495, found: 393.1496.

methyl 4-(butylsulfinyl)-3,5-dimethylbenzoate (1i):



1i

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 884 mg, 66% yield.

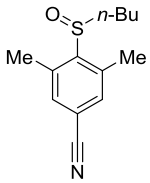
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 (s, 2H), 3.90 (s, 3H), 3.28 – 3.22 (m, 1H), 2.84 – 2.78 (m, 1H), 2.60 (s, 6H), 1.81 – 1.64 (m, 2H), 1.56 – 1.43 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.4, 143.3, 138.7, 131.8, 131.0, 52.5, 52.2, 25.8, 22.0, 19.4, 13.8.

IR (neat): 2955, 2931, 2871, 1719, 1569, 1435, 1406, 1306, 1214, 1017, 756.

HRMS (APCI -TOF): calculated for [$C_{14}H_{20}O_3SNa$ ($M + Na^+$)]: 291.1025, found: 291.1059.

4-(butylsulfinyl)-3,5-dimethylbenzonitrile (1j):



1j

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as white solid, m.p. 67 – 68 ℃, 846 mg, 72% yield.

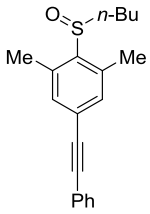
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 (s, 2H), 3.29 – 3.17 (m, 1H), 2.82 – 2.75 (m, 1H), 2.56 (s, 6H), 1.82 – 1.63 (m, 2H), 1.57 – 1.38 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 143.8, 139.5, 133.1, 117.8, 114.2, 52.0, 25.5, 21.8, 19.0, 13.6.

IR (neat): 2957, 2923, 2855, 2220, 1560, 1442, 1379, 1077, 1031, 881, 607.

HRMS (APCI -TOF): calculated for [$C_{13}H_{17}NOSNa$ ($M + Na^+$)]: 258.0923, found: 258.0953.

2-(butylsulfinyl)-1,3-dimethyl-5-(phenylethynyl)benzene (1k):



1k

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 1.1 g, 73% yield.

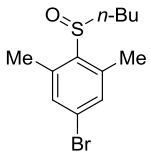
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.49 (m, 2H), 7.36 – 7.31 (m, 3H), 7.20 (s, 2H), 3.29 – 3.23 (m, 1H), 2.86 – 2.80 (m, 1H), 2.54 (s, 6H), 1.81 – 1.62 (m, 2H), 1.56 – 1.42 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.6, 138.4, 132.9, 131.8, 128.7, 128.5, 125.8, 122.8, 91.3, 88.3, 52.3, 25.8, 22.0, 19.2, 13.8.

IR (neat): 2958, 2928, 2971, 2232, 1598, 1588, 1074, 1026, 909, 871, 755.

HRMS (APCI -TOF): calculated for [$C_{20}H_{22}OSNa$ ($M + Na^+$)]: 333.1284, found: 333.1302.

5-bromo-2-(butylsulfinyl)-1,3-dimethylbenzene (1l):



1l

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 1.2 g, 82% yield.

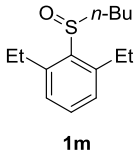
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (s, 2H), 3.26 – 3.21 (m, 1H), 2.84 – 2.78, 1H), 2.54 (s, 6H), 1.79 – 1.65 (m, 2H), 1.54 – 1.44 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.4, 137.5, 132.9, 125.8, 52.3, 25.8, 22.1, 19.2, 13.8.

IR (neat): 3051, 2957, 2928, 2870, 1561, 1457, 1398, 1379, 1246, 1075, 1029, 832.

HRMS (APCI -TOF): calculated for [$C_{12}H_{17}BrOSNa$ ($M + Na^+$)]: 311.0076, found: 311.0027.

2-(butylsulfinyl)-1,3-diethylbenzene (1m):



1m

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 892 mg, 75% yield.

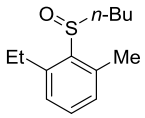
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 -7.29 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 3.41 – 3.30 (m, 1H), 3.07 (s, 2H), 2.97 – 2.89 (m, 2H), 2.82 – 2.75 (m, 1H), 1.84 – 1.66 (m, 2H), 1.57 – 1.43 (m, 2H), 1.26 (t, *J* = 7.5 Hz, 6H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.2, 138.1, 131.3, 128.6, 54.0, 26.3, 25.3, 22.1, 16.4, 13.8.

IR (neat): 2940, 2930, 2871, 1579, 1458, 1401, 1379, 1073, 1030, 801, 739.

HRMS (APCI -TOF): calculated for [$C_{14}H_{22}OSNa$ ($M + Na^+$)]: 261.1284, found: 261.1314.

2-(butylsulfinyl)-1-ethyl-3-methylbenzene (1n):



1n

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 862 mg, 77% yield.

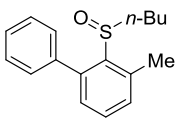
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.26 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 3.39 – 3.29 (m, 1H), 3.03 – 2.80 (m, 3H), 2.66 (s, 3H), 1.87 – 1.67 (m, 2H), 1.60 – 1.42 (m, 2H), 1.27 (t, *J* = 7.5 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 144.8, 138.8, 131.1, 130.6, 128.4, 26.1, 25.6, 22.1, 19.4, 16.5, 13.8.

IR (neat): 2959, 2929, 2870, 1580, 1458, 1380, 1073, 1029, 784, 756, 732.

HRMS (APCI -TOF): calculated for [$C_{13}H_{20}OSNa$ ($M + Na^+$)]: 247.1127, found: 247.1167.

2-(butylsulfinyl)-3-methyl-1,1'-biphenyl (1o):



1o

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 1.1 g, 81% yield.

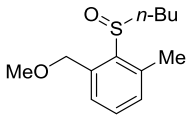
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.36 (m, 4H), 7.31 – 7.24 (m, 3H), 7.13 – 7.09 (m, 1H), 3.24 – 3.18 (m, 1H), 2.85 (s, 3H), 2.83 – 2.78 (m, 1H), 1.62 – 1.50 (m, 2H), 1.36 – 1.23 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 143.1, 139.9, 139.5, 138.3, 132.8, 130.5, 129.7, 128.8, 128.0, 127.7, 52.4, 25.8, 21.7, 18.9, 13.6.

IR (neat):

HRMS (APCI -TOF): calculated for [$C_{17}H_{20}OSNa$ ($M + Na^+$)]: 295.1127, found: 296.1162.

2-(butylsulfinyl)-1-(methoxymethyl)-3-methylbenzene (1p):



1p

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as white solid, m.p. 48 – 49 ℃, 864 mg, 72% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.27 (m, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 4.71 (d, *J* = 11.3 Hz, 1H), 4.57 (s, 1H), 3.40 – 3.32 (m, 4H), 2.85 – 2.78 (m, 1H), 2.65 (s, 3H), 1.88 – 1.73 (m, 2H), 1.60 – 1.43 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).kk

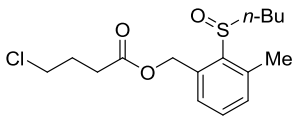
^{13}C NMR (151 MHz, $CDCl_3$): δ 139.9, 139.1, 137.9, 132.9, 130.7, 128.1, 58.1, 52.9, 26.2, 21.9,

19.0, 13.8.

IR (neat): 2954, 2927, 2869, 1582, 1453, 1389, 1087, 1029, 797, 777.

HRMS (APCI -TOF): calculated for [$C_{13}H_{20}O2SNa$ (M + Na^+)]: 263.1076, found: 263.1125.

2-(butylsulfinyl)-3-methylbenzyl 4-chlorobutanoate (1q):



1q

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as colorless oil, 974 mg, 59% yield.

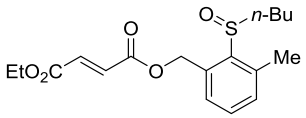
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.32 (m, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 5.67 (d, *J* = 11.1 Hz, 1H), 5.37 (d, *J* = 12.9 Hz, 1H), 3.58 (t, *J* = 6.3 Hz, 2H), 3.49 – 3.34 (m, 1H), 2.91 – 2.76 (m, 1H), 2.57 (s, 3H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.16 – 2.02 (m, 2H), 1.91 – 1.67 (m, 2H), 1.61 – 1.43 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.1, 139.5, 138.4, 136.4, 132.6, 131.1, 128.8, 62.9, 53.1, 44.1, 31.2, 27.6, 26.0, 22.1, 19.3, 13.8.

IR (neat): 2958, 2930, 2871, 1733, 1583, 1459, 1169, 1141, 1073, 784, 730.

HRMS (APCI -TOF): calculated for [$C_{16}H_{23}ClO_3SNa$ (M + Na^+)]: 353.0949, found: 353.0957.

2-(butylsulfinyl)-3-methylbenzyl ethyl fumarate (1r):



1r

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as white solid, m.p. 88 – 89 ℃, 1.1 g, 62% yield.

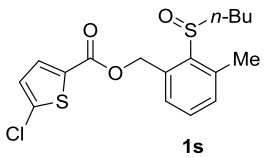
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.30 (m, 2H), 7.19 (d, *J* = 6.8 Hz, 1H), 6.85 (s, 2H), 5.78 (s, 1H), 5.50 (d, J = 12.9 Hz, 1H), 4.27 – 4.13 (m, 2H), 3.47 – 3.29 (m, 1H), 2.82 (s, 1H), 2.56 (s, 3H), 1.90 – 1.80 (m, 1H), 1.76 – 1.66 (m, 1H), 1.57 – 1.41 (m, 2H), 1.29 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 164.8, 164.4, 139.6, 138.3, 135.9, 134.4, 133.1, 132.7, 131.1, 128.9, 63.6, 61.5, 53.2, 26.0, 22.0, 19.2, 14.2, 13.8.

IR (neat):

HRMS (APCI -TOF): calculated for [$C_{18}H_{24}O_5SNa$ (M + Na^+)]: 375.1237, found: XXXXX

2-(butylsulfinyl)-3-methylbenzyl 5-chlorothiophene-2-carboxylate (1s):



1s

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as light yellow semi solid, 1.2 g, 67% yield.

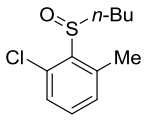
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 4.0 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.20 (d, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 4.0 Hz, 1H), 5.86 (s, 1H), 5.58 (d, *J* = 13.0 Hz, 1H), 3.47 – 3.42 (m, 1H), 2.87 – 2.81 (m, 1H), 2.58 (s, 3H), 1.92 – 1.72 (m, 2H), 1.54 – 1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.7, 139.6, 138.4, 137.8, 136.2, 133.5, 132.7, 131.5, 131.1, 128.9, 127.5, 63.6, 53.2, 26.1, 22.1, 19.3, 13.8

IR (neat): 2958, 2929, 2870, 1707, 1421, 1272, 1243, 1081, 1032, 783, 711.

HRMS (APCI -TOF): calculated for [$C_{17}H_{19}ClO_3S_2Na$ (M + Na^+)]: 393.0356, found: 393.0364.

2-(butylsulfinyl)-1-chloro-3-methylbenzene (1t):



1t

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as white solid, m.p. 62 – 64 ℃, 886 mg, 77% yield.

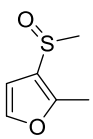
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 2H), 7.12 – 7.09 (m, 1H), 3.30 – 3.23 (m, 1H), 3.01 – 2.95 (m, 1H), 2.67 (s, 3H), 1.83 – 1.70 (m, 2H), 1.58 – 1.43 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 141.5, 137.8, 133.0, 131.8, 131.5, 128.5, 52.4, 25.6, 21.9, 18.6, 13.7.

IR (neat): 2951, 2900, 2869, 1582, 1453, 1389, 1075, 1029, 797, 720.

HRMS (APCI -TOF): calculated for [$C_{11}H_{15}ClOSNa$ (M + Na^+)]: 253.0424, found: 253.0409.

2-methyl-3-(methylsulfinyl)furan (1u):



1u

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as light yellow semi solid, 518 mg, 72% yield.

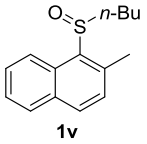
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, *J* = 2.1 Hz, 1H), 6.67 (d, *J* = 2.0 Hz, 1H), 2.76 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.2, 142.6, 123.7, 106.2, 40.9, 12.3.

IR (neat): 3448, 3110, 2996, 1586, 1515, 1418, 1388, 1035, 1011, 939, 888, 738.

HRMS (APCI -TOF): calculated for [$C_6H_8O_2SNa$ (M + Na^+)]: 167.0137, found: 167.0136.

1-(butylsulfinyl)-2-methylnaphthalene (1v):



1v

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as light yellow semi solid, 947 mg, 77% yield.

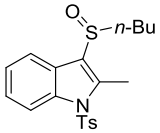
^{1}H NMR (600 MHz, $CDCl_3$): δ 9.08 (s, 1H), 7.88 – 7.82 (m, 2H), 7.60 – 7.49 (m, 2H), 7.32 – 7.22 (m, 1H), 3.62 – 3.48 (m, 1H), 3.10 – 3.04 (m, 1H), 2.73 (s, 3H), 1.90 – 1.75 (m, 1H), 1.71 – 1.60 (m, 1H), 1.57 – 1.43 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 137.4, 134.2, 133.3, 131.9, 131.2, 129.3, 129.0, 127.3, 126.0, 123.6, 52.8, 25.9, 22.0, 20.0, 13.8.

IR (neat): 2960, 2930, 2872, 1961, 1596, 1447, 1270, 1167, 1054, 859, 710, 686

HRMS (APCI -TOF): calculated for [$C_{15}H_{18}OSNa$ (M + Na^+)]: 269.0971, found: 269.0968

3-(butyllsulfinyl)-2-methyl-1-tosyl-1H-indole (1w):



1w

Following general procedure, the title compound was prepared from 5 mmol of corresponding aryl sulfide and was obtained as light yellow semi solid, 1.1 g, 63% yield.

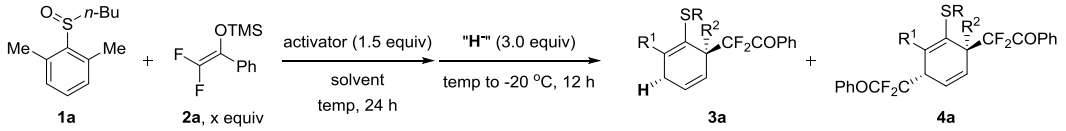
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.18 (m, 4H), 3.00 (s, 3H), 2.75 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.8, 138.3, 136.5, 135.6, 130.3, 126.6, 125.3, 124.8, 124.2, 120.8, 119.8, 114.8, 40.2, 21.7, 13.6.

IR (neat): 2956, 2927, 2871, 1691, 1596, 1447, 1275, 1091, 1045, 910, 713, 686.

HRMS (APCI -TOF): calculated for [$C_{17}H_{17}NO_3S_2Na$ (M + Na^+)]: 370.0542, found: 370.0541.

3 Optimization of reaction conditions



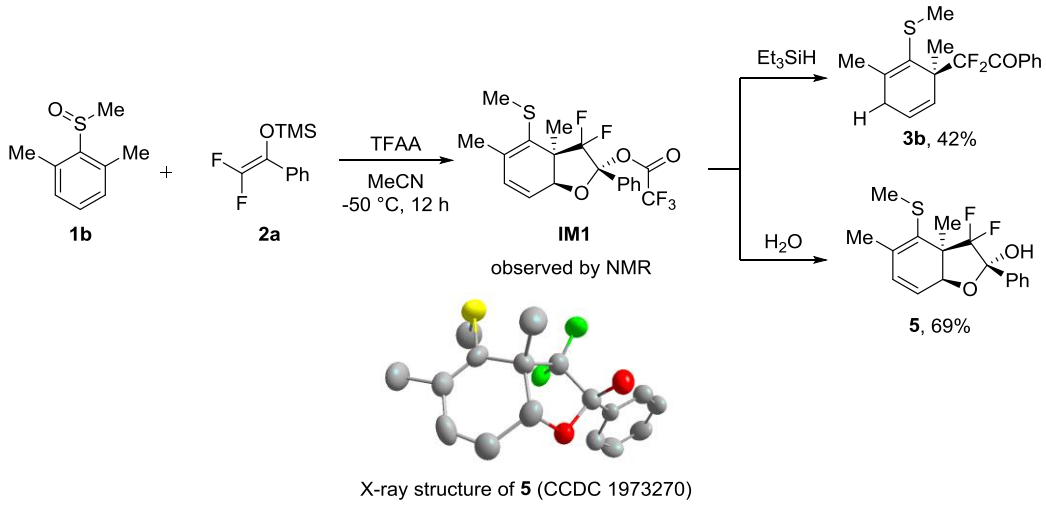
1a **2a**, x equiv **3a** **4a**

entry	activator	solvent	temp (°C)	"**H**"	x (equiv) of **2a**	yield of **3a** (%)	yield of **4a** (%)
1	TFAA	DCM	-78	Et_3SiH	1.5	0	0
2	TFAA	$CHCl_3$	-60	Et_3SiH	1.5	0	0
3	TFAA	MeCN	-50	Et_3SiH	1.5	47	15
6	TFAA	MeCN/DCM (1/1)	-50	Et_3SiH	1.5	19	26
7	TFAA	MeCN/DCM (10/1)	-50	Et_3SiH	1.5	50	20
8	TFAA	MeCN/DCM (9/1)	-50	Et_3SiH	1.5	65	5
9	TFAA	MeCN/DCM (8/1)	-50	Et_3SiH	1.5	27	29
10	TFAA	MeCN/DCM (9/1)	-40	Et_3SiH	1.5	47	23
11	TFAA	MeCN/DCM (9/1)	-50	$(MeO)_3SiH$	1.5	43	9
12	TFAA	MeCN/DCM (9/1)	-50	*i*-Pr_3SiH	1.5	54	9
13	TFAA	MeCN/DCM (9/1)	-50	L-selectride	1.5	0	0
14	TFAA	MeCN/DCM (9/1)	-50	DIBAL-H	1.5	32	trace
15	TFAA	MeCN/DCM (9/1)	-50	Et_3SiH	2.0	58	16
17	Ts_2O	MeCN/DCM (9/1)	-50	Et_3SiH	1.5	0	trace
18	Tf_2O	MeCN/DCM (9/1)	-50	Et_3SiH	1.5	0	17
19	$(ClF_2CO)_2O$	MeCN/DCM (9/1)	-50	Et_3SiH	1.5	61	10
20	Tf_2O	DCM	-78	none	3.0	0	48
21	Tf_2O	MeCN	-50	none	3.0	0	19
22	Tf_2O	DCM	-50	none	3.0	0	35
23	Tf_2O	DCM	-100	none	3.0	0	73
24	Tf_2O	DCM	-100	none	2.5	0	66

General procedure for entries 1 to 19: To a stirred solution of sulfoxide **1a** (63 mg, 0.3 mmol) and difluoroenol silyl ether **2a** (1.5 to 2.0 equiv) in indicated solvent (3 mL) was added anhydride (1.5 equiv) at indicated temperature (-50 to -78 ℃). The mixture was stirred for 24 h. After that, to the mixture was added reducing agent "H" (3.0 equiv), and the resulting mixture was then slowly warmed up to -20 ℃. After stirring for 12 h, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel giving the title compounds **3a** and **4a**.

General procedure for entries 20 to 24: To a stirred solution of sulfoxide **1a** (63 mg, 0.3 mmol) and difluoroenol silyl ether **2a** (1.5 to 2.0 equiv) in indicated solvent (3 mL) was added Tf_2O (76 μL, 1.5 equiv) at indicated temperature (-50 to -100 ℃). The mixture was stirred for 24 h. After that, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel giving the title compound **4a**.

4 Identification of dearomatized key intermediate IM1.

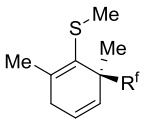


X-ray structure of **5** (CCDC 1973270)

To a stirred solution of sulfoxide **1b** (17 mg, 0.1 mmol) and difluoroenol silyl ether **2a** (36 mg, 1.5 equiv) in CD_3CN/DCM (0.45/0.05 mL) was added TFAA (21 μL, 1.5 equiv) at -50 ℃. The NMR tube charged with reaction mixture was kept at -50 ℃ for 24 h. After that, the reaction mixture was brought for NMR analysis. The obtained ^{1}H, ^{13}C, and ^{19}F-NMR spectrum were shown at page S17.

Reduction: to the obtained mixture of **IM1** was added Et_3SiH (35 mg, 3 equiv), and the resulting mixture was then slowly warmed up to -20 ℃. After stirring for 12 h, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel giving the title compound **3b**, as light yellow oil, 15 mg, 42% yield

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.45 – 7.39 (m, 2H), 5.87 – 5.78 (m, 1H), 5.67 (d, *J* = 9.9, 1H), 2.70 – 2.56 (m, 2H), 2.10 (s, 3H), 1.94 (s, 3H), 1.63 (s, 3H).



3b

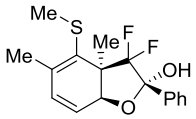
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.8 (t, *J* = 28.7 Hz), 145.9, 134.8, 133.6, 130.2 (t, *J* = 6.0 Hz), 128.8, 128.3, 127.7, 126.6, 120.5 (t, *J* = 262.7 Hz), 49.6 (t, *J* = 21.1 Hz), 34.8, 22.6, 22.2, 22.1, 20.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.7 (s, 1F), -104. 8(s, 1F).

IR (neat): 3037, 2980, 2920, 1691, 1596, 1577, 1447, 1092, 1050, 910, 686.

HRMS (ESI-TOF): calculated for [$C_{17}H_{18}F_2OSNa$ ($M + Na^+$)]: 331.0939, found: 331.0939.

Hydrolysis: to the obtained mixture of **IM1** was added at. aq. $NaHCO_3$ (0.5 mL). The mixture was warmed to 0 ℃. After that, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel giving the title compound **5**, as light yellow solid, 22 mg, m.p. 87 – 89 ^{o}C, 69% yield. (Rf = 0.23, eluent: PE/EtOAc = 10/1). The crystal of **5** was obtained by crystallization from DCM and hexane at room temperature.



5

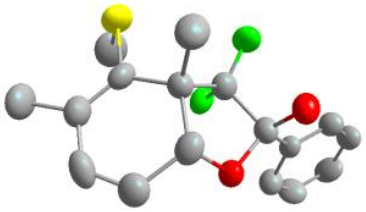
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 – 7.59 (m, 2H), 7.42 – 7.34 (m, 3H), 6.04 (d, *J* = 9.8 Hz, 1H), 5.88 (dd, *J* = 9.7, 3.8 Hz, 1H), 4.71 (d, *J* = 3.9 Hz, 1H), 3.22 (bs, 1H), 2.15 (s, 3H), 2.11 (s, 3H), 1.58 (d, *J* = 2.0 Hz, 3H).

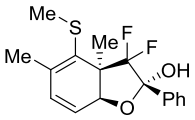
^{13}C NMR (151 MHz, $CDCl_3$): δ 136.8, 135.5, 131.1, 129.9, 129.5, 128.3, 126.9, 125.9 (t, *J* = 271.3 Hz), 121.8, 98.4 (m), 79.6, 50.1 (t, *J* = 21.1 Hz), 23.7 (dd, *J* = 9.0, 1.5 Hz), 21.1, 18.8 (d, *J* = 6.0 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -101.1 (d, *J* = 231.8 Hz, 1F), -121.3 (d, *J* = 231.8 Hz, 1F).

IR (neat): 3371, 2927, 1576, 1448, 1234, 1142, 1102, 1064, 1018, 976, 921, 709.

HRMS (ESI-TOF): calculated for [$C_{17}H_{18}F_2O_2SNa$ (M + Na^+)]: 347.0888, found: 347.0879.





5

Bond precision	c-c=0.00105 Å Wavelength=0.71073	
Cell	a=8.497 (3) b=13.357 (5) c=13.775 (5) α=90 β=85.689 (14) γ=90	
Temperature	294 K	
	Calculated	Reported
Volumn	1559.0(10)	1559.0(10)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	
Moiety formula	C17 H18 F2 O2 S	C17 H18 F2 O2 S
Sum formula	C17 H18 F2 O2 S	C17 H18 F2 O2 S
Mr	324.37	324.37
Dx,g cm^{-3}	1.382	1.382

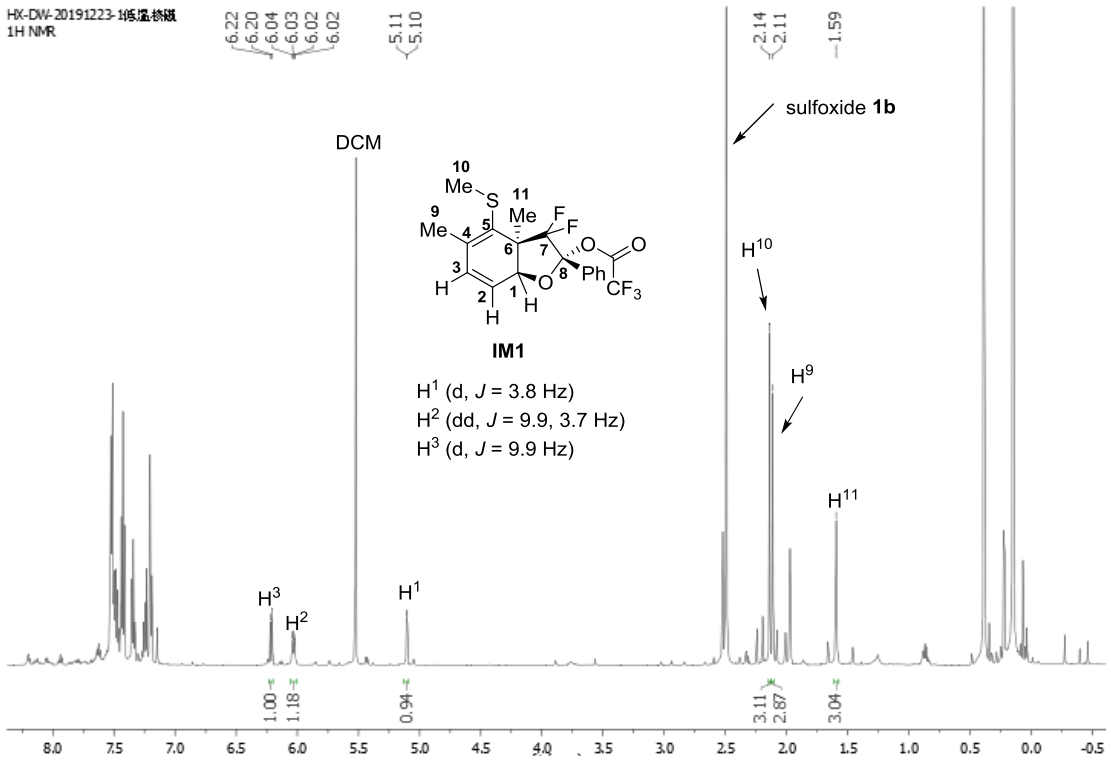
Z	4	4
Mu (mm^{-1})	0.233	0.233
F000	680.0	680.0
F000’	680.88	
h,k,lmax	9,14,14	9,14,14
Nref	1941	1895
Tmin,Tmax	0.954,0.975	0.954,0.975
Tmin’	0.937	

Correction method= # Reported T Limits: Tmin=0.954 Tmax=0.975
AbsCorr = EMPIRICAL

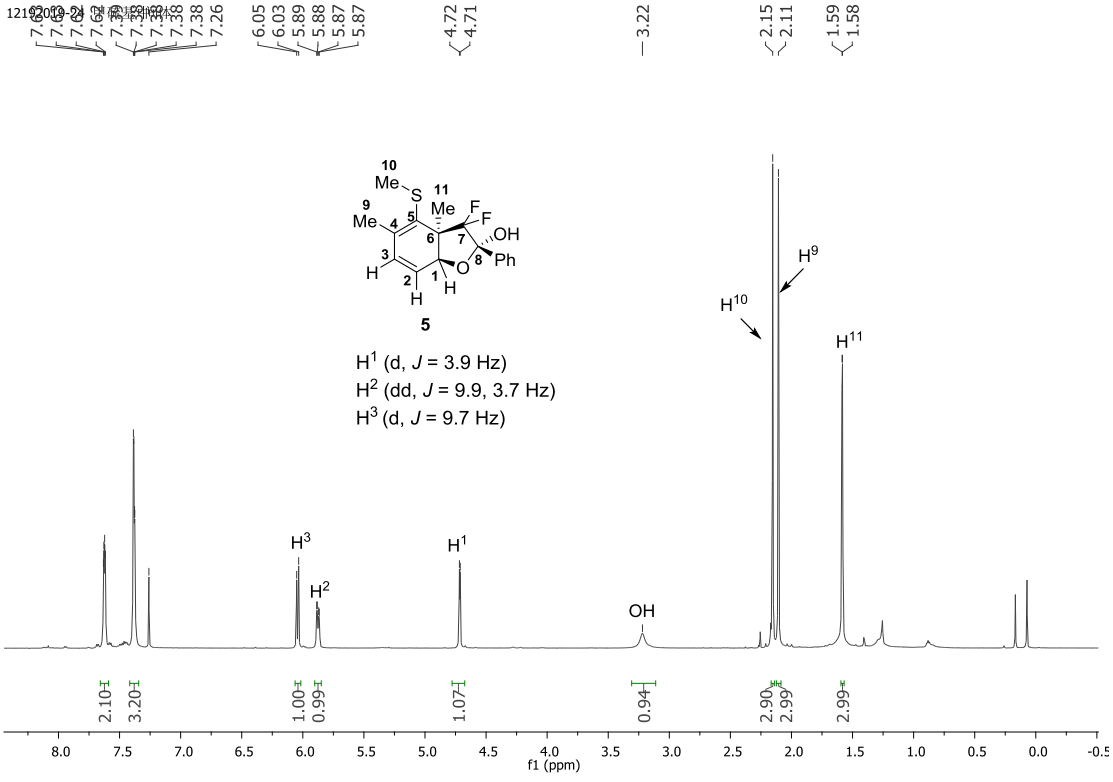
Data completeness= 0.976 Theta(max)= 22.130
R(reflections)= 0.937 wR2(reflections)= 0.2022(1895)
S = 1.011 Npar= 199

Crystallographic data (excluding structural factors) for compound **5** also has been deposited at the Cambridge Crystallographic Data Centre under the deposition number CCDC 1973270.

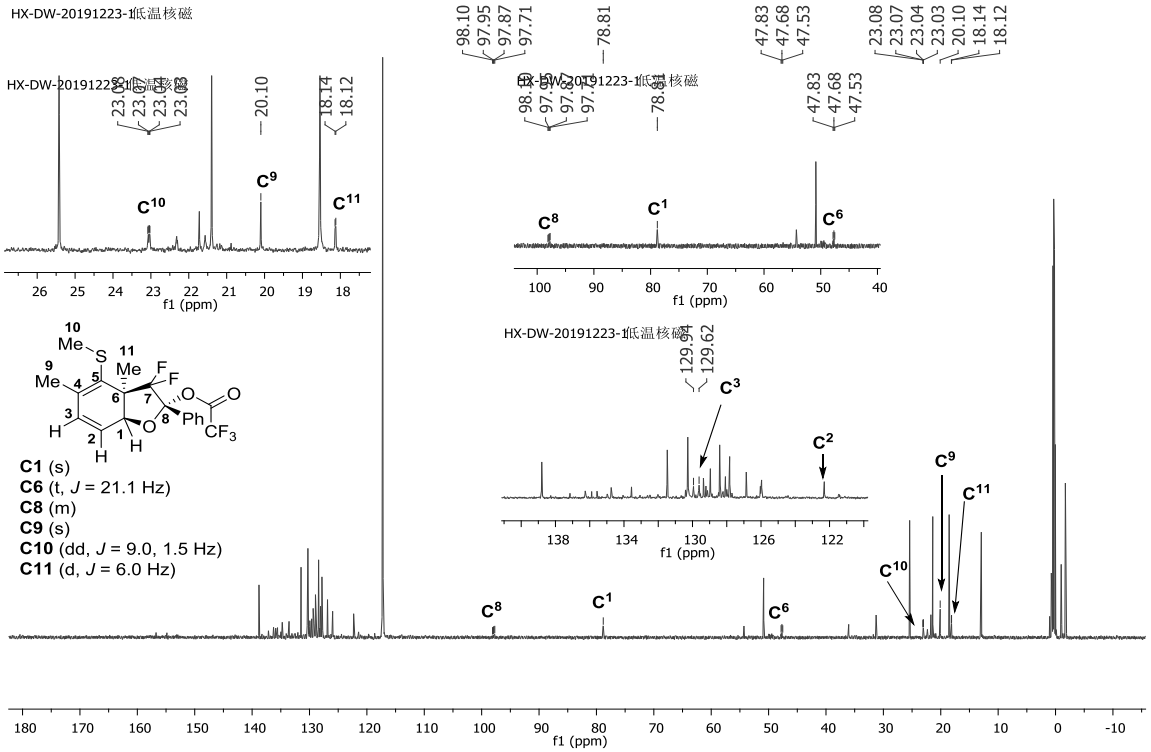
In-situ ^{1}H-NMR analysis of IM1



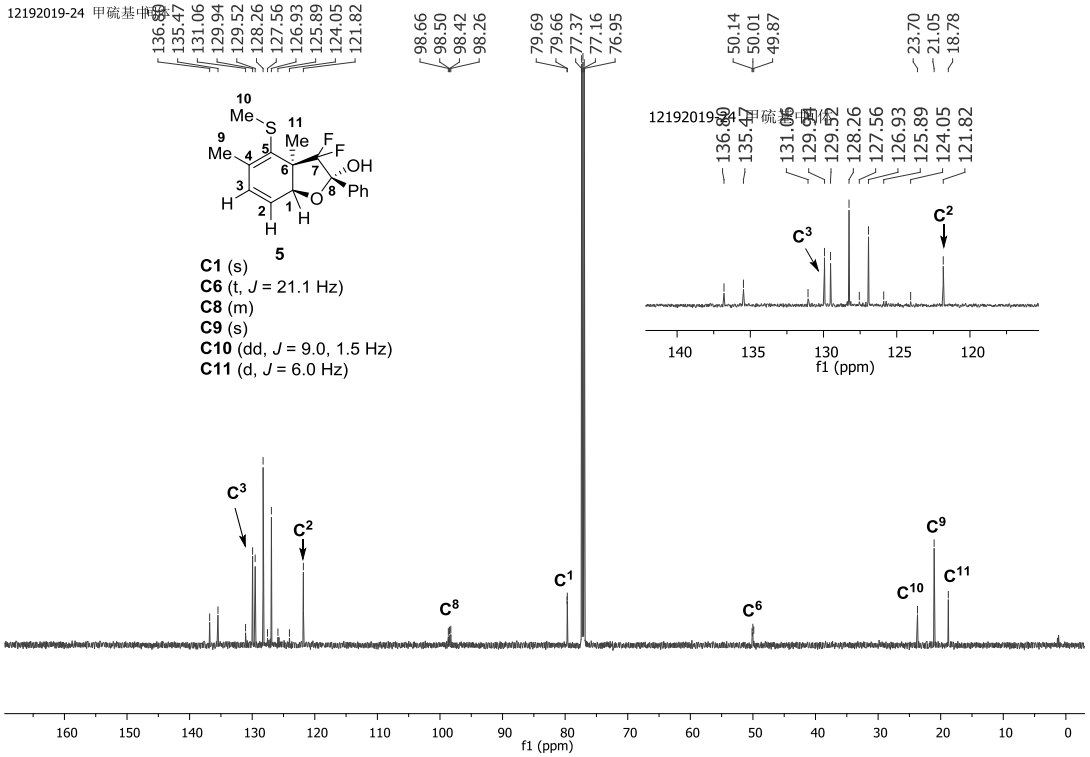
^{1}H-NMR analysis of 5



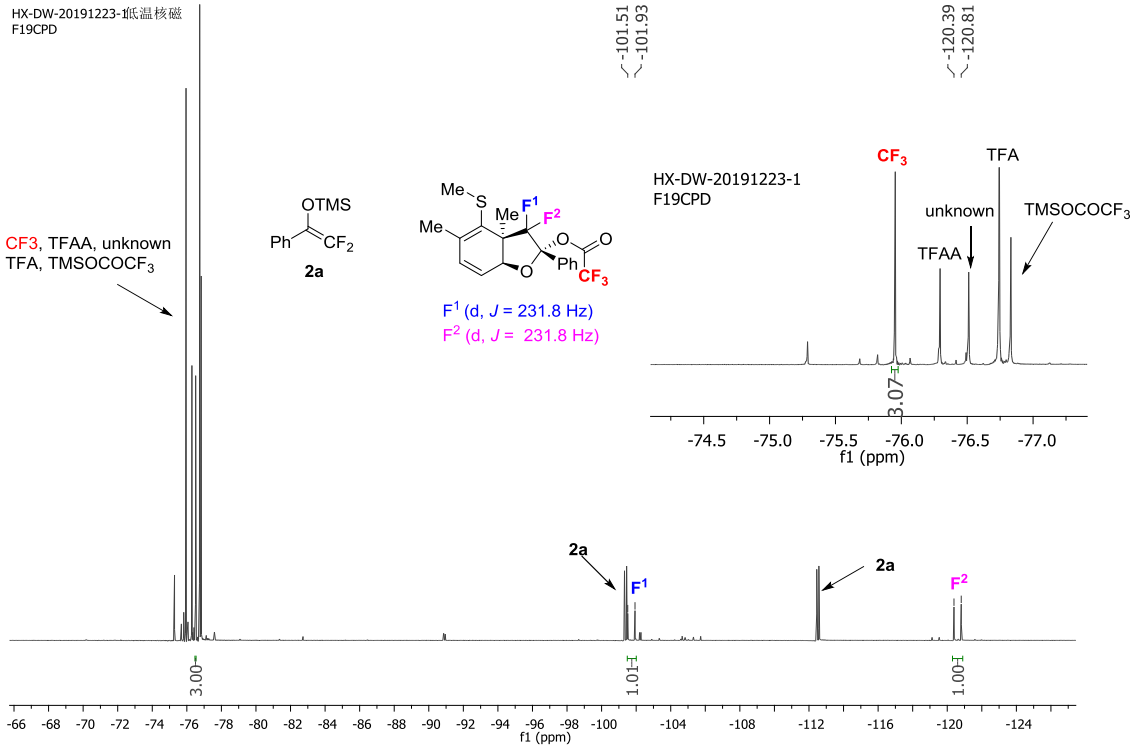
In-situ ^{13}C-NMR analysis of IM1



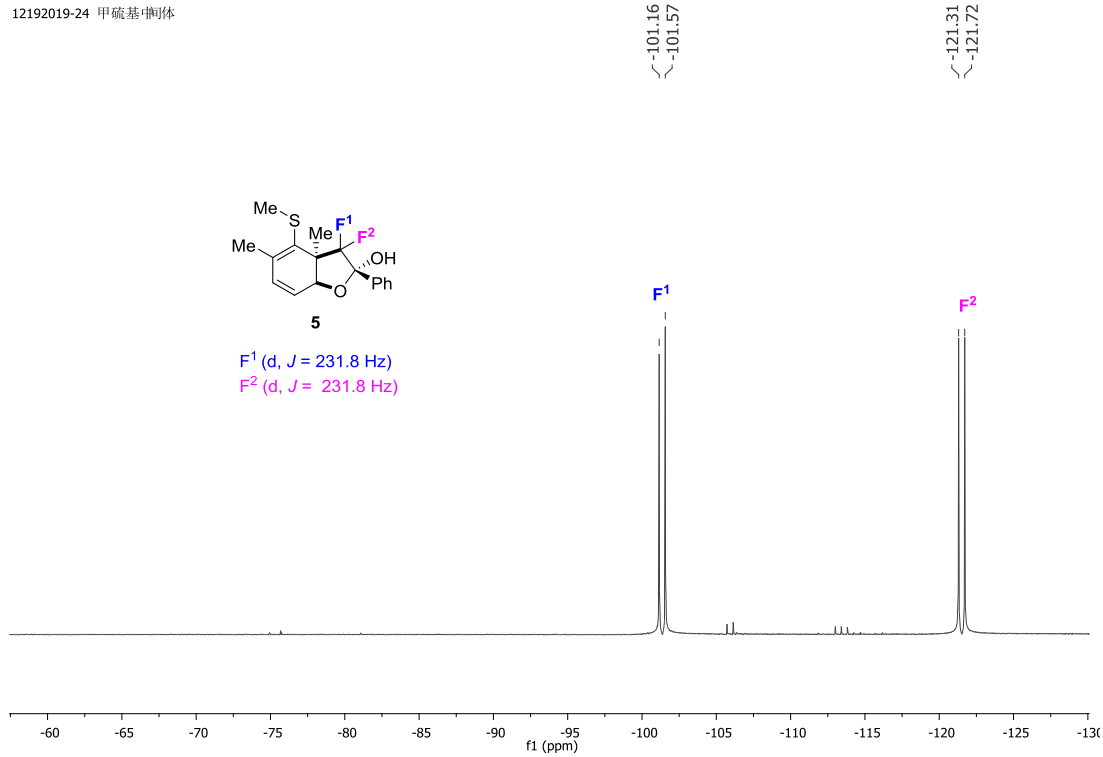
^{13}C-NMR analysis of 5



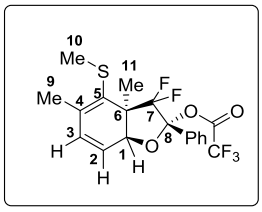
In-situ ^{19}-NMR analysis of IM1

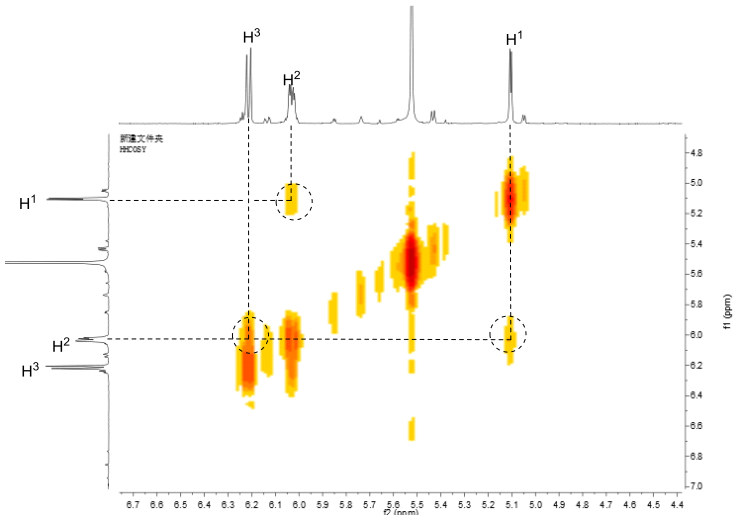


^{19}-NMR analysis of 5

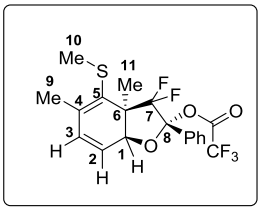


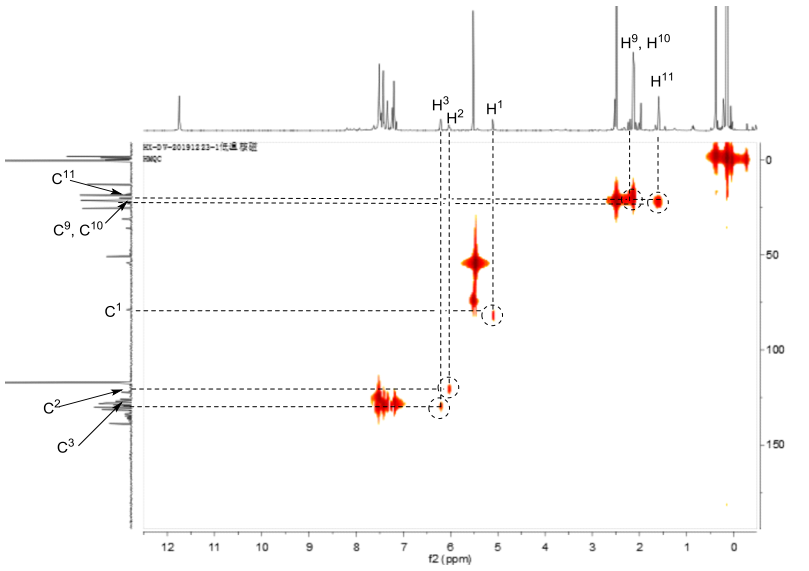
In-situ COSEY-NMR analysis of IM1

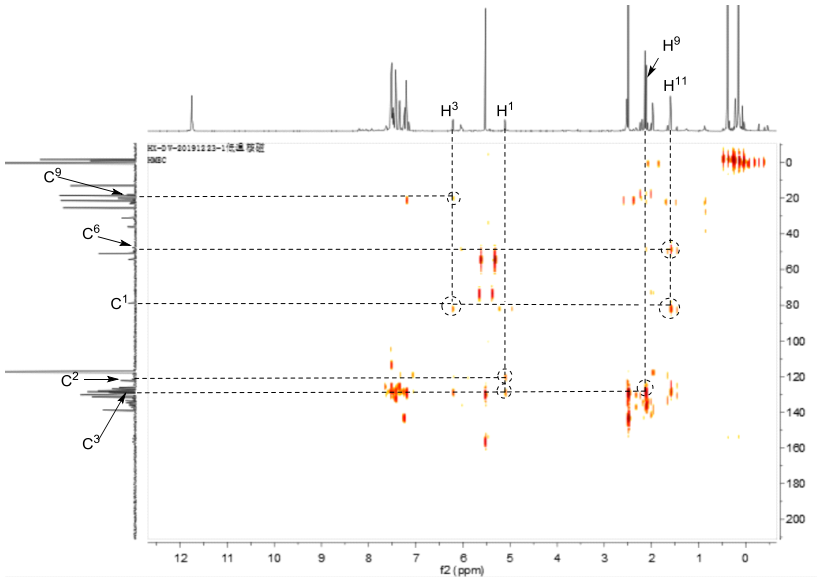




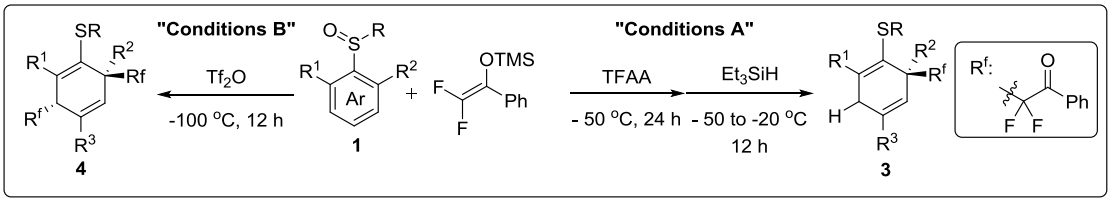
In-situ HMQC AND HMQC analysis OF IM1







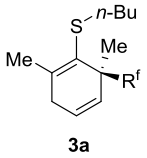
5 General procedure for the dearomative mono- and dual-difluoroalkylation of aryl sulfoxides



General procedure A for "**Conditions A**": To a stirred solution of sulfoxide **1** (0.3 mmol) and difluoroenol silyl ether **2a** (103 mg, 1.5 equiv) in MeCN/DCM (9/1, 3 mL) was added TFAA (63 μL, 1.5 equiv) at -50 ℃. The mixture was then stirred at -50 ℃ for 24 h. After that, to the mixture was added Et_3SiH (104 mg, 3.0 equiv), and the resulting mixture was then slowly warmed up to -20 ℃. After stirring for 12 h, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel giving the title compound **3** (Note: After Et3SiH was added, reaction mixture was slowly warmed up to 0 ℃ for **1i**, **1j**, **1q**, **1r** ,**1s** or 20 ℃ for **1k**).

General procedure B for "**Conditions B**": To a stirred solution of sulfoxide **1** (0.3 mmol) and difluoroenol silyl ether **2a** (205 mg, 3.0 equiv) in DCM (3 mL) was added Tf_2O (76 μL, 1.5 equiv) at -100 ℃. The mixture was stirred for 12 h. After that, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel giving the title compound **4**.

2-(2-(butylthio)-1,3-dimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (3a):



3a

Following the general procedure A, the title compound was obtained as light yellow oil, 68 mg, 65% yield. (Rf = 0.28, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.43 – 7.38 (m, 2H), 5.83 – 5.79 (m, 1H), 5.68 – 5.65 (m, 1H), 2.65 – 2.62 (m, 1H), 2.58 – 2.51 (m, 3H), 1.91 (s, 3H), 1.63 (s, 3H), 1.52 – 1.46 (m, 2H), 1.39 – 1.32 (m 2H), 0.87 (t, *J* = 7.3 Hz, 3H).

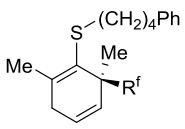
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.8 (t, *J* = 28.7 Hz), 145.9, 134.7, 133.3, 130.2 (t, *J* = 6.0 Hz), 128.9, 126.9, 126.6, 120.5 (t, *J* = 262.7 Hz), 49.4 (t, *J* = 21.1 Hz), 36.9, 34.9, 31.6, 22.6, 22.4, 22.2, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.1 (d, *J* = 254.3 Hz, 1F), -104.7 (d, *J* = 204.3 Hz, 1F).

IR (neat): 3057, 2958, 2930, 2872, 1694, 1597, 1448, 1101, 1043, 912, 821.

HRMS (ESI-TOF): calculated for [$C_{20}H_{24}F_2OSNa$ ($M + Na^+$)]: 373.1408, found: 373.1407.

2-(1,3-dimethyl-2-((4-phenylbutyl)thio)cyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (3c):



3c

Following the general procedure A, the title compound was obtained as light yellow oil, 73 mg, 57% yield. (Rf = 0.26, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, J = 7.7 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.48 – 7.41 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.15 (m, 3H), 5.87 – 5.83 (m, 1H), 5.71 (dd, *J* = 9.9, 2.4 Hz, 1H), 2.68 – 2.54 (m, 6H), 1.93 (s, 3H), 1.75 – 1.68 (m, 2H), 1.66 (s, 3H), 1.62 – 1.56 (m, 2H).

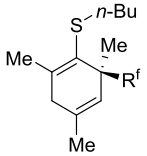
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.9 (t, *J* = 28.7 Hz), 146.1, 142.3, 134.7, 133.5, 130.3 (t, *J* = 6.0 Hz), 128.9, 128.5, 128.4, 128.3, 126.7, 126.6, 125.9, 120.5 (t, *J* = 262.7 Hz), 49.4 (t, *J* = 21.1 Hz), 36.9, 35.7, 34.9, 30.8, 29.1, 22.6, 22.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.1 (d, *J* = 254.3 Hz, 1F), -104.7 (d, *J* = 204.3 Hz, 1F).

IR (neat): 3025, 2931, 2854, 1691, 1596, 1447, 1367, 1092, 1050, 910, 733, 679.

HRMS (ESI-TOF): calculated for [$C_{26}H_{28}F_2OSNa$ ($M + Na^+$)]: 449.1721, found: 449.1718.

2-(2-(butylthio)-1,3,5-trimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (3d):



3d

Following the general procedure A, the title compound was obtained as light yellow oil, 86 mg, 79% yield. (Rf = 0.28, eluent: PE/EtOAc = 30/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.42 – 7.37 (m, 2H), 5.32 (s, 1H), 2.61 – 2.33 (m, 4H), 1.91 (s, 3H), 1.59 (s, 3H), 1.57 (s, 3H), 1.53 – 1.46 (m, 2H), 1.40 – 1.33 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

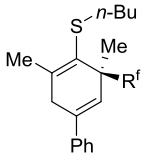
^{13}C NMR (151 MHz, $CDCl_3$): δ 191.0 (t, *J* = 28.7 Hz), 145.6, 134.8, 133.4, 134.3, 130.2 (t, *J* = 6.0 Hz), 128.1, 126.8, 123.8, 120.7 (t, *J* = 262.7 Hz), 49.9 (t, *J* = 21.1 Hz), 39.5, 36.8, 31.7, 22.4, 22.33, 22.26, 22.22, 13.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.2 (d, *J* = 254.3 Hz, 1F), -104.8 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2956, 2929, 2871, 1692, 1596, 1446, 1272, 1089, 1048, 914, 714, 687.

HRMS (ESI-TOF): calculated for [$C_{21}H_{26}F_2OSNa$ ($M + Na^+$)]: 387.1565, found: 387.1559.

2-(4-(butylthio)-3,5-dimethyl-3,6-dihydro-[1,1'-biphenyl]-3-yl)-2,2-difluoro-1-phenylethan-1-one (3e):



3e

Following the general procedure A, the title compound was obtained as light yellow oil, 73 mg, 57% yield. (Rf = 0.25, eluent: PE/EtOAc = 30/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.38 – 7.34 (m, 2H), 7.32 – 7.25 (m, 5H), 5.97 (d, *J* = 2.4 Hz, 1H), 3.02 (d, *J* = 21.9 Hz, 1H), 2.88 (d, *J* = 21.9, 1H), 2.63 – 2.55 (m, 2H), 2.02 (s, 3H), 1.72 (s, 3H), 1.56 – 1.50 (m, 2H), 1.43 – 1.36 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

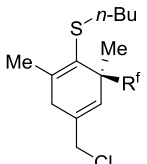
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.8 (t, *J* = 28.7 Hz), 145.8, 139.6, 136.6, 134.7, 130.2 (t, *J* = 6.0 Hz), 128.5, 128.3, 127.6, 126.7, 125.6, 125.5, 120.7 (t, *J* = 262.7 Hz), 50.4 (t, *J* = 21.1 Hz), 37.1, 36.9, 31.7, 22.7, 22.6, 22.3, 13.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.3 (s, 2F).

IR (neat): 2955, 2928, 2870, 1691, 1596, 1446, 1272, 1094, 1049, 889, 714, 687.

HRMS (ESI-TOF): calculated for [$C_{26}H_{28}F_2OSNa$ ($M + Na^+$)]: 449.1721, found: 449.1722.

2-(2-(butylthio)-5-(chloromethyl)-1,3-dimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenyl ethan-1-one (3f):



3f

Following the general procedure A, the title compound was obtained as light yellow oil, 84 mg, 71% yield. (Rf = 0.30, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.45 – 7.38 (m, 2H), 5.73 (s, 1H), 3.96 (d, *J* = 11.6 Hz, 1H), 3.90 (d, *J* = 11.6 Hz, 1H), 2.77 (d, *J* = 22.2 Hz, 1H), 2.62 – 2.48 (m, 3H), 1.96 (s, 3H), 1.63 (s, 3H), 1.52 – 1.46 (m, 2H), 1.40 – 1.33 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

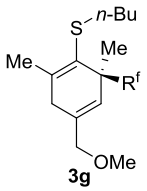
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.6 (t, *J* = 28.7 Hz), 145.2, 134.6, 134.1, 133.7, 130.2 (t, *J* = 6.0 Hz), 128.4, 128.3, 126.5, 120.7 (t, *J* = 262.7 Hz), 50.2 (t, *J* = 21.1 Hz), 47.8, 36.9, 35.5, 31.6, 22.5, 22.2, 22.1, 13.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.9 (d, *J* = 254.3 Hz, 1F), -104.5 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2956, 2929, 2870, 1691, 1596, 1446, 1262, 1100, 1045, 906, 715, 687.

HRMS (ESI-TOF): calculated for [$C_{21}H_{25}ClF_2OSNa$ ($M + Na^+$)]: 421.1175, found: 421.1174.

2-(2-(butylthio)-5-(methoxymethyl)-1,3-dimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (3g):



Following the general procedure A, the title compound was obtained as light yellow oil, 85 mg, 72% yield. (Rf = 0.43, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.51 (m, 1H), 7.42 – 7.38 (m, 2H), 5.63 (s, 1H), 3.77 (d, *J* = 12.1 Hz, 1H), 3.73 (d, *J* = 12.1 Hz, 1H), 3.26 (s, 3H), 2.65 (d, *J* = 22.3 Hz, 1H), 2.56 – 2.45 (m, 3H), 1.92 (s, 3H), 1.63 (s, 3H), 1.51 – 1.44 (m, 2H), 1.38 – 1.31 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

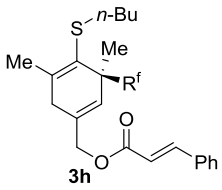
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.8 (t, *J* = 28.7 Hz), 145.7, 135.0, 134.7, 133.5, 130.2 (t, *J* = 6.0 Hz), 128.3, 126.7, 125.9, 120.5 (t, *J* = 262.7 Hz), 75.2, 58.0, 50.0 (t, *J* = 21.1 Hz), 36.9, 35.4, 31.6, 22.5, 22.3, 22.2, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.0 (d, *J* = 254.3 Hz, 1F), -104.6 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2956, 292 9, 2870, 1691, 1596, 1446, 1262, 1100, 1045, 906, 715, 687.

HRMS (ESI-TOF): calculated for [$C_{22}H_{28}F_2O_2SNa$ ($M + Na^+$)]: 417.1670, found: 417.1667.

(4-(butylthio)-3-(1,1-difluoro-2-oxo-2-phenylethyl)-3,5-dimethylcyclohexa-1,4-dien-1-yl)methyl cinnamate (3h):



Following the general procedure A, the title compound was obtained as light yellow oil, 109 mg, 68% yield. (Rf = 0.33, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 16.0 Hz, 1H), 7.55 – 7.51 (m, 3H), 7.43 – 7.36 (m, 5H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.74 (s, 1H), 4.55 (s, 2H), 2.66 (d, *J* = 22.3 Hz, 1H), 2.60 – 2.50 (m, 3H), 1.97 (s, 3H), 1.66 (s, 3H), 1.54 – 1.47 (m, 2H), 1.40 – 1.34 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 190.6 (t, *J* = 28.7 Hz), 166.6, 145.4, 145.0, 134.6, 134.3, 133.6, 133.1, 130.5, 130.2 (t, *J* = 6.0 Hz), 129.0, 128.3, 128.2, 127.0, 126.8, 120.4 (t, *J* = 262.7 Hz), 117.7, 66.5, 49.9 (t, *J* = 21.1 Hz), 36.8, 35.4, 31.6, 22.5, 22.2, 13.8.

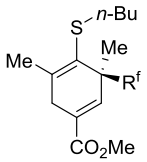
^{19}F NMR (565 MHz, $CDCl_3$) δ -104.4 (s, 2F).

IR (neat): 2955, 2928, 2870, 1710, 1692, 1635, 1596, 1447, 1154, 1094, 766, 713.

HRMS (ESI-TOF): calculated for [$C_{30}H_{32}F_2O_3SNa$ ($M + Na^+$)]: 533.1932, found: 533.1931.

methyl

4-(butylthio)-3-(1,1-difluoro-2-oxo-2-phenylethyl)-3,5-dimethylcyclohexa-1,4-diene-1-carboxylate (3i):



3i

Following the general procedure A, the title compound was obtained as light yellow oil, 73 mg, 59% yield. (Rf = 0.41, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.43 – 7.38 (m, 2H), 6.83 (d, *J* = 2.4 Hz, 1H), 3.73 (s, 3H), 3.00 (d, *J* = 22.8 Hz, 1H), 2.77 (d, *J* = 22.8, 1H), 2.53 – 2.43 (m, 2H), 1.97 (s, 3H), 1.67 (s, 3H), 1.48 – 1.42 (m, 2H), 1.38 – 1.30 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

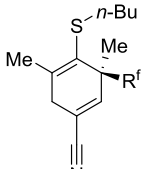
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.1 (t, *J* = 28.7 Hz), 166.3, 145.8, 138.8, 134.2, 133.8, 130.2 (t, *J* = 6.0 Hz), 129.4, 128.4, 125.8, 119.9 (t, *J* = 262.7 Hz), 52.0, 50.8 (t, *J* = 21.1 Hz), 36.9, 34.0, 31.5, 22.6, 22.2, 21.9, 13.9

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.2 (d, *J* = 254.3 Hz, 1F), -104.2 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2954, 2871, 1717, 1692, 1596, 1436, 1267, 1100, 1044, 906, 711,

HRMS (ESI-TOF): calculated for [$C_{22}H_{26}F_2O_3SNa$ ($M + Na^+$)]: 431.1463, found: 431.1458.

4-(butylthio)-3-(1,1-difluoro-2-oxo-2-phenylethyl)-3,5-dimethylcyclohexa-1,4-diene-1-carbonitrile (3j):



3j

Following the general procedure A, the title compound was obtained as light yellow oil, 45 mg, 40% yield. (Rf = 0.19, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.61 – 7.58 (m, 1H), 7.48 – 7.42 (m, 2H), 6.58 (s, 1H), 2.88 (s, 2H), 2.53 – 2.45 (m, 2H), 2.01 (s, 3H), 1.66 (s, 3H), 1.49 – 1.43 (m, 2H), 1.36 – 1.30 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

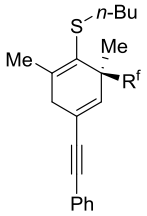
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.4 (t, *J* = 28.7 Hz), 144.4, 143.7, 134.2, 133.7, 130.2 (t, *J* = 6.0 Hz), 128.6, 126.3, 119.3 (t, *J* = 262.7 Hz), 117.4, 112.2, 50.5 (t, *J* = 21.1 Hz), 36.9, 35.6, 31.5, 22.4, 22.1, 21.8, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -102.7 (d, *J* = 254.3 Hz, 1F), -103.4 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2957, 2930, 2871, 2221, 1691, 1596, 1447, 1274, 1108, 1044, 907, 715.

HRMS (ESI-TOF): calculated for [$C_{21}H_{23}F_2NOSNa$ ($M + Na^+$)]: 398.1361, found: 398.1359.

2-(2-(butylthio)-1,3-dimethyl-5-(phenylethynyl)cyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (3k):



3k

Following the general procedure A, the title compound was obtained as light yellow oil, 71.5 mg, 53% yield. (Rf = 0.21, eluent: PE/EtOAc = 30/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.39 (m, 4H), 7.33 – 7.28 (m, 3H), 6.11 (s, 1H), 2.90 – 2.78 (m, 2H), 2.57 – 2.49 (m, 2H), 1.98 (s, 3H), 1.67 (s, 3H), 1.53 – 1.46 (m, 2H), 1.39 – 1.33 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

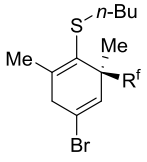
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.4 (t, *J* = 28.7 Hz), 145.5, 134.6, 134.4, 133.7, 133.2, 131.8, 131.6, 130.2 130.2 (t, *J* = 6.0 Hz), 128.6, 123.1, 122.0, 120.4 (t, *J* = 262.7 Hz), 89.8, 88.4, 50.6 (t, *J* = 21.1 Hz), 38.6, 37.0, 31.6, 22.5, 22.3, 22.2, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.4 (d, *J* = 254.3 Hz, 1F), -104.0 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2955, 2926, 2870, 1691, 1596, 1447, 1272, 1100, 1044, 754, 687.

HRMS (ESI-TOF): calculated for [$C_{28}H_{28}F_2OSNa$ ($M + Na^+$)]: 473.1721, found: 473.1722.

2-(5-bromo-2-(butylthio)-1,3-dimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (3l):



3l

Following the general procedure A, the title compound was obtained as light yellow oil, 83 mg, 65% yield. (Rf = 0.32, eluent: PE/EtOAc = 30/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.58 – 7.55 (m, 1H), 7.46 – 7.42 (m, 2H), 6.01 (s, 1H), 3.01 – 2.85 (m, 2H), 2.59 – 2.46 (m, 2H), 1.95 (s, 3H), 1.63 (s, 3H), 1.53 – 1.44 (m, 2H), 1.38 – 1.32 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H).

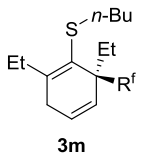
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.2 (t, *J* = 28.7 Hz), 145.0, 134.4, 133.8, 130.2 (t, *J* = 6.0 Hz), 129.9, 128.4, 126.6, 121.6, 119.6 (t, *J* = 262.7 Hz), 52.7 (t, *J* = 21.1 Hz), 43.5, 36.8, 31.6, 22.2, 22.1, 22.0, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.7 (d, *J* = 254.3 Hz, 1F), -104.2 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2955, 2928, 2870, 1691, 1596, 1447, 1271, 1097, 1047, 712, 662.

HRMS (ESI-TOF): calculated for [$C_{20}H_{23}BrF_2OSNa$ ($M + Na^+$)]: 451.0513, found: 451.0512.

2-(2-(butylthio)-1,3-diethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (3m):



3m

Following the general procedure A, the title compound was obtained as light yellow oil, 70 mg, 62% yield. (Rf = 0.41, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.44 – 7.38 (m, 2H), 5.96 – 5.80 (m, 1H), 5.49 (d, *J* = 10.0, 1H), 2.72 – 2.51 (m, 6H), 2.43 – 2.36 (m, 1H), 1.80 – 1.73 (m, 1H), 1.56 – 1.49 (m, 2H), 1.41 – 1.34 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.72 (t, *J* = 7.4 Hz, 3H).

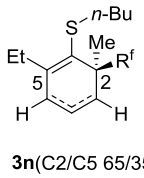
^{13}C NMR (151 MHz, $CDCl_3$): δ 191.0 (t, *J* = 28.7 Hz), 152.3, 134.9, 133.5, 130.4 (t, *J* = 6.0 Hz), 129.3, 127.1, 124.6, 120.5 (t, *J* = 262.7 Hz), 53.8 (t, *J* = 21.1 Hz), 37.0, 31.9, 31.8, 29.4, 25.2, 22.3, 13.9, 12.7, 8.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -102.5 (d, *J* = 254.3 Hz, 1F), -103.4 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2955, 2928, 2870, 1691, 1596, 1447, 1271, 1097, 1047, 712, 662.

HRMS (ESI-TOF): calculated for [$C_{22}H_{28}F_2OSNa$ ($M + Na^+$)]: 401.1721, found: 401.1726.

2-(2-(butylthio)-3-ethyl-1-methylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (3n):



3n(C2/C5 65/35)

Following the general procedure A, the title compound was obtained as a mixture of C2/C5 65/35, light yellow oil, 69 mg, 63% yield. (Rf = 0.32, eluent: PE/EtOAc = 30/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 – 7.94 (m, 2H), 7.57 – 7.52 (m, 1H), 7.44 – 7.37 (m, 2H), 5.88 – 5.83 (m, 3H), 5.68 (d, *J* = 9.8 Hz, 0.66H), 5.49 (d, *J* = 10.0 Hz, 0.32H), 2.69 – 2.51 (m, 5H), 2.30 – 2.24 (m, 0.66H), 1.95 (s, 1H), 1.77 – 1.73 (m, 0.38H), 1.64 (s, 2.14H), 1.55 – 1.46 (m, 2H), 1.40 – 1.30 (m, 2H), 0.92 – 0.84 (m, 5H), 0.74 – 0.70 (t, *J* = 7.4 Hz, 1H).

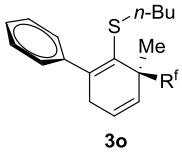
^{13}C NMR (151 MHz, $CDCl_3$): δ 191.2 (t, *J* = 28.7 Hz), 190.7 (t, *J* = 28.7 Hz), 151.7, 146.3, 134.9, 134.6, 133.6, 133.4, 130.4 (t, *J* = 6.0 Hz), 130.2 (t, *J* = 6.0 Hz), 128.8, 128.3, 128.2, 128.1, 127.2, 126.9, 126.2, 125.4, 120.6 (t, *J* = 262.7 Hz), 120.5 (t, *J* = 262.7 Hz), 53.7 (t, *J* = 21.1 Hz), 49.8 (t, *J* = 21.1 Hz), 38.1, 36.2, 34.9, 31.9, 31.7, 31.6, 29.2, 25.2, 22.9, 22.4, 22.3, 13.9, 13.8, 12.4, 8.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.0 – -104.8 (m, 2F).

IR (neat): 2959, 2931, 2872, 1691, 1596, 1447, 1059, 907, 729, 686.

HRMS (ESI-TOF): calculated for [$C_{21}H_{26}F_2OSNa$ ($M + Na^+$)]: 387.1565, found: 387.1562.

2-(2-(butylthio)-3-methyl-3,6-dihydro-[1,1'-biphenyl]-3-yl)-2,2-difluoro-1-phenylethan-1-one (3o):



3o

Following the general procedure A, the title compound was obtained as light yellow oil, 91.5 mg, 74% yield. (Rf = 0.27, eluent: PE/EtOAc = 30/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.62 – 7.62 (m, 1H), 7.48 – 7.43 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 7.14 – 7.11 (m, 2H), 5.92 – 5.87 (m, 1H), 5.77 (d, *J* = 9.9 Hz, 1H), 3.04 – 2.77 (m, 2H), 2.17 – 2.03 (m, 2H), 1.71 (s, 3H), 1.19 – 1.01 (m, 4H), 0.70 (t, *J* = 7.3 Hz, 3H).

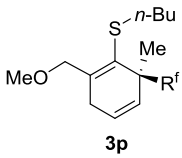
^{13}C NMR (151 MHz, $CDCl_3$): δ 191.6 (t, *J* = 28.7 Hz), 147.0, 142.6, 133.8, 130.4 (t, *J* = 6.0 Hz), 129.7, 128.7, 128.5, 129.1, 128.0, 127.7, 127.1, 126.9, 120.5 (t, *J* = 262.7 Hz), 49.4 (t, *J* = 21.1 Hz), 36.2, 36.1, 31.2, 22.5, 21.9, 13.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.5 (d, *J* = 254.3 Hz, 1F), -104.2 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2959, 2931, 2872, 1691, 1596, 1447, 1059, 907, 729, 686.

HRMS (ESI-TOF): calculated for [$C_{25}H_{26}F_2OSNa$ ($M + Na^+$)]: 435.1565, found: 435.1559.

2-(2-(butylthio)-3-(methoxymethyl)-1-methylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (3p):



3p

Following the general procedure A, the title compound was obtained as light yellow oil, 63 mg, 55% yield. (Rf = 0.20, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.44 – 7.39 (m, 2H), 5.91 – 5.87 (m, 1H), 5.66 (d, *J* = 9.8 Hz, 1H), 4.33 (d, *J* = 11.9 Hz, 1H), 4.24 (d, *J* = 11.9 Hz, 1H), 3.26 (s, 3H), 2.88 (dd, *J* = 23.1, 4.5 Hz, 1H), 2.67 (d, *J* = 23.2 Hz, 1H), 2.57 – 2.52 (m, 2H), 1.64 (s, 3H), 1.52 – 1.47 (m, 2H), 1.39 – 1.32 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

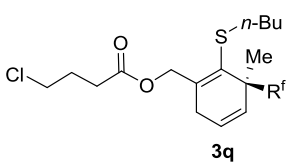
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.6 (t, *J* = 28.7 Hz), 146.8, 134.6, 133.7, 130.4 (t, *J* = 6.0 Hz), 130.2, 128.4, 127.2, 120.4 (t, *J* = 262.7 Hz), 73.9, 58.3, 49.6 (t, *J* = 21.1 Hz), 38.2, 31.6, 30.5, 22.4, 22.2, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.7 (d, *J* = 254.3 Hz, 1F), -104.3 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2956, 2927, 2871, 1691, 1596, 1447, 1275, 1091, 1045, 910, 713, 686.

HRMS (ESI-TOF): calculated for [$C_{21}H_{26}F_2O_2SNa$ ($M + Na^+$)]: 403.1514, found: 403.1508

(2-(butylthio)-3-(1,1-difluoro-2-oxo-2-phenylethyl)-3-methylcyclohexa-1,4-dien-1-yl)methyl 4-chlorobutanoate (3q):



3q

Following the general procedure A, the title compound was obtained as light yellow oil, 76 mg, 54% yield. (Rf = 0.37, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.45 – 7.41 (m 2H), 5.92 – 5.84 (m, 1H), 5.68 (d, J = 9.8 Hz, 1H), 5.02 (d, *J* = 12.7 Hz, 1H), 4.94 (d, *J* = 12.7 Hz, 1H), 3.61 (t, *J* = 6.3 Hz, 2H), 2.78 – 2.72 (m, 1H), 2.68 – 2.61 (m, 1H), 2.59 – 2.54 (m, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.16 – 2.04 (m, 2H), 1.65 (s, 3H), 1.53 – 1.47 (m, 2H), 1.37 – 1.32 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H).

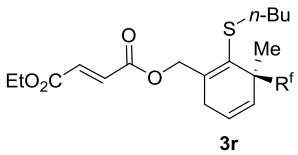
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.4 (t, *J* = 28.7 Hz), 172.5, 144.0, 134.5, 133.8, 132.2, 130.4 (t, *J* = 6.0 Hz), 128.6, 128.4, 126.5, 120.2 (t, *J* = 262.7 Hz), 66.2, 49.7 (t, *J* = 21.1 Hz), 44.2, 38.3, 31.6, 31.2, 30.5, 27.7, 22.3, 22.2, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.7 (d, *J* = 254.3 Hz, 1F), -104.4 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2957, 2927, 2871, 1734, 1691, 1596, 1447, 1169, 1094, 1044, 912, 714, 687.

HRMS (ESI-TOF): calculated for [$C_{24}H_{29}ClF_2O_3SNa$ ($M + Na^+$)]: 493.1386, found: 493.1384.

(2-(butylthio)-3-(1,1-difluoro-2-oxo-2-phenylethyl)-3-methylcyclohexa-1,4-dien-1-yl)methyl ethyl maleate (3r):



3r

Following the general procedure A, the title compound was obtained as light yellow oil, 84 mg, 57% yield. (Rf = 0.34, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.44 – 7.40 (m, 2H), 6.83 (s, 2H), 5.88 – 5.85 (m, 1H), 5.68 (dd, *J* = 9.8, 2.4 Hz, 1H), 5.11 (d, *J* = 12.7 Hz, 1H), 5.05 (d, *J* = 12.8 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.77 – 2.72 (m, 1H), 2.67 – 2.61 (m, 1H), 2.60 – 2.55 (m, 2H), 1.65 (s, 3H), 1.53 – 1.46 (m, 2H), 1.36 – 1.28 (m, 5H),

0.86 (t, *J* = 7.4 Hz, 3H).

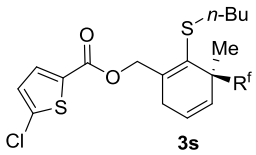
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.3 (t, *J* = 28.7 Hz), 164.9, 164.7, 143.5, 134.4, 134.3, 133.8, 133.1, 132.7, 130.3 (t, *J* = 6.0 Hz), 128.5, 128.4, 126.3, 120.1 (t, *J* = 262.7 Hz), 66.8, 61.5, 49.7 (t, *J* = 21.1 Hz), 38.3, 31.6, 30.5, 22.2, 22.1, 14.2, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.8 (d, *J* = 254.3 Hz, 1F), -104.3 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2957, 2927, 2871, 1734, 1691, 1596, 1447, 1169, 1094, 1044, 912, 714, 687.

HRMS (ESI-TOF): calculated for [$C_{26}H_{30}F_2O_5SNa$ ($M + Na^+$)]: 515.1674, found: 515.1670.

(2-(butylthio)-3-(1,1-difluoro-2-oxo-2-phenylethyl)-3-methylcyclohexa-1,4-dien-1-yl)methyl 5-chlorothiophene-2-carboxylate (3s):



3s

Following the general procedure A, the title compound was obtained as light yellow oil, 79.5 mg, 52% yield. (Rf = 0.51, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.60 – 7.52 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 4.0 Hz, 1H), 5.91 – 5.85 (m, 1H), 5.69 (dd, *J* = 9.8, 2.4 Hz, 1H), 5.19 (d, *J* = 12.8 Hz, 1H), 5.13 (d, *J* = 12.8 Hz, 1H), 2.85 – 2.79 (m, 1H), 2.73 – 2.67 (m, 1H), 2.64 – 2.57 (m, 2H), 1.67 (s, 3H), 1.55 – 1.48 (m, 2H), 1.37 – 1.32 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

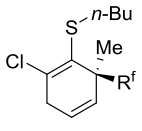
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.5 (t, *J* = 28.7 Hz), 160.9, 143.8, 137.8, 134.5, 133.8, 133.4, 132.4, 131.5, 130.3 (t, *J* = 6.0 Hz), 128.5, 128.4, 127.5, 126.4, 120.2 (t, *J* = 262.7 Hz), 66.6, 49.7 (t, *J* = 21.1 Hz), 38.2, 31.7, 30.5, 22.2, 22.1, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.8 (d, *J* = 254.3 Hz, 1F), -104.4 (d, *J* = 204.3 Hz, 1F).

IR (neat): 2956, 2928, 2871, 1707, 1691, 1596, 1447, 1421, 1274, 1243, 1085, 909, 737, 686.

HRMS (ESI-TOF): calculated for [$C_{25}H_{25}ClF_2O_3S_2Na$ ($M + Na^+$)]: 533.0794, found: 533.0794.

2-(2-(butylthio)-3-chloro-1-methylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (3t):



3t

Following the general procedure A, the title compound was obtained as light yellow oil, 63 mg, 55% yield. (Rf = 0.41, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.47 – 7.43 (m, 2H), 5.79 – 5.74 (m, 1H), 5.67 (d, *J* = 9.9 Hz, 1H), 3.06 – 2.96 (m, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 1.64 (s, 3H), 1.57 – 1.48 (m, 2H), 1.41 – 1.35 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

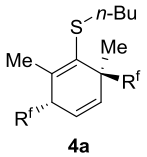
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.1 (t, *J* = 28.7 Hz), 142.4, 134.3, 133.9, 130.3 (t, *J* = 6.0 Hz), 128.5, 128.4, 125.9, 119.6 (t, *J* = 262.7 Hz), 51.1 (t, *J* = 21.1 Hz), 37.2, 35.7, 31.5, 22.4, 22.2, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.1 (d, *J* = 254.3 Hz, 1F), -104.1 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2959, 2920, 2870, 1705, 1596, 1447, 1271, 1097, 1047, 712, 660.

HRMS (ESI-TOF): calculated for [$C_{19}H_{21}ClF_2OSNa$ ($M + Na^+$)]: 393.0862, found: 393.0866.

2,2'-(2-(butylthio)-1,3-dimethylcyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4a):



4a

Following the general procedure B, the title compound was obtained as light yellow oil, 110 mg, 73% yield. (Rf = 0.46, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.90 (d, *J* = 7.9 Hz, 2H), 7.64 – 7.62 (m, 1H), 7.56 – 7.54 (m, 1H), 7.49 – 7.47 (m, 2H), 7.44 – 7.42 (m, 2H), 5.95 (d, *J* = 10.3 Hz, 1H), 5.70 (dd, *J* = 10.3, 3.4 Hz, 1H), 3.62 – 3.58 (m, 1H), 2.60 – 2.58 (m, 1H), 2.47 – 2.43 (m, 1H), 2.05 (s, 3H), 1.57 (s, 3H), 1.54 – 1.47 (m, 2H), 1.41 – 1.33 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

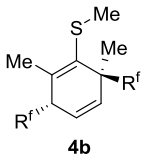
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.5 (t, *J* = 28.7 Hz), 189.2 (t, *J* = 28.7 Hz), 138.0, 134.8, 134.5, 134.4, 133.5, 132.8, 132.6, 130.2 (t, *J* = 3.0 Hz), 130.0 (t, *J* = 3.0 Hz), 128.9, 128.4, 121.3 (t, *J* = 6.0 Hz), 119.6 (t, *J* = 255.2 Hz), 118.6 (t, *J* = 255.2 Hz), 49.7 (t, *J* = 21.1 Hz), 47.7 (t, *J* = 21.1 Hz), 36.5, 31.6, 23.1, 22.3, 22.2, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -97.9 (d, *J* = 273.5 Hz, 1F), -100.9 (d, *J* = 273.5 Hz, 1F), -103.7 (d, *J* = 259.9 Hz, 1F), -103.8 (d, *J* = 259.9 Hz, 1F).

IR (neat): 3057, 2958, 2930, 2872, 1694, 1597, 1448, 1101, 1043, 912, 821.

HRMS (ESI-TOF): calculated for [$C_{28}H_{28}F_4O_2SNa$ ($M + Na^+$)]: 527.1638, found: 527.1664.

2,2'-(1,3-dimethyl-2-(methylthio)cyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4b):



4b

Following the general procedure B, the title compound was obtained as light yellow oil, 76 mg, 55% yield. (Rf = 0.44, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.90 (d, *J* = 7.9 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.57 – 7.54 (m, 1H), 7.50 – 7.46 (m, 2H), 7.44 – 7.40 (m, 2H), 5.95 (d, *J* = 10.3 Hz, 1H), 5.70 (dd, *J* = 10.3, 3.4 Hz, 1H), 3.66 – 3.59 (m, 1H), 2.60 – 2.58 (m, 1H), 2.47 – 2.43 (m, 1H), 2.09 – 2.07 (m, 6H), 1.57 (s, 3H).

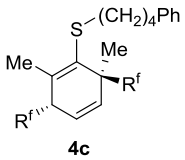
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.5 (t, *J* = 28.7 Hz), 189.2 (t, *J* = 28.7 Hz), 138.3, 135.4, 134.8, 134.5, 133.6, 132.8, 132.5, 130.2 (t, *J* = 3.0 Hz), 130.0 (t, *J* = 3.0 Hz), 128.9, 128.4, 121.4, 119.6 (t, *J* = 255.2 Hz), 118.6 (t, *J* = 255.2 Hz), 49.9 (t, *J* = 21.1 Hz), 47.7 (t, *J* = 21.1 Hz), 22.6, 21.9, 19.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -97.7 (d, *J* = 273.5 Hz, 1F), -100.2 (d, *J* = 273.5 Hz, 1F), -103.4 (d, *J* = 259.9 Hz, 1F), -103.9 (d, *J* = 259.9 Hz, 1F).

IR (neat): 3063, 2988, 2924, 1693, 1596, 1448, 1101, 1043, 714, 685, 672.

HRMS (ESI-TOF): calculated for [$C_{25}H_{22}F_4O_2SNa$ ($M + Na^+$)]: 485.1169, found: 485.1191.

2,2'-(1,3-dimethyl-2-((4-phenylbutyl)thio)cyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4c):



4c

Following the general procedure B, the title compound was obtained as light yellow oil, 104 mg, 60% yield. (Rf = 0.44, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.58 – 7.54 (m, 1H), 7.51 – 7.47 (m, 2H), 7.45 – 7.41 (m, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 5.97 (d, *J* = 10.4 Hz, 1H), 5.73 (dd, *J* = 10.3, 3.4 Hz, 1H), 3.63 (dd, *J* = 16.7, 9.0 Hz, 1H), 2.70 – 2.58 (m, 3H), 2.55 – 2.46 (m, 1H), 2.07 (s, 3H), 1.74 – 1.67 (m, 2H), 1.65 – 1.57 (m, 5H).

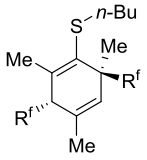
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.4 (t, *J* = 28.7 Hz), 189.2 (t, *J* = 28.7 Hz), 142.2, 138.2, 134.8, 134.5, 134.3, 133.6, 132.7, 132.6, 130.4 (t, *J* = 3.0 Hz), 129.9 (t, *J* = 3.0 Hz), 128.9, 128.5, 128.4, 128.3, 125.9, 121.3 (t, *J* = 6.0 Hz), 119.6 (t, *J* = 255.2 Hz), 118.6 (t, *J* = 255.2 Hz), 49.7 (t, *J* = 21.1 Hz), 47.8 (t, *J* = 21.1 Hz), 36.6, 35.6, 30.7, 29.1, 23.1, 22.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -97.6 (d, *J* = 271.2 Hz, 1F), -100.9 (d, *J* = 271.2 Hz, 1F), -103.2 (d, *J* = 259.9 Hz, 1F), -103.8 (d, *J* = 259.9 Hz, 1F).

IR (neat): 3063, 2931, 2856, 1694, 1597, 1448, 1102, 1043, 908, 821.

HRMS (ESI-TOF): calculated for [$C_{34}H_{32}F_4O_2SNa$ ($M + Na^+$)]: 603.1951, found: 603.1986.

2,2'-(2-(butylthio)-1,3,5-trimethylcyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4d):



4d

Following the general procedure B, the title compound was obtained as light yellow oil, 112 mg, 72% yield. (Rf = 0.40, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.54 – 7.46 (m, 3H), 7.43 – 7.38 (m, 2H), 5.81 (s, 1H), 3.70 – 3.66 (m, 1H), 2.58 – 2.51 (m, 1H), 2.45 – 2.39 (m, 1H), 2.01 (s, 3H), 1.64 (s, 3H), 1.54 (s, 3H), 1.50 – 1.45 (m, 2H), 1.37 – 1.30 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

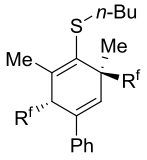
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.6 (t, *J* = 28.7 Hz), 189.9 (t, *J* = 28.7 Hz), 137.5, 135.4, 135.2, 134.5, 133.1, 132.9, 130.2, 129.8 (t, *J* = 3.0 Hz), 128.9, 128.3, 120.5 (t, *J* = 261.2 Hz), 117.9 (t, *J* = 261.2 Hz), 52.2 (t, *J* = 21.1 Hz), 50.9 (t, *J* = 21.1 Hz), 36.1, 31.7, 24.1, 23.5, 22.1, 21.3, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -98.2 (d, *J* = 271.2 Hz, 1F), -98.5 (d, *J* = 271.2 Hz, 1F), -102.6 (d, *J* = 259.9 Hz, 1F), -104.5 (d, *J* = 259.9 Hz, 1F).

IR (neat): 3158, 2929, 2872, 1696, 1597, 1447, 1104, 1065, 1047, 910, 872.

HRMS (ESI-TOF): calculated for [$C_{29}H_{30}F_4O_2SNa$ ($M + Na^+$)]: 541.1795, found: 541.1819.

2,2'-(4-(butylthio)-3,5-dimethyl-2,5-dihydro-[1,1'-biphenyl]-2,5-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4e):



4e

Following the general procedure B, the title compound was obtained as light yellow solid, m.p. 72 – 74 ℃, 96 mg, 55% yield. (Rf = 0.38, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.47 – 7.44 (m, 1H), 7.36 – 7.30 (m, 4H), 7.14 – 7.06 (m, 3H), 7.02 – 6.98 (m, 2H), 6.11 (s, 1H), 4.44 – 4.40 (m, 1H), 2.68 – 2.63 (m, 1H), 2.58 – 2.53 (m, 1H), 2.22 (s, 3H), 1.74 (s, 3H), 1.56 – 1.54 (m, 2H), 1.41 – 1.36 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 190.2 (t, *J* = 28.7 Hz), 189.0 (t, *J* = 28.7 Hz), 139.6, 137.8, 135.1, 134.9, 134.1, 134.3, 132.7 (m), 129.8 (t, *J* = 3.0 Hz), 128.5, 128.3, 128.2, 128.1, 127.7, 127.0, 120.1 (t, *J* = 259.7 Hz), 117.9 (t, *J* = 259.7 Hz), 51.8 (t, *J* = 21.1 Hz), 50.2 (t, *J* = 21.1 Hz), 36.3,

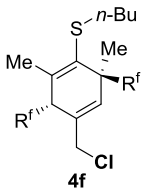
31.7, 24.3, 22.2, 21.5, 13.8

^{19}F NMR (565 MHz, $CDCl_3$) δ -96.7 (d, *J* = 259.9 Hz, 1F), -101.4 (d, *J* = 259.7 Hz, 1F), -101.9 (d, *J* = 265.6 Hz, 1F), -103.9 (d, *J* = 265.6 Hz, 1F).

IR (neat): 2959, 2920, 2849, 1698, 1684, 1597, 1449, 713, 692.

HRMS (ESI-TOF): calculated for [$C_{34}H_{32}F_4O_2SNa$ ($M + Na^+$)]: 603.1951, found: 603.1974.

2,2'-(2-(butylthio)-5-(chloromethyl)-1,3-dimethylcyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4f):



4f

Following the general procedure B, the title compound was obtained as light yellow oil, 99.5 mg, 60% yield. (Rf = 0.19, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 7.7 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.56 – 7.48 (m, 3H), 7.43 – 7.39 (m, 2H), 6.29 (s, 1H), 4.28 (d, *J* = 11.8 Hz, 1H), 4.25 – 4.19 (m, 1H), 4.07 (d, *J* = 12.0 Hz, 1H), 2.62 – 2.56 (m, 1H), 2.44 – 2.38 (m, 1H), 1.95 (s, 3H), 1.61 (s, 3H), 1.51 – 1.42 (m, 2H), 1.36 – 1.30 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

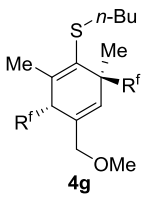
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.0 (t, *J* = 28.7 Hz), 189.1 (t, *J* = 28.7 Hz), 136.9, 135.1, 134.8, 134.7, 133.7, 132.5, 130.2 (t, *J* = 3.0 Hz), 129.9 (t, *J* = 3.0 Hz), 129.0, 128.8, 128.4, 119.2 (t, *J* = 261.2 Hz), 118.5 (t, *J* = 261.2 Hz), 51.3 (t, *J* = 21.1 Hz), 48.2, 48.1 (t, *J* = 21.1 Hz), 36.2, 31.6, 23.9, 22.1, 21.2, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -96.5 (d, *J* = 271.2 Hz, 1F), -100.1 (d, *J* = 265.6 Hz, 1F), -101.6 (d, *J* = 271.2 Hz, 1F), -103.6 (d, *J* = 265.6 Hz, 1F).

IR (neat): 2958, 2929, 2872, 1697, 1597, 1448, 1264, 1152, 1065, 1064.

HRMS (ESI-TOF): calculated for [$C_{29}H_{29}ClF_4O_2SNa$ ($M + Na^+$)]: 575.1405, found: 575.1437.

2,2'-(2-(butylthio)-5-(methoxymethyl)-1,3-dimethylcyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4g):



4g

Following the general procedure B, the title compound was obtained as light yellow oil, 86 mg, 52% yield. (Rf = 0.36, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.50 – 7.46 (m, 3H), 7.43 – 7.39 (m, 2H), 6.17 (s, 1H), 4.17 –

4.12 (m, 1H), 3.89 (d, *J* = 11.8 Hz, 1H), 3.75 (d, *J* = 12.0 Hz, 1H), 3.03 (s, 3H), 2.62 – 2.57 (m, 1H), 2.53 – 2.47 (m, 1H), 2.06 (s, 3H), 1.64 (s, 3H), 1.53 – 1.46 (m, 2H), 1.38 – 1.32 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

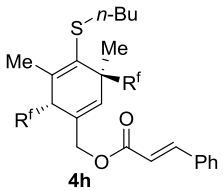
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.2 (t, *J* = 28.7 Hz), 188.9 (t, *J* = 28.7 Hz), 138.0, 135.0, 134.7, 134.2, 132.2, 132.8, 132.7, 130.2 (t, *J* = 3.0 Hz), 129.9 (t, *J* = 3.0 Hz), 129.2, 128.8, 128.4, 119.3 (t, *J* = 261.2 Hz), 118.7 (t, *J* = 261.2 Hz), 75.2, 57.4, 51.3 (t, *J* = 21.1 Hz), 48.2 (t, *J* = 21.1 Hz), 36.3, 31.6, 24.3, 22.1, 21.7, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -96.8 (d, *J* = 271.2 Hz, 1F), -100.0 (d, *J* = 265.6 Hz, 1F), -101.4 (d, *J* = 271.2 Hz, 1F), -103.4 (d, *J* = 265.6 Hz, 1F).

IR (neat): 2962, 2928, 2875, 1700, 1597, 1448, 1378, 1264, 1104, 1065, 1064.

HRMS (ESI-TOF): calculated for [$C_{30}H_{32}F_4O_3SNa$ ($M + Na^+$)]: 571.1900, found: 571.1924.

(4-(butylthio)-3,6-bis(1,1-difluoro-2-oxo-2-phenylethyl)-3,5-dimethylcyclohexa-1,4-dien-1-yl) methyl cinnamate (4h):



4h

Following the general procedure B, the title compound was obtained as light yellow solid, m.p. 74 – 76 ℃, 102 mg, 51% yield. (Rf = 0.25, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.53 – 7.49 (m, 1H), 7.49 – 7.35 (m, 9H), 6.31 (s, 1H), 6.19 (d, *J* = 16.0 Hz, 1H), 4.76 (d, *J* = 13.1 Hz, 1H), 4.58 (d, *J* = 13.1 Hz, 1H), 4.21 – 4.15 (m, 1H), 2.63 – 2.55 (m, 1H), 2.52 – 2.43 (m, 1H), 2.05 (s, 3H), 1.64 (s, 3H), 1.53 – 1.47 (m, 2H), 1.39 – 1.31 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 189.9 (t, *J* = 28.7 Hz), 188.9 (t, *J* = 28.7 Hz), 166.3, 145.2, 137.3, 134.9, 134.6, 134.3, 134.0, 133.3, 132.4, 130.5, 130.3 (t, *J* = 3.0 Hz), 129.9 (t, *J* = 3.0 Hz), 129.0, 128.9, 128.3, 128.2, 127.6, 120.2 (t, *J* = 261.2 Hz), 118.5 (t, *J* = 261.2 Hz), 117.6, 66.6, 51.1 (t, *J* = 21.1 Hz), 48.5 (t, *J* = 21.1 Hz), 36.2, 31.6, 24.1, 22.1, 21.5, 13.8.

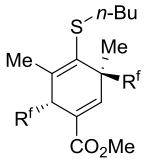
^{19}F NMR (565 MHz, $CDCl_3$) δ -97.2 (d, *J* = 271.2 Hz, 1F), -98.4 (d, *J* = 271.2 Hz, 1F), -101.6 (d, *J* = 271.2 Hz, 1F), -103.7 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2956, 2925, 2853, 1719, 1712, 1636, 1598, 1448, 1101, 1055.

HRMS (ESI-TOF): calculated for [$C_{38}H_{36}F_4O_4SNa$ ($M + Na^+$)]: 687.2163, found: 687.2175.

methyl

4-(butylthio)-3,6-bis(1,1-difluoro-2-oxo-2-phenylethyl)-3,5-dimethylcyclohexa-1,4-diene-1-carboxylate (4i):



4i

Following the general procedure B, the title compound was obtained as light yellow oil, 115 mg, 68% yield. (Rf = 0.28, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.9 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.56 – 7.49 (m, 3H), 7.44 – 7.40 (m, 2H), 7.35 (s, 1H), 4.60 – 4.54 (m, 1H), 3.62 (s, 3H), 2.64 – 2.59 (m, 1H), 2.55 – 2.49 (m, 1H), 2.08 (s, 3H), 1.69 (s, 3H), 1.52 – 1.43 (m, 2H), 1.37 – 1.30 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

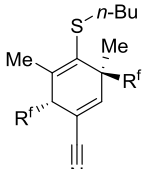
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.9 (t, *J* = 28.7 Hz), 188.8 (t, *J* = 28.7 Hz), 166.3, 143.9, 137.7, 134.5, 134.3, 133.6, 133.5, 132.5, 130.3 (t, *J* = 3.0 Hz), 129.9 (t, *J* = 3.0 Hz), 128.9, 128.4, 124.4, 120.2 (t, *J* = 261.2 Hz), 118.8 (t, *J* = 261.2 Hz), 52.2, 52.1 (t, *J* = 21.1 Hz), 47.6 (t, *J* = 21.1 Hz), 36.3, 31.6, 23.7, 22.1, 20.9, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -98.6 (d, *J* = 265.6 Hz, 1F), -101.1 (d, *J* = 271.2 Hz, 1F), -101.6 (d, *J* = 265.6 Hz, 1F), -102.7 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2955, 2872, 1701, 1597, 1448, 1112, 1045, 907, 822, 711.

HRMS (ESI-TOF): calculated for [$C_{30}H_{30}F_4O_4SNa$ ($M + Na^+$)]: 585.1693, found: 585.1719.

4-(butylthio)-3,6-bis(1,1-difluoro-2-oxo-2-phenylethyl)-3,5-dimethylcyclohexa-1,4-diene-1-carbonitrile (4j):



4j

Following the general procedure B, the title compound was obtained as light yellow oil, 103 mg, 65% yield. (Rf = 0.26, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.69 – 7.65 (m, 1H), 7.61 – 7.58 (m, 1H), 7.55 – 7.51 (m, 2H), 7.48 – 7.44 (m, 2H), 7.06 (s, 1H), 4.25 – 4.12 (m, 1H), 2.59 – 2.54 (m, 1H), 2.50 – 2.43 (m, 1H), 2.04 (s, 3H), 1.62 (s, 3H), 1.49 – 1.43 (m, 2H), 1.34 – 1.29 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 189.1 (t, *J* = 28.7 Hz), 188.1 (t, *J* = 28.7 Hz), 150.4, 135.9, 135.0, 134.0, 133.9, 133.7, 132.1, 130.2 (t, *J* = 3.0 Hz), 130.0 (t, *J* = 3.0 Hz), 129.1, 128.7, 119.2 (t, *J* = 261.2 Hz), 118.2 (t, *J* = 261.2 Hz), 117.5, 106.8, 51.7 (t, *J* = 21.1 Hz), 48.6 (t, *J* = 21.1 Hz), 36.3,

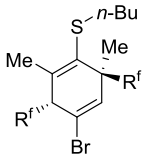
31.5, 23.5, 22.0, 21.2, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -96.3 (d, *J* = 276.9 Hz, 1F), -99.8 (d, *J* = 276.9 Hz, 1F), -100.7 (d, *J* = 276.9 Hz, 1F), -102.1 (d, *J* = 276.9 Hz, 1F).

IR (neat): 2958, 2926, 2872, 2224, 1697, 1596, 1448, 1153, 1114, 1068, 1046.

HRMS (ESI-TOF): calculated for [$C_{29}H_{27}F_4NO_2SNa$ (M + Na^+)]: 552.1591, found: 552.1614.

2,2'-(5-bromo-2-(butylthio)-1,3-dimethylcyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4l):



4l

Following the general procedure B, the title compound was obtained as light yellow oil, 119 mg, 68% yield. (Rf = 0.49, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 7.7 Hz, 2H), 7.68 – 7.62 (m, 1H), 7.59 – 7.54 (m, 1H), 7.53 – 7.48 (m, 2H), 7.47 – 7.41 (m, 2H), 6.53 (s, 1H), 4.25 – 4.19 (m, 1H), 2.65 – 2.59 (m, 1H), 2.56 – 2.43 (m, 1H), 2.12 (s, 3H), 1.63 (s, 3H), 1.55 – 1.45 (m, 2H), 1.38 – 1.31 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

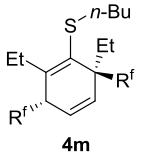
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.8 (t, *J* = 28.7 Hz), 189.1 (t, *J* = 28.7 Hz), 137.6, 136.5 t, *J* = 7.6 Hz), 134.7, 134.6, 134.5, 133.6, 132.9, 130.2 (t, *J* = 3.0 Hz), 129.9 (t, *J* = 3.0 Hz), 128.9, 128.5, 118.6 (t, *J* = 261.2 Hz), 116.9 (t, *J* = 261.2 Hz), 114.4, 55.1 (t, *J* = 21.1 Hz), 54.1 (t, *J* = 21.1 Hz), 36.3, 31.5, 24.1, 22.1, 21.1, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -97.3 (d, *J* = 265.6 Hz, 1F), -101.5 (d, *J* = 271.2 Hz, 1F), -102.3 (d, *J* = 265.6 Hz, 1F), -103.2 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2958, 2929, 1697, 1577, 1448, 1111, 1044, 907, 873, 713.

HRMS (ESI-TOF): calculated for [$C_{28}H_{27}F_4NaO_2SNa$ (M + Na^+)]: 605.0743, found: 605.0779.

2,2'-(2-(butylthio)-1,3-diethylcyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4m):



4m

Following the general procedure B, the title compound was obtained as light yellow oil, 104 mg, 65% yield. (Rf = 0.55, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, J = 7.8 Hz, 0.87H), 8.05 – 8.00 (m, 4.8 Hz, 2H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.58 – 7.45 (m, 3H), 7.44 – 7.34 (m, 2H), 5.87 – 5.80 (m, 1H), 5.74 (dd, *J* = 10.5, 3.4 Hz, 0.6H), 5.61 (d, *J* = 10.2 Hz, 0.38H), 4.15

– 4.06 (m, 0.39H), 3.94 – 3.86 (m, 0.6H), 3.34 – 3.18 (m, 1H), 2.71 – 2.65 (m, 1.42H), 2.58 – 2.38 (m, 1.68H), 2.33 – 2.20 (m, 1H), 1.95 – 1.88 (m, 0.62H), 1.77 – 1.71 (m, 0.43H), 1.58 – 1.32 (m, 4H), 1.10 (t, *J* = 7.4 Hz, 1.2H), 0.95 – 0.84 (m, 5H), 0.77 (t, *J* = 7.5 Hz, 1.92H), 0.60 (t, *J* = 7.5 Hz, 1.2H).

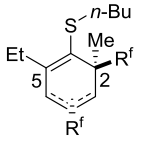
^{13}C NMR (151 MHz, $CDCl_3$): δ 191.1 (t, *J* = 28.7 Hz), 190.2 (t, *J* = 28.7 Hz), 190.1 (t, *J* = 28.7 Hz), 189.5 (t, *J* = 28.7 Hz), 145.4, 145.1, 134.8, 134.7, 134.5, 134.4, 133.7, 133.6, 132.8, 132.3, 131.8, 130.8, 130.6, 130.4, 130.3, 128.9, 128.8, 128.4, 124.8, 123.2, 120.5 – 117.0 (m), 55.2, (t, *J* = 21.1 Hz), 54.3 (t, *J* = 21.1 Hz), 43.3 (t, *J* = 21.1 Hz), 42.9 (t, *J* = 21.1 Hz), 37.8, 36.7, 31.8, 31.3, 28.5, 28.1, 26.0, 25.5, 22.3, 22.2, 13.9, 13.8, 12.9, 12.5, 9.0, 8.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -96.7 – -103.8 (m, 4F)

IR (neat): 3057, 2958, 2930, 2872, 1694, 1597, 1448, 1101, 1043, 912, 821.

HRMS (ESI-TOF): calculated for [$C_{30}H_{32}F_4O_2SNa$ ($M + Na^+$)]: 555.1951, found: 555.1961.

2,2'-(2-(butylthio)-3-ethyl-1-methylcyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4n):



4n(C2/C5 85/15)

Following the general procedure B, the title compound was obtained as a mixture of C2/C5 85/15, light yellow oil, 95 mg, 61% yield. (Rf = 0.53, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.9 Hz, 0.37H), 8.01 (d, *J* = 7.9 Hz, 1.84H), 7.96 (d, *J* = 7.9 Hz, 1.62H), 7.91 (d, *J* = 7.9 Hz, 0.19H), 7.64 – 7.62 (m, 1H), 7.56 – 7.54 (m, 1H), 7.49 – 7.47 (m, 2H), 7.44 – 7.42 (m, 2H), 6.02(d, *J* = 10.3 Hz, 0.85H), 5.85 (dd, *J* = 10.3, 4.0 Hz, 0.15H), 5.71 (dd, *J* = 10.3, 3.9 Hz, 0.85H), 5.66 (d, *J* = 10.3 Hz, 0.13H), 3.97 – 3.92 (m, 1H), 3.25 – 3.18 (m, 1H), 2.65 – 2.50 (m, 2H), 2.25 – 2.18 (m, 1H), 1.97 (s, 0.36H), 1.57 (s, 2.64H), 1.54 – 1.47 (m, 2H), 1.41 – 1.33 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 2.59H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.61 (t, *J* = 7.3 Hz, 0.40H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 190.0 (t, *J* = 28.7 Hz), 189.2 (t, *J* = 28.7 Hz), 144.1, 134.8, 134.6, 134.4, 133.5, 133.4, 133.3, 133.2, 132.7, 131.6, 130.6, 130.3, 130.19, 130.17, 129.9, 128.9, 128.8, 128.34, 128.30, 120.9, 120.8, 119.6 (t, *J* = 255.2 Hz), 118.6 (t, *J* = 255.2 Hz), 50.6 (t, *J* = 21.1 Hz), 43.6 (t, *J* = 21.1 Hz), 37.8, 35.3, 31.8, 31.5, 31.1, 28.1, 23.7, 22.2, 21.8, 13.8, 12.6.

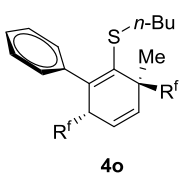
^{19}F NMR (565 MHz, $CDCl_3$) δ -97.7 (d, *J* = 273.5 Hz, 1F, C5), -102.1 (d, *J* = 273.5 Hz, 1F, C5),

-102.2 (d, *J* = 273.5 Hz, 1F, C5), -103.2 (d, *J* = 273.5 Hz, 1F, C5).

IR (neat): 2959, 2931, 2873, 1693, 1597, 1448, 1102, 1042, 731, 686.

HRMS (ESI-TOF): calculated for [$C_{29}H_{30}F_4O_2SNa$ ($M + Na^+$)]: 541.1795, found: 541.1818.

2,2'-(6-(butylthio)-5-methyl-2,5-dihydro-[1,1'-biphenyl]-2,5-diyl)bis(2,2-difluoro-1-phenyleth an-1-one) (4o):



4o

Following the general procedure B, the title compound was obtained as light yellow oil, 73 mg, 43% yield. (Rf = 0.51, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.68 – 7.62 (m, 2H), 7.57 – 7.52 (m, 2H), 7.38 – 7.34 (m, 2H), 7.16 – 7.08 (m, 5H), 6.27 (d, *J* = 10.3 Hz, 1H), 6.02 (dd, *J* = 10.3, 3.5 Hz, 1H), 4.59 – 4.43 (m, 1H), 2.02 – 1.92 (m, 2H), 1.67 (s, 3H), 0.92 – 0.81 (m, 4H), 0.58 (t, *J* = 7.1 Hz, 3H).

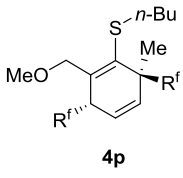
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.4 (t, *J* = 28.7 Hz), 188.5 (t, *J* = 28.7 Hz), 140.4, 140.2, 136.0, 134.7, 134.0, 133.4, 132.5, 130.2 (t, *J* = 3.0 Hz), 129.9 (t, *J* = 3.0 Hz), 129.6, 128.4, 128.1, 127.4, 120.6, 120.5, 119.2 (t, *J* = 261.2 Hz), 118.2 (t, *J* = 261.2 Hz), 51.4 (t, *J* = 21.1 Hz), 48.2 (t, *J* = 21.1 Hz), 36.2, 30.6, 23.4, 21.9, 13.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -98.3 (d, *J* = 271.2 Hz, 1F), -98.8 (d, *J* = 282.5 Hz, 1F), -101.7 (d, *J* = 282.5 Hz, 1F), -102.8 (d, *J* = 271.2 Hz, 1F).

IR (neat):

HRMS (ESI-TOF): calculated for [$C_{33}H_{30}F_4O_2SNa$ ($M + Na^+$)]: 589.1795, found: 589.1810.

2,2'-(2-(butylthio)-3-(methoxymethyl)-1-methylcyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4p):



4p

Following the general procedure B, the title compound was obtained as light yellow oil, 91 mg, 57% yield. (Rf = 0.43, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.57 – 7.54 (m, 1H), 7.51 – 7.47 (m, 2H), 7.43 – 7.39 (m, 2H), 6.02 (d, *J* = 10.4 Hz, 1H), 5.83 (dd, *J* = 10.4, 3.8 Hz, 1H), 4.52 (d, *J* = 12.1 Hz, 1H), 4.24 – 4.14 (m, 2H), 2.99 (s, 3H), 2.65 – 2.55 (m, 1H), 2.54 – 2.46 (m, 1H), 1.65 (s, 3H), 1.58 – 1.49 (m, 2H), 1.37 – 1.35 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

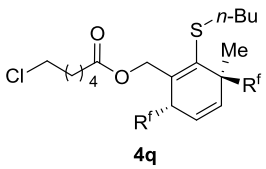
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.2 (t, *J* = 28.7 Hz), 188.2 (t, *J* = 28.7 Hz), 138.4, 137.7, 134.6, 134.2, 133.7, 132.7, 132.2, 130.2 (t, *J* = 3.0 Hz), 130.1 (t, *J* = 3.0 Hz), 128.7, 128.4, 121.0, 119.2 (t, *J* = 261.2 Hz), 118.2 (t, *J* = 261.2 Hz), 72.5, 57.4, 50.0 (t, *J* = 21.1 Hz), 42.8 (t, *J* = 21.1 Hz), 38.1, 31.7, 29.9, 22.3, 22.1, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -100.2 (d, *J* = 271.2 Hz, 1F), -102.1 (d, *J* = 282.5 Hz, 1F), -102.2 (d, *J* = 282.5 Hz, 1F), -103.5 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3057, 2962, 2928, 1697, 1597, 1448, 1101, 1072, 1043, 911, 829.

HRMS (ESI-TOF): calculated for [$C_{29}H_{30}F_4O_3SNa$ ($M + Na^+$)]: 557.1744, found: 557.1767.

(2-(butylthio)-3,6-bis(1,1-difluoro-2-oxo-2-phenylethyl)-3-methylcyclohexa-1,4-dien-1-yl)methyl 4-chlorobutanoate (4q):



4q

Following the general procedure B, the title compound was obtained as light yellow oil, 97 mg, 52% yield. (Rf = 0.27, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.58 – 7.54 (m, 1H), 7.51 – 7.48 (m, 2H), 7.45 – 7.40 (m, 2H), 5.99 (d, *J* = 10.3 Hz, 1H), 5.72 (dd, *J* = 10.3, 3.9 Hz, 1H), 5.38 (d, *J* = 12.9 Hz, 1H), 4.88 (d, *J* = 13.0 Hz, 1H), 4.18 – 4.05 (m, 1H), 3.57 (t, *J* = 6.3 Hz, 2H), 2.67 – 2.62 (m, 1H), 2.53 – 2.48 (m, 1H), 2.42 – 2.36 (m, 2H), 2.08 – 2.02 (m, 2H), 1.63 (s, 3H), 1.57 – 1.51 (m, 2H), 1.41 – 1.35 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

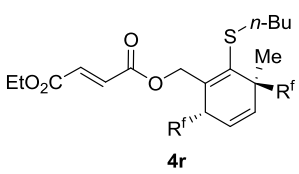
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.2 (t, *J* = 28.7 Hz), 188.7 (t, *J* = 28.7 Hz), 171.9, 140.2, 135.7, 134.7, 134.6, 133.8, 130.2 (t, *J* = 3.0 Hz), 130.1 (t, *J* = 3.0 Hz), 129.0, 128.5, 120.7, 119.2 (t, *J* = 261.2 Hz), 118.3 (t, *J* = 261.2 Hz), 95.4, 50.1 (t, *J* = 21.1 Hz), 44.1, 43.1 (t, *J* = 21.1 Hz), 38.2, 31.7, 31.2, 29.8, 27.7, 22.2, 22.1, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -98.4 (d, *J* = 271.2 Hz, 1F), -102.3 (d, *J* = 282.5 Hz, 1F), -102.6 (d, *J* = 282.5 Hz, 1F), -103.5 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2958, 2919, 2849, 1736, 1696, 1597, 1448, 1107, 1043, 912, 821.

HRMS (ESI-TOF): calculated for [$C_{32}H_{33}ClF_4O_4SNa$ ($M + Na^+$)]: 647.1616, found: 647.1646.

(2-(butylthio)-3,6-bis(1,1-difluoro-2-oxo-2-phenylethyl)-3-methylcyclohexa-1,4-dien-1-yl)methyl ethyl fumarate (4r):



4r

Following the general procedure B, the title compound was obtained as light yellow solid, m.p. 88 – 89 ℃, 128 mg, 66% yield. (Rf = 0.25, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.56 – 7.52 (m, 1H), 7.49 – 7.45 (m, 2H), 7.43 – 7.39 (m, 2H), 6.78 (d, *J* = 15.8 Hz, 1H), 6.72 (d, *J* = 15.8 Hz, 1H), 5.99 (d, *J* = 10.2 Hz, 1H), 5.72 (dd, *J* = 10.4, 3.8 Hz, 1H), 5.47 (d, *J* = 13.0 Hz, 1H), 4.98 (d, *J* = 13.0 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.13 – 4.06 (m, 1H), 2.68 – 2.62 (m, 1H), 2.54 – 2.49 (m, 1H), 1.63 (s, 3H), 1.57 – 1.51 (m, 2H), 1.40 – 1.31 (m, 5H), 0.89 (t, *J* = 7.3 Hz, 3H).

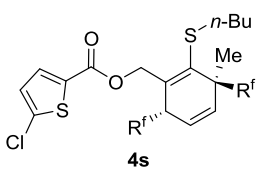
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.9 (t, *J* = 28.7 Hz), 188.5 (t, *J* = 28.7 Hz), 164.8, 164.1, 140.9, 135.0, 134.8, 134.4, 134.1, 133.8, 132.9, 132.5, 132.3, 130.07 (t, *J* = 3.0 Hz), 130.05 (t, *J* = 3.0 Hz), 129.0, 128.4, 120.5, 119.9 (t, *J* = 261.2 Hz), 118.2 (t, *J* = 261.2 Hz), 66.1, 61.6, 50.0 (t, *J* = 21.1 Hz), 43.1 (t, *J* = 21.1 Hz), 38.3, 31.7, 22.2, 22.1, 14.2, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -98.8 (d, *J* = 271.2 Hz, 1F), -102.5 (d, *J* = 271.2 Hz, 1F), -102.6 (d, *J* = 271.2 Hz, 1F), -103.6 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2958, 2930, 2870, 1719, 1701, 1645, 1596, 1447, 1291, 1255, 1148, 1035, 976, 913, 714, 686.

HRMS (ESI-TOF): calculated for [$C_{34}H_{34}F_4O_6SNa$ ($M + Na^+$)]: 669.1904, found: 669.1900.

(2-(butylthio)-3,6-bis(1,1-difluoro-2-oxo-2-phenylethyl)-3-methylcyclohexa-1,4-dien-1-yl)methyl 5-chlorothiophene-2-carboxylate (4s):



4s

Following the general procedure B, the title compound was obtained as light yellow solid, m.p. 69 – 71 ℃, 119.5 mg, 60% yield,. (Rf = 0.36, eluent: PE/EtOAc = 10/1). The crystal of **4s** was obtained by crystallization from DCM and hexane at room temperature. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.54 – 7.49 (m, 2H), 7.44 – 7.35 (m, 4H), 6.92 (d, *J* = 4.0 Hz, 1H), 6.01 (d, *J* = 10.3 Hz, 1H), 5.72 (dd,

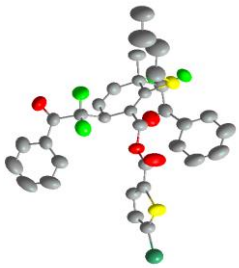
J = 10.3, 3.9 Hz, 1H), 5.52 (d, *J* = 12.8 Hz, 1H), 5.07 (d, *J* = 12.8 Hz, 1H), 4.18 – 4.12 (m, 1H), 2.70 – 2.64 (m, 1H), 2.58 – 2.51 (m, 1H), 1.65 (s, 3H), 1.59 – 1.52 (m, 2H), 1.40 – 1.33 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

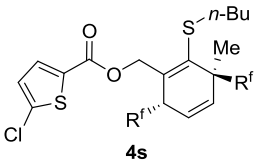
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.0 (t, *J* = 28.7 Hz), 188.5 (t, *J* = 28.7 Hz), 160.3, 141.0, 137.8, 135.4, 134.7, 134.6, 133.7, 133.3, 132.6, 132.3, 130.2 (t, *J* = 3.0 Hz), 130.0 (t, *J* = 3.0 Hz), 128.9, 128.5, 127.4, 120.5, 119.2 (t, *J* = 261.2 Hz), 118.2 (t, *J* = 261.2 Hz), 66.2, 50.1 (t, *J* = 21.1 Hz), 43.2 (t, *J* = 21.1 Hz), 38.3, 31.8, 22.2, 22.1, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -98.7 (d, *J* = 271.2 Hz, 1F), -102.8 (d, *J* = 271.2 Hz, 1F), -102.9 (d, *J* = 271.2 Hz, 1F), -103.7 (d, *J* = 271.2 Hz, 1F).

IR (neat): 2929, 2854, 1714, 1702, 1687, 1423, 1270, 1688, 1061, 912, 826.

HRMS (ESI-TOF): calculated for [$C_{33}H_{29}ClF_4O_4S_2Na$ (M + Na^+)]: 687.1024, found: 687.1042.





4s

Bond precision	c-c=0.0048 Å	Wavelength=0.71073
Cell	a=10.2039 (5)	b=13.2445 (5) c=13.5012 (6)
	α=66.799(1)	β=70.330(1) γ=75.627(1)
Temperature	294 K	
	Calculated	Reported
Volumn	1569.19(12)	1569.19(12)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C33 H29 Cl F4 O4 S2	C33 H29 Cl F4 O4 S2
Sum formula	C33 H29 Cl F4 O4 S2	C33 H29 Cl F4 O4 S2
Mr	665.13	665.13
Dx,g cm^{-3}	1.408	1.408
Z	2	2
Mu (mm^{-1})	0.316	0.316
F000	688.0	688.0
F000’	689.17	

h,k,lmax	13,17,17	13,17,17
Nref	7180	7140
Tmin,Tmax	0.903,0.954	0.903,0.954
Tmin'	0.887	

Correction method= # Reported T Limits: Tmin=0.903 Tmax=0.954
AbsCorr = EMPIRICAL

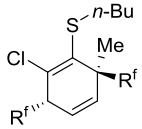
Data completeness= 0.994 Theta(max)= 27.460
R(reflections)= 0.0537(5151) wR2(reflections)= 0.1818(7140)
S = 1.021 Npar= 397

Crystallographic data (excluding structural factors) for compound **4s** also has been deposited at the Cambridge Crystallographic Data Centre under the deposition number CCDC 1973271.

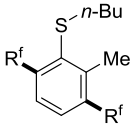
2,2'-2-meth

2,2'-(2-(butylthio)-3-chloro-1-methylcyclohexa-2,5-diene-1,4-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (4t)

and 2,2'-(2-(butylthio)-3-methyl-1,4-phenylene)bis(2,2-difluoro-1-phenylethan-1-one) (4t'):



4t



4t'

Following the general procedure B, the title compound was obtained as the mixture of 4q and 4q' with the ratio of 1.3/1, light yellow oil, 110 mg, 72% yield. (Rf = 0.46, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.7 Hz, 4H, **4t'**), 8.04 (d, *J* = 7.8 Hz, 2H, **4t**), 7.96 (d, *J* = 7.8 Hz, 2H, **4t**), 7.83 (s, 2H, **4t'**), 7.67 – 7.56 (m, 4H, **4t**&**4t'**), 7.52 – 7.43 (m, 8H, **4t**&**4t'**), 6.07 (d, *J* = 10.4 Hz, 1H, **4t**), 5.89 (dd, *J* = 10.3, 3.5 Hz, 1H, **4t**), 4.28 – 4.14 (m, 1H, **4t**), 2.77 – 2.68 (m, 2H, **4t**), 2.50 (s, 3H, **4t'**), 2.44 (t, *J* = 7.4 Hz, 2H, **4t'**), 1.67 (s, 3H, **4t**), 1.53 – 1.47 (m, 2H, **4t**), 1.37 – 1.29 (m, 4H, **4t'**), 1.24 – 1.18 (m, 2H, **4t'**), 0.86 (t, *J* = 7.4 Hz, 3H, **4t**), 0.78 (t, *J* = 7.3 Hz, 3H, **4t'**).

^{13}C NMR (151 MHz, $CDCl_3$): δ 189.6 – 188.4 (m), 143.1, 136.7, 135.7, 135.5, 134.6, 134.4, 134.1, 133.9, 133.8, 133.6, 132.8, 132.2, 132.1, 130.4, 130.2, 130.0, 128.9, 128.8, 128.6, 126.9, 124.3, 120.9, 118.9 – 116.5 (m), 51.7 (t, *J* = 21.1 Hz, **4t**), 49.2 (t, *J* = 21.1 Hz, **4t**), 36.3 (**4t'**), 35.8 (**4t**), 31.5 (**4t**), 30.7 (**4t'**), 22.14 (**4t**), 22.10 (**4t**), 22.0 (**4t'**), 17.9 (**4t'**), 13.74 (**4t**), 13.67 (**4t'**).

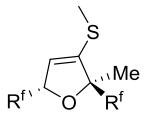
^{19}F NMR (565 MHz, $CDCl_3$) δ -93.3 (s, 2F, **4t'**), -95.6 (s, 2F, **4t'**), -98.2 (d, *J* = 271.2 Hz, 1F, **4t**),

-101.1 (d, *J* = 282.5 Hz, 1F, **4t**), -103.2 (d, *J* = 282.5 Hz, 1F, **4t**), -104.7 (d, *J* = 271.2 Hz, 1F, **4t**).

IR (neat): 2958, 2929, 2872, 1701, 1597, 1448, 1254, 1125, 1057, 908, 870, 816.

HRMS (ESI-TOF): calculated for **4t** [$C_{27}H2_5ClF_4O_2SNa$ (M + Na^+)]: 547.1092, found: 547.1122; **4t'** [$C_{27}H_{24}F_4O_2SNa$ (M + Na^+)]: 511.1325, found: 511.1353.

1,1'-(2-methyl-3-(methylthio)-2,5-dihydrofuran-2,5-diyl)bis(2,2-difluoro-2-phenylethan-1-one) (4u):



4u

Following the general procedure B, the title compound was obtained as light yellow oil, 78 mg, 61% yield. (Rf = 0.35, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.9 Hz, 2H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.68 – 7.64 (m, 1H), 7.63 – 7.59 (m, 1H), 7.52 – 7.48 (m, 2H), 7.47 – 7.43 (m, 2H), 5.38 (s, 1H), 5.09 – 5.03 (m, 1H), 2.40 (s, 3H), 1.61 (s, 3H).

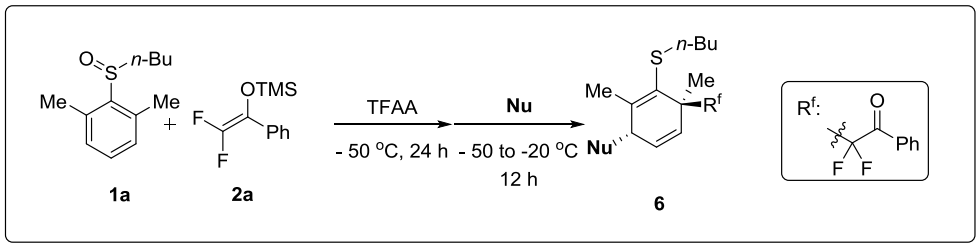
^{13}C NMR (151 MHz, $CDCl_3$): δ 189.7 (t, *J* = 28.7 Hz), 189.0 (t, *J* = 28.7 Hz), 144.3, 134.6, 134.2, 133.6, 132.5, 130.6, 130.3, 128.8, 128.5, 117.0 (t, *J* = 261.2 Hz), 116.9 (t, *J* = 261.2 Hz), 113.4, 93.0 (t, *J* = 21.1 Hz), 85.3 (t, *J* = 21.1 Hz), 29.8, 20.3, 16.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -106.2 (d, *J* = 271.2 Hz, 1F), -108.7 (d, *J* = 271.2 Hz, 1F), -108.9 (d, *J* = 271.2 Hz, 1F), -113.6 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3077, 2923, 1693, 1596, 1448, 1280, 1113, 1069, 913, 825, 711.

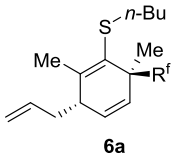
HRMS (ESI-TOF): calculated for [$C_{22}H_{18}F_4O_3SNa$ (M + Na^+)]: 461.0805, found: 461.0803.

6 General procedure for mono-difluoroalkylative dearomatization of aryl sulfoxide 1a



To a stirred solution of sulfoxide **1a** (63 mg, 0.3 mmol) and difluoroenol silyl ether **2a** (103 mg, 1.5 equiv) in MeCN/DCM (9/1, 3 mL) was added TFAA (63 μL, 1.5 equiv) at -50 ℃. The mixture was then stirred at -50 ℃ for 24 h. After that, to the mixture was added different nucleophiles (2 equiv), and the resulting mixture was then slowly warmed up to -20 ℃. After stirring for 12 h, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel giving the title compound **6**.

2-(4-allyl-2-(butylthio)-1,3-dimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (6a):



6a

Following the general procedure, the title compound was obtained as light yellow oil, 76 mg, 65% yield. (Rf = 0.29, eluent: PE/EtOAc = 30/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.41 (m, 2H), 5.86 (dd, *J* = 10.0, 4.2 Hz, 1H), 5.82 – 5.74 (m, 1H), 5.66 (d, *J* = 10.0 Hz, 1H), 5.03 – 4.92 (m, 2H), 2.78 – 2.72 (m, 1H), 2.58 – 2.46 (m, 3H), 2.10 (s, 3H), 2.03 – 1.97 (m, 1H), 1.58 (s, 3H), 1.50 – 1.45 (m, 2H), 1.38 – 1.32 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H).

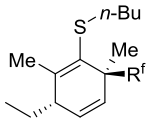
^{13}C NMR (151 MHz, $CDCl_3$): δ 191.0 (t, *J* = 28.7 Hz), 148.3, 136.2, 134.8, 133.6, 130.7 (t, *J* = 3.0 Hz), 128.4, 128.2, 128.1, 127.8, 119.9 (t, *J* = 261.2 Hz), 116.8, 50.2 (t, *J* = 21.1 Hz), 43.9, 39.1, 36.8, 31.5, 22.9, 22.3, 21.2, 13.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -102.9 (s, 2F).

IR (neat): 2956, 2928, 2870, 1691, 1596, 1447, 1275, 1094, 1042, 910, 713, 686.

HRMS (ESI-TOF): calculated for [$C_{23}H_{28}F_2OSNa$ ($M + Na^+$)]: 413.1721, found: 413.1721.

2-(2-(butylthio)-4-ethyl-1,3-dimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (6b):



6b

Following the general procedure, the title compound was obtained as light yellow oil, 74 mg, 65% yield. (Rf = 0.23, eluent: PE/EtOAc = 30/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.43 – 7.38 (m, 2H), 5.72 (dd, *J* = 10.1, 1.5 Hz, 1H), 5.56 (dd, *J* = 10.1, 2.7 Hz, 1H), 2.57 – 2.49 (m, 2H), 2.45 – 2.40 (m, 1H), 1.84 (s, 3H), 1.64 – 1.57 (m, 4H), 1.53 – 1.44 (m, 3H), 1.38 – 1.32 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.62 (t, *J* = 7.4 Hz, 3H).

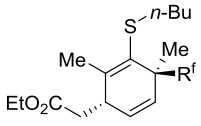
^{13}C NMR (151 MHz, $CDCl_3$): δ 191.0 (t, *J* = 28.7 Hz), 146.9, 135.1, 133.3, 130.5, 130.1 (t, *J* = 3.0 Hz), 129.3, 128.5, 128.2, 120.4 (t, *J* = 261.2 Hz), 49.3 (t, *J* = 21.1 Hz), 42.8, 36.8, 31.7, 25.4, 23.1, 22.2, 20.8, 13.8, 8.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.2 (d, *J* = 254.3 Hz, 1F), -105.0 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2958, 2930, 2871, 1692, 1596, 1447, 1276, 1094, 1041, 912, 804, 713, 687.

HRMS (ESI-TOF): calculated for [$C_{22}H_{28}F_2OSNa$ ($M + Na^+$)]: 401.1721, found: 401.1719.

ethyl-3-(butylthio)-4-(1,1-difluoro-2-oxo-2-phenylethyl)-2,4-dimethylcyclohexa-2,5-dien-1-yl) acetate (6c):



6c

Following the general procedure, the title compound was obtained as light yellow oil, 80 mg, 62% yield. (Rf = 0.20, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.40 (m, 2H), 5.93 (dd, *J* = 9.9, 4.3 Hz, 1H), 5.69 (d, *J* = 10.0 Hz, 1H), 4.21 – 4.08 (m, 2H), 3.26 – 3.17 (m, 1H), 2.67 (dd, *J* = 15.9, 4.1 Hz, 1H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.23 (dd, *J* = 15.9, 10.2 Hz, 1H), 2.08 (s, 3H), 1.58 (s, 3H), 1.52 – 1.43 (m, 2H), 1.38 – 1.31 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H).

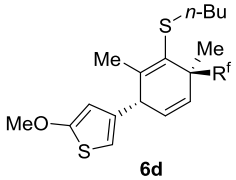
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.6 (t, *J* = 28.7 Hz), 172.3, 147.3, 134.6, 133.7, 130.6, 130.1, 129.1, 128.7, 128.4, 119.7 (t, *J* = 261.2 Hz), 60.8, 50.0 (t, *J* = 21.1 Hz), 40.5, 39.1, 36.7, 31.5, 22.7, 22.3, 20.9, 14.3, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -102.7 (d, *J* = 254.3 Hz, 1F), -103.2 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2957, 2930, 2871, 1730, 1691, 1596, 1447, 1368, 1271, 1153, 1093, 1040, 910, 737, 687.

HRMS (ESI-TOF): calculated for [$C_{24}H_{30}F_2O_3SNa$ (M + Na^+)]: 459.1776, found: 459.1784.

2-(butylthio)-4-(5-methoxythiophen-3-yl)-1,3-dimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (6d):



6d

Following the general procedure, the title compound was obtained as light yellow oil, 98 mg, 71% yield. (Rf = 0.31, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.45 – 7.41 (m, 2H), 6.39 (d, *J* = 3.8 Hz, 1H), 5.94 (d, *J* = 3.8 Hz, 1H), 5.80 – 5.71 (m, 2H), 3.81 (s, 3H), 3.72 (s, 1H), 2.52 – 2.46 (m, 2H), 1.77 (s, 3H), 1.70 (s, 3H), 1.52 – 1.47 (m, 2H), 1.38 – 1.31 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H).

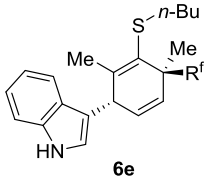
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.7 (t, *J* = 28.7 Hz), 165.9 146.1, 134.9, 133.6, 132.8, 130.1 (t, *J* = 3.0 Hz), 130.0, 128.3, 127.0, 122.3, 120.1 (t, *J* = 261.2 Hz), 102.6, 60.1, 49.1 (t, *J* = 21.1 Hz), 45.4, 36.5, 31.7, 22.7, 22.2, 21.9, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.8 (d, *J* = 254.3 Hz, 1F), -104.5 (d, *J* = 254.3 Hz, 1F).

IR (neat): 2955, 2931, 2871, 1691, 1596, 1560, 1501, 1447, 1208, 1094, 1036, 908, 806, 729, 687.

HRMS (ESI-TOF): calculated for [$C_{25}H_{28}F_2O_2S_2Na$ (M + Na^+)]: 485.1391, found: 485.1378.

2-(2-(butylthio)-4-(1H-indol-3-yl)-1,3-dimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (6e):



6e

Following the general procedure, the title compound was obtained as light yellow oil, 91 mg, 65% yield. (Rf = 0.21, eluent: PE/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (bs, 1H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.51 – 7.41 (m, 3H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.07 – 7.01 (m, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 5.84 (dd, *J* = 9.9, 2.4 Hz, 1H), 5.78 (dd, *J* = 9.9, 2.4 Hz, 1H), 3.88 (s, 1H), 2.52 (t, *J* = 7.5 Hz, 2H), 1.84 (s, 3H), 1.71 (s, 3H), 1.54 – 1.45 (m, 2H), 1.36 – 1.30 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 191.1 (t, *J* = 28.7 Hz), 148.1, 136.6, 134.9, 133.6, 131.5, 130.2 (t,

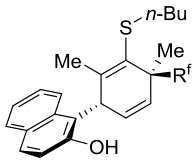
J = 3.0 Hz), 128.3, 127.5, 126.6, 126.5, 122.4, 122.3, 120.6 (t, *J* = 261.2 Hz), 119.4, 119.1, 118.8, 111.5, 49.4 (t, *J* = 21.1 Hz), 41.4, 36.7, 31.8, 22.6, 22.2, 22.1, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.8 (d, *J* = 271.2 Hz, 1F), -104.6 (d, *J* = 271.2 Hz, 1F).

IR (neat): 3408, 2955, 2870, 1688, 1595, 1454, 1275, 1092, 1039, 909, 811, 735, 687.

HRMS (ESI-TOF): calculated for [$C_{28}H_{29}F_2NOSNa$ (M + Na^+)]: 488.1830, found: 488.1832.

2-(2-(butylthio)-4-(2-hydroxynaphthalen-1-yl)-1,3-dimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (6f):



6f (2/1 dr)

Following the general procedure B, the title compound was obtained as light yellow oil, 74 mg, 51% yield. (Rf = 0.37, eluent: PE/EtOAc = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 – 8.06 (m, 2H), 7.89 – 7.77 (m, 2H), 7.76 – 7.68 (m, 1H), 7.65 – 7.60 (m, 1H), 7.59 – 7.55 (m, 0.45H), 7.55 – 7.49 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 0.84H), 7.37 (t, *J* = 7.4 Hz, 0.67H), 7.29 – 7.22 (m, 1.18H, overlap with protons of $CDCl_3$), 7.07 – 7.01 (m, 1H), 6.03 (dd, *J* = 9.8, 2.6 Hz, 0.64H), 5.89 – 5.77 (m, 1.43H), 5.45 (s, 1H), 4.84 (s, 0.39H), 4.60 (s, 0.63H), 2.65 – 2.47 (m, 2H), 1.89 (s, 1.21H), 1.82 (s, 1.97H), 1.71 (s, 2H), 1.60 (s, 1.25H), 1.56 – 1.47 (m, 2H), 1.40 – 1.35 (m, 1H), 1.34 – 1.28 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 1.95H), 0.83 (t, *J* = 7.4 Hz, 1.2H).

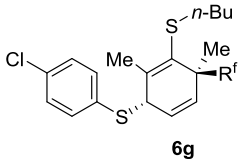
^{13}C NMR (151 MHz, $CDCl_3$): δ 191.3 (t, *J* = 28.7 Hz), 190.5 (t, *J* = 28.7 Hz), 153.5, 150.5, 150.2, 147.8, 134.7, 134.5, 134.0, 133.7, 133.6, 132.9, 132.5, 130.4, 130.2, 129.9, 129.8, 129.5, 129.2, 129.1, 128.7, 128.5, 128.4, 127.2, 126.4, 125.8, 123.7, 123.4, 123.3, 121.9, 120.1 (t, *J* = 261.2 Hz), 119.6 (t, *J* = 261.2 Hz), 118.9, 117.9, 117.7, 50.0 (t, *J* = 21.1 Hz), 49.4 (t, *J* = 21.1 Hz), 40.6, 40.5, 36.9, 36.5, 31.9, 31.7, 22.7, 22.3, 22.2, 22.1, 21.4, 21.3, 13.8, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.8 – -105.6 (m, 2F).

IR (neat): 3438, 2955, 2927, 2870, 1681, 1625, 1596, 1513, 1446, 1271, 1095, 1040, 909, 803, 716, 686.

HRMS (ESI-TOF): calculated for [$C_{30}H_{30}F_2O_2SNa$ (M + Na^+)]: 515.1827, found: 515.1828.

2-(2-(butylthio)-4-((4-chlorophenyl)thio)-1,3-dimethylcyclohexa-2,5-dien-1-yl)-2,2-difluoro-1-phenylethan-1-one (6g):



6g

Following the general procedure, the title compound was obtained as light yellow oil, 96 mg, 65% yield. (Rf = 0.26, eluent: PE/EtOAc = 30/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ (d, *J* = 7.7 Hz, 0.30H), 7.89 (d, *J* = 7.7 Hz, 1.70H), 7.62 – 7.54 (m, 1H), 7.50 – 7.36 (m, 2.37H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 1.62H), 6.01 (dd, *J* = 9.8, 4.2 Hz, 0.12H), 5.93 (dd, *J* = 10.0, 2.7 Hz, 0.84H), 5.79 (d, *J* = 9.8 Hz, 0.15H), 5.74 (d, *J* = 10.0 Hz, 0.84H), 4.06 (s, 0.12H), 3.79 (s, 0.85H), 2.38 – 2.32 (m, 1H), 2.28 (s, 0.40H), 2.16 – 2.02 (m, 3.62H), 1.42 – 1.26 (m, 4.31H), 1.20 (s, 2.84H), 0.90 (t, *J* = 7.2 Hz, 3H).

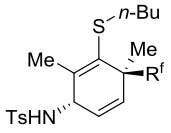
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.5 (t, *J* = 28.7 Hz), 143.7, 142.6, 136.9, 135.2, 135.0, 134.4, 133.7, 133.5, 133.0, 130.7 (t, *J* = 3.0 Hz), 130.0 (t, *J* = 3.0 Hz), 129.8, 129.3, 129.2, 128.8, 128.4, 128.3, 128.0, 127.8, 119.6 (t, *J* = 261.2 Hz), 52.6, 51.5, 49.3 (t, *J* = 21.1 Hz), 36.9, 36.7, 31.6, 31.4, 22.4, 22.3, 22.2, 21.9, 21.7, 13.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -101.3 (d, *J* = 271.2 Hz, 0.25F), -102.3 (d, *J* = 271.2 Hz, 0.25F), -104.2 (s, 3.46F).

IR (neat): 2956, 2928, 2871, 1692, 1596, 1474, 1173, 1092, 1013, 907, 805, 726, 688.

HRMS (ESI-TOF): calculated for [$C_{26}H_{27}ClF_2OS_2Na$ ($M + Na^+$)]: 515.1052, found: 515.1057.

N-(3-(butylthio)-4-(1,1-difluoro-2-oxo-2-phenylethyl)-2,4-dimethylcyclohexa-2,5-dien-1-yl)-4-methylbenzenesulfonamide (6h):



6h

Following the general procedure, the title compound was obtained as light yellow oil, 101 mg, 65% yield. (Rf = 0.23, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.75 (d, *J* = 9.9 Hz, 1H), 5.33 (dd, *J* = 9.9, 4.4 Hz, 1H), 4.84 (d, *J* = 10.0 Hz, 1H), 4.22 (dd, *J* = 10.1, 4.4 Hz, 1H), 2.53 – 2.37 (m, 5H), 2.03 (s, 3H), 1.51 (s, 3H), 1.45 – 1.37 (m, 2H), 1.32 – 1.26 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).

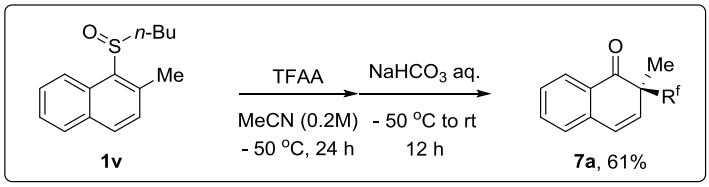
^{13}C NMR (151 MHz, $CDCl_3$): δ 190.0 (t, *J* = 28.7 Hz), 143.7, 143.6, 138.6, 134.4, 135.5, 132.7, 132.3, 130.4 (t, *J* = 3.0 Hz), 129.9, 128.7, 127.1, 125.9, 118.8 (t, *J* = 261.2 Hz), 52.3, 48.6 (t, *J* = 21.1 Hz), 36.3, 31.5, 22.1, 21.7, 19.9, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -101.3 (d, *J* = 254.3 Hz, 1F), -101.8 (d, *J* = 254.3 Hz, 1F).

IR (neat): 3326, 2956, 2871, 1692, 1596, 1447, 1330, 1156, 1093, 1044, 906, 814, 713, 662.

HRMS (ESI-TOF): calculated for [$C_{27}H_{31}F_2NO_3S_2Na$ (M + Na^+)]: 542.1606, found: 542.1601.

2-(1,1-difluoro-2-oxo-2-phenylethyl)-2-methylnaphthalen-1(2H)-one (7a):



1v **7a**, 61%

To a stirred solution of sulfoxide **1v** (74 mg, 0.3 mmol) and difluoroenol silyl ether **2a** (103 mg, 1.5 equiv) in MeCN (1.5 mL) was added TFAA (63 μL, 1.5 equiv) at -50 ℃. The mixture was then stirred for 24 h. After that, to the mixture was added $NaHCO_3$ (1.0 mL), and the resulting mixture was then slowly warmed up to rt. After stirring for 12 h, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel giving the title compound **7a** as light yellow oil, 48 mg, 61% yield. (Rf = 37, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 – 8.03 (m, 3H), 7.64 – 7.56 (m, 2H), 7.50 – 7.39 (m, 3H), 7.31 (d, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 9.9 Hz, 1H), 6.22 (d, *J* = 9.9 Hz, 1H), 1.56 (s, 3H).

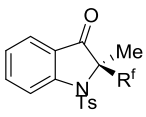
^{13}C NMR (151 MHz, $CDCl_3$): δ 196.9, 187.7 (t, *J* = 28.7 Hz), 137.7, 134.6, 134.5, 132.5 (m), 131.9, 130.5 (t, *J* = 3.0 Hz), 129.3, 128.7, 127.9, 127.4, 125.9, 120.1, 120.0 (t, *J* = 261.2 Hz), 53.0 (t, *J* = 21.1 Hz), 19.4 (m).

^{19}F NMR (565 MHz, $CDCl_3$) δ -101.0 (d, *J* = 254.3 Hz, 1F), -103.4 (d, *J* = 254.3 Hz, 1F).

IR (neat): 3059, 2936, 1677, 1596, 1448, 1291, 1145, 1064, 945, 785, 713, 684.

HRMS (ESI-TOF): calculated for [$C_{19}H_{14}F_2O_2Na$ (M + Na^+)]: 335.0854, found: 335.0854.

2-(1,1-difluoro-2-oxo-2-phenylethyl)-2-methyl-1-tosylindolin-3-one (7b):



7b

Following a similar procedure for the synthesis of **7b**, the title compound was obtained as light yellow oil, 78 mg, 57% yield. (Rf = 0.29, eluent: PE/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.71 – 7.65 (m, 3H), 7.63 – 7.58 (m, 1H), 7.45 – 7.39 (m, 2H), 7.29 – 7.25 (m, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.26 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 193.1, 187.7 (t, *J* = 28.7 Hz), 152.6, 144.8, 137.2, 134.5, 132.3,

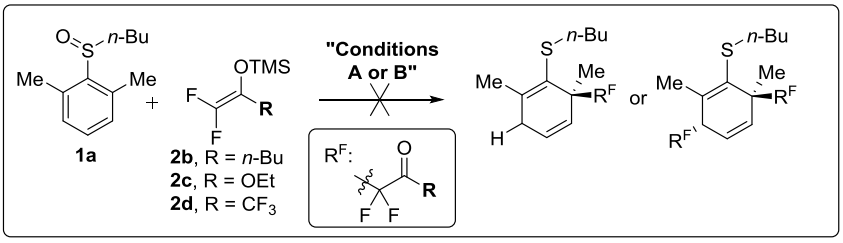
130.4, 130.3, 129.7, 128.5, 127.1, 124.9, 124.6, 123.9, 116.9 (t, J = 261.2 Hz), 116.5, 29.8, 21.6, 17.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.1 (s, 1F), -103.6 (s, 1F).

IR (neat): 2923, 2853, 1722, 1692, 1611, 1596, 1466, 1322, 1166, 1084, 1067, 750, 714, 659, 575.

HRMS (ESI-TOF): calculated for [$C_{24}H_{19}F_2NO_4SNa$ (M + Na^+)]: 478.0895, found: 478.0891.

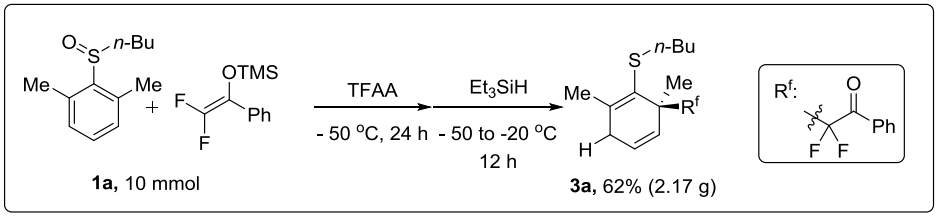
7 Examination of difluoroenol silly ethers 2b-2d.



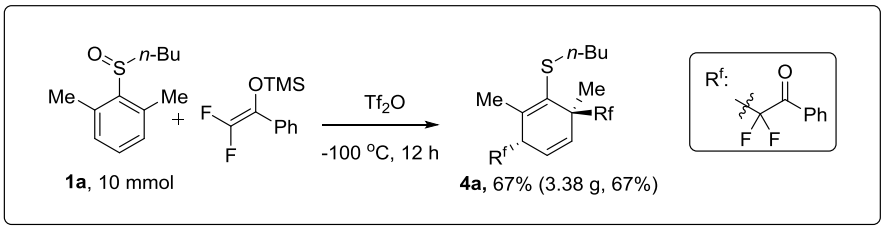
Following the general procedure A and B, the reaction of sulfoxide **1a** (63 mg, 0.3 mmol) with difluoroenol silly ethers **2b**-**2d** was carried out. The progress of the reaction was monitored by TLC. During the whole process, no expected product was determined from these reactions.

8 Gram-scale reactions and conversion of product 3a to highly substituted difluoroalkylated cyclohexenones.

8.1 Gram-scale reactions for the synthesis of 3a and 4a

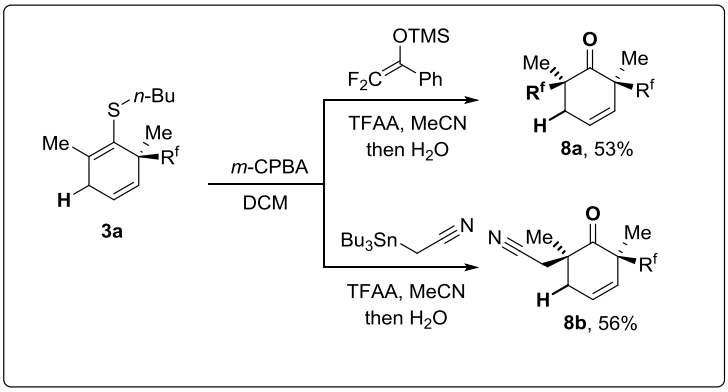


Following the general procedure A, the reaction of sulfoxide **1a** (2.1 g, 10 mmol) produced the title compound **3a**, 2.17 g, 62% yield.



Following the general procedure B, the reaction of sulfoxide **1a** (2.1 g, 10 mmol) produced the title compound **4a**, 3.38 g, 67% yield.

8.2 Conversion of products 3a to highly substituted difluoroalkylated cyclohexenones.

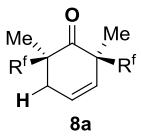


To a solution of sulfide **3a** (70 mg, 0.2 mmol) in DCM (2 mL, 0.1 M) was added a solution of *m*-CPBA (38 mg, 1.1 equiv.) in DCM (0.44 mL, 0.5 M) at 0 °C. After sulfides **3a** was completely consumed, the reaction was quenched with sat. aq. $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with

brine, dried over Na_2SO_4, filtrated and concentrated in vacuum. The obtained sulfoxides were directly used for the next step.

To the solution of sulfoxides obtained following the above procedure was added nucleophiles difluoroenol silyl ether **2a** (69 mg, 1.5 equiv) or α-stannyl nitrile (99 mg, 1.5 equiv), and TFAA (42 μL, 1.5 equiv) at -40 ℃. After stirring for 12 h, sat. aq. $NaHCO_3$ (1.0 mL) was added, and the resulting mixture was then slowly warmed up to rt and kept stirring for another 12 h. After that, the mixture was passed through a short silica gel column and concentrated under vacuum. The obtained residue was further purified by flash chromatography on silica gel giving compound **8a** or **8b**.

2,2'-(1,3-dimethyl-2-oxocyclohex-4-ene-1,3-diyl)bis(2,2-difluoro-1-phenylethan-1-one) (8a):



8a

Following the general procedure, the title compound 8a was obtained as light yellow oil, 46 mg, 53% yield. (Rf = 0.55, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.7 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.59 (dd, *J* = 15.6, 7.5 Hz, 2H), 7.45 (dd, *J* = 15.8, 8.0 Hz, 4H), 6.06 – 5.90 (m, 2H), 2.99 – 2.94 (m, 1H), 2.50 – 2.41 (m, 1H), 1.66 (s, 3H), 1.58 (d, *J* = 1.3 Hz, 3H).

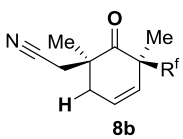
^{13}C NMR (151 MHz, $CDCl_3$): δ 207.7, 188.9 (t, *J* = 28.7 Hz), 188.7 (t, *J* = 28.7 Hz), 134.3, 134.2, 133.1, 130.4, 130.3, 128.7, 128.6, 127.9, 125.5, 119.8 (t, *J* = 261.2 Hz), 119.1 (t, *J* = 261.2 Hz), 54.6 (t, *J* = 21.1 Hz), 52.3 (t, *J* = 21.2 Hz), 31.6, 20.8, 20.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -99.8 (d, *J* = 254.3 Hz, 1F), -101.8 (d, *J* = 254.3 Hz, 1F), -102.4 (d, *J* = 254.3 Hz, 1F), -104.4 (d, *J* = 254.3 Hz, 1F).

IR (neat): 3062, 2950, 2852, 1701, 1596, 1449, 1298, 1147, 1051, 994, 844, 709, 659.

HRMS (ESI-TOF): calculated for [$C_{24}H_{20}F_4O_3Na$ ($M + Na^+$)]: 455.1241, found: 455.1240.

2-(5-(1,1-difluoro-2-oxo-2-phenylethyl)-1,5-dimethyl-6-oxocyclohex-3-en-1-yl)acetonitrile (8b):



8b

Following the general procedure, the title compound **8b** was obtained as light yellow oil, 53 mg, 56% yield. (Rf = 43, eluent: PE/EtOAc = 10/1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.50 – 7.44 (m, 2H), 6.05 – 5.95 (m, 1H), 5.63 – 5.59 (m, 1H), 3.03 (d, *J* = 17.0 Hz, 1H), 2.86 (d, *J* = 17.0 Hz, 1H), 2.70 (d, *J* = 17.0 Hz, 1H), 2.51 (dd, *J* = 17.0, 6.6 Hz, 1H), 1.52 (d, *J* = 1.5 Hz,

3H), 1.36 (s, 3H).

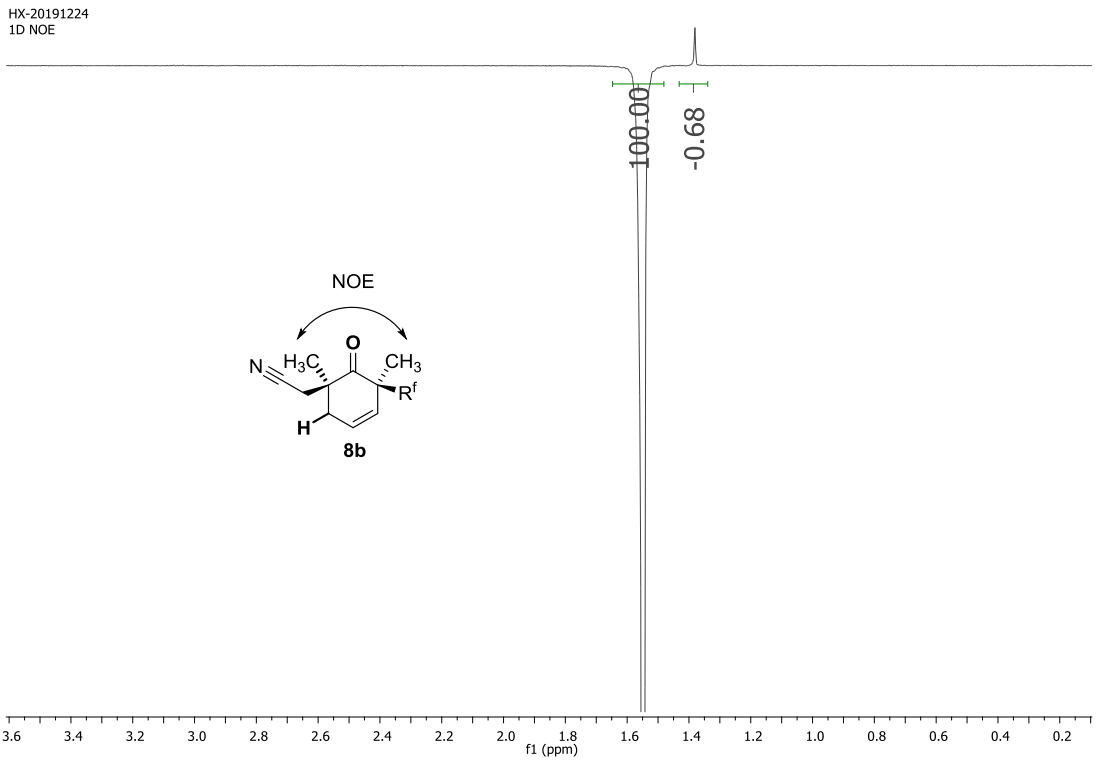
^{13}C NMR (151 MHz, $CDCl_3$): δ 208.7, 188.0 (t, *J* = 28.7 Hz), 134.9, 131.5, 130.5, 128.8, 128.1, 127.1, 120.1 (t, *J* = 261.2 Hz), 118.2, 50.7 (t, *J* = 21.1 Hz), 45.2, 36.5, 26.7, 24.2, 20.0, 19.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -96.6 (d, *J* = 254.3 Hz, 1F), -102.5 (d, *J* = 254.3 Hz, 1F).

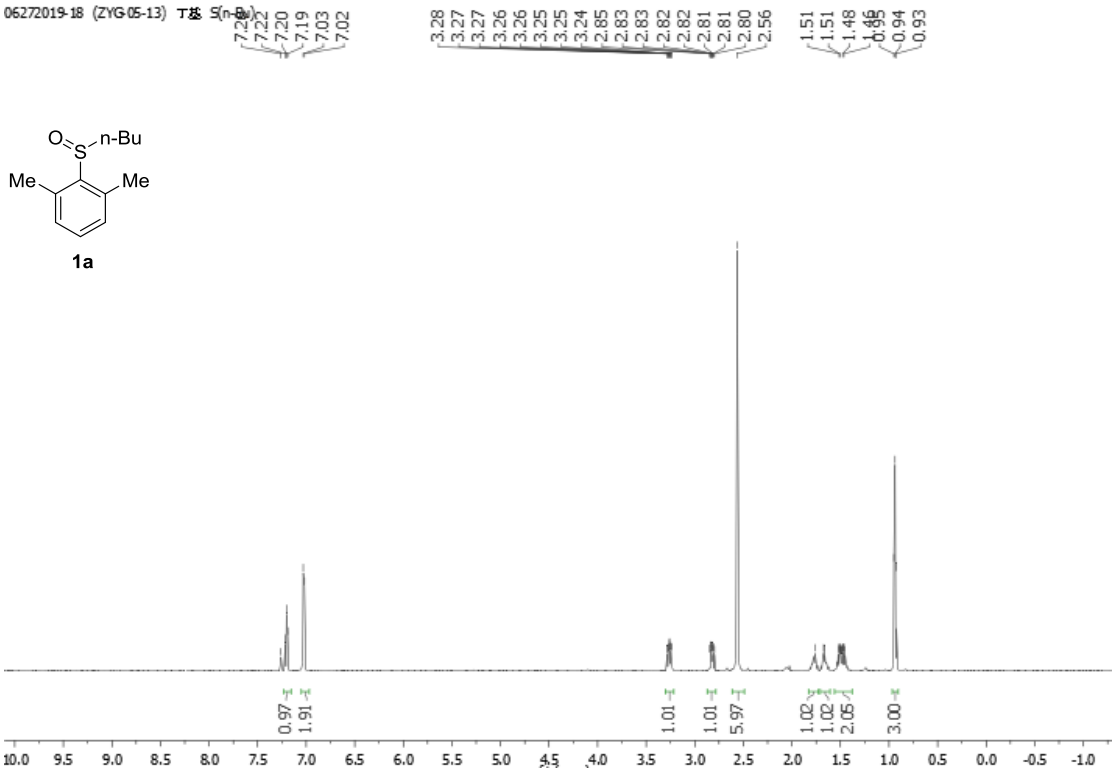
IR (neat): 2982, 2939, 2245, 1693, 1596, 1448, 1203, 1149, 1064, 1003, 930, 882, 711, 648.

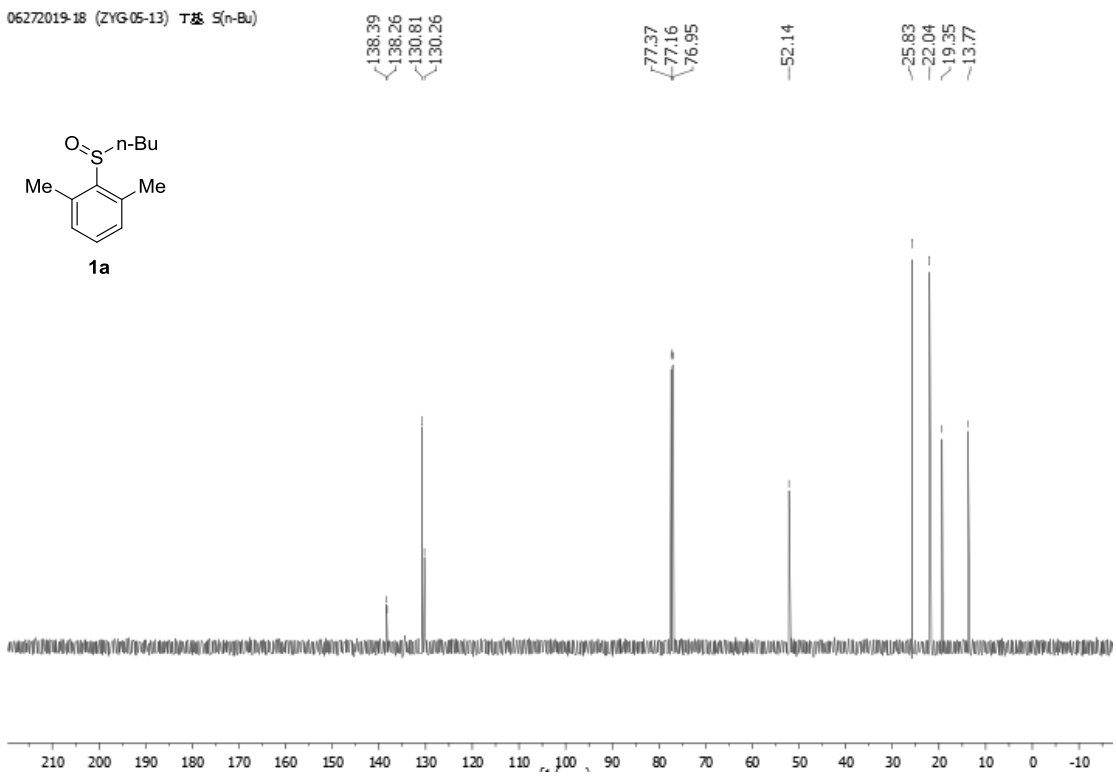
HRMS (ESI-TOF): calculated for [$C_{18}H_{17}F_2NO_2Na$ (M + Na^+)]: 340.1120, found: 340.1117

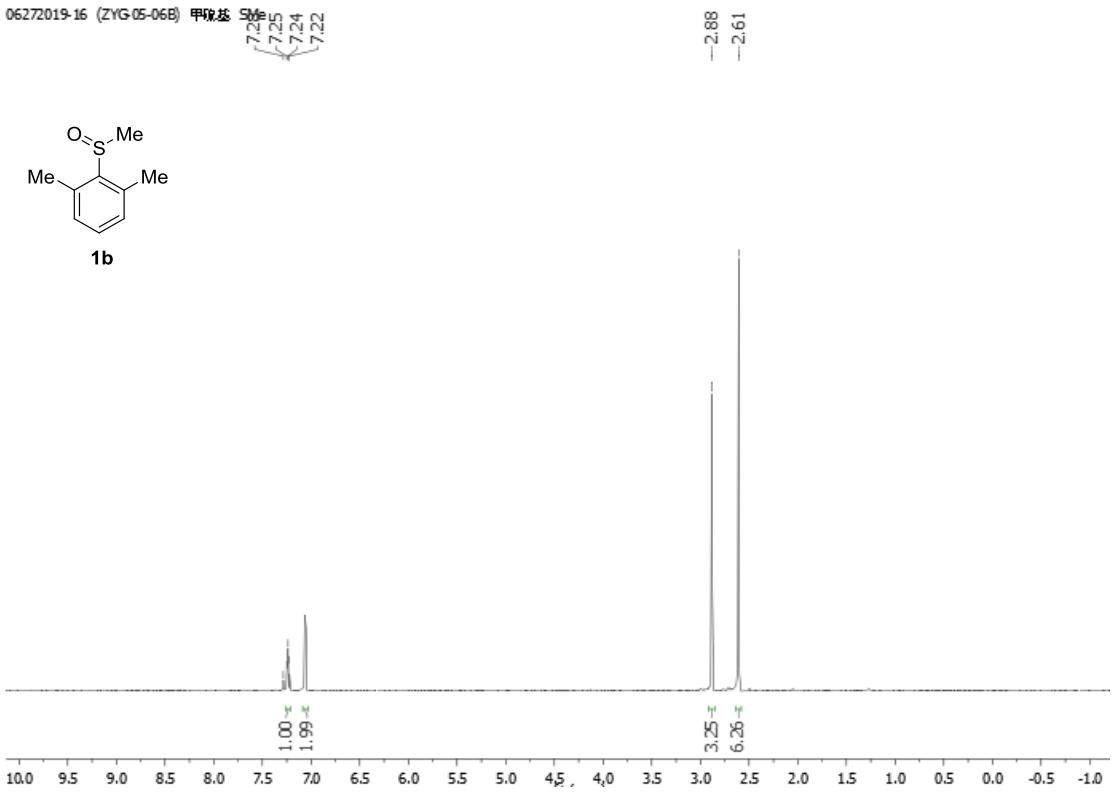
The relative configuration of **8b** was assigned according to the NOE analysis, and the corresponding spectrum was shown as blow.

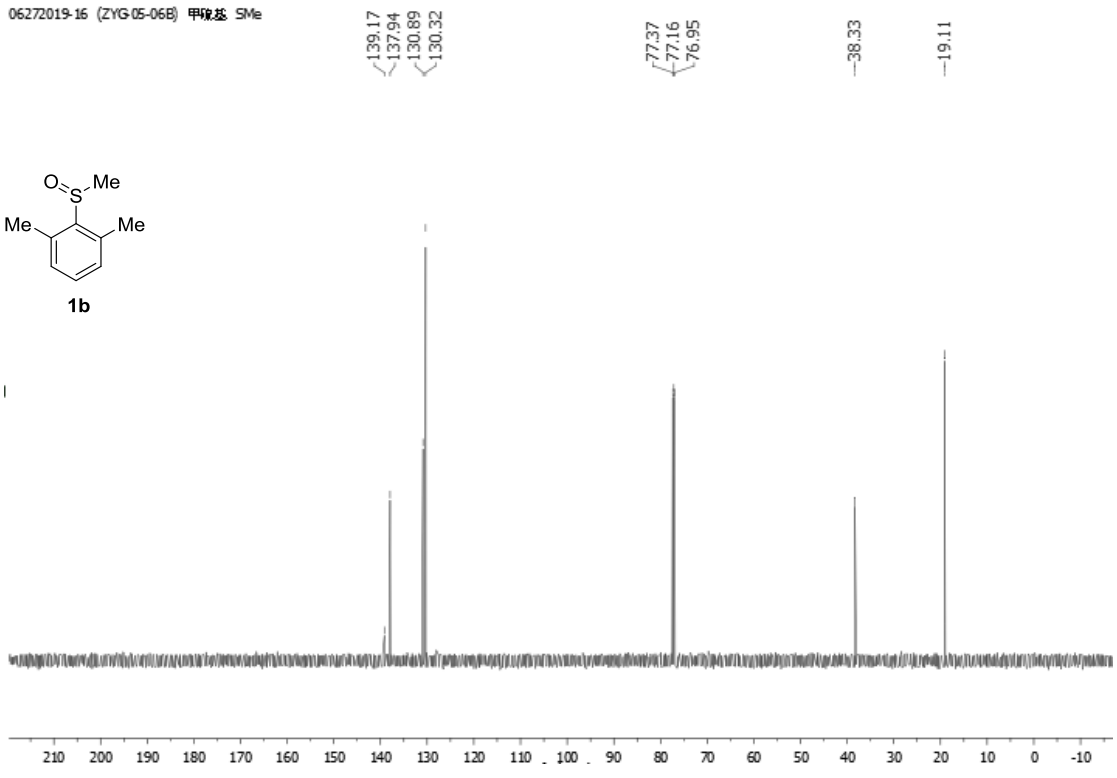


9 NMR spectra

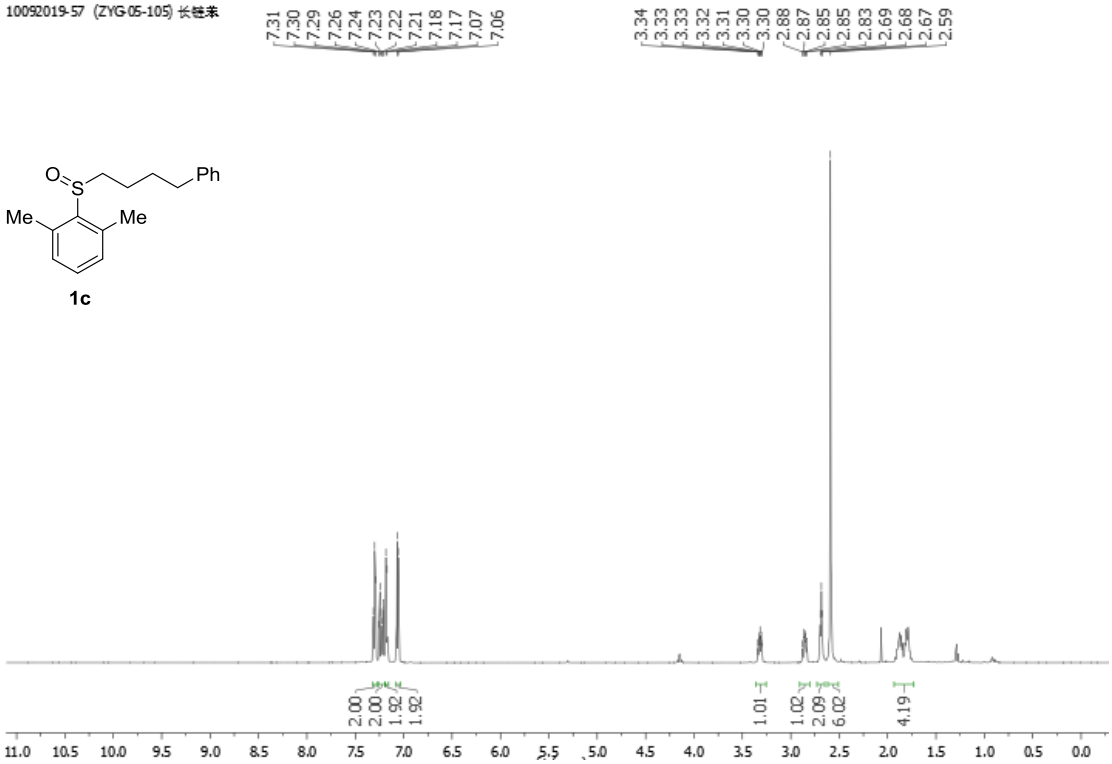





06272019-16 (ZYG-05-06B) 甲硫基 SMe
7.26
7.25
7.24
7.22
2.88
2.61
O
S
Me
Me
Me
1b
1.00
1.99
3.25
6.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

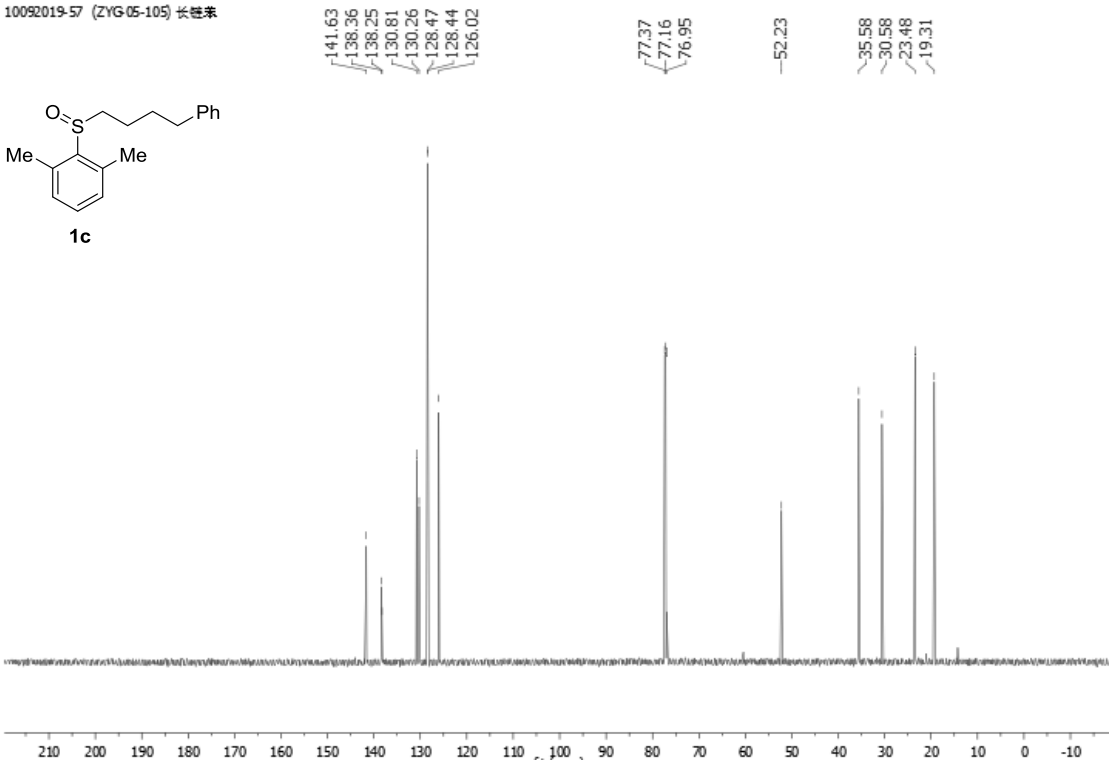

06272019-16 (ZYG-05-06B) 甲硫基 SMe
139.17
137.94
130.89
130.32
77.37
77.16
76.95
38.33
19.11
O
S
Me
Me
Me
1b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

10092019-57 (ZYG-05-105) 长链苯

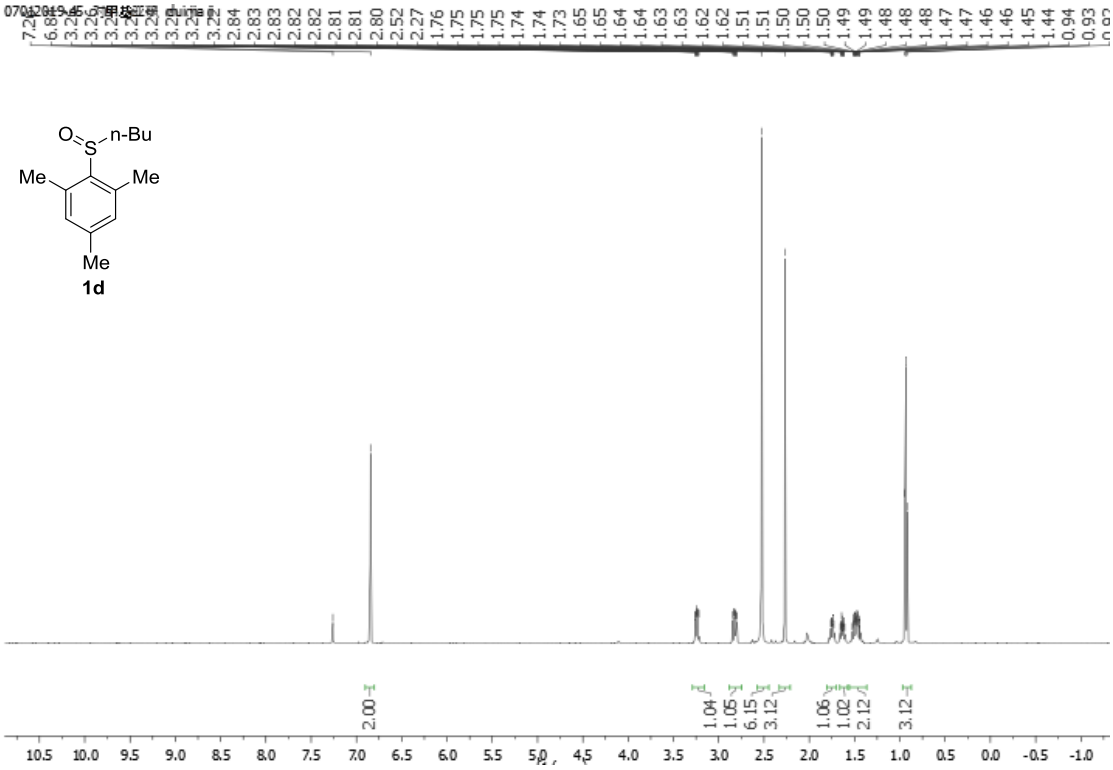


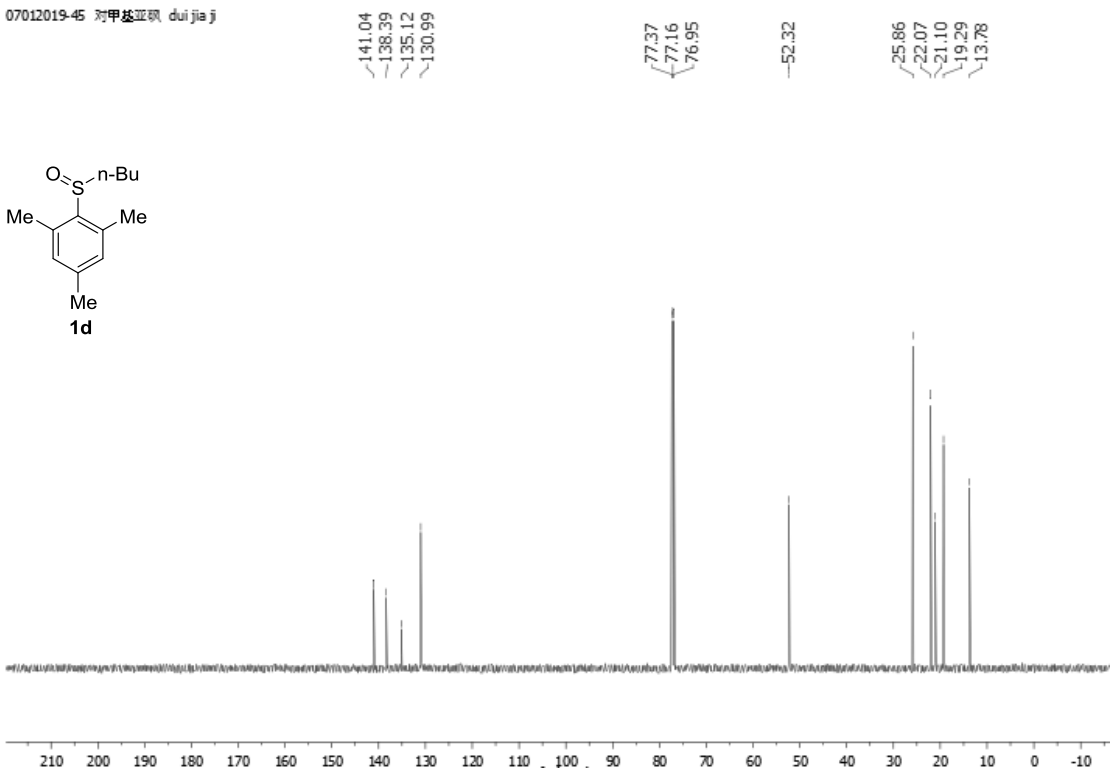
1c

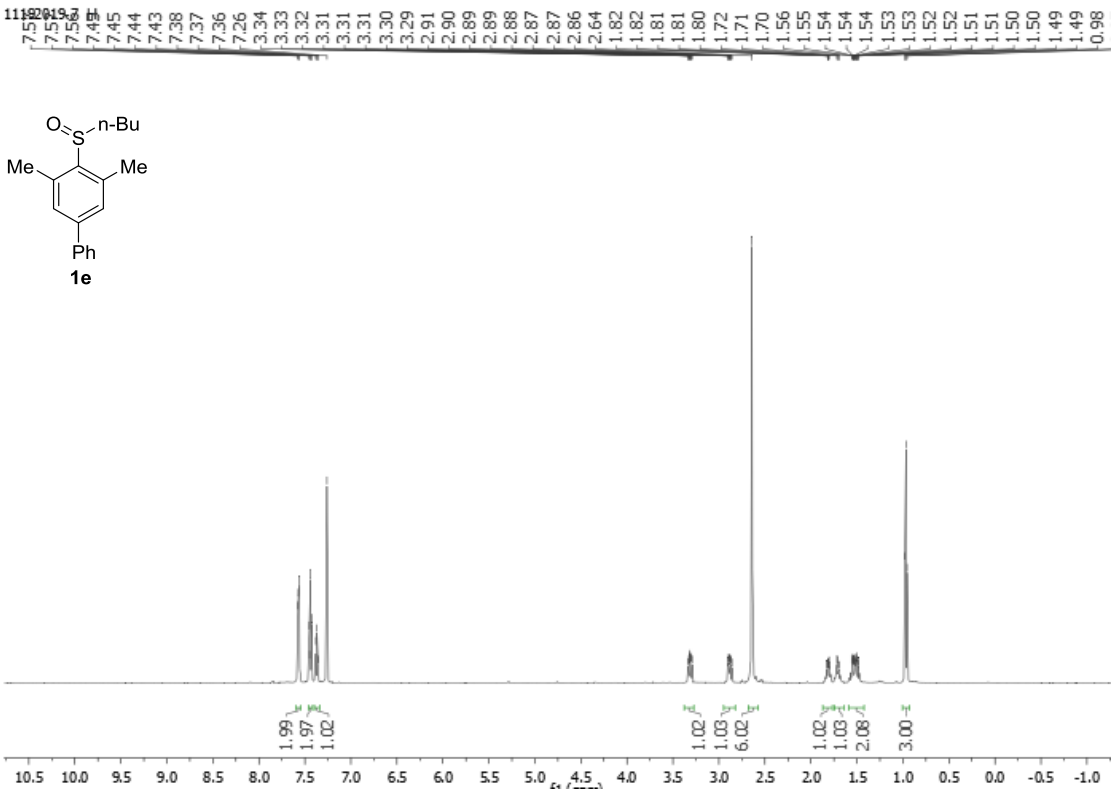
10092019-57 (ZYG-05-105) 长链苯

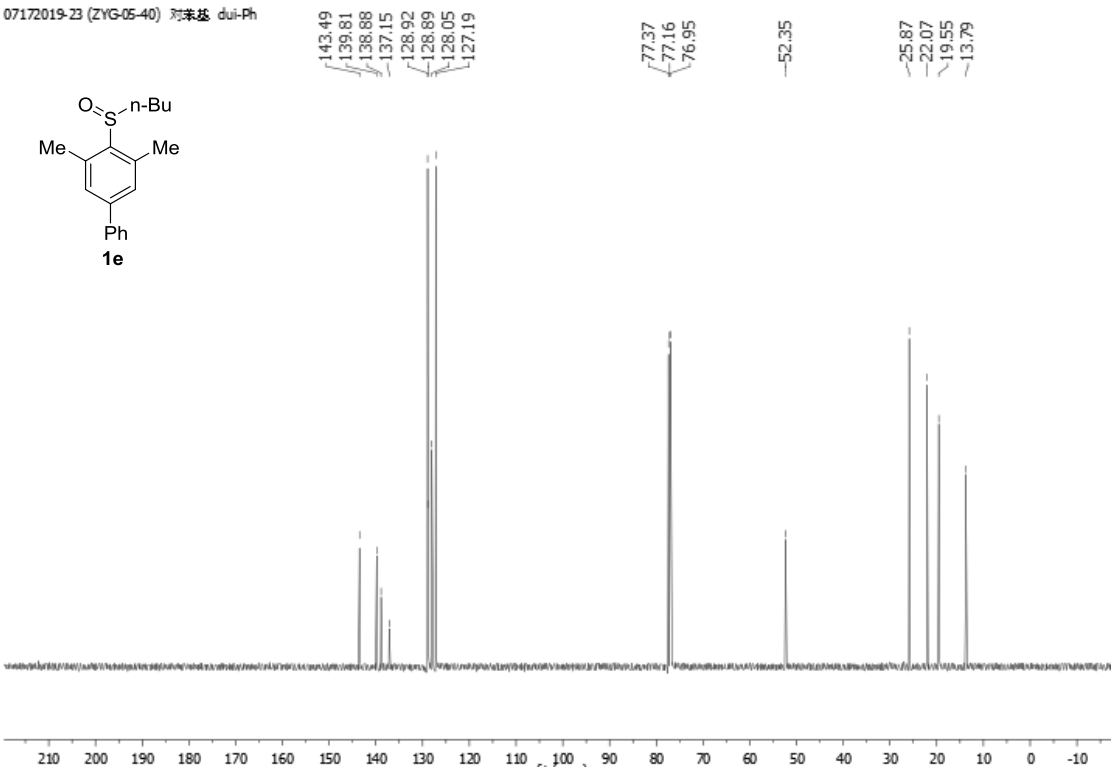


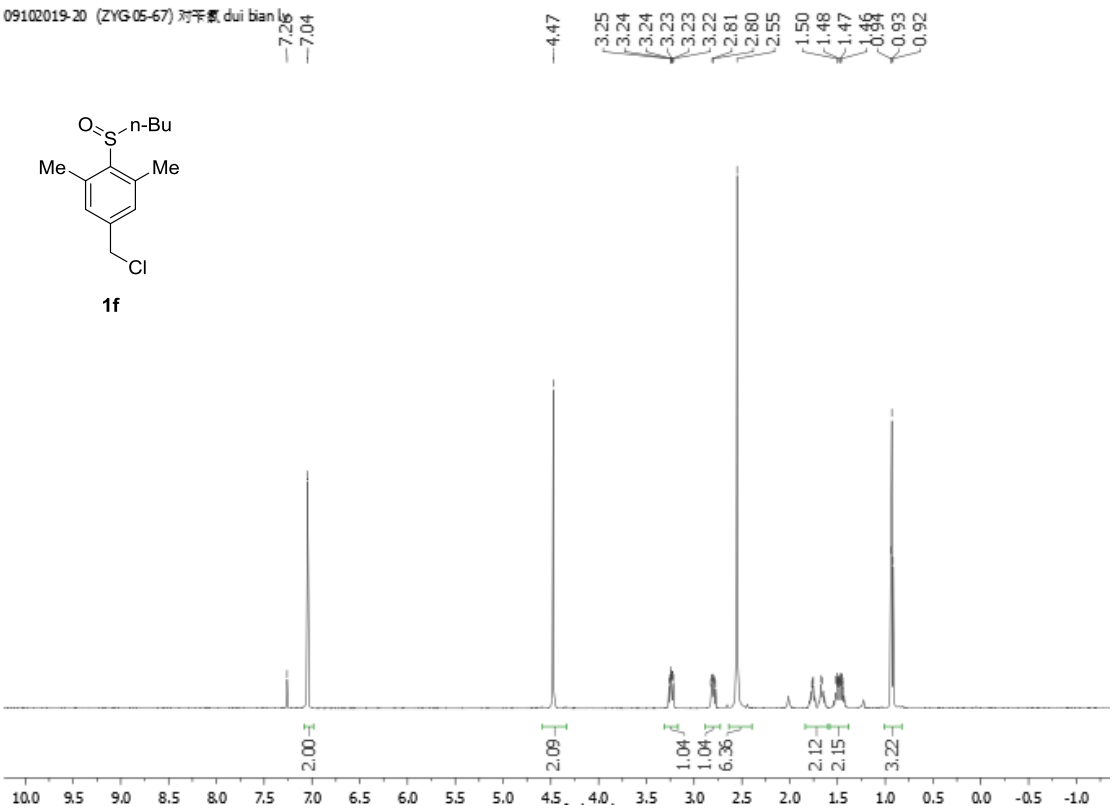
1c


n-Bu
Me
Me
Me
1d
2.00
1.04
1.05
6.15
3.12
1.06
1.02
2.12
3.12

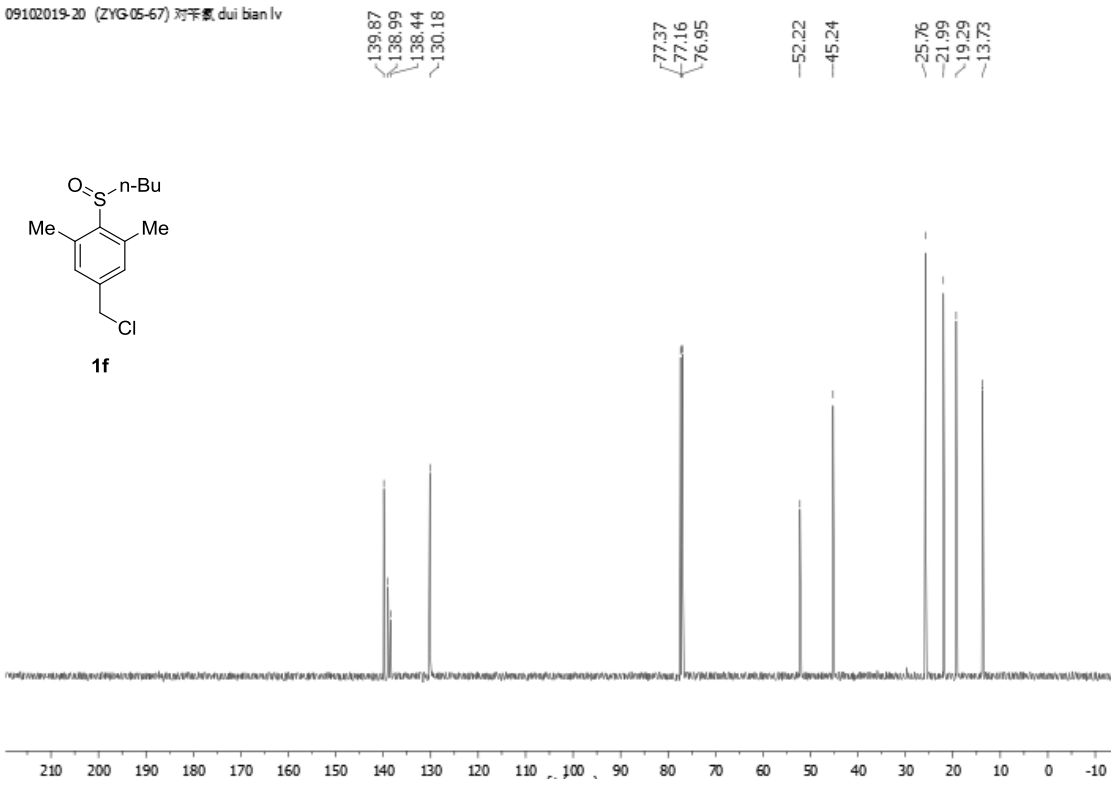

07012019-45 对甲基亚砜 dui jia ji
141.04
138.39
135.12
130.99
77.37
77.16
76.95
52.32
25.86
22.07
21.10
19.29
13.78
n-Bu
Me
Me
Me
1d


n-Bu
Me
Me
Ph
1e


07172019-23 (ZYG-05-40) 对苯基 dui-Ph
n-Bu
Me
Me
Ph
1e

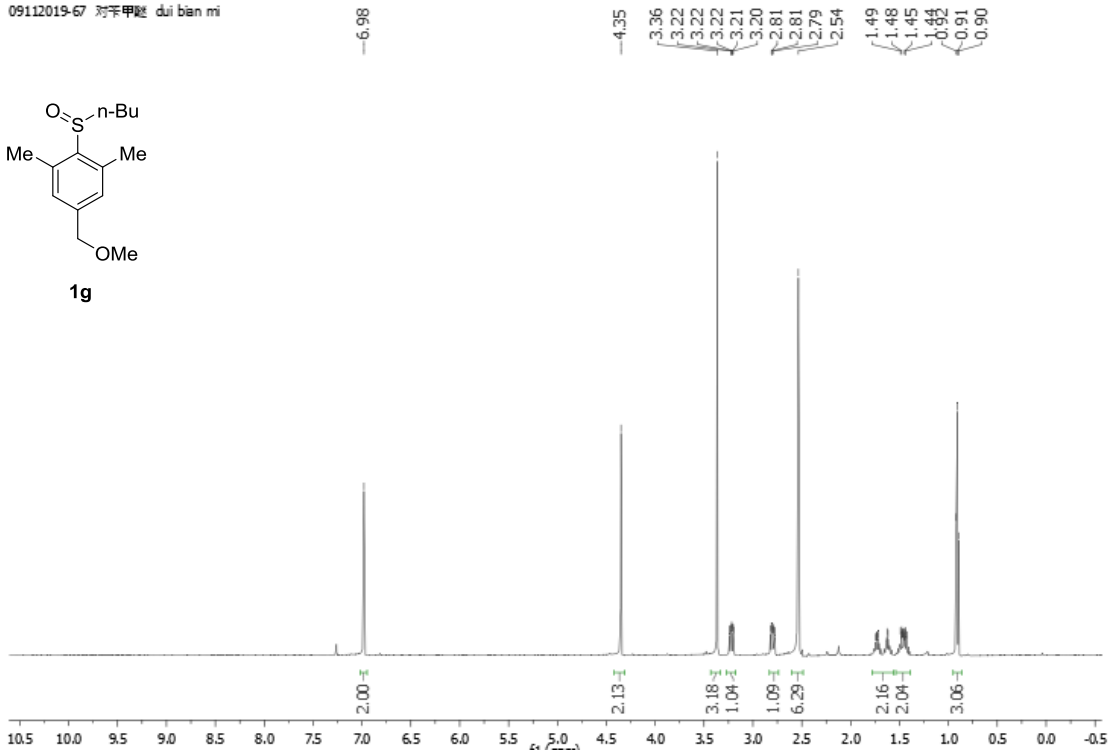

09102019-20 (ZYG-05-67) 对苄氯 dui bian lv
7.26
7.04
4.47
3.25
3.24
3.24
3.23
3.23
3.22
2.81
2.80
2.55
1.50
1.48
1.47
1.46
0.94
0.93
0.92
O
S
n-Bu
Me
Me
Cl
2.00
2.09
1.04
1.04
6.36
2.12
2.15
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

1f


09102019-20 (ZYG-05-67) 对苄氯 dui bian lv
139.87
138.99
138.44
130.18
77.37
77.16
76.95
52.22
45.24
25.76
21.99
19.29
13.73
O
S
n-Bu
Me
Me
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

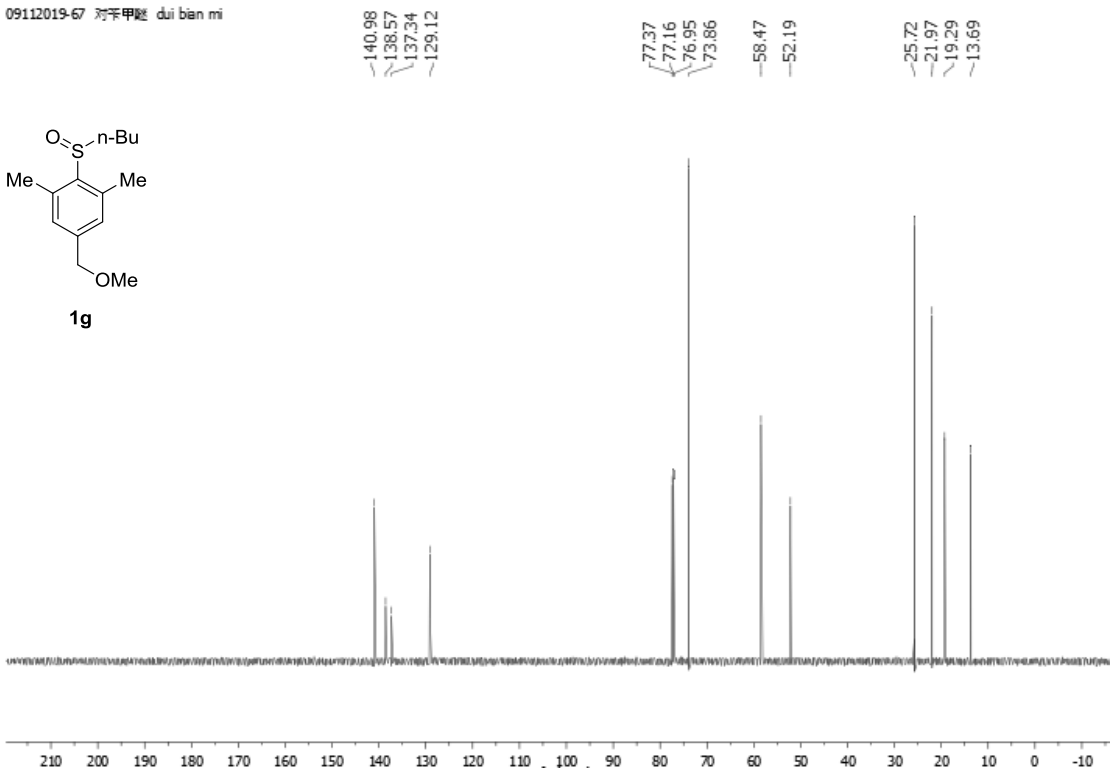
1f

09112019-67 对苄甲醚 dui bian mi

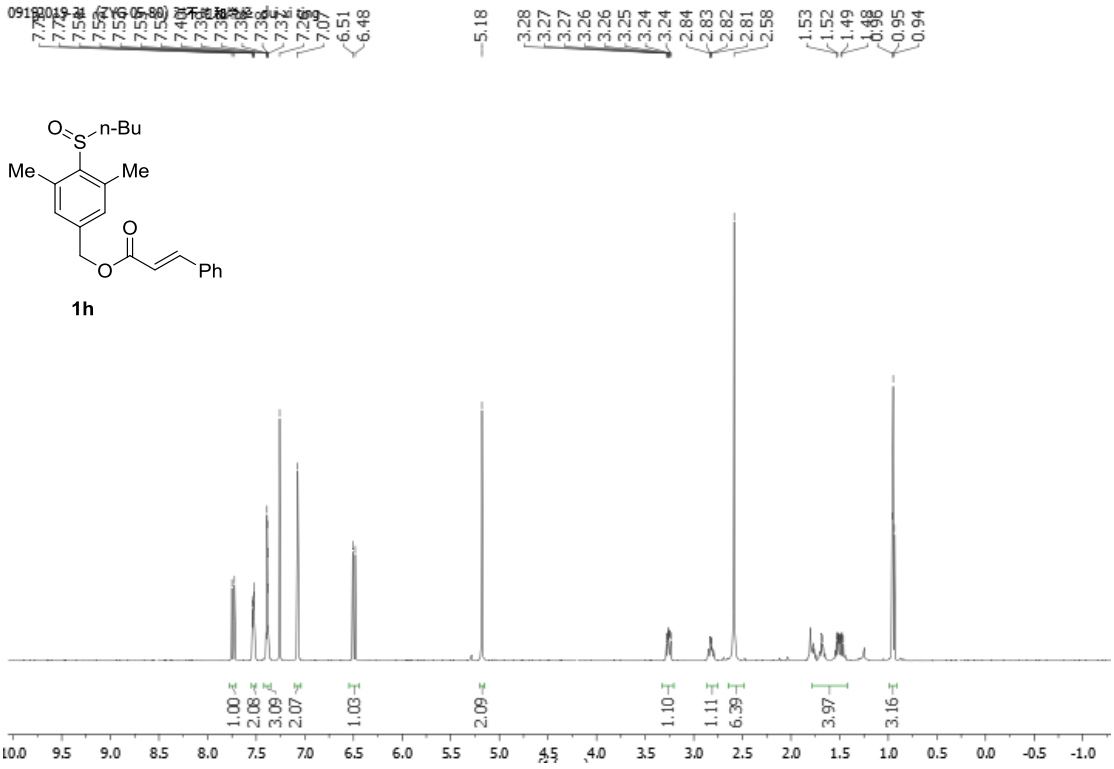


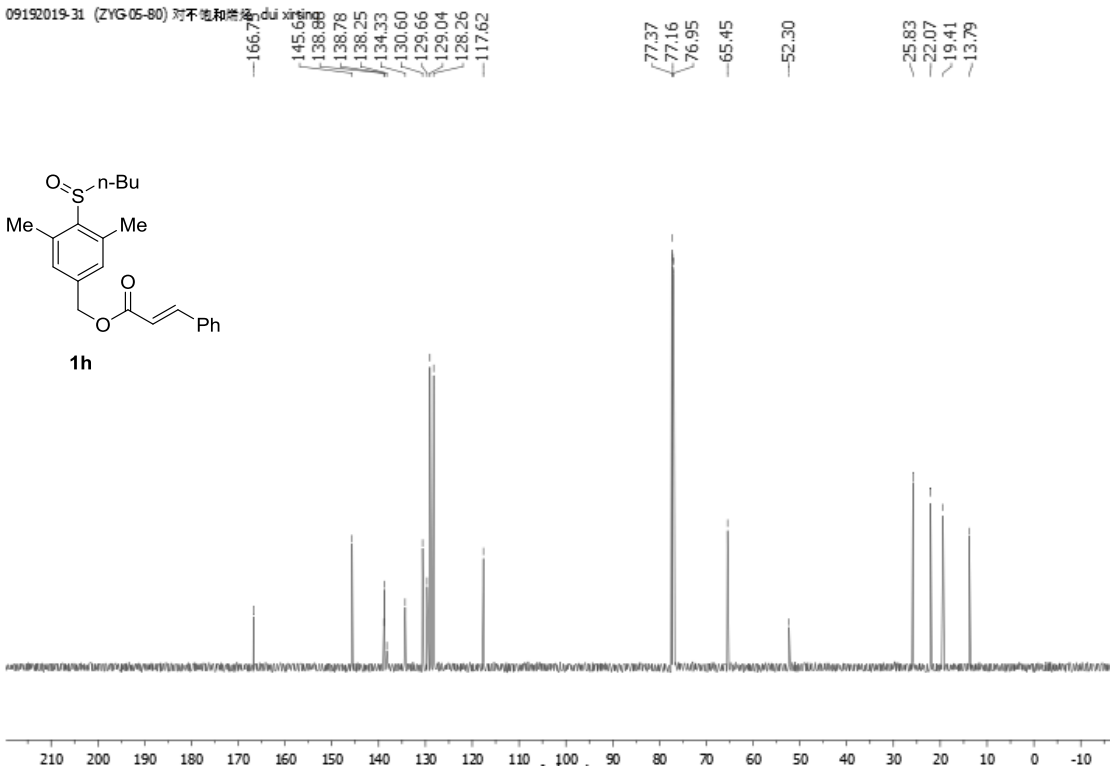
1g

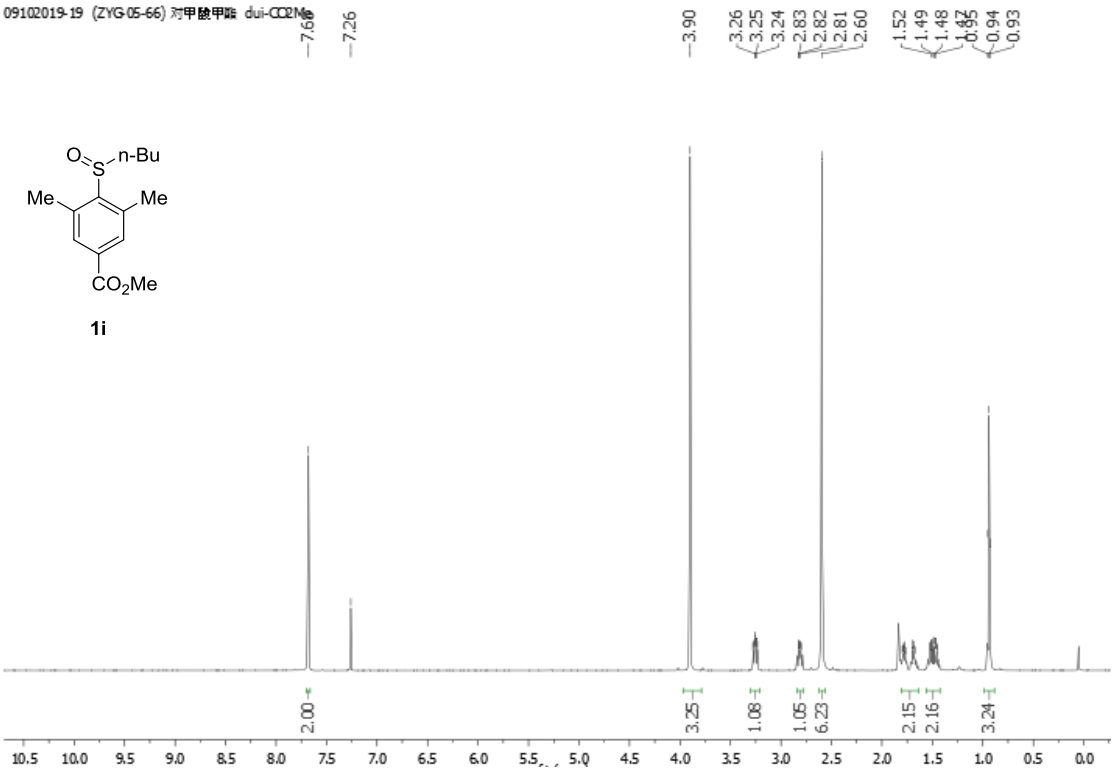
09112019-67 对苄甲醚 dui bian mi



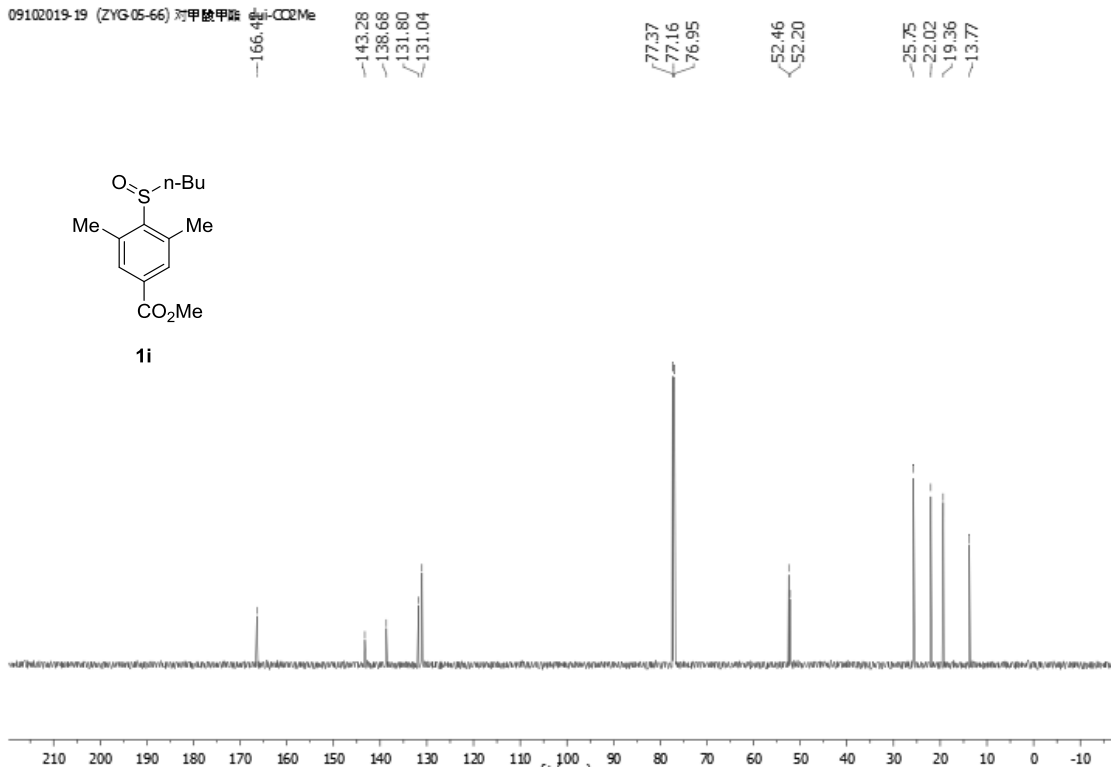
1g


n-Bu
Me
Me
O
Ph
1h

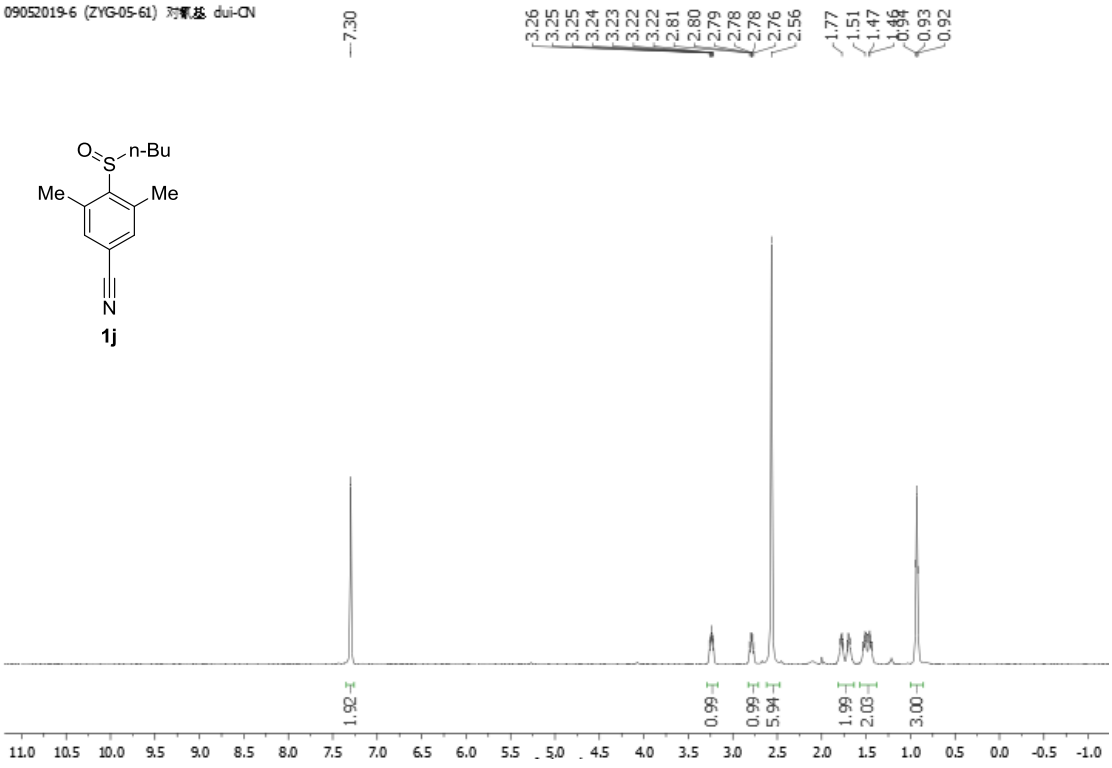

n-Bu
Me
Me
O
Ph
1h

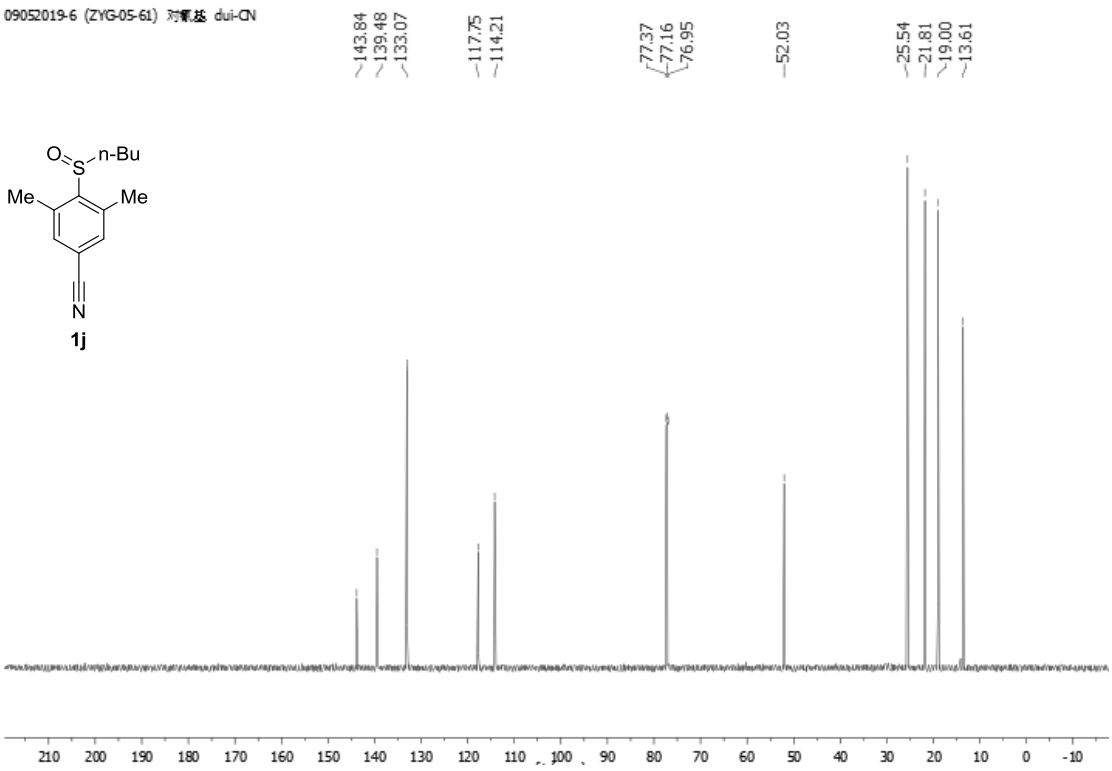

09102019-19 (ZYG-05-66) 对甲酸甲酯 dui-CO2Me
7.68
7.26
3.90
3.26
3.25
3.24
2.83
2.82
2.81
2.60
1.52
1.49
1.48
1.47
0.95
0.94
0.93
O
S
n-Bu
Me
Me
CO2Me
2.00
3.25
1.08
1.05
6.23
2.15
2.16
3.24
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

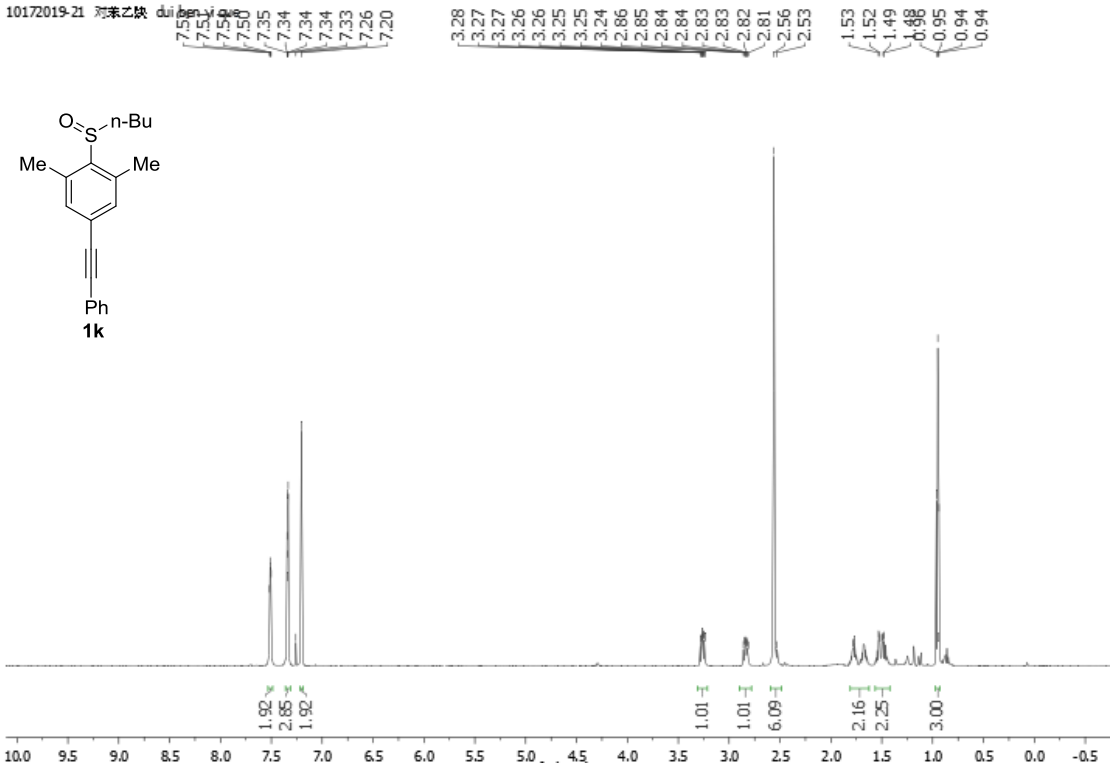
1i

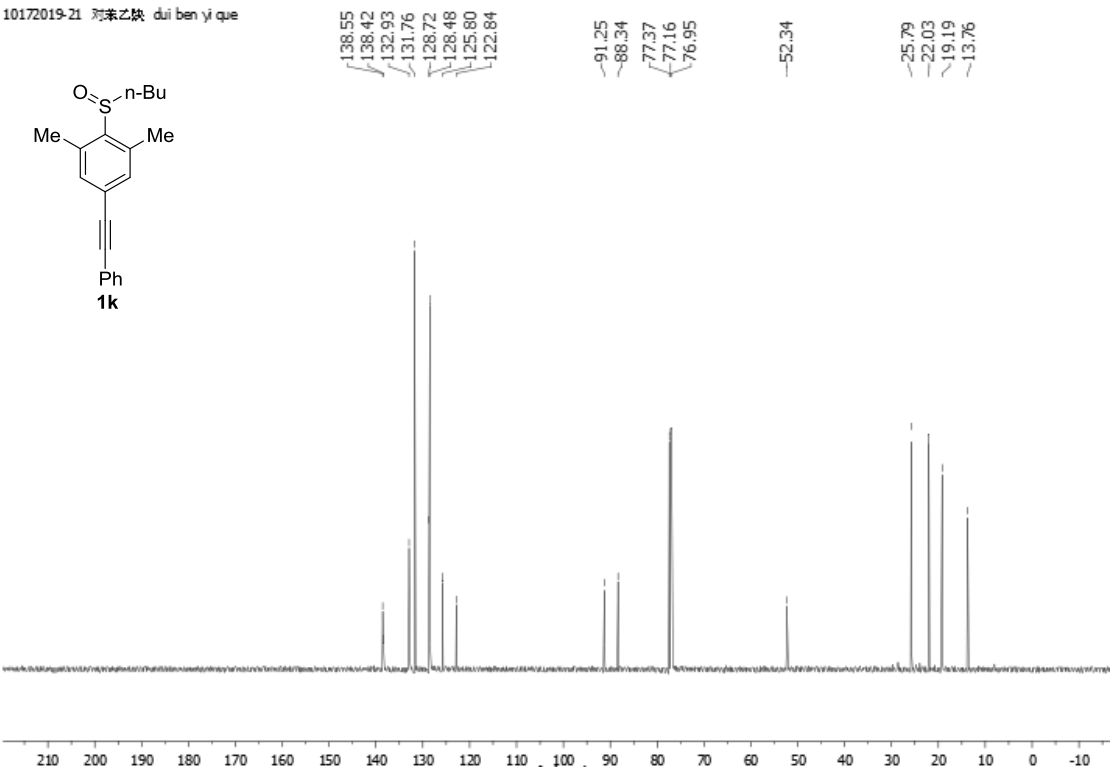

09102019-19 (ZYG-05-66) 对甲酸甲酯 dui-CO2Me
166.42
143.28
138.68
131.80
131.04
77.37
77.16
76.95
52.46
52.20
25.75
22.02
19.36
13.77
O
S
n-Bu
Me
Me
CO2Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

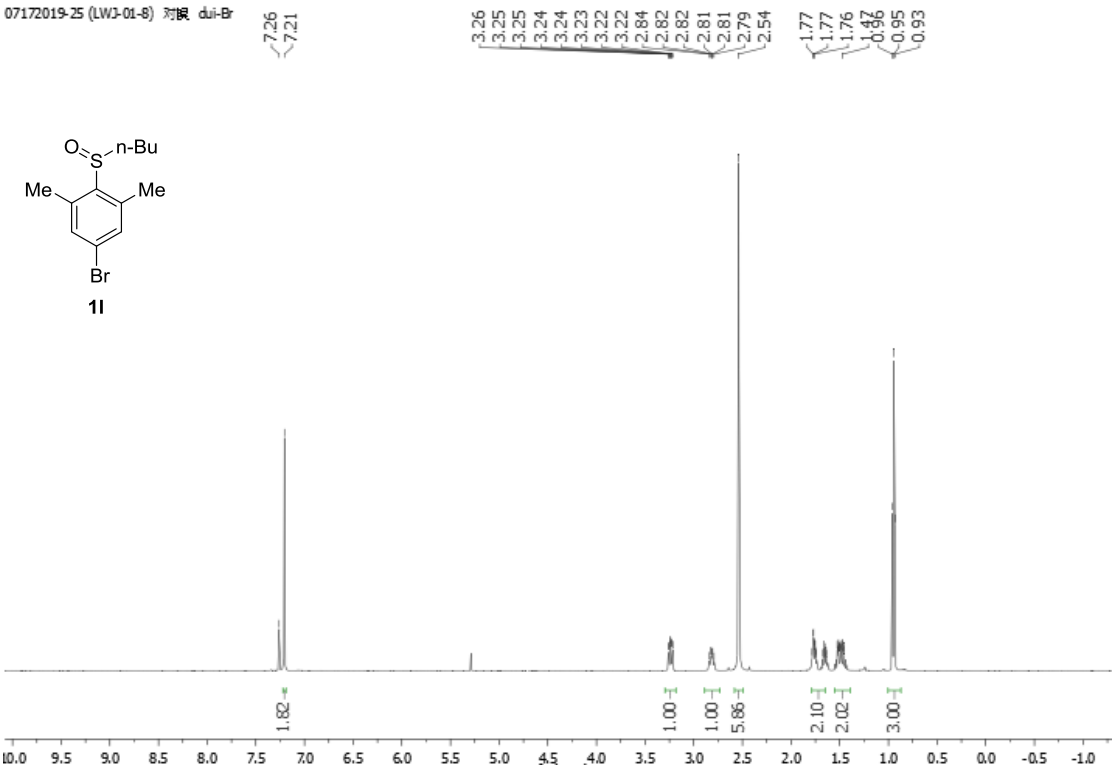
1i

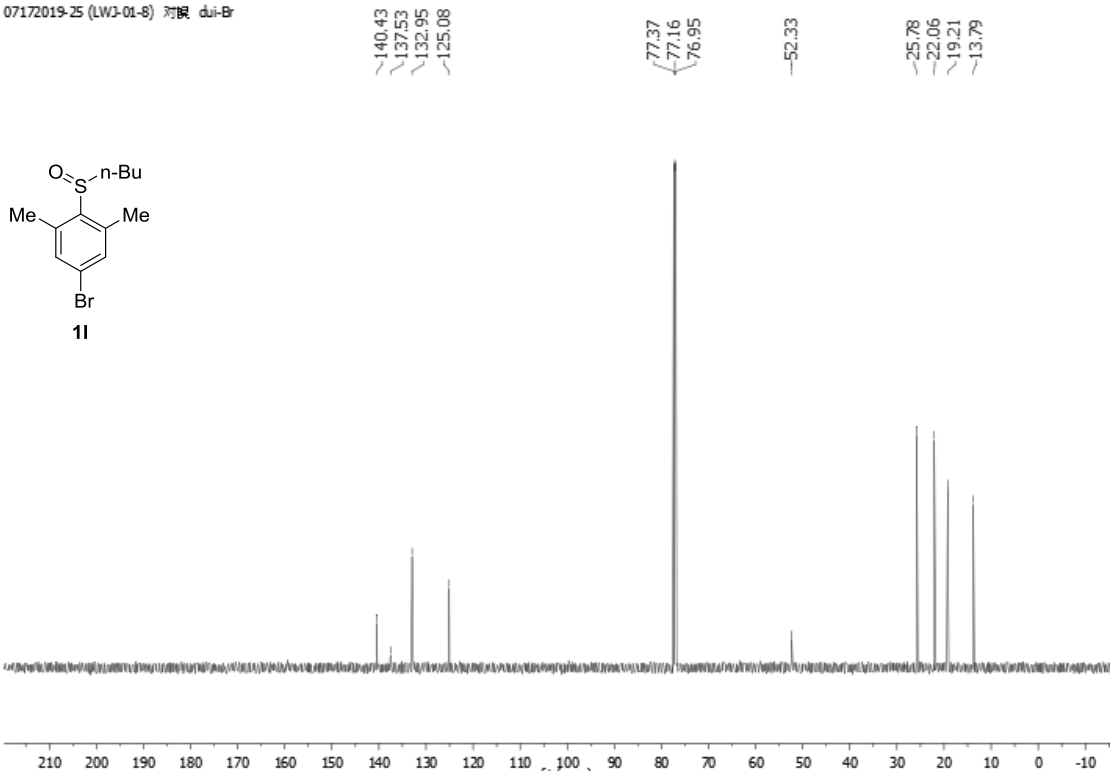

09052019-6 (ZYG-05-61) 对氰基 dui-CN
7.30
3.26
3.25
3.25
3.24
3.23
3.22
3.22
2.81
2.80
2.79
2.78
2.78
2.76
2.56
1.77
1.51
1.47
1.46
0.94
0.93
0.92
O
S
n-Bu
Me
Me
N
1j
1.92
0.99
0.99
5.94
1.99
2.03
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

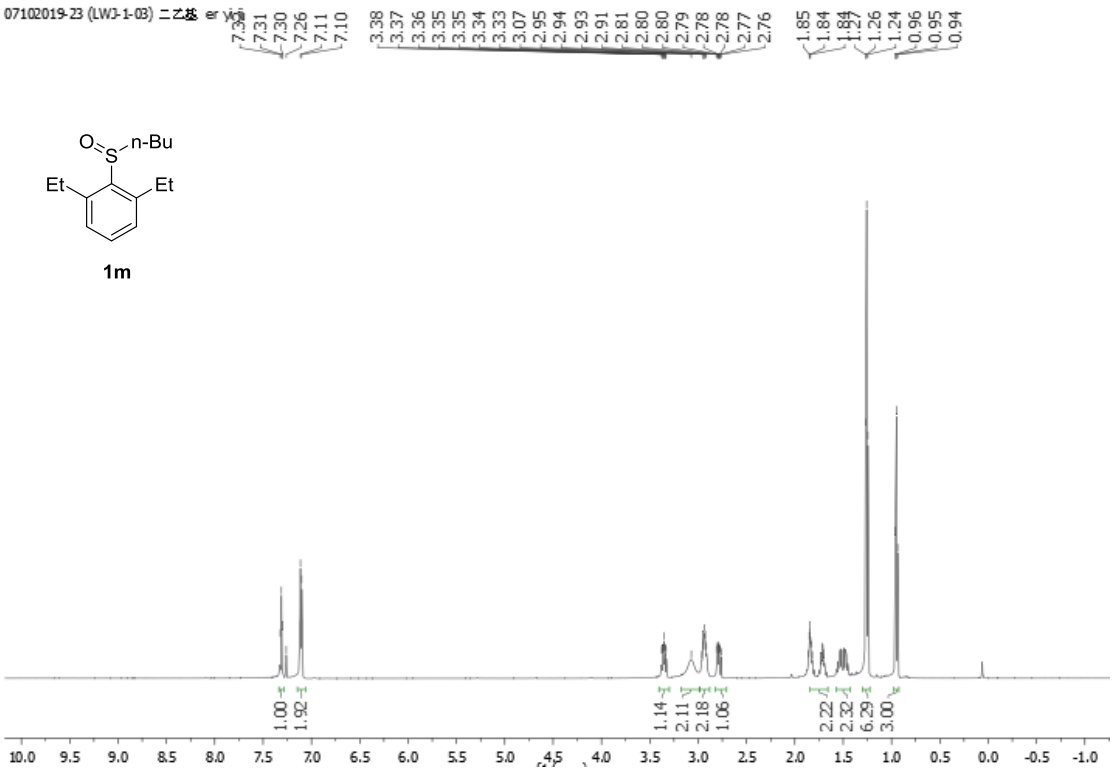

09052019-6 (ZYG-05-61) 对氰基 dui-CN
143.84
139.48
133.07
117.75
114.21
77.37
77.16
76.95
52.03
25.54
21.81
19.00
13.61
O
S
n-Bu
Me
Me
N
1j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

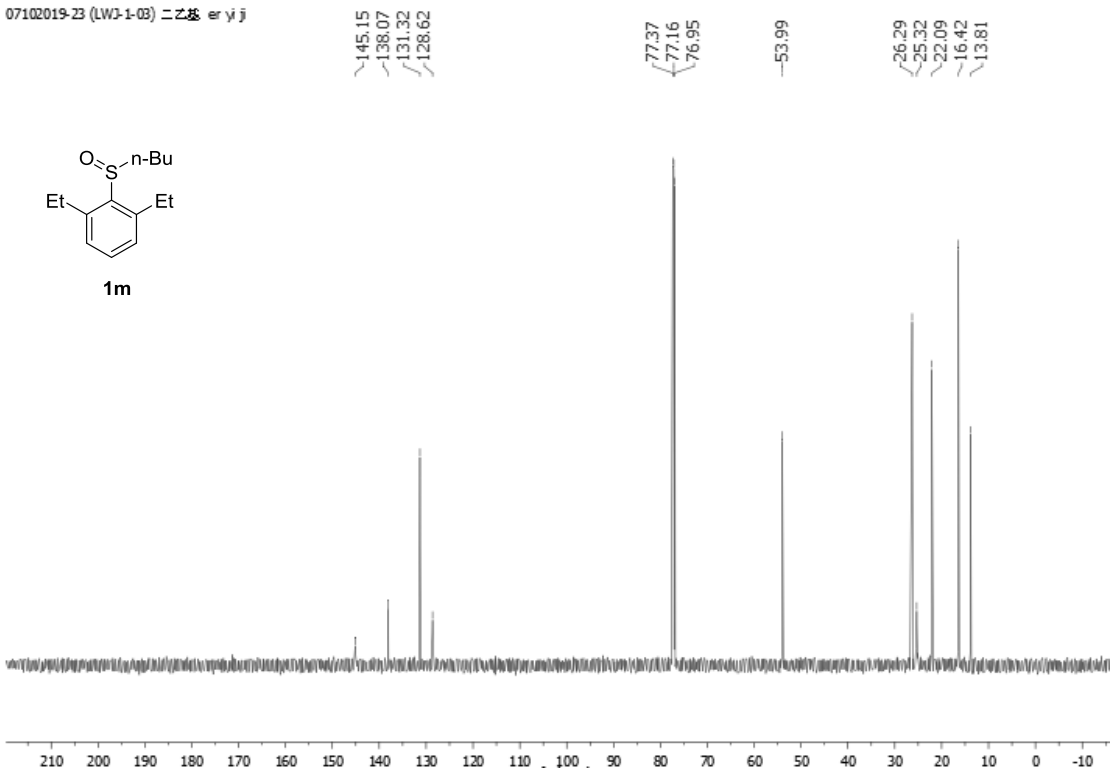

10172019-21 对苯乙炔 dui ben yi que
7.51
7.50
7.35
7.34
7.34
7.33
7.26
7.20
3.28
3.27
3.27
3.26
3.26
3.25
3.25
3.24
2.86
2.85
2.84
2.84
2.83
2.83
2.82
2.81
2.56
2.53
1.53
1.52
1.49
1.48
0.95
0.94
0.94
n-Bu
Me
Me
Ph
1k
1.92
2.85
1.92
1.01
1.01
6.09
2.16
2.25
3.00

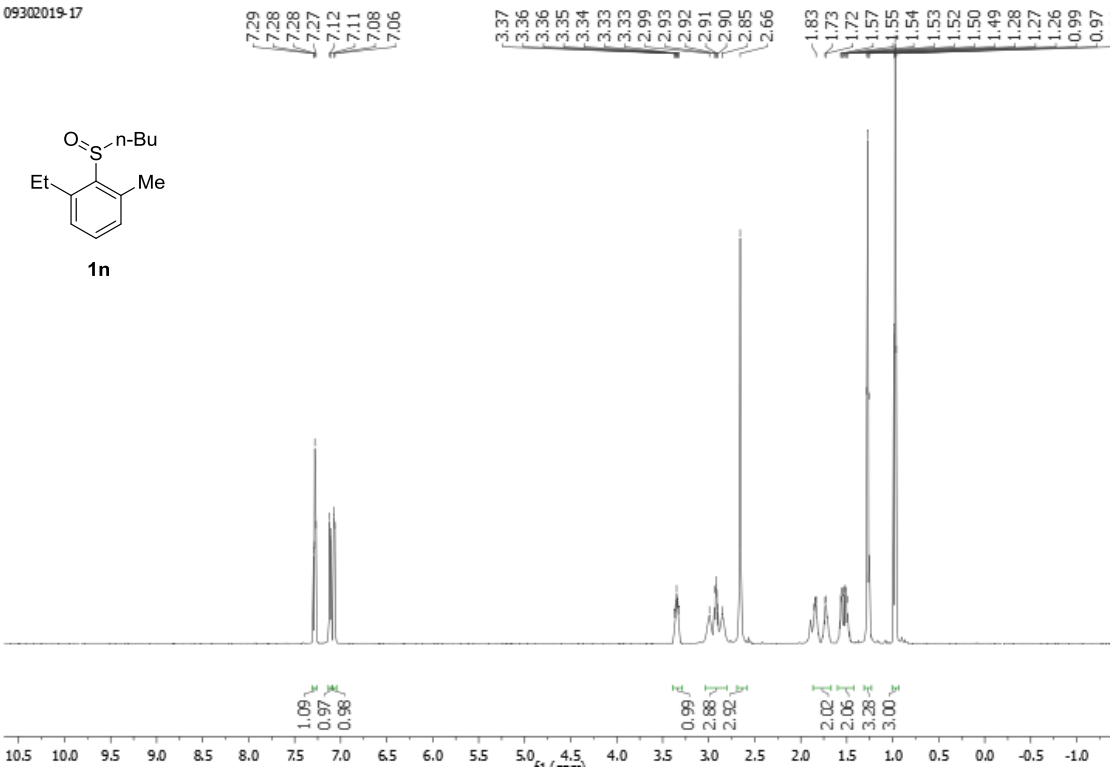

10172019-21 对苯乙炔 dui ben yi que
138.55
138.42
132.93
131.76
128.72
128.48
125.80
122.84
91.25
88.34
77.37
77.16
76.95
52.34
25.79
22.03
19.19
13.76
n-Bu
Me
Me
Ph
1k

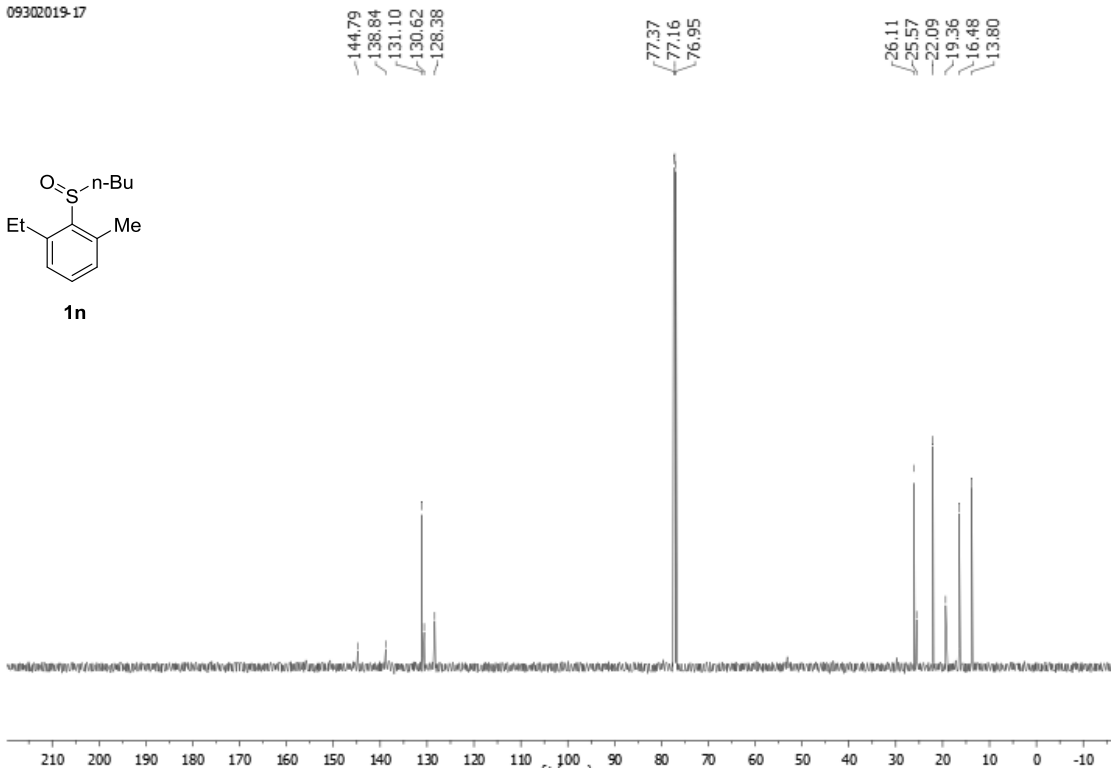

07172019-25 (LWJ-01-8) 对溴 dui-Br
7.26
7.21
3.26
3.25
3.25
3.24
3.24
3.23
3.22
3.22
2.84
2.82
2.82
2.81
2.81
2.79
2.54
1.77
1.77
1.76
1.47
0.96
0.95
0.93
n-Bu
Me
Me
Br
1l
1.82
1.00
1.00
5.86
2.10
2.02
3.00

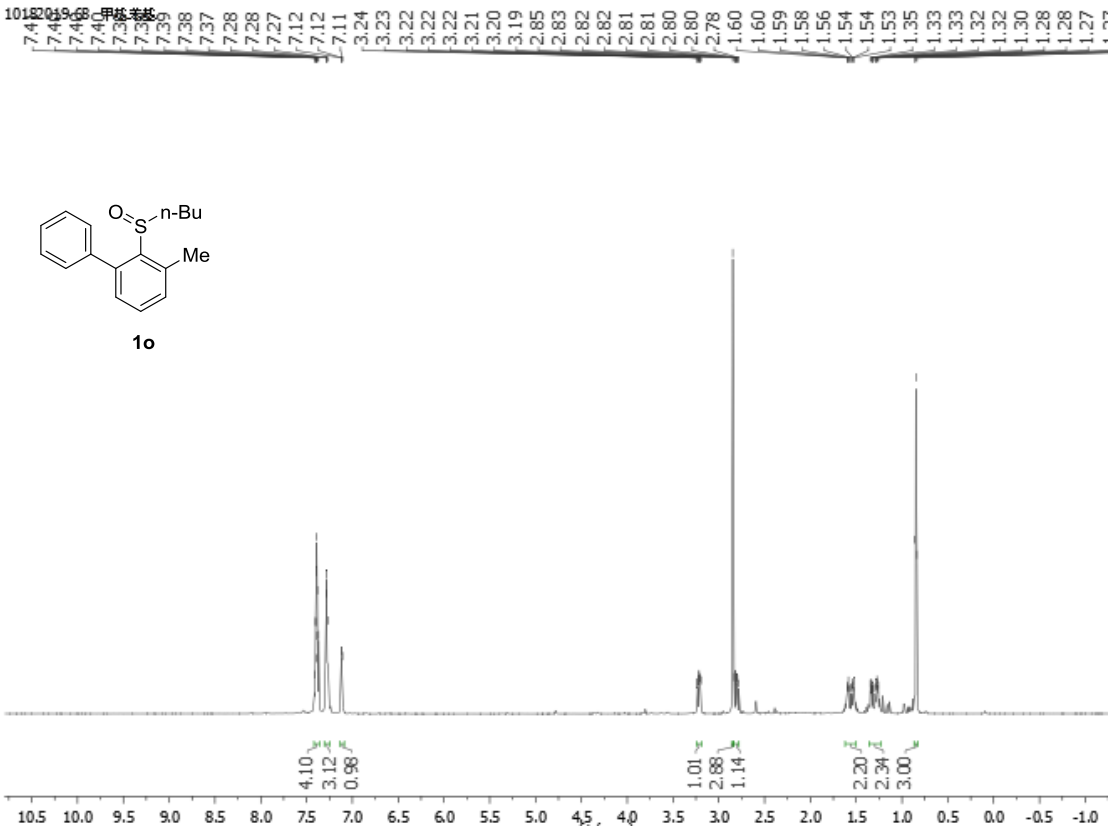

07172019-25 (LWJ-01-8) 对溴 dui-Br
140.43
137.53
132.95
125.08
77.37
77.16
76.95
52.33
25.78
22.06
19.21
13.79
n-Bu
Me
Me
Br
1l

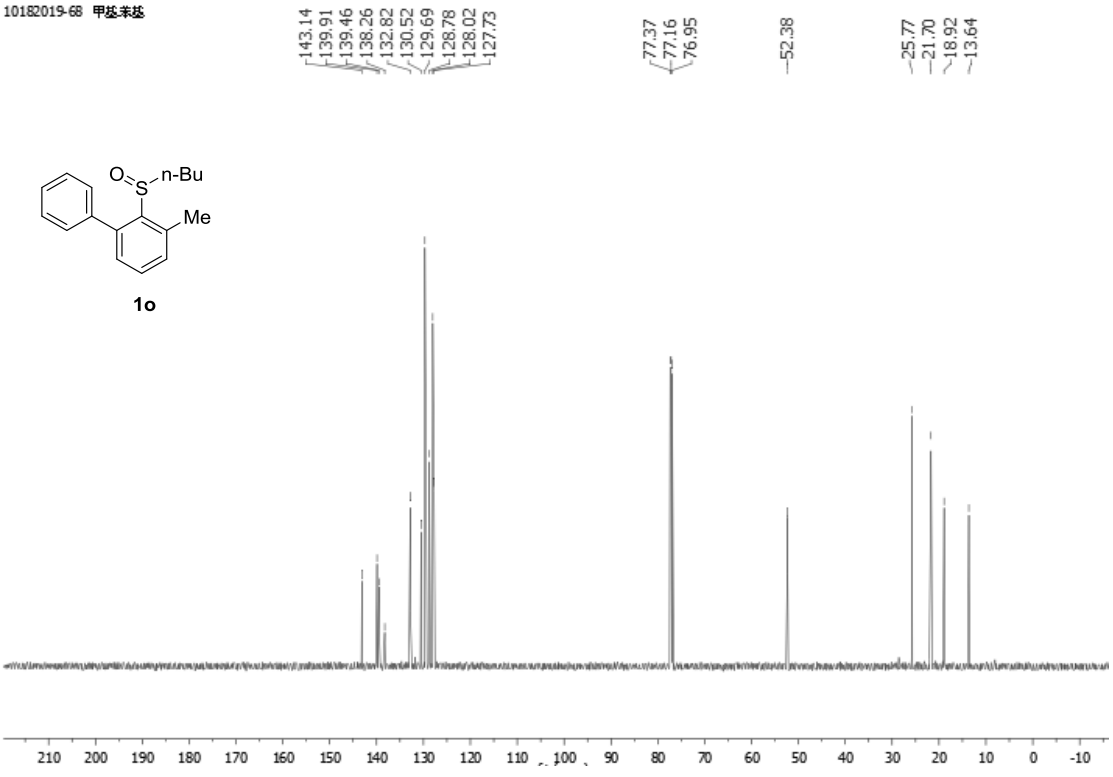

07102019-23 (LWJ-1-03) 二乙基 er yi ji
7.31
7.30
7.26
7.11
7.10
3.38
3.37
3.36
3.35
3.34
3.33
3.07
2.95
2.94
2.93
2.91
2.81
2.80
2.80
2.79
2.78
2.78
2.77
2.76
1.85
1.84
1.84
1.27
1.26
1.24
0.96
0.95
0.94
O
S
n-Bu
Et
Et
1m
1.00
1.92
1.14
2.11
2.18
1.06
2.22
2.32
6.29
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
-0.5
-1.0

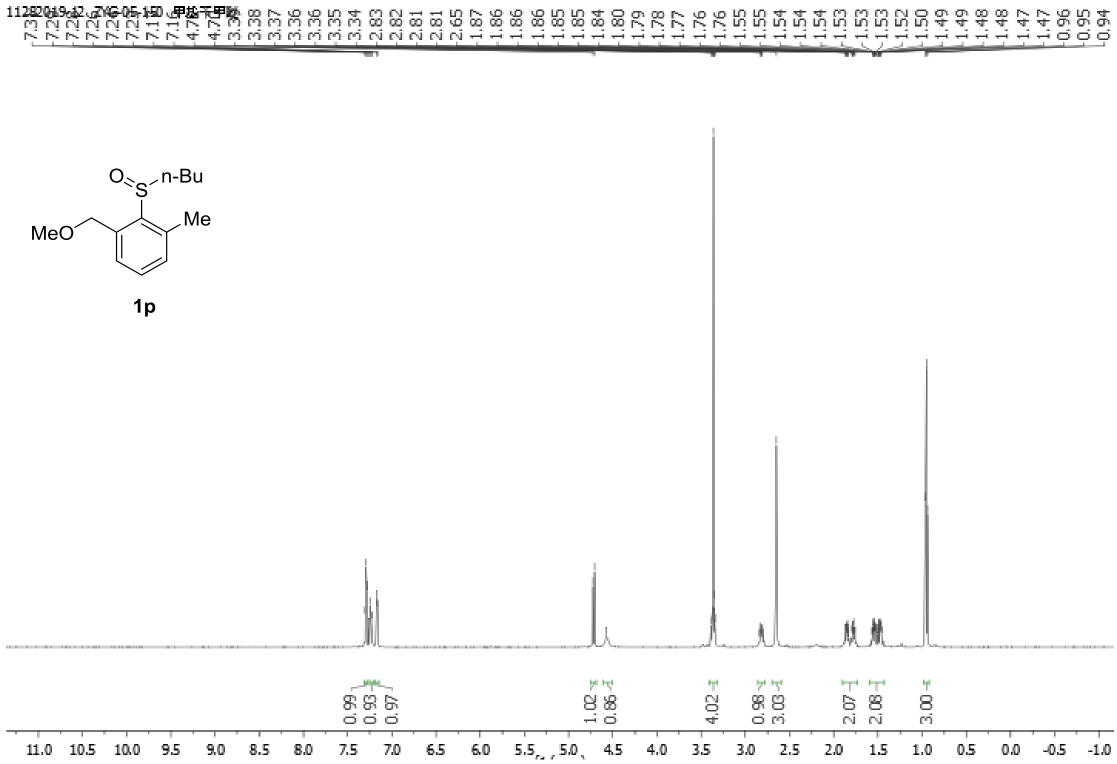

07102019-23 (LWJ-1-03) 二乙基 er yi ji
145.15
138.07
131.32
128.62
77.37
77.16
76.95
53.99
26.29
25.32
22.09
16.42
13.81
O
S
n-Bu
Et
Et
1m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

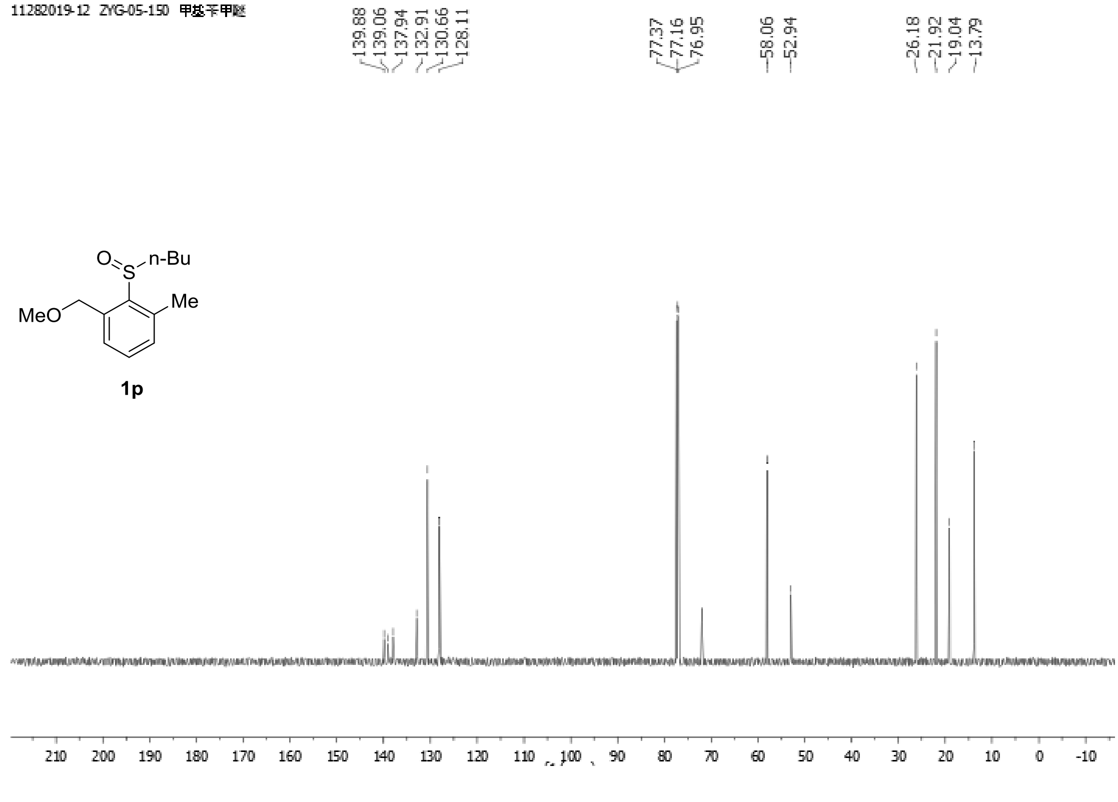

09302019-17
7.29
7.28
7.28
7.27
7.12
7.11
7.08
7.06
3.37
3.36
3.36
3.35
3.34
3.33
3.33
2.99
2.93
2.92
2.91
2.90
2.85
2.66
1.83
1.73
1.72
1.57
1.55
1.54
1.53
1.52
1.50
1.49
1.28
1.27
1.26
0.99
0.97
O
S
n-Bu
Et
Me
1n
1.09
0.97
0.98
0.99
2.88
2.92
2.02
2.06
3.28
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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 -0.5 -1.0

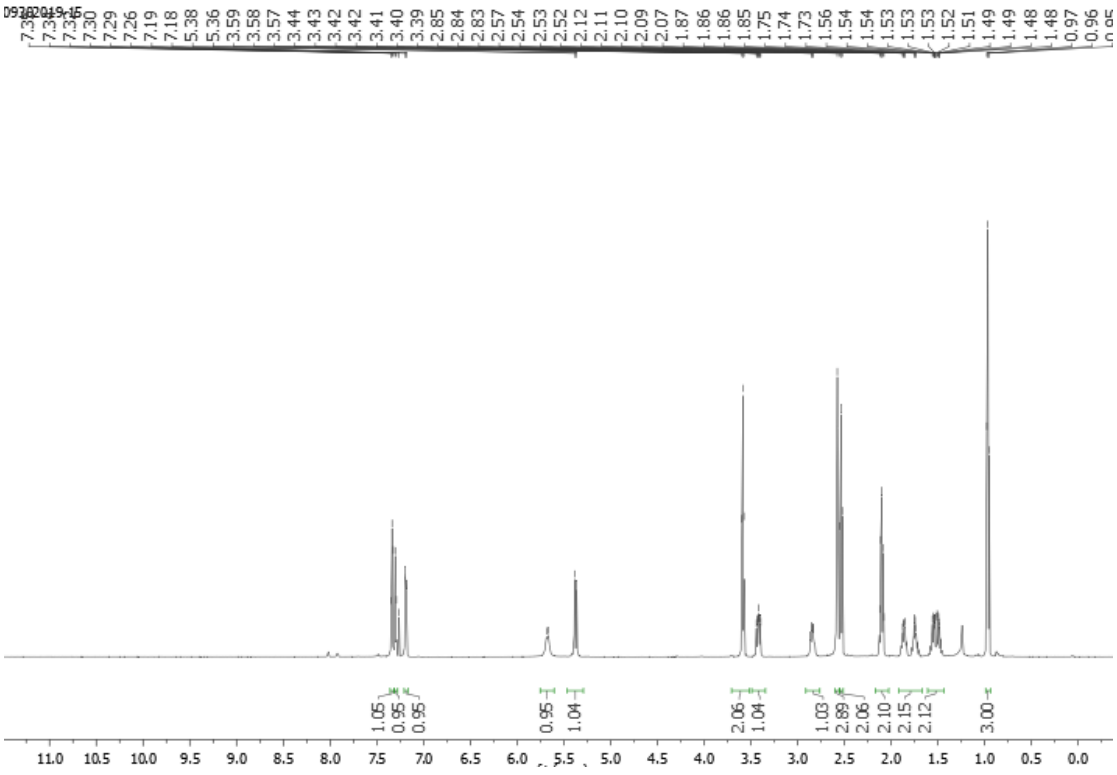

09302019-17
144.79
138.84
131.10
130.62
128.38
77.37
77.16
76.95
26.11
25.57
22.09
19.36
16.48
13.80
O
S
n-Bu
Et
Me
1n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

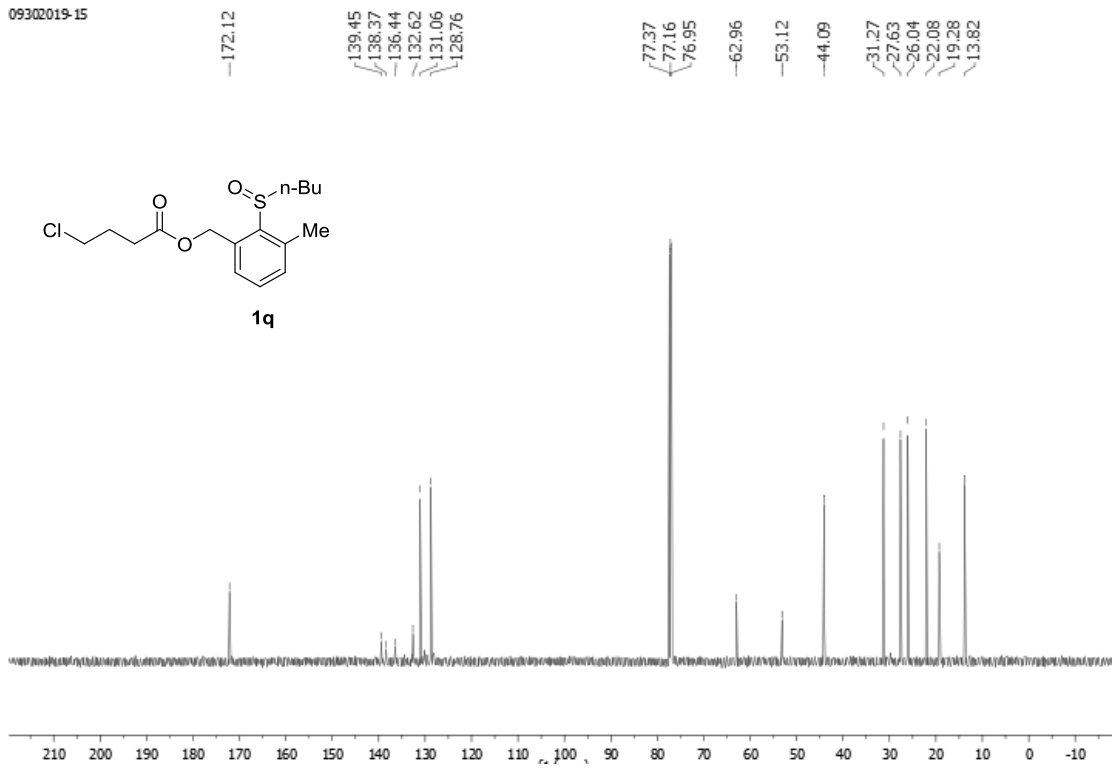

10182019-68 甲基苯基
7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.37 7.28 7.28 7.27 7.12 7.11
3.24 3.23 3.22 3.22 3.22 3.21 3.20 3.19 2.85 2.83 2.82 2.82 2.81 2.81 2.80 2.80 2.78 1.60 1.60 1.59 1.58 1.56 1.54 1.54 1.53 1.35 1.33 1.33 1.32 1.32 1.30 1.28 1.28 1.27
n-Bu
O
S
Me
1o
4.10 3.12 0.98 1.01 2.88 1.14 2.20 2.34 3.00
10.5 10.0 9.5 9.0 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 -0.5 -1.0


10182019-68 甲基苯基
143.14 139.91 139.46 138.26 132.82 130.52 129.69 128.78 128.02 127.73
77.37 77.16 76.95
52.38
25.77 21.70 18.92 13.64
n-Bu
O
S
Me
1o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


11282019-12 ZYG-05-150
7.30 7.29 7.26 7.26 7.24 7.22 7.16 7.16 4.71 4.70 3.38 3.37 3.36 3.35 3.35 3.34 2.83 2.82 2.81 2.81 2.65 1.87 1.86 1.86 1.86 1.85 1.85 1.84 1.80 1.79 1.78 1.77 1.76 1.76 1.55 1.55 1.54 1.54 1.54 1.53 1.53 1.53 1.52 1.50 1.49 1.49 1.48 1.48 1.47 1.47 0.96 0.95 0.94
O
S
n-Bu
Me
MeO
1p
0.99 0.93 0.97 1.02 0.86 4.02 0.98 3.03 2.07 2.08 3.00
11.0 10.5 10.0 9.5 9.0 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 -0.5 -1.0

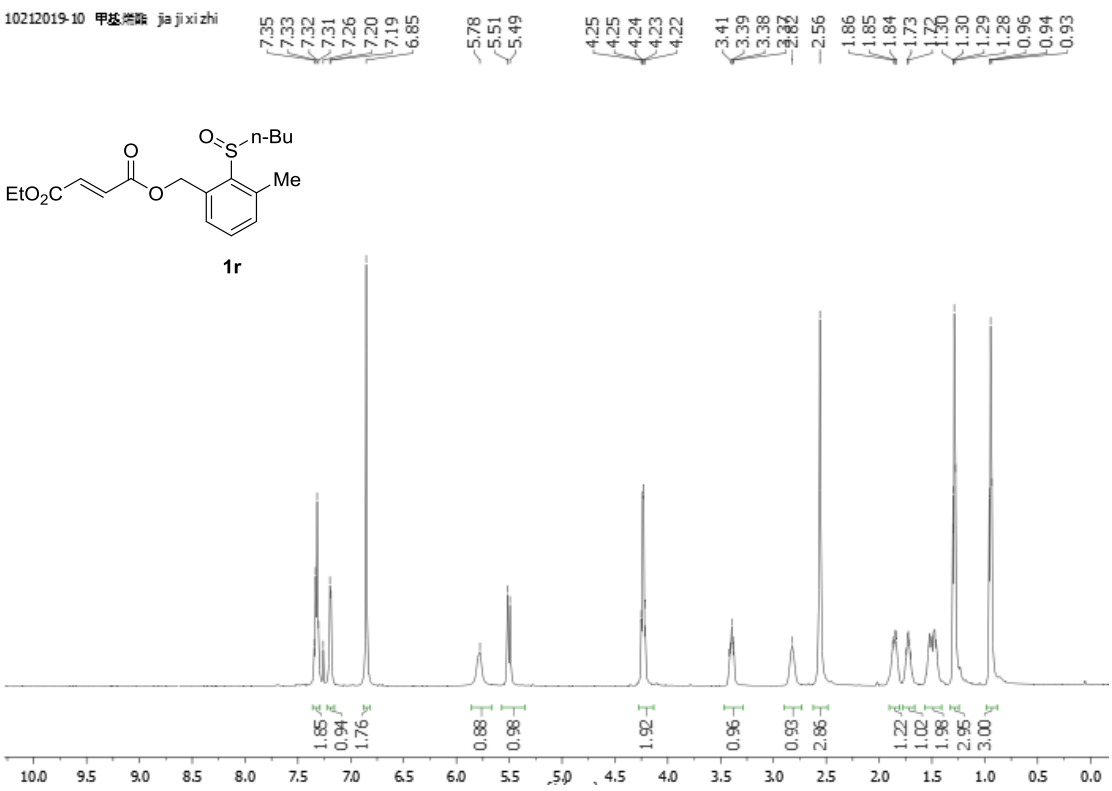

11282019-12 ZYG-05-150 甲基苄甲醚
139.88 139.06 137.94 132.91 130.66 128.11
77.37 77.16 76.95
58.06 52.94
26.18 21.92 19.04 13.79
O
S
n-Bu
Me
MeO
1p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10





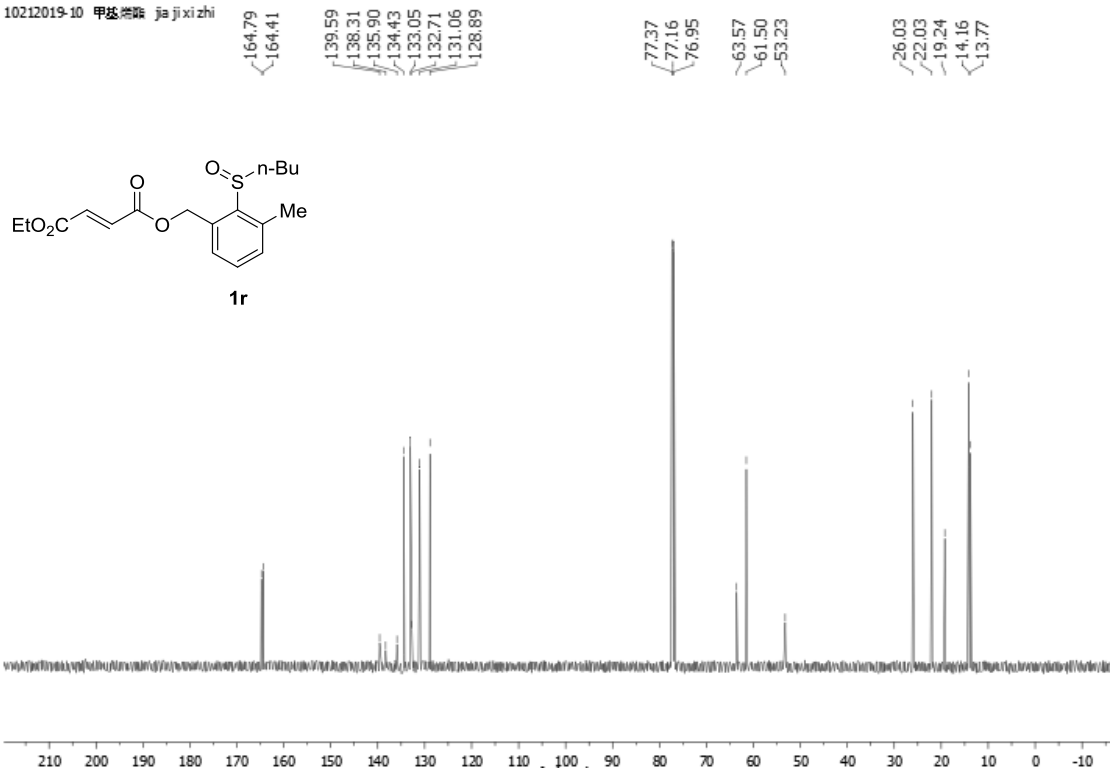
1q

10212019-10 甲基苯酯 jia ji xi zhi

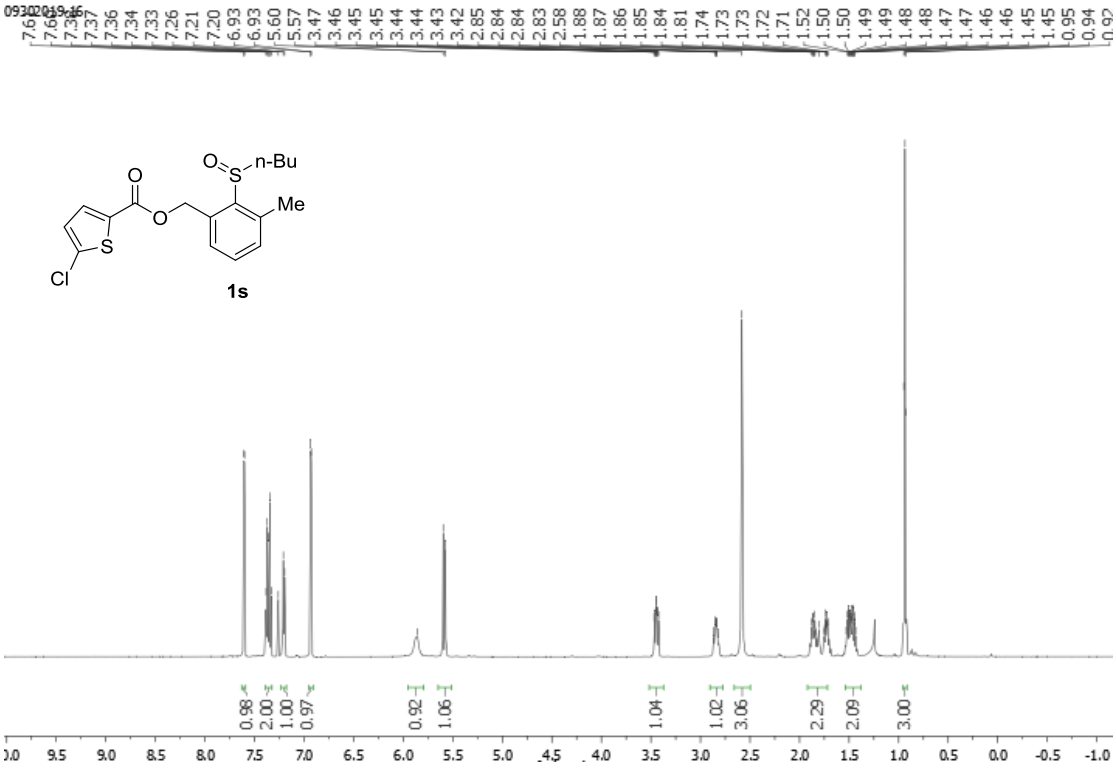


1r

10212019-10 甲基苯酯 jia ji xi zhi



1r


09302019-16
7.61
7.60
7.38
7.37
7.36
7.34
7.33
7.26
7.21
7.20
6.93
6.93
5.60
5.57
3.47
3.46
3.45
3.45
3.44
3.44
3.43
3.42
2.85
2.84
2.84
2.83
2.58
1.88
1.87
1.86
1.85
1.84
1.81
1.74
1.73
1.73
1.72
1.71
1.52
1.50
1.50
1.49
1.49
1.48
1.48
1.47
1.47
1.46
1.46
1.45
1.45
0.95
0.94
0.92
O
O
S
n-Bu
Me
O
S
Cl
1s
0.98
2.00
1.00
0.97
0.92
1.06
1.04
1.02
3.06
2.29
2.09
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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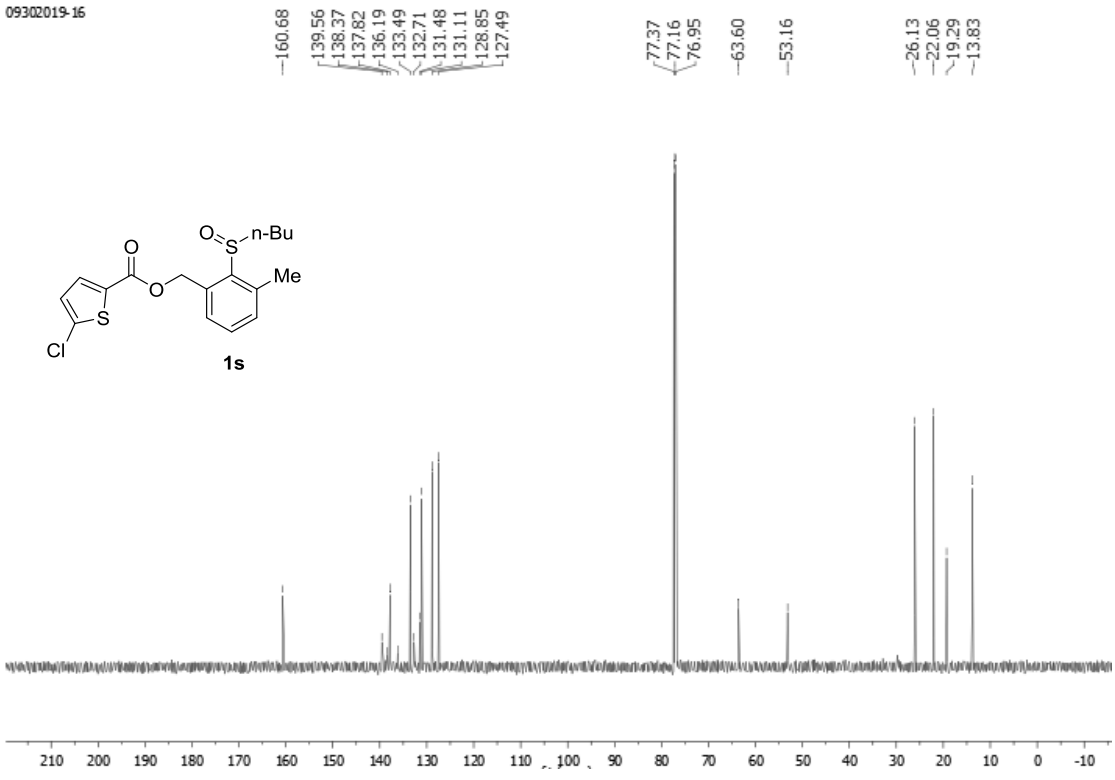
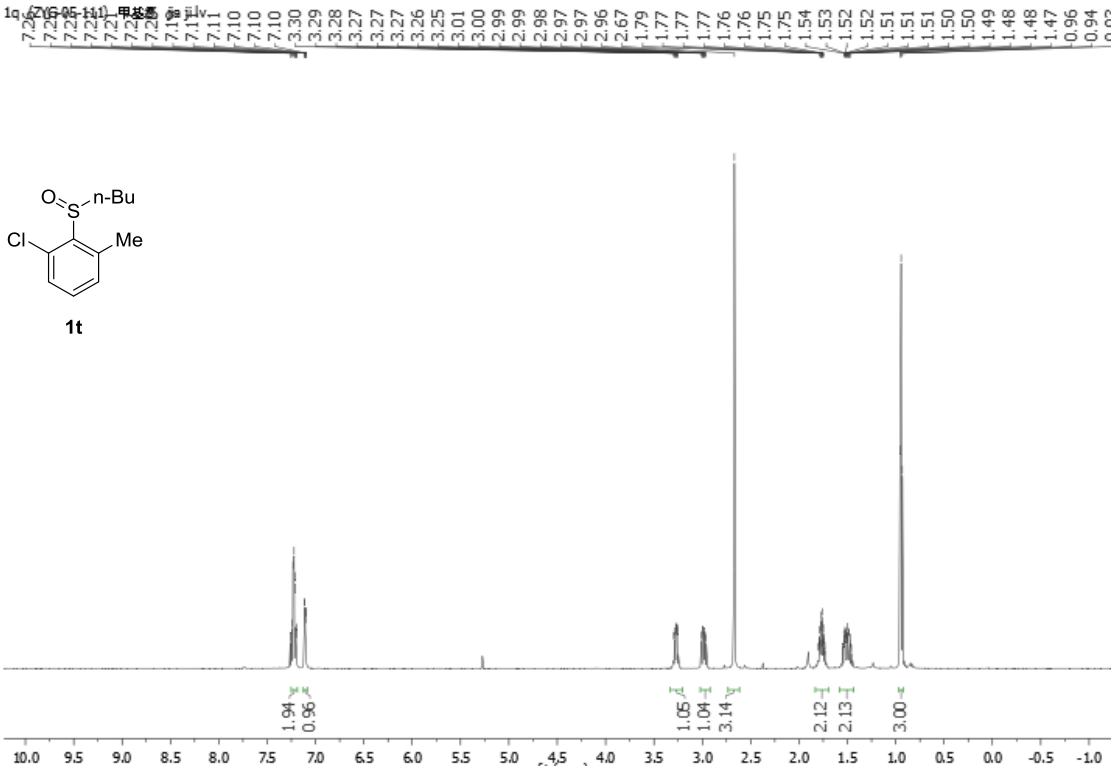
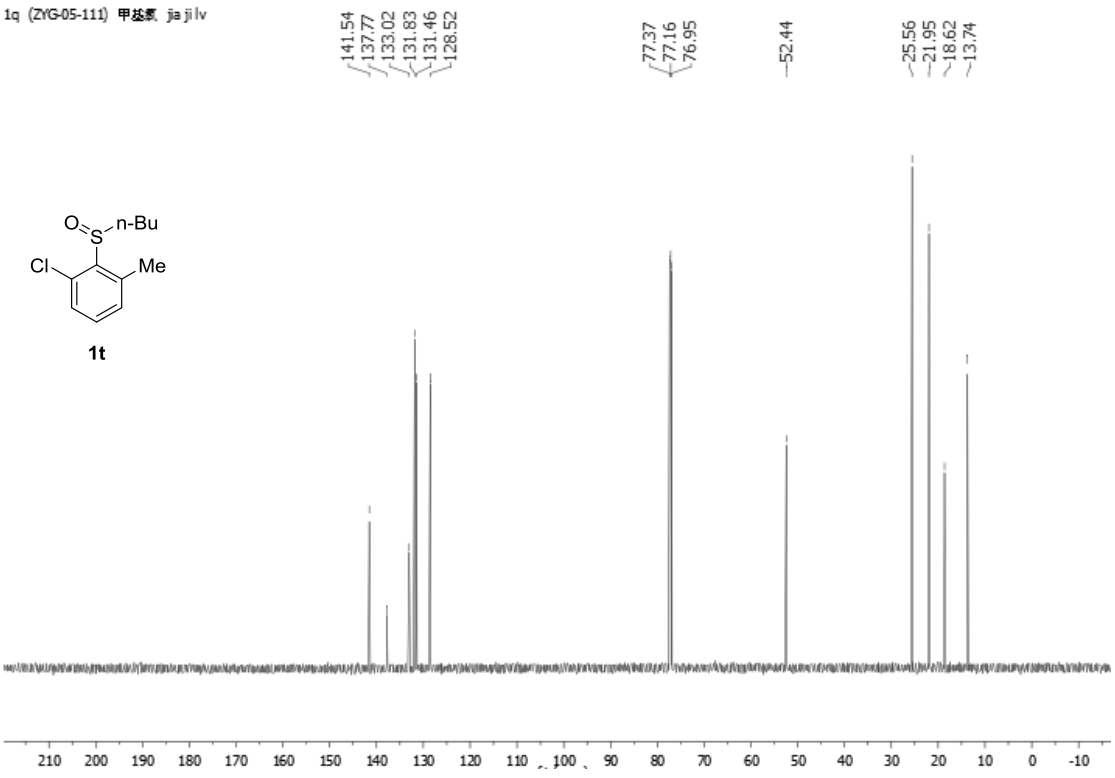
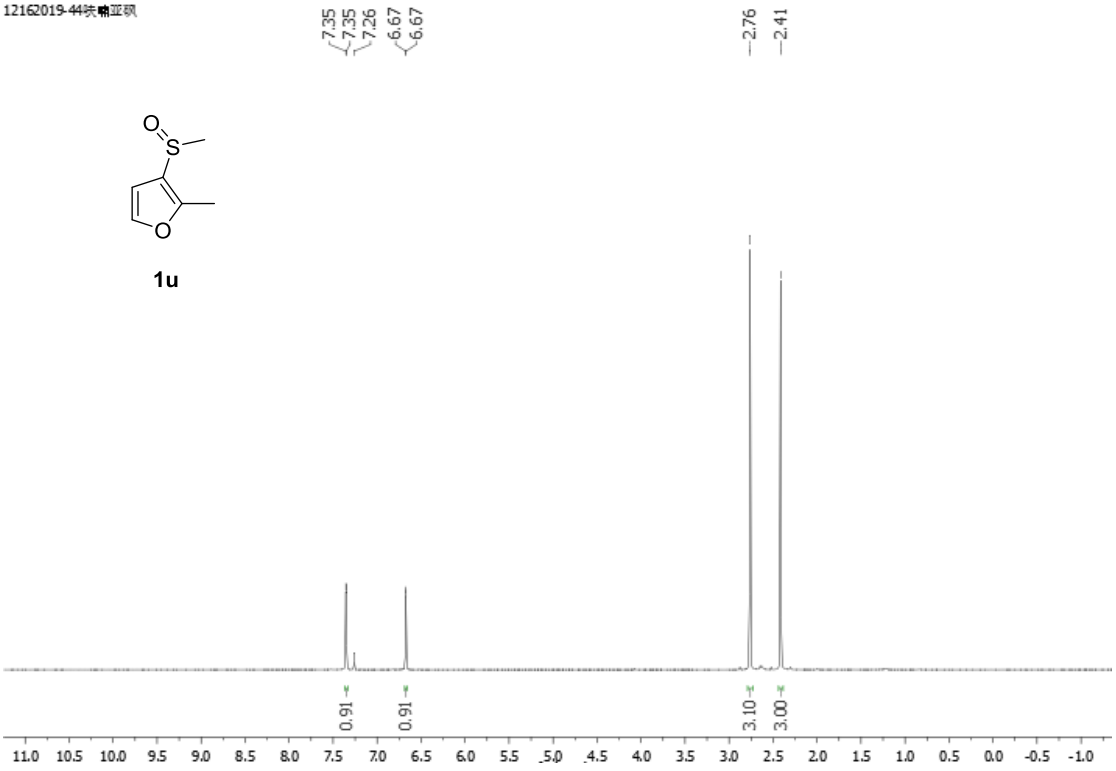
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


09302019-16
160.68
139.56
138.37
137.82
136.19
133.49
132.71
131.48
131.11
128.85
127.49
77.37
77.16
76.95
63.60
53.16
26.13
22.06
19.29
13.83
O
O
S
n-Bu
Me
O
S
Cl
1s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


1q (ZYG-05-111) 甲基素 jia ji lv
n-Bu
Cl
Me
1t
1.94
0.96
1.05
1.04
3.14
2.12
2.13
3.00

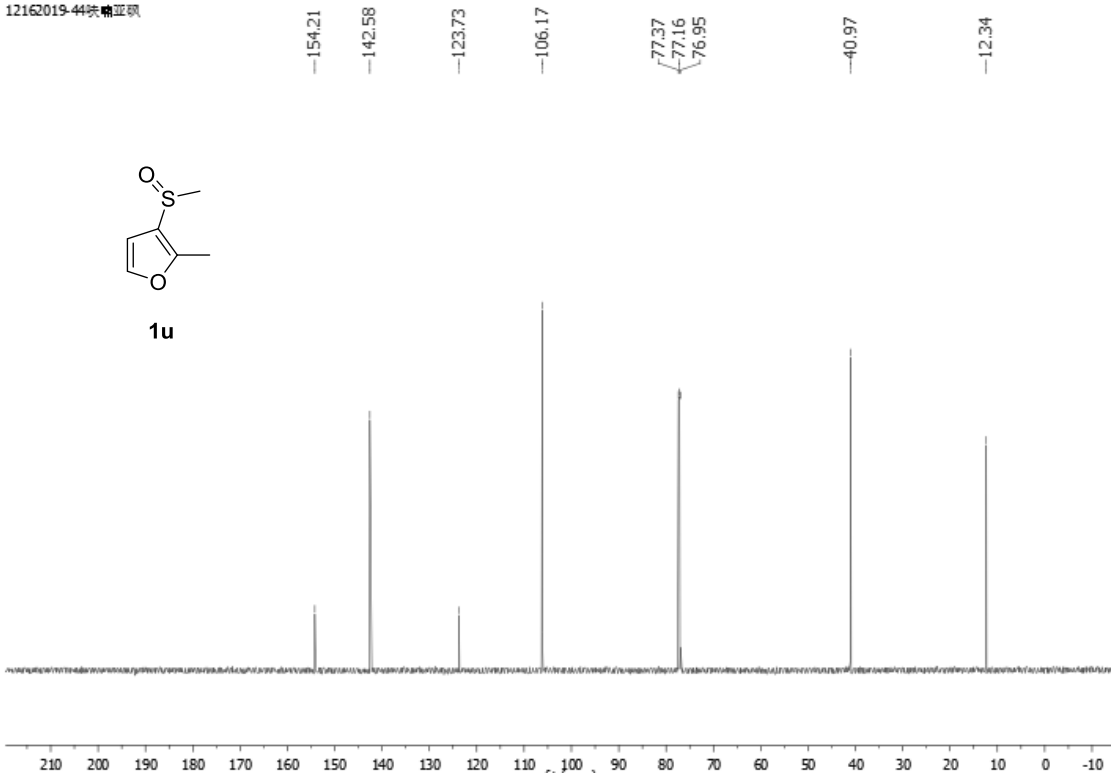

1q (ZYG-05-111) 甲基素 jia ji lv
141.54
137.77
133.02
131.83
131.46
128.52
77.37
77.16
76.95
52.44
25.56
21.95
18.62
13.74
n-Bu
Cl
Me
1t

12162019-44铁硝亚砜



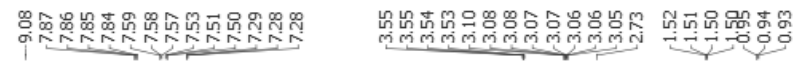
1u

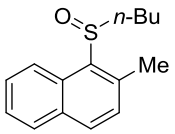
12162019-44铁硝亚砜



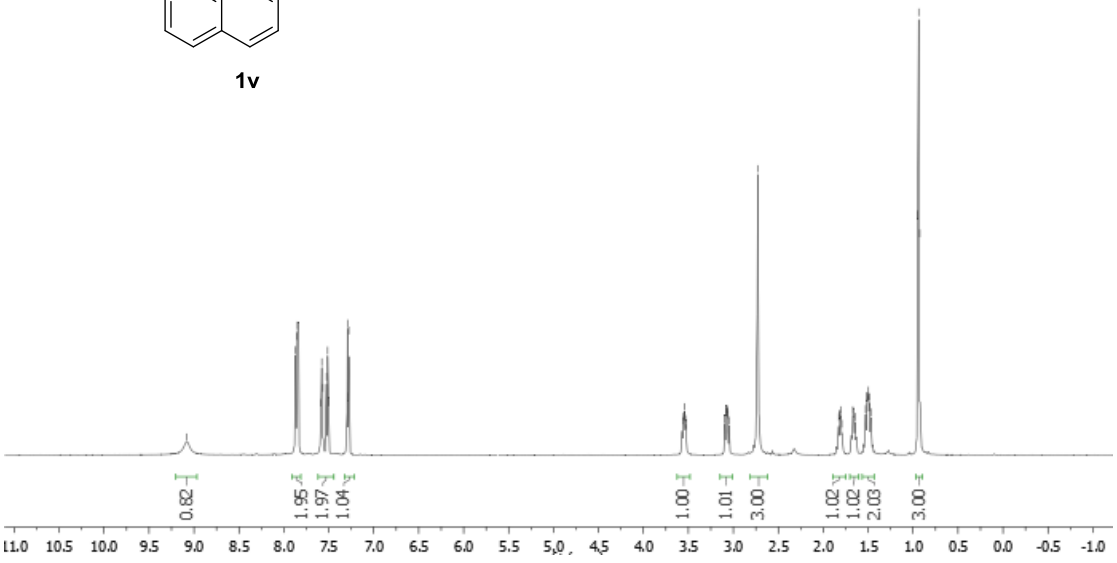
1u

12162019-45苯亚砜

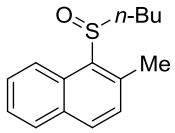




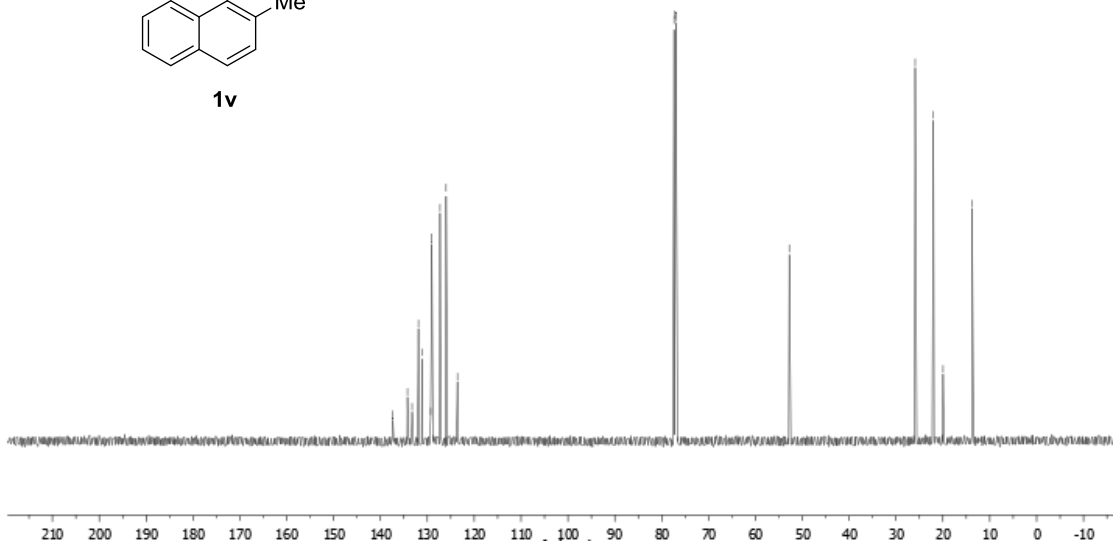
1v

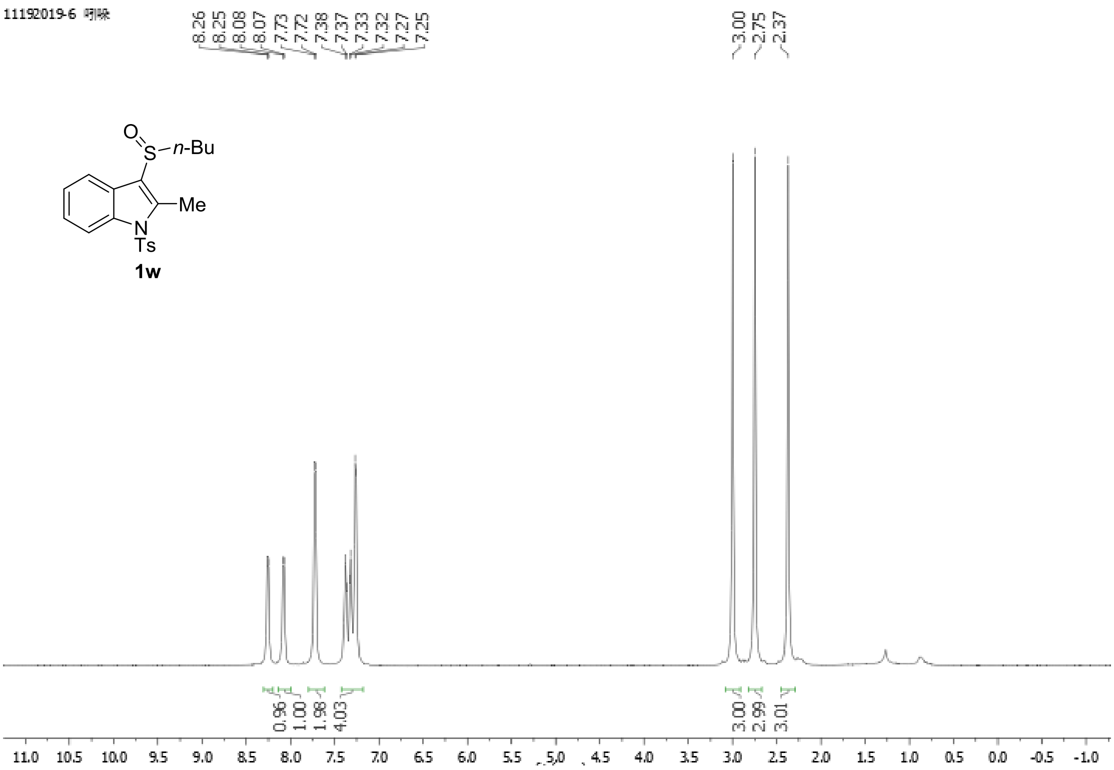


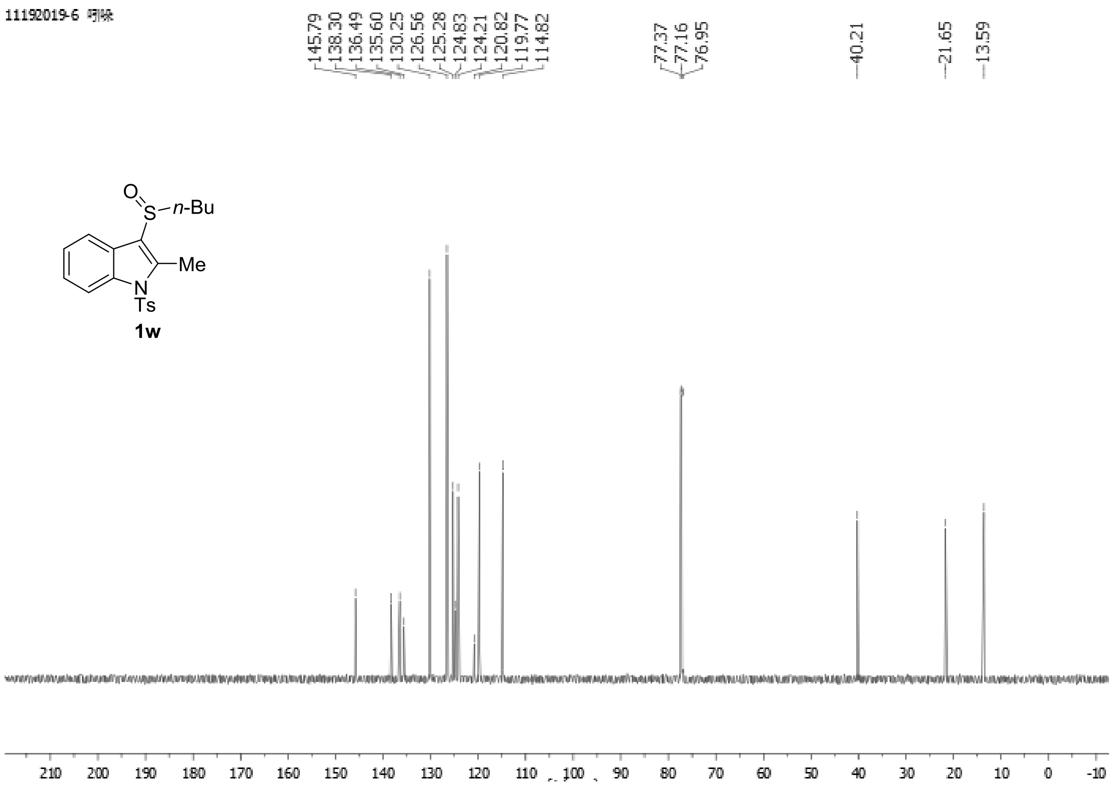
12162019-45苯亚砜



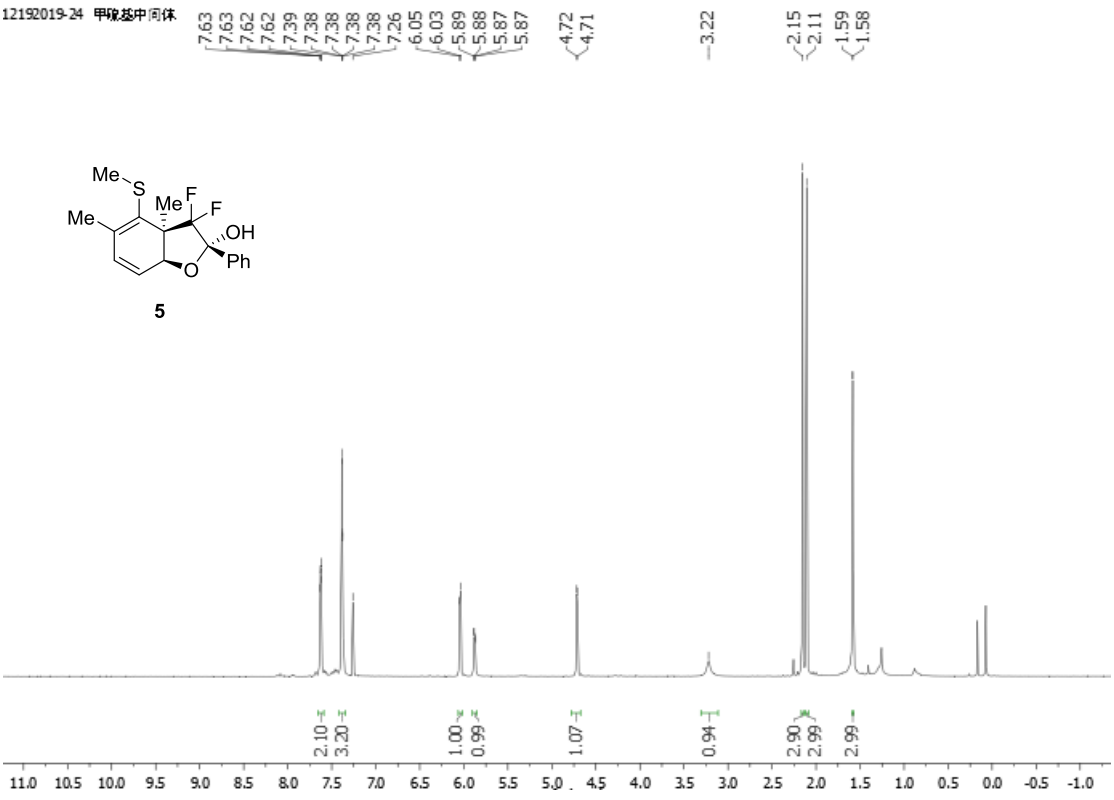
1v




11192019-6 吲哚
8.26 8.25 8.08 8.07 7.73 7.72 7.38 7.37 7.33 7.32 7.27 7.25
3.00 2.75 2.37
O
S
n-Bu
Me
N
Ts
1w
0.96 1.00 1.98 4.03
3.00 2.99 3.01
11.0 10.5 10.0 9.5 9.0 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 -0.5 -1.0

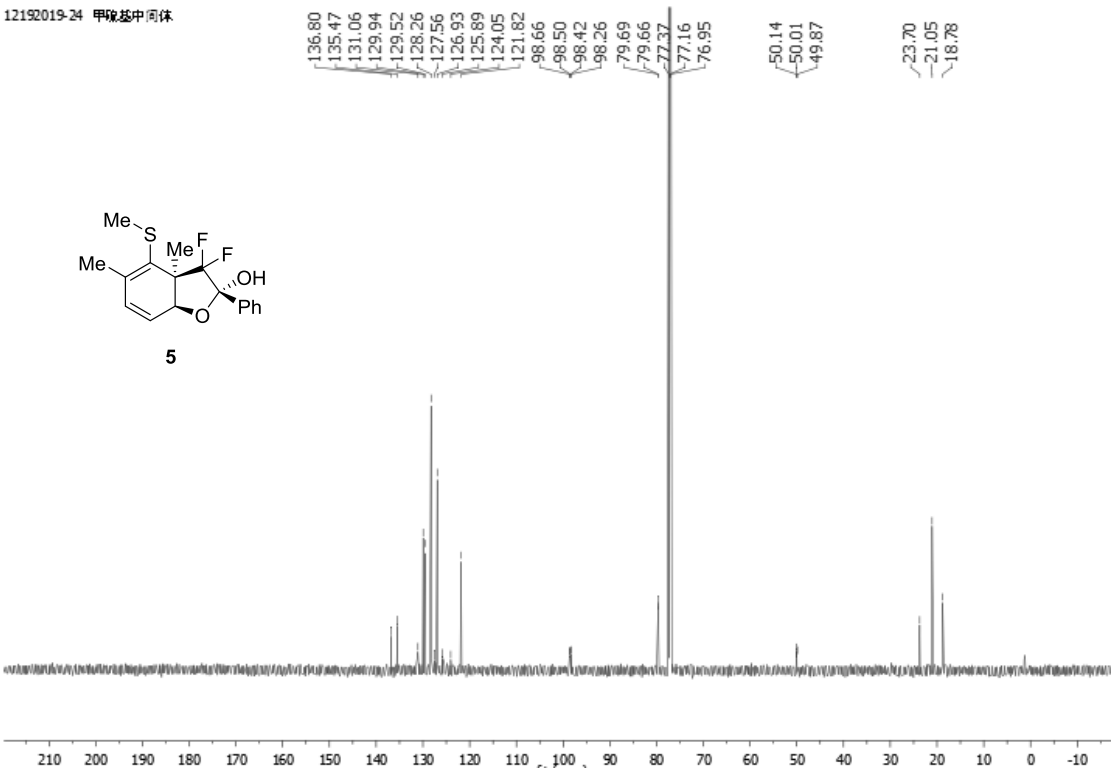

11192019-6 吲哚
145.79 138.30 136.49 135.60 130.25 126.56 125.28 124.83 124.21 120.82 119.77 114.82
77.37 77.16 76.95
40.21
21.65
13.59
O
S
n-Bu
Me
N
Ts
1w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

12192019-24 甲硫基中间体



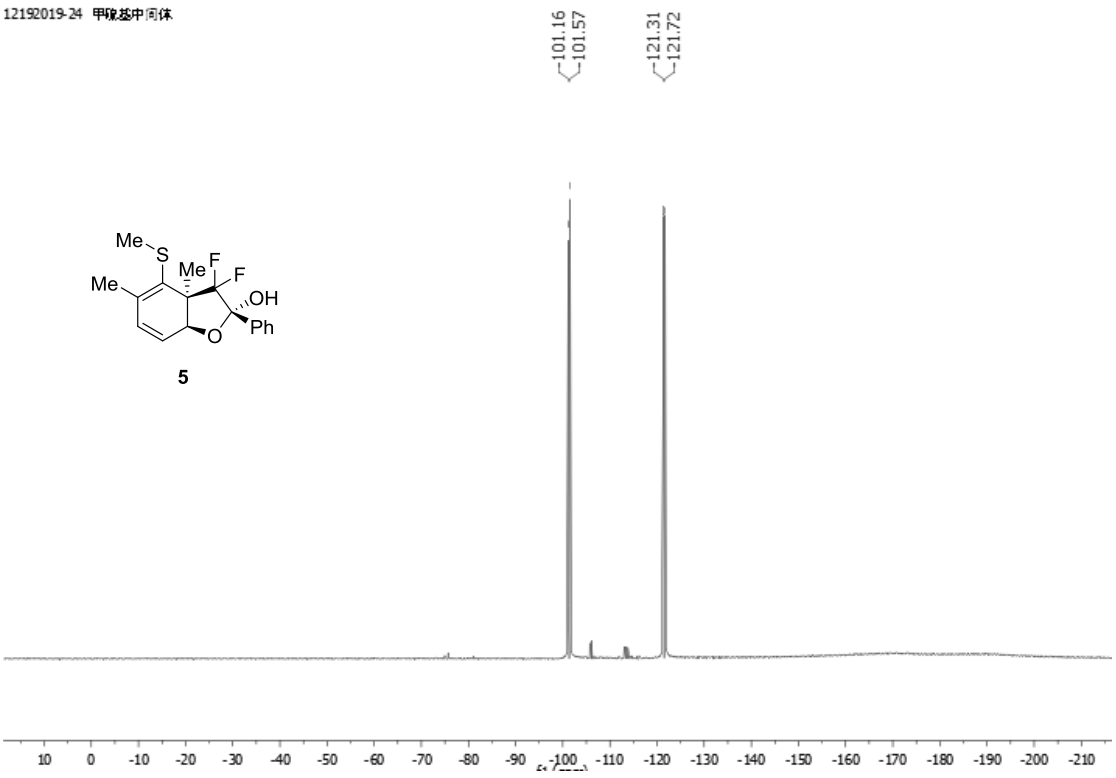
5

12192019-24 甲硫基中间体



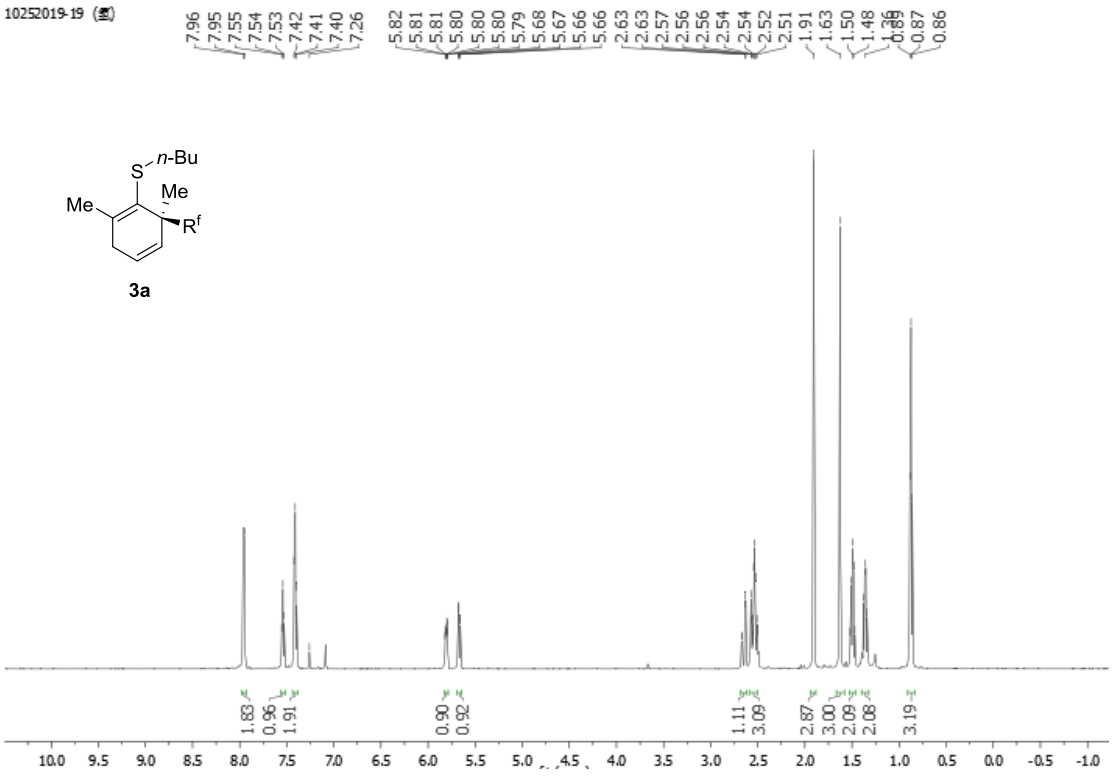
5

12192019-24 甲氧基中间体

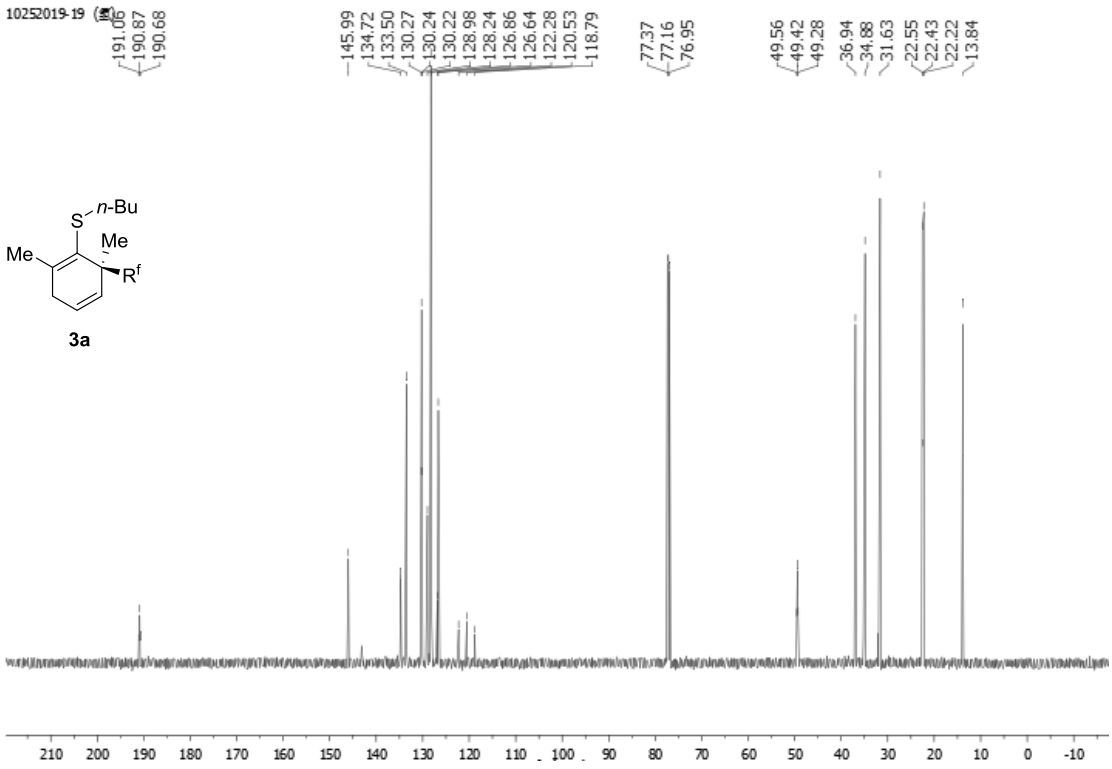


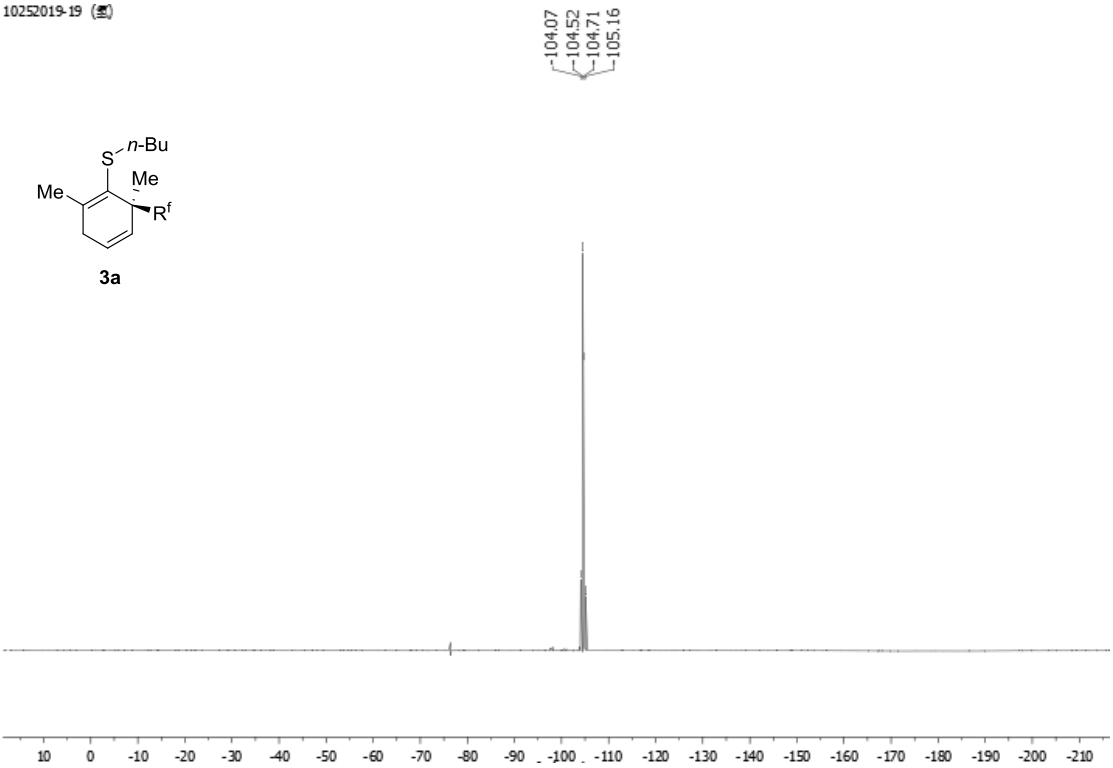
5

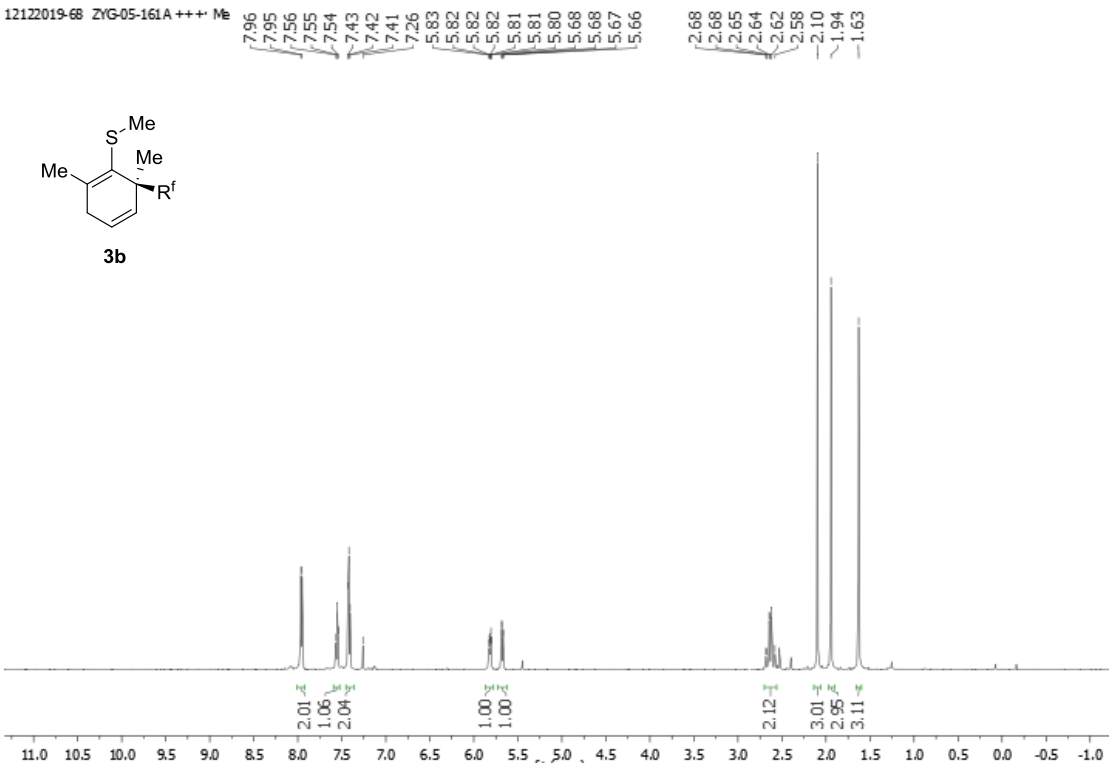
10252019-19 (氢)

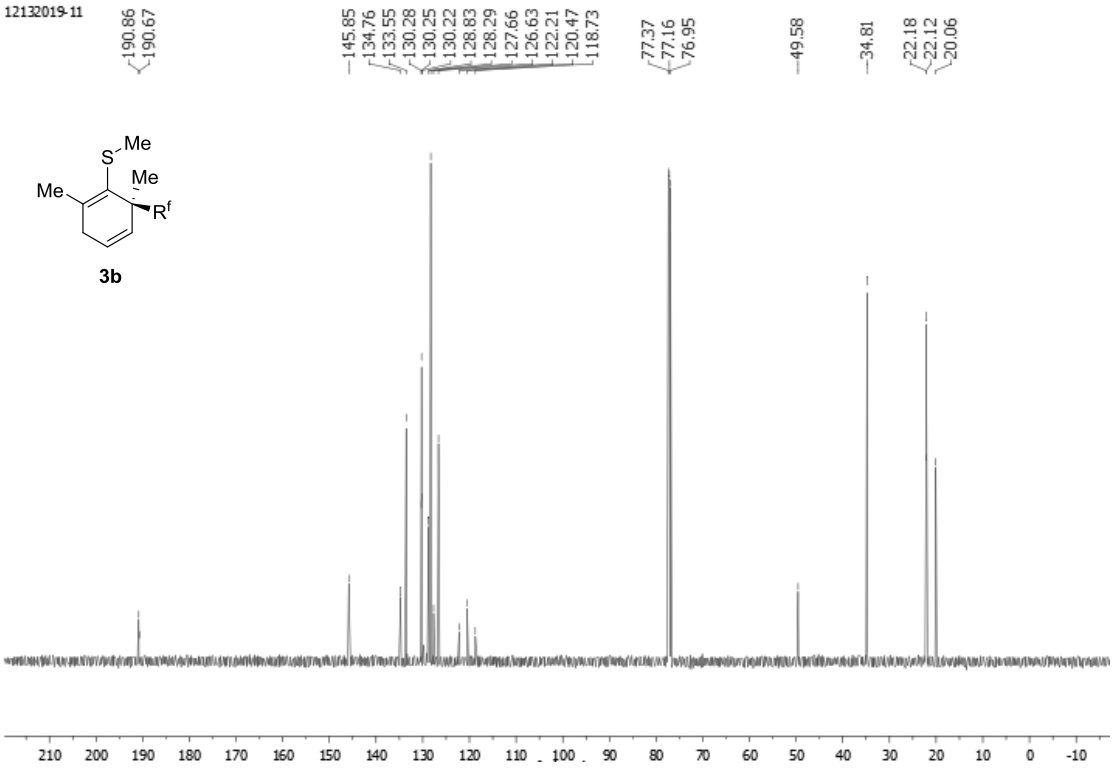


3a

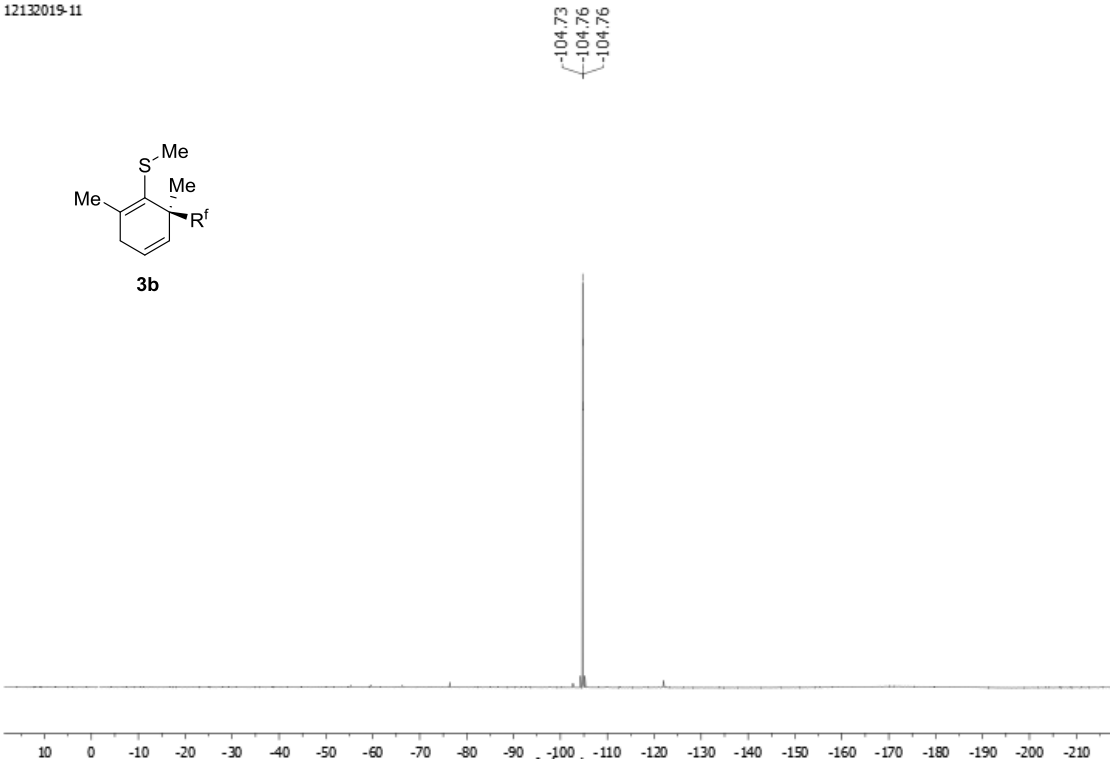

10252019-19 (
191.06
190.87
190.68
145.99
134.72
133.50
130.27
130.24
130.22
128.98
128.24
126.86
126.64
122.28
120.53
118.79
77.37
77.16
76.95
49.56
49.42
49.28
36.94
34.88
31.63
22.55
22.43
22.22
13.84
n-Bu
S
Me
Me
Rf
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


10252019-19 (
104.07
104.52
104.71
105.16
n-Bu
S
Me
Me
Rf
3a
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

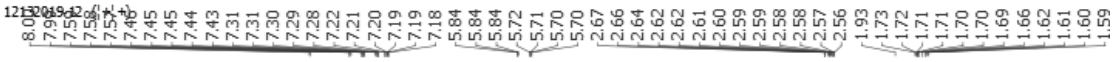

12122019-6B ZYG-05-161A +++ Me
7.96
7.95
7.56
7.55
7.54
7.43
7.42
7.41
7.26
5.83
5.82
5.82
5.82
5.81
5.81
5.80
5.68
5.68
5.67
5.66
2.68
2.68
2.65
2.64
2.62
2.58
2.10
1.94
1.63
Me
S
Me
Me
Rf
3b
2.01
1.06
2.04
1.00
1.00
2.12
3.01
2.95
3.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

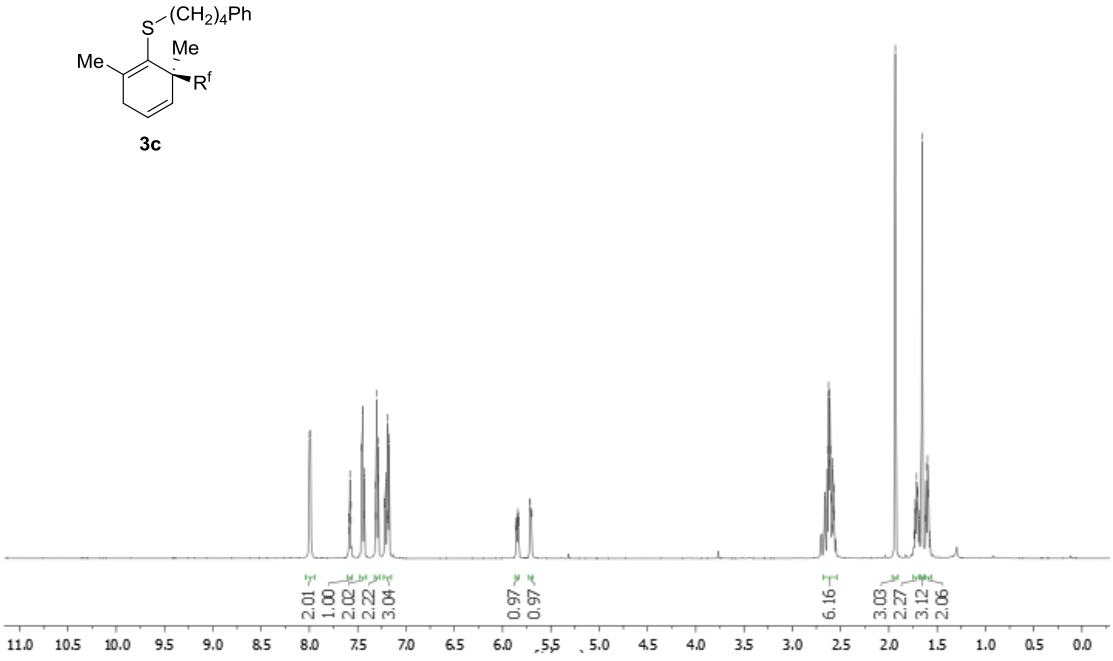

12132019-11
190.86
190.67
145.85
134.76
133.55
130.28
130.25
130.22
128.83
128.29
127.66
126.63
122.21
120.47
118.73
77.37
77.16
76.95
49.58
34.81
22.18
22.12
20.06
Me
S
Me
Me
Rf
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

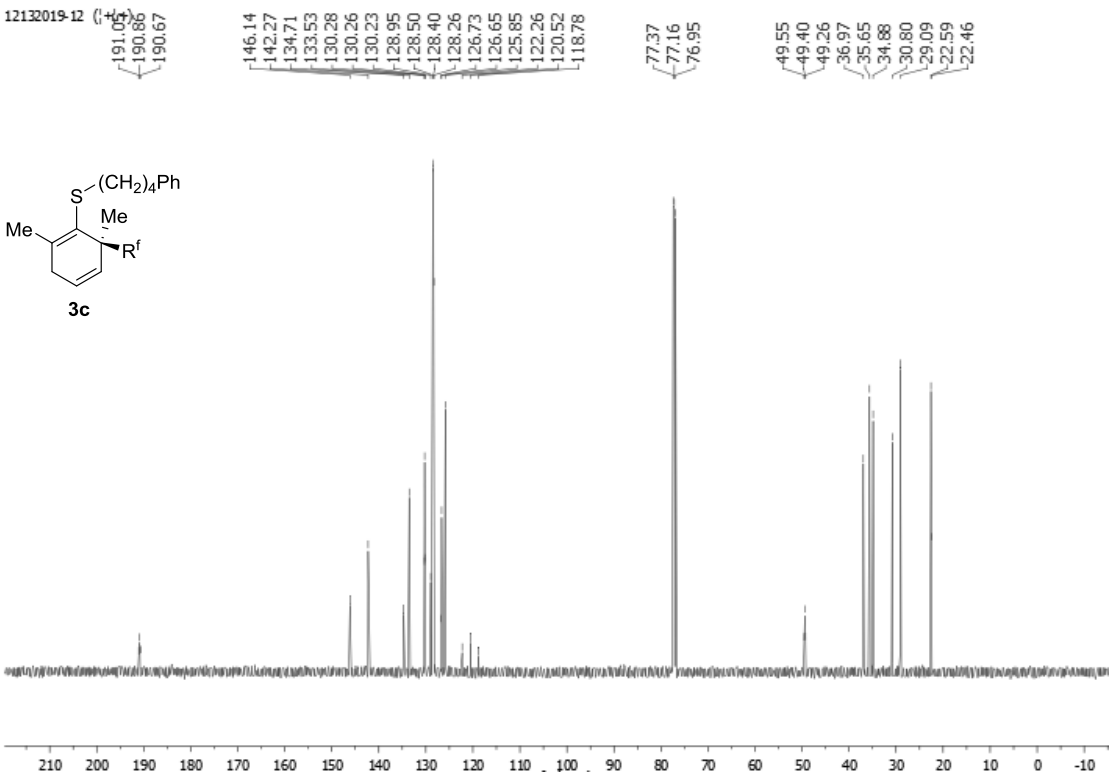
12132019-11

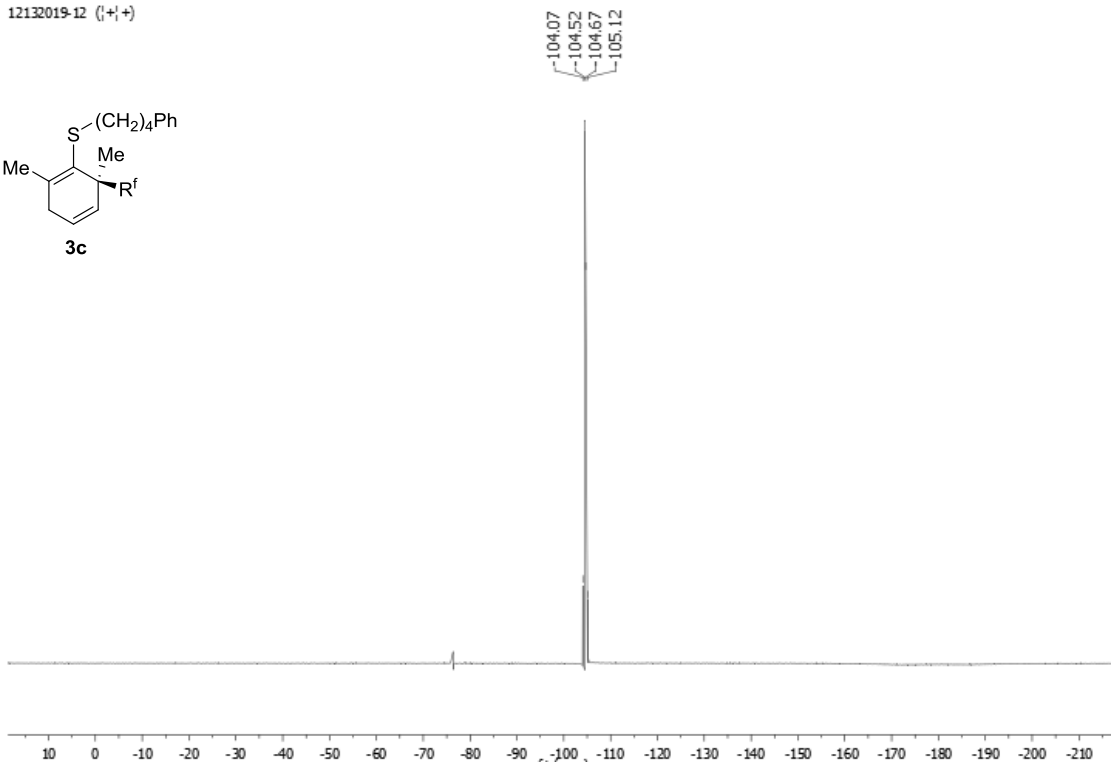


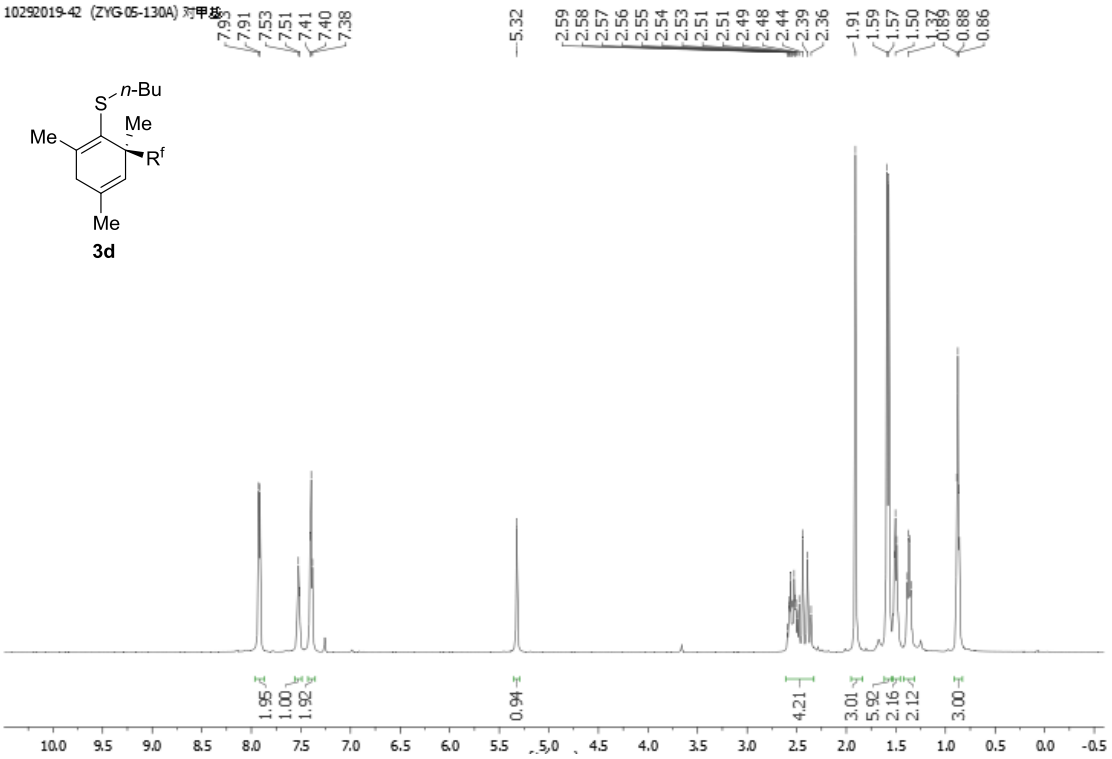
12132019-12



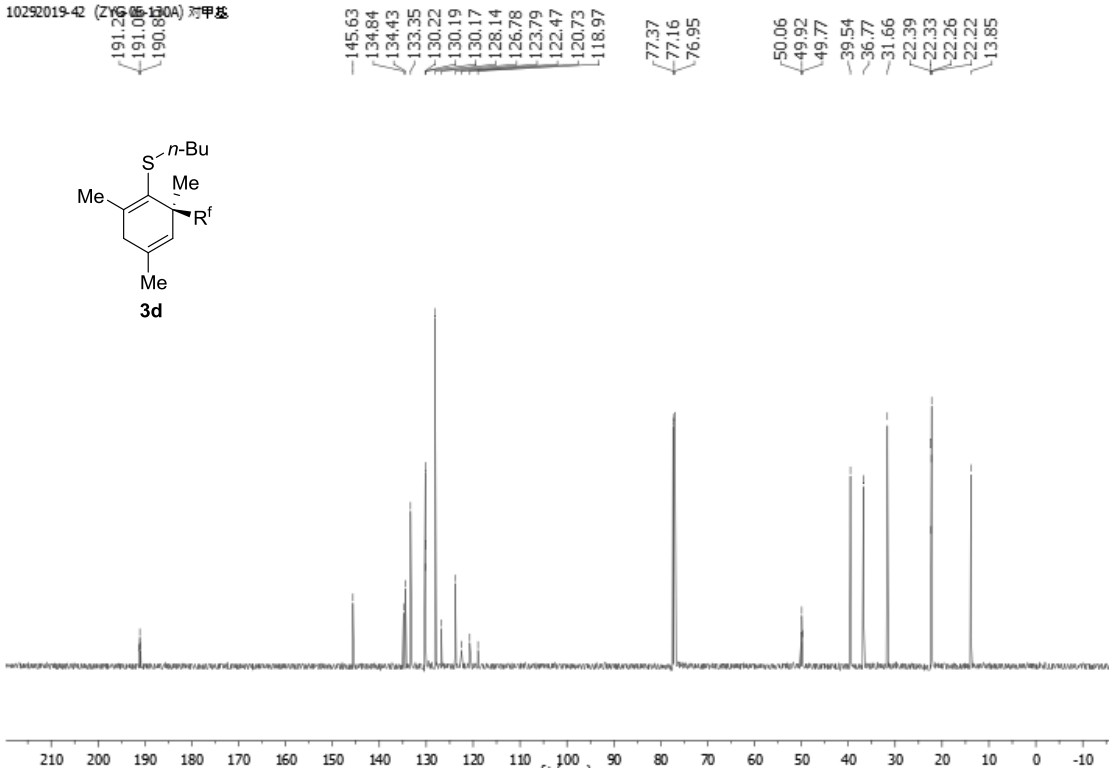



12132019-12 (1+/+)
191.05
190.86
190.67
146.14
142.27
134.71
133.53
130.28
130.26
130.23
128.95
128.50
128.40
128.26
126.73
126.65
125.85
122.26
120.52
118.78
77.37
77.16
76.95
49.55
49.40
49.26
36.97
35.65
34.88
30.80
29.09
22.59
22.46
S
(CH2)4Ph
Me
Me
Rf
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

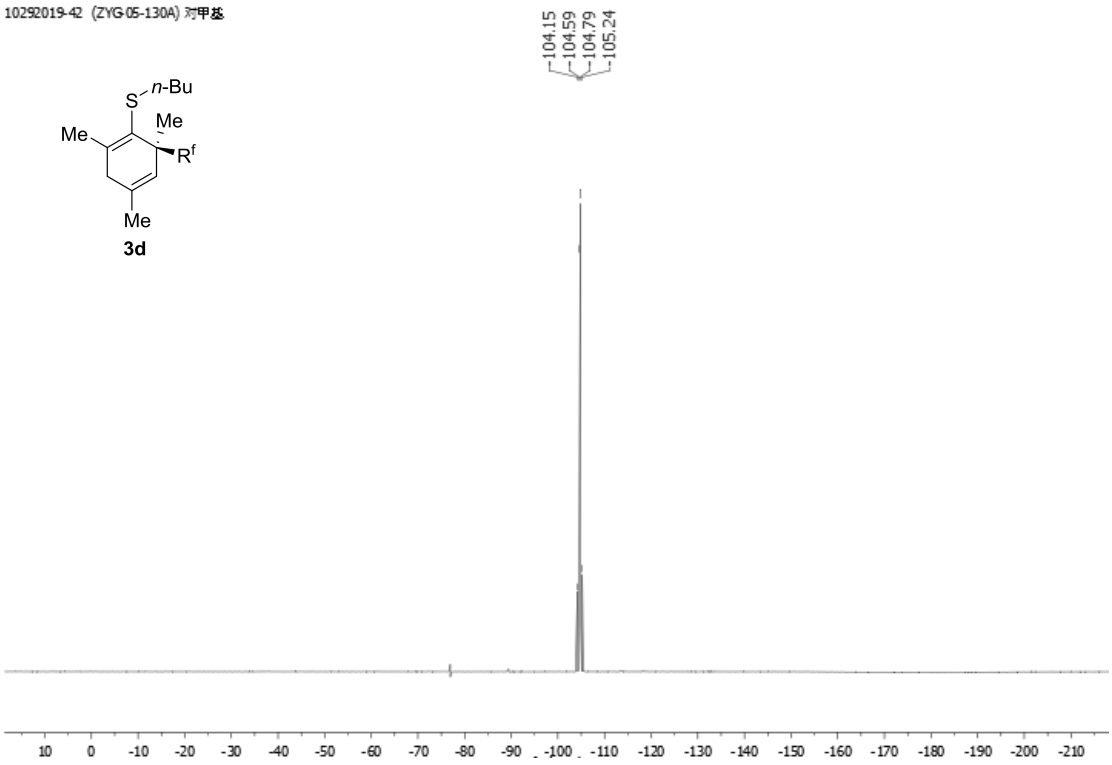

12132019-12 (1+/+)
104.07
104.52
104.67
105.12
S
(CH2)4Ph
Me
Me
Rf
3c
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


10292019-42 (ZYG-05-130A) 对甲基
7.93
7.91
7.53
7.51
7.41
7.40
7.38
5.32
2.59
2.58
2.57
2.56
2.55
2.54
2.53
2.51
2.51
2.49
2.48
2.44
2.39
2.36
1.91
1.59
1.57
1.50
1.37
0.89
0.88
0.86
S
n-Bu
Me
Me
R^f
Me
1.95
1.00
1.92
0.94
4.21
3.01
5.92
2.16
2.12
3.00
10.0
9.5
9.0
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
-0.5

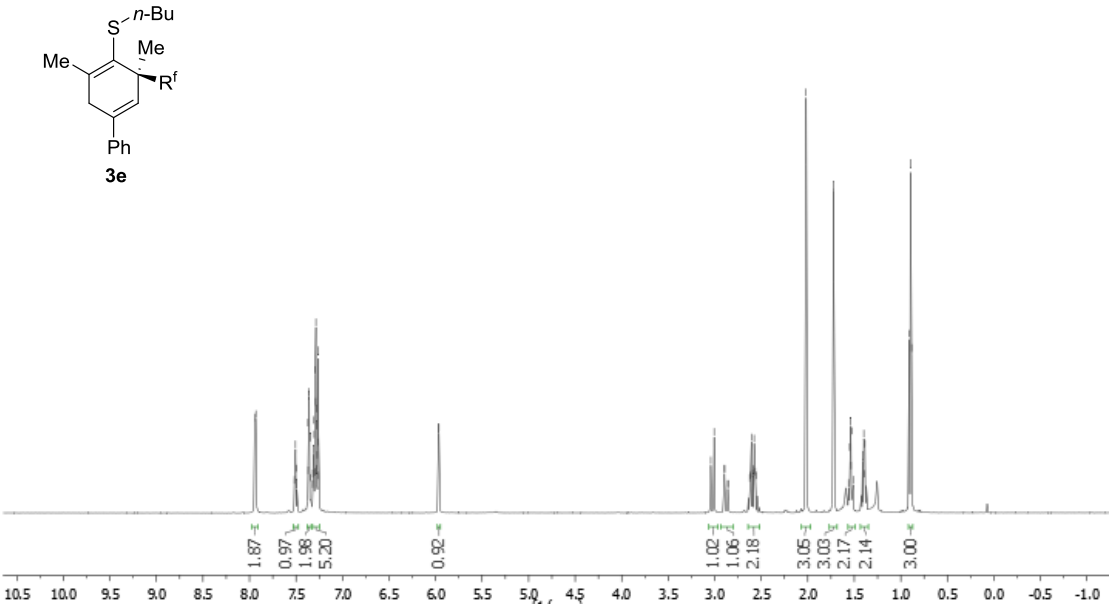
3d

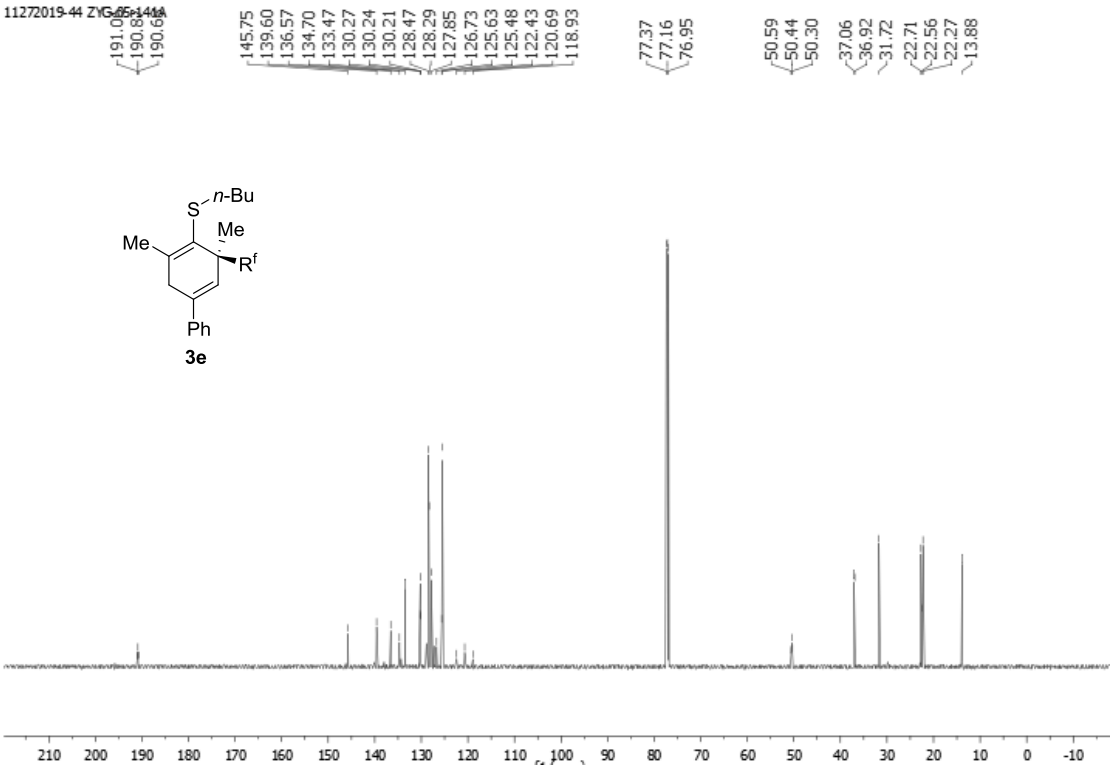

10292019-42 (ZYG-05-130A) 对甲基
191.24
191.06
190.88
145.63
134.84
134.43
133.35
130.22
130.19
130.17
128.14
126.78
123.79
122.47
120.73
118.97
77.37
77.16
76.95
50.06
49.92
49.77
39.54
36.77
31.66
22.39
22.33
22.26
22.22
13.85
S
n-Bu
Me
Me
R^f
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

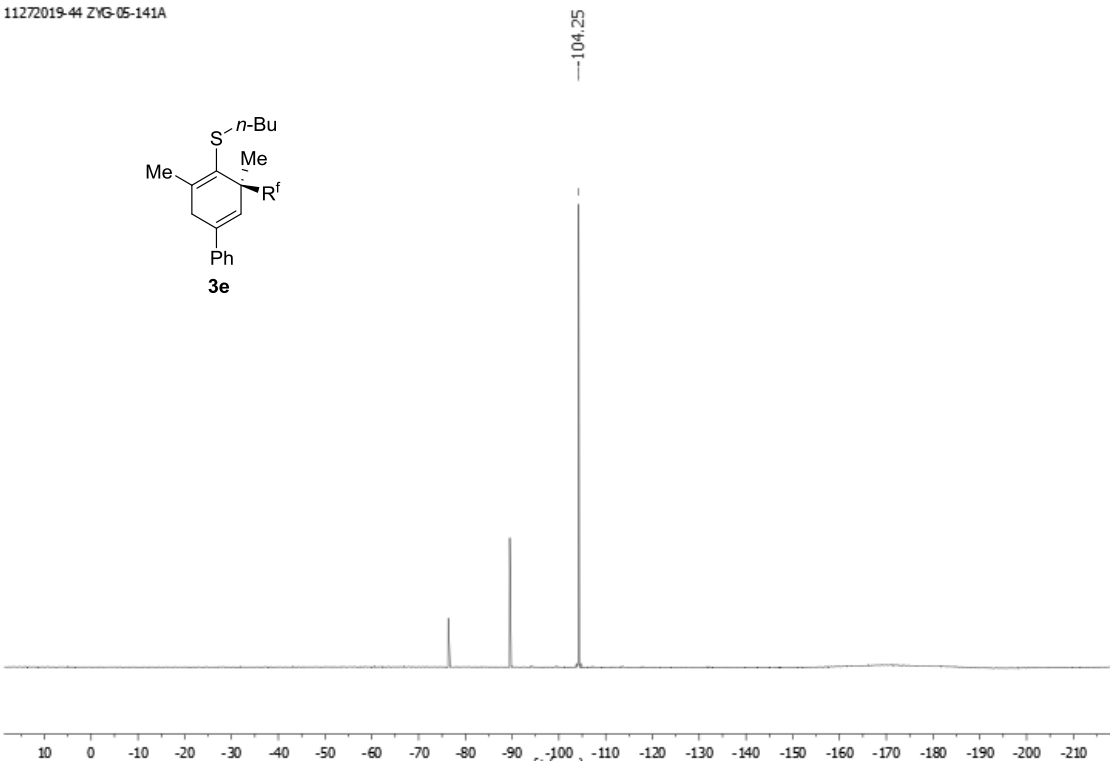
3d

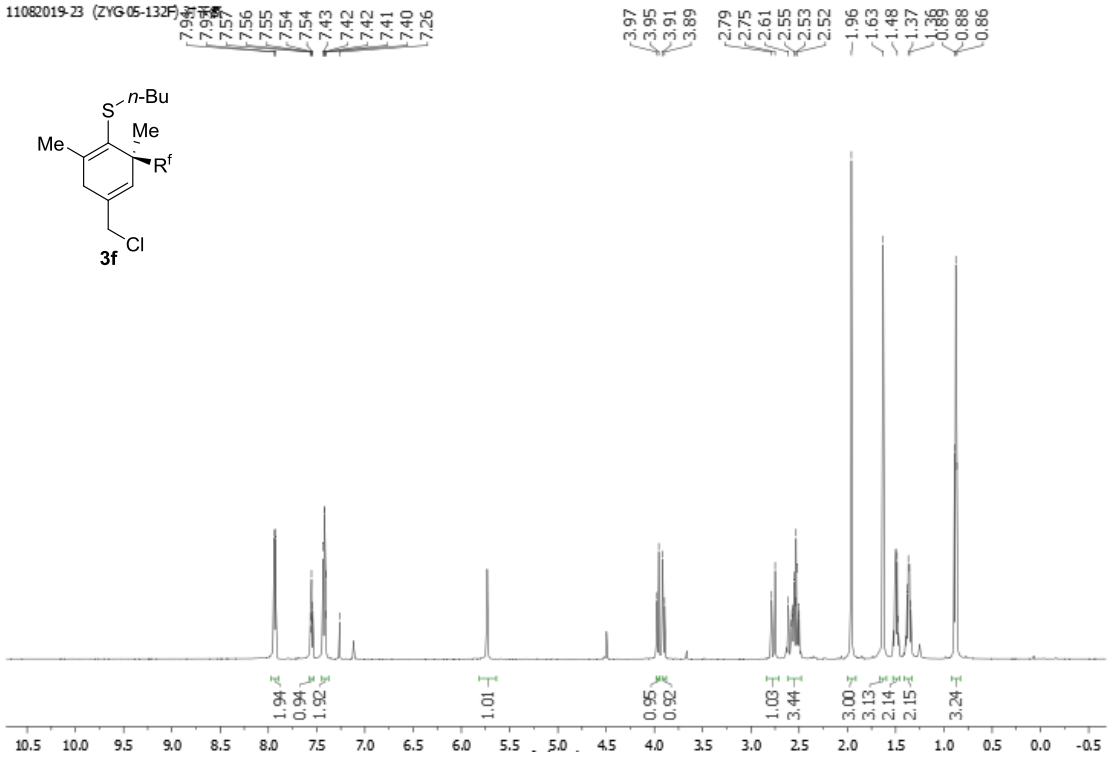

10292019-42 (ZYG-05-130A) 对甲基
104.15
104.59
104.79
105.24
n-Bu
S
Me
Me
R^f
Me
3d

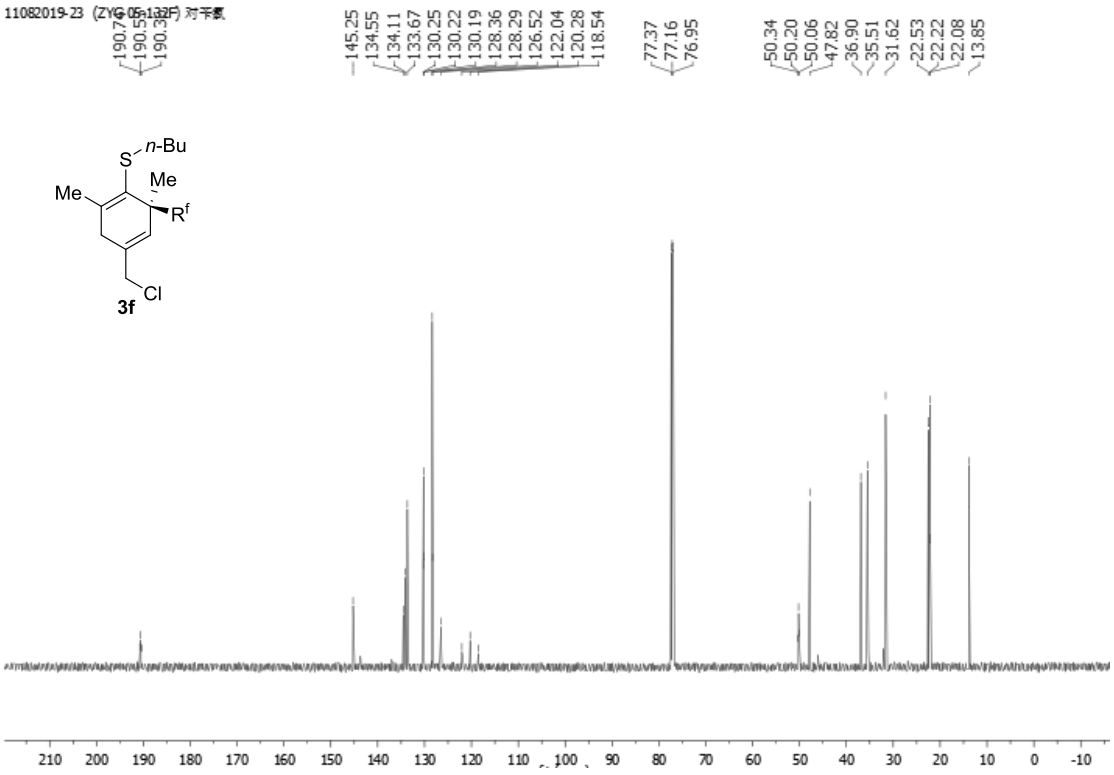

7.94
7.93
7.52
7.51
7.48
7.37
7.37
7.36
7.36
7.35
7.35
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.26
5.97
5.96
3.04
3.01
2.90
2.89
2.62
2.62
2.61
2.59
2.59
2.58
2.56
2.56
2.02
1.72
1.55
1.54
1.53
1.52
1.51
1.41
1.40
1.39
1.39
0.91
0.90
0.88


n-Bu
S
Me
Me
R^f
Ph
3e
1.87
0.97
1.98
5.20
0.92
1.02
1.06
2.18
3.05
3.03
2.17
2.14
3.00


11272019-44 ZYG-05-141A
191.08
190.85
190.64
145.75
139.60
136.57
134.70
133.47
130.27
130.24
130.21
128.47
128.29
127.85
126.73
125.63
125.48
122.43
120.69
118.93
77.37
77.16
76.95
50.59
50.44
50.30
37.06
36.92
31.72
22.71
22.56
22.27
13.88
S
n-Bu
Me
Me
R^f
Ph
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

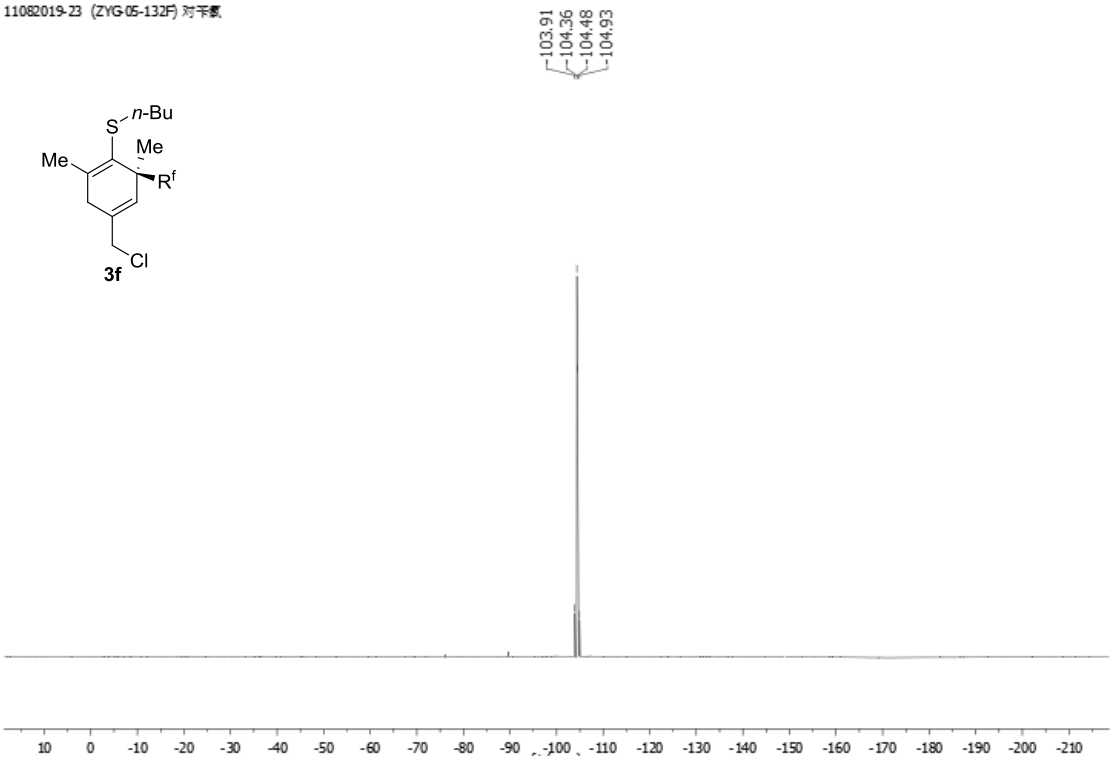

11272019-44 ZYG-05-141A
-104.25
S
n-Bu
Me
Me
R^f
Ph
3e
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


11082019-23 (ZYG-05-132F)
7.94
7.57
7.56
7.55
7.54
7.54
7.43
7.42
7.42
7.41
7.40
7.26
3.97
3.95
3.91
3.89
2.79
2.75
2.61
2.55
2.53
2.52
1.96
1.63
1.48
1.37
1.36
0.89
0.88
0.86
n-Bu
S
Me
Me
Rf
Cl
3f
1.94
0.94
1.92
1.01
0.95
0.92
1.03
3.44
3.00
3.13
2.14
2.15
3.24
10.5
10.0
9.5
9.0
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
-0.5

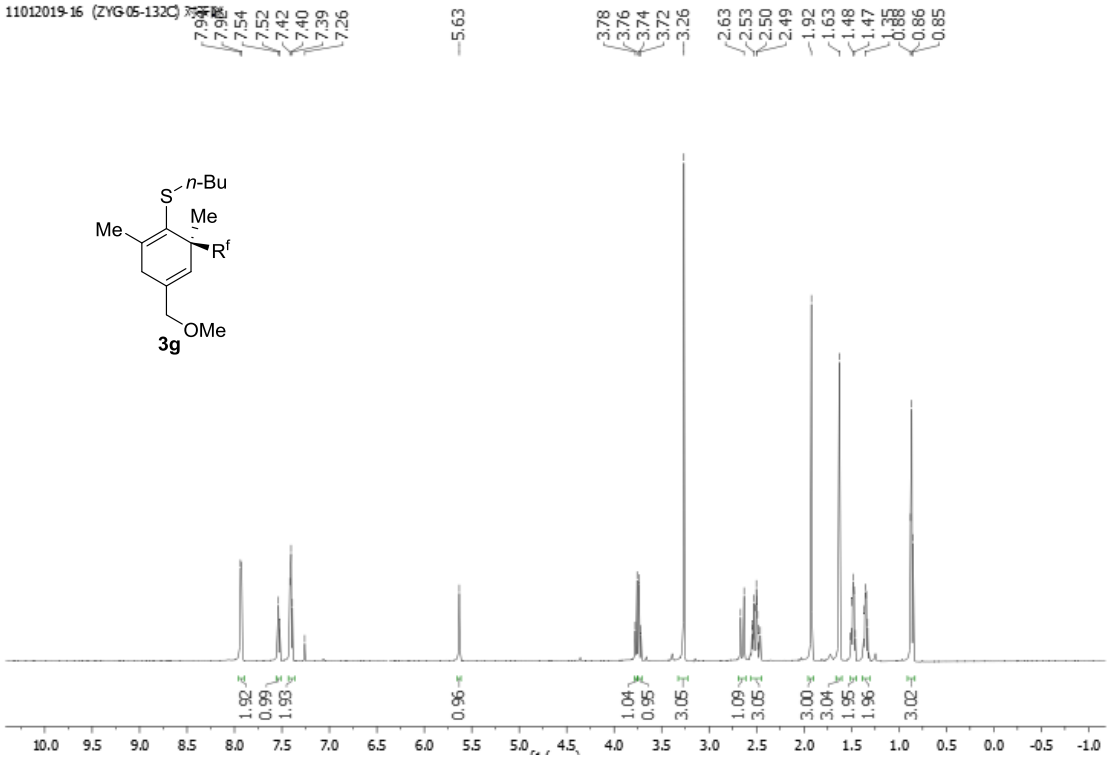

11082019-23 (ZYG-05-132F)
190.74
190.58
190.38
145.25
134.55
134.11
133.67
130.25
130.22
130.19
128.36
128.29
126.52
122.04
120.28
118.54
77.37
77.16
76.95
50.34
50.20
50.06
47.82
36.90
35.51
31.62
22.53
22.22
22.08
13.85
n-Bu
S
Me
Me
Rf
Cl
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

11082019-23 (ZYG-05-132F) 对平氟

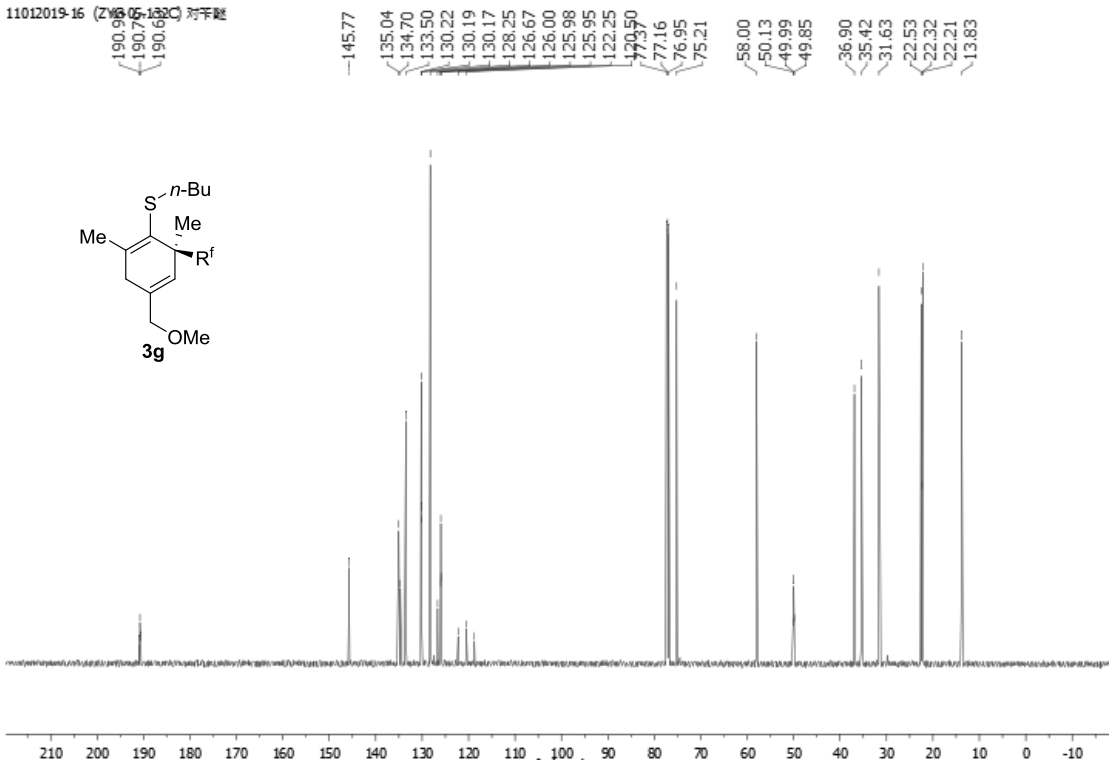
3f

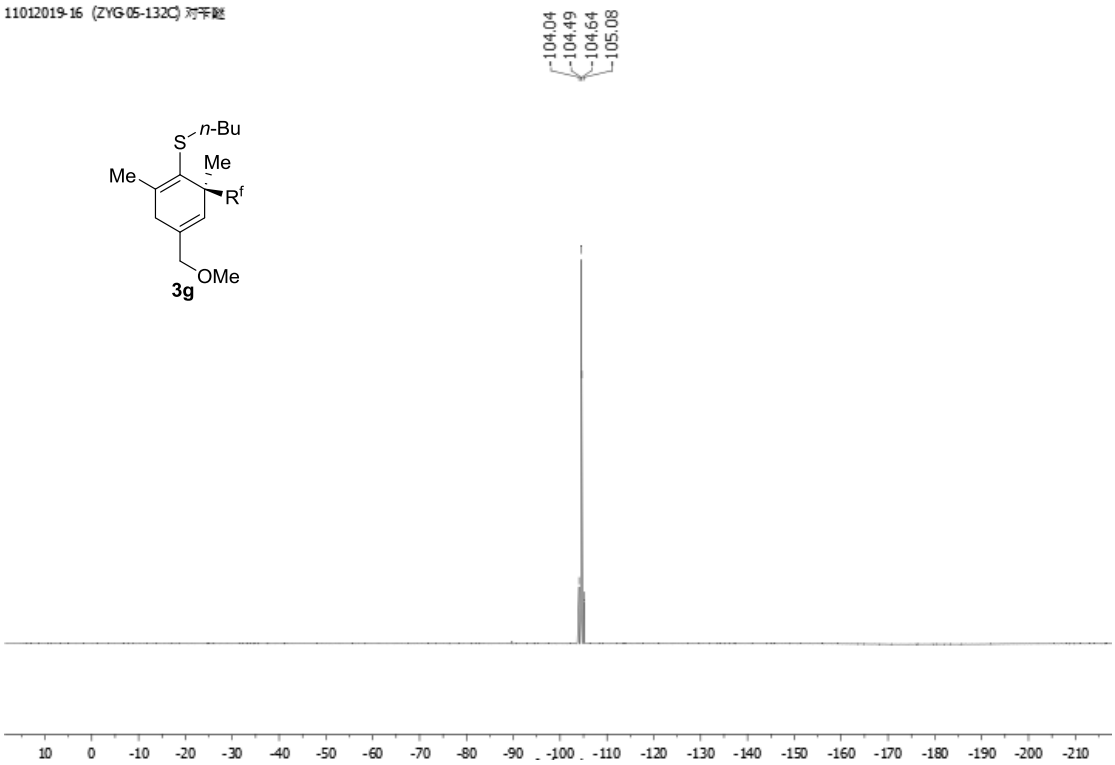


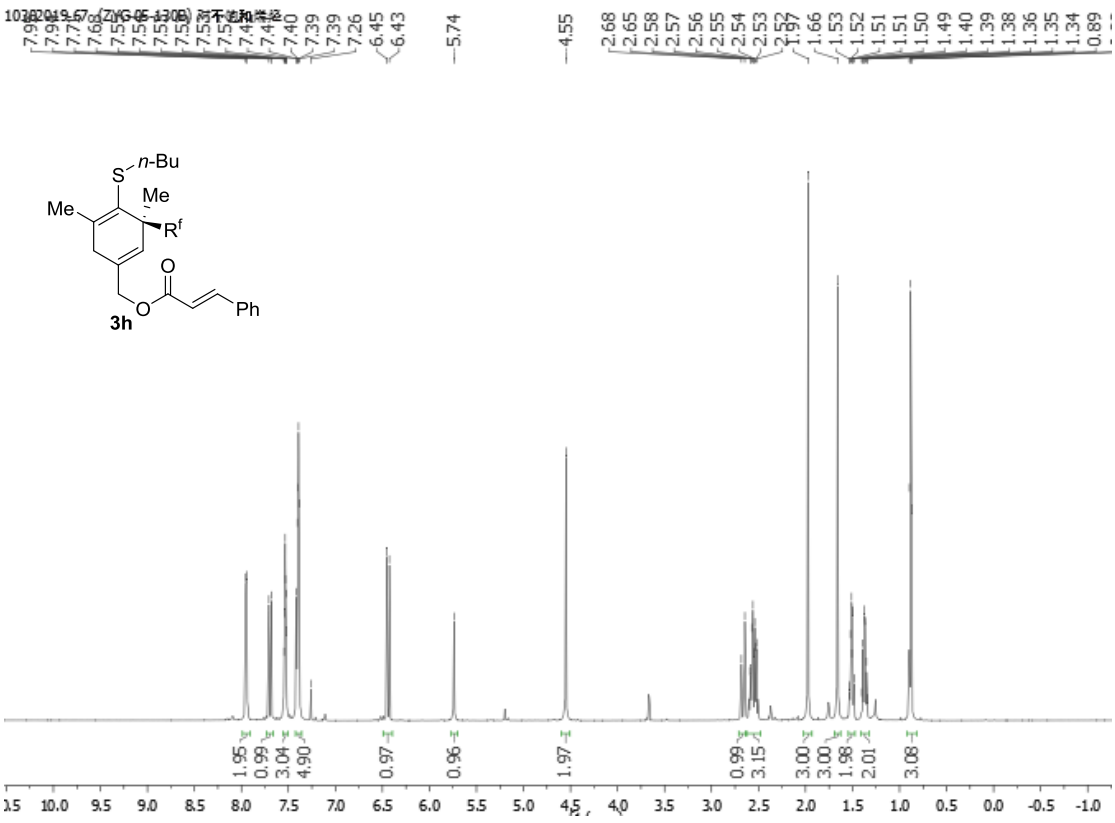
11012019-16 (ZYG-05-132C) 对氟

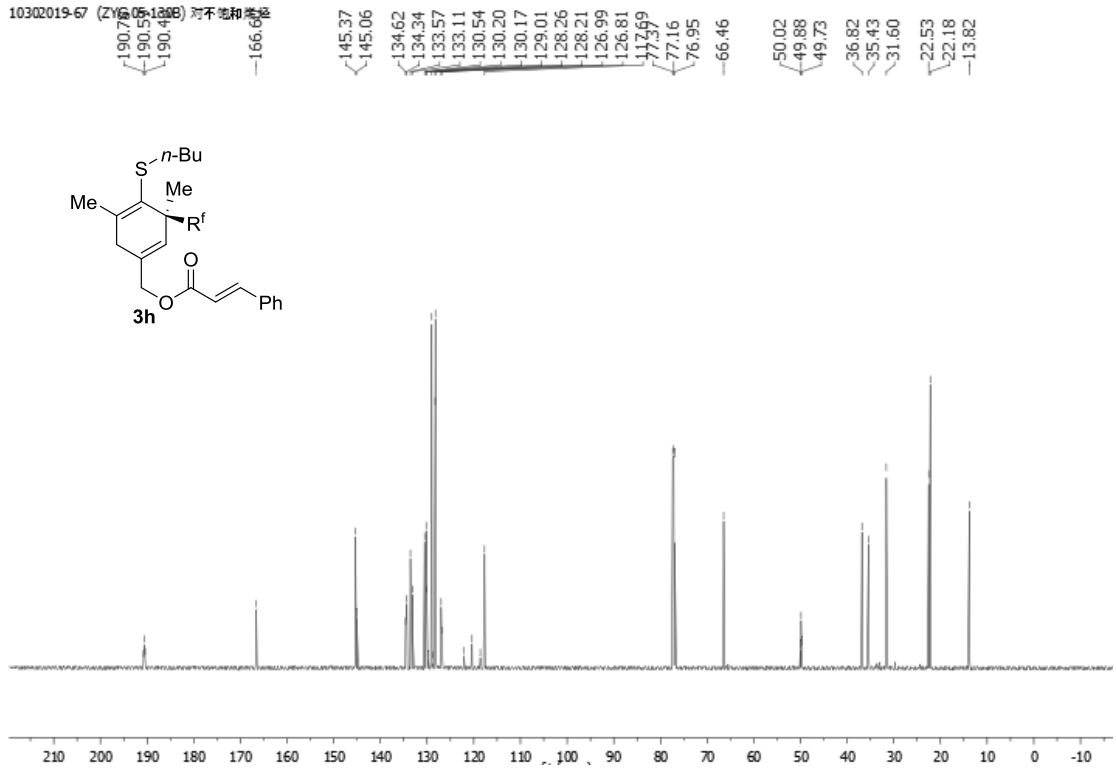


3g

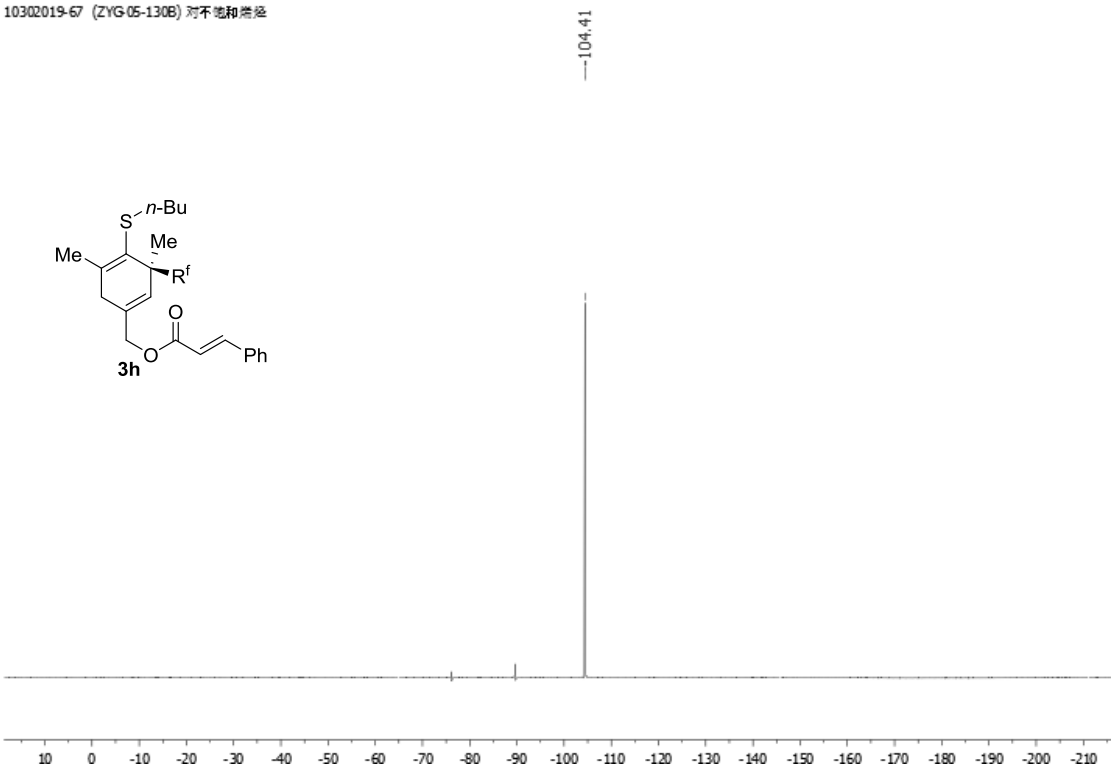

11012019-16 (ZYG-05-132C) 对干燥
190.96
190.70
190.62
145.77
135.04
134.70
133.50
130.22
130.19
130.17
128.25
126.67
126.00
125.98
125.95
122.25
120.50
77.37
77.16
76.95
75.21
58.00
50.13
49.99
49.85
36.90
35.42
31.63
22.53
22.32
22.21
13.83
S
n-Bu
Me
Me
Rf
OMe
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


11012019-16 (ZYG-05-132C) 对干燥
104.04
104.49
104.64
105.08
S
n-Bu
Me
Me
Rf
OMe
3g
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

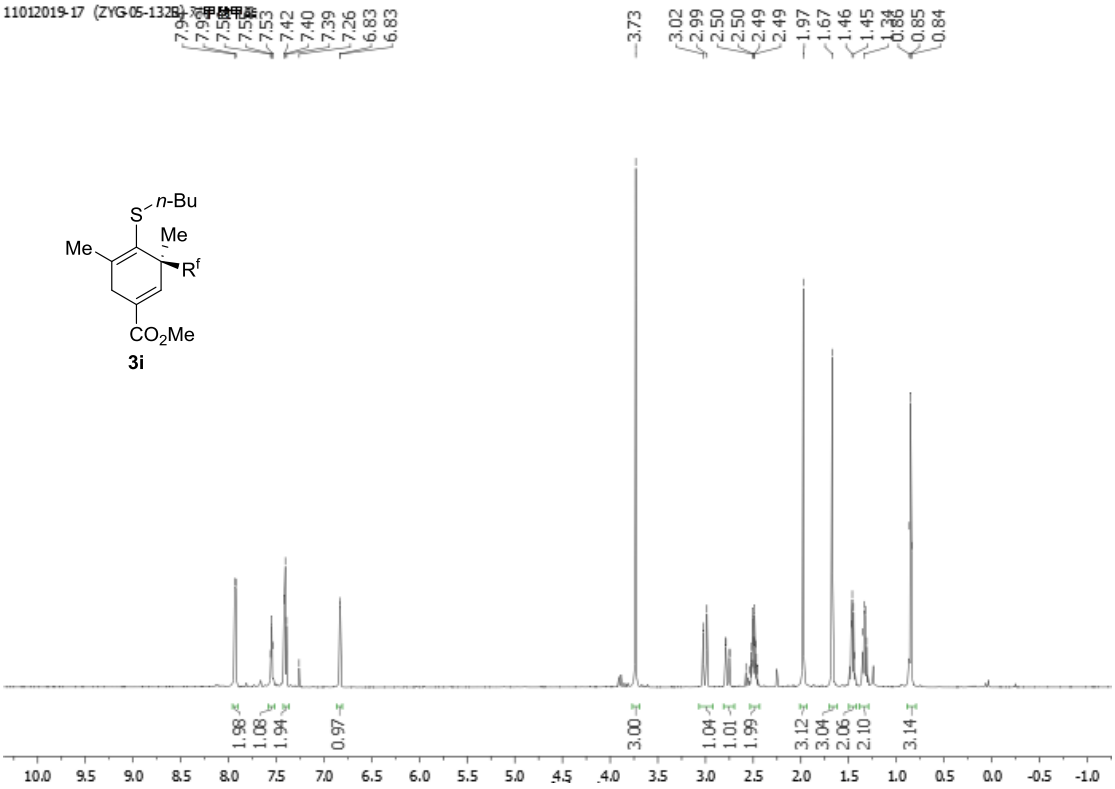

n-Bu
S
Me
Me
R^f
O
O
Ph
3h


n-Bu
S
Me
Me
R^f
O
O
Ph
3h

10302019-67 (ZYG-05-130B) 对不饱和底物

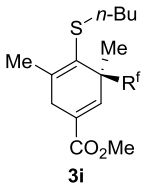


11012019-17 (ZYG-05-132B) 对甲酸甲酯

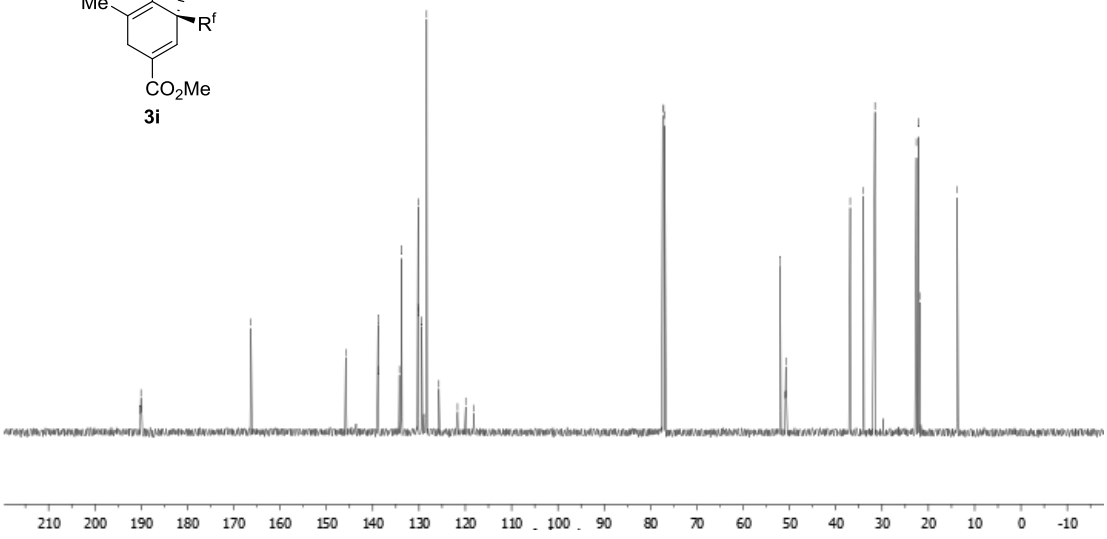


11012019-32

190.25
190.06
189.86
166.31
145.82
138.83
138.81
134.23
133.77
130.21
130.19
130.16
129.41
128.36
125.71
121.68
119.92
118.17
77.37
77.16
76.95
52.02
50.93
50.78
50.64
36.88
34.02
31.54
22.59
22.16
21.88
13.78



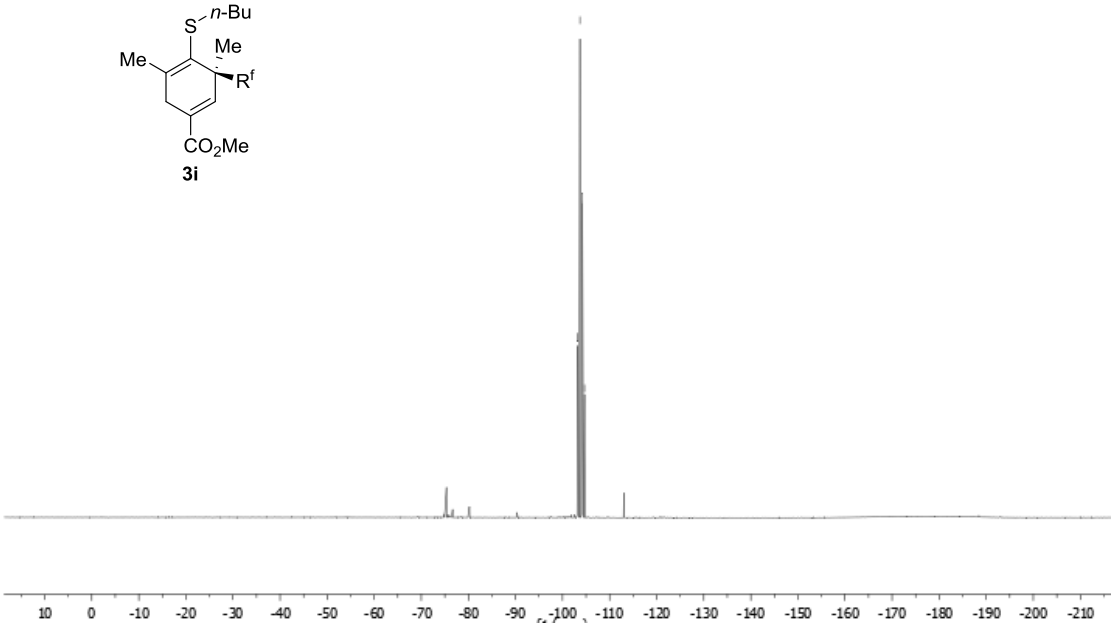
3i

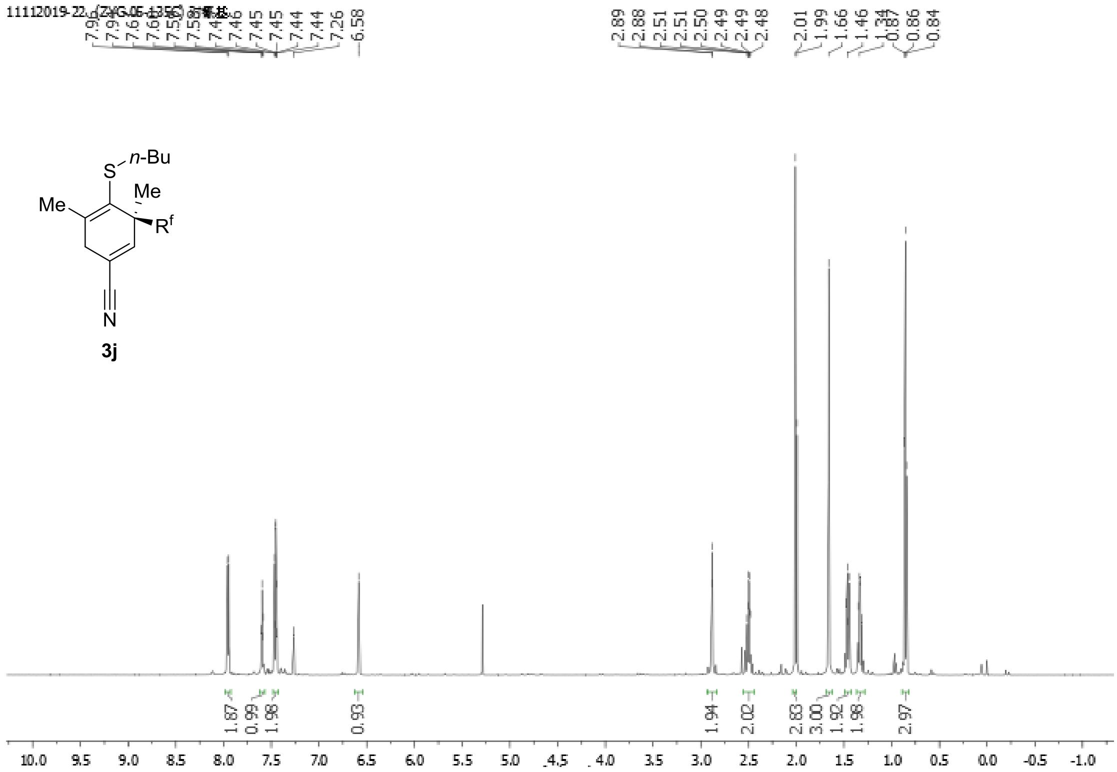


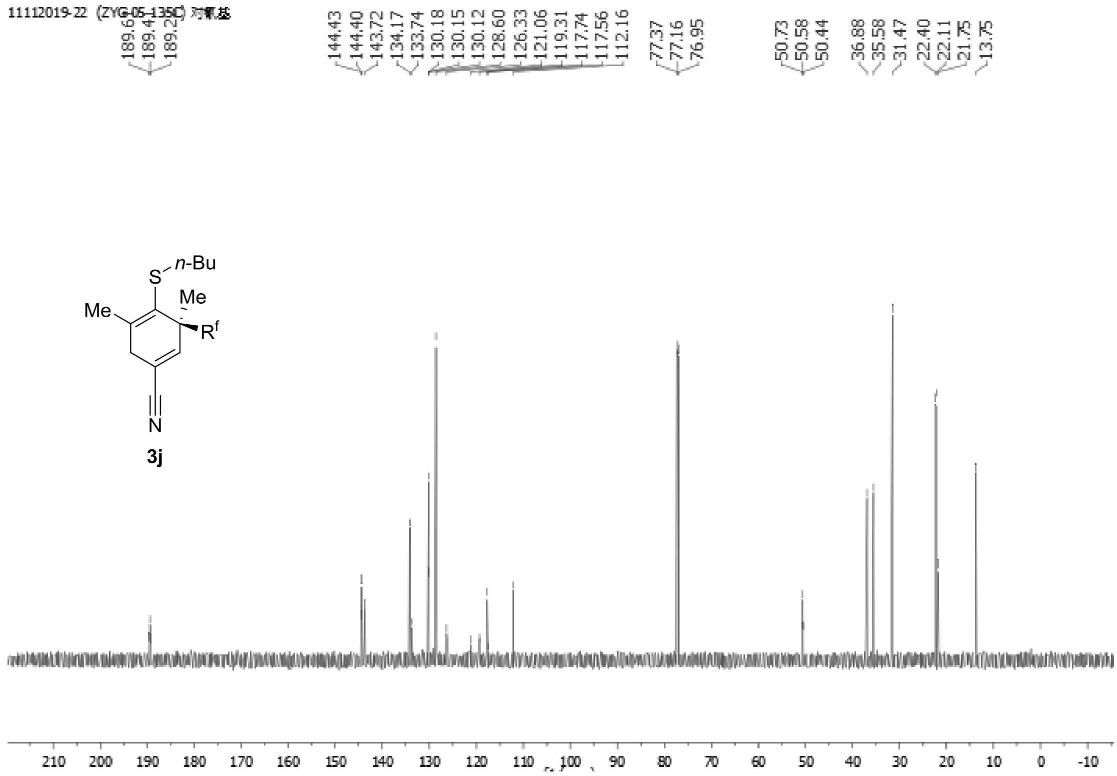
11012019-32

103.24
103.70
104.22
104.68

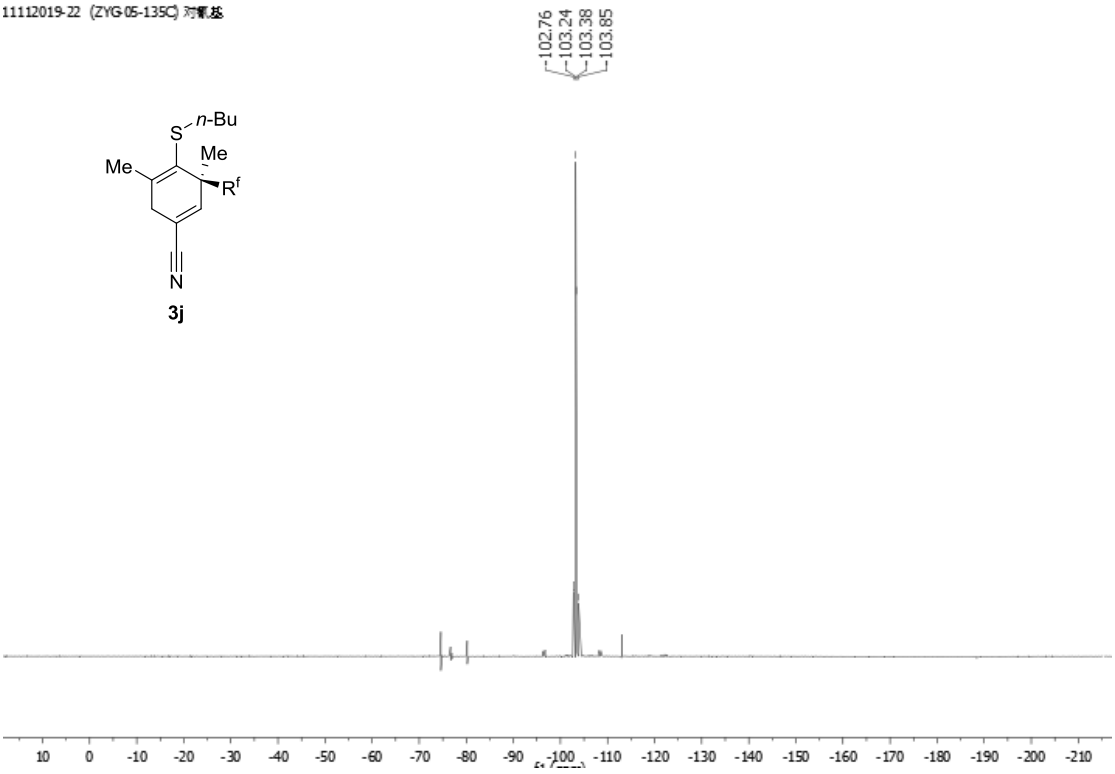
3i




11112019-22 (ZYG-05-135C)
7.94 7.60 7.59 7.46 7.45 7.45 7.44 7.44 7.26 6.58
2.89 2.88 2.51 2.51 2.50 2.49 2.49 2.48
2.01 1.99 1.66 1.46 1.34 0.87 0.86 0.84
S n-Bu
Me
Me
Rf
N
3j
1.87 0.99 1.98 0.93 1.94 2.02 2.83 3.00 1.92 1.98 2.97
10.0 9.5 9.0 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 -0.5 -1.0

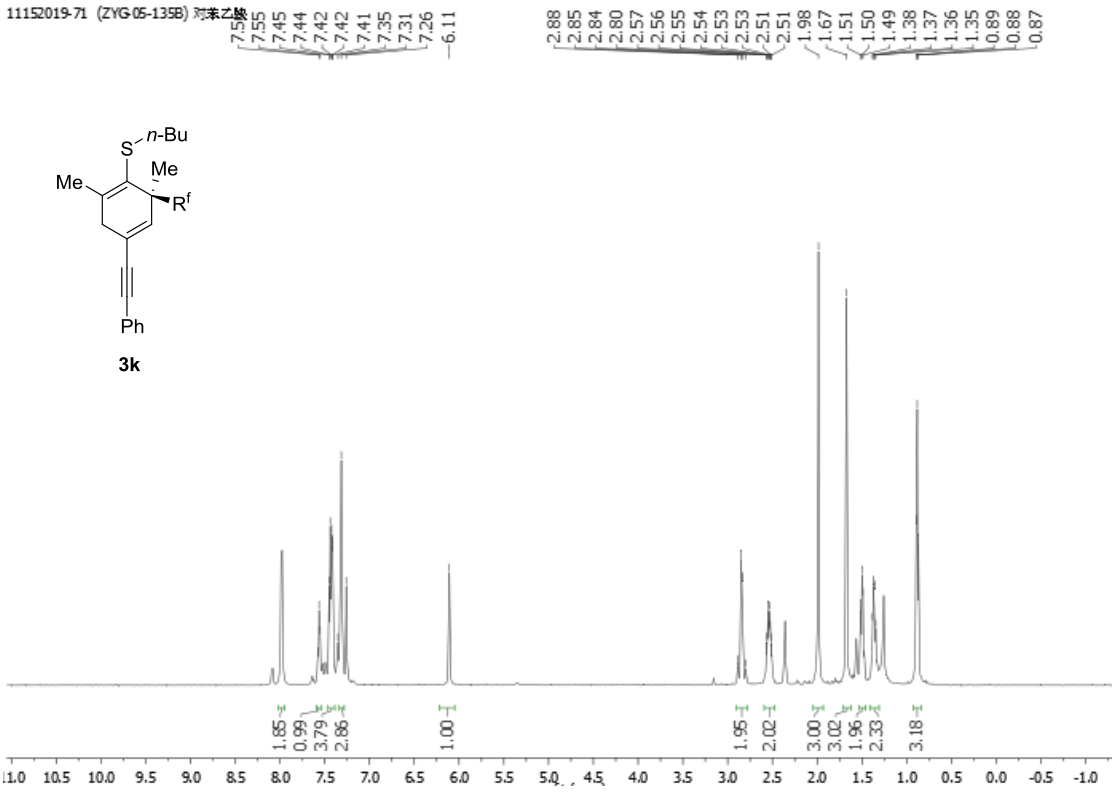

11112019-22 (ZYG-05-135C)
189.6 189.4 189.2
144.43 144.40 143.72 134.17 133.74 130.18 130.15 130.12 128.60 126.33 121.06 119.31 117.74 117.56 112.16
77.37 77.16 76.95
50.73 50.58 50.44
36.88 35.58 31.47 22.40 22.11 21.75 13.75
S n-Bu
Me
Me
Rf
N
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

11112019-22 (ZYG-05-135C) 对氟苯

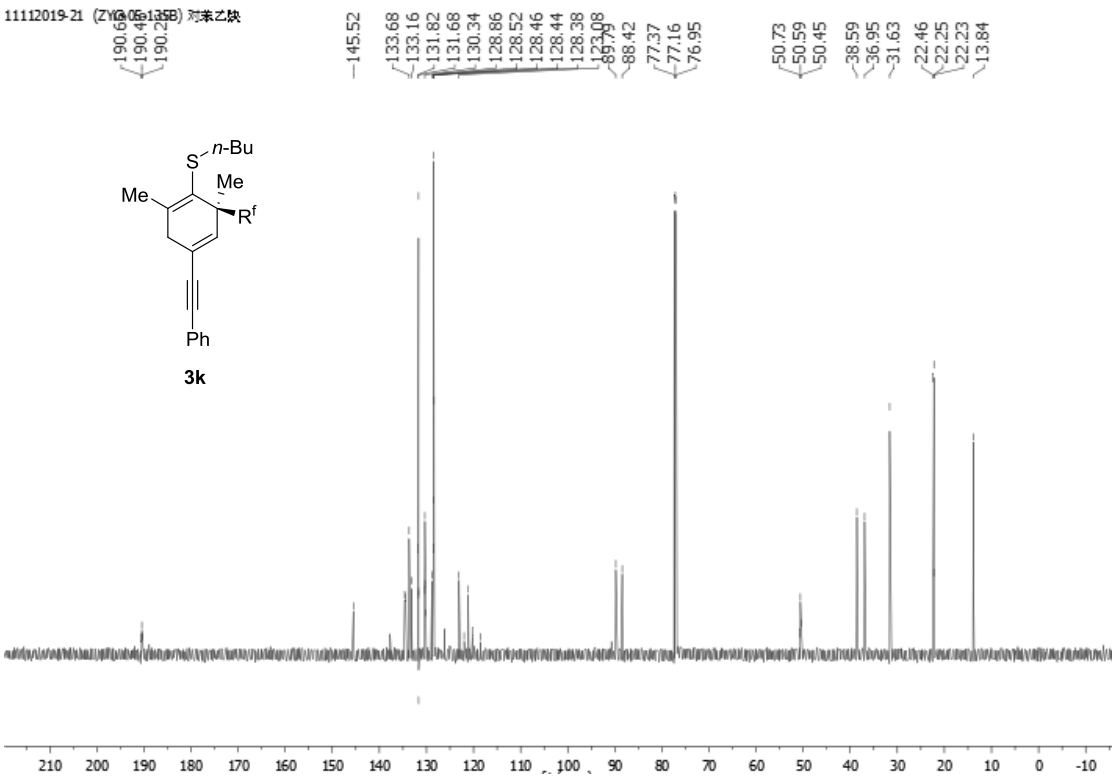


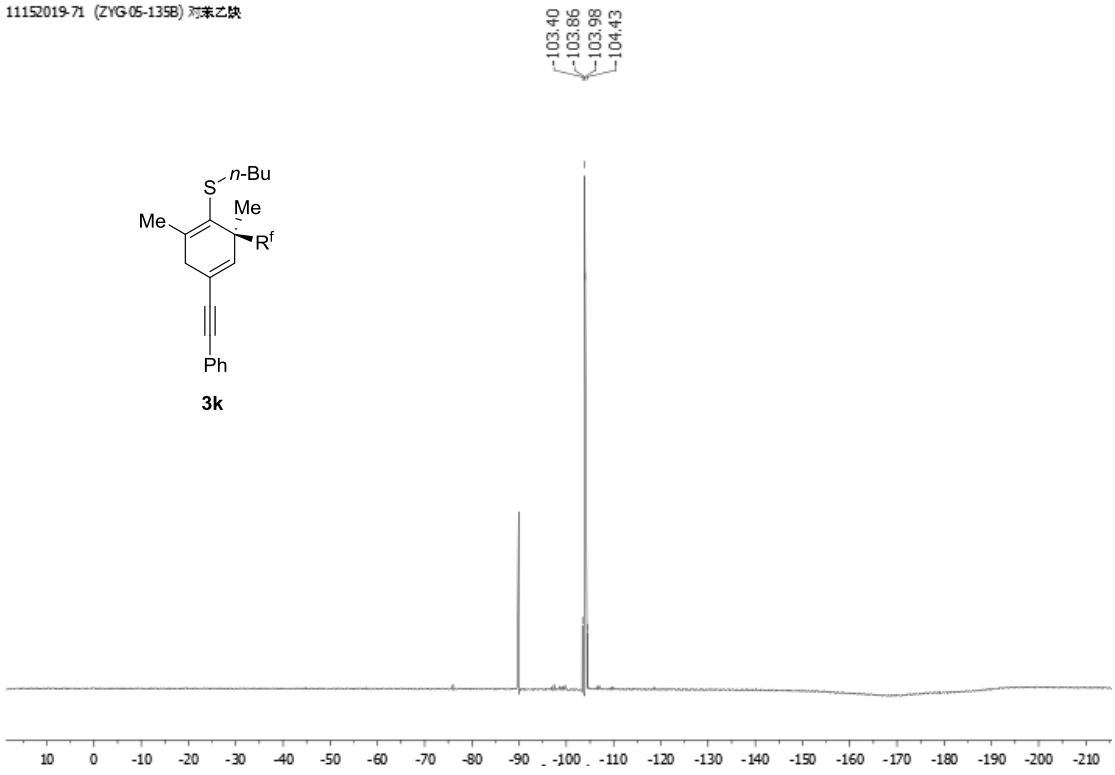
3j

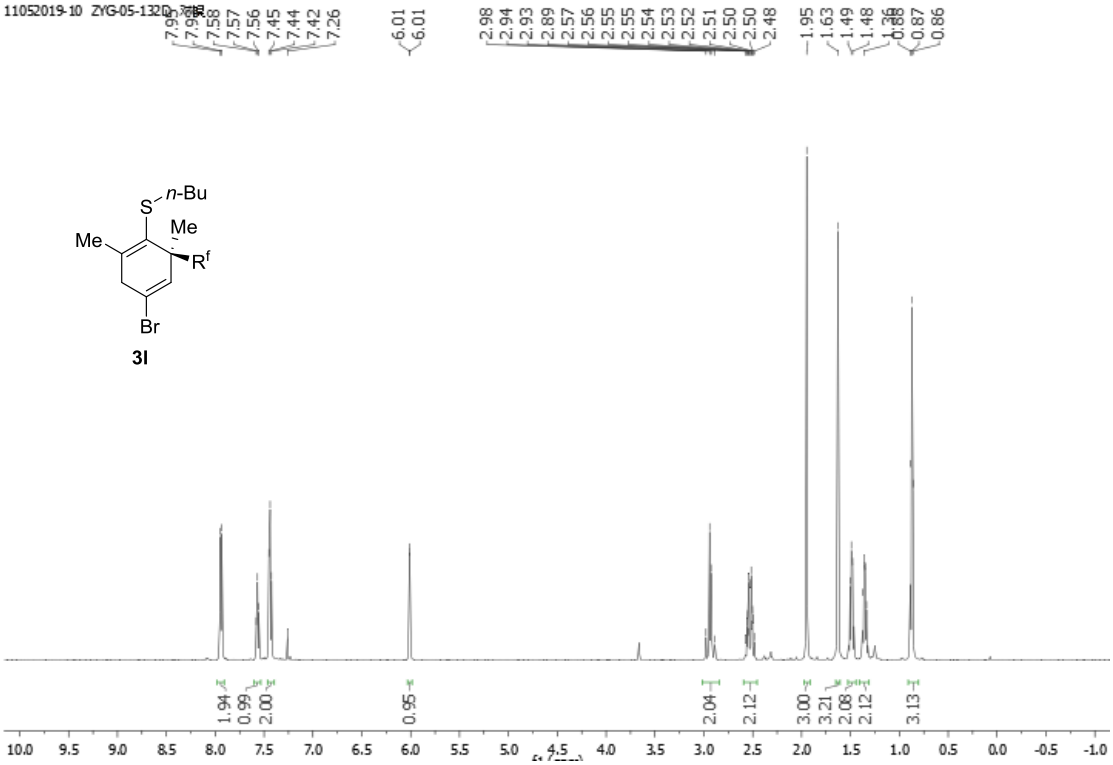
11152019-71 (ZYG-05-135B) 对苯乙炔

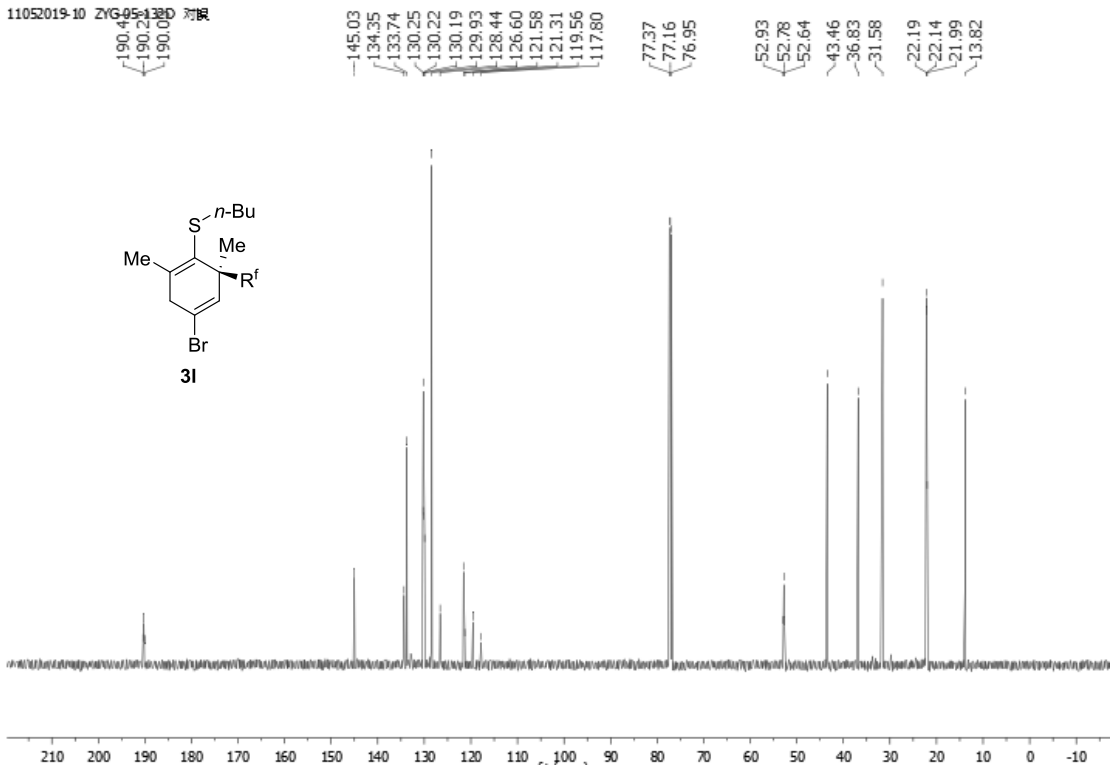


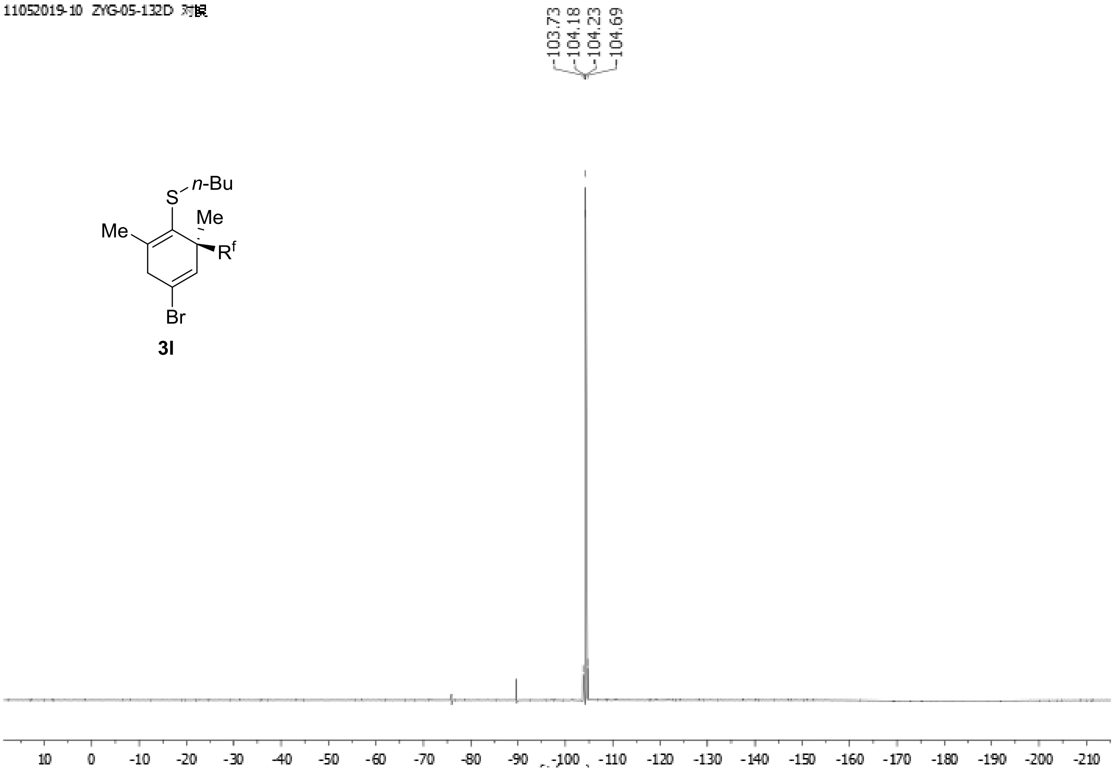
3k


11112019-21 (ZYG-05-135B) 对苯乙炔
190.60
190.45
190.25
145.52
133.68
133.16
131.82
131.68
130.34
128.86
128.52
128.46
128.44
128.38
123.08
89.79
88.42
77.37
77.16
76.95
50.73
50.59
50.45
38.59
36.95
31.63
22.46
22.25
22.23
13.84
S
n-Bu
Me
Me
R^f
Ph
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

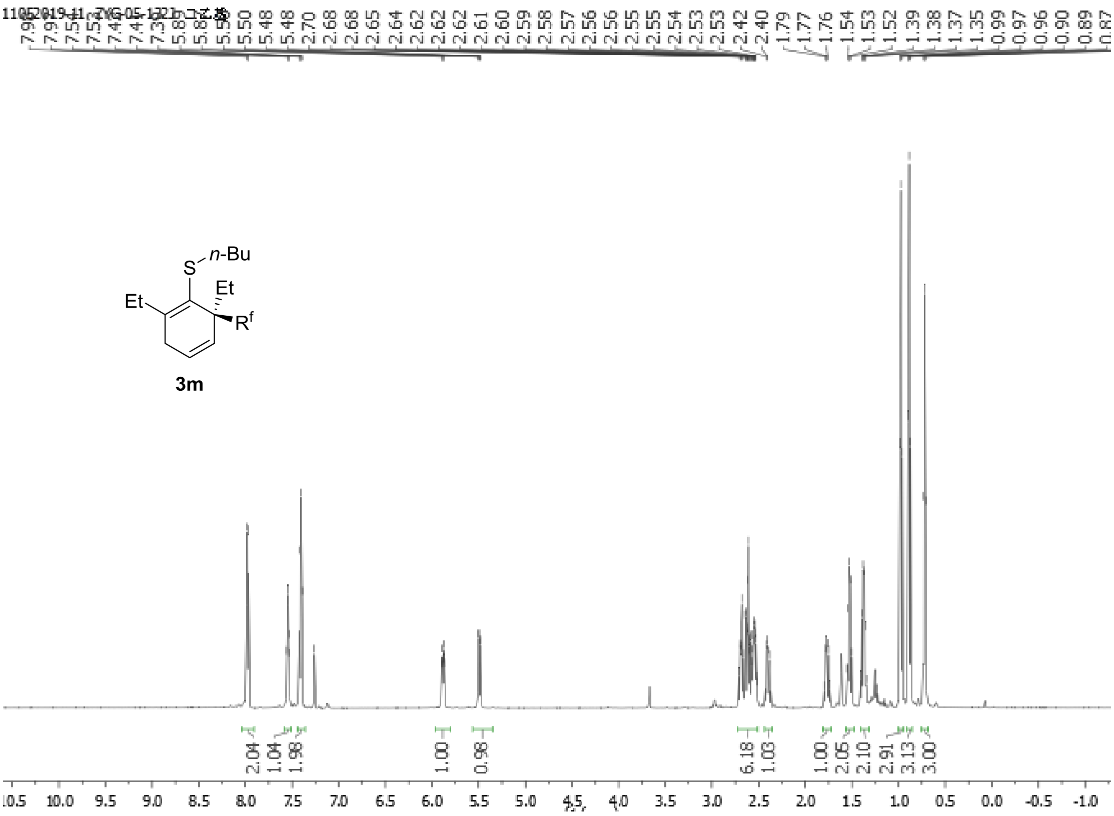

11152019-71 (ZYG-05-135B) 对苯乙炔
103.40
103.86
103.98
104.43
S
n-Bu
Me
Me
R^f
Ph
3k
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


11052019-10 ZYG-05-132D
7.58
7.57
7.56
7.45
7.44
7.42
7.26
6.01
6.01
2.98
2.94
2.93
2.89
2.57
2.56
2.55
2.55
2.54
2.53
2.52
2.51
2.50
2.50
2.48
1.95
1.63
1.49
1.48
0.88
0.87
0.86
n-Bu
S
Me
Me
Rf
Br
3l
1.94
0.99
2.00
0.95
2.04
2.12
3.00
3.21
2.08
2.12
3.13


11052019-10 ZYG-05-132D
145.03
134.35
133.74
130.25
130.22
130.19
129.93
128.44
126.60
121.58
121.31
119.56
117.80
77.37
77.16
76.95
52.93
52.78
52.64
43.46
36.83
31.58
22.19
22.14
21.99
13.82
n-Bu
S
Me
Me
Rf
Br
3l

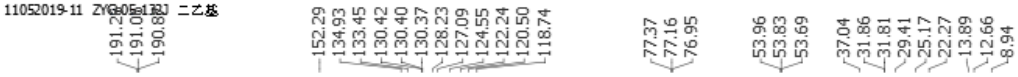

11052019-10 ZYG-05-132D
-103.73
-104.18
-104.23
-104.69
S n-Bu
Me
Me
R^f
Br
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

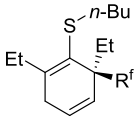
3l


S n-Bu
Et
Et
R^f
2.04
1.04
1.98
1.00
0.98
6.18
1.03
1.00
2.05
2.10
2.91
3.13
3.00
10.5 10.0 9.5 9.0 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 -0.5 -1.0

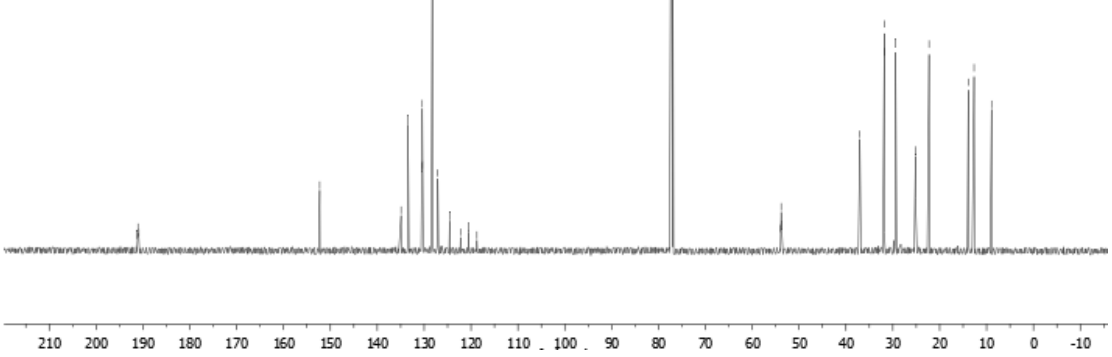
3m

11052019-11 ZYG-05-132J 二乙基



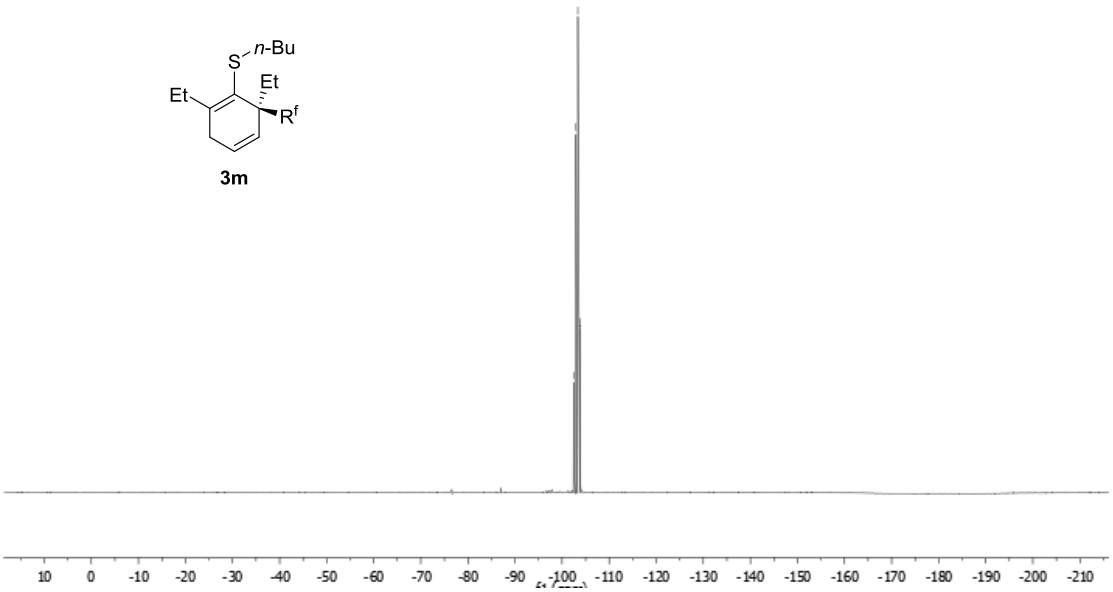


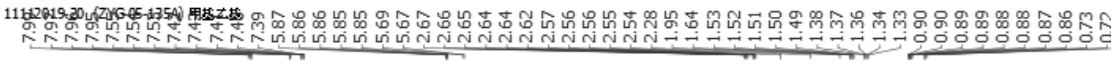
3m

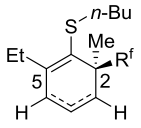


11052019-11 ZYG-05-132J 二乙基

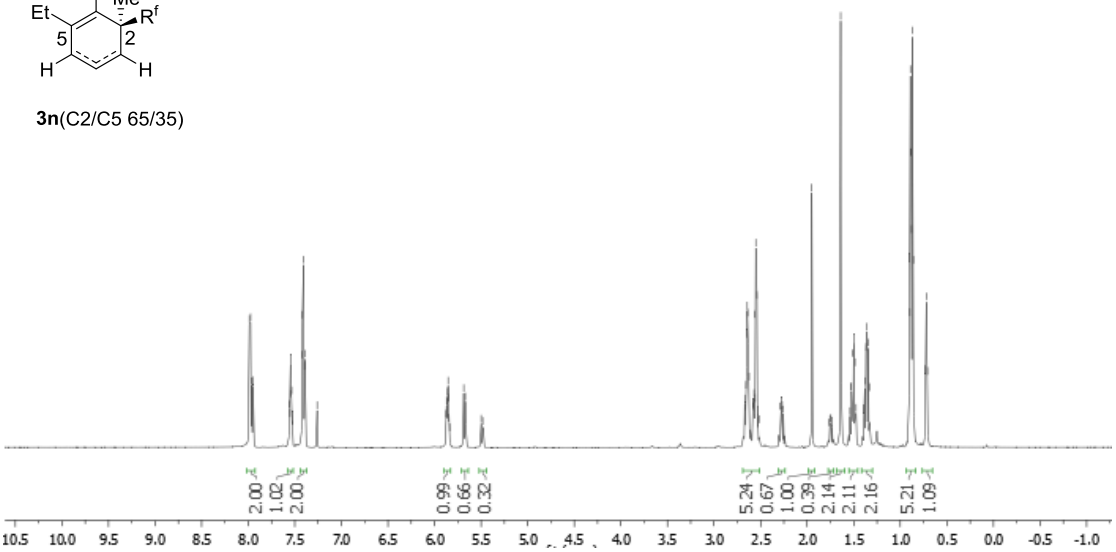
3m

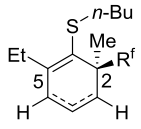




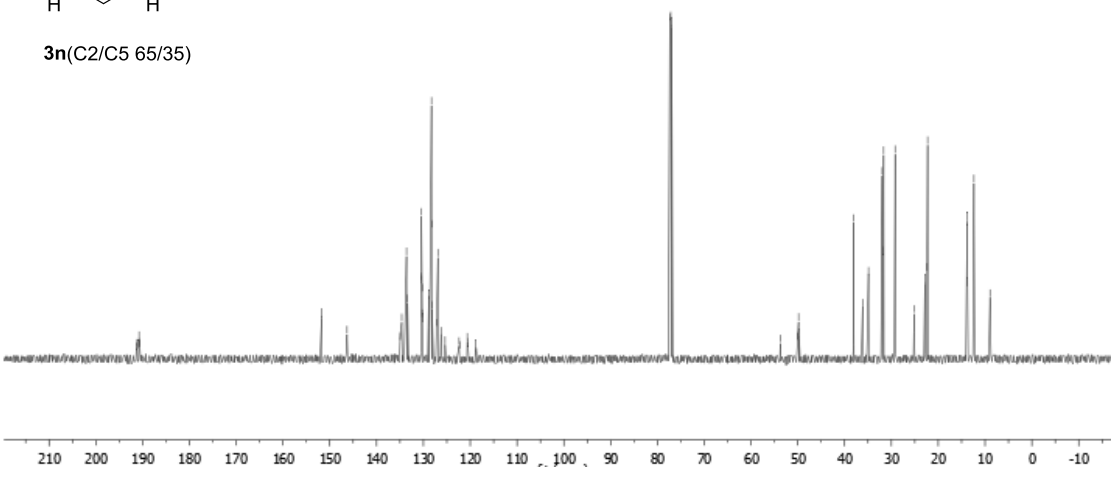


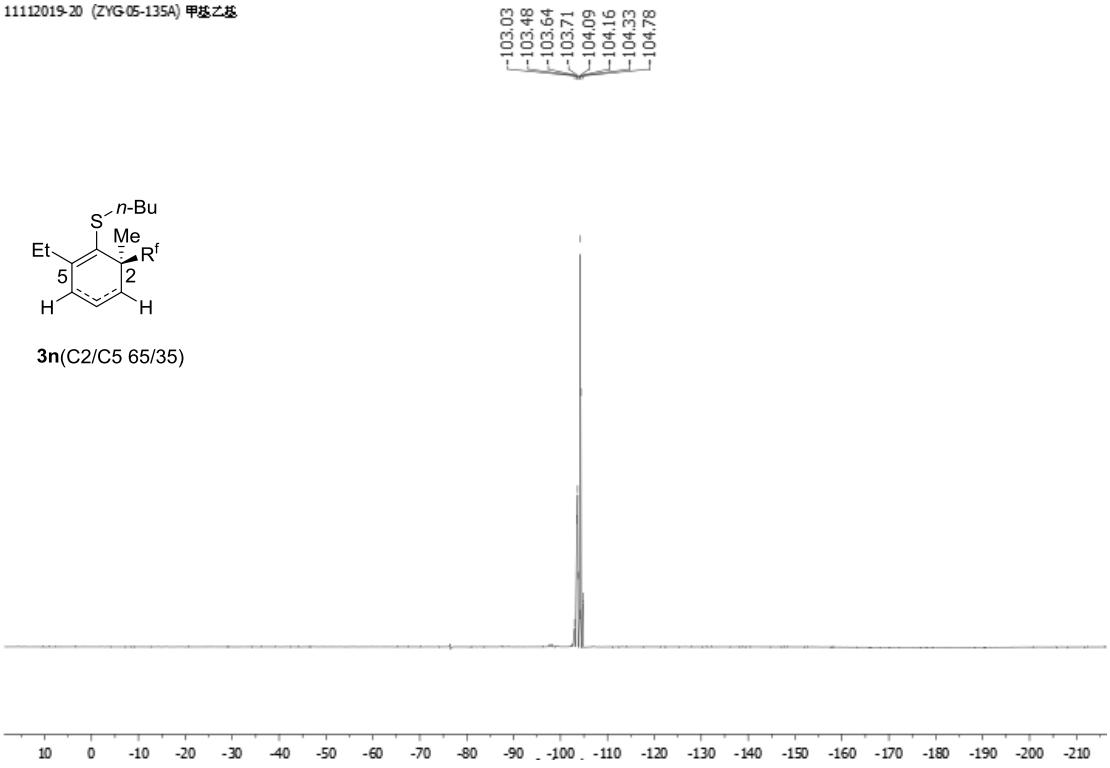
3n(C2/C5 65/35)



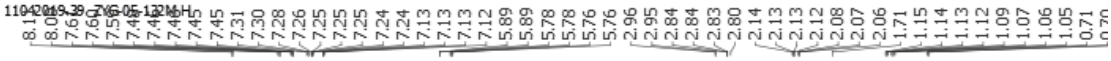


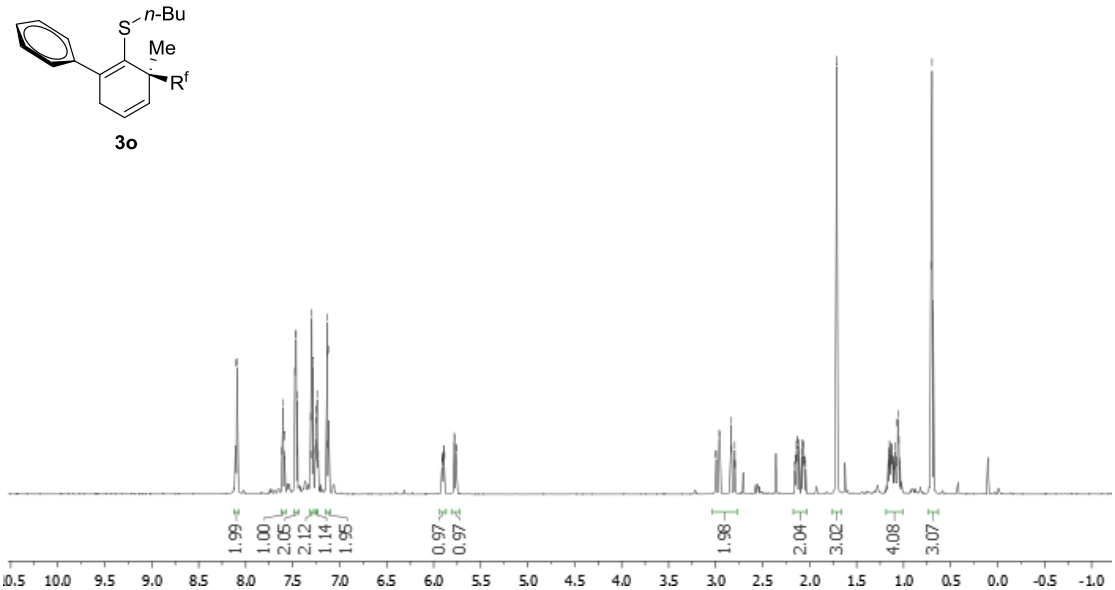
3n(C2/C5 65/35)





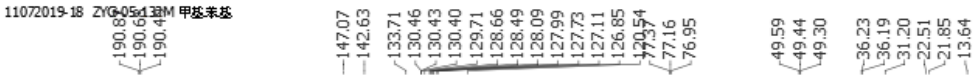
3n(C2/C5 65/35)

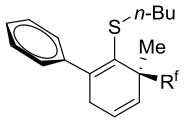




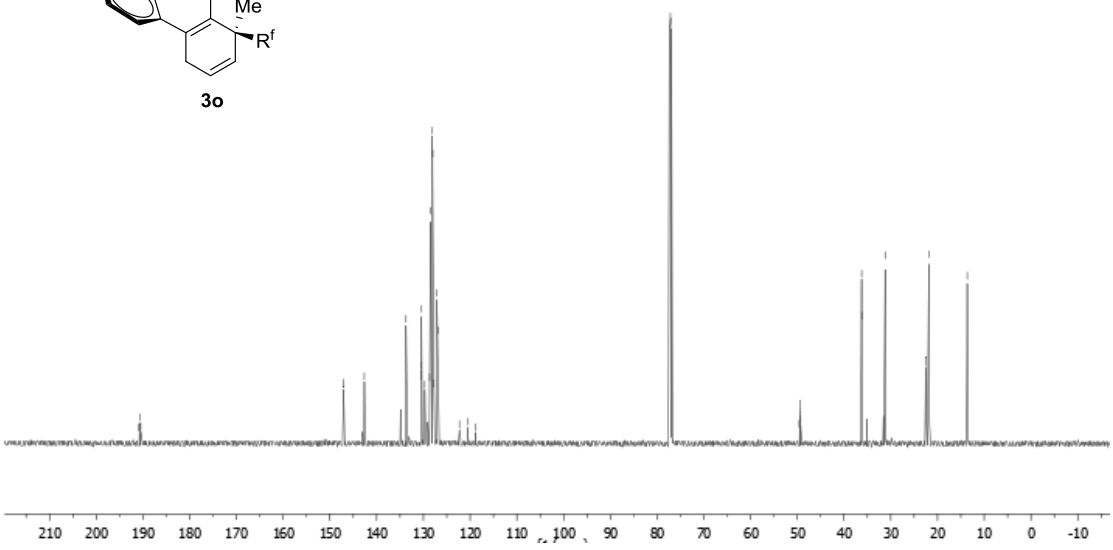
3o

11072019-18 ZYG-05-132M 甲基苯基

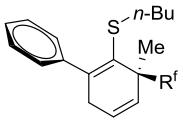




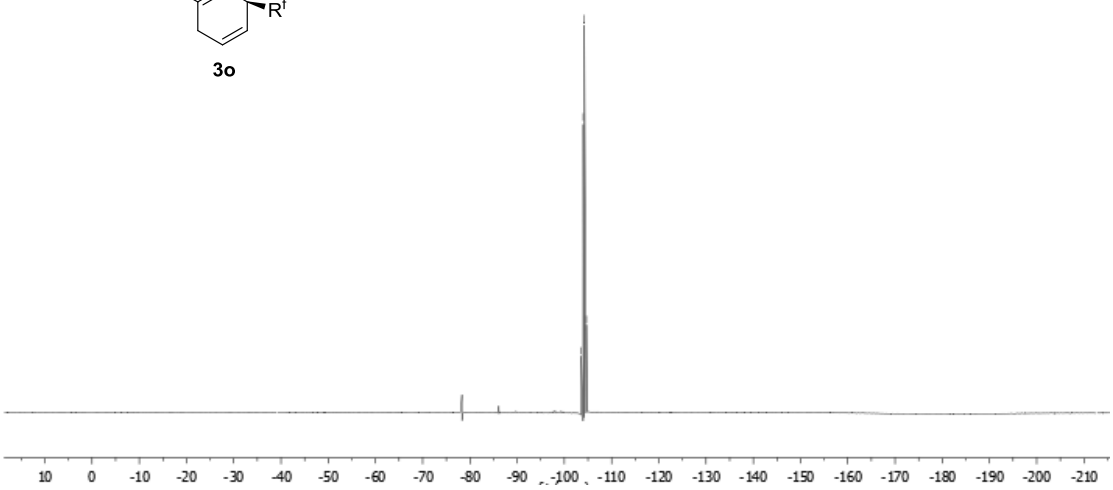
3o



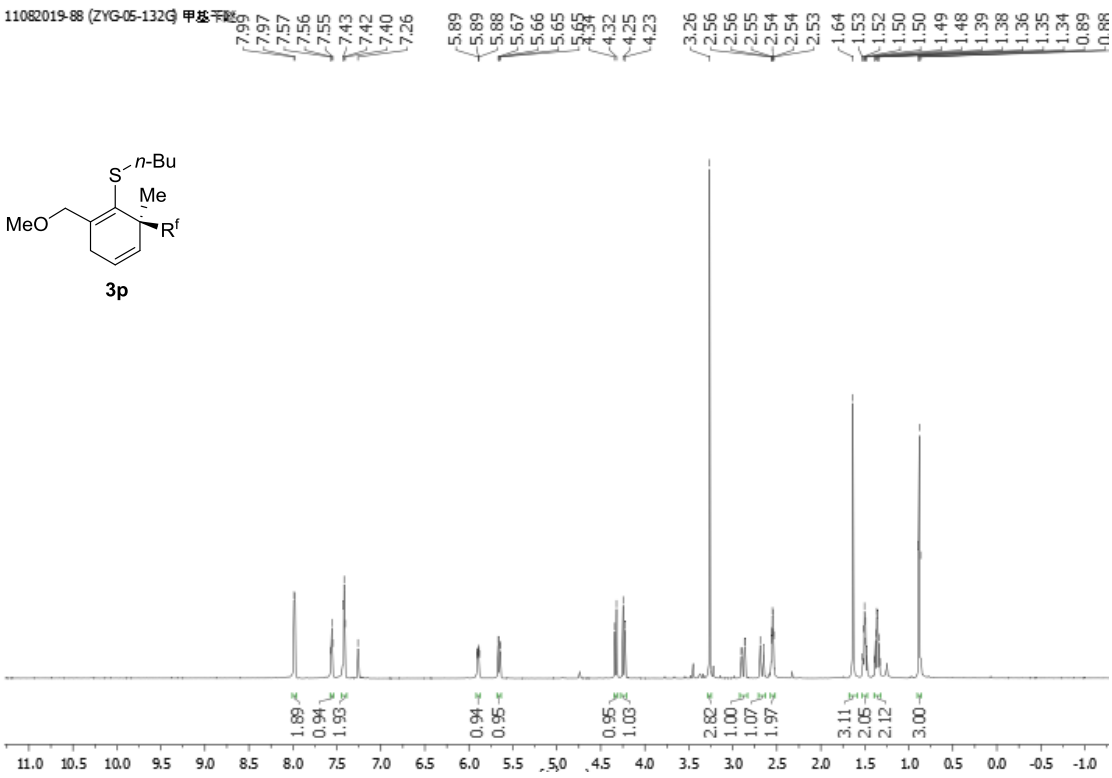
11072019-18 ZYG-05-132M 甲基苯基



3o

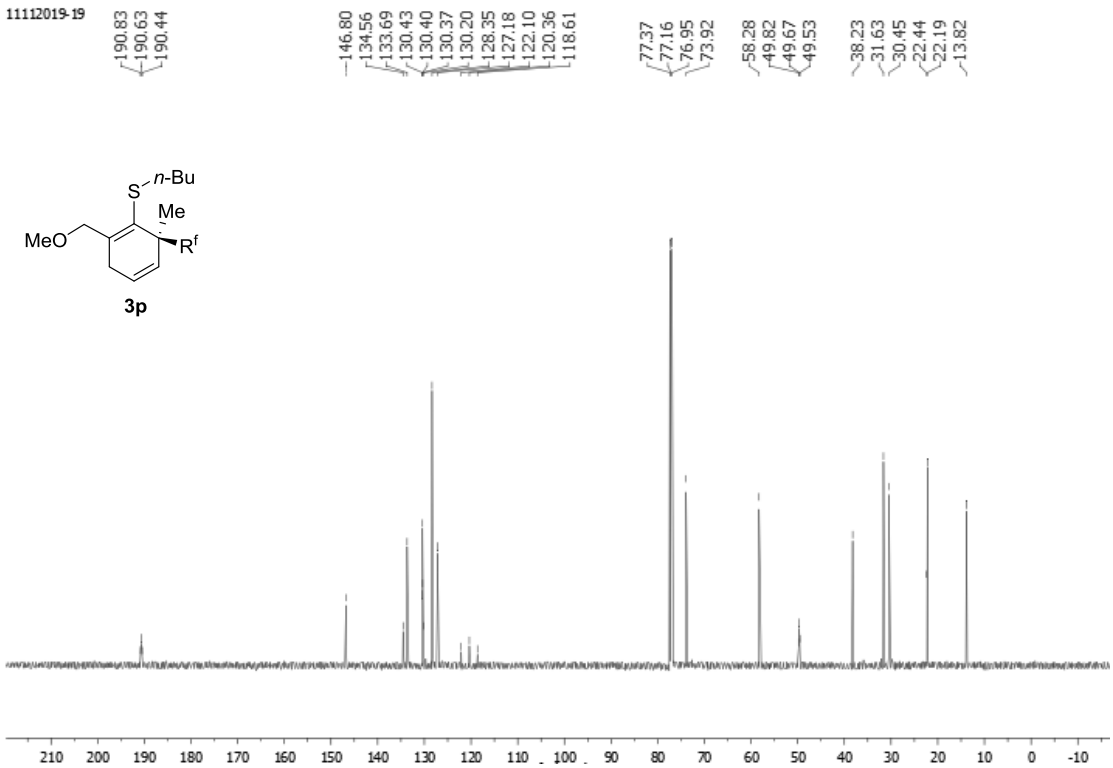


11082019-88 (ZYG-05-132G) 甲苯干燥

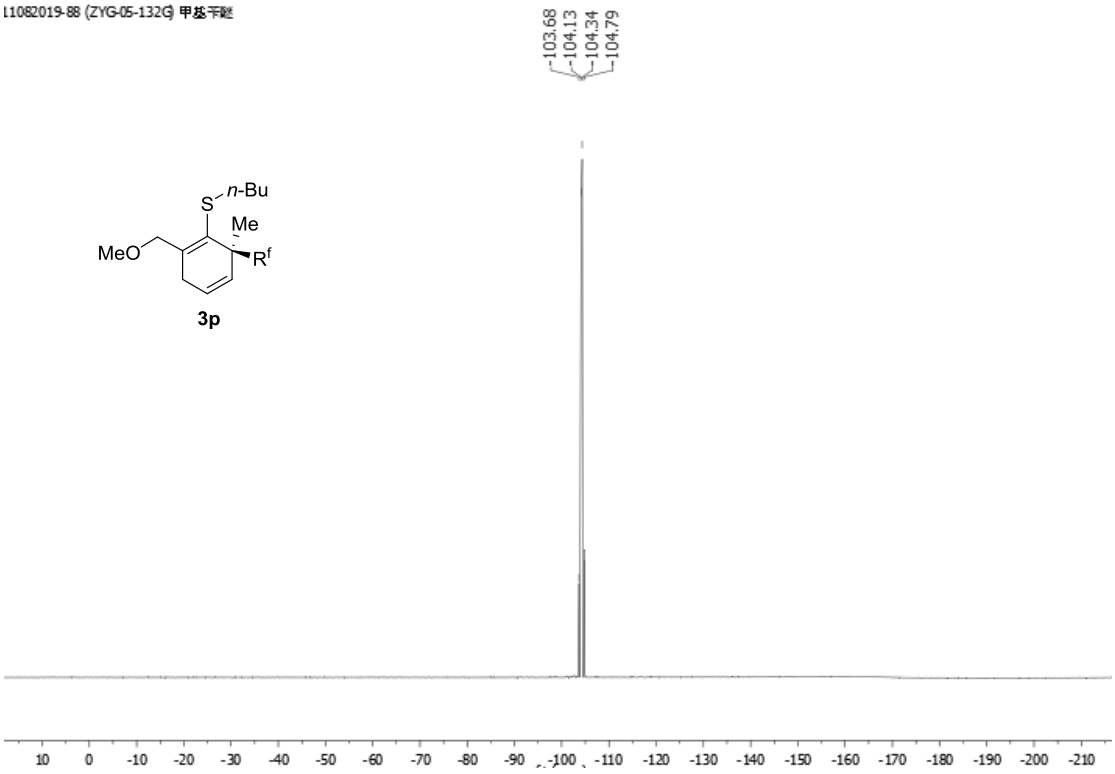


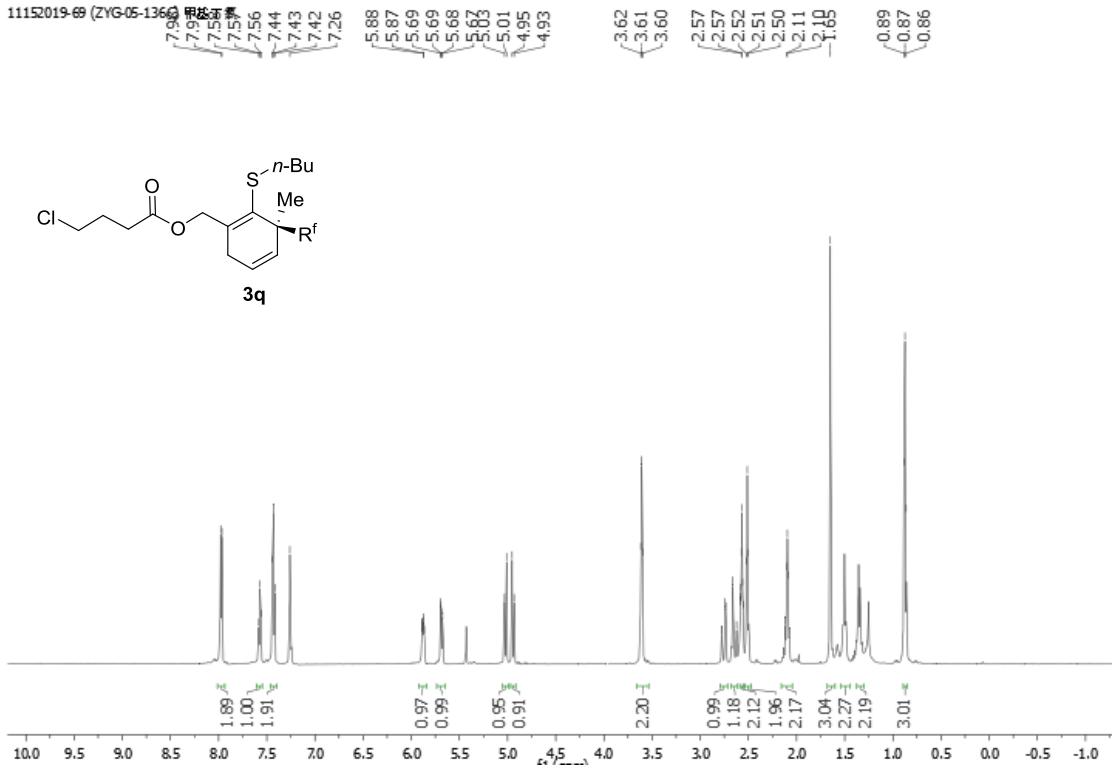
3p

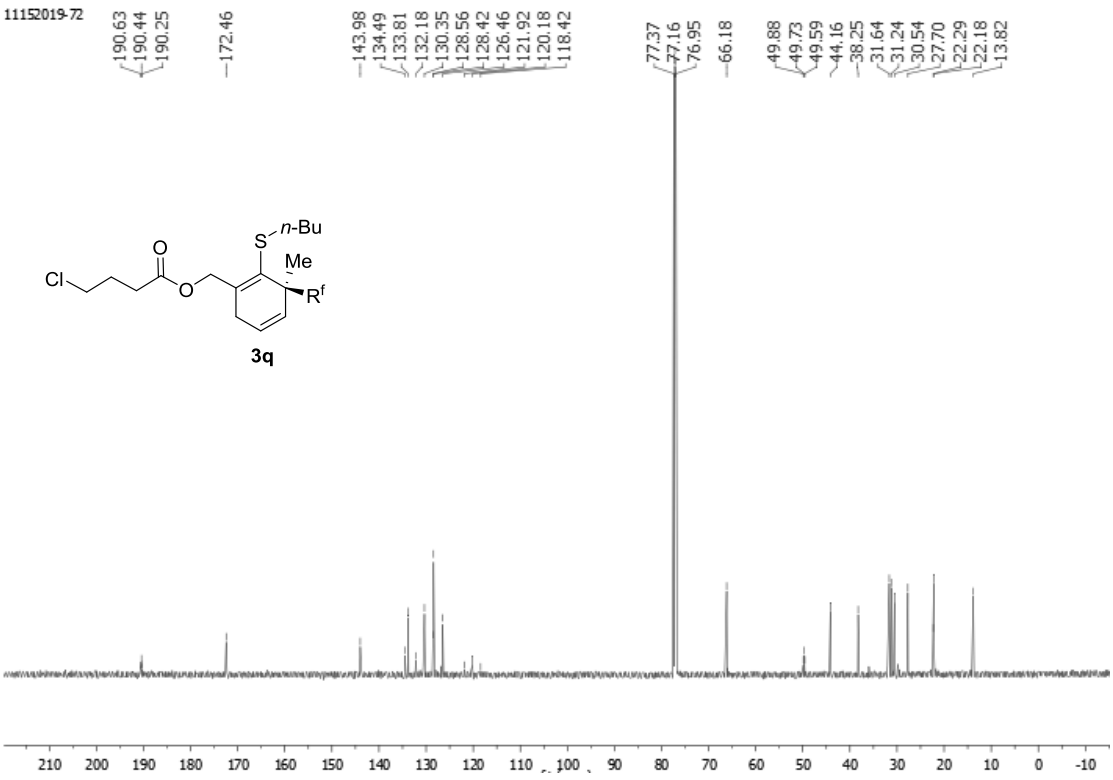
11112019-19



3p


103.68
104.13
104.34
104.79
n-Bu
S
Me
MeO
Rf
3p


7.96
7.92
7.58
7.56
7.44
7.43
7.42
7.26
5.88
5.87
5.69
5.69
5.68
5.67
5.03
5.01
4.95
4.93
3.62
3.61
3.60
2.57
2.57
2.52
2.51
2.50
2.11
2.10
1.65
0.89
0.87
0.86
n-Bu
S
Me
O
Cl
O
Rf
3q
1.89
1.00
1.91
0.97
0.99
0.95
0.91
2.20
0.99
1.18
2.12
1.96
2.17
3.04
2.27
2.19
3.01


11152019-72
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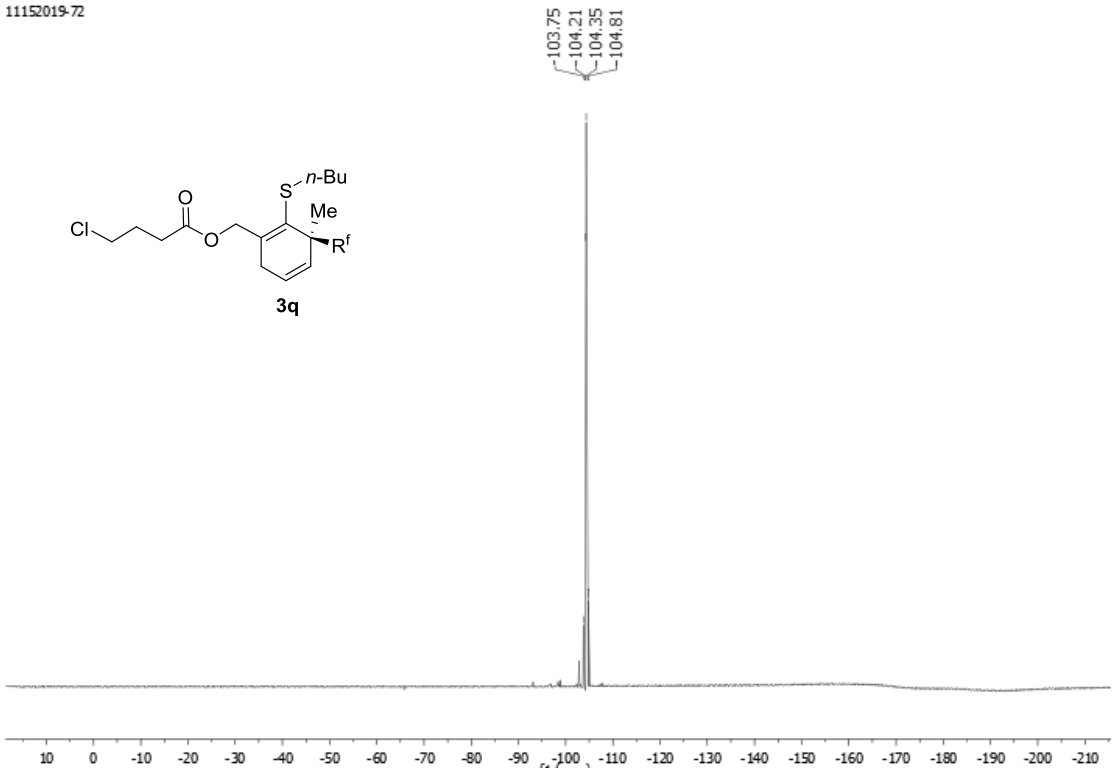
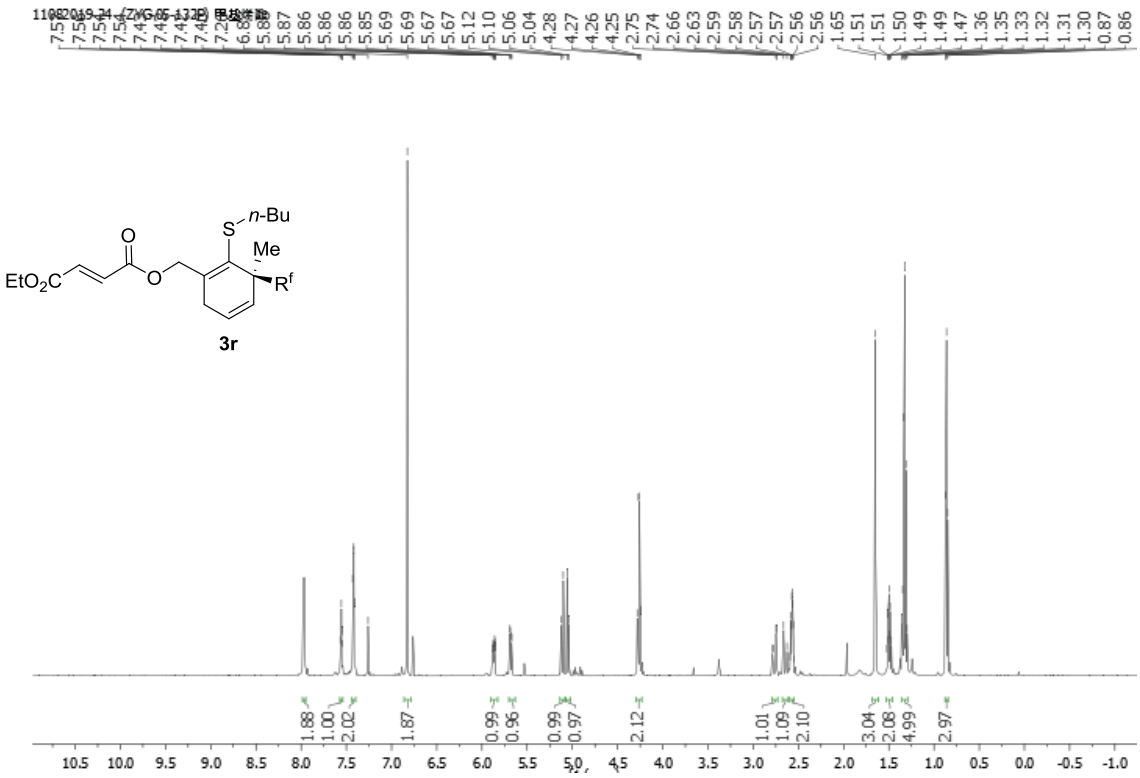
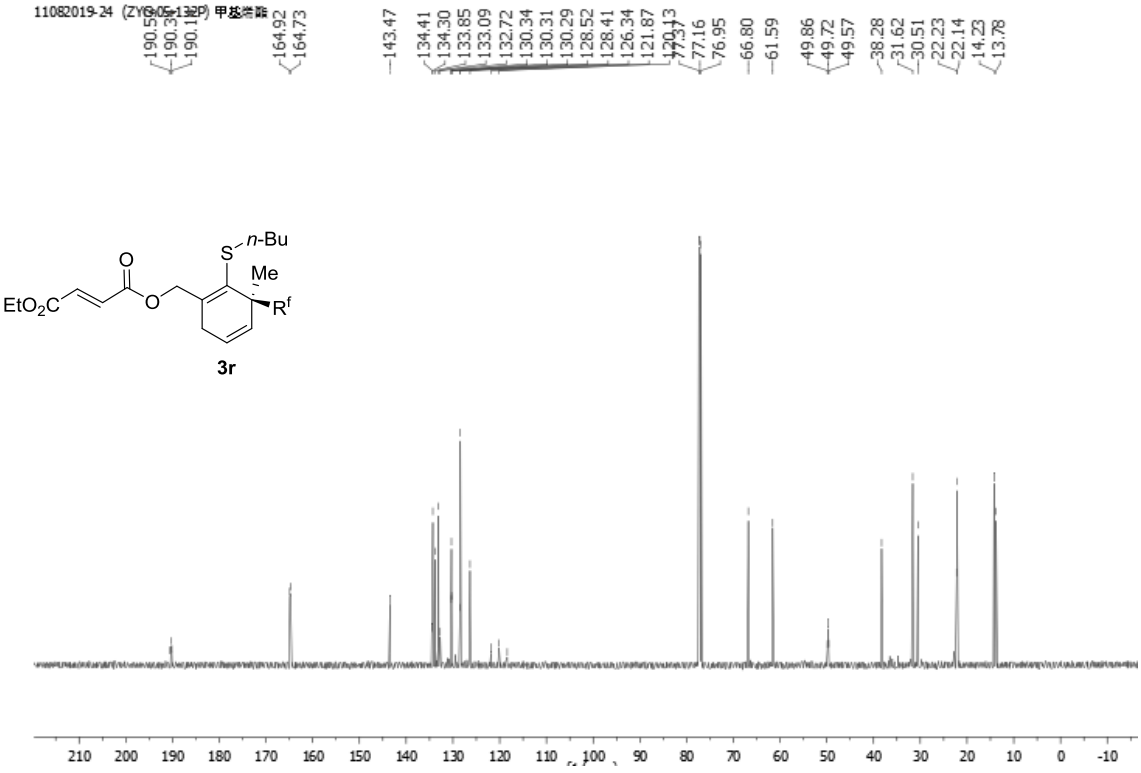
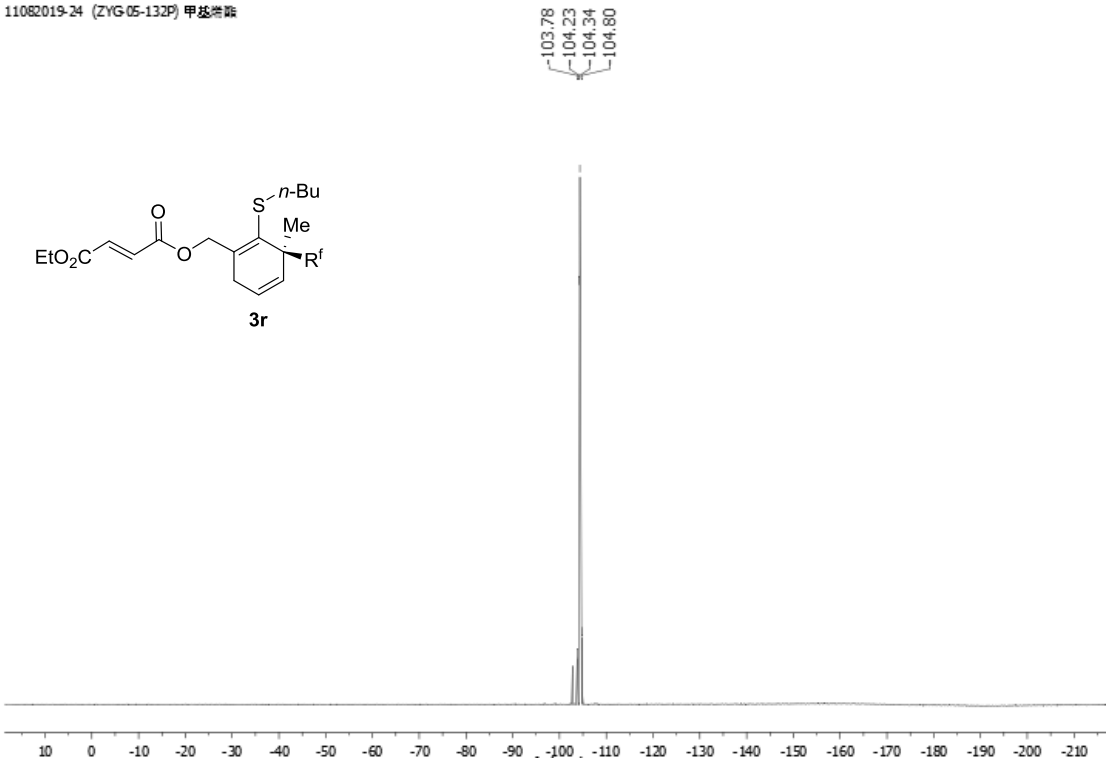
190.44
190.25
172.46
143.98
134.49
133.81
132.18
130.35
128.56
128.42
126.46
121.92
120.18
118.42
77.37
77.16
76.95
66.18
49.88
49.73
49.59
44.16
38.25
31.64
31.24
30.54
27.70
22.29
22.18
13.82
n-Bu
S
Me
Rf
O
O
Cl
3q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


11152019-72
103.75
104.21
104.35
104.81
n-Bu
S
Me
Rf
O
O
Cl
3q
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

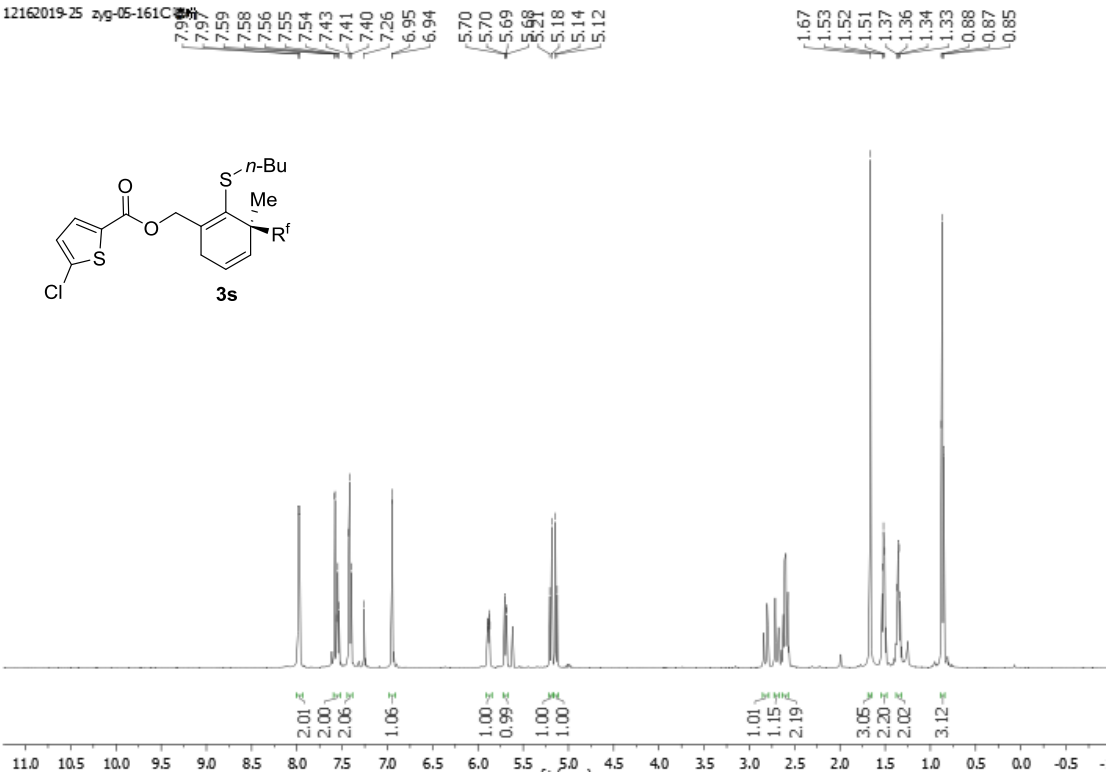

n-Bu
S
Me
O
EtO2C
O
Rf
3r

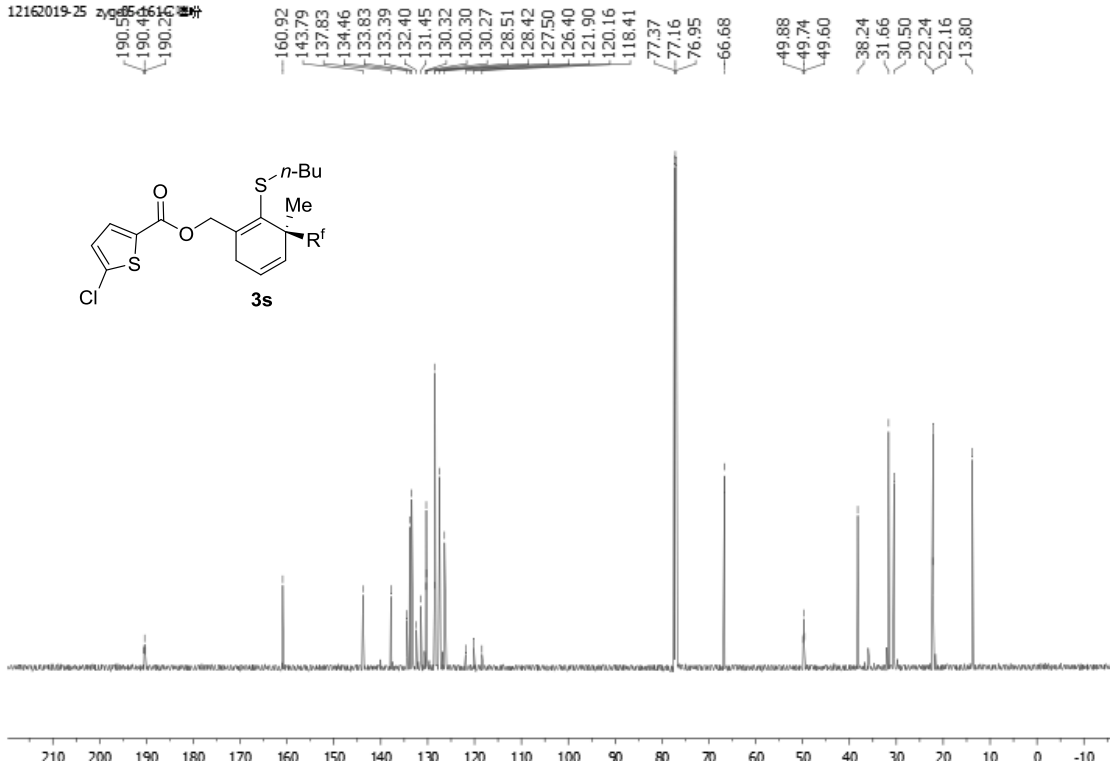

n-Bu
S
Me
O
EtO2C
O
Rf
3r

11082019-24 (ZYG-05-132P) 甲基萘酯

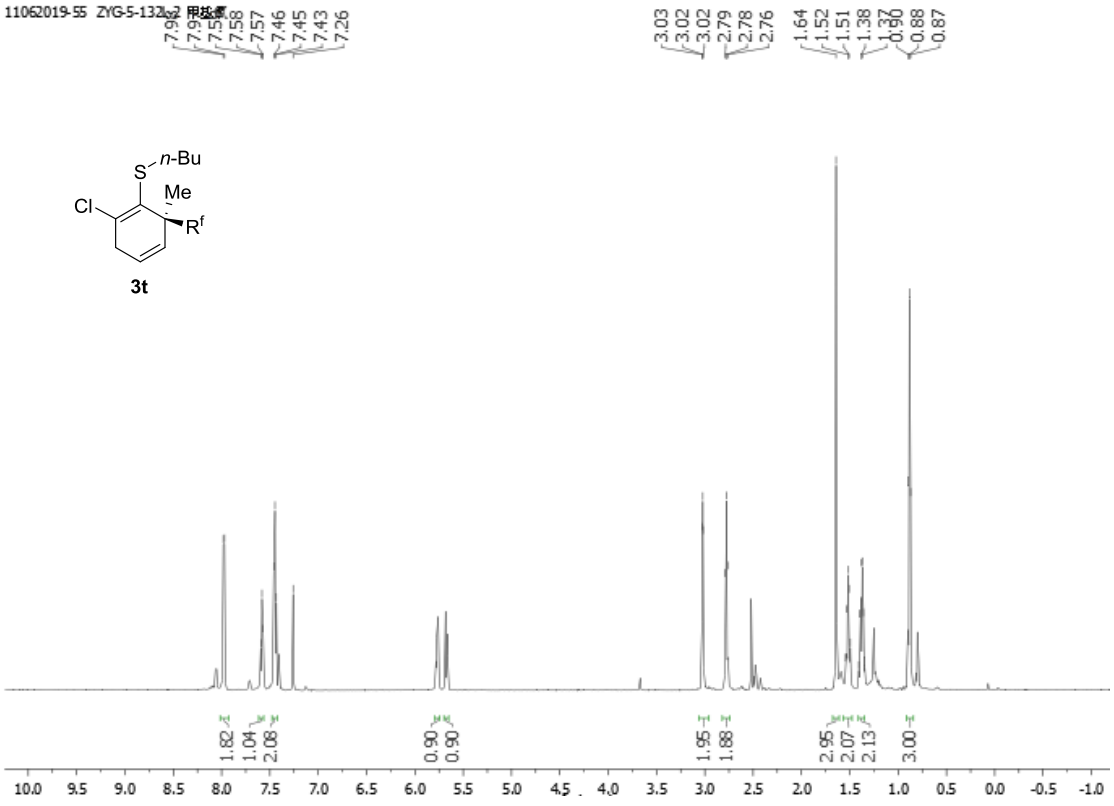


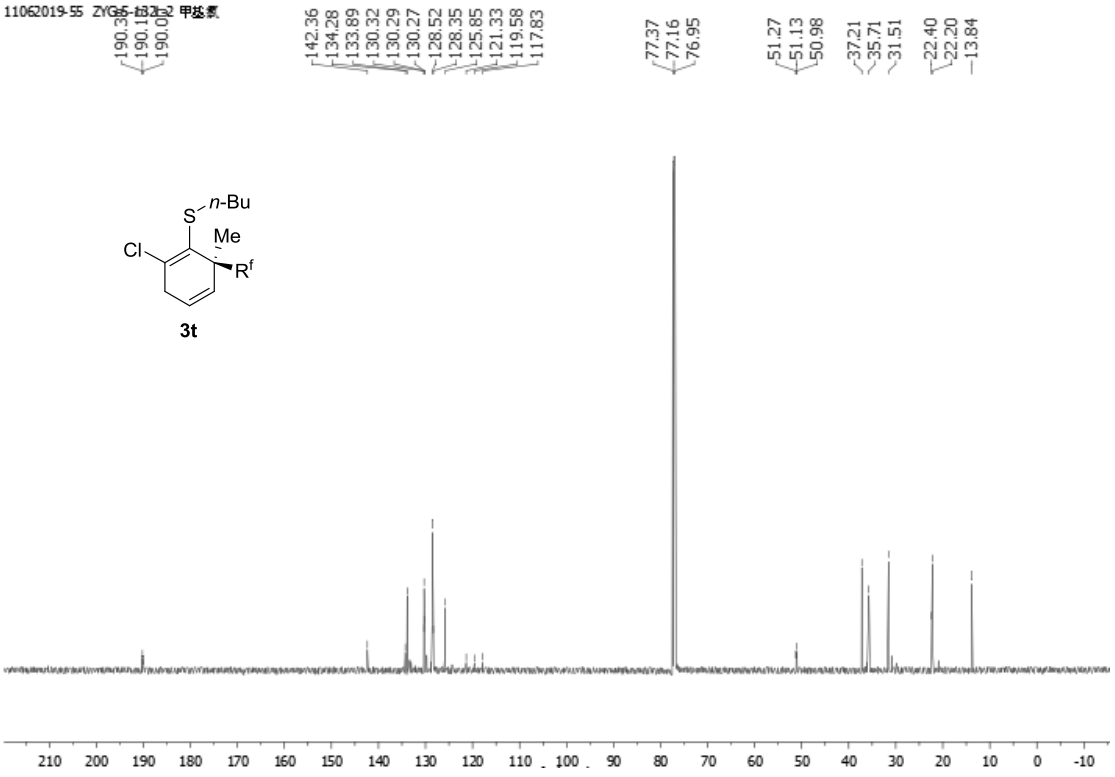
12162019-25 zyg-05-161C萘环

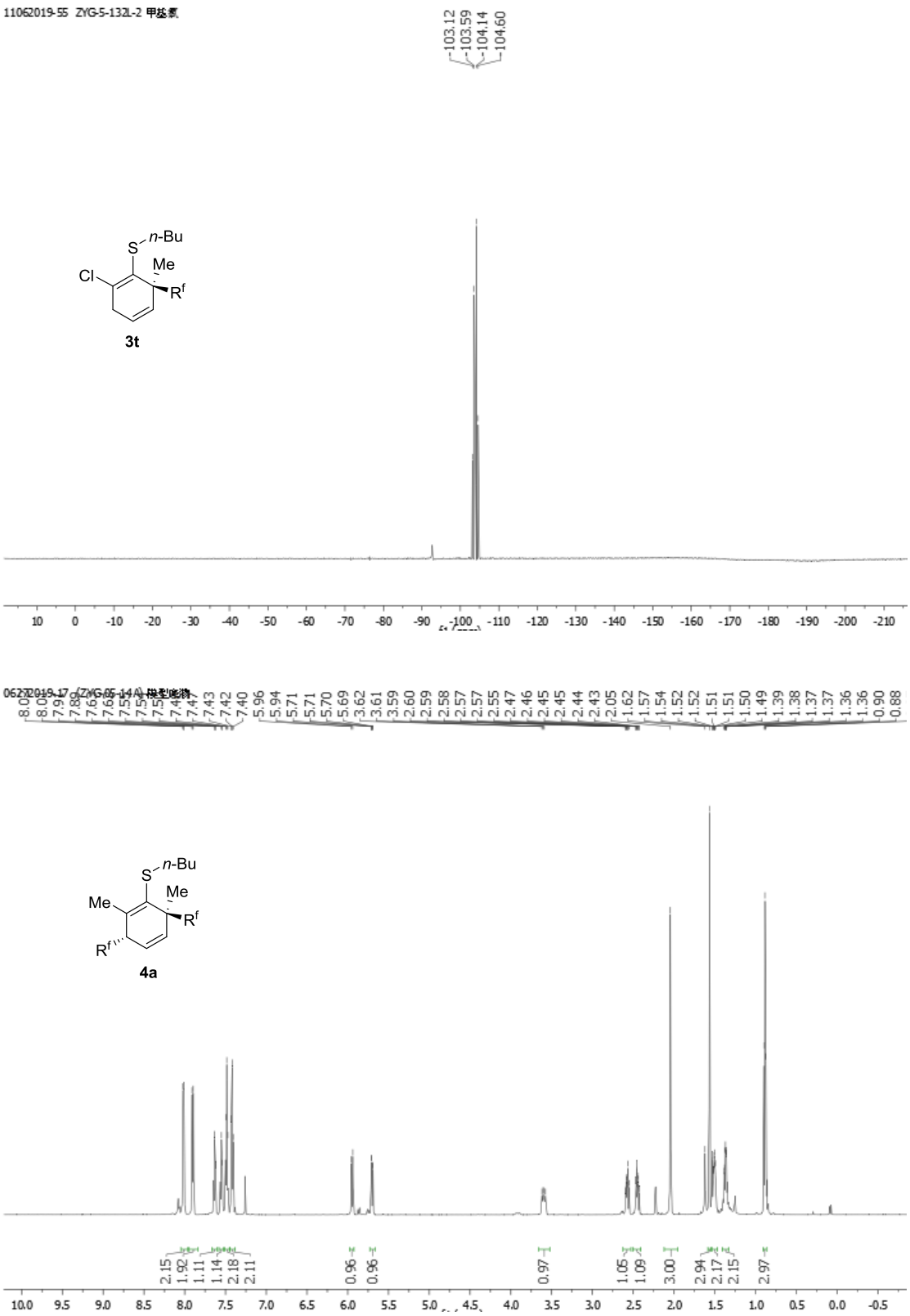


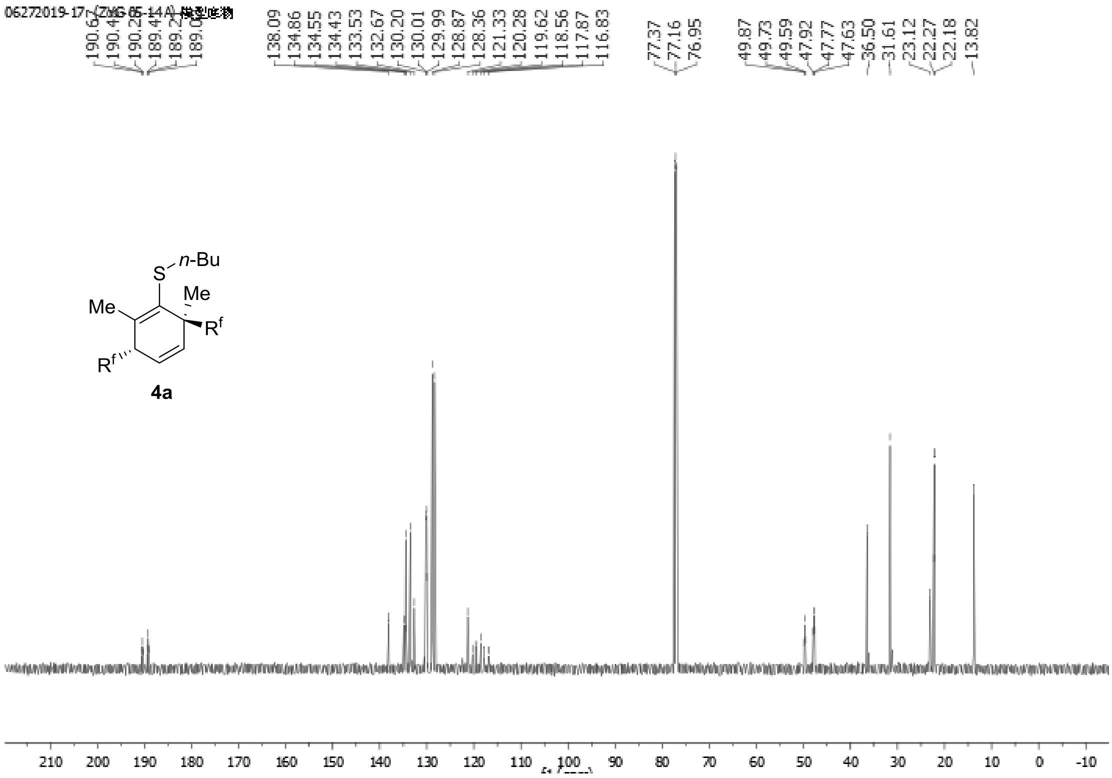

12162019-25
190.50
190.40
190.22
160.92
143.79
137.83
134.46
133.83
133.39
132.40
131.45
130.32
130.30
130.27
128.51
128.42
127.50
126.40
121.90
120.16
118.41
77.37
77.16
76.95
66.68
49.88
49.74
49.60
38.24
31.66
30.50
22.24
22.16
13.80
n-Bu
S
Me
O
O
S
Cl
Rf
3s

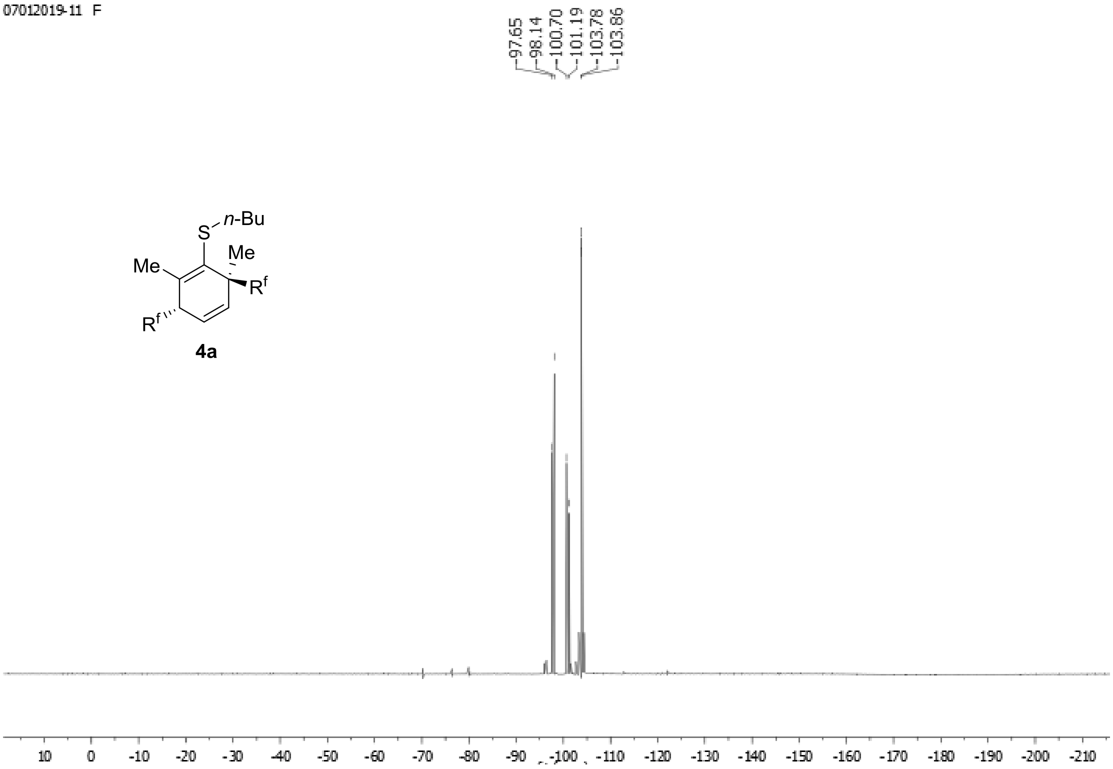

12162019-25
103.82
104.27
104.42
104.88
n-Bu
S
Me
O
O
S
Cl
Rf
3s

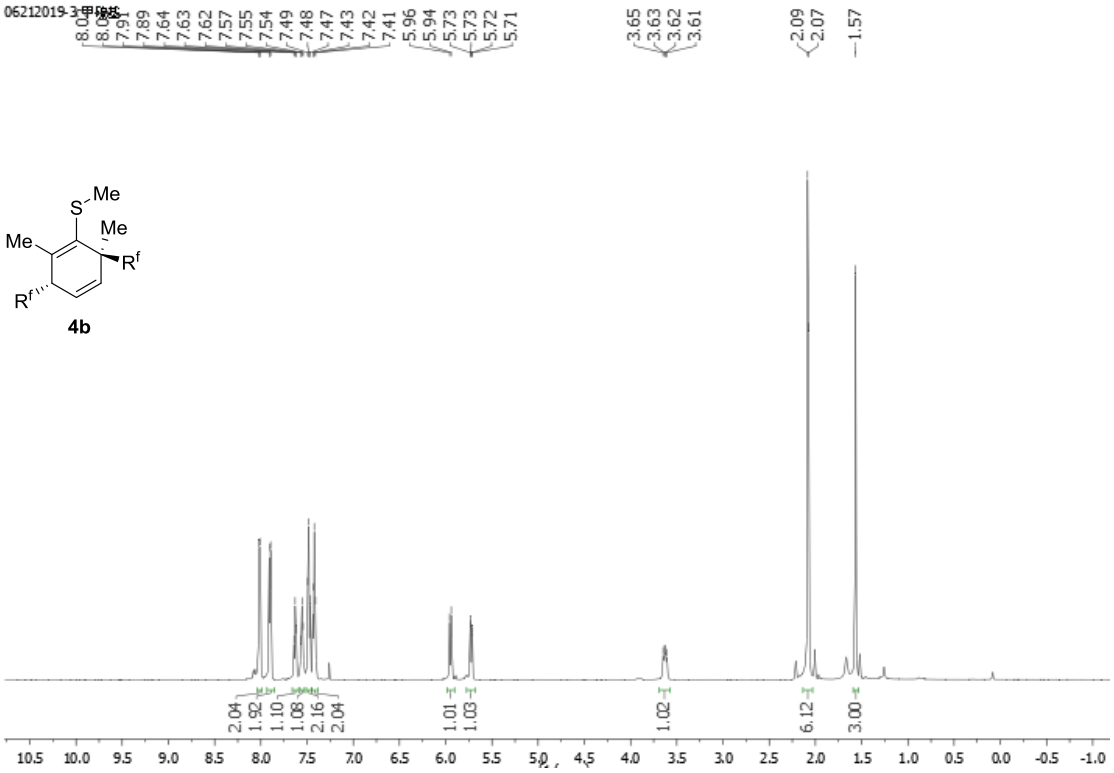

11062019-55 ZYG-5-132-2 甲基苯
7.94
7.57
7.46
7.45
7.43
7.26
3.03
3.02
3.02
2.79
2.78
2.76
1.64
1.52
1.51
1.38
1.37
0.90
0.88
0.87
S
n-Bu
Me
Cl
R^f
3t
1.82
1.04
2.08
0.90
0.90
1.95
1.88
2.95
2.07
2.13
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

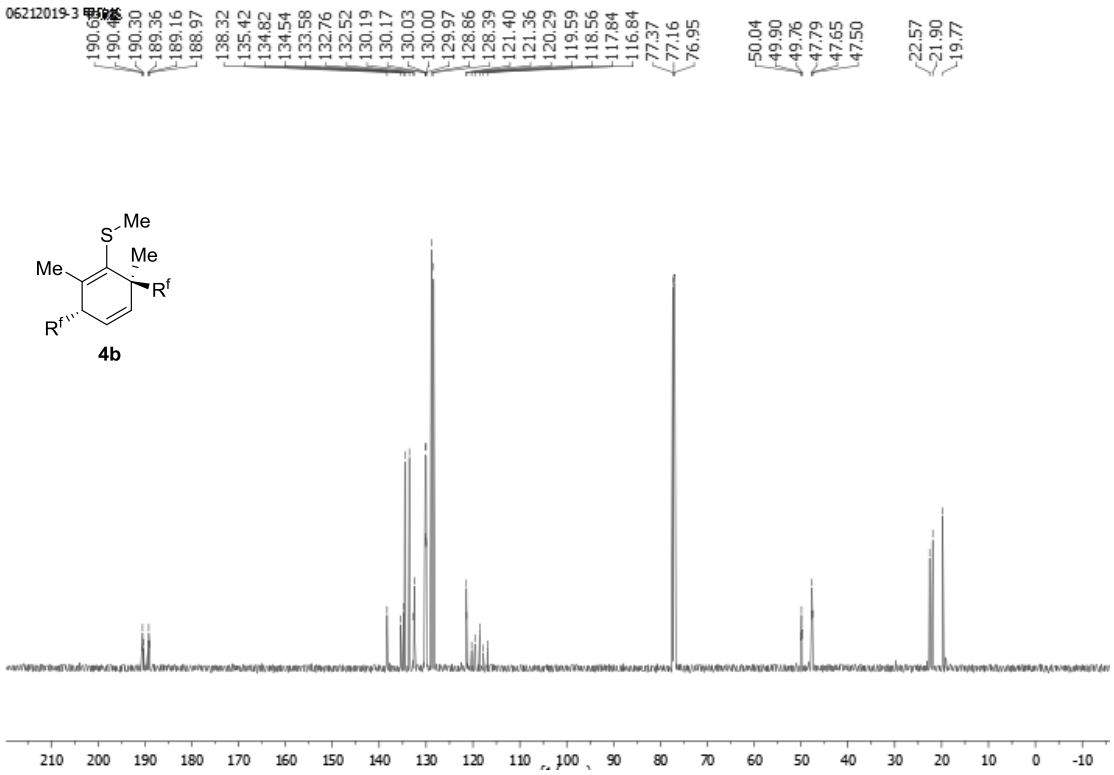

11062019-55 ZYG-5-132-2 甲基苯
190.36
190.18
190.00
142.36
134.28
133.89
130.32
130.29
130.27
128.52
128.35
125.85
121.33
119.58
117.83
77.37
77.16
76.95
51.27
51.13
50.98
37.21
35.71
31.51
22.40
22.20
13.84
S
n-Bu
Me
Cl
R^f
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


11062019-55 ZYG-5-132L-2 甲基氢
103.12
103.59
104.14
104.60
n-Bu
S
Me
Cl
Rf
3t
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
8.07 8.05 7.91 7.88 7.63 7.61 7.55 7.53 7.50 7.48 7.47 7.43 7.42 7.40 5.96 5.94 5.71 5.70 5.69 3.62 3.61 3.59 2.60 2.59 2.58 2.57 2.57 2.55 2.47 2.46 2.45 2.45 2.44 2.43 2.05 1.62 1.57 1.54 1.52 1.52 1.51 1.51 1.50 1.49 1.39 1.38 1.37 1.37 1.36 1.36 0.90 0.88
n-Bu
S
Me
Me
Rf
Rf
4a
2.15 1.92 1.11 1.14 2.18 2.11 0.96 0.96 0.97 1.05 1.09 3.00 2.94 2.17 2.15 2.97
10.0 9.5 9.0 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 -0.5


06272019-17
190.6
190.4
190.20
189.4
189.2
189.0
138.09
134.86
134.55
134.43
133.53
132.67
130.20
130.01
129.99
128.87
128.36
121.33
120.28
119.62
118.56
117.87
116.83
77.37
77.16
76.95
49.87
49.73
49.59
47.92
47.77
47.63
36.50
31.61
23.12
22.27
22.18
13.82
S
n-Bu
Me
Me
R^f
R^f
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


07012019-11 F
-97.65
-98.14
-100.70
-101.19
-103.78
-103.86
S
n-Bu
Me
Me
R^f
R^f
4a
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


8.01
8.00
7.91
7.89
7.64
7.63
7.62
7.57
7.55
7.54
7.49
7.48
7.47
7.43
7.42
7.41
5.96
5.94
5.73
5.72
5.71
3.65
3.63
3.62
3.61
2.09
2.07
1.57
Me
S
Me
Me
R^f
R^f
4b
2.04
1.92
1.10
1.08
2.16
2.04
1.01
1.03
1.02
6.12
3.00


190.63
190.30
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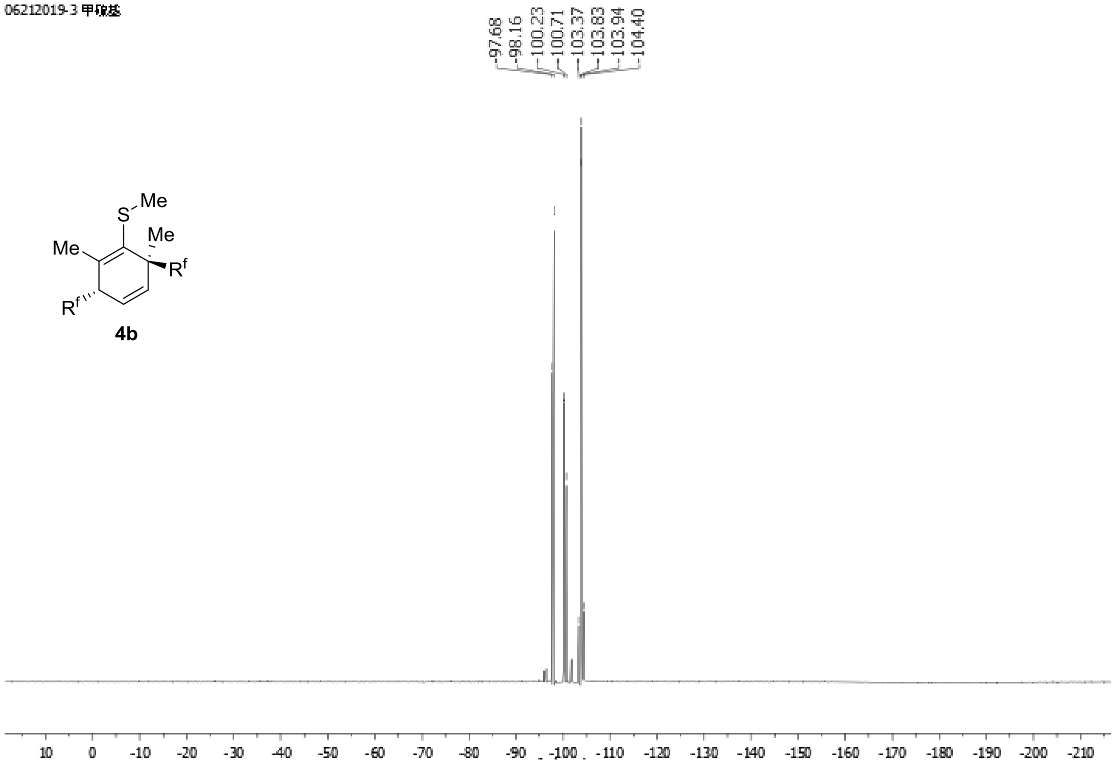
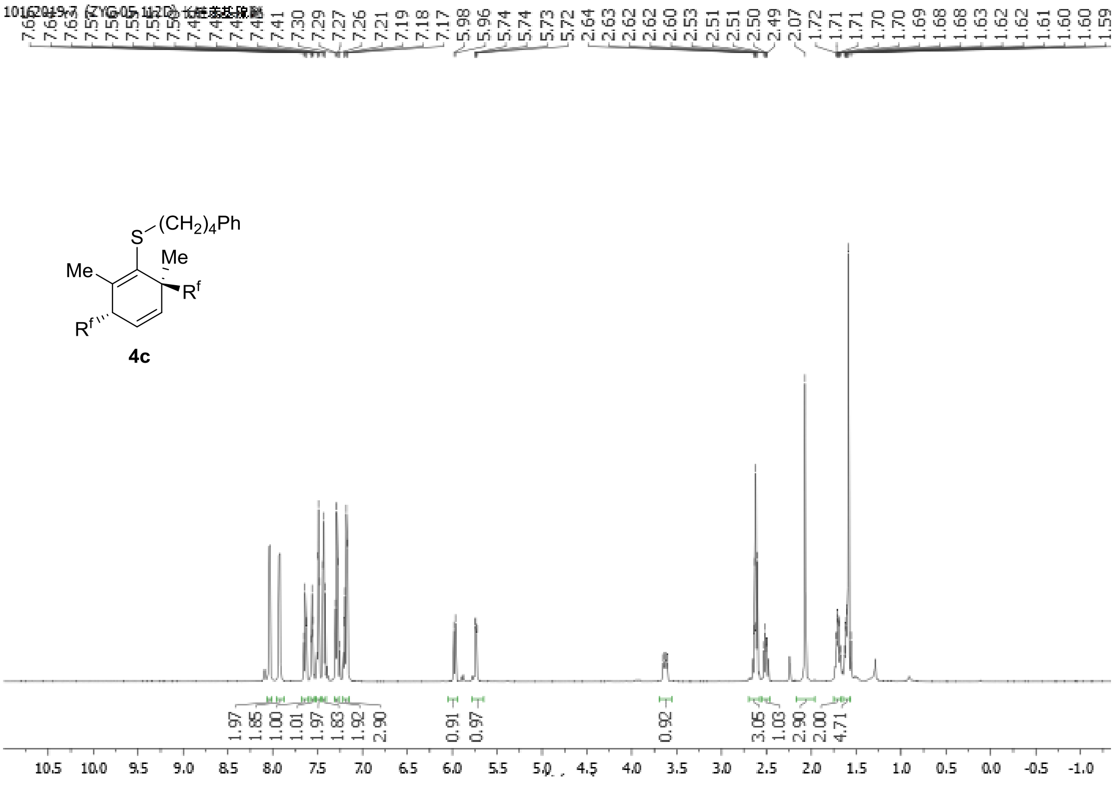
189.16
188.97
138.32
135.42
134.82
134.54
133.58
132.76
132.52
130.19
130.17
130.03
130.00
129.97
128.86
128.39
121.40
121.36
120.29
119.59
118.56
117.84
116.84
77.37
77.16
76.95
50.04
49.90
49.76
47.79
47.65
47.50
22.57
21.90
19.77
Me
S
Me
Me
R^f
R^f
4b


06212019-3
-97.68
-98.16
-100.23
-100.71
-103.37
-103.83
-103.94
-104.40
S
Me
Me
Me
Rf
Rf
4b
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


7.41
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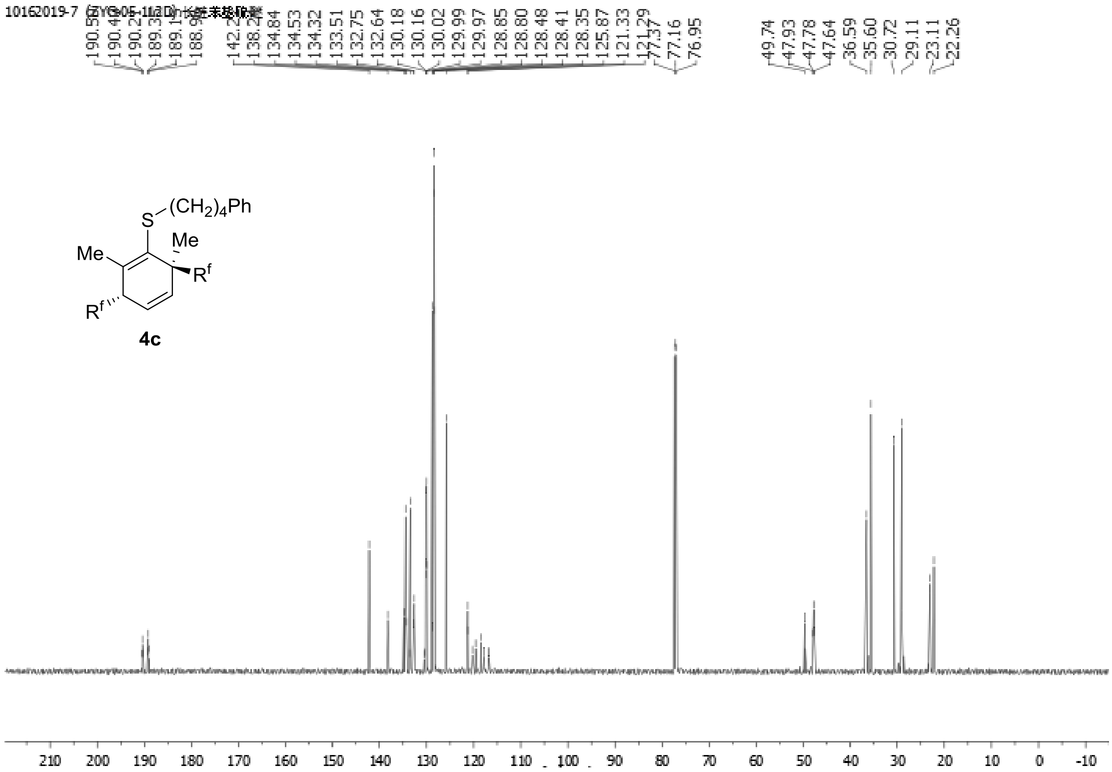
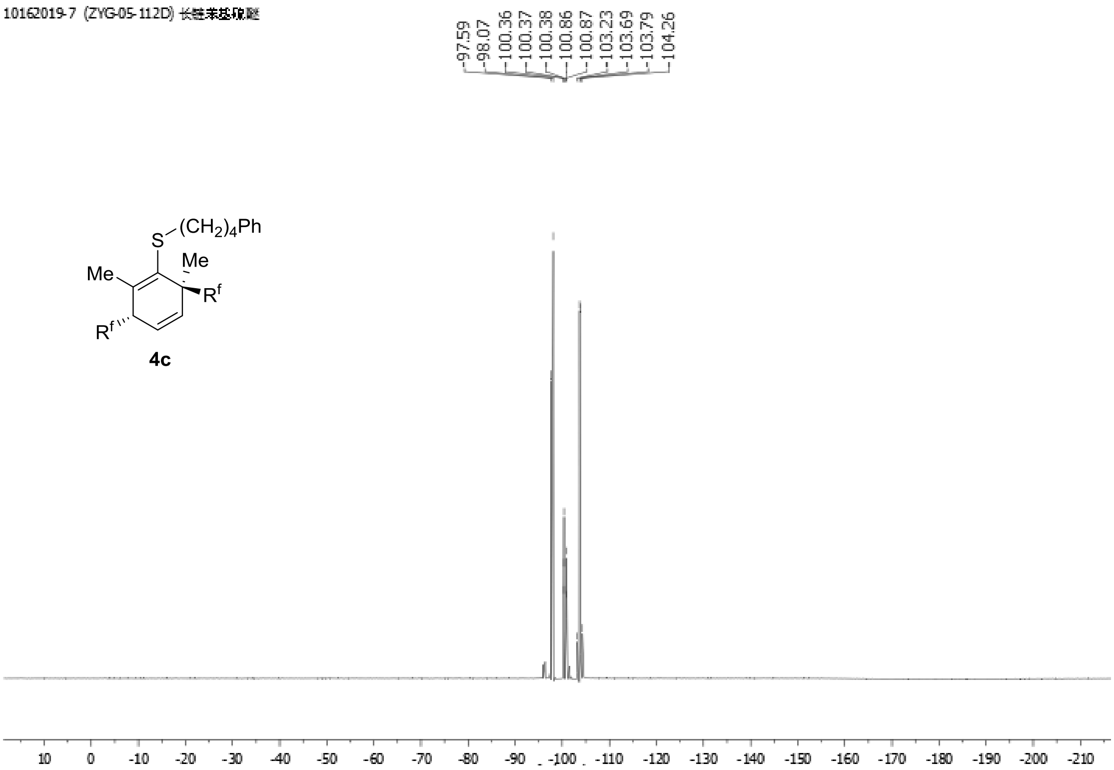
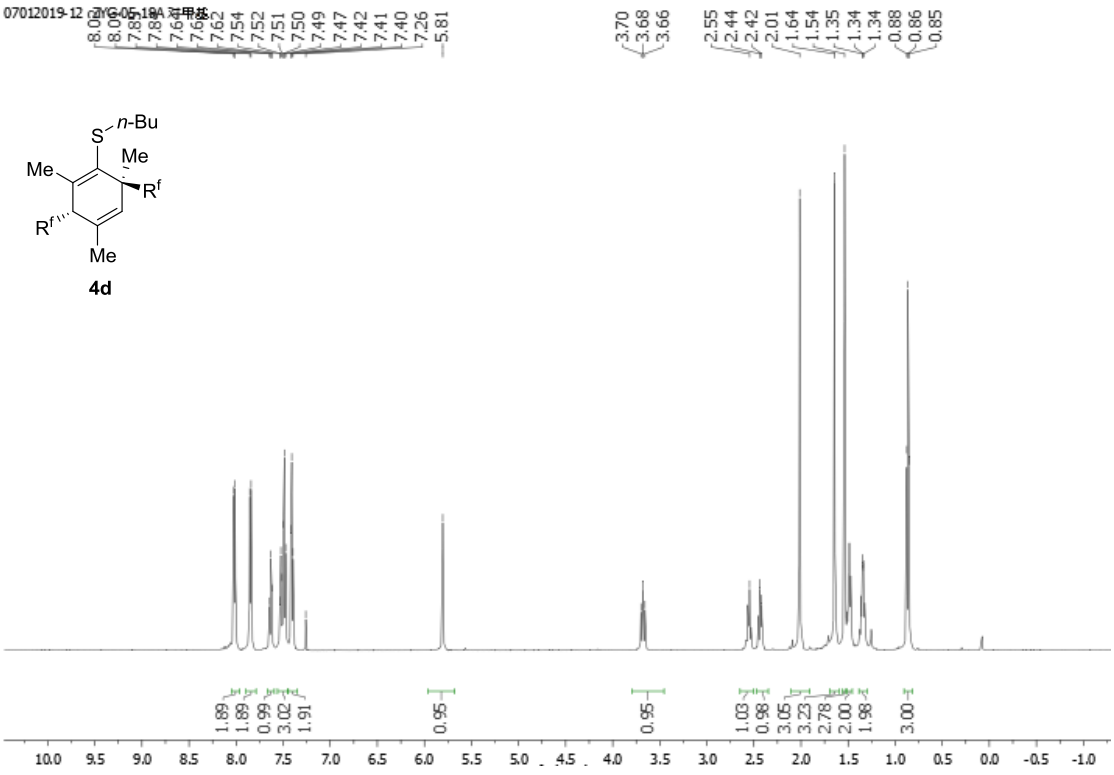
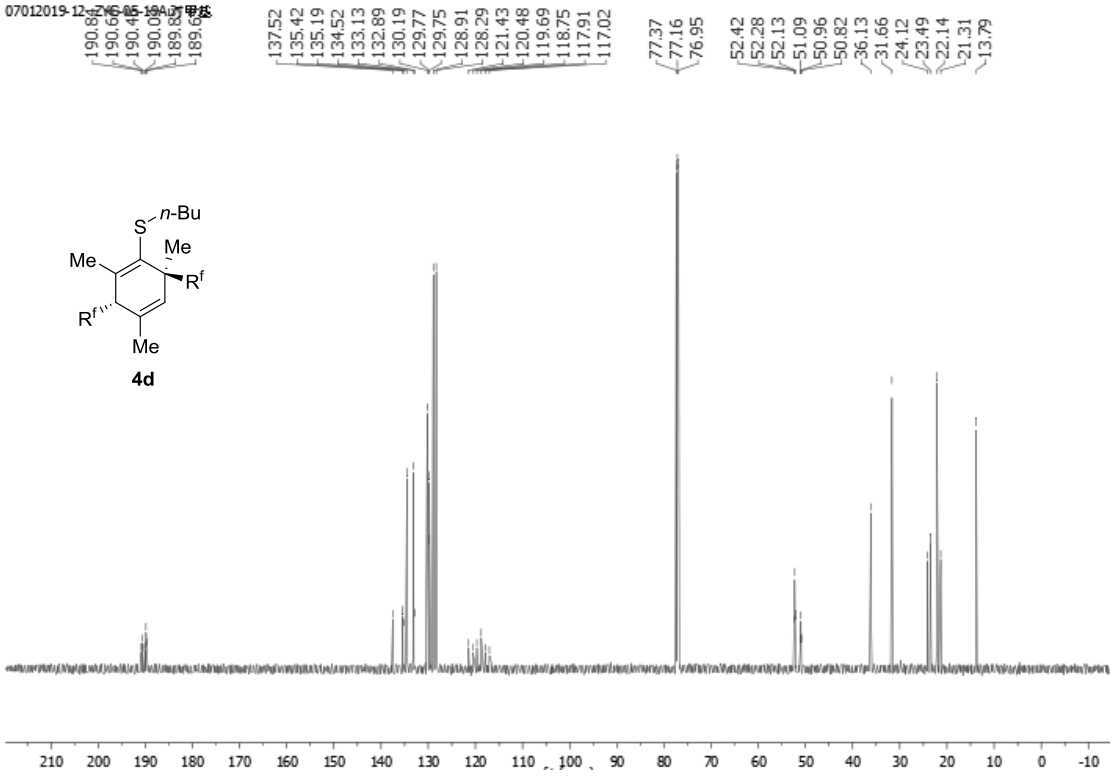
7.29
7.27
7.26
7.21
7.19
7.18
7.17
5.98
5.96
5.74
5.74
5.73
5.72
2.64
2.63
2.62
2.60
2.53
2.51
2.51
2.50
2.49
2.07
1.72
1.71
1.71
1.70
1.70
1.69
1.68
1.68
1.63
1.62
1.62
1.61
1.60
1.60
1.59
S
(CH2)4Ph
Me
Me
Rf
Rf
4c
1.97
1.85
1.00
1.01
1.97
1.83
1.92
2.90
0.91
0.97
0.92
3.05
1.03
2.90
2.00
4.71
10.5 10.0 9.5 9.0 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 -0.5 -1.0


10162019-7
134.84
134.53
134.32
133.51
132.75
132.64
130.18
130.16
130.02
129.99
129.97
128.85
128.80
128.48
128.41
128.35
125.87
121.33
77.37
77.16
76.95
49.74
47.93
47.78
47.64
36.59
35.60
30.72
29.11
23.11
22.26
S
(CH2)4Ph
Me
Me
Rf
Rf
4c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

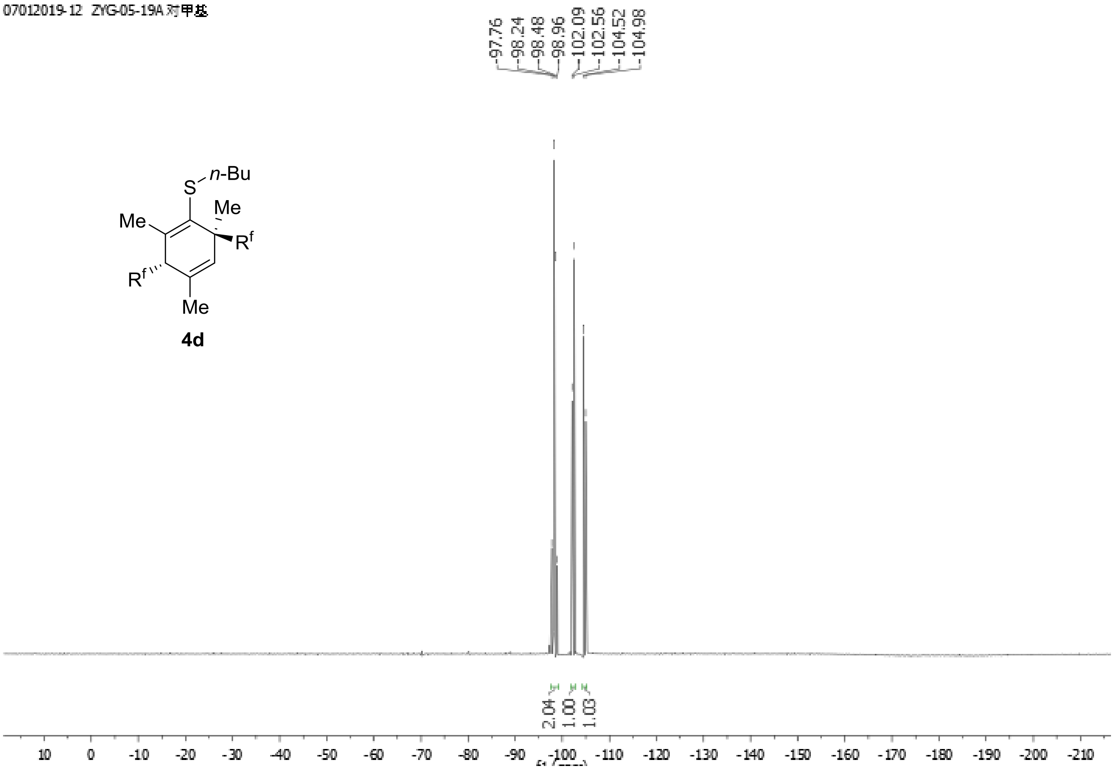

10162019-7 (ZYG-05-112D) 长链苯基硫醚
-97.59
-98.07
-100.36
-100.37
-100.38
-100.86
-100.87
-103.23
-103.69
-103.79
-104.26
S
(CH2)4Ph
Me
Me
Rf
Rf
4c
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210



4d

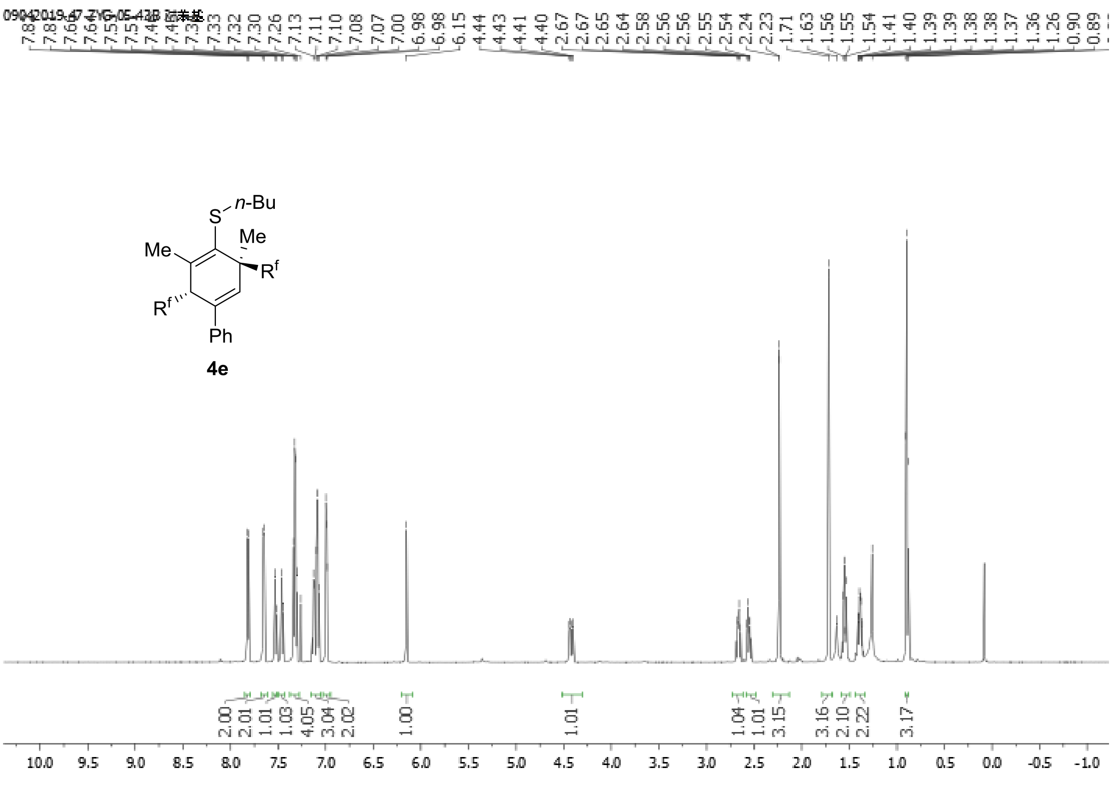


4d



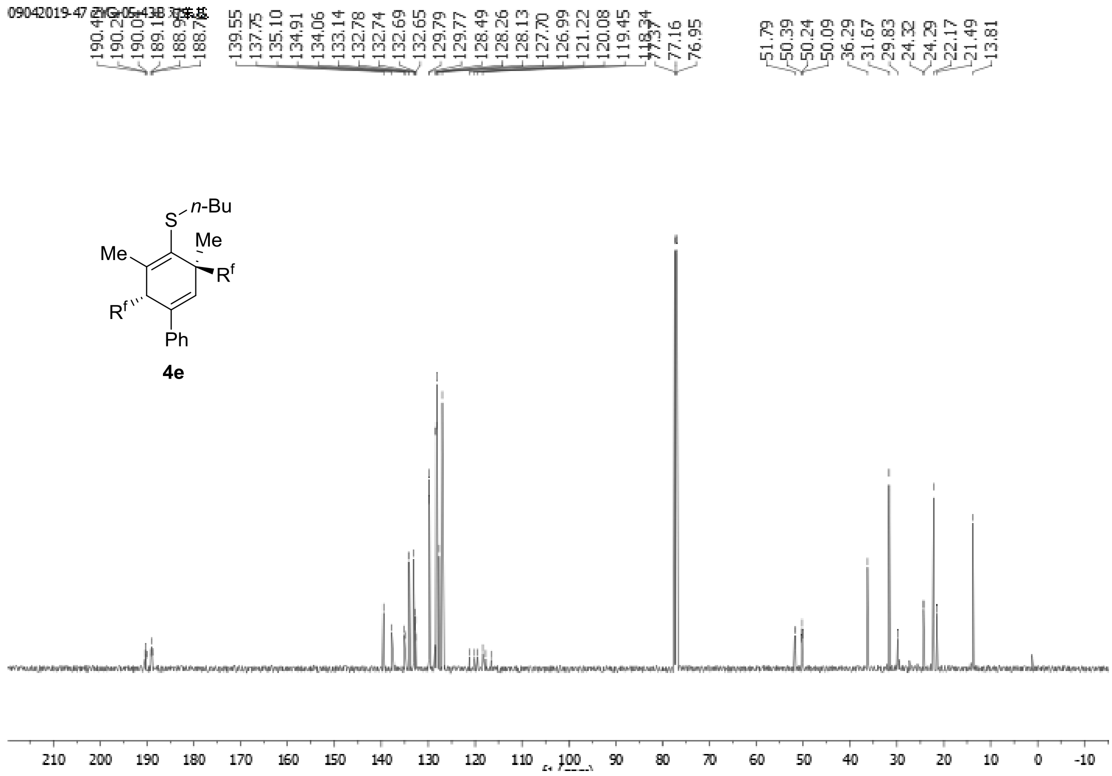
07012019-12 ZYG-05-19A
S
n-Bu
Me
Me
R^f
R^f
Me

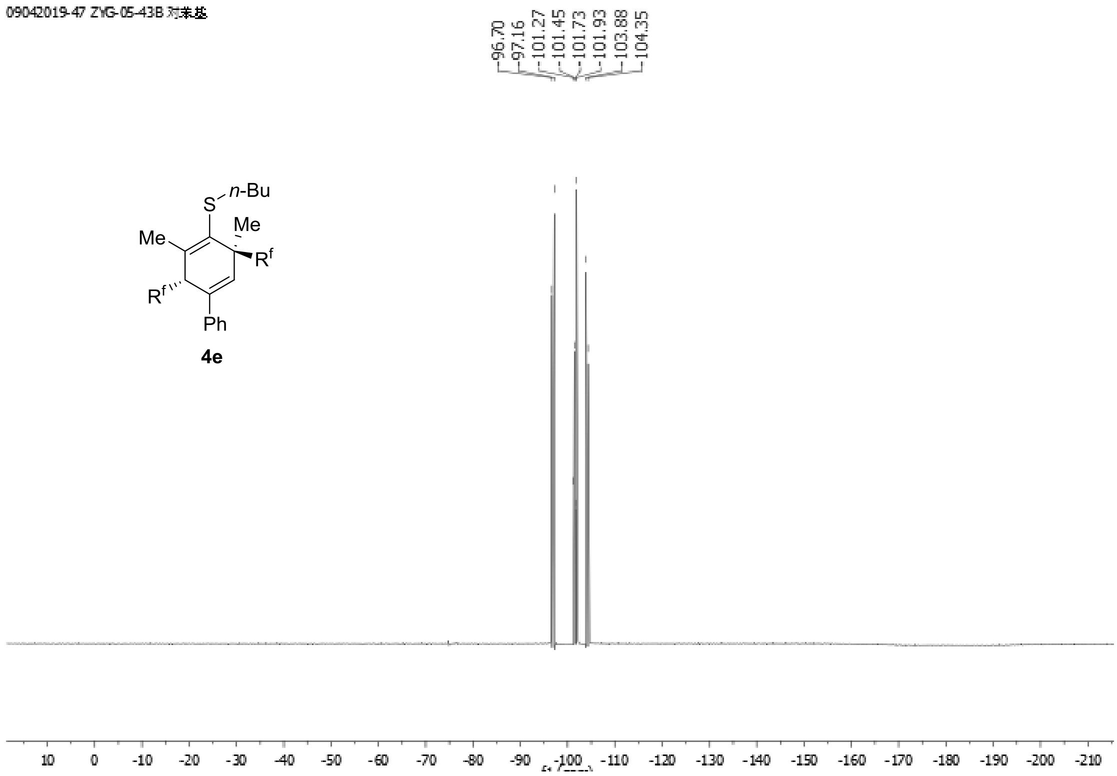
4d

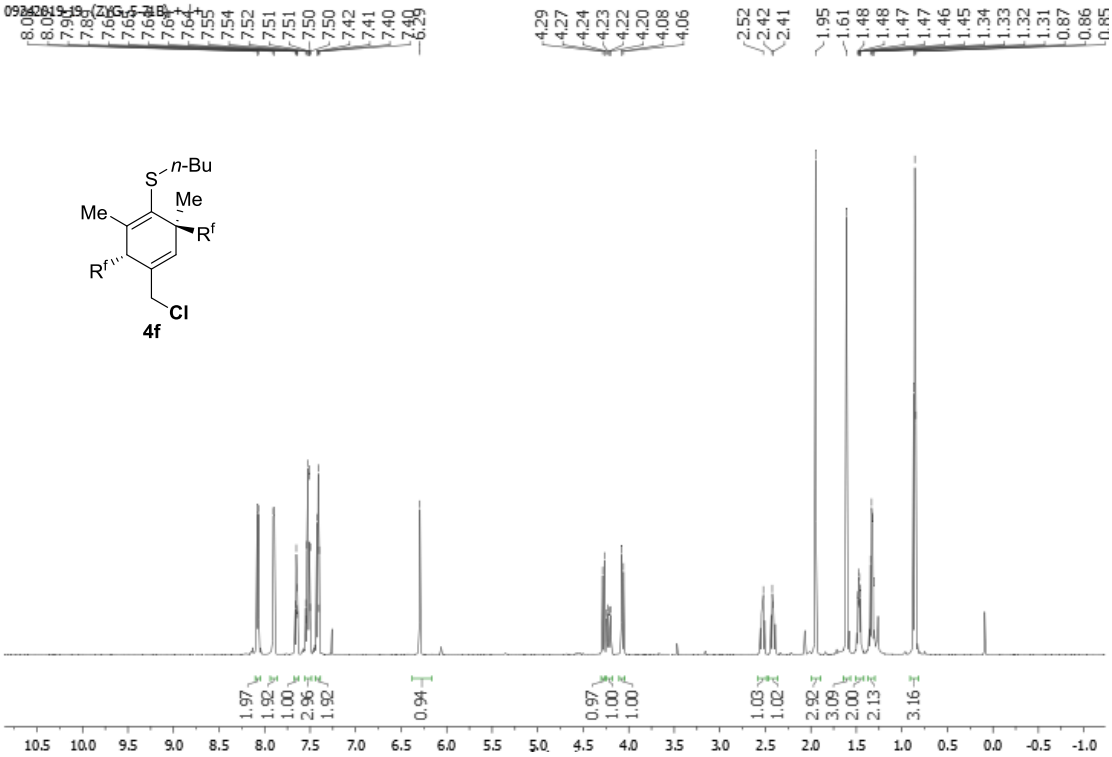


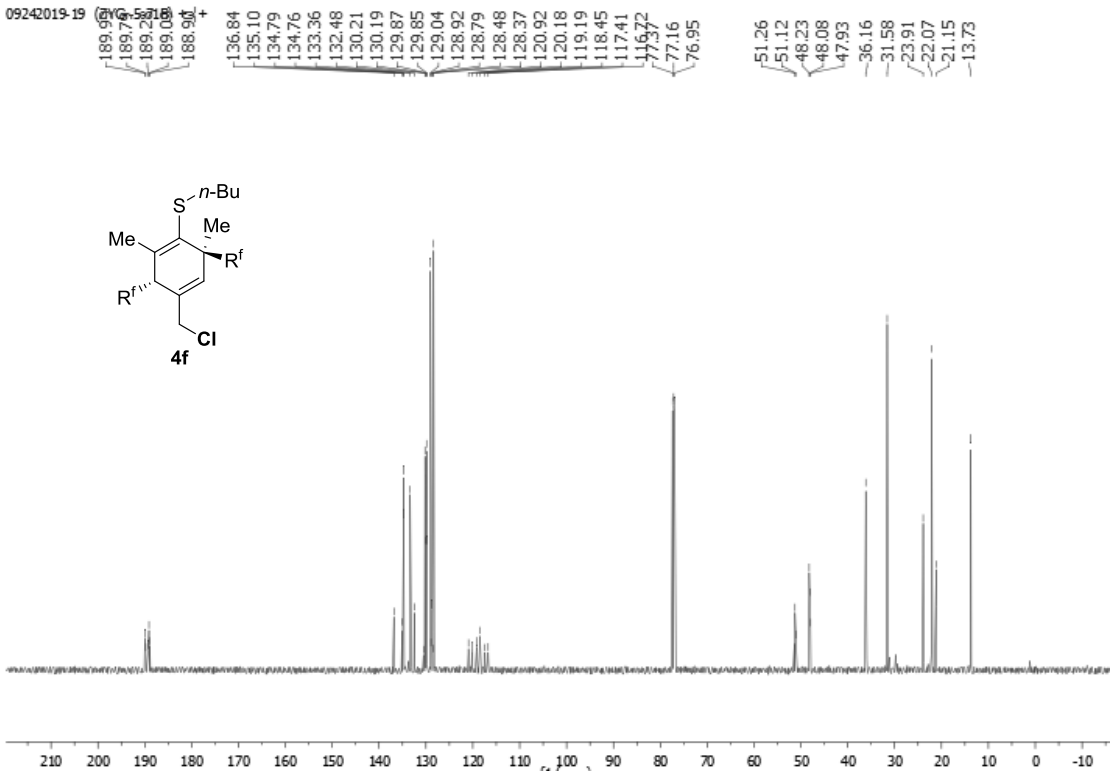
09042019-47 ZYG-05-43B
S
n-Bu
Me
Me
R^f
R^f
Ph

4e


09042019-47 ZYG-05-43B
190.4 190.2 190.0 189.1 188.9 188.7 139.55 137.75 135.10 134.91 134.06 133.14 132.78 132.74 132.69 132.65 129.79 129.77 128.49 128.26 128.13 127.70 126.99 121.22 120.08 119.45 118.34 77.37 77.16 76.95 51.79 50.39 50.24 50.09 36.29 31.67 29.83 24.32 24.29 22.17 21.49 13.81
S n-Bu
Me
Me
Rf
Rf
Ph
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

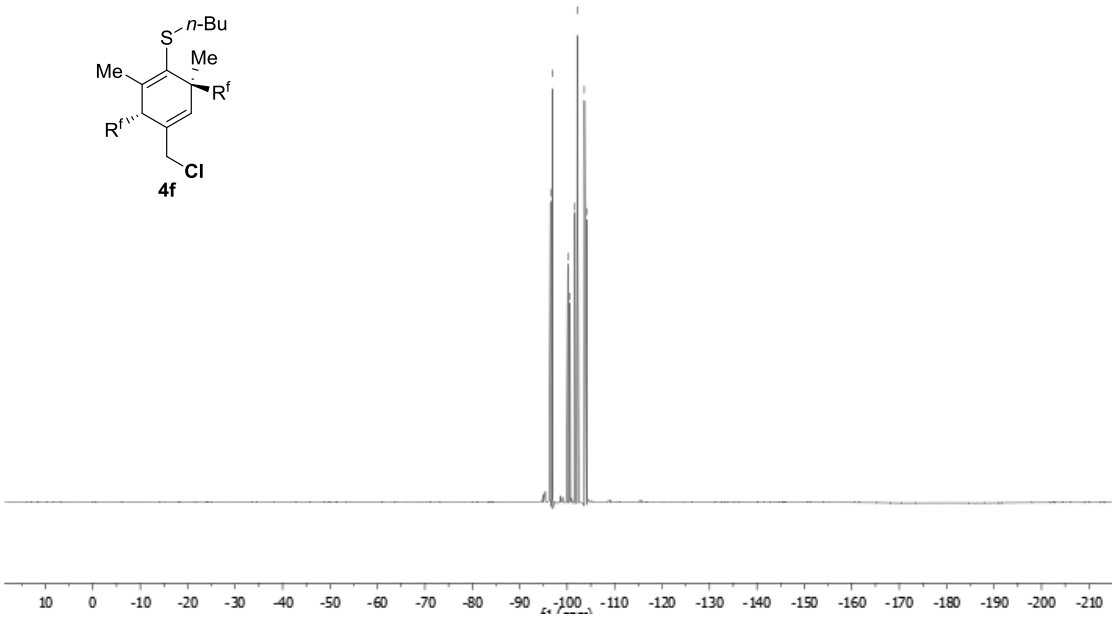

09042019-47 ZYG-05-43B
-96.70 -97.16 -101.27 -101.45 -101.73 -101.93 -103.88 -104.35
S n-Bu
Me
Me
Rf
Rf
Ph
4e
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


4f

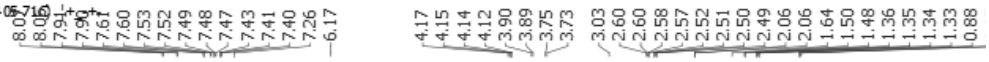

4f

09242019-19 (ZYG-5-71B) +-¦+

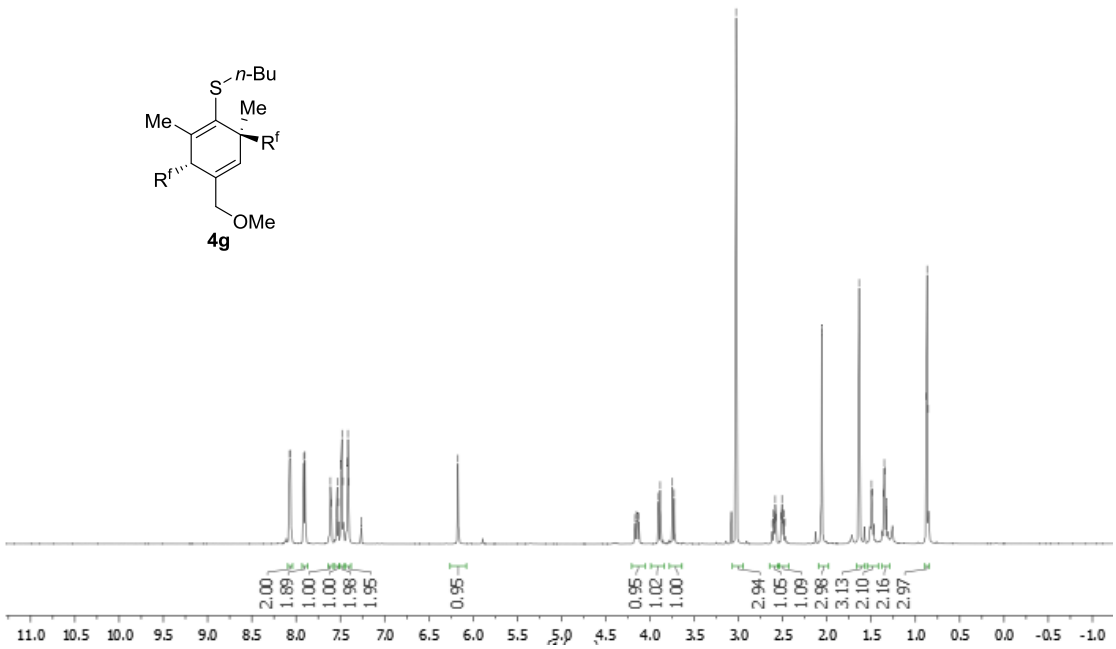
4f

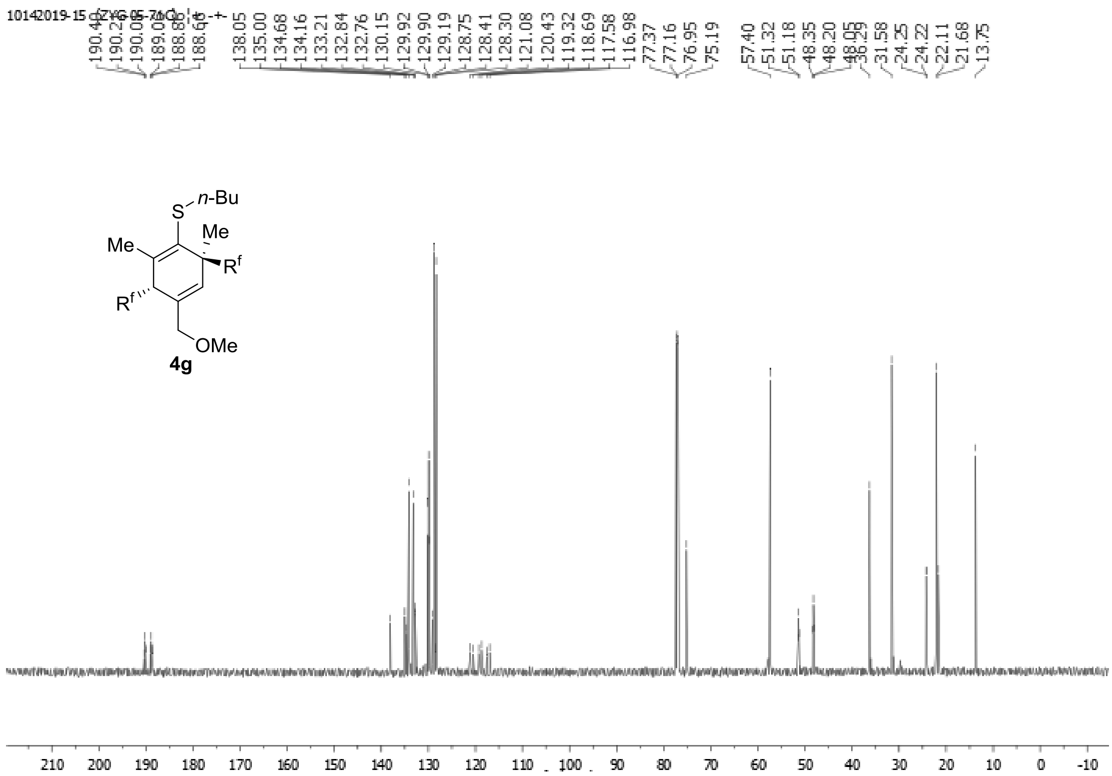


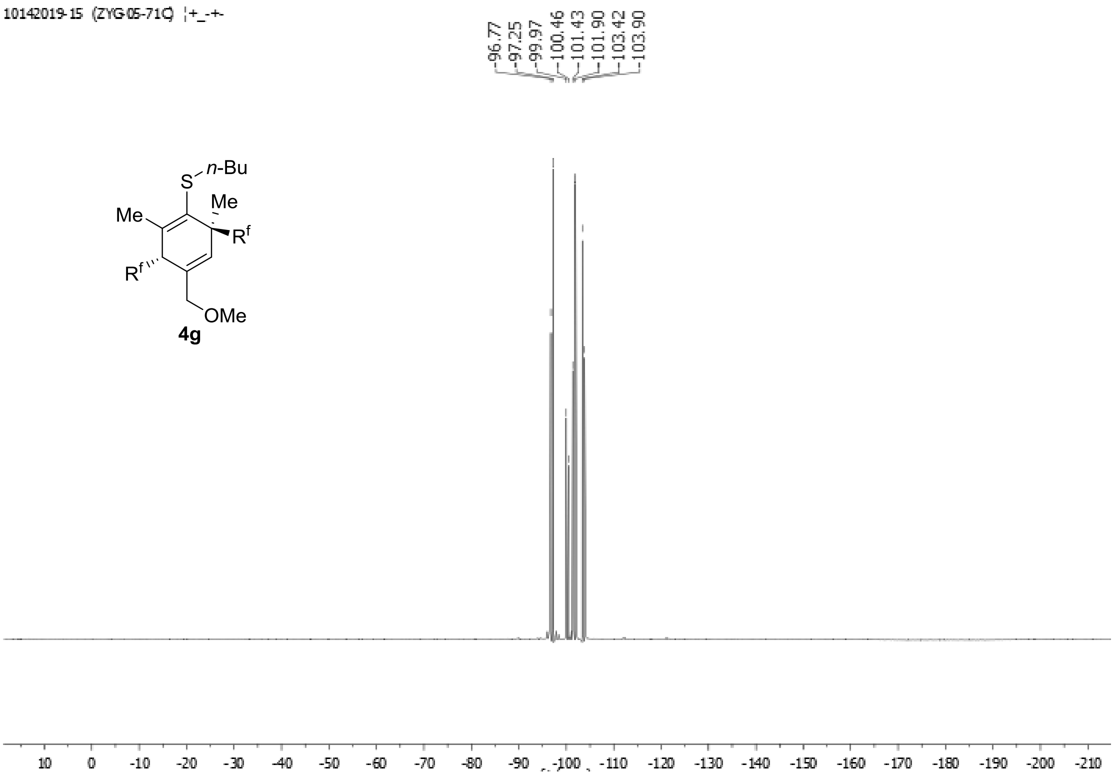
10142019-15 (ZYG-05-71C)

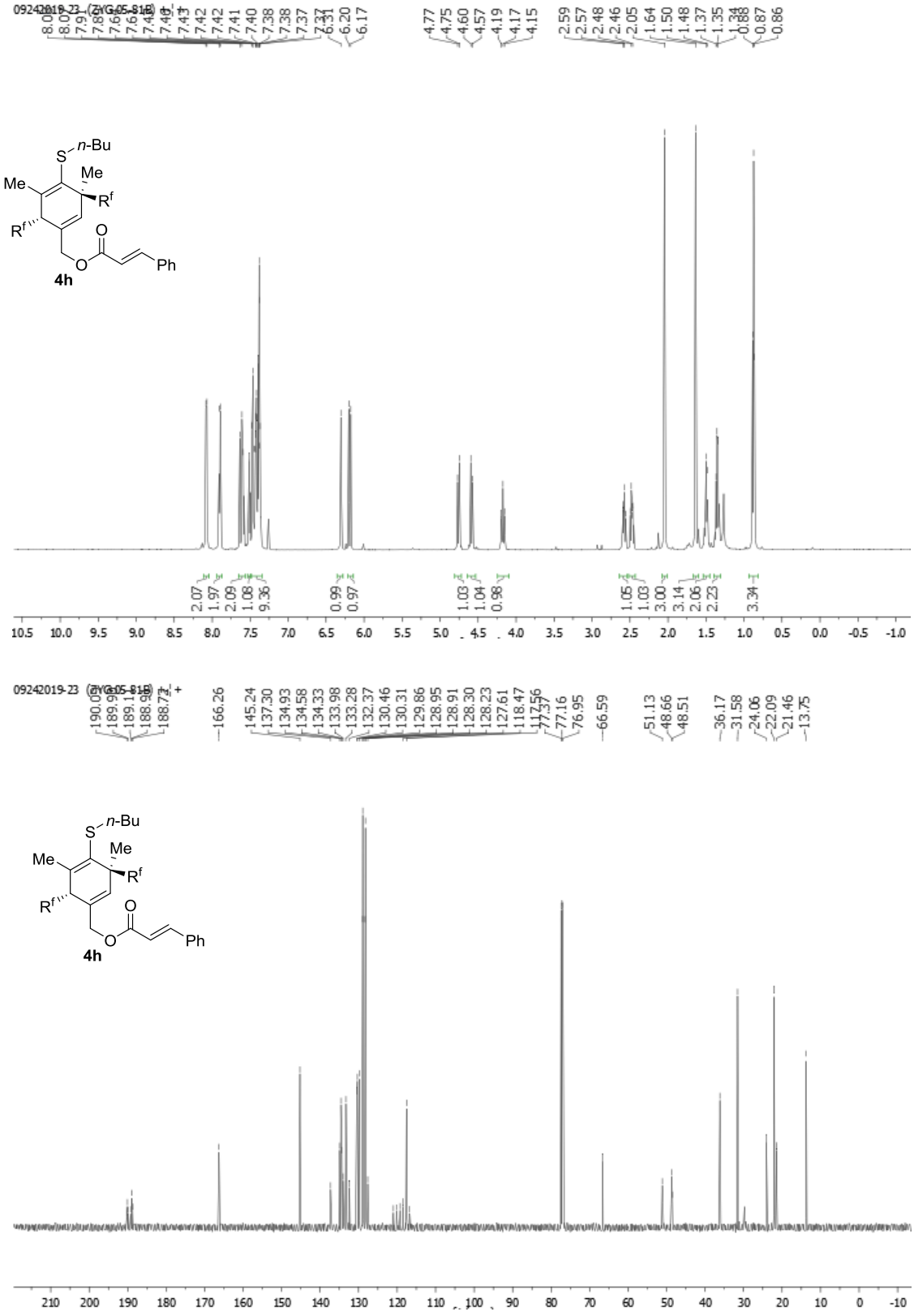


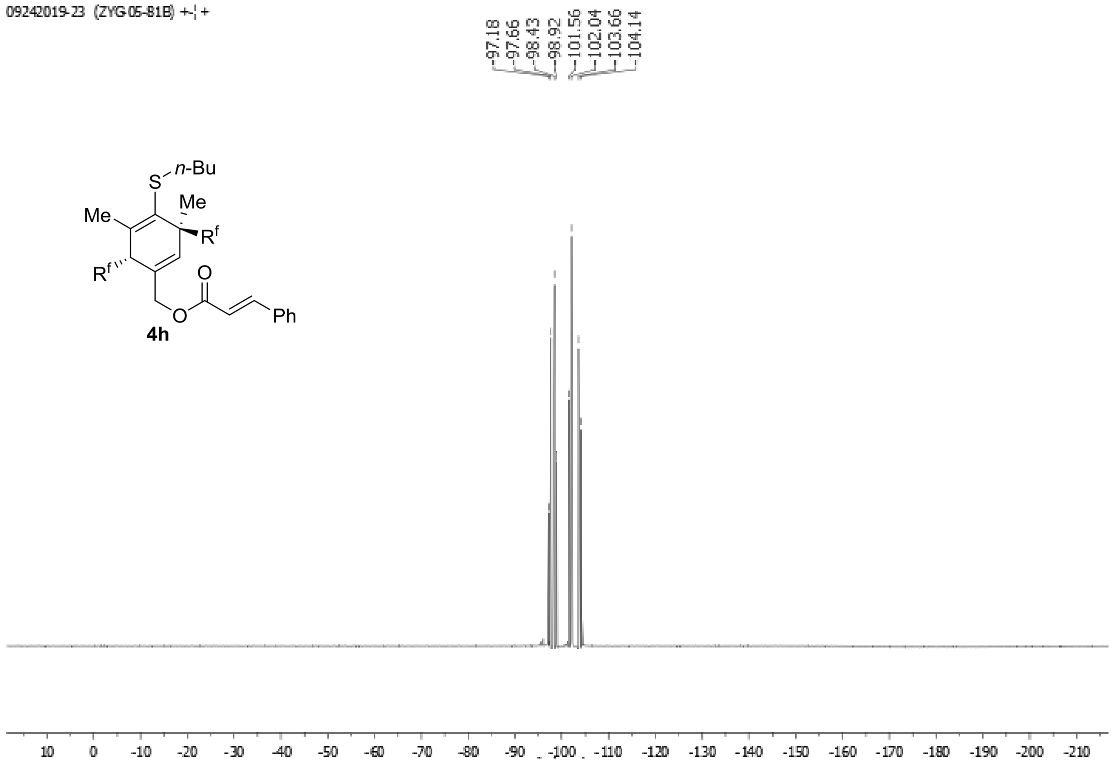
4g

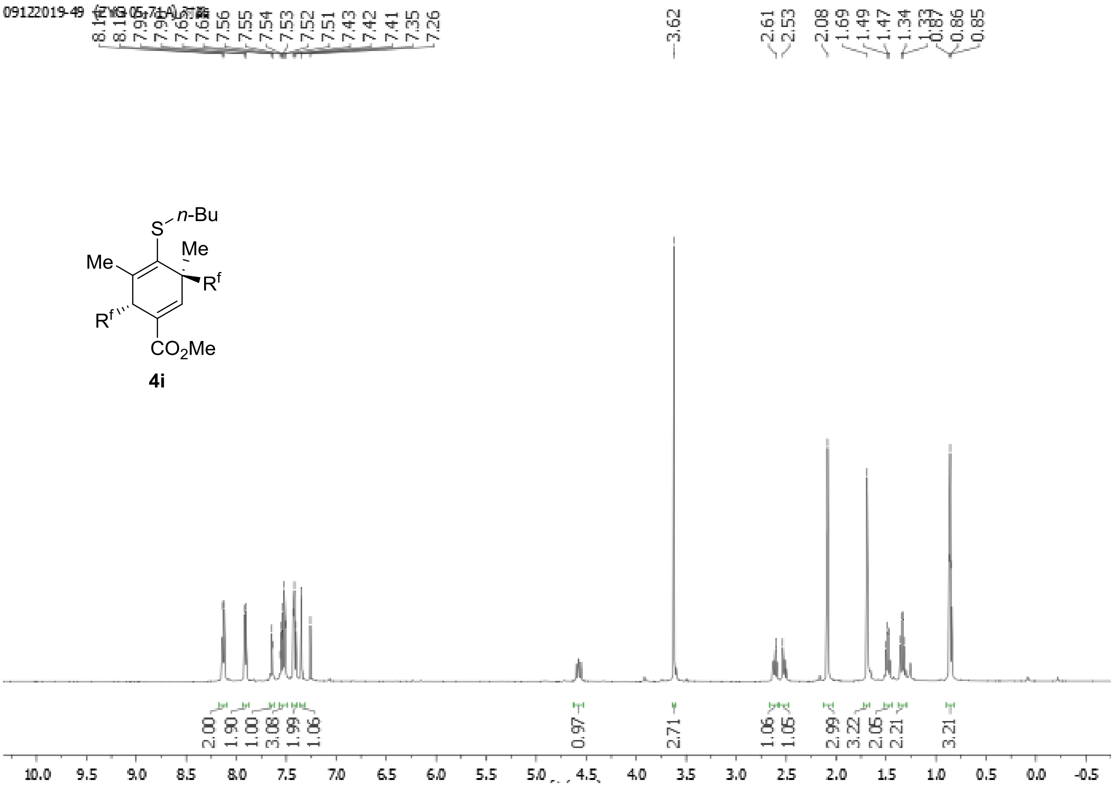


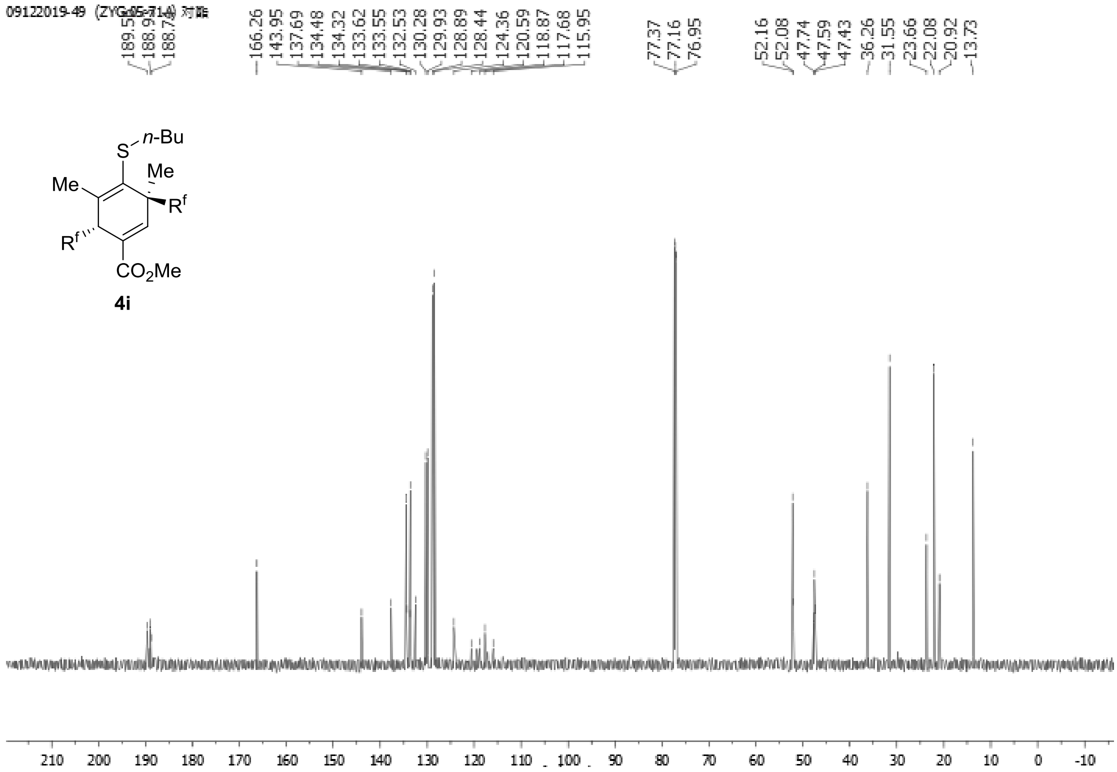

10142019-15 (ZYG-05-71C)
190.42
190.25
190.08
189.05
188.88
188.64
138.05
135.00
134.68
134.16
133.21
132.84
132.76
130.15
129.92
129.90
129.19
128.75
128.41
128.30
121.08
120.43
119.32
118.69
117.58
116.98
77.37
77.16
76.95
75.19
57.40
51.32
51.18
48.35
48.20
48.05
36.29
31.58
24.25
24.22
22.11
21.68
13.75
S
n-Bu
Me
Me
R^f
R^f
OMe
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

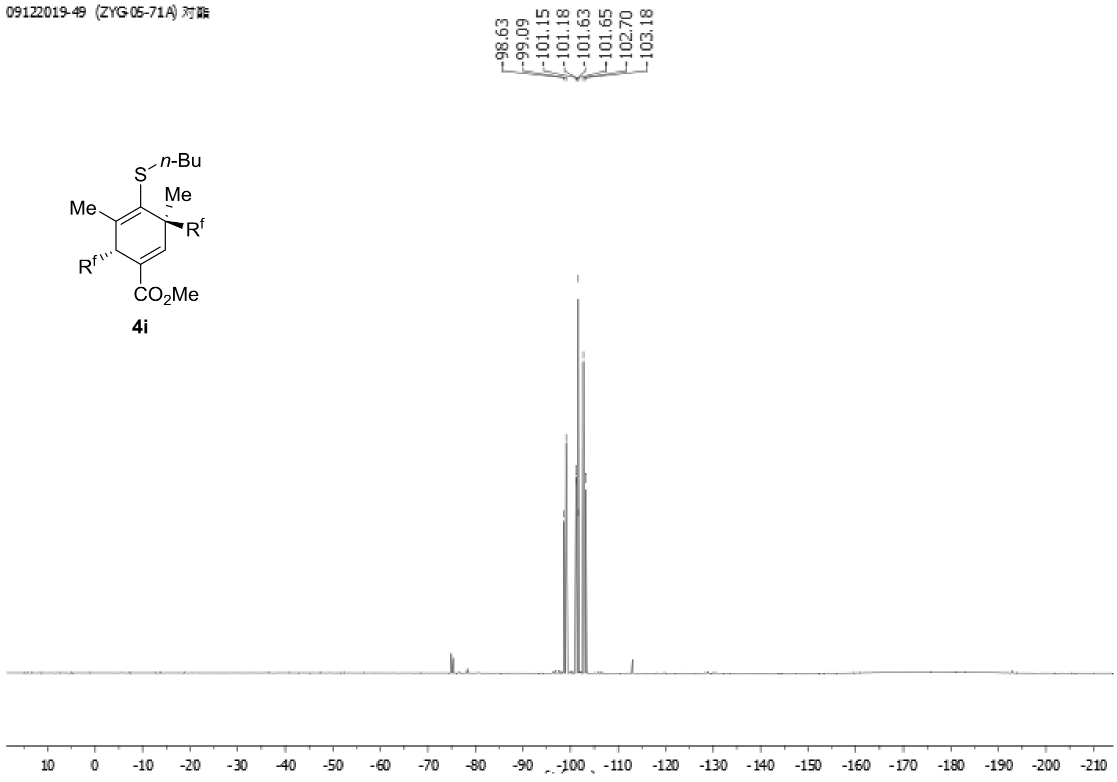

10142019-15 (ZYG-05-71C)
-96.77
-97.25
-99.97
-100.46
-101.43
-101.90
-103.42
-103.90
S
n-Bu
Me
Me
R^f
R^f
OMe
4g
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

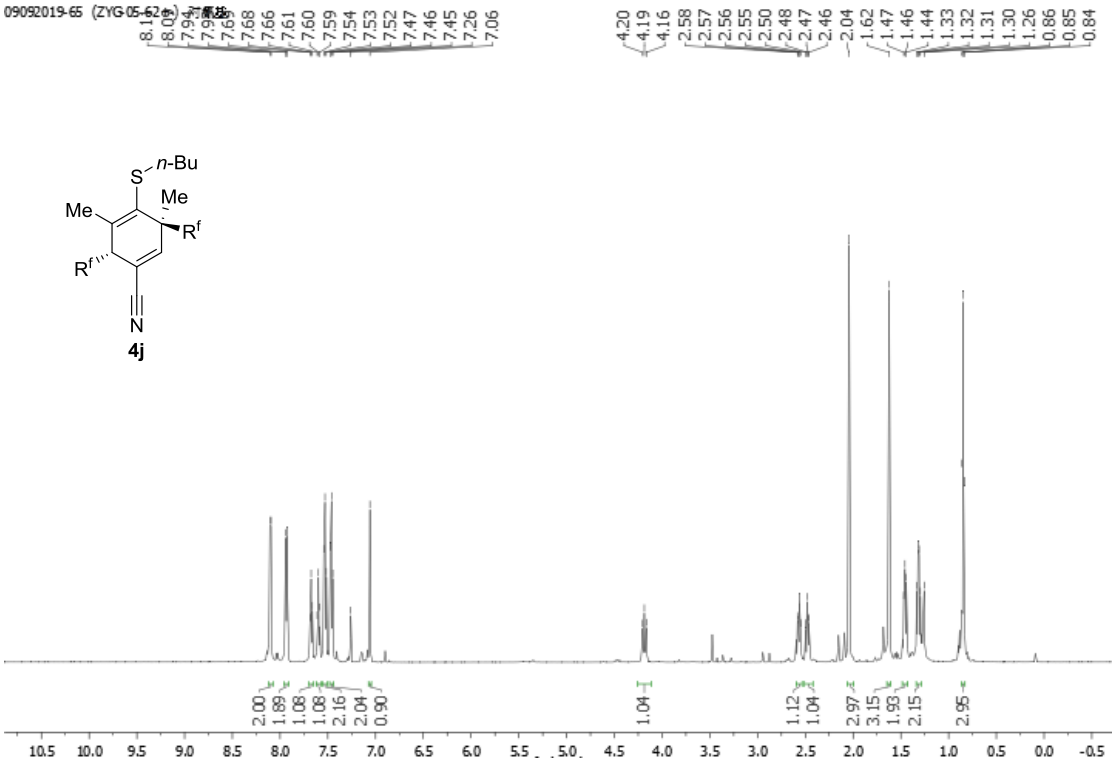

4h
4h

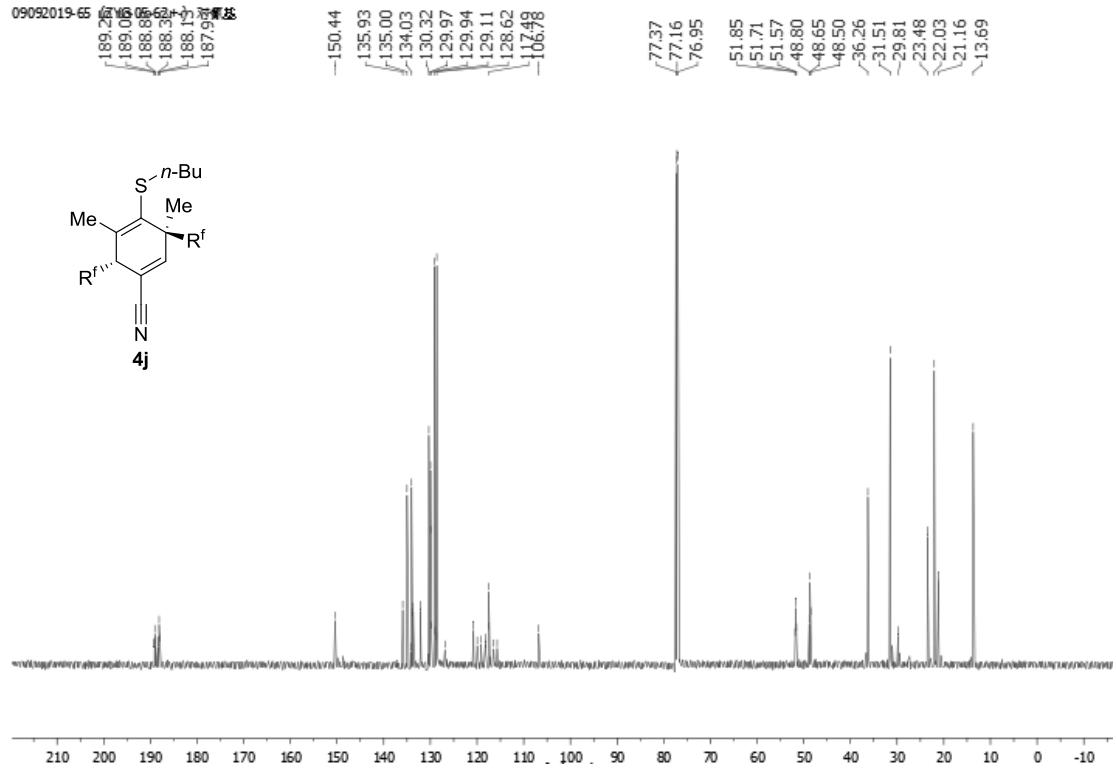

09242019-23 (ZYG-05-81B)
-97.18
-97.66
-98.43
-98.92
-101.56
-102.04
-103.66
-104.14
S
n-Bu
Me
Me
R^f
R^f
O
O
Ph
4h
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

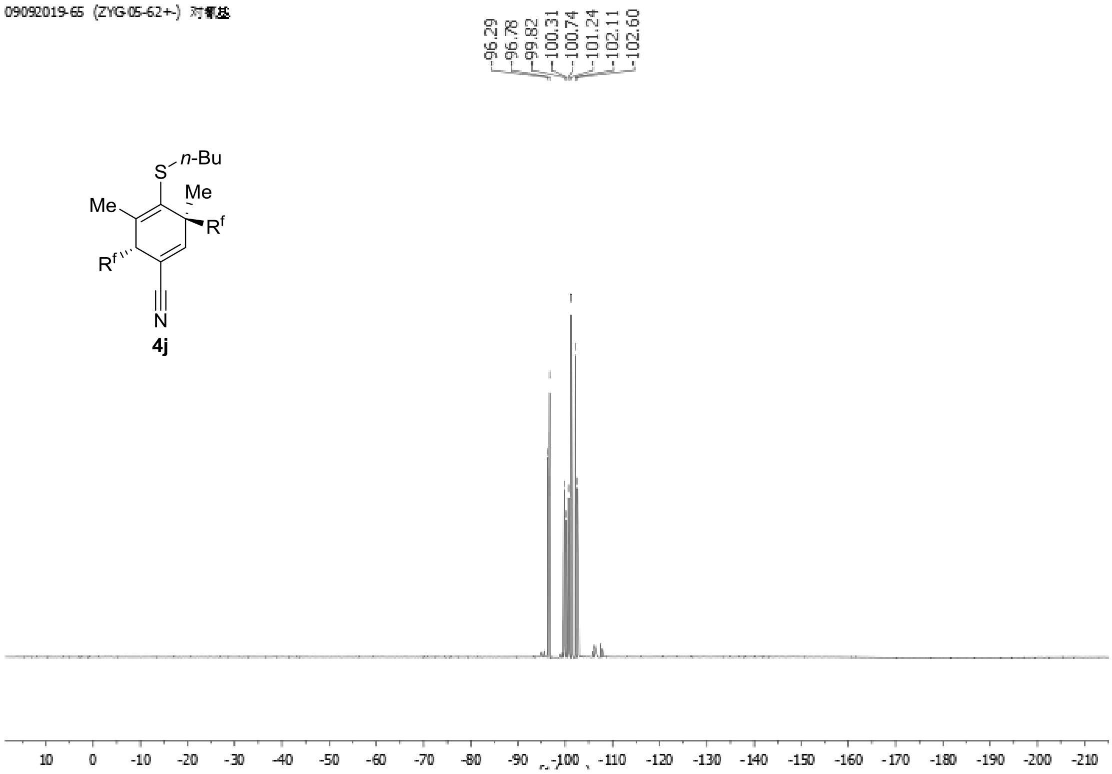

09122019-49
7.56
7.55
7.54
7.53
7.52
7.51
7.43
7.42
7.41
7.35
7.26
3.62
2.61
2.53
2.08
1.69
1.49
1.47
1.34
1.33
0.87
0.86
0.85
S
n-Bu
Me
Me
R^f
R^f
CO_2Me
4i
2.00
1.90
1.00
3.08
1.99
1.06
0.97
2.71
1.06
1.05
2.99
3.22
2.05
2.21
3.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


09122019-49 (ZYG-05-71A)
189.5
188.9
188.7
166.26
143.95
137.69
134.48
134.32
133.62
133.55
132.53
130.28
129.93
128.89
128.44
124.36
120.59
118.87
117.68
115.95
77.37
77.16
76.95
52.16
52.08
47.74
47.59
47.43
36.26
31.55
23.66
22.08
20.92
13.73
S
n-Bu
Me
Me
R^f
R^f
CO_2Me
4i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

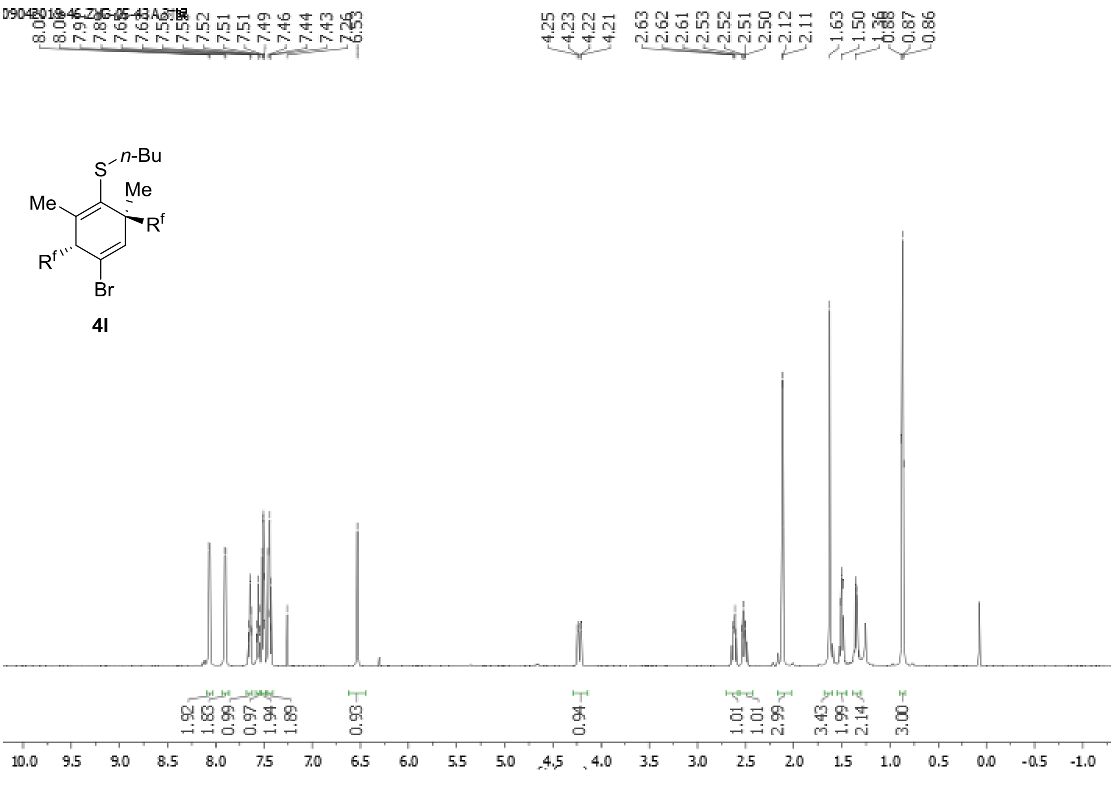

09122019-49 (ZYG-05-71A)
-98.63
-99.09
-101.15
-101.18
-101.63
-101.65
-102.70
-103.18
S
n-Bu
Me
Me
R^f
R^f
CO_2Me
4i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


09092019-65 (ZYG-05-62e)
8.14
8.09
7.94
7.89
7.68
7.66
7.61
7.60
7.59
7.54
7.53
7.52
7.47
7.46
7.45
7.26
7.06
4.20
4.19
4.16
2.58
2.57
2.56
2.55
2.50
2.48
2.47
2.46
2.04
1.62
1.47
1.46
1.44
1.33
1.32
1.31
1.30
1.26
0.86
0.85
0.84
S
n-Bu
Me
Me
R^f
R^f
N
4j
2.00
1.89
1.08
1.08
2.16
2.04
0.90
1.04
1.12
1.04
2.97
3.15
1.93
2.15
2.95
10.5
10.0
9.5
9.0
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
-0.5

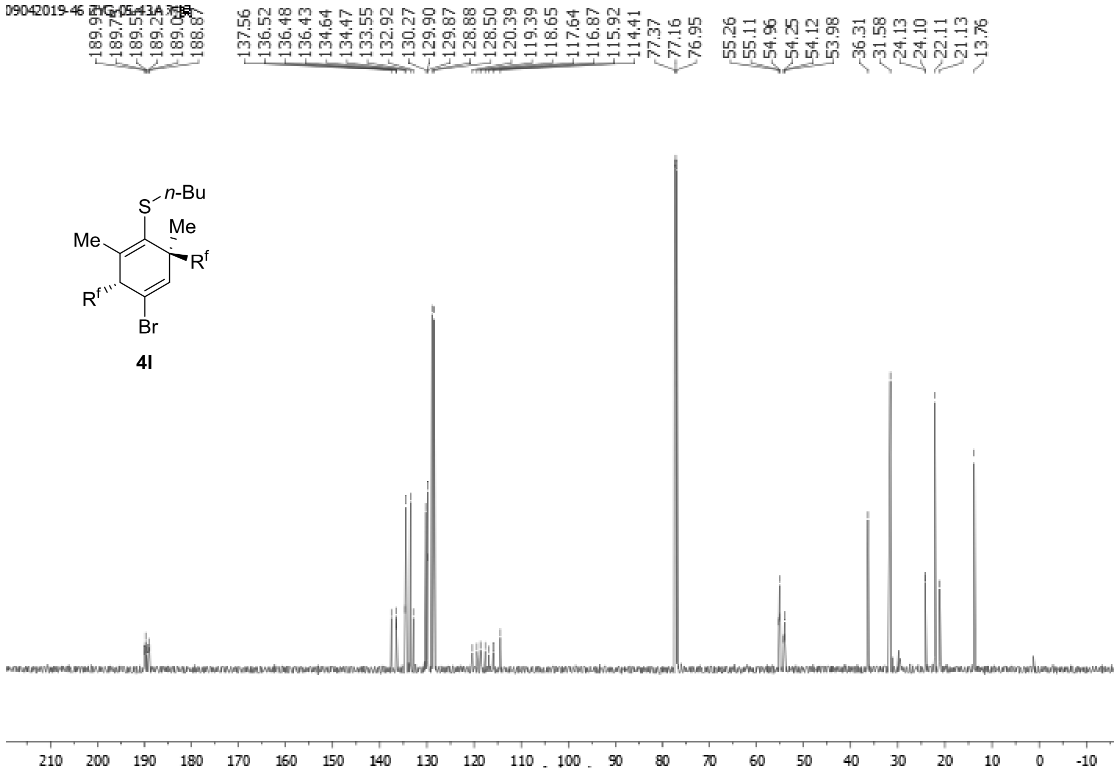

09092019-65
189.26
189.08
188.88
188.37
188.15
187.93
150.44
135.93
135.00
134.03
130.32
129.97
129.94
129.11
128.62
117.49
106.78
77.37
77.16
76.95
51.85
51.71
51.57
48.80
48.65
48.50
36.26
31.51
29.81
23.48
22.03
21.16
13.69
S
n-Bu
Me
Me
R^f
R^f
N
4j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

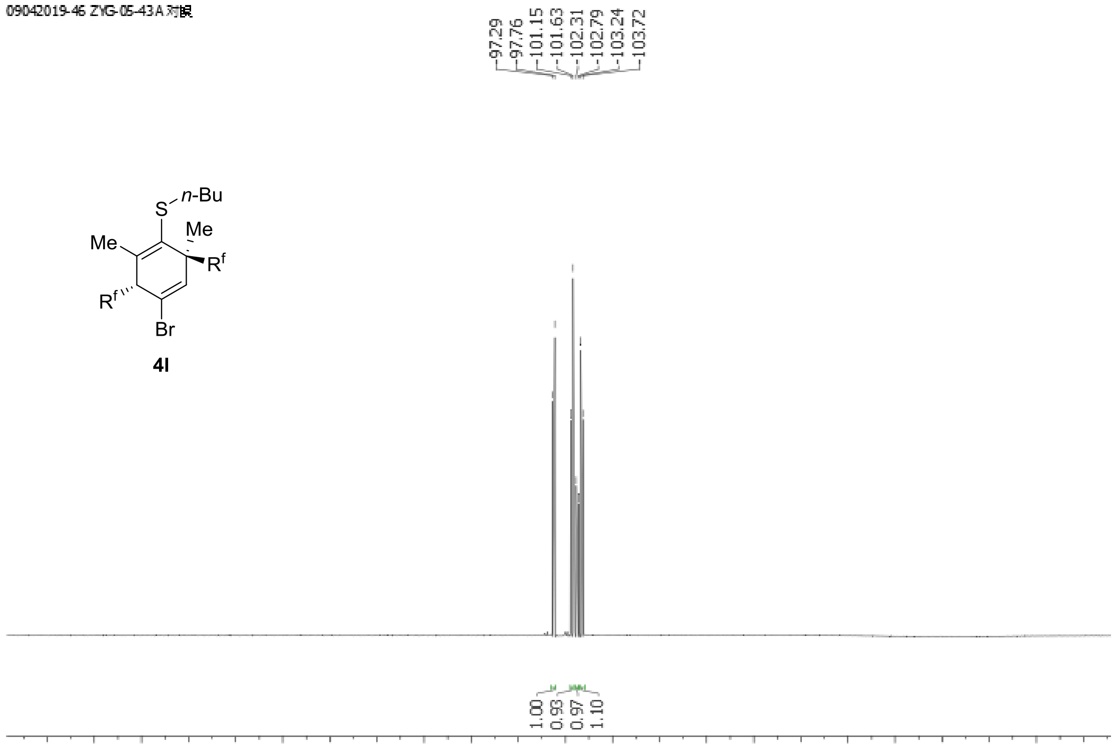

09092019-65 (ZYG-05-62+-)
-96.29
-96.78
-99.82
-100.31
-100.74
-101.24
-102.11
-102.60
S
n-Bu
Me
Me
R^f
R^f
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

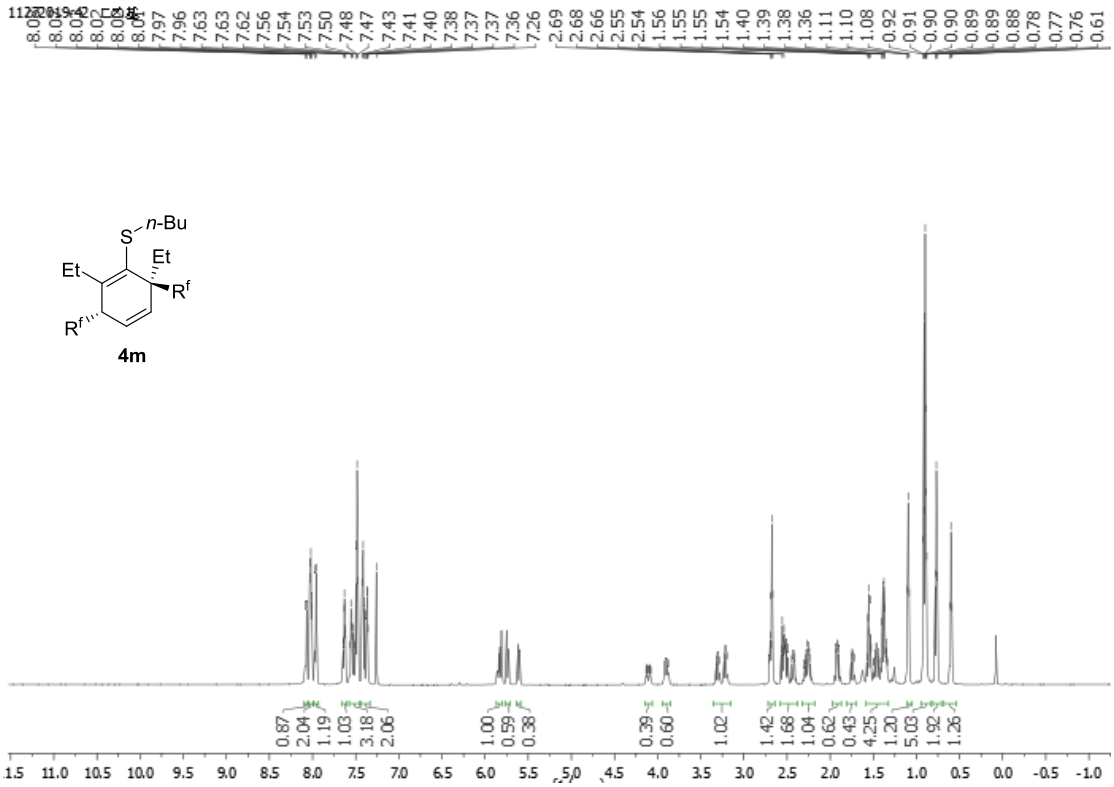
4j

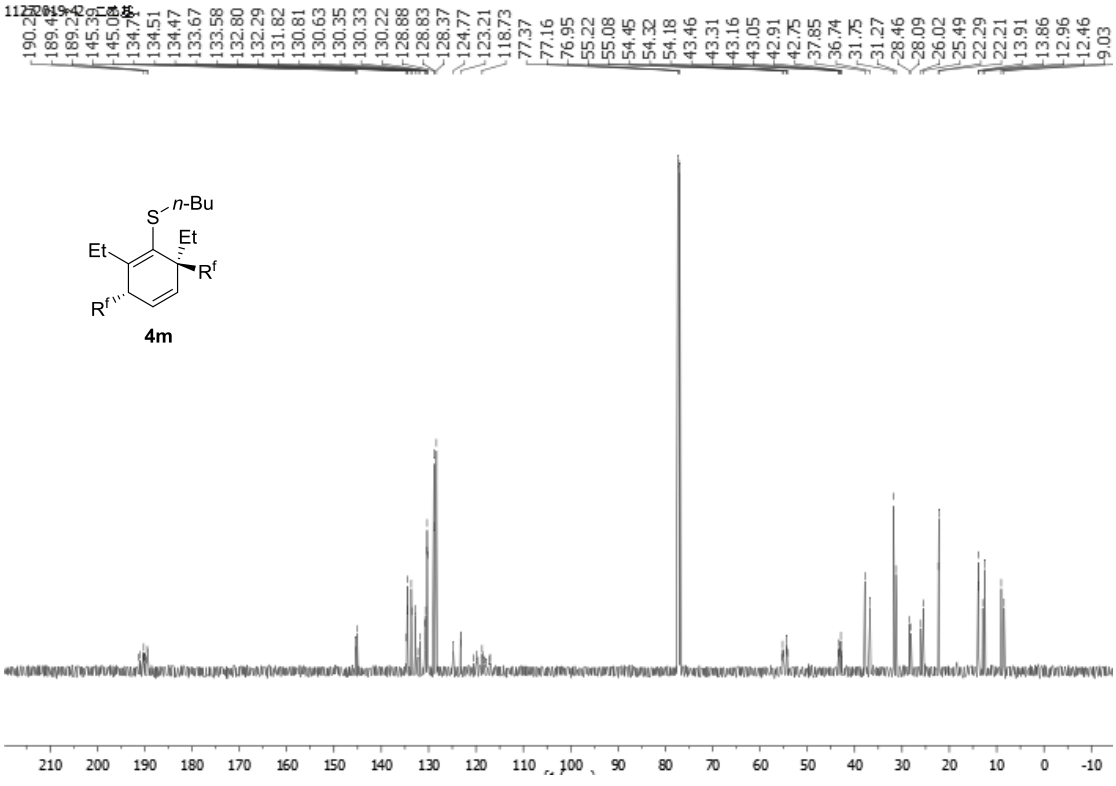

8.07 8.06 7.91 7.89 7.65 7.63 7.57 7.55 7.52 7.51 7.51 7.49 7.46 7.44 7.43 7.26 6.53
4.25 4.23 4.22 4.21
2.63 2.62 2.61 2.53 2.52 2.51 2.50 2.12 2.11
1.63 1.50 1.36 0.88 0.87 0.86
S
n-Bu
Me
Me
R^f
R^f
Br
1.92 1.83 0.99 0.97 1.94 1.89 0.93 0.94 1.01 1.01 2.99 3.43 1.99 2.14 3.00
10.0 9.5 9.0 8.5 8.0 7.5 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 -0.5 -1.0

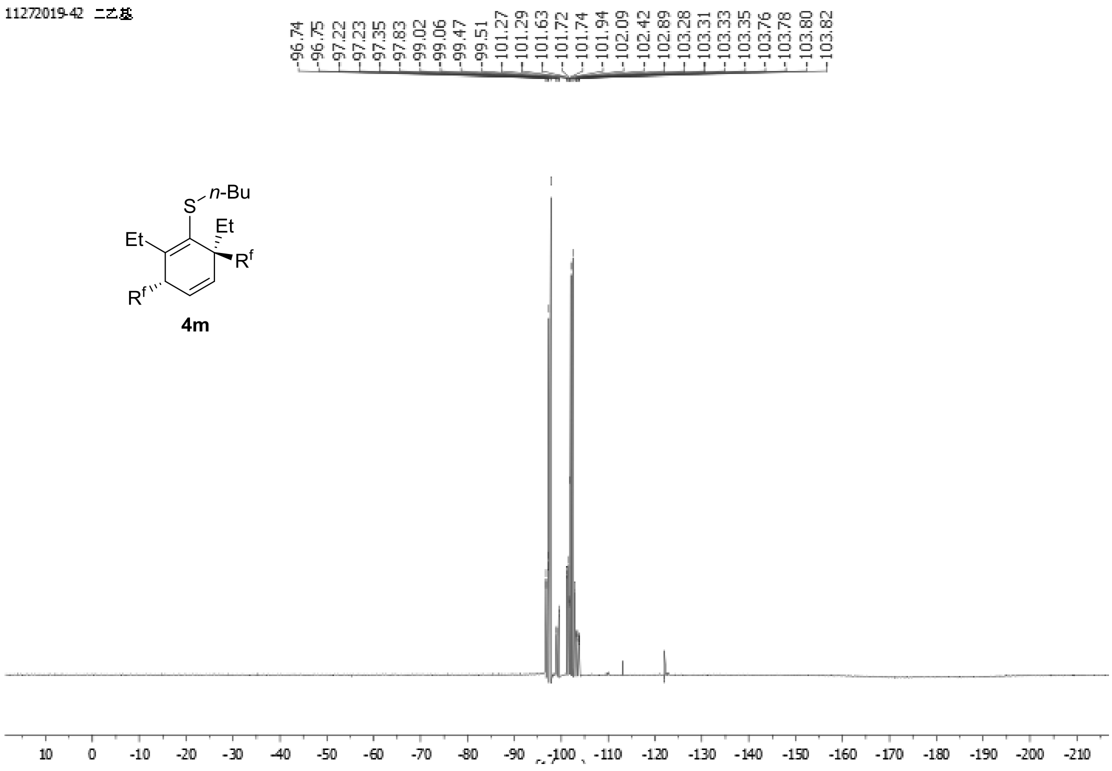
4l


09042019-46 ZYG-05-43A
137.56 136.52 136.48 136.43 134.64 134.47 133.55 132.92 130.27 129.90 129.87 128.88 128.50 120.39 119.39 118.65 117.64 116.87 115.92 114.41
77.37 77.16 76.95
55.26 55.11 54.96 54.25 54.12 53.98
36.31 31.58 24.13 24.10 22.11 21.13 13.76
S n-Bu
Me
Me
R^f
R^f
Br
4l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

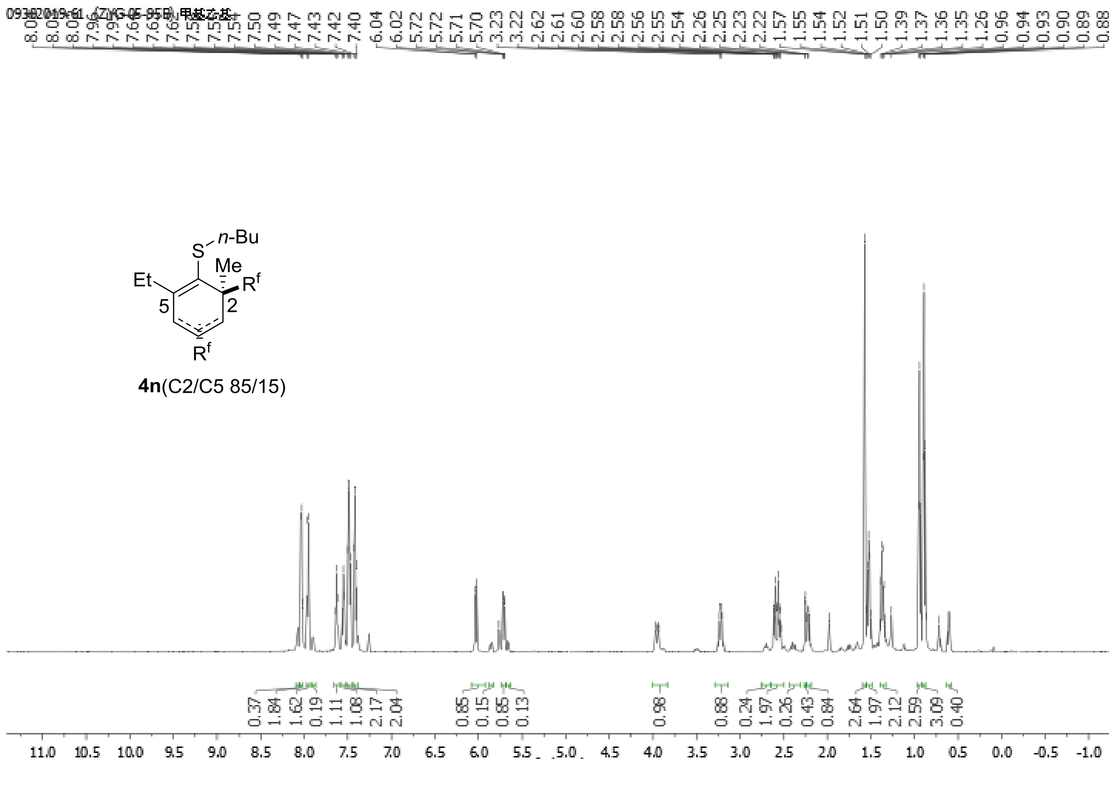

09042019-46 ZYG-05-43A
-97.29 -97.76 -101.15 -101.63 -102.31 -102.79 -103.24 -103.72
S n-Bu
Me
Me
R^f
R^f
Br
4l
1.00 0.93 0.97 1.10
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


4m

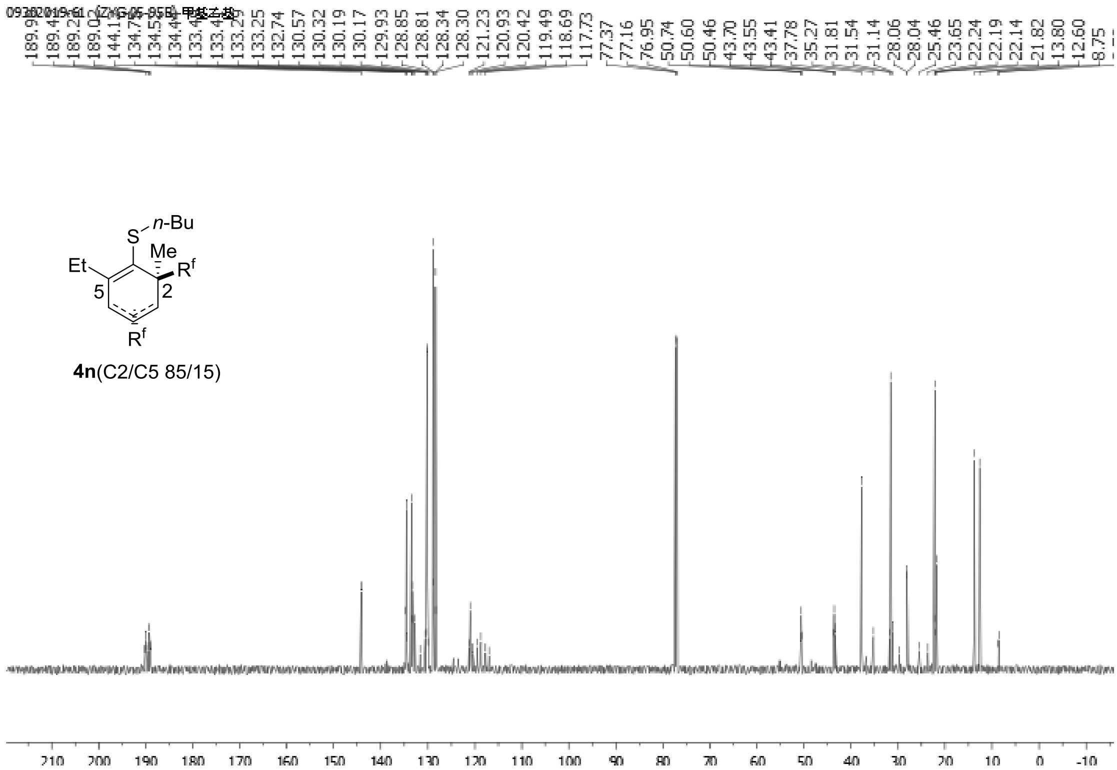

4m

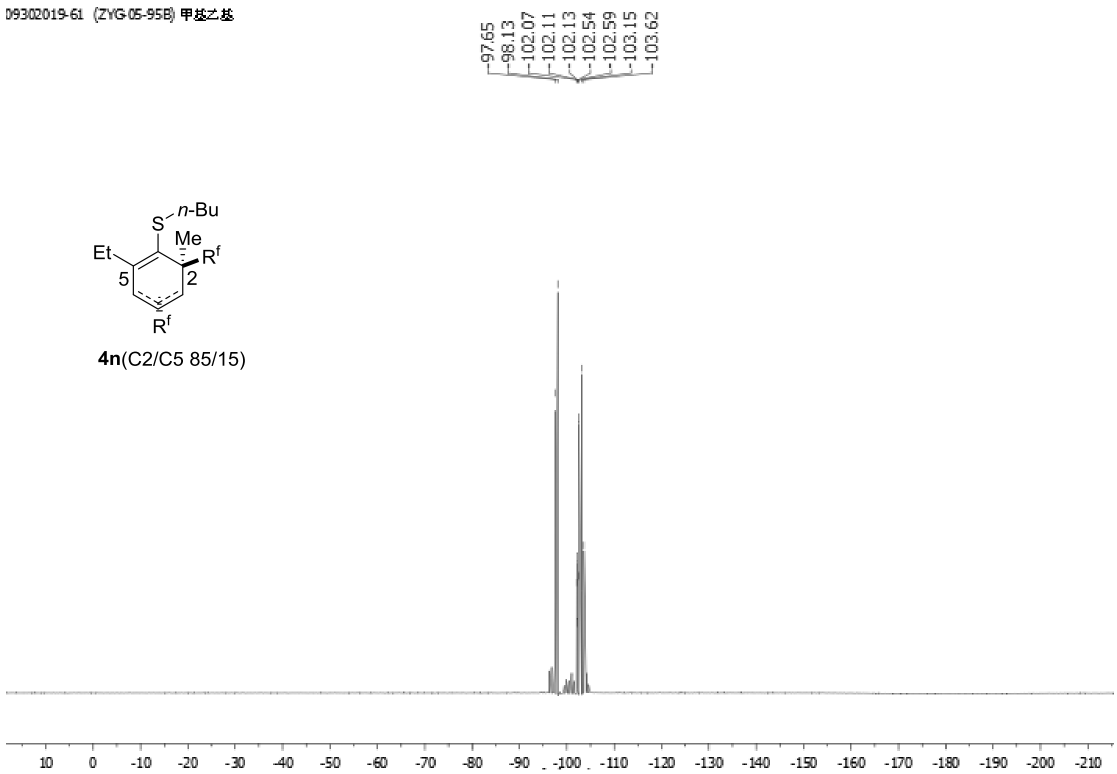


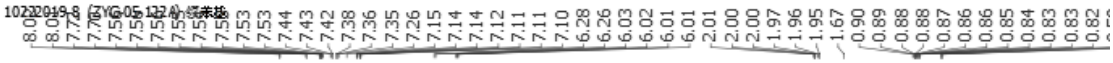
-96.74
-96.75
-97.22
-97.23
-97.35
-97.83
-99.02
-99.06
-99.47
-99.51
-101.27
-101.29
-101.63
-101.72
-101.74
-101.94
-102.09
-102.42
-102.89
-103.28
-103.31
-103.33
-103.35
-103.76
-103.78
-103.80
-103.82
S n-Bu
Et
Et
R f
R f
4m
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

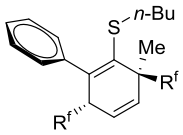


S n-Bu
Me
Et
R f
5
2
R f
4n(C2/C5 85/15)
0.37 1.84 1.62 0.19 1.11 1.08 2.17 2.04 0.85 0.15 0.85 0.13 0.98 0.88 0.24 1.97 0.26 0.43 0.84 2.64 1.97 2.12 2.59 3.09 0.40
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

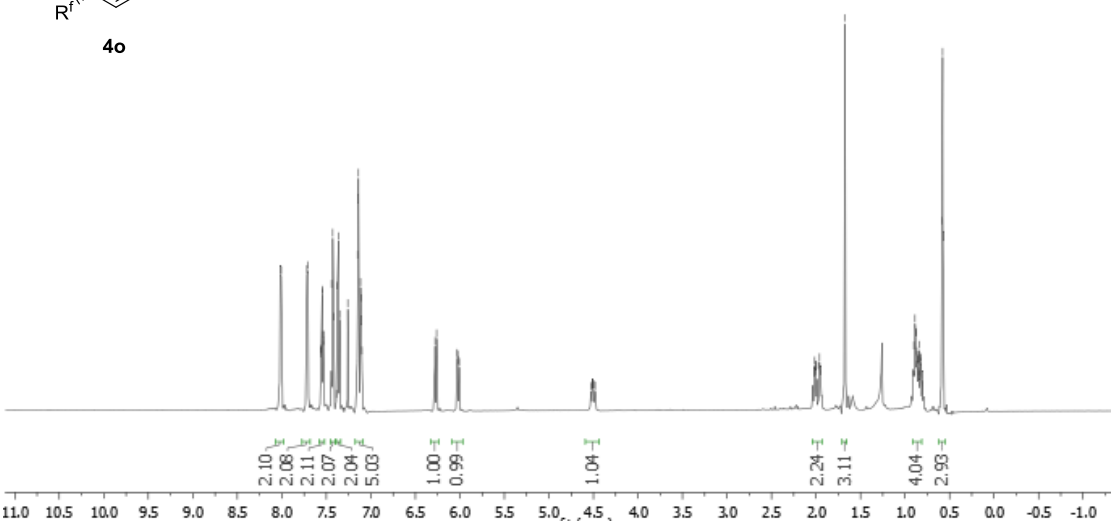

09302019-61 (ZYG-05-95B) 甲基乙基
189.93
189.47
189.28
189.02
144.11
134.75
134.53
134.44
133.47
133.41
133.29
133.25
132.74
130.57
130.32
130.19
130.17
129.93
128.85
128.81
128.34
128.30
121.23
120.93
120.42
119.49
118.69
117.73
77.37
77.16
76.95
50.74
50.60
50.46
43.70
43.55
43.41
37.78
35.27
31.81
31.54
31.14
28.06
28.04
25.46
23.65
22.24
22.19
22.14
21.82
13.80
12.60
8.75
S
n-Bu
Me
Et
R^f
5
2
R^f
4n(C2/C5 85/15)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

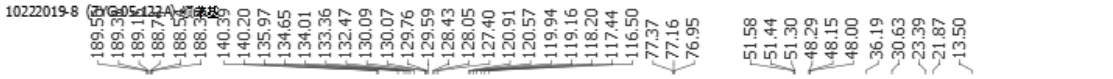

09302019-61 (ZYG-05-95B) 甲基乙基
-97.65
-98.13
-102.07
-102.11
-102.13
-102.54
-102.59
-103.15
-103.62
S
n-Bu
Me
Et
R^f
5
2
R^f
4n(C2/C5 85/15)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

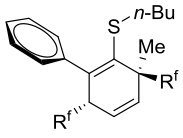




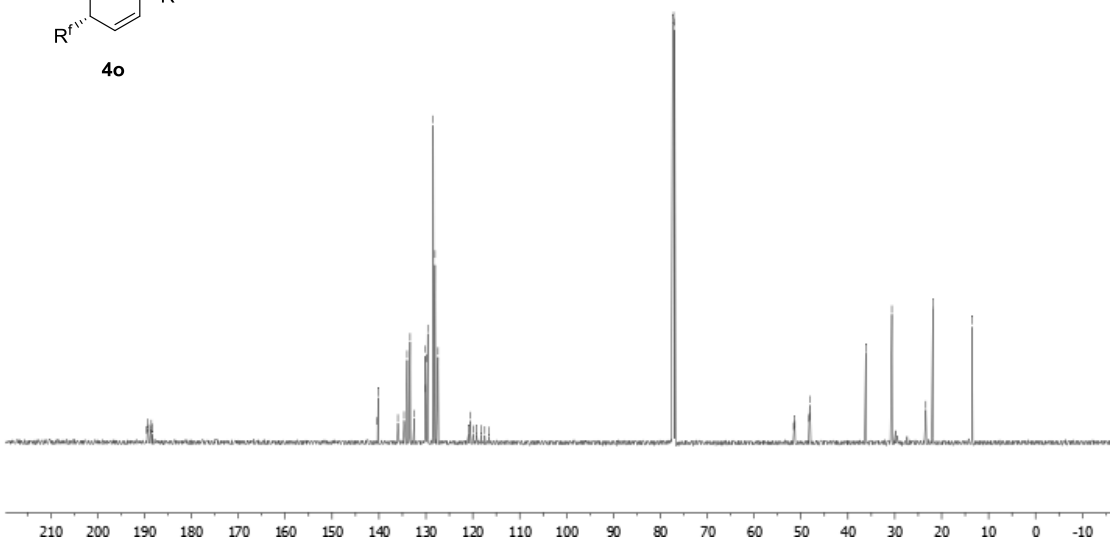
4o



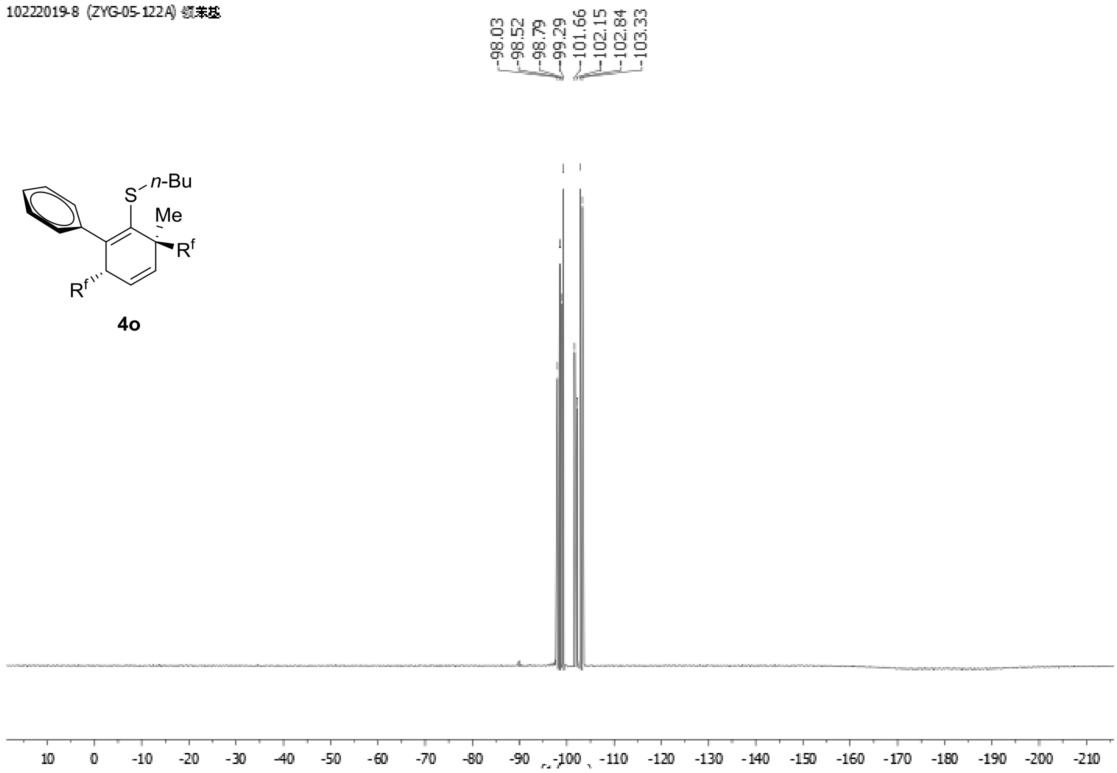




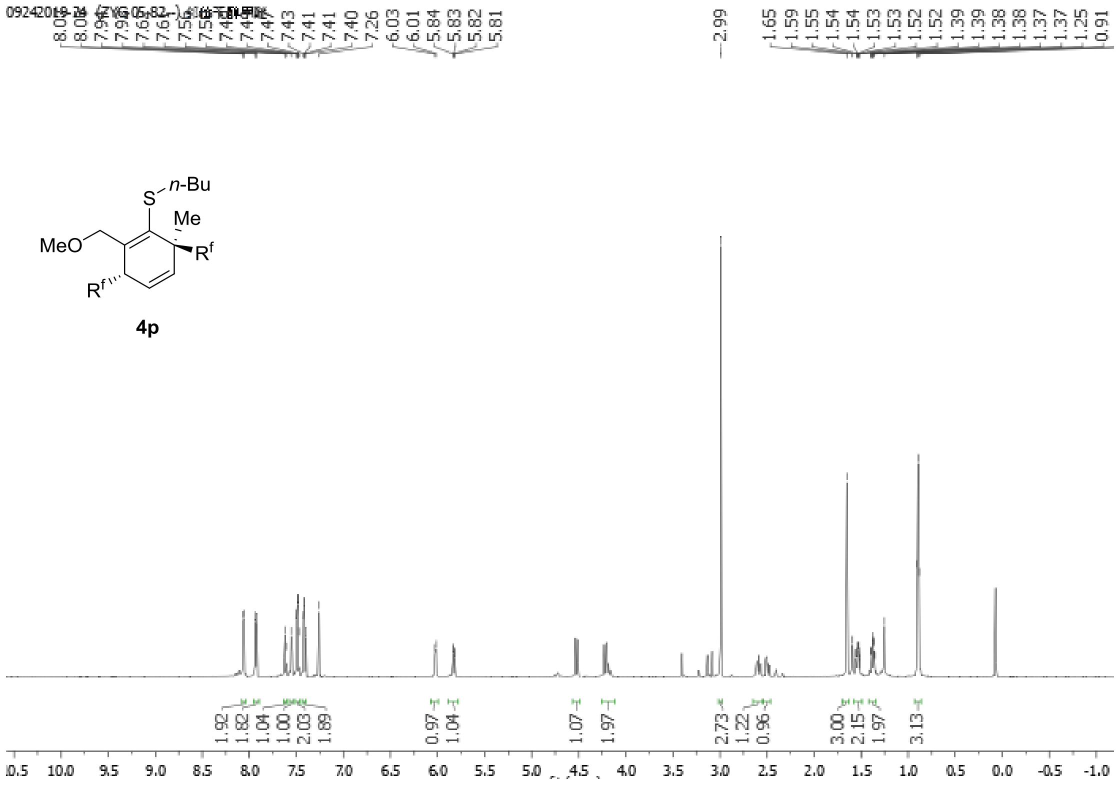
4o



10222019-8 (ZYG-05-122A)

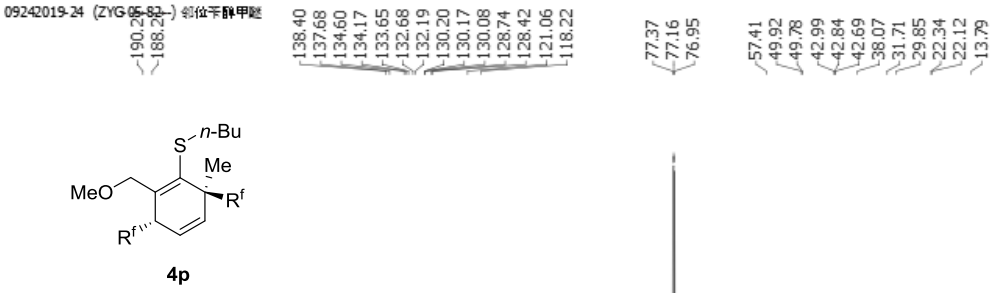


4o

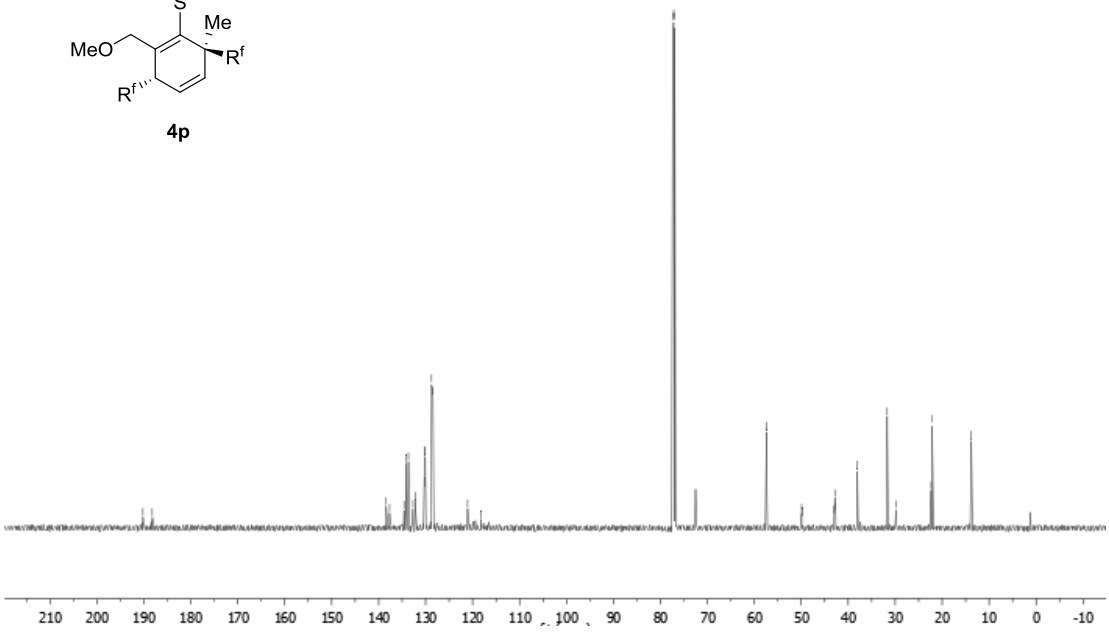


4p

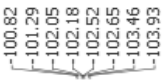
09242019-24 (ZYG-05-82--) 邻位干酵甲醛

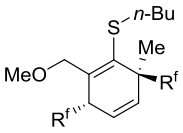


4p

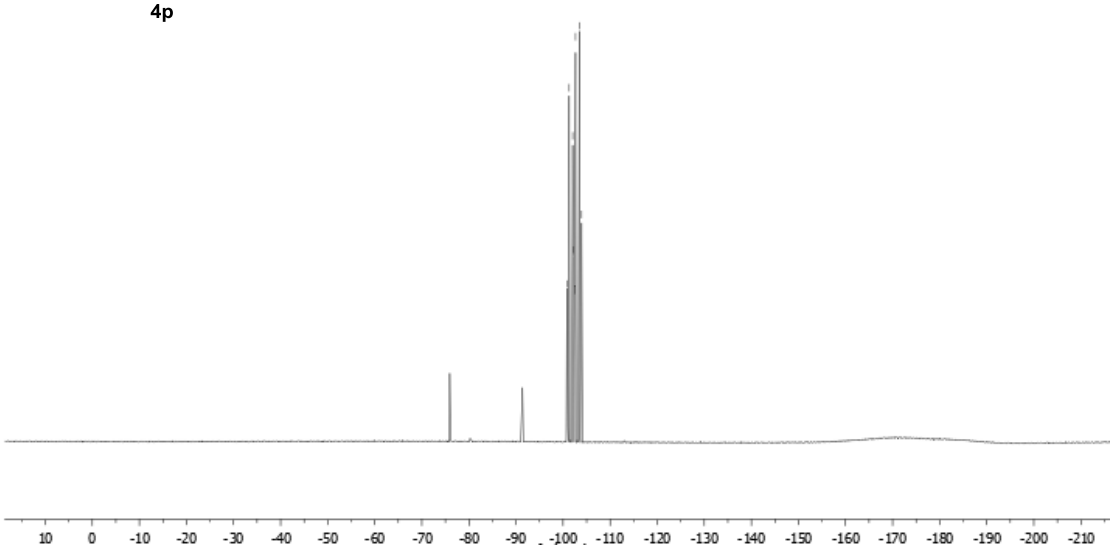


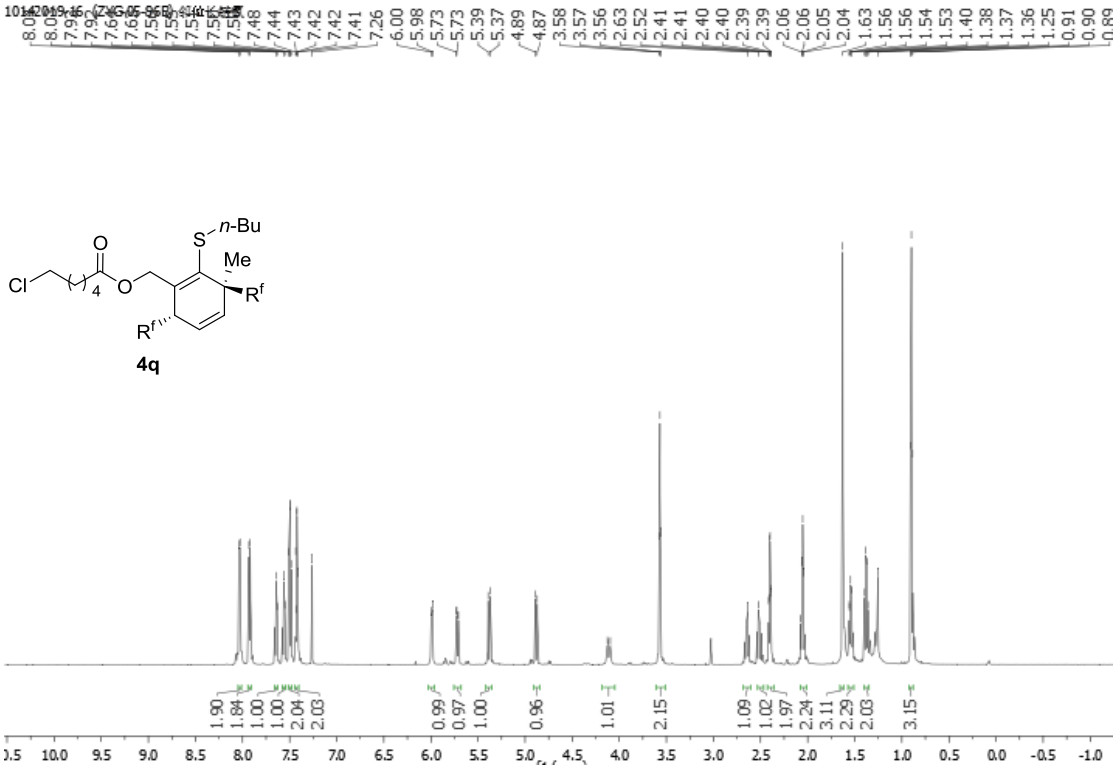
09242019-24 (ZYG-05-82--) 邻位干酵甲醛

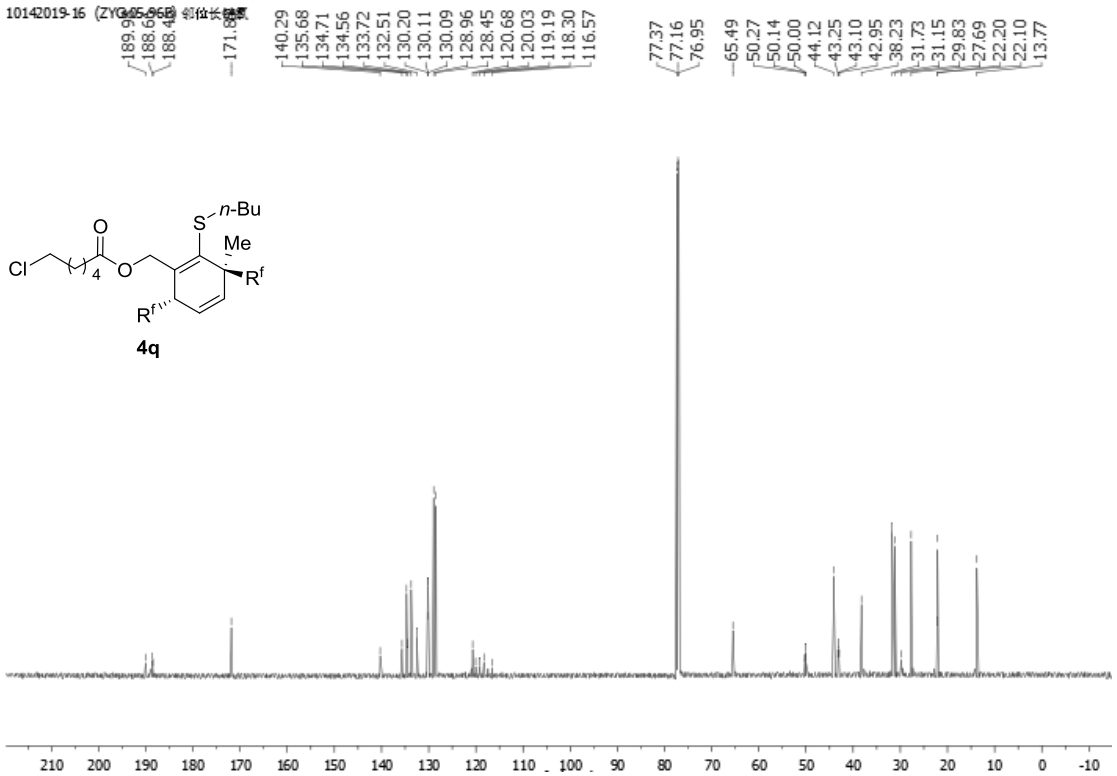




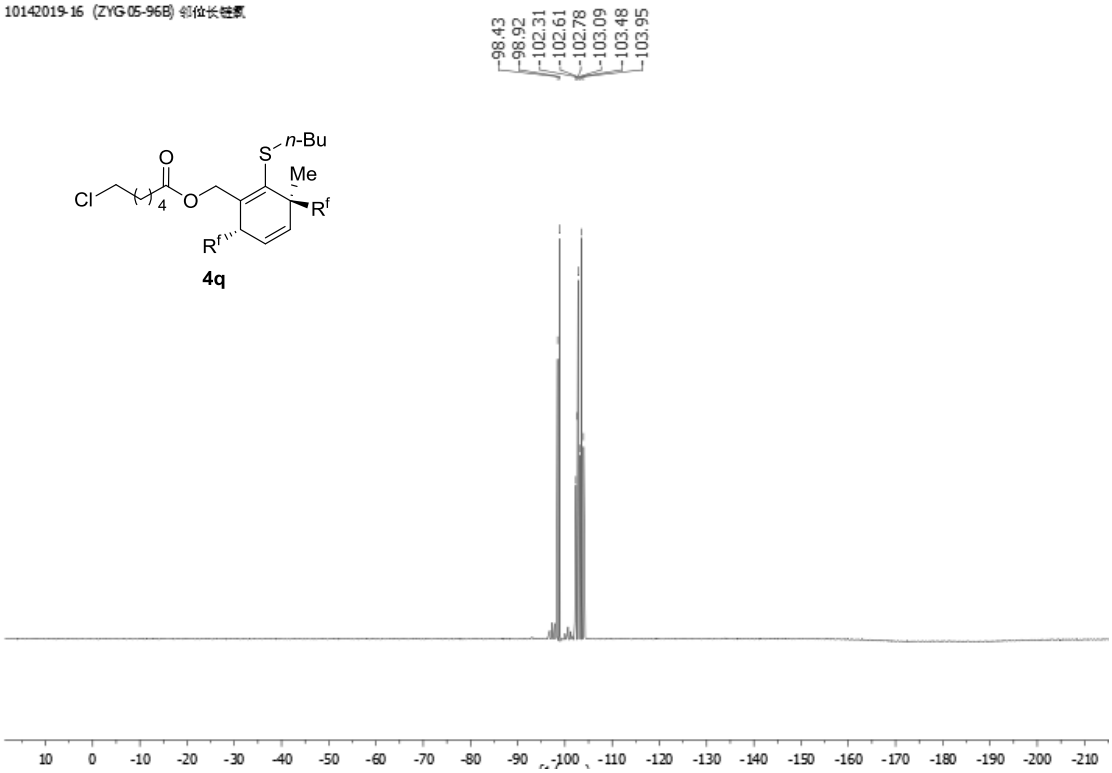
4p




4q
1.90
1.84
1.00
1.00
2.04
2.03
0.99
0.97
1.00
0.96
1.01
2.15
1.09
1.02
1.97
2.24
3.11
2.29
2.03
3.15


4q

10142019-16 (ZYG-05-96B) 邻位长链氢



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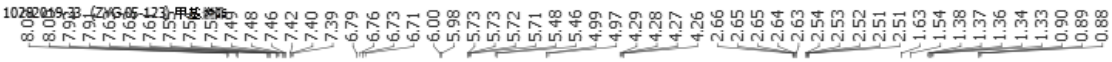

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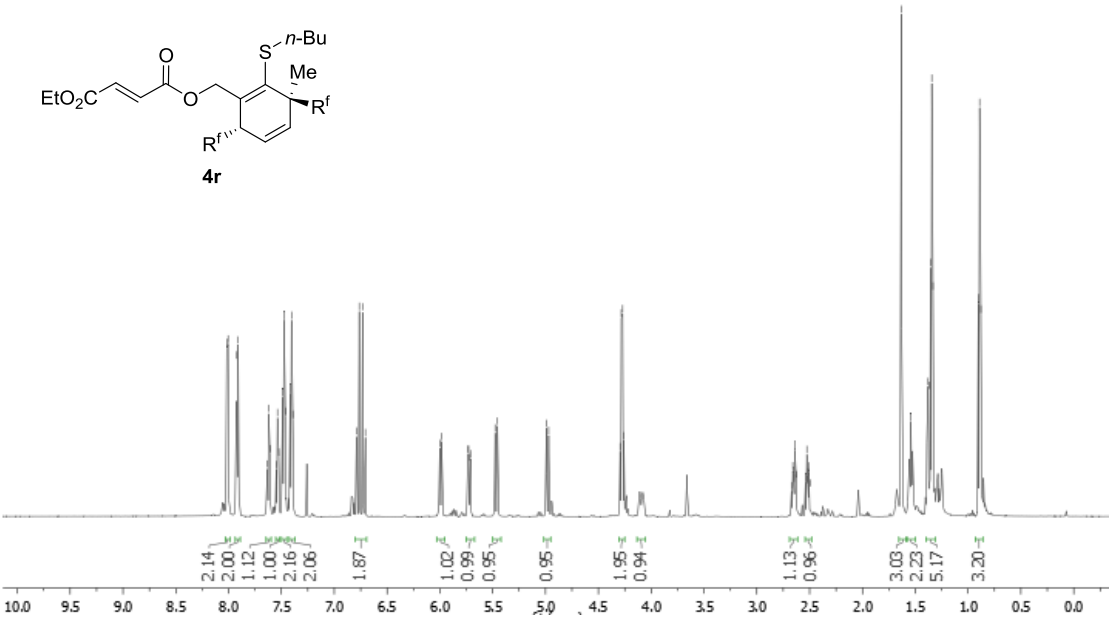

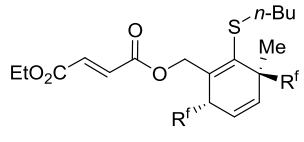

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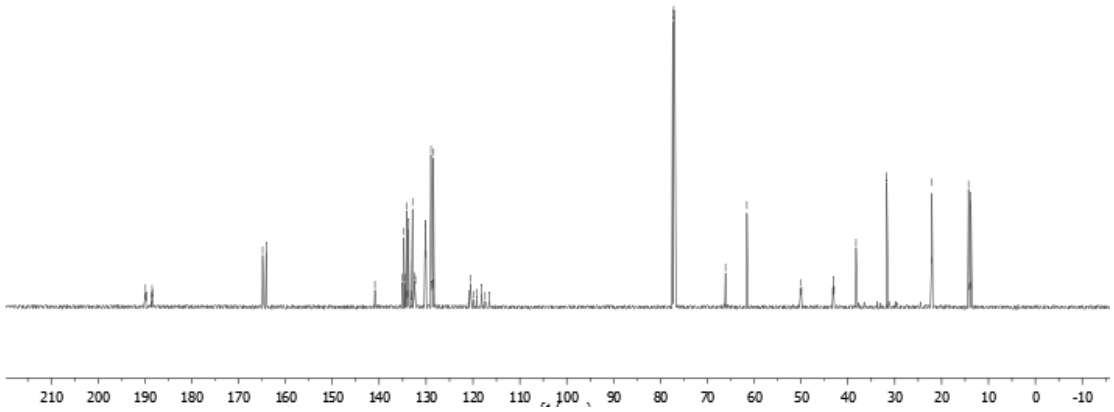

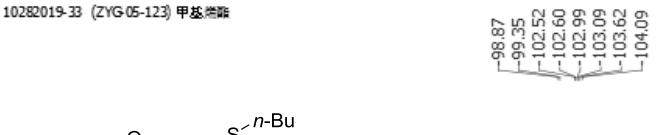

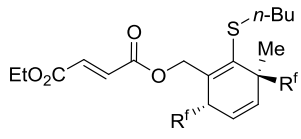

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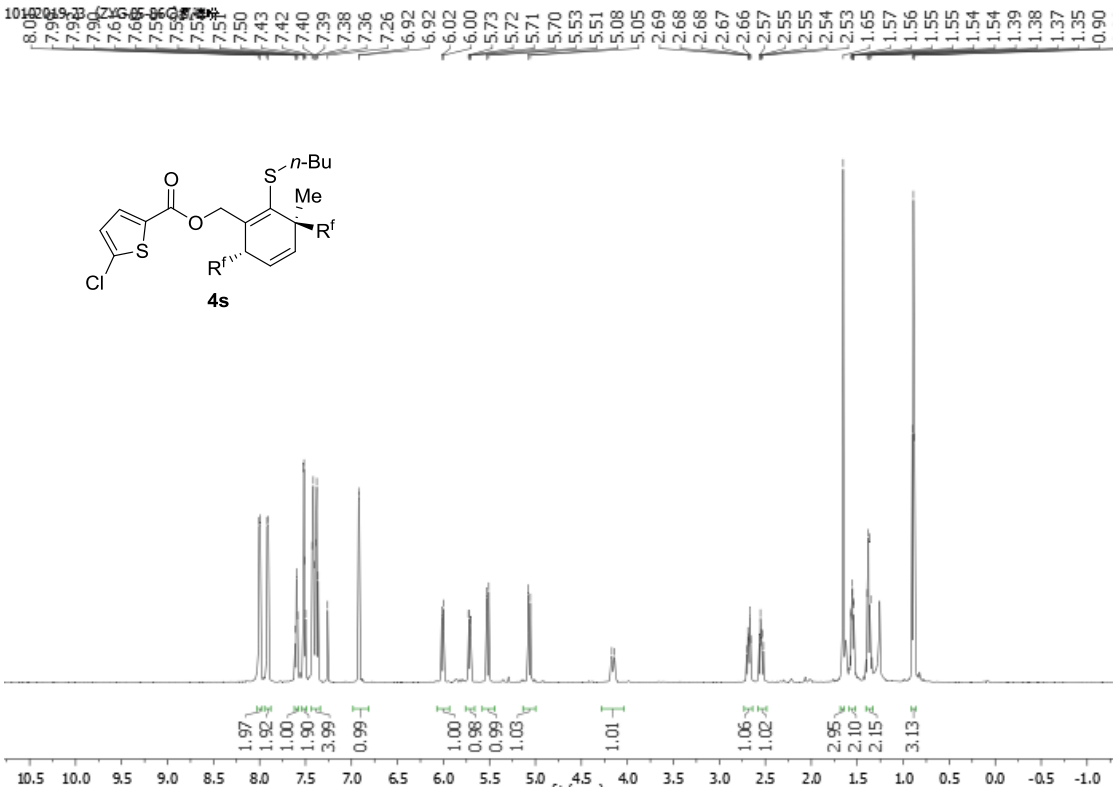
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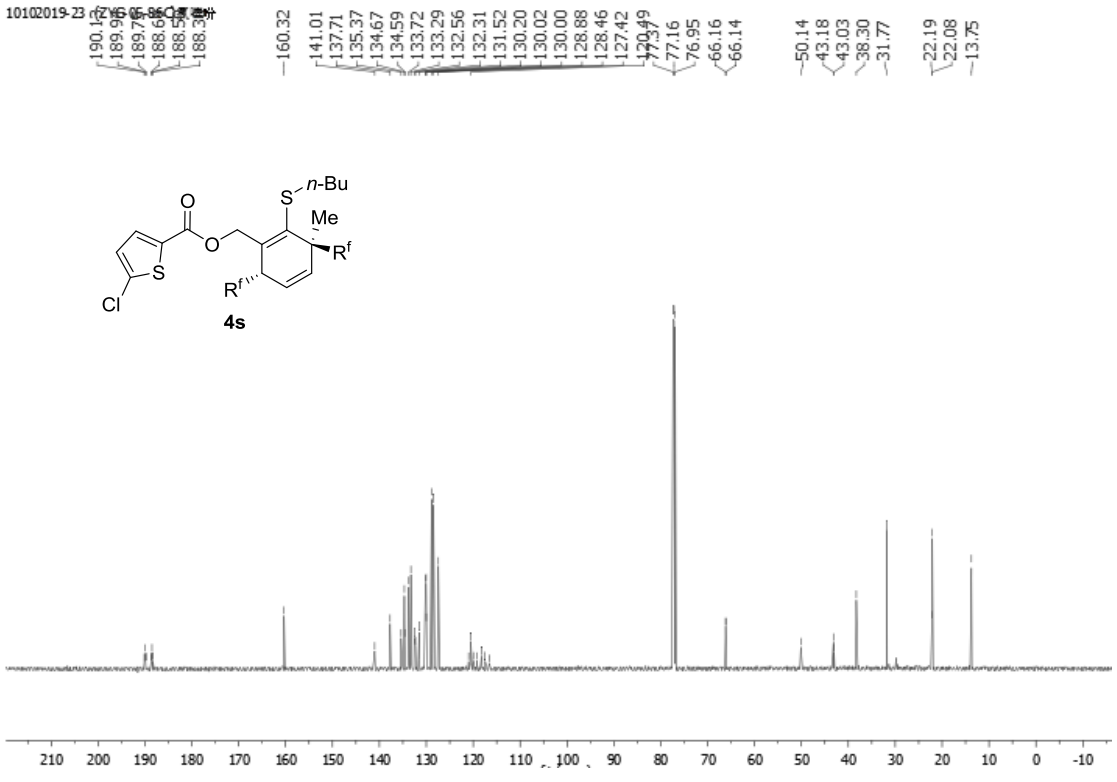
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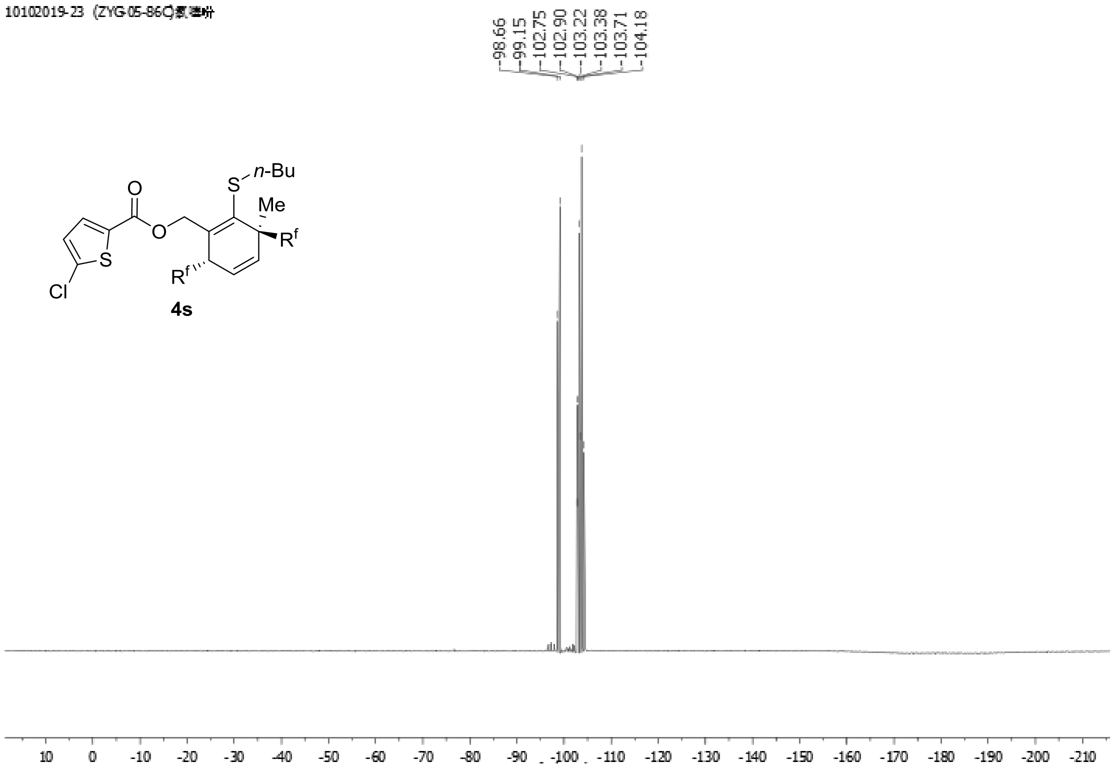
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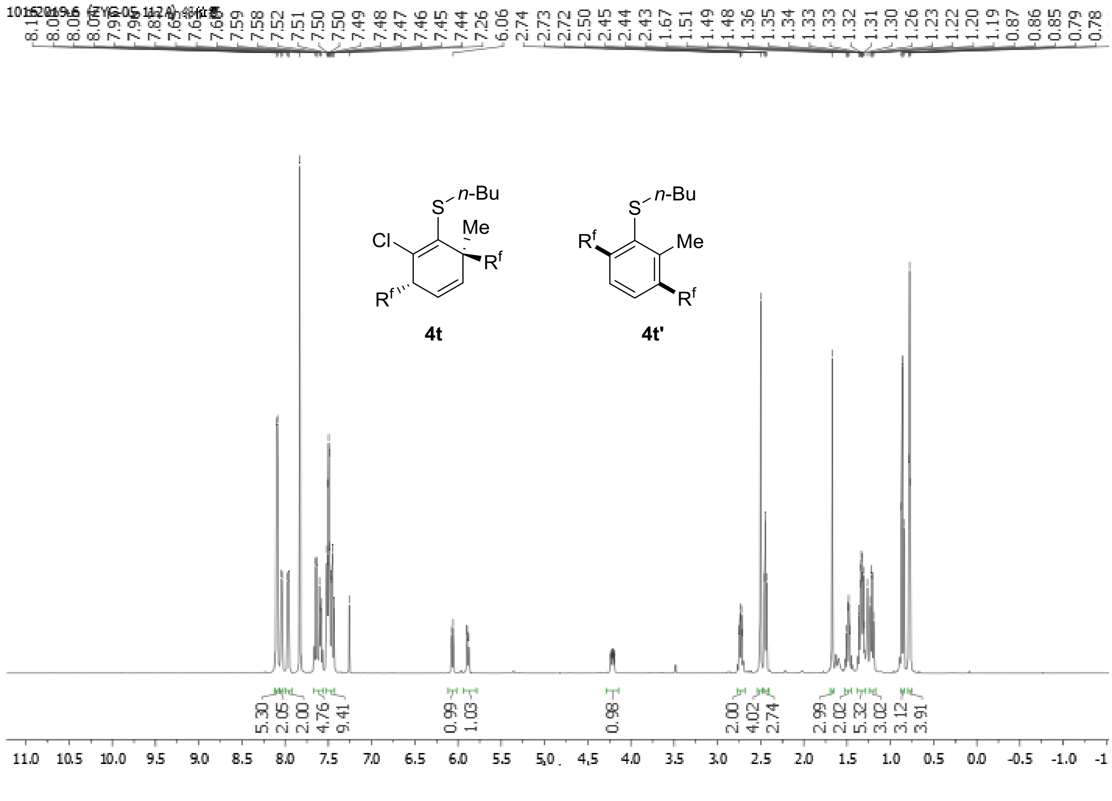
-98.66
-99.15
-102.75
-102.90
-103.22
-103.38
-103.71
-104.18
S n-Bu
O
Me
O
R^f
S
R^f
Cl
4s
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210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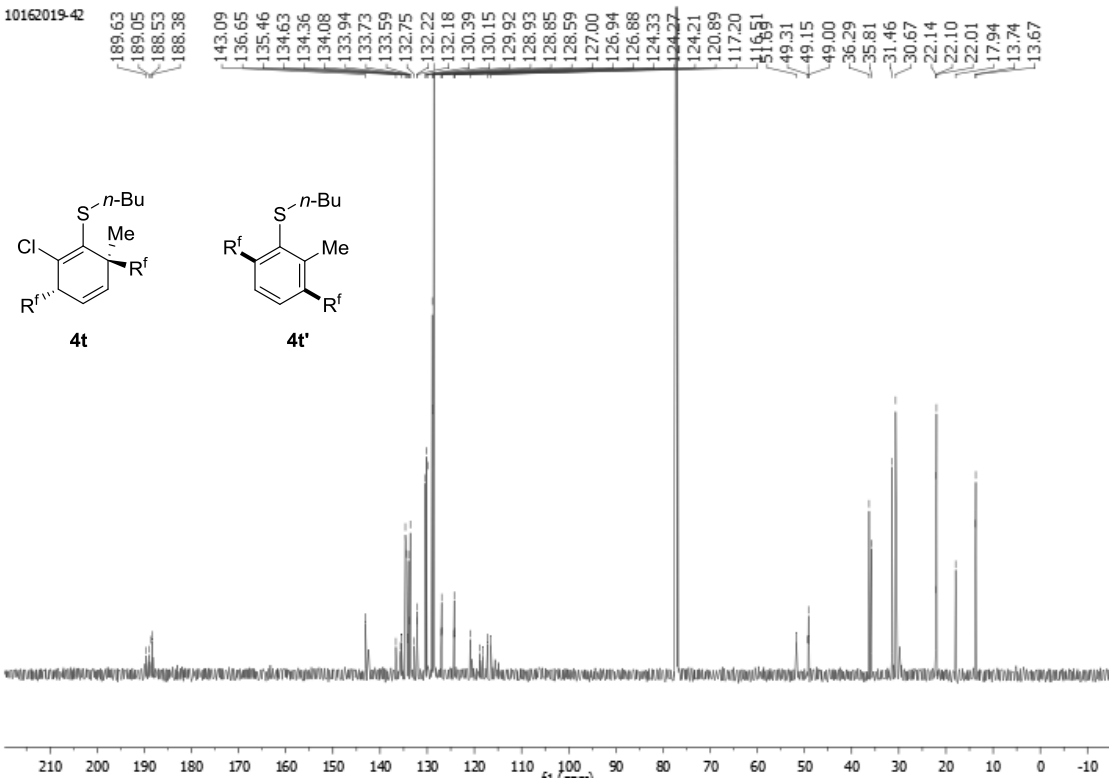
2.74 2.73 2.72 2.50 2.45 2.44 2.43 1.67 1.51 1.49 1.48 1.36 1.35 1.34 1.33 1.33 1.32 1.31 1.30 1.26 1.23 1.22 1.20 1.19 0.87 0.86 0.85 0.79 0.78
S n-Bu
Cl
Me
R^f
R^f
4t
S n-Bu
R^f
Me
R^f
4t'
5.30 2.05 2.00 4.76 9.41 0.99 1.03 0.98 2.00 4.02 2.74 2.99 2.02 5.32 3.02 3.12 3.91
11.0 10.5 10.0 9.5 9.0 8.5 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 -0.5 -1.0 -1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132.18
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126.94
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124.21
120.89
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116.51
51.69
49.31
49.15
49.00
36.29
35.81
31.46
30.67
22.14
22.10
22.01
17.94
13.74
13.67
n-Bu
S
Me
Cl
Rf
4t
4t'
210
200
190
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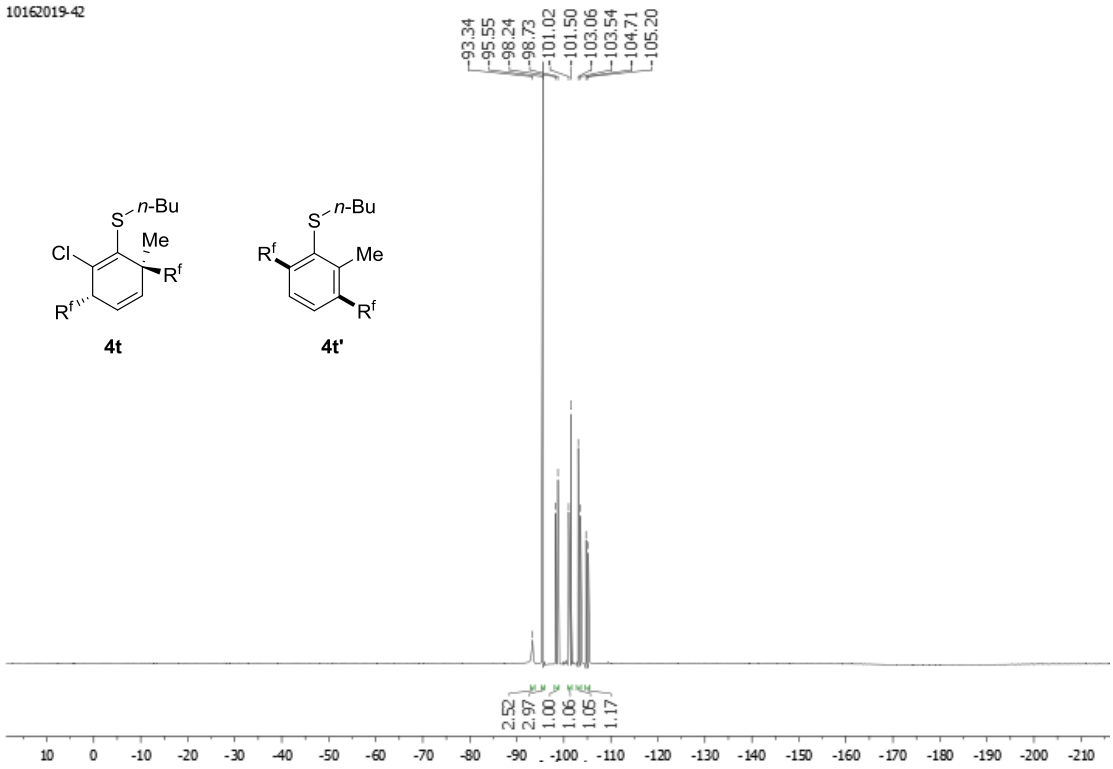
-10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103.06
103.54
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105.20
n-Bu
S
Me
Cl
Rf
4t
4t'
2.52
2.97
1.00
1.06
1.05
1.17
10
0
-10
-20
-30
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-60
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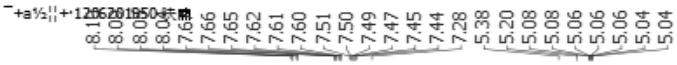
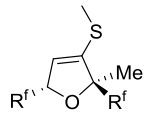
-210





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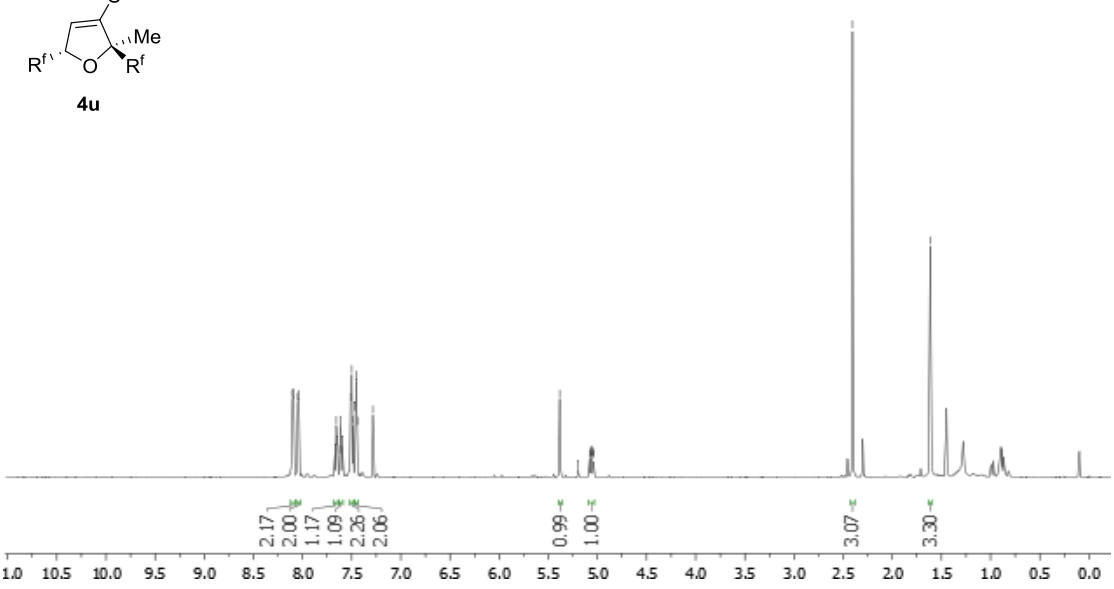

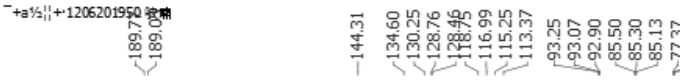

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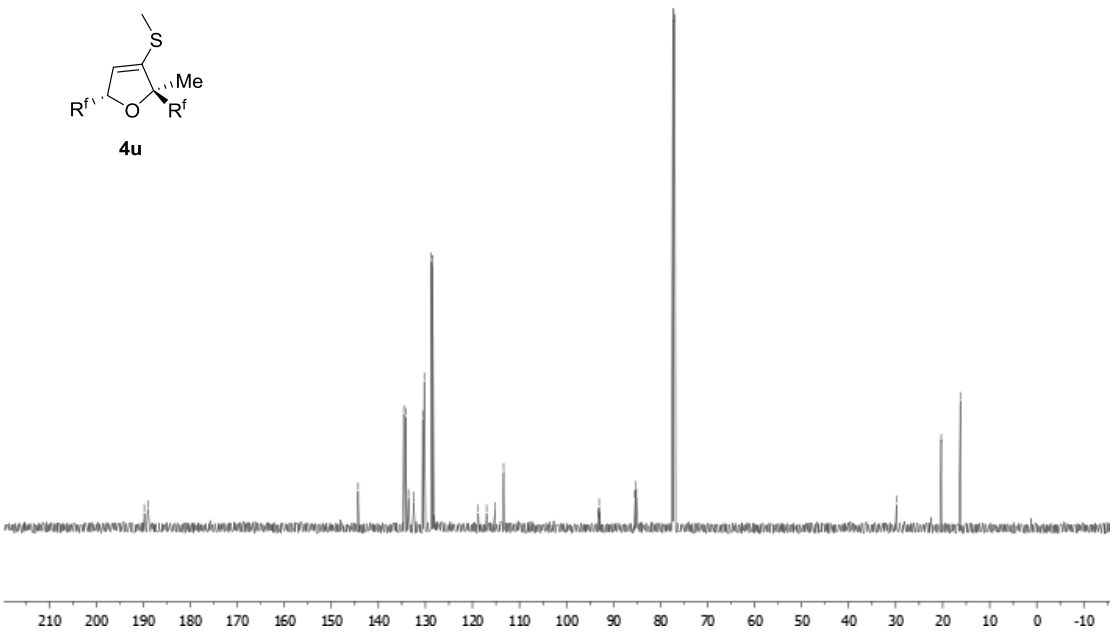

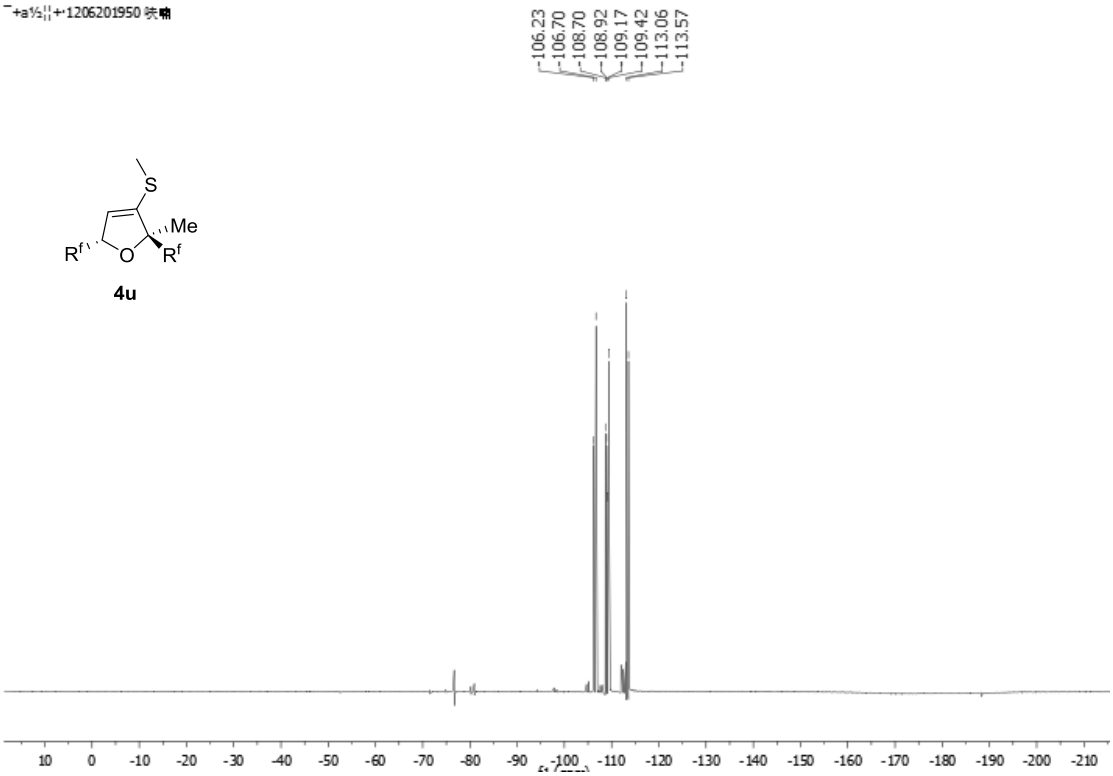
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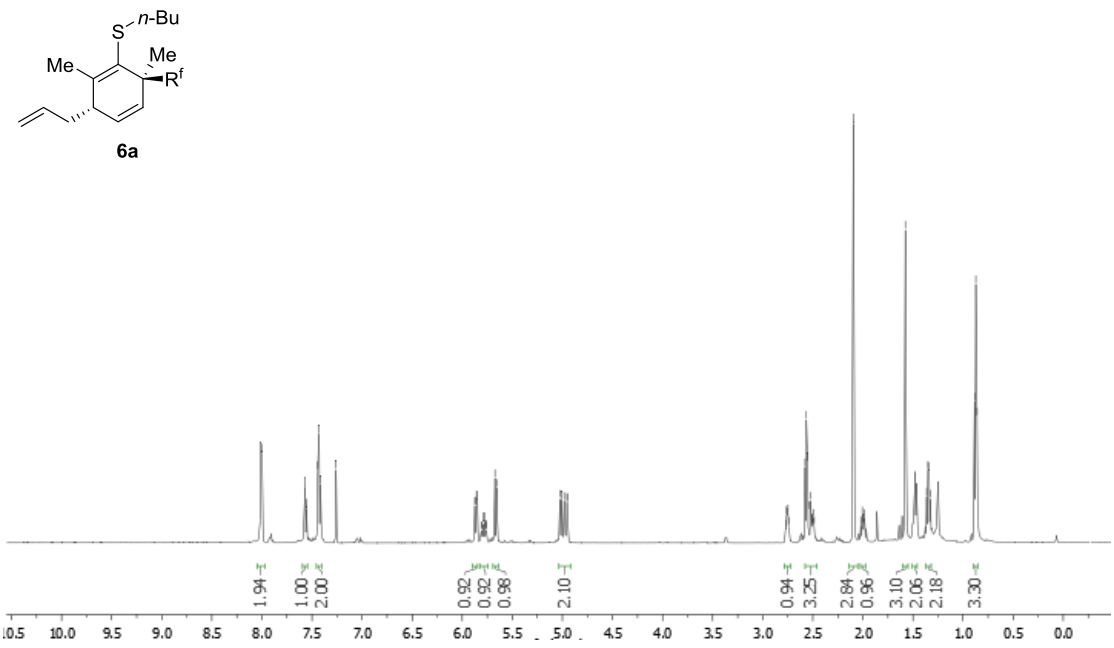
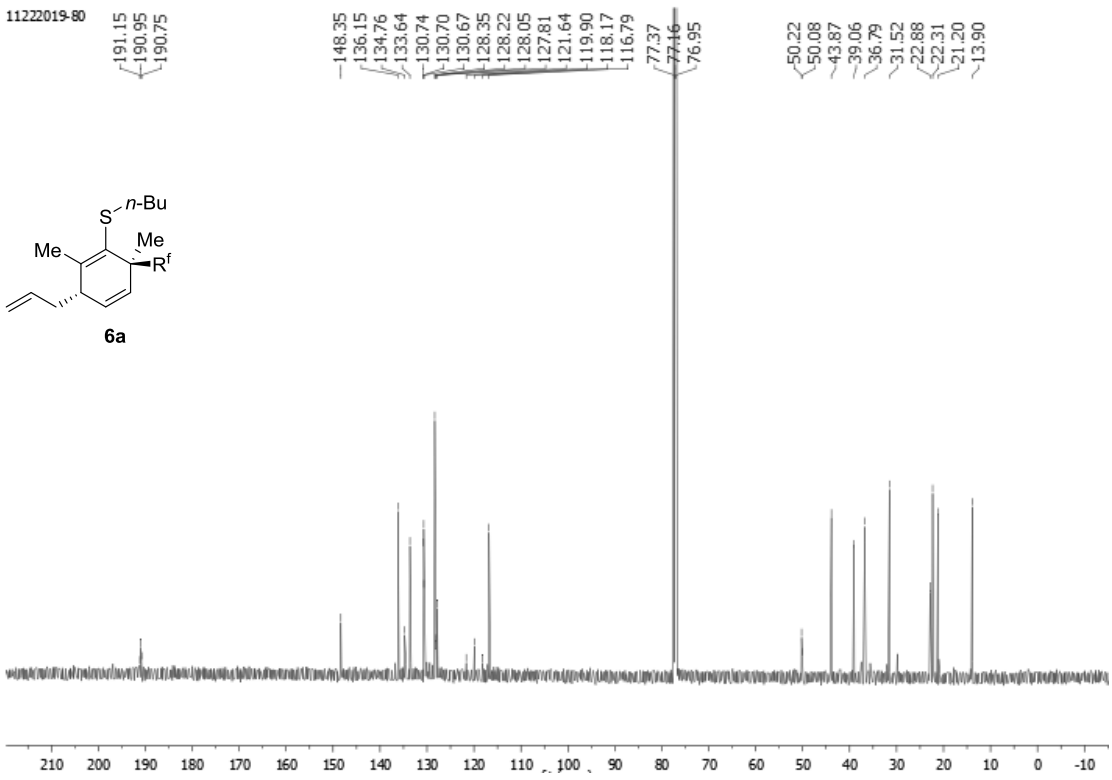
113.57
S
Me
Rf
O
Rf

4u


n-Bu
S
Me
Me
Rf

6a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128.05
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121.64
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118.17
116.79
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77.16
76.95
50.22
50.08
43.87
39.06
36.79
31.52
22.88
22.31
21.20
13.90
S
n-Bu
Me
Me
Rf
6a
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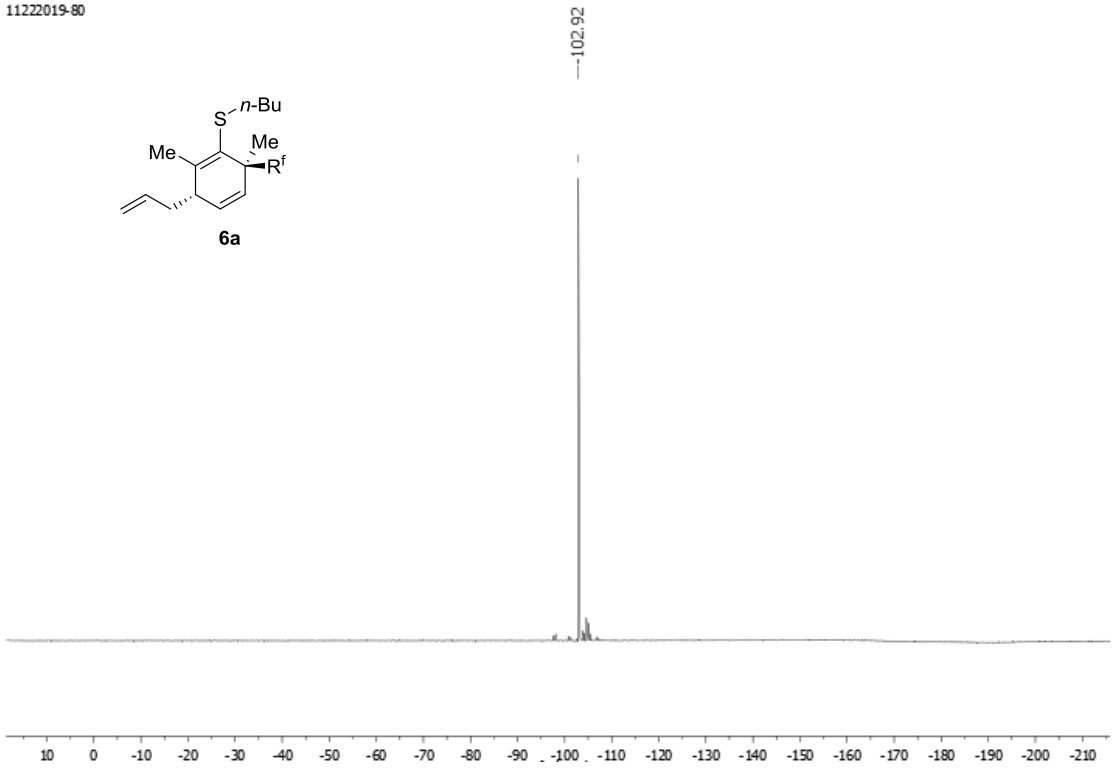
11222019-80
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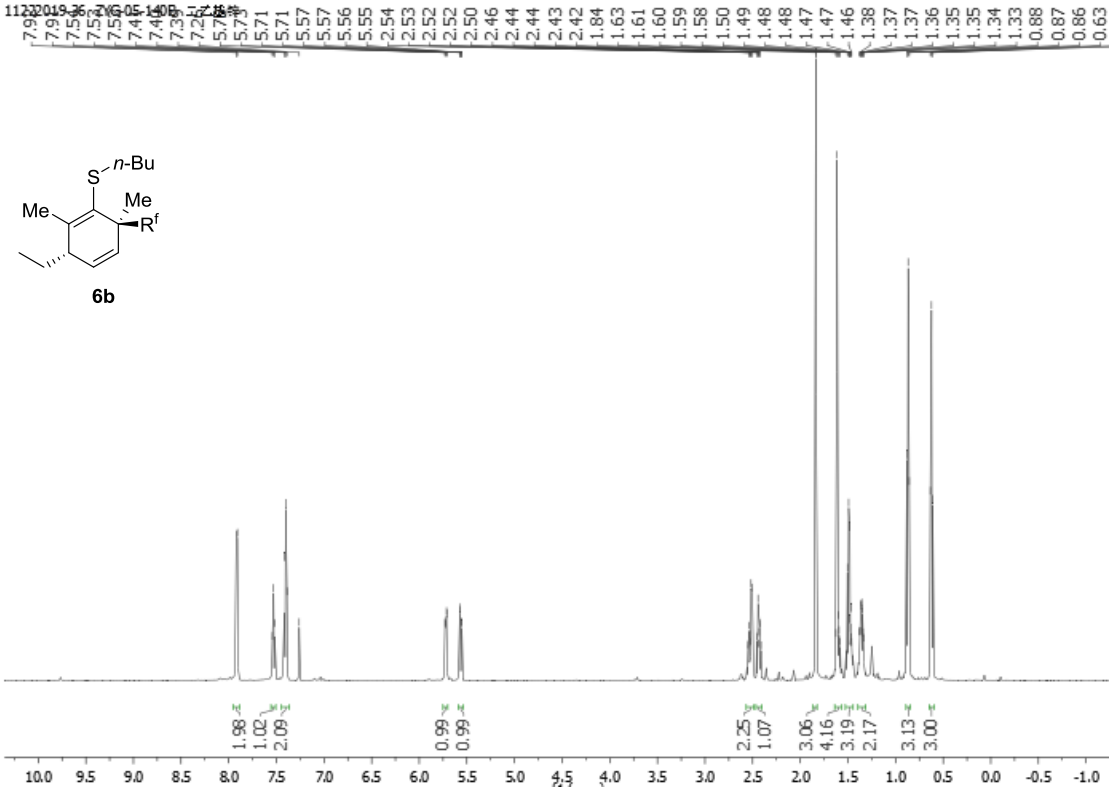
S
n-Bu
Me
Me
Rf
6a
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210



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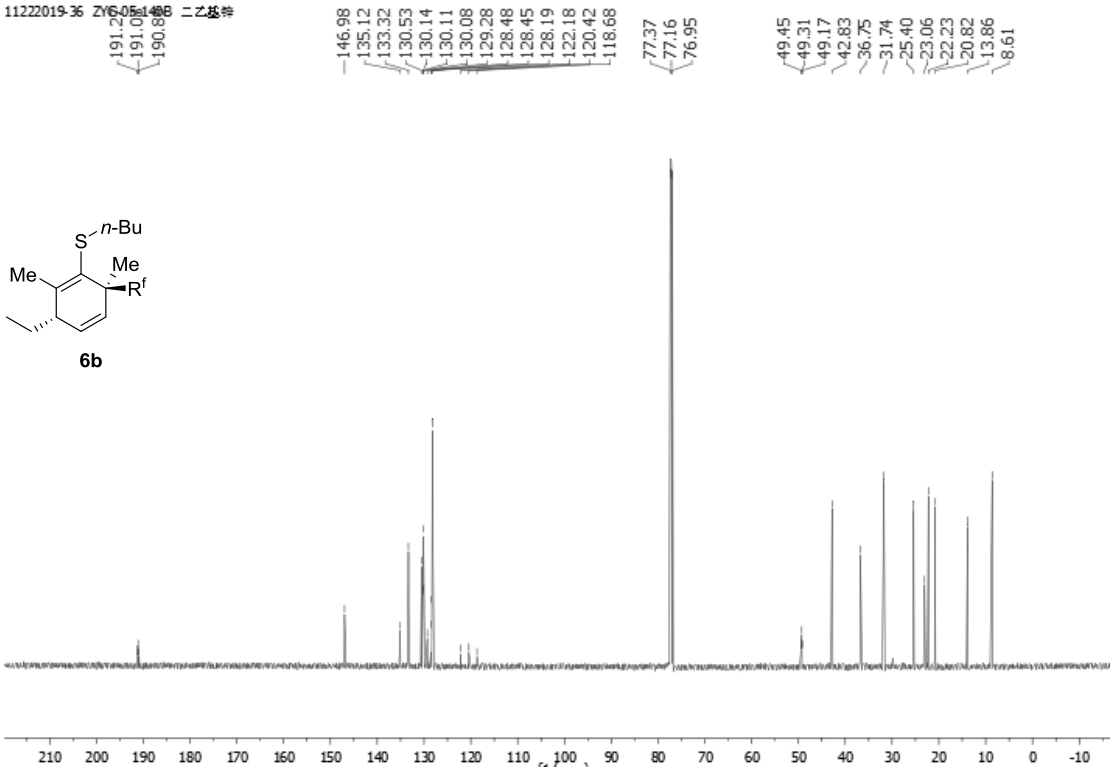
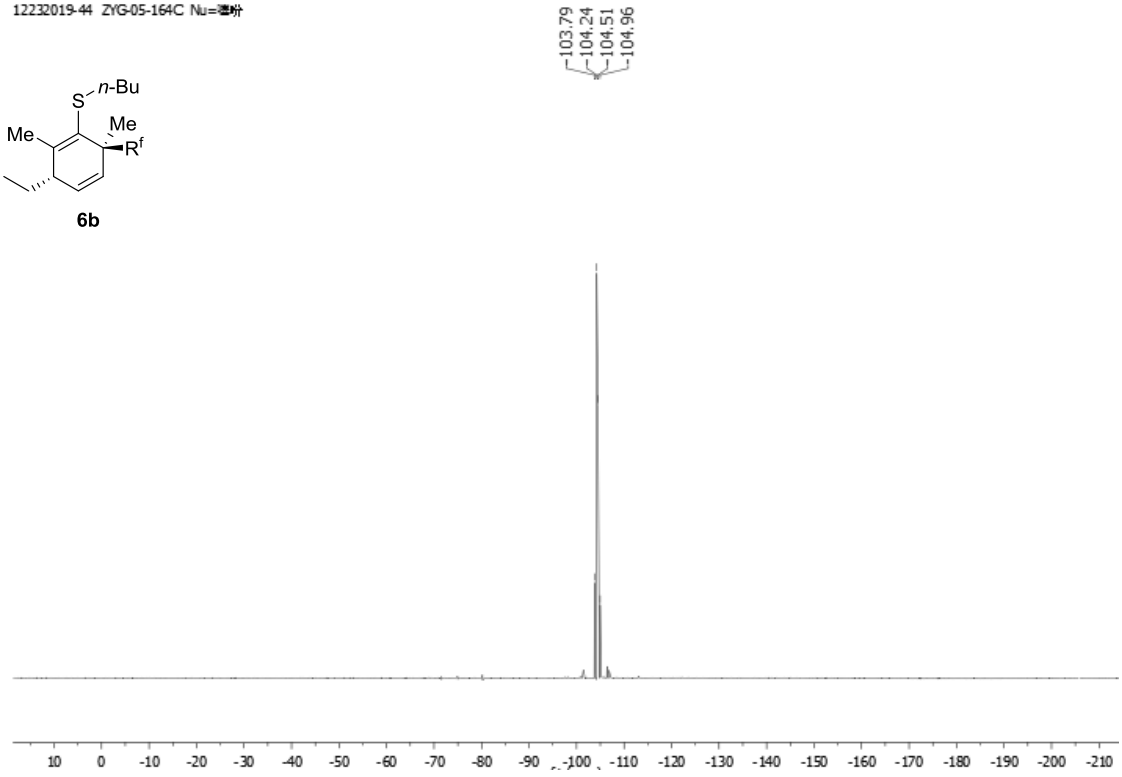


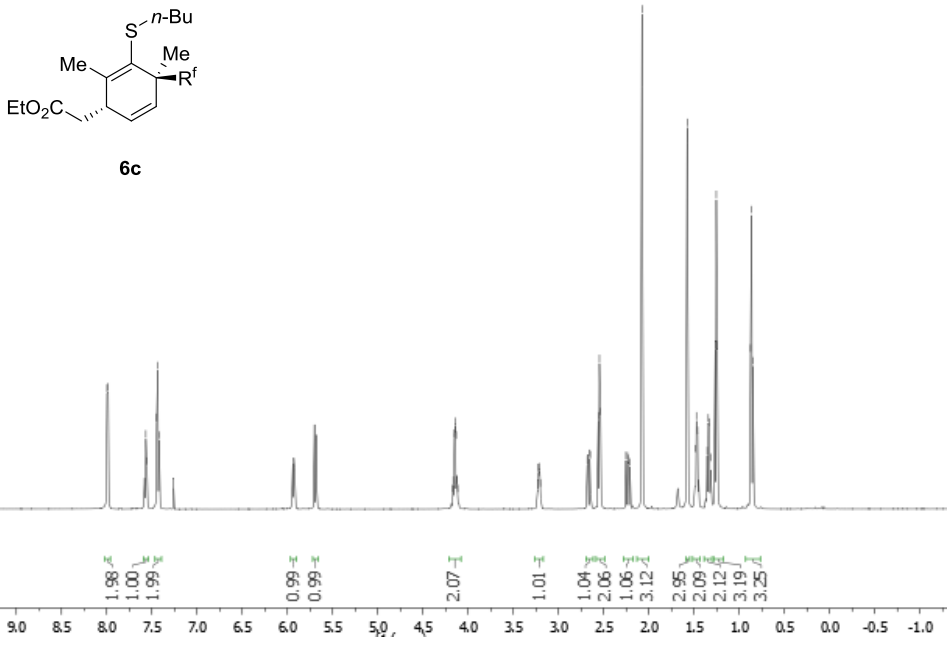
6b

12232019-44 ZYG-05-164C Nu=

6b

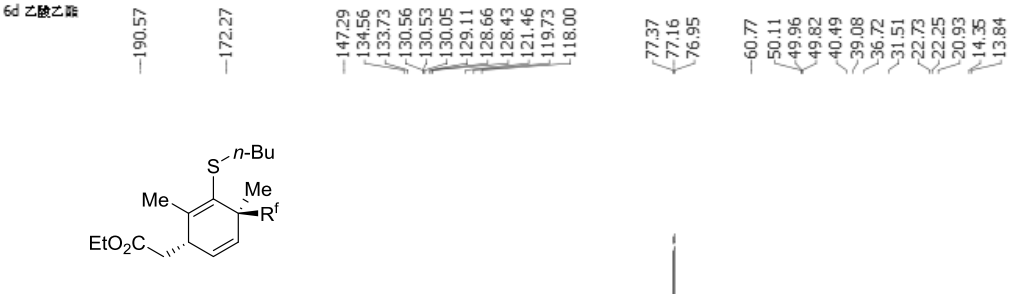


6d 乙酸乙酯



6c

6d 乙酸乙酯



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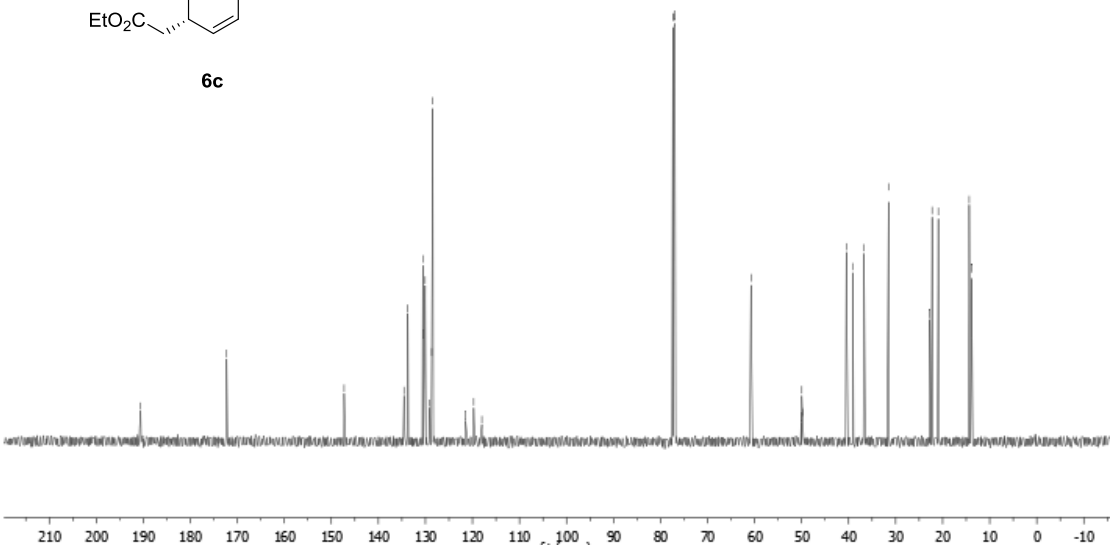

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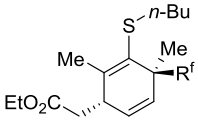

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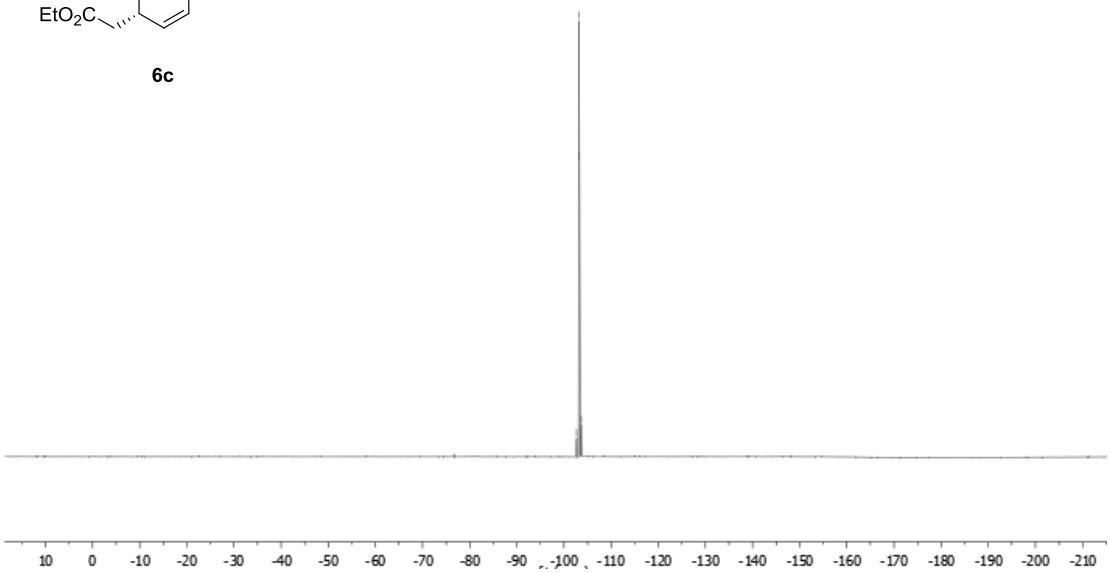
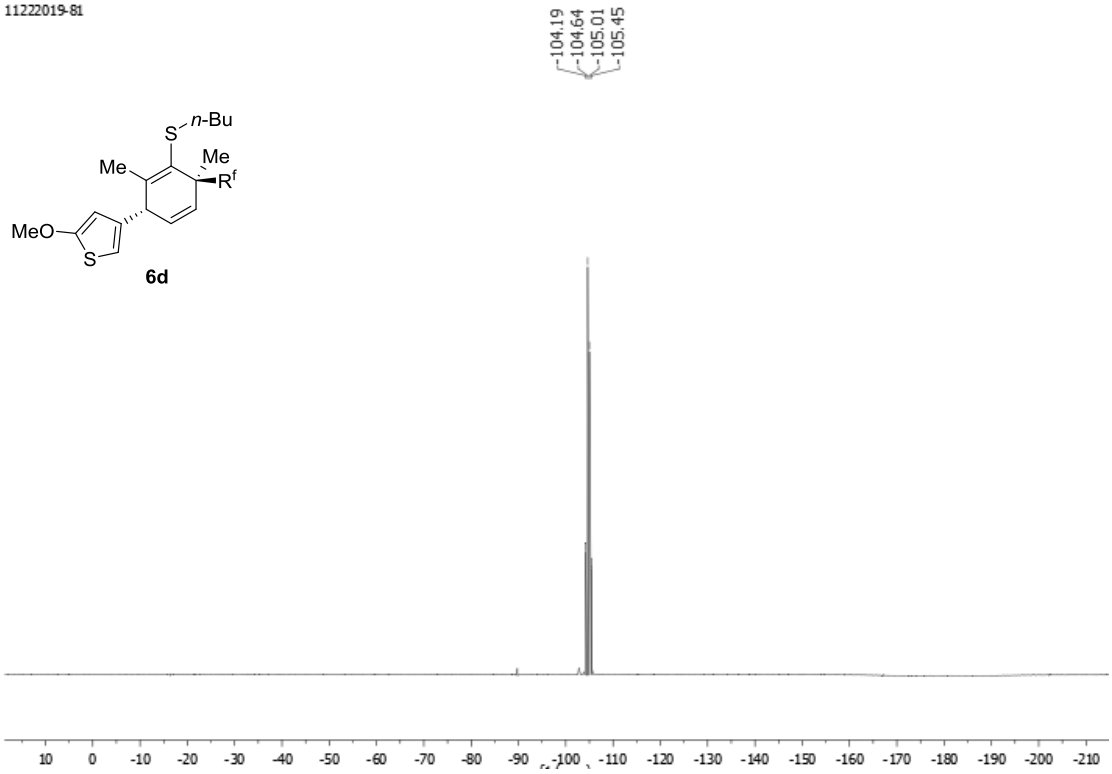
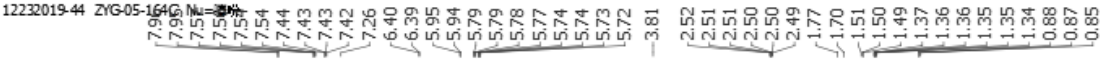


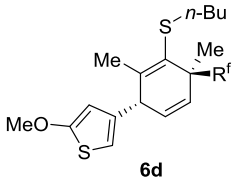
11222019-81



6d

12232019-44 ZYG-05-164C





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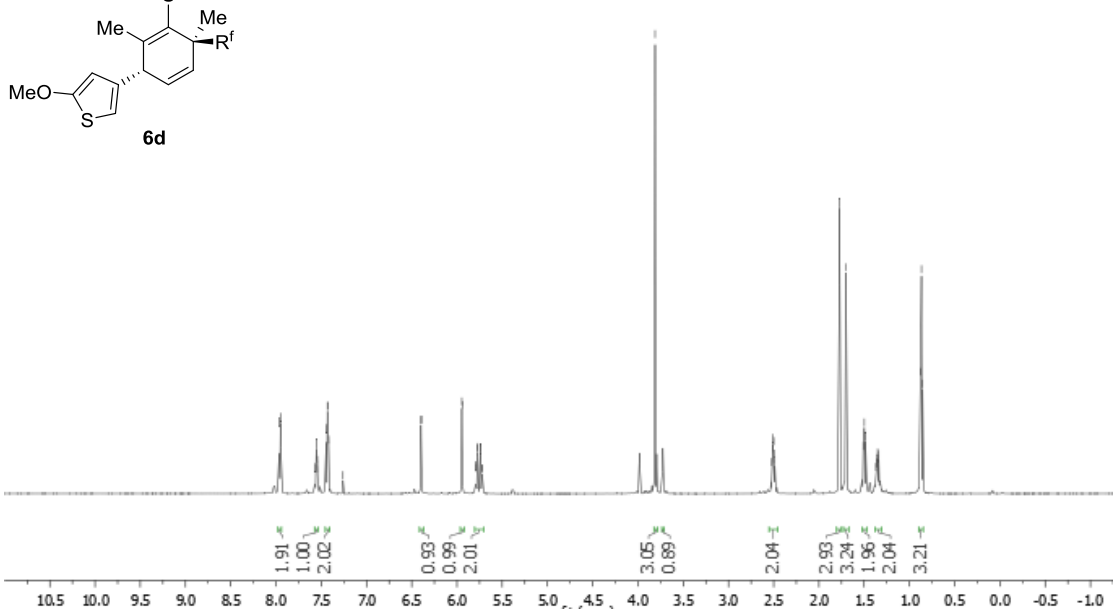

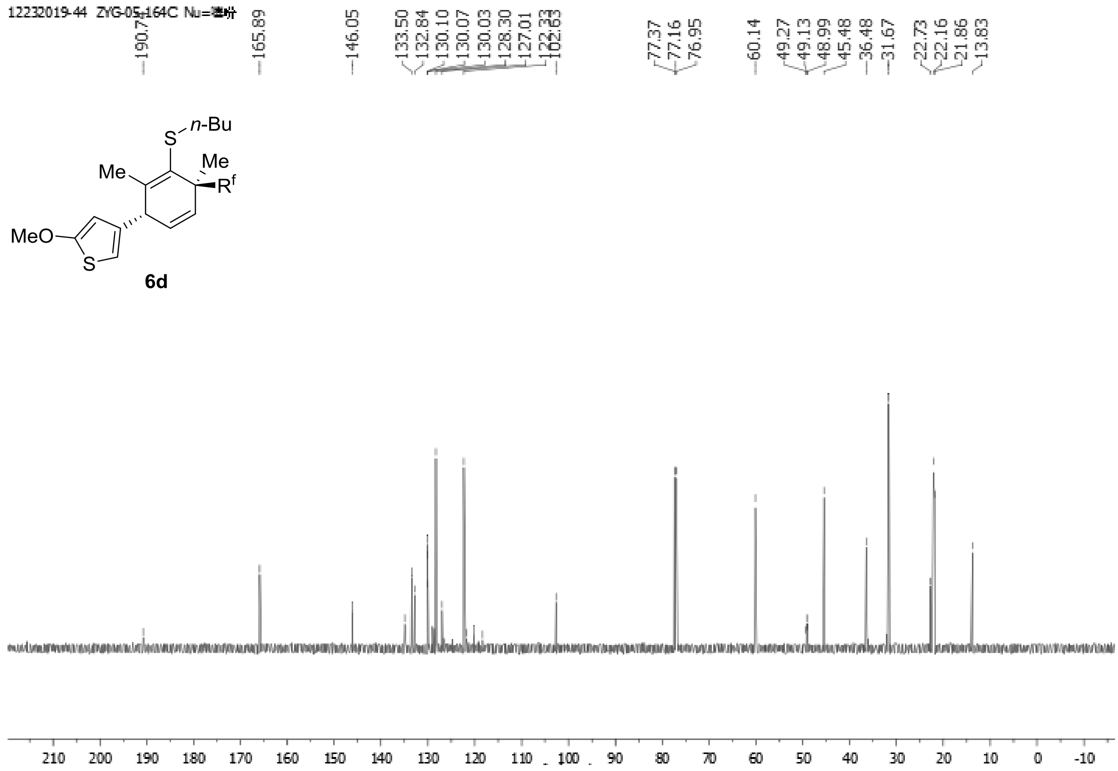
12232019-44 ZYG-05-164C
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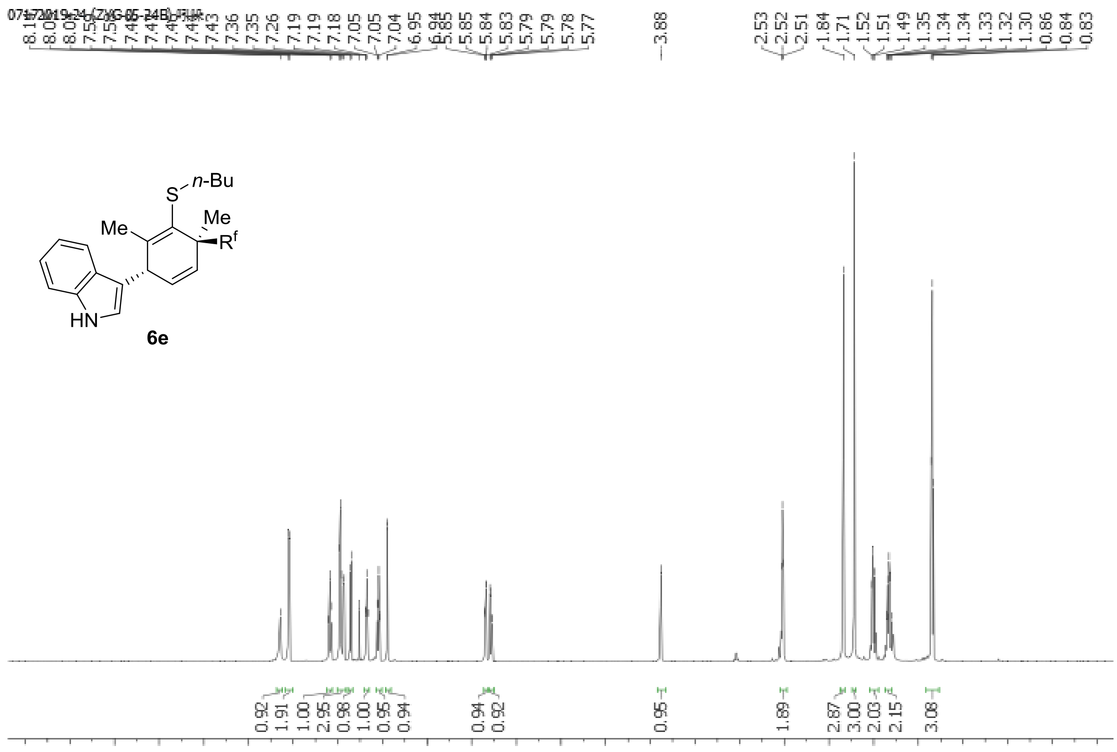
49.13
48.99
45.48
36.48
31.67
22.73
22.16
21.86
13.83
S
n-Bu
Me
Me
R^f
MeO
S
6d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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1.52
1.51
1.49
1.35
1.34
1.33
1.32
1.30
0.86
0.84
0.83
S
n-Bu
Me
Me
R^f
HN
6e
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2.95
0.98
1.00
0.95
0.94
0.94
0.92
0.95
1.89
2.87
3.00
2.03
2.15
3.08
11.0 10.5 10.0 9.5 9.0 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 -0.5 -1.0

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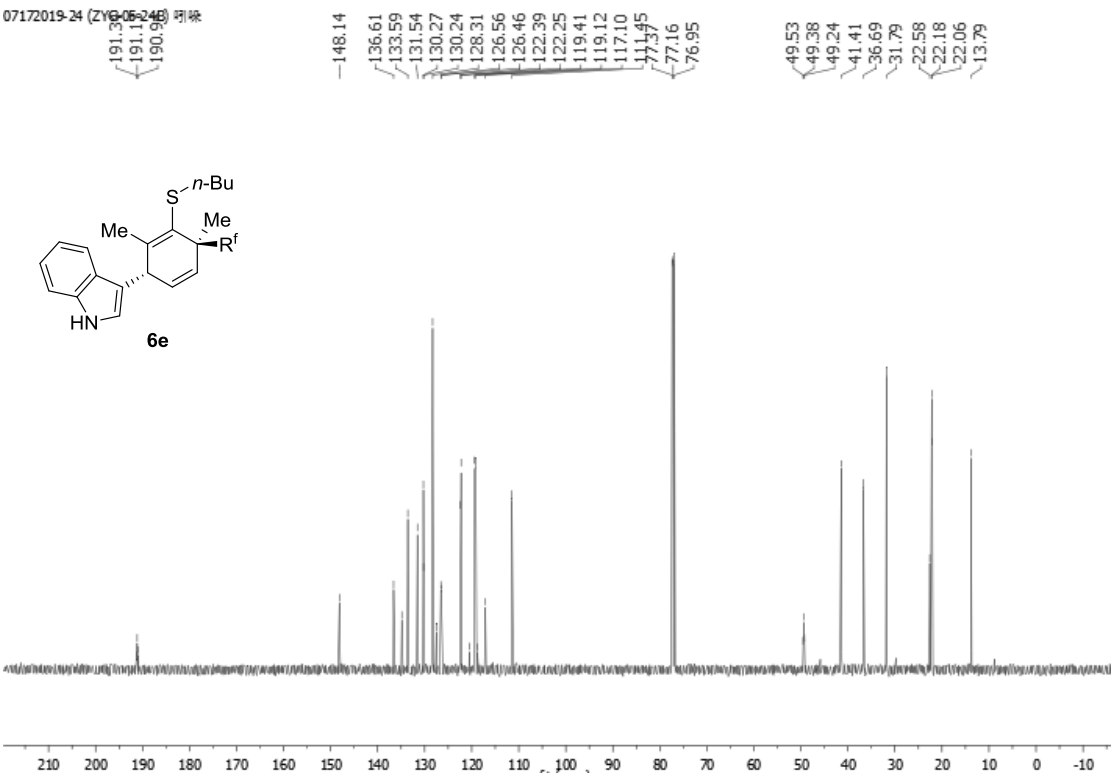
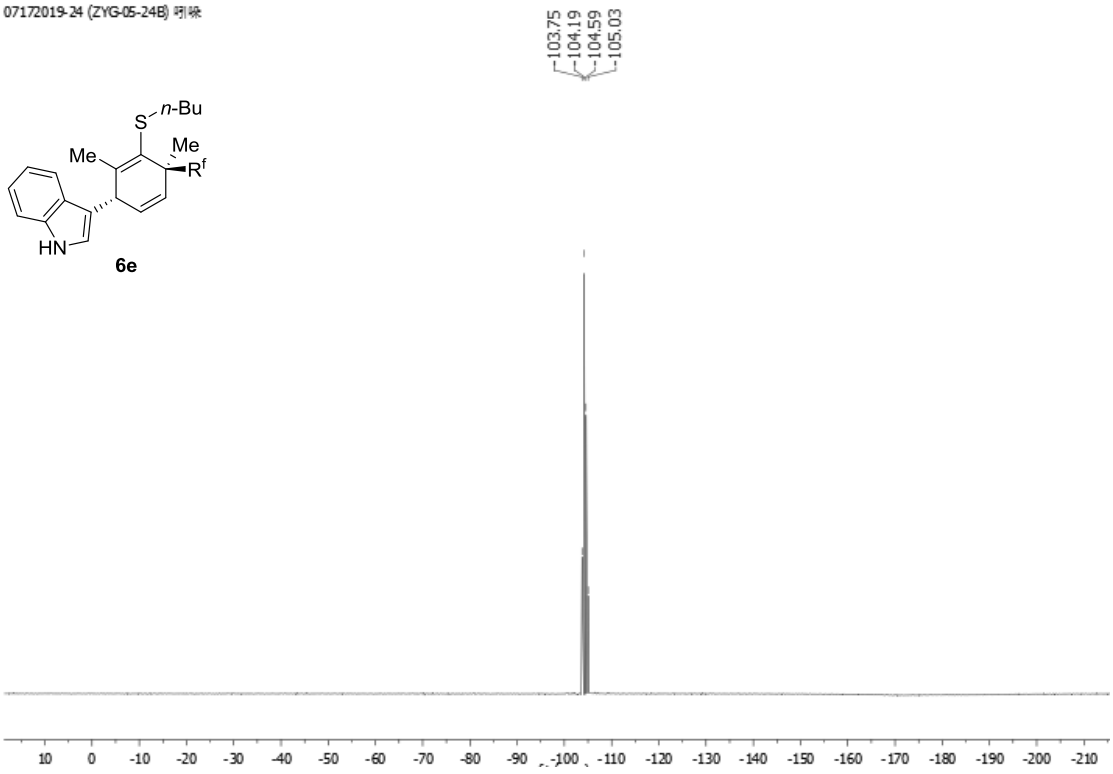
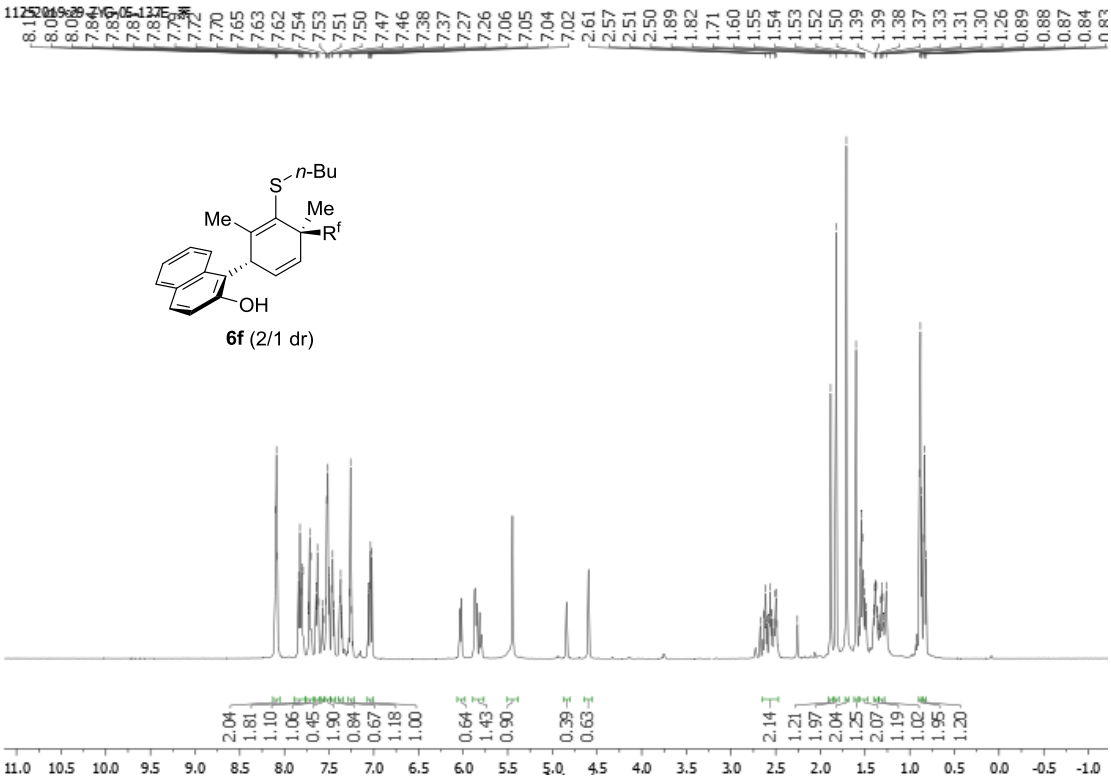
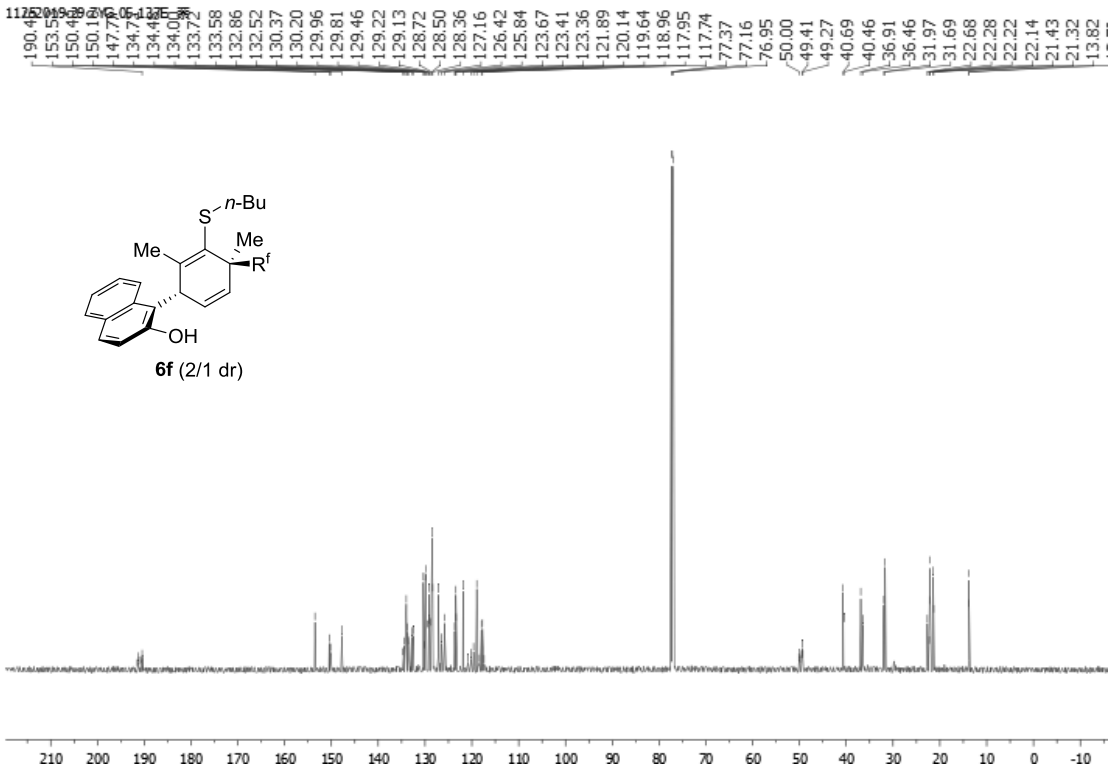


07172019-24 (ZYG-05-24B) 可录



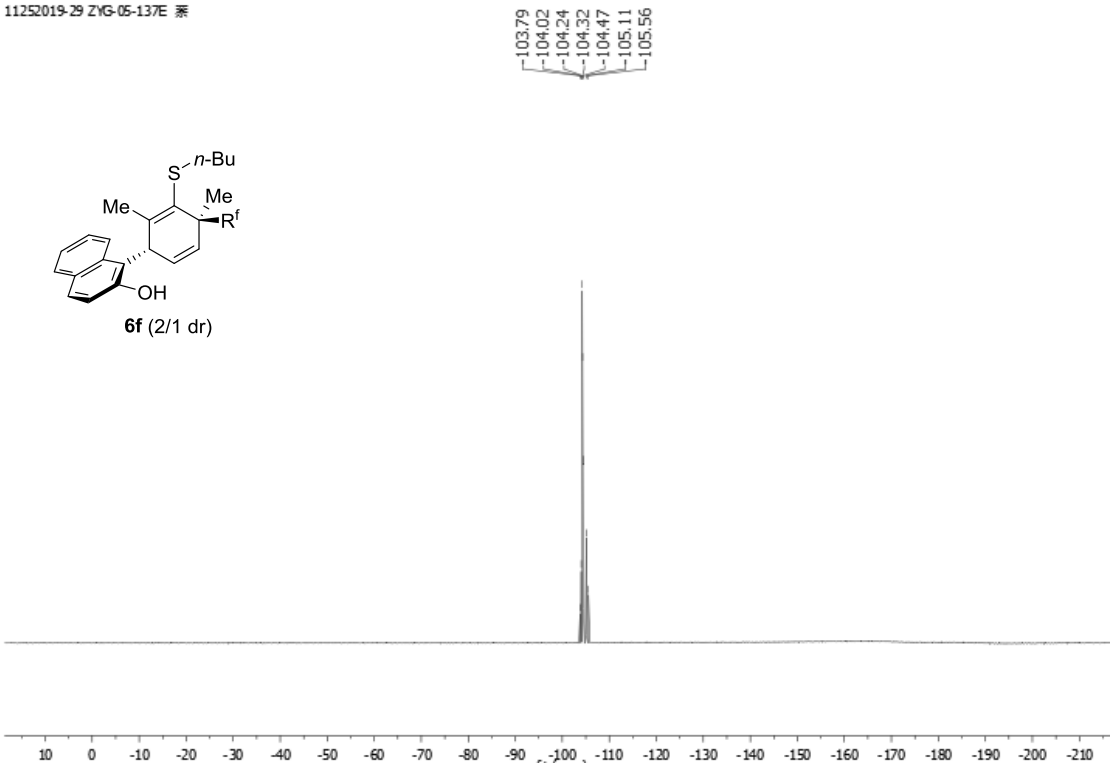


6f (2/1 dr)

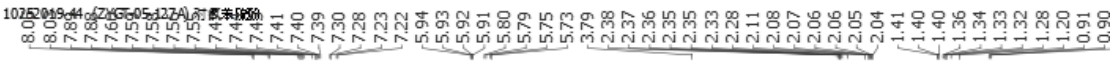


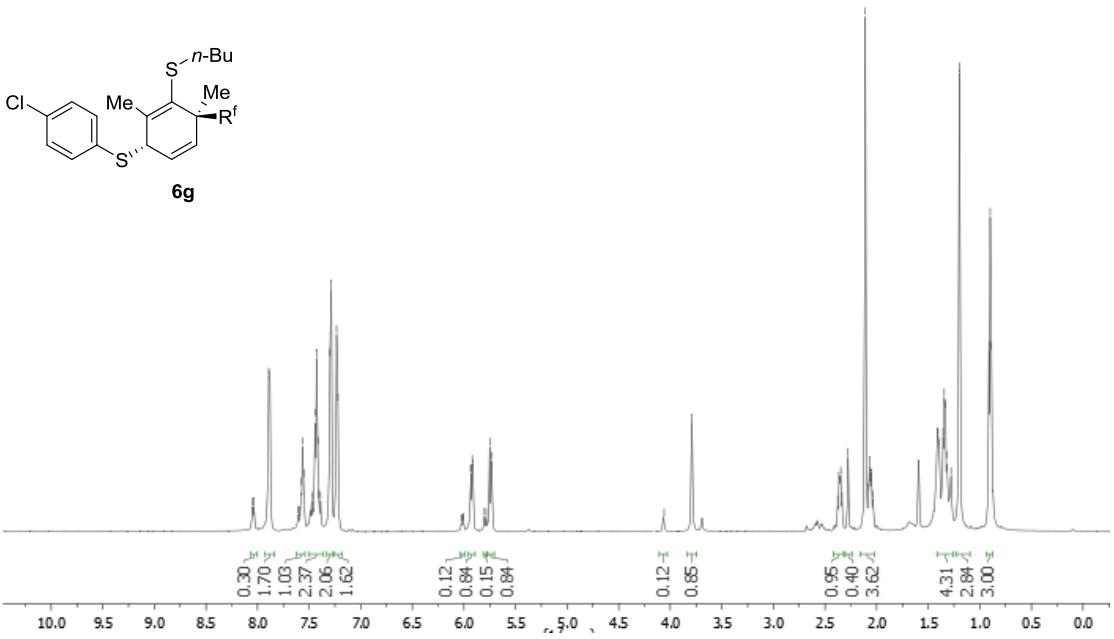
6f (2/1 dr)

11252019-29 ZYG-05-137E



6f (2/1 dr)





6g

10252019-72

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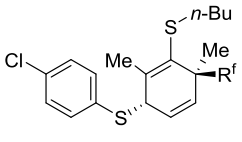
13.84



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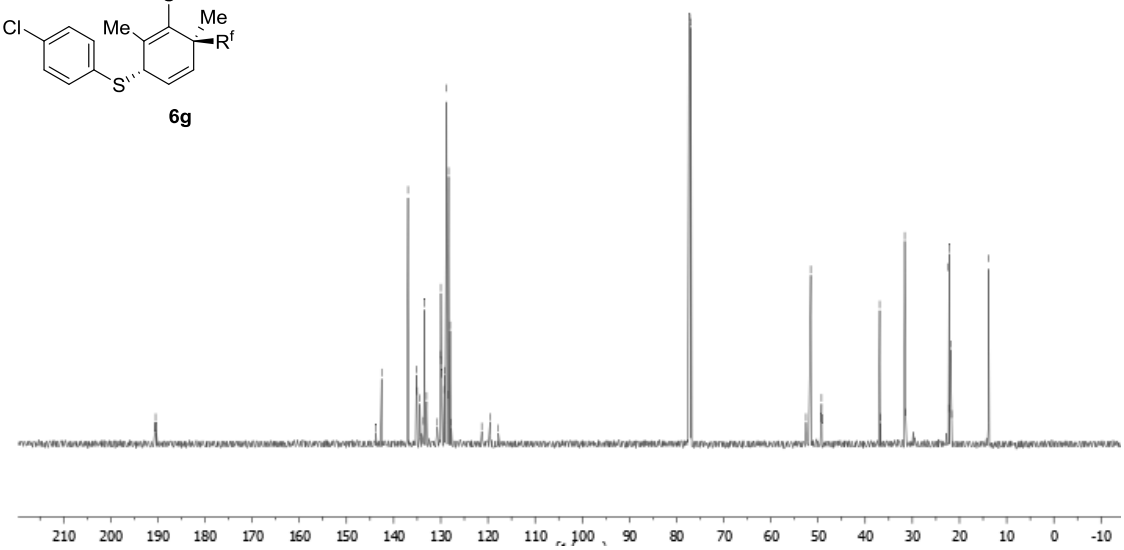

10252019-72

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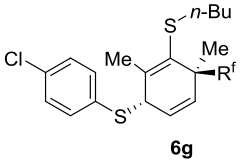
104.20



6g

0.49
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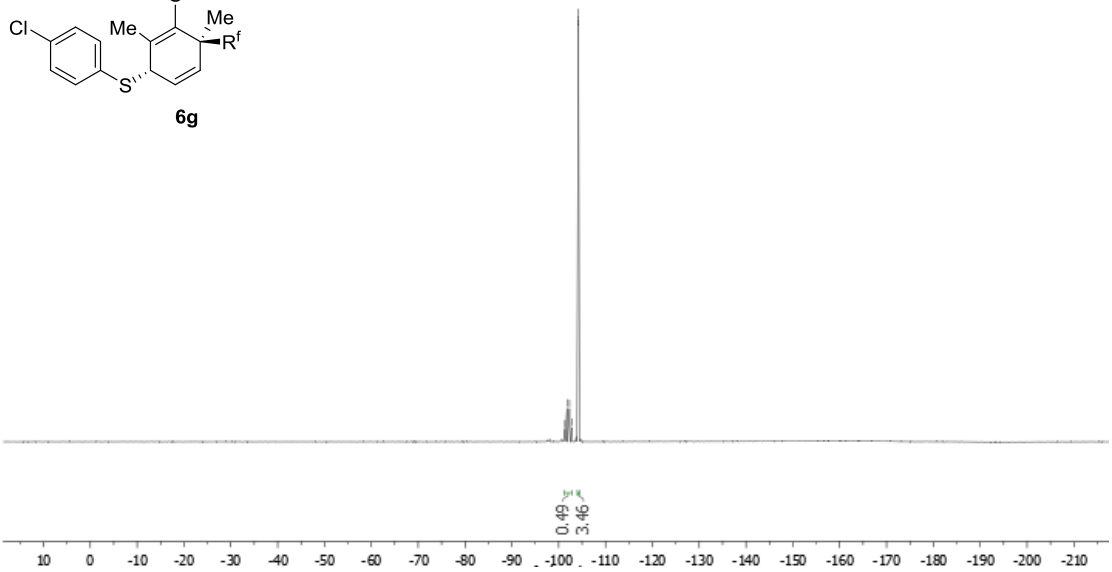

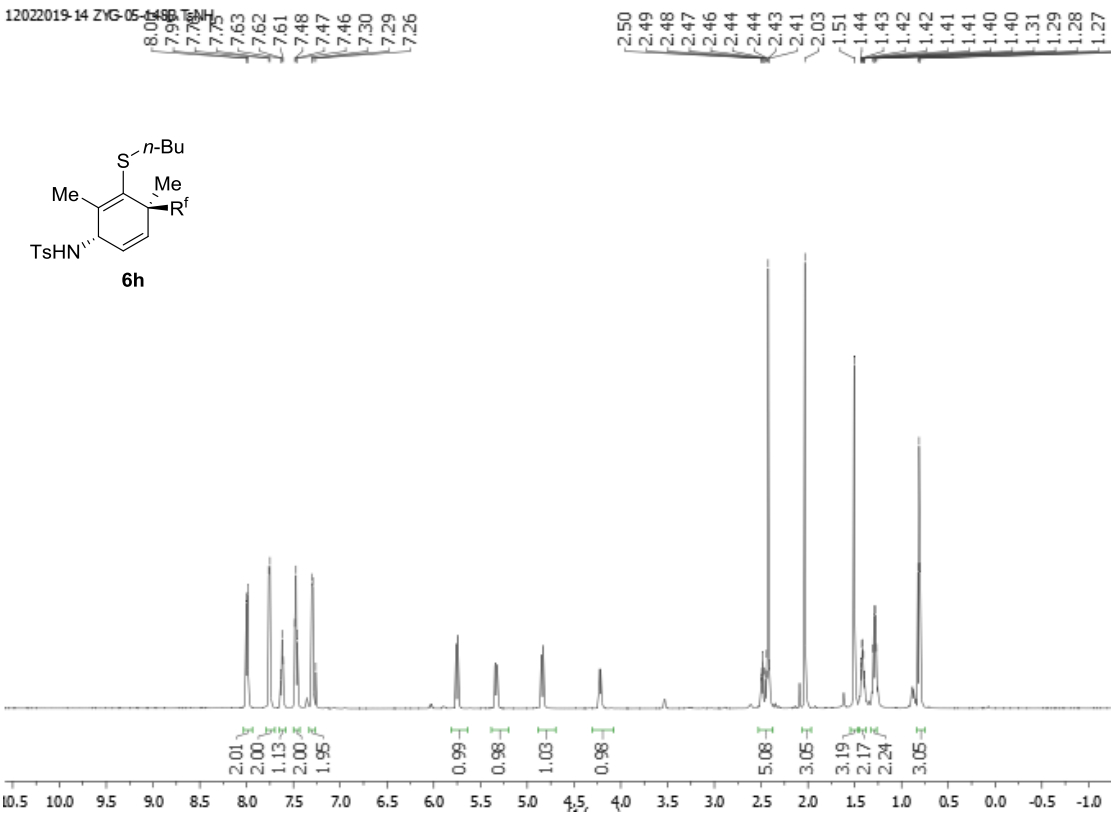
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7.62
7.61
7.48
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7.30
7.29
7.26
2.50
2.49
2.48
2.47
2.46
2.44
2.44
2.43
2.41
2.03
1.51
1.44
1.43
1.42
1.42
1.41
1.41
1.40
1.40
1.31
1.29
1.28
1.27
n-Bu
S
Me
Me
Rf
TsHN
6h
2.01
2.00
1.13
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0.98
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3.05
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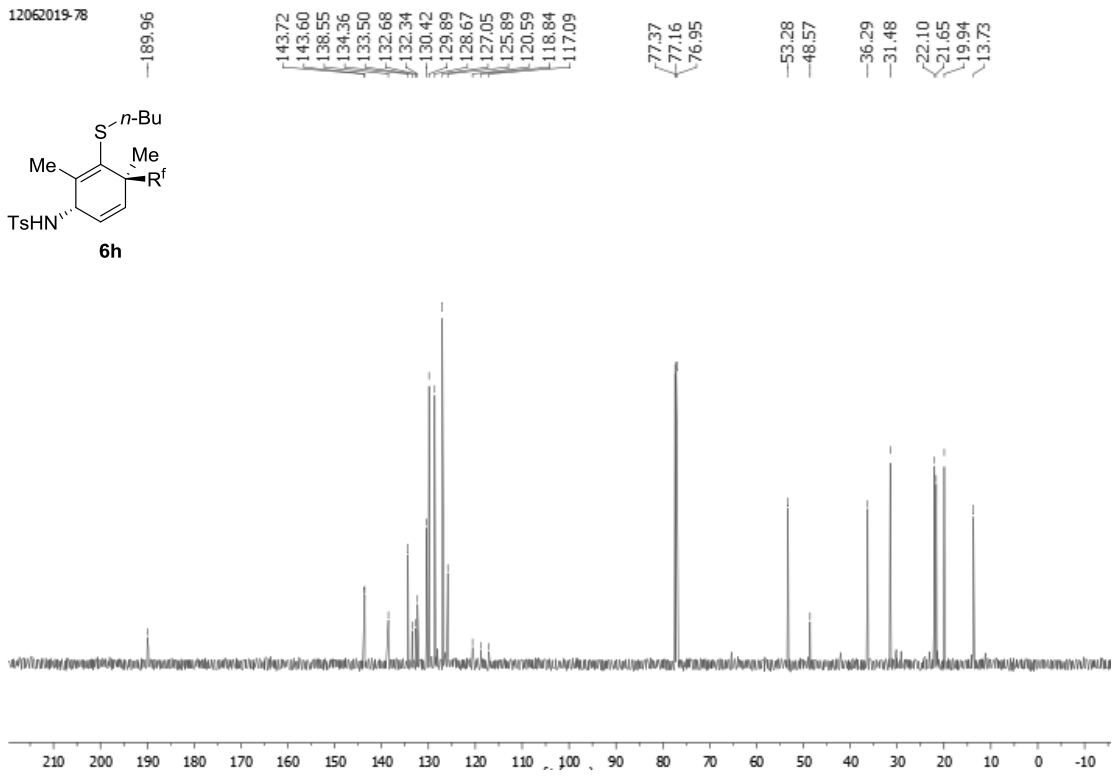
2.17
2.24
3.05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125.89
120.59
118.84
117.09
77.37
77.16
76.95
53.28
48.57
36.29
31.48
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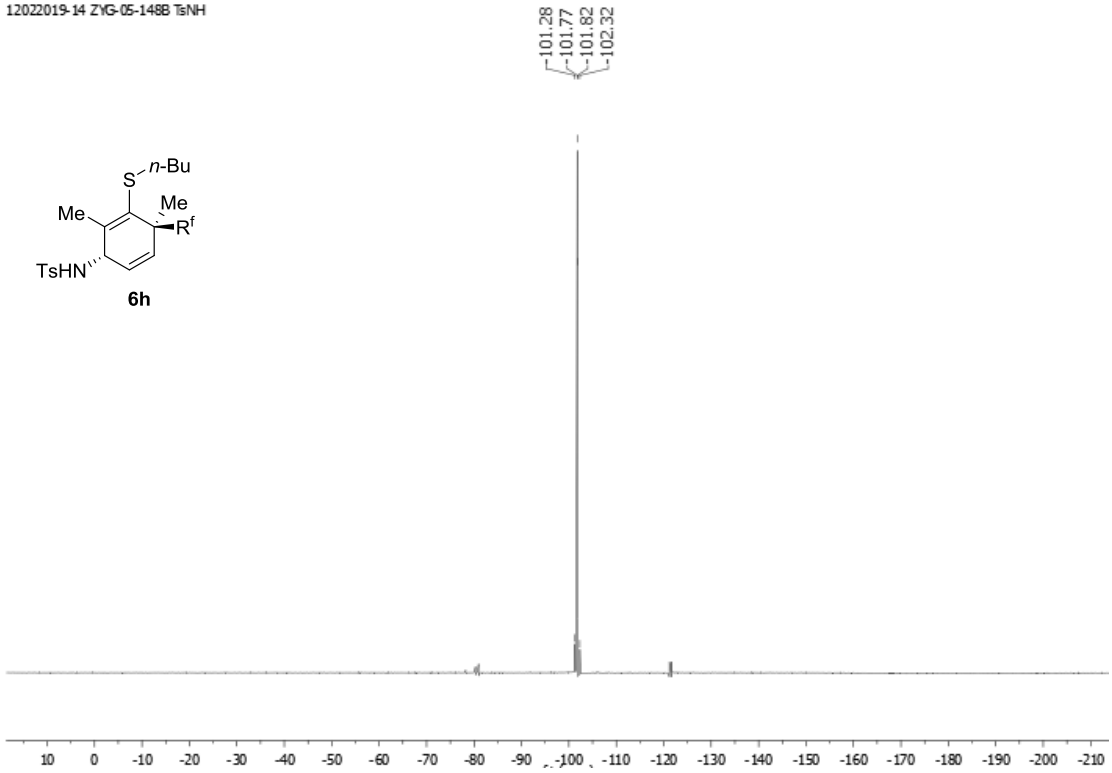
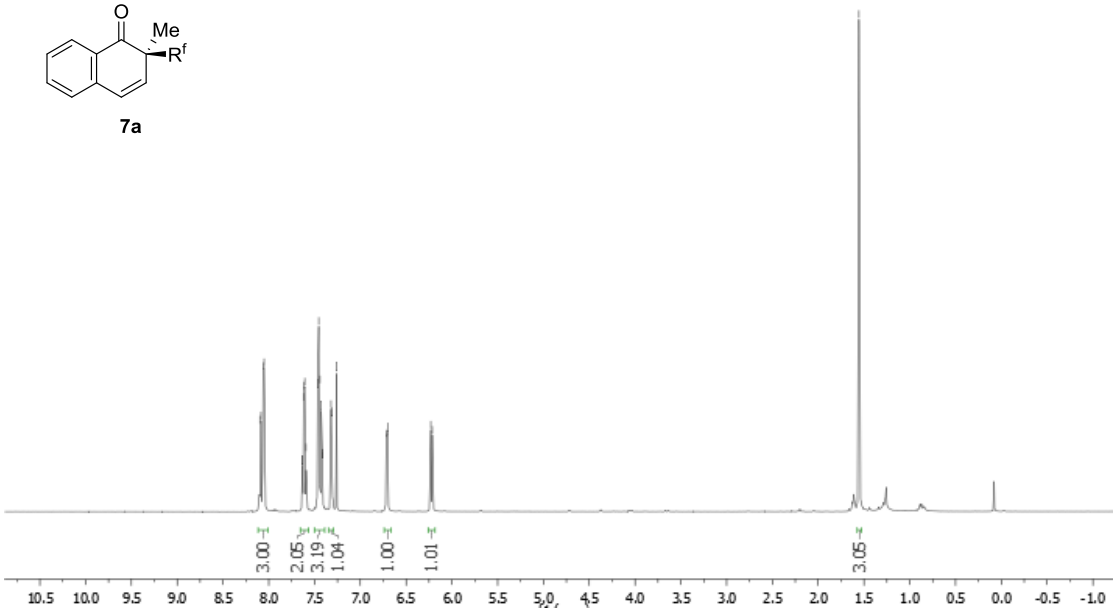
13.73
n-Bu
S
Me
Me
Rf
TsHN
6h

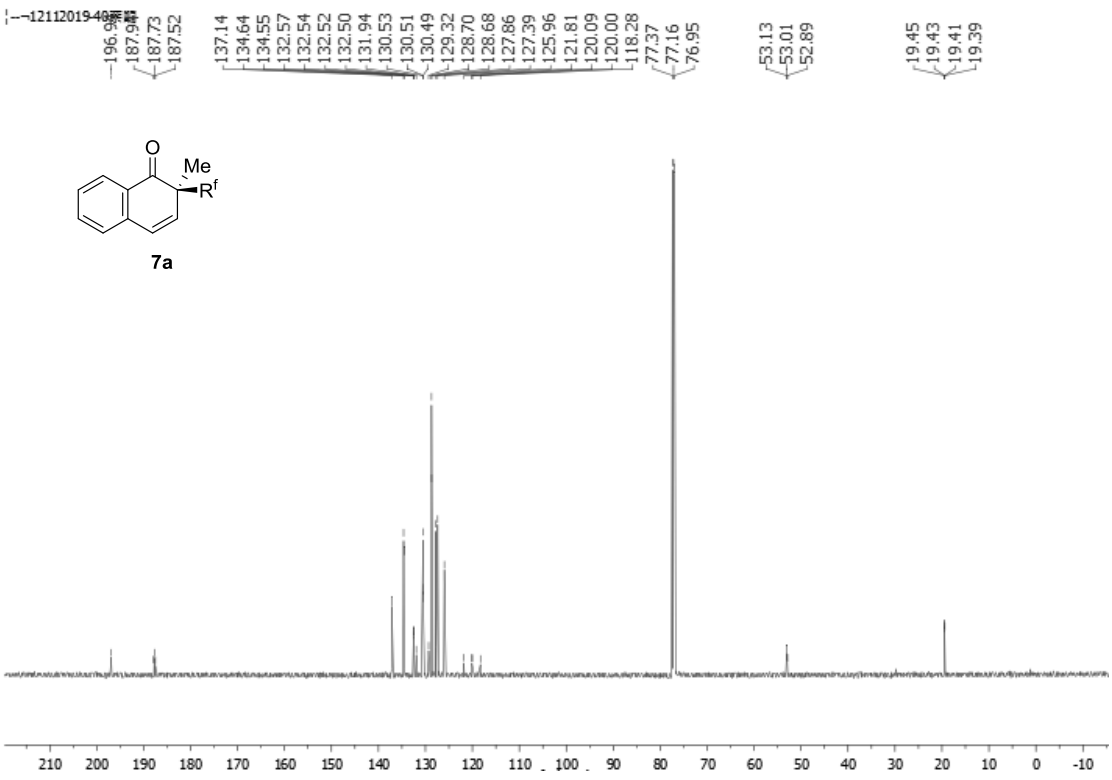
12022019-14 ZYG-05-148B TsNH



6h

7a




12112019-40茶霸
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187.52
137.14
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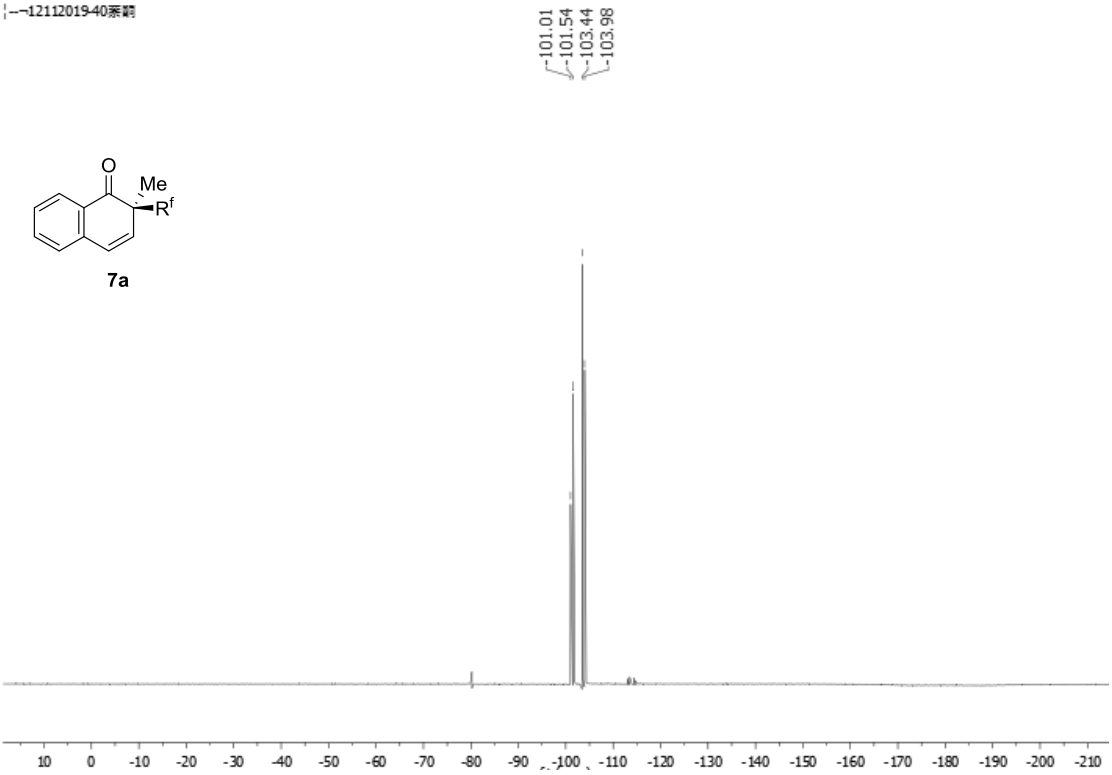
132.50
131.94
130.53
130.51
130.49
129.32
128.70
128.68
127.86
127.39
125.96
121.81
120.09
120.00
118.28
77.37
77.16
76.95
53.13
53.01
52.89
19.45
19.43
19.41
19.39
O
Me
Rf
7a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


12112019-40茶霸
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101.54
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103.98
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Rf
7a
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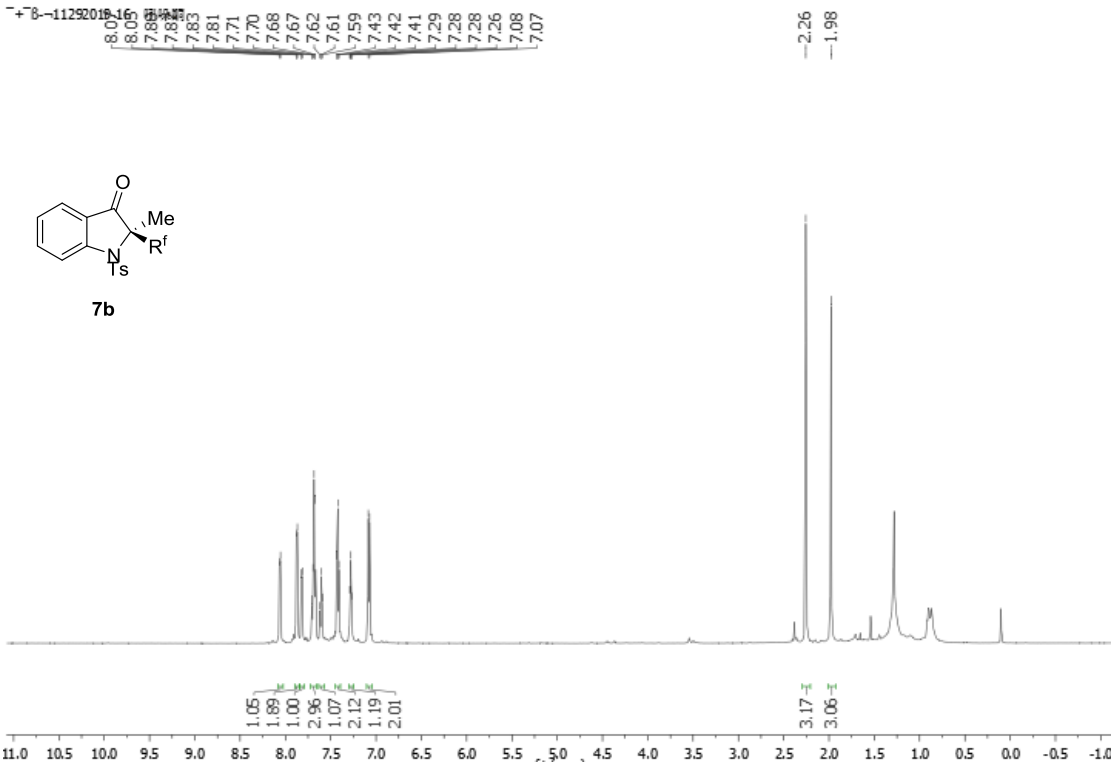
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7.61
7.59
7.43
7.42
7.41
7.29
7.28
7.28
7.26
7.08
7.07
2.26
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O
Me
Rf
N
Ts
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1.89
1.00
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1.07
2.12
1.19
2.01
3.17
3.06
11.0
10.5
10.0
9.5
9.0
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
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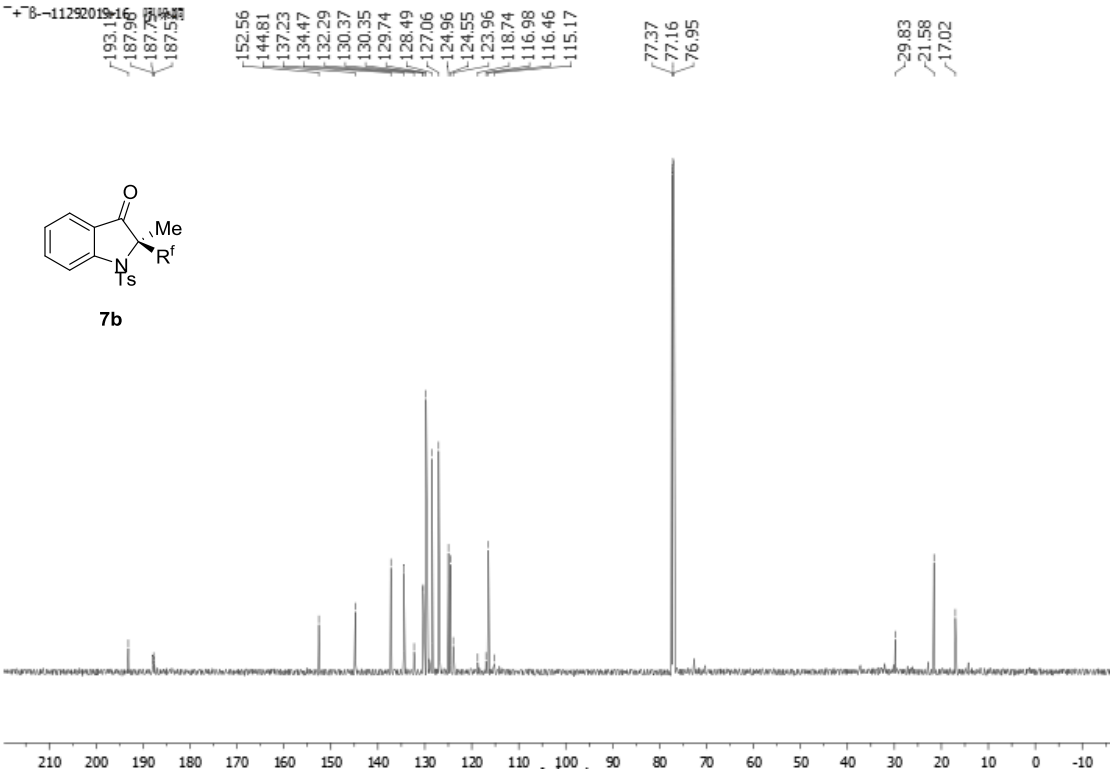
0.0
-0.5

7b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128.49
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124.96
124.55
123.96
118.74
116.98
116.46
115.17
77.37
77.16
76.95
29.83
21.58
17.02
O
Me
Rf
N
Ts
210
200
190
180
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30
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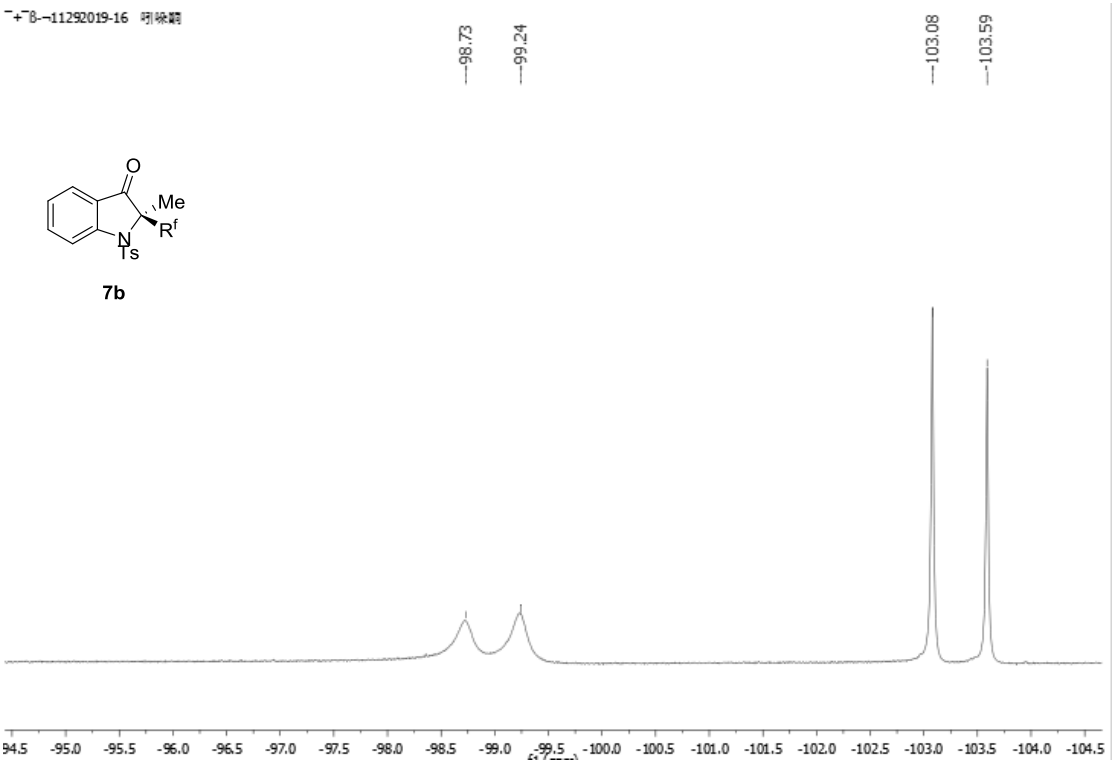
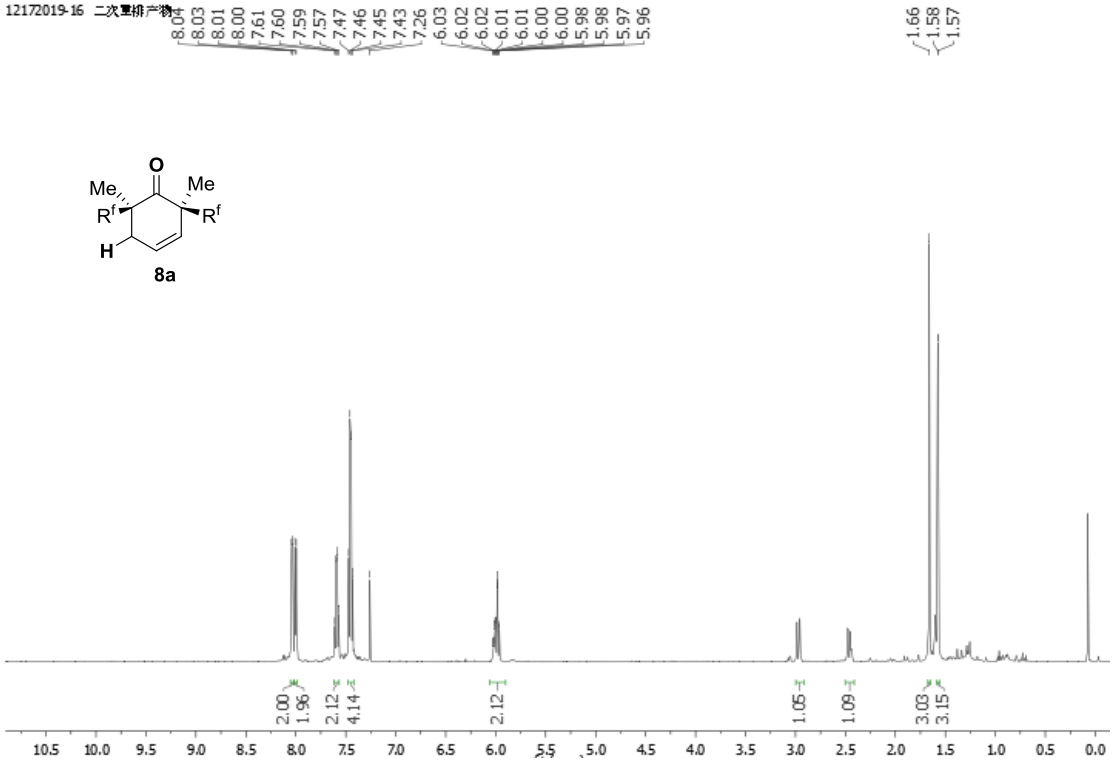
0
-10

7b


-98.73
-99.24
-103.08
-103.59
O
Me
Rf
N
Ts
7b
94.5 -95.0 -95.5 -96.0 -96.5 -97.0 -97.5 -98.0 -98.5 -99.0 -99.5 -100.0 -100.5 -101.0 -101.5 -102.0 -102.5 -103.0 -103.5 -104.0 -104.5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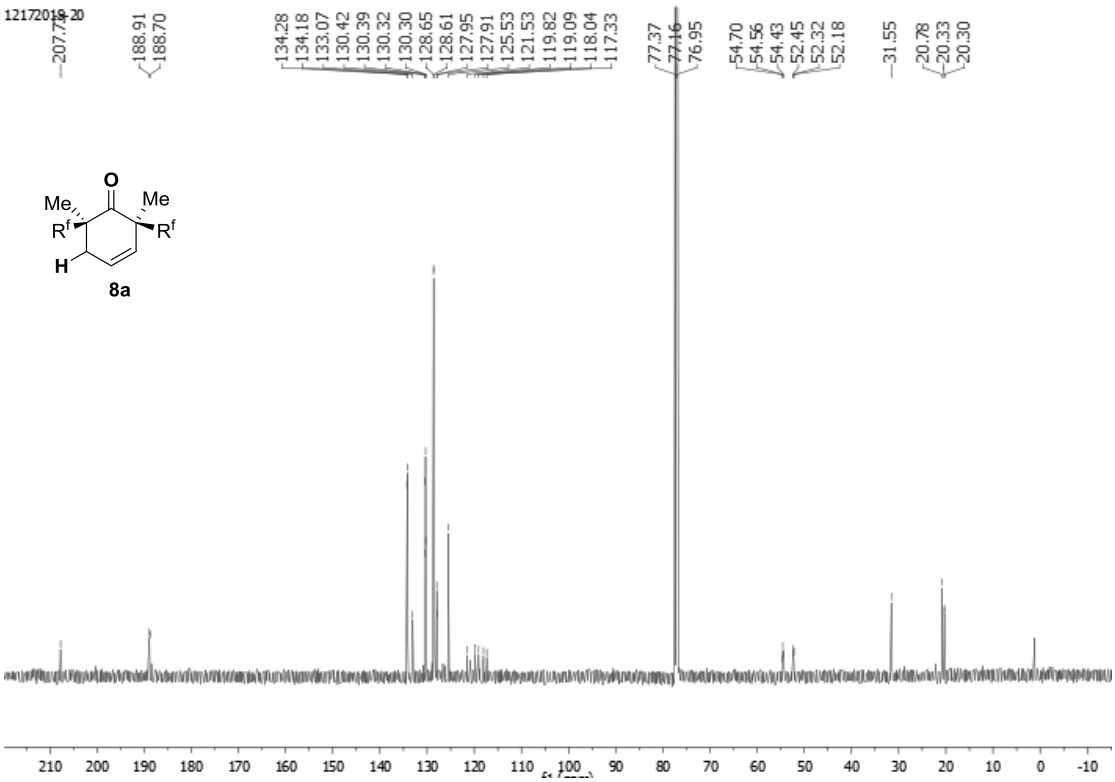
7.26
6.03
6.02
6.02
6.01
6.01
6.00
6.00
5.98
5.98
5.97
5.96
1.66
1.58
1.57
O
Me
Me
Rf
Rf
H
8a
2.00
1.96
2.12
4.14
2.12
1.05
1.09
3.03
3.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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77.16
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54.70
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54.43
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52.18
31.55
20.78
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Me
Rf
Rf
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8a
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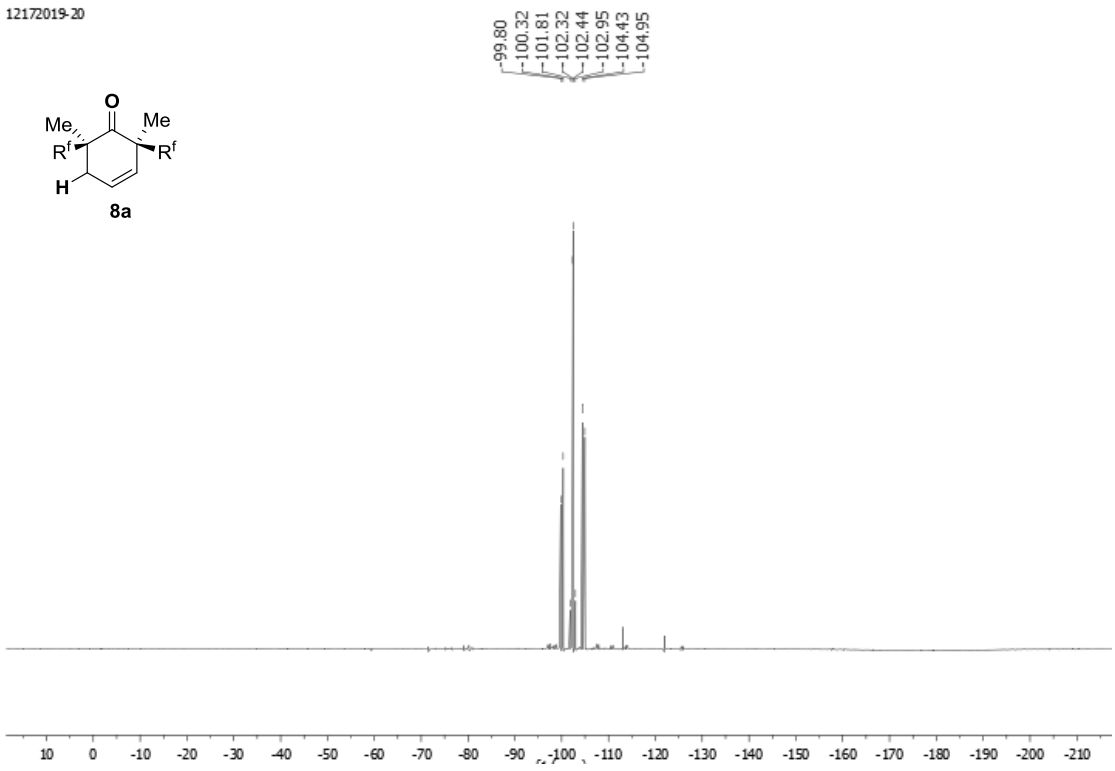
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Me
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Rf
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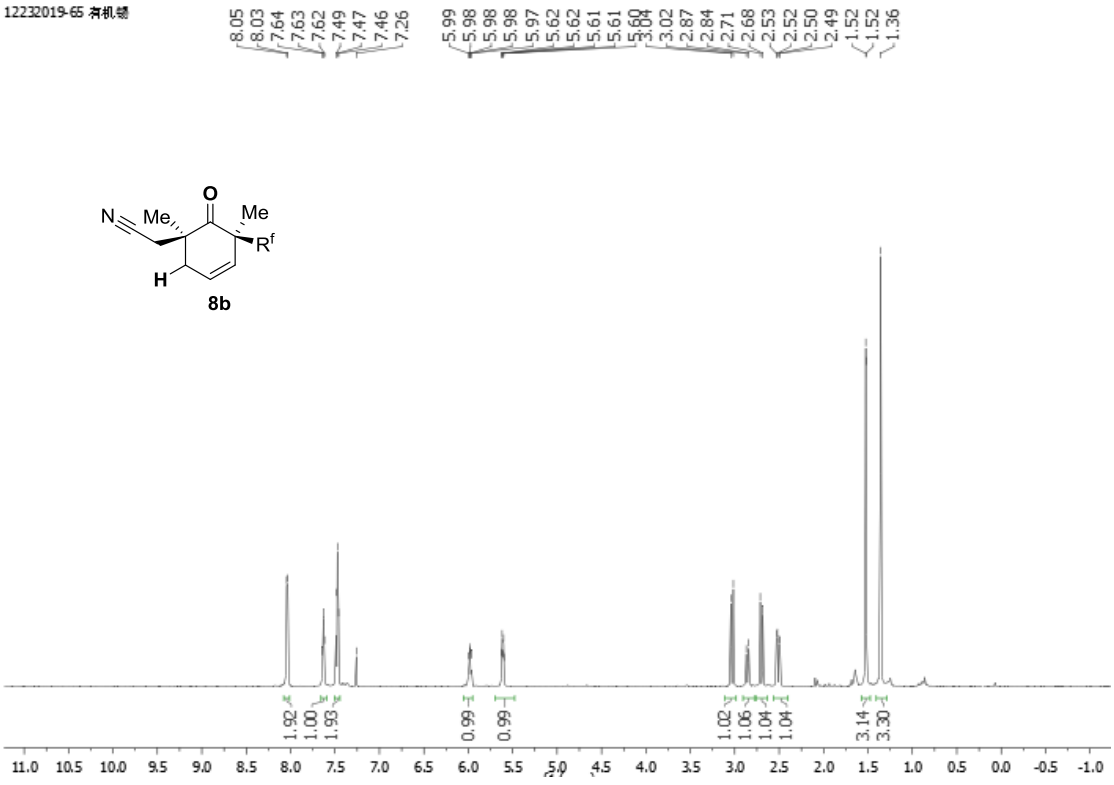
12232019-65 有机锁
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R^f
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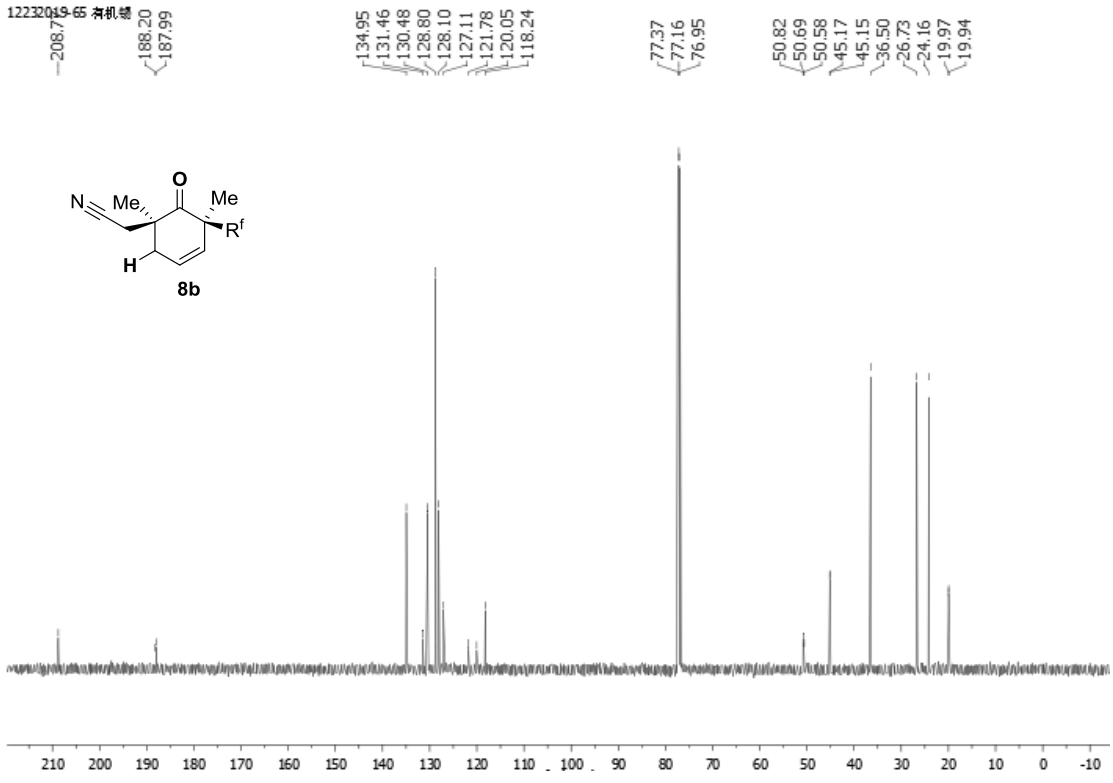
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R^f
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8b
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200
190
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120
110
100
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20
10
0
-10

12232019-65 有机物