Photoinduced Fragmentation-Rearrangement Sequence of Cycloketoxime Esters

(Supporting Information)

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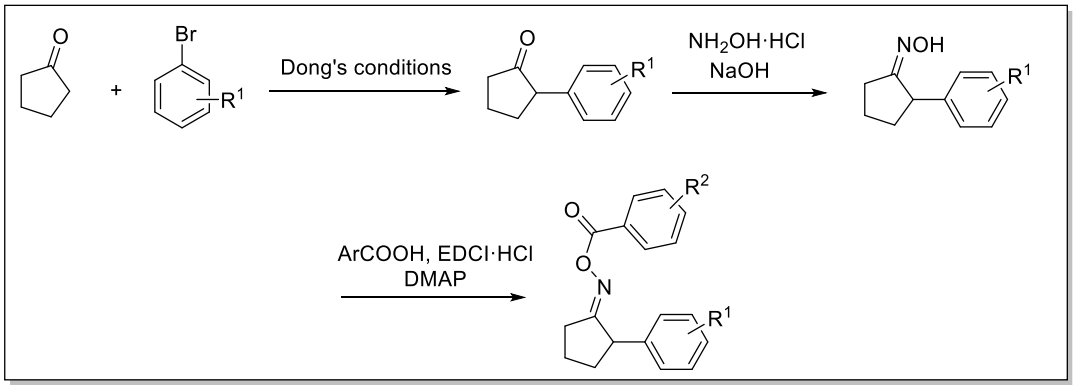
1. General Information.

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 a 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. Photoredox catalysis *fac*-[$Ir(ppy)_3$] was purchased from Adamas-beta,and $Cu(OTf)_2$ was purchased from TCI. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Preparation of Cycloketoxime Esters



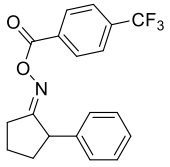
2-Arylcyclopentan-1-one *O*-benzoyl oximes were obtained from the correspounding 2-arylcyclopentan-1-ones, which were synthesized from the corresponding cyclopentane and aryl bromides according to the reported procedure[1].

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 12-24 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 (1.0 equiv) was dissolved in abs EtOH (0.25 M) and treated with NaOH (2.0 equiv) in H_2O (0.5 M) followed by hydroxylamine hydrochloride (1.5 equiv). The mixture was allowed to stir at room temperature 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 (20.0 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*-(4-(trifluoromethyl)benzoyl) oxime (1aa)

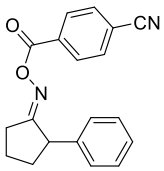


1aa

According to the general procedure, **1aa** was prepared from the commercially available cyclopentanone (5.0 mmol) and phenyl

bromide 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.

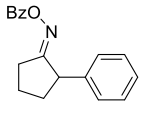
4-((((2-Phenylcyclopentylidene)amino)oxy)carbonyl)benzonitrile (1ba)



1ba

According to the general procedure, **1ba** was prepared from the commercially available cyclopentanone (2.0 mmol) and phenyl bromide as a white solid (385 mg, 63%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 4.06 (t, *J* = 7.1 Hz, 1H), 2.98 – 2.90 (m, 1H), 2.85 – 2.76 (m, 1H), 2.38 – 2.30 (m, 1H), 2.11 – 1.82 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.4, 162.2, 140.0, 133.2, 132.3, 130.0, 128.6, 127.8, 126.9, 117.9, 116.6, 49.2, 34.7, 30.1, 22.5; **ATR-FTIR (cm $^{-1}$):** 1745, 1280, 1243, 1070, 904; **HRMS m/z (ESI)** calcd for $C_{19}H_{16}N_2NaO_2$ $(M + Na)^+$ 327.1104, found 327.1101.

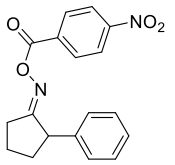
2-Phenylcyclopentan-1-one *O*-benzoyl oxime (1ca)



1ca

According to the general procedure, **1ca** was prepared from the commercially available cyclopentanone (5.0 mmol) and phenyl bromide 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, 1690, 1290, 1211, 1058, 915; **HRMS m/z (ESI)** calcd for $C_{18}H_{17}NNaO_2$ $(M + Na)^+$ 302.1151, found 302.1151.

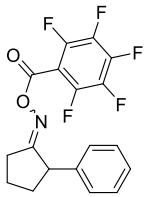
2-Phenylcyclopentan-1-one *O*-benzoyl oxime (1da)



1da

According to the general procedure, **1da** was prepared from the commercially available cyclopentanone (2.0 mmol) and phenyl bromide as a yellow solid (391 mg, 60%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.26 – 7.20 (m, 1H), 4.07 (t, *J* = 7.2 Hz, 1H), 3.00 – 2.92 (m, 1H), 2.87 – 2.78 (m, 1H), 2.39 – 2.30 (m, 1H), 2.12 – 1.75 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.5, 161.9, 150.6, 140.0, 134.7, 130.6, 128.6, 127.8, 126.9, 123.7, 49.3, 34.7, 30.1, 22.5; **ATR-FTIR (cm^{-1}):**1745, 1690, 1281, 1210, 1061, 852; **HRMS m/z (ESI)** calcd for $C_{18}H_{16}N_2NaO_4$ $(M + H)^+$ 347.1002, found 347.1006.

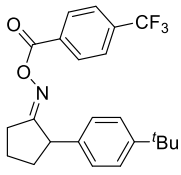
2-Phenylcyclopentan-1-one *O*-perfluorobenzoyl oxime (1ea)



1ea

According to the general procedure, **1ea** was prepared from the commercially available cyclopentanone (2.0 mmol) and phenyl bromide 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, 1651, 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-(*tert*-Butyl)phenyl)cyclopentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1ab)

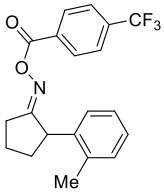


1ab

According to the general procedure, **1ab** was prepared from the commercially available cyclopentanone (5.0 mmol) and 1-bromo-4-(tert-butyl)benzene as a white solid (1.1 g, 55%): **^{1}H**

NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.04 (t, *J* = 7.3 Hz, 1H), 2.97 – 2.91 (m, 1H), 2.85 – 2.78 (m, 1H), 2.40 – 2.22 (m, 1H), 2.15 – 1.97 (m, 2H), 1.93 – 1.78 (m, 1H), 1.31 (s, 9H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.4, 162.6, 149.6, 136.9, 134.5 (q, *J* = 32.7 Hz), 132.5, 129.9, 127.4, 125.5 (q, *J* = 3.3 Hz), 123.5 (q, *J* = 272.7 Hz), 48.8, 34.5, 34.3.31.3, 29.9, 22.5; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):**1750, 1601, 1545, 1460, 1261, 1066, 756; **HRMS m/z (ESI)** calcd for $C_{23}H_{24}F_3NNaO_2$ $(M + Na)^+$ 426.1651, found 426.1650.

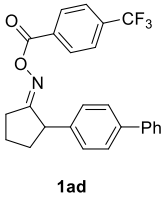
2-(*O*-tolyl)cyclopentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1ac)



1ac

According to the general procedure, **1ac** was prepared from the commercially available cyclopentanone (5.0 mmol) and 1-bromo-2-methylbenzene as a white solid (650 mg, 36%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.21 – 7.08 (m, 4H), 4.22 (t, *J* = 7.3 Hz, 1H), 3.02 – 2.83 (m, 2H), 2.40 (s, 3H), 2.36 – 2.26 (m, 1H), 2.07 – 2.01 (m, 1H), 1.94 – 1.83 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.7, 162.6, 139.4, 135.9, 134.6 (q, *J* = 32.8 Hz), 132.5, 130.6, 129.9, 127.1, 126.8, 126.2, 125.5 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 270.4 Hz), 46.5, 34.0, 30.5, 22.5, 19.9; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):**1749, 1601, 1515, 1460, 1383, 1066, 741; **HRMS m/z (ESI)** calcd for $C_{20}H_{18}F_3NNaO_2$ $(M + Na)^+$ 384.1182, found 384.1185.

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

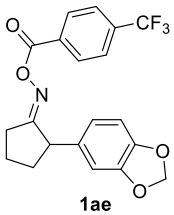


1ad

According to the general procedure, **1ad** was prepared from the commercially available cyclopentanone (5.0 mmol) and 4-bromo-1,1'-biphenyl as a white solid (953 mg, 45%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.19 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.54 (m, 4H), 7.48 – 7.38 (m, 4H), 7.34 (t, *J* = 7.4 Hz, 1H), 4.11 (t, *J* = 7.6 Hz, 1H), 3.01 – 2.94 (m, 1H), 2.88 – 2.81 (m, 1H), 2.41 – 2.34 (m, 1H), 2.14 – 2.03 (m, 2H),

1.92 – 1.87 (m, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.2, 162.6, 140.8, 139.8, 139.1, 134.6 (q, *J* = 32.8 Hz), 132.5, 129.9, 128.7, 128.3, 127.4, 127.2, 127.0, 125.5 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 272.8 Hz), 49.0, 34.7, 30.0, 22.5; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):**1748, 1650, 1550, 1454, 1260, 712; **HRMS m/z (ESI)** calcd for $C_{25}H_{20}F_3NNaO_2$ $(M + Na)^+$ 446.1338, found 446.1340.

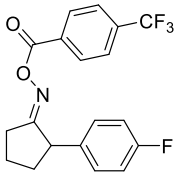
2-(Benzo[*d*][1,3]dioxol-5-yl)cyclopentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1ae)



1ae

According to the general procedure, **1ae** was prepared from the commercially available cyclopentanone (5.0 mmol) and 5-bromobenzo[*d*][1,3]dioxole as a yellow solid (768 mg, 39%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 6.90 – 6.63 (m, 3H), 5.92 (q, *J* = 1.3 Hz, 2H), 3.97 (t, *J* = 7.1 Hz, 1H), 2.95 – 2.89 (m, 1H), 2.81 – 2.74 (m, 1H), 2.32 – 2.27 (m, 1H), 2.06 – 1.93 (m, 2H), 1.87 – 1.80 (m, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.2, 162.5, 147.8, 146.4, 134.5 (q, *J* = 32.6 Hz), 133.7, 132.5, 129.9, 125.5 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz), 121.0, 108.3, 108.2, 100.9, 49.0, 34.8, 29.9, 22.4; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):**1752, 1611, 1511, 1324, 1248, 1075, 746; **HRMS m/z (ESI)** calcd for $C_{20}H_{16}F_3NNaO_4$ $(M + Na)^+$ 414.0924, found 414.0930.

2-(4-Fluorophenyl)cyclopentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1af)

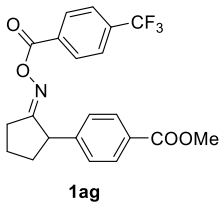


1af

According to the general procedure, **1af** was prepared from the commercially available cyclopentanone (5.0 mmol) and 1-bromo-4-fluorobenzene as a white solid (723 mg, 40%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 4.03 (t, *J* = 7.3 Hz, 1H), 2.98 – 2.92 (m, 1H), 2.83 – 2.76 (m, 1H), 2.37 – 2.31 (m, 1H), 2.05 – 1.97 (m, 2H), 1.91 – 1.83 (m, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.0, 162.7 (d, *J* = 20.7 Hz), 160.8, 135.7 (d, *J* = 3.3 Hz), 134.6 (q, *J* = 32.8 Hz), 132.4, 129.9, 129.4 (d, *J* = 8.0 Hz), 125.5 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz), 115.4 (d, *J* = 21.4 Hz), 48.6, 34.8,

29.9, 22.4; **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.2, -116.1; **ATR-FTIR (cm^{-1}):**1749, 1640, 1451, 1263, 708; **HRMS m/z (ESI)** calcd for $C_{19}H_{15}F_4NNaO_2$ $(M + Na)^+$ 388.0931, found 388.0933.

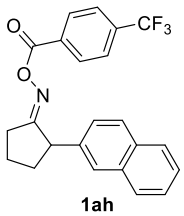
Methyl -4-(2-(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclopentyl)benzoate (1ag)



1ag

According to the general procedure, **1ag** was prepared from the commercially available cyclopentanone (5.0 mmol) and methyl 4-bromobenzoate as a yellow solid (674 mg, 33%): **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.17 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.01 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.00 – 2.87 (m, 1H), 2.84 – 2.73 (m, 1H), 2.36 – 2.23 (m, 1H), 2.07 – 1.96 (m, 2H), 1.90 – 1.80 (m, 1H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 178.4, 162.6, 158.4, 134.6 (q, *J* = 32.7 Hz), 132.5, 131.9, 129.9, 128.8, 125.5 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz), 114.0, 55.2, 48.5, 34.6, 29.9, 22.4; **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.1; **ATR-FTIR (cm^{-1}):**1749, 1721, 1550, 1450, 1015, 832; **HRMS m/z (ESI)** calcd for $C_{21}H_{18}F_3NNaO_4$ $(M + H)^+$ 428.1080, found 428.1085.

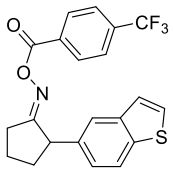
2-(Naphthalen-2-yl)cyclopentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1ah)



1ah

According to the general procedure, **1ah** was prepared from the commercially available cyclopentanone (5.0 mmol) and 2-bromonaphthalene as a white solid (1.0 g, 51%): **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.18 (d, *J* = 8.1 Hz, 2H), 7.88 – 7.79 (m, 3H), 7.77 – 7.72 (m, 3H), 7.50 – 7.42 (m, 3H), 4.24 (t, *J* = 7.7 Hz, 1H), 3.02 – 2.96 (m, 1H), 2.91 – 2.84 (m, 1H), 2.44 – 2.37 (m, 1H), 2.22 – 2.15 (m, 1H), 2.11 – 2.03 (m, 1H), 1.97 – 1.86 (m, 1H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 178.1, 162.6, 137.4, 134.6 (q, *J* = 32.9 Hz), 133.4, 132.5, 132.4, 130.0, 128.4, 127.8, 127.6, 126.4, 126.1, 126.2, 125.7, 125.5 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz), 49.4, 34.6, 30.1, 22.6; **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.1; **ATR-FTIR (cm^{-1}):** 1749, 1515, 1462, 1270, 1089, 756; **HRMS m/z (ESI)** calcd for $C_{23}H_{18}F_3NNaO_2$ $(M + Na)^+$ 420.1182, found 420.1185.

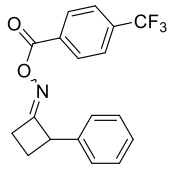
2-(Benzo[*b*]thiophen-5-yl)cyclopentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1ai)



1ai

According to the general procedure, **1ai** was prepared from the commercially available cyclopentanone (5.0 mmol) and 5-bromobenzo[*b*]thiophene as a white solid (870 mg, 43%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.69 (m, 3H), 7.43 (d, *J* = 5.4 Hz, 1H), 7.35 – 7.28 (m, 2H), 4.19 (t, *J* = 7.9 Hz, 1H), 3.02 – 2.94 (m, 1H), 2.91 – 2.78 (m, 1H), 2.43 – 2.35 (m, 1H), 2.20 – 2.02 (m, 2H), 1.95 – 1.83 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.3, 162.6, 139.9, 138.4, 136.2, 134.6 (q, *J* = 32.7 Hz), 132.5, 129.9, 126.8, 125.5 (q, *J* = 3.7 Hz), 124.4, 123.8, 123.5 (q, *J* = 272.8 Hz), 122.7, 49.2, 34.9, 30.0, 22.5; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 1747, 1511, 1411, 1277, 1074, 860; **HRMS m/z (ESI)** calcd for $C_{21}H_{16}F_3NNaO_2S$ $(M + Na)^+$ 426.0746, found 426.0750.

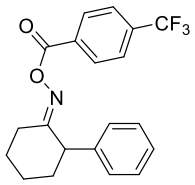
2-Phenylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1aj) (*E*/*Z* mixture)



1aj

According to the general procedure, **1aj** was prepared from the corresponding ketone which was synthesized according to the reported literature[2] as a brown solid (3.0 mmol, 553 mg, 55%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 8.2 Hz, 1.35H), 7.73 (d, *J* = 8.4 Hz, 1.38H), 7.51 – 7.46 (m, 1.3H), 7.43 – 7.24 (m, 5H), 4.72 – 4.53 (m, 1H), 3.30 – 3.07 (m, 2H), 2.68 – 2.58 (m, 1H), 2.34 – 2.16 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.6, 169.9, 162.7, 138.9, 138.4, 134.7 (q, *J* = 32.8 Hz), 132.3, 130.0, 129.8, 129.0, 128.7, 127.4, 127.3, 127.2, 127.1, 125.5 (q, *J* = 3.7 Hz), 125.2 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 272.7 Hz), 51.4, 49.6, 29.5, 29.3, 24.4, 23.2; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.15 , -63.19; **ATR-FTIR (cm $^{-1}$):**1750, 1654, 1501, 1454, 1266, 708; **HRMS m/z (ESI)** calcd for $C_{18}H_{14}F_3NNaO_2$ $(M + Na)^+$ 356.0869, found 356.0873.

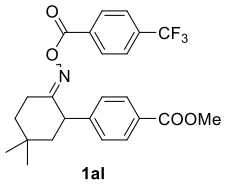
2-Phenylcyclohexan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1ak)



1ak

According to the general procedure, **1ak** was prepared from the commercially available ketone (2.0 mmol, CAS:1444-65-1) as a white solid (594 mg, 82%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.19 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.32 – 7.24 (m, 1H), 4.02 (t, *J* = 4.9 Hz, 1H), 2.98 – 2.93 (m, 1H), 2.57 – 2.44 (m, 1H), 2.37 – 2.32 (m, 1H), 2.12 – 2.05 (m, 1H), 1.88 – 1.68 (m, 4H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.1, 163.0, 138.7, 134.6 (q, *J* = 32.7 Hz), 132.7, 130.0, 128.6, 127.7, 126.8, 125.5 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 273.1 Hz), 45.5, 31.0, 26.4, 25.4, 22.1; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm^{-1}):**1748, 1635, 1515, 1464, 1260, 1110, 710; **HRMS m/z (ESI)** calcd for $C_{20}H_{19}F_3NO_2$ $(M + H)^+$ 362.1362, found 362.1366.

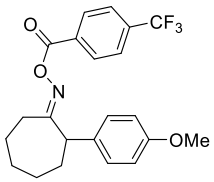
Methyl 4-(5,5-dimethyl-2-(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclohexyl) benzoate (1al) (*E*/*Z* mixture)



1al

According to the general procedure, **1al** was prepared from the corresponding ketone which was synthesized according to the reported literature[3] as a white solid (3.0 mmol, 906 mg, 68%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 8.1 Hz, 1.5H), 8.03 – 7.98 (m, 2H), 7.72 – 7.68 (m, 2H), 7.55 (d, *J* = 8.3 Hz, 0.52H), 7.41 (d, *J* = 8.3 Hz, 1.51H), 7.31 (d, *J* = 8.2 Hz, 0.56H), 4.42 (t, *J* = 7.0 Hz, 0.34H), 3.90 (s, 3H), 3.88 – 3.86 (m, 0.64H), 3.16 (dt, *J* = 15.2, 4.4 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.04 – 1.98 (m, 1H), 1.90 – 1.59 (m, 3H), 1.18 (s, 2H), 1.04 (s, 1H), 1.02 (s, 2H), 0.85 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 170.0, 167.0, 162.7, 146.1, 144.7, 132.6, 130.2, 129.9, 129.8, 129.7, 128.8, 126.7, 125.5 (q, *J* = 3.6 Hz), 125.4, 125.3, 52.0, 47.0, 45.5, 44.1, 40.9, 38.0, 36.9, 31.1, 30.9, 30.2, 30.1, 29.2, 27.5, 25.1, 23.7; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.17 , -63.24; **ATR-FTIR (cm^{-1}):**1747, 1720, 1600, 1545, 1462, 1380, 1260, 1069, 720; **HRMS m/z (ESI)** calcd for $C_{24}H_{24}F_3NNaO_4$ $(M + Na)^+$ 470.1550, found 470.1556.

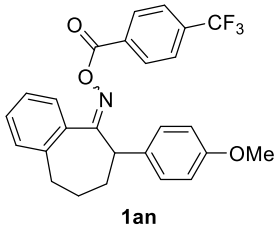
2-(4-Methoxyphenyl)cycloheptan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1am)



1am

According to the general procedure, **1am** was prepared from the corresponding ketone which was synthesized according to the reported literature[3] as a brown solid (3.0 mmol, 739 mg, 61%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.06 (dd, *J* = 10.8, 6.7 Hz, 1H), 3.79 (s, 3H), 3.12 – 3.08 (m, 1H), 2.39 – 2.33 (m, 1H), 2.10 (td, *J* = 12.5, 2.4 Hz, 1H), 1.99 – 1.90 (m, 4H), 1.62 – 1.55 (m, 1H), 1.46 – 1.39 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.9, 162.8, 158.5, 134.6 (q, *J* = 32.7 Hz), 132.7, 132.5, 129.9, 128.3, 125.5 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.7 Hz), 113.9, 55.2, 47.6, 30.9, 30.7, 27.4, 26.3, 25.4; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.2; **ATR-FTIR (cm^{-1}):** 1747, 1600, 1515, 1462, 1293, 1201, 1060, 855; **HRMS m/z (ESI)** calcd for $C_{22}H_{22}F_3NNaO_3$ $(M + Na)^+$ 428.1444, found 428.1444.

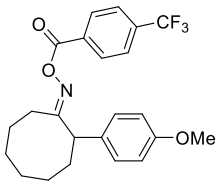
6-(4-Methoxyphenyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1an) (*E*/*Z* mixture)



1an

According to the general procedure, **1an** was prepared from the corresponding ketone which was synthesized according to the reported literature[3] as a brown solid (3.0 mmol, 670 mg, 49%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.68 – 7.54 (m, 3H), 7.47 – 7.32 (m, 2H), 7.24 – 7.21 (m, 2H), 6.87 – 6.80 (m, 2H), 4.28 – 4.24 (m, 1H), 3.78 (s, 3H), 2.97 – 2.74 (m, 2H), 2.12 – 1.62 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.3, 162.6, 158.3, 138.9, 134.8, 134.3, 133.0, 132.3, 130.7, 130.1, 129.9, 129.6, 129.3, 129.0, 128.5, 128.5, 128.1, 127.0, 125.7, 125.3 (q, *J* = 3.9 Hz), 114.2, 113.9, 55.3, 44.7, 31.9, 30.5, 24.0; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.1, -63.2; **ATR-FTIR (cm^{-1}):**1752, 1611, 1511, 1324, 1248, 1075, 747; **HRMS m/z (ESI)** calcd for $C_{26}H_{22}F_3NNaO_3$ $(M + Na)^+$ 476.1444, found 476.1447.

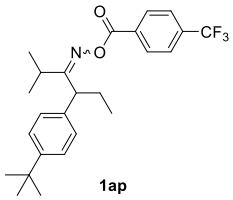
2-(4-Methoxyphenyl)cyclooctan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1ao)



1ao

According to the general procedure, **1ao** was prepared from the corresponding ketone which was synthesized according to the reported literature[3] as a brown solid (3.0 mmol, 695 mg, 55%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.94 (dd, *J* = 12.7, 3.1 Hz, 1H), 3.78 (s, 3H), 2.79 (dt, *J* = 12.7, 4.1 Hz, 1H), 2.38 – 2.24 (m, 1H), 2.09 – 2.00 (m, 2H), 1.91 – 1.72 (m, 6H), 1.51 – 1.40 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.9, 162.8, 158.7, 134.6 (q, *J* = 32.9 Hz), 132.7, 132.2, 129.9, 128.5, 125.6 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.7 Hz), 113.9, 55.2, 47.7, 27.1, 26.8, 26.4, 26.3, 24.8, 24.8; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.2; **ATR-FTIR (cm $^{-1}$):**1748, 1545, 1460, 1290, 1209, 1066, 741; **HRMS m/z (ESI)** calcd for $C_{23}H_{24}F_3NNaO_3$ $(M + Na)^+$ 442.1600, found 442.1602.

4-(4-(*tert*-Butyl)phenyl)-2-methylhexan-3-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1ap) (*E*/*Z* mixture)



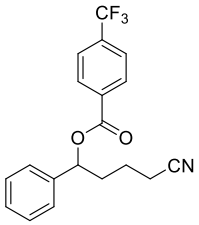
1ap

According to the general procedure, **1ap** was prepared from the corresponding ketone which was synthesized according to the reported literature[3] as a colorless (3.0 mmol, 562 mg, 43%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 8.1 Hz, 0.6H), 8.08 (d, *J* = 8.1 Hz, 1.38H), 7.76 – 7.70 (m, 2H), 7.38 – 7.28 (m, 2.59H), 7.20 (d, *J* = 8.3 Hz, 1.41H), 4.46 – 4.29 (m, 0.69H), 3.61 (t, *J* = 7.6 Hz, 0.24H), 3.06 – 2.99 (m, 0.23H), 2.67 – 2.60 (m, 0.68H), 2.19 – 1.84 (m, 2H), 1.31 – 1.28 (m, 11H), 1.20 (d, *J* = 7.0 Hz, 1H), 1.05 (t, *J* = 7.4 Hz, 2H), 0.99 – 0.94 (m, 3H), 0.90 (d, *J* = 7.1 Hz, 1H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.9, 175.1, 162.8, 150.0, 150.0, 136.7, 135.6, 134.5 (q, *J* = 32.7 Hz), 132.8, 130.0, 128.1, 127.5, 125.5, 125.4, 123.5 (q, *J* = 272.8 Hz), 50.7, 46.9, 34.4, 32.1, 31.3, 31.3, 30.5, 26.7, 24.0, 22.0, 21.7, 19.4, 19.3, 12.7, 12.4; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.15, -63.16; **ATR-FTIR (cm $^{-1}$):**1749, 1601, 1515, 1467, 1071, 741; **HRMS m/z (ESI)** calcd for $C_{25}H_{30}F_3NNaO_2$ $(M + Na)^+$ 456.2121,

found 456.2126.

3. Experimental Procedures and Characterization of Photoinduced Fragmentation-Rearrangement

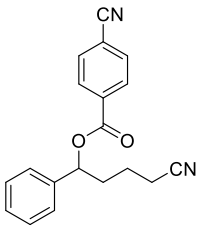
4-Cyano-1-phenylbutyl 4-(trifluoromethyl)benzoate (2aa)



2aa

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1aa** (0.2 mmol, 69.4 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 10:1) to afford 56.1 mg (81%) of **2aa** as a colorless oil: **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.19 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.32 (m, 5H), 6.04 (dd, *J* = 7.6, 5.9 Hz, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.30 – 2.22 (m, 1H), 2.15 – 2.08 (m, 1H), 1.86 – 1.67 (m, 2H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 164.5, 139.2, 134.6 (q, *J* = 32.7 Hz), 133.2, 130.0, 128.8, 128.5, 126.2, 125.4 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz), 119.1, 76.1, 35.2, 21.6, 16.9; **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 2246, 1727, 1412, 1590, 1515, 1462, 1171, 1064, 775; **HRMS m/z (ESI)** calcd for $C_{19}H_{17}F_3NO_2$ $(M + H)^+$ 348.1206, found 348.1203.

4-Cyano-1-phenylbutyl 4-cyanobenzoate (2ba)

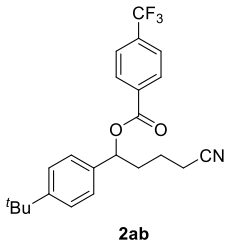


2ba

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ba** (0.2 mmol, 60.8 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 5:1) to afford 46.6 mg (77%) of **2ba** as a colorless oil: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.32 (m, 5H), 6.02 (dd, *J* = 7.5, 6.1 Hz, 1H), 2.39 (t, *J* = 7.1 Hz, 2H), 2.29 – 2.21 (m, 1H), 2.14 – 2.08 (m, 1H), 1.83 – 1.66 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.0, 139.0, 133.7, 132.2, 130.0, 128.8, 128.5, 126.2, 119.0, 117.8, 116.5, 76.4, 35.0, 21.5, 16.9; **ATR-FTIR (cm $^{-1}$):** 2245, 2224, 1722, 1659, 1632, 1412, 1310, 1019, 762; **HRMS m/z (ESI)** calcd for $C_{19}H_{16}N_2NaO_2$ $(M + Na)^+$ 327.1104, found 327.1099.

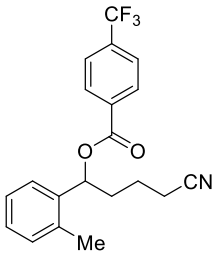
1-(4-(*tert*-Butyl)phenyl)-4-cyanobutyl 4-(trifluoromethyl)benzoate (2ab)



2ab

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ab** (0.2 mmol, 80.6 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 10:1) to afford 62.5 mg (78%) of **2ab** as a colorless oil: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.34 (m, 4H), 6.03 (dd, *J* = 7.5, 6.1 Hz, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.29 – 2.22 (m, 1H), 2.14 – 2.07 (m, 1H), 1.84 – 1.68 (m, 2H), 1.31 (s, 9H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.5, 151.5, 136.1, 134.5 (q, *J* = 32.6 Hz), 133.3, 130.0, 126.1, 125.7, 125.4 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 272.8 Hz), 119.1, 76.0, 35.1, 31.2, 21.7, 16.9; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 2246, 1723, 1513, 1432, 1324, 1245, 1066, 775; **HRMS m/z (ESI)** calcd for $C_{23}H_{24}F_3NNaO_2$ $(M + Na)^+$ 426.1651, found 426.1655.

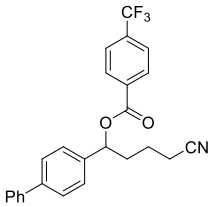
4-Cyano-1-(o-tolyl)butyl 4-(trifluoromethyl)benzoate (2ac)



2ac

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ab** (0.2 mmol, 60.1 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 10:1) to afford 60.1 mg (83%) of **2ab** as a yellow oil: **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.19 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.42 (m, 1H), 7.24 – 7.18 (m, 3H), 6.26 (dd, *J* = 8.2, 5.2 Hz, 1H), 2.49 (s, 3H), 2.42 (t, *J* = 7.1 Hz, 2H), 2.27 – 2.19 (m, 1H), 2.11 – 2.04 (m, 1H), 1.91 – 1.83 (m, 1H), 1.80 – 1.71 (m, 1H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 164.5, 137.8, 134.9, 134.6 (q, *J* = 32.6 Hz), 133.2, 130.7, 130.0, 128.2, 126.5, 125.5 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 272.7 Hz), 72.9, 34.6, 21.7, 19.2, 17.0; **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):**2247, 1725, 1603, 1556, 1328, 1068, 766; **HRMS m/z (ESI)** calcd for $C_{20}H_{19}F_3NO_2$ $(M + H)^+$ 362.1362, found 362.1361.

1-([1,1'-Biphenyl]-4-yl)-4-cyanobutyl 4-(trifluoromethyl)benzoate (2ad)

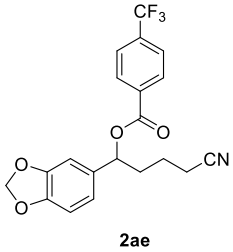


2ad

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ad** (0.2 mmol, 84.6 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 7:1) to afford 56.9 mg (67%) of **2ab** as a colorless oil: **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.22 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.58 (m, 4H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 6.09 (dd, *J* = 7.5, 6.0 Hz, 1H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.34 – 2.27 (m, 1H), 2.19 – 2.12 (m, 1H), 1.89 – 1.73 (m, 2H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 164.5, 141.5, 140.4, 138.2, 134.6 (q, *J* = 32.6 Hz),

133.2, 130.0, 128.8, 127.5, 127.1, 126.7, 125.5 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 272.8 Hz), 119.1, 76.0, 35.1, 21.6, 17.0; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 2247, 1725, 1596, 1536, 1469, 1085, 796; **HRMS m/z (ESI)** calcd for $C_{25}H_{20}F_3NNaO_2$ $(M + Na)^+$ 446.1338, found 446.1334.

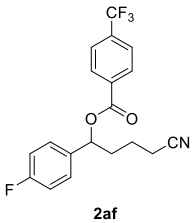
1-(Benzo[*d*][1,3]dioxol-5-yl)-4-cyanobutyl 4-(trifluoromethyl)benzoate (2ae)



2ae

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ae** (0.2 mmol, 78.2 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 5:1) to afford 67.4 mg (86%) of **2ag** as a colorless oil: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.2 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 6.91 – 6.88 (m, 2H), 6.79 (d, *J* = 7.9 Hz, 1H), 5.96 – 5.95 (m, 2H), 5.92 (dd, *J* = 7.5, 6.3 Hz, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.26 – 2.18 (m, 1H), 2.09 – 2.02 (m, 1H), 1.82 – 1.66 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.4, 148.0, 147.7, 134.6 (q, *J* = 32.6 Hz), 133.2, 133.0, 130.0, 125.4 (q, *J* = 3.8 Hz), 123.5 (q, *J* = 272.8 Hz), 120.3, 119.1, 108.3, 106.6, 101.2, 76.1, 35.1, 21.6, 16.9; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 2246, 1722, 1565, 1413, 1336, 1069, 765; **HRMS m/z (ESI)** calcd for $C_{20}H_{16}F_3NNaO_4$ $(M + Na)^+$ 414.0924, found 414.0925.

4-Cyano-1-(4-fluorophenyl)butyl 4-(trifluoromethyl)benzoate (2af)

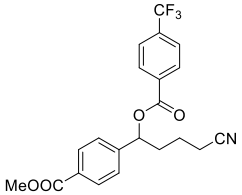


2af

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1af** (0.2 mmol, 73.0 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 7:1) to afford 40.2 mg (55%) of **2af** as a colorless oil: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.00 (dd, *J* = 7.8, 5.9 Hz, 1H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.29 – 2.21 (m, 1H), 2.12 – 2.04 (m, 1H), 1.84 – 1.67 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.5, 162.6 (d, *J* = 247.5 Hz), 135.1 (d, *J* = 3.1 Hz), 134.7 (q, *J* = 32.7 Hz), 133.0, 130.0, 128.2 (d, *J* = 8.2 Hz), 125.5 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz), 119.0, 115.8 (d, *J* = 21.7 Hz), 75.5, 35.1, 21.6, 17.0; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.2, -113.0; **ATR-FTIR (cm $^{-1}$):**2247, 1723, 1068, 1550, 1466, 1069, 758; **HRMS m/z (ESI)** calcd for $C_{19}H_{15}F_4NNaO_2$ $(M + Na)^+$ 388.0931, found 388.0926.

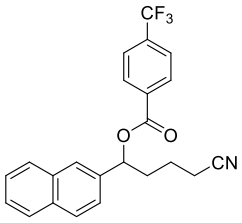
4-Cyano-1-(4-(methoxycarbonyl)phenyl)butyl 4-(trifluoromethyl)benzoate (2ag)



2ag

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ag** (0.2 mmol, 81.0 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 7:1) to afford 56.5 mg (70%) of **2ag** as a yellow oil: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.98 (t, *J* = 6.9 Hz, 1H), 3.80 (s, 3H), 2.39 (t, *J* = 7.1 Hz, 2H), 2.29 – 2.21 (m, 1H), 2.12 – 2.05 (m, 1H), 1.82 – 1.64 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.5, 159.7, 134.5 (q, *J* = 32.6 Hz), 133.3, 131.2, 130.0, 127.8, 125.4 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 272.8 Hz), 119.1, 114.1, 75.9, 55.2, 35.0, 21.7, 16.9; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):**2246, 1720, 1515, 1412, 1066, 747; **HRMS m/z (ESI)** calcd for $C_{21}H_{18}F_3NNaO_4$ $(M + Na)^+$ 428.1080, found 428.1083.

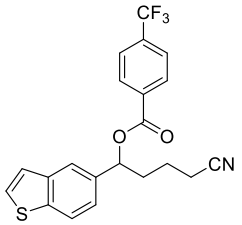
4-Cyano-1-(naphthalen-2-yl)butyl 4-(trifluoromethyl)benzoate (2ah)



2ah

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ag** (0.2 mmol, 79.4 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 7:1) to afford 58.6 mg (74%) of **2ah** as a colorless oil: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.21 (d, *J* = 8.1 Hz, 2H), 7.90 – 7.83 (m, 4H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.50 (m, 3H), 6.21 (t, *J* = 7.0 Hz, 1H), 2.41 (t, *J* = 7.1 Hz, 2H), 2.37 – 2.31 (m, 1H), 2.25 – 2.16 (m, 1H), 1.91 – 1.69 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.5, 136.5, 134.6 (q, *J* = 32.7 Hz), 133.2, 133.0, 130.0, 128.8, 128.0, 127.7, 126.5, 126.4, 125.7, 125.5 (q, *J* = 3.7 Hz), 123.7, 123.5 (q, *J* = 272.8 Hz), 119.0, 76.3, 35.0, 21.7, 17.0. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 2247, 1724, 1609, 1566, 1411, 1077, 699; **HRMS m/z (ESI)** calcd for $C_{23}H_{18}F_3NNaO_2$ $(M + Na)^+$ 420.1182, found 420.1183.

1-(Benzo[*b*]thiophen-5-yl)-4-cyanobutyl 4-(trifluoromethyl)benzoate (2ai)

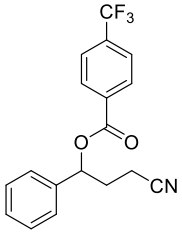


2ai

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ai** (0.2 mmol, 90.2 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 7:1) to afford 68.9 mg (76%) of **2ai** as a colorless oil: **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 9.3 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 5.4 Hz, 1H), 7.42 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.34 (d, *J* = 5.5 Hz, 1H), 6.16 (t, *J* = 7.0 Hz, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.37 – 2.30 (m, 1H), 2.21 – 2.14 (m, 1H), 1.87 – 1.69 (m, 2H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 164.5, 139.7, 139.6, 135.4,

134.5 (q, *J* = 32.7 Hz), 133.2, 130.0, 127.5, 125.4 (q, *J* = 3.6 Hz), 123.7, 123.5 (q, *J* = 272.9 Hz), 122.9, 122.3, 121.6, 119.1, 76.4, 35.3, 21.6, 16.9; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 2245, 1721, 1510, 1375, 1276, 1065, 703; **HRMS m/z (ESI)** calcd for $C_{21}H_{16}F_3NNaO_2S$ $(M + H)^+$ 426.0746, found 426.0748.

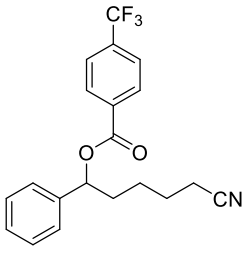
3-Cyano-1-phenylpropyl 4-(trifluoromethyl)benzoate (2aj)



2aj

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1aj** (0.2 mmol, 66.6 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 10:1) to afford 35.8 mg (54%) of **2aj** as a colorless oil: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.21 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.35 (m, 5H), 6.11 (t, *J* = 5.9 Hz, 1H), 2.49 – 2.30 (m, 4H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.3, 138.2, 134.8 (q, *J* = 32.7 Hz), 132.9, 130.2, 129.0, 128.8, 126.1, 125.5 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 272.8 Hz), 118.8, 32.0, 13.7; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.2; **ATR-FTIR (cm $^{-1}$):**2246, 1726, 1611, 1510, 1507, 1436, 1066, 788; **HRMS m/z (ESI)** calcd for $C_{18}H_{14}F_3NNaO_2$ $(M + Na)^+$ 356.0869, found 356.0864.

5-Cyano-1-phenylpentyl 4-(trifluoromethyl)benzoate (2ak)

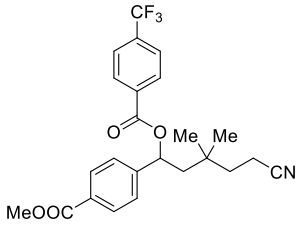


2ak

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ak** (0.2 mmol, 72.2 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 10:1) to afford 34.9 mg (48%) of **2ak** as a

colorless oil: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.31 (m, 5H), 6.00 (t, *J* = 6.8 Hz, 1H), 2.34 (t, *J* = 7.0 Hz, 2H), 2.17 – 2.10 (m, 1H), 2.01 – 1.94 (m, 1H), 1.75 – 1.69 (m, 2H), 1.64 – 1.45 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.6, 139.7, 134.5 (q, *J* = 32.8 Hz), 133.4, 130.0, 128.7, 128.3, 126.3, 125.4 (q, *J* = 3.6 Hz), 123.6 (d, *J* = 272.7 Hz), 119.3, 76.8, 35.5, 25.1, 24.6, 17.0; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 2247, 1726, 1516, 1466, 1079, 762; **HRMS m/z (ESI)** calcd for $C_{20}H_{18}F_3NNaO_2$ $(M + Na)^+$ 384.1182, found 384.1177.

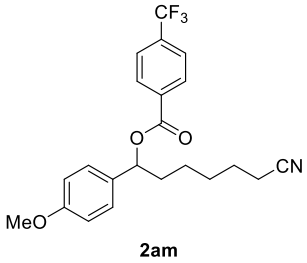
6-Cyano-1-(4-methoxyphenyl)hexyl 4-(trifluoromethyl)benzoate (2al)



2al

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1al** (0.2 mmol, 89.5 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 7:1) to afford 48.5 mg (54%) of **2al** as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.1 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 6.14 (dd, *J* = 9.3, 3.1 Hz, 1H), 3.90 (s, 3H), 2.43 – 2.25 (m, 2H), 2.19 (dd, *J* = 15.1, 9.3 Hz, 1H), 1.82 – 1.65 (m, 3H), 1.03 (d, *J* = 7.2 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 164.3, 146.1, 134.8 (q, *J* = 32.8 Hz), 132.9, 130.1, 130.1, 130.0, 126.1, 125.6 (q, *J* = 3.6 Hz), 123.5 (d, *J* = 272.8 Hz), 120.0, 74.1, 52.2, 47.4, 37.8, 33.1, 26.8, 26.8, 12.4; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.2; **ATR-FTIR (cm $^{-1}$):** 2246, 1727, 1720, 1600, 1545, 1412, 1383, 1264, 1070, 852; **HRMS m/z (ESI)** calcd for $C_{24}H_{24}F_3NNaO_4$ $(M + Na)^+$ 470.1550, found 470.1556.

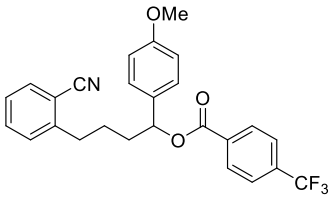
6-Cyano-1-(4-methoxyphenyl)hexyl 4-(trifluoromethyl)benzoate (2am)



2am

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1am** (0.2 mmol, 81.0 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 7:1) to afford 51.6 mg (63%) of **2am** as a colorless oil: **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 5.95 (t, *J* = 7.0 Hz, 1H), 3.80 (s, 3H), 2.31 (t, *J* = 7.0 Hz, 2H), 2.14 – 2.07 (m, 1H), 1.96 – 1.89 (m, 1H), 1.67 – 1.61 (m, 2H), 1.54 – 1.28 (m, 4H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 164.6, 159.5, 134.3 (q, *J* = 32.6 Hz), 133.6, 132.0, 129.9, 127.9, 125.3 (q, *J* = 3.6 Hz), 123.6 (q, *J* = 272.7 Hz), 119.6, 113.9, 76.9, 55.2, 35.8, 28.3, 25.2, 24.8, 17.0; **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 2247, 1727, 1514, 1327, 1085, 1065, 786; **HRMS m/z (ESI)** calcd for $C_{22}H_{22}F_3NNaO_3$ $(M + Na)^+$ 428.1444, found 428.1445.

4-(2-Cyanophenyl)-1-(4-methoxyphenyl)butyl 4-(trifluoromethyl)benzoate (2an)

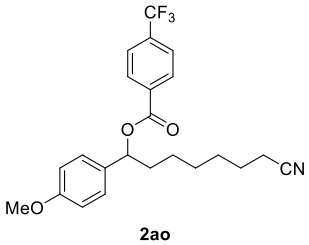


2an

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1an** (0.2 mmol, 90.6 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 7:1) to afford 69.1 mg (76%) of **2an** as a colorless oil: **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.17 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.59 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.49 (td, *J* = 7.7, 1.3 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.27 (m, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.01 – 5.98 (m, 1H), 3.79 (s,

3H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.22 – 2.15 (m, 1H), 2.04 – 1.96 (m, 1H), 1.87 – 1.65 (m, 2H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 164.6, 159.4, 145.7, 134.3 (q, *J* = 32.7 Hz), 133.6, 132.8, 132.8, 131.9, 130.0, 129.3, 127.9, 126.6, 125.3 (q, *J* = 3.6 Hz), 123.6 (q, *J* = 272.7 Hz), 118.0, 113.9, 112.3, 76.7, 55.2, 35.6, 34.1, 26.9; **^{19}F NMR (471 MHz, CDCl$_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 2246, 2224, 1727, 1565, 1512, 1413, 1066, 778; **HRMS m/z (ESI)** calcd for $C_{26}H_{22}F_3NNaO_3$ $(M + Na)^+$ 476.1444, found 476.1444.

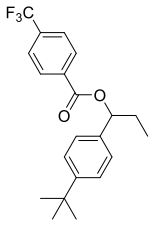
7-Cyano-1-(4-methoxyphenyl)heptyl 4-(trifluoromethyl)benzoate (2ao)



2ao

Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ao** (0.2 mmol, 83.3 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. 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 (PE : EA = 7:1) to afford 57.9 mg (69%) of **2ao** as a colorless oil: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.16 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.94 (t, *J* = 7.0 Hz, 1H), 3.80 (s, 3H), 2.31 (t, *J* = 7.1 Hz, 2H)., 2.12 – 2.05 (m, 1H), 1.95 – 1.87 (m, 1H), 1.66 – 1.59 (m, 2H), 1.48 – 1.26 (m, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.7, 159.5, 134.4 (q, *J* = 32.7 Hz), 133.8, 132.2, 130.0, 128.0, 125.4 (q, *J* = 3.4 Hz), 123.6 (q, *J* = 272.6 Hz), 119.7, 114.0 , 77.0, 55.3, 36.0, 28.5, 25.3, 25.2, 17.1; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):**2246, 1725, 1514, 1332, 1277, 1066, 795; **HRMS m/z (ESI)** calcd for $C_{23}H_{24}F_3NNaO_3$ $(M + Na)^+$ 442.1600, found 442.1595.

1-(4-(*tert*-Butyl)phenyl)propyl 4-(trifluoromethyl)benzoate (2ap)

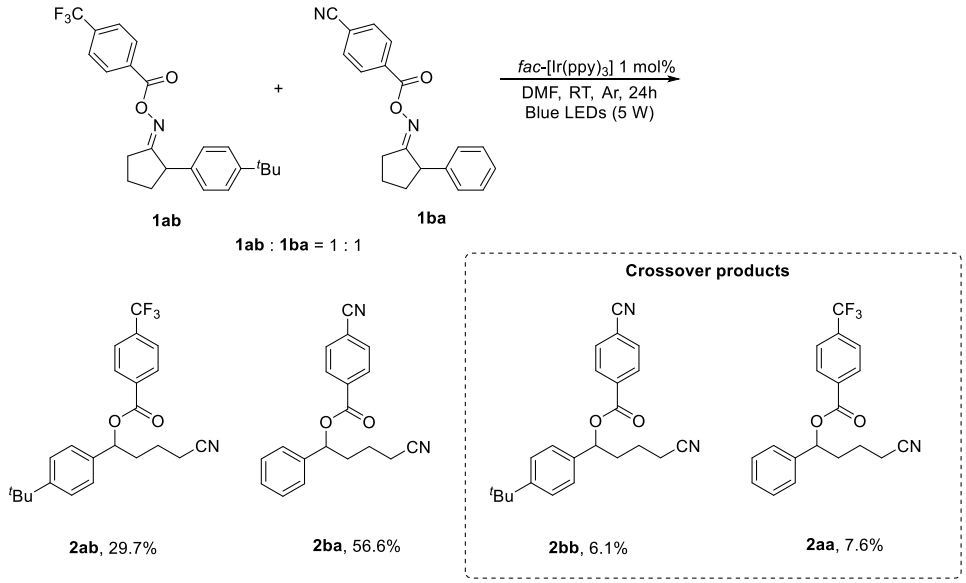


2ap

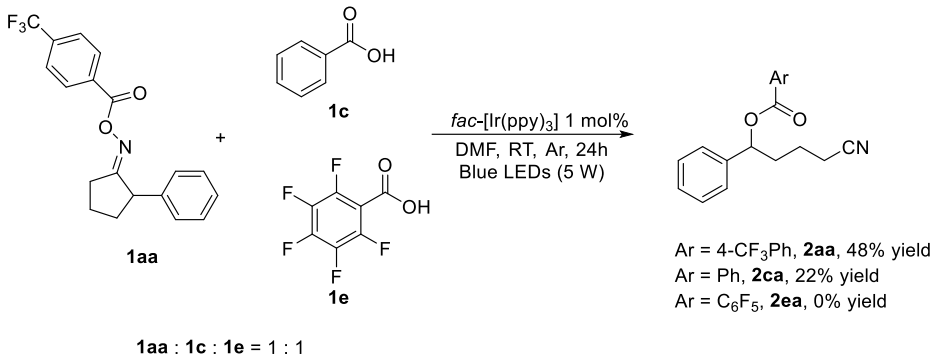
Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ap** (0.2 mmol, 86.7 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute

dry 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 for 24 h at room temperature. 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 (PE : EA = 50:1) to afford 37.3 mg (51%) of **2ap** as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.33 (m, 4H), 5.96 – 5.88 (m, 1H), 2.13 – 2.04 (m, 1H), 2.02 – 1.91 (m, 1H), 1.31 (s, 9H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 151.0, 137.0, 134.3 (d, *J* = 32.7 Hz), 133.8, 130.0, 126.3, 125.4, 125.4 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 272.5 Hz), 78.6, 34.5, 31.3, 30.0, 10.1; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.1; **ATR-FTIR (cm $^{-1}$):** 1725, 1545, 1512, 1460, 1380, 1259, 1052, 756; **HRMS m/z (ESI)** calcd for $C_{21}H_{23}F_3NaO_2$ $(M + Na)^+$ 387.1542, found 387.1545.

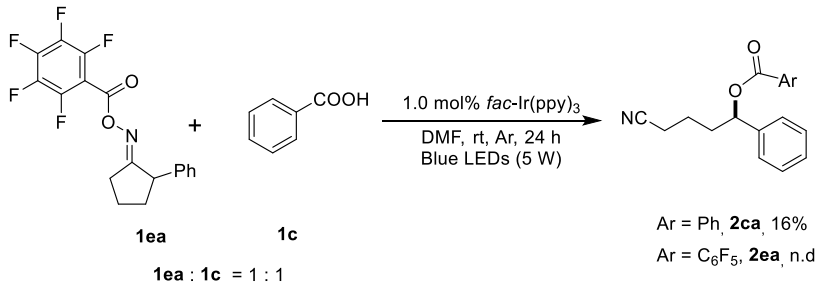
4. Mechanistic Experiments



Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ab** (0.1 mmol, 40.3 mg), **1ba** (0.1 mmol, 30.4 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. The yield was determined by GC-MS.



Flame-dried 25 mL Schlenk tube filled with argon was charged with **1aa** (0.2 mmol, 69.4 mg), **1c** (0.2 mmol, 24.4 mg), **1e** (0.2 mmol, 42.4 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. The yield was determined by GC-MS.



Flame-dried 25 mL Schlenk tube filled with argon was charged with **1ea** (0.2 mmol, 73.8 mg), **1c** (0.2 mmol, 24.4 mg), *fac*-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry 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 for 24 h at room temperature. The yield was determined by GC-MS.

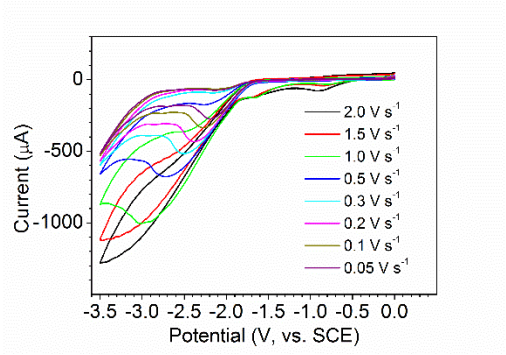
5. Electrochemical studies

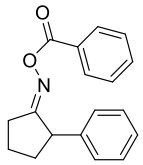
General Experimental Detail

Cyclic voltammograms were recorded in a single cell, constructed from a glass vial, fitted with three electrodes. A glassy carbon disk electrode was used as a working electrode and a platinum wire was used as a counter electrode. The potential was recorded with the reference electrode saturated calomel electrode (SCE) immersed in

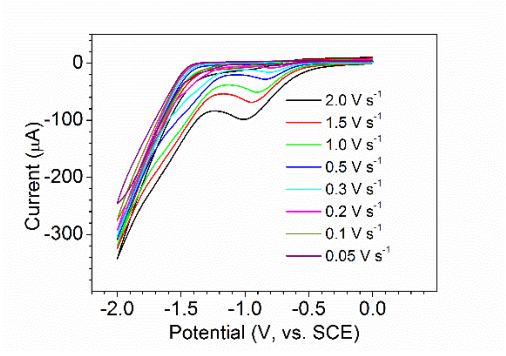
0.1 M solution of Et_4NClO_4 in 10 ml DMF. And the concentration of cycloketoxime esters is 0.05 M. The solutions were deoxygenated with a stream of nitrogen for 15 min before each experiment. Samples were examined at 8 different scan rates 0.05 V s^{-1} – 2.00 V s^{-1}. As a result, we have used the $E_p$max (potential corresponding to the maximum reductive current in the voltammogram from the fastest scan-rate, 2 V s^{-1}).

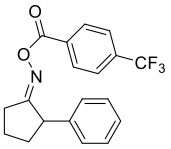
Cyclic voltammograms



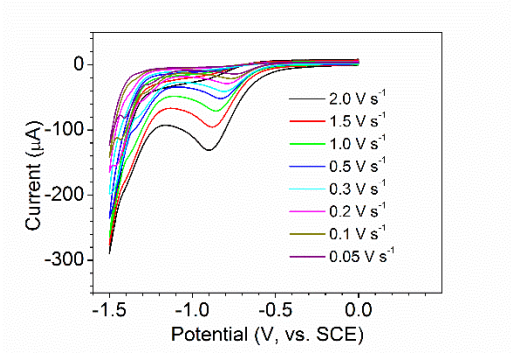


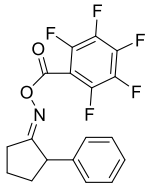
E_p = -2.56 V



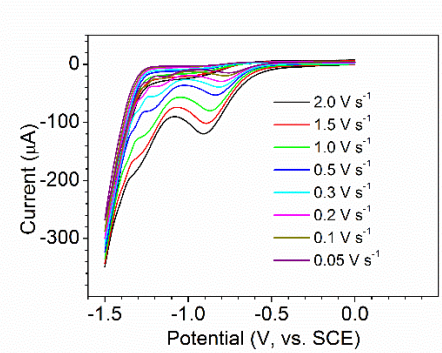


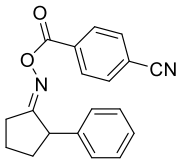
E_p = -1.00 V





E_p = -0.88 V





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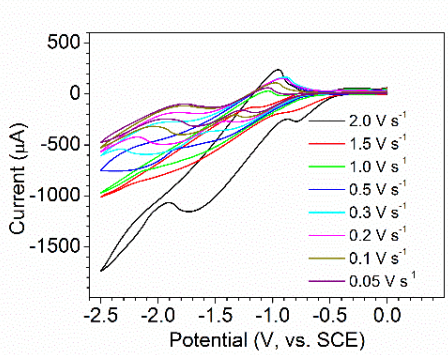
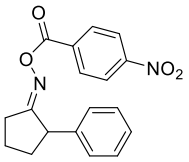




E_p = -1.72 V

6. References

[1] Y. Xu, T.-S. Su, Z.-X. Huang, G.-B. Dong, *Angew. Chem. Int. Ed.*, **2016**, *55*, 2559.

[2] L. Yu, J.-D. Meng, L. Xia, R. Guo, *J. Org. Chem.*, **2009**, *74*, 5087.

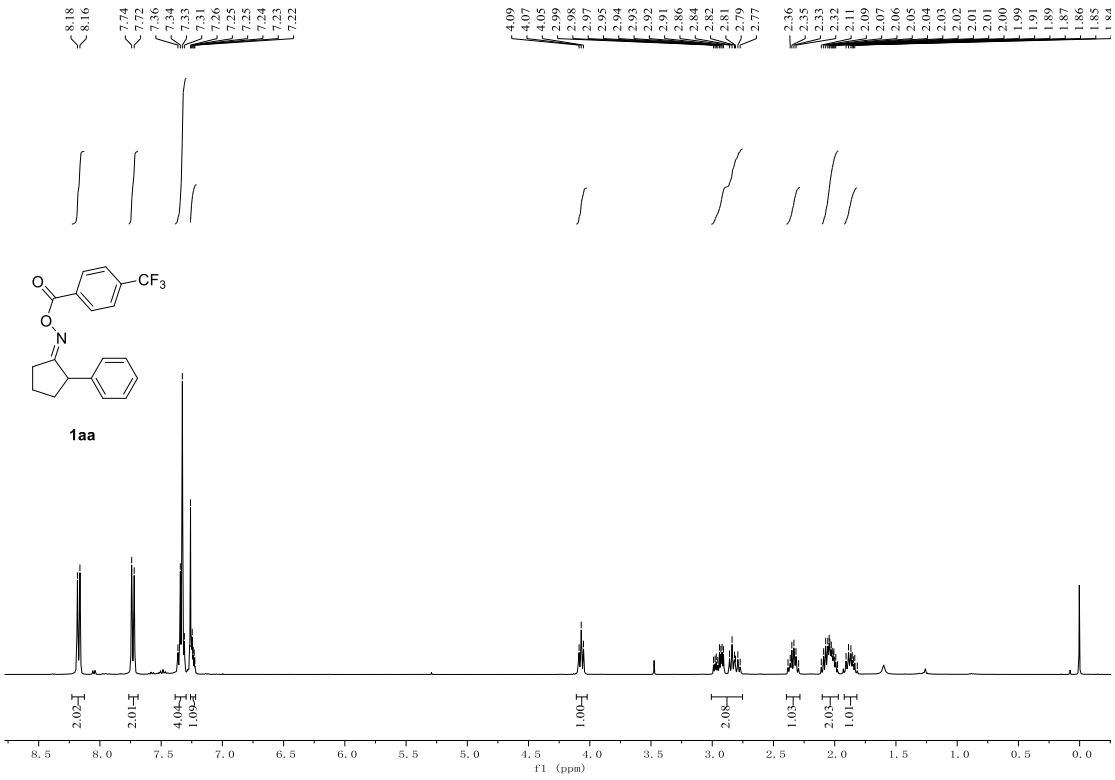
[3] J. M. Fox, X.-H. Huang, A. Chieffi, S. L. Buchwald, *J. Am. Chem. Soc.*, **2000**, *122*, 1360.

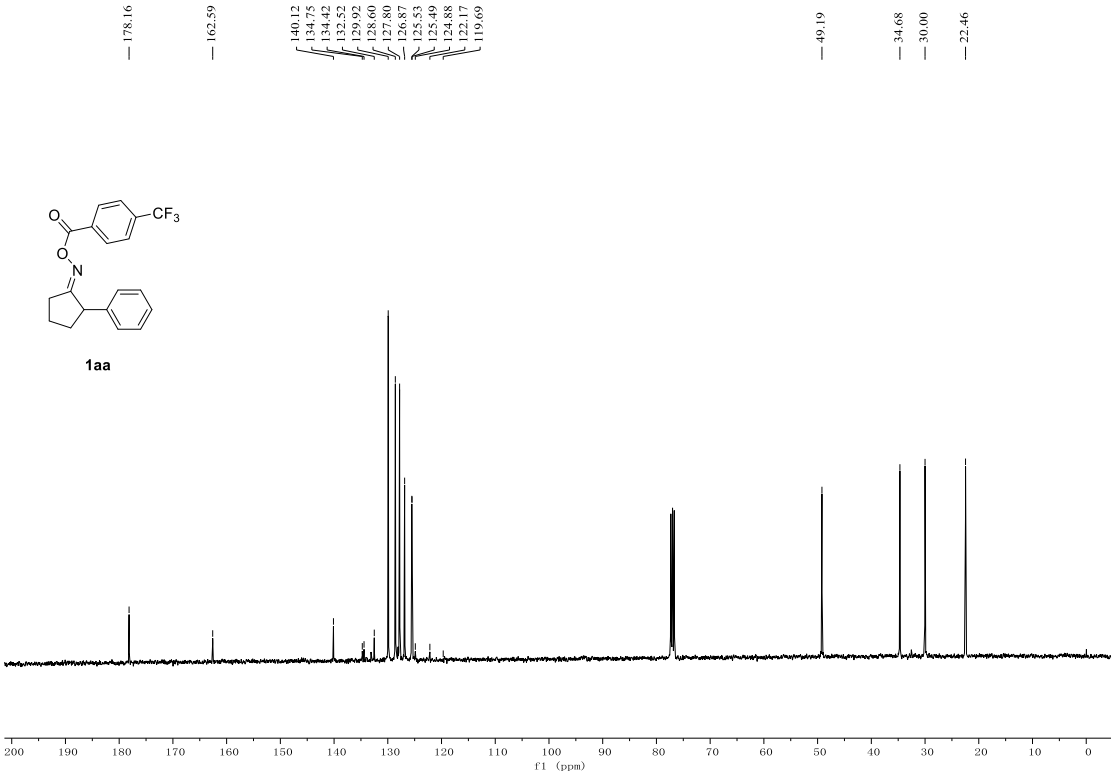
[4] D. C. Moebius, J. S. Kingsbury, *J. Am. Chem. Soc.*, **2009**, *131*, 878.

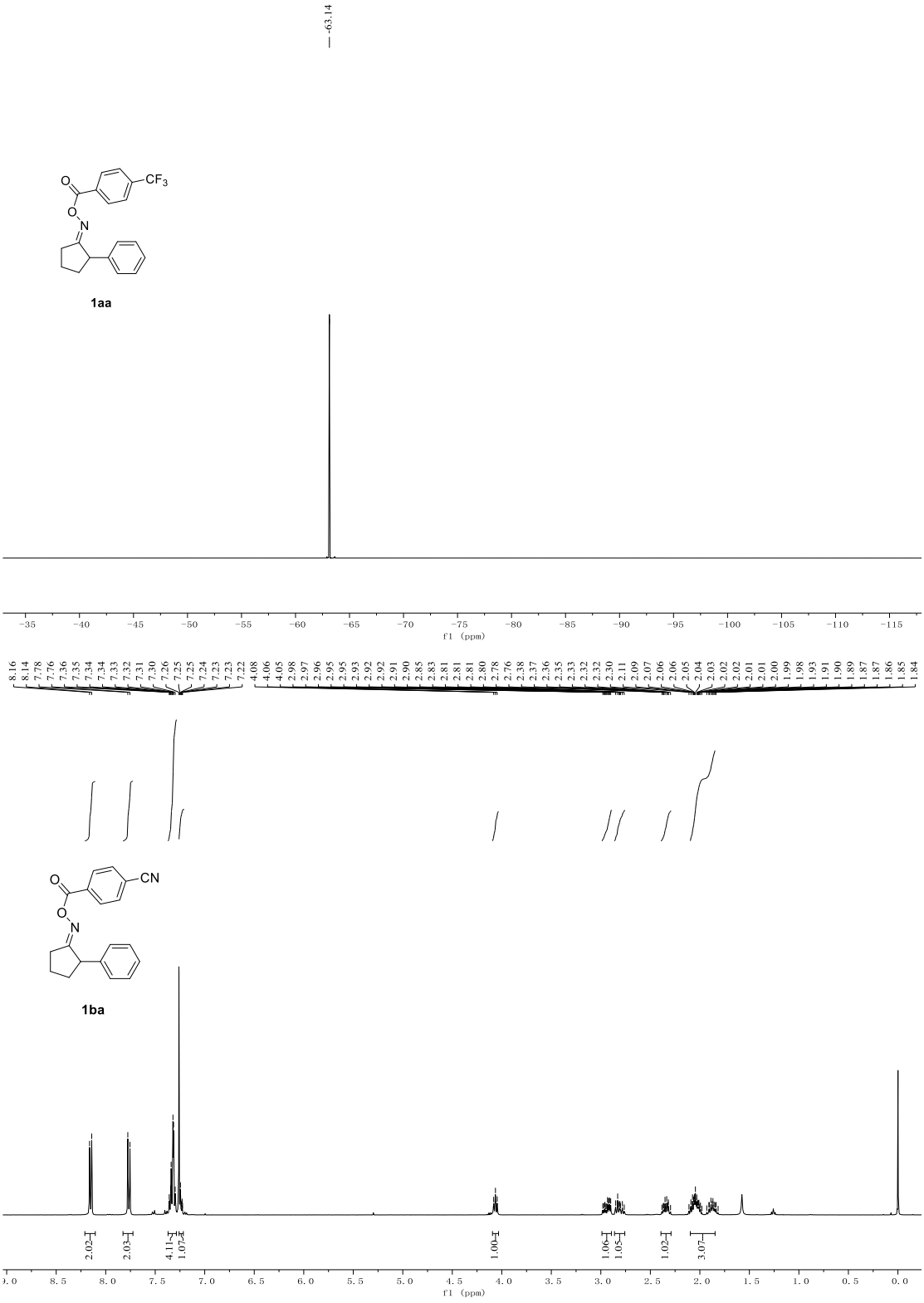
[5] R. Soni, J.-M. Collinson, G. C. Clarkson, M. Wills, *Org. Lett.*, **2011**, *13*, 4304.

[6] H. E. Zimmerman, E. E. Nesterov, *J. Am. Chem. Soc.*, **2002**, *124*, 2818.

7. Copies of NMR Spectra



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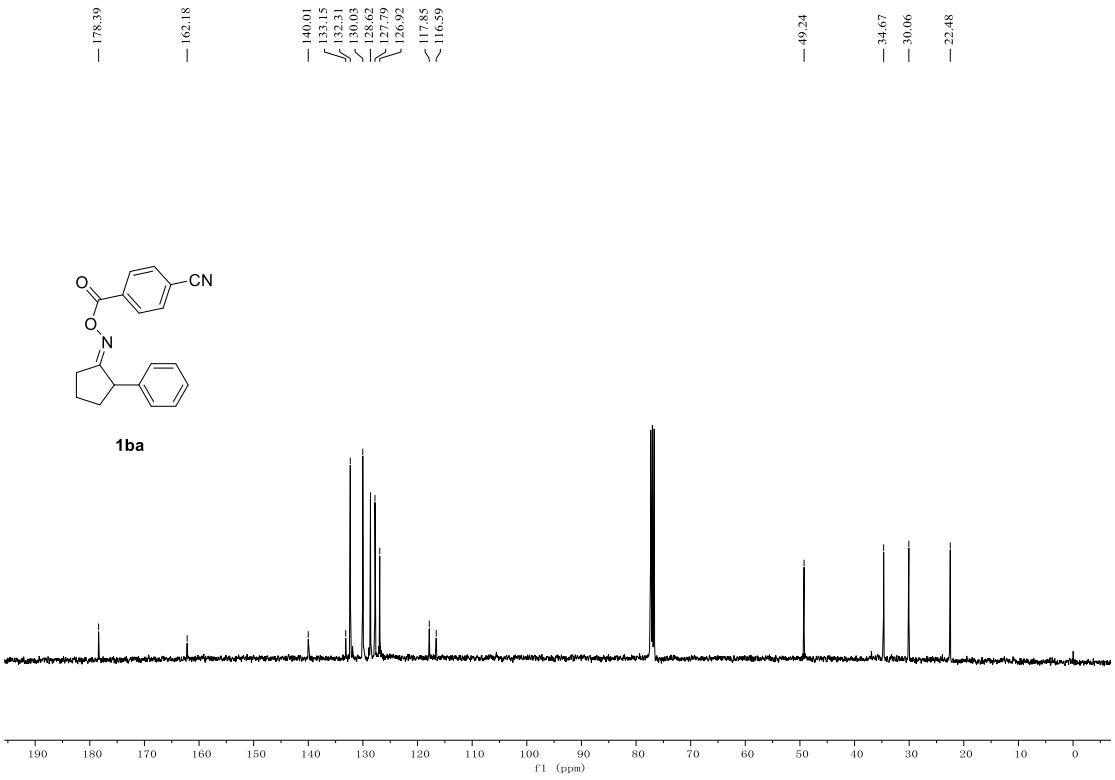
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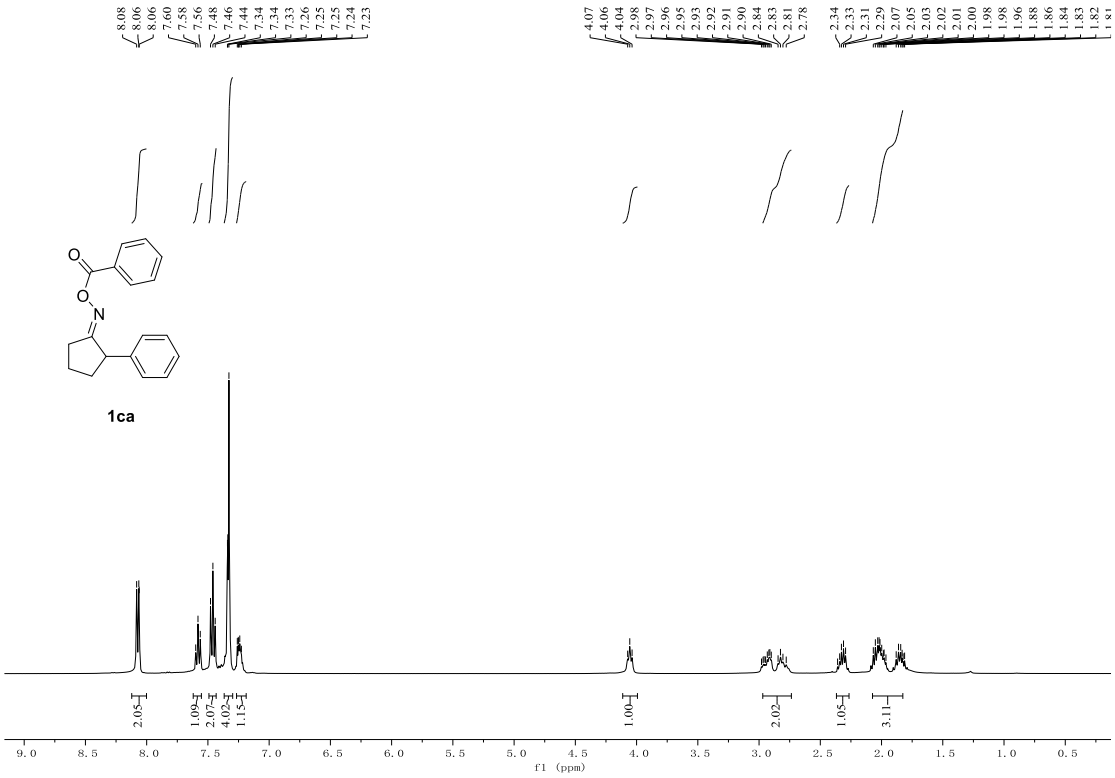
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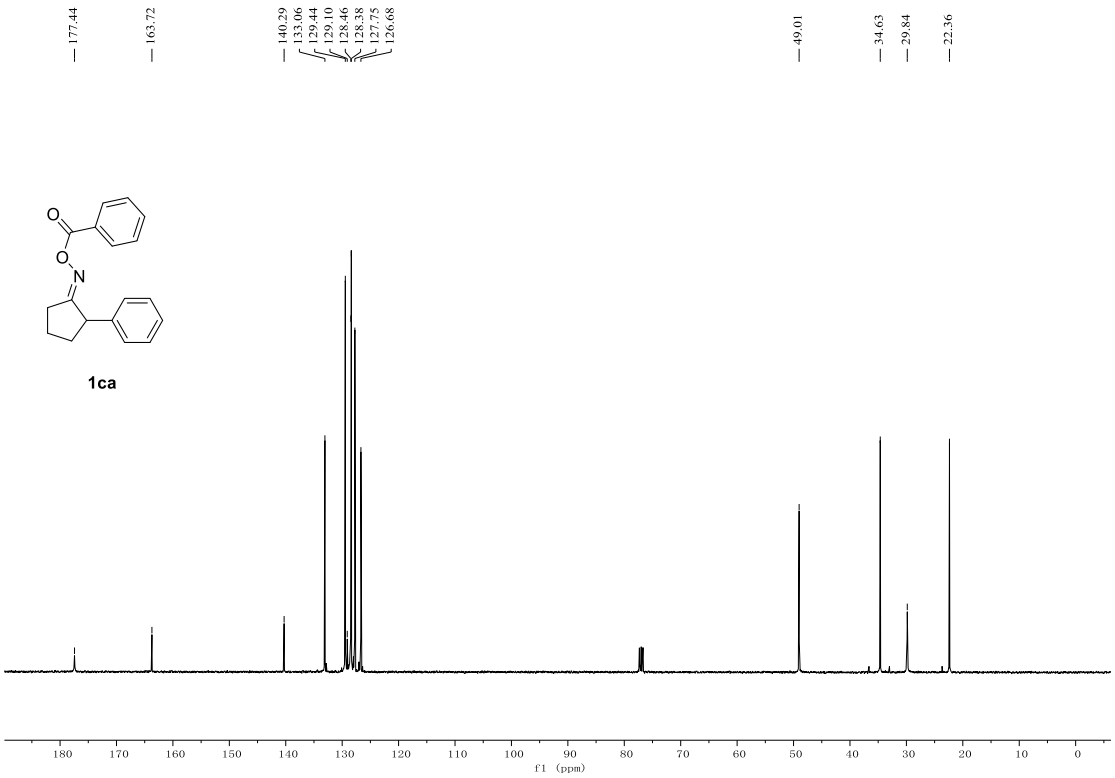
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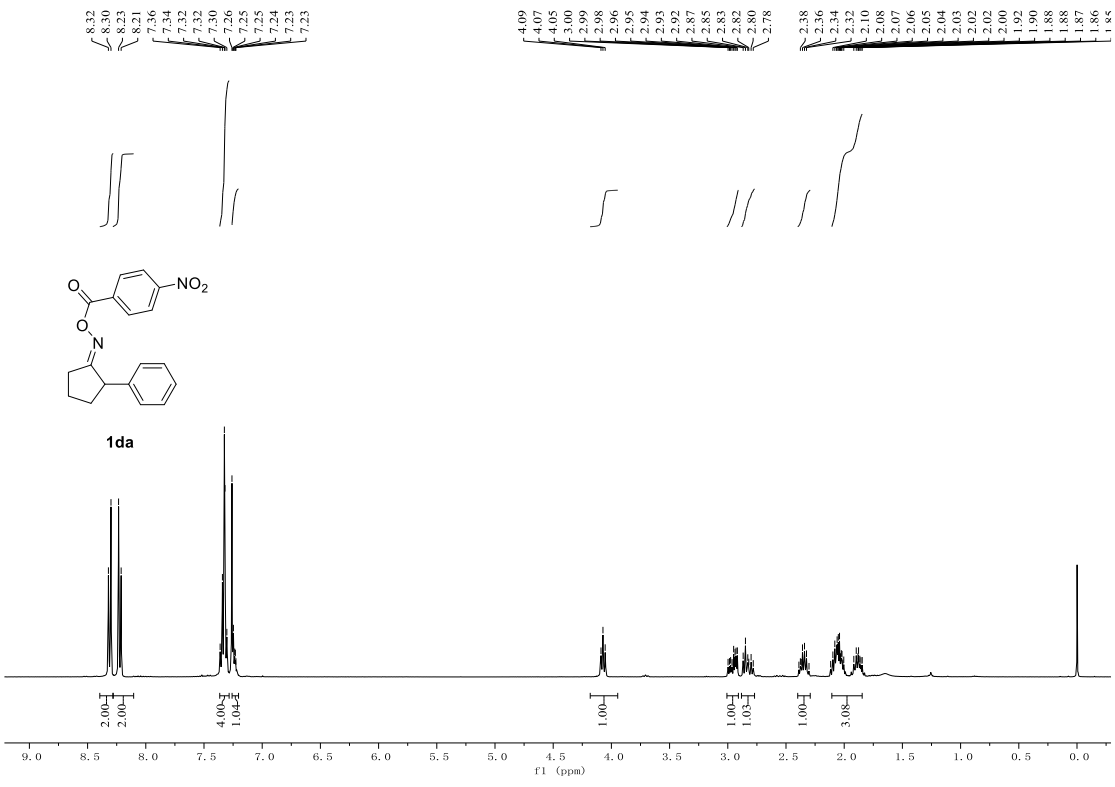
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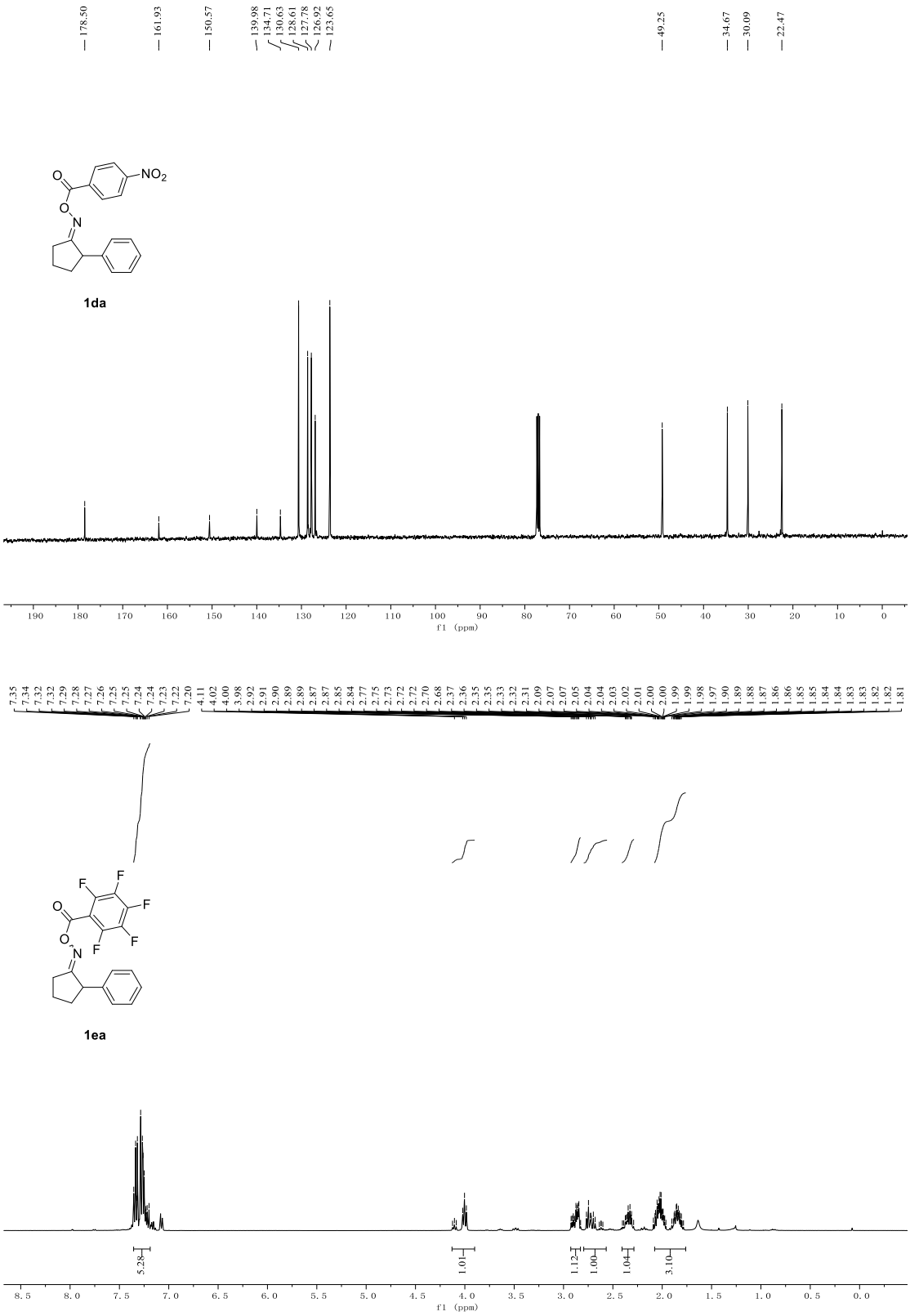
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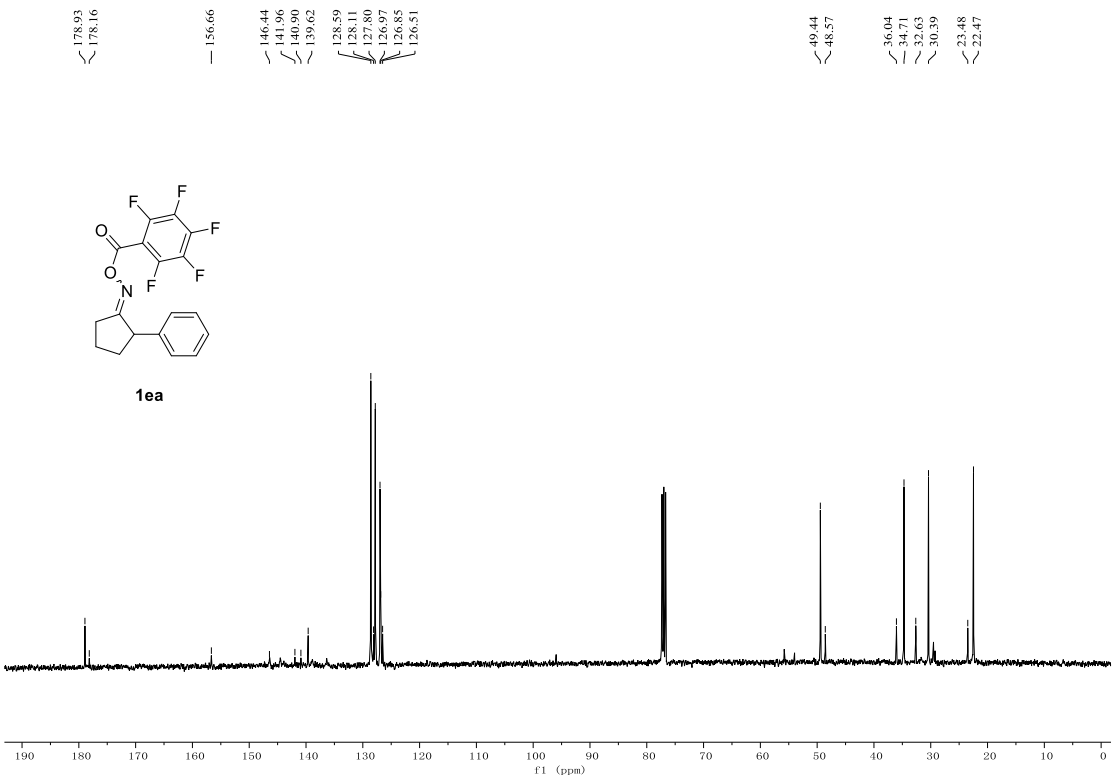
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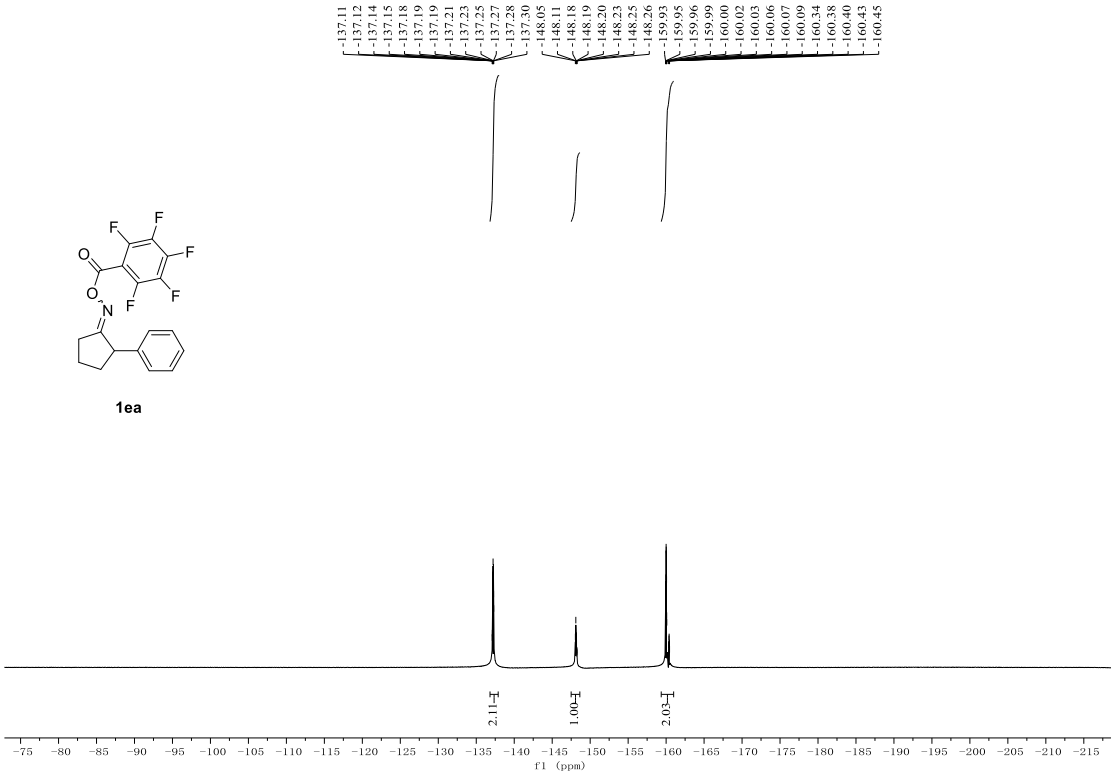
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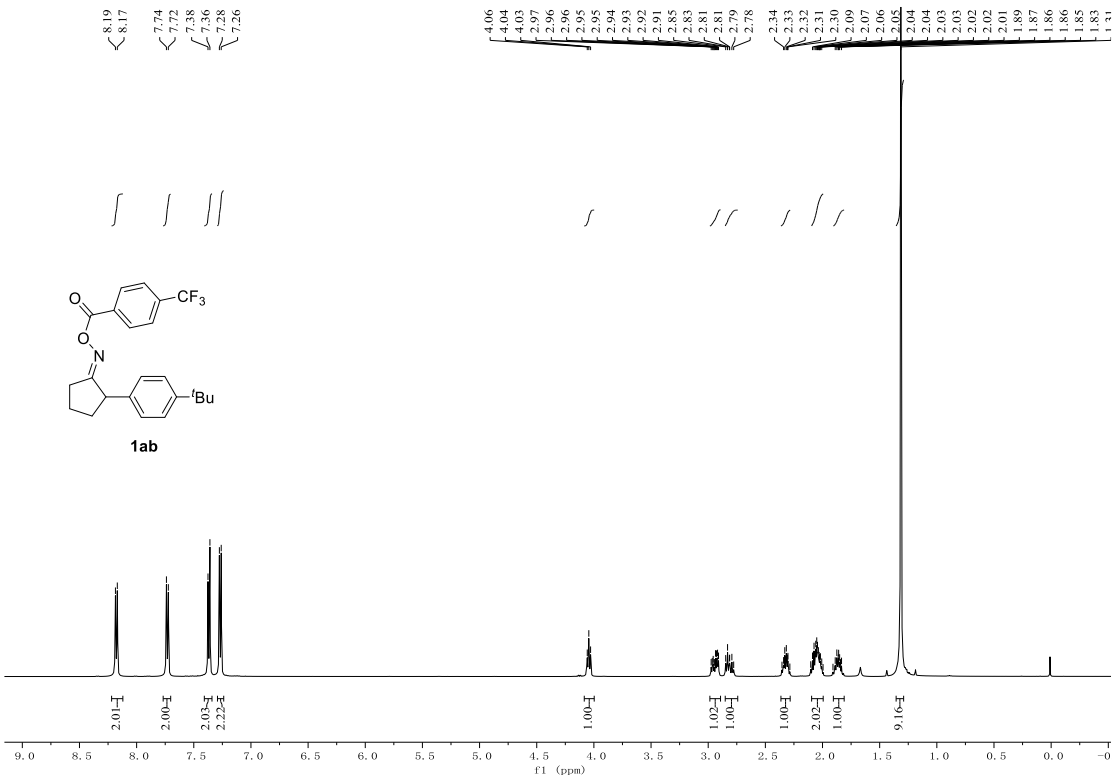
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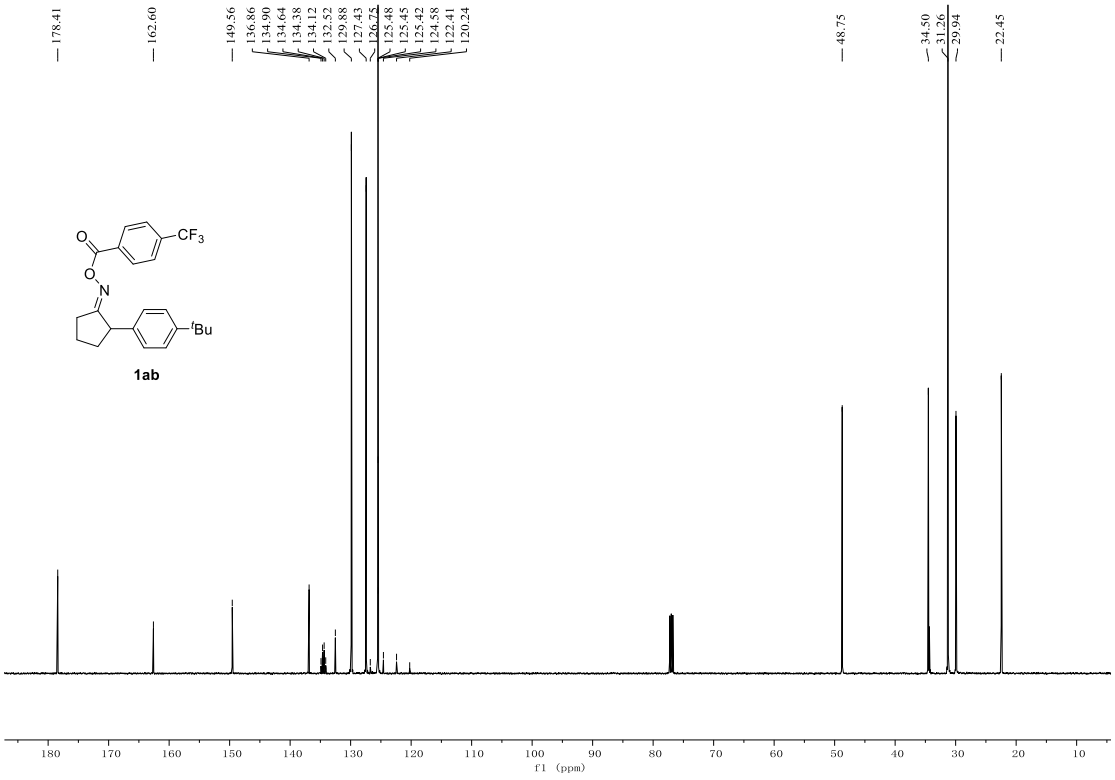
2.06
2.05
2.04
2.04
2.03
2.03
2.02
2.02
2.01
1.89
1.87
1.86
1.86
1.85
1.83
CF3
O
O
N
tBu
1ab
2.01
2.00
2.03
2.22
1.00
1.02
1.00
1.00
2.02
1.00
9.16
f1 (ppm)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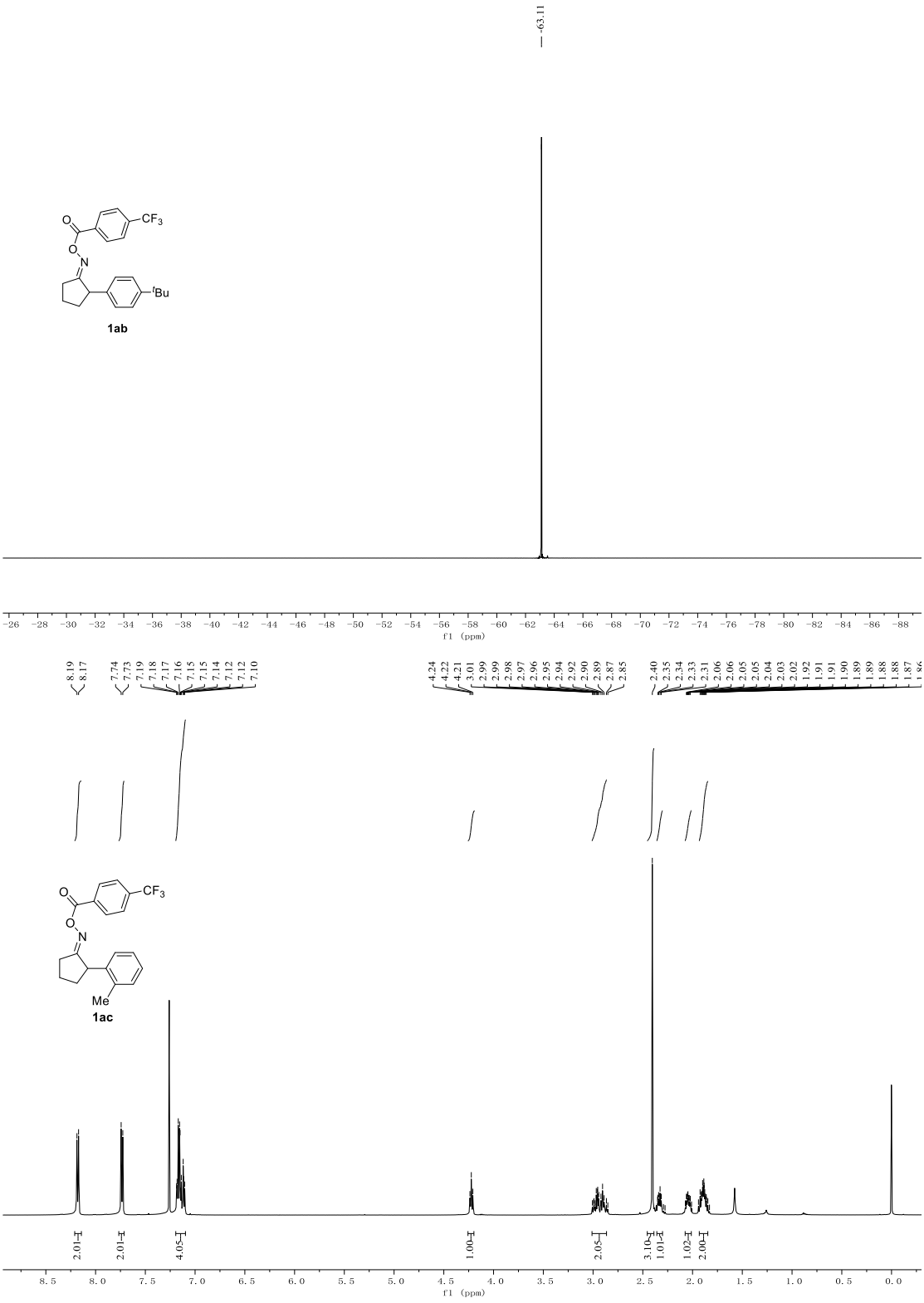
134.64
134.38
134.12
132.52
129.88
127.43
126.75
125.48
125.45
125.42
124.58
122.41
120.24
48.75
34.50
31.26
29.94
22.45
CF3
O
O
N
tBu
1ab
f1 (ppm)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O
N
tBu
1ab
f1 (ppm)
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8.17
7.74
7.73
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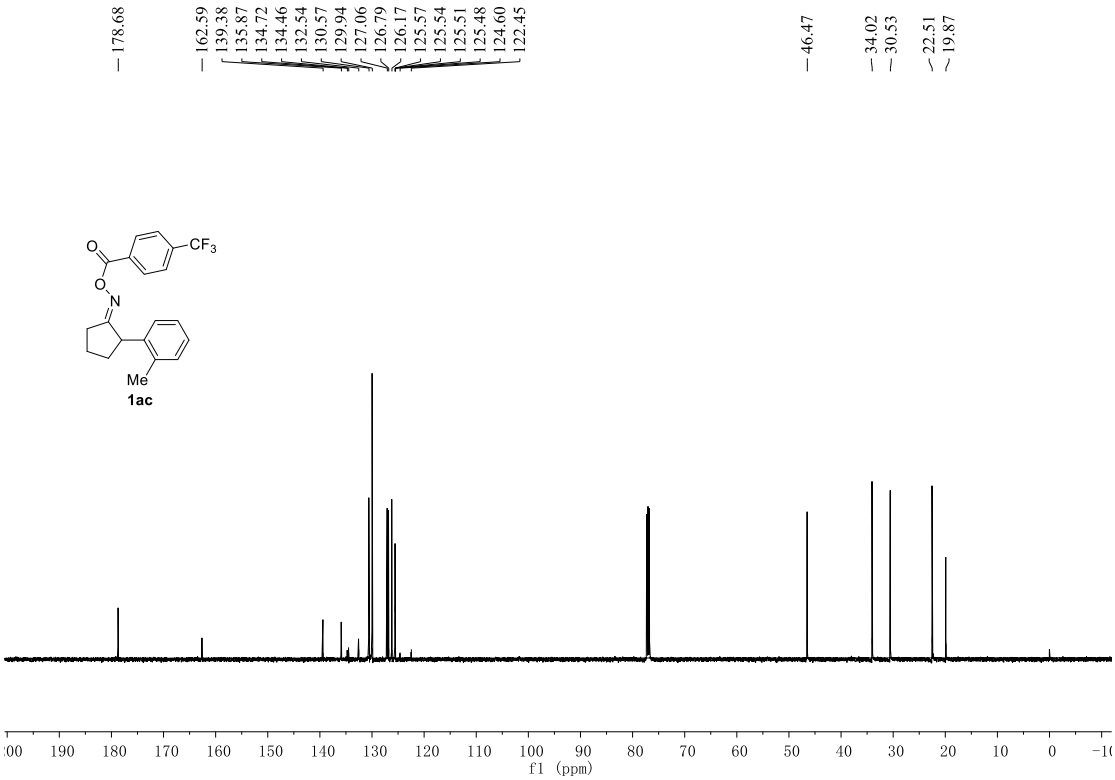
7.18
7.17
7.16
7.15
7.15
7.14
7.12
7.12
7.10
4.24
4.22
4.21
3.01
2.99
2.99
2.98
2.97
2.96
2.95
2.94
2.92
2.90
2.89
2.87
2.85
2.40
2.35
2.34
2.33
2.31
2.06
2.06
2.05
2.05
2.04
2.03
2.02
1.92
1.91
1.91
1.90
1.89
1.89
1.88
1.88
1.87
CF3
O
O
N
Me
1ac
2.01
2.01
4.05
1.00
2.05
3.10
1.01
1.02
2.00
f1 (ppm)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132.54
130.57
129.94
127.06
126.79
126.17
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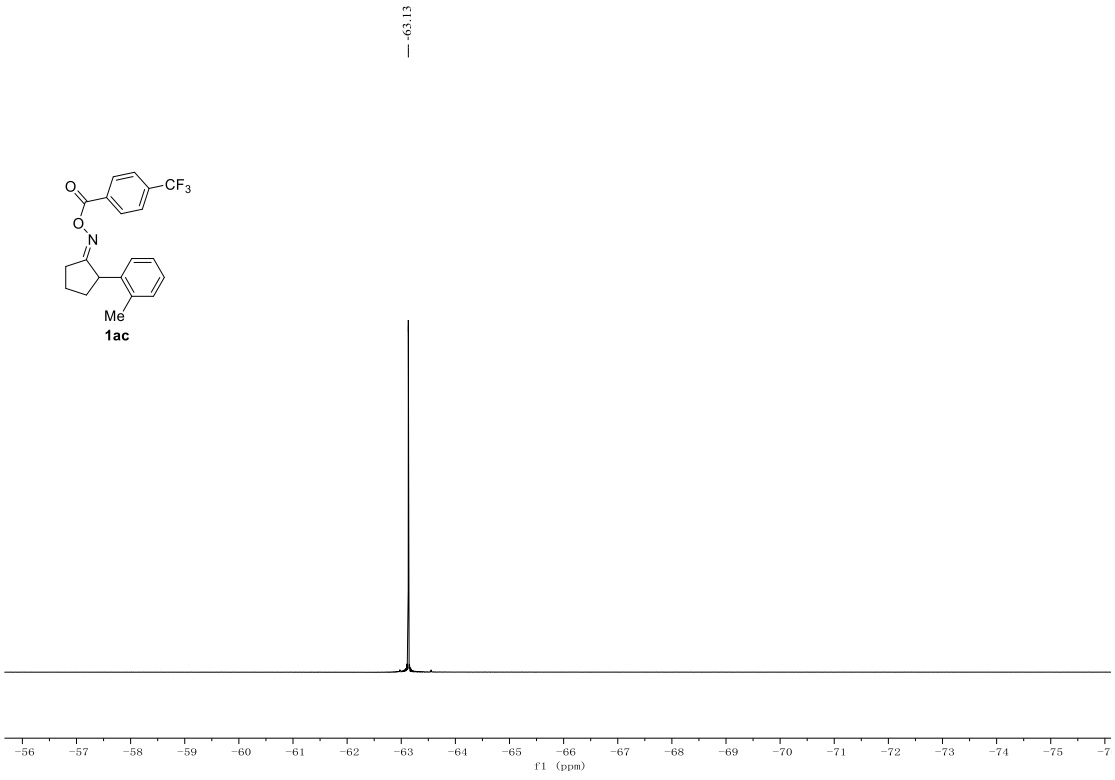
125.54
125.51
125.48
124.60
122.45
46.47
34.02
30.53
22.51
19.87
CF3
O
O
N
Me
1ac
f1 (ppm)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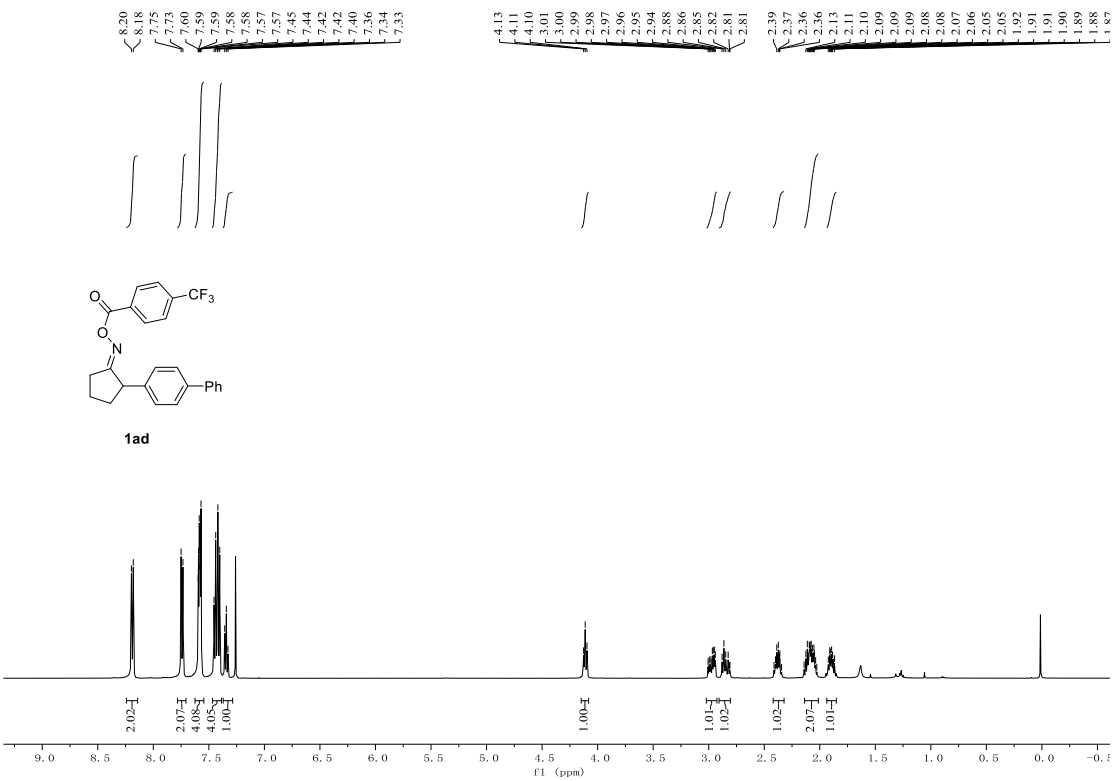
CF3
O
O
N
Me
1ac
f1 (ppm)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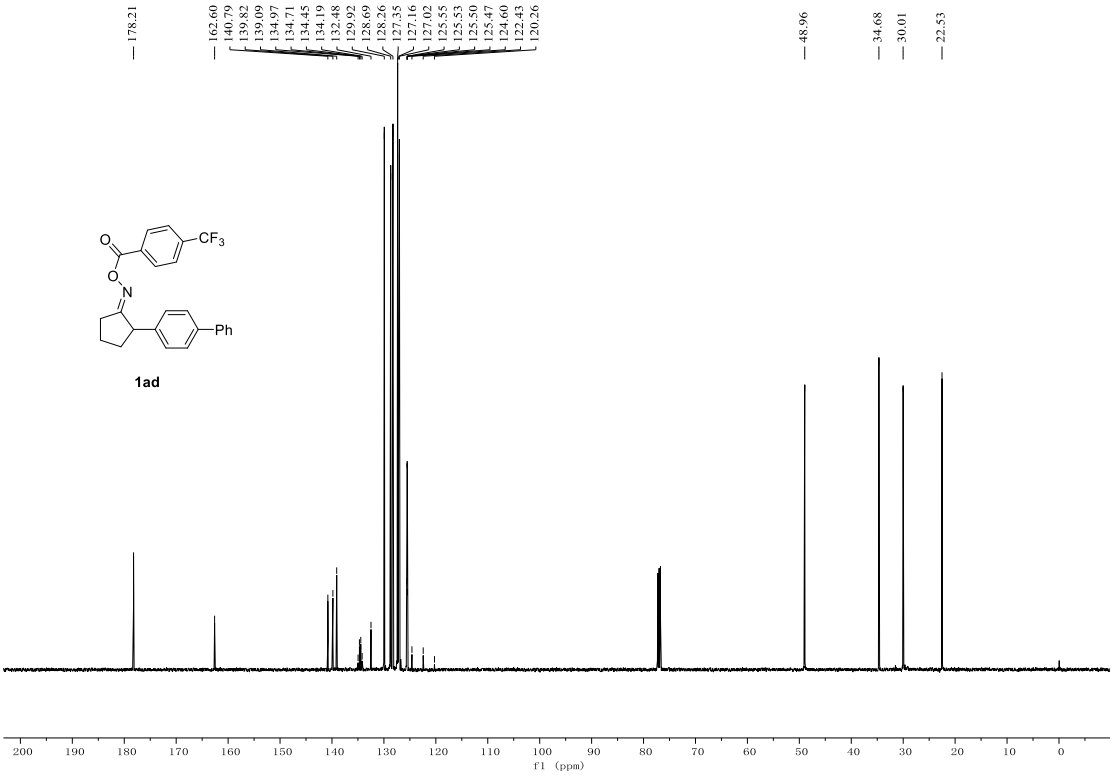
7.75
7.73
7.60
7.59
7.59
7.58
7.58
7.57
7.57
7.45
7.44
7.42
7.42
7.40
7.36
7.34
7.33
4.13
4.11
4.10
3.01
3.00
2.99
2.98
2.97
2.96
2.95
2.94
2.88
2.86
2.85
2.82
2.81
2.81
2.39
2.37
2.36
2.36
2.13
2.11
2.10
2.09
2.09
2.09
2.08
2.08
2.07
2.06
2.05
2.05
1.92
1.91
1.91
1.90
1.89
1.88
O
O
N
CF3
Ph
1ad
2.02
2.07
4.08
4.05
1.00
1.00
1.01
1.02
1.02
2.07
1.01
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)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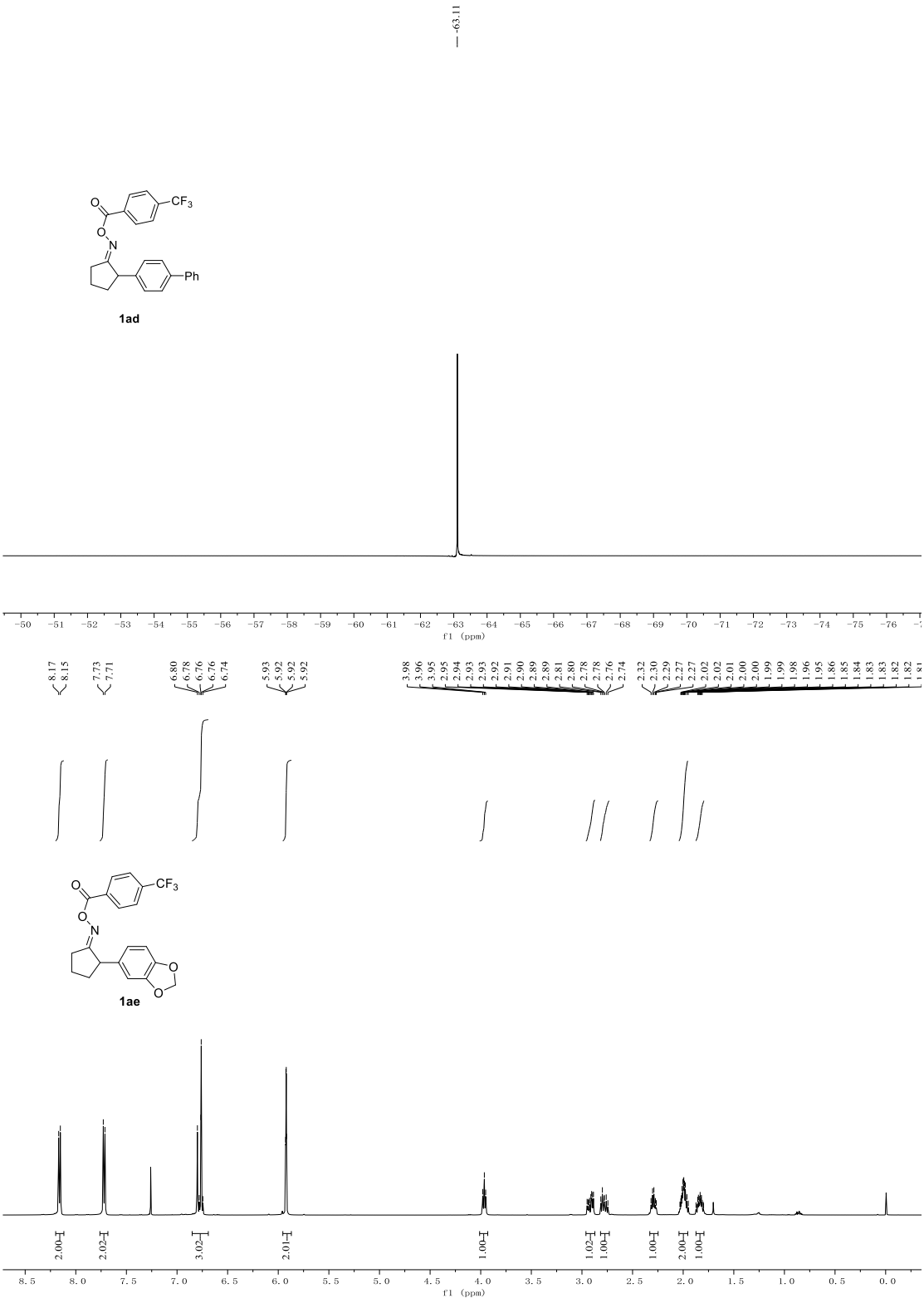
134.71
134.45
134.19
132.48
129.92
128.69
128.26
127.35
127.16
127.02
125.55
125.53
125.50
125.47
124.60
122.43
120.26
48.96
34.68
30.01
22.53
O
O
N
CF3
Ph
1ad
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-63.11
1ad
f1 (ppm)
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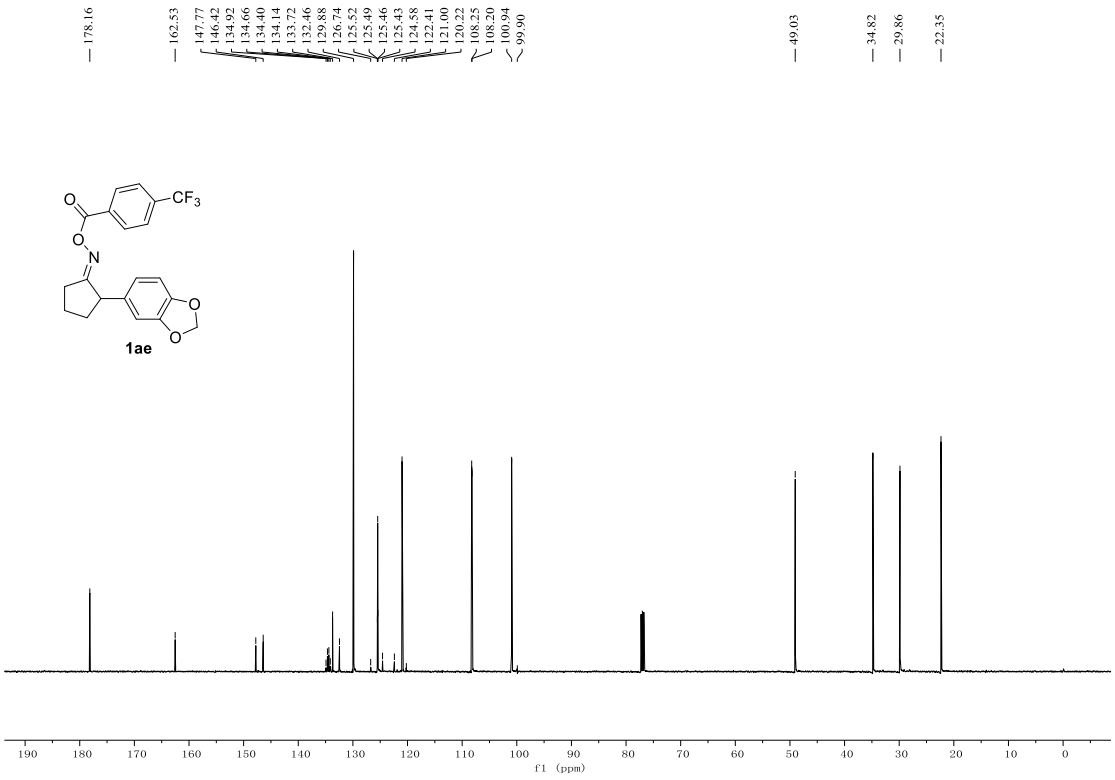
8.15
7.73
7.71
6.80
6.78
6.76
6.76
6.74
5.93
5.92
5.92
5.92
3.98
3.96
3.95
3.95
2.94
2.93
2.93
2.92
2.91
2.90
2.89
2.89
2.81
2.80
2.78
2.78
2.76
2.74
2.32
2.30
2.29
2.27
2.27
2.02
2.02
2.01
2.00
2.00
1.99
1.99
1.98
1.96
1.95
1.86
1.85
1.84
1.83
1.83
1.82
1.82
1ae
2.00
2.02
3.02
2.01
1.00
1.02
1.00
1.00
2.00
1.00
f1 (ppm)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134.66
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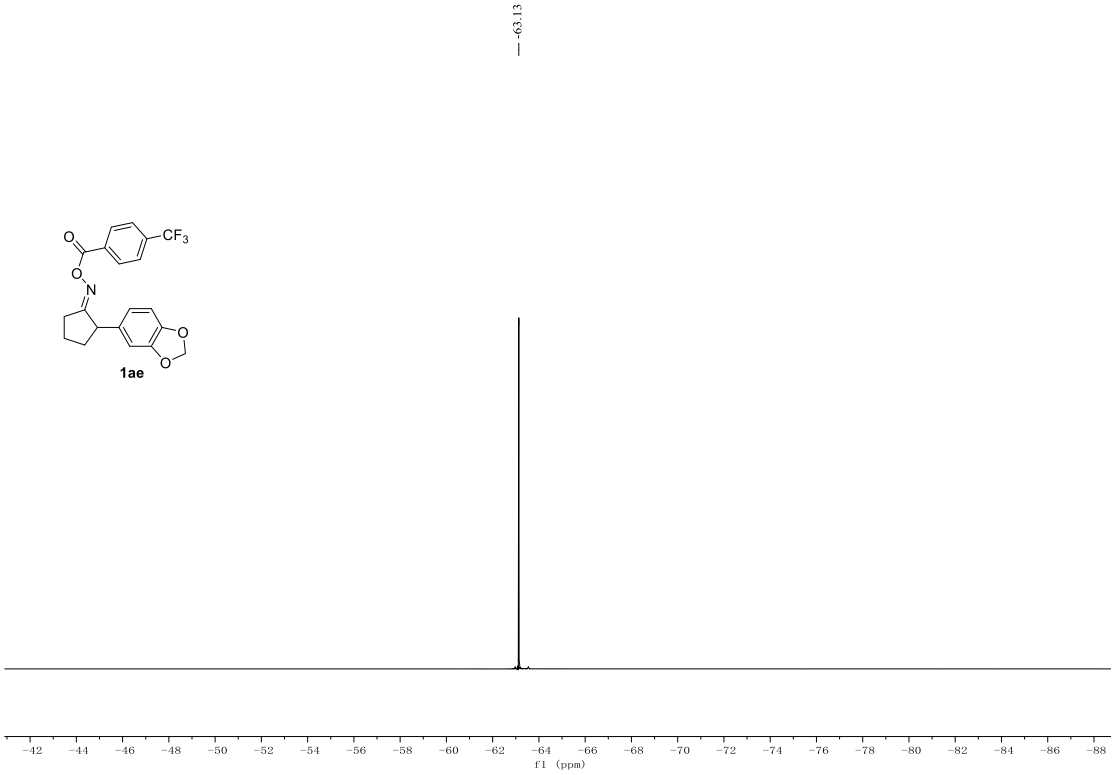
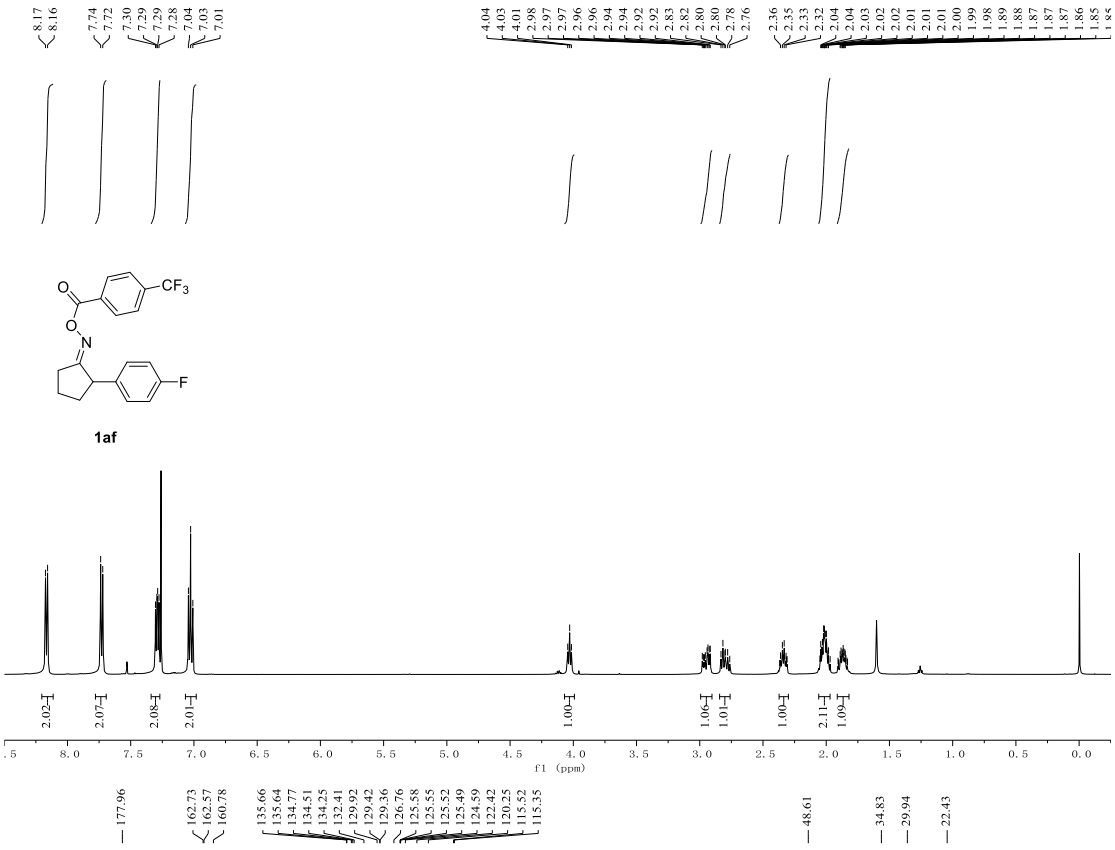
134.14
133.72
132.46
129.88
126.74
125.52
125.49
125.46
125.43
124.58
122.41
121.00
120.22
108.25
108.20
100.94
99.90
49.03
34.82
29.86
22.35
O
CF3
O
N
O
O
1ae
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-63.13
O
CF3
O
N
O
O
1ae
-42
-44
-46
-48
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
f1 (ppm)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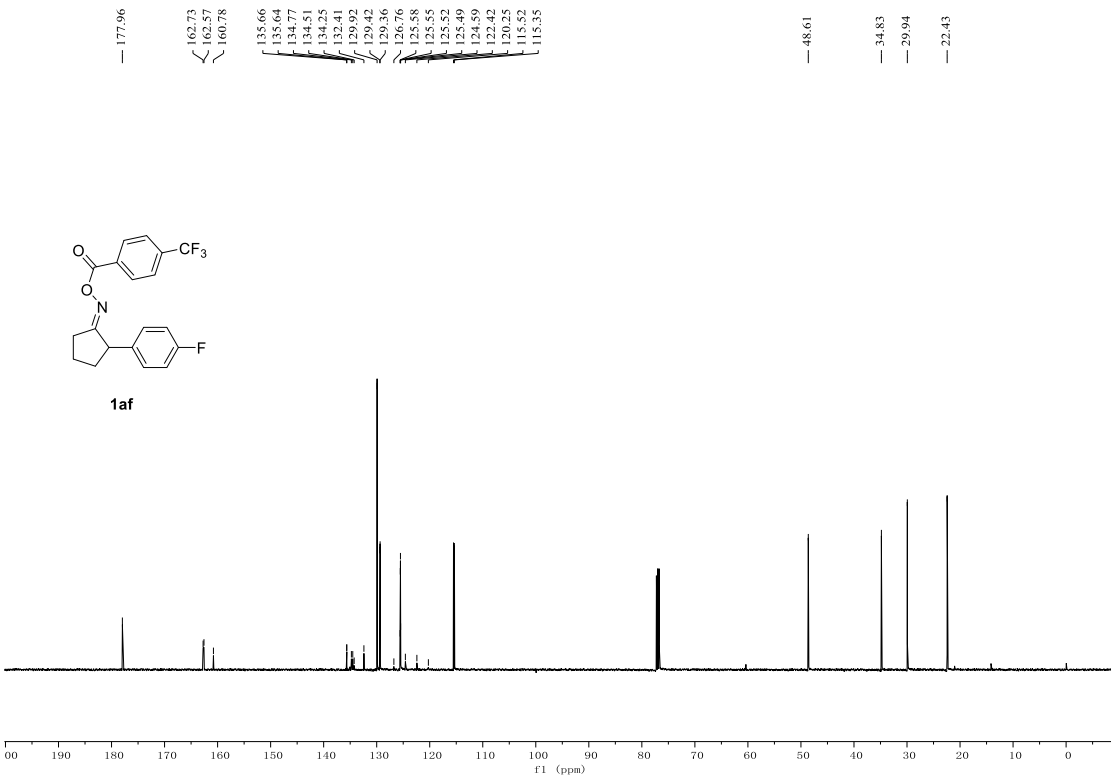
8.16
7.74
7.72
7.30
7.29
7.29
7.28
7.04
7.03
7.01
4.04
4.03
4.01
2.98
2.97
2.97
2.96
2.96
2.94
2.94
2.92
2.92
2.83
2.82
2.80
2.80
2.78
2.76
2.36
2.35
2.33
2.32
2.04
2.04
2.03
2.02
2.02
2.01
2.01
2.00
1.99
1.98
1.89
1.88
1.87
1.87
1.87
1.86
1.85
O
O
N
CF3
F
1af
2.02
2.07
2.08
2.01
1.00
1.06
1.01
1.00
2.11
1.09
f1 (ppm)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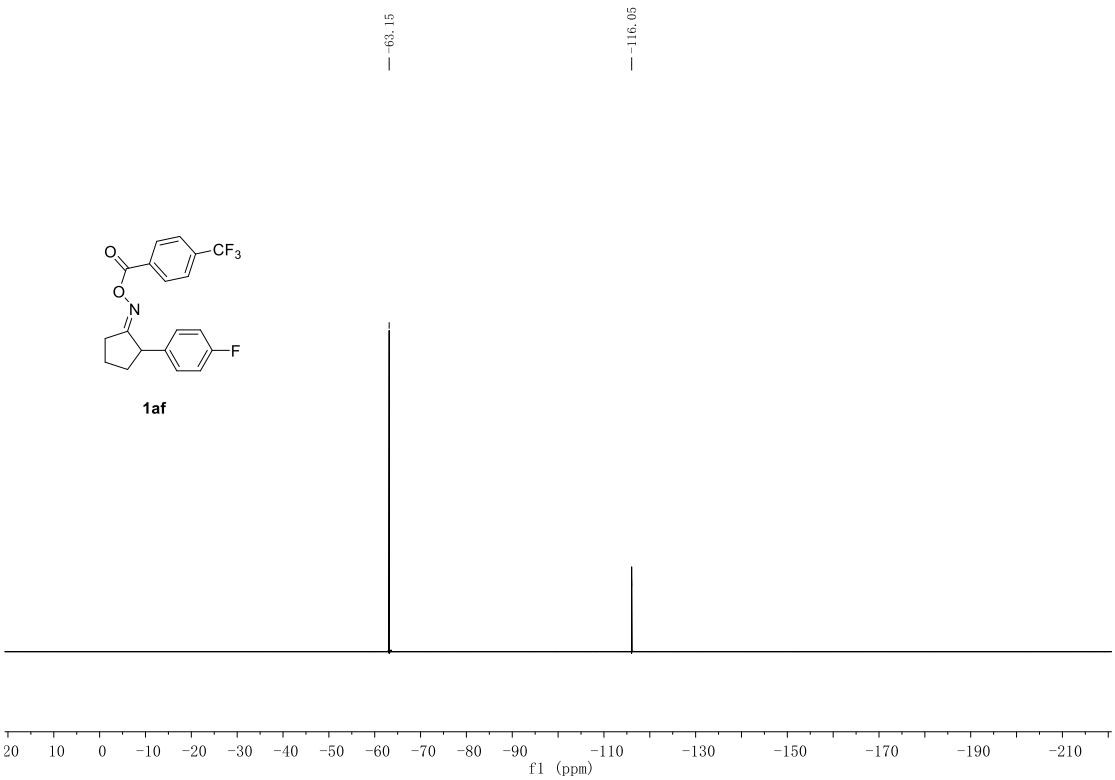
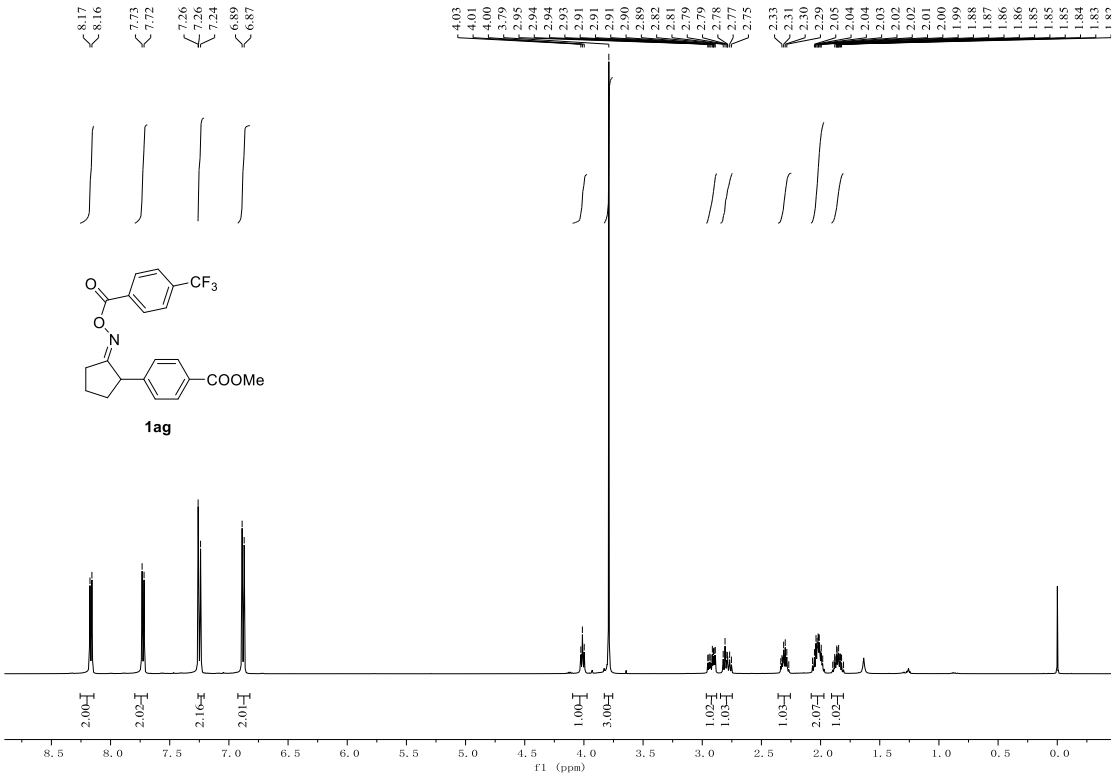
132.41
129.92
129.42
129.36
126.76
125.58
125.55
125.52
125.49
124.59
122.42
120.25
115.52
115.35
48.61
34.83
29.94
22.43
f1 (ppm)

O
O
N
CF3
F
1af
f1 (ppm)


-63.15
-116.05
O
CF3
O
N
F
1af
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)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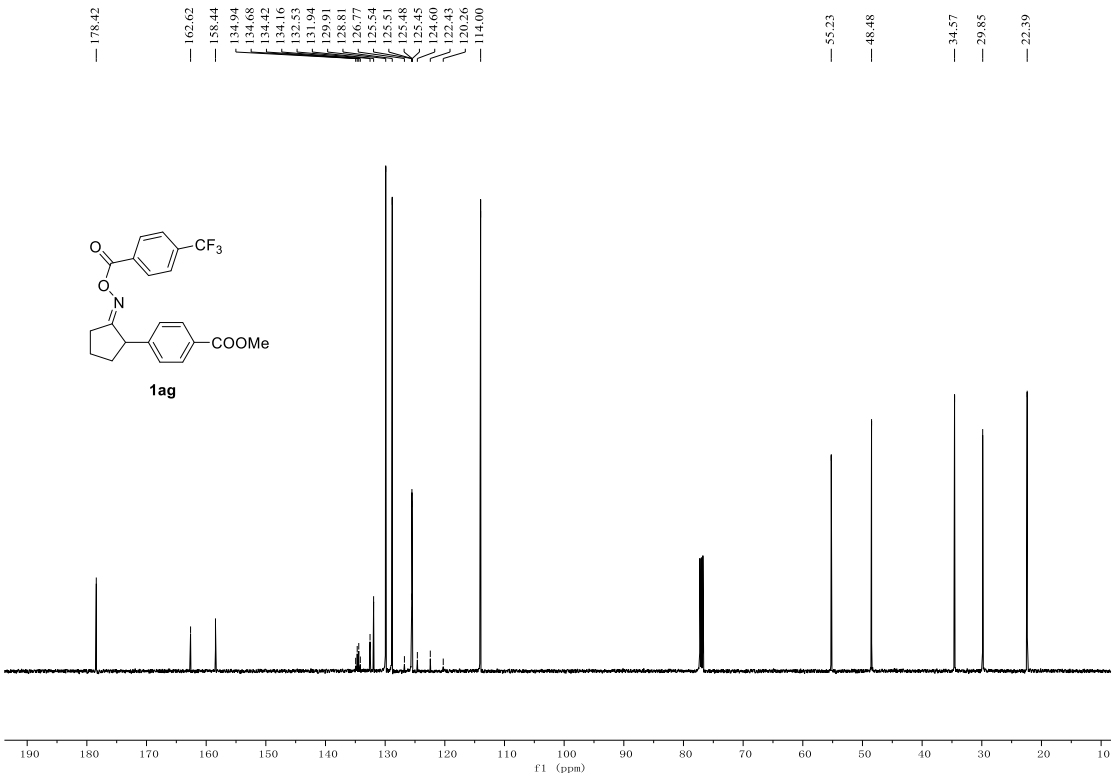
8.16
7.73
7.72
7.26
7.26
7.24
6.89
6.87
4.03
4.01
4.00
3.79
2.95
2.94
2.94
2.93
2.91
2.91
2.91
2.90
2.89
2.82
2.81
2.79
2.79
2.78
2.77
2.75
2.33
2.31
2.30
2.29
2.05
2.04
2.04
2.03
2.02
2.02
2.01
2.00
1.99
1.88
1.87
1.86
1.86
1.85
1.85
1.85
1.84
1.83
O
CF3
O
N
COOMe
1ag
2.00
2.02
2.16
2.01
1.00
3.00
1.02
1.03
1.03
2.07
1.02
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)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158.44
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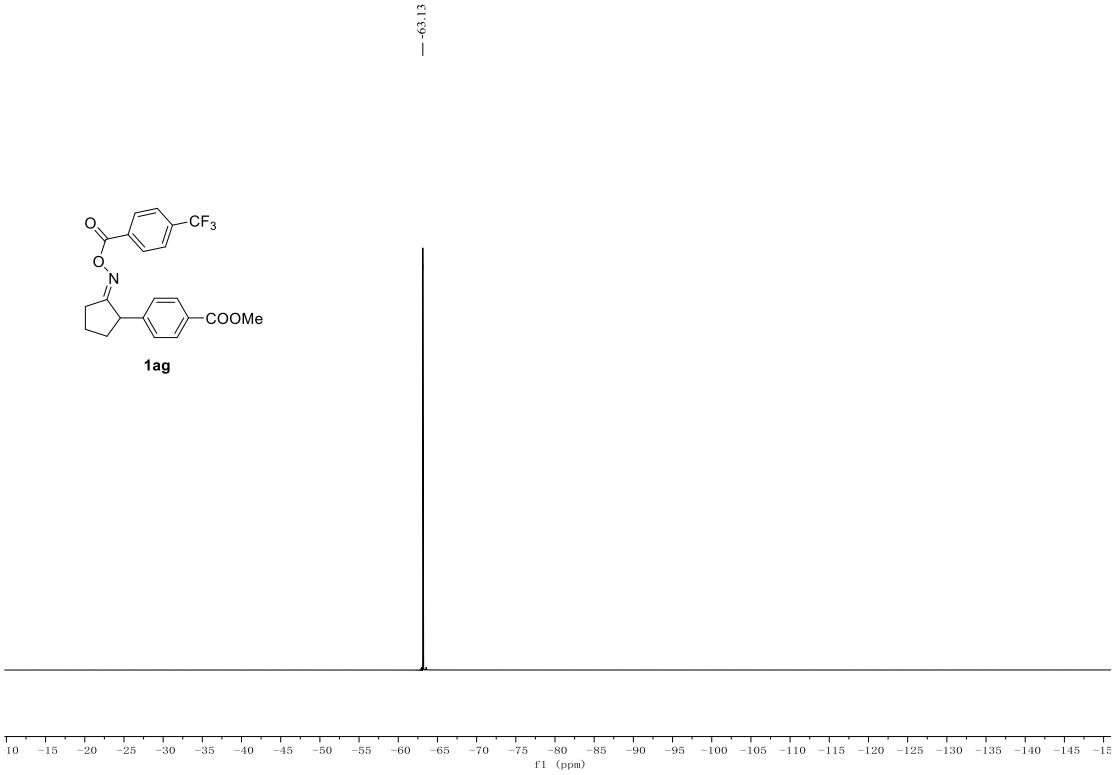
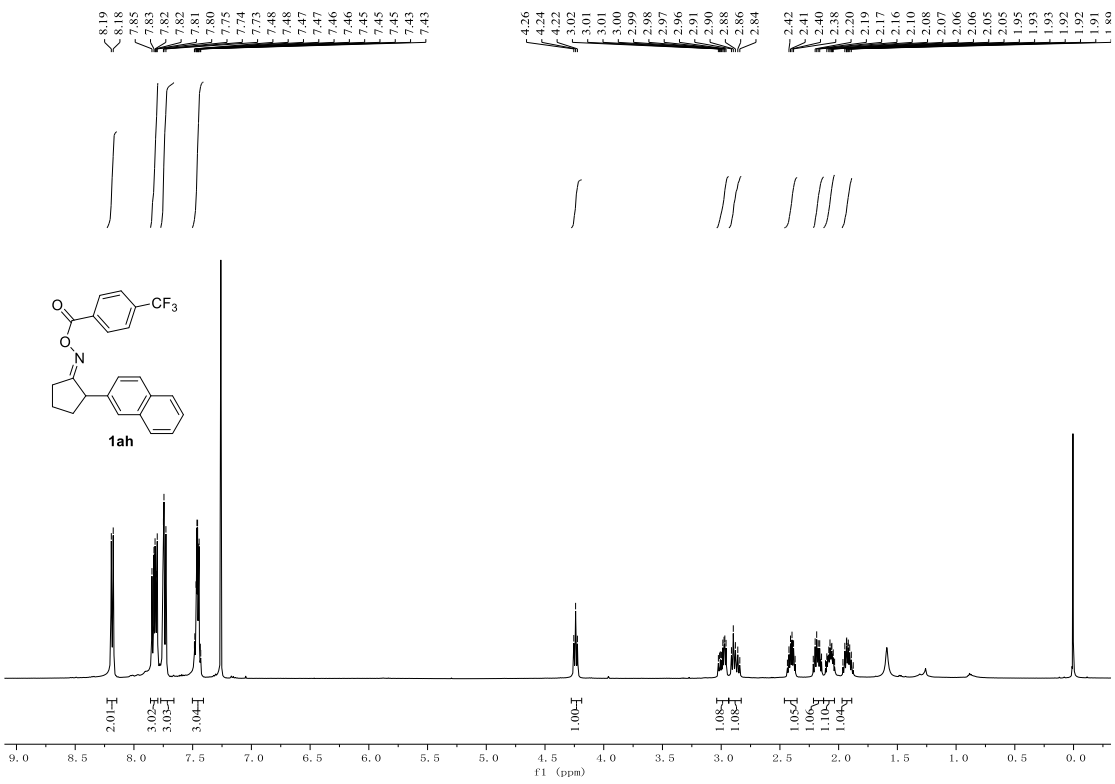
134.68
134.42
134.16
132.53
131.94
129.91
128.81
126.77
125.54
125.51
125.48
125.45
124.60
122.43
120.26
114.00
55.23
48.48
34.57
29.85
22.39
O
O
N
CF3
COOMe
1ag
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-63.13
O
O
N
CF3
COOMe
1ag
10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -15
f1 (ppm)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8.18
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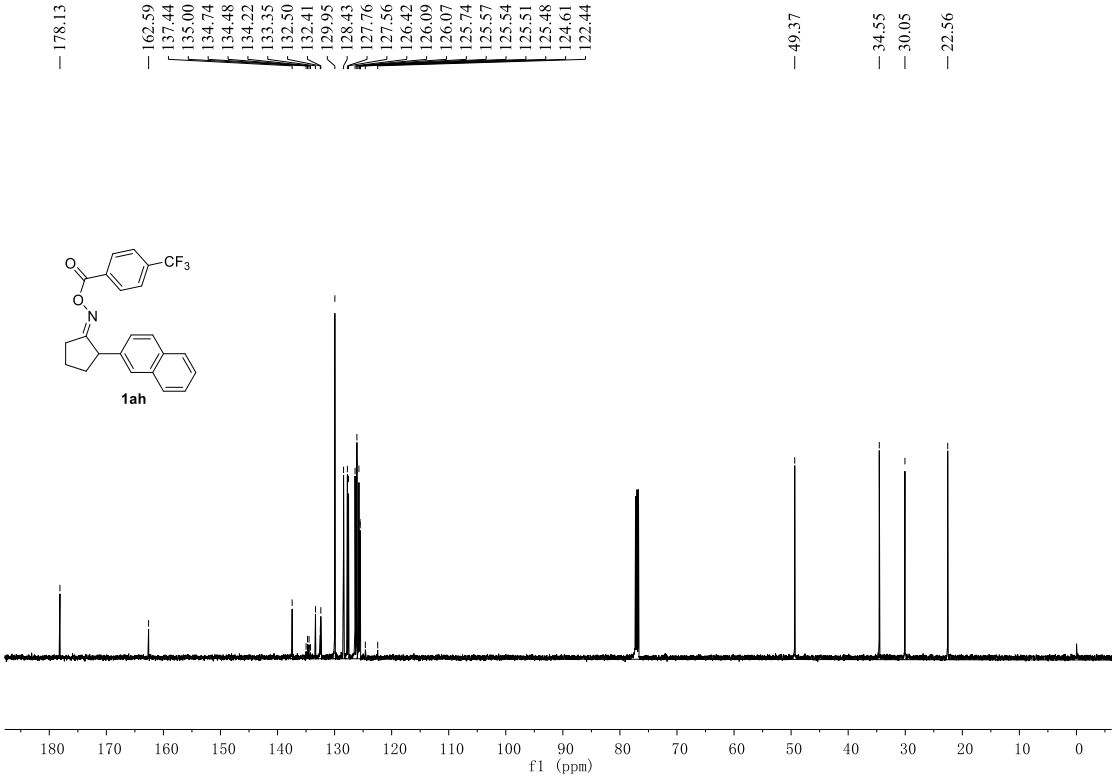
7.82
7.81
7.80
7.75
7.74
7.73
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.43
7.43
4.26
4.24
4.22
3.02
3.01
3.01
3.00
2.99
2.98
2.97
2.96
2.91
2.90
2.88
2.86
2.84
2.42
2.41
2.40
2.38
2.20
2.19
2.17
2.16
2.10
2.08
2.07
2.06
2.06
2.05
2.05
1.95
1.93
1.93
1.92
1.92
1.91
CF3
1ah
2.01
3.02
3.03
3.04
1.00
1.08
1.08
1.05
1.06
1.10
1.04
f1 (ppm)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135.00
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133.35
132.50
132.41
129.95
128.43
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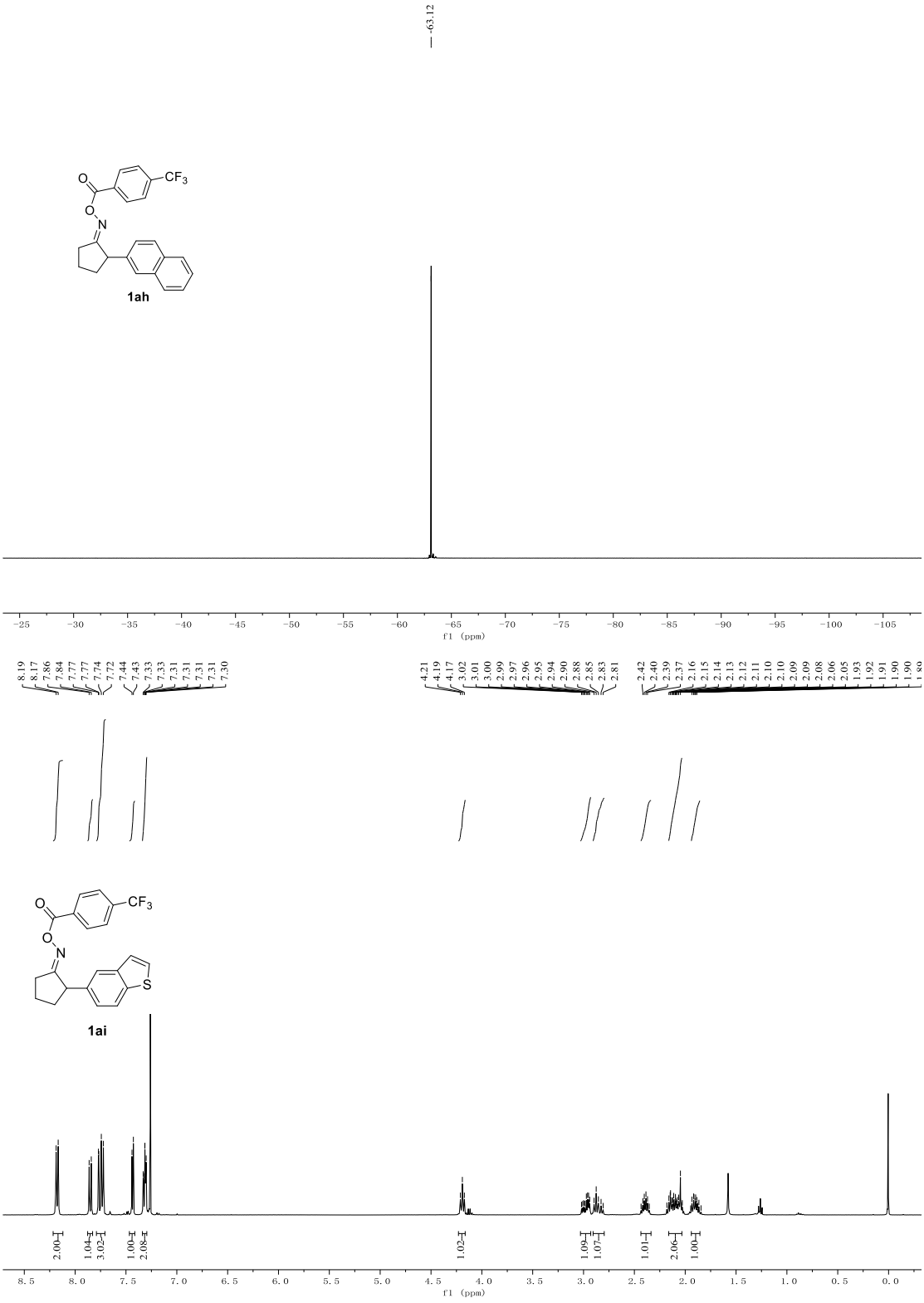
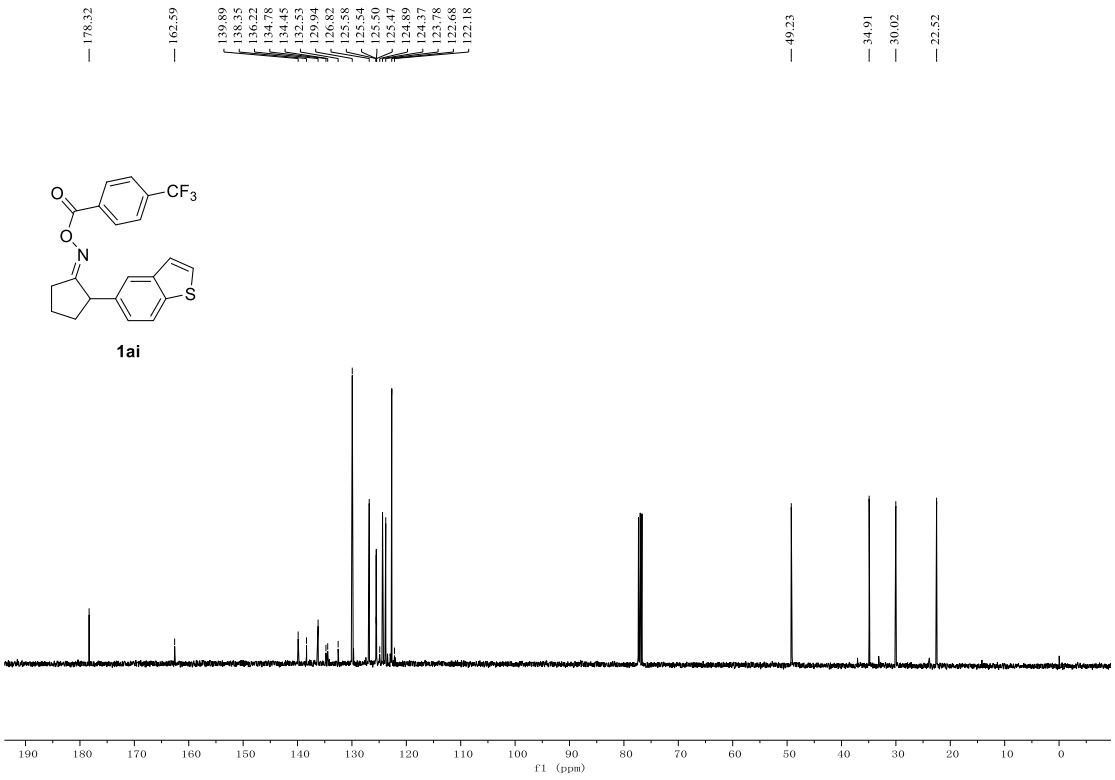
127.56
126.42
126.09
126.07
125.74
125.57
125.54
125.51
125.48
124.61
122.44
49.37
34.55
30.05
22.56
CF3
1ah
f1 (ppm)


-63.12
1ah
f1 (ppm)
1ai
f1 (ppm)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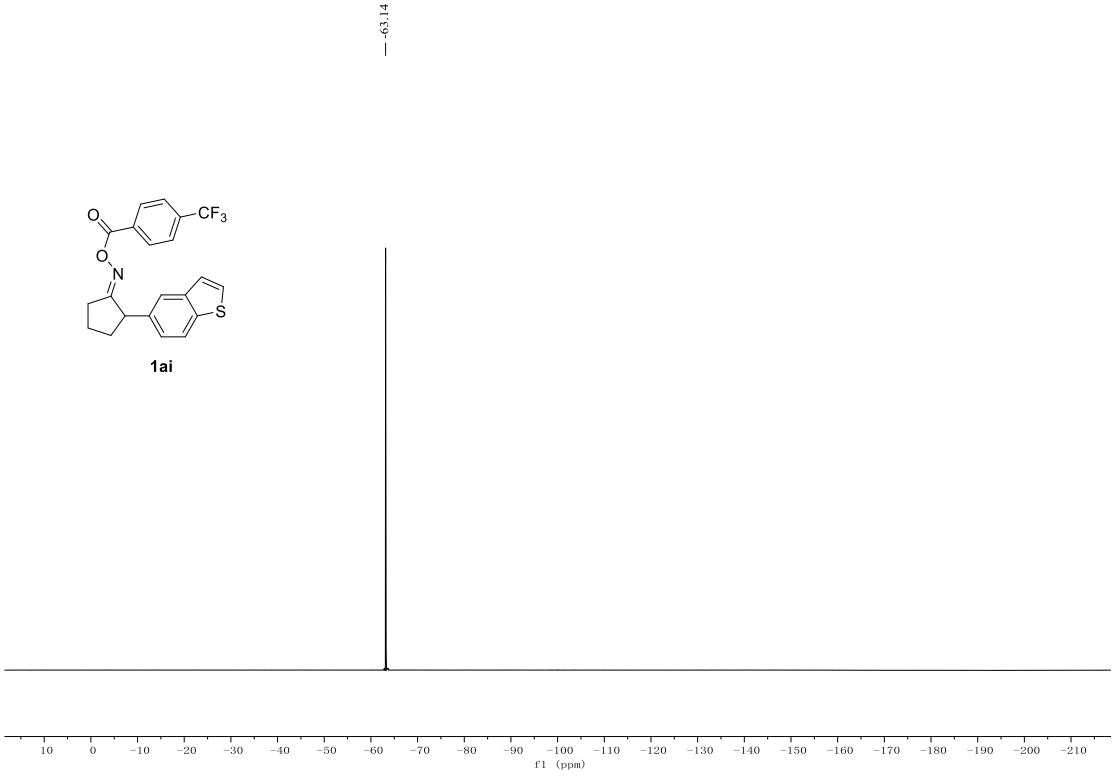
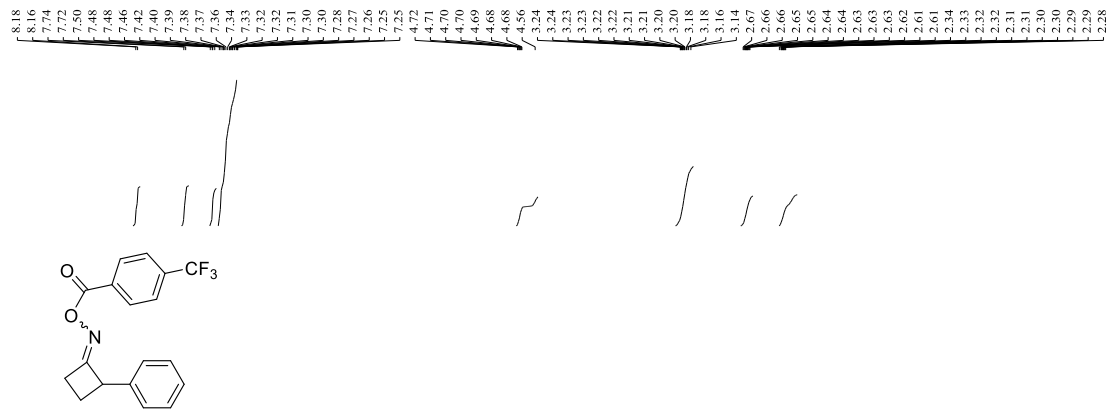
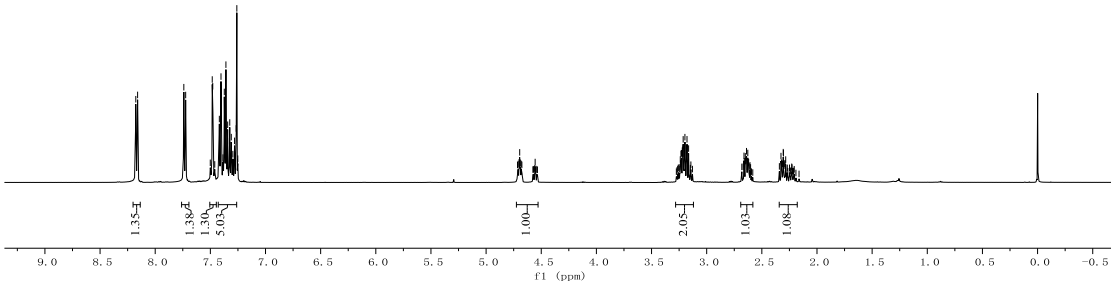
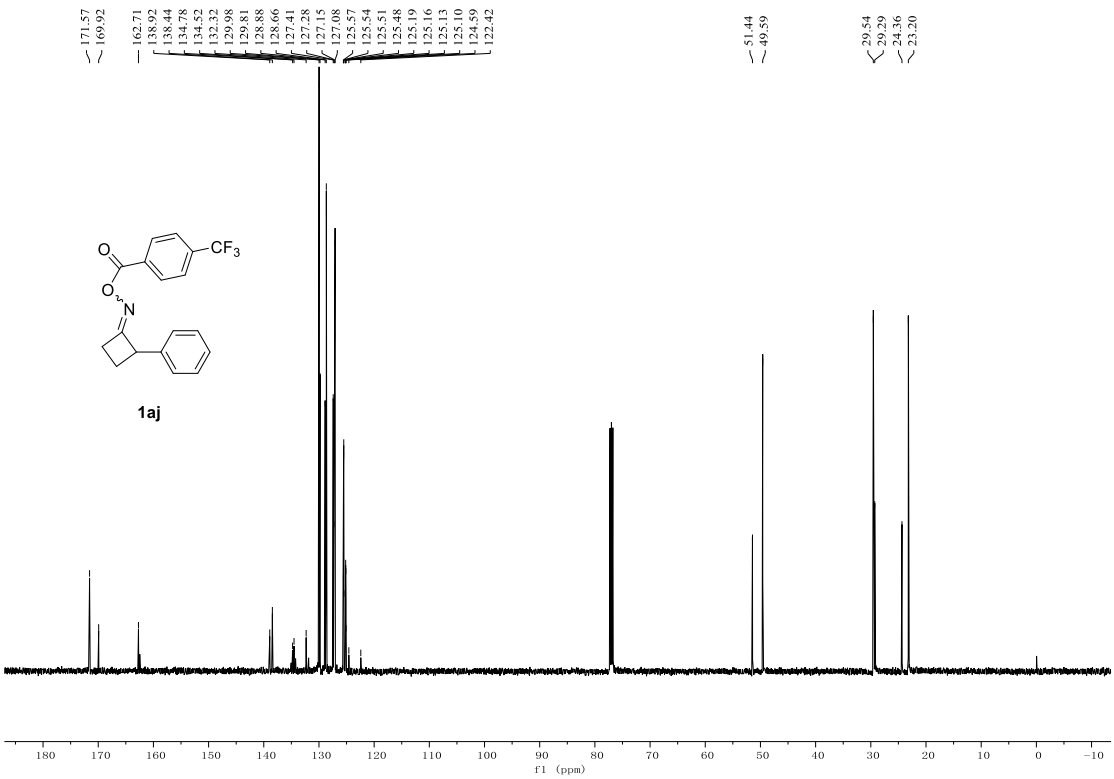
138.35
136.22
134.78
134.45
132.53
129.94
126.82
125.58
125.54
125.50
125.47
124.89
124.37
123.78
122.68
122.18
49.23
34.91
30.02
22.52
O
CF3
O
N
S
1ai
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.14
O
CF3
O
N
S
1ai
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

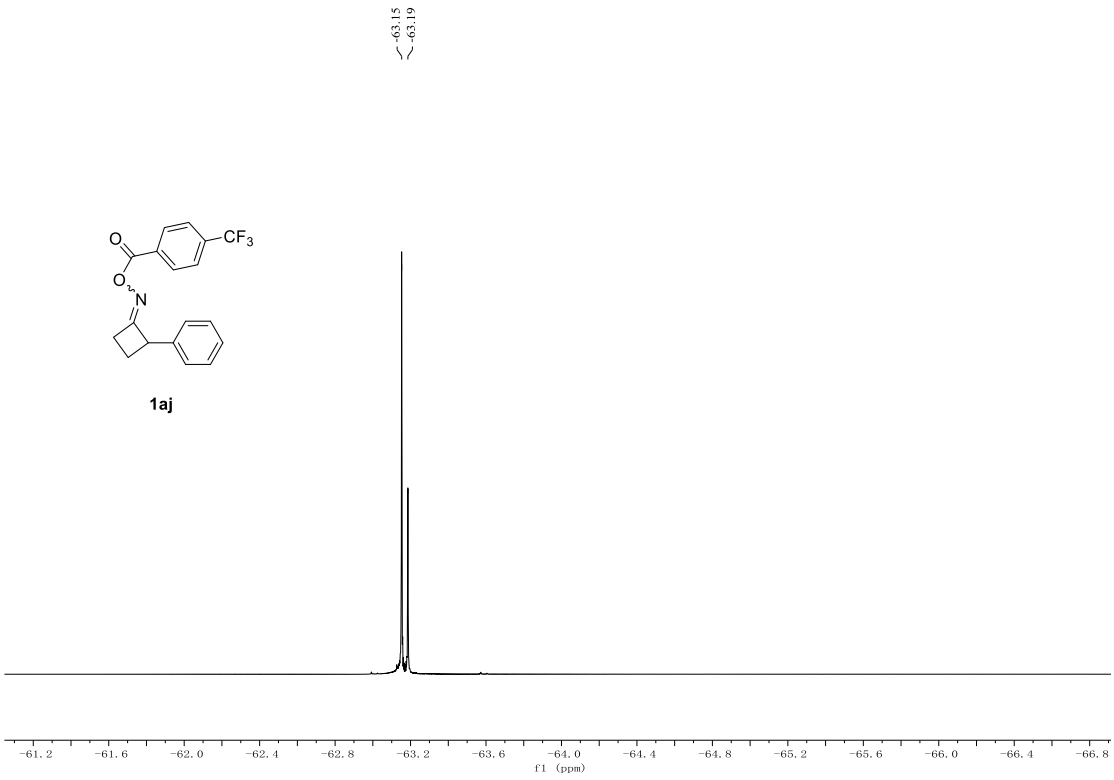


1aj





1aj


-63.15
-63.19
CF3
O
O
N
1aj
-61.2
-61.6
-62.0
-62.4
-62.8
-63.2
-63.6
-64.0
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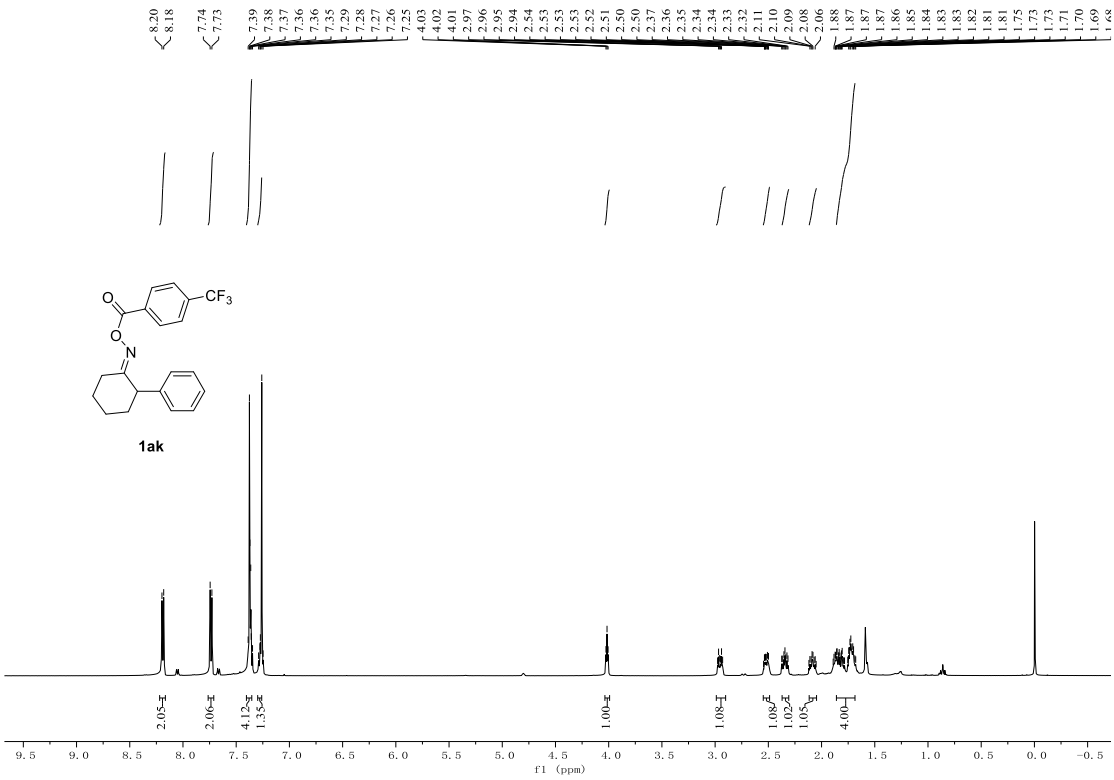
-64.8
-65.2
-65.6
-66.0
-66.4
-66.8
f1 (ppm)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7.35
7.29
7.28
7.27
7.26
7.25
4.03
4.02
4.01
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2.95
2.94
2.54
2.53
2.53
2.53
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2.33
2.32
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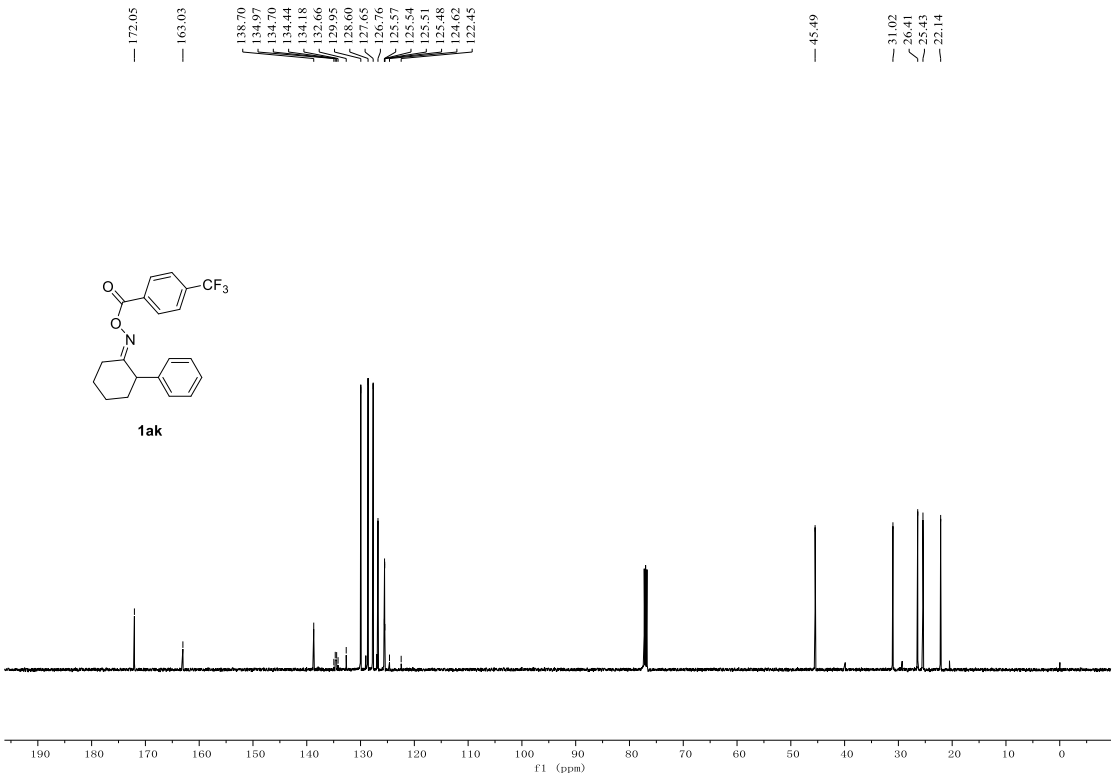
2.10
2.09
2.08
2.06
1.88
1.87
1.87
1.87
1.86
1.85
1.84
1.83
1.83
1.82
1.81
1.81
1.75
1.73
1.73
1.71
1.70
1.69
CF3
O
O
N
1ak
2.05
2.06
4.12
1.35
1.00
1.08
1.08
1.02
1.05
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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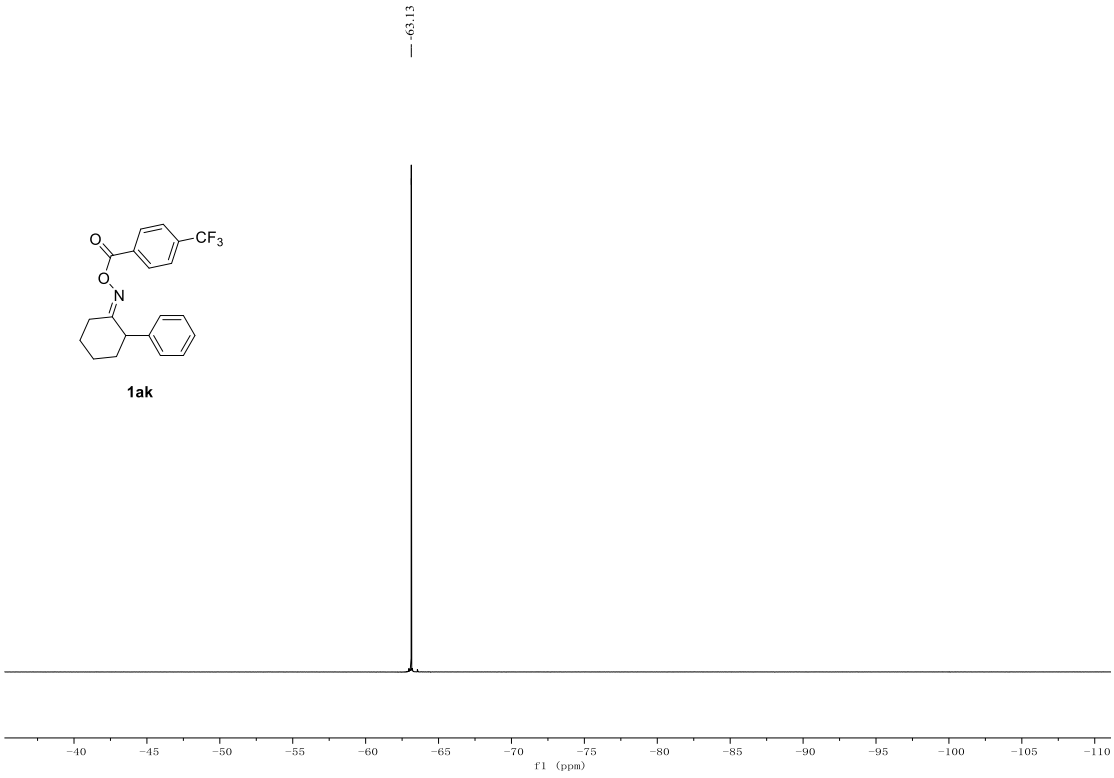
138.70
134.97
134.70
134.44
134.18
132.66
129.95
128.60
127.65
126.76
125.57
125.54
125.51
125.48
124.62
122.45
45.49
31.02
26.41
25.43
22.14
CF3
O
O
N
1ak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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CF3
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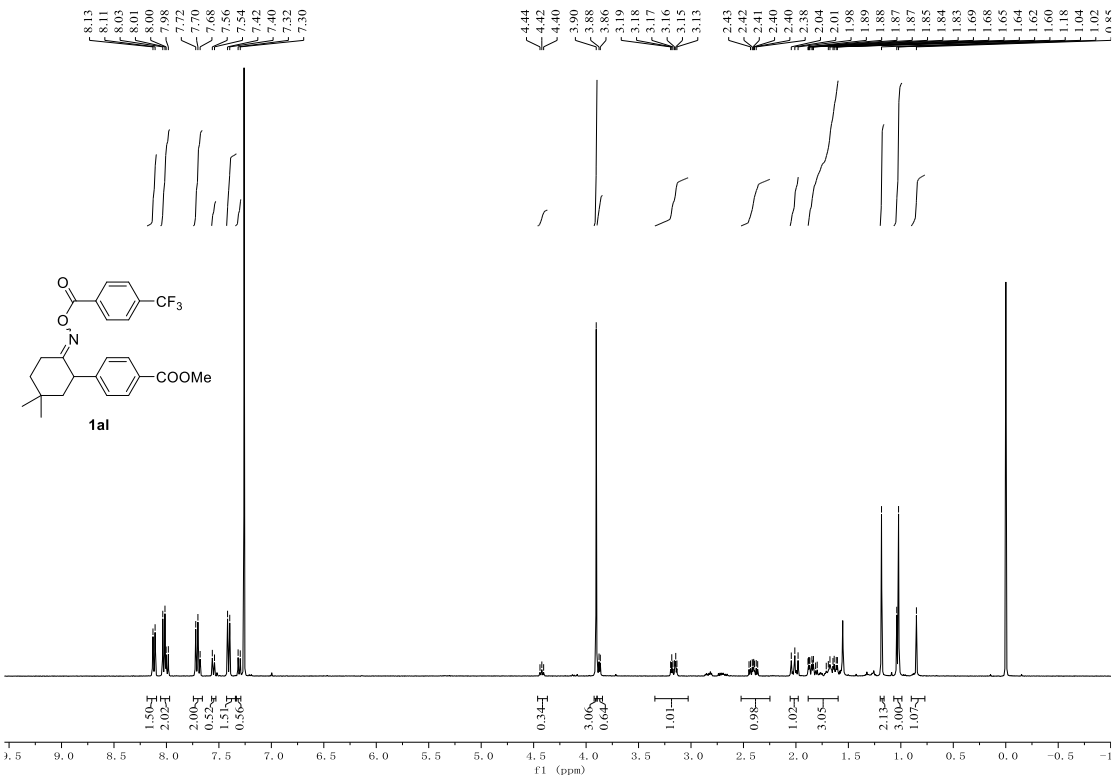
O
N
1ak
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110
f1 (ppm)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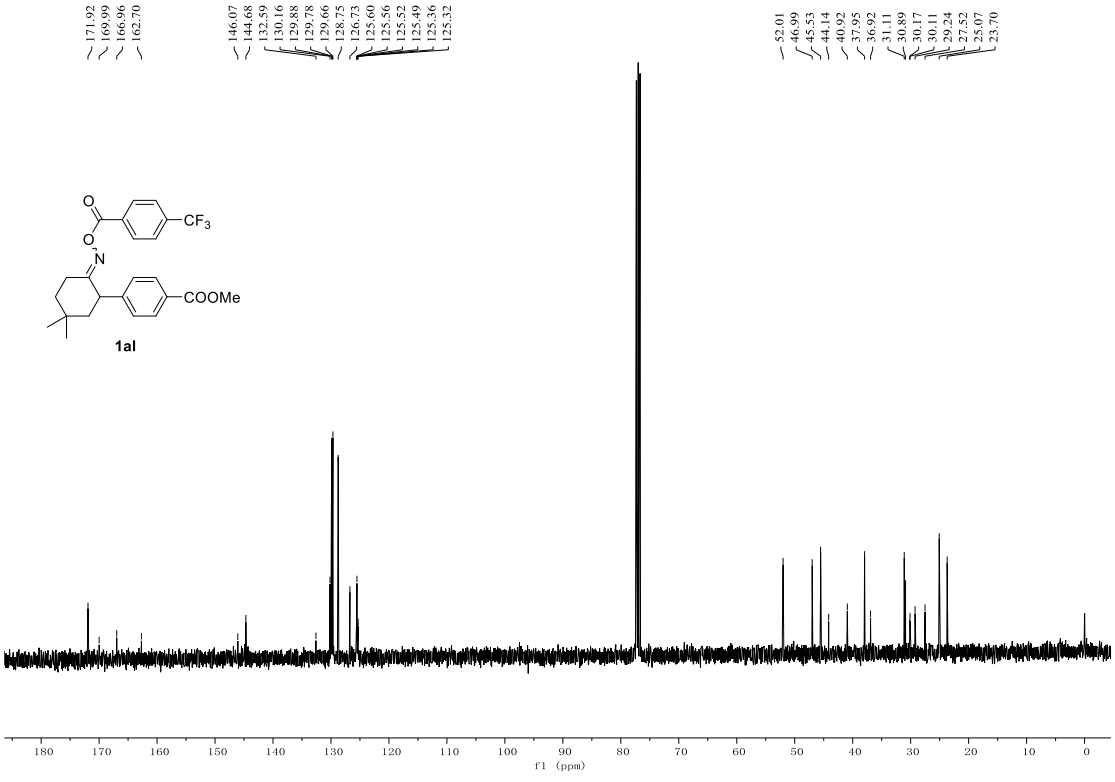
8.03
8.01
8.00
7.98
7.72
7.70
7.68
7.56
7.54
7.42
7.40
7.32
7.30
4.44
4.42
4.40
3.90
3.88
3.86
3.19
3.18
3.17
3.16
3.15
3.13
2.43
2.42
2.41
2.40
2.40
2.38
2.04
2.01
1.98
1.89
1.88
1.87
1.87
1.85
1.84
1.83
1.69
1.68
1.65
1.64
1.62
1.60
1.18
1.04
1.02
O
O
N
CF3
COOMe
1al
1.50
2.02
2.00
0.52
1.51
0.56
0.34
3.06
0.64
1.01
0.98
1.02
3.05
2.13
3.00
1.07
f1 (ppm)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166.96
162.70
146.07
144.68
132.59
130.16
129.88
129.78
129.66
128.75
126.73
125.60
125.56
125.52
125.49
125.36
125.32
52.01
46.99
45.53
44.14
40.92
37.95
36.92
31.11
30.89
30.17
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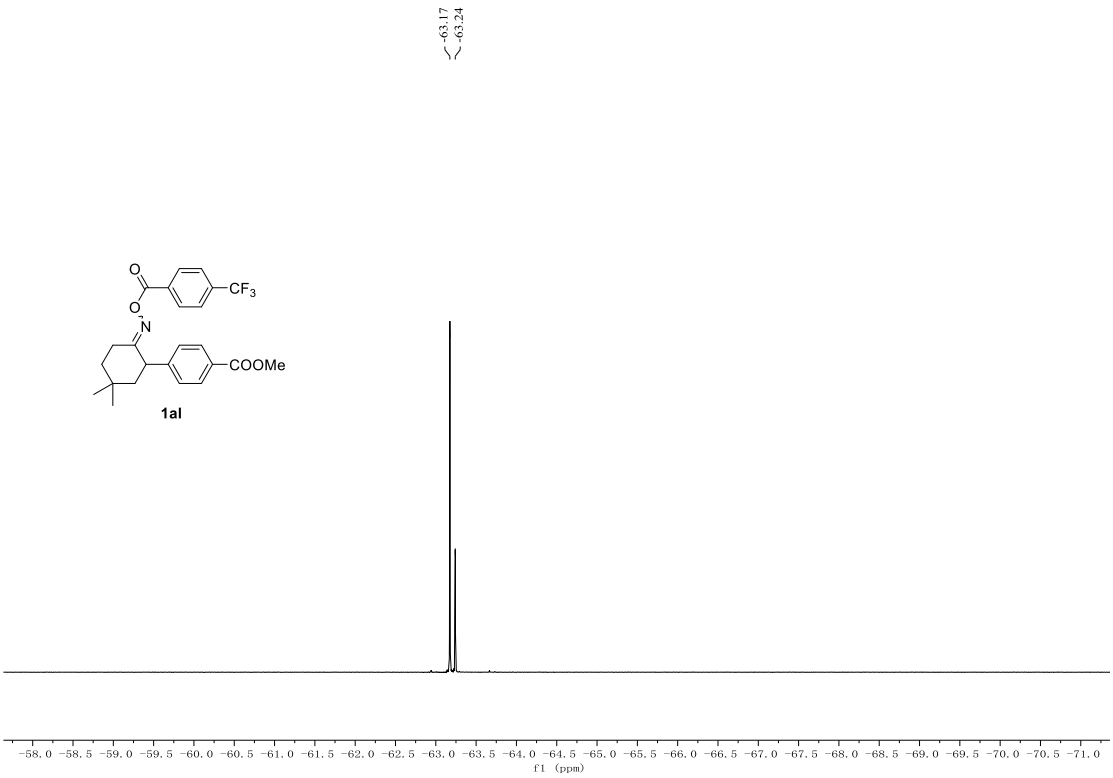
O
O
N
CF3
COOMe
1al
f1 (ppm)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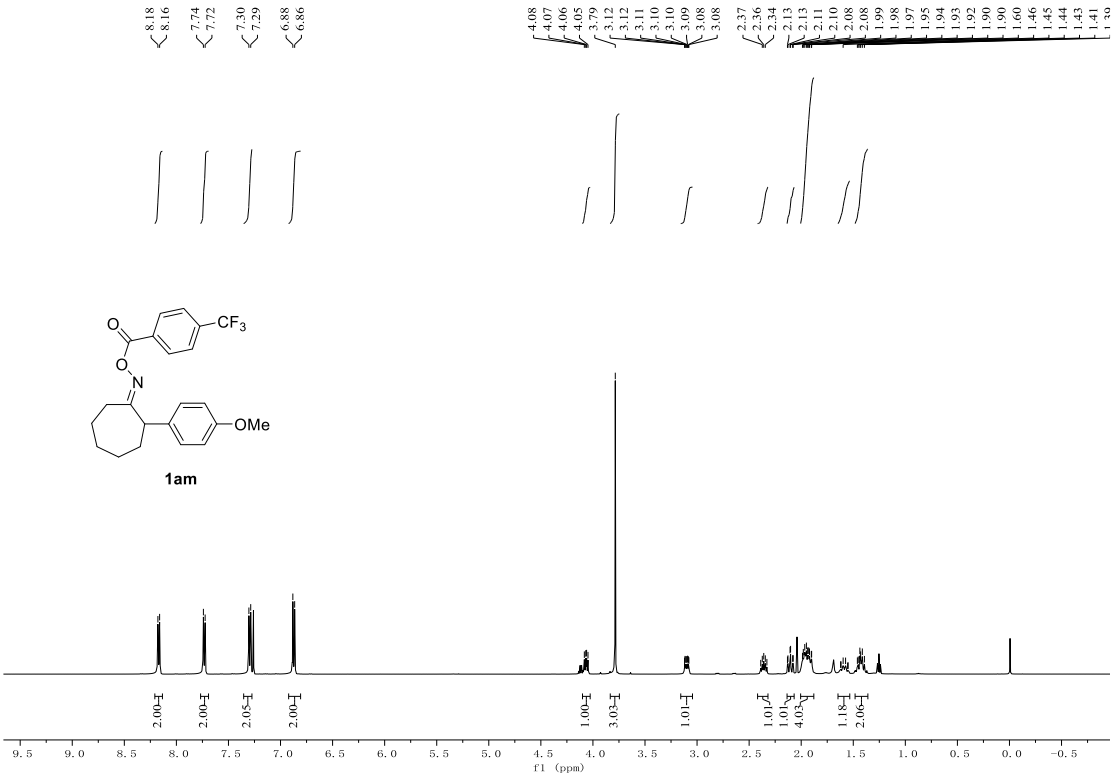
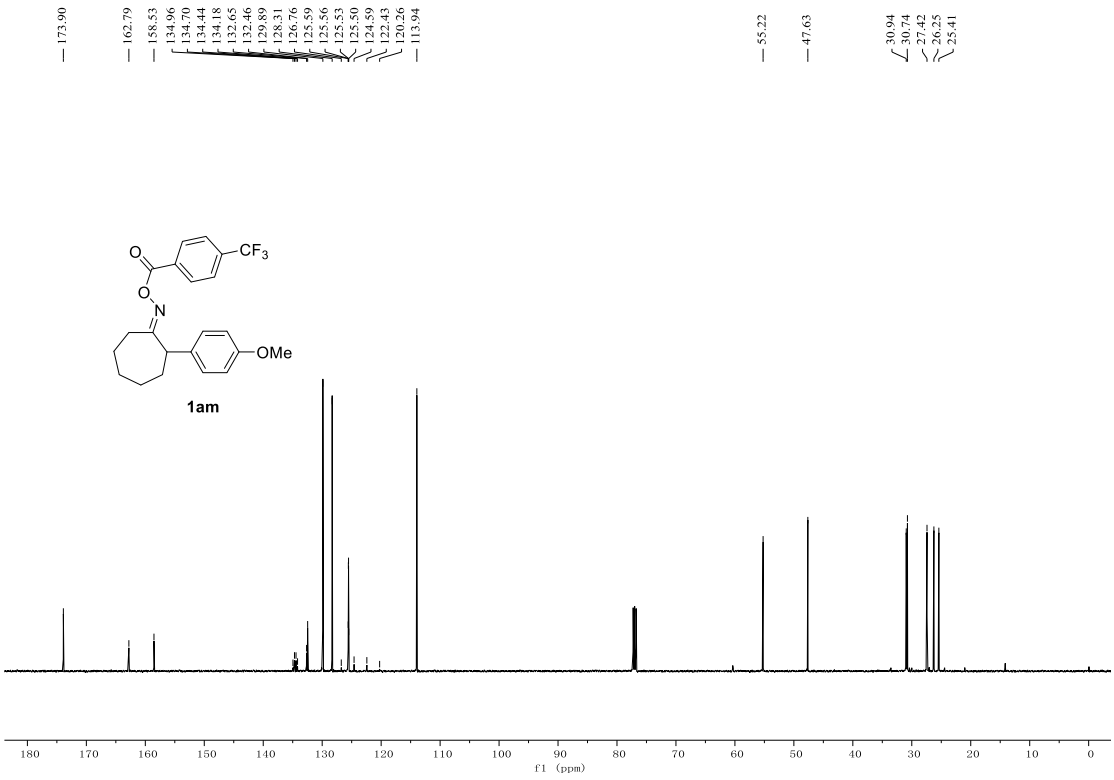
-63.24
CF3
COOMe
1al
f1 (ppm)


8.18
8.16
7.74
7.72
7.30
7.29
6.88
6.86
CF3
OMe
1am
2.00
2.00
2.05
2.00
1.00
3.03
1.01
1.01
1.01
4.03
1.18
2.06
f1 (ppm)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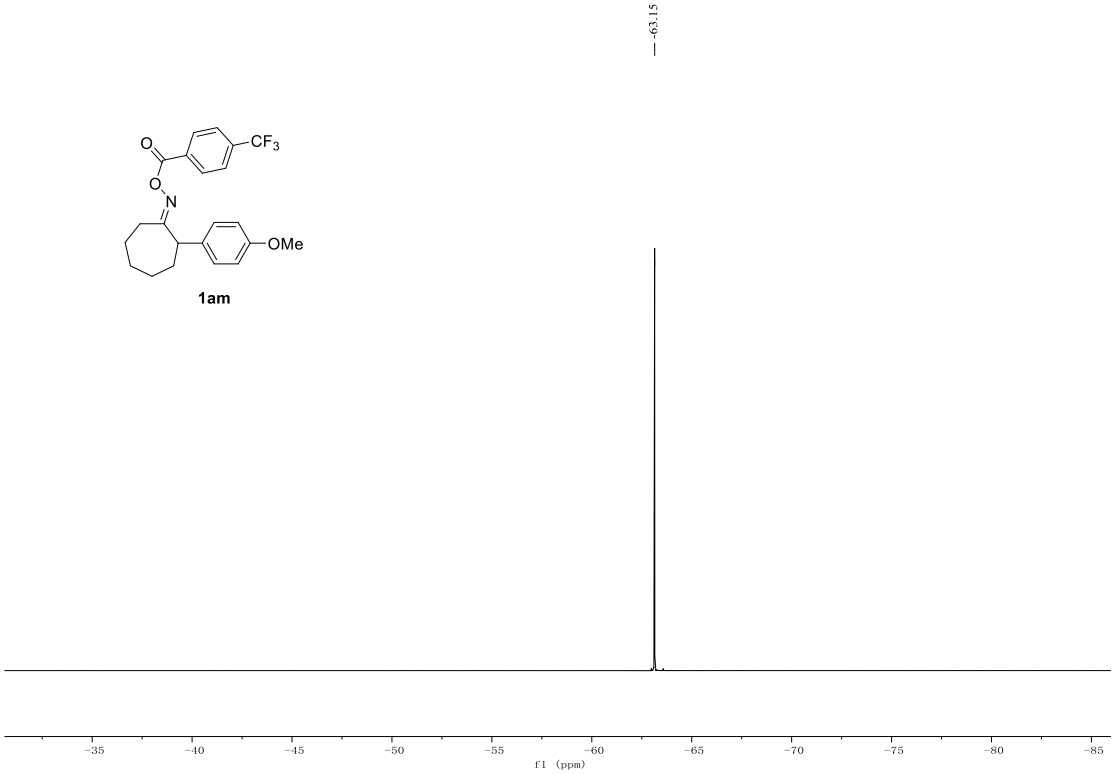
134.70
134.44
134.18
132.65
132.46
129.89
128.31
126.76
125.59
125.56
125.53
125.50
124.59
122.43
120.26
113.94
55.22
47.63
30.94
30.74
27.42
26.25
25.41
CF3
O
O
N
OMe
1am
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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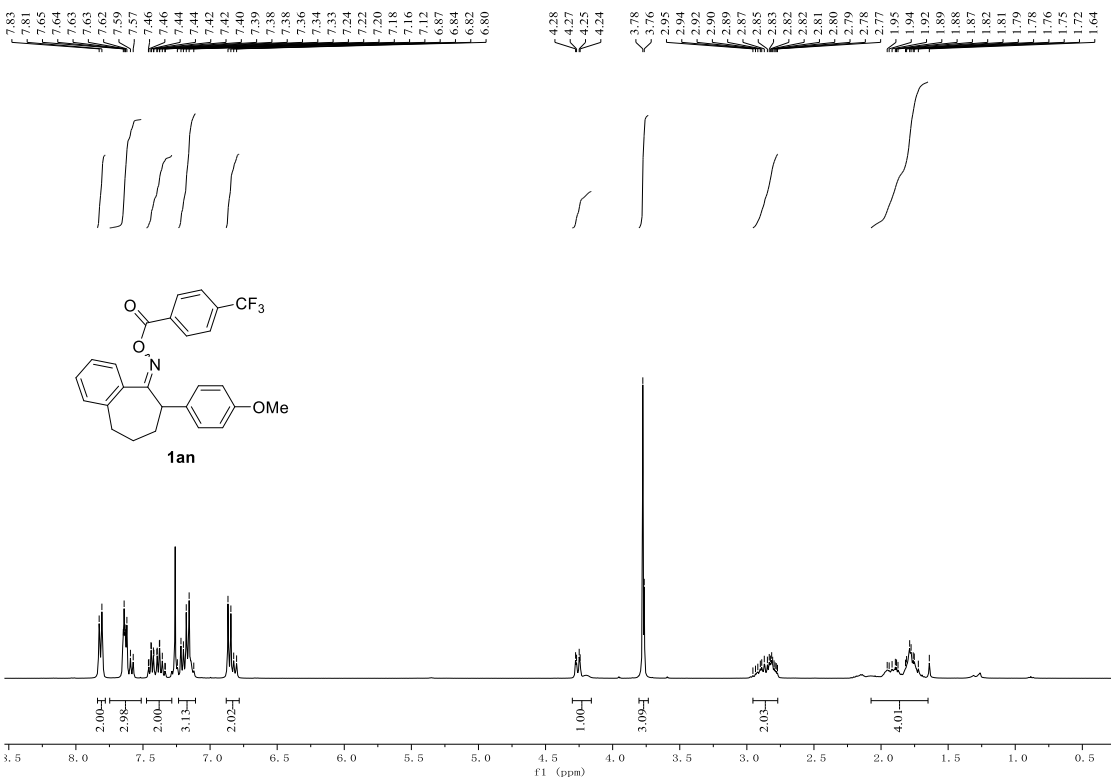
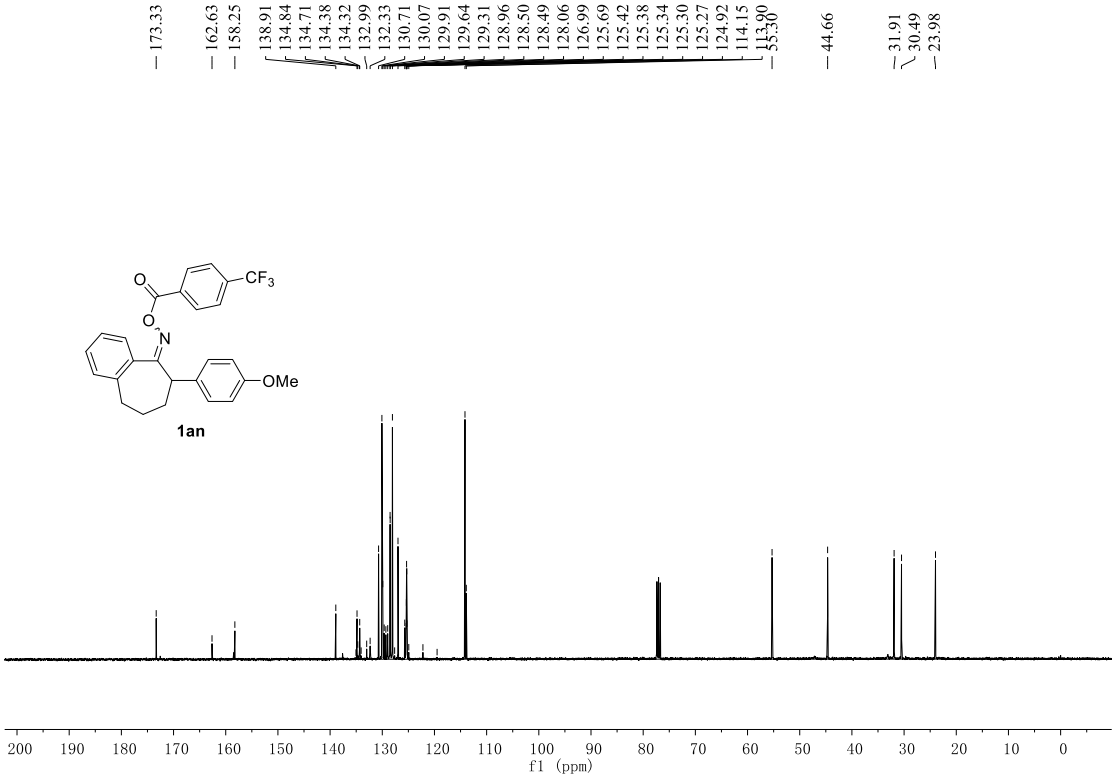
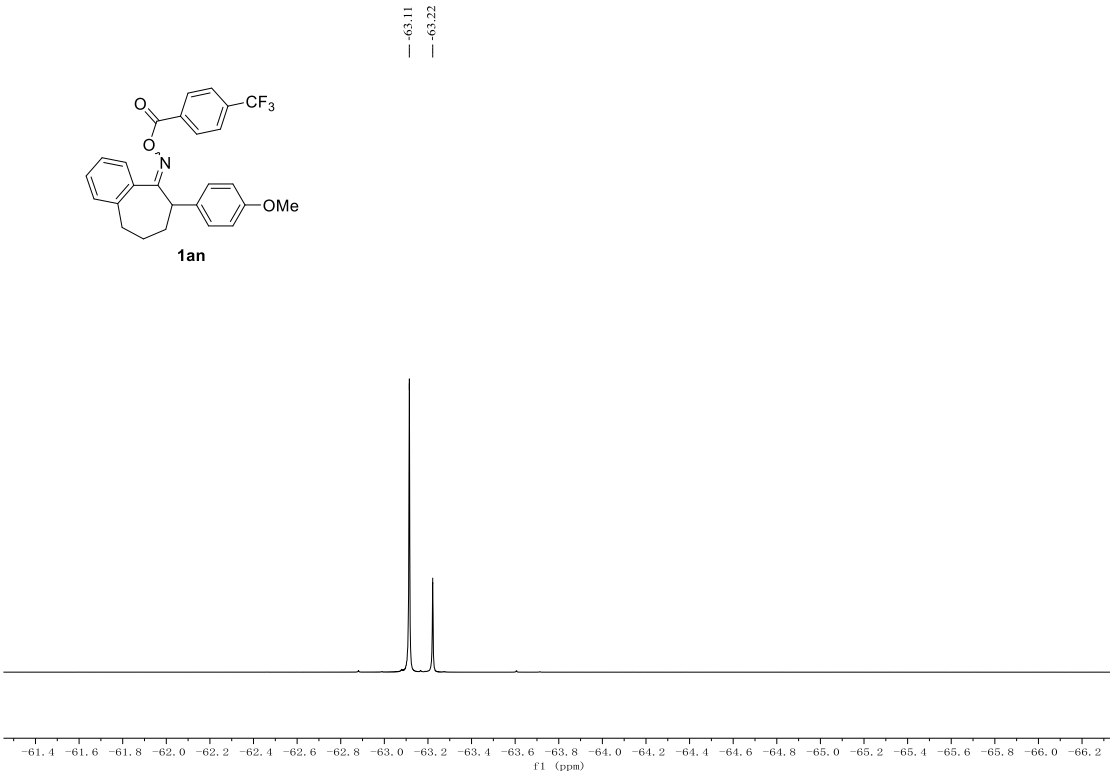
CF3
O
O
N
OMe
1am
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
f1 (ppm)


7.83 7.81 7.65 7.64 7.63 7.63 7.62 7.59 7.57 7.46 7.46 7.44 7.44 7.42 7.42 7.40 7.39 7.38 7.38 7.36 7.34 7.33 7.24 7.22 7.20 7.18 7.16 7.12 6.87 6.84 6.82 6.80
4.28 4.27 4.25 4.24
3.78 3.76 2.95 2.94 2.92 2.90 2.89 2.87 2.85 2.83 2.82 2.82 2.81 2.80 2.79 2.78 2.77 1.95 1.94 1.92 1.89 1.88 1.87 1.82 1.81 1.79 1.78 1.76 1.75 1.72 1.64
O
O
N
CF3
OMe
1an
2.00 2.98 2.00 3.13 2.02 1.00 3.09 2.03 4.01
f1 (ppm)


173.33 162.63 158.25 138.91 134.84 134.71 134.38 134.32 132.99 132.33 130.71 130.07 129.91 129.64 129.31 128.96 128.50 128.49 128.06 126.99 125.69 125.42 125.38 125.34 125.30 125.27 124.92 114.15 113.90 55.30 44.66 31.91 30.49 23.98
O
O
N
CF3
OMe
1an
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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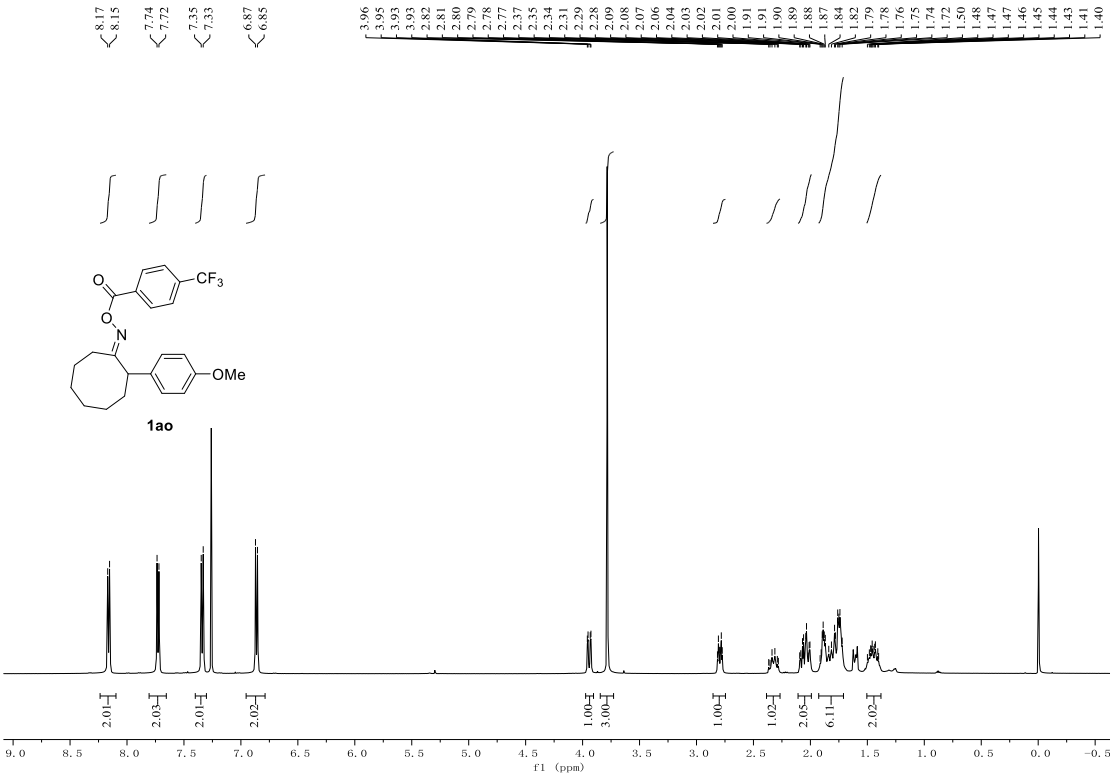
-63.22
CF3
O
O
N
OMe
1an
f1 (ppm)


8.17
8.15
7.74
7.72
7.35
7.33
6.87
6.85
CF3
O
O
N
OMe
1ao
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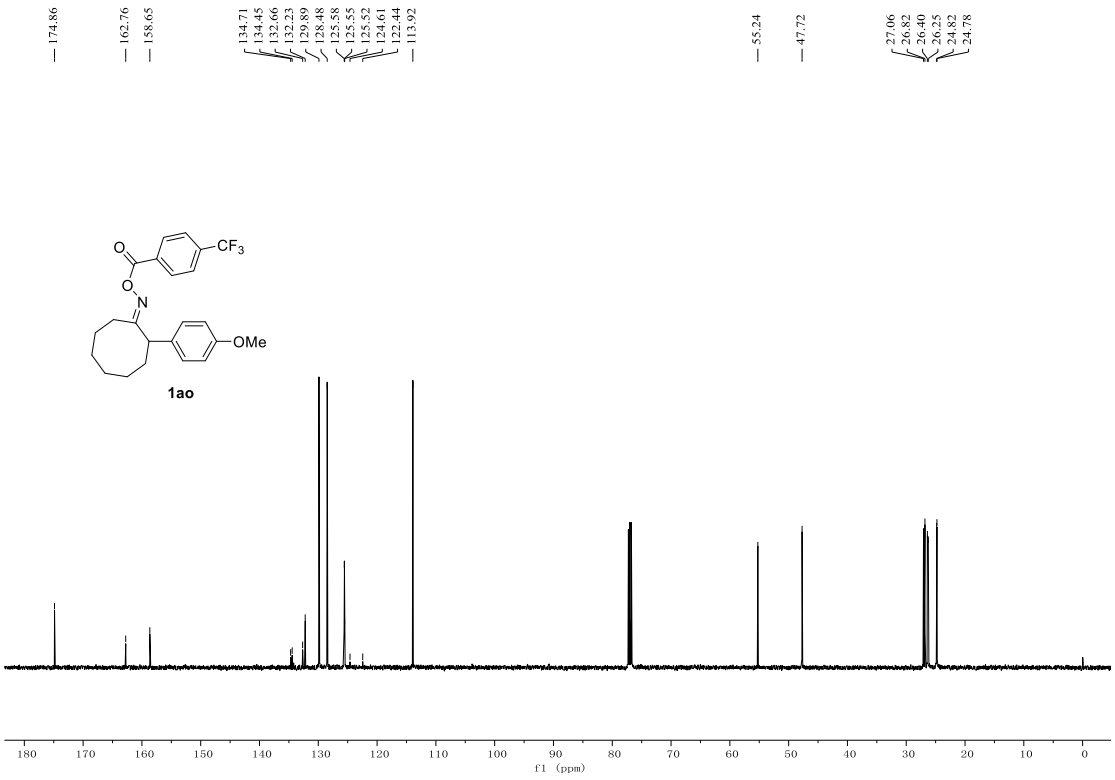
1.02
2.05
6.11
2.02
f1 (ppm)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132.23
129.89
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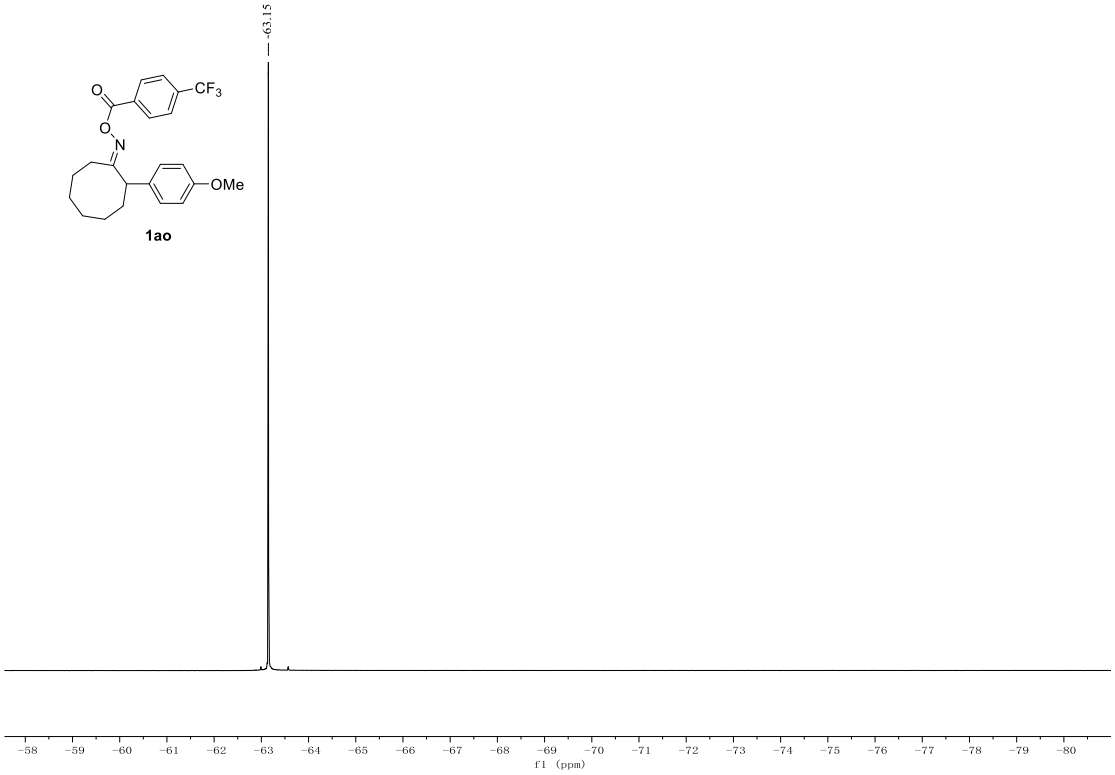
125.58
125.55
125.52
124.61
122.44
113.92
55.24
47.72
27.06
26.82
26.40
26.25
24.82
24.78
CF3
O
O
N
OMe
1ao
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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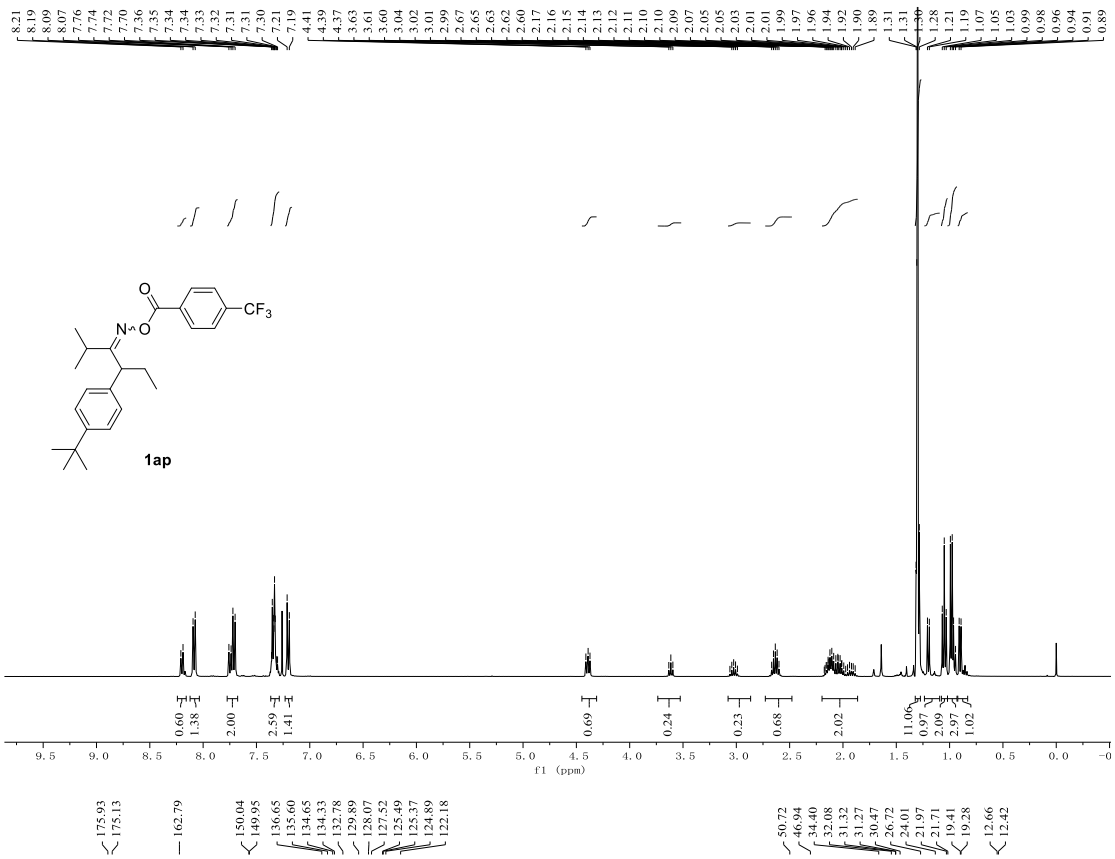
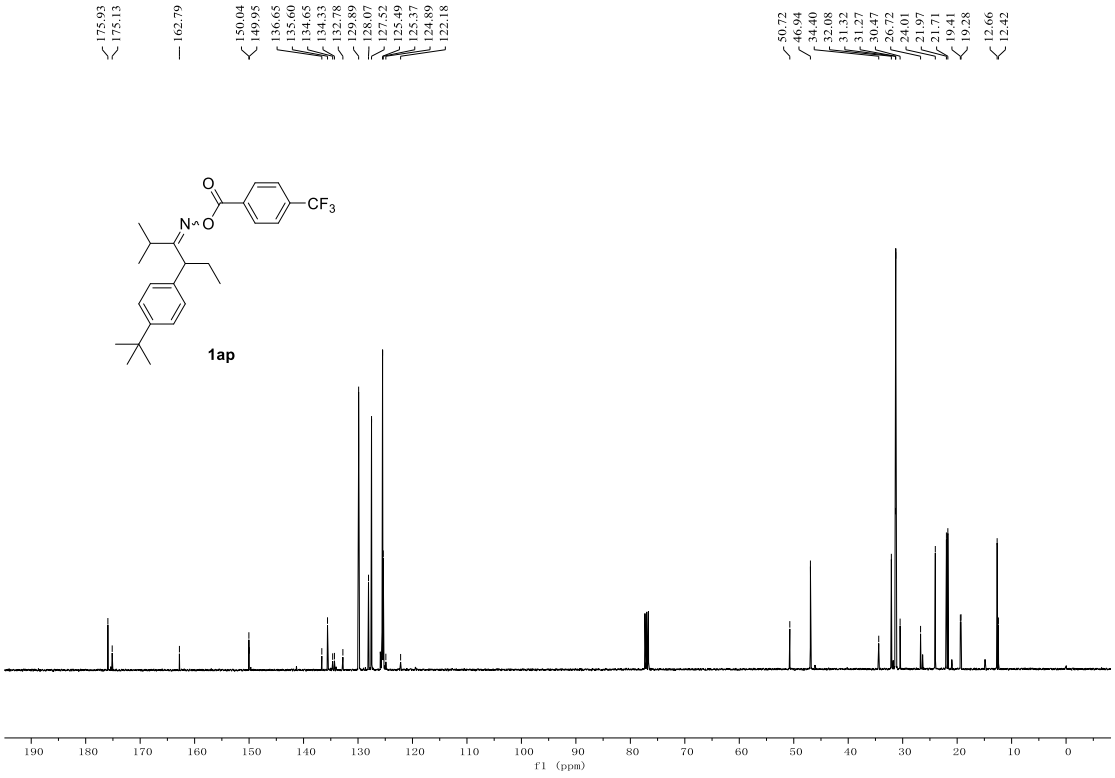
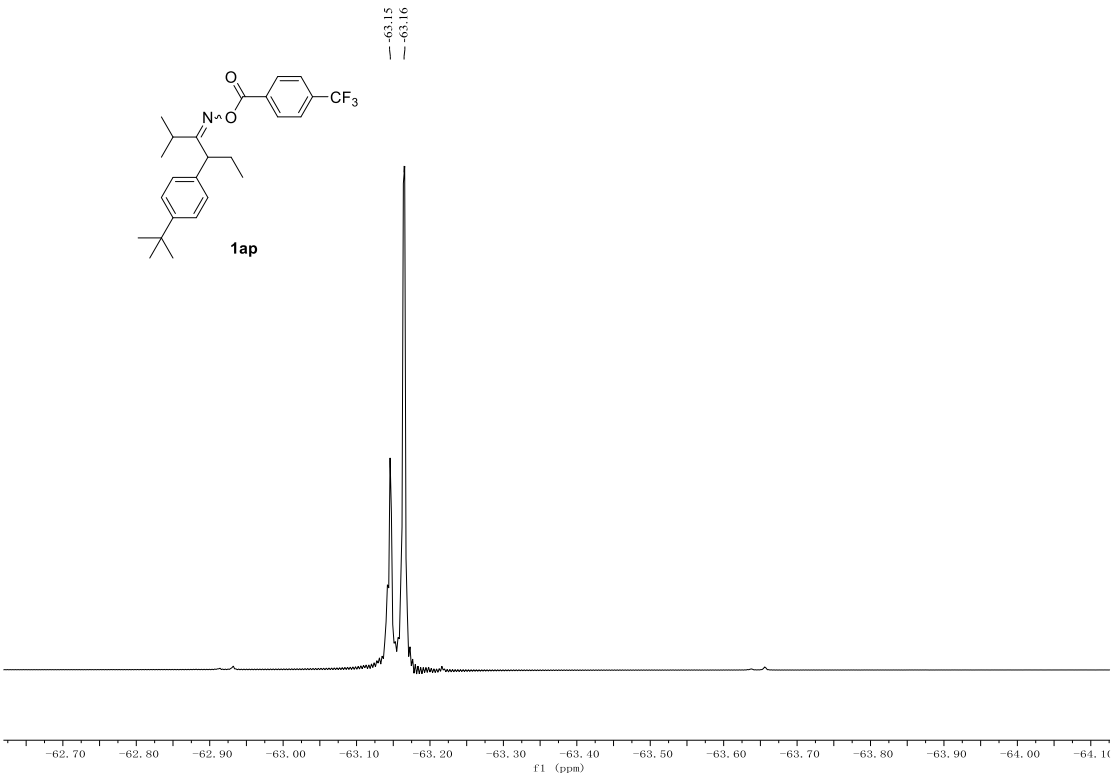
CF3
O
O
N
OMe
1ao
-58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80
f1 (ppm)


1ap
f1 (ppm)


1ap
f1 (ppm)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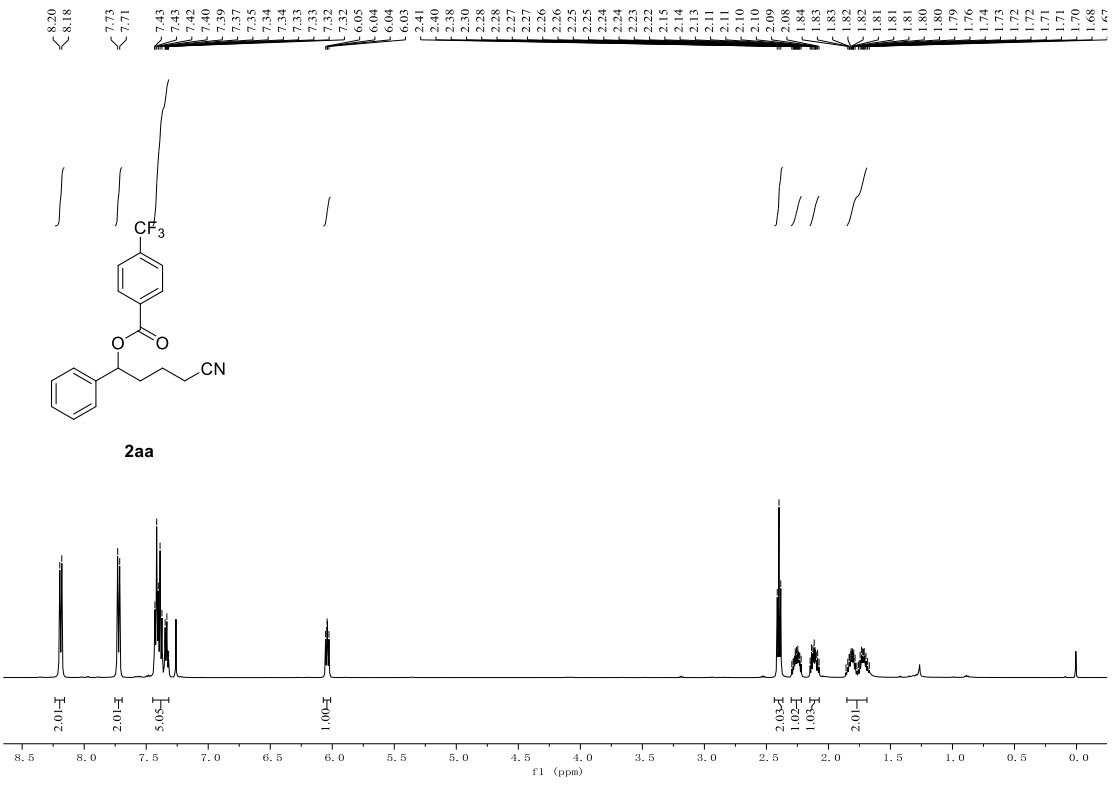
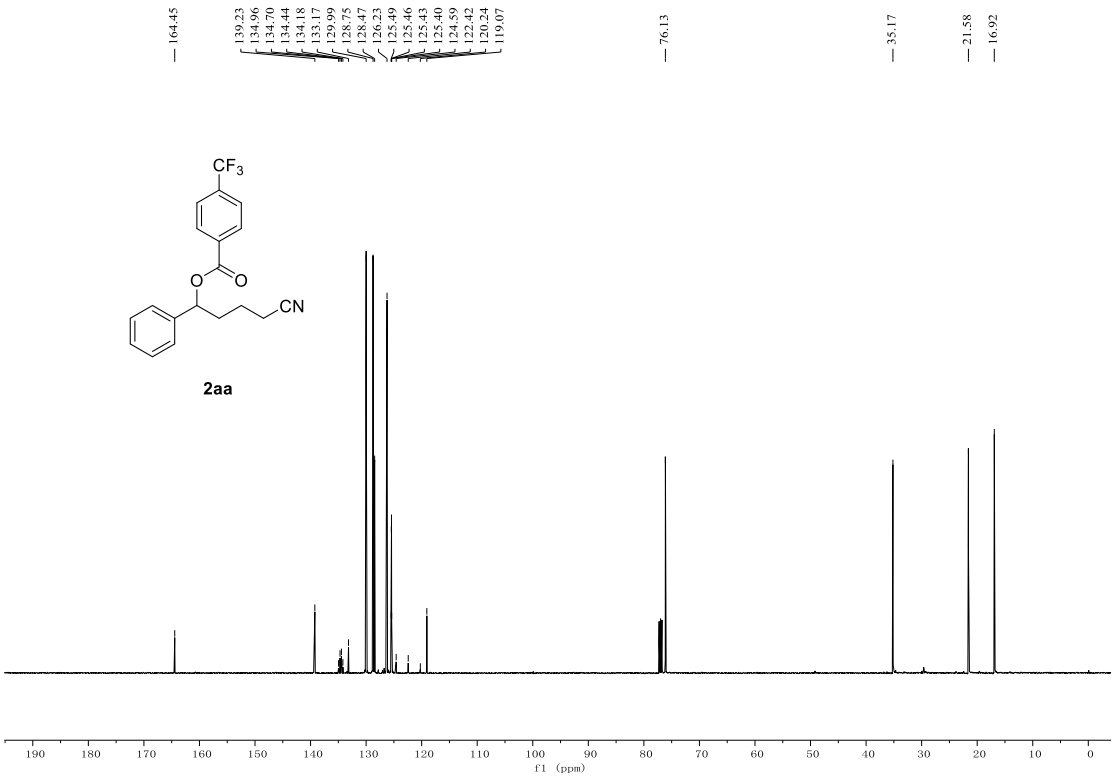
-63.16
CF3
1ap
-62.70
-62.80
-62.90
-63.00
-63.10
-63.20
-63.30
-63.40
-63.50
-63.60
-63.70
-63.80
-63.90
-64.00
f1 (ppm)


CF3
O
O
CN
2aa
2.01
2.01
5.05
1.00
2.03
1.02
1.03
2.01
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
0.0
f1 (ppm)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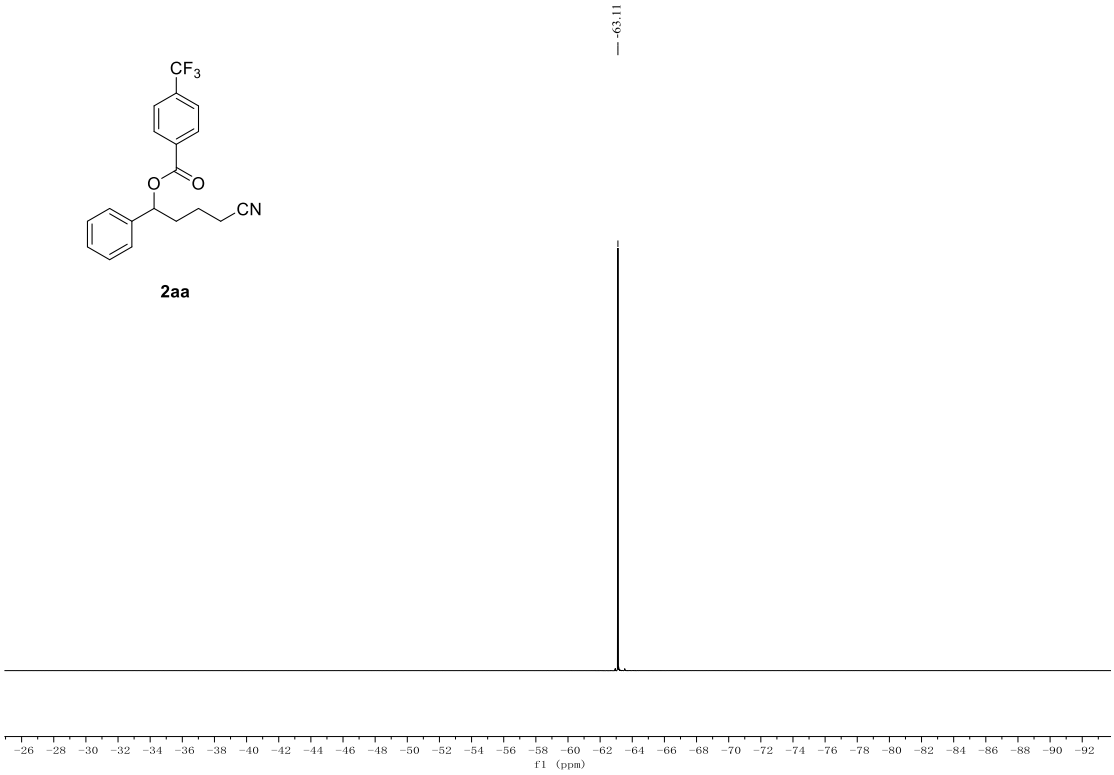
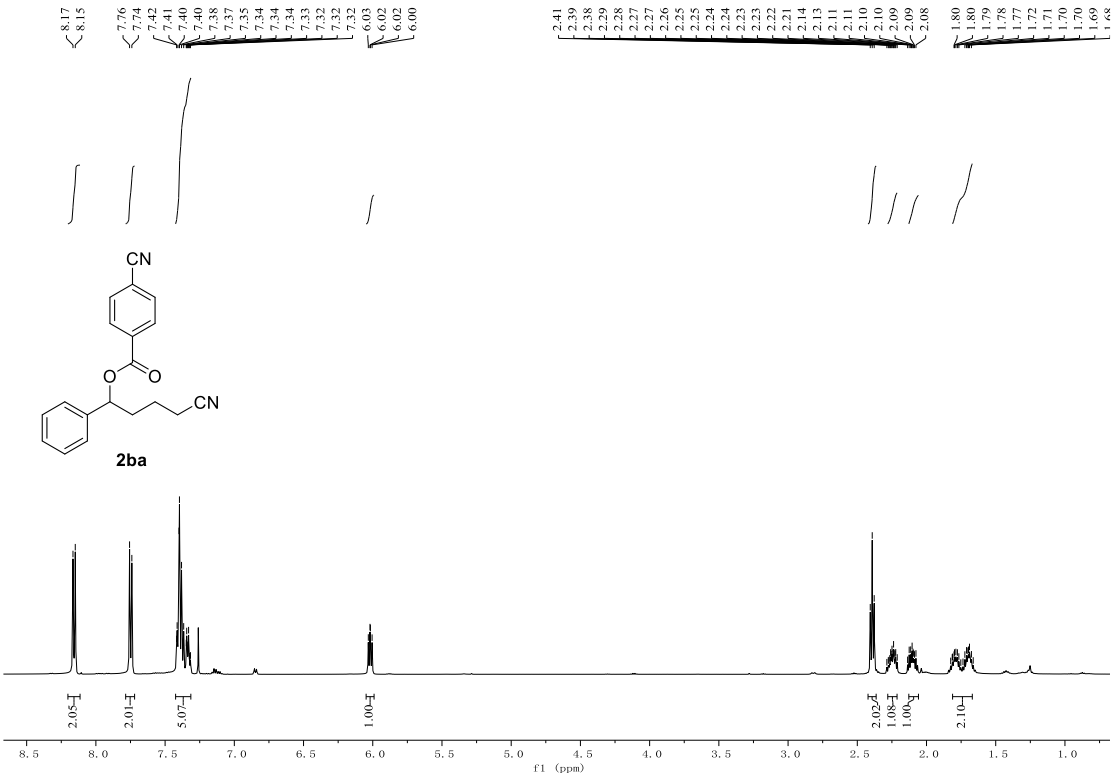
139.23
134.96
134.70
134.44
134.18
133.17
129.99
128.75
128.47
126.23
125.49
125.46
125.43
125.40
124.59
122.42
120.24
119.07
76.13
35.17
21.58
16.92
CF3
O
O
CN
2aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.11
CF3
O
O
CN
2aa
-26 -28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92
f1 (ppm)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7.41
7.40
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7.38
7.37
7.35
7.34
7.34
7.33
7.32
7.32
6.03
6.02
6.02
6.00
2.41
2.39
2.38
2.29
2.28
2.27
2.27
2.26
2.25
2.25
2.24
2.24
2.23
2.23
2.22
2.21
2.14
2.13
2.11
2.11
2.10
2.10
2.09
2.09
2.08
1.80
1.80
1.79
1.78
1.77
1.72
1.71
1.70
1.70
1.69
CN
O
O
CN
2ba
2.05
2.01
5.07
1.00
2.02
1.08
1.00
2.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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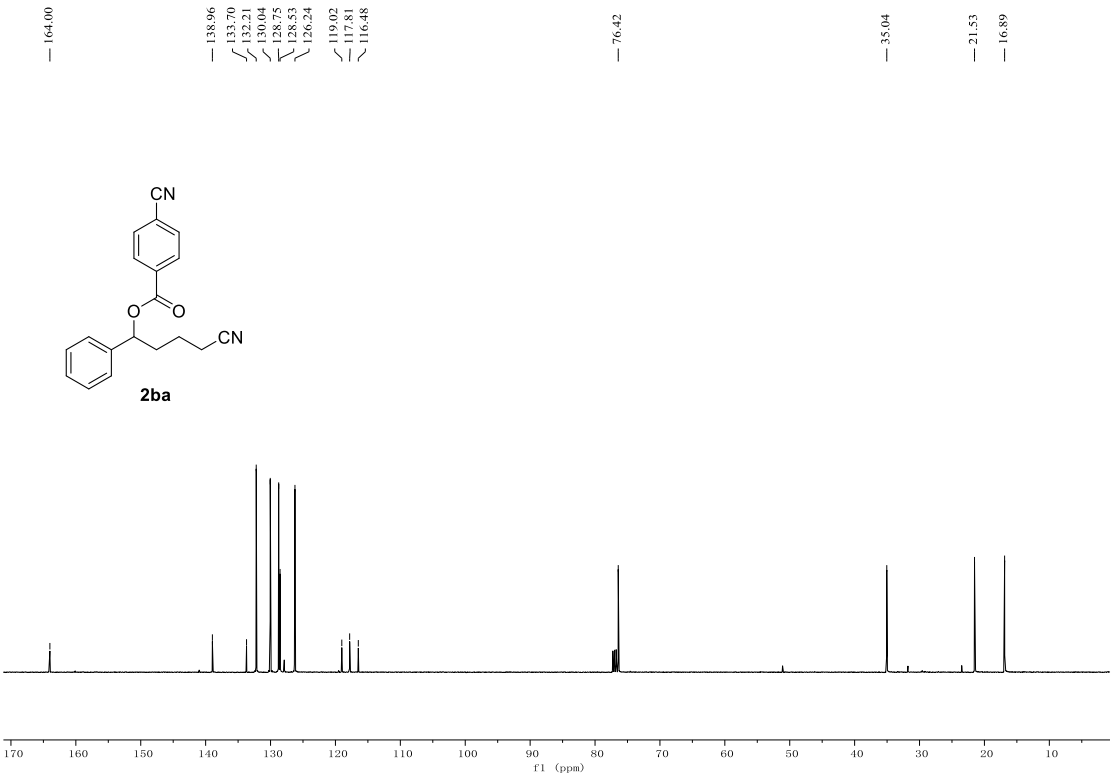
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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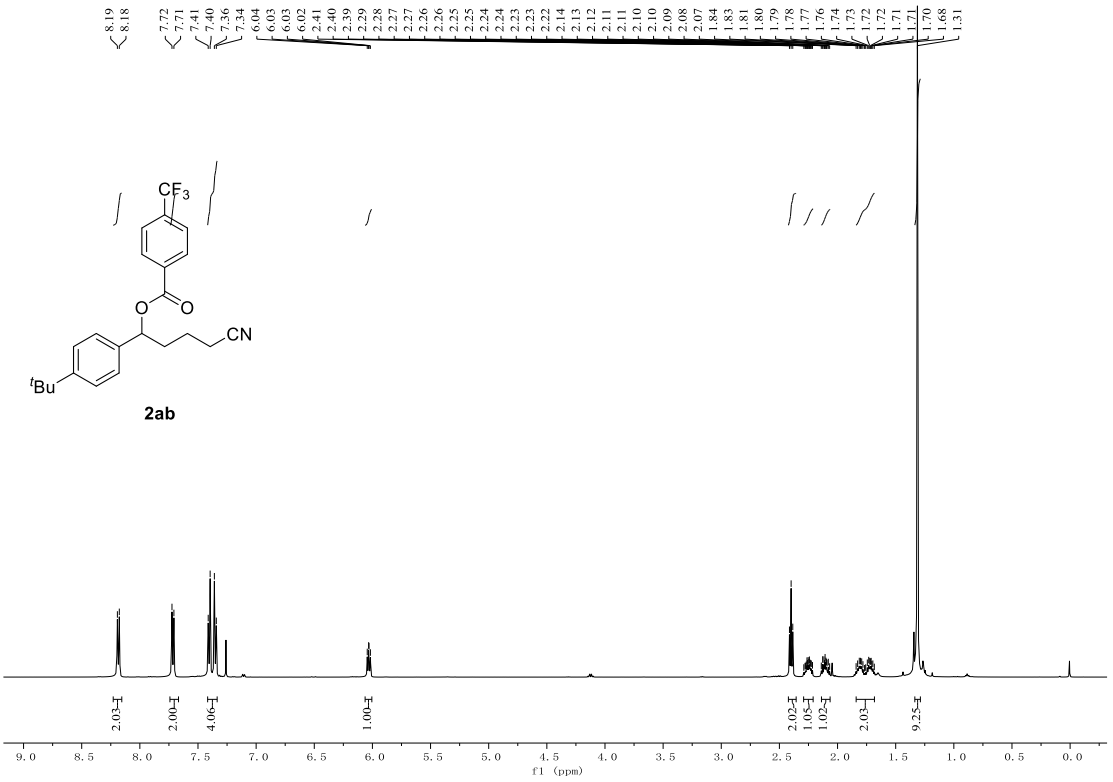
132.21
130.04
128.75
128.53
126.24
119.02
117.81
116.48
76.42
35.04
21.53
16.89
CN
O
O
CN
2ba
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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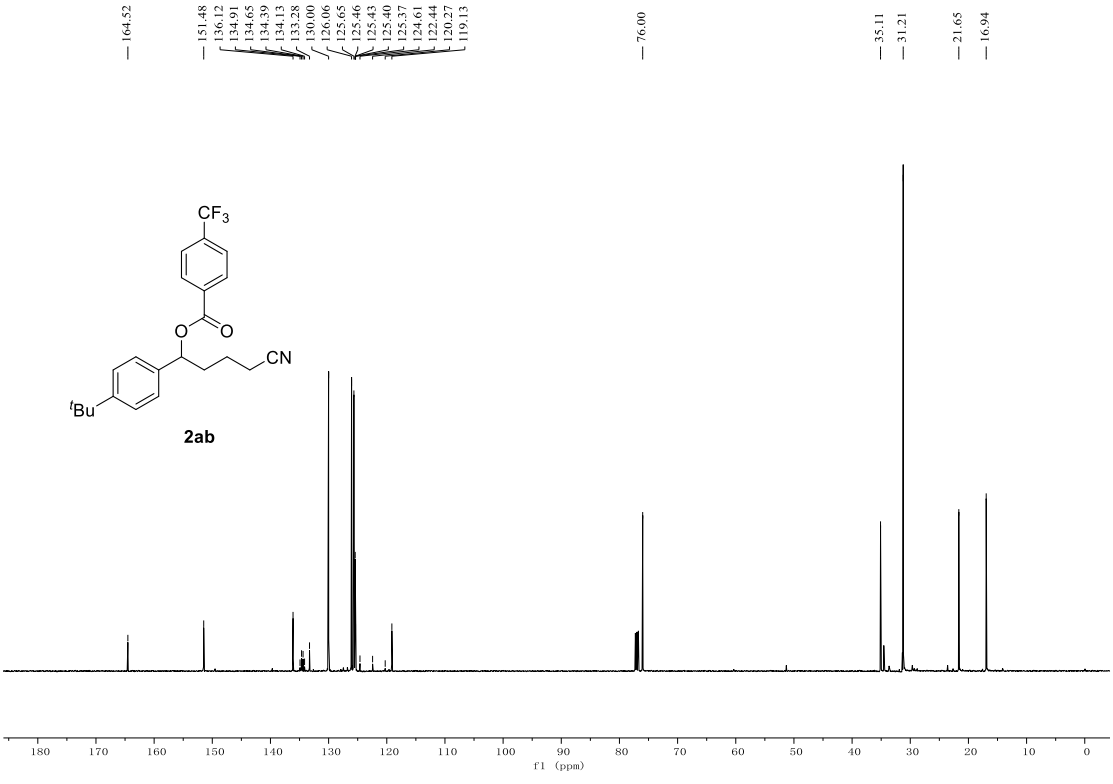
7.72
7.71
7.41
7.40
7.36
7.34
6.04
6.03
6.03
6.02
2.41
2.40
2.39
2.29
2.28
2.27
2.27
2.26
2.26
2.25
2.25
2.24
2.24
2.23
2.23
2.22
2.14
2.13
2.12
2.11
2.11
2.10
2.10
2.09
2.08
2.07
1.84
1.83
1.81
1.80
1.79
1.78
1.77
1.76
1.74
1.73
1.72
1.72
1.71
1.71
1.70
1.68
1.31
CF3
O
O
CN
tBu
2ab
2.03
2.00
4.06
1.00
2.02
1.05
1.02
2.03
9.25
f1 (ppm)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134.91
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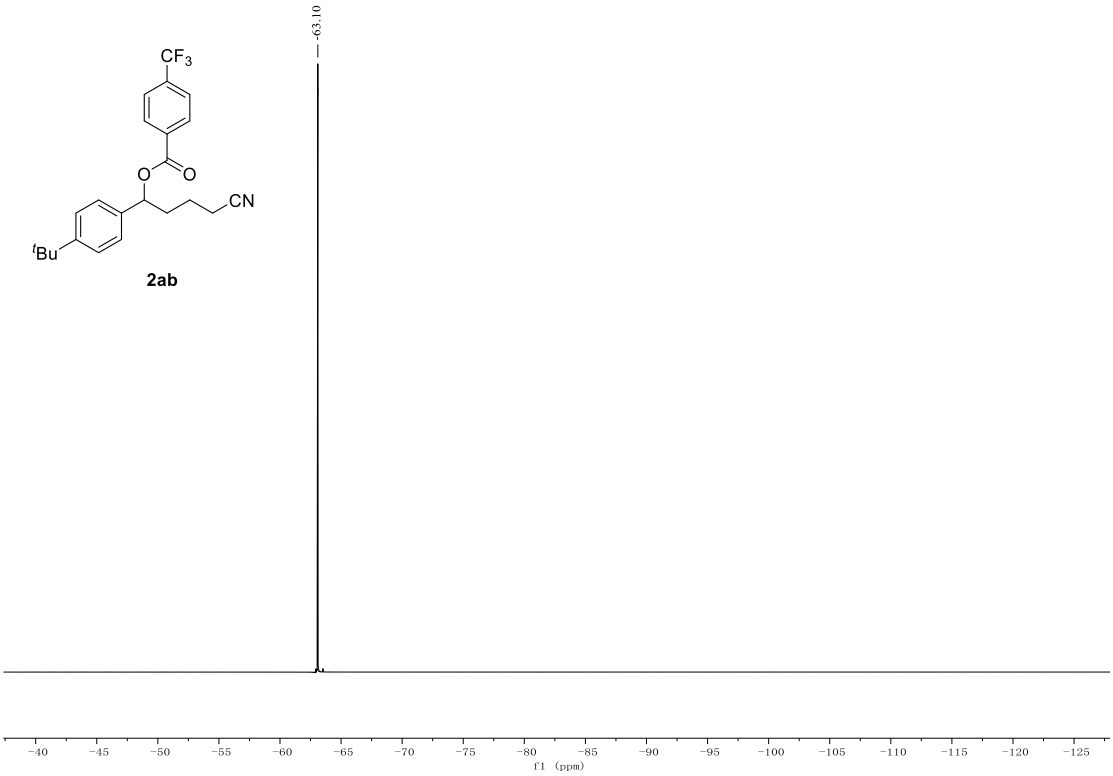
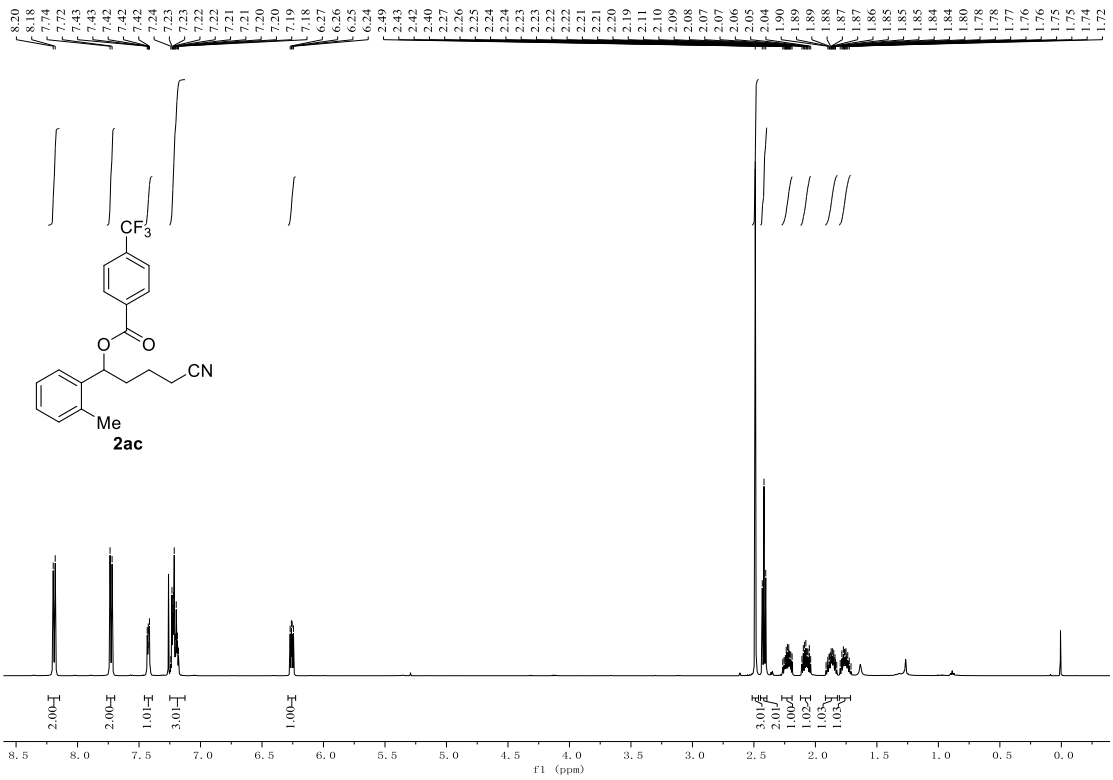
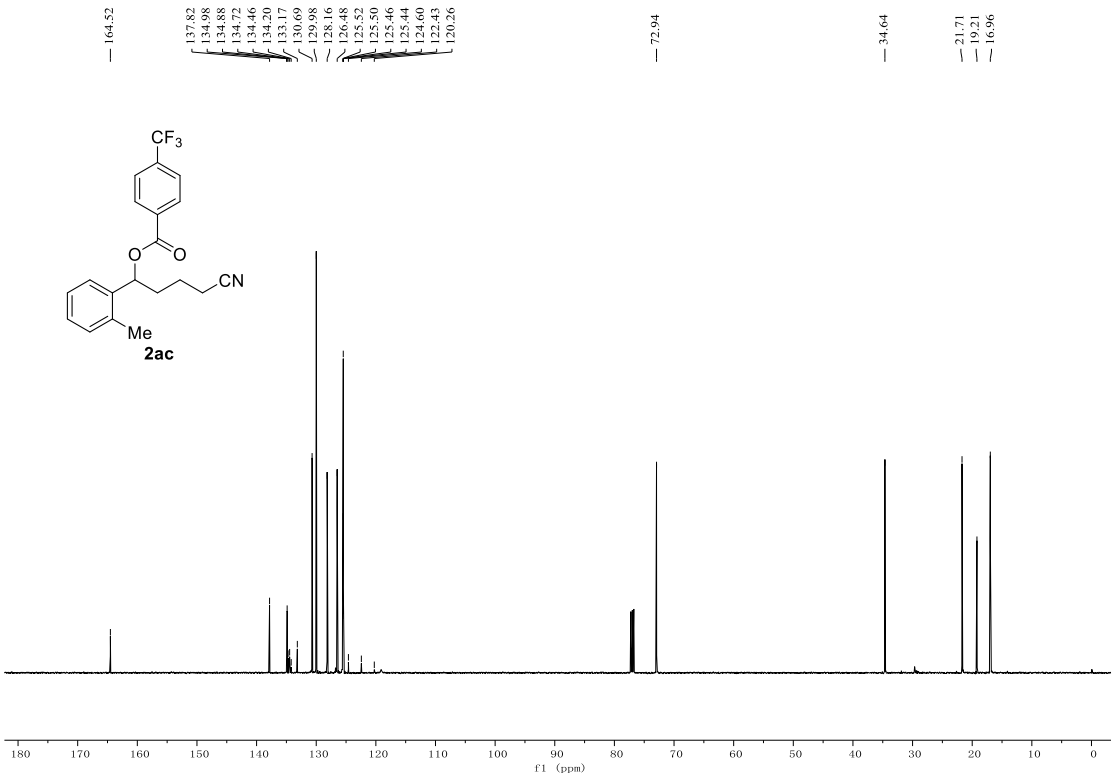
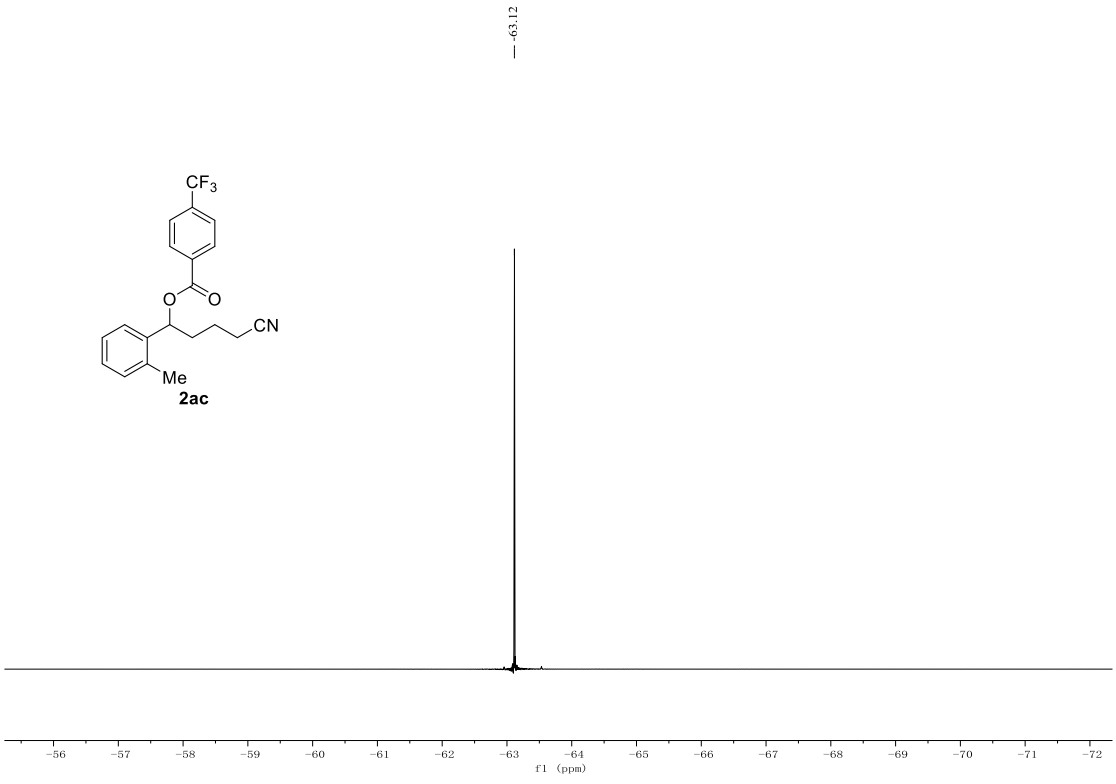
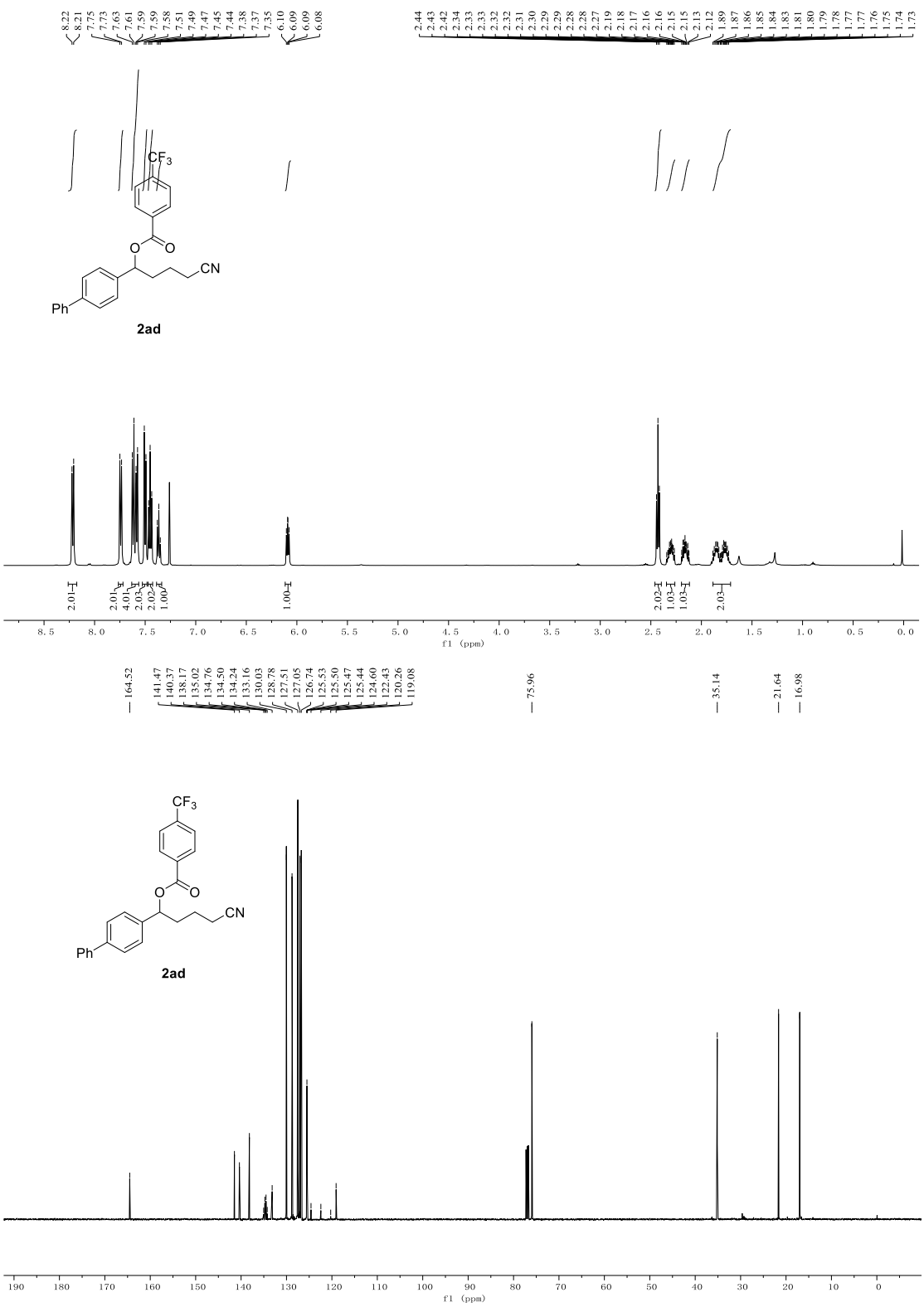
134.39
134.13
133.28
130.00
126.06
125.65
125.46
125.43
125.40
125.37
124.61
122.44
120.27
119.13
76.00
35.11
31.21
21.65
16.94
CF3
O
O
CN
tBu
2ab
f1 (ppm)


-63.10
CF3
O
O
CN
tBu
2ab
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125
f1 (ppm)


8.20 8.18 7.74 7.72 7.43 7.43 7.42 7.42 7.42 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.18 6.27 6.26 6.25 6.24
2.49 2.43 2.42 2.40 2.27 2.26 2.25 2.24 2.24 2.23 2.23 2.22 2.22 2.21 2.21 2.20 2.19 2.11 2.10 2.09 2.08 2.07 2.07 2.06 2.05 2.04 1.90 1.89 1.89 1.88 1.87 1.87 1.86 1.85 1.85 1.85 1.84 1.84 1.80 1.78 1.78 1.77 1.76 1.76 1.75 1.75 1.74 1.72
CF3
O
O
CN
Me
2ac
2.00 2.00 1.01 3.01 1.00 3.01 2.01 1.00 1.02 1.03 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
f1 (ppm)


164.52
137.82
134.98
134.88
134.72
134.46
134.20
133.17
130.69
129.98
128.16
126.48
125.52
125.50
125.46
125.44
124.60
122.43
120.26
72.94
34.64
21.71
19.21
16.96
CF3
O
O
CN
Me
2ac
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-63.12
CF3
O
O
CN
Me
2ac
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
f1 (ppm)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8.21
7.75
7.73
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7.61
7.59
7.59
7.59
7.58
7.51
7.49
7.47
7.45
7.44
7.38
7.37
7.35
6.10
6.09
6.09
6.08
2.44
2.43
2.42
2.34
2.33
2.32
2.32
2.31
2.30
2.29
2.29
2.28
2.28
2.27
2.19
2.18
2.17
2.16
2.16
2.15
2.15
2.13
2.12
1.89
1.87
1.86
1.85
1.84
1.83
1.81
1.80
1.79
1.78
1.77
1.77
1.76
1.75
1.74
1.73
CF3
O
O
CN
Ph
2ad
2.01
2.01
4.01
2.03
2.02
1.00
1.00
2.02
1.03
1.03
2.03
f1 (ppm)
164.52
141.47
140.37
138.17
135.02
134.76
134.50
134.24
133.16
130.03
128.78
127.51
127.05
126.74
125.53
125.50
125.47
125.44
124.60
122.43
120.26
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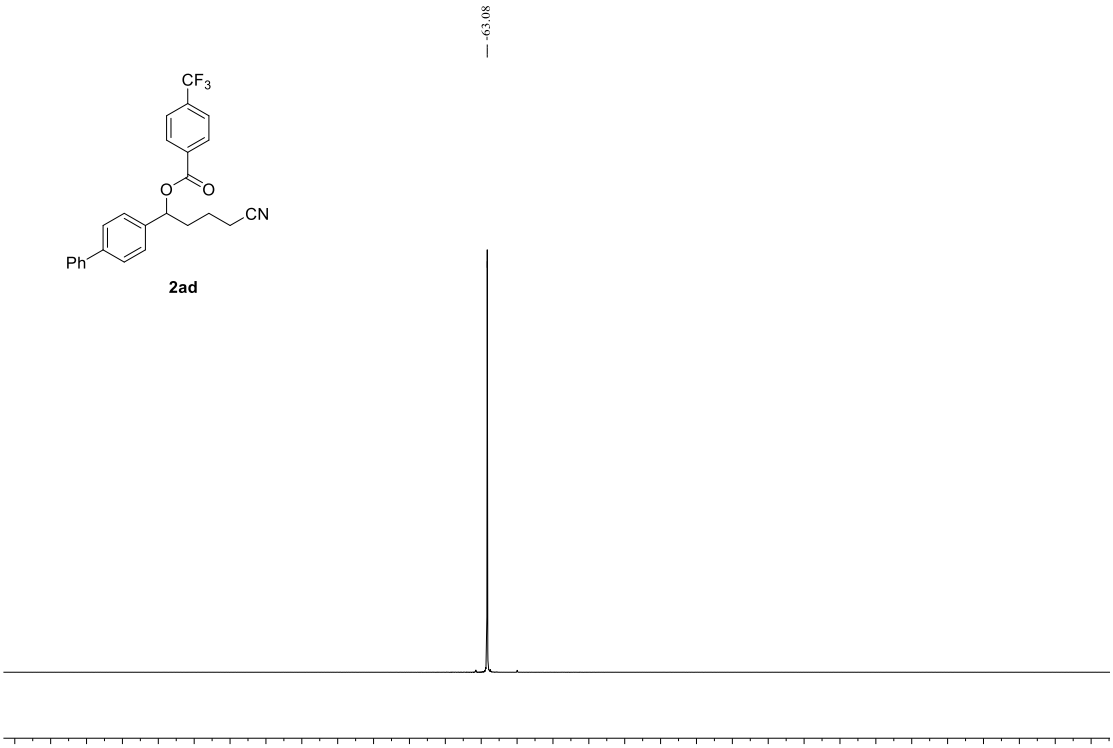
75.96
35.14
21.64
16.98
CF3
O
O
CN
Ph
2ad
f1 (ppm)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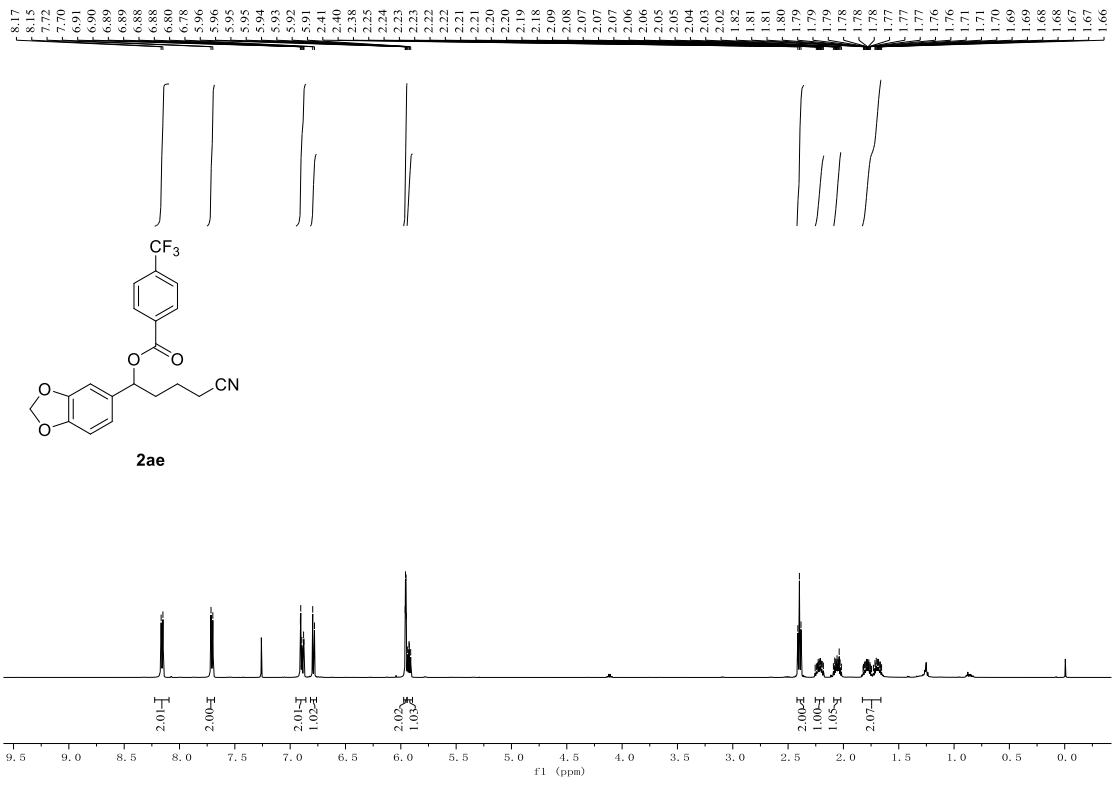
O
O
CN
Ph
2ad
-56.5 -57.5 -58.5 -59.5 -60.5 -61.5 -62.5 -63.5 -64.5 -65.5 -66.5 -67.5 -68.5 -69.5 -70.5 -71.5
f1 (ppm)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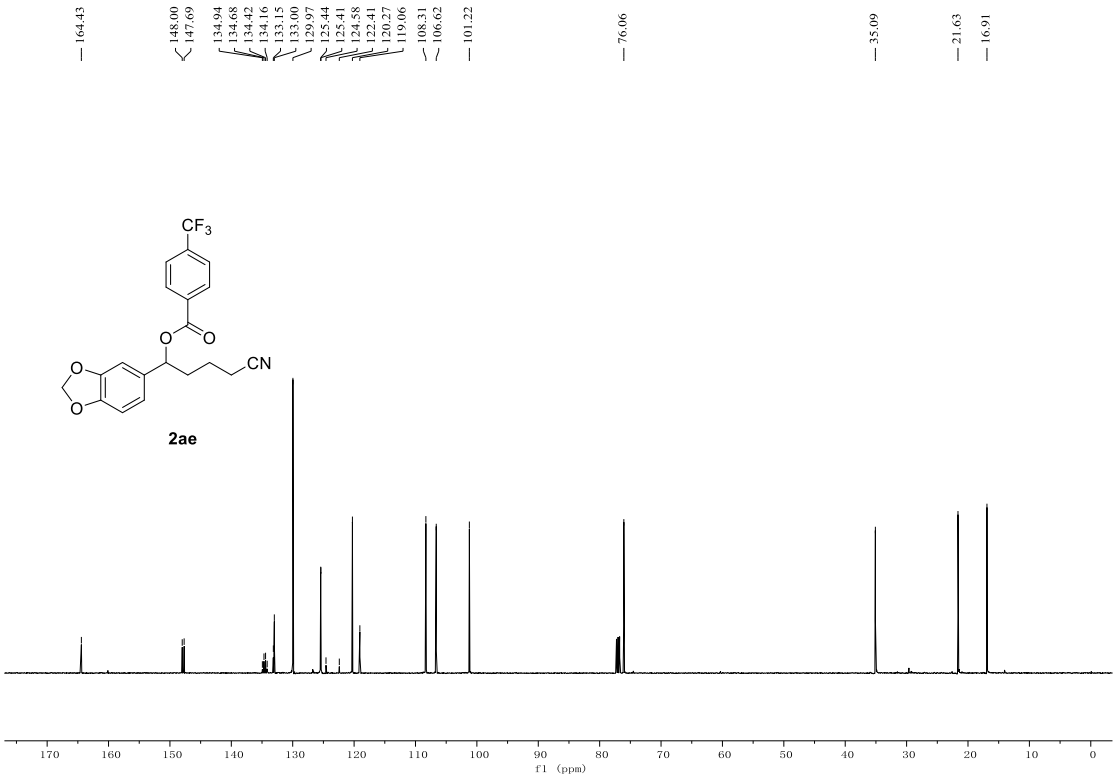
CF3
O
O
CN
O
O
2ae
2.01 2.00 2.01 1.02 2.02 1.03 2.00 1.00 1.05 2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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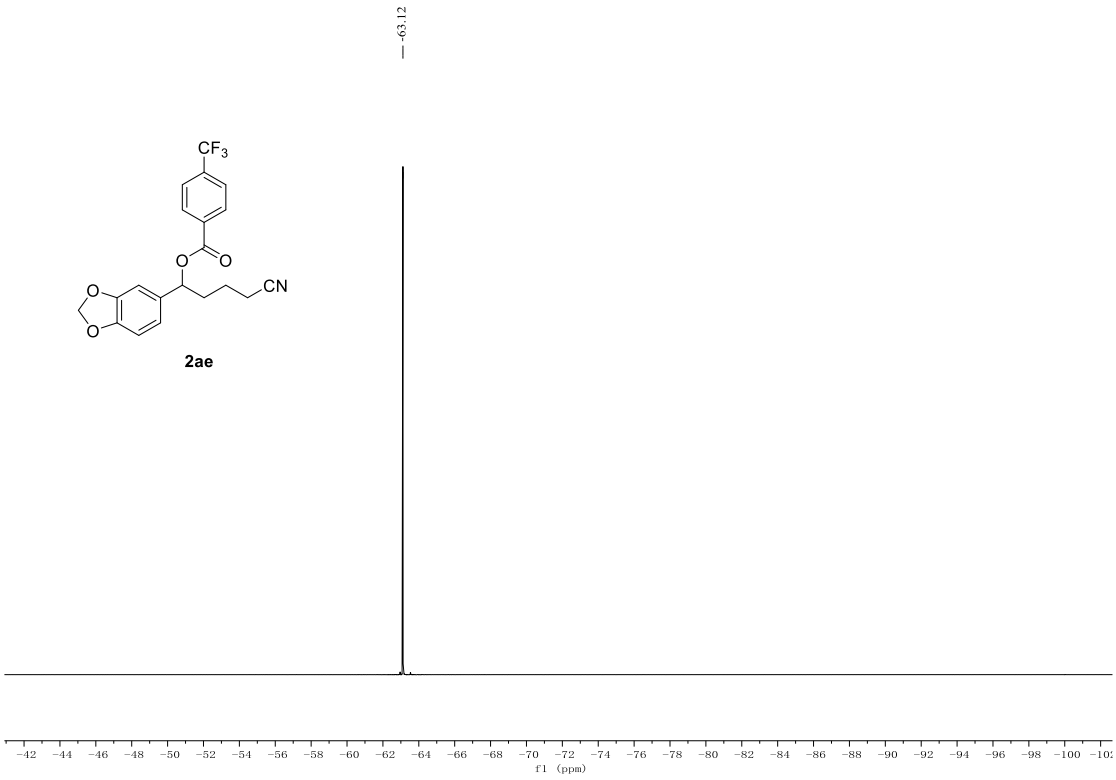
147.69
134.94
134.68
134.42
134.16
133.15
133.00
129.97
125.44
125.41
124.58
122.41
120.27
119.06
108.31
106.62
101.22
76.06
35.09
21.63
16.91
CF3
O
O
O
O
CN
2ae
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-63.12
CF3
O
O
O
O
CN
2ae
-42
-44
-46
-48
-50
-52
-54
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-58
-60
-62
-64
-66
-68
-70
-72
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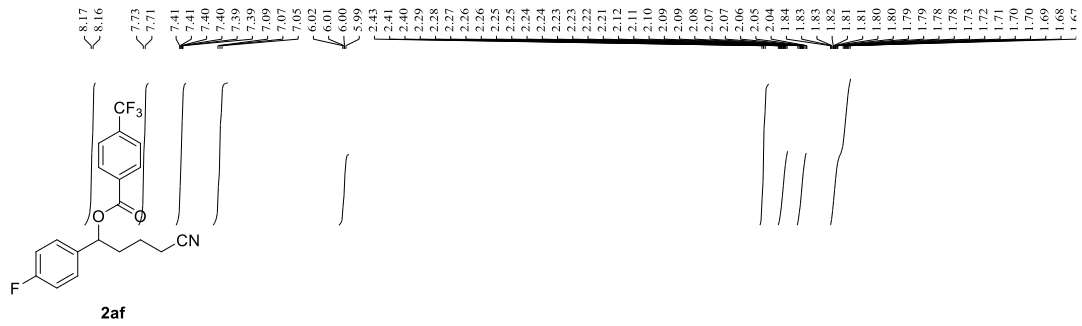
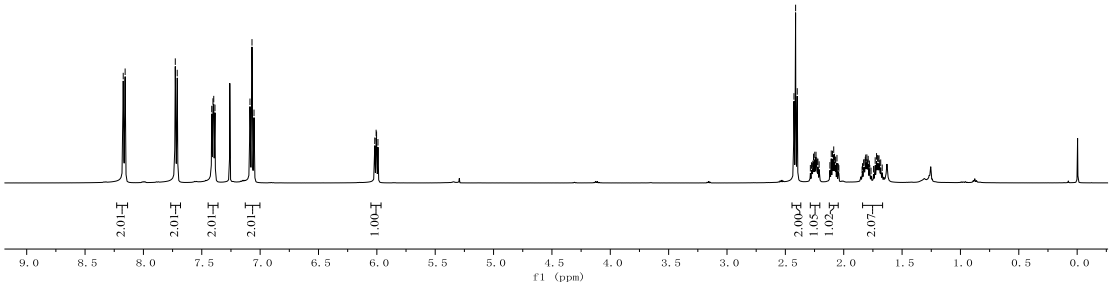
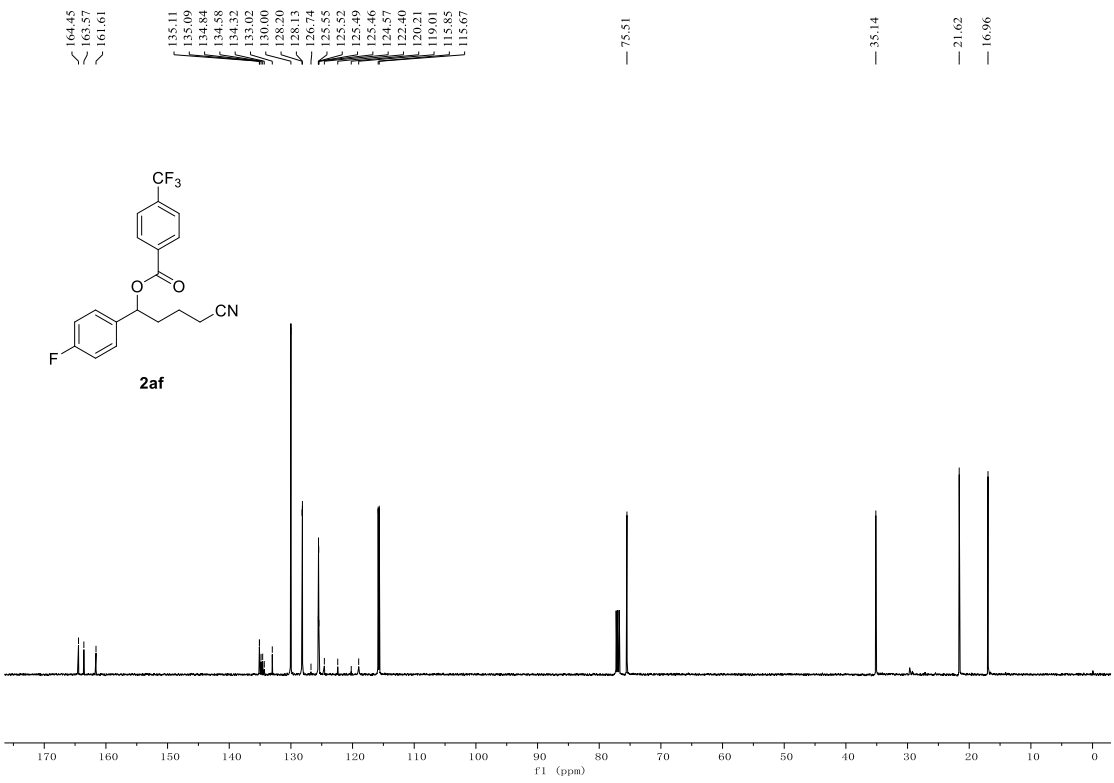
-92
-94
-96
-98
-100
f1 (ppm)

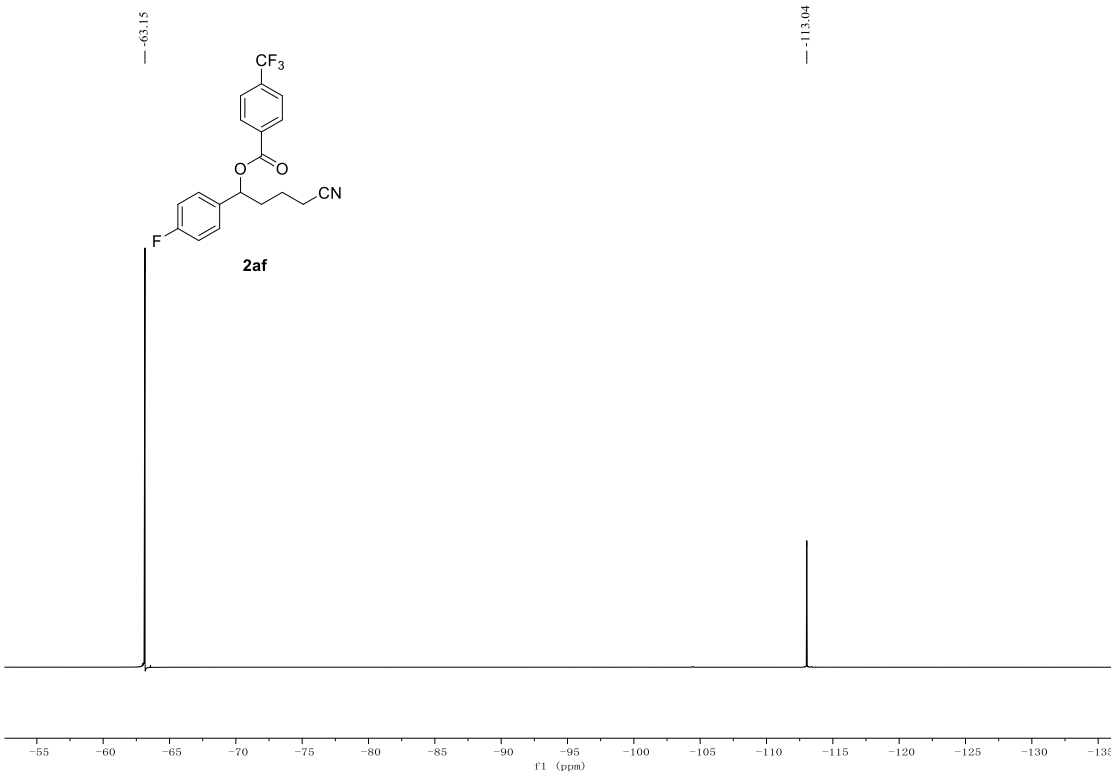

CF3
O
O
CN
F

2af


2.01
2.01
2.01
2.01
1.00
2.00
1.05
1.02
2.07
f1 (ppm)


CF3
O
O
CN
F
f1 (ppm)

2af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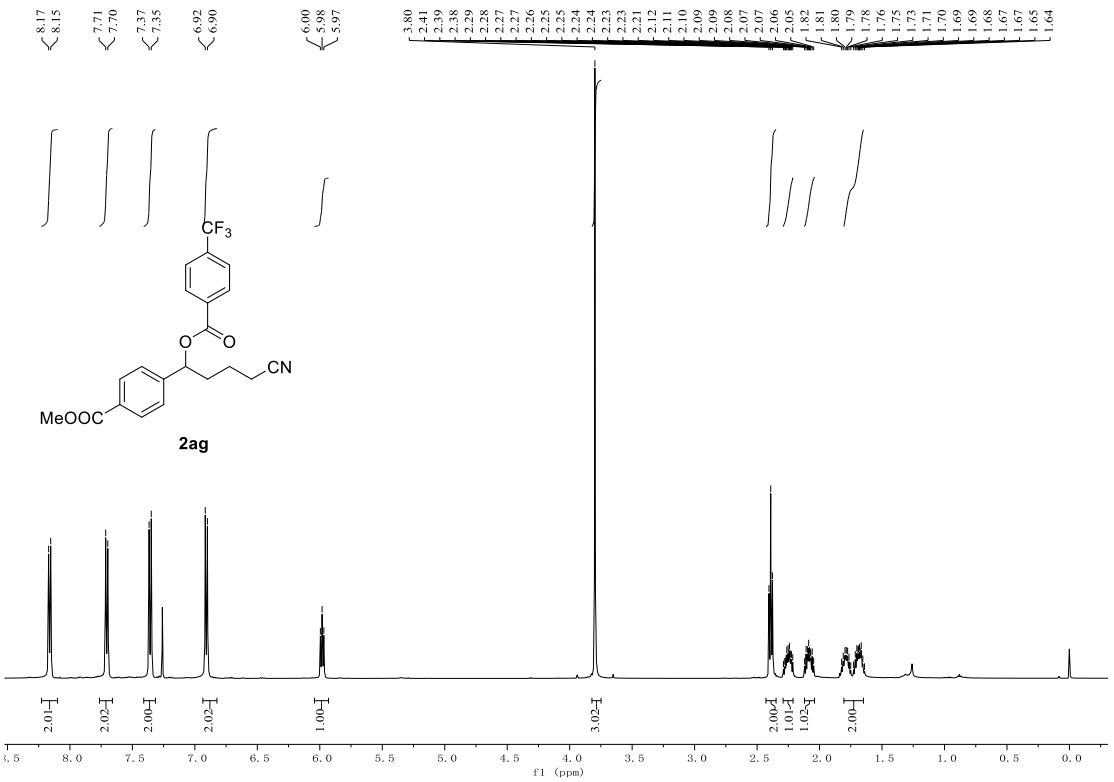
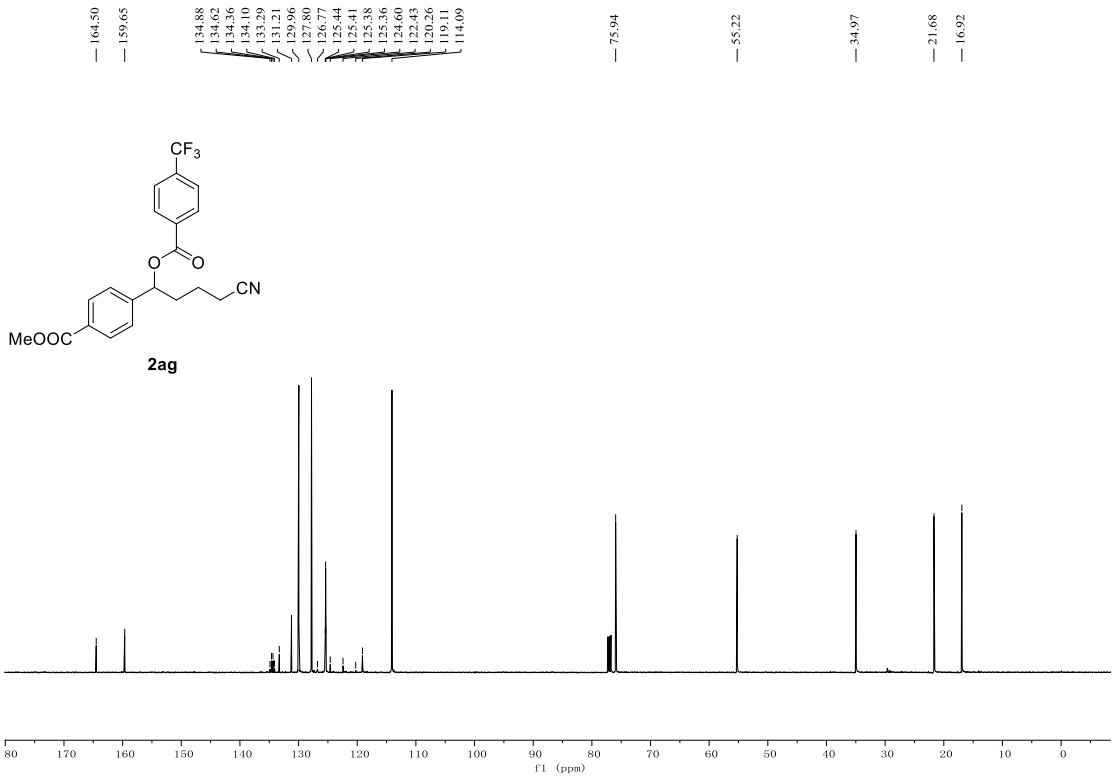
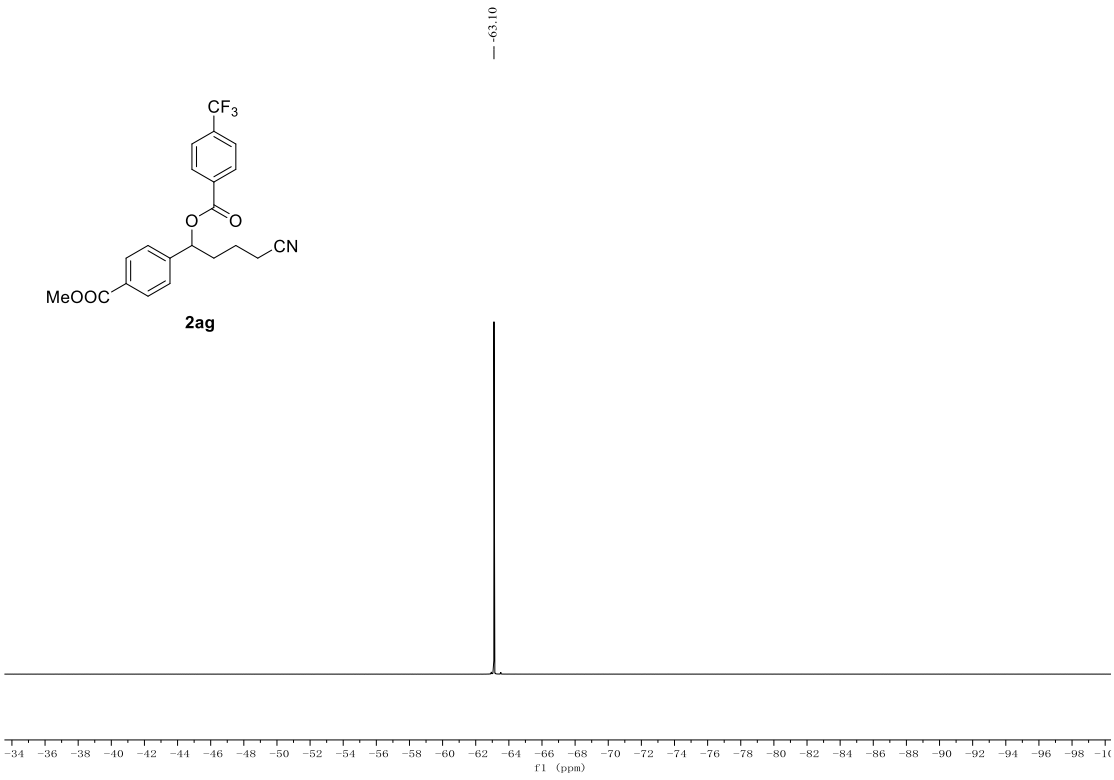
-113.04
CF3
O
O
CN
F
2af
f1 (ppm)


8.17
8.15
7.71
7.70
7.37
7.35
6.92
6.90
6.00
5.98
5.97
3.80
CF3
O
O
CN
MeOOC
2ag
2.01
2.02
2.00
2.02
1.00
3.02
2.00
1.01
1.02
2.00
f1 (ppm)


164.50
159.65
134.88
134.62
134.36
134.10
133.29
131.21
129.96
127.80
126.77
125.44
125.41
125.38
125.36
124.60
122.43
120.26
119.11
114.09
75.94
55.22
34.97
21.68
16.92
CF3
O
O
CN
MeOOC
2ag
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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CF3
O
O
CN
MeOOC
2ag
-34
-36
-38
-40
-42
-44
-46
-48
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
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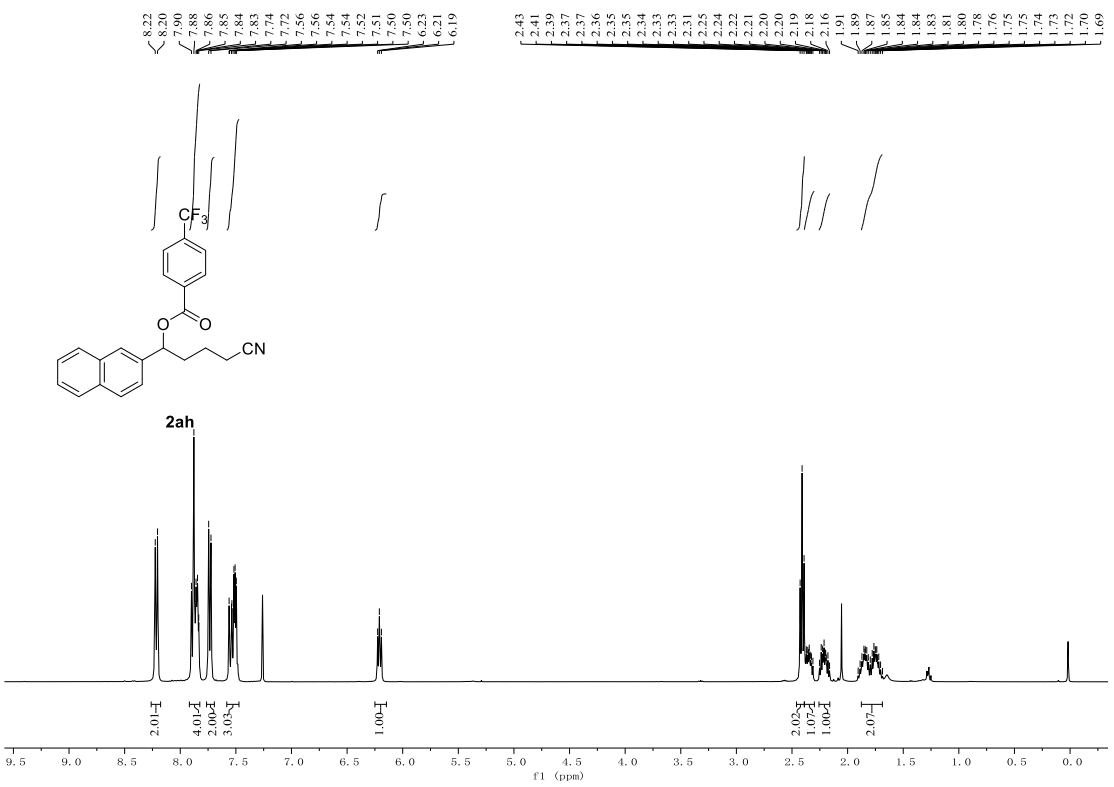
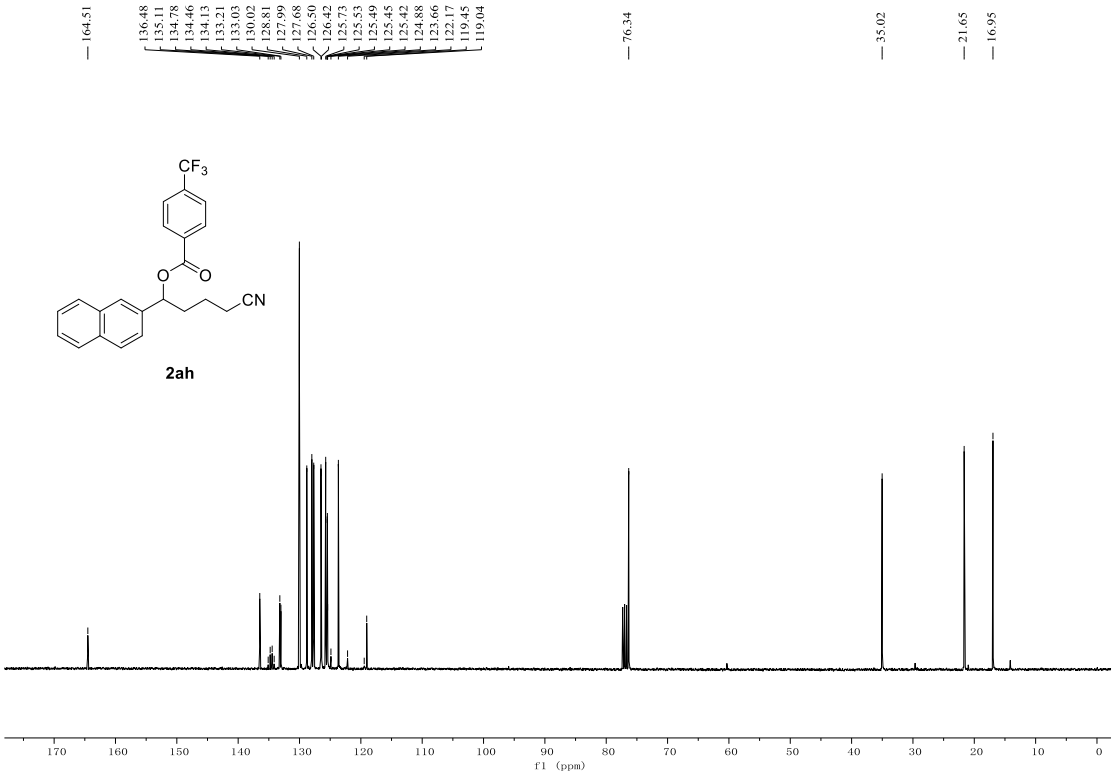
-90
-92
-94
-96
-98
f1 (ppm)


8.22
8.20
7.90
7.88
7.86
7.85
7.84
7.83
7.74
7.72
7.56
7.56
7.54
7.54
7.52
7.51
7.50
7.50
6.23
6.21
6.19
2.43
2.41
2.39
2.37
2.37
2.36
2.35
2.35
2.34
2.33
2.33
2.31
2.25
2.24
2.22
2.21
2.20
2.20
2.19
2.18
2.16
1.91
1.89
1.87
1.85
1.84
1.84
1.83
1.81
1.80
1.78
1.76
1.75
1.75
1.74
1.73
1.72
1.70
1.69
CF3
O
O
CN
2ah
2.01
4.01
2.00
3.03
1.00
2.02
1.07
1.00
2.07
f1 (ppm)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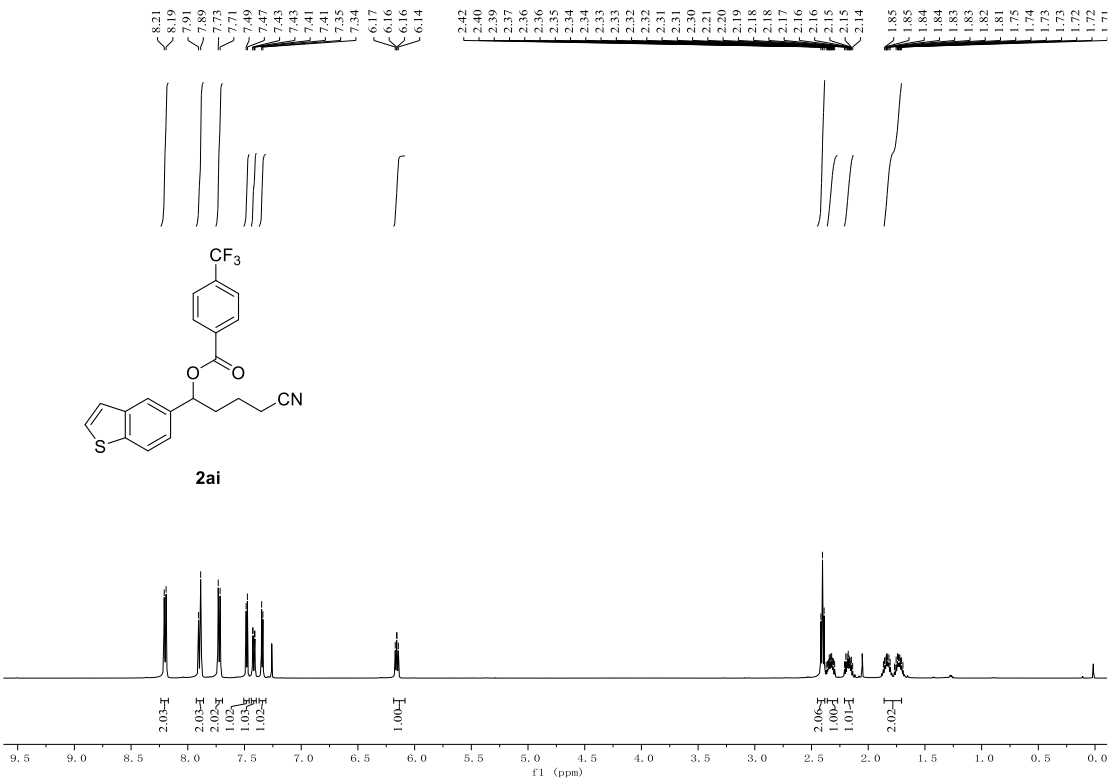
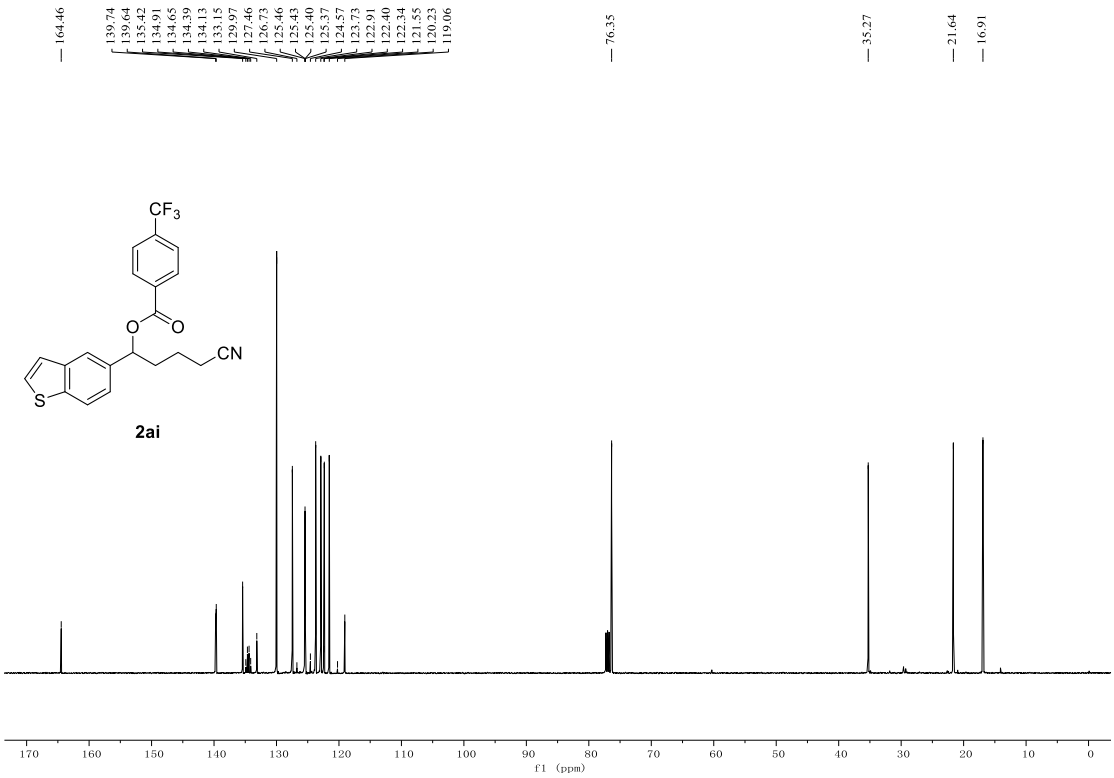
136.48
135.11
134.78
134.46
134.13
133.21
133.03
130.02
128.81
127.99
127.68
126.50
126.42
125.73
125.53
125.49
125.45
125.42
124.88
123.66
122.17
119.45
119.04
76.34
35.02
21.65
16.95
CF3
O
O
CN
2ah
f1 (ppm)


-63.10
CF3
O
O
CN
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

2ah


8.21 8.19 7.91 7.89 7.73 7.71 7.49 7.47 7.43 7.43 7.41 7.41 7.35 7.34 6.17 6.16 6.16 6.14
2.42 2.40 2.39 2.37 2.36 2.36 2.35 2.34 2.34 2.33 2.33 2.32 2.32 2.31 2.31 2.30 2.21 2.20 2.19 2.18 2.18 2.17 2.16 2.16 2.15 2.15 2.14
1.85 1.85 1.84 1.84 1.83 1.83 1.82 1.81 1.75 1.74 1.73 1.73 1.72 1.72 1.71
CF3
O
O
CN
S
2.03 2.03 2.02 1.02 1.03 1.02 1.00 2.06 1.00 1.01 2.02
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)

2ai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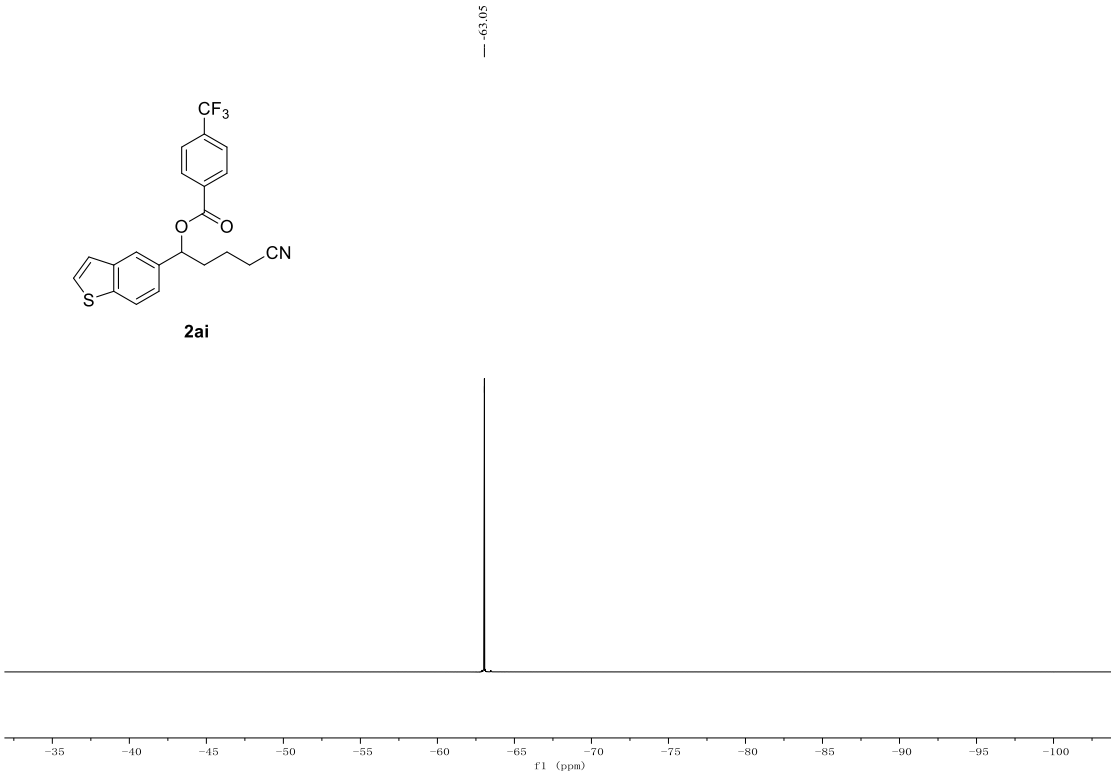
134.39
134.13
133.15
129.97
127.46
126.73
125.46
125.43
125.40
125.37
124.57
123.73
122.91
122.40
122.34
121.55
120.23
119.06
76.35
35.27
21.64
16.91
CF3
O
O
CN
S
2ai
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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CF3
O
O
CN
S
2ai
-35
-40
-45
-50
-55
-60
-65
-70
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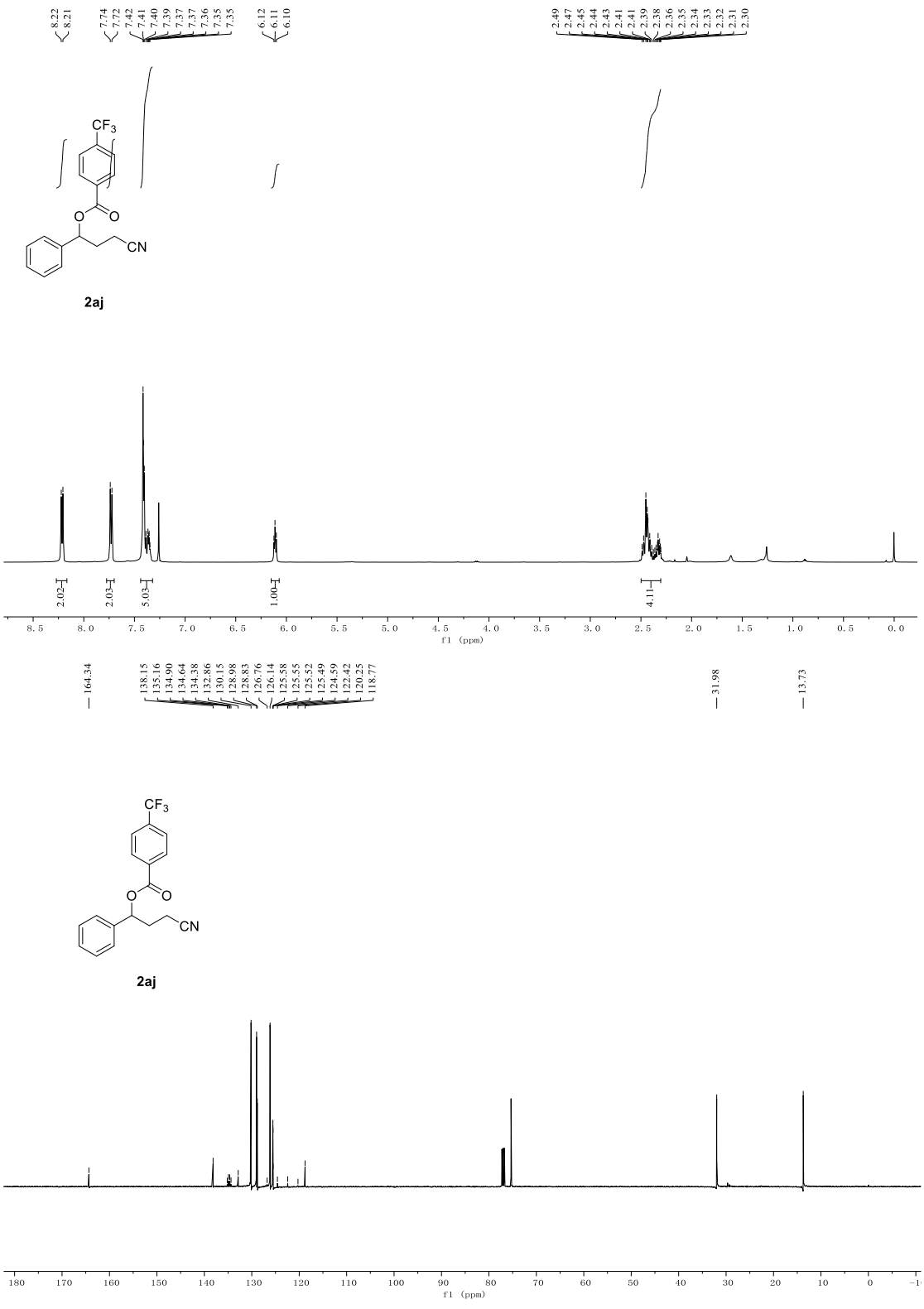
-80
-85
-90
-95
-100
f1 (ppm)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7.72
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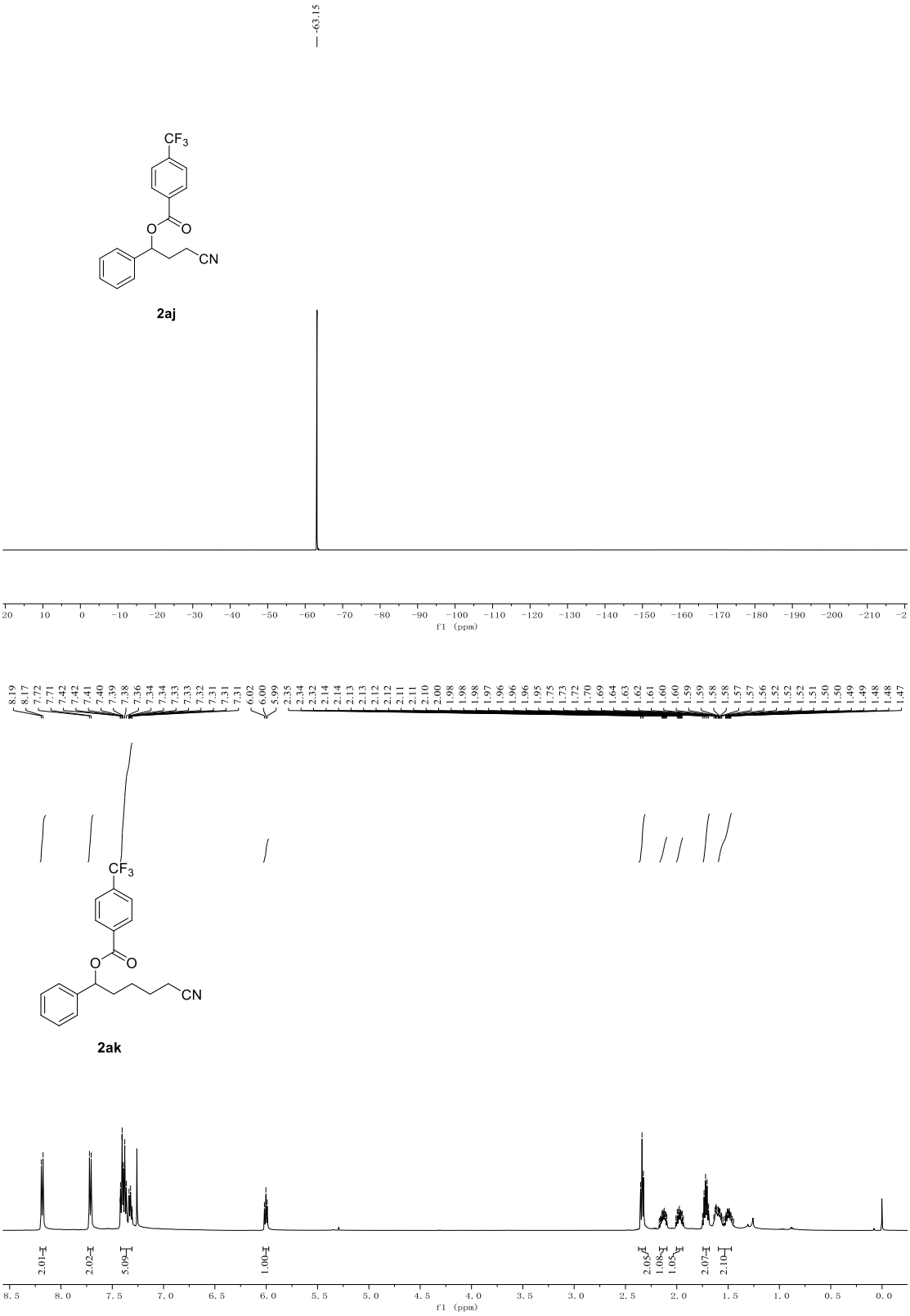
7.41
7.40
7.39
7.37
7.37
7.36
7.35
7.35
6.12
6.11
6.10
2.49
2.47
2.45
2.44
2.43
2.41
2.41
2.39
2.38
2.36
2.35
2.34
2.33
2.32
2.31
2.30
CF3
O
O
CN
2aj
2.02
2.03
5.03
1.00
4.11
f1 (ppm)
164.34
138.15
135.16
134.90
134.64
134.38
132.86
130.15
128.98
128.83
126.76
126.14
125.58
125.55
125.52
125.49
124.59
122.42
120.25
118.77
31.98
13.73
CF3
O
O
CN
2aj
f1 (ppm)


-63.15
CF3
O
O
CN
2aj
f1 (ppm)
8.19
8.17
7.72
7.71
7.42
7.42
7.41
7.40
7.39
7.38
7.36
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.31
6.02
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1.98
1.97
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1.96
1.96
1.95
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1.72
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1.52
1.52
1.52
1.51
1.50
1.50
1.49
1.49
1.48
1.48
1.47
CF3
O
O
CN
2ak
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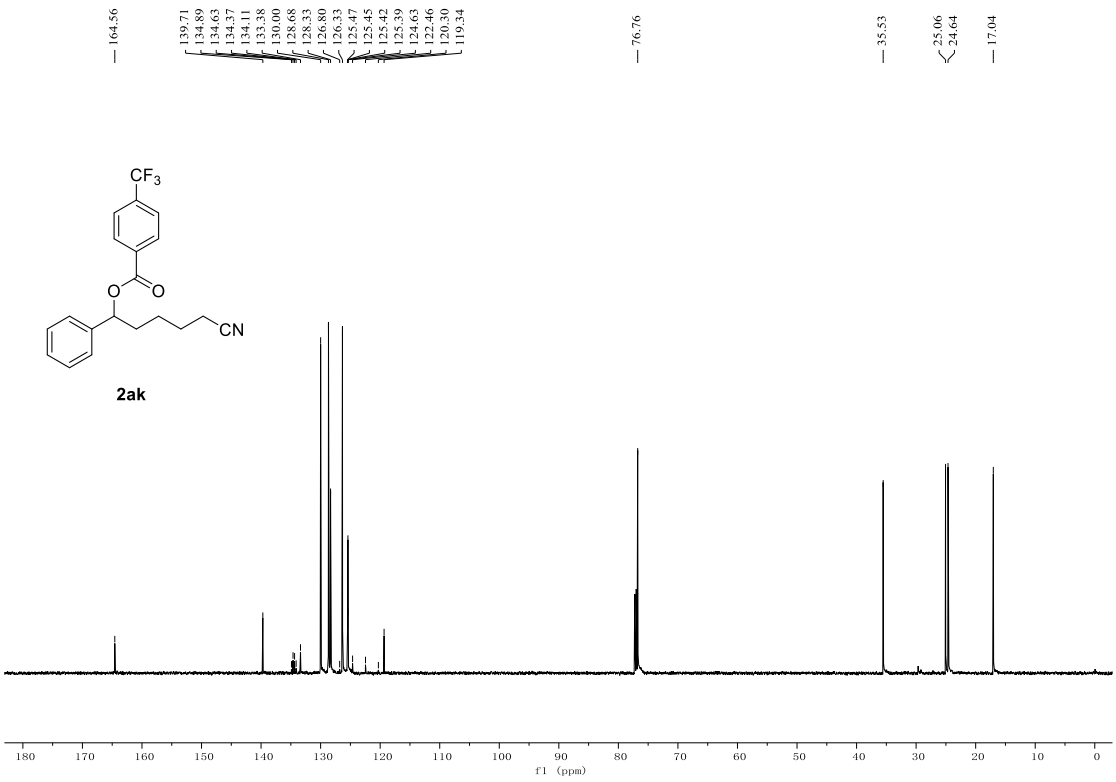
2.02
5.09
1.00
2.05
1.08
1.05
2.07
2.10
f1 (ppm)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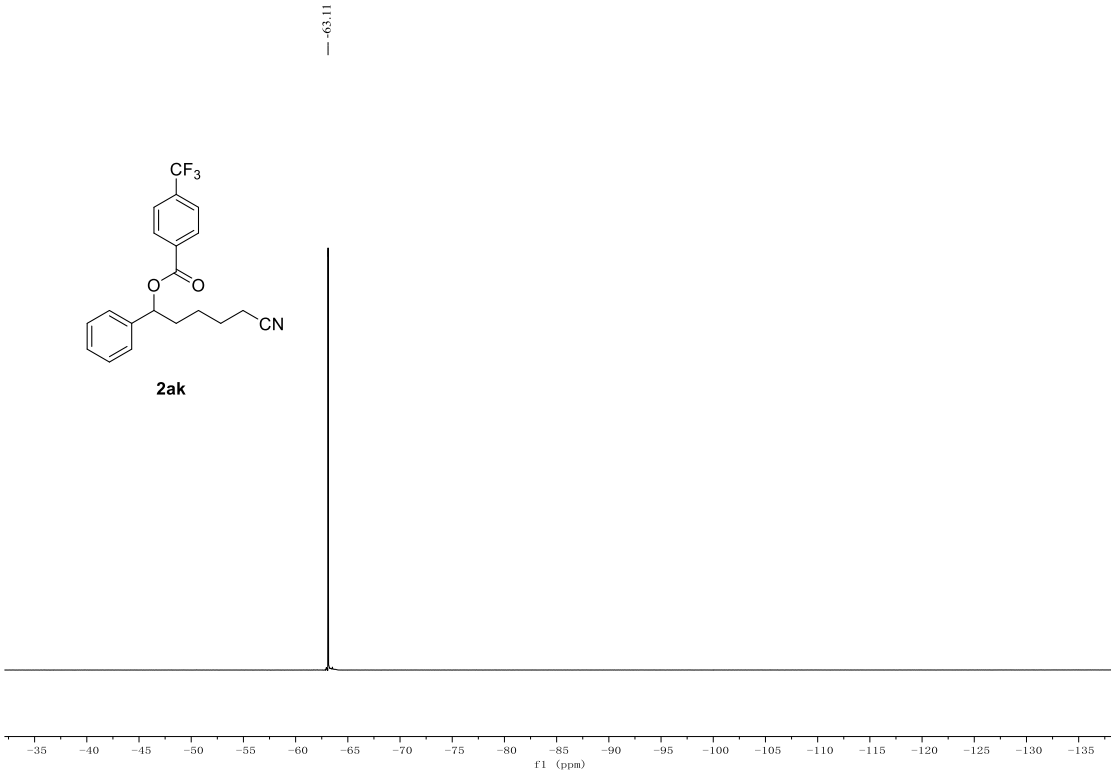
128.33
126.80
126.33
125.47
125.45
125.42
125.39
124.63
122.46
120.30
119.34
76.76
35.53
25.06
24.64
17.04
CF3
O
O
CN
2ak
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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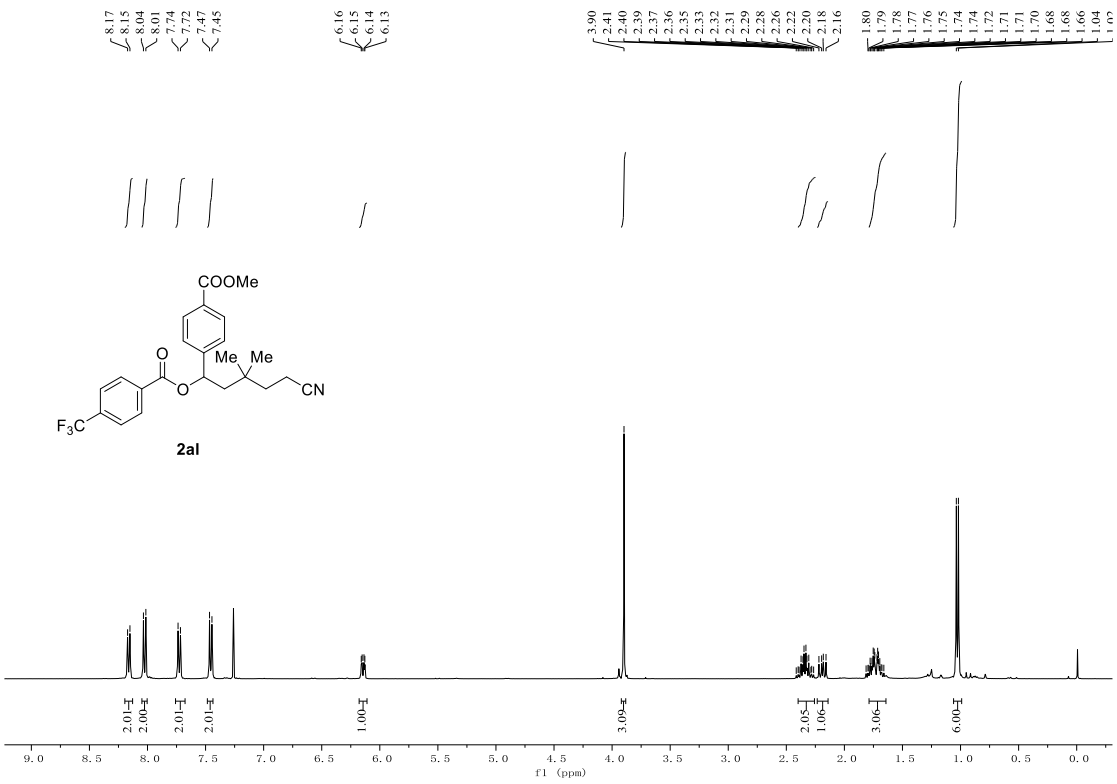
CF3
O
O
CN
2ak
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135
f1 (ppm)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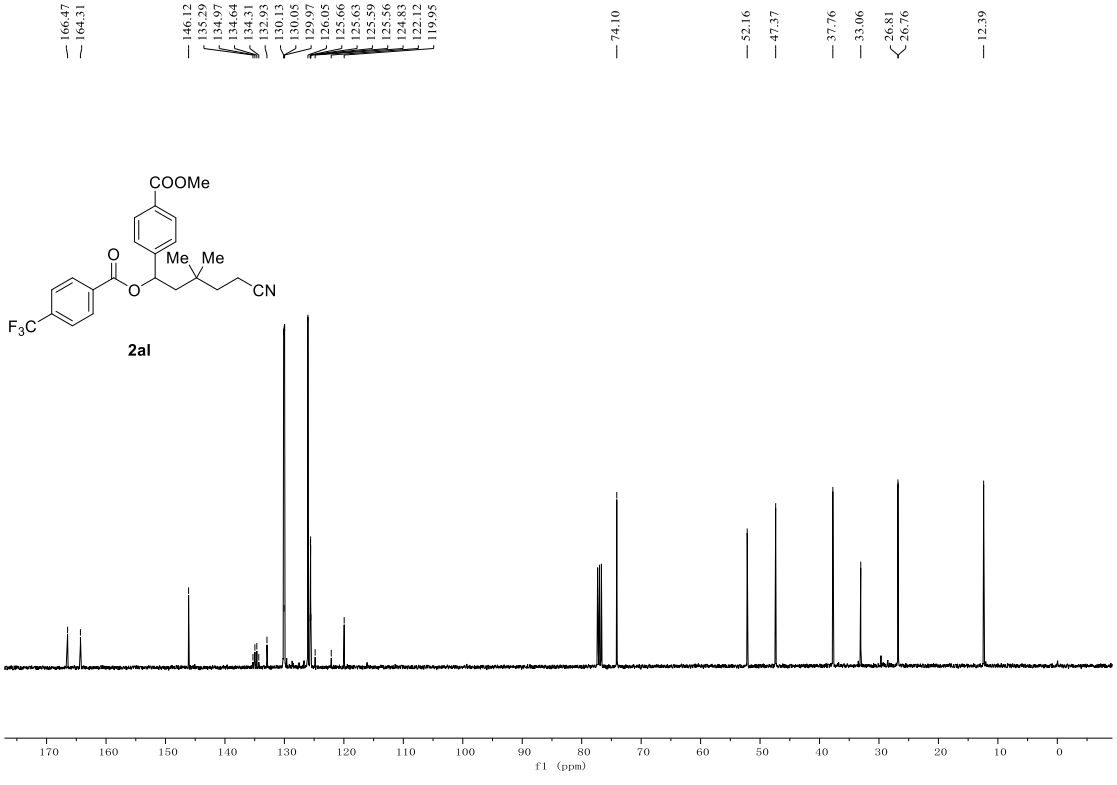
7.72
7.47
7.45
6.16
6.15
6.14
6.13
3.90
2.41
2.40
2.39
2.37
2.36
2.35
2.33
2.32
2.31
2.29
2.28
2.26
2.22
2.20
2.18
2.16
1.80
1.79
1.78
1.77
1.76
1.75
1.74
1.74
1.72
1.71
1.71
1.70
1.68
1.68
1.66
1.04
COOMe
Me
Me
O
O
CN
F3C
2al
2.01
2.00
2.01
2.01
1.00
3.09
2.05
1.06
3.06
6.00
f1 (ppm)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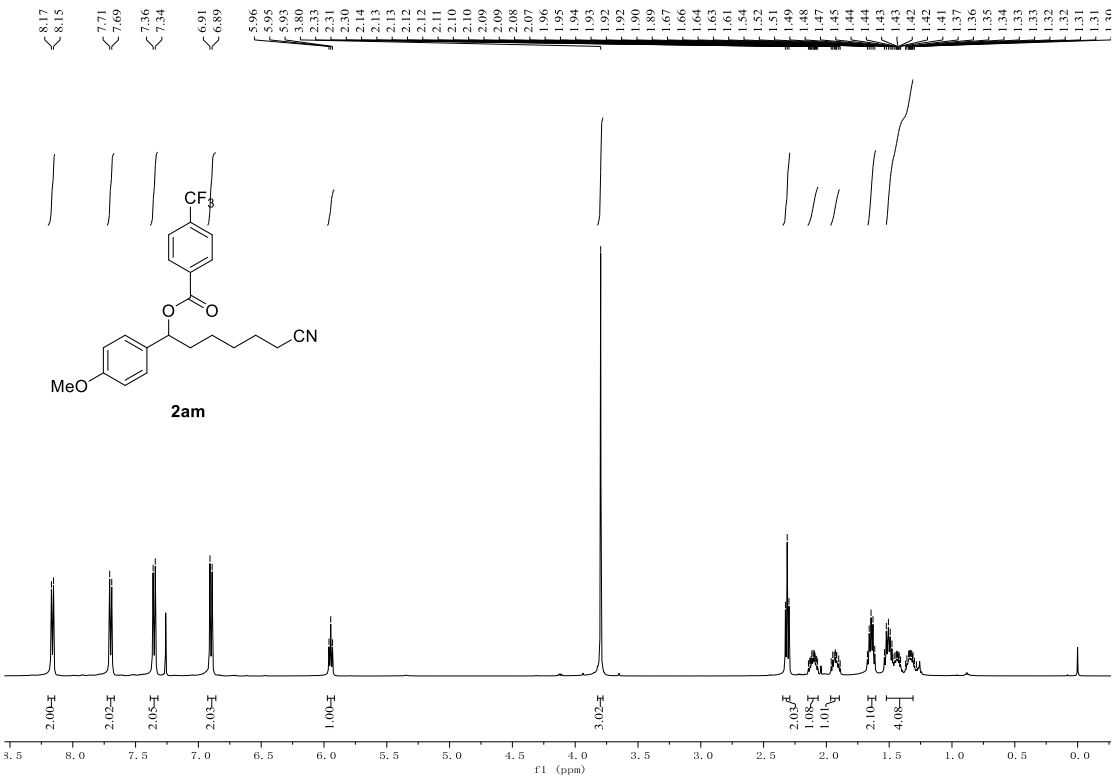
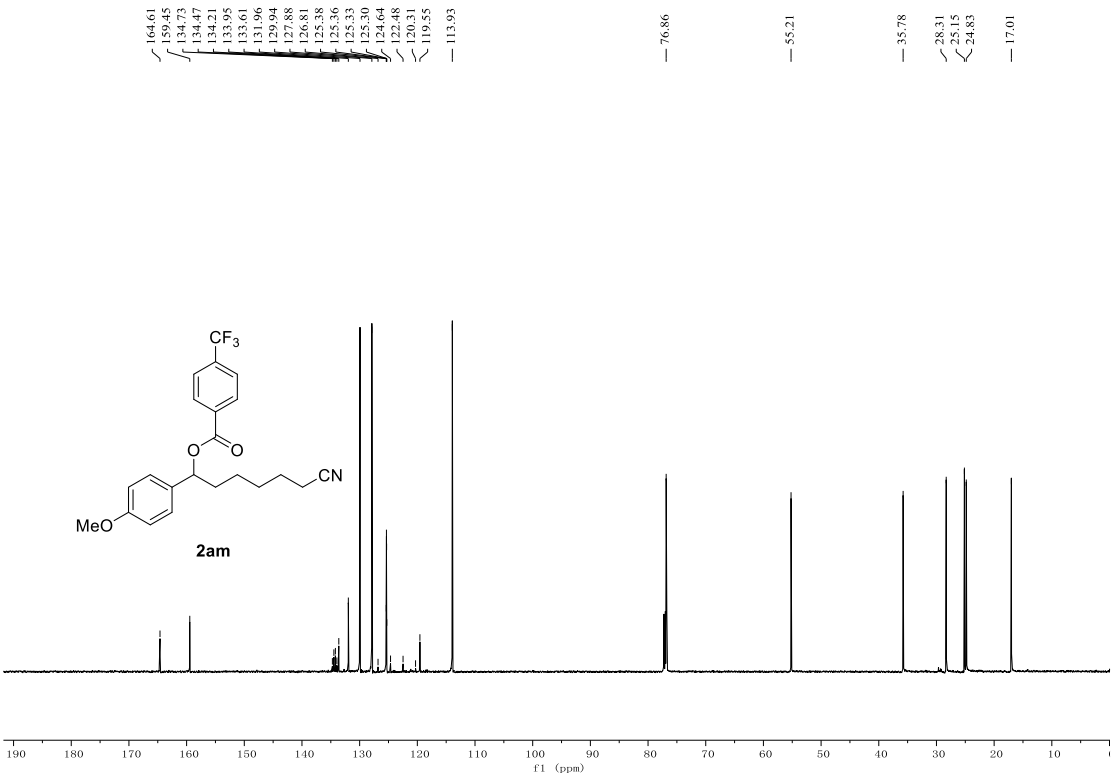
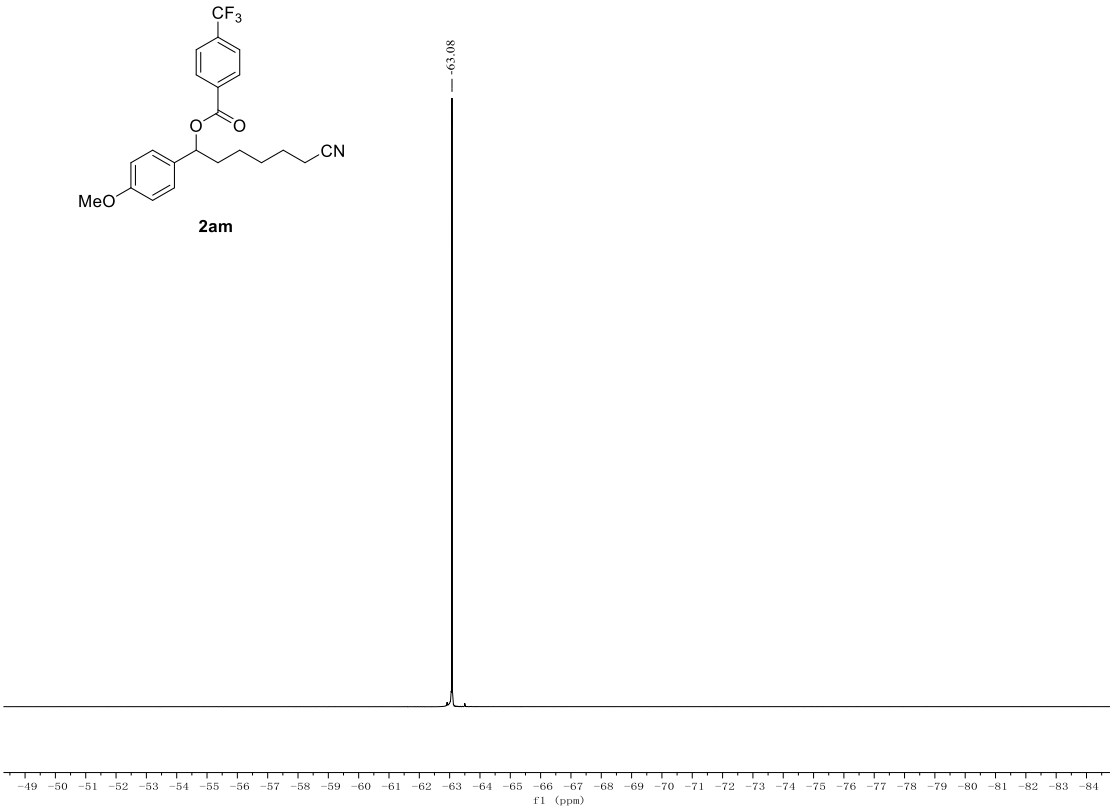
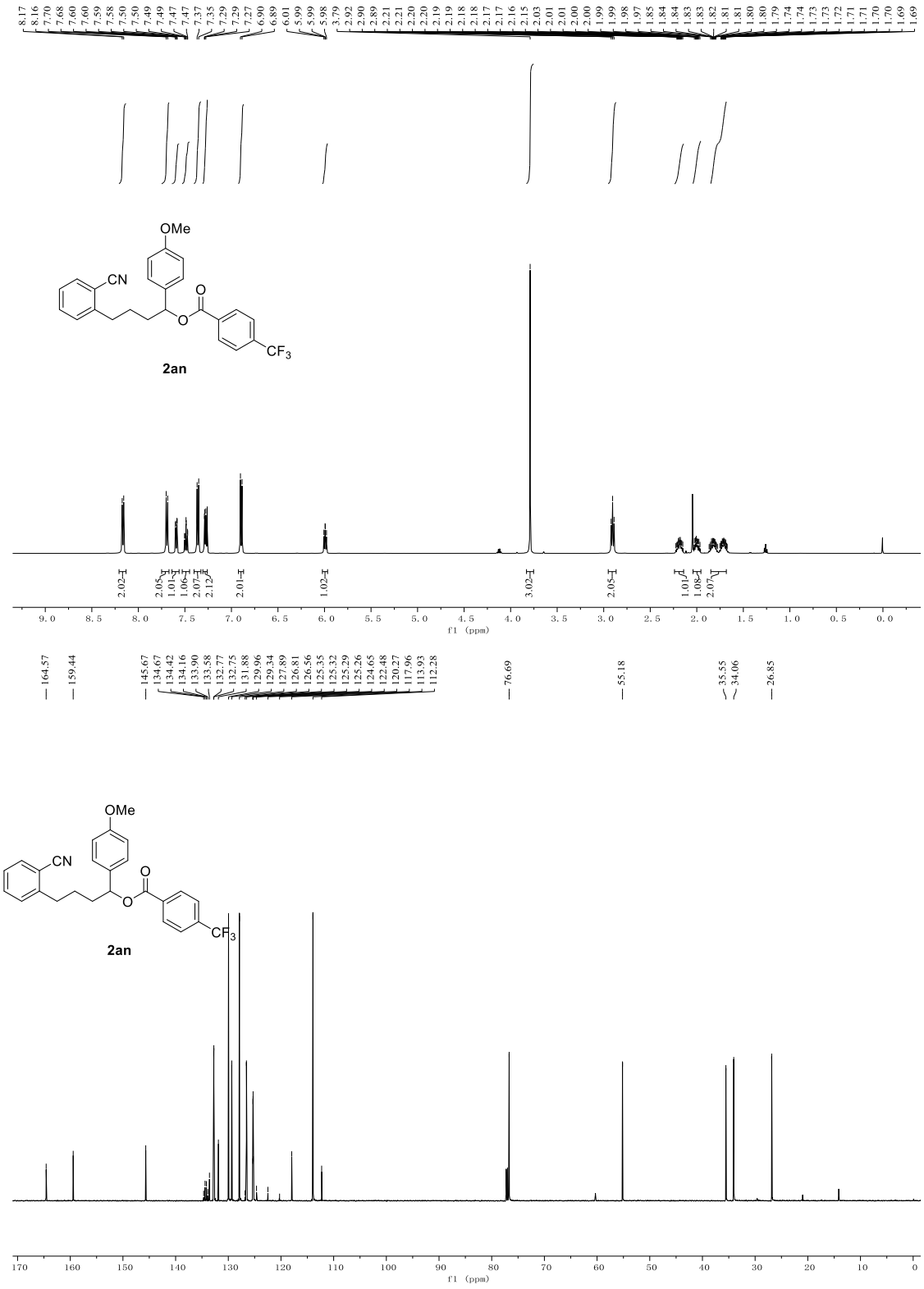
146.12
135.29
134.97
134.64
134.31
132.93
130.13
130.05
129.97
126.05
125.66
125.63
125.59
125.56
124.83
122.12
119.95
74.10
52.16
47.37
37.76
33.06
26.81
26.76
12.39
COOMe
Me
Me
O
O
CN
F3C
2al
f1 (ppm)

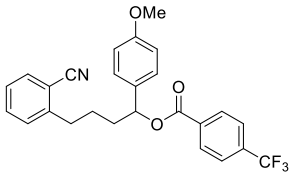

-63.17
COOMe
Me Me
O
O
CN
F3C
2al
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.17
8.15
7.71
7.69
7.36
7.34
6.91
6.89
CF3
O
O
CN
MeO
2am
2.00
2.02
2.05
2.03
1.00
3.02
2.03
1.08
1.01
2.10
4.08
3.5 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)


164.61
159.45
134.73
134.47
134.21
133.95
133.61
131.96
129.94
127.88
126.81
125.38
125.36
125.33
125.30
124.64
122.48
120.31
119.55
113.93
76.86
55.21
35.78
28.31
25.15
24.83
17.01
CF3
O
O
CN
MeO
2am
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

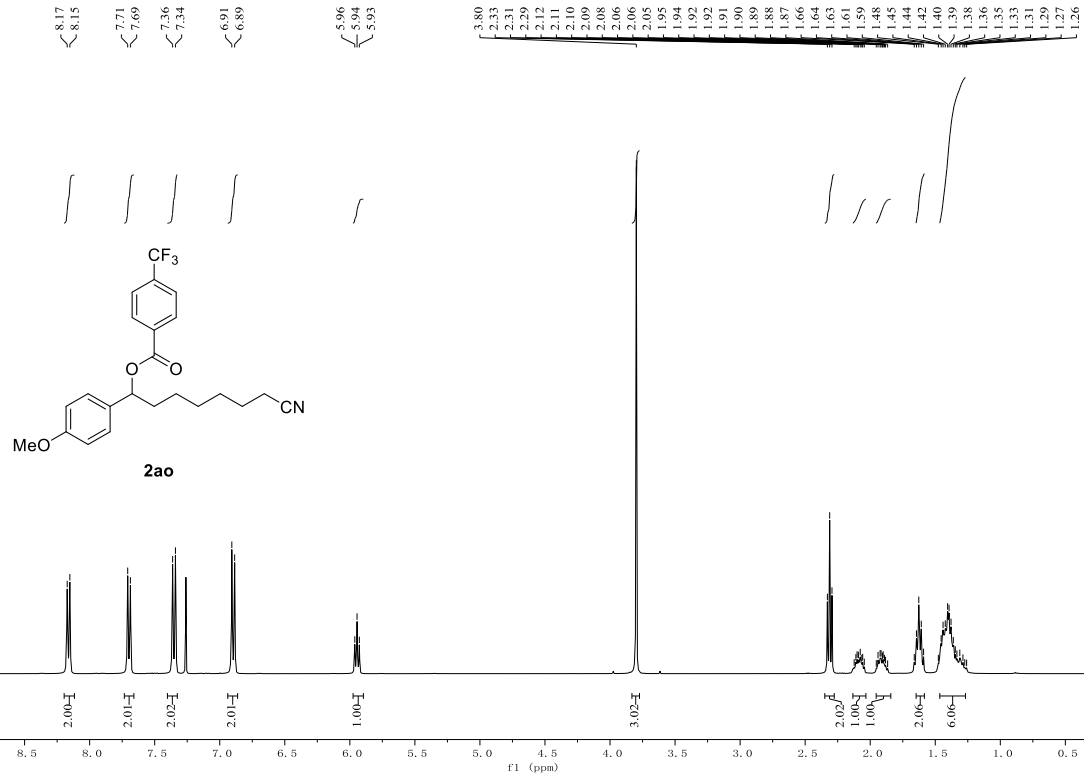

CF3
O
O
CN
MeO
2am
-63.08
-49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84
f1 (ppm)


OMe
CN
O
O
CF3
2an
f1 (ppm)
OMe
CN
O
O
CF3
2an
f1 (ppm)


OMe
CN
O
O
CF3

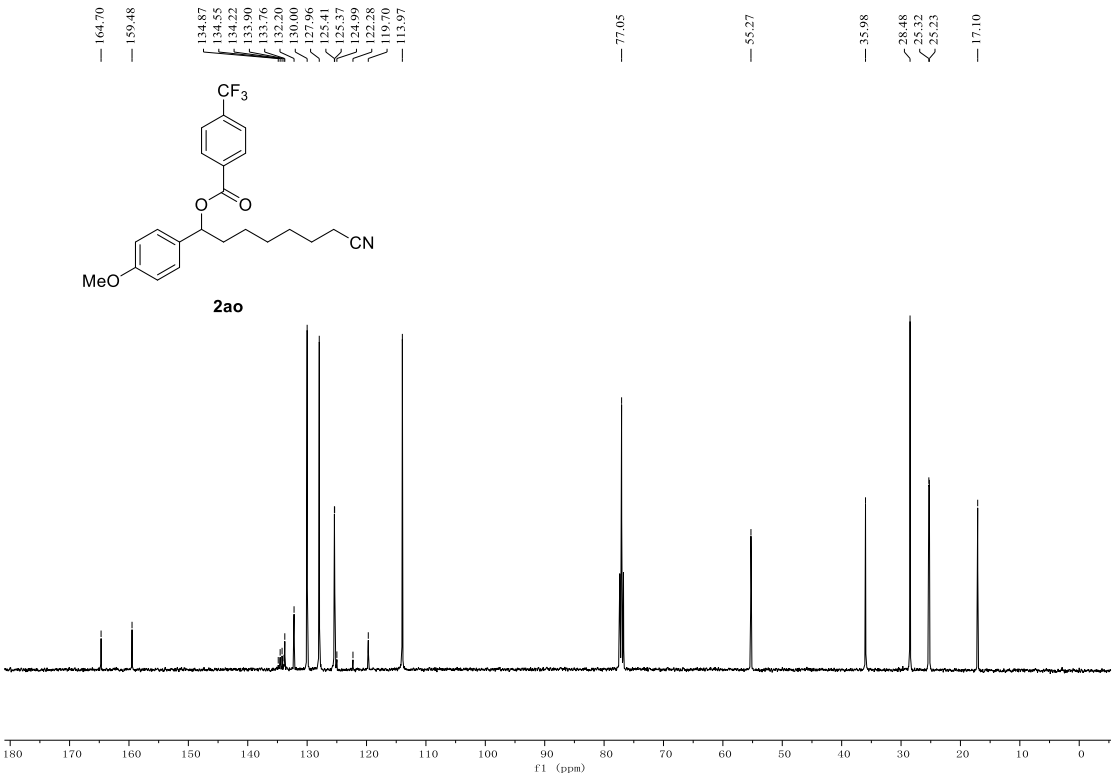
2an

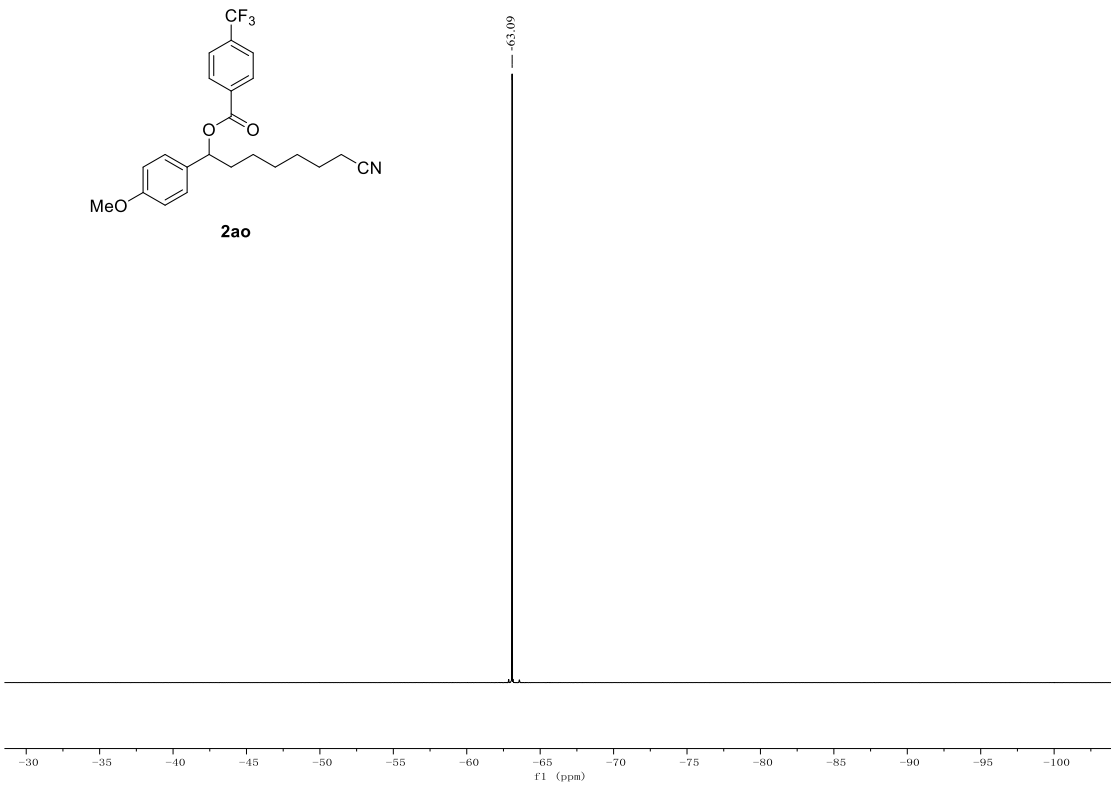
-63.06
-49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79
f1 (ppm)

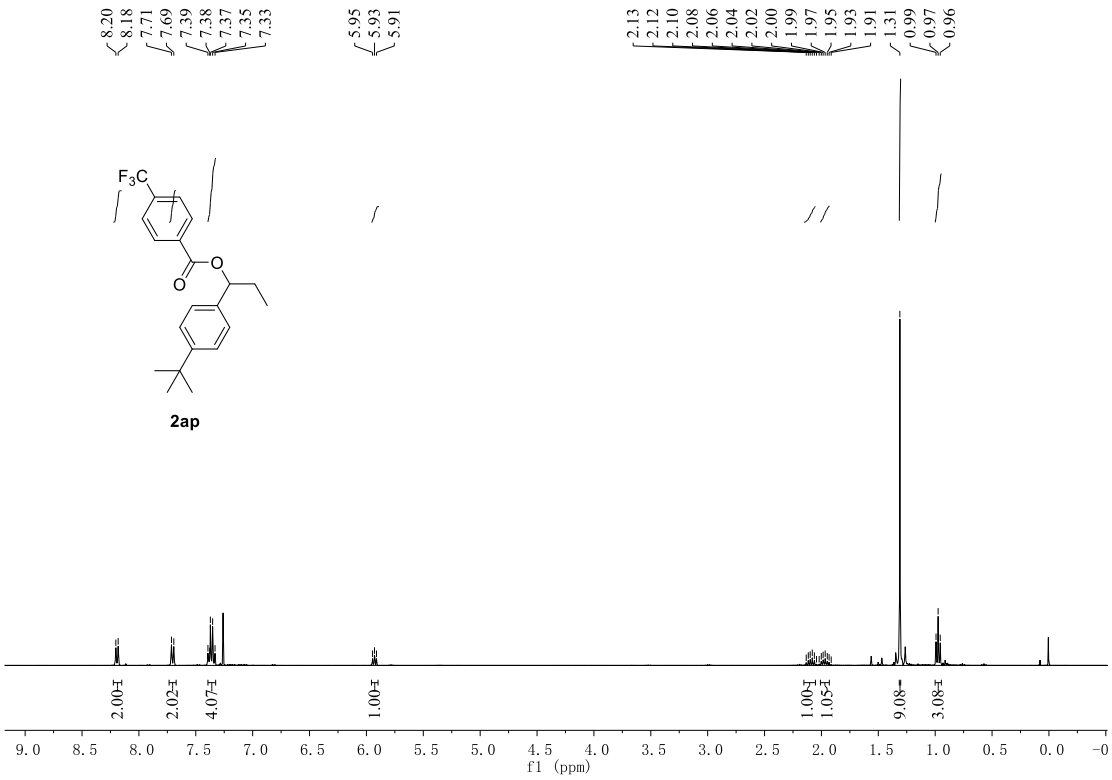

8.17
8.15
7.71
7.69
7.36
7.34
6.91
6.89
5.96
5.94
5.93
3.80
2.33
2.31
2.29
2.12
2.11
2.10
2.09
2.08
2.06
2.06
2.05
1.95
1.94
1.92
1.92
1.91
1.90
1.89
1.88
1.87
1.66
1.64
1.63
1.61
1.59
1.48
1.45
1.44
1.42
1.40
1.39
1.38
1.36
1.35
1.33
1.31
1.29
1.27
1.26
2.00
2.01
2.02
2.01
1.00
3.02
2.02
1.00
1.00
2.06
6.06
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)

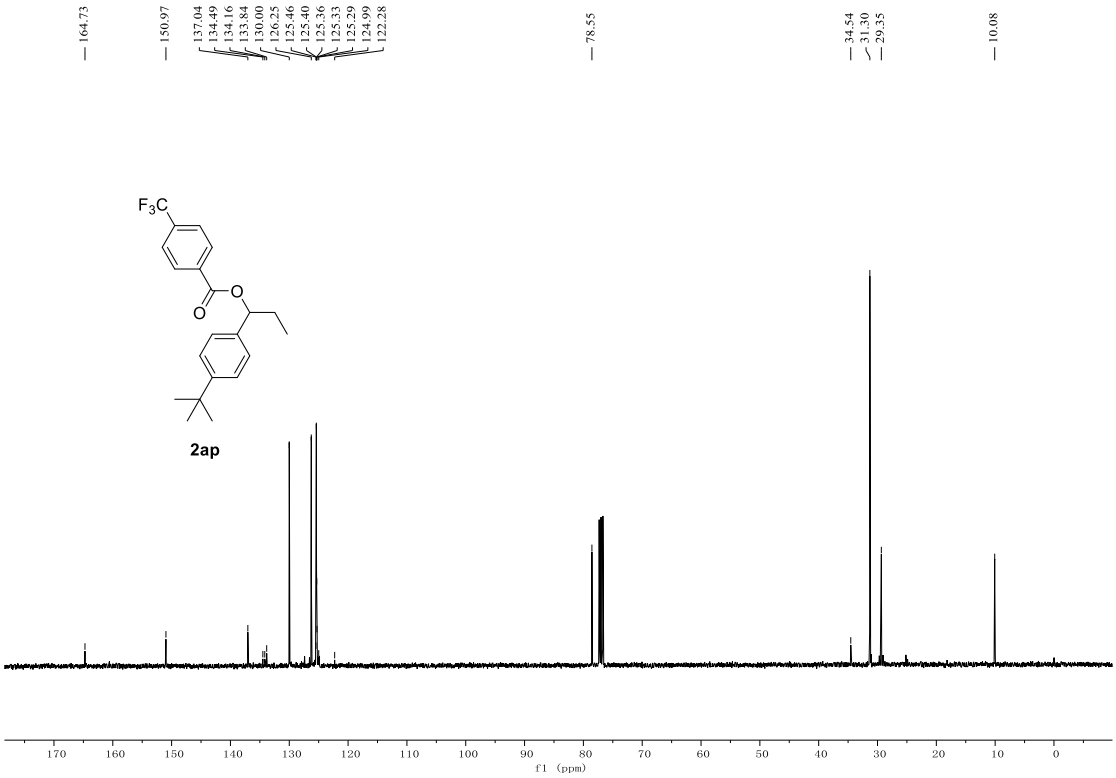
CF3
O
O
CN
MeO

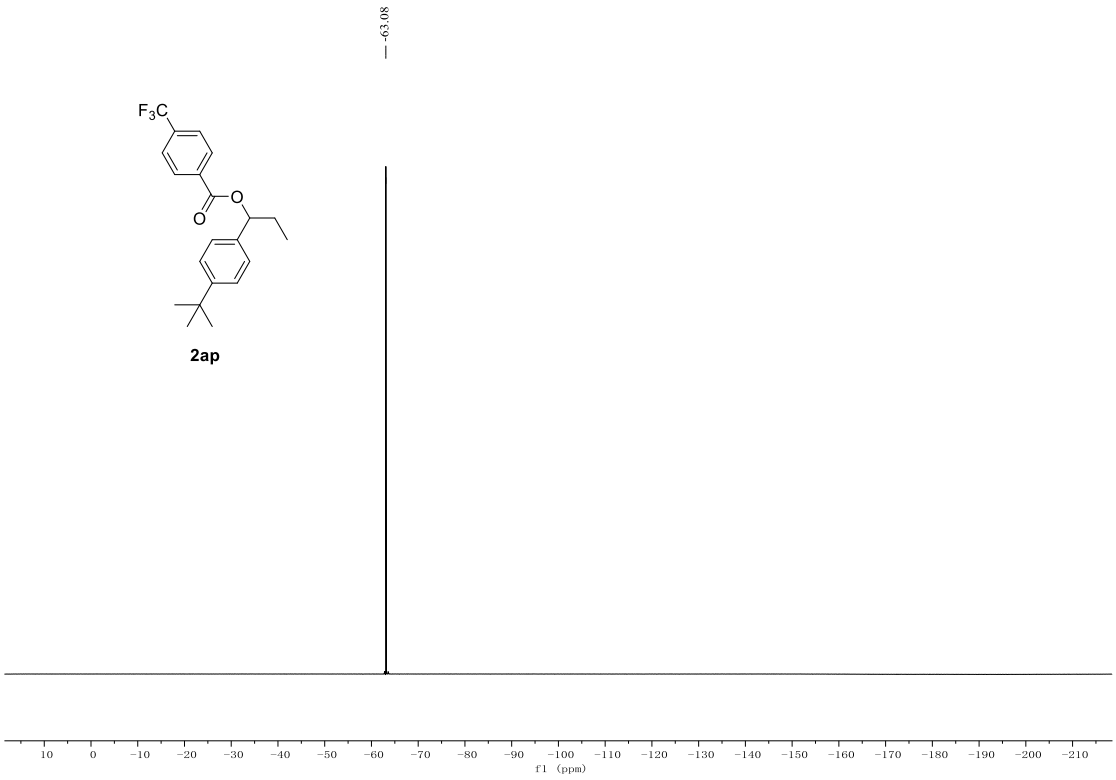
2ao


164.70
159.48
134.87
134.55
134.22
133.90
133.76
132.20
130.00
127.96
125.41
125.37
124.99
122.28
119.70
113.97
77.05
55.27
35.98
28.48
25.32
25.23
17.10
CF3
O
O
CN
MeO
2ao
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CF3
O
O
CN
MeO
2ao
-63.09
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100
f1 (ppm)


8.20
8.18
7.71
7.69
7.39
7.38
7.37
7.35
7.33
5.95
5.93
5.91
2.13
2.12
2.10
2.08
2.06
2.04
2.02
2.00
1.99
1.97
1.95
1.93
1.91
1.31
0.99
0.97
0.96
F3C
O
O
2ap
2.00
2.02
4.07
1.00
1.00
1.05
9.08
3.08
f1 (ppm)


164.73
150.97
137.04
134.49
134.16
133.84
130.00
126.25
125.46
125.40
125.36
125.33
125.29
124.99
122.28
78.55
34.54
31.30
29.35
10.08
F3C
O
O
2ap
f1 (ppm)


-63.08
F3C
O
O
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

2ap