Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Peroxide- and Transition Metal-free Electrochemical Synthesis of α,β-Epoxy Ketones

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1. General information

Electrochemical reactions were carried out in undivided cells under air. All air- and water-sensitive reactions were carried out under a nitrogen or argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates (60F-254) that were analyzed by fluorescence upon 254 nm irradiation or by staining with $KMnO_4$ (200 mL H_2O of 1.5 g of $KMnO_4$, 10 g of K_2CO_3, and 1.25 mL of 10% aqueous NaOH). Silica gel (60, particle size 0.040 - 0.063 mm) was used for flash column chromatography. All the chemicals were purchased commercially and used without further purification. Anhydrous THF was distilled from sodium and benzophenone. Yields refer to the isolated yields after silica gel flash column chromatography, unless otherwise stated. NMR spectra were recorded on either a 400 MHz (^{1}H, 400 MHz; ^{13}C, 101 MHz) or 500 MHz (^{1}H, 500 MHz; ^{13}C, 126 MHz) or 600 MHz (^{1}H, 600 MHz; ^{13}C, 151 MHz) Bruker AVANCE Ⅲ spectrometer. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HR-MS) were obtained from a MALDI-TOF mass spectrometer. All the IR spectra were recorded with a FTIR spectrometer.

Table S1. Scope of the ketone substrates

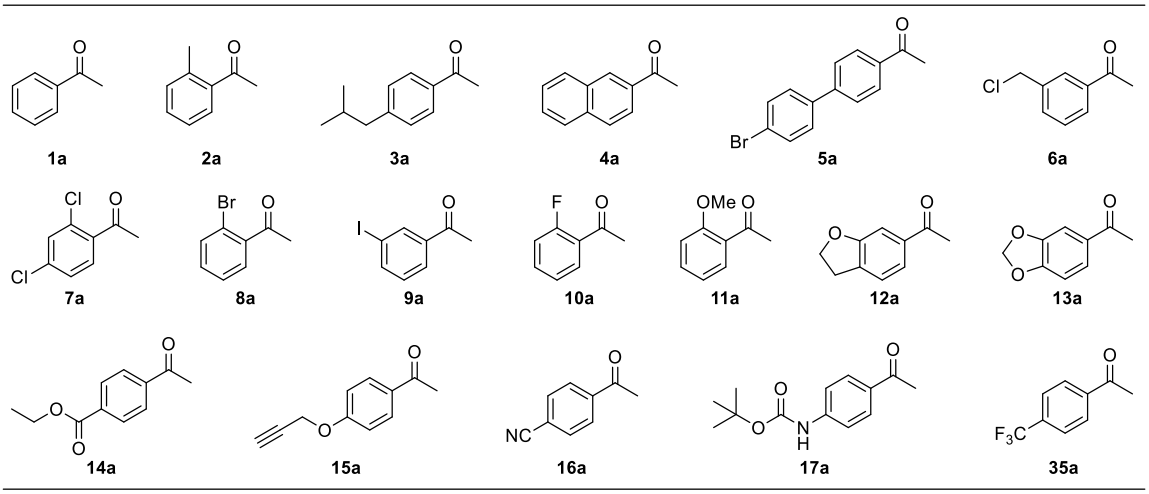
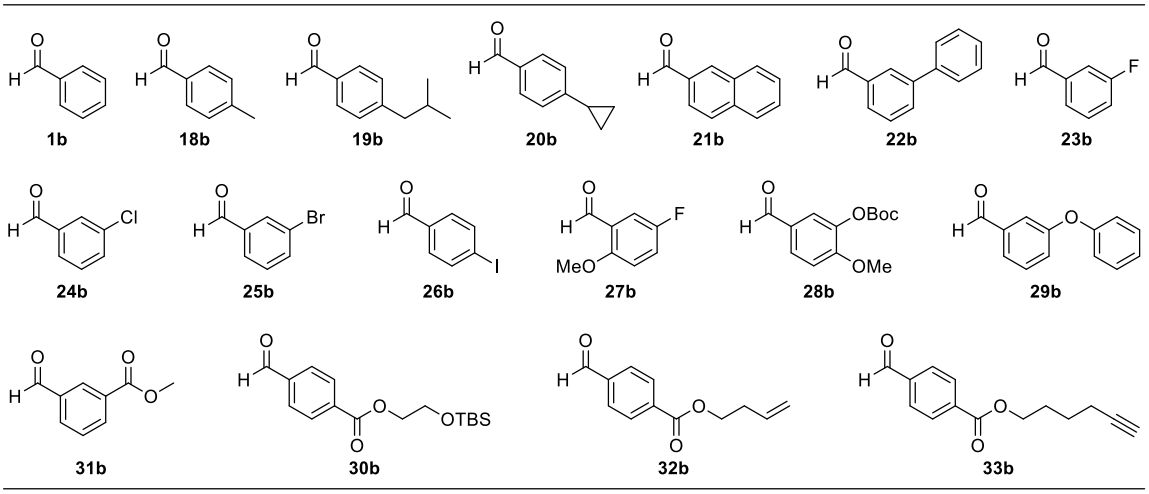
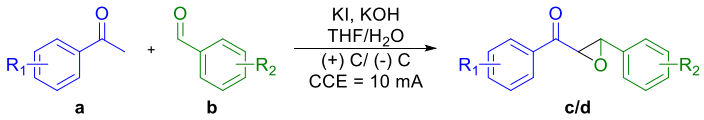


Table S2. Scope of the aldehyde substrates

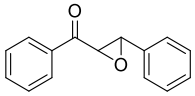


2. General procedures for the electrochemical synthesis of α,β-epoxy ketones



The electrolysis was carried out under constant current conditions in an undivided cell under air, with a graphite rodlike anode and cathode (4 mm × 6 cm). Ketone **a** (3 mmol, 1.0 equiv.), aldehyde **b** (3 mmol, 1.0 equiv.), KI (6 mmol, 2.0 equiv.) and KOH (0.6 mmol, 0.2 equiv.) were dissolved in a THF (15 mL) / H_2O (15 mL) mixture. Electrolysis was performed at rt (25 °C) with a constant current of 10 mA maintained for 4–12 h. The reaction was monitored by TLC. After electrolysis, electrodes were moved out and washed with ethanol (2 × 50 mL) in an ultrasonic bath. The reaction mixture was extracted by ethyl acetate (3 × 15 mL). The combined organic phases were washed by saturated $Na_2S_2O_3$ aqueous solution (45 mL) followed by saturated NaCl aqueous solution (45 mL) and was dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography (hexanes/EtOAc) of the residue provided the product **c** and **d**.

Phenyl(3-phenyloxiran-2-yl)methanone (1c, d)



The compound was synthesized from **1a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **1c** (a white solid, 298 mg, 44%) and *cis*-product **1d** (a white solid, 213 mg, 32%). *Trans*-product **1c**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.63 (s, 1H), 7.50 (s, 2H), 7.47 – 7.33 (m, 5H), 4.31 (s, 1H), 4.09 (s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 193.1, 135.5, 134.0, 129.1, 128.9, 128.8, 128.3, 125.8, 61.0, 59.4. IR (ATR): 3070, 3041, 3025, 2926, 2852, 1688, 1595, 1452, 1413, 1231, 1180, 1004, 889, 751, 697, 668, 591, 527cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{12}NaO_2$ $[M+Na]^+$: 247.0735, found: 247.0733. *Cis*-product **1d**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.25-7.19 (m, 3H), 4.51 (s, 1H), 4.51 (s, 1H). IR (ATR): 2961, 2926, 2859, 1682,1 452, 1231, 981, 911, 751, 738, 694, 652, 531 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{12}NaO_2$ $[M+Na]^+$: 247.0735, found: 247.0732.

The assignment for the *trans*- and *cis*-epoxide is based the shielding effects of aromatic ring[1,2] that lead to the difference of chemical shifts between H_A and H_B. As shwon below, H_A of the *trans*-product was influenced by the shielding impact of the neighbouring aromatic ring more than that in the cis-product, which shifts the signal to a more upfield region. In the ^{1}H NMR spectrum, the signal of H_A and H_B in (±)-**1c** are at 4.09 and 4.31 ppm (the difference is 0.21 ppm), while in (±)-**1d**, the signal of H_A and H_B overlap at 4.49 ppm due to their similar chemical environment. This observation is consistent with analysis of shielding effects and NMR data are consistent with that reported in the literature[3,4]. In general, the chemical shift differences between H_A and H_B of the *trans*-products are higher than 0.1 ppm (0.14 – 0.31 ppm) and that in the *cis*-product are less than 0.1 ppm (0.00 – 0.09 ppm). For **7c** and **7d**, the chemical shift differences are similar, and they were assigned based on the order of elution in column chromatography (the *trans*-products have higher R_f values in all the cases).

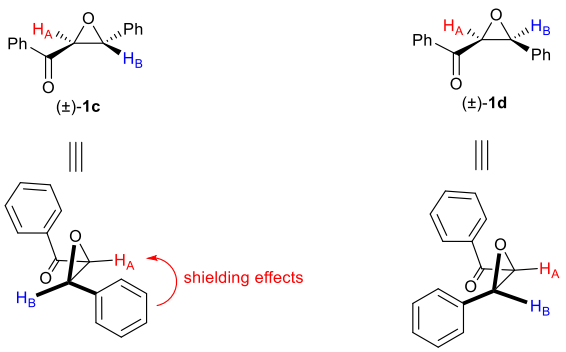
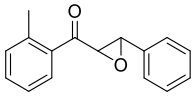


Table S3. Chemical shifts of epoxide protons in the literature

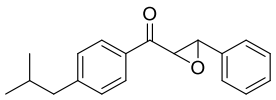
Compound	Chemical shifts of epoxide protons in the literature	Reference
1c	4.30, 4.07	3
1d	4.51, 4.49	4
3c	4.30, 4.07	5
4c	4.44, 4.15	6
11c	4.31, 4.00 4.31, 4.01	7 8
18c	4.32, 4.06	9
21c	4.40, 4.24	10
23c	4.19, 4.00	11
24c	4.26, 4.06	12
25c	4.26, 4.06	13
29c	4.16, 4.02	14

(3-Phenyloxiran-2-yl)(o-tolyl)methanone (2c)



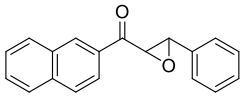
The compound was synthesized from **2a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded only the *trans*-product **2c** (a white solid, 536 mg, 75%). *Trans*-product **2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.28-7.25 (m, 4H), 7.18 (d, *J* = 7.6 Hz, 1H), 4.50 (d, *J* = 4.8 Hz, 1H), 4.35 (d, *J* = 4.8 Hz, 1H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 195.4, 138.9, 135.4, 132.9, 131.9, 129.1, 128.4, 128.1, 126.5, 125.6, 61.7, 59.0, 20.4. IR (ATR): 2967, 2929, 1685, 1452, 1221, 975, 914, 748, 703, 652, 534, 460 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{14}NaO_2$ $[M+Na]^+$: 261.0891, found: 261.0889.

(4-Isobutylphenyl)(3-phenyloxiran-2-yl)methanone (3c, d)



The compounds were synthesized from **3a** and **1b** according to the general procedures for the electrosynthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **3c** (a colorless oil, 463 mg, 55%) and *cis*-product **3d** (a colorless oil, 67 mg, 8%). *Trans*-product **3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 6.8 Hz, 5H), 7.16 (t, *J* = 2.4 Hz, 2H), 4.21 (d, *J* = 2.0 Hz, 1H), 3.98 (d, *J* = 2.0 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.84-1.77 (m, 1H), 0.81 (d, *J* = 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 191.6, 147.7, 134.6, 132.2, 128.5, 127.9, 127.7, 127.3, 124.7, 59.9, 58.2, 44.4, 29.0, 21.2. IR (ATR): 3030, 2969, 2931, 1688, 1451, 1375, 1211, 977, 928, 748, 733, 653, 534, 512, 459 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{19}H_{20}NaO_2$ $[M+Na]^+$: 303.1361, found: 303.1366. *Cis*-product **3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.27 – 7.09 (m, 7H), 4.41 (s, 1H), 4.41 (s, 1H), 2.47 (d, *J* = 7.2 Hz, 1H), 2.40 (d, *J* = 7.2 Hz, 1H), 1.86 – 1.75 (m, 1H), 0.83 (d, *J* = 6.4 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 191.8, 149.3, 133.3, 133.0, 129.7, 129.4, 128.6, 128.4, 128.1, 126.5, 60.9, 58.7, 45.5, 30.0, 22.3. IR (ATR): 2965, 2930, 1683, 1449, 1355, 1219, 969, 925, 744, 719, 638, 527, 457 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{19}H_{20}NaO_2$ $[M+Na]^+$: 303.1361, found: 303.1364. The NMR data of **3c** is consistent with that reported in the literature.[5]

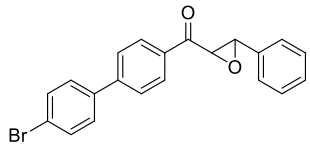
Naphthalen-2-yl(3-phenyloxiran-2-yl)methanone (4c, d)



The compounds were synthesized from **4a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **3c** (a white solid, 469.1 mg, 57%) and cis product **4d** (a white solid, 246.8 mg, 30%). *Trans*-product **4c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.06 (d, *J* = 8.5 Hz,

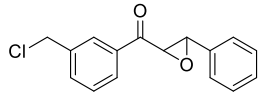
1H), 7.96 – 7.88 (m, 3H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.43 (s, 5H), 4.45 (s, 1H), 4.17 (s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 192.9, 135.9, 135.6, 132.8, 132.4, 130.4, 129.7, 129.1, 128.9, 128.8, 127.9, 127.1, 125.9, 123.6, 61.0, 59.5. IR (ATR): 2929, 2849, 1675, 1461, 1276, 1180, 1122, 889, 751, 710, 591, 470 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{19}H_{14}NaO_2$ [M+Na]+: 297.0891, found: 297.0895. *Cis*-product **4d**: ^1H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.0 Hz, 1H), 7.84 (d, *J* = 7.0 Hz, 2H), 7.58 (dt, *J* = 24.0, 7.0 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.23 – 7.18 (m, 3H), 4.64 (d, *J* = 6.5 Hz, 1H), 4.59 (d, *J* = 4.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 191.9, 135.8, 133.0, 132.8, 132.3, 130.2, 129.6, 128.8, 128.7, 128.4, 128.2, 127.8, 126.9, 126.4, 123.4, 61.0, 58.8. IR (ATR): 2961, 2923, 2849, 1723, 1685, 1455, 1279, 1125, 914, 822, 754, 700, 591, 473 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{19}H_{14}NaO_2$ $[M+Na]^+$: 297.0891, found: 297.0894. The NMR data of **4c** is consistent with that reported in the literature.[6]

(4'-Bromo-[1,1'-biphenyl]-4-yl)(3-phenyloxiran-2-yl)methanone (5d)



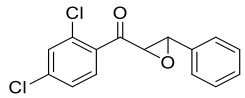
The compound was synthesized from **5a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded only the *cis*-product **5d** (a white solid, 590 mg, 52%). *Cis*-product **5d**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (t, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 5.5 Hz,4H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 7.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 3H), 4.52 (s, 1H), 4.51 (s, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 191.5, 145.1, 134.4, 132.9, 132.1, 128.8, 128.5, 128.2, 127.1, 126.4, 122.8, 60.9, 58.7. IR (ATR): 2980, 2926, 1736, 1691, 1605, 1375, 1228, 1045, 981, 914, 815, 732, 700, 665, 534 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{21}H_{15}BrNaO_2$ $[M+Na]^+$: 401.0153, found: 401.0158.

(3-(Chloromethyl)phenyl)(3-phenyloxiran-2-yl)methanone (6c, d)



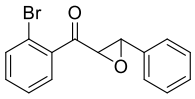
The compounds were synthesized from **6a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **6c** (a colorless oil, 491 mg, 60%) and the *cis*-product **6d** (a pale-yellow oil, 90 mg, 11%). *Trans*-product **6c**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.63 (d, *J* = 6.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 3.2 Hz, 5H), 4.59 (s, 2H), 4.30 (s, 1H), 4.06 (s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 192.7, 138.5, 135.8, 135.3, 134.0, 129.4, 129.1, 128.8, 125.8, 61.0, 59.5, 45.4. IR (ATR): 3070, 2926, 1679, 1605, 1445, 1400, 1253, 1173, 1042, 876, 754, 690, 665, 572, 527 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{13}ClNaO_2$ $[M+Na]^+$: 295.0502, found: 295.0505. *Cis*-product **6d**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.16 – 7.03 (m, 3H), 4.42 (s, 1H), 4.42 (s, 1H), 4.39 – 4.35 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 191.6, 138.2, 135.9, 133.7, 132.8, 129.2, 128.5, 128.2, 128.0, 126.4, 60.9, 58.7, 45.3. IR (ATR): 3059, 2913, 1677, 1698, 1431, 1378, 1235, 1156, 1023, 865, 744, 663, 633, 549, 497 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{13}ClNaO_2$ $[M+Na]^+$: 295.0502, found: 295.0506.

(2,4-Dichlorophenyl)(3-phenyloxiran-2-yl)methanone (7c, d)



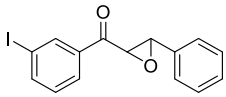
The compounds were synthesized from **7a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **7c** (a white solid, 589 mg, 67%) and the *cis*-product **7d** (a white solid, 88 mg, 10%). *Trans*-product **7c**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 7.39 – 7.33 (m, 6H), 4.14 (s, 1H), 4.08 (s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 195.1, 138.8, 135.0, 134.7, 133.2, 131.4, 130.3, 129.2, 128.7, 127.6, 125.8, 62.9, 60.4. IR (ATR): 3089, 3031, 1682, 1583, 1455, 1407, 1381, 1215, 1103, 1061, 879, 870, 847, 828, 754, 729, 697, 684, 575, 543 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{10}Cl_2NaO_2$ $[M+Na]^+$: 314.9956, found: 314.9957. *Cis*-product **7d**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 10.0 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.29-7.24 (m, 5H), 4.53 – 4.51 (m, 1H), 4.46 – 4.45 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 193.3, 138.7, 134.5, 133.3, 132.4, 131.4, 130.3, 128.5, 128.1, 127.3, 126.7, 62.1, 59.9. IR (ATR): 3055, 2979, 1668, 1581, 1443, 1397, 1380, 1200, 1179, 1103, 1042, 875, 868, 844, 819, 739, 717, 693, 674, 566, 533 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{10}Cl_2NaO_2$ $[M+Na]^+$: 314.9956, found: 314.9957.

(2-Bromophenyl)(3-phenyloxiran-2-yl)methanone (8c, d)



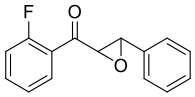
The compounds were synthesized from **8a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **8c** (a yellow solid, 528 mg, 58%) and the *cis*-product **8d** (a yellow oil, 136 mg, 15%). *Trans*-product **8c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.6 Hz, 2H), 7.66 (d, *J* = 6.0 Hz, 2H), 7.41 (d, *J* = 12.8 Hz, 5H), 7.28 (s, 2H), 4.25 (s, 1H), 4.10 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.3, 135.2, 134.1, 132.2, 129.8, 129.1, 128.8, 125.7, 61.0, 59.4. IR (ATR): 3089, 3063, 3035, 2958, 2929, 1675, 1583, 1397, 1241, 1228, 1180, 1065, 1004, 882, 748, 697, 524, 467 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{11}BrNaO_2$ $[M+Na]^+$: 324.9840, found: 324.9840. *Cis*-product **8d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.16 (dt, *J* = 35.0, 7.5 Hz, 5H), 4.41 (d, *J* = 4.5 Hz, 1H), 4.36 (d, *J* = 6.0 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 191.3, 134.1, 132.7, 132.0, 129.6, 129.0, 128.5, 128.2, 126.3, 60.8, 58.6. IR (ATR): 3065, 3054, 3029, 2939, 2921, 1669, 1577, 1369, 1224, 1221, 1177, 1059, 996, 874, 744, 687, 512, 457 cm^{-1}. HR-MS (ESI) m/z calc. for HR-MS (ESI) m/z calc. for $C_{15}H_{11}BrNaO_2$ $[M+Na]^+$: 324.9840, found: 324.9843.

(3-Iodophenyl)(3-phenyloxiran-2-yl)methanone (9c)



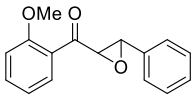
The compound was synthesized from **9a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded only the *trans*-product **9c** (a white solid, 725 mg, 69%). *Trans*-product **9c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.96 (dd, *J* = 12.0, 8.0 Hz, 2H), 7.41 (d, *J* = 7.0 Hz, 3H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.26-7.22 (m, 1H), 4.23 (d, *J* = 1.5 Hz, 1H), 4.08 (d, *J* = 1.5 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 190.9, 141.7, 136.1, 134.1, 129.4, 128.1, 127.8, 126.5, 124.7, 93.6, 59.8, 58.5. IR (ATR): 3060, 2929, 2849, 1685, 1560, 1426, 1221, 997, 892, 754, 694, 598, 527 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{11}INaO_2$ $[M+Na]^+$: 372.9701, found: 372.9703.

(2-Fluorophenyl)(3-phenyloxiran-2-yl)methanone (10c)



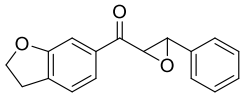
The compound was synthesized from **10a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded only the *trans*-product **10c** (a white solid, 530 mg, 73%). *Trans*-product **10c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, *J* = 7.6 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.38 (d, *J* = 6.4 Hz, 5H), 7.28 (dd, *J* = 13.6, 6.8 Hz, 1H), 7.16 – 7.11 (m, 1H), 4.32 (dd, *J* = 4.4, 2.0 Hz, 1H), 4.08 (d, *J* = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.1, 163.3, 161.2, 135.6, 135.6, 135.5, 130.6, 129.0, 128.6, 128.0, 126.6, 125.9, 124.9, 124.8, 124.1, 116.7, 116.5, 63.0, 59.9. IR (ATR): 2964, 2916, 1669, 1605, 1496, 1442, 1404, 1247, 1116, 1071, 1020, 940, 870, 815, 754, 690, 527cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{11}FNaO_2$ $[M+Na]^+$: 265.0641, found: 265.0639.

(2-Methoxyphenyl)(3-phenyloxiran-2-yl)methanone (11c, d)



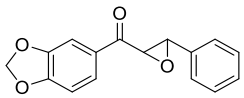
The compounds were synthesized from **11a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **11c** (a white solid, 511 mg, 67%) and the *cis*-product **11d** (a yellow solid, 99 mg, 13%). *Trans*-product **11c**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.51 (m, 1H), 7.38 (tt, *J* = 8.2, 4.0 Hz, 5H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 4.31 (s, 1H), 4.01 (s, 1H), 3.60 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 194.8, 159.6, 136.4, 134.9, 130.6, 128.7, 128.5, 125.9, 125.7, 121.0, 111.5, 64.5, 59.8, 55.6. IR (ATR): 3066, 2980, 2932, 1672, 1592, 1484, 1461, 1436, 1285, 1250, 1209, 1154, 1026, 898, 774, 754, 742, 700, 652, 595, 502 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{15}O_3$ $[M+H]^+$: 255.1021, found: 255.1024.*Cis* product **11d**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.28 – 7.25 (m, 2H), 7.22 – 7.21 (m, 1H), 6.95 – 6.92 (m, 2H), 4.56 (d, *J* = 4.8 Hz, 1H), 4.47 (d, *J* = 4.8 Hz, 1H), 3.98 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 192.8, 159.3, 134.7, 133.6, 130.6, 128.0, 127.9, 126.6, 125.7, 120.8, 111.5, 64.0, 59.2, 55.6. IR (ATR): 2942, 2839, 1669, 1595, 1484, 1464, 1442, 1285, 1244, 1205, 1157, 1023, 981, 908, 748, 697, 646 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{15}O_3$ $[M+H]^+$: 255.1021, found: 255.1023. The NMR data of **11c** is consistent with that reported in the literature.[7,8]

(2,3-dihydrobenzofuran-6-yl)(3-phenyloxiran-2-yl)methanone (12c)



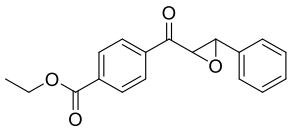
The compound was synthesized from **12a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 15:1) afforded only the *trans*-product **12c** (a white solid, 575 mg, 72%). *Trans*-product **12c**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.86 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.40 – 7.35 (m, 5H), 6.80 (d, *J* = 8.4 Hz, 1H), 4.66 (t, *J* = 8.4 Hz, 2H), 4.24 (d, *J* = 1.8 Hz, 1H), 4.05 (d, *J* = 1.8 Hz, 1H), 3.24 (t, *J* = 8.4 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 191.1, 165.2, 135.7, 130.5, 128.9, 128.2, 125.7, 109.4, 77.4, 77.1, 76.9, 72.4, 60.8, 59.1, 28.9. IR (ATR): 3469, 2983, 2932, 1730, 1679, 1455, 1375, 1253, 1154, 1087, 930, 847, 751, 700, 585, cm^{-1}. HR-MS (ESI) m/z calc. for $C_{17}H_{14}NaO_3$ [M+Na]$^{+}$: 289.0841, found: 289.0840.

Benzo[d][1,3]dioxol-5-yl(3-phenyloxiran-2-yl)methanone (13c)



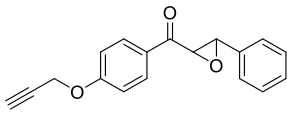
The compound was synthesized from **13a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 10:1) afforded the *trans*-product **13c** (an orange solid, 595 mg, 74%). *Trans*-product **13c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.45 (d, *J* = 4.8 Hz, 1H), 7.36 (t, *J* = 4.0 Hz, 5H), 6.82 (dd, *J* = 8.0, 6.4 Hz, 1H), 6.03 (d, *J* = 6.0 Hz, 2H), 4.22 – 4.21 (m, 1H), 4.05 – 4.04 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 190.9, 152.6, 148.4, 135.5, 130.3, 129.0, 128.7, 125.8, 125.0, 108.1, 107.9, 102.1, 60.8, 59.2. IR (ATR): 2913, 1739, 1656, 1599, 1490, 1429, 1346, 1247, 1116, 1033, 930, 886, 815, 636, 559, 508, 419 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{12}NaO_4$ [M+Na]$^{+}$: 291.0633, found: 291.0635.

Ethyl 4-(3-phenyloxirane-2-carbonyl)benzoate (14c, d)



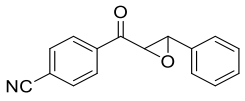
The compounds were synthesized from **14a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 10:1) afforded the *trans*-product **14c** (a white solid, 533 mg, 60%) and the *cis*-product **14d** (a colorless oil, 80 mg, 9%). *Trans*-product **14c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (t, *J* = 9.0 Hz, 2H), 8.07 (d, *J* = 7.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.37 (m, 4H), 4.41 (q, *J* = 7.0 Hz, 2H), 4.29 (s, 1H), 4.09 (s, 1H), 1.42 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.9, 165.5, 138.4, 135.2, 135.0, 130.0, 129.2, 128.8, 128.2, 125.8, 61.6, 61.2, 59.5, 14.2. IR (ATR): 2996, 2913, 1711, 1685, 1410, 1362, 1276, 1106, 1020, 854, 767, 697, 591 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{18}H_{16}NaO_4$ [M+Na]$^{+}$: 319.0946, found: 319.0950. *Cis*-product **14d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.8 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 6.8, 2.8 Hz, 2H), 7.27 – 7.24 (m, 3H), 4.56 (d, *J* = 4.8 Hz, 1H), 4.52 (d, *J* = 4.8 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.9, 165.5, 138.4, 135.2, 135.0, 129.9, 129.2, 128.8, 128.2, 125.8, 61.6, 61.2, 59.5, 14.2. IR (ATR): 2983, 2932, 1717, 1688, 1269, 1228, 1109, 1017, 892, 774, 754, 700, 598 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{18}H_{16}NaO_4$ [M+Na]$^{+}$: 319.0946, found: 319.0949.

(3-Phenyloxiran-2-yl)(4-(prop-2-yn-1-yloxy)phenyl)methanone (15c, d)



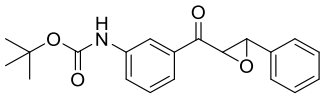
The compounds were synthesized from **15a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **15c** (a colorless oil, 551 mg, 66%) and the *cis*-product **15d** (a colorless oil, 175 mg, 21%). *Trans*-product **15c**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 2H), 7.41 – 7.39 (m, 5H), 7.04 (d, *J* = 9.0 Hz, 2H), 4.77 (d, *J* = 2.4 Hz, 2H), 4.26 (d, *J* = 1.8 Hz, 1H), 4.07 (d, *J* = 1.8 Hz, 1H), 2.57 (t, *J* = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 191.4, 162.0, 135.6, 130.7, 129.2, 129.0, 128.7, 125.8, 115.0, 77.5, 76.4, 60.9, 59.2, 55.9. IR (ATR): 3290, 3063, 2983, 2929, 1736, 1679, 1599, 1423, 1225, 1173, 1004, 882, 751, 694, 598, 511 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{18}H_{14}NaO_3$ [M+Na]$^{+}$: 301.0841, found: 301.0841. *Cis*-product **15d**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.18 (m, 3H), 6.96 (d, *J* = 9.0 Hz, 2H), 4.72 (s, 1H), 4.72 (s, 1H), 4.46(dd, *J* = 2.4, 15 Hz, 2H), 2.55 (t, *J* = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 190.4, 161.7, 133.1, 130.4, 129.3, 128.4, 128.1, 126.4, 114.8, 77.5, 76.3, 60.8, 58.6, 55.8. IR (ATR): 3294, 2980, 1733, 1685, 1599, 1228, 1167, 1020, 985, 700, 537 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{18}H_{14}NaO_3$ [M+Na]$^{+}$: 301.0841, found: 301.0841.

4-(3-Phenyloxirane-2-carbonyl)benzonitrile (16c)



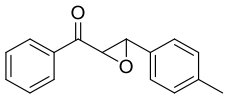
The compound was synthesized from **16a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 15:1) afforded only the *trans*-product **16c** (a pale-yellow oil, 456 mg, 61%). *Trans*-product **16c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.42 (s 3H), 7.37 (d, *J*= 7.5, 2H), 4.24 (s, 1H), 4.10 (s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 192.3, 138.2, 134.8, 132.7, 129.3, 128.9, 125.7, 117.6, 117.2, 77.3, 77.0, 76.7, 61.3, 59.5. IR (ATR): 3051, 2926, 2849, 2232, 1685, 1416, 1228, 1010, 892, 758, 697, 547, 518 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{11}NNaO_2$ $[M+Na]^+$: 272.0687, found: 272.0691.

***tert*-Butyl (4-(3-phenyloxirane-2-carbonyl)phenyl)carbamate (17c)**



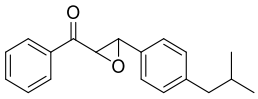
The compound was synthesized from **17a** and **1b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 8:1) afforded only the *trans*-product **17c** (a white solid, 916 mg, 90%). *Trans*-product **17c**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.61 (s, 1H), 8.11 (s, 1H), 7.68 (dd, *J* = 34.0, 8.2 Hz, 2H), 7.45 – 7.38 (m, 5H), 4.70 (d, *J* = 2.0 Hz, 1H), 4.12 (d, *J* = 2.0 Hz, 1H), 1.46 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO) δ 193.3, 140.6, 136.1, 129.8, 129.0, 126.8, 123.9, 122.6, 117.5, 79.9, 60.5, 58.9, 28.5. IR (ATR): 3351, 2977, 2935, 1730, 1666, 1535, 1496, 1304, 1231, 1157, 1074, 786, 754, 722, 697, 674, 655, 527cm^{-1}. HR-MS (ESI) m/z calc. for $C_{20}H_{22}NO_4$ $[M+H]^+$: 340.1549, found: 340.1547.

Phenyl(3-(p-tolyl)oxiran-2-yl)methanone (18c, d)



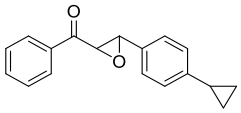
The compounds were synthesized from **1a** and **18b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **18c** (a white solid, 458 mg, 64%) and the *cis*-product **18d** (a white solid, 57 mg, 8%). *Trans*-product **18c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.22 (m, 4H), 4.32 (d, *J* = 1.6 Hz, 1H), 4.07 (d, *J* = 1.6 Hz, 1H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 193.2, 139.1, 135.5, 133.9, 132.4, 129.4, 128.8, 128.3, 125.8, 61.0, 59.5, 21.3. IR (ATR): 2958, 2929, 1727, 1675, 1452, 1234, 1071, 886, 754, 687, 668, 527, 403 cm^{-1}. HR-MS (ESI) m/z calc. for$C_{16}H_{14}NaO_2$ $[M+Na]^+$: 261.0891, found: 261.0893. *Cis*-product **18d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.49 (s, 1H), 4.49 (s, 1H), 2.25 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 192.1, 138.2, 135.5, 133.6, 129.9, 128.9, 128.7, 128.1, 126.3, 61.0, 58.8, 21.1. IR (ATR): 3479, 2919, 2855, 1685, 1448, 1238, 988, 921, 809, 764, 703, 658, 533, 489 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{14}NaO_2$ $[M+Na]^+$: 261.0891, found: 261.0890. The NMR data of **18c** is consistent with that reported in the literature.[9]

(3-(4-Isobutylphenyl)oxiran-2-yl)(phenyl)methanone (19c, d)



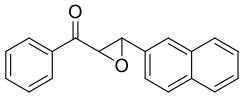
The compounds were synthesized from **1a** and **19b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **19c** (a colorless oil, 505 mg, 60%) and the *cis*-product **19d** (a colorless oil, 67 mg, 8%). *Trans*-product **19c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 7.0 Hz, 2H), 4.31 (s, 1H), 4.05 (s, 1H), 2.50 (d, *J* = 7.0 Hz, 2H), 1.91-1.83 (m, 1H), 0.92 (d, *J* = 6.5 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 193.2, 142.9, 135.5, 133.9, 132.7, 129.5, 128.8, 128.3, 125.6, 61.0, 59.5, 45.1, 30.2, 22.3. IR (ATR): 3029, 2979, 2891, 1752, 1683, 1622, 1256, 1218, 978, 909, 883, 752, 694, 688, 527, 489 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{19}H_{20}NaO_2$ $[M+Na]^+$: 303.1361, found: 303.1363. *Cis*-product **19d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.41 (t, *J* = 7.0 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 2H), 4.49 (s, 1H), 4.49 (s, 1H), 2.36 (d, *J* = 7.0 Hz, 2H), 1.81-1.73 (m, 1H), 0.81 (d, *J* = 6.5 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 192.3, 142.1, 135.7, 133.6, 130.3, 129.0, 128.9, 128.6, 128.1, 126.2, 61.0, 58.8, 45.0, 30.2, 22.3. IR (ATR): 3021, 2951, 2875, 1744, 1668, 1616, 1233, 1203, 969, 911, 852, 721, 683, 661, 503, 470 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{19}H_{20}NaO_2$ $[M+Na]^+$: 303.1361, found: 303.1365.

(3-(4-Cyclopropylphenyl)oxiran-2-yl)(phenyl)methanone (20c, d)



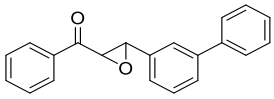
The compounds were synthesized from **1a** and **20b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **20c** (a colorless oil, 500 mg, 63 %) and the *cis*-product **20d** (a colorless oil, 119 mg, 15 %). *Trans*-product **20c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.21 (s, 1H), 3.95 (s, 1H), 1.86 – 1.80 (m, 1H), 0.93 – 0.89 (m, 2H), 0.63 (q, *J* = 4.5 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 193.2, 145.3, 135.5, 133.9, 132.4, 128.8, 128.3, 126.0, 125.8, 61.0, 59.4, 15.3, 9.5, 9.5. IR (ATR): 3050, 3021, 2860, 1749, 1682, 1642, 1261, 1210, 954, 809, 764, 681, 574 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{18}H_{16}NaO_2$ [M+Na]$^+$: 287.1048, found: 287.1044. *Cis*-product **20d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 7.5 Hz, 2H), 4.48 (s, 1H), 4.48 (s, 1H), 1.82 – 1.76 (m, 1H), 0.90 (q, *J* = 5.0 Hz, 2H), 0.61 (q, *J* = 4.5 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 191.0, 143.3, 134.5, 132.6, 128.7, 127.6, 127.1, 125.4, 124.4, 60.0, 57.8, 14.1, 8.2. IR (ATR): 3045, 3012, 2869, 1723, 1668, 1619, 1233, 1203, 969, 925, 742, 661, 530 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{18}H_{16}NaO_2$ [M+Na]$^+$: 287.1048, found: 287.1045.

(3-(Naphthalen-2-yl)oxiran-2-yl)(phenyl)methanone(21c, d)



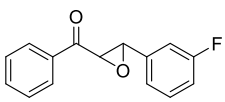
The compounds were synthesized from **1a** and **21b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **21c** (a white solid, 461 mg, 56%) and the *cis*-product **21d** (a white solid, 230 mg, 28%). *Trans*-product **21c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (t, *J* = 11.6 Hz, 2H), 7.90 – 7.87 (m, 4H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.42 (m, 5H), 4.43 (d, *J* = 8.8 Hz, 1H), 4.27 (d, *J* = 6.8 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 193.0, 135.5, 134.0, 133.6, 133.1, 132.9, 128.9, 128.4, 127.8, 126.6, 125.9, 122.4, 61.2, 59.7. IR (ATR): 2961, 2923, 2852, 1679, 1455, 1231, 988, 831, 758, 748, 687, 643, 473 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{19}H_{14}NaO_2$ [M+Na]$^+$: 297.0891, found: 297.0889. *Cis*-product **21d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 3H), 7.78 – 7.70 (m, 3H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.44 – 7.37 (m, 5H), 4.68 (d, *J* = 4.8 Hz, 1H), 4.59 (d, *J* = 4.8 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 191.9, 135.4, 133.7, 133.2, 132.8, 130.4, 128.7, 127.6, 126.2, 126.1, 123.7, 61.2, 58.9. IR (ATR): 2959, 2923, 2848, 1669, 1447, 1228, 988, 826, 745, 739, 678, 633, 469 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{19}H_{14}NaO_2$ [M+Na]$^+$: 297.0891, found: 297.0894. The NMR data of **21c** is consistent with that reported in the literature.[10]

(3-([1,1'-biphenyl]-3-yl)oxiran-2-yl)(phenyl)methanone (22c)



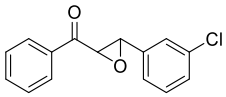
The compound was synthesised from **1a** and **22b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **22c** (a white solid, 694 mg, 77%). *Trans*-product **22c**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.63 (dd, *J* = 8.4, 1.2 Hz, 5H), 7.48 (dt, *J* = 15.0, 7.8 Hz, 5H), 7.40 – 7.37 (m, 2H), 4.38 (d, *J* = 1.8 Hz, 1H), 4.18 (d, *J* = 1.8 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 193.0, 141.9, 140.4, 136.1, 135.5, 134.1, 129.3, 128.9, 128.4, 127.9, 127.7, 127.2, 124.7, 124.5, 61.0, 59.4. IR (ATR): 3057, 2929, 2855, 1733, 1685, 1595, 1455, 1231, 1007, 876, 761, 694, 617 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{21}H_{16}NaO_2$ [M+Na]$^+$: 323.1048, found: 323.1052.

(3-(3-fluorophenyl)oxiran-2-yl)(phenyl)methanone (23c)



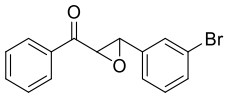
The compound was synthesized from **1a** and **24b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded only the *trans*-product **24c** (a yellow solid, 545 mg, 75%). *Trans*-product **23c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.07 – 7.04 (m, 2H), 4.27 (s, 1H), 4.08 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.6, 164.1, 162.2, 162.1, 138.2, 135.3, 134.1, 130.4, 128.9, 128.3, 121.7, 116.1, 112.6, 112.4, 60.8, 58.6. IR (ATR): 2961, 2926, 1745, 1675, 1605, 1477, 1439, 1401, 1240, 1089, 1071, 1010, 938, 875, 834, 749, 696, 521 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{11}FNaO_2$ [M+Na]$^+$: 265.0641, found: 265.0643. The NMR data of **23c** is consistent with that reported in the literature.[11]

(3-(3-Chlorophenyl)oxiran-2-yl)(phenyl)methanone (24c, d)



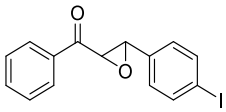
The compounds were synthesized from **1a** and **24b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **24c** (a yellow solid, 449 mg, 58%) and the *cis*-product **24d** (a yellow oil, 108 mg, 14%). *Trans*-product **24c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.22– 7.14 (m, 4H), 4.16 (s, 1H), 3.93 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.6, 137.7, 135.3, 134.8, 134.1, 130.1, 129.1, 128.9, 128.3, 125.7, 124.1, 60.7, 58.5. IR (ATR): 3029, 3011, 1682, 1583, 1455, 1407, 1381, 1215, 1103, 1061, 879, 870, 847, 828, 754, 729, 697, 684, 575, 543 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{11}ClNaO_2$ [M+Na]$^{+}$: 281.0345, found: 281.0341. *Cis*-product **24d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.33 (s, 1H), 7.26 – 7.16 (m, 3H), 4.51 (d, *J* = 5.0 Hz, 1H), 4.47 (d, *J* = 4.5 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 191.6, 135.0, 134.2, 133.9, 129.5, 128.8, 128.1, 126.7, 124.6, 60.7, 57.9. IR (ATR): 3030, 2989, 1678, 1575, 1457, 1410, 1372, 1210, 1095, 998, 864, 832, 739, 689, 547, 513 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{11}ClNaO_2$ [M+Na]$^{+}$: 281.0345, found: 281.0343. The NMR data of **24c** is consistent with that reported in the literature.[12]

(3-(3-Bromophenyl)oxiran-2-yl)(phenyl)methanone (25c, d)



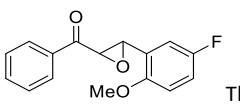
The compounds were synthesized from **1a** and **25b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **25c** (a white solid, 527 mg, 58%) and the *cis*-product **25d** (a white solid,118 mg, 13%). *Trans*-product **25c**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.50 – 7.48 (m, 4H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 6.4 Hz, 1H), 4.27 (d, *J* = 1.8 Hz, 1H), 4.05 (d, *J* = 1.8 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 192.6, 137.9, 135.3, 134.1, 132.1, 130.3, 128.9, 128.6, 128.4, 124.6, 123.0, 60.8, 58.4. IR (ATR): 3081, 3059, 3030, 2949, 2919, 1675, 1580, 1393, 1238, 1228, 1096, 1064, 1001, 878, 732, 679, 521, 458 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{11}BrNaO_2$ [M+Na]$^{+}$: 324.9840, found: 324.9840. *Cis*-product **25d**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.44 (d, *J* = 6.6 Hz, 2H), 7.30 (dd, *J* = 27.6, 7.2 Hz, 2H), 7.10 (s, 1H), 4.54 (s, 1H), 4.47 (s, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 191.6, 135.3, 135.3, 133.9, 131.6, 129.7, 129.6, 128.8, 128.0, 125.1, 122.2, 60.7, 57.8. IR (ATR): 3057, 3027, 3010, 2928, 2910, 1665, 1564, 1356, 1212, 1119, 1079, 998, 878, 727, 647, 501, 447 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{11}BrNaO_2$ [Na+H]$^{+}$: 324.9840, found: 324.9840. The NMR data of **25c** is consistent with that reported in the literature.[13]

(3-(4-Iodophenyl)oxiran-2-yl)(phenyl)methanone (26c)



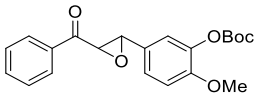
The compound was synthesized from **1a** and **24b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded only the *trans*-product **26c** (a white solid, 756 mg, 72%). *Trans*-product **26c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.25 (s, 1H), 4.04 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.7, 137.9, 135.3, 134.1, 128.9, 128.3, 127.5, 94.7, 60.2, 58.8. IR (ATR): 2987, 2929, 1736, 1653, 1368, 1234, 1045, 802, 738, 694, 611, 506, 422 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{11}INaO_2$ [M+H]+: 372.9701, found: 372.9703.

(3-(3-fluoro-4-methoxyphenyl)oxiran-2-yl)(phenyl)methanone (27c)



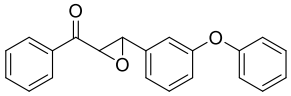
The compound was synthesized from **1a** and **27b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 15:1) afforded only the *trans*-product **27c** (a pale-yellow solid, 678 mg, 82%). *Trans*-product **27c**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.02-6.99 (m, 2H), 6.84 (dd, *J* = 8.4, 4.0 Hz, 1H), 4.36 (s, 1H), 4.15 (d, *J* = 1.8 Hz, 1H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 193.2, 158.2, 156.3, 154.2, 135.5, 133.9, 128.8, 128.4, 125.9, 115.7, 115.5, 112.5, 112.3, 111.4, 60.4, 55.9, 55.1. IR (ATR): 3070, 2945, 2913, 2843, 1656, 1496, 1292, 1256, 1183, 1066, 882, 815, 722, 690 630, 566, 524, 460 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{13}FNaO_3$ [M+Na]$^{+}$: 295.0746, found: 295.0749.

5-(3-Benzoyloxiran-2-yl)-2-methoxyphenyl tert-butyl carbonate (28c)



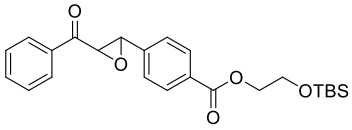
The compound was synthesized from **1a** and **28b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 10:1) afforded only the *trans*-product **28c** (a white solid, 921 mg, 83%). *Trans*-product **28c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 2H), 7.15 (d, *J* = 9.5 Hz, 1H), 6.98 – 6.95 (m, 2H), 4.25 (s, 1H), 4.07 (s, 1H), 3.88 (s, 3H), 1.56 (s, 9H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 192.7, 151.7, 151.4, 140.7, 135.3, 134.4, 134.1, 128.9, 128.3, 122.8, 118.3, 109.2, 83.7, 61.0, 59.0, 56.0, 27.6. IR (ATR): 2980, 2935, 1759, 1691, 1375, 1253, 1148, 1033, 892, 738, 694 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{21}H_{23}O_6$ $[M+H]^+$: 371.1495, found: 371.1495.

(3-(3-Phenoxyphenyl)oxiran-2-yl)(phenyl)methanone (29c, d)



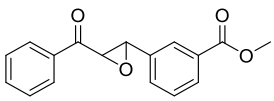
The compounds were synthesized from **1a** and **29b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **29c** (a white solid, 550 mg, 58%) and the *cis*-product **29d** (a white solid, 133 mg, 14%). *Trans*-product **29c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 3H), 7.14 (dd, *J* = 18.5, 7.5 Hz, 2H), 7.05 – 7.00 (m, 4H), 4.27 (s, 1H), 4.06 (s, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 192.9, 158.0, 156.6, 137.6, 135.4, 134.0, 130.2, 129.9, 128.9, 128.4, 123.7, 120.4, 119.2, 115.7, 60.9, 59.0. IR (ATR): 2961, 1739, 1691, 1586, 1490, 1228, 1045, 690, 614, 489 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{21}H_{16}NaO_3$ $[M+Na]^+$: 339.0997, found: 339.0999. *Cis*-product **29d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 3H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.85 (d, *J* = 11.5 Hz, 3H), 4.47 (s, 1H), 4.47 (s, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 191.7, 157.0, 156.8, 135.4, 134.9, 133.7, 129.7, 129.0, 128.7, 128.1, 123.3, 121.2, 119.0, 118.8, 116.8, 60.7, 58.2. IR (ATR): 2961, 2929, 1730, 1691, 1583, 1452, 1271, 1228, 1119, 1077, 889, 748, 694, 658, 499 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{21}H_{16}NaO_3$ $[M+Na]^+$: 339.0997, found: 339.1002. The NMR data of **29c** is consistent with that reported in the literature.[14]

2-((*tert*-Butyldimethylsilyl)oxy)ethyl 4-(3-benzoyloxiran-2-yl)benzoate (30c)



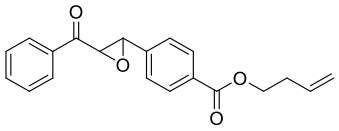
The compound was synthesized from **1a** and **30b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded only the *trans*-product **30c** (a colorless oil, 101 mg, 79%). *Trans*-product **30c:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 4.42 (t, *J* = 5.0 Hz, 2H), 4.29 (s, 1H), 4.15 (s, 1H), 3.96 (t, *J* = 5.0 Hz, 2H), 0.91 (s, 9H), 0.09 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 192.6, 166.0, 140.5, 135.3, 134.1, 130.9, 130.1, 128.9, 128.4, 125.7, 66.4, 61.3, 60.9, 58.7, 25.8, 18.3, 1.0, -5.27. IR (ATR): 2929, 2859, 1717, 1448, 1276, 1100, 1007, 956, 834, 774, 700, 668 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{24}H_{30}NaO_5Si$ $[M+Na]^+$: 449.1760, found: 449.1759.

Methyl 3-(3-benzoyloxiran-2-yl)benzoate (31c)



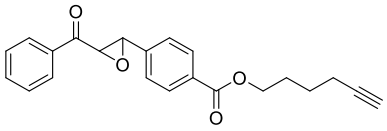
The compound was synthesized from **1a** and **31b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 15:1) afforded only the *trans*-product **31c** (a white solid, 567 mg, 67%). *Trans*-product **31c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 2H), 8.01 (d, *J* = 8.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.19 (m, 1H), 4.32 (s, 1H), 4.15 (s, 1H), 3.94 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 192.7, 166.5, 136.0, 135.3, 134.1, 130.8, 130.1, 128.9, 128.4, 127.3, 126.9, 60.8, 58.8, 52.3. IR (ATR): 2929, 2852, 1992, 1720, 1691, 1602, 1452, 1288, 1237, 1199, 1109, 758, 703 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{17}H_{14}NaO_4$ $[M+Na]^+$: 305.0790, found: 305.0790.

But-3-en-1-yl 4-(3-benzoyloxiran-2-yl)benzoate (32c, d)



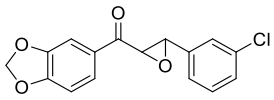
The compounds were synthesized from **1a** and **32b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **32c** (a colorless oil, 648 mg, 67%) and the *cis*-product **32d** (a colorless oil, 135 mg, 14%). *Trans*-product **32c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.97 (m, 4H), 7.61 (t, *J* = 6.8 Hz, 1H), 7.49 – 7.26 (m, 4H), 5.86 (ddt, *J* = 16.8, 10.0, 6.4 Hz, 1H), 5.19 – 5.08 (m, 2H), 4.37 (t, *J* = 6.8 Hz, 2H), 4.28 (d, *J* = 2.0 Hz, 1H), 4.12 (d, *J* = 2.0 Hz, 1H), 2.52 (qd, *J* = 6.8, 3.2 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.6, 165.9, 140.5, 135.3, 134.2, 133.9, 130.9, 130.0, 128.9, 128.3, 125.7, 117.4, 64.1, 60.9, 58.7, 33.1. IR (ATR): 3070, 2961, 1717, 1272, 1237, 1106, 1004, 918, 758, 706, 668, 527 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{20}H_{18}NaO_4$ [M+Na]$^+$: 345.1103, found: 345.1105. *Cis*-product **32d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 4H), 5.83 (ddt, *J* = 17.0, 10.5, 6.5 Hz, 1H), 5.16 – 5.07 (m, 2H), 4.55 (s, 1H), 4.55 (s, 1H), 4.31 (t, *J* = 6.5 Hz, 2H), 2.47 (q, *J* = 6.5 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 191.4, 166.0, 138.0, 135.2, 133.9, 129.4, 128.8, 128.0, 126.5, 117.3, 77.3, 77.0, 76.8, 64.0, 60.8, 58.2, 33.0. IR (ATR): 2983, 1714, 1276, 1228, 1103, 985, 918, 770, 697, 658, 547, 467 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{20}H_{18}NaO_4$ [M+Na]$^+$: 345.1103, found: 345.1107.

Hex-5-yn-1-yl 4-(3-benzoyloxiran-2-yl)benzoate (33c, d)



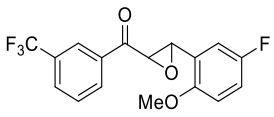
The compounds were synthesised from **1a** and **33b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded the *trans*-product **33c** (a colorless oil, 722 mg, 70%) and the *cis*-product **33d** (a colorless oil, 146 mg, 14%). *Trans*-product **33c**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07-7.99 (m, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 4.36 (t, *J* = 6.4 Hz, 2H), 4.30 (s, 1H), 4.14 (s, 1H), 2.29 (td, *J* = 7.2, 6.4, 3.6 Hz, 2H), 2.00 (t, *J* = 2.4 Hz, 1H), 1.92 (p, *J* = 6.6 Hz, 2H), 1.70 (p, *J* = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.6, 166.0, 140.5, 135.3, 134.2, 130.9, 130.0, 128.9, 128.4, 127.4, 83.8, 68.9, 64.7, 61.0, 58.7, 27.7, 25.0, 18.1. IR (ATR): 3511, 3294, 2939, 1714, 1445, 1269, 1234, 1119, 1020, 767, 703, 636, 585 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{22}H_{20}NaO_4$ [M+Na]$^+$: 371.1259, found: 371.1257. *Cis*-product **33d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.41 (dd, *J* = 7.5, 5.5 Hz, 4H), 4.55 (s, 1H), 4.55 (s, 1H), 4.28 (t, *J* = 6.5 Hz, 2H), 2.25 (td, *J* = 7.0, 2.5 Hz, 2H), 1.96 (t, *J* = 2.5 Hz, 1H), 1.85 (dt, *J* = 14.5, 6.5 Hz, 2H), 1.65 (p, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 191.4, 166.1, 137.9, 135.2, 133.9, 130.4, 129.4, 128.8, 128.0, 126.5, 83.8, 68.8, 64.5, 60.8, 58.2, 27.7, 24.9, 18.0. IR (ATR): 3514, 3300, 2942, 1717, 1448, 1375, 1276, 1231, 1116, 761, 703, 636 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{22}H_{20}NaO_4$ [M+Na]$^+$: 371.1259, found: 371.1261.

Benzo[d][1,3]dioxol-5-yl(3-(3-chlorophenyl)oxiran-2-yl)methanone (34c)



The compound was synthesised from **13a** and **24b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 15:1) afforded only the *trans*-product **34c** (a yellow solid, 681 mg, 75%). *Trans*-product **34c**:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 7.34 (s, 3H), 7.26 (t, *J* = 6.5 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 2H), 4.18 (s, 1H), 4.04 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 190.4, 152.7, 148.5, 137.7, 134.9, 130.2, 130.0, 129.2, 125.7, 125.1, 124.1, 108.2, 107.9, 102.1, 60.6, 58.3. IR (ATR): 3284, 2955, 1704, 1445, 1273, 1253, 1039, 892, 786, 761, 627 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{11}ClNaO_4$ [M+Na]$^+$: 325.0244, found: 325.0245.

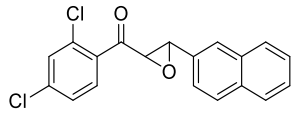
(3-(5-Fluoro-2-methoxyphenyl)oxiran-2-yl)(4-(trifluoromethyl)phenyl)methanone (35c)



The compound was synthesised from **35a** and **27b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 15:1) afforded only the *trans*-product **34c** (a yellow solid, 633 mg, 62%). *Trans*-product **35c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.67 (t, *J*

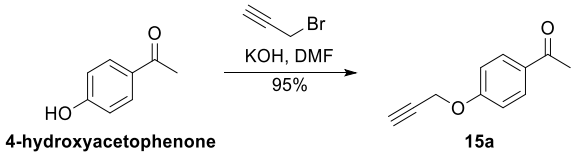
= 7.6 Hz, 1H), 7.02 (td, *J* = 7.2, 6.8, 2.8 Hz, 2H), 6.92 – 6.80 (m, 1H), 4.36 (s, 1H), 4.12 (s, 1H), 3.82 (s, 3H).$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 191.3, 155.4, 155.0, 153.1, 134.9, 130.5, 129.2, 129.2, 128.5, 124.5, 124.4, 124.3, 124.2, 124.2, 121.6, 121.5, 114.8, 111.6, 111.4, 110.3, 110.2, 59.5, 54.8, 54.3. IR (ATR): 3284, 1714, 1685, 1493, 1330, 1167, 1129, 1068, 1029, 809, 716, 697, 575 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{17}H_{12}F_4NaO_3$ $[M+Na]^+$: 363.0620, found: 363.0622.

(3-(chloromethyl)phenyl)(3-(naphthalen-2-yl)oxiran-2-yl)methanone (36d)



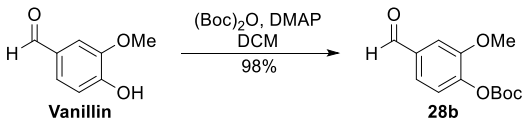
The compound was synthesized from **7a** and **21b** according to the general procedures for the electrochemical synthesis of α,β-epoxy ketones. Purification by column chromatography on silica gel (hexanes:EtOAc = 20:1) afforded only the *cis*-product **36d** (a white solid, 741 mg, 72%). *Cis*-product **36c**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 4H), 7.63 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.52 – 7.51 (m, 2H), 7.43 (s, 1H), 7.39 – 7.35 (m, 2H), 4.25 (s, 1H), 4.25 (s, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 194.8, 138.8, 134.5, 133.5, 133.2, 132.9, 132.4, 131.2, 130.2, 128.7, 127.8, 127.8, 127.6, 126.6, 126.5, 125.9, 122.3, 62.9, 60.6. IR (ATR): 2987, 1739, 1583, 1378, 1241, 1045, 847, 822, 633, 604, 485 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{19}H_{12}Cl_2NaO_2$ $[M+Na]^+$: 365.0112, found: 365.0115.

3. Synthesis of substrates



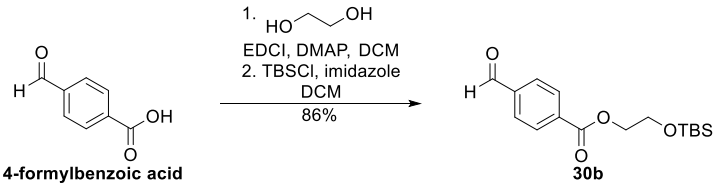
4-hydroxyacetophenone **15a**

4-hydroxylacetophenone (1.5 g, 11.0 mmol) was dissolved in DMF (22 mL). KOH (678.7 mg, 12.1 mmol) and 3-bromopropyne (1.42 mL, 16.5 mmol) were added. The mixture was stirred at rt for 3 hours. The reaction was quenched by saturated NH_4Cl aqueous solution (30 mL), and then extracted with ethyl acetate (3 × 20 mL). The combined organic phase was washed with saturated NaCl aqueous solution (3 × 60 mL) to remove DMF and then dried with Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography (hexanes/EtOAc = 10:1) of the crude mixture provided a colorless oil (1.8 g, 95%) as the product. **15a**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 4.76 (d, *J* = 2.4 Hz, 2H), 2.56 (s, 4H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 196.7, 161.2, 131.0, 130.5, 114.5, 77.7, 76.1, 55.8, 26.3. IR (ATR): 3226, 2977, 2846 1759, 1688, 1656, 1602, 1509, 1420, 1384, 1279, 1241, 1135, 1122, 1033, 1013, 822, 732, 588 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{11}H_{10}NaO_2$ $[M+Na]^+$: 197.0578, found: 197.0574.



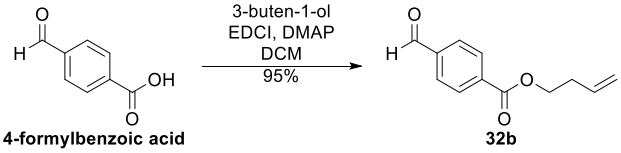
Vanillin **28b**

Vanillin (2.0 g, 13.14 mmol) was dissolved in DCM (26 mL). DMAP (321.1 mg, 2.63 mmol) and Di-*tert*-butyl dicarbonate (3.02 mL, 13.14 mmol) were added. The mixture stirred at rt for 15 minutes. The reaction was quenched by water (30 mL), and then extracted with DCM (3 × 20 mL). The combined organic phases were washed with saturated NaCl aqueous solution (60 mL) and dried with Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography (hexanes/EtOAc = 10:1) of the crude mixture provided a white solid (3.25 g, 98%) as the product. **28b**: ^1H NMR (600 MHz, $CDCl_3$) δ 9.93 (d, *J* = 1.2 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.31 – 7.27 (m, 1H), 3.91 (dd, *J* = 4.2, 1.2 Hz, 3H), 1.55 (dd, *J* = 3.6, 1.2 Hz, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 191.0, 152.0, 150.6, 145.1, 135.0, 124.7, 123.0, 110.8, 84.1, 56.1, 27.5. IR (ATR): 2977, 2846, 1762, 1698, 1602, 1506, 1384, 1253, 1116, 1033, 892, 777, 732, 639 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{13}H_{16}NaO_5$ $[M+Na]^+$: 275.0895, found: 275.0899.



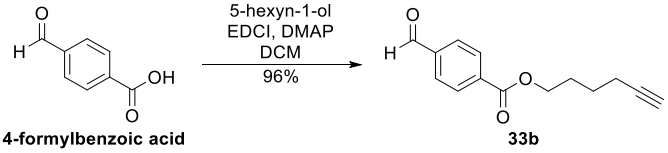
4-formylbenzoic acid **30b**

4-Formylbenzoic acid (2.0 g, 13.0 mmol) was dissolved in DCM (43 mL). EDCI (2.99 g, 15.6 mmol) and DMAP (317 mg, 2.6 mmol) were added at rt. After stirring for a while, excessive ethylene glycol (7.5 mL, 130 mmol) was added. The reaction was stirred for half of an hour at rt, and then quenched by water (30 mL), followed by extracting with DCM (3 × 20 mL). The combined organic phases were washed with saturated NaCl aqueous solution (60 mL) and dried with Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography (hexanes/EtOAc = 10:1) of the residue provided the intermediate ester. The crude ester was dissolved in DCM (43 mL). TBSCl (2.35 g, 15.6mmol) and imidazole (1.15 g, 16.9 mmol) were added at rt. After string for 3 hours, the reaction was quenched by water (30 mL), and then extracted with DCM (3 × 20 mL). The combined organic phases were washed with saturated NaCl aqueous solution (60 mL) and dried with Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography (hexanes/EtOAc = 30:1) of the crude mixture provided a colorless oil (3.45 g, 86%) as the product. **30b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.22 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 4.44 (d, *J* = 2.0 Hz, 2H), 3.96 (d, *J* = 2.0 Hz, 2H), 0.90 (s, 9H), 0.08 (s, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 191.5, 165.3, 139.0, 135.0, 130.1, 129.3, 66.6, 61.0, 25.7, -3.6, -5.4. IR (ATR): 2983, 2846, 1754, 1269, 1202, 1103, 1020, 921, 818, 754, 687 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{16}H_{25}O_4Si$ $[M+H]^+$: 309.1522, found: 309.1526.



4-formylbenzoic acid **32b**

4-Formylbenzoic acid (2.0 g, 13.0 mmol) was dissolved in DCM (43 mL). EDCI (2.99 g, 15.6 mmol) and DMAP (317 mg, 2.6 mmol) were added at rt. After stirring for a while, 3-buten-1-ol (1.3 mL, 15.6 mmol) was added. The reaction was stirred for half of an hour at rt, and then quenched by water (30 mL), followed by extracting with DCM (3 × 20 mL). The combined organic phases were washed with saturated NaCl aqueous solution (60 mL) and dried with Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography (hexanes/EtOAc = 20:1) of the residue provided a colorless oil (2.5 g, 12.4 mmol, 95%) as the product. **32b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.09 (dt, *J* = 5.6, 2.4 Hz, 1H), 8.17 (td, *J* = 7.2, 6.0, 3.0 Hz, 2H), 7.94 (ddd, *J* = 8.4, 4.8, 1.8 Hz, 2H), 5.88 (dtt, *J* = 15.0, 6.6, 4.2 Hz, 1H), 5.20 – 5.16 (m, 1H), 5.12 (dtd, *J* = 8.4, 2.8, 1.2 Hz, 1H), 4.42 – 4.39 (m, 2H), 2.54 (t, J = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 191.7, 165.4, 139.1, 135.2, 133.8, 130.1, 129.4, 117.5, 64.5, 33.0. IR (ATR): 2983, 2846, 1754, 1269, 1202, 1103, 1020, 921, 818, 754, 687 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{12}H_{12}NaO_3$ $[M+Na]^+$: 227.0684, found: 227.0686.

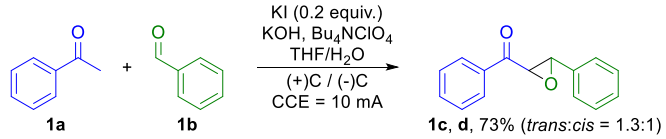


4-formylbenzoic acid **33b**

4-Formylbenzoic acid (2.0 g, 13.0 mmol) was dissolved in DCM (43 mL). EDCI (2.99 g, 15.6 mmol) and DMAP (317 mg, 2.6 mmol) were added at rt. After stirring for a while, 5-hexyn-1-ol (1.7 mL, 15.6 mmol) was added. The reaction was stirred for half of an hour at rt, and then quenched by water (30 mL), followed by extracting with DCM (3 × 20 mL). The combined organic phases were washed with saturated NaCl aqueous solution (60 mL) and dried with Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography (hexanes/EtOAc = 20:1) of the residue provided a colorless oil (2.80 g, 12.5 mmol, 96%) as the product. **33b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 2H), 7.88 – 7.87 (m, 2H), 4.32 – 4.31 (m, 2H), 2.23 – 2.21 (m, 2H), 1.96 (d, *J* = 2.4 Hz, 1H), 1.86 (d, *J* = 5.4 Hz, 2H), 1.64 (t, *J* = 13.2 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 191.7, 165.5, 139.1, 135.2, 130.1, 129.5, 83.7, 69.0, 65.1, 27.6, 24.9, 18.1. IR (ATR): 3290, 2948, 1688, 1253, 1154, 1125, 1100, 988, 914, 838, 809, 758, 636 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{14}H_{14}NaO_3$ $[M+Na]^+$: 253.0841, found: 253.0843.

4. Mechanistic studies

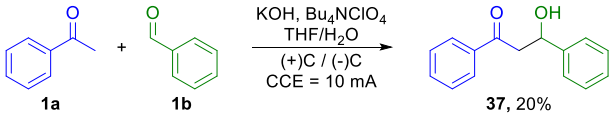
a)



1a **1b** **1c**, **d**, 73% (*trans*:*cis* = 1.3:1)

The electrolysis was carried out in an undivided cell under air, with a graphite rodlike anode and cathode (4 mm × 6 cm). Ketone **1a** (3 mmol, 0.35 mL), aldehyde **1b** (3 mmol, 0.30 mL), KI (99.6 mg, 0.6 mmol), Bu_4NClO_4 (1.85 g, 5.5 mmol) and KOH (33.6 mg, 0.6 mmol) were dissolved in a THF/H_2O (1:1, 30 mL) mixture. Electrolysis was performed at rt with a constant current of 10 mA maintained for 7 hours. After electrolysis, electrodes were moved out and washed with ethanol (2 × 50 mL) in an ultrasonic bath. The solution of reaction was extracted by ethyl acetate (3 × 15 mL). The combined organic phases were washed by saturated $Na_2S_2O_3$ aqueous solution (45 mL) and saturated NaCl aqueous solution (45 mL). The organic solvent was dried by Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography of the residue (hexanes/EtOAc = 20:1) provided **1c** (*trans*-product: 275.5 mg, 41%) and **1d** (*cis*-product 215.0 mg, 32%) as the products.

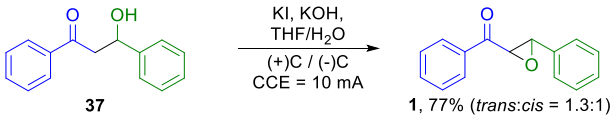
b)



1a **1b** **37**, 20%

The electrolysis was carried out in an undivided cell under air, with a graphite rodlike anode and cathode (4 mm × 6 cm). Ketone **1a** (3 mmol, 0.35 mL), aldehyde **1b** (3 mmol, 0.30 mL), KOH (33.6 mg, 0.6 mmol) and Bu_4NClO_4 (2.05 g, 6.0 mmol) were dissolved in a THF/H_2O (1:1, 30 mL) mixture. Electrolysis was performed at rt with a constant current of 10 mA maintained for 7 h. After electrolysis, electrodes were moved out and washed with ethanol (2 × 50 mL) in an ultrasonic bath. The solution of reaction was extracted by ethyl acetate (3 × 15 mL). The combined organic phases were washed by saturated $Na_2S_2O_3$ aqueous solution (45 mL) and saturated NaCl aqueous solution (45 mL). The organic solvent was dried by Na_2SO_4. After filtration and concentration under reduced pressure, flash chromatography on silica gel (hexanes/EtOAc = 20:1) provided **37** (136 mg, 20%) as the product. **37**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 15.0, 7.0 Hz, 4H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 5.35 (t, *J* = 6.0 Hz, 1H), 3.37 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.23, 142.96, 136.59, 133.69, 128.74, 128.19, 127.72, 127.16, 125.78, 70.07, 47.41. IR (ATR): 3473, 3063, 3028, 2916, 1675, 1599, 1448, 1356, 1266, 1209, 1061, 1020, 748, 700, 687, 611, 575, 550 cm^{-1}. HR-MS (ESI) m/z calc. for $C_{15}H_{14}NaO_2$ [M+Na]$^+$: 249.0891, found: 249.0890.

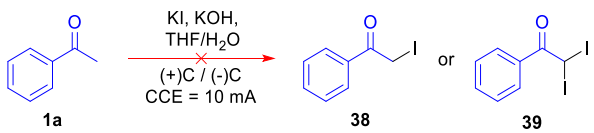
c)



37 **1**, 77% (*trans*:*cis* = 1.3:1)

The electrolysis was carried out in an undivided cell under air, with a graphite rodlike anode and cathode (4 mm × 6 cm). β-hydroxyl ketone **37** (679 mg, 3 mmol), KI (996 mg, 6 mmol), KOH (33.6 mg, 0.6 mmol) were dissolved in a THF/H_2O (1:1, 30 mL) mixture. Electrocatalysis was performed at rt with a constant current of 10 mA maintained for 7 h. After electrolysis, electrodes were moved out and washed with ethanol (2 × 50 mL) in an ultrasonic bath. The solution of reaction was extracted by ethyl acetate (3 × 15 mL). the combined organic phases were washed by saturated $Na_2S_2O_3$ aqueous solution (45 mL) and saturated NaCl aqueous solution (45 mL). The organic phase was dried by Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography (hexanes/EtOAc = 20:1) of the residue provided **1c** (*trans*-product: 295.9 mg, 44%) and **1d** (*cis*-product 221.9 mg, 33%) as the products.

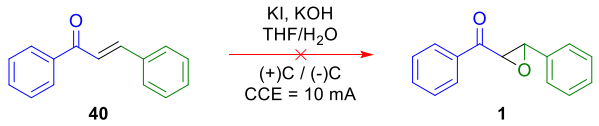
d)



1a **38** **39**

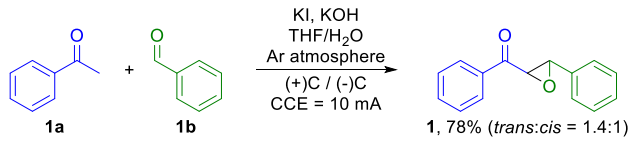
The electrolysis was carried out in an undivided cell under air, with a graphite rodlike anode and cathode (4 mm × 6 cm). Ketone **1a** (3 mmol, 0.35 mL), KI (996 mg, 6 mmol), KOH (33.6 mg, 0.6 mmol) were dissolved in a THF/H_2O (1:1, 30 mL) mixture. Electrocatalysis was performed at rt with a constant current of 10 mA maintained for 7 h. No desired product was detected by TLC (hexanes/EtOAc = 5:1).

e)



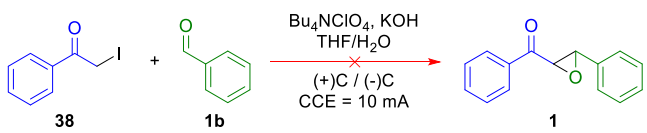
Compound **40** was prepared according to the reference, and the NMR data is consistent with that was reported in the literature.[15] The electrolysis was carried out in an undivided cell under air, with a graphite rodlike anode and cathode (4 mm × 6 cm). Unsaturated ketone **40** (3 mmol, 624 mg), KI (996 mg, 6.0 mmol), KOH (33.6 mg, 0.6 mmol) were dissolved in a THF/H_2O (1:1, 30 mL) mixture. Electrocatalysis was performed at rt with a constant current of 10 mA maintained for 7 h. No desired product was detected by TLC (hexanes/EtOAc = 5:1).

f)



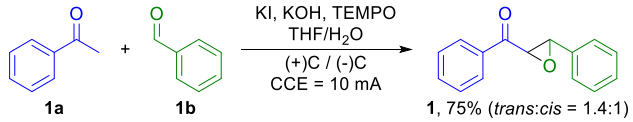
Ketone **1a** (3 mmol, 0.35 mL), aldehyde **1b** (3 mmol, 0.3 mL), KI (996 mg, 6 mmol) and KOH (33.6 mg, 0.6 mmol) were dissolved in a THF/H_2O (1:1, 30 mL) mixture. graphite rodlike anode and cathode (4 mm × 6 cm) were put into reaction cell. The whole cell was treated with ultrasound to remove the gas in the solvent, then Ar flowed through the cell for 3 minutes. at last, the cell was sealed and Ar balloon was used to maintain the pressure of cell. Electrolysis was performed at rt with a constant current of 10 mA maintained for 7 h. After electrolysis, electrodes were moved out and washed with ethanol (2 × 50 mL) in an ultrasonic bath. The solution of reaction was extracted by ethyl acetate (3 × 15 mL). the combined organic phases were washed by saturated $Na_2S_2O_3$ aqueous solution (45 mL) and saturated NaCl aqueous solution (45 mL). The organic phase was dried by Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography (hexanes/EtOAc = 20:1) provided **1c** (*trans*-product: 309 mg, 46%) and **1d** (*cis*-product 215 mg, 32%) as the products.

g)



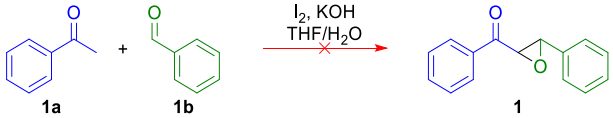
Compound **38** was prepared according to the reference, and the NMR data is consistent with that was reported in the literature.[16] The electrolysis was carried out in an undivided cell under air, with a graphite rodlike anode and cathode (4 mm × 6 cm). Ketone **38** (3 mmol, 738 mg), aldehyde **1b** (3 mmol, 0.30 mL), Bu_4NClO_4 (2.05 g, 6.0 mmol), KOH (33.6 mg, 0.6 mmol) were dissolved in a THF/H_2O (1:1, 30 mL) mixture. Electrocatalysis was performed at rt with a constant current of 10 mA maintained for 7 h. No desired product was detected by TLC (hexanes/EtOAc = 5:1).

h)



The electrolysis was carried out in an undivided cell under air, with a graphite rodlike anode and cathode (4 mm × 6 cm). Ketone **1a** (3 mmol, 0.35 mL), aldehyde **1b** (3 mmol, 0.30 mL), KI (996 mg, 6 mmol), KOH (33.6 mg, 0.6 mmol) and TEMPO (468.7 mg, 3 mmol) were dissolved in a THF/H_2O (1:1, 30 mL) mixture. Electrocatalysis was performed at rt (25 °C) with a constant current of 10 mA maintained for 10 h. After electrolysis, electrodes were moved out and washed with ethanol (2 × 50 mL) in an ultrasonic bath. The solution of reaction was extracted by ethyl acetate (3 × 15 mL). the combined organic phases were washed by saturated $Na_2S_2O_3$ aqueous solution (45 mL) and saturated NaCl aqueous solution (45 mL). The organic solvent was dried by Na_2SO_4. After filtration and concentration under reduced pressure, silica gel flash column chromatography of the residue (hexanes/EtOAc = 20:1) provided **1a** (*trans*-product: 296 mg, 44%) and **1d** (*cis*-product 208 mg, 31%) as the products.

i)



The reaction was carried out in an undivided cell under air. Ketone **1a** (3 mmol, 0.35 mL), aldehyde **1b** (3 mmol, 0.35 mL), I_2 (761.4 mg, 3 mmol) and KOH (33.6 mg, 0.6 mmol) were dissolved in a THF/H_2O (1:1, 30 mL) mixture. No desired product was detected by TLC (hexanes/EtOAc = 5:1).

5. Cyclic voltammetry

Cyclic voltammetry was carried out in a glass cell with CHI660E potentiostat. A graphite rod (diameter is 3.0 mm) was used as a working electrode. A glassy carbon electrode (diameter is 3.0 mm) was used as a counter electrode. $HgCl/Hg_2Cl_2/Cl^-$ electrode (diameter is 3.0 mm) was used as a reference electrode. Supporting Electrolyte: 0.2 M Bu_4NClO_4 in THF/H_2O (5%); Init E (V) = -0.2; High E (V) = 1.2; Low E (V) = -0.2; Scan Rate (V/s) = 0.02, Segment = 4; Sample Interval (V) = 0.001; Quiet Time (sec) = 2; Sensitivity (A/V) = 0.0001.

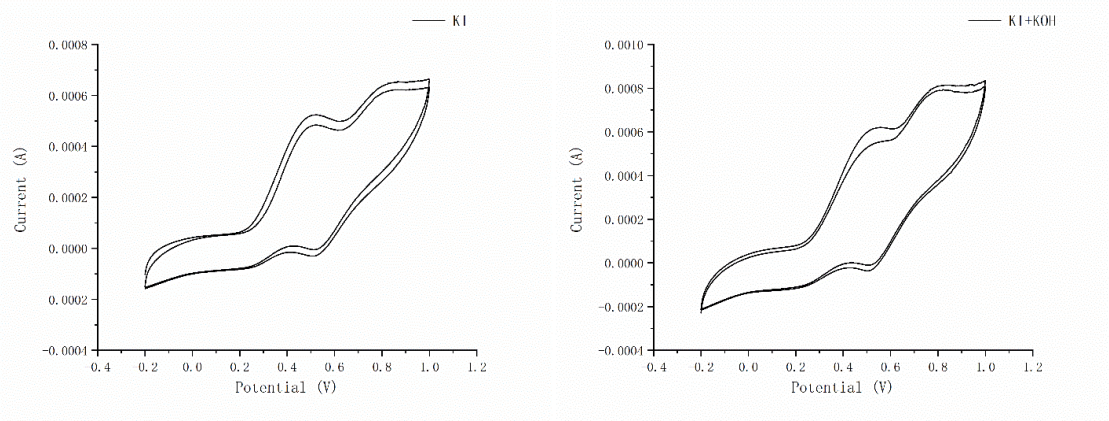


Figure S-1. Left: Cyclic voltammetry of KI (5 mM). Right: Cyclic voltammetry of KI (5 mM) with KOH (1 mM)

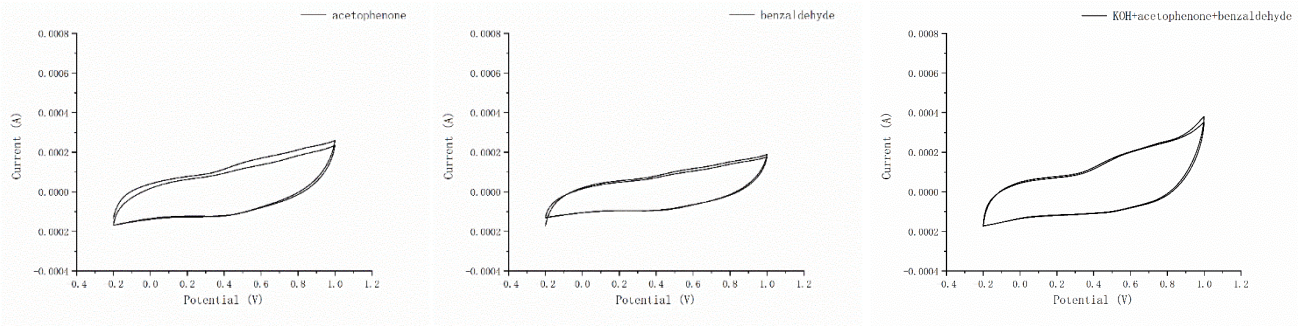


Figure S-2. Cyclic voltammetry of: acetophenone (5 mM), left; benzaldehyde (5 mM), medium; KOH (1 mM), acetophenone (5 mM), benzaldehyde (5 mM), right.

6. *In vitro* studies for anticancer activity

Gastric cancer stem cell culture

Fresh isolated, primary tumor-derived GCSC which from a GAC patient was obtained from Dr. Xianming Mo, grown and maintained as previously described.[17]

HGC27 were cultured in Dulbecco's modified Eagle medium (DMEM, Gibco, Rockville, MD, USA) containing 10% fetal bovine serum (FBS, Gibco, Rockville, MD, USA), 100 U/mL penicillin and 100 mg/mL streptomycin in a humid incubator with 5% CO2 at 37°C.

Cell Proliferation Assay

The CCK-8 (Dojindo, Kumamoto, Japan) assay was conducted according to the manufacturer's protocol. Briefly, The above cells (5×103 cells per well) were plated in 96-well plates in triplicate. CCK-8 reagent was added at 48 hours after adding compounds, and the cells were cultured for a further 1.5 hours at 37°C. Absorbance at 450 nm was measured using a microplate reader.

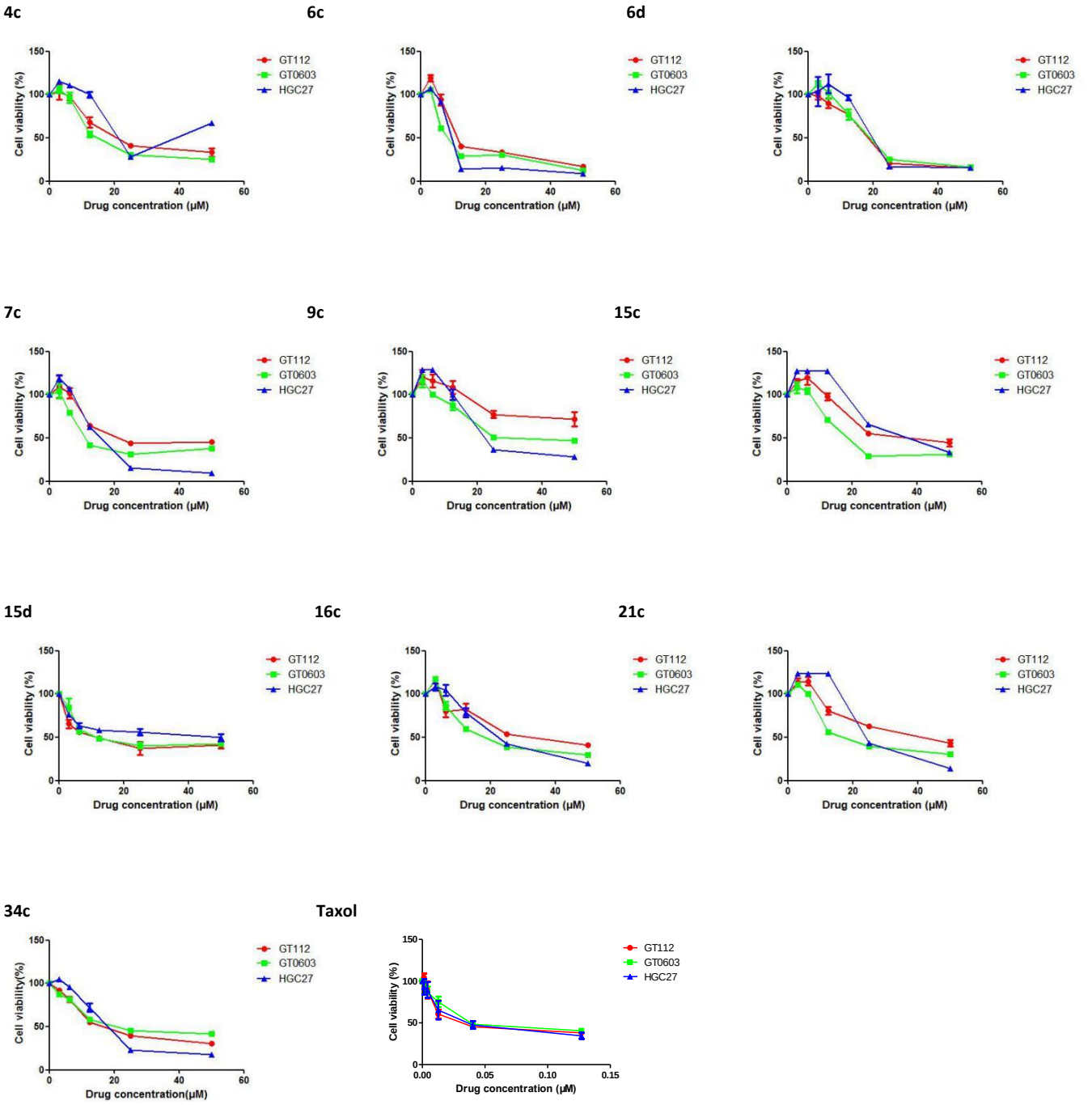


Figure S-7. Inhibitory effects of synthesized epoxides on different cancer cell lines.

Table S4. *In vitro* cancer growth inhibition of synthesized epoxides. [a]

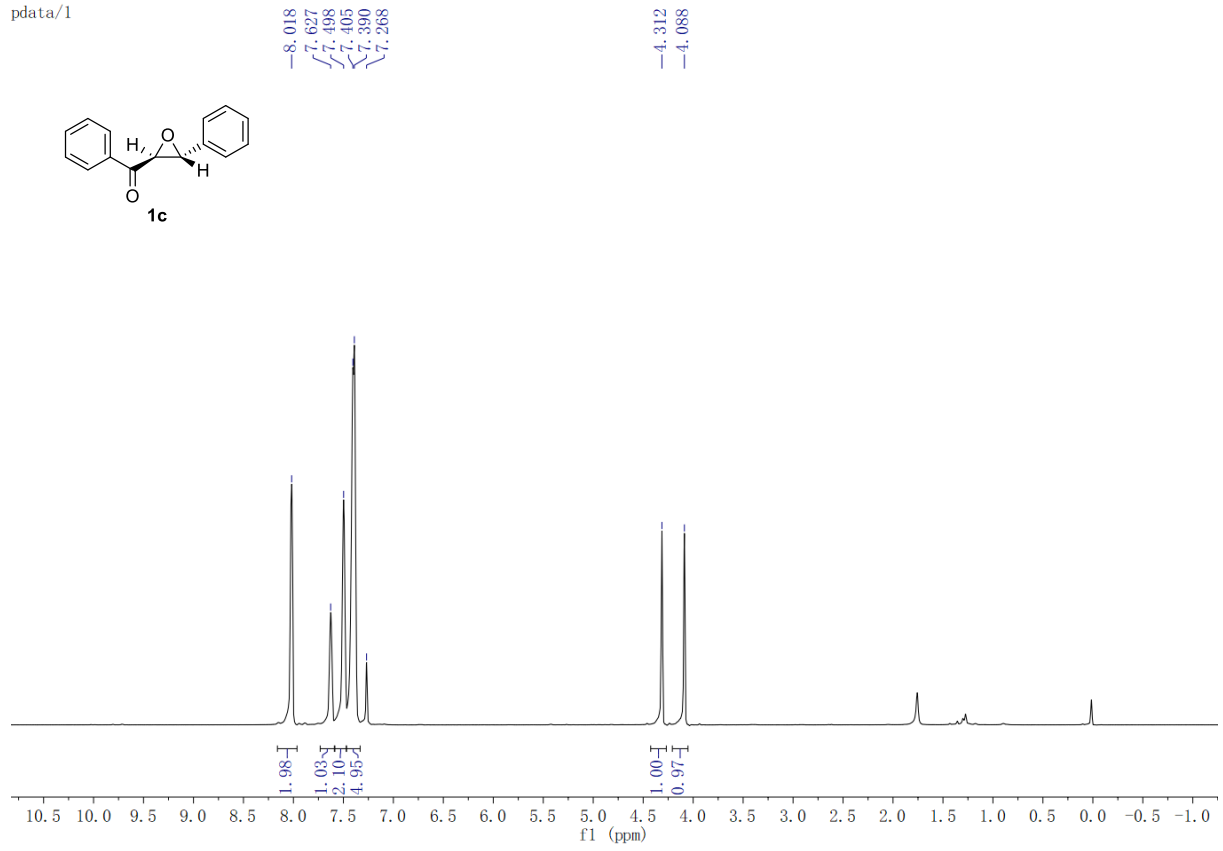
Compound	GT112	GT0603	HGC27
4c	24.08	17.19	44.73
6c	14.48	9.952	9.293
6d	17.48	18.62	19.81
7c	29.17	16.18	15.05
9c	29.98	22.19	20.78
15c	38.00	20.57	37.23
15d	12.12	17.08	42.85
16c	33.32	20.38	23.16
21c	38.36	20.92	24.74
34c	25.01	17.53	18.80
Paclitaxel	0.04	0.05	0.04

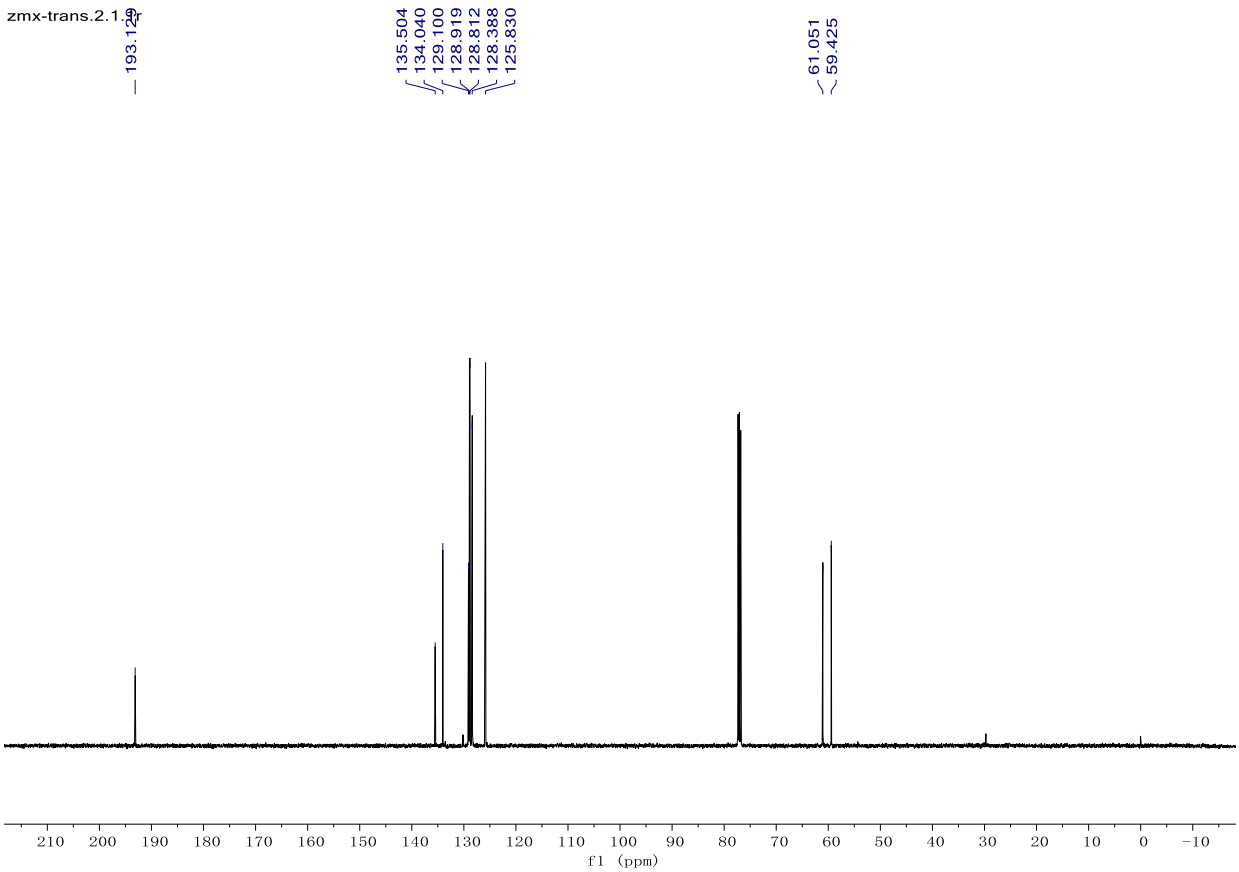
[a] Experiments were conducted in triplicate and results are expressed as mean IC_{50} values in μM.

7. References:

1. M. Matsugi, K. Itoh, M. Nojima, Y. Hagimoto and Y. Kita, Determination of absolute configuration of trans-2-arylcyclohexanols using remarkable aryl-induced 1H NMR shifts in diastereomeric derivatives. *Tetrahedron Lett.* 2001, **42**, 6903–6905.
2. C. Anson, D. Thamattoor. Influence of Substituents on the through-space shielding of aromatic rings. *J. Org. Chem.* 2012, **77**, 1693−1700.
3. W. Liu, Y. Li, K. Liu and Z. Li, Iron-catalyzed carbonylation-peroxidation of alkenes with aldehydes and hydroperoxides. *J. Am. Chem. Soc.*, 2011, **133**, 10756-10759.
4. B. Lygo, S. D. Gardiner, M. C. McLeoda and D. C. M. To, Diastereo- and enantioselective synthesis of α,β-epoxyketones using aqueous NaOCl in conjunction with dihydrocinchonidine derived phase-transfer catalysis at room temperature. Scope and limitations. *Org. Biomol. Chem.*, 2007, **5**, 2283-2290.
5. X. Chen, B. Gao, Y. Su and H. Huang, Enantioselective epoxidation of electron-deficient alkenes catalyzed by manganese complexes with chiral N4 Ligands derived from rigid chiral diamines. *Adv. Synth. Catal.* 2017, **359**, 2535-2541.
6. A. Lattanzi, Enantioselective epoxidation of α,β-Enones promoted by α,α-diphenyl-L-prolinol as bifunctional organocatalyst. *Org. Lett.* 2005, **7**, 2579–2582
7. V. Ashokkumara and A. Siva. One-pot synthesis of α,β-epoxy ketones through domino reaction between alkenes and aldehydes catalyzed by proline based chiral organocatalysts. *Org. Biomol. Chem.* 2017,**15**, 2551-2561
8. Q. Ke, B. Zhang, B. Hu, Y. Jin and G. Lu, A transition-metal-free, one-pot procedure for the synthesis of α,β-epoxy ketones by oxidative coupling of alkenes and aldehydes via base catalysis. *Chem. Commun.* 2015, **51**, 1012-1015
9. Y. Wu, G. Zhou, Q. Meng, X. Tang, G. Liu, H. Yin, J. Zhao, F. Yang, Z. Yu and Y. Luo, Visible light-Induced aerobic epoxidation of α,β-unsaturated ketones mediated by amidines. *J. Org. Chem.* 2018, **83**, 13051-13062.
10. Y. Liu; B. Provencher, K. Bartelson, J. Keith and L. Deng, Highly enantioselective asymmetric Darzens reactions with a phase transfer catalyst. *Chem. Sci.* 2011, **2**, 1301-1304
11. S. Jew, J. Lee, B. Jeong, M. Yoo, M. Kim, Y. Lee, J. Lee, S. Choi, K. Lee, M. Lah and H. Park, Highly enantioselective epoxidation of 2,4-diarylenones by using dimeric cinchona phase-transfer catalysts: Enhancement of enantioselectivity by surfactants. *Angew. Chem. Int. Edit.* 2005, **44**, 1383-1385.
12. A. Mako, Z. Rapi, G. Keglevich, A. Szoellosy, L. Drahos, L Hegedus and P. Bako, Asymmetric epoxidation of substituted chalcones and chalcone analogues catalyzed by α-d-glucose- and α-d-mannose-based crown ethers. *Tetrahedron: Asymmetry* 2010, **21**, 919-925.
13. J. Li and X. Liu. An efficient and practical synthesis of 2,3-epoxyl-1,3-diaryl-1-propanone by combination of phase transfer catalyst and ultrasound irradiation. *Ultrasonics Sonochemistry* 2008, **15**, 330-333
14. G. Kumaraswamy, M. N. V. Sastry, J. Nivedita; K. R. Kumar and M. Vairamani, Enantioenriched (S)-6,6′-diphenylBinol-Ca: a novel and efficient chirally modified metal complex for asymmetric epoxidation of α,β-unsaturated enones. *Tetrahedron: Asymmetry.* 2003, **14**, 3797-3803.
15. Y.-L. Zhang, B.-Y. Li, R. Yang, L.-Y. Xia, A.-L. Fan, Y.-C. Chu, L.-J.Wang, Z.-C. Wang, A.-Q. Jiang and H.-L. Zhu, A class of novel tubulin polymerization inhibitors exert effective anti-tumor activity via mitotic catastrophe. *Eur. J. Med. Chem.*, 2019, **163**, 896–910.
16. P. Zhao, X. Wu, X. Geng, C. Wang, Y. Zhou, Y.-D. Wu and A.-X. Wu, I_2/PhI$(OAc)_2$ Copromoted Amination Reaction: Synthesis of α-Dicarbonylsulfoximine Derivatives by Incorporating an Intact Dimethyl Sulfoxide, *J. Org. Chem.*, 2019, **84**, 8322–8329.
17. T. Chen, K. Yang, J. Yu, W. Meng, D. Yuan, F. Bi, F. Liu, J. Liu, B. Dai, X. Chen, F. Wang, F. Zeng, H. Xu, J. Hu and X. Mo, Identification and expansion of cancer stem cells in tumor tissues and peripheral blood derived from gastric adenocarcinoma patients, *Cell Res*., 2012, **22**, 248–258.

8. NMR spectra



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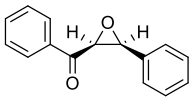
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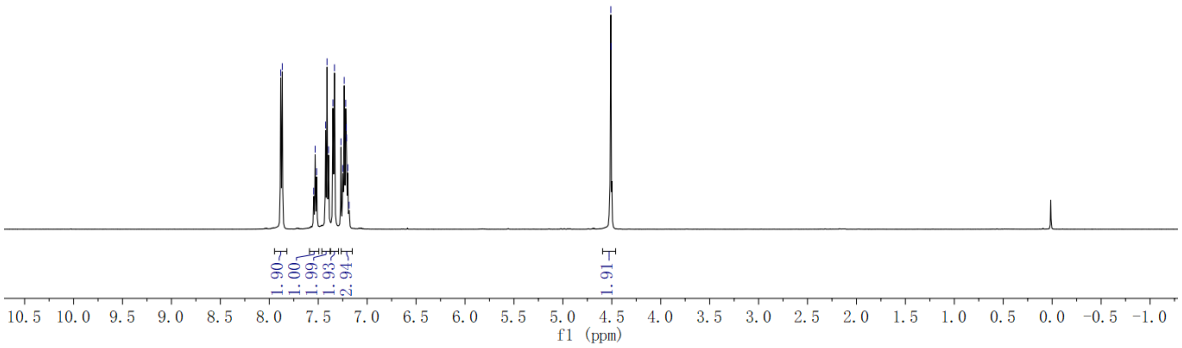
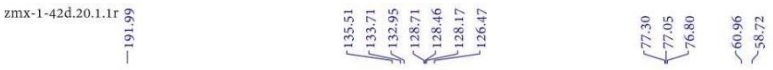
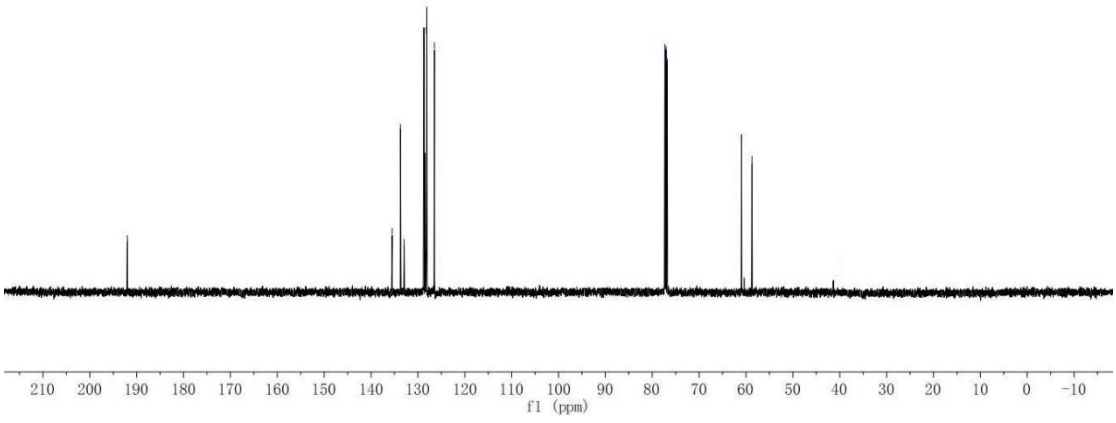
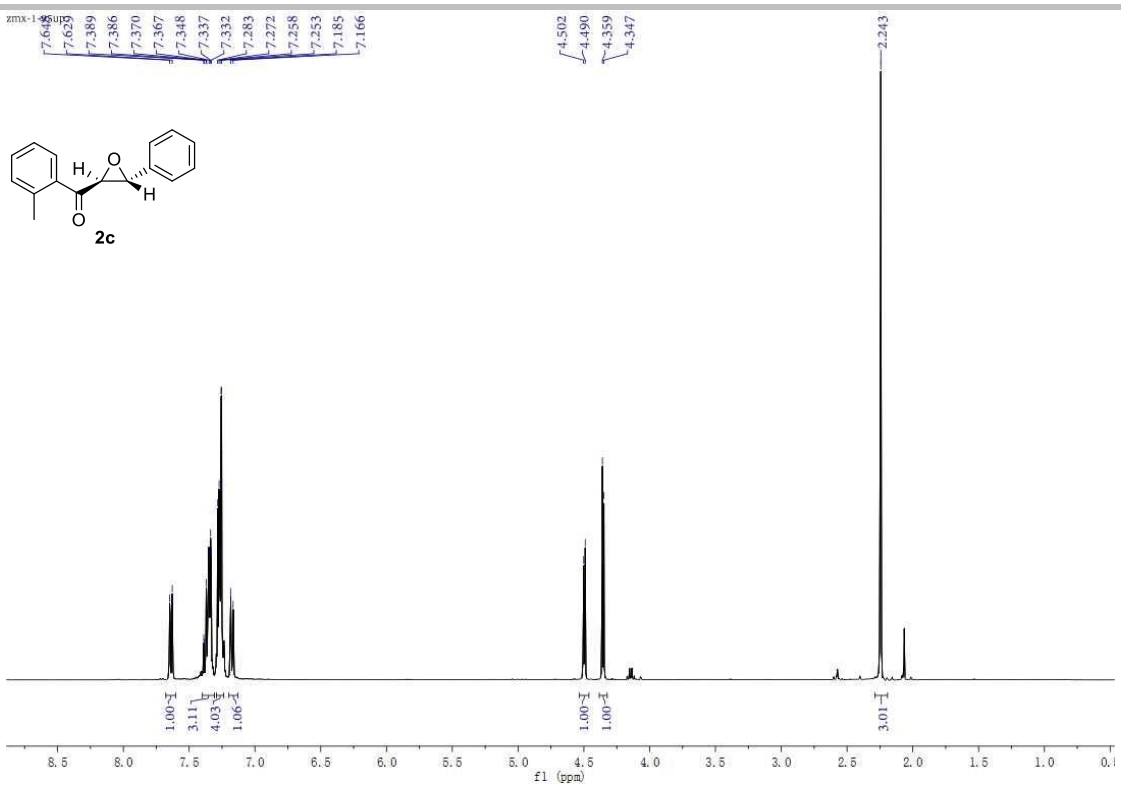
O

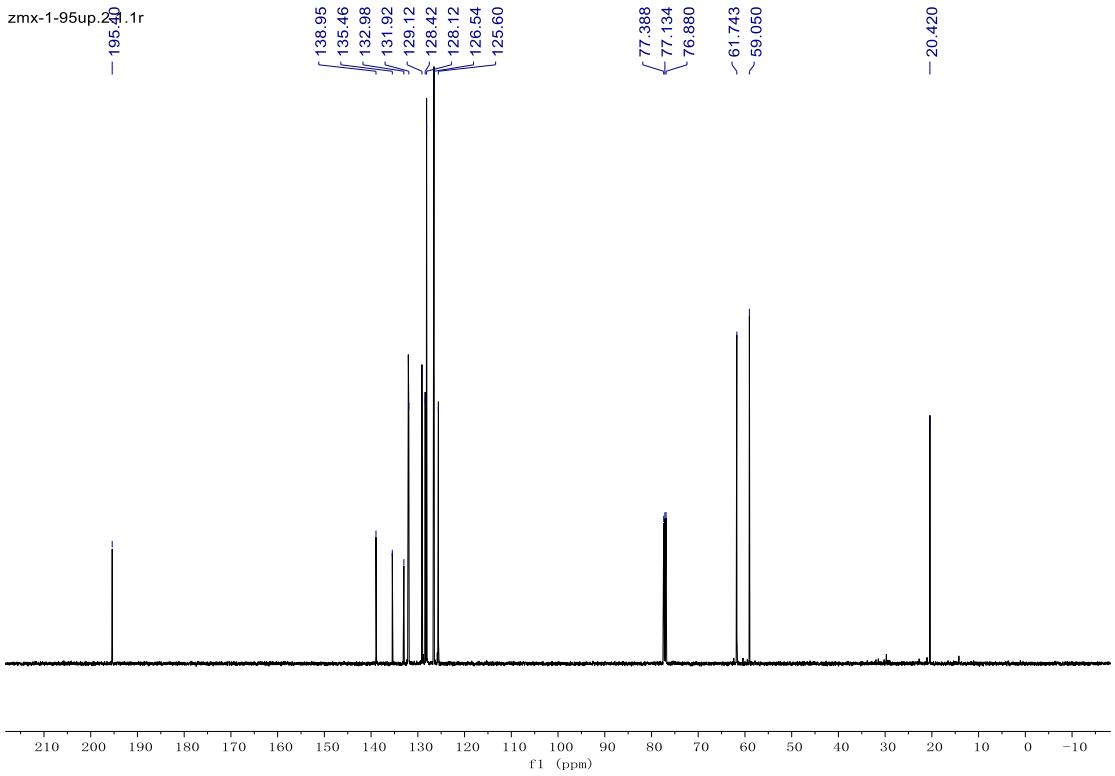
1d

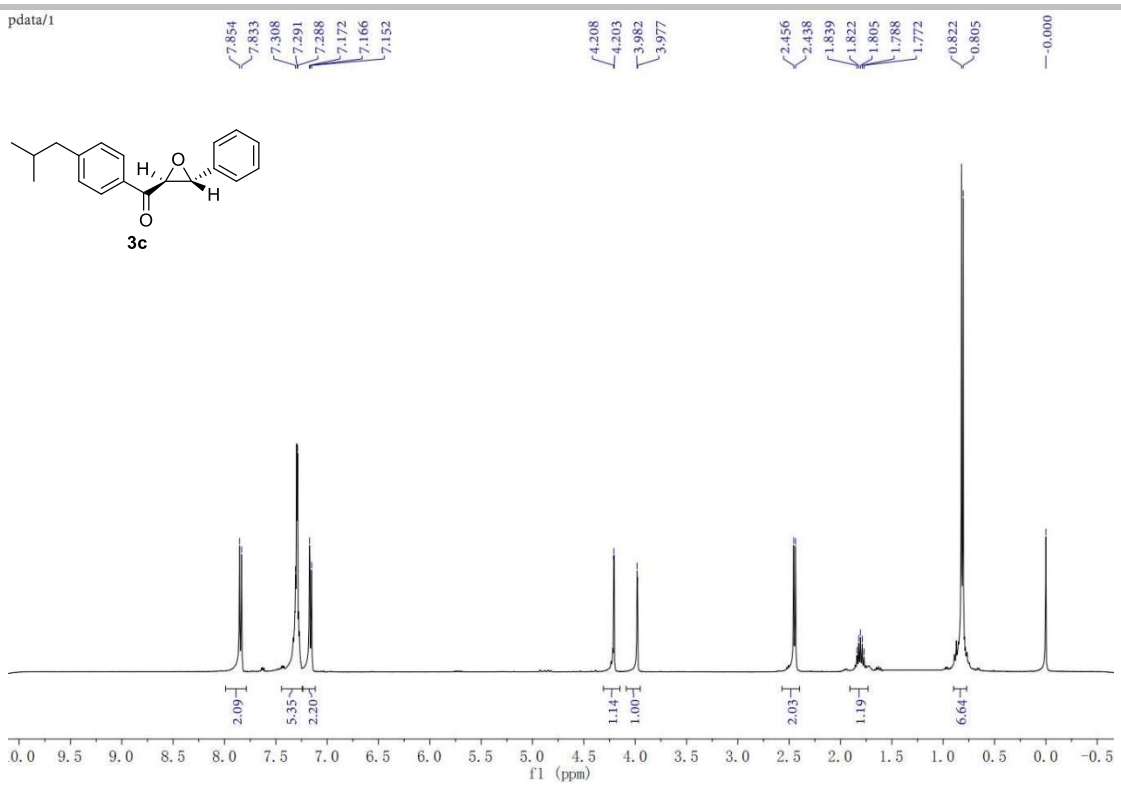

1. 90
1. 00
1. 99
1. 93
2. 94
1. 91
10. 5 10. 0 9. 5 9. 0 8. 5 8. 0 7. 5 7. 0 6. 5 6. 0 5. 5 5. 0 4. 5 4. 0 3. 5 3. 0 2. 5 2. 0 1. 5 1. 0 0. 5 0. 0 -0. 5 -1. 0
f1 (ppm)

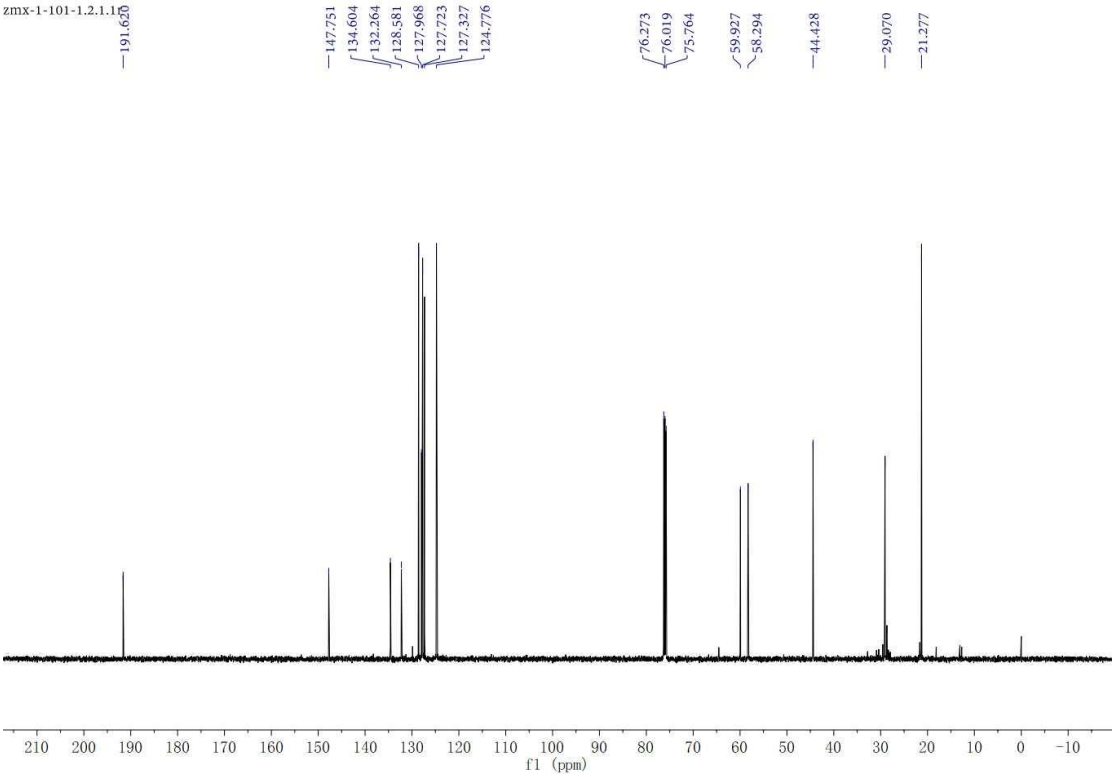

zmx-1-42d.20.1.1r
191.99
135.51
133.71
132.95
128.71
128.46
128.17
126.47
77.30
77.05
76.80
60.96
58.72

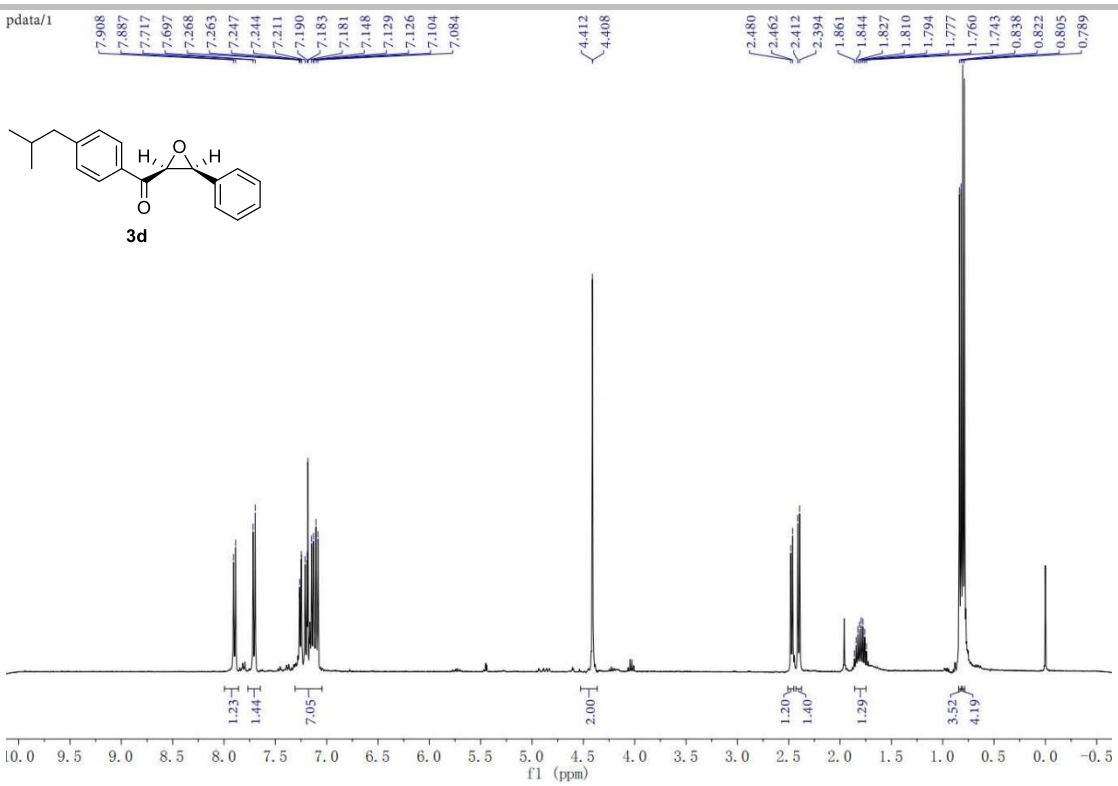

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

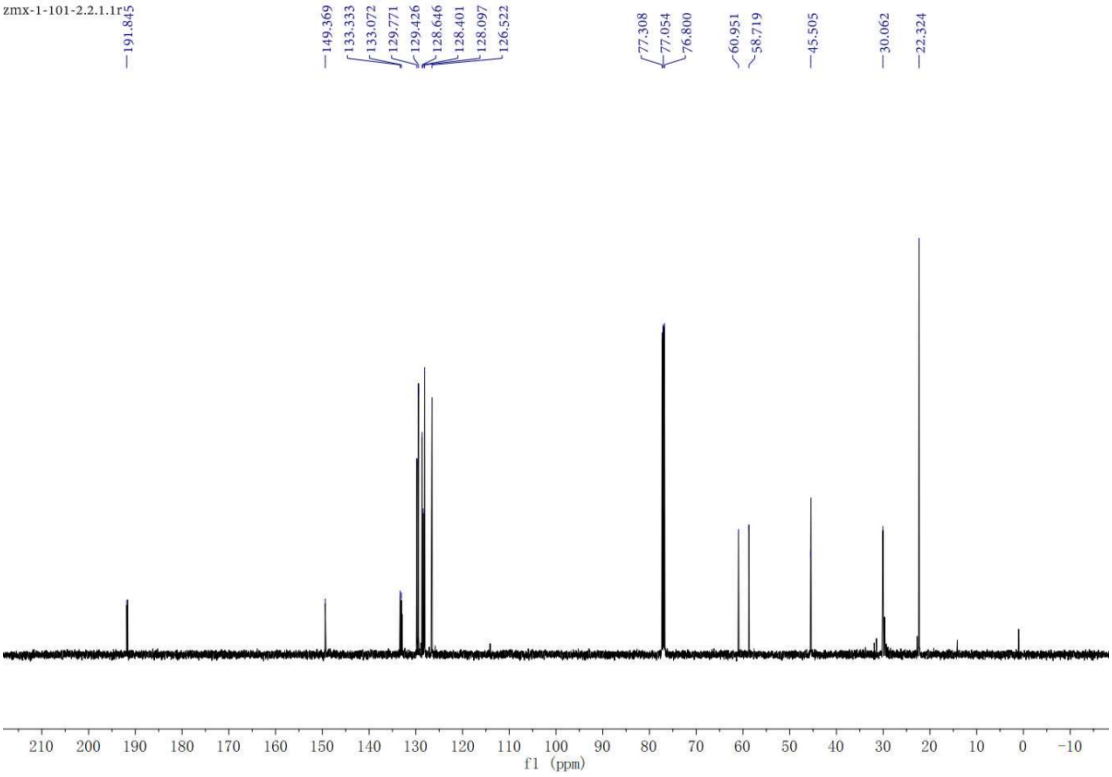

7.644
7.629
7.389
7.386
7.370
7.367
7.348
7.337
7.332
7.283
7.272
7.258
7.253
7.185
7.166
4.502
4.490
4.359
4.347
2.243
H
O
H
O
2c
1.00
3.11
4.03
1.06
1.00
1.00
3.01
f1 (ppm)

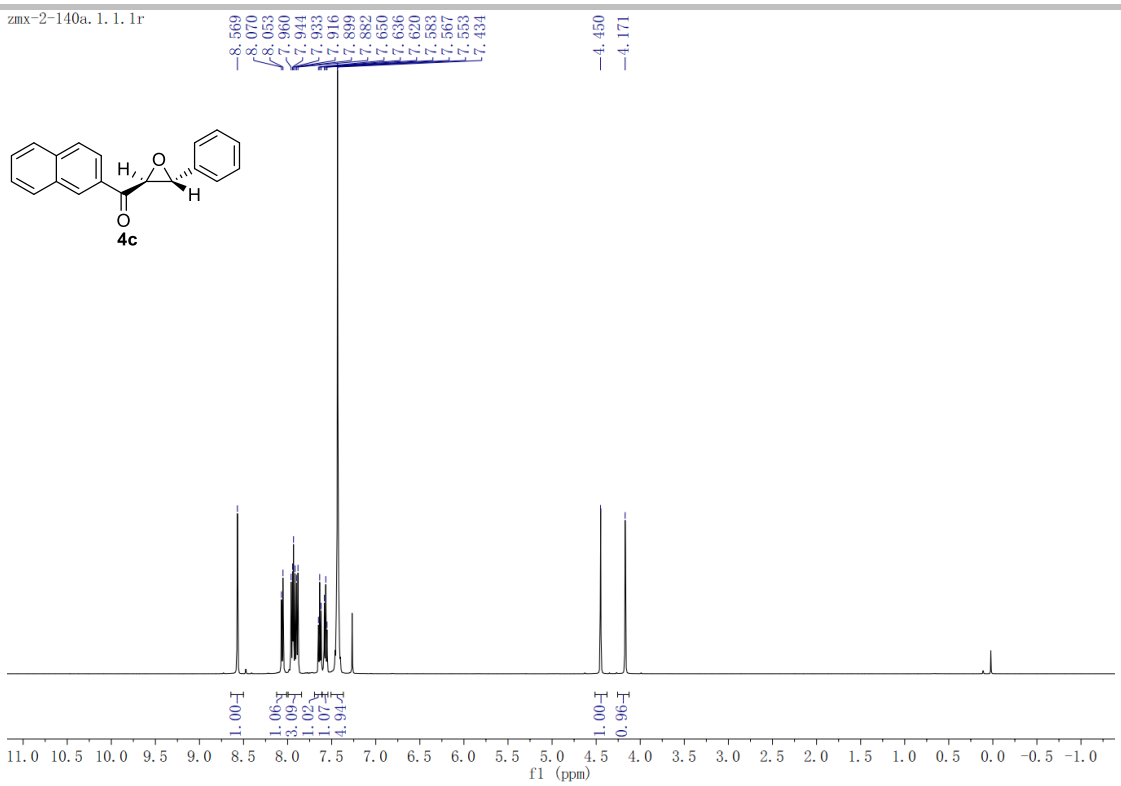

zmx-1-95up.2
195.440
138.95
135.46
132.98
131.92
129.12
128.42
128.12
126.54
125.60
77.388
77.134
76.880
61.743
59.050
20.420
f1 (ppm)

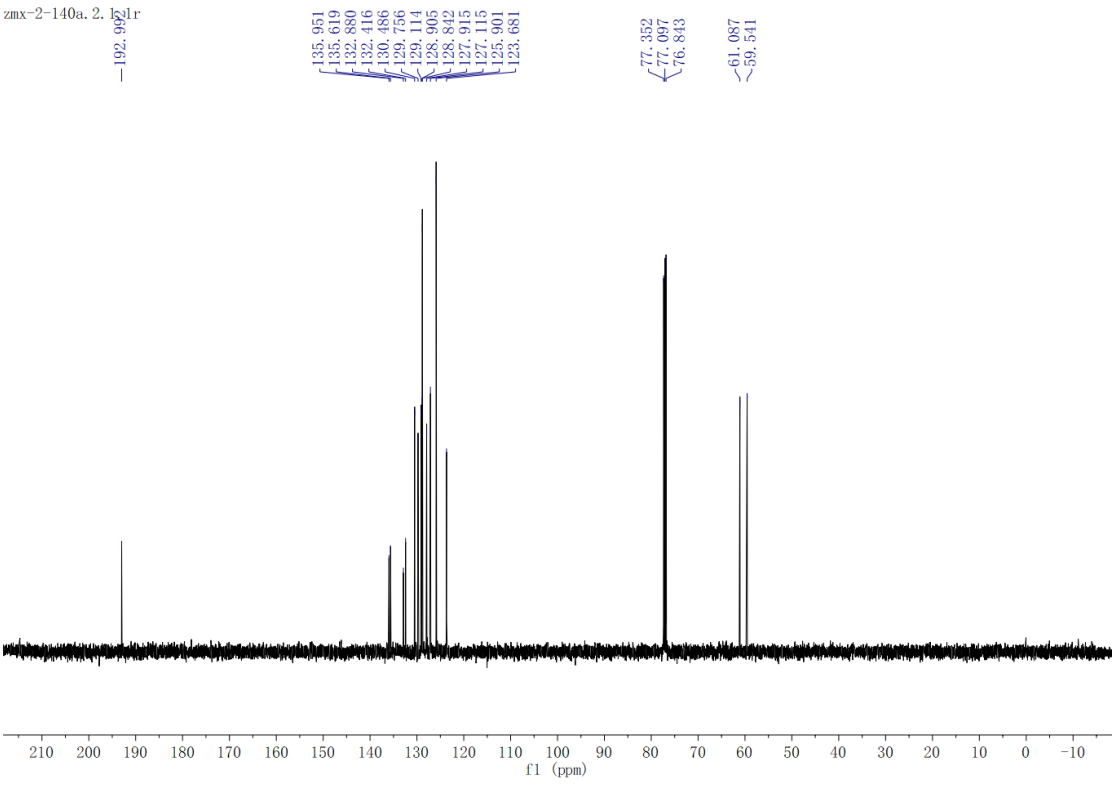

pdata/1
7.854
7.833
7.308
7.291
7.288
7.172
7.166
7.152
4.208
4.203
3.982
3.977
2.456
2.438
1.839
1.822
1.805
1.788
1.772
0.822
0.805
-0.000
3c
2.09
5.35
2.20
1.14
1.00
2.03
1.19
6.64
f1 (ppm)


zmx-1-101-1.2.1.1
191.620
147.751
134.604
132.264
128.581
127.968
127.723
127.327
124.776
76.273
76.019
75.764
59.927
58.294
44.428
29.070
21.277
f1 (ppm)


pdata/1
7.908
7.887
7.717
7.697
7.268
7.263
7.247
7.244
7.211
7.190
7.183
7.181
7.148
7.129
7.126
7.104
7.084
4.412
4.408
2.480
2.462
2.412
2.394
1.861
1.844
1.827
1.810
1.794
1.777
1.760
1.743
0.838
0.822
0.805
0.789
H
O
H
O
3d
1.23
1.44
7.05
2.00
1.20
1.40
1.29
3.52
4.19
f1 (ppm)


zmx-1-101-2.2.1.1r
191.845
149.369
133.333
133.072
129.771
129.426
128.646
128.401
128.097
126.522
77.308
77.054
76.800
60.951
58.719
45.505
30.062
22.324
f1 (ppm)

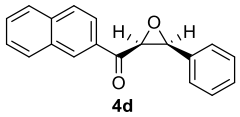

zmx-2-140a. 1. 1. 1r
8.569
8.070
8.053
7.960
7.944
7.933
7.916
7.899
7.882
7.650
7.636
7.620
7.583
7.567
7.553
7.434
4.450
4.171
H
O
H
O
4c
1.00
1.06
3.09
1.02
1.07
4.94
1.00
0.96
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


zmx-2-140a. 2. 1r
192.992
135.951
135.619
132.880
132.416
130.486
129.756
129.114
128.905
128.842
127.915
127.115
125.901
123.681
77.352
77.097
76.843
61.087
59.541
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

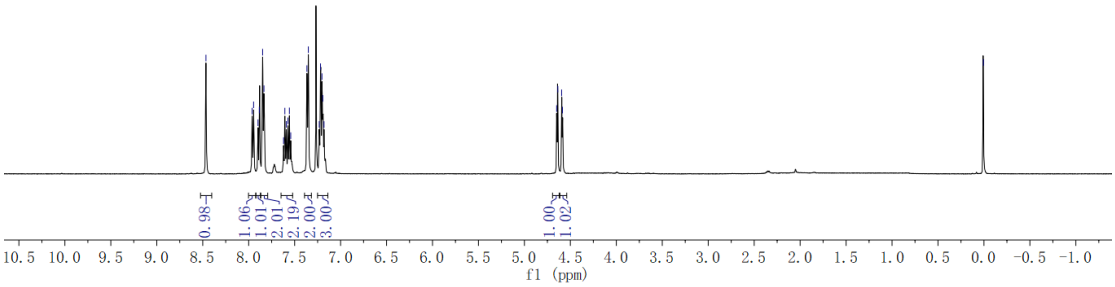
ZMX-2-140b-again.1.1.1r

8.465
7.963
7.947
7.898
7.884
7.848
7.834
7.620
7.606
7.590
7.573
7.557
7.543
7.366
7.351
7.232
7.218
7.203
7.194
7.180
4.649
4.636
4.595
4.586

0.006



4d



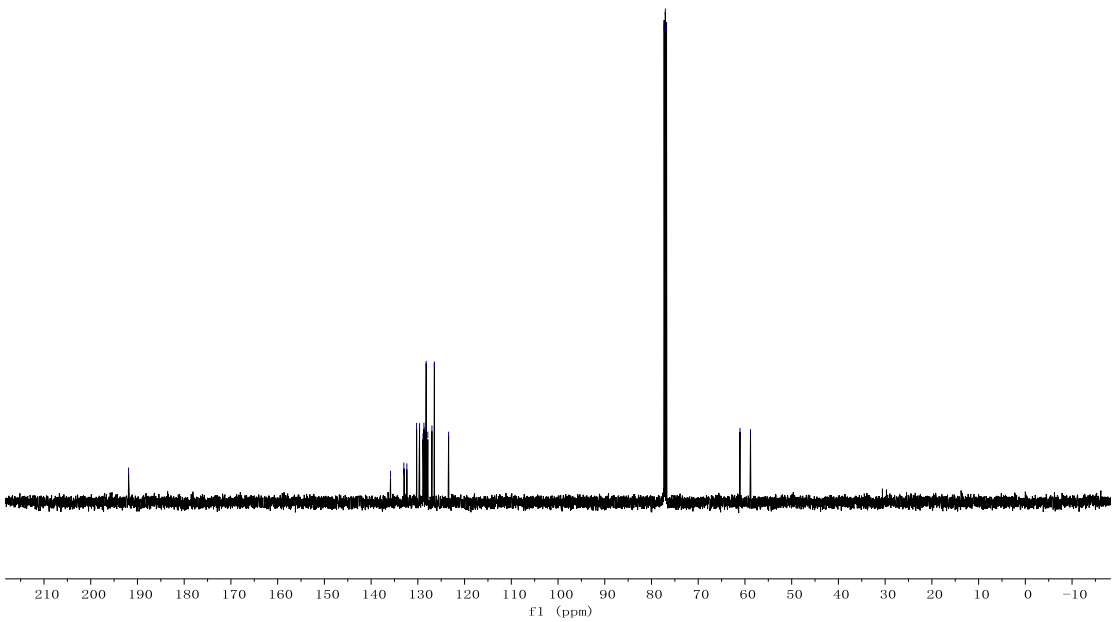
ZMX-2-140b-again.2.1.1r

191.903

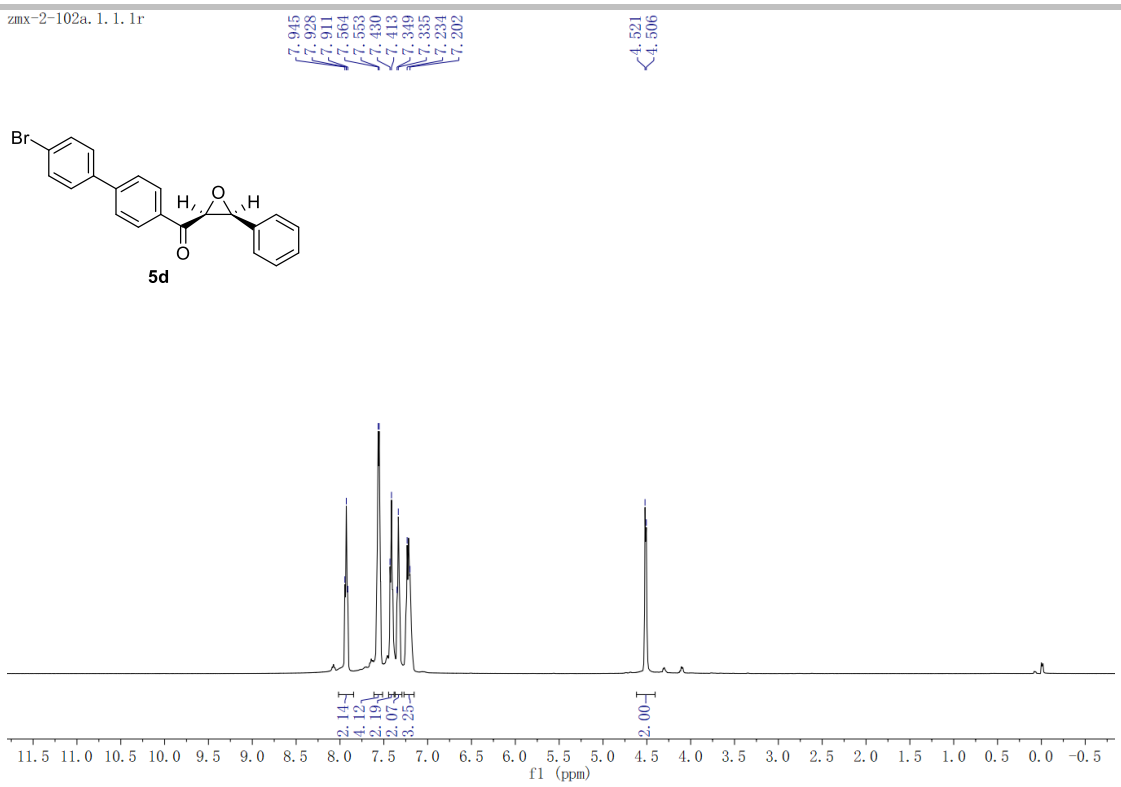
135.843
132.999
132.863
132.349
130.264
129.636
128.888
128.697
128.479
128.212
127.870
126.985
126.457
123.419

77.291
77.038
76.784

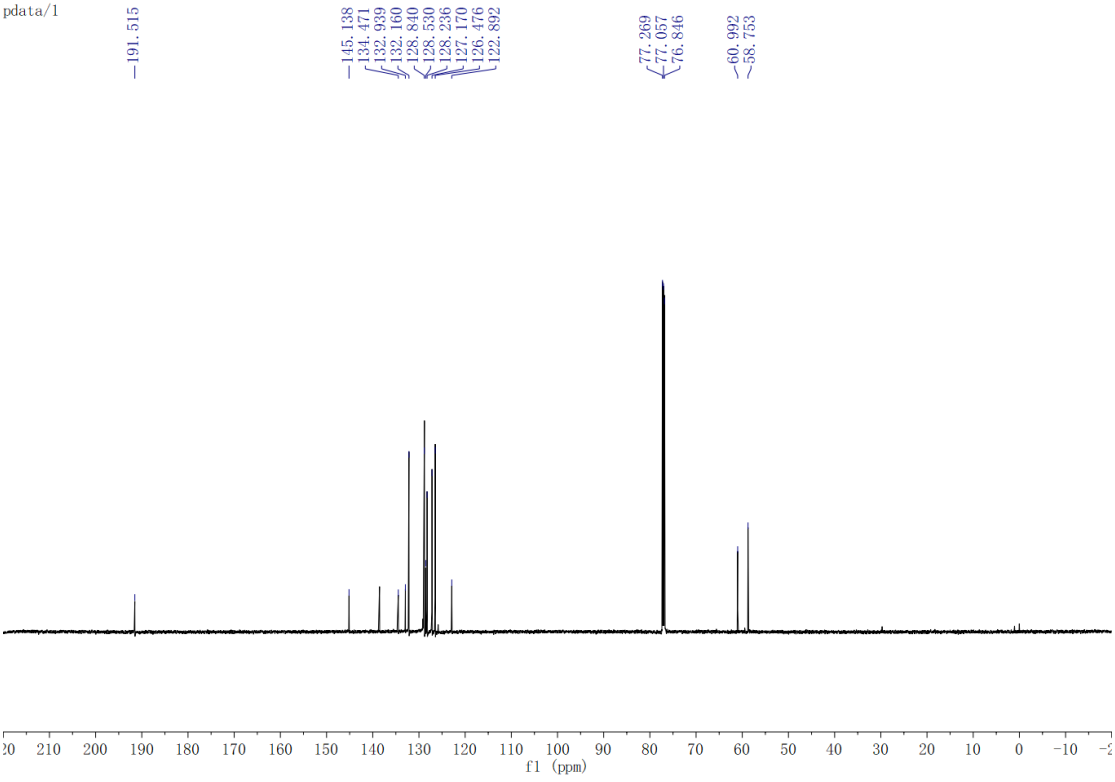
61.063
58.813

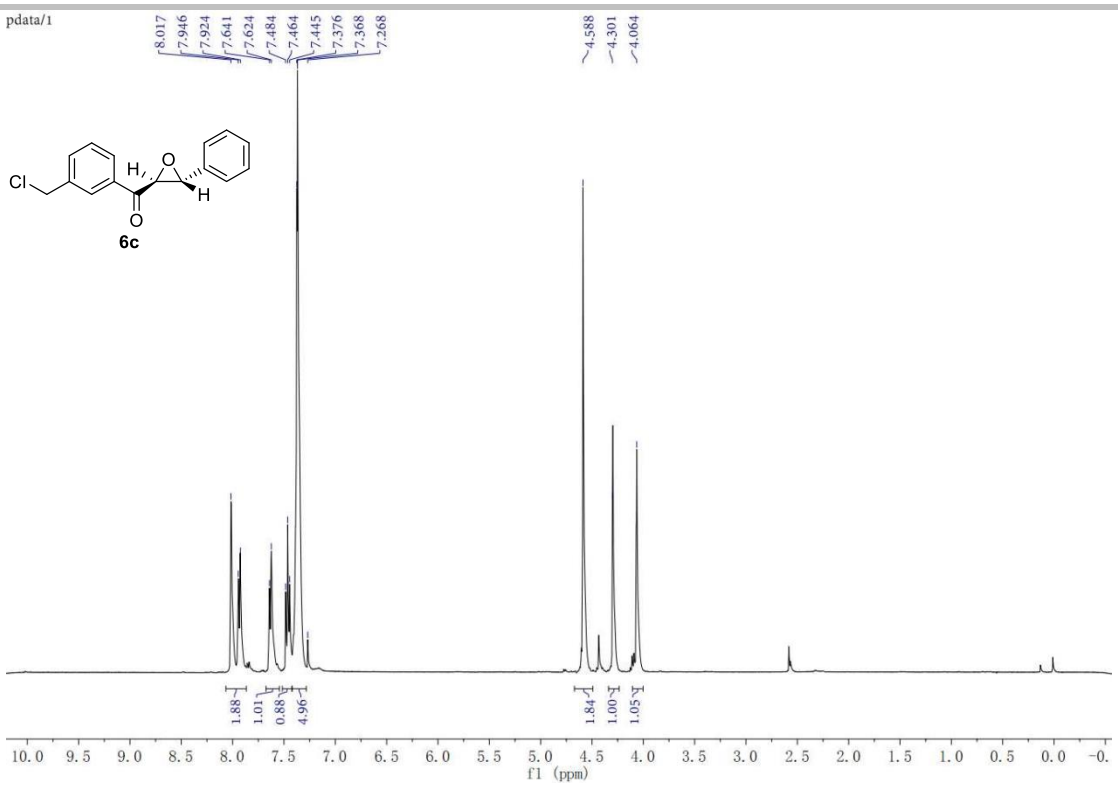


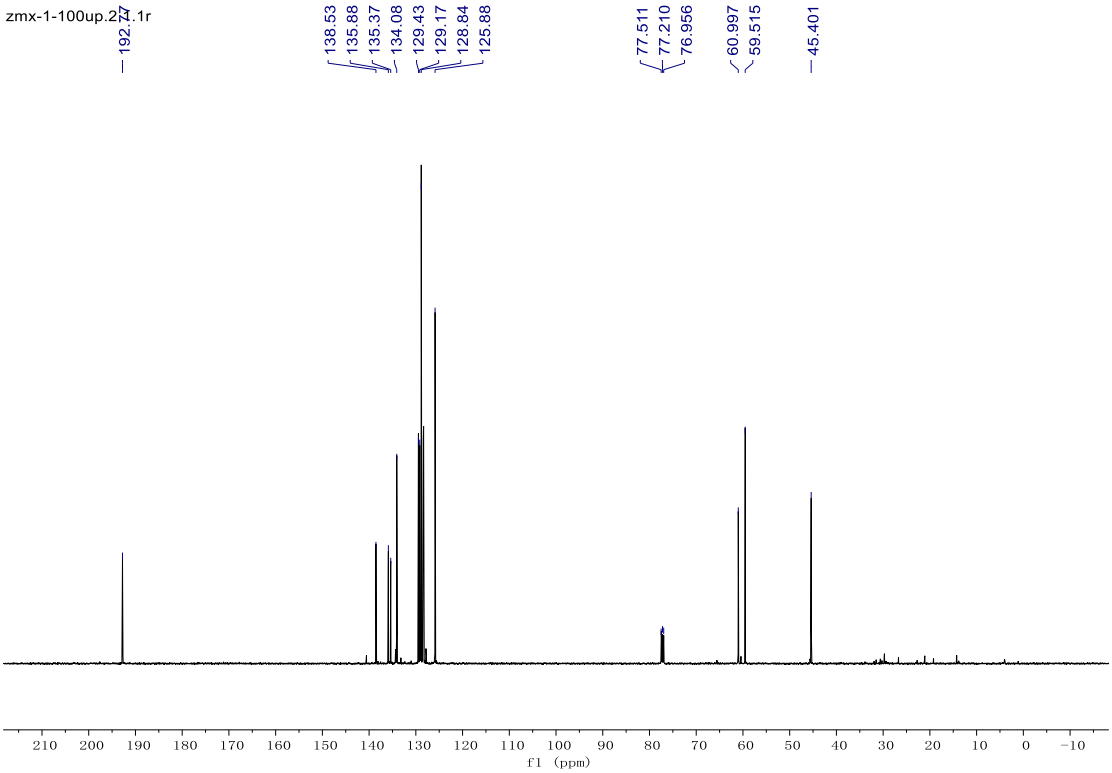
zmx-2-102a.1.1.1r

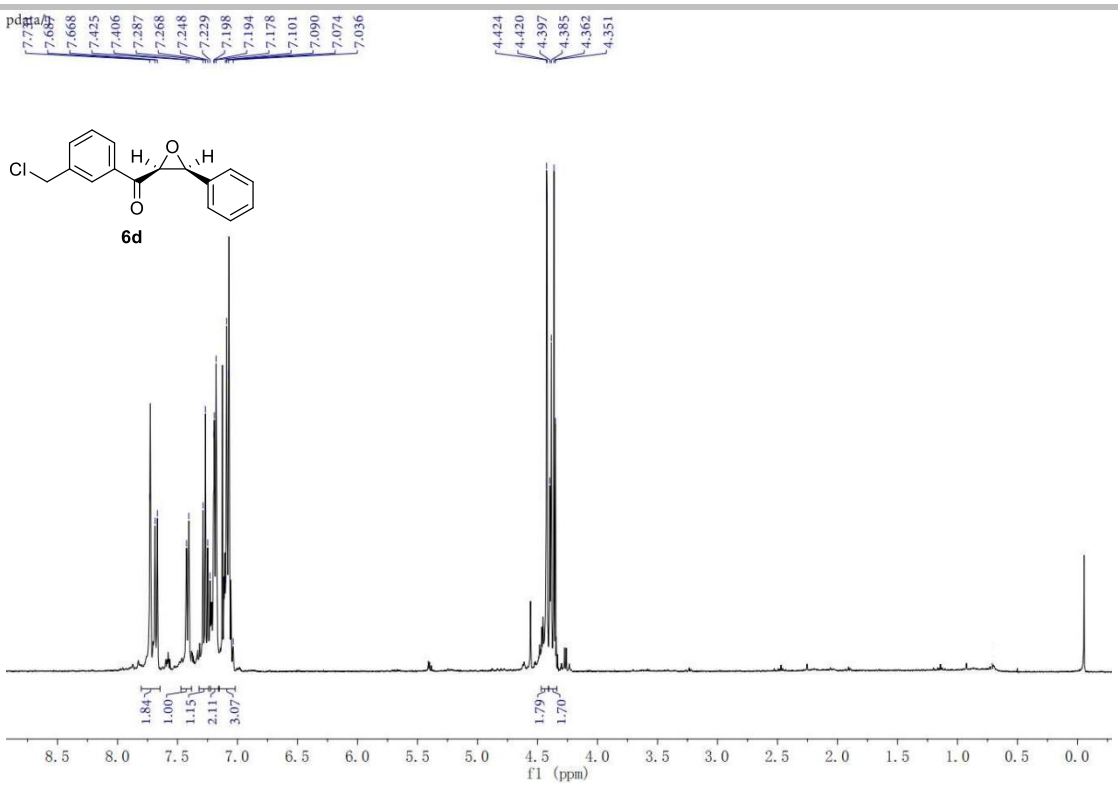


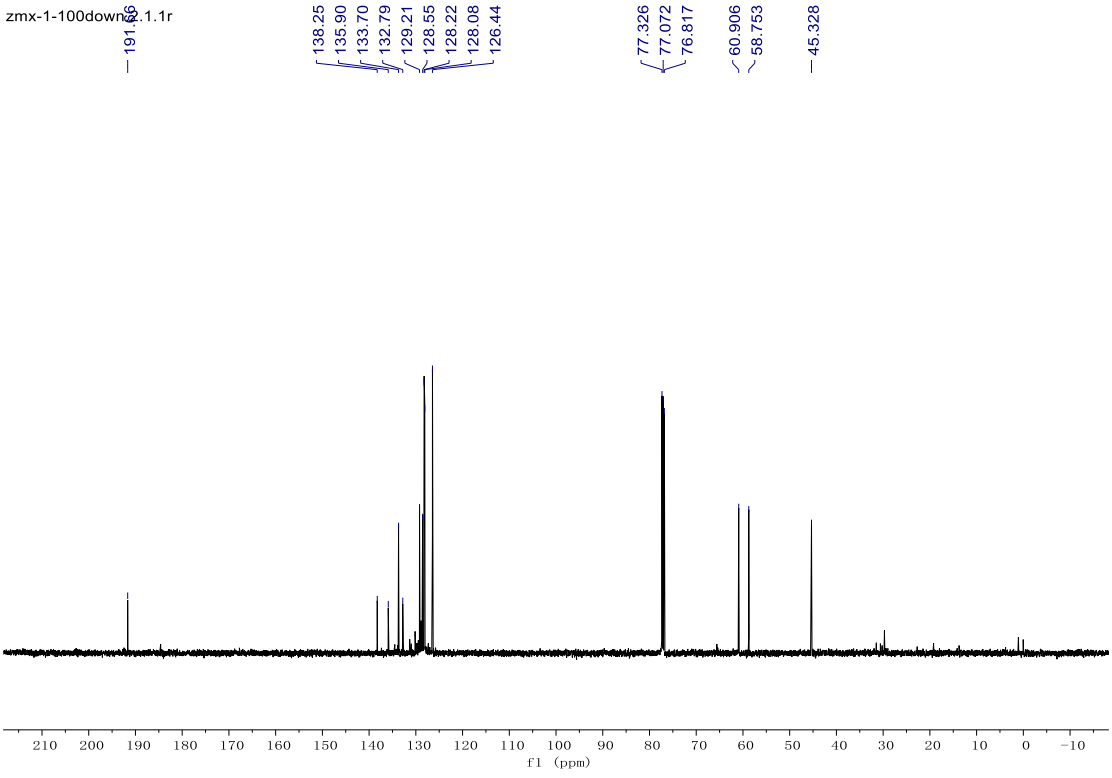
pdata/1

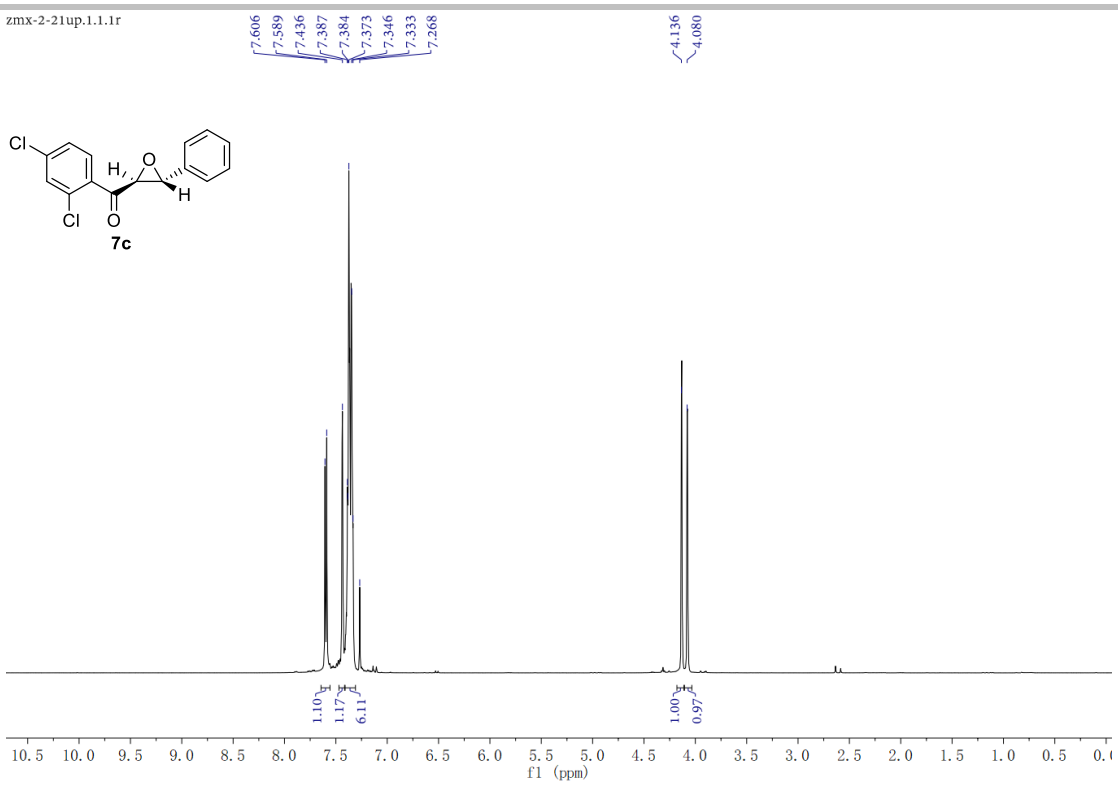


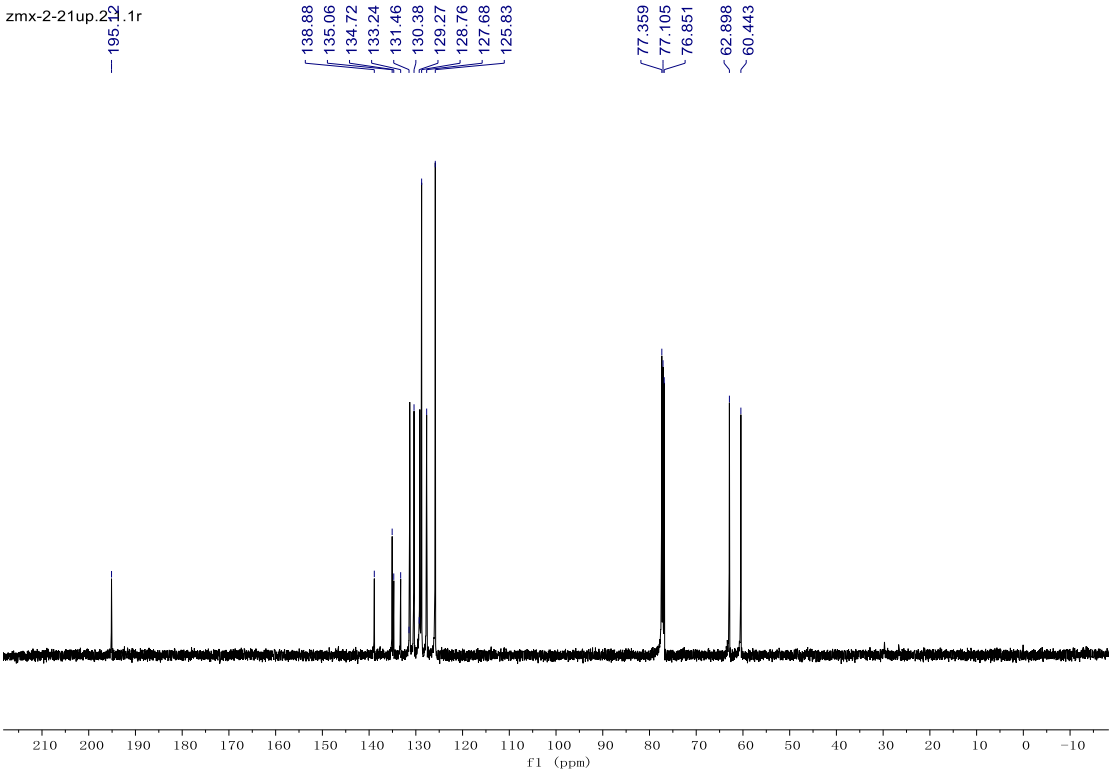

pdata/1
8.017
7.946
7.924
7.641
7.624
7.484
7.464
7.445
7.376
7.368
7.268
4.588
4.301
4.064
Cl
H
O
H
O
6c
1.88
1.01
0.88
4.96
1.84
1.00
1.05
f1 (ppm)


zmx-1-100up.2
192.27
138.53
135.88
135.37
134.08
129.43
129.17
128.84
125.88
77.511
77.210
76.956
60.997
59.515
45.401
f1 (ppm)

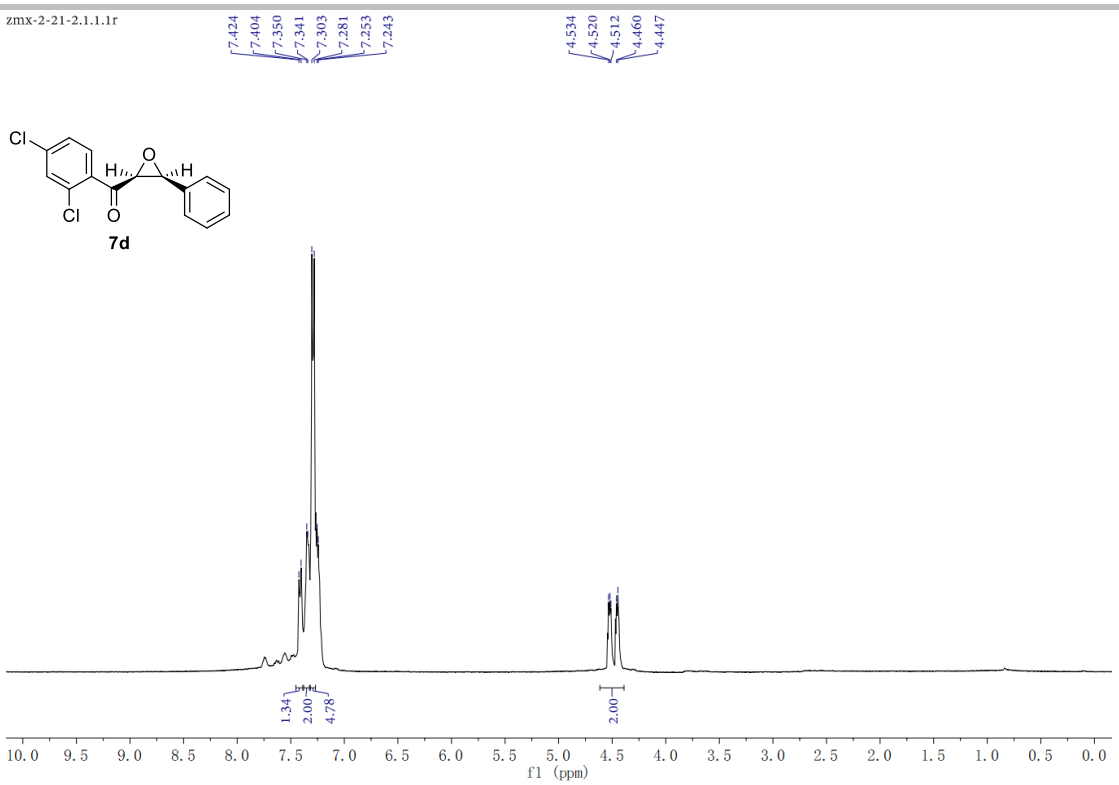

pdata/1
7.714
7.697
7.668
7.425
7.406
7.287
7.268
7.248
7.229
7.198
7.194
7.178
7.101
7.090
7.074
7.036
4.424
4.420
4.397
4.385
4.362
4.351
Cl
H
O
H
O
6d
1.84
1.00
1.15
2.11
3.07
1.79
1.70
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


zmx-1-100down2.1.1r
191.466
138.25
135.90
133.70
132.79
129.21
128.55
128.22
128.08
126.44
77.326
77.072
76.817
60.906
58.753
45.328
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

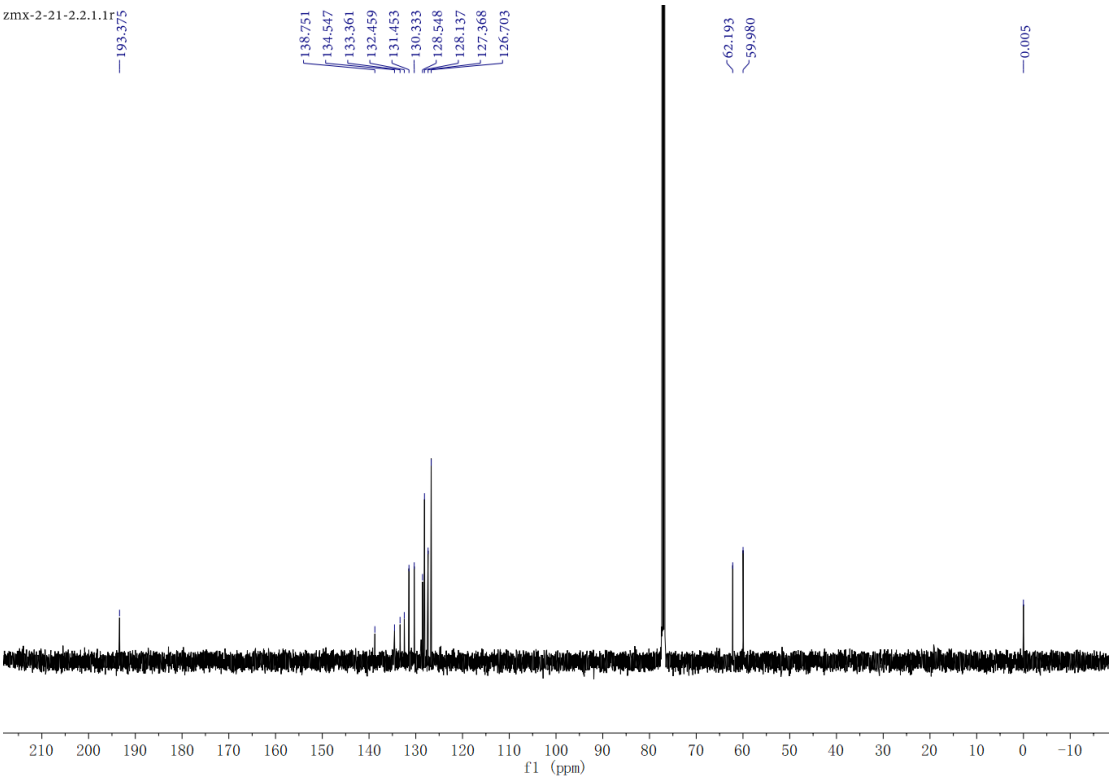

zmx-2-21up.1.1.1r
7.606
7.589
7.436
7.387
7.384
7.373
7.346
7.333
7.268
4.136
4.080
Cl
H
O
H
Cl
O
7c
1.10
1.17
6.11
1.00
0.97
f1 (ppm)

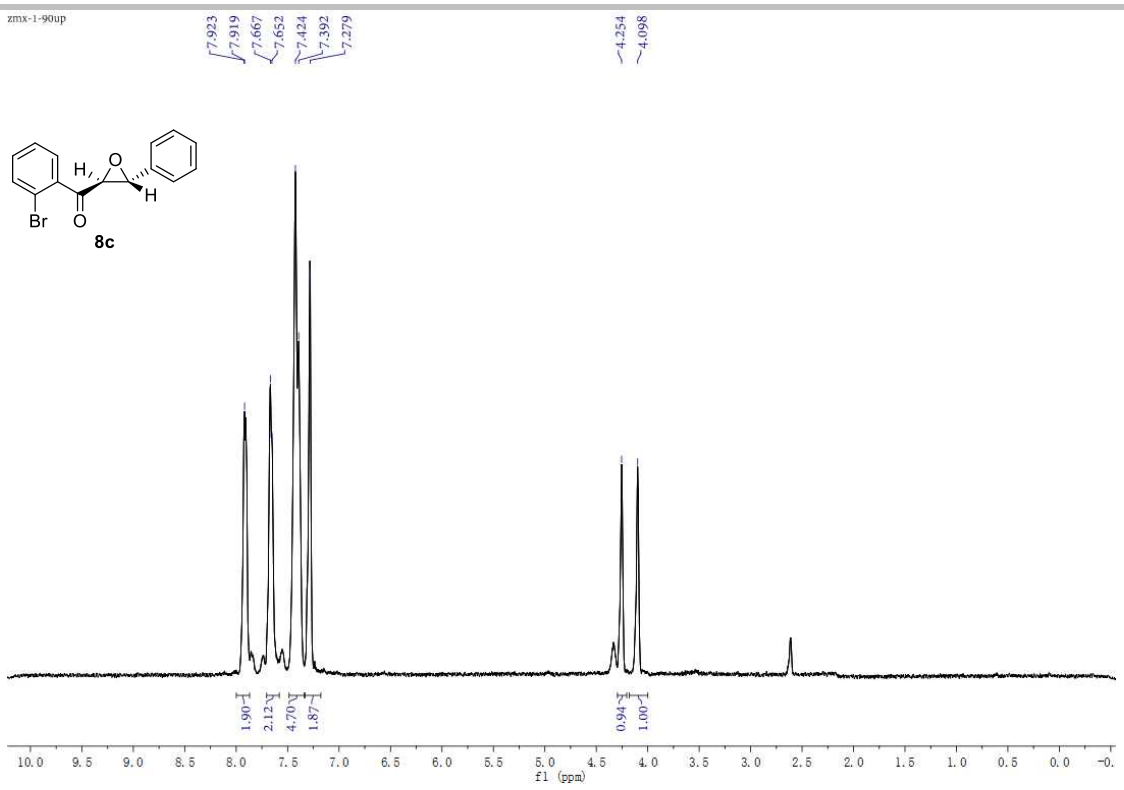

zmx-2-21up.2.1.1r
195.12
138.88
135.06
134.72
133.24
131.46
130.38
129.27
128.76
127.68
125.83
77.359
77.105
76.851
62.898
60.443
f1 (ppm)

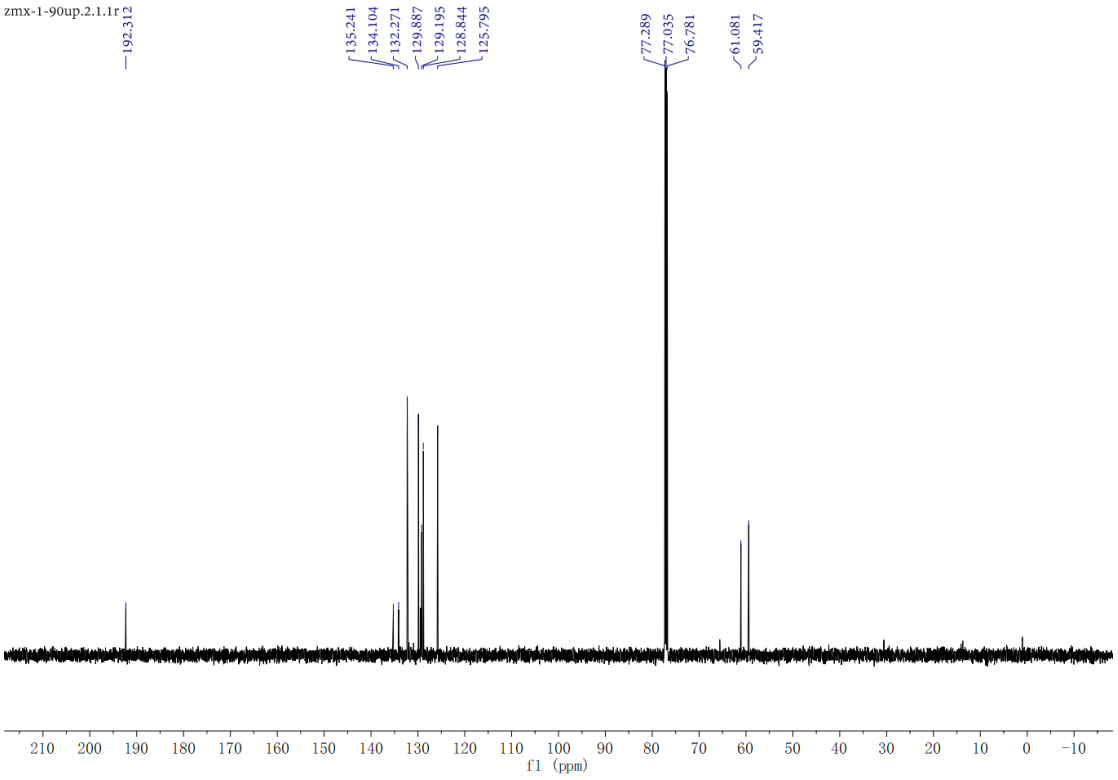
zmx-2-21-2.1.1.1r



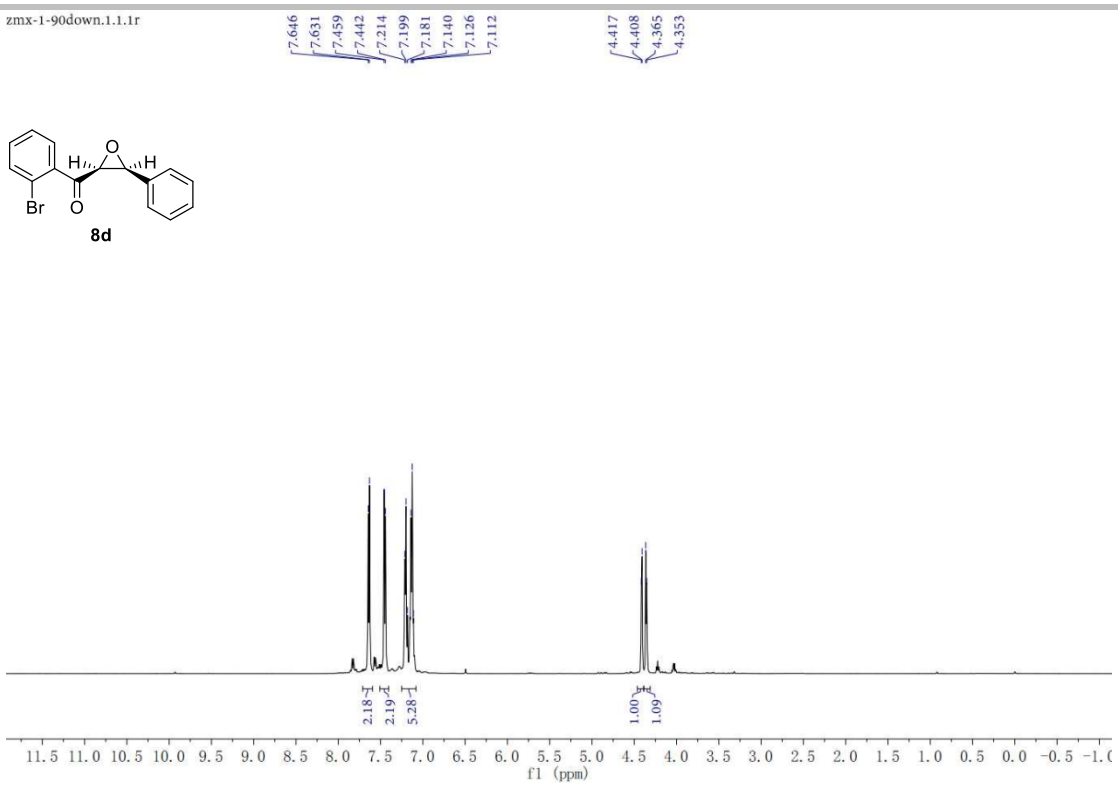
zmx-2-21-2.2.1.1r




zmx-1-90up
7.923
7.919
7.667
7.652
7.424
7.392
7.279
4.254
4.098
H
O
H
Br
O
8c
1.90
2.12
4.70
1.87
0.94
1.00
f1 (ppm)

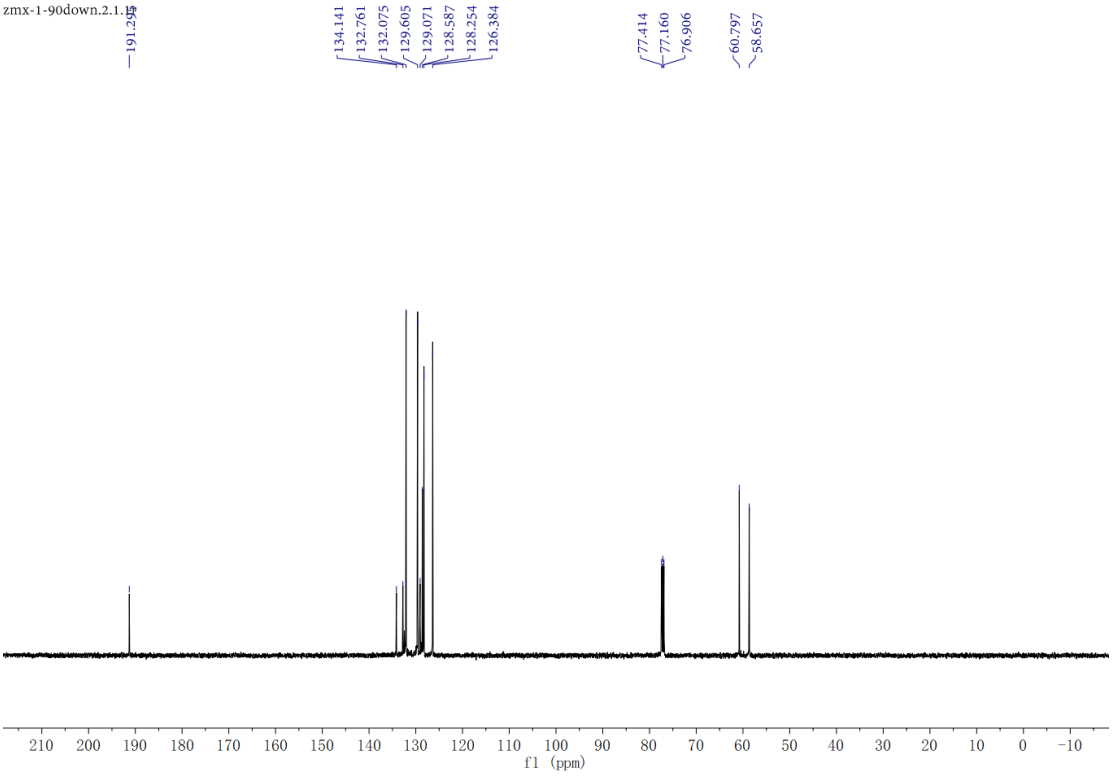

zmx-1-90up.2.1.1r2
192.312
135.241
134.104
132.271
129.887
129.195
128.844
125.795
77.289
77.035
76.781
61.081
59.417
f1 (ppm)

zmx-1-90down.1.1.1r



8d

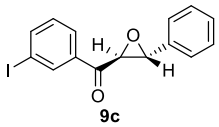
zmx-1-90down.2.1.1r



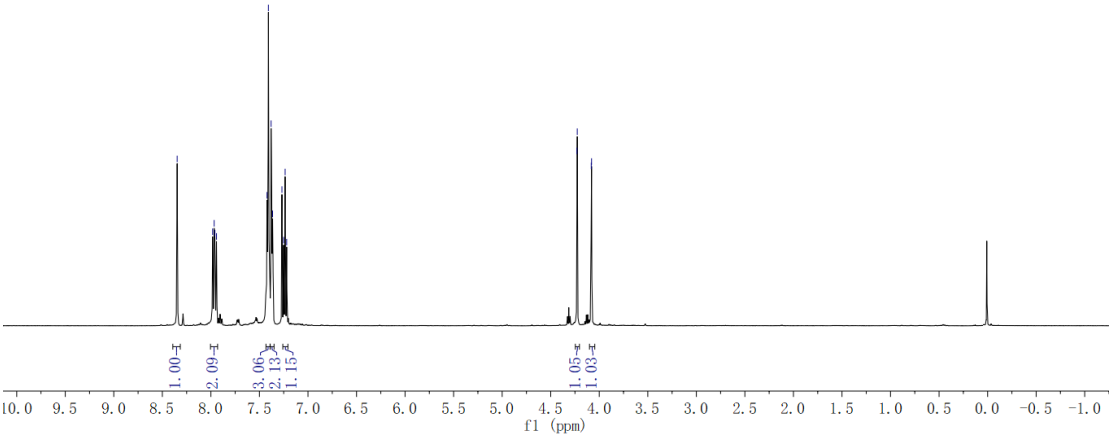
zmx-2-133a-again.1.1.1r

8.347
7.983
7.967
7.959
7.942
7.422
7.408
7.380
7.364
7.268
7.251
7.235
7.219

4.230
4.227
4.083
4.079



9c



zmx-2-133a-again.2.1.1r

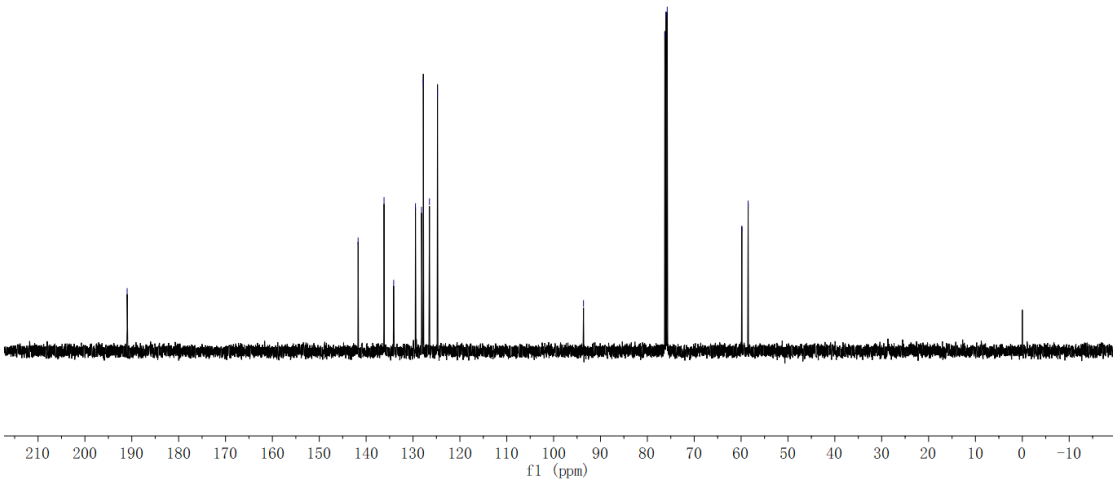
190.993

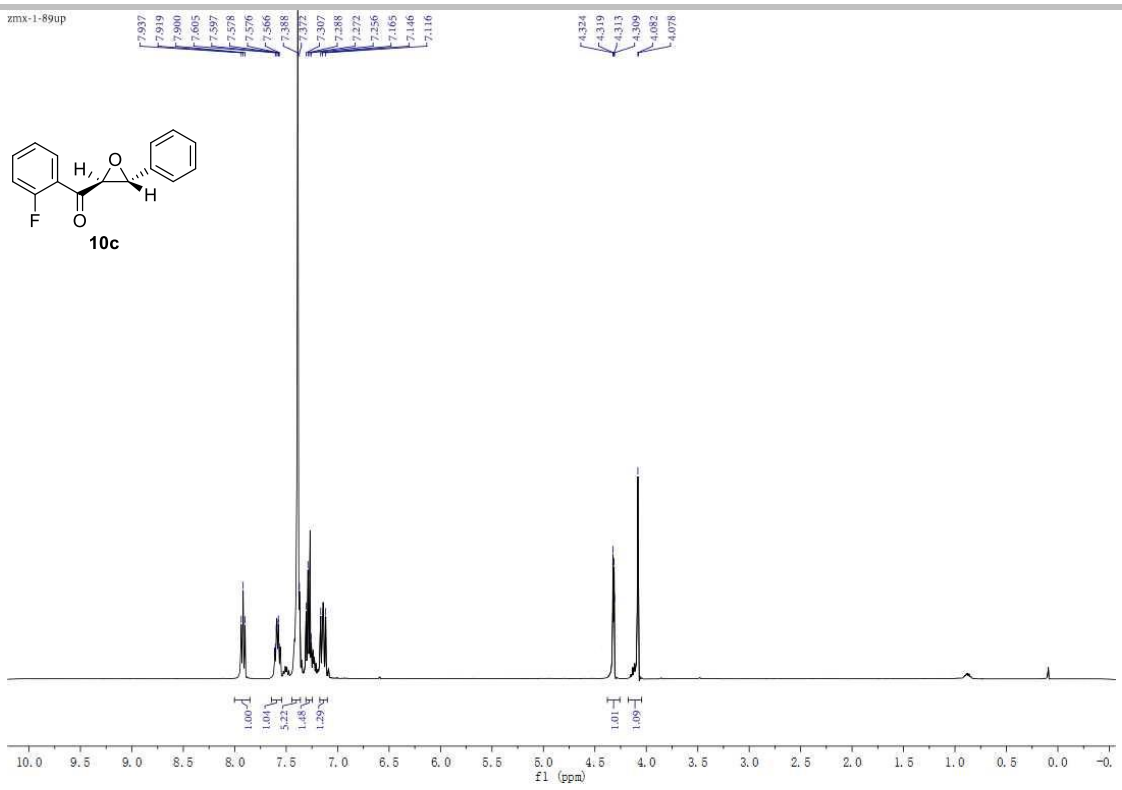
141.708
136.179
134.129
129.479
128.171
127.804
126.496
124.778

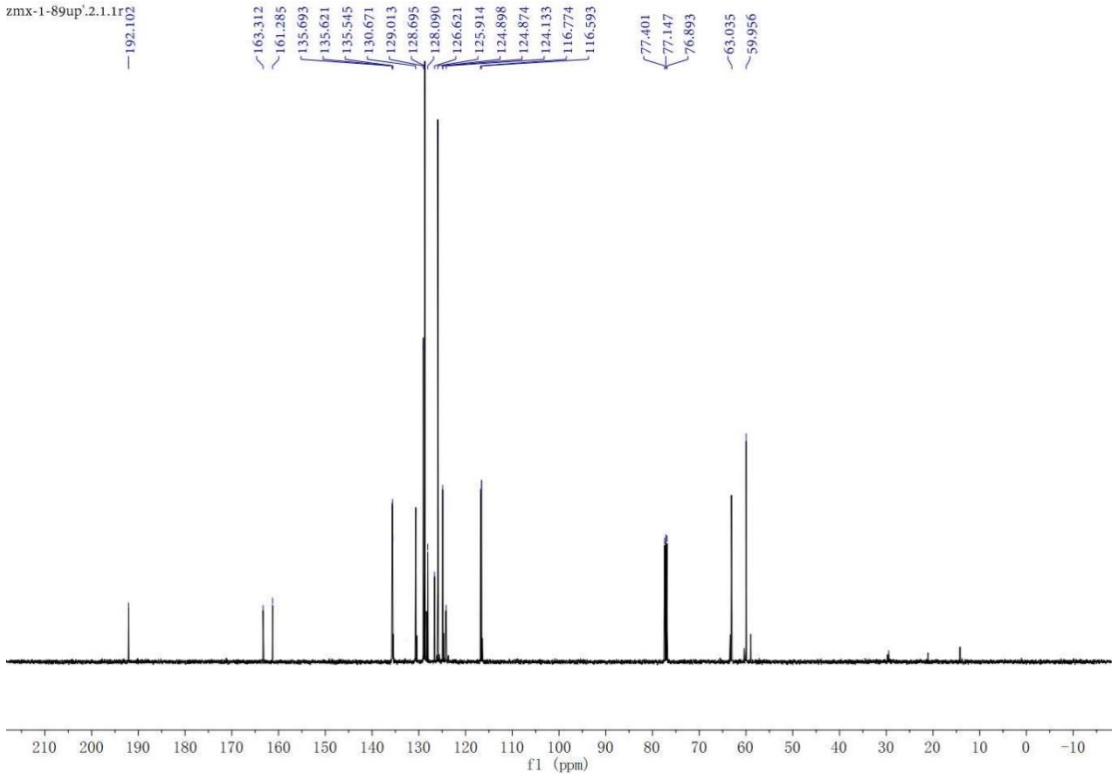
93.629

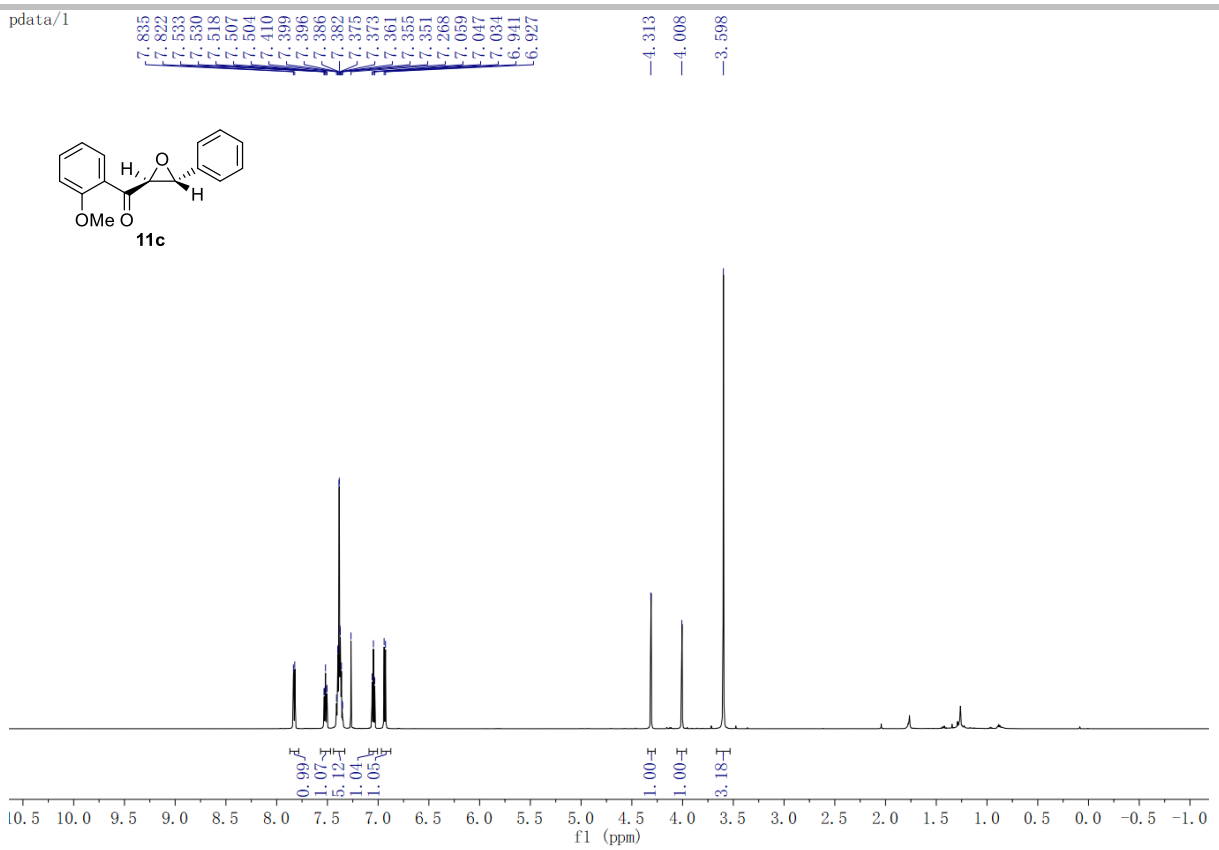
76.269
76.015
75.761

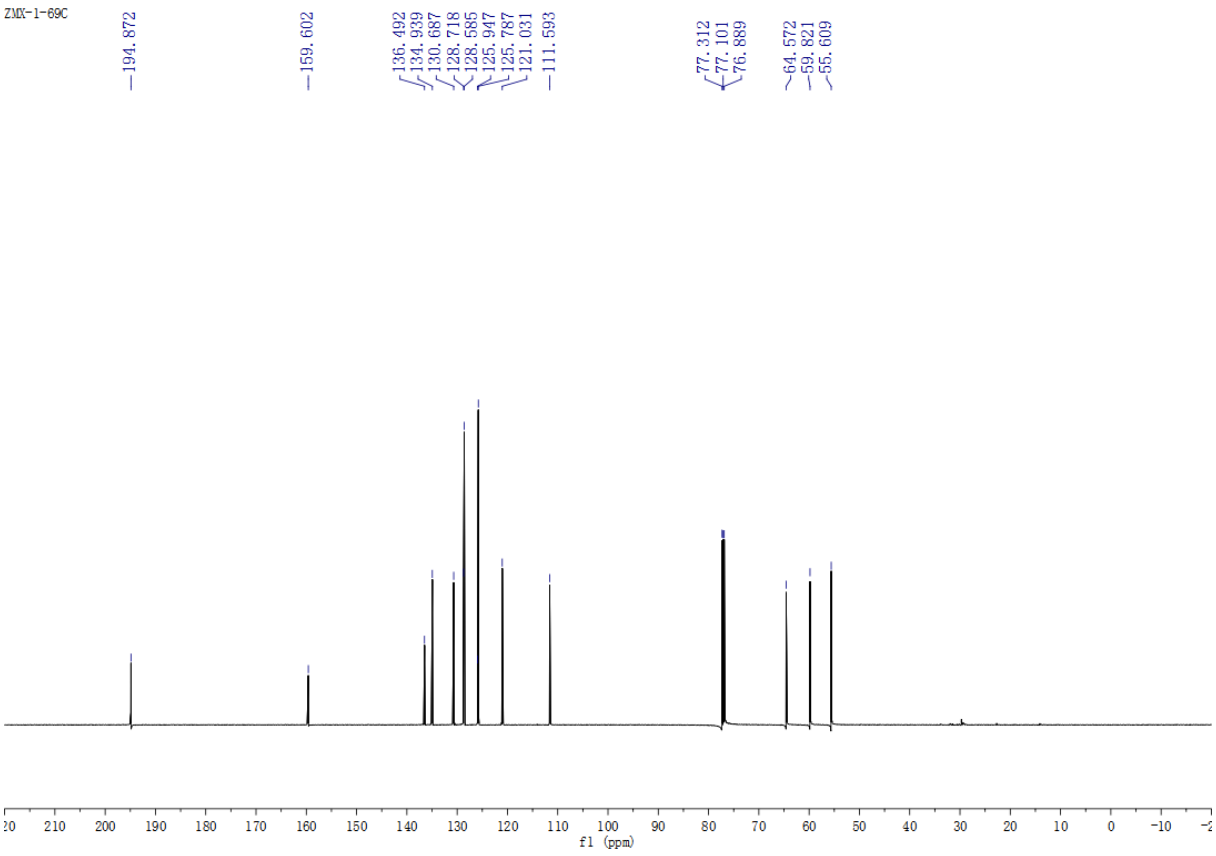
59.841
58.496

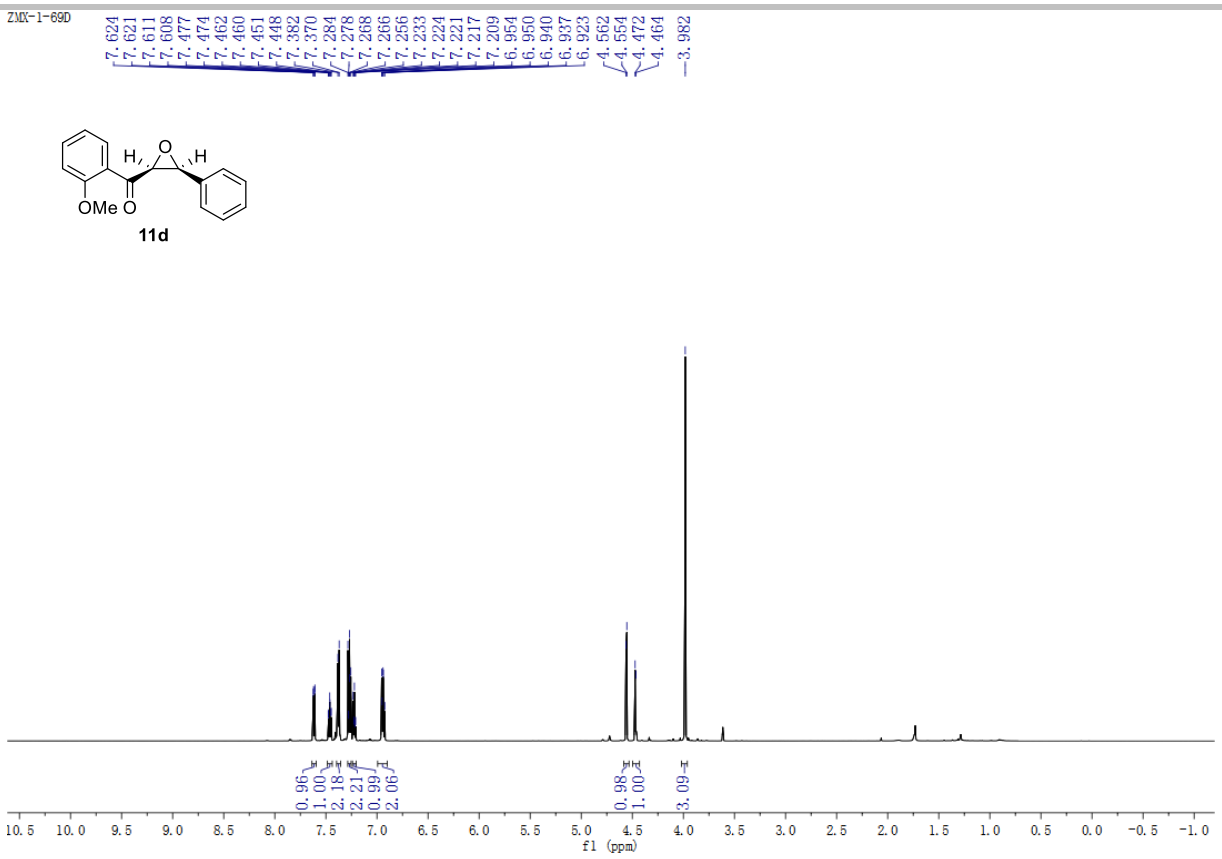


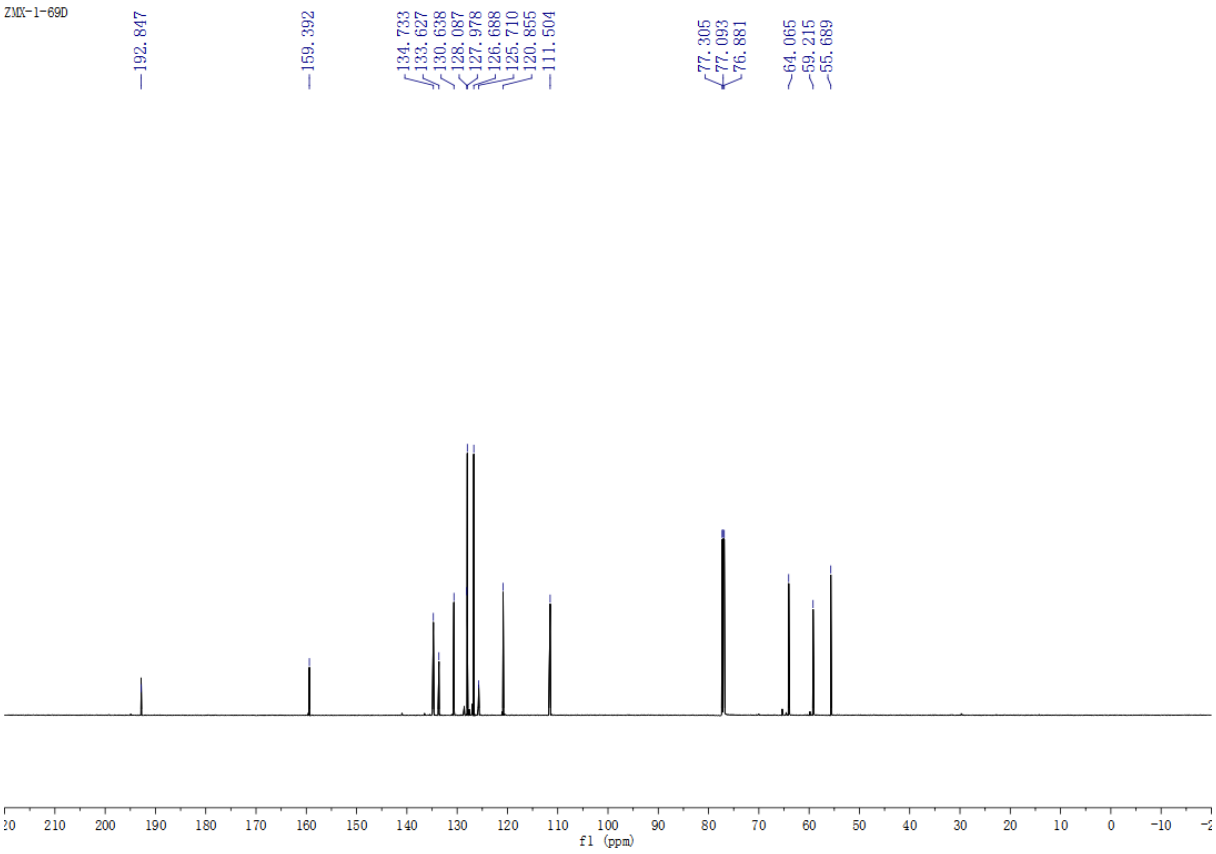

zmx-1-89up
7.937
7.919
7.900
7.605
7.597
7.578
7.576
7.566
7.388
7.372
7.307
7.288
7.272
7.256
7.165
7.146
7.116
4.324
4.319
4.313
4.309
4.082
4.078
H
O
H
F
O
10c
1.00
1.04
5.22
1.48
1.29
1.01
1.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


zmx-1-89up'.2.1.1r
192.102
163.312
161.285
135.693
135.621
135.545
130.671
129.013
128.695
128.090
126.621
125.914
124.898
124.874
124.133
116.774
116.593
77.401
77.147
76.893
63.035
59.956
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

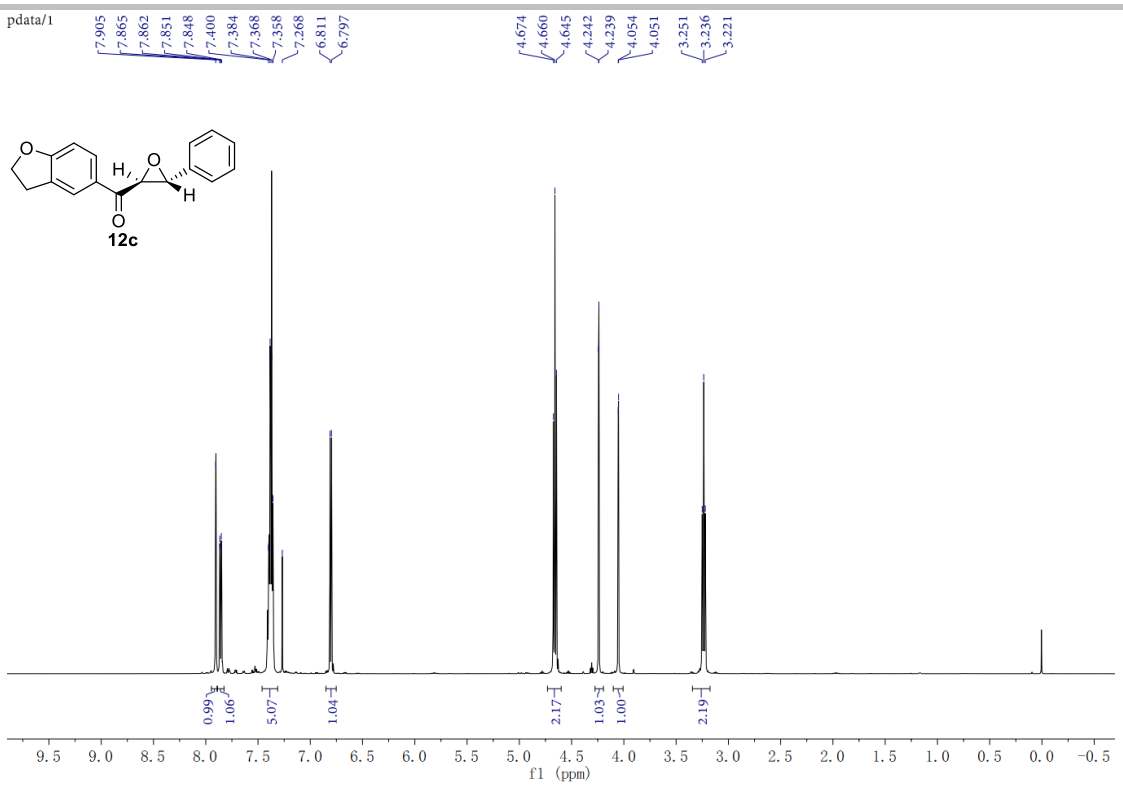

pdata/1
7.835
7.822
7.533
7.530
7.518
7.507
7.504
7.410
7.399
7.396
7.386
7.382
7.375
7.373
7.361
7.355
7.351
7.268
7.059
7.047
7.034
6.941
6.927
4.313
4.008
3.598
OMe O
11c
0.99
1.07
5.12
1.04
1.05
1.00
1.00
3.18
f1 (ppm)


ZMX-1-69C
194.872
159.602
136.492
134.939
130.687
128.718
128.585
125.947
125.787
121.031
111.593
77.312
77.101
76.889
64.572
59.821
55.609
f1 (ppm)

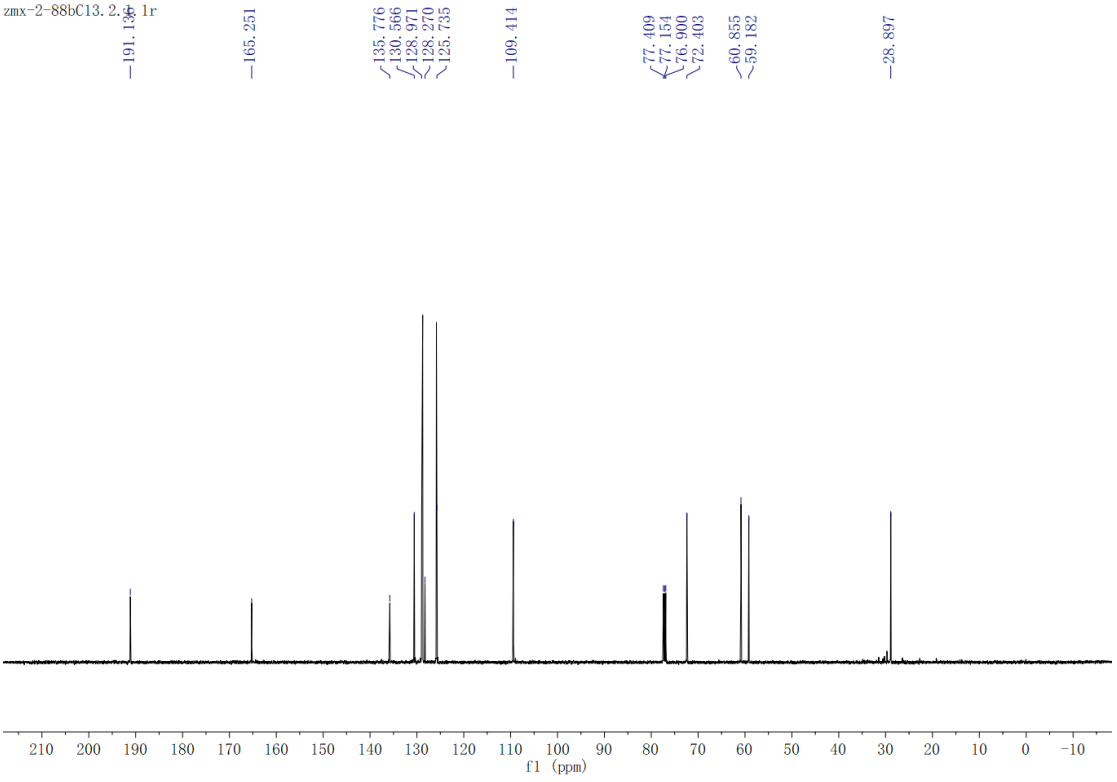

ZMX-1-69D
7.624
7.621
7.611
7.608
7.477
7.474
7.462
7.460
7.451
7.448
7.382
7.370
7.284
7.278
7.268
7.266
7.256
7.233
7.224
7.221
7.217
7.209
6.954
6.950
6.940
6.937
6.923
4.562
4.554
4.472
4.464
3.982
H
O
H
OMe
O
11d
0.96
1.00
2.18
2.21
0.99
2.06
0.98
1.00
3.09
f1 (ppm)

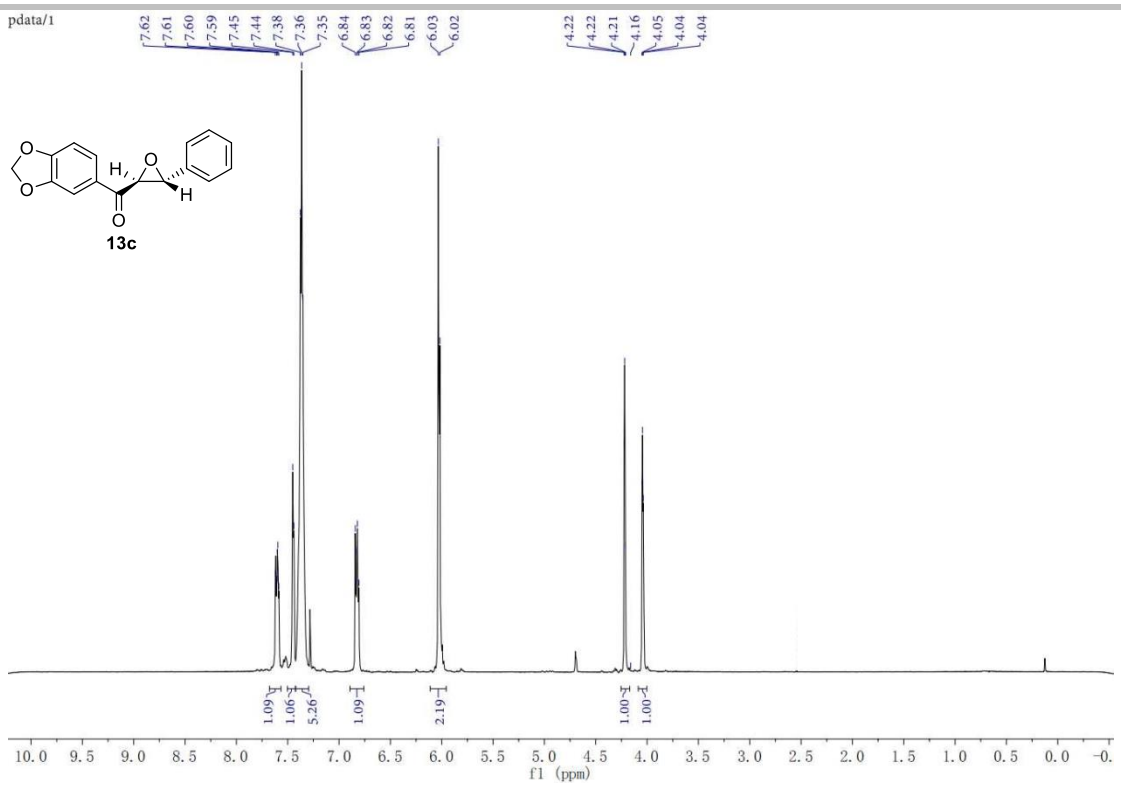

ZMX-1-69D
192.847
159.392
134.733
133.627
130.638
128.087
127.978
126.688
125.710
120.855
111.504
77.305
77.093
76.881
64.065
59.215
55.689
f1 (ppm)

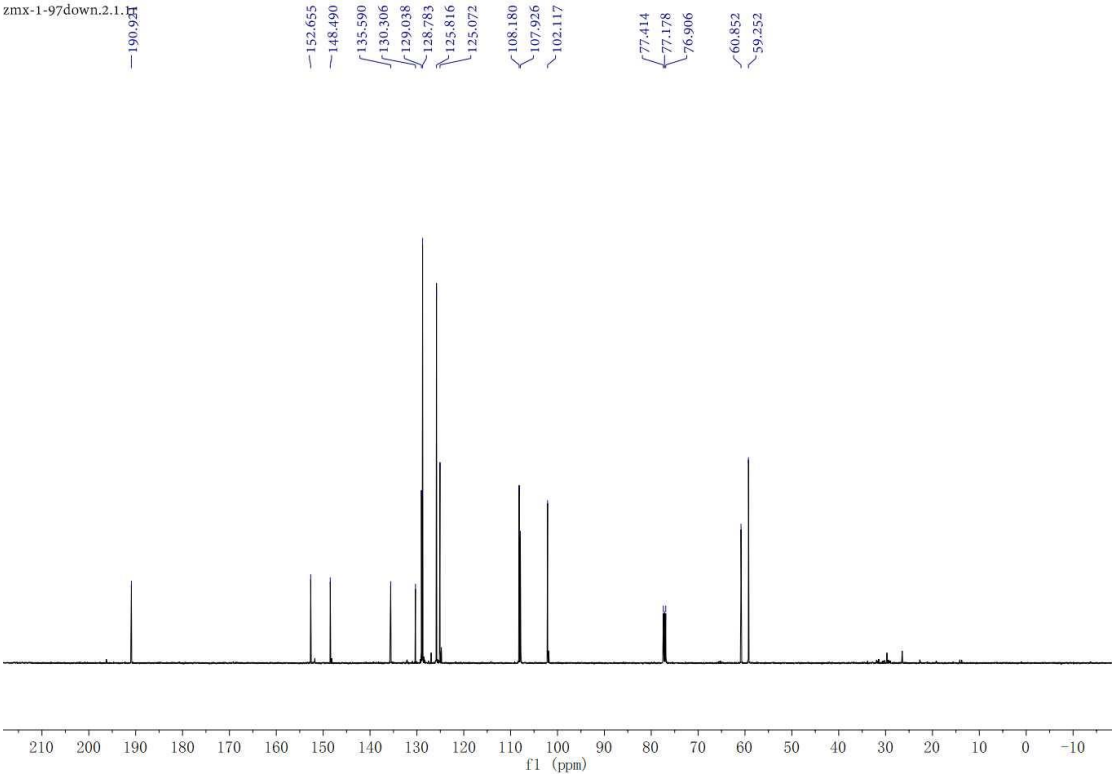
pdata/1

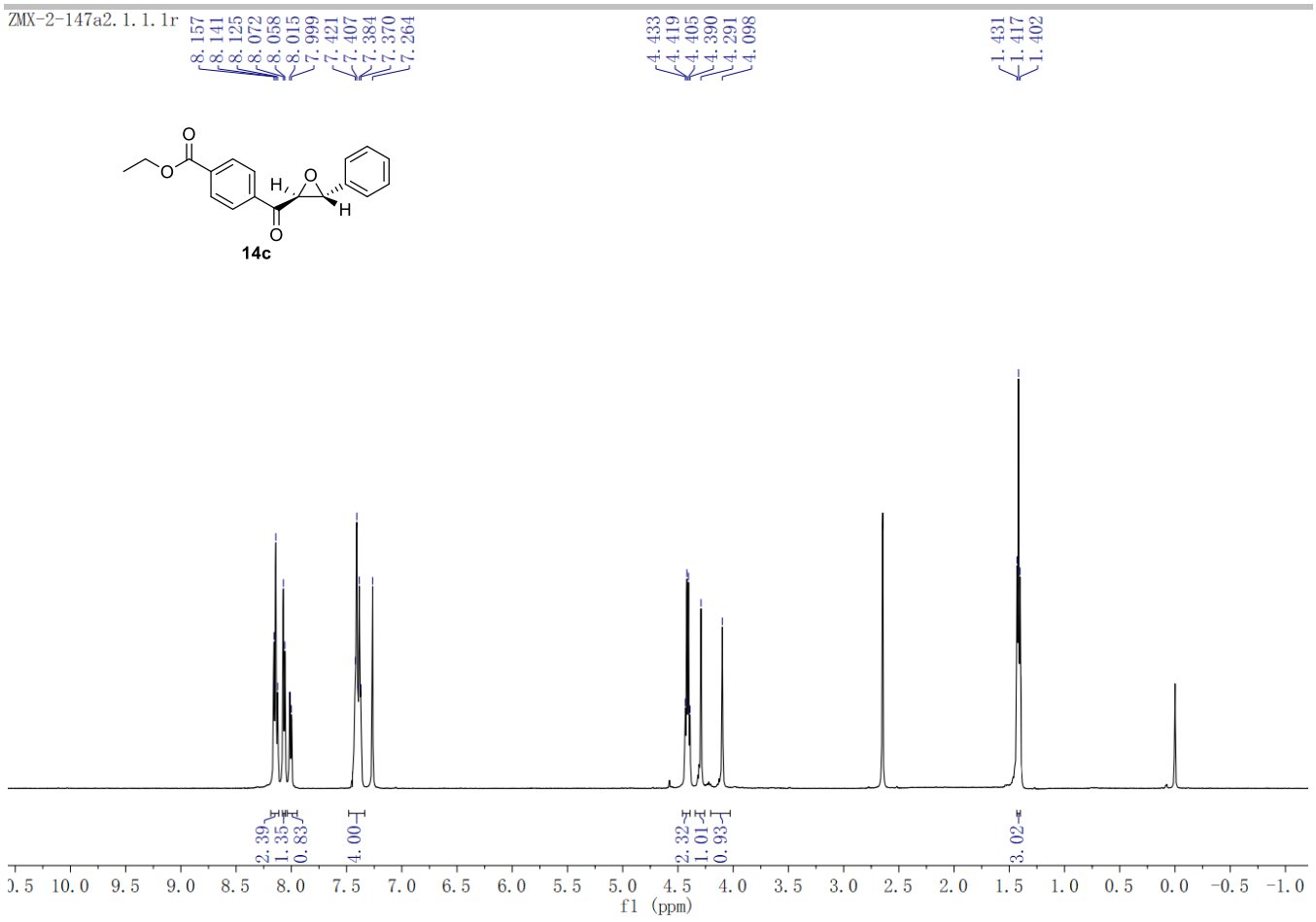


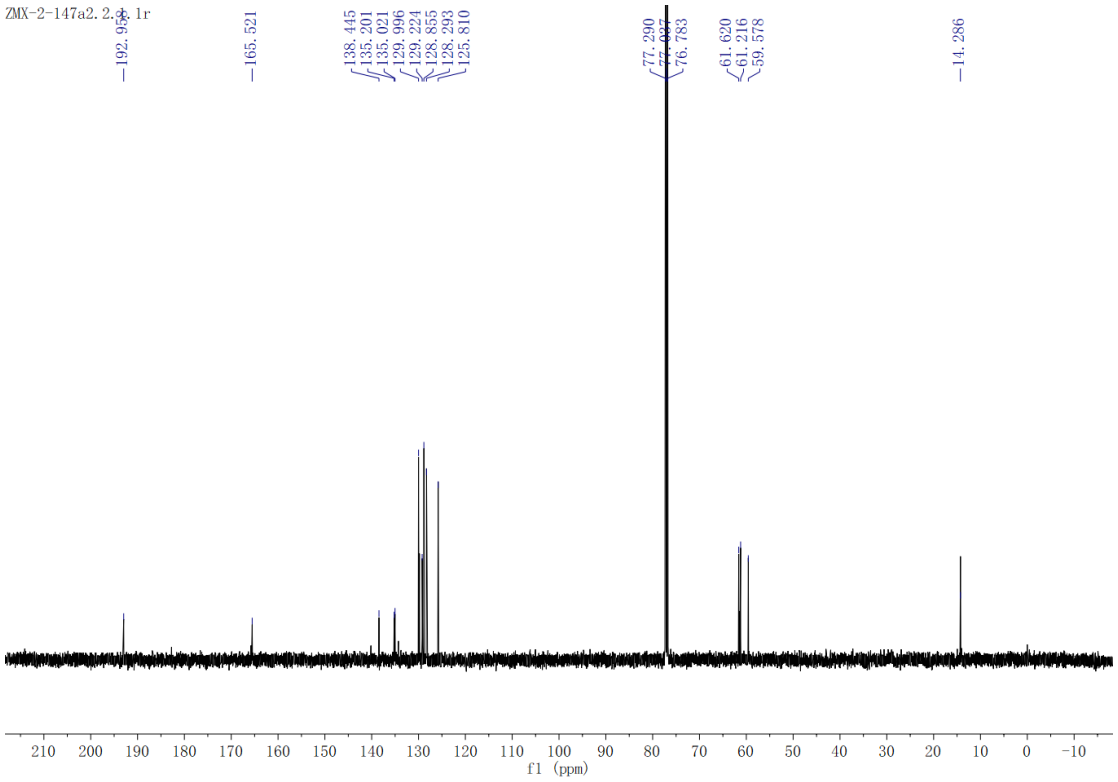
zmx-2-88bC13.2.4.1r

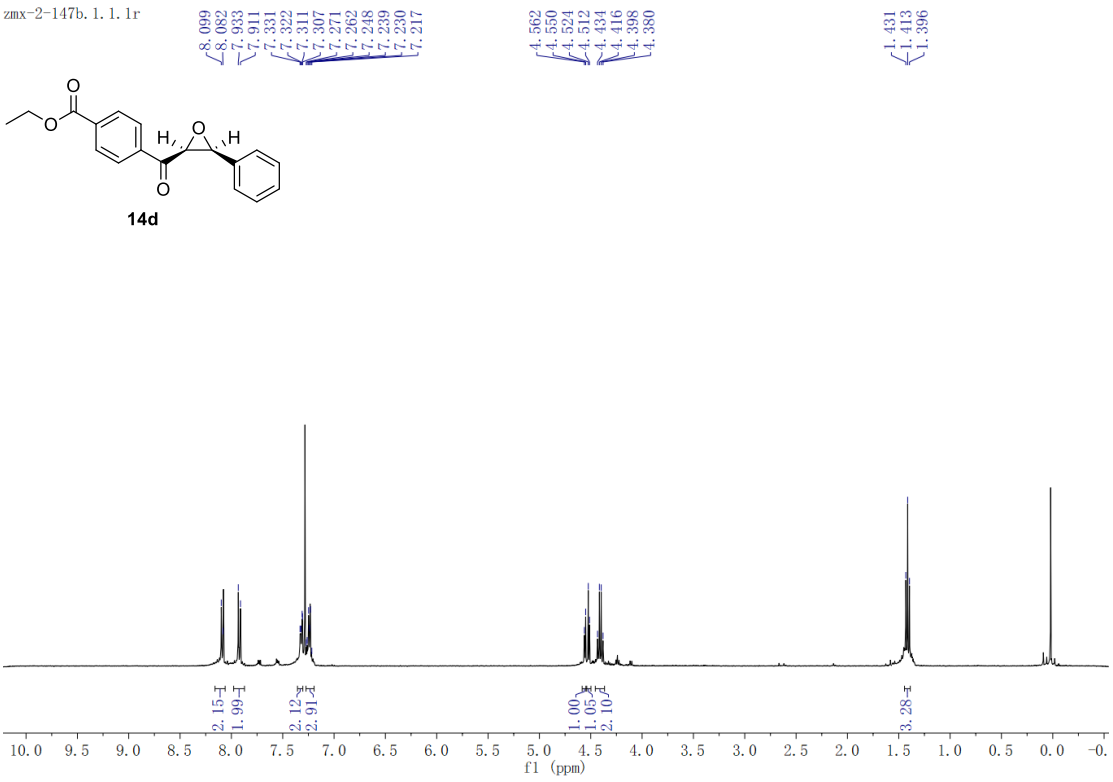


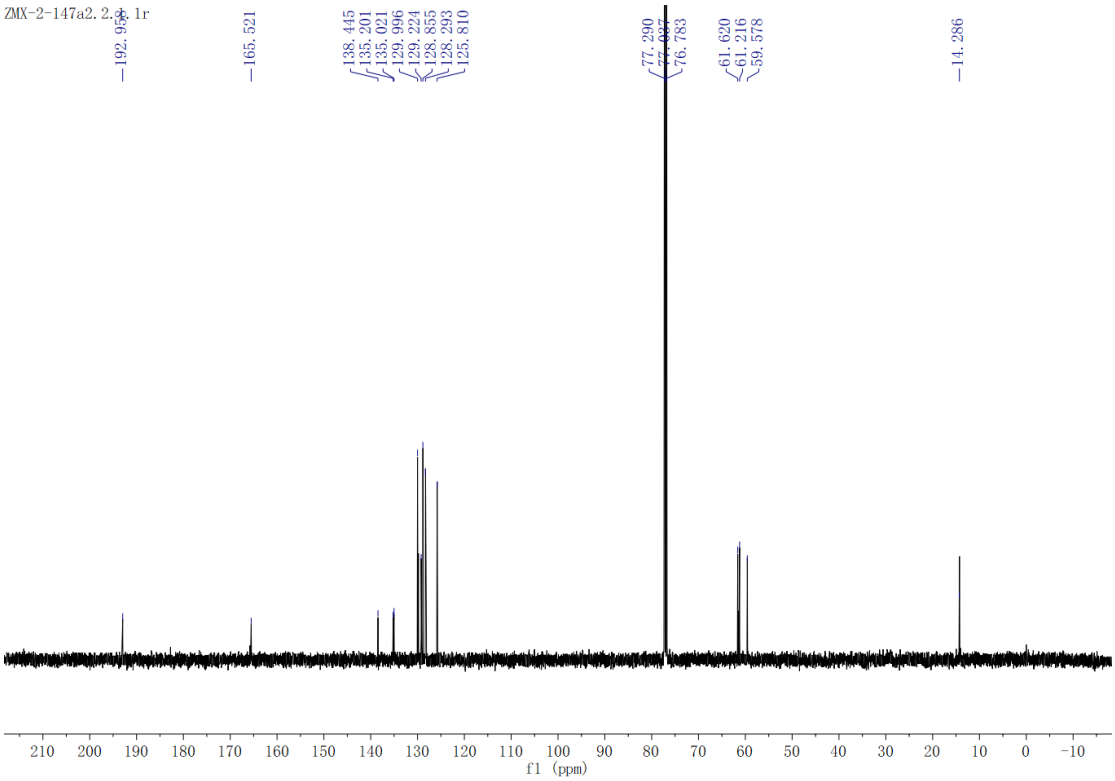

pdata/1
7.62
7.61
7.60
7.59
7.45
7.44
7.38
7.36
7.35
6.84
6.83
6.82
6.81
6.03
6.02
4.22
4.22
4.21
4.16
4.05
4.04
4.04
13c
1.09
1.06
5.26
1.09
2.19
1.00
1.00
f1 (ppm)

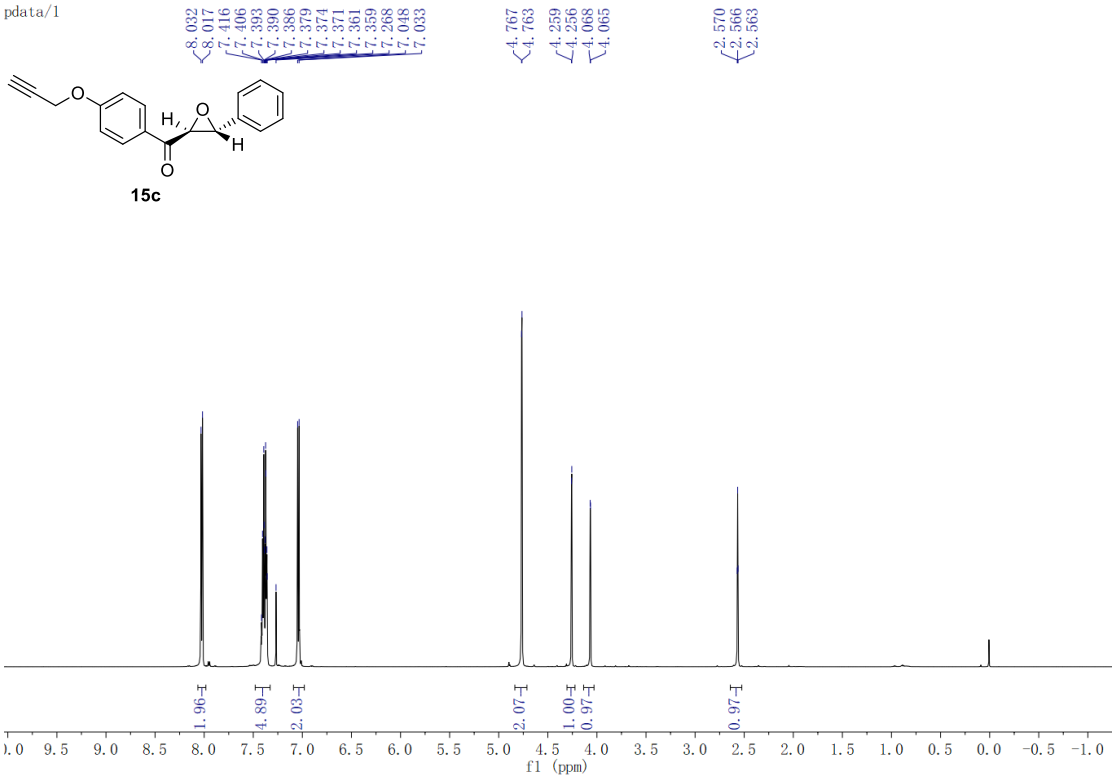

zmx-1-97down.2.1.1
190.93
152.655
148.490
135.590
130.306
129.038
128.783
125.816
125.072
108.180
107.926
102.117
77.414
77.178
76.906
60.852
59.252
f1 (ppm)

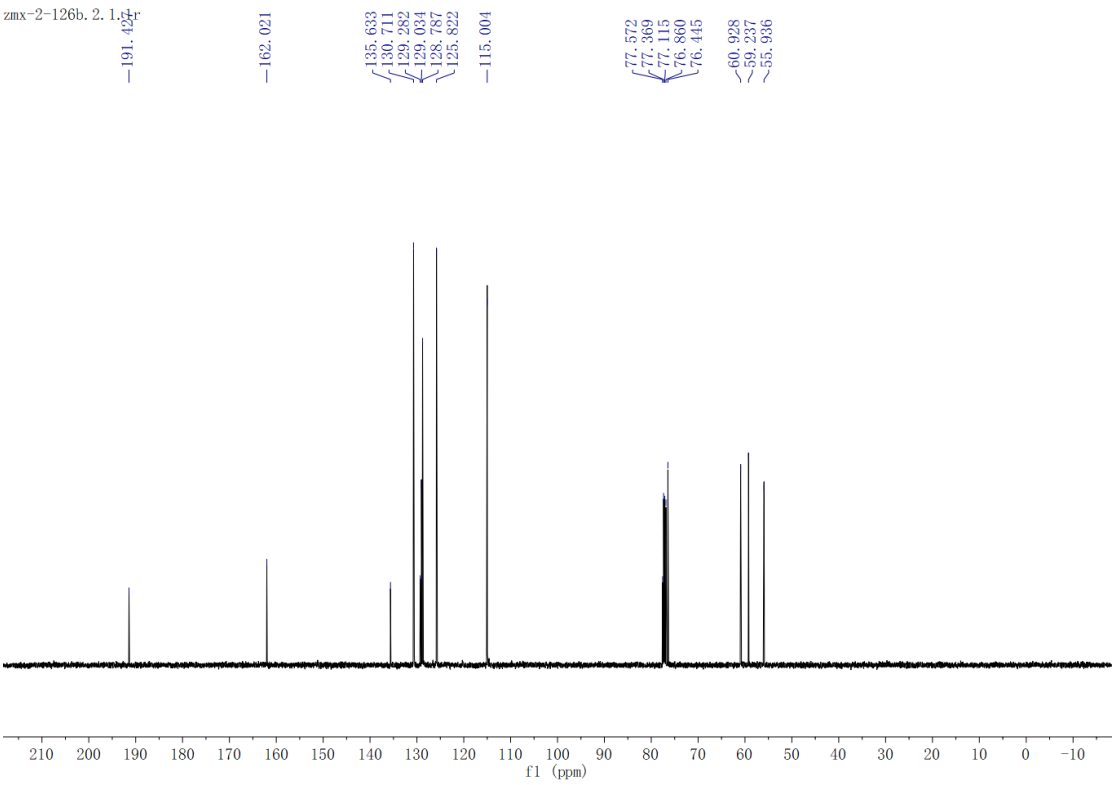

ZMX-2-147a2.1.1.1r
8.157
8.141
8.125
8.072
8.058
8.015
7.999
7.421
7.407
7.384
7.370
7.264
4.433
4.419
4.405
4.390
4.291
4.098
1.431
1.417
1.402
14c
2.39
1.35
0.83
4.00
2.32
1.01
0.93
3.02
f1 (ppm)


ZMX-2-147a2.2.1r
192.958
165.521
138.445
135.201
135.021
129.996
129.224
128.855
128.293
125.810
77.290
77.083
76.783
61.620
61.216
59.578
14.286
f1 (ppm)


zmx-2-147b.1.1.1r
8.099
8.082
7.933
7.911
7.331
7.322
7.311
7.307
7.271
7.262
7.248
7.239
7.230
7.217
4.562
4.550
4.524
4.512
4.434
4.416
4.398
4.380
1.431
1.413
1.396
14d
2.15
1.99
2.12
2.91
1.00
1.05
2.10
3.28
f1 (ppm)

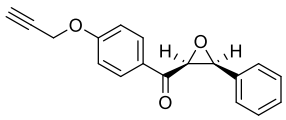

ZMX-2-147a2.2.1.1r
192.958
165.521
138.445
135.201
135.021
129.996
129.224
128.855
128.293
125.810
77.290
77.037
76.783
61.620
61.216
59.578
14.286
f1 (ppm)


pdata/1
8.032
8.017
7.416
7.406
7.393
7.390
7.386
7.379
7.374
7.371
7.361
7.359
7.268
7.048
7.033
4.767
4.763
4.259
4.256
4.068
4.065
2.570
2.566
2.563
15c
1.96
4.89
2.03
2.07
1.00
0.97
0.97
f1 (ppm)

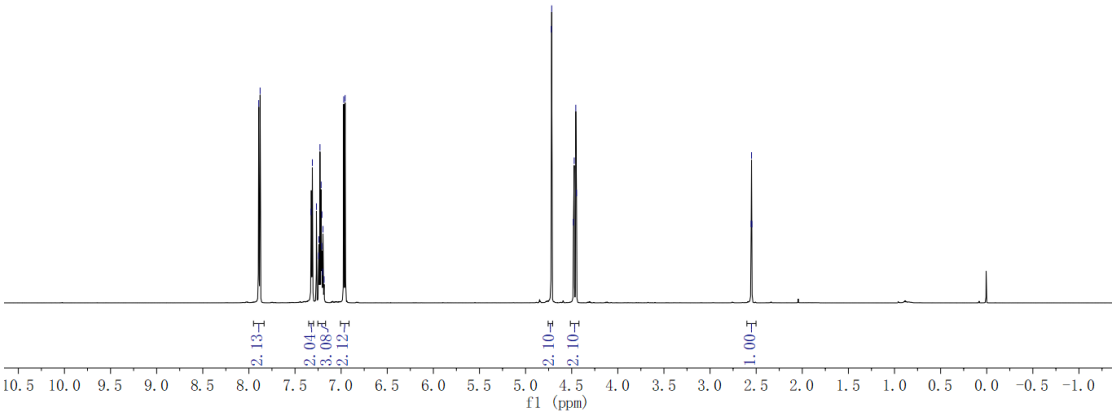

zmx-2-126b.2.1.fr
191.424
162.021
135.633
130.711
129.282
129.034
128.787
125.822
115.004
77.572
77.369
77.115
76.860
76.445
60.928
59.237
55.936
f1 (ppm)

pdata/1

7.893
7.878
7.326
7.312
7.268
7.244
7.241
7.229
7.217
7.211
7.208
7.201
7.197
7.185
6.971
6.957
4.721
4.717
4.481
4.473
4.456
4.448
2.554
2.550
2.546

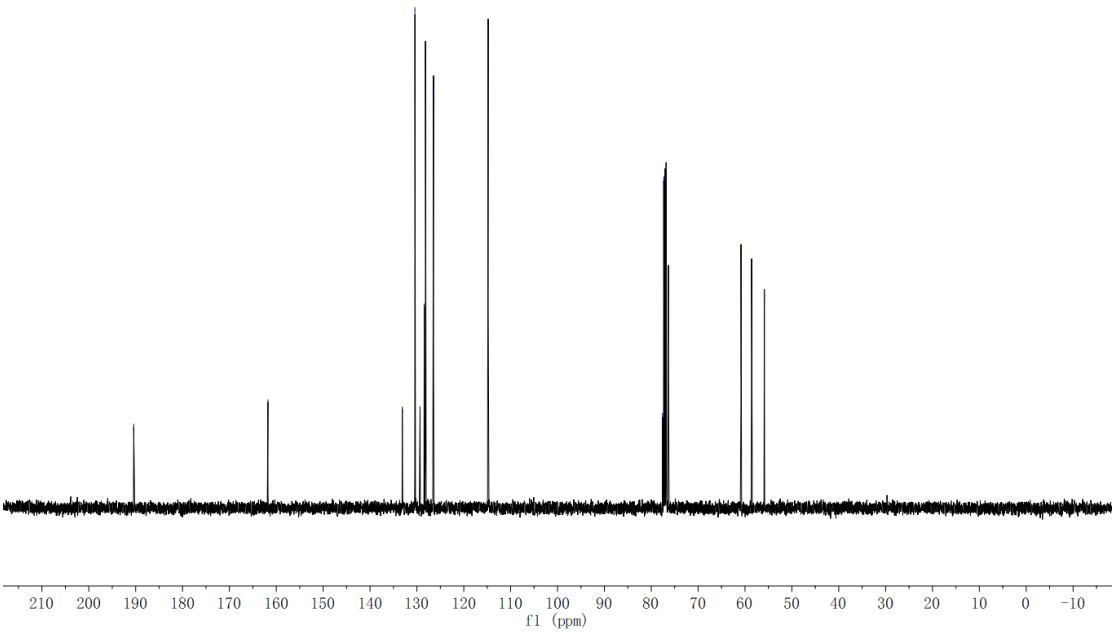


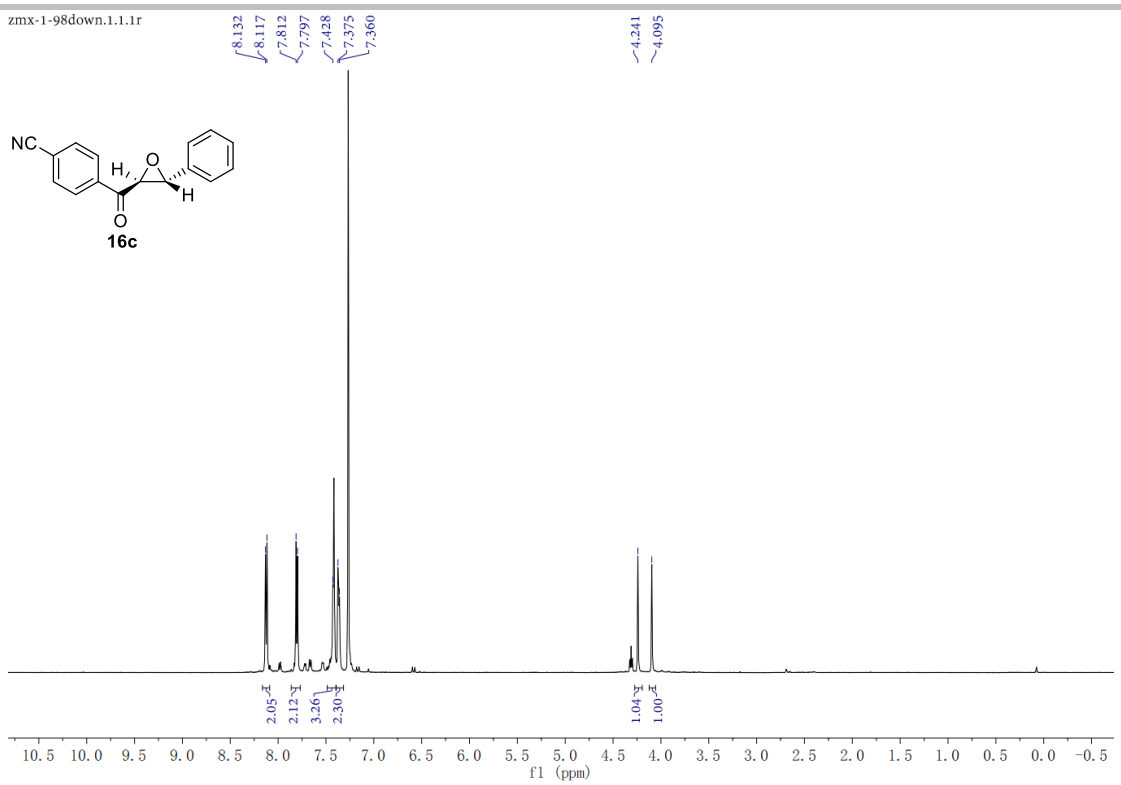
15d

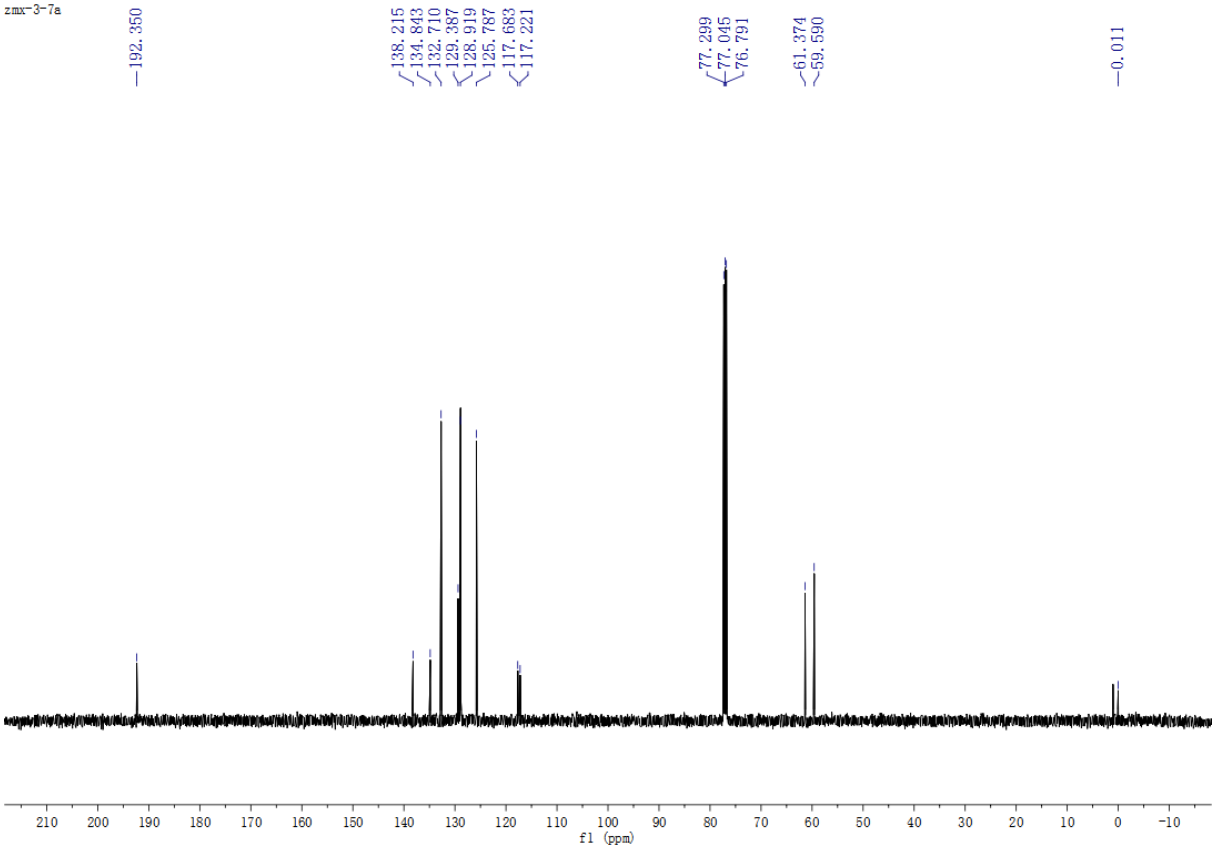


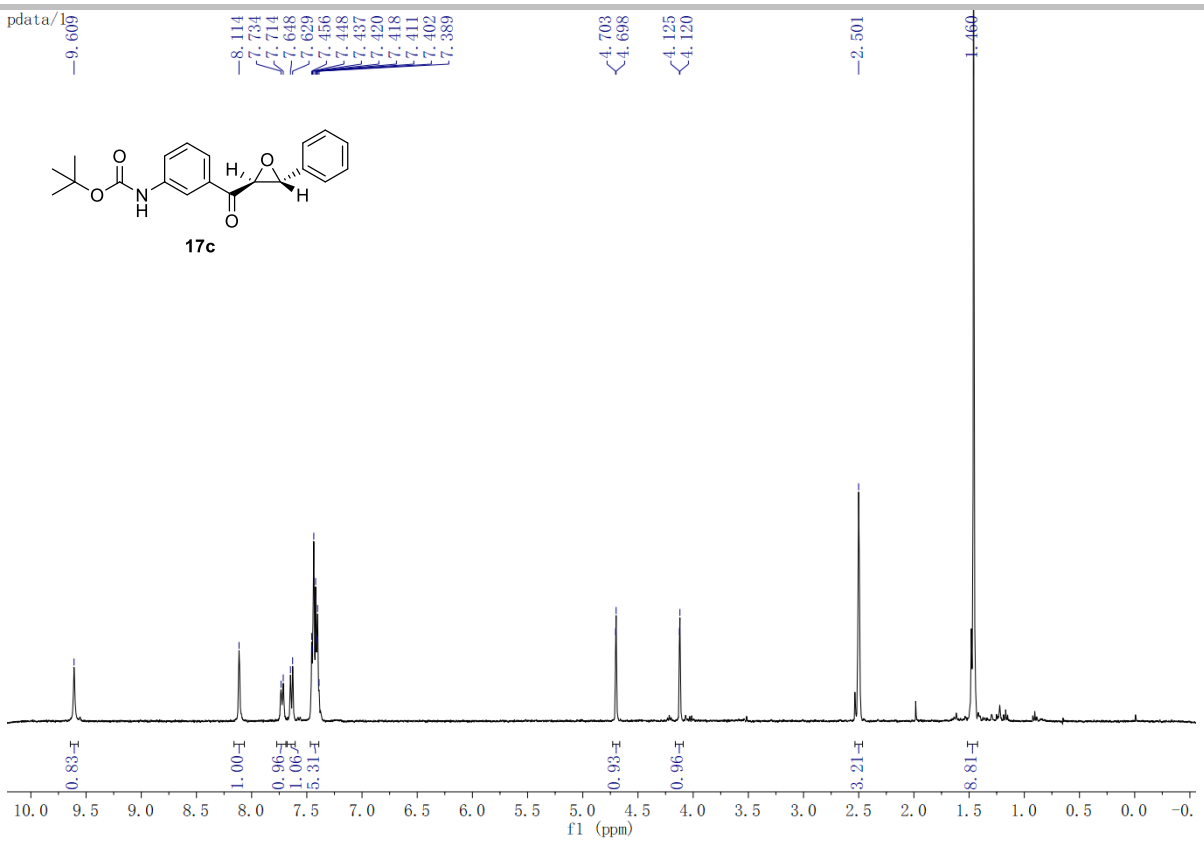
zmx-2-126c.2.1.1zr

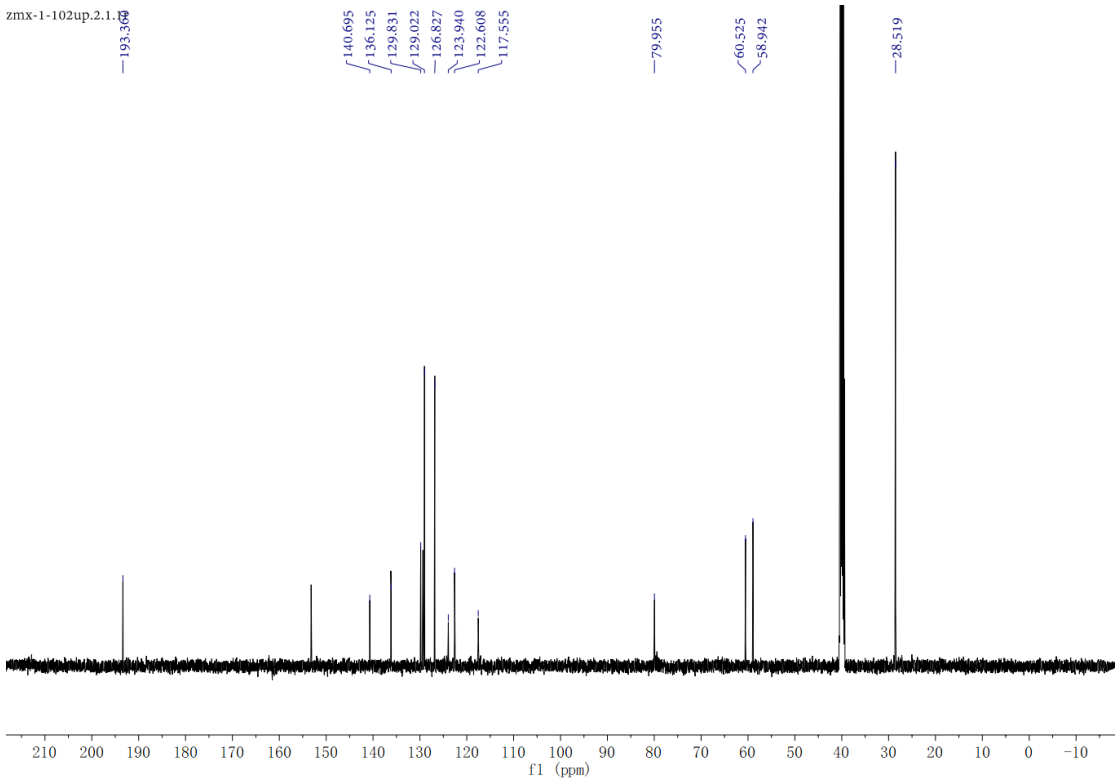
190.412
161.777
133.114
130.422
129.323
128.426
128.175
126.452
114.796
77.588
77.337
77.083
76.829
76.343
60.854
58.596
55.871




zmx-1-98down.1.1.1r
8.132
8.117
7.812
7.797
7.428
7.375
7.360
4.241
4.095
NC
H
O
H
O
16c
2.05
2.12
3.26
2.30
1.04
1.00
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
f1 (ppm)

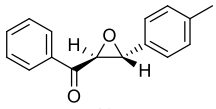

zmx-3-7a
192.350
138.215
134.843
132.710
129.387
128.919
125.787
117.683
117.221
77.299
77.045
76.791
61.374
59.590
0.011
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


pdata/1
9.609
8.114
7.734
7.714
7.648
7.629
7.456
7.448
7.437
7.420
7.418
7.411
7.402
7.389
4.703
4.698
4.125
4.120
2.501
1.460
17c
0.83
1.00
0.96
1.06
5.31
0.93
0.96
3.21
8.81
f1 (ppm)

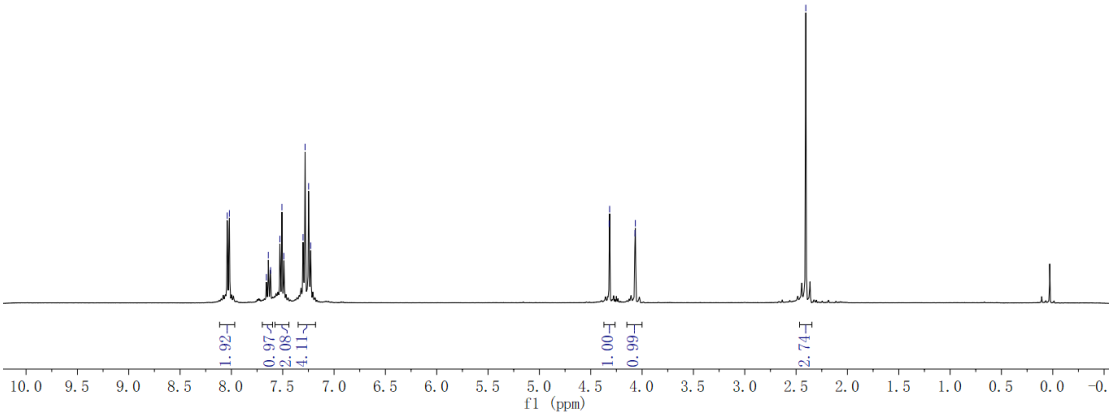

zmx-1-102up.2.1.fid
193.364
140.695
136.125
129.831
129.022
126.827
123.940
122.608
117.555
79.955
60.525
58.942
28.519
f1 (ppm)

zmx-2-151a.1.1.1r

8.040
8.019
7.659
7.640
7.619
7.528
7.508
7.489
7.302
7.282
7.248
7.228
4.320
4.316
4.069
4.065
2.405

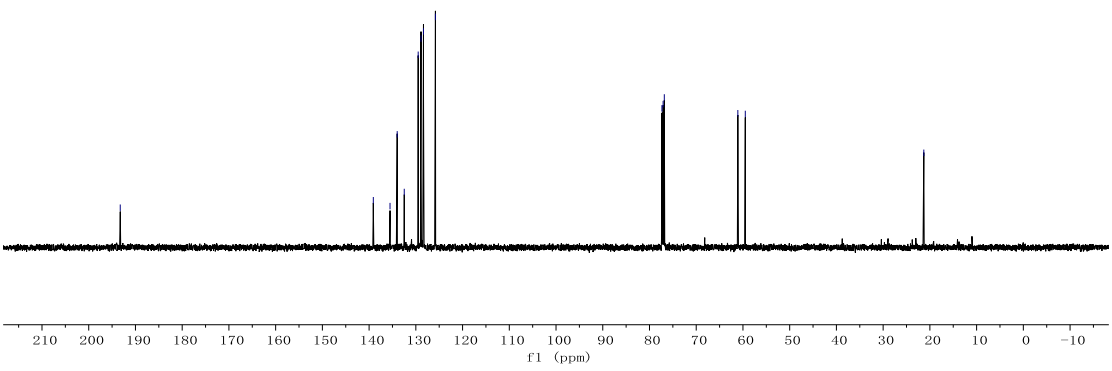


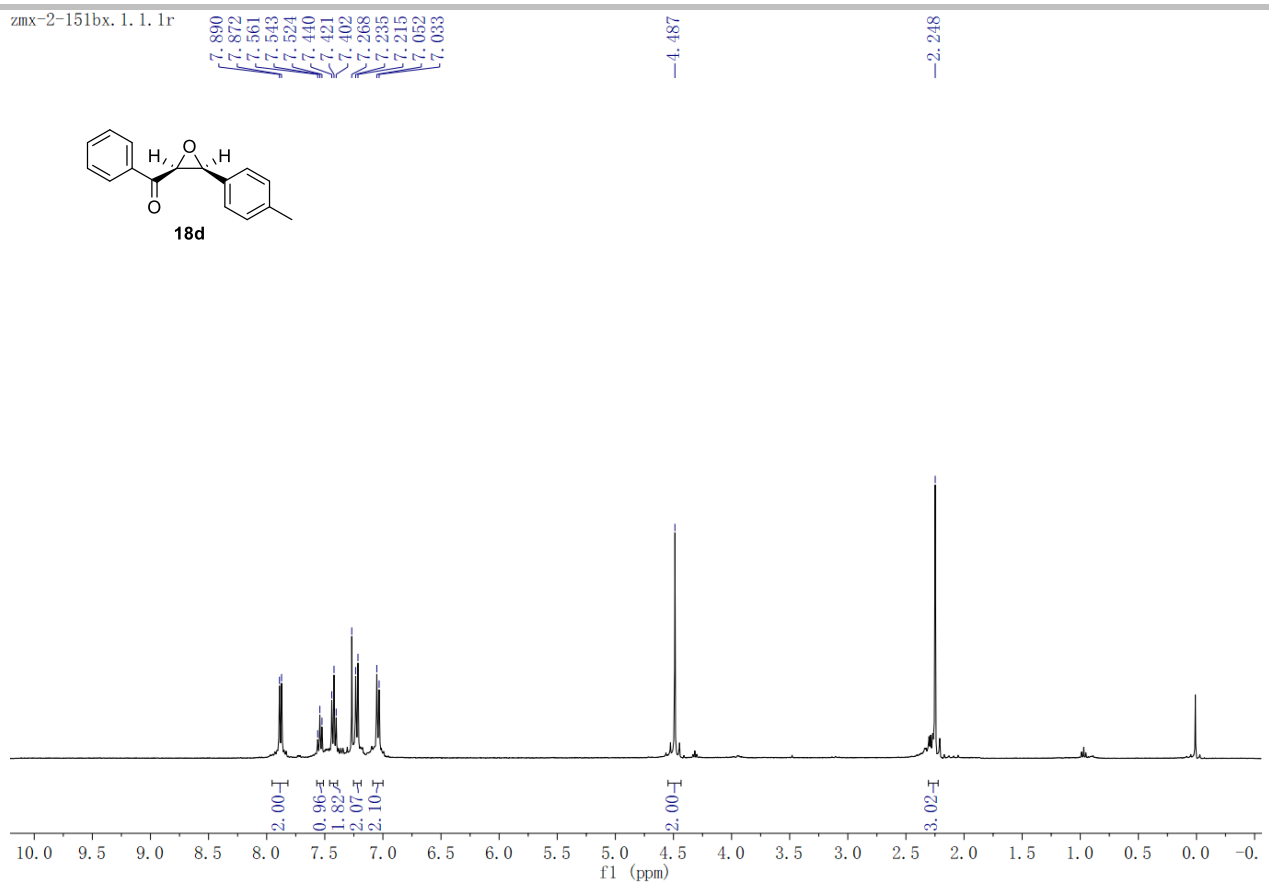
18c

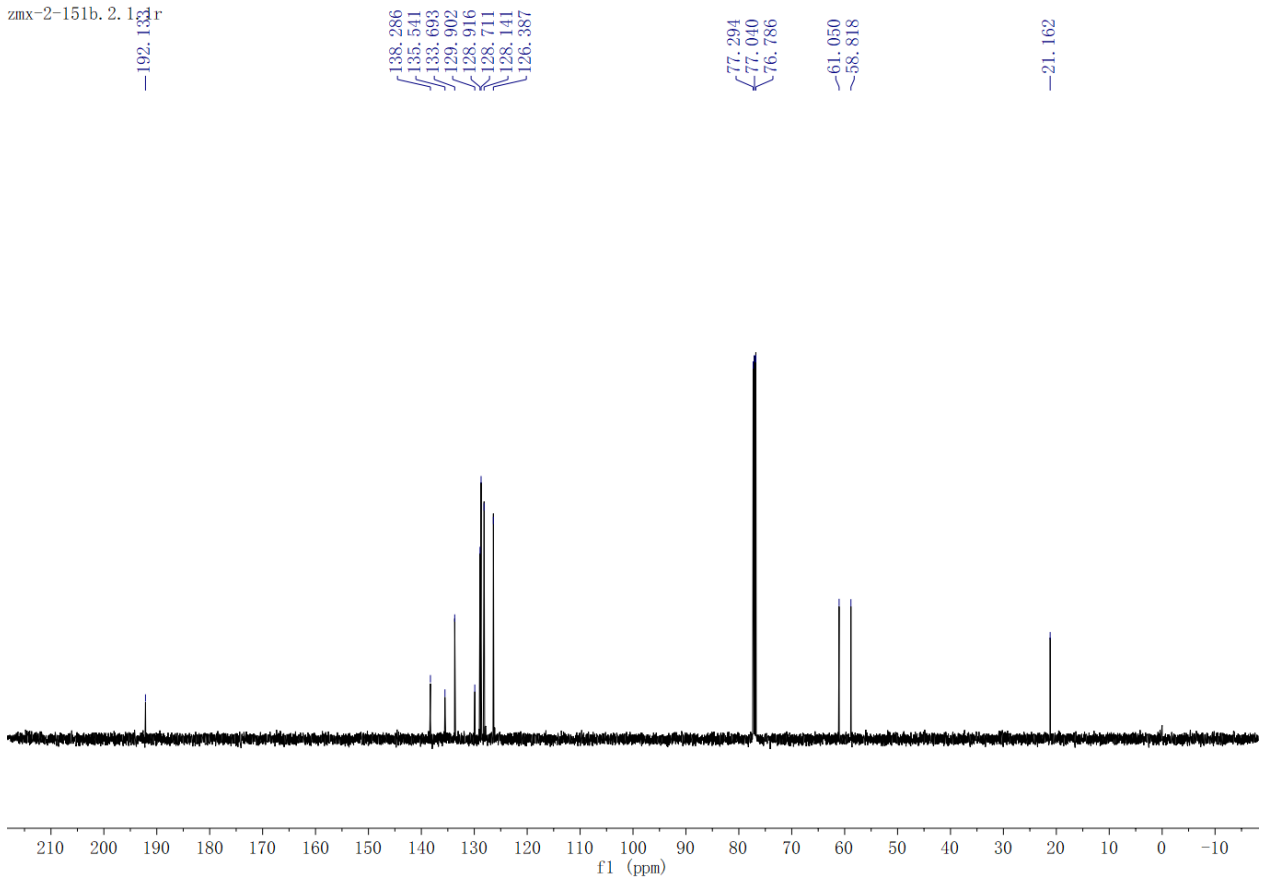


zmx-2-151a.2.1.1r

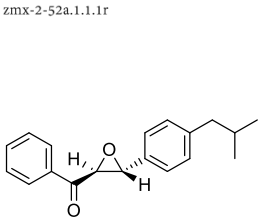
193.255
139.099
135.524
133.988
132.479
129.495
128.893
128.363
125.809
77.337
77.082
76.828
61.094
59.497
21.297




zmx-2-151bx.1.1.1r
7.890
7.872
7.561
7.543
7.524
7.440
7.421
7.402
7.268
7.235
7.215
7.052
7.033
4.487
2.248
18d
2.00
0.96
1.82
2.07
2.10
2.00
3.02
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.
f1 (ppm)

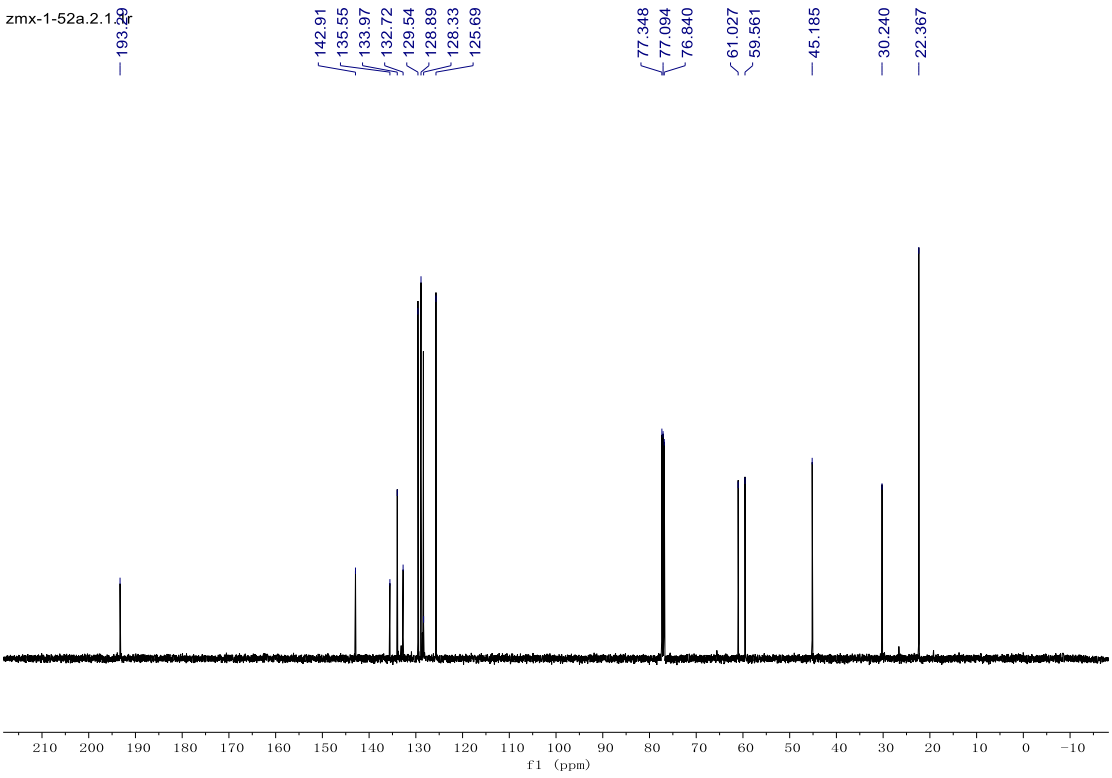

zmx-2-151b.2.1.1r
192.132
138.286
135.541
133.693
129.902
128.916
128.711
128.141
126.387
77.294
77.040
76.786
61.050
58.818
21.162
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

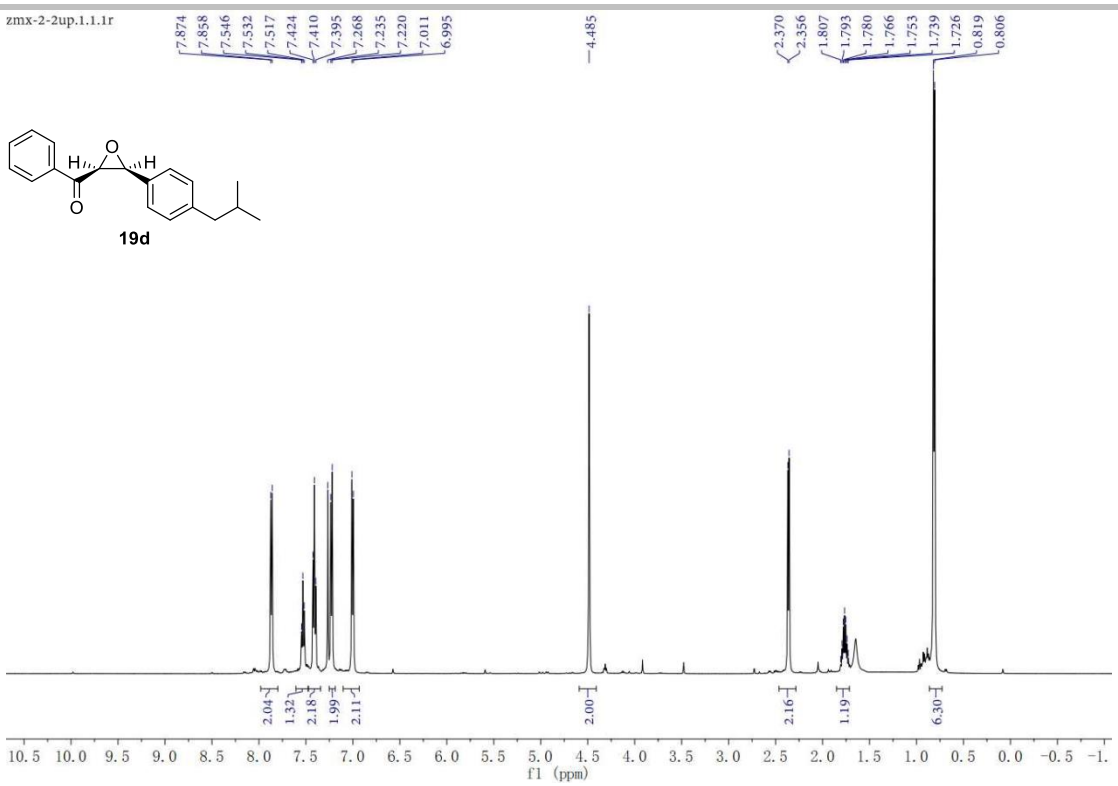
zmx-2-52a.1.1.1r

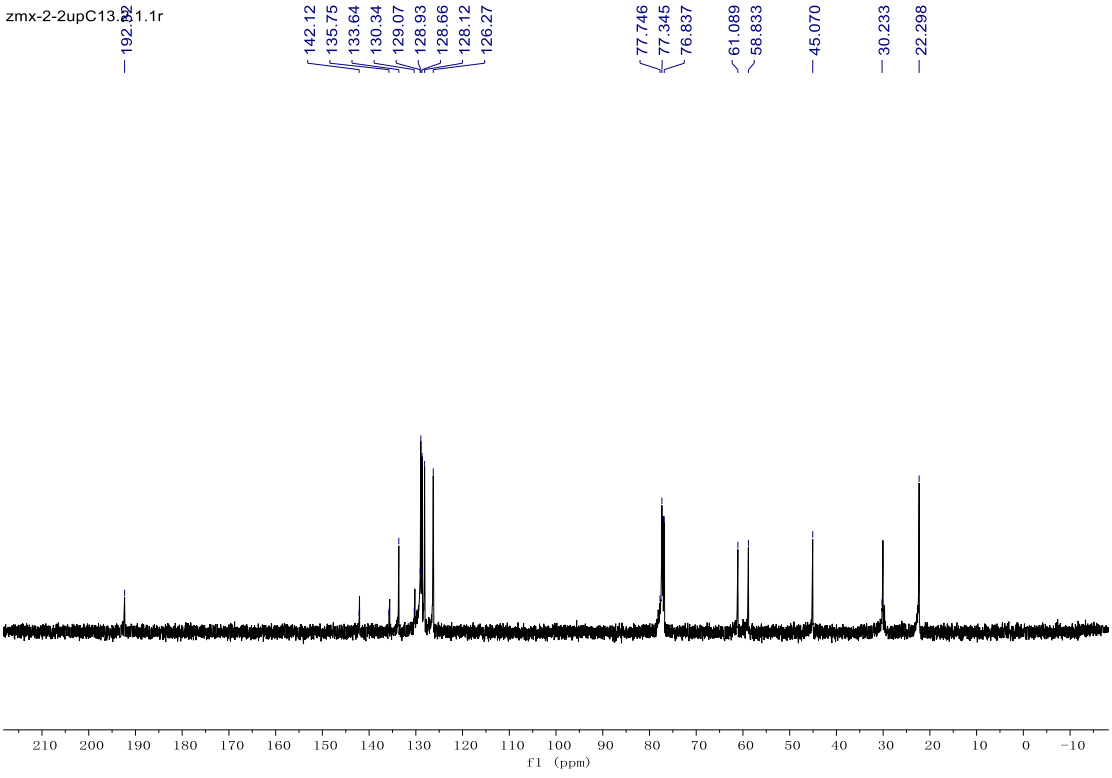


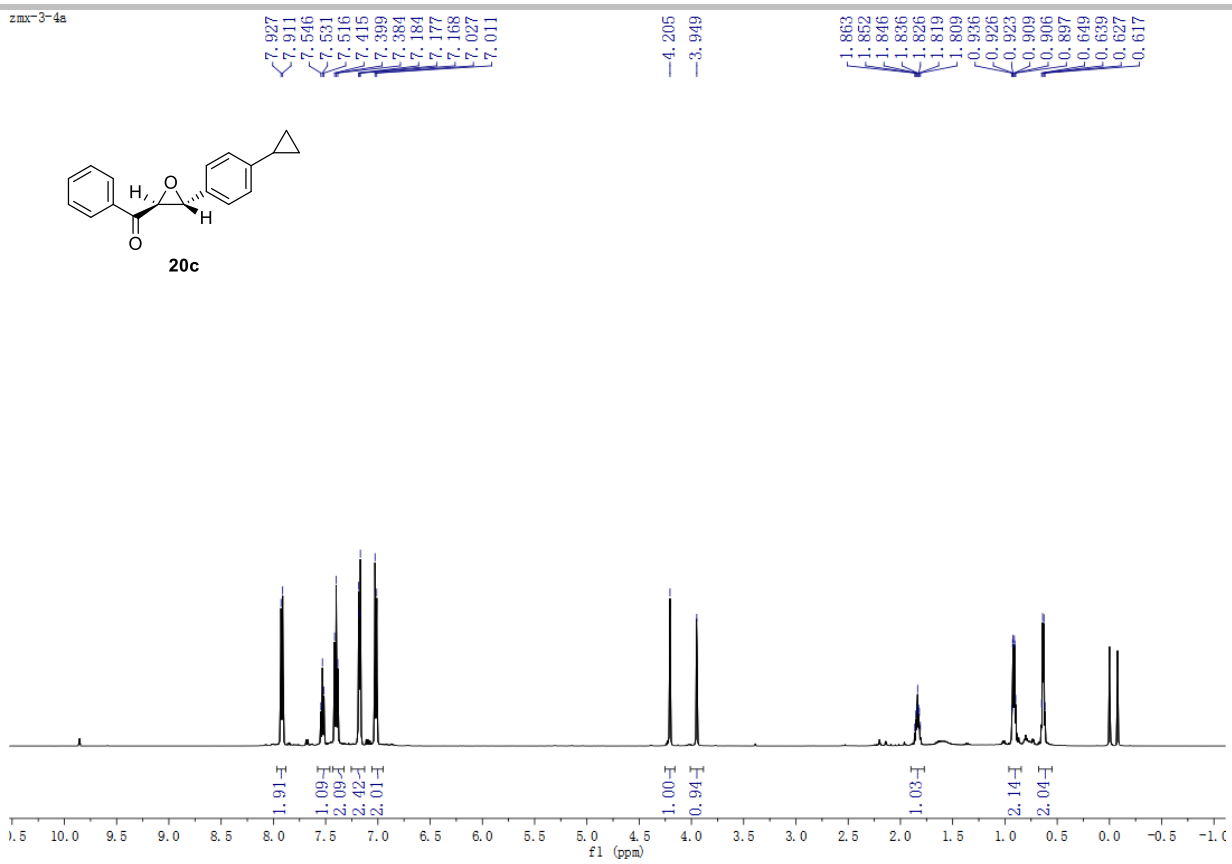
19c

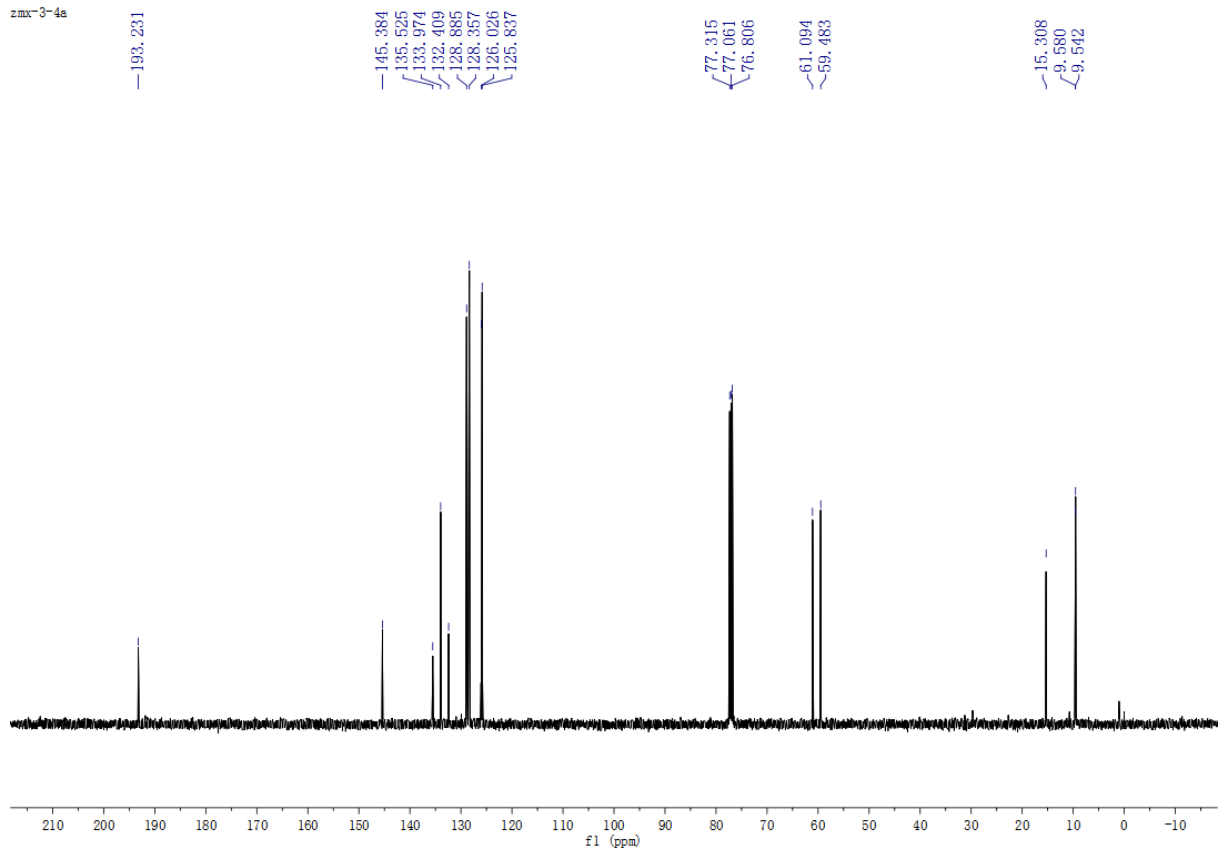
zmx-1-52a.2.1.1r

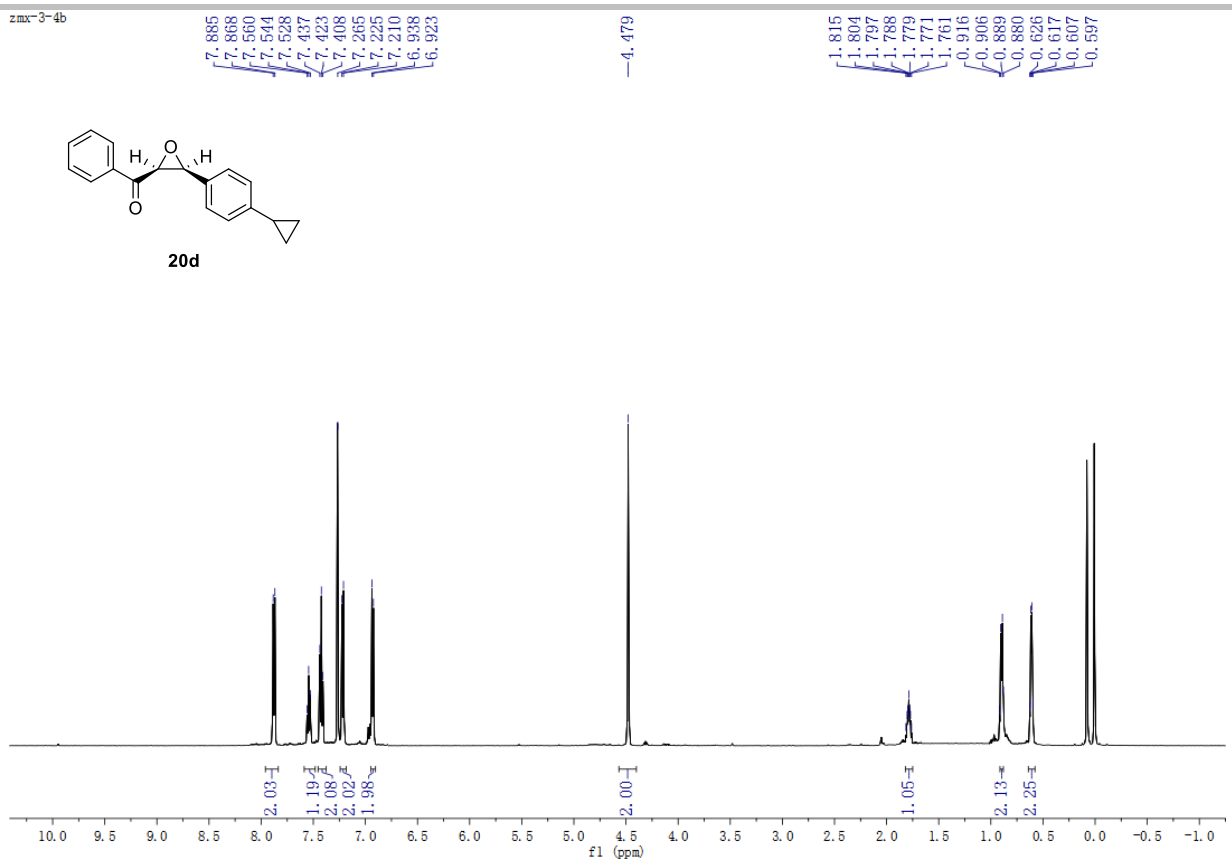


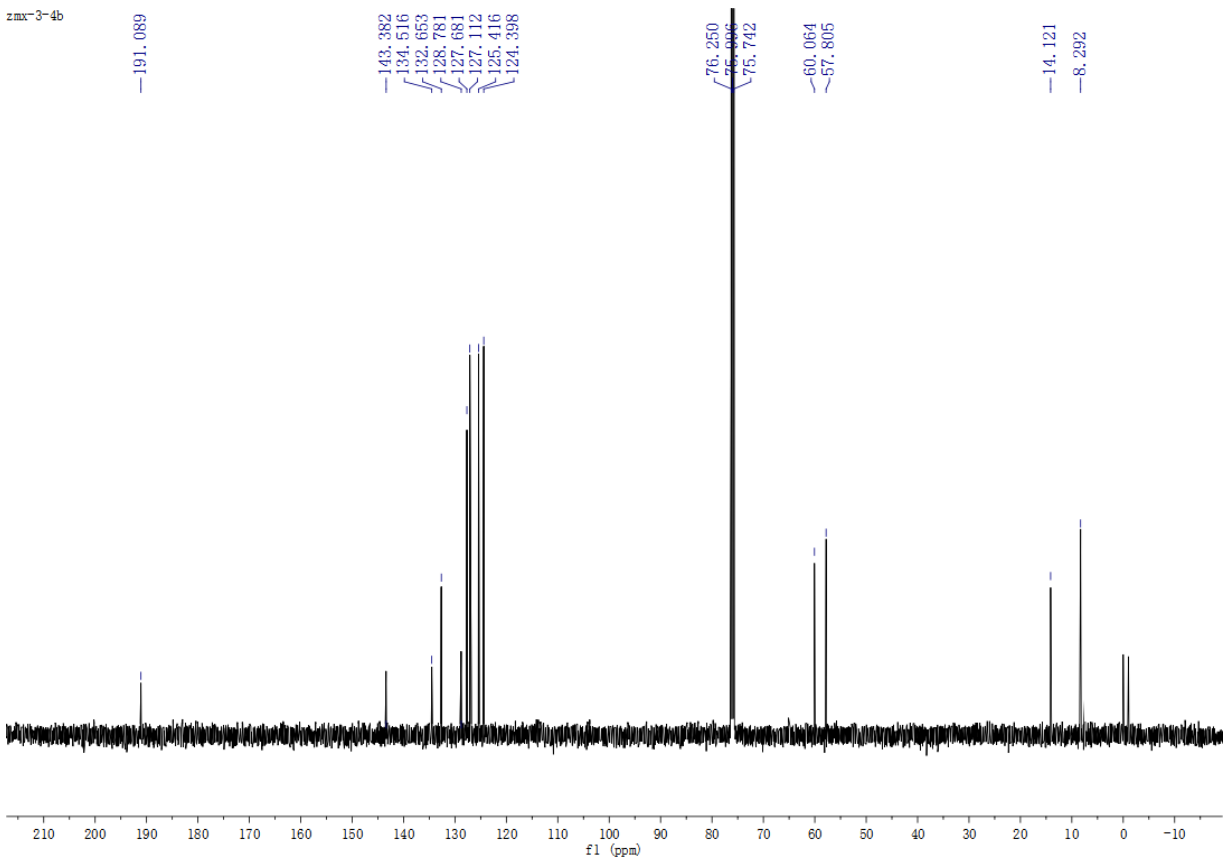

zmx-2-2up.1.1.1r
7.874
7.858
7.546
7.532
7.517
7.424
7.410
7.395
7.268
7.235
7.220
7.011
6.995
4.485
2.370
2.356
1.807
1.793
1.780
1.766
1.753
1.739
1.726
0.819
0.806
19d
2.04
1.32
2.18
1.99
2.11
2.00
2.16
1.19
6.30
f1 (ppm)

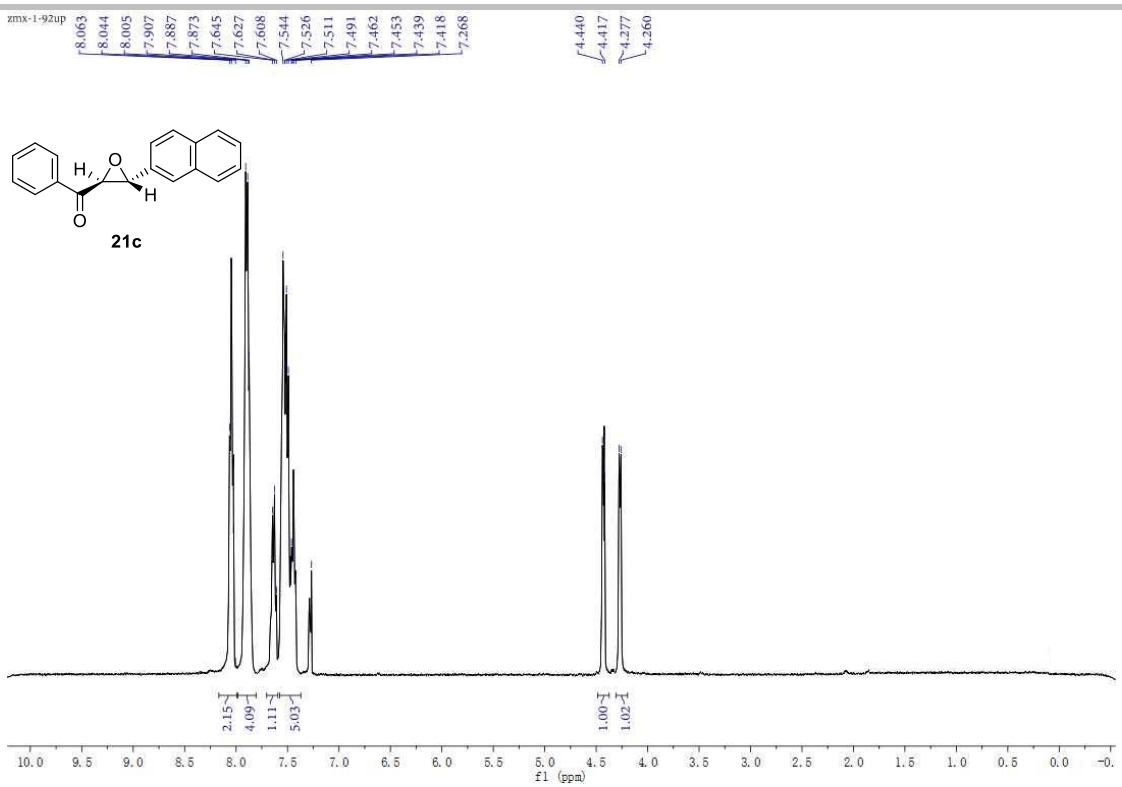

zmx-2-2upC13.1.1r
192.822
142.12
135.75
133.64
130.34
129.07
128.93
128.66
128.12
126.27
77.746
77.345
76.837
61.089
58.833
45.070
30.233
22.298
f1 (ppm)

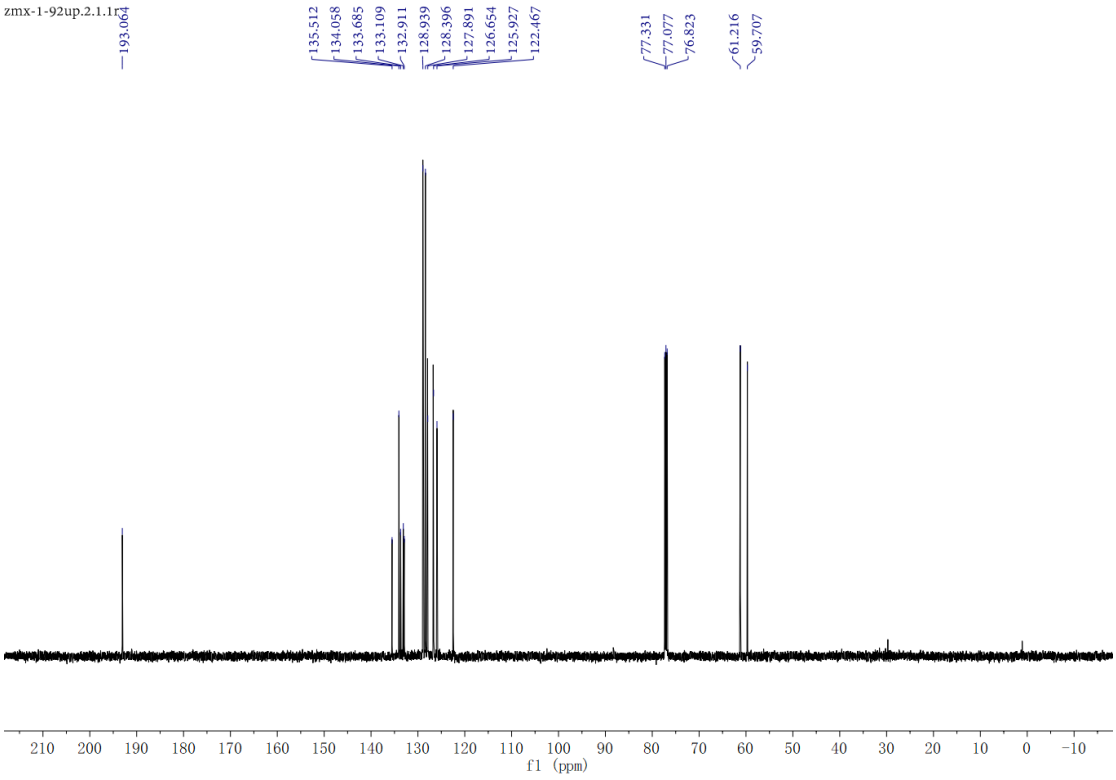

zmx-3-4a
7.927
7.911
7.546
7.531
7.516
7.415
7.399
7.384
7.184
7.177
7.168
7.027
7.011
4.205
3.949
1.863
1.852
1.846
1.836
1.826
1.819
1.809
0.936
0.926
0.923
0.909
0.906
0.897
0.649
0.639
0.627
0.617
H
O
H
O
20c
1.91
1.09
2.09
2.42
2.01
1.00
0.94
1.03
2.14
2.04
f1 (ppm)

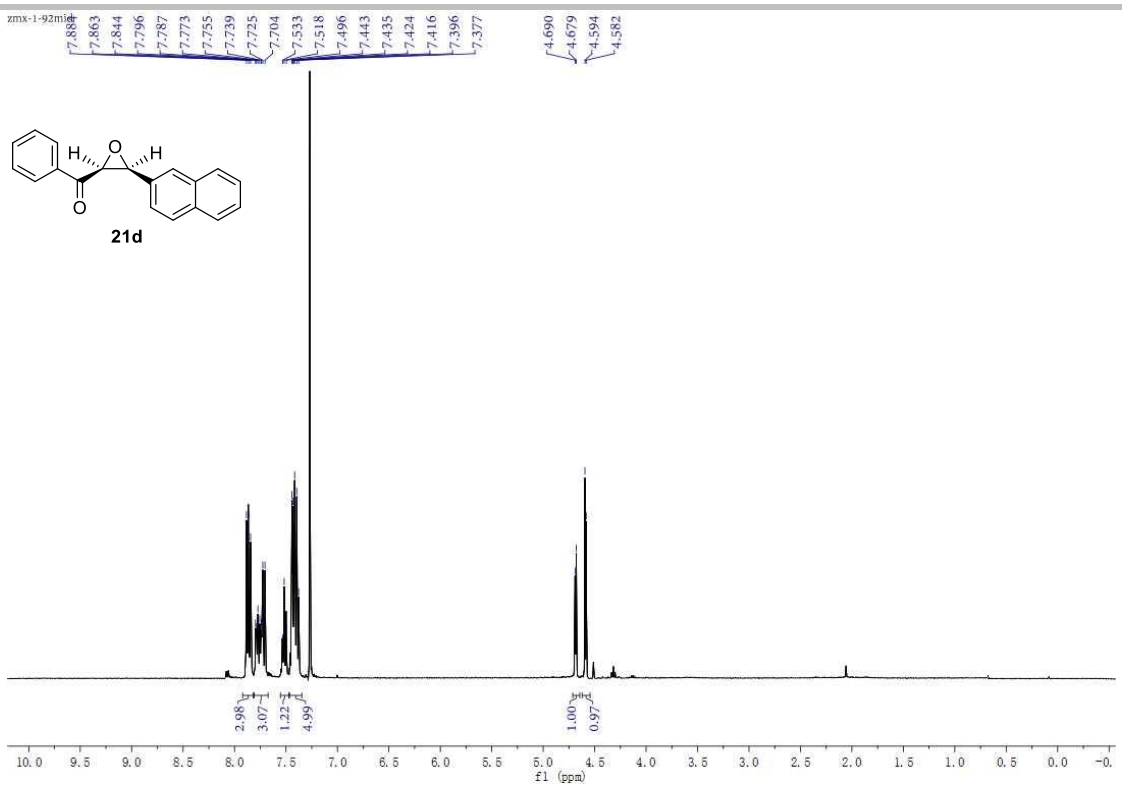

zmx-3-4a
193.231
145.384
135.525
133.974
132.409
128.885
128.357
126.026
125.837
77.315
77.061
76.806
61.094
59.483
15.308
9.580
9.542
f1 (ppm)

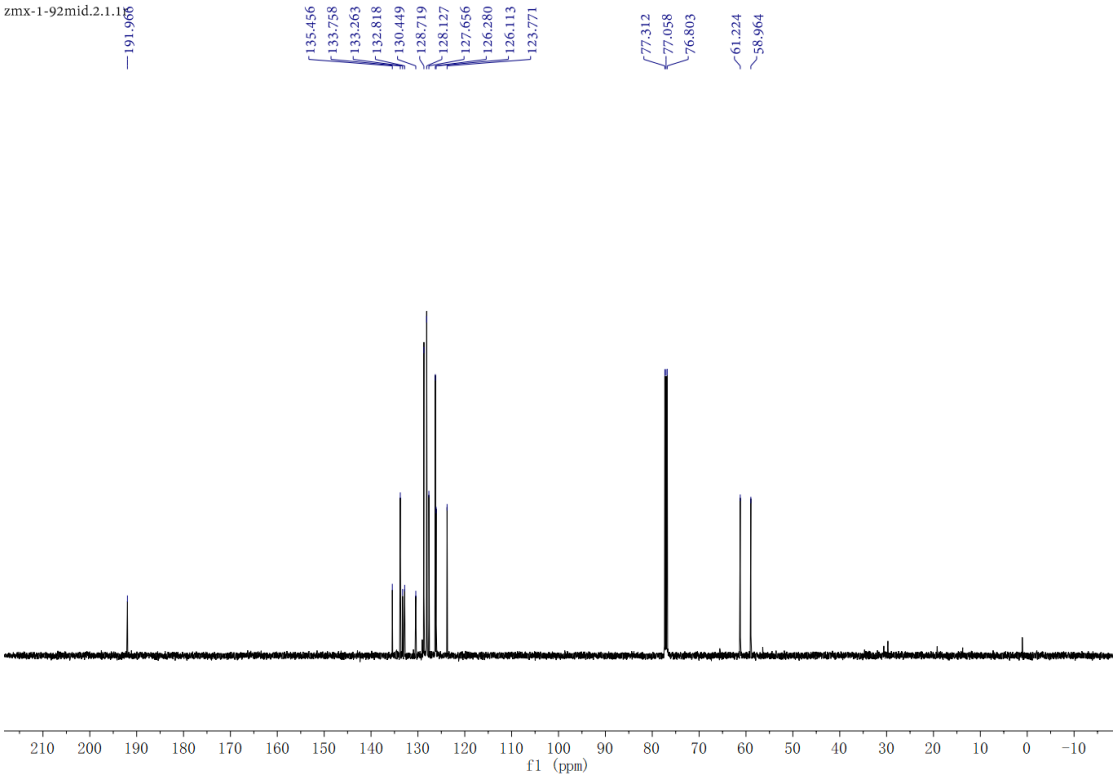

zmx-3-4b
7.885
7.868
7.560
7.544
7.528
7.437
7.423
7.408
7.265
7.225
7.210
6.938
6.923
4.479
1.815
1.804
1.797
1.788
1.779
1.771
1.761
0.916
0.906
0.889
0.880
0.626
0.617
0.607
0.597
H
O
H
O
20d
2.03
1.19
2.08
2.02
1.98
2.00
1.05
2.13
2.25
f1 (ppm)


zmx-3-4b
191.089
143.382
134.516
132.653
128.781
127.681
127.112
125.416
124.398
76.250
75.996
75.742
60.064
57.805
14.121
8.292
f1 (ppm)

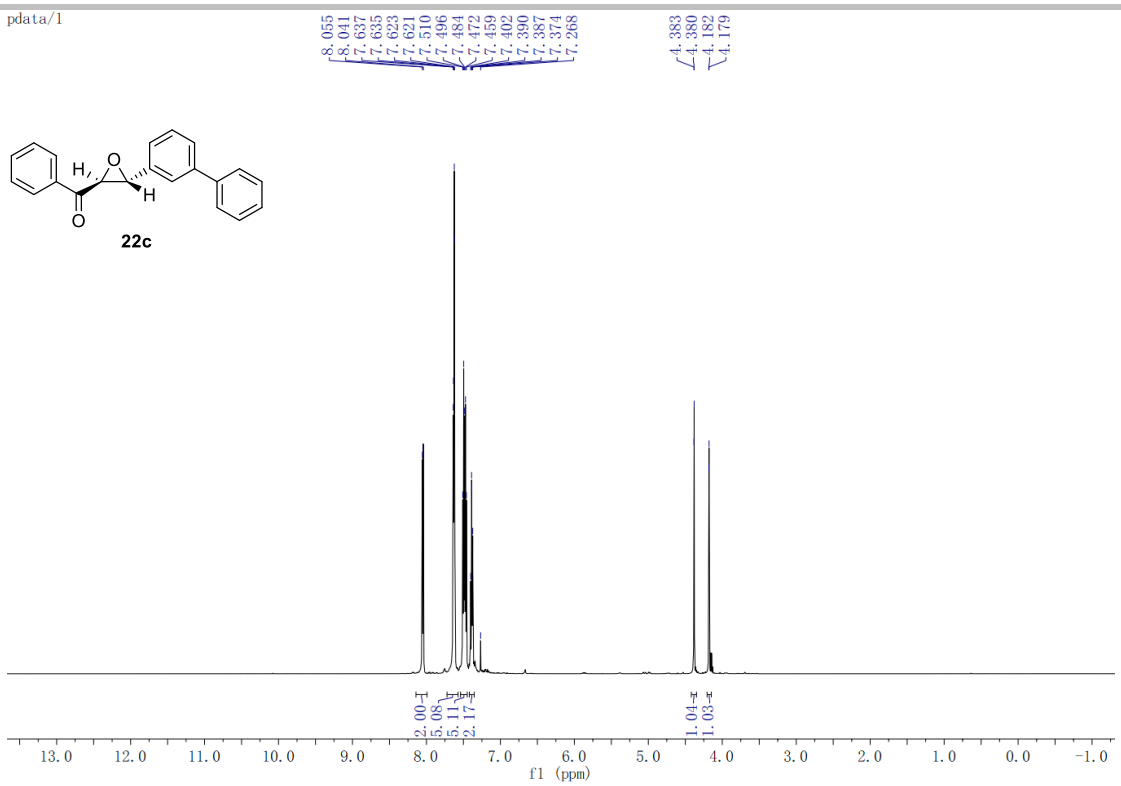

zmx-1-92up
8.063
8.044
8.005
7.907
7.887
7.873
7.645
7.627
7.608
7.544
7.526
7.511
7.491
7.462
7.453
7.439
7.418
7.268
4.440
4.417
4.277
4.260
21c
2.15
4.09
1.11
5.03
1.00
1.02
f1 (ppm)


zmx-1-92up.2.1.1
193.064
135.512
134.058
133.685
133.109
132.911
128.939
128.396
127.891
126.654
125.927
122.467
77.331
77.077
76.823
61.216
59.707
f1 (ppm)

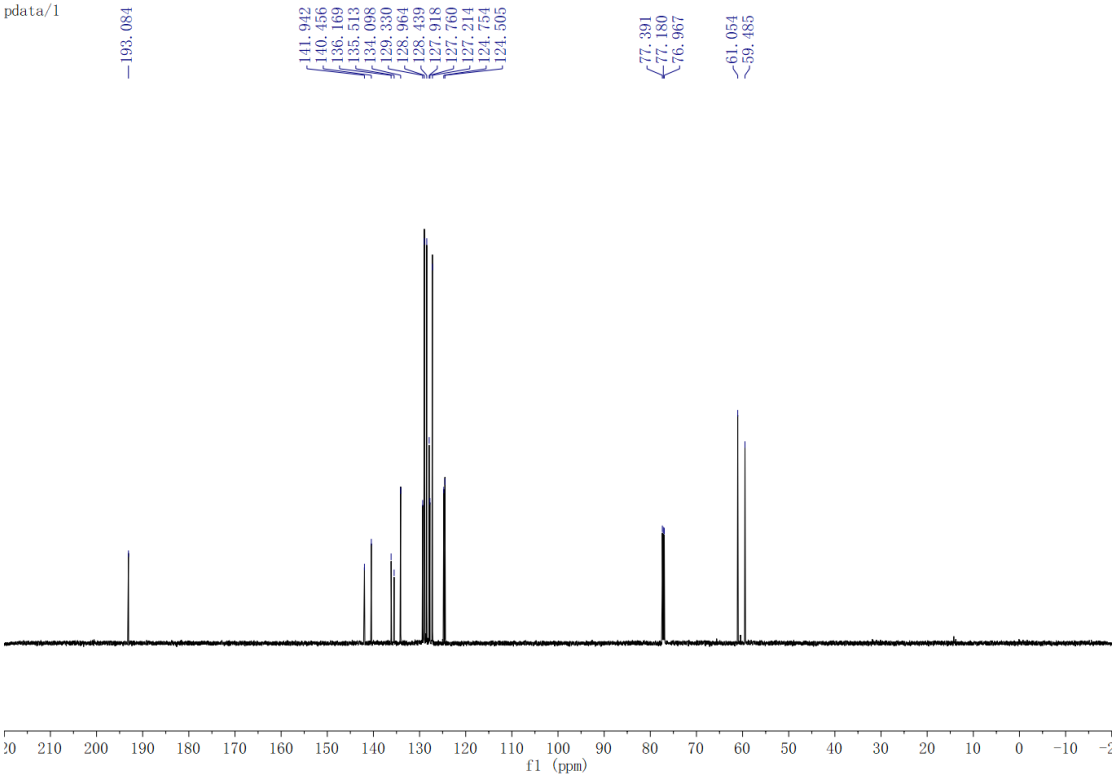

zmx-1-92mid
7.881
7.863
7.844
7.796
7.787
7.773
7.755
7.739
7.725
7.704
7.533
7.518
7.496
7.443
7.435
7.424
7.416
7.396
7.377
4.690
4.679
4.594
4.582
H
O
H
O
21d
2.98
3.07
1.22
4.99
1.00
0.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


zmx-1-92mid.2.1.1
191.966
135.456
133.758
133.263
132.818
130.449
128.719
128.127
127.656
126.280
126.113
123.771
77.312
77.058
76.803
61.224
58.964
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

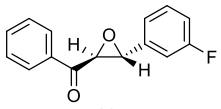
pdata/1



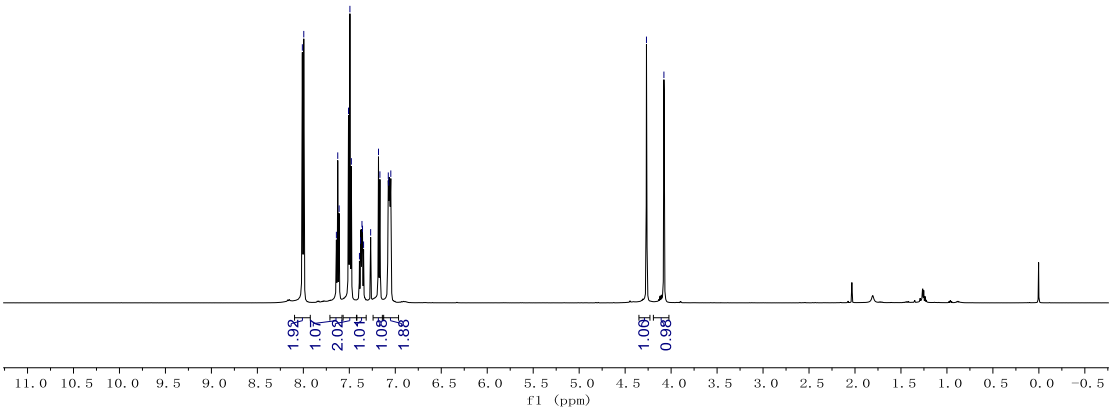
pdata/1



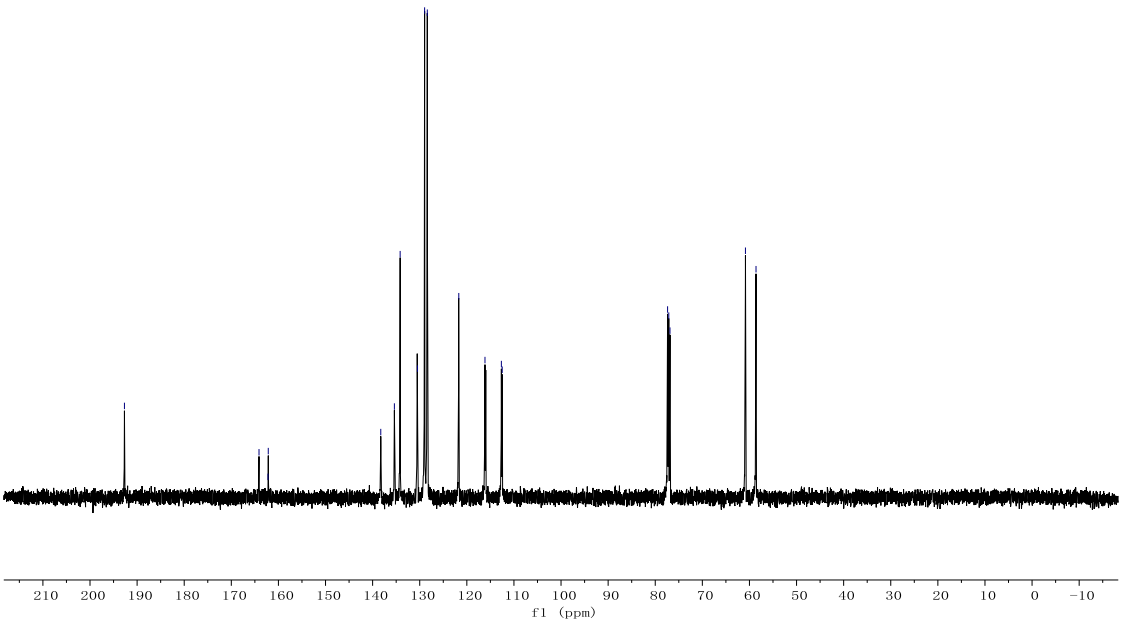
zmx-2-42a.1.1.1r

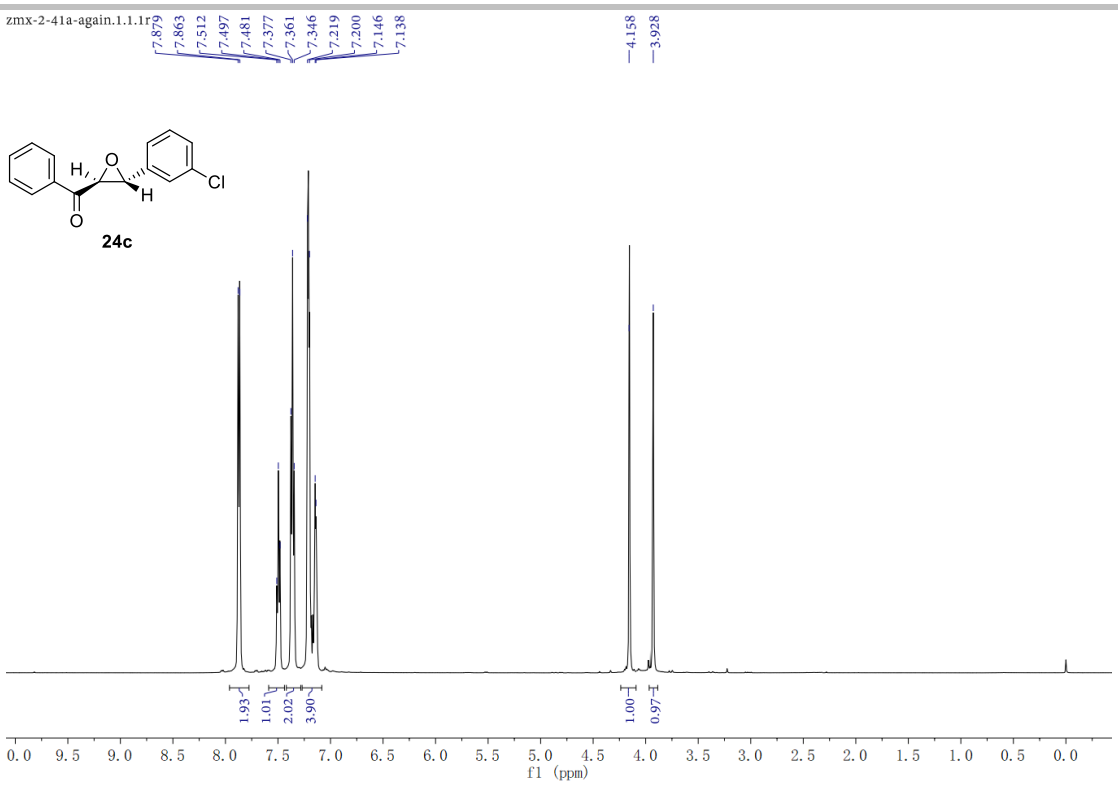


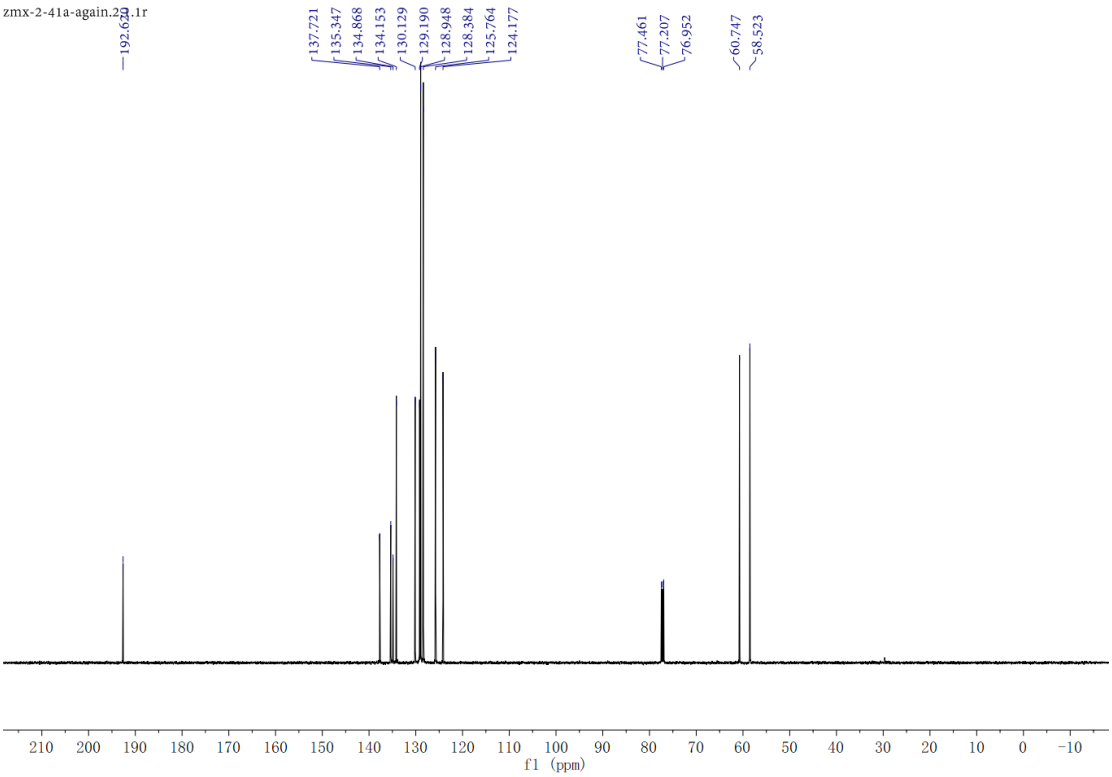
23c

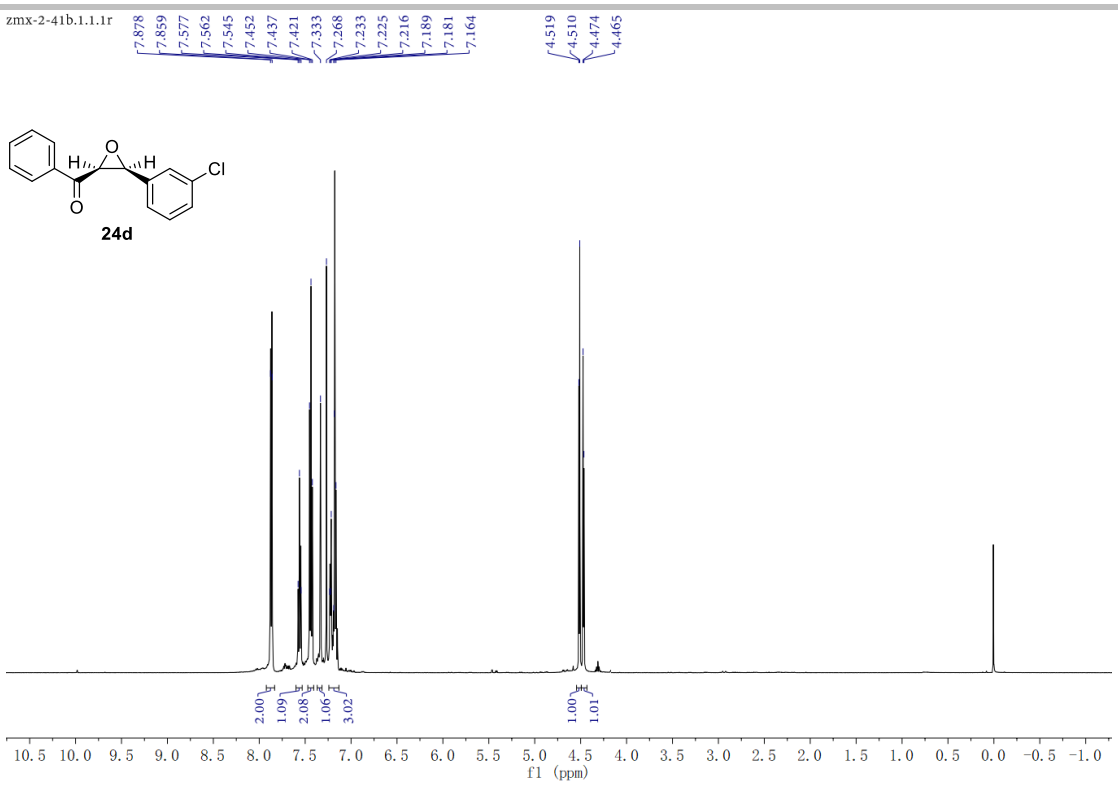


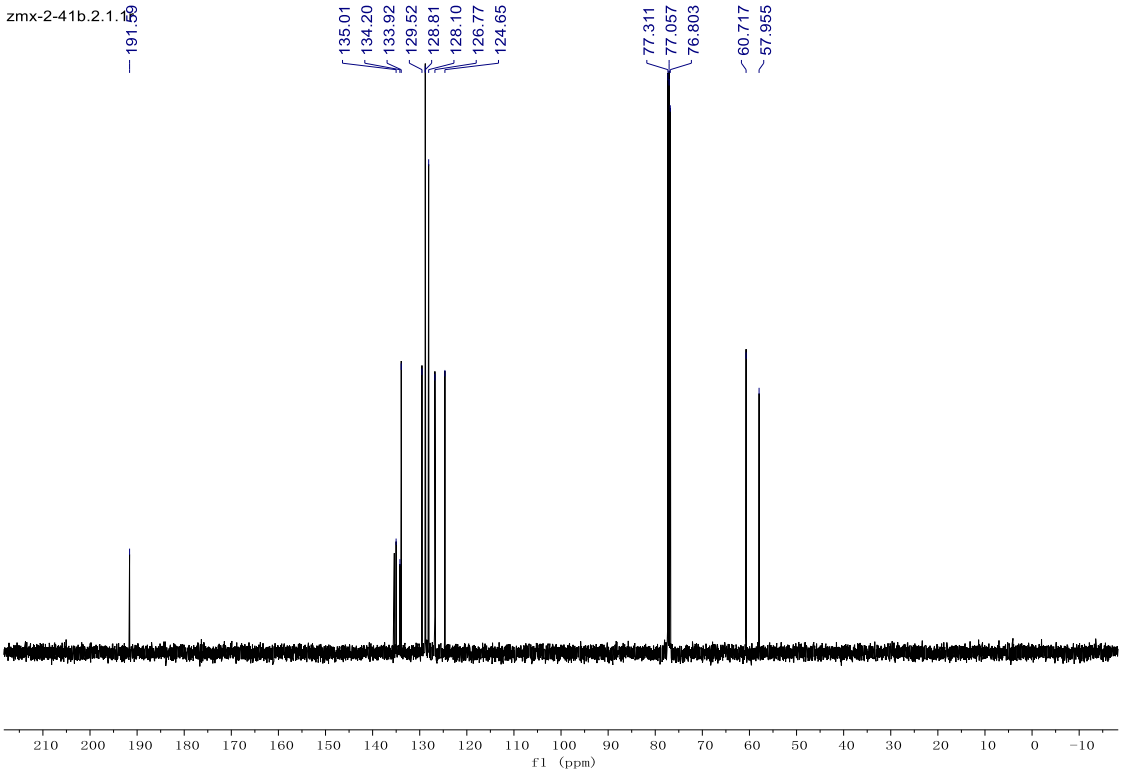
zmx-2-42a.2.1.1r




zmx-2-41a-again.1.1.1r
7.879
7.863
7.512
7.497
7.481
7.377
7.361
7.346
7.219
7.200
7.146
7.138
4.158
3.928
H
O
H
Cl
O
24c
1.93
1.01
2.02
3.90
1.00
0.97
0.0 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
f1 (ppm)


zmx-2-41a-again.2.1.1r
192.624
137.721
135.347
134.868
134.153
130.129
129.190
128.948
128.384
125.764
124.177
77.461
77.207
76.952
60.747
58.523
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

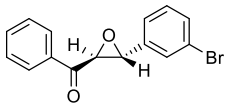

zmx-2-41b.1.1.1r
7.878
7.859
7.577
7.562
7.545
7.452
7.437
7.421
7.333
7.268
7.233
7.225
7.216
7.189
7.181
7.164
4.519
4.510
4.474
4.465
H
O
H
Cl
O
24d
2.00
1.09
2.08
1.06
3.02
1.00
1.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


zmx-2-41b.2.1.1r
191.59
135.01
134.20
133.92
129.52
128.81
128.10
126.77
124.65
77.311
77.057
76.803
60.717
57.955
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

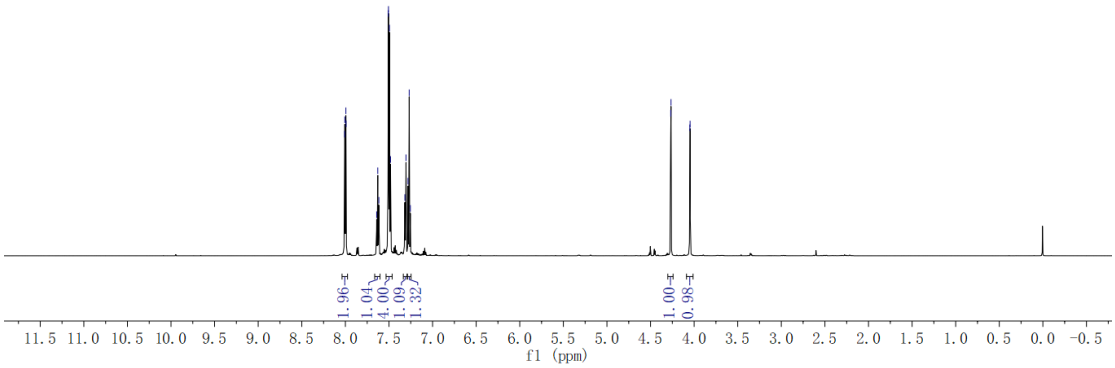
pdata/1

8.008
8.006
7.994
7.992
7.641
7.628
7.616
7.508
7.506
7.495
7.482
7.318
7.305
7.282
7.268
7.255

4.268
4.265
4.049
4.046



25c



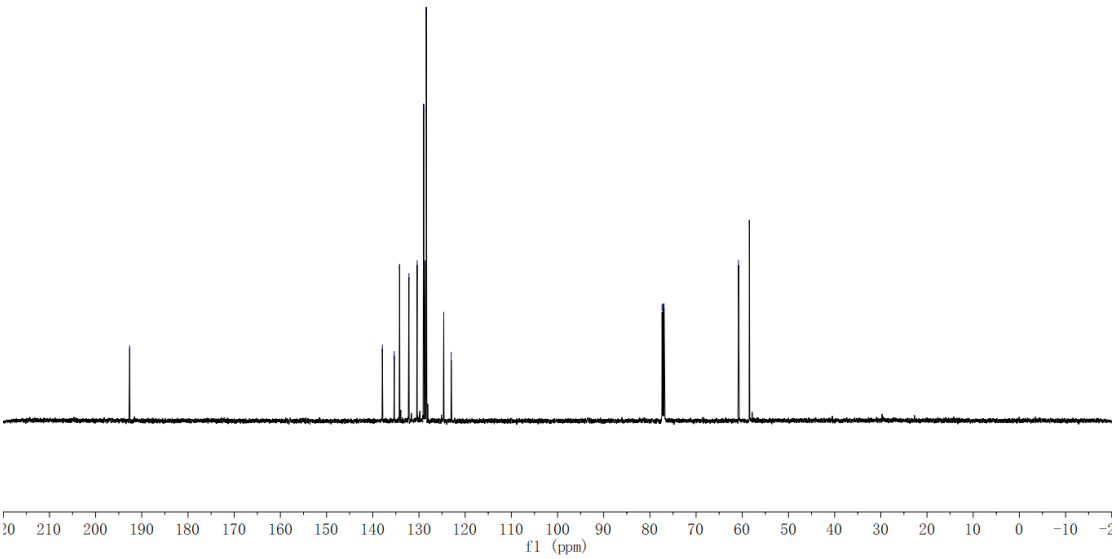
pdata/1

192.631

137.922
135.351
134.193
132.173
130.388
128.978
128.670
128.409
124.630
123.009

77.361
77.149
76.937

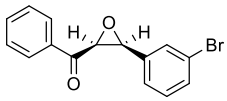
60.805
58.460



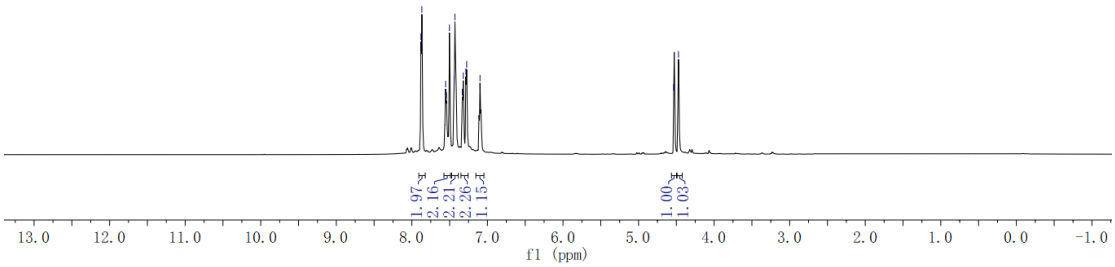
pdata/1

7.880
7.868
7.554
7.542
7.503
7.440
7.430
7.332
7.320
7.285
7.275
7.098

4.536
4.472



25d



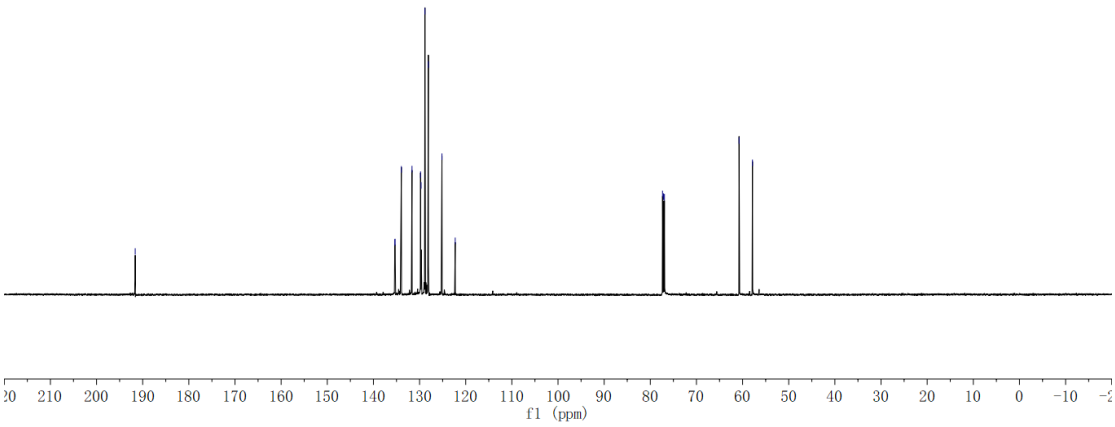
pdata/1

191.621

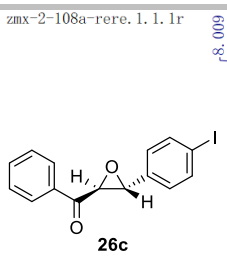
135.370
135.300
133.950
131.641
129.788
129.672
128.834
128.093
125.149
122.275

77.352
77.141
76.929

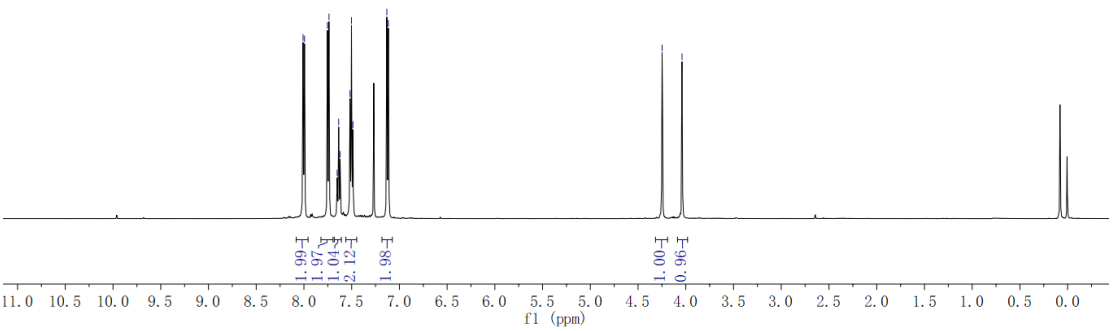
60.759
57.860



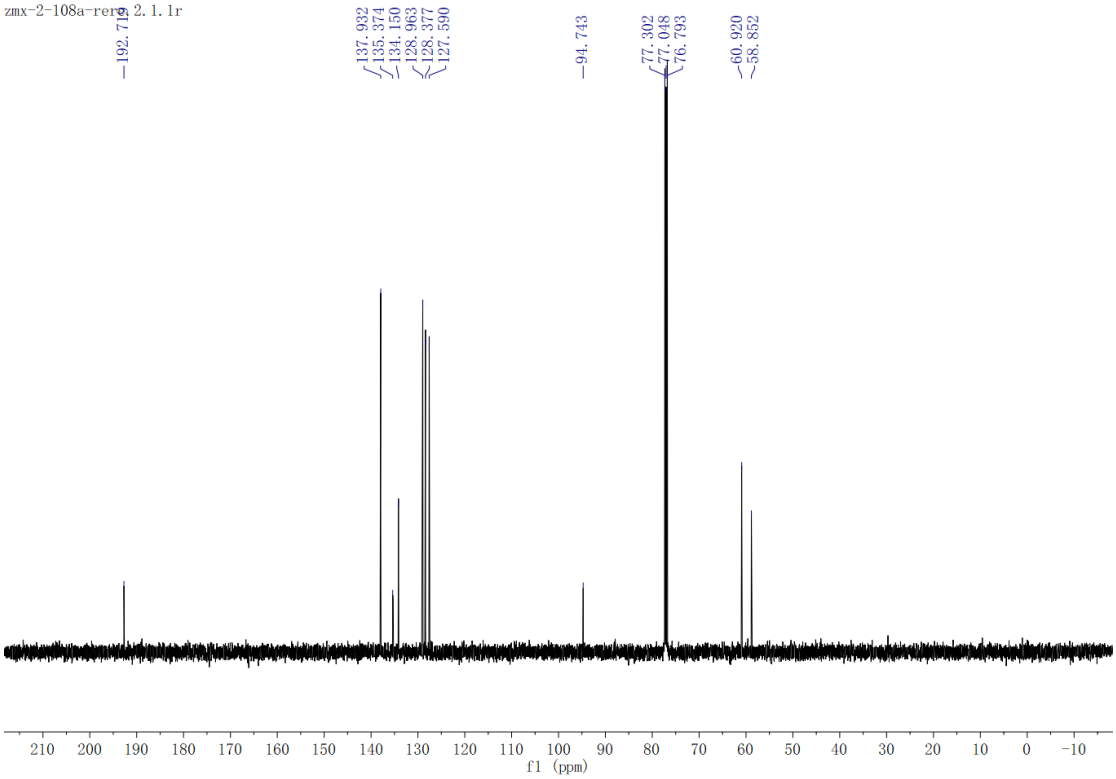
zmx-2-108a-rere.1.1.1r



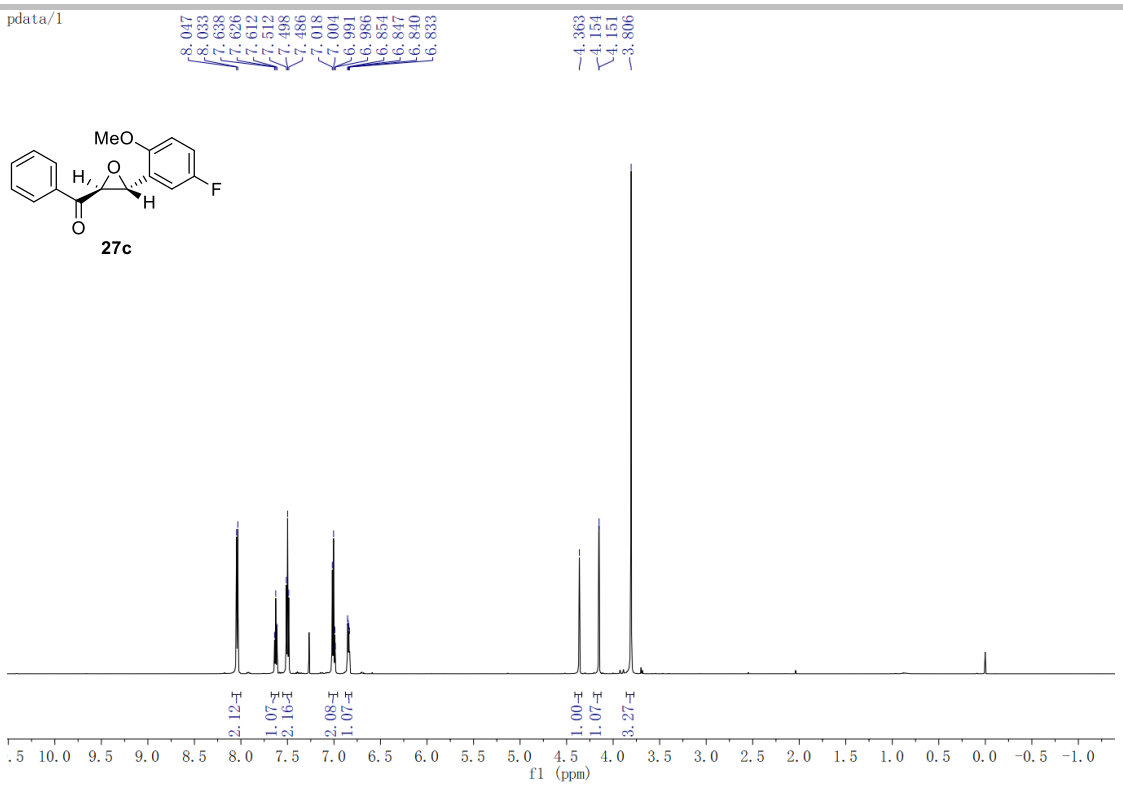
26c



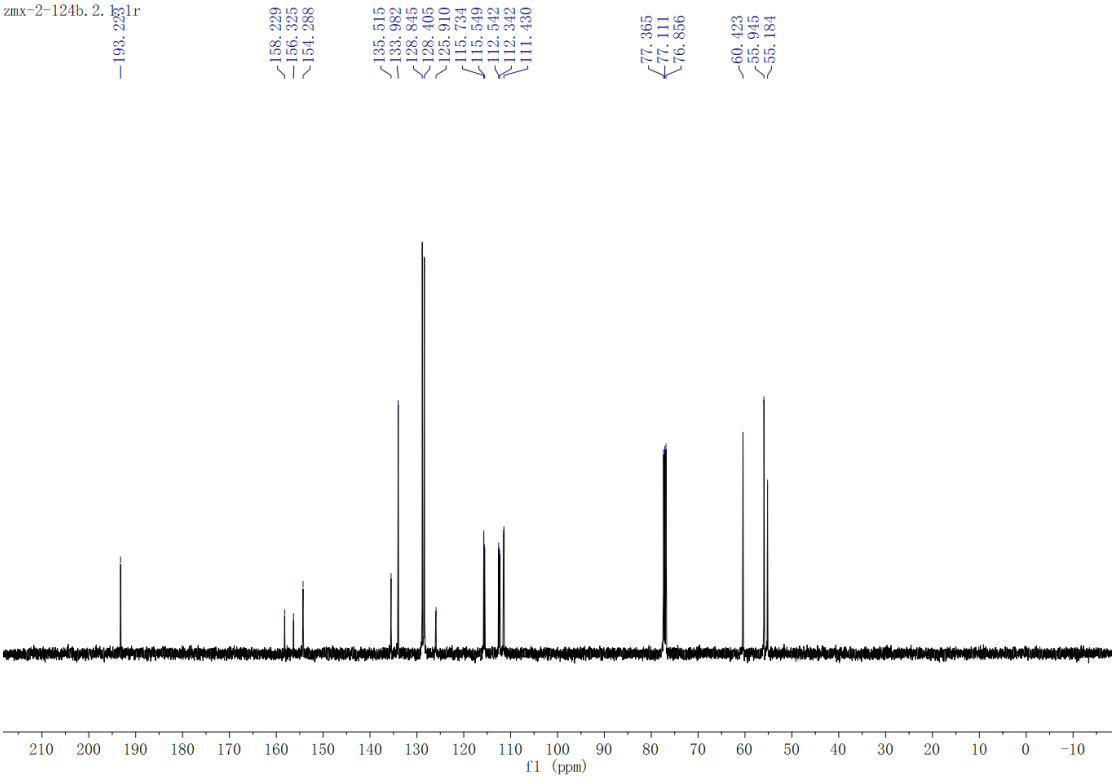
zmx-2-108a-rere2.1.1r

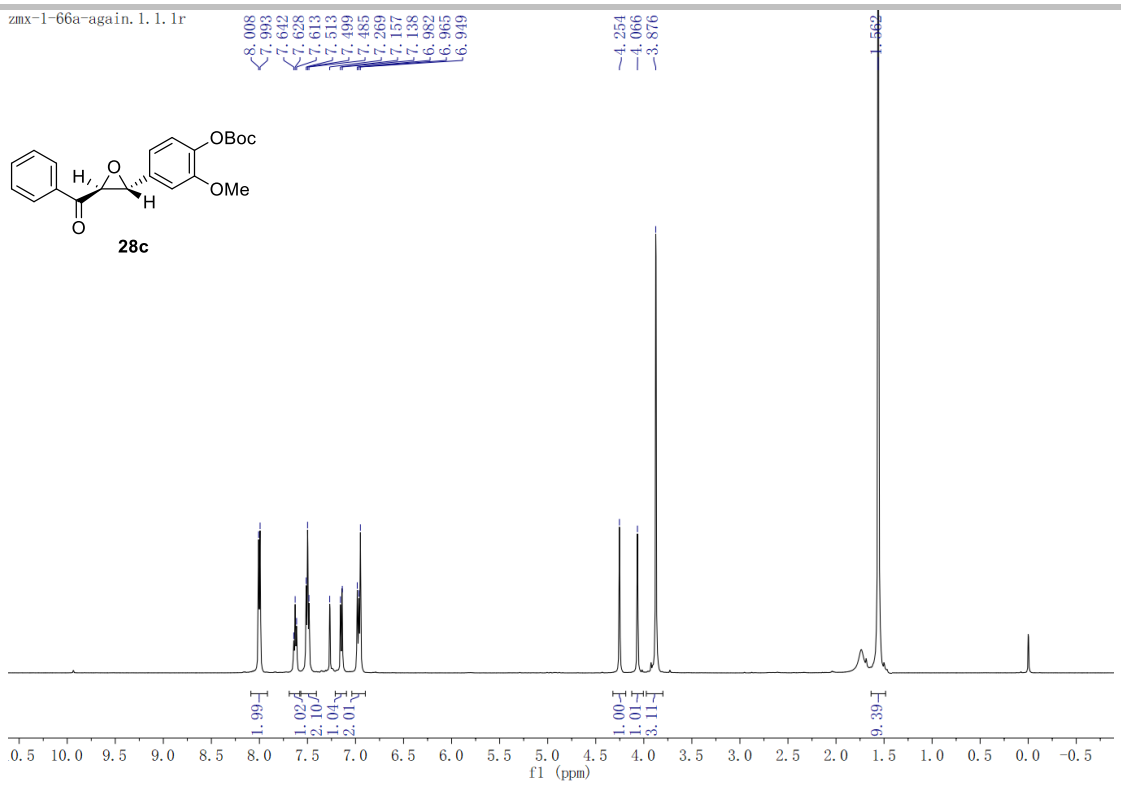


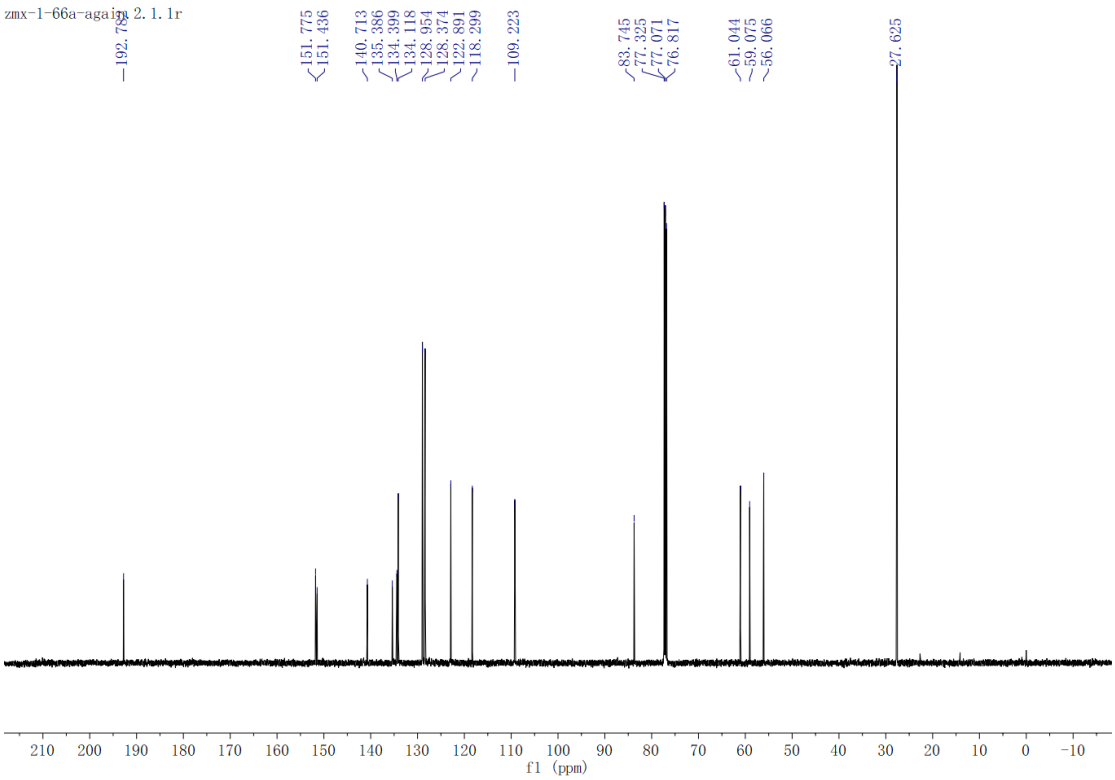
pdata/1

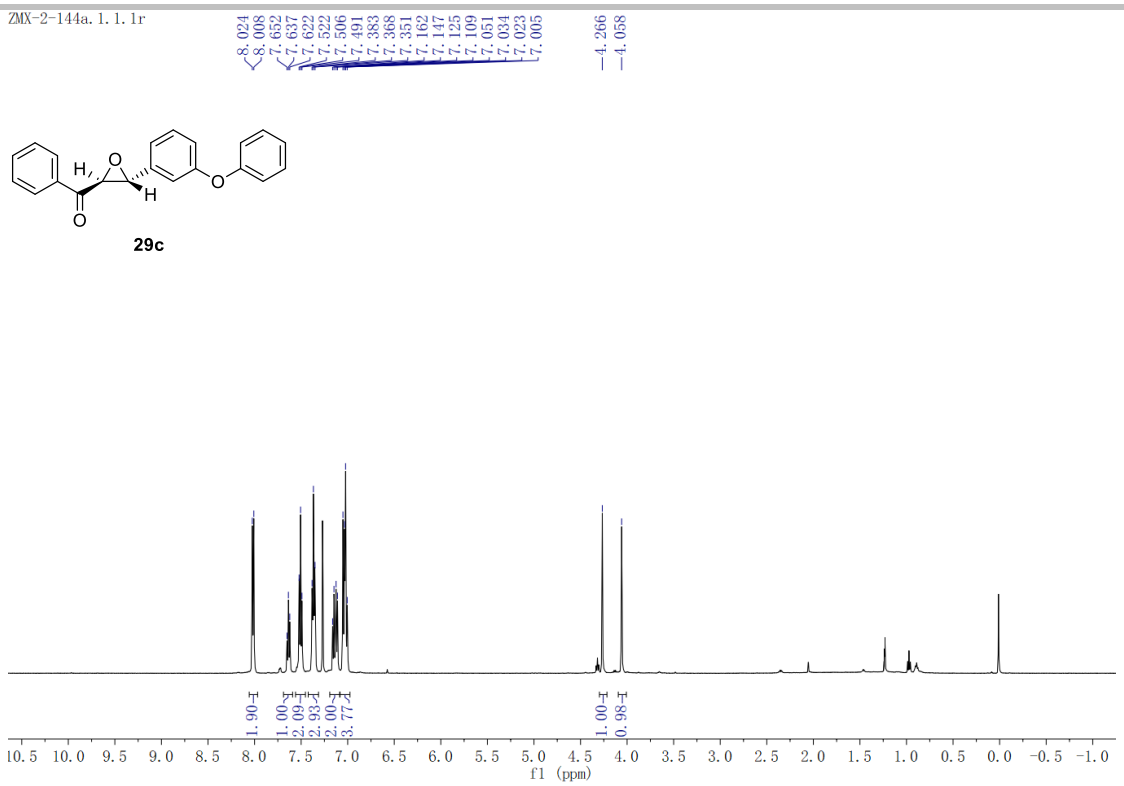


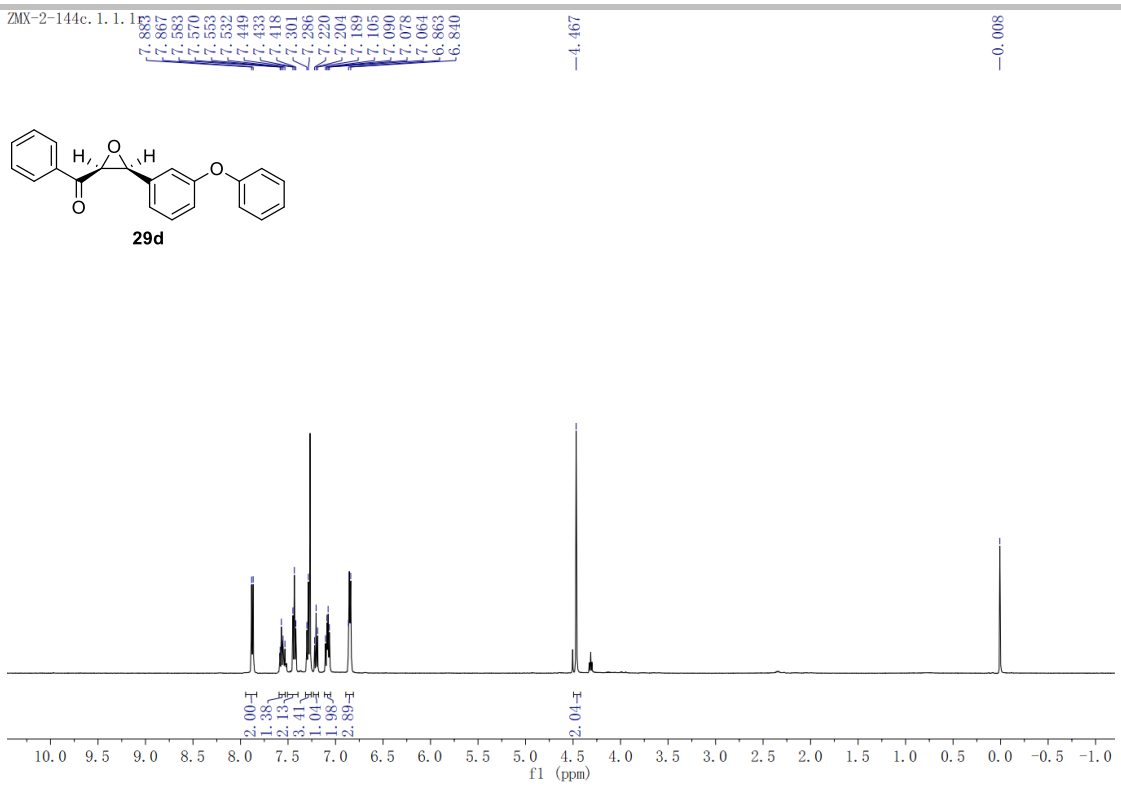
zmx-2-124b.2.1r

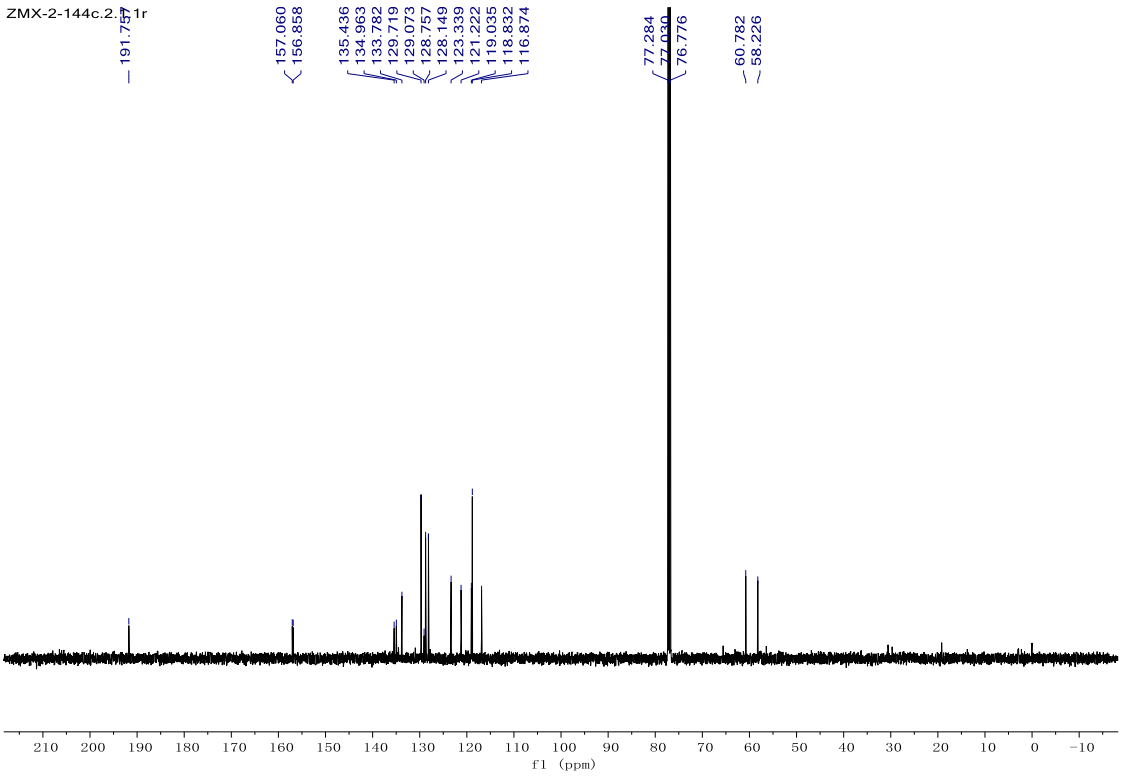


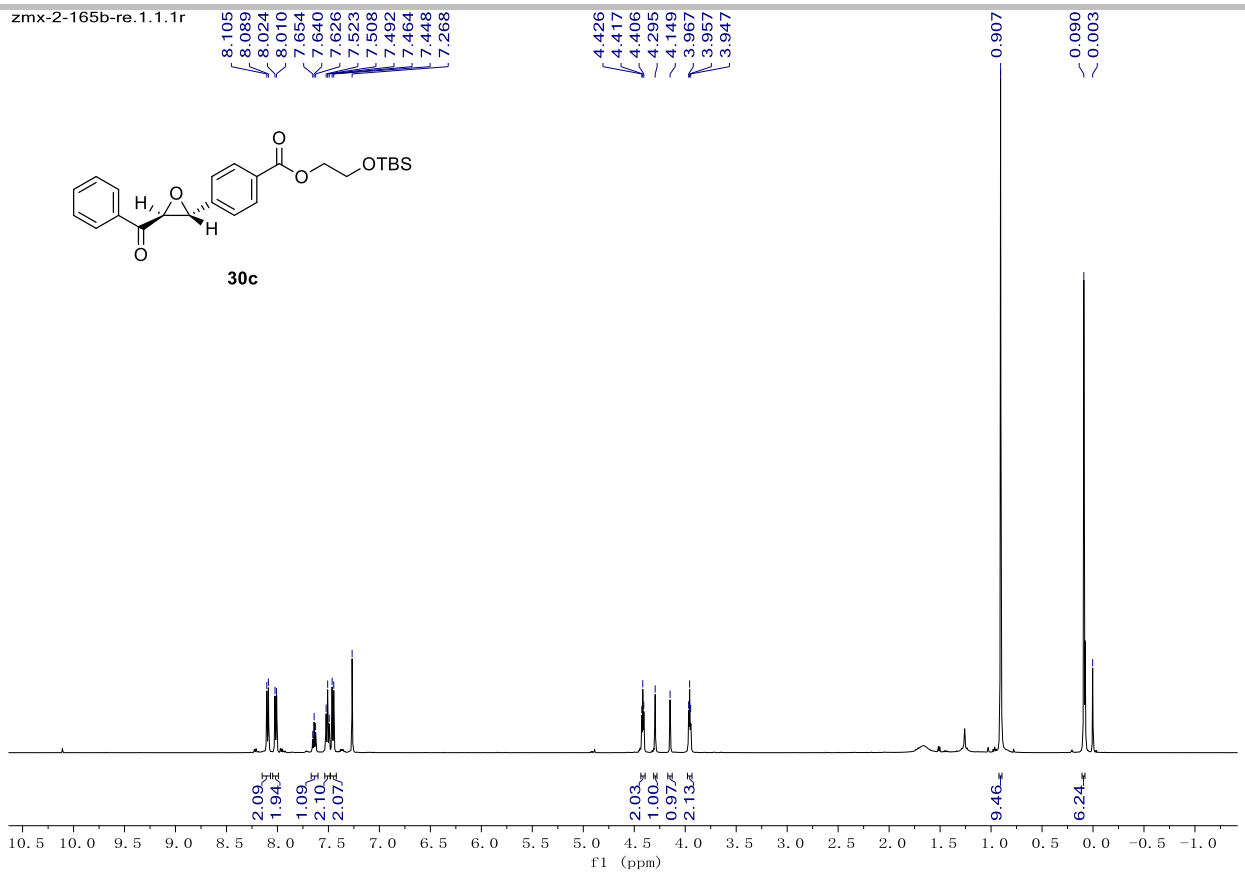

zmx-1-66a-again.1.1.1r
8.008
7.993
7.642
7.628
7.613
7.513
7.499
7.485
7.269
7.157
7.138
6.982
6.965
6.949
4.254
4.066
3.876
1.562
OBoc
OMe
H
O
H
O
28c
1.99
1.02
2.10
1.04
2.01
1.00
1.01
3.11
9.39
f1 (ppm)

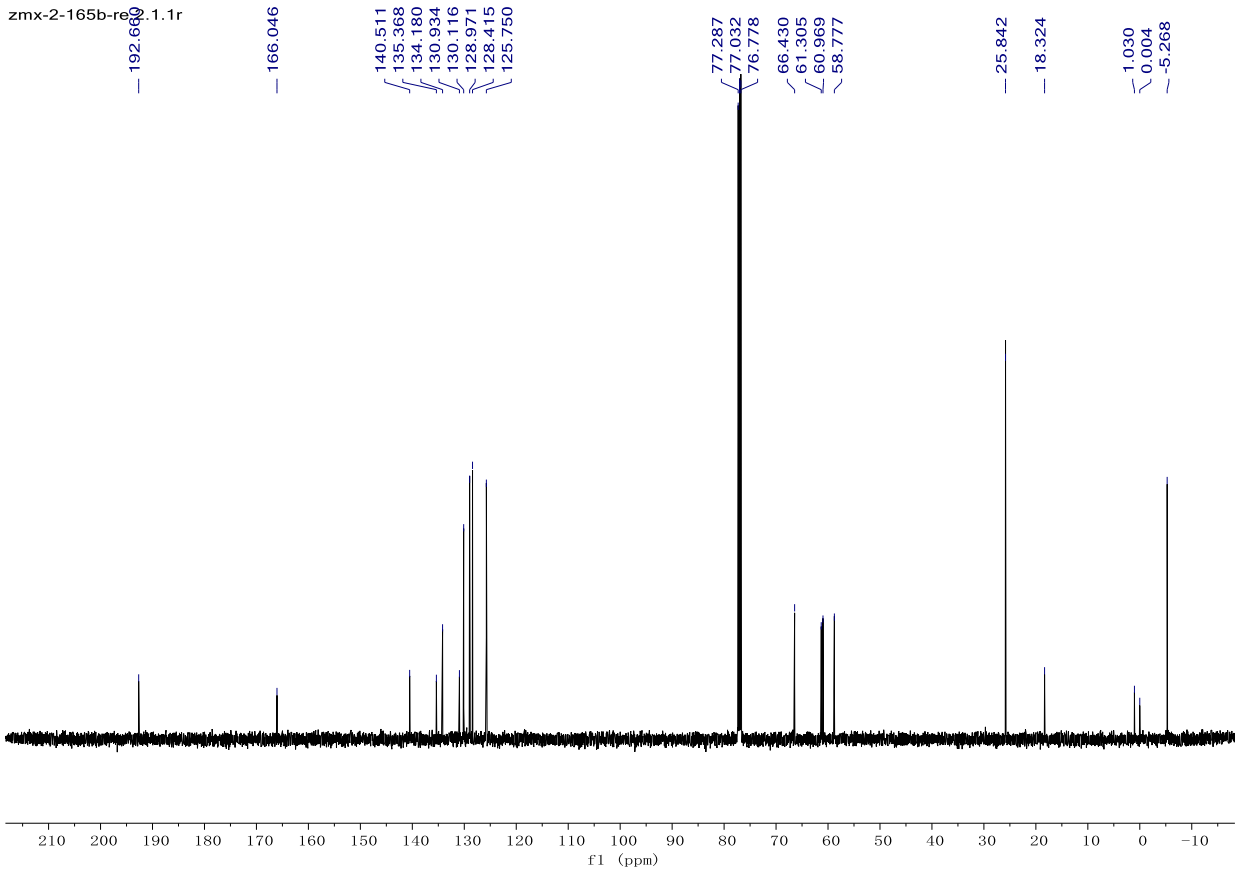

zmx-1-66a-again 2.1.1r
192.782
151.775
151.436
140.713
135.386
134.399
134.118
128.954
128.374
122.891
118.299
109.223
83.745
77.325
77.071
76.817
61.044
59.075
56.066
27.625
f1 (ppm)


ZMX-2-144a.1.1.1r
8.024
8.008
7.652
7.637
7.622
7.522
7.506
7.491
7.383
7.368
7.351
7.162
7.147
7.125
7.109
7.051
7.034
7.023
7.005
4.266
4.058
H
O
H
O
O
29c
1.90
1.00
2.09
2.93
2.00
3.77
1.00
0.98
f1 (ppm)
ZMX-2-144a.2
1.1r
192.957
158.042
156.605
137.625
135.437
134.070
130.199
129.915
128.921
128.407
123.786
120.470
119.258
115.764
77.294
77.039
76.785
60.920
59.006
f1 (ppm)


ZMX-2-144c.1.1.1r
7.883
7.867
7.583
7.570
7.553
7.532
7.449
7.433
7.418
7.301
7.286
7.220
7.204
7.189
7.105
7.090
7.078
7.064
6.863
6.840
4.467
0.008
H
O
H
O
O
29d
2.00
1.38
2.13
3.41
1.04
1.98
2.89
2.04
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
f1 (ppm)


ZMX-2-144c.2.1.1r
191.757
157.060
156.858
135.436
134.963
133.782
129.719
129.073
128.757
128.149
123.339
121.222
119.035
118.832
116.874
77.284
77.030
76.776
60.782
58.226
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

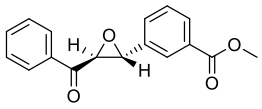

zmx-2-165b-re.1.1.1r
8.105
8.089
8.024
8.010
7.654
7.640
7.626
7.523
7.508
7.492
7.464
7.448
7.268
4.426
4.417
4.406
4.295
4.149
3.967
3.957
3.947
0.907
0.090
0.003
O
O
OTBS
H
O
H
O
30c
2.09
1.94
1.09
2.10
2.07
2.03
1.00
0.97
2.13
9.46
6.24
f1 (ppm)


zmx-2-165b-re.1.1.1r
192.600
166.046
140.511
135.368
134.180
130.934
130.116
128.971
128.415
125.750
77.287
77.032
76.778
66.430
61.305
60.969
58.777
25.842
18.324
1.030
0.004
-5.268
f1 (ppm)

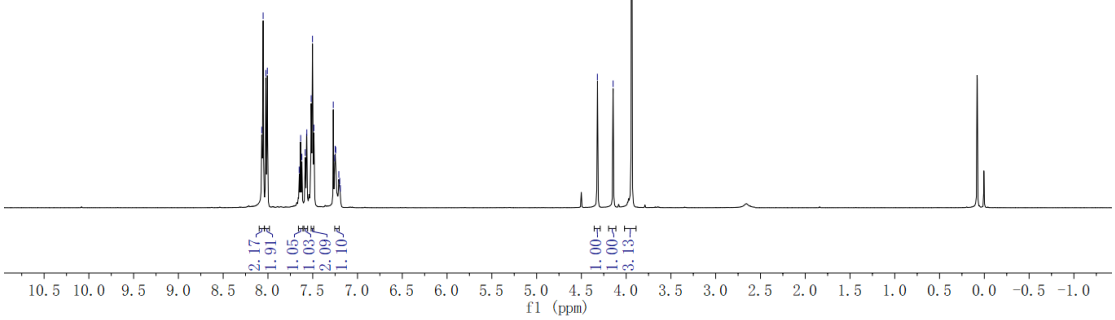
zmx-2-109b-re.1.1.1r

8.069
8.054
8.023
8.007
7.651
7.635
7.622
7.583
7.566
7.517
7.503
7.487
7.270
7.255
7.249
7.243
7.208
7.199
7.192

4.321
4.146
3.940



31c



zmx-2-109b-re.1.1.1r

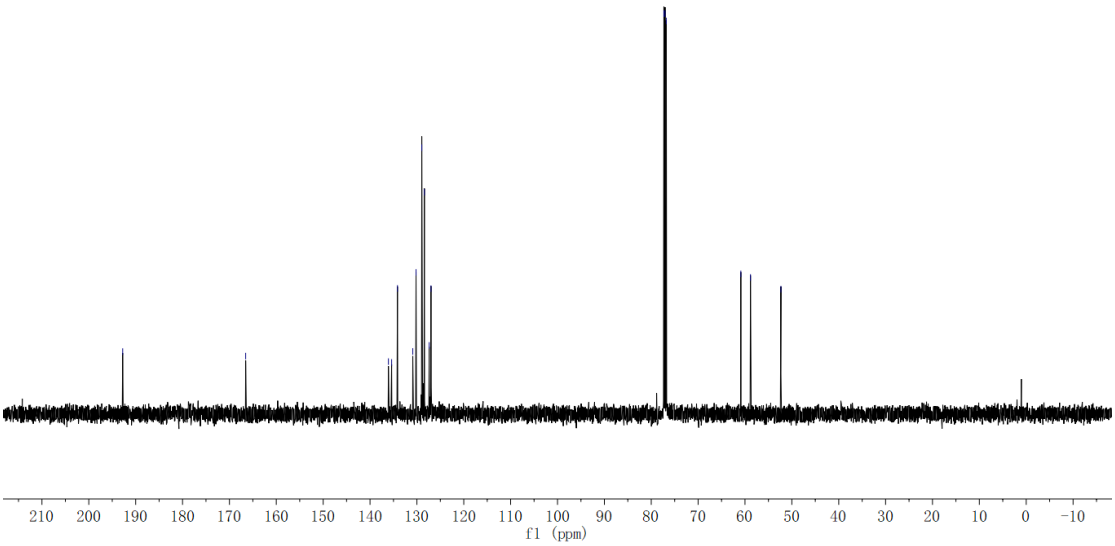
192.776

166.527

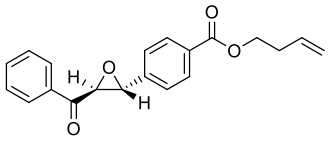
136.080
135.389
134.147
130.877
130.183
128.955
128.403
127.381
126.991

77.303
77.049
76.795

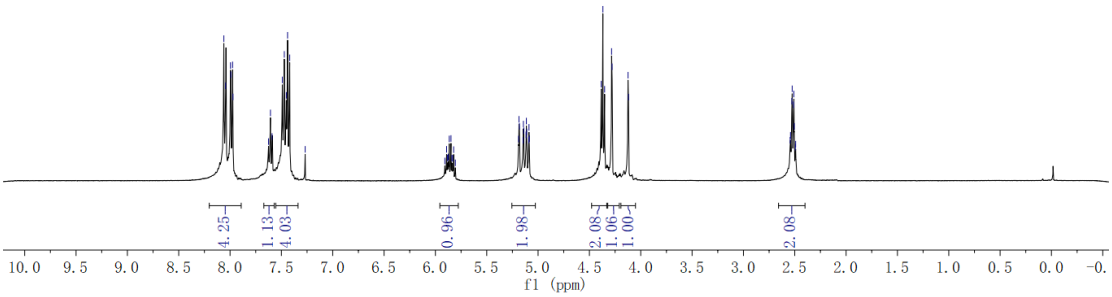
60.883
58.832
52.336



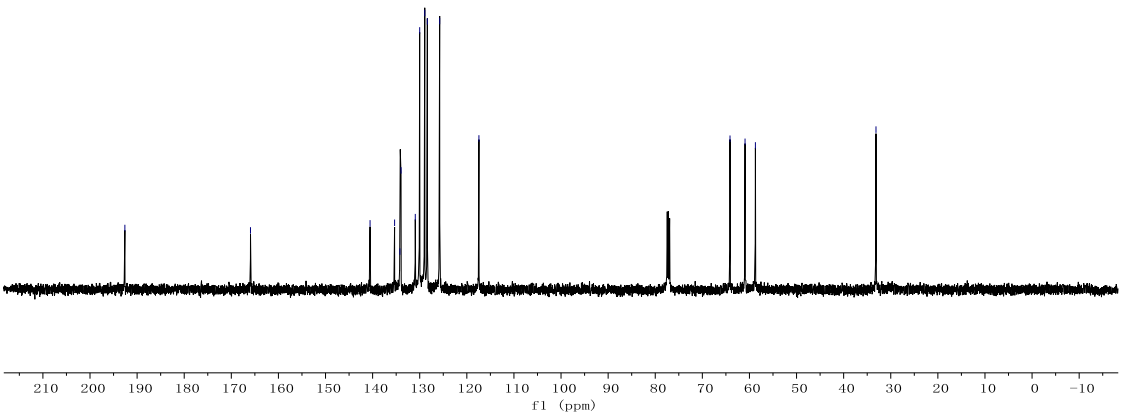
zmx-2-145b.1.1.1r

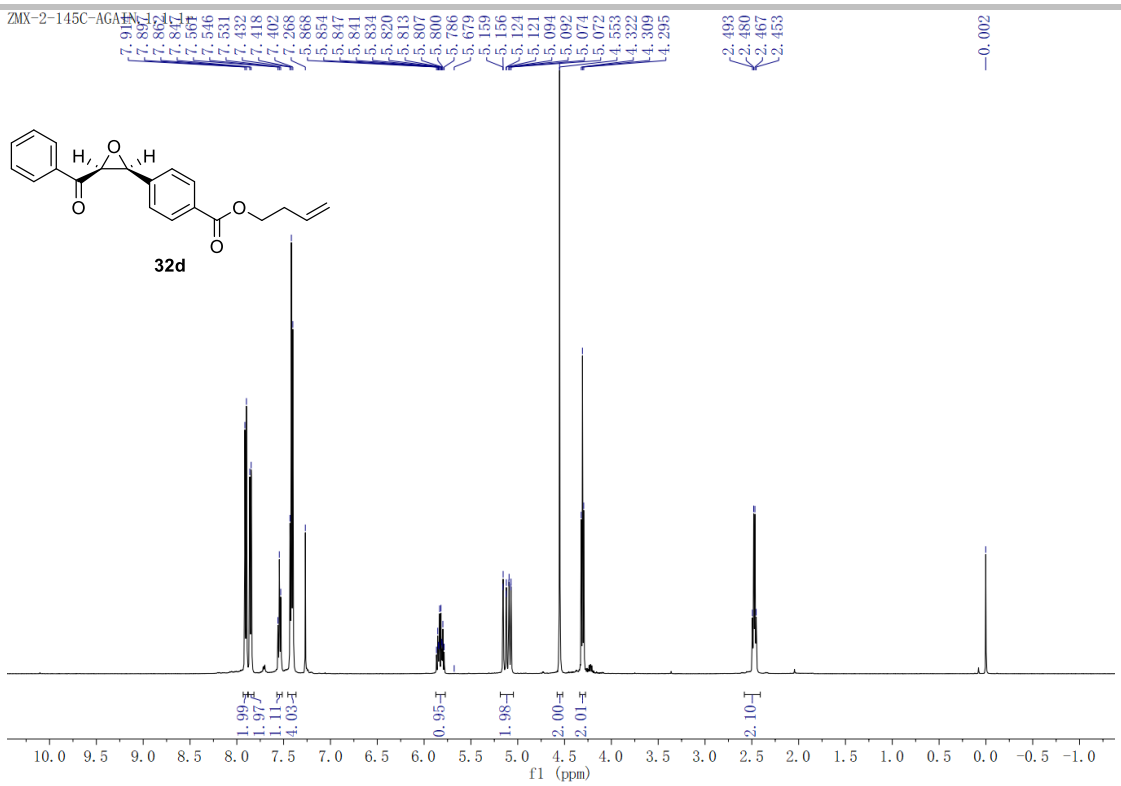


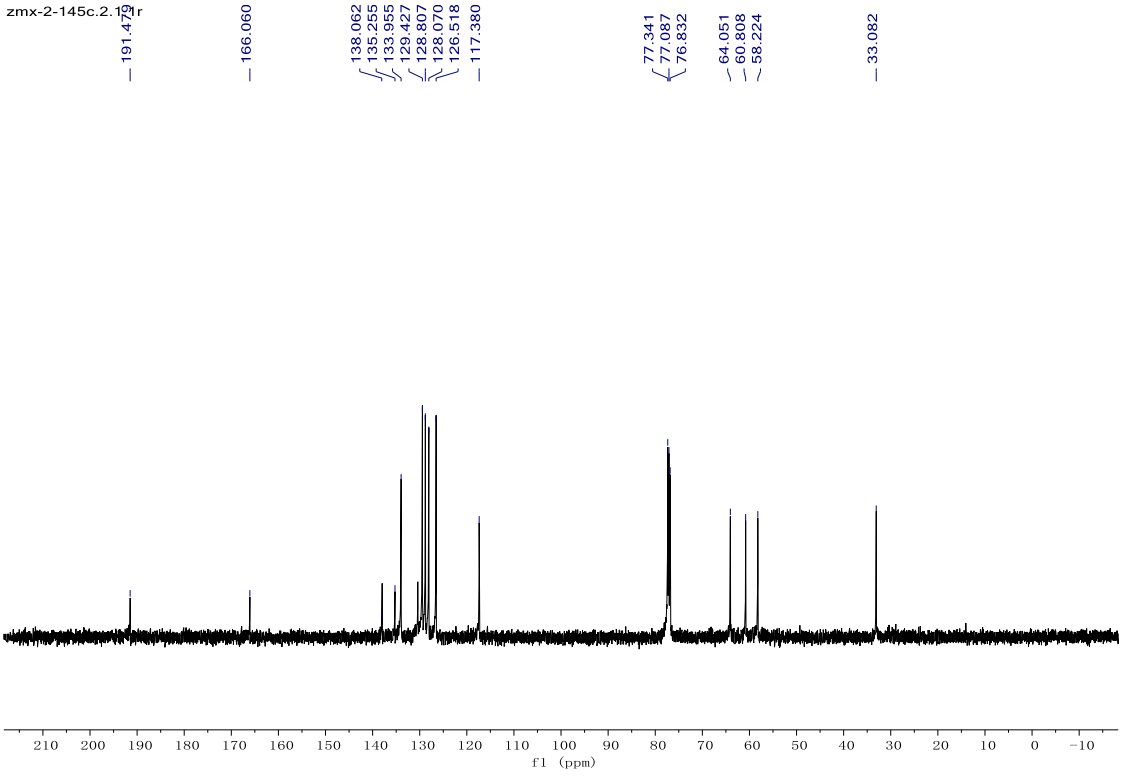
32c



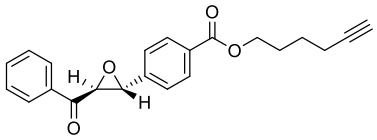
zmx-2-145b.2.1.1r



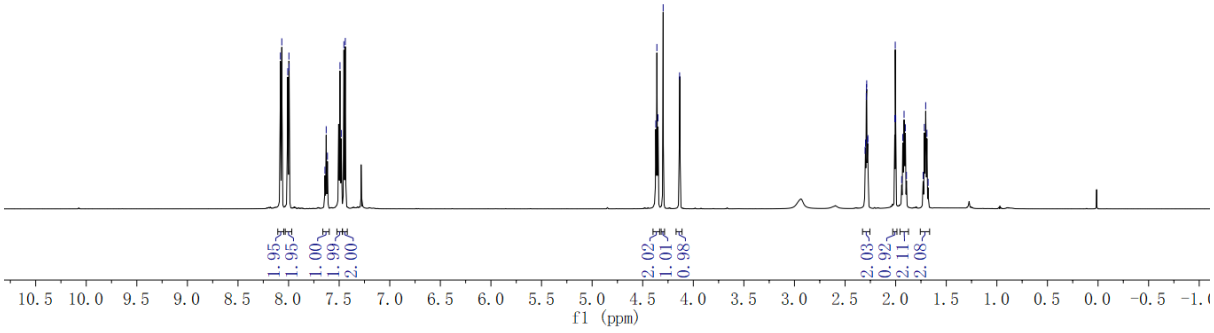

ZMX-2-145C-AGAIN-1
7.919
7.895
7.882
7.847
7.561
7.546
7.531
7.432
7.418
7.402
7.268
5.868
5.854
5.847
5.841
5.834
5.820
5.813
5.807
5.800
5.786
5.679
5.159
5.156
5.124
5.121
5.094
5.092
5.074
5.072
4.553
4.322
4.309
4.295
2.493
2.480
2.467
2.453
0.002
32d
1.99
1.97
1.11
4.03
0.95
1.98
2.00
2.01
2.10
f1 (ppm)


zmx-2-145c.2.11r
191.479
166.060
138.062
135.255
133.955
129.427
128.807
128.070
126.518
117.380
77.341
77.087
76.832
64.051
60.808
58.224
33.082
f1 (ppm)

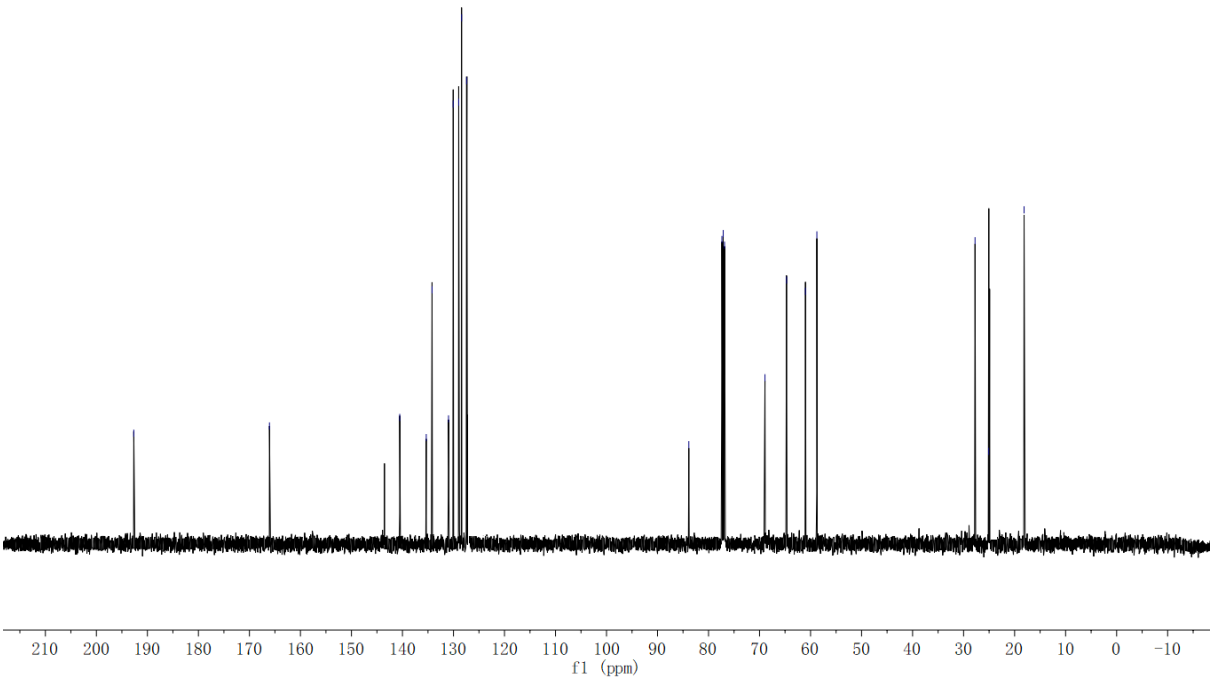
pdata/1

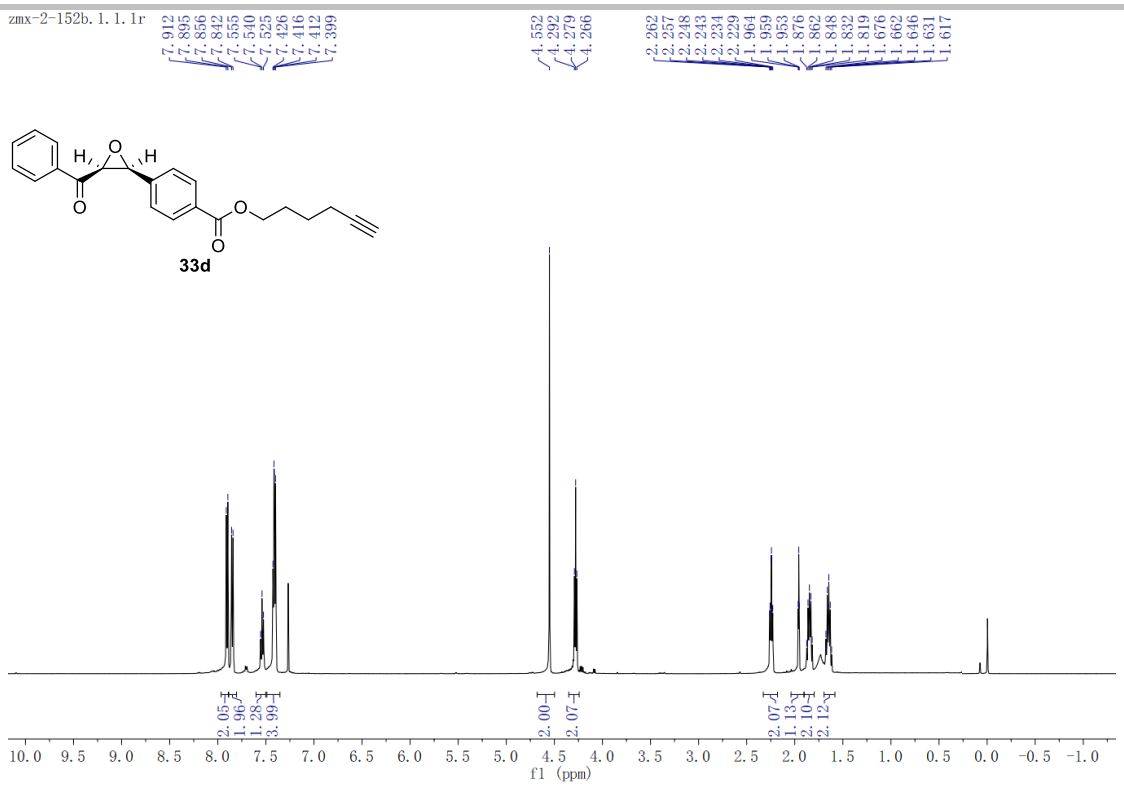


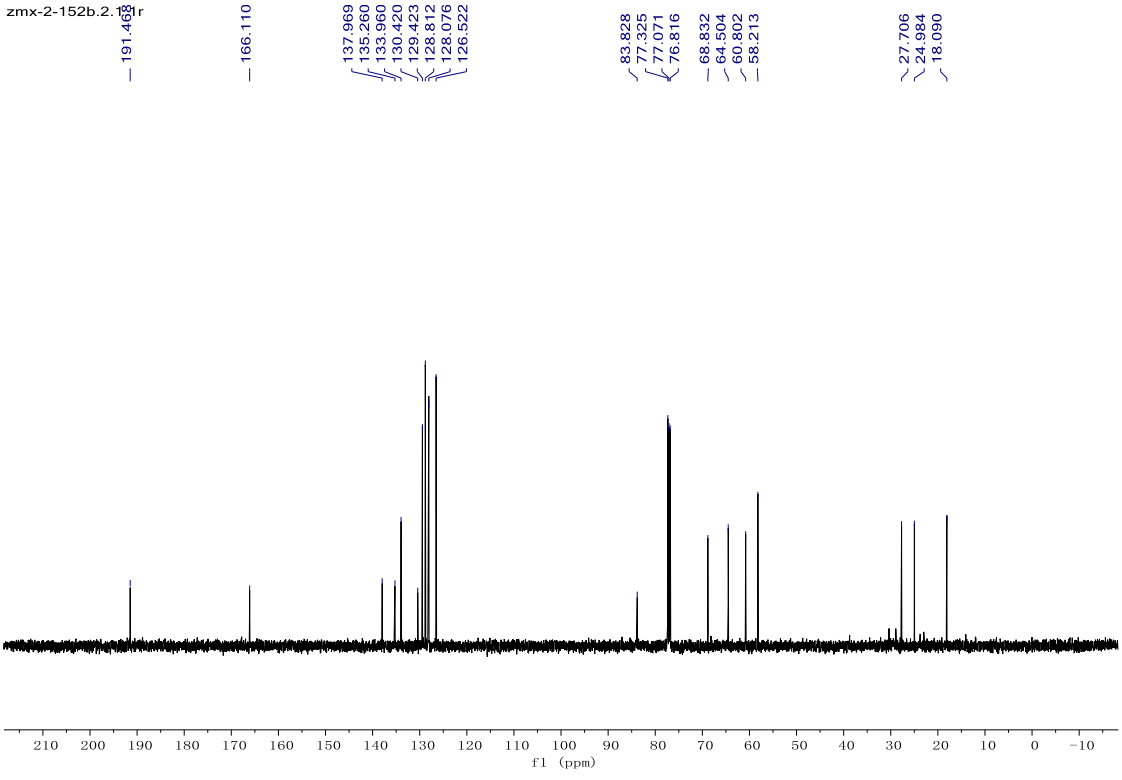
33c



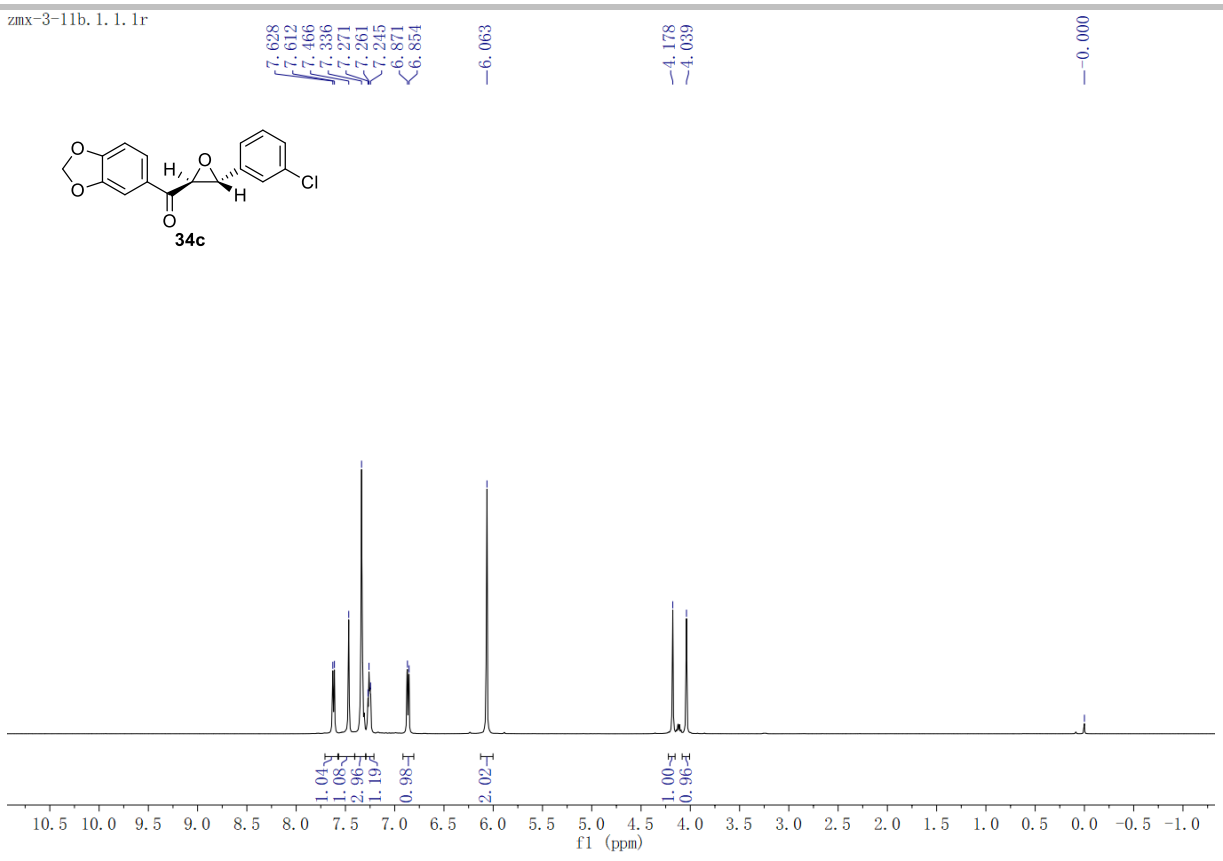
zmx-2-151bx.2.10.1r



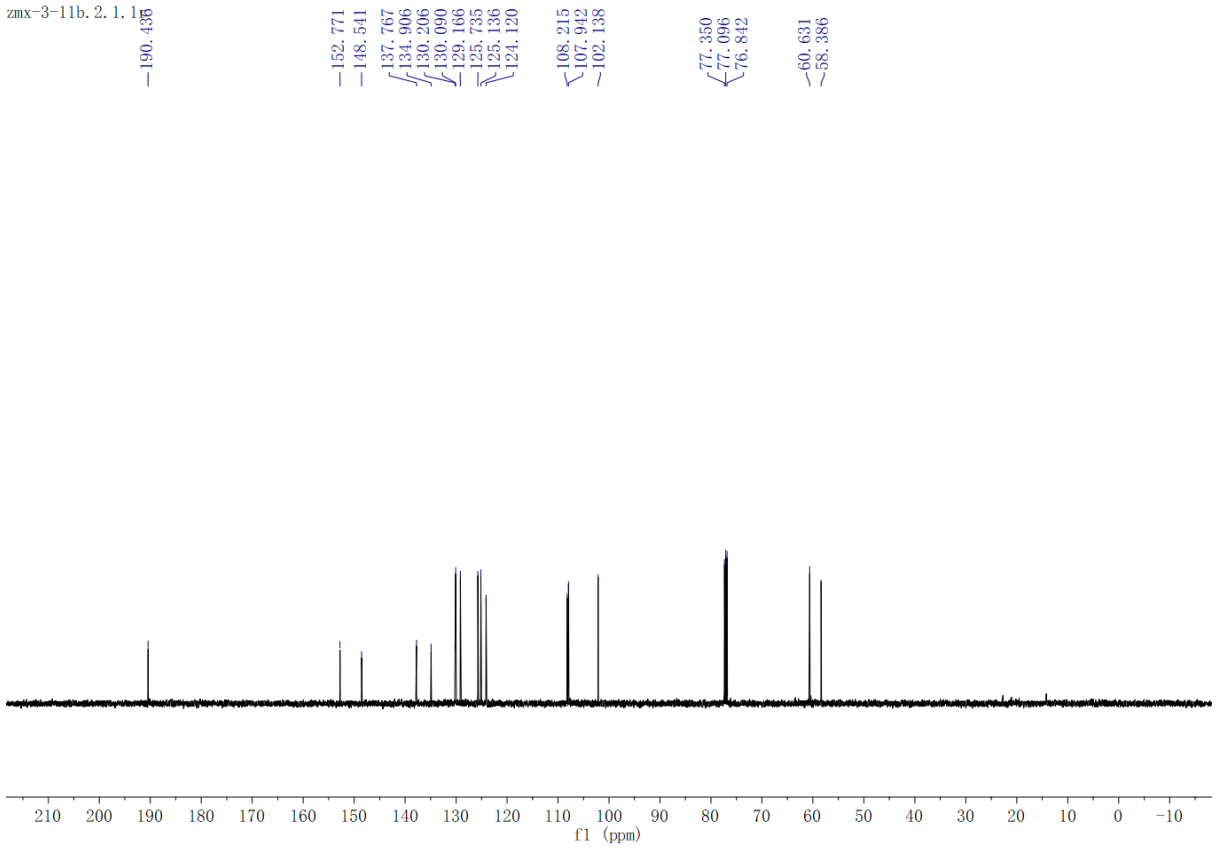

zmx-2-152b.1.1.1r
7.912
7.895
7.856
7.842
7.555
7.540
7.525
7.426
7.416
7.412
7.399
4.552
4.292
4.279
4.266
2.262
2.257
2.248
2.243
2.234
2.229
1.964
1.959
1.953
1.876
1.862
1.848
1.832
1.819
1.676
1.662
1.646
1.631
1.617
H
O
H
O
O
O
33d
2.05
1.96
1.28
3.99
2.00
2.07
2.07
1.13
2.10
2.12
10.0 9.5 9.0 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
f1 (ppm)

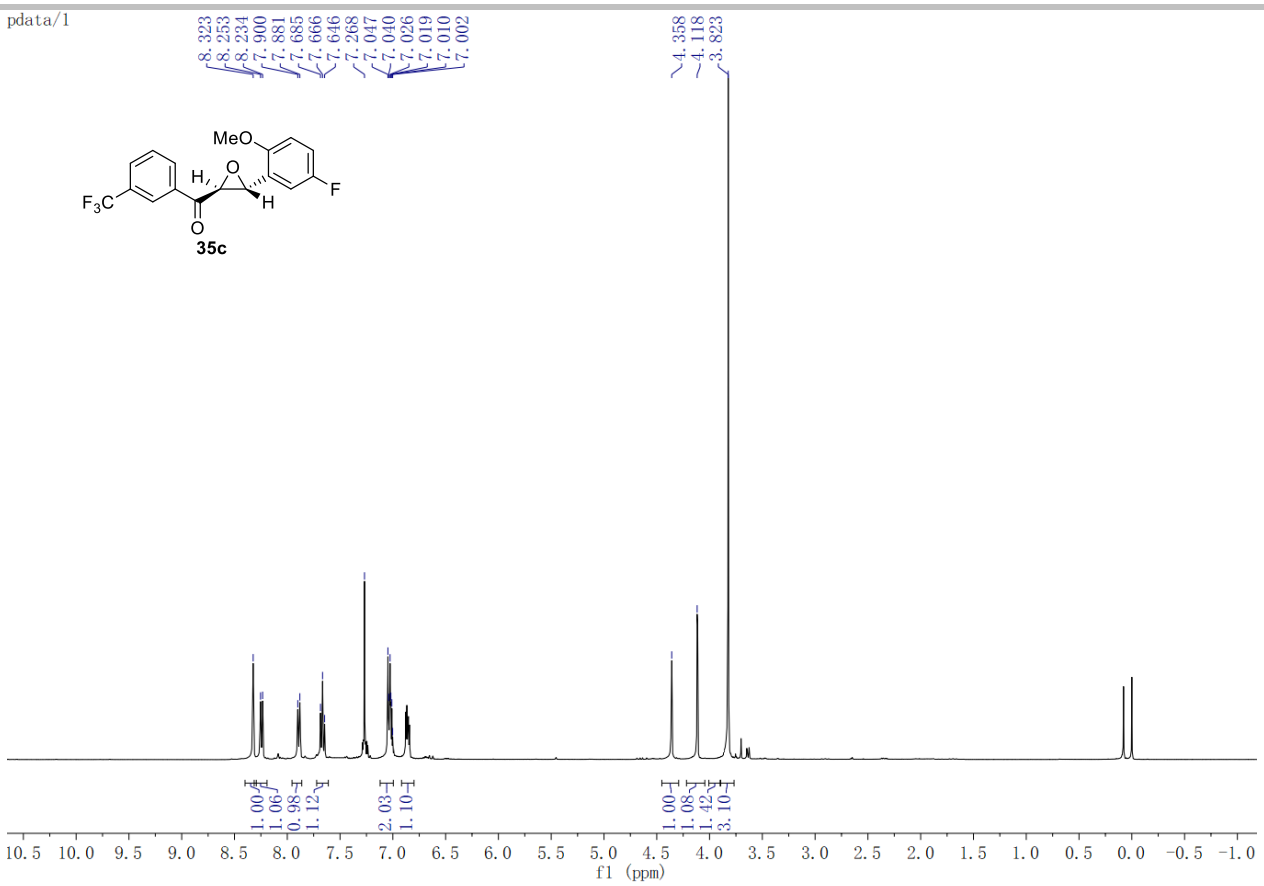

zmx-2-152b.2.1.1r
191.463
166.110
137.969
135.260
133.960
130.420
129.423
128.812
128.076
126.522
83.828
77.325
77.071
76.816
68.832
64.504
60.802
58.213
27.706
24.984
18.090
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

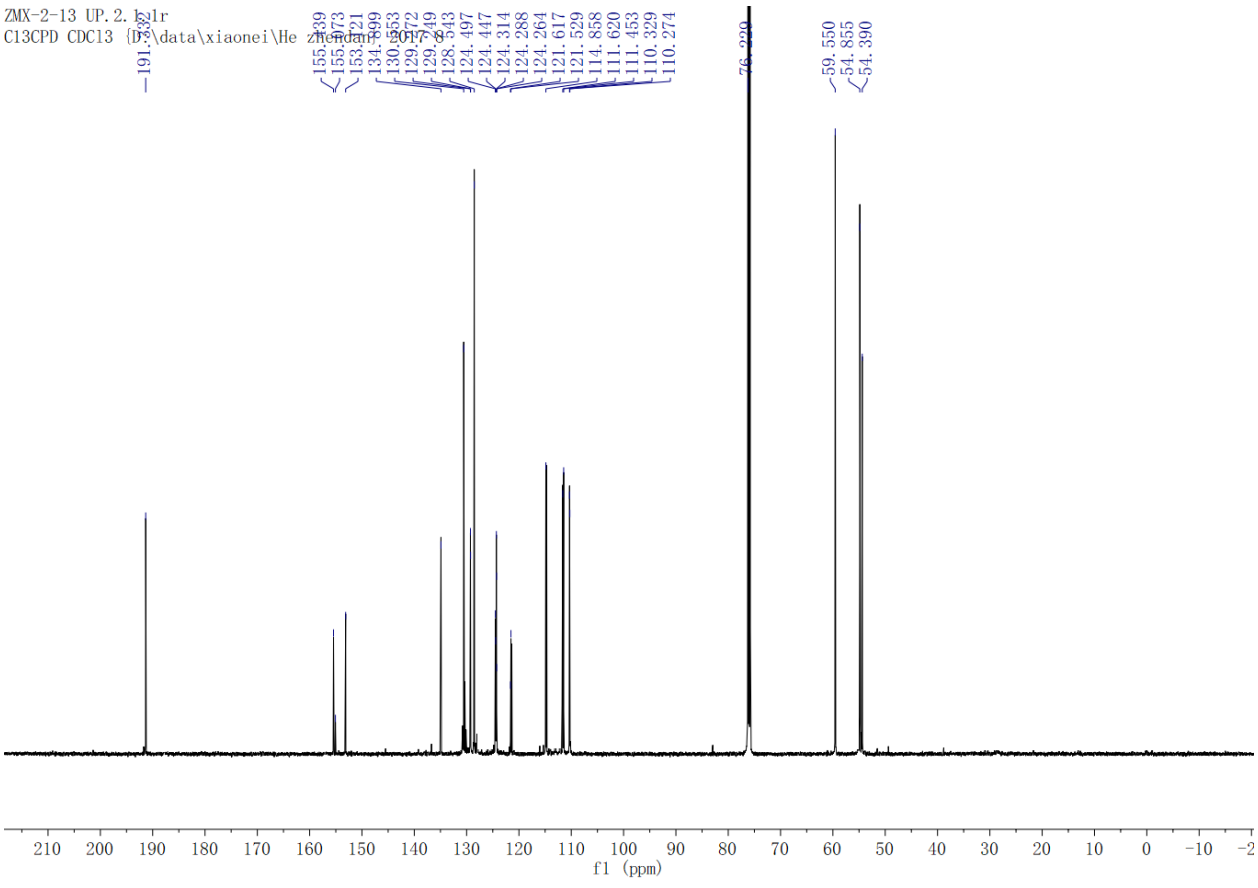
zmx-3-11b.1.1.1r



zmx-3-11b.2.1.1r



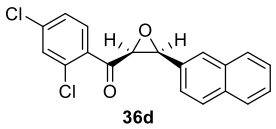

pdata/1
8.323
8.253
8.234
7.900
7.881
7.685
7.666
7.646
7.268
7.047
7.040
7.026
7.019
7.010
7.002
4.358
4.118
3.823
MeO
H
O
F
F3C
H
O
35c
1.00
1.06
0.98
1.12
2.03
1.10
1.00
1.08
1.42
3.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


ZMX-2-13 UP.2.10r
C13CPD CDCl3 {D:\data\xiaonei\He zhendan 2017 8
191.337
155.439
155.073
153.121
134.599
130.253
129.972
129.749
128.843
124.497
124.447
124.314
124.288
124.264
121.617
121.529
114.858
111.620
111.453
110.329
110.274
76.229
59.550
54.855
54.390
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

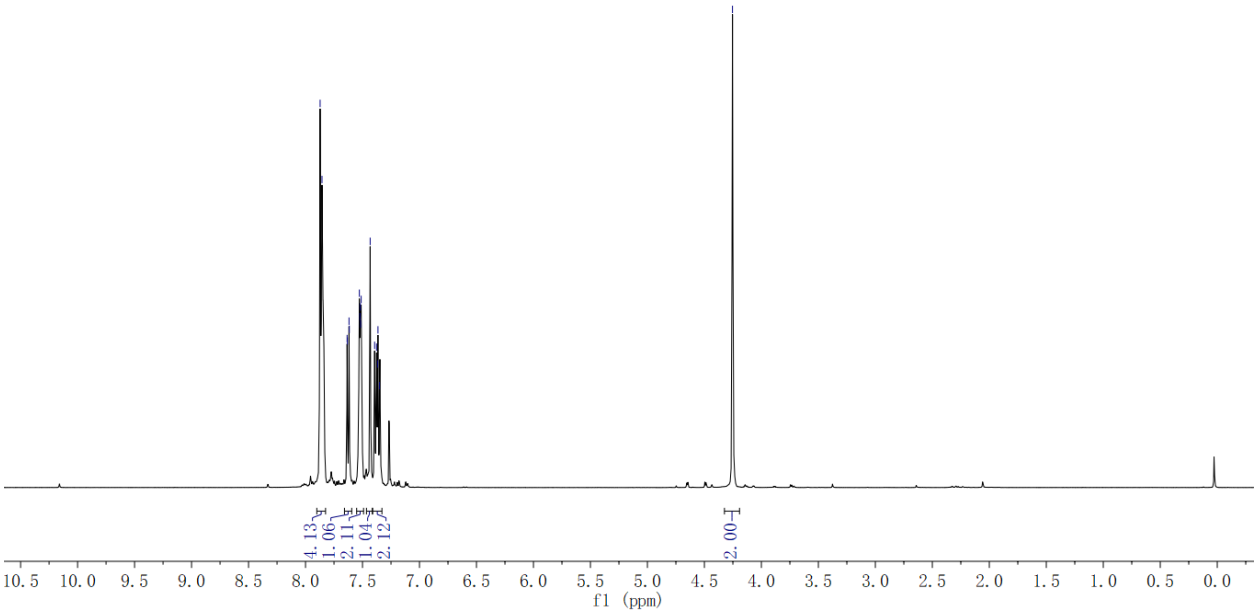
zmx-3-14b.1.1.1r

7.872
7.855
7.635
7.633
7.618
7.616
7.528
7.522
7.519
7.517
7.512
7.433
7.394
7.377
7.367
7.364
7.351

4.254



36d

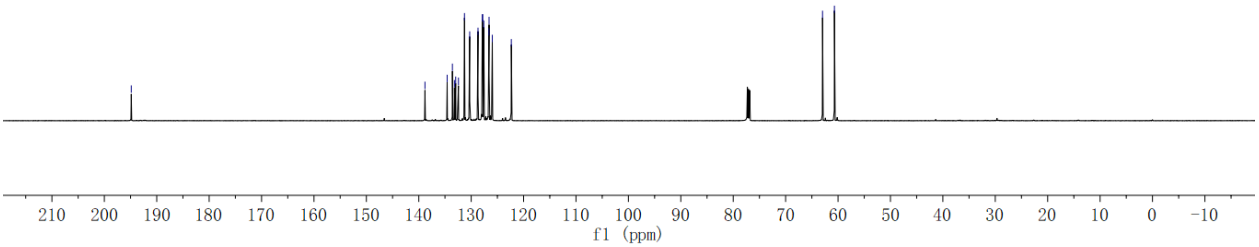


ZMX-2-14B.2.1.1r
C13CPD CDCl3 - D:\data\xiaonei\He zhendan - 2017

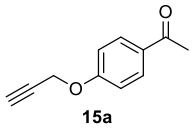
194.662

138.620
134.584
133.196
132.959
132.529
131.981
130.287
128.700
127.883
127.795
127.598
126.617
126.592
125.972
122.344

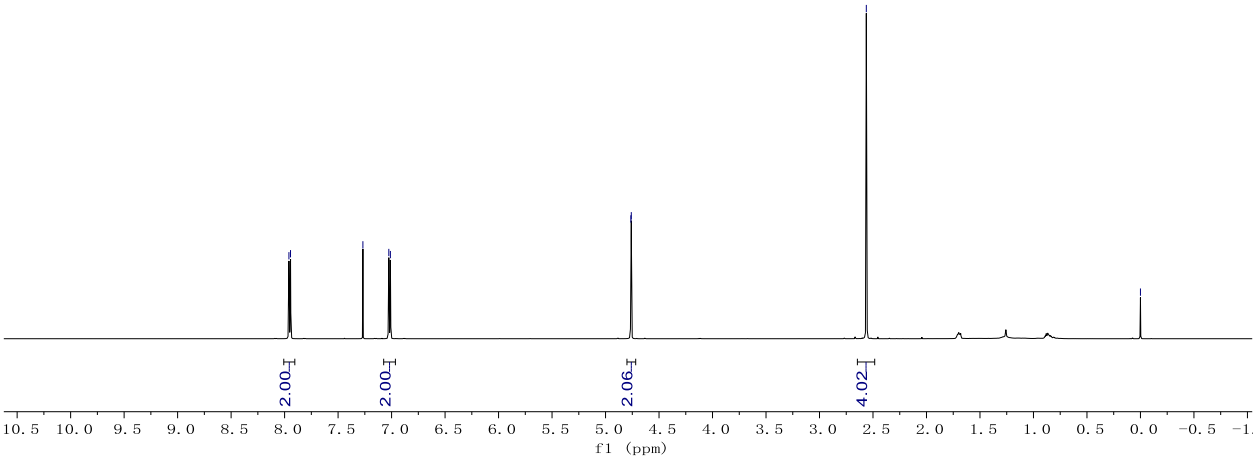
62.957
60.691



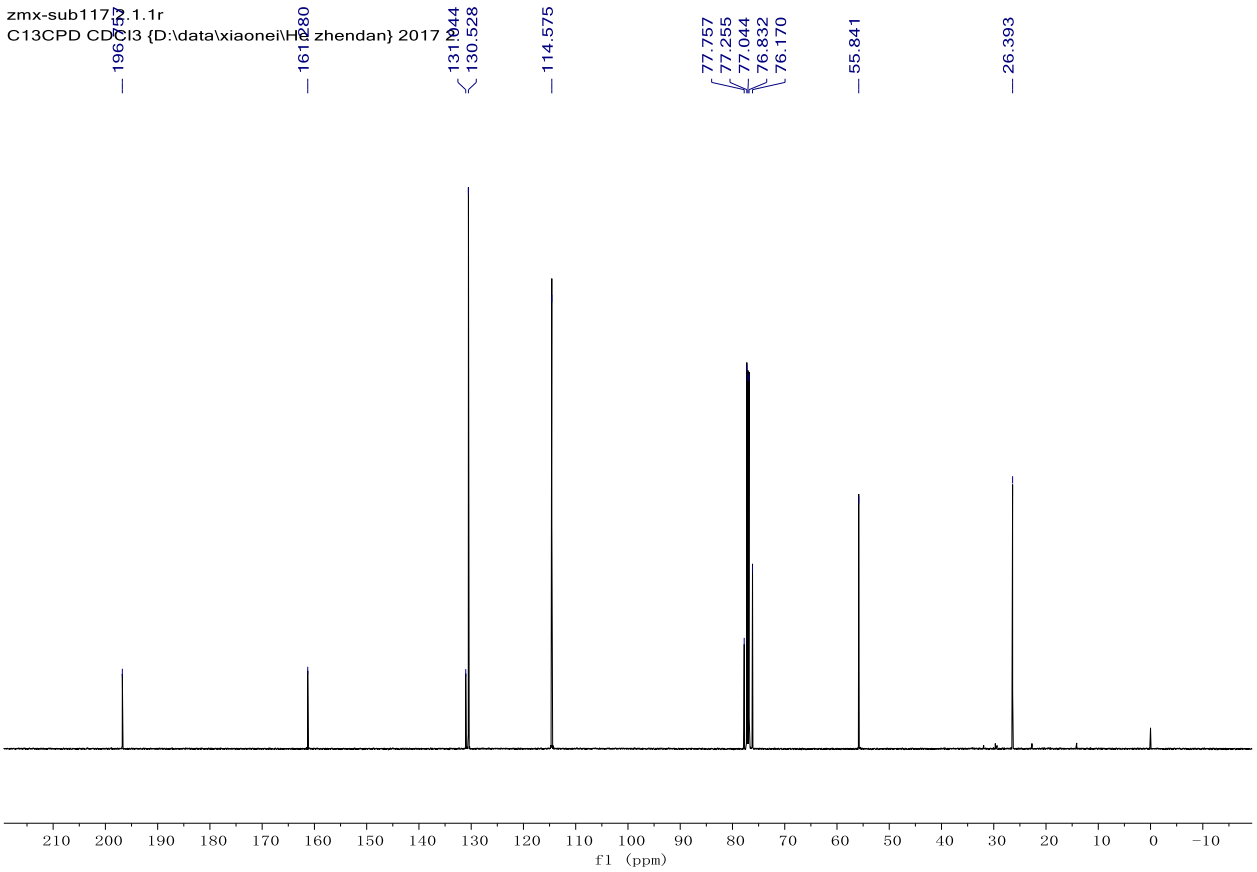
zmx-sub117.1.1.1r
PROTON CDCl3 {D:\data\xiaonei\He zhendan} 2017 2

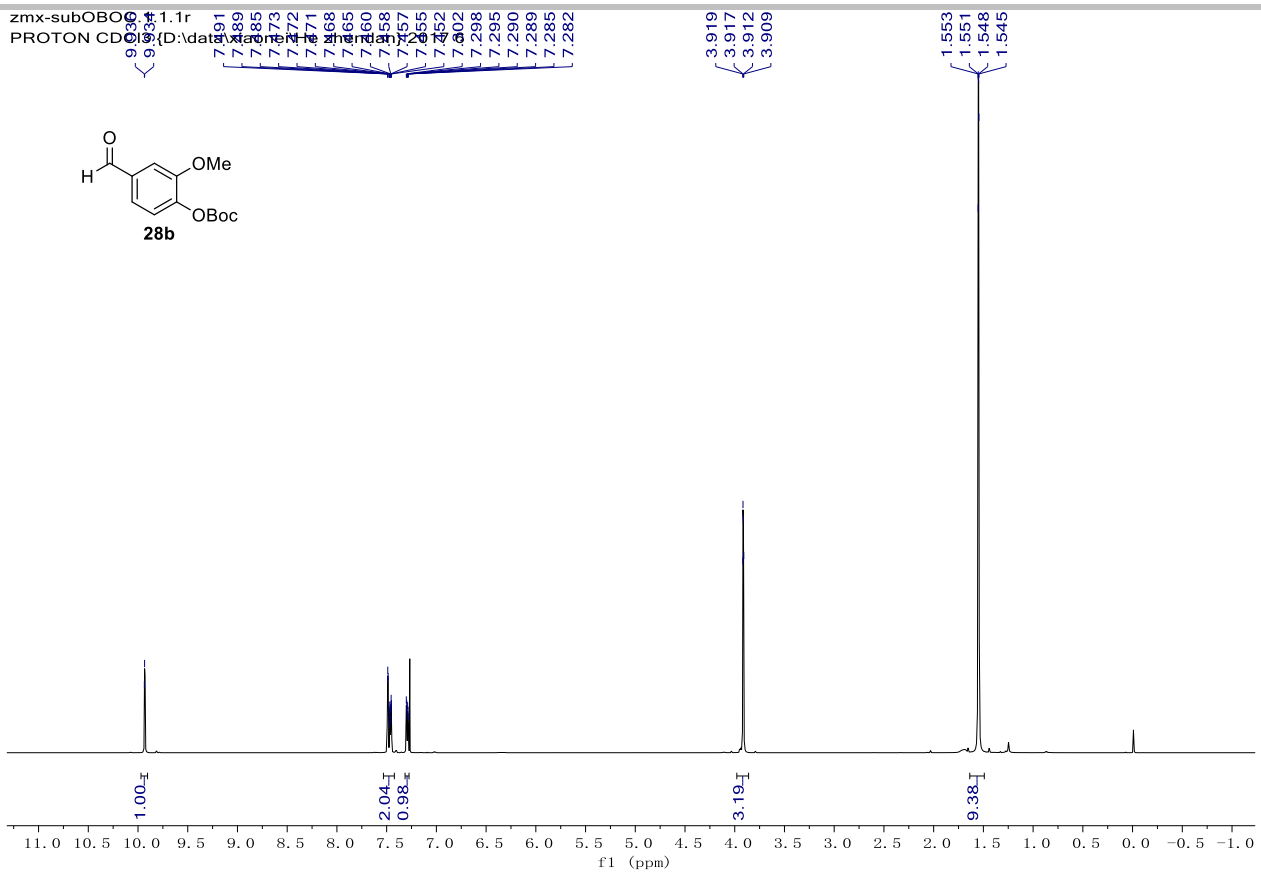


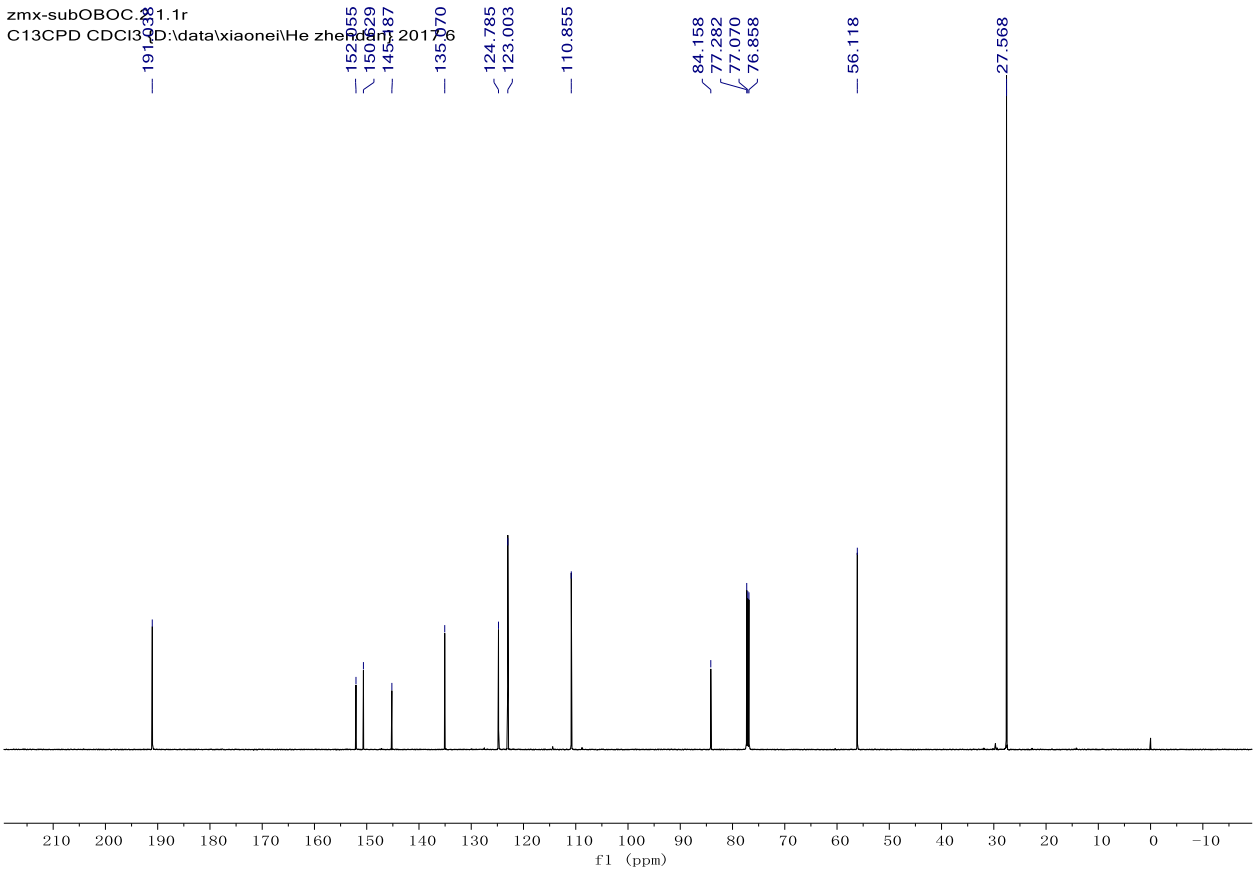
15a

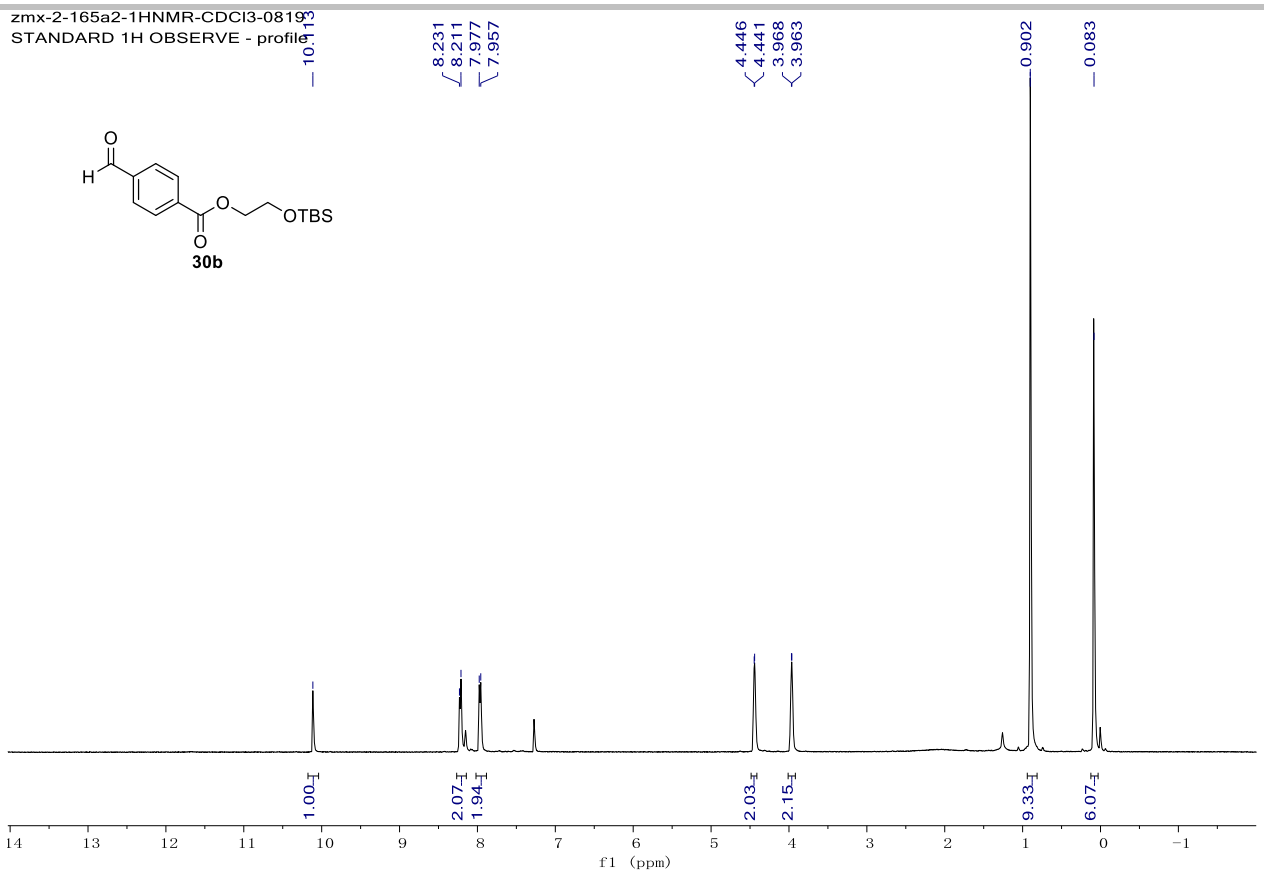


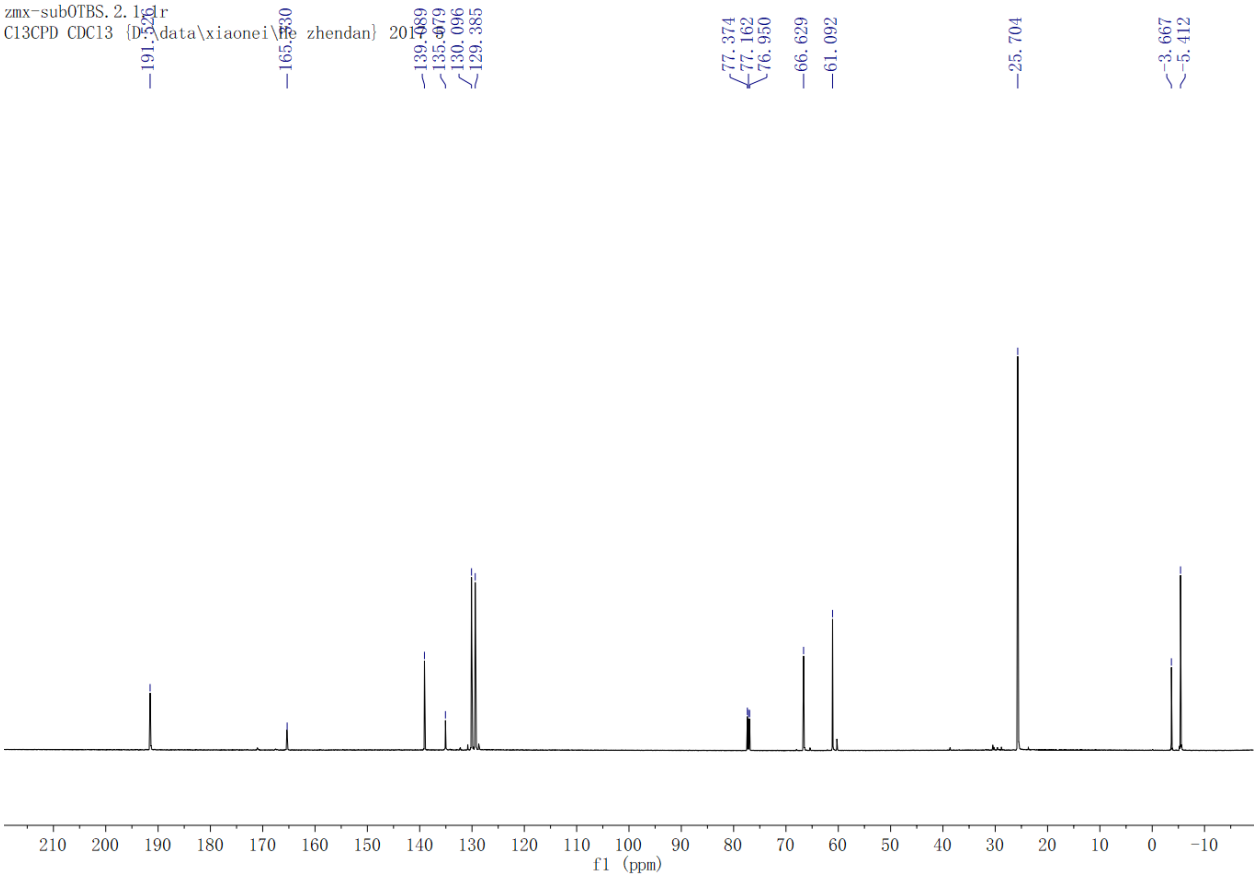
zmx-sub117.1.1.1r
C13CPD CDCl3 {D:\data\xiaonei\He zhendan} 2017 2

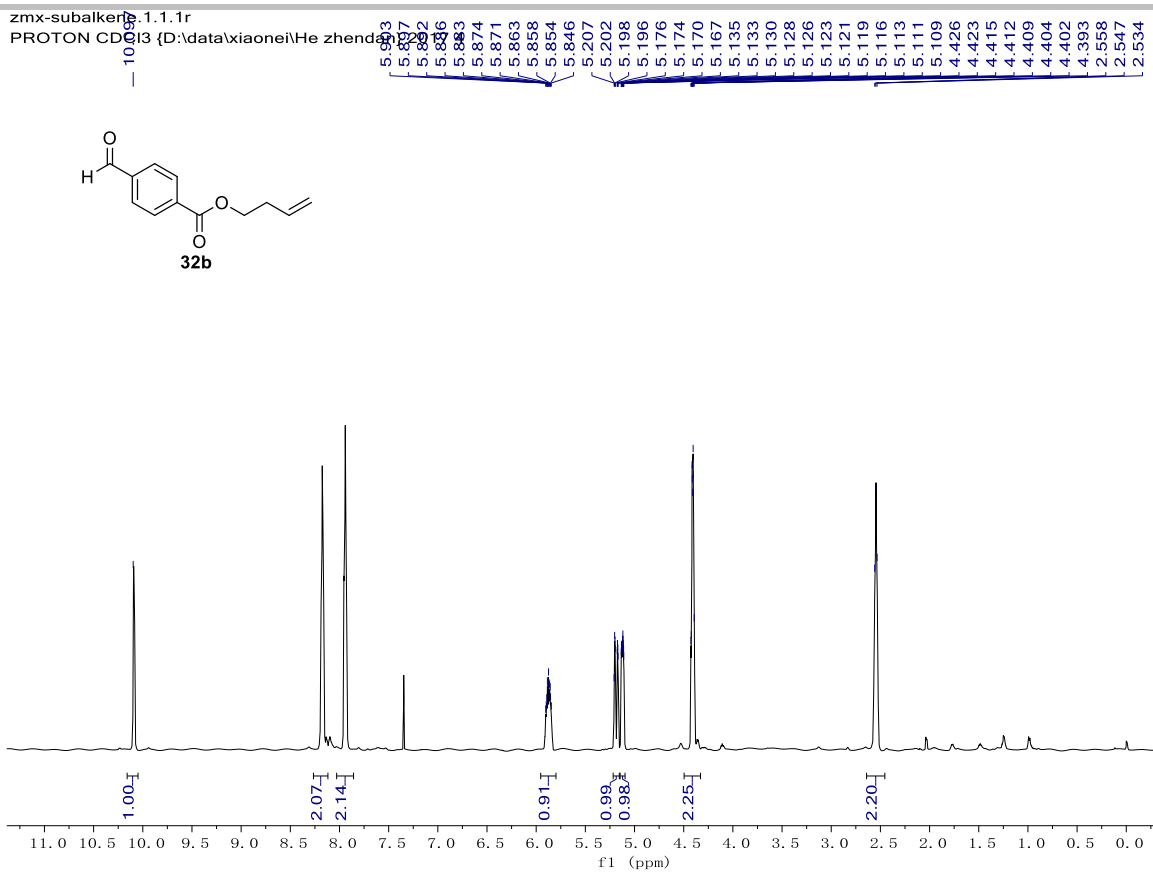



zmx-subOBOC.10.1.1r
PROTON CDCl3 {D:\data\xiaonei\He zhendan} 2017-6
9.934
9.931
7.791
7.789
7.785
7.773
7.772
7.771
7.768
7.765
7.760
7.758
7.757
7.755
7.752
7.702
7.298
7.295
7.290
7.289
7.285
7.282
3.919
3.917
3.912
3.909
1.553
1.551
1.548
1.545
O
H
OMe
OBoc
28b
1.00
2.04
0.98
3.19
9.38
f1 (ppm)

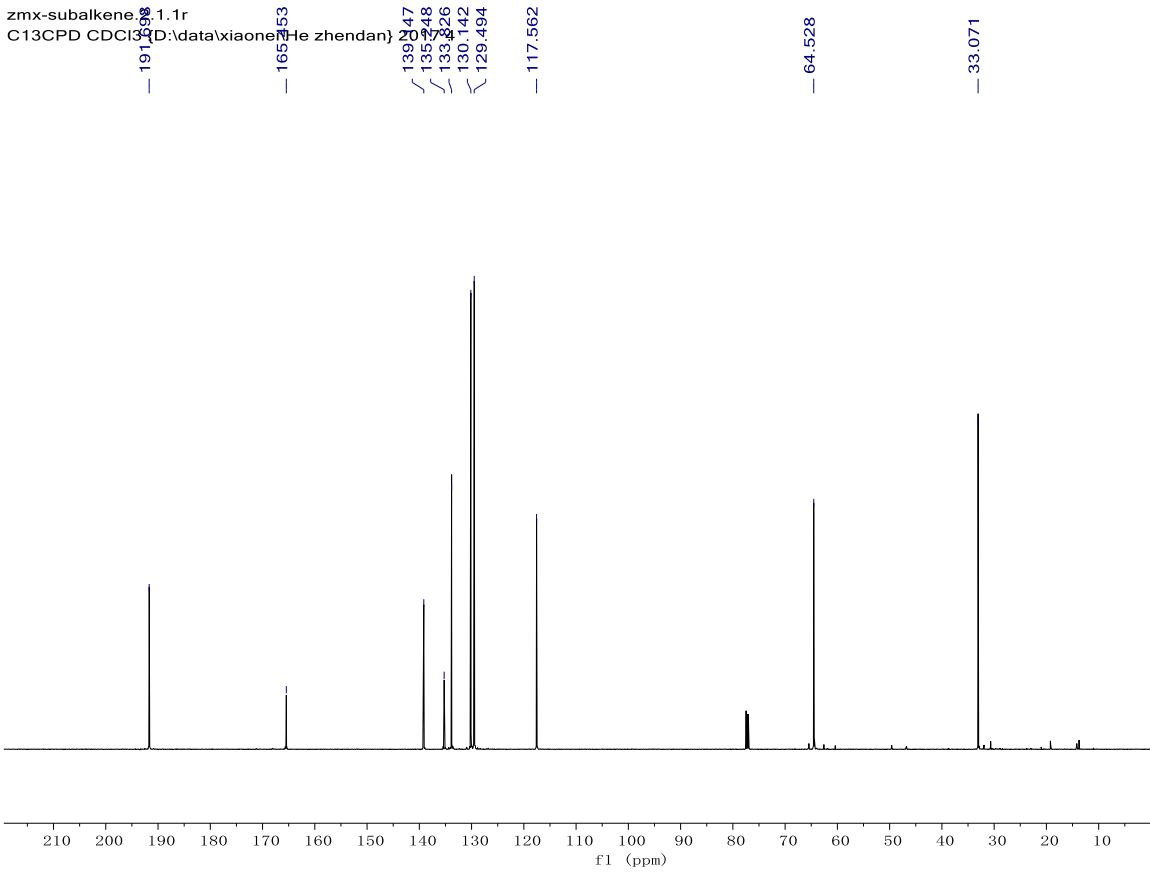

zmx-subOBOC.10.1.1r
C13CPD CDCl3 {D:\data\xiaonei\He zhendan} 2017-6
191.038
152.455
150.029
145.187
135.770
124.785
123.003
110.855
84.158
77.282
77.070
76.858
56.118
27.568
f1 (ppm)

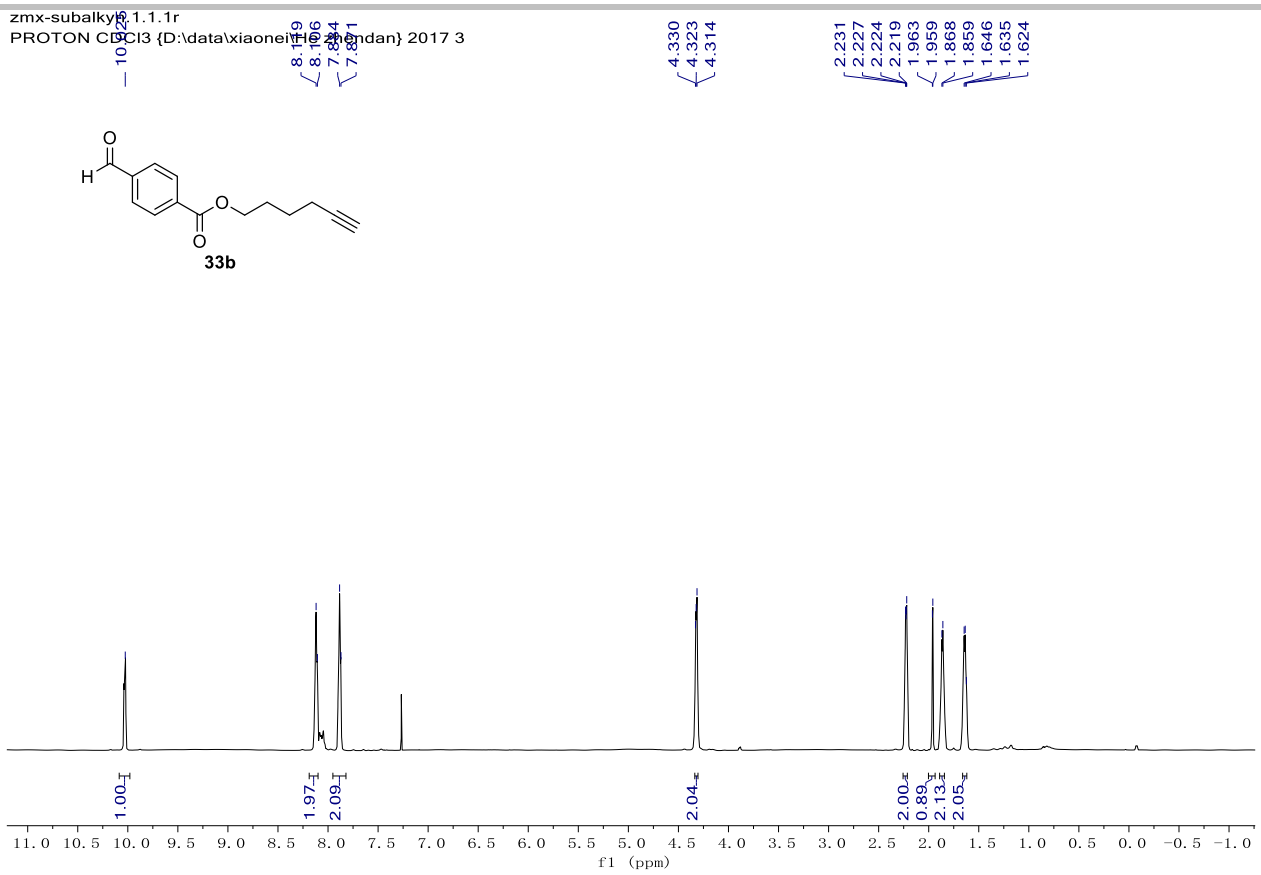

zmx-2-165a2-1HNMR-CDCl3-08192
STANDARD 1H OBSERVE - profile
10.13
8.231
8.211
7.977
7.957
4.446
4.441
3.968
3.963
0.902
0.083
O
H
O
O
OTBS
30b
1.00
2.07
1.94
2.03
2.15
9.33
6.07
f1 (ppm)

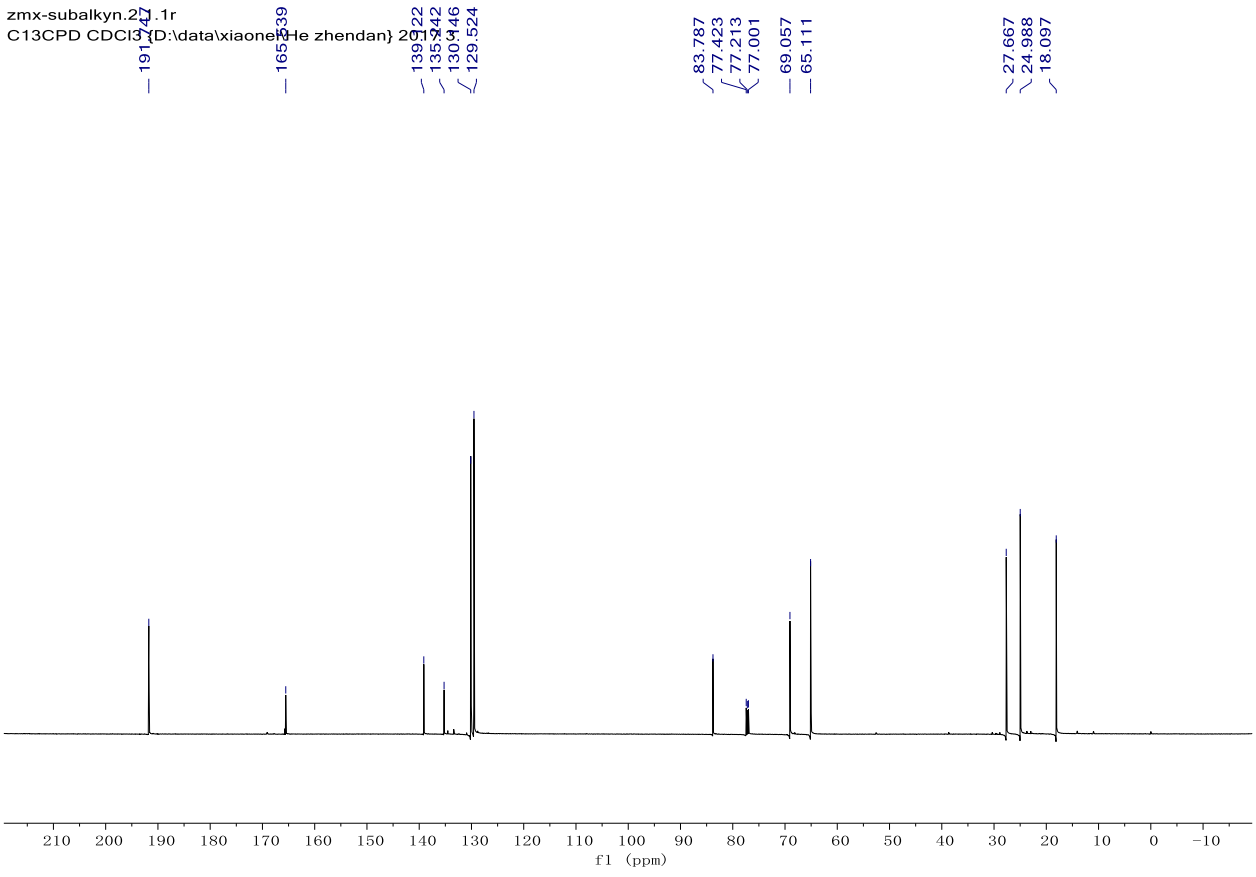

zmx-subOTBS.2.1
C13CPD CDCl3 {D:\data\xiaonei\he zhendan} 2015
191.526
165.730
139.089
135.479
130.096
129.385
77.374
77.162
76.950
66.629
61.092
25.704
-3.667
-5.412
f1 (ppm)


zmx-subalkene.1.1.1r
PROTON CDCl3 {D:\data\xiaonei\He zhendan} 2014
10.034
5.993
5.837
5.822
5.836
5.883
5.874
5.871
5.863
5.858
5.854
5.846
5.207
5.202
5.198
5.196
5.176
5.174
5.170
5.167
5.135
5.133
5.130
5.128
5.126
5.123
5.121
5.119
5.116
5.113
5.111
5.109
4.426
4.423
4.415
4.412
4.409
4.404
4.402
4.393
2.558
2.547
2.534
1.00
2.07
2.14
0.91
0.99
0.98
2.25
2.20
f1 (ppm)

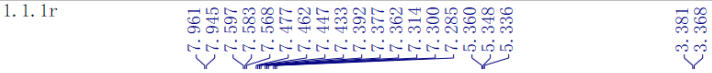
32b

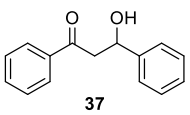

zmx-subalkene.1.1.1r
C13CPD CDCl3 {D:\data\xiaonei\He zhendan} 2014
191.298
165.153
139.447
135.348
133.426
130.142
129.494
117.562
64.528
33.071
f1 (ppm)


zmx-subalkyn.1.1.1r
PROTON CDCl3 {D:\data\xiaonei\He zhendan} 2017 3
10.026
8.119
8.106
7.884
7.881
4.330
4.323
4.314
2.231
2.227
2.224
2.219
1.963
1.959
1.868
1.859
1.646
1.635
1.624
O
H
O
O
33b
1.00
1.97
2.09
2.04
2.00
0.89
2.13
2.05
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
f1 (ppm)

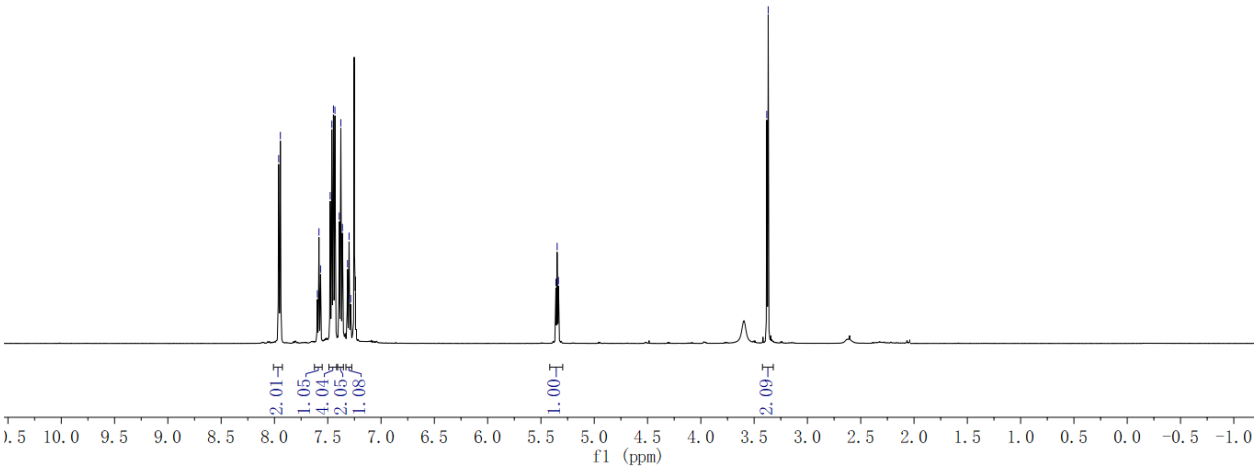

zmx-subalkyn.2.1.1r
C13CPD CDCl3 {D:\data\xiaonei\He zhendan} 2017
191.421
165.439
139.122
135.342
130.446
129.524
83.787
77.423
77.213
77.001
69.057
65.111
27.667
24.988
18.097
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

zmx-3-6.1.1.1r





37



zmx-3-6.2.1.1r