Supporting Information

KCC-1 Supported Palladium Nanoparticles as an Efficient and Sustainable Nanocatalyst for Carbonylative Suzuki-Miyaura Cross-Coupling

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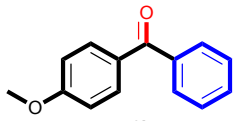
I Characterization data of products

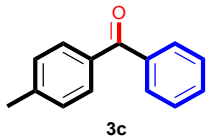


3b

(4-methoxyphenyl)(phenyl)methanone (3b)

59.3 mg, yield 56%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 3.92 (s, 3H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 195.4, 163.1, 138.2, 132.4, 131.8, 130.0, 129.6, 128.1, 113.4, 55.4. **GCMS** (EI, 70 eV): *m/z* (%): 212 (40), 135 (100), 105 (14), 77 (36).

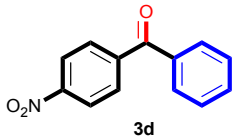


3c

phenyl(*p*-tolyl)methanone (3c)

51.0 mg, yield 52%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J = 7.7 Hz, 2H), 7.75 (d, J = 7.9 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 2.47 (s, 3H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 196.4, 143.1, 137.8, 134.7, 132.0, 130.2, 129.8, 128.8, 128.1, 21.5. **GCMS** (EI, 70 eV): *m/z* (%): 196 (73), 119 (100), 105 (42), 91 (47), 77 (34).

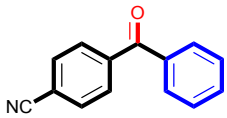


3d

(4-nitrophenyl)(phenyl)methanone (3d)

57.9 mg, yield 51%

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 7.7 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.7 Hz, 2H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 194.7, 149.7, 142.8, 136.1, 133.4, 130.6, 130.0, 128.6, 123.4. **GCMS** (EI, 70 eV): *m/z* (%): 227 (55), 150 (19), 105 (100), 77 (58).

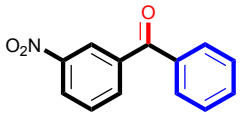


3e

4-benzoylbenzonitrile (3e)

50.7 mg, yield 49%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.82 (dd, *J* = 7.9, 4.6 Hz, 4H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 194.9, 141.1, 136.2, 133.2, 132.0, 130.1, 129.9, 128.5, 117.9, 115.5. **GCMS** (EI, 70 eV): *m/z* (%): 207 (38), 130 (27), 105 (100), 77 (47).

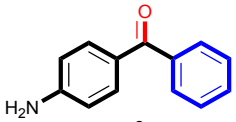


3f

(3-nitrophenyl)(phenyl)methanone (3f)

54.5 mg, yield 48%

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.48 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 7.7 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.71 (dt, J = 22.5, 7.7 Hz, 2H), 7.57 (t, J = 7.6 Hz, 2H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 194.0, 148.0, 138.9, 136.1, 135.3, 133.2, 129.9, 129.5, 128.6, 126.6, 124.6. **GCMS** (EI, 70 eV): *m/z* (%): 227 (23), 105 (100), 150 (11), 77 (50).

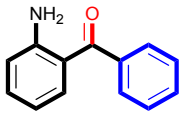


3g

(4-aminophenyl)(phenyl)methanone (3g)

59.1 mg, yield 60%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.3 Hz, 4H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 4.16 (s, 2H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 195.2, 150.9, 138.7, 132.8, 131.3, 129.4, 127.9, 127.2, 113.5. **GCMS** (EI, 70 eV): *m/z* (%): 197 (39), 120 (100), 92 (24), 65 (25).

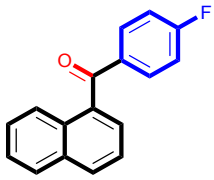


3h

(2-aminophenyl)(phenyl)methanone (3h)

38.4 mg, yield 39%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 3H), 7.32 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.10 (s, 2H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 199.0, 150.8, 140.0, 134.5, 134.1, 130.9, 129.0, 127.9, 118.0, 116.9, 115.4. **GCMS** (EI, 70 eV): *m/z* (%): 197 (65), 196 (100), 120 (48), 92 (31), 77 (36).

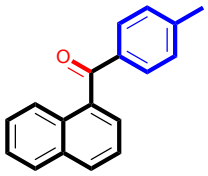


3i

(4-fluorophenyl)(naphthalen-1-yl)methanone (3i)

73.8 mg, yield 59%

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.97 – 7.90 (m, 3H), 7.57 (dt, *J* = 19.1, 6.9 Hz, 4H), 7.16 (t, *J* = 8.5 Hz, 2H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 196.3, 165.7 (J_{C-F} = 254 Hz), 136.0, 134.5, 133.6, 132.9 (J_{C-F} = 10 Hz, 2C), 131.2, 130.7, 128.3, 127.3, 127.2, 126.4, 125.4, 124.2, 115.5 (J_{C-F} = 21 Hz, 2C). **GCMS** (EI, 70 eV): *m/z* (%): 250 (88), 155 (77), 127 (100), 95 (61), 75 (24).



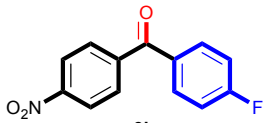
3j

naphthalen-1-yl(*p*-tolyl)methanone (3j)

68.9 mg, yield 56%

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.75 (d, 2H), 7.51 (dt, *J* = 17.9, 8.7 Hz, 4H), 7.28 – 7.20 (m, 2H), 2.41 (s, 3H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 197.7, 144.1, 136.6, 135.6, 133.6, 130.9, 130.8, 130.5, 129.1, 128.3, 127.2, 127.0, 126.3,

125.6, 124.3, 21.7. **GCMS** (EI, 70 eV): *m/z* (%): 246 (100), 245 (55), 231 (69), 155 (59), 127 (66), 119 (73), 91 (46).

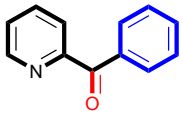


3k

(4-fluorophenyl)(4-nitrophenyl)methanone (3k)

69.8mg, yield 57%

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.23 (t, *J* = 8.4 Hz, 2H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 193.2, 165.8 (J_{C-F} = 256.1 Hz), 149.7, 142.6, 132.7 (J_{C-F} = 9.4 Hz), 132.4, 130.4, 123.5, 115.9 (J_{C-F} = 21.6 Hz). **GCMS** (EI, 70 eV): *m/z* (%): 245 (51), 150 (17), 123 (100), 95 (58), 75 (22).

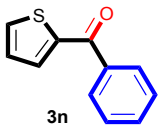


3m

phenyl(pyridin-2-yl)methanone (3m)

36.6mg, yield 40%

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.5 Hz, 1H), 8.13 – 8.05 (m, 3H), 7.93 (t, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 193.8, 155.0, 148.4, 136.9, 136.1, 132.8, 130.9, 128.0, 126.0, 124.5. **GCMS** (EI, 70 eV): *m/z* (%): 183 (40), 155 (77), 105 (80), 77 (100), 51 (32).

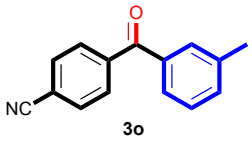


3n

phenyl(thiophen-2-yl)methanone (3n)

36.7mg, yield 39%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 4.9 Hz, 1H), 7.68 (d, *J* = 3.8 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 4.4 Hz, 1H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 188.1, 143.5, 138.0, 134.7, 134.1, 132.1, 129.0, 128.3, 127.8. **GCMS** (EI, 70 eV): *m/z* (%): 188 (60), 111 (100), 105 (39), 77 (40), 51 (18).

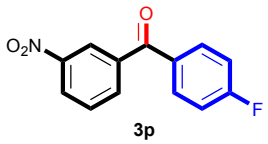


3o

4-(3-methylbenzoyl)benzonitrile (3o)

63.0mg, yield 57%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.63 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 2.46 (s, 3H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 195.1, 141.3, 138.5, 136.2, 134.0, 132.0, 130.3, 130.1, 128.3, 127.2, 117.9, 115.4, 21.2. **GCMS** (EI, 70 eV): *m/z* (%): 221 (31), 119 (100), 91 (36), 65 (18).

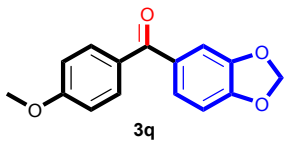


3p

(4-fluorophenyl)(3-nitrophenyl)methanone (3p)

67.4mg, yield 55%

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 7.88 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.74 (t, *J* = 7.9 Hz, 1H), 7.24 (t, *J* = 8.4 Hz, 2H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 192.58, 165.79 (J_{C-F} = 256.1 Hz), 148.0, 138.8, 135.1, 132.6 (J_{C-F} = 9.4 Hz), 132.4, 129.6, 126.6, 124.4, 115.9 (J_{C-F} = 22.0 Hz). **GCMS** (EI, 70 eV): *m/z* (%): 245 (23), 123 (100), 95 (39), 75 (13).

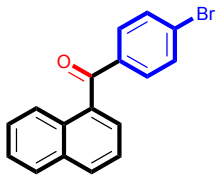


3q

benzo[*d*][1,3]dioxol-5-yl(4-methoxyphenyl)methanone (3q)

76.8mg, yield 60%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.33 (m, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.09 (s, 2H), 3.91 (s, 3H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 194.0, 162.8, 151.0, 147.7, 132.4, 132.2, 130.4, 126.1, 113.4, 109.8, 107.6, 101.7, 55.4. **GCMS** (EI, 70 eV): *m/z* (%): 256 (74), 225 (15), 149 (44), 135 (100), 107 (13), 77 (21).

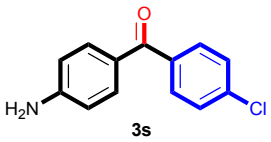


3r

(4-bromophenyl)(naphthalen-1-yl)methanone (3r)

91.7mg, yield 59%

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 18.0, 8.1 Hz, 2H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.51 (m, 4H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 196.8, 137.0, 135.7, 133.6, 131.8, 131.7, 131.5, 130.7, 128.4, 128.4, 127.7, 127.3, 126.5, 125.4, 124.3. **GCMS** (EI, 70 eV): *m/z* (%): 310 (52), 231 (71), 183 (22), 155 (100), 127 (87), 101 (35)

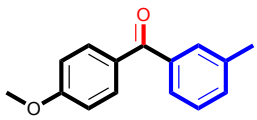


3s

(4-aminophenyl)(4-chlorophenyl)methanone (3s)

62.5mg, yield 54%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 4.8 Hz, 2H), 7.70 (d, *J* = 4.7 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 4.19 (s, 2H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 194.0, 151.0, 137.6, 137.0, 132.8, 130.9, 128.3, 126.9, 113.6. **GCMS** (EI, 70 eV): *m/z* (%): 231 (10), 120 (40), 92 (8), 65 (8).

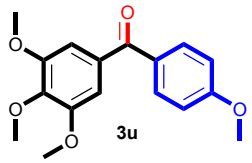


3t

(4-methoxyphenyl)(*m*-tolyl)methanone (3t)

65.6mg, yield 58%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.62 – 7.53 (m, 2H), 7.43 – 7.35 (m, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 3H), 2.45 (s, 3H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 195.7, 163.0, 138.2, 137.9, 132.5, 132.4, 130.1, 130.1, 127.8, 126.9, 113.4, 55.4, 21.2. **GCMS** (EI, 70 eV): *m/z* (%): 226 (33), 135 (100), 119 (15), 91 (17), 77 (18).



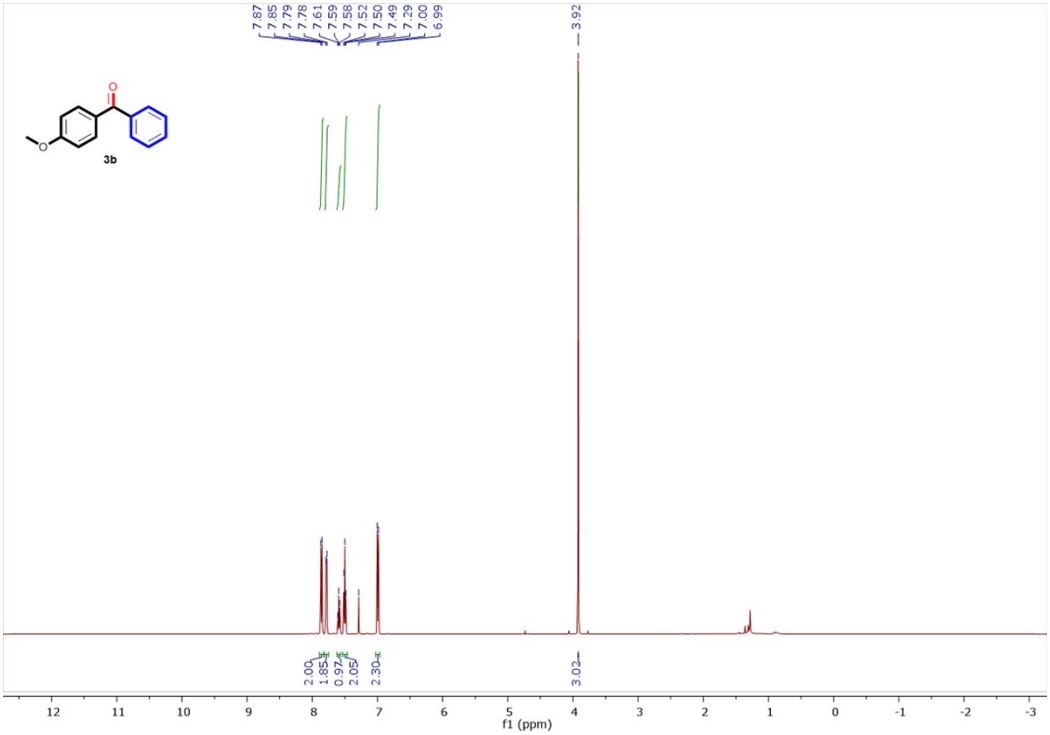
(4-methoxyphenyl)(3,4,5-trimethoxyphenyl)methanone (3u)

92.2mg, yield 61%

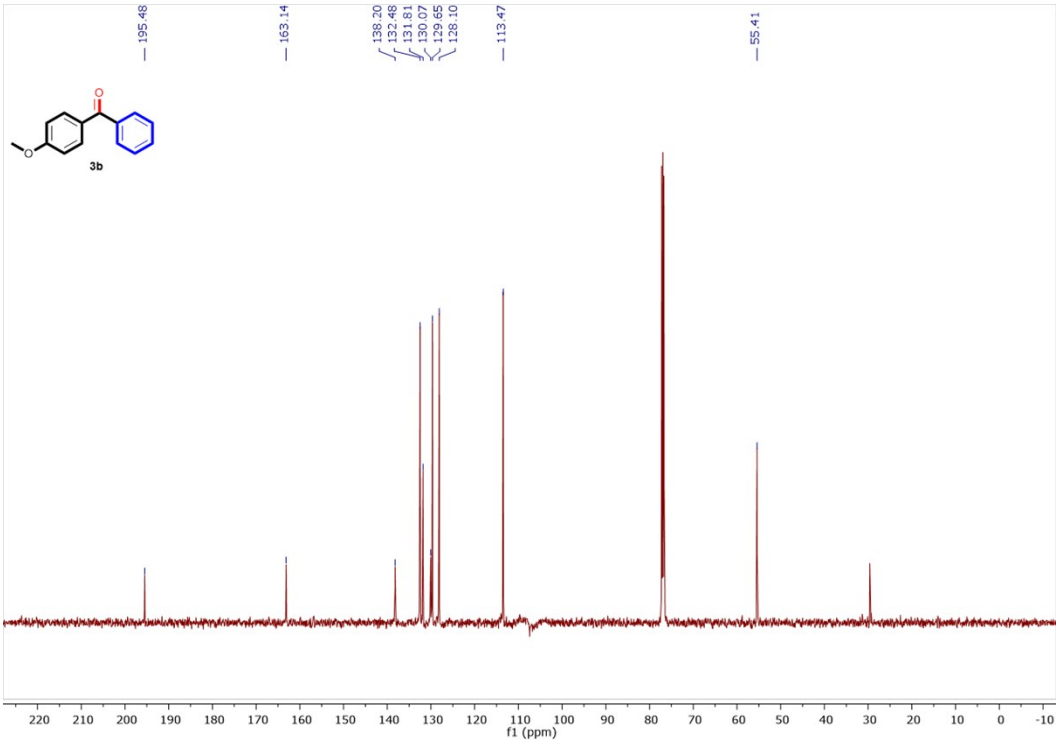
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.7 Hz, 2H), 6.98 (s, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 3.84 (s, 6H). **^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$)**: δ 194.6, 163.0, 152.7, 141.4, 133.28, 132.3, 130.1, 113.4, 107.3, 60.8, 56.2, 55.4.

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

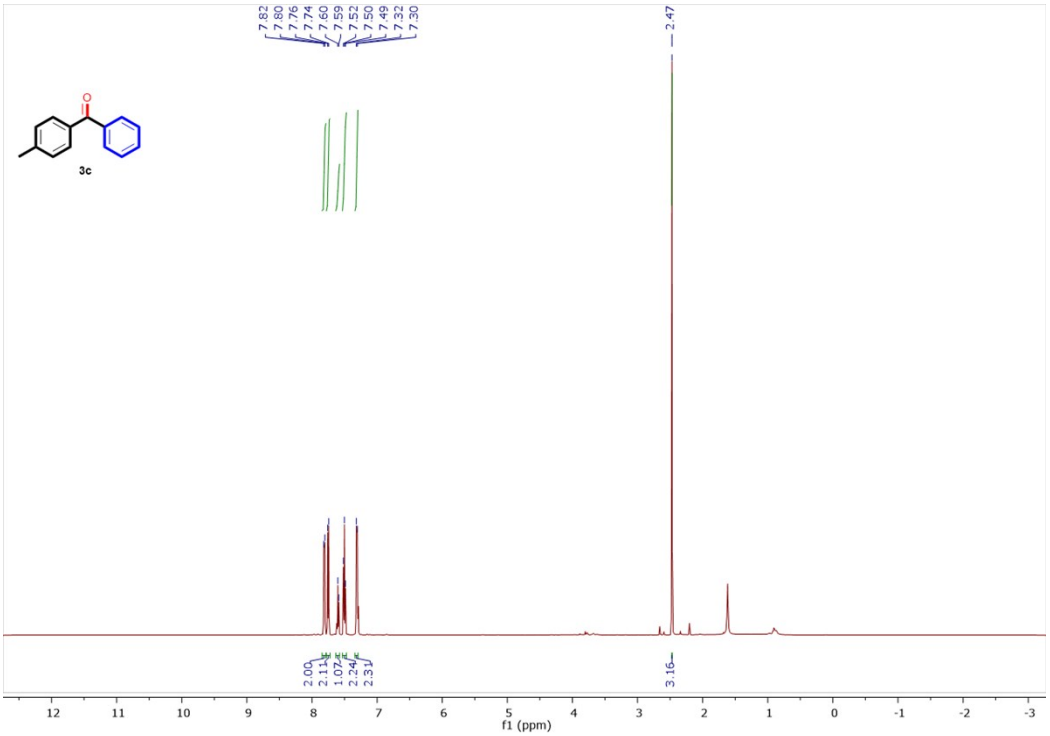
(4-methoxyphenyl)(phenyl)methanone (3b) (^{1}H NMR)



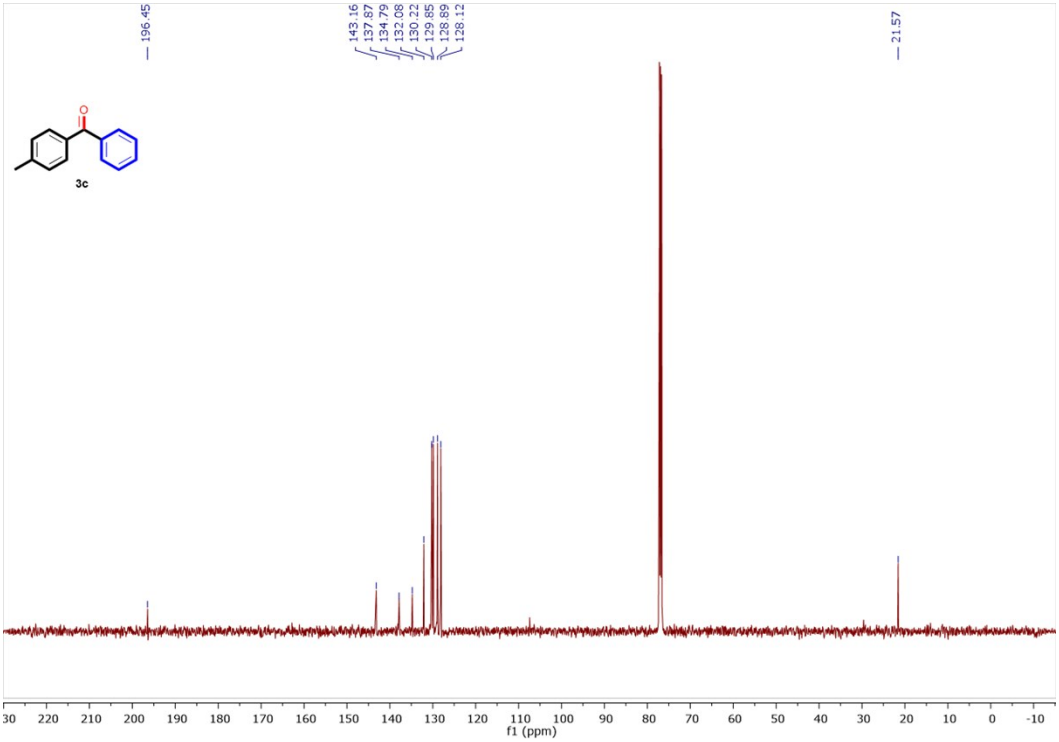
(4-methoxyphenyl)(phenyl)methanone (3b) (^{13}C NMR)



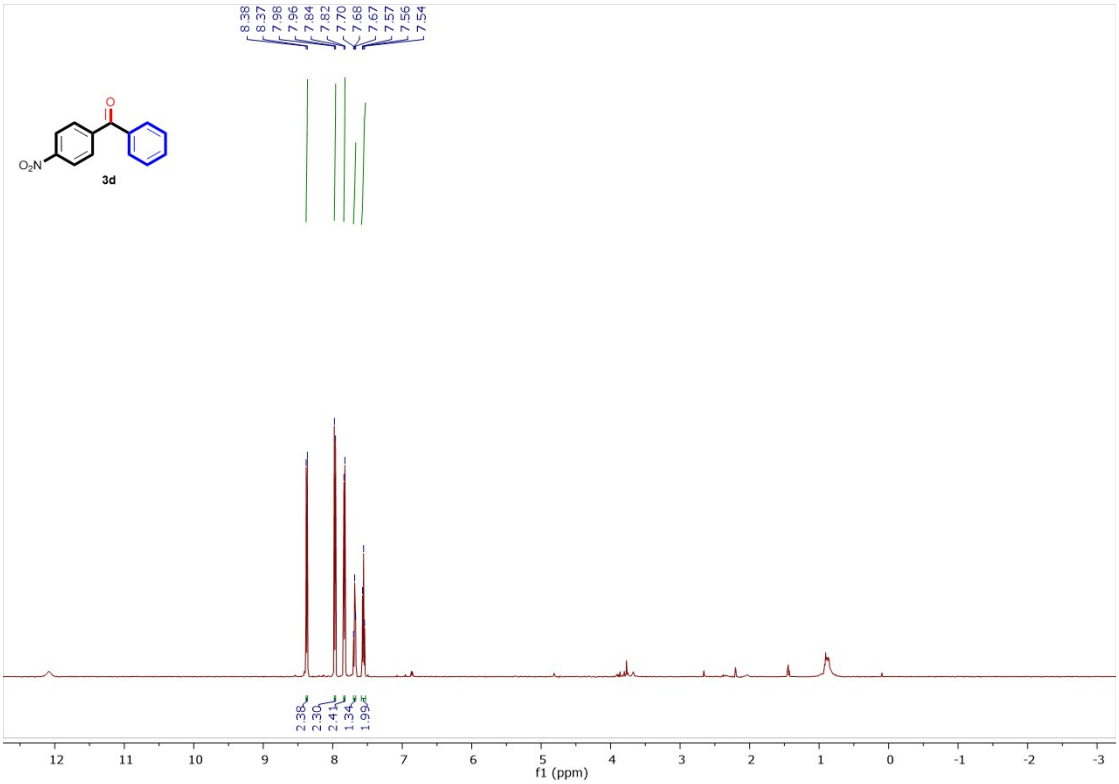
phenyl(*p*-tolyl)methanone (3c) (^{1}H NMR)



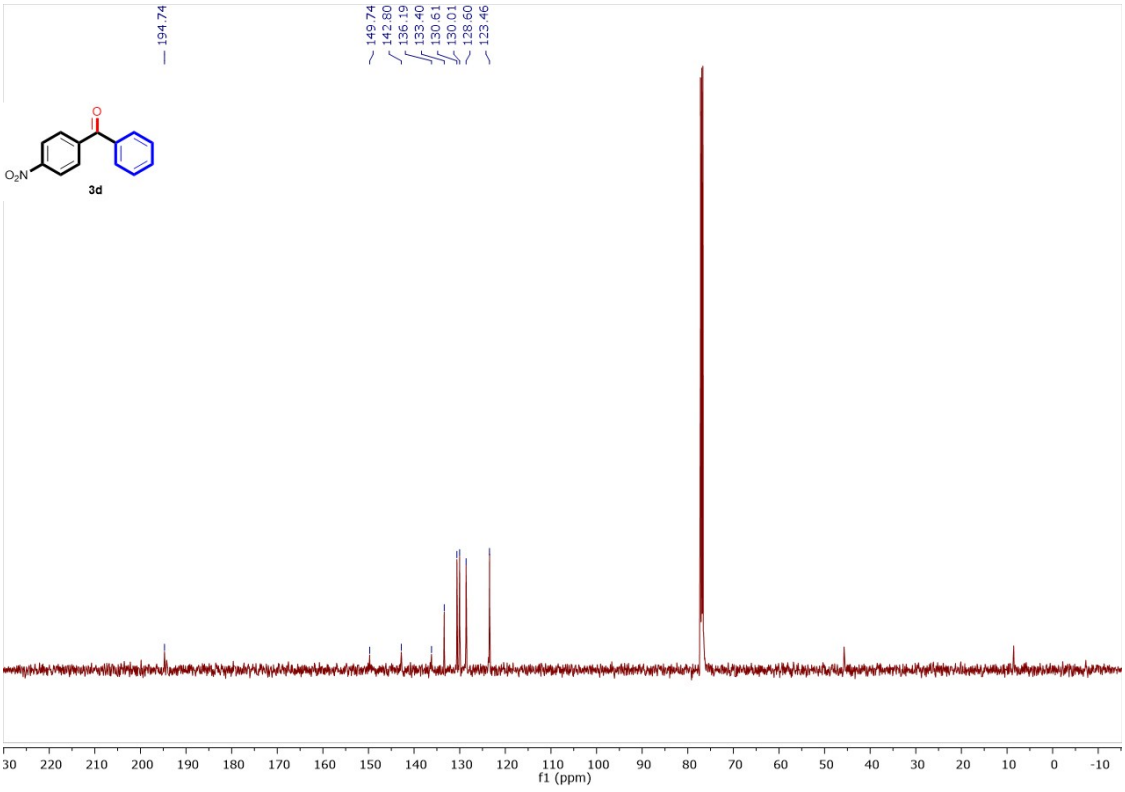
phenyl(*p*-tolyl)methanone (3c) (^{13}C NMR)



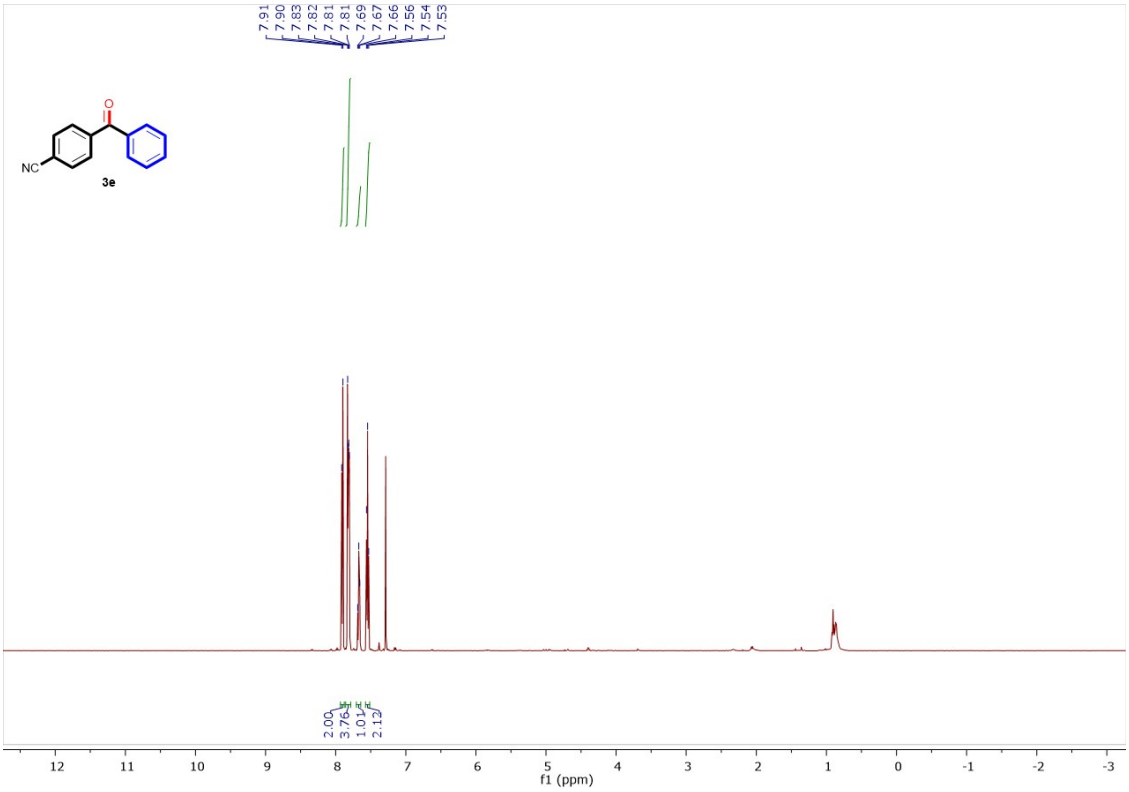
(4-nitrophenyl)(phenyl)methanone (3d) (^{1}H NMR)



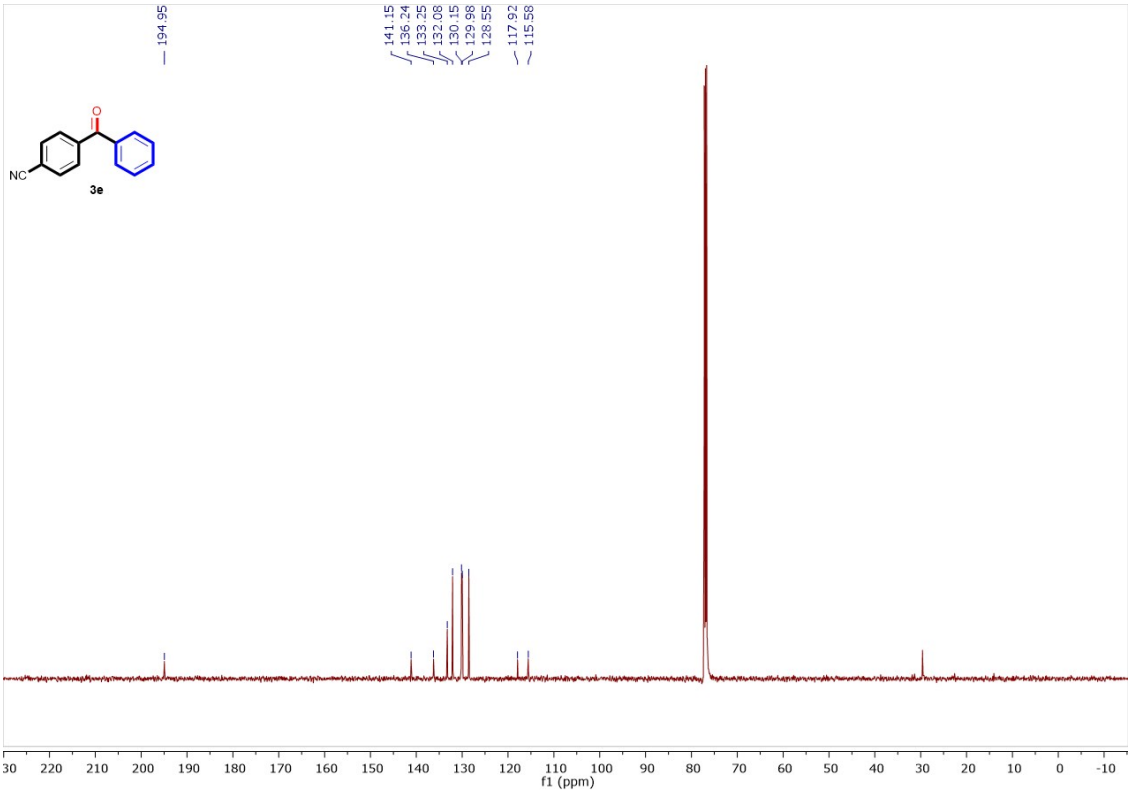
(4-nitrophenyl)(phenyl)methanone (3d) (^{13}C NMR)



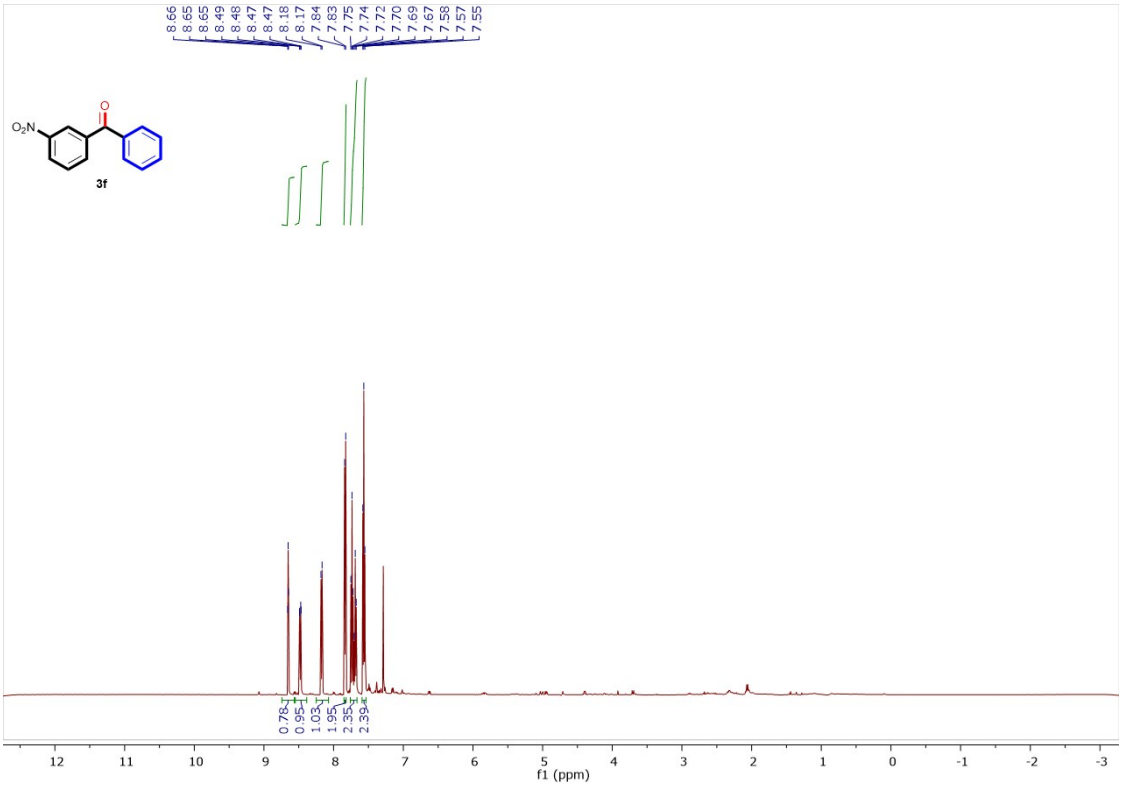
4-benzoylbenzonitrile (3e) (^{1}H NMR)



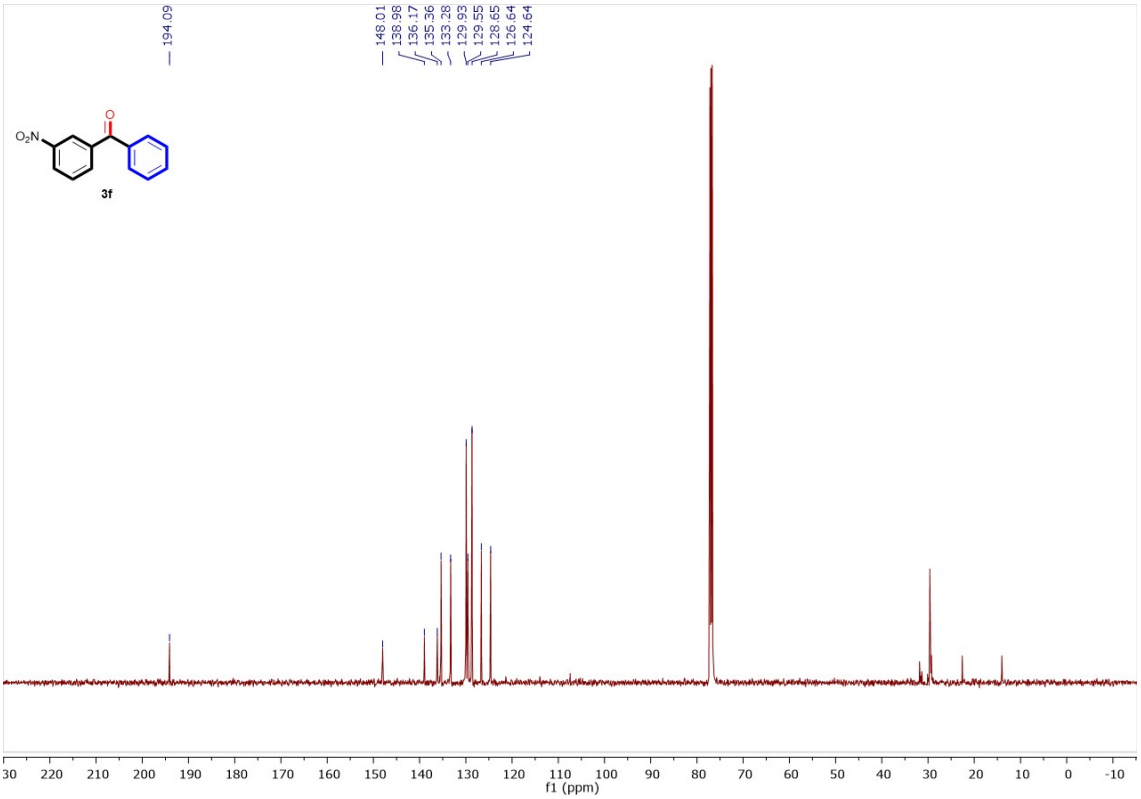
4-benzoylbenzonitrile (3e) (^{13}C NMR)



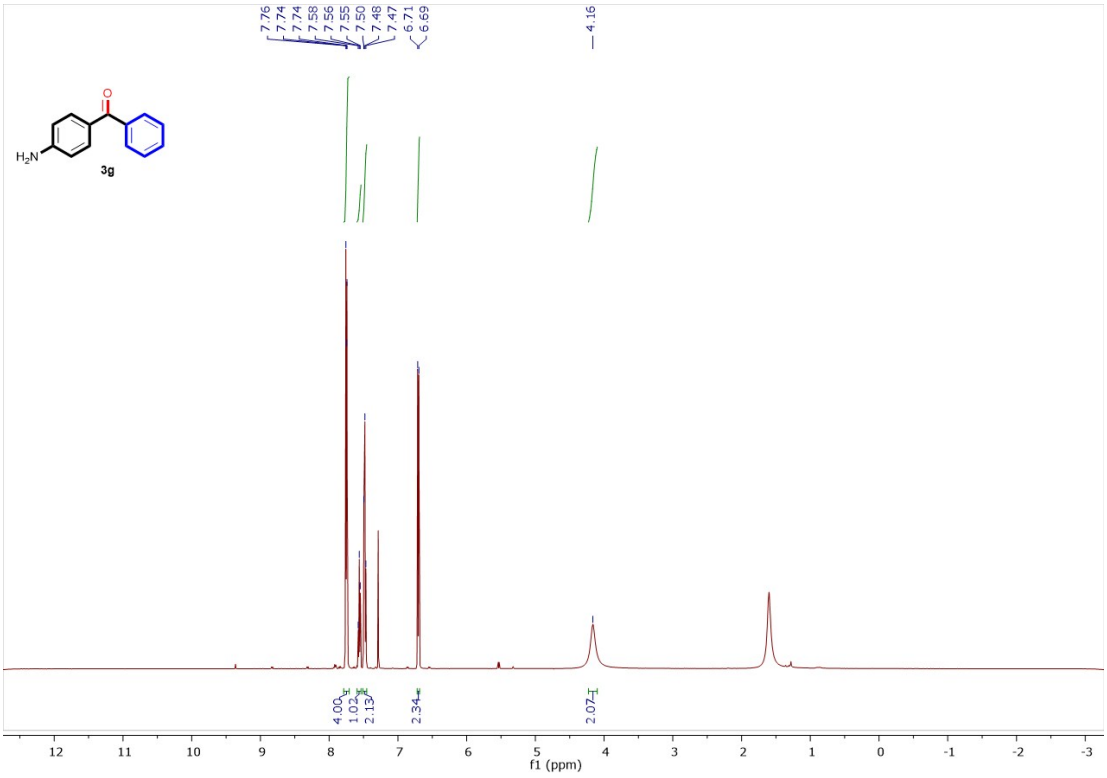
(3-nitrophenyl)(phenyl)methanone (3f) (^{1}H NMR)



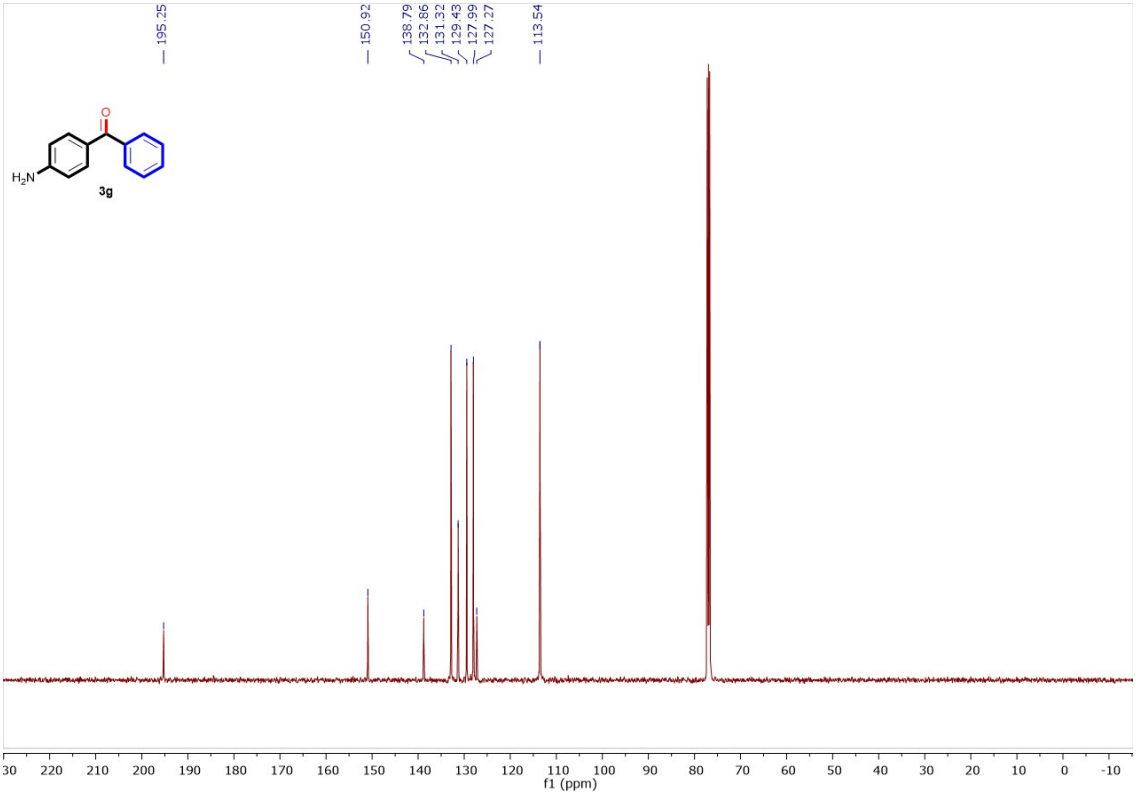
(3-nitrophenyl)(phenyl)methanone (3f) (^{13}C NMR)



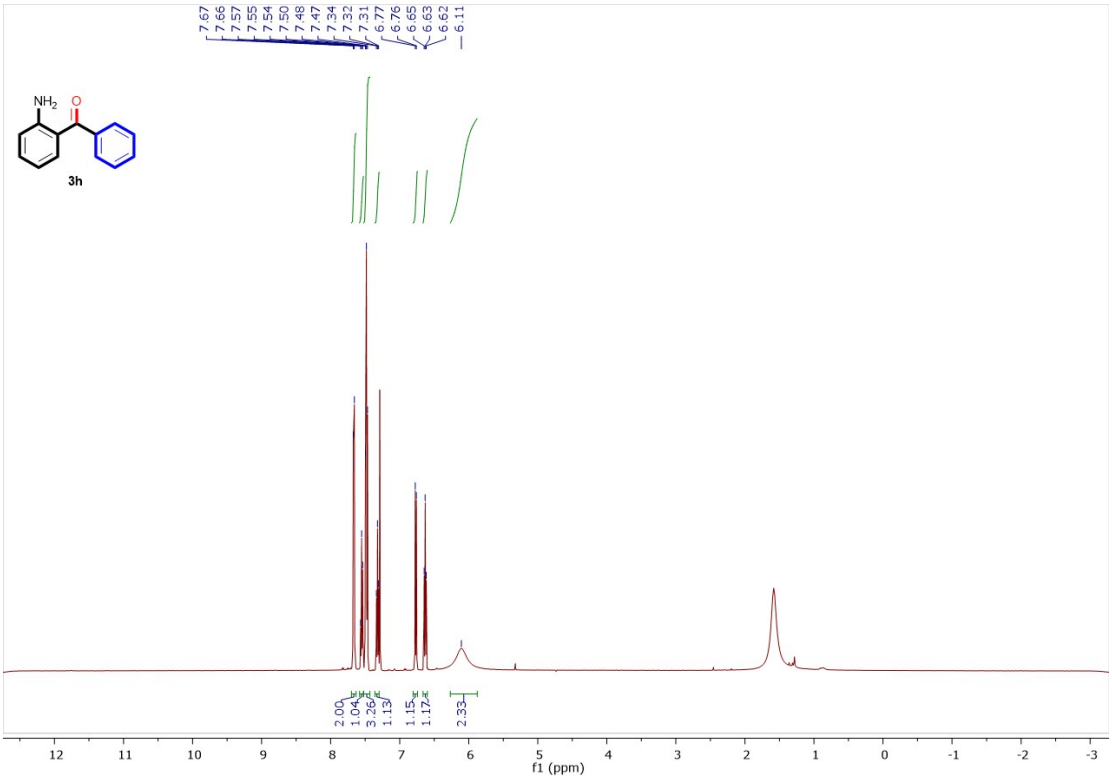
(4-aminophenyl)(phenyl)methanone (3g) (^{1}H NMR)



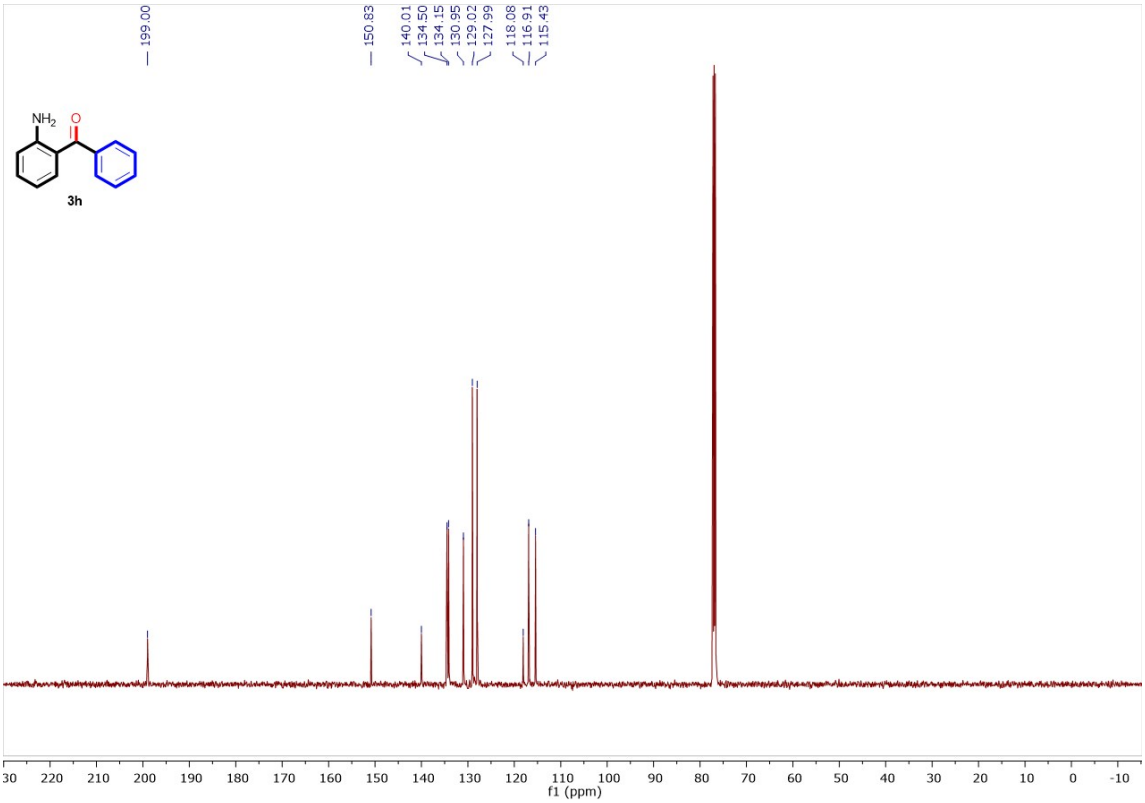
(4-aminophenyl)(phenyl)methanone (3g) (^{13}C NMR)



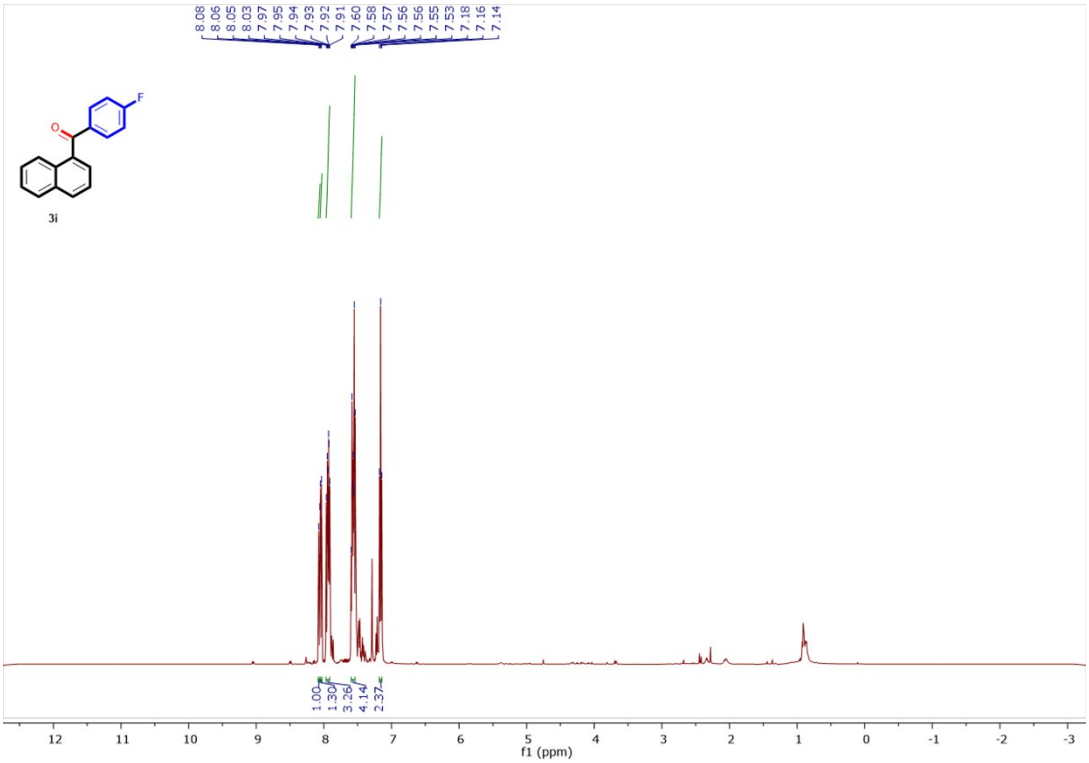
(2-aminophenyl)(phenyl)methanone (3h) (^{1}H NMR)



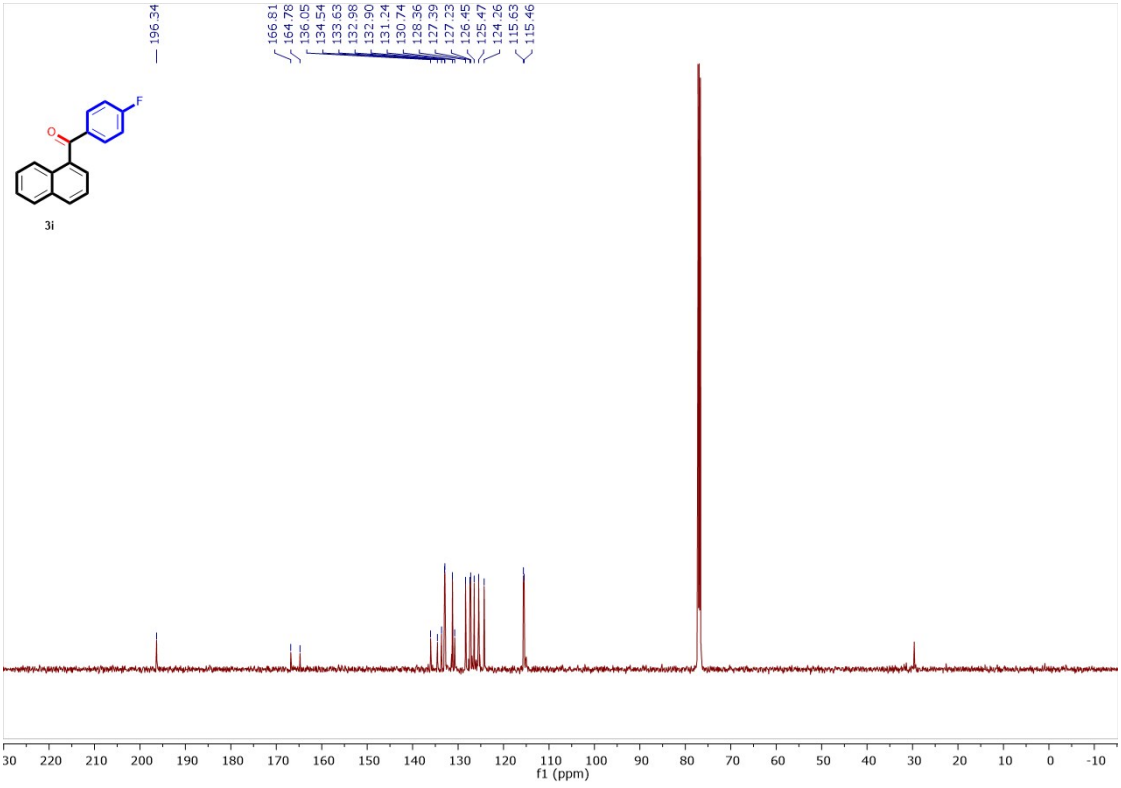
(2-aminophenyl)(phenyl)methanone (3h) (^{13}C NMR)



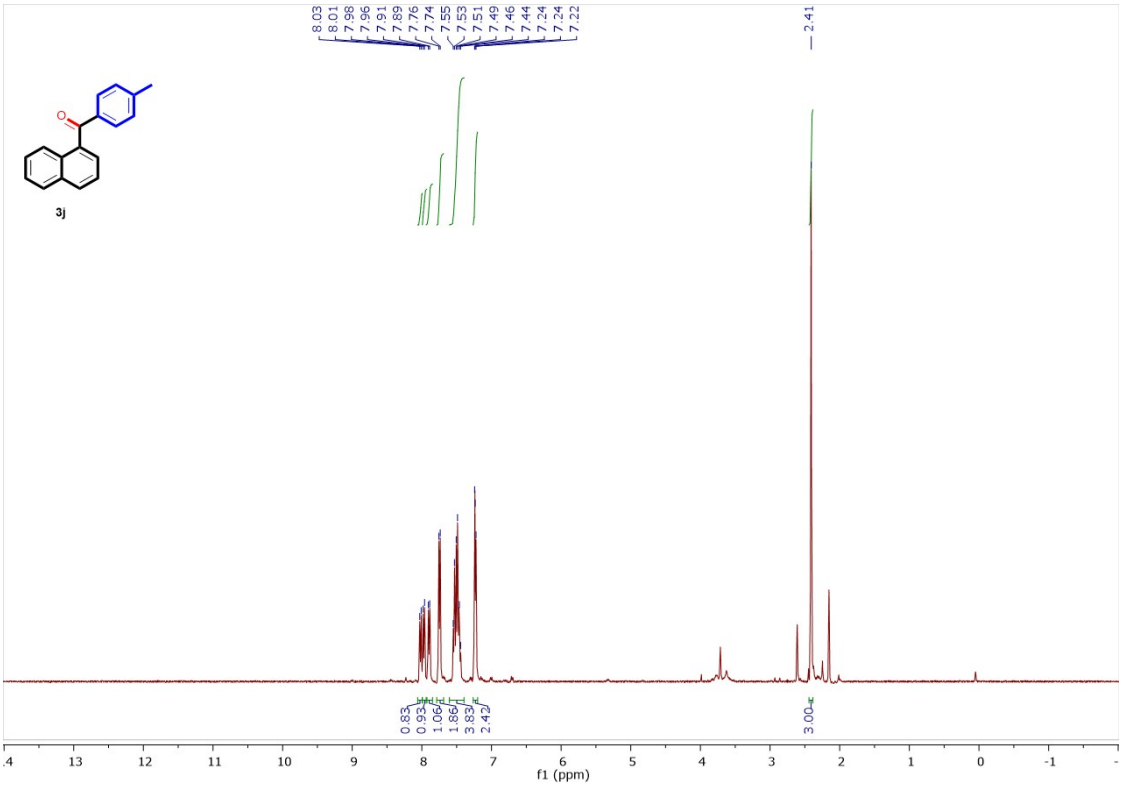
(4-fluorophenyl)(naphthalen-1-yl)methanone (3i) (^{1}H NMR)



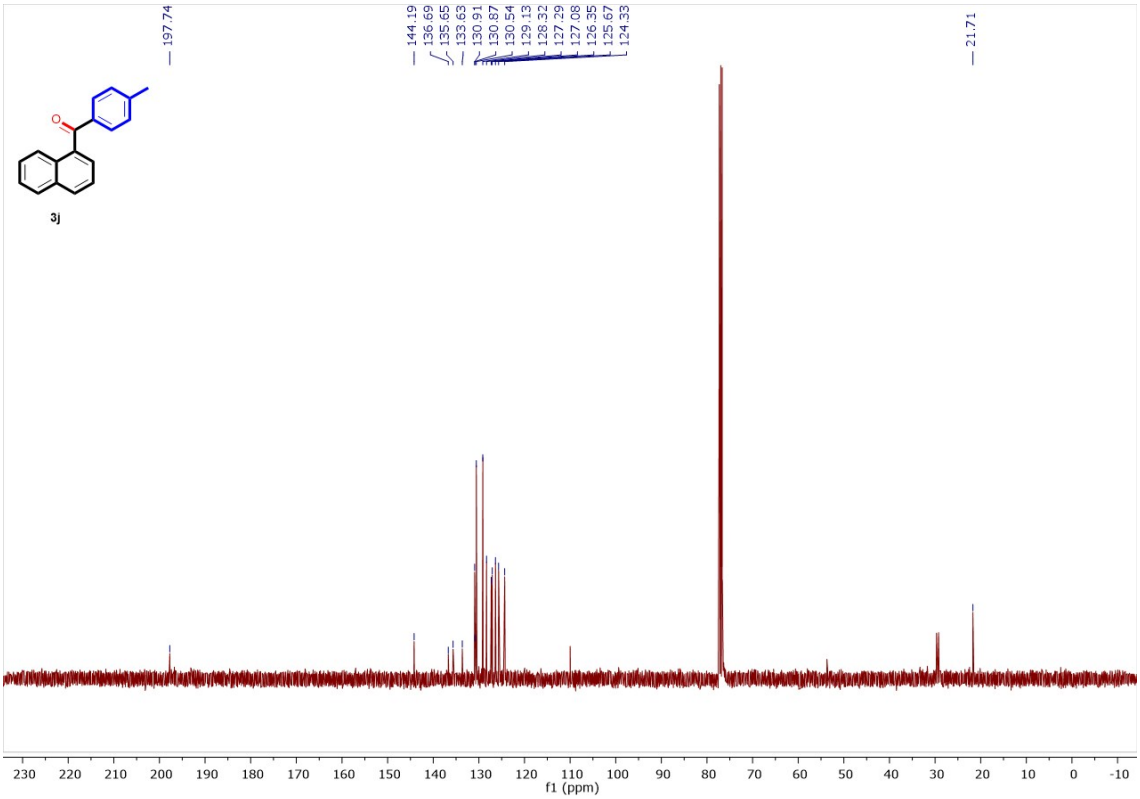
(4-fluorophenyl)(naphthalen-1-yl)methanone (3i) (^{13}C NMR)



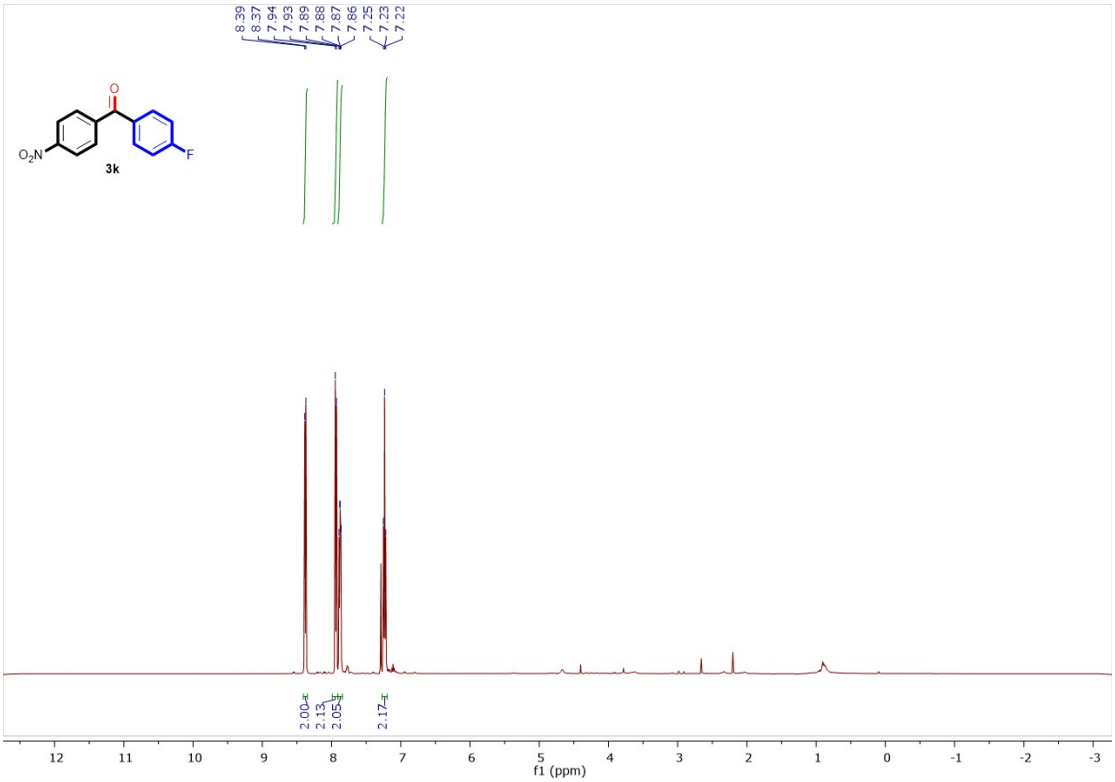
naphthalen-1-yl(*p*-tolyl)methanone (3j) (^{1}H NMR)



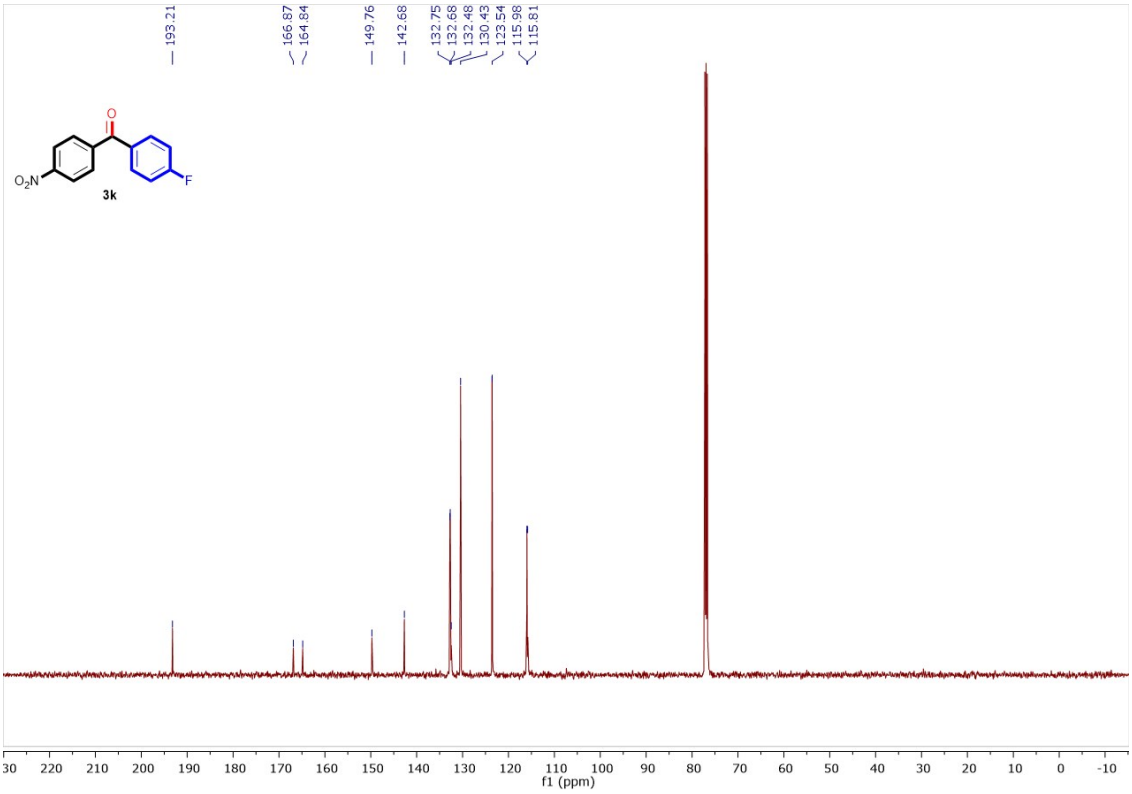
naphthalen-1-yl(*p*-tolyl)methanone (3j) (^{13}C NMR)



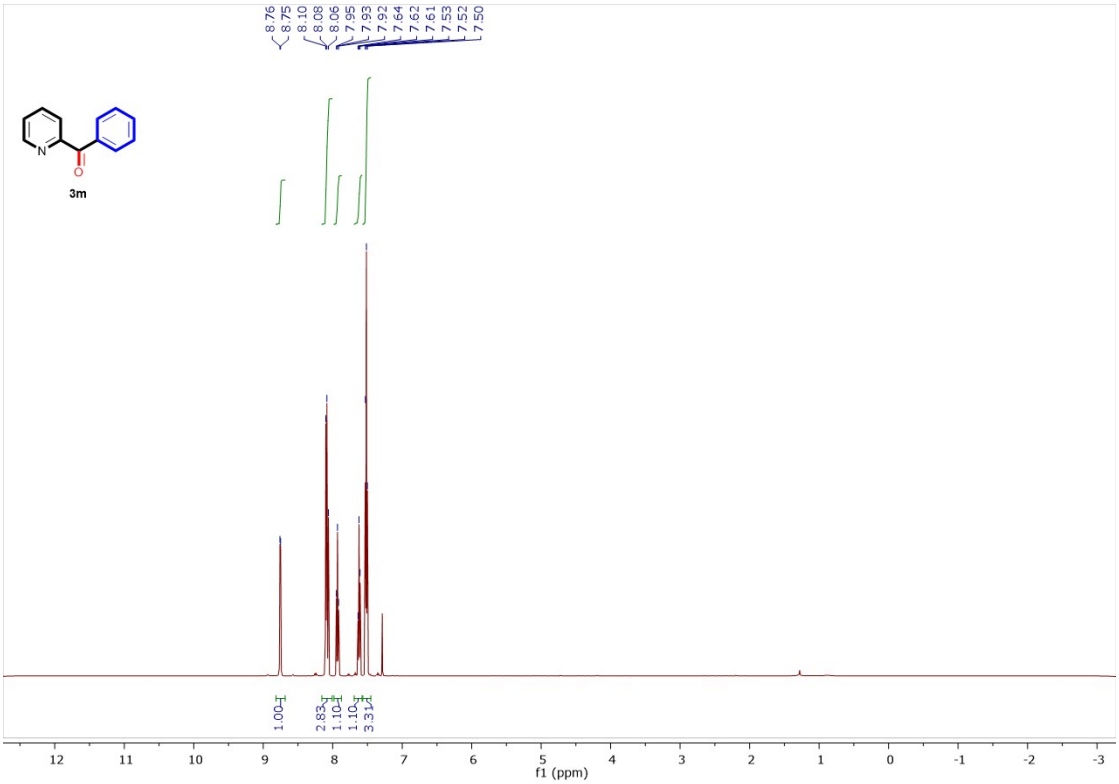
(4-fluorophenyl)(4-nitrophenyl)methanone (3k) (^{1}H NMR)



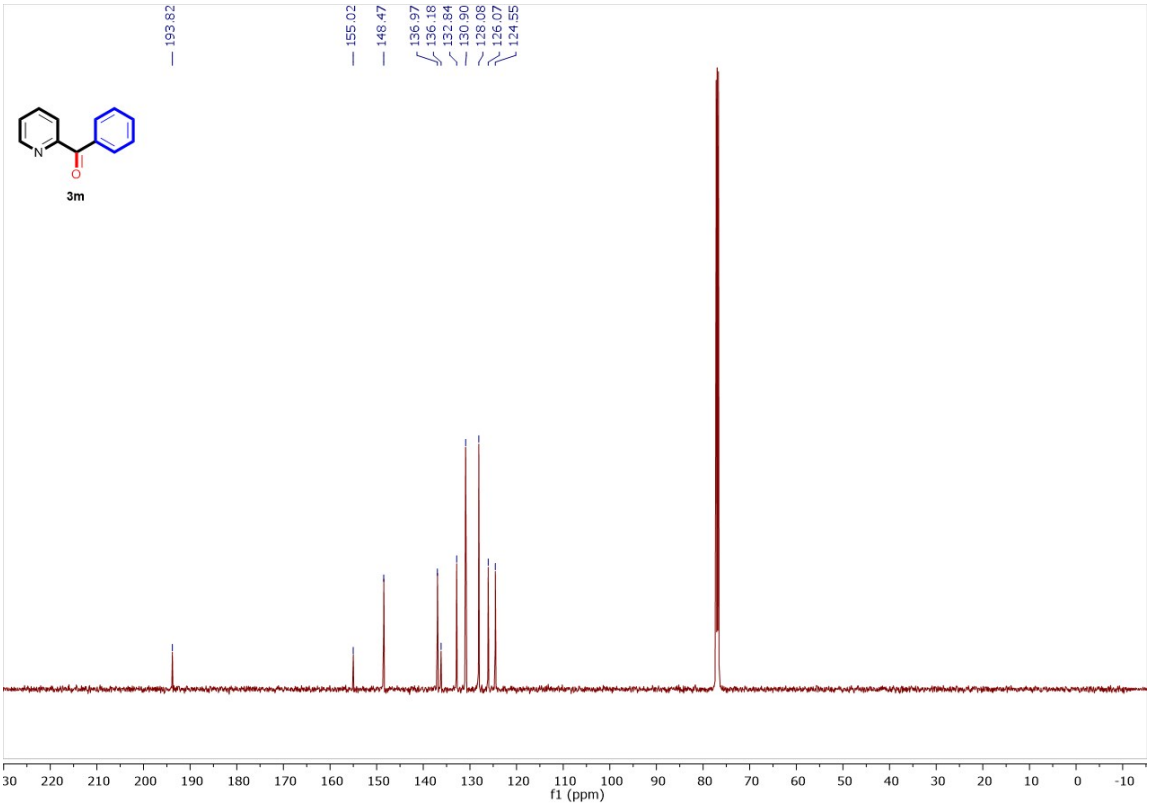
(4-fluorophenyl)(4-nitrophenyl)methanone (3k) (^{13}C NMR)



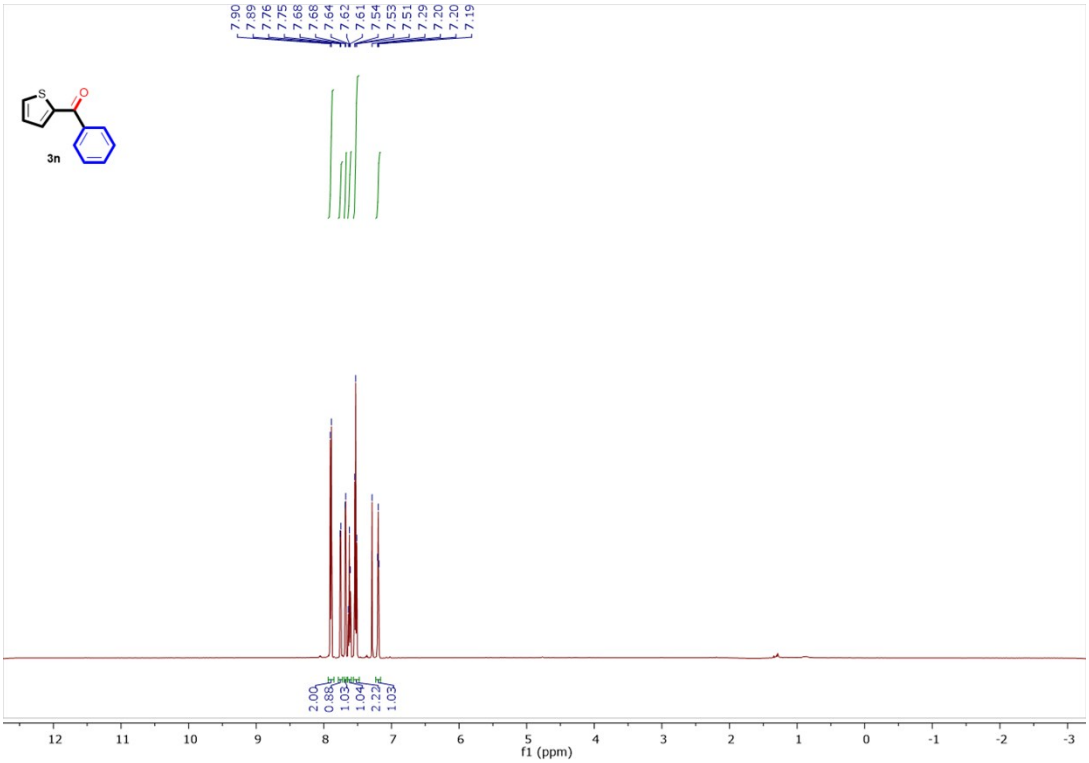
phenyl(pyridin-2-yl)methanone (3m) (^{1}H NMR)



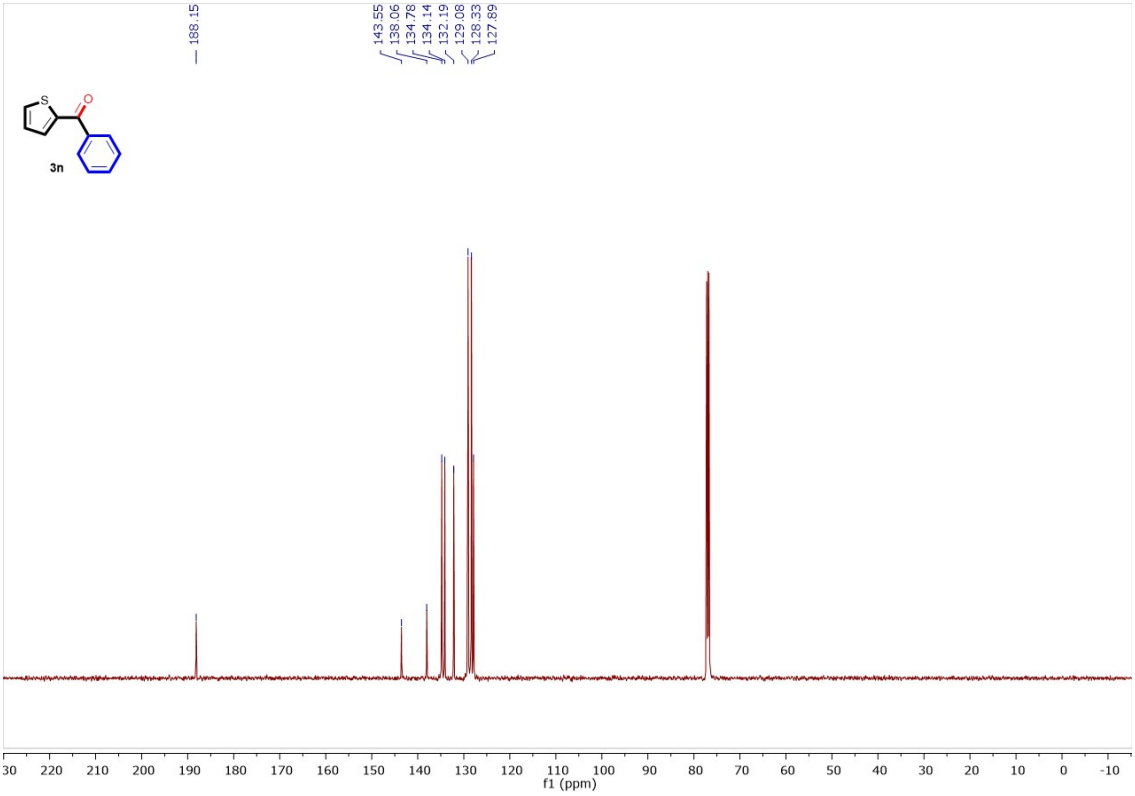
phenyl(pyridin-2-yl)methanone (3m) (^{13}C NMR)



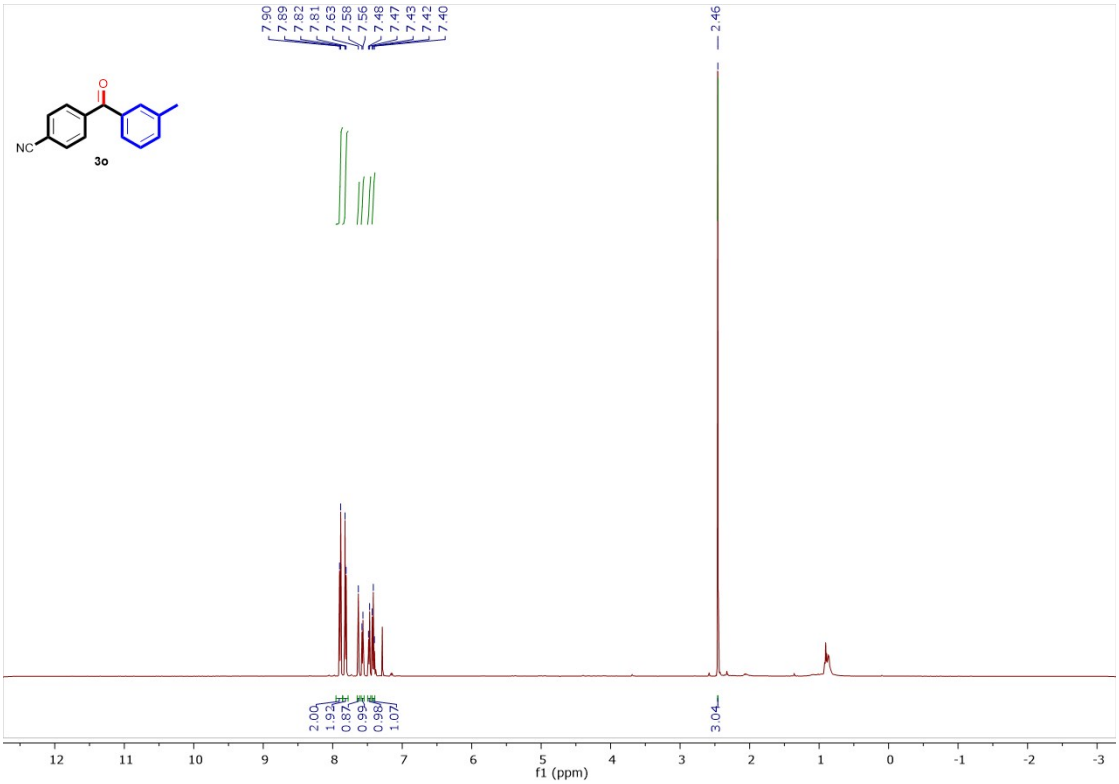
phenyl(thiophen-2-yl)methanone (3n) (^{1}H NMR)



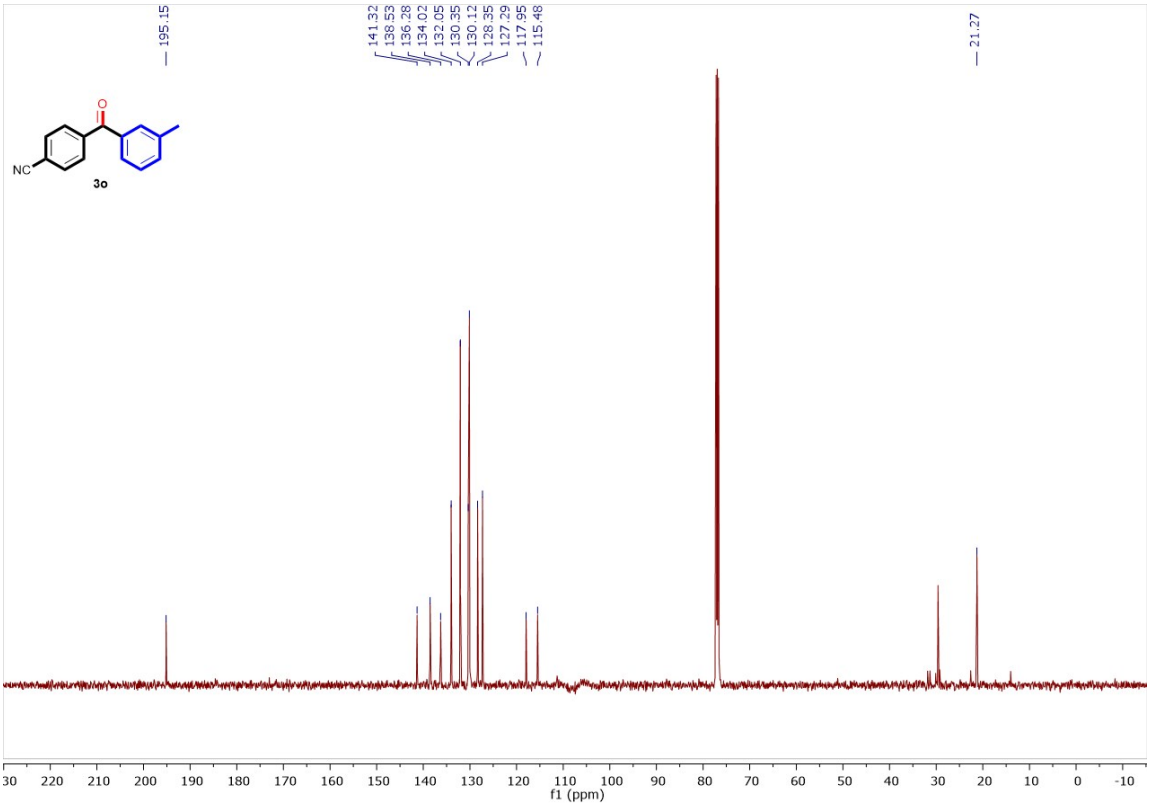
phenyl(thiophen-2-yl)methanone (3n) (^{13}C NMR)



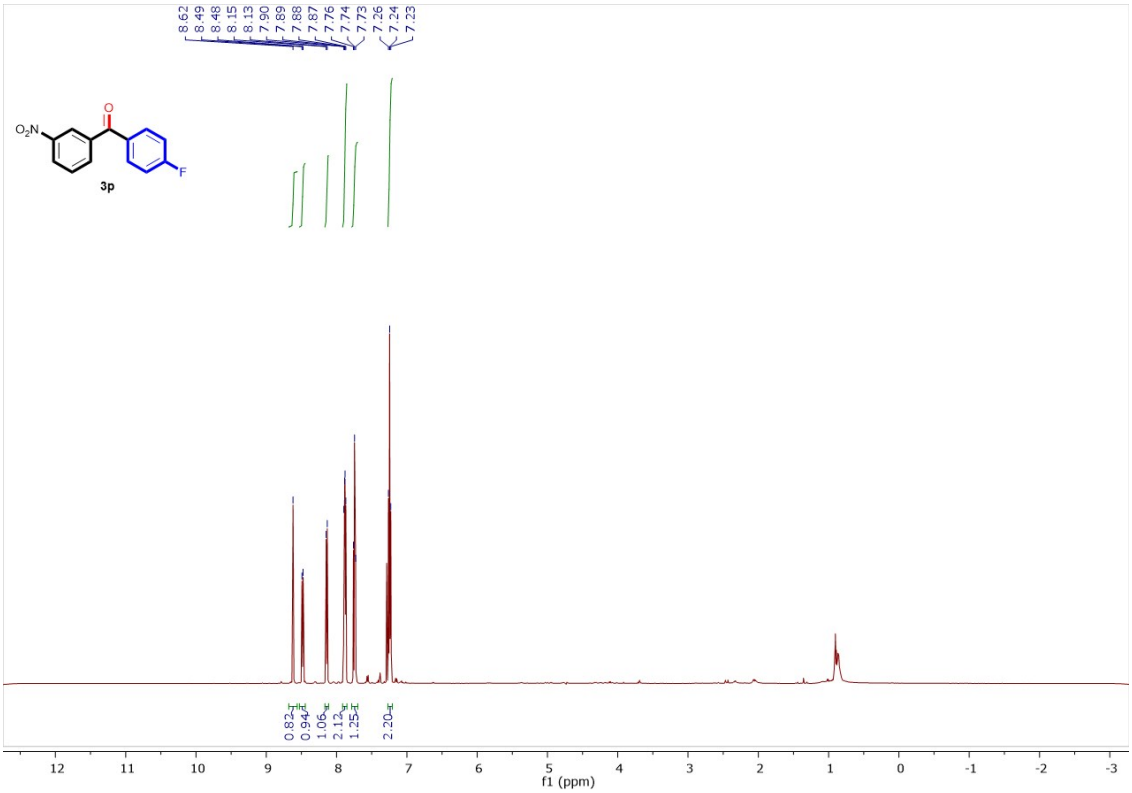
4-(3-methylbenzoyl)benzonitrile (3o) (^{1}H NMR)



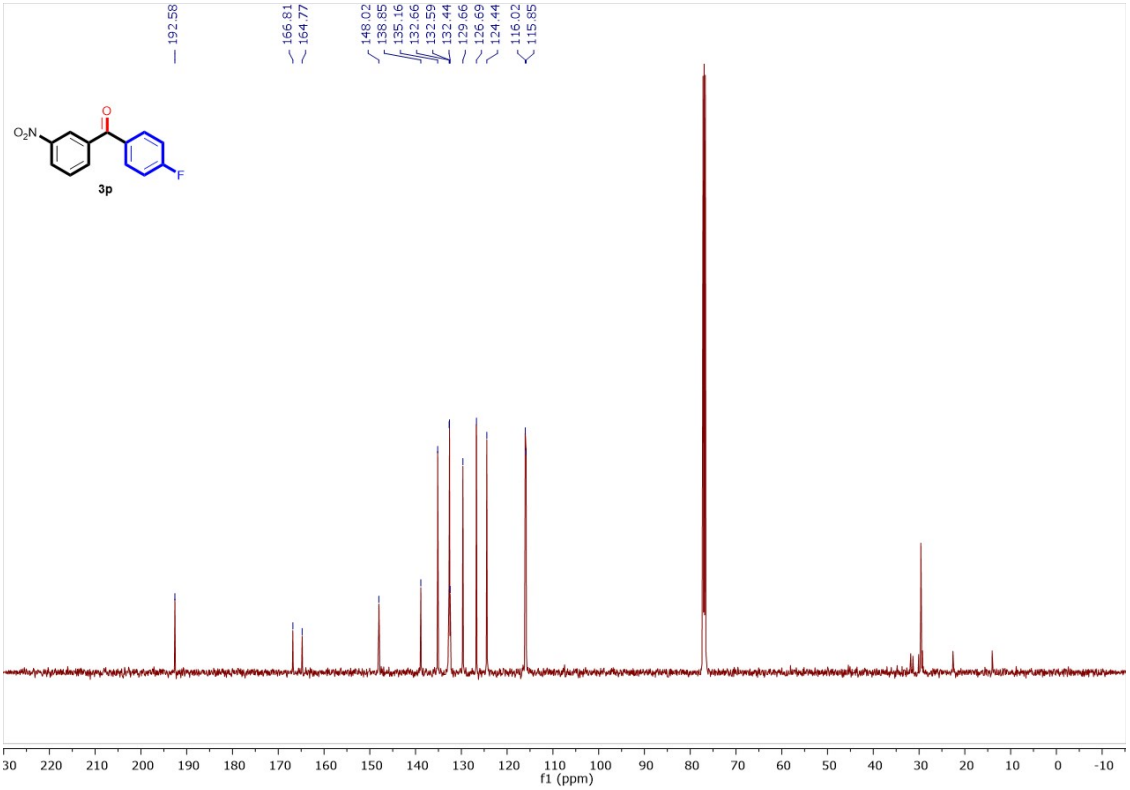
4-(3-methylbenzoyl)benzonitrile (3o) (^{13}C NMR)



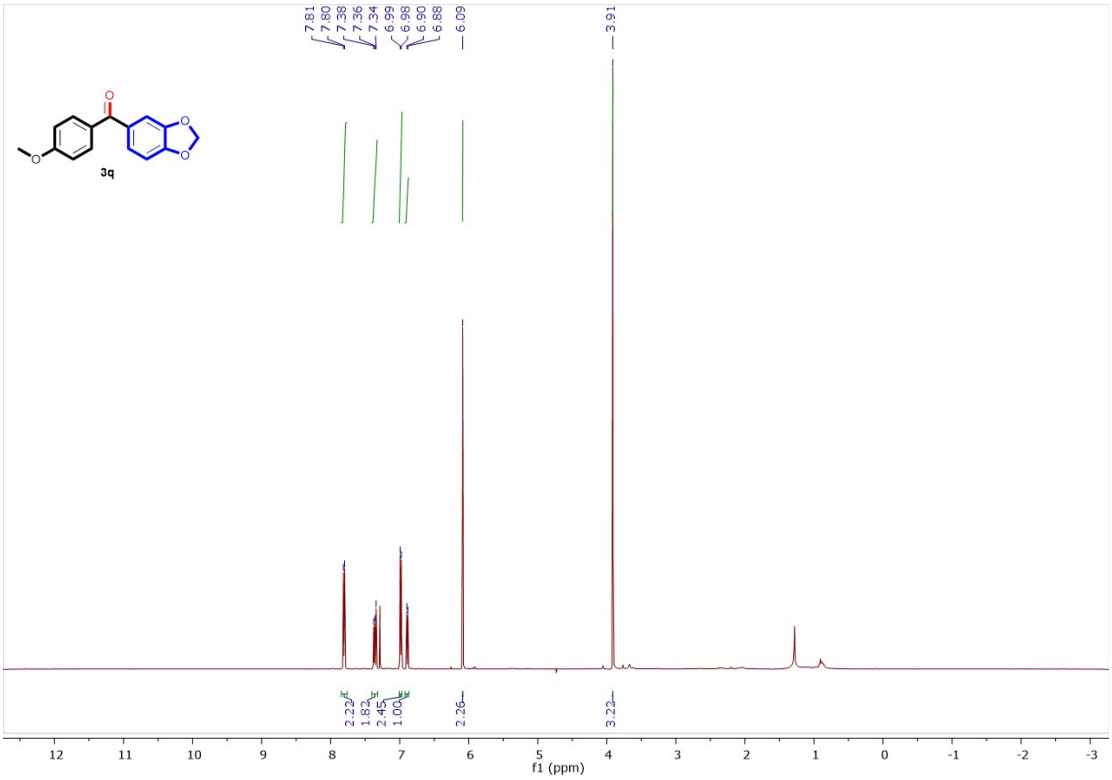
(4-fluorophenyl)(3-nitrophenyl)methanone (3p) (^{1}H NMR)



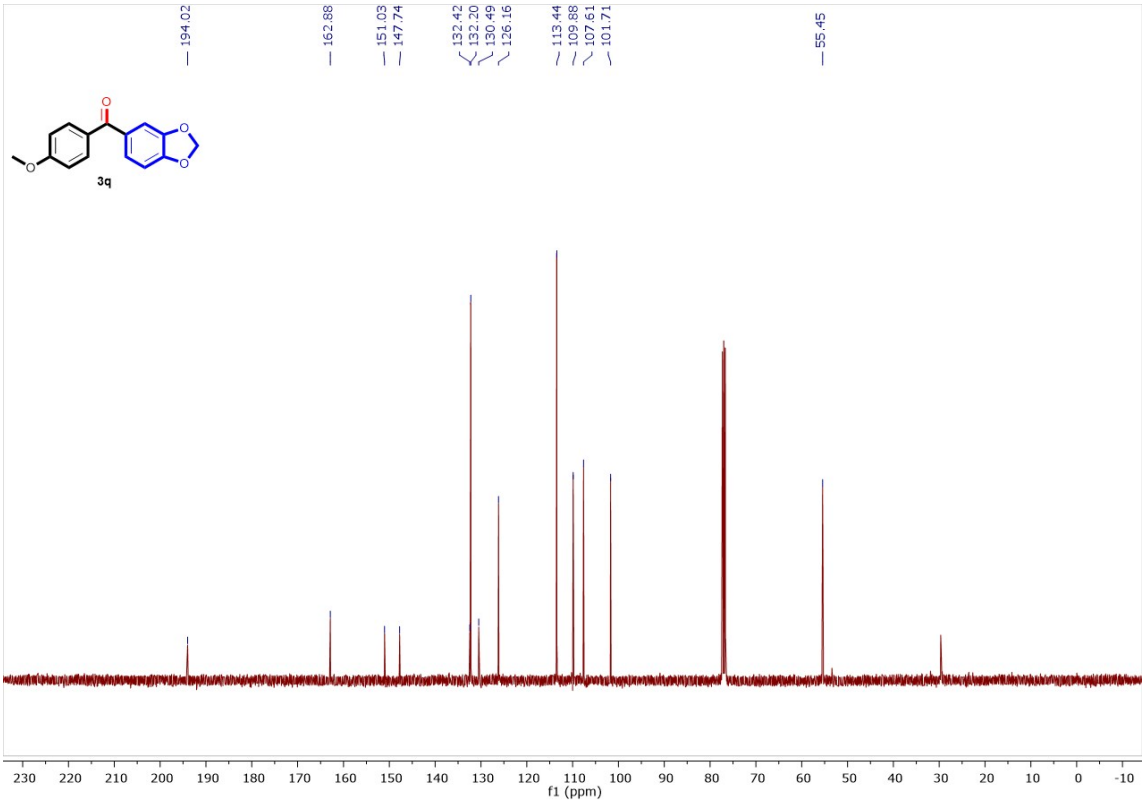
(4-fluorophenyl)(3-nitrophenyl)methanone (3p) (^{13}C NMR)



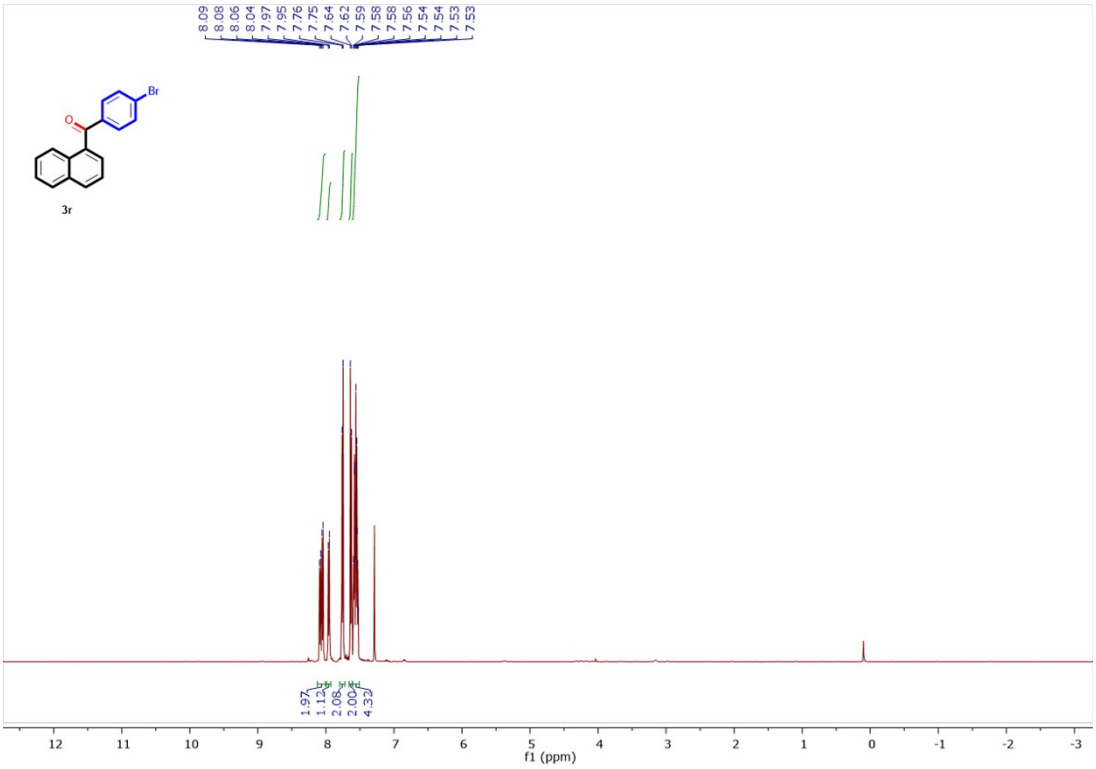
benzo[*d*][1,3]dioxol-5-yl(4-methoxyphenyl)methanone (3q) (^{1}H NMR)



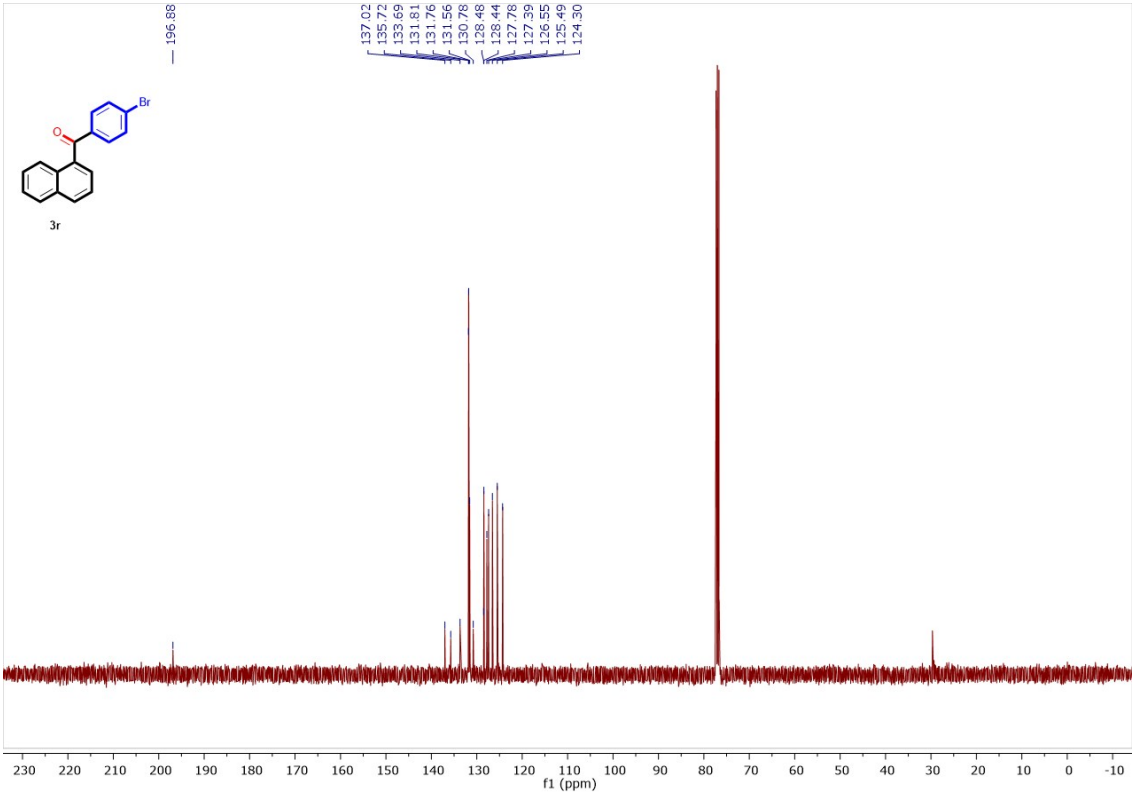
benzo[*d*][1,3]dioxol-5-yl(4-methoxyphenyl)methanone (3q) (^{13}C NMR)



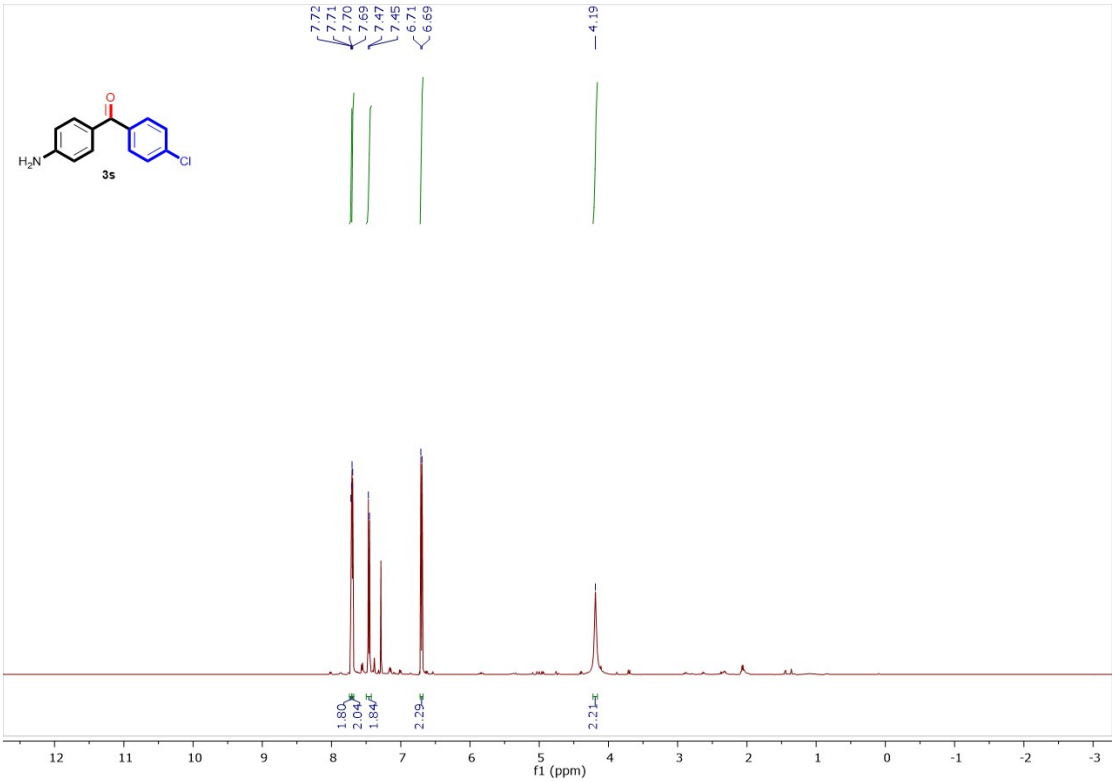
(4-bromophenyl)(naphthalen-1-yl)methanone (3r) (^{1}H NMR)



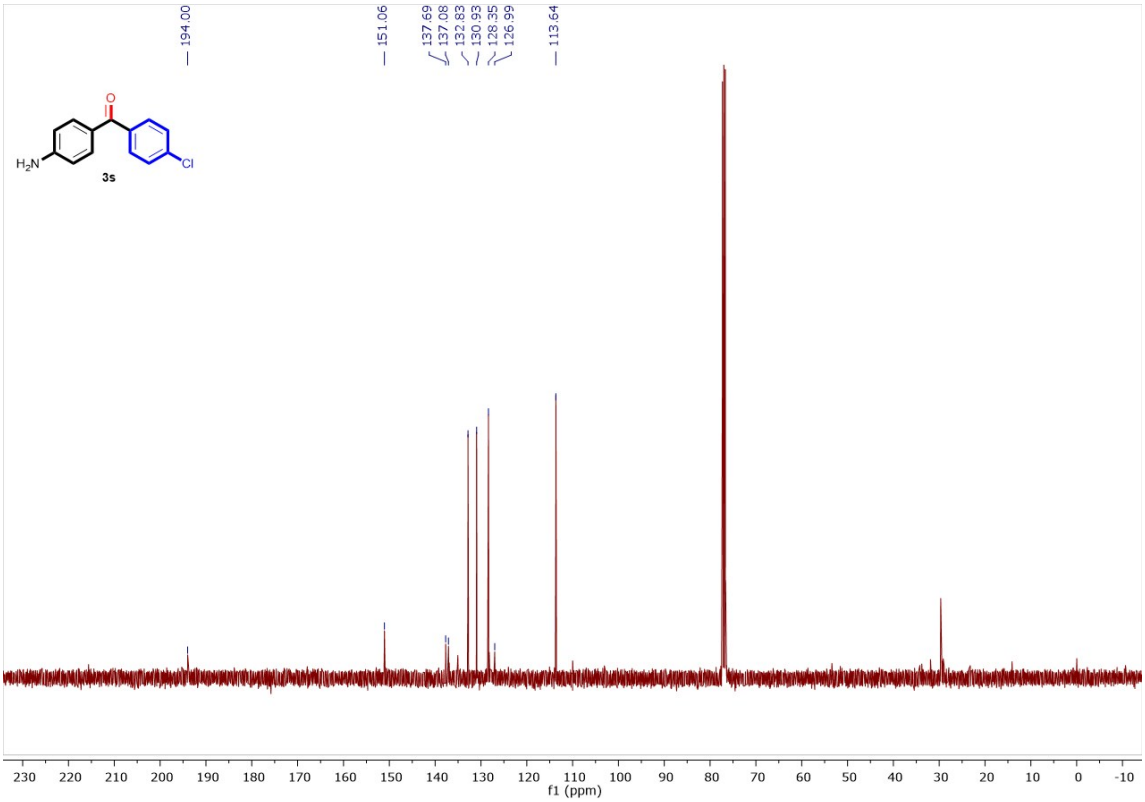
(4-bromophenyl)(naphthalen-1-yl)methanone (3r) (^{13}C NMR)



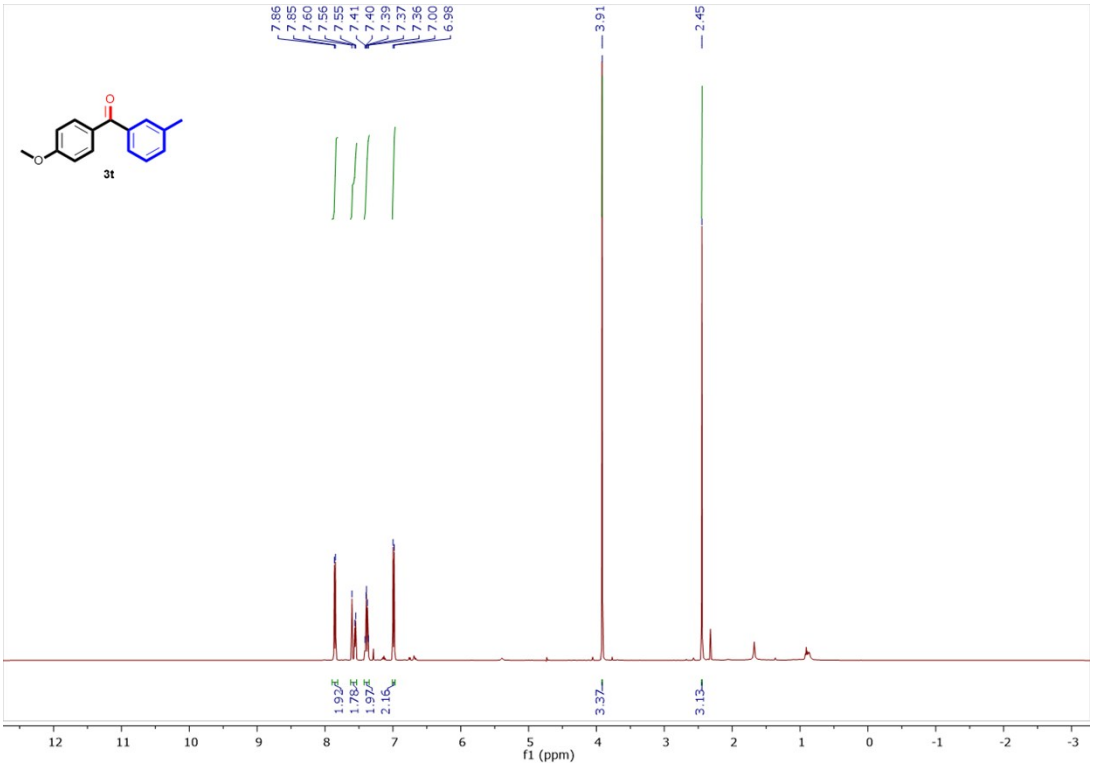
(4-aminophenyl)(4-chlorophenyl)methanone (3s) (^{1}H NMR)



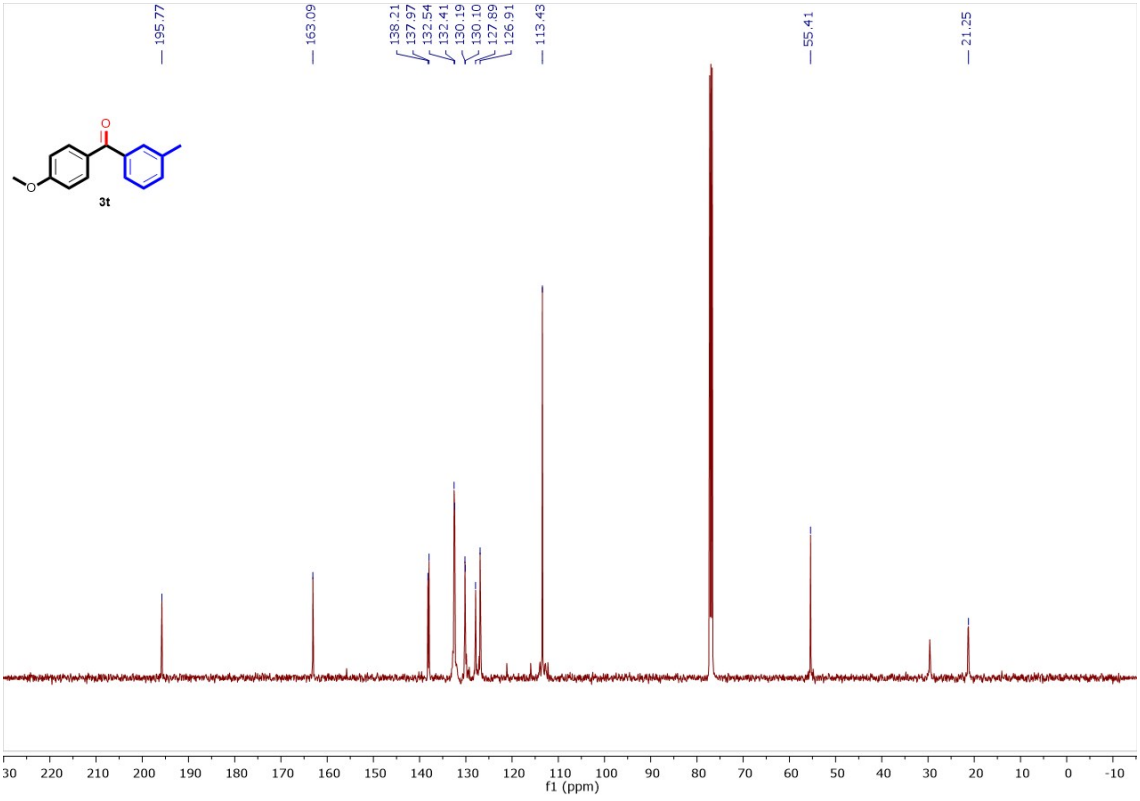
(4-aminophenyl)(4-chlorophenyl)methanone (3s) (^{13}C NMR)



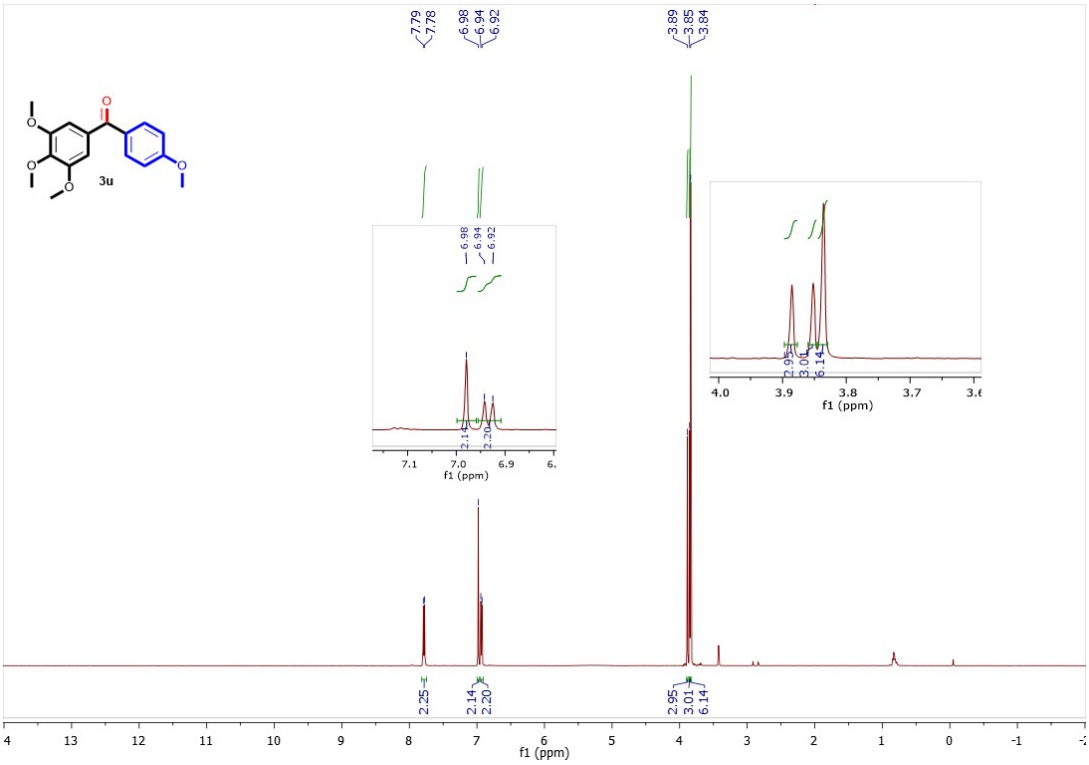
(4-methoxyphenyl)(*m*-tolyl)methanone (3t) (^{1}H NMR)



(4-methoxyphenyl)(*m*-tolyl)methanone (3t) (^{13}C NMR)



(4-methoxyphenyl)(3,4,5-trimethoxyphenyl)methanone (3u) (^{1}H NMR)



(4-methoxyphenyl)(3,4,5-trimethoxyphenyl)methanone (3u) (^{13}C NMR)

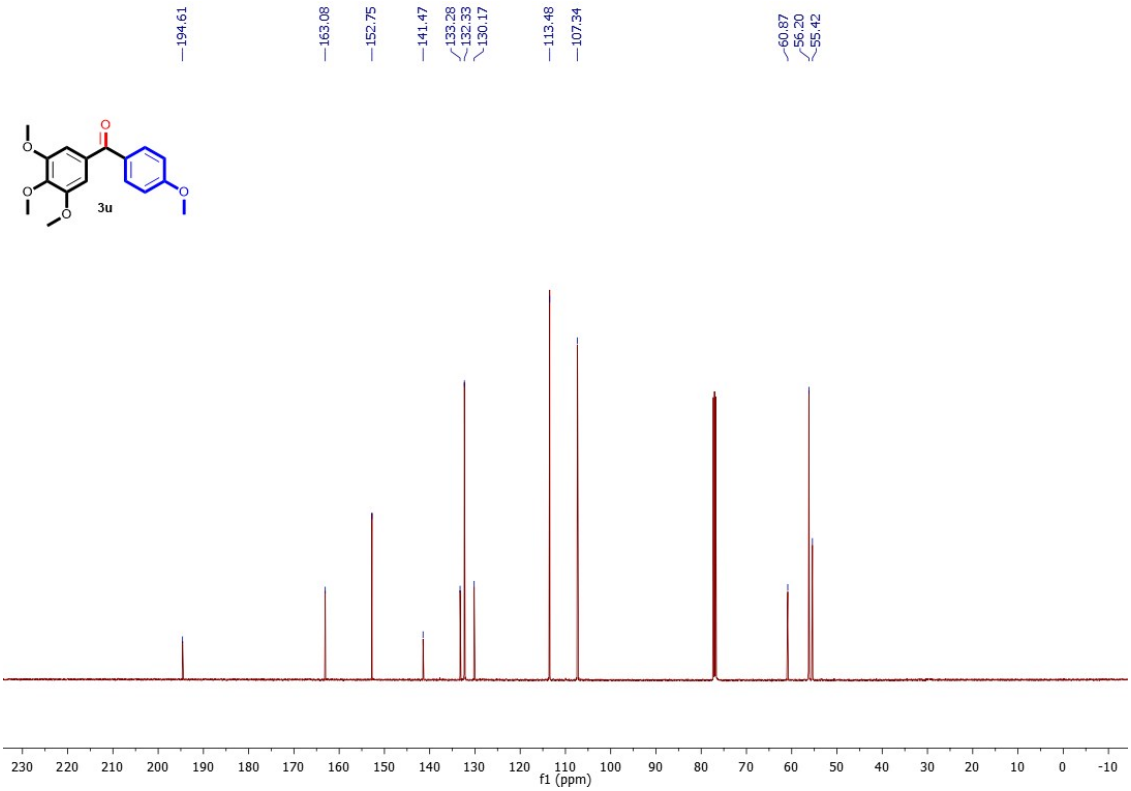


Figure SI 1. TEM image of KCC-1-PEI/Pd (0.1%) catalyst after 10 cycles of reaction.

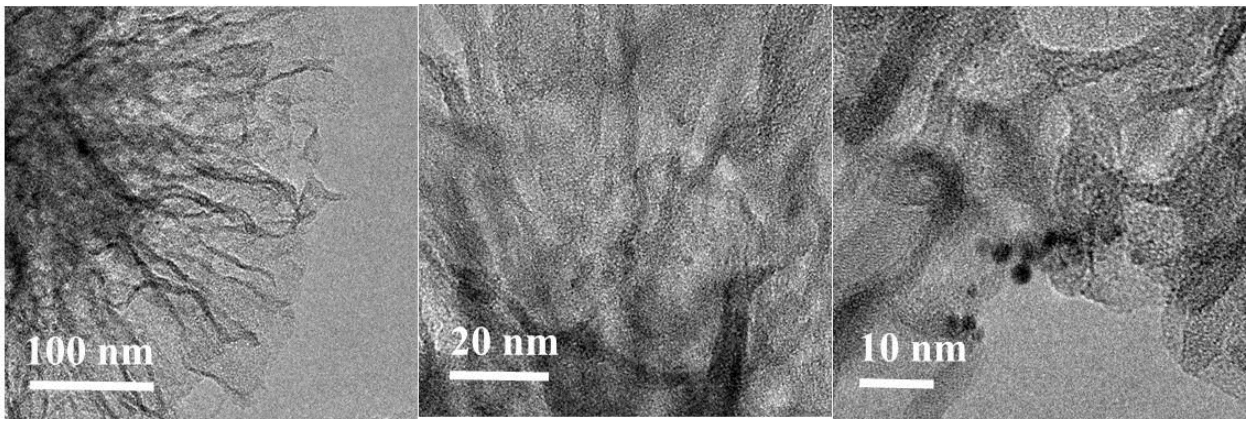


Table SI 1. Recycling study of KCC-1-PEI/Pd (0.1%) for carboylative Suzuki-Miyaura cross-coupling between iodobenzene and phenylboronic acid.

Run	Conversion[b] (%)	Selectivity[b] (%)	TON[c]	TOF (h^{-1})
1	54	85	4019	669
2	55	89	4286	714
3	54	88	4161	693
4	55	88	4238	706
5	54	86	4066	677
6	54	88	4161	693
7	53	87	4037	672
8	51	86	3840	640
9	46	85	3423	570
10	45	86	3388	564

[a]Reaction conditions: **1a** (5 mmol), **2a** (7.5 mmol), CO (2 bar), KCC-1-PEI/Pd (50 mg 0.1% Pd), K_2CO_3 (15 mmol), anisole (20 mL) at 100 °C for 6 h. [b]Determined by GC-MS. [c] mol product per mol Pd.

Figure SI 2. A drawing showing the chemical structure of the KCC-1-PEI