Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Photocarboxylation of Remote C−H Bond through Nitrogen-Centred Radicals 1,5-Hydrogen Atom Transfer

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Contents

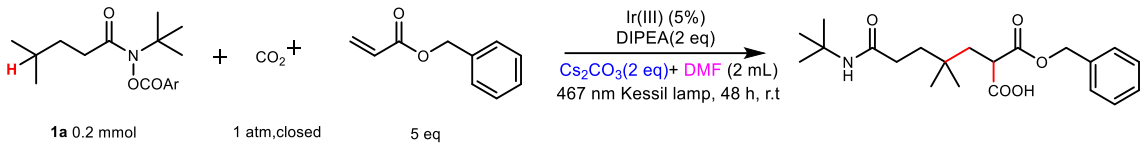
1. General information

Unless otherwise noted, all experiments were carried out under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. All solvents were purchased from J&K Scientific and stored in a nitrogen-filled glovebox over 4Å molecular sieves. Bis(catecholato)diboron (B_2cat_2) was purchased from Beijing Innochem Science & Technology co., LTD (Innochem) and stored in the glovebox. Purification of the products was conducted by column chromatography on silica gel (200 - 300 mesh, in some cases 300-400 mesh were used, from Qingdao, China). Thin-layer chromatography (TLC) was performed on silica gel plates (10 - 40 μm) purchased from WISH CHEMICAL, using UV light (254/ 366 nm) or phosphomolybdic acid (PMA) in ethanol (5%) for detection. The substrates were purchased from commercial sources unless otherwise noted.

NMR spectra were measured on a Bruker ARX400 (^{1}H at 400 MHz, ^{13}C at 101 MHz,) magnetic resonance spectrometer. The chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $CHCl_3$, δH (7.26 ppm) and δC (77.00 ppm); Coupling constants are reported in Hertz (Hz). Data for 1H NMR spectra are reported as follows: chemical shift (ppm, referenced to protium; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). HRMS data were obtained on a VG ZAB-HS mass spectrometer, Brucker Apex IV FTMS spectrometer. GC-MS or FID data were measured using the Agilent Technologies 7890B GC and the Agilent Technologies 5977B MSD. The FID yields were all based on standard curves with 5 points and minimum 0.996 R^2 value (or 4 points and minimum 0.997 R^2 value).

2. Complementary Reaction Optimization Data

Table S1 Optimization of reaction conditions of three-component Photocarboxylation[a]



entry	acrylic ester (equiv)	PC (equiv)	light source	additive (equiv)	yield[b] (%)
1	2.0	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (2%)	456 nm	DIPEA (2.0)	42%
2	2.0	$Ir(p\text{-}F\text{-}ppy)_3$ (2%)	456 nm	DIPEA (2.0)	35%
3	2.0	$(Ir[dF(CF_3)ppy]_2(4,4'\text{-}CF_3bpy)PF_6$ (2%)	456 nm	DIPEA (2.0)	32%
4	2.0	Eosin Y (2%)	456 nm	DIPEA (2.0)	47%
5	2.0	4CzIPN (2%)	456 nm	DIPEA (2.0)	29%
6	2.0	$[Ir(dFCF_3ppy)_2\text{-}(5,5'\text{-}dCF_3bpy)]PF_6$ (2%)	456 nm	DIPEA (2.0)	27%
7	2.0	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ (2%)	456nm	DIPEA (2.0)	23%
8	5.0	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (2%)	456 nm	DIPEA (2.0)	58%
9	5.0	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (2%)	467 nm	DIPEA (2.0)	71%
10	5.0	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (2%)	467 nm	DBU (2.0)	trace
11	5.0	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (2%)	467 nm	DMAP (2.0)	10.5%

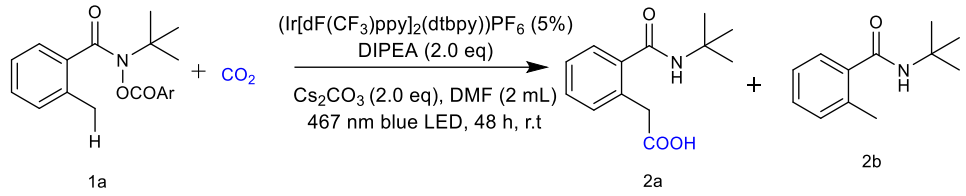
12[c]	**5.0**	(Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5%)	**467 nm**	**DIPEA (2.0)**	**82% (75%)**
13	5.0	none	467 nm	DIPEA (2.0)	none
14	5.0	(Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5%)	none	DIPEA (2.0)	trace
15	5.0	(Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5%)	467 nm	none	none

a: Reaction Condition: **1a** (0.2 mmol), acrylic ester (Benzyl acrylate), photocatalyst, DMF (N,N-Dimethylformamide) (2 mL), additive, then irradiated by Kessil 40 W blue LED for 24 h. After the reaction, the resulting mixture was diluted with 3 mL EA and quenched by 3 mL 1 N HCl, then stirred for 5 min. The reaction mixture was extracted by EA six times and the combined organic phases were concentratedin vacuo.

b: NMR yield, the yield in bracket is isolated yield.

c: The reaction time was 48 h.

Table S2 Optimization of reaction conditions of remote benzylic C-H bond carboxylation



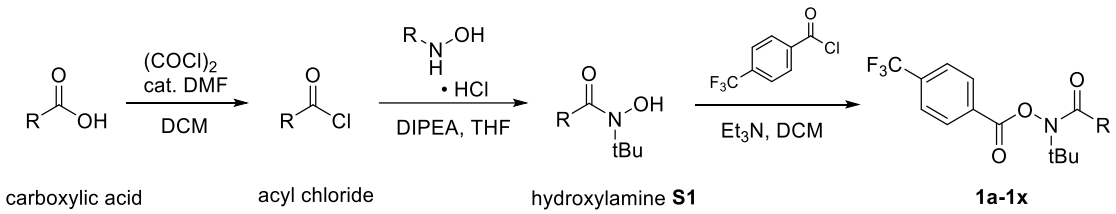
Entry	Deviations	Yields [%][(b)]	
		2 a	**2 b**
1	none	75 (71)	20
2	no light	trace	trace
3	no $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	trace	63
4	N_2 instead of CO_2	trace	85
5	no Cs_2CO_3	67	23
6	4CzIPN instead of $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	45	44
7	no DIPEA	trace	55
8	Eosin Y instead of $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	32	55
9	CH_3CN instead of DMF	44	50
10	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (2%)	65	18
11	24 h	67	19

[a] Reaction condition: 1a (0.2 mmol), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5%), DIPEA (1.0 eq), Cs_2CO_3(2.0 eq), DMF (2 mL), irradiation by Kessil 40 W blue LED for 48 h under 1 atm CO_2 at ambient temperature. [b] 1H NMR yields using 1,1,2,2-tetrachloroethane as an internal standard and yields of isolated products in parentheses. DMF= N,N-Dimethylformamide, DIPEA= N,N-Diisopropylethylamine, 4CzIPN=2,4,5,6-tetrakis(carbazol-9- yl)-1,3-dicyanobenzene, Eosin Y= Solvent Red 43.

3. General Procedure for Carbocarboxylation of substrates

A 50 mL Schlenk tube equipped with a magnetic stir bar was added substrate(0.2 mmol 1eq), alkene(1 mmol, 5 eq), base (0.4 mmol, 2 eq), PC (5%), DIPEA(0.4 mmol, 2 eq),solvent (2 ml) in glovebox. Then the Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfilled with CO_2 for three times. Then, the reaction was placed under a blue LED (2-meter strips, 18 W) and irradiated for 48 hr. at rt. The reaction was quenched with 1 M HCl , then extracted 3 times with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography isolation on silica gel or prepared TLC to give the product.

4. Preparation of substrates



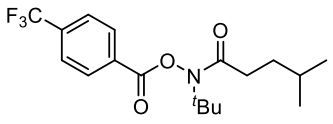
The procedure was according to the literature[1].

Step 1: To a solution of carboxylic acid (1.0 equiv) and 3-5 drops of anhydrous DMF in anhydrous CH_2Cl_2 (0.5 M) at 0 ˚C, oxalyl chloride (1.5 equiv) was added dropwise over 10 minutes. The reaction was vigorously stirred at room temperature for 3 h. The solvent was removed in vacuum. Anhydrous CH_2Cl_2 was added to remove the residual oxalyl chloride in vacuum. Then the resulting acyl chloride was dissolved in anhydrous DCM and used directly for the next step without further purification.

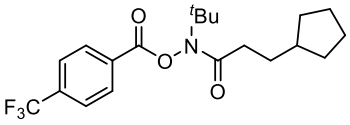
Step 2: A solution of the N-(tert-butyl)hydroxylamine hydrochloride (1.0 equiv, or N-isopropylhydroxylamine hydrochloride for **1f**, or N-cyclohexylhydroxylamine hydrochloride for **1g**) in anhydrous THF (0.4 M) was cooled to 0 ºC, treated with DIPEA (2.0 equiv) and stirred for 15 minutes. The acyl chloride (1.0 equiv) in anhydrous acetonitrile was added dropwise over 15 minutes. The mixture was allowed to warm to room temperature overnight. The mixture was diluted with saturated $NaHCO_3$ and EtOAc, the layers were separated. The aqueous layer was extracted with EtOAc (2 x), the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine, successively, and then evaporated. Purification by column chromatography on silica gel eluting with Petroleum ether and EtOAc gave the hydroxylamine **S1**.

Step 3: To a solution of hydroxylamine **S1** (1.05 equiv) in anhydrous CH_2Cl_2 (0.35 M) at 0 ˚C, Et_3N (1.5 equiv) was added dropwise. 4-trifluoromethyl-benzoyl chloride (1.0 equiv) was then added dropwise over 5 minutes. The reaction was vigorously stirred at room temperature for 2 h. After removing the solvent, the resulting residue was added saturated $NaHCO_3$ and THF and stirred for 30 minutes. Then, the layers were separated. The aqueous layer was extracted with EtOAc again, the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine, successively, and then evaporated. Purification by column chromatography on silica gel gave **1a-1p**.

5. Structures of hydroxylamine derivatives



1a



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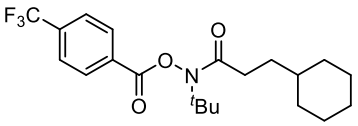

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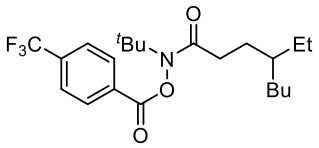

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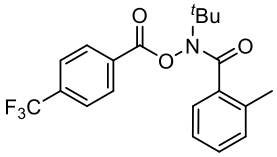

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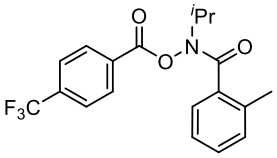

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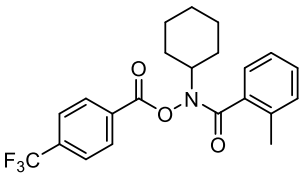

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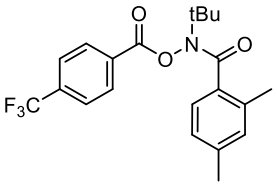

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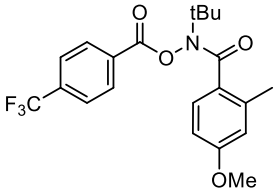

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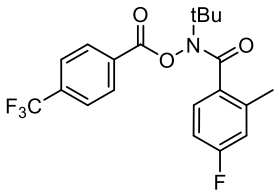

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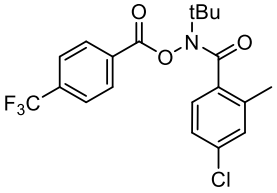

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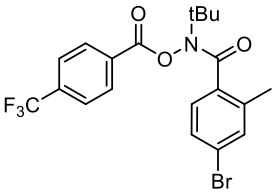

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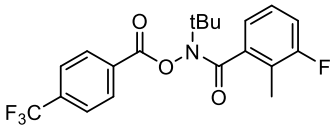

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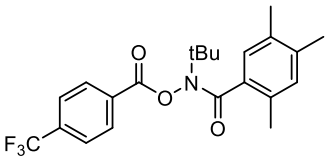

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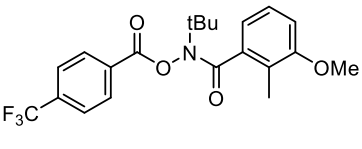

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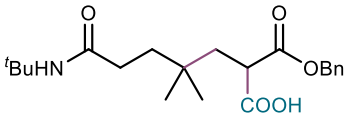
6. Structures of carboxylation products



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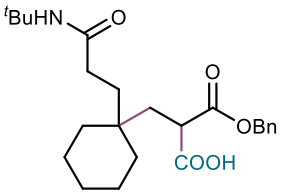

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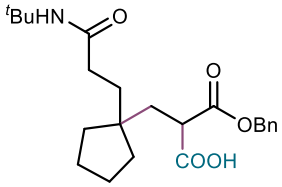

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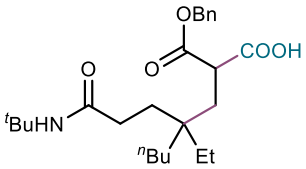

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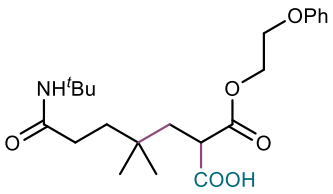

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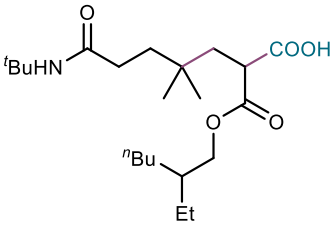

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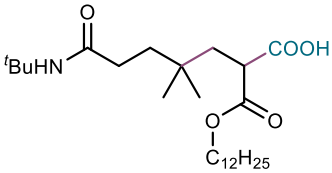

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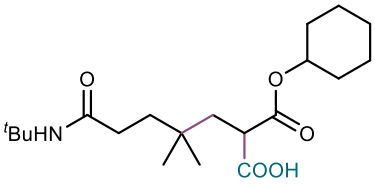

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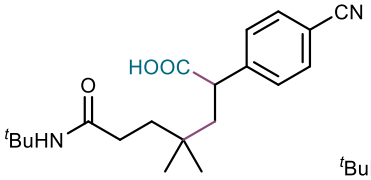

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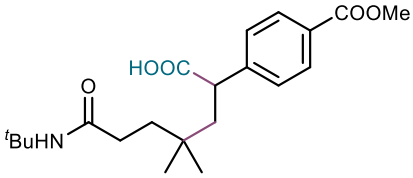

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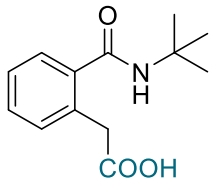

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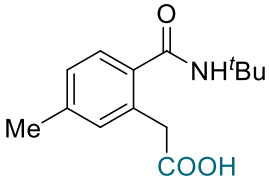

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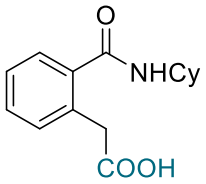

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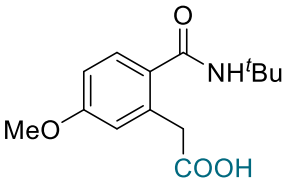

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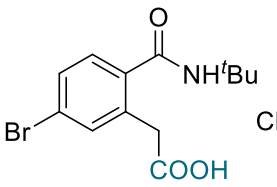

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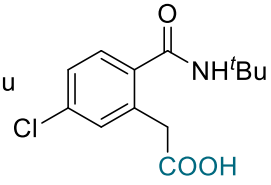

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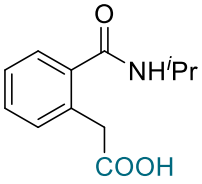

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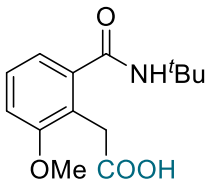

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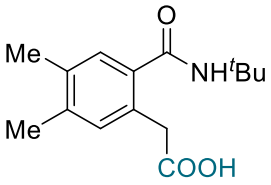
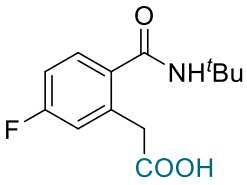
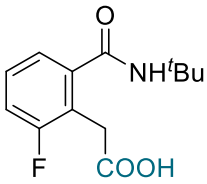


3i

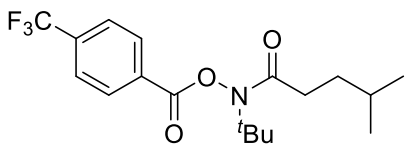


3j



3k

7. Analytical Data of the Substrates and Products



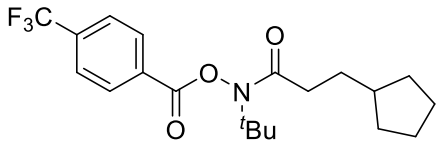
1a

N-(tert-butyl)-4-methyl-N-((4-(trifluoromethyl)benzoyl)oxy)pentanamide (1a) 76% overall yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 2.26 (dt, J = 15.0, 7.1 Hz, 1H), 2.10 (dt, J = 18.1, 7.0 Hz, 1H), 1.48 (s, 12H), 0.84 –0.76 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.11, 164.63, 135.88 (q, J = 33.0 Hz), 130.49, 130.27, 126.14 (q, J = 3.7 Hz), 123.44 (q, J = 272.9 Hz), 62.95, 33.01, 32.36, 27.64, 27.59, 22.46, 22.37.

All data matched that reported in the literature[1].



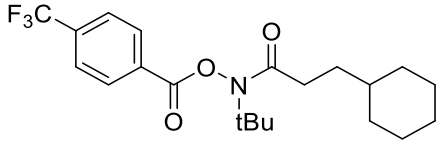
1b

N-(tert-butyl)-3-cyclopentyl-N-((4-(trifluoromethyl)benzoyl)oxy)propanamide (1b) 54% overall yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 2.28 (dt, J = 15.3, 7.5 Hz, 1H), 2.11 (dt, J = 15.7, 7.5 Hz, 1H), 1.71 – 1.53 (m, 5H), 1.52 – 1.37 (m, 13H), 1.05 – 0.92 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.97, 164.58, 135.79 (q, J = 33.0 Hz), 130.45, 130.29, 126.07 (q, J = 3.7 Hz), 123.41 (q, J = 272.9 Hz), 62.86, 39.58, 33.55, 32.50, 32.45, 30.35, 27.52, 25.04.

All data matched that reported in the literature[1].



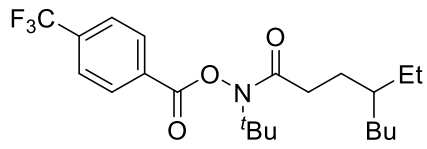
1c

N-(tert-butyl)-3-cyclohexyl-N-((4-(trifluoromethyl)benzoyl)oxy)propanamide (1c) 70% overall yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 2.26 (dt, J = 15.8, 7.8 Hz, 1H), 2.10 (dt, J = 15.8, 7.7 Hz, 1H), 1.66 – 1.52 (m, 5H), 1.52 – 1.40 (m, 11H), 1.20 – 1.01 (m, 4H), 0.91 – 0.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.26, 164.61, 135.86 (q, J = 33.0 Hz), 130.50, 130.30, 126.12 (q, J = 3.7 Hz), 123.44 (q, J = 272.9 Hz), 62.95, 37.15, 33.21, 33.15, 31.81, 31.60, 27.60, 26.58, 26.27.

All data matched that reported in the literature[1].



1d

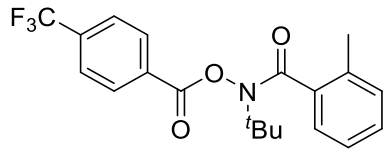
N-(tert-butyl)-4-ethyl-N-((4-(trifluoromethyl)benzoyl)oxy)octanamide (1d)

37% overall yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 2.23 (dt, J = 16.1, 8.0 Hz, 1H), 2.09 (dt, J = 15.8, 8.0 Hz, 1H), 1.59 – 1.53 (m, 2H), 1.49 (s, 9H), 1.23 – 1.11 (m, 9H), 0.85 – 0.75 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.20, 164.59, 135.82 (q, J = 33.0 Hz), 130.44, 130.29, 126.05 (q, J = 3.7 Hz), 123.40 (q, J = 272.9 Hz), 62.87, 38.39, 32.58, 32.00, 28.75, 27.67, 27.52, 25.73, 23.01, 13.98, 10.69.

All data matched that reported in the literature[1].



1e

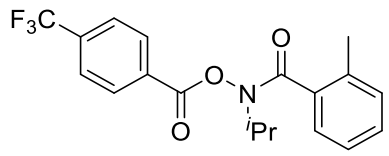
N-(tert-butyl)-2-methyl-N-((4-(trifluoromethyl)benzoyl)oxy)benzamide (1e)

14% overall yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.7 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 7.4 Hz, 1H), 7.10 – 6.98 (m, 3H), 2.42 (s, 3H), 1.61 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.49, 164.27, 136.10, 135.20 (q, J = 32.9 Hz) , 134.71 ,130.09, 130.05, 129.76, 129.01, 125.72, 125.56 (q, J = 3.7 Hz), 125.16, 123.30 (q, J = 272.9 Hz), 63.08, 27.61, 18.89.

All data matched that reported in the literature[1].



1f

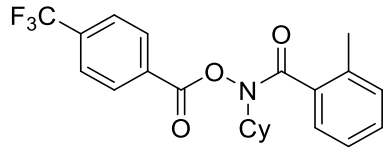
N-isopropyl-2-methyl-N-((4-(trifluoromethyl)benzoyl)oxy)benzamide (1f)

28% overall yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.09 (m, 4H), 4.44 (s, 1H), 2.49 (s, 3H),, 1.29 (d, J = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.34,135.44 (q, *J* = 32.8 Hz), 134.43,130.74, 130.53, 130.43, 129.92, 126.44,125.79 (q, *J* = 3.8 Hz), 123.53 (d, *J* = 272.8 Hz), 20.00, 19.21.

All data matched that reported in the literature[1].



1g

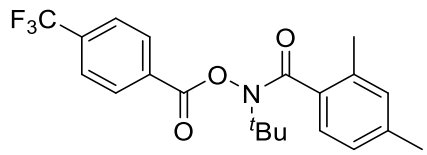
N-cyclohexyl-2-methyl-N-((4-(trifluoromethyl)benzoyl)oxy)benzamide (1g)

45% overall yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.12 (m, 3H), 4.73 – 3.49 (m, 1H), 2.48 (s, 3H), 2.11 – 1.92 (m, 2H), 1.79 (d, *J* = 12.8 Hz, 2H), 1.59 (d, *J* = 13.2 Hz, 2H), 1.34 – 1.15 (m, 2H), 1.13 – 0.95 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.36, δ 135.26 (q, *J* = 32.8 Hz), 134.39, 132.70, 131.60, 130.52, 130.40, 130.26, 129.70, 129.44, 126.24, 125.67 (q, *J* = 3.7 Hz), 123.40 (q, *J* = 272.9 Hz), 30.32, 25.34, 25.02, 19.07.

All data matched that reported in the literature[1].



1h

N-(tert-butyl)-2,4-dimethyl-N-((4-(trifluoromethyl)benzoyl)oxy)benzamide (1h)

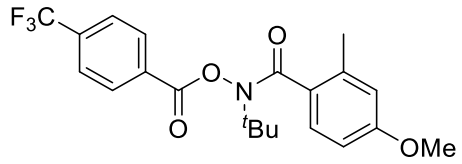
30% overall yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H),

7.11 (d, J = 7.8 Hz, 1H), 6.89 (s, 1H), 6.82 (d, J = 7.8 Hz, 1H), 2.38 (s, 3H), 2.16 (s, 3H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.76, 164.31, 138.86, 135.17 (q, J = 32.7 Hz), 133.25, 130.81, 130.24, 129.84, 125.86, 125.77, 125.56 (q, J = 3.9 Hz), 123.33 (q, J = 272.9 Hz), 63.03, 27.70, 21.10, 18.89.

All data matched that reported in the literature[2].



1i

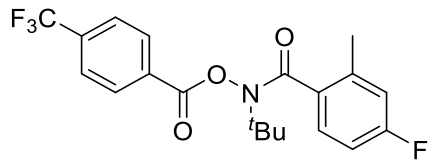
N-(tert-butyl)-4-methoxy-2-methyl-N-((4-(trifluoromethyl)benzoyl)oxy)benzamide (1i)

30% overall yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 1H), 6.62 (d, J = 2.7 Hz, 1H), 6.56 (dd, J = 8.4, 2.7 Hz, 1H), 3.68 (s, 3H), 2.42 (s, 3H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.59, 164.40, 159.99, 135.32 (q, J = 33.0 Hz), 130.29, 129.97, 128.69, 127.81, 125.73 (q, J = 3.9 Hz), 123.42 (q, J = 272.9 Hz), 115.66, 110.48, 63.10, 55.18, 27.85, 19.41.

All data matched that reported in the literature[2].



1j

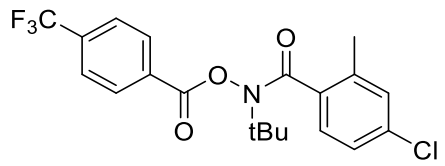
N-(tert-butyl)-4-fluoro-2-methyl-N-((4-(trifluoromethyl)benzoyl)oxy)benzamide (1j)

25% overall yield, colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.21 (dd, *J* = 8.4, 5.8 Hz, 1H), 6.79 (dd, *J* = 9.7, 2.3 Hz, 1H), 6.73 (td, *J* = 8.4, 2.3 Hz, 1H), 2.42 (s, 3H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.54, 164.16, 162.60 (q, *J* = 248.3 Hz), 137.8, 135.31 (q, *J* = 33.0 Hz), 132.10, 129.80, 127.91 (q, *J* = 8.8 Hz), 125.74 (q, *J* = 3.7 Hz), 124.61, 123.26 (d, *J* = 272.9 Hz), 121.90, 116.92 (q, *J* = 21.4 Hz), 112.15 (q, *J* = 21.7 Hz) , 63.24, 27.63, 19.06.

All data matched that reported in the literature[2].



1k

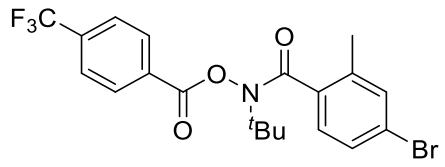
N-(tert-butyl)-4-chloro-2-methyl-N-((4-(trifluoromethyl)benzoyl)oxy)benzamide (1k)

14% overall yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.09 (s, 1H), 7.02 (dd, *J* = 8.2, 1.5 Hz, 1H), 2.40 (s, 3H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ170.34, 164.16, 136.85, 135.52 (q, *J* = 33.0 Hz), 134.71, 134.47, 130.12, 129.84, 129.77, 127.29, 125.78 (q, *J* = 3.7 Hz), 125.36, 123.26 (q, *J* = 273.0 Hz), 63.33, 27.62, 18.84.

All data matched that reported in the literature[2].



1l

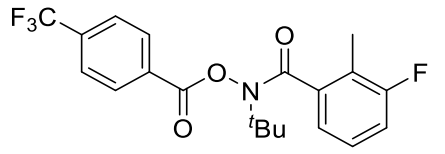
4-bromo-N-(tert-butyl)-2-methyl-N-((4-(trifluoromethyl)benzoyl)oxy)benzamide (1l)

10% overall yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 2.1 Hz, 1H), 7.18 (dd, J = 8.2, 2.1 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 2.40 (s, 3H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.46, 164.28, 137.18, 135.64 (q, J = 33.0 Hz), 135.06, 133.14, 129.96, 129.87, 128.40, 127.57, 125.90 (q, J = 3.9 Hz), 123.37 (q, J = 273.1 Hz), 123.13, 63.46, 27.73, 18.89.

HRMS (ESI) (m/z): Calcd. $C_{20}H_{20}BrF_3NO_3^+$ $[M+H]^+$: 458.0500. Found: 458.0573



1m

N-(tert-butyl)-3-fluoro-2-methyl-N-((4-

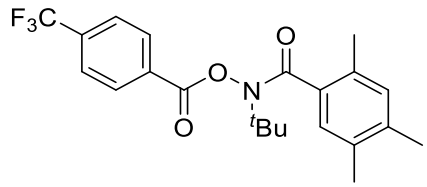
(trifluoromethyl)benzoyl)oxy)benzamide (1m)

32% overall yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.01 (q, J = 3.3 Hz, 2H), 6.85 (ddt, J = 9.5, 5.9, 3.7 Hz, 1H), 2.32 (d, J = 2.1 Hz, 3H), 1.61 (s, 9H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.87, 164.13, 160.82 (q, J = 245.5 Hz), 138.23, 135.45 (q, J = 32.9 Hz), 129.80, 127.32, 126.73 (q, J = 6.8 Hz), 125.70 (q, J = 3.7 Hz), 123.25 (q, J = 272.9 Hz), 121.47, 121.44, 115.67 (q, J = 22.7 Hz), 63.37, 27.57, 11.16.

HRMS (ESI) (m/z): Calcd. $C_{20}H_{20}F_4NO_3^+$ $[M+H]^+$: 398.1301. Found: 398.1373.



1n

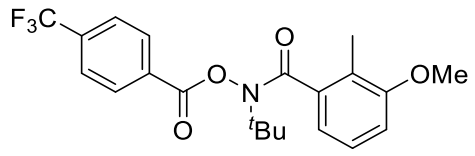
N-(tert-butyl)-2,4,5-trimethyl-N-((4-(trifluoromethyl)benzoyl)oxy)benzamide (1n)

18% overall yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 6.99 (s, 1H), 6.83 (s, 1H), 2.35 (s, 3H), 2.06 (d, J = 8.2 Hz, 6H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.80, 164.31, 137.43, 135.09 (q, J = 32.8 Hz), 133.50, 133.19, 131.34, 130.33, 129.82, 127.05, 125.47 (q, J = 3.7 Hz), 123.33 (q, J = 272.9 Hz), 119.26, 62.96, 27.68, 19.32, 18.83, 18.37.

HRMS (ESI) (m/z): Calcd. $C_{22}H_{25}F_3NO_3^+$ $[M+H]^+$: 408.1708. Found: 408.1782.



1o

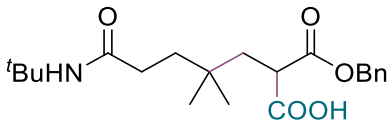
N-(tert-butyl)-3-methoxy-2-methyl-N-((4-(trifluoromethyl)benzoyl)oxy)benzamide (1o)

15% overall yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 6.1 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.06 – 6.94 (m, 1H), 6.82 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 8.1 Hz, 1H), 3.71 (s, 3H), 2.27 (s, 3H), 1.62 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.31, 164.23, 157.44, 135.12 (q, J = 32.9 Hz), 130.19, 129.82, 127.39, 125.49 (q, J = 3.7 Hz), 123.32 (d, J = 272.9 Hz), 117.82, 110.51, 63.10, 55.42, 27.54, 12.39

HRMS (ESI) (m/z): Calcd. $C_{21}H_{23}F_3NO_4^+$ $[M+H]^+$: 410.1501. Found: 410.1573.



2a

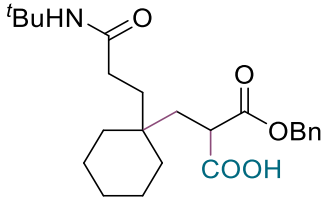
2-((benzyloxy)carbonyl)-7-(tert-butylamino)-4,4-dimethyl-7-oxoheptanoic acid (2a)

Yield : 82%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.48 (s, 1H), 5.17 (s, 2H), 3.49 (t, J = 6.1 Hz, 1H), 2.06 (ddd, J = 14.3, 10.7, 7.2 Hz, 2H), 2.00 – 1.88 (m, 2H), 1.60 – 1.44 (m, 2H), 1.33 (s, 9H), 0.84 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.91, 172.89, 170.38, 135.36, 128.55, 128.36, 128.31, 128.15, 67.29, 51.37, 48.18, 39.04, 37.27, 32.85, 32.59, 28.71, 26.76, 26.68.

HRMS (ESI) (m/z): Calcd. $C_{21}H_{32}NO_5^+$ $[M+H]^+$: 378.2202. Found: 378.2275.



2b

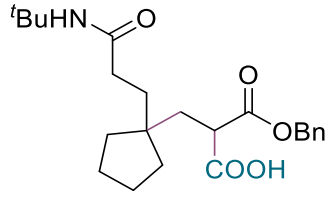
3-(benzyloxy)-2-((1-(3-(tert-butylamino)-3-oxopropyl)cyclohexyl)methyl)-3-oxopropanoic acid (2b)

Yield : 76%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 7.33 (q, J = 3.7, 3.3 Hz, 5H), 5.69 (s, 1H), 5.16 (d, J = 4.2 Hz, 2H), 3.44 (q, J = 7.9, 6.8 Hz, 1H), 2.17 – 1.91 (m, 4H), 1.61 – 1.52 (m, 4H), 1.44 – 1.13 (m, 14H).

^{13}C NMR (101 MHz, $CDCl_3$) δδ 174.23, 173.15, 170.91, 135.42, 128.55, 128.29, 128.16, 67.19, 51.18, 47.53, 35.43, 35.13, 31.62, 28.71, 26.11, 21.30.

HRMS (ESI) (m/z): Calcd. $C_{24}H_{36}NO_5^+$ $[M+H]^+$: 418.2515 Found: 418.2588.



2c

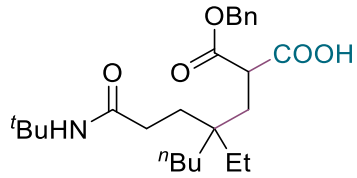
3-(benzyloxy)-2-((1-(3-(tert-butylamino)-3-oxopropyl)cyclopentyl)methyl)-3-oxopropanoic acid (2c)

Yield : 81%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 7.36 – 7.31 (m, 6H), 5.66 (s, 1H), 5.21 – 5.12 (m, 2H), 3.45 (t, *J* = 5.9 Hz, 1H), 2.15 – 1.97 (m, 4H), 1.58 (tt, *J* = 9.2, 4.0 Hz, 4H), 1.40 – 1.20 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.08, 173.13, 170.56, 135.29, 128.58, 128.36, 128.14, 67.33, 51.30, 48.82, 45.00, 37.31, 37.26, 28.70, 24.05, 24.02.

HRMS (ESI) (m/z): Calcd. $C_{23}H_{34}NO_5^+$ $[M+H]^+$: 404.2359 Found: 404.2427.



2d

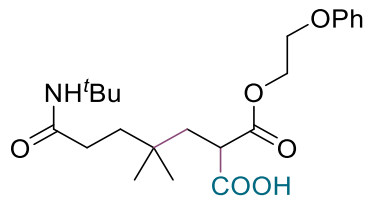
2-((benzyloxy)carbonyl)-4-(3-(tert-butylamino)-3-oxopropyl)-4-ethyloctanoic acid (2d)

Yield : 79%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.36 – 7.30 (m, 5H), 5.65 (d, *J* = 4.7 Hz, 1H), 5.23 – 5.11 (m, 2H), 3.45 (t, *J* = 5.9 Hz, 1H), 2.08 – 1.80 (m, 4H), 1.48 – 1.37 (m, 2H), 1.32 (d, *J* = 4.2 Hz, 9H), 1.22 – 1.02 (m, 8H), 0.91 – 0.65 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.97, 170.38, 135.24, 128.59, 128.39, 128.25, 128.16, 77.37, 77.05, 76.73, 67.40, 51.26, 47.39, 37.91, 37.74, 35.05, 34.12, 32.05, 31.82, 28.72, 28.03, 24.82, 23.41, 14.08, 7.32.

HRMS (ESI) (m/z): Calcd. $C_{25}H_{40}NO_5^+$ $[M+H]^+$: 434.2828 Found: 434.2894.



2e

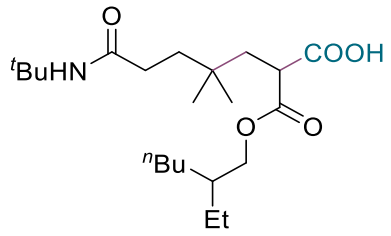
7-(tert-butylamino)-4,4-dimethyl-7-oxo-2-((2-phenoxyethoxy)carbonyl)heptanoic acid (2e)

Yield : 66%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.27 (t, *J* = 6.3, 5.5, 2.6 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 2H), 5.59 (s, 1H), 4.54 – 4.41 (m, 2H), 4.18 (t, *J* = 4.9 Hz, 2H), 3.46 (t, *J* = 7.2, 5.0 Hz, 1H), 2.12 – 2.03 (m, 2H), 2.02 – 1.84 (m, 2H), 1.62 – 1.41 (m, 2H), 1.31 (s, 9H), 0.85 (d, *J* = 3.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.88, 172.63, 170.55, 158.38, 129.53, 129.47, 121.22, 114.69, 114.63, 65.51, 63.72, 51.37, 48.09, 39.06, 37.25, 32.85, 32.55, 28.76, 28.70, 26.72, 26.69, 19.47.

HRMS (ESI) (m/z): Calcd. $C_{22}H_{34}NO_6^+$ $[M+H]^+$: 408.2308 Found: 408.2393.



2f

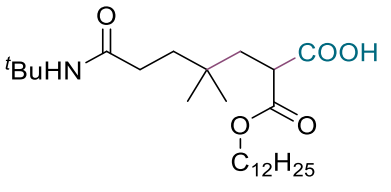
7-(tert-butylamino)-2-(((2-ethylhexyl)oxy)carbonyl)-4,4-dimethyl-7-oxoheptanoic acid (2f)

Yield : 71%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 5.60 (s, 1H), 4.12 – 4.00 (m, 2H), 3.42 (t, *J* = 6.1 Hz, 1H), 2.16 – 2.05 (m, 2H), 2.01 – 1.84 (m, 2H), 1.65 – 1.46 (m, 3H), 1.43 – 1.22 (m, 19H), 0.93 – 0.85 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.76, 173.73, 170.58, 68.07, 68.05, 51.34, 48.13, 39.02, 38.61, 37.26, 32.83, 32.61, 30.25, 28.85, 28.82, 28.71, 26.74, 26.67, 23.68, 22.98, 22.94, 22.91, 14.04, 10.92, 10.90.

HRMS (ESI) (m/z): Calcd. $C_{22}H_{42}NO_5^+$ $[M+H]^+$: 400.2985 Found: 400.3057.



2g

7-(tert-butylamino)-2-((dodecyloxy)carbonyl)-4,4-dimethyl-7-oxoheptanoic acid (2g)

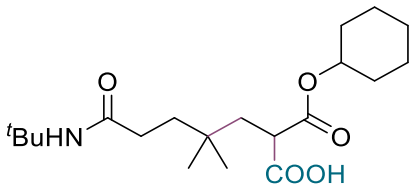
Yield : 71%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 5.60 (s, 1H), 4.13 (t, *J* = 6.8 Hz, 2H), 3.42 (t, *J* = 6.9, 5.3 Hz, 1H), 2.18 – 2.05 (m, 2H), 1.93 (qd, *J* = 14.5, 6.1 Hz,

2H), 1.64 (p, *J* = 7.0 Hz, 2H), 1.55 – 1.44 (m, 2H), 1.30 (d, *J* = 30.3 Hz, 28H), 0.88 (d, *J* = 2.8 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.81, 173.54, 170.52, 65.88, 51.36, 48.11, 39.04, 37.22, 32.85, 32.61, 31.92, 29.65, 29.64, 29.59, 29.51, 29.35, 29.20, 28.71, 28.38, 26.78, 26.70, 25.78, 22.69, 14.12.

HRMS (ESI) (m/z): Calcd. $C_{26}H_{50}NO_5^+$ $[M+H]^+$: 456.3611 Found: 456.3680.



2h

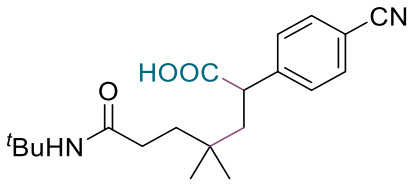
7-(tert-butylamino)-2-((cyclohexyloxy)carbonyl)-4,4-dimethyl-7-oxoheptanoic acid (2)

Yield : 71%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 5.61 (s, 1H), 4.82 (tt, J = 8.7, 3.8 Hz, 1H), 3.39 (dd, J = 7.0, 5.2 Hz, 1H), 2.09 (q, J = 7.6, 6.7 Hz, 2H), 1.97 (dd, J = 14.4, 7.2 Hz, 1H), 1.92 – 1.78 (m, 5H), 1.77 – 1.66 (m, 4H), 1.61 – 1.39 (m, 8H), 1.34 (d, J = 4.0 Hz, 14H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.76, 173.74, 169.92, 73.94, 51.30, 48.42, 38.98, 37.21, 32.87, 32.64, 31.24, 31.19, 28.71, 26.81, 25.30, 23.55, 23.52.

HRMS (ESI) (m/z): Calcd. $C_{20}H_{36}NO_5^+$ $[M+H]^+$: 370.2515 Found: 370.2585.



2i

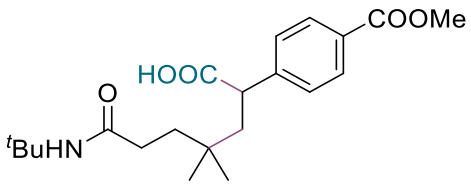
7-(tert-butylamino)-2-(4-cyanophenyl)-4,4-dimethyl-7-oxoheptanoic acid (2i)

Yield : 71%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.49 – 7.43 (m, 2H), 5.42 (s, 1H), 3.75 (dd, *J* = 8.2, 4.4 Hz, 1H), 2.29 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.13 – 1.94 (m, 2H), 1.62 – 1.45 (m, 3H), 1.31 (s, 9H), 0.83 (d, *J* = 3.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.08, 173.58, 146.48, 132.36, 128.91, 118.72, 110.89, 51.40, 48.07, 44.62, 37.22, 33.42, 32.63, 28.69, 27.16, 26.94.

HRMS (ESI) (m/z): Calcd. $C_{20}H_{36}NO_5^+$ $[M+H]^+$: 370.2515 Found: 370.2585.



2j

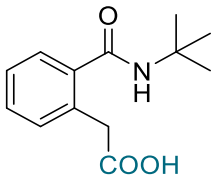
7-(tert-butylamino)-2-(4-(methoxycarbonyl)phenyl)-4,4-dimethyl-7-oxoheptanoic acid (2j)

Yield : 75%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.39 (m, 2H), 5.51 (s, 1H), 3.90 (d, *J* = 1.8 Hz, 4H), 3.74 (dd, *J* = 8.3, 4.4 Hz, 1H), 2.29 (dd, *J* = 14.3, 8.3 Hz, 1H), 2.14 – 1.96 (m, 1H), 1.62 – 1.41 (m, 3H), 1.30 (s, 9H), 0.85 (d, *J* = 4.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ178.09, 176.68, 174.01, 166.89, 166.76, 145.63, 142.89, 130.16, 129.99, 129.51, 129.10, 128.14, 128.04, 52.20, 52.15, 51.53, 47.65, 46.41, 46.09, 44.39, 37.46, 33.44, 32.70, 29.94, 28.66, 27.06, 26.91.

HRMS (ESI) (m/z): Calcd. $C_{21}H_{32}NO_5^+$ $[M+H]^+$: 377.2202 Found: 378.2274.



3a

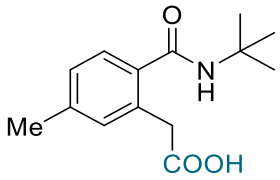
2-(2-(tert-butylcarbamoyl)phenyl)acetic acid (3a)

75% overall yield, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 4.9 Hz, 3H), 7.33 (td, *J* = 7.9, 6.6, 3.9 Hz, 1H), 6.14 (s, 1H), 3.72 (s, 2H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.51, 171.10, 163.16, 135.55, 132.97, 131.54, 131.37, 127.74, 127.62, 52.96, 41.68, 36.80, 31.69, 28.54.

All data matched that reported in the literature[3].



3b

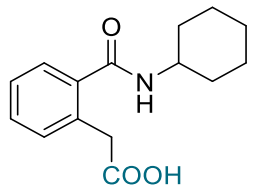
2-(2-(tert-butylcarbamoyl)-5-methylphenyl)acetic acid (3b)

67% overall yield, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.11 (s, 1H), 3.68 (s, 2H), 2.35 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.79, 171.29, 142.24, 133.45, 132.53, 132.31, 128.44, 127.34, 52.98, 42.15, 28.82, 28.62, 21.20.

All data matched that reported in the literature[3].



3c

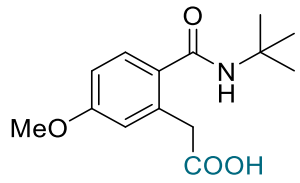
2-(2-(cyclohexylcarbamoyl)phenyl)acetic acid (3c)

82% overall yield, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 1H), 7.39 (ddd, *J* = 16.0, 7.6, 1.5 Hz, 2H), 7.32 – 7.26 (m, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 3.94 (th, *J* = 13.9, 3.7 Hz, 1H), 3.69 (s, 2H), 2.02 (dq, *J* = 11.9, 3.6 Hz, 2H), 1.78 (dp, *J* = 11.1, 3.7 Hz, 2H), 1.67 (dt, *J* = 12.9, 3.7 Hz, 1H), 1.48 – 1.12 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.02, 170.44, 134.49, 133.36, 131.63, 127.81, 127.72, 77.40, 77.08, 76.76, 49.86, 42.04, 32.65, 25.34, 24.84.

HRMS (ESI) (m/z): Calcd. $C_{15}H_{20}NO_3^+$ $[M+H]^+$: 262.1365. Found: 262.1438.



3d

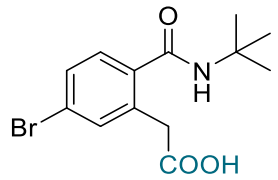
2-(2-(tert-butylcarbamoyl)-5-methoxyphenyl)acetic acid (3d)

64% overall yield, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.6 Hz, 1H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.81 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.06 (s, 1H), 3.82 (s, 3H), 3.71 (s, 2H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.62, 171.01, 161.86, 135.79, 129.05, 127.36, 116.43, 113.79, 55.57, 52.94, 42.49, 28.64.

All data matched that reported in the literature[3].



3e

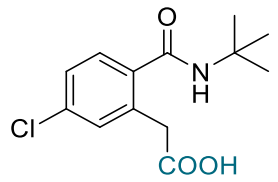
2-(5-bromo-2-(tert-butylcarbamoyl)phenyl)acetic acid (3e)

57% overall yield, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 5.6 Hz, 2H), 7.36 – 7.28 (m, 1H), 6.15 (s, 1H), 3.72 (s, 2H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.60, 171.21, 135.26, 133.43, 131.84, 131.67, 127.85, 127.28, 53.11, 42.11, 28.60..

All data matched that reported in the literature[3].



3f

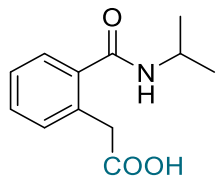
2-(2-(tert-butylcarbamoyl)-5-chlorophenyl)acetic acid (3f)

64% overall yield, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 2H), 7.29 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.28 (s, 1H), 3.70 (s, 2H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.20, 170.09, 137.57, 135.12, 133.78, 131.75, 130.53, 128.70, 128.00, 125.49, 53.25, 41.64, 28.57.

All data matched that reported in the literature[3].



3g

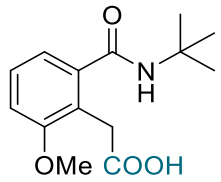
2-(2-(isopropylcarbamoyl)phenyl)acetic acid (3g)

64% overall yield, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 3H), 7.36 – 7.29 (m, 1H), 6.29 (s, 1H), 4.28 (dt, *J* = 13.3, 6.7 Hz, 1H), 3.72 (s, 2H), 1.31 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.55, 170.59, 134.27, 133.62, 131.89, 131.87, 127.89, 127.41, 43.07, 42.20, 22.46.

HRMS (ESI) (m/z): Calcd. $C_{12}H_{16}NO_3^+$ $[M+H]^+$: 222.1052. Found: 222.1124.



3h

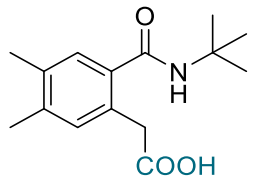
2-(2-(tert-butylcarbamoyl)-6-methoxyphenyl)acetic acid (3h)

57% overall yield, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 1H), 7.04 – 6.94 (m, 2H), 6.08 (s, 1H), 3.88 (s, 3H), 3.75 (s, 2H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.09, 170.86, 158.70, 137.36, 128.80, 121.93, 118.61, 113.18, 56.09, 52.96, 35.21, 28.62.

HRMS (ESI) (m/z): Calcd. $C_{14}H_{20}NO_4^+$ $[M+H]^+$: 266.1314. Found: 266.1386.



3i

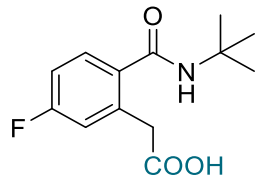
2-(2-(tert-butylcarbamoyl)-4,5-dimethylphenyl)acetic acid (3i)

60% overall yield, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 7.17 (s, 1H), 3.65 (s, 2H), 2.26 (d, *J* = 3.5 Hz, 6H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.13, 171.36, 140.94, 136.41, 133.08, 132.47, 130.89, 130.56, 128.24, 125.55, 52.94, 41.74, 28.65, 19.57, 19.35.

HRMS (ESI) (m/z): Calcd. $C_{15}H_{22}NO_3^+$ $[M+H]^+$: 264.1521. Found: 264.1596.



3j

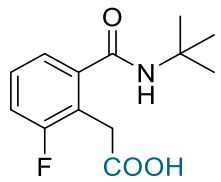
2-(2-(tert-butylcarbamoyl)-5-fluorophenyl)acetic acid (3j)

61% overall yield, colorless liquid.

^{1}H NMR(400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.6, 5.5 Hz, 1H), 7.12 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.00 (td, *J* = 8.2, 2.6 Hz, 1H), 6.22 (s, 1H), 3.70 (s, 2H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.93, 170.22, 163.92 (d, *J* = 253.5 Hz), 136.39, 136.31, 131.58, 131.54, 129.67, 129.58, 118.82, 118.60, 114.98, 114.76, 53.21, 42.00, 28.57.

HRMS (ESI) (m/z): Calcd. $C_{13}H_{17}FNO_3^+$ $[M+H]^+$: 254.1114. Found: 254.1186.



3j

2-(2-(tert-butylcarbamoyl)-6-fluorophenyl)acetic acid (3k)

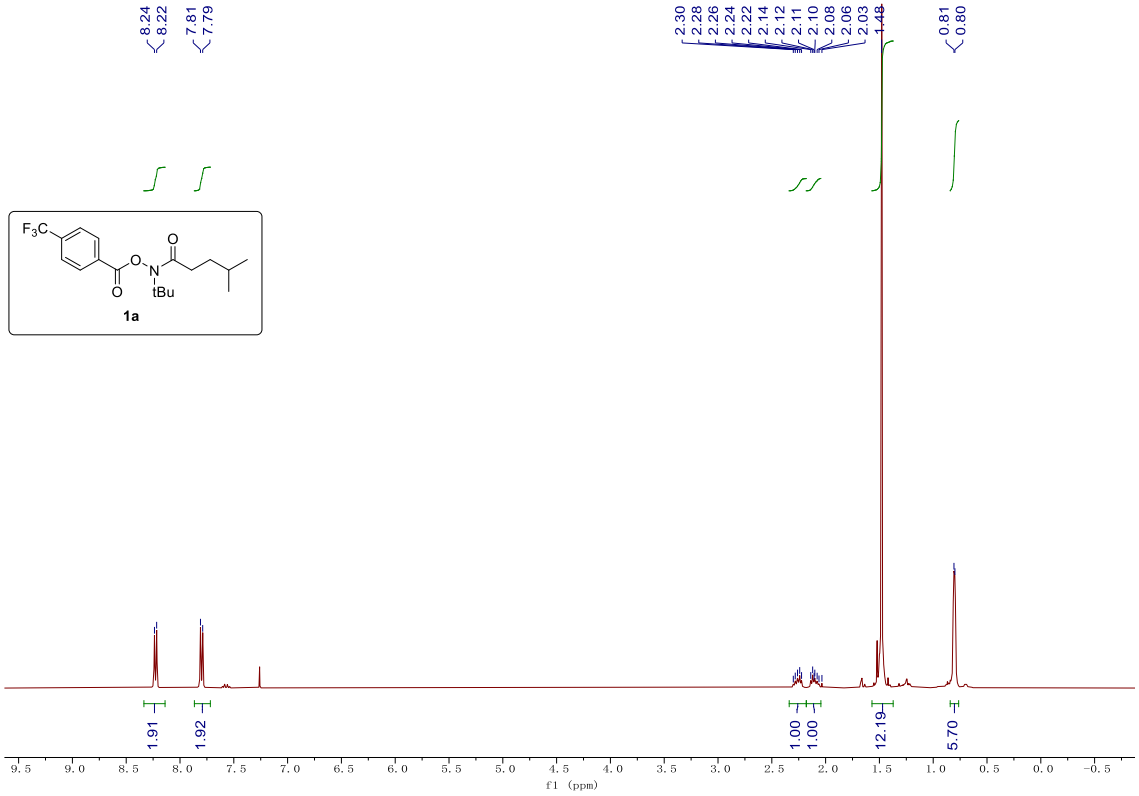
58% overall yield, colorless liquid.

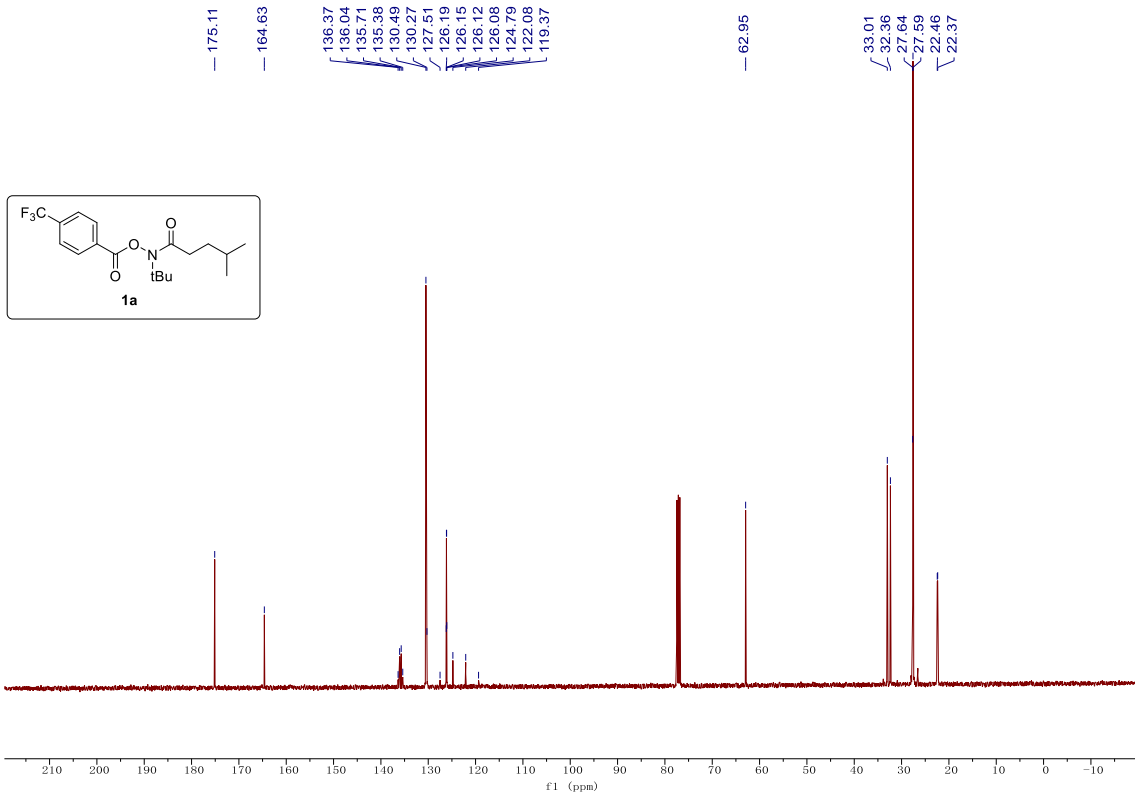
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 1H), 7.28 – 7.15 (m, 2H), 6.19 (s, 1H), 3.79 (s, 2H), 1.49 (s, 9H).

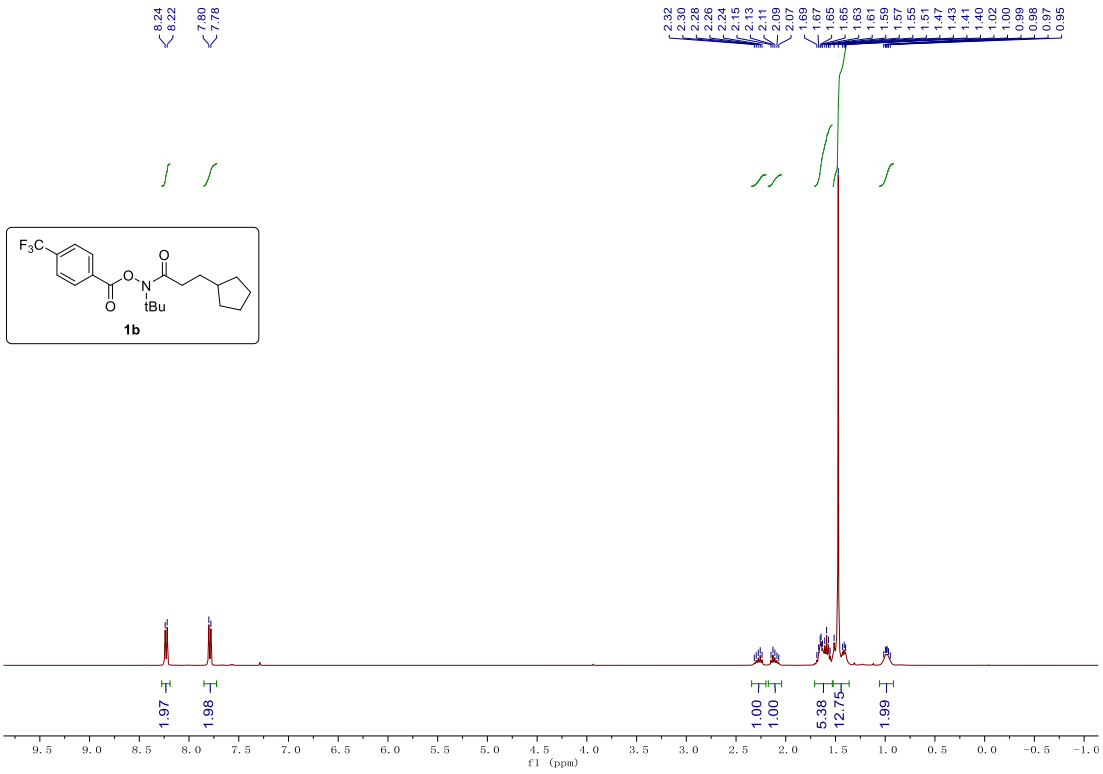
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.67, 169.56, 161.55 (d, *J* = 250.5 Hz), 137.98, 129.35, 129.26, 122.83, 122.79, 120.78 (d, *J* = 17.5 Hz), 118.30 (d, *J* = 22.8 Hz), 53.12, 33.98, 33.95, 28.58.

HRMS (ESI) (m/z): Calcd. $C_{13}H_{17}FNO_3^+$ $[M+H]^+$: 254.1114. Found: 254.1186.

8. NMR Spectra of New Compounds and Products



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2.26
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2.15
2.13
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2.07
1.69
1.67
1.65
1.65
1.63
1.61
1.59
1.57
1.55
1.51
1.47
1.43
1.41
1.40
1.02
1.00
0.99
0.98
0.97
0.95
F3C
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O
N
O
tBu
1b
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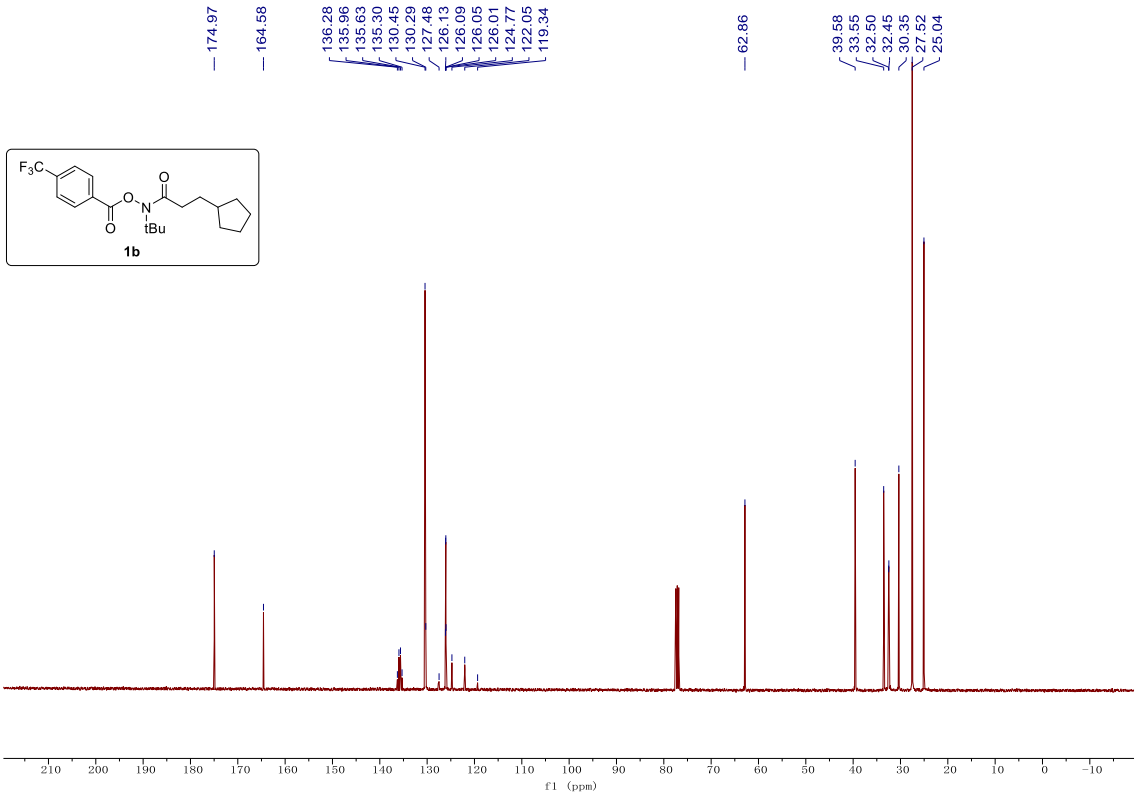
1.98
1.00
1.00
5.38
12.75
1.99
f1 (ppm)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124.77
122.05
119.34
62.86
39.58
33.55
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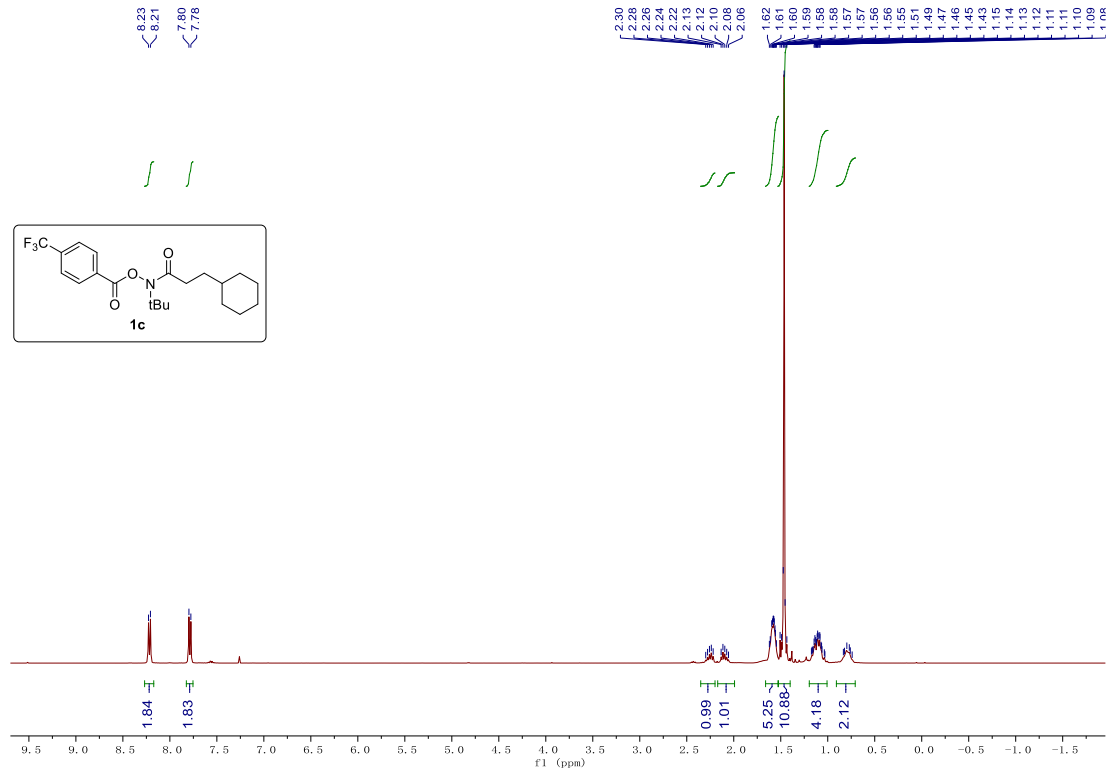
30.35
27.52
25.04
F3C
O
O
N
O
tBu
1b
f1 (ppm)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2.06
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1.61
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1.58
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1.47
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1.13
1.12
1.11
1.10
1.09
F3C
O
O
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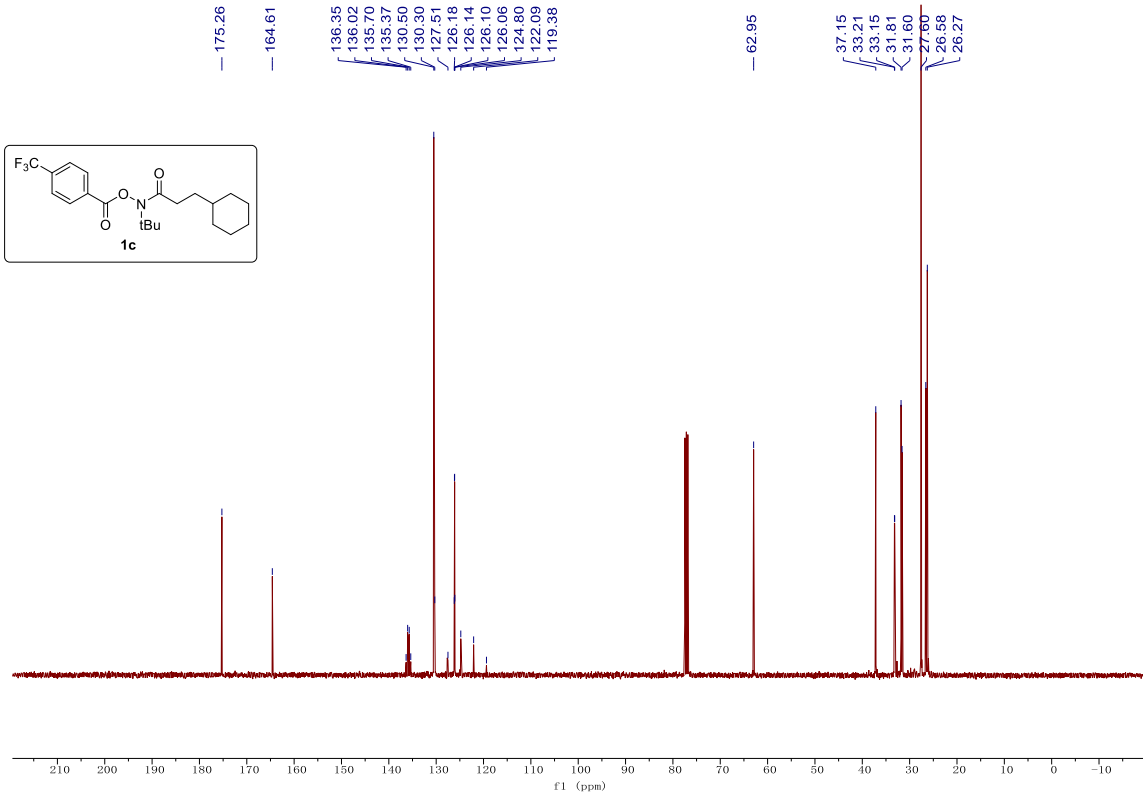
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124.80
122.09
119.38
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33.21
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26.27
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N
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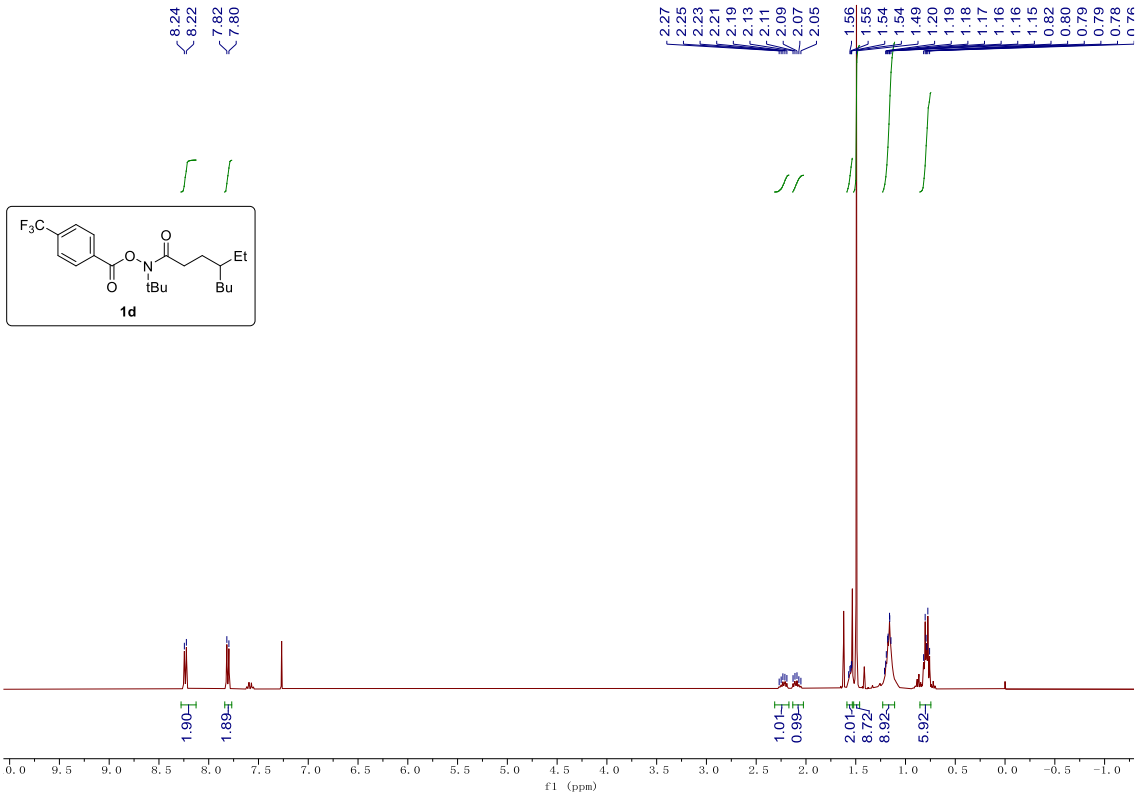
1c
f1 (ppm)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2.07
2.05
1.56
1.55
1.54
1.54
1.49
1.20
1.19
1.18
1.17
1.16
1.16
1.15
0.82
0.80
0.79
0.79
0.78
F3C
O
O
N
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Et
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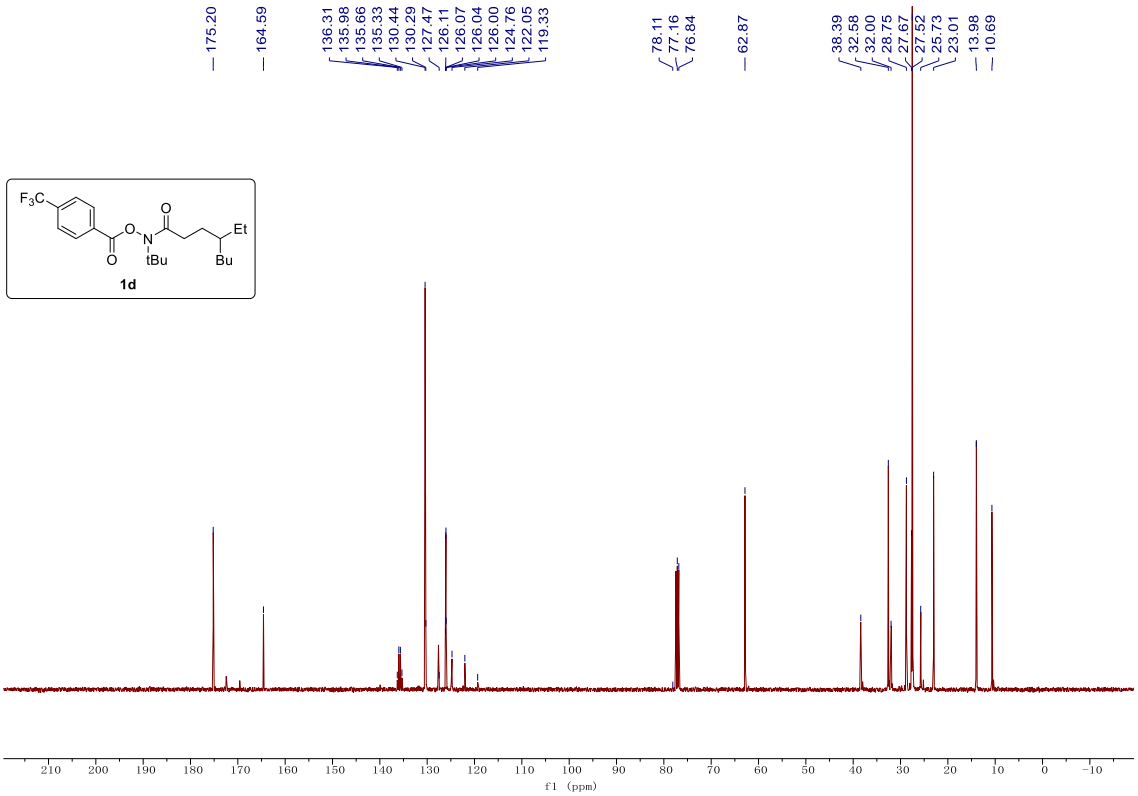
5.92
f1 (ppm)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122.05
119.33
78.11
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76.84
62.87
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32.00
28.75
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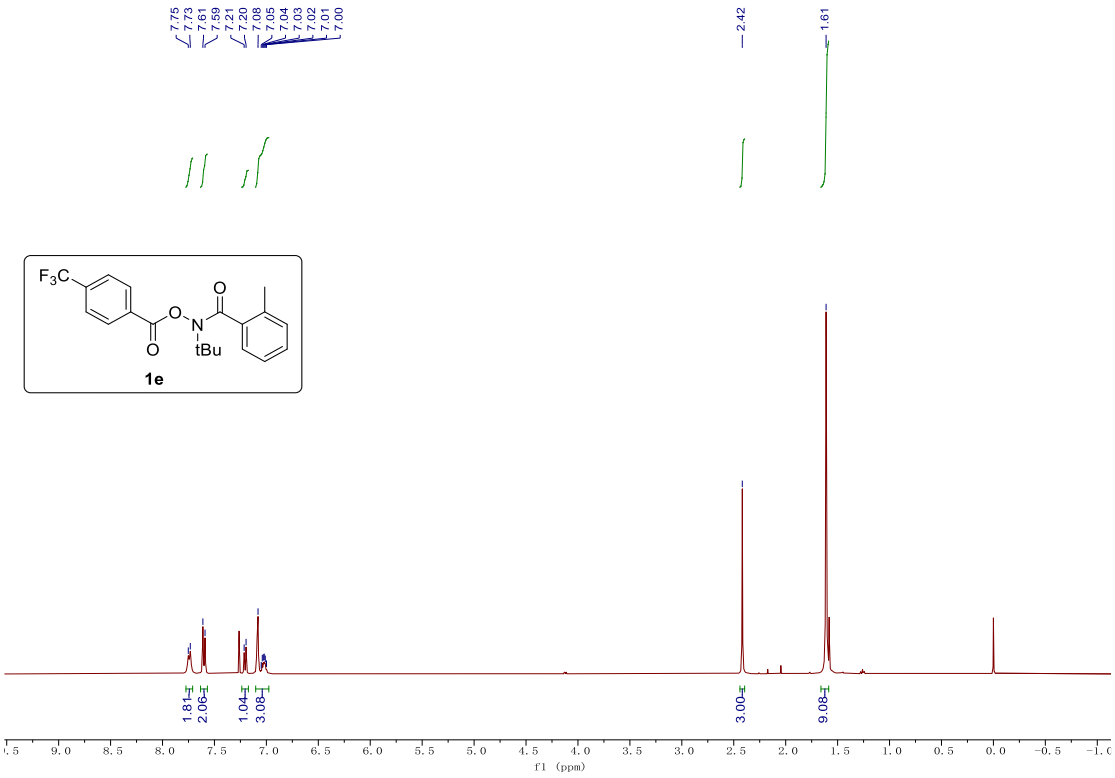
Et
Bu
1d
f1 (ppm)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7.00
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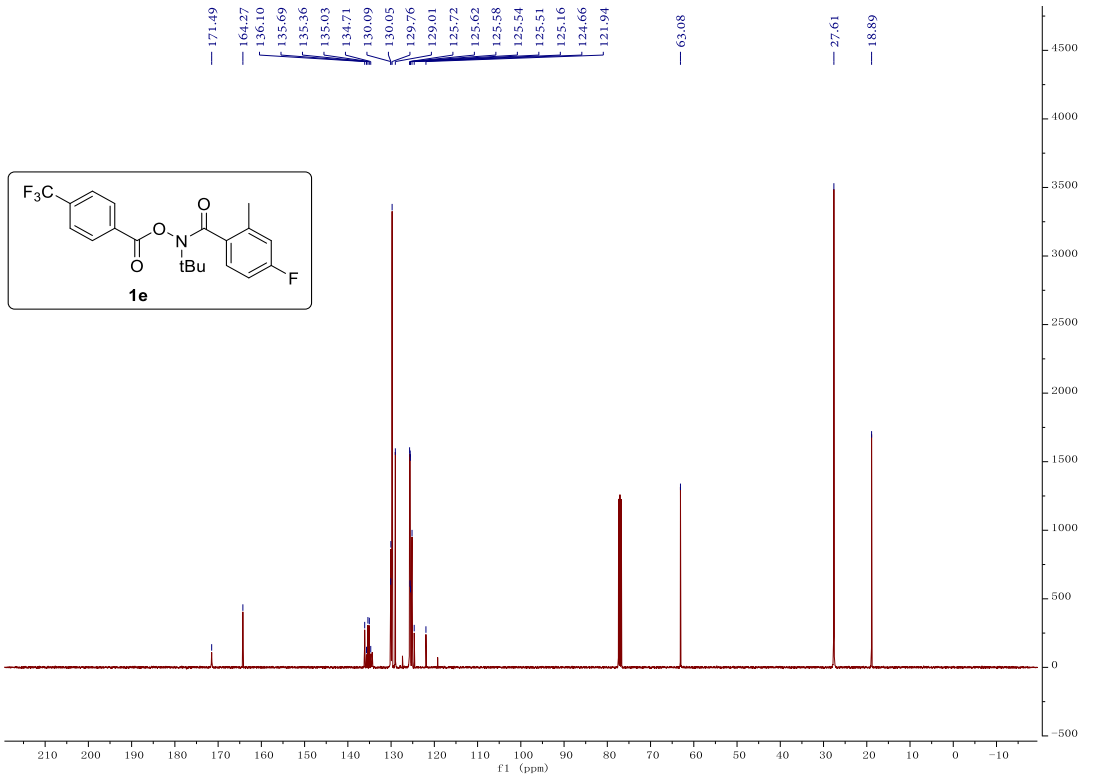
f1 (ppm)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125.54
125.51
125.16
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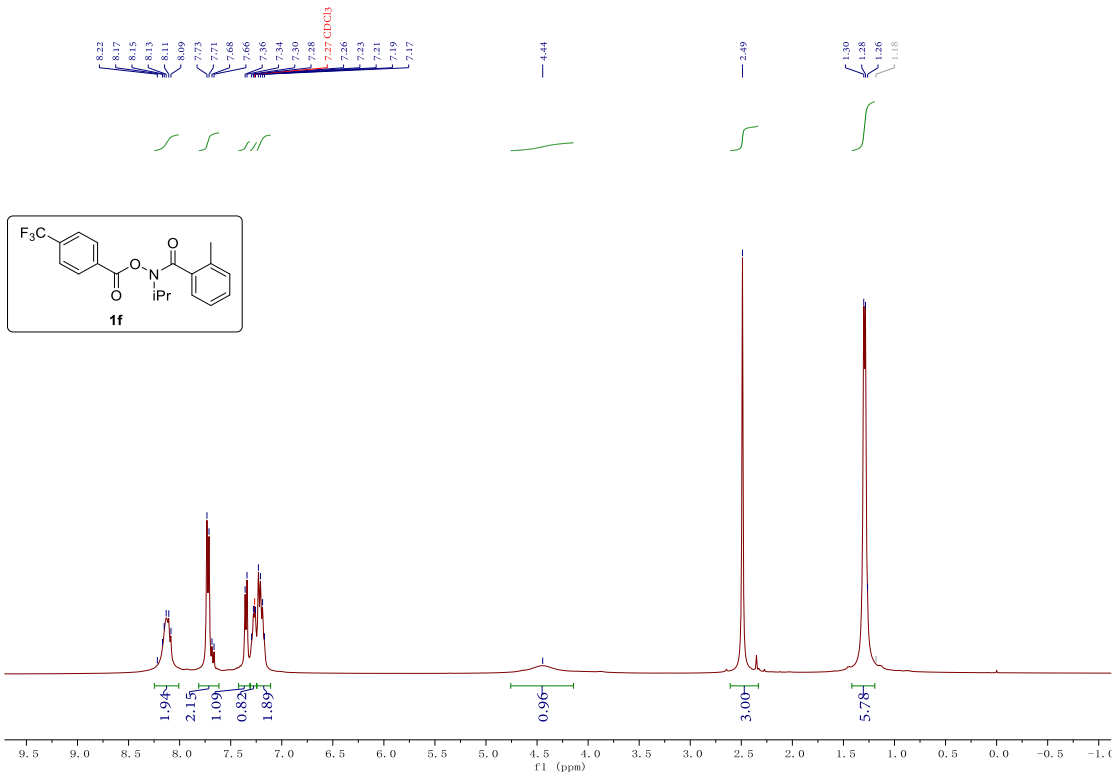
N
O
tBu
F
1e
f1 (ppm)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7.30
7.28
7.27 CDCl3
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7.23
7.21
7.19
7.17
4.44
2.49
1.30
1.28
1.26
1.18
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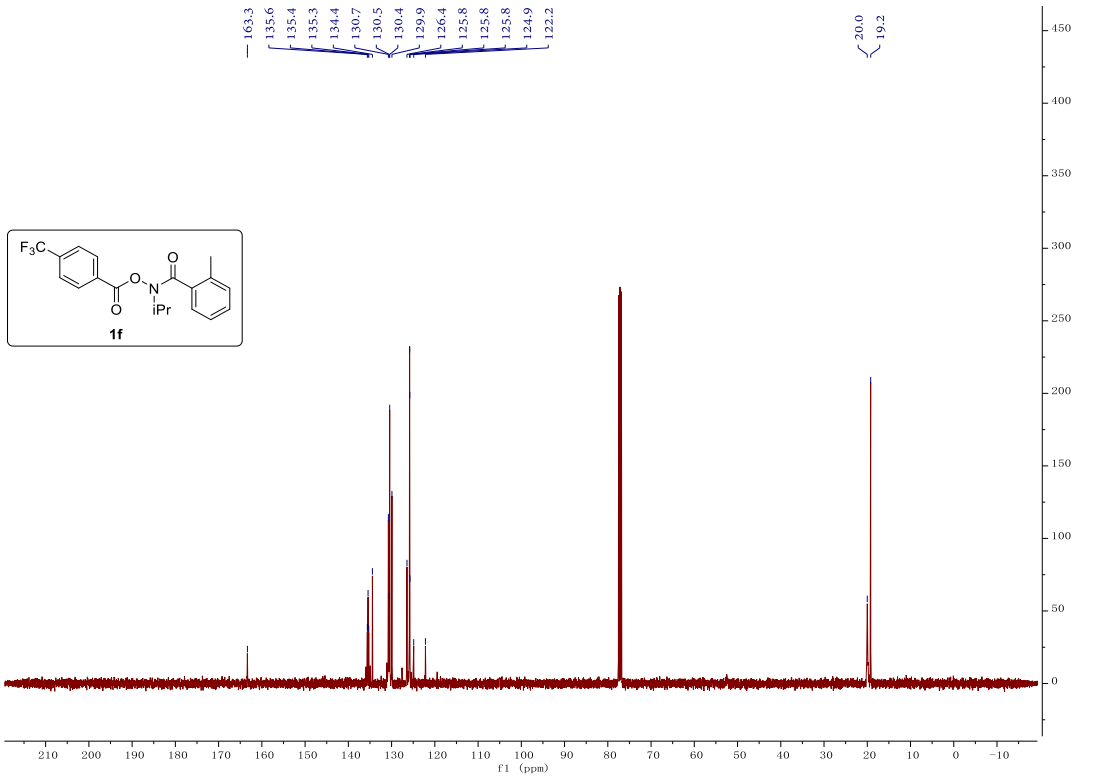
f1 (ppm)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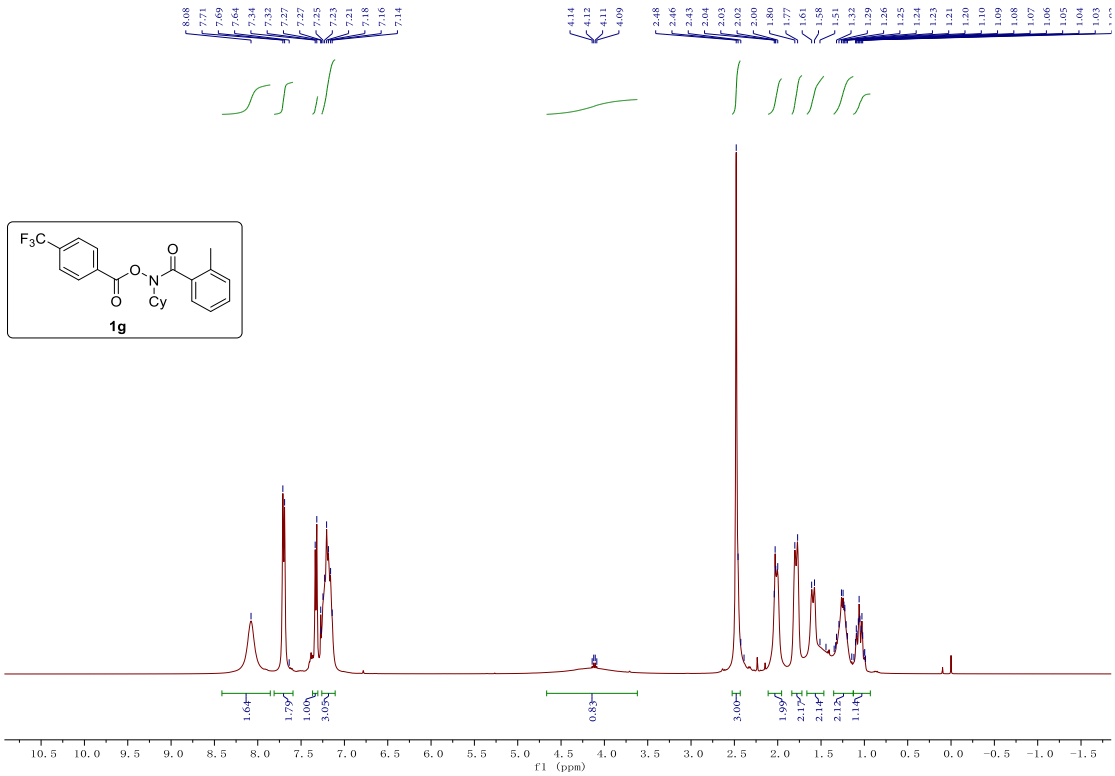
1f
f1 (ppm)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2.02
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1.20
1.10
1.09
1.08
1.07
1.06
1.05
1.04
1.03
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O
O
N
Cy
O
1g
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1.79
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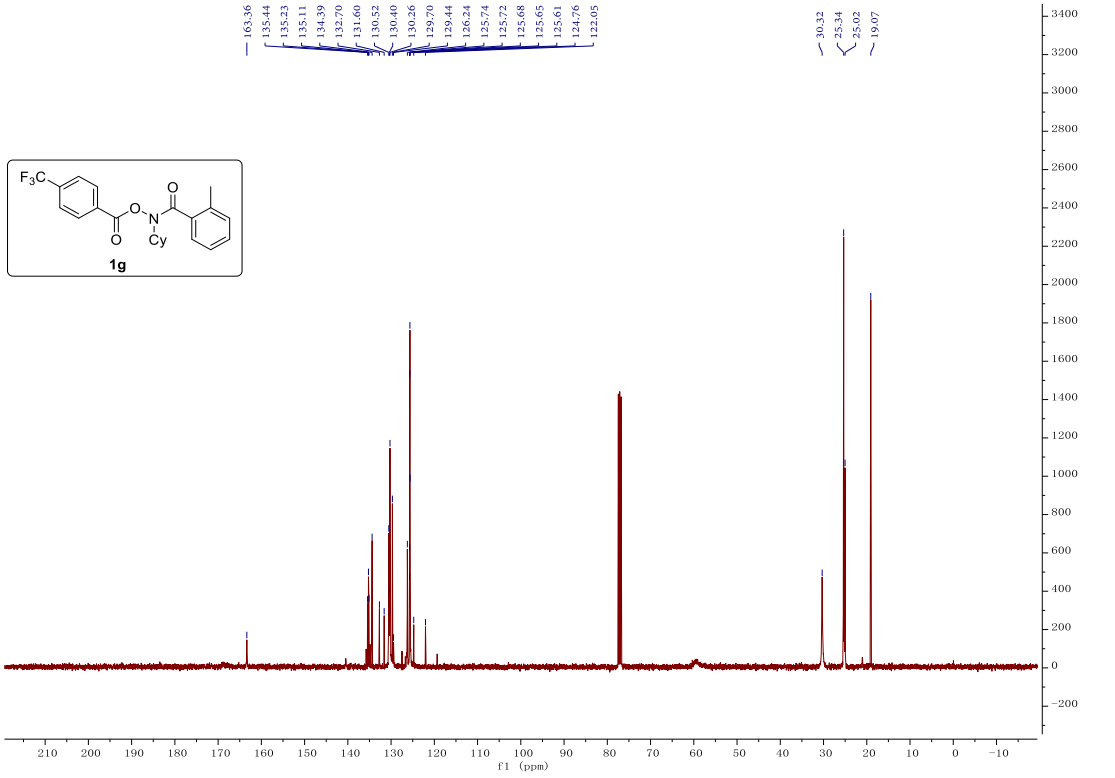
3.05
0.83
3.00
1.99
2.17
2.14
2.12
1.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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125.61
124.76
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3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
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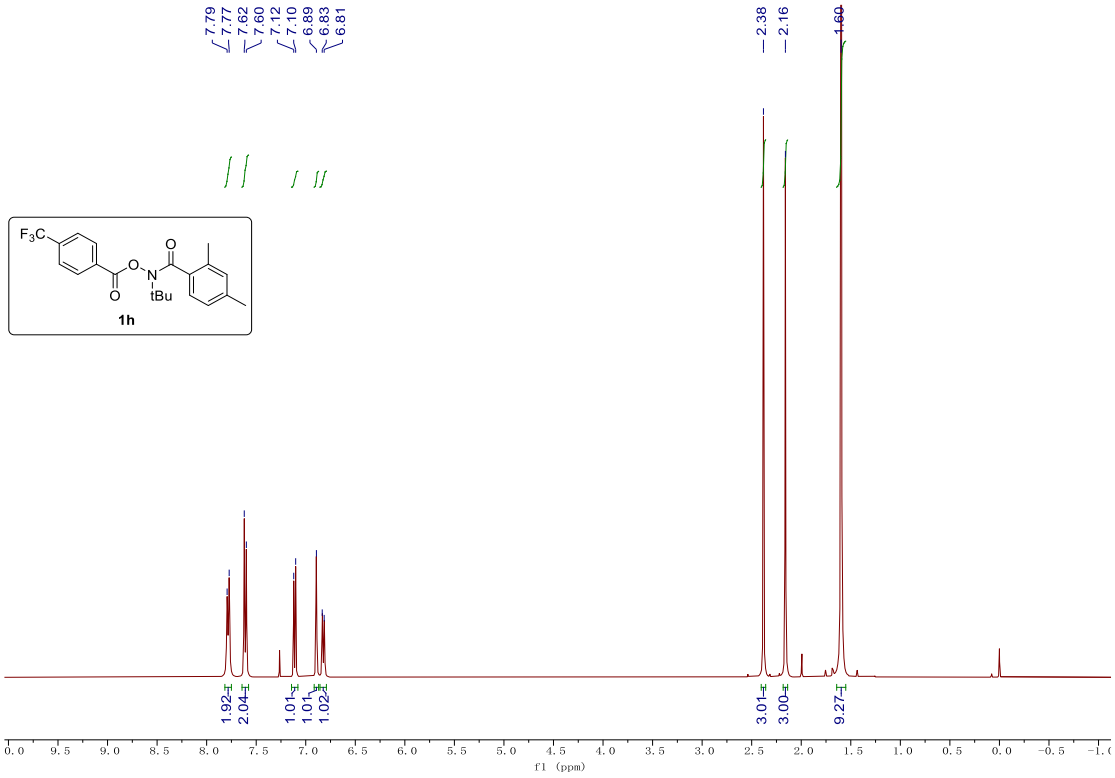
f1 (ppm)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O
O
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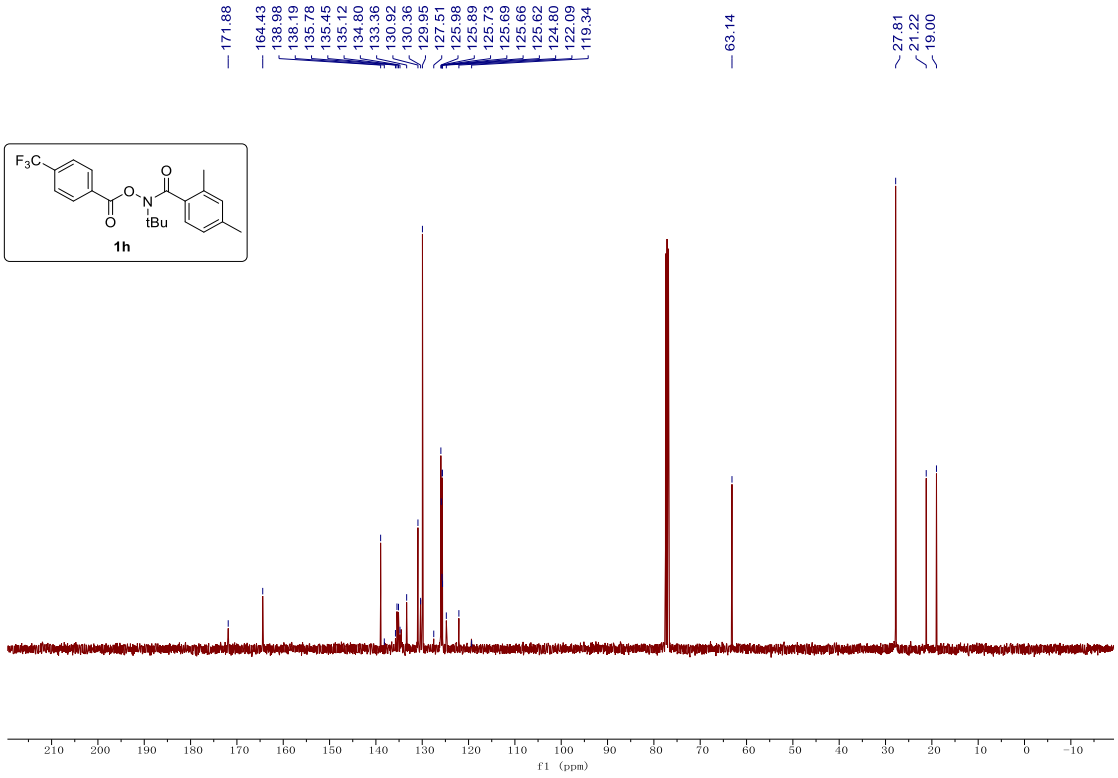
f1 (ppm)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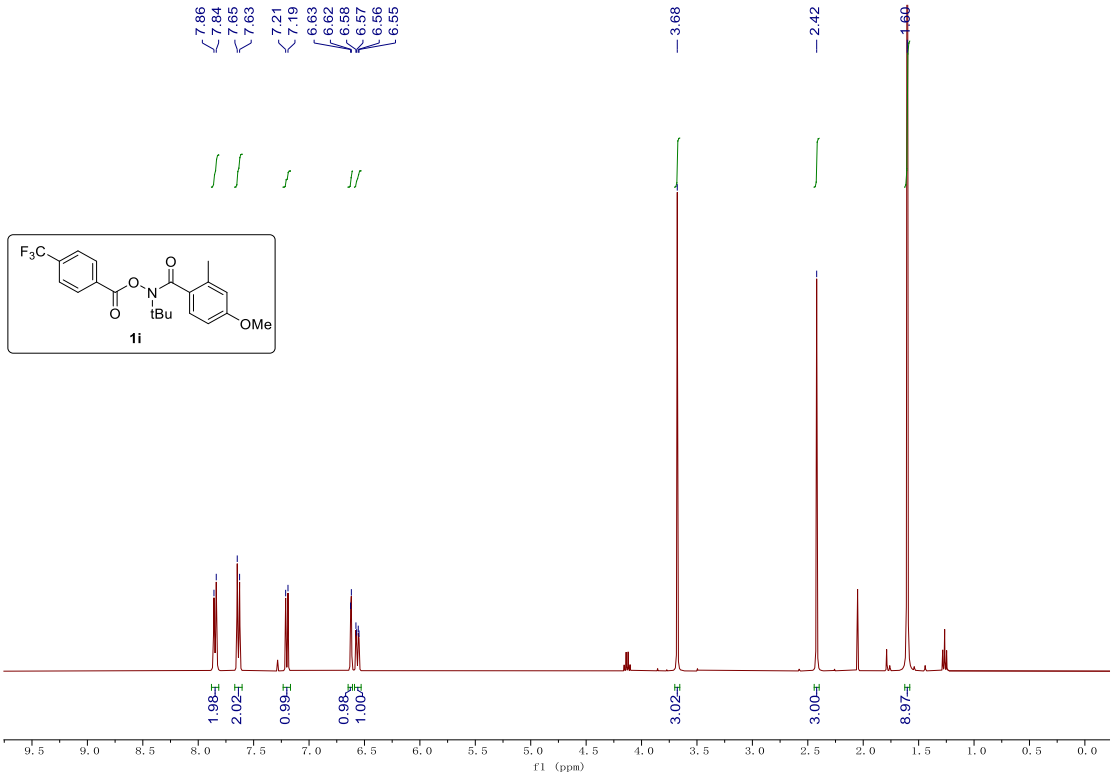
f1 (ppm)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O
O
N
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OMe
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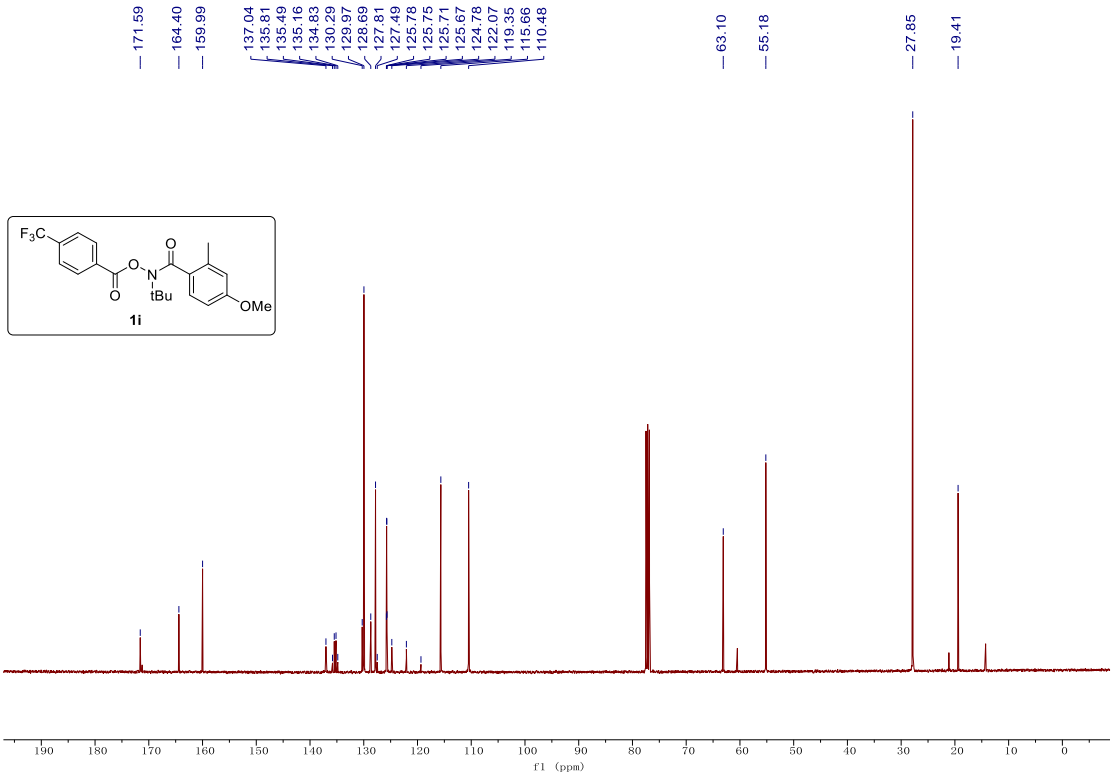
f1 (ppm)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N
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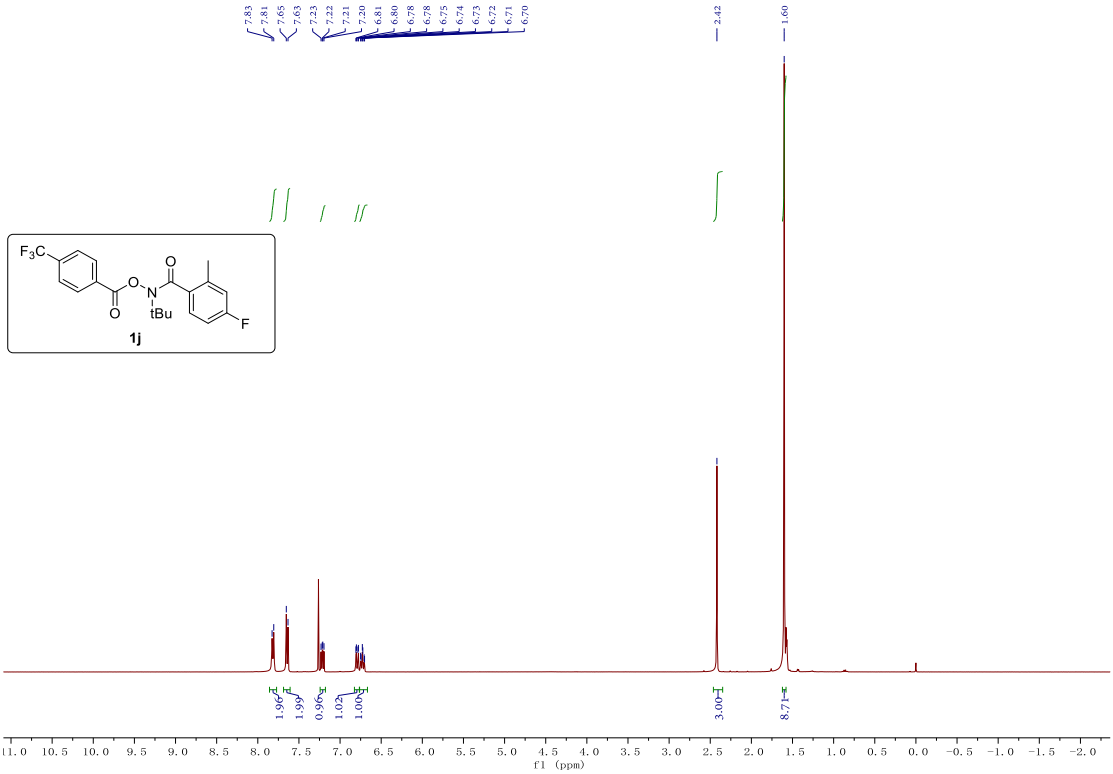
1i
f1 (ppm)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6.71
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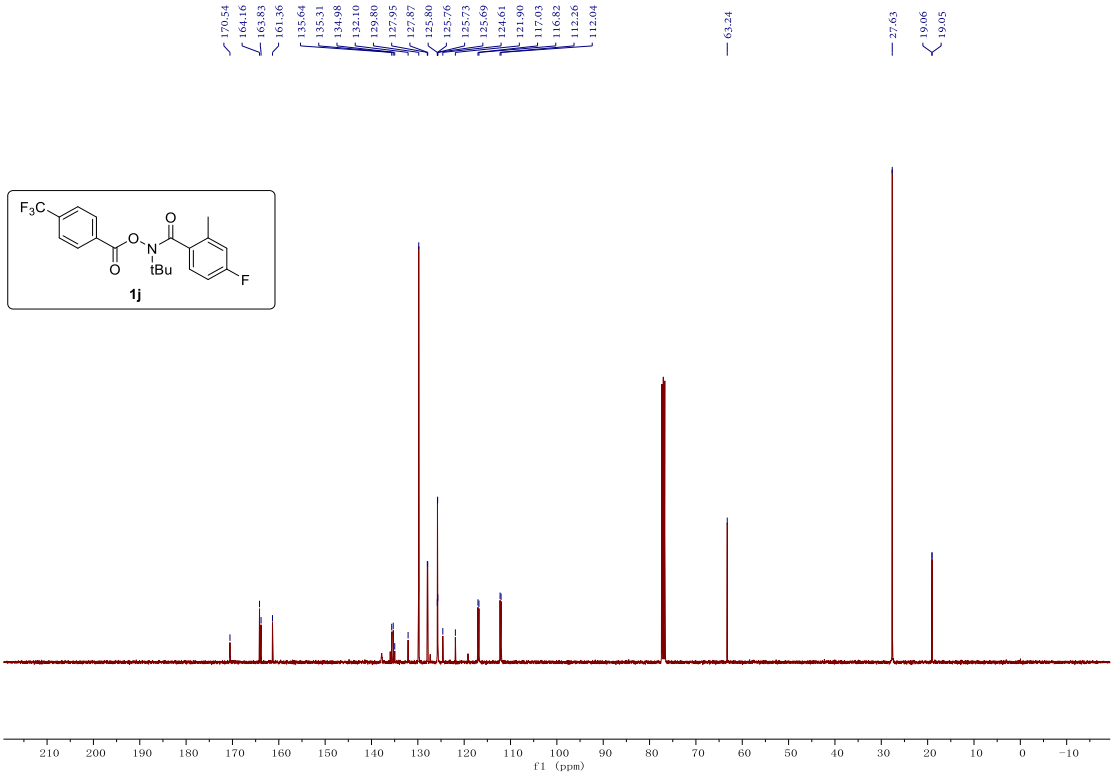
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121.90
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116.82
112.26
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O
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N
tBu
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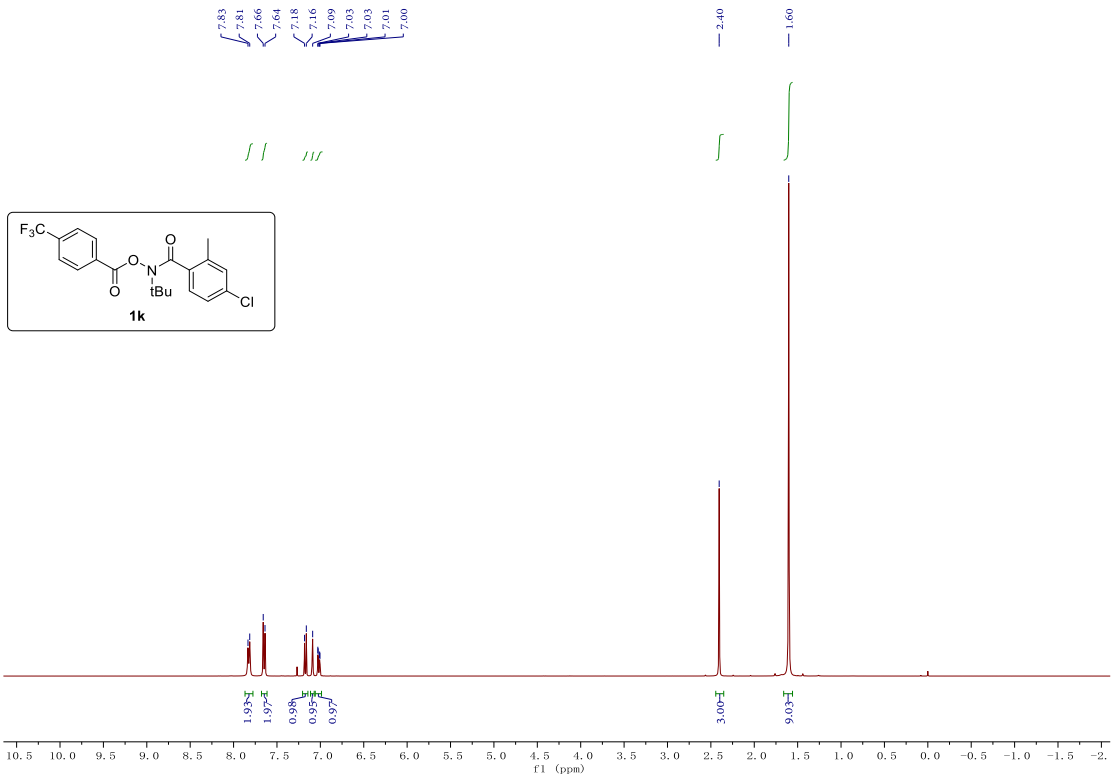
F
1j
f1 (ppm)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F3C
O
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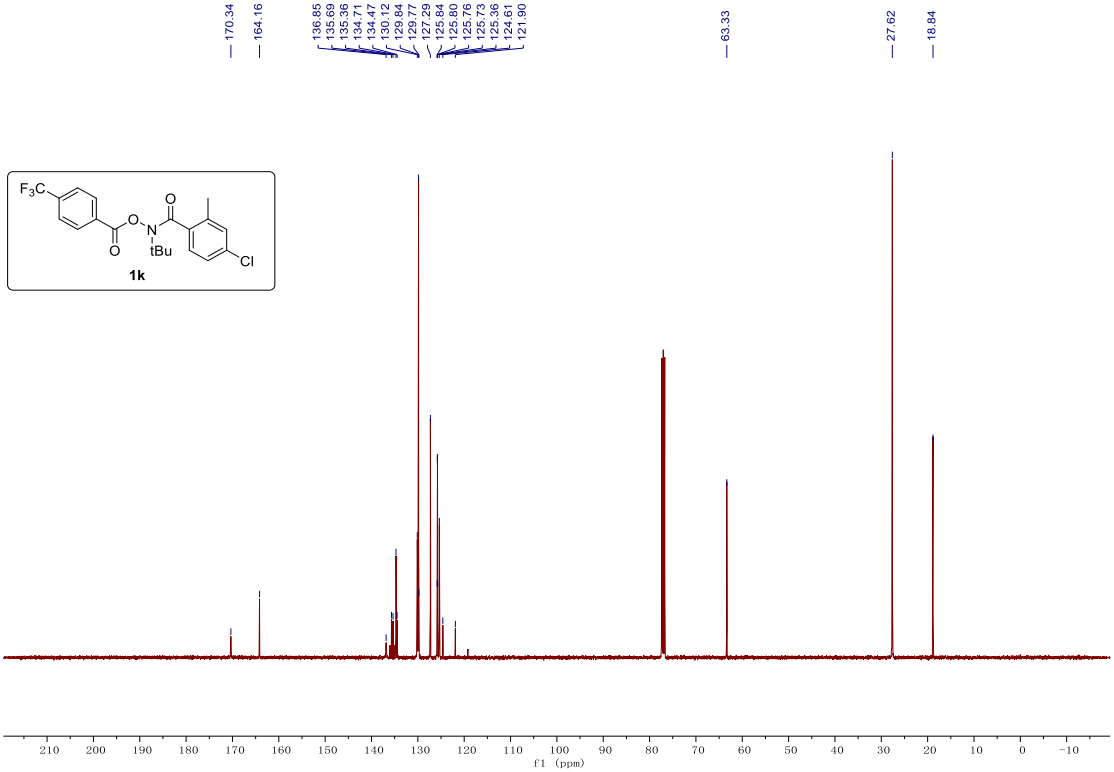
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125.76
125.73
125.36
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27.62
18.84
F3C
O
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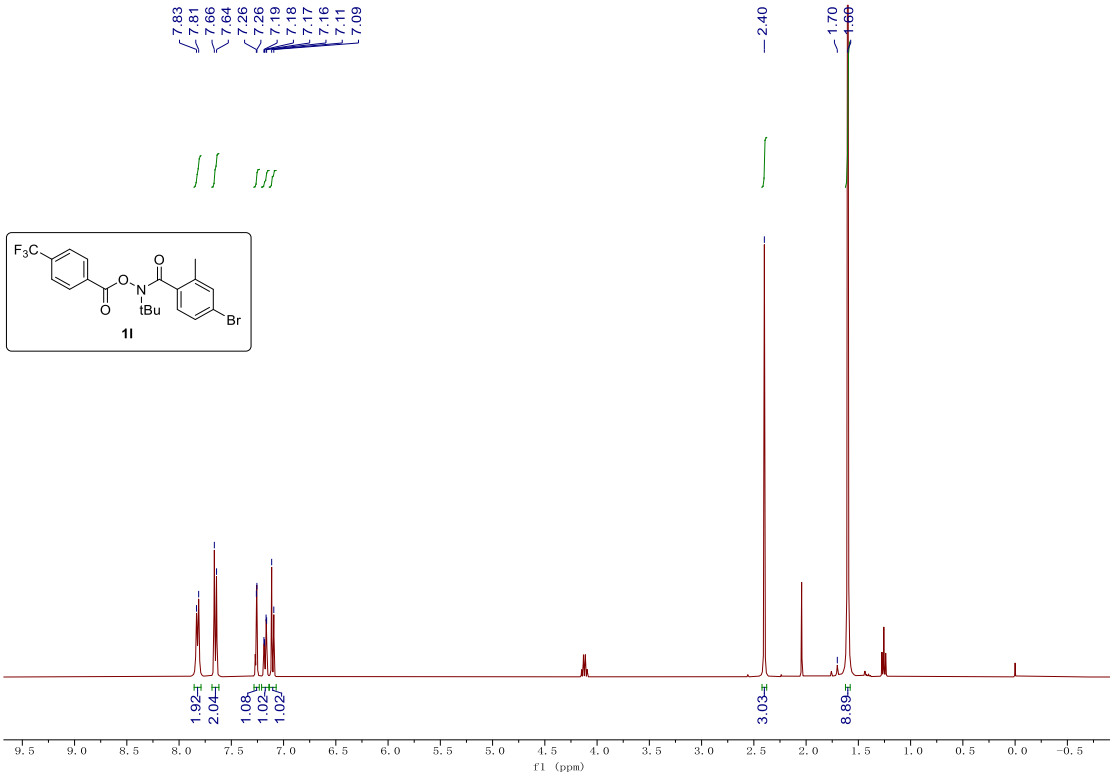
N
tBu
O
Cl
1k
f1 (ppm)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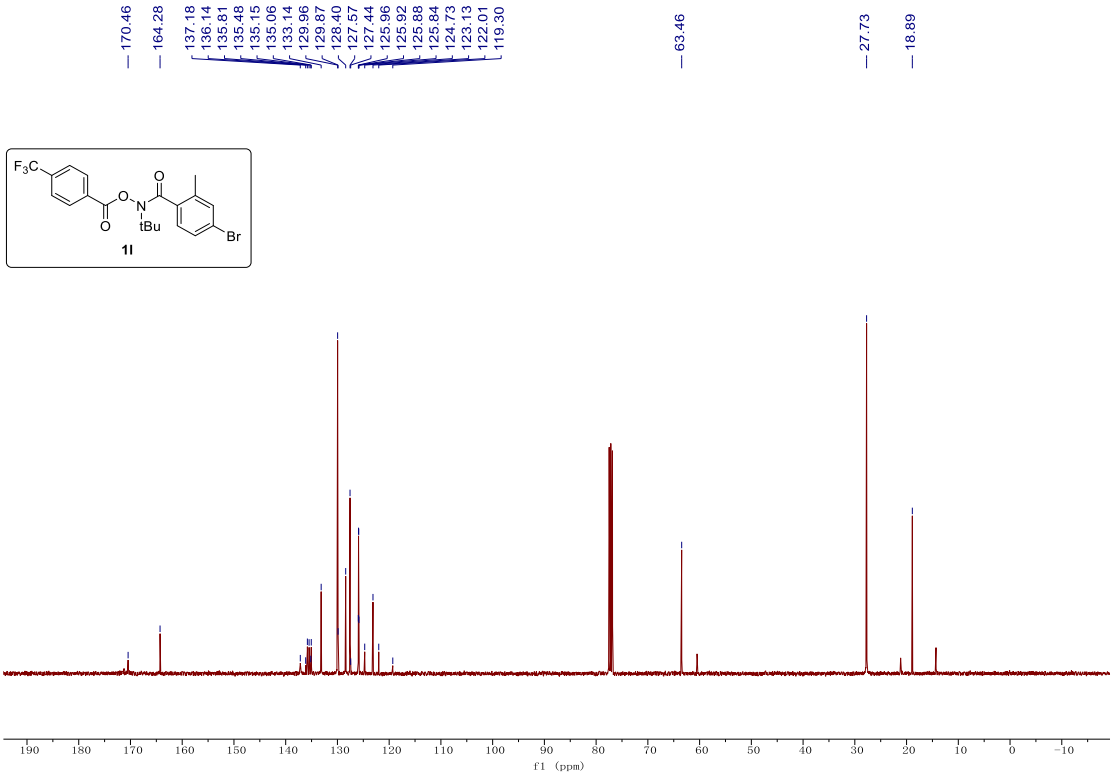
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63.46
27.73
18.89
F3C
O
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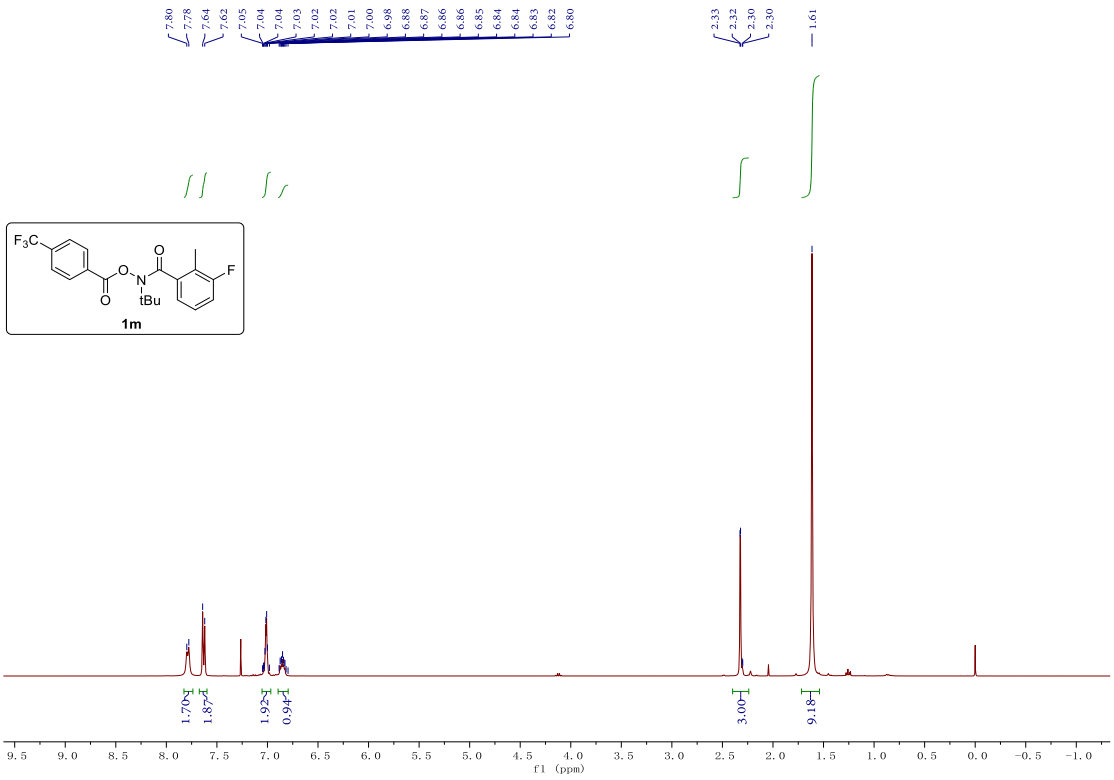
N
tBu
O
Br
1l
f1 (ppm)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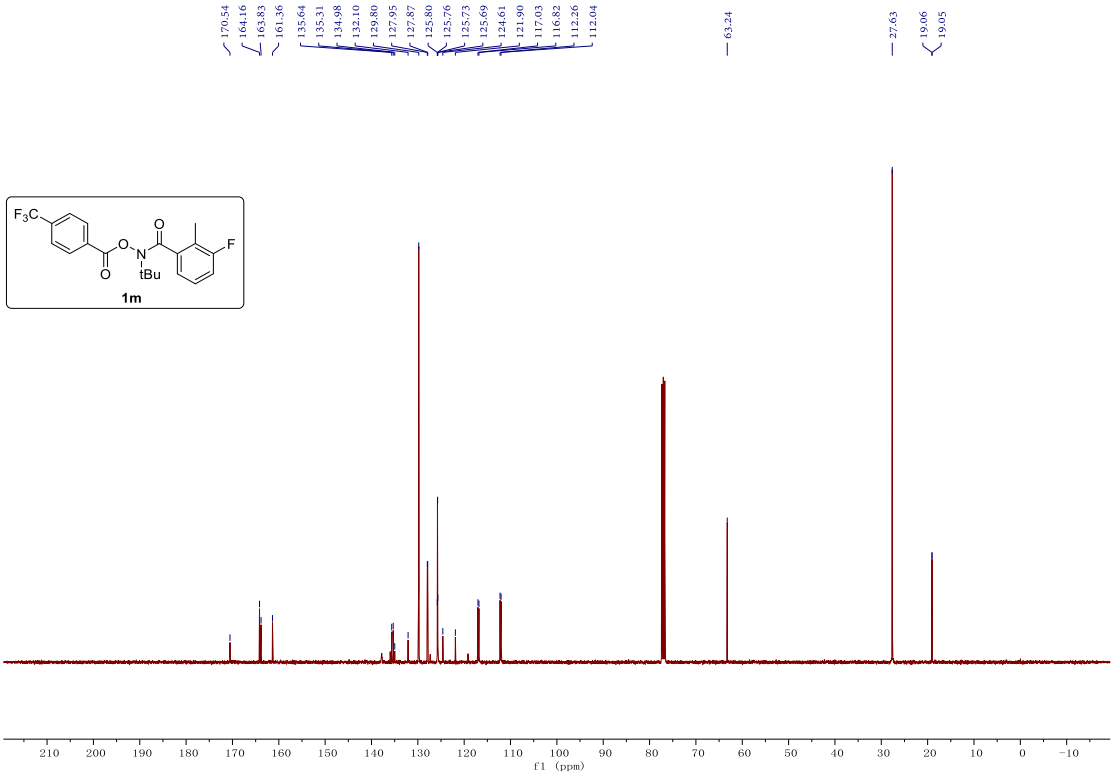
7.78
7.64
7.62
7.05
7.04
7.04
7.03
7.02
7.02
7.01
7.00
6.98
6.88
6.87
6.86
6.86
6.85
6.84
6.84
6.83
6.82
6.80
2.33
2.32
2.30
2.30
1.61
F3C
O
O
N
O
tBu
F
1m
1.70
1.87
1.92
0.94
3.00
9.18
f1 (ppm)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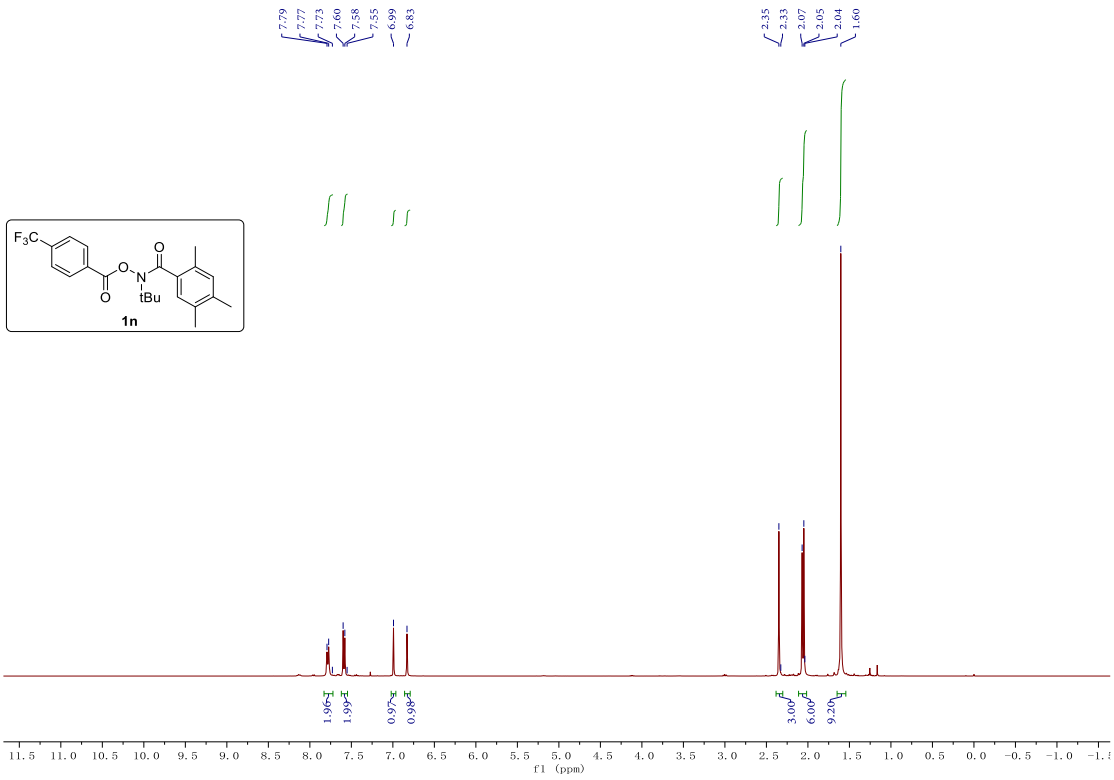
163.83
161.36
135.64
135.31
134.98
132.10
129.80
127.95
127.87
125.80
125.76
125.73
125.69
124.61
121.90
117.03
116.82
112.26
112.04
63.24
27.63
19.06
19.05
F3C
O
O
N
O
tBu
F
1m
f1 (ppm)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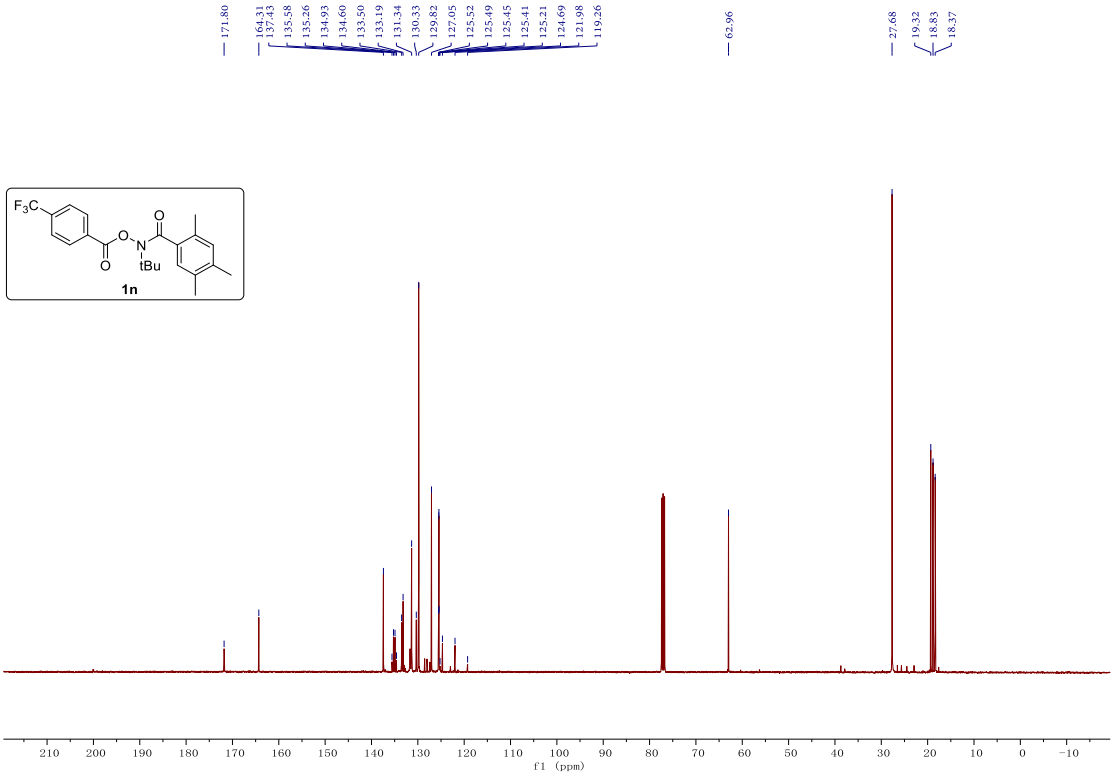
7.55
6.99
6.83
2.35
2.33
2.07
2.05
2.04
1.60
F3C
O
O
N
O
tBu
1n
1.96
1.99
0.97
0.98
3.00
6.00
9.20
f1 (ppm)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137.43
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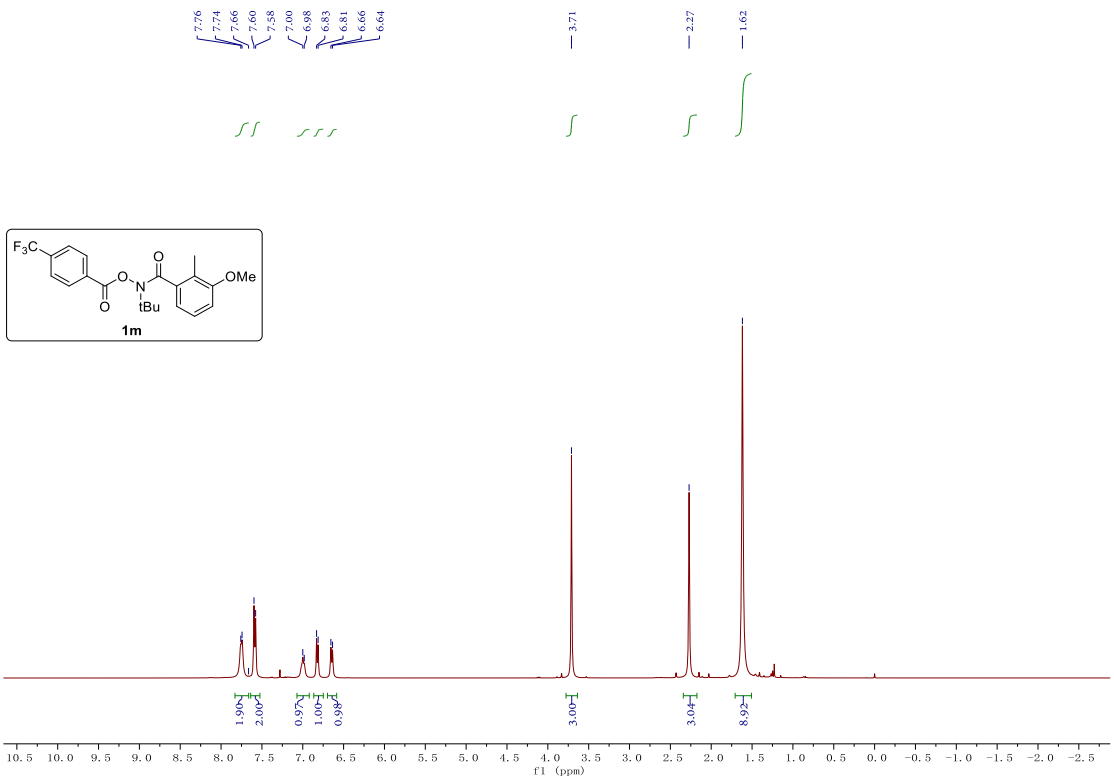
133.50
133.19
131.34
130.33
129.82
127.05
125.52
125.49
125.45
125.41
125.21
124.69
121.98
119.26
62.96
27.68
19.32
18.83
18.37
F3C
O
O
N
O
tBu
1n
f1 (ppm)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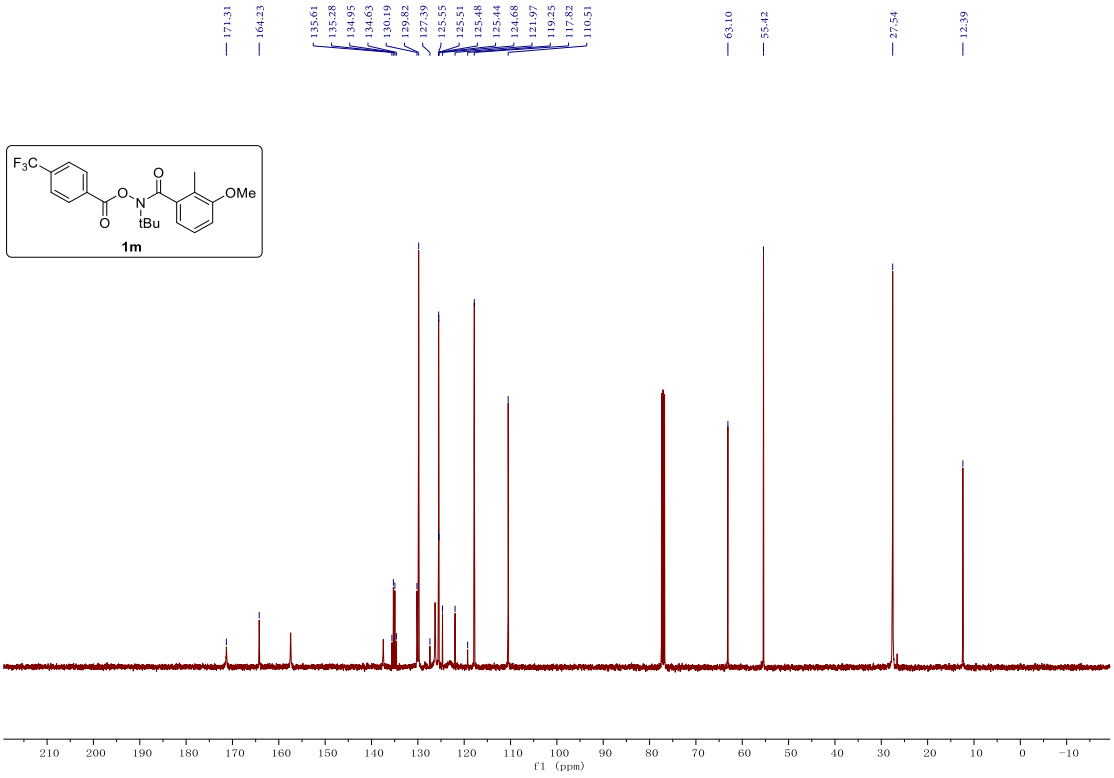
7.74
7.66
7.60
7.58
7.00
6.98
6.83
6.81
6.66
6.64
3.71
2.27
1.62
F3C
O
O
N
tBu
O
OMe
1m
1.90
2.00
0.97
1.00
0.98
3.00
3.04
8.92
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)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164.23
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135.28
134.95
134.63
130.19
129.82
127.39
125.55
125.51
125.48
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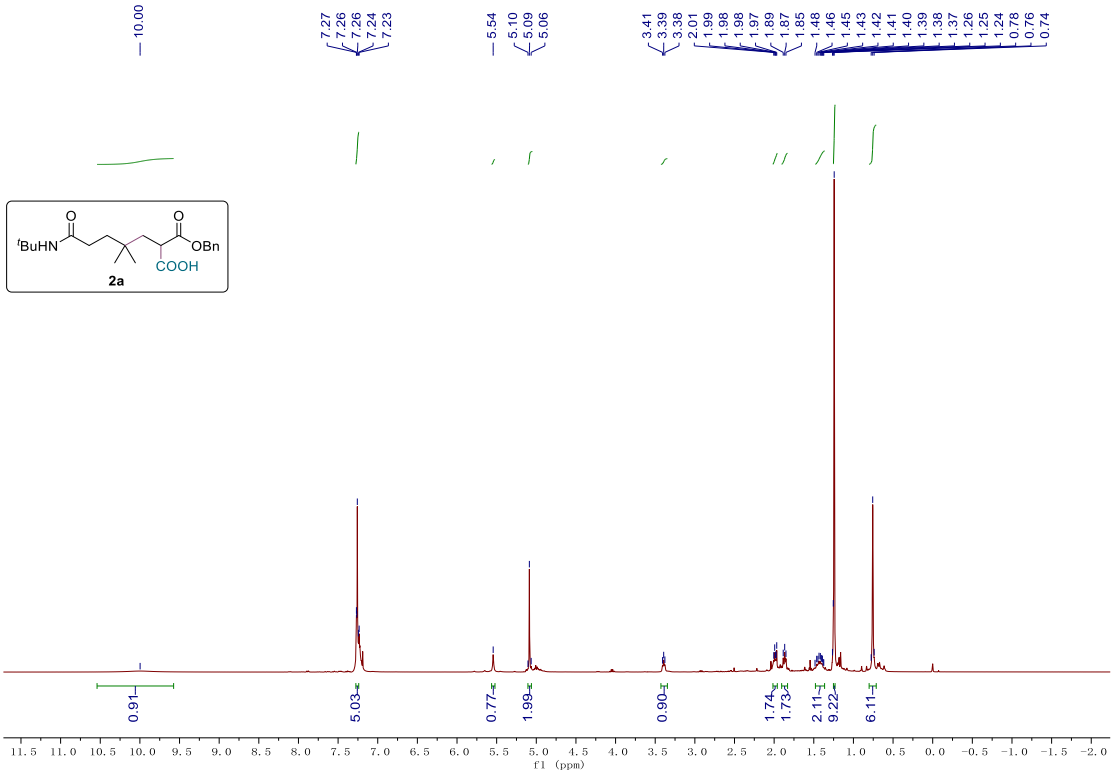
124.68
121.97
119.25
117.82
110.51
63.10
55.42
27.54
12.39
F3C
O
O
N
tBu
O
OMe
1m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.26
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7.23
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5.10
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5.06
3.41
3.39
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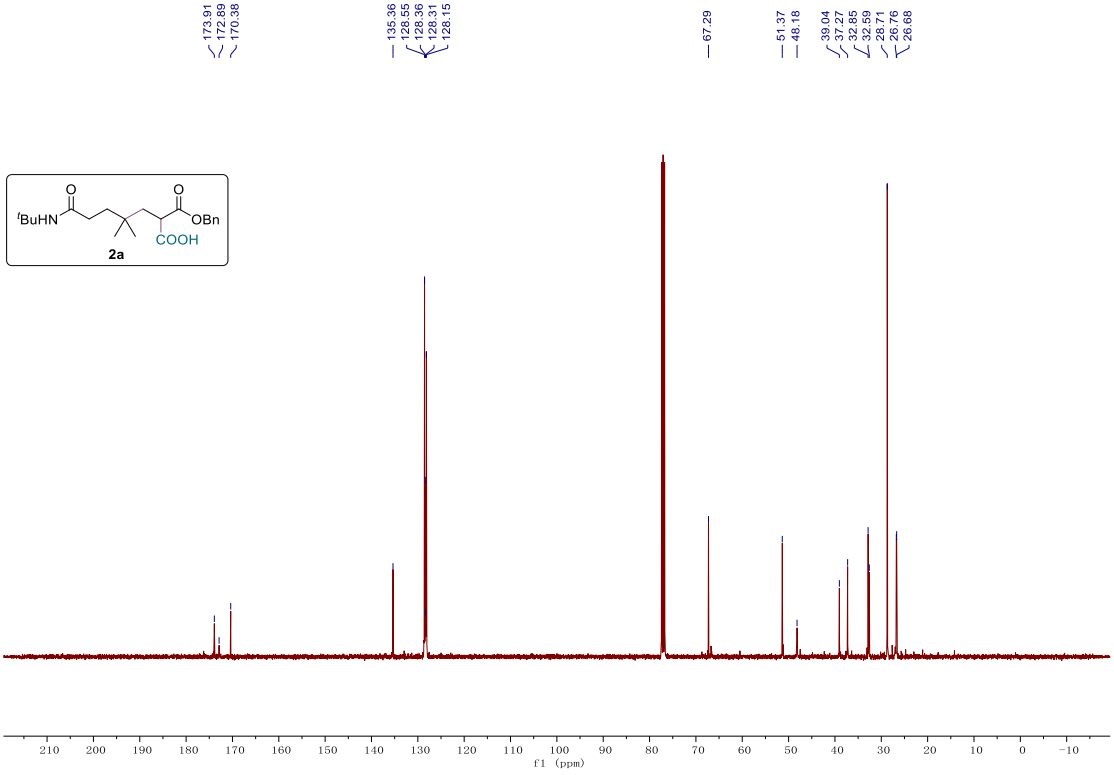
2.01
1.99
1.98
1.98
1.97
1.89
1.87
1.85
1.48
1.46
1.45
1.43
1.42
1.41
1.40
1.39
1.38
1.37
1.26
1.25
1.24
0.78
0.76
0.74
tBuHN
OBn
COOH
2a
0.91
5.03
0.77
1.99
0.90
1.74
1.73
2.11
9.22
6.11
f1 (ppm)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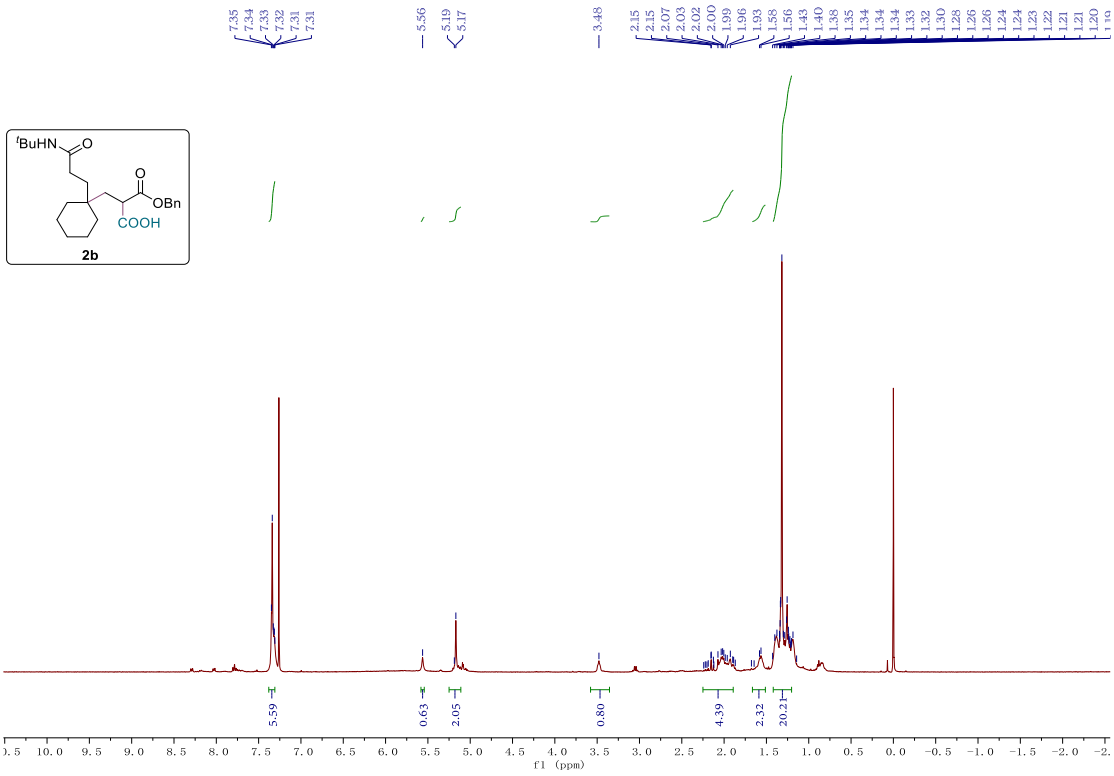
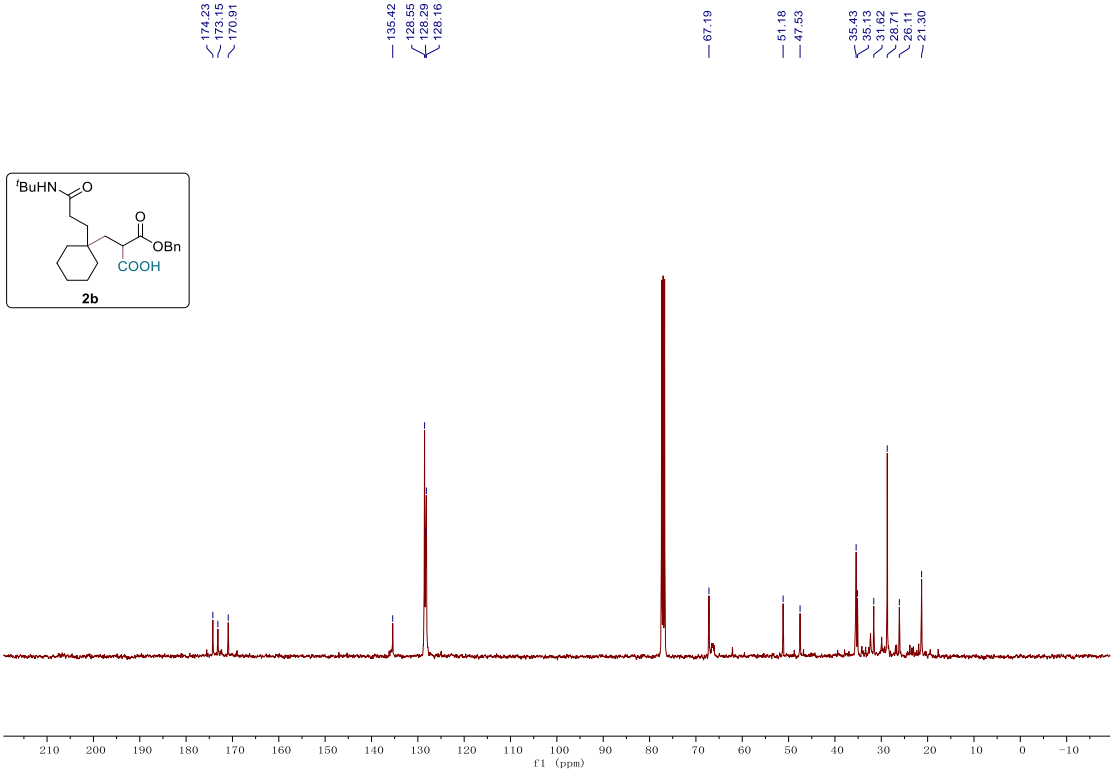
172.89
170.38
135.36
128.55
128.36
128.31
128.15
67.29
51.37
48.18
39.04
37.27
32.85
32.59
28.71
26.76
26.68
tBuHN
OBn
COOH
2a
f1 (ppm)


7.35
7.34
7.33
7.32
7.31
7.31
5.56
5.19
5.17
3.48
2.15
2.15
2.07
2.03
2.02
2.00
1.99
1.96
1.93
1.58
1.56
1.43
1.40
1.38
1.35
1.34
1.34
1.33
1.32
1.30
1.28
1.26
1.26
1.24
1.24
1.23
1.22
1.21
1.21
1.20
tBuHN
O
O
OBn
COOH
2b
5.59
0.63
2.05
0.80
4.39
2.32
20.21
f1 (ppm)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173.15
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135.42
128.55
128.29
128.16
67.19
51.18
47.53
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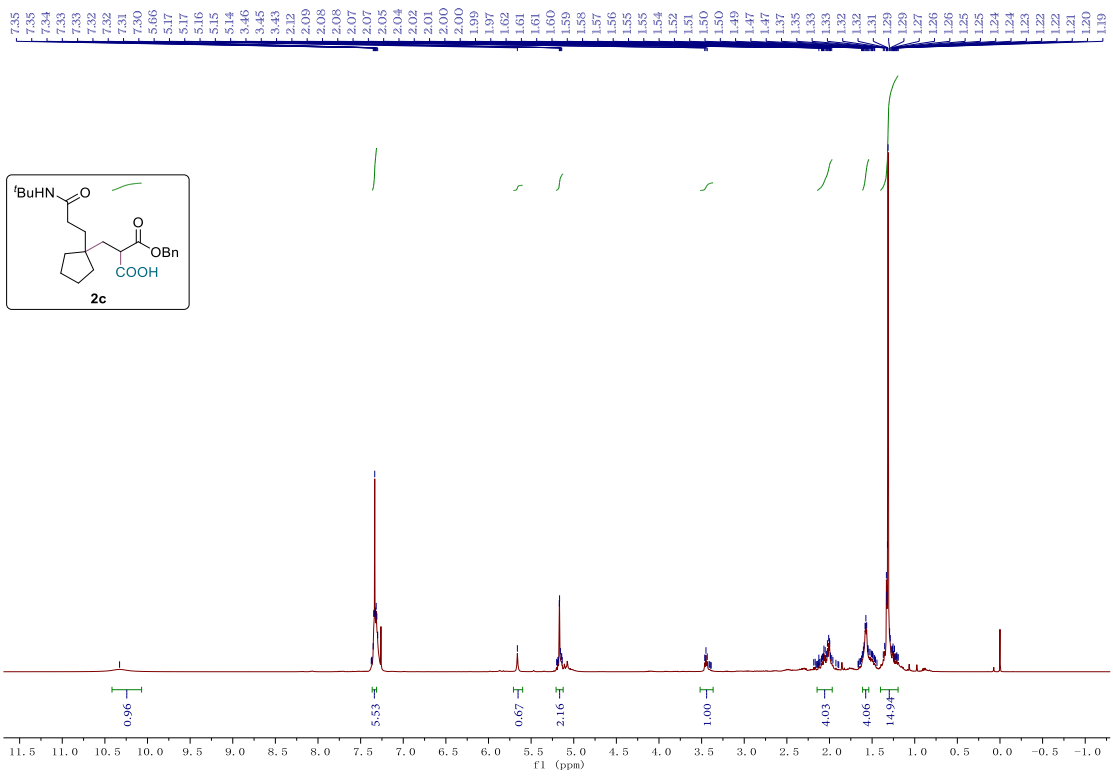
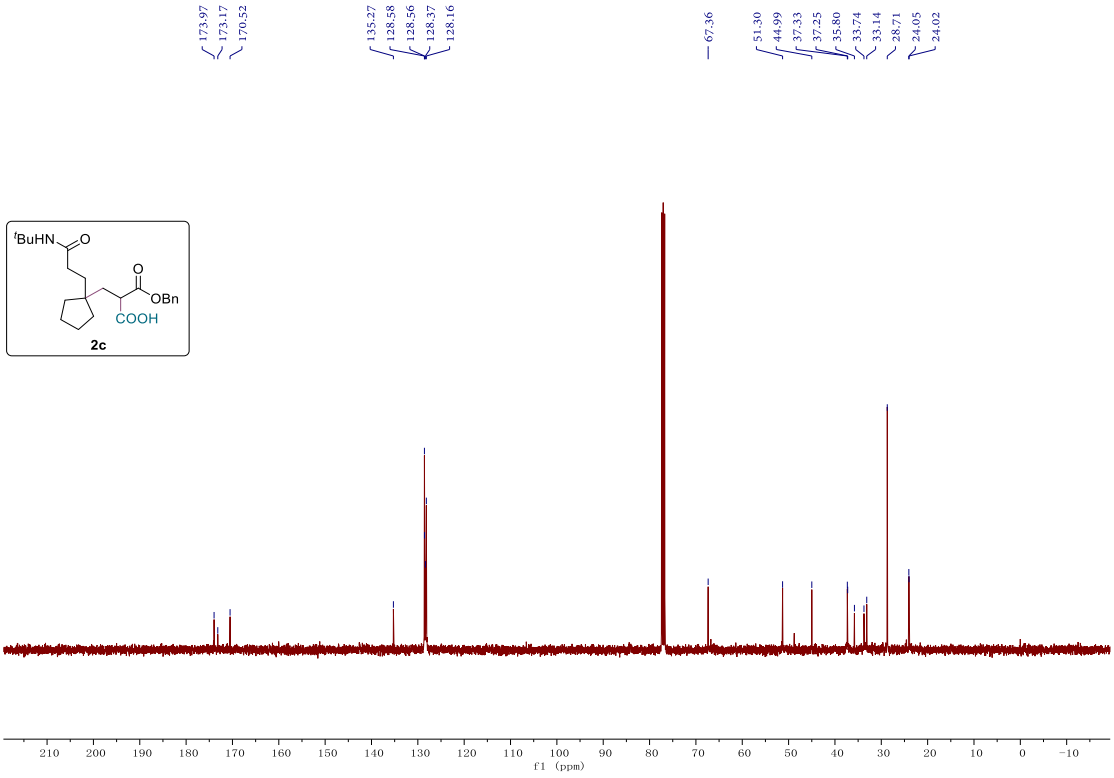
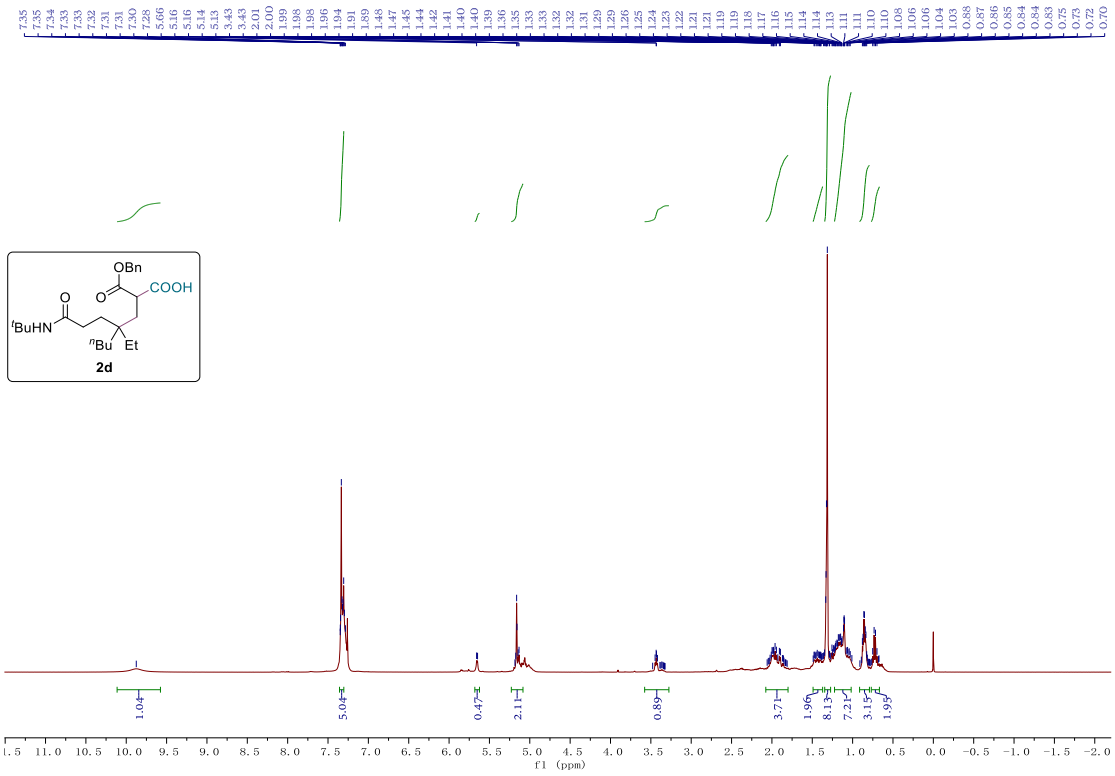
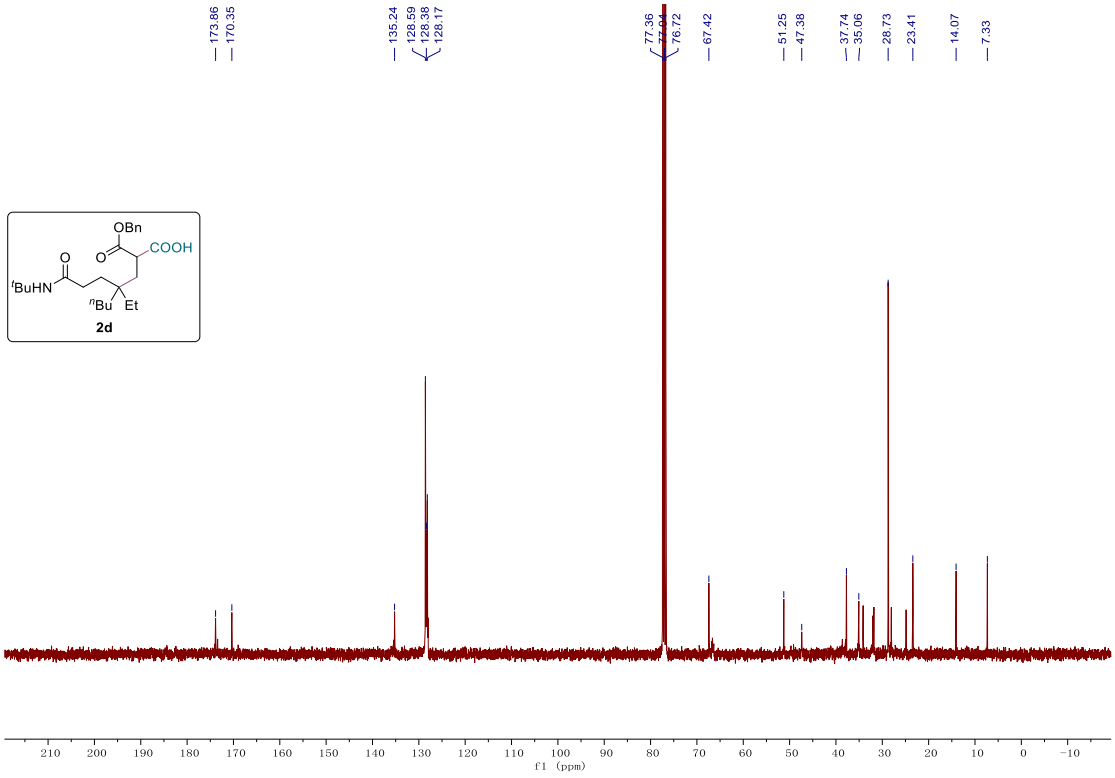
35.13
31.62
28.71
26.11
21.30
tBuHN
O
O
OBn
COOH
2b
f1 (ppm)


7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.30 5.66 5.17 5.17 5.16 5.15 5.14 3.46 3.45 3.43 2.12 2.09 2.08 2.08 2.07 2.07 2.05 2.04 2.02 2.01 2.00 2.00 1.99 1.97 1.62 1.61 1.61 1.60 1.59 1.58 1.57 1.56 1.55 1.55 1.54 1.52 1.51 1.50 1.50 1.49 1.47 1.47 1.37 1.35 1.33 1.33 1.32 1.32 1.31 1.29 1.29 1.27 1.26 1.26 1.25 1.25 1.24 1.24 1.23 1.22 1.22 1.21 1.20 1.19
tBuHN
O
O
OBn
COOH
2c
0.96
5.53
0.67
2.16
1.00
4.03
4.06
14.94
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


173.97 173.17 170.52 135.27 128.58 128.56 128.37 128.16 67.36 51.30 44.99 37.33 37.25 35.80 33.74 33.14 28.71 24.05 24.02
tBuHN
O
O
OBn
COOH
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OBn
O
O
COOH
tBuHN
nBu
Et
2d
1.04
5.04
0.47
2.11
0.89
3.71
1.96
8.13
7.21
3.15
1.95
f1 (ppm)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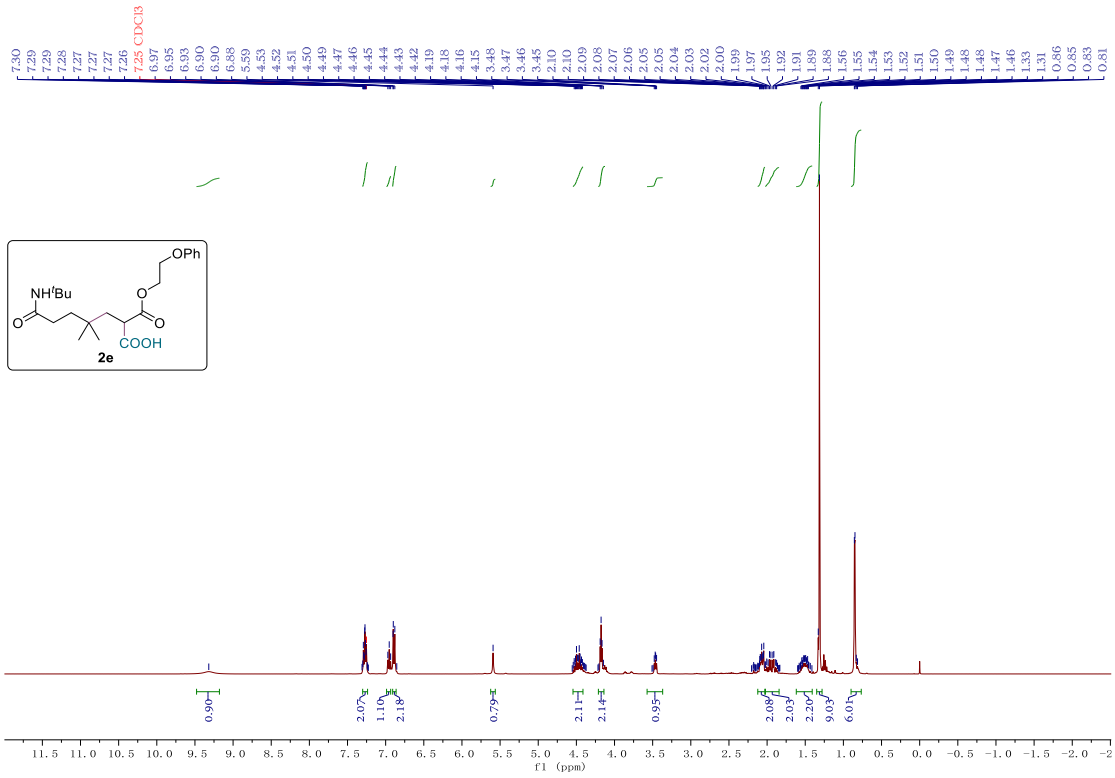
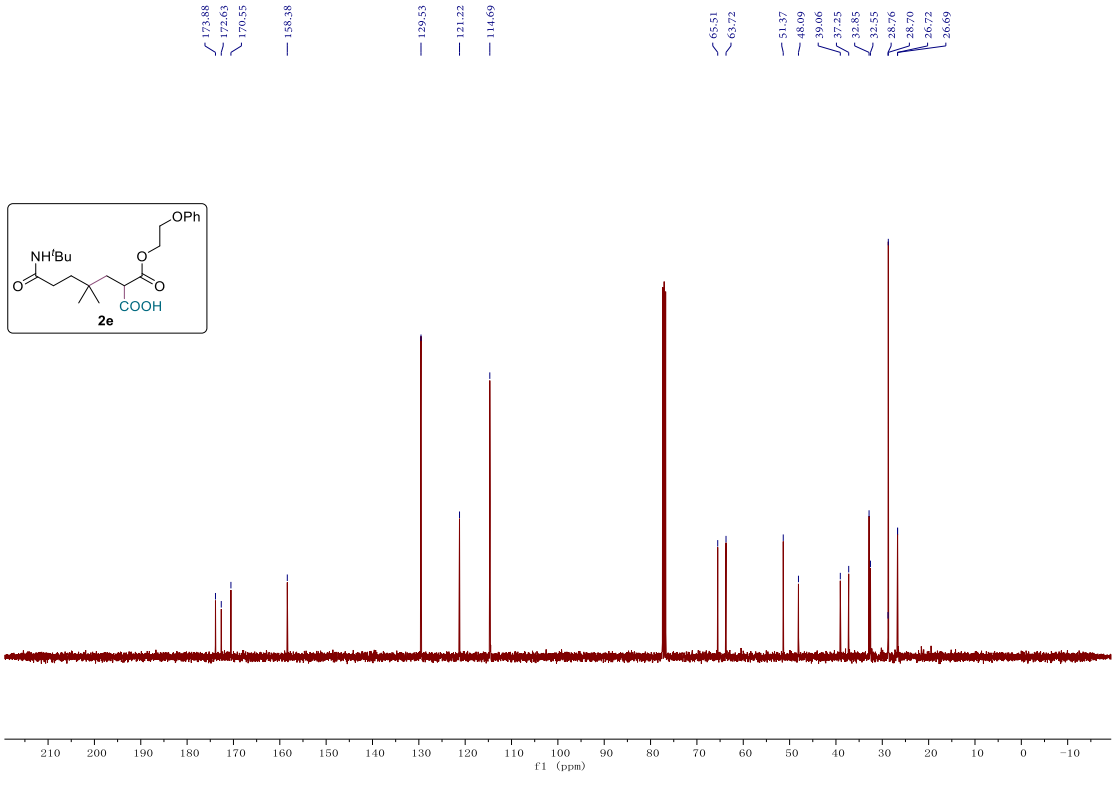
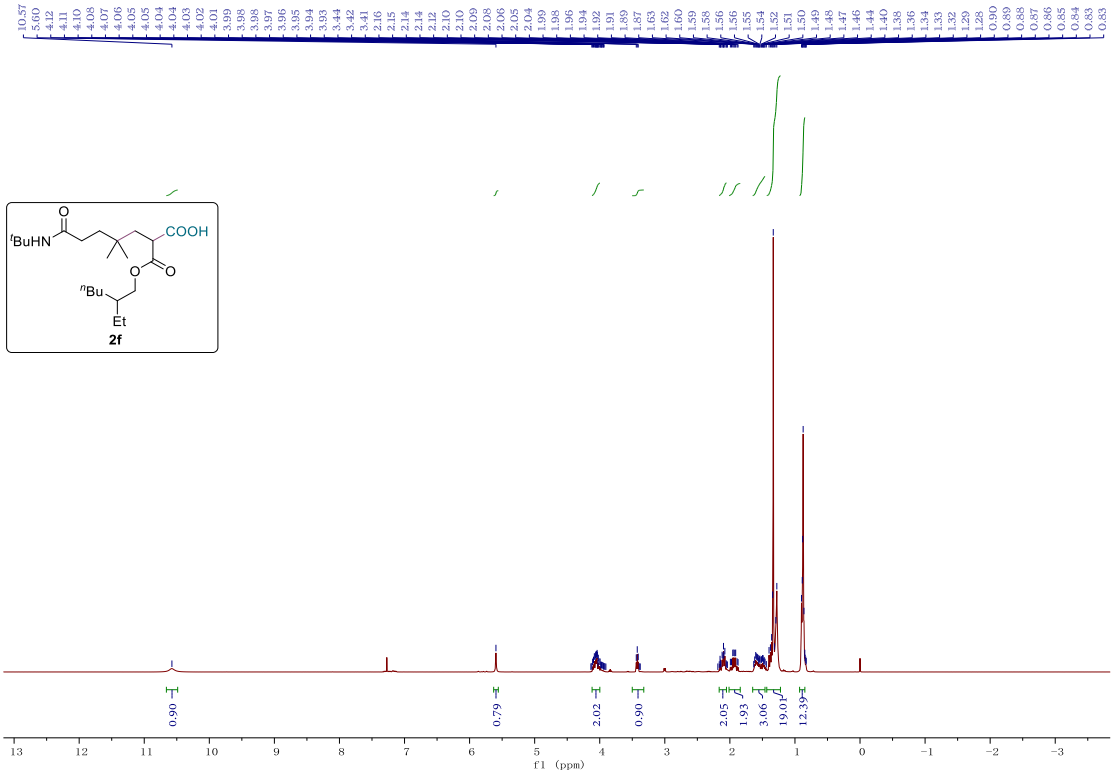
170.35
135.24
128.59
128.38
128.17
77.36
77.04
76.72
67.42
51.25
47.38
37.74
35.06
28.73
23.41
14.07
7.33
OBn
O
O
COOH
tBuHN
nBu
Et
2d
f1 (ppm)


7.30 7.29 7.29 7.28 7.27 7.27 7.27 7.26 7.25 CDCl3 6.97 6.95 6.93 6.90 6.90 6.88 5.59 4.53 4.52 4.51 4.50 4.49 4.47 4.46 4.45 4.44 4.43 4.42 4.19 4.18 4.16 4.15 3.48 3.47 3.46 3.45 2.10 2.09 2.08 2.07 2.06 2.05 2.05 2.04 2.03 2.02 2.00 1.99 1.97 1.95 1.92 1.91 1.89 1.88 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.48 1.48 1.47 1.46 1.33 1.31 0.86 0.85 0.83 0.81
OPh
NH^{t}Bu
O
O
O
COOH
2e
0.90 2.07 1.10 2.18 0.79 2.11 2.14 0.95 2.08 2.03 2.20 9.03 6.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2
f1 (ppm)


173.88 172.63 170.55 158.38 129.53 121.22 114.69 65.51 63.72 51.37 48.09 39.06 37.25 32.85 32.55 28.76 28.70 26.72 26.69
OPh
NH^{t}Bu
O
O
O
COOH
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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4.08
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4.06
4.05
4.05
4.04
4.04
4.03
4.02
4.01
3.99
3.98
3.98
3.97
3.96
3.95
3.94
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3.42
3.41
2.16
2.15
2.14
2.12
2.10
2.10
2.09
2.08
2.06
2.05
2.04
1.99
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1.96
1.94
1.92
1.91
1.89
1.87
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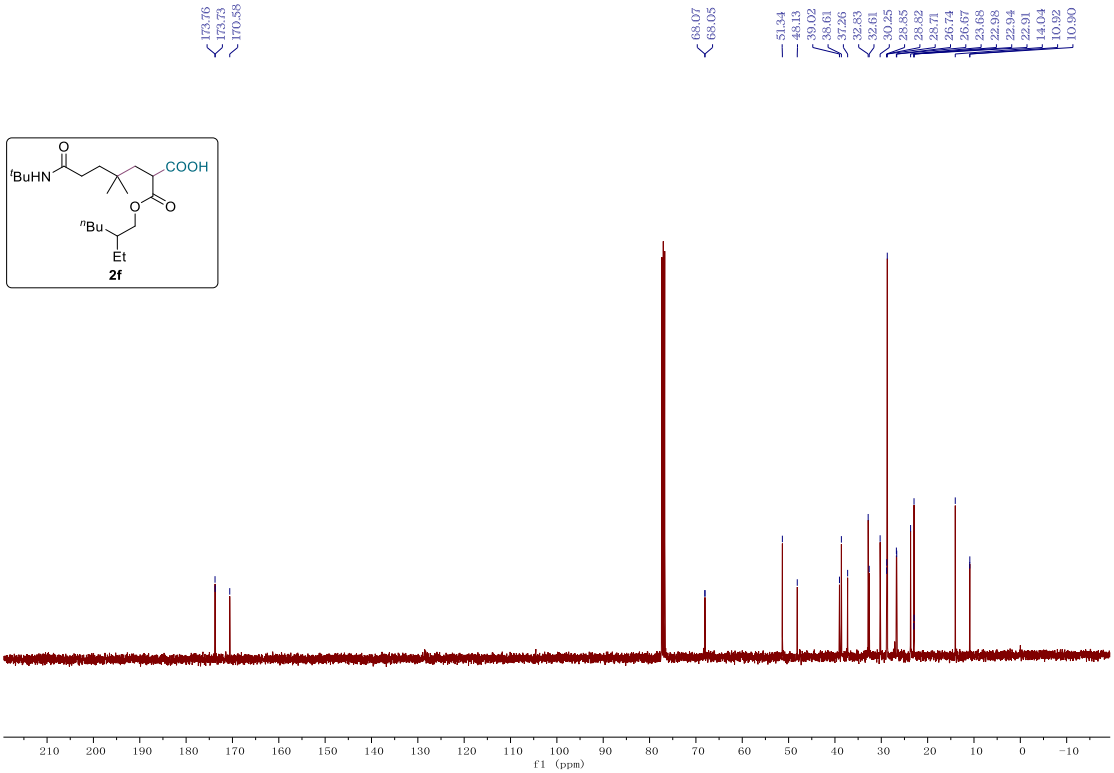
1.49
1.48
1.47
1.46
1.44
1.40
1.38
1.36
1.34
1.33
1.32
1.29
1.28
0.90
0.89
0.88
0.87
0.86
0.85
0.84
0.83
0.83
tBuHN
COOH
nBu
Et
2f
0.90
0.79
2.02
0.90
2.05
1.93
3.06
19.01
12.39
f1 (ppm)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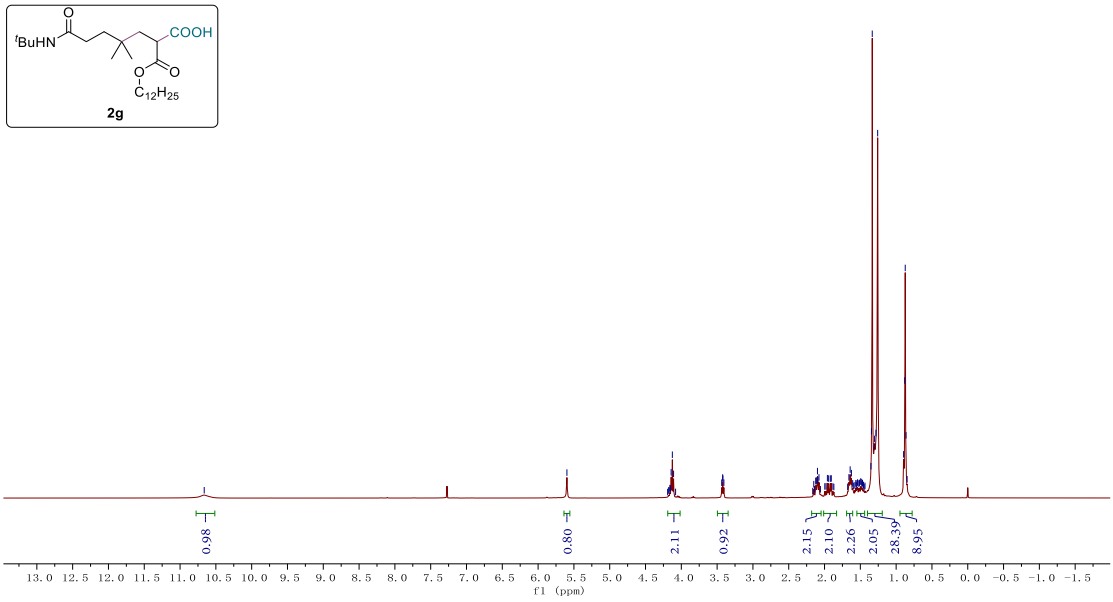
170.58
68.07
68.05
51.34
48.13
39.02
38.61
37.26
32.83
32.61
30.25
28.85
28.82
28.71
25.74
25.67
23.68
22.98
22.94
22.91
14.04
10.92
10.90
tBuHN
COOH
nBu
Et
2f
f1 (ppm)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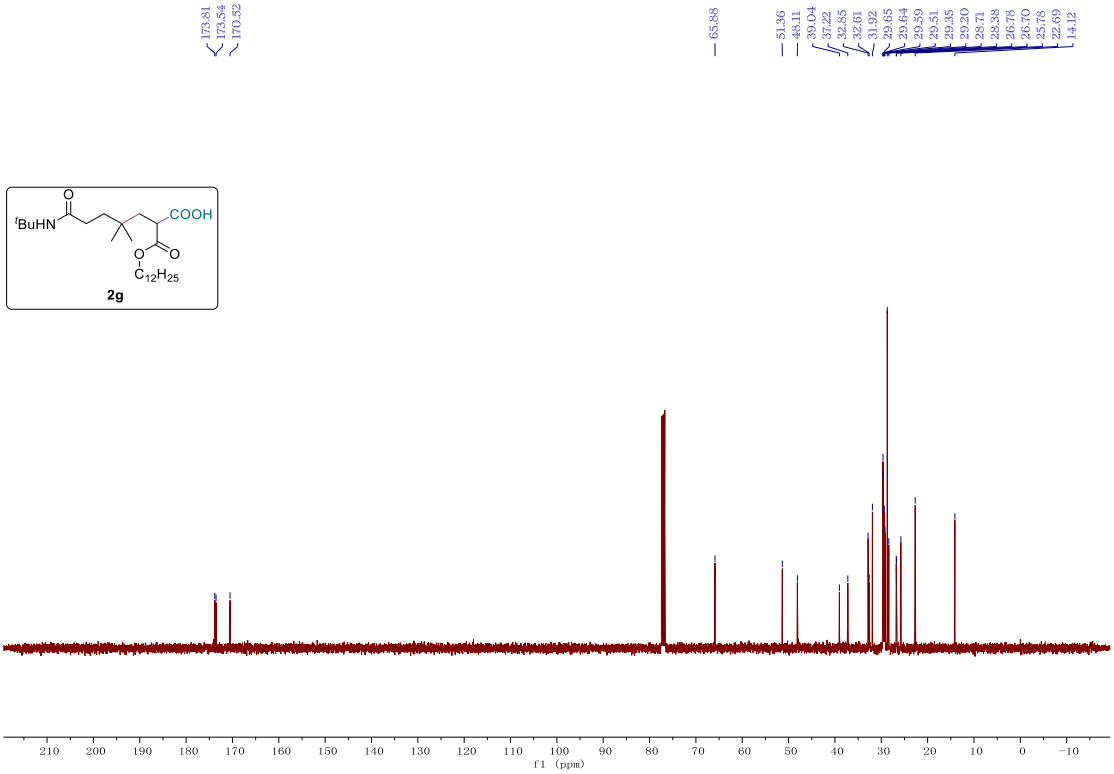
5.60
4.19 4.18 4.17 4.16 4.15 4.14 4.13 4.11 4.08
3.44 3.42 3.42 3.41 2.12 2.12 2.11 2.10 2.09 2.08 1.96 1.94 1.92 1.91 1.66 1.64 1.62 1.61 1.56 1.55 1.54 1.52 1.51 1.50 1.49 1.47 1.47 1.35 1.34 1.33 1.31 1.31 1.30 1.28 1.26 0.90 0.88 0.87 0.86 0.85
COOH
tBuHN
O
O
O
C12H25
2g
0.98
0.80
2.11
0.92
2.15
2.10
2.26
2.05
28.39
8.95
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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170.52
65.88
51.36
48.11
39.04
37.22
32.85
32.61
31.92
29.65
29.64
29.59
29.51
29.35
29.20
28.71
28.38
26.78
26.70
25.78
22.69
14.12
COOH
tBuHN
O
O
O
C12H25
2g
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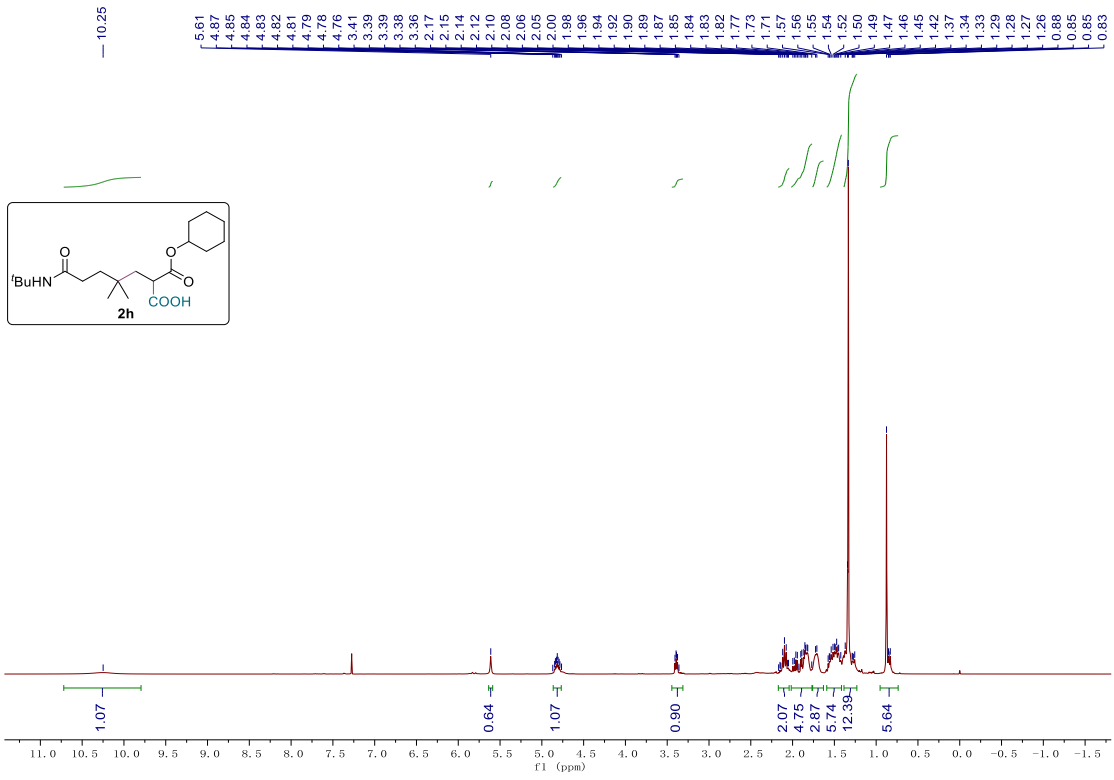
f1 (ppm)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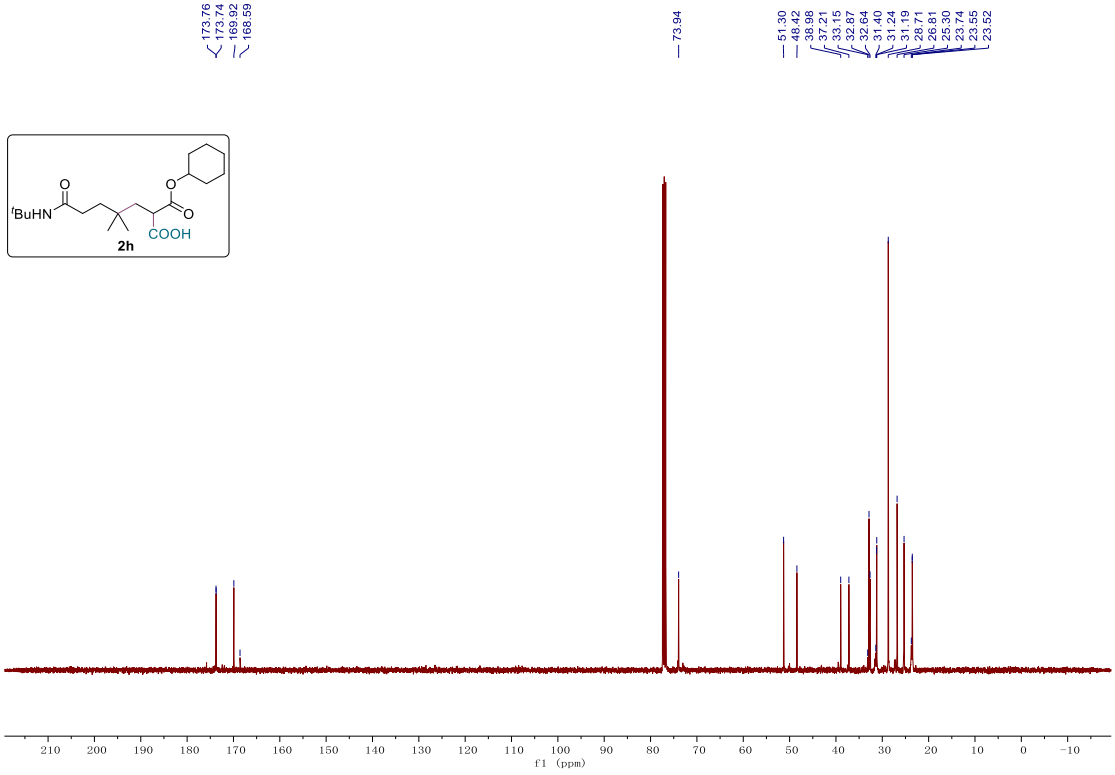
4.85
4.84
4.83
4.82
4.81
4.79
4.78
4.76
3.41
3.39
3.39
3.38
3.36
2.17
2.15
2.14
2.12
2.10
2.08
2.06
2.05
2.00
1.98
1.96
1.94
1.92
1.90
1.89
1.87
1.85
1.84
1.83
1.82
1.77
1.73
1.71
1.57
1.56
1.55
1.54
1.52
1.50
1.49
1.47
1.46
1.45
1.42
1.37
1.34
1.33
1.29
1.28
1.27
1.26
0.88
0.85
0.85
0.83
tBuHN
O
O
O
COOH
2h
1.07
0.64
1.07
0.90
2.07
4.75
2.87
5.74
12.39
5.64
f1 (ppm)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173.74
169.92
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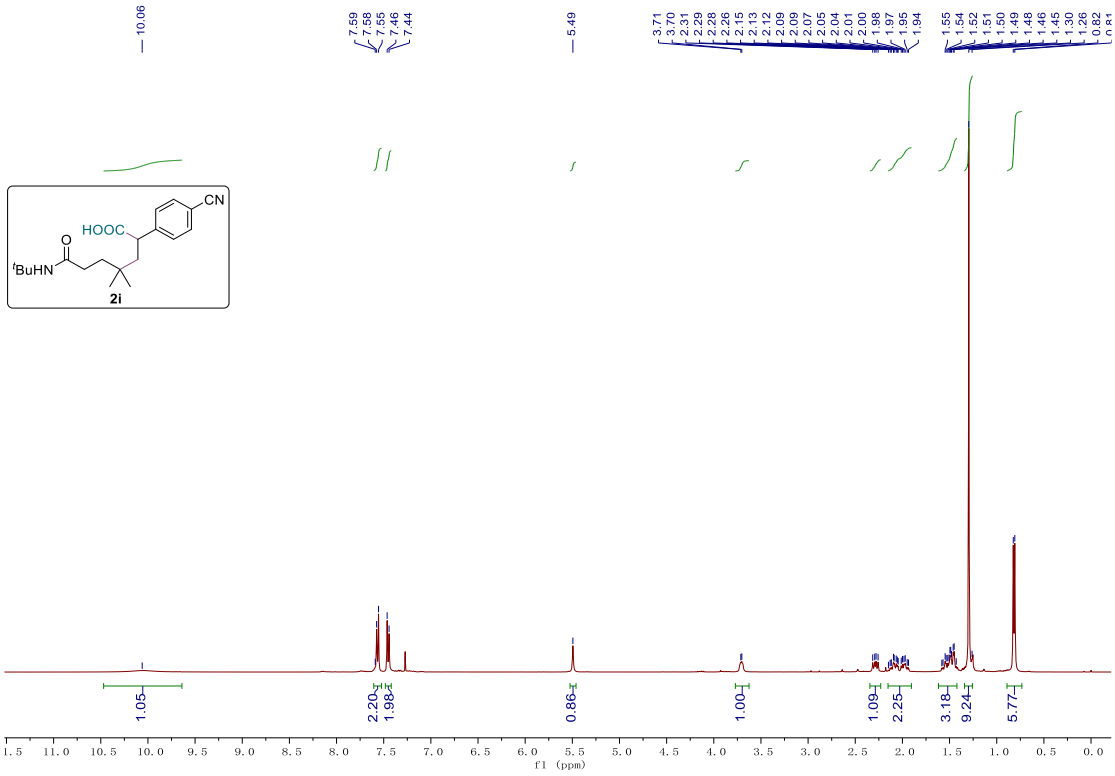
73.94
51.30
48.42
38.98
37.21
33.15
32.87
32.64
31.40
31.24
31.19
28.71
26.81
25.30
23.74
23.55
23.52
tBuHN
O
O
O
COOH
2h
f1 (ppm)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7.58
7.55
7.46
7.44
5.49
3.71
3.70
2.31
2.29
2.28
2.26
2.15
2.13
2.12
2.09
2.09
2.07
2.05
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2.00
1.98
1.97
1.95
1.94
1.55
1.54
1.52
1.51
1.50
1.49
1.48
1.46
1.45
1.30
1.26
0.82
0.81
CN
HOOC
O
tBuHN
2i
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1.98
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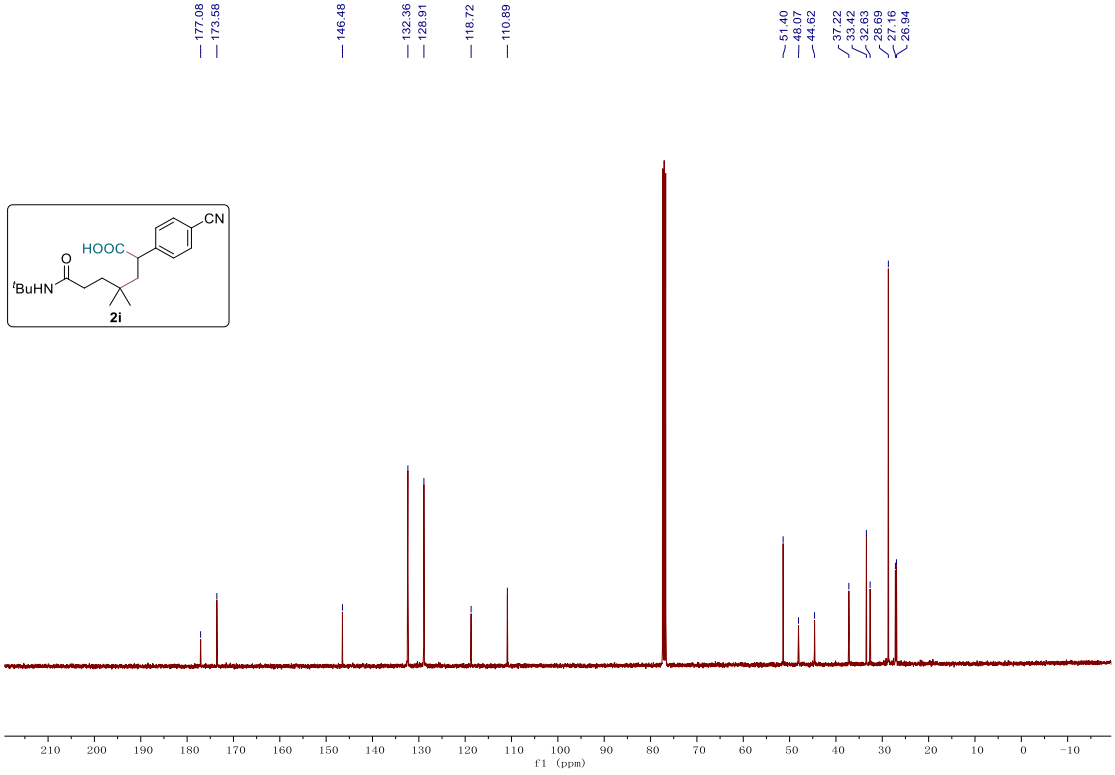
1.00
1.09
2.25
3.18
9.24
5.77
f1 (ppm)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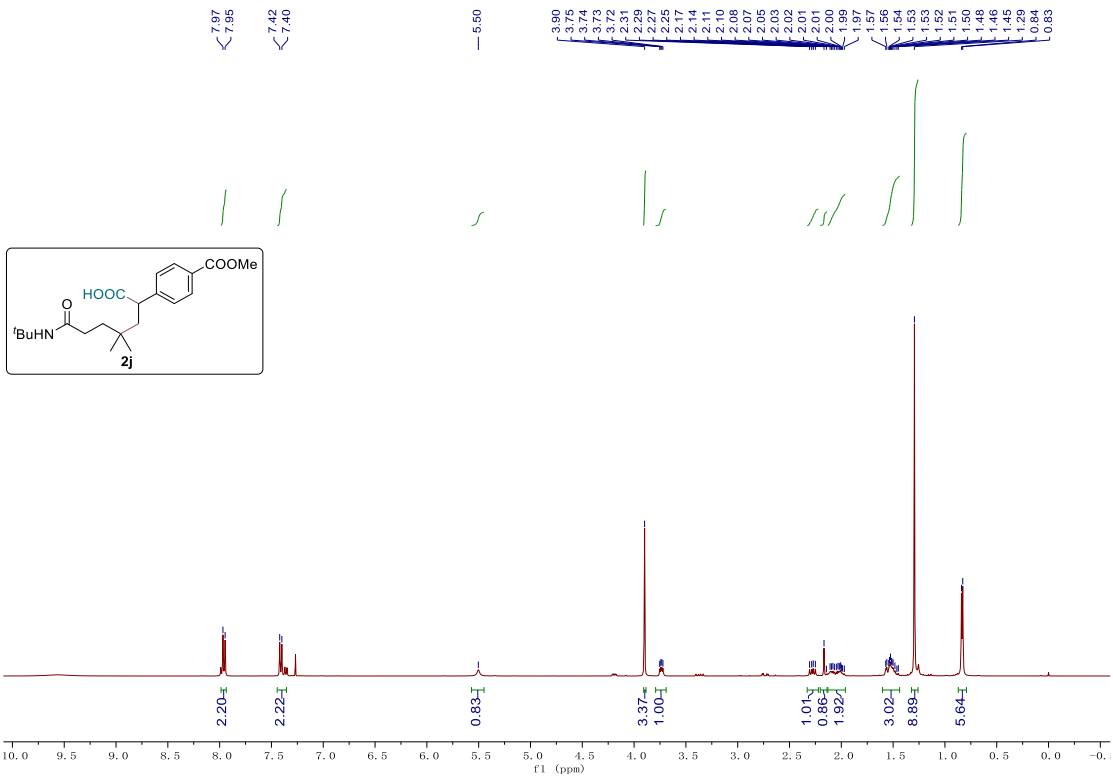
27.16
26.94
CN
HOOC
O
tBuHN
2i
f1 (ppm)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3.74
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2.31
2.29
2.27
2.25
2.17
2.14
2.11
2.10
2.08
2.07
2.05
2.03
2.02
2.01
2.01
2.00
1.99
1.97
1.57
1.56
1.54
1.53
1.53
1.52
1.51
1.50
1.48
1.46
1.45
1.29
0.84
0.83
COOMe
HOOC
O
tBuHN
2j
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1.00
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3.02
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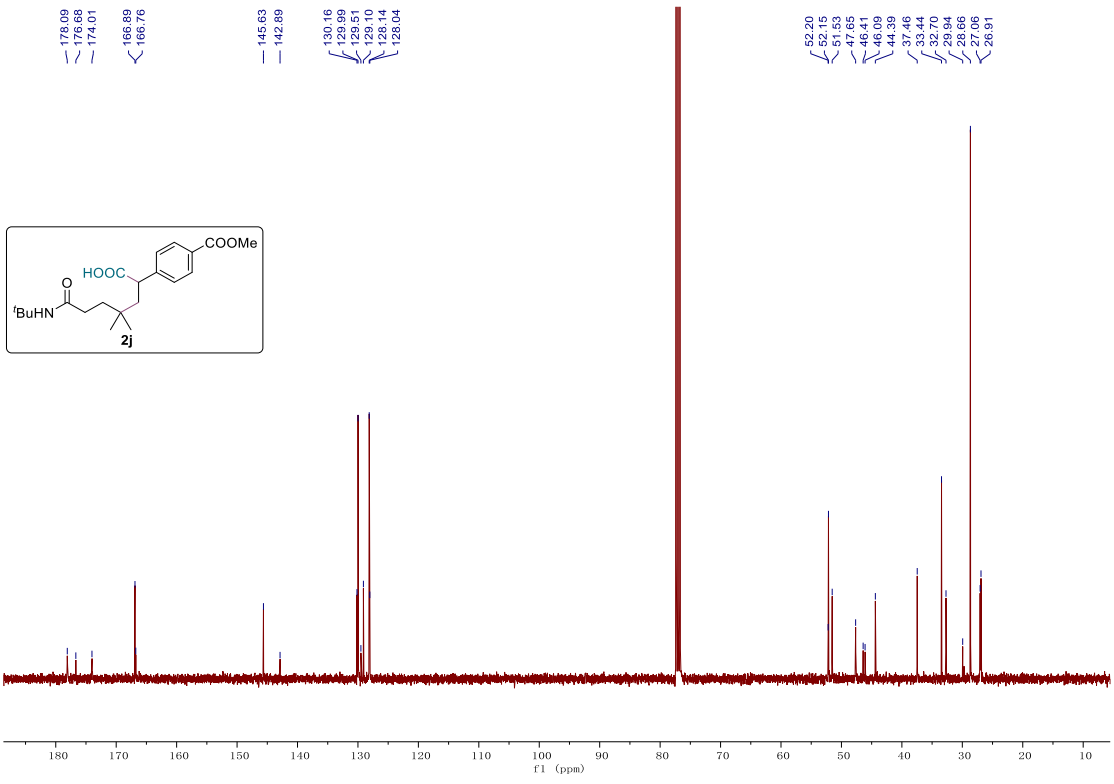
5.64
f1 (ppm)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52.20
52.15
51.53
47.65
46.41
46.09
44.39
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33.44
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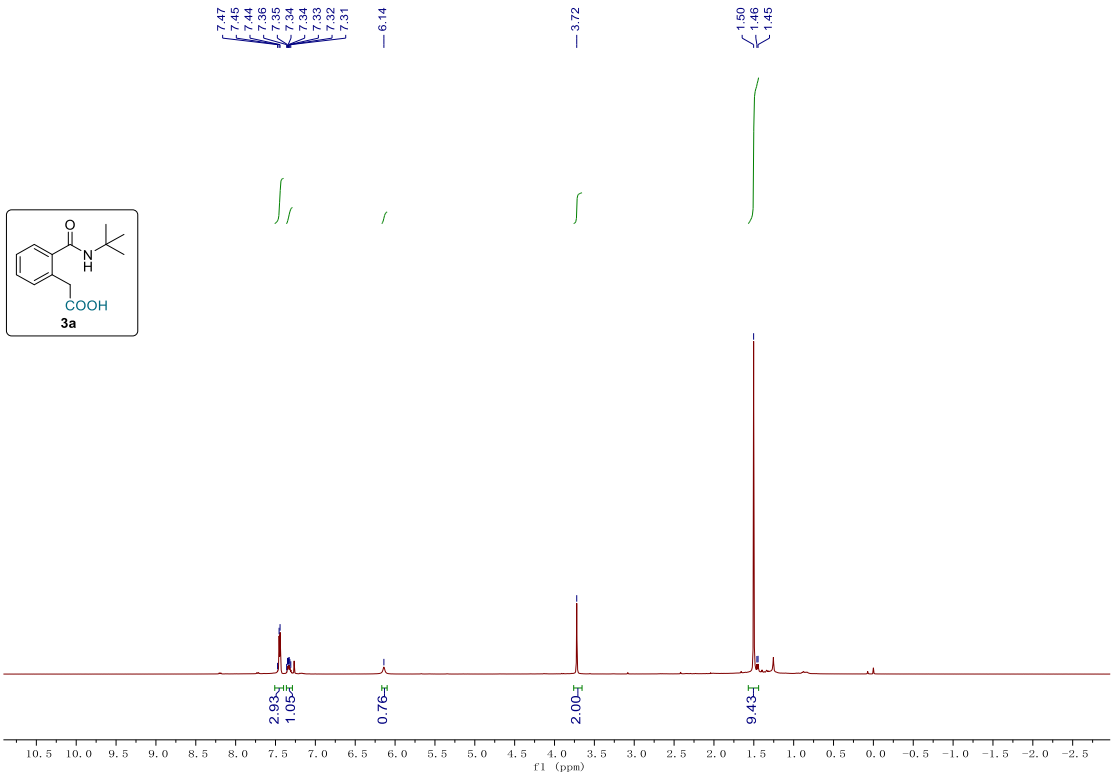
28.66
27.06
26.91
COOMe
HOOC
O
tBuHN
2j
f1 (ppm)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7.34
7.33
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7.31
6.14
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O
N
H
COOH
3a
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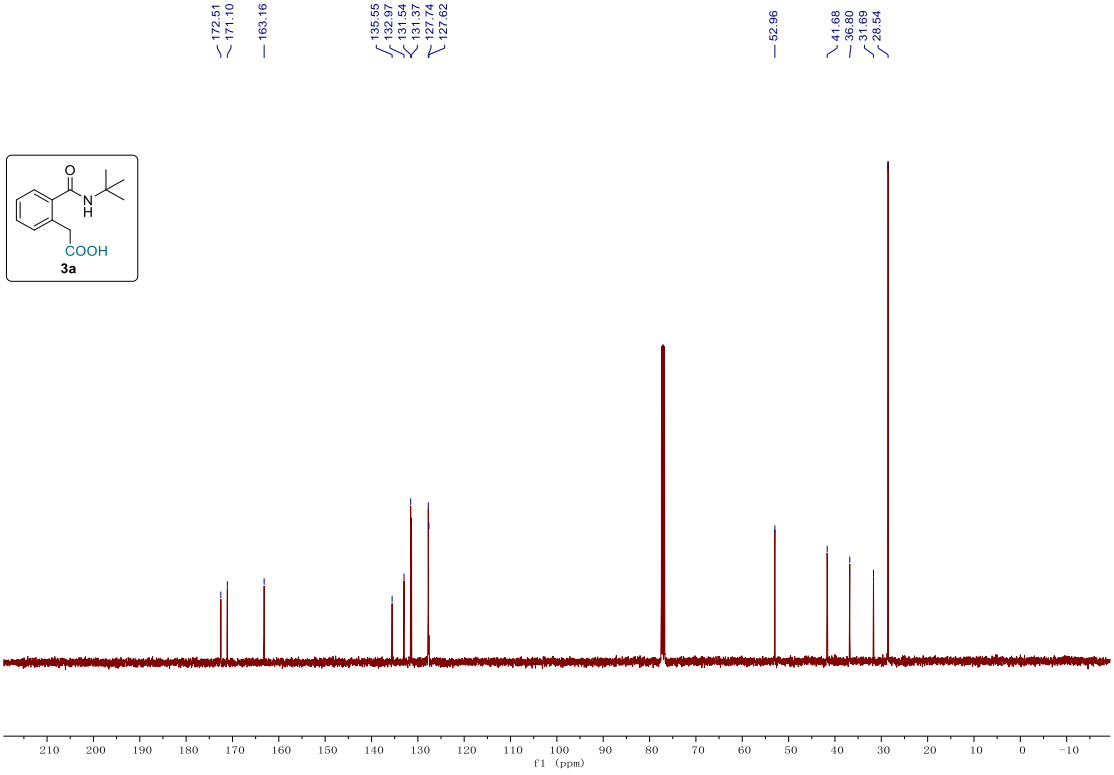
9.43
f1 (ppm)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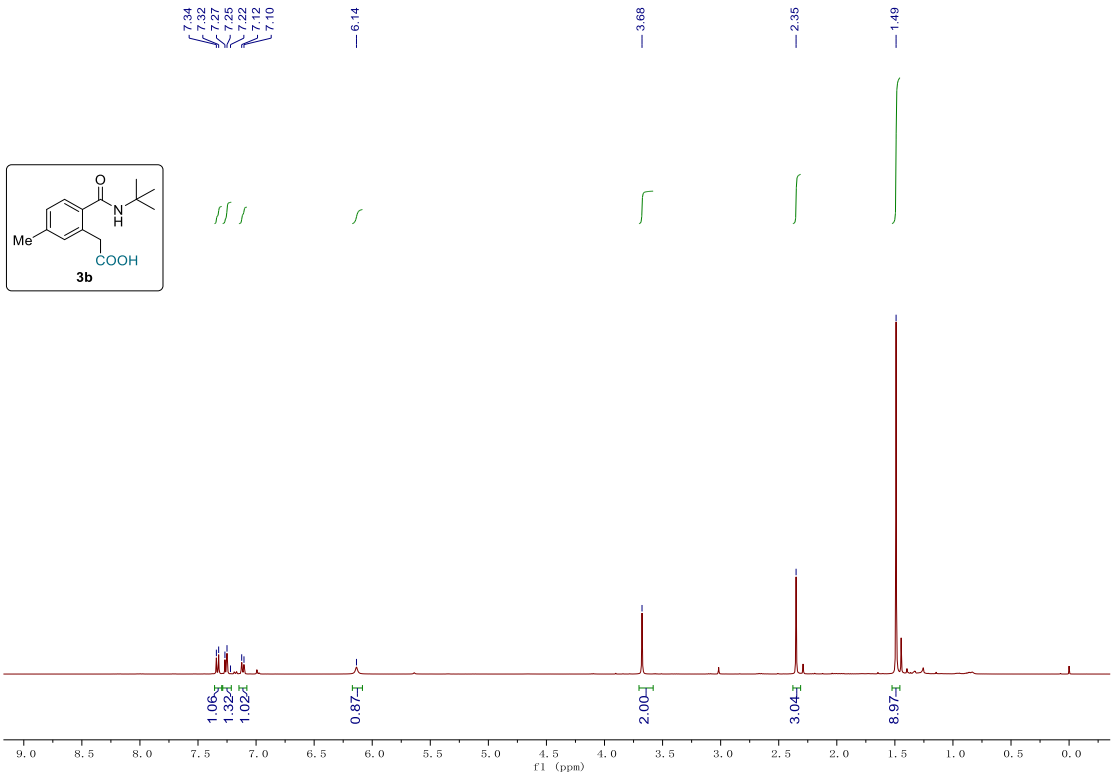
28.54
O
N
H
COOH
3a
f1 (ppm)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7.32
7.27
7.25
7.22
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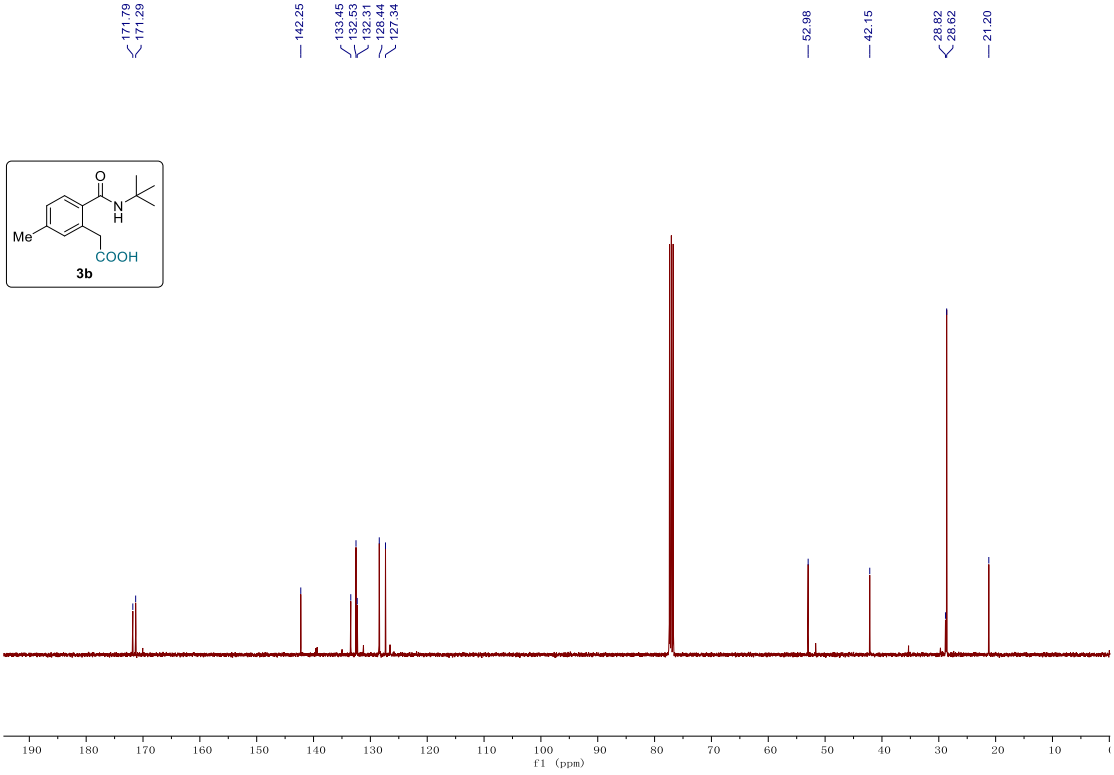
7.10
6.14
3.68
2.35
1.49
O
N
H
Me
COOH
3b
1.06
1.32
1.02
0.87
2.00
3.04
8.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.31
128.44
127.34
52.98
42.15
28.82
28.62
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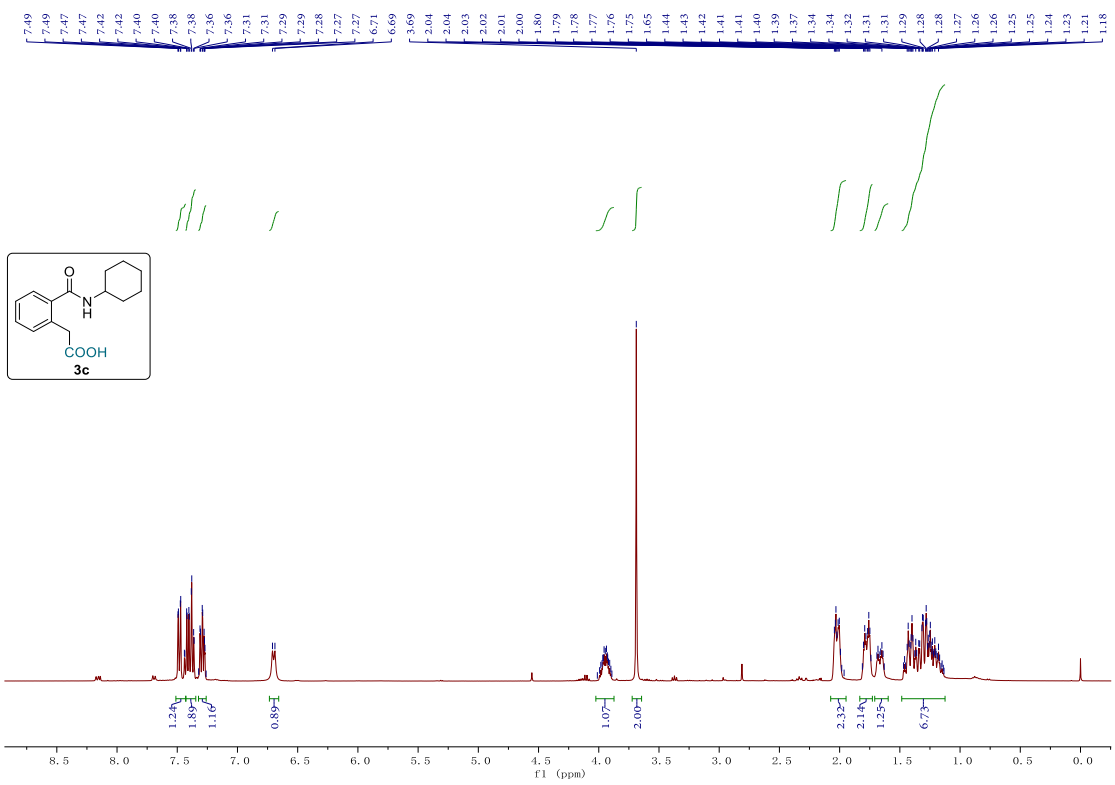
O
N
H
Me
COOH
3b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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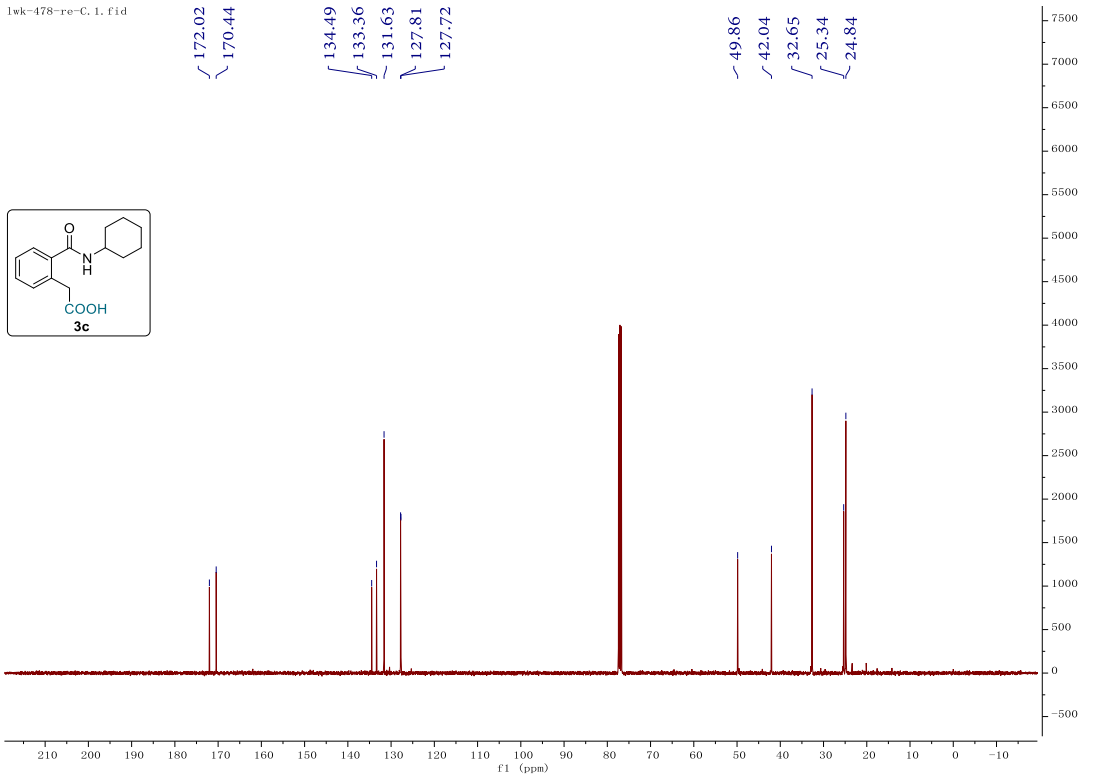
3.69 2.04 2.04 2.03 2.02 2.01 2.00 1.80 1.79 1.78 1.77 1.76 1.75 1.65 1.44 1.43 1.42 1.41 1.41 1.40 1.39 1.37 1.34 1.34 1.32 1.31 1.31 1.29 1.28 1.28 1.27 1.26 1.26 1.25 1.25 1.24 1.23 1.21 1.18
O
N
H
COOH
3c
1.24 1.89 1.16 0.89 1.07 2.00 2.32 2.14 1.25 6.73
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


lwk-478-re-C.1.fid
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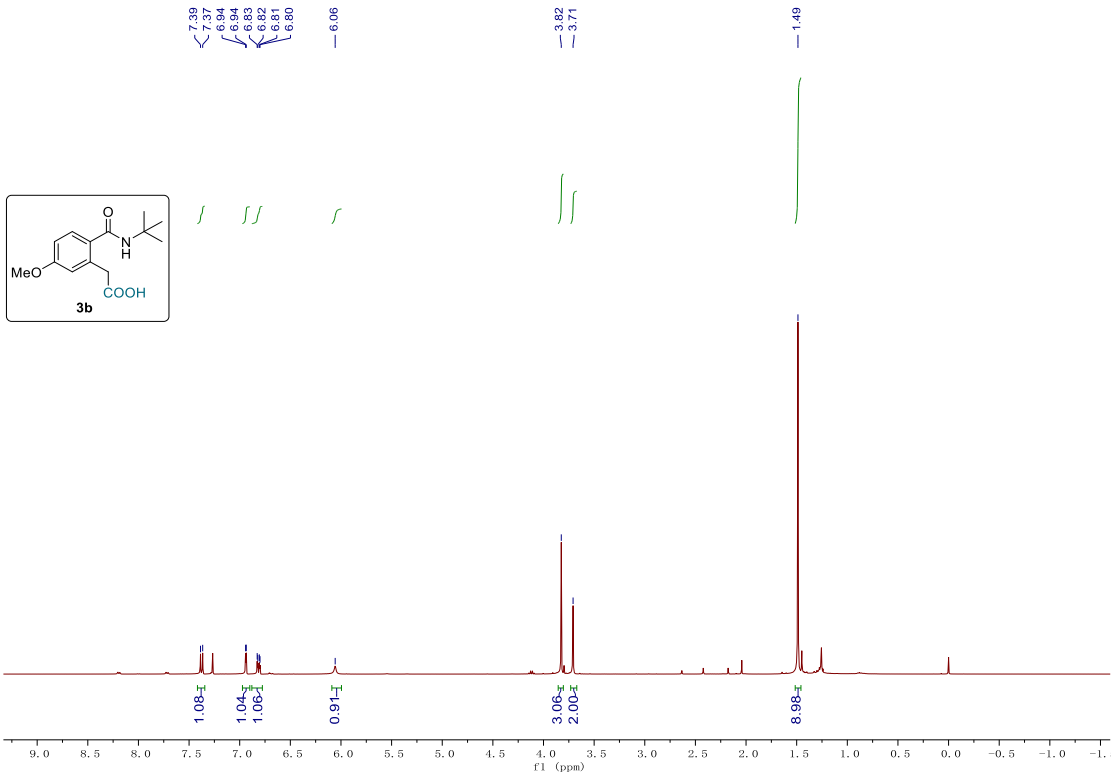
O
N
H
COOH
3c
7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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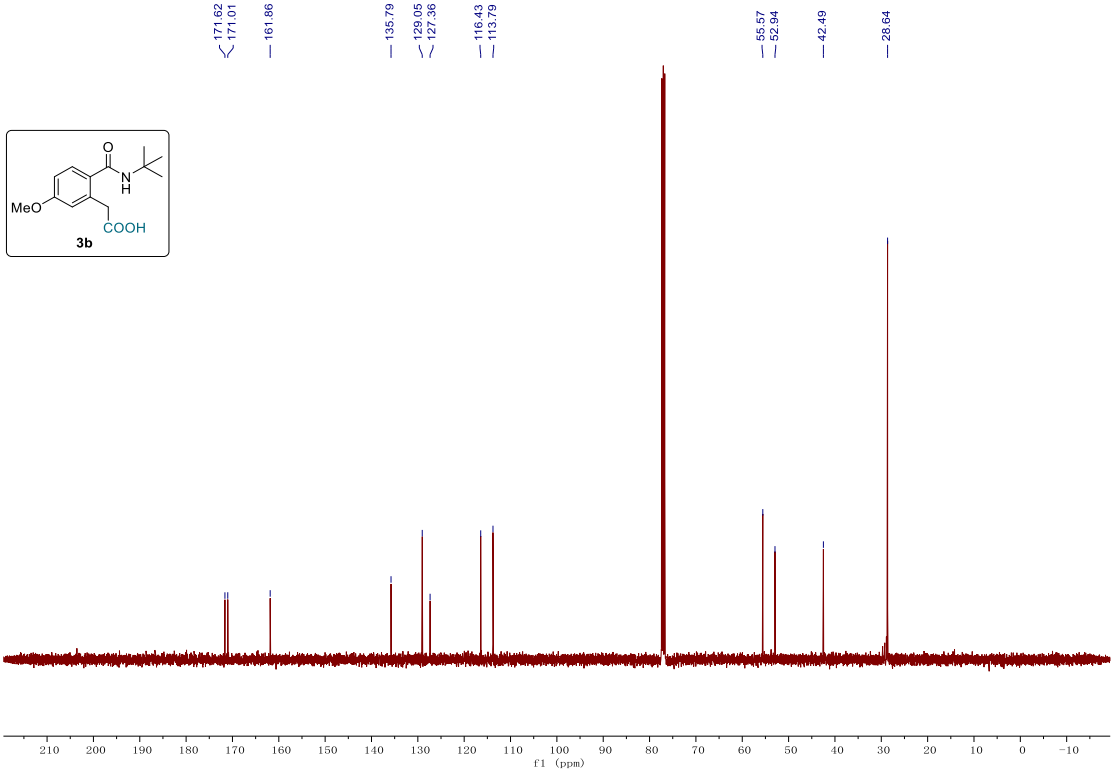
7.37
6.94
6.94
6.83
6.82
6.81
6.80
6.06
3.82
3.71
1.49
MeO
COOH
3b
1.08
1.04
1.06
0.91
3.06
2.00
8.98
f1 (ppm)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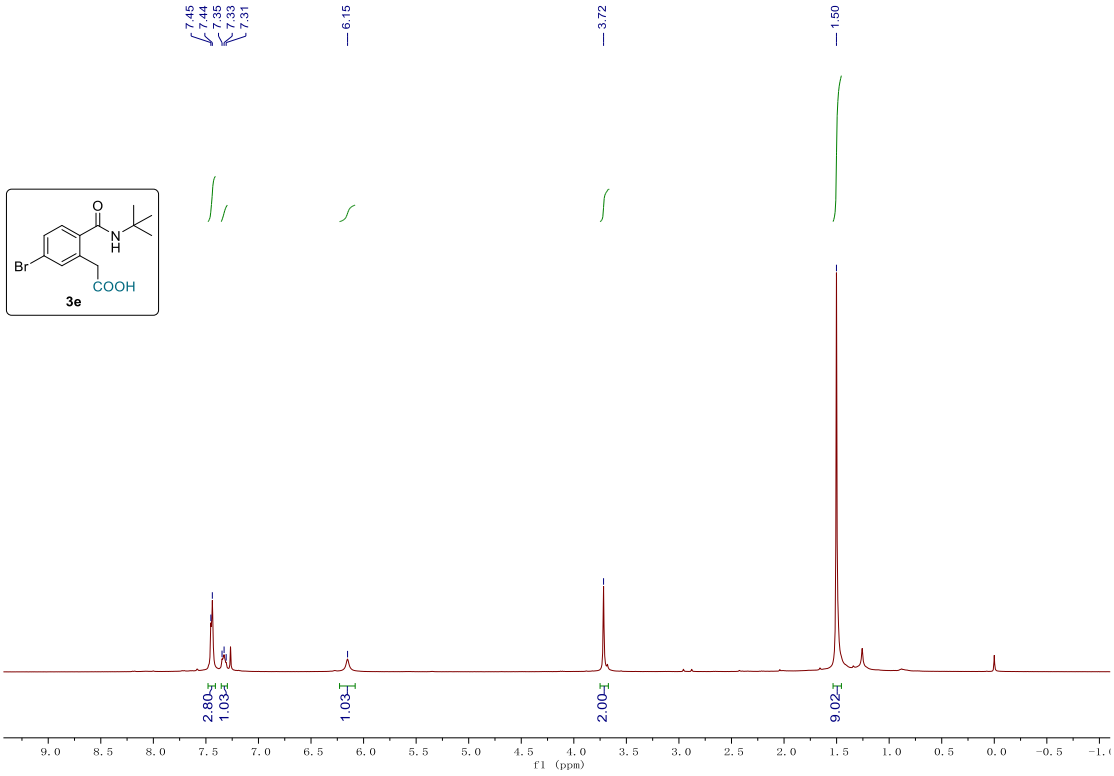
171.01
161.86
135.79
129.05
127.36
116.43
113.79
55.57
52.94
42.49
28.64
MeO
COOH
3b
f1 (ppm)


7.45
7.44
7.35
7.33
7.31
6.15
3.72
1.50
Br
O
N
H
COOH
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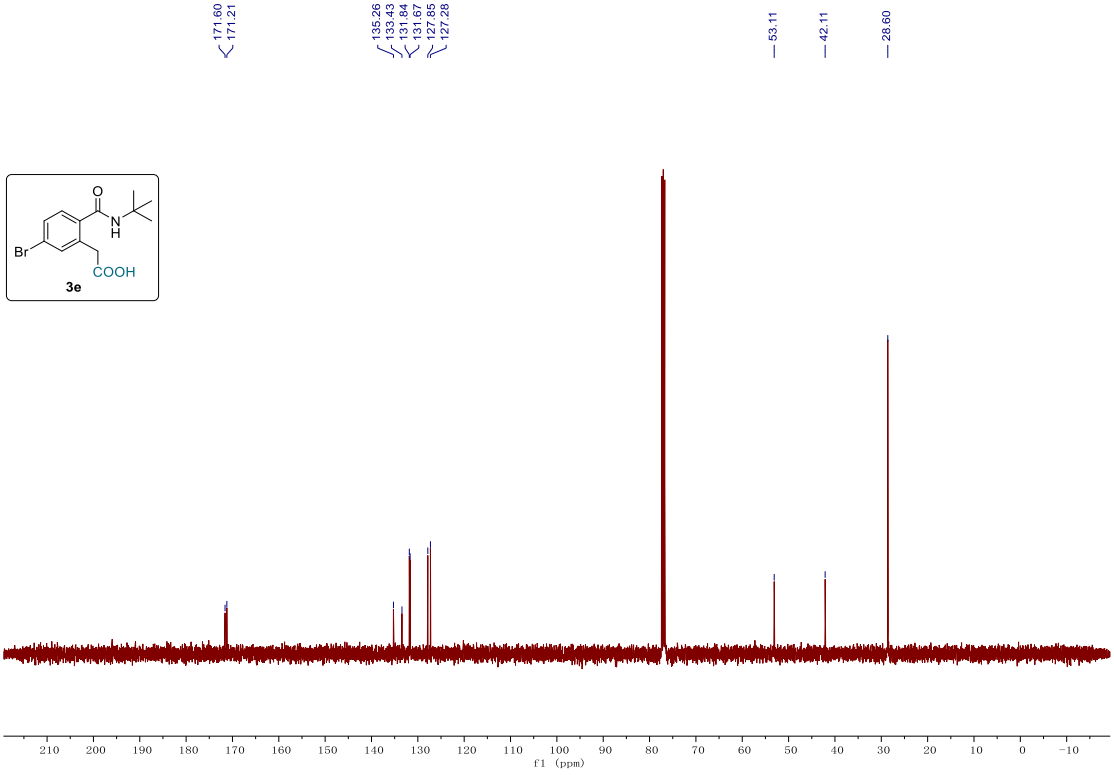
1.03
1.03
2.00
9.02
f1 (ppm)


171.60
171.21
135.26
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131.67
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127.28
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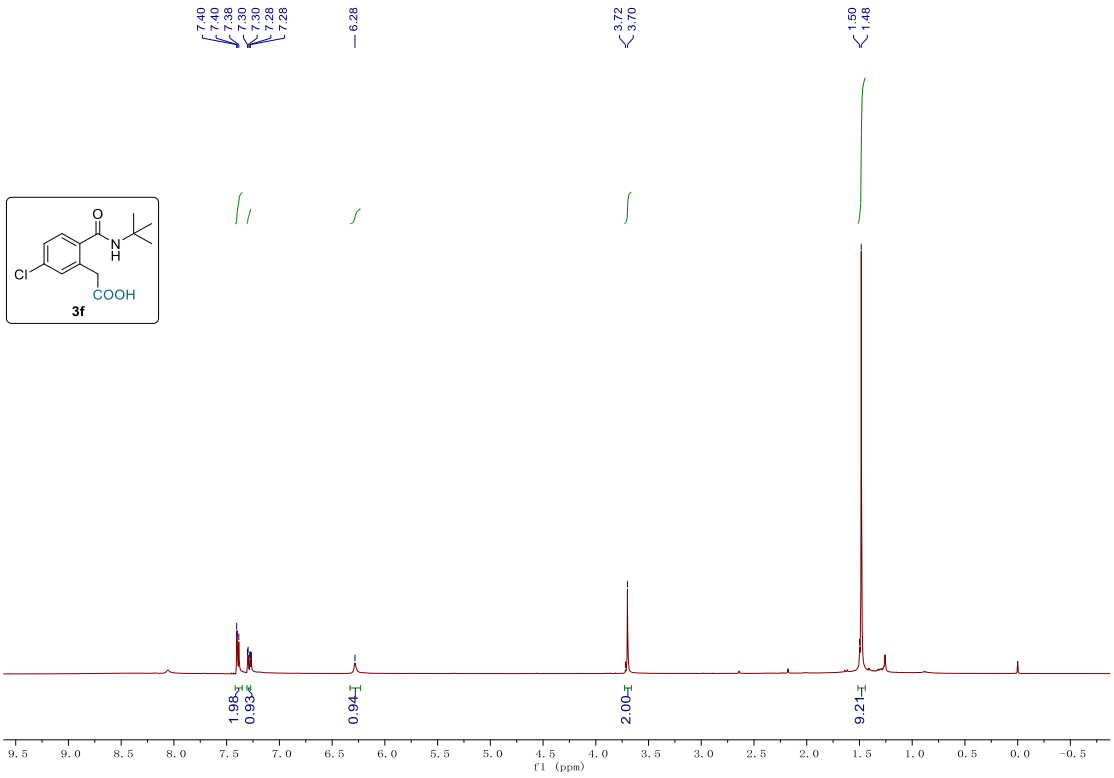
42.11
28.60
Br
O
N
H
COOH
3e
f1 (ppm)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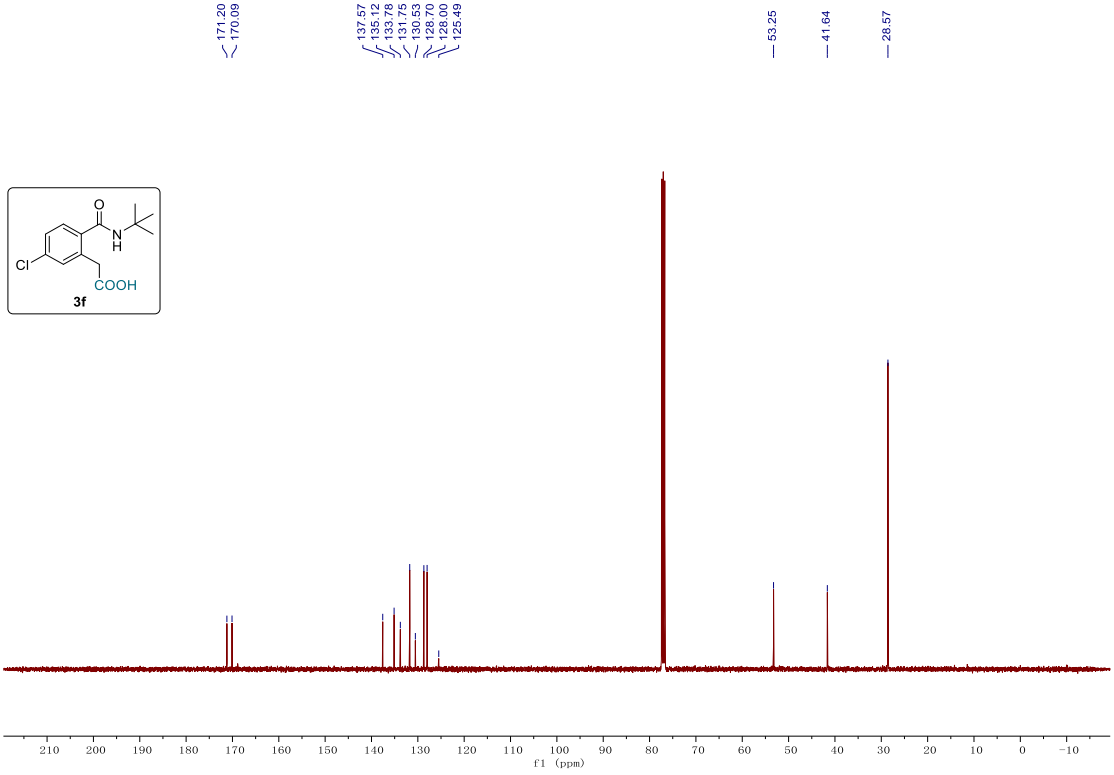
7.40
7.38
7.30
7.30
7.28
7.28
6.28
3.72
3.70
1.50
1.48
Cl
O
N
H
COOH
3f
1.98
0.93
0.94
2.00
9.21
f1 (ppm)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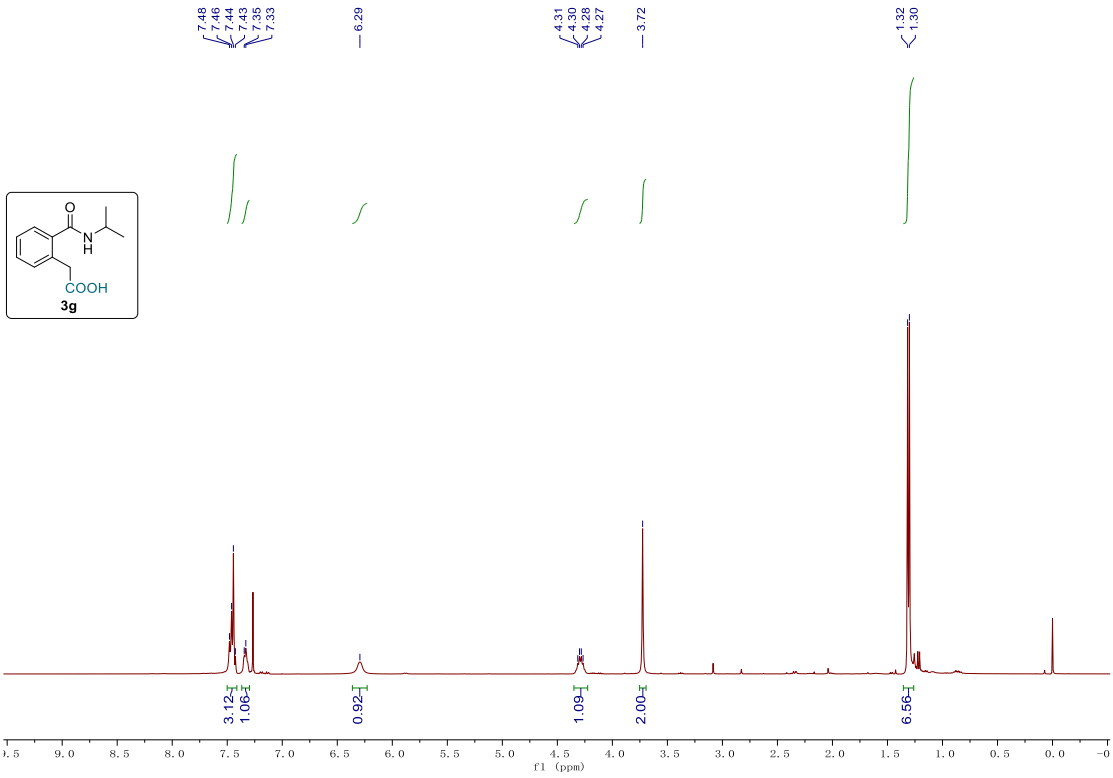
170.09
137.57
135.12
133.78
131.75
130.53
128.70
128.00
125.49
53.25
41.64
28.57
Cl
O
N
H
COOH
3f
f1 (ppm)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7.46
7.44
7.43
7.35
7.33
6.29
4.31
4.30
4.28
4.27
3.72
1.32
1.30
COOH
3g
3.12
1.06
0.92
1.09
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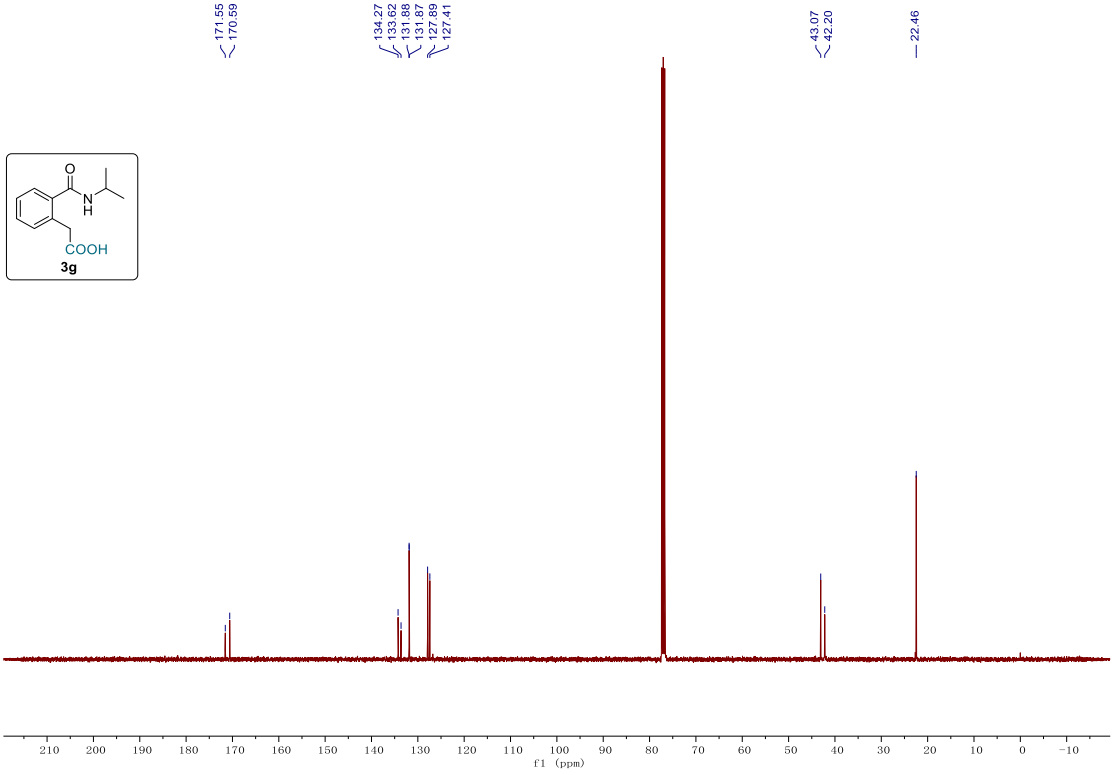
6.56
f1 (ppm)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170.59
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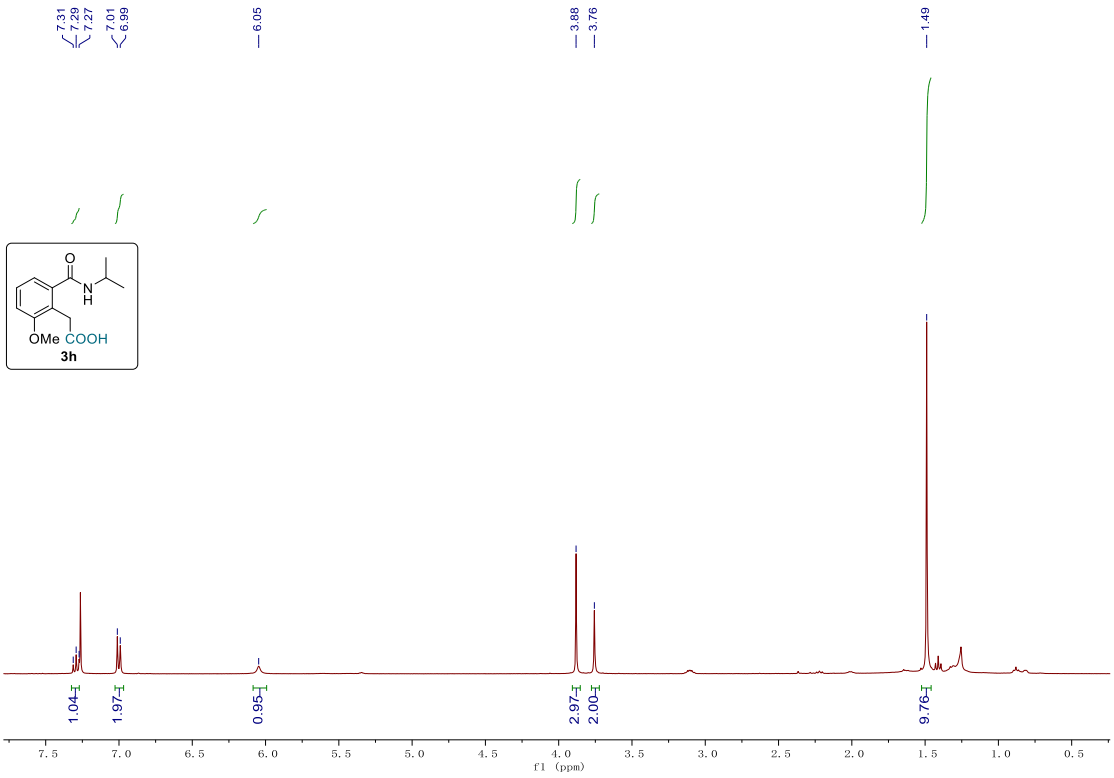
131.88
131.87
127.89
127.41
43.07
42.20
22.46
COOH
3g
f1 (ppm)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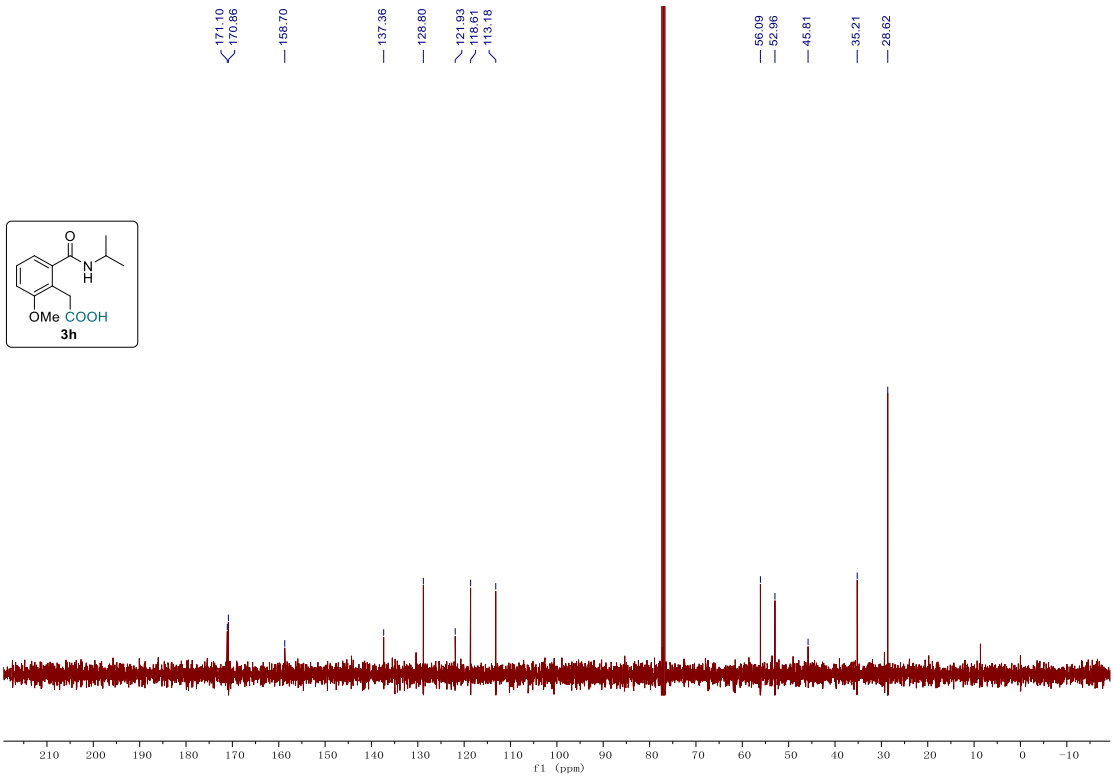
7.29
7.27
7.01
6.99
6.05
3.88
3.76
1.49
OMe COOH
3h
1.04
1.97
0.95
2.97
2.00
9.76
f1 (ppm)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113.18
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45.81
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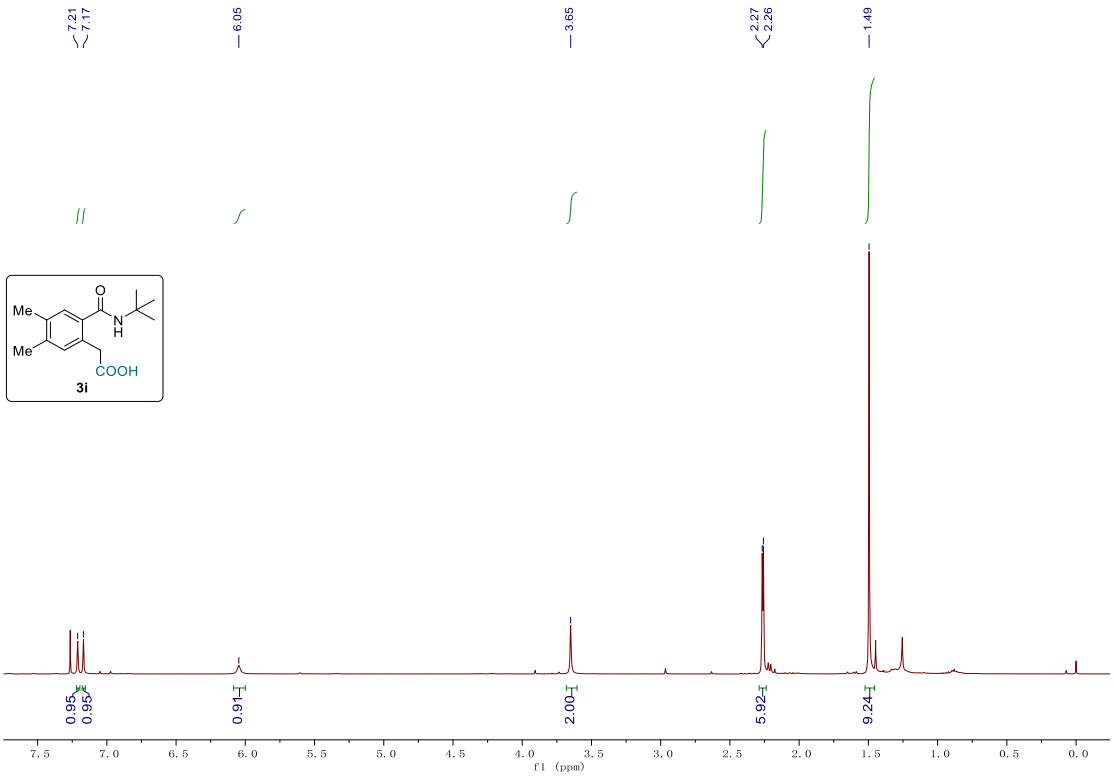
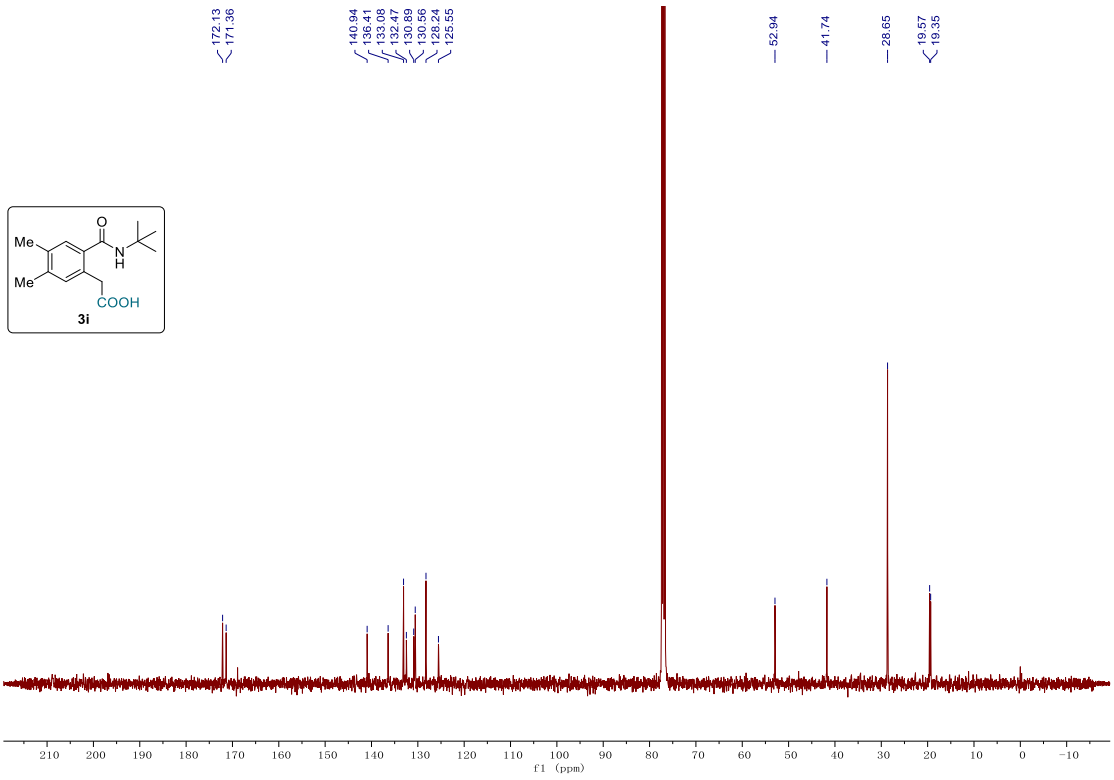
28.62
OMe COOH
3h
f1 (ppm)


7.21
7.17
6.05
3.65
2.27
2.26
1.49
Me
Me
O
N
H
COOH
3i
0.95
0.99
0.91
2.00
5.92
9.24
f1 (ppm)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132.47
130.89
130.56
128.24
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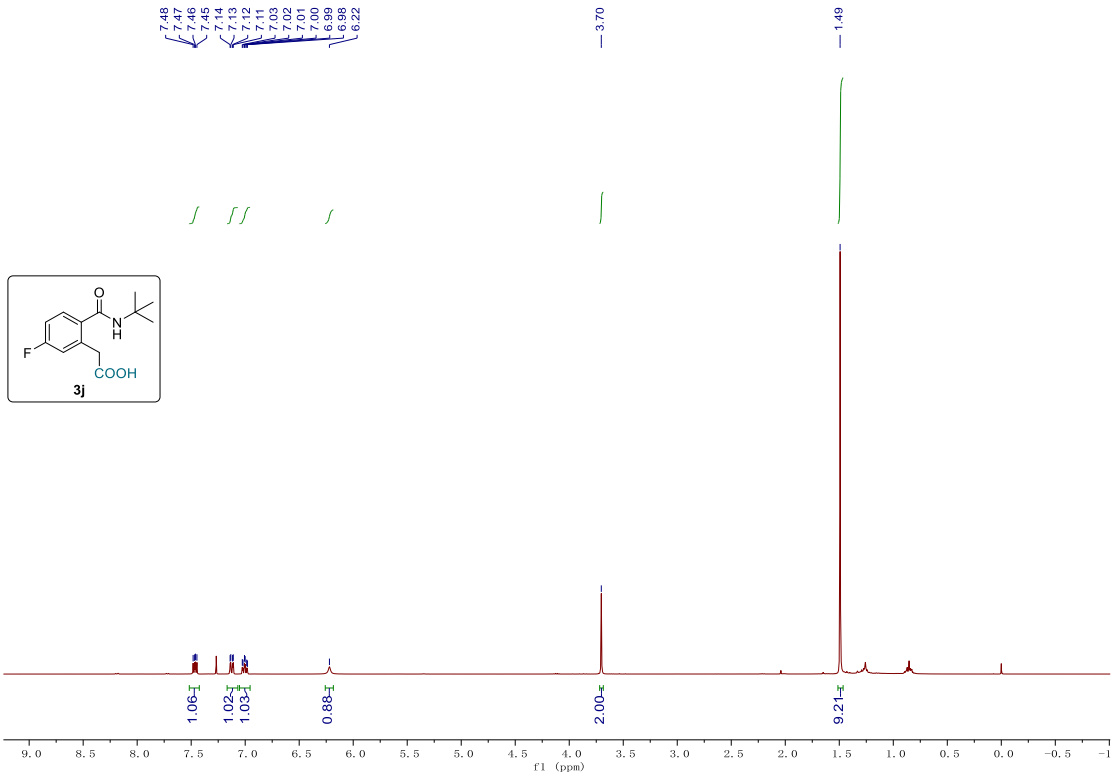
52.94
41.74
28.65
19.57
19.35
Me
Me
O
N
H
COOH
3i
f1 (ppm)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7.47
7.46
7.45
7.14
7.13
7.12
7.11
7.03
7.02
7.01
7.00
6.99
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1.49
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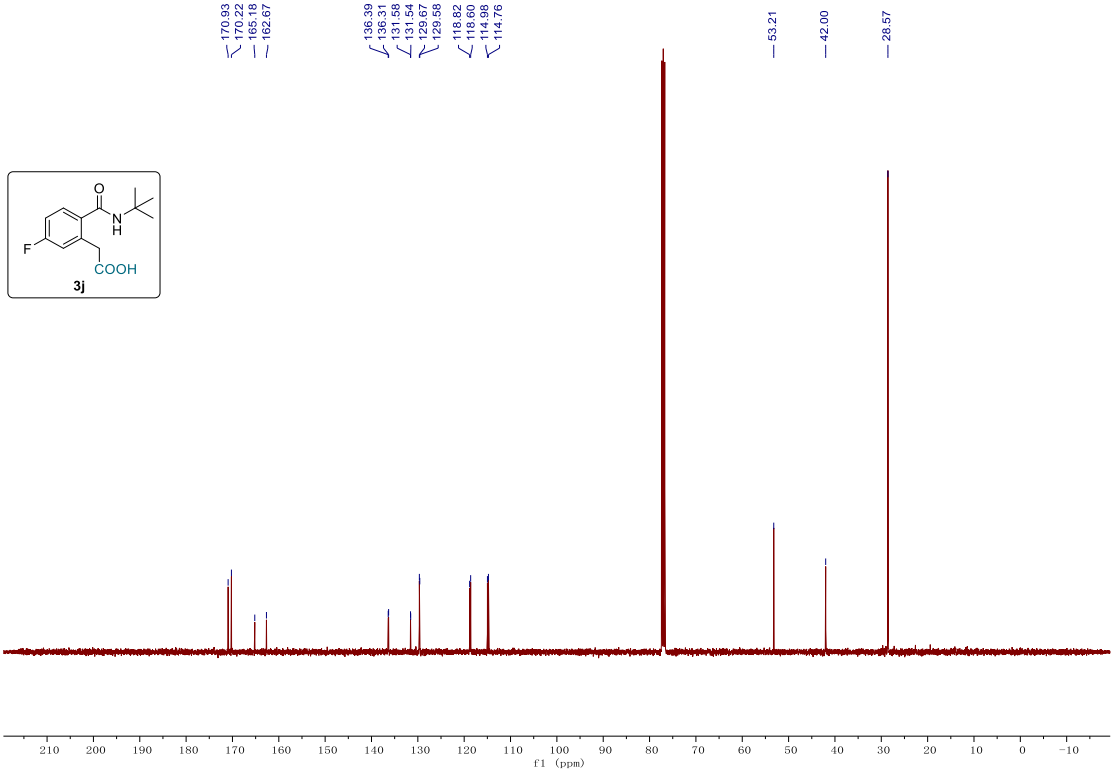
0.88
2.00
9.21
f1 (ppm)
3j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170.22
165.18
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136.31
131.58
131.54
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118.82
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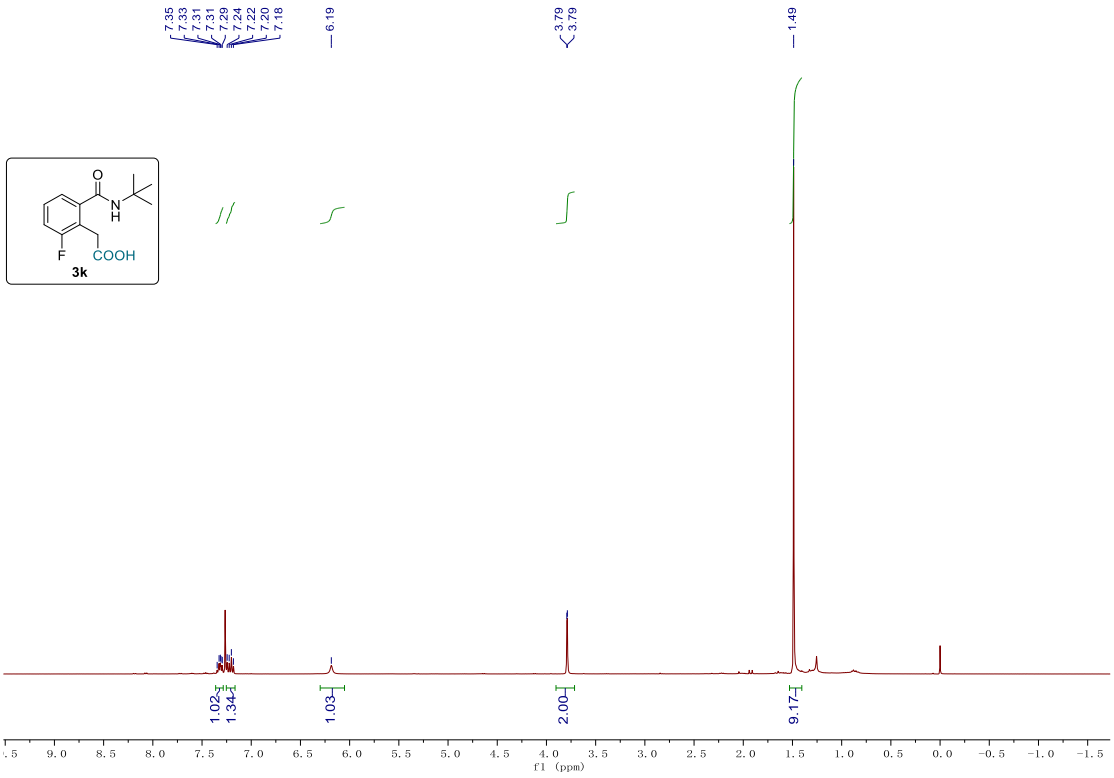
114.98
114.76
53.21
42.00
28.57
f1 (ppm)
3j


7.35
7.33
7.31
7.29
7.24
7.22
7.20
7.18
6.19
3.79
3.79
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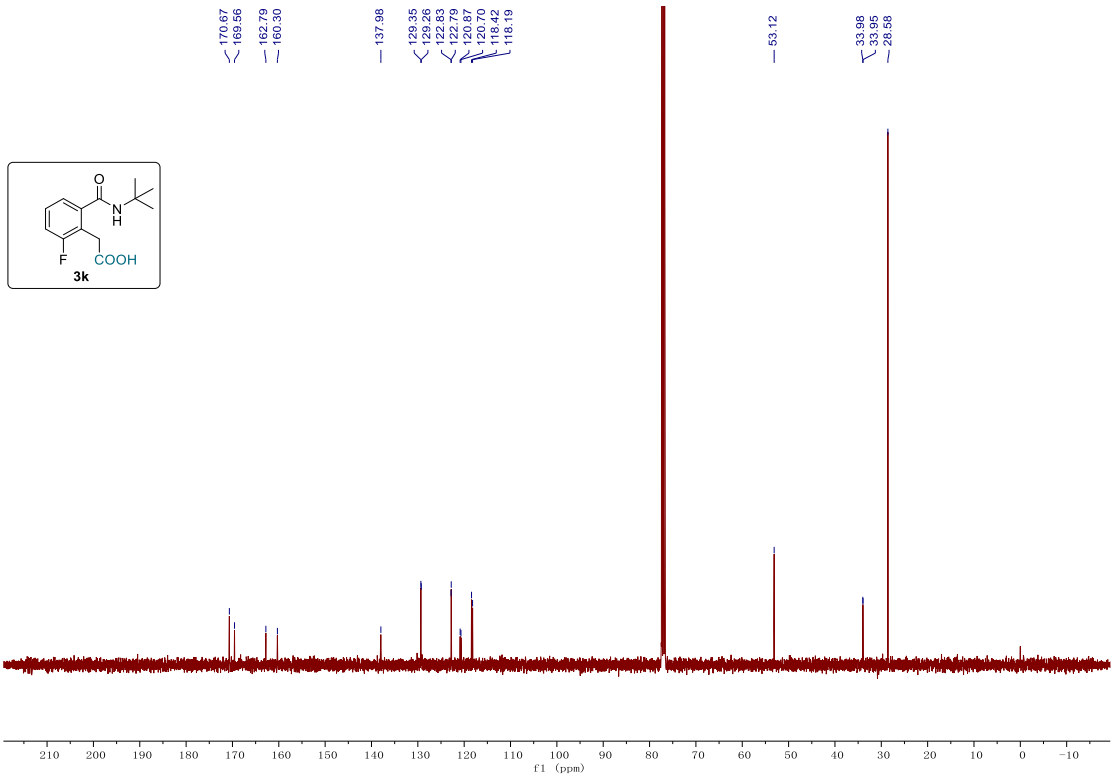
O
N
H
F
COOH
3k
1.02
1.34
1.03
2.00
9.17
f1 (ppm)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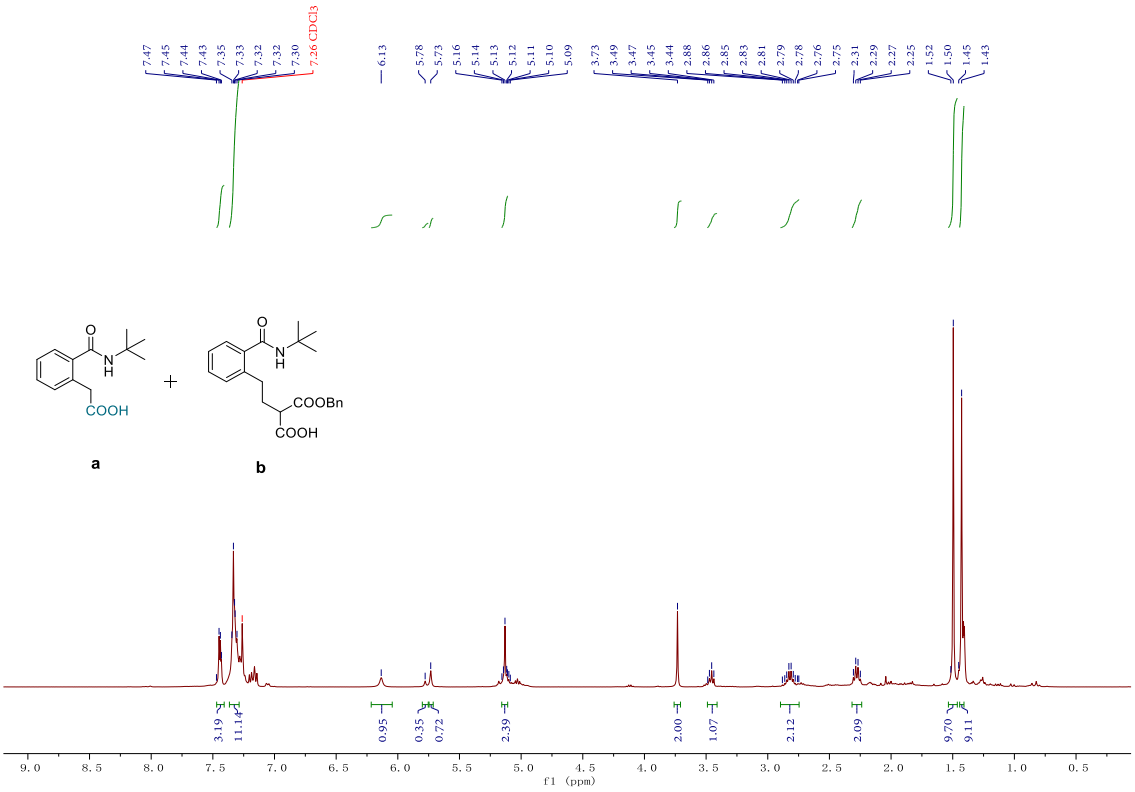
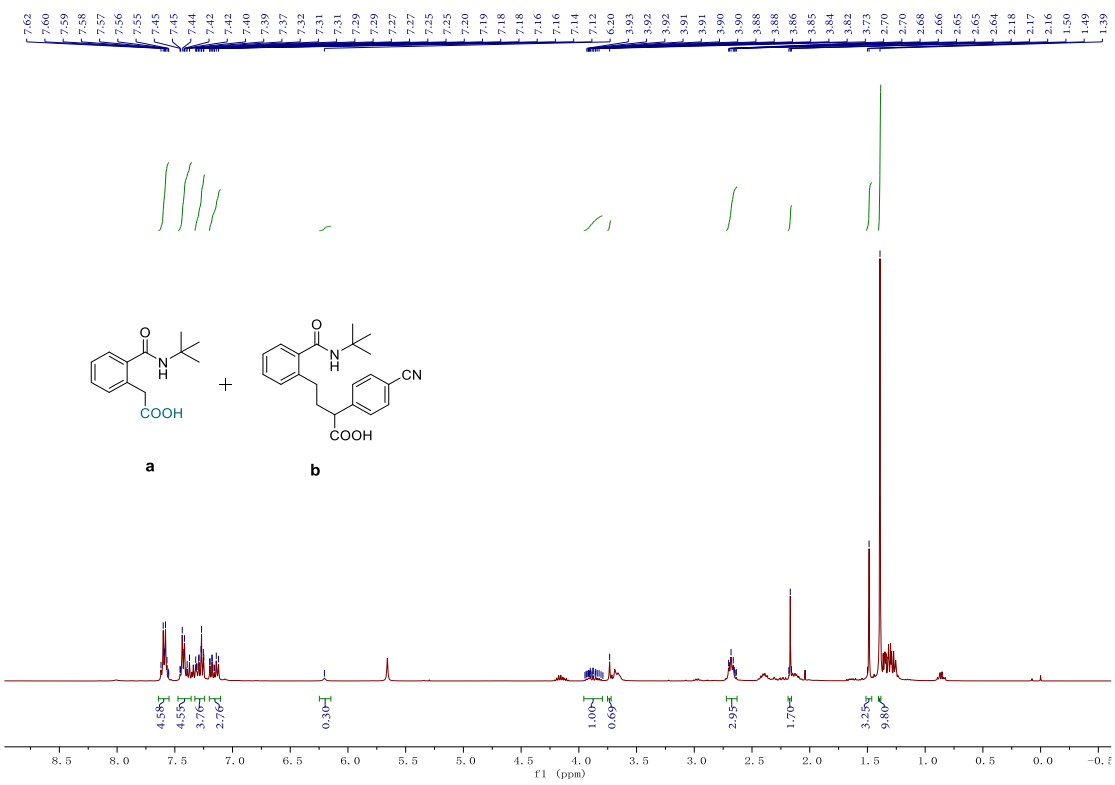
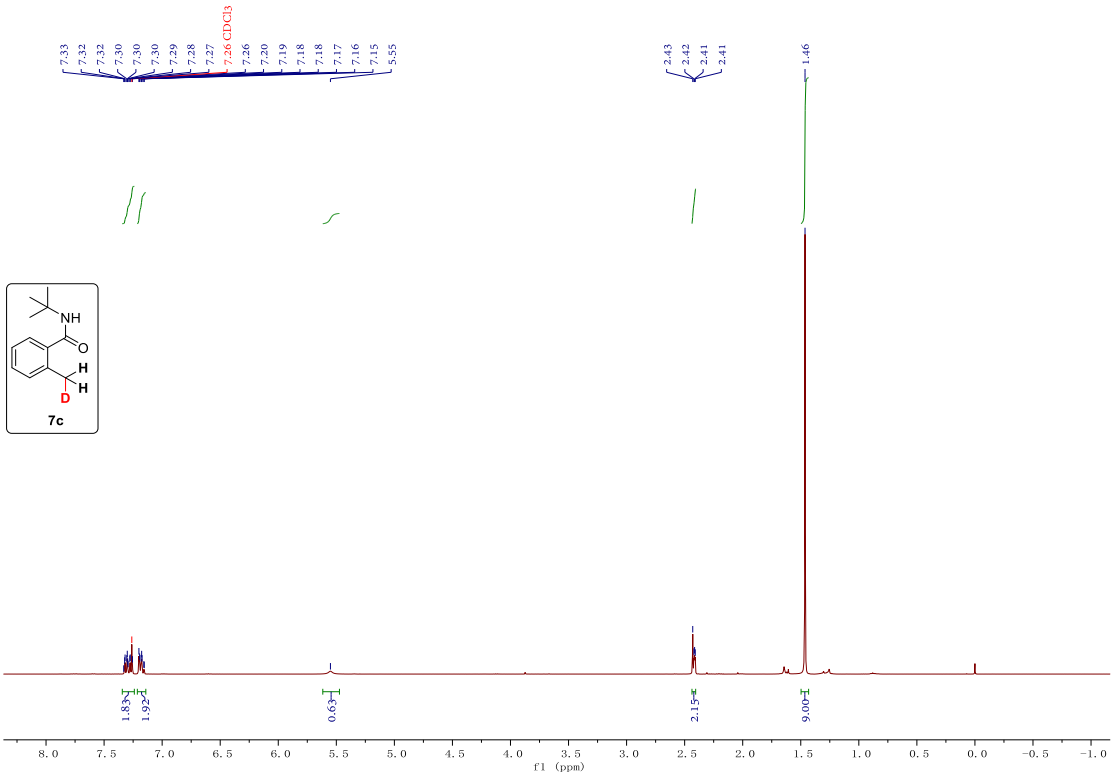
169.56
162.79
160.30
137.98
129.35
129.26
122.83
122.79
120.87
120.70
118.42
118.19
53.12
33.98
33.95
28.58
O
N
H
F
COOH
3k
f1 (ppm)



^{1}H HMR of mixture (a:b molar ratio = 1:1)



^{1}H HMR of mixture (a:b molar ratio = 1:3)


7.33
7.32
7.32
7.30
7.30
7.30
7.29
7.28
7.27
7.26 CDCl3
7.26
7.20
7.19
7.18
7.18
7.17
7.16
7.15
5.55
2.43
2.42
2.41
2.41
1.46
NH
O
H
H
D
7c
1.83
1.92
0.63
2.15
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

8. References

1. Chen, H.; Guo, L.; Yu, S., Primary, Secondary, and Tertiary gamma-C(sp(3))-H Vinylation of Amides via Organic Photoredox-Catalyzed Hydrogen Atom Transfer. *Org Lett* **2018,** *20* (19), 6255-6259.
2. Ruan, X.-Y.; Zhang, T.; Li, W.-A.; Yin, Y.-Z.; Han, Z.-Y.; Gong, L.-Z., Photoinduced and palladium-catalyzed hydrogen atom transfer triggered 1,2-difunctionalization of 1,3-dienes with hydroxamides. *Science China Chemistry* **2022,** *65* (5), 863-869.
3. Xia Y, Liu Z, Feng S, et al. Ir (III)-catalyzed aromatic C–H bond functionalization via metal carbene migratory insertion[J]. The Journal of Organic Chemistry, 2015, 80(1): 223-236.