Copper-Catalyzed Beckmann-Type Fragmentation of Less-Strained Cycloketoxime Esters

(Supporting Information)

Binlin Zhao*,[a] Yukun Zheng,[a] Cheng Chen,[b] Mengning Wang, [a] Mengtao Ma,[a] Zhuangzhi Shi[b]

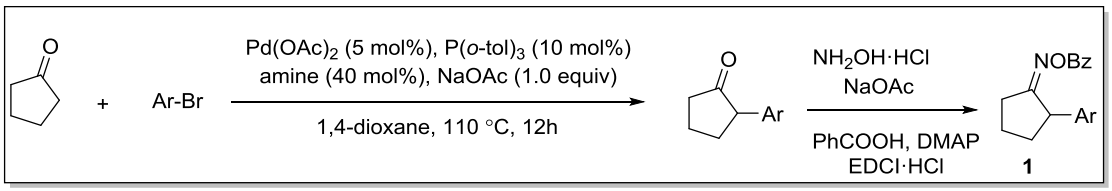
[a.]Department of Chemistry and Materials Science, College of Science, Nanjing Forestry University, Nanjing 210037, China.

[b.]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China.

1. General Information

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. All new compounds were fully characterized. NMR-spectra were recorded on Bruker ARX-400 MHz, ARX-500 MHz or ARX-600 MHz Associated. ^{1}H NMR spectra data were reported as δ values in ppm relative to chloroform (δ 7.26) if collected in $CDCl_3$. ^{13}C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.00). ^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doublet of quartets); app (apparent); br (broad). Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). All reactions were carried out in flame-dried 25-mL Schlenk tubes with Teflon screw caps under argon. $Cu(OTf)_2$ was purchased from TCI. Dry 1,4-dioxane, MeOH and DMSO were purchased from Adamas-beta. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Preparation of Cycloketoxime Esters



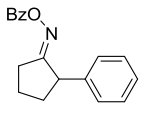
2-Arylcyclopentan-1-one *O*-benzoyl oximes were obtained from the correspounding 2-arylcyclopentanone, which were synthesized from the corresponding aryl bromide and cyclopentanone by the reported procedure[1]. The following experimental procedure is typical: flame-dried 50 mL schlenk tube filled with argon, $Pd(OAc)_2$ (56.2 mg, 0.25 mmol, 0.05 equiv), P(*o*-tol)$_3$ (152 mg, 0.5 mmol, 0.1 equiv), NaOAc (410.0

mg, 5.0 mmol, 1.0 equiv), cyclopentanones (5.0 mmol, 1.0 equiv), aryl bromides (6.5 mmol, 1.3 equiv), pyrrolidine (128.3 μL, 1.5 mmol, 0.3 equiv), 1,1,3,3-tetramethylbutylamine (250.0 μL, 1.5 mmol, 0.3 equiv) and 1,4-dioxane (25.0 mL), the tube was then sealed and heated at 110 °C under stirring for 12 hours, before cooled to room temperature. The mixture was filtered through a small plug of silica gel and eluted with ethyl acetate. The filtrate was then concentrated under vacuo and further purified by flash column chromatography to give the arylation product.

The ketone (5.30 g, 24.5 mmol) was dissolved in abs EtOH (0.25 M) and treated with NaOH (2.0 equiv) in H_2O (3.3 M) followed by hydroxylamine hydrochloride (1.5 equiv). The mixture was allowed to stir at room temperature until until the reaction was complete (TLC monitoring). The residue was diluted with water and extracted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to give the crude material, which were used in the next step without further purification.

To a solution of ketoxime in DCM (0.1 M) was added the carboxylic acid (1.5 equiv) followed by EDCI (2.5 equiv) and DMAP (10.0 mol%). The mixture was stirred at room temperature under Ar until the reaction was complete (TLC monitoring). The mixture was diluted with water and extracted with DCM. The aqueous layer was extracted with DCM and the combined organic extracts were washed with brine, dried over Na_2SO_4, the solvent was removed under vacuum and the residue was subjected to column chromatography on SiO_2 with EtOAc–hexane as an eluent to give 2-arylcyclopentan-1-one *O*-benzoyl oximes (**1**).

2-Phenylcyclopentan-1-one *O*-benzoyl oxime (1aa)[2]

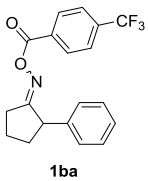


1aa

According to the general procedure, **1aa** was prepared from the commercially available cyclopentanone (5.0 mmol) as a white solid (750 mg, 53%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.33 (m, 4H), 7.26 – 7.22 (m, 1H), 4.05 (t, *J* = 7.2 Hz, 1H), 2.98 – 2.78 (m, 2H), 2.36 – 2.29 (m, 1H), 2.05 – 1.98 (m, 2H),

1.88 – 1.79 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.5, 163.7, 140.3, 133.1, 129.5, 129.1, 128.5, 128.4, 127.8, 126.7, 49.0, 34.6, 29.8, 22.4; **ATR-FTIR (cm $^{-1}$):**1746, 1290, 1211, 1058, 915; **HRMS m/z (ESI)** calcd for $C_{18}H_{17}NNaO_2$ $(M + Na)^+$ 302.1151, found 302.1151.

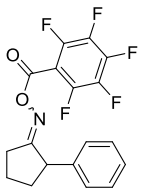
2-Phenylcyclopentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1ba)[2]



1ba

According to the general procedure, **1ba** was prepared from the commercially available cyclopentanone (5.0 mmol) as a white solid (1.0 g, 58%) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 6.6 Hz, 4H), 7.26 – 7.21 (m, 1H), 4.07 (t, *J* = 7.2 Hz, 1H), 3.01 – 2.74 (m, 2H), 2.38 – 2.29 (m, 1H), 2.13 – 1.94 (m, 2H), 1.93 – 1.79 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.2, 162.6, 140.1, 134.6 (q, *J* = 32.7 Hz), 132.5, 129.9, 128.6, 127.8, 126.9, 125.5 (q, *J* = 3.5 Hz), 123.5 (q, *J* = 272.8 Hz), 49.2, 34.7, 30.0, 22.5; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 1748, 1511, 1324, 1242, 1066, 696; **HRMS m/z (ESI)** calcd for $C_{19}H_{16}F_3NNaO_2$ $(M + Na)^+$ 370.1025, found 370.1028.

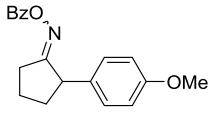
2-Phenylcyclopentan-1-one *O*-perfluorobenzoyl oxime (1ca) [2]



1ca

According to the general procedure, **1ea** was prepared from the commercially available cyclopentanone (2.0 mmol) as a brown solid (395 mg, 53%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.17 (m, 5H), 4.12 – 3.98 (m, 1H), 2.92 – 2.83 (m, 1H), 2.77 – 2.60 (m, 1H) , 2.40 – 2.29 (m, 1H) 2.09 – 1.78 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.9, 178.2, 156.7, 146.4, 142.0, 140.9, 139.6, 128.6, 128.1, 127.8, 127.0, 126.9, 126.5, 49.4, 48.6, 36.0, 34.7, 32.6, 30.4, 23.5, 22.5; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -137.11 – -137.30 (m, 2F), -148.05 – -148.26 (m, 1F), -159.93 – -160.45 (m, 2F); **ATR-FTIR (cm $^{-1}$):**1760, 1524, 1500, 1420, 1325, 1062; **HRMS m/z (ESI)** calcd for $C_{18}H_{12}F_5NNaO_2$ $(M + Na)^+$ 392.0680, found 392.0681.

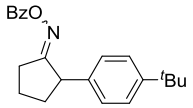
2-(4-Methoxyphenyl)cyclopentan-1-one *O*-benzoyl oxime (1ab)[3]



1ab

According to the general procedure, **1ab** was prepared from cyclopentanone (3.0 mmol) as a white solid (420.2 mg, 45%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 7.4 Hz, 1.51H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 0.5H), 6.86 (t, *J* = 8.6 Hz, 2H), 4.10 – 3.99 (m, 1H), 3.79 (s, 3H), 2.94 – 2.76 (m, 2H), 2.37 – 2.27 (m, 1H), 2.04 – 1.80 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.7, 175.9, 163.8, 158.4, 158.2, 133.8, 133.1, 132.9, 132.2, 129.5, 129.5, 129.2, 128.8, 128.4, 128.1, 128.1, 114.1, 114.0, 55.3, 55.2, 48.4, 47.7, 36.7, 34.6, 32.9, 29.8, 23.6, 22.4; **ATR-FTIR (cm $^{-1}$):** 1740, 1545, 1451, 1263, 1025, 708; **HRMS m/z (ESI)** calcd for $C_{19}H_{20}NO_3$ $(M + H)^+$ 310.1428, found 310.1432.

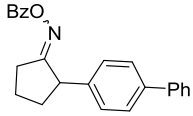
2-(4-(*tert*-Butyl)phenyl)cyclopentan-1-one *O*-benzoyl oxime (1ac)[3]



1ac

According to the general procedure, **1ac** was prepared from cyclopentanone (3.0 mmol) as a white solid (570.6 mg, 57%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 – 8.05 (m, 1H), 7.58 – 7.41 (m, 2H), 7.37 – 7.32 (m, 3H), 7.27 – 7.19 (m, 2H), 7.14 – 7.12 (m, 1H), 4.07 – 4.03 (m, 1H), 2.97 – 2.75 (m, 2H), 2.44 – 2.26 (m, 1H), 2.09 – 1.74 (m, 3H), , 1.30 (s, 4.60H), 1.29 (s, 4.40H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.8, 175.9, 163.9, 163.8, 149.5, 149.4, 138.6, 137.2, 133.1, 132.8, 129.5, 129.5, 129.3, 128.8, 128.4, 128.0, 127.5, 126.8, 125.6, 125.5, 48.6, 48.3, 36.7, 34.5, 34.4, 33.1, 31.4 31.3, 29.9, 23.8, 22.5; **ATR-FTIR (cm $^{-1}$):** 1739, 1550, 1454, 1378, 1260, 715; **HRMS m/z (ESI)** calcd for $C_{22}H_{26}NO_2$ $(M + H)^+$ 336.1958, found 336.1955.

2-([1,1'-Biphenyl]-4-yl)cyclopentan-1-one *O*-benzoyl oxime (1ad)[3]

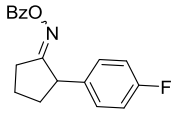


1ad

According to the general procedure, **1ad** was prepared from cyclopentanone (3.0 mmol) as a white solid (448.4 mg, 42%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.55 (m,

4.5H), 7.49 – 7.40 (m, 5.5H), 7.36 – 7.33 (m, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.17 (m, 1H), 4.18 – 4.09 (m, 1H), 3.00 – 2.79 (m, 2H), 2.50 – 2.32 (m, 1H), 2.14 – 1.80 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.6, 175.5, 163.9, 163.8, 140.9, 140.8, 140.7, 139.7, 139.5, 139.4, 133.2, 132.9, 129.6, 129.5, 128.8, 128.7, 128.5, 128.3, 128.1, 127.6, 127.5, 127.3, 127.2, 127.1, 127.0, 126.9, 48.9, 48.4, 36.7, 34.7, 33.1, 29.9, 23.8, 22.5; **ATR-FTIR (cm $^{-1}$):** 1742, 1732, 1501, 1454, 1266, 708; **HRMS m/z (ESI)** calcd for $C_{24}H_{22}NO_2$ $(M + H)^+$ 356.1645, found 356.1652.

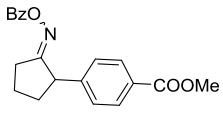
2-(4-Fluorophenyl)cyclopentan-1-one *O*-benzoyl oxime (1ae)[4]



1ae

According to the general procedure, **1ae** was prepared from cyclopentanone (3.0 mmol) as a white solid (448.4 mg, 42%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 – 8.05 (m, 2H), 7.60 – 7.56 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.04 – 7.00 (m, 2H), 4.02 (t, *J* = 7.6 Hz, 1H), 2.99 – 2.91 (m, 1H), 2.83 – 2.74 (m, 1H), 2.36 – 2.29 (m, 1H), 2.04 – 1.81 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.3, 163.8, 161.71 (d, *J* = 245.0 Hz), 135.9 (d, *J* = 2.8 Hz), 133.2, 129.5, 129.4 (d, *J* = 8.0 Hz), 129.1, 128.5, 115.4 (d, *J* = 21.4 Hz), 48.5, 34.8, 29.8, 22.4; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -116.3; **ATR-FTIR (cm $^{-1}$):** 1738, 1644, 1495, 1454, 1266, 708; **HRMS m/z (ESI)** calcd for $C_{18}H_{16}FNNaO_2$ $(M + Na)^+$ 320.1057, found 320.1060.

Methyl 4-(2-((benzoyloxy)imino)cyclopentyl)benzoate (1af)

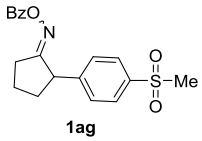


1af

According to the general procedure, **1af** was prepared from cyclopentanone (3.0 mmol) as a white solid (416.6 mg, 41%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 – 7.99 (m, 3H), 7.59 (t, *J* = 7.4 Hz, 0.5H), 7.48 – 7.36 (m, 3.5H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 4.14 (dt, *J* = 28.1, 7.7 Hz, 1H), 3.90 (s, 3H), 3.00 – 2.75 (m, 2H), 2.48 – 2.33 (m, 1H), 2.07 – 1.79 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.8, 174.9, 147.0, 145.7, 133.2, 133.1, 130.2, 129.9, 129.6, 129.3, 128.5, 128.2, 128.0, 127.2, 126.9, 52.1, 52.0, 49.1,

48.5, 36.5, 34.8, 33.0, 30.0, 23.8, 22.6; **ATR-FTIR (cm $^{-1}$):** 1738, 1635, 1505, 1464, 1260, 1110, 710; **HRMS m/z (ESI)** calcd for $C_{20}H_{20}NO_4$ $(M + H)^+$ 338.1387, found 338.1385.

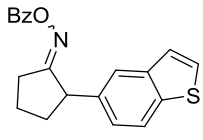
2-(4-(Methylsulfonyl)phenyl)cyclopentan-1-one *O*-benzoyl oxime (1ag)



1ag

According to the general procedure, **1ag** was prepared from cyclopentanone (3.0 mmol) as a white solid (479.8 mg, 45%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 – 8.04 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 4.14 – 4.08 (m, 1H), 3.04 (s, 3H), 3.02 – 2.98 (m, 1H), 2.89 – 2.79 (m, 1H), 2.43 – 2.39 (m, 1H), 2.08 – 1.87 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.6, 174.5, 148.0, 146.8, 139.0, 138.9, 133.4, 133.3, 129.6, 129.2, 129.1, 128.6, 128.2, 128.1, 128.0, 127.8, 127.4, 49.4, 48.5, 44.6, 44.4, 36.6, 35.2, 33.0, 30.1, 23.9, 22.7; **ATR-FTIR (cm $^{-1}$):** 1740, 1545, 1495, 1502, 1382, 1254, 723; **HRMS m/z (ESI)** calcd for $C_{19}H_{20}NO_4S$ $(M + H)^+$ 358.1108, found 358.1112.

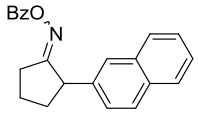
2-(3-((Benzoyloxy)imino)-1-methylcyclobutyl)ethyl acetate (1ah)[4]



1ah

According to the general procedure, **1ah** was prepared from cyclopentanone (3.0 mmol) as a white solid (489.1 mg, 49%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 – 8.06 (m, 1H), 7.84 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.77 – 7.67 (m, 1H), 7.61 – 7.56 (m, 0.5H), 7.48 – 7.42 (m, 2H), 7.38 – 7.24 (m, 3H), 7.20 (dd, *J* = 8.3, 1.7 Hz, 0.5H), 7.07 – 7.03 (m, 1H), 4.25 – 4.17 (m, 1H), 3.02 – 2.82 (m, 2H), 2.50 – 2.33 (m, 1H), 2.16 – 1.80 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.6, 175.6, 163.9, 163.8, 140.0, 139.9, 138.2, 137.9, 136.5, 133.1, 132.8, 129.6, 129.4, 129.2, 128.6, 128.5, 128.0, 127.1, 126.7, 124.4, 123.8, 123.7, 123.6, 122.9, 122.7, 122.6, 122.0, 49.1, 48.7, 37.0, 34.9, 33.1, 29.9, 23.8, 22.5; **ATR-FTIR (cm $^{-1}$):** 1741, 1738, 1595, 1454, 1254, 1035, 732; **HRMS m/z (ESI)** calcd for $C_{20}H_{17}NNaO_2S$ $(M + Na)^+$ 358.0872, found 358.0875.

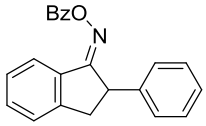
2-(Naphthalen-2-yl)cyclopentan-1-one *O*-benzoyl oxime (1ai) [4]



1ai

According to the general procedure, **1ai** was prepared from cyclopentanone (3.0 mmol) as a white solid (541.5 mg, 55%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 – 8.07 (m, 1H), 7.84 – 7.78 (m, 3H), 7.75 – 7.68 (m, 1H), 7.61 – 7.42 (m, 4H), 7.34 – 7.28 (m, 1H), 7.24 – 7.22 (m, 1H), 6.96 – 6.93 (m, 1H), 4.30 – 4.22 (m, 1H), 3.03 – 2.83 (m, 2H), 2.51 – 2.34 (m, 1H), 2.21 – 1.81 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.4, 175.4, 163.8, 163.8, 139.1, 137.7, 133.5, 133.4, 133.1, 132.8, 132.4, 132.1, 129.6, 129.3, 129.2, 128.7, 128.5, 128.5, 128.3, 127.9, 127.8, 127.6, 127.5, 127.5, 126.4, 126.3, 126.1, 126.0, 125.7, 125.6, 125.4, 36.6, 34.5, 33.1, 29.9, 23.8, 22.5; **ATR-FTIR (cm^{-1}):** 1739, 1545, 1465, 1260, 1120, 716; **HRMS m/z (ESI)** calcd for $C_{18}H_{17}NNaO_2$ $(M + Na)^+$ 352.1308, found 352.1312.

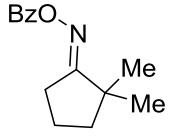
2-Phenyl-2,3-dihydro-1*H*-inden-1-one *O*-benzoyl oxime (1aj)



1aj

According to the general procedure, **1aj** was prepared from 2-phenyl-2,3-dihydro-1*H*-inden-1-one obtained from 2,3-dihydro-1*H*-inden-1-one according to the reported procedure[6] as a yellow solid (3.0 mmol scale, 420.1 mg, 43%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.43 – 7.39 (m, 2H), 7.33 – 7.11 (m, 9H), 4.58 (dd, *J* = 8.7, 3.0 Hz, 1H), 3.62 (dd, *J* = 17.2, 8.7 Hz, 1H), 2.97 (dd, *J* = 17.2, 2.9 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.4, 163.9, 148.4, 142.0, 134.5, 133.0, 132.5, 129.5, 128.9, 128.8, 128.2, 127.6, 126.9, 126.8, 125.5, 123.6, 47.0, 40.4; **ATR-FTIR (cm^{-1}):** 1740, 1545, 1502, 1265, 1145, 726; **HRMS m/z (ESI)** calcd for $C_{22}H_{17}NNaO_2$ $(M + Na)^+$ 350.1151, found 350.1152.

2,2-Dimethylcyclopentan-1-one *O*-benzoyl oxime (1ak)[5]

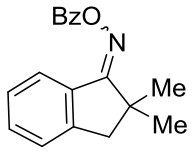


1ak

According to the general procedure, **1ak** was prepared from the corresponding 2,2-dimethylcyclopentan-1-one (2.0 mmol) as a white solid (407.9 mg, 88%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 – 8.03 (m,

2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.43 (m, 2H), 2.77 (td, *J* = 7.6, 2.1 Hz, 2H), 1.87 – 1.80 (m, 2H), 1.73 – 1.70 (m, 2H), 1.31 (s, 3H), 1.30 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.7, 163.9, 133.0, 129.5, 128.6, 128.4, 43.3, 41.0, 28.9, 26.3, 20.7; **ATR-FTIR (cm $^{-1}$):** 1741, 1595, 1460, 1262, 1152, 725; **HRMS m/z (ESI)** calcd for $C_{14}H_{18}NO_2$ $(M + H)^+$ 232.1332, found 232.1335.

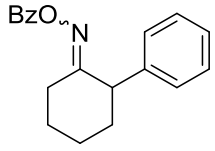
2,2-Dimethyl-2,3-dihydro-1*H*-inden-1-one *O*-benzoyl oxime (1al)



1al

According to the general procedure, **1al** was prepared from the corresponding 2,2-dimethyl-2,3-dihydro-1-inden-1-one obtained from 2,3-dihydro-1*H*-inden-1-one according to the reported procedure[7] as a white solid (3.0 mmol scale, 407.9 mg, 88%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (d, *J* = 7.9 Hz, 0.65H), 8.16 – 8.11 (m, 2H), 7.96 (d, *J* = 7.8 Hz, 0.34H), 7.65 – 7.60 (m, 1H), 7.55 – 7.42 (m, 3H), 7.37 – 7.27 (m, 2H), 3.03 (s, 0.7H), 3.01 (s, 1.3H), 1.62 (s, 2.1H), 1.48 (s, 4.0H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.4, 173.2, 164.5, 164.2, 147.7, 146.8, 134.2, 133.2, 133.1, 132.4, 132.2, 131.7, 129.8, 129.7, 129.6, 129.2, 128.7, 127.3, 126.1, 125.3, 123.8, 47.8, 46.1, 44.7, 43.6, 28.1, 26.2; **ATR-FTIR (cm $^{-1}$):** 1739, 1601, 1545, 1459, 1252, 732; **HRMS m/z (ESI)** calcd for $C_{18}H_{18}NO_2$ $(M + H)^+$ 280.1332, found 280.1333.

2-Phenylcyclohexan-1-one *O*-benzoyl oxime (1am)[5]

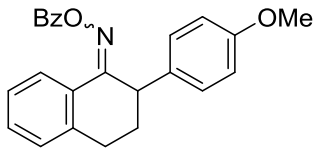


1am

According to the general procedure, **1am** was prepared from the corresponding 2-phenylcyclohexan-1-one (2.0 mmol) as a white solid (435.9 mg, 74%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 – 7.96 (m, 2H), 7.61 – 7.52 (m, 1H), 7.49 – 7.34 (m, 5H), 7.31 – 7.23 (m, 2H), 4.86 (s, 0.4H), 4.03 (t, *J* = 4.8 Hz, 0.6H), 3.04 – 2.98 (m, 0.6H), 2.74 – 2.71 (m, 0.4H), 2.54 – 2.49 (m, 1H), 2.34 – 2.24 (m, 1H), 2.11 – 1.63 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.3, 170.5, 164.2, 138.9, 138.0, 133.1, 133.1, 129.6, 128.9, 128.6, 128.5, 127.6, 127.1, 126.7, 126.6, 45.3, 39.6, 30.9, 29.4, 29.1, 26.5, 26.4, 25.3, 22.1,

20.6; **ATR-FTIR (cm^{-1}):** 1738, 1598, 1502, 1378, 1249, 1125, 726; **HRMS m/z (ESI)** calcd for $C_{19}H_{19}NNaO_2$ $(M + Na)^+$ 316.1308, found 316.1312.

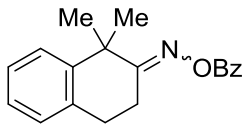
2-(4-Methoxyphenyl)-3,4-dihydronaphthalen-1(2*H*)-one *O*-benzoyl oxime (1an)



1an

According to the general procedure, **1an** was prepared from the corresponding 2-(4-methoxyphenyl)-3,4-dihydronaphthalen-1(2*H*)-one obtained from 3,4-dihydronaphthalen-1(2*H*)-one according to the reported procedure[8] as a white solid (3.0 mmol scale, 466.8 mg, 42%) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.44 – 8.42 (m, 1H), 7.77 – 7.75 (m, 2H), 7.54 – 7.50 (m, 1H), 7.41 – 7.31 (m, 4H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.84 – 6.82 (m, 2H), 4.77 (t, *J* = 4.5 Hz, 1H), 3.76 (s, 3H), 2.82 – 2.63 (m, 2H), 2.32 – 2.23 (m, 1H), 2.12 – 2.06 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.7, 163.4, 158.3, 140.8, 133.1, 132.0, 130.9, 129.6, 129.2, 129.0, 128.8, 128.3, 126.7, 126.1, 114.0, 55.2, 40.2, 30.3, 25.3; **ATR-FTIR (cm^{-1}):** 1742, 1602, 1545, 1502, 1338, 1246, 1020, 730; **HRMS m/z (ESI)** calcd for $C_{24}H_{22}NO_3$ $(M + H)^+$ 372.1594, found 372.1599.

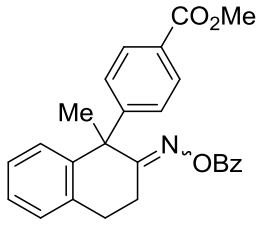
1,1-Dimethyl-3,4-dihydronaphthalen-2(1*H*)-one *O*-benzoyl oxime (1ao)



1ao

According to the general procedure, **1ao** was prepared from the corresponding 1,1-dimethyl-3,4-dihydronaphthalen-2(1*H*)-one obtained from 3,4-dihydronaphthalen-2(*1*H)-one according to the reported procedure[9] as a white solid (3.0 mmol scale, 498.9 mg, 68%)**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 – 8.08 (m, 2H), 7.61 – 7.57 (m, 1H), 7.50 – 7.43 (m, 3H), 7.30 – 7.26 (m, 1H), 7.22 – 7.15 (m, 2H), 3.07 – 3.03 (m, 4H), 1.69 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.0, 163.9, 143.0, 135.4, 133.1, 129.5, 128.5, 128.2, 127.1, 126.4, 125.2, 41.9, 27.9, 27.6, 24.2; **ATR-FTIR (cm^{-1}):** 1740, 1560, 1500, 1380, 1245, 1123, 721; **HRMS m/z (ESI)** calcd for $C_{19}H_{19}NNaO_2$ $(M + Na)^+$ 316.1308, found 316.1311.

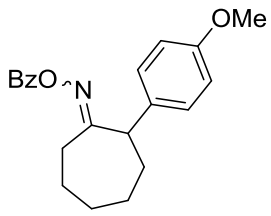
Methyl 4-(2-((benzoyloxy)imino)-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzoate (1ap)



1ap

According to the general procedure, **1ao** was prepared from the corresponding methyl 4-(1-methyl-2-*oxo*-1,2,3,4-tetrahydronaphthalen-1-yl)benzoate obtained from 3,4-dihydronaphthalen-2(*1*H)-one according to the reported procedure[8,9] as a white solid (3.0 mmol scale, 394.2 mg, 32%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.10 – 8.08 (m, 2H), 7.91 – 7.89 (m, 2H), 7.63 – 7.58 (m, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.33 (td, *J* = 7.4, 1.1 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.16 – 7.14 (m, 2H), 3.88 (s, 3H), 2.97 – 2.93 (m, 2H), 2.68 – 2.62 (m, 1H), 2.28 – 2.20 (m, 1H), 2.02 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 171.6, 166.8, 163.8, 149.7, 139.6, 138.3, 133.3, 130.0, 129.6, 129.2, 128.8, 128.6, 128.2, 127.8, 127.2, 126.5, 126.3, 52.1, 51.6, 26.5, 26.1, 25.6; **ATR-FTIR (cm^{-1}):** 1739, 1698, 1505, 1375, 1251, 1025, 732; **HRMS m/z (ESI)** calcd for $C_{26}H_{23}NNaO_4$ $(M + Na)^+$ 436.1519, found 436.1520.

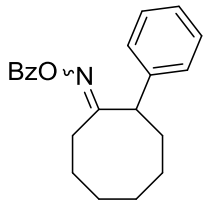
2-(4-Methoxyphenyl)cycloheptan-1-one O-benzoyl oxime (1aq)



1aq

According to the general procedure, **1aq** was prepared from the corresponding 2-(4-methoxyphenyl)cycloheptan-1-one obtained from cycloheptanone according to the reported procedure[8] as a white solid (3.0 mmol scale, 433.2 mg, 43%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.07 – 8.05 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.09 – 4.05 (m, 1H), 3.78 (s, 3H), 3.14 – 3.10 (m, 1H), 2.39 – 2.32 (m, 1H), 2.11 – 2.05 (m, 1H), 1.98 – 1.88 (m, 4H), 1.63 – 1.57 (m, 1H), 1.46 – 1.39 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.2, 164.0, 158.5, 133., 132.7, 129.5, 129.4, 128.5, 128.3, 113.9, 55.2, 47.6, 31.0, 30.8, 27.4, 26.2, 25.4; **ATR-FTIR (cm^{-1}):** 1741, 1602, 1543, 1246, 1025, 735; **HRMS m/z (ESI)** calcd for $C_{21}H_{24}NO_3$ $(M + H)^+$ 338.1751, found 338.1753.

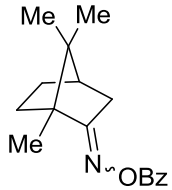
2-Phenylcyclooctan-1-one *O*-benzoyl oxime (1ar)



1ar

According to the general procedure, **1ar** was prepared from the corresponding 2-phenylcyclooctan-1-one obtained from cycloheptanone according to the reported procedure[10] as a white solid (3.0 mmol scale, 599.3 mg, 62%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 – 8.04 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 4.01 (dd, *J* = 12.7, 3.2 Hz, 1H), 2.84 (dt, *J* = 12.5, 4.2 Hz, 1H), 2.46 – 2.31 (m, 1H), 2.11 – 2.01 (m, 2H), 1.94 – 1.72 (m, 6H), 1.53 – 1.40 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.9, 163.8, 140.5, 133.1, 129.5, 129.3, 128.5, 127.4, 127.0, 48.5, 26.9, 26.8, 26.5, 26.2, 24.8; **ATR-FTIR (cm^{-1}):** 1739, 1552, 1462, 1242, 732; **HRMS m/z (ESI)** calcd for $C_{21}H_{23}NNaO_2$ $(M + Na)^+$ 344.1621, found 344.1622.

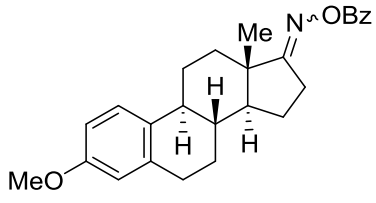
1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one *O*-benzoyl oxime (3)[5]



3

According to the general procedure, **3** was prepared from Camphor (3.0 mmol) as a white solid (672.4 mg, 83%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 – 8.03 (m, 2H), 7.58 – 7.54 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 2.75 (dt, *J* = 18.1, 3.8 Hz, 1H), 1.97 (t, *J* = 4.3 Hz, 1H), 1.91 – 1.77 (m, 3H), 1.63 – 1.57 (m, 1H), 1.32 – 1.25 (m, 1H), 1.19 (s, 3H), 0.96 (s, 3H), 0.87 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.9, 164.0, 132.9, 129.5, 129.4, 128.4, 53.2, 48.7, 43.5, 34.9, 32.4, 27.1, 19.5, 18.4, 11.0; **ATR-FTIR (cm^{-1}):** 1738, 1545, 1460, 1382, 1244, 1125, 732; **HRMS m/z (ESI)** calcd for $C_{17}H_{22}NO_2$ $(M + H)^+$ 272.1645, found 272.1646.

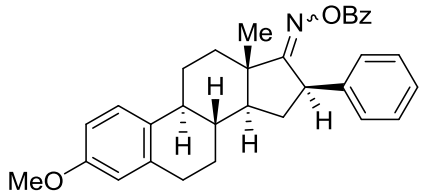
(8R,9S,13S,14S)-3-Methoxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one *O*-benzoyl oxime (8)



8

According to the general procedure, **8** was prepared from Estrone 3-methyl ether (1.0 mmol) as a white solid (307.5 mg, 76%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 – 8.05 (m, 2H), 7.60 – 7.56 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.65 (d, *J* = 2.6 Hz, 1H), 3.79 (s, 3H), 2.92 – 2.75 (m, 4H), 2.46 – 2.31 (m, 3H), 2.00 – 1.95 (m, 2H), 1.86 – 1.70 (m, 2H), 1.60 – 1.44 (m, 4H), 1.09 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.5, 164.0, 157.6, 137.6, 133.0, 132.0, 129.5, 128.4, 126.4, 113.9, 111.5, 55.2, 52.8, 45.6, 43.8, 38.2, 33.7, 29.6, 27.3, 27.2, 26.1, 22.8, 17.1; **ATR-FTIR (cm^{-1}):** 1740, 1542, 1464, 1376, 1227, 1012, 752; **HRMS m/z (ESI)** calcd for $C_{26}H_{29}NNaO_2$ $(M + Na)^+$ 426.2040, found 426.2043.

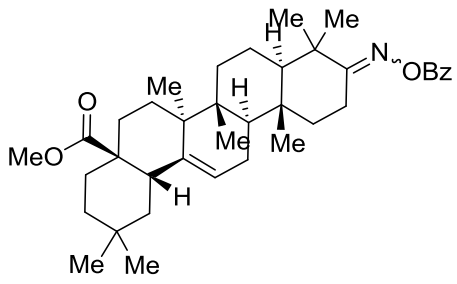
(8R,9S,13S,14S)-3-Methoxy-13-methyl-16-phenyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one *O*-benzoyl oxime (9)



9

According to the general procedure, **9** was prepared from (8R,9S,13S,14S)-3-methoxy-13-methyl-16-phenyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one obtained from Estrone 3-methyl ether according to the reported procedure[8] as a white solid (2.0 mmol scale, 394.3 mg, 41%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.40 (m, 1H), 7.35 – 7.30 (m, 4H), 7.26 – 7.18 (m, 6H), 6.74 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 4.26 – 4.22 (m, 1H), 3.79 (s, 3H), 2.89 – 2.87 (m, 2H), 2.54 – 2.34 (m, 4H), 1.97 – 1.90 (m, 2H), 1.71 – 1.58 (m, 5H), 1.51 – 1.46 (m, 1H), 1.27 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.4, 163.8, 157.6, 141.1, 137.6, 132.7, 132.0, 129.4, 129.0, 128.6, 128.1, 127.1, 126.3, 113.8, 111.5, 55.2, 51.6, 48.4, 46.3, 43.8, 37.8, 34.8, 34.3, 29.6, 27.2, 26.2, 16.8; **ATR-FTIR (cm^{-1}):** 1740, 1542, 1464, 1376, 1227, 1012, 752; **HRMS m/z (ESI)** calcd for $C_{32}H_{34}NO_3$ $(M + H)^+$ 480.2533, found 480.2536.

Methyl (4aS,6aS,6bR,8aR,12aR,12bR,14bS)-10-((benzoyloxy)imino)-2,2,6a,6b,9,9,12a-heptamethyl-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2*H*)-carboxylate (12)

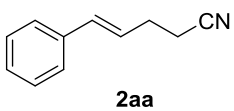


9

According to the general procedure, **12** was prepared from methyl (4aS,6aS,6bR,8aR,12aR,12bR,14bS)-2,2,6a,6b,9,9,12a-heptamethyl-10-oxo-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2*H*)-carboxylate obtained from Oleanic acid according to the reported procedure[11] as a white solid (2.0 mmol scale, 926.4 mg, 79%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 – 8.04 (m, 2H), 7.59 – 7.55 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.29 (t, *J* = 3.4 Hz, 1H), 3.63 (s, 3H), 3.08 – 3.02 (m, 1H), 2.86 (dd, *J* = 13.8, 4.2 Hz, 1H), 2.48 – 2.40 (m, 1H), 2.00 – 1.86 (m, 3H), 1.81 – 1.75 (m, 2H), 1.69 – 1.58 (m, 9H), 1.54 – 1.47 (m, 4H), 1.35 (s, 3H), 1.20 (s, 3H), 1.16 – 1.15 (m, 1H), 1.12 (s, 3H), 1.09 – 0.08 (m, 1H), 1.05 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H), 0.77 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.2, 176.2, 164.2, 144.0, 133.0, 129.7, 129.5, 128.4, 122.0, 55.8, 51.5, 47.1, 46.7, 45.8, 41.7, 41.6, 41.3, 39.3, 38.7, 37.0, 33.8, 33.1, 32.3, 30.7, 27.6, 27.2, 26.9, 25.8, 23.6, 23.5, 23.2, 23.0, 19.9, 19.0, 16.8, 15.1; **ATR-FTIR (cm^{-1}):** 1739, 1465, 1383, 1246, 1035, 702; **HRMS m/z (ESI)** calcd for $C_{38}H_{54}NO_4$ $(M + H)^+$ 588.4047, found 588.4050.

3. Experimental Procedures and Characterization of Products

(*E*)-5-Phenylpent-4-enenitrile (2aa)[12]

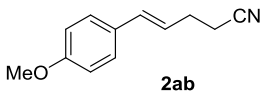


2aa

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1aa** (55.8 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under

vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to afford 25.9 mg (83%) of **2aa** as a yellow oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 – 7.23 (m, 4H), 7.19 – 7.15 (m, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.11 (dt, *J* = 15.8, 6.7 Hz, 1H), 2.52 – 2.40 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.5, 132.9, 128.5, 127.6, 126.2, 125.4, 119.1, 28.7, 17.5; **ATR-FTIR (cm $^{-1}$):** 3005, 2925, 2247, 1605, 1545, 1510, 1255, 766; **HRMS m/z (ESI)** calcd for $C_{11}H_{12}N$ $(M + H)^+$ 158.0964, found 158.0968.

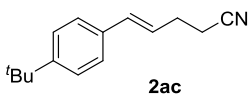
(*E*)-5-(4-methoxyphenyl)pent-4-enenitrile (2ab)



2ab

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ab** (61.9 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to afford 32.5 mg (87%) of **2ab** as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.04 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.80 (s, 3H), 2.56 – 2.46 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.2, 132.2, 129.3, 127.4, 123.2, 119.2, 113.9, 55.2, 28.7, 17.6; **ATR-FTIR (cm $^{-1}$):** 2927, 2248, 1596, 1540, 1510, 1246, 1025, 760; **HRMS m/z (ESI)** calcd for $C_{12}H_{14}NO$ $(M + H)^+$ 188.1070, found 188.1072.

(*E*)-5-(4-(*tert*-Butyl)phenyl)pent-4-enenitrile (2ac)

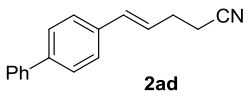


2ac

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ac** (67.1 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly.

The crude product was purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to afford 33.1 mg (78%) of **2ac** as a colorless oil: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.37 – 7.31 (m, 4H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.8, 6.7 Hz, 1H), 2.57 – 2.49 (m, 4H), 1.33 (s, 9H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 150.9, 133.9, 132.7, 126.0, 125.6, 124.7, 119.3, 34.6, 31.3, 28.9, 17.7; **ATR-FTIR (cm $^{-1}$):** 2925, 2247, 1598, 1515, 1498, 1338, 1246, 763; **HRMS m/z (ESI)** calcd for $C_{15}H_{20}N$ $(M + H)^+$ 214.1590, found 214.1593.

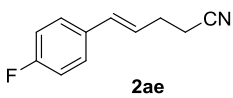
(*E*)-5-([1,1'-Biphenyl]-4-yl)pent-4-enenitrile (2ad)



2ad

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ad** (71.2 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to afford 35.3 mg (76%) of **2ad** as a white solid: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 – 7.56 (m, 4H), 7.47 – 7.44 (m, 4H), 7.38 – 7.34 (m, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.8, 6.7 Hz, 1H), 2.62 – 2.50 (m, 4H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 140.5, 140.4, 135.5, 132.5, 128.8, 127.3, 127.2, 126.9, 126.7, 125.5, 119.1, 28.8, 17.5; **ATR-FTIR (cm $^{-1}$):** 2925, 2247, 1596, 1506, 1450, 1265, 1238, 760; **HRMS m/z (ESI)** calcd for $C_{17}H_{16}N$ $(M + H)^+$ 234.1277, found 234.1281.

(*E*)-5-(4-Fluorophenyl)pent-4-enenitrile (2ae)

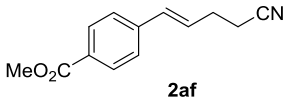


2ae

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ae** (59.5 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude

product was purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to afford 25.2 mg (72%) of **2ae** as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.30 (m, 2H), 7.02 – 6.97 (m, 2H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8, 6.6 Hz, 1H), 2.57 – 2.48 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.3 (d, *J* = 246.9 Hz), 132.7, 131.8, 127.73 (d, *J* = 8.0 Hz), 125.17 (d, *J* = 2.2 Hz), 119.1, 115.4 (d, *J* = 21.7 Hz), 28.7, 17.5; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -114.3; **ATR-FTIR (cm $^{-1}$):** 2928, 2249, 1595, 1510, 1465, 1264, 1229, 755; **HRMS m/z (ESI)** calcd for $C_{11}H_{11}FN$ $(M + H)^+$ 176.0870, found 176.0875.

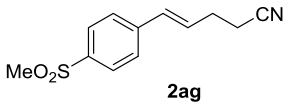
Methyl (*E*)-4-(4-cyanobut-1-en-1-yl)benzoate (2af)



2af

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1af** (67.5 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10 : 1) to afford 32.7 mg (76%) of **2af** as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.90 (s, 3H), 2.61 – 2.50 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.8, 140.9, 133.5, 132.1, 129.9, 128.2, 126.1, 118.9, 52.0, 28.7, 17.3; **ATR-FTIR (cm $^{-1}$):** 3005, 2928, 2247, 1721, 1610, 1591, 1506, 1460, 1260, 1025, 748; **HRMS m/z (ESI)** calcd for $C_{13}H_{14}NO_2$ $(M + H)^+$ 216.1019, found 216.1022.

(*E*)-5-(4-(Methylsulfonyl)phenyl)pent-4-enenitrile (2ag)

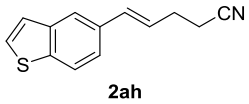


2ag

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ag** (71.5 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was

then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 3 : 1) to afford 33.2 mg (71%) of **2ag** as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.36 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.04 (s, 3H), 2.63 – 2.52 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.9, 139.1, 131.3, 129.8, 127.7, 127.0, 118.8, 44.5, 28.7, 17.2; **ATR-FTIR (cm $^{-1}$):** 3010, 2931, 2248, 1605, 1595, 1506, 1465, 1235, 762; **HRMS m/z (ESI)** calcd for $C_{12}H_{14}NO_2S$ $(M + H)^+$ 236.0740, found 236.0742.

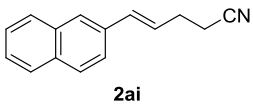
(*E*)-5-(Benzo[*b*]thiophen-5-yl)pent-4-enenitrile (2ah)



2ah

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ah** (67.1 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10 : 1) to afford 27.8 mg (65%) of **2ah** as a yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 1.4 Hz, 1H), 7.44 (d, *J* = 5.4 Hz, 1H), 7.40 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.31 (dd, *J* = 5.4, 0.5 Hz, 1H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.7, 6.7 Hz, 1H), 2.63 – 2.51 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.0, 139.0, 133.0, 127.0, 125.1, 123.9, 122.5, 122.3, 121.6, 119.2, 28.8, 17.6; **ATR-FTIR (cm $^{-1}$):** 3005, 2927, 2246, 1596, 1510, 1460, 1220, 758; **HRMS m/z (ESI)** calcd for $C_{13}H_{12}NS$ $(M + H)^+$ 214.0685, found 214.0688.

(*E*)-5-(Naphthalen-2-yl)pent-4-enenitrile (2ai)

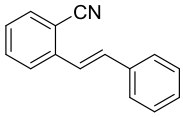


2ai

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ai** (65.8 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed

mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to afford 22.8 mg (54%) of **2ai** as a white solid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 – 7.79 (m, 3H), 7.72 (s, 1H), 7.58 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.50 – 7.43 (m, 2H), 6.68 (d, *J* = 15.8 Hz, 1H), 6.31 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.64 – 2.59 (m, 2H), 2.55 – 2.51 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.0, 133.5, 133.0, 128.2, 127.9, 127.6, 126.3, 126.2, 125.9, 125.8, 123.3, 119.2, 28.9, 17.5; **ATR-FTIR (cm $^{-1}$):** 3010, 2928, 2247, 1605, 1556, 1503, 1446, 1138, 762; **HRMS m/z (ESI)** calcd for $C_{15}H_{14}N$ $(M + H)^+$ 208.1121, found 208.1123.

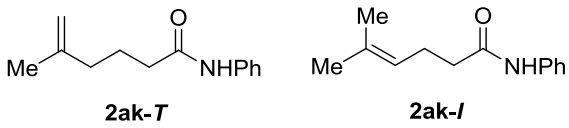
(*E*)-2-Styrylbenzonitrile (2aj)



2aj

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ai** (65.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to afford 37.5 mg (92%) of **2ai** as a yellow oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.57 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.52 – 7.48 (m, 3H), 7.38 (d, *J* = 16.2 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.27 – 7.18 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.5, 136.1, 133.3, 133.1, 132.7, 128.8, 128.7, 127.5, 127.1, 125.2, 124.0, 118.0, 111.2; **ATR-FTIR (cm $^{-1}$):** 3006, 2248, 1601, 1596, 1500, 1465, 753; **HRMS m/z (ESI)** calcd for $C_{15}H_{14}N$ $(M + H)^+$ 206.0964, found 206.0968.

5-Methyl-*N*-phenylhex-5-enamide (2ak-*T*) and 5-Methyl-*N*-phenylhex-4-enamide (2ak-*I*)

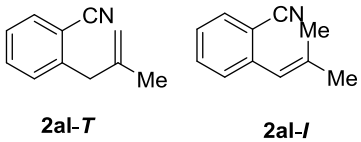


2ak-*T* **2ak-*I***

T : *I* = 8 : 1

1) Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ak** (46.2 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. **2)** The obtained crude product was dissolved in EtOH (5 mL) and a solution of NaOH (25%) (2 mL) was added. The resulting cloudy reaction mixture was stirred at reflux under Ar for 48 h. Then the biphasic mixture was cooled to rt and acidified to pH = 1 by careful addition of conc HCl. The mixture was extracted with Et_2O (15 mL * 3) and the combined organic phases were dried with $MgSO_4$, filtered and evaporated in vacuo affording a crude carboxylic acid product that was used without further purification. **3)** The carboxylic acid (0.2 mmol) was dissolved in CH_2Cl_2 (2 mL) and the reaction mixture was cooled to 0 ℃, before EDCI•HCl (1.35 equiv) was added, followed by DMAP (10 mol%), aniline (0.2 mol) and NEt_3 (1.5 equiv). The reaction mixture was allowed to warm to room temperature and stirred for 14 h, after which saturated NH_4Cl was added to the reaction mixture was extracted with CH_2Cl_2(15 mL * 3) and the combined organic phases were dried with MgSO4, filtered and evaporated in vacuo. The crude reaction mixture was purified by flash column chromatography on silica gel (PE : EA = 2 : 1) to afford 25.7 mg (63%) of **2ak** as a yellow solid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (br s, 1H), 7.53 – 7.49 (m, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.14 (d, *J* = 5.8 Hz, 0.8H), 4.75 (s, 0.1H), 4.70 (s, 0.1H), 2.42 – 2.31 (m, 4H), 1.70 (s, 3H), 1.63 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.2, 138.0, 133.6, 128.9, 126.6, 124.1, 122.5, 119.8, 110.7, 57.2, 37.6, 32.2, 30.7, 25.9, 24.2, 17.7; **ATR-FTIR (cm $^{-1}$):** 3345, 2928, 1688, 1596, 1506, 1465, 1230, 1025, 746; **HRMS m/z (ESI)** calcd for $C_{13}H_{18}NO$ $(M + H)^+$ 204.1383, found 204.1386.

2-(2-Methylallyl)benzonitrile (2al-*T*) and 2-(2-Methylprop-1-en-1-yl)benzonitrile (2al-*I*)

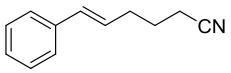


2al-*T* **2al-*I***

T : *I* = 2.3 : 1

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1al** (55.8 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to afford 20.5 mg (65%) of **2al** as a yellow oil: **^{1}H NMR (400 MHz, $CDCl_3$, *T*)** δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.36 – 7.25 (m, 2H), 4.89 (s, 1H), 4.69 (s, 1H), 3.55 (s, 2H), 1.74 (s, 3H); **^{1}H NMR (400 MHz, $CDCl_3$, *I*)** δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.36 – 7.25 (m, 2H), 6.44 (s, 1H), 1.97 (d, *J* = 1.3 Hz, 3H), 1.81 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.5, 143.0, 142.3, 140.4, 132.8, 132.6, 132.1, 130.0, 129.7, 126.8, 126.3, 121.6, 113.2, 42.5, 26.5, 22.2, 19.6; **ATR-FTIR (cm^{-1}):** 3005, 2248, 1598, 1556, 1505, 1380, 1265, 752; **HRMS m/z (ESI)** calcd for $C_{11}H_{12}N$ $(M + H)^+$ 158.0964, found 158.0966.

(*E*)-6-Phenylhex-5-enenitrile (2am)[13]

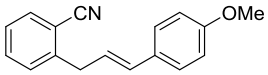


2am

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1am** (58.6 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to afford 19.4 mg (57%) of **2am** as a yellow oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.28 (m, 4H), 7.25 – 7.20 (m, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.17 – 6.08 (m, 1H), 2.43 – 2.35 (m, 4H), 1.90 – 1.80 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.1, 132.0,

128.6, 127.6, 127.3, 126.0, 119.5, 31.7, 25.0, 16.4; **ATR-FTIR (cm $^{-1}$):**2929, 2247, 1652, 1541, 1508, 1457, 743; **HRMS m/z (ESI)** calcd for $C_{12}H_{13}NNa$ $(M + Na)^+$ 194.0940, found 194.0936.

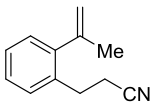
(*E*)-2-(3-(4-Methoxyphenyl)allyl)benzonitrile (2an)



2an

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1an** (74.2 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10 : 1) to afford 30.5 mg (61 %) of **2an** as a yellow oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.53 (td, *J* = 7.7, 1.3 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.28 (m, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.17 (dt, *J* = 15.7, 7.0 Hz, 1H), 3.80 (s, 3H), 3.75 (d, *J* = 6.9 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.1, 144.3, 132.9, 132.8, 131.9, 129.7, 129.6, 127.3, 126.7, 124.2, 118.0, 113.9, 112.4, 55.2, 37.7; **ATR-FTIR (cm $^{-1}$):**3002, 2996, 2248, 1602, 1545, 1500, 1460, 1379, 1056, 751; **HRMS m/z (ESI)** calcd for $C_{17}H_{16}NO$ $(M + H)^+$ 250.1226, found 250.1230.

3-(2-(Prop-1-en-2-yl)phenyl)propanenitrile (2ao)

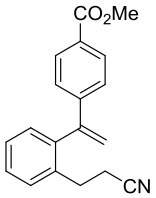


2ao

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ao** (58.6 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to afford 21.3 mg (62 %) of **2ao** as a yellow oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.19 – 7.14 (m,

1H), 7.08 – 7.05 (m, 1H), 5.18 – 5.16 (m, 1H), 4.79 – 4.78 (m, 1H), 2.93 (t, *J* = 7.7 Hz, 2H), 2.51 (t, *J* = 7.7 Hz, 2H), 1.99 – 1.98 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.8, 143.7, 134.5, 129.0, 128.5, 127.4, 127.2, 119.3, 115.7, 28.8, 25.2, 19.1; **ATR-FTIR (cm $^{-1}$):** 3008, 2989, 2246, 1596, 1542, 1515, 1465, 1383, 1246, 762; **HRMS m/z (ESI)** calcd for $C_{12}H_{13}NNa$ $(M + Na)^+$ 194.0940, found 194.0942.

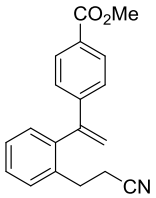
Methyl 4-(1-(2-(2-cyanoethyl)phenyl)vinyl)benzoate (2ap)



2ap

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ap** (82.7 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10 : 1) to afford 45.9 mg (79 %) of **2ap** as a yellow oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.25 (m, 6H), 5.93 (d, *J* = 0.9 Hz, 1H), 5.37 (d, *J* = 0.9 Hz, 1H), 3.90 (s, 3H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.6, 147.6, 144.5, 140.6, 135.8, 130.7, 129.9, 129.6, 129.4, 128.5, 127.5, 126.2, 118.9, 117.9, 52.1, 29.0, 18.2; **ATR-FTIR (cm $^{-1}$):** 3010, 2985, 2247, 1689, 1605, 1546, 1501, 1464, 1375, 1235, 1025, 752; **HRMS m/z (ESI)** calcd for $C_{19}H_{18}NO_2$ $(M + H)^+$ 292.1332, found 292.1333.

Methyl 4-(1-(2-(2-cyanoethyl)phenyl)vinyl)benzoate (2ap)

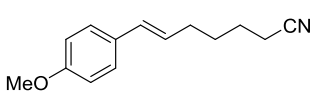


2ap

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ap** (82.7 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel

(PE : EA = 10 : 1) to afford 45.9 mg (79 %) of **2ap** as a yellow oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.25 (m, 6H), 5.93 (d, *J* = 0.9 Hz, 1H), 5.37 (d, *J* = 0.9 Hz, 1H), 3.90 (s, 3H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.6, 147.6, 144.5, 140.6, 135.8, 130.7, 129.9, 129.6, 129.4, 128.5, 127.5, 126.2, 118.9, 117.9, 52.1, 29.0, 18.2; **ATR-FTIR (cm $^{-1}$):** 3010, 2985, 2247, 1689, 1605, 1546, 1501, 1464, 1375, 1235, 1025, 752; **HRMS m/z (ESI)** calcd for $C_{19}H_{18}NO_2$ $(M + H)^+$ 292.1332, found 292.1333.

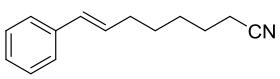
(*E*)-7-(4-Methoxyphenyl)hept-6-enenitrile (2aq)



2aq

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1aq** (67.5 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10 : 1) to afford 32.1 mg (75 %) of **2aq** as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.03 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.80 (s, 3H), 2.36 (t, *J* = 7.0 Hz, 2H), 2.26 – 2.21 (m, 2H), 1.73 – 1.68 (m, 2H), 1.65 – 1.61 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.7, 131.9, 130.0, 127.1, 127.0, 119.6, 113.9, 55.2, 31.9, 28.3, 24.7, 16.9; **ATR-FTIR (cm $^{-1}$):** 2989, 2248, 1600, 1553, 1509, 1466, 1383, 1246, 1015, 756; **HRMS m/z (ESI)** calcd for $C_{14}H_{18}NO$ $(M + H)^+$ 216.1383, found 216.1388.

(*E*)-8-Phenyloct-7-enenitrile (2ar)

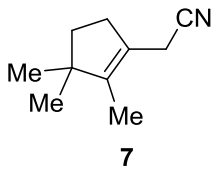


2ar

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1ar** (64.2 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by

TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to afford 26.9 mg (68 %) of **2ar** as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.28 (m, 4H), 7.22 – 7.18 (m, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.35 (t, *J* = 7.1 Hz, 2H), 2.26 – 2.21 (m, 2H), 1.72 – 1.66 (m, 2H), 1.55 – 1.50 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.6, 130.2, 130.1, 128.5, 126.9, 125.9, 119.7, 32.6, 28.4, 28.1, 25.2, 17.1; **ATR-FTIR (cm $^{-1}$):** 3005, 2986, 2247, 1595, 1546, 1502, 1458, 1376, 1244, 753; **HRMS m/z (ESI)** calcd for $C_{14}H_{17}NNa$ $(M + Na)^+$ 222.1253, found 222.1256.

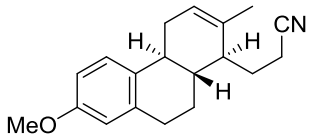
2-(2,3,3-Trimethylcyclopent-1-en-1-yl)acetonitrile (7)[14]



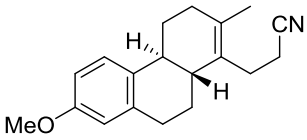
7

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **3** (54.2 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to afford 23.4 mg (79 %) of **7** as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.08 (s, 2H), 2.35 – 2.33 (m, 2H), 1.70 – 1.67 (m, 2H), 1.54 (s, 3H), 0.98 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.7, 121.5, 117.8, 47.2, 38.3, 32.4, 26.2, 17.4, 9.6; **ATR-FTIR (cm $^{-1}$):** 3005, 2986, 2247, 1246, 732; **HRMS m/z (ESI)** calcd for $C_{10}H_{16}N$ $(M + H)^+$ 150.1277, found 150.1276.

3-((1S,4aS,10aS)-7-Methoxy-2-methyl-1,4,4a,9,10,10a-hexahydrophenanthren-1-yl)propanenitrile (10-*L*) and 3-((4aS,10aR)-7-Methoxy-2-methyl-3,4,4a,9,10,10a-hexahydrophenanthren-1-yl)propanenitrile (10-*R*)



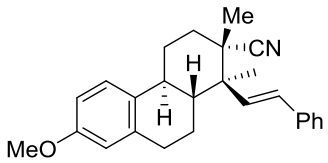
10-*L*



10-*R*

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **8** (80.6 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to afford 49.6 mg (79 %) of **10** as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$-*L*)** δ 7.24 – 7.15 (m, 1H), 6.74 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.67 – 6.62 (m, 1H), 5.74 (d, *J* = 6.2 Hz, 1H), 3.79 (s, 3H), 2.96 – 2.92 (m, 2H), 2.88 – 2.42 (m, 3H), 2.40 – 2.05 (m, 5H), 1.90 – 1.82 (m, 1H), 1.72 (s, 3H), 1.50 – 1.32 (m, 2H); **^{1}H NMR (400 MHz, $CDCl_3$-*R*)** δ 7.24 – 7.15 (m, 1H), 6.74 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.67 – 6.62 (m, 1H), 3.79 (s, 3H), 2.96 – 2.92 (m, 2H), 2.88 – 2.42 (m, 4H), 2.40 – 2.05 (m, 5H), 1.90 – 1.82 (m, 1H), 1.72 (s, 3H), 1.50 – 1.32 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.6, 157.5, 137.7, 137.6, 133.3, 132.7, 131.7, 131.5, 128.0 127.3, 126.1, 125.7, 120.4, 119.6, 113.5, 113.3, 112.1, 111.4, 55.2, 44.2, 43.3, 41.0, 40.6, 39.1, 38.5, 32.8, 31.6, 30.3, 30.0, 27.4, 27.0, 24.9, 24.3, 21.2, 19.6, 16.4, 11.9; **ATR-FTIR (cm $^{-1}$):** 3003, 2988, 2248, 1605, 1596, 1546, 1505, 1378, 1240, 1025, 755; **HRMS m/z (ESI)** calcd for $C_{19}H_{23}NNaO$ $(M + Na)^+$ 304.1672, found 304.1677.

(1S,2S,4aS,10aR)-7-Methoxy-1,2-dimethyl-1-((*E*)-styryl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-2-carbonitrile (11)

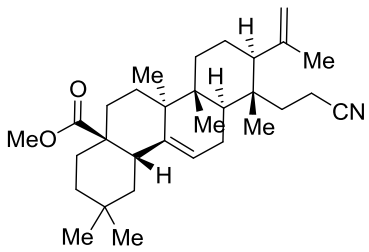


11

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **9** (95.8 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room

temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10 : 1) to afford 63.8 mg (89 %) of **11** as a white solid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.34 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.66 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.55 (d, *J* = 2.6 Hz, 1H), 5.93 (dd, *J* = 15.8, 9.6 Hz, 1H), 3.69 (s, 3H), 2.76 – 2.73 (m, 2H), 2.35 – 2.27 (m, 3H), 2.13 – 2.07 (m, 2H), 1.96 – 1.91 (m, 1H), 1.43 – 1.35 (m, 2H), 1.30 (s, 3H), 1.28 – 1.24 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.8, 137.8, 136.7, 134.8, 130.9, 128.5, 127.6, 127.5, 126.4, 126.2, 125.2, 113.6, 111.8, 55.2, 52.6, 42.2, 38.2, 37.8, 37.0, 29.8, 27.8, 24.8, 17.2; **ATR-FTIR (cm $^{-1}$):** 3003, 2988, 2248, 1605, 1596, 1546, 1505, 1378, 1240, 1025, 755; **HRMS m/z (ESI)** calcd for $C_{26}H_{30}NO$ $(M + H)^+$ 372.2322, found 372.2325.

Methyl (1S,2S,4aR,4bS,6aS,10aS,12aR)-1-(2-cyanoethyl)-1,4a,4b,9,9-pentamethyl-2-(prop-1-en-2-yl)-1,3,4,4a,4b,5,6,7,8,9,10,10a,12,12a-tetradecahydrochrysene-6a(2*H*)-carboxylate (13)

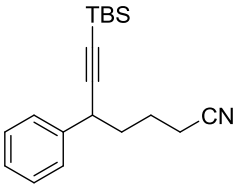


13

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **12** (117.6 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 130 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10 : 1) to afford 82.8 mg (89 %) of **13** as a white solid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.29 (t, *J* = 3.4 Hz, 1H), 4.88 (s, 1H), 4.64 (s, 1H), 3.61 (s, 3H), 2.87 (dd, *J* = 13.8, 3.9 Hz, 1H), 2.38 – 2.16 (m, 2H), 1.99 – 1.87 (m, 3H), 1.80 – 1.75 (m, 2H), 1.73 (s, 3H), 1.69 – 1.66 (m, 2H), 1.62 – 1.57 (m, 3H), 1.49 – 1.35 (m, 4H), 1.33 – 1.24 (m, 3H), 1.20 – 1.17 (m, 1H), 1.13 (s, 3H), 1.11 – 1.03 (m, 2H), 0.92 (s, 3H), 0.91 (s, 3H), 0.89 (s, 3H), 0.77 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.2,

146.8, 144.0, 121.6, 120.2, 114.1, 51.5, 50.6, 46.6, 45.7, 42.1, 41.3, 39.4, 39.0, 37.8, 34.4, 33.8, 33.0, 32.3, 31.2, 30.6, 27.6, 25.7, 24.1, 23.6, 23.5, 22.9, 19.0, 16.9, 11.5; **ATR-FTIR (cm $^{-1}$):** 3008, 2985, 2247, 1686, 1465, 1378, 1246, 1012, 732; **HRMS m/z (ESI)** calcd for $C_{31}H_{47}NNaO_2$ $(M + Na)^+$ 488.3499, found 488.3508.

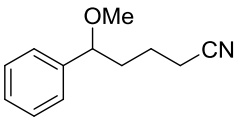
7-(*tert*-Butyldimethylsilyl)-5-phenylhept-6-ynenitrile (15)



15

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1aa** (55.8 mg, 0.2 mmol), alkynyl sulfone[15] (84.1 mg, 0.3 mmol), Zn-Cu couple (2.6 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 80 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to afford 29.1 mg (49 %) of **15** as a yellow oil: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.31 (m, 4H), 7.27 – 7.23 (m, 1H), 3.74 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.36 (t, *J* = 6.9 Hz, 2H), 2.38 – 1.78 (m, 4H), 0.96 (s, 9H), 0.12 (d, *J* = 1.5 Hz, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.7, 128.6, 127.3, 127.0, 119.4, 107.3, 86.6, 38.0, 37.2, 26.1, 23.0, 16.9, -4.5; **ATR-FTIR (cm $^{-1}$):** 2992, 2247, 2103, 1452, 1383, 1245, 1125, 750; **HRMS m/z (ESI)** calcd for $C_{19}H_{27}NNaSi$ $(M + Na)^+$ 320.1805, found 320.1802.

5-Methoxy-5-phenylpentanenitrile (16)

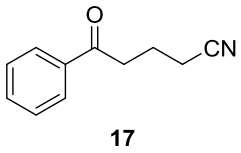


16

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1aa** (55.8 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry MeOH (1.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10 : 1) to afford (22.6 mg, 60 %) of **16** as a colorless oil: **^{1}H NMR (500 MHz, $CDCl_3$)**

δ 7.35 (t, *J* = 7.3 Hz, 2H), 7.30 – 7.26 (m, 3H), 4.13 (dd, *J* = 7.6, 4.3 Hz, 1H), 3.20 (s, 3H), 2.39 – 2.28 (m, 2H), 1.94 – 1.86 (m, 1H), 1.82 – 1.75 (m, 2H), 1.75 – 1.63 (m, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.3, 128.5, 127.8, 126.4, 119.6, 82.9, 56.6, 36.9, 21.9, 17.0; **ATR-FTIR (cm $^{-1}$):** 2985, 2246, 1598, 1545, 1378, 1246, 1145, 1025, 745; **HRMS m/z (ESI)** calcd for $C_{12}H_{16}NO$ $(M + H)^+$ 190.1226, found 190.1225.

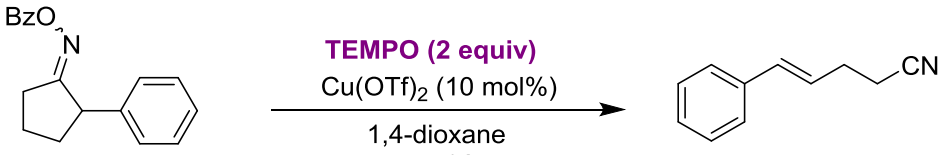
5-*oxo*-5-phenylpentanenitrile (17)



17

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1aa** (55.8 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry DMSO (1.0 mL) were added under Ar. The formed mixture was stirred at 80 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 7 : 1) to afford (19.1 mg, 60 %) of **17** as a colorless oil: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.11 (p, *J* = 6.9 Hz, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 198.1, 136.3, 133.4, 128.7, 127.9, 119.4, 36.3, 19.6, 16.6; **ATR-FTIR (cm $^{-1}$):** 1684, 1597, 1580, 1449, 1374, 1235, 1058, 756; **HRMS m/z (ESI)** calcd for $C_{11}H_{11}NNaO$ $(M + Na)^+$ 196.0733, found 196.0732.

4. Mechanistic Experiments

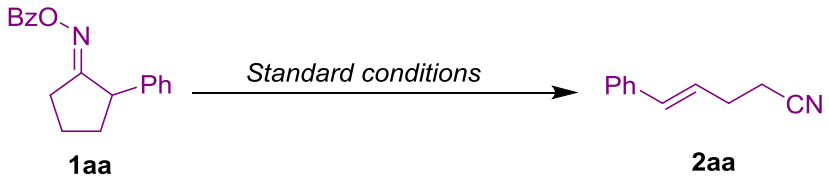


1aa **2aa**, ND

Flame-dried 25 mL Schlenk tube filled with argon, cycloketoxime ester **1aa** (55.8 mg, 0.2 mmol), TEMPO (62.5 mg, 0.4 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), absolute dry 1, 4-dioxane (1.0 mL) were added under Ar. The formed mixture was stirred at 100

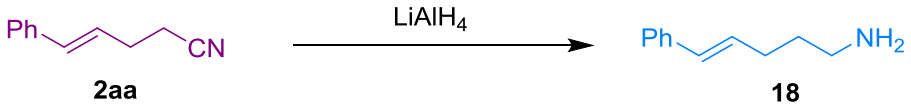
℃ under Ar for 12 h. The resulting mixture was analysed by GC-MS, and no desired product **2aa** was detected, which indicated that a radical intermediate was involved in this catalytic cycle.

5. Synthetic Application



1aa **2aa**

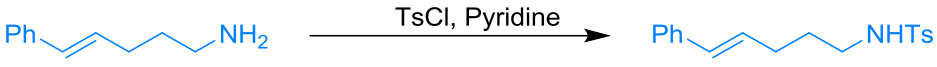
Flame-dried 50 mL Schlenk tube filled with argon, cycloketoxime ester **1aa** (700.0 mg, 2.5 mmol), $Cu(OTf)_2$ (90.0 mg, 10 mol%), absolute dry 1, 4-dioxane (13.0 mL) were added under Ar. The formed mixture was stirred at 100 ℃ under Ar for 12 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to afford 306.9 mg (78%) of **2aa** as a yellow oil.



2aa **18**

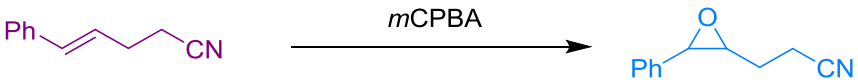
A flame dried Schlenk equipped with a sirrer bar and a reflux condenser is charged with $LiAlH_4$ (22.8 mg, 0.6 mmol), Et_2O (2.0 mL) is added carefully and the mixture is cooled to 0 ℃ with an external ice/water cooling bath. **2aa** (31.4 mg, 0.2 mmol) dissolved in Et_2O (0.5 mL) and added carefully to the $LiAlH_4$ suspension. The mixture is heated to reflux for 2 h and cooled to 0 ℃ afterwards. A solution of NaOH (10% in water) is added carefully until a white solid precipitates. After filtration over Na_2SO4 and evaporation of the solvent, **18** is obtained in quantitive yields as a yellow oil:**^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.7, 6.9 Hz, 1H), 2.75 (t, *J* = 7.0 Hz, 2H), 2.26 (q, *J* = 7.3 Hz, 2H), 1.63 (p, *J* = 7.3 Hz, 2H), 1.33 (br s, 2H); **^{13}C**

NMR (151 MHz, $CDCl_3$) δ 137.4, 130.1, 129.8, 128.2, 126.6, 125.7, 41.5, 33.1, 30.1. The spectroscopic data matched those reported in the literature.[16]



18 **20**

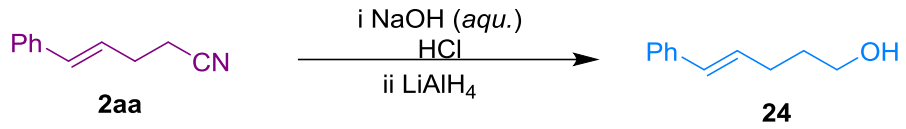
The prepared **18** (0.2 mmol) was dissolved in pyrdine (2.0 mL) and the respective tosyl chloride (0.3 mmol, 57.2 mg) is added at 0 ℃. The solution stirred overnight at room temperature. CH_2Cl_2 is added, and the mixture is washed three times with a hydrochloride solution (10% HCI in water). The organic layer is dried over Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was then purified by flash chromatography on silica gel (PE : EA=5 :1) to afford 50.5 mg (80%) of **20** as a colorless oil: **^{1}H NMR (600 MHz,$CDCl_3$)** δ 7.76 (d, *J* = 8.3 Hz, 1H), 7.29 – 7.28 (m, 6H), 7.21 – 7.18 (m, 1H), 6.35 – 6.28 (m, 1H), 6.08 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.86 – 4.82 (m, 1H), 2.99 (q, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 2.24 – 2.16 (m, 2H), 1.65 (p, *J* = 7.1 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 143.1, 137.1, 136.7, 130.7, 129.4, 128.7, 128.2, 126.8, 126.8, 125.7, 42.3, 29.5, 28.9, 21.2. The spectroscopic data matched those reported in the literature.[17]



2aa (±)-**22**

To a stirred solution of the **2aa** (31.4 mg, 0.2 mmol) in CH_2Cl_2 (1.5 mL) was added $NaHCO_3$ (50.4 mg, 0.6 mmol,) then *m*-CPBA (85wt%, 60.9 mg, 0.3 mmol) in one portion at room temperature, and the resulting white slurry was stirred, which was monitored by TLC analysis. The mixture was then cooled to 0 ℃ in an ice bath and 5% w/v aq. Na_2SO_3 (1.5 mL) was added in one portion. The biphasic mixture was stirred at 0 ℃ for 5 min, then at room temperature for 15 min, then the layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated. The residue was purified

by flash chromatography (PE : EA = 7 : 1) to afford 28.4 mg (82%) of (±)-**22** as a yellow oil: **^{1}H NMR (600 MHz,CDCl$_3$)** 7.32 – 7.27 (m, 3H), 7.26 – 7.20 (m, 2H), 3.69 (d, *J* = 2.1 Hz, 1H), 3.03 (t, *J* = 2.1 Hz, 1H), 2.50 (dd, *J* = 6.4, 1.7 Hz, 2H), 2.14 – 2.05 (m, 1H), 1.91 (dd, *J* = 13.9, 6.8 Hz, 1H).; **^{13}C NMR (151 MHz, CDCl$_3$)** δ 136.2, 128.3, 128.2, 125.3, 118.6, 60.1, 58.2, 28.0, 13.6. The spectroscopic data matched those reported in the literature.[18]



A solution of **2aa** (31.4 mg, 0 .2 mmol) and 25% aqueous sodium hydroxide (1.5 mL) in methanol (4.5 mL) was stirred at reflux for 16 h. The reaction mixture was cooled to room temperature. Water and EtOAc was added to the reaction mixture, and the two layers were separated. The pH of the aqueous layer was adjusted to 3 with 10% HCl, and the product was extracted with EtOAc. The organic layer was washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was used for the next step without further purification.

$LiAlH_4$ (0.24 mmol, 9.1 mg) was suspended in dry diethyl ether (2.0 mL) and an solution of carboxylie acid generated above in Et_2O was added dropwise while cooling the reaction in an ice bath. The reaction mixture was stirred at room temperature for 3 h, 10% HCl was added to the reaction mixture to acidity soltion, stirred for 2 h. The two layers were separated and the aqueous layer was extracted with ether. The combined organic layers were washed with saturated $NaHCO_3$, and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the product was purified by flash chromatography on silica gel (PE : EA = 3 : 1) to afford 21.1 mg (65%) of **24** as a colourless oil: **^{1}H NMR (600 MHz,CDCl$_3$)** δ 7.38 – 7.28 (m, 4H), 7.21 (d, *J* = 7.2 Hz, 1H), 6.48 – 6.39 (m, 1H), 6.24 (d, *J* = 15.8 Hz, 1H), 3.72 (t, *J* = 6.5 Hz, 2H), 2.34 – 2.30 (m, 2H), 1.81 – 1.71 (m, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 137.4, 130.2, 129.8, 128.3, 126.7, 125.7, 62.2, 32.0, 29.1. The spectroscopic data matched those reported in the literature.[19]

6. References

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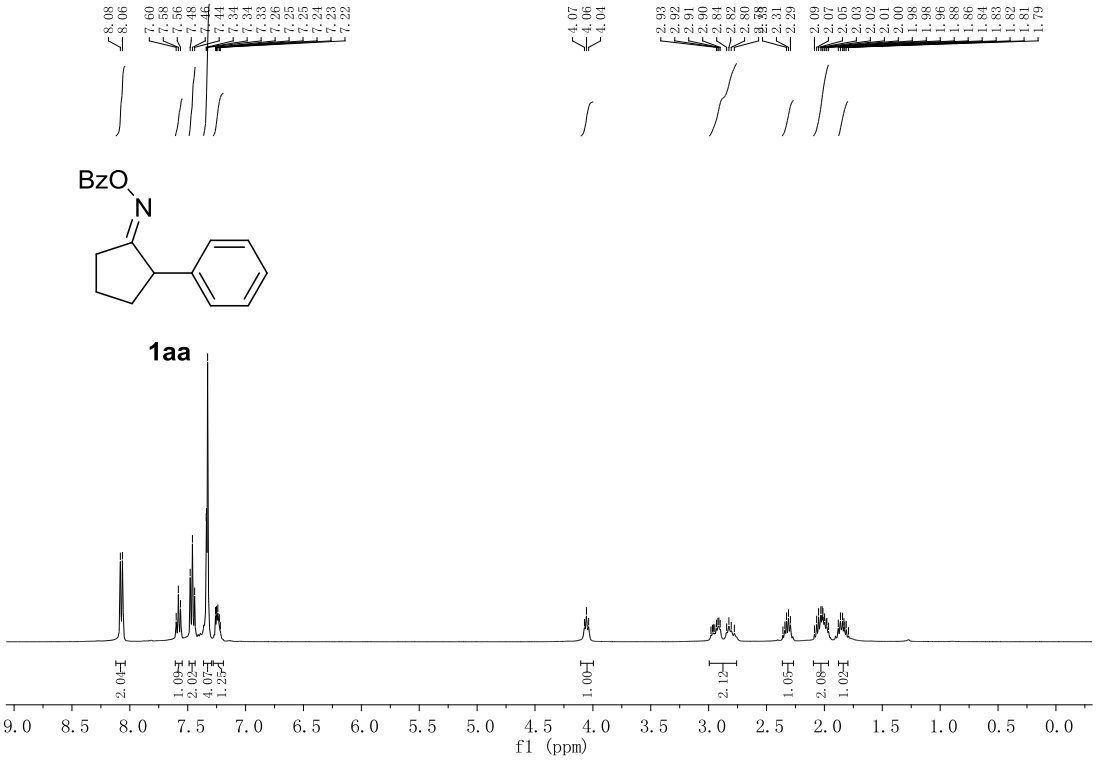
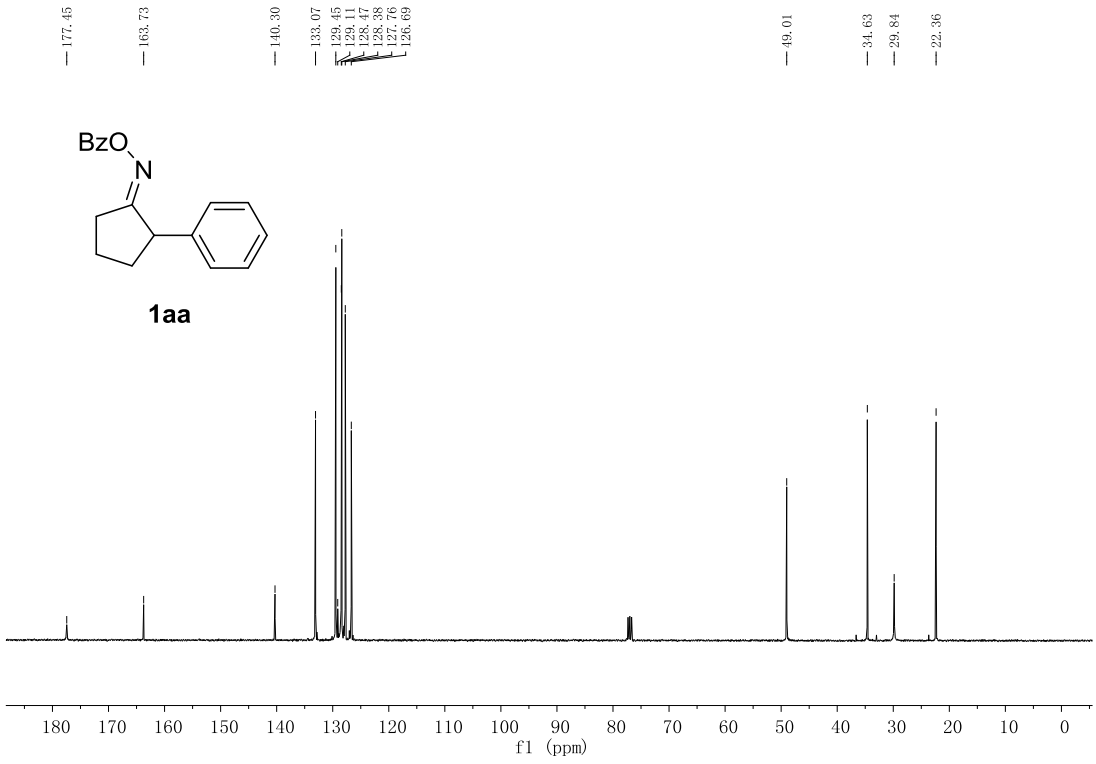
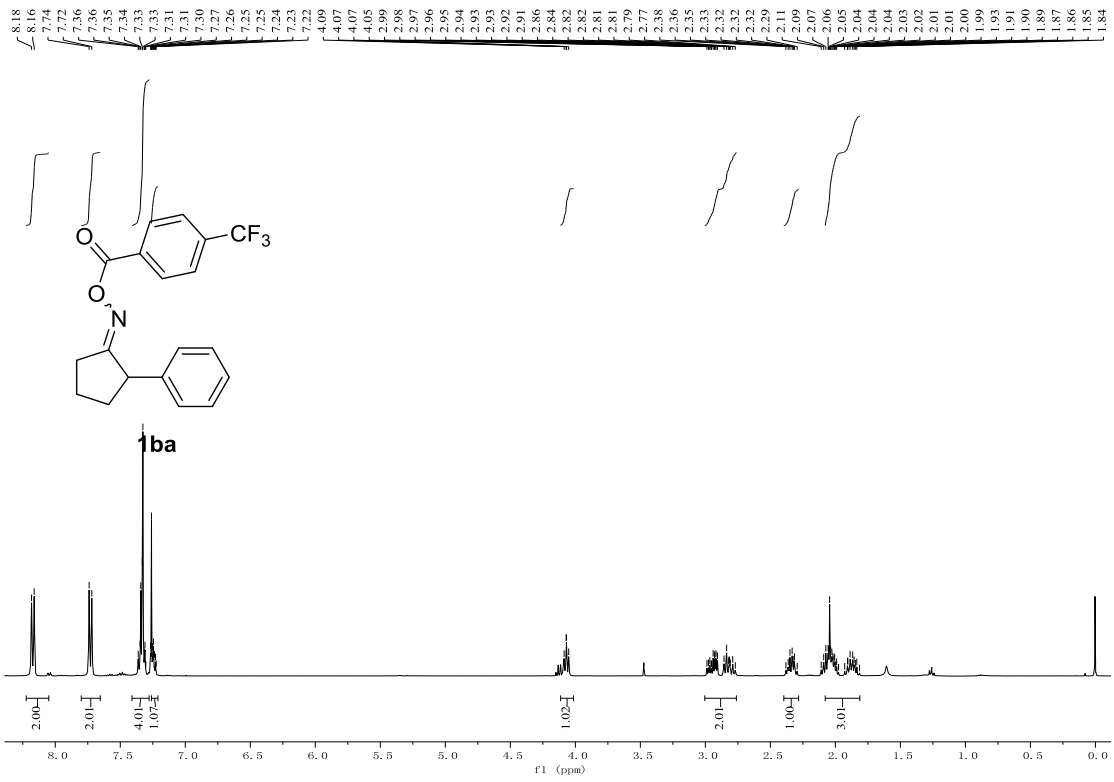
7. Copies of NMR Spectra



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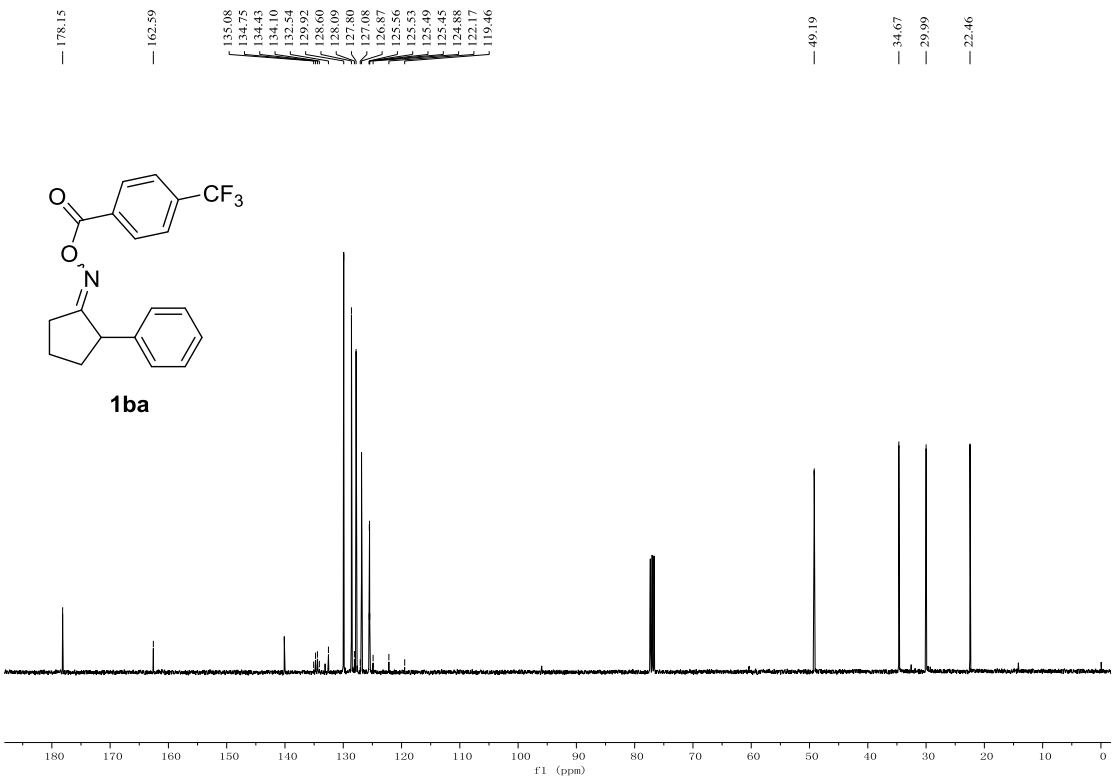
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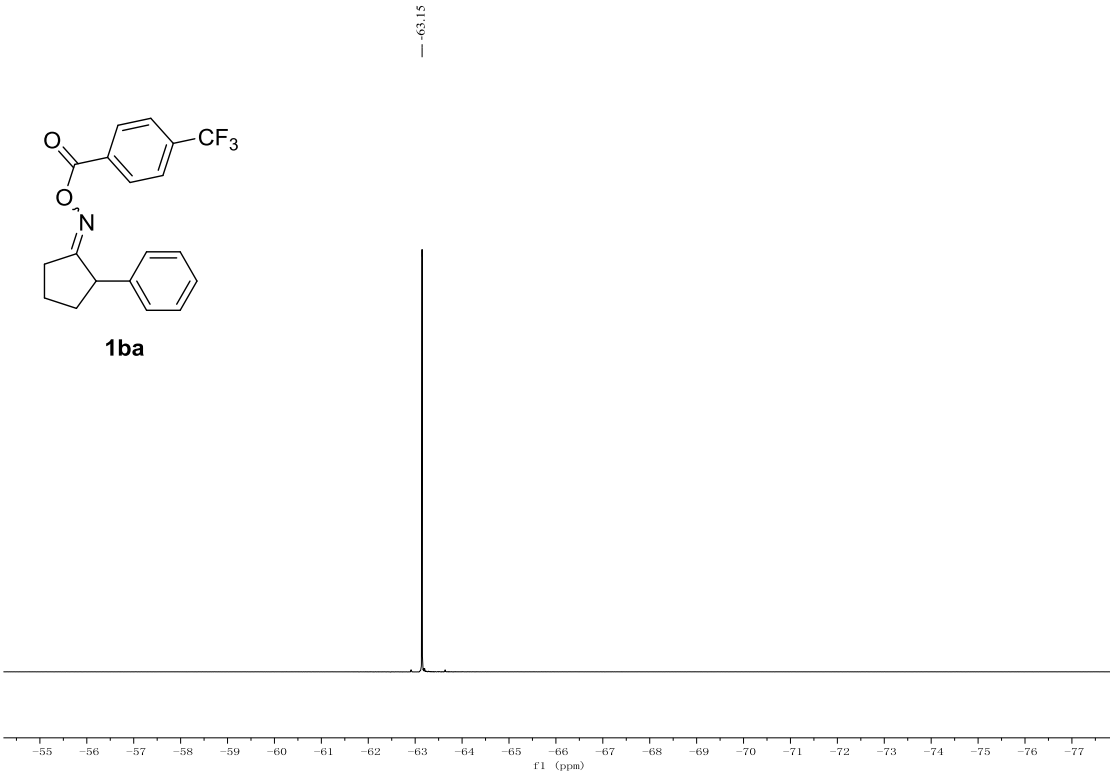
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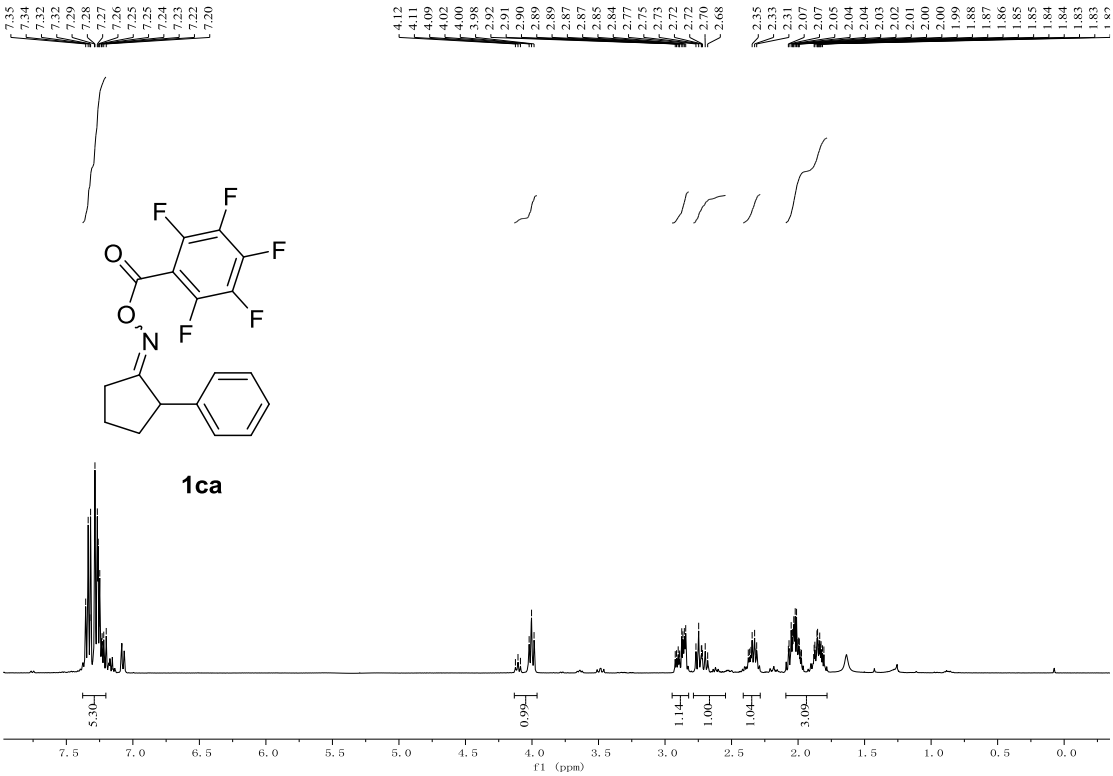
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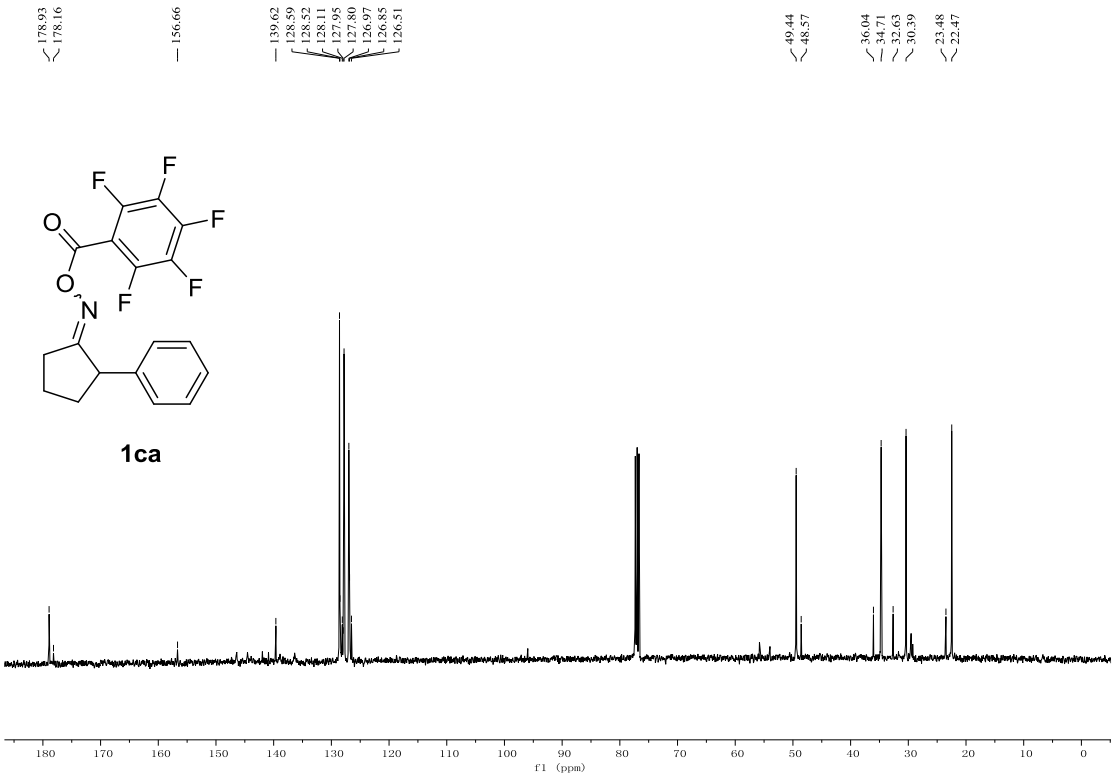
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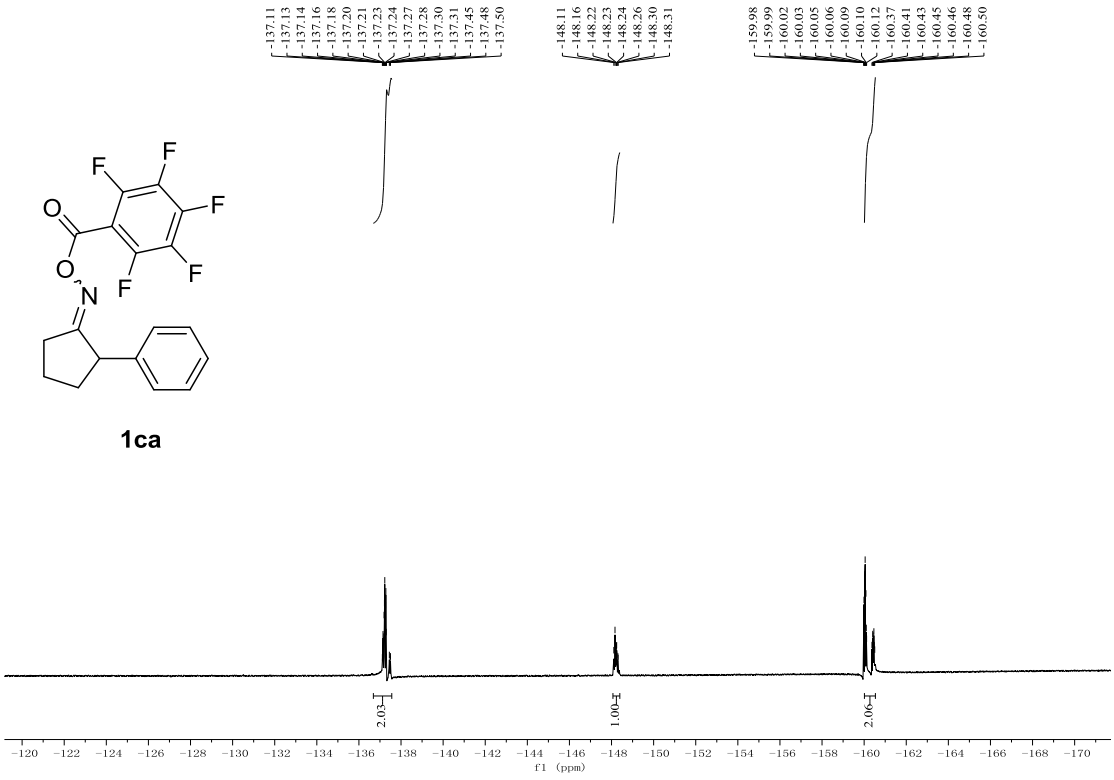
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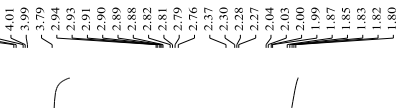
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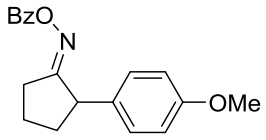
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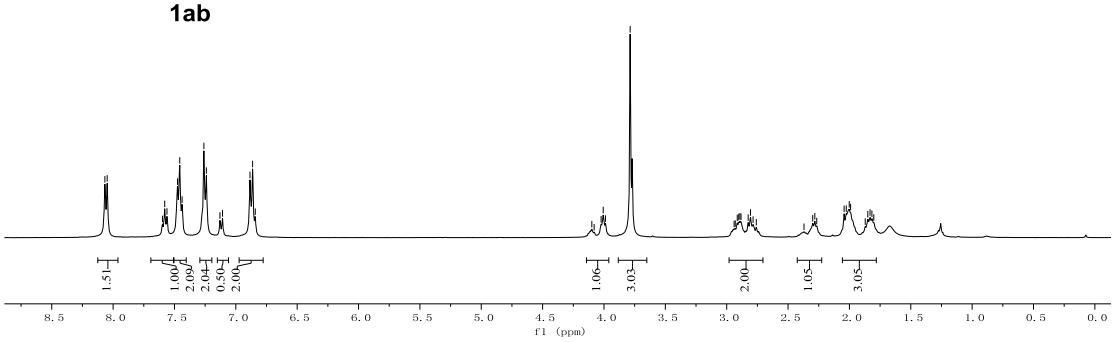
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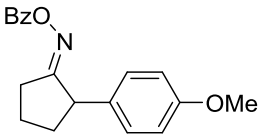
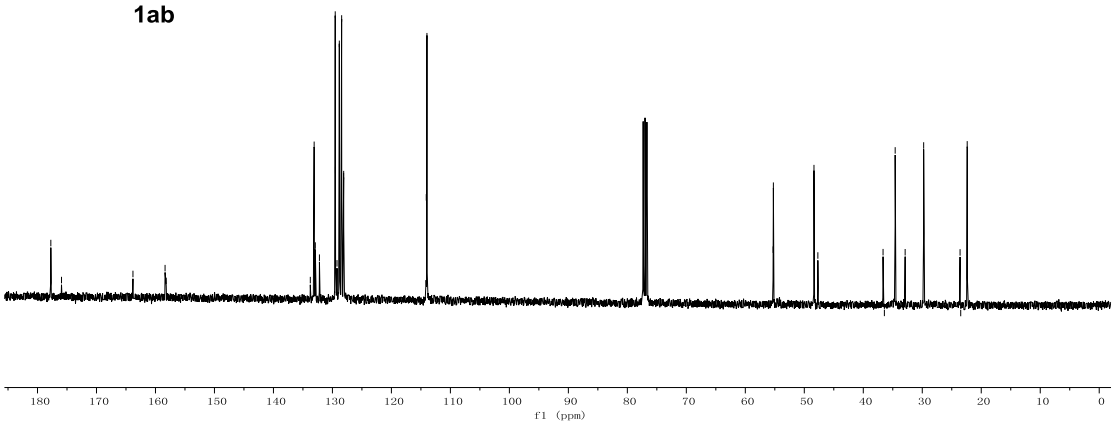
22.38


BzO
N
OMe

1ab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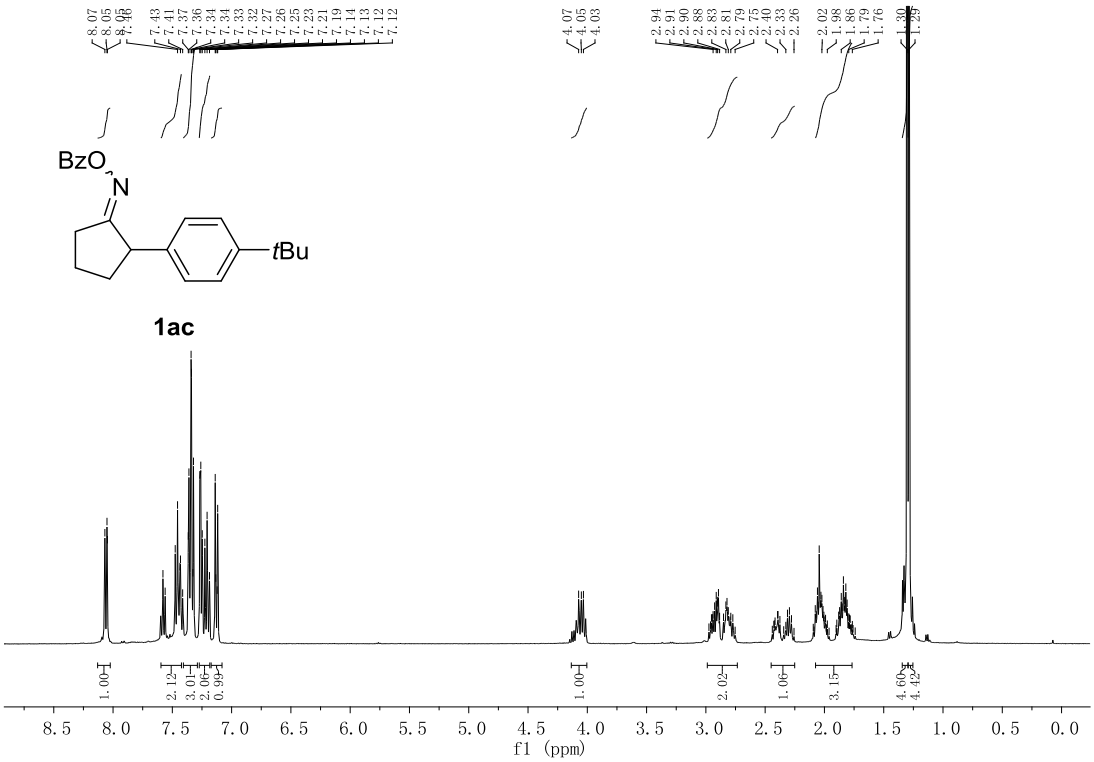
0
f1 (ppm)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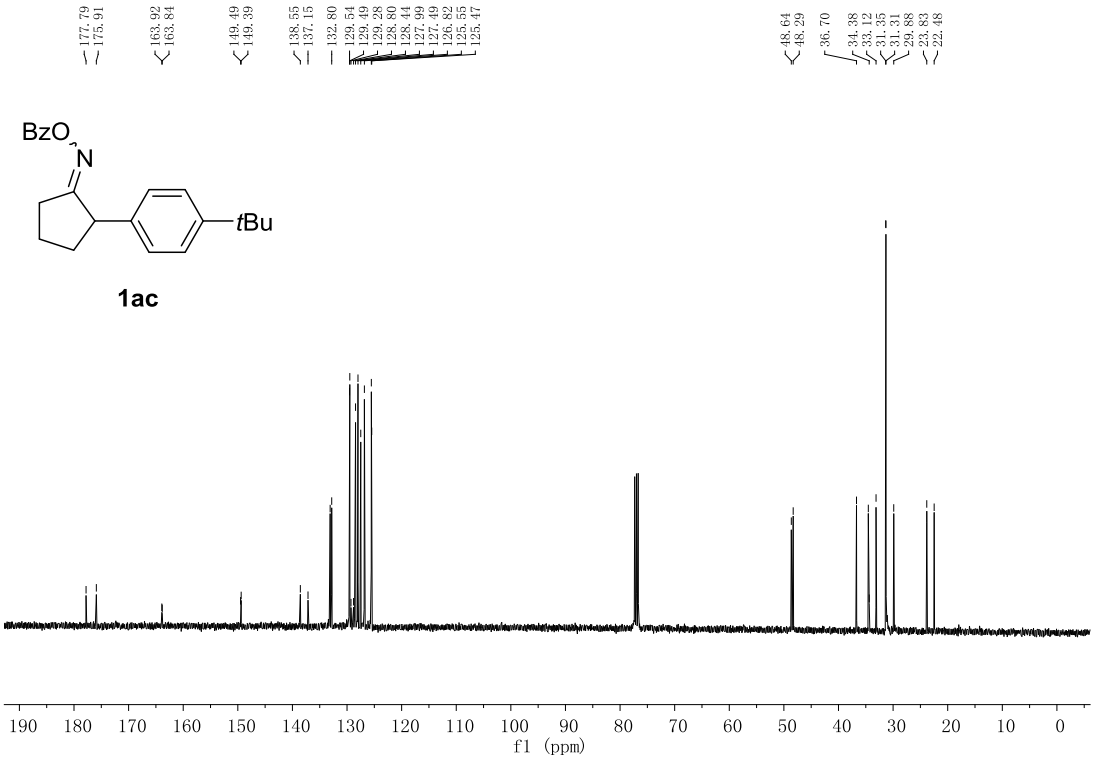
N
tBu
1ac
f1 (ppm)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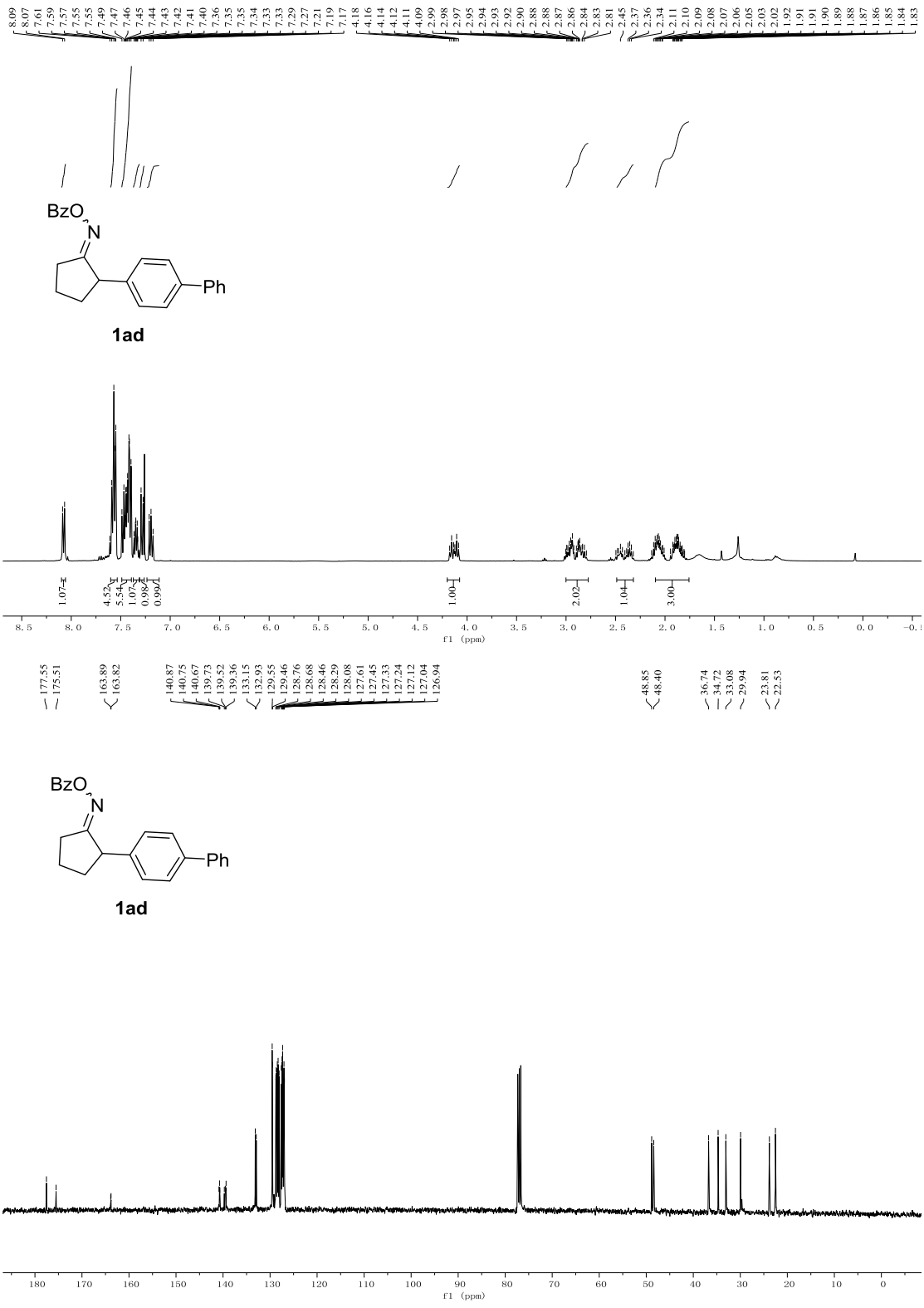
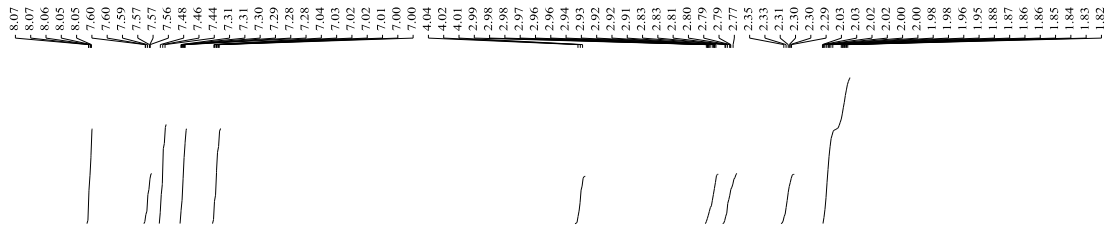
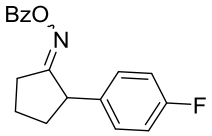
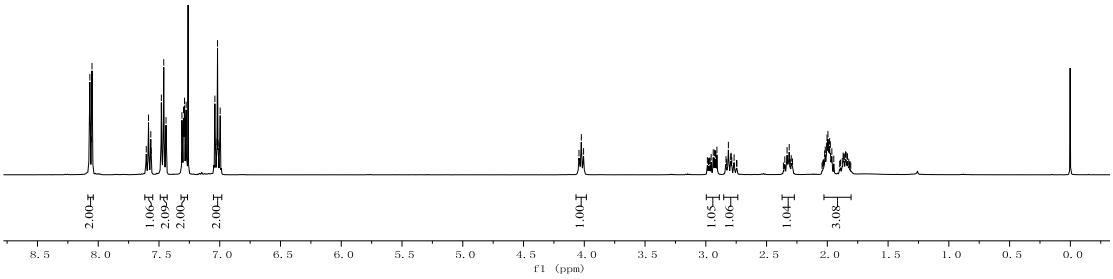
1ac
f1 (ppm)


BzO
N
Ph
1ad
f1 (ppm)
BzO
N
Ph
1ad
f1 (ppm)




BzO
N
F

1ae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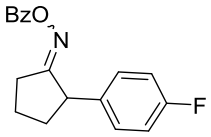
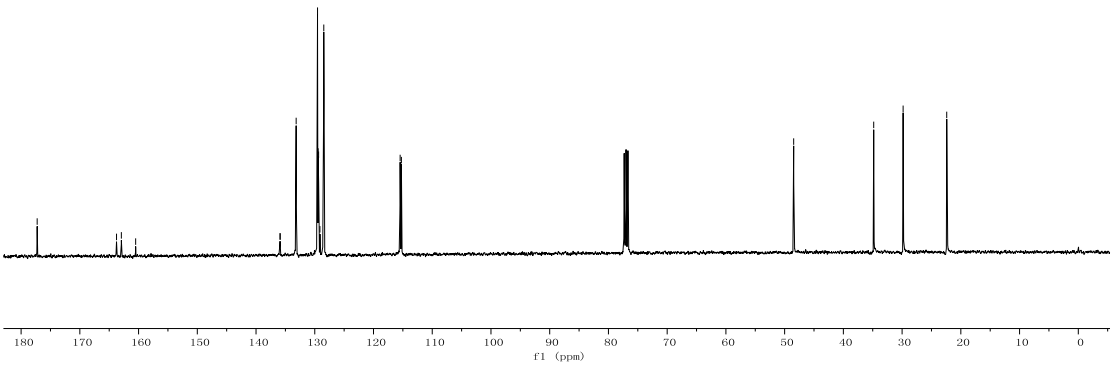
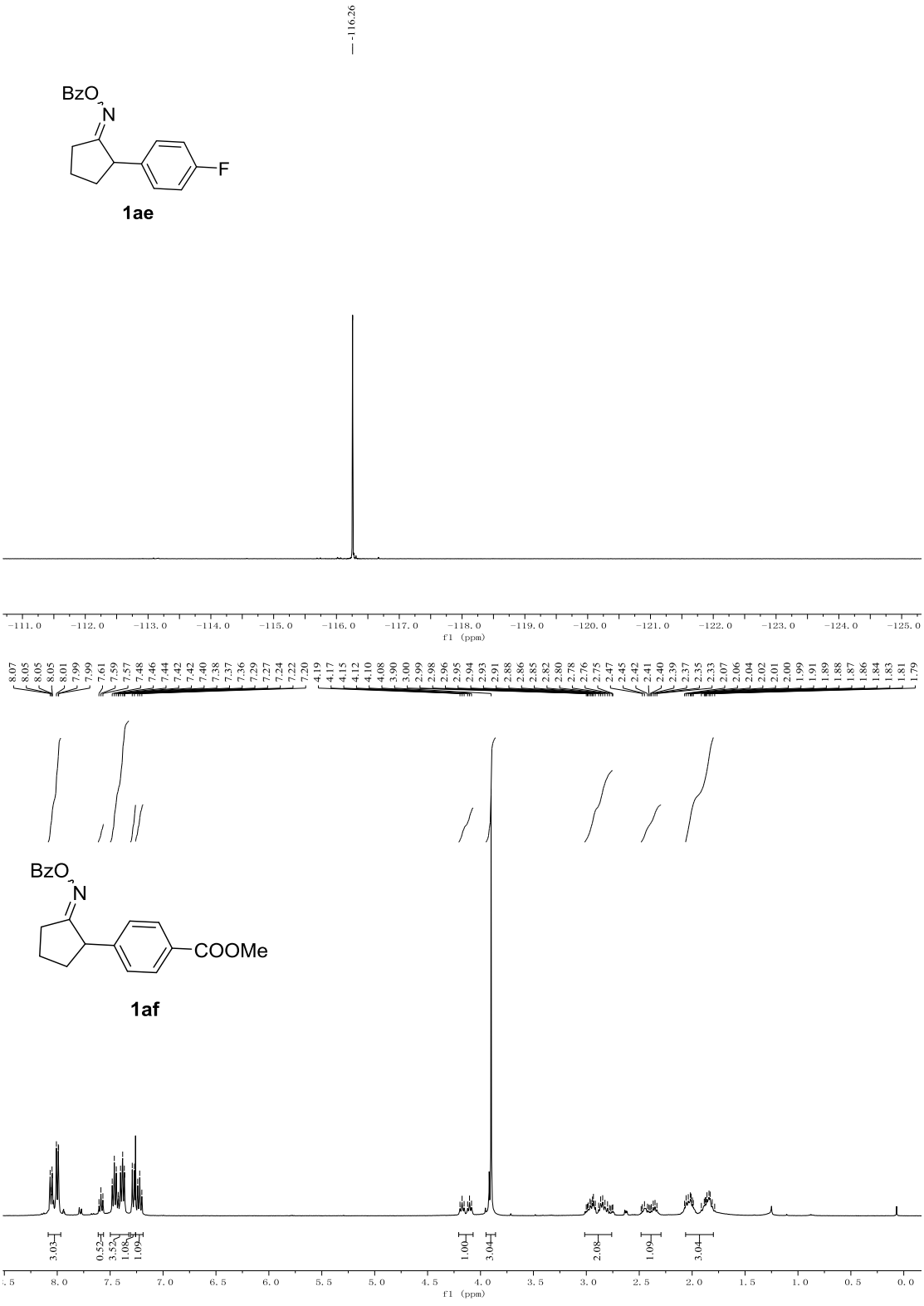
2.00
1.00
1.05
1.06
1.04
3.08
f1 (ppm)


177.26
163.75
162.93
160.50
135.91
135.89
133.17
129.53
129.43
129.35
129.12
128.46
115.46
115.25
48.46
34.83
29.83
22.40


BzO
N
F

1ae


f1 (ppm)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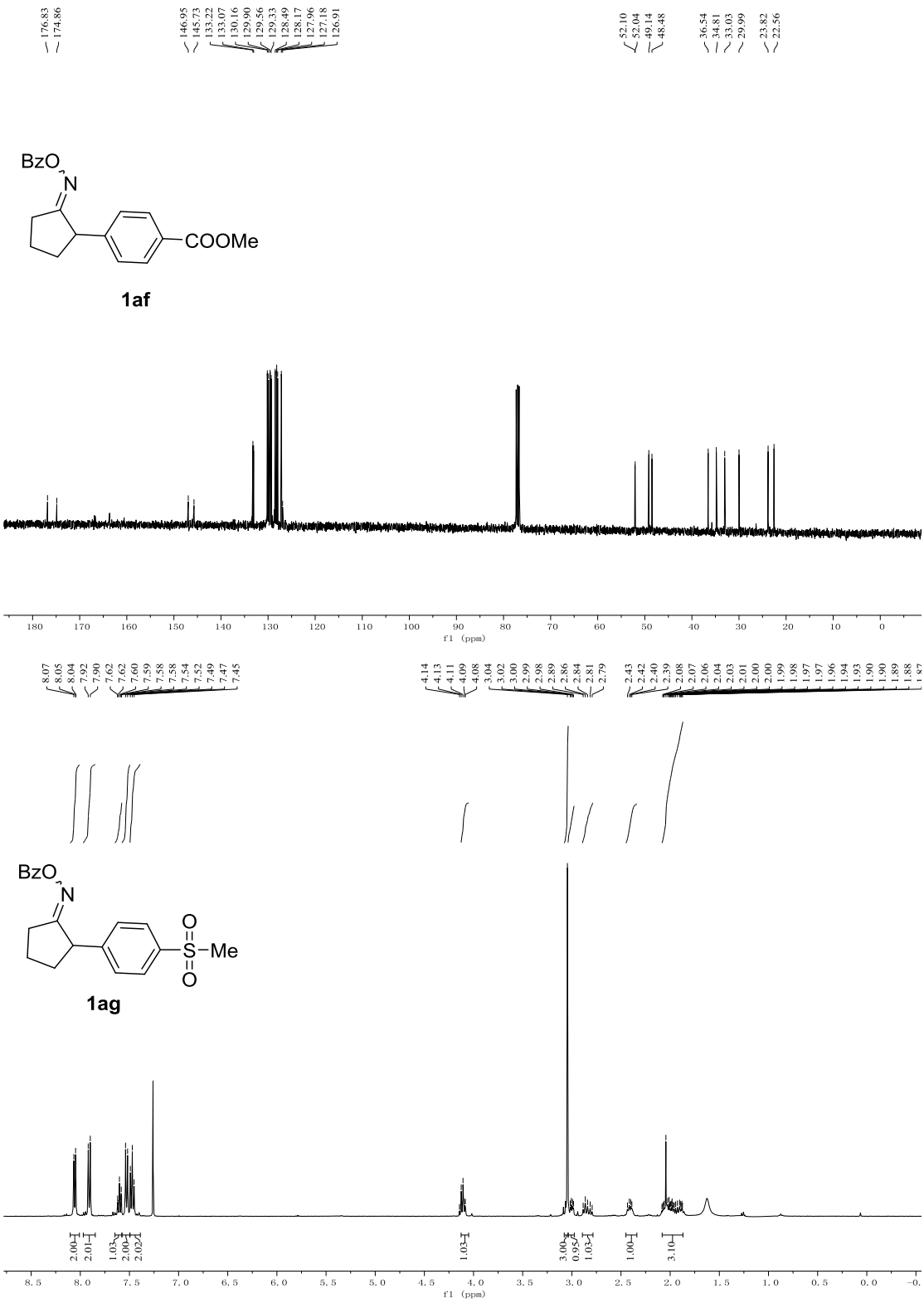
N
F
1ae
f1 (ppm)
BzO
N
COOMe
1af
f1 (ppm)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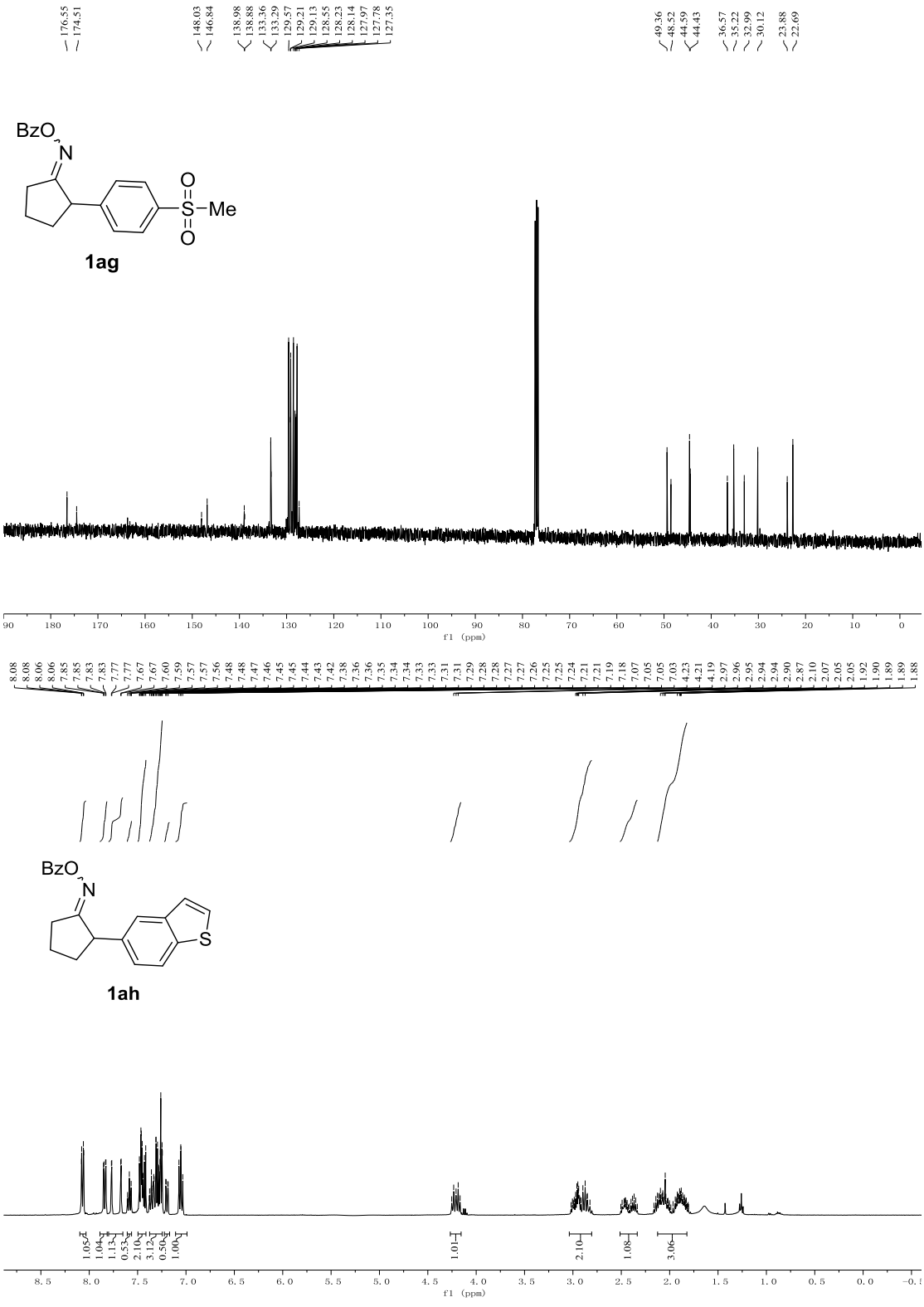
129.90
129.56
129.33
128.49
128.17
127.96
127.18
126.91
52.10
52.04
49.14
48.48
36.54
34.81
33.03
29.99
23.82
22.56
BzO
N
COOMe
1af
f1 (ppm)
8.07
8.05
8.04
7.92
7.90
7.62
7.62
7.60
7.59
7.58
7.58
7.54
7.52
7.49
7.47
7.45
4.14
4.13
4.11
4.09
4.08
3.04
3.02
3.00
2.99
2.98
2.89
2.86
2.84
2.81
2.79
2.43
2.42
2.40
2.39
2.08
2.07
2.06
2.04
2.03
2.01
2.00
2.00
1.99
1.98
1.97
1.97
1.96
1.94
1.93
1.90
1.90
1.89
1.88
BzO
N
O
S
Me
O
1ag
2.00
2.01
1.03
2.00
2.02
1.03
3.00
0.95
1.03
1.00
3.10
f1 (ppm)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138.88
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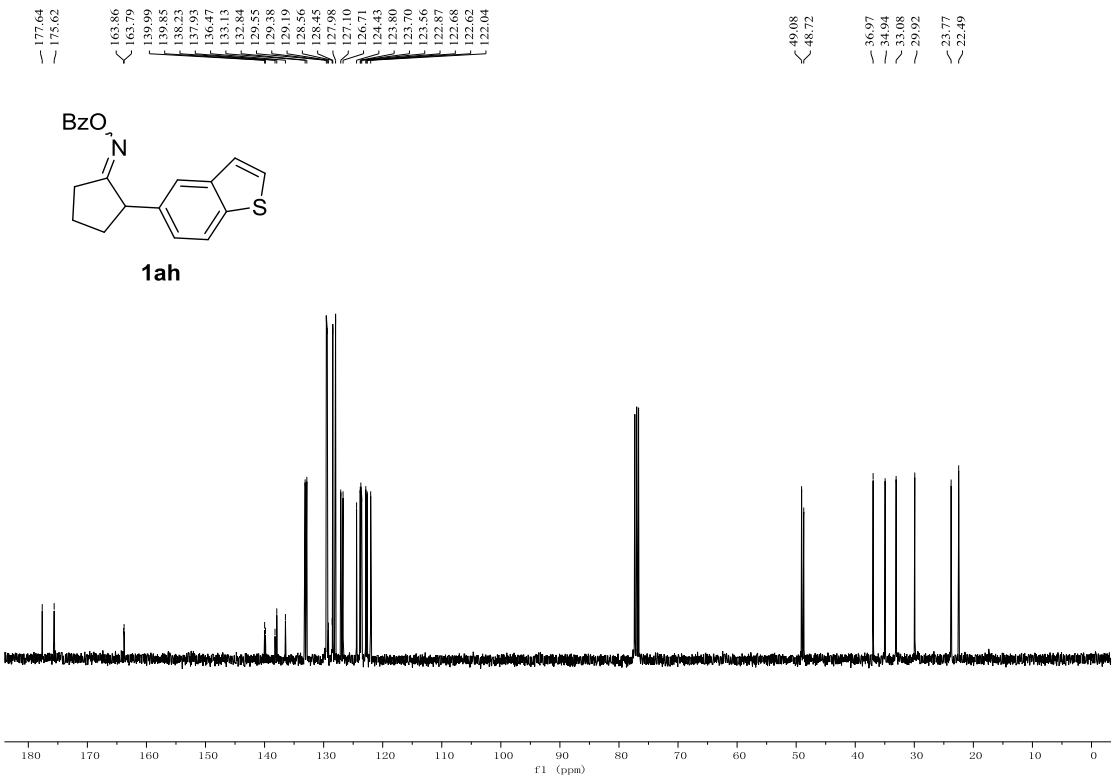
133.29
129.57
129.21
129.13
128.55
128.23
128.14
127.97
127.78
127.35
49.36
48.52
44.59
44.43
36.57
35.22
32.99
30.12
23.88
22.69
BzO
N
O
S
Me
O
1ag
f1 (ppm)
BzO
N
S
1ah
1.05
1.04
1.13
0.53
2.10
3.12
0.50
1.00
1.01
2.10
1.08
3.06
f1 (ppm)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163.86
163.79
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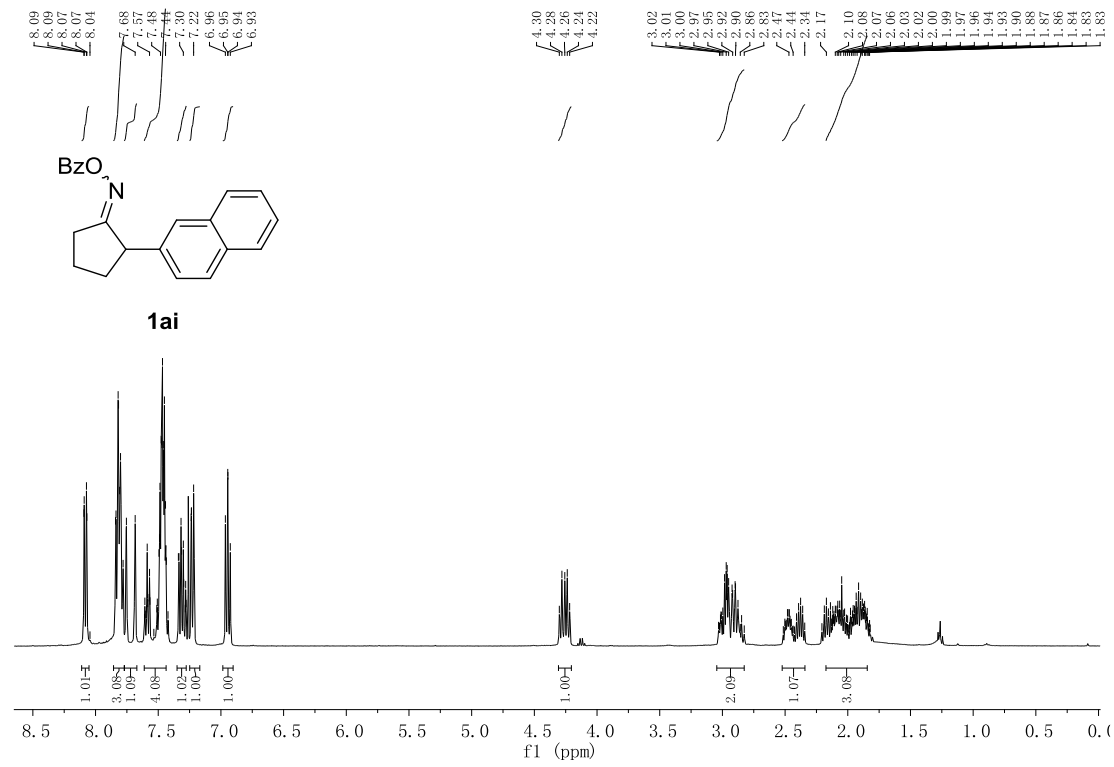
139.85
138.23
137.93
136.47
133.13
132.84
129.55
129.38
129.19
128.56
128.45
127.98
127.10
126.71
124.43
123.80
123.70
123.56
122.87
122.68
122.62
122.04
49.08
48.72
36.97
34.94
33.08
29.92
23.77
22.49
BzO
N
S
1ah
f1 (ppm)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8.09
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8.07
8.04
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7.48
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7.30
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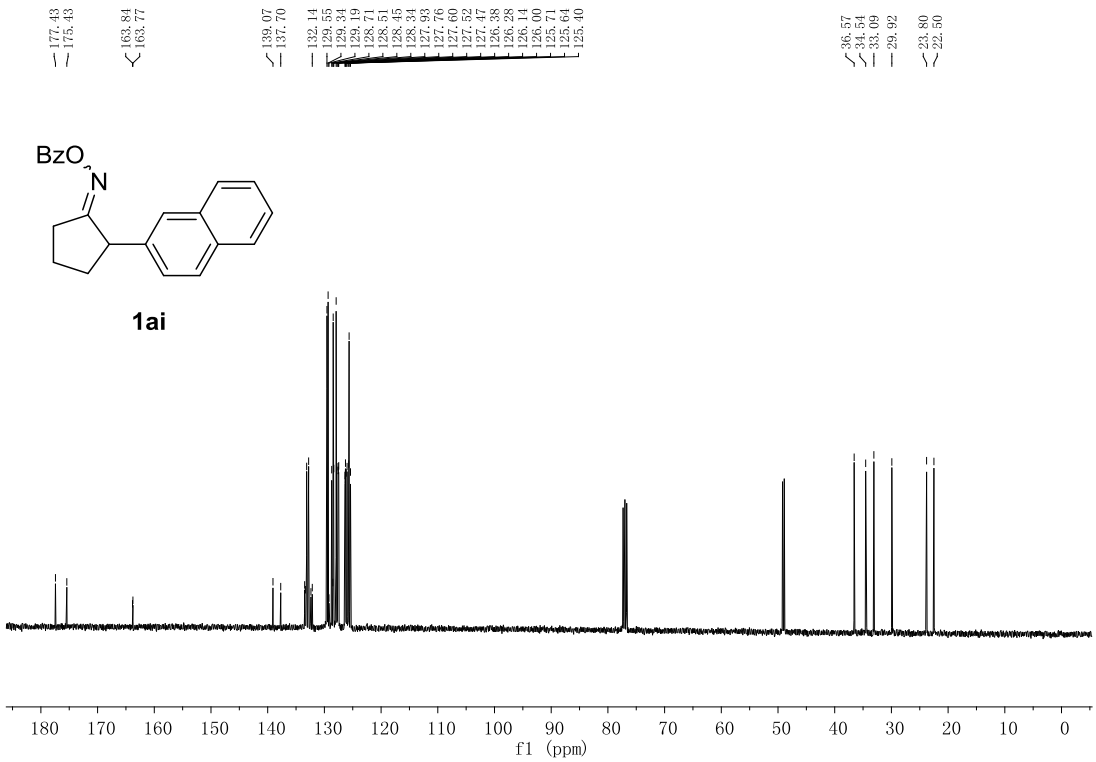
6.96
6.95
6.94
6.93
4.30
4.28
4.26
4.24
4.22
3.02
3.01
3.00
2.97
2.95
2.92
2.90
2.86
2.83
2.47
2.44
2.34
2.17
2.10
2.08
2.07
2.06
2.03
2.02
2.00
1.99
1.97
1.96
1.94
1.93
1.90
1.88
1.87
1.86
1.84
1.83
1.83
BzO
N
1ai
1.01
3.08
1.09
4.08
1.02
1.00
1.00
1.00
2.09
1.07
3.08
f1 (ppm)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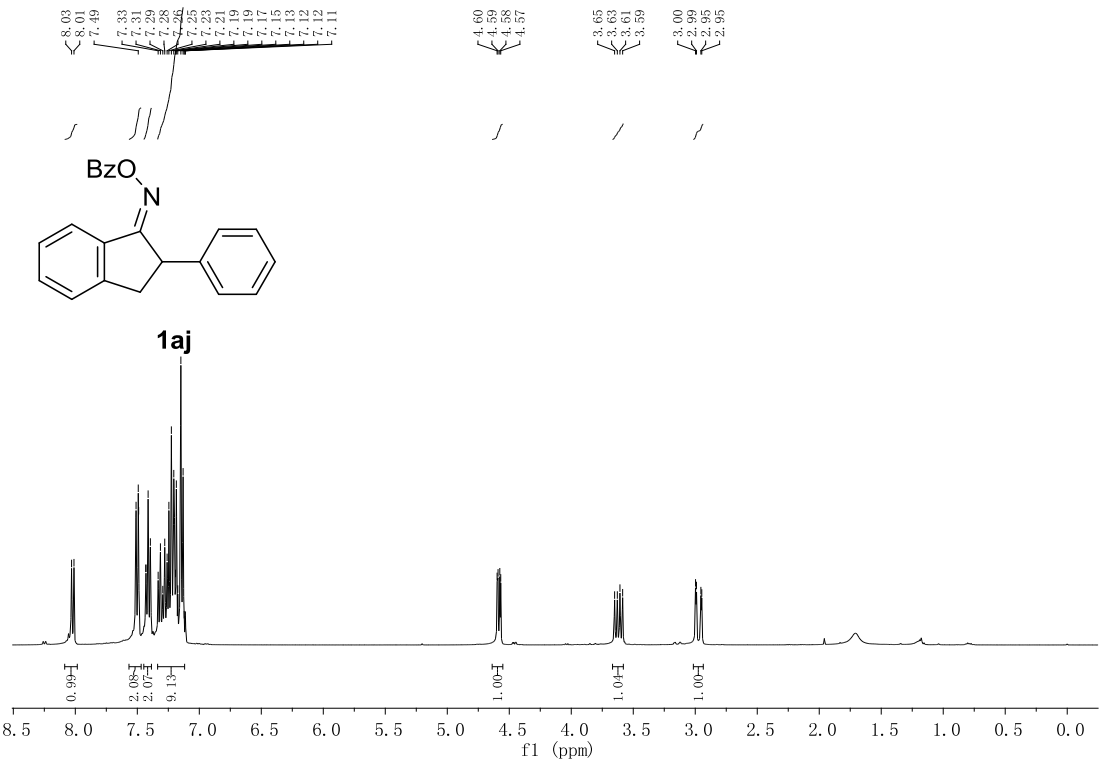
132.14
129.55
129.34
129.19
128.71
128.51
128.45
128.34
127.93
127.76
127.60
127.52
127.47
126.38
126.28
126.14
126.00
125.71
125.64
125.40
36.57
34.54
33.09
29.92
23.80
22.50
BzO
N
1ai
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.01
7.49
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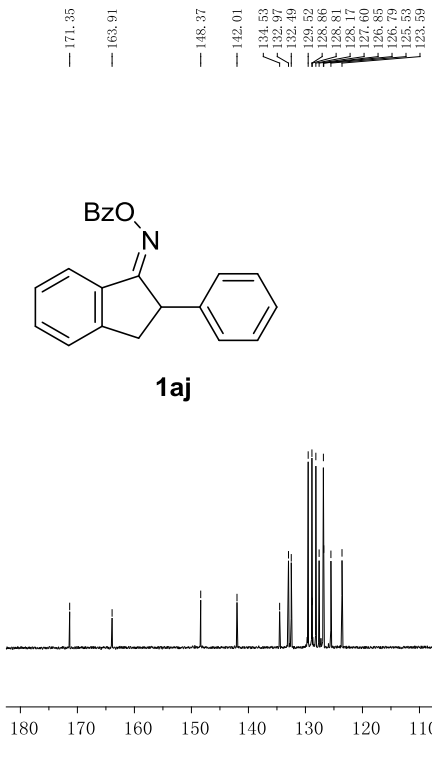
7.26
7.25
7.23
7.21
7.19
7.19
7.17
7.15
7.13
7.12
7.12
7.11
4.60
4.59
4.58
4.57
3.65
3.63
3.61
3.59
3.00
2.99
2.95
2.95
BzO
N
1aj
0.99
2.08
2.07
9.13
1.00
1.04
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.97
132.49
129.52
128.86
128.81
128.17
127.60
126.85
126.79
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123.59
47.00
40.37
BzO
N
1aj
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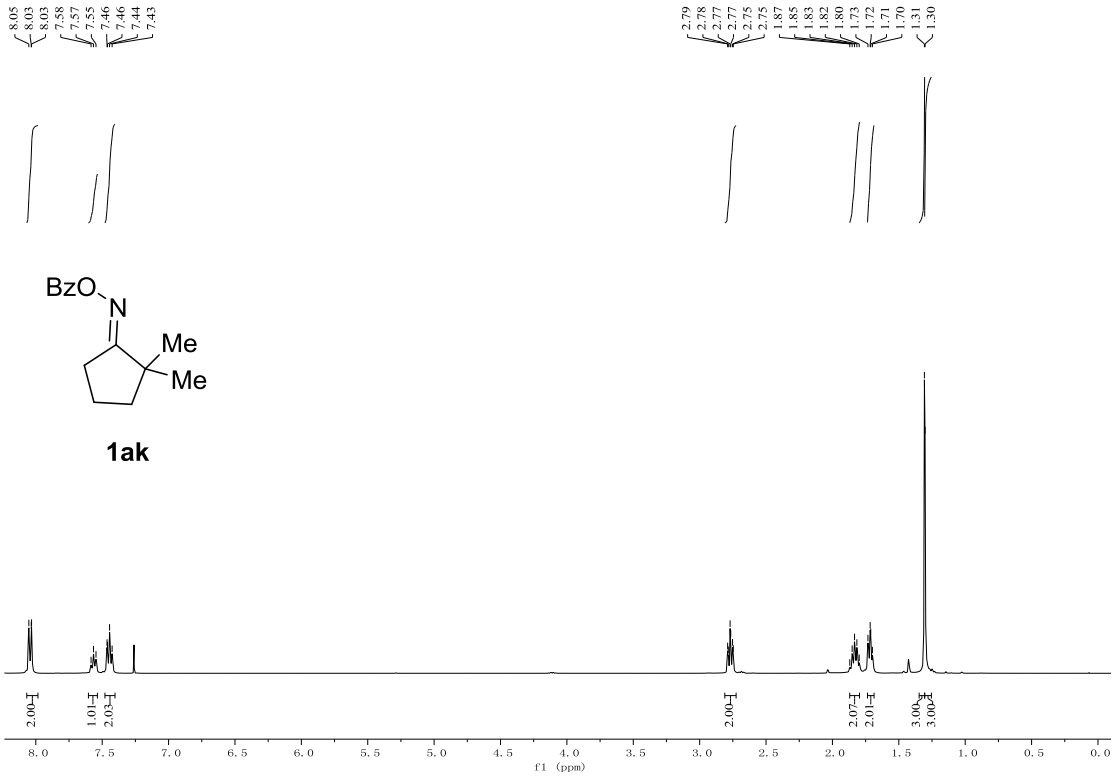
f1 (ppm)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7.46
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7.43
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2.77
2.75
2.75
1.87
1.85
1.83
1.82
1.80
1.73
1.72
1.71
1.70
1.31
1.30
BzO
N
Me
Me
1ak
2.00
1.01
2.03
2.00
2.07
2.01
3.00
3.00
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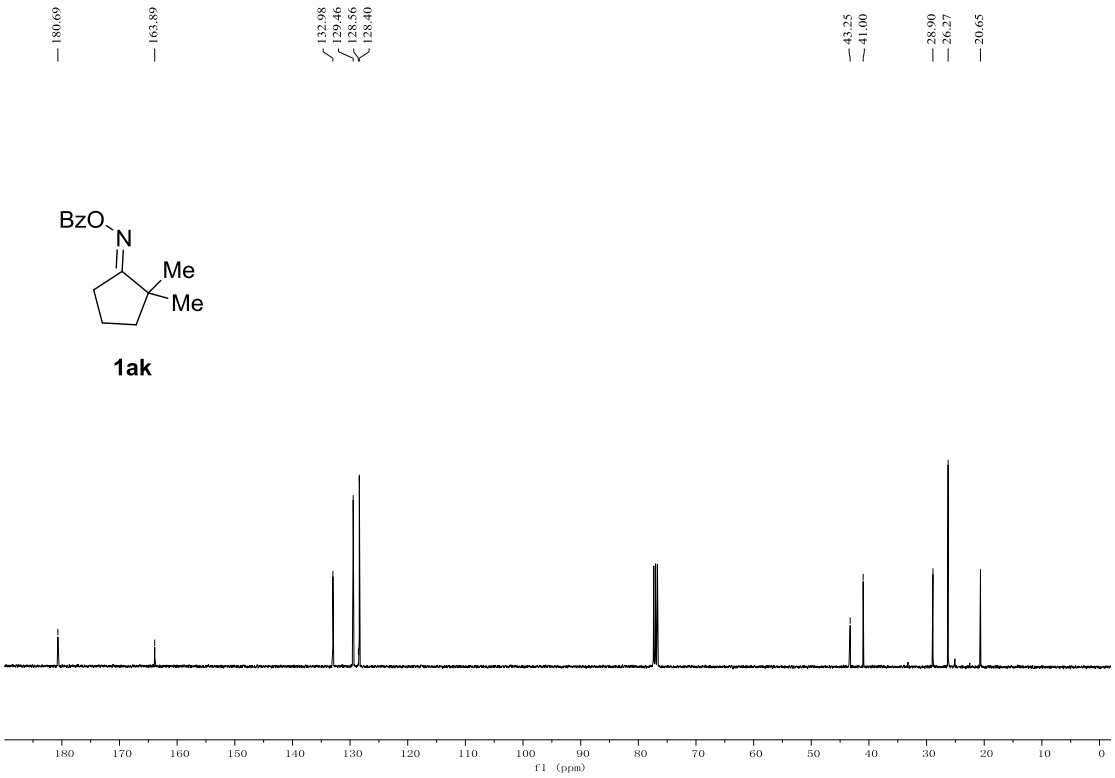
f1 (ppm)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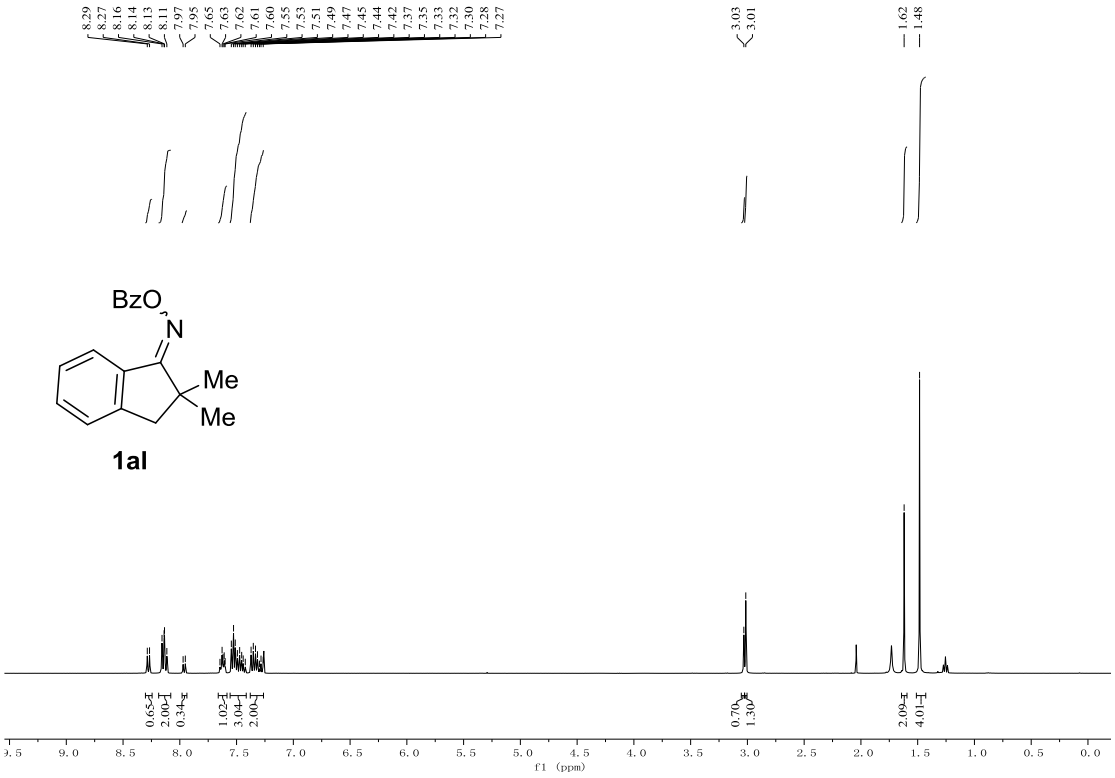
28.90
26.27
20.65
BzO
N
Me
Me
1ak
f1 (ppm)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7.62
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7.60
7.55
7.53
7.51
7.49
7.47
7.45
7.44
7.42
7.37
7.35
7.33
7.32
7.30
7.28
7.27
3.03
3.01
1.62
1.48
BzO
N
Me
Me
1al
0.65
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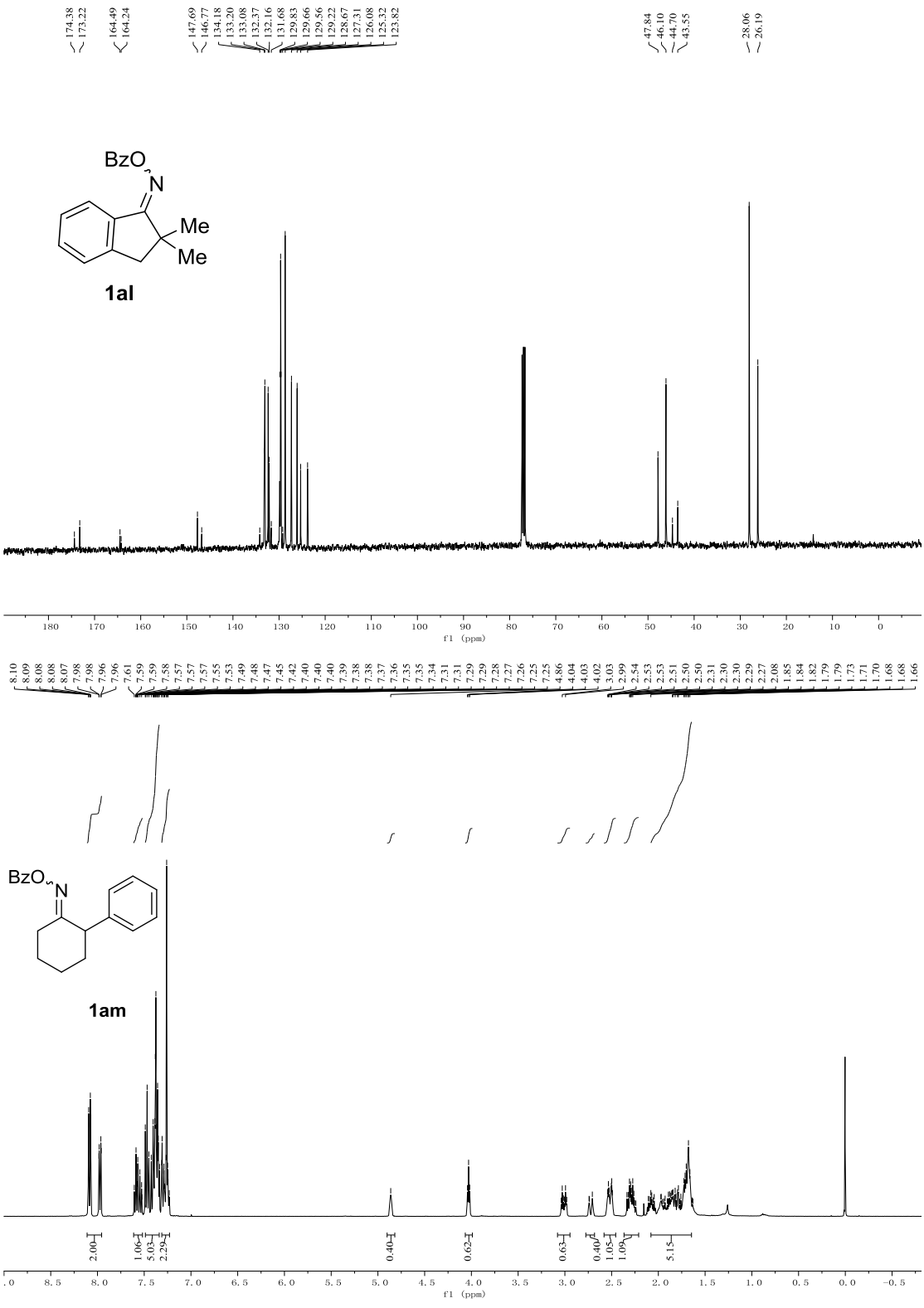
0.34
1.02
3.04
2.00
0.70
1.30
2.09
4.01
f1 (ppm)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129.83
129.66
129.56
129.22
128.67
127.31
126.08
125.32
123.82
47.84
46.10
44.70
43.55
28.06
26.19
BzO
N
Me
Me
1al
f1 (ppm)
8.10
8.09
8.08
8.08
8.07
7.98
7.98
7.96
7.96
7.61
7.59
7.59
7.58
7.57
7.57
7.57
7.55
7.53
7.49
7.48
7.47
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7.36
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4.02
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2.50
2.50
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2.30
2.29
2.27
2.08
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1.84
1.82
1.79
1.79
1.73
1.71
1.70
1.68
1.68
1.66
BzO
N
1am
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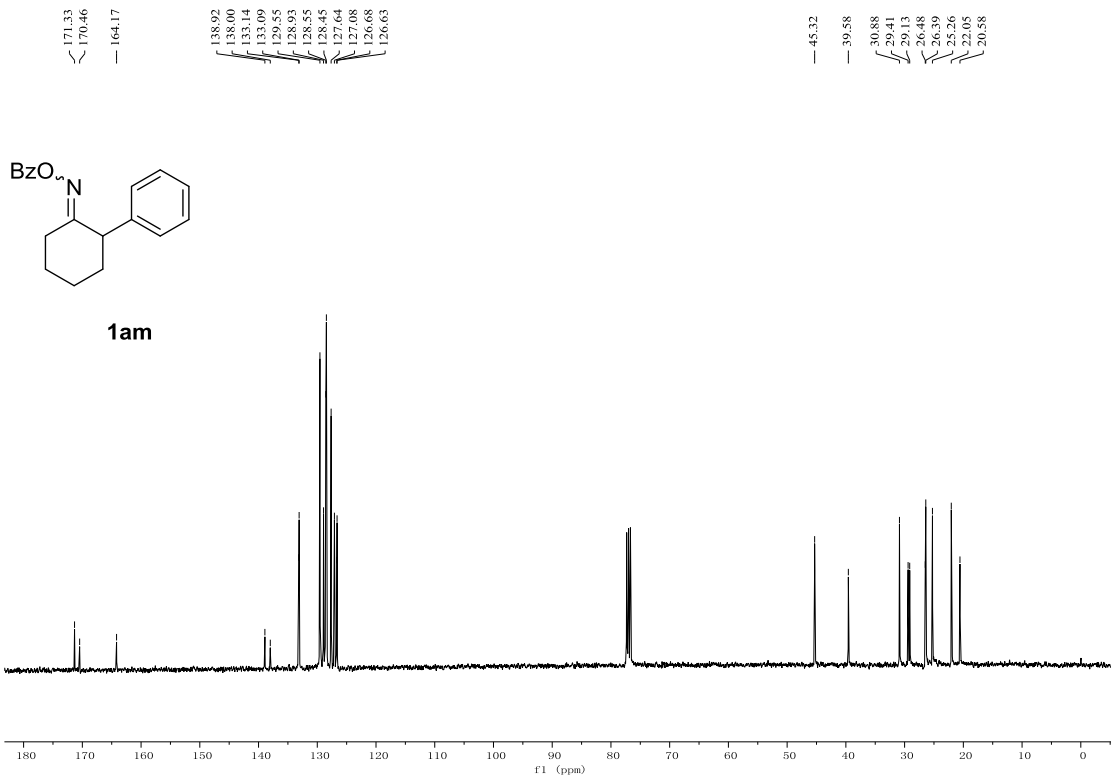
0.63
0.40
1.05
1.09
5.15
f1 (ppm)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127.64
127.08
126.68
126.63
45.32
39.58
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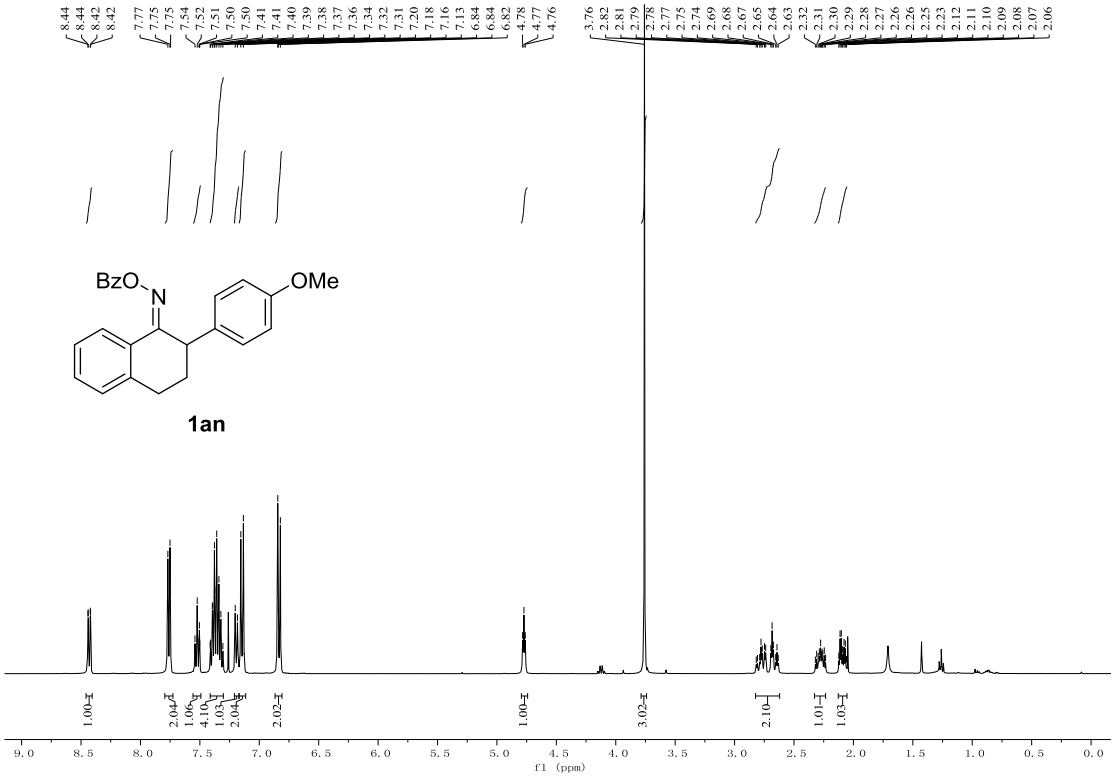
29.13
26.48
26.39
25.26
22.05
20.58
BzO
N
1am
f1 (ppm)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7.41
7.41
7.40
7.39
7.38
7.37
7.36
7.34
7.32
7.31
7.20
7.18
7.16
7.13
6.84
6.84
6.82
4.78
4.77
4.76
3.76
2.82
2.81
2.79
2.78
2.77
2.75
2.74
2.69
2.68
2.67
2.65
2.64
2.63
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2.31
2.30
2.29
2.28
2.27
2.26
2.26
2.25
2.23
2.12
2.11
2.10
2.09
2.08
2.07
2.06
BzO
N
OMe
1an
1.00
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1.06
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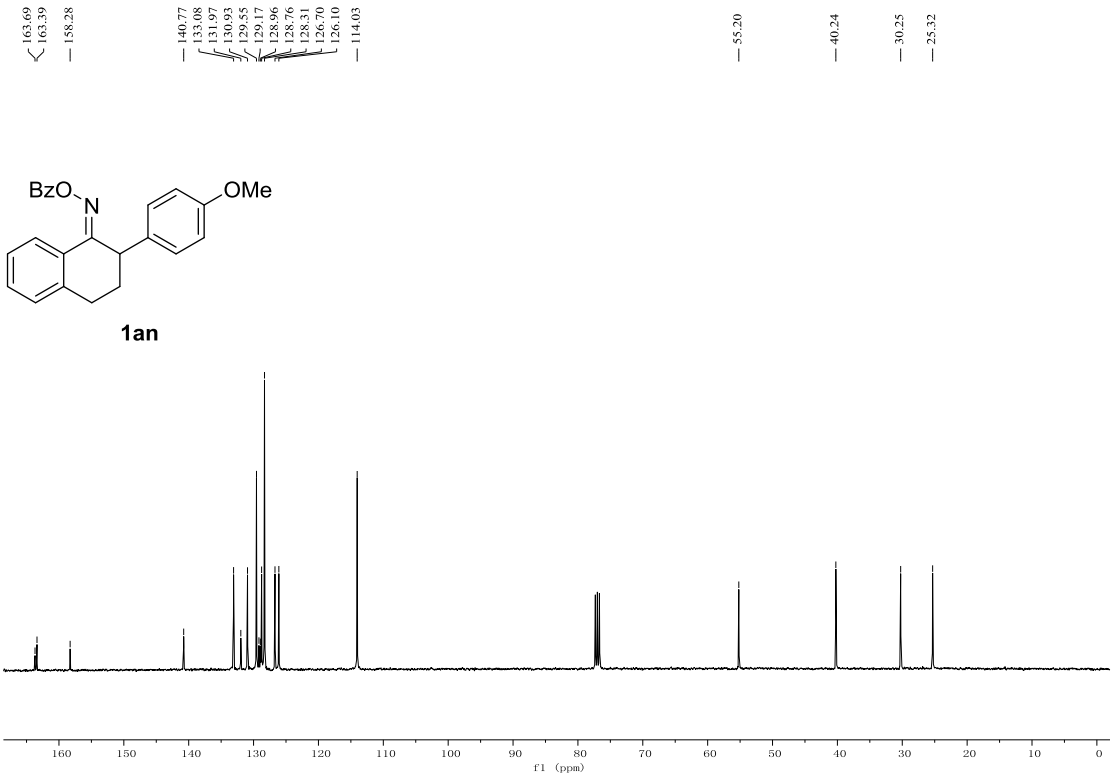
1.03
2.04
2.02
1.00
3.02
2.10
1.01
1.03
f1 (ppm)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129.55
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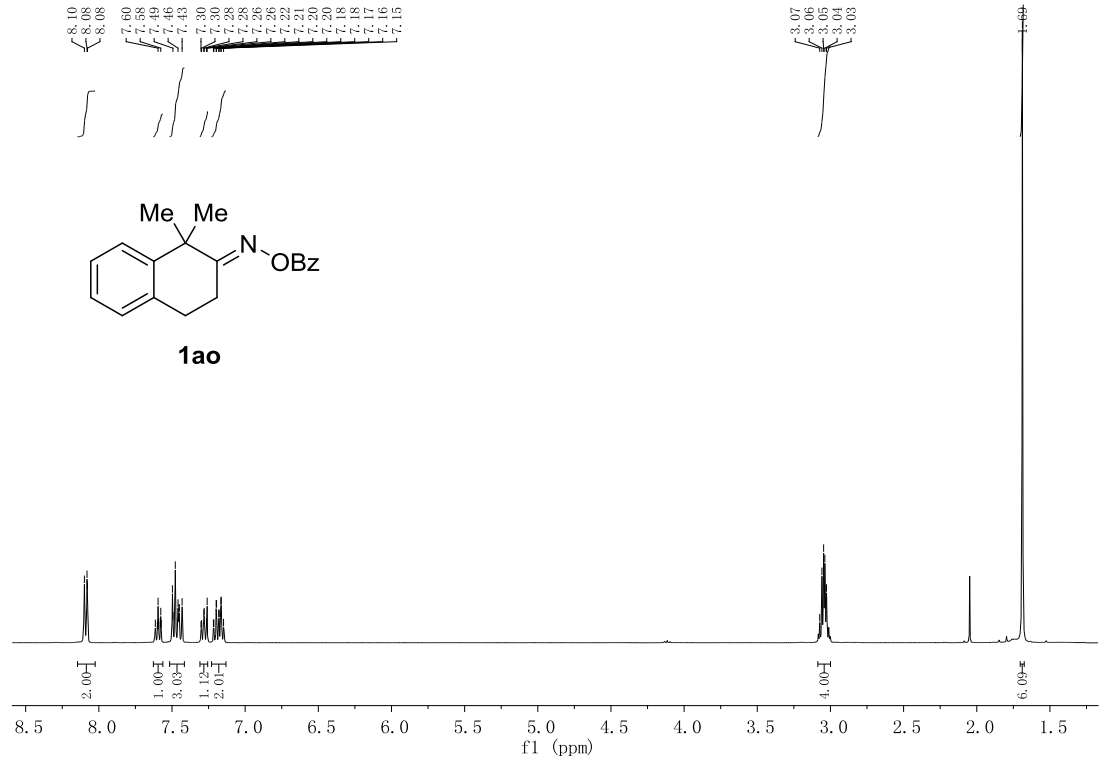
128.96
128.76
128.31
126.70
126.10
114.03
55.20
40.24
30.25
25.32
BzO
N
OMe
1an
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.08
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7.43
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7.30
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7.28
7.26
7.26
7.22
7.21
7.20
7.20
7.18
7.18
7.17
7.16
7.15
3.07
3.06
3.05
3.04
3.03
1.69
Me
Me
N
OBz
1ao
2.00
1.00
3.03
1.12
2.01
4.00
6.09
8.5
8.0
7.5
7.0
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4.0
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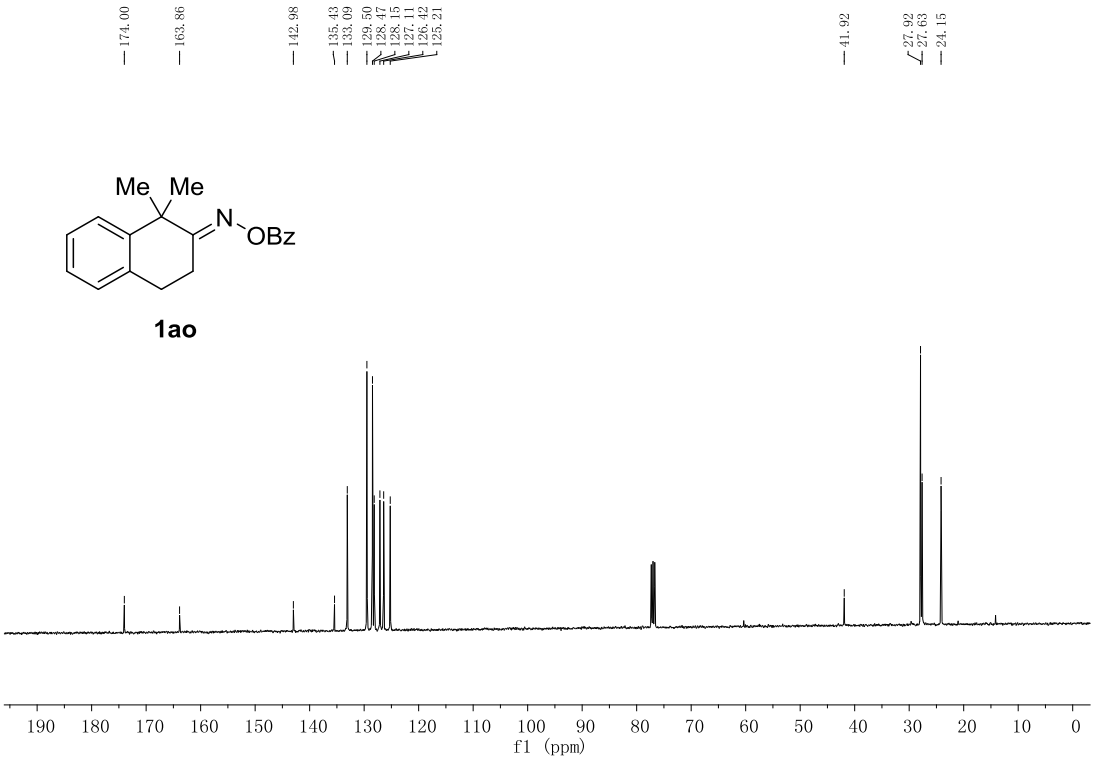
3.0
2.5
2.0
1.5
f1 (ppm)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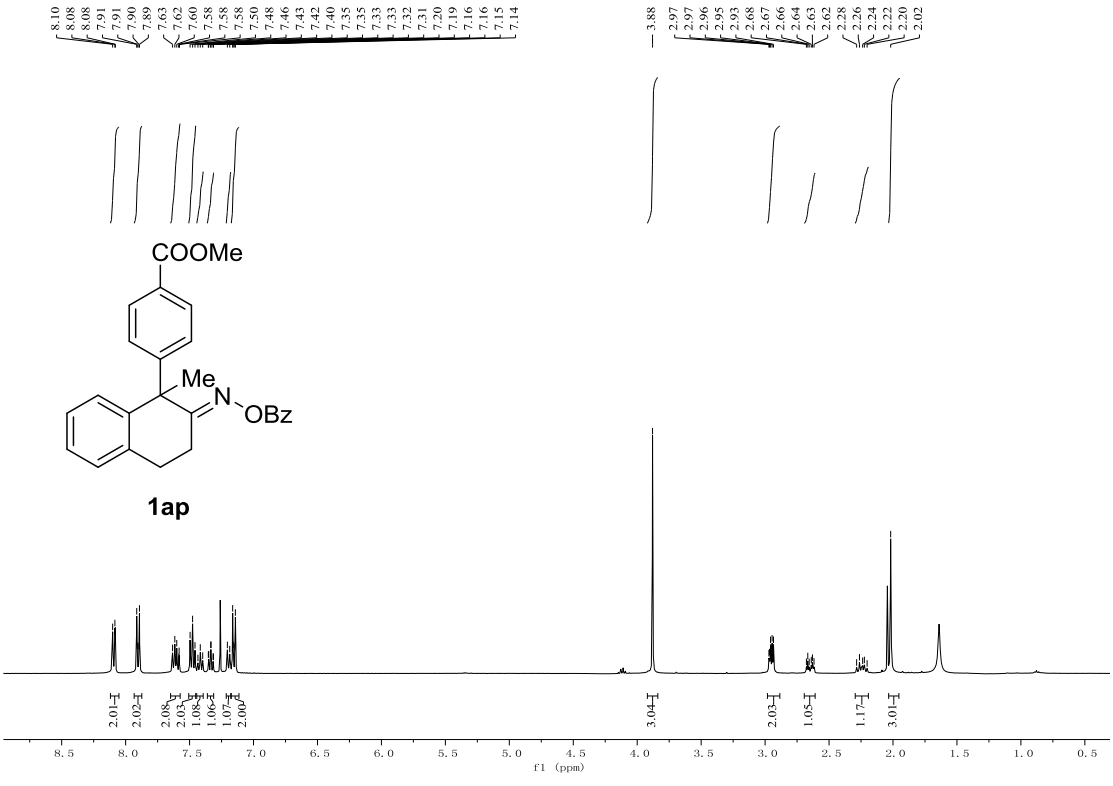
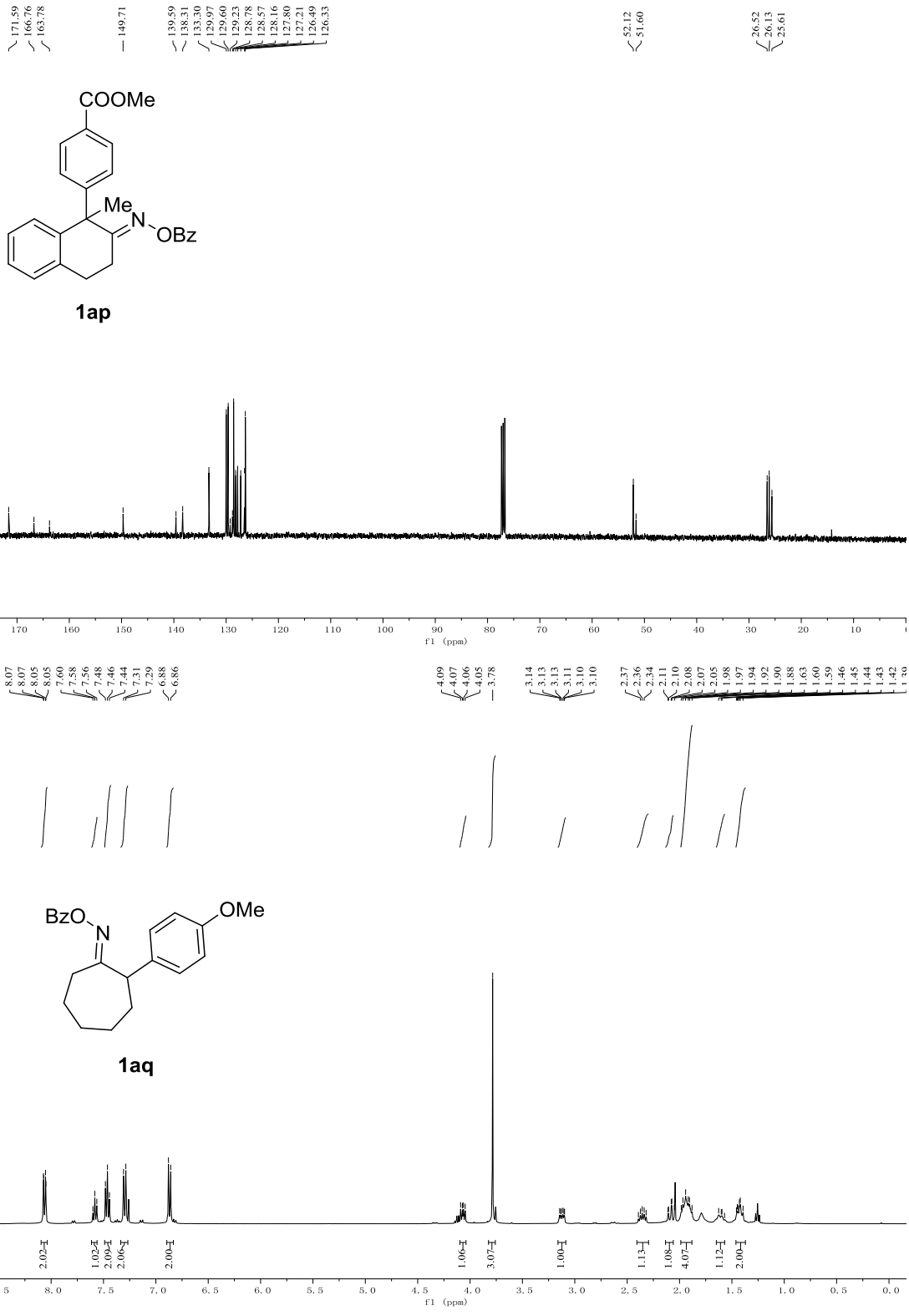
125.21
41.92
27.92
27.63
24.15
Me
Me
N
OBz
1ao
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.10
8.08
8.08
7.91
7.91
7.90
7.89
7.63
7.62
7.60
7.58
7.58
7.58
7.50
7.48
7.46
7.43
7.42
7.40
7.35
7.35
7.33
7.33
7.32
7.31
7.20
7.19
7.16
7.16
7.15
7.14
3.88
2.97
2.97
2.96
2.95
2.93
2.68
2.67
2.66
2.64
2.63
2.62
2.28
2.26
2.24
2.22
2.20
2.02
COOMe
Me
N
OBz
1ap
2.01
2.02
2.08
2.03
1.08
1.06
1.07
2.00
3.04
2.03
1.05
1.17
3.01
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
f1 (ppm)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163.78
149.71
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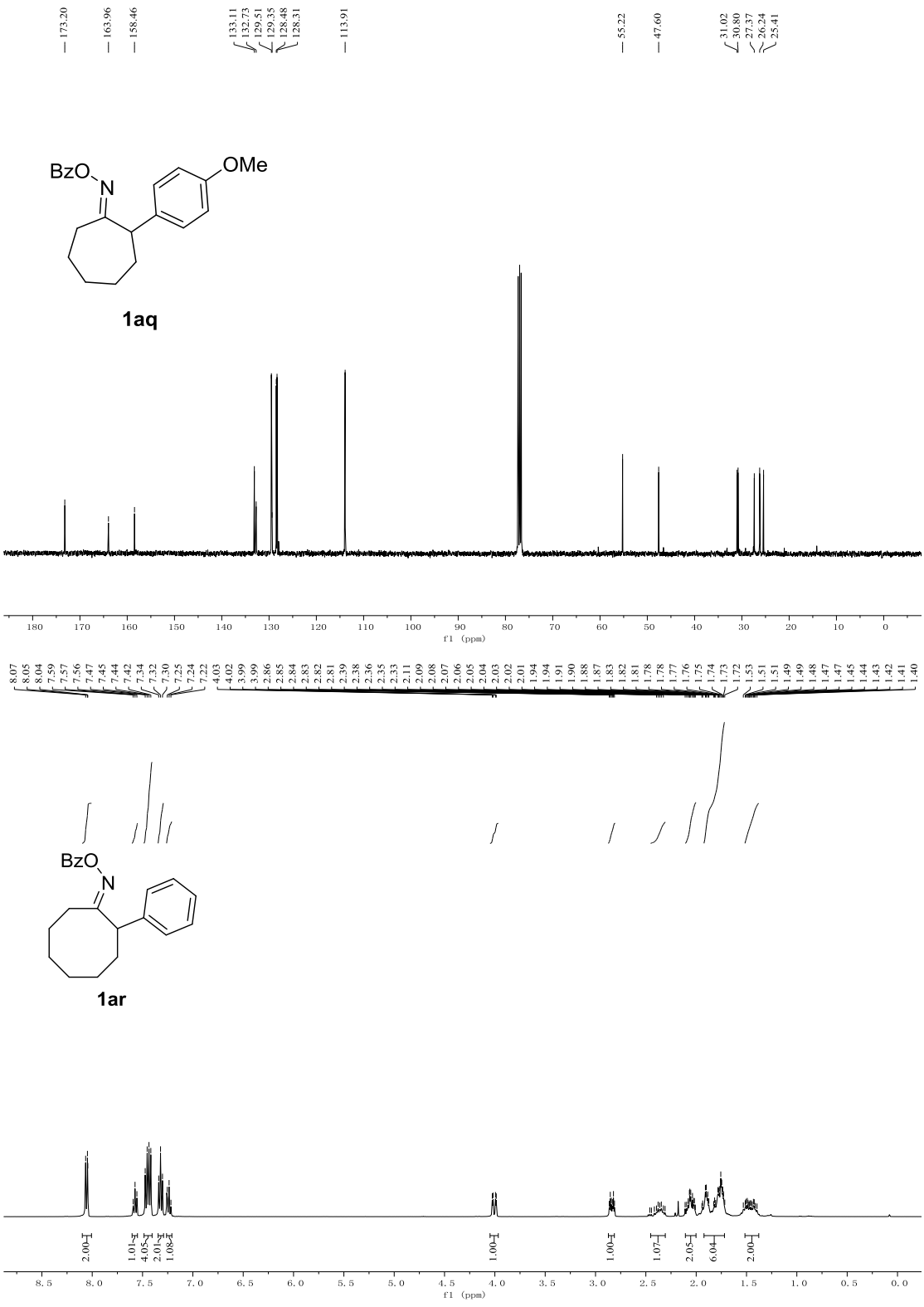
138.31
133.30
129.97
129.60
129.23
128.78
128.57
128.16
127.80
127.21
126.49
126.33
52.12
51.60
26.52
26.13
25.61
COOMe
Me
N
OBz
1ap
f1 (ppm)
8.07
8.07
8.05
8.05
7.60
7.58
7.56
7.48
7.46
7.44
7.31
7.29
6.88
6.86
4.09
4.07
4.06
4.05
3.78
3.14
3.13
3.13
3.11
3.10
3.10
2.37
2.36
2.34
2.11
2.10
2.08
2.07
2.05
1.98
1.97
1.94
1.92
1.90
1.88
1.63
1.60
1.59
1.46
1.45
1.44
1.43
1.42
BzO
N
OMe
1aq
2.02
1.02
2.09
2.06
2.00
1.06
3.07
1.00
1.13
1.08
4.07
1.12
2.00
f1 (ppm)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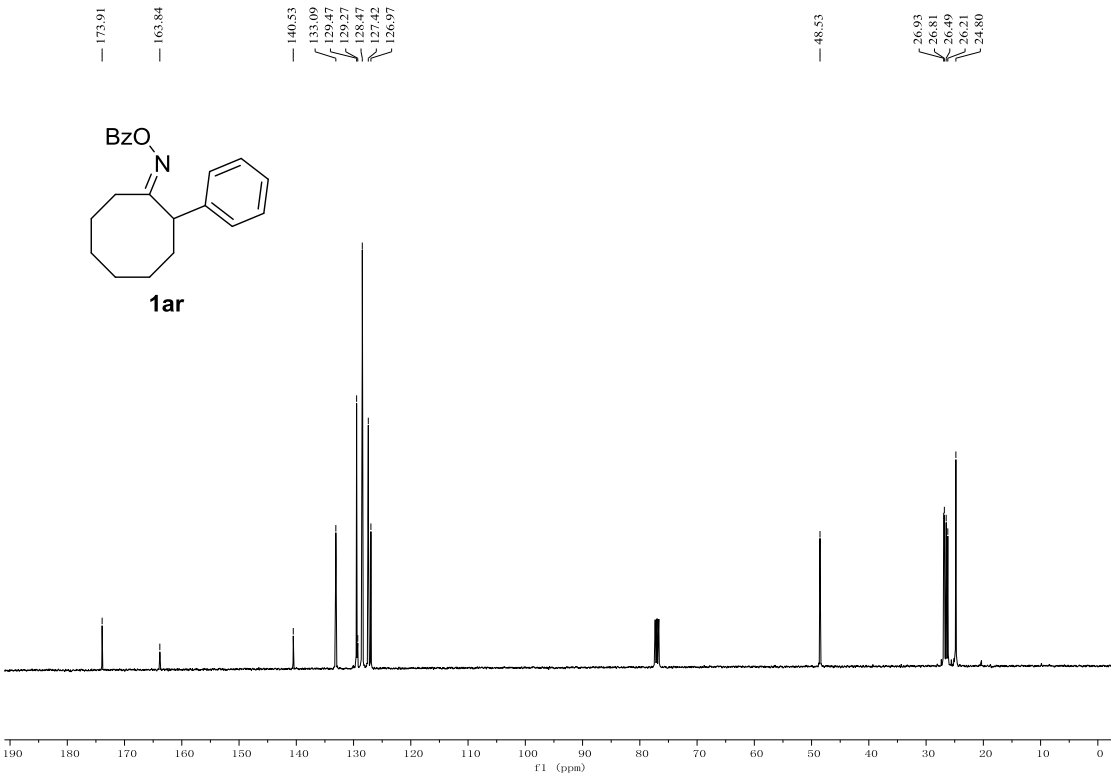
163.96
158.46
133.11
132.73
129.51
129.35
128.48
128.31
113.91
55.22
47.60
31.02
30.80
27.37
26.24
25.41
BzO
N
OMe
1aq
f1 (ppm)
8.07
8.05
8.04
7.59
7.57
7.56
7.47
7.45
7.44
7.42
7.34
7.32
7.30
7.25
7.24
7.22
4.03
4.02
3.99
3.99
2.86
2.85
2.84
2.83
2.82
2.81
2.39
2.38
2.36
2.35
2.33
2.11
2.09
2.08
2.07
2.06
2.05
2.04
2.03
2.02
2.01
1.94
1.94
1.91
1.90
1.88
1.87
1.83
1.82
1.81
1.78
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.53
1.51
1.51
1.49
1.49
1.48
1.47
1.47
1.45
1.44
1.43
1.42
1.41
1.40
BzO
N
1ar
2.00
1.01
4.05
2.01
1.08
1.00
1.00
1.07
2.05
6.04
2.00
f1 (ppm)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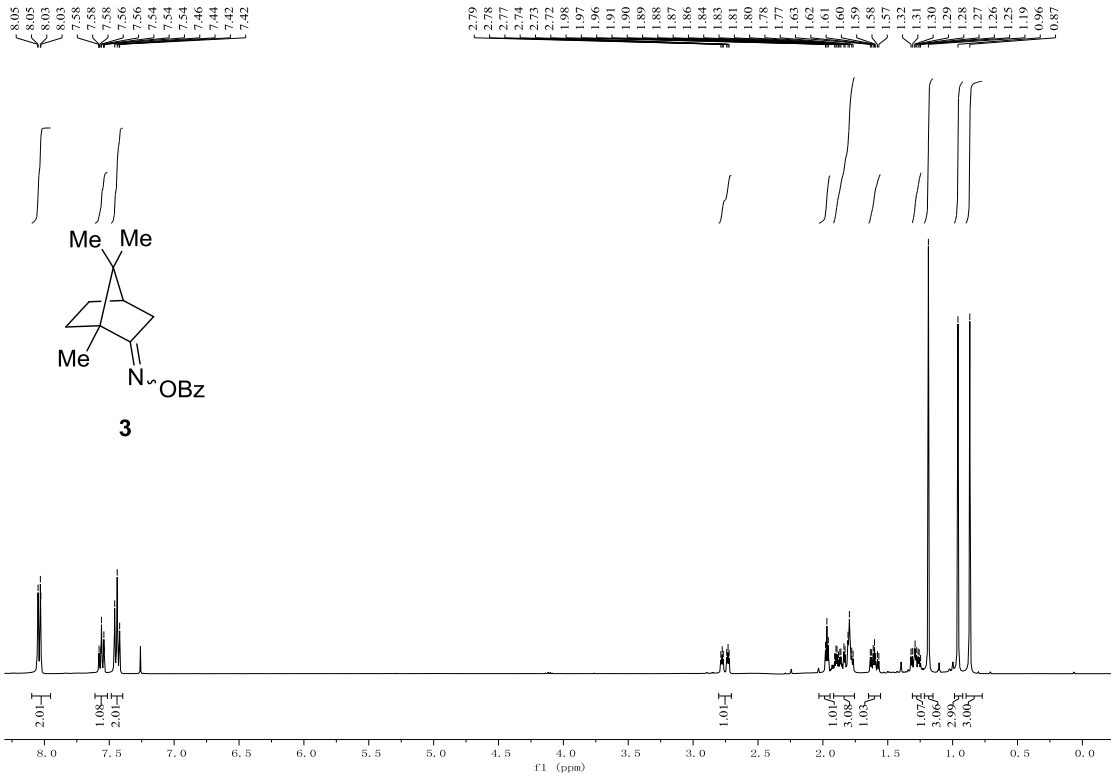
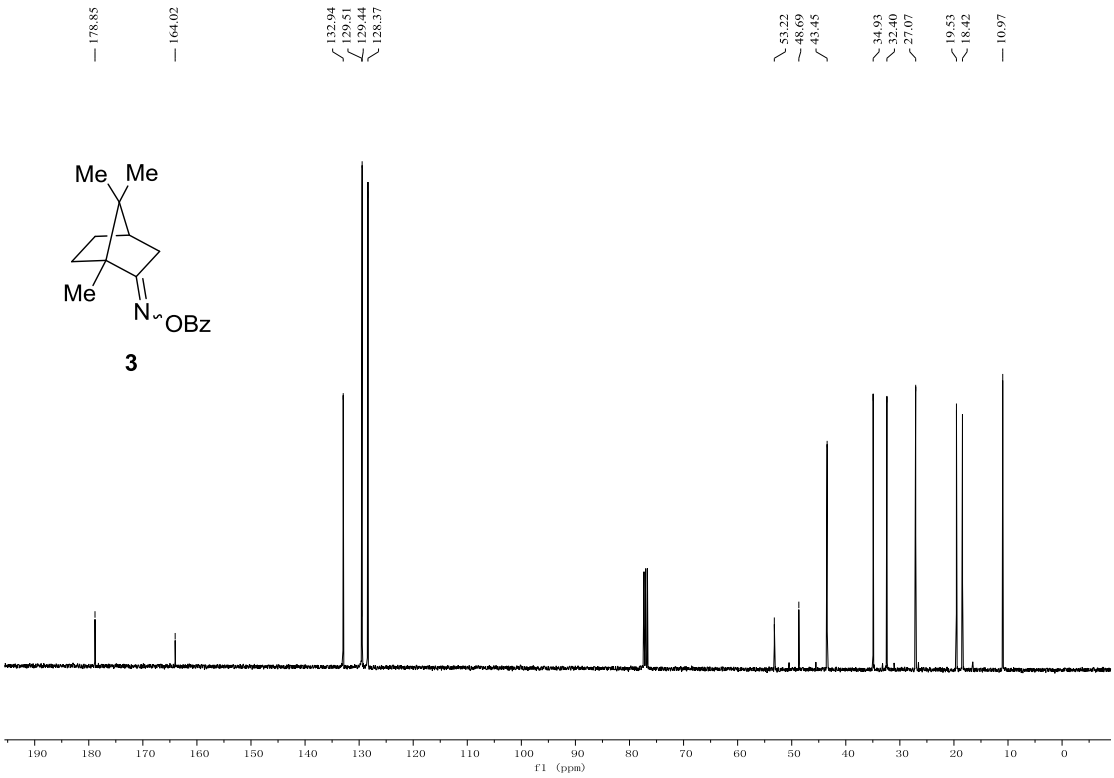
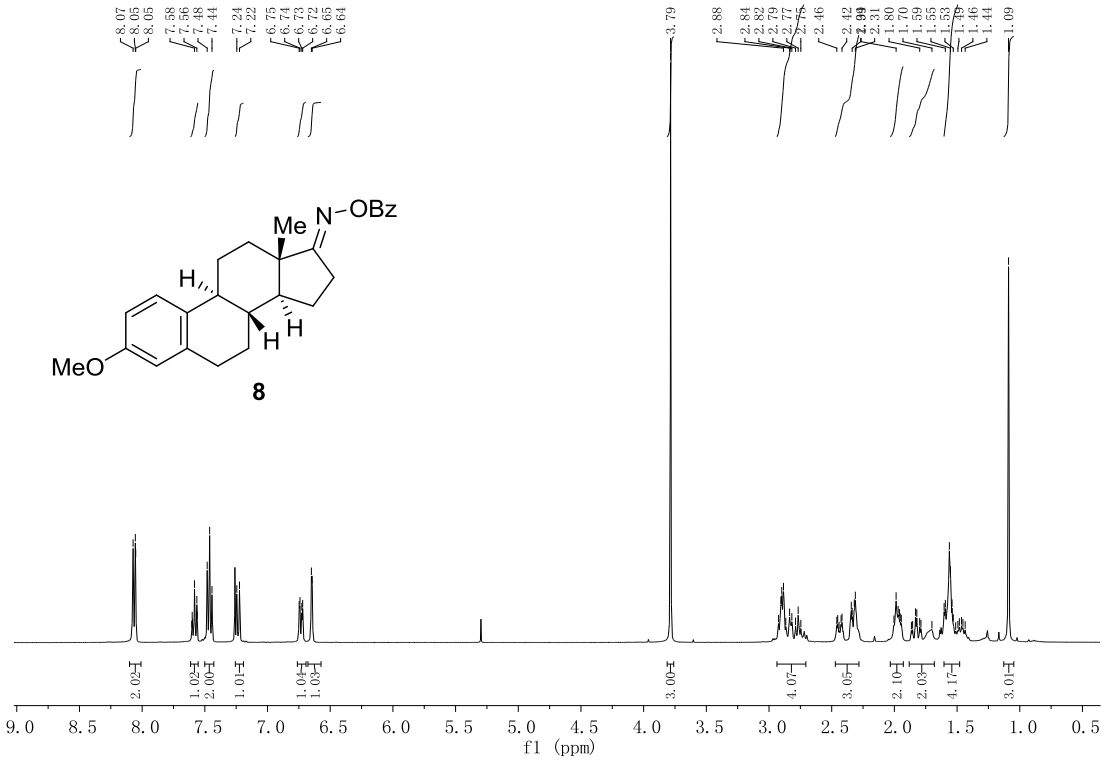
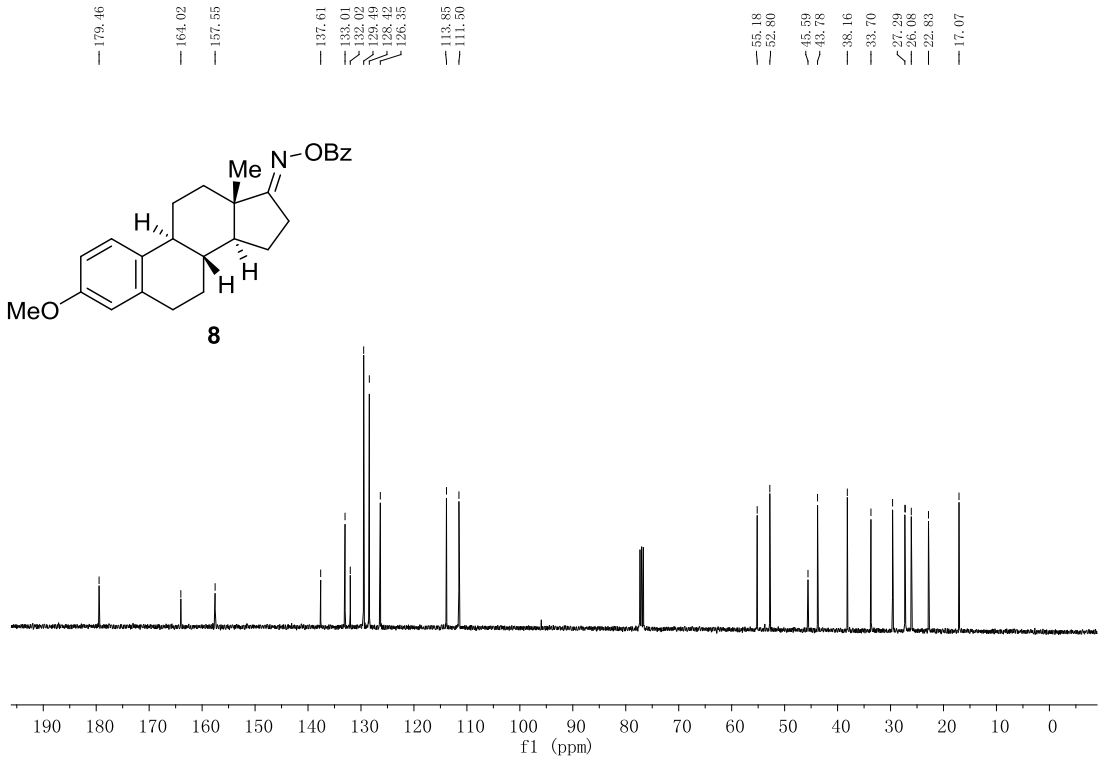
163.84
140.53
133.09
129.47
129.27
128.47
127.42
126.97
48.53
26.93
26.81
26.49
26.21
24.80
BzO
N
1ar
f1 (ppm)


Me
Me
Me
N
OBz
3
f1 (ppm)


178.85
164.02
132.94
129.51
129.44
128.37
53.22
48.69
43.45
34.93
32.40
27.07
19.53
18.42
10.97
Me
Me
Me
N
OBz
3
f1 (ppm)


8.07
8.05
8.05
7.58
7.56
7.48
7.44
7.24
7.22
6.75
6.74
6.73
6.72
6.65
6.64
3.79
2.88
2.84
2.82
2.79
2.77
2.46
2.42
2.31
1.80
1.70
1.59
1.55
1.53
1.46
1.44
1.09
Me
N
OBz
H
H
MeO
8
2.02
1.02
2.00
1.01
1.04
1.03
3.00
4.07
3.05
2.10
2.03
4.17
3.01
f1 (ppm)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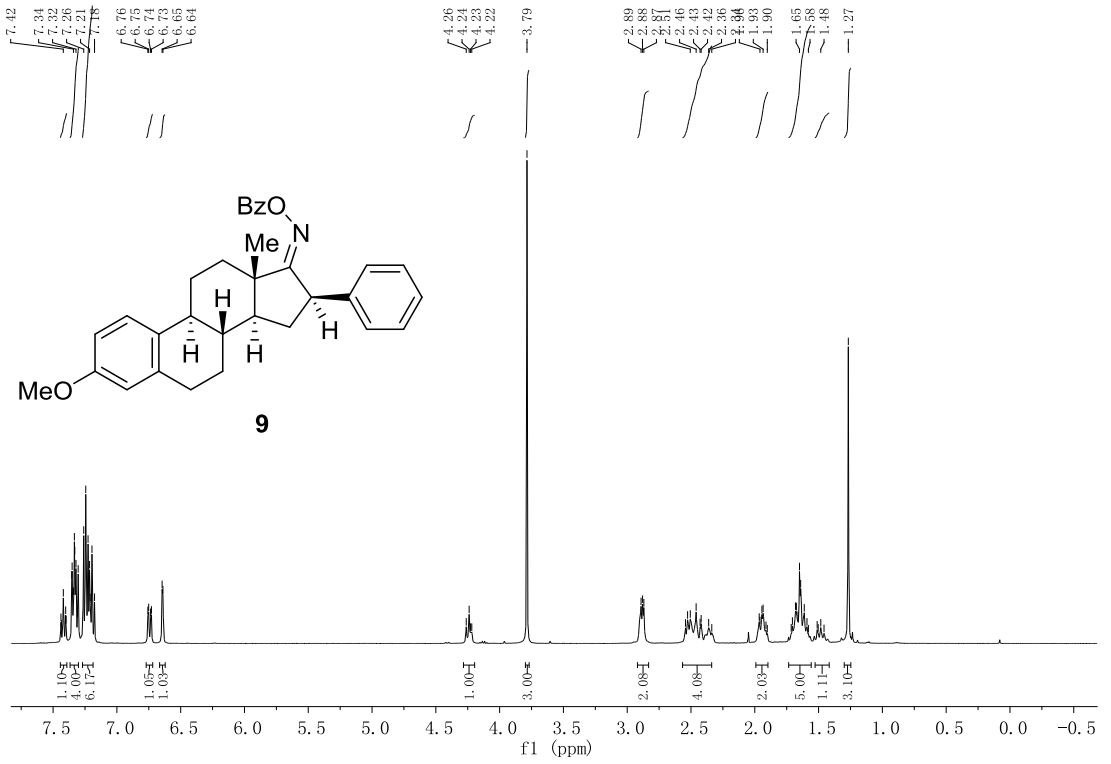
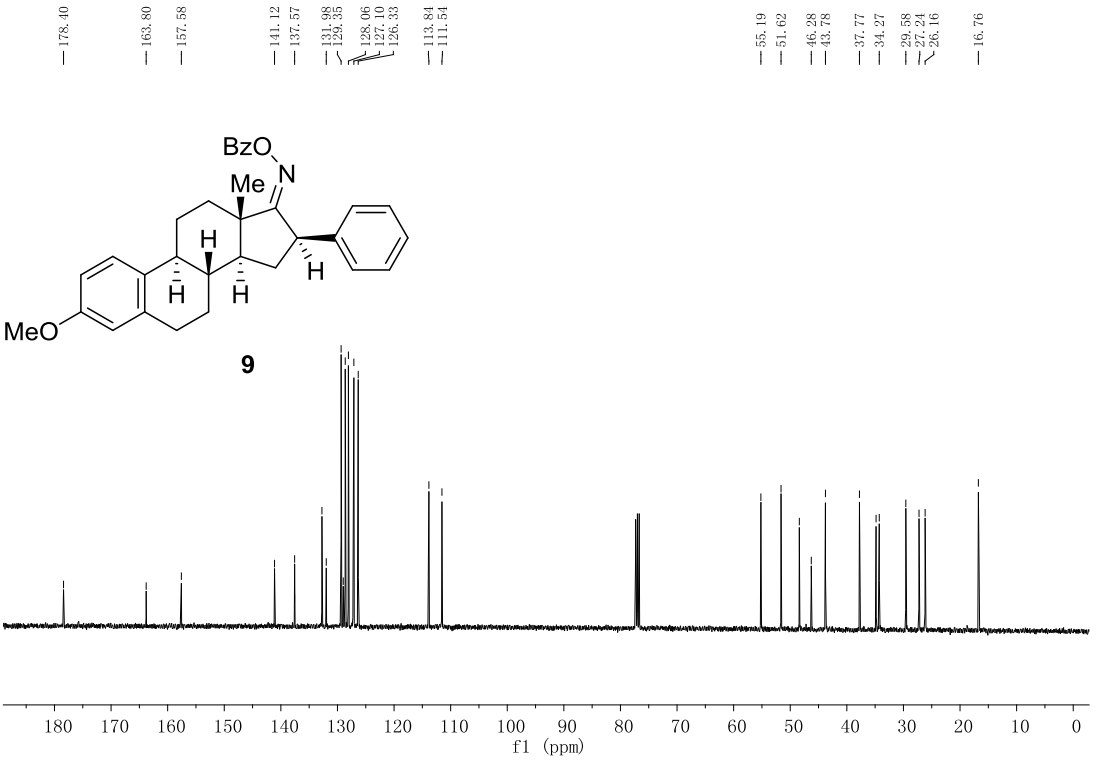
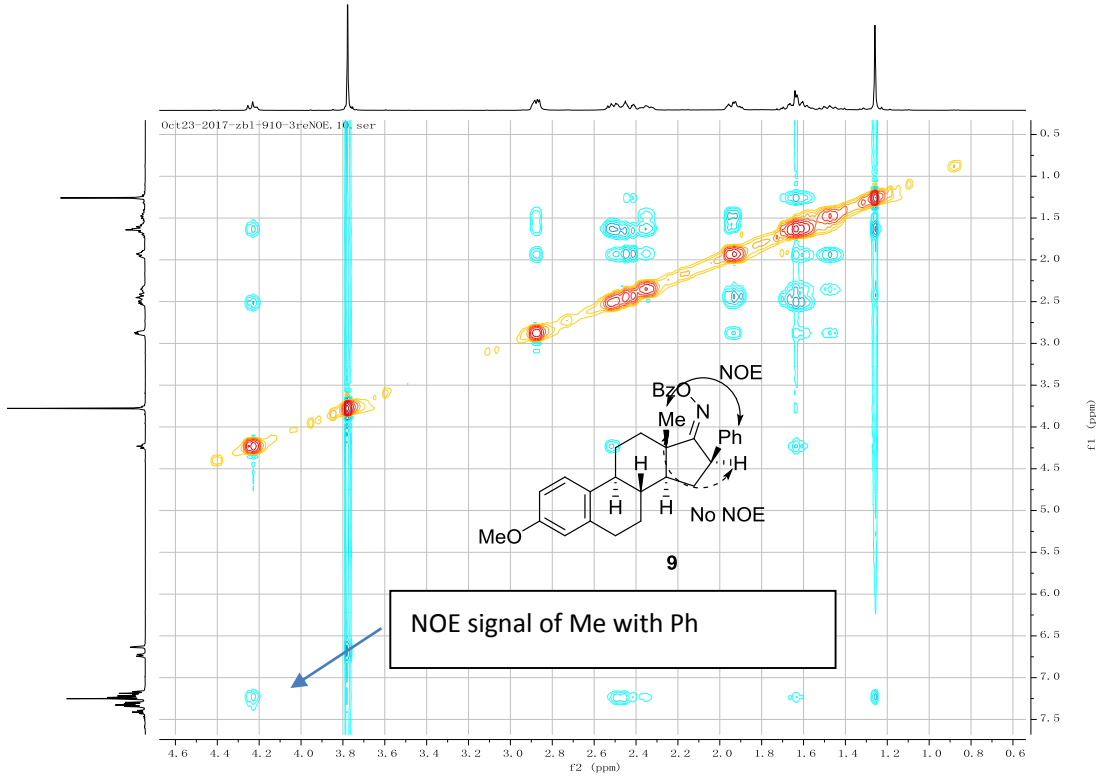
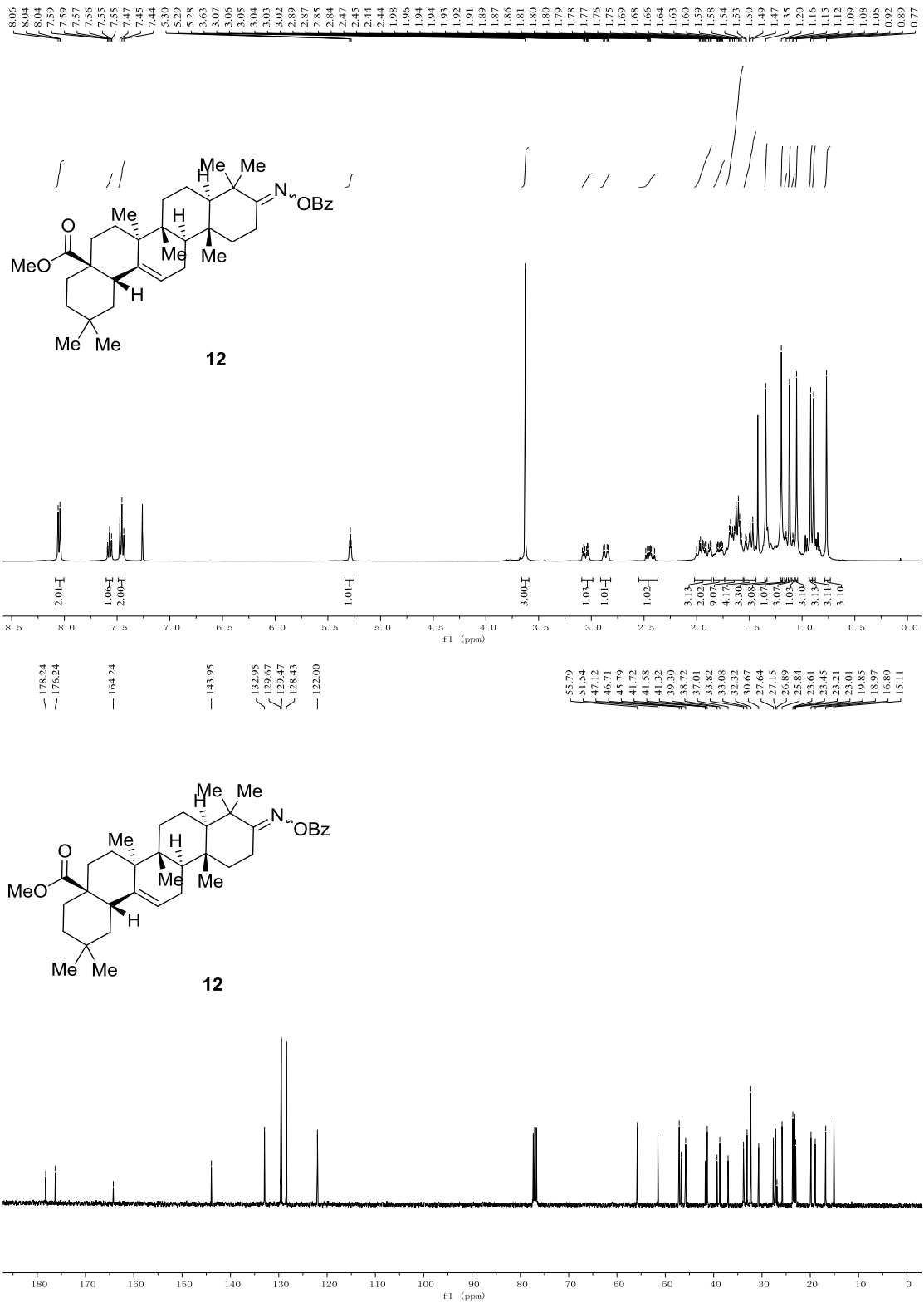
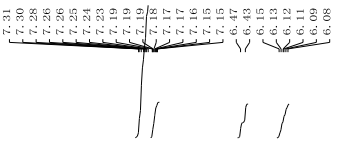
164.02
157.55
137.61
133.01
132.02
129.49
128.42
126.35
113.85
111.50
55.18
52.80
45.59
43.78
38.16
33.70
27.29
26.08
22.83
17.07
Me
N–OBz
H
H
H
MeO
8
f1 (ppm)


7.42
7.34
7.32
7.26
7.21
7.18
6.76
6.75
6.74
6.73
6.65
6.64
4.26
4.24
4.23
4.22
3.79
2.89
2.88
2.51
2.46
2.43
2.42
2.36
1.93
1.90
1.65
1.58
1.48
1.27
BzO
N
Me
H
H
H
H
MeO
9
1.10
4.00
6.17
1.05
1.03
1.00
3.00
2.08
4.08
2.03
5.00
1.11
3.10
f1 (ppm)


178.40
163.80
157.58
141.12
137.57
131.98
129.35
128.06
127.10
126.33
113.84
111.54
55.19
51.62
46.28
43.78
37.77
34.27
29.58
27.24
26.16
16.76
BzO
N
Me
H
H
H
MeO
9
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Oct23-2017-zb1+910-3reNOE.10 ser
NOE
BzO
N
Me
Ph
H
H
H
No NOE
MeO
9
NOE signal of Me with Ph
4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
f2 (ppm)
f1 (ppm)


12
f1 (ppm)
12
f1 (ppm)


7.31
7.30
7.28
7.26
7.26
7.25
7.24
7.23
7.19
7.19
7.18
7.17
7.17
7.16
7.15
7.15
6.47
6.43
6.15
6.13
6.12
6.11
6.09
6.08


2.52
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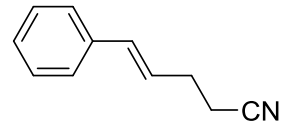
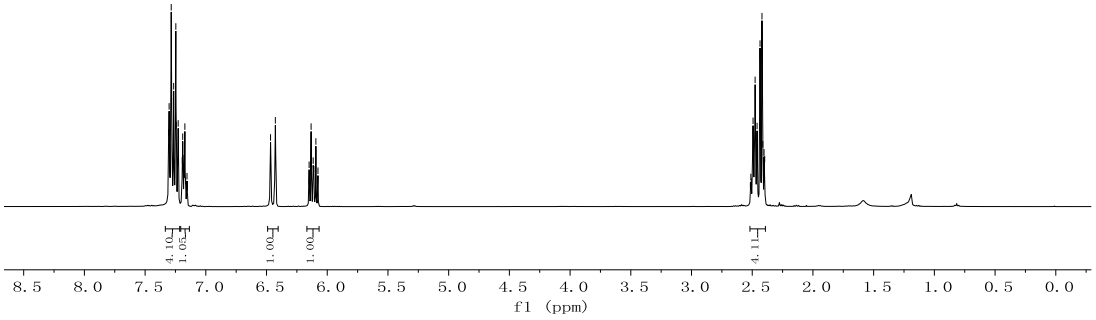
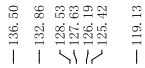
2.44
2.43
2.42
2.41
2.40
2.40

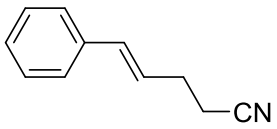

CN

2aa

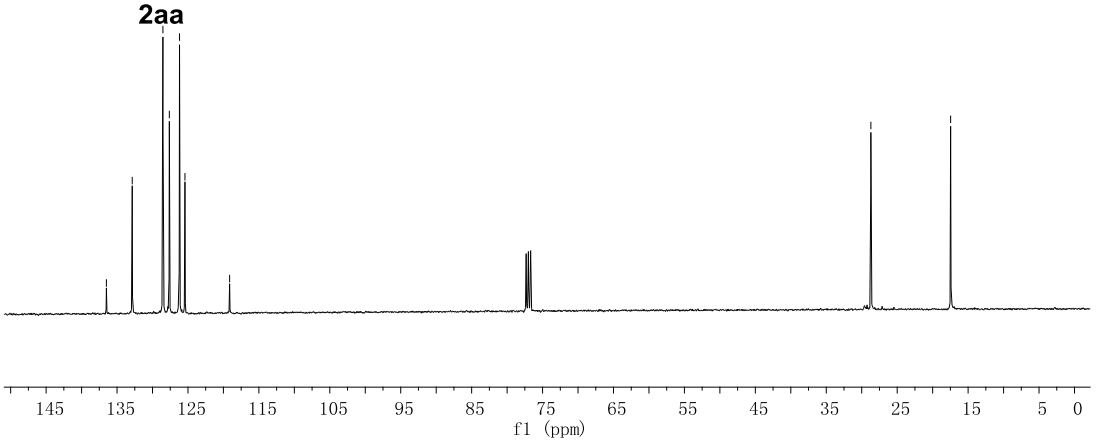

4.10
1.05
1.00
1.00
4.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

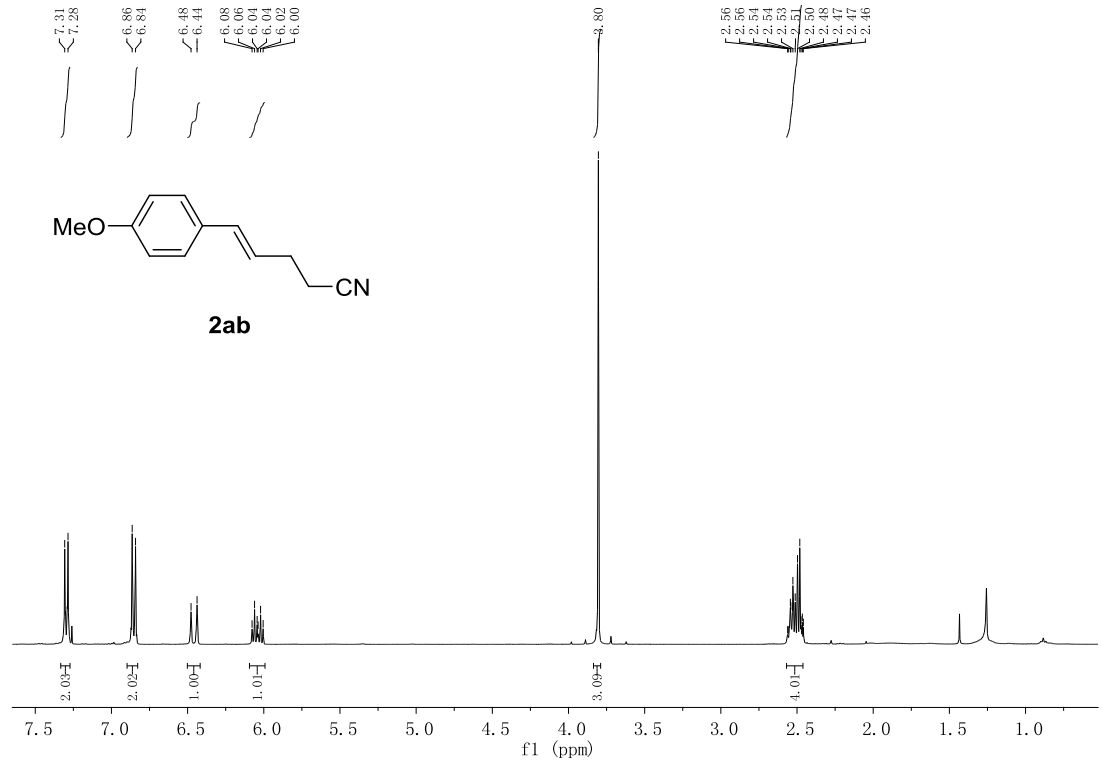

136.50
132.86
128.53
127.63
126.19
125.42
119.13

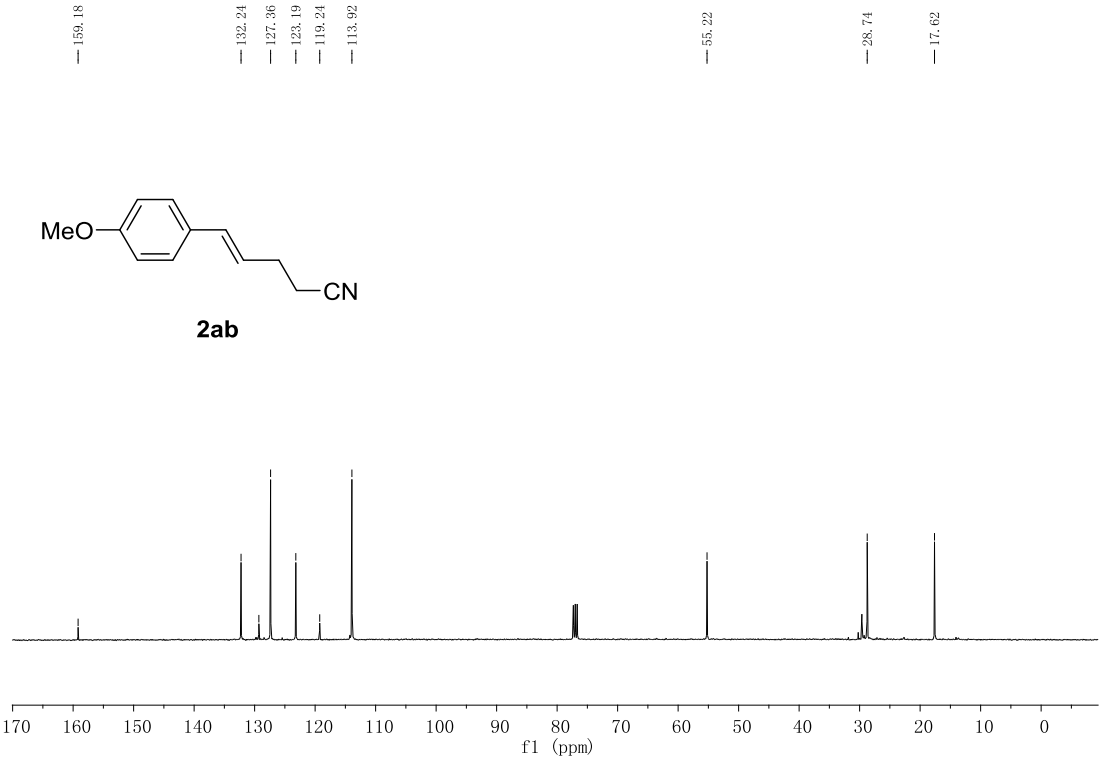

28.71
17.46

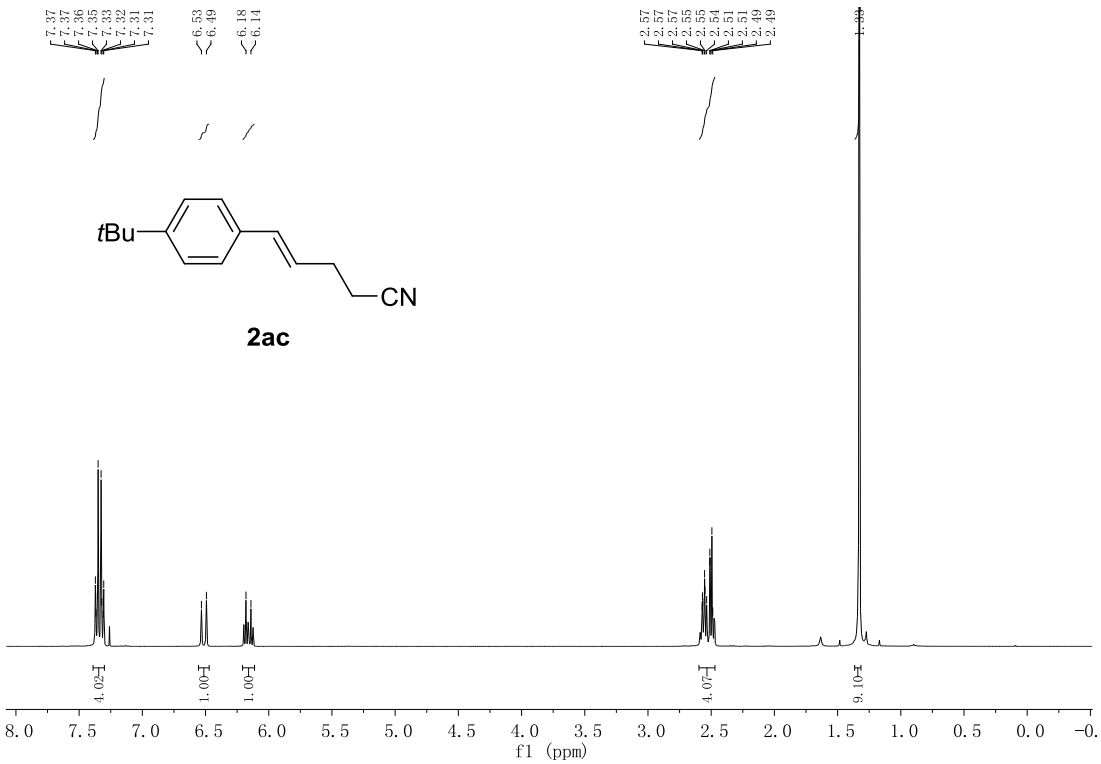

CN

2aa


145
135
125
115
105
95
85
75
65
55
45
35
25
15
5
0
f1 (ppm)


7.31
7.28
6.86
6.84
6.48
6.44
6.08
6.06
6.04
6.04
6.02
6.00
3.80
2.56
2.56
2.54
2.54
2.53
2.51
2.50
2.48
2.47
2.47
2.46
MeO
CN
2ab
2.03
2.02
1.00
1.01
3.09
4.01
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
f1 (ppm)


159.18
132.24
127.36
123.19
119.24
113.92
55.22
28.74
17.62
MeO
CN
2ab
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37
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7.36
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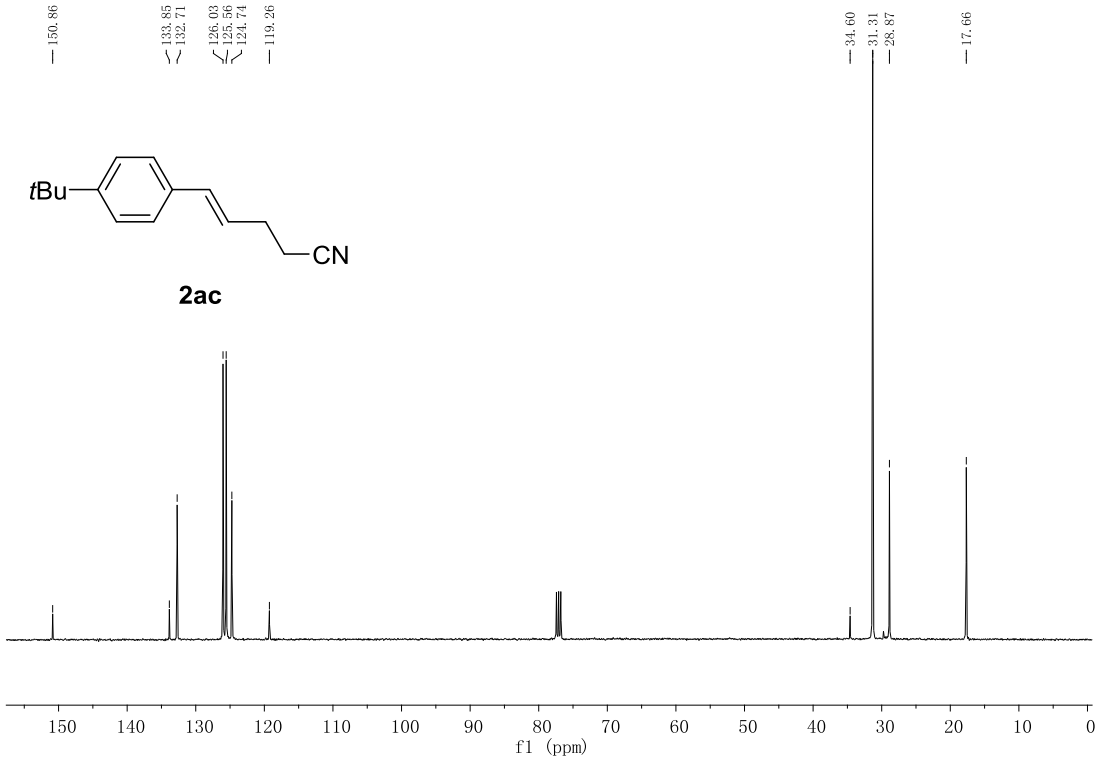
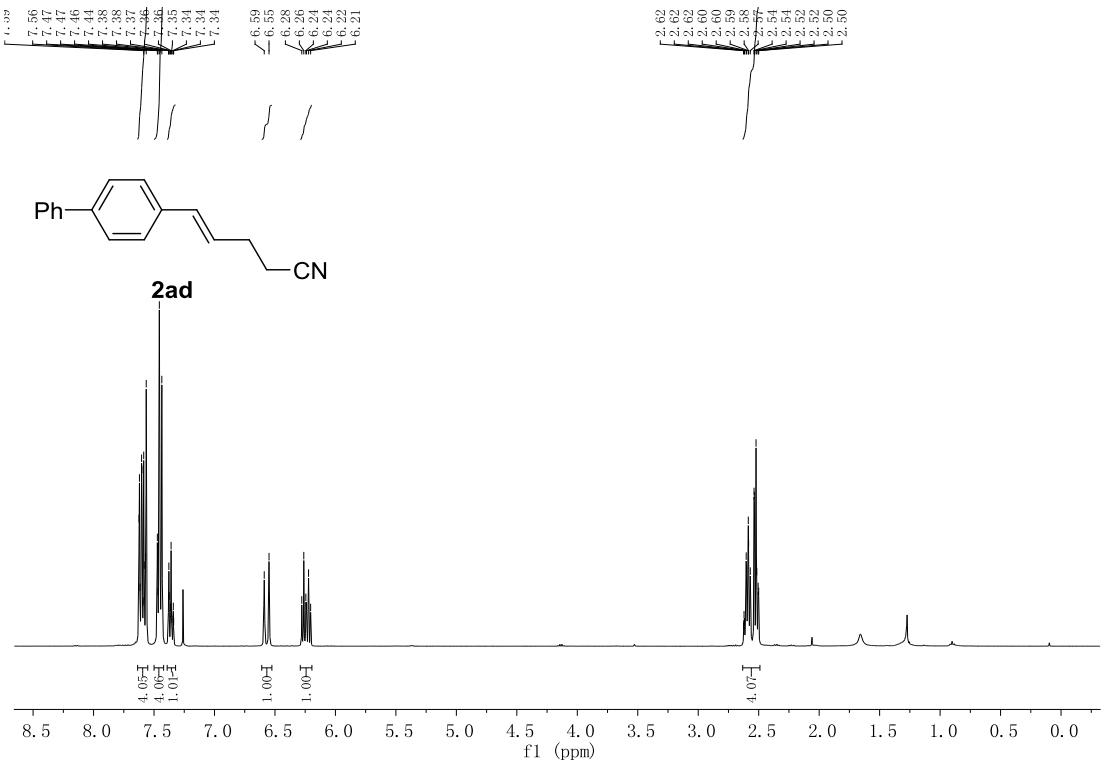
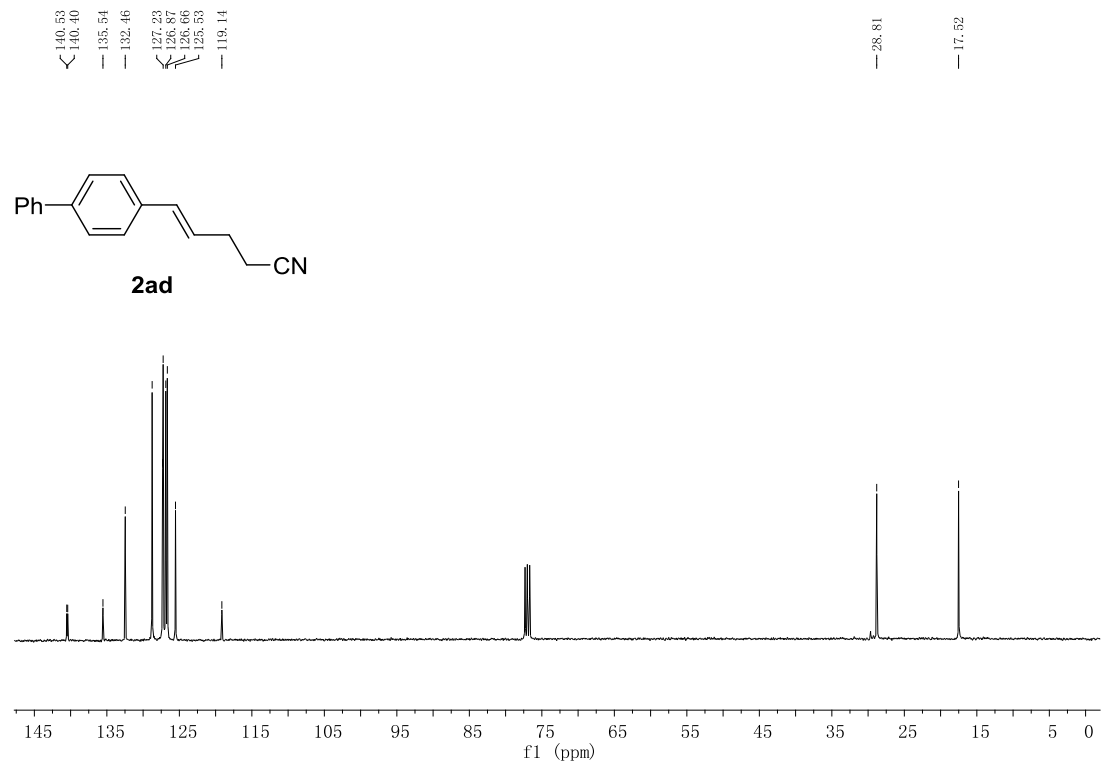
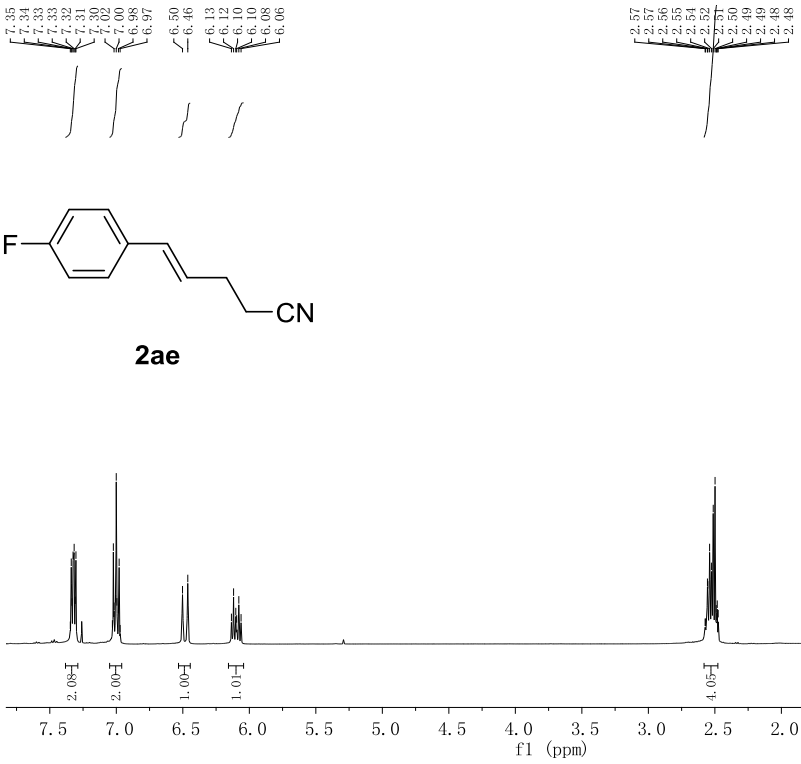
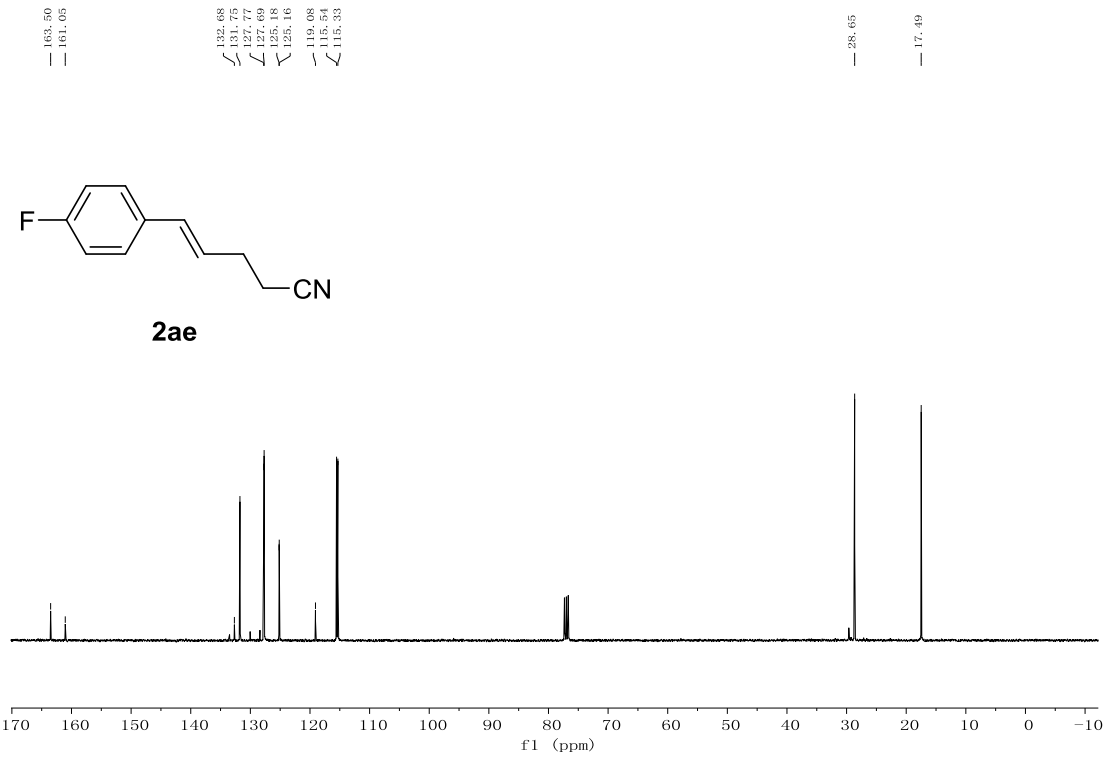
7.32
7.31
7.31
6.53
6.49
6.18
6.14
2.57
2.57
2.57
2.55
2.55
2.54
2.51
2.51
2.49
2.49
1.33
tBu
CN
2ac
4.02
1.00
1.00
4.07
9.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.
f1 (ppm)

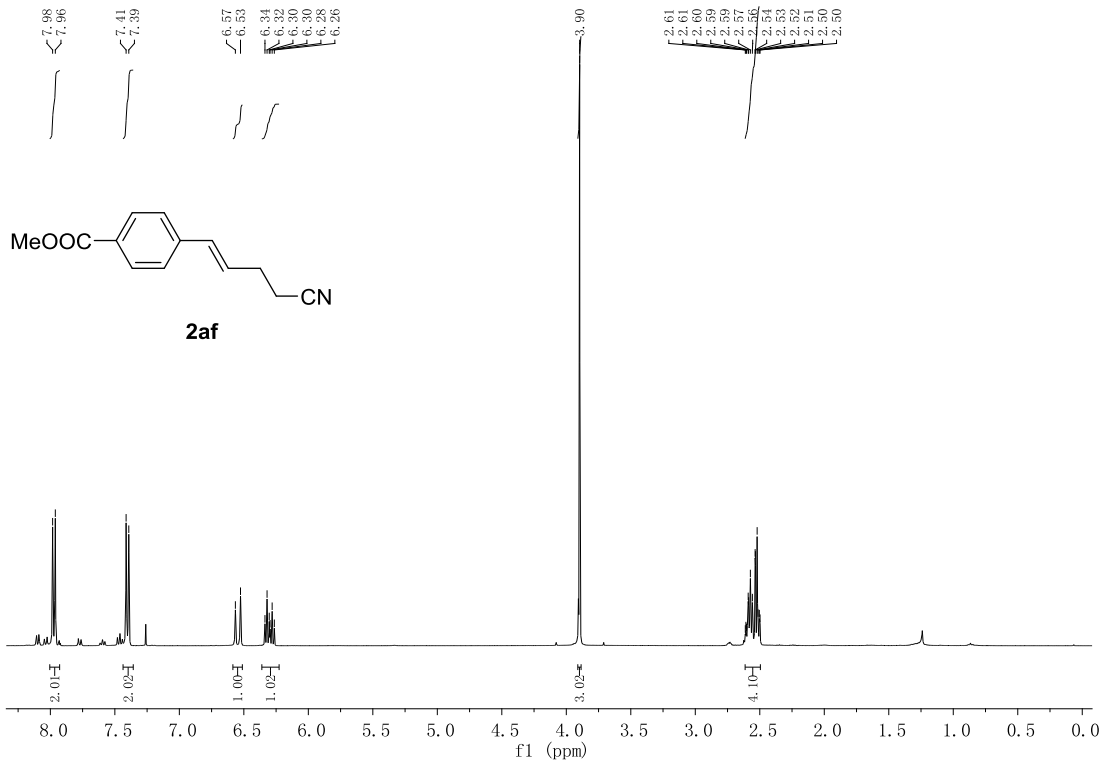

150.86
133.85
132.71
126.03
125.56
124.74
119.26
34.60
31.31
28.87
17.66
tBu
CN
2ac
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

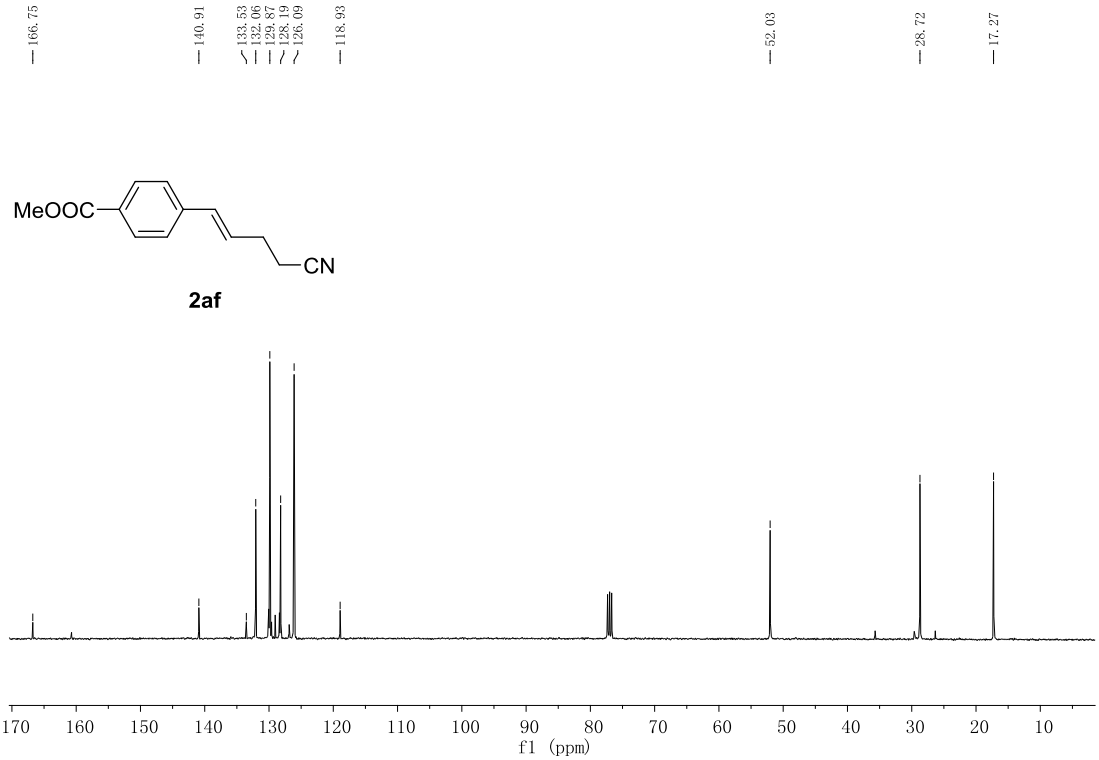

Ph
CN
2ad
4.05
4.06
1.01
1.00
1.00
4.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

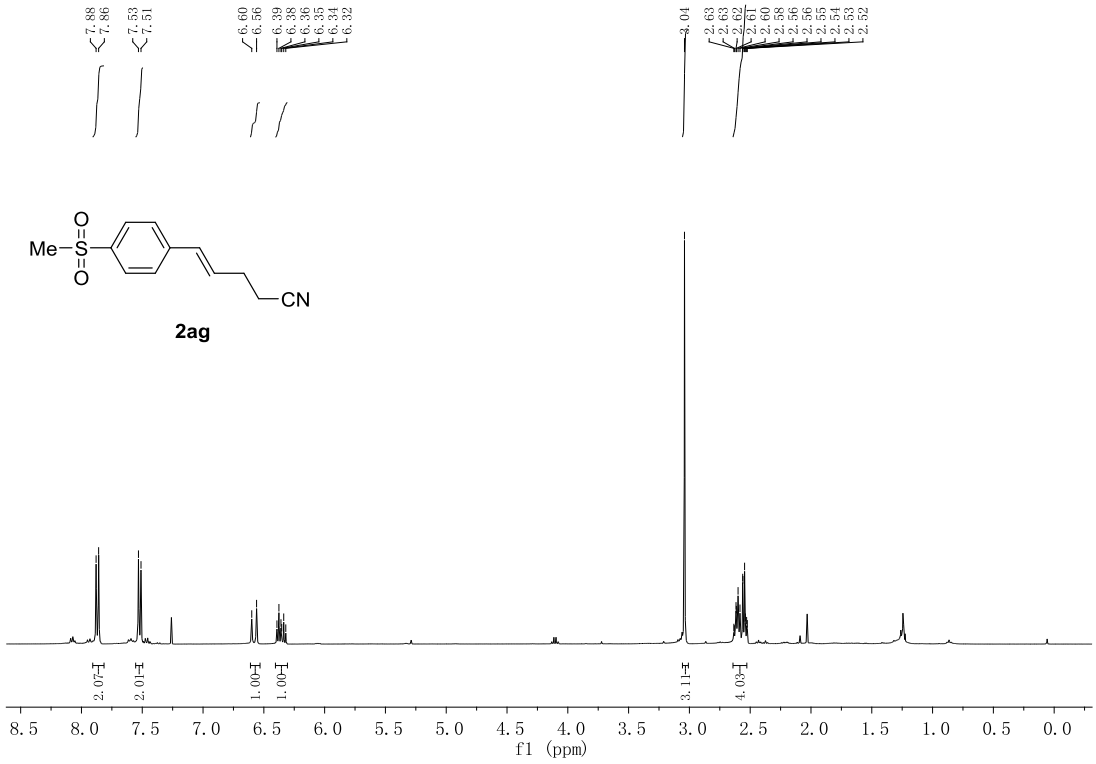

140.53
140.40
135.54
132.46
127.23
126.87
126.66
125.53
119.14
28.81
17.52
Ph
CN
2ad
145 135 125 115 105 95 85 75 65 55 45 35 25 15 5 0
f1 (ppm)

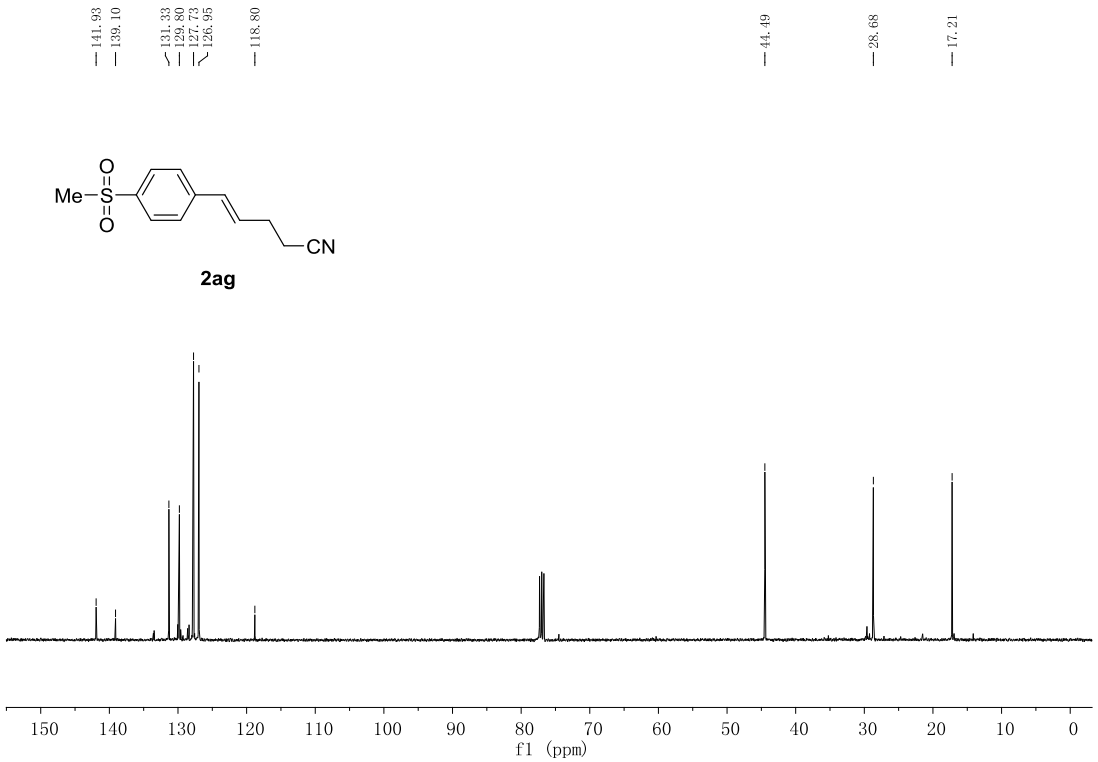

7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.02
7.00
6.98
6.97
6.50
6.46
6.13
6.12
6.10
6.10
6.08
6.06
2.57
2.57
2.56
2.55
2.54
2.52
2.51
2.50
2.49
2.49
2.48
2.48
F
CN
2ae
2.08
2.00
1.00
1.01
4.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
-114.32
F
CN
2ae
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
f1 (ppm)


163.50
161.05
132.68
131.75
127.77
127.69
125.18
125.16
119.08
115.54
115.33
28.65
17.49
F
CN
2ae
f1 (ppm)

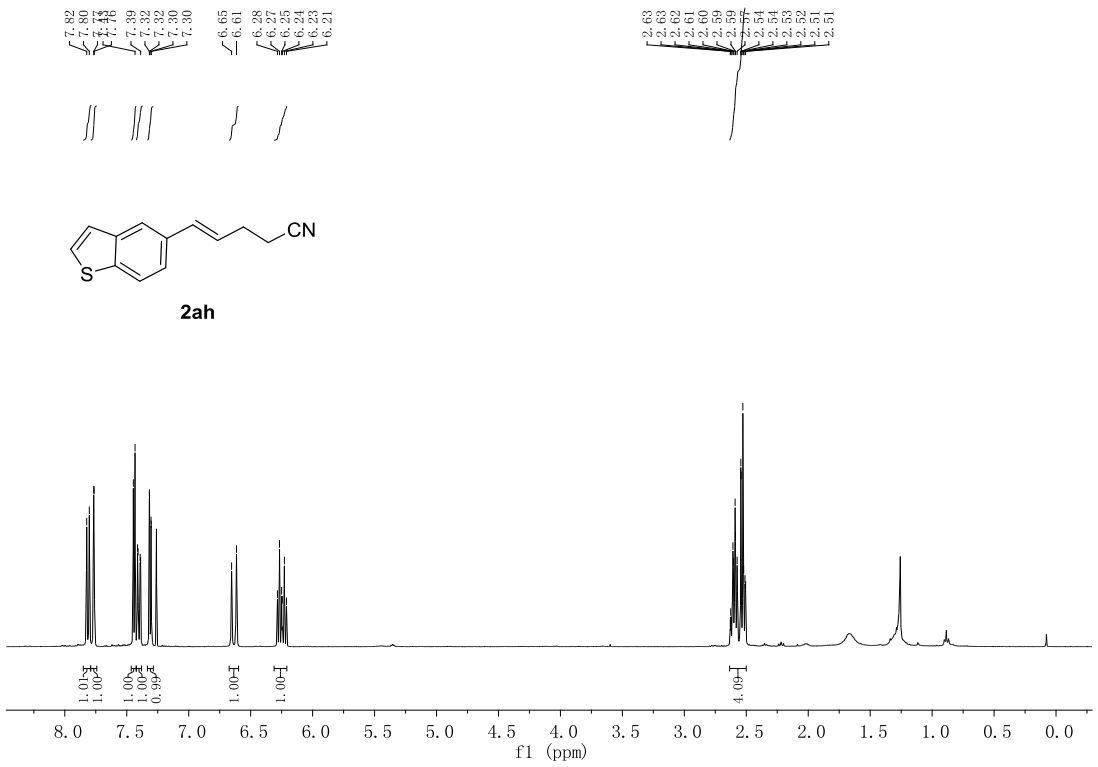

7.98
7.96
7.41
7.39
6.57
6.53
6.34
6.32
6.30
6.28
6.26
3.90
2.61
2.61
2.60
2.59
2.59
2.57
2.56
2.54
2.53
2.52
2.51
2.50
2.50
MeOOC
CN
2af
2.01
2.02
1.00
1.02
3.02
4.10
f1 (ppm)


166.75
140.91
133.53
132.06
129.87
128.19
126.09
118.93
52.03
28.72
17.27
MeOOC
CN
2af
f1 (ppm)


7.88
7.86
7.53
7.51
6.60
6.56
6.39
6.38
6.36
6.35
6.34
6.32
3.04
2.63
2.63
2.62
2.61
2.60
2.58
2.56
2.56
2.55
2.54
2.53
2.52
Me
S
O
O
CN
2ag
2.07
2.01
1.00
1.00
3.11
4.03
f1 (ppm)

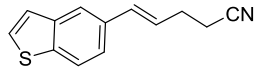

141.93
139.10
131.33
129.80
127.73
126.95
118.80
44.49
28.68
17.21
Me
S
O
O
CN
f1 (ppm)

2ag

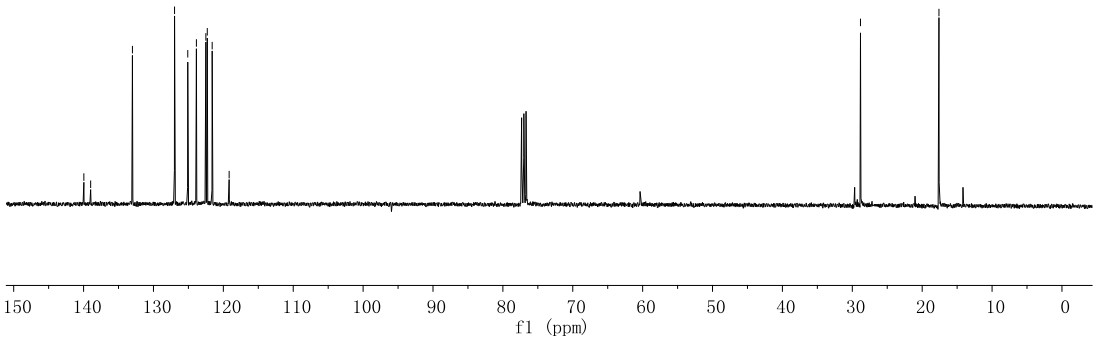

7.82
7.80
7.46
7.44
7.39
7.32
7.32
7.30
7.30
6.65
6.61
6.28
6.27
6.25
6.24
6.23
6.21
2.63
2.63
2.62
2.61
2.60
2.59
2.59
2.57
2.54
2.54
2.53
2.52
2.51
2.51
S
CN
1.01
1.00
1.00
1.00
0.99
1.00
1.00
4.09
f1 (ppm)

2ah

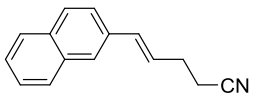

139.96
138.99
133.01
126.98
123.86
122.50
122.30
121.60
119.17
28.83
17.60


CN
S

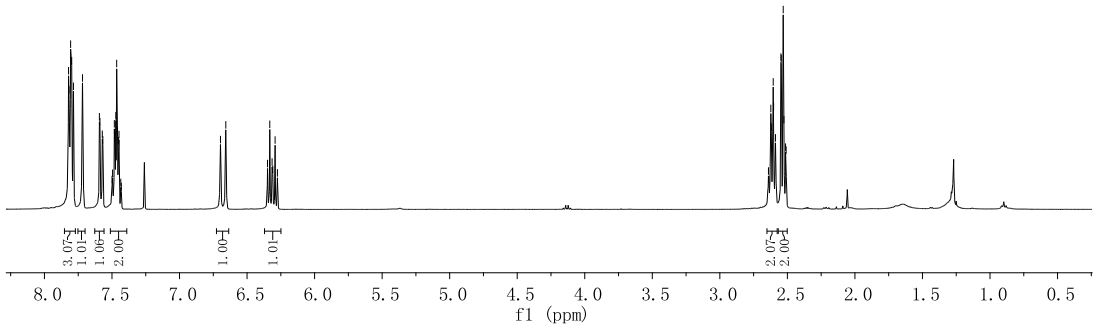
2ah

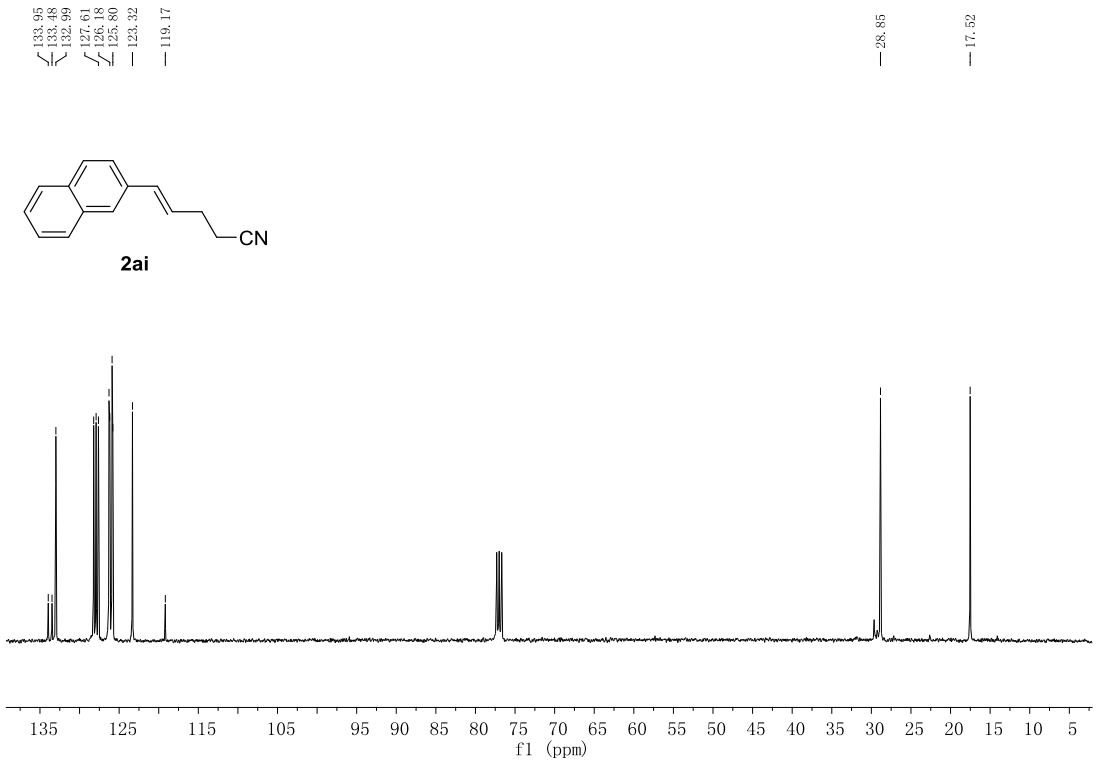

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

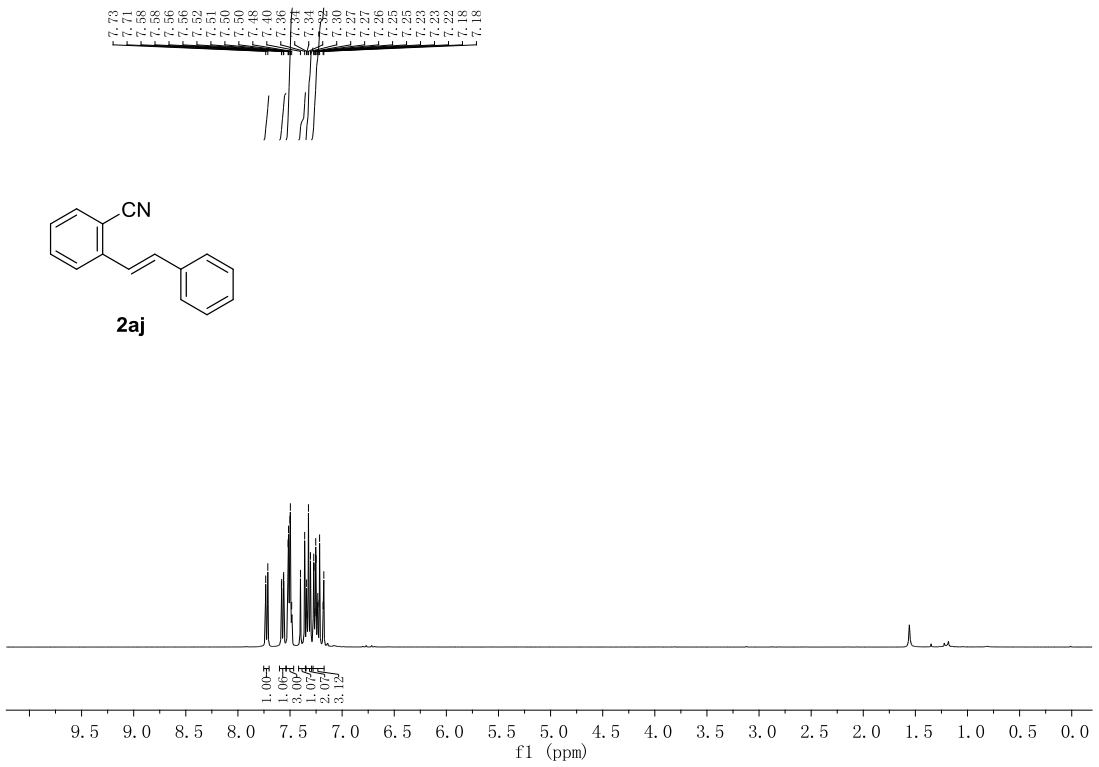

7.82
7.82
7.81
7.80
7.79
7.72
7.57
7.50
7.47
7.45
7.43
6.70
6.66
6.35
6.33
6.31
6.31
6.29
6.28
2.64
2.64
2.62
2.62
2.60
2.60
2.59
2.59
2.55
2.55
2.53
2.53
2.51
2.51

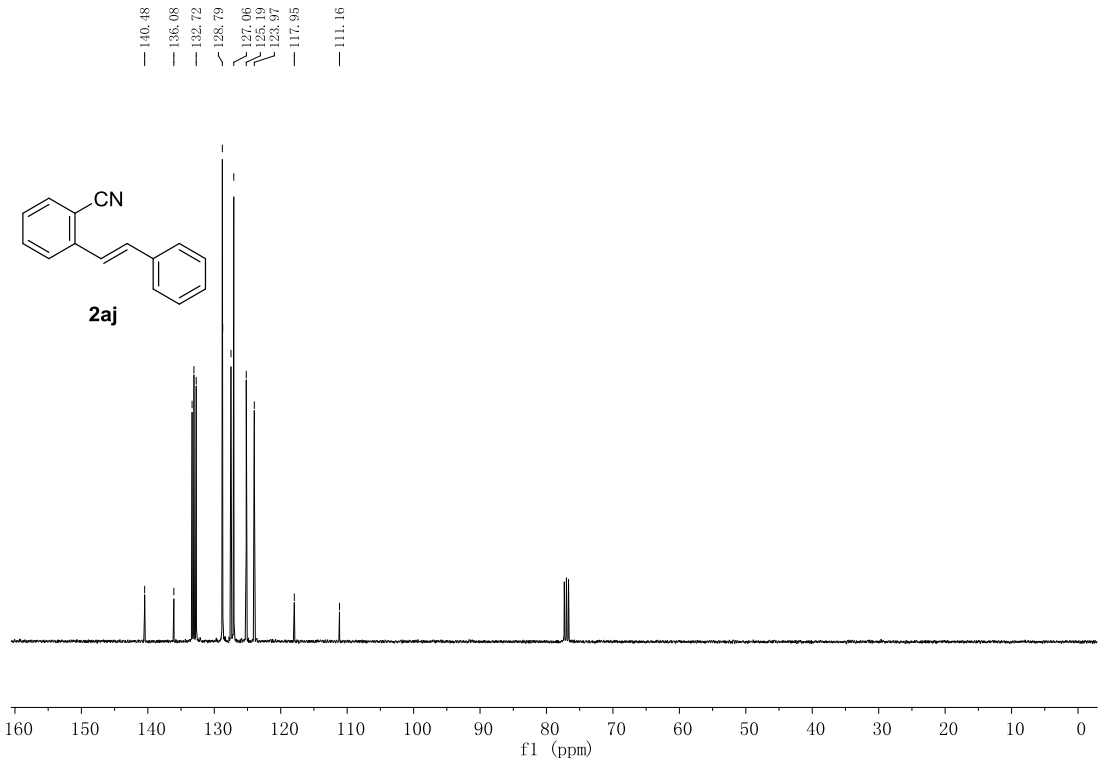

CN

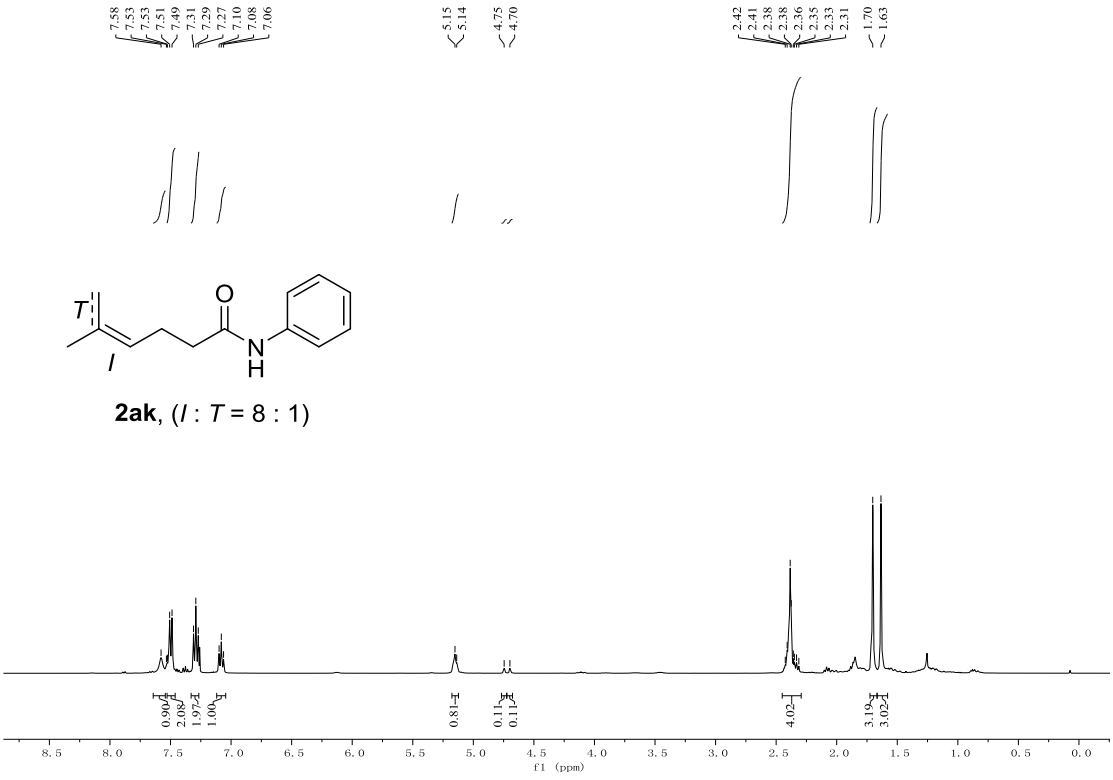
2ai

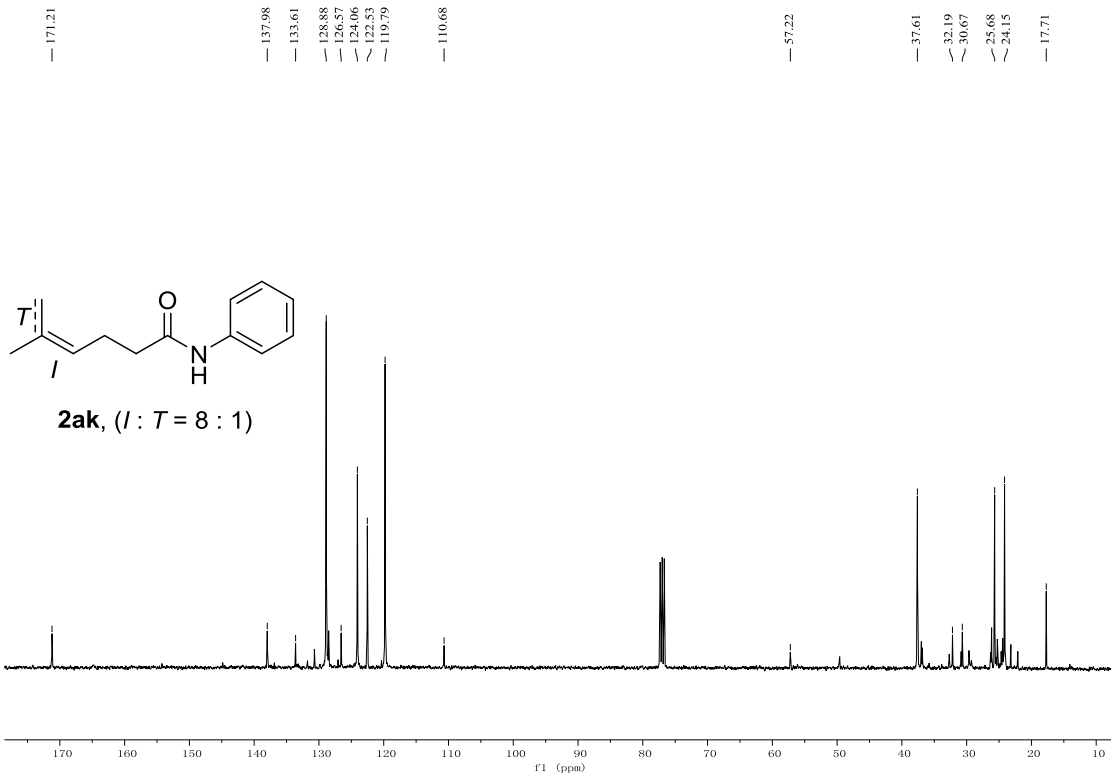

3.07
1.10
1.00
2.00
1.00
1.10
2.07
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


133.95
133.48
132.99
127.61
126.18
125.80
123.32
119.17
28.85
17.52
CN
2ai
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

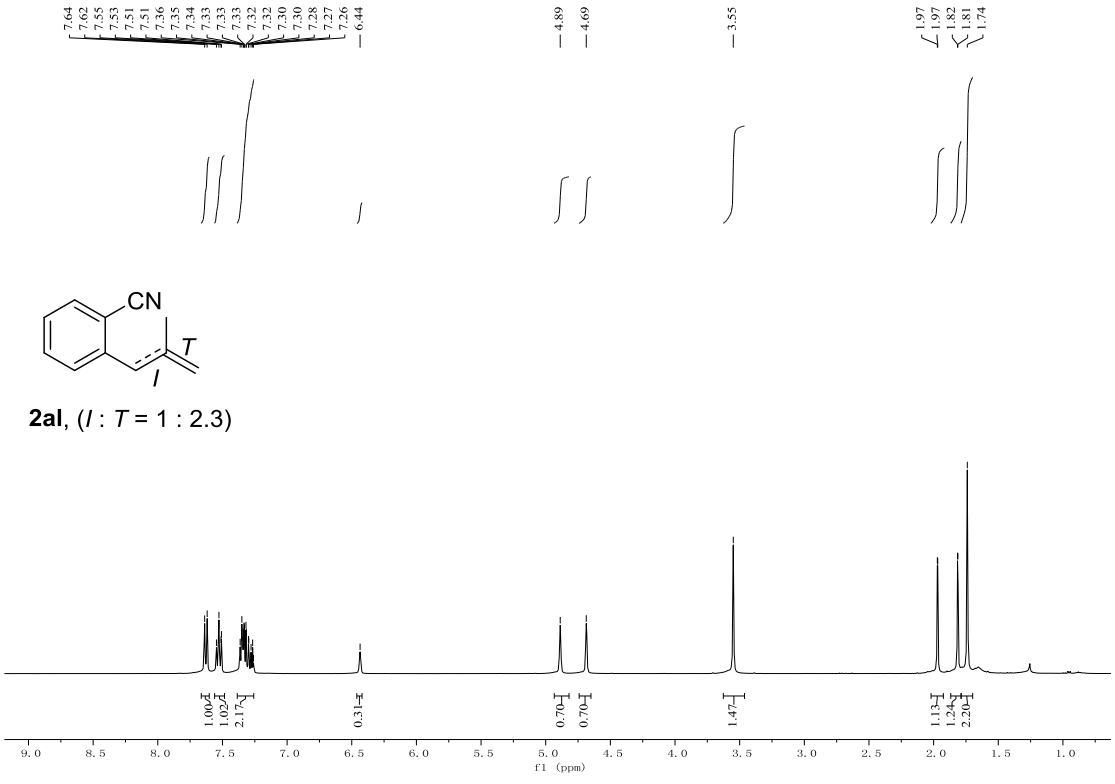

7.73
7.71
7.58
7.58
7.56
7.56
7.52
7.51
7.50
7.50
7.48
7.40
7.36
7.34
7.32
7.30
7.27
7.27
7.26
7.25
7.23
7.23
7.22
7.18
7.18
CN
2aj
1.00
1.06
3.00
1.07
2.07
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


140.48
136.08
132.72
128.79
127.06
125.19
123.97
117.95
111.16
CN
2aj
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

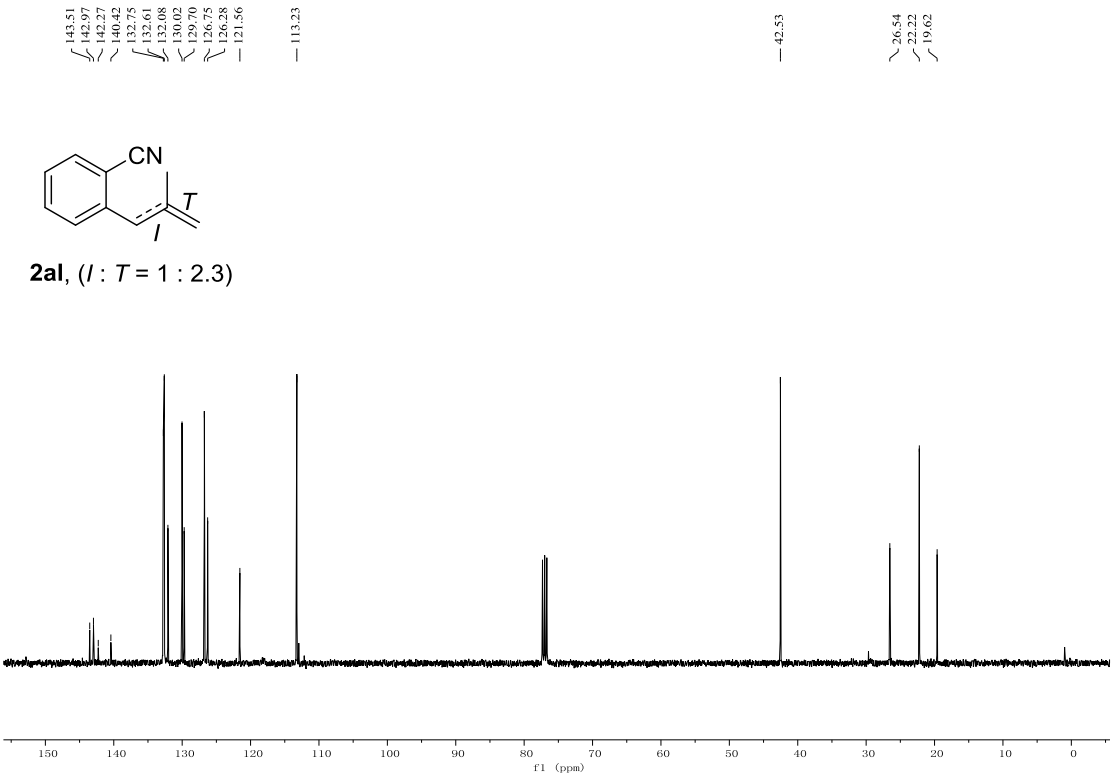

7.58
7.53
7.53
7.51
7.49
7.31
7.29
7.27
7.10
7.08
7.06
5.15
5.14
4.75
4.70
2.42
2.41
2.38
2.38
2.36
2.35
2.33
2.31
1.70
1.63
O
N
H
T
I
2ak, (I : T = 8 : 1)
0.90
2.08
1.97
1.00
0.81
0.11
0.11
4.02
3.19
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



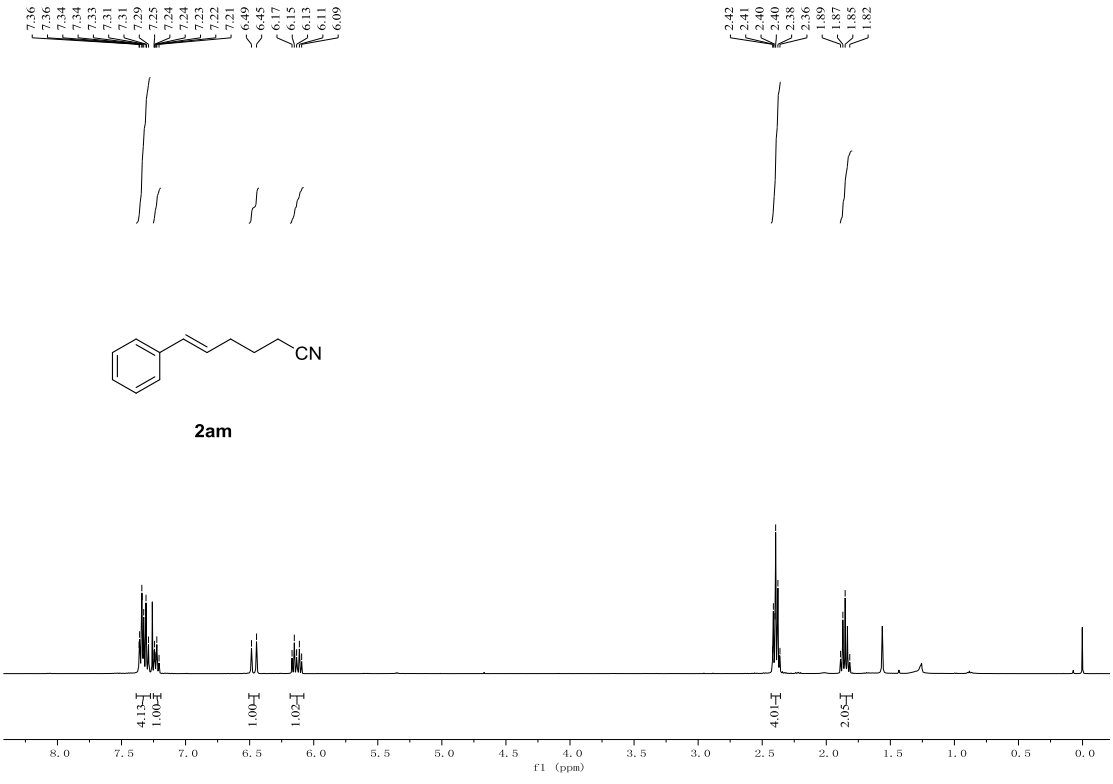
2ak, (*I* : *T* = 8 : 1)



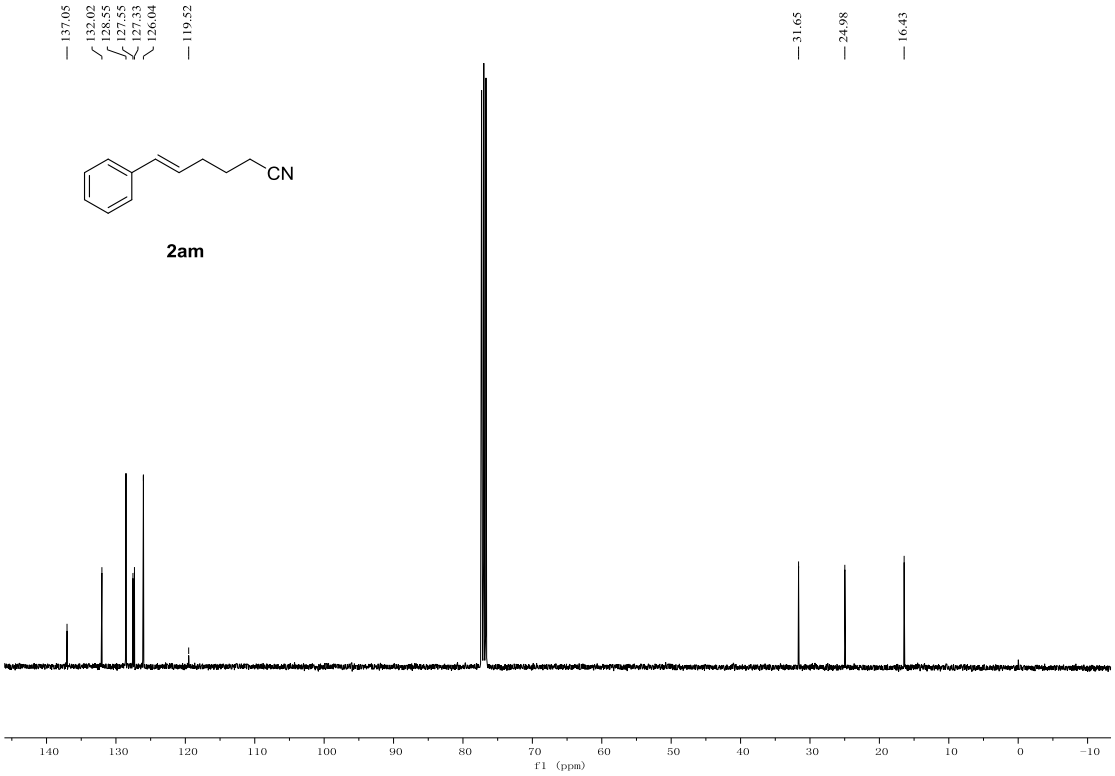
2al, (*I* : *T* = 1 : 2.3)

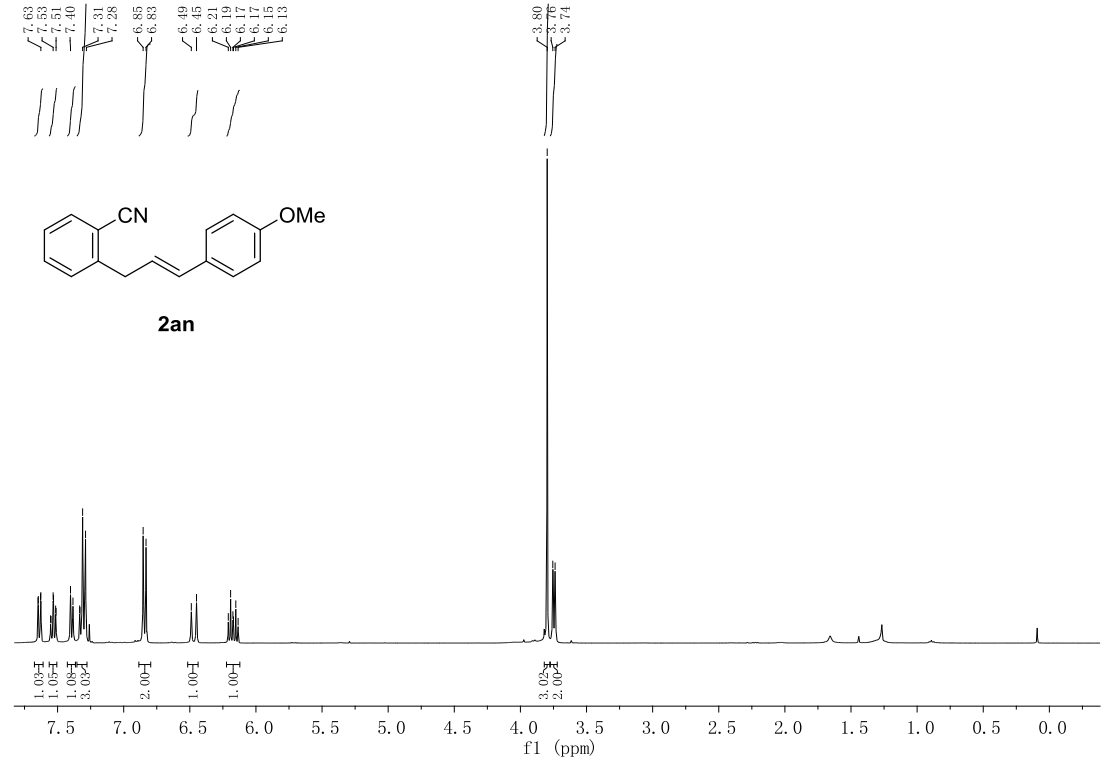


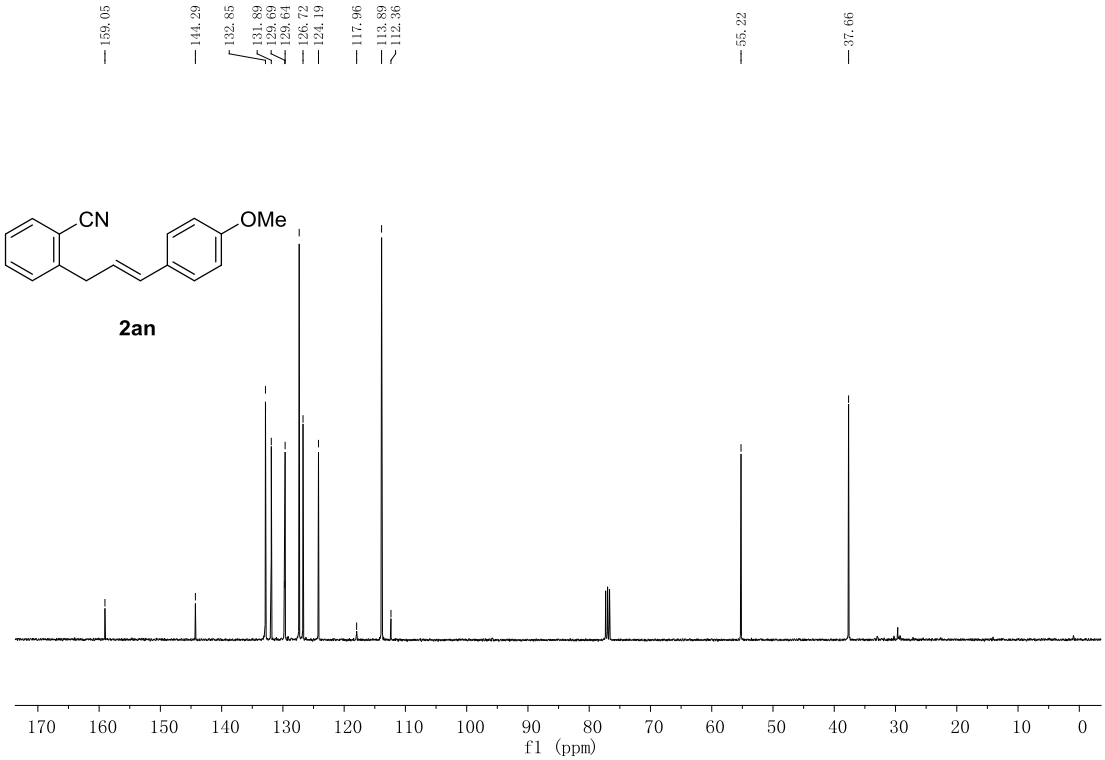
2al, (*I* : *T* = 1 : 2.3)

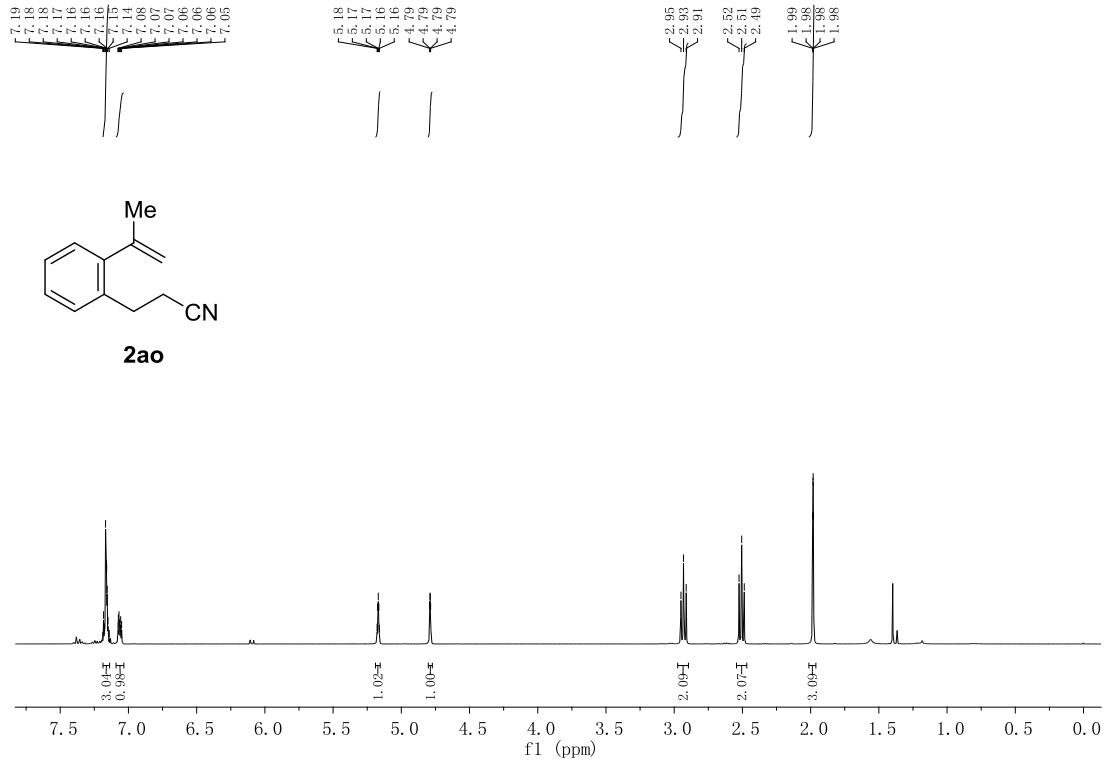


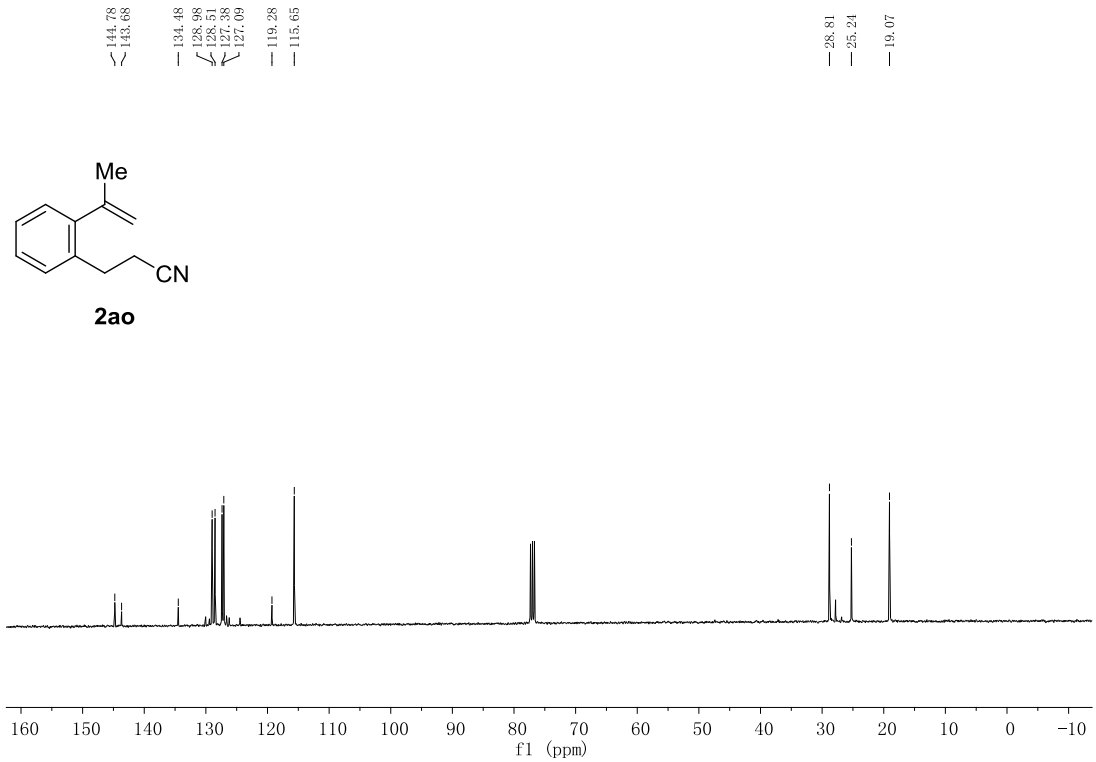
2am


137.05
132.02
128.55
127.55
127.33
126.04
119.52
31.65
24.98
16.43
CN
2am
f1 (ppm)

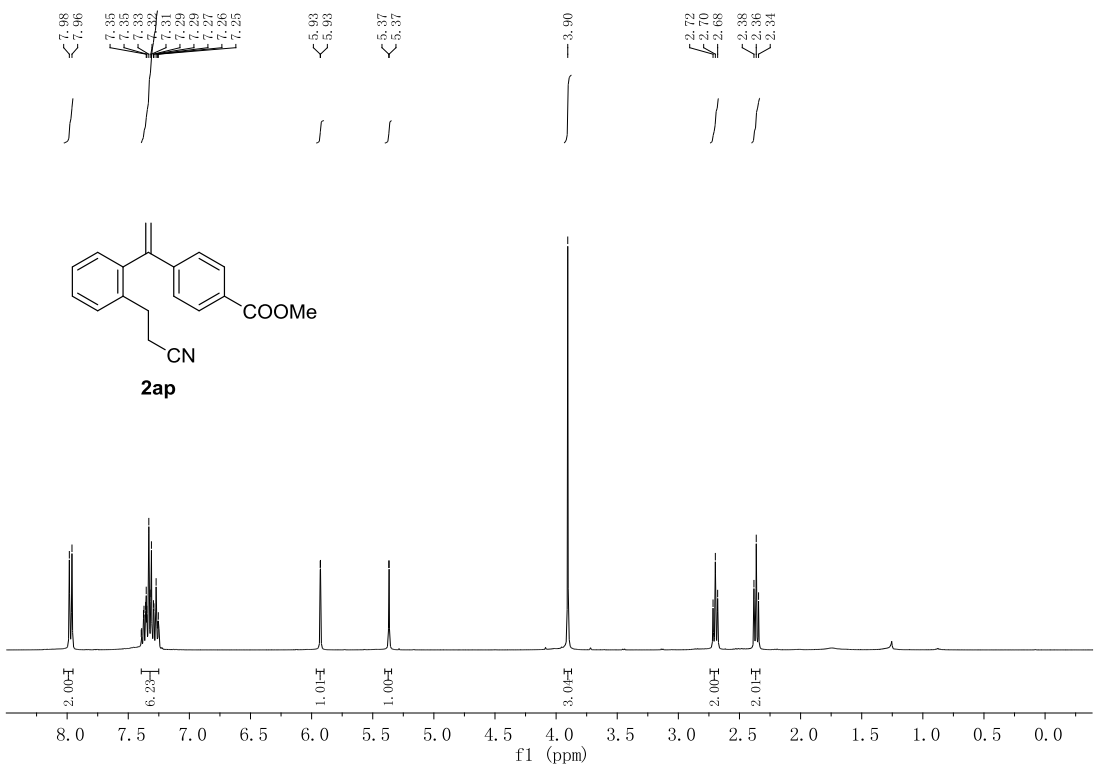

7.63
7.53
7.51
7.40
7.31
7.28
6.85
6.83
6.49
6.45
6.21
6.19
6.17
6.17
6.15
6.13
3.80
3.76
3.74
CN
OMe
2an
1.03
1.05
1.09
3.03
2.00
1.00
1.00
3.02
2.00
f1 (ppm)


159.05
144.29
132.85
131.89
129.69
129.64
126.72
124.19
117.96
113.89
112.36
55.22
37.66
CN
OMe
2an
f1 (ppm)

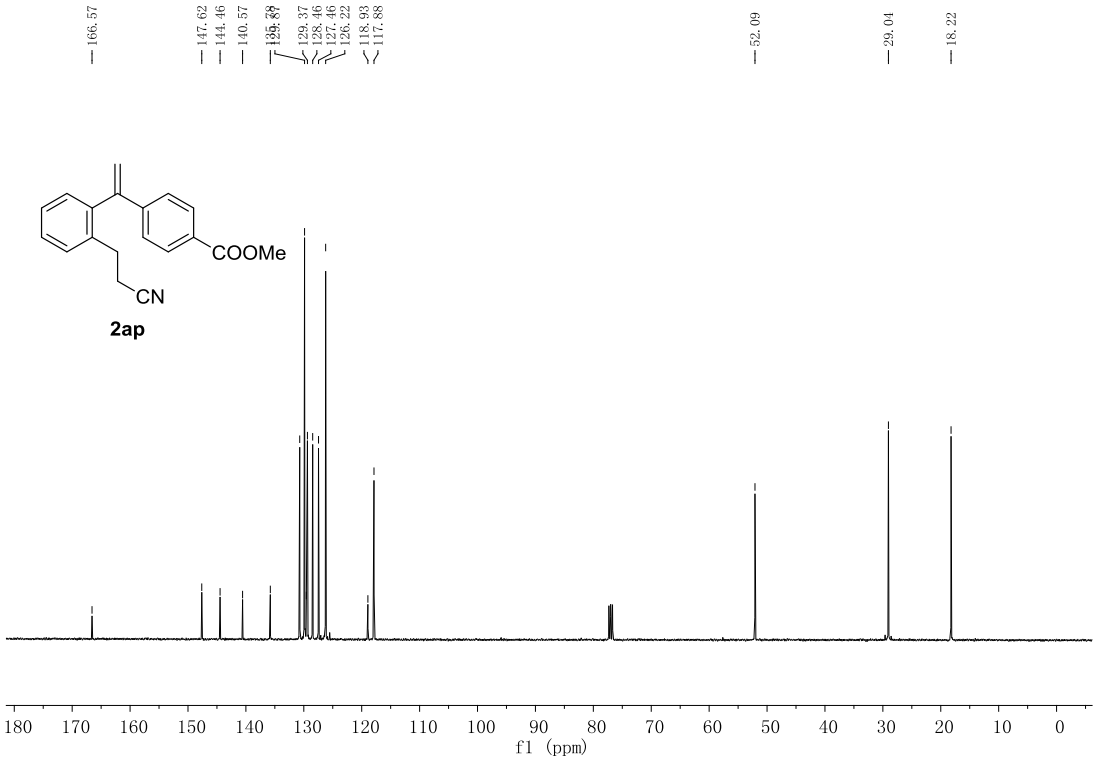

7.19
7.18
7.18
7.17
7.16
7.16
7.16
7.15
7.14
7.08
7.07
7.07
7.06
7.06
7.06
7.05
5.18
5.17
5.17
5.16
5.16
4.79
4.79
4.79
4.79
2.95
2.93
2.91
2.52
2.51
2.49
1.99
1.98
1.98
1.98
Me
CN
2ao
3.04
0.98
1.02
1.00
2.09
2.07
3.09
f1 (ppm)

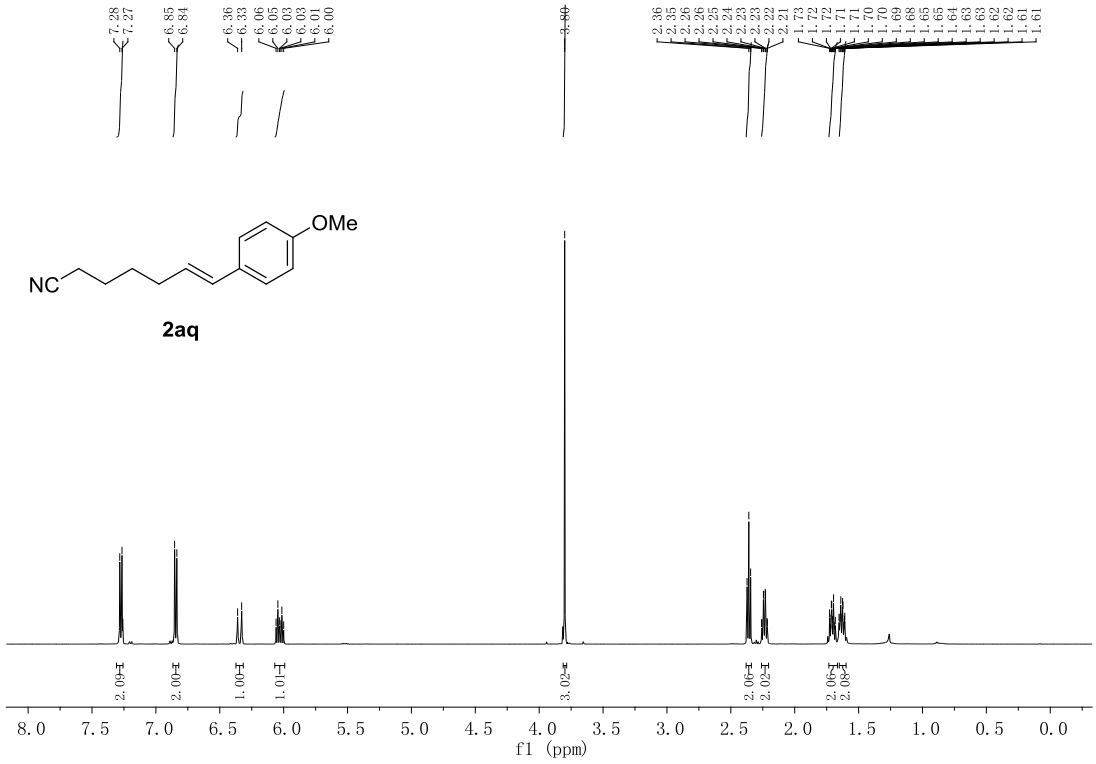

144.78
143.68
134.48
128.98
128.51
127.38
127.09
119.28
115.65
28.81
25.24
19.07
Me
CN
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

2ao


7.98
7.96
7.35
7.35
7.33
7.32
7.31
7.29
7.29
7.27
7.26
7.25
5.93
5.93
5.37
5.37
3.90
2.72
2.70
2.68
2.38
2.36
2.34
COOMe
CN
2.00
6.23
1.01
1.00
3.04
2.00
2.01
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)

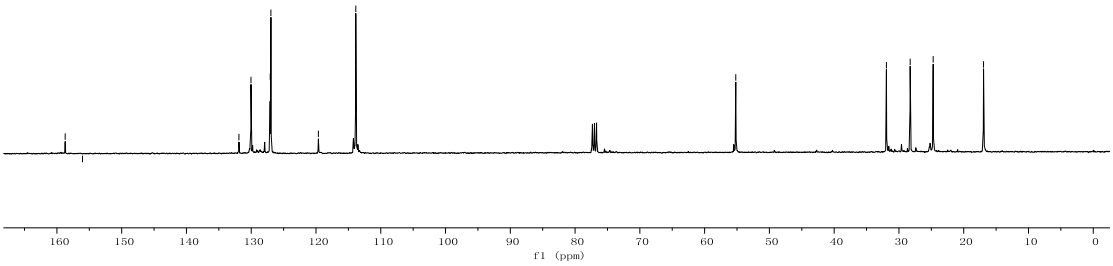
2ap


166.57
147.62
144.46
140.57
135.87
129.37
128.46
127.46
126.22
118.93
117.88
52.09
29.04
18.22
COOMe
CN
2ap
f1 (ppm)

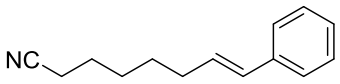

7.28
7.27
6.85
6.84
6.36
6.33
6.06
6.05
6.03
6.01
6.00
3.80
2.36
2.35
2.26
2.25
2.24
2.23
2.22
2.21
1.73
1.72
1.71
1.70
1.69
1.68
1.65
1.64
1.63
1.62
1.61
OMe
NC
2aq
2.09
2.00
1.00
1.01
3.02
2.06
2.02
2.06
2.08
f1 (ppm)


158.72
156.05
131.90
130.04
127.07
126.96
119.63
113.86
55.19
31.93
28.27
24.71
16.94
OMe
NC

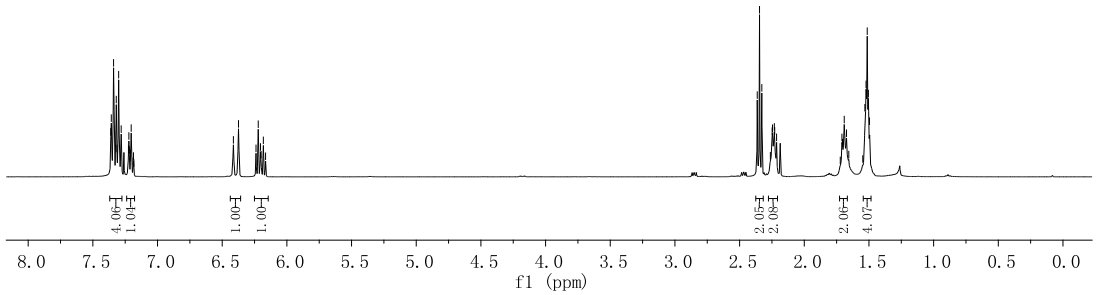
2aq

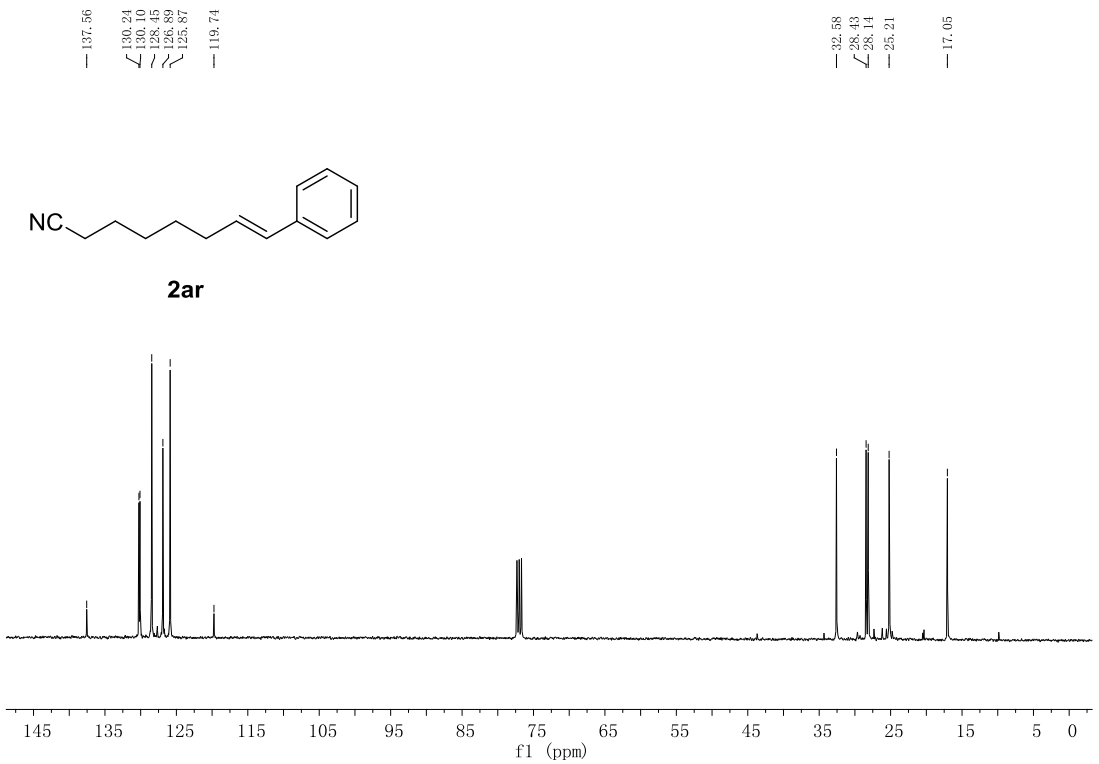

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

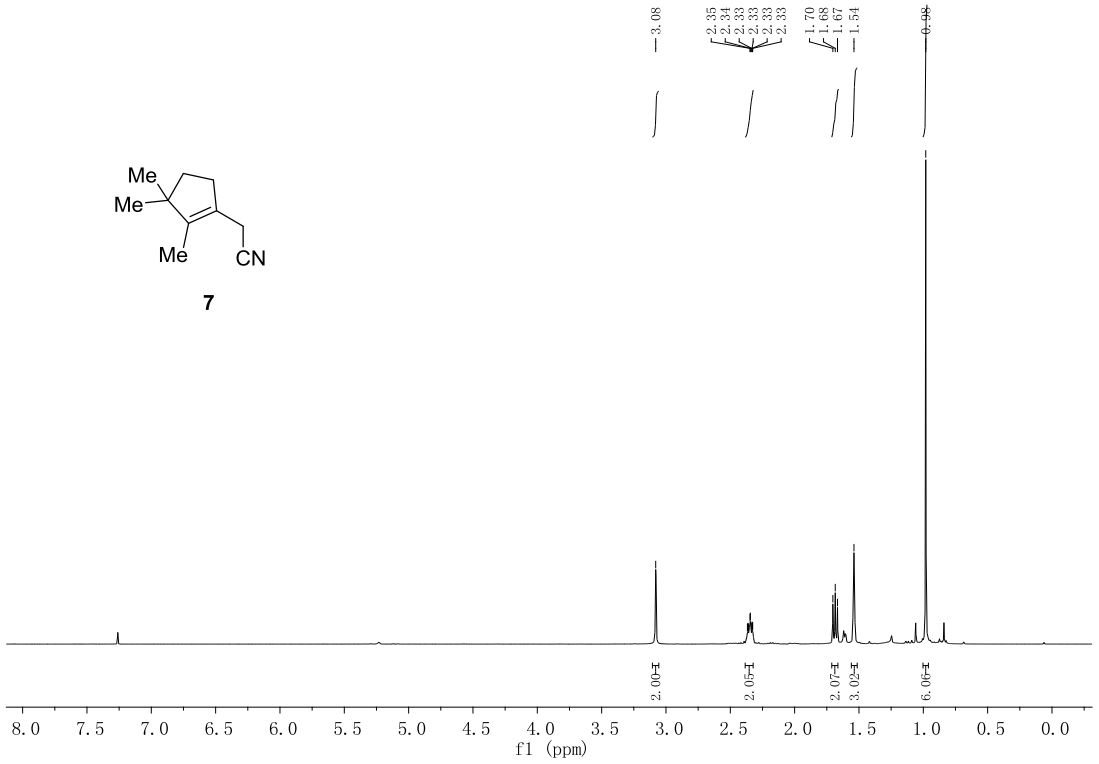

7.34
7.32
7.31
7.30
7.28
7.22
7.22
7.22
7.21
7.20
7.19
7.19
7.18
6.41
6.37
6.24
6.22
6.20
6.20
6.18
6.16
2.36
2.35
2.33
2.26
2.25
2.25
2.23
2.23
2.21
1.72
1.71
1.70
1.69
1.67
1.66
1.55
1.53
1.52
1.51
1.50
1.50

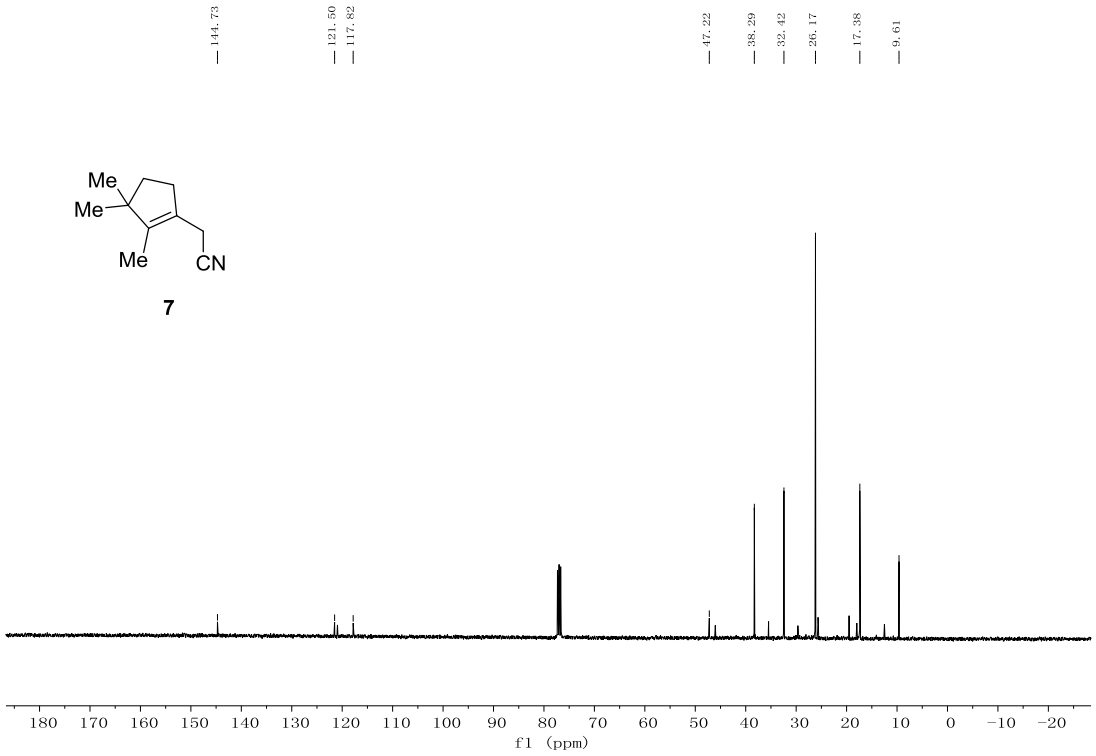

NC

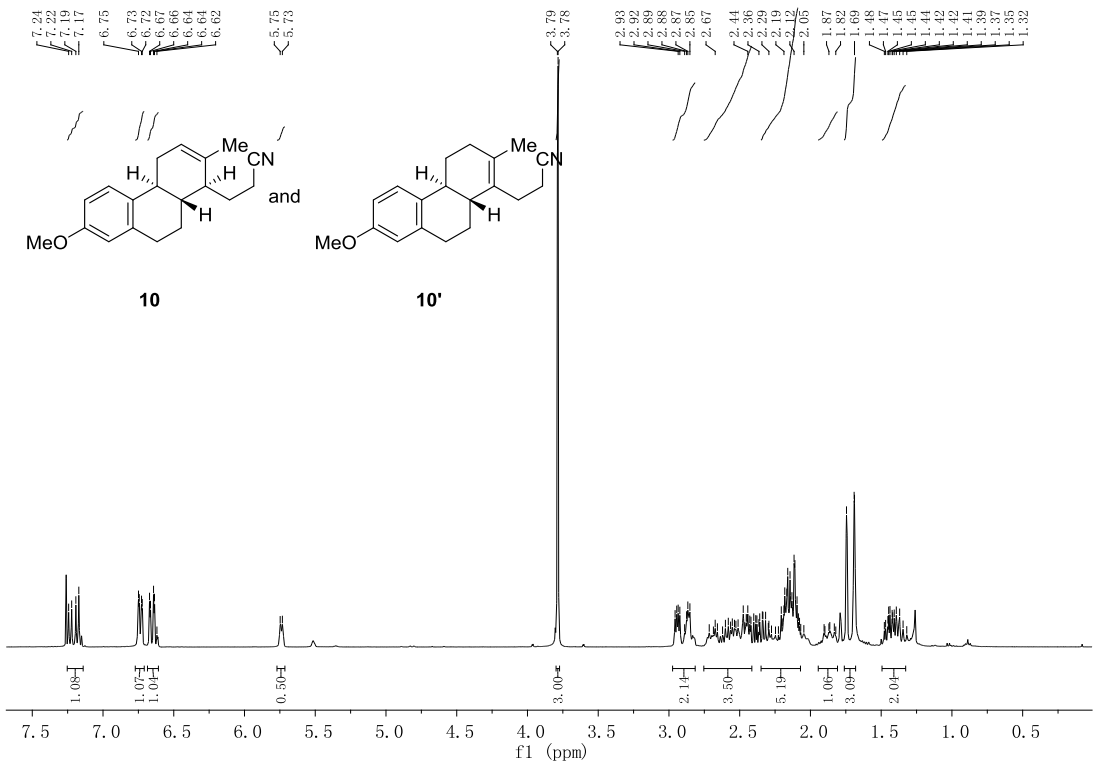
2ar

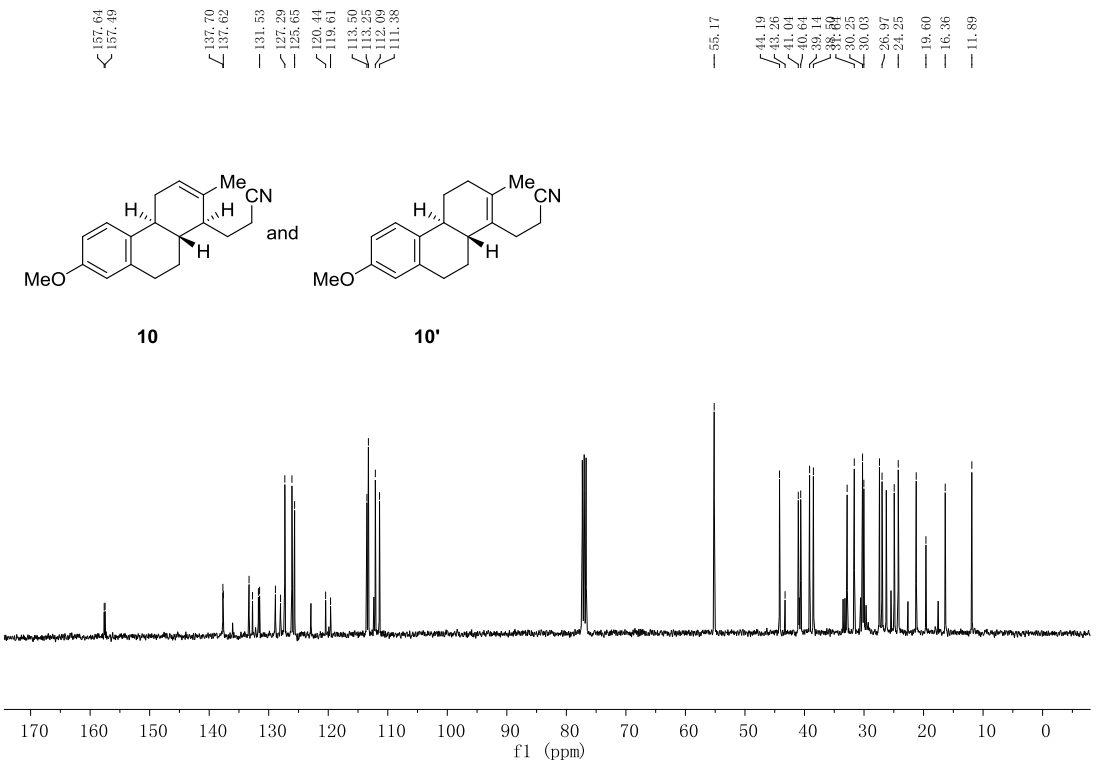

4.06
1.04
1.00
1.00
2.05
2.08
2.06
4.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

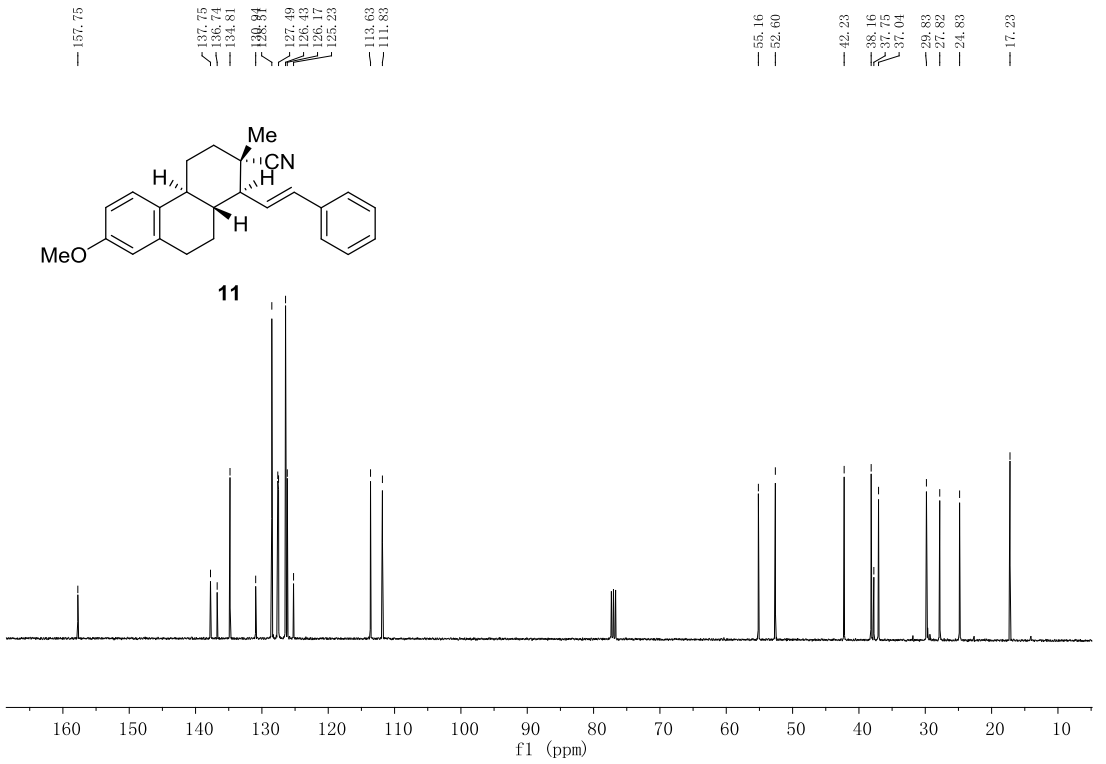

137.56
130.24
130.10
128.45
126.89
125.87
119.74
32.58
28.43
28.14
25.21
17.05
NC
2ar
145 135 125 115 105 95 85 75 65 55 45 35 25 15 5 0
f1 (ppm)

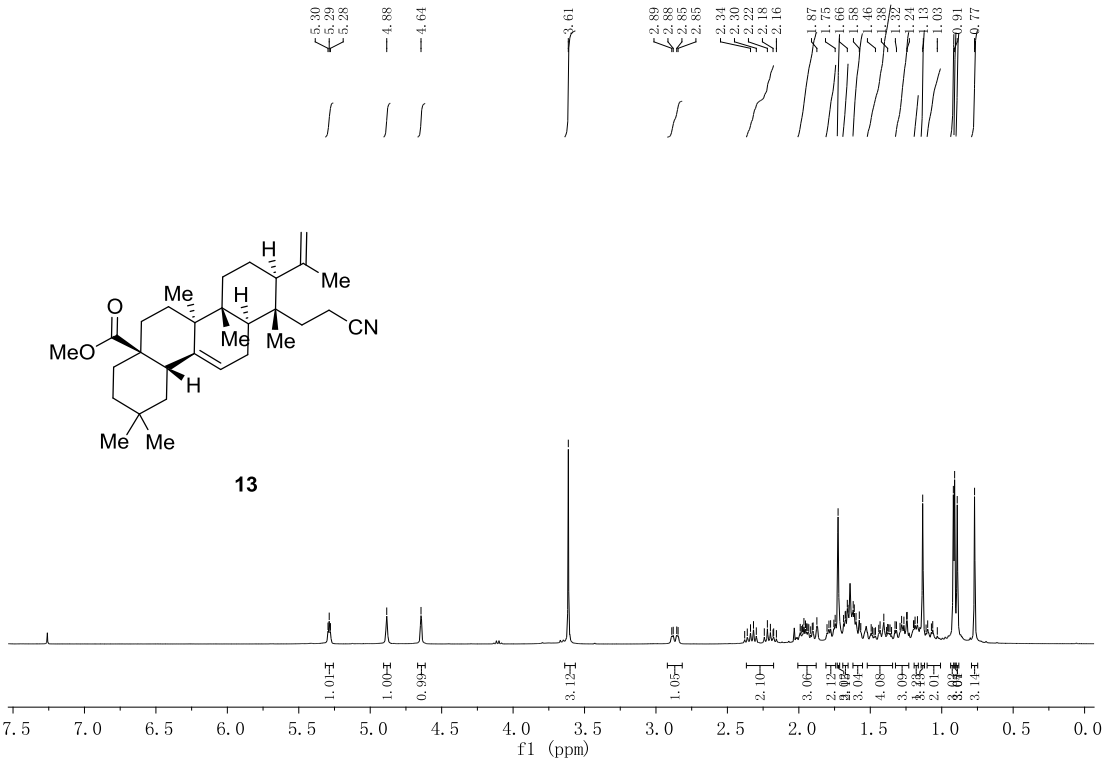

3.08
2.35
2.34
2.33
2.33
2.33
2.33
1.70
1.68
1.67
1.54
0.98
Me
Me
Me
CN
7
2.00
2.05
2.07
3.02
6.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

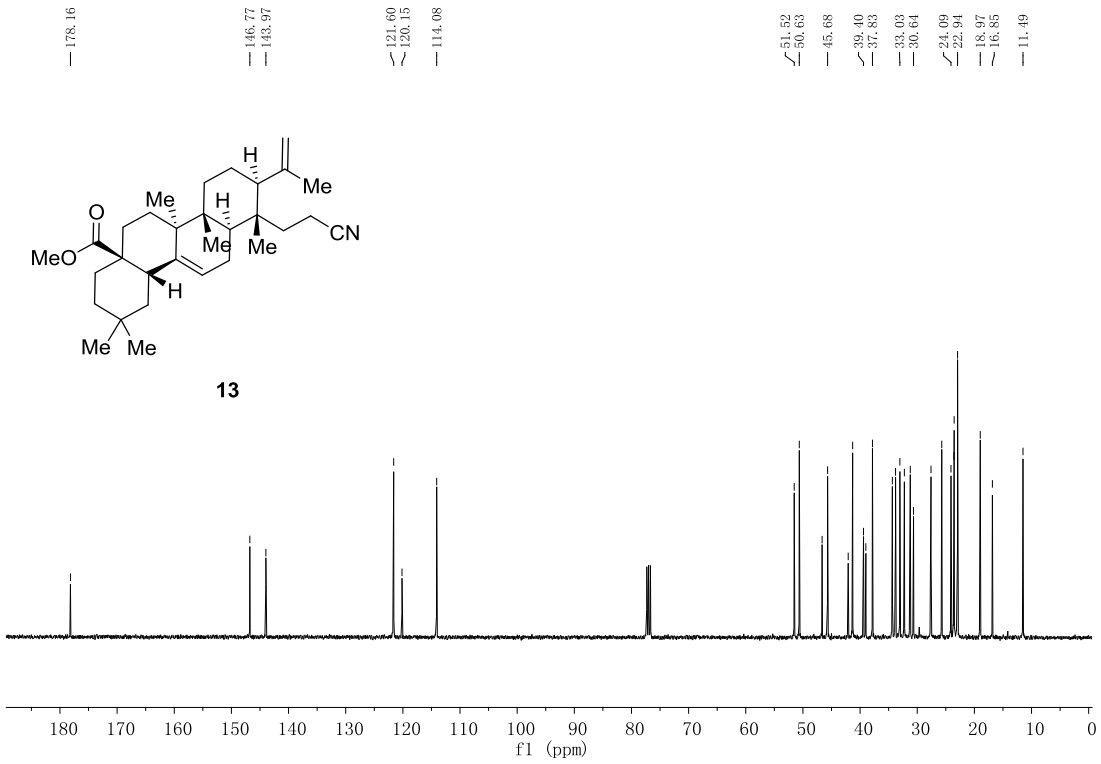

144.73
121.50
117.82
47.22
38.29
32.42
26.17
17.38
9.61
Me
Me
Me
CN
7
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

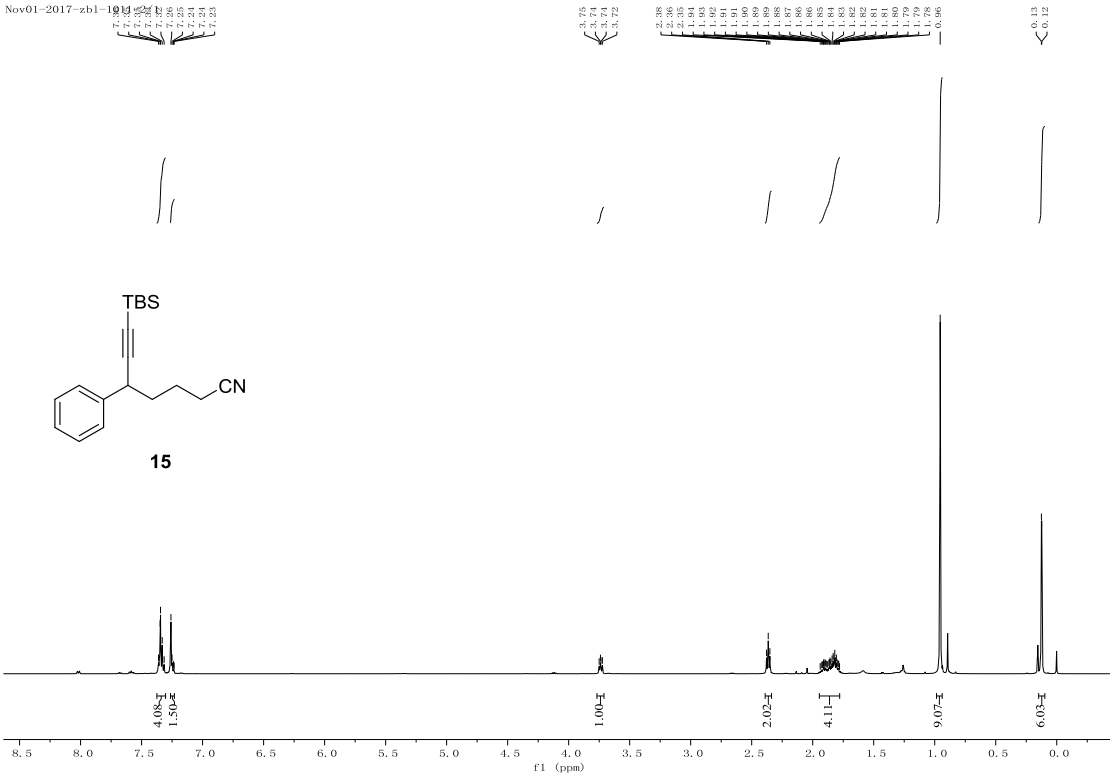

7.24
7.22
7.19
7.17
6.75
6.73
6.72
6.67
6.66
6.64
6.64
6.62
5.75
5.73
3.79
3.78
2.93
2.92
2.89
2.88
2.87
2.85
2.67
2.44
2.36
2.29
2.19
2.12
2.05
1.87
1.82
1.69
1.48
1.47
1.45
1.45
1.44
1.42
1.42
1.41
1.39
1.37
1.35
1.32
Me
CN
H
H
H
MeO
and
10
10'
1.08
1.07
1.04
0.50
3.00
2.14
3.50
5.19
1.06
3.09
2.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

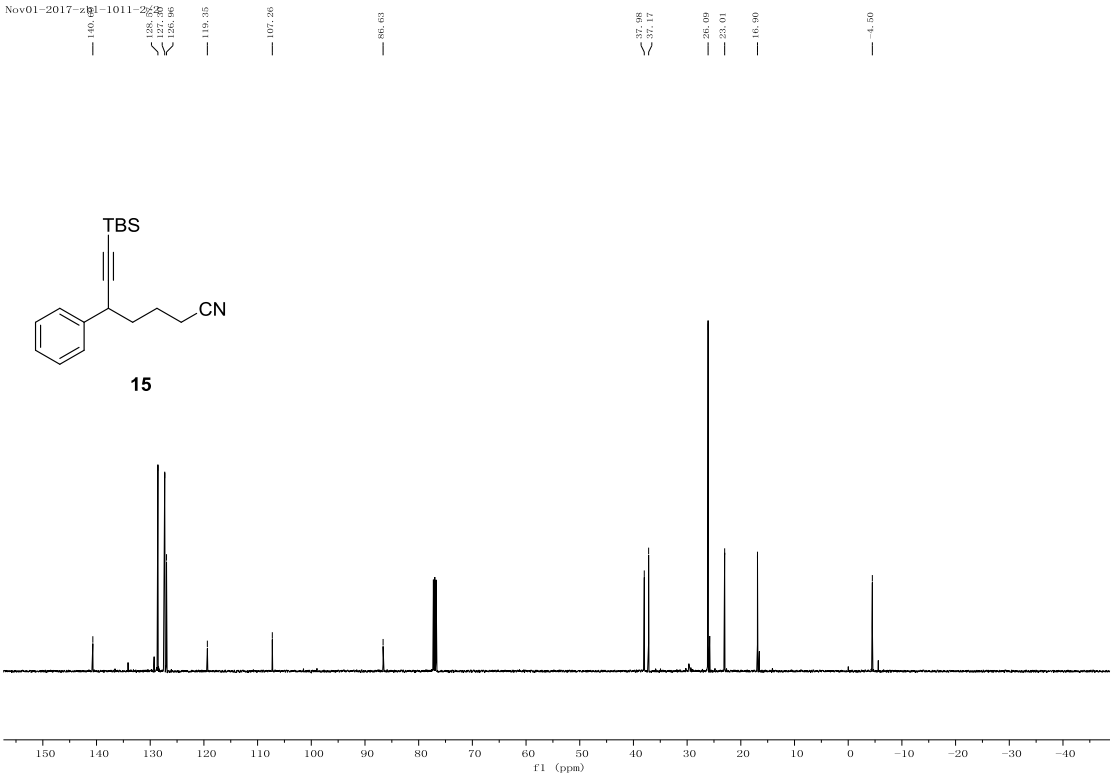

157.64
157.49
137.70
137.62
131.53
127.29
125.65
120.44
119.61
113.50
113.25
112.09
111.38
55.17
44.19
43.26
41.04
40.64
39.14
30.25
30.03
26.97
24.25
19.60
16.36
11.89
Me
CN
H
H
H
MeO
and
Me
CN
H
H
MeO
10
10'
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.12
7.10
6.64
6.62
6.58
6.55
6.55
5.96
5.94
5.92
5.90
3.69
2.76
2.74
2.73
2.33
2.29
2.27
2.07
1.95
1.93
1.91
1.43
1.40
1.40
1.38
1.37
1.37
1.36
1.35
1.30
1.28
1.27
1.27
1.25
1.24
Me
CN
H
H
H
MeO
11
2.03
2.06
1.09
1.00
1.05
1.02
0.97
1.00
3.03
2.03
3.07
2.01
1.08
2.11
3.02
1.01
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)

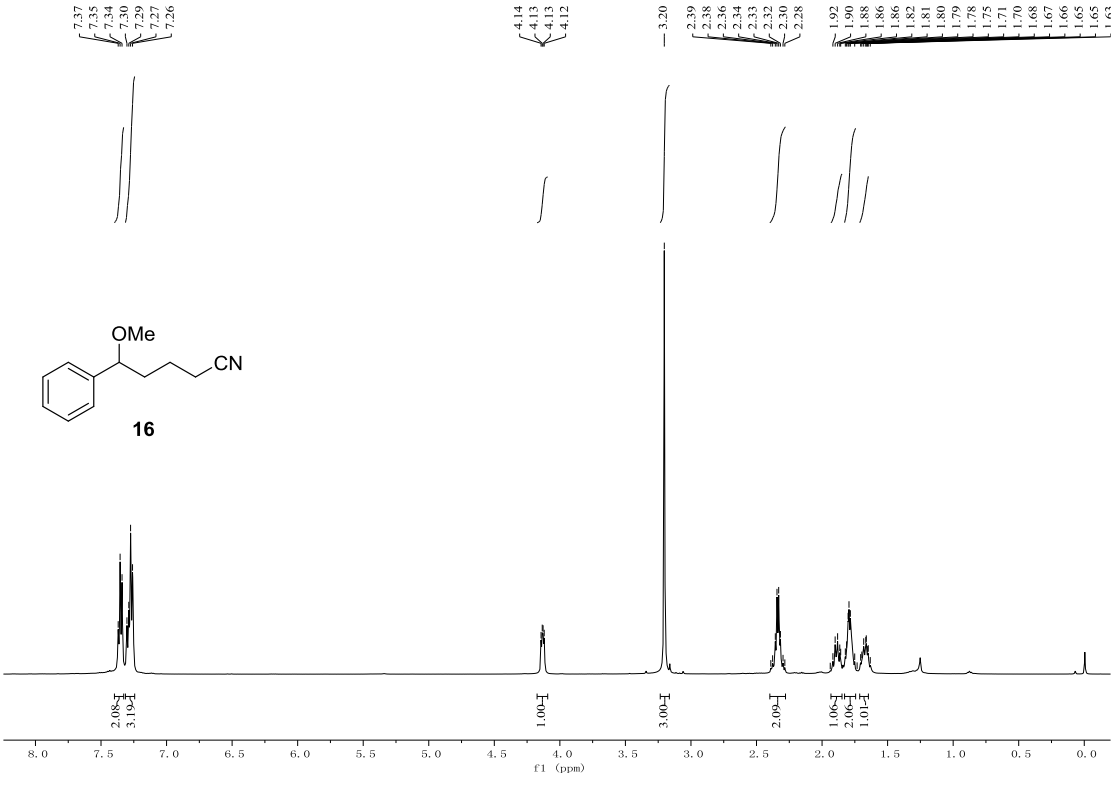

157.75
137.75
136.74
134.81
130.94
128.81
127.49
126.43
126.17
125.23
113.63
111.83
55.16
52.60
42.23
38.16
37.75
37.04
29.83
27.82
24.83
17.23
Me
CN
H
H
H
MeO
11
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

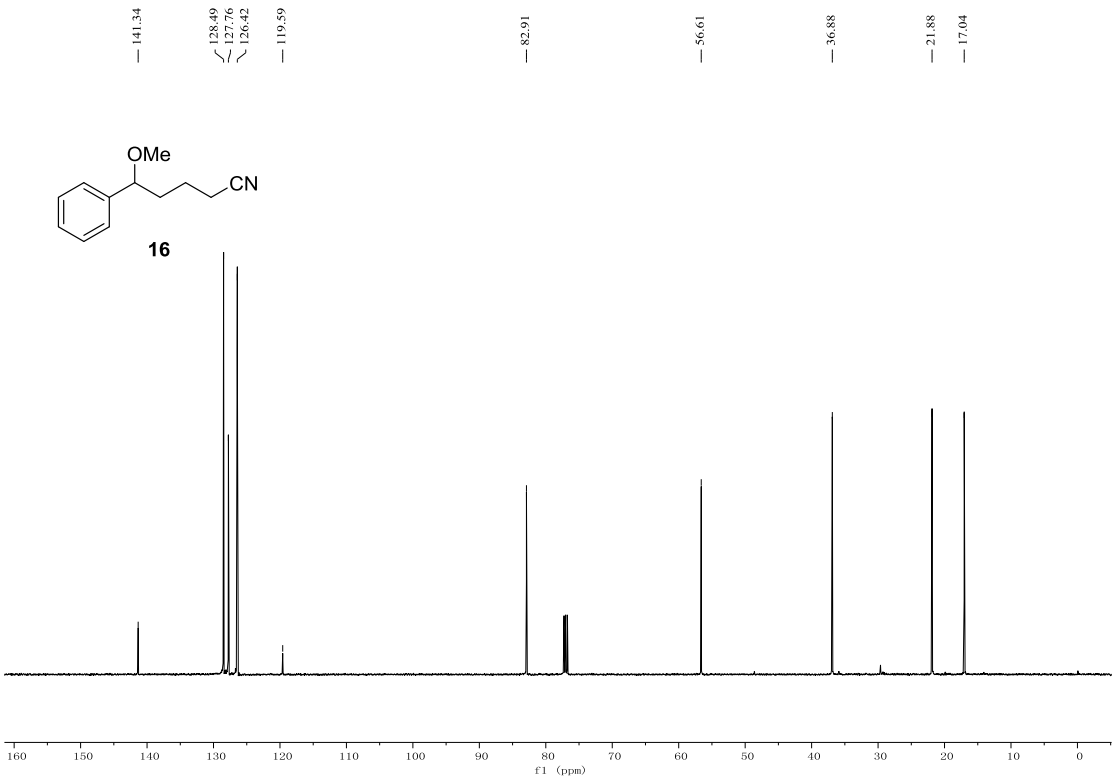

5.30
5.29
5.28
4.88
4.64
3.61
2.89
2.88
2.85
2.85
2.34
2.30
2.22
2.18
2.16
1.87
1.75
1.66
1.58
1.46
1.38
1.32
1.24
1.13
1.03
0.91
0.77
H
Me
O
Me
H
Me
Me
CN
MeO
H
Me
Me
13
1.01
1.00
0.99
3.12
1.05
2.10
3.06
4.08
3.14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

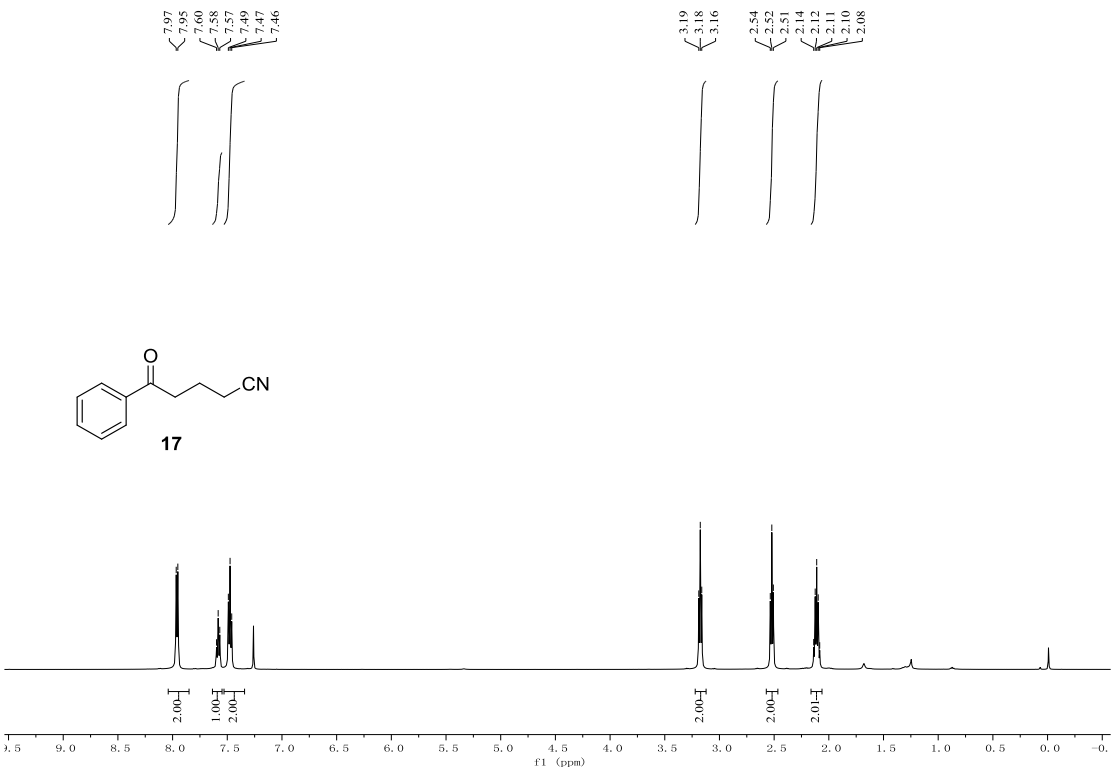

178.16
146.77
143.97
121.60
120.15
114.08
51.52
50.63
45.68
39.40
37.83
33.03
30.64
24.09
22.94
18.97
16.85
11.49
H
Me
Me
H
O
MeO
Me
Me
CN
H
Me
Me
13
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

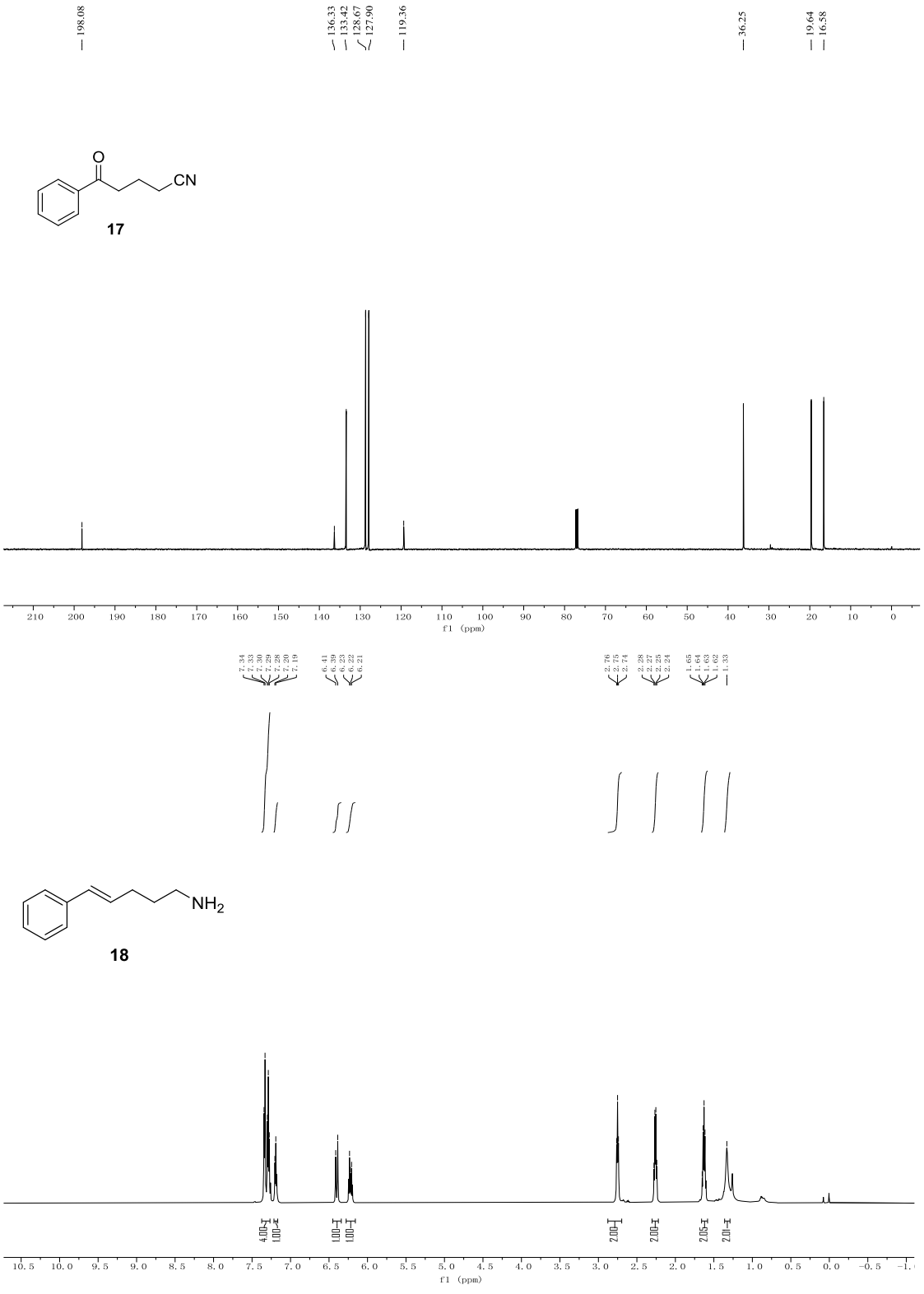

Nov01-2017-zb1-1H
7.45
7.43
7.36
7.34
7.26
7.25
7.24
7.23
3.75
3.74
3.71
3.72
2.38
2.36
2.35
1.94
1.93
1.92
1.91
1.90
1.89
1.88
1.87
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.78
0.96
0.13
0.12
TBS
CN
15
4.08
1.50
1.00
2.02
4.11
9.07
6.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

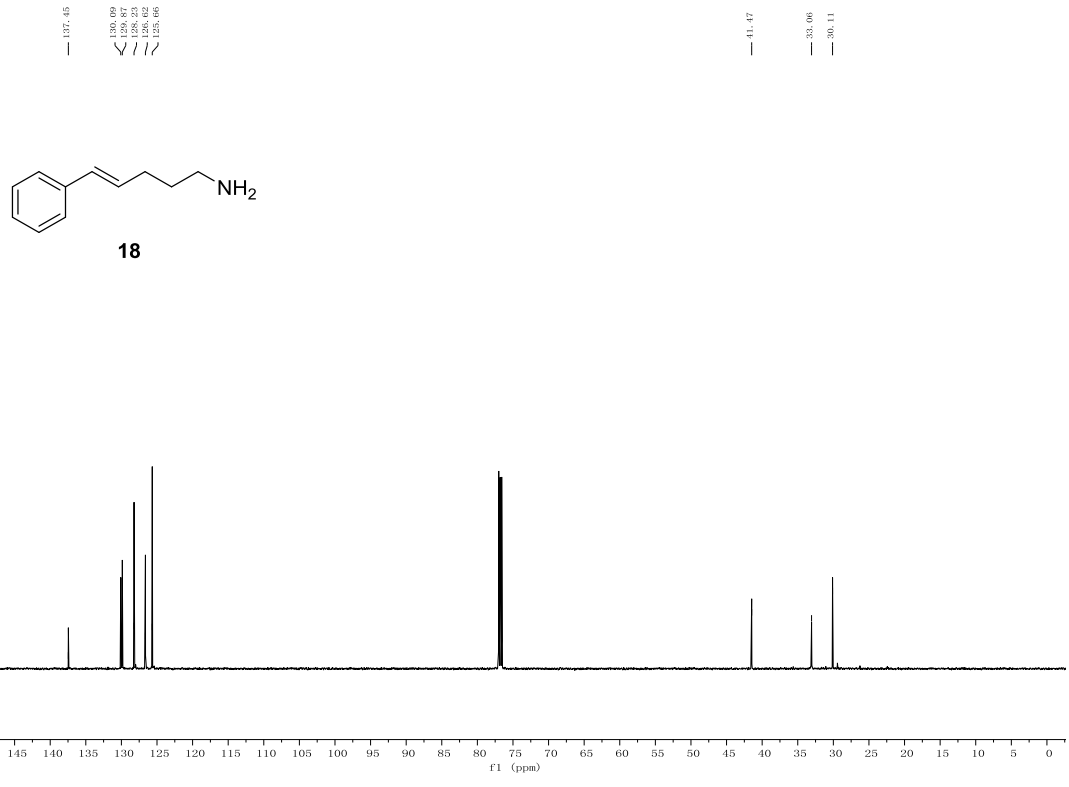

Nov01-2017-zjl-1011-2
140.68
128.67
127.39
126.96
119.35
107.26
86.63
37.98
37.17
26.09
23.01
16.90
-4.59
TBS
CN
15
f1 (ppm)

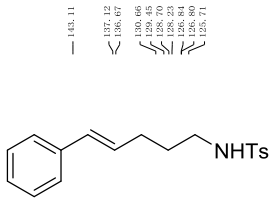

7.37
7.35
7.34
7.30
7.29
7.27
7.26
4.14
4.13
4.13
4.12
3.20
2.39
2.38
2.36
2.34
2.33
2.32
2.30
2.28
1.92
1.90
1.88
1.86
1.86
1.82
1.81
1.80
1.79
1.78
1.75
1.71
1.70
1.68
1.67
1.66
1.65
1.65
OMe
CN
16
2.08
3.19
1.00
3.00
2.09
1.06
2.06
1.01
f1 (ppm)


141.34
128.49
127.76
126.42
119.59
82.91
56.61
36.88
21.88
17.04
OMe
CN
16
f1 (ppm)

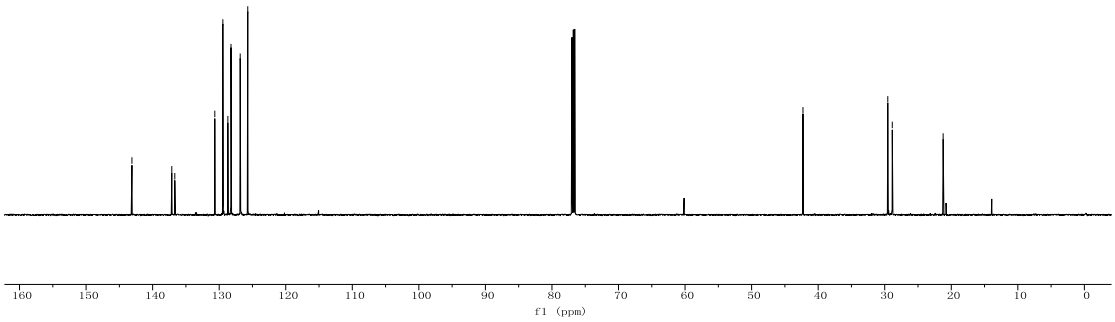

7.97
7.95
7.60
7.58
7.57
7.49
7.47
7.46
3.19
3.18
3.16
2.54
2.52
2.51
2.14
2.12
2.11
2.10
2.08
O
CN
17
2.00
1.00
2.00
2.00
2.00
2.01
f1 (ppm)

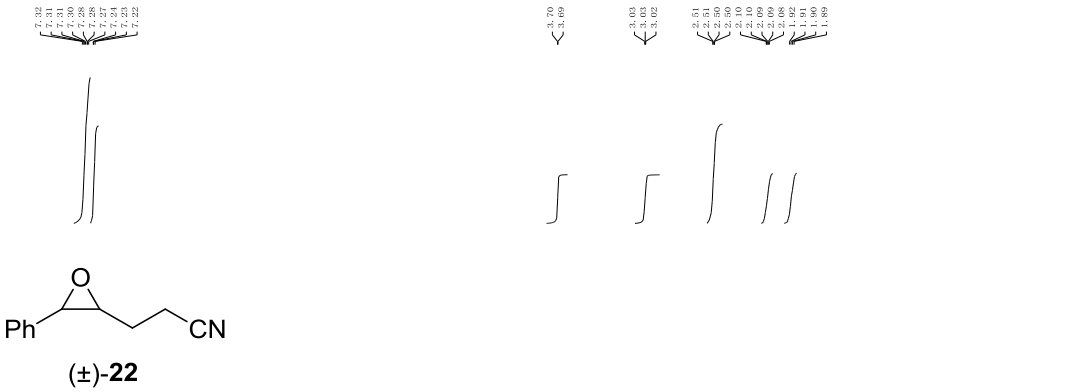

198.08
136.33
133.42
128.67
127.90
119.36
36.25
19.64
16.58
O
CN
17
f1 (ppm)
7.34
7.33
7.30
7.29
7.28
7.20
7.19
6.41
6.39
6.23
6.22
6.21
2.76
2.75
2.74
2.28
2.27
2.25
2.24
1.65
1.64
1.63
1.62
1.33
NH2
18
4.00
1.00
1.00
1.00
2.00
2.00
2.05
2.01
f1 (ppm)


137.45
130.09
129.87
128.23
126.62
125.66
41.47
33.06
30.11
NH2
18
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)
pdata/1
wmn-NHTs
7.77
7.76
7.29
7.28
7.28
7.21
7.20
7.20
7.19
7.18
6.34
6.33
6.33
6.31
6.10
6.09
6.08
6.07
6.06
6.05
4.84
4.83
3.00
2.99
2.98
2.97
2.40
2.22
2.22
2.21
2.21
2.20
2.19
2.18
1.67
1.66
1.65
1.63
1.62
NHTs
20
2.00
6.10
1.00
1.00
1.03
1.03
2.10
3.08
2.08
2.09
.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)

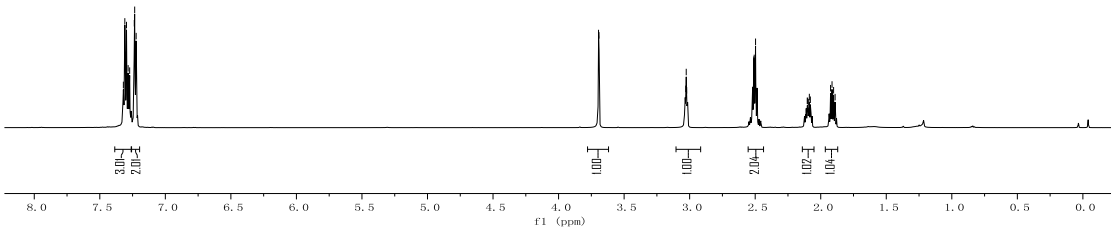


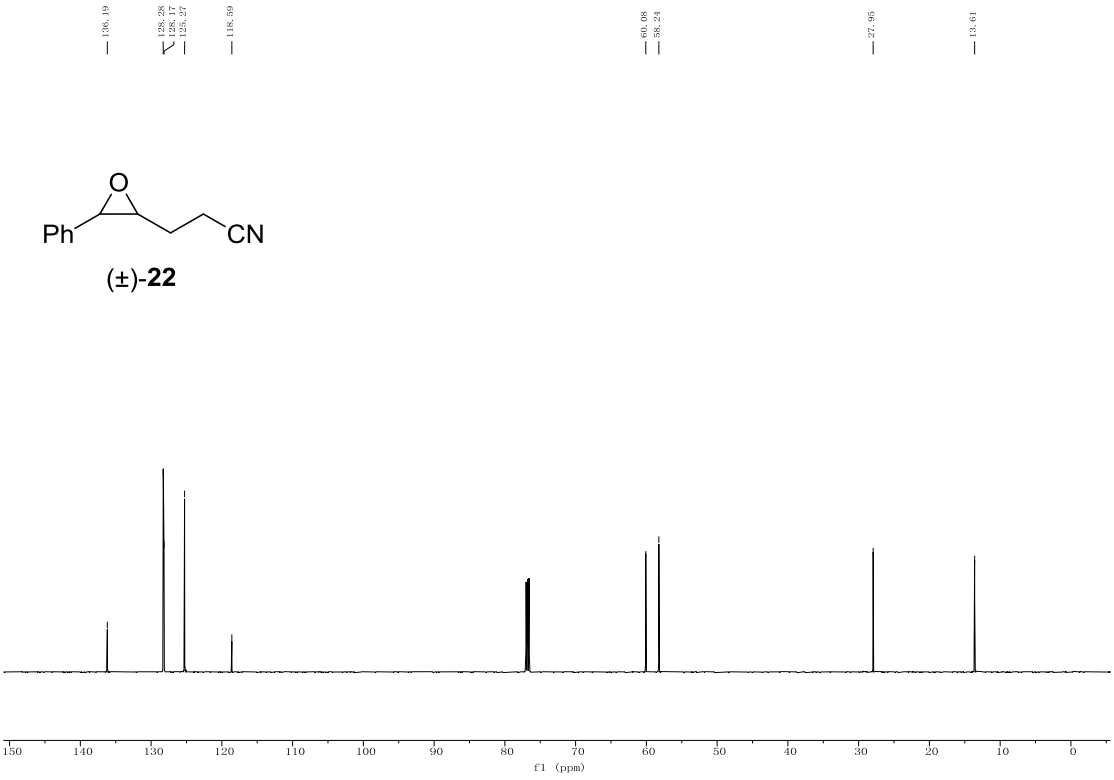
20





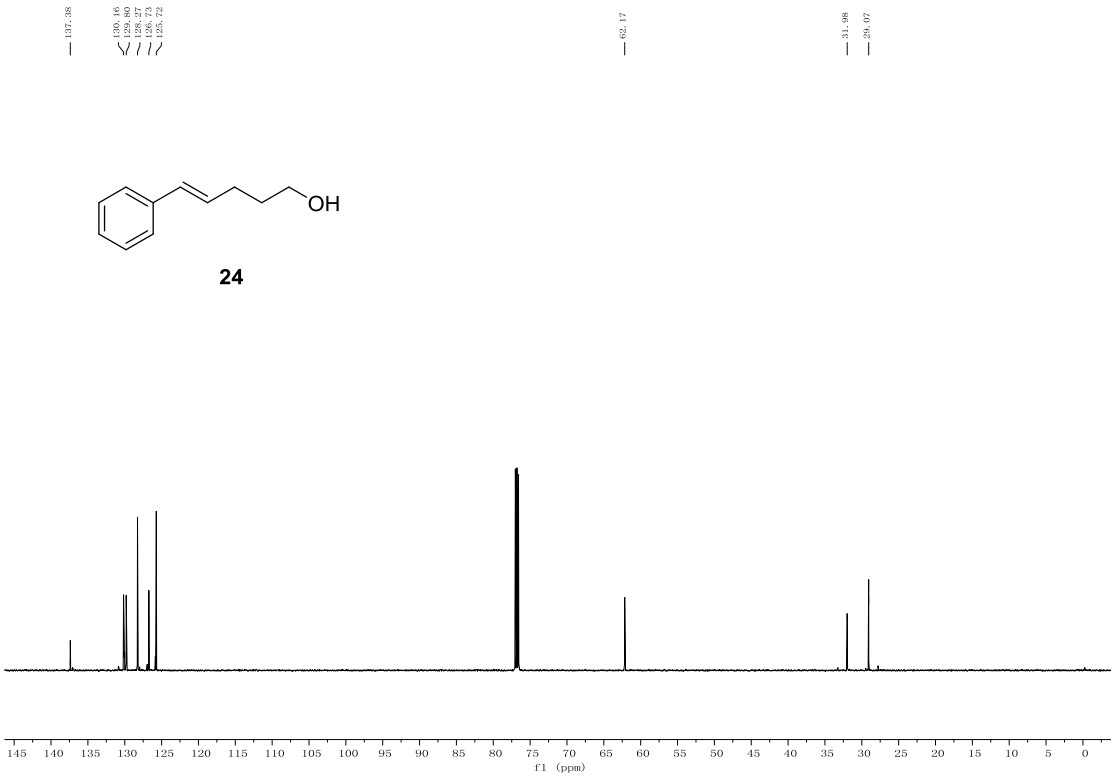
(±)-**22**




136.19
128.28
128.17
125.27
118.89
60.08
58.24
27.95
13.61
O
Ph
CN
f1 (ppm)
7.36
7.35
7.35
7.34
7.31
7.31
7.30
7.29
7.22
7.20
6.44
6.42
6.44
6.41
6.25
6.22
3.73
3.72
3.71
2.34
2.33
2.32
2.31
2.31
2.30
1.77
1.76
1.75
OH
4.07
1.00
1.00
1.00
2.00
2.02
2.02
f1 (ppm)

(±)-**22**

24


137.38
130.16
128.80
128.27
126.73
125.72
62.17
31.98
29.07
OH
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

24