Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

HBr-Catalyzed C-Si Bond Cleavage of Benzylsilanes and Subsequent Oxidation into Benzoic Acids with Air as Terminal Oxidant

Jing Sun,[a,b,e] Yu Wang,[c,e] Liqiong Han,[a] Dawen Xu,[a] Yiyong Chen,[a] Xinhua Peng,[b] and Hao Guo*[a,d]

[a] Department of Chemistry, Fudan University, 220 Handan Road, Shanghai, 200433, P. R. China. Tel: +86-21-55664361, Fax: +86-21-55664361, E-mail: Hao_Guo@fudan.edu.cn

[b] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, P. R. China

[c] Department of Head and Neck Surgery, Fudan University Shanghai Cancer Center; Department of Oncology, Shanghai Medical College, Fudan University, Shanghai, P. R. China

[d] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences

[e] They contributed equally.

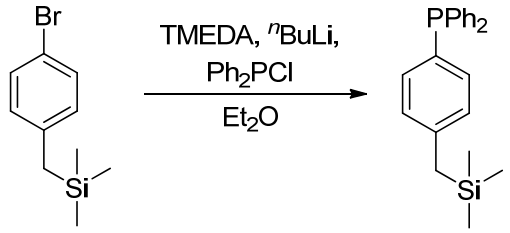
Supplementary Information

Experimental Section

General experimental methods

All reactions were carried out using a PLS-SXE300UV reactor with Xe lamp (300 W) as the irradiation source. Melting points were determined on a WRS-2 apparatus. IR spectra were recorded on a Avatar 360 FT-IR spectrometer. ^{1}H (400 MHz), ^{13}C (100 MHz), ^{19}F (376 MHz), and ^{31}P (162 MHz) NMR spectra of samples in $CDCl_3$ (unless stated otherwise) were recorded on an AVANCE III 400 spectrometer. MS (EI, 70 eV) determinations were carried out on a HP 5973 spectrometer. HRMS (EI) determinations were carried out on a Water GCT CA176 spectrometer. HRMS (ESI) determinations were carried out on a Bruker Daltonics micrOTOF Ⅱ spectrometer. Compound **1f** was commercial available. Compounds **1a**,[1] **1b**,[2] **1c**,[3] **1d**,[4] **1e**,[5] **1g**,[6] **1h**,[7] **1j**,[8] **1k**,[9] **1l**,[10] **1m**,[11] **1n**,[12] **1q**,[5] **1r**,[5] **1s**,[5] **1t**,[5] **4**,[13] and **5**[14] were prepared according to literature procedures.

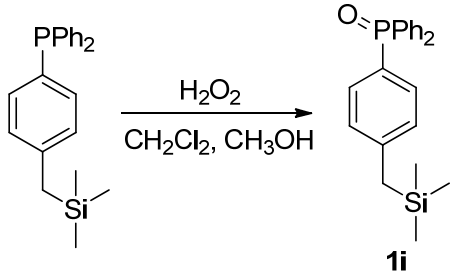
Synthesis of diphenyl(4-((trimethylsilyl)methyl)phenyl)phosphine



A solution of (4-bromobenzyl)trimethylsilane (187 mg, 0.77 mmol) in anhydrous Et_2O (20 mL) was cooled with ice-salt bath. Then TMEDA (0.4 mL, 2.7 mmol) and *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol) were added subsequently. The reaction mixture was stirred for 1.5 hour, then warmed to rt, and stirred for another 1 hour at rt. After which the reaction mixture was cooled with ice-salt bath, and then chlorodiphenylphosphine (0.5 mL, 2.8 mmol) was added dropwise and stirred for 1 hour with ice-salt bath. Then the mixture was allowed to warm to rt and stirred for 13 hours. The solvent was removed under reduced pressure. Purification by silica gel chromatography (eluent: petroleum ether) afforded a white solid (192 mg, 72%); mp 84.2-84.8 ^{o}C (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 10 H), 7.24-7.17 (m, 2 H), 7.01 (d, J = 7.2 Hz, 2 H), 2.12 (s, 2 H), 0.03 (s, 9 H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 141.8, 137.9 (d, J_{PC} = 10.3 Hz), 133.9 (d, J_{PC} = 19.7 Hz), 133.7 (d, J_{PC} = 19.0 Hz), 131.4 (d, J_{PC} = 8.1 Hz), 128.5 (d, J_{PC} = 5.8 Hz), 128.4, 128.3, 27.2, -1.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ -6.4 ppm; IR (neat) 1595, 1494, 1476, 1436 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}PSi$ 349.1541, found. 349.1532.

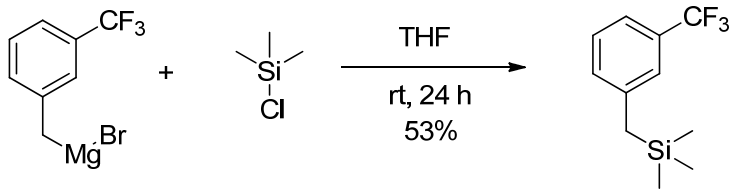
Synthesis of diphenyl(4-((trimethylsilyl)methyl)phenyl)phosphine oxide (1i)



1i

Diphenyl(4-((trimethylsilyl)methyl)phenyl)phosphine (350 mg, 1.0 mmol) was added to a solution of H_2O_2 (30%) (0.4 mL), methanol (15 mL), and dichloromethane (15 mL). After stirred for 2 hours at rt, it was quenched with saturated Na_2CO_3 solution (10 mL). The resulting mixture was extracted with dichloromethane (20 mL). The organic layer was washed with water (10 mL), dried over $MgSO_4$, and concentrated to dryness. Purification by silica gel chromatography (eluent: ethyl acetate) afforded **1i** as a white solid (300 mg, 82%); mp 152.9-154.4 ^oC (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.62 (m, 4 H), 7.56-7.42 (m, 8 H), 7.09-7.04 (m, 2 H), 2.14 (s, 2 H), -0.02 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 133.0 (d, J_{PC} = 103.6 Hz), 132.1 (d, J_{PC} = 9.5 Hz), 131.8, 128.4 (d, J_{PC} = 11.6 Hz), 128.1 (d, J_{PC} = 12.4 Hz), 127.3 (d, J_{PC} = 108.0 Hz), 27.8, -1.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.6 ppm; IR (neat) 1601, 1473, 1433 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}OPSi$ 365.1491, found. 365.1482.

Synthesis of (3-(trifluoromethyl)benzyl)trimethylsilane (1o)

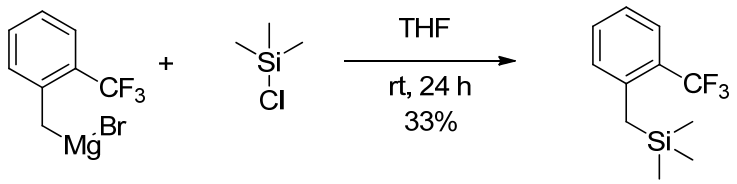


1o

Under argon atmosphere, Mg (121 mg, 5.0 mmol), anhydrous THF (3 mL), chlorotrimethylsilane (691 μL, 8.0 mmol), and a drop of I_2 were added into a dry 50

mL Schlenk flask. The mixture was stirred at rt for 15 min. Then a solution of 1-(bromomethyl)-3-(trifluoromethyl)benzene (611 μL, 4.0 mmol) in anhydrous THF (7 mL) was added dropwise. After stirred at rt for 24 hours, the reaction was quenched by water (10 mL) and HCl (aq., 1 M) (10 mL). The mixture was extracted with ethyl acetate (30 mL x 3). The combined organic layer was dried over $MgSO_4$. Filtration, concentration, and purification by flash chromatography on silica gel (eluent: petroleum ether) afforded **1o** as a colorless oil (491 mg, 53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 2 H), 7.24 (s, 1 H), 7.17 (d, J = 6.0 Hz, 1 H), 2.15 (s, 2 H), 0.00 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7 (s), 131.3 (s), 130.5 (q, J = 31.5 Hz), 128.5 (q, J = 2.8 Hz), 124.5 (q, J = 3.8 Hz), 124.4 (q, J = 270.8 Hz), 120.8 (q, J = 3.8 Hz), 27.2 (s), -2.12 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 ppm; IR (neat) 1593, 1491, 1445, 1424 cm^{-1}; MS (EI, 70 eV) m/z 232 (M^+ 6.46), 140 (100); HRMS (EI, 70 eV) calcd for $C_{11}H_{15}F_3Si$ 232.0895, found. 232.0892.

Synthesis of (2-(trifluoromethyl)benzyl)trimethylsilane (1p)



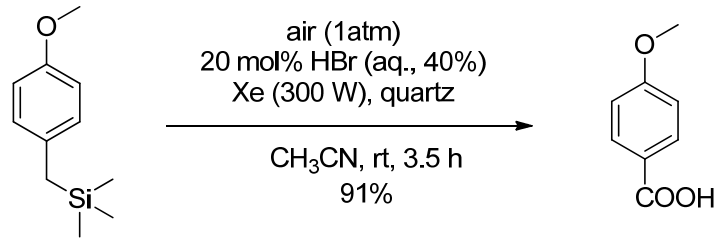
1p

Under argon atmosphere, Mg (125 mg, 5.2 mmol), anhydrous THF (3 mL), chlorotrimethylsilane (700 μL, 8.1 mmol), and a drop of I_2 were added into a dry 50 mL Schlenk flask. The mixture was stirred at rt for 15 min. Then a solution of 1-(bromomethyl)-2-(trifluoromethyl)benzene (969 mg, 3.9 mmol) in anhydrous THF (6 mL) was added dropwise. After stirred at rt for 24 hours, the reaction was quenched by water (10 mL) and HCl (aq., 1 M) (10 mL). The mixture was extracted with CH_2Cl_2 (30 mL x 3). The combined organic layer was dried over $MgSO_4$. Filtration, concentration, and purification by flash chromatography on silica gel (eluent: petroleum ether) afforded **1p** as a colorless oil (302 mg, 33%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1 H), 7.44-7.37 (m, 1 H), 7.22-7.15 (m, 2 H), 2.39 (s, 2 H), 0.07 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2 (q, J = 2.2 Hz), 131.2 (q, J = 1.5 Hz), 130.5 (s), 127.3 (q, J = 29.2 Hz), 126.1 (q, J = 5.8 Hz), 124.8 (q, J = 272.1

Hz), 124.0 (s), 23.7 (q, J = 1.5 Hz), -1.37 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.1 ppm; IR (neat) 1607, 1577, 1491, 1455 cm^{-1}; MS (EI, 70 eV) m/z 232 (M^+ 1.32), 140 (100); HRMS (EI, 70 eV) calcd for $C_{11}H_{15}F_3Si$ 232.0895, found. 232.0900.

Typical Procedure I for the photoreaction.

Synthesis of 4-methoxybenzoic acid (3a)[15]

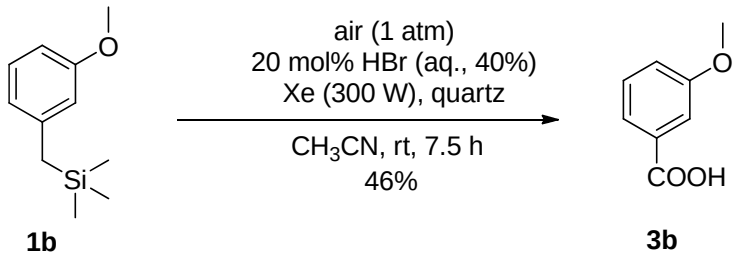


1a **3a**

(4-Methoxybenzyl)trimethylsilane (38 mg, 0.20 mmol), anhydrous acetonitrile (10 mL), and HBr (aq., 40%) (5.9 μL, 0.04 mmol) were added to a dry quartz reaction flask which was equipped with a magnetic stirrer and a condenser. The mixture was irradiated by a Xe lamp (300 W) at rt in the open air. The photoreaction was completed after 3.5 hours as monitored by TLC (eluent: petroleum ether : ethyl acetate = 10:1). The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 3:1→1:1) to afford **3a** as a solid (27 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 2 H), 6.95 (d, J = 8.0 Hz, 2 H), 3.88 (s, 3 H).

The following compounds were prepared according to typical procedure I.

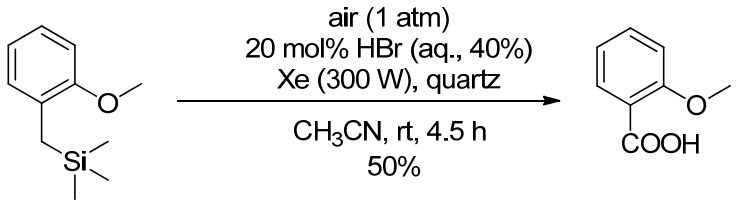
(1) 3-Methoxybenzoic acid (3b)[16]



1b **3b**

The reaction of **1b** (39 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3b** as a solid (14 mg, 46%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 1 H), 7.65-7.62 (m, 1 H), 7.43-7.35 (m, 1 H), 7.19-7.13 (m, 1 H), 3.88 (s, 3 H).

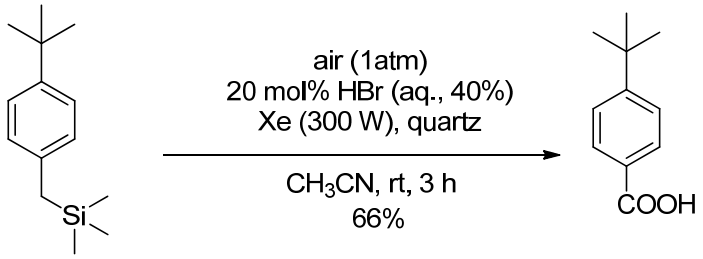
(2) 2-Methoxybenzoic acid (3c)[17]



1c **3c**

The reaction of **1c** (38 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3c** as a solid (15 mg, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.88 (brs, 1 H), 8.20-8.17 (m, 1 H), 7.61-7.56 (m, 1 H), 7.17-7.05 (m, 2 H), 4.09 (s, 3 H).

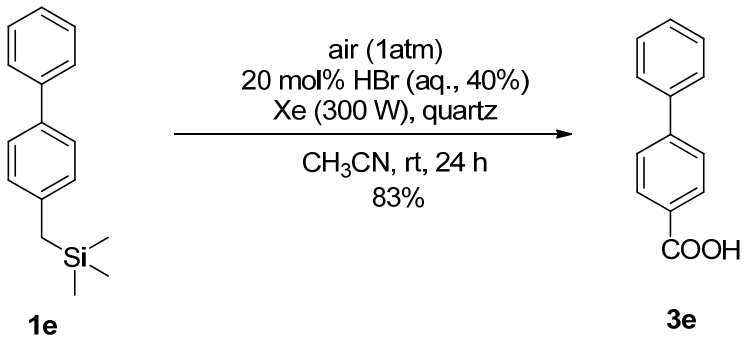
(3) 4-*Tert*-butylbenzoic acid (3d)[18]



1d **3d**

The reaction of **1d** (43 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3d** as a solid (23 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.8 Hz, 2 H), 7.49 (d, J = 8.8 Hz, 2 H), 1.35 (s, 9 H).

(4) 4-Phenylbenzoic acid (3e)[19]



1e **3e**

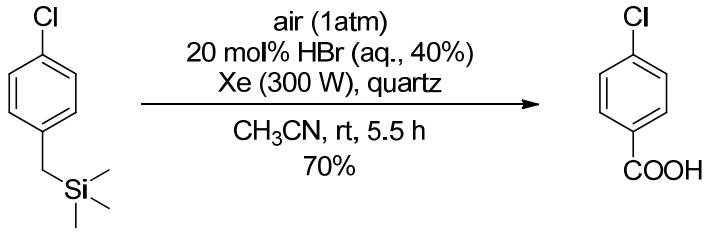
The reaction of **1e** (47 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3e** as a solid (32 mg, 83%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.99 (brs, 1 H), 8.03 (d, J = 8.4 Hz, 2 H), 7.80 (d, J = 8.4 Hz, 2 H), 7.74 (d, J = 6.8 Hz, 2 H), 7.54-7.47 (m, 2 H), 7.46-7.40 (m, 1 H).

(5) Benzoic acid (3f)[20]

1f **3f**

The reaction of **1f** (33 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3f** as a solid (18 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (brs, 1 H), 8.13 (d, J = 8.0 Hz, 2 H), 7.65-7.55 (m, 1 H), 7.54-7.30 (m, 2 H).

(6) 4-Chlorobenzoic acid (3g)[16]



1g **3g**

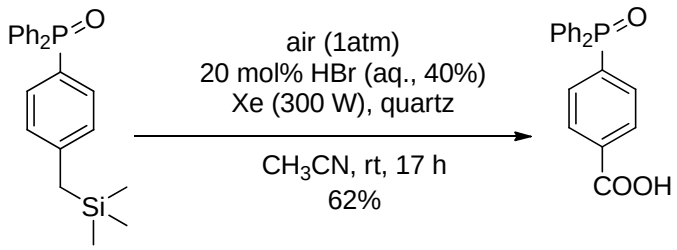
The reaction of **1g** (40 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3g** as a solid (22 mg, 70%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.12 (brs, 1 H), 7.95 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 8.4 Hz, 2 H).

(7) 4-Fluorobenzoic acid (3h)[15]

1h **3h**

The reaction of **1h** (35 mg, 0.19 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3h** as a solid (22 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.10 (m, 2 H), 7.20-7.09 (m, 2 H).

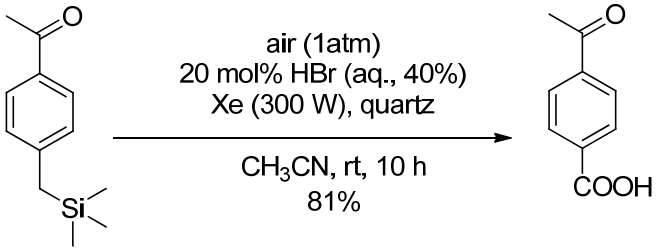
(8) 4-(Diphenylphosphoryl)benzoic acid (3i)[21]



1i **3i**

The reaction of **1i** (71 mg, 0.19 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3i** as a solid (39 mg, 62%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11-8.05 (m, 2 H), 7.78-7.69 (m, 2 H), 7.68-7.52 (m, 10 H).

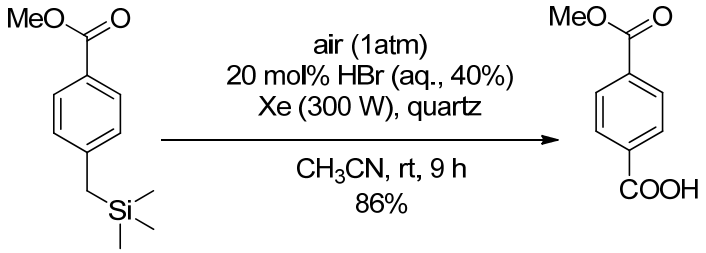
(9) 4-Acetylbenzoic acid (3j)[22]



1j **3j**

The reaction of **1j** (39 mg, 0.19 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3j** as a solid (25 mg, 81%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.33 (brs, 1 H), 8.06 (s, 4 H), 2.63 (s, 3 H).

(10) 4-(Methoxycarbonyl)benzoic acid (3k)[23]



1k **3k**

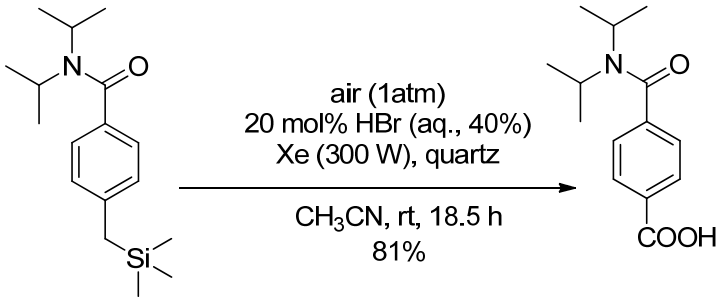
The reaction of **1k** (43 mg, 0.19 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3k** as a solid (30 mg, 86%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (s, 4 H), 3.88 (s, 3 H).

(11) 4-(Ethoxycarbonyl)benzoic acid (3l)[24]

1l **3l**

The reaction of **1l** (46 mg, 0.19 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3l** as a solid (34 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.12 (m, 4 H), 4.42 (q, J = 7.2 Hz, 2 H), 1.43 (t, J = 7.2 Hz, 3 H).

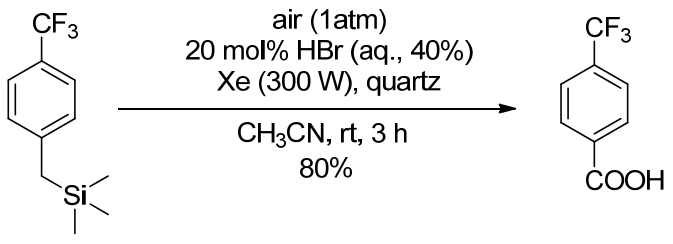
(12) 4-(Diisopropylcarbamoyl)benzoic acid (3m)



1m **3m**

The reaction of **1m** (55 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3m** as a solid (40 mg, 81%); mp 251.1-252.9 ^{o}C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (brs, 1 H), 8.11 (d, J = 8.4 Hz, 2 H), 7.41 (d, J = 8.4 Hz, 2 H), 3.75 (brs, 1 H), 3.56 (brs, 1 H), 1.56 (brs, 6 H), 1.15 (brs, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.2, 143.4, 130.5, 129.8, 125.7, 50.7, 45.8, 20.6; IR (neat) 1705, 1632, 1473, 1439 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{20}NO_3$ 250.1443, found. 250.1433.

(13) 4-(Trifluoromethyl)benzoic acid (3n)[23]

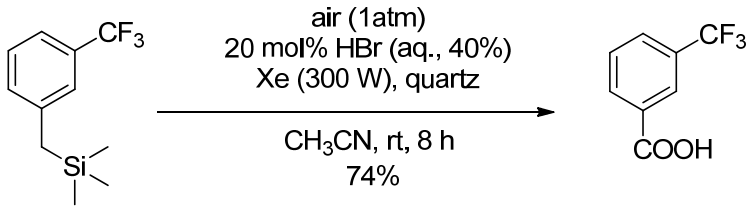


1n **3n**

The reaction of **1n** (46 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in

anhydrous acetonitrile (10 mL) afforded **3n** as a solid (30 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.0 Hz, 2 H), 7.76 (d, J = 8.0 Hz, 2 H).

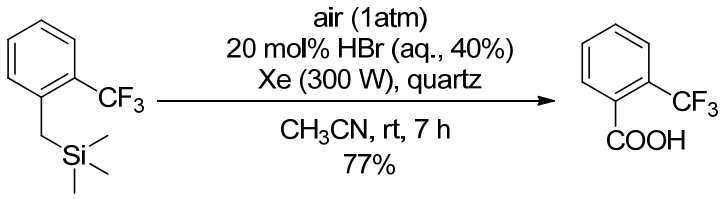
(14) 3-(Trifluoromethyl)benzoic acid (3o)[23]



1o **3o**

The reaction of **1o** (46 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 µL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3o** as a solid (28 mg, 74%); ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1 H), 8.31 (d, J = 8.0 Hz, 1 H), 7.89 (d, J = 7.2 Hz, 1 H), 7.81-7.50 (m, 1 H).

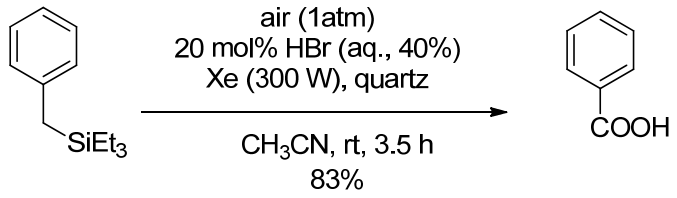
(15) 2-(Trifluoromethyl)benzoic acid (3p)[23]



1p **3p**

The reaction of **1p** (46 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 µL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3p** as a solid (29 mg, 77%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.58 (brs, 1 H), 7.85-7.69 (m, 4 H).

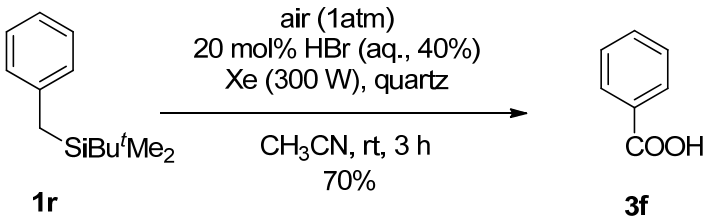
(16) Synthesis of benzoic acid (3f)[20] **from 1q**



1q **3f**

The reaction of **1q** (41 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 µL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3f** as a solid (20 mg, 83%).

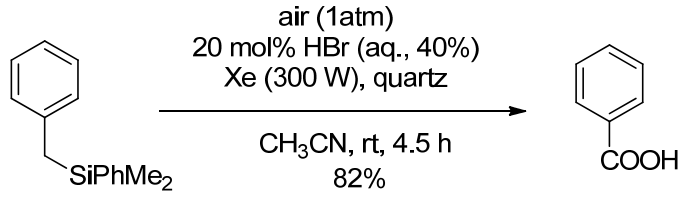
(17) Synthesis of benzoic acid (3f)[20] **from 1r**



1r **3f**

The reaction of **1r** (41 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3f** as a solid (17 mg, 70%).

(18) Synthesis of benzoic acid (3f)[20] from 1s



1s **3f**

The reaction of **1s** (45 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3f** as a solid (20 mg, 82%).

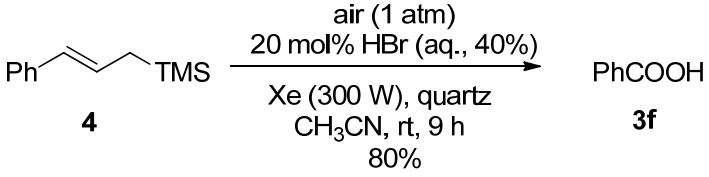
(19) Synthesis of benzoic acid (3f)[20] from 1t

1t **3f**

The reaction of **1t** (59 mg, 0.20 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3f** as a solid (15 mg, 60%).

(20) Synthesis of benzoic acid (3f)[20] from 4

The reaction of **4** (39 mg, 0.21 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in anhydrous acetonitrile (10 mL) afforded **3f** as a solid (20 mg, 80%).



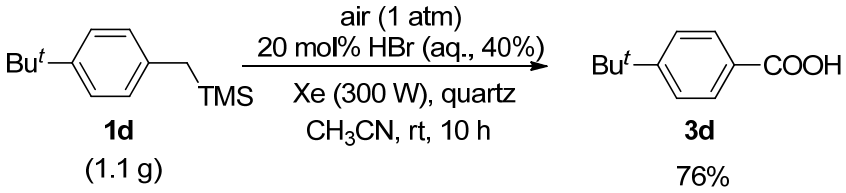
4 **3f**

(21) Synthesis of benzoic acid (3f)[20] from 5

The reaction of **5** (42 mg, 0.22 mmol) and HBr (aq., 40%) (5.9 μL, 0.04 mmol) in

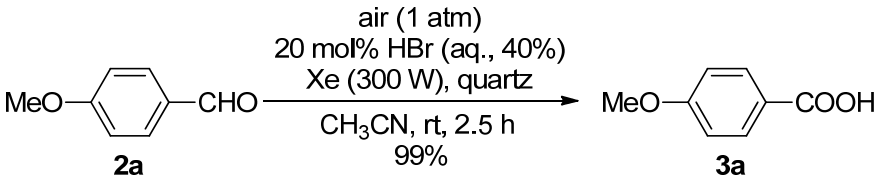
anhydrous acetonitrile (10 mL) afforded **3f** as a solid (23 mg, 86%).

Gram-scale synthesis of 3d



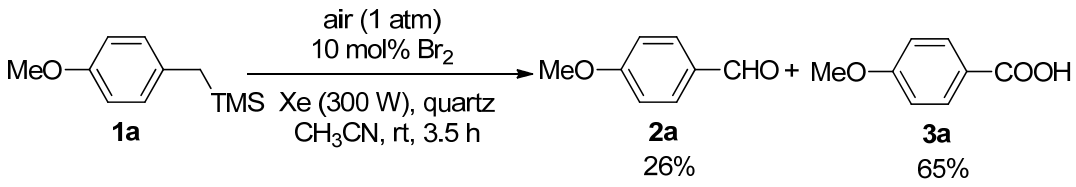
The reaction of **1d** (1.10 g, 5.0 mmol) and HBr (aq., 40%) (148 μL, 1.0 mmol) in anhydrous acetonitrile (60 mL) afforded **3d** as a solid (677 mg, 76%).

The conversion of 2a to 3a under Conditions A



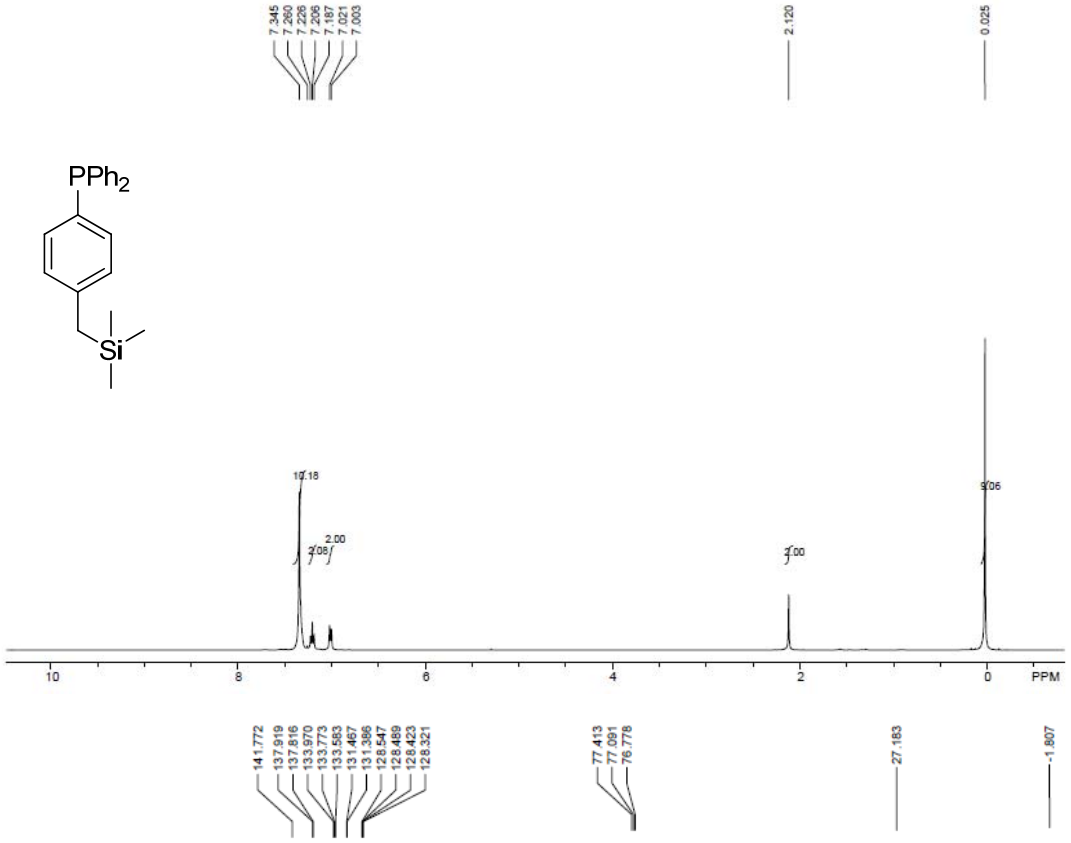
2a (29 mg, 0.21 mmol), anhydrous acetonitrile (10 mL), and HBr (aq., 40%) (5.9 μL, 0.04 mmol) were added to a dry quartz reaction flask which was equipped with a magnetic stirrer and a condenser. The mixture was irradiated by a Xe lamp (300 W) at rt in the open air. The photoreaction was completed after 2.5 hours as monitored by TLC (eluent: petroleum ether : ethyl acetate = 10:1). The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 3:1) to afford **3a** as a solid (32 mg, 99%).

The photooxidation of 1a under the catalysis of Br_2



1a (39 mg, 0.20 mmol), anhydrous acetonitrile (10 mL), and Br_2 (6.4 mg/mL in CH_3CN) (0.5 mL, 0.02 mmol) were added to a dry quartz reaction flask which was equipped with a magnetic stirrer and a condenser. The mixture was irradiated by a Xe

lamp (300 W) at rt in the open air. The photoreaction was completed after 3.5 hours as monitored by TLC (eluent: petroleum ether : ethyl acetate = 10:1). The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 3:1→ethyl acetate) to afford **2a** (7 mg, 26%) and **3a** (20 mg, 65%).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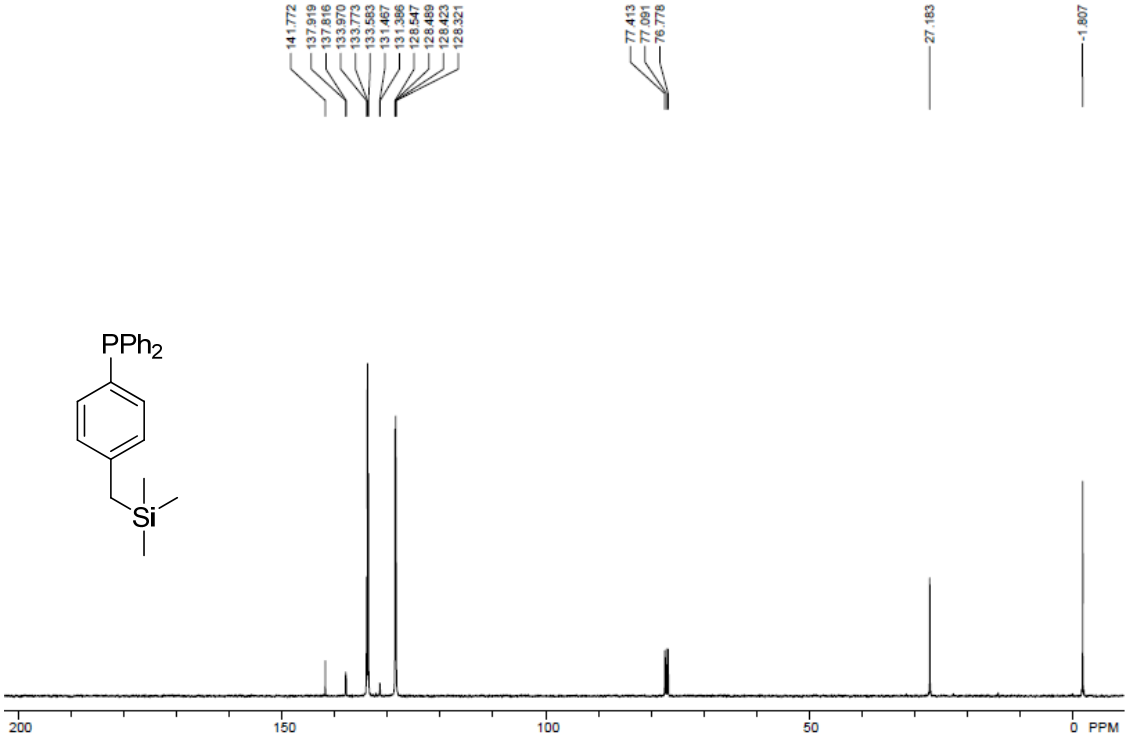
7.260
7.226
7.206
7.187
7.021
7.003
2.120
0.025
PPh2
Si
10.18
2.06
2.00
2.00
9.06
10
8
6
4
2
0
PPM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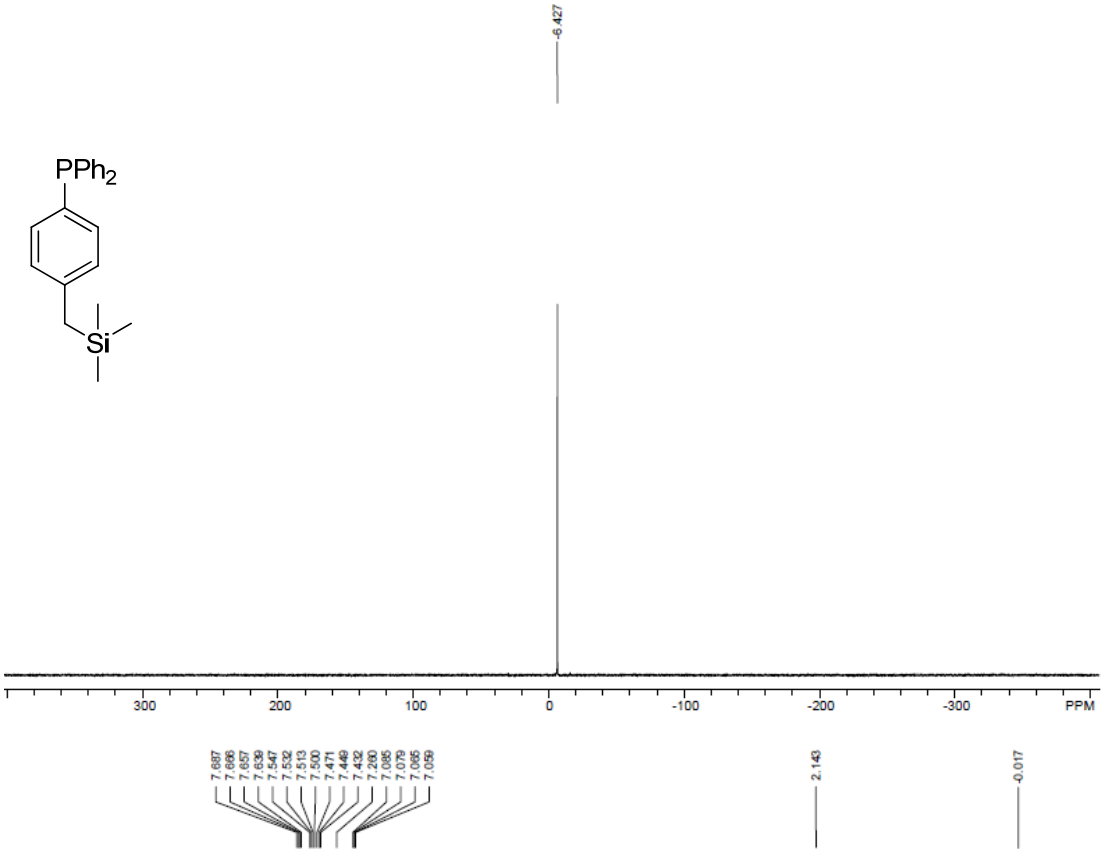
137.816
133.970
133.773
133.583
131.467
131.386
128.547
128.489
128.423
128.321
77.413
77.091
76.778
27.183
-1.807
PPh2
Si
200
150
100
50
0
PPM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PPh2
Si
300
200
100
0
-100
-200
-300
PPM
7.687
7.666
7.657
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7.547
7.532
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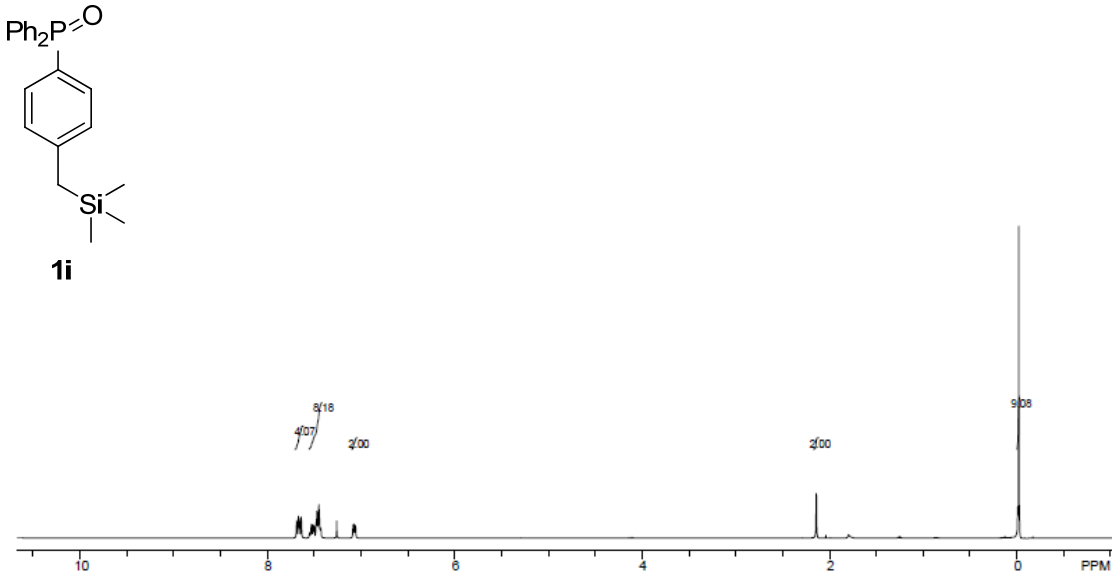
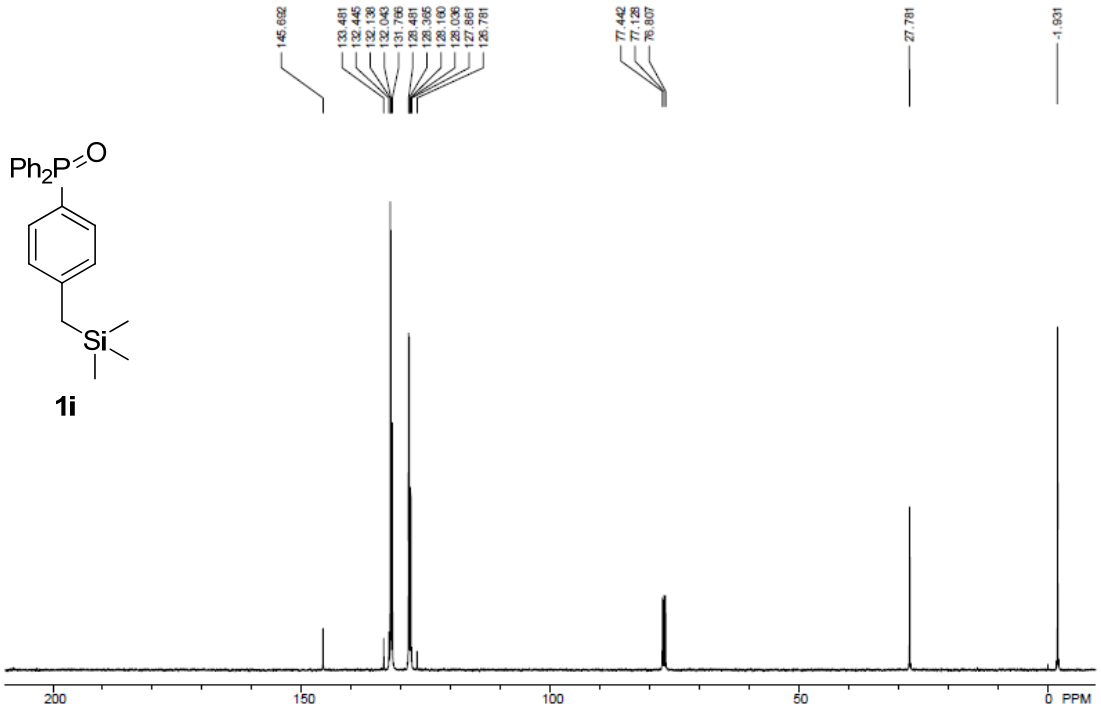
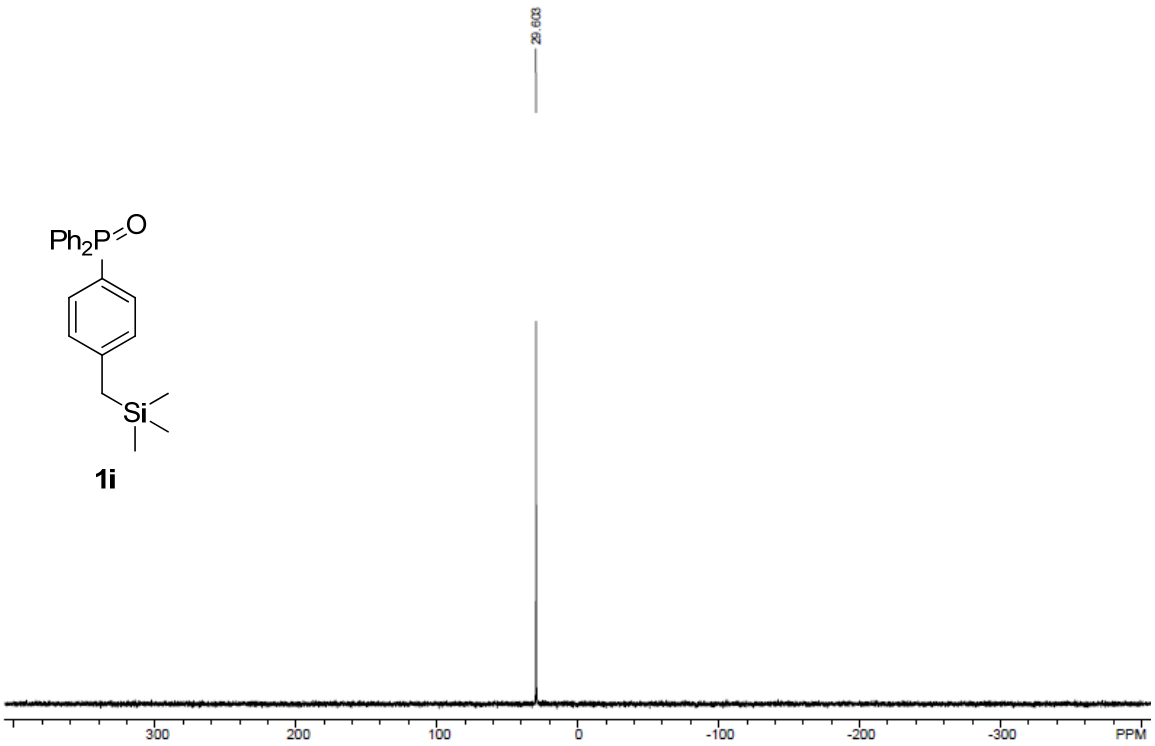
7.079
7.065
7.059
2.143
-0.017


Ph2P
O
Si
8.18
4.07
2.00
2.00
9.08
10
8
6
4
2
0
PPM

1i


145.692
133.481
132.445
132.138
132.043
131.766
128.481
128.365
128.160
128.036
127.861
126.781
77.442
77.128
76.807
27.781
-1.931
Ph2P=O
Si
1i
200
150
100
50
0 PPM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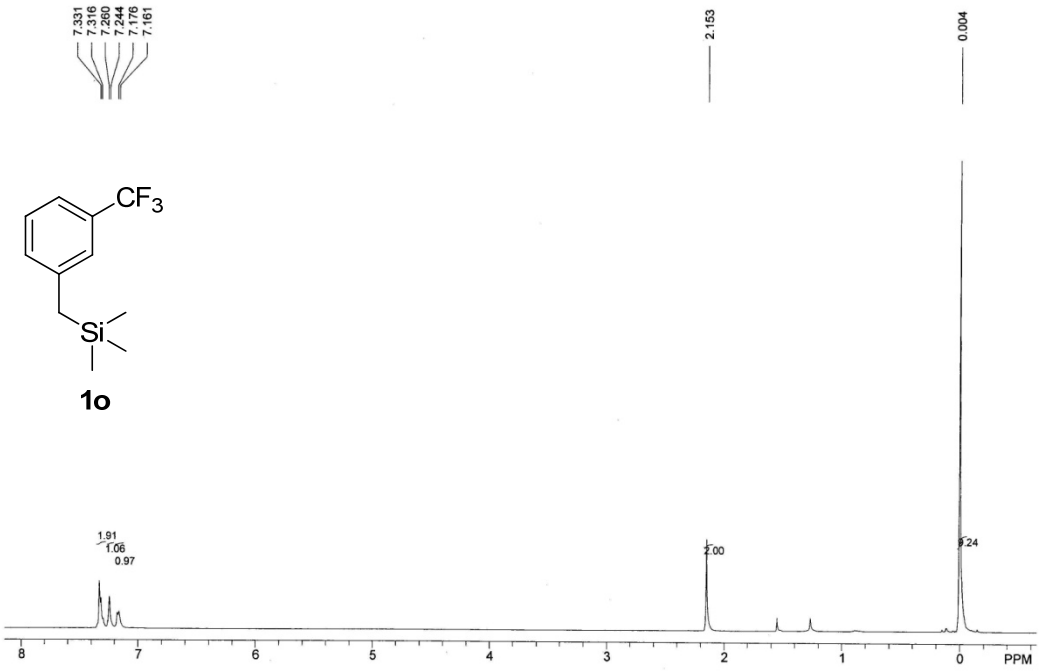
Ph2P=O
Si
1i
300
200
100
0
-100
-200
-300
PPM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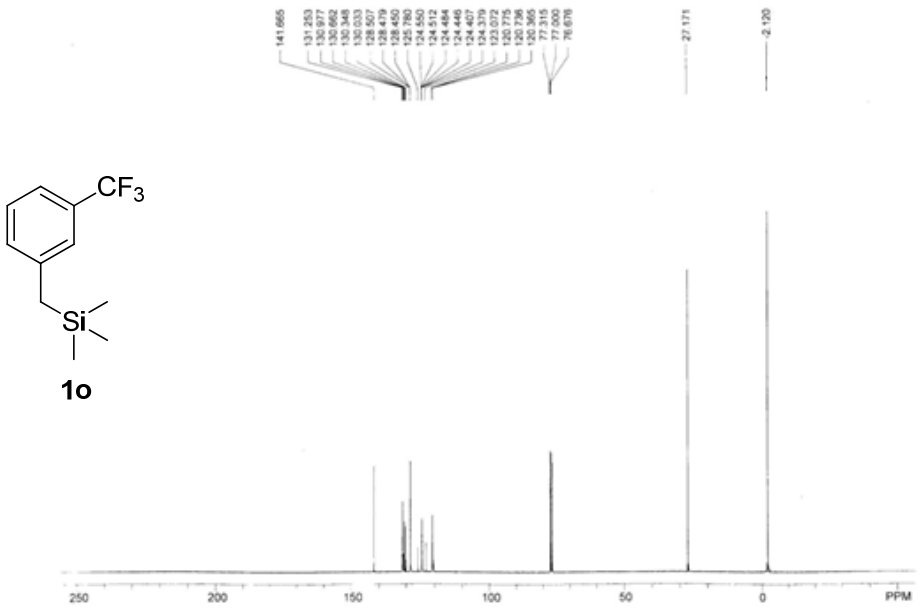
7.316
7.260
7.244
7.176
7.161
2.153
0.004
CF3
Si
1o
1.91
1.06
0.97
2.00
9.24
8
7
6
5
4
3
2
1
0
PPM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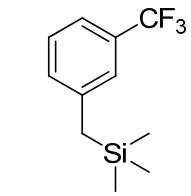
131.253
130.977
130.662
130.348
130.033
128.507
128.419
128.405
125.780
124.550
124.512
124.484
124.446
124.407
124.379
124.272
120.775
120.738
120.365
77.315
77.000
76.676
27.171
-2.120
CF3
Si
1o
250
200
150
100
50
0
PPM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Si

1o

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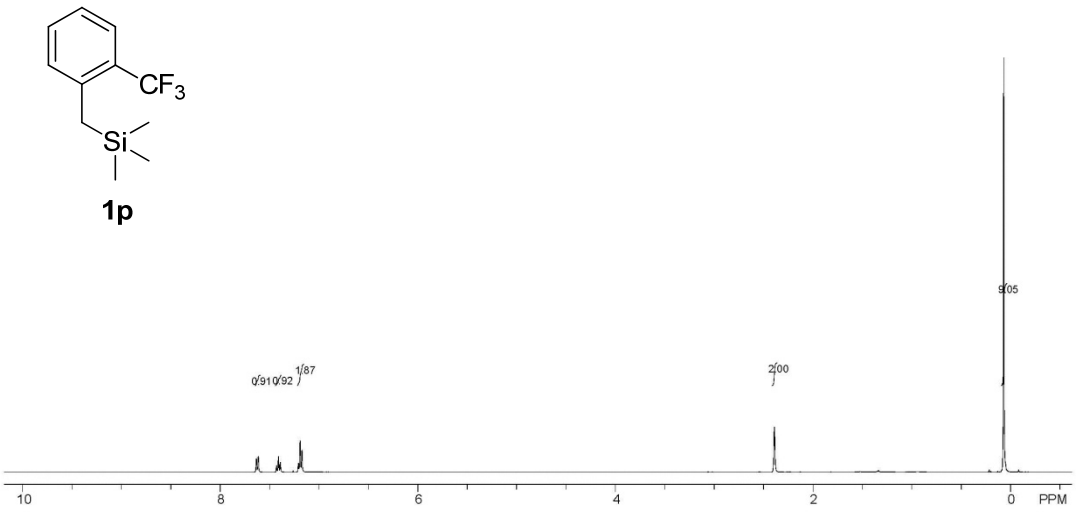
100
50
0
-50
-100
PPM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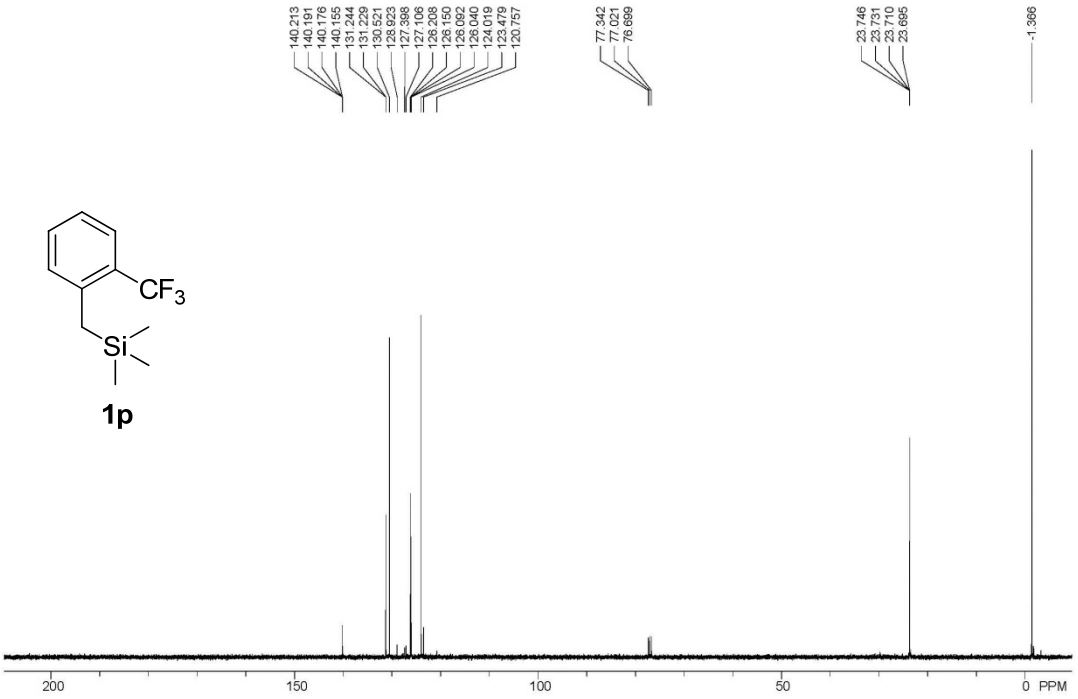
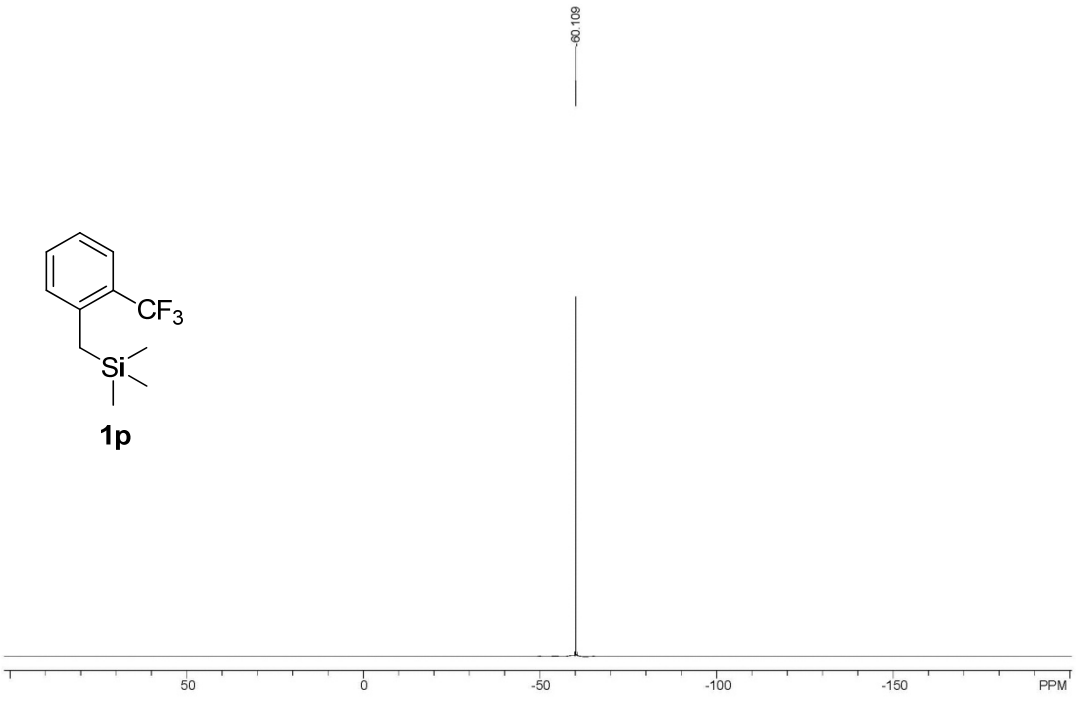
7.614
7.430
7.411
7.392
7.209
7.192
7.173
2.391
0.070
9.05
0.91
0.92
1.87
2.00
10
8
6
4
2
0
PPM

CF3
Si

1p


140.213
140.191
140.176
140.155
131.244
131.229
130.521
128.923
127.398
127.106
126.208
126.150
126.092
126.040
124.019
123.479
120.757
77.342
77.021
76.699
23.746
23.731
23.710
23.695
1.366
CF3
Si
200
150
100
50
0 PPM

1p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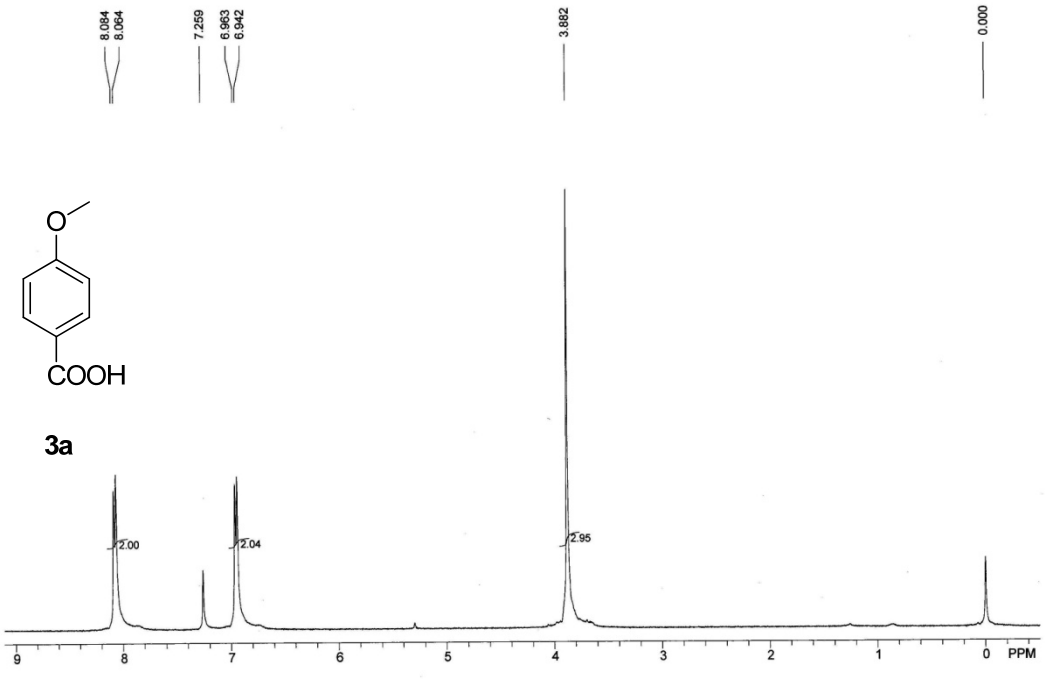
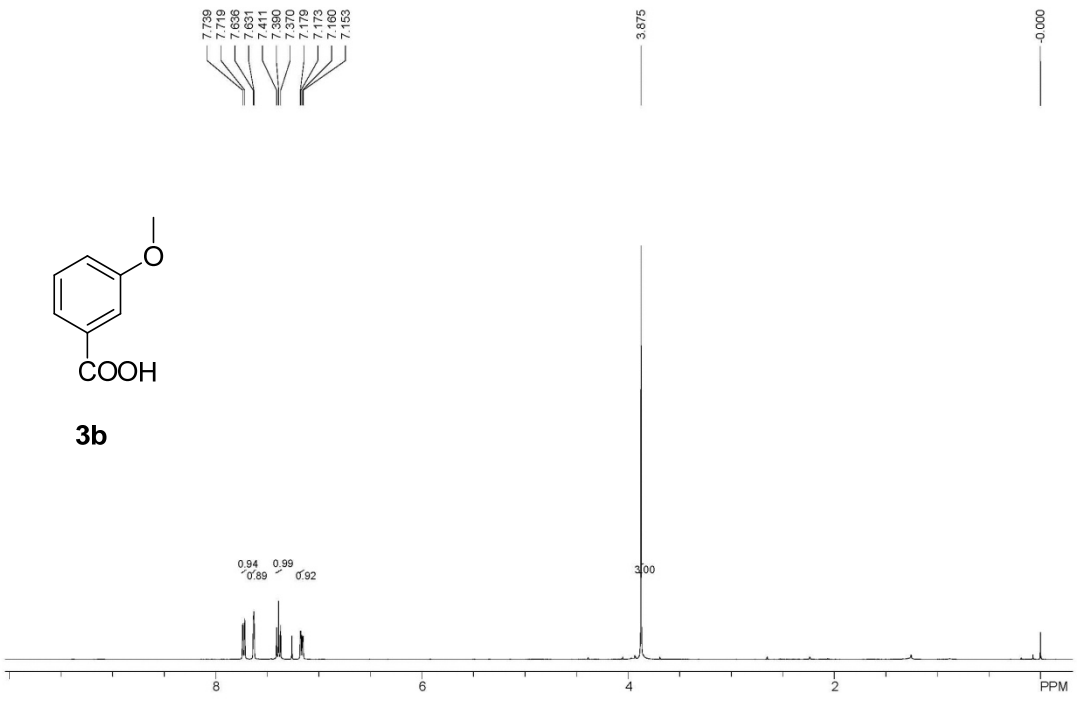
Si
50
0
-50
-100
-150
PPM

1p


8.084
8.064
7.259
6.963
6.942
3.882
0.000
O
COOH
2.00
2.04
2.95
9
8
7
6
5
4
3
2
1
0
PPM

3a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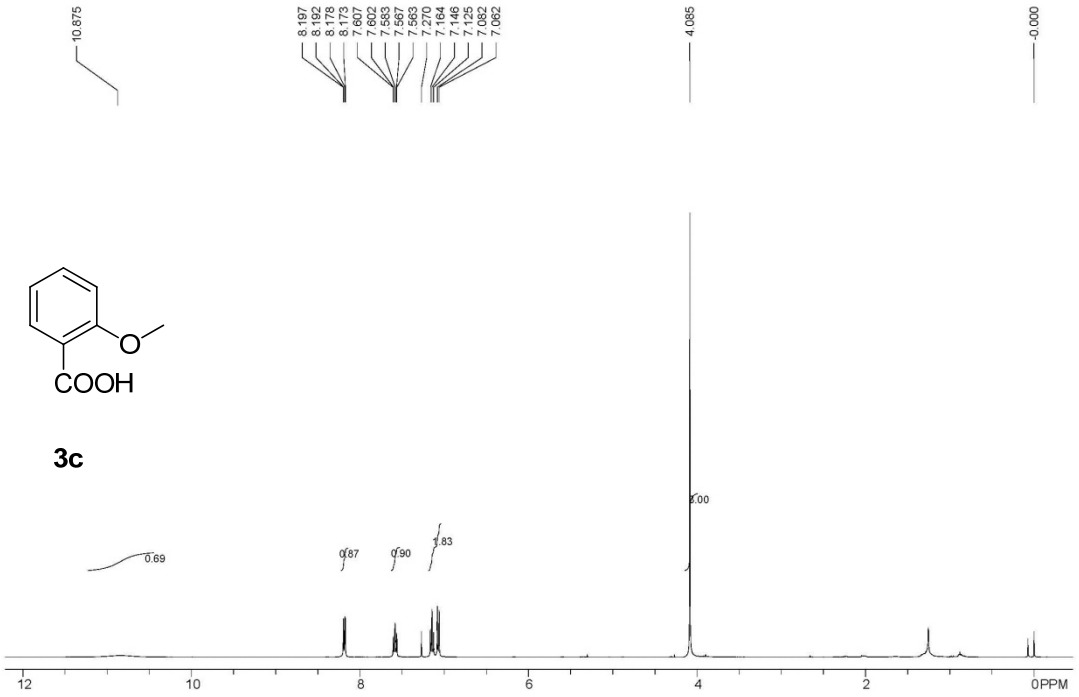
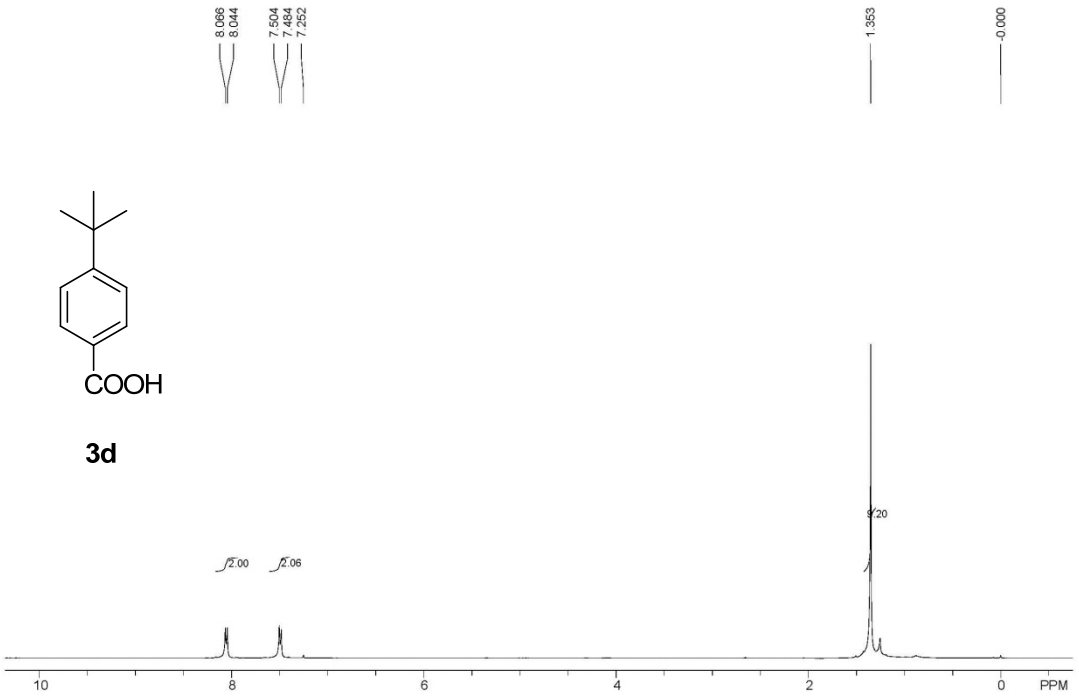
7.719
7.636
7.631
7.411
7.390
7.370
7.179
7.173
7.160
7.153
3.875
0.000
O
COOH
0.94
0.89
0.99
0.92
3.00
8
6
4
2
PPM

3b


10.875
8.197
8.192
8.178
8.173
7.607
7.602
7.583
7.567
7.563
7.270
7.164
7.146
7.125
7.082
7.062
4.085
-0.000
O
COOH
0.69
0.87
0.90
1.83
3.00
12
10
8
6
4
2
0PPM

3c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7.504
7.484
7.252
1.353
-0.000
COOH
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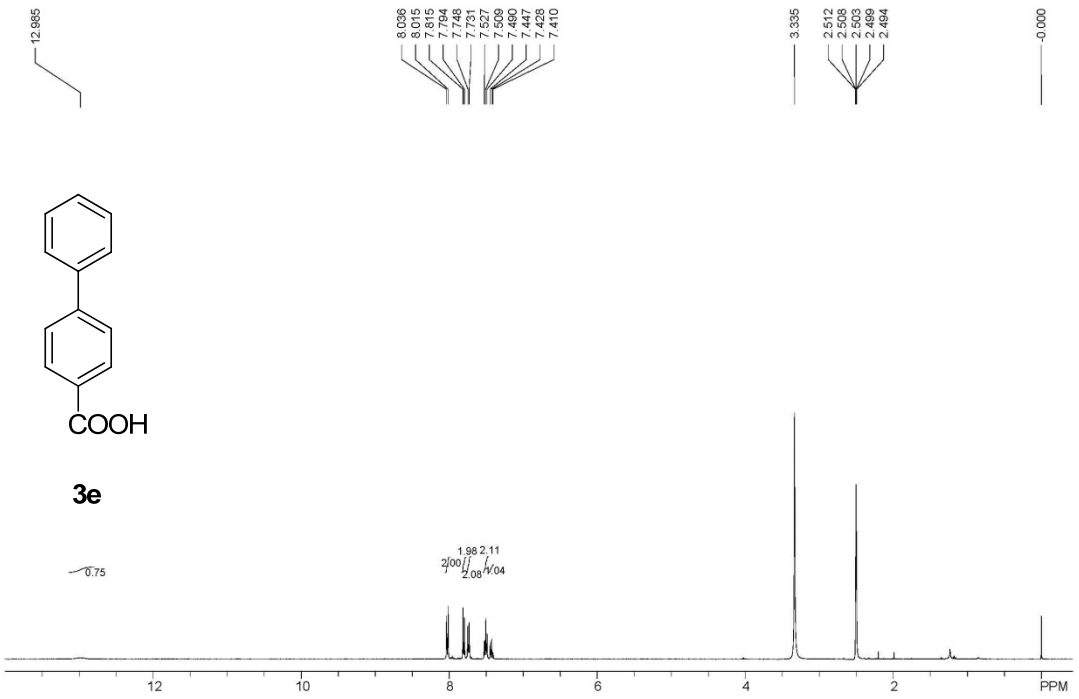
2.06
9.20
10
8
6
4
2
0
PPM

3d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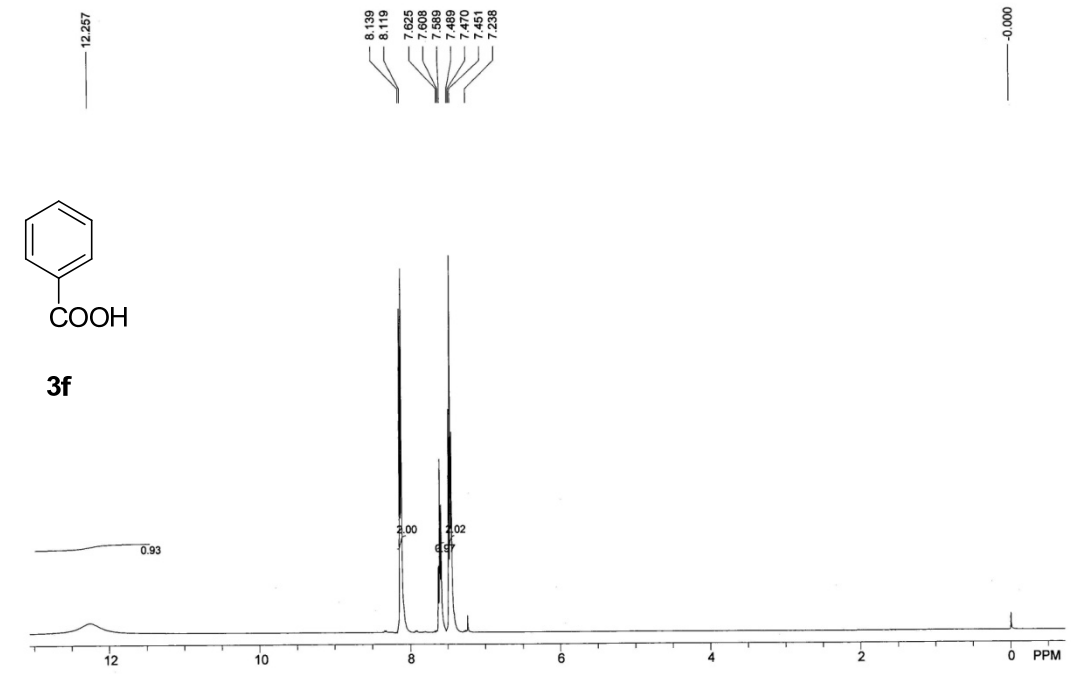
8.015
7.815
7.794
7.748
7.731
7.527
7.509
7.490
7.447
7.428
7.410
3.335
2.512
2.508
2.503
2.499
2.494
-0.000
COOH
0.75
1.98
2.11
2.00
2.08
2.04
12
10
8
6
4
2
PPM

3e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8.119
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7.608
7.589
7.489
7.470
7.451
7.238
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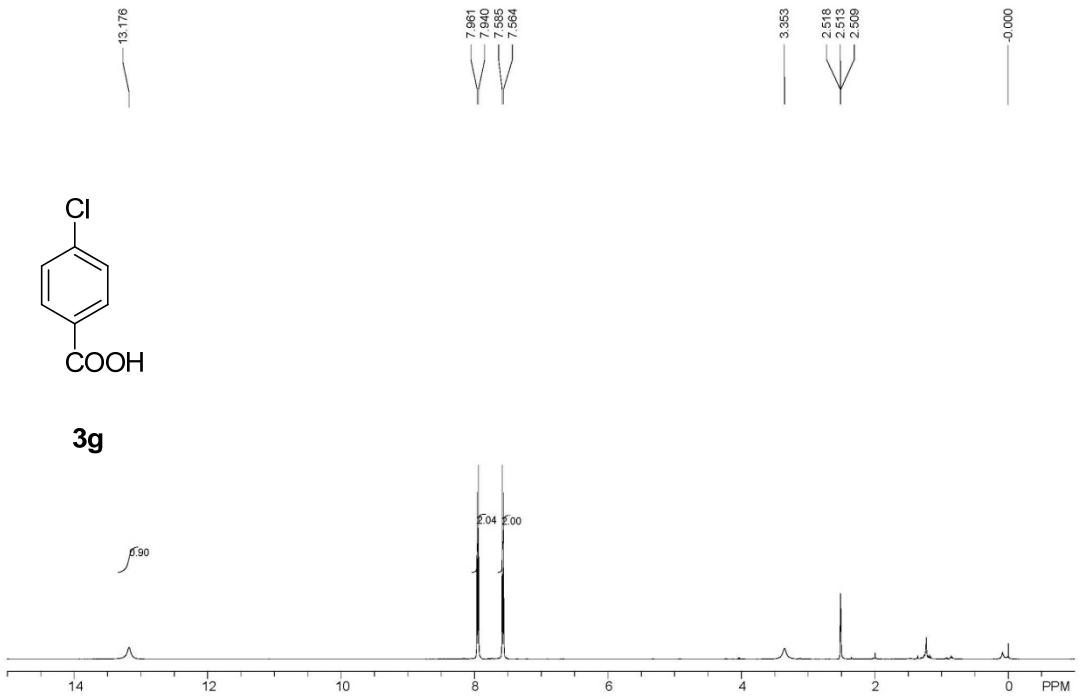
COOH
0.93
2.00
2.02
6.97
12
10
8
6
4
2
0
PPM

3f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7.940
7.585
7.564
3.353
2.518
2.513
2.509
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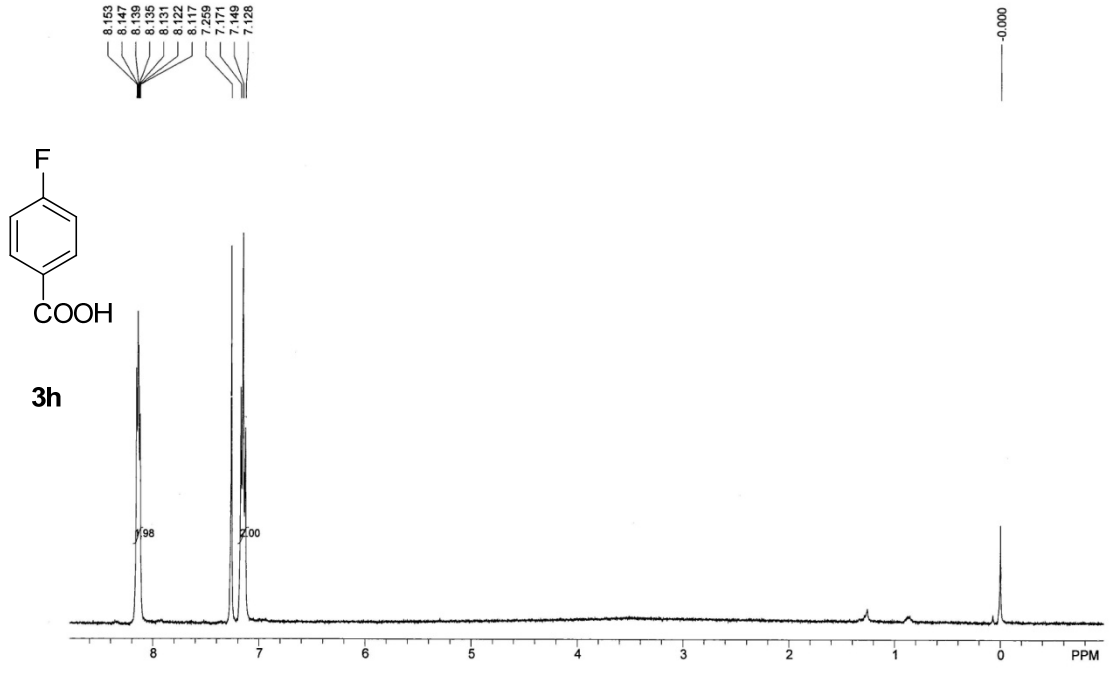
Cl
COOH
3g
0.90
2.04
2.00
14
12
10
8
6
4
2
0
PPM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8.131
8.122
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7.259
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7.149
7.128
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COOH
3h
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2.00
8
7
6
5
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3
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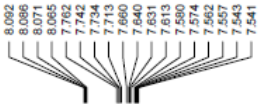
1
0
PPM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8.065
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7.562
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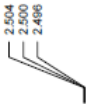
7.543
7.541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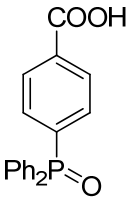
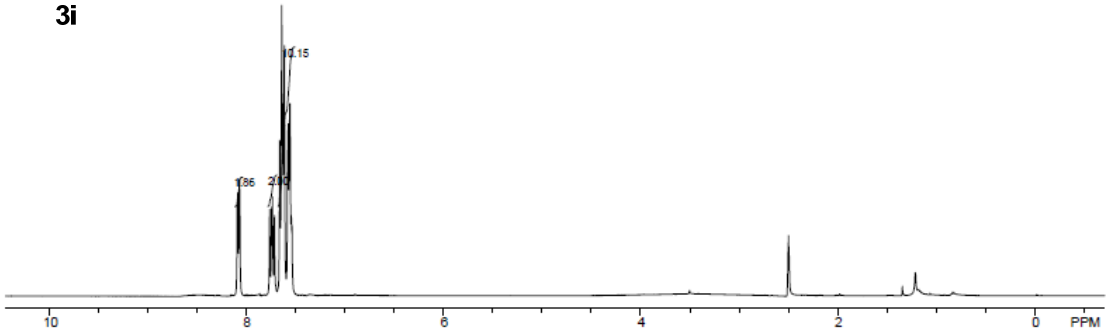
2.500
2.496


COOH
Ph2P
O

3i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8
6
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2
0
PPM


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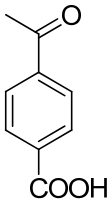
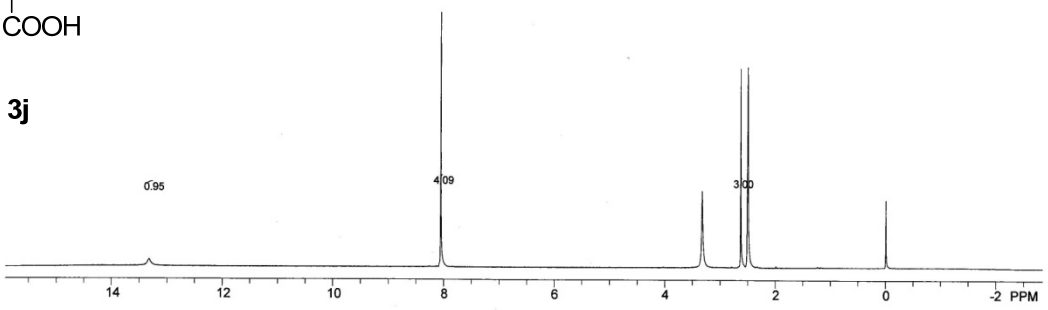
0.000


O
COOH

3j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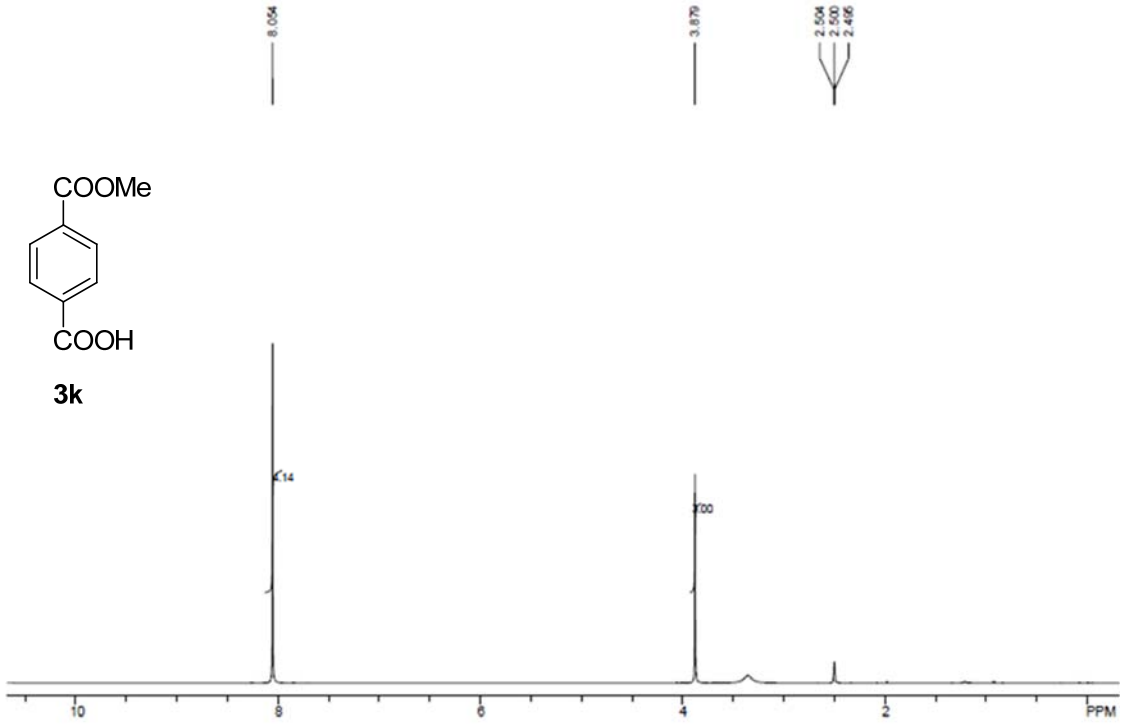
3.00
14
12
10
8
6
4
2
0
-2 PPM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2.496
COOMe
COOH
3k
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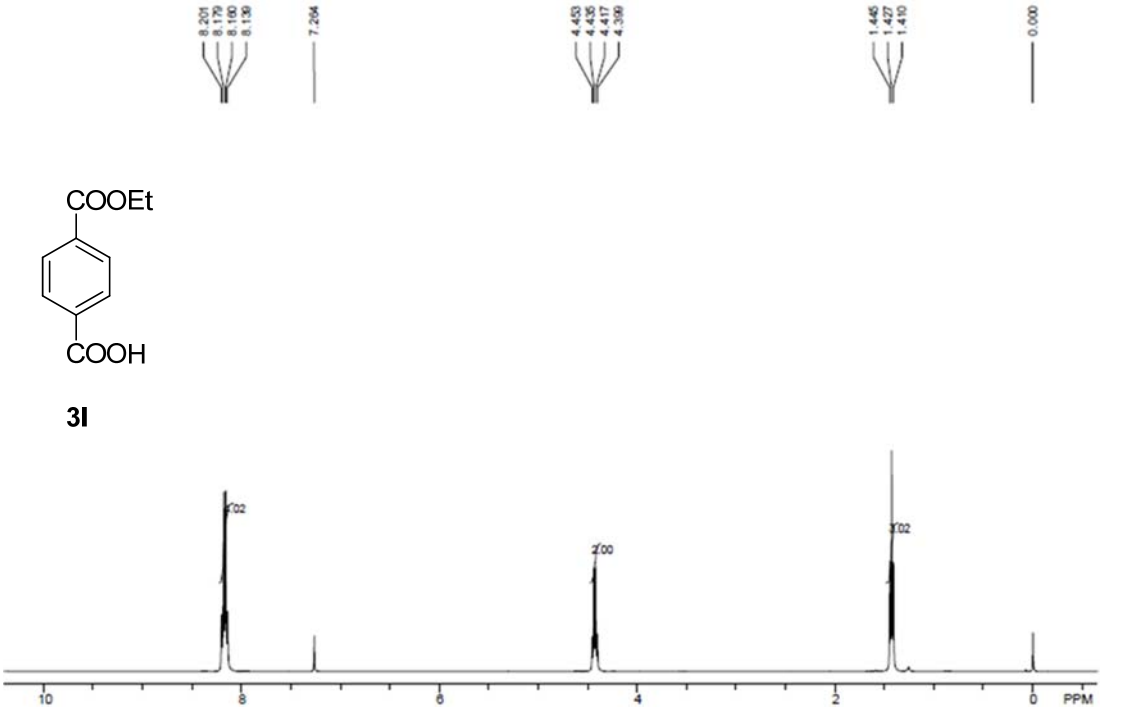
2.00
10
8
6
4
2
PPM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1.427
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COOH
3l
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2.00
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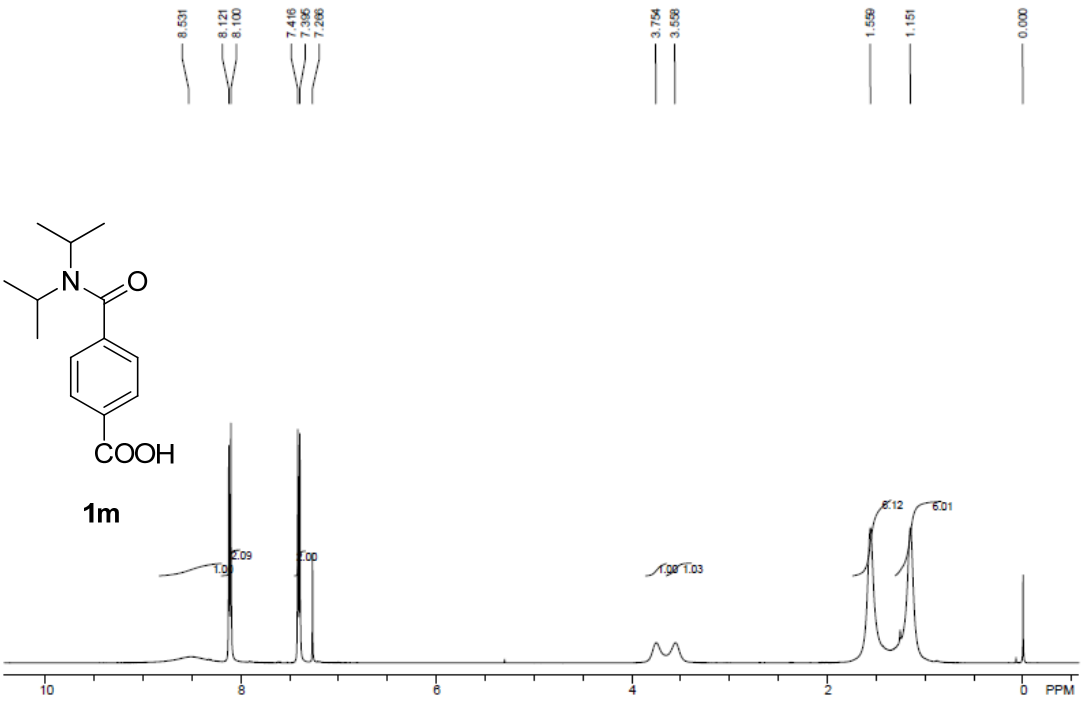
10
8
6
4
2
0
PPM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7.266
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3.558
1.559
1.151
0.000
N
O
COOH
1m
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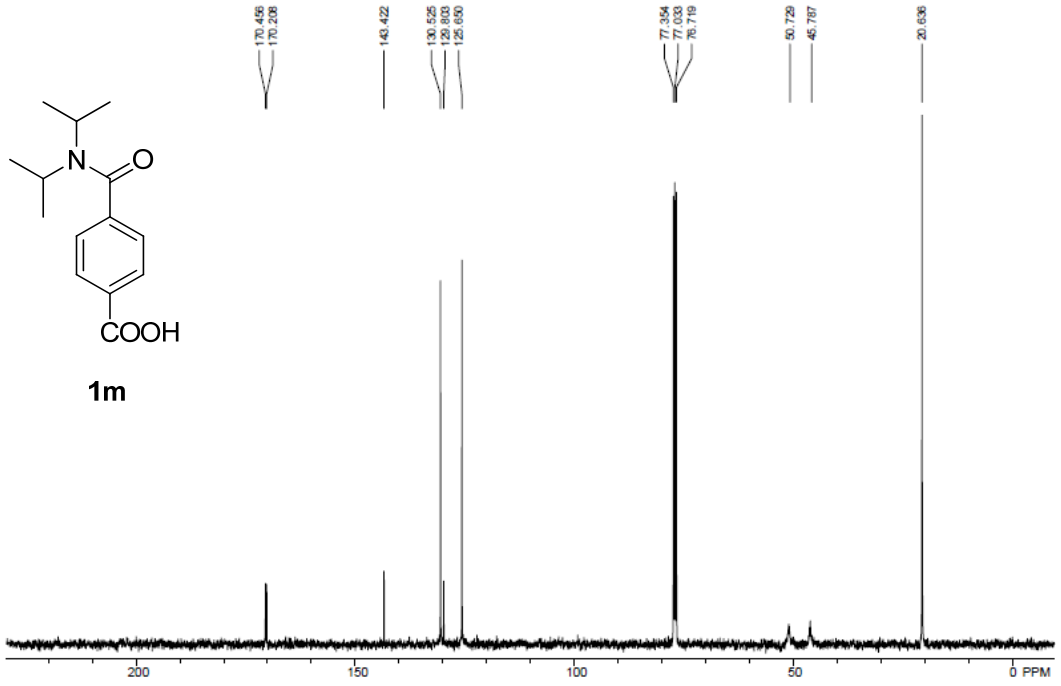
2.00
1.00
1.03
6.12
6.01
10
8
6
4
2
0
PPM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129.803
125.650
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77.033
76.719
50.729
45.787
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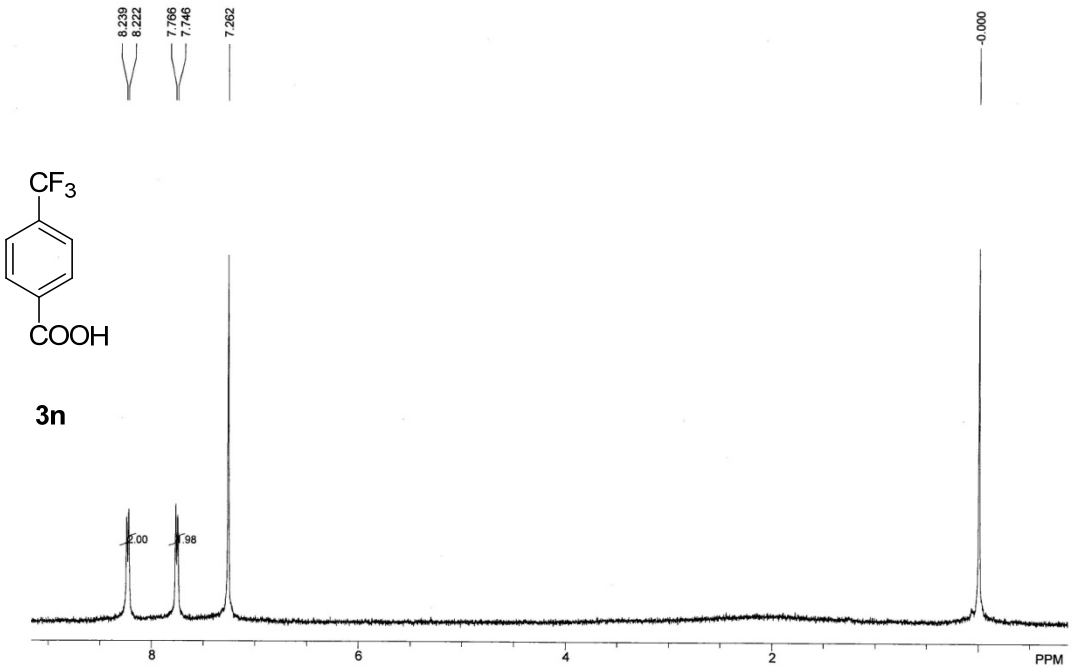
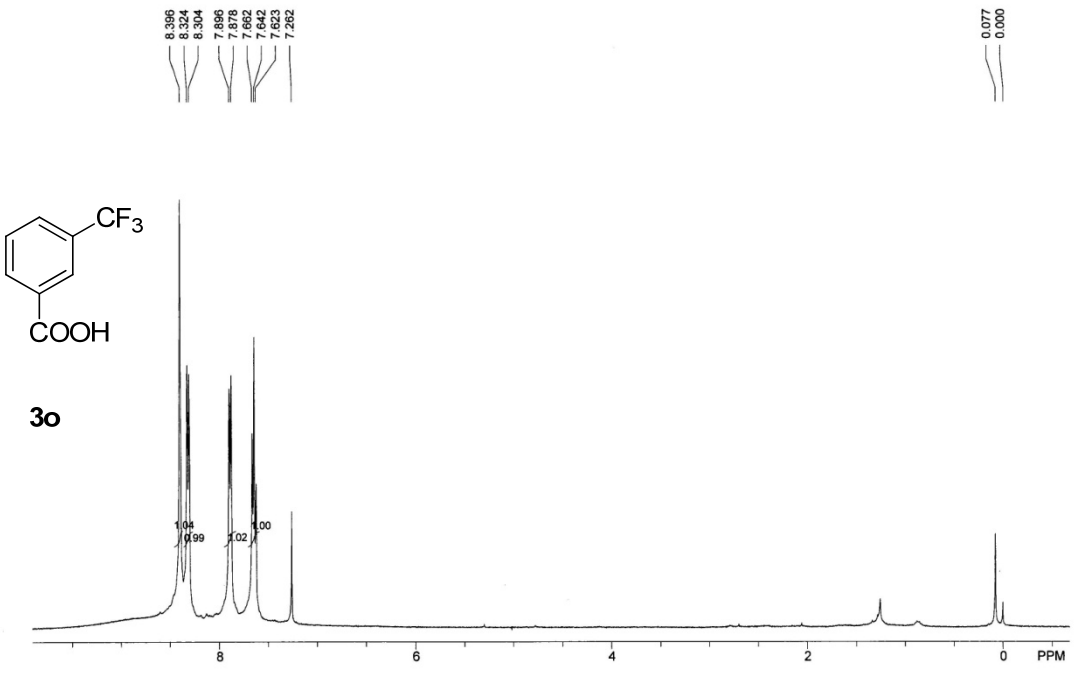
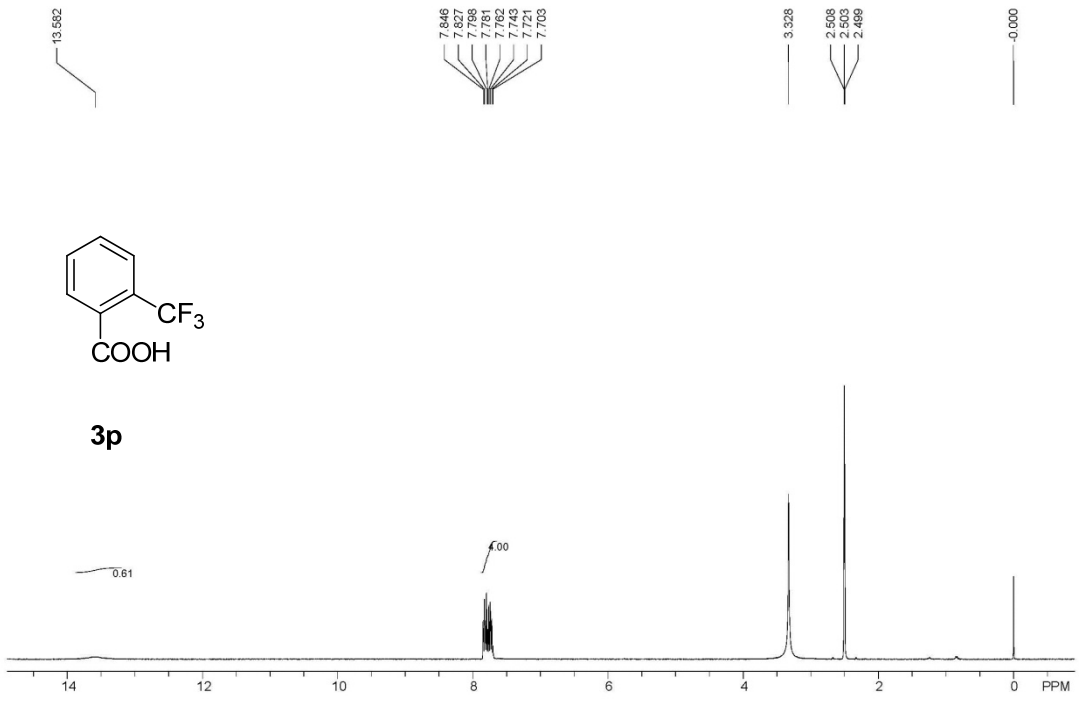
O
COOH
1m
200
150
100
50
0
PPM


8.239
8.222
7.766
7.746
7.262
0.000
CF3
COOH
3n
2.00
1.98
8
6
4
2
PPM


8.396
8.324
8.304
7.896
7.878
7.662
7.642
7.623
7.262
0.077
0.000
CF3
COOH
3o
1.04
0.99
1.02
1.00
8
6
4
2
0
PPM


13.582
7.846
7.827
7.798
7.781
7.762
7.743
7.721
7.703
3.328
2.508
2.503
2.499
0.000
CF3
COOH
3p
0.61
4.00
14
12
10
8
6
4
2
0
PPM

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