Supporting information

Room-Temperature Cobalt-Catalyzed Arylation of Aromatic Acid: Overriding *Ortho*-Selectivity via Oxidative Assembly of Carboxylate and Aryl Titanate Reagents Using Oxygen

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General remarks.

All NMR spectra were collected using a 400 MHz (100 MHz for ^{13}C spectroscopy) and all spectra recorded with tetramethylsilane as an internal standard unless otherwise noted. High resolution mass spectra (HRMS) were obtained with a microTOF (ESI). Infrared data were acquired using an FT-IR spectrophotometer. Melting points were recorded on a microscopic instrument and uncorrected.

The corresponding glassware used for aryl magnesium reagents or lithium reagents was oven dried (120 ^{o}C) and cooled under a stream of argon gas. Aryl Grignard reagents such as phenyl magnesium or 4-methoxyphenyl magnesium were prepared according to standard procedure. Functionalized aryl Grignard reagents such as 2-cyanophenyl magnesium chloride or 4-(ethoxycarbonyl)phenyl magnesium chloride were prepared via iodine-magnesium exchange using *i*-PrMgCl·LiCl according to Knochel's method.[1] All the Grignard reagents were titrated before use.[2]

Typical procedure (3ad)

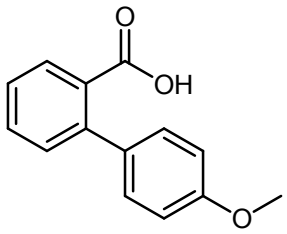
Under Ar atmosphere, a solution of *i*-PrMgCl·LiCl (5 mmol, 1.0 M in THF) was added dropwise to a solution of ethyl 4-iodobenzoate (1380 mg, 5 mmol) in 10 mL THF at –40 ^{o}C and stirred for 1h at that temperature. A solution of $Ti(OEt)_4$ (570 mg, 2.5 mmol) in 10 mL THF added dropwise to that mixture. The stirring was continued for 1 h and then the temperature was allowed to come to 0 ^{o}C.

In another three neck flask, a solution of $Ti(OEt)_4$ (570 mg, 2.5 mmol) in 10 mL THF was added dropwise to 5 mmol Lithium (2-carboxylatophenyl) lithium (prepared from benzoic acid via direct metalation using 2.2 equiv. s-BuLi/TMEDA (1:1) according to the literature[3]). The temperature of this mixture was allowed to come to 0 ^{o}C during 1 h. The above-prepared Grignard reagent was added in and stirred at room temperature for 0.5 h. To the resulting mixture a solution of $CoCl_2$ (48.8 mg, 0.38

mmol), DMPU (195 mg, 1.5 mmol) in THF (5 ml) was added in at one portion. The Ar atmosphere was changed into O_2 atmosphere (applied by an oxygen bag). The thus-obtained mixture was stirred at room temperature until the completion of the reaction (monitored by TLC). The reaction was quenched with diluted HCl solution and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated to yield the crude compound, which was purified by column chromatography to yield the desired product **3ad**.

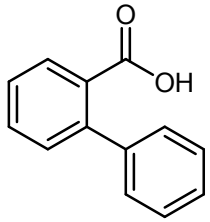
Characterization Data

4'-Methoxy-[1,1'-biphenyl]-2-carboxylic acid (3aa)



As described in the typical procedure for **3ad**, the product was isolated as a white solid in 75% yield. m.p. = 136–138 °C (lit. 138–140 °C); R_f = 0.35 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 2977, 1701, 1609, 1243; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 7.92 (d, J =7.6 Hz, 1H) , 7.52–7.56 (m, 1H), 7.35–7.39 (m, 2H) , 7.26 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) (ppm) 169.8, 158.6, 140.4, 133.0, 132.3, 130.6, 130.3, 129.4, 128.9, 126.7, 113.6, 55.1. Data was consistent with that reported in the literature. [4]

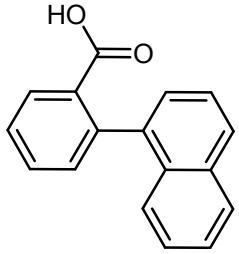
[1,1'-Biphenyl]-2-carboxylic acid (3ab)



As described in the typical procedure for **3ad**, the product was isolated as a white solid in 80% yield. m.p. = 110–112 °C (lit. 108–110 °C); R_f = 0.34 (petroleum

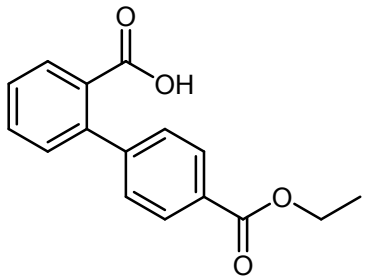
ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 1693, 1596, 1483, 1295, 750, 700; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 7.94 (d, J = 7.5 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.35–7.44 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 173.8, 143.5, 141.0, 134.8, 132.4, 131.2, 130.7, 129.3, 128.5, 128.1, 127.3, 127.22, 127.18. Data was consistent with that reported in the literature. [4]

2-(Naphthalen-1-yl)benzoic acid (3ac)



As described in the typical procedure for **3ad**, the product was isolated as a white solid in 72% yield. m.p. = 174.4–175.6 °C (lit. 174–175 °C); R_f = 0.32 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3410, 3056, 1701, 1602, 1303, 754; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 11.48 (br s, 1H), 8.13–8.11 (m, 1H), 8.06–7.83 (m, 2H), 7.68–7.60 (m, 1H), 7.53–7.42 (m, 3H), 7.38–7.29 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 171.3, 142.2, 139.3, 134.9, 133.5, 132.5, 132.4, 132.3, 130.0, 128.2, 127.7, 127.3, 126.1, 126.0, 125.6, 125.5, 125.2. Data was consistent with that reported in the literature.[5]

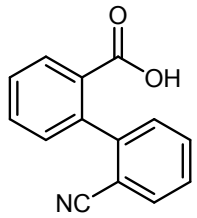
4'-(Ethoxycarbonyl)-[1,1'-biphenyl]-2-carboxylic acid (3ad)



As described in the typical procedure for **3ad**, the product was isolated as a white solid in 73% yield. m.p. = 113.6–114.3 °C; R_f = 0.42 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3392, 3061, 2987, 1705, 1693, 1280, 754; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 8.07 (d, J = 8.2Hz, 1H), 8.00 (d, J = 1.1Hz,

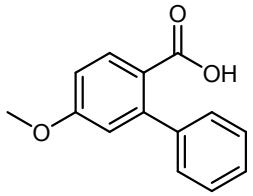
1H), 7.99 (d, J = 1.1 Hz, 1H), 7.61–7.57 (m, 1H), 7.48–7.45 (m, 1H), 7.40–7.34 (m, 3H), 4.40 (q, J = 7.2 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 172.2, 166.5, 145.8, 142.6, 132.3, 131.04, 131.00, 129.4, 129.3, 128.9, 128.5, 127.8, 61.0, 14.4. Data was consistent with that reported in the literature.[6]

2'-Cyano-[1,1'-biphenyl]-2-carboxylic acid (3ae)



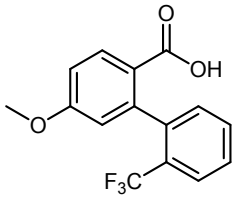
As described in the typical procedure for **3ad**, the product was isolated as a white solid in 65% yield. m.p. = 170.4–172.3 °C (lit. 170–172 °C); R_f = 0.38 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3433, 3267, 3051, 2229, 1701, 1602, 1433, 1384, 1095, 692, 521; ^{1}H NMR ($CDCl_3$, 400 MHz) (ppm) 8.12 (d, J = 7.4 Hz, 1H), 7.63–7.58 (m, 3H), 7.48 (t, J = 7.8 Hz, 1H), 7.34–7.24 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 171.0, 135.0, 134.9, 133.7, 132.2, 132.1, 130.2, 130.0, 128.6, 128.52, 128.49, 127.9, 119.2, 117.6. Data was consistent with that reported in the literature.[7]

5-Methoxy-[1,1'-biphenyl]-2-carboxylic acid (3bb)



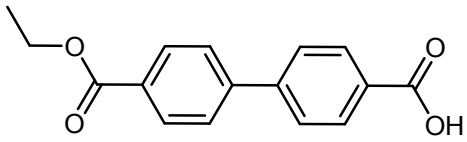
As described in the typical procedure for **3ad**, the product was isolated as a white solid in 71% yield. m.p. = 174.6–174.8 °C (lit. 171-173 °C); R_f = 0.33 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3431, 2918, 1697, 1602, 1317, 1114, 754; ^{1}H NMR ($CDCl_3$, 400 MHz) (ppm) 8.02 (d, J = 8.7 Hz, 1H), 7.39–7.31 (m, 5H), 6.94–6.91 (m, 1H), 6.28 (d, J = 2.6 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 171.7, 162.4, 146.4, 141.4, 133.5, 128.4, 127.9, 127.4, 120.3, 116.7, 112.7, 55.5. Data was consistent with that reported in the literature.[8]

5-Methoxy-2'-(trifluoromethyl)-[1, 1'-biphenyl]-2-carboxylic acid [9] (3bf)



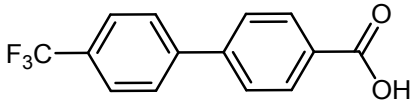
As described in **3bb**, the product was isolated as a yellow solid in 75% yield. m.p. = 115.3–116.2 °C; R_f = 0.36 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3400, 2954, 1691, 1676. 1602, 1317, 1168, 763; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 8.07 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.52–7.42 (m, 2H), 7.19 (d, J = 7.5 Hz, 1H), 6.96–6.93 (m, 1H), 6.73,(d, J = 2.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 170.8, 162.6, 143.6, 140.4, 133.3, 130.9, 130.4, 128.0–127.3 (q), 127.2, 125.7–125.6 (q), 125.2, 123.0, 120.8 (d), 113.2, 55.5.

4'-(Ethoxycarbonyl)-[1, 1'-biphenyl]-4-carboxylic acid (3cd)



The Grignard reagent of 4-Iodobenzoic acid was prepared via I-Mg exchange method following the general procedure for **3ad**. The product was isolated as a white solid in 77% yield. m.p. = 185.7–187.4 °C; R_f = 0.46 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3437, 3072, 2981, 1707, 1674, 1606, 1274, 1099, 756; ^1H NMR (DMSO-d_6, 400 MHz) (ppm) 13.11 (br s, 1H), 8.08–8.06 (m, 4H), 7.90–7.86 (m, 4H), 4.35 (q, J = 7.0 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) (ppm) 167.5, 165.9, 143.9, 143.4, 130.9, 130.5, 130.3, 130.0, 127.7, 127.6, 61.3, 14.6. Data was consistent with that reported in the literature.[10]

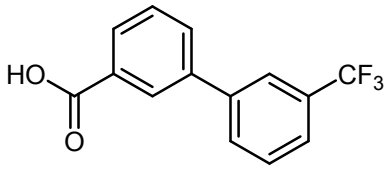
4'-(Trifluoromethyl)-[1, 1'-biphenyl]-4-carboxylic acid (3cg)



As described in **3cd**, the product was isolated as a yellow solid in 88% yield. m.p. = 120.6–121.7 °C (lit. 120.0–121.1 °C); R_f = 0.43 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3412, 3078, 1689, 1608, 1323, 1128, 1070, 835; ^1H NMR (DMSO-d_6, 400 MHz) (ppm) 13.06 (br s, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.96 (d,

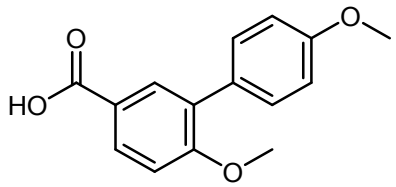
J = 7.9 Hz, 2H), 7.89–7.85 (m, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz) (ppm) 167.5, 143.5, 143.1, 131.0, 130.5, 128.3, 127.8, 126.3(d), 125.8, 123.7. Data was consistent with that reported in the literature.[11]

3'-(Trifluoromethyl)-[1, 1'-biphenyl]-3-carboxylic acid (3dh)



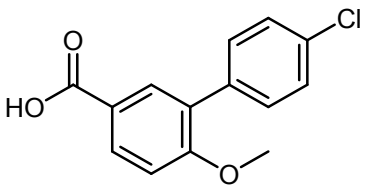
As described in **3cd**, the product was isolated as a yellow solid in 76% yield. m.p. = 163.4–164.5 °C; R_f = 0.37 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3431, 3088, 1701, 1685, 1568, 1313, 1124, 750; ^{1}H NMR ($CDCl_3$, 400 MHz) (ppm) 8.35 (s, 1H), 8.25 (s, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.87–7.80 (m, 1H), 7.75–7.73 (m, 1H), 7.67–7.57 (m, 1H), 7.36 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 170.9, 140.2, 136.8, 133.2, 132.5, 131.2, 130.5, 130.1, 129.7, 129.5, 129.3, 128.8, 124.0, 122.6. Data was consistent with that reported in the literature.[12]

4', 6-Dimethoxy-[1,1'-biphenyl]-3-carboxylic acid[13] (3ba)



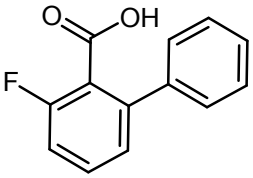
4-Methoxybenzoic acid was lithiated n-BuLi/t-BuOLi according to the reported procedure[14] and the cross-coupling was conducted as described in **3ad**. The product was isolated as a white solid in 69% yield. m.p. = 167.4–168.3 °C; R_f = 0.33 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3433, 3034, 2984, 1695, 1602, 1257, 1026, 823; ^{1}H NMR ($CDCl_3$, 400 MHz) (ppm) 8.09–8.07 (m, 2H), 7.48 (d, *J* = 6.6 Hz, 2H), 7.01 (d, *J* = 9.2 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 171.4, 160.9, 159.0, 132.8, 131.1, 130.6, 130.4, 129.7, 121.6, 113.6, 110.6, 55.8, 55.3.

4'-Chloro-6-methoxy-[1, 1'-biphenyl]-3-carboxylic acid (3bi)



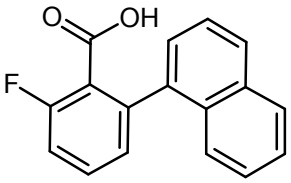
As described in **3ba**, the product was isolated as a white solid in 55% yield. m.p. = 187.4–188.3 °C; R_f = 0.35 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3431, 3292, 1685, 1606, 1435, 1271, 1024, 628; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 8.11 (dd, J = 8.6 Hz, 2.2 Hz, 1H), 8.05 (d, J = 2.2 Hz, 1H), 7.47 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.7 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 171.1, 160.8, 135.5, 132.8, 131.8, 131.4, 130.8, 128.3, 121.7, 111.1, 110.8, 56.5. MS (HRMS) *m/z* calcd. for $C_{14}H_{11}ClO_3$ 261.0324 $[M-H]^-$, found 261.0313.

3-Fluoro-[1, 1'-biphenyl]-2-carboxylic acid (3eb)



2-Fluorobenzoic acid was lithiated using 2.2 equiv. *s*-BuLi at –78 °C and the cross-coupling was conducted following the general procedure for **3ad**. The product was isolated as a white solid in 81% yield. m.p. = 115.3–117.5 °C (lit. 115–117 °C); R_f = 0.40 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3412, 3011, 1707, 1614, 1462, 1257, 756; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 7.62–7.42 (m, 6H), 7.31 (dd, J = 8.3 Hz, 2.5 Hz, 1H), 7.13 (t, J = 9.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 170.9, 160.9, 142.9, 132.8, 132.4, 131.8, 128.6, 128.3, 128.2, 125.9, 114.9. Data was consistent with that reported in the literature.[15]

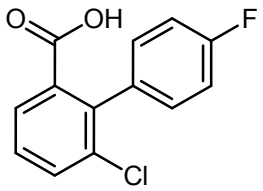
2-Fluoro-6-(naphthalen-1-yl)benzoic acid (3ec)



As described in **3eb**, the product was isolated as a white solid in 76% yield .m.p. = 178.4–180.0 °C; R_f = 0.40 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR

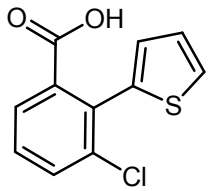
(cm^{-1}, KBr): 3433, 3066, 1701, 1602, 1303, 754; ^{1}H NMR ($CDCl_3$, 400 MHz) (ppm) 9.23 (br s, 1H), 8.06–8.02 (m, 1H), 7.90–7.60 (m, 4H), 7.50–7.18 (m, 4H), 7.16–7.11 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 169.0, 161.6, 135.8, 135.7, 132.8, 132.54, 132.46, 129.0, 124.17, 124.15, 120.4, 117.3, 117.1, 115.2, 115.1. MS (HRMS) *m/z* calcd. for $C_{17}H_{11}FO_2$ 265.0670 [M-H]$^-$, found 265.0667.

6-Chloro-4'-fluoro-[1, 1'-biphenyl]-2-carboxylic acid (3fj)



3-Chlorobenzoic acid was lithiated using 2.2 equiv. TMPLi according to the reported procedure[16] and the cross-coupling was conducted following the general procedure for **3ad**. The product was isolated as a white solid in 77% yield. m.p. = 116.7–116.9 °C; R_f = 0.37 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3421, 3074, 1703, 1512, 1436, 702; ^{1}H NMR ($CDCl_3$, 400 MHz) (ppm) 11.22 (br s, 1H), 7.89 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.66 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.41–7.39 (m, 1H), 7.21–7.17 (m, 2H), 7.10 (t, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 172.1, 163.4, 140.5, 133.9, 133.6, 132.0, 130.7, 130.6, 129.9, 128.6, 115.1. MS (HRMS) *m/z* calcd. for $C_{13}H_8ClFO_2$ 249.0124 [M-H]$^-$, found 249.0139.

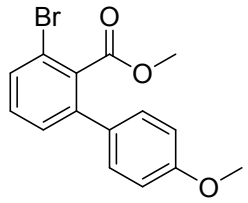
3-Chloro-2-(thiophen-2-yl)benzoic acid (3fk)



As described in **3fj**, the product was isolated as a yellow solid in 67% yield. m.p. = 108.8–109.4 °C; R_f = 0.34 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3527, 3068, 1665, 1608, 1433, 1253, 750; ^{1}H NMR ($CDCl_3$, 400 MHz) (ppm) 10.94 (br s, 1H), 7.88 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.71 (dd, *J* = 7.7 Hz, 1.5 Hz, 1H), 7.21–7.17 (m, 2H), 7.39 (t, *J* = 7.9 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 171.0, 157.9, 141.5, 137.8, 137.0, 132.5, 129.4,

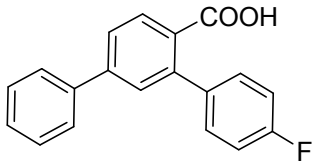
129.1, 128.9, 122.5, 119.7. MS (HRMS) *m/z* calcd. for $C_{11}H_7ClO_2S$ 236.9783 $[M-H]^-$, found 236.9779.

Methyl 3-bromo-4'-methoxy-[1, 1'-biphenyl]-2-carboxylate (3ga)



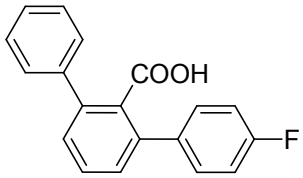
The lithium reagent of 2-bromobenzoic acid was prepared using 2 equiv. TMPLi according to the reported procedure[17] and the cross-coupling was conducted following the general procedure. The product acid was esterified using methanol and isolated as a yellow solid in 49% yield. m.p. = 87.8–89.4 °C; R_f = 0.48 (petroleum ether/ethyl acetate = 20:1). IR (cm^{-1}, KBr): 3031, 2987, 1723, 1608, 1512, 1381, 764; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 7.54 (dd, *J* = 6.3 Hz, 2.8 Hz, 1H), 7.31–7.29 (m, 4H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 168.4, 159.5, 141.5, 135.2, 131.7, 131.0, 130.5, 129.5, 128.7, 119.6, 113.9, 55.3, 52.5. Anal. Calcd. for $C_{15}H_{13}BrO_3$: C, 56.10; H, 4.08. Found: C, 56.22; H, 3.99. MS (ESI): $[M+H]^+$ [m/z 322 (100%), 320 (31%)].

4''-Fluoro-[1,1':3',1''-terphenyl]-4'-carboxylic acid (3hj)



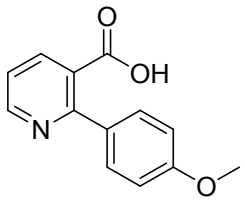
Biphenyl-4-carboxylic acid was lithiated using *s*-BuLi/TMEDA according to the reported method[18] and the cross-coupling was conducted following the general procedure. The product was isolated as a white solid in 85% yield. m.p. = 215.7–216.4 °C; R_f = 0.34 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3402, 3011, 1690, 1484, 1197, 764; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 8.22 (d, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.31–7.13 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 168.1, 161.5, 141.9, 140.4, 135.4, 135.3, 131.6, 131.4, 129.0, 128.32, 128.27, 128.1, 127.63, 127.56, 115.6. Anal. Calcd. for $C_{19}H_{13}FO_2$: C, 78.07; H, 4.48. Found: C, 78.25; H, 4.29. MS (ESI): $[M+H]^+$ (m/z 293).

4-Fluoro-[1, 1':3', 1''-terphenyl]-2'-carboxylic acid (3ij)



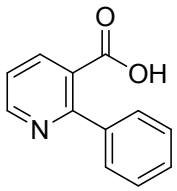
The product was prepared as described in **3hj** and isolated as a white solid in 76% yield. m.p. = 243.4–245.1 °C; R_f = 0.37 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3443, 3030, 1687, 1593, 1217, 833; ^1H NMR ($CDCl_3$, 400 MHz) (ppm); 8.15 (d, J = 7.6 Hz, 2H), 7.50 (t, J = 7.7 Hz, 1H), 7.41–7.30 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 169.8, 161.7, 139.4, 135.4, 135.3, 132.9, 132.8, 131.6, 131.4, 129.43, 129.39, 128.1, 127.6, 119.6, 115.6. Anal. Calcd. for $C_{19}H_{13}FO_2$: C, 78.07; H, 4.48. Found: C, 78.17; H, 4.22. MS (ESI): $[M+H]^+$ (m/z 293).

2-(4-Methoxyphenyl)nicotinic acid (3ja)



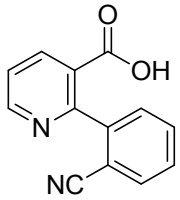
3-Pyridinecarboxylic acid was lithiated with n-BuLi/TMPLi in THF at −50 °C according to the literature [19] and the cross-coupling conducted following the general procedure. The product was isolated as a yellow solid in 89% yield. m.p. = 254.3–255.4 °C; R_f = 0.27 (petroleum ether/ethyl acetate/acetic acid = 1:1:0.01). IR (cm^{-1}, KBr): 3431, 3008, 1699, 1606, 1429, 1251, 840; ^1H NMR (DMSO-d_6, 400 MHz) (ppm) 13.19 (br s, 1H), 8.71 (d, J = 3.4 Hz, 1H), 8.05 (d, J = 7.4 Hz, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.43–7.40 (m, 1H), 7.01 (d, J = 8.1 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) (ppm) 170.0, 160.2, 156.6, 151.1, 137.6, 132.5, 130.5, 128.4, 121.9, 114.0, 55.7. Data was consistent with that reported in the literature.[20]

2-Phenylnicotinic acid (3jb)



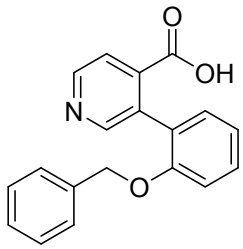
As described in **3ja**, the product was isolated as a yellow solid in 92% yield (915 mg), m.p. = 167.6–168.4 °C (lit. 168–169 °C); R_f = 0.30 (petroleum ether/ethyl acetate/acetic acid = 1:1:0.01). IR (cm^{-1}, KBr): 3431, 3055, 2918, 1705, 1578, 1440, 1280, 754; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 10.14 (br s, 1H), 8.84 (dd, J = 4.9 Hz, 1.7 Hz, 1H), 8.25–8.22 (m, 1H), 7.53–7.52 (m, 2H), 7.43–7.38 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 170.8, 158.9, 150.8, 139.5, 138.6, 129.1, 128.8, 128.2, 126.9, 122.1. Data was consistent with that reported in the literature.[21]

2-(2-Cyanophenyl)nicotinic acid (3je)



As described in **3ja**, the product was isolated as a yellow solid in 83% yield (834 mg), m.p. = 198.6–199.3 °C; R_f = 0.33 (petroleum ether/ethyl acetate/acetic acid = 1:1:0.01).. IR (cm^{-1}, KBr): 3385, 3170, 2225, 1658, 1577, 1402, 704; ^1H NMR (DMSO-d_6, 400 MHz) (ppm) 8.50 (dd, J = 4.8 Hz, 2.8 Hz, 1H), 8.13 (dd, J = 7.6 Hz, 2.0 Hz, 1H), 7.88 (d, J = 7.1 Hz, 2H), 7.54–7.50 (m, 1H), 7.47–7.43 (m, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) (ppm) 166.9, 152.3, 150.4, 143.7, 139.2, 134.7, 131.7, 128.7, 128.0, 123.8, 117.4, 114.9, 104.3. Anal. Calcd. for $C_{13}H_8N_2O_2$: C, 69.64; H, 3.60; N, 12.49. Found: C, 69.72; H, 3.46; N, 12.55. MS (ESI): $[M+H]^+$ (m/z 225).

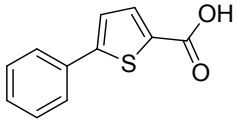
3-(2-(Benzyloxy)phenyl)isonicotinic acid (3kl)



As described in **3ja**, the product was isolated as a yellow solid in 77% yield. m.p. = 187.7–188.3 °C. R_f = 0.43 (petroleum ether/ethyl acetate/acetic acid = 1:1:0.01). IR (cm^{-1}, KBr):3412, 3010, 1668, 1612, 1432, 1110, 837; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 13.41 (br s, 1H), 8.50 (dd, J = 5.0 Hz, 0.6 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H),

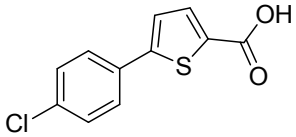
7.85–7.78 (m, 3H), 7.35–7.22 (m, 4H), 7.04 (d, J = 1.0 Hz, 1H), 7.02–6.89 (m, 2H), 5.19 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 167.3, 151.6, 149.3, 136.7, 136.4, 135.2, 129.2, 129.0, 128.7, 128.5, 128.4, 127.2, 126.3, 125.4, 119.3, 116.4, 70.1. MS (HRMS) *m/z* calcd. for $C_{19}H_{15}NO_3$ 306.1125 $[M+H]^+$, found 306.1127.

5-Phenylthiophene-2-carboxylic acid (3lb)



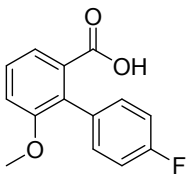
Thiophene-2-carboxylic acid was prepared using LDA according to the literature[22] and the cross-coupling was conducted following the general procedure. The product was isolated as a white solid in 80% yield. m.p. = 187.3–187.8 °C (lit. 187–188 °C); R_f = 0.40 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3446, 3018, 1701, 1660, 1539, 1290, 746; ^{1}H NMR ($CDCl_3$, 400 MHz) (ppm) 7.87 (d, J = 4.0 Hz, 1H), 7.67–7.65 (m, 2H), 7.45–7.33 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 167.4, 153.1, 136.0, 133.3, 131.2, 129.2, 129.1, 126.4, 123.9. Data was consistent with that reported in the literature.[23]

5-(4-Chlorophenyl)thiophene-2-carboxylic acid (3li)



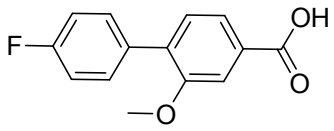
As described in **3lb**, the product was isolated as a white solid in 68% yield. m.p. = 252.7–253.6 °C (lit. 253–254 °C); R_f = 0.40 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3421, 3099, 1653, 1535, 1311, 1093, 810, 752; ^{1}H NMR (DMSO-d_6, 400 MHz) (ppm) 13.10 (br s, 1H), 7.77 (d, J = 6.8 Hz, 2H), 7.72 (d, J = 3.1 Hz, 1H), 7.60 (d, J = 3.1 Hz, 1H), 7.52 (d, J = 6.8 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) (ppm) 163.2, 148.6, 134.8, 134.4, 133.9, 132.2, 129.7, 128.0, 125.7. Data was consistent with that reported in the literature.[23]

4'-Fluoro-6-methoxy-[1, 1'-biphenyl]-2-carboxylic acid[24] (3mj)



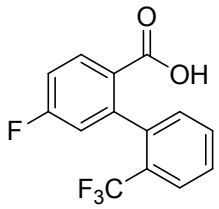
3-Methoxybenzoic acid was lithiated at C2 using TMPLi according to the literature[14] and the cross-coupling was conducted following the general procedure. The product was isolated as a white solid in 81% yield. m.p. = 196.6–198.7 °C. R_f = 0.37 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3336, 3061, 1707, 1490, 1219, 887; ^1H NMR ($CDCl_3$, 400 MHz) (ppm); 8.14 (d, J = 7.9 Hz, 1H), 7.50–7.44 (m, 2H), 7.36–7.33 (m, 2H), 7.14 (t, J = 8.7 Hz, 2H), 3.82 (s, 3H);^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 168.2, 160.9, 158.9, 132.6(d), 129.0(d), 128.5, 123.3, 123.1, 120.5(d), 115.3, 115.1, 55.4. MS (HRMS) *m/z* calcd. for $C_{14}H_{11}FO_3$ 245.0619 $[M-H]^-$, found 245.0619.

4'-Fluoro-2-methoxy-[1, 1'-biphenyl]-4-carboxylic acid (4mj)



3-Methoxybenzoic acid was lithiated at C4 using n-BuLi/t-BuOK (1:1.4 equiv.) a according to the literature[14] and the cross-coupling was conducted following the general procedure. The product was isolated as a white solid in 73% yield, m.p. = 178.3–179.1 °C; R_f = 0.38 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3446, 3290, 1691, 1436, 1006, 753; ^1H NMR (DMSO-d_6, 400 MHz) (ppm) 10.10 (br s, 1H), 7.63–7.59 (m, 3H), 7.49–7.47 (m, 3H), 7.39 (s, 1H), 3.38 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) (ppm) 167.5, 154.8, 136.8, 132.4, 131.6, 131.3, 131.1, 130.8, 128.5, 120.9, 117.2, 55.5. MS (HRMS) *m/z* calcd. for $C_{14}H_{11}FO_3$ 245.0619 $[M-H]^-$, found 245.0619.

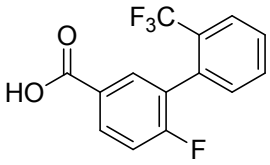
5-Fluoro-2'-(trifluoromethyl)-[1, 1'-biphenyl]-2-carboxylic acid (3nf)



4-Fluorobenzoic acid was lithiated at C2 using 2.2 equiv. s-BuLi at –78 °C according to the literature[25] and the cross-coupling was conducted following the general procedure. The product was isolated as a yellow solid in 72% yield. m.p. =

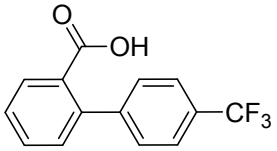
164.5–165.4 °C; R_f = 0.43 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3421, 3066, 1692, 1600, 1435, 766; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 8.32 (s, 1H), 7.57–7.53 (m, 3H), 7.46–7.42 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 167.7, 167.1, 136.5, 134.4, 131.1, 129.7, 129.5, 127.2, 126.4, 125.4, 124.7, 124.1, 115.2, 110.7. Anal. Calcd. for $C_{14}H_8F_4O_2$: C, 59.16; H, 2.84. Found: C, 59.12; H, 2.86. MS (ESI): $[M+H]^+$ (m/z 285).

6-Fluoro-2'-(trifluoromethyl)-[1, 1'-biphenyl]-3-carboxylic acid (4nf)



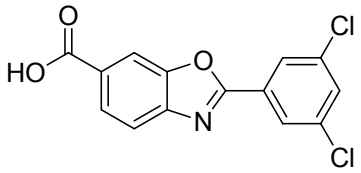
4-Fluorobenzoic acid was lithiated at C3 using using TMPLi at according to the literature[25] and the cross-coupling was conducted following the general procedure. The product was isolated as a yellow solid in 69% yield (950 mg), m.p. = 177.7–178.2 °C; Rf = 0.41 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01).IR (cm^{-1}, KBr): 3435, 3095, 1686, 1593, 1265, 767; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 11.52 (br s, 1H), 8.17–8.08 (m, 3H), 7.46 (t, J = 6.4 Hz, 2H), 7.16–7.11 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 169.2, 164.0, 131.4, 131.3, 130.6, 130.0, 129.6, 128.0, 127.7, 127.6, 127.3, 126.2, 124.0, 114.7. Anal. Calcd. for $C_{14}H_8F_4O_2$: C, 59.16; H, 2.84. Found: C, 59.21; H, 2.77. MS (ESI): $[M+H]^+$ (m/z 285).

4'-(Trifluoromethyl)-[1, 1'-biphenyl]-2-carboxylic acid (Xenalipin)



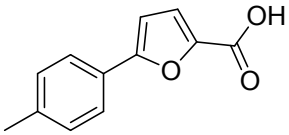
As described in **3aa**, the product was isolated as a white solid in 77% yield. m.p. = 165.7–166.2 °C (lit. 165–166 °C); Rf = 0.41 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3399, 3070, 1686, 1452, 1321, 1066, 708; ^1H NMR ($CDCl_3$, 400 MHz) (ppm) 10.41 (br s, 1H), 8.12–7.92 (m, 2H), 7.67–7.60 (m, 2H), 7.52–7.44 (m, 3H), 7.35–7.33(m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) (ppm) 172.2, 142.4, 133.9, 132.5, 131.2, 130.2, 129.2, 128.9, 128.5, 128.0, 125.02–124.93 (q), 119.5. Data was consistent with that reported in the literature.[26]

2-(3, 5-Dichlorophenyl)benzo[d]oxazole-6-carboxylic acid (Tafamidis)



Benzo[d]oxazole-6-carboxylic acid was lithiated at C2 using 3 equiv. TMPLi at –50 ^{o}C according to the reported procedure and the product was isolated as a white solid in 61% yield. m.p. = 200.4–202.7 °C; R_f = 0.37 (petroleum ether/ethyl acetate/acetic acid = 6:1:0.01). IR (cm^{-1}, KBr): 3383, 1685, 1608, 1224, 769; ^{1}H NMR (DMSO-d$_6$, 400 MHz) (ppm) 8.27 (s, 1H), 8.18 (d, *J* = 6.8 Hz, 1H), 8.04–8.02 (m, 1H), 7.94 (s, 1H), 7.88 (d, *J* = 1.6 Hz, 1H), 7.67 (dd, *J* = 6.8 Hz, 5.2 Hz, 1H); ^{13}C NMR (DMSO-d$_6$, 100 MHz) (ppm) 167.2, 162.1, 150.1, 145.0, 137.8, 133.7, 131.4, 128.6, 126.8, 124.3, 120.5, 112.6. Data was consistent with that reported in the literature. [27]

5-(*p*-Tolyl)furan-2-carboxylic acid (5)



Furan-2-carboxylic acid was lithiated at C5 using LDA according to the literature[28] The product was isolated as a white solid in 88% yield (888 mg), m.p. = 184.6–185.2 °C (lit. 185–186 °C); R_f = 0.42 (petroleum ether/ethyl acetate/acetic acid = 5:1:0.01). IR (cm^{-1}, KBr): 3445, 3024, 1664, 1485, 1165, 806, 758; ^{1}H NMR (DMSO-d$_6$, 400 MHz) (ppm) 13.07 (br s, 1H), 7.70 (d, *J* = 6.4 Hz, 2H), 7.31–7.28 (m, 3H), 7.07 (d, *J* = 2.8 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (DMSO-d$_6$, 100 MHz) (ppm) 159.8, 157.0, 144.2, 139.1, 130.1, 127.0, 124.8, 120.4, 107.7, 21.4. Data was consistent with that reported in the literature.[29]

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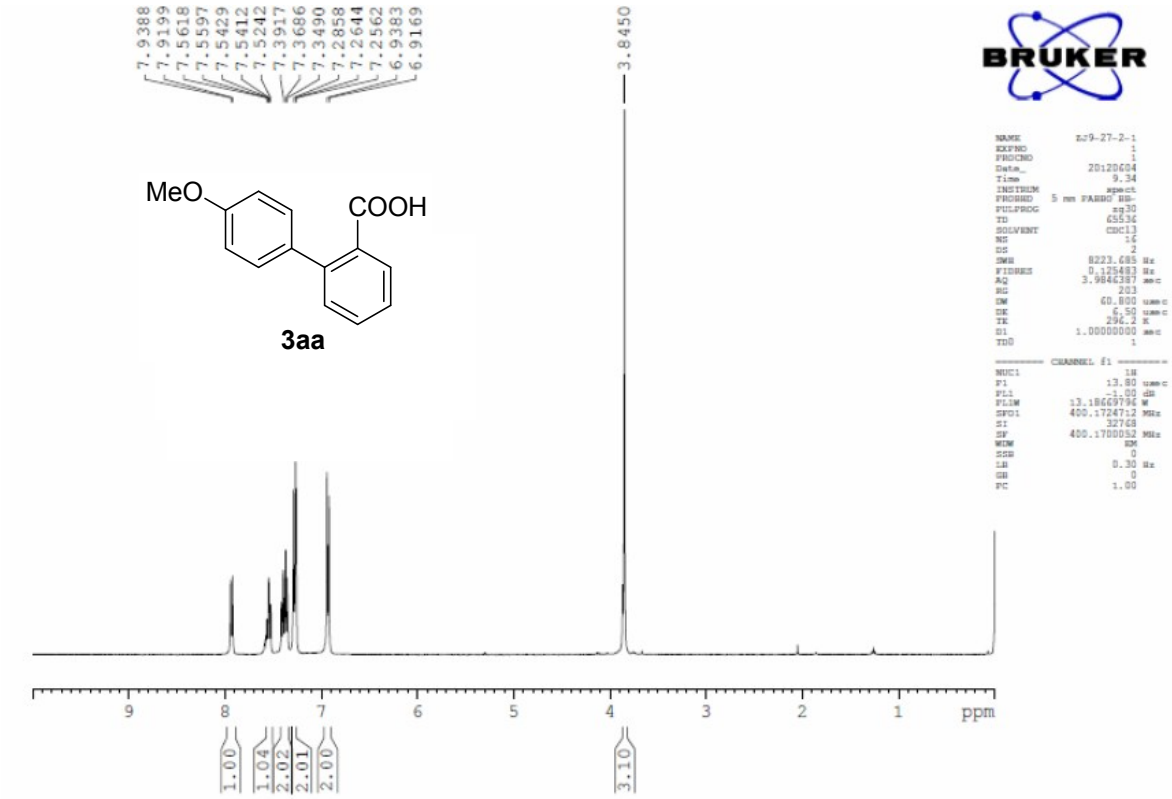
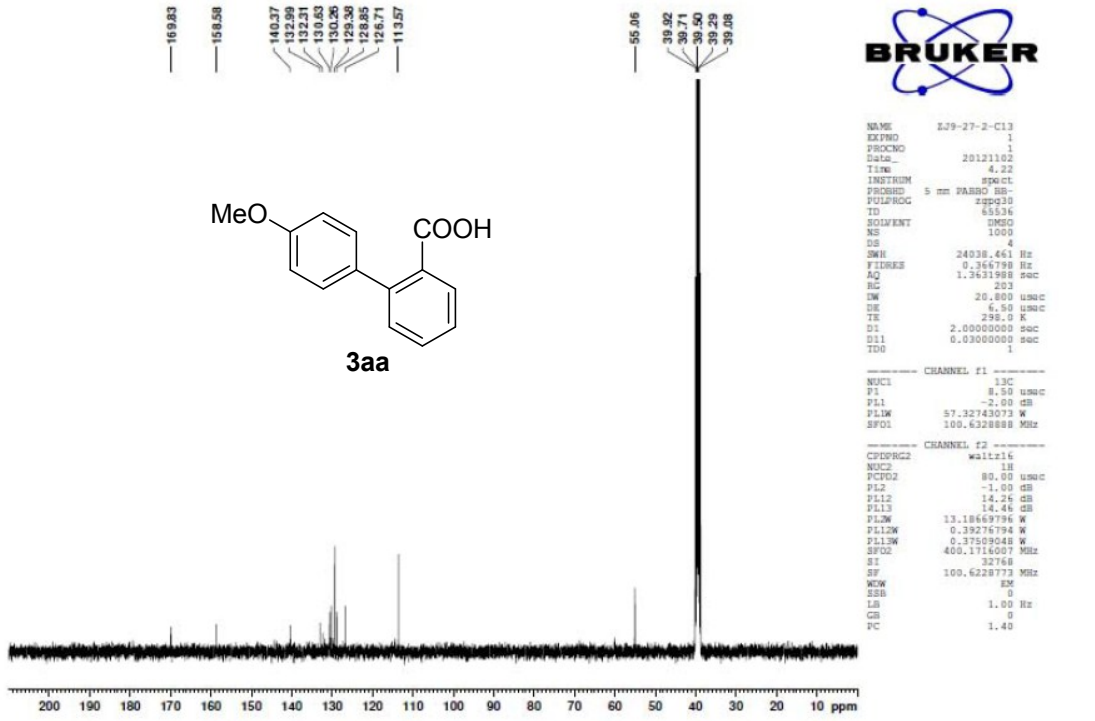
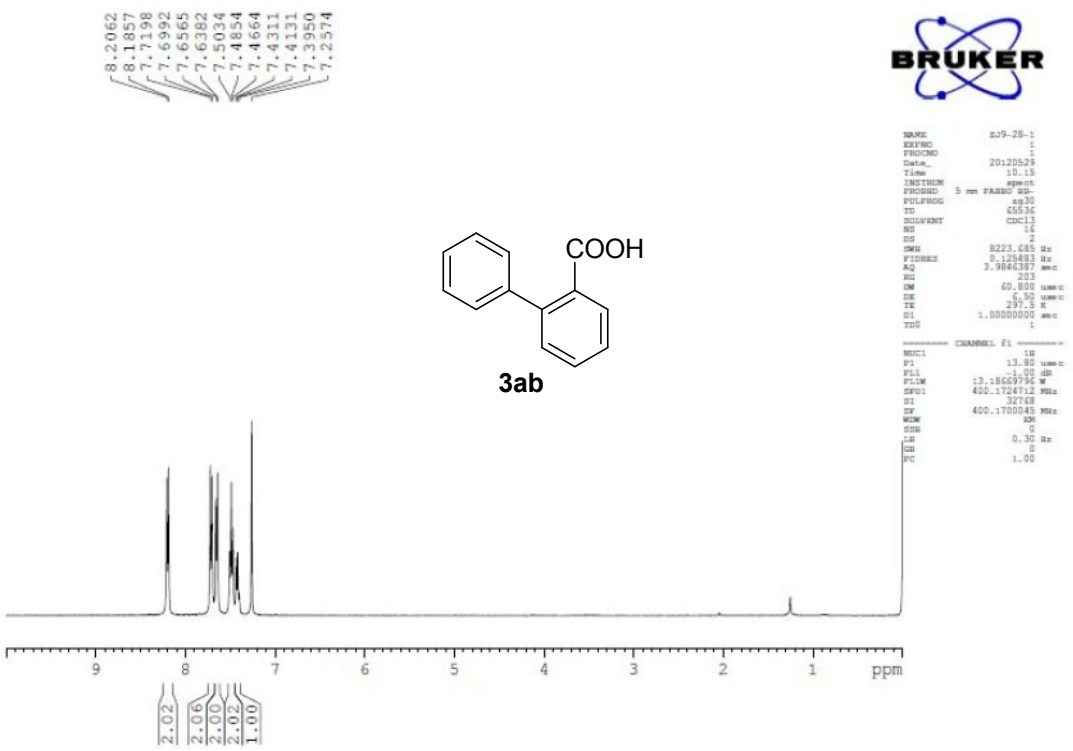
V. Copies of ^{1}H NMR and ^{13}C NMR spectra



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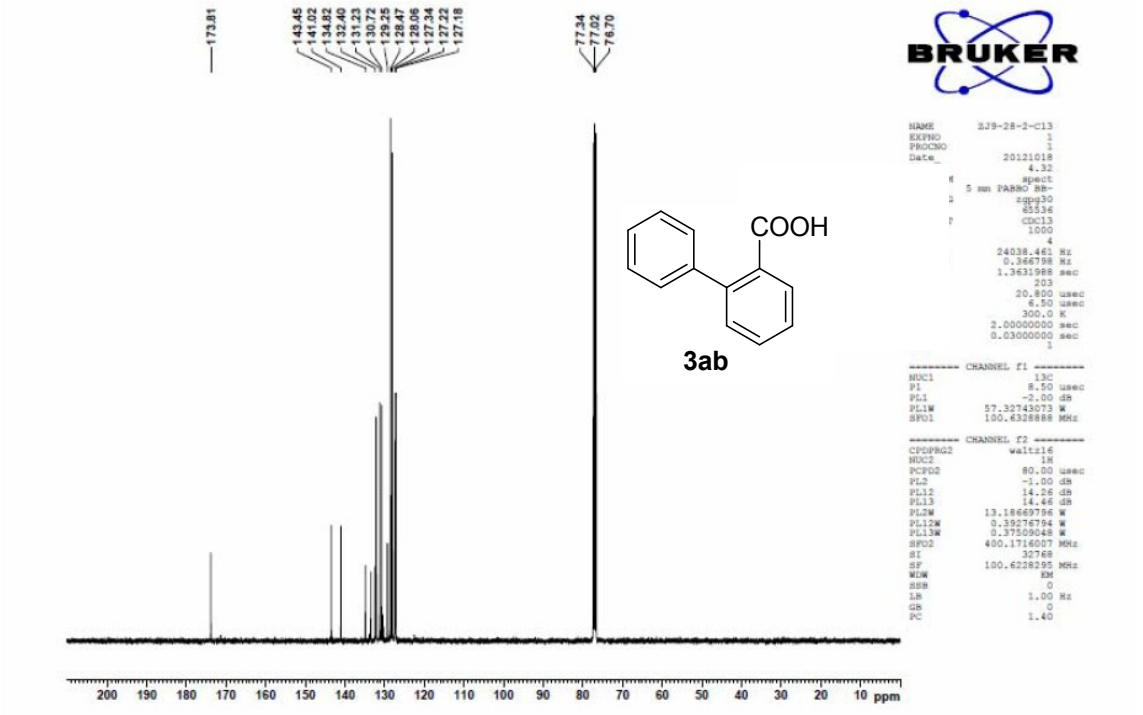
7.4131
7.3950
7.2574
COOH
3ab
9
8
7
6
5
4
3
2
1
ppm
2.02
2.06
2.00
2.02
1.00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141.02
134.82
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131.23
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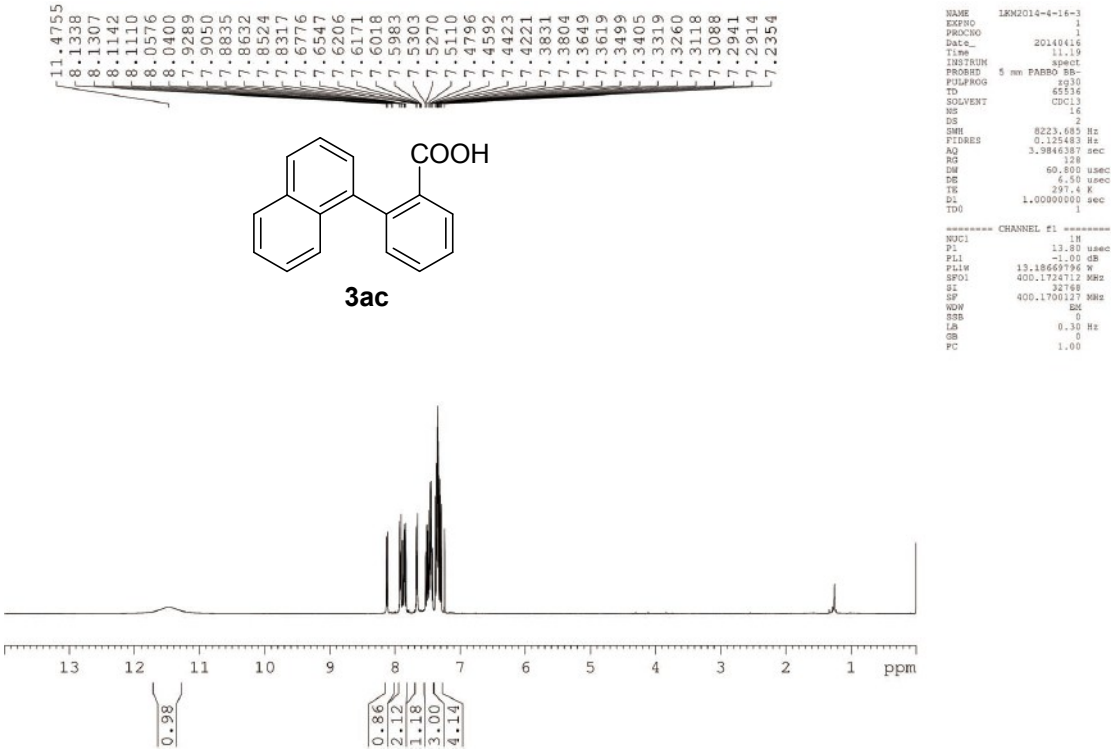
128.06
127.34
127.22
127.18
77.34
77.02
76.70
COOH
3ab
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.1307
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7.8632
7.8524
7.8317
7.6776
7.6547
7.6206
7.6171
7.6018
7.5983
7.5303
7.5270
7.5110
7.4796
7.4592
7.4423
7.4221
7.3831
7.3804
7.3649
7.3619
7.3499
7.3405
7.3319
7.3260
7.3118
7.3088
7.2941
7.2914
7.2354
COOH
3ac
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EXPNO 1
PROCNO 1
Date_ 20140416
Time 11.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 128
DW 60.800 usec
DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700127 MHz
WDW EM
SSB 0
LB 0.30 Hz
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0.86
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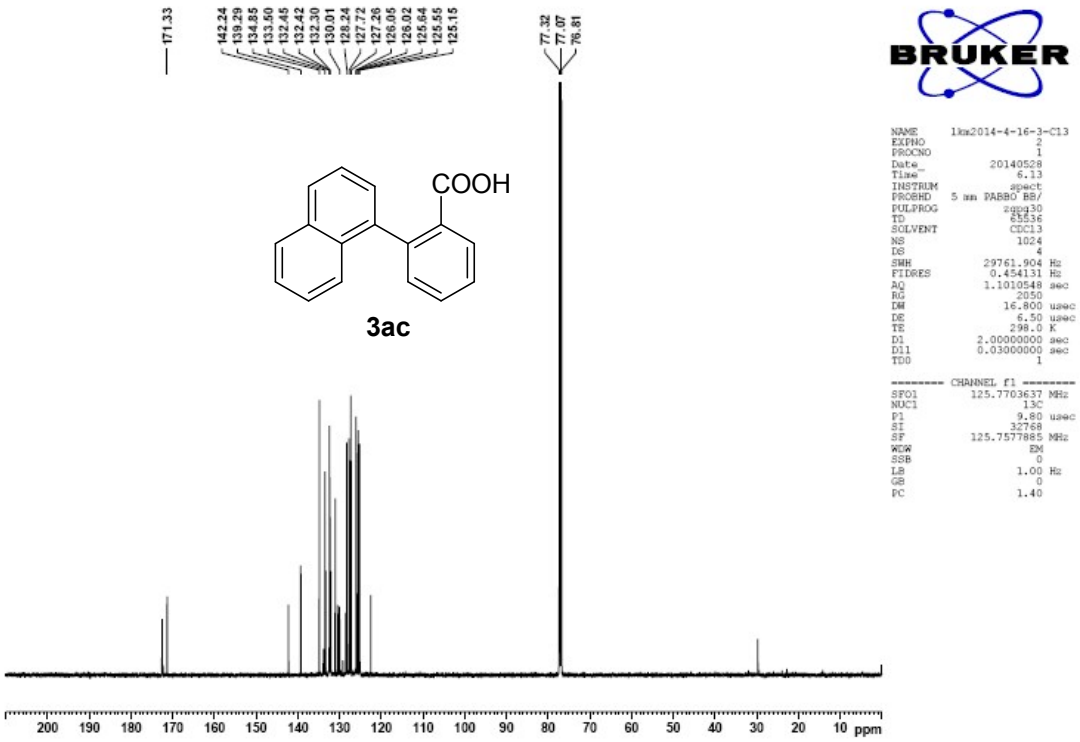
3.00
4.14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132.30
130.01
128.24
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126.06
126.02
125.64
125.55
125.15
77.32
77.07
76.81
COOH
3ac
BRUKER
NAME 1km2014-4-16-3-C13
EXPNO 2
PROCNO 1
Date_ 20140528
Time 6.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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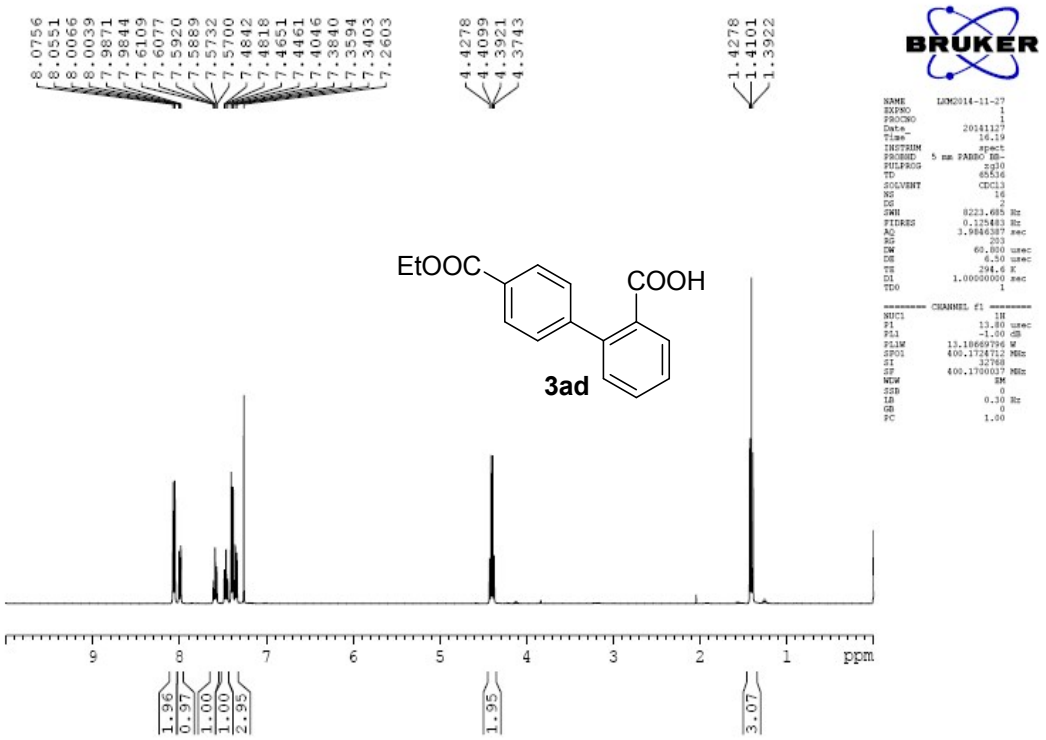
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7.5700
7.4842
7.4818
7.4651
7.4461
7.4046
7.3840
7.3594
7.3403
7.2603
4.4278
4.4099
4.3921
4.3743
1.4278
1.4101
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BRUKER
EtOOC
COOH
3ad
ppm
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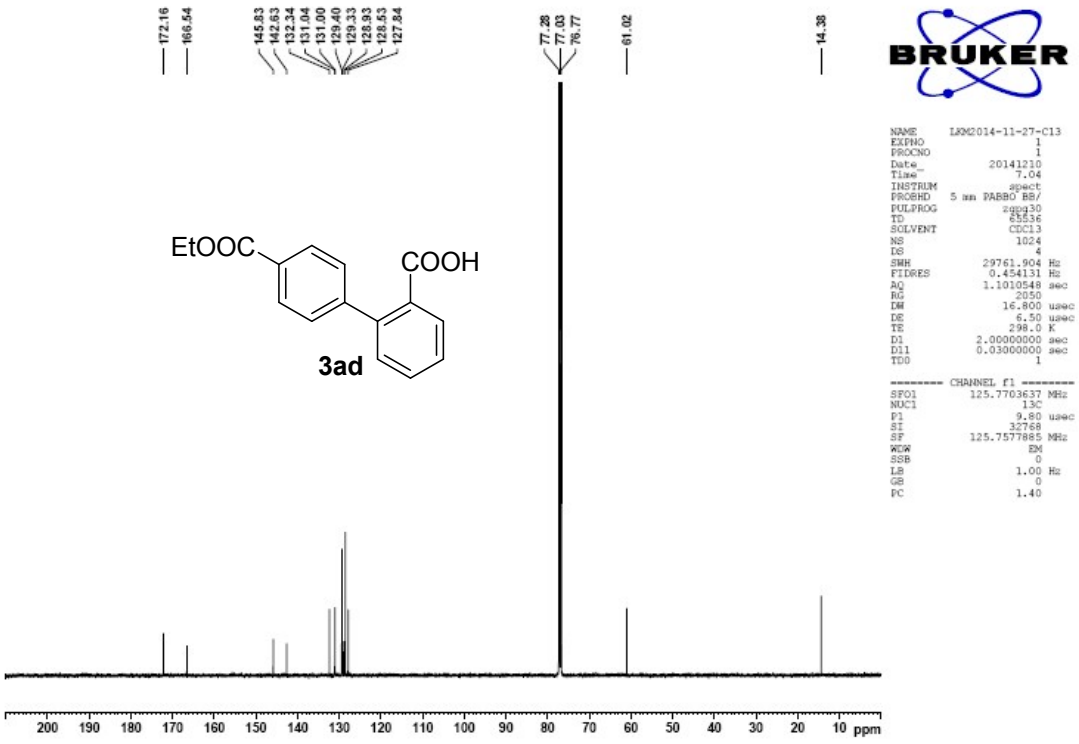
0.97
1.00
1.00
2.95
1.95
3.07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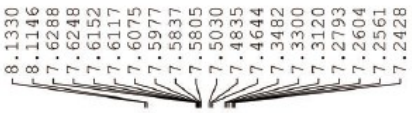
77.03
76.77
61.02
14.38
BRUKER
EtOOC
COOH
3ad
ppm



```
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PROCNO                     1
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INSTRUM                spect
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PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846307 sec
RG                      203
DW                   60.800 usec
DE                    6.50 usec
TE                  298.5 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.80 usec
PL1                    -1.00 dB
PLW1              13.10669796 W
SFO1              400.1724712 MHz
SI                      32768
SF                400.1700056 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

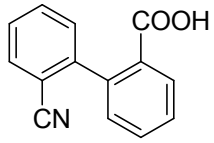

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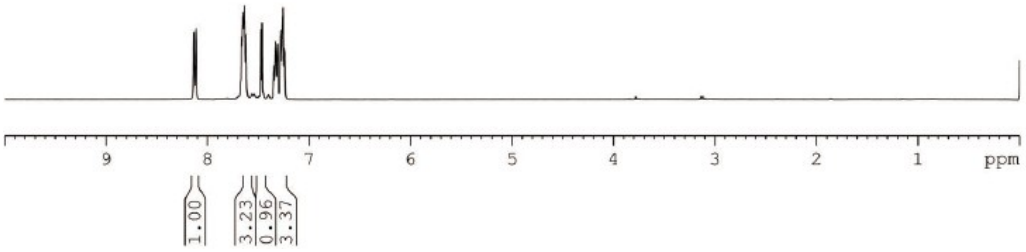

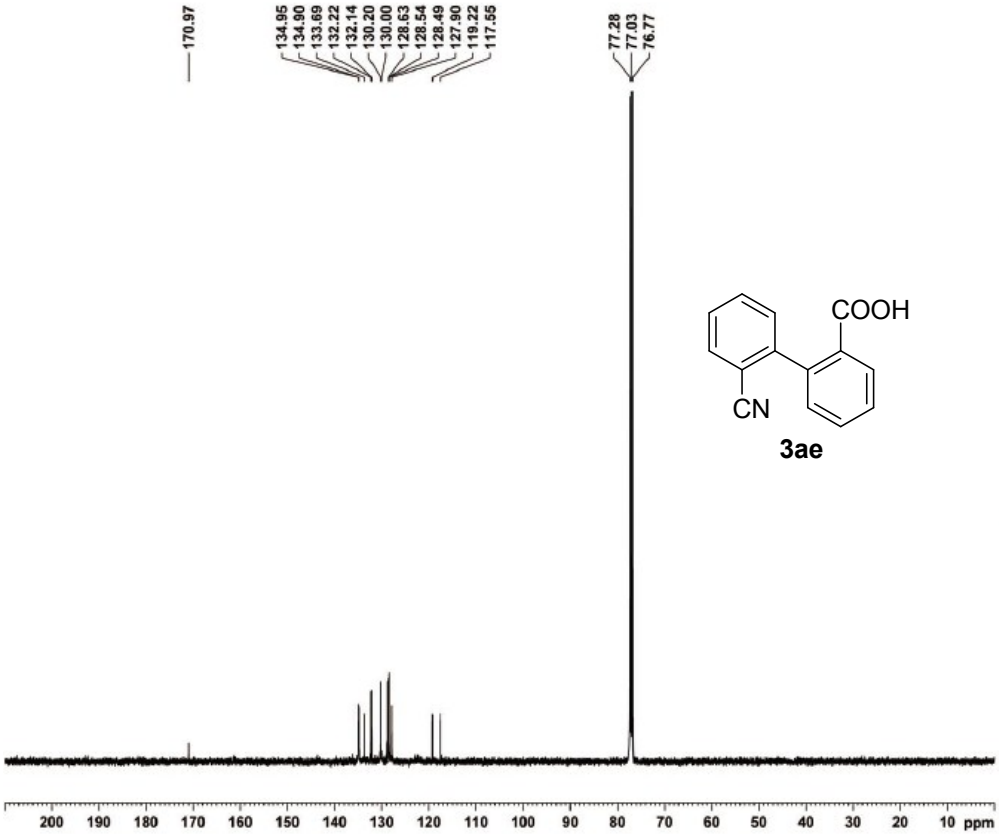

```
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PROCNO                        1
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Time                       4.15
INSTRUM                   spect
PROBHD      5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010548 sec
RG                      2050
DW                   16.800 usec
DE                    6.50 usec
TE                  298.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1              125.7703637 MHz
NUC1                      13C
P1                     9.80 usec
SI                      32768
SF                125.7577885 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```
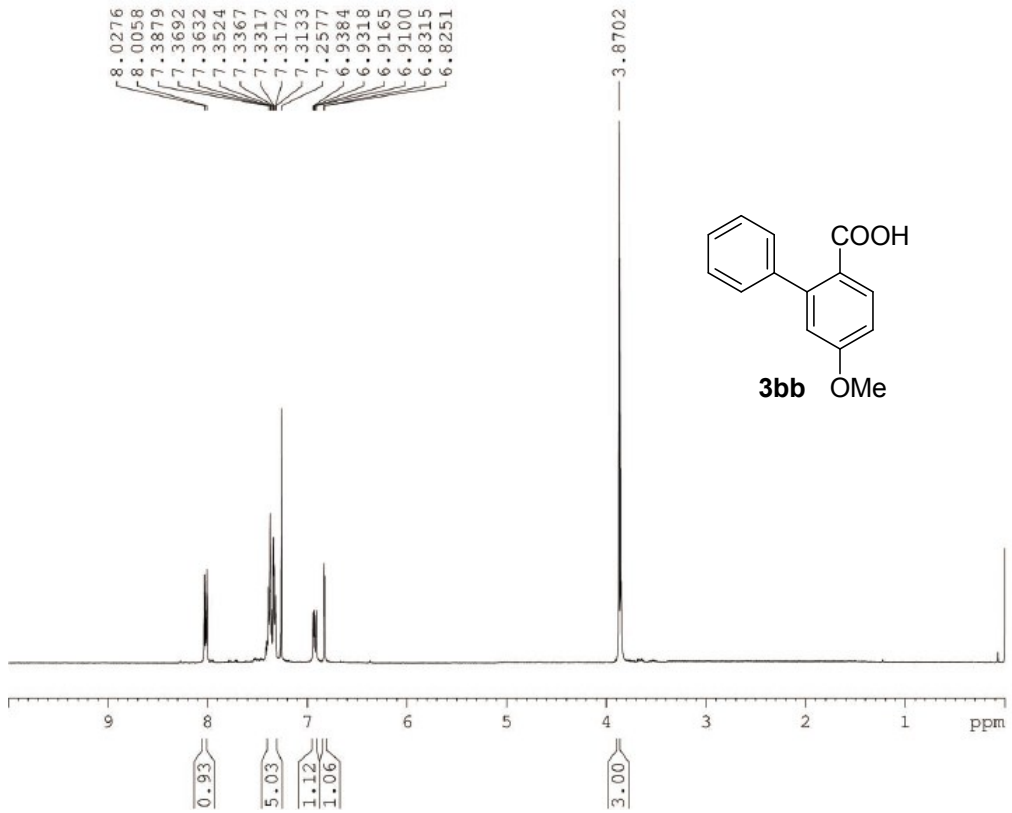
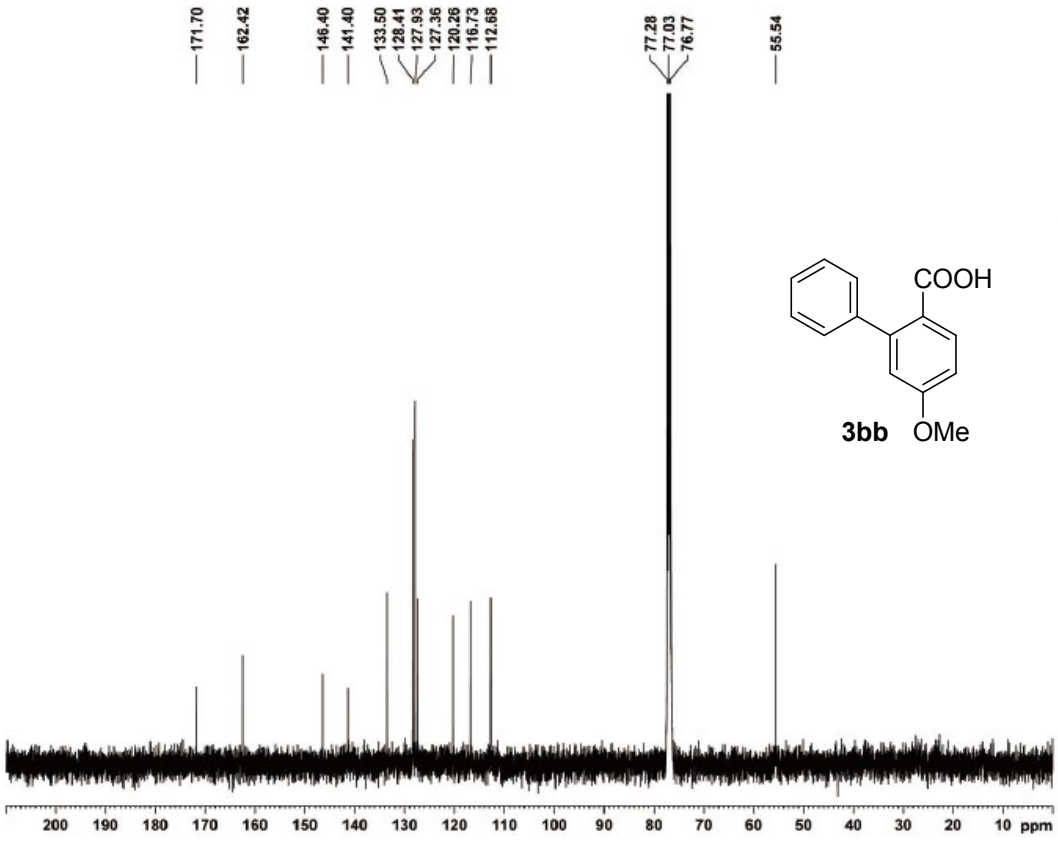


3ae

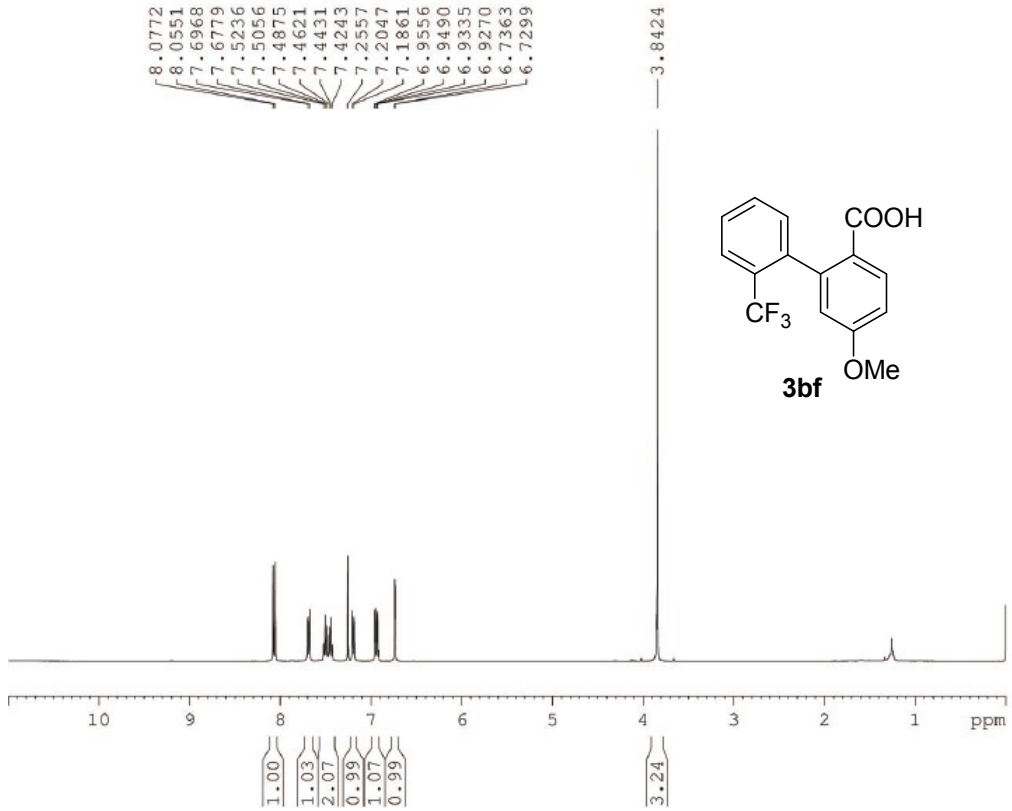



```
NAME        LKM2014-9-12-2
EXPNO                    1
PROCNO                   1
Date_             20140912
Time                  9.38
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    203
DW                 60.800 usec
DE                  6.50 usec
TE                 298.4 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.80 usec
PL1                 -1.00 dB
PL1W          13.18669796 W
SFO1          400.1724712 MHz
SI                   32768
SF            400.1700048 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



BRUKER

```
NAME        LKM2014-9-12-2-C13
EXPNO                    1
PROCNO                   1
Date_             20140912
Time                 21.42
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH              29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010548 sec
RG                   2050
DW                 16.800 usec
DE                  6.50 usec
TE                 298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7703637 MHz
NUC1                   13C
P1                   9.80 usec
SI                   32768
SF            125.7577885 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```




```
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EXPNO                      1
PROCNO                     1
Date_               20140416
Time                   11.40
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      181
DW                   60.800 usec
DE                    6.50 usec
TE                   297.4 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.80 usec
PL1                    -1.00 dB
PL1W            13.18669796 W
SFO1             400.1724712 MHz
SI                      32768
SF               400.1700047 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```
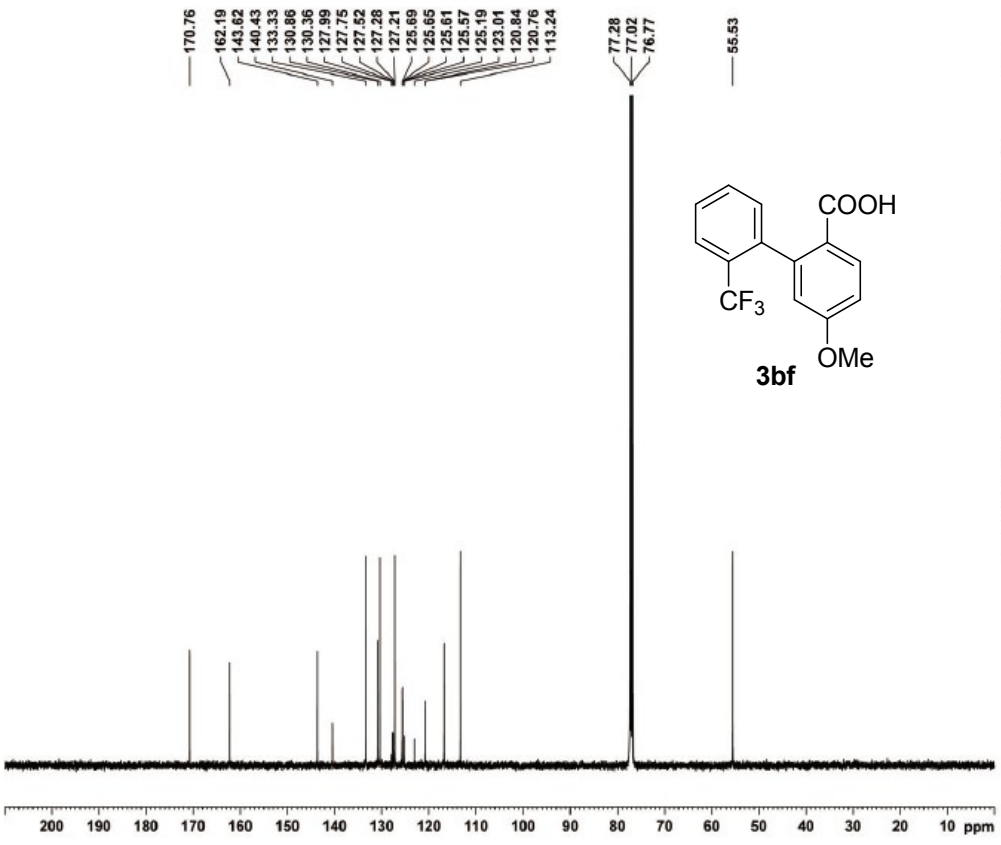
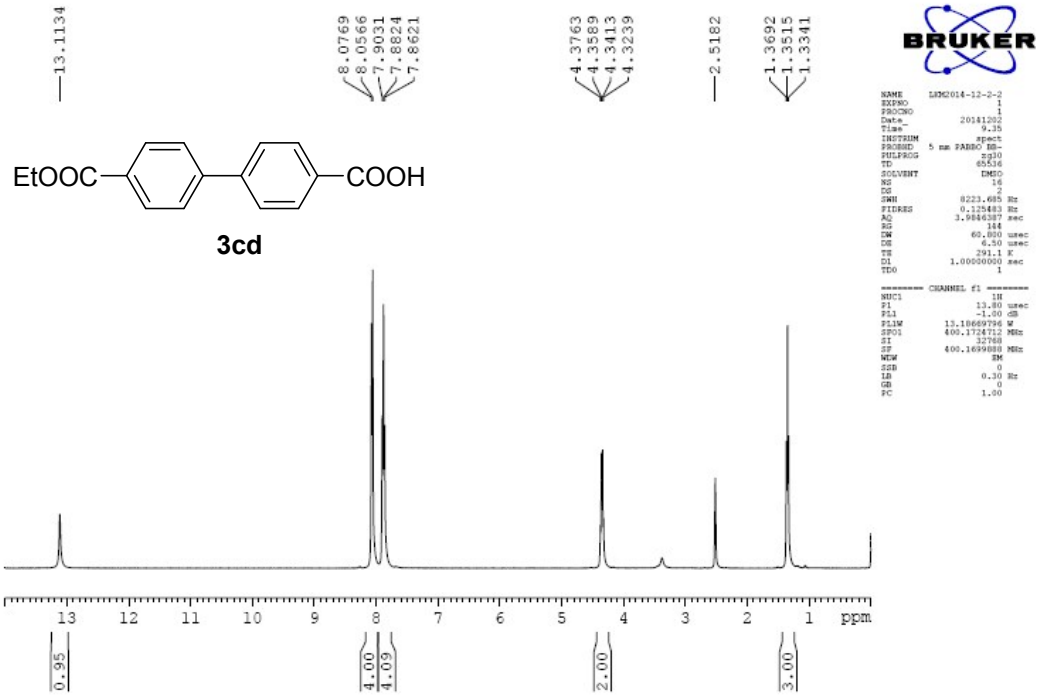



BRUKER

```
NAME          LKM2014-4-16-7-C13
EXPNO                      6
PROCNO                     1
Date_               20140528
Time                   9.15
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               29761.904 Hz
FIDRES            0.454131 Hz
AQ                1.1010548 sec
RG                      2050
DW                   16.800 usec
DE                    6.50 usec
TE                   297.9 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            125.7703637 MHz
NUC1                      13C
P1                     9.80 usec
SI                      32768
SF              125.7577885 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```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4.3413
4.3239
2.5182
1.3692
1.3515
1.3341
EtOOC
COOH
3cd
BRUKER
NAME LKM2014-12-2-2
EXPNO 1
PROCNO 1
Date_ 20141202
Time_ 9.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 144
DW 60.800 usec
DE 6.50 usec
TE 291.1 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PLW 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1699886 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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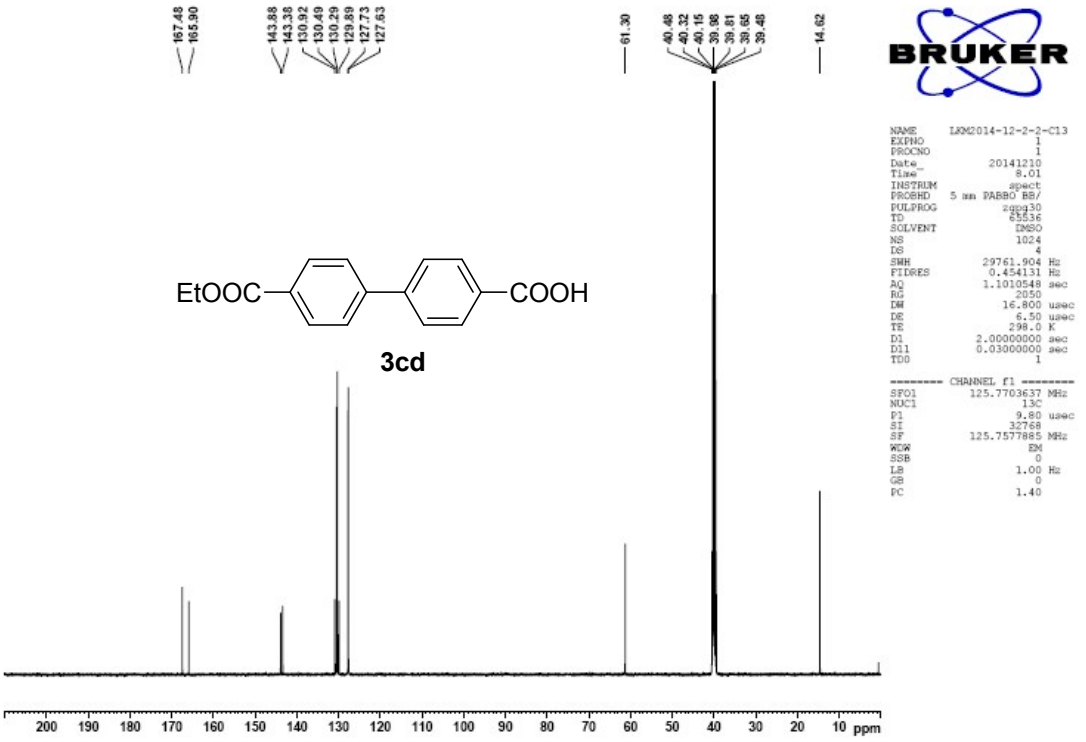
4.00
4.09
2.00
3.00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127.73
127.63
61.30
40.48
40.32
40.15
39.98
39.81
39.65
39.48
14.62
EtOOC
COOH
3cd
BRUKER
NAME LKM2014-12-2-2-C13
EXPNO 1
PROCNO 1
Date_ 20141210
Time_ 8.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
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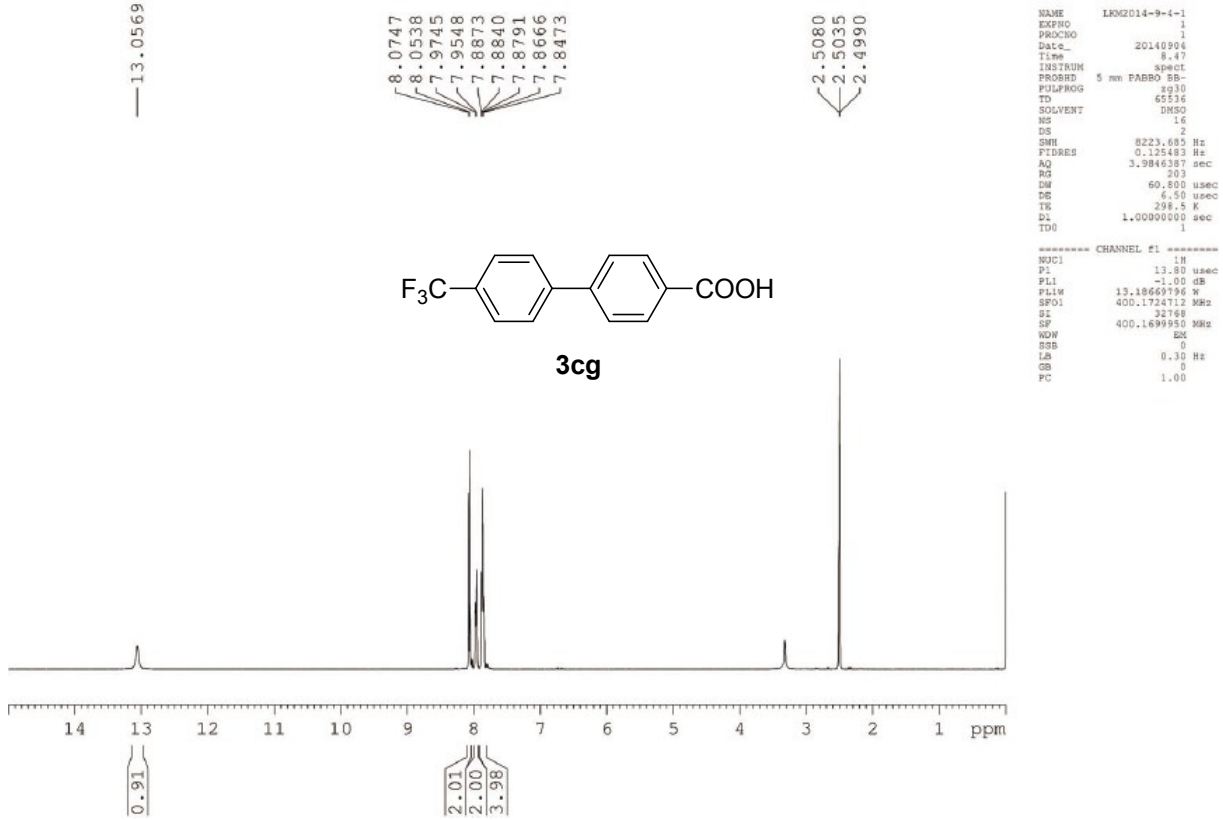


```
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PROCNO                   1
Date_             20140904
Time                  8.47
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    203
DW                60.800 usec
DE                 6.50 usec
TE                298.5 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.80 usec
PL1                -1.00 dB
PL1W          13.18669796 W
SFO1         400.1724712 MHz
SI                   32768
SF           400.1699950 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

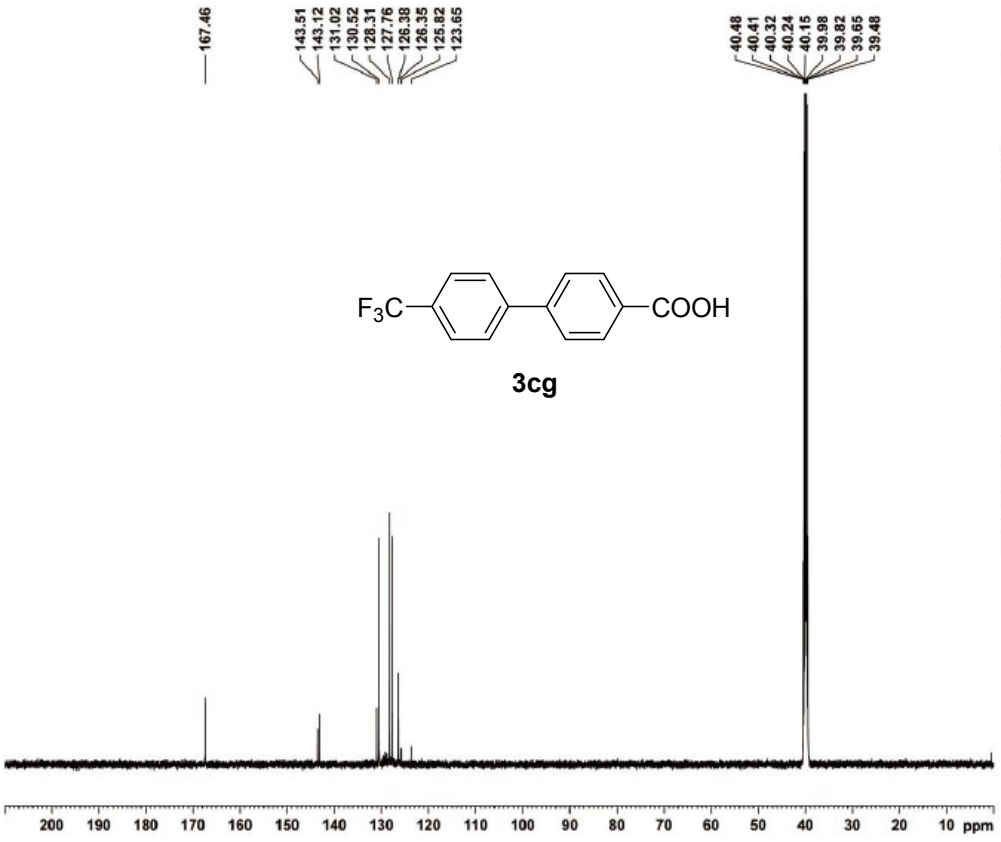


```
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PROCNO                   1
Date_             20140911
Time                 14.44
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                  65536
SOLVENT              DMSO
NS                    727
DS                      4
SWH              29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010548 sec
RG                   2050
DW                16.800 usec
DE                 6.50 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                   13C
P1                  9.80 usec
SI                   32768
SF           125.7577885 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```
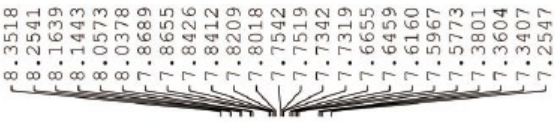
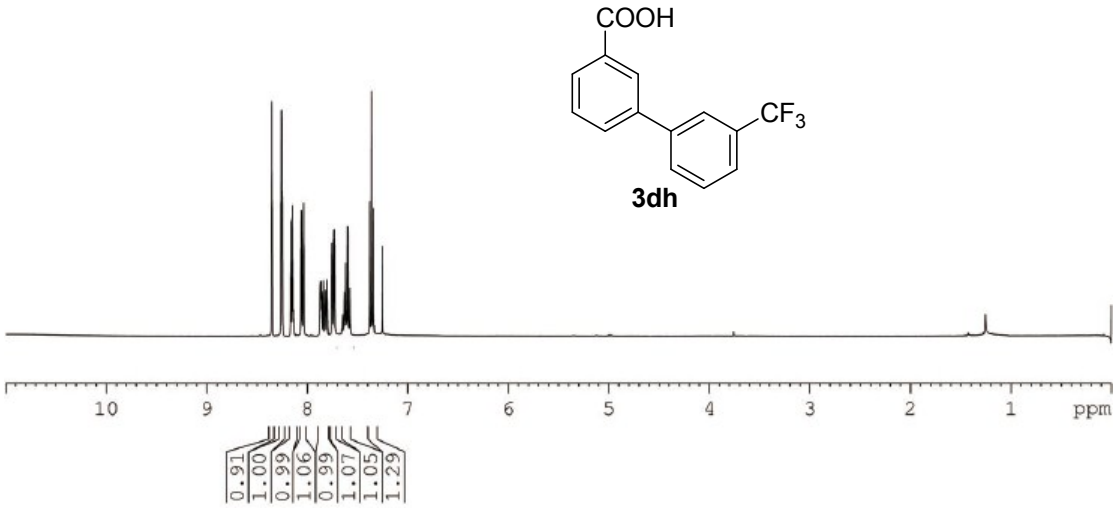
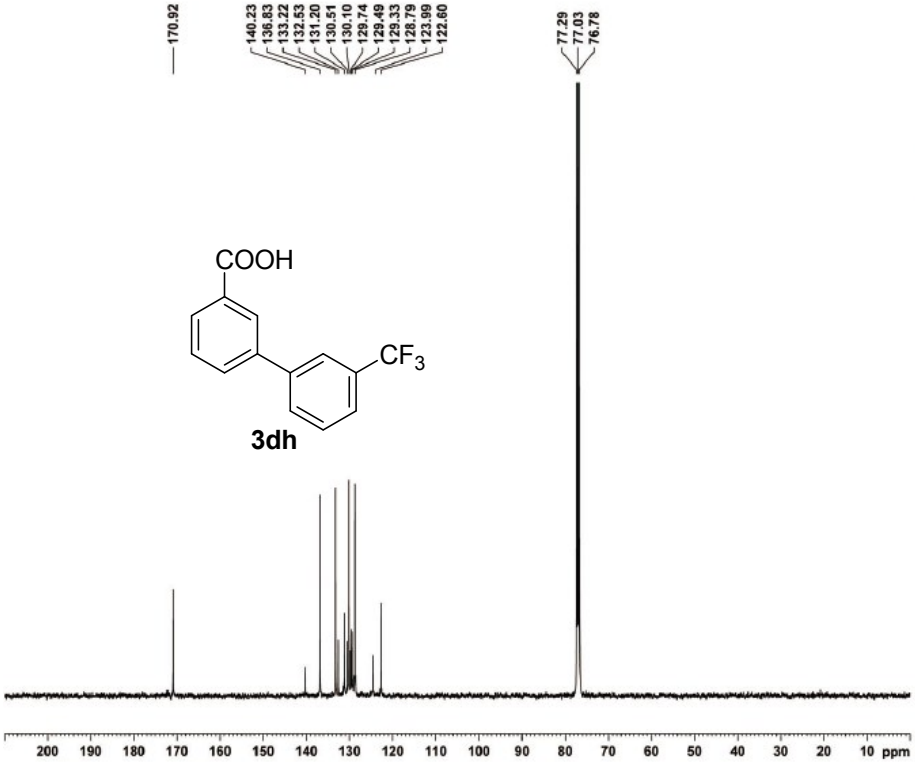
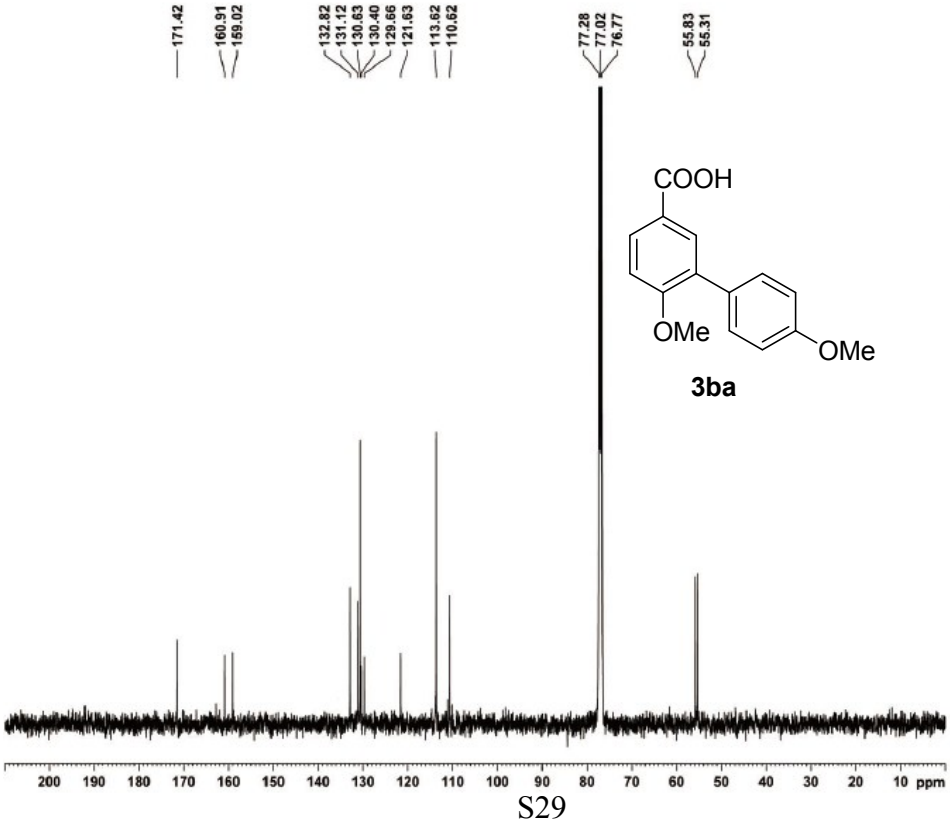





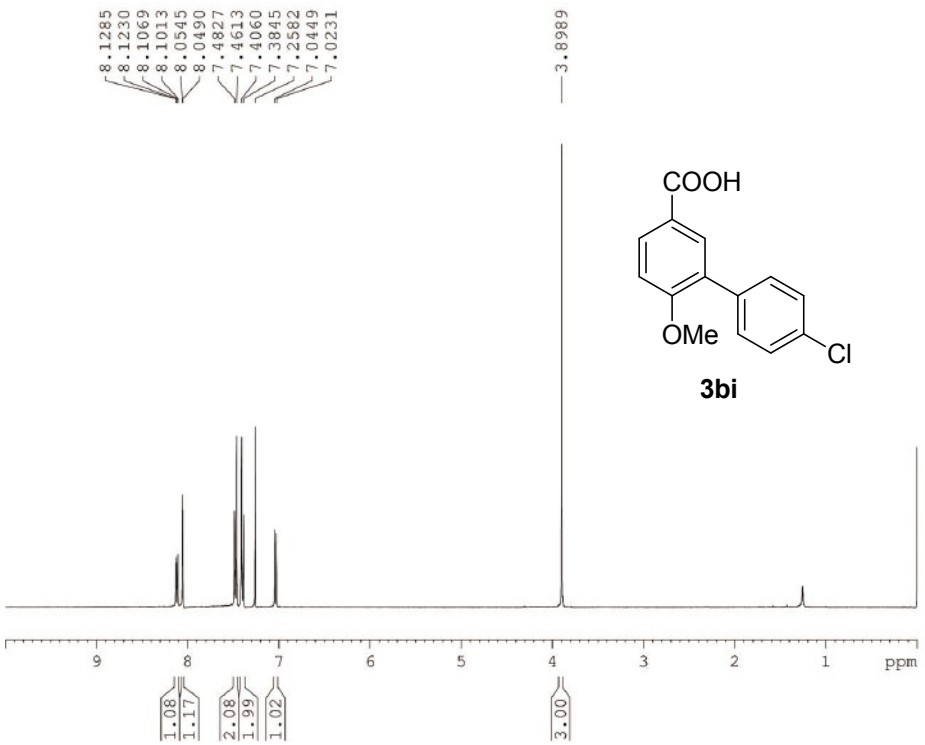


NAME	LKM2014-9-4-2-C13
EXPNO	1
PROCNO	1
Date_	20140912
Time	10.05
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	2050
DW	16.800 usec
DE	6.50 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	125.7703637 MHz
NUC1	13C
P1	9.80 usec
SI	32768
SF	125.7577885 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

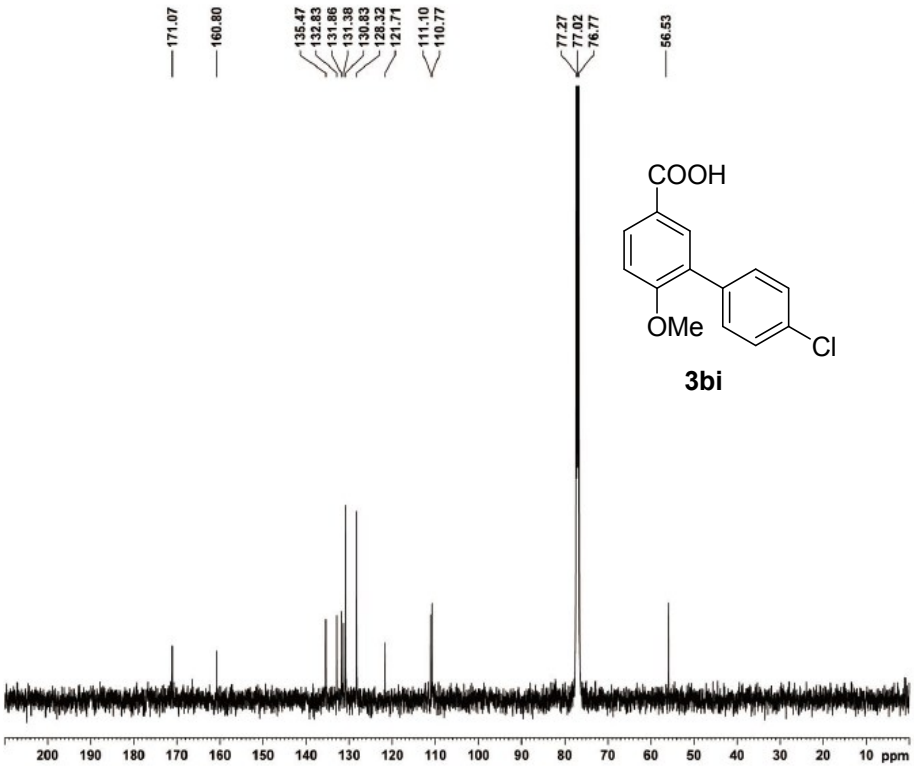

```
NAME        LKM2014-9-1-7
EXPNO               1
PROCNO              1
Date_        20140901
Time            15.22
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG         zg30
TD             65536
SOLVENT         CDCl3
NS                 16
DS                  2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ           3.9846387 sec
RG                203
DW             60.800 usec
DE              6.50 usec
TE             298.6 K
D1          1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              13.80 usec
PL1             -1.00 dB
PL1W       13.18669796 W
SFO1        400.1724712 MHz
SI               32768
SF          400.1700048 MHz
WDW                EM
SSB                 0
LB              0.30 Hz
GB                  0
PC               1.00
```



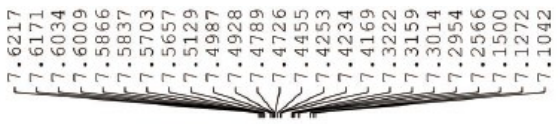

```
NAME        LKM2014-9-1-7-C13
EXPNO               1
PROCNO              1
Date_        20140903
Time            12.08
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD             65536
SOLVENT         CDCl3
NS               1024
DS                  4
SWH          29761.904 Hz
FIDRES       0.454131 Hz
AQ           1.1010548 sec
RG               2050
DW             16.800 usec
DE              6.50 usec
TE             297.4 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                 1

========== CHANNEL f1 ==========
SFO1       125.7703637 MHz
NUC1               13C
P1              9.80 usec
SI               32768
SF         125.7577885 MHz
WDW                EM
SSB                 0
LB              3.00 Hz
GB                  0
PC               1.40
```

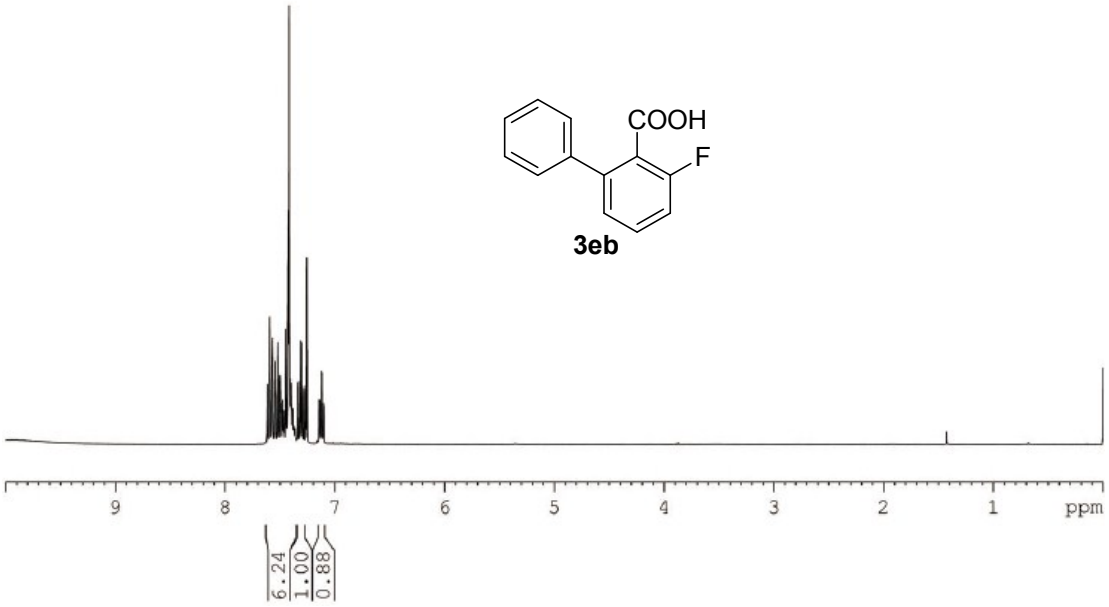


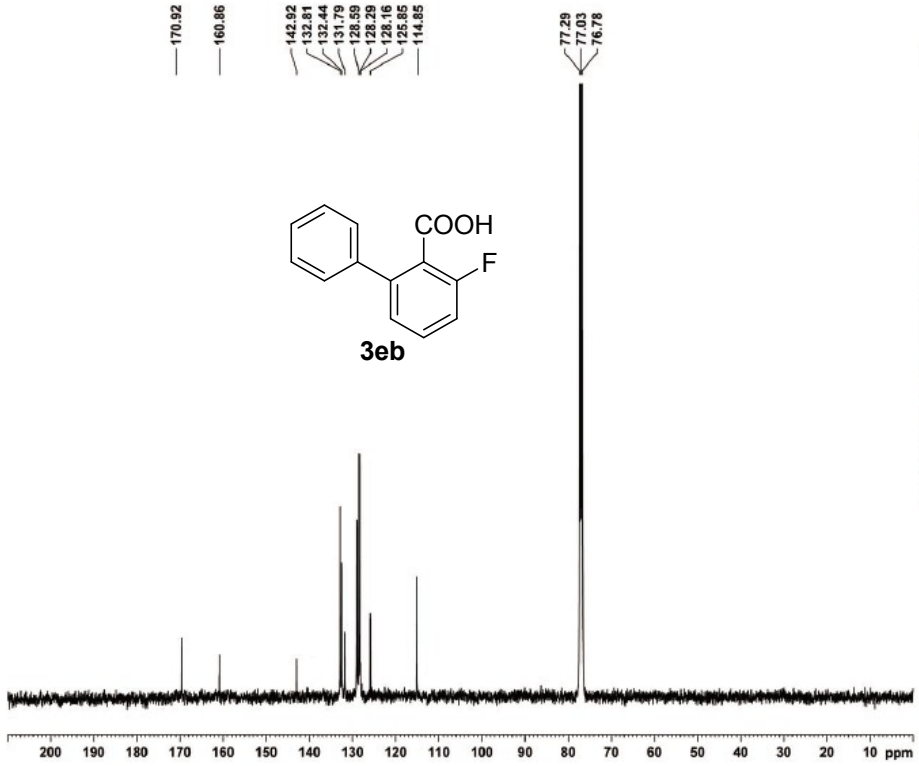

```
NAME        LKM2014-9-1-8
EXPNO               1
PROCNO              1
Date_        20140901
Time            15.45
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                 16
DS                  2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ           3.9846387 sec
RG                203
DW             60.800 usec
DE              6.50 usec
TE             298.1 K
D1          1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              13.80 usec
PL1             -1.00 dB
PL1W       13.18669796 W
SFO1      400.1724712 MHz
SI              32768
SF        400.1700047 MHz
WDW               EM
SSB                0
LB              0.30 Hz
GB                 0
PC              1.00
```



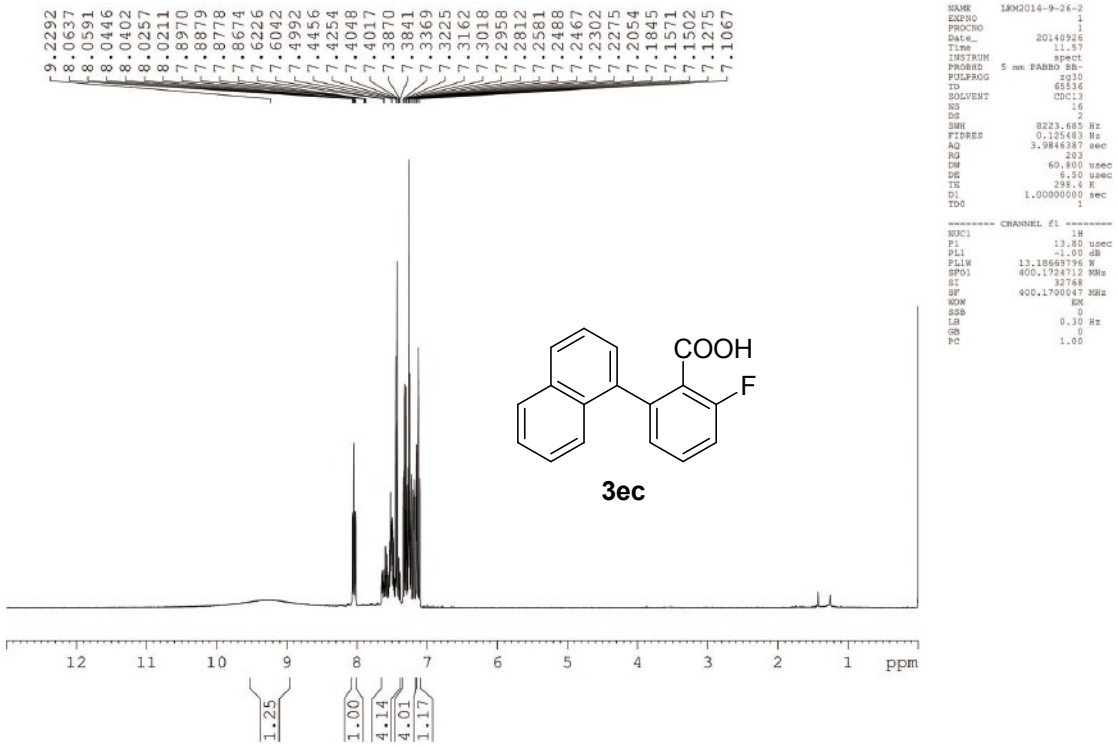

```
NAME      LKM2014-9-1-8-C13
EXPNO               1
PROCNO              1
Date_        20140903
Time            15.33
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD              65536
SOLVENT          CDCl3
NS               1024
DS                  4
SWH         29761.904 Hz
FIDRES       0.454131 Hz
AQ           1.1010548 sec
RG                2050
DW             16.800 usec
DE              6.50 usec
TE             297.3 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      125.7703637 MHz
NUC1               13C
P1              9.80 usec
SI              32768
SF        125.7577885 MHz
WDW               EM
SSB                0
LB              3.00 Hz
GB                 0
PC              1.40
```



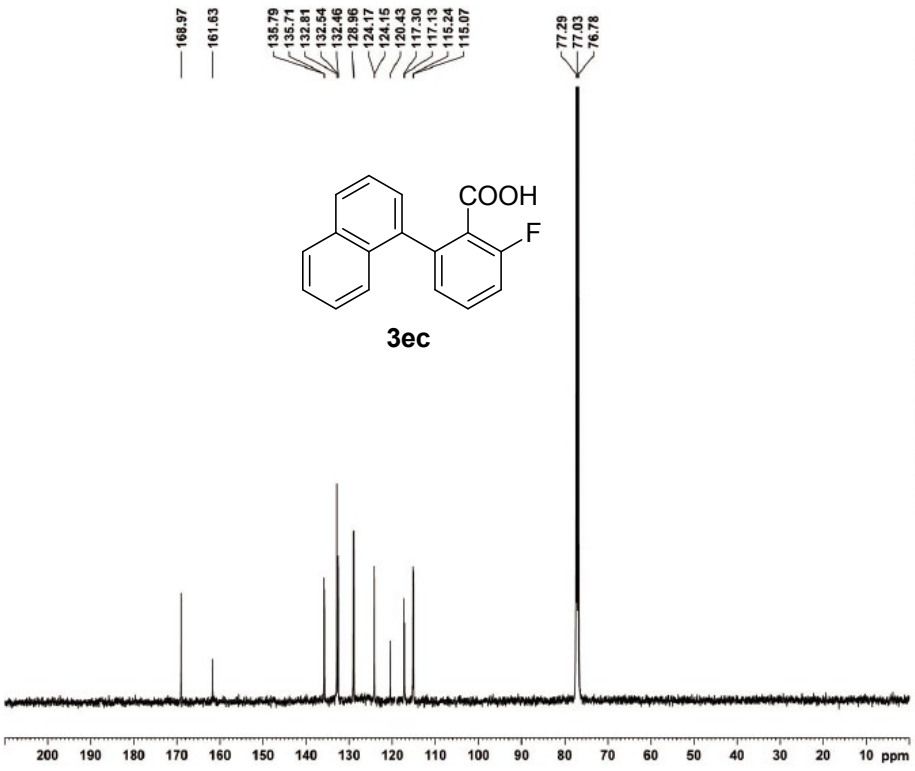




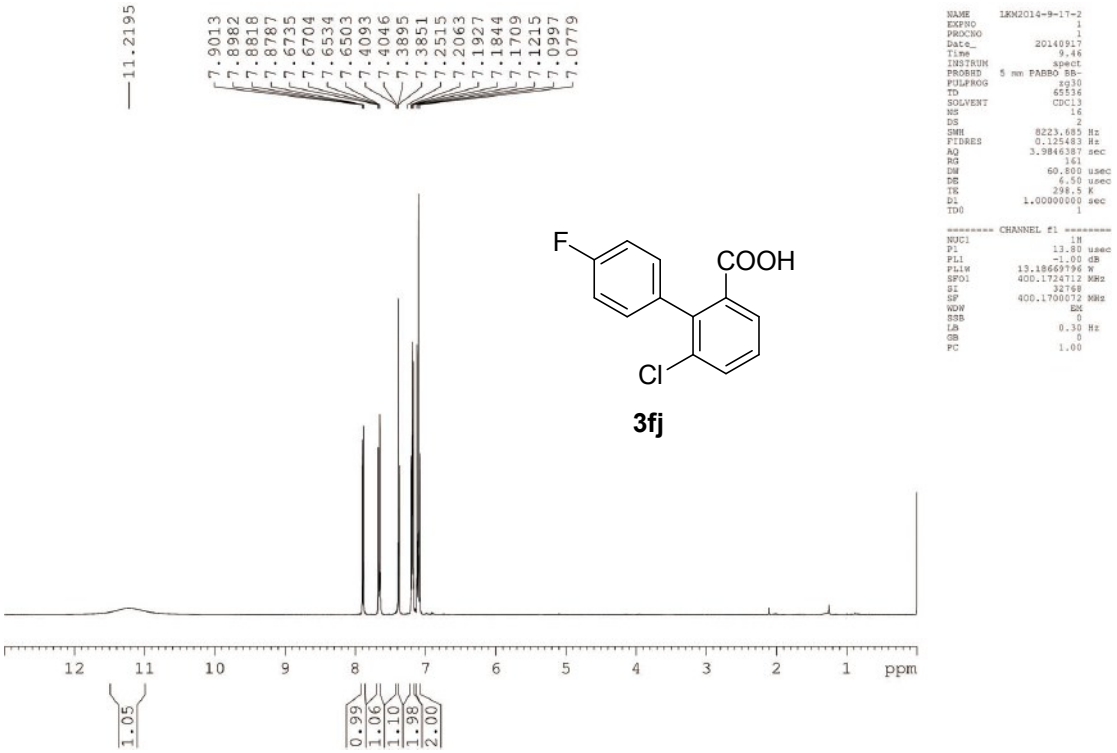

```
NAME          LKM2014-9-1-4-C13
EXPNO                         1
PROCNO                        1
Date_              20140903
Time               11.10
INSTRUM            spect
PROBHD     5 mm PABBO BB/
PULPROG            zgpg30
TD                 65536
SOLVENT            CDCl3
NS                 1024
DS                 4
SWH                29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010548 sec
RG                 2050
DW                 16.800 usec
DE                 6.50 usec
TE                 297.4 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                1

======== CHANNEL f1 ========
SFO1               125.7703637 MHz
NUC1               13C
P1                 9.80 usec
SI                 32768
SF                 125.7577885 MHz
WDW                EM
SSB                0
LB                 3.00 Hz
GB                 0
PC                 1.40
```



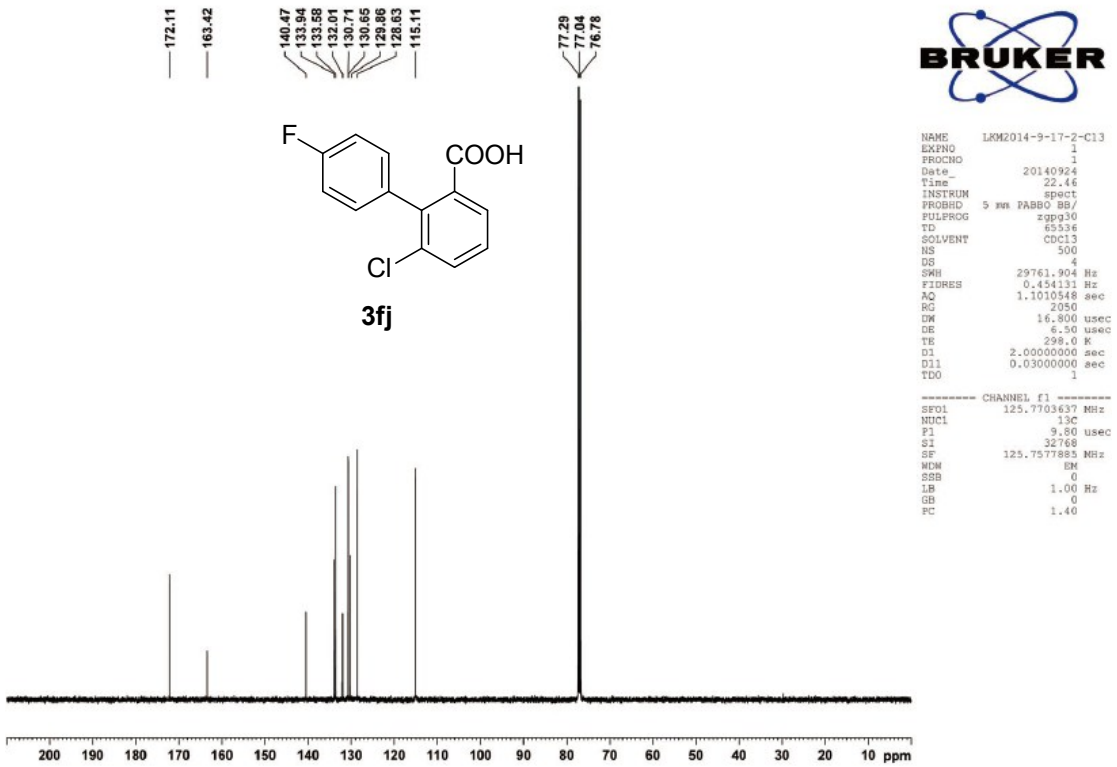

```
NAME          LKM2014-9-26-2
EXPNO                      1
PROCNO                     1
Date_               20140926
Time                   11.57
INSTRUM                spect
PROBHD  5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                       203
DW                  60.800 usec
DE                   6.50 usec
TE                  298.4 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.80 usec
PL1                    -1.00 dB
PL1W            13.18669796 W
SFO1             400.1324712 MHz
SI                       32768
SF               400.1300047 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```



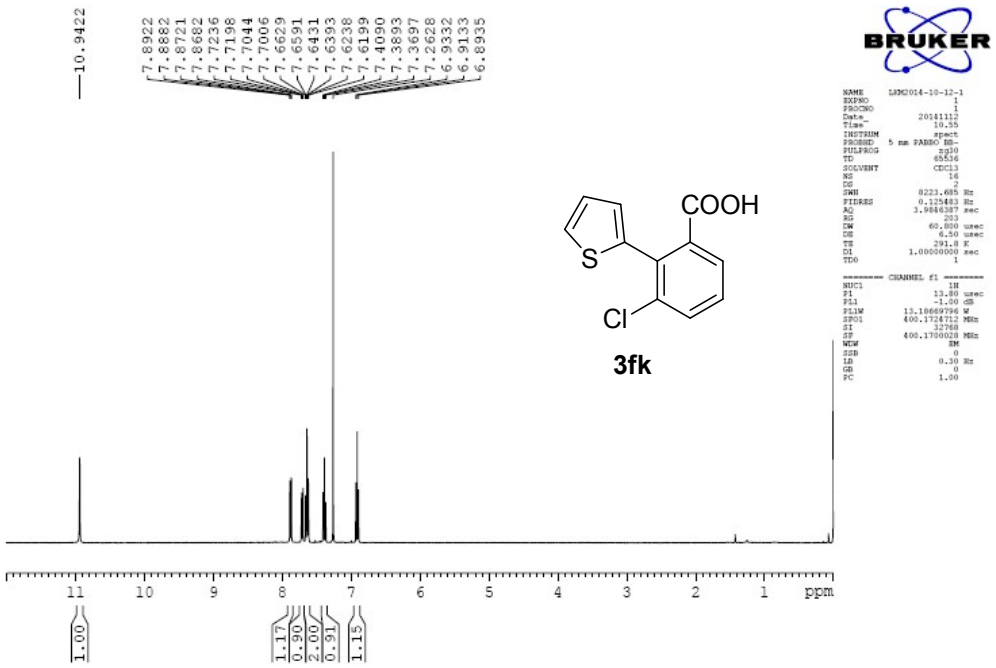

```
NAME          LKM2014-9-26-2-C13
EXPNO                      1
PROCNO                     1
Date_               20141029
Time                   5.12
INSTRUM                spect
PROBHD  5 mm PABBO BB/
PULPROG                zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010548 sec
RG                      2050
DW                  16.800 usec
DE                   6.50 usec
TE                  298.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            125.7703637 MHz
NUC1                      13C
P1                      9.80 usec
SI                       32768
SF              125.7577885 MHz
WDW                       EM
SSB                        0
LB                      3.00 Hz
GB                         0
PC                      1.40
```

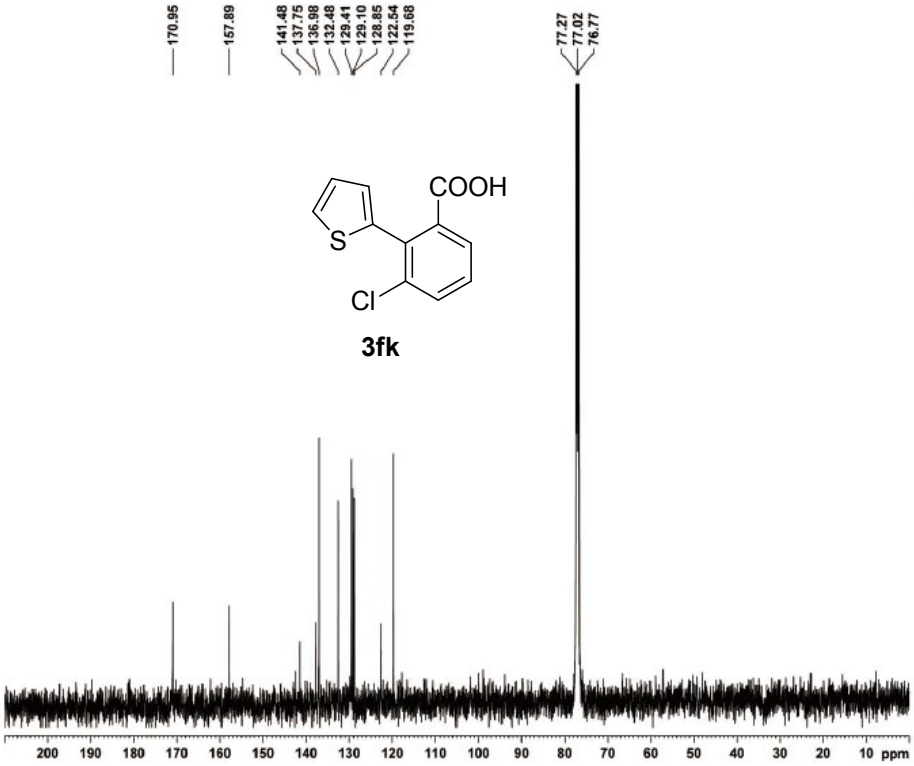


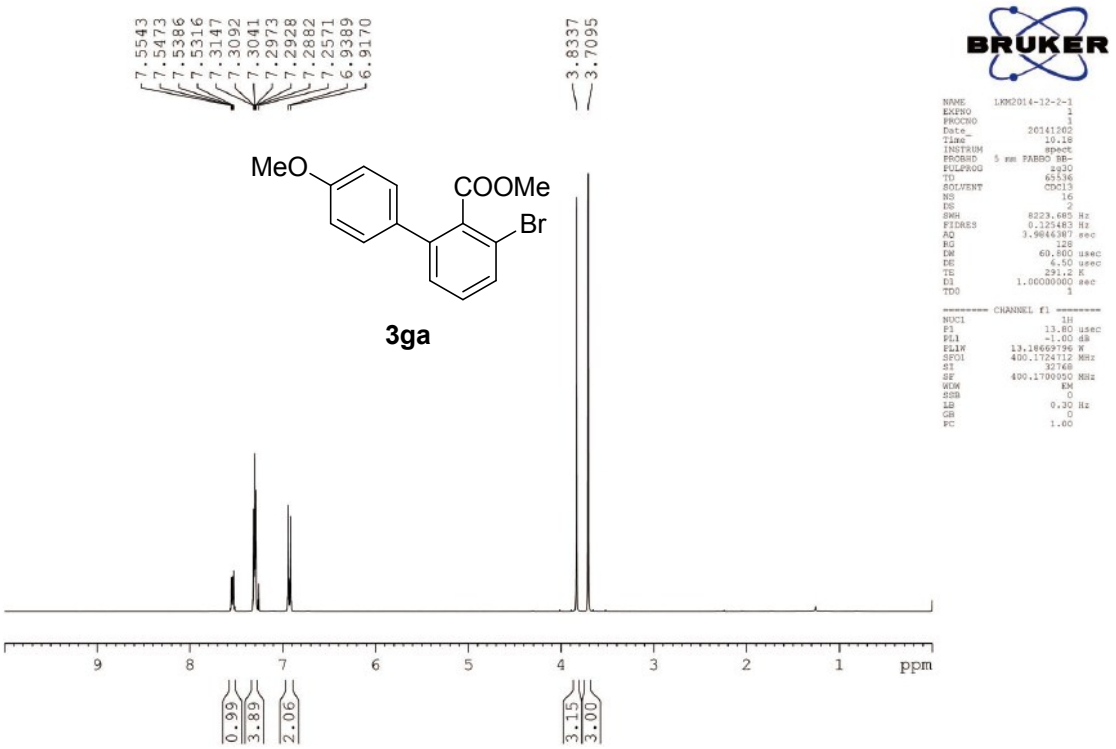

```
NAME        LKM2014-9-17-2
EXPNO               1
PROCNO              1
Date_        20140917
Time              9.46
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                 16
DS                  2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ           3.9846387 sec
RG                161
DW             60.800 usec
DE              6.50 usec
TE             298.5 K
D1          1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              13.80 usec
PL1             -1.00 dB
PLW1       13.18669796 W
SFO1      400.1734712 MHz
SI              32768
SF        400.1700072 MHz
WDW                EM
SSB                 0
LB              0.30 Hz
GB                  0
PC              1.00
```



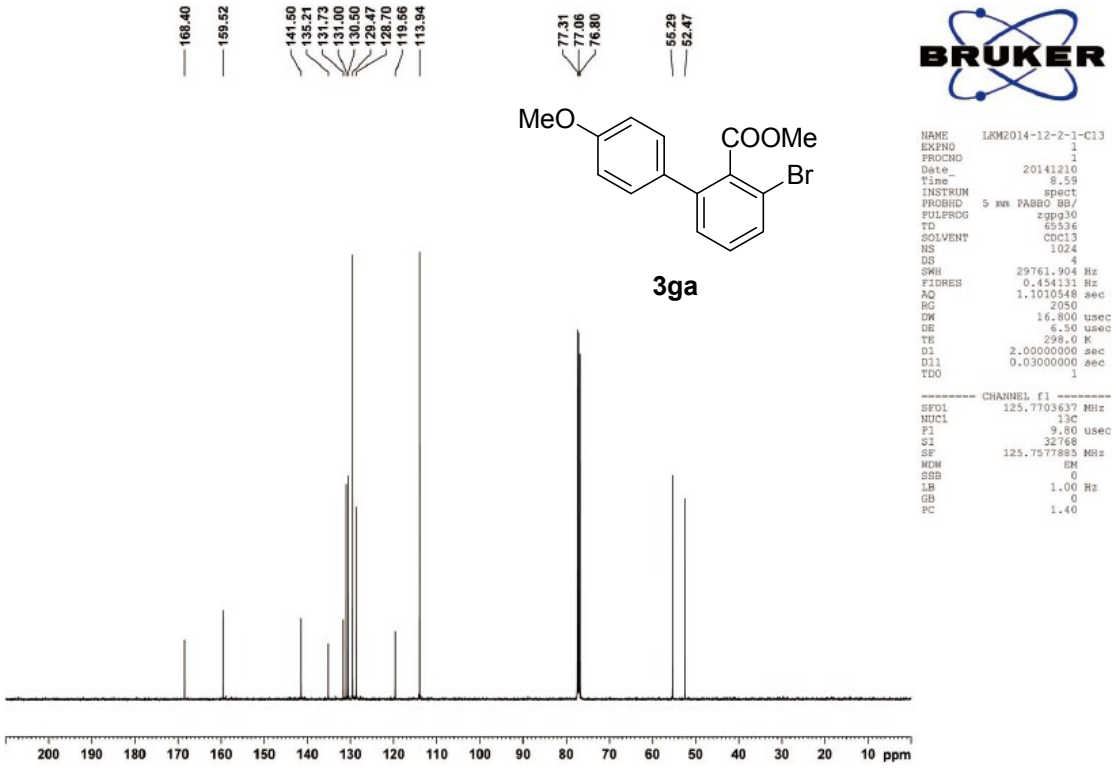

```
NAME        LKM2014-9-17-2-C13
EXPNO               1
PROCNO              1
Date_        20140924
Time              22.46
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD              65536
SOLVENT          CDCl3
NS                500
DS                  4
SWH          29761.904 Hz
FIDRES       0.454131 Hz
AQ           1.1010548 sec
RG                2050
DW             16.800 usec
DE              6.50 usec
TE             298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      125.7703637 MHz
NUC1               13C
P1              9.80 usec
SI              32768
SF        125.7577885 MHz
WDW                EM
SSB                 0
LB              1.00 Hz
GB                  0
PC              1.40
```


10.9422
7.8922
7.8882
7.8721
7.8682
7.7236
7.7198
7.7044
7.7006
7.6629
7.6591
7.6431
7.6393
7.6238
7.6199
7.4090
7.3893
7.3697
7.2628
6.9332
6.9133
6.8935
COOH
S
Cl
3fk
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.17
0.90
2.00
0.91
1.15

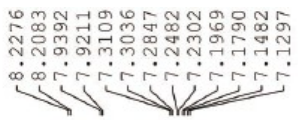

170.95
157.89
141.48
137.75
136.98
132.48
129.41
129.10
128.85
122.54
119.68
77.27
77.02
76.77
COOH
S
Cl
3fk
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

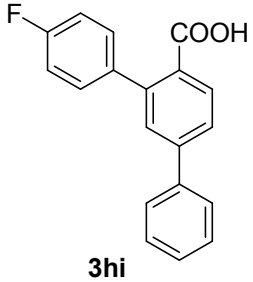

7.5543
7.5473
7.5386
7.5316
7.3147
7.3092
7.3041
7.2973
7.2928
7.2882
7.2571
6.9389
6.9170
3.8337
3.7095
MeO
COOMe
Br
3ga
9
8
7
6
5
4
3
2
1
ppm
0.99
3.89
2.06
3.15
3.00

NAME LKM2014-12-2-1
EXPNO 1
PROCNO 1
Date_ 20141202
Time 10.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 128
DW 60.800 usec
DE 6.50 usec
TE 291.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.10669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700050 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

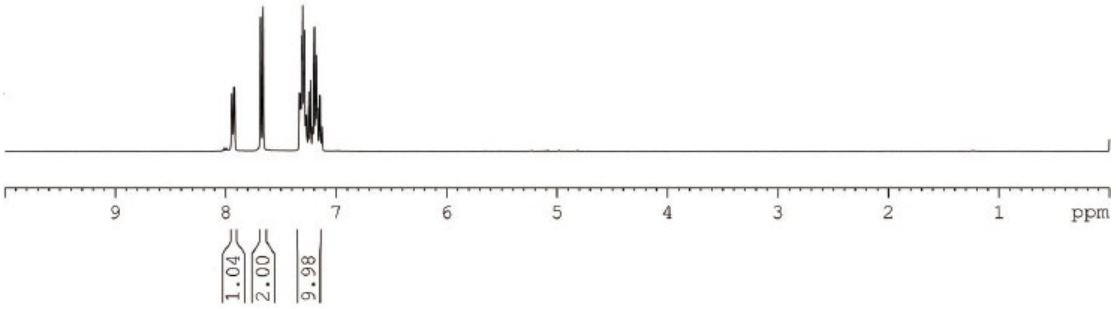

168.40
159.52
141.50
135.21
131.73
131.00
130.50
129.47
128.70
119.56
113.94
77.31
77.06
76.80
55.29
52.47
MeO
COOMe
Br
3ga
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

NAME LKM2014-12-2-1-C13
EXPNO 1
PROCNO 1
Date_ 20141210
Time 8.59
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

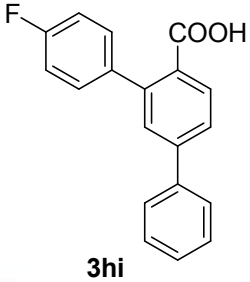

8.2276
8.2083
7.9392
7.9211
7.3109
7.3036
7.2847
7.2482
7.2302
7.1969
7.1790
7.1482
7.1297


F
COOH

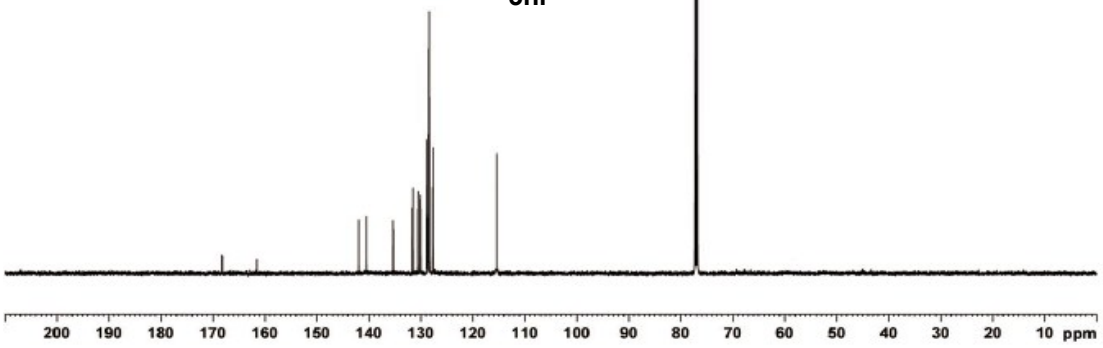
3hi

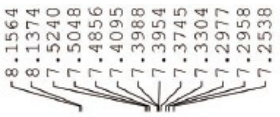

9
8
7
6
5
4
3
2
1
ppm
1.04
2.00
9.98

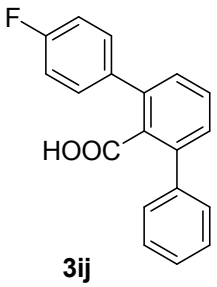

168.08
161.47
141.88
140.36
135.35
135.25
131.59
131.44
129.00
128.32
128.27
128.06
127.63
127.56
115.56
77.31
77.05
76.80


F
COOH

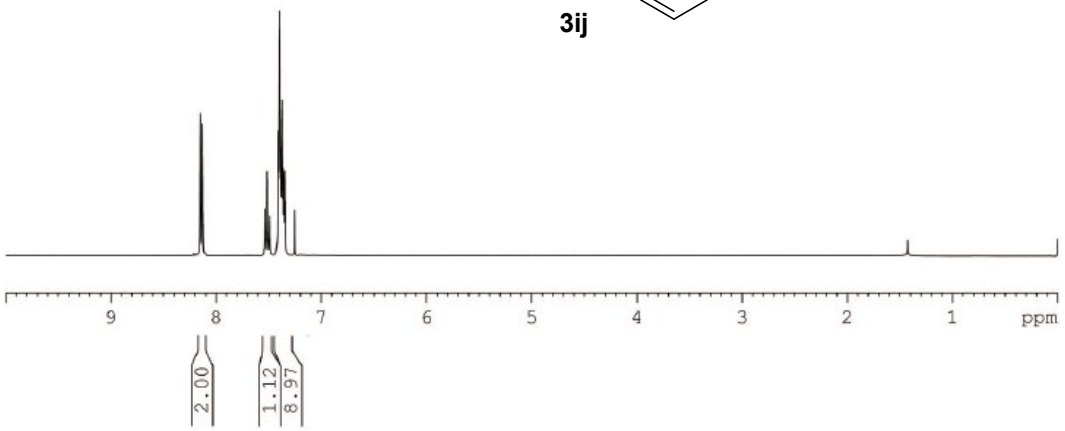
3hi


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.1564
8.1374
7.5240
7.5048
7.4856
7.4095
7.3988
7.3954
7.3745
7.3304
7.2977
7.2958
7.2538

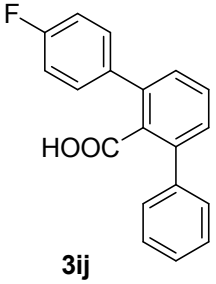

F
HOOC

3ij

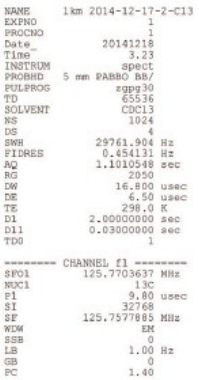

9
8
7
6
5
4
3
2
1
ppm
2.00
1.12
8.97

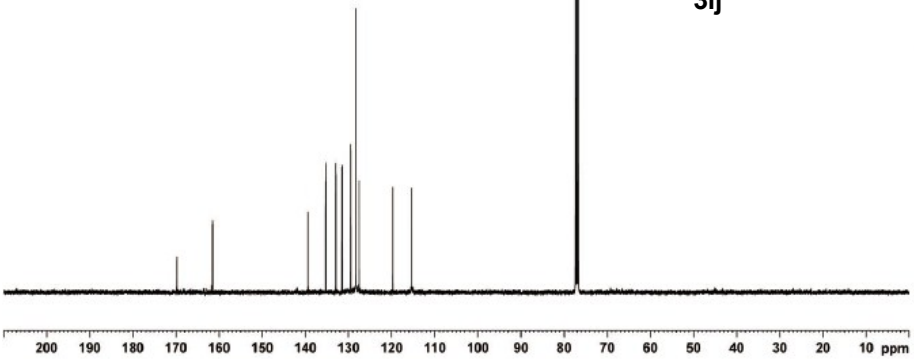

169.76
161.71
139.37
135.35
135.25
132.89
132.83
131.59
131.44
129.43
129.39
128.06
127.56
119.63
115.56
77.31
77.05
76.80

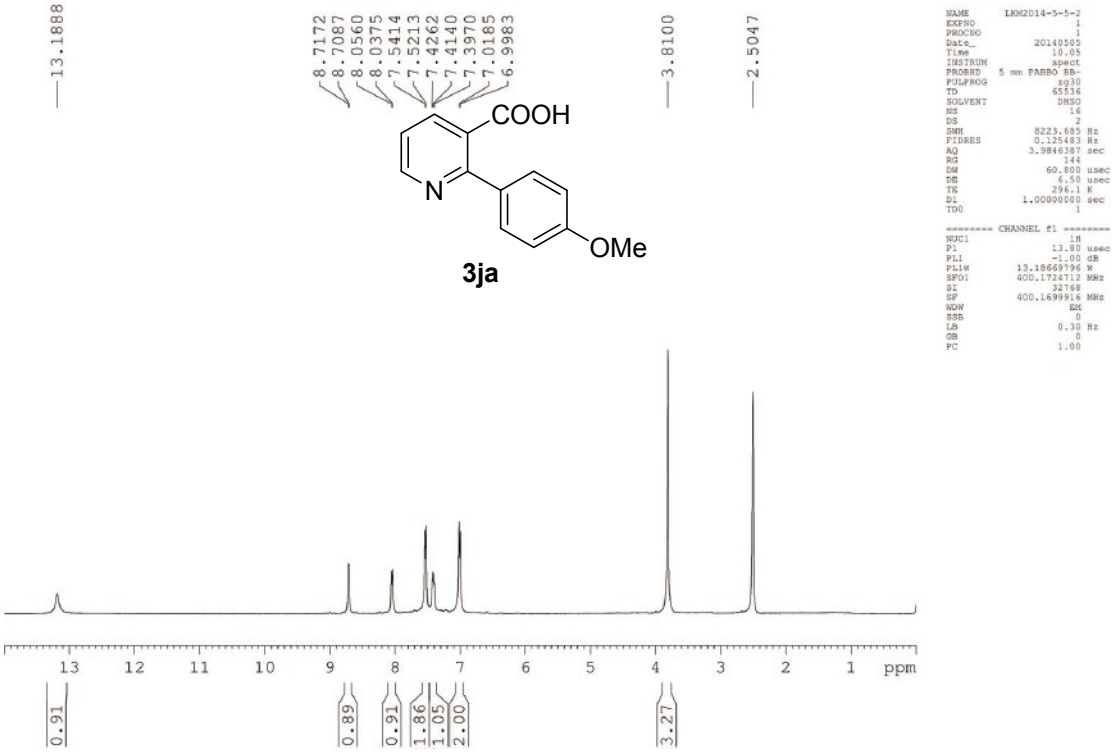

BRUKER

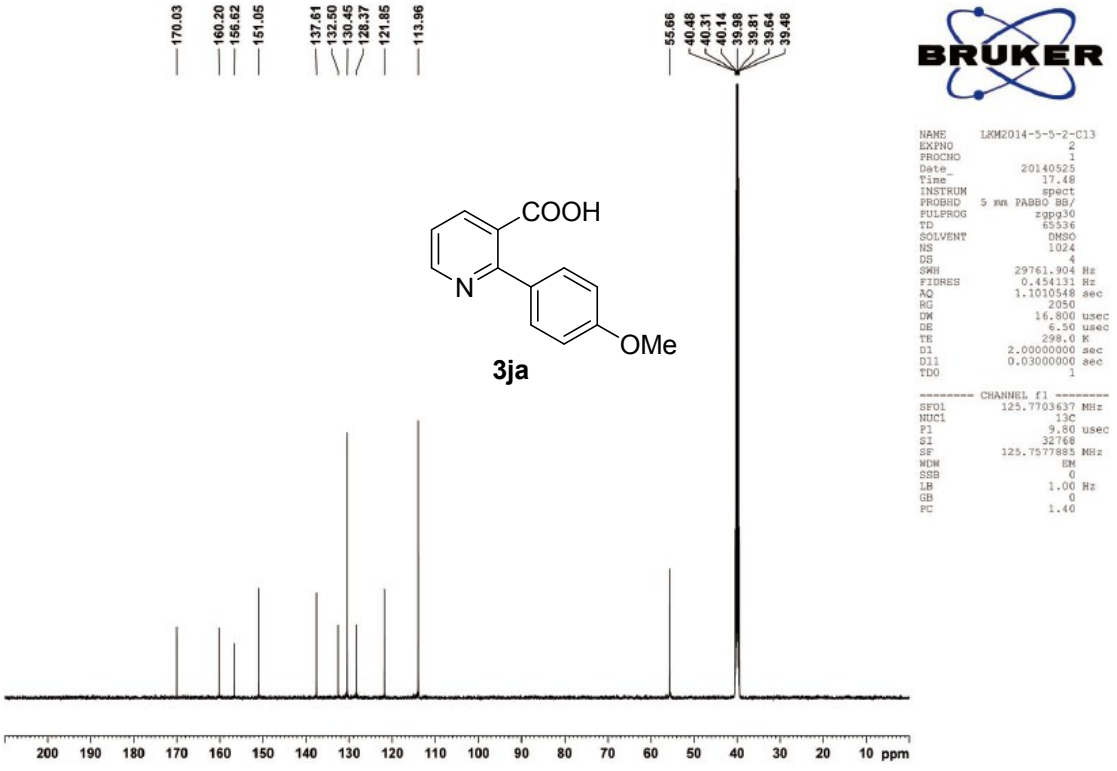

F
HOOC

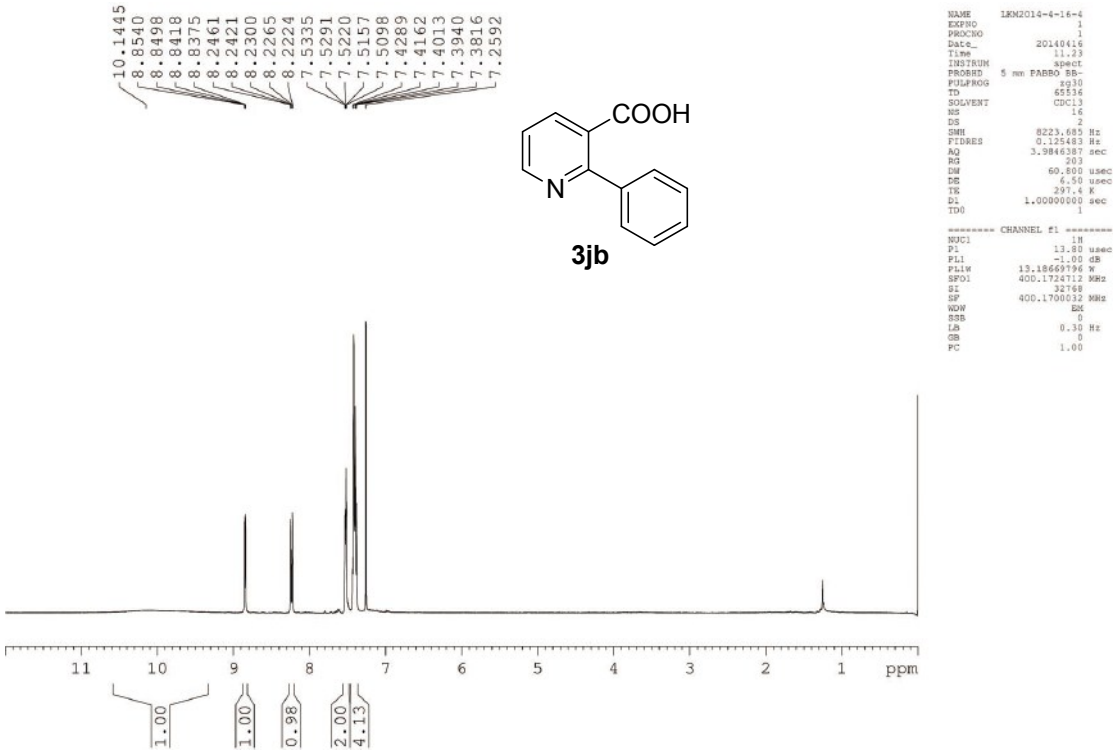
3ij

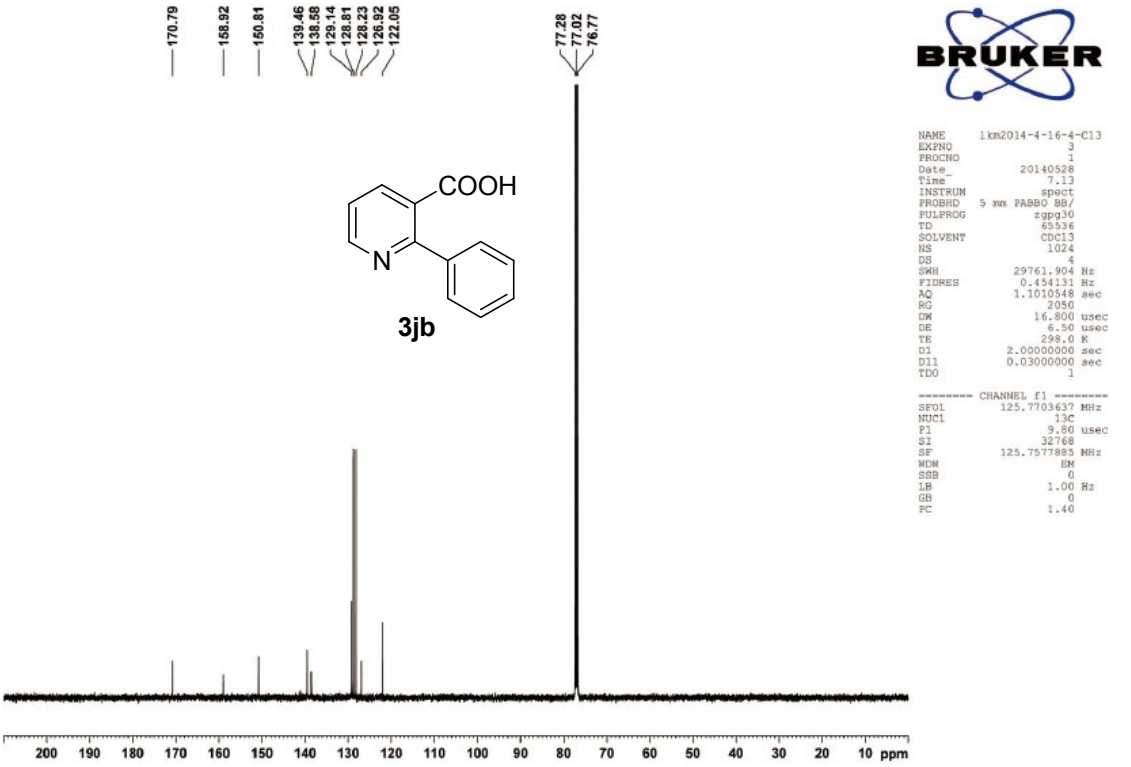

NAME 1km 2014-12-17-2-C13
EXPNO 1
PROCNO 1
Date_ 20141218
Time 3.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

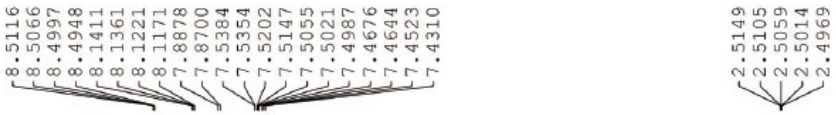

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

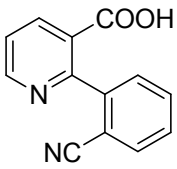

13.1888
8.7172
8.7087
8.0560
8.0375
7.5414
7.5213
7.4262
7.4140
7.3970
7.0185
6.9983
3.8100
2.5047
COOH
N
OMe
3ja
NAME LKM2014-5-5-2
EXPNO 1
PROCNO 1
Date_ 20140505
Time 10.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 144
DW 60.800 usec
DE 6.50 usec
TE 296.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1699916 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.91
0.89
0.91
1.86
1.05
2.00
3.27


170.03
160.20
156.62
151.05
137.61
132.50
130.45
128.37
121.85
113.96
55.66
40.48
40.31
40.14
39.98
39.81
39.64
39.48
COOH
N
OMe
3ja
BRUKER
NAME LKM2014-5-5-2-C13
EXPNO 2
PROCNO 1
Date_ 20140525
Time 17.48
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

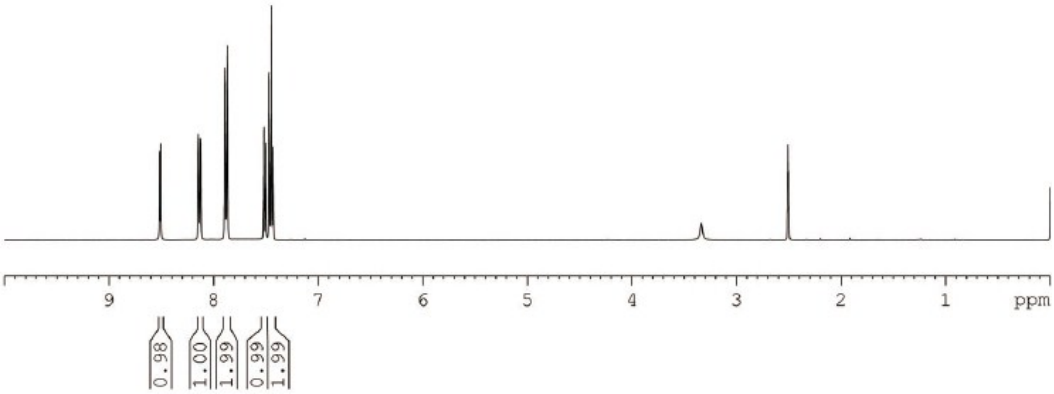

10.1445
8.8540
8.8498
8.8418
8.8375
8.2461
8.2421
8.2300
8.2265
8.2224
7.5335
7.5291
7.5220
7.5157
7.5098
7.4289
7.4162
7.4013
7.3940
7.3816
7.2592
COOH
N
3jb
NAME lkm2014-4-16-4
EXPNO 1
PROCNO 1
Date_ 20140416
Time 11.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700032 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.00 0.98 2.00 4.13

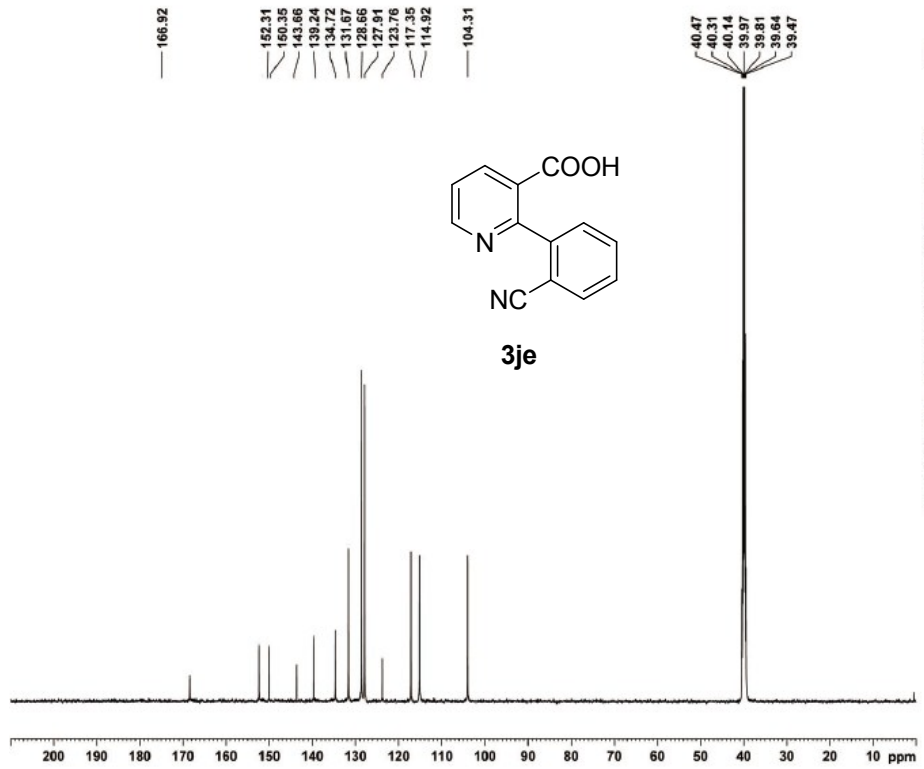

170.79
158.92
150.81
139.46
138.58
129.14
128.81
128.23
126.92
122.05
77.28
77.02
76.77
COOH
N
3jb
BRUKER
NAME lkm2014-4-16-4-C13
EXPNO 3
PROCNO 1
Date_ 20140528
Time 7.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm





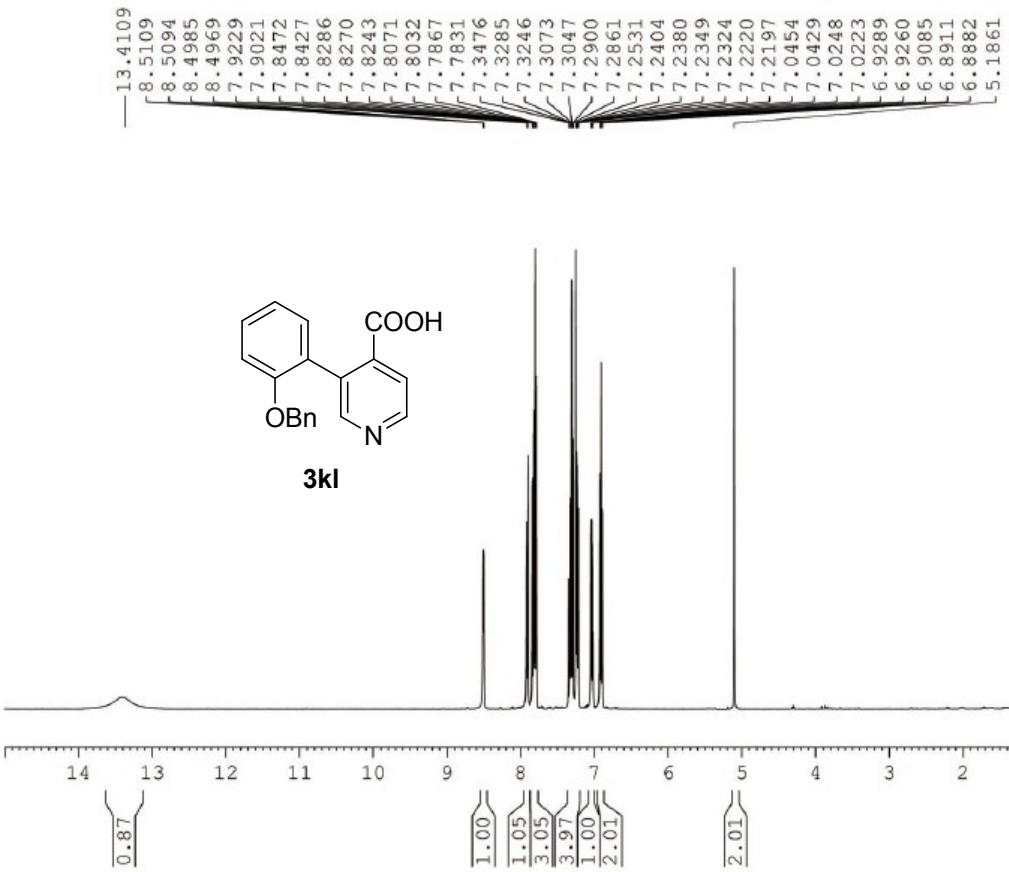
3je

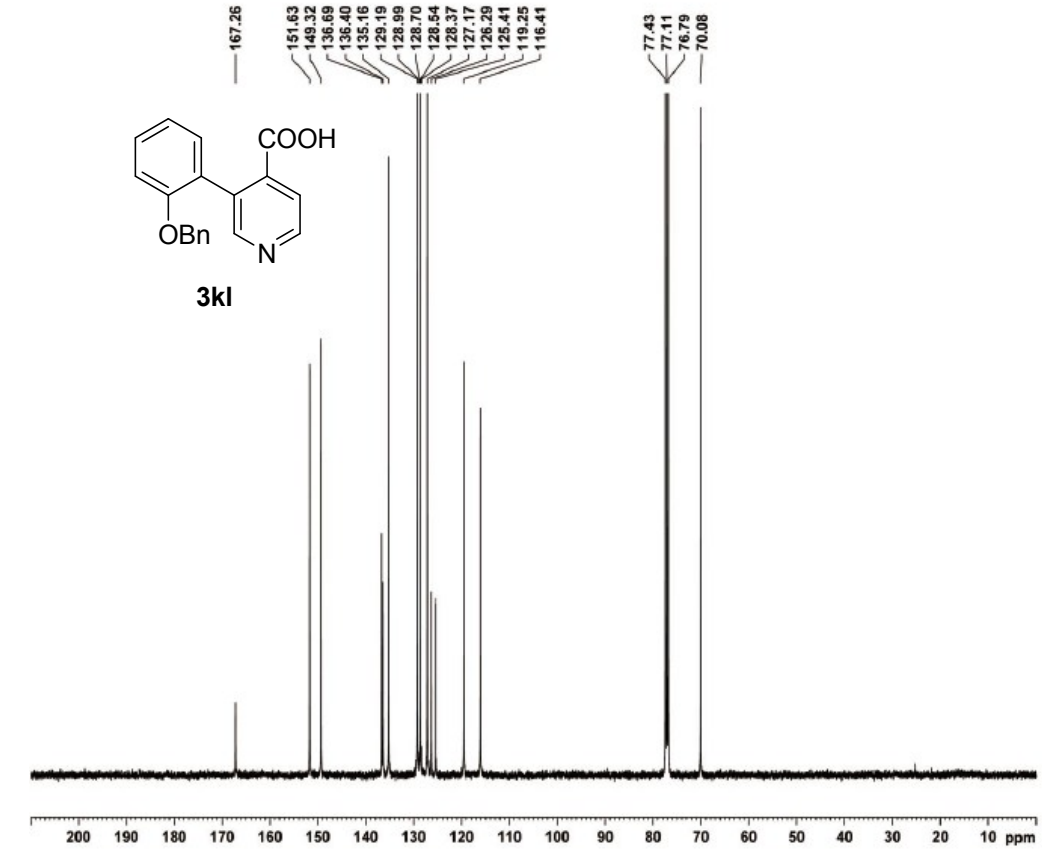


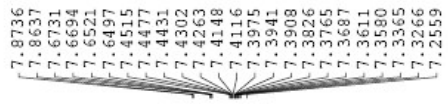


3je

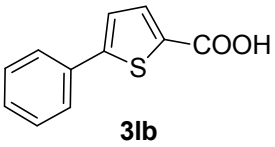

```
NAME        LKM2014-9-1-2-C13
EXPNO                       1
PROCNO                      1
Date_                20140903
Time                     9.54
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  DMSO
NS                        787
DS                          4
SWH                 29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010548 sec
RG                       2050
DW                     16.800 usec
DE                      6.50 usec
TE                     297.0 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1                125.7703637 MHz
NUC1                        13C
P1                      9.80 usec
SI                       32768
SF                  125.7577885 MHz
WDW                         EM
SSB                          0
LB                      3.00 Hz
GB                           0
PC                      1.40
```


13.4109
8.5109
8.5094
8.4985
8.4969
7.9229
7.9021
7.8472
7.8427
7.8286
7.8270
7.8243
7.8071
7.8032
7.7867
7.7831
7.3476
7.3285
7.3246
7.3073
7.3047
7.2900
7.2861
7.2531
7.2404
7.2380
7.2349
7.2324
7.2220
7.2197
7.0454
7.0429
7.0248
7.0223
6.9289
6.9260
6.9085
6.8911
6.8882
5.1861
COOH
OBn
N
3kl
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.87
1.00
1.05
3.05
3.97
1.00
2.01
2.01

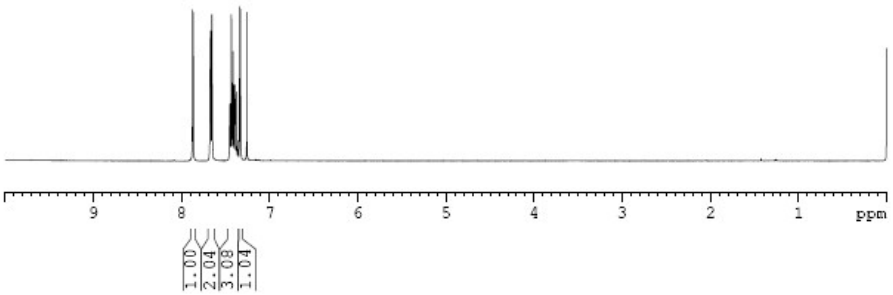

167.26
151.63
149.32
136.69
136.40
135.16
129.19
128.99
128.70
128.54
128.37
127.17
126.29
125.41
119.25
116.41
77.43
77.11
76.79
70.08
COOH
OBn
N
3kl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.8736
7.8637
7.6731
7.6694
7.6521
7.6497
7.4515
7.4477
7.4431
7.4302
7.4263
7.4148
7.4116
7.3975
7.3941
7.3908
7.3826
7.3765
7.3687
7.3611
7.3580
7.3365
7.3266
7.2559


NAME LKM2014-4-16-5
EXPNO 1
PROCNO 1
Date_ 20140416
Time 11.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PLW 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700045 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

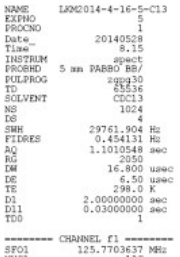

COOH
S

3lb


9
8
7
6
5
4
3
2
1
ppm
1.00
2.04
3.08
1.04


167.41
153.06
135.99
133.27
131.19
129.17
129.06
126.35
123.93
77.28
77.03
76.77

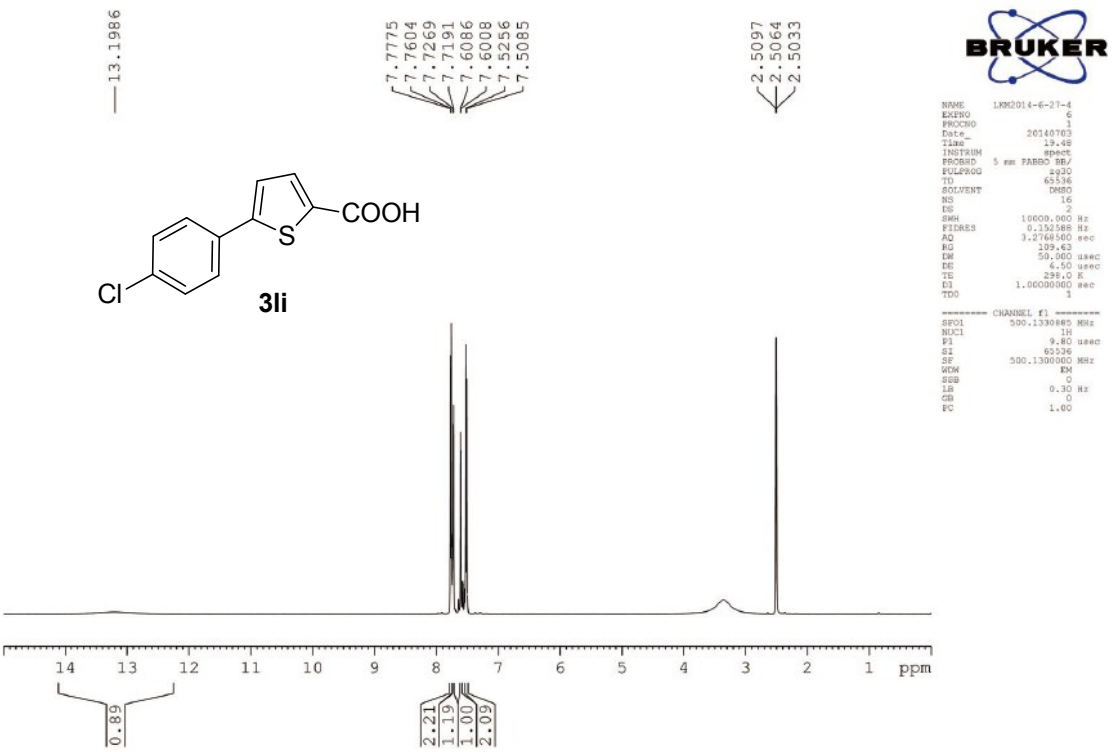

BRUKER

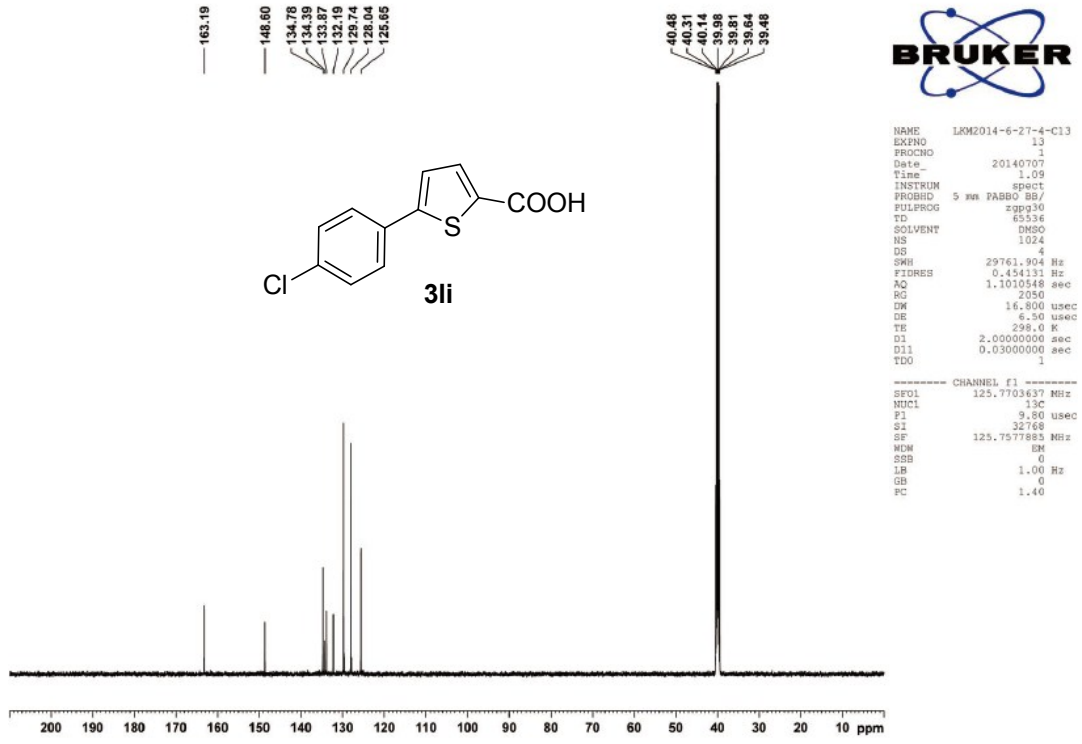

NAME LKM2014-4-16-5-C13
EXPNO 5
PROCNO 1
Date_ 20140528
Time 8.15
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

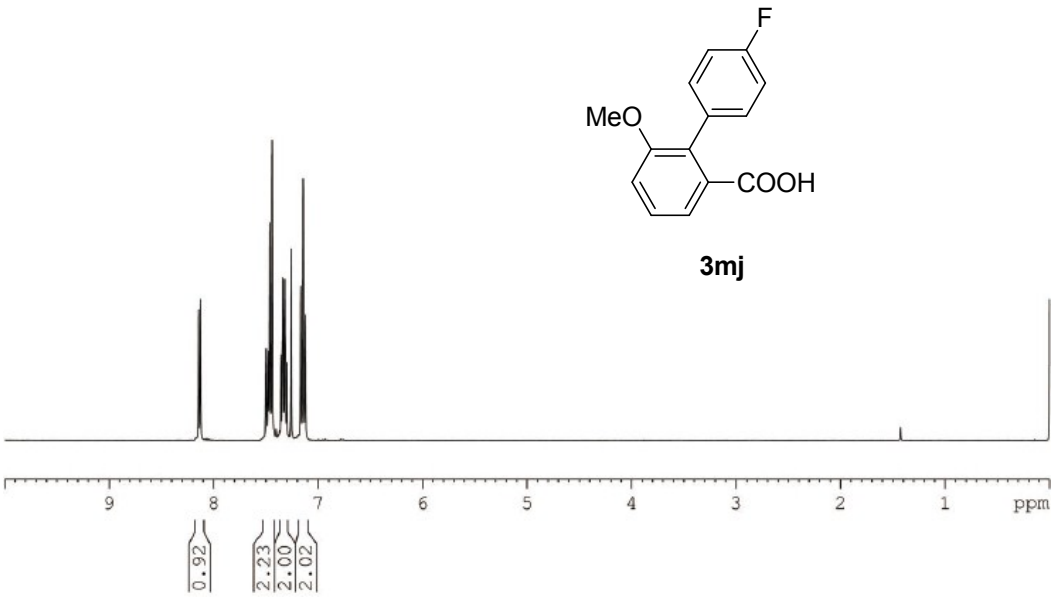
COOH
S

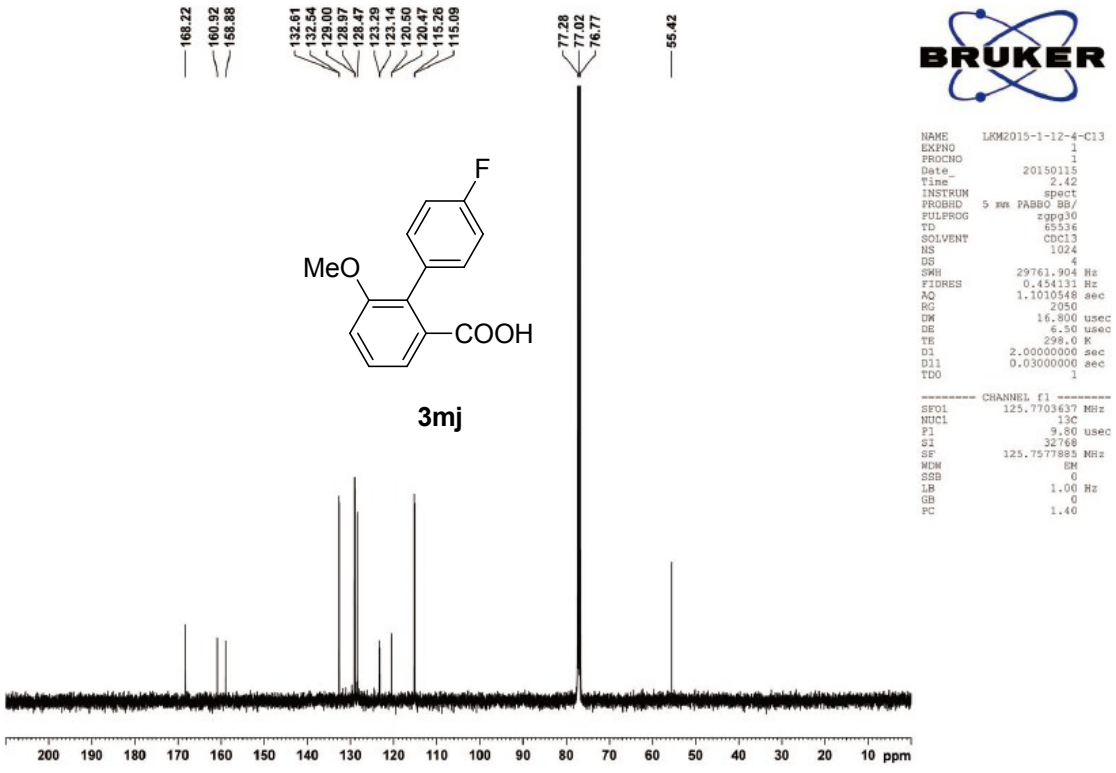
3lb

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

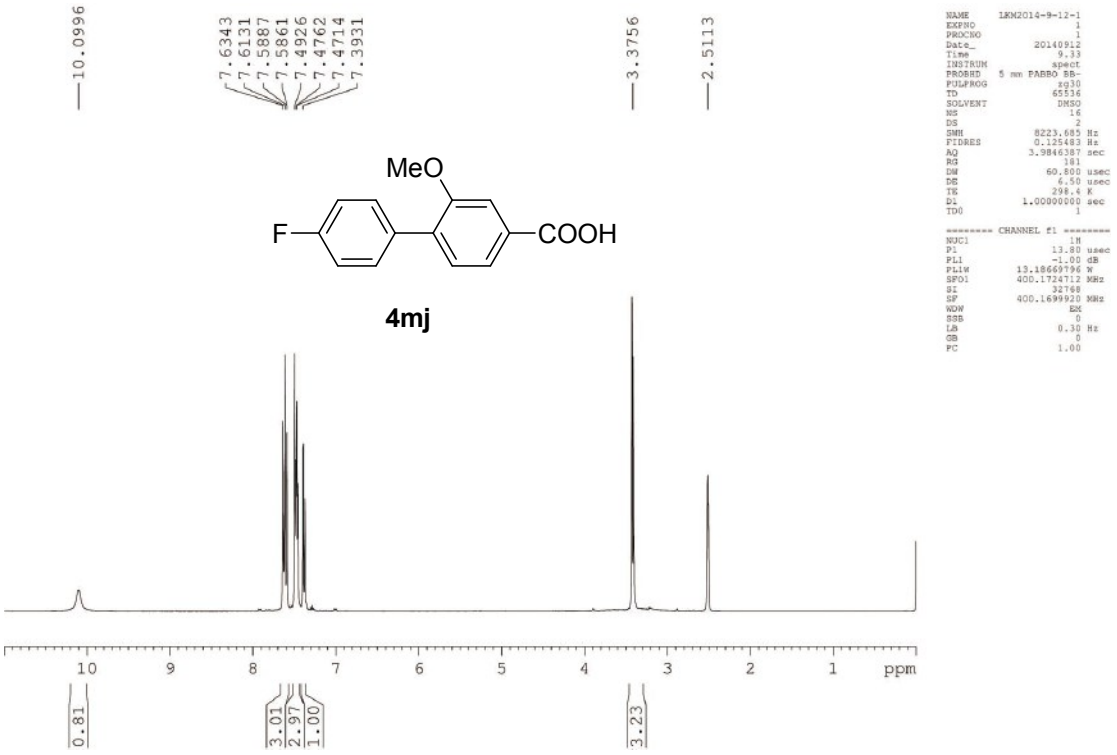

13.1986
7.7775
7.7604
7.7269
7.7191
7.6086
7.6008
7.5256
7.5085
2.5097
2.5064
2.5033
COOH
S
Cl
3li
BRUKER
NAME LKM2014-6-27-4
EXPNO 6
PROCNO 1
Date_ 20140703
Time_ 19.48
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 109.63
DW 50.000 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 9.80 usec
SI 65536
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.89
2.21
1.19
1.00
2.09


163.19
148.60
134.78
134.39
133.87
132.19
129.74
128.04
125.65
40.48
40.31
40.14
39.98
39.81
39.64
39.48
COOH
S
Cl
3li
BRUKER
NAME LKM2014-6-27-4-C13
EXPNO 13
PROCNO 1
Date_ 20140707
Time_ 1.09
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

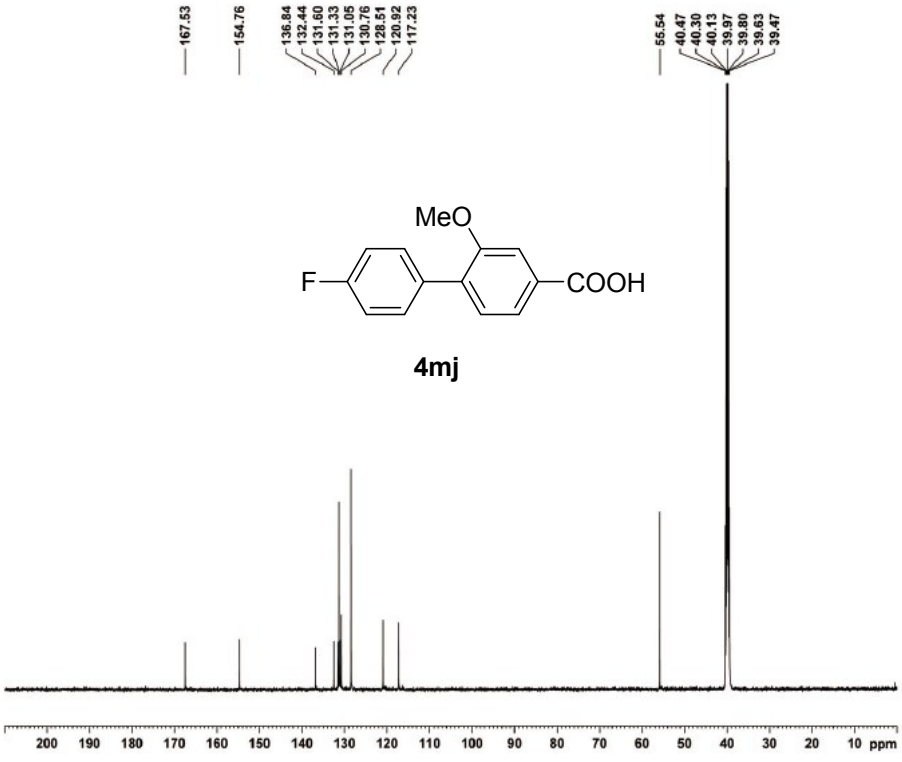




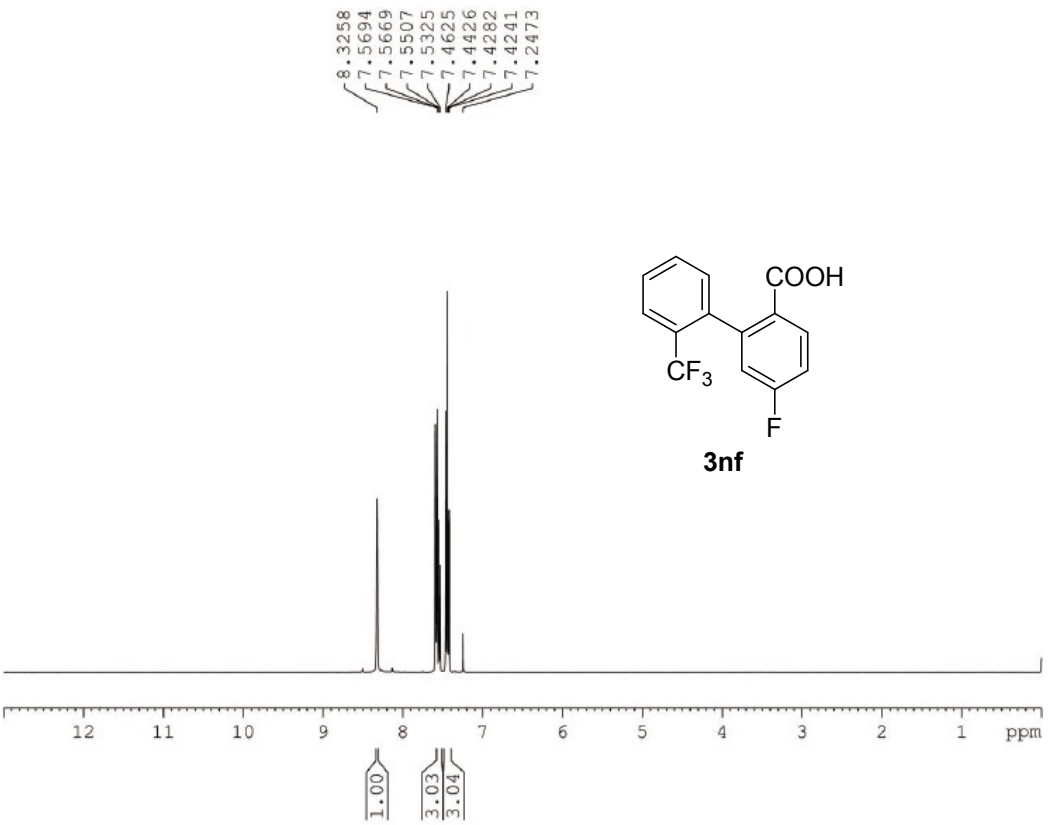

```
NAME          LKM2015-1-12-4-C13
EXPNO                          1
PROCNO                         1
Date_                   20150115
Time                        2.42
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                   zpg30
TD                         65536
SOLVENT                    CDCl3
NS                          1024
DS                             4
SWH                    29761.904 Hz
FIDRES                 0.454131 Hz
AQ                     1.1010548 sec
RG                          2050
DW                        16.800 usec
DE                         6.50 usec
TE                       298.0 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 125.7703637 MHz
NUC1                        13C
P1                         9.80 usec
SI                         32768
SF                   125.7577885 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

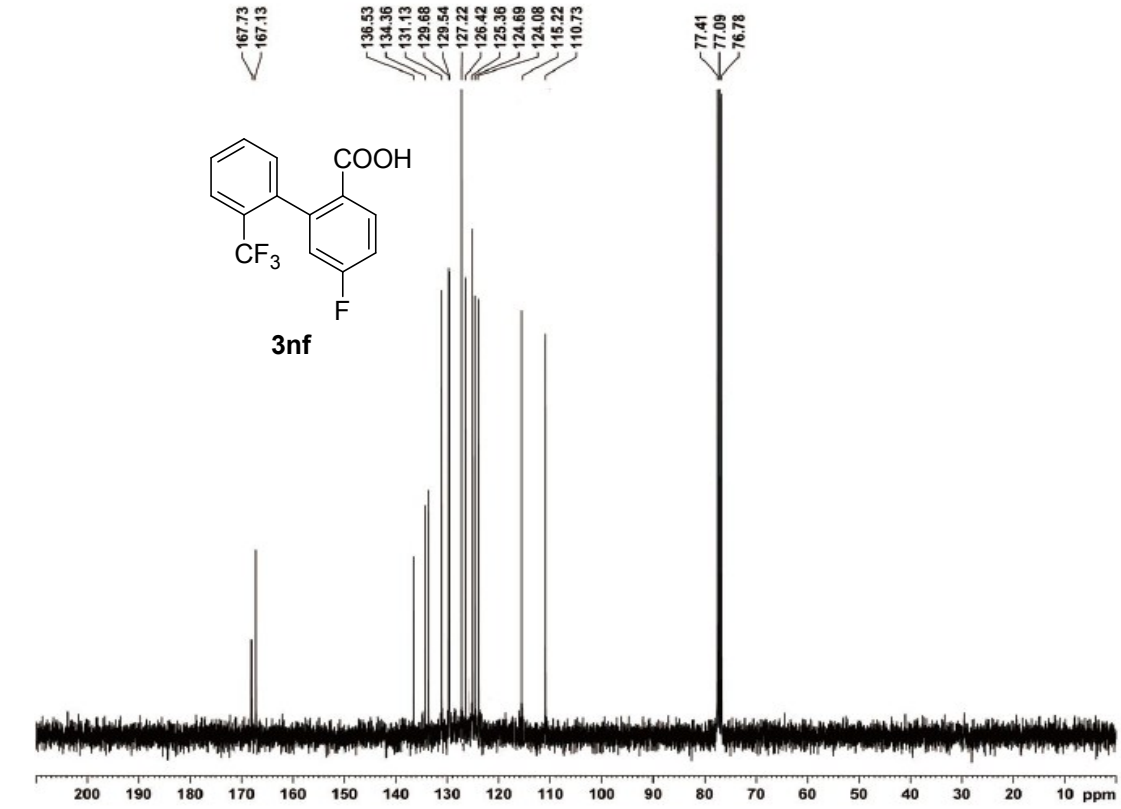


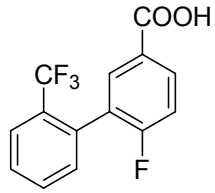

```
NAME        LKM2014-9-12-1
EXPNO               1
PROCNO              1
Date_        20140912
Time             9.33
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          DMSO
NS                 16
DS                  2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ           3.9846387 sec
RG                 161
DW              60.800 usec
DE               6.50 usec
TE              298.4 K
D1           1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1                1H
P1               13.80 usec
PL1              -1.00 dB
PL1W        13.18669796 W
SFO1        400.1724712 MHz
SI              32768
SF          400.1699920 MHz
WDW                 EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```



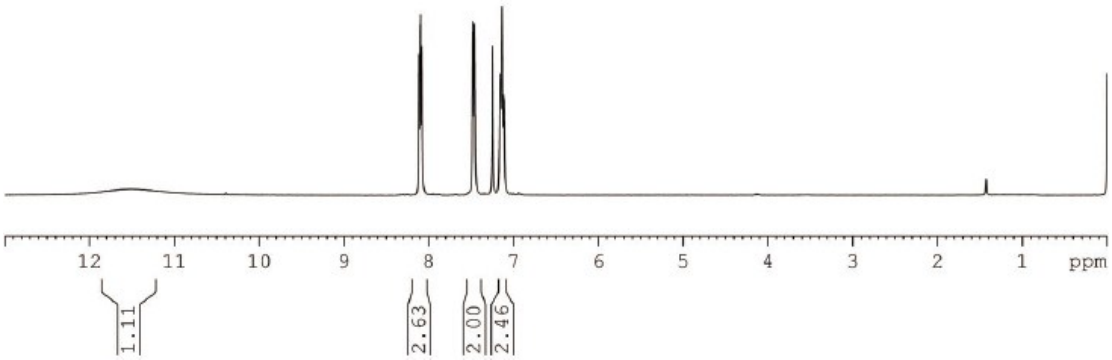

```
NAME        LKM2014-9-12-1-C13
EXPNO               1
PROCNO              1
Date_        20140912
Time             20.42
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD              65536
SOLVENT          DMSO
NS                1024
DS                   4
SWH          29761.904 Hz
FIDRES       0.454131 Hz
AQ           1.1010548 sec
RG                2050
DW              16.800 usec
DE               6.50 usec
TE              298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1        125.7703637 MHz
NUC1                13C
P1               9.80 usec
SI              32768
SF          125.7577885 MHz
WDW                 EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

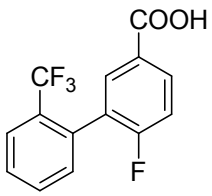

8.3258
7.5694
7.5669
7.5507
7.5325
7.4625
7.4426
7.4282
7.4241
7.2473
COOH
CF3
F
3nf
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.03
3.04


167.73
167.13
136.53
134.36
131.13
129.68
129.54
127.22
126.42
125.36
124.69
124.08
115.22
110.73
77.41
77.09
76.78
COOH
CF3
F
3nf
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm



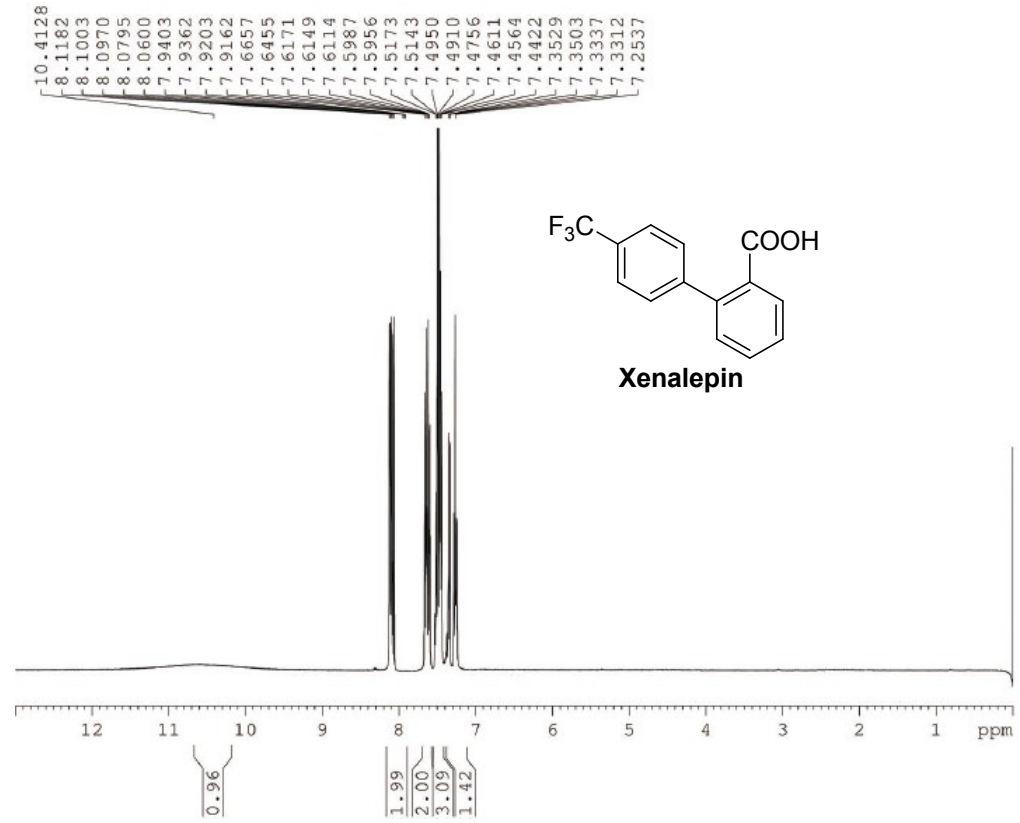
4nf





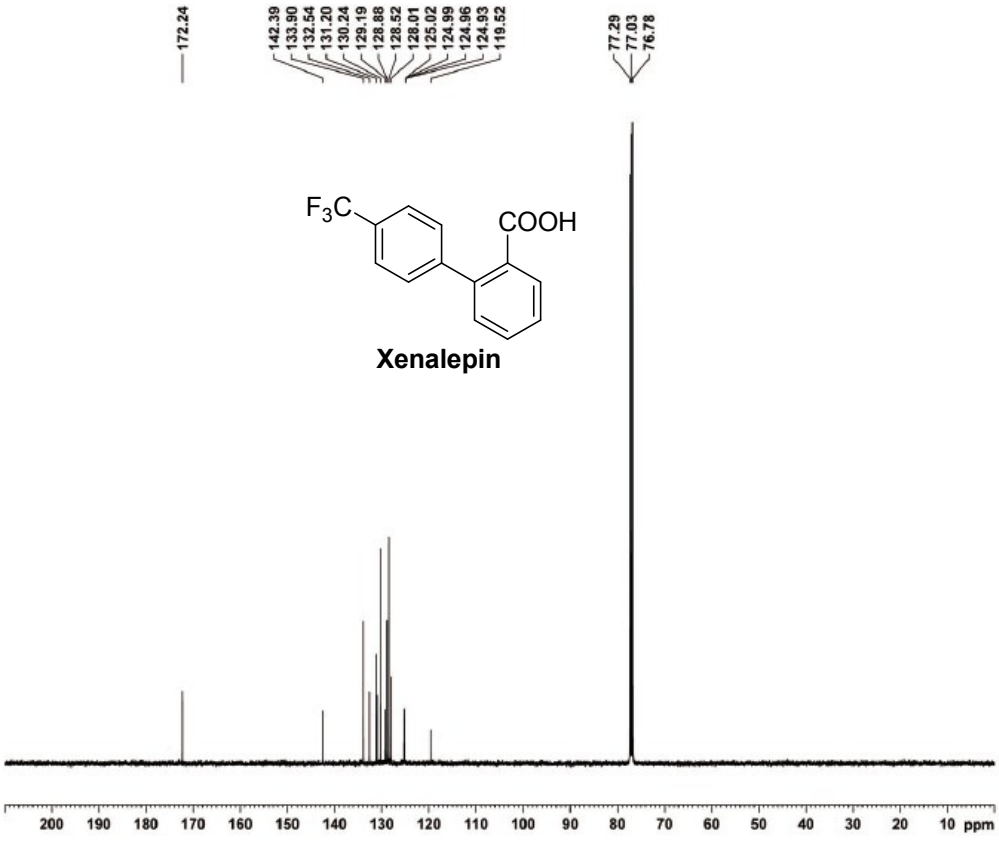
4nf


```
NAME          LRM2015-1-14-3-C13-1
EXPNO                            1
PROCNO                           1
Date_                     20150115
Time                          4.38
INSTRUM                      spect
PROBHD    5 mm PABBO BB/
PULPROG                   zgpg30
TD                             65536
SOLVENT                      CDCl3
NS                              1024
DS                                 4
SWH                       29761.904 Hz
FIDRES                        0.454131 Hz
AQ                            1.1010548 sec
RG                              2050
DW                            16.800 usec
DE                             6.50 usec
TE                            298.0 K
D1                        2.00000000 sec
D11                       0.03000000 sec
TD0                                1

======== CHANNEL f1 ========
SFO1                  125.7703637 MHz
NUC1                          13c
P1                            9.80 usec
SI                           32768
SF                    125.7577885 MHz
WDW                             EM
SSB                              0
LB                            1.00 Hz
GB                               0
PC                            1.40
```



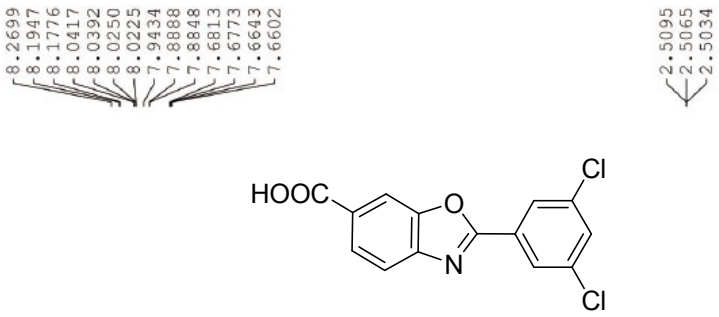
Xenalepin

```
NAME        LKM2014-9-23-1
EXPNO               1
PROCNO              1
Date_        20140923
Time             9.55
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                 16
DS                  2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ           3.9846387 sec
RG                203
DW             60.800 usec
DE              6.50 usec
TE             299.0 K
D1          1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              13.80 usec
PL1             -1.00 dB
PLW1        13.18669796 W
SFO1       400.1724712 MHz
SI              32768
SF         400.1700063 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

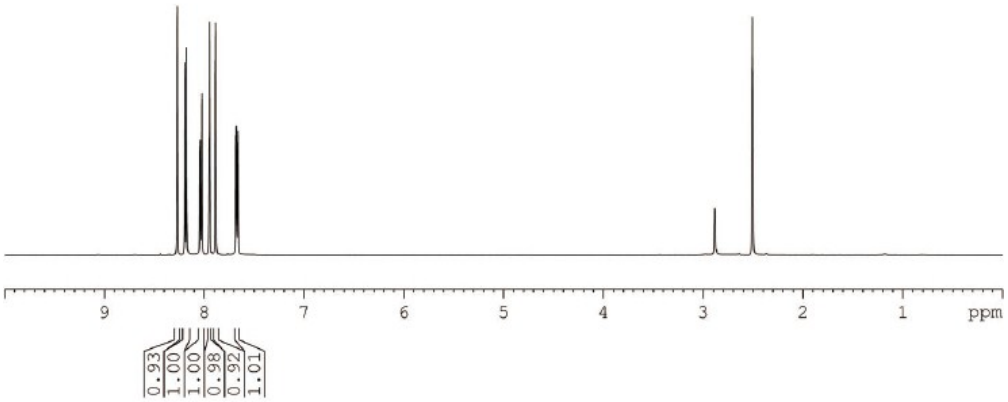


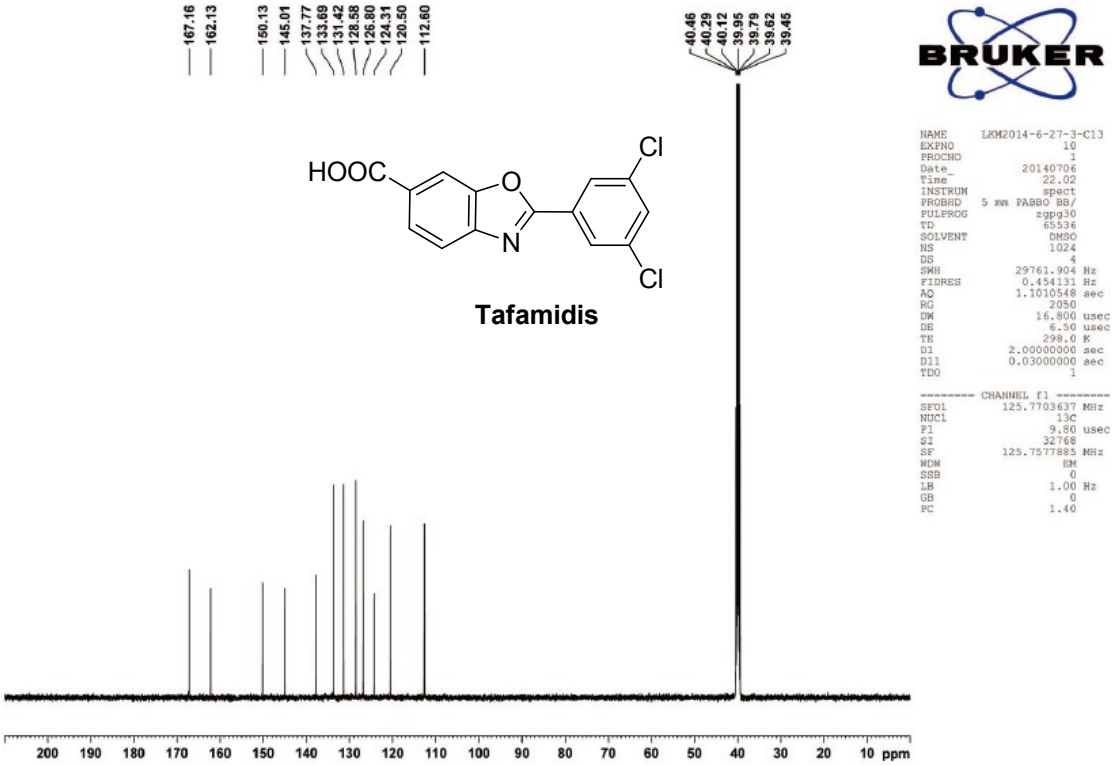
Xenalepin

```
NAME        LKM2014-9-23-1-C13
EXPNO               1
PROCNO              1
Date_        20140924
Time            23.17
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD              65536
SOLVENT          CDCl3
NS                500
DS                  4
SWH         29761.904 Hz
FIDRES       0.454131 Hz
AQ           1.1010548 sec
RG                2050
DW             16.800 usec
DE              6.50 usec
TE             298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1       125.7703637 MHz
NUC1               13C
P1              9.80 usec
SI              32768
SF         125.7577885 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



Tafamidis

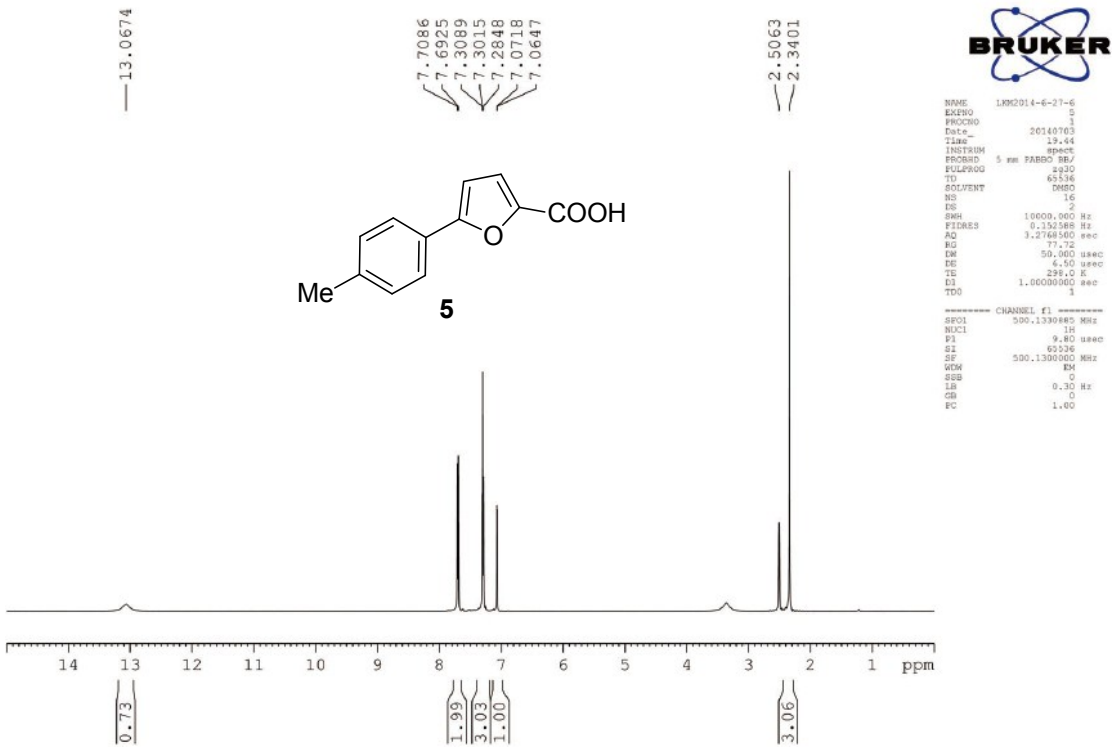


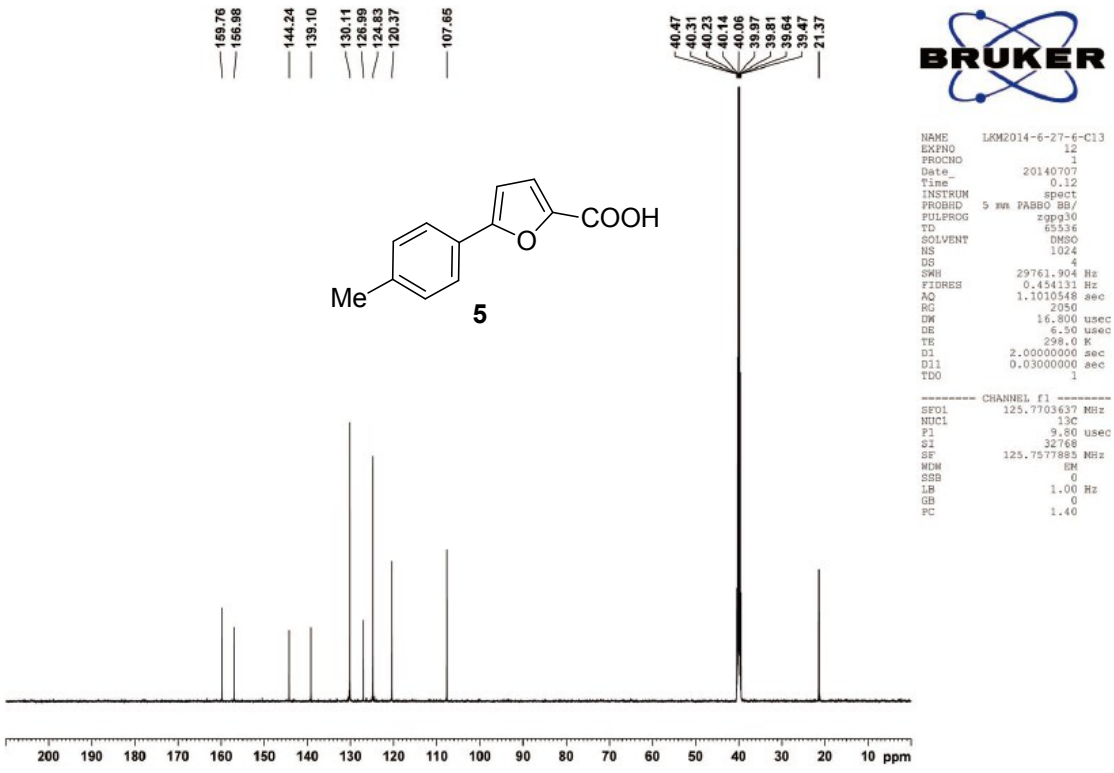


Tafamidis

BRUKER

```
NAME          LKM2014-6-27-3-C13
EXPNO                         10
PROCNO                         1
Date_                   20140706
Time                       22.02
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                   zgpg30
TD                         65536
SOLVENT                     DMSO
NS                          1024
DS                             4
SWH                   29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010548 sec
RG                          2050
DW                      16.800 usec
DE                       6.50 usec
TE                        298.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                125.7703637 MHz
NUC1                        13C
P1                         9.80 usec
SI                        32768
SF                  125.7577885 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```


13.0674
7.7086
7.6925
7.3089
7.3015
7.2848
7.0718
7.0647
2.5063
2.3401
COOH
O
Me
5
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.73
1.99
3.03
1.00
3.06
NAME LKM2014-6-27-6
EXPNO 5
PROCNO 1
Date_ 20140703
Time 13.44
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 77.72
DW 50.000 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 9.80 usec
SI 65536
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


159.76
156.98
144.24
139.10
130.11
126.99
124.83
120.37
107.65
40.47
40.31
40.23
40.14
40.06
39.97
39.81
39.64
39.47
21.37
COOH
O
Me
5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
NAME LKM2014-6-27-6-C13
EXPNO 12
PROCNO 1
Date_ 20140707
Time 0.12
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40