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Radical-Induced Ring-Opening and Reconstruction of Cyclobutanone Oxime Esters

(Supporting Information)

Panpan Wang,[a,b,c] Binlin Zhao,[b,c] Yu Yuan, [a,] *and Zhuangzhi Shi,[b,] *

[a] *College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China, E-mail: yyuan@yzu.edu.cn*

[b]*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China, E-mail: shiz@nju.edu.cn*

[c]*These authors contributed equally.*

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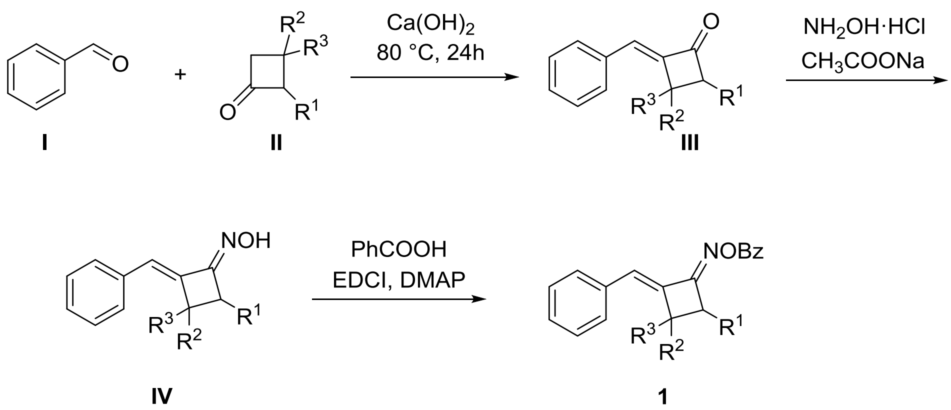
1. General Information

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 ARX-400 MHz or ARX-500 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. The $Cu(OTf)_2$ was purchased from TCI. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Preparation of benzylidene cyclobutan *O*-benzoyl oxime Substrates



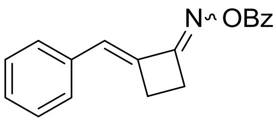
Benzylidene cyclobutan *O*-benzoyl oximes were obtained from the correspounding cyclobutanones, which were commercial available or produced by the reduction of *α*,*α*-dichlorocyclobutanones synthesized from the corresponding alkenes by the reported procedure[1].

To a 25 mL Schlenk tube was added $Ca(OH)_2$ (1 mmol, 20 mol%). A solution of aldehyde **I** (5.0 mmol, 1.0 equiv) and cyclobutanone **II** (15.0 mmol, 3.0 equiv) in 10 mL of anhydrous ethanol were then injected via a syringe under N_2. The mixture was then stirred at 80 ^{o}C for 24 hours under N_2[2]. The solvent was evaporated under vacuum and the residue was purified through flash column chromatogram to give products **III**. The product was used in the next step.

To a stirred solution of benzylidenecyclobutan **III** (1.0 equiv) in water mixture ethanol (1.0 M, H_2O : EtOH = 3 : 7) was added hydroxylamine hydrochloride (1.5 equiv) and NaOAc (1.8 equiv) at 100 ^{o}C. After stirring for 12 h, quenching the reaction with $NaHCO_3$ and extracted with EtOAc[3]. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure to give the crude material **IV**, which were used in the next step without further purification.

To a mixture of cyclobutanone oxime **IV** (1.0 equiv), benzoic acid (1.5 equiv) and DCM (0.5 M) in a 30-mL one-necked flask was added EDCI (2.5 equiv) and DMAP (20 mol%) at rt for 12 h[4]. Then NaOH (0.5 equiv) was added to the above solution, and the mixture was diluted with DCM. The organic layer was washed with water and dried over $MgSO_4$. 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 substrates **1**.

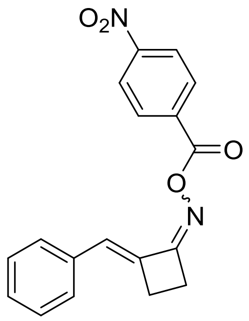
2-((*E*) Benzylidene)cyclobutan-1-one *O*-benzoyl oxime (1a)



1a

According to the general procedure, **1a** (*E/Z* mixture) was prepared from the commercially available benzaldehyde (CAS:100-52-7, 20.0 mmol) and cyclobutanone (CAS: 1191-95-3, 60.0 mmol) as a white solid (3.4 g, 62%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 – 8.04 (m, 2H), 7.67 – 7.29 (m, 8H), 7.27 – 7.23 (m, 1H), 3.25 – 3.12 (m, 2H), 3.10 – 2.98 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.4, 164.0, 162.9, 135.7, 135.5, 134.9, 134.5, 134.4, 133.4, 133.3, 129.7, 129.7, 129.3, 129.2, 129.1, 129.1, 129.0, 128.9, 128.9, 128.8, 128.7, 128.5, 127.3, 30.4, 29.5, 27.0, 26.1; **ATR-FTIR (cm $^{-1}$)** 2929**,** 1742, 1639, 1591, 1449, 1250, 1060, 700; **HRMS m/z (ESI)** calcd for $C_{18}H_{15}NO_2$ ((M + Na)$^+$ 300.0995, found 300.0999.

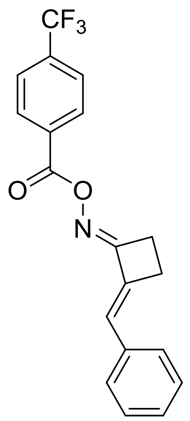
2-((*E*) Benzylidene)cyclobutan-1-one *O*-(4-nitrobenzoyl) oxime (1a')



1a'

According to the general procedure, **1a'** (*E/Z* mixture) was prepared from the commercially available benzaldehyde (CAS: 100-52-7, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (821 mg, 51%): **^{1}H NMR (400 MHz, CDCl$_3$)** 8.37 (d, *J* = 8.9 Hz, 2H), 8.28 (d, *J* = 8.9 Hz, 2H), 7.44 – 7.34 (m, 6H), 3.21 – 3.12 (m, 2H), 3.07 – 2.98 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 163.8, 162.5, 150.7, 135.3, 135.0, 134.7, 134.2, 131.7, 130.8, 129.7, 129.2, 129.2, 129.0, 128.9, 128.8, 128.7, 128.7, 128.5, 128.3, 123.9, 29.5, 28.9, 26.1, 26.0; **ATR-FTIR (cm $^{-1}$)** 3171**,** 1740, 1525, 700, 549; **HRMS m/z (ESI)** calcd for $C_{18}H_{14}N_2O_4$ (M + Na)$^+$ 345.0846, found 345.0850.

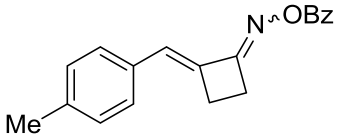
2-((*E*) Benzylidene)cyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1a")



1a"

According to the general procedure, **1a"** was prepared from the commercially available benzaldehyde (CAS: 100-52-7, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (828 mg, 48%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.18 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.32 (m, 5H), 7.25 (t, *J* = 2.8 Hz, 1H), 3.23 (dd, *J* = 9.3, 6.5 Hz, 2H), 3.08 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 167.0, 162.8, 135.4, 134.7 (t, *J* = 32.8 Hz) 134.5, 132.3, 130.1, 129.1, 129.0, 128.9, 127.8, 125.6 (q, *J* = 4.0 Hz), 123.5(q, *J* = 273.7 Hz), 30.4, 27.0; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -63.2; **ATR-FTIR (cm $^{-1}$)** 3069, 1749, 1642, 1584, 1507, 861, 764; **HRMS m/z (ESI)** calcd for $C_{18}H_{14}F_3NO_2$ (M + H)$^+$ 346.1049, found 346.1051.

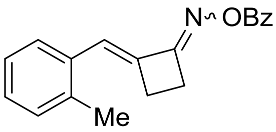
2-((*E*)-4-Methylbenzylidene)cyclobutan-1-one *O*-benzoyl oxime (1b)



1b

According to the general procedure, **1b** (*E/Z* mixture) was prepared from the commercially available 4-methylbenzaldehyde (CAS: 104-87-0, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (889 mg, 60%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.03 (m, 2H), 7.59 – 7.32 (m, 4H), 7.25 (s, 1H), 7.20 – 7.07 (m, 3H), 3.17 – 3.02 (m, 2H), 2.94 (m, 2H), 2.30 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 166.6, 164.3, 164.003, 163.1, 139.7, 139.2, 134.5, 133.7, 133.3, 133.2, 133.0, 132.8, 129.7, 129.7, 129.6, 129.2, 129.1, 129.0, 128.7, 128.5, 127.3, 30.4, 29.5, 26.9, 26.0, 21.5, 21.4; **ATR-FTIR (cm $^{-1}$)** 3154, 1742, 1586, 1250, 1063, 866, 701; **HRMS m/z (ESI)** calcd for $C_{19}H_{17}NO_2$ (M + H)$^+$ 292.1332 , found 292.1335.

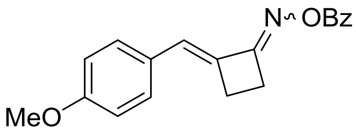
2-((*E*)-2-Methylbenzylidene)cyclobutan-1-one *O*-benzoyl oxime (1c)



1c

According to the general procedure, **1c** (*E/Z* mixture) was prepared from the commercially available 2-methylbenzaldehyde (CAS: 529-20-4, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (844 mg, 58%): **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.97 – 7.88 (m, 2H), 7.43 (d, J = 7.3 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.06 (dd, J = 5.1, 3.4 Hz, 3H), 3.03 (dd, J = 9.3, 6.5 Hz, 2H), 2.86 (m, 2H), 2.26 (s,3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 166.7, 164.0, 133.9, 133.4, 133.3, 130.9, 130.9, 129.7, 129.6, 128.9, 128.9, 128.6, 128.6, 127.4, 127.2, 126.3, 126.1, 124.5, 30.2, 29.4, 27.0, 26.0, 20.1, 19.9; **ATR-FTIR (cm $^{-1}$)** 3153, 1742, 1552, 1062, 706, 555; **HRMS m/z (ESI)** calcd for $C_{19}H_{17}NO_2$ (M + Na)$^+$ 314.1151, found 314.1156.

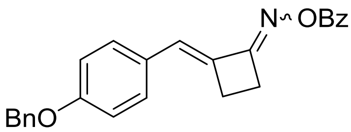
2-((*E*)-4-Methoxybenzylidene)cyclobutan-1-one *O*-benzoyl oxime (1d)



1d

According to the general procedure, **1d** (*E/Z* mixture) was prepared from the commercially available *p*-anisaldehyde (CAS: 123-11-5, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (782 mg, 51%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.23 – 8.08 (m, 2H), 7.70 – 7.59 (m, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.33 (m, 3H), 7.02 – 6.87 (m, 2H), 3.85 (s, 3H), 3.13 (m, 2H), 2.96 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.3, 163.1, 160.5, 134.3, 133.3, 131.8, 130.8, 129.7, 129.2, 128.7, 128.5, 114.4, 55.4, 29.4, 25.9; **ATR-FTIR (cm^{-1})** 3181, 2315, 1742, 1512, 1248, 879, 701; **HRMS m/z (ESI)** calcd for $C_{19}H_{17}NO_3$ $(M + H)^+$ 308.1281, found 308.1283.

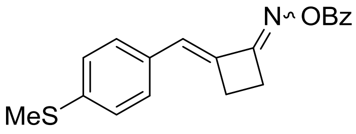
2-((*E*)-4-(Benzyloxy)benzylidene)cyclobutan-1-one *O*-benzoyl oxime (1e)



1e

According to the general procedure, **1e** (*E/Z* mixture) was prepared from the commercially available 4-benzyloxybenzaldehyde (CAS: 4397-53-9, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (1.2 g, 64%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 – 8.04 (m, 2H), 7.75 (t, *J* = 2.8 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.42 – 7.29 (m, 5H), 7.25 (d, *J* = 1.2 Hz, 1H), 6.98 – 6.89 (m, 2H), 5.14 (s, 2H), 3.21 – 3.15 (m, 2H), 3.03 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.0, 164.1, 157.0, 136.6, 134.4, 133.2, 130.2, 129.7, 129.2, 128.7, 128.5, 128.1, 127.4, 124.9, 122.1, 120.7, 112.5, 70.3, 30.2, 27.0; **ATR-FTIR (cm^{-1})** 3181, 2314, 1741, 1453, 1250, 1061, 860; **HRMS m/z (ESI)** calcd for $C_{25}H_{21}NO_3$ $(M + Na)^+$ 406.1414, found 406.1417.

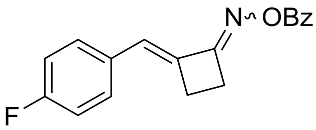
2-((*E*)-4-(Methylthio)benzylidene)cyclobutan-1-one *O*-benzoyl oxime (1f)



1f

According to the general procedure, **1f** (*E/Z* mixture) was prepared from the commercially available 4-(methylthio)benzaldehyde (CAS: 3446-89-7, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (743 mg, 46%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 – 7.98 (m, 2H), 7.64 – 7.53 (m, 1H), 7.48 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.17 (m, 3H), 3.27 – 3.17 (m, 2H), 3.05 (m, 2H), 2.50 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.3, 163.1, 160.5, 134.3, 133.3, 131.8, 130.8, 129.7, 129.2, 128.7, 128.5, 114.4, 55.4, 29.43, 25.9; **ATR-FTIR (cm $^{-1}$)** 3171, 2314, 1736, 1518, 1254, 1058, 810, 703; **HRMS m/z (ESI)** calcd for $C_{19}H_{17}NO_2S$ $(M + H)^+$ 324.1053, found 324.1055.

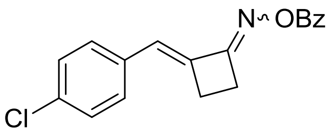
2-((*E*)-4-Fluorobenzylidene)cyclobutan-1-one *O*-benzoyl oxime (1g)



1g

According to the general procedure, **1g** (*E/Z* mixture) was prepared from the commercially available 4-fluorobenzaldehyde (CAS: 459-57-4, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (856 mg, 58%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 – 8.10 (m, 2H), 7.68 – 7.62 (m, 1H), 7.53 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.10 (t, *J* = 8.6 Hz, 2H), 3.16 (dd, *J* = 9.2, 6.1 Hz, 2H), 2.98 (td, *J* = 7.5, 6.7, 2.6 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.2, 163.1 (d, *J* = 251.5 Hz,), 133.4, 133.2, 131.0 (d, *J* = 8.1 Hz), 129.7, 128.7, 116.1 (d, *J* = 22.2 Hz,), 29.5, 25.9; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -110.3; **ATR-FTIR (cm $^{-1}$)** 3069, 1745, 1641, 1595, 1506, 1246, 1063, 884, 707; **HRMS m/z (ESI)** calcd for $C_{18}H_{14}FNO_2$ $(M + H)^+$ 296.1081, found 296.1084.

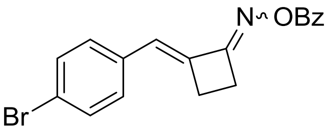
2-((*E*)-4-Chlorobenzylidene)cyclobutan-1-one *O*-benzoyl oxime (1h)



1h

According to the general procedure, **1h** (*E/Z* mixture) was prepared from the commercially available 4-chlorobenzaldehyde (CAS: 104-88-1, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (918 mg, 59%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.18 – 7.99 (m, 2H), 7.64 – 7.55 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.29 (m, 4H), 7.19 (t, *J* = 2.7 Hz, 1H), 3.22 (m, 2H), 3.04 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 166.1, 163.9, 135.5, 134.7, 134.0, 133.4, 130.1, 129.7, 129.1, 128.5, 125.9, 125.1, 30.4, 26.9; **ATR-FTIR (cm $^{-1}$)** 3168, 1742, 1522, 1249, 1069, 881, 706, 519; **HRMS m/z (ESI)** calcd for $C_{18}H_{14}ClNO_2$ $(M + H)^+$ 312.0786, found 312.0788.

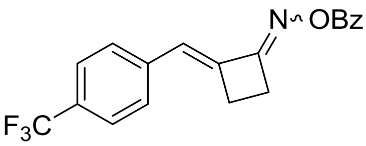
2-((*E*)-4-Bromobenzylidene)cyclobutan-1-one *O*-benzoyl oxime (1i)



1i

According to the general procedure, **1i** (*E/Z* mixture) was prepared from the commercially available 4-bromobenzaldehyde (CAS: 1122-91-4, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (1.03 g, 58%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.12 (dt, *J* = 7.0, 1.4 Hz, 2H), 7.70 – 7.61 (m, 1H), 7.53 (m, 4H), 7.37 (t, *J* = 2.8 Hz, 1H), 7.27 (t, *J* = 4.2 Hz, 2H), 3.22 – 3.11 (m, 2H), 2.97 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.2, 162.6, 135.1, 134.5, 133.4, 133.1, 132.1, 130.5, 129.7, 128.8, 123.6, 29.5, 26.1; **ATR-FTIR (cm $^{-1}$)** 3156, 1740, 1485, 1250, 1062, 882, 702; **HRMS m/z (ESI)** calcd for $C_{18}H_{14}BrNO_2$ $(M + Na)^+$ 378.0100, found 378.0104.

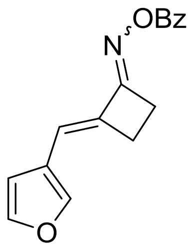
2-((*E*)-4-(Trifluoromethyl)benzylidene)cyclobutan-1-one *O*-benzoyl oxime (1j)



1j

According to the general procedure, **1j** (*E/Z* mixture) was prepared from the commercially available 4-(trifluoromethyl)benzaldehyde (CAS: 455-19-6, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (724 mg, 41%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.14 – 8.02 (m, 2H), 7.66 – 7.57 (m, 3H), 7.53 – 7.45 (m, 4H), 7.26 (s, 1H), 3.26 (m, 2H), 3.10 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 165.7, 163.9, 138.8, 137.8, 133.4, 130.3(q, *J* = 32.3 Hz), 129.7, 129.0, 128.6, 125.7 (q, *J*=4.0 Hz), 125.5, 123.9 (q, *J*=272.7 Hz), 30.5, 27.1; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.7; **ATR-FTIR (cm $^{-1}$)** 3186, 2312, 1740, 1454, 1324, 1117, 901; **HRMS m/z (ESI)** calcd for $C_{19}H_{14}F_3NO_2$ $(M + H)^+$ 346.1049, found 346.1051.

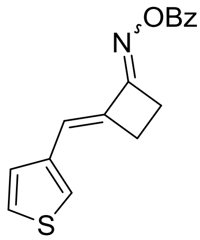
(2*E*)-2-(Furan-3-ylmethylene)cyclobutan-1-one *O*-benzoyl oxime (1k)



1k

According to the general procedure, **1k** (*E/Z* mixture) was prepared from the commercially available 3-furaldehyde (CAS: 498-60-2, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (950 mg, 60%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 – 8.08 (m, 2H), 7.65 – 7.55 (m, 2H), 7.54 – 7.41 (m, 3H), 7.12 – 7.07 (m, 1H), 6.52 (dd, *J* = 8.6, 1.8 Hz, 1H), 3.16 (m, 2H), 2.90 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.9, 164.3, 164.0, 162.5, 144.3, 144.1, 143.9, 143.5, 133.7, 133.3, 129.6, 129.1, 129.0, 128.7, 128.6, 128.5, 124.7, 122.6, 122.3, 117.9, 108.9, 29.7, 28.8, 26.0, 25.2; **ATR-FTIR (cm^{-1})** 3134, 1740, 1643, 1449, 1259, 871, 706; **HRMS m/z (ESI)** calcd for $C_{16}H_{13}NO_3$ $(M + H)^+$ 268.0968, 268.0969.

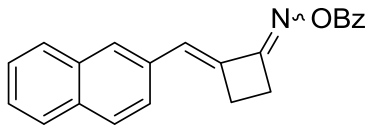
(2*E*)-2-(Thiophen-3-ylmethylene)cyclobutan-1-one *O*-benzoyl oxime (1l)



1l

According to the general procedure, **1l** (*E/Z* mixture) was prepared from the commercially available 3-thiophenecarboxaldehyde (CAS: 498-62-4, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (708 mg, 50%): **^{1}H NMR (400 MHz, $CDCl_3$)** **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (m, 2H), 7.65 – 7.05 (m, 7H), 3.07 (m, 2H), 2.92 – 2.78 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.2, 163.2, 162.9, 161.8, 136.8, 136.6, 132.5, 132.3, 132.2, 132.1, 128.6, 128.1, 129.0, 127.7, 127.5, 127.4, 127.2, 126.2, 125.9, 125.8, 125.6, 125.5, 120.3, 28.8, 27.9, 25.4, 24.6; **ATR-FTIR (cm^{-1})** 3183, 2315, 1739, 1516, 1061, 883, 706, 547; **HRMS m/z (ESI)** calcd for $C_{16}H_{13}NO_2S$ $(M + H)^+$ 284.0740, found 284.0741.

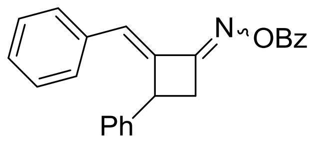
2-(Naphthalen-2-ylmethylene)cyclobutan-1-one *O*-benzoyl oxime (1m)



1m

According to the general procedure, **1m** (*E/Z* mixture) was prepared from the commercially available 2-naphthaldehyde (CAS: 66-99-9, 5.0 mmol) and cyclobutanone (CAS: 1191-95-3, 15.0 mmol) as a white solid (410 mg, 25%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 – 7.99 (m, 2H), 7.77 (m, 5H), 7.56 – 7.39 (m, 6H), 3.22 – 3.17 (m, 2H), 3.12 (dt, *J* = 8.8, 2.2 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.4, 162.9, 134.1, 132.3, 132.2, 132.1, 128.6, 128.5, 127.5, 127.4, 126.7, 126.4, 125.9, 125.6, 124.5, 29.4, 26.1; **ATR-FTIR (cm $^{-1}$)** 3061, 2926, 1738, 1591, 1453, 1172, 1062, 859, 705; **HRMS m/z (ESI)** calcd for $C_{22}H_{17}NO_2$ $(M + H)^+$ 328.1332, found 328.1334.

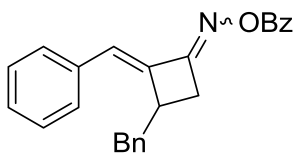
2-((*E*)-Benzylidene)-3-phenylcyclobutan-1-one *O*-benzoyl oxime (1n)



1n

According to the general procedure, **1n** (*E/Z* mixture) was prepared from the commercially available styrene (CAS: 100-42-5, 5.0 mmol) as a white solid (212 mg, 12%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.25 – 8.02 (m, 2H), 7.78 – 7.40 (m, 4H), 7.37 – 7.25 (m, 4H), 7.25 – 7.15 (m, 6H), 4.60 – 4.41 (m, 1H), 3.71 (m, 1H), 3.03 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.1, 164.0, 141.0, 140.9, 136.7, 136.4, 134.3, 133.4, 133.3, 133.2, 130.1, 123.0, 129.7, 129.6, 129.5, 129.3, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 127.1, 127.0, 126.4, 44.2, 43.1, 41.2, 40.3; **ATR-FTIR (cm $^{-1}$)** 3181, 2315, 1742, 1518, 1252, 1056, 702; **HRMS m/z (ESI)** calcd for $C_{24}H_{19}NO_2$$(M + H)^+$ 354.1489, found 354.1488.

3-Benzyl-2-((*E*)-benzylidene)cyclobutan-1-one *O*-benzoyl oxime (1o)

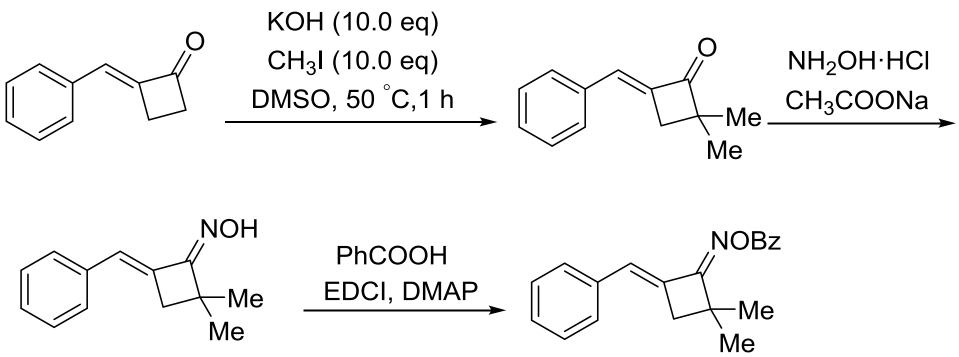


1o

According to the general procedure, **1o** (*E/Z* mixture) was prepared from the commercially available allylbenzene (CAS: 300-57-2, 5.0 mmol) as a white solid (275 mg, 15%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.11 (m, 1H), 8.06 – 8.03 (m, 1H), 7.58 – 7.31 (m, 11H), 7.24 – 7.15 (m, 3H), 3.81 – 3.68 (m, 1H), 3.45 – 3.33 (m, 1H), 3.27 – 3.15 (m, 1H), 2.89 – 2.78 (m, 1H), 2.66 – 2.57 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.9, 164.2, 164.0, 161.5, 138.9, 138.3, 138.0, 135.4, 135.1, 134.9, 133.4, 133.3, 129.7, 129.4, 129.0, 128.9, 128.7, 128.5, 127.9, 126.6, 40.2, 39.0, 37.1, 35.9, 35.1; **ATR-FTIR (cm $^{-1}$)** 3168, 2315, 1741, 1518, 1246, 1055, 877, 699**; HRMS m/z (ESI)** calcd for $C_{25}H_{21}NO_2$ $(M + Na)^+$ 390.1465, found 390.1470.

4-((*E*)-Benzylidene)-2,2-dimethylcyclobutan-1-one *O*-benzoyl oxime (1q)

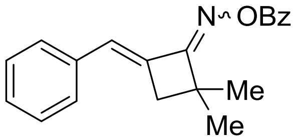


To a 100 mL flask was added KOH (2.8 g, 50 mmol) and DMSO (10 mL). To this was added CH_3I (7.1 g, 50 mmol) and (*E*)-2-benzylidenecyclobutan-1-one (0.79 g, 5 mmol) in DMSO (10 mL) through an addition funnel. The suspension was stirred at 50 °C for 1 h. The resulting mixture was washed by water and then extracted with ethyl acetate. Combined organic dried over $MgSO_4$. 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 (*E*)-4-benzylidene-2,2-dimethylcyclobutan-1-one.[5]

To a stirred solution of (*E*)-4-benzylidene-2,2-dimethylcyclobutan-1-one (1.0 equiv) in water mixture ethanol (1.0 M, H_2O : EtOH = 3 : 7) was added hydroxylamine hydrochloride (1.5 equiv) and NaOAc (1.8 equiv) at 100°C. After stirring for 12 h, quenching the reaction with $NaHCO_3$ and extracted with EtOAc[3]. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure to give the crude material, which were used in the next step without further purification.

To a mixture of cyclobutanone oxime (1.0 equiv), benzoic acid (1.5 equiv) and DCM (0.5 M) in a 30-mL one-necked flask was added EDCI (2.5 equiv) and DMAP(20 mol%) at rt[4]. After stirring for 12 h, NaOH (0.5 equiv) was added to the above solution, and the mixture was diluted with DCM. The organic layer was washed with water and dried over $MgSO_4$. 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 4-((*E*)-benzylidene)-2,2-dimethylcyclobutan-1-one *O*-benzoyl oxime (**1q**).

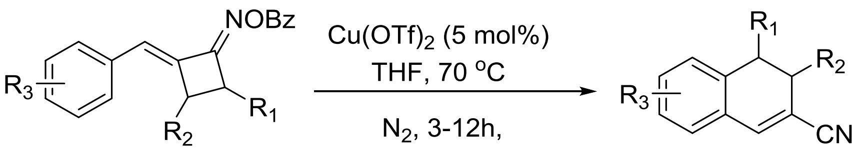
4-((*E*)-Benzylidene)-2,2-dimethylcyclobutan-1-one *O*-benzoyl oxime (1p)



1p

According to the general procedure, **1q** was prepared from (*E*)-2-benzylidenecyclobutan-1-one (790 mg, 5.0 mmol) as a white solid (275 mg, 18%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 – 7.99 (m, 2H), 7.67 – 7.57 (m, 1H), 7.50 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.43 – 7.29 (m, 6H), 2.84 (d, *J* = 2.8 Hz, 2H), 1.59 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.1, 164.1, 135.8, 133.3, 130.8, 129.6, 129.1, 129.0, 128.9, 128.8, 128.7, 47.7, 42.2, 24.8; **ATR-FTIR (cm $^{-1}$)** 3180**,** 2315, 1743, 1519, 1250, 1055, 701; **HRMS m/z (ESI)** calcd for $C_{20}H_{19}NO_2(M + H)^+$ 306.1489, found 306.1490.

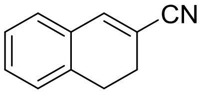
3. Experimental Procedures and Characterization of Products



1 **2**

Flame-dried 25 mL Schlenk tube filled with nitrogen, benzylidenecyclobutan-1-one O-benzoyl oxime 1 (0.2 mmol), $Cu(OTf)_2$ (3.6 mg, 5 mol%), dry THF (2.0 mL) were added under Ar. The formed mixture was stirred at 70 ℃ under N_2 for 3-12h 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 the corresponding product.

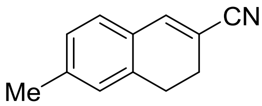
3,4-Dihydronaphthalene-2-carbonitrile (2a)



2a

According to the experimental procedure, **2a** was prepared from **1a** as a white solid (26.5 mg, 85%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.23 – 7.12 (m, 2H), 7.11 – 7.04 (m, 3H), 2.82 (t, *J* = 8.3 Hz, 2H), 2.45 (td, *J* = 8.2, 1.6 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.6, 135.3, 131.1, 130.2, 127.9, 127.0, 119.6, 109.5, 26.6, 24.6; **ATR-FTIR (cm^{-1})** 3062, 2943, 2841, 2210, 1689, 1618, 1565, 1292, 905; **HRMS m/z (ESI)** calcd for $C_{11}H_9N$ $(M + H)^+$ 156.0808, found 156.0806.

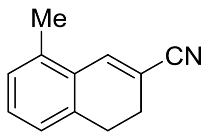
6-Methyl-3,4-dihydronaphthalene-2-carbonitrile (2b)



2b

According to the experimental procedure, **2b** was prepared from **1b** as a white solid (27.7 mg, 82%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.07 (t, *J* = 1.4 Hz, 1H), 6.95 (d, *J* = 1.1 Hz, 2H), 6.90 (t, *J* = 1.1 Hz, 1H), 2.85 (t, *J* = 8.2 Hz, 2H), 2.43 (td, *J* = 8.2, 1.6 Hz, 2H), 2.26 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.6, 139.7, 134.4, 127.8, 127.6, 126.9, 126.7, 118.9, 107.3, 25.7, 23.7, 20.5; **ATR-FTIR (cm^{-1})** 2940, 2314, 2198, 1742, 1554, 1428, 1140, 896; **HRMS m/z (ESI)** calcd for $C_{12}H_{11}N$ $(M + H)^+$ 170.0964, found 170.0963.

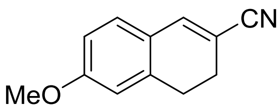
8-Methyl-3,4-dihydronaphthalene-2-carbonitrile (2c)



2c

According to the experimental procedure, **2c** was prepared from **1c** as a white solid (27.4 mg, 81%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 (q, *J* = 1.5 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 2.79 (t, *J* = 8.2 Hz, 2H), 2.42 (td, *J* = 8.2, 1.7 Hz, 2H), 2.29 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.7, 135.8, 135.4, 129.9, 129.6, 129.0, 125.8, 120.0, 109.5, 27.4, 24.3, 18.8; **ATR-FTIR (cm $^{-1}$)** 3181, 2315, 2208, 1519, 1466, 899, 427**; HRMS m/z (ESI)** calcd for $C_{12}H_{11}N$ $(M + H)^+$ 170.0964, found 170.0963.

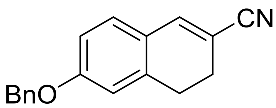
6-Methoxy-3,4-dihydronaphthalene-2-carbonitrile (2d)



2d

According to the experimental procedure, **2d** was prepared from **1d** as a white solid (24.1 mg, 65%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.13 (d, *J* = 1.7 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.74 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.70 (d, *J* = 2.6 Hz, 1H), 3.82 (s, 3H), 2.86 (t, *J* = 8.2 Hz, 2H), 2.50 (td, *J* = 8.2, 1.6 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.1, 141.3, 137.5, 129.5, 124.5, 120.2, 114.2, 111.9, 106.3, 55.4, 27.3, 24.5; **ATR-FTIR (cm $^{-1}$)** 3181, 2314, 2199, 1699, 1558, 1430, 880**; HRMS m/z (ESI)** calcd for $C_{12}H_{11}NO$ $(M + H)^+$ 186.0913, found 186.0908.

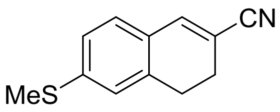
6-(Benzyloxy)-3,4-dihydronaphthalene-2-carbonitrile (2e)



2e

According to the experimental procedure, **2e** was prepared from **1e** as a white solid (48.0 mg, 92%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (t, *J* = 1.4 Hz, 1H), 7.43 (d, *J* = 4.4 Hz, 4H), 7.40 – 7.33 (m, 1H), 7.22 (dd, *J* = 8.4, 7.5 Hz, 1H), 6.84 – 6.75 (m, 2H), 5.10 (s, 2H), 2.87 (t, *J* = 8.3, 2H), δ 2.50 (td, *J* = 8.3, 1.6 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.9, 136.0, 135.4, 135.3, 130.1, 127.7, 127.1, 126.3, 119.6, 119.5, 119.2, 109.5, 106.9, 69.3, 26.0, 23.2; **ATR-FTIR (cm $^{-1}$)** 3288, 2947, 2314, 2207, 1693, 1571, 1462, 1054, 909; **HRMS m/z (ESI)** calcd for $C_{18}H_{15}NO$ $(M + H)^+$ 262.1226, found 262.1225.

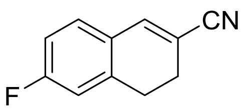
6-(Methylthio)-3,4-dihydronaphthalene-2-carbonitrile (2f)



2f

According to the experimental procedure, **2f** was prepared from **1f** as a white solid (21.3 mg, 53%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.06 (s, 1H), 6.98 (d, *J* = 2.3 Hz, 2H), 6.94 (s, 1H), 2.79 (t, *J* = 8.2 Hz, 2H), 2.45 (t, *J* = 8.2 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.8, 141.2, 135.9, 128.2, 128.0, 125.1, 123.9, 119.9, 108.2, 26.9, 24.6, 15.2; **ATR-FTIR (cm $^{-1}$)** 3183, 2314, 2199, 1699, 1558, 1430, 880; **HRMS m/z (ESI)** calcd for $C_{12}H_{11}NS$ $(M + H)^+$ 202.0685, found 202.0680.

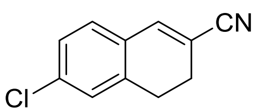
6-Fluoro-3,4-dihydronaphthalene-2-carbonitrile (2g)



2g

According to the experimental procedure, **2g** was prepared from **1g** as a white solid (28.7 mg, 83%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 (s, 1H), 7.15 – 7.07 (m, 1H), 6.96 – 6.82 (m, 2H), 2.90 (t, *J* = 8.3 Hz, 2H), 2.58 – 2.46 (t, *J* = 8.2Hz, 2H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.5(d, *J* = 252.5 Hz) , 140.6 (d, *J* = 1.6 Hz), 138.2 (t, *J* = 8.2 Hz), 129.8 (d, *J* = 8.7 Hz), 127.5 (d, *J* = 3.1 Hz), 115.4 (d, *J* = 22.3 Hz), 114.0 (d, *J* = 21.9 Hz), 108.8 (d, *J* = 2.8 Hz), 26.9 (d, *J* = 1.8 Hz), 24.2; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -109.1; **ATR-FTIR (cm $^{-1}$)** 2948, 2206, 1740, 1574, 1489, 1237, 1136, 946; **HRMS m/z (ESI)** calcd for $C_{11}H_8FN$ $(M + H)^+$ 174.0714, found 174.0716.

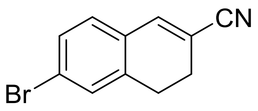
6-Chloro-3,4-dihydronaphthalene-2-carbonitrile (2h)



2h

According to the experimental procedure, **2h** was prepared from **1h** as a white solid (33.6 mg, 89%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.22 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 2.90 (t, *J* = 8.3 Hz, 2H), 2.55 (td, *J* = 8.3, 1.7 Hz, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.5, 137.1, 135.8, 129.6, 129.0, 128.2, 127.3, 119.4, 110.0, 26.6, 24.4; **ATR-FTIR (cm $^{-1}$)** 3124, 2956, 2315, 2204, 1745, 1550, 1481, 1086, 874; **HRMS m/z (ESI)** calcd for $C_{11}H_8ClN$ (M + Na)$^+$ 212.0237, found 212.0241.

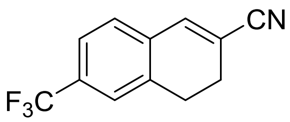
6-Bromo-3,4-dihydronaphthalene-2-carbonitrile (2i)



2i

According to the experiment procedure, **2i** was prepared from **1i** as a white solid (37.7 mg, 81%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.40 – 7.29 (m, 2H), 7.13 (d, *J* = 1.8 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 2.88 (t, *J* = 8.3 Hz, 2H), 2.52 (td, *J* = 8.3, 1.7 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.6, 136.24, 130.1, 129.3, 129.0, 128.2, 123.2, 118.3, 109.2, 25.5, 23.4; **ATR-FTIR (cm $^{-1}$)** 3180, 2932, 2314, 2210, 1690, 1552, 1436, 1187, 895, 776; **HRMS m/z (ESI)** calcd for $C_{11}H_8BrN$ (M + H)$^+$ 233.9913, found 233.9912.

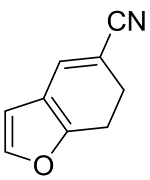
6-(Trifluoromethyl)-3,4-dihydronaphthalene-2-carbonitrile (2j)



2j

According to the experimental procedure, **2j** was prepared from **1j** as a white solid (29.5 mg, 66%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.42 (d, *J* = 7.9 Hz, 1H), 7.35 (s, 1H), 7.22 – 7.16 (m, 1H), 7.14 (d, *J* = 1.9 Hz, 1H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.52 (t, *J* = 8.0 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 140.1 , 136.0 , 134.1, 131.6 (d, *J* = 32.4 Hz), 128.0 , 124.75 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 3.9 Hz), 123.7 (q, *J* = 273.7 Hz) , 118.9, 112.5 , 26.5 , 24.5; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.9; **ATR-FTIR (cm $^{-1}$)** 3290, 2206, 1690, 1560, 1324, 1068, 899, 427; **HRMS m/z (ESI)** calcd for $C_{12}H_9F_3N$ (M + H)$^+$ 224.0682, found 224.0680.

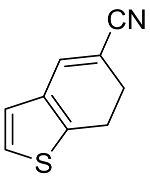
6,7-Dihydrobenzofuran-5-carbonitrile (2k)



2k

According to the experimental procedure, **2k** was prepared from **1k** as a white solid (20.9 mg, 72%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.30 (d, *J* = 2.0, 1H), 7.04 (t, *J* = 1.7 Hz, 1H), 6.33 (d, *J* = 1.9 Hz, 1H), 2.92 (t, *J* = 9.6 Hz, 2H), 2.73 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 154.2, 142.5, 136.2, 119.9, 116.1, 108.1, 102.9, 26.1, 21.2; **ATR-FTIR (cm $^{-1}$)** 2978, 2318, 1708, 1400, 1251, 1057, 887; **HRMS m/z (ESI)** calcd for C_9H_7NO (M + H)$^+$ 146.0600, found 146.0598.

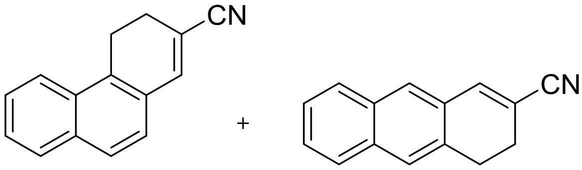
6,7-Dihydrobenzo[*b*]thiophene-5-carbonitrile (2l)



2l

According to the experimental procedure, **2l** was prepared from **1l** as a white solid (25.2 mg, 78%): **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.17 (t, *J* = 1.7 Hz, 1H), 7.11 (d, *J* = 5.1 Hz, 1H), 6.91 (d, *J* = 5.1 Hz, 1H), 3.00 (t, *J* = 9.0 Hz, 2H), 2.64 (td, *J* = 9.0, 1.6 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.5, 136.6, 132.9, 125.7, 123.4, 120.1, 105.3, 25.6, 22.7; **ATR-FTIR (cm $^{-1}$)** 3113, 2314, 2207, 1694, 1594, 1431, 1178, 715; **HRMS m/z (ESI)** calcd for C_9H_7NS (M + H)$^+$ 162.0372, found 162.0371.

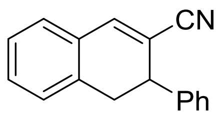
3,4-Dihydrophenanthrene-2-carbonitrile (2m) and 3,4-Dihydroanthracene-2-carbonitrile (2m')



2m **2m'**

According to the experimental procedure, **2m** and **2m'** were prepared from **1m** as a white solid (36.9 mg, 90% **2m: 2m'** = 93 : 7 (NMR analysis): **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.05 (d, *J* = 8.4 Hz, 1H) **2n** product, 7.86 (d, *J* = 8.0 Hz, 1H) **2n** product, 7.75 (d, *J* = 8.3 Hz, 1H) **2n** product, 7.56 (m, 2H) **2n** product, 7.31 (t, *J* = 1.7 Hz, 1H) **2n** product, 7.28 (d, *J* = 8.2 Hz, 1H) **2n** product, 3.34 (t, *J* = 8.8 Hz, 2H) **2n** product, 2.70 (td, *J* = 8.9, 1.7 Hz, 2H) **2n** product; **^{13}C NMR (126 MHz, CDCl$_3$)** δ 141.2, 133.5, 130.9, 129.9, 127.8, 127.2, 126.2, 125.8, 125.7, 124.5, 122.8, 118.7, 107.8, 23.3, 21.2; **ATR-FTIR (cm $^{-1}$)** 3057, 2316, 2206, 1700, 1511, 1256, 1119, 952; **HRMS m/z (ESI)** calcd for $C_{15}H_{11}N$ (M + H)$^+$ 206.0964, found 206.0963.

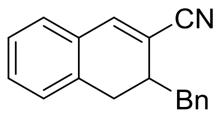
3-Phenyl-3,4-dihydronaphthalene-2-carbonitrile (2n)



2n

According to the experimental procedure, **2n** was prepared from **1n** as a white solid (16.2 mg, 35%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.24 (m, 7H), 7.19 – 7.09 (m, 2H), 6.98 – 6.83 (m, 1H), 4.24 (dd, J = 9.6, 7.6 Hz, 1H), 2.89 – 2.78 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.2, 141.7, 138.1, 131.3, 130.7, 128.8, 128.4, 128.2, 127.4, 127.2, 119.4, 108.6, 43.0, 32.9; **ATR-FTIR (cm^{-1})** 3184, 2923, 2315, 1703, 1517, 706, 552; **HRMS m/z (ESI)** calcd for $C_{17}H_{13}N$ $(M + H)^+$ 232.1121, found 232.1124.

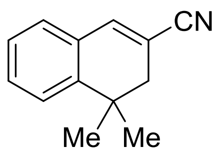
3-Benzyl-3,4-dihydronaphthalene-2-carbonitrile (2o)



2o

According to the experimental procedure, **2o** was prepared from **1o** as a white solid (26.9 mg, 55%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 – 7.10 (m, 7H), 6.97 (m, 3H), 3.06 – 2.98 (m, 1H), 2.80 – 2.72 (m, 1H), 2.68 – 2.59 (m, 1H), 2.51 (d, J = 2.8 Hz, 1H), 2.32 (dd, J = 17.0, 3.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.3, 139.1, 138.9, 130.3, 129.2, 128.5, 128.4, 128.1, 127.3, 126.5, 119.8, 107.6, 40.7, 38.9, 28.6.; **ATR-FTIR (cm^{-1})** 3027, 2929, 2315, 2208, 1698, 1496, 1447, 907; **HRMS m/z (ESI)** calcd for $C_{18}H_{15}N$ $(M + H)^+$ 246.1277, found 246.1278.

4,4-Dimethyl-3,4-dihydronaphthalene-2-carbonitrile (2p)

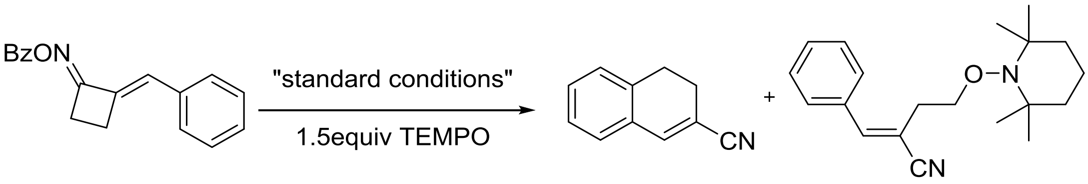


2p

According to the experimental procedure, **2p** was prepared from **1p** as a white solid (24.5 mg, 67%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.32 (m, 2H), 7.25 – 7.11 (m, 3H), 2.42 (d, J = 1.6 Hz, 2H), 1.29 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.6, 143.5, 140.4, 130.0, 127.6, 125.7, 123.1, 118.8, 107.3, 38.4, 32.6, 27.0; **ATR-FTIR (cm^{-1})** 3063, 2965, 2314, 2209, 1692, 1625, 1563, 1131, 904**; HRMS m/z (ESI)** calcd for $C_{13}H_{13}N$ $(M + H)^+$ 184.1126, found 184.1125.

4. Mechanistic Experiments

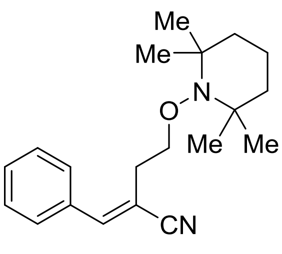
(a) TEMPO trapping experiment



1a 2a 3

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone *O*-benzoyl oxime (**1a**, 55.4 mg, 0.2 mmol), $Cu(OTf)_2$ (3.6 mg, 5 mol%), TEMPO (46.8 mg, 0.3 mmol), dry THF (2.0 mL) were added under Ar. The formed mixture was stirred at 70 ℃ 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 to afford 1.5 mg (<5%) of **2a** and 49.9 mg (80%) of **3** as a white solid.

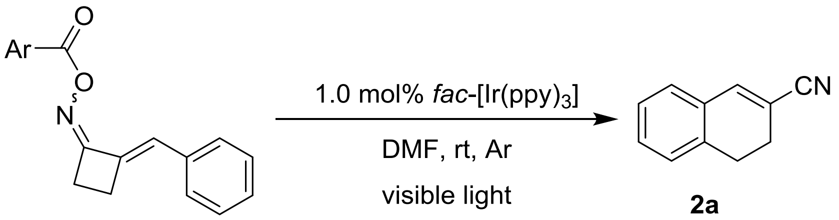
(*E*)-2-Benzylidene-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanenitrile (3)



3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.45 – 7.34 (m, 3H), 7.32 (s, 1H), 4.06 (t, *J* = 6.2 Hz, 2H), 2.68 (td, *J* = 6.2, 1.2 Hz, 2H), 1.56 – 1.29 (m, 6H), 1.20 (s, 6H), 1.10 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.5, 134.0, 129.3, 128.6, 120.5, 113.2, 73.5, 59.9, 39.6, 33.1, 29.5, 20.3, 17.1; **ATR-FTIR (cm $^{-1}$)** 2973, 2933, 2214, 1693, 1457, 1254, 1056, 934; **HRMS m/z (ESI)** calcd for $C_{20}H_{28}N_2O$ $(M + Na)^+$ 335.2094, found 335.2099.

(b). Photo-induced experiments



1

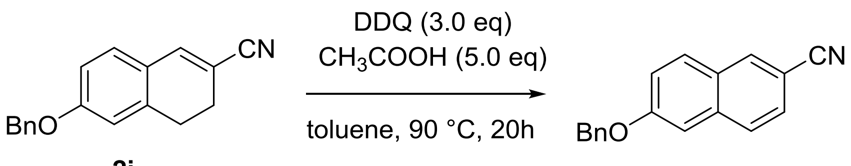
0.1 mmol

2a

Ar= Ph **1a**	trace
Ar=4-NO_2Ph **1a'**	45%
Ar=4-CF_3Ph **1a''**	61%

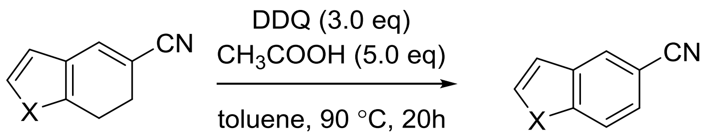
These reactions were carried out according to the reported literature[6]: flame-dried 25 mL Schlenk tube filled with argon was charged with **1** (0.2 mmol), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg) and DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip as monitored by TLC. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel to afford **2a**.

5. Synthetic Application and Transformations



2i

4, 96%

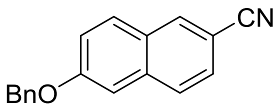


2k, **X=O** — **5**, 97%

2l, **X=S** — **6**, 95%

To a mixture of acetic acid (60 mg, 5.0 eq), DDQ (136.2 mg, 3.0 eq) and product **2i** (0.2 mmol) was stirred in toluene (2 mL) at 90^{o}C in 25 mL Schlenk tube.[7] After stirring for 20 h, the mixture was diluted with ethyl acetate and washed with water and NaOH solution (1 mol/L, 3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was further purified by flash chromatography on silica gel affording the desired product.

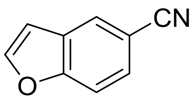
6-(Benzyloxy)-2-naphthonitrile (4)



4

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.71 (m, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.61 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.49 – 7.37 (m, 4H), 6.99 (d, *J* = 7.6 Hz, 1H), 5.27 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.5, 136.2, 135.7, 129.5, 129.1, 128.8, 128.7, 128.3, 127.4, 127.0, 124.8, 120.3, 119.7, 108.5, 106.7, 70.4; **ATR-FTIR (cm $^{-1}$)** 3196, 2224, 1692, 1628, 1571, 1454, 1193, 990; **HRMS m/z (ESI)** calcd for $C_{18}H_{13}NO$ $(M + H)^+$ 260.1070, found 260.1068.

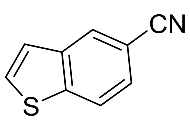
Benzofuran-5-carbonitrile (5)[8]



5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, *J* = 1.2 Hz, 1H), 7.75 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 1.5 Hz, 2H), 6.85 (d, *J* = 1.8, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.6, 147.1, 128.0, 126.4, 119.4, 112.7, 106.8, 106.6; **ATR-FTIR (cm $^{-1}$)** 3185, 2920, 2225, 1775, 1658, 1630, 1463, 1073, 769; **HRMS m/z (ESI)** calcd for C_9H_5NO $(M + Na)^+$ 166.0263, found 166.0258.

Benzo[*b*]thiophene-5-carbonitrile (6)[9]



6

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.97 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.61 (d, *J* = 5.5 Hz, 1H), 7.56 (dt, *J* = 8.4, 1.1 Hz, 1H), 7.41 (d, *J* = 5.5 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.8, 139.3, 129.1, 128.2, 126.2, 123.7, 123.5, 119.4, 108.0; **ATR-FTIR (cm $^{-1}$)** 3087, 2314, 2225, 1702, 1539, 1418, 1048, 898, 701; **HRMS m/z (ESI)** calcd for C_9H_5NS $(M + H)^+$ 160.0215, found 160.0215.

6. References

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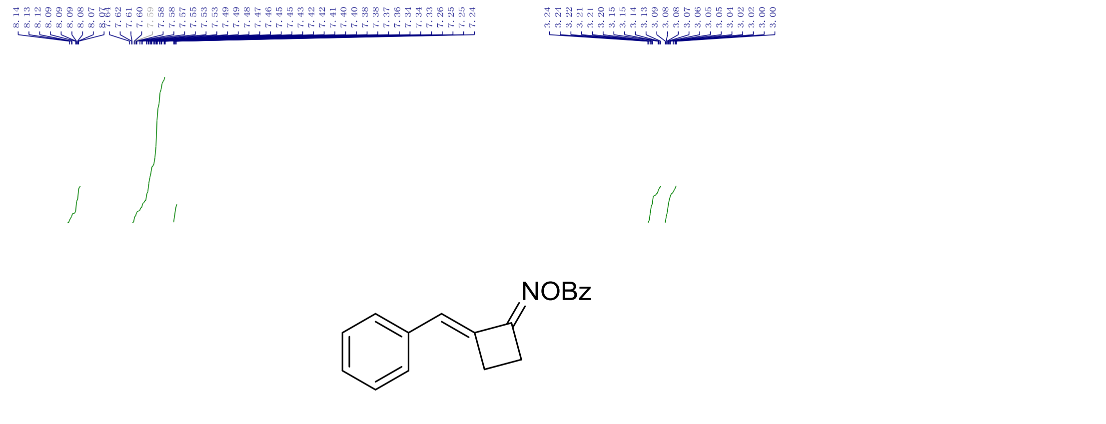
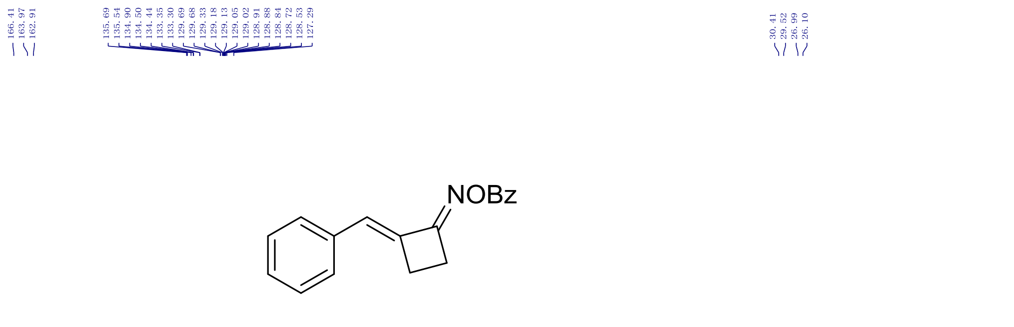
7. Copies of NMR Spectra



1a



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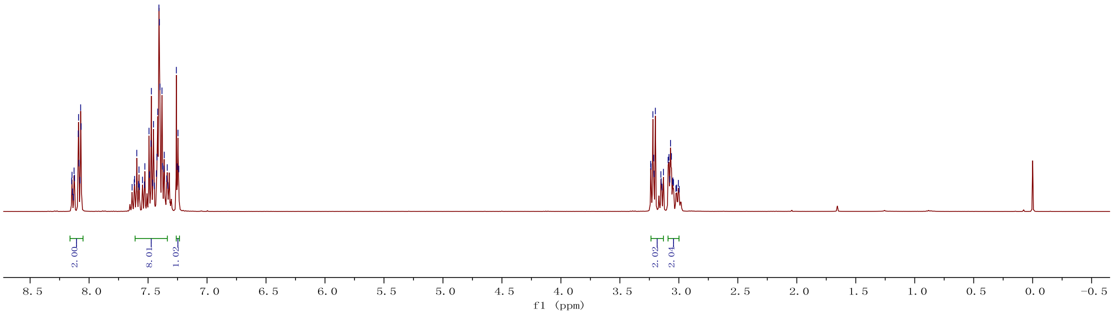

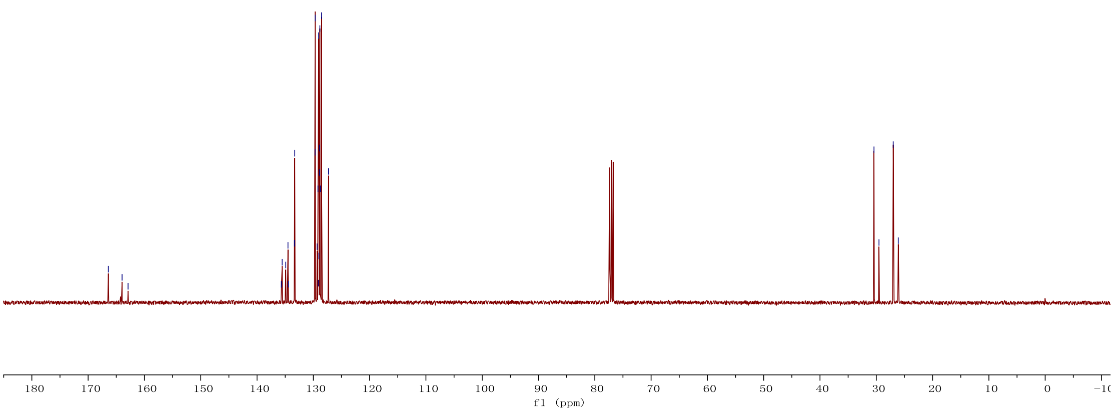

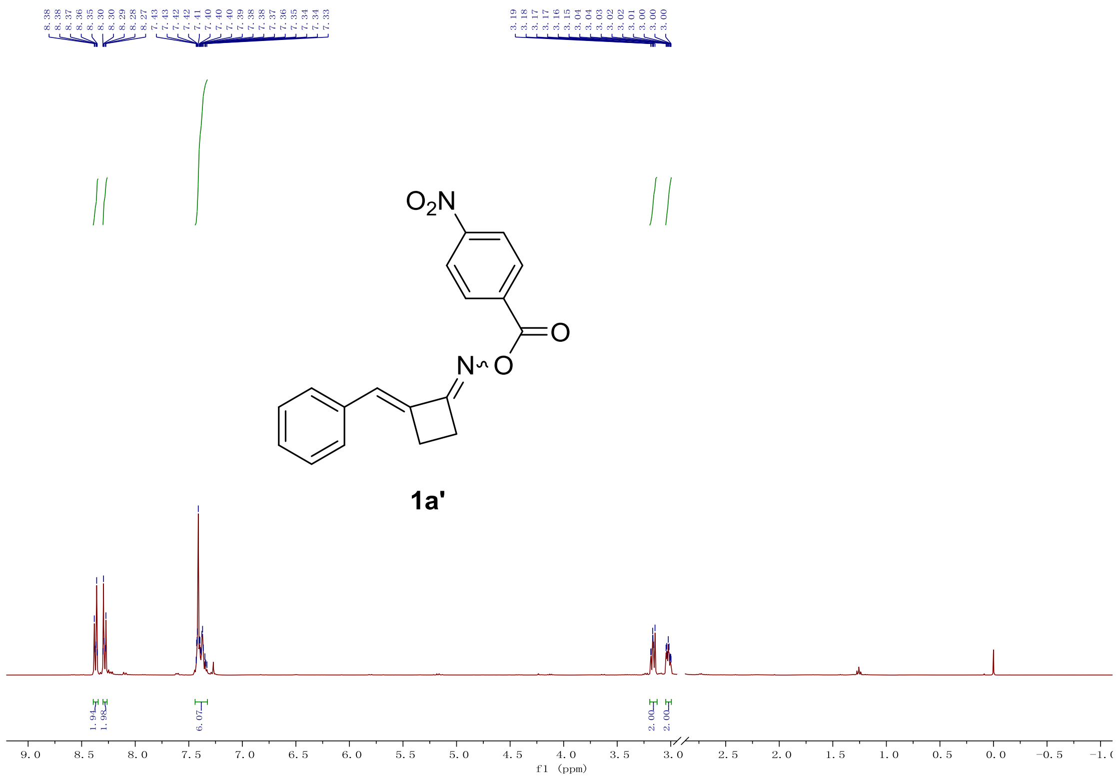

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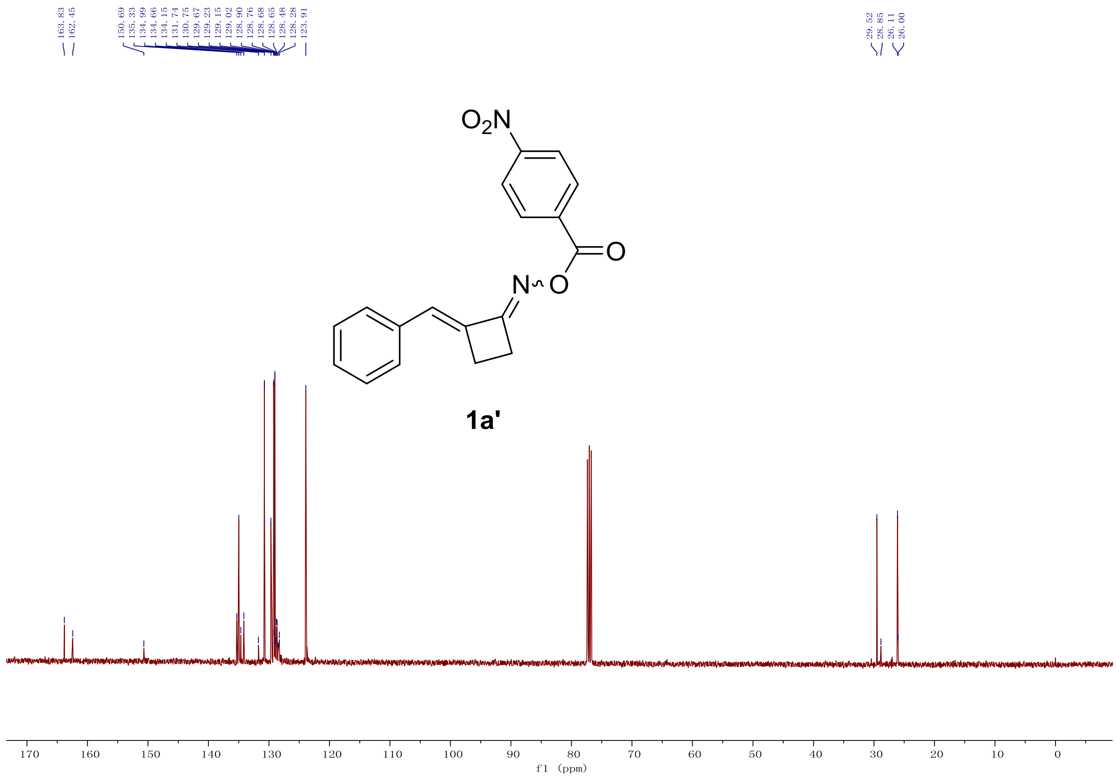

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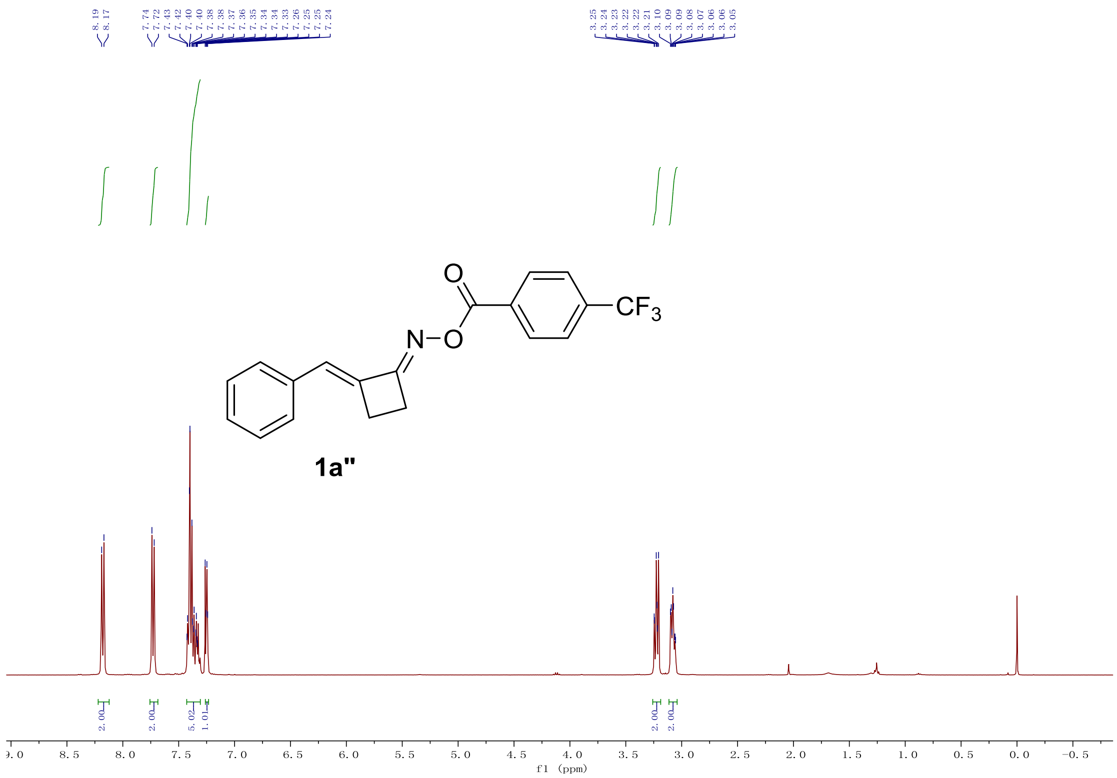
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3.21
3.10
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3.09
3.08
3.07
3.06
3.06
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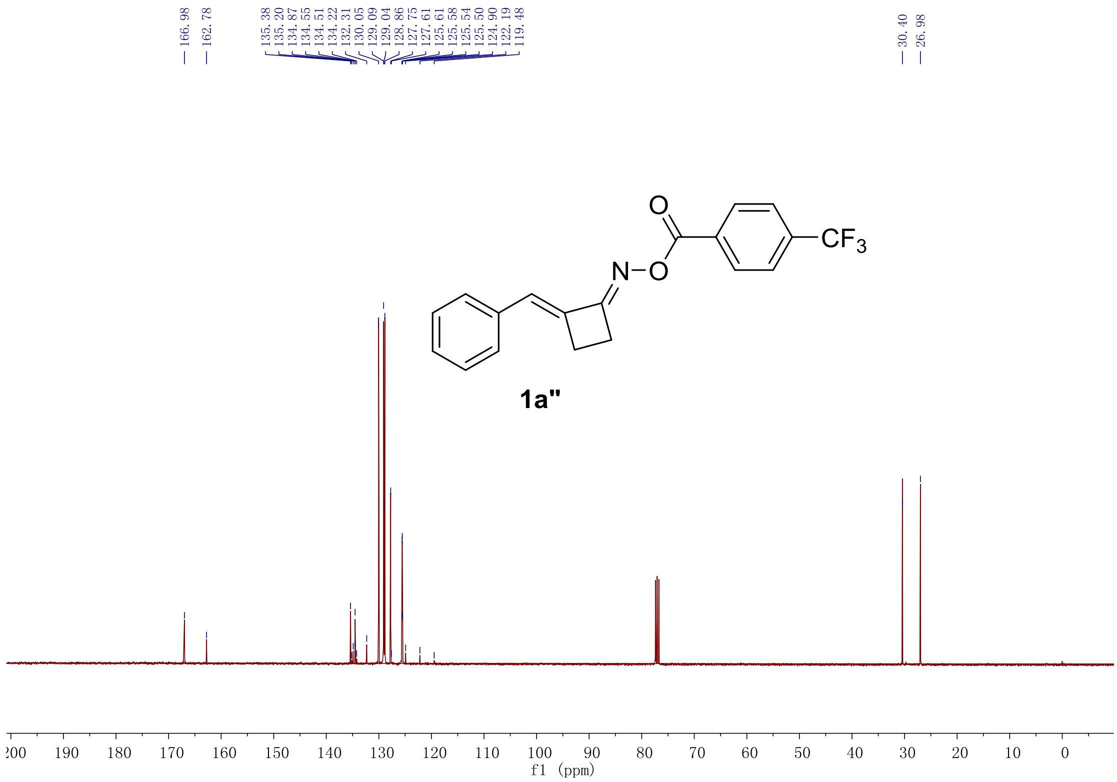
f1 (ppm)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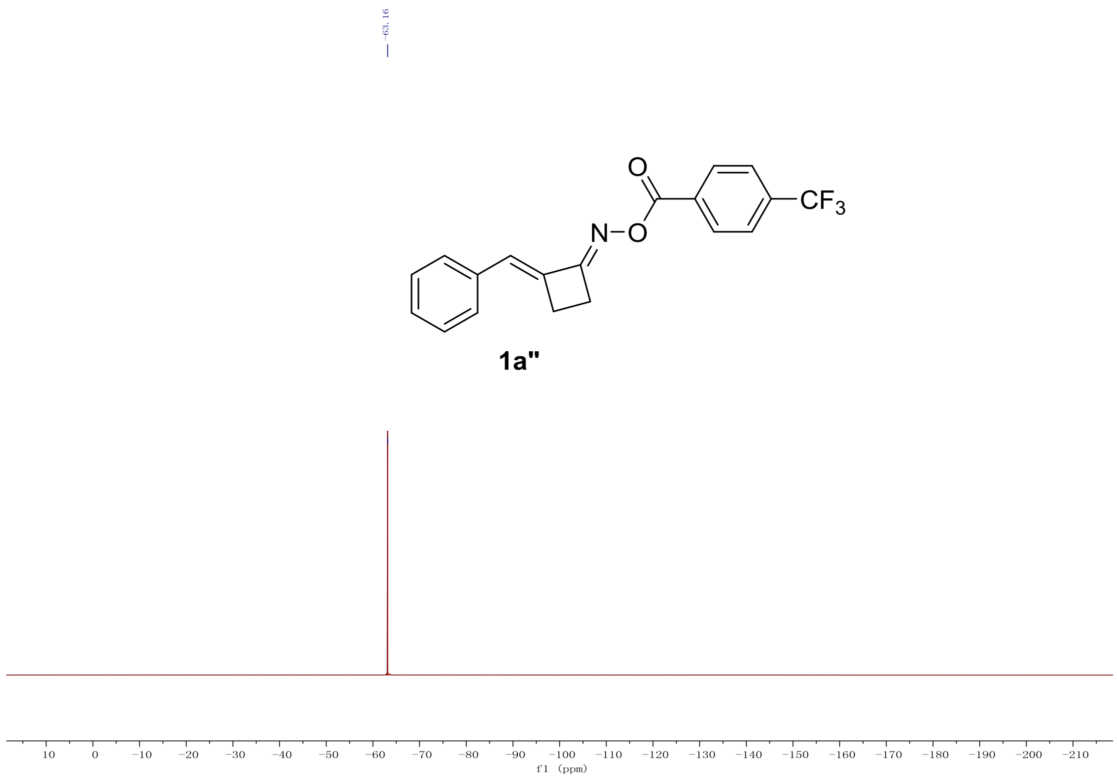
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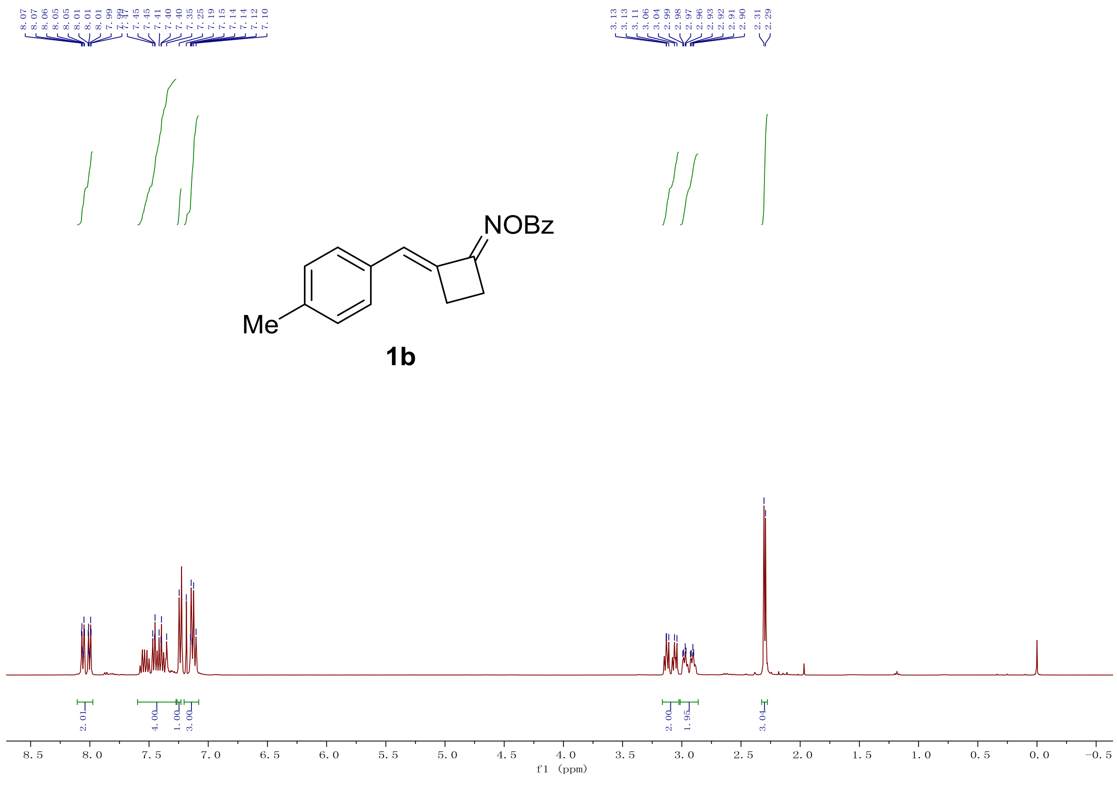
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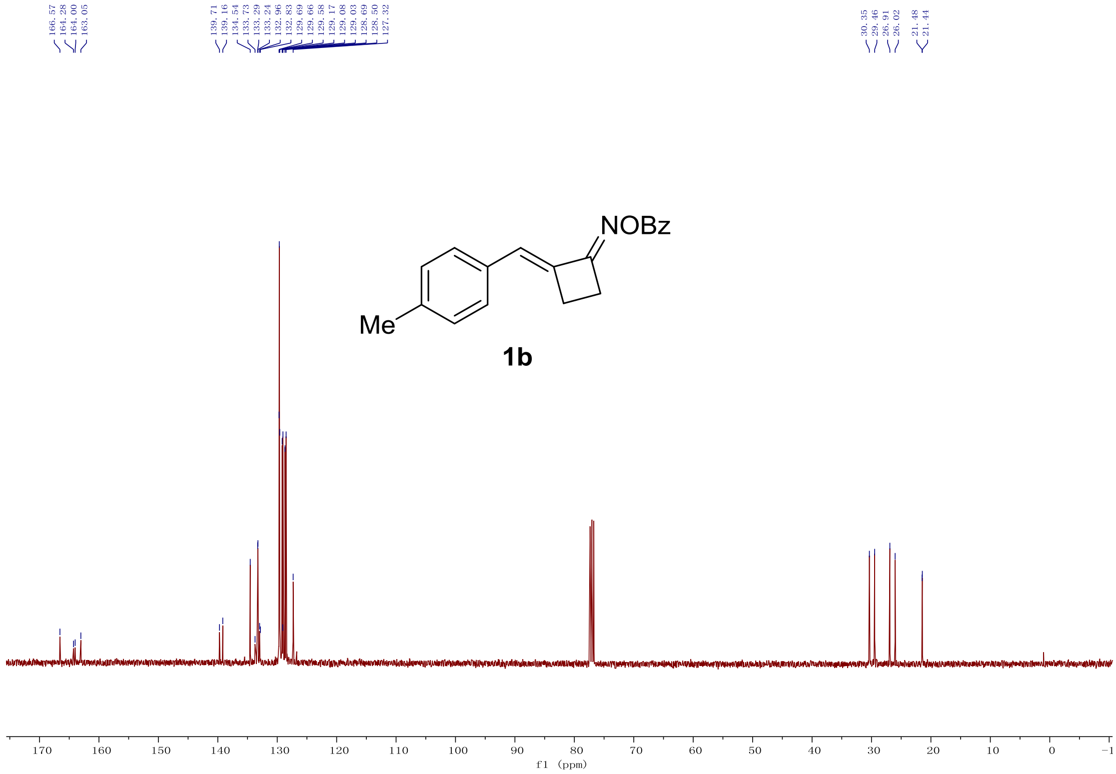
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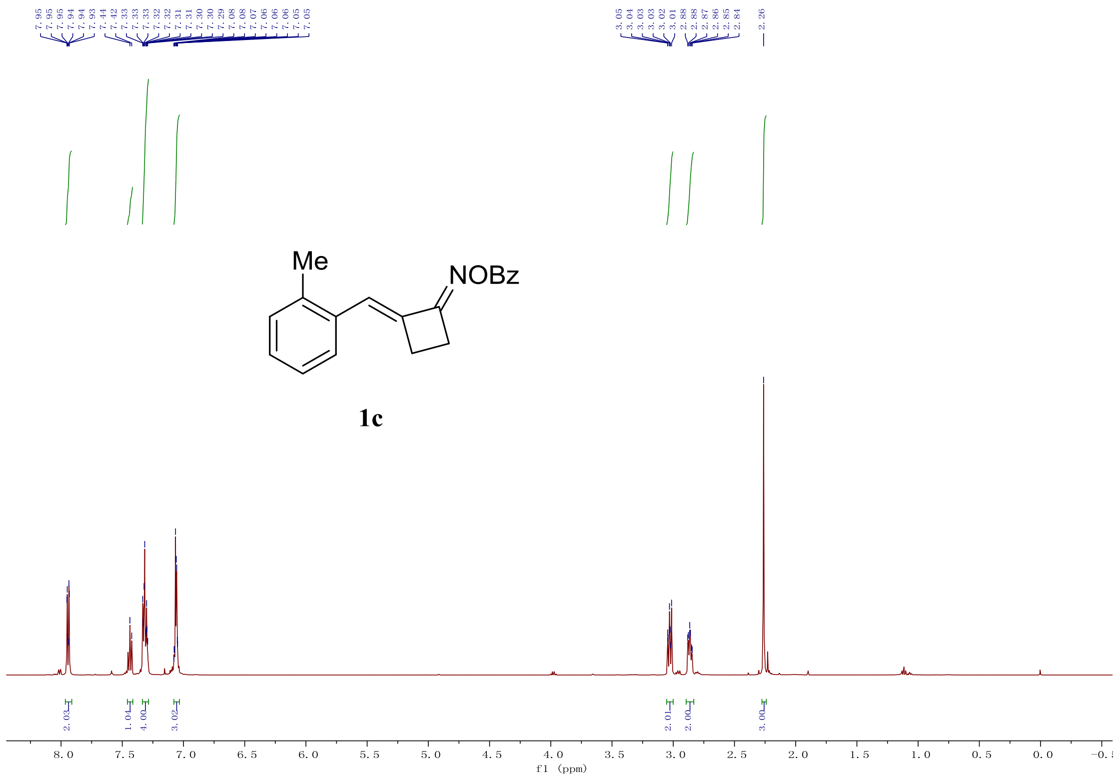
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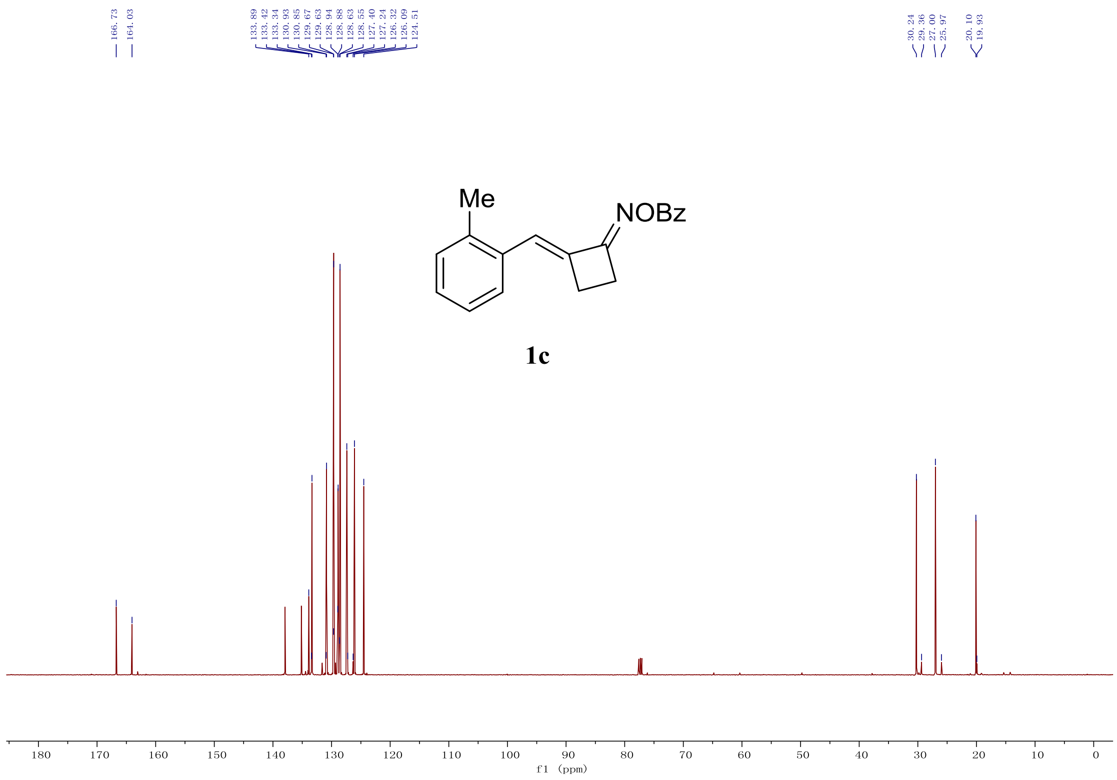
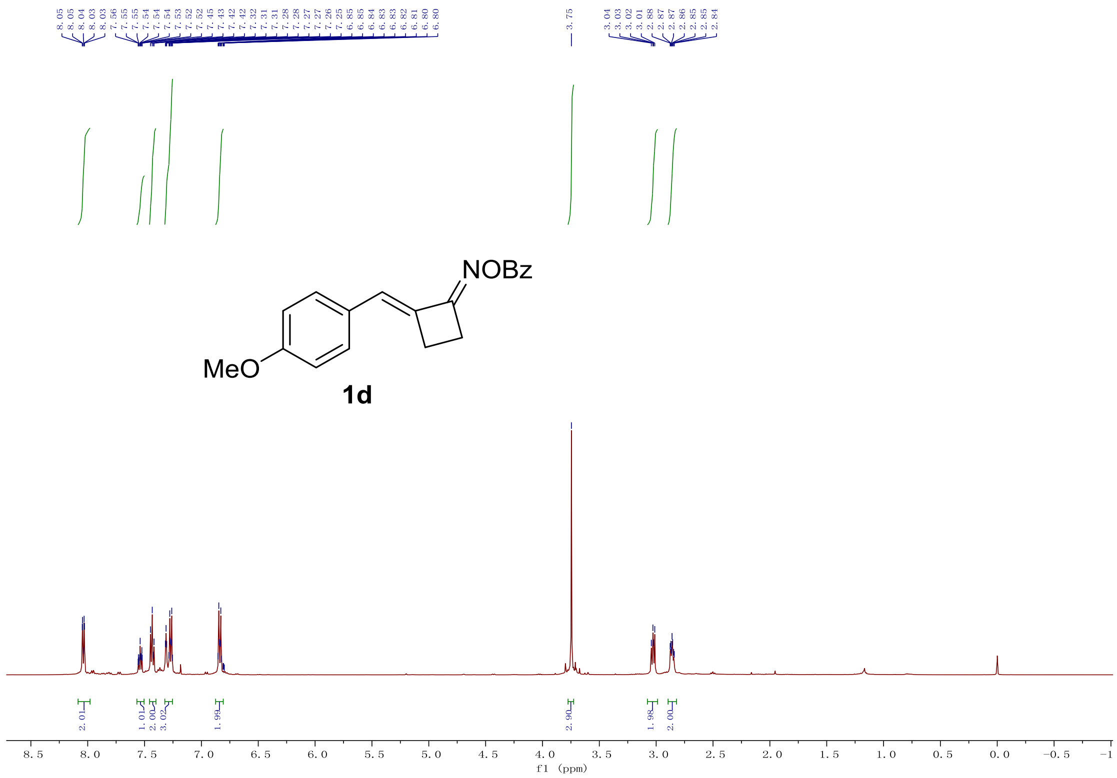
3.00
f1 (ppm)


Me
NOBz
1c
f1 (ppm)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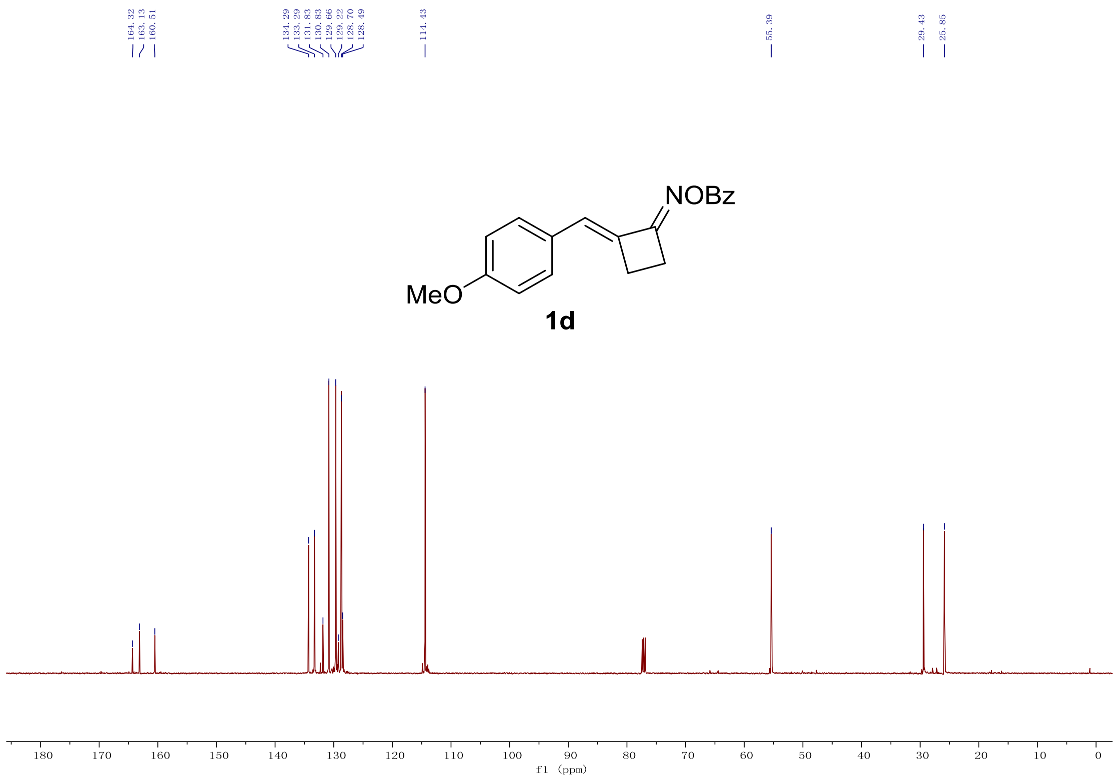
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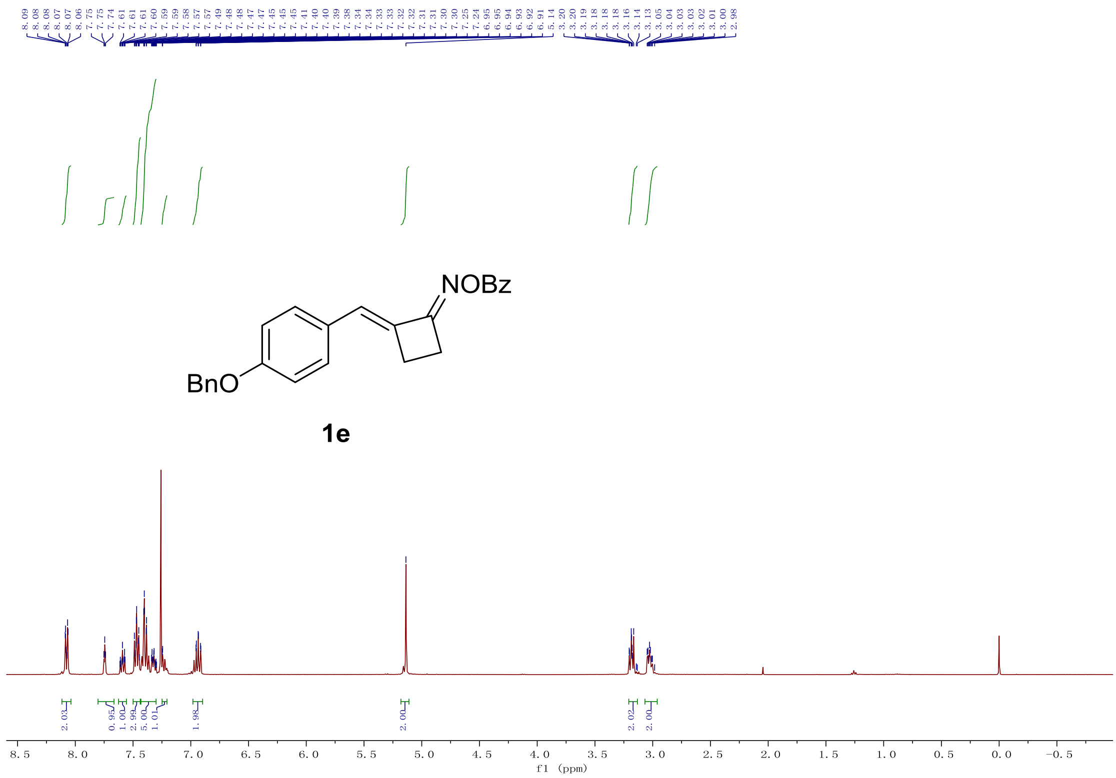
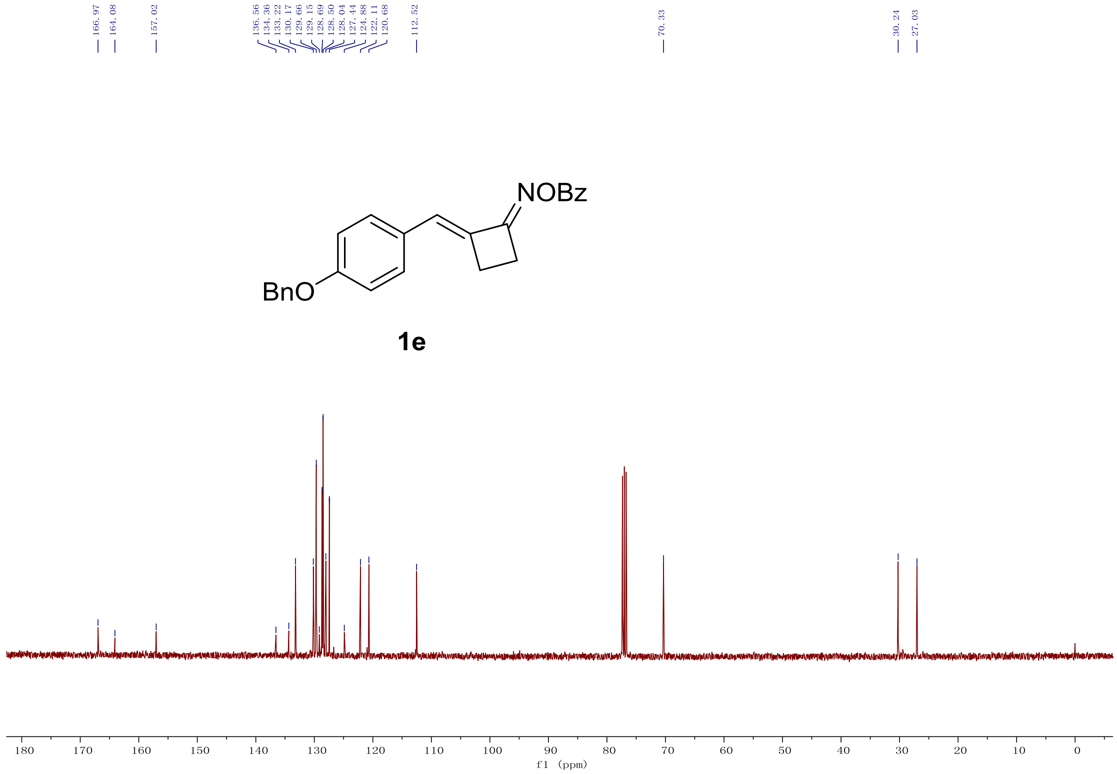
1d


8.09 8.08 8.08 8.07 8.07 8.06 7.75 7.74 7.61 7.61 7.61 7.60 7.59 7.59 7.58 7.57 7.57 7.49 7.48 7.48 7.47 7.47 7.45 7.45 7.45 7.41 7.40 7.40 7.39 7.38 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.25 7.24 6.95 6.94 6.93 6.92 6.91 5.14 3.20 3.20 3.19 3.18 3.18 3.16 3.14 3.13 3.05 3.04 3.03 3.03 3.02 3.01 3.00 2.98
NOBz
BnO
2.03 0.95 1.00 2.00 5.00 1.01 1.98 2.00 2.02 2.00
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 -0.5
f1 (ppm)

1e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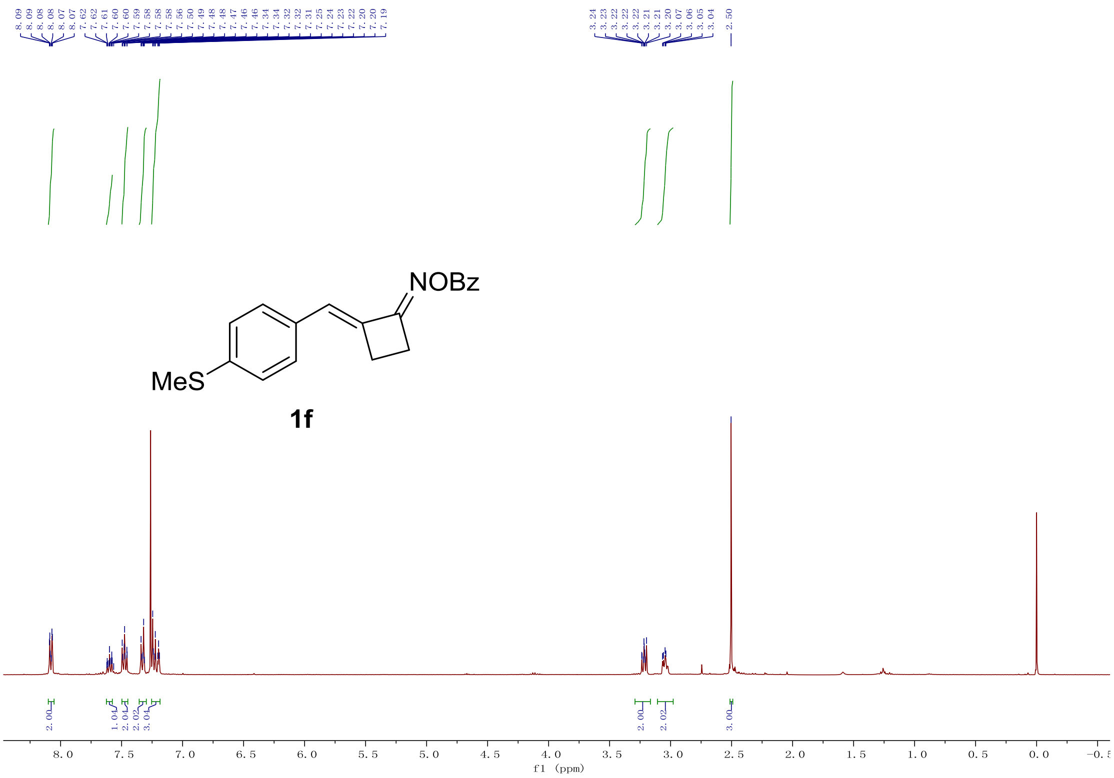
128.50
128.04
127.44
124.88
122.11
120.68
112.52
70.33
30.24
27.03
NOBz
BnO
f1 (ppm)

1e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8.09
8.08
8.08
8.07
8.07
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7.61
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7.60
7.59
7.58
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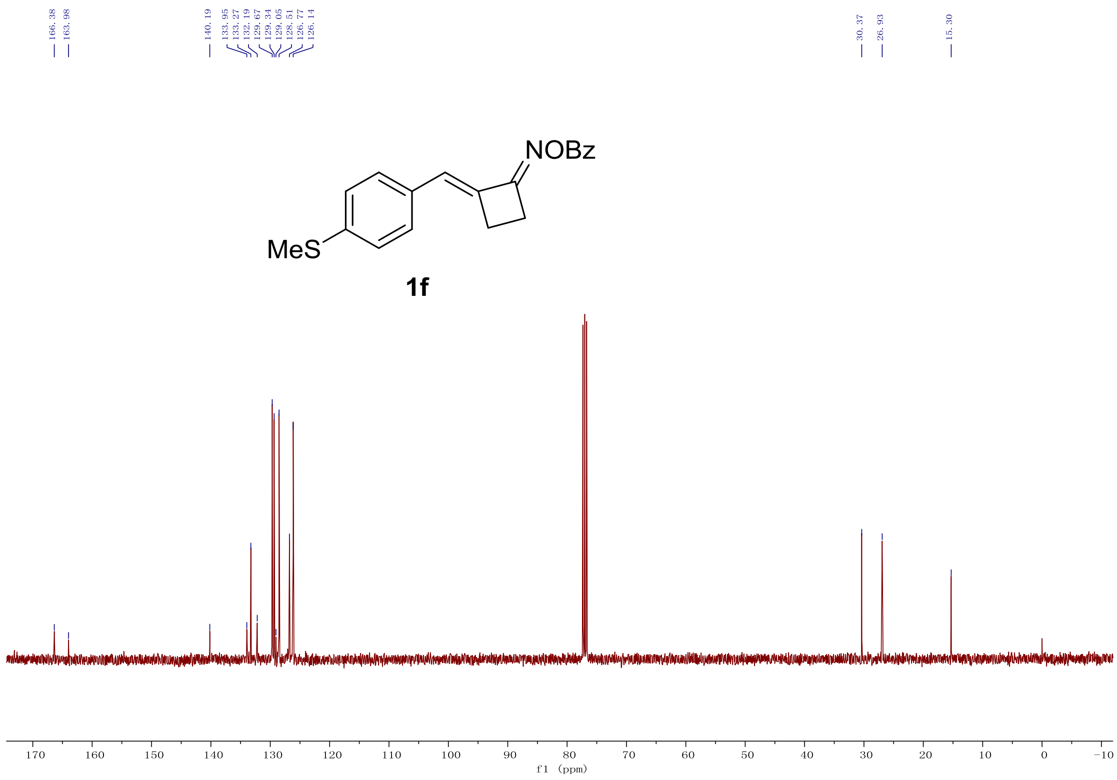
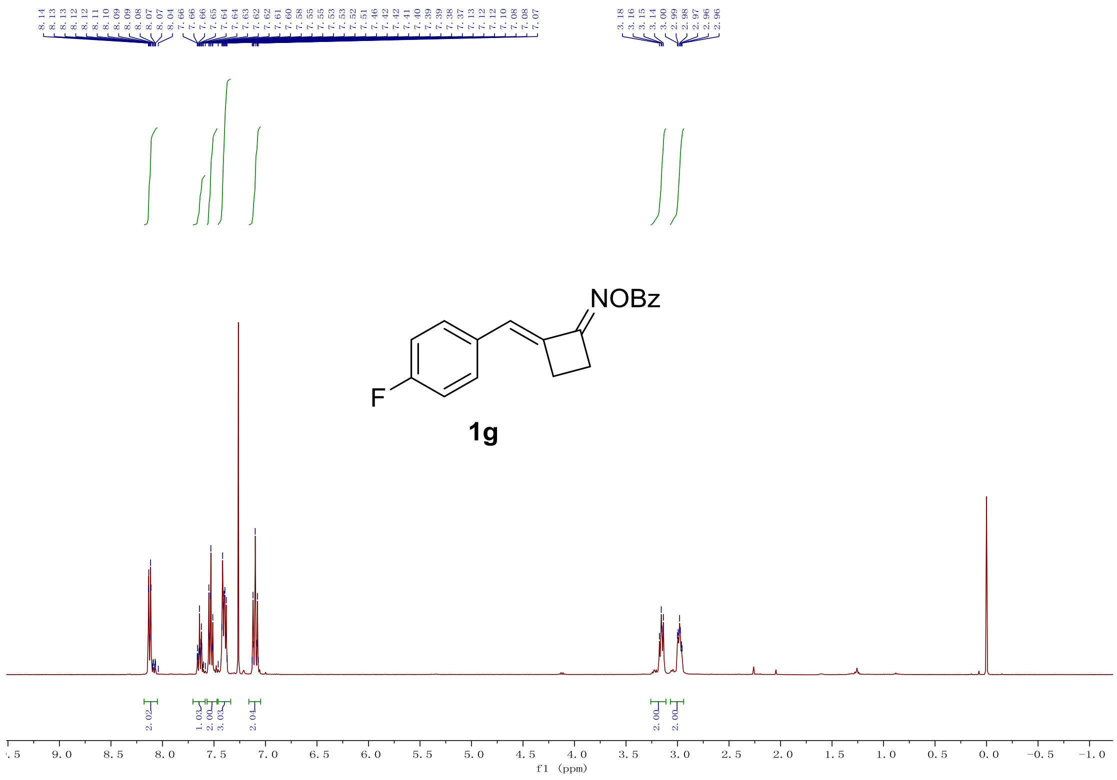
7.56
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.34
7.34
7.32
7.32
7.31
7.25
7.24
7.23
7.22
7.20
7.20
7.19
3.24
3.23
3.22
3.22
3.22
3.21
3.21
3.20
3.07
3.06
3.05
3.04
2.50
NOBz
MeS
2.00
1.04
2.04
2.02
3.04
2.00
2.02
3.00
f1 (ppm)

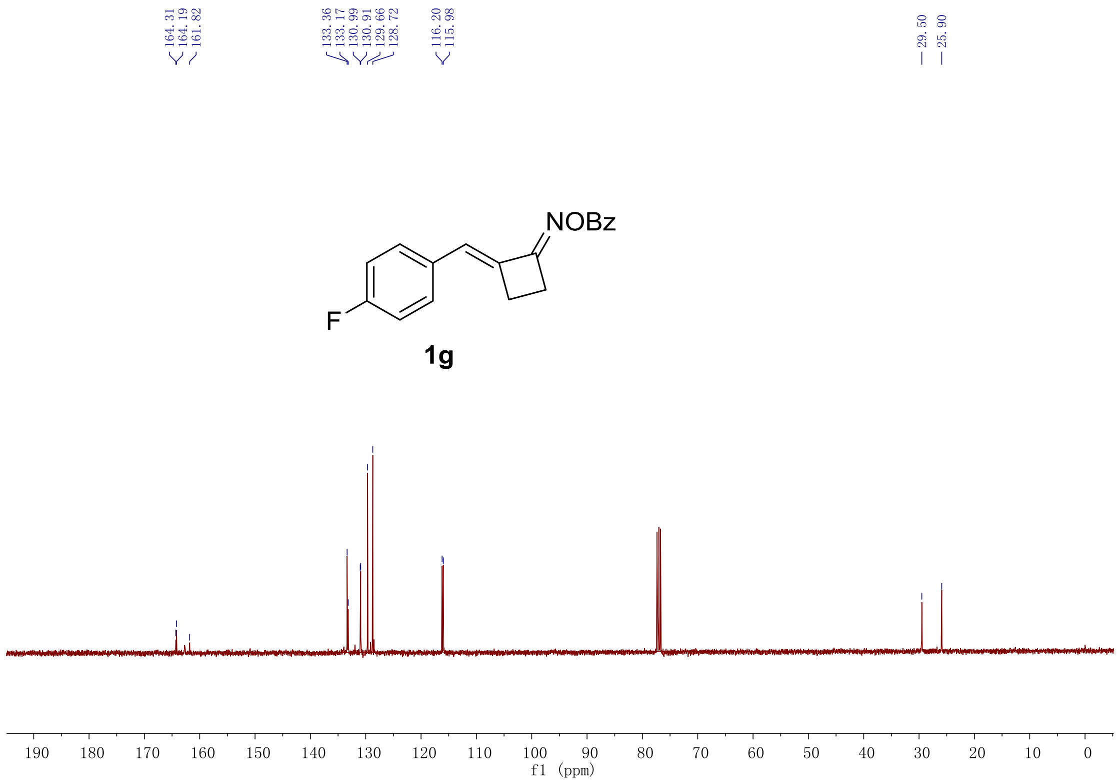
1f



166.38
163.98
140.19
133.95
133.27
132.19
129.67
129.34
129.05
128.51
126.77
126.14
30.37
26.93
15.30
NOBz
MeS
1f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



8.14 8.13 8.13 8.12 8.12 8.11 8.10 8.09 8.09 8.08 8.07 8.07 8.04 7.66 7.66 7.65 7.64 7.64 7.63 7.62 7.62 7.61 7.60 7.58 7.55 7.55 7.53 7.53 7.52 7.51 7.46 7.42 7.42 7.41 7.40 7.39 7.39 7.38 7.37 7.13 7.12 7.12 7.10 7.08 7.08 7.07
3.18 3.16 3.15 3.14 3.00 2.99 2.98 2.97 2.96 2.96
NOBz
F
1g
2.02
1.03
2.00
3.03
2.04
2.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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164.19
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133.36
133.17
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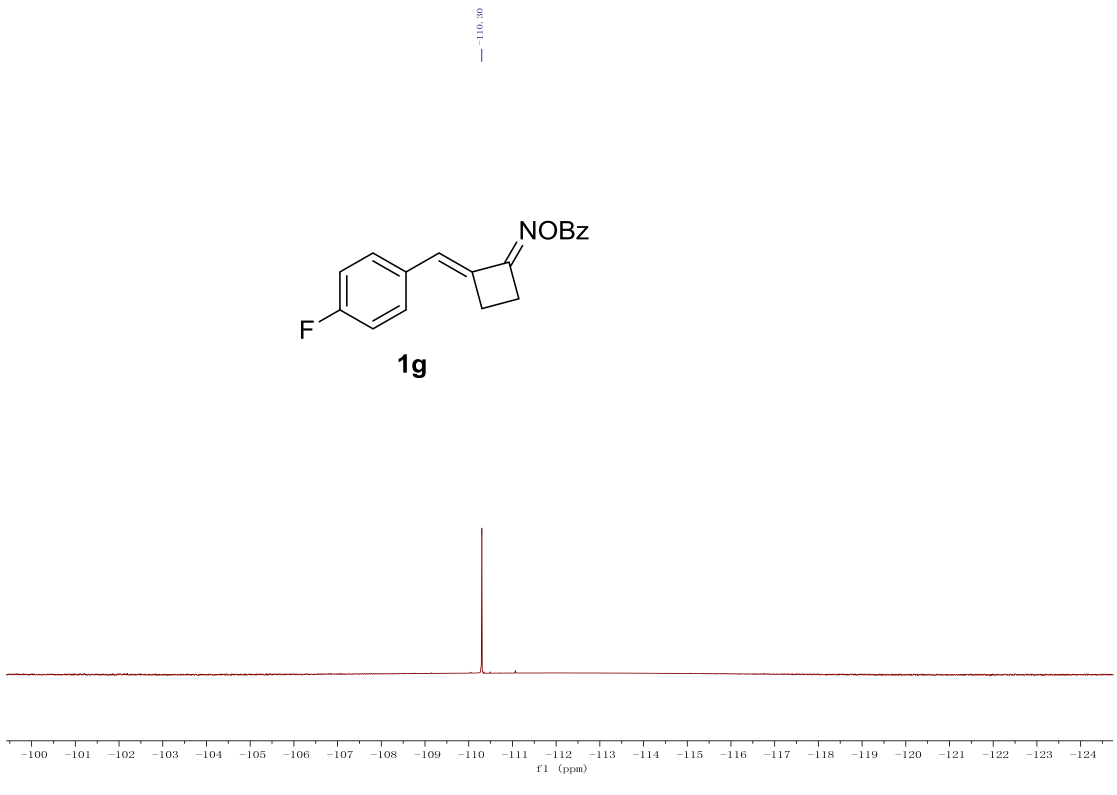
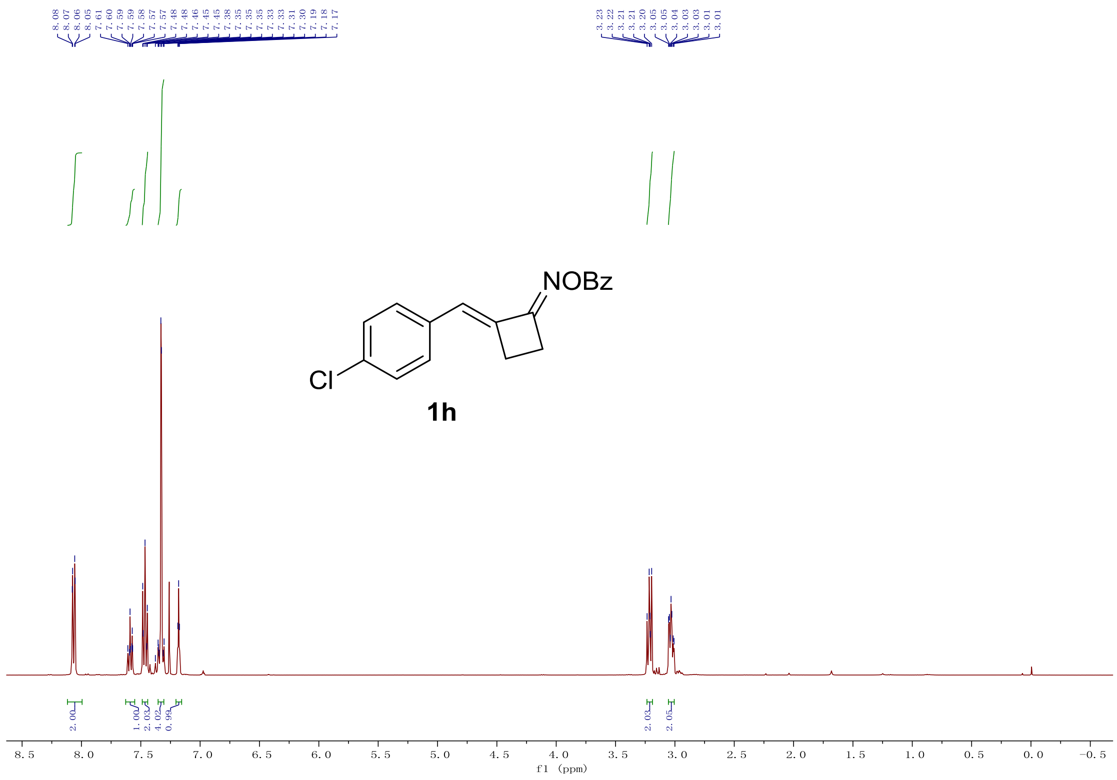
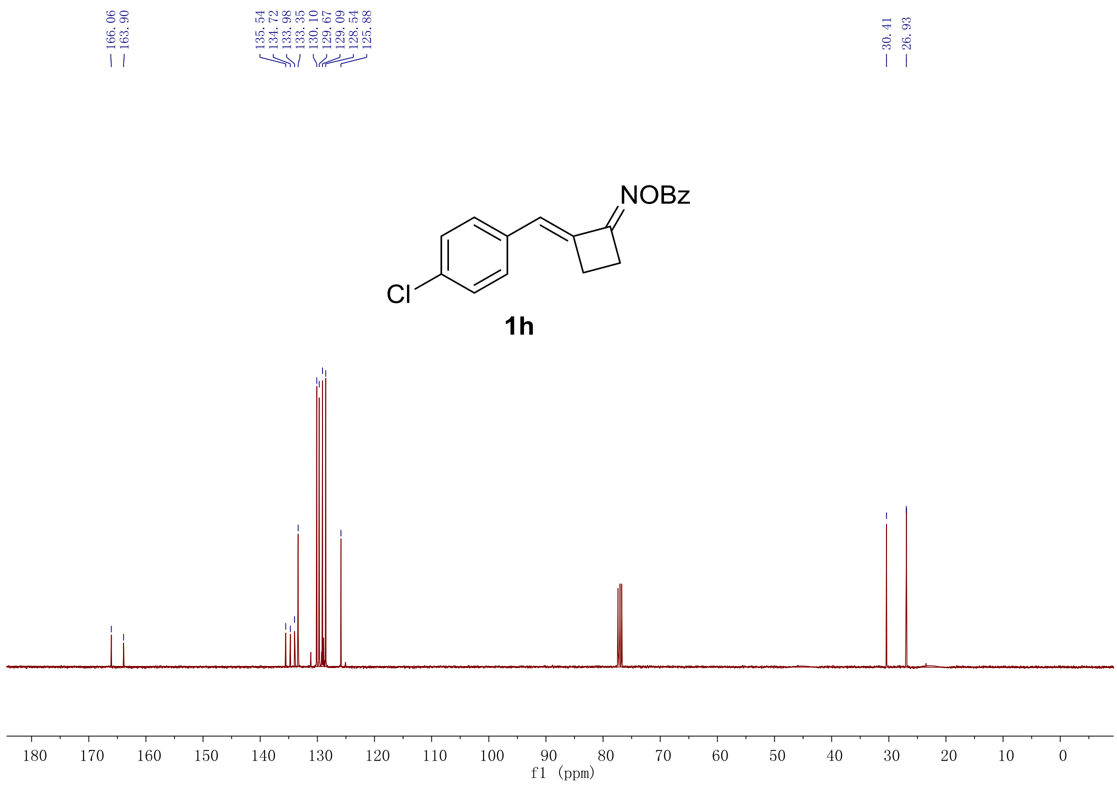
129.66
128.72
116.20
115.98
29.50
25.90
NOBz
F
1g
f1 (ppm)

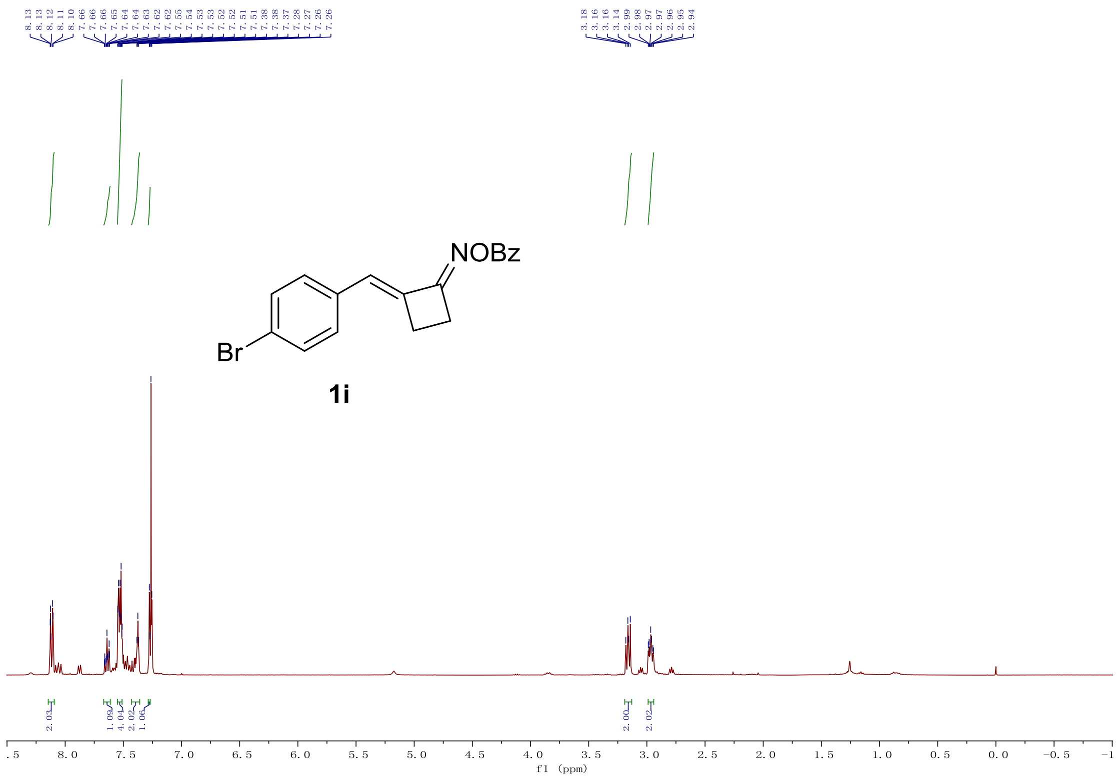

-110.30
NOBz
F
1g
f1 (ppm)

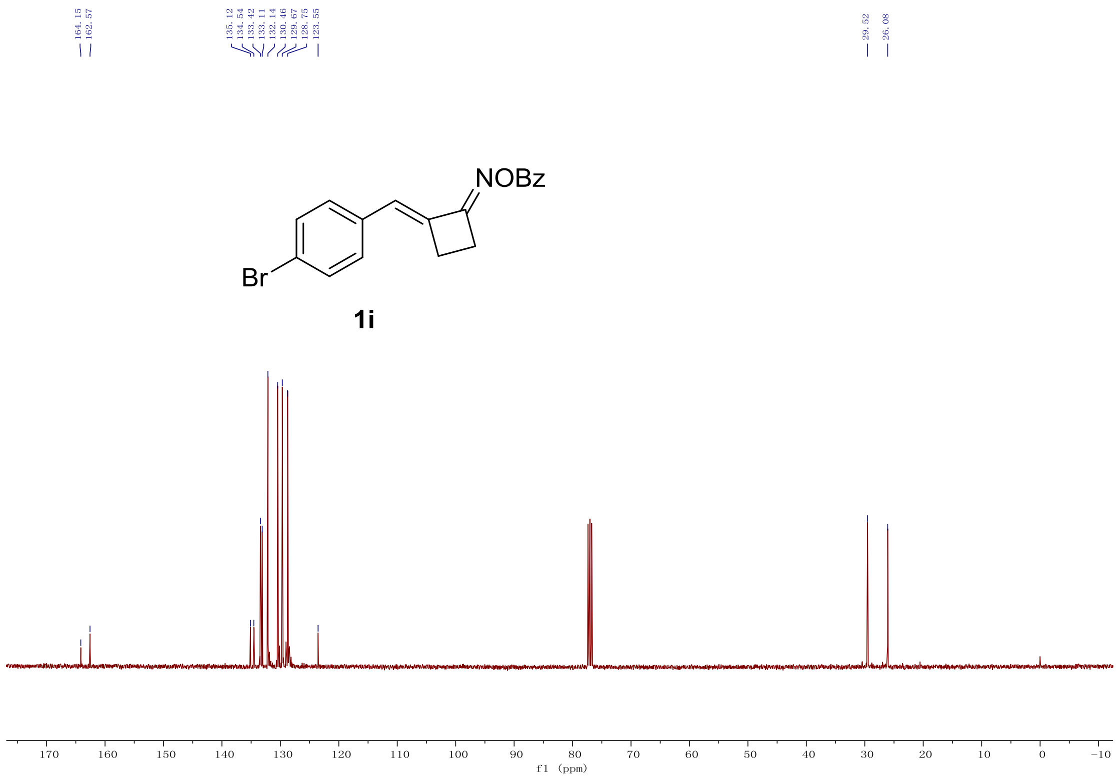


1h



1h


NOBz
Br
1i
f1 (ppm)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162.57
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134.54
133.42
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130.46
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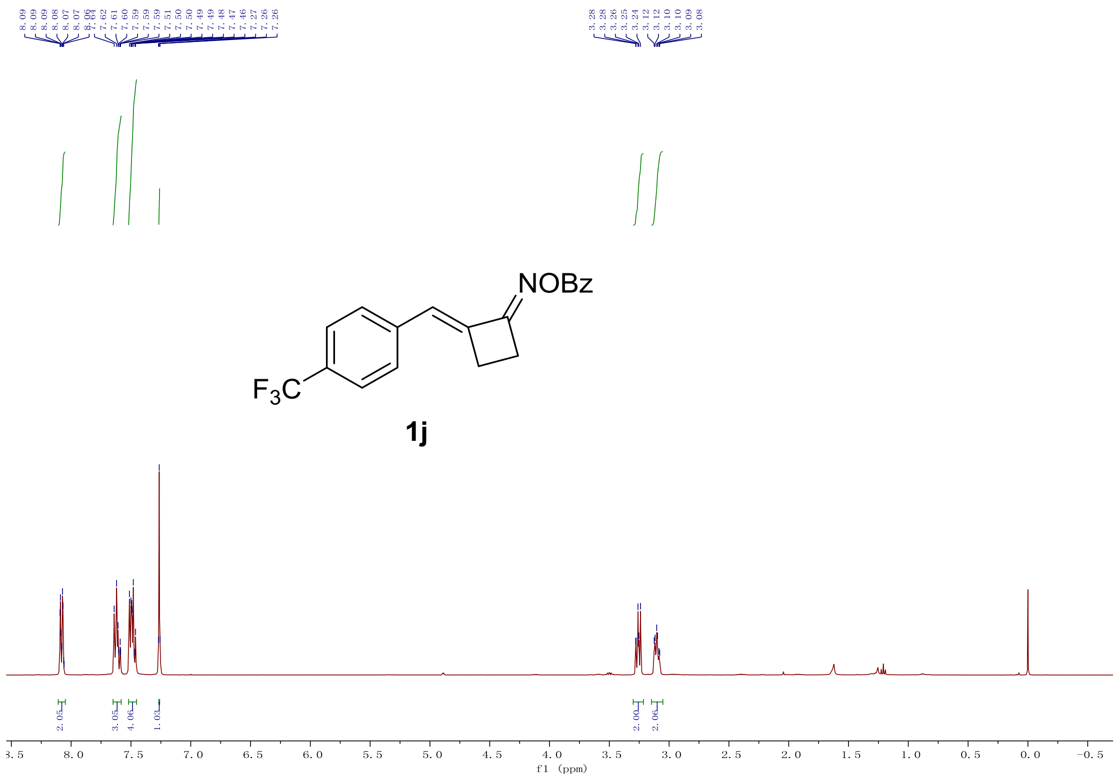
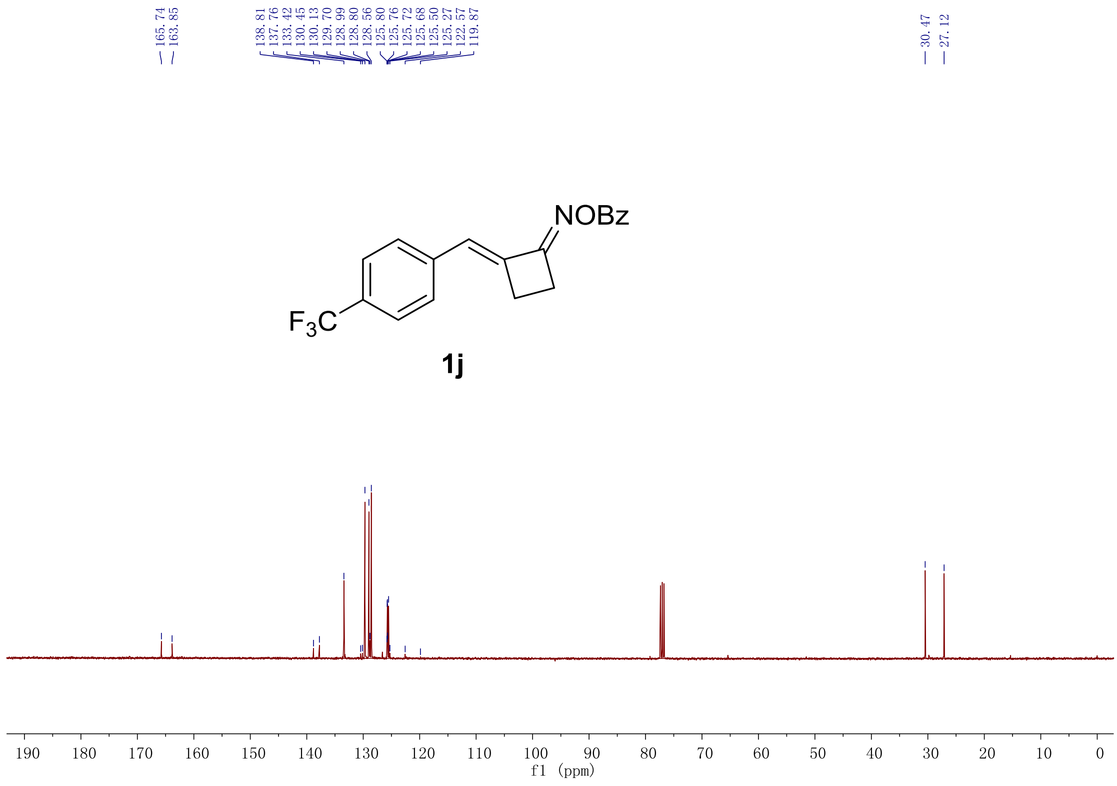
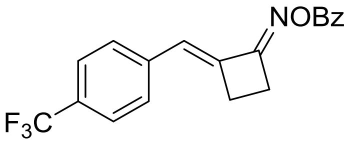
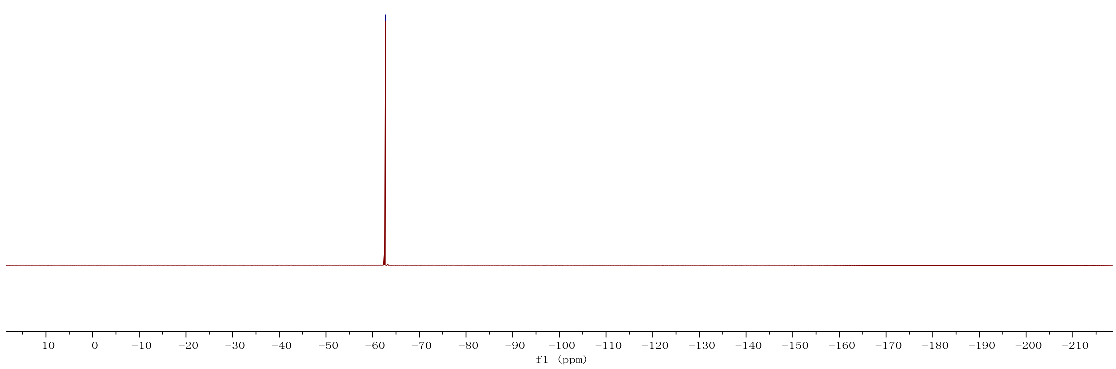
128.75
123.55
29.52
26.08
NOBz
Br
1i
f1 (ppm)

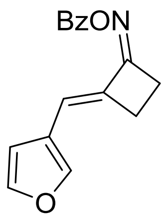

8.09 8.09 8.09 8.08 8.07 8.07 8.06 7.64 7.62 7.61 7.60 7.59 7.59 7.59 7.51 7.50 7.50 7.49 7.49 7.48 7.47 7.46 7.27 7.26 7.26
3.28 3.28 3.26 3.25 3.24 3.12 3.12 3.10 3.10 3.09 3.08
NOBz
F3C
1j
2.05 3.05 4.06 1.03 2.00 2.06
f1 (ppm)


165.74 163.85
138.81 137.76 133.42 130.45 130.13 129.70 128.99 128.80 128.56 125.80 125.76 125.72 125.68 125.50 125.27 122.57 119.87
30.47 27.12
NOBz
F3C
1j
f1 (ppm)

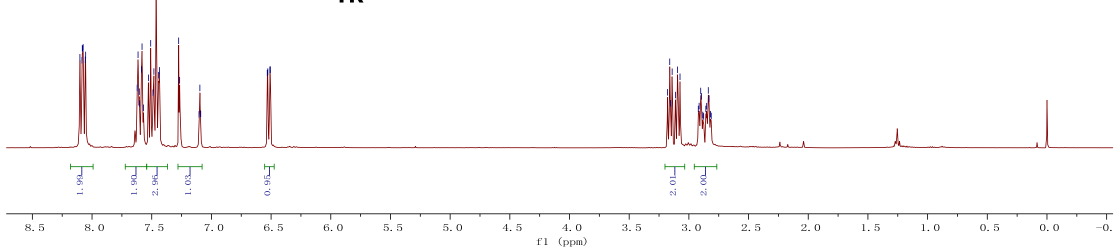


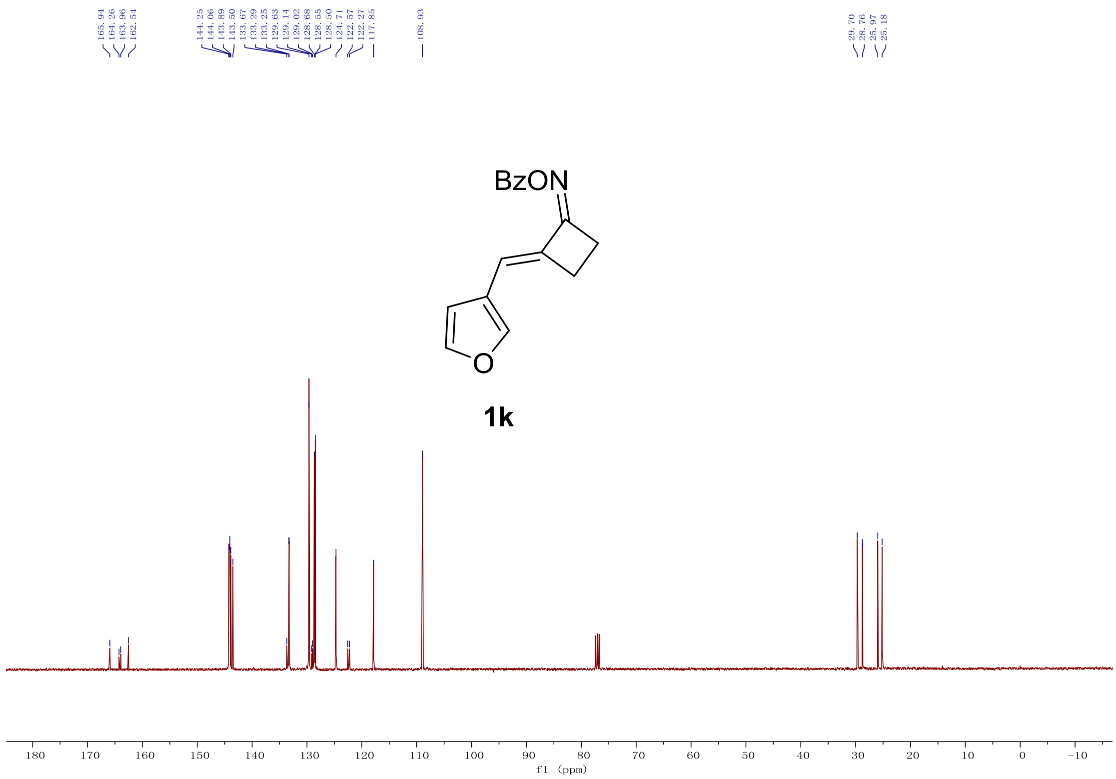
1j





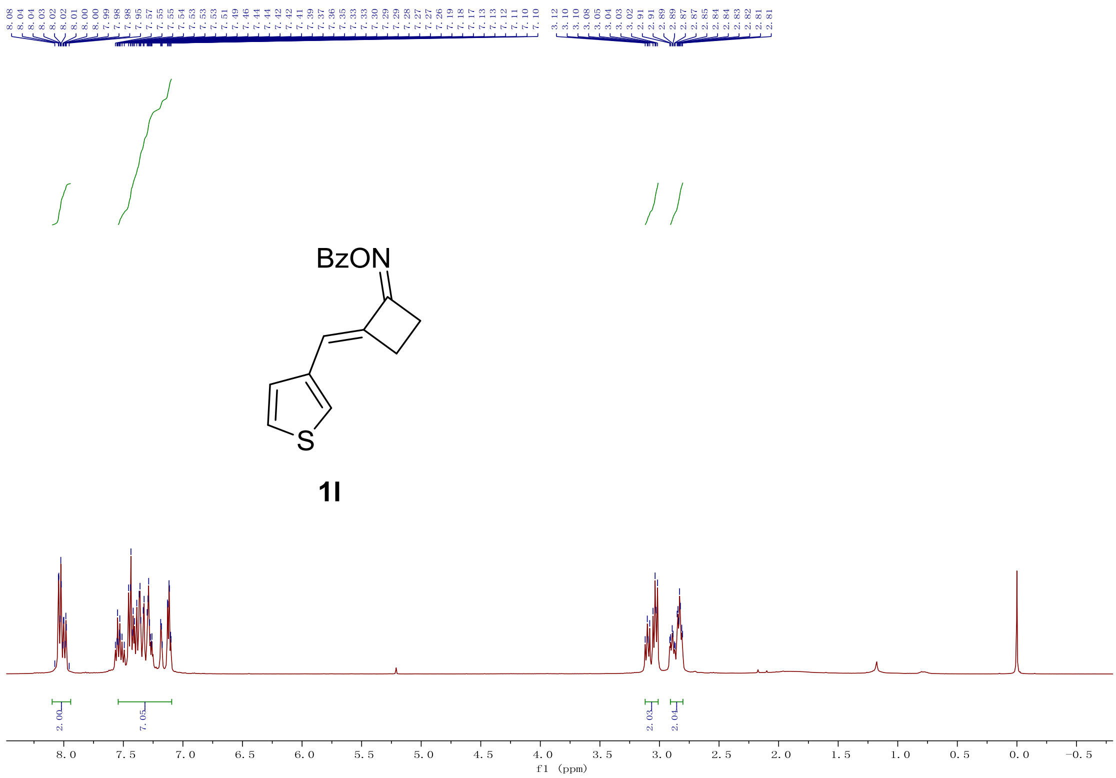
1k





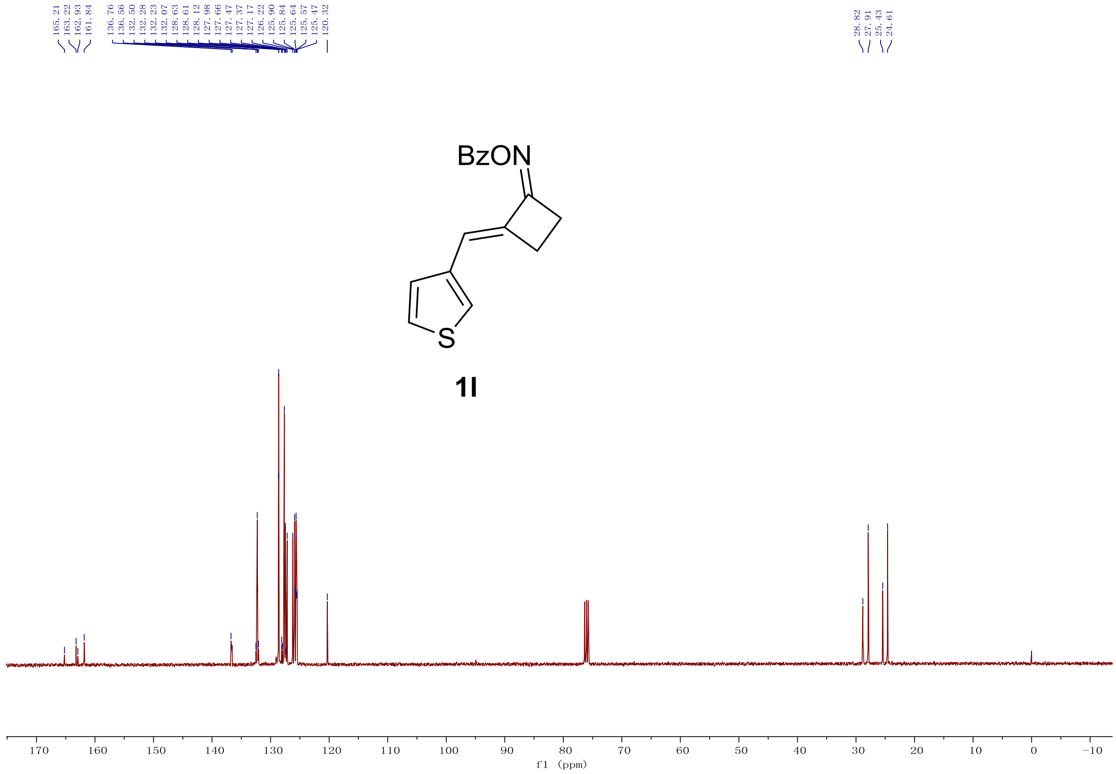
165.94
164.26
163.96
162.54
144.25
144.06
143.89
143.50
133.67
133.29
133.25
129.63
129.14
129.02
128.68
128.55
128.50
124.71
122.57
122.27
117.85
108.93
29.70
28.76
25.97
25.18
BzON
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1k



8.08 8.04 8.04 8.03 8.02 8.02 8.01 8.00 8.00 7.99 7.98 7.98 7.95 7.57 7.55 7.55 7.54 7.53 7.53 7.53 7.51 7.49 7.46 7.44 7.44 7.42 7.42 7.41 7.39 7.37 7.36 7.35 7.33 7.33 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.19 7.18 7.17 7.13 7.13 7.12 7.11 7.10 7.10
3.12 3.10 3.10 3.08 3.05 3.04 3.03 3.02 2.91 2.91 2.89 2.89 2.87 2.87 2.85 2.84 2.84 2.83 2.82 2.81 2.81
BzON
S
2.00
7.05
2.03
2.04
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

1l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162.93
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136.76
136.56
132.50
132.28
132.23
132.07
128.63
128.61
128.12
127.98
127.66
127.47
127.37
127.17
126.22
125.90
125.84
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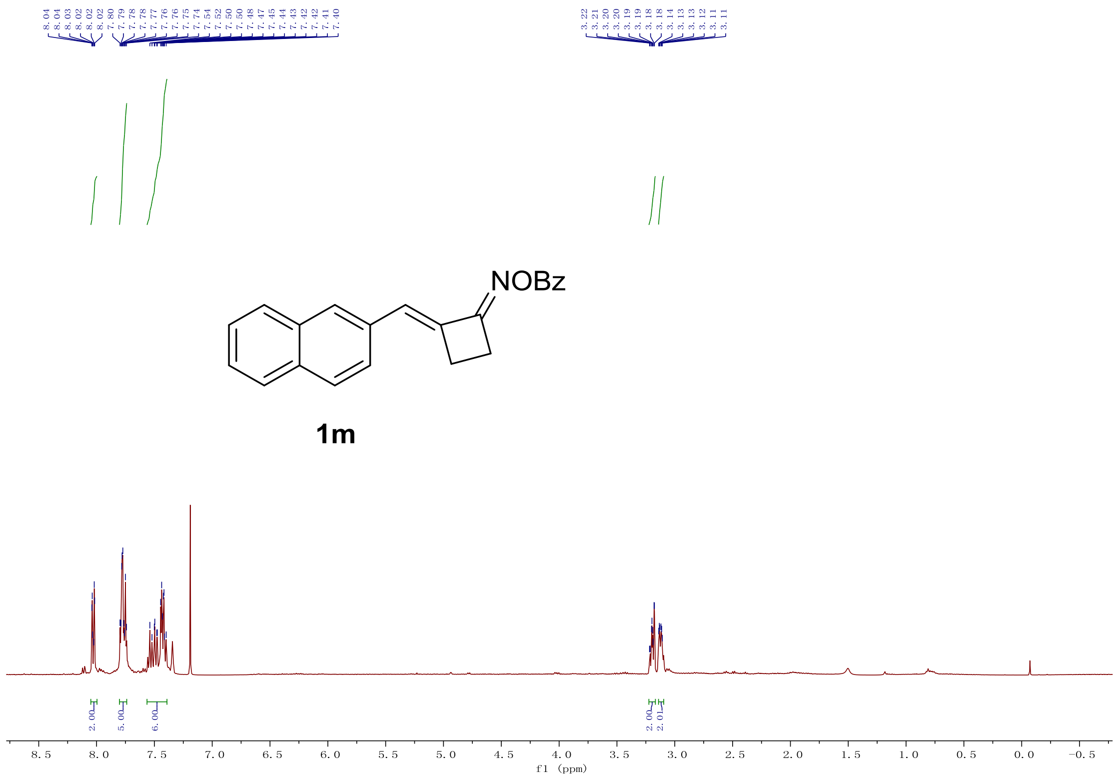
125.57
125.47
120.32
28.82
27.91
25.43
24.61
BzON
S
1l
f1 (ppm)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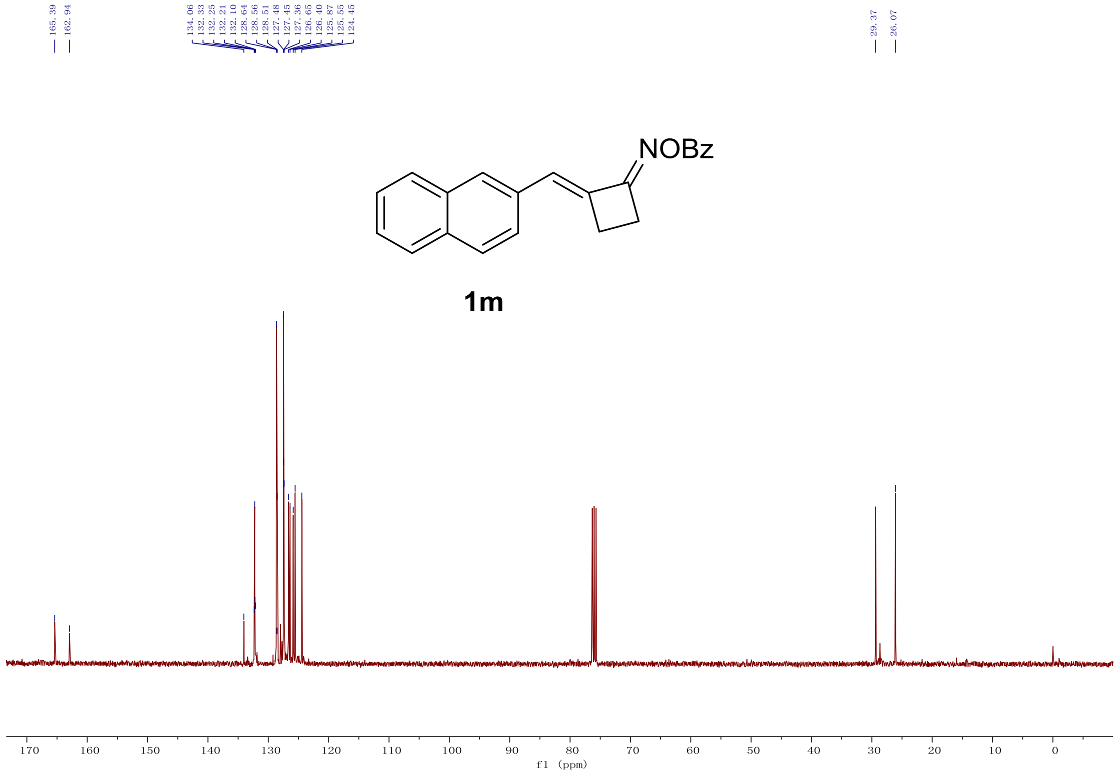
8.04
8.03
8.02
8.02
8.02
7.80
7.79
7.78
7.78
7.77
7.76
7.76
7.75
7.74
7.54
7.52
7.50
7.50
7.48
7.47
7.45
7.44
7.43
7.42
7.41
7.40
3.22
3.21
3.20
3.19
3.19
3.18
3.18
3.14
3.13
3.13
3.12
3.11
3.11
NOBz
1m
2.00
5.00
6.00
2.00
2.01
f1 (ppm)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128.51
127.48
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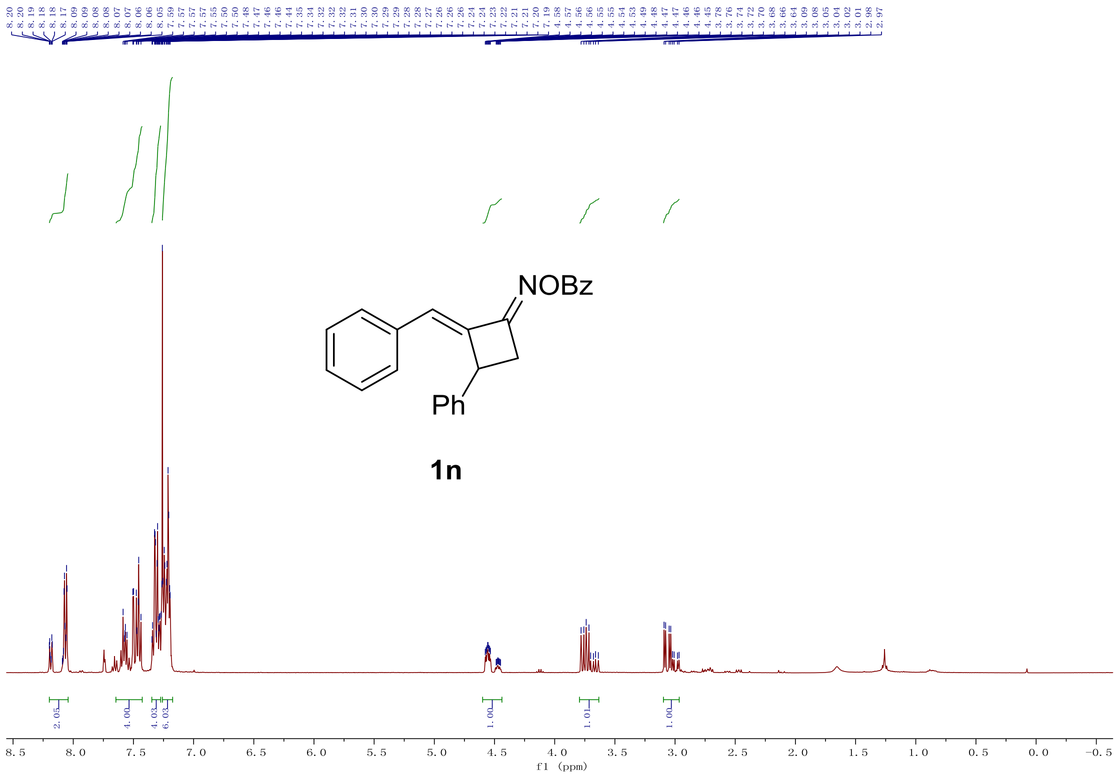
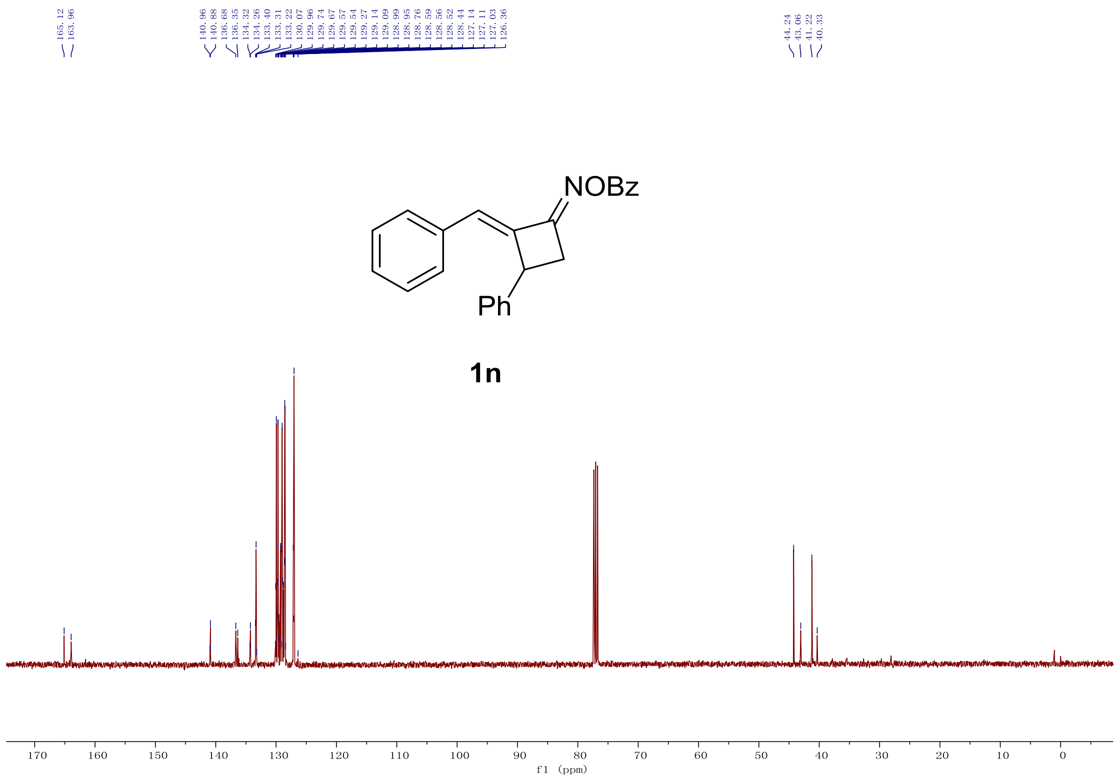
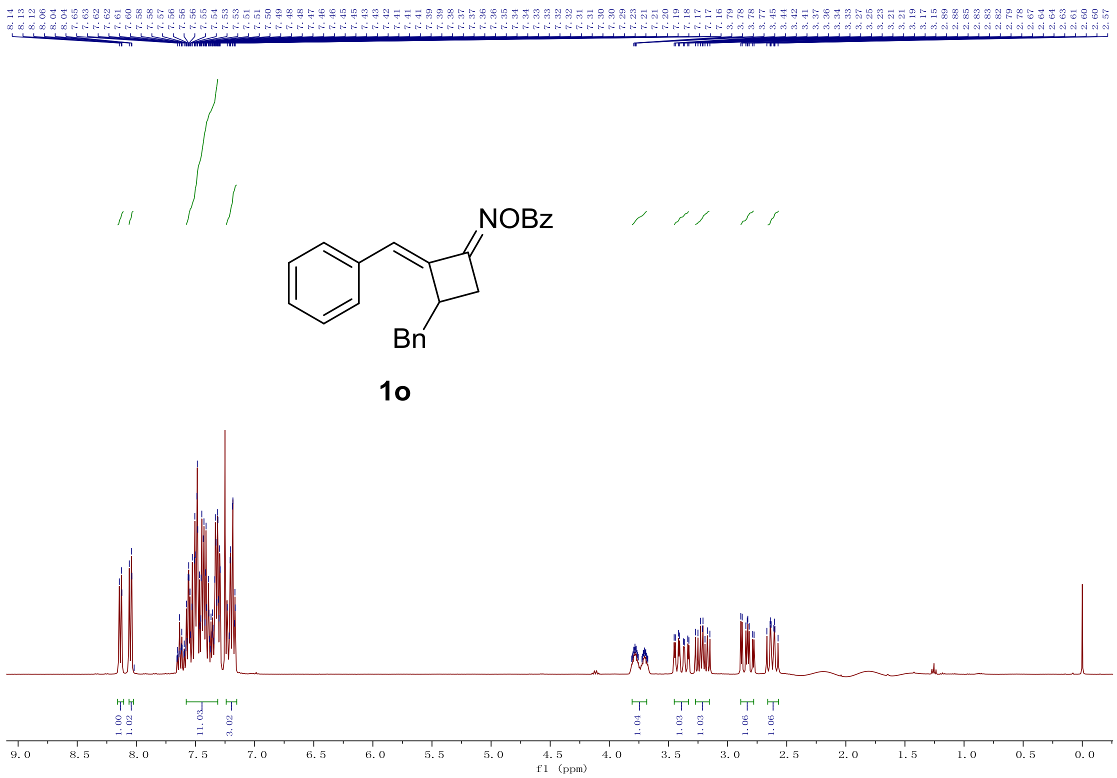
126.40
125.87
125.55
124.45
29.37
26.07
NOBz
1m
f1 (ppm)

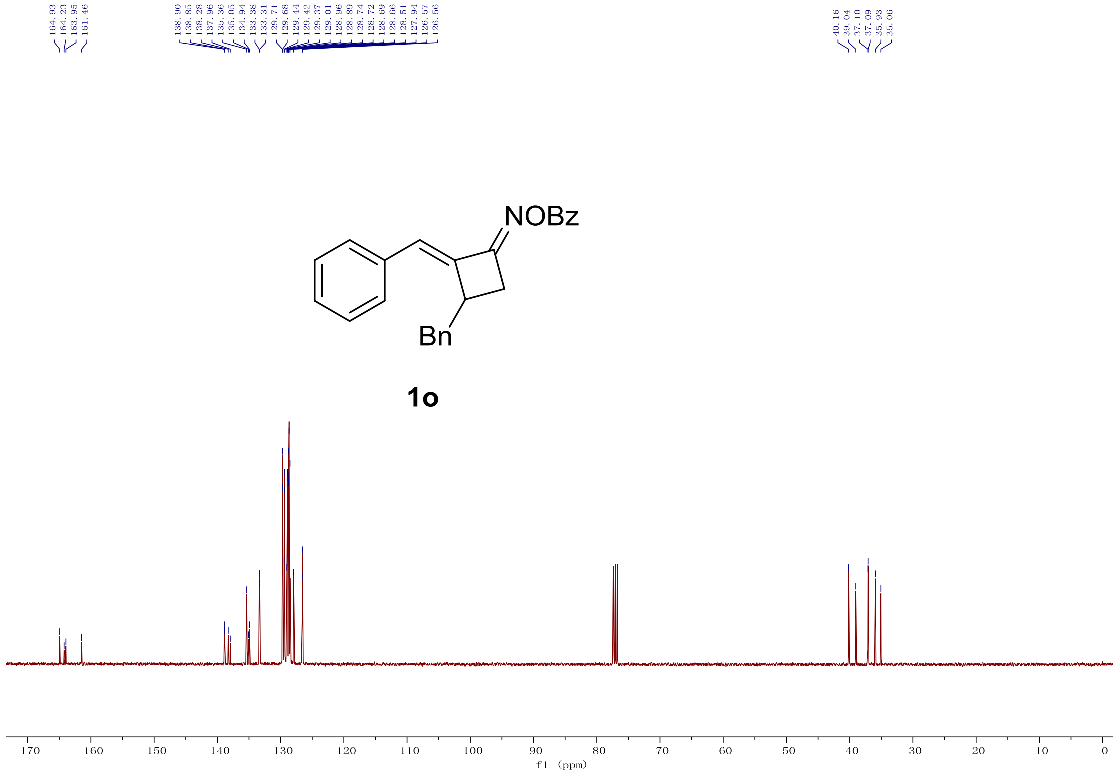

NOBz
Ph
1n
f1 (ppm)



1n



1o



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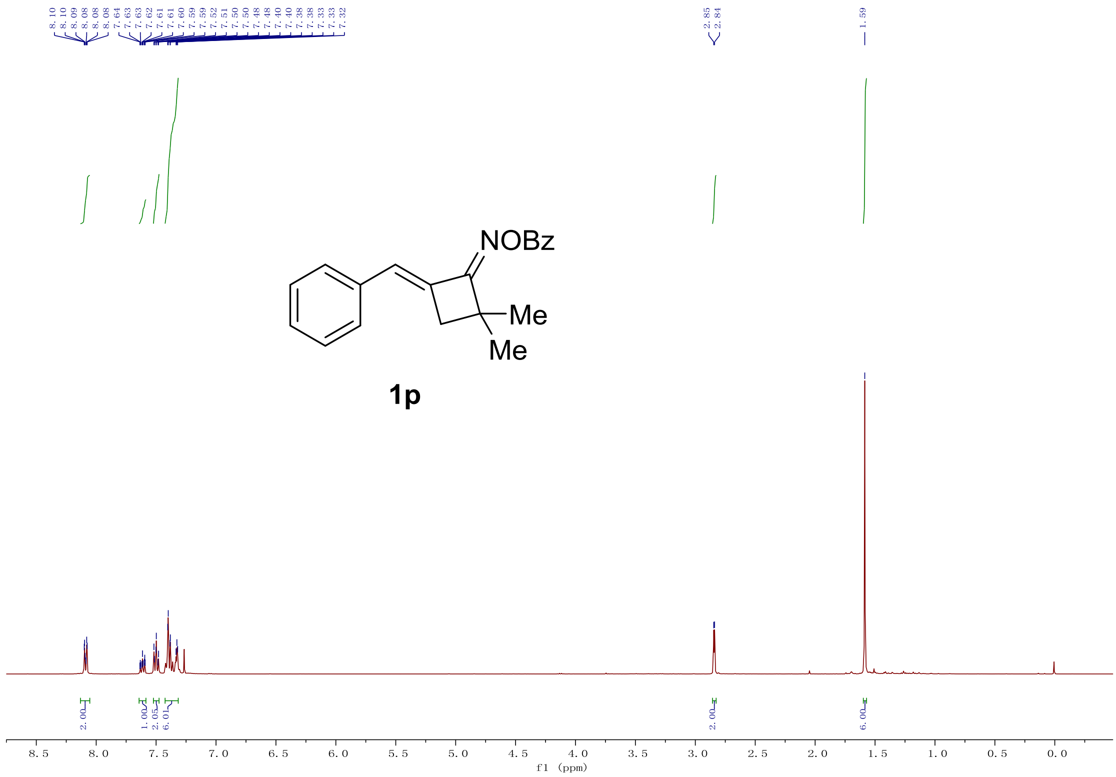
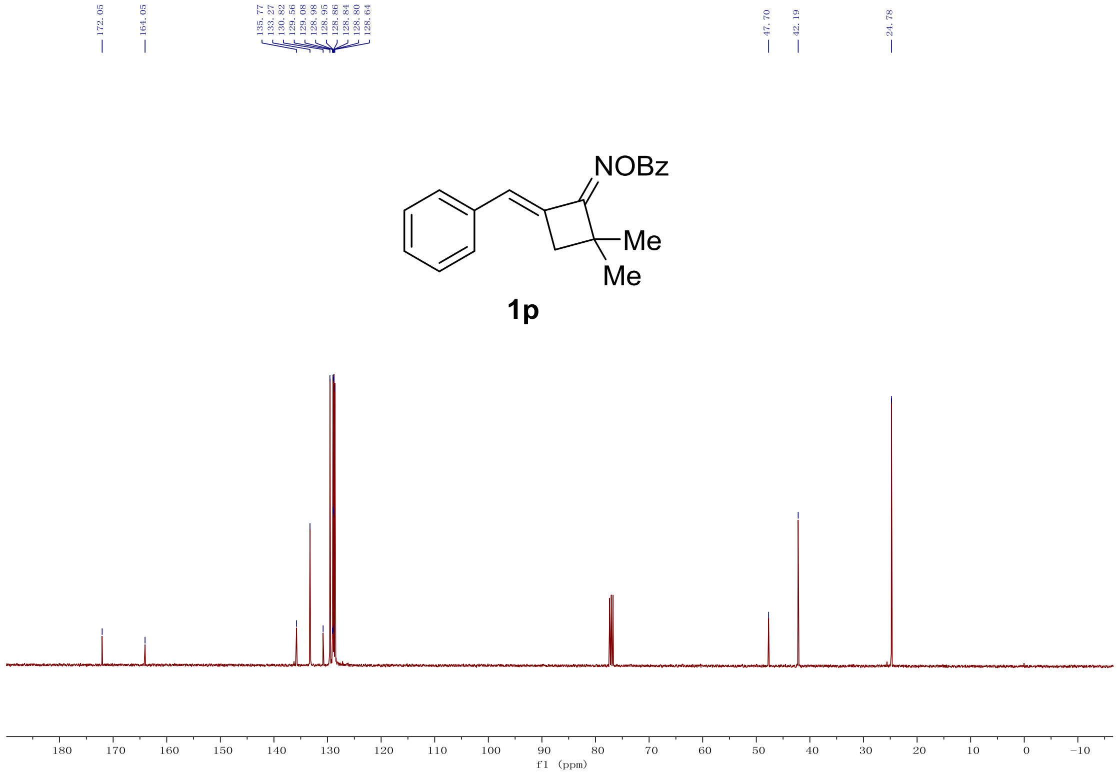


1p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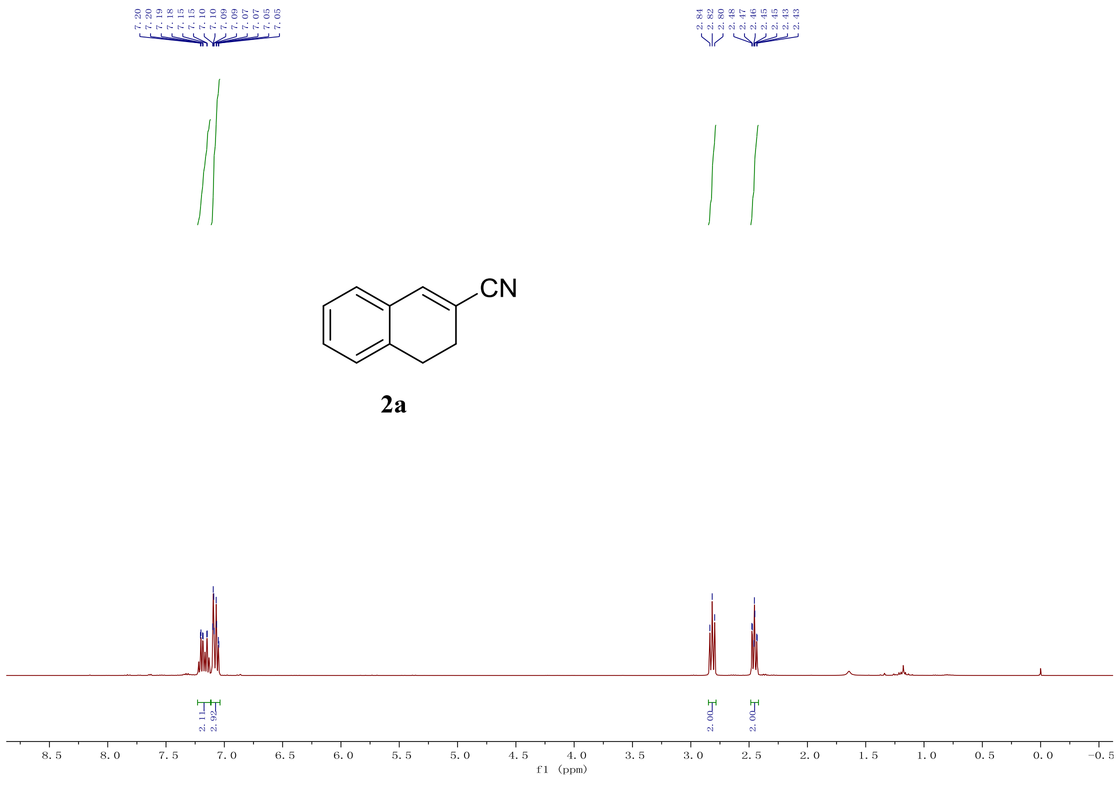
133.27
130.82
129.56
129.08
128.98
128.95
128.86
128.84
128.80
128.64
47.70
42.19
24.78
NOBz
Me
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

1p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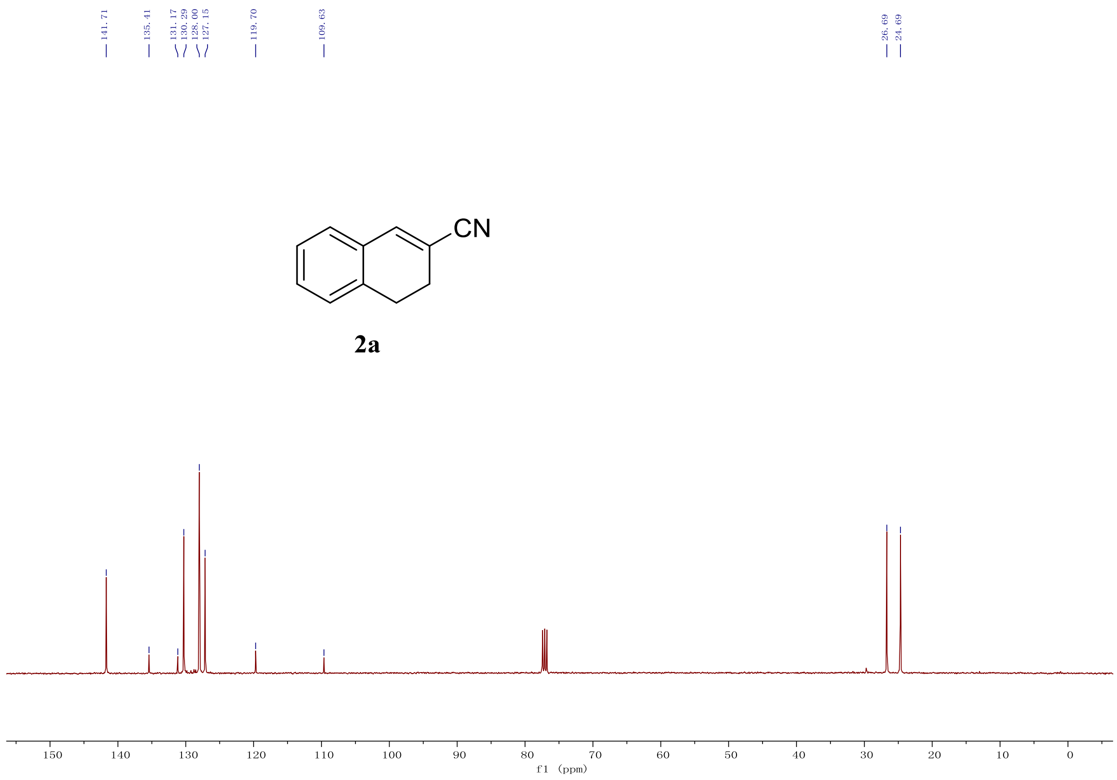
7.15
7.10
7.10
7.09
7.09
7.07
7.07
7.05
7.05
2.84
2.82
2.80
2.48
2.47
2.46
2.45
2.45
2.43
2.43
CN
2.11
2.92
2.00
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

2a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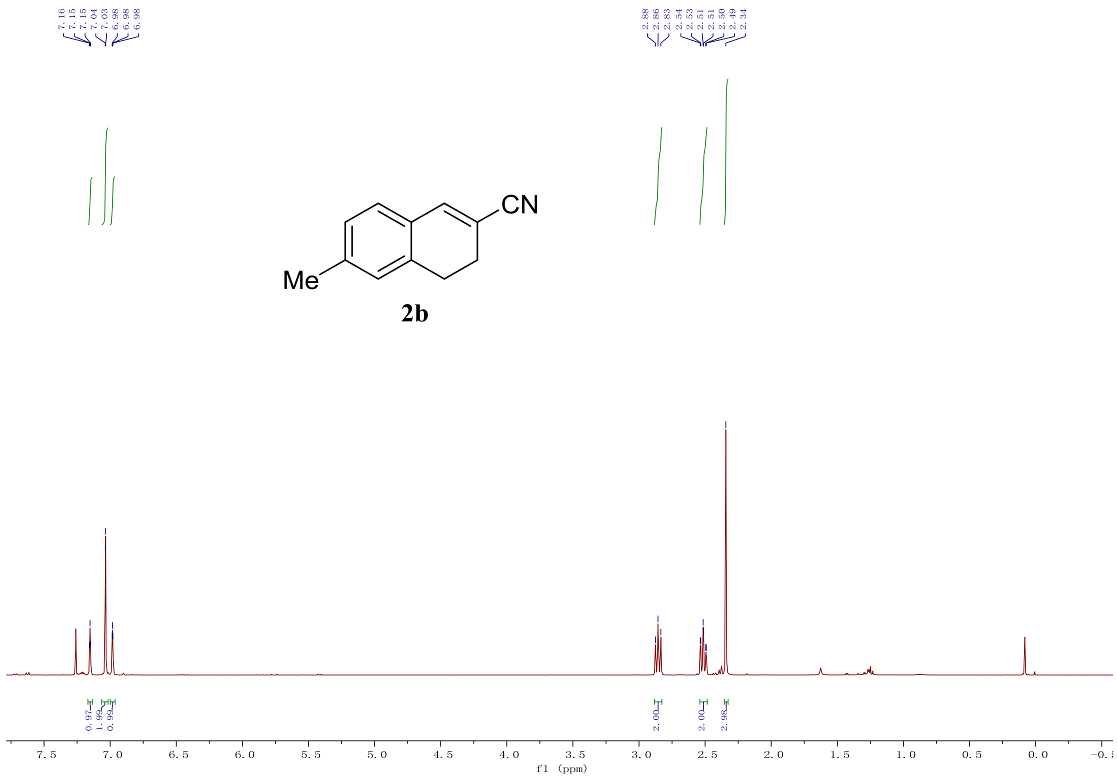
26.69
24.69
CN
f1 (ppm)

2a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7.15
7.04
7.03
6.98
6.98
6.98
2.88
2.86
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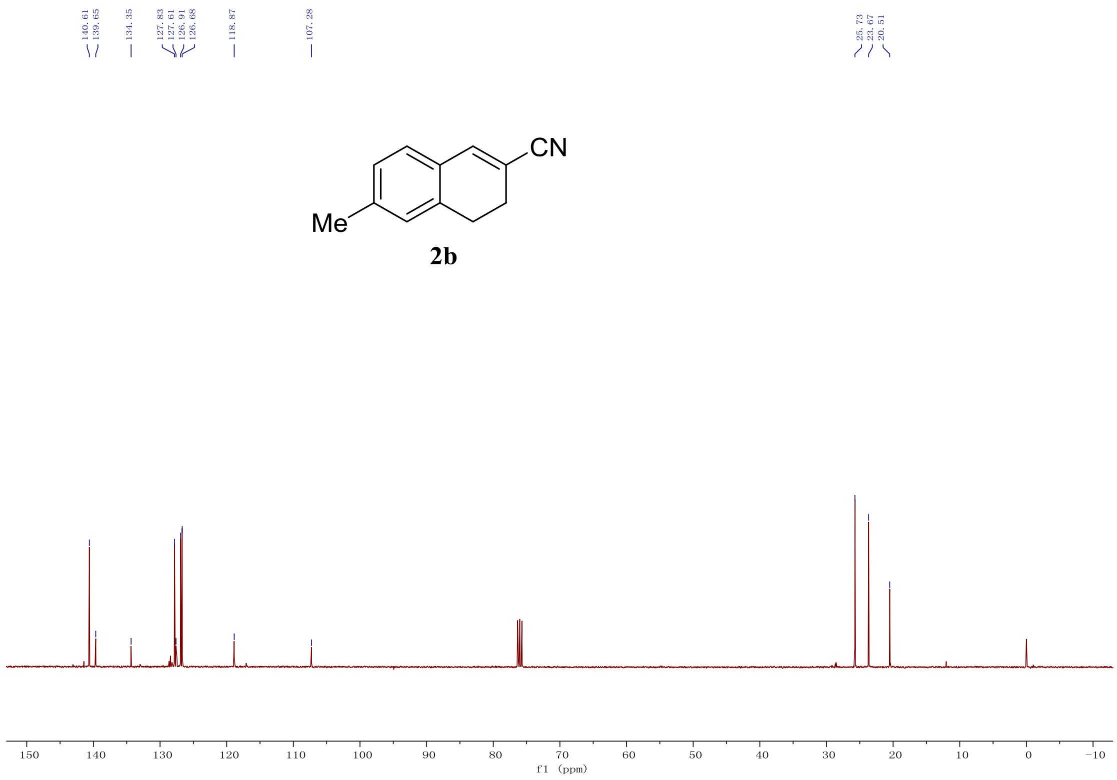
2.54
2.53
2.51
2.51
2.50
2.49
2.34
CN
Me
f1 (ppm)

2b


140.61
139.65
134.35
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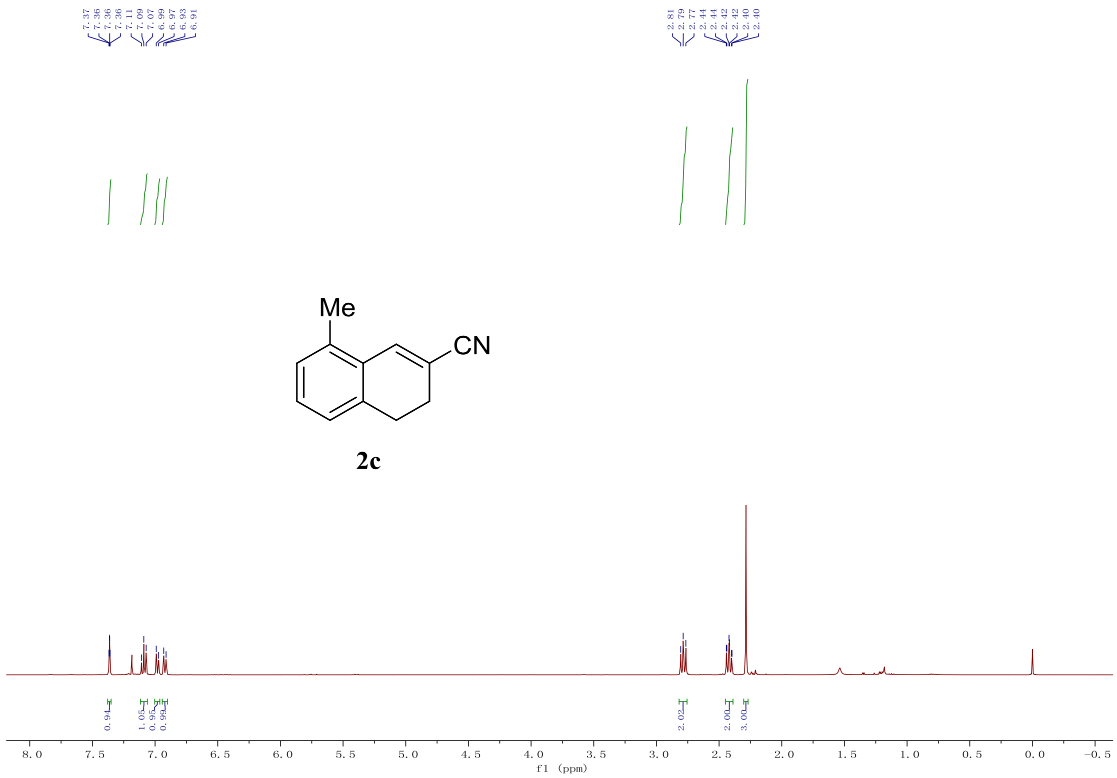
127.61
126.91
126.68
118.87
107.28
25.73
23.67
20.51
CN
Me
2b
f1 (ppm)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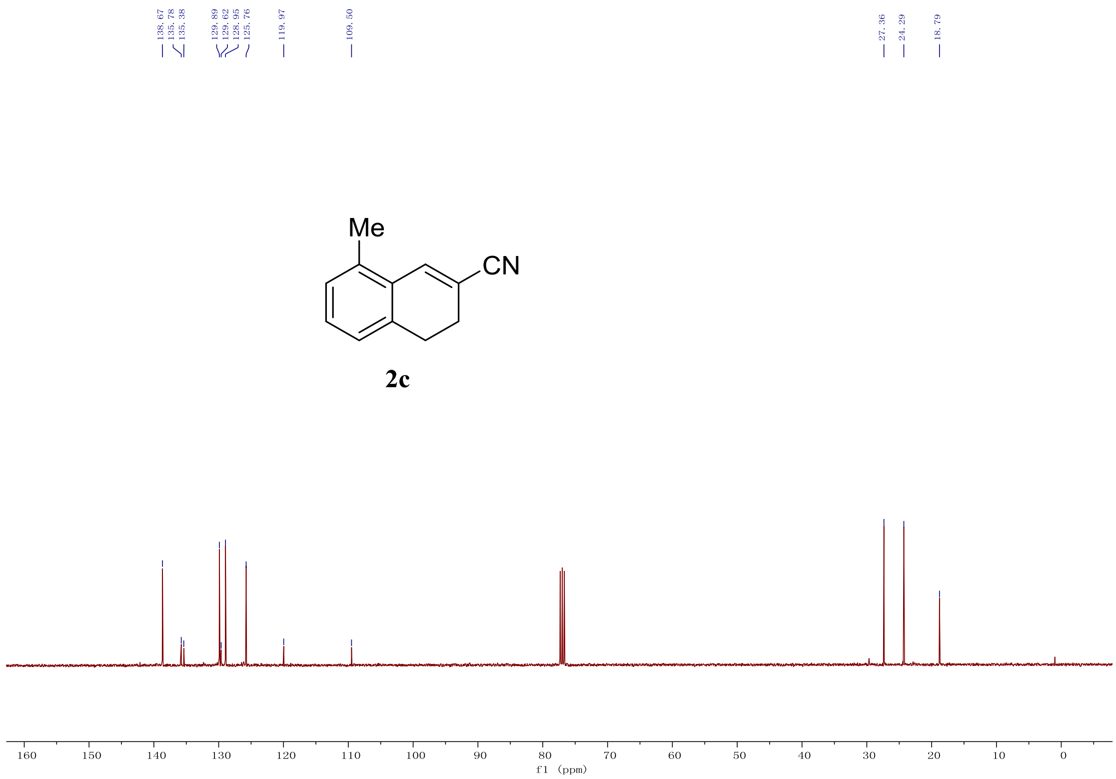
7.36
7.36
7.36
7.11
7.09
7.07
6.99
6.97
6.93
6.91
2.81
2.79
2.77
2.44
2.42
2.42
2.42
2.40
Me
CN
2c
0.94
1.05
0.95
0.94
2.02
2.00
3.00
f1 (ppm)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125.76
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109.50
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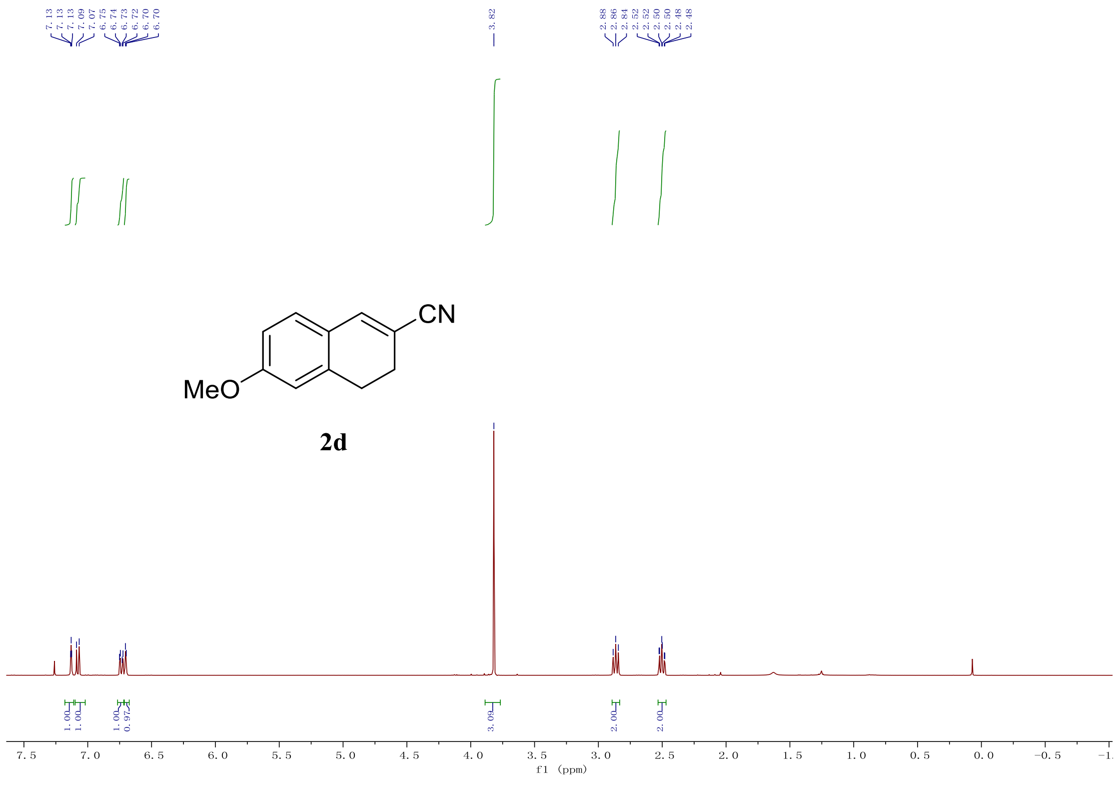
24.29
18.79
Me
CN
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2c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7.13
7.13
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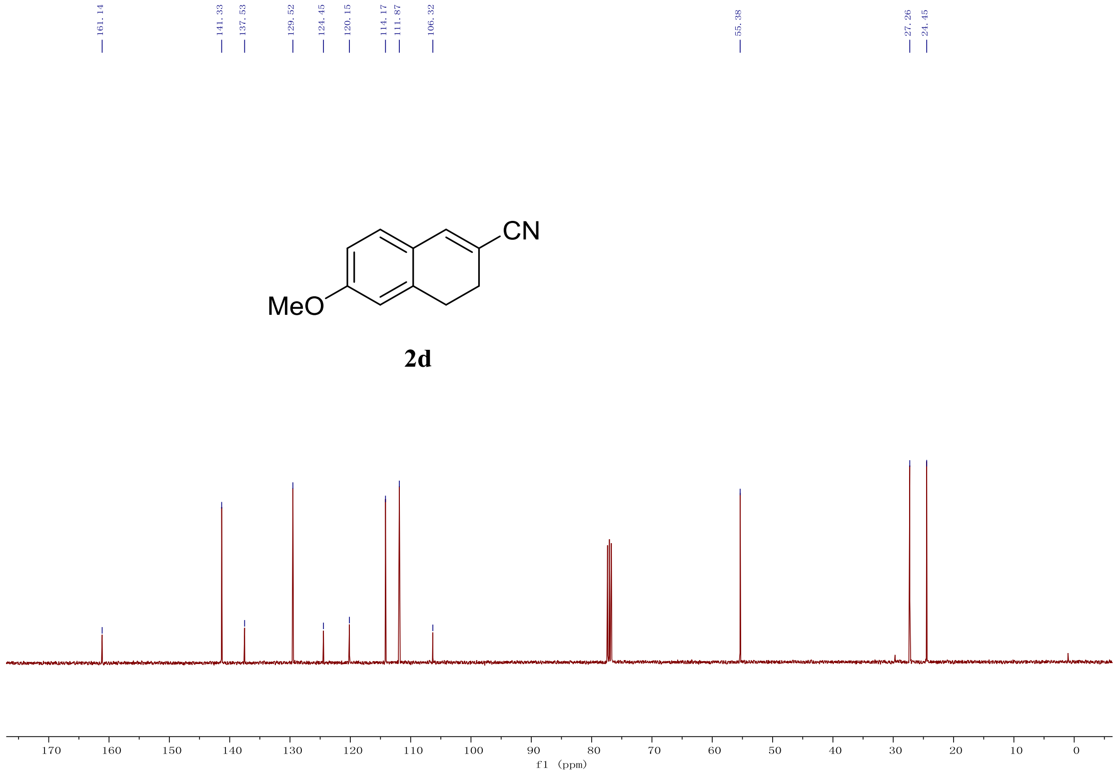
7.07
6.75
6.74
6.73
6.72
6.70
6.70
3.82
2.88
2.86
2.84
2.52
2.52
2.50
2.50
2.48
2.48
CN
MeO
1.00
1.00
1.00
0.97
3.09
2.00
2.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

2d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129.52
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120.15
114.17
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55.38
27.26
24.45
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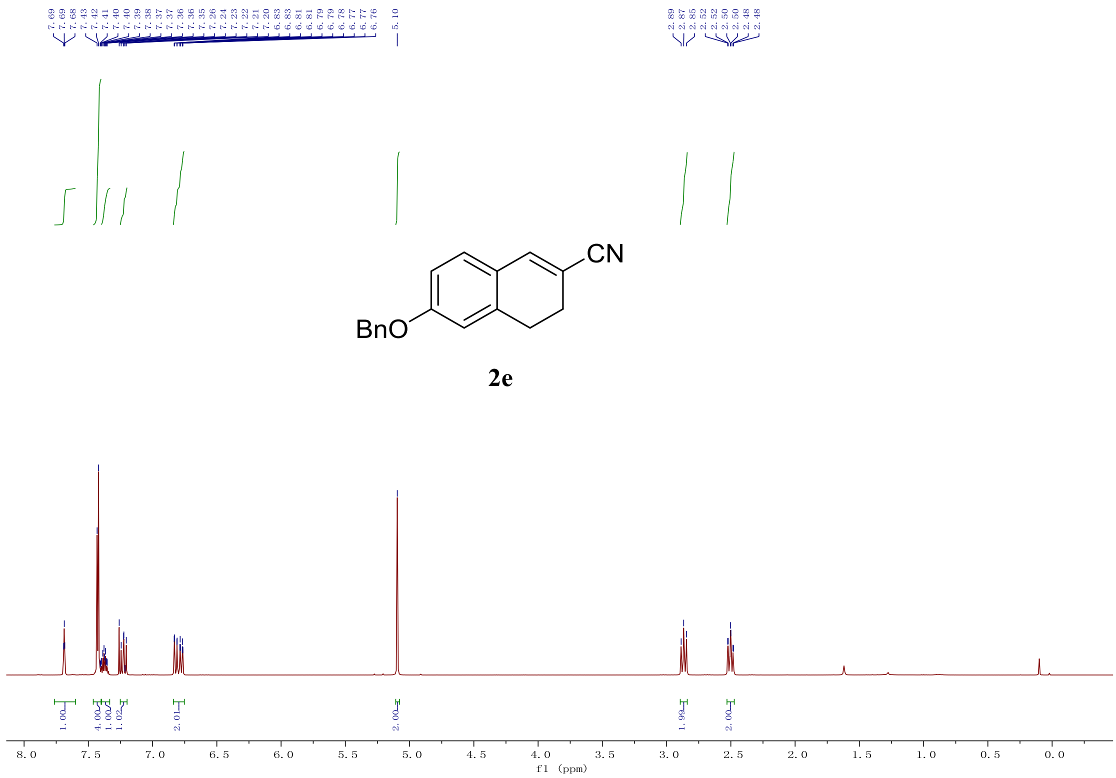
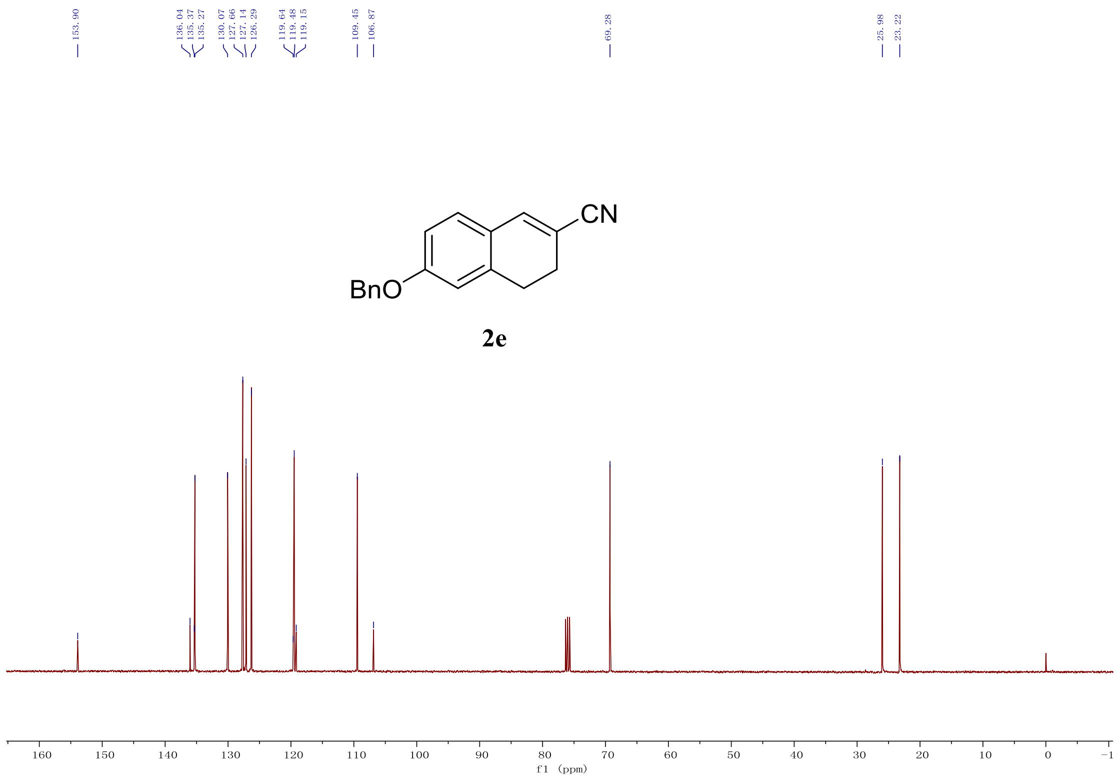
f1 (ppm)
CN
MeO

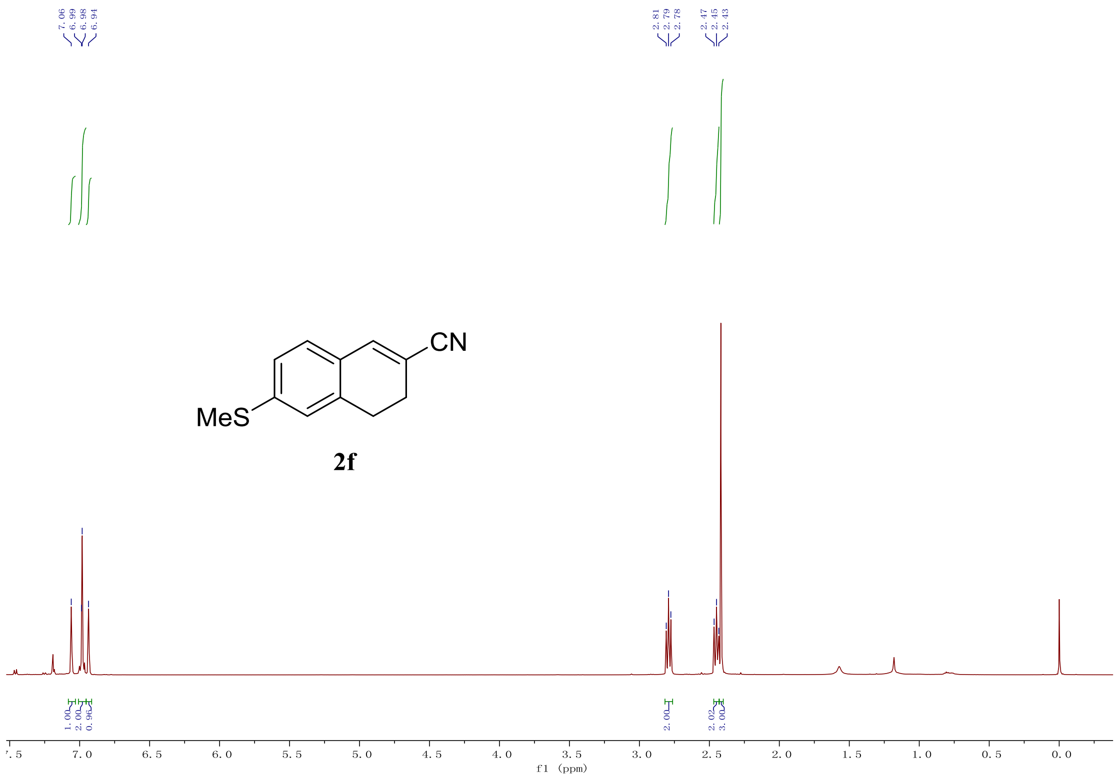
2d


7.69 7.69 7.68 7.43 7.42 7.41 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.26 7.24 7.23 7.22 7.21 7.20 6.83 6.81 6.81 6.79 6.79 6.78 6.77 6.77 6.76
5.10
2.89 2.87 2.85 2.52 2.52 2.50 2.50 2.48 2.48
1.00 4.00 1.00 1.02 2.01 2.00 1.99 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 0.0
f1 (ppm)
CN
BnO

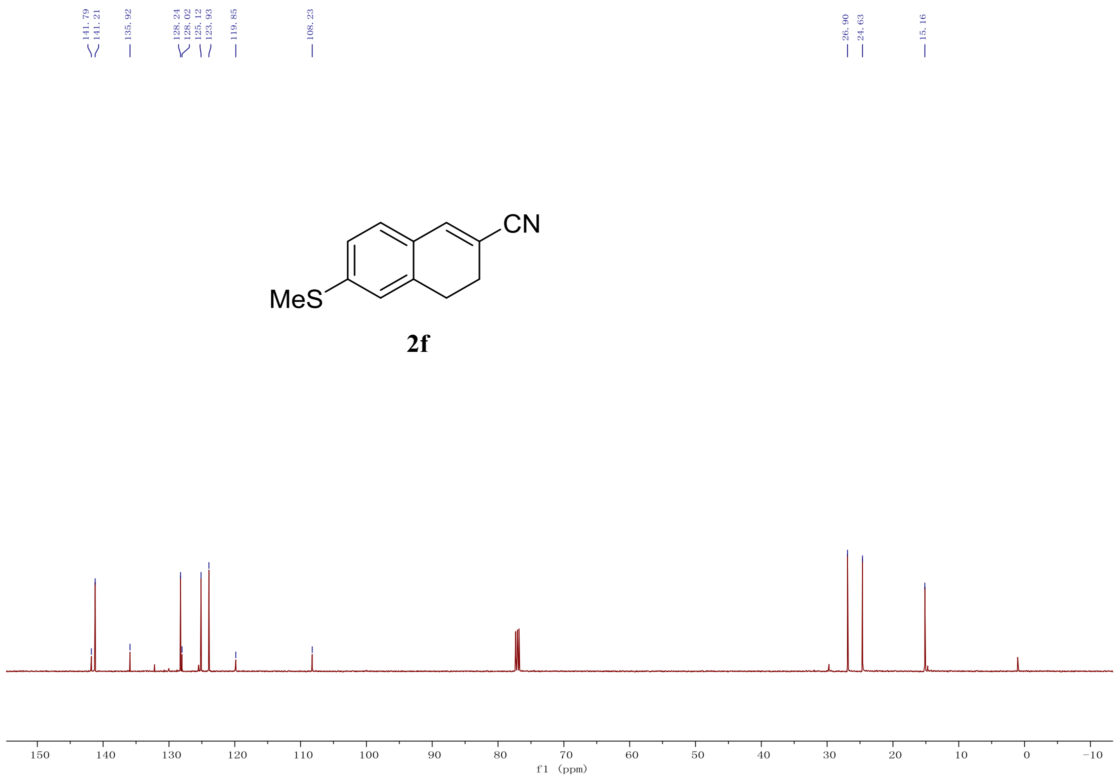
2e



2e



2f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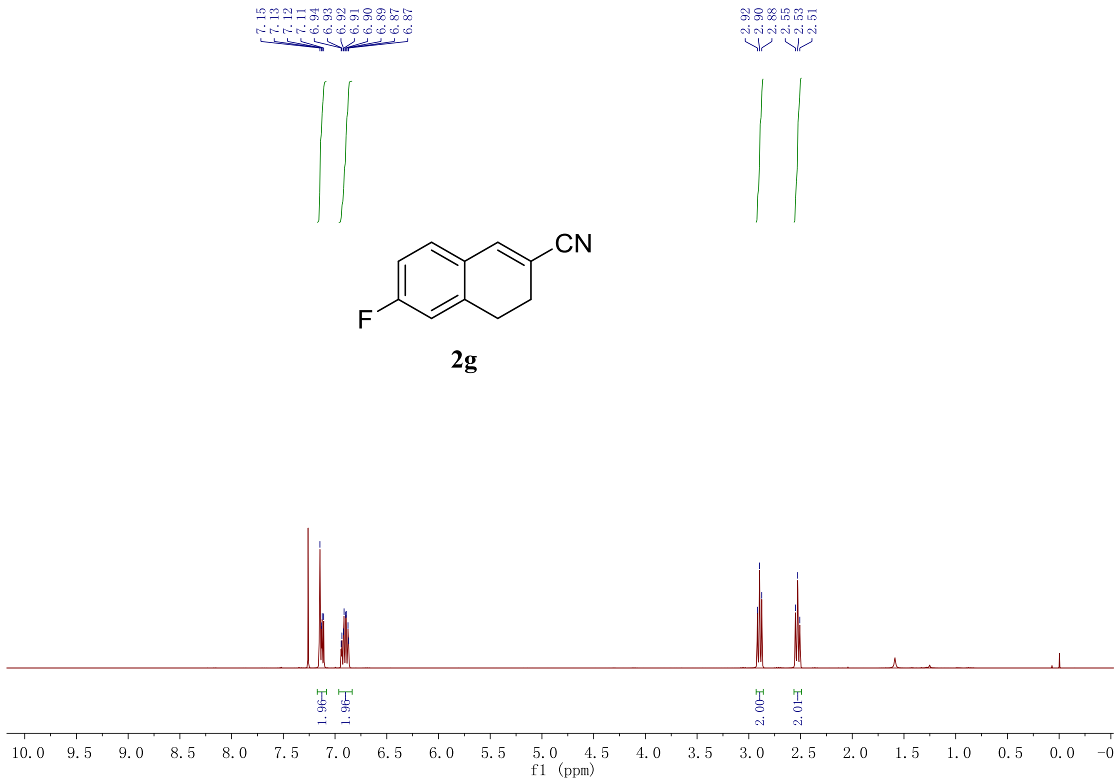
128.24
128.02
125.12
123.93
119.85
108.23
26.90
24.63
15.16
CN
MeS
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

2f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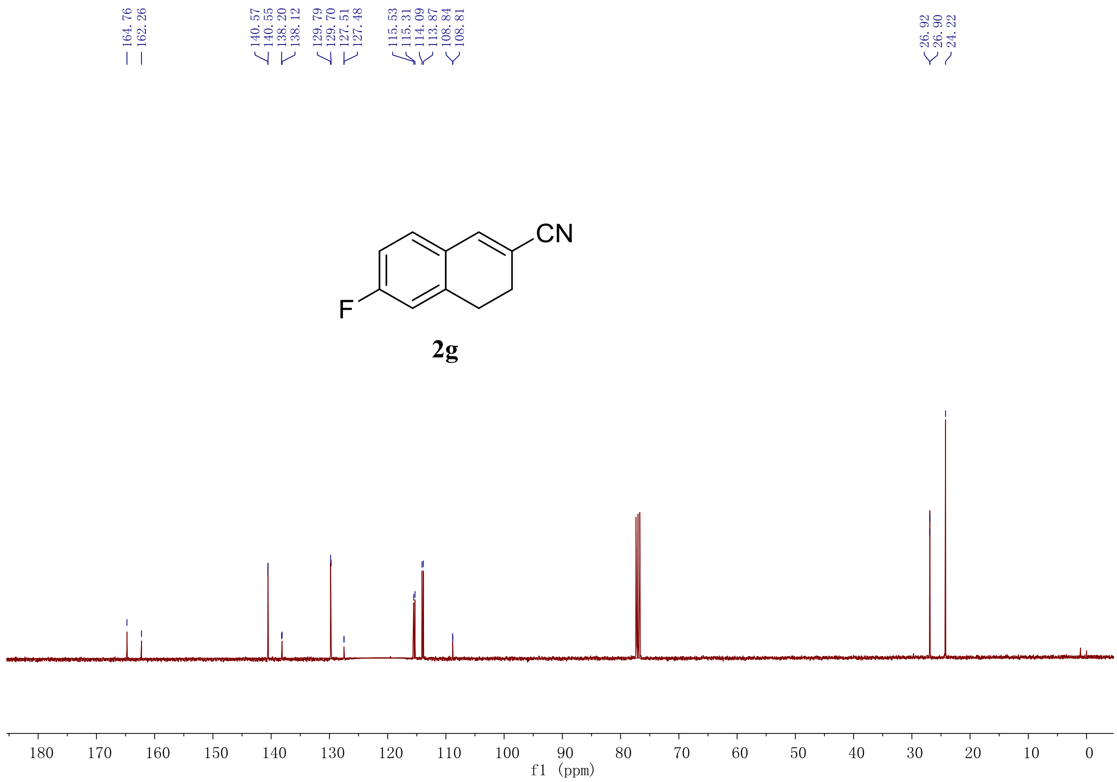
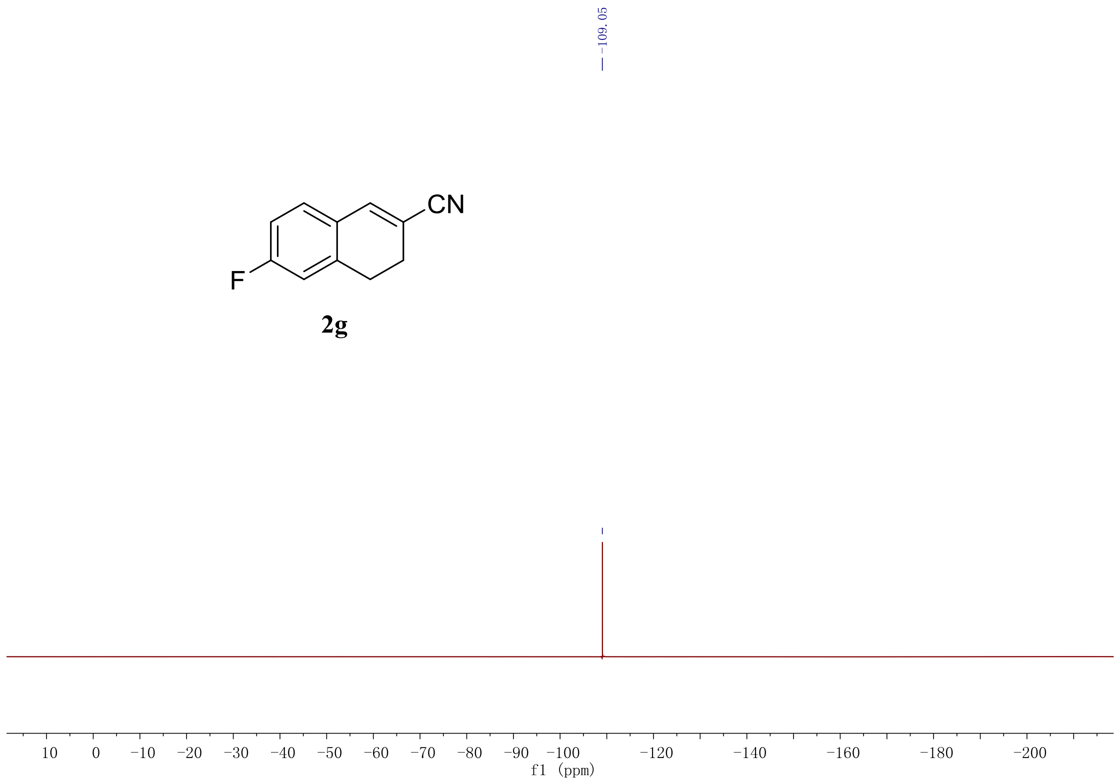
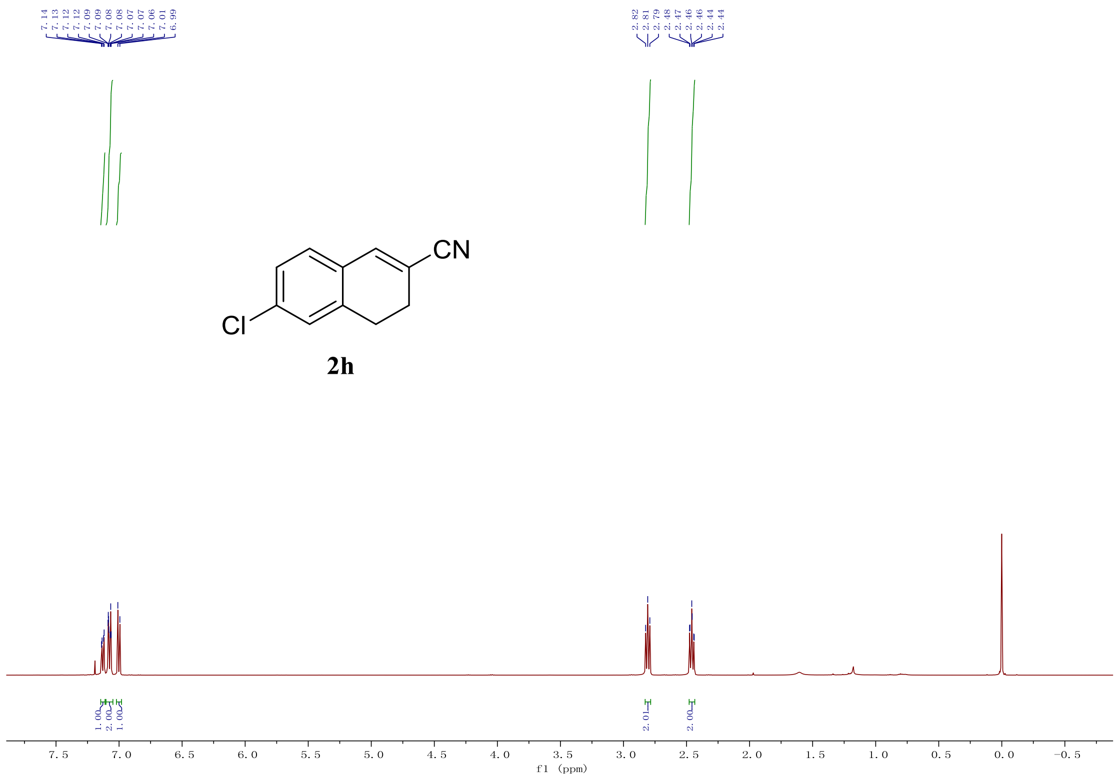
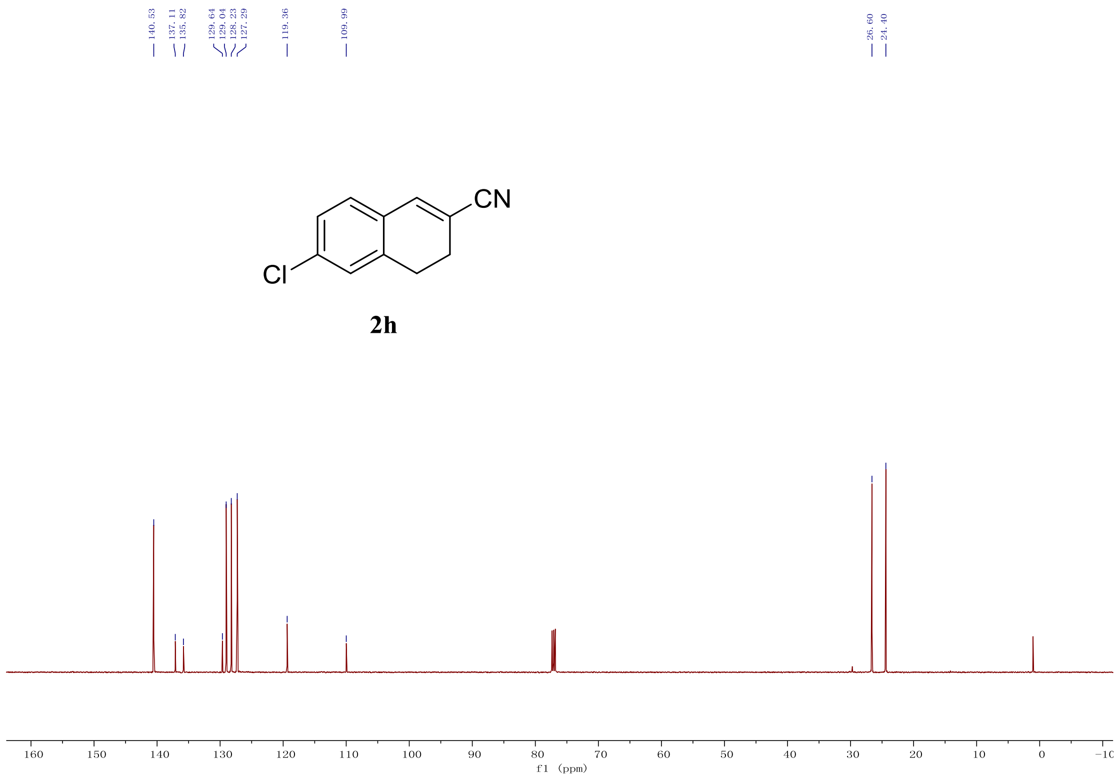
7.13
7.12
7.11
6.94
6.93
6.92
6.91
6.90
6.89
6.87
6.87
2.92
2.90
2.88
2.55
2.53
2.51
CN
F
1.96
1.96
2.00
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

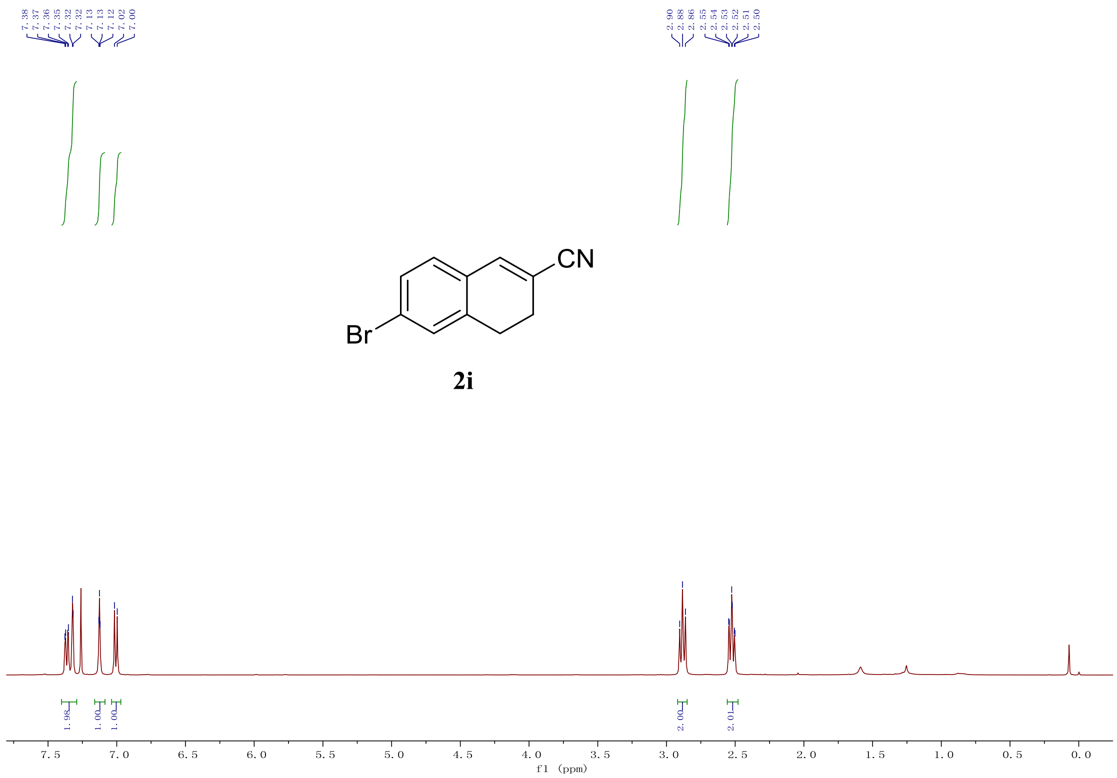
2g


164.76
162.26
140.57
140.55
138.20
138.12
129.79
129.70
127.51
127.48
115.53
115.31
114.09
113.87
108.84
108.81
26.92
26.90
24.22
CN
F
2g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

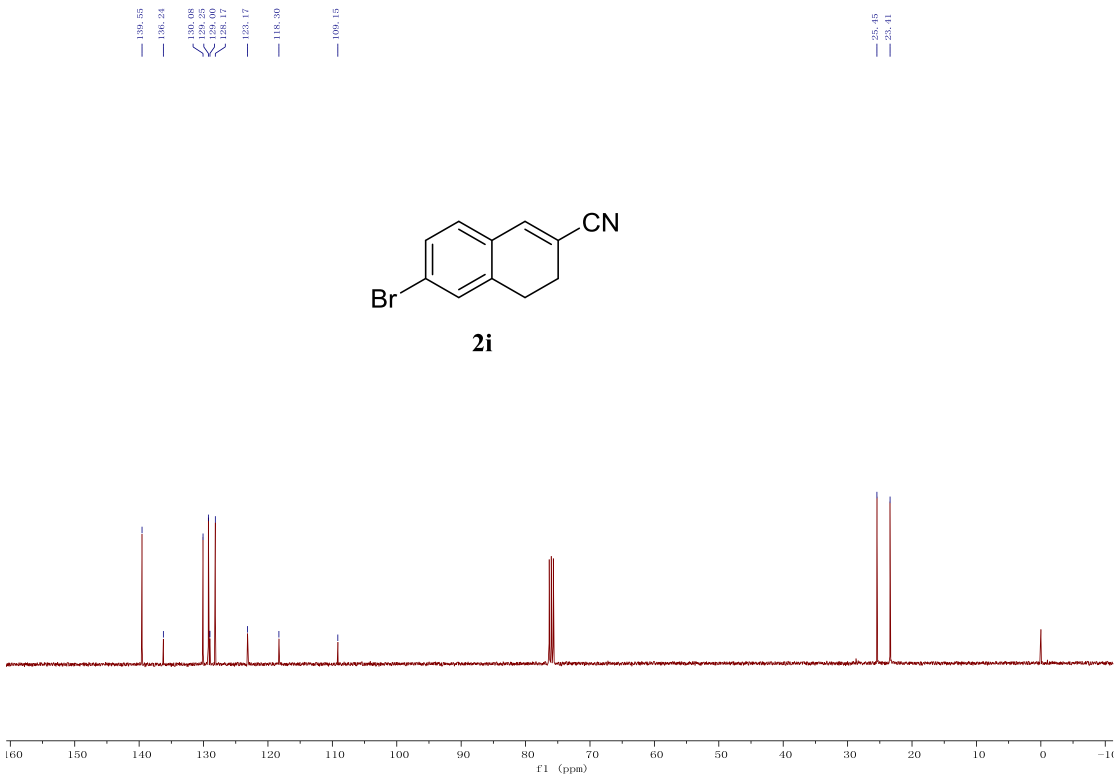

-109.05
CN
F
2g
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)


7.14
7.13
7.12
7.12
7.09
7.09
7.08
7.08
7.07
7.07
7.06
7.01
6.99
2.82
2.81
2.79
2.48
2.47
2.46
2.46
2.44
2.44
CN
Cl
2h
1.00
2.00
1.00
2.01
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

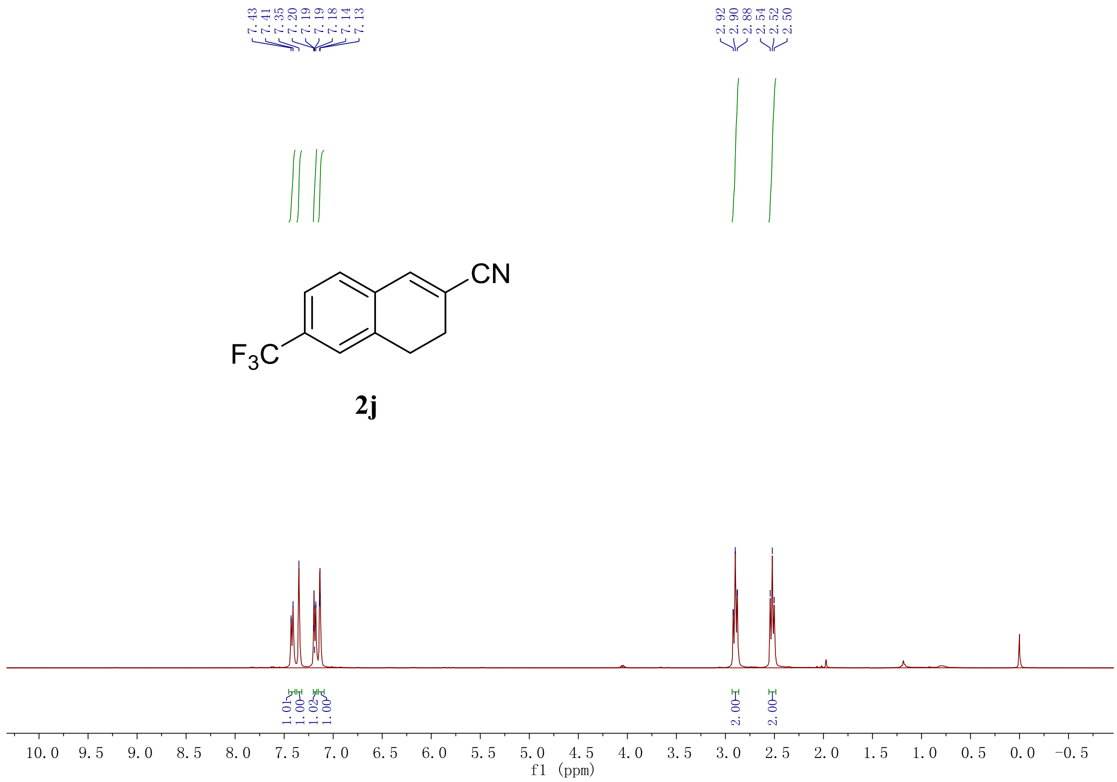

140.53
137.11
135.82
129.64
129.04
128.23
127.29
119.36
109.99
26.60
24.40
CN
Cl
2h
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

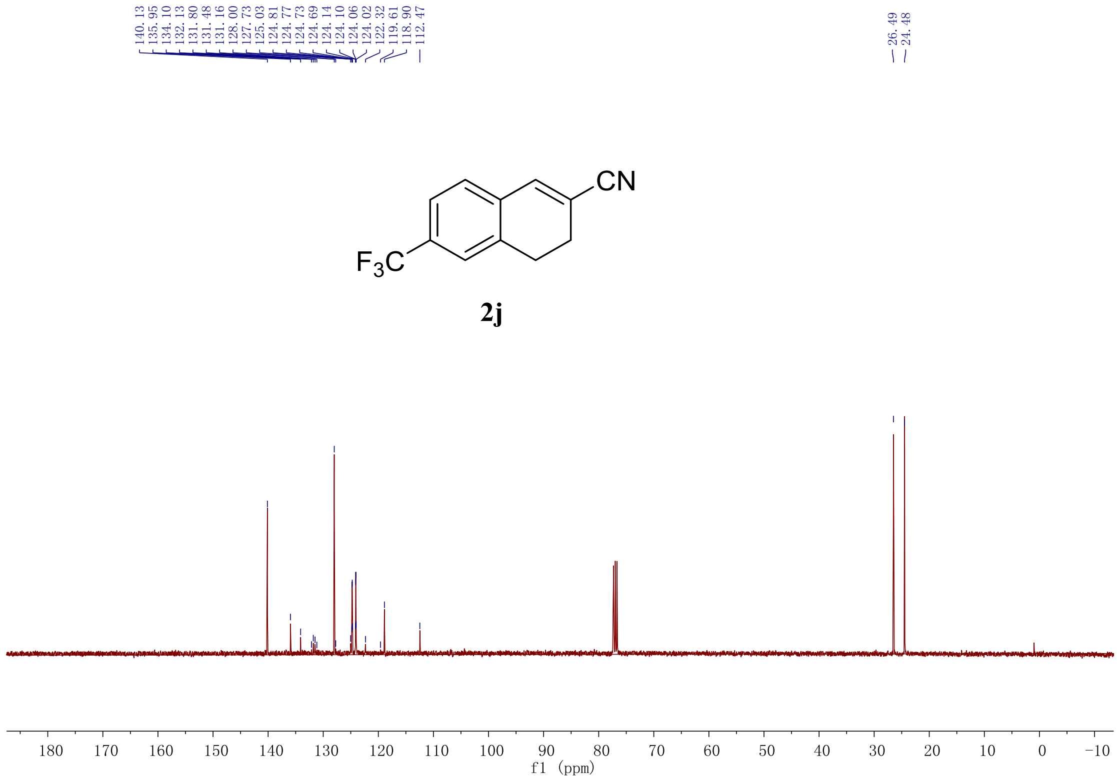


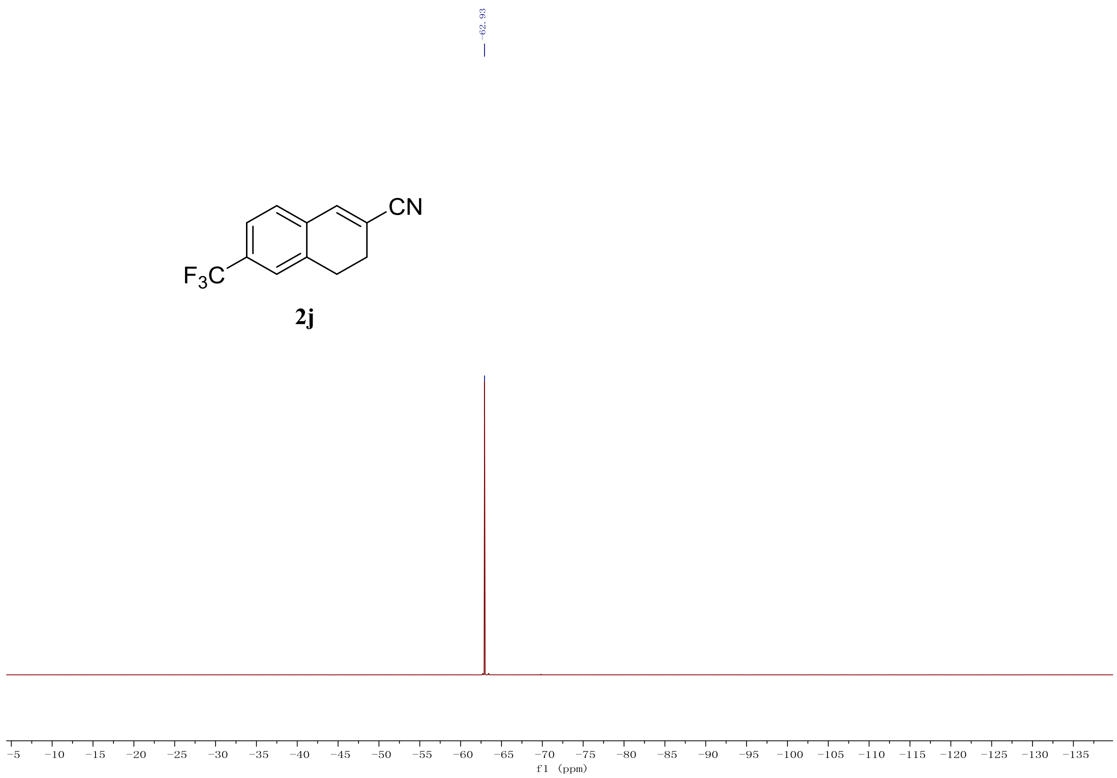
7.38
7.37
7.36
7.35
7.32
7.32
7.13
7.13
7.12
7.02
7.00
2.90
2.88
2.86
2.55
2.54
2.53
2.52
2.51
2.50
CN
Br
2i
1.98
1.00
1.00
2.00
2.01
f1 (ppm)



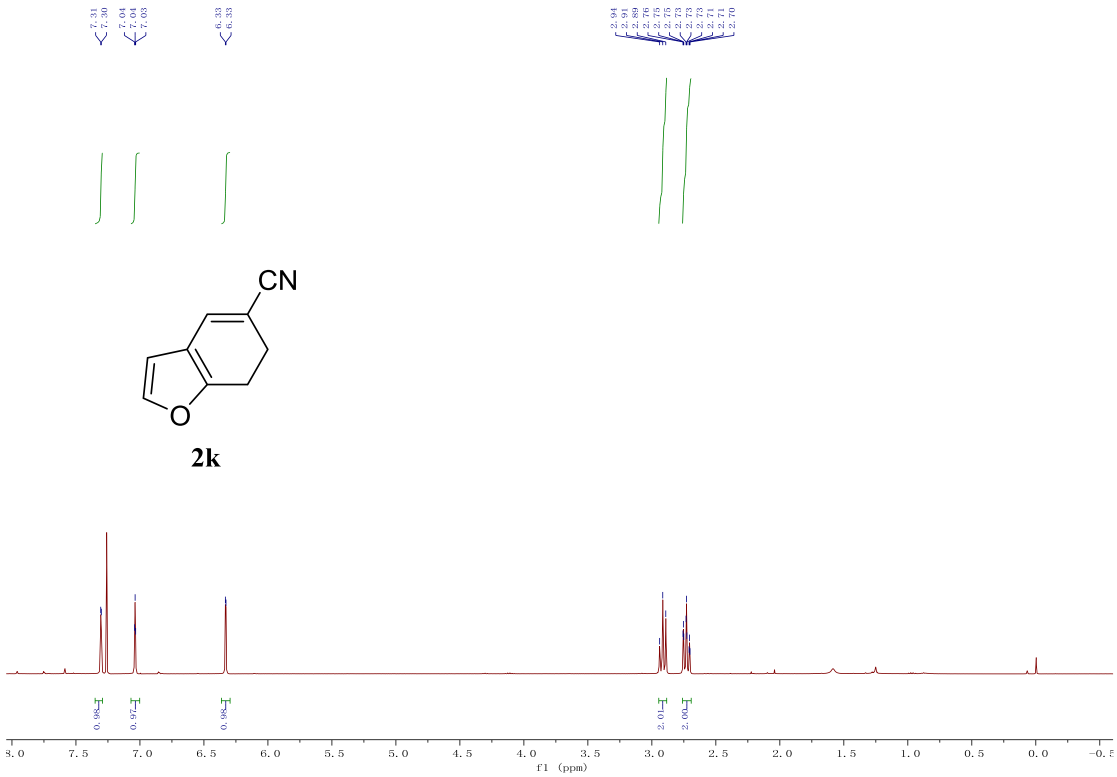
139.55
136.24
130.08
129.25
129.00
128.17
123.17
118.30
109.15
25.45
23.41
CN
Br
2i
f1 (ppm)


7.43
7.41
7.35
7.20
7.19
7.19
7.18
7.14
7.13
2.92
2.90
2.88
2.54
2.52
2.50
CN
F3C
2j
1.01
1.00
1.02
1.00
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

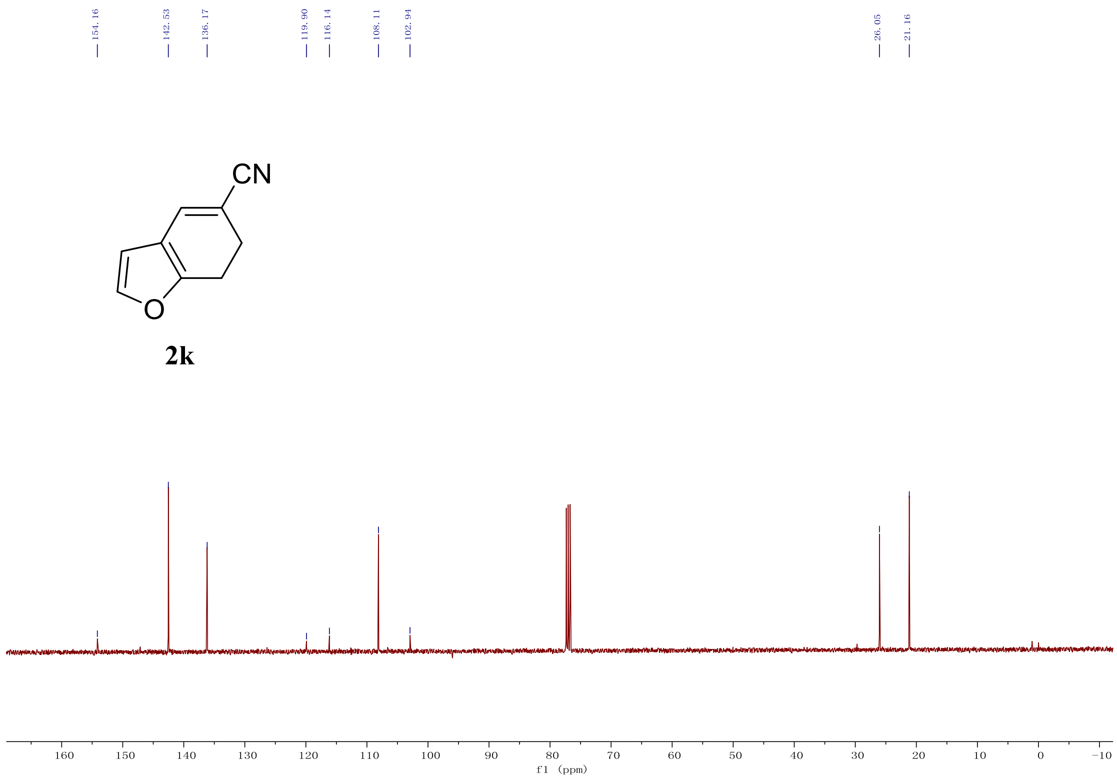

140.13
135.95
134.10
132.13
131.80
131.48
131.16
128.00
127.73
125.03
124.81
124.77
124.73
124.69
124.14
124.10
124.06
124.02
122.32
119.61
118.90
112.47
26.49
24.48
CN
F3C
2j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

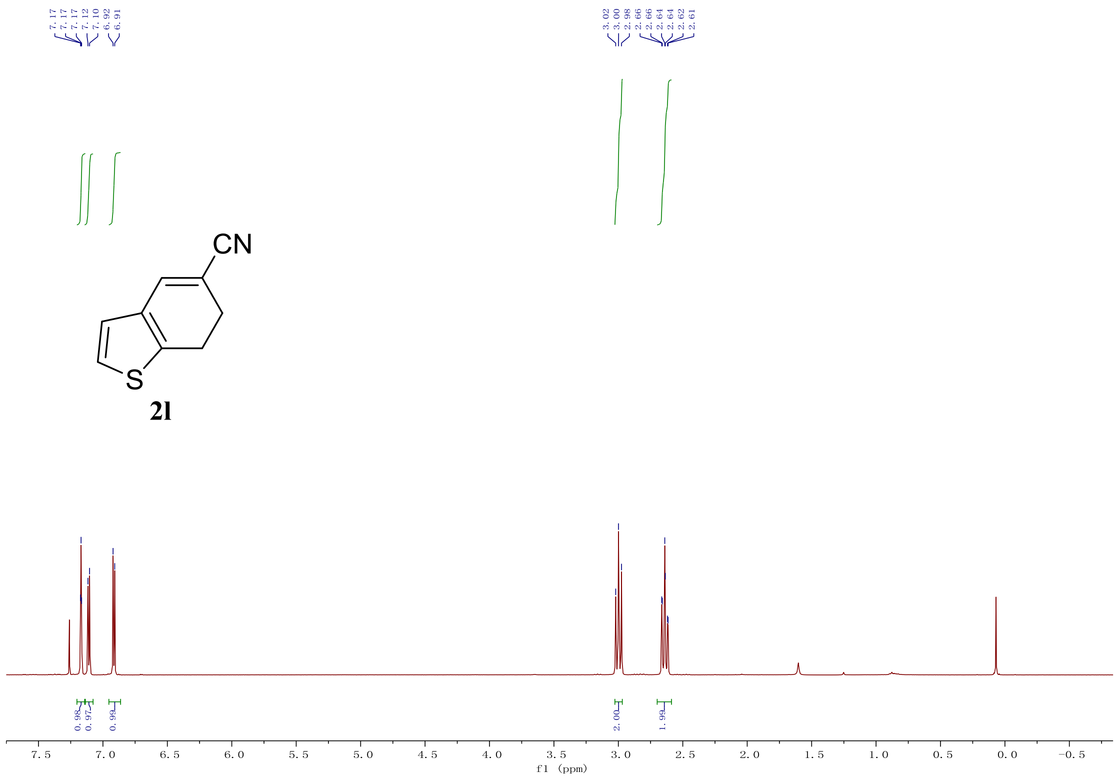


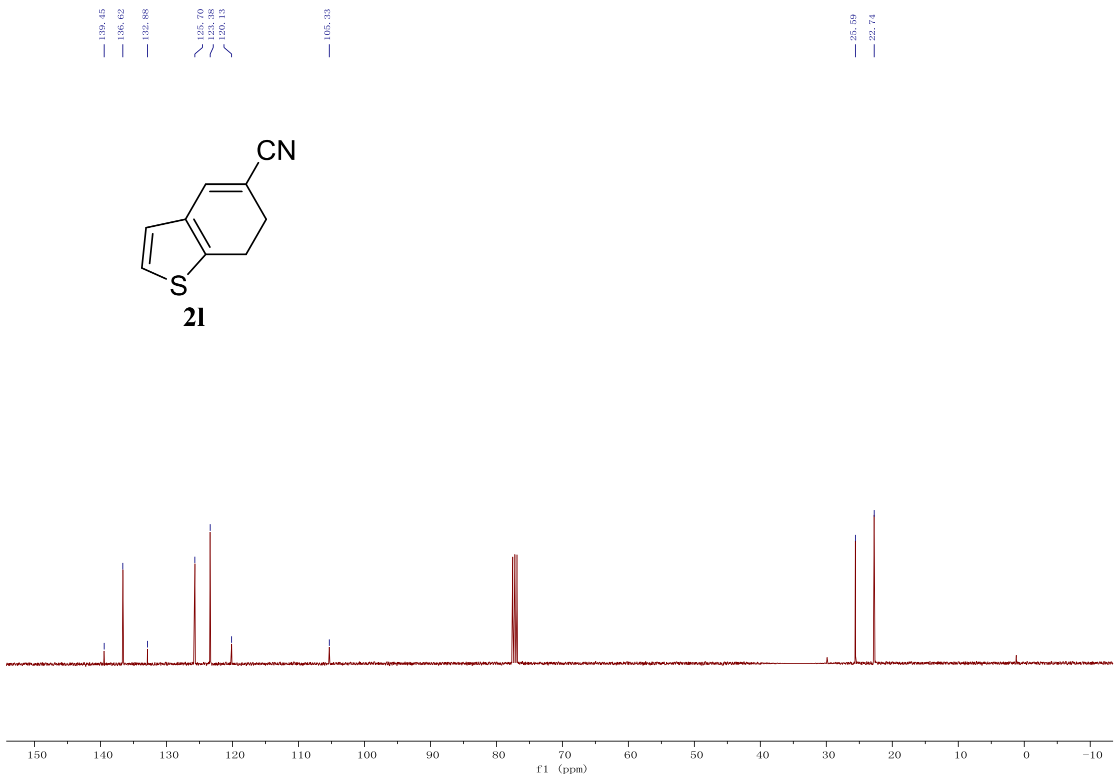
2j

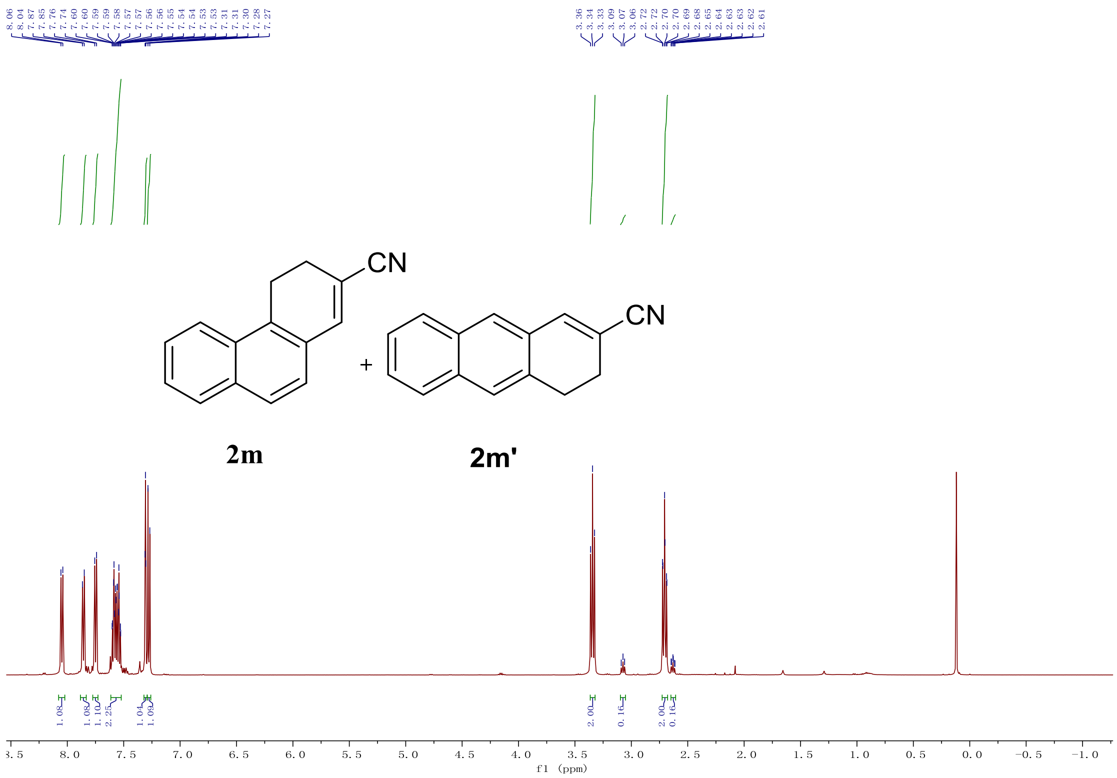


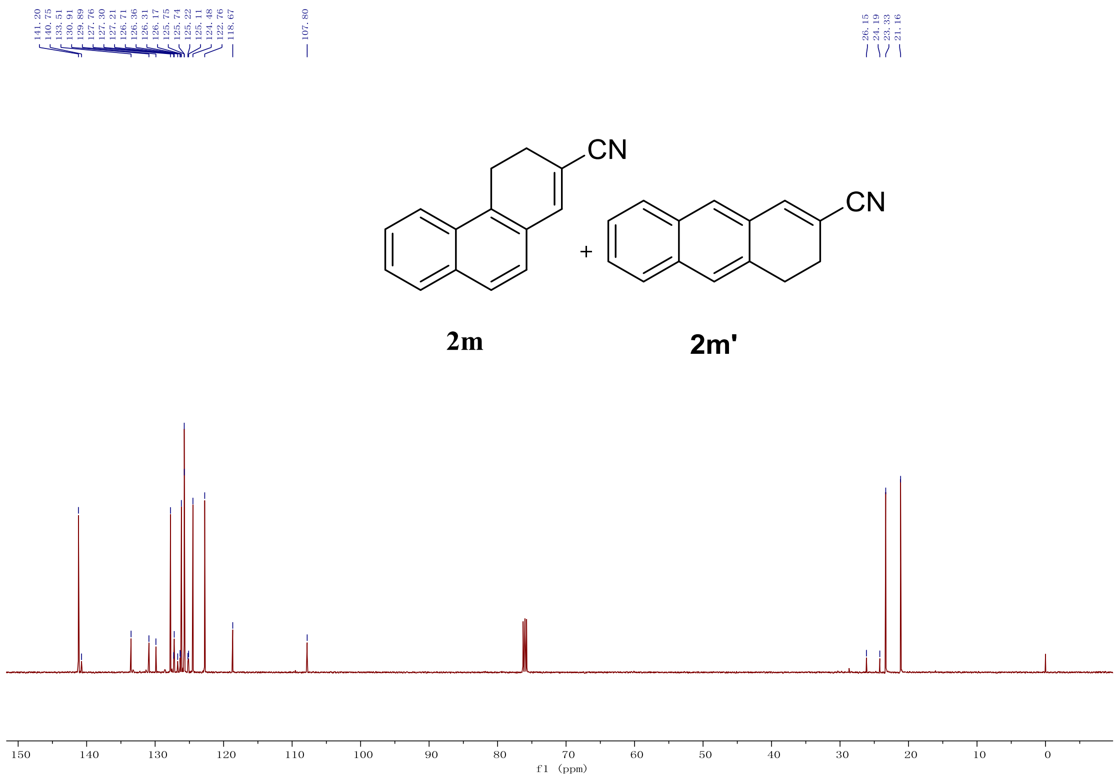
2k


154.16
142.53
136.17
119.90
116.14
108.11
102.94
26.05
21.16
CN
O
2k
f1 (ppm)

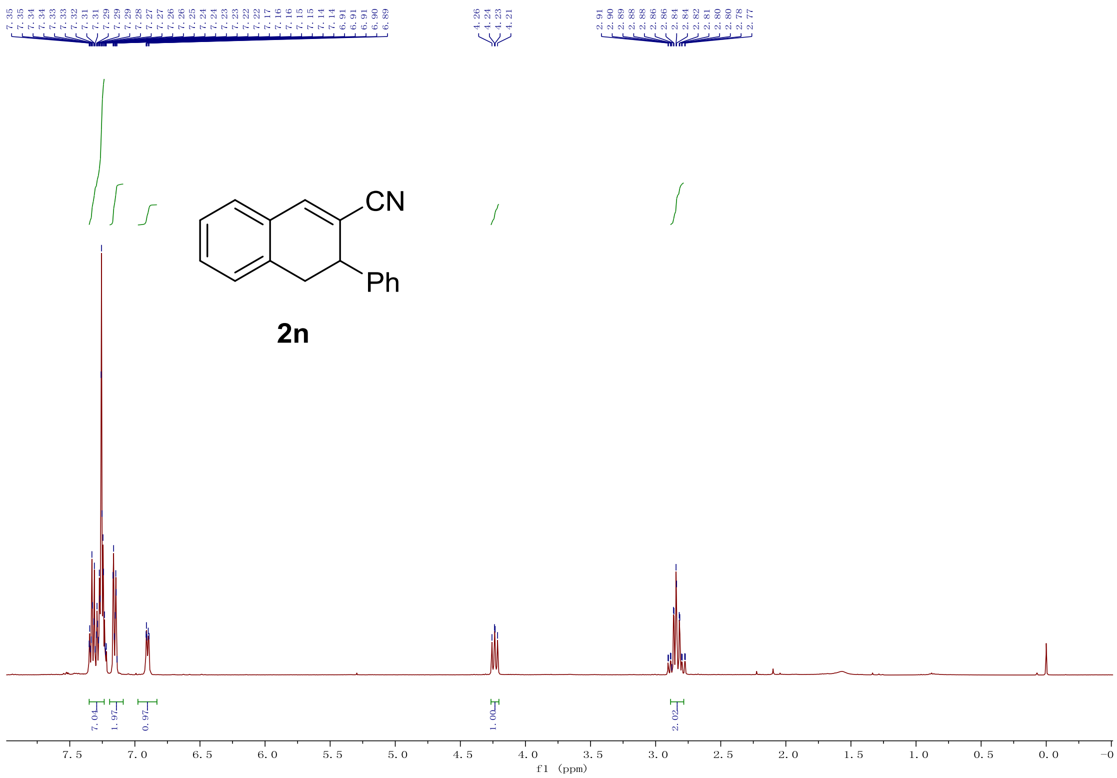

7.17
7.17
7.17
7.12
7.10
6.92
6.91
3.02
3.00
2.98
2.66
2.66
2.64
2.64
2.62
2.61
CN
S
2l
0.98
0.97
0.99
2.00
1.99
f1 (ppm)


139.45
136.62
132.88
125.70
123.38
120.13
105.33
25.59
22.74
CN
S
2l
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

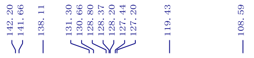

8.06 8.04 7.87 7.85 7.76 7.74 7.60 7.60 7.59 7.58 7.57 7.57 7.56 7.55 7.54 7.54 7.53 7.53 7.31 7.31 7.30 7.28 7.27
3.36 3.34 3.33 3.09 3.07 3.06 2.72 2.72 2.70 2.70 2.69 2.68 2.65 2.64 2.63 2.63 2.62 2.61
CN
+
CN
2m
2m'
1.08
1.08
1.10
2.25
1.04
1.09
2.00
0.16
2.00
0.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

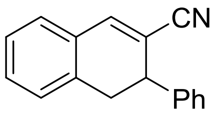


141.20
140.75
133.51
130.91
129.89
127.76
127.30
127.21
126.71
126.36
126.31
126.17
125.75
125.74
125.22
125.11
124.48
122.76
118.67
107.80
26.15
24.19
23.33
21.16
CN
+
CN
2m
2m'
f1 (ppm)

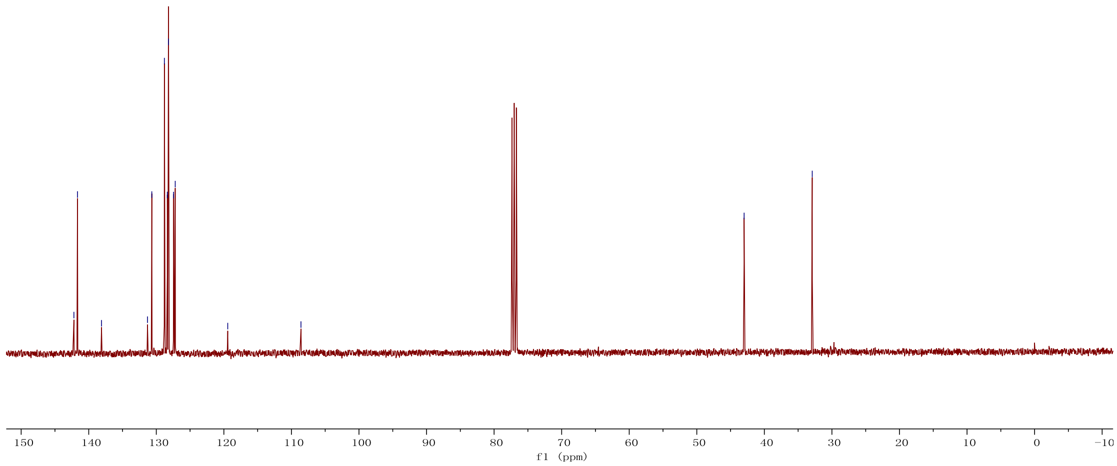


7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.17
7.16
7.15
7.15
7.14
6.91
6.91
6.91
6.90
6.89
4.26
4.24
4.23
4.21
2.91
2.90
2.89
2.88
2.86
2.86
2.84
2.84
2.82
2.81
2.80
2.80
2.78
2.77
CN
Ph
2n
7.04
1.97
0.97
1.00
2.02
f1 (ppm)

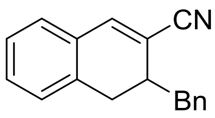

142.20
141.66
138.11
131.30
130.66
128.80
128.37
128.20
127.44
127.20
119.43
108.59
42.99
32.91


CN
Ph

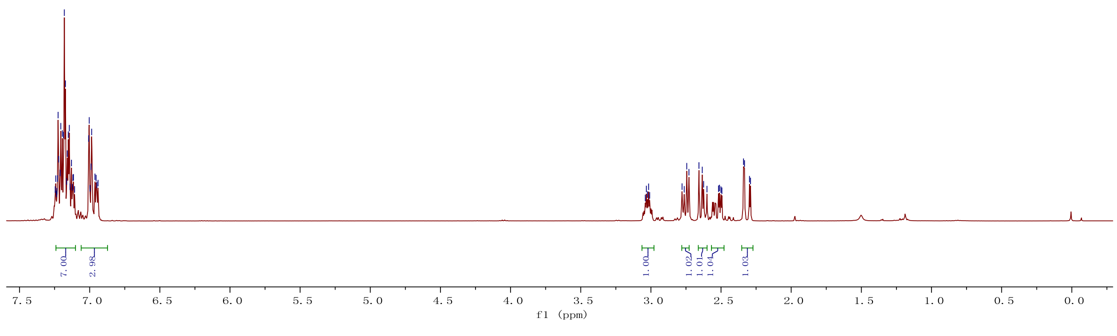
2n

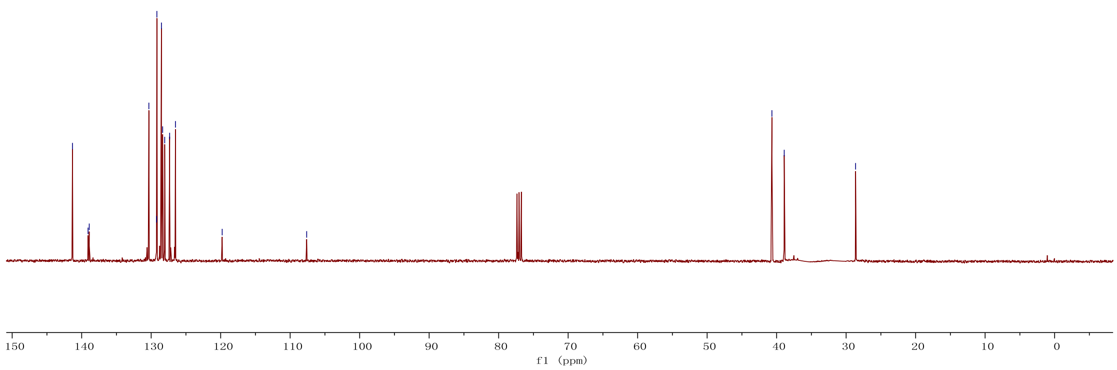

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.19
7.19
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.12
7.12
7.12
7.12
7.11
7.01
7.00
7.00
6.99
6.99
6.96
6.95
6.95
6.94
3.04
3.03
3.02
3.02
3.01
2.78
2.76
2.74
2.73
2.66
2.63
2.62
2.60
2.52
2.51
2.50
2.49
2.34
2.33
2.30
2.29

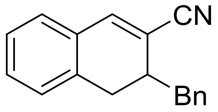

CN
Bn

2o


7.00
2.98
1.00
1.02
1.01
1.04
1.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

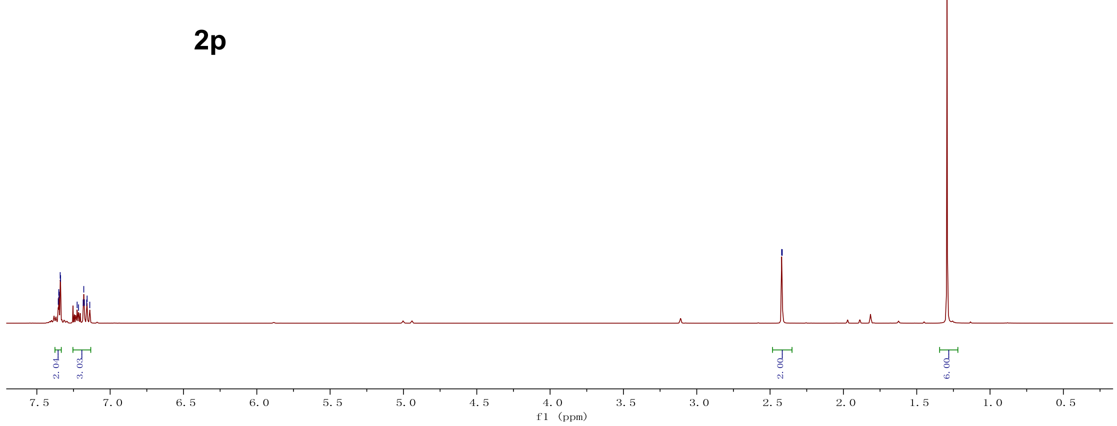


141.32
139.08
138.91
130.33
129.22
129.18
128.52
128.35
128.05
127.34
126.51
119.78
107.62
40.68
38.91
28.64
f1 (ppm)

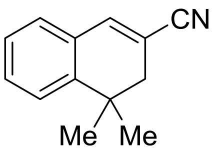


CN
Bn

2o

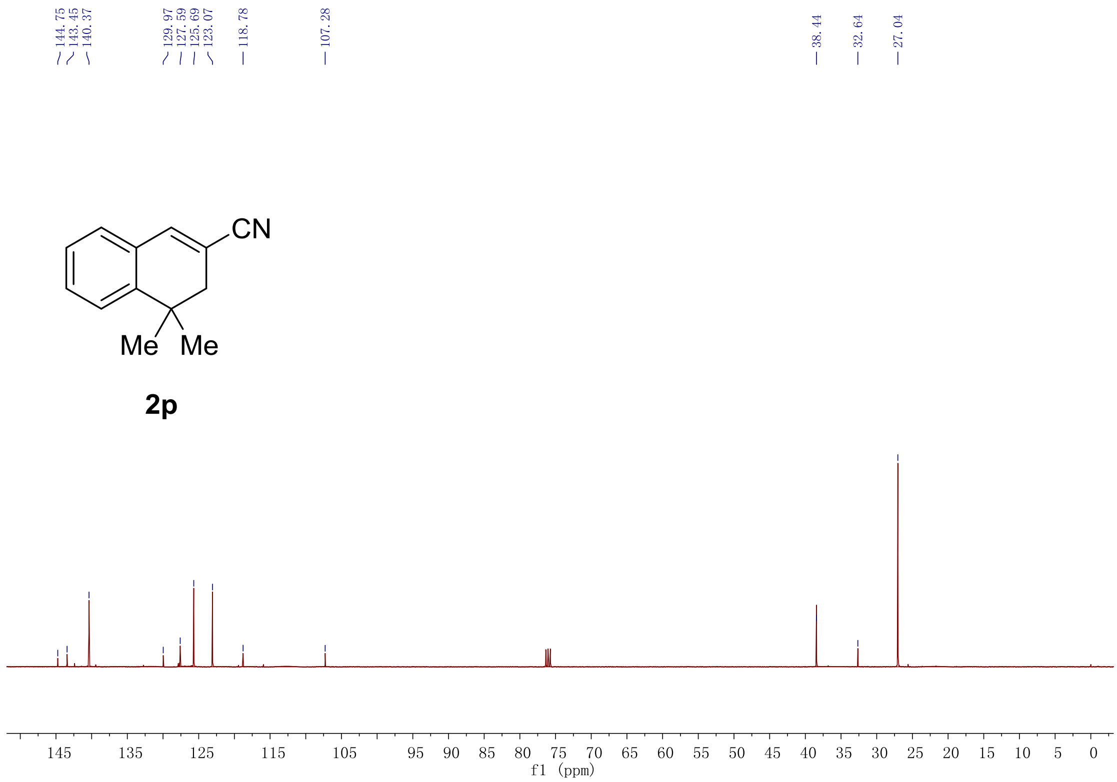


7.35
7.35
7.34
7.34
7.23
7.22
7.18
7.18
7.18
7.16
7.14
2.42
2.42
1.29
2.04
3.03
2.00
6.00
f1 (ppm)

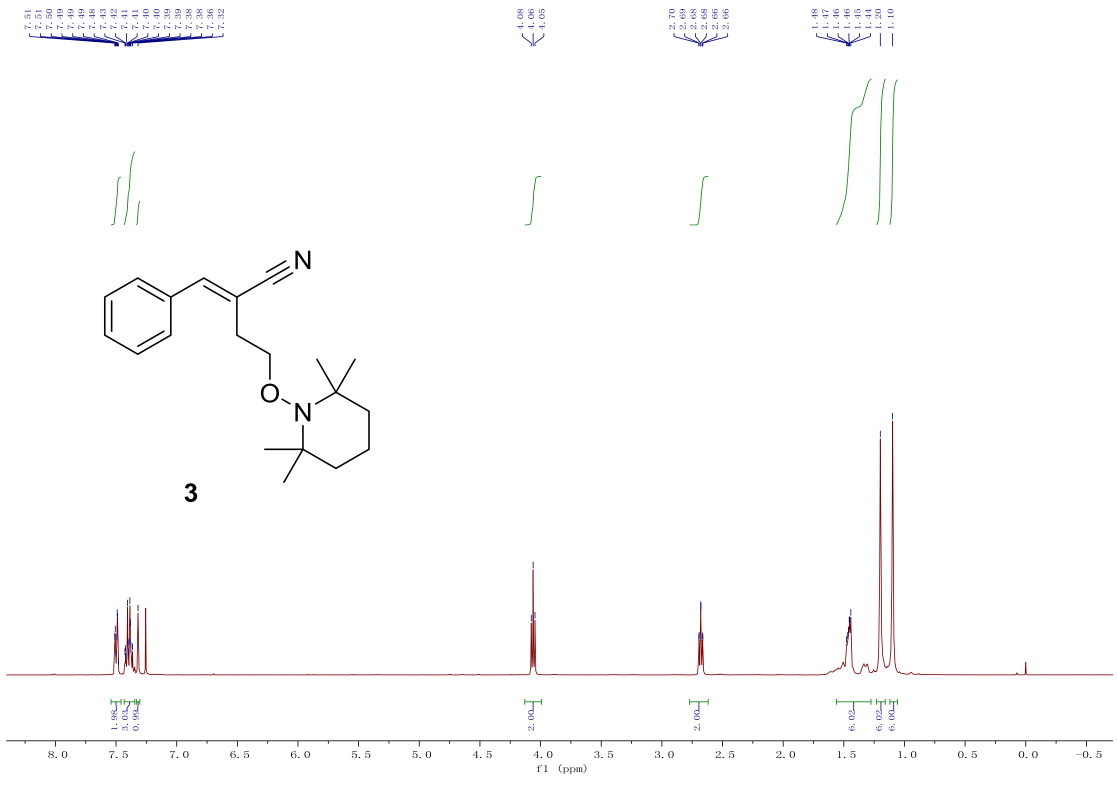


CN
Me
Me

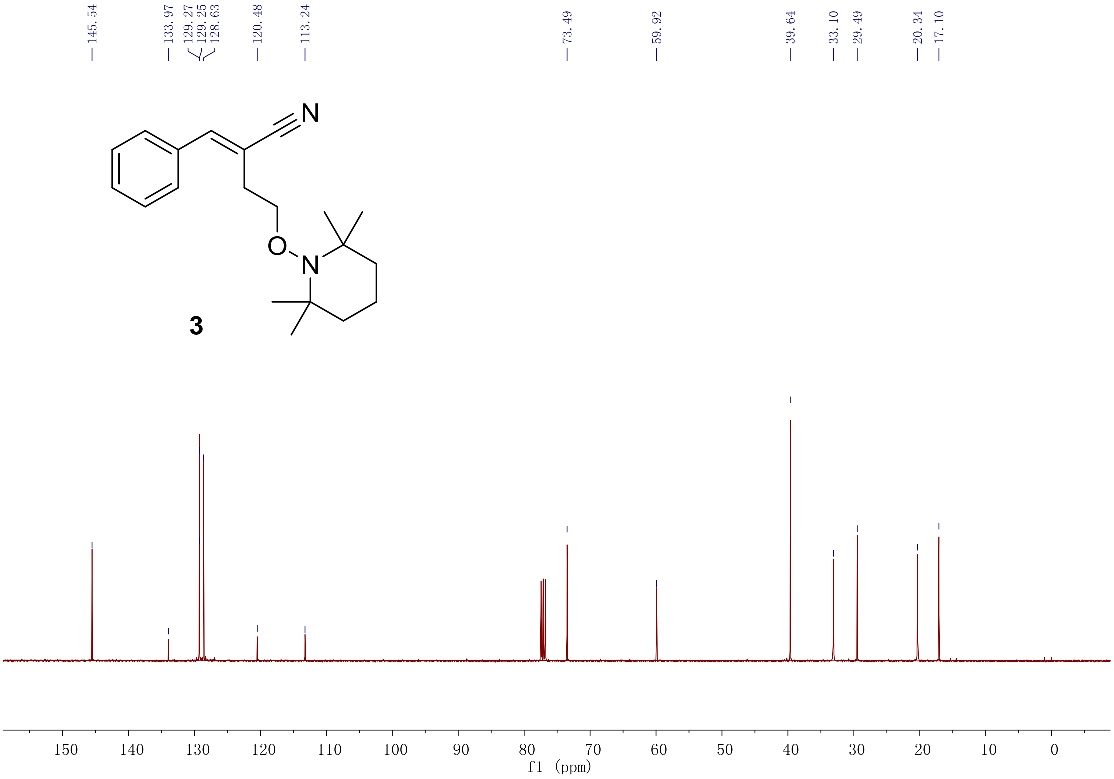
2p



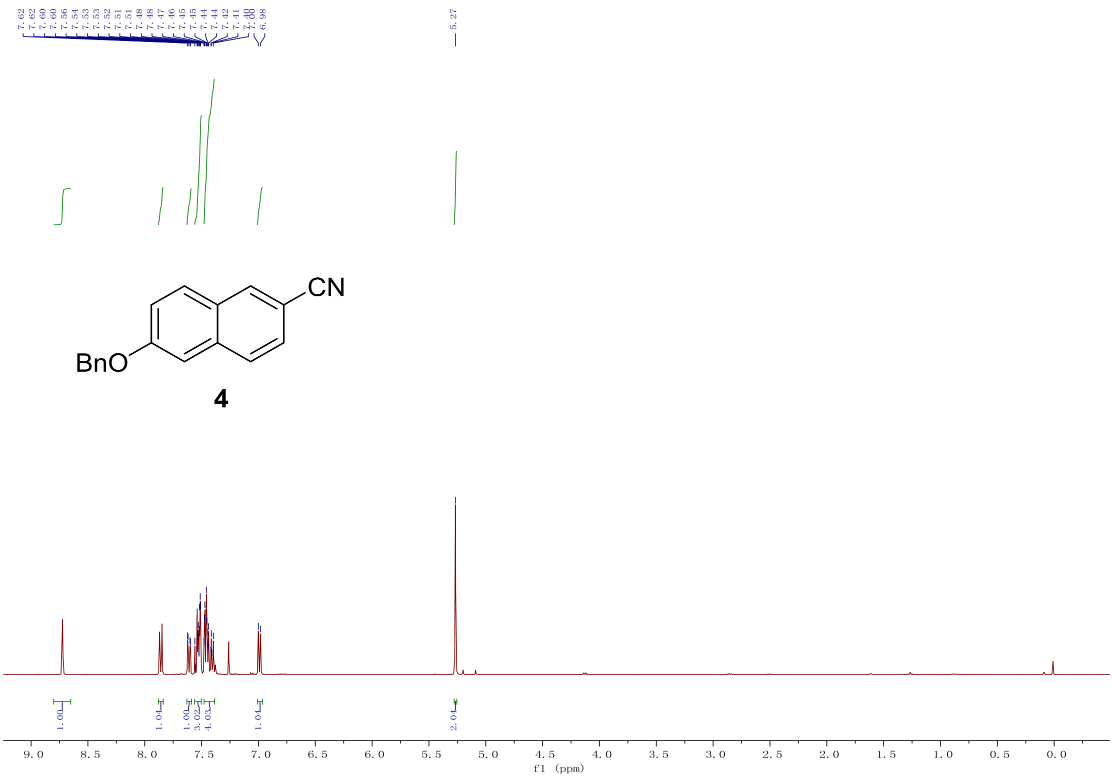
2p



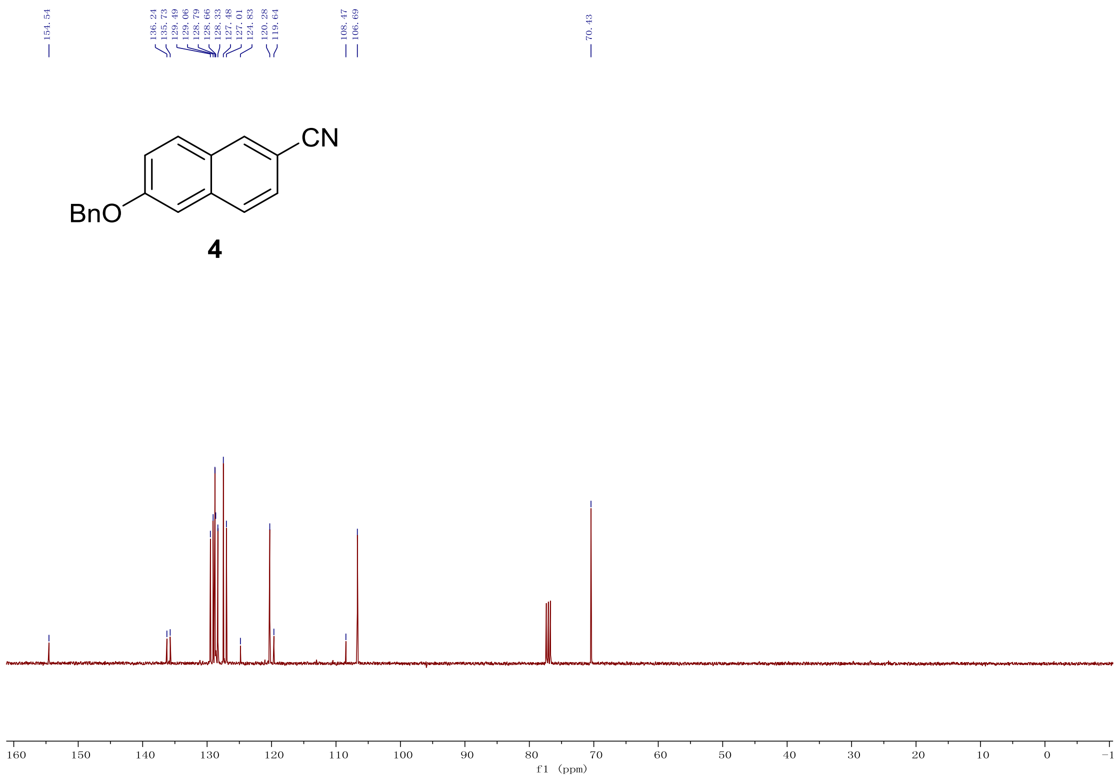
3

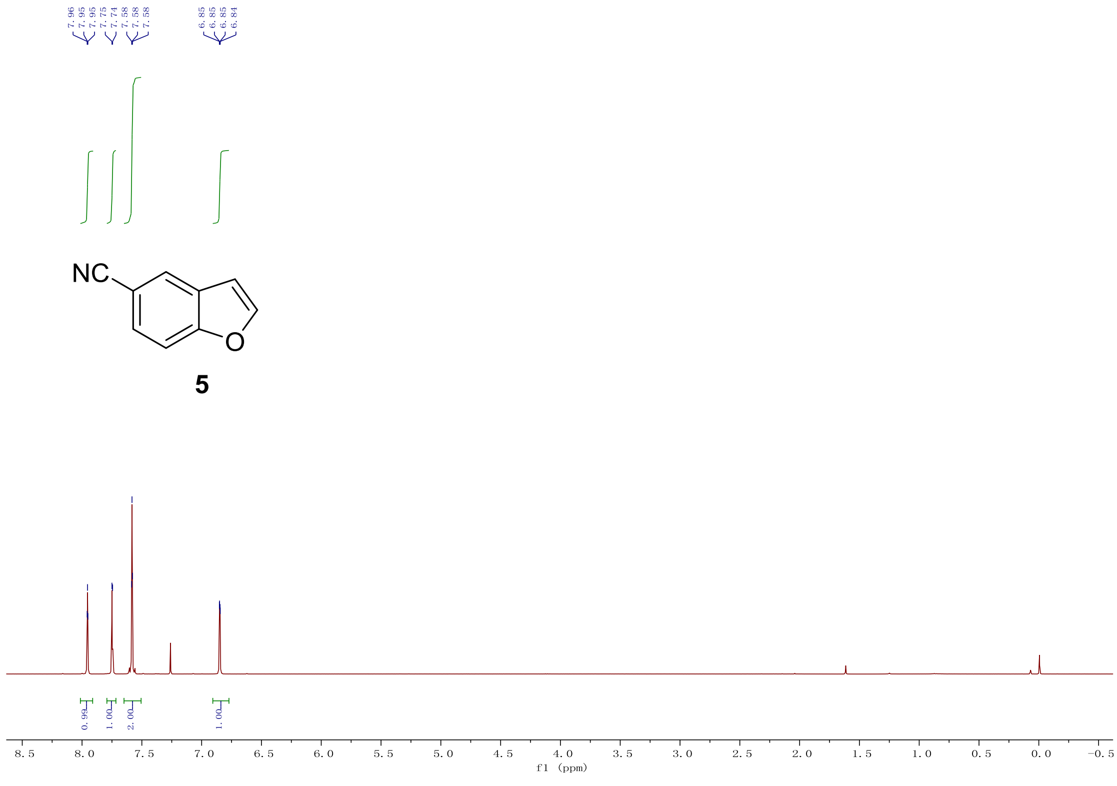

145.54
133.97
129.27
129.25
128.63
120.48
113.24
73.49
59.92
39.64
33.10
29.49
20.34
17.10
N
O
N
f1 (ppm)

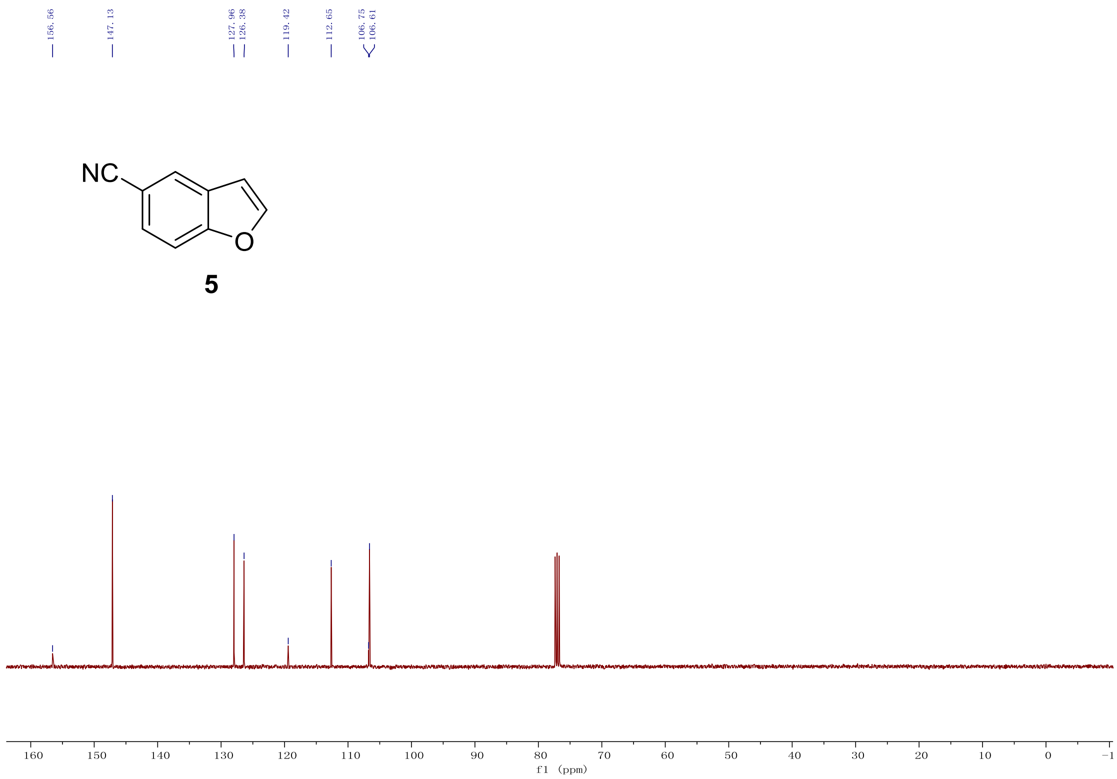
3


7.62
7.62
7.60
7.56
7.54
7.53
7.52
7.51
7.48
7.47
7.46
7.45
7.45
7.44
7.44
7.42
7.41
7.00
6.98
5.27
CN
BnO
1.00
1.04
1.00
3.02
4.03
1.04
2.04
f1 (ppm)

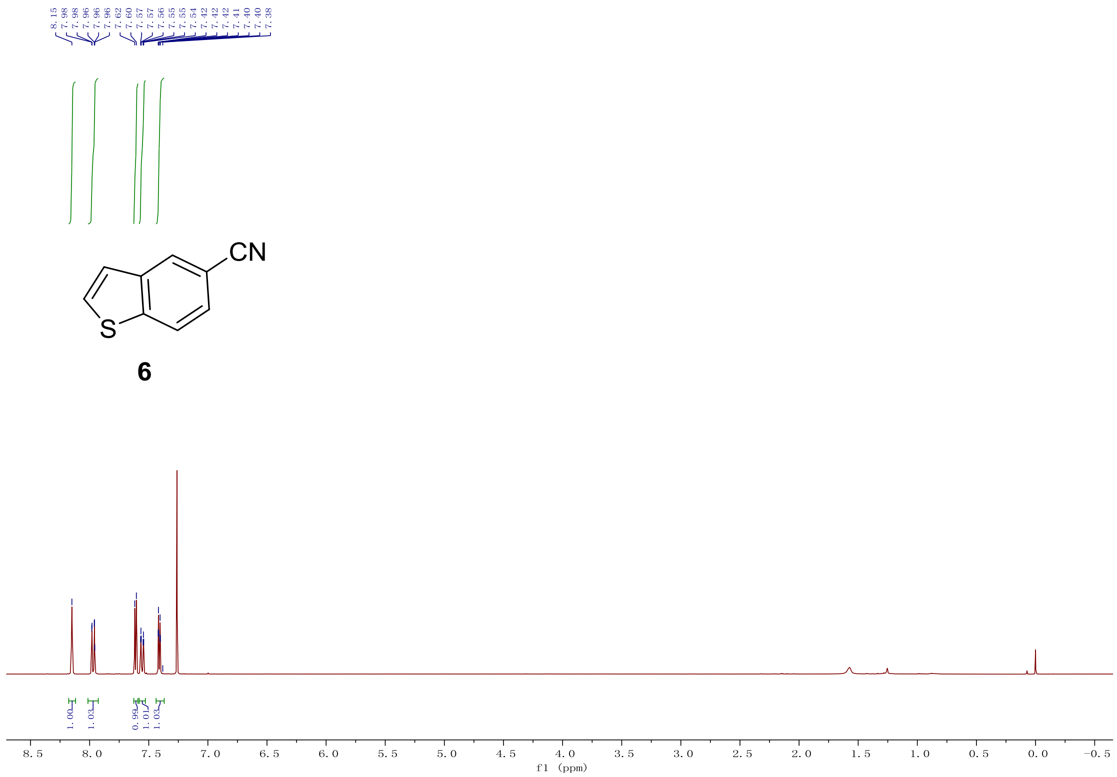
4



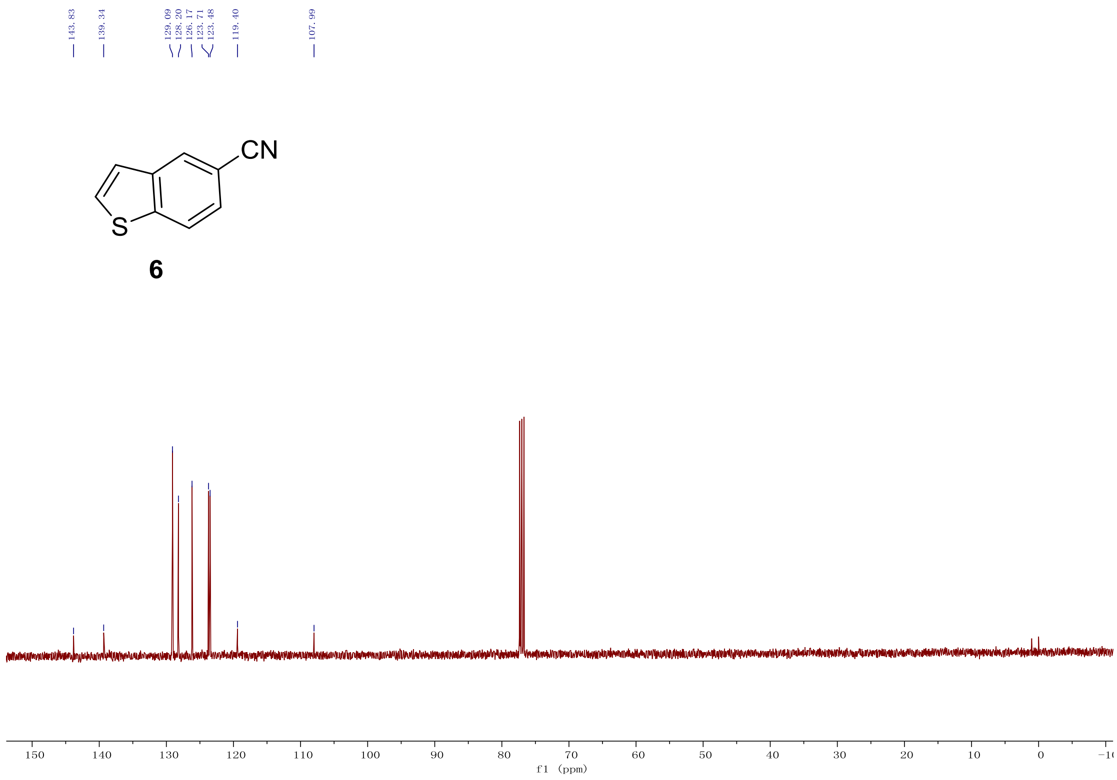



156.56
147.13
127.96
126.38
119.42
112.65
106.75
106.61
NC
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

5


8.15
7.98
7.98
7.96
7.96
7.96
7.62
7.60
7.57
7.57
7.56
7.55
7.55
7.54
7.42
7.42
7.42
7.41
7.40
7.40
7.38
CN
S
1.00
1.03
0.99
1.01
1.03
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 -0.5
f1 (ppm)

6



143.83
139.34
129.09
128.20
126.17
123.71
123.48
119.40
107.99
CN
S
6
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)