Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Pd/C Catalyzed Phenoxycarbonylation Using *N*-Formylsaccharin as a CO Surrogate in Propylene Carbonate as a Sustainable Solvent

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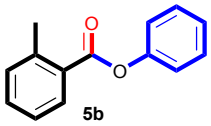
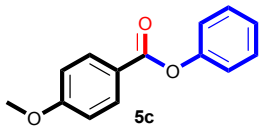
I Characterization data of products



phenyl 2-methylbenzoate (5b)

30.2 mg, yield 57%

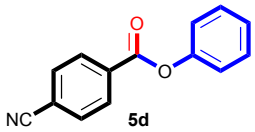
GCMS (EI, 70 eV): *m/z* (%): 212 (16.5), 91 (41.71), 65 (13.24), 39 (3.78), 119 (100%)



phenyl 4-methoxybenzoate (5c)

40.5 mg, yield 71%

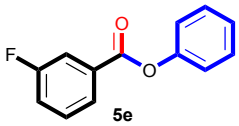
GCMS (EI, 70 eV): *m/z* (%): 228 (2.31), 135 (100), 107 (12.10), 92 (8.71), 77 (14.01), 64 (4.36), 39 (1.74)



phenyl 4-cyanobenzoate (5d)

25.6 mg, yield 46%

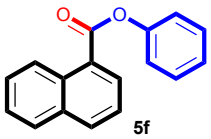
GCMS (EI, 70 eV): m/z (%): 223 (14.76), 130 (100), 131 (10.06), 102 (33.76), 75(5.01), 39 (3.16)



phenyl 3-fluorobenzoate (5e)

37.8 mg, yield 70%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 0H), 7.51 – 7.39 (m, 5H), 7.38 – 7.27 (m, 1H), 7.20 (d, *J* = 8.2 Hz, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 163.8, 150.7, 130.2 (*J* = 7.7 Hz), 129.5, 126.0, 125.8 (*J* = 3.2 Hz), 121.5, 120.7, 120.5, 117.1, 116.9. **GCMS** (EI, 70 eV): *m/z* (%): 216 (9.95), 123 (100), 124 (8.22), 95 (42.32), 75 (9.25), 39 (2.94)

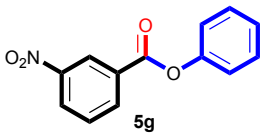


5f

phenyl 1-naphthoate (5f)

40.3 mg, yield 65%

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (d, *J* = 8.7 Hz, 1H), 8.47 (d, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.64 (ddd, *J* = 8.7, 6.8, 1.5 Hz, 1H), 7.57 (tt, *J* = 7.2, 2.4 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.33 – 7.26 (m, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 165.8, 150.9, 134.2, 133.9, 131.6, 131.1, 129.5, 128.6, 128.1, 126.3, 125.9, 125.8, 125.7, 124.5, 121.8. **GCMS** (EI, 70 eV): *m/z* (%): 248 (6.23), 155 (100), 156 (12.32), 127 (56.01), 126 (8.32), 101 (2.77), 77 (4.64).

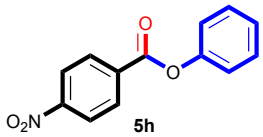


5g

phenyl 3-nitrobenzoate (5g)

38.9 mg, yield 64%

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (s, 1H), 8.50 (dd, *J* = 10.6, 8.5 Hz, 2H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.27 (m, 1H), 7.25 – 7.20 (m, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 163.0, 150.4, 148.3, 135.7, 131.3, 129.8, 129.6, 127.9, 126.3, 125.0, 121.4. **GCMS** (EI, 70 eV): *m/z* (%): 243 (21.66), 150 (100), 151 (8.79), 104 (32.57), 76 (18.80), 50 (5.65).

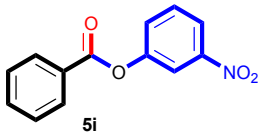


5h

phenyl 4-nitrobenzoate (5h)

33.4 mg, yield 55%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (t, *J* = 6.0 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.20 (m, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 163.3, 150.8, 150.4, 134.9, 131.2, 129.6, 126.4, 123.7, 121.3. **GCMS** (EI, 70 eV): *m/z* (%): 243 (15.13), 150 (100), 151 (8.75), 120 (19.82), 104 (30.09), 76 (19.02), 50 (5.89).

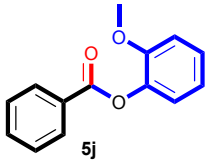


5i

3-nitrophenyl benzoate (5i)

40.7 mg, yield 67%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 – 8.18 (m, 2H), 8.18 – 8.09 (m, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 164.5, 151.2, 148.8, 134.1, 130.2, 130.0, 128.7, 128.5, 128.2, 120.8, 117.56. **GCMS** (EI, 70 eV): *m/z* (%): 243 (0.13), 213 (0.6), 105 (100), 106 (7.45), 77 (33.94), 51 (7.75).

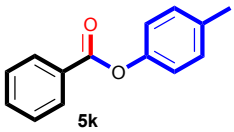


5j

2-methoxyphenyl benzoate (5j)

42.7 mg, yield 75%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 – 8.18 (m, 2H), 7.66 – 7.59 (m, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.15 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.04 – 6.97 (m, 2H), 3.81 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 164.7, 151.3, 139.9, 133.4, 130.2, 129.4, 128.4, 126.9, 122.9, 120.7, 112.4, 55.84. **GCMS** (EI, 70 eV): *m/z* (%): 228 (10.32), 105 (100), 106 (7.87), 77 (33.38), 51 (6.48).

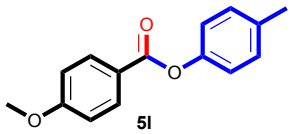


5k

***p*-tolyl benzoate (5k)**

44.0 mg, yield 83%

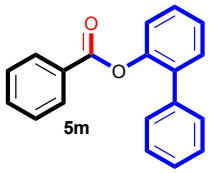
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.1 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 2.37 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: 165.3, 148.6, 135.5, 133.4, 130.1, 129.9, 129.6, 128.5, 121.3, 20.9. **GCMS** (EI, 70 eV): *m/z* (%): 212 (8.81), 105 (100), 106 (7.78), 77 (34.10), 51 (6.70).



***p*-tolyl 4-methoxybenzoate (5l)**

37.5 mg, yield 62%

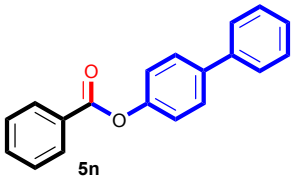
GCMS (EI, 70 eV): *m/z* (%): 242 (4.30), 135 (100), 136 (9.31), 107 (10.45), 92 (7.67), 77 (13.92), 51 (1.23).



[1,1'-biphenyl]-2-yl benzoate (5m)

58.2 mg, yield 85%

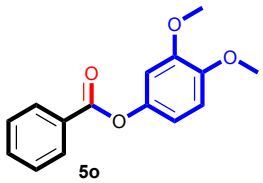
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 6.9 Hz, 1H), 7.50 – 7.21 (m, 11H), 6.98 (t, *J* = 7.3 Hz, 1H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 165.1, 147.9, 137.4, 133.4, 130.0, 129.2, 129.0, 128.9, 128.4, 128.4, 128.2, 127.8, 127.3, 123.0, 120.7. **GCMS** (EI, 70 eV): *m/z* (%): 274 (18.12), 169 (1.48), 139 (3.09), 105 (100), 106 (8.39), 77 (26.11), 51 (3.36). **HRMS**: Calculated for $C_{19}H_{14}O_2$ [M + H]$^+$ 275.1067, found 275.1068.



[1,1'-biphenyl]-4-yl benzoate (5n)

61.7 mg, yield 90%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 3H), 7.56 (d, *J* = 5.1 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.33 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 165.2, 150.3, 140.3, 139.0, 133.6, 130.1, 129.5, 128.7, 128.5, 128.1, 127.3, 127.0, 121.7. **GCMS** (EI, 70 eV): 274 (19.26%), 105 (100%), 77 (36.92%), 51 (4.63%).

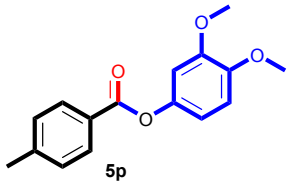


5o

3,4-dimethoxyphenyl benzoate (5o)

42.6 mg, yield 66%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 6.91 – 6.59 (m, 3H), 3.88 (s, 3H), 3.86 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 165.5, 149.3, 146.8, 144.5, 133.5, 130.1, 129.5, 128.5, 112.9, 111.1, 105.8, 56.1, 55.9. **GCMS** (EI, 70 eV): *m/z* (%): 258 (19.05), 125 (1.86), 105 (100), 106 (7.79), 77 (28.04), 51 (4.18). **HRMS**: Calculated for $C_{15}H_{14}O_4$ $[M + H]^+$ 259.0965, found 259.0964.

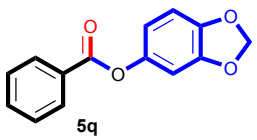


5p

3,4-dimethoxyphenyl 4-methylbenzoate (5p)

34.0 mg, yield 50%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 6.91 – 6.84 (m, 1H), 6.74 (dd, *J* = 4.1, 2.0 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 2.44 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 165.5, 154.9, 149.3, 146.8, 144.3, 130.1, 129.2, 126.7, 112.9, 111.1, 105.8, 56.1, 55.9, 21.7. **GCMS** (EI, 70 eV): *m/z* (%): 272 (9.88), 153 (0.78), 125 (1.70), 119 (100), 120 (9.30), 91 (27.37), 65 (8.35), 39 (2.07). **HRMS**: Calculated for $C_{16}H_{16}O_4$ $[M + H]^+$ 295.0941, found 295.0945.

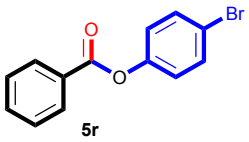


5q

benzo[*d*][1,3]dioxol-5-yl benzoate (5q)

31.4 mg, yield 52%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dd, *J* = 20.1, 8.1 Hz, 2H), 7.61 (dt, *J* = 13.6, 7.4 Hz, 1H), 7.48 (p, *J* = 8.2 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.75 (s, 1H), 6.70 – 6.65 (m, 1H), 5.95 (s, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 165.4, 148.0, 145.4, 145.2, 133.7, 130.1, 128.5, 128.4, 114.0, 108.0, 103.9, 101.7. **GCMS** (EI, 70 eV): *m/z* (%): 242 (14.50), 137 (2.15), 105 (100), 106 (8.20), 77 (36.24), 51 (6.99).

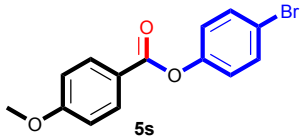


5r

4-bromophenyl benzoate (5r)

56.1 mg, yield 81%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.9 Hz, 2H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.52 (q, *J* = 8.0 Hz, 4H), 7.11 (d, *J* = 8.8 Hz, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 164.8, 149.9, 133.7, 132.5, 130.1, 129.1, 128.6, 123.5, 118.9. **GCMS** (EI, 70 eV): *m/z* (%): 276 (2.55), 105 (100), 106 (7.83), 77 (31.34), 51 (7.18).

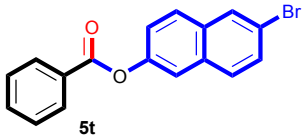


5s

4-bromophenyl 4-methoxybenzoate (5s)

57.5 mg, yield 75%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 164.5, 164.0, 150.0, 132.4, 132.3, 123.6, 121.3, 118.7, 113.8, 55.5. **GCMS** (EI, 70 eV): *m/z* (%): 306 (1.07), 136 (9.81), 135 (100), 107 (10.64), 92 (8.62), 77 (11.85), 63 (4.36), 50 (1.24).

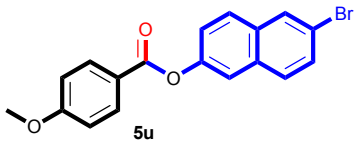


5t

6-bromonaphthalen-2-yl benzoate (5t)

41.7 mg, yield 51%

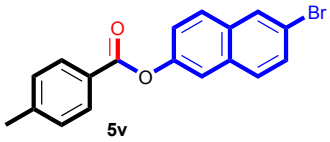
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.3 Hz, 2H), 8.02 (s, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.73 – 7.61 (m, 3H), 7.59 – 7.47 (m, 3H), 7.41 – 7.33 (m, 1H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 165.1, 148.8, 133.7, 132.4, 132.2, 130.1, 129.9, 129.8, 129.3, 129.2, 128.6, 128.5, 122.3, 119.6, 118.7. **GCMS** (EI, 70 eV): *m/z* (%): 326 (6.63%), 105 (100%), 77 (28.71%).



6-bromonaphthalen-2-yl 4-methoxybenzoate (5u)

63.4 mg, yield 71%

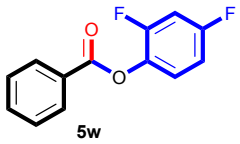
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.9 Hz, 2H), 8.01 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 160.1, 159.2, 144.2, 127.6, 127.5, 127.4, 125.1, 125.0, 124.5, 123.7, 117.8, 116.8, 114.7, 114.0, 109.1, 50.7. **GCMS** (EI, 70 eV): *m/z* (%): 356 (2.14), 135 (100), 136 (8.67), 114 (2.96), 107 (7.69), 92 (6.05),77 (10.38). **HRMS**: Calculated for $C_{18}H_{13}BrO_3$ $[M + H]^+$ 357.0121, found 357.0122.



6-bromonaphthalen-2-yl 4-methylbenzoate (5v)

58.0 mg, yield 68%

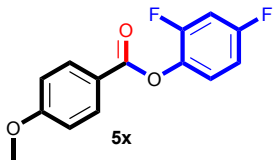
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.6 Hz, 2H), 8.02 (s, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.35 (dd, *J* = 19.3, 8.6 Hz, 3H), 2.46 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 165.2, 148.9, 144.6, 132.4, 132.2, 130.2, 129.9, 129.8, 129.3, 129.2, 128.4, 126.5, 122.4, 119.5, 118.8, 21.7. **GCMS** (EI, 70 eV): **HRMS**: Calculated for $C_{18}H_{13}BrO_2$ $[M + Na]^+$ 362.9991, found 362.9993.



2,4-difluorophenyl benzoate (5w)

46.2 mg, yield 79%

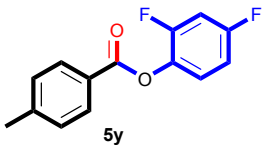
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.22 (dd, *J* = 11.3, 5.5 Hz, 1H), 7.01 – 6.87 (m, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 164.1, 161.4 (d, *J* = 10.4 Hz), 158.9 (d, *J* = 10.2 Hz), 155.4 (d, *J* = 12.5 Hz), 133.9, 130.3, 128.6, 128.4, 124.3 (dd, *J* = 9.9, 1.9 Hz), 111.2 (dd, *J* = 23.1, 3.8 Hz), 105.1 (dd, *J* = 26.9, 22.3 Hz). **GCMS** (EI, 70 eV): *m/z* (%): 234 (1.16), 129 (1.43), 105 (100), 106 (7.91), 77 (43.31), 51 (11.88). **HRMS**: Calculated for $C_{13}H_8F_2O_2$ $[M + H]^+$ 235.0565, found 235.0564



2,4-difluorophenyl 4-methoxybenzoate (5x)

56.1 mg, yield 85%

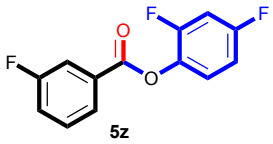
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.9 Hz, 2H), 7.21 (ddd, *J* = 14.1, 7.6, 3.3 Hz, 1H), 7.03 – 6.85 (m, 4H), 3.89 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 159.4, 156.5 (d, *J* = 10.6 Hz), 154.0 (d, *J* = 10.4 Hz), 150.7 (d, *J* = 12.4 Hz), 148.2 (d, *J* = 12.4 Hz), 127.7, 119.7 (d, *J* = 11.9 Hz), 115.9, 109.1, 106.4 (dd, *J* = 23.0, 3.8 Hz), 100.3 (dd, *J* = 27.0, 22.4 Hz), 50.7. **GCMS** (EI, 70 eV): *m/z* (%): 264 (1.07), 136 (10.11), 135 (100), 129 (1.19), 107 (13.73), 92 (10.55), 77 (15.54), 51 (1.90). **HRMS**: Calculated for $C_{14}H_{10}F_2O_3$ $[M + H]^+$ 265.0671, found 265.0675.



2,4-difluorophenyl 4-methylbenzoate (5y)

49.6 mg, yield 80%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.20 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.00 – 6.86 (m, 2H), 2.45 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 159.4, 156.5 (d, *J* = 10.9 Hz), 154.1 (d, *J* = 10.8 Hz), 148.2 (d, *J* = 12.8 Hz), 140.1, 125.6, 124.6, 120.9, 119.6 (dd, *J* = 9.9, 1.9 Hz), 106.4 (dd, *J* = 23.0, 3.8 Hz), 100.7 – 99.9 (m), 17.0 . **GCMS** (EI, 70 eV): *m/z* (%): 248 (0.99), 129 (1.65), 120 (9.87), 119 (100), 101 (3.60), 91 (40.42), 65 (13.8), 51 (2.54). **HRMS**: Calculated for $C_{14}H_{10}F_2O_2$ $[M + H]^+$ 249.0722, found 249.0728.

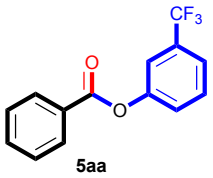


2,4-difluorophenyl 3-fluorobenzoate (5z)

56.1 mg, yield 89%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 10.1 Hz, 1H), 7.50 (q, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 8.9 Hz, 1H), 7.22 (td, *J* = 8.7, 5.7 Hz, 1H), 7.03 – 6.87 (m, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 159.0, 156.7 (d, *J* = 10.4 Hz), 154.3 (d, *J* = 10.5 Hz), 150.5 (d, *J* = 12.5 Hz), 148.0 (d, *J* = 12.6 Hz), 125.7 (d, *J* = 7.5 Hz), 125.6 (d, *J* = 7.8 Hz), 121.3 (d, *J* = 3.1 Hz), 119.5 (d, *J* = 11.8 Hz), 116.3 (d, *J* = 21.2 Hz), 112.4 (d, *J* = 23.4 Hz), 106.6 (dd, *J* = 23.0, 3.9 Hz), 100.5 (dd, *J* = 26.9, 22.3 Hz). **^{19}F NMR (500 MHz, $CDCl_3$)**: δ -111.3 – -111.9 (m), -112.0 – -112.5 (m), -123.3 (td, *J* = 9.4, 6.6 Hz). **GCMS** (EI,

70 eV): *m/z* (%): 252 (51.5), 129 (1.89), 123.15 (100), 124 (8.45), 101 (5.16), 95 (43.99), 75 (14.08), 51 (2.86). **HRMS**: Calculated for $C_{13}H_7F_3O_2$ [M + Na]$^+$ 275.0290, found 275.0288.

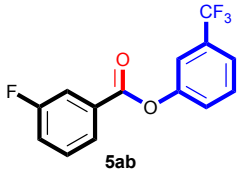


5aa

3-(trifluoromethyl)phenyl benzoate (5aa)

55.2 mg, yield 83%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.48 (m, 5H), 7.43 (d, *J* = 6.7 Hz, 1H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 164.7, 150.9, 133.9, 132.3 – 131.3 (m), 130.2, 130.0, 128.9, 128.6, 125.3, 124.8, 122.7 (q, *J* = 3.8 Hz), 119.0 (q, *J* = 4.0 Hz). **GCMS** (EI, 70 eV): *m/z* (%): 266 (1.02), 247 (4.72), 161 (0.79), 133 (1.97), 105 (100), 106 (8.36), 77 (41.55), 51 (11.76).

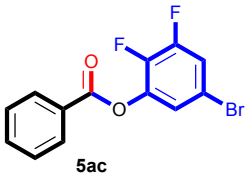


5ab

3-(trifluoromethyl)phenyl 3-fluorobenzoate (5ab)

63.9 mg, yield 90%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.91 – 7.83 (m, 1H), 7.59 – 7.47 (m, 4H), 7.45 – 7.33 (m, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 163.8, 161.3, 150.7, 132.0 (d, *J* = 32.9 Hz), 131.0 (d, *J* = 7.7 Hz), 130.4, 130.3, 130.1, 125.9 (d, *J* = 3.1 Hz), 125.2, 122.9 (q, *J* = 4.0 Hz), 121.0 (d, *J* = 21.3 Hz), 118.9 (q, *J* = 3.9 Hz), 117.0 (d, *J* = 23.3 Hz). **^{19}F NMR (500 MHz, $CDCl_3$)**: δ -62.7, -111.6 (td, J = 8.9, 5.6 Hz). **GCMS** (EI, 70 eV): *m/z* (%): 284 (2.17), 265 (4.54), 133 (1.80), 123 (100), 124 (8.46), 113 (2.14), 95 (43.27), 75 (13.85), 50 (2.26). **HRMS**: Calculated for $C_{14}H_8F_4O_2$ [M + Na]$^+$ 307.0353, found 307.0355.



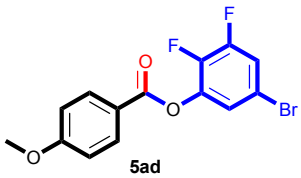
5ac

5-bromo-2,3-difluorophenyl benzoate (5ac)

50.0 mg, yield 64%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.2 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.27 (dd, *J* = 15.5, 6.2 Hz, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 163.4, 152.3 (d, *J* = 11.8 Hz), 149.8 (d, *J* = 11.5 Hz), 144.1 (d, *J* = 14.6 Hz), 134.3, 130.4, 128.7, 127.8, 122.5 (d, *J* = 3.7 Hz), 118.3 (d, *J* = 20.3

Hz), 114.8. **GCMS** (EI, 70 eV): *m/z* (%): 312 (1.13), 178 (1.52), 106 (8.54), 105 (100), 77 (37.62), 51 (11.59), 50 (4.51). **HRMS**: Calculated for $C_{13}H_7BrF_2O_2$ $[M + H]^+$ 312.9670, found 312.9674.

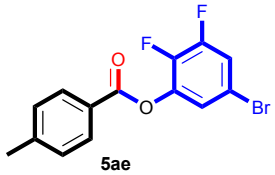


5ad

5-bromo-2,3-difluorophenyl 4-methoxybenzoate (5ad)

57.4 mg, yield 67%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.26 (q, *J* = 6.7, 4.5 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 164.4, 163.0, 151.1 (dd, *J* = 253.6, 11.9 Hz), 143.0 (dd, *J* = 252.6, 14.8 Hz), 140.3, 132.6, 122.6 (d, *J* = 3.6 Hz), 119.9, 118.2, 118.0, 114.0, 55.5. **GCMS** (EI, 70 eV): *m/z* (%): 342 (0.25), 344 (0.25), 179 (1.09), 136 (10.17), 135 (100), 107 (10.74), 92 (8.7), 77 (12.18), 50 (2.09). **HRMS**: Calculated for $C_{14}H_9BrF_2O_3$ $[M + Na]^+$ 364.9595, found 364.9595.

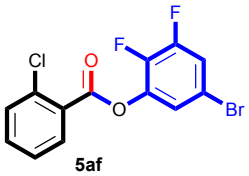


5ae

5-bromo-2,3-difluorophenyl 4-methylbenzoate (5ae)

49.8 mg, yield 61%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.22 (m, 2H), 2.45 (s, 3H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 163.4, 151.1 (dd, *J* = 253.6, 11.7 Hz), 145.3, 142.9 (dd, *J* = 252.9, 14.1 Hz), 140.3 (dd, *J* = 10.9, 2.9 Hz), 130.5, 129.4, 125.0, 122.6 (d, *J* = 3.7 Hz), 118.2 (d, *J* = 20.3 Hz), 114.9 (dd, *J* = 9.6, 5.1 Hz), 21.8. **GCMS** (EI, 70 eV): *m/z* (%): 326 (0.30), 328 (0.30), 181 (1.20), 119 (100), 120 (9.48), 91 (36.68), 65 (13.14), 50 (1.85), 39 (3.03). **HRMS**: Calculated for $C_{14}H_9BrF_2O_2$ $[M + Na]^+$ 348.9646, found 348.9647.



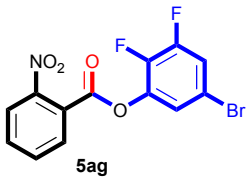
5af

5-bromo-2,3-difluorophenyl 2-chlorobenzoate (5af)

50.3 mg, yield 58%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 3.8 Hz, 2H), 7.36 (dt, *J* = 8.3, 4.4 Hz, 1H), 7.26 (t, *J* = 5.6 Hz, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 161.83 , 152.41 – 149.68 (m),

142.82 (dd, *J* = 253.3, 14.3 Hz), 139.84 (d, *J* = 13.9 Hz), 134.95 , 133.99 , 132.27 , 131.55 , 127.24 , 126.87 , 122.50 , 118.55 (d, *J* = 20.3 Hz), 115.06 (dd, *J* = 9.6, 5.1 Hz). **^{19}F NMR (500 MHz, $CDCl_3$)**: δ -131.5 – -134.3 (m), -149.4 – -152.5 (m). **GCMS** (EI, 70 eV): *m/z* (%): **HRMS:** Calculated for $C_{13}H_6BrClF_2O_2$ $[M + Na]^+$ 368.9100, found 368.9099.



5ag

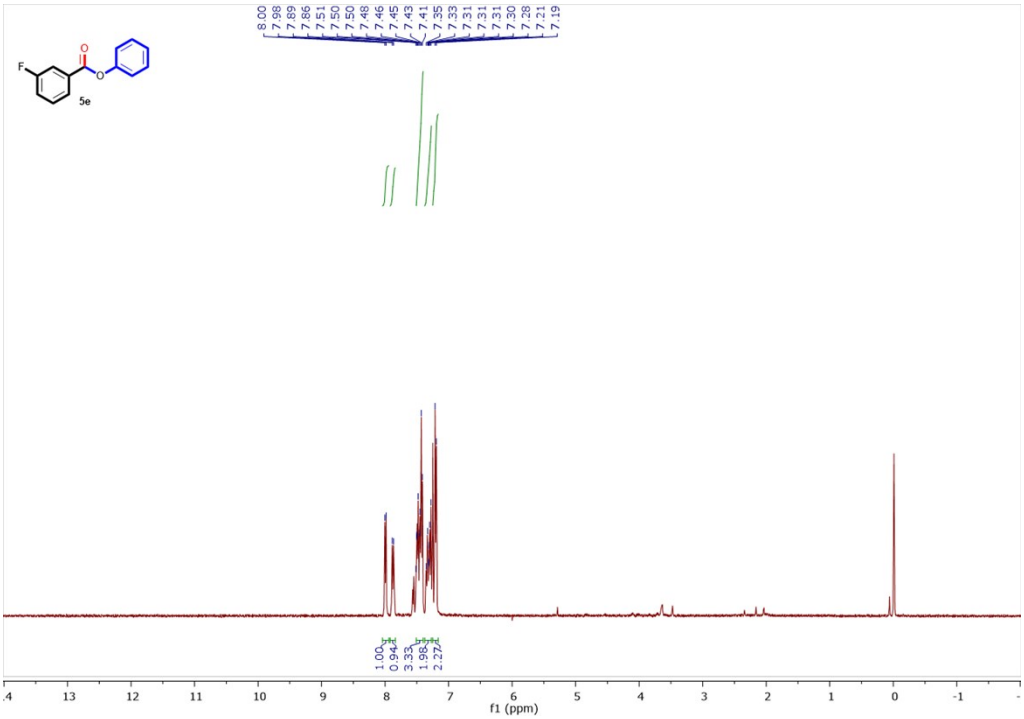
5-bromo-2,3-difluorophenyl 2-nitrobenzoate (5ag)

43.8 mg, yield 49%

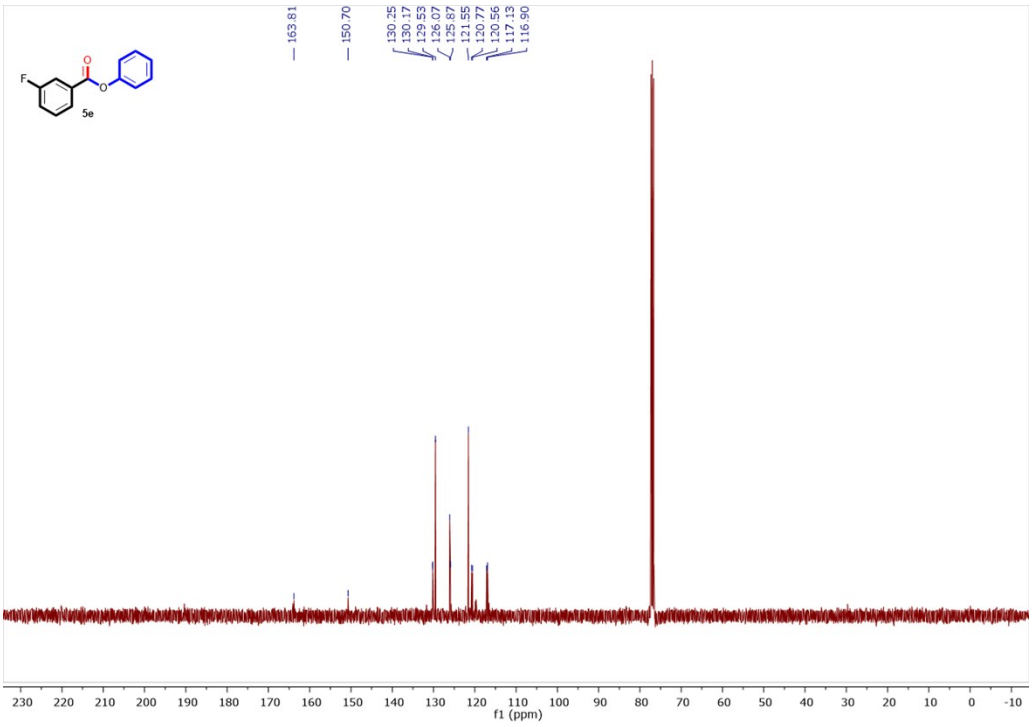
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.1 Hz, 1H), 7.75 (dt, *J* = 16.8, 7.5 Hz, 2H), 7.34 – 7.25 (m, 2H). **^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$)**: δ 162.44 , 150.99 (dd, *J* = 254.3, 11.6 Hz), 148.22 – 143.72 (m), 142.11 – 138.73 (m), 133.58 , 132.76 , 130.17 , 125.86 , 124.39 , 122.08 (d, *J* = 3.7 Hz), 119.07 , 118.87 , 115.23 (dd, *J* = 9.4, 5.1 Hz). **GCMS** (EI, 70 eV): *m/z* (%): **HRMS**: Calculated for $C_{13}H_6BrF_2NO_4$ $[M + Na]^+$ 379.9340, found 379.9340.

II Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

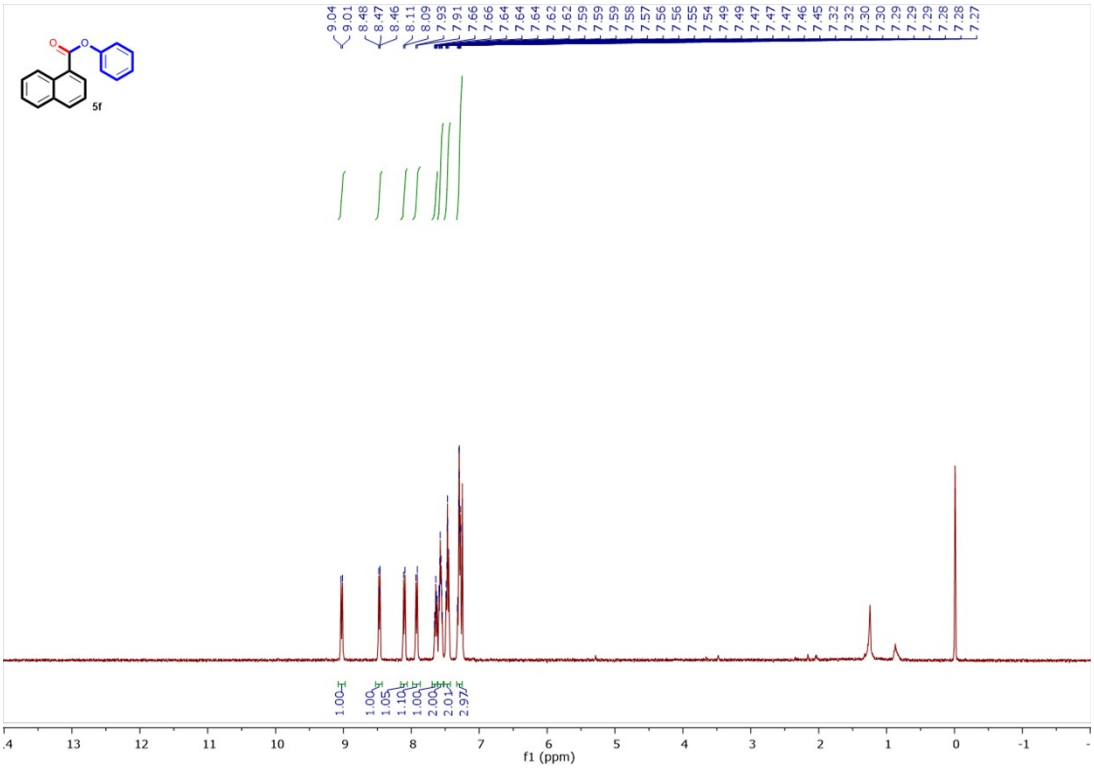
phenyl 3-fluorobenzoate (5e) (^{1}H NMR)



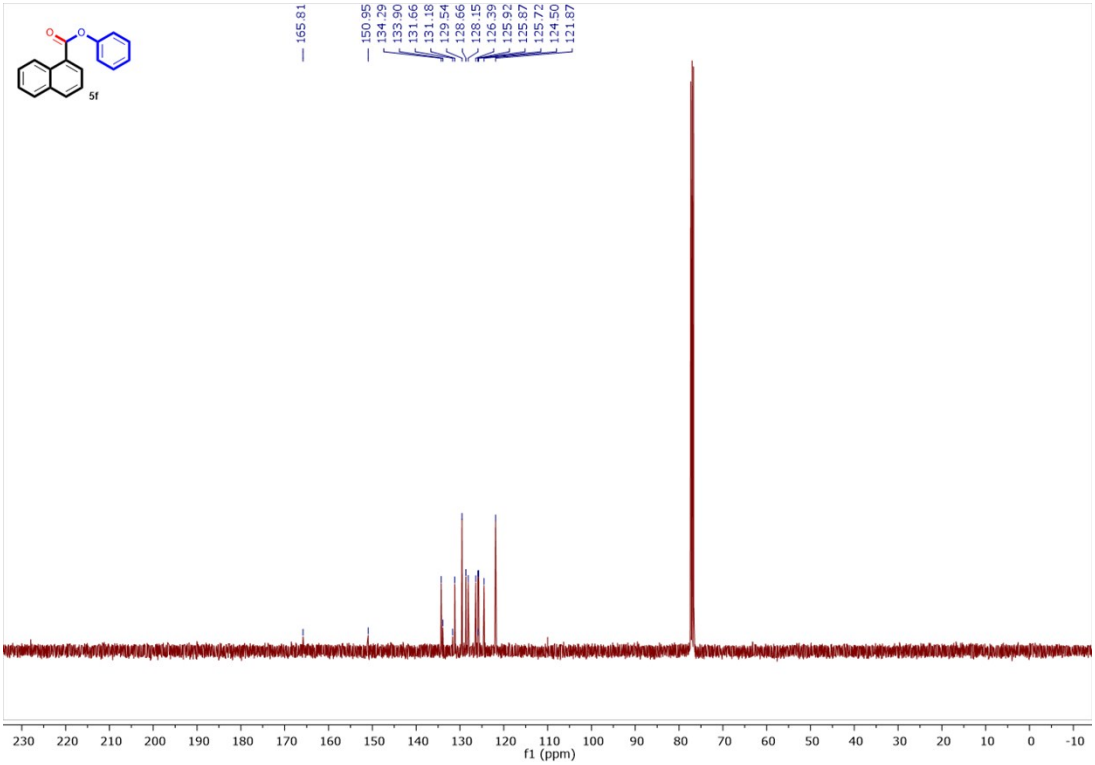
phenyl 3-fluorobenzoate (5e) (^{13}C NMR)



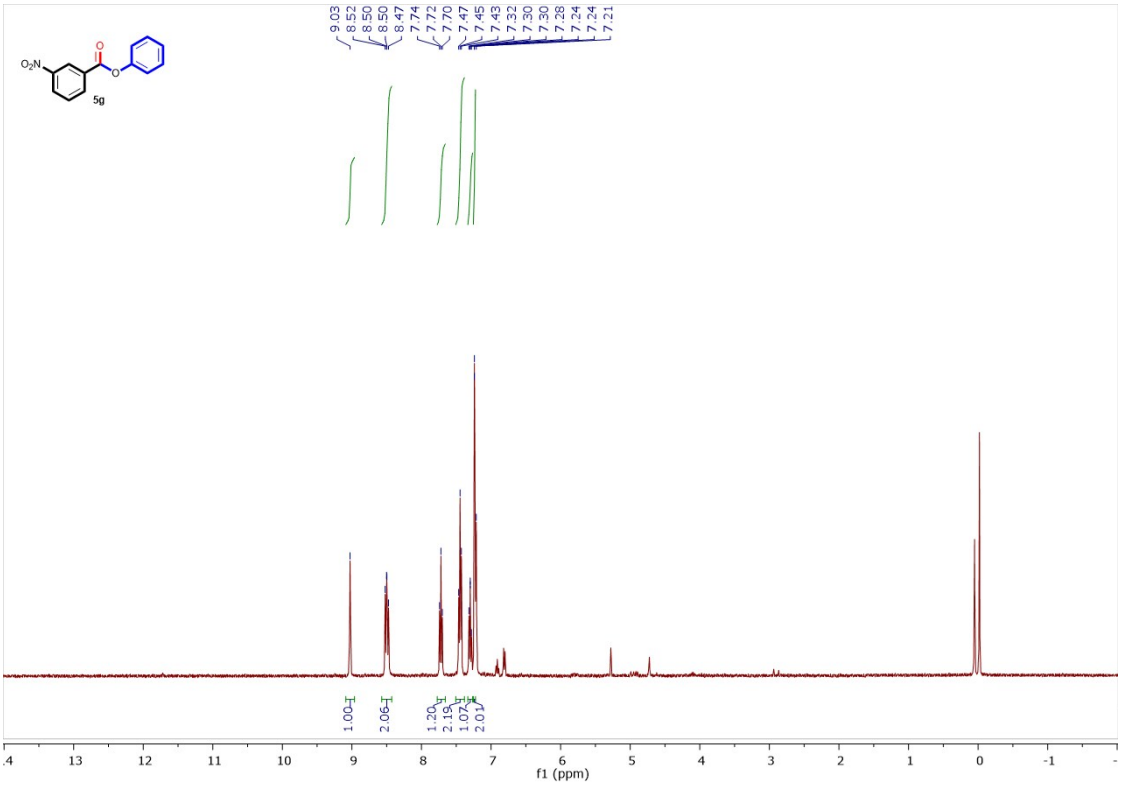
phenyl 1-naphthoate (5f) (^{1}H NMR)



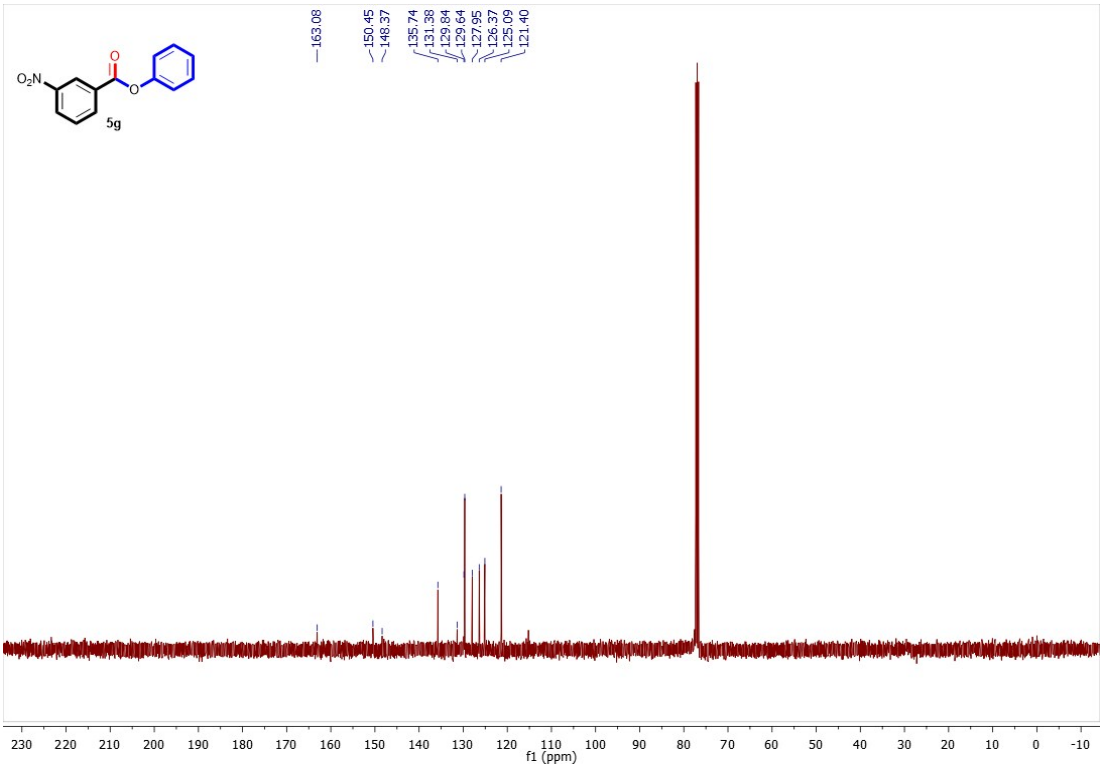
phenyl 1-naphthoate (5f) (^{13}C NMR)



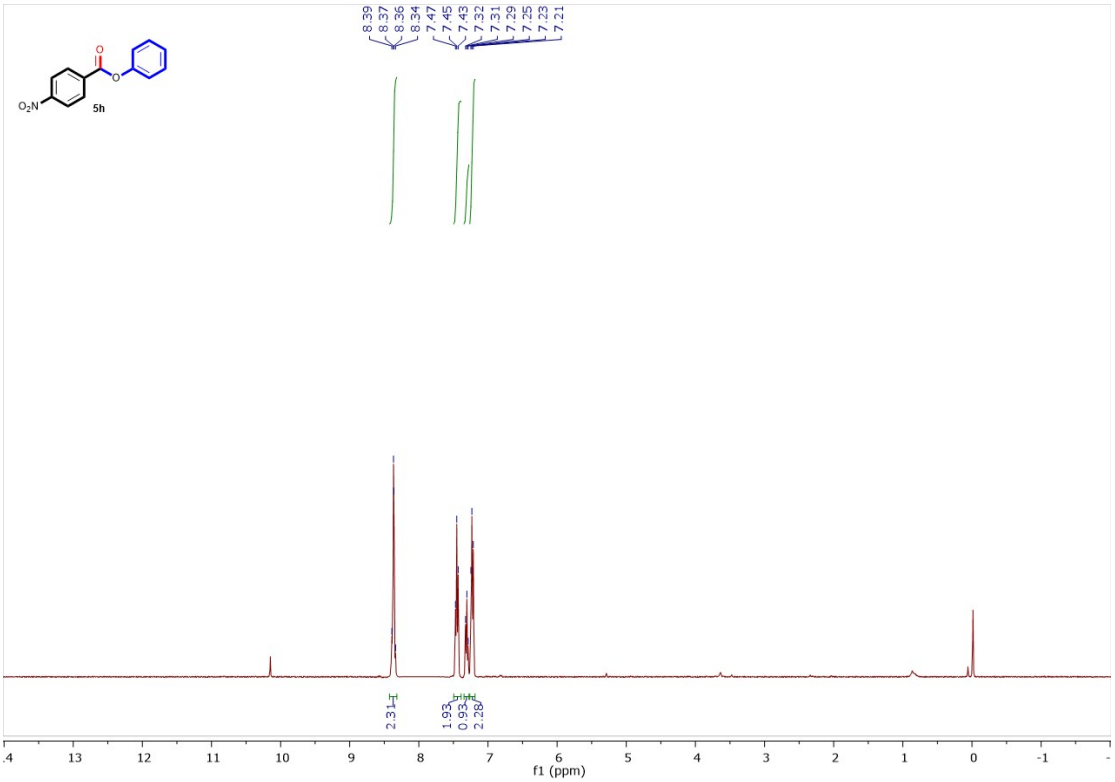
phenyl 3-nitrobenzoate (5g) (^{1}H NMR)



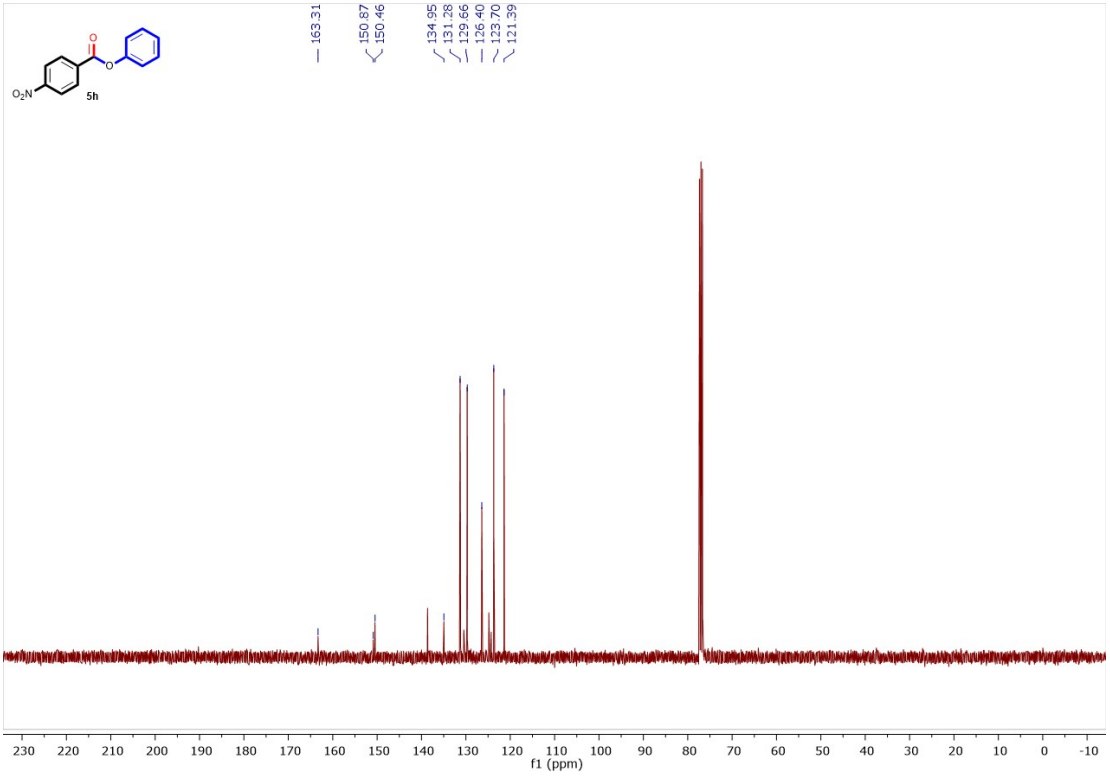
phenyl 3-nitrobenzoate (5g) (^{13}C NMR)



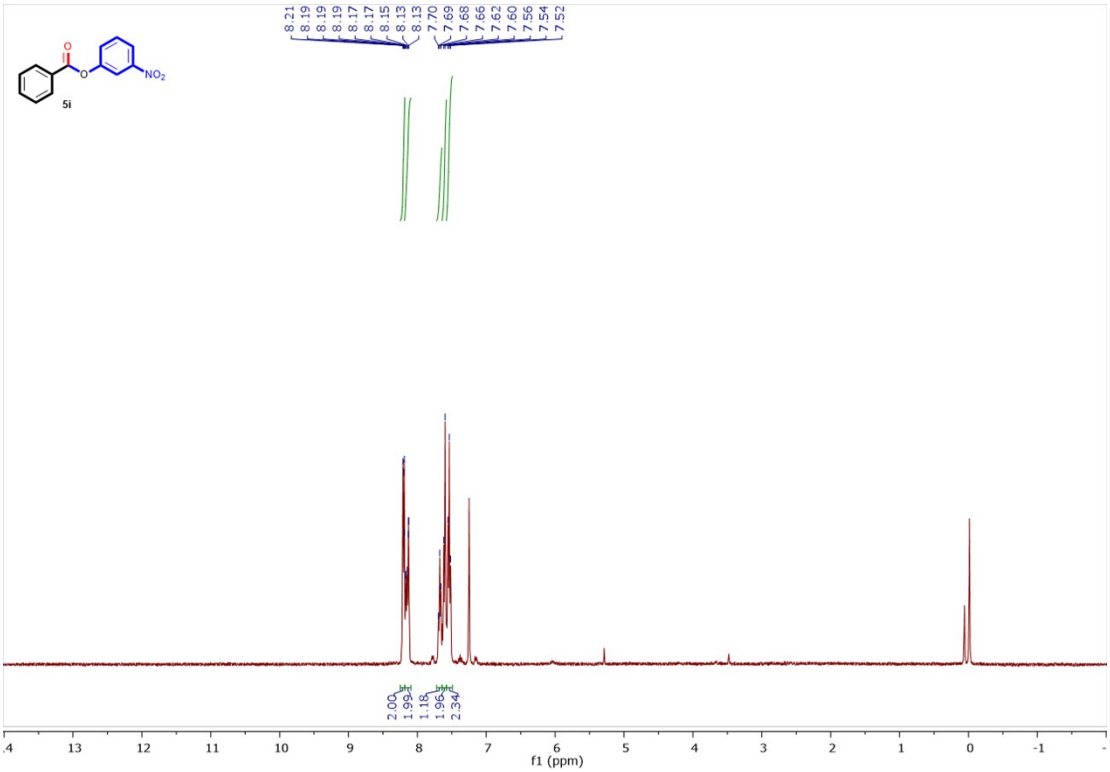
phenyl 4-nitrobenzoate (5h) (^{1}H NMR)



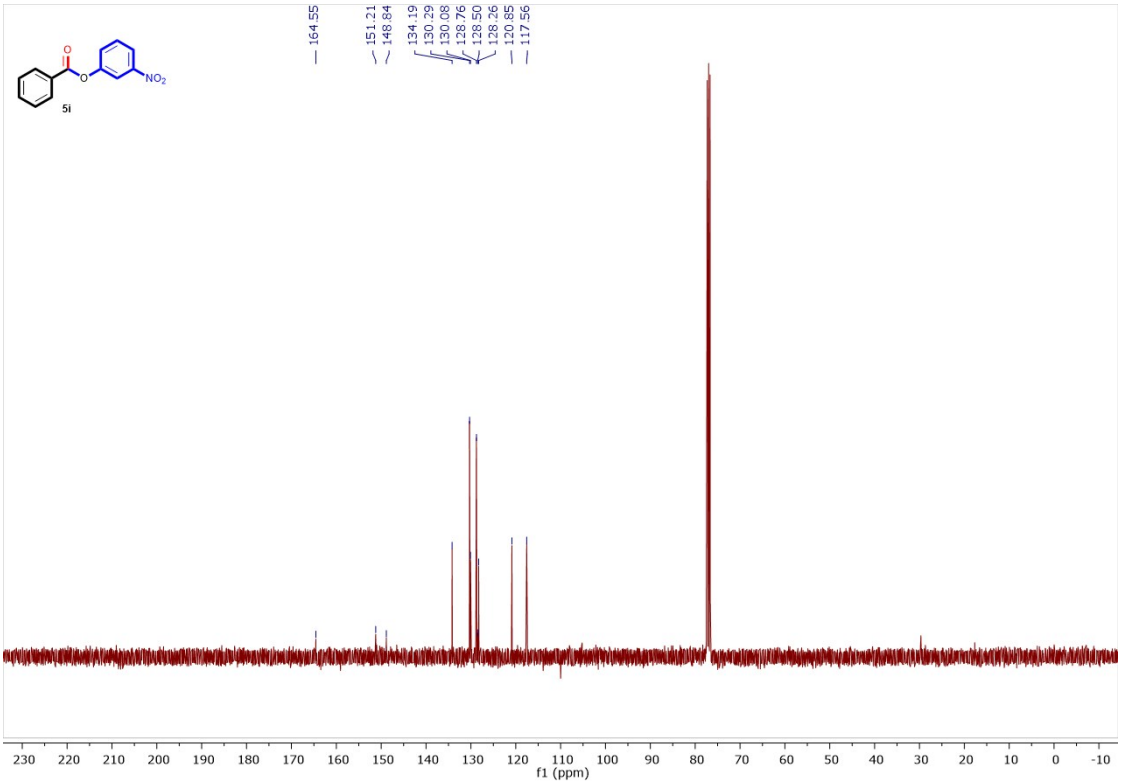
phenyl 4-nitrobenzoate (5h) (^{13}C NMR)



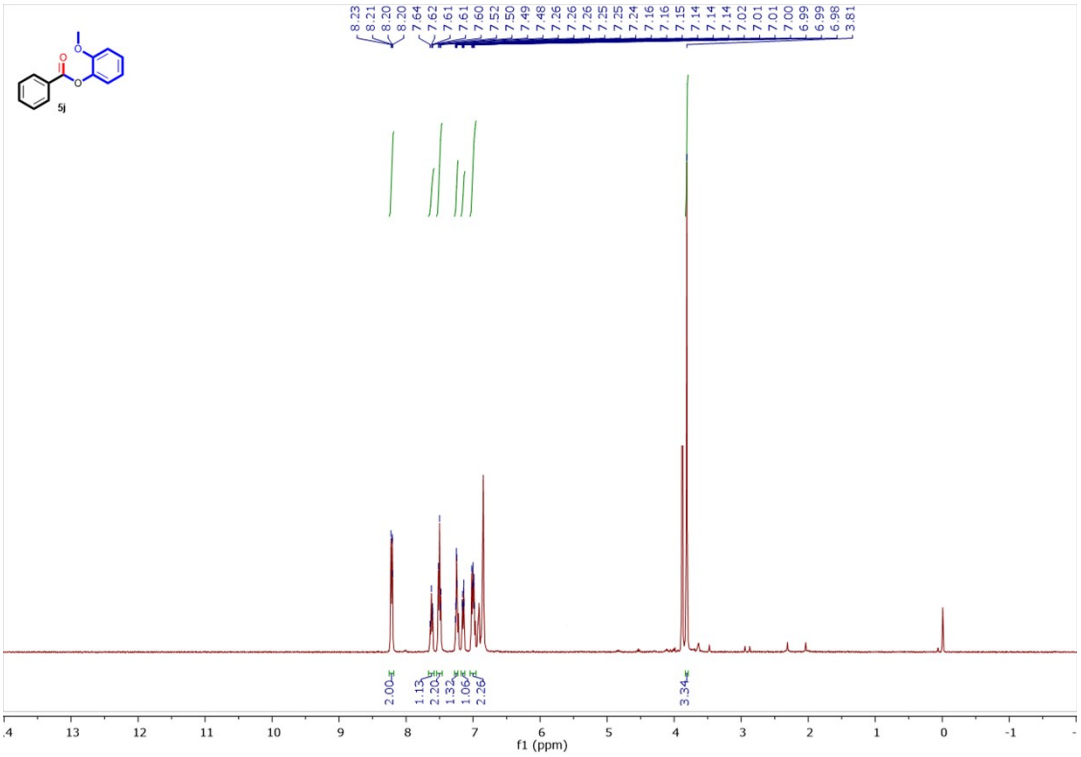
3-nitrophenyl benzoate (5i) (^{1}H NMR)



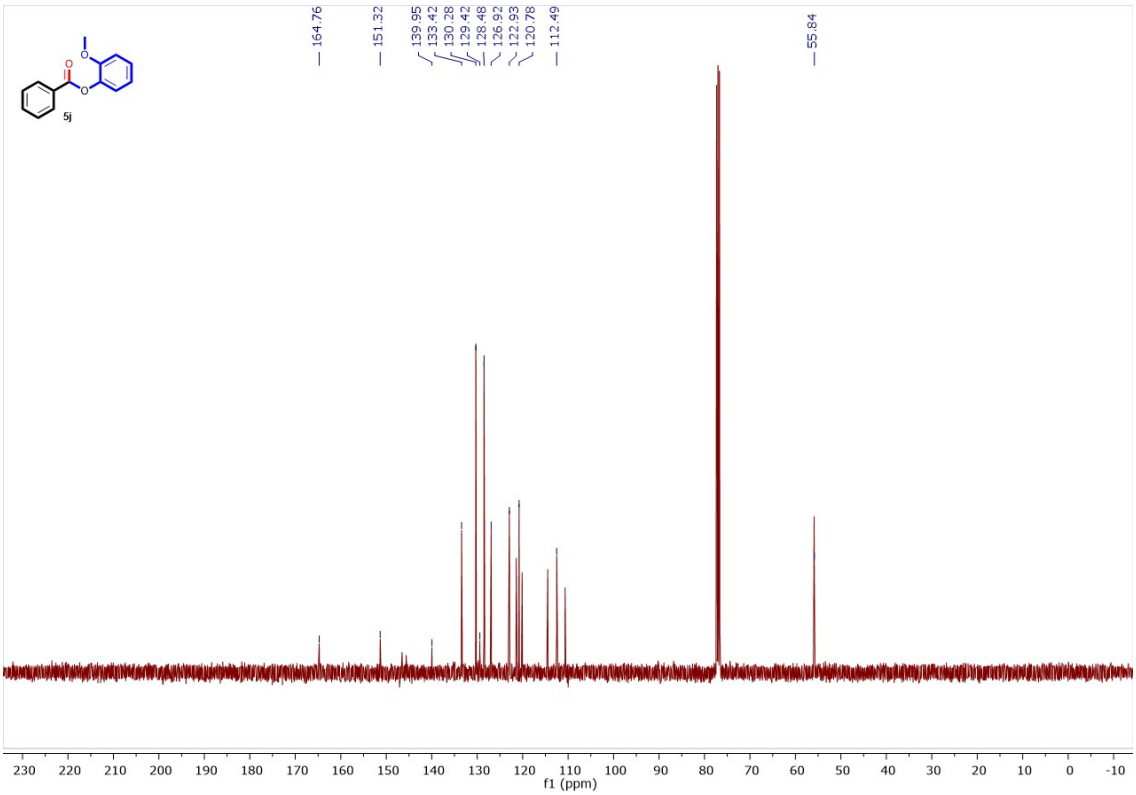
3-nitrophenyl benzoate (5i) (^{13}C NMR)



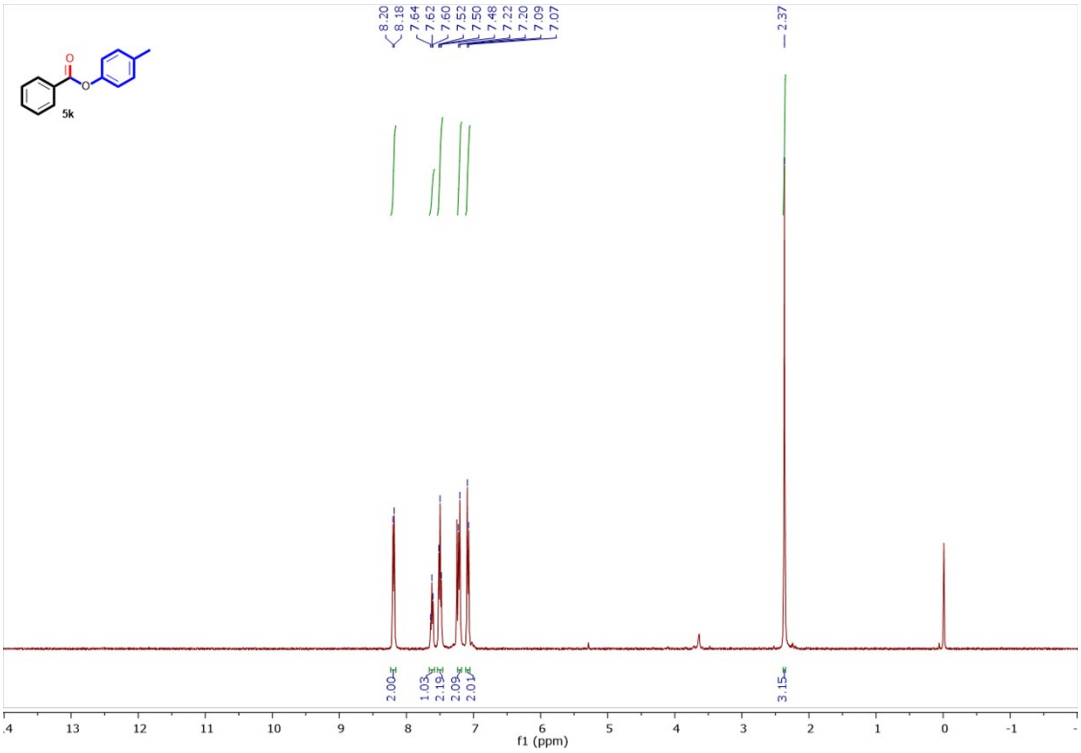
2-methoxyphenyl benzoate (5j) (^{1}H NMR)



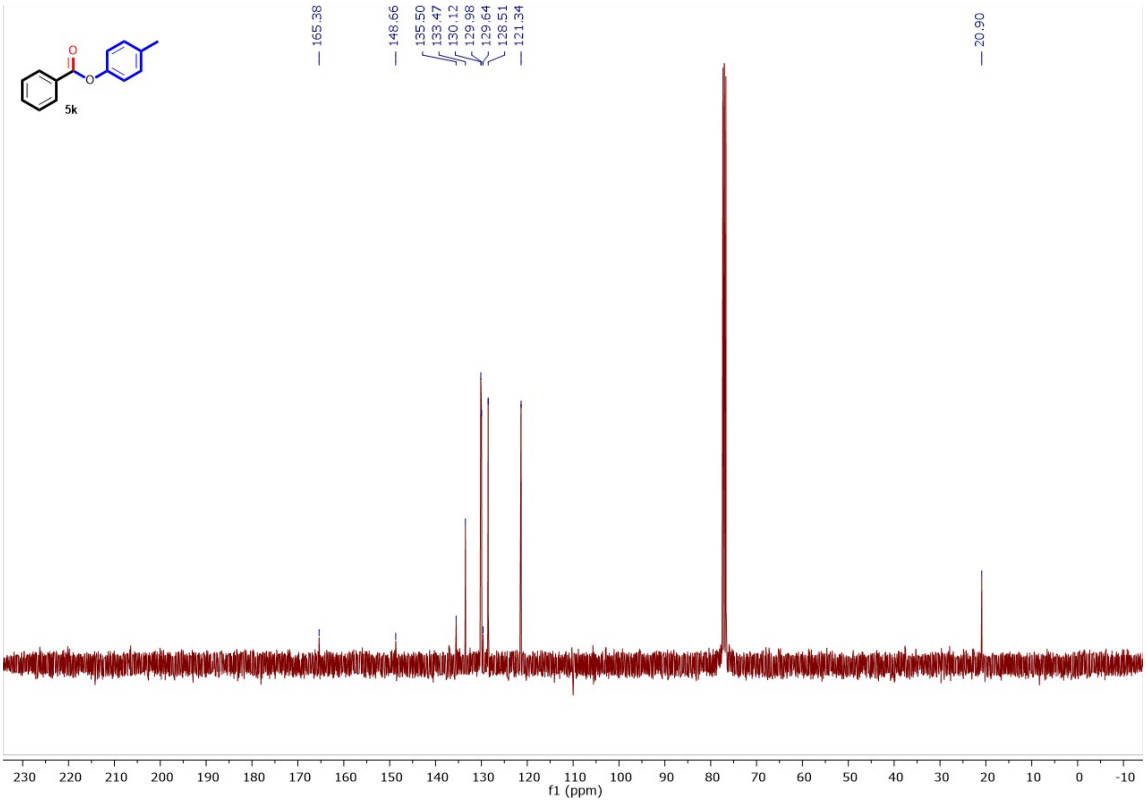
2-methoxyphenyl benzoate (5j) (^{13}C NMR)



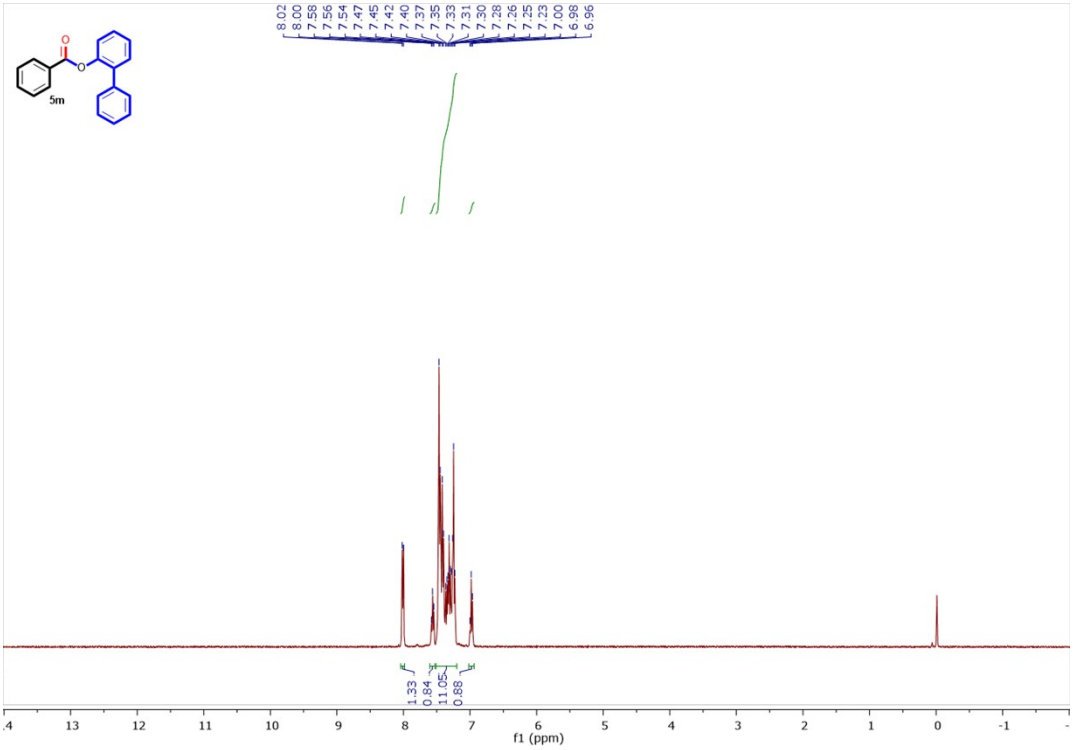
***p*-tolyl benzoate (5k) (^{1}H NMR)**



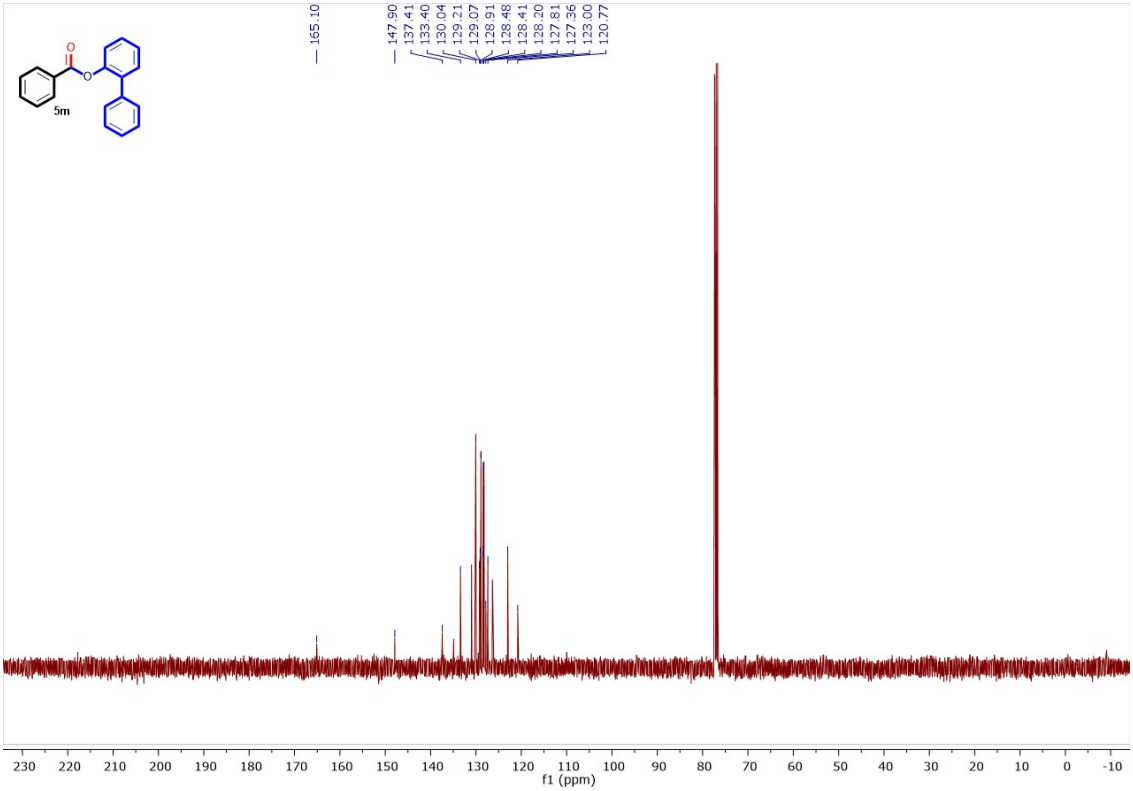
***p*-tolyl benzoate (5k) (^{13}C NMR)**



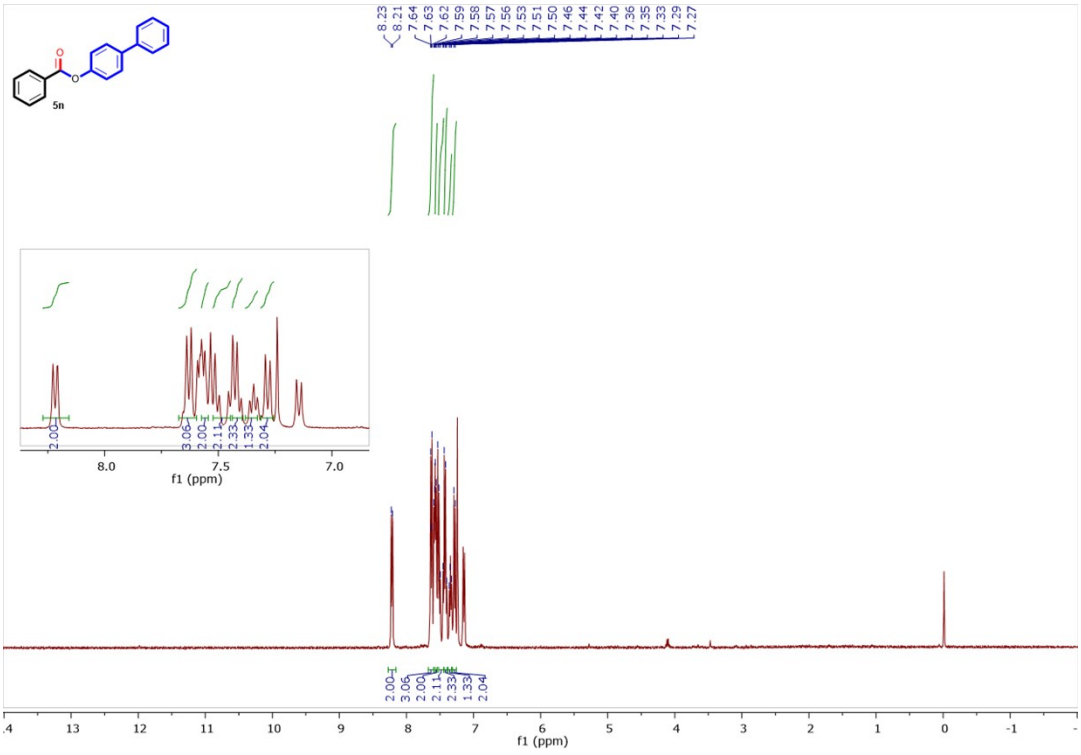
[1,1'-biphenyl]-2-yl benzoate (5m) (^{1}H NMR)



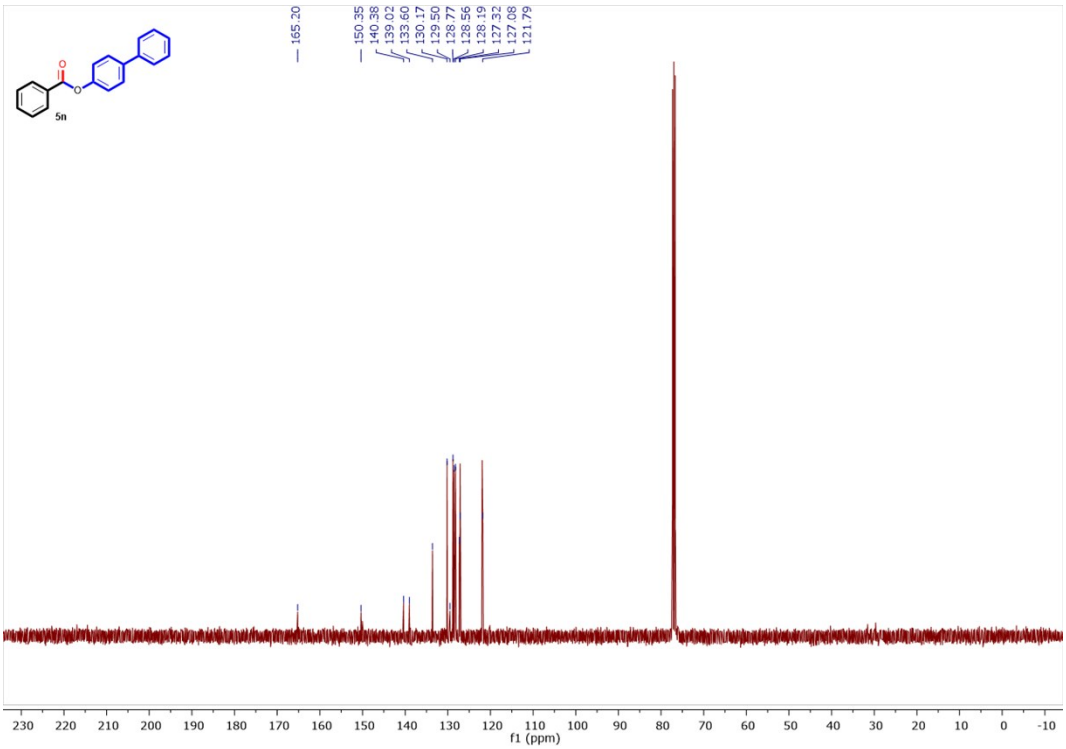
[1,1'-biphenyl]-2-yl benzoate (5m) (^{13}C NMR)



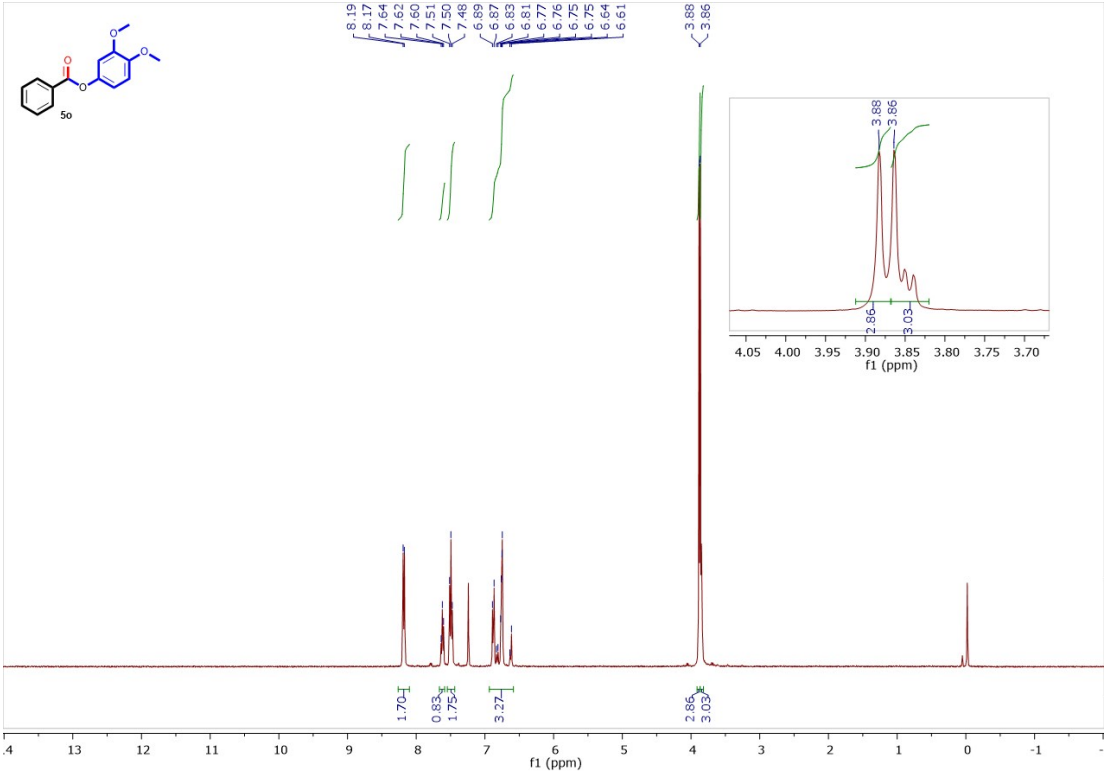
[1,1'-biphenyl]-4-yl benzoate (5n) (^{1}H NMR)



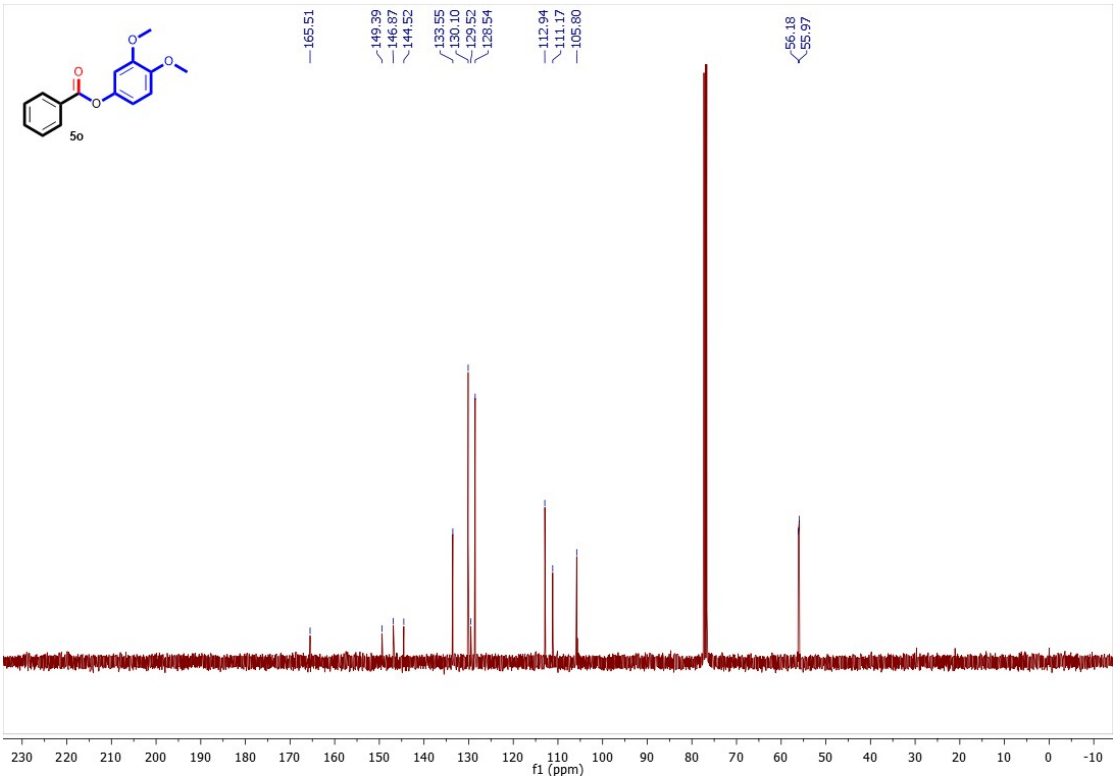
[1,1'-biphenyl]-4-yl benzoate (5n) (^{13}C NMR)



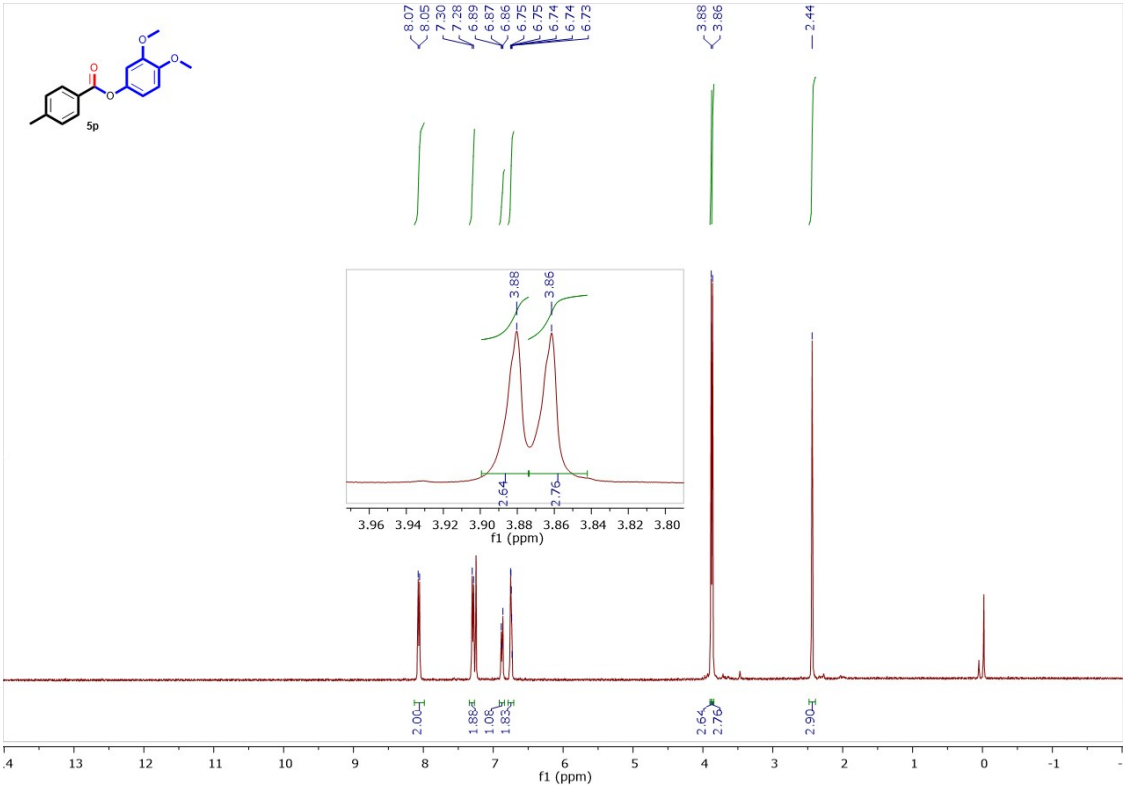
3,4-dimethoxyphenyl benzoate (5o) (^{1}H NMR)



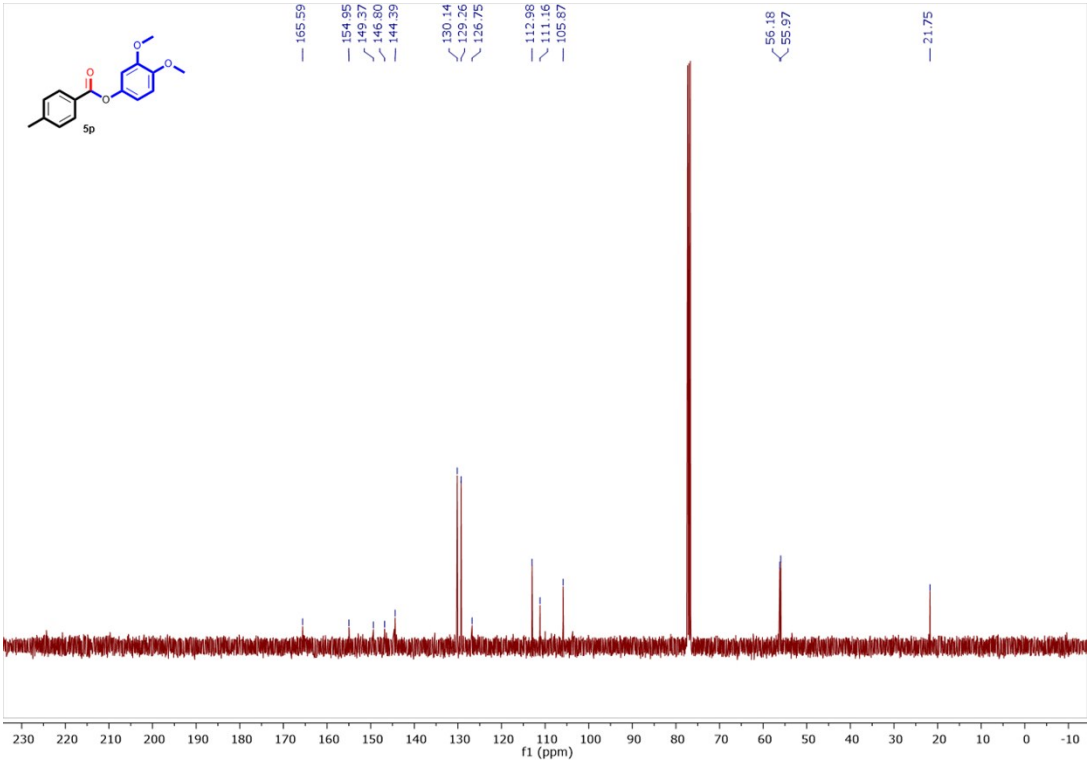
3,4-dimethoxyphenyl benzoate (5o) (^{13}C NMR)



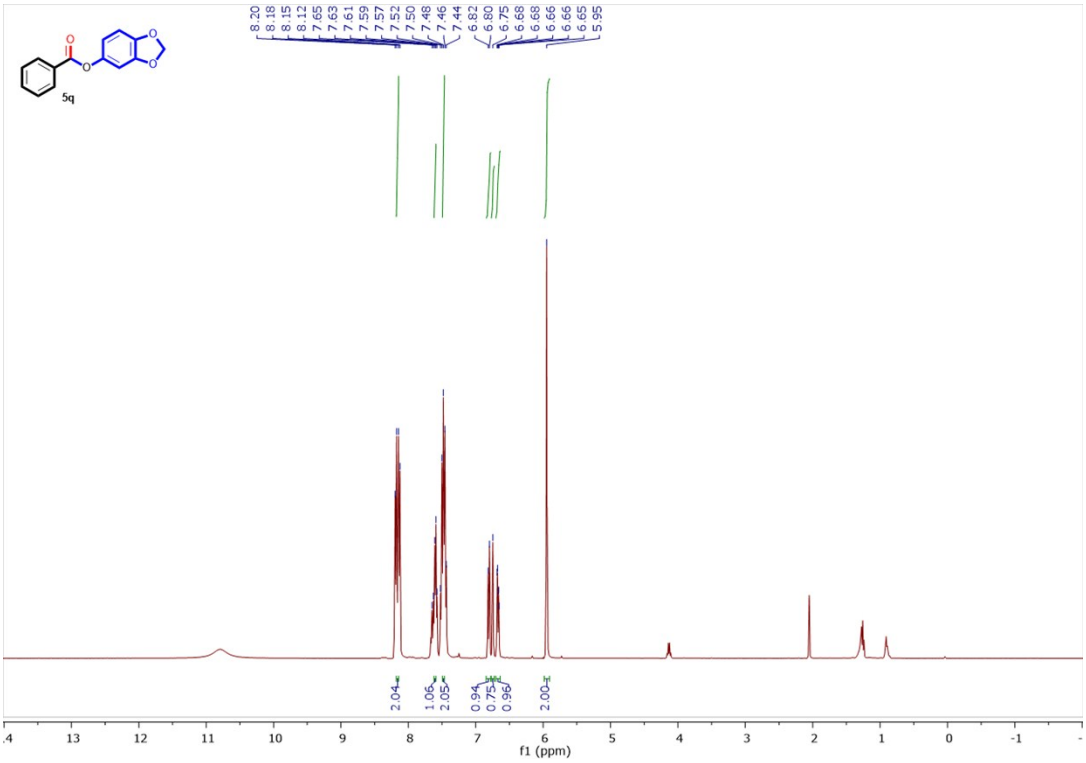
3,4-dimethoxyphenyl 4-methylbenzoate (5p) ^{1}H NMR



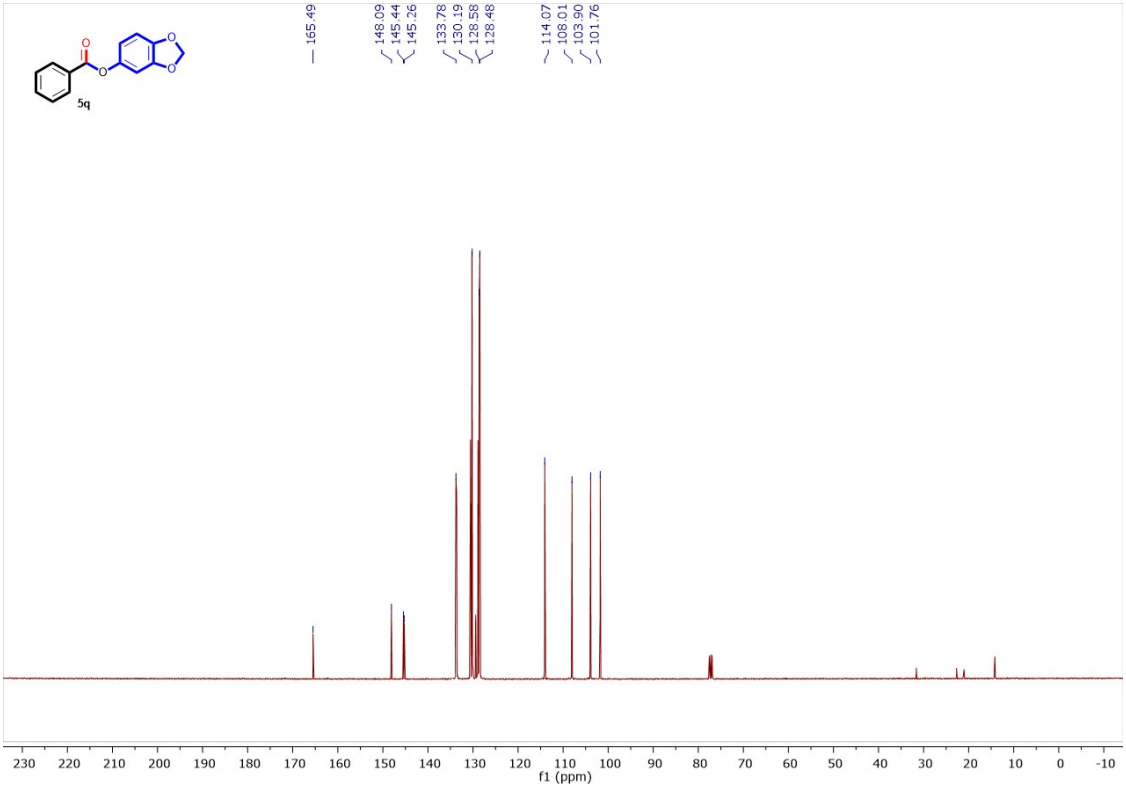
3,4-dimethoxyphenyl 4-methylbenzoate (5p) ^{13}C NMR



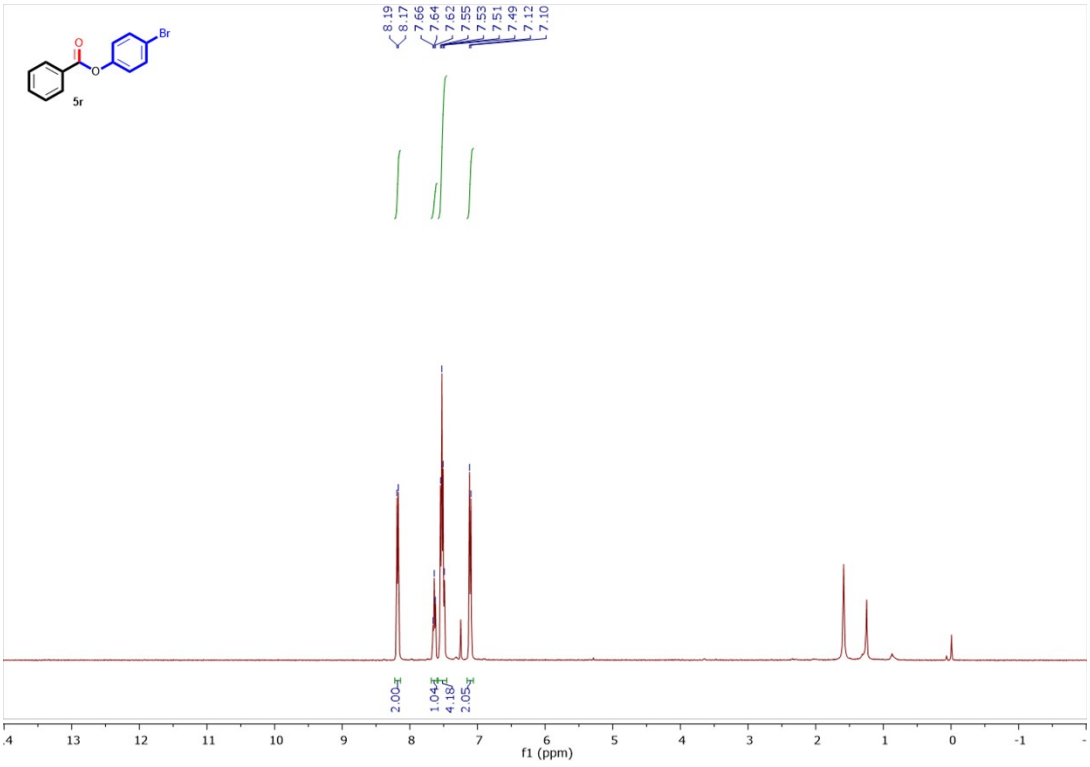
benzo[*d*][1,3]dioxol-5-yl benzoate (5q) ^{1}H NMR



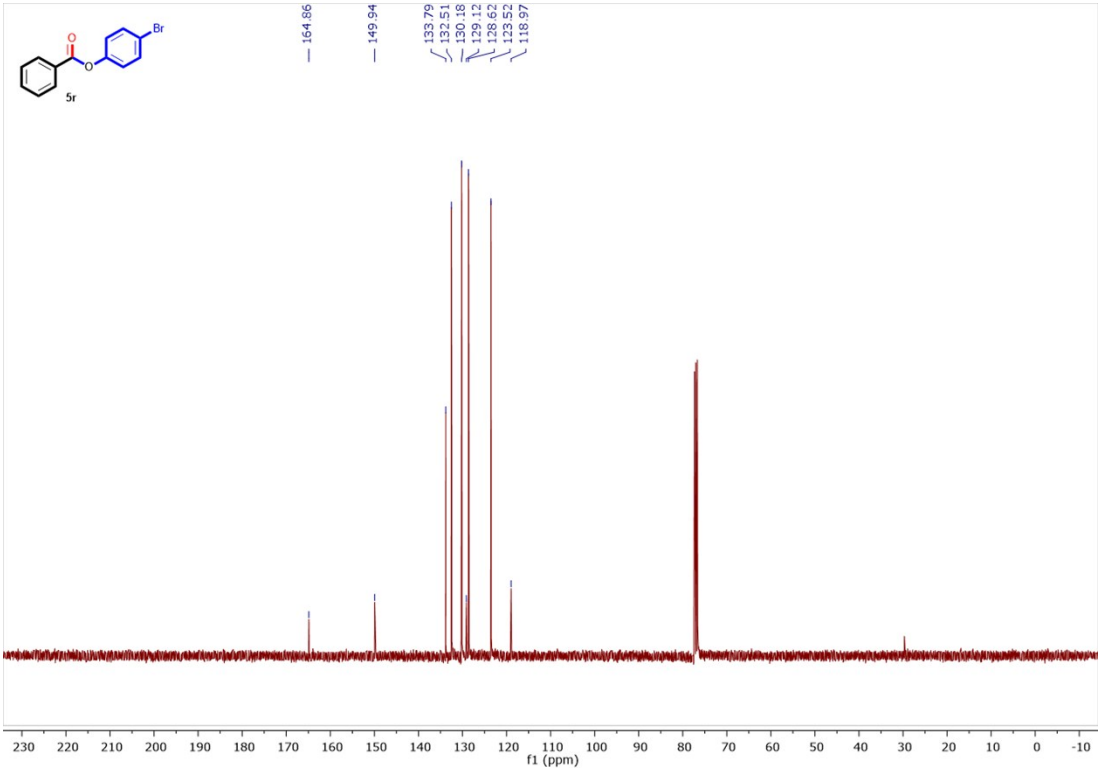
benzo[*d*][1,3]dioxol-5-yl benzoate (5q) ^{13}C NMR



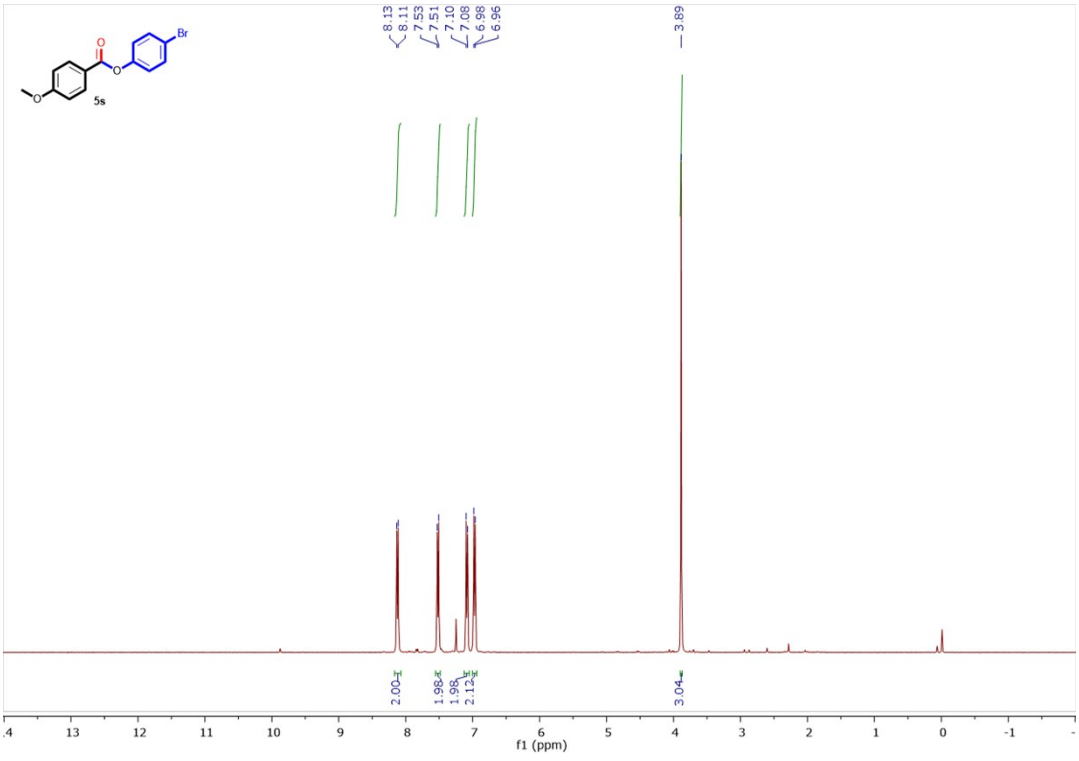
4-bromophenyl benzoate (5r) ^{1}H NMR



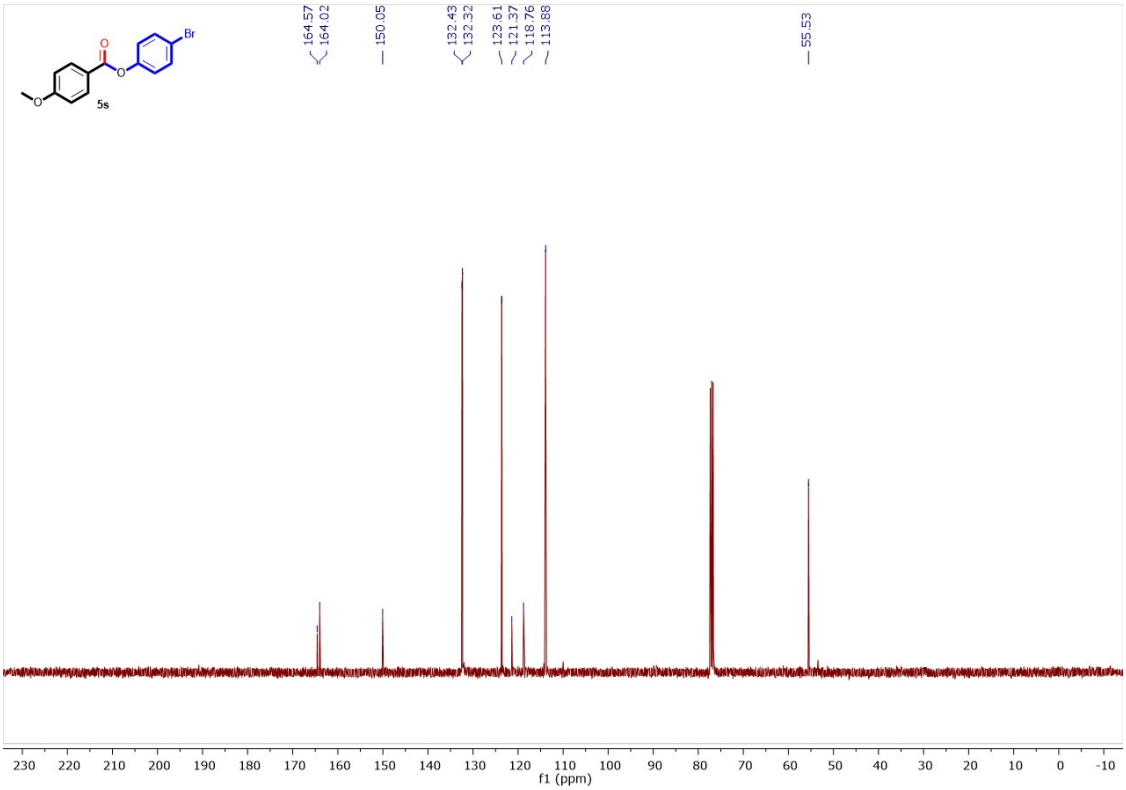
4-bromophenyl benzoate (5r) ^{13}C NMR



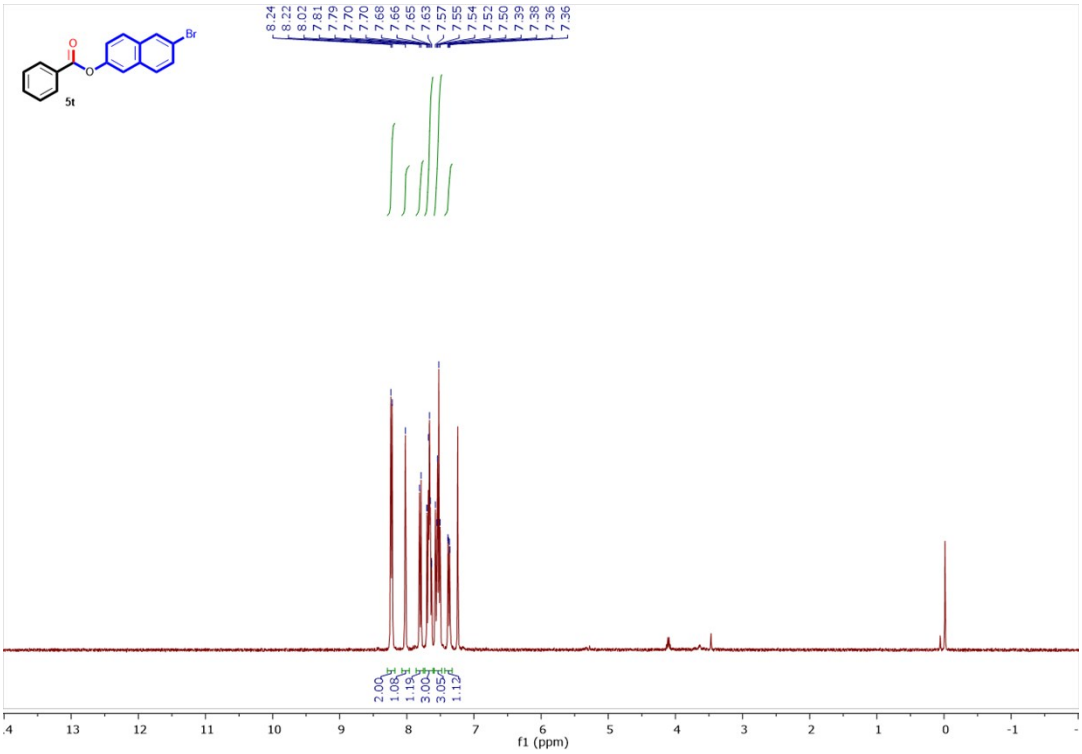
4-bromophenyl 4-methoxybenzoate (5s) ^{1}H NMR



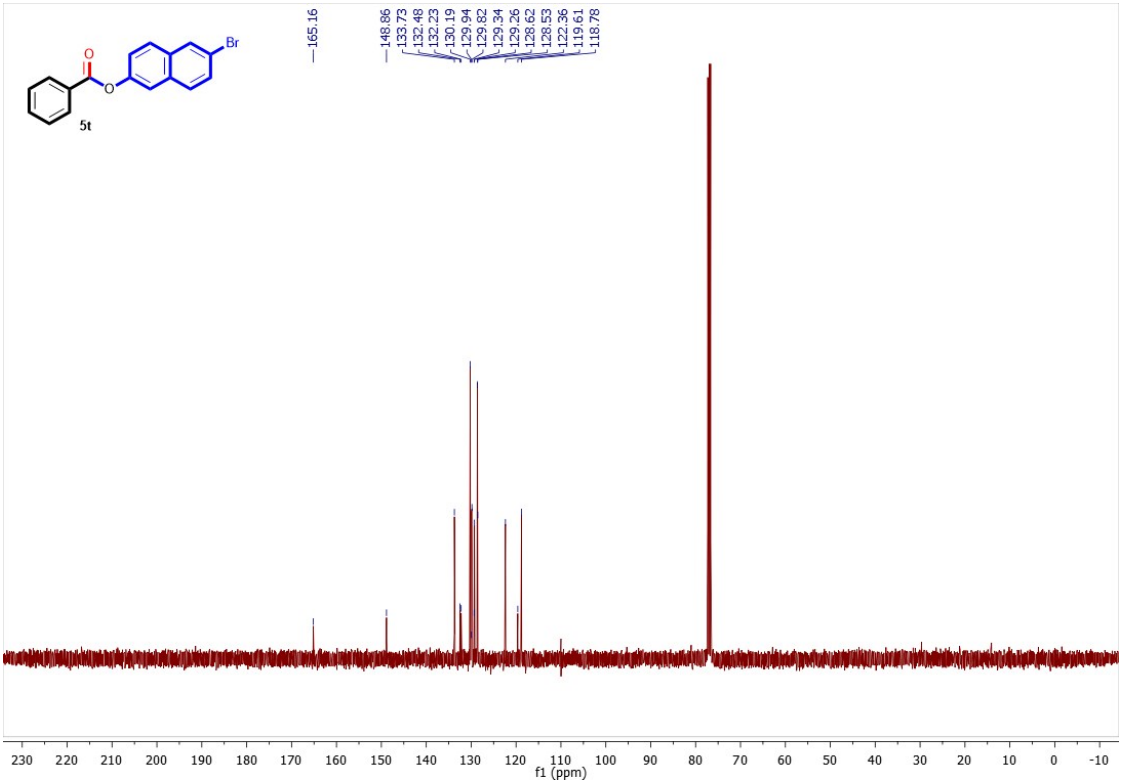
4-bromophenyl 4-methoxybenzoate (5s) ^{13}C NMR



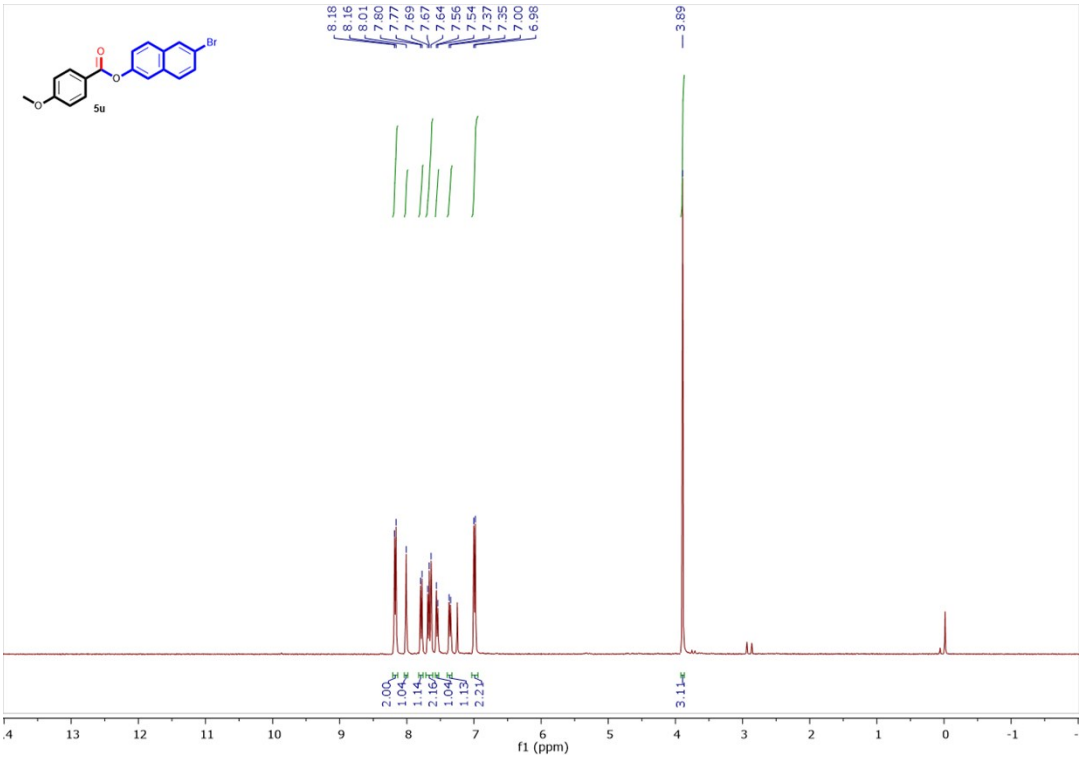
6-bromonaphthalen-2-yl benzoate (5t) ^{1}H NMR



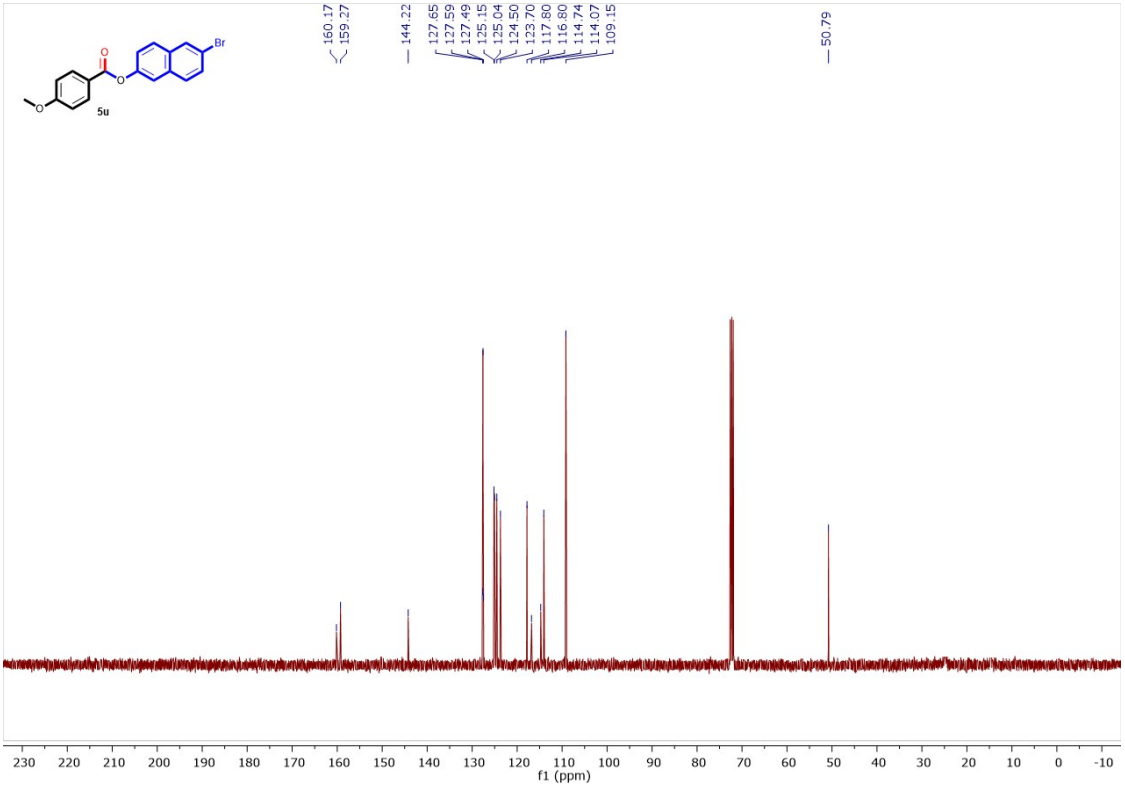
6-bromonaphthalen-2-yl benzoate (5t) ^{13}C NMR



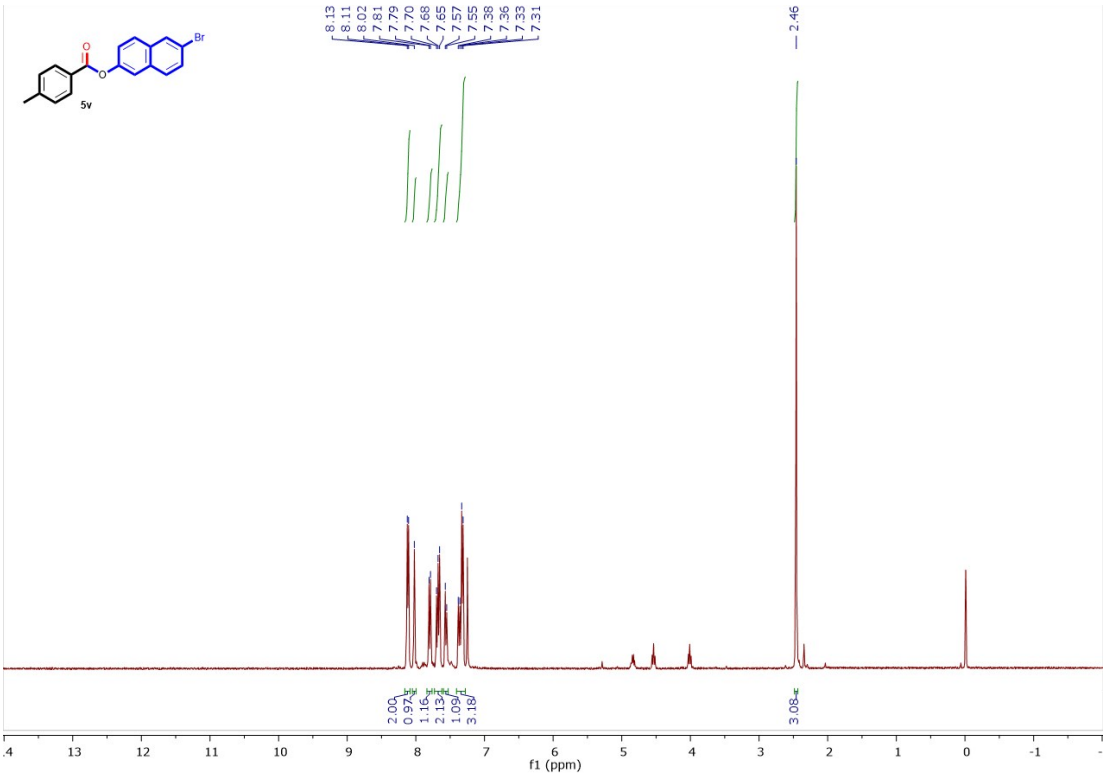
6-bromonaphthalen-2-yl 4-methoxybenzoate (5u) ^{1}H NMR



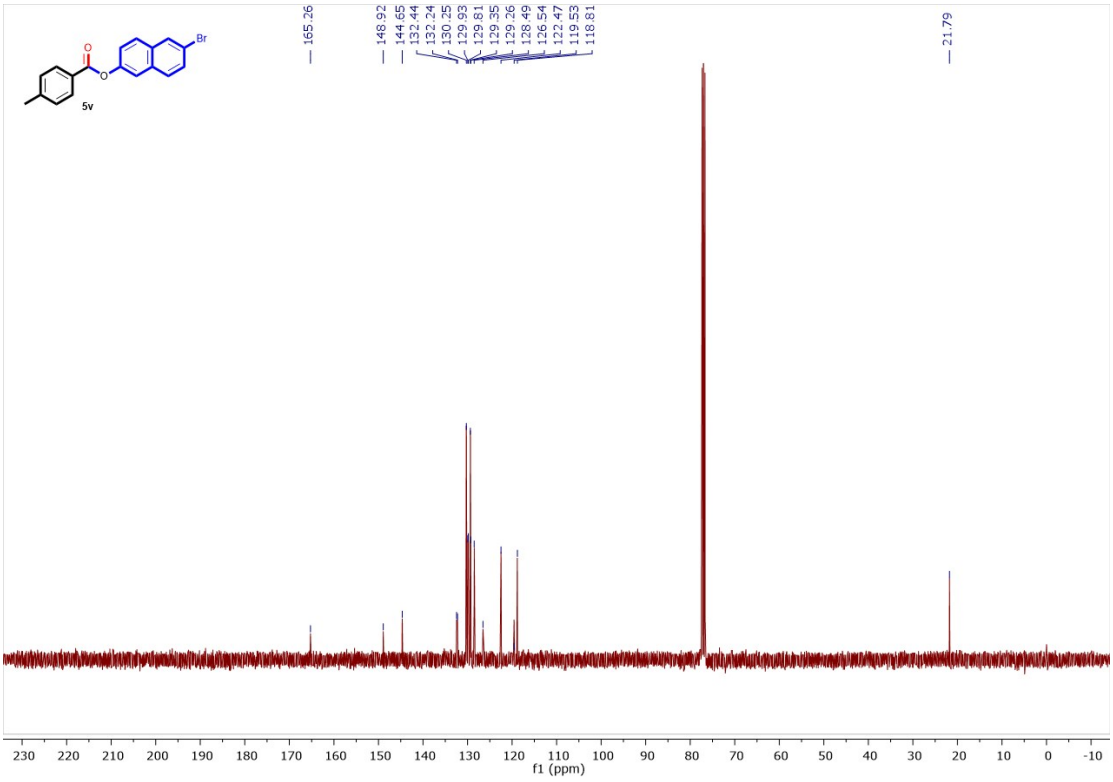
6-bromonaphthalen-2-yl 4-methoxybenzoate (5u) ^{13}C NMR



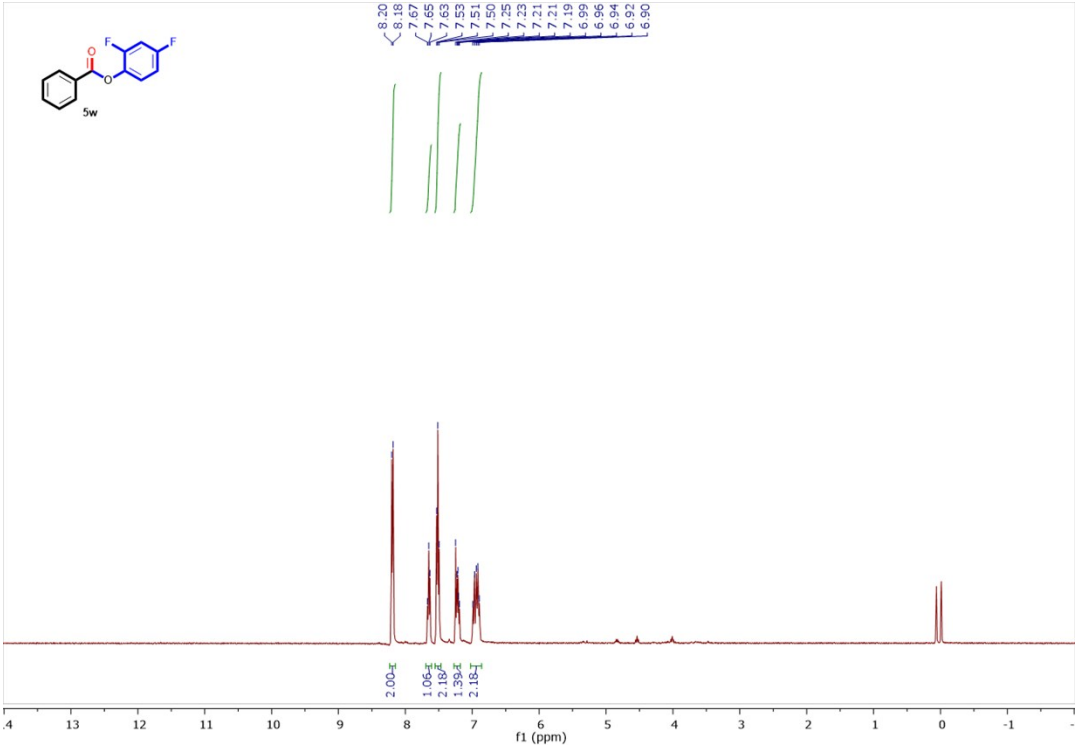
6-bromonaphthalen-2-yl 4-methylbenzoate (5v) ^{1}H NMR



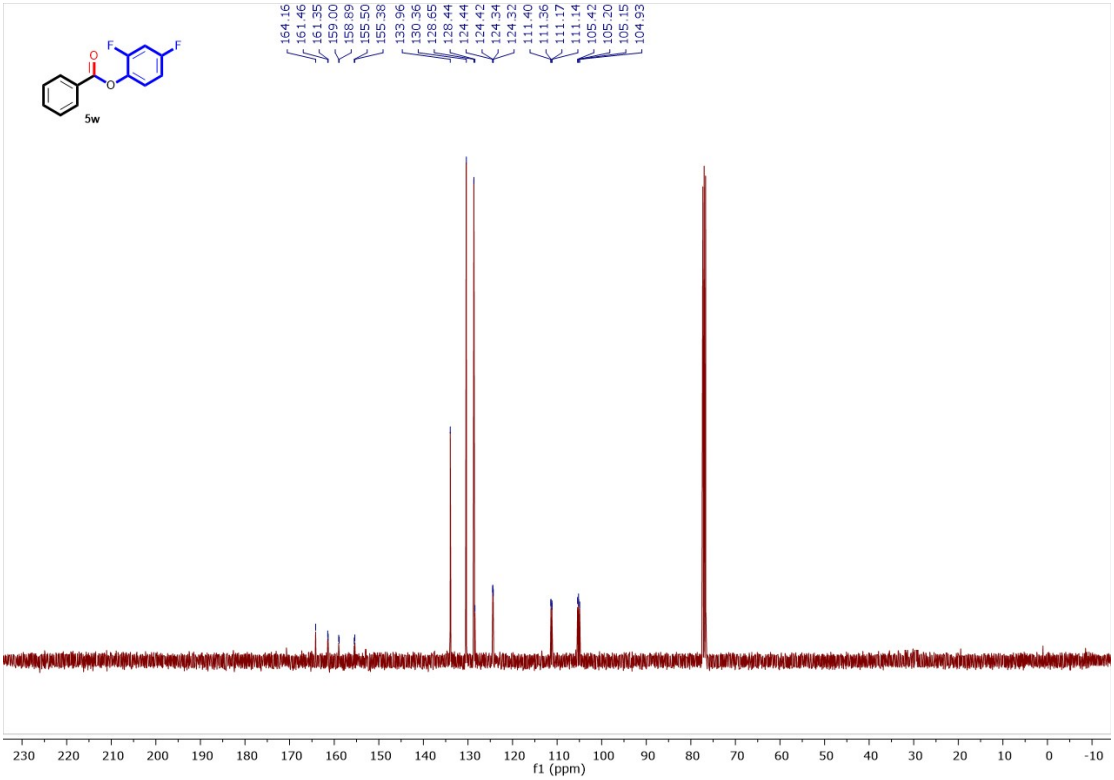
6-bromonaphthalen-2-yl 4-methylbenzoate (5v) ^{13}C NMR



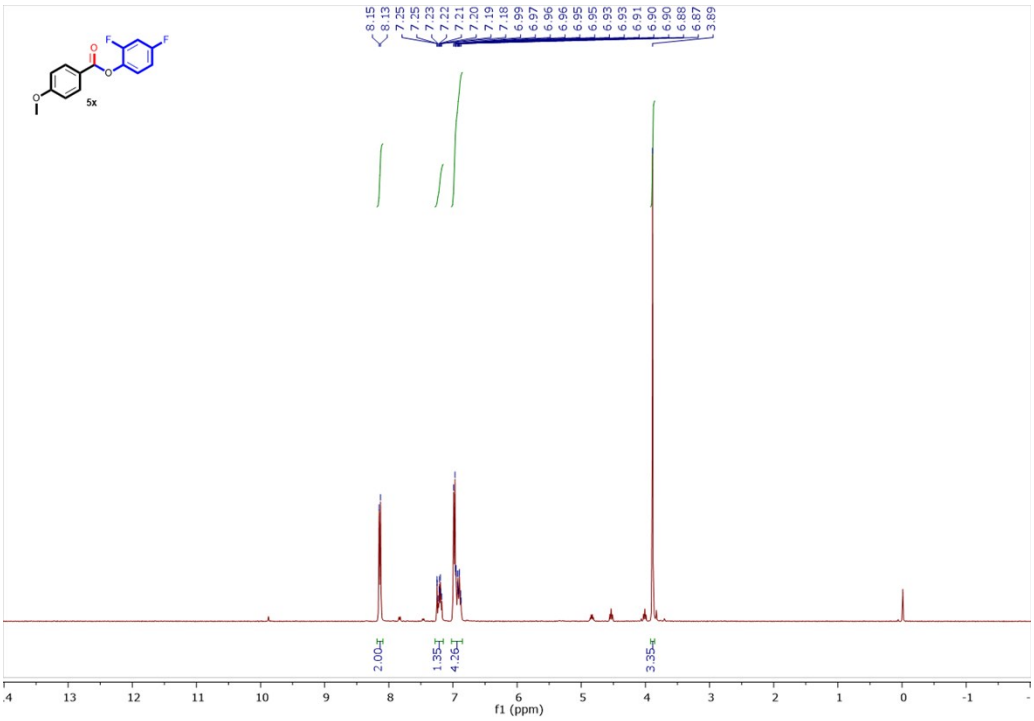
2,4-difluorophenyl benzoate (5w) ^{1}H NMR



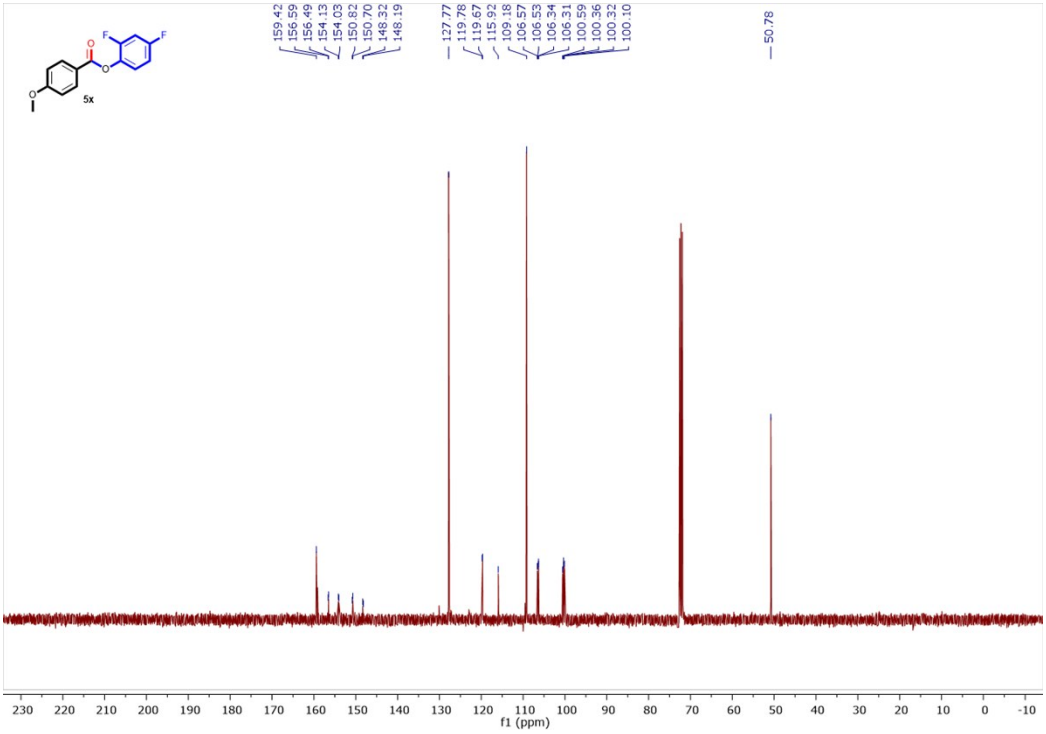
2,4-difluorophenyl benzoate (5w) ^{13}C NMR



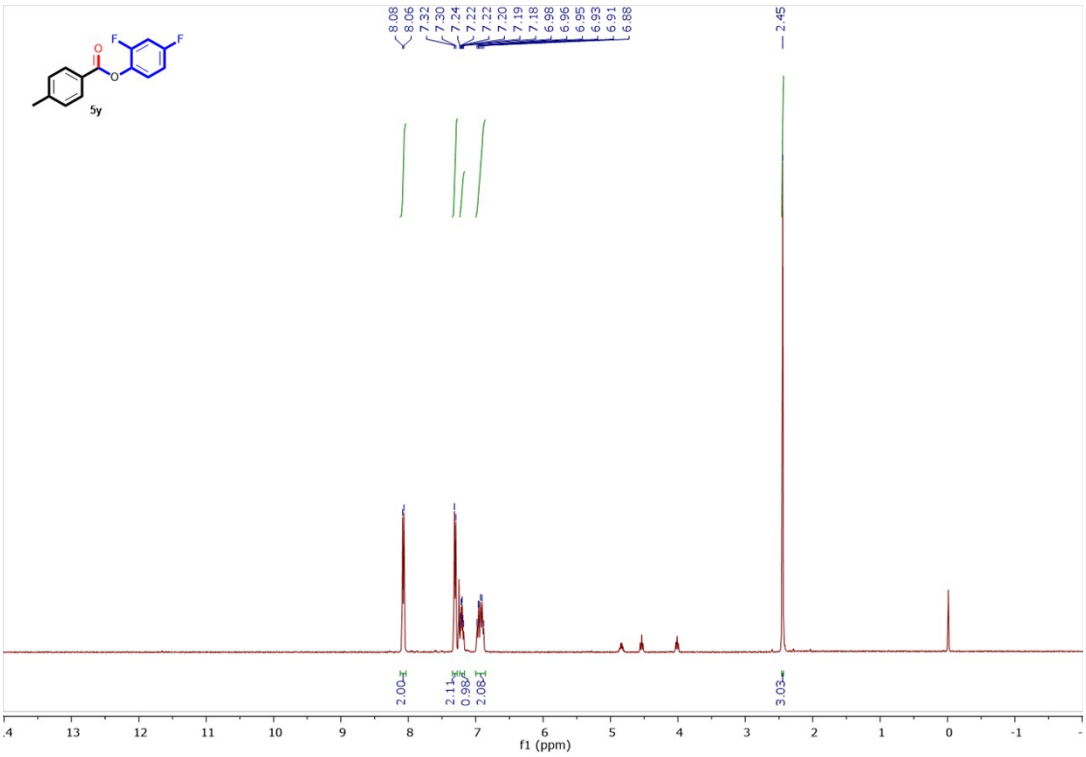
2,4-difluorophenyl 4-methoxybenzoate (5x) ^{1}H NMR



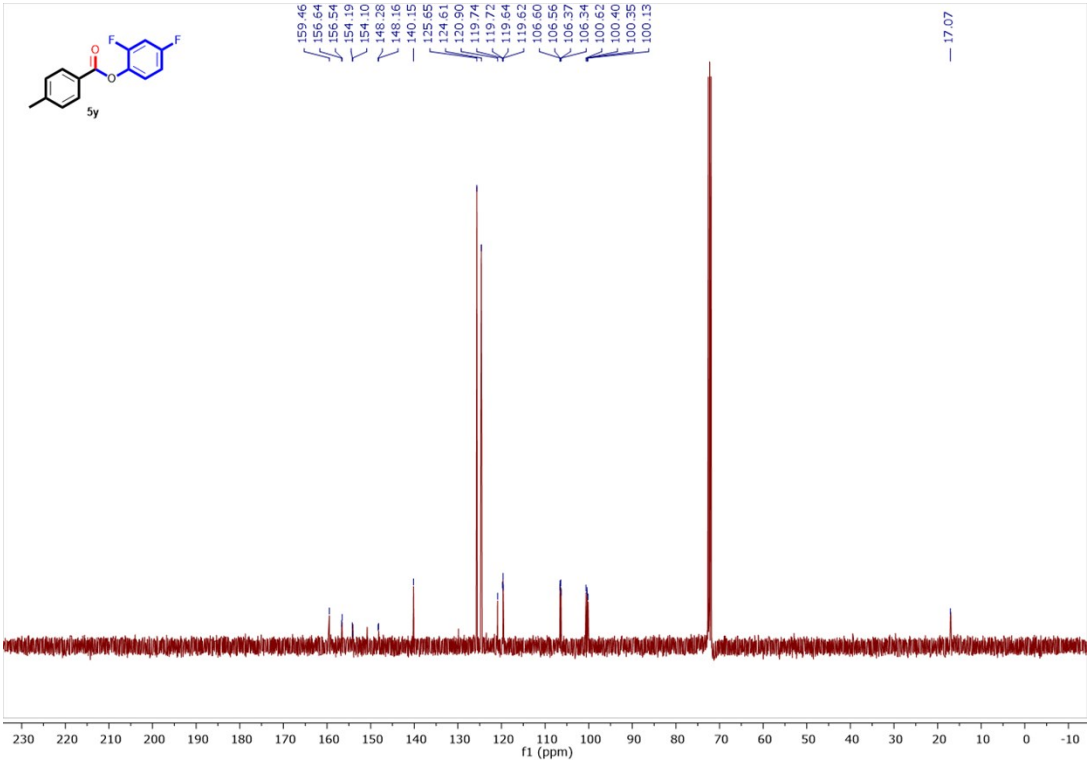
2,4-difluorophenyl 4-methoxybenzoate (5x) ^{13}C NMR



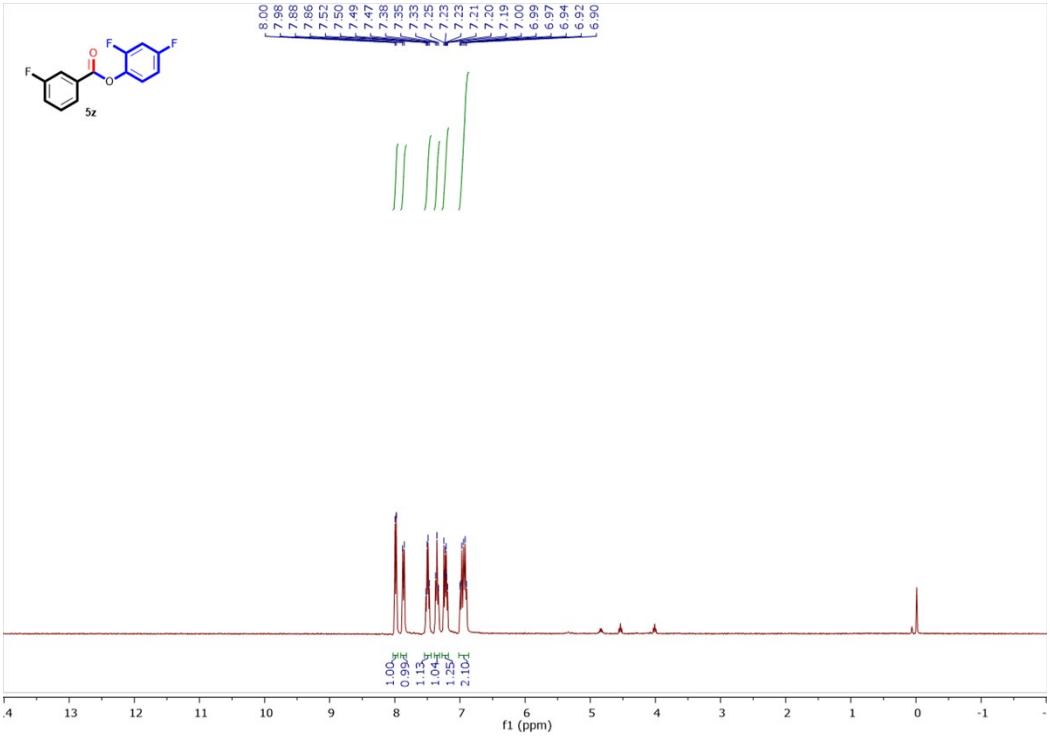
2,4-difluorophenyl 4-methylbenzoate (5y) ^{1}H NMR



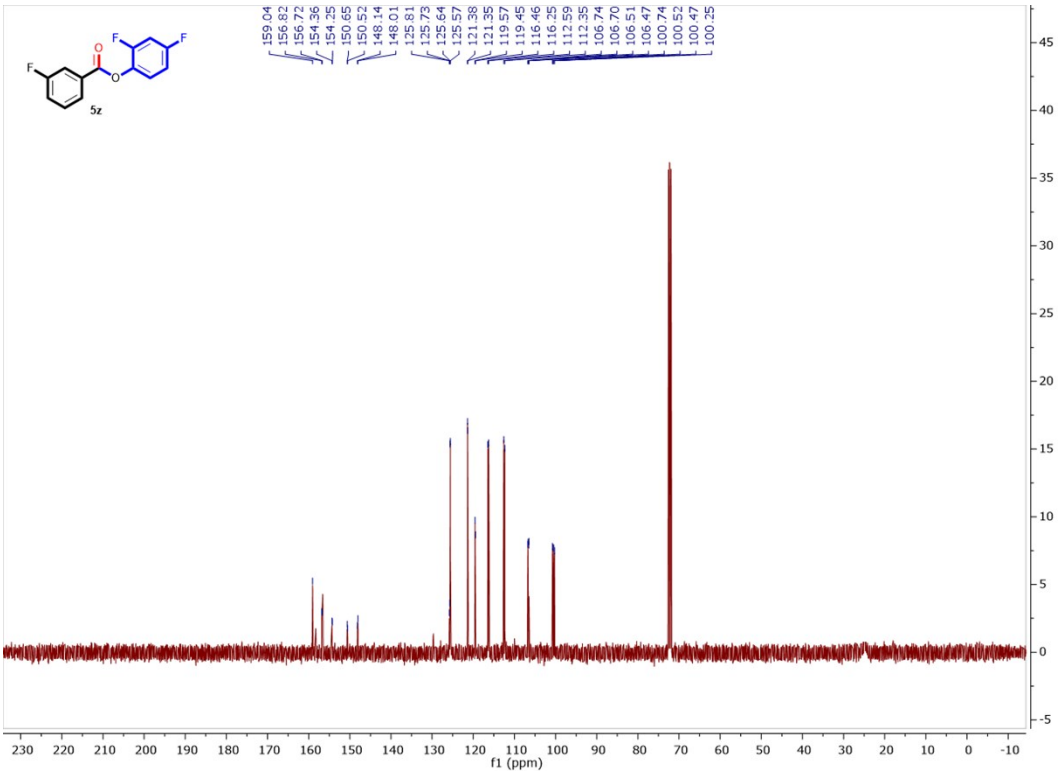
2,4-difluorophenyl 4-methylbenzoate (5y) ^{13}C NMR



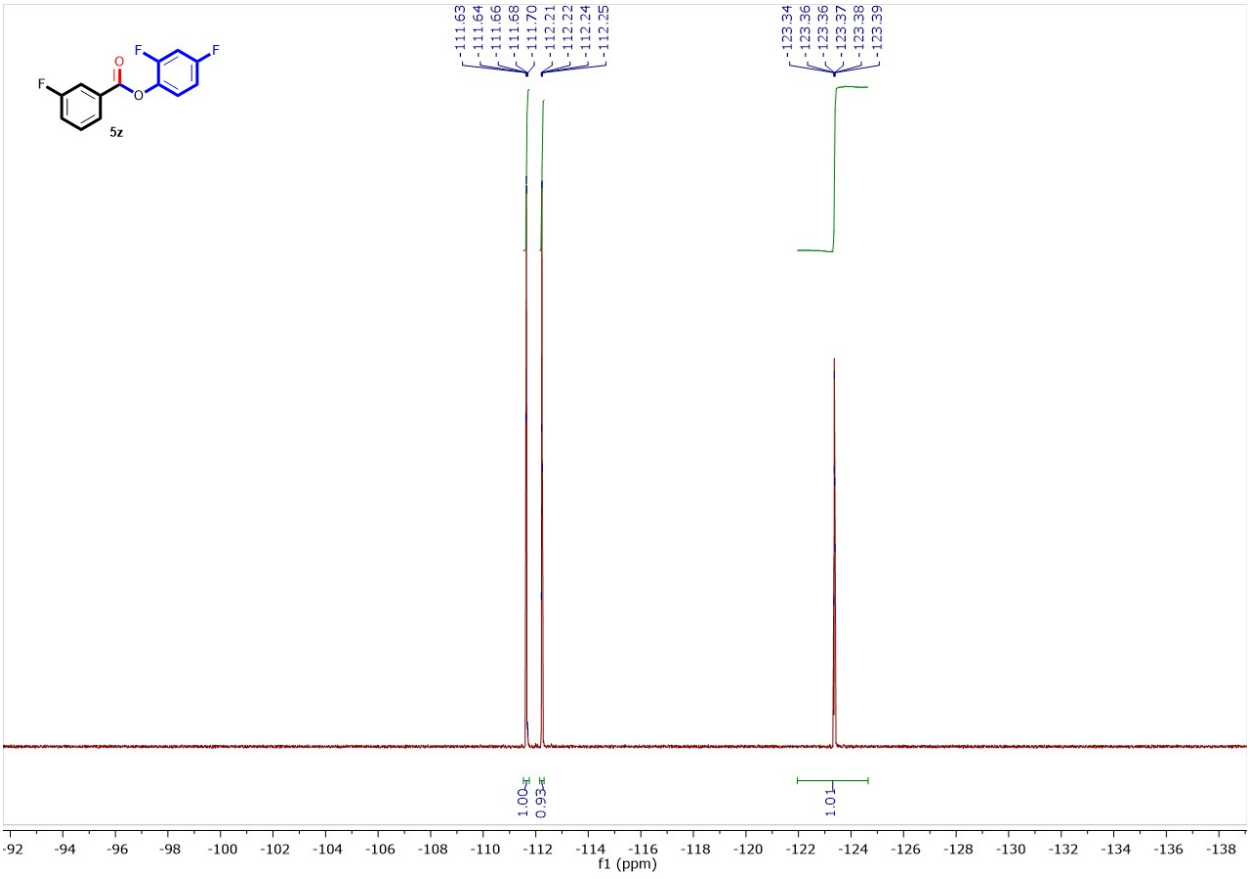
2,4-difluorophenyl 3-fluorobenzoate (5z) ^{1}H NMR



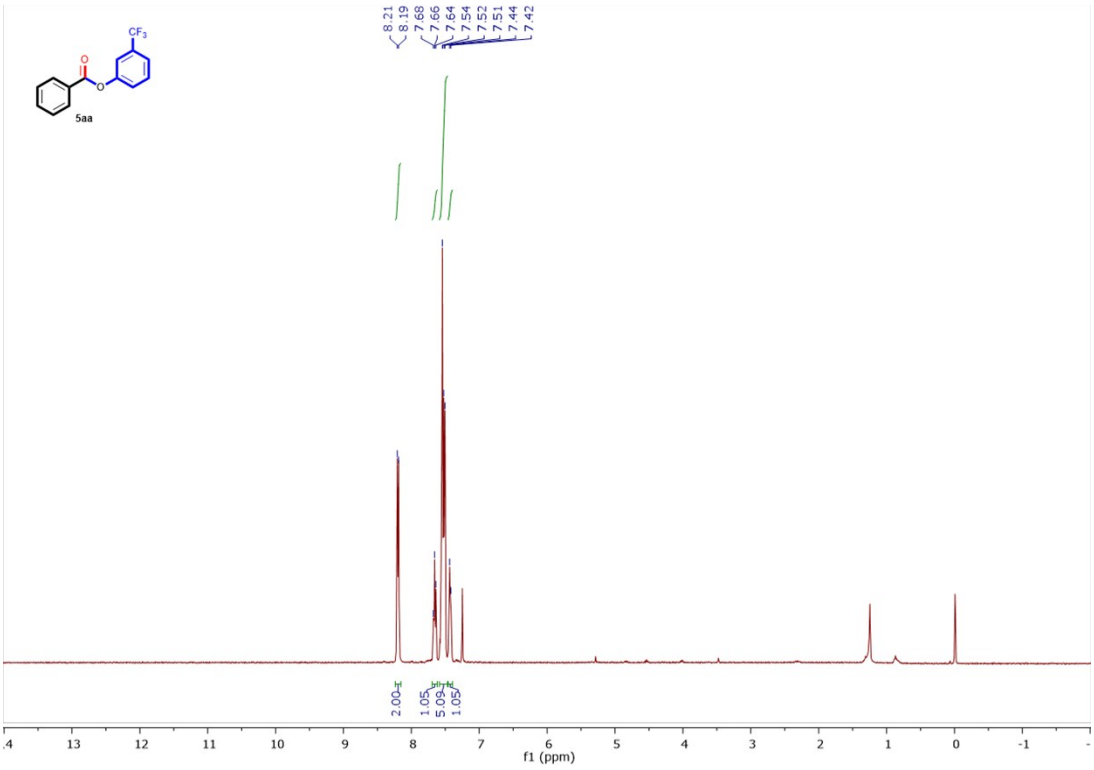
2,4-difluorophenyl 3-fluorobenzoate (5z) ^{13}C NMR



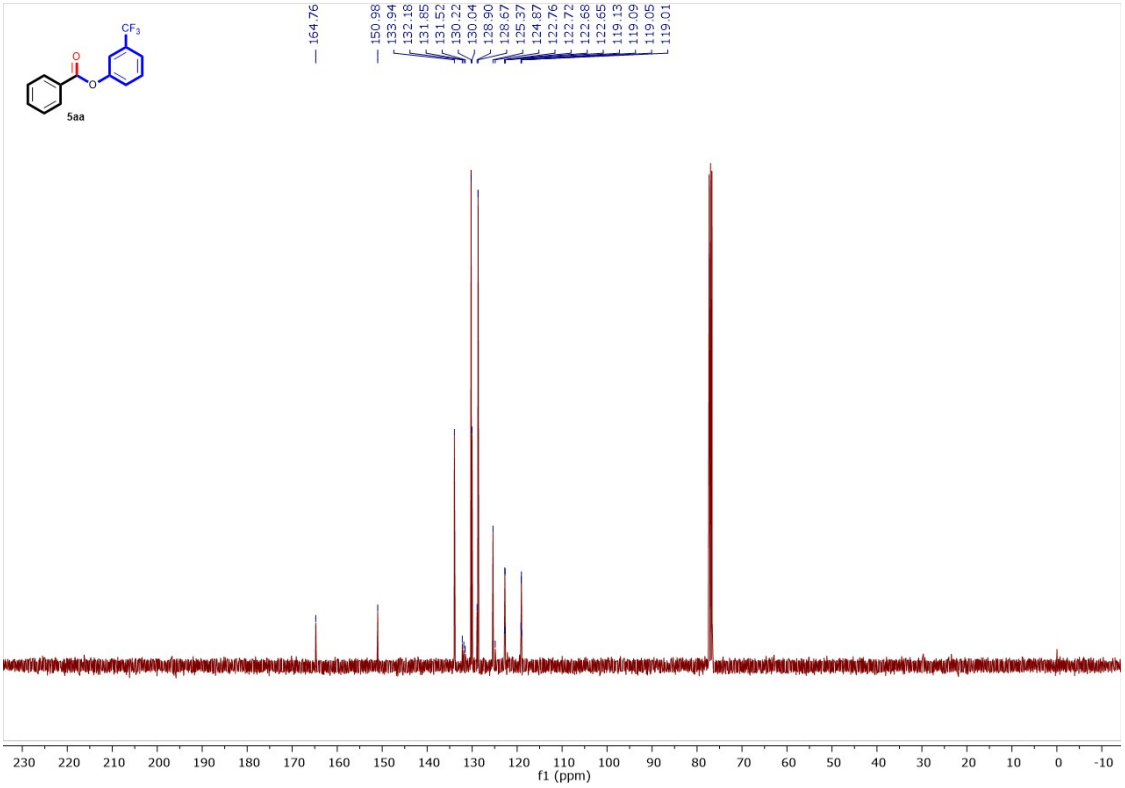
2,4-difluorophenyl 3-fluorobenzoate (5z) ^{19}F NMR



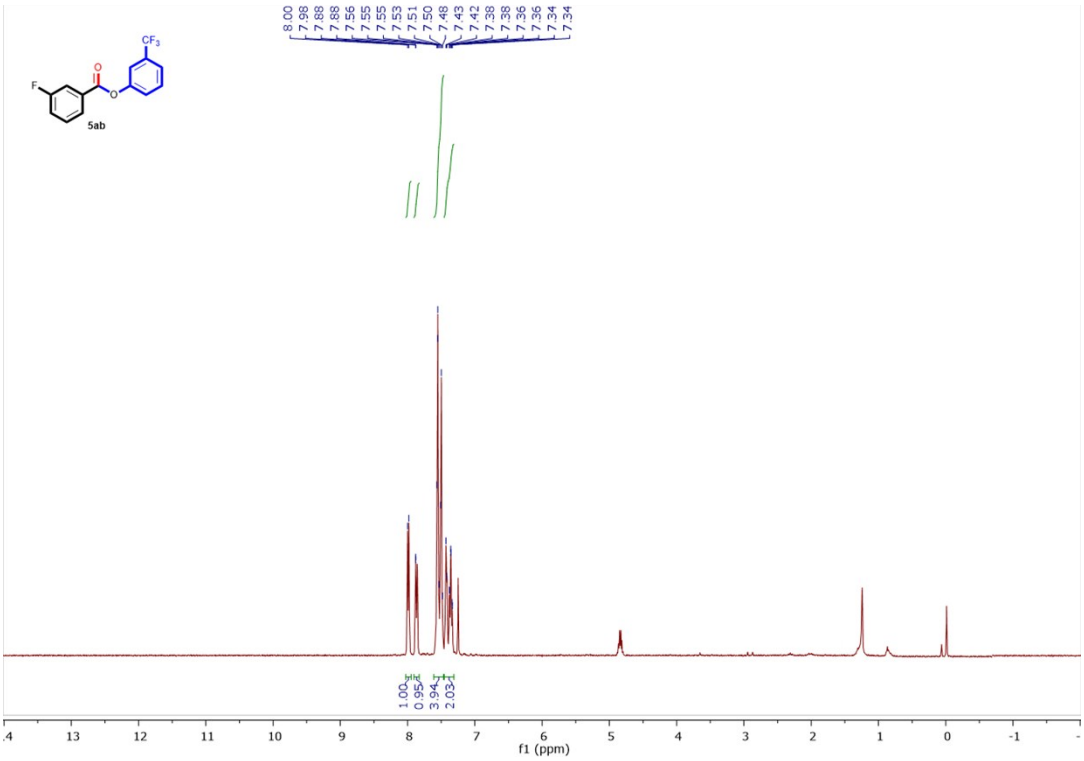
3-(trifluoromethyl)phenyl benzoate (5aa) ^{1}H NMR



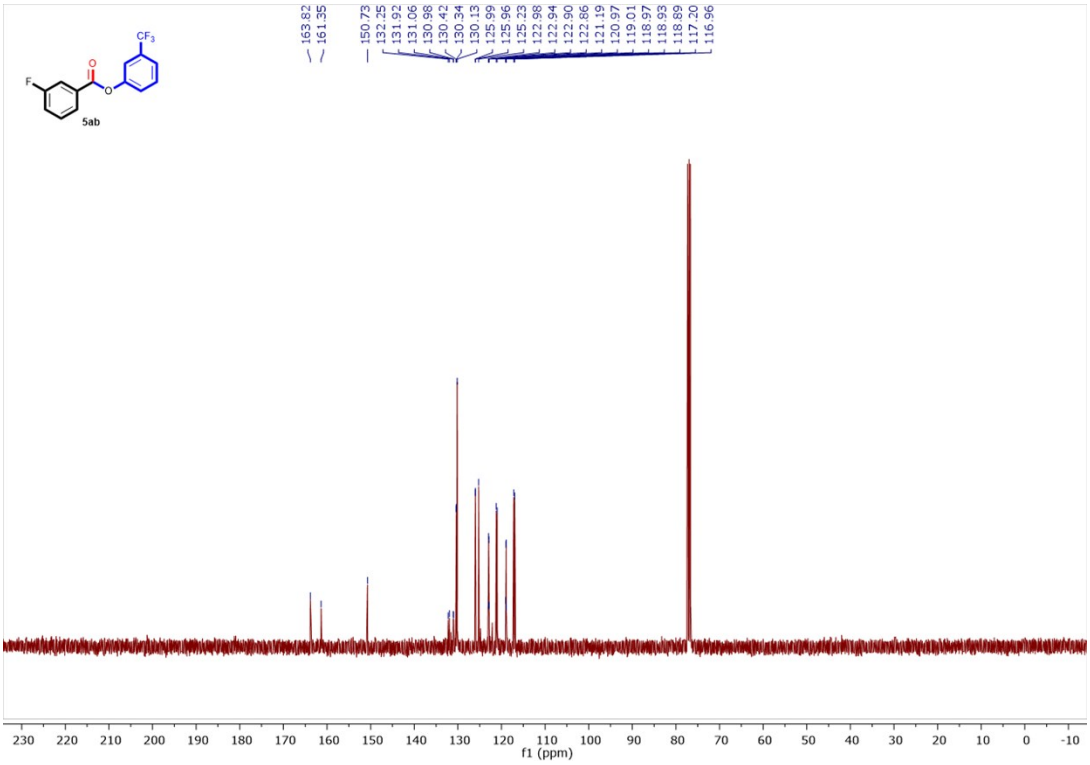
3-(trifluoromethyl)phenyl benzoate (5aa) ^{13}C NMR



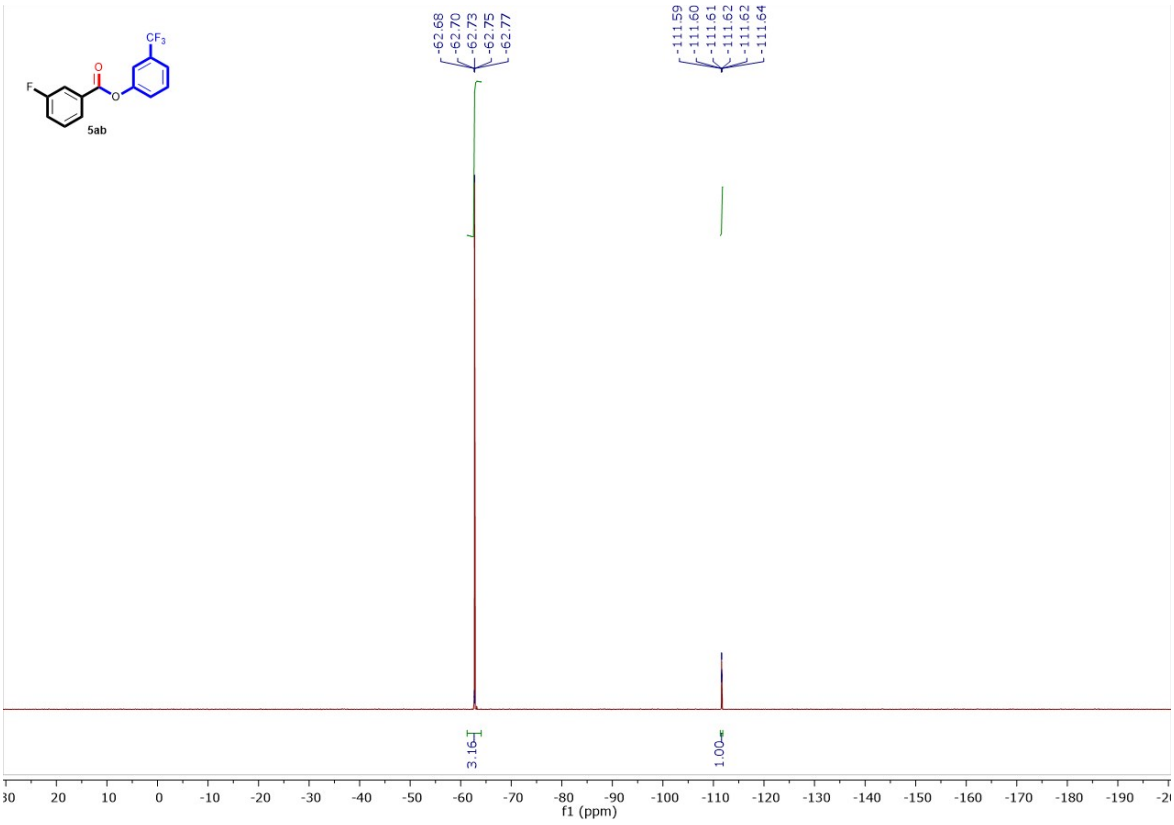
3-(trifluoromethyl)phenyl 3-fluorobenzoate (5ab) ^{1}H NMR



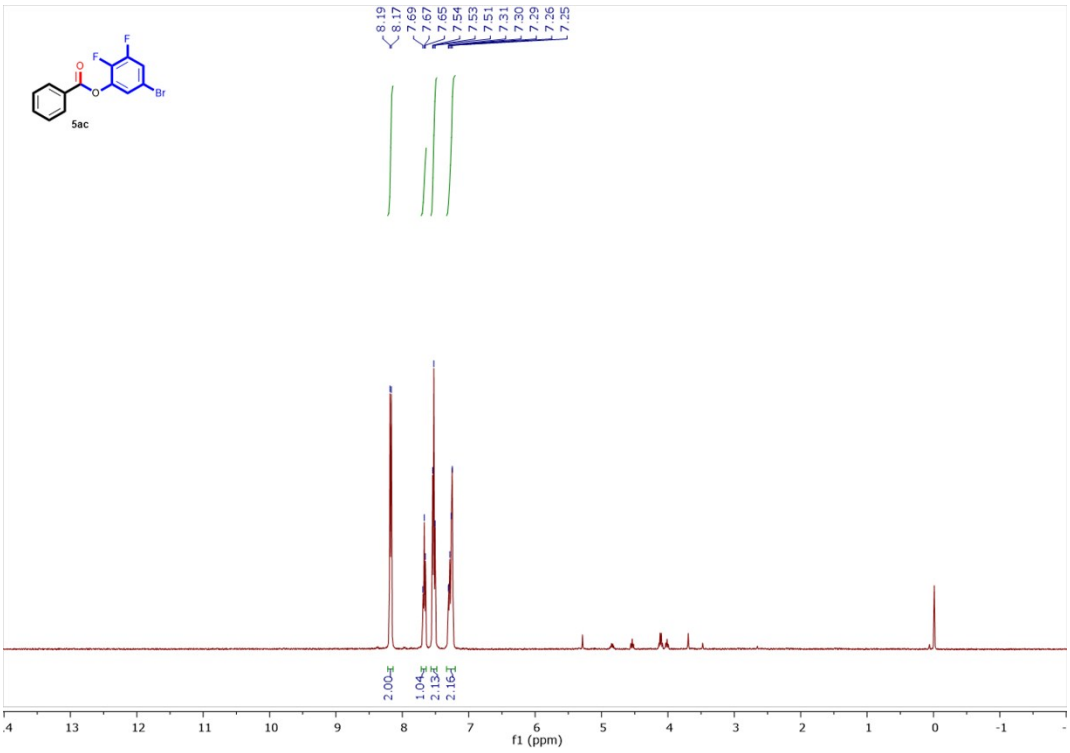
3-(trifluoromethyl)phenyl 3-fluorobenzoate (5ab) ^{13}C NMR



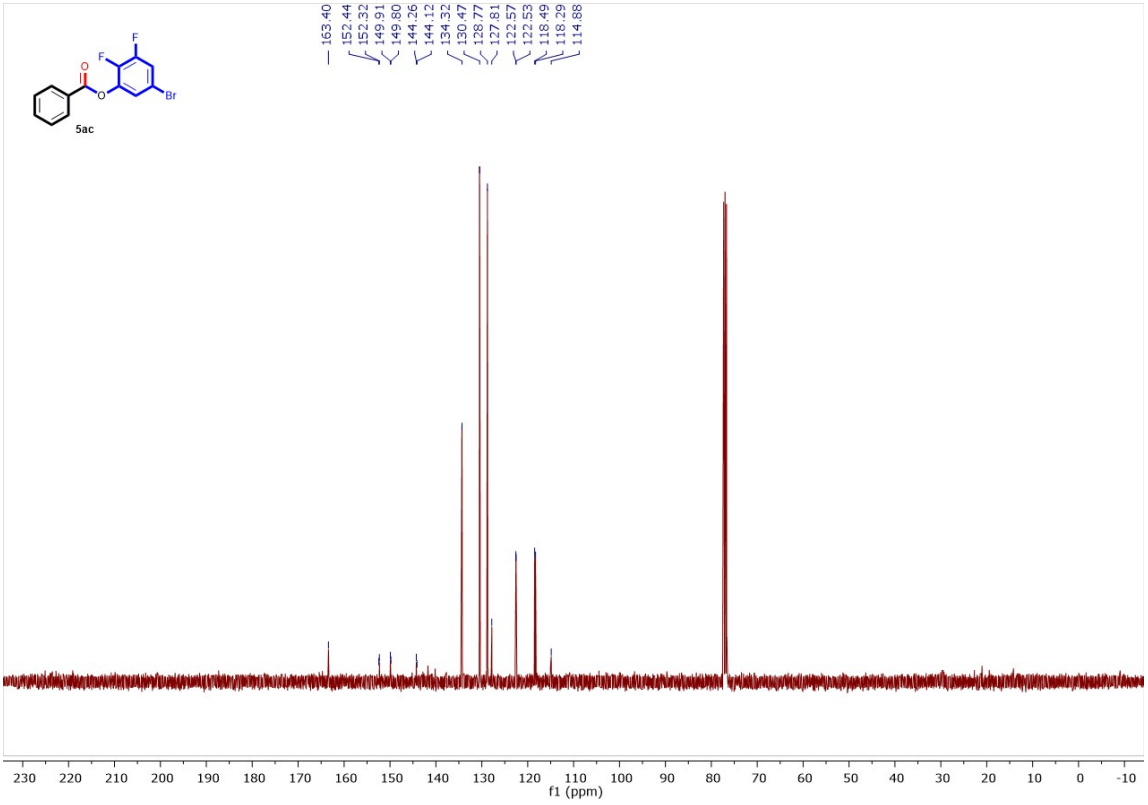
3-(trifluoromethyl)phenyl 3-fluorobenzoate (5ab) ^{19}F NMR



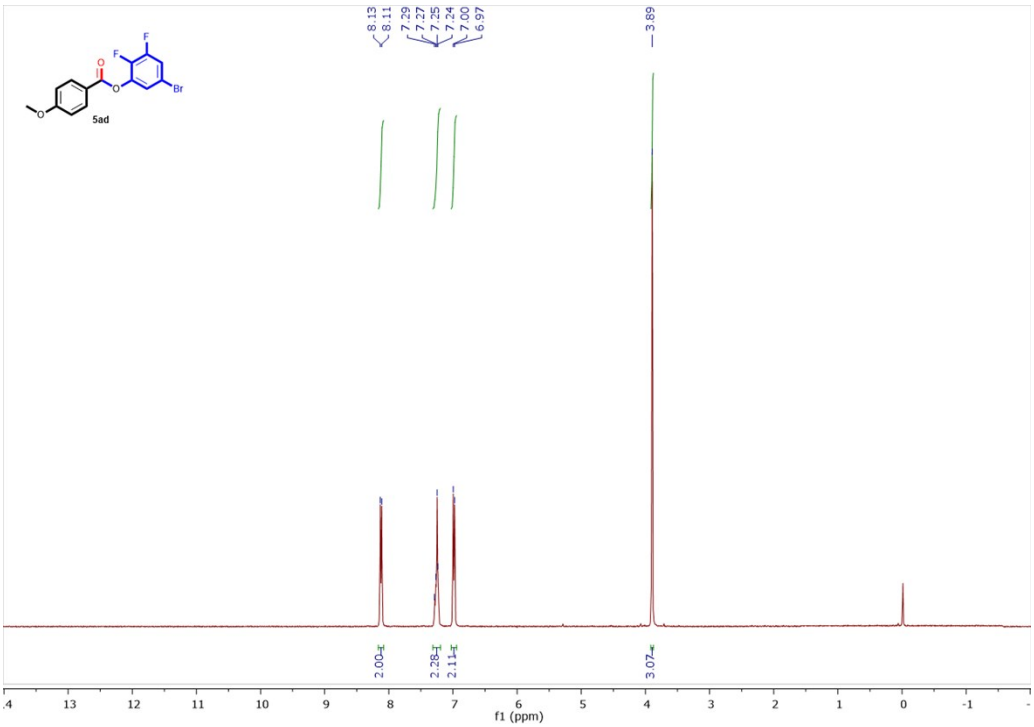
5-bromo-2,3-difluorophenyl benzoate (5ac) ^{1}H NMR



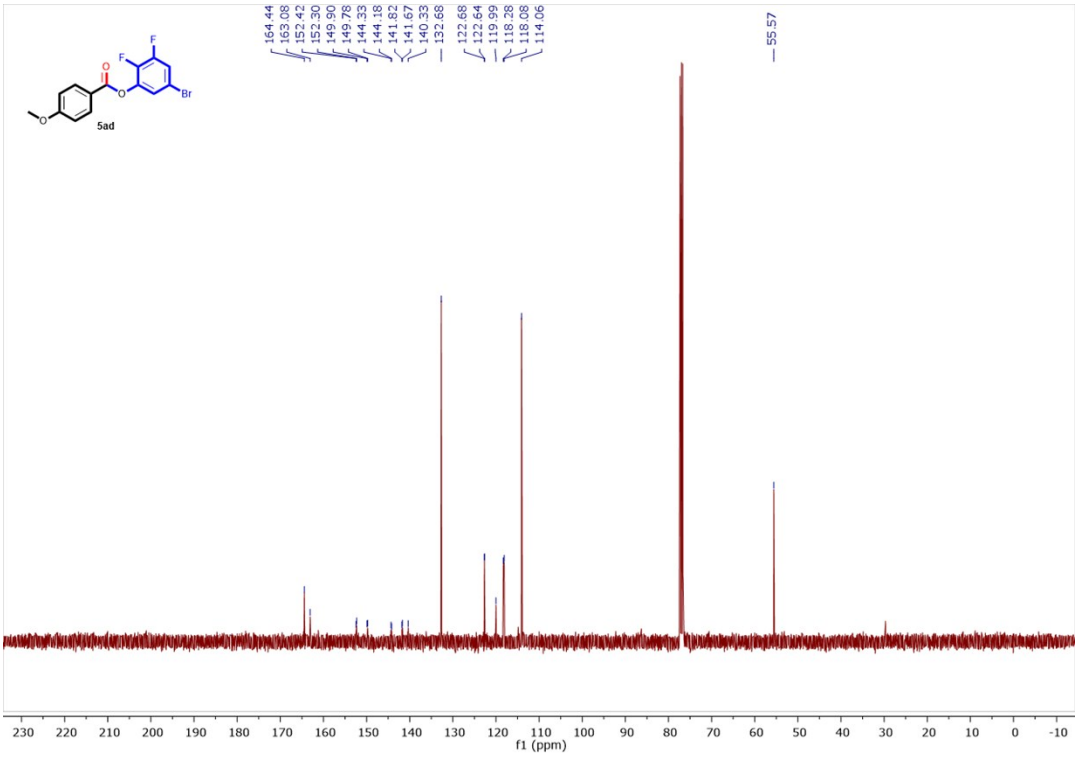
5-bromo-2,3-difluorophenyl benzoate (5ac) ^{13}C NMR



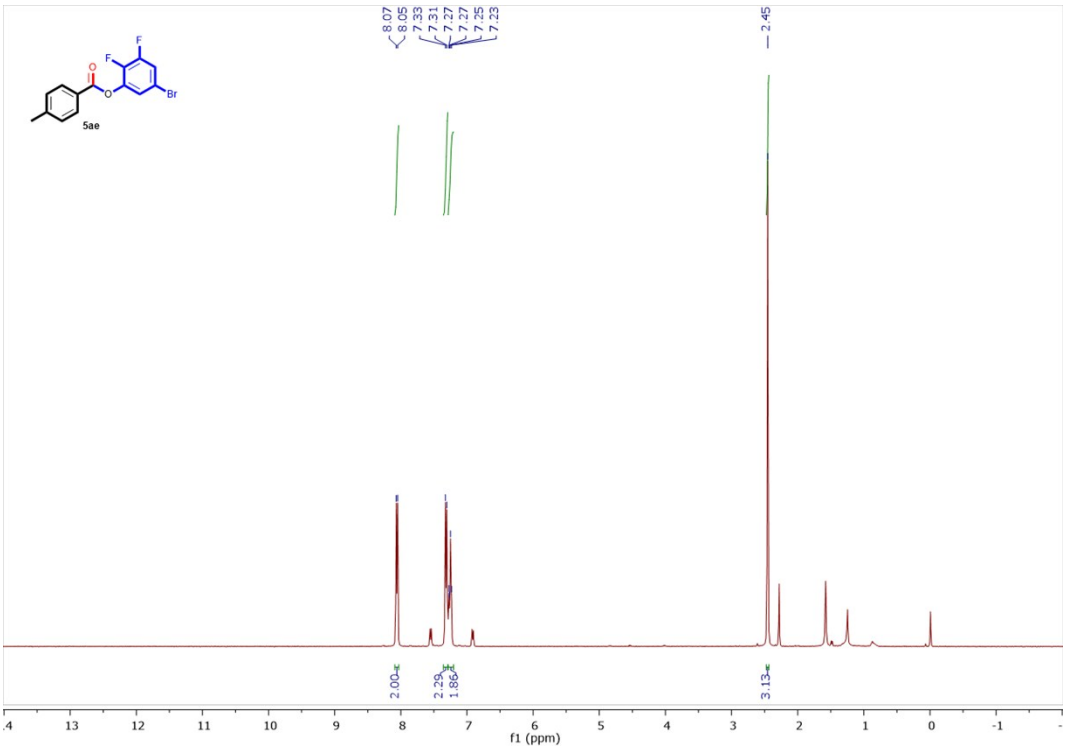
5-bromo-2,3-difluorophenyl 4-methoxybenzoate (5ad) ^{1}H NMR



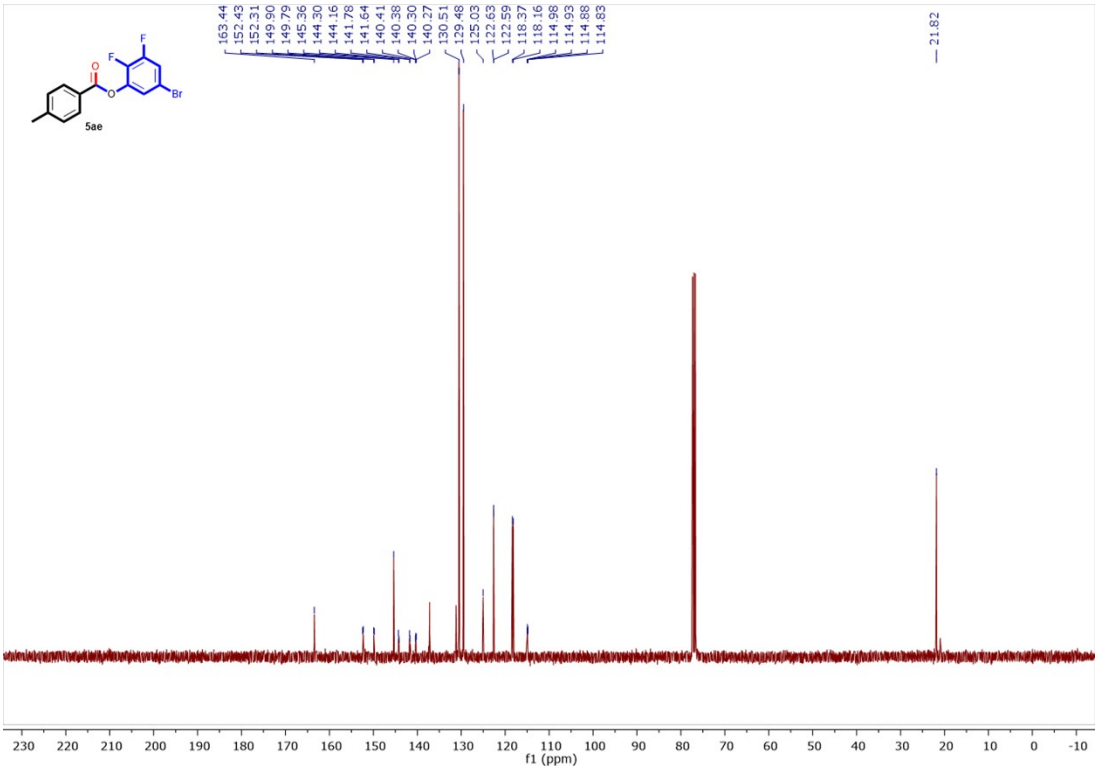
5-bromo-2,3-difluorophenyl 4-methoxybenzoate (5ad) ^{13}C NMR



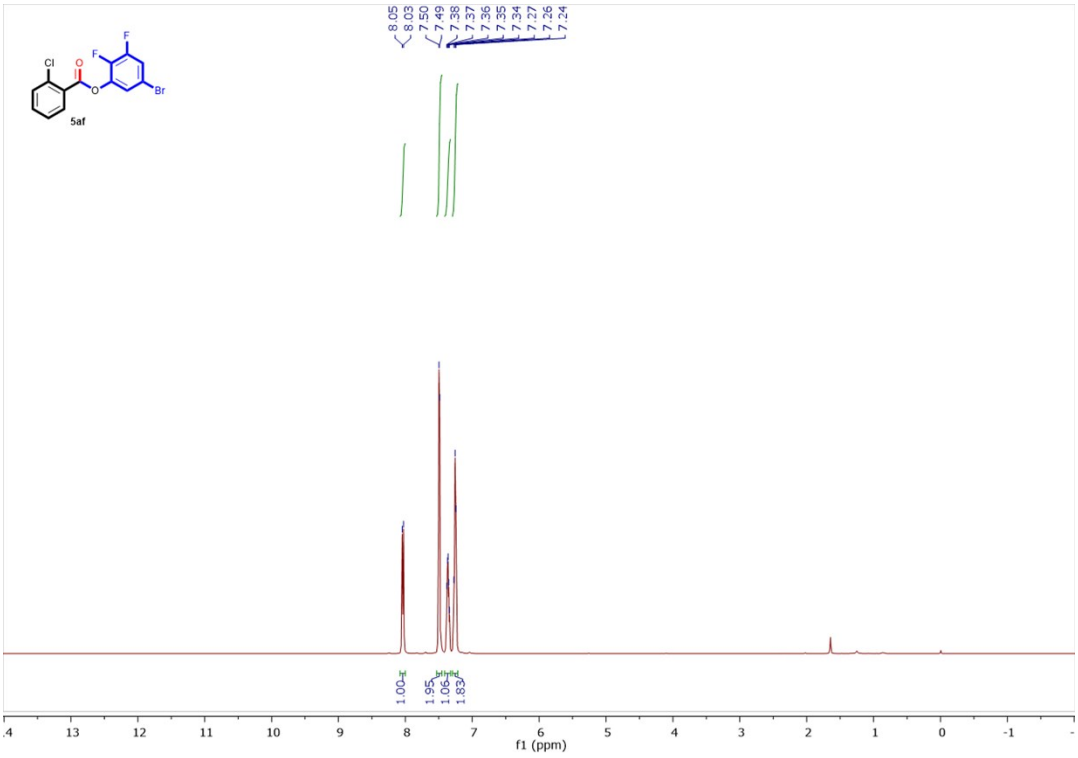
5-bromo-2,3-difluorophenyl 4-methylbenzoate (5ae) ^{1}H NMR



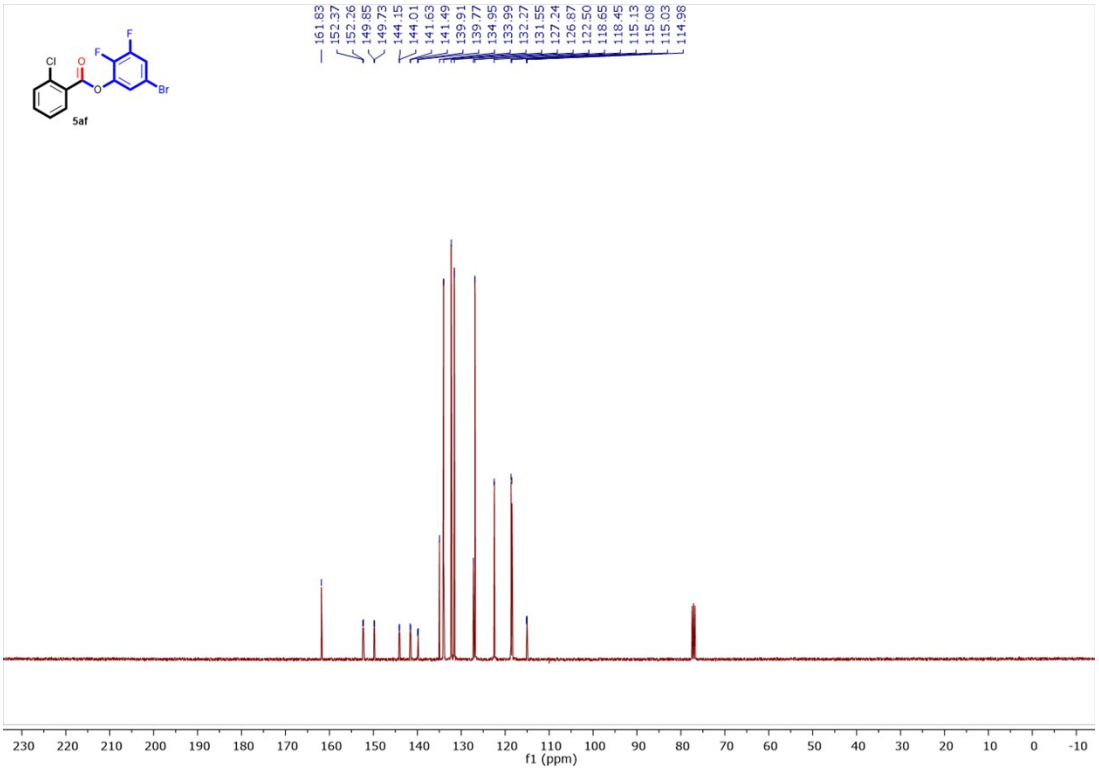
5-bromo-2,3-difluorophenyl 4-methylbenzoate (5ae) ^{13}C NMR



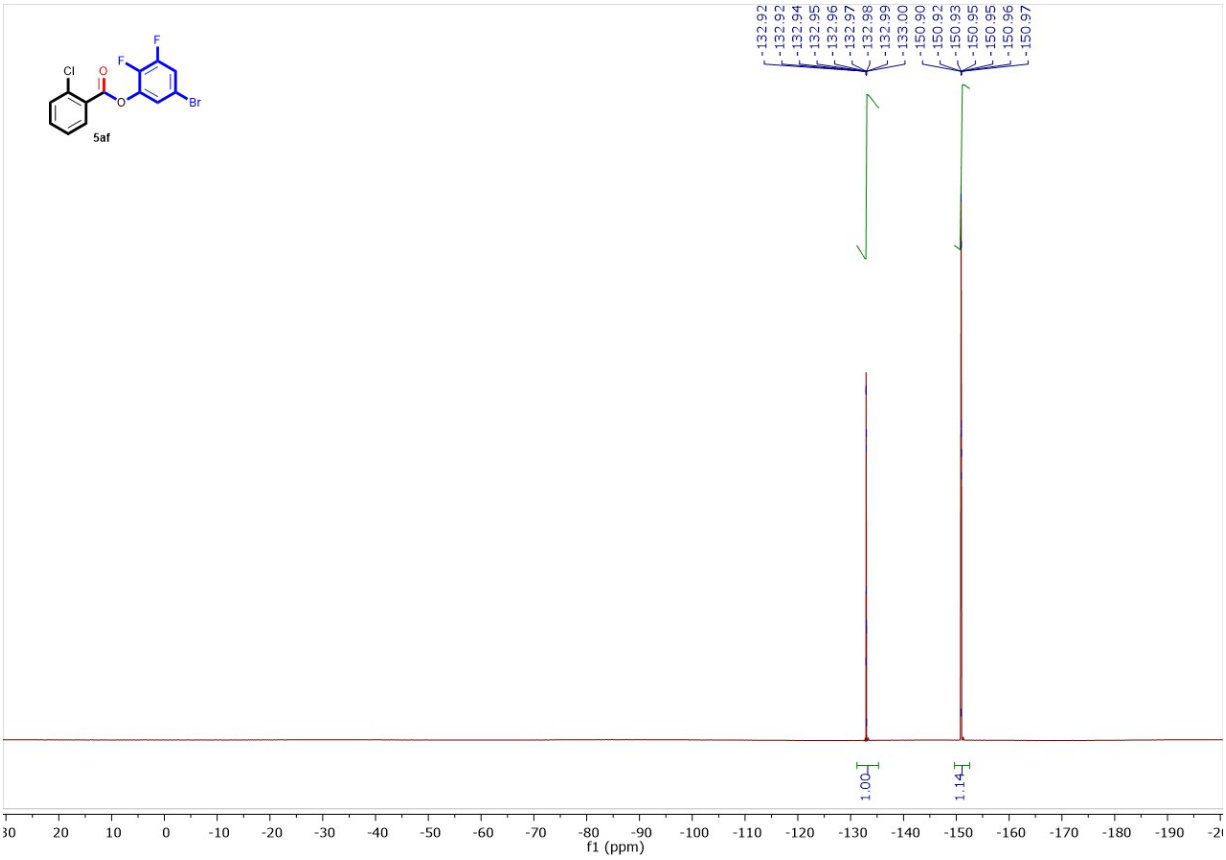
5-bromo-2,3-difluorophenyl 2-chlorobenzoate (5af) ^{1}H NMR



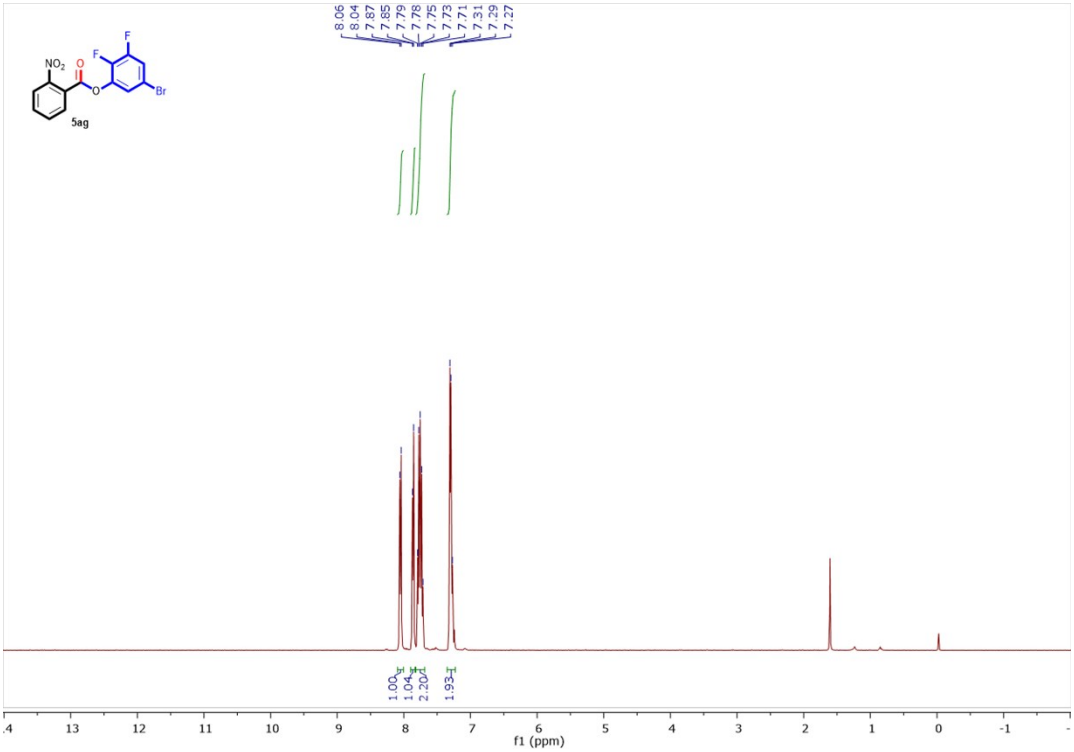
5-bromo-2,3-difluorophenyl 2-chlorobenzoate (5af) ^{13}C NMR



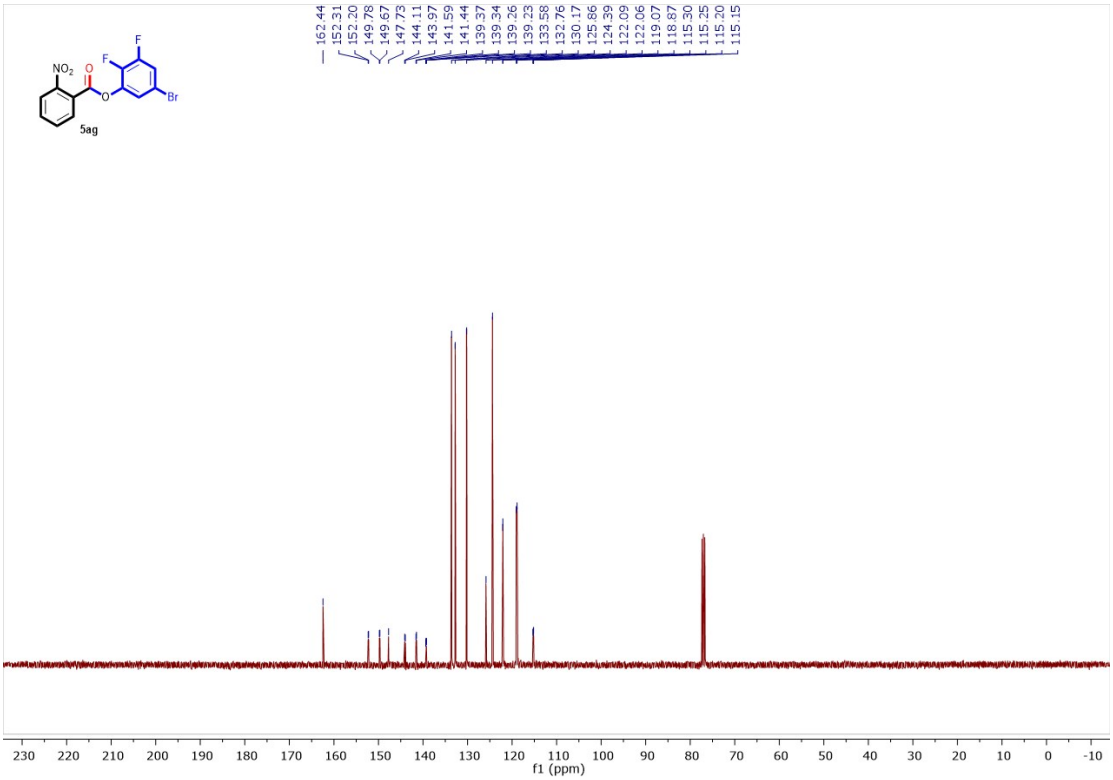
5-bromo-2,3-difluorophenyl 2-chlorobenzoate (5af) ^{19}F NMR

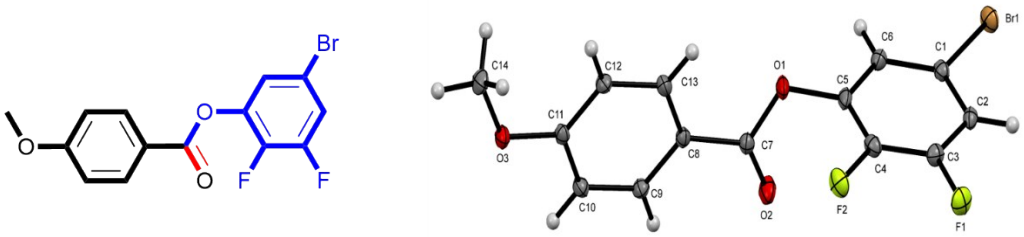


5-bromo-2,3-difluorophenyl 2-nitrobenzoate (5ag) ^{1}H NMR



5-bromo-2,3-difluorophenyl 2-nitrobenzoate (5ag) ^{13}C NMR





5ad

Figure 1. ORTEP diagram of **5ad** (CCDC 1512468).

Table 1. Crystal data and structure refinement for 5ad (CCDC 1512468).

Identification code	S_44 (CCDC 1512468)
Empirical formula	$C_{14}H_9BrF_2O_3$
Formula weight	343.12
Temperature	110(2)
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 6.6847(5) Å α = 71.172°
	b = 8.2593(7) Å β = 85.353°
	c = 12.7076(12) Å γ = 72.077°
Volume	631.70 $Å^3$
Z	2
Density (calculated)	1.804 g/cm^3
Absorption coefficient	3.282 mm^{-1}
F(000)	340
Crystal size	0.15 × 0.14 × 0.12 mm^3
Index ranges	-9<=h<=9, -11<=k<=11, -18<=l<=18
Theta range for data collection	2.72° to 30.47°
Reflection collected	3420
Independent reflections	3870 [R(int) = 0.0604]
Completeness to theta = 30.47°	99.8%
Absorption correction	MULTI-SCAN
Refinement method	SHELXL-2014 (Sheldrick 2014)
Data / restraints / parameters	3870/0/182
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0575
R indices (all data)	R1 = 0.0363, wR2 = 0.0600
Extinction coefficient	n/a
Largest diff. peak and hole	0.375 and -0.577 $e.Å^{-3}$