Supporting Information

Regioselective construction of diverse and multifunctionalized 2-hydroxybenzophenones for sun protection by indium(III)-catalyzed benzannulation

Hongyun Cai, Likai Xia, and Yong Rok Lee*

School of Chemical Engineering, Yeungnam University, Gyeongsan 712-749, Republic of Korea

To whom correspondence should be addressed.
E-mail: yrlee@yu.ac.kr; Tel: +82-53-810-2529; Fax: +82-53-810-4631.

Table of Contents

List of Tables and Graphics

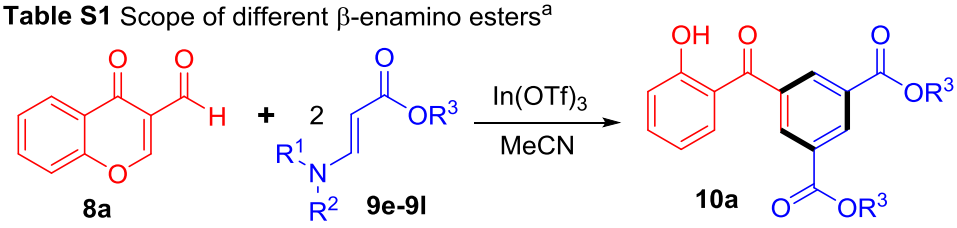
I. General information

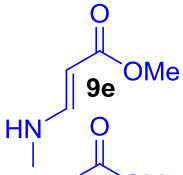
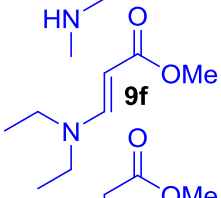
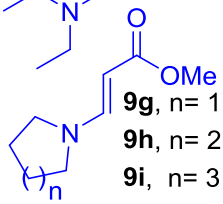
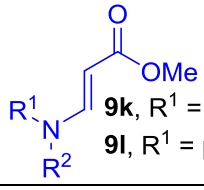
Solvents and all other chemicals, otherwise not mentioned, were purchased from Sigma-Aldrich, Fluka, or Tokyo Chemical Industry (TCI), and used as received. β-enamino esters **9** and chromene diene **13** were prepared according to the known methods.[s1,s2] All experiments were carried out in air. Merck precoated silica gel plates (Art. 5554) containing a fluorescent indicator were used for analytical thin layer chromatography (TLC). Flash column chromatography was performed using silica gel 9385 (Merck). The nuclear magnetic resonance (NMR) spectra were obtained on Bruker Model DPX-300, Varian VNS-300, or Varian VNS-600 spectrometers. The ^{1}H NMR spectra were recorded at 300/600 MHz and the chemical shifts were reported in parts per million (δ) relative to tetramethyl silane (TMS) (0 ppm) as the internal standard or relative to the resonance of the residual protonated solvent (^{1}H: $CDCl_3$, δ = 7.24 ppm). The following abbreviations were used to describe the signal patterns where appropriate: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). The coupling constants, *J*, are reported in Hertz (Hz). The ^{13}C NMR spectra were obtained at 75/150 MHz and are referenced to the internal solvent signals (^{13}C: $CDCl_3$, δ = 77.0). All melting points were obtained on a Fisher-Johns melting point apparatus and were uncorrected. The Fourier transform infrared (FT-IR) spectra were recorded on a Jasco FTIR 5300 spectrophotometer. High-resolution Mass Spectrometry **(**HRMS) was performed on a JEOL JMS-600 mass spectrometer (positive ion EI mode) at the Korean Basic Science Institute.

II. Investigation of the substrate scope of β-enamino esters

The substrate scope of β-enamino esters **9e-9l** was further investigated (Table S1). A reaction of 3-formylchromone (**8a**) with **9e** in the presence of 5 mol% of $In(OTf)_3$ in MeCN at room temperature for 24 h gave no desired product, but intractable reaction mixtures were obtained (entry 1). When **9f** was used, the desired product **10a** was produced in lower yield (48%), probably due to the steric hindrance of *N*,*N*-diethyl groups (entry 2). Further examinations of a variety of β-enamino esters **9g-9j** bearing bulky cyclic rings showed that the yield of **10a** decreased significantly with increasing ring size of amine substituents (entries 3-6). In the cases of β-enamino esters **9k-9l** bearing bulkier groups, no desired products were isolated (entries 7 and 8). These observations suggest that *N*-alkyl substituents on the β-enamino esters play an important role in determining their reactivity with 3-formylchromone.

Table S1 Scope of different β-enamino esters[a]



Entry	β-Enamino esters	Conditions	yield (%)[b]
1	 **9e**	rt, 24 h	0
2	 **9f**	rt, 12 h	48
3	 **9g**, n= 1	50 °C, 12 h	82
4	**9h**, n= 2	50 °C, 12 h	72
5	**9i**, n= 3	50 °C, 12 h	25
6	**9j**, n= 4	50 °C, 12 h	12
7	 **9k**, R^1 = R^2 = benzyl	50 °C, 12 h	0
8	**9l**, R^1 = phenyl, R^2 = Me	50 °C, 12 h	0

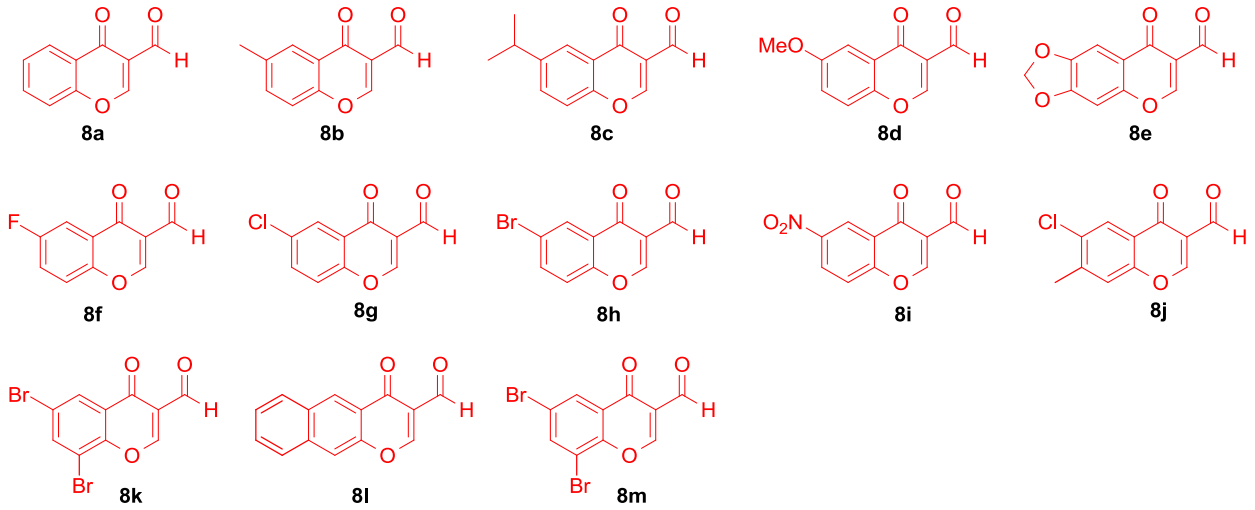
[a] Reaction conditions: Chromene-3-carbaldehyde (0.5 mmol), β-enamino ester (1.1 mmol), catalyst $In(OTf)_3$ (5 mol%), acetonitrile (5.0 mL).

[b] Isolated yields.

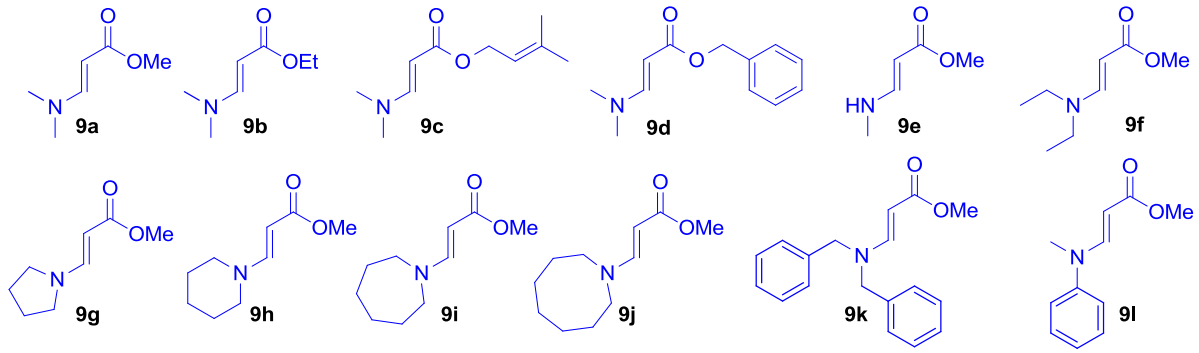
III. General Experimental Procedures and Analytical Data for 2-Hydroxybenzophenone 10 and 12

Indium(III) trifluoromethanesulfonate [Synonym: $In(OTf)_3$, Indium(III) triflate, Trifluoromethanesulfonic acid indium(III) salt, Tris(trifluoromethanesulfonato)indium, Sigma-Aldrich, >99.0%, 5.0 mol%] was added to a stirred solution of chromene-3-carbaldehyde **8** (0.5 mmol) and the corresponding β-enamino ester **9** or β-enamino ketone **11** (1.1 mmol) in MeCN (3.0 mL) at room temperature. The reaction mixture was stirred for 4–12 h. When the reaction was complete as indicated by TLC (hexane–EtOAc, 4:1, v/v), water (10 mL) was added and the solution was extracted with ethyl acetate (10 mL x 3). The products were obtained after evaporation of the solvent and purification by column chromatography on silica gel using hexane-ethyl acetate (4:1, v /v).

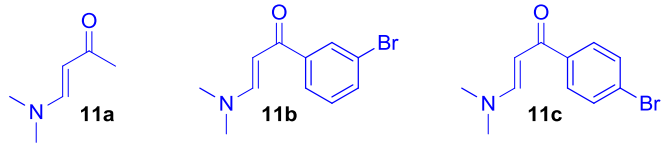
3-formylchromones



β-enamino esters



β-enamino ketones



Chromen-4-ones

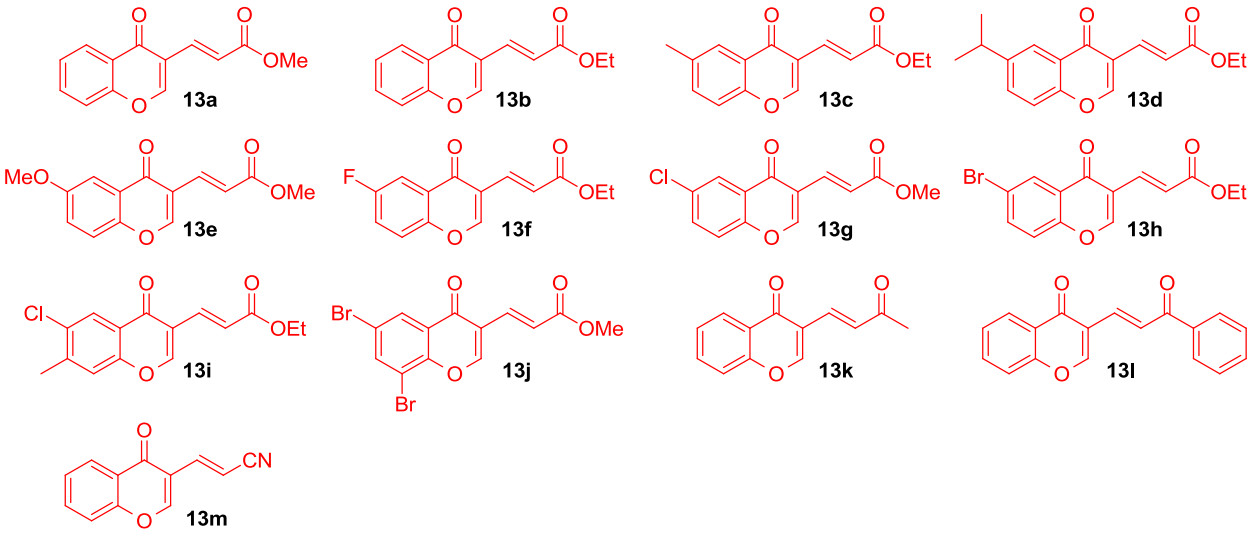
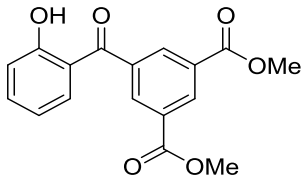
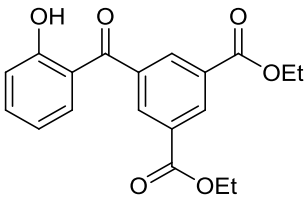


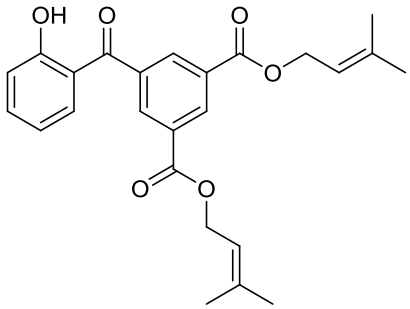
Fig. S1 Complete list of building blocks used for the preparation of 2-hydroxybenzophenones.



Dimethyl 5-(2-hydroxybenzoyl)isophthalate (10a). Yellow solid; yield 267 mg; 85%; mp 105-106 ℃; IR (KBr): $\tilde{\nu}$ = 2921, 2858, 1714, 1627, 1447, 1293, 1229, 747, 656 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.77 (s, 1H), 8.83 (s, 1H), 8.46 (s, 2H), 7.51 (dd, *J* = 8.1, 7.5 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.86 (dd, *J* = 7.8, 7.5 Hz, 1H), 3.94 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.40, 165.21, 163.28, 138.49, 136.96, 133.79, 133.33, 133.00, 131.01, 119.08, 118.64, 118.52, 52.65 ppm; HRMS (EI^+): *m/z*: calcd for $C_{17}H_{14}O_6$: 314.0790, Found: 314.0789.

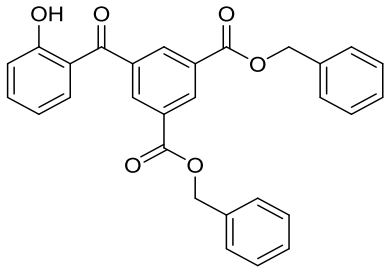


Diethyl 5-(2-hydroxybenzoyl)isophthalate (10b). Yellow solid; yield 315 mg; 92%; mp 108-109 ℃; IR (KBr): $\tilde{\nu}$ = 3423, 3081, 2978, 2922, 1715, 1616, 1448, 1223, 1114, 1015, 865, 741, 705, 655 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.81 (s, 1H), 8.84 (s, 1H), 8.46 (s, 2H), 7.52 (dd, *J* = 7.8, 7.5 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 4H), 1.40 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.64, 164.84, 163.33, 138.45, 136.98, 133.65, 133.27, 133.08, 131.37, 119.08, 118.65, 118.60, 61.78, 14.25 ppm; HRMS (EI^+): *m/z*: calcd for $C_{19}H_{18}O_6$: 342.1103, Found: 342.1105.

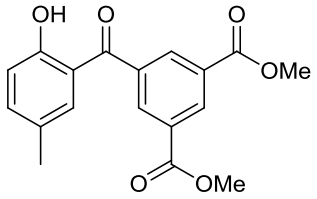


Bis(3-methylbut-2-en-1-yl) 5-(2-hydroxybenzoyl)isophthalate (10c). Yellow solid; yield 342 mg; 81%; mp 132-133 ℃; IR (KBr): $\tilde{\nu}$ = 3405, 3069, 2951, 1709, 1622, 1446, 1348, 1223, 1116, 956, 918, 742, 693, 520 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.81 (s, 1H), 8.84 (s, 1H), 8.45 (s, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H),

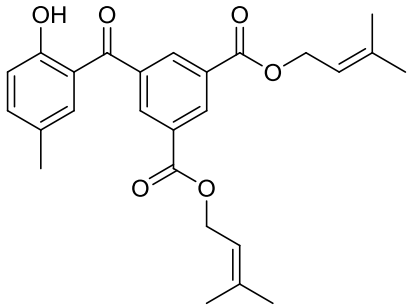
7.05 (d, *J* = 8.4 Hz, 1H), 6.86 (dd, *J* = 7.8, 7.5 Hz, 1H), 5.44 (t, *J* = 7.2 Hz, 2H), 4.84 (d, *J* = 7.2 Hz, 4H), 1.75 (s, 12H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.63, 164.85, 163.29, 139.81, 138.37, 136.91, 133.61, 133.36, 133.08, 131.37, 119.03, 118.59, 118.58, 118.09, 62.54, 25.72, 18.05 ppm; HRMS (EI^+): *m/z*: calcd for $C_{25}H_{26}O_6$: 422.1729, Found: 422.1729.



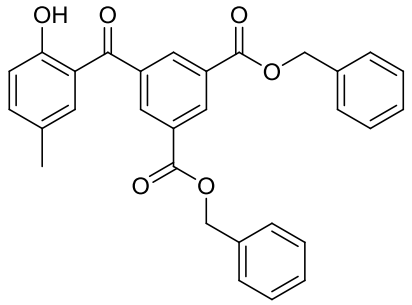
Dibenzyl 5-(2-hydroxybenzoyl)isophthalate (10d). Yellow solid; yield 363mg; 78%; mp 124-125 ℃; IR (KBr): ṽ = 3417, 3079, 2924, 1715, 1617, 1446, 1222, 1121, 946, 735, 656, 530, 449 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.82 (s, 1H), 8.93 (s, 1H), 8.52 (s, 2H), 7.53 (dd, *J* =7.5, 7.2 Hz, 1H), 7.46-7.32 (m, 11H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.87 (t, *J* = 7.5, 7.2 Hz, 1H), 5.41 (s, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.36, 164.56, 163.31, 138.54, 136.97, 135.30, 133.87, 133.43, 132.99, 131.09, 128.60, 128.45, 128.31, 119.02, 118.63, 118.53, 67.37 ppm; HRMS (EI^+): *m/z*: calcd for $C_{29}H_{22}O_6$: 466.1416, Found: 466.1418.



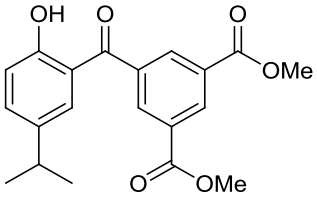
Dimethyl 5-(2-hydroxy-5-methylbenzoyl)isophthalate (10e). Yellow solid; yield 269 mg; 82%; mp 138-139 ℃; IR (KBr): ṽ = 3435, 3084, 2956, 1721, 1628, 1488, 1444, 1353, 1217, 1113, 991, 954, 749, 672, 539, 459 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.59 (s, 1H), 8.83 (s, 1H), 8.45 (s, 2H), 7.51 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.18 (s, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 6H), 2.21 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.42, 165.26, 161.26, 138.72, 138.11, 133.65, 133.18, 132.55, 130.99, 128.26, 118.40, 118.25, 52.63, 20.42 ppm; HRMS (EI^+): *m/z*: calcd for $C_{18}H_{16}O_6$: 328.0947, Found: 328.0948.



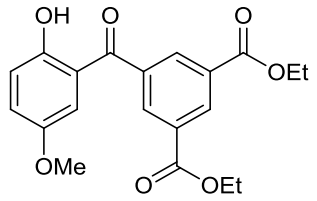
Bis(3-methylbut-2-en-1-yl) 5-(2-hydroxy-5-methylbenzoyl)isophthalate (10f). Yellow solid; yield 314 mg; 72%; mp 78-79 °C; IR (KBr): $\tilde{\nu}$ = 3417, 3088, 2975, 2918, 1720, 1634, 1483, 1445, 1331, 1287, 1210, 1108, 940, 826, 790, 732, 664, 534, 452 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.65 (s, 1H), 8.86 (s, 1H), 8.45 (s, 2H), 7.34 (d, J = 8.4 Hz, 1H), 7.19 (s, 1H), 6.98 (d, J = 8.7 Hz, 1H), 5.45 (dd, J = 7.2, 6.9 Hz, 2H), 4.85 (d, J = 7.2 Hz, 4H), 2.21 (s, 3H), 1.77 (s, 12H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.71, 164.99, 161.32, 139.93, 138.63, 138.13, 133.57, 133.32, 132.71, 131.42, 128.28, 118.43, 118.37, 118.14, 62.59, 25.79, 20.46, 18.13 ppm; HRMS (EI^+): *m/z*: calcd for $C_{26}H_{28}O_6$: 436.1886, Found: 436.1888.



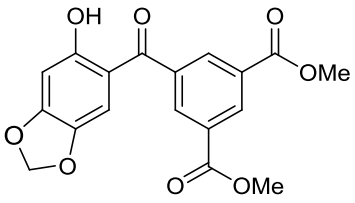
Dibenzyl 5-(2-hydroxy-5-methylbenzoyl)isophthalate (10g). Yellow solid; yield 360 mg; 75%; mp 106-107 °C; IR (KBr): $\tilde{\nu}$ = 3405, 3069, 2939, 1711, 1630, 1483, 1452, 1346, 1282, 1244, 1213, 1115, 963, 919, 748, 698, 667, 527 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.62 (s, 1H), 8.92 (s, 1H), 8.50 (s, 2H), 7.45-7.34 (m, 11H), 7.18 (s, 1H), 6.98 (d, J = 8.4 Hz, 1H), 5.40 (s, 4H), 2.21 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.41, 164.69, 161.36, 138.80, 138.19, 135.37, 133.85, 133.45, 132.61, 131.15, 128.68, 128.53, 128.37, 128.29, 118.48, 118.31, 67.44, 20.43 ppm; HRMS (EI^+): *m/z*: calcd for $C_{30}H_{24}O_6$: 480.1573, Found: 480.1576.



Dimethyl 5-(2-hydroxy-5-isopropylbenzoyl)isophthalate (10h). Yellow solid; yield 278 mg; 78%; mp 83-84 ℃; IR (KBr): ṽ = 3435, 3084, 2957, 1728, 1631, 1478, 1445, 1349, 1236, 998, 838, 721, 666, 584 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.58 (s, 1H), 8.85 (s, 1H), 8.50 (s, 2H), 7.41 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.27 (d, *J* = 1.8 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 3.95 (s, 6H), 2.83-2.74 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.15, 165.25, 161.43, 139.35, 138.55, 135.57, 134.05, 133.37, 131.01, 130.20, 118.44, 118.18, 52.62, 33.05, 23.80 ppm; HRMS (EI^+): *m/z*: calcd for $C_{20}H_{20}O_6$: 356.1260, Found:356.1257.

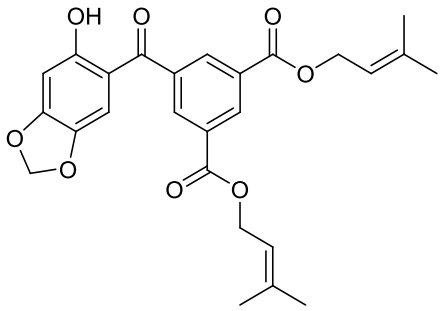


Diethyl 5-(2-hydroxy-5-methoxybenzoyl)isophthalate (10i). Brown solid; yield 268 mg; 72%; mp 115-116 ℃; IR (KBr): ṽ = 3405, 3081, 2924, 1711, 1480, 1209, 1109, 1017, 847, 731, 443 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.43 (s, 1H), 8.85 (s, 1H), 8.50 (s, 2H), 7.17 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 1H), 6.90 (d, *J* = 3.0 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 4H), 3.66 (s, 3H), 1.40 (s, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.09, 164.83, 157.78, 151.65, 138.41, 133.67, 133.38, 131.43, 125.14, 119.64, 118.02, 115.20, 61.81, 55.84, 14.28 ppm; HRMS (EI^+): *m/z*: calcd for $C_{20}H_{20}O_7$: 372.1209, Found: 372.1212.

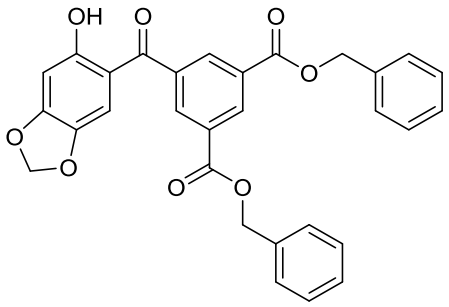


Dimethyl 5-(6-hydroxybenzo[*d*][1,3]dioxole-5-carbonyl)isophthalate (**10j**). Yellow solid; yield 272 mg; 76%; mp 176-177 ℃; IR (KBr): ṽ = 3435, 3079, 2958, 2916, 1725, 1625, 1480, 1427, 1312, 1239, 1212, 1159, 1033, 997, 928, 745, 697, 540 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 12.77 (s, 1H), 8.81 (d, *J* = 1.8 Hz, 1H), 8.41 (d, *J* = 1.8 Hz, 2H), 6.74 (s, 1H), 6.53 (d, 1H), 5.97 (s, 2H), 3.95 (s, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.22, 165.32, 163.74, 155.23,

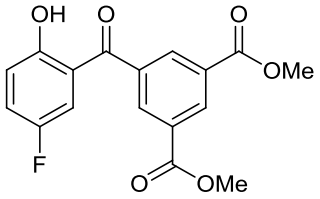
140.62, 138.97, 133.35, 132.94, 131.07, 111.14, 109.06, 102.13, 99.02, 52.65 ppm; HRMS (EI^+): *m/z*: calcd for $C_{18}H_{14}O_8$: 358.0689, Found: 358.0686.



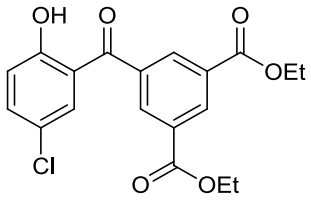
Bis(3-methylbut-2-en-1-yl) 5-(6-hydroxybenzo[*d*][1,3]dioxole-5-carbonyl)isophthalate (10k). Yellow solid; yield 317 mg; 68%; mp 130-131 ℃; IR (KBr): ṽ = 3417, 3074, 2919, 1718, 1623, 1472, 1429, 1231, 1154, 1113, 1037, 962, 929, 826, 742, 695, 534, 450, 428 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 12.80 (s, 1H), 8.82 (t, *J* = 1.5 Hz, 1H), 8.39 (d, *J* = 1.5 Hz, 2H), 6.74 (s, 1H), 6.53 (s, 1H), 5.97 (s, 2H), 5.48-5.42 (m, 2H), 4.84 (d, *J* = 7.2 Hz, 4H), 1.77 (s, 6H), 1.76 (s, 6 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.49, 164.98, 163.68, 155.19, 140.58, 139.88, 138.80, 133.19, 132.98, 131.39, 118.14, 111.20, 109.17, 102.11, 98.97, 62.58, 25.79, 18.12 ppm; HRMS (EI^+): *m/z*: calcd for $C_{26}H_{26}O_8$: 466.4628, Found: 466.1626.



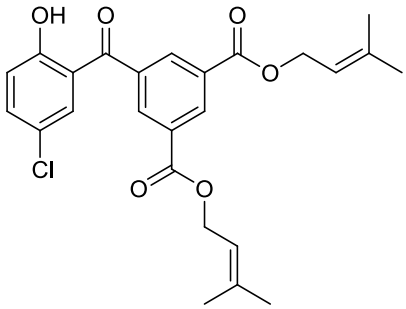
Dibenzyl 5-(6-hydroxybenzo[*d*][1,3]dioxole-5-carbonyl)isophthalate (10l). Orange solid; yield 367 mg; 72%; mp 172-173 ℃; IR (KBr): ṽ = 3441, 3072, 2922, 1726, 1628, 1238, 1200, 1039, 749, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 12.76 (s, 1H), 8.87 (d, *J* = 1.8 Hz, 1H), 8.43 (d, *J* = 1.8 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 4H), 7.42-7.34 (m, 6H), 6.72 (s, 1H), 6.54(s, 1H), 5.97 (s, 2H), 5.39 (s, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.23, 164.72, 163.77, 155.29, 140.65, 139.04, 135.38, 133.47, 133.10, 131.16, 128.68, 128.52, 128.39, 111.18, 109.07, 102.13, 99.03, 67.45 ppm; HRMS (EI^+): *m/z*: calcd for $C_{30}H_{22}O_8$: 510.1315, Found: 510.1313.



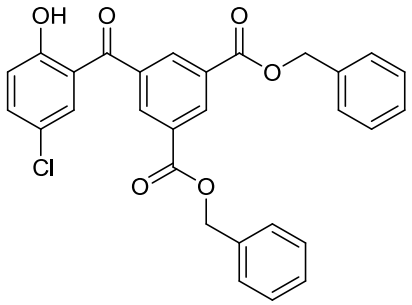
Dimethyl 5-(5-fluoro-2-hydroxybenzoyl)isophthalate (10m). Yellow solid; yield 276 mg; 83%; mp 135-136 ℃; IR (KBr): ṽ = 3453, 3076, 2924, 2859, 1720, 1624, 1463, 1232, 1186, 1114, 951, 736, 672, 553, 462 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.51 (s, 1H), 8.87 (d, J = 1.5 Hz, 1H), 8.46 (d, J = 1.5 Hz, 2H), 7.31-7.25 (m, 1H), 7.11 (dd, J = 8.7, 3 Hz, 1H), 7.05 (dd, J = 9.0, 4.5 Hz, 1H), 3.96 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.62 (d, J = 2.3 Hz), 165.13, 159.53 (d, J = 1.5 Hz), 154.63 (d, J = 238.5 Hz), 138.02, 133.69, 133.62, 131.28, 124.74 (d, J = 24.0 Hz), 120.14 (d, J = 7.5 Hz), 118.06 (d, J = 6.8 Hz), 117.62 (d, J = 23.3 Hz), 52.75 ppm; HRMS (EI^+): *m/z*: calcd for $C_{17}H_{13}O_6$: 332.0696, Found: 332.0694.



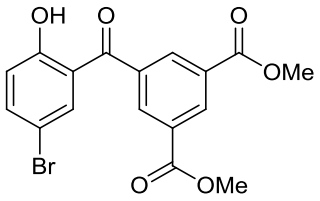
Diethyl 5-(5-chloro-2-hydroxybenzoyl)isophthalate (10n). Yellow solid; yield 320 mg; 85%; mp 131-132 ℃; IR (KBr): ṽ = 3411, 3076, 2984, 1713, 1622, 1526, 1459, 1210, 1105, 1015, 855, 741, 694, 626, 532, 467 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.69 (s, 1H), 8.86 (s, 1H), 8.44 (s, 2H), 7.59 (dd, J = 9.0, 2.4 Hz, 1H), 7.53 (d, J = 2.4 Hz, 1H), 6.98 (d, J = 9.0 Hz, 1H), 4.42 (q, J = 7.2 Hz, 4H), 1.40 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.70, 164.66, 162.21, 139.64, 137.76, 134.84, 133.63, 133.46, 131.63, 120.71, 119.90, 110.63, 61.85, 14.24 ppm; HRMS (EI^+): *m/z*: calcd for $C_{19}H_{17}ClO_6$: 376.0714, Found: 376.0711.



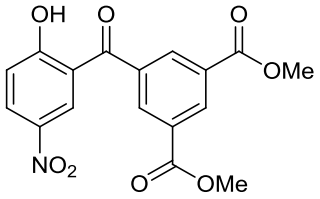
Bis(3-methylbut-2-en-1-yl) 5-propionylisophthalate (10o). Yellow solid; yield 375 mg; 82%; mp 77-78 ℃; IR (KBr): ṽ = 3423, 3081, 2976, 1735, 1628, 1461, 1355, 1251, 1216, 1170, 965, 831, 743, 707, 646, 535, 455 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.67 (s, 1H), 8.86 (s, 1H), 8.43 (s, 2H), 7.44 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 1H), 5.44 (t, *J* = 7.2 Hz, 2H), 4.84 (d, *J* = 7.2 Hz, 4H), 1.75 (s,12 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.78, 164.69, 161.73, 139.95, 137.72, 136.82, 133.71, 133.42, 131.80, 131.62, 123.75, 120.29, 119.23, 118.05, 62.60, 25.73, 18.07 ppm; HRMS (EI^+): *m/z*: calcd for $C_{25}H_{25}ClO_6$: 456.1340, Found: 456.1338.



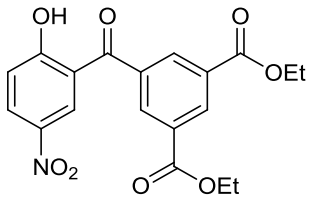
Dibenzyl 5-(5-chloro-2-hydroxybenzoyl)isophthalate (10p). Yellow solid; yield 401 mg; 80%; mp 122-123 ℃; IR (KBr): ṽ = 3429, 3071, 2953, 1722, 1633, 1462, 1342, 1212, 966, 912, 828, 737, 699, 593, 522 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.68 (s, 1H), 8.94 (s, 1H), 8.50 (s, 2H), 7.49-7.32 (m, 12H), 7.04 (d, *J* = 8.7 Hz, 1H), 5.41 (s, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.55, 164.45, 161.78, 137.89, 136.94, 135.25, 133.90, 133.75, 131.76, 131.36, 128.67, 128.52, 128.35, 123.81, 120.38, 119.17, 67.51 ppm; HRMS (EI^+): *m/z*: calcd for $C_{29}H_{21}ClO_6$: 500.1027, Found: 500.1024.



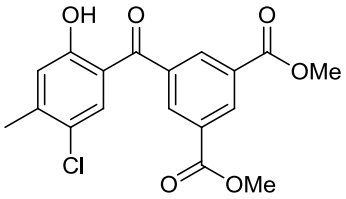
Dimethyl 5-(5-bromo-2-hydroxybenzoyl)isophthalate (10q). Yellow solid; yield 322 mg; 82%; mp 113-114 ℃; IR (KBr): ṽ = 3435, 3086, 2956, 1729, 1633, 1524, 1447, 1244, 1202, 989, 949, 705, 647, 460 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.66 (s, 1H), 8.87 (s, 1H), 8.45 (s, 2H), 7.47 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 1H), 3.97 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.69, 165.12, 161.78, 137.94, 136.96, 133.72, 133.59, 131.78, 131.30, 123.85, 120.39, 119.22, 52.78 ppm; HRMS (EI^+): *m/z*: calcd for $C_{17}H_{13}BrO_6$: 391.9896, Found: 391.9894.



Dimethyl 5-(2-hydroxy-5-nitrobenzoyl)isophthalate (10r). Yellow solid; yield 302 mg; 84%; mp 158-159 ℃; IR (KBr): ṽ = 3329, 3067, 2924, 1733, 1639, 1447, 1337, 1246, 1168, 993, 749, 685, 409 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 12.24 (brs, 1H), 8.93 (s, 1H), 8.50 (s, 2H), 8.42 (s, 1H), 8.39 (d, *J* = 2.7 Hz, 1H), 7.21 (d, *J* = 2.7 Hz, 1H), 3.98 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.76, 167.83, 164.92, 139.71, 137.11, 134.35, 133.68, 131.69, 131.50, 129.04, 119.88, 117.57, 52.86 ppm; HRMS (EI^+): *m/z*: calcd for $C_{17}H_{13}NO_8$: 359.0641, Found: 359.0638.

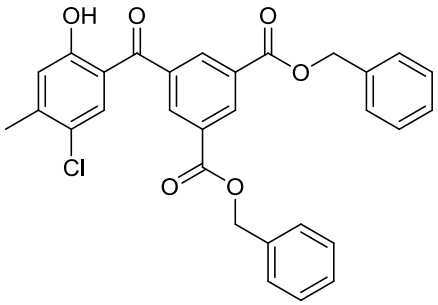


Diethyl 5-(2-hydroxy-5-nitrobenzoyl)isophthalate (10s). Yellow solid; yield 352 mg; 91%; mp 132-133 ℃; IR (KBr): ṽ = 3424, 3074, 2923, 1721, 1455, 1328, 1230, 1102, 1018, 751, 701, 634 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 12.31 (s, 1H), 8.87 (s, 1H), 8.46 (s, 2H), 8.40 (d, *J* = 2.4 Hz, 1H), 8.36 (dd, *J* = 9.3, 2.4 Hz, 1H), 7.16 (d, *J* = 9.3 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 4H), 1.38 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.73, 167.69, 164.37, 139.58, 136.86, 134.10, 133.46, 131.86, 131.33, 128.95, 119.72, 117.49, 61.88, 14.15 ppm; HRMS (EI^+): *m/z*: calcd for $C_{19}H_{17}NO_8$: 387.0954, Found: 387.0953.

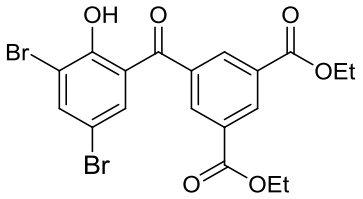


Dimethyl 5-(5-chloro-2-hydroxy-4-methylbenzoyl)isophthalate (10t). Yellow solid; yield 294 mg; 81%; mp 155-156 ℃; IR (KBr): ṽ = 3429, 3079, 2925, 2854, 1720, 1624, 1468, 1437, 1321, 1222, 1162, 985, 927, 740, 705, 590, 524, 470 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.64 (s, 1H), 8.84 (s, 1H), 8.43 (s, 2H), 7.35 (s, 1H), 6.94 (s, 1H), 3.95 (s, 6H), 2.36 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.16, 165.12, 161.67, 146.55, 138.13, 133.51,

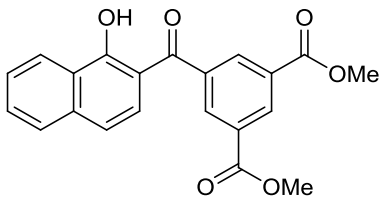
133.48, 132.12, 131.18, 124.46, 120.66, 117.51, 52.69, 20.86 ppm; HRMS (EI^+): *m/z*: calcd for $C_{18}H_{15}ClO_6$: 362.0557, Found: 362.0559.



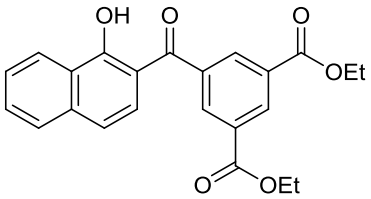
Dibenzyl 5-((2Z,3E)-4-chloro-2-(hydroxymethylene)but-3-enoyl)isophthalate (10u). Yellow solid; yield 376 mg; 75%; mp 121-122 ℃; IR (KBr): ῦ = 3423, 3072, 2925, 1716, 1625, 1480, 1345, 1304, 1222, 1164, 971, 904, 876, 733, 694, 586, 450 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.68 (s, 1H), 8.93 (s, 1H), 8.49 (s, 2H), 7.46-7.34 (m, 11H), 6.97 (s, 1H), 5.41 (s, 4H), 2.39 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.06, 164.48, 161.70, 146.56, 138.12, 135.30, 133.67 (2 Ar-C), 132.13, 131.28, 128.64, 128.47, 128.30, 124.45, 120.69, 117.51, 67.44, 20.86 ppm; HRMS (EI^+): *m/z*: calcd for $C_{30}H_{23}ClO_6$: 514.1183, Found: 514.1182.



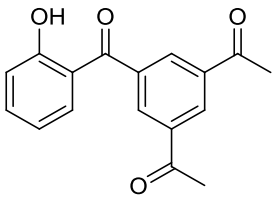
Diethyl 5-(3,5-dibromo-2-hydroxybenzoyl)isophthalate (10v). Yellow solid; yield 390 mg; 78%; mp 119-120 ℃; IR (KBr): ῦ = 3417, 3081, 2930, 1720, 1623, 1432, 1357, 1225, 1111, 1013, 874, 752, 694, 464 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 12.26 (s, 1H), 8.86 (s, 1H), 8.44 (s, 2H), 7.87 (d, *J* = 2.1 Hz, 1H), 7.51 (d, *J* = 2.1 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 4H), 1.40 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.32, 164.48, 158.69, 141.88, 137.17, 134.12, 133.92, 133.51, 131.68, 120.24, 113.47, 110.56, 61.89, 14.22 ppm; HRMS (EI^+): *m/z*: calcd for $C_{19}H_{16}Br_2O_6$: 497.9314, Found: 497.9314.



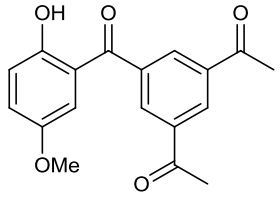
Dimethyl 5-(1-hydroxy-2-naphthoyl)isophthalate (10w). Yellow solid; yield 273 mg; 75%; mp 172-173 ℃; IR (KBr): ῦ = 3436, 3076, 2923, 2854, 1724, 1603, 1572, 1456, 1237, 1004, 800, 731, 572, 486cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.67 (s, 1H), 8.81 (s, 1H), 8.48-8.44 (m, 3H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.50 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.13, 165.37, 164.33, 138.89, 137.50, 133.84, 133.18, 131.07, 130.79, 127.52, 126.41, 126.24, 125.20, 124.58, 118.56, 112.12, 52.69 ppm; HRMS (EI$^+$): *m/z*: calcd for $C_{21}H_{16}O_6$: 364.0947, Found: 364.1946.



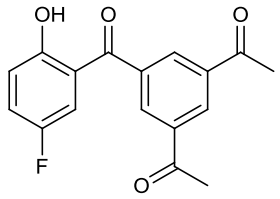
Diethyl 5-(1-hydroxy-2-naphthoyl)isophthalate (10x). Yellow solid; yield 306 mg; 78%; mp 102-103 ℃; IR (KBr): ῦ = 3424, 3064, 2921, 2854, 1715, 1604, 1546, 1384, 1235, 1114, 1017, 816, 729, 570, 418 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.69 (s, 1H), 8.82 (s, 1H), 8.47-8.45 (m, 3H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 7.2, 6.9 Hz, 1H), 7.51 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 4H), 1.36 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.34, 164.97, 164.32, 138.80, 137.51, 133.67, 133.11, 131.39, 130.77, 127.52, 136.47, 126.23, 125.21, 124.59, 118.53, 112.18, 61.79, 14.29 ppm; HRMS (EI$^+$): *m/z*: calcd for $C_{23}H_{20}O_6$: 392.1260, Found: 392.1262.



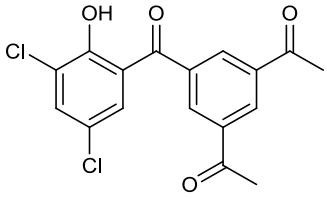
1,1'-(5-(2-Hydroxybenzoyl)-1,3-phenylene)diethanone (12a). Yellow solid; yield 212 mg; 75%; mp 133-134 ℃; IR (KBr): ῦ = 3356, 3074, 3004, 1683, 1619, 1592, 1443, 1348, 1221, 1164, 991, 905, 767, 585 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.75 (s, 1H), 8.67 (s, 1H), 8.38 (s, 2H), 7.53 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.87 (dd, *J* = 8.1, 7.2 Hz, 1H), 2.68 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.64, 196.29, 163.34, 138.86, 137.57, 137.14, 132.94, 132.47, 130.51, 119.17, 118.76, 118.53, 26.80 ppm; HRMS (EI$^+$): *m/z*: calcd for $C_{17}H_{14}O_4$: 282.0892, Found: 282.0894.



1,1'-(5-(2-Hydroxy-5-methoxybenzoyl)-1,3-phenylene)diethanone (12b). Yellow solid; yield 218 mg; 70%; mp 175-176 ℃; IR (KBr): ṽ = 3356, 3072, 2293, 1686, 1582, 1480, 1357, 1272, 1215, 1144, 1026, 988, 796, 759, 674, 597, 558 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.36 (s, 1H), 8.69 (s, 1H), 8.43 (s, 2H), 7.18 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.88 (d, *J* = 3.0 Hz, 1H), 3.67 (s, 3H), 2.70 (s, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 199.13, 196.26, 157.83, 151.77, 138.92, 137.70, 132.51, 130.60, 125.18, 119.77, 118.04, 115.29, 55.91, 26.84 ppm; HRMS (EI^+): *m/z*: calcd for $C_{18}H_{16}O_5$: 312.3166, Found: 312.3166.

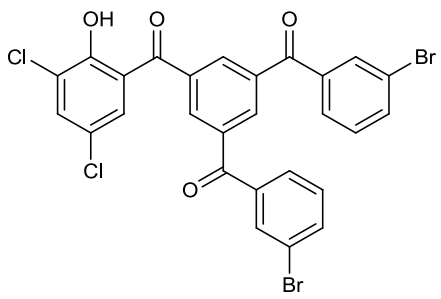


1,1'-(5-(5-Fluoro-2-hydroxybenzoyl)-1,3-phenylene)diethanone (12c). Yellow solid; yield 249 mg; 83%; mp 122-123 ℃; IR (KBr): ṽ = 3356, 3060, 2292, 1685, 1620, 1581, 1470, 1429, 1343, 1266, 1225, 1181, 994, 899, 835, 785, 738, 677, 586, 550, 485 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.46 (s, 1H), 8.68 (d, *J* = 1.8 Hz, 1H), 8.37 (d, *J* = 1.8 Hz, 2H), 7.29-7.27 (m, 1H), 7.09 (dd, *J* = 8.4, 3 Hz, 1H), 7.05 (dd, *J* = 9.0, 4.2 Hz, 1H), 2.68 (s, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.80 (d, *J* = 1.1 Hz), 196.08, 159.54, 155.64 (d, *J* = 238.0 Hz), 138.35, 137.76, 132.22, 130.80, 124.84 (d, *J* = 24.2 Hz), 120.21 (d, *J* = 7.9 Hz), 118.03 (d, *J* = 5.9 Hz), 117.51 (d, *J* = 23.1 Hz), 26.76 ppm; HRMS (EI^+): *m/z*: calcd for $C_{17}H_{13}FO_4$: 300.2811, Found: 300.2811.

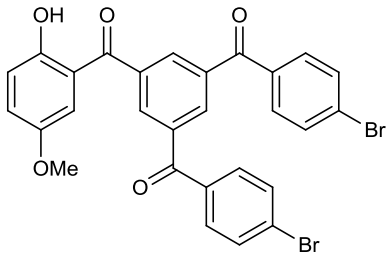


1,1'-(5-(3,5-Dichloro-2-hydroxybenzoyl)-1,3-phenylene)diethanone (12d). Yellow solid; yield 263 mg; 75%; mp 158-159 ℃; IR (KBr): ṽ = 3374, 3072, 1691, 1631, 1590, 1425, 1358, 1333, 1268, 1219, 1159, 1014, 909, 786, 747, 678, 588, 506, 466 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.99 (s, 1H), 8.66 (s, 1H), 8.32 (s, 2H), 7.56 (d, *J* = 2.4 Hz,

1H), 7.28 (s, 1H), 2.65 (s, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.56, 195.91, 157.45, 137.85, 136.46, 133.25, 132.26, 131.18, 130.32, 124.46, 123.73, 119.80, 26.76 ppm; HRMS (EI^+): *m/z*: calcd for $C_{17}H_{12}Cl_2O_4$: 351.1808, Found: 351.1808.



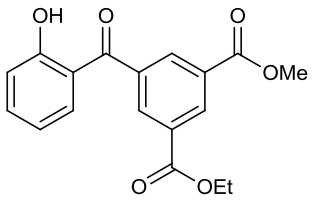
(5-(2-Hydroxy-5-methoxybenzoyl)-1,3-phenylene)bis((4-bromophenyl)methanone) (12e). Green solid; yield 538 mg; 85%; mp 100-101 ℃; IR (KBr): ṽ = 3320, 3069, 1731, 1663, 1633, 1591, 1567, 1425, 1340, 1279, 1223, 1160, 1041, 909, 799, 737, 680, 644, 564, 471, 426 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 12.00 (s, 1H), 8.36 (s, 1H), 8.25 (s, 2H), 7.97 (t, *J* = 1.8 Hz, 2H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.04, 192.66, 157.52, 137.97, 137.90, 137.62, 136.58, 136.33, 134.13, 133.42, 132.69, 130.27, 130.25, 128.46, 124.61, 123.75, 123.24, 119.73 ppm; HRMS (EI^+): *m/z*: calcd for $C_{27}H_{14}Br_2Cl_2O_4$: 633.1117, Found: 633.1117.



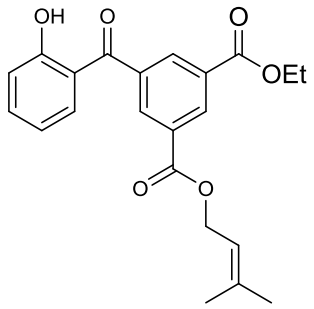
(5-(2-Hydroxy-5-methoxybenzoyl)-1,3-phenylene)bis((4-bromophenyl)methanone) (12f). Yellow solid; yield 487 mg; 82%; mp 194-195 ℃; IR (KBr): ṽ = 3314, 3096, 2924, 2856, 1660, 1584, 1483, 1396, 1316, 1277, 1224, 1172, 1066, 1035, 1001, 946, 838, 788, 748, 707, 666, 605, 553, 463 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.31 (s, 1H), 8.32 (s, 1H), 8.26 (s, 2H), 7.70 (d, *J* = 8.4 Hz, 4H), 7.66 (d, *J* = 8.4 Hz, 4H), 7.17 (dd, *J* = 8.4, 3 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.97 (d, *J* = 3.0 Hz, 1H), 3.72 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.72, 193.52, 157.68, 151.70, 138.51, 137.98, 134.91, 133.43, 133.34, 132.13, 131.48, 128.74, 124.75, 119.71, 117.99, 115.79, 55.98 ppm; HRMS (EI^+): *m/z*: calcd for $C_{28}H_{18}Br_2O_5$: 594.2475, Found: 594.2475.

IV. General Experimental Procedures and Analytical Data for 2-Hydroxybenzophenone 14

Indium(III) trifluoromethanesulfonate was added to a stirred solution of chromene diene **13** (0.5 mmol) and the corresponding β-enamino ester **9** or β-enamino ketone **11** (0.6 mmol) in MeCN (3.0 mL) at room temperature. The reaction mixture was stirred for 2–8 h. When the reaction was complete as indicated by TLC (hexane–EtOAc, 4:1, v/v), water (10 mL) was added and the solution was extracted with ethyl acetate (10 mL x 3). The products were obtained after evaporation of the solvent and purification by column chromatography on silica gel using hexane-ethyl acetate (4:1, v /v).

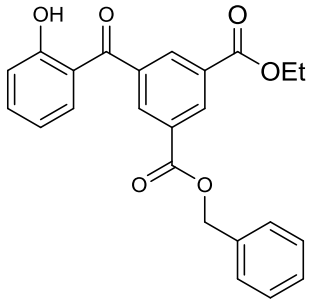


1-Ethyl 3-methyl 5-(2-hydroxybenzoyl)isophthalate (14a). Yellow solid; yield 298 mg; 91%; mp 99-100 ℃; IR (KBr): ṽ = 3421, 3081, 2958, 2924, 1719, 1622, 1438, 1345, 1234, 1161, 1105, 1024, 997, 739, 655, 465 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.80 (s, 1H), 8.84 (t, *J* = 1.8 Hz, 1H), 8.47 (d, *J* = 1.8 Hz, 1H), 8.45 (t, *J* = 1.8 Hz, 1H), 7.51 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.95 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 199.52, 165.29, 164.74, 163.30, 138.46, 136.98, 133.77, 133.68, 133.29, 133.04, 131.41, 130.92, 119.08, 118.64, 118.55, 61.78, 52.65, 14.23 ppm; HRMS (EI^+): *m/z*: calcd for $C_{18}H_{16}O_6$: 328.0947, Found: 328.0947.

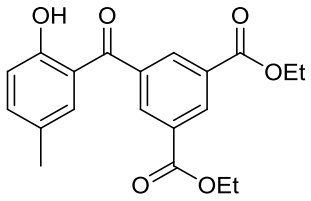


1-Ethyl 3-(3-methylbut-2-en-1-yl) 5-(2-hydroxybenzoyl)isophthalate (14b). Yellow solid; yield 344 mg; 90%; mp 78-79 ℃; IR (KBr): ṽ = 3421, 3081, 2981, 2935, 1718, 1619, 1481, 1445, 1280, 1227, 1161, 1109, 1024, 950, 867, 739, 704, 653, 539, 456 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.83 (s, 1H), 8.86 (t, *J* = 1.5 Hz, 1H), 8.47 (d, *J* = 1.5

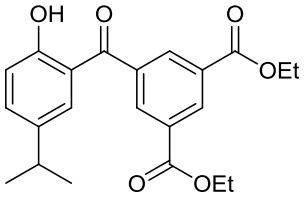
Hz, 2H), 7.53 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.45 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 1H), 5.45 (t, *J* = 7.2 Hz, 1H), 4.85 (d, *J* = 7.2 Hz, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.77 (s, 3H), 1.76 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.72, 164.93, 164.90, 163.35, 139.94, 138.45, 137.02, 133.71, 133.65, 133.38, 133.14, 131.44, 131.36, 119.12, 118.67, 118.63, 118.09, 62.64, 61.80, 25.80, 18.03, 14.28 ppm; HRMS (EI^+): *m/z*: calcd for $C_{22}H_{22}O_6$: 382.4065, Found: 382.4065.



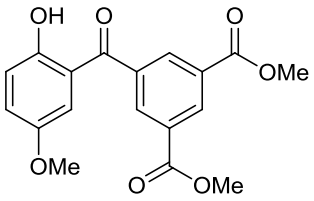
1-Benzyl 3-ethyl 5-(2-hydroxybenzoyl)isophthalate (14c). White solid; yield 356 mg; 88%; mp 74-75 ℃; IR (KBr): ṽ = 3422, 3079, 2984, 2934, 1714, 1623, 1445, 1345, 1281, 1223, 1162, 1108, 1023, 955, 870, 739, 696, 655, 589 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.82 (s, 1H), 8.89 (d, *J* = 1.5 Hz, 1H), 8.49 (dd, *J* = 3.6, 1.5 Hz, 2H), 7.53 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.46-7.34 (m, 6H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 1H), 5.41 (s, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.59, 164.80, 164.74, 163.34, 138.52, 137.06, 135.34, 133.85, 133.79, 133.43, 133.10, 131.43, 131.06, 128.67, 128.54, 128.43, 119.13, 118.69, 118.58, 67.45, 61.84, 14.26 ppm; HRMS (EI^+): *m/z*: calcd for $C_{24}H_{20}O_6$: 404.4120, Found: 404.4120.



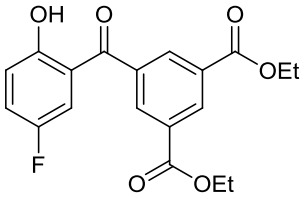
Diethyl 5-(2-hydroxy-5-methylbenzoyl)isophthalate (14d). Yellow solid; yield 328 mg; 92%; mp 147-148 ℃; IR (KBr): ṽ = 3412, 3081, 2985, 2926, 1710, 1632, 1486, 1211, 1106, 1016, 736, 664 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.64 (s, 1H), 8.85 (s, 1H), 8.60 (s, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.20 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 4H), 2.22 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.66, 164.93, 161.35, 138.69, 138.15, 133.57, 133.18, 132.68, 131.40, 128.29, 118.45, 118.37, 61.78, 20.45, 14.28 ppm; HRMS (EI^+): *m/z*: calcd for $C_{20}H_{20}O_6$: 356.1260, Found: 356.1257.



Diethyl 5-(2-hydroxy-5-isopropylbenzoyl)isophthalate (14e). Yellow solid; yield 330 mg; 86%; mp 124-125 ℃; IR (KBr): ṽ = 3427, 3069, 2963, 1723, 1632, 1475, 1358, 1227, 1023, 749, 718, 584, 473 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.63 (s, 1H), 8.87 (s, 1H), 8.51 (s, 2H), 7.42 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.30 (d, *J* = 1.8 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 4H), 2.87-2.73 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 6H), 1.15 (d, *J* = 6.9 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.33, 164.85, 161.48, 139.36, 138.44, 135.61, 133.94, 133.43, 131.36, 130.24, 118.45, 118.23, 61.74, 33.09, 23.86, 14.25 ppm; HRMS (EI^+): *m/z*: calcd for $C_{22}H_{24}O_6$: 384.1573, Found: 384.1574.

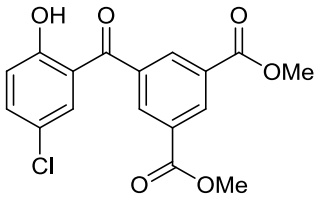


Dimethyl 5-(2-hydroxy-5-methoxybenzoyl)isophthalate (14f). Orange solid; yield 279 mg; 81%; mp 137-138 ℃; IR (KBr): ṽ = 3427, 3088, 2921, 2852, 1716, 1623, 1441, 1253, 1194, 1045, 986, 732, 674, 559, 444 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.35 (s, 1H), 8.82 (s, 1H), 8.49 (s, 2H), 7.14 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 6.86 (d, *J* = 3.0 Hz, 1H), 3.94 (s, 6H), 3.64 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.83, 165.18, 157.65, 151.59, 138.44, 133.77, 133.37, 131.03, 124.95, 119.56, 117.94, 115.21, 55.78, 52.66 ppm; HRMS (EI^+): *m/z*: calcd for $C_{18}H_{16}O_7$: 344.0896, Found: 344.0896.

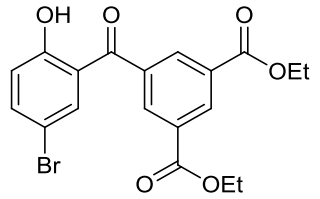


Diethyl 5-(5-fluoro-2-hydroxybenzoyl)isophthalate (14g). Yellow solid; yield 313 mg; 87%; mp 85-86 ℃; IR (KBr): ṽ = 3429, 3086, 2923, 2857, 1717, 1475, 1354, 1204, 1111, 1015, 841, 792, 738, 672, 481, 441 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.54 (s, 1H), 8.86 (s, 1H), 8.46 (s, 2H), 7.30-7.27 (m, 1H), 7.12 (dd, *J* = 8.7, 3.0 Hz, 1H), 7.05 (dd, *J* = 9.0, 4.5 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 4H), 1.40 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.81 (d,

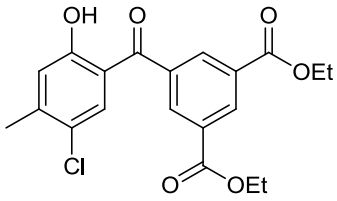
J = 2.3 Hz), 164.71, 159.51 (d, *J* = 1.5 Hz), 154.62 (d, *J* = 237.7 Hz), 137.90, 133.58, 133.45, 131.57, 124.71 (d, *J* = 24.0 Hz), 120.09 (d, *J* = 7.5 Hz), 118.09 (d, *J* = 6.0 Hz), 117.67 (d, *J* = 24.0 Hz), 61.87, 14.25 ppm; HRMS (EI^+): *m/z*: calcd for $C_{19}H_{17}FO_6$: 360.1009, Found: 360.1011.



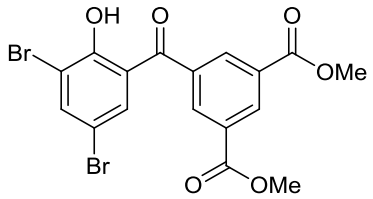
Dimethyl 5-(5-chloro-2-hydroxybenzoyl)isophthalate (14h). Yellow solid; yield 300 mg; 86%; mp 129-130 ℃; IR (KBr): ῦ = 3448, 3084, 2925, 2859, 1731, 1624, 1453, 1347, 1213, 992, 936, 823, 742, 696, 626, 532, 481 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.68 (s, 1H), 8.87 (s, 1H), 8.45 (s, 2H), 7.59 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 3.97 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.61, 165.11, 162.20, 139.71, 137.91, 134.79, 133.72, 133.59, 131.30, 120.75, 119.86, 110.68, 52.78 ppm; HRMS (EI^+): *m/z*: calcd for $C_{17}H_{13}ClO_6$: 348.0401, Found: 348.0403.



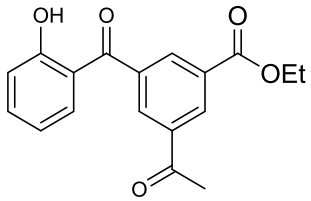
Diethyl 5-(5-bromo-2-hydroxybenzoyl)isophthalate (14i). Yellow solid; yield 349 mg; 83%; mp 134-135 ℃; IR (KBr): ῦ = 3414, 3074, 2984, 1714, 1616, 1458, 1211, 1105, 1015, 851, 744, 705, 641, 466 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.67 (s, 1H), 8.86 (s, 1H), 8.44 (s, 2H), 7.45 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 4H), 1.40 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.78, 164.66, 161.76, 137.78, 136.87, 133.59, 133.43, 131.81, 131.61, 123.79, 120.33, 119.24, 61.84, 14.23 ppm; HRMS (EI^+): *m/z*: calcd for $C_{19}H_{17}BrO_6$: 420.0209, Found: 420.0207.



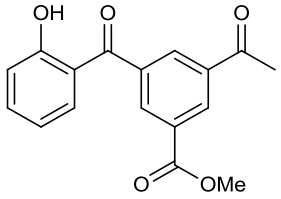
Diethyl 5-(5-chloro-2-hydroxy-4-methylbenzoyl)isophthalate (14j). Yellow solid; yield 321 mg; 82%; mp 136-137 ℃; IR (KBr): ṽ = 3422, 3081, 2992, 2926, 1723, 1620, 1471, 1349, 1231, 1118, 1018, 930, 862, 699, 594, 512, 486 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.69 (s, 1H), 8.85 (s, 1H), 8.43 (s, 2H), 7.37 (s, 1H), 6.96 (s, 1H), 4.42 (q, *J* = 7.2 Hz, 4H), 2.38 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.35, 164.72, 161.70, 146.54, 138.01, 133.44, 133.39, 132.21, 131.52, 124.46, 120.66, 117.56, 61.81, 20.90, 14.25 ppm; HRMS (EI^+): *m/z*: calcd for $C_{20}H_{19}ClO_6$: 390.0870, Found: 390.0872.



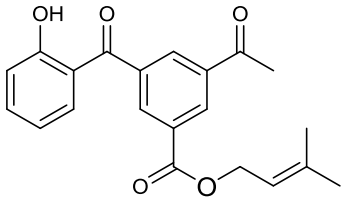
Dimethyl 5-(3,5-dibromo-2-hydroxybenzoyl)isophthalate (14k). Yellow solid; yield 368 mg; 78%; mp 200-201 ℃; IR (KBr): ṽ = 3422, 3072, 2926, 2859, 1728, 1632, 1428, 1335, 1248, 1171, 996, 885, 742, 691, 528, 418 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 12.24 (s, 1H), 8.88 (s, 1H), 8.45 (s, 2H), 7.90 (d, *J* = 1.8 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 3.97 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.29, 164.98, 158.77, 142.01, 137.41, 134.10, 134.05, 133.65, 131.46, 120.30, 113.59, 110.67, 52.81 ppm; HRMS (EI^+): *m/z*: calcd for $C_{17}H_{12}Br_2O_6$: 469.9001, Found: 469.9004.



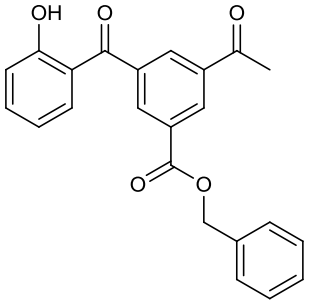
Ethyl 3-acetyl-5-(2-hydroxybenzoyl)benzoate (14l). Yellow solid; yield 287 mg; 92%; mp 58-59 ℃; IR (KBr): ṽ = 3356, 3079, 2983, 1714, 1683, 1622, 1561, 1441, 1358, 1287, 1231, 1165, 1030, 974, 910, 761, 707, 658, 595, 534 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 11.79 (s, 1H), 8.75 (d, *J* = 1.5 Hz, 1H), 8.48 (d, *J* = 1.2 Hz, 1H), 8.38 (d, *J* = 1.5 Hz, 1H), 7.53 (dd, *J* = 7.2, 6.9 Hz, 1H), 7.44 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.88 (dd, *J* = 7.8, 7.2 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 2.68 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.68, 196.24, 164.87, 163.35, 138.68, 137.44, 137.08, 133.77, 133.03, 132.27, 132.01, 131.54, 119.14, 118.71, 118.57, 61.88, 26.83, 14.26 ppm; HRMS (EI^+): *m/z*: calcd for $C_{18}H_{16}O_5$: 312.3166, Found: 312.3166.



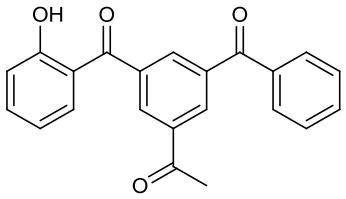
Methyl 3-acetyl-5-(2-hydroxybenzoyl)benzoate (14m). Yellow solid; yield 274 mg; 92%; mp 79-80 ℃; IR (KBr): ῦ = 3361, 3069, 2953, 1722, 1695, 1623, 1524, 1488, 1442, 1350, 1278, 1228, 960, 755, 662, 597 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.78 (s, 1H), 8.75 (dd, *J* = 1.5, 1.2 Hz, 1H), 8.47 (dd, *J* = 1.5, 1.2 Hz, 1H), 8.39 (d, *J* = 1.5 Hz, 1H), 7.52 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.43 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.87 (dd, *J* = 8.1, 0.9 Hz, 1H), 3.96 (s, 3H), 2.68 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.55, 196.16, 165.31, 163.31, 138.69, 137.46, 137.06, 133.80, 132.99, 132.38, 132.05, 132.09, 119.14, 118.69, 118.51, 52.73, 26.81 ppm; HRMS (EI^+): *m/z*: calcd for $C_{17}H_{14}O_5$: 298.2901, Found: 298.2901.



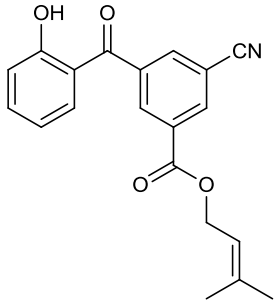
3-Methylbut-2-en-1-yl 3-acetyl-5-(2-hydroxybenzoyl)benzoate (14n). Yellow solid; yield 299 mg; 85%; oil; IR (KBr): ῦ = 3373, 3079, 2975, 2924, 1723, 1695, 1628, 1445, 1349, 1283, 1231, 1164, 926, 762 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.80 (s, 1H), 8.76 (dd, *J* = 1.8, 1.2 Hz, 1H), 8.48 (t, *J* = 1.2 Hz, 1H), 8.38 (d, *J* = 1.8 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 7.8 Hz, 1H), 5.45 (t, *J* = 6.6 Hz, 1H), 4.86 (d, *J* = 6.6 Hz, 2H), 2.68 (s, 3H), 1.78 (s, 3H), 1.77 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 199.73, 196.26, 164.95, 163.40, 140.02, 138.73, 137.49, 137.08, 133.81, 133.06, 132.23, 132.08, 131.67, 119.15, 118.74, 118.64, 118.07, 62.72, 26.83, 25.79, 18.13 ppm; HRMS (EI^+): *m/z*: calcd for $C_{21}H_{20}O_5$: 352.3805, Found: 352.3805.



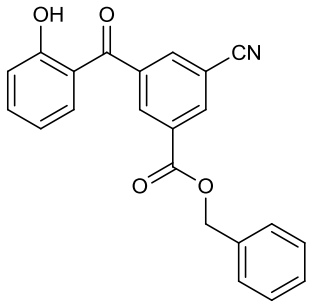
Benzyl 3-acetyl-5-(2-hydroxybenzoyl)benzoate (14o). Yellow solid; yield 307 mg; 82%; mp 118-119 ℃; IR (KBr): ṽ = 3366, 3072, 2963, 1725, 1695, 1628, 1449, 1352, 1285, 1230, 1167, 758, 701 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.79 (s, 1H), 8.78 (s, 1H), 8.51 (s, 1H), 8.39 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.44-7.43 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.87 (t, *J* = 7.8 Hz, 1H), 5.41 (s, 2H), 2.67 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.55, 196.16, 164.72, 163.31, 138.71, 137.44, 137.09, 135.25, 133.85, 132.99, 132.43, 132.10, 131.20, 128.66, 128.55, 128.42, 119.12, 118.70, 118.51, 67.50, 26.82 ppm; HRMS (EI^+): *m/z*: calcd for $C_{23}H_{18}O_5$: 374.3860, Found: 374.3860.



1-(3-Benzoyl-5-(2-hydroxybenzoyl)phenyl)ethanone (14p). Yellow solid; yield 313 mg; 91%; mp 145-146 ℃; IR (KBr): ṽ = 3369, 3063, 2924, 1738, 1691, 1661, 1625, 1483, 1444, 1347, 1283, 1233, 1152, 1008, 976, 908, 801, 760, 713, 652, 592, 532 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.78 (s, 1H), 8.54 (d, *J* = 1.8 Hz, 1H), 8.43 (d, *J* = 1.8 Hz, 1H), 8.22 (d, *J* = 1.8 Hz, 1H), 7.80 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.54-7.49 (m, 4H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.89 (t, *J* = 8.4 Hz, 1H), 2.68 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 199.63, 196.26, 194.76, 163.35, 138.56, 138.43, 137.35, 137.15, 136.30, 134.02, 133.34, 133.02, 132.16, 131.77, 130.02, 128.70, 119.16, 118.75, 118.54, 26.83 ppm; HRMS (EI^+): *m/z*: calcd for $C_{22}H_{16}O_4$: 344.3600, Found: 344.3600.



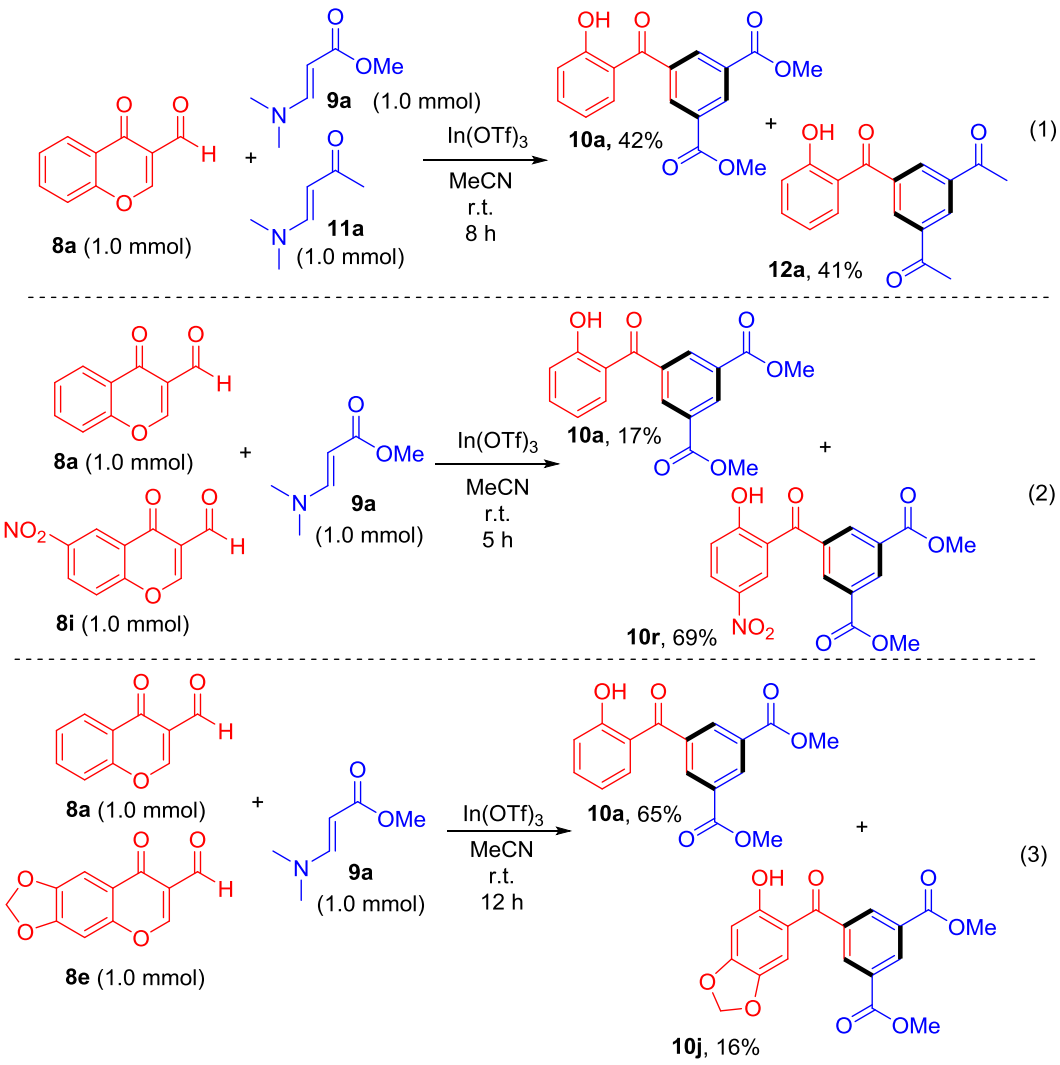
3-Methylbut-2-en-1-yl 3-cyano-5-(2-hydroxybenzoyl)benzoate (14q). Yellow solid; yield 271 mg; 81%; oil; IR (KBr): ṽ = 3431, 3074, 2975, 2932, 2237, 1724, 1628, 1484, 1446, 1379, 1344, 1278, 1233, 1158, 1120, 945, 760, 09, 662 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.63 (s, 1H), 8.49 (s, 1H), 8.48 (s, 1H), 8.07 (s, 1H), 7.55 (dd, *J* = 8.4, 7.8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.90 (dd, *J* = 7.8, 7.2 Hz, 1H), 5.43 (t, *J* = 7.2 Hz, 1H), 4.84 (d, *J* = 7.2 Hz, 2H), 1.77 (s, 3H), 1.76 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.04, 163.70, 163.38, 140.58, 139.21, 137.45, 135.76, 135.62, 133.59, 132.72, 132.25, 119.29, 118.88, 118.17, 117.63, 116.96, 113.37, 62.98, 25.77, 18.10 ppm; HRMS (EI^+): *m/z*: calcd for $C_{20}H_{17}NO_4$: 335.3533, Found: 335.3533.



Benzyl 3-cyano-5-(2-hydroxybenzoyl)benzoate (14r). White solid; yield 268 mg; 75%; mp 102-103 ℃; IR (KBr): ṽ = 3431, 3076, 2230, 1723, 1525, 1588, 1487, 1445, 1340, 1275, 1226, 1191, 1156, 1123, 985, 734, 700, 661 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.63 (s, 1H), 8.53 (t, *J* = 1.5 Hz, 1H), 8.51 (t, *J* = 1.5 Hz, 1H), 8.09 (t, *J* = 1.5 Hz, 1H), 7.56 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.39 (m, 6H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.91 (dd, *J* = 8.1, 7.2 Hz, 1H), 5.40 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.95, 163.56, 163.46, 139.36, 137.54, 135.99, 135.68, 134.88, 133.71, 132.71, 131.95, 128.79, 128.78, 128.56, 119.34, 118.97, 118.19, 116.92, 113.53, 67.95 ppm; HRMS (EI^+): *m/z*: calcd for $C_{22}H_{15}NO_4$: 357.3588, Found: 357.3588.

V. Control Experiments

To understand the chemoselectivity and mechanism of this reaction, control experiments were carried out between 3-formylchromones and β-enamino esters or β-enamino ketones (Scheme S1). For example, a reaction of **8a** (1.0 mmol) with β-aminoacrylate **9a** (1.0 mmol) and β-enaminoketone **11a** (1.0 mmol) under the optimized reaction conditions for 8 h provided products **10a** and **12a** in 42 and 41% yield, respectively (eq. 1, Scheme S1). This result did not show any significant difference in chemoselectivity between the different β-aminoacrylate and β-enaminoketone. Further control experiments were attempted to check the reactivity of the different 3-formylchromones. The reaction of β-enamino ester **9a** with 3-formylchromones **8a** (1.0 mmol) and **8i** (1.0 mmol) bearing an electron-withdrawing group afforded 2-hydroxybenzophenones **10a** and **10r** in 17 and 69% yield, respectively (eq. 2, Scheme S1), whereas treatment with 3-formylchromones **8a** (1.0 mmol) and **8e** (1.0 mmol) bearing electron-donating groups afforded compounds **10a** and **10j** in 65 and 16% yield, respectively (eq. 3, Scheme S1). These results suggested that molecules bearing an electron-withdrawing group on the chromone skeleton possess superior chemoselectivity compared to those bearing no substituent or electron-donating groups.

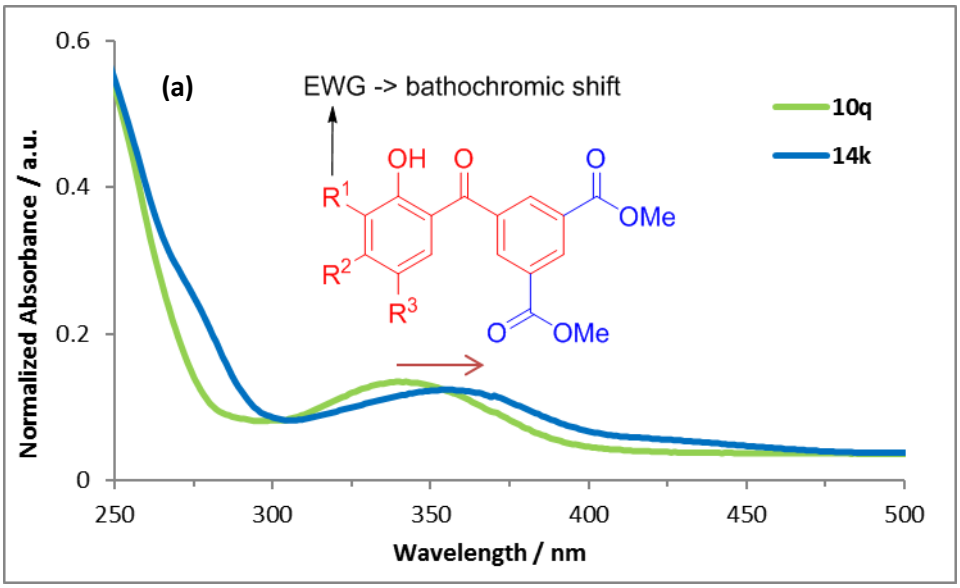


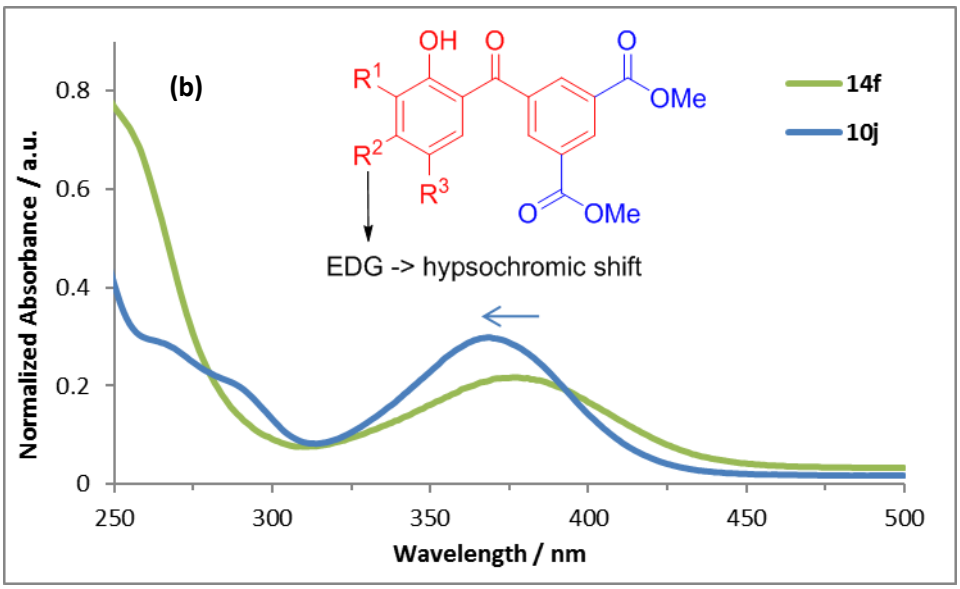
Scheme S1 Control experiments for the chemoselectivity between 4-oxo-4*H*-chromene-3-carbaldehydes and β-enamino carbonyls.

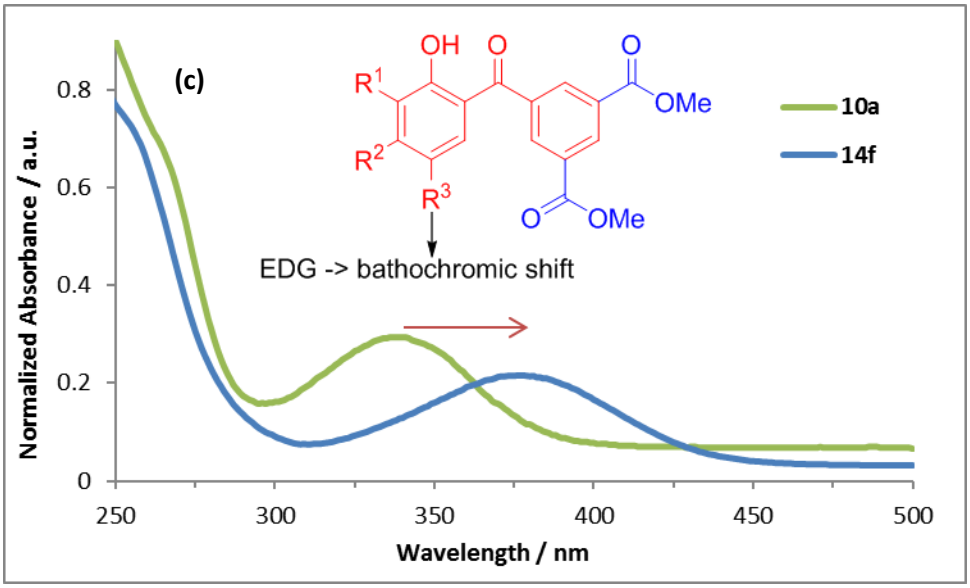
VI. Application as sun protection materials

Spectrophotometric measurements section

Absorbance spectra of the tested compounds were recorded at room temperature (298 K) on a UV/vis spectrophotometer (Optizen UV-3200). Tested compounds and oxybenzone (Aldrich, analytical standard, ≥ 98% pure) were prepared in an ethanol solvent (Sigma-Aldrich, ≥99.8% pure) at a concentration of 50 μM. The data were corrected for solvent background by the instrument's calibration using the solvent as a blank. The absorption spectra of samples in solution were obtained in the range of 250-500 nm (for the measurements and determinations of typical parameters for sun protection materials: UVA/UVB, 290-400 nm) using 1 cm quartz cell, and ethanol as a blank. The absorption data were obtained in the range of 250-500/290-400, every 1 nm, and 3 determinations were made at each point, followed by the data analysis (Table S2).[s3] Critical wavelength is defined as the wavelength λ_c where the area under the spectrum from 290 nm (the approximate lower wavelength limit of terrestrial sunlight) to λ_c, is 90% of the integral of the absorbance spectrum from 290 to 400 nm. Similar to the critical wavelength, the UVA/UVB-ratio is also a reduction of the complete spectral information to one number, characterizing in some way the shape of the spectrum in terms of the amount of UVA-coverage in relation to the amount of UVB-coverage. The *in vitro* SPF is used for rating the protection strength of sun protection materials. Most of the tested compounds showed similar or higher UV protection power than oxybenzone (OBZ, $SPF_{in\ vitro}$ = 2.12, at 25μM). Especially, compounds **10r**, **10s**, **10w**, and **10x** exhibited excellent protection power ($SPF_{in\ vitro,}$ range: 1.80-2.26, at 25μM), which were suitable for UVB protection. Compounds **12e** and **12f** also showed potent UVB protection strength. Compounds **10e**, **10f**, **10h-10k**, **and 10n** displayed good protection against UVA ($SPF_{in\ vitro,}$ range: 1.20-1.60, at 25μM).


(a)
EWG -> bathochromic shift
10q
14k
Normalized Absorbance / a.u.
Wavelength / nm
0.6
0.4
0.2
0
250
300
350
400
450
500
OH
O
O
OMe
O
OMe
R1
R2
R3


(b)
14f
10j
EDG -> hypsochromic shift
Normalized Absorbance / a.u.
Wavelength / nm
0.8
0.6
0.4
0.2
0
250
300
350
400
450
500
OH
O
O
OMe
O
OMe
R1
R2
R3


(c)
10a
14f
EDG -> bathochromic shift
Normalized Absorbance / a.u.
Wavelength / nm
0.8
0.6
0.4
0.2
0
250
300
350
400
450
500
OH
O
O
OMe
O
OMe
R1
R2
R3

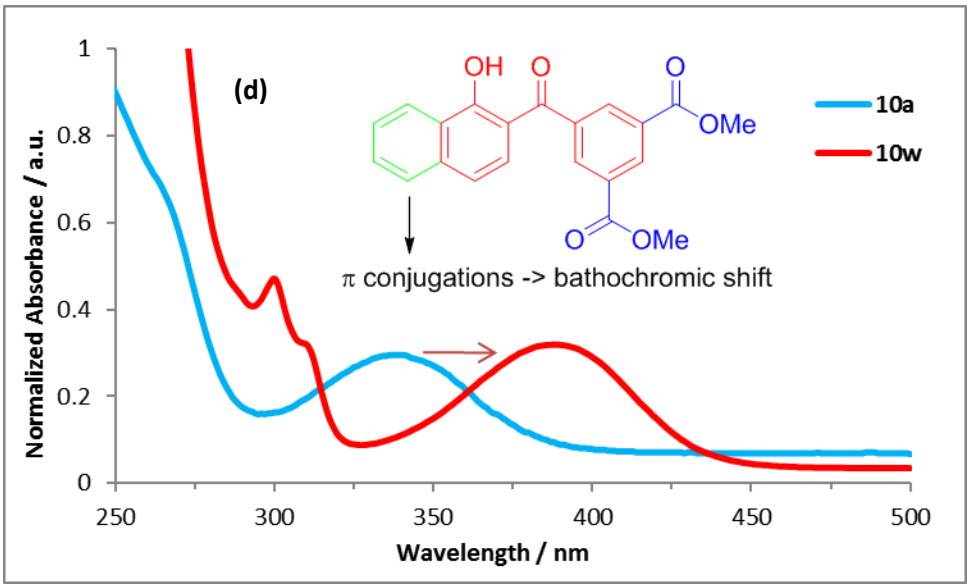


Fig. S2 Substituent effects on the UV absorbance spectra.

Table S2 Typical parameters of sun protection materials[s3]

Compound	**λ_c (nm)**	**UVA/UVB**	**$SPF_{in\ vitro}$**
10a	377	1.06	1.25 ± 0.04
10b	376	1.07	1.27 ± 0.04
10c	373	1.08	1.37 ± 0.06
10d	380	1.00	1.19 ± 0.01
10e	379	1.85	1.27 ± 0.04
10f	383	1.46	1.21 ± 0.04
10g	384	1.31	1.19 ± 0.03
10h	381	1.55	1.29 ± 0.04
10i	390	1.74	1.17 ± 0.01
10j	388	1.79	1.60 ± 0.09

10k	388	1.78	1.36 ± 0.06
10l	387	0.99	1.16 ± 0.03
10m	379	1.22	1.25 ± 0.04
10n	391	1.86	1.21 ± 0.01
10o	385	1.03	1.12 ± 0.02
10p	383	1.07	1.14 ± 0.01
10q	380	1.12	1.24 ± 0.02
10r	384	0.48	1.81 ± 0.06
10s	382	0.42	2.26 ± 0.05
10t	381	1.18	1.18 ± 0.06
10u	383	1.05	1.15 ± 0.06
10v	385	1.15	1.22 ± 0.08
10w	391	0.61	1.92 ± 0.08
10x	391	0.62	1.87 ± 0.08
12a	372	1.03	1.44 ± 0.09
12b	389	1.27	1.21 ± 0.04
12c	375	0.64	1.55 ± 0.05
12d	384	1.02	1.23 ± 0.04

12e	382	0.62	1.31 ± 0.04
12f	388	0.74	1.14 ± 0.06
14a	378	0.90	1.24 ± 0.05
14b	374	1.07	1.34 ± 0.05
14c	379	0.95	1.20 ± 0.02
14d	378	1.15	1.23 ± 0.08
14e	381	1.51	1.24 ± 0.02
14f	391	1.86	1.21 ± 0.07
14g	377	1.27	1.33 ± 0.05
14h	380	1.15	1.21 ± 0.01
14i	380	1.13	1.20 ± 0.03
14j	379	1.27	1.23 ± 0.04
14k	386	1.00	1.17 ± 0.06
14l	372	0.95	1.42 ± 0.07
14m	371	1.04	1.48 ± 0.04
14n	373	1.04	1.38 ± 0.08
14o	379	1.04	1.21 ± 0.01
14p	370	0.79	1.61 ± 0.02

14q	378	1.02	1.23 ± 0.01
14r	377	1.05	1.25 ± 0.02
OBZ	363	0.46	2.12 ± 0.04

Theoretical investigations

Molecular structures were built based on CCDC 918116,[s4] and the geometries were successively optimized at the semiempirical PM6, RHF/AM1, RHF/3-21G and DFT/(B3LYP/6-31G++**) levels of theory. Geometries of all structures were fully optimized and normal mode analysis was used to confirm the nature of the stationary points and to evaluate the thermochemical properties. Reported thermochemical properties include zero-point energies (ZPEs) without scaling and were calculated at 1 atm and 298.15 K. Free energies in solution were computed on the structures optimized in the gas phase at the B3LYP/6-311G++** level of theory with the Integral-Equation-Formalism Polarizable Continuum Model (IEF-PCM) using ethanol as solvent.[s5] Cartesian coordinates based on the bond lengths and angles of the optimized structures of the tested compound were used as inputs for theoretical studies of absorption spectra by means of PCM-TD-DFT at the same level of theory as B3LYP/6-311G++**. The lowest 12 singlet−singlet excitations have been computed with their respective wavelengths, transition energies, main transition configurations, and oscillator strengths. All the calculations were run with Gaussian 09[s6] at the Supercomputing Center of Korea Institute of Science and Technology Information.

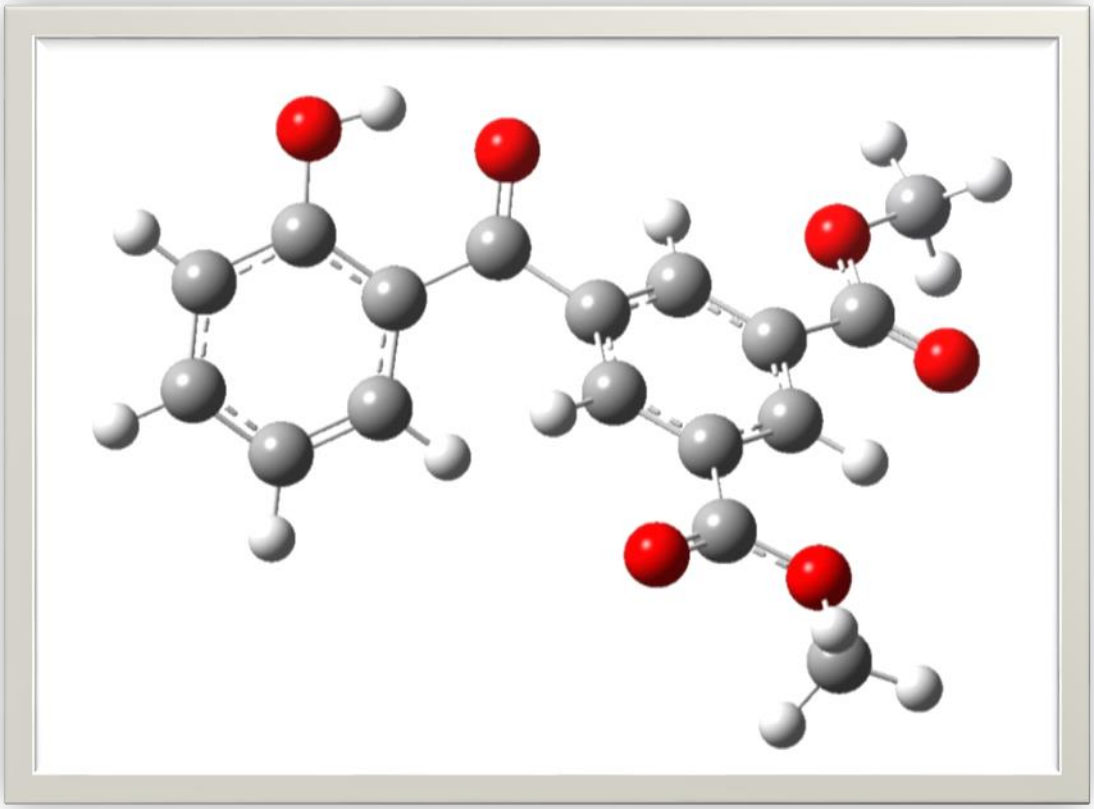


Fig. S3 DFT/B3LYP/6-311G++** calculated structure for compound **10a**, with implicit IEF-PCM solvation (EtOH).

Calculations with implicit IEF-PCM solvation (EtOH)

Dimethyl 5-(2-hydroxybenzoyl)isophthalate (**10a**)

B3LYP/6-311G++** Geometry

O	-4.31960900	-1.60831500	-1.37130400
O	-1.75864500	-1.95729000	-1.32849600
O	2.90647100	3.11821900	-0.13813900
O	4.36834700	-1.54378100	0.45477000
O	0.75186300	3.64218700	-0.52776500
O	2.81162700	-3.16601800	0.34081200
C	-3.81093800	1.13650300	1.70302100
C	-5.08296900	0.82030500	1.20515100
C	-5.23454300	-0.08887600	0.17000200
C	-4.11180000	-0.70389700	-0.39579400
C	-2.80841600	-0.35894300	0.06014000
C	-2.69447900	0.55348300	1.13192800
C	-1.63807600	-0.98312600	-0.56879000
C	-0.25659800	-0.45940500	-0.32298900
C	0.03833100	0.90306300	-0.38113100
C	0.77413200	-1.38222300	-0.12086700
C	2.08572900	-0.94123800	0.05893800
C	2.37566900	0.42434100	0.00213200
C	1.35506300	1.34621700	-0.22817300
C	1.61483000	2.81434900	-0.31756600
C	3.21430200	-1.88921700	0.30462600
C	3.25590200	4.52007900	-0.20493000
C	3.83674700	-4.16056000	0.56851300
H	-3.44343900	-2.00097900	-1.59410800
H	-5.96263200	1.28010700	1.64109100
H	-6.21380500	-0.35460000	-0.20906300
H	-1.71483800	0.78427600	1.52856100
H	-0.73993300	1.63149800	-0.56725600
H	0.54703000	-2.43917100	-0.09757600
H	4.32858400	4.55718000	-0.03455200
H	2.72360600	5.07687400	0.56674300

H	3.00764600	4.92245800	-1.18739700
H	4.32019700	-3.98825100	1.53049700
H	3.31699800	-5.11498000	0.56513000
H	4.57924300	-4.12330700	-0.22904400
H	3.39605400	0.75588500	0.13359700
H	-3.70246200	1.82786800	2.52909300

B3LYP/6-311G++** Energy + ZPE = -1107.700605

B3LYP/6-311G++** Free energy in EtOH = -1107.752642

Number of imaginary frequencies = 0

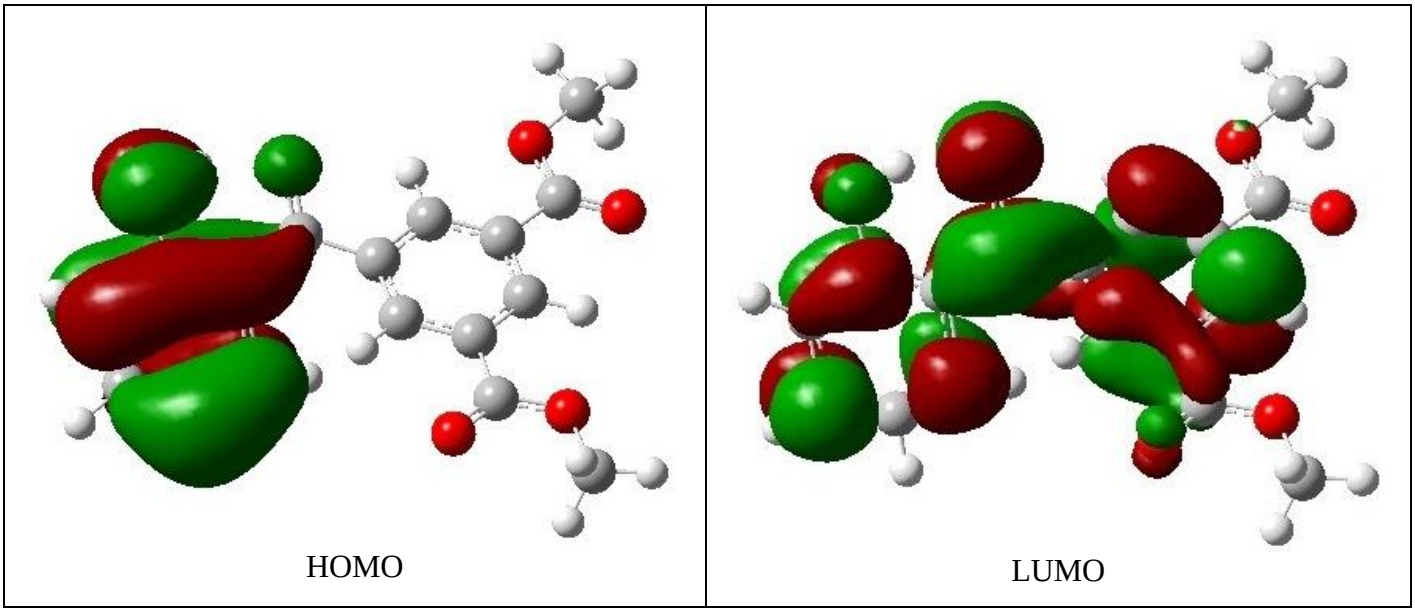


Fig. S4 View of the ground/excited state frontier molecular orbitals (MOs) of compound **10a** generated from TD-DFT/B3PW91/6-311G++** geometry optimization.

Table S3 $\lambda^{(1)}_{max}$ (in nm) Provided by TD-B3LYP, TD-B3PW91, TD-PBE0, TD-M062X, and TD-CAM-B3LYP/6-311G++** in ethanol[a]

Compound	$\lambda^{(1)}_{max}$					
	B3LYP	B3PW91	PBE0	M062X	CAM-B3LYP	Experimental
10a	348 nm	344 nm	336 nm	303 nm	307 nm	341 nm

[a] All geometries are obtained at the B3LYP/6-311G++** level. During the calculations, bulk solvent effects are modelized by the IEF-PCM model.

VII. References

s1. (*a*) Y. Jiang, V. Z. Y. Khong, E. Lourdusamy and C.-M. Park, *Chem. Commun.*, 2012, **48**, 3133-3135; (*b*) E. Lourdusamy, L. Yao and C.-M. Park, *Angew. Chem., Int. Ed.*, 2010, **49**, 7963-7967.

s2. (*a*) V. Eschenbrenner-Lux, P. Küchler, S. Ziegler, K. Kumar and H. Waldmann, *Angew. Chem., Int. Ed.*, 2014, **53**, 2134-2137; (*b*) W. M. Abdou, M. D. Khidre and M. R. Mahran, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1991, **61**, 83-90.

s3. (*a*) J. Batzer, A. Bleckmann, H. Lerg, F. Schwanke and T. Schlager, *Int. J. Cosmet. Sci.*, 2015; (*b*) E. A. Dutra, D. A. Goncalves da Costa e Oliveira, E. R. M. Kedor-Hackmann and M. I. R. M. Santoro, *Rev. Bras. Cienc. Farm.*, 2004, **40**, 381-385; (*c*) J. Akrman, L. Kubáč, H. Bendová, D. Jírová and K. Kejlová, *Int. J. Cosmet. Sci.*, 2009, **31**, 119-129; (*d*) P. Schuch André, S. Moraes Maria Carolina, T. Yagura and F. M. Menck Carlos, *Environ. Sci. Technol.*, 2014, **48**, 11584-11590.

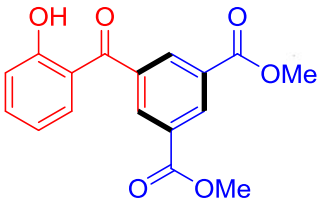
s4. A. Bari, S. S. Ali, A. Kadi, I. A. Hashmi and S. W. Ng, *Chem. Heterocycl. Compd.*, 2014, **49**, 1723-1731.

s5. (*a*) T. N. V. Karsili, B. Marchetti, M. N. R. Ashfold and W. Domcke, *J. Phys. Chem. A*, 2014, **118**, 11999-12010; (*b*) B. A. M. Corrêa, A. S. Gonçalves, A. M. T. de Souza, C. A. Freitas, L. M. Cabral, M. G. Albuquerque, H. C. Castro, E. P. dos Santos and C. R. Rodrigues, *J. Phys. Chem. A*, 2012, **116**, 10927-10933; (*c*) B. M. Baughman, E. Stennett, R. E. Lipner, A. C. Rudawsky and S. J. Schmidtke, *J. Phys. Chem. A*, 2009, **113**, 8011-8019; (*d*) J. Preat, D. Jacquemin, V. Wathelet, J.-M. André and E. A. Perpète, *J. Phys. Chem. A*, 2006, **110**, 8144-8150.

s6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.

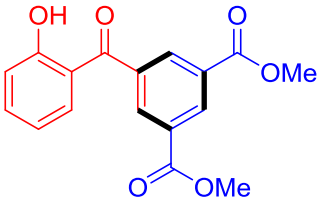
VIII. ^{1}H NMR and ^{13}C NMR Spectra for All Compounds: 10, 12 and 14

^{1}H NMR of Compound **10a**

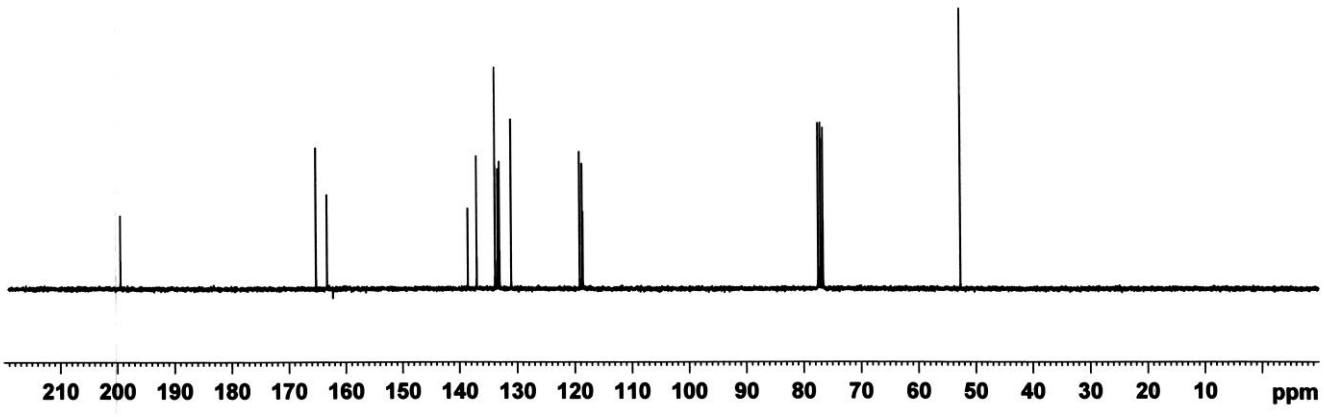


300 MHz, $CDCl_3$

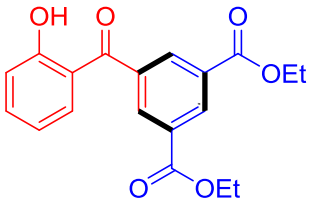
^{13}C NMR of Compound **10a**



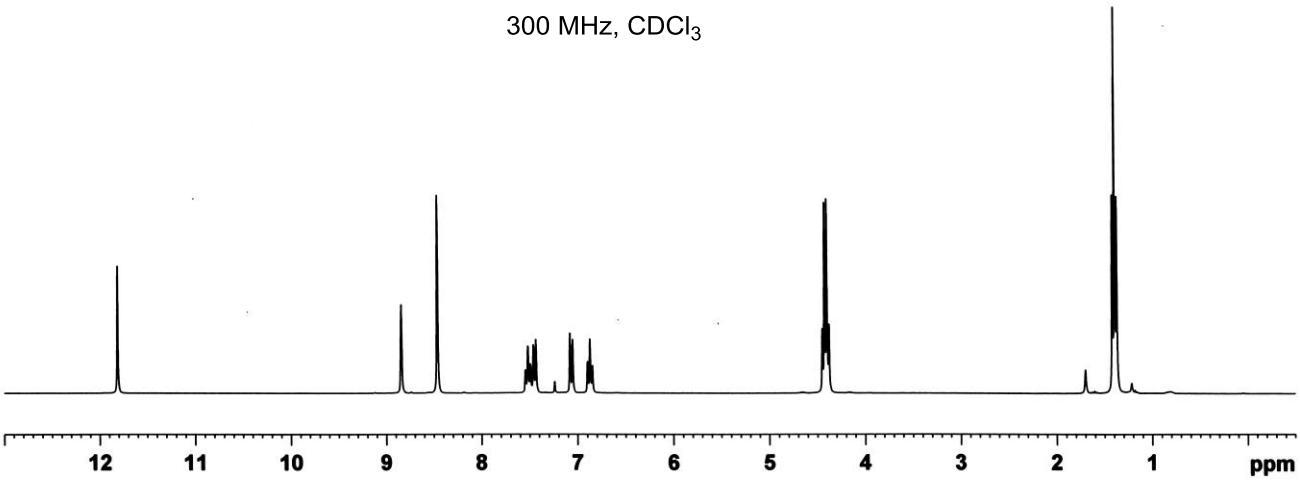
75 MHz, $CDCl_3$



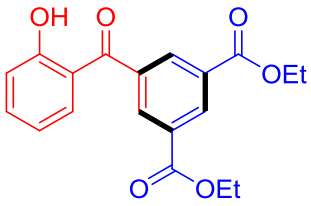
^{1}H NMR of Compound **10b**



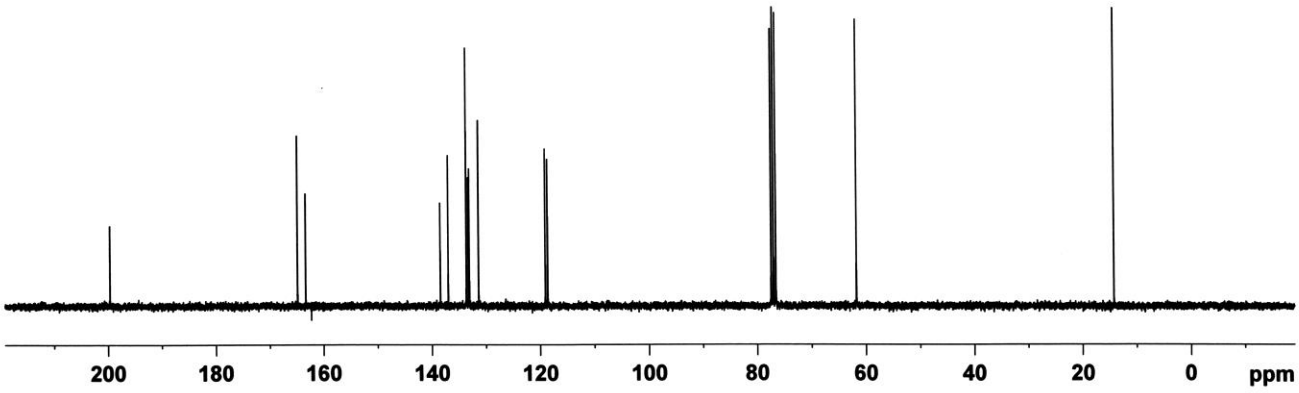
300 MHz, $CDCl_3$



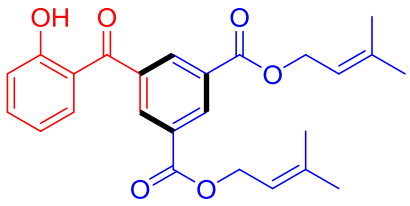
^{13}C NMR of Compound **10b**



75 MHz, $CDCl_3$

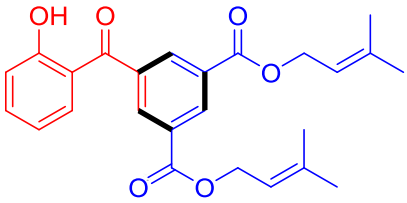


^{1}H NMR of Compound **10c**

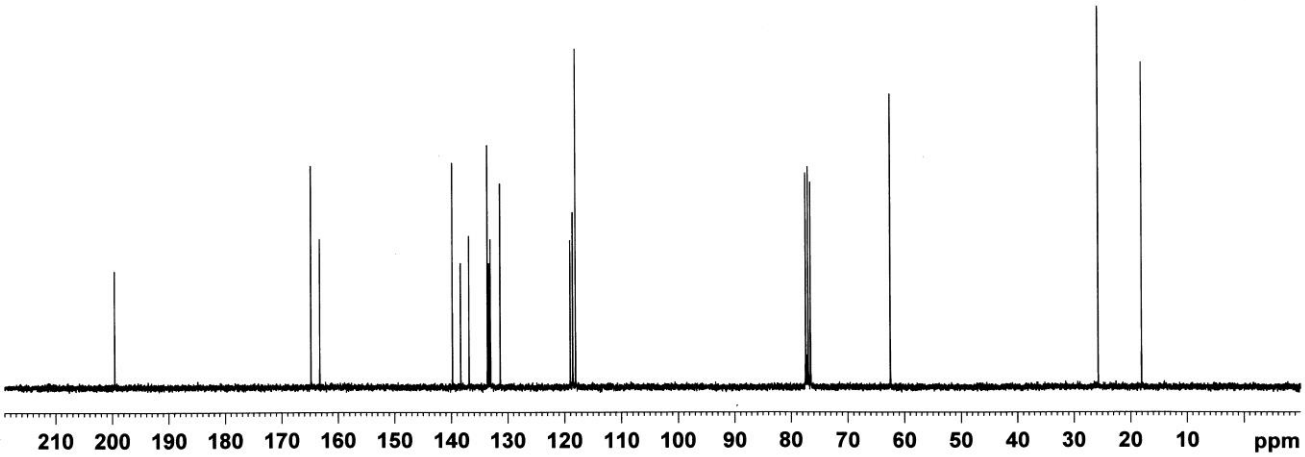


300 MHz, $CDCl_3$

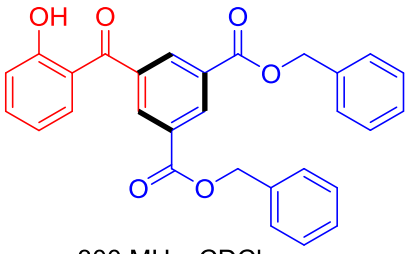
^{13}C NMR of Compound **10c**



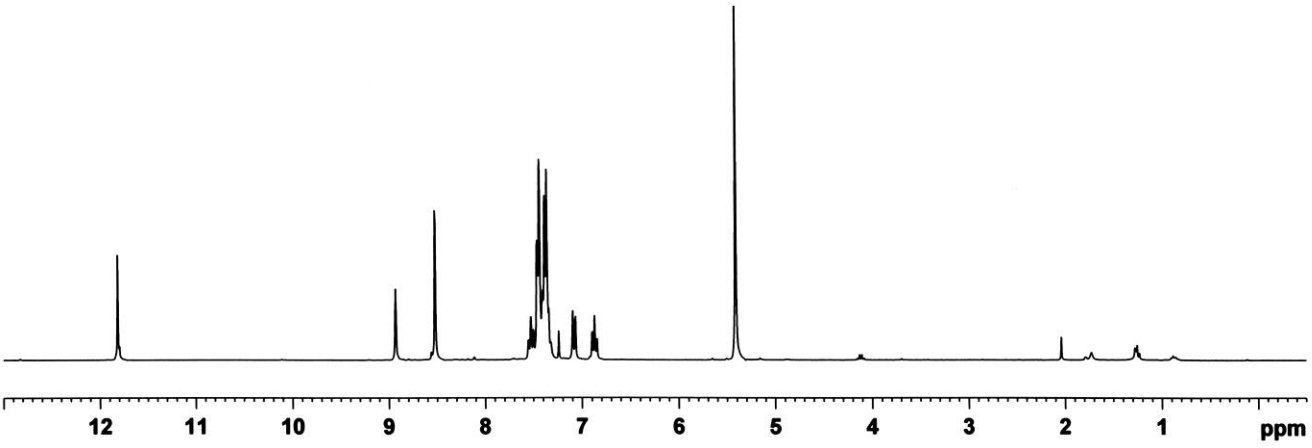
75 MHz, $CDCl_3$



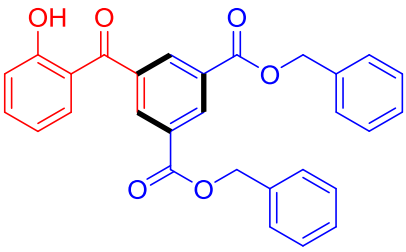
^{1}H NMR of Compound **10d**



300 MHz, $CDCl_3$

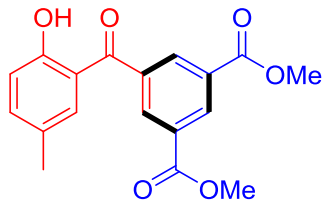


^{13}C NMR of Compound **10d**

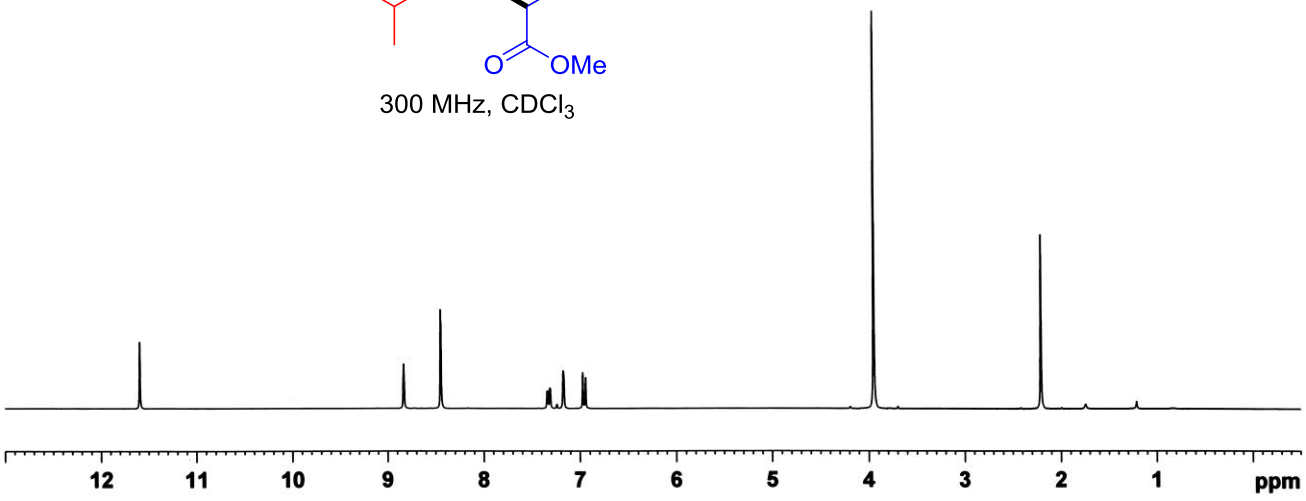


75 MHz, $CDCl_3$

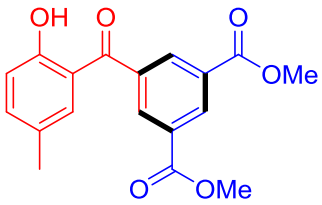
^{1}H NMR of Compound **10e**



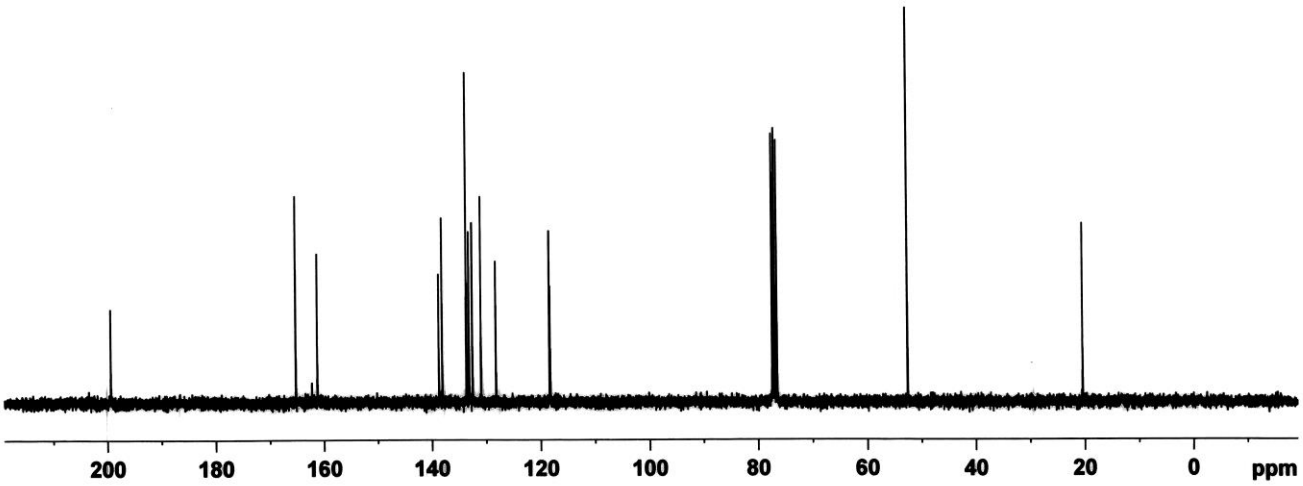
300 MHz, $CDCl_3$



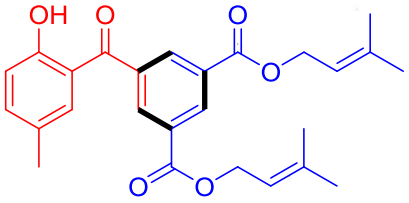
^{13}C NMR of Compound **10e**



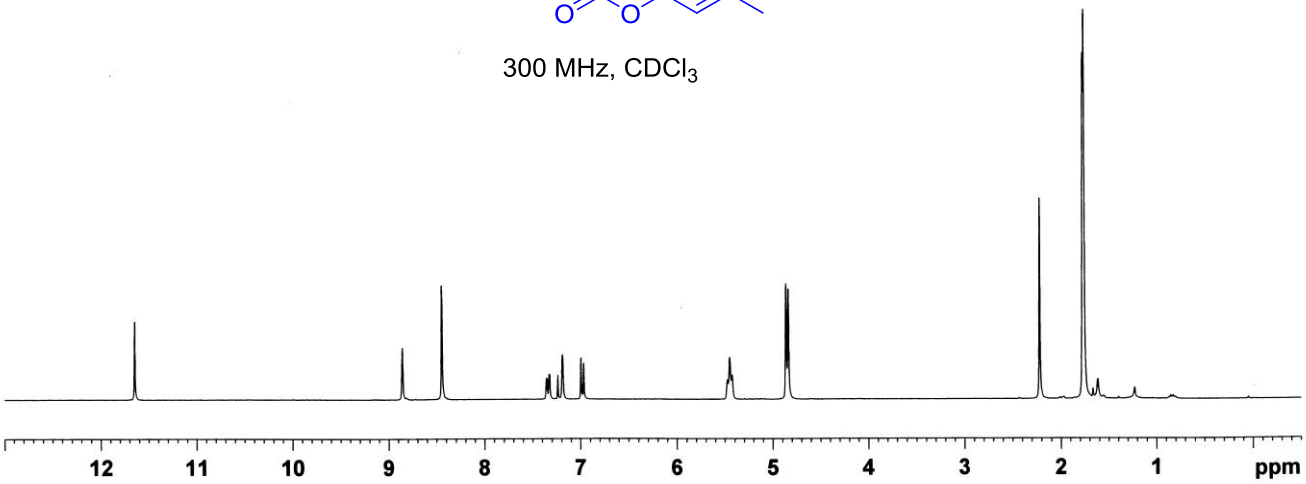
75 MHz, $CDCl_3$



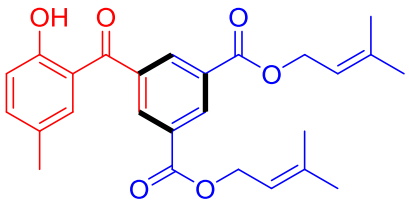
^{1}H NMR of Compound **10f**



300 MHz, $CDCl_3$

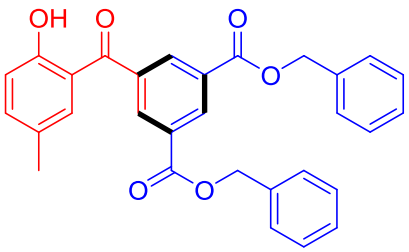


^{13}C NMR of Compound **10f**

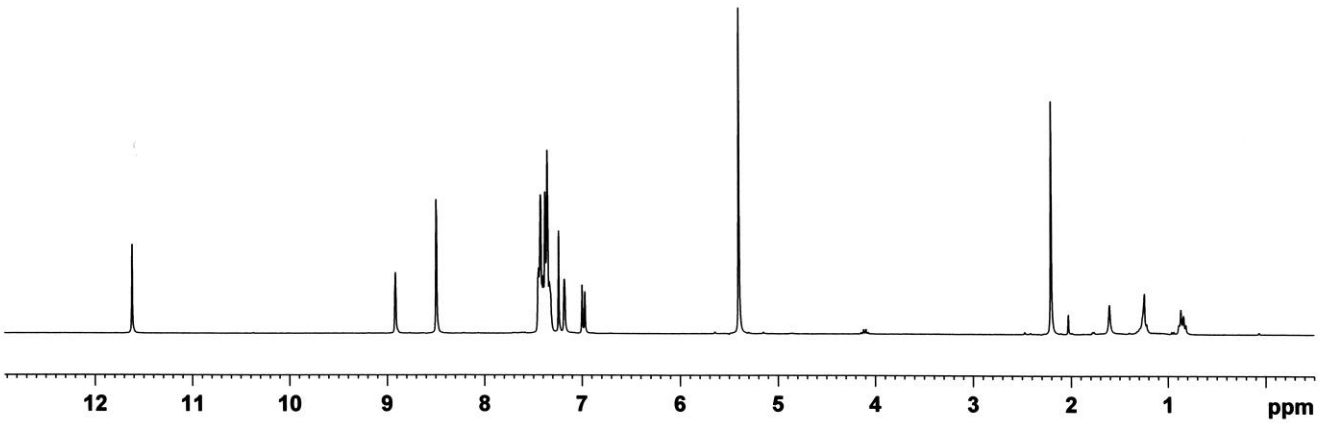


75 MHz, $CDCl_3$

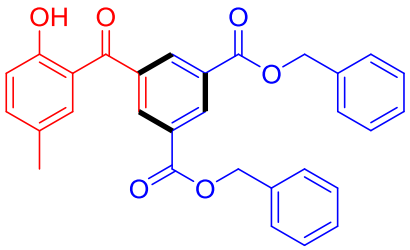
^{1}H NMR of Compound **10g**



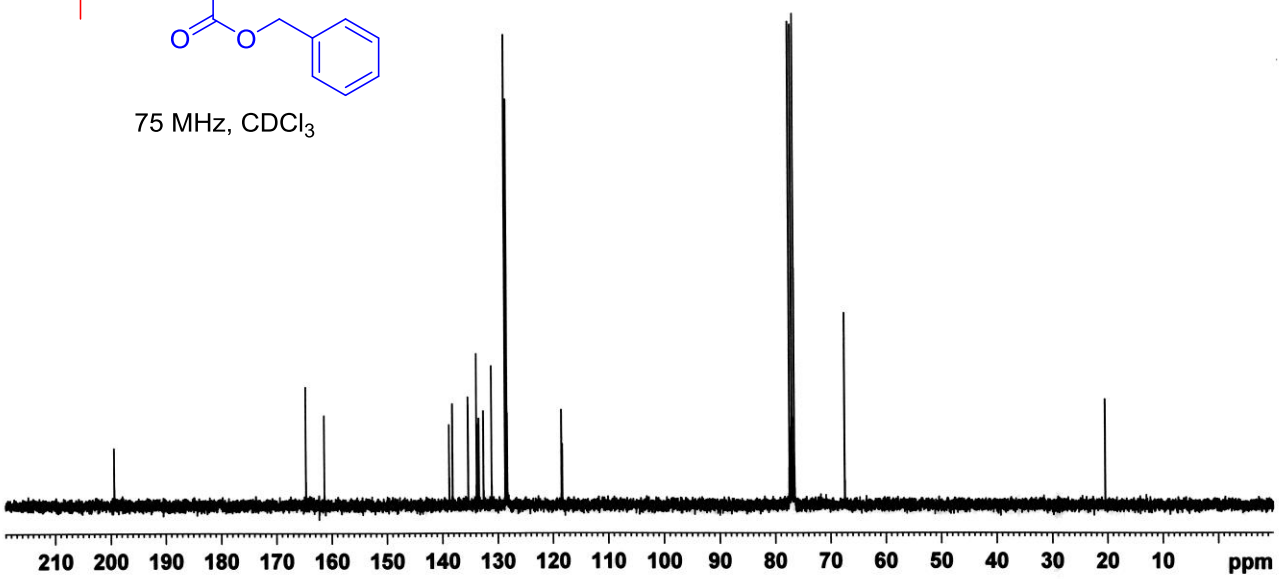
300 MHz, $CDCl_3$



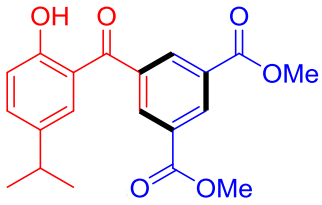
^{13}C NMR of Compound **10g**



75 MHz, $CDCl_3$

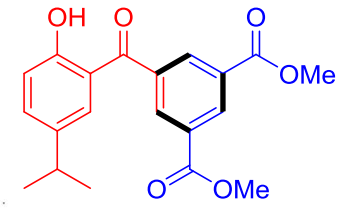


^{1}H NMR of Compound **10h**

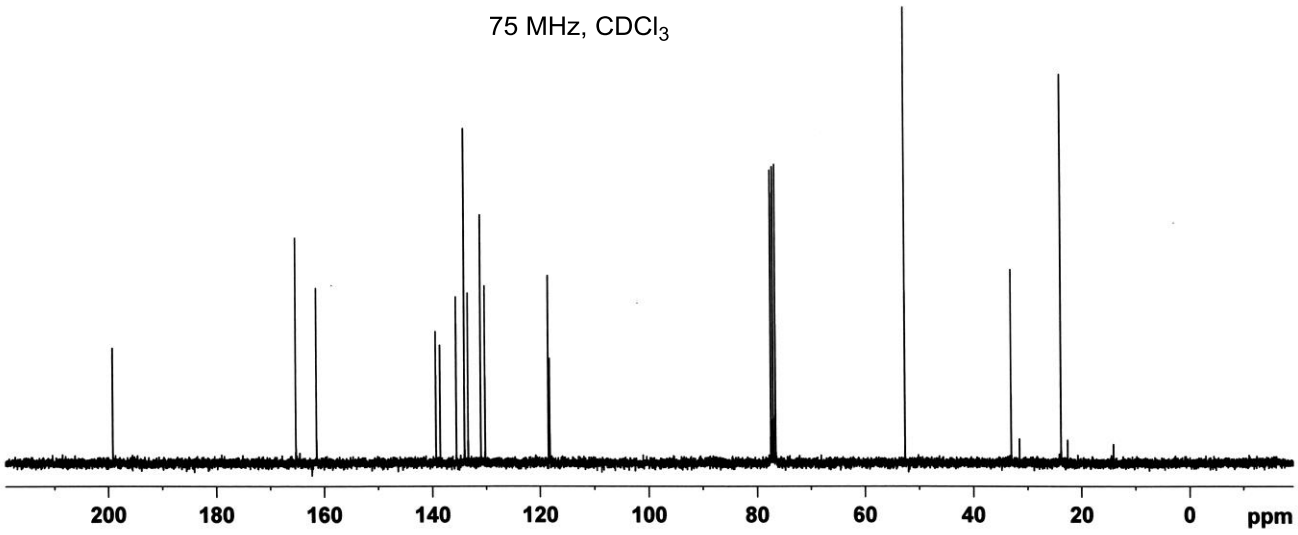


300 MHz, $CDCl_3$

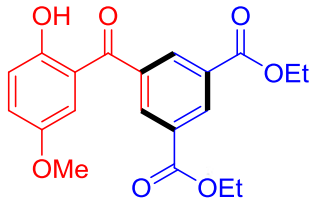
^{13}C NMR of Compound **10h**



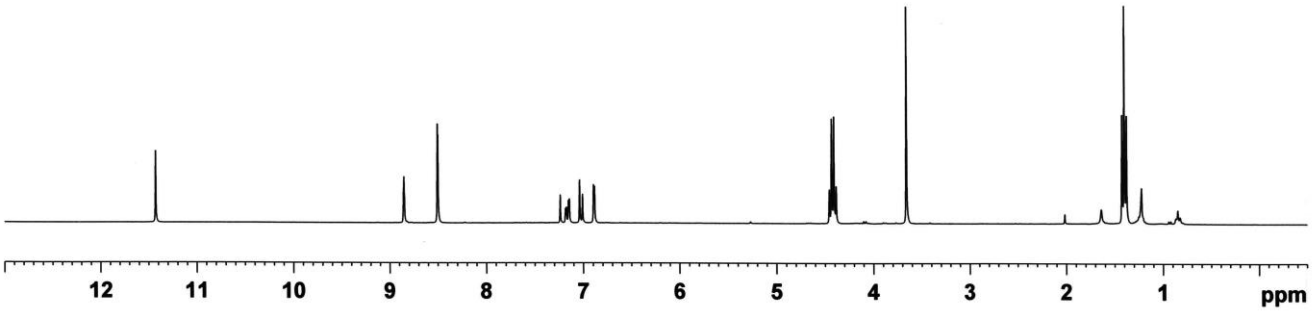
75 MHz, $CDCl_3$



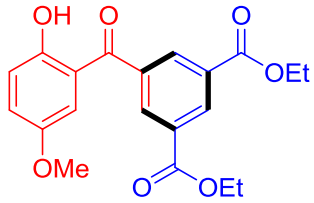
^{1}H NMR of Compound **10i**



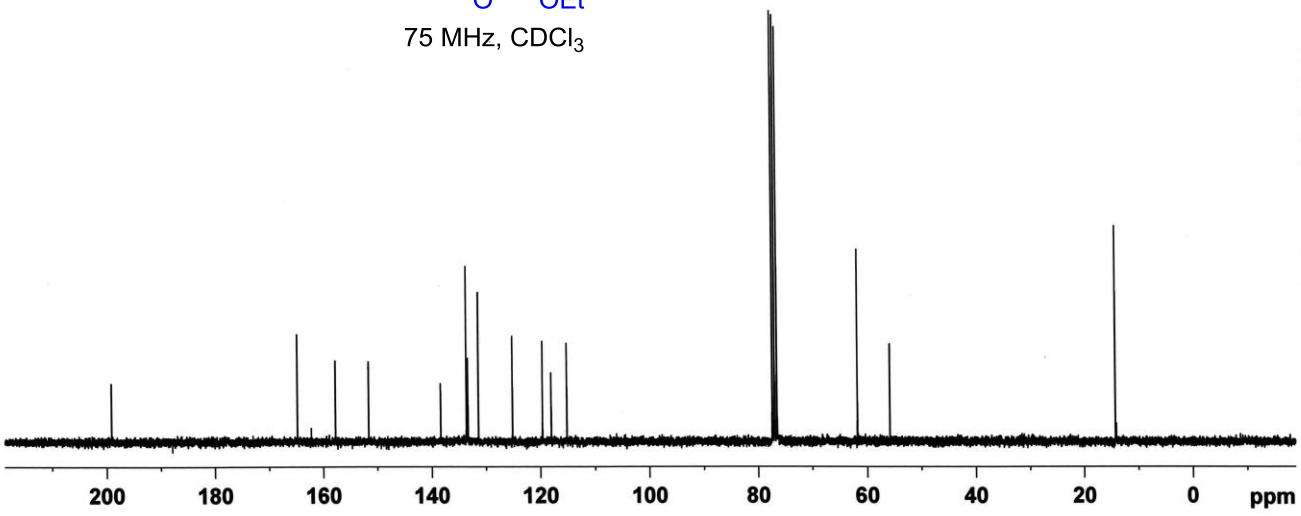
300 MHz, $CDCl_3$



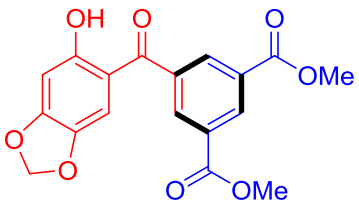
^{13}C NMR of Compound **10i**



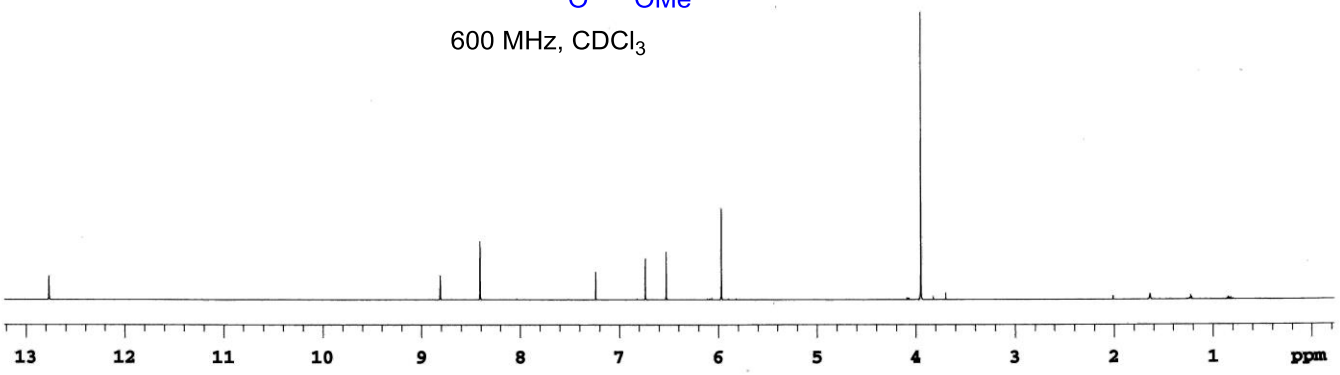
75 MHz, $CDCl_3$



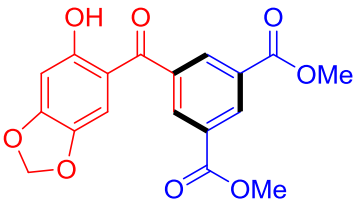
^{1}H NMR of Compound **10j**



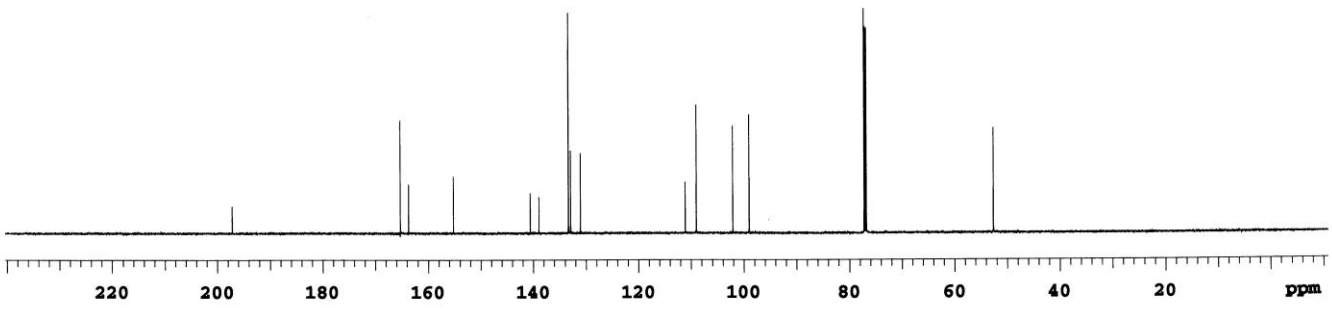
600 MHz, $CDCl_3$



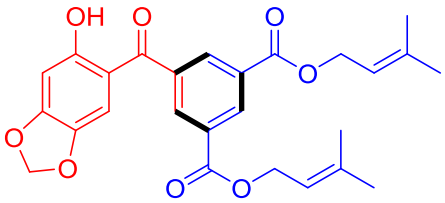
^{13}C NMR of Compound **10j**



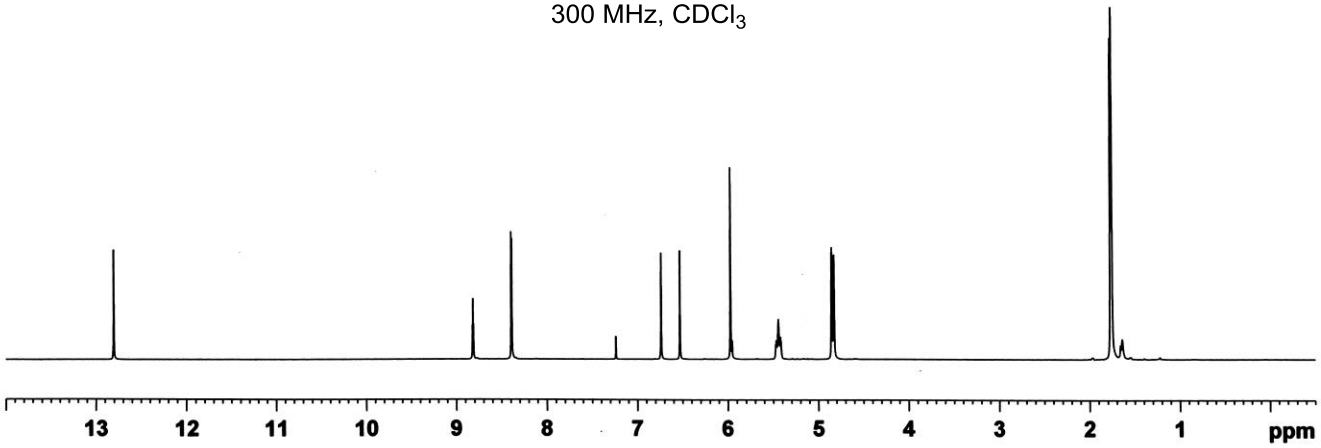
150 MHz, $CDCl_3$



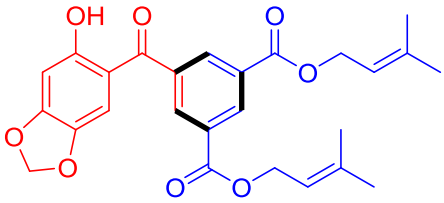
^{1}H NMR of Compound **10k**



300 MHz, $CDCl_3$

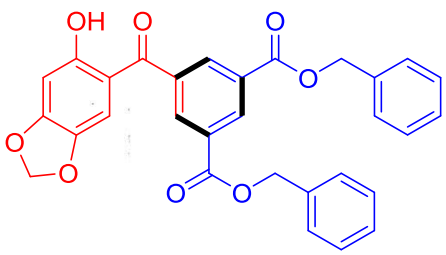


^{13}C NMR of Compound **10k**

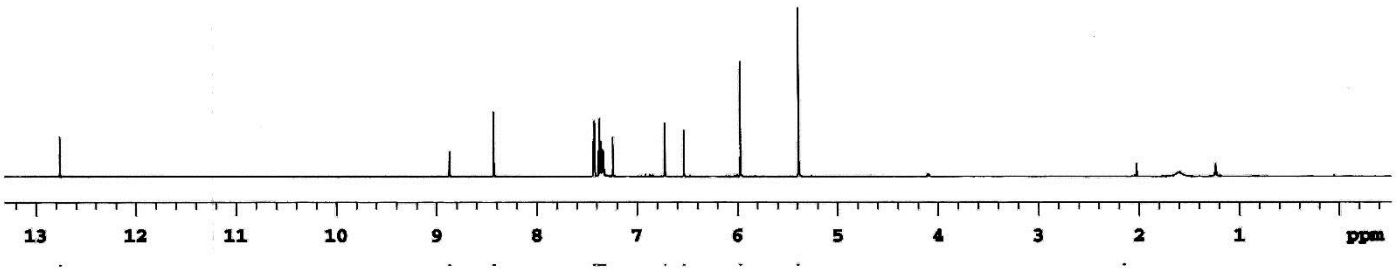


75 MHz, $CDCl_3$

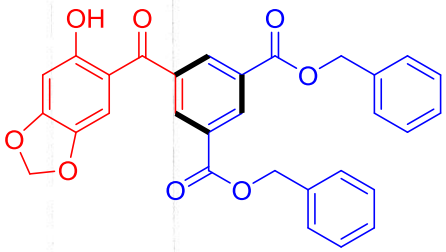
^{1}H NMR of Compound **10l**



600 MHz, $CDCl_3$

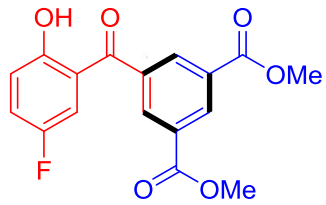


^{13}C NMR of Compound **10l**



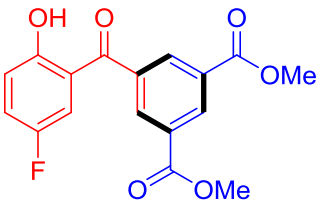
150 MHz, $CDCl_3$

^{1}H NMR of Compound **10m**

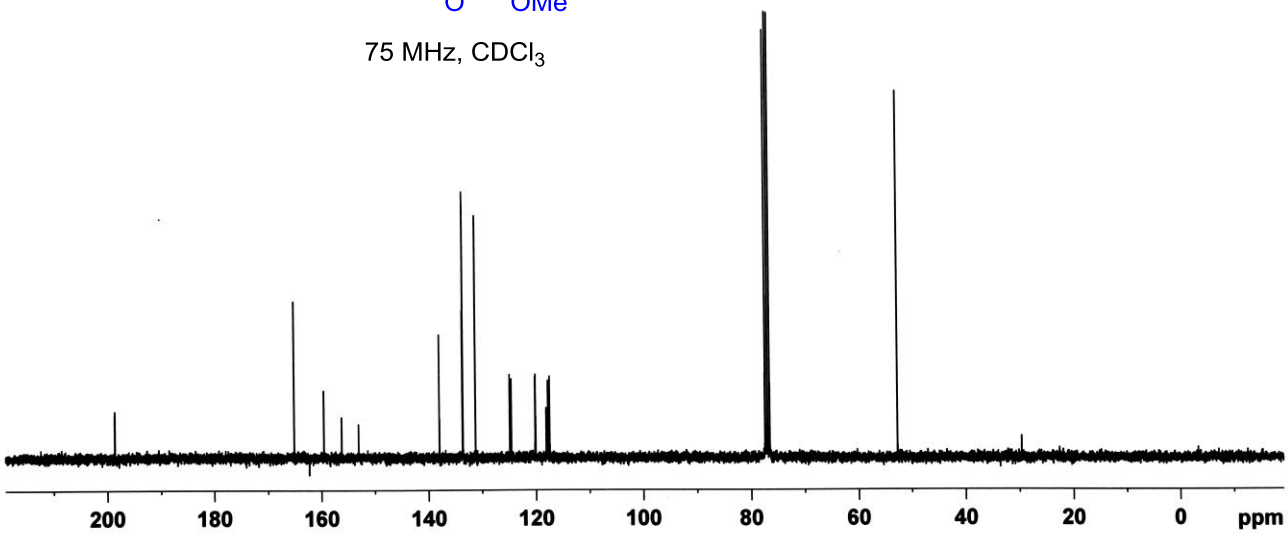


300 MHz, $CDCl_3$

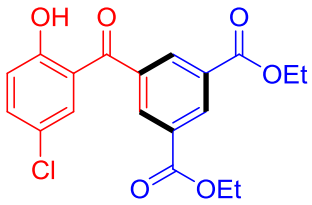
^{13}C NMR of Compound **10m**



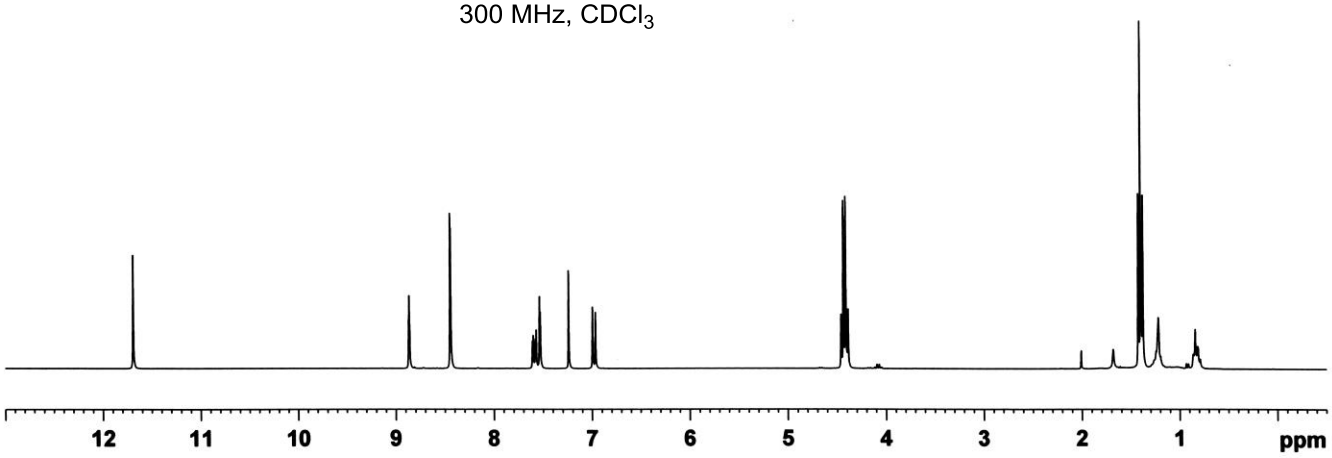
75 MHz, $CDCl_3$



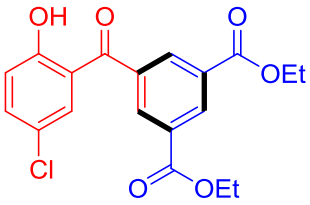
^{1}H NMR of Compound **10n**



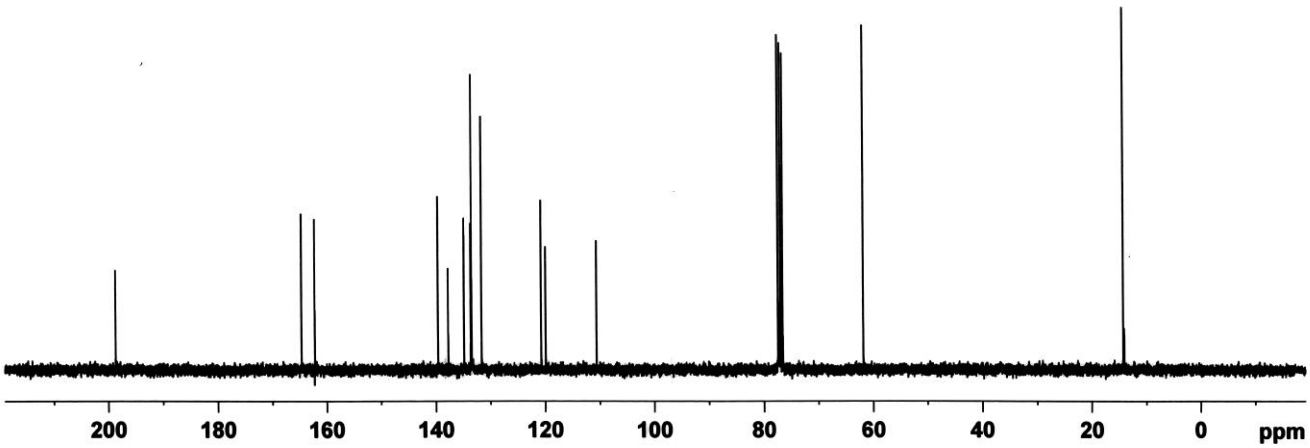
300 MHz, $CDCl_3$



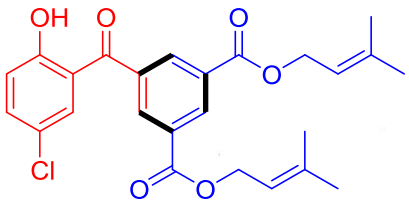
^{13}C NMR of Compound **10n**



150 MHz, $CDCl_3$

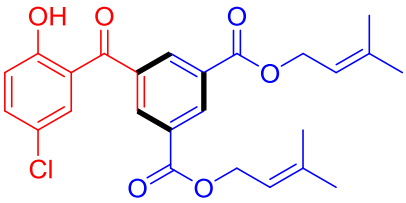


^{1}H NMR of Compound **10o**

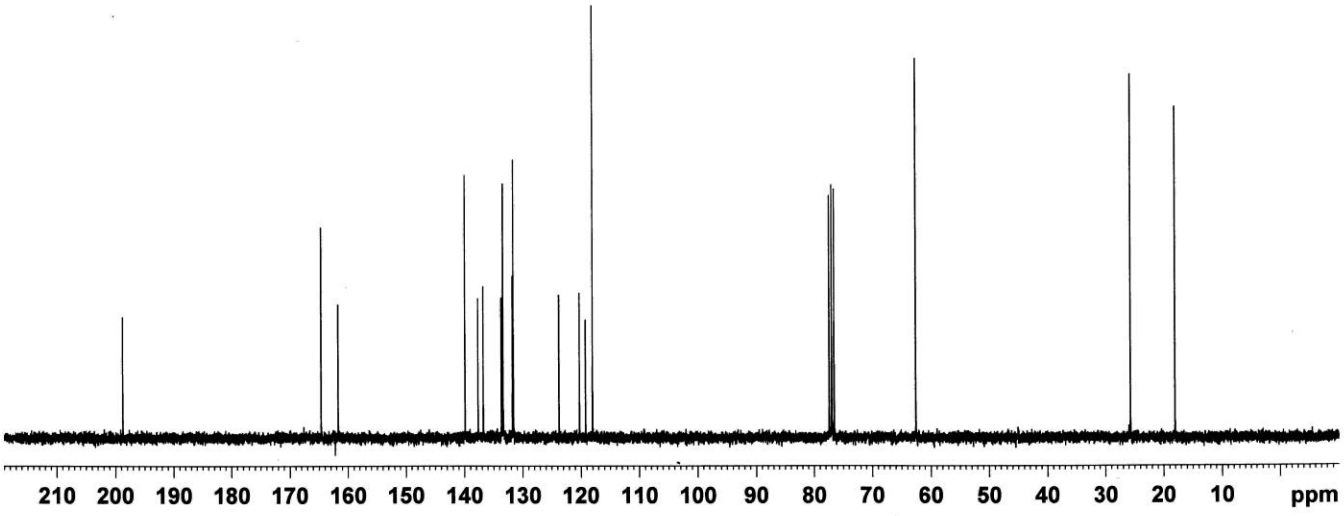


300 MHz, $CDCl_3$

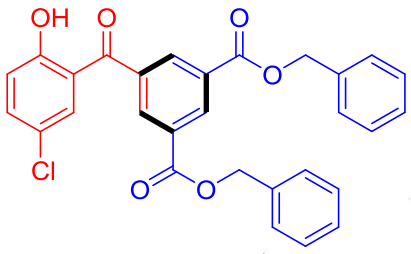
^{13}C NMR of Compound **10o**



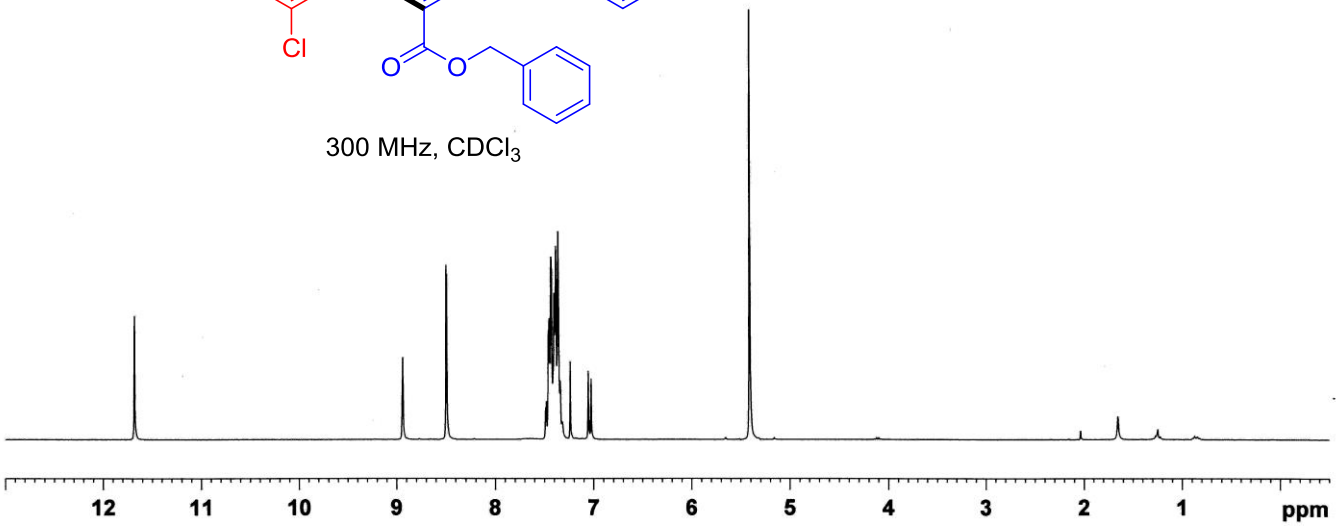
75 MHz, $CDCl_3$



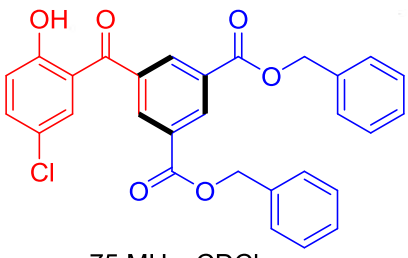
^{1}H NMR of Compound **10p**



300 MHz, $CDCl_3$

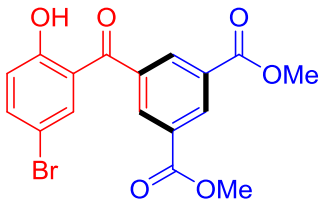


^{13}C NMR of Compound **10p**



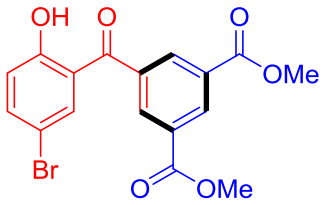
75 MHz, $CDCl_3$

^{1}H NMR of Compound **10q**



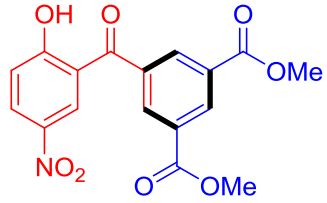
300 MHz, $CDCl_3$

^{13}C NMR of Compound **10q**

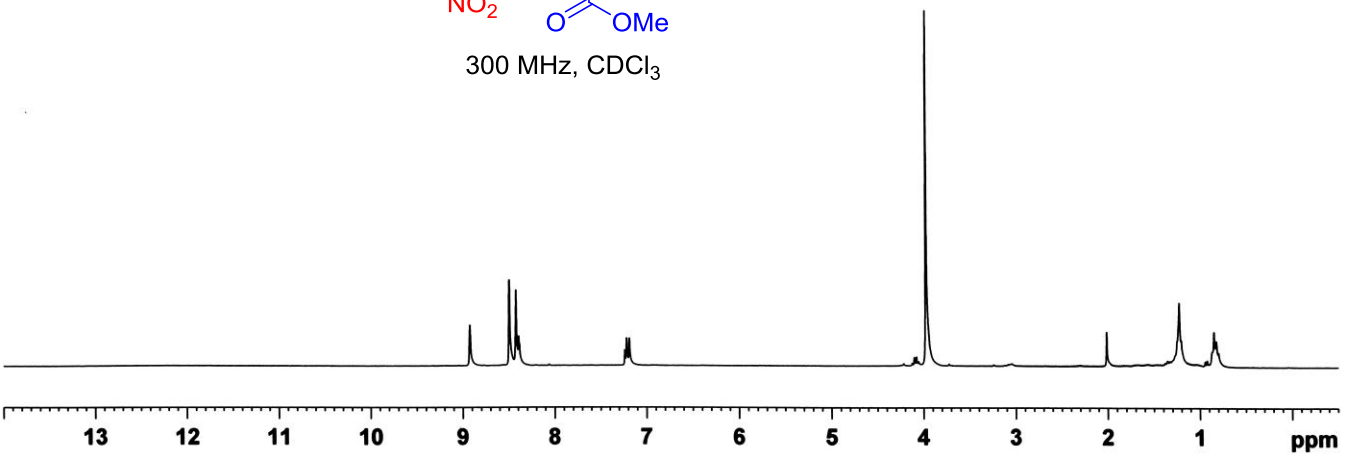


75 MHz, $CDCl_3$

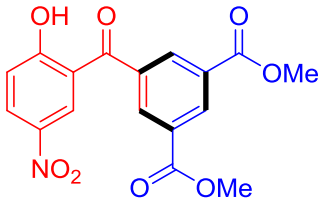
^{1}H NMR of Compound **10r**



300 MHz, $CDCl_3$

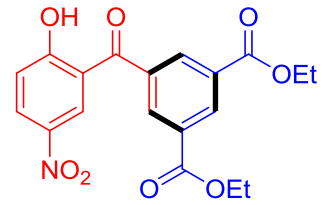


^{13}C NMR of Compound **10r**

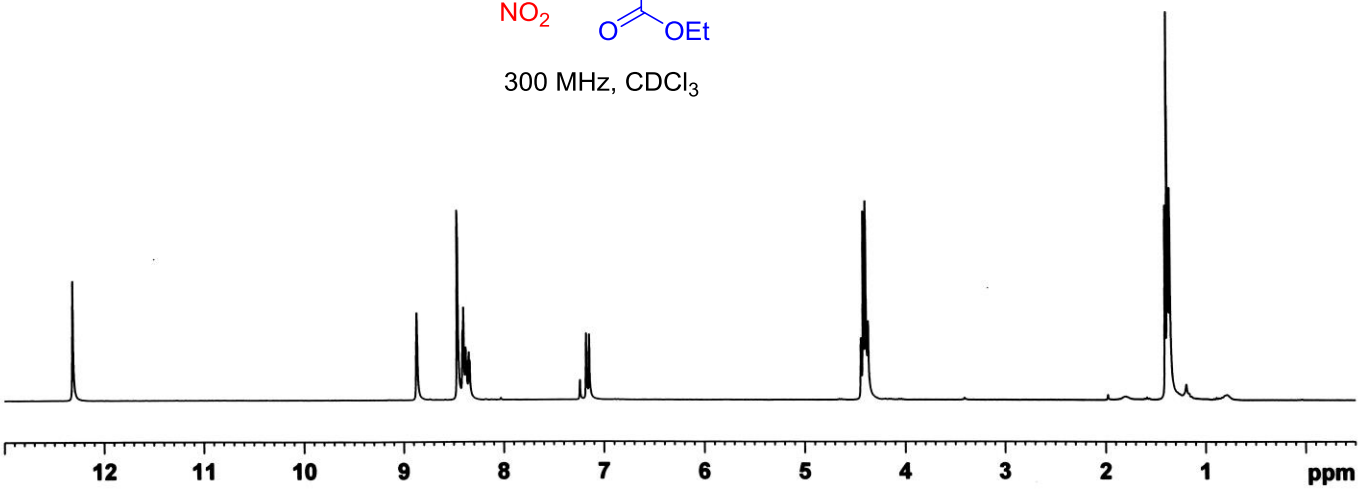


75 MHz, $CDCl_3$

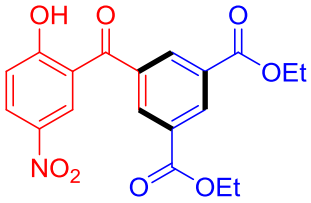
^{1}H NMR of Compound **10s**



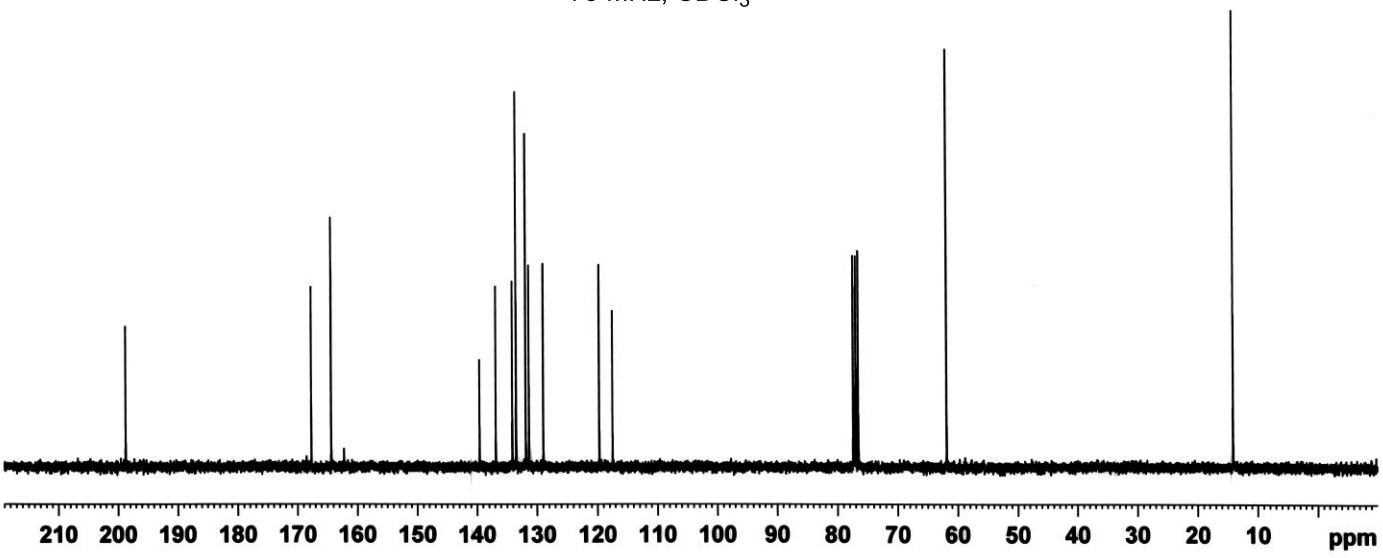
300 MHz, $CDCl_3$



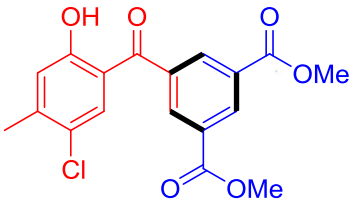
^{13}C NMR of Compound **10s**



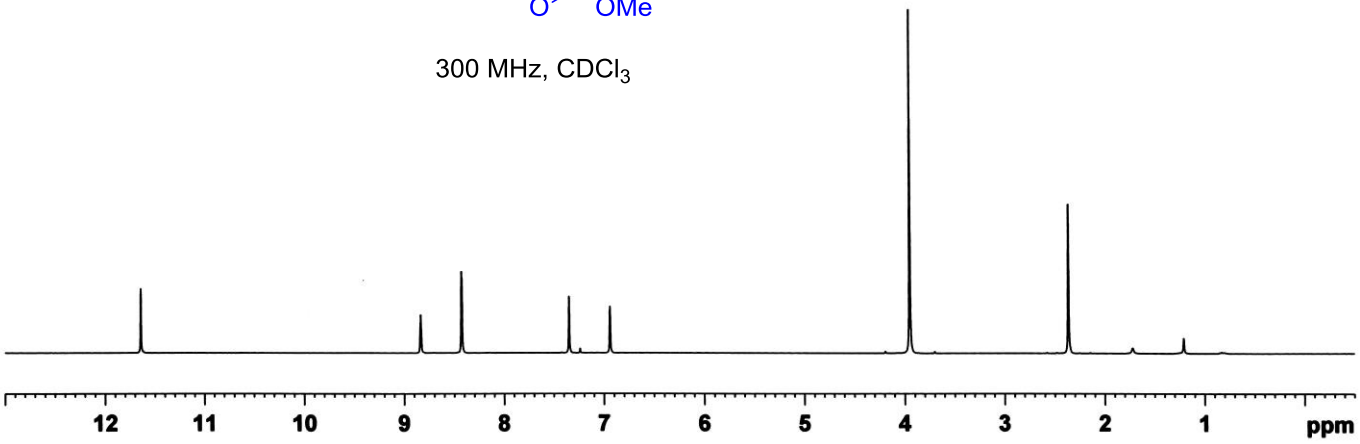
75 MHz, $CDCl_3$



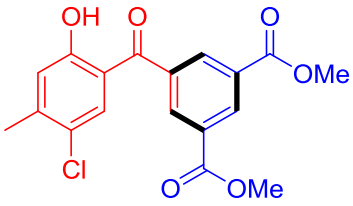
^{1}H NMR of Compound **10t**



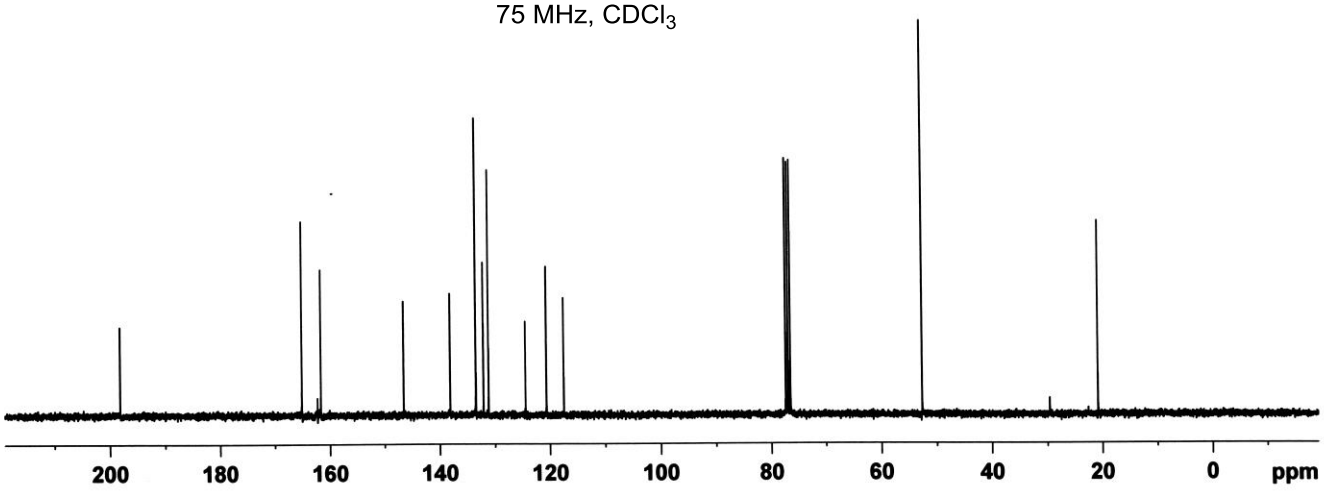
300 MHz, $CDCl_3$



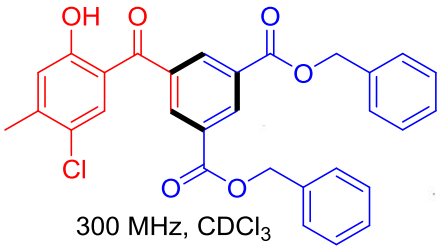
^{13}C NMR of Compound **10t**



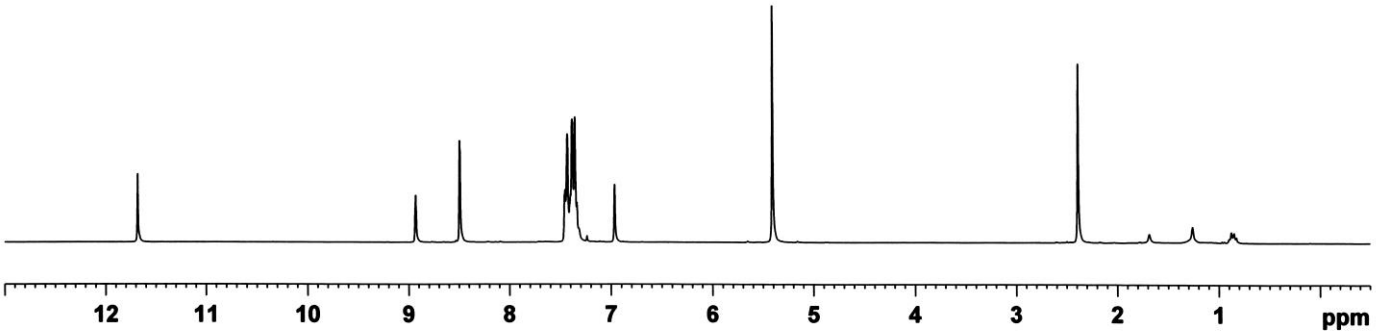
75 MHz, $CDCl_3$



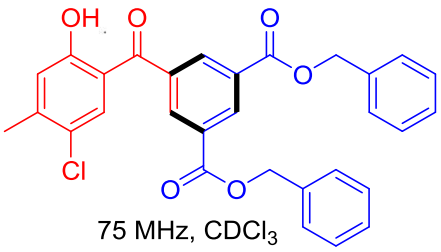
^{1}H NMR of Compound **10u**



300 MHz, $CDCl_3$

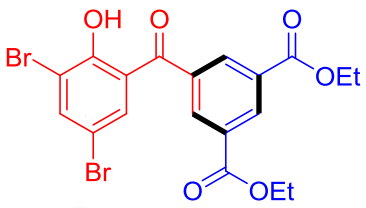


^{13}C NMR of Compound **10u**

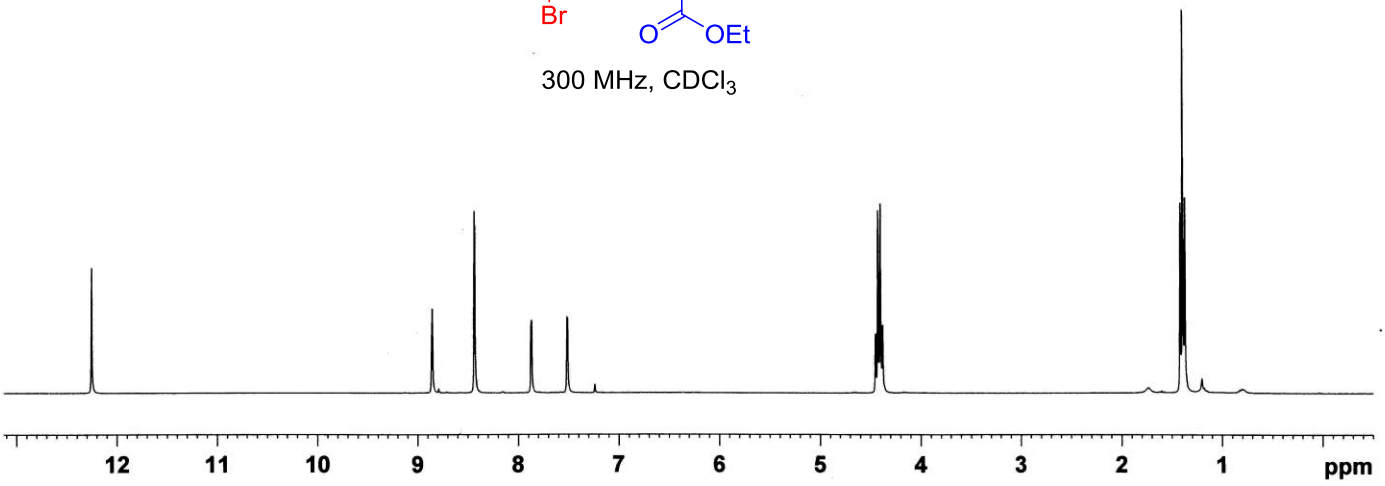


75 MHz, $CDCl_3$

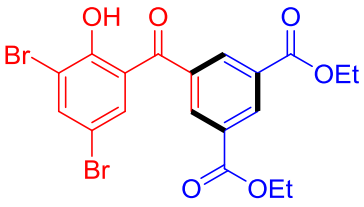
^{1}H NMR of Compound **10v**



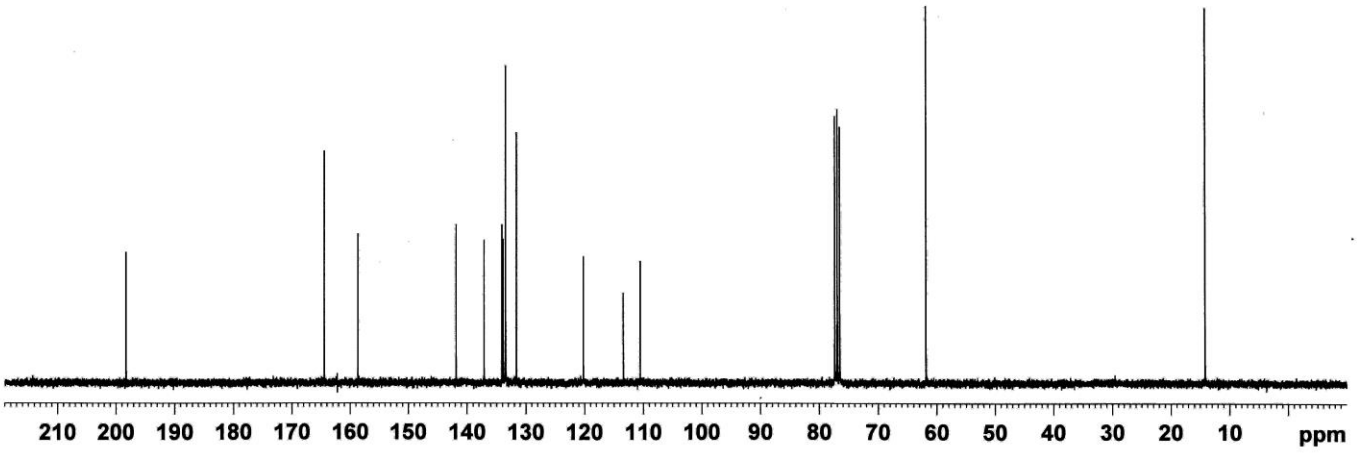
300 MHz, $CDCl_3$



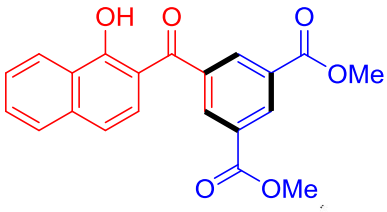
^{13}C NMR of Compound **10v**



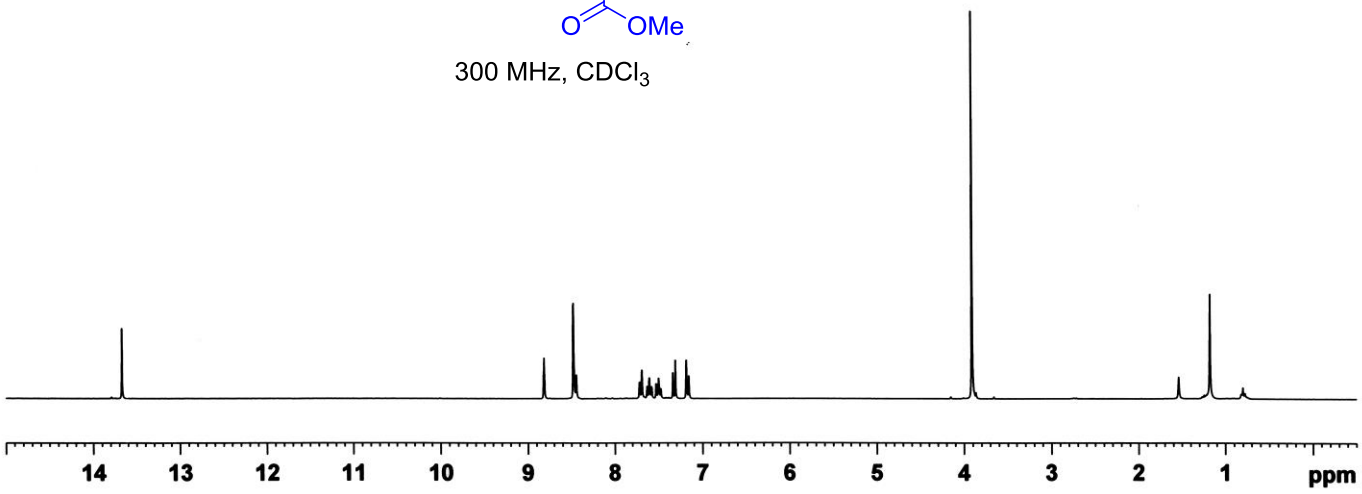
75 MHz, $CDCl_3$



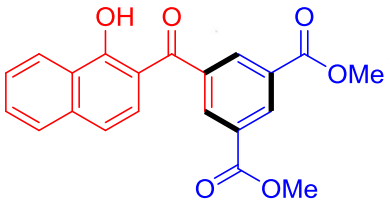
^{1}H NMR of Compound **10w**



300 MHz, $CDCl_3$

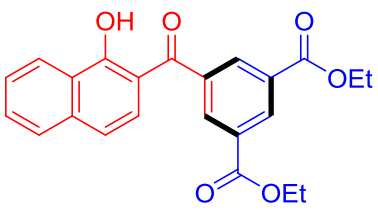


^{13}C NMR of Compound **10w**

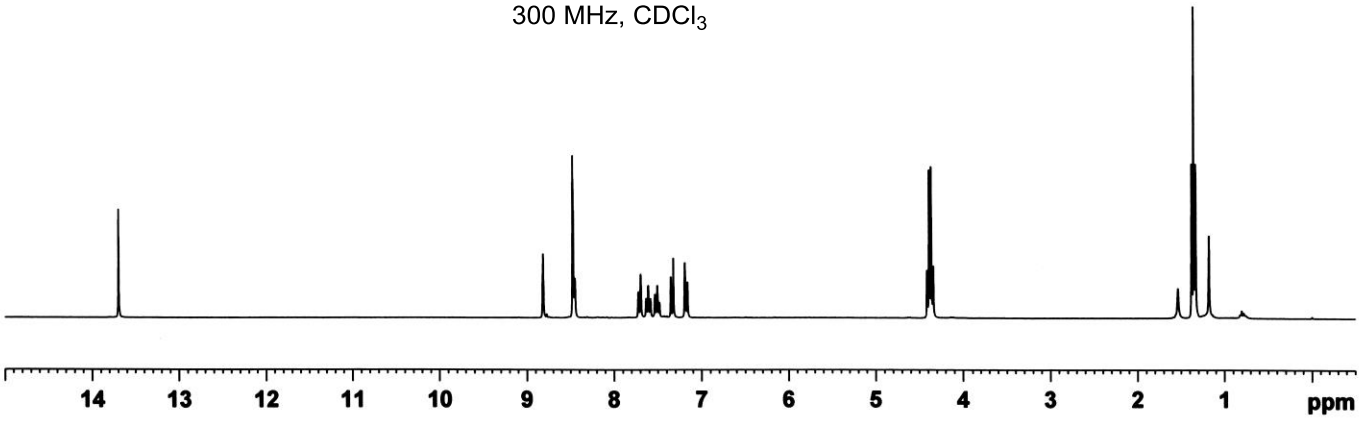


75 MHz, $CDCl_3$

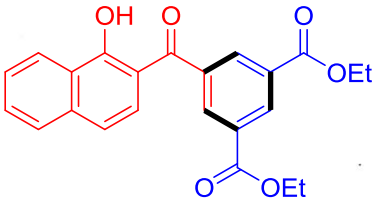
^{1}H NMR of Compound **10x**



300 MHz, $CDCl_3$

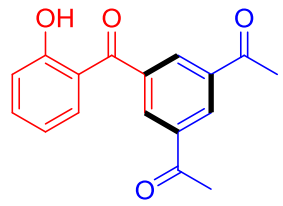


^{13}C NMR of Compound **10x**

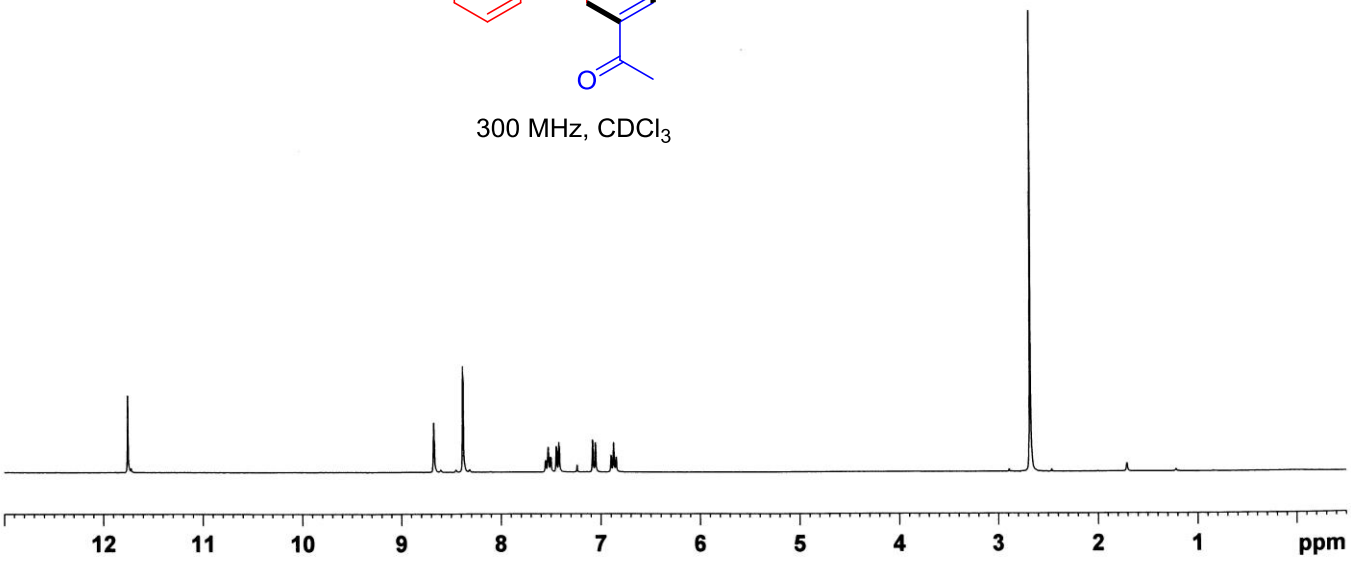


75 MHz, $CDCl_3$

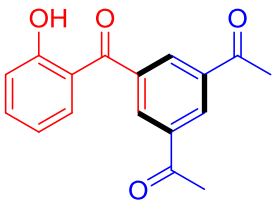
^{1}H NMR of Compound **12a**



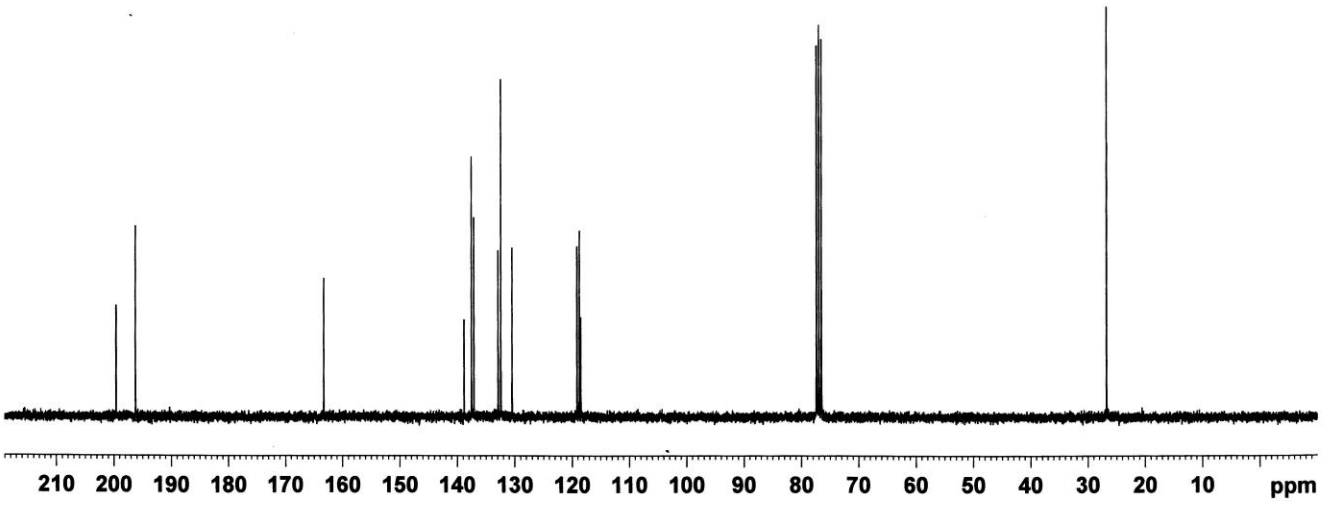
300 MHz, $CDCl_3$



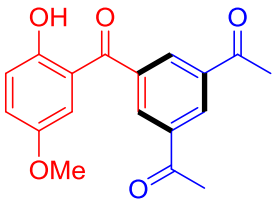
^{13}C NMR of Compound **12a**



75 MHz, $CDCl_3$

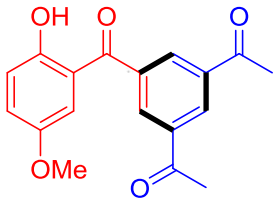


^{1}H NMR of Compound **12b**



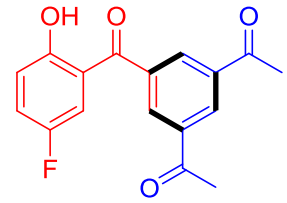
600 MHz, $CDCl_3$

^{13}C NMR of Compound **12b**



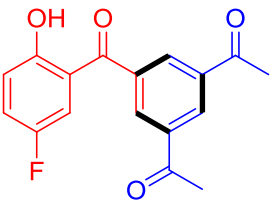
150 MHz, $CDCl_3$

^{1}H NMR of Compound **12c**

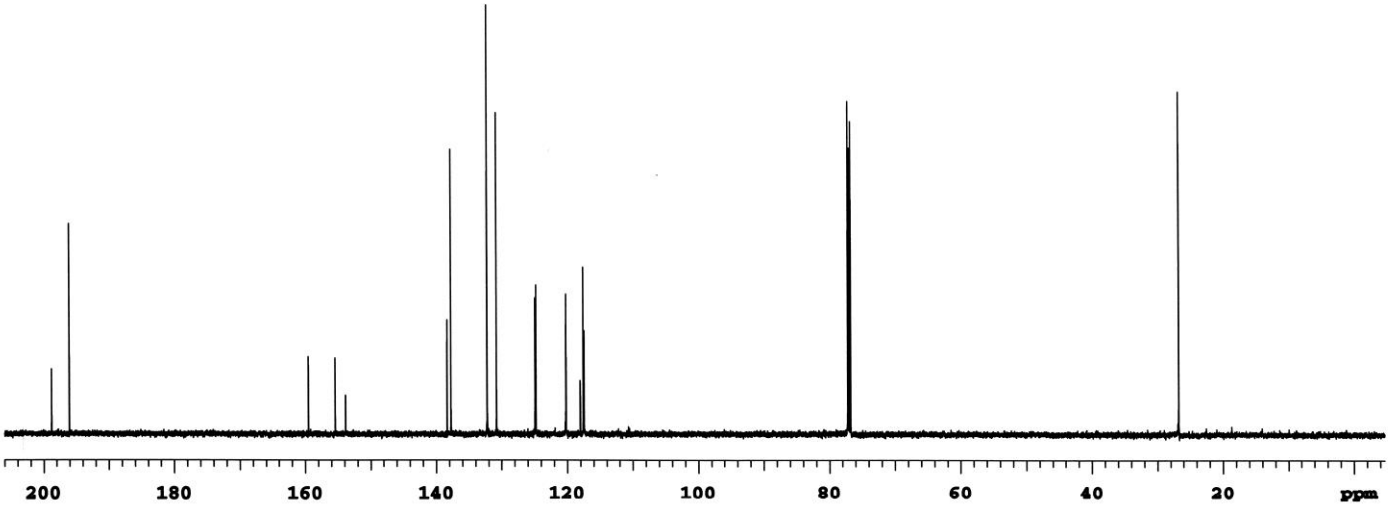


600 MHz, $CDCl_3$

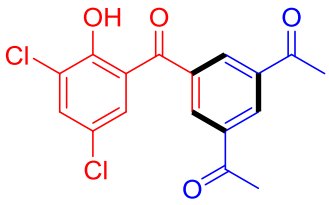
^{13}C NMR of Compound **12c**



150 MHz, $CDCl_3$

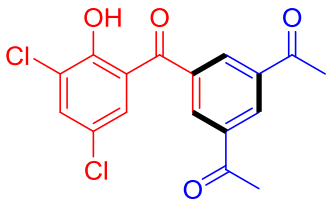


^{1}H NMR of Compound **12d**

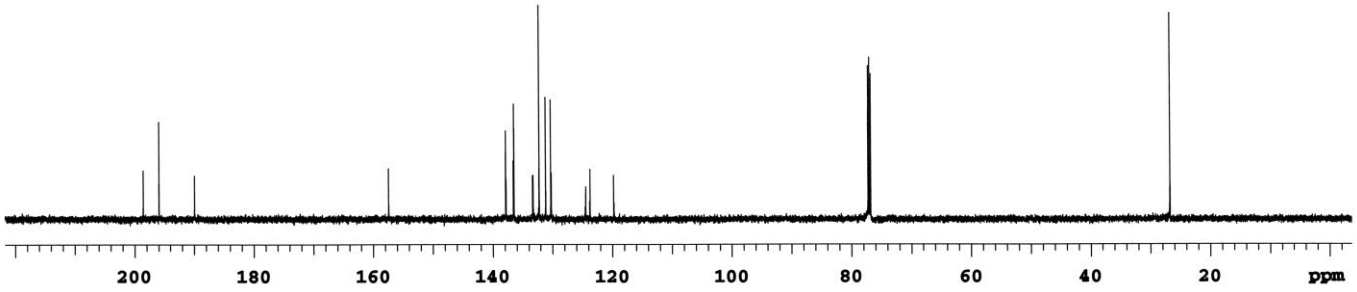


600 MHz, $CDCl_3$

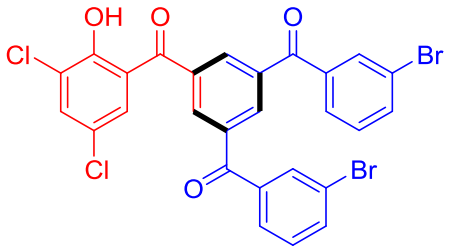
^{13}C NMR of Compound **10d**



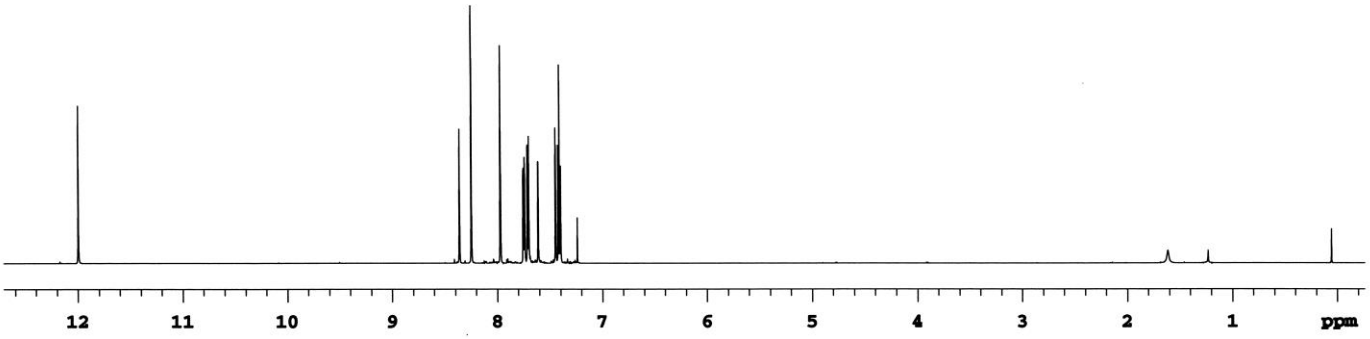
150 MHz, $CDCl_3$



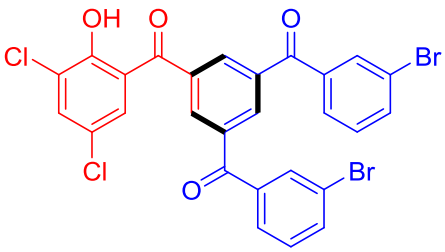
^{1}H NMR of Compound **12e**



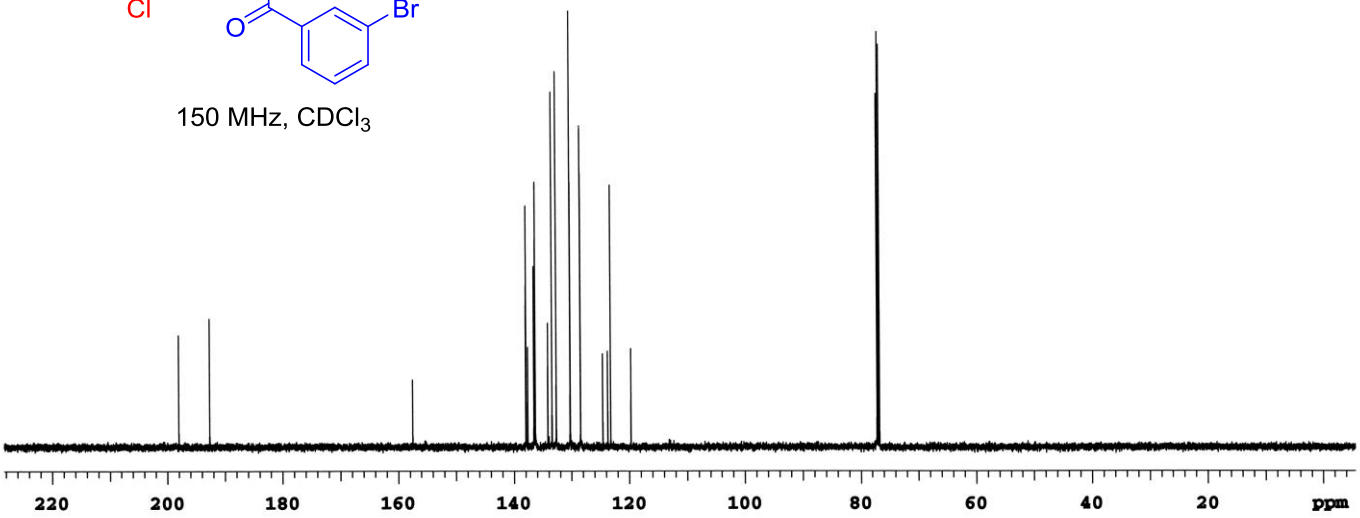
600 MHz, $CDCl_3$



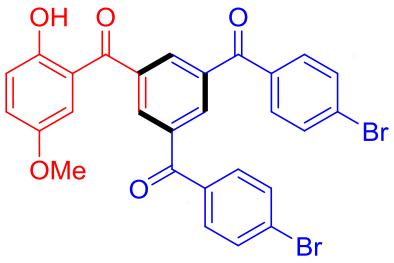
^{13}C NMR of Compound **12e**



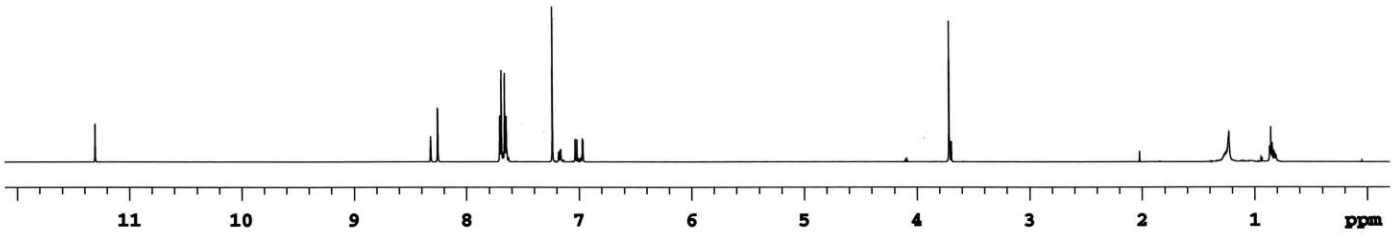
150 MHz, $CDCl_3$



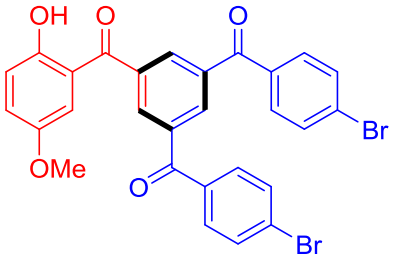
^{1}H NMR of Compound **12f**



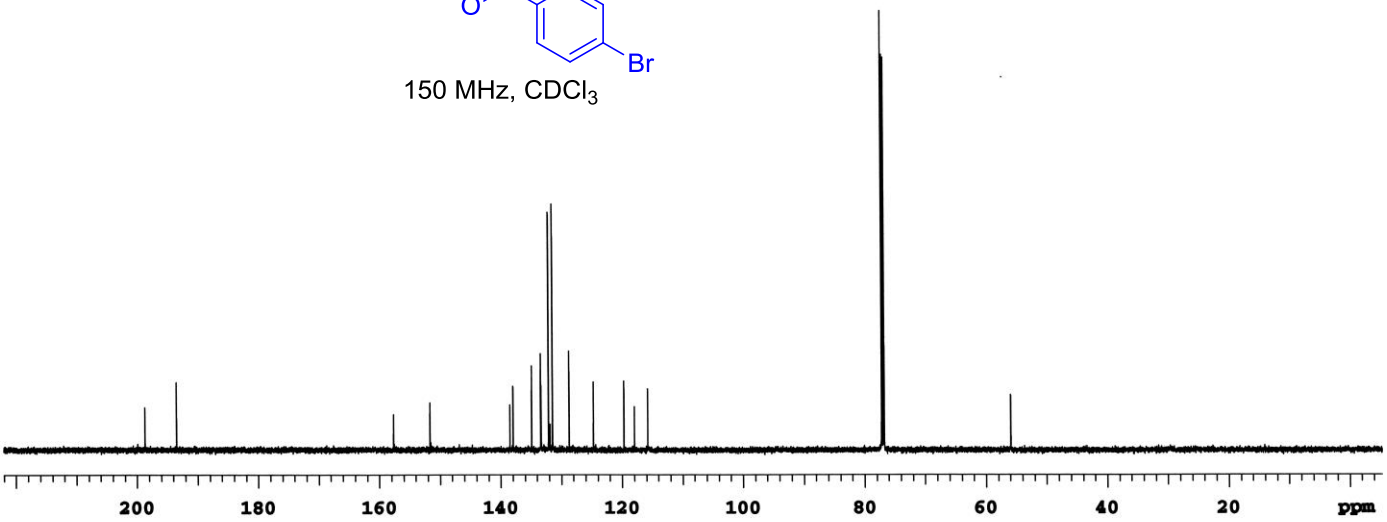
600 MHz, $CDCl_3$



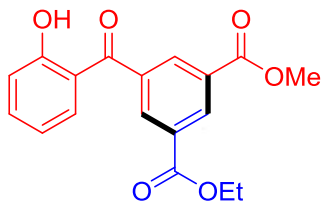
^{13}C NMR of Compound **12f**



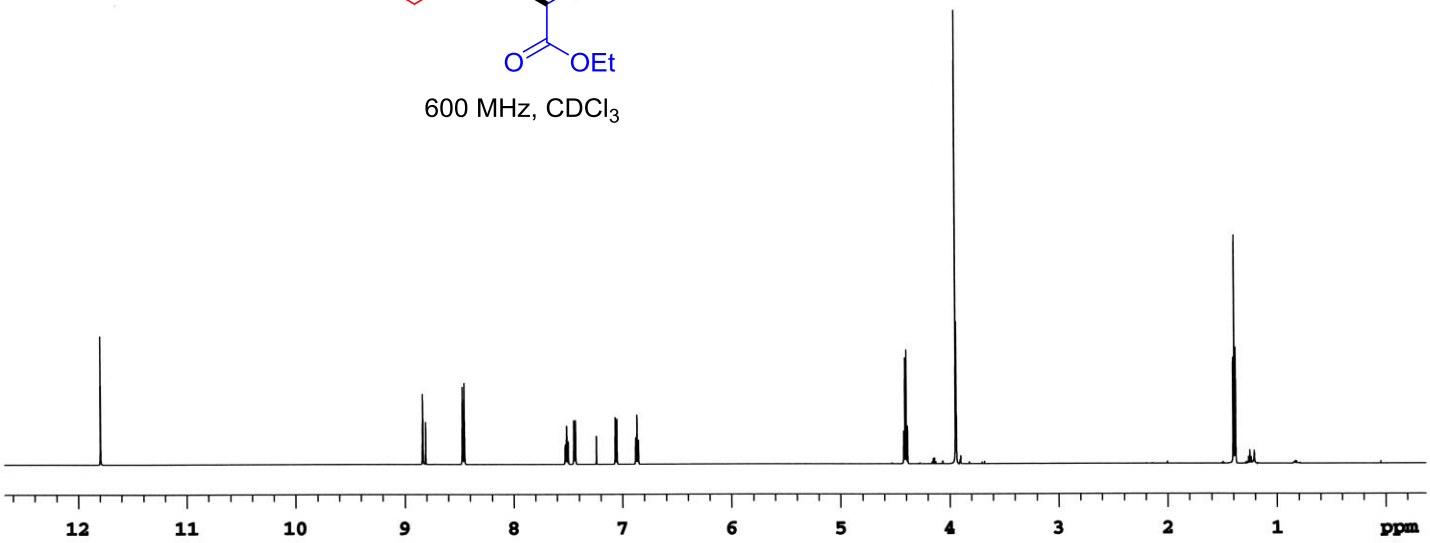
150 MHz, $CDCl_3$



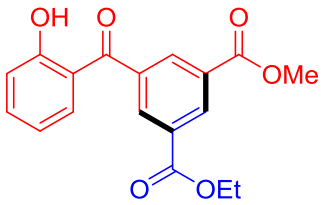
^{1}H NMR of Compound **14a**



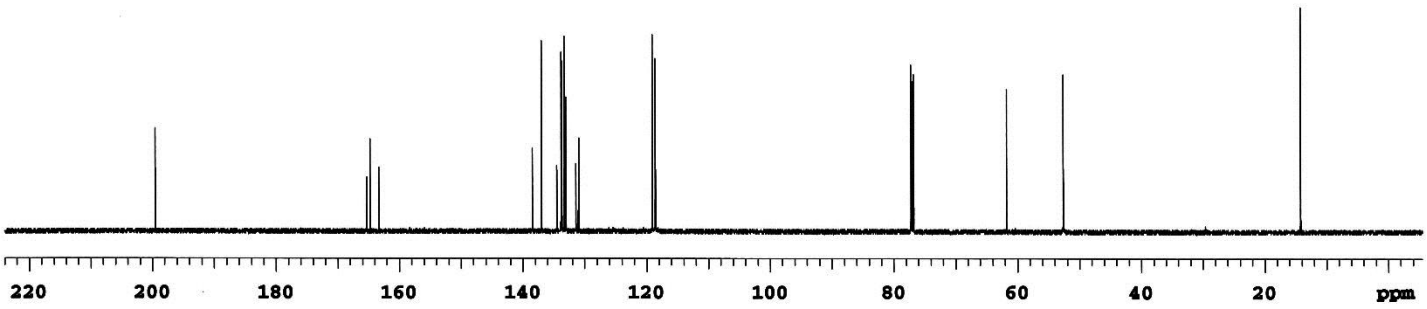
600 MHz, $CDCl_3$



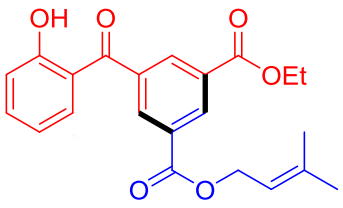
^{13}C NMR of Compound **14a**



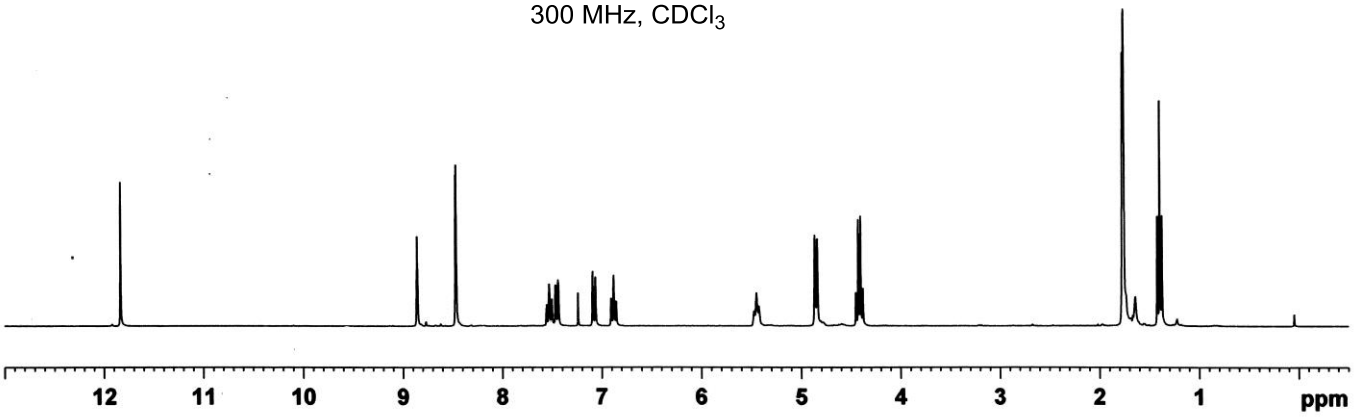
150 MHz, $CDCl_3$



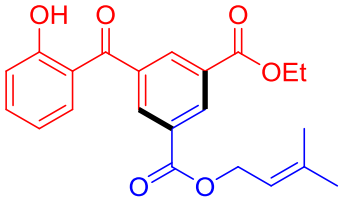
^{1}H NMR of Compound **14b**



300 MHz, $CDCl_3$

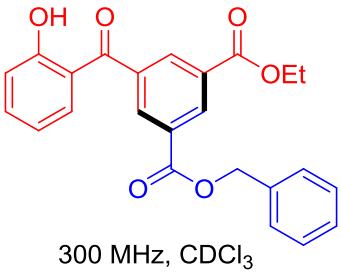


^{13}C NMR of Compound **14b**

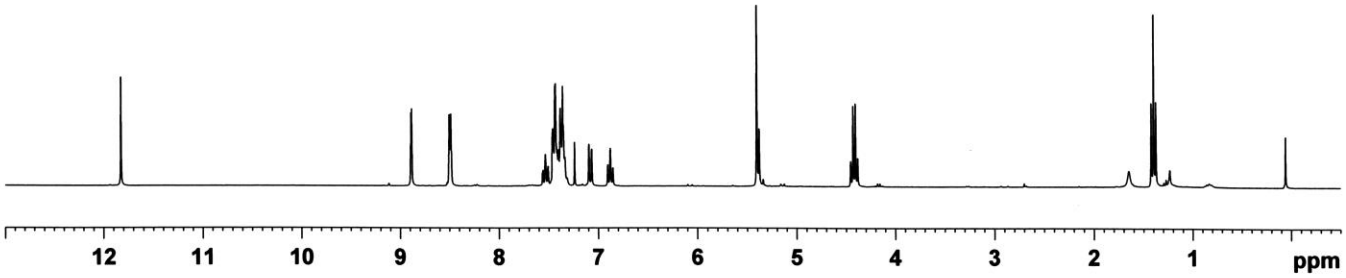


75 MHz, $CDCl_3$

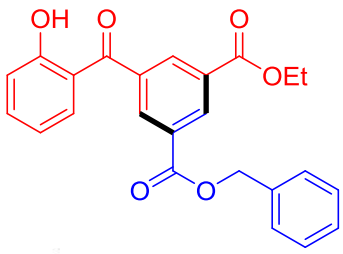
^{1}H NMR of Compound **14c**



300 MHz, $CDCl_3$

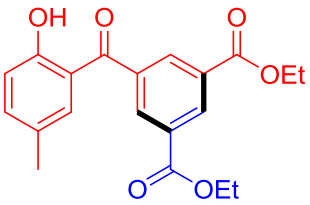


^{13}C NMR of Compound **14c**

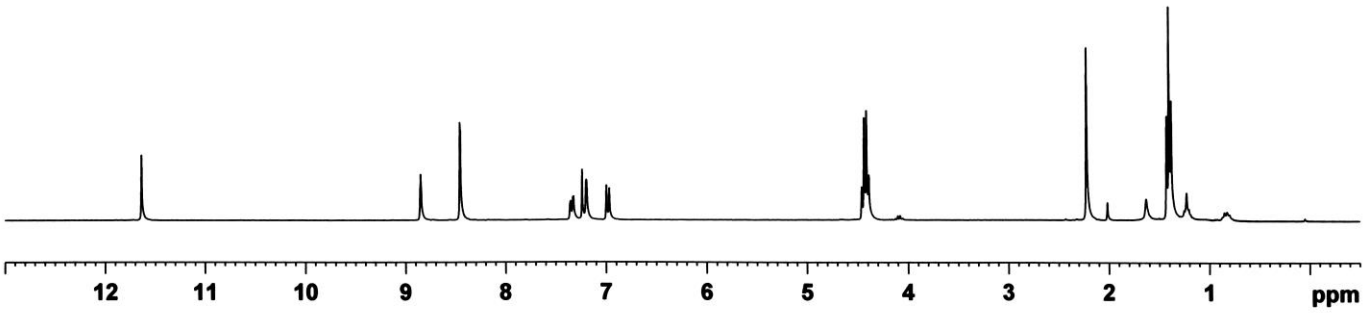


75 MHz, $CDCl_3$

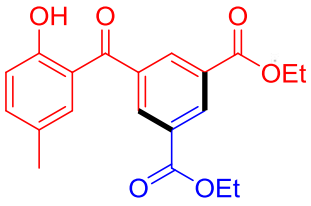
^{1}H NMR of Compound **14d**



300 MHz, $CDCl_3$

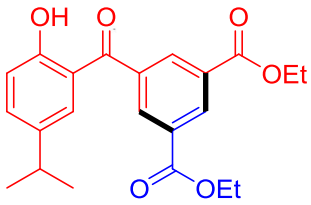


^{13}C NMR of Compound **14d**

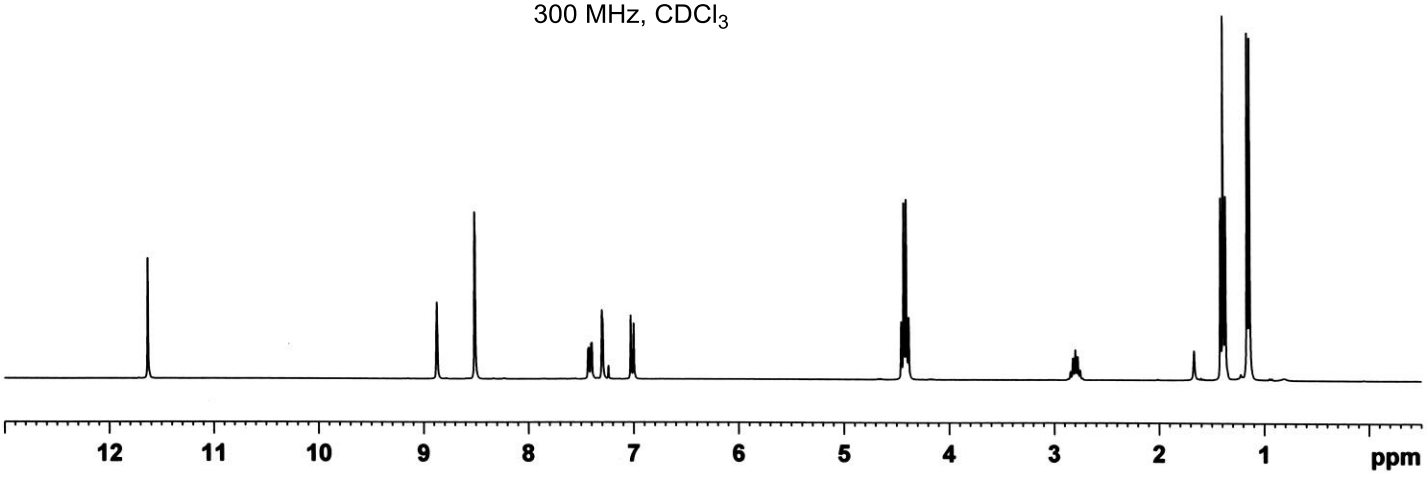


75 MHz, $CDCl_3$

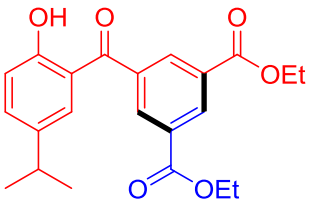
^{1}H NMR of Compound **14e**



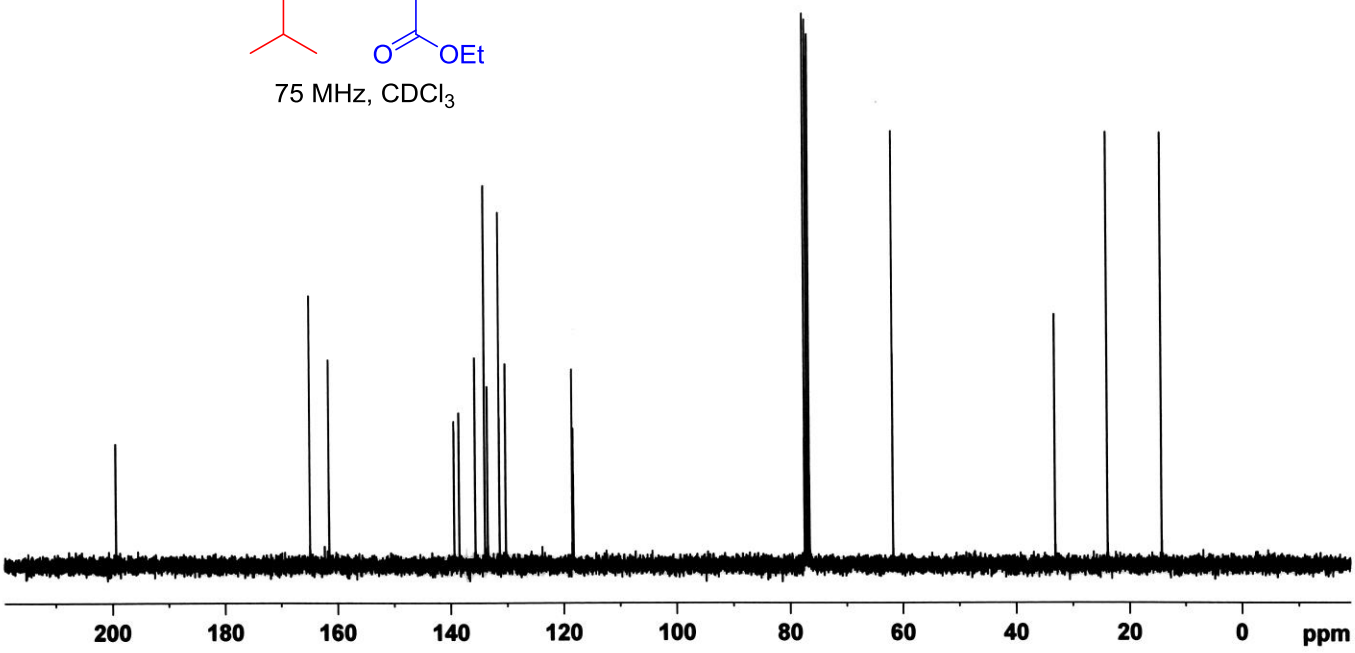
300 MHz, $CDCl_3$



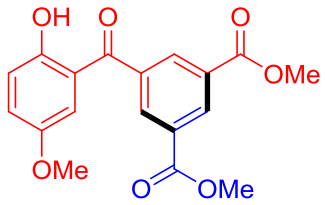
^{13}C NMR of Compound **14e**



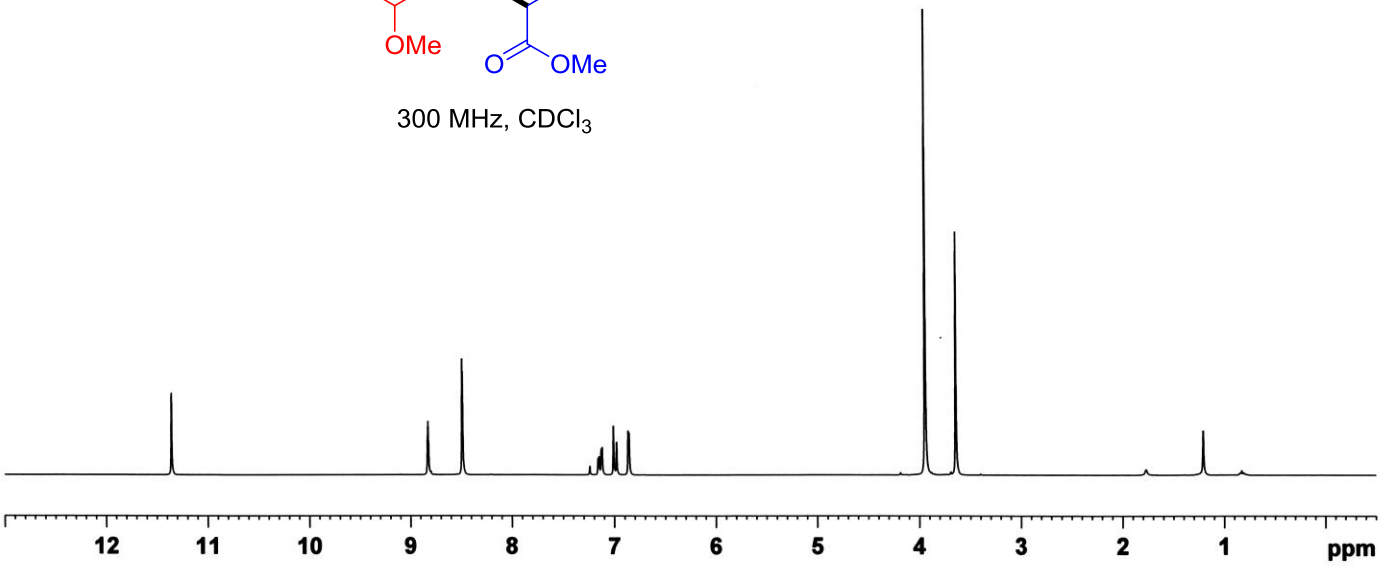
75 MHz, $CDCl_3$



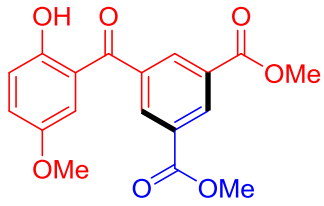
^{1}H NMR of Compound **14f**



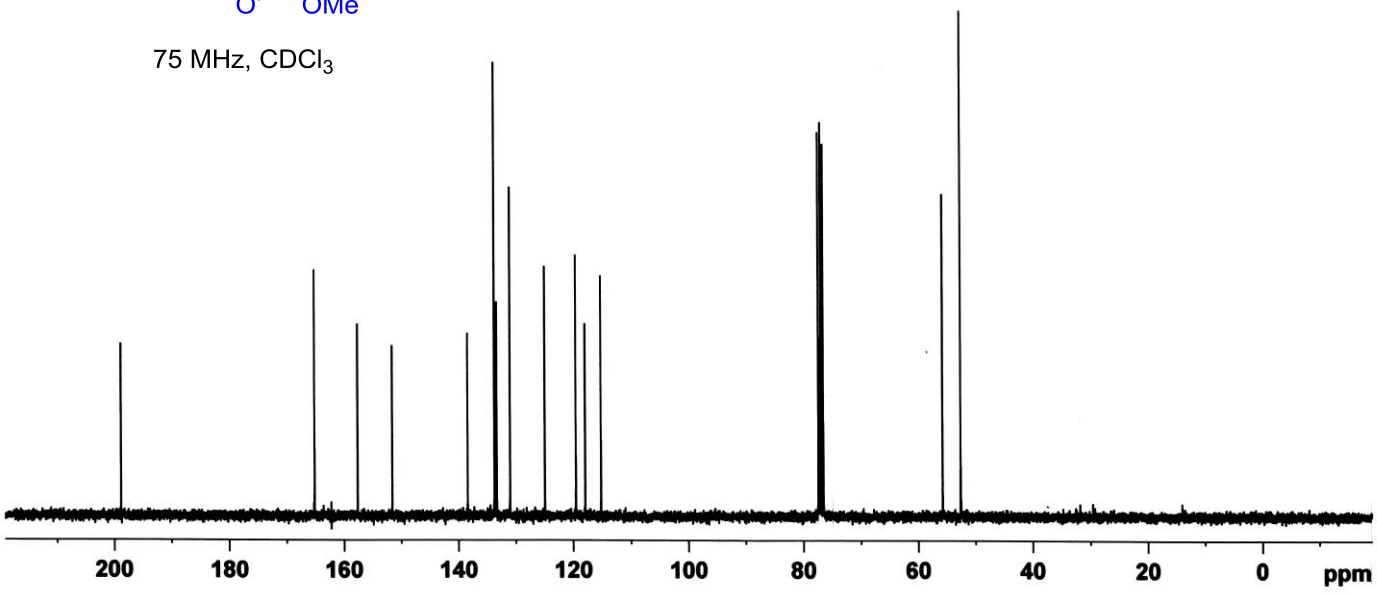
300 MHz, $CDCl_3$



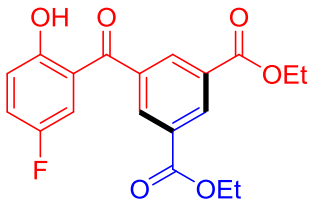
^{13}C NMR of Compound **14f**



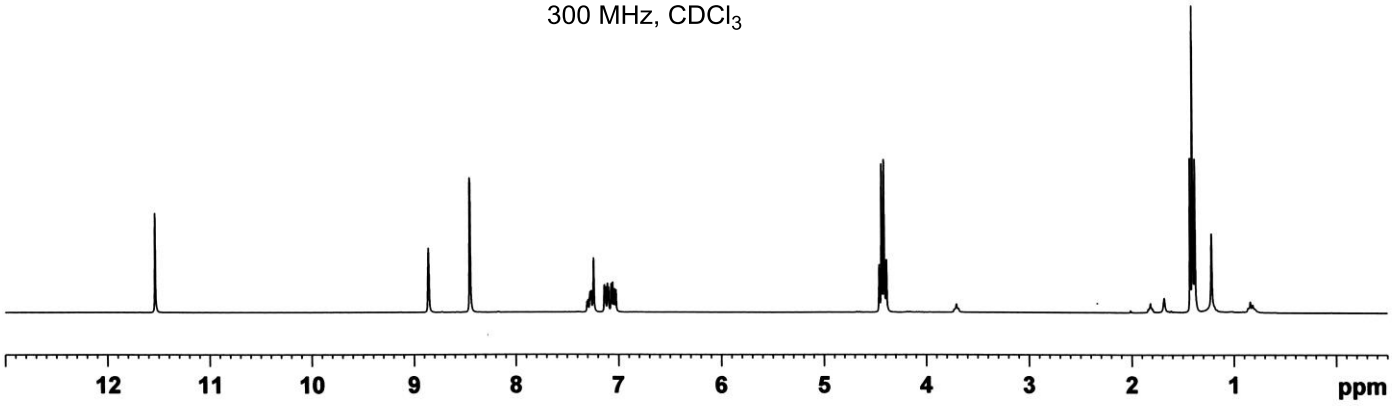
75 MHz, $CDCl_3$



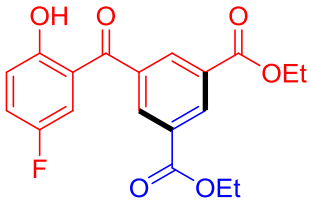
^{1}H NMR of Compound **14g**



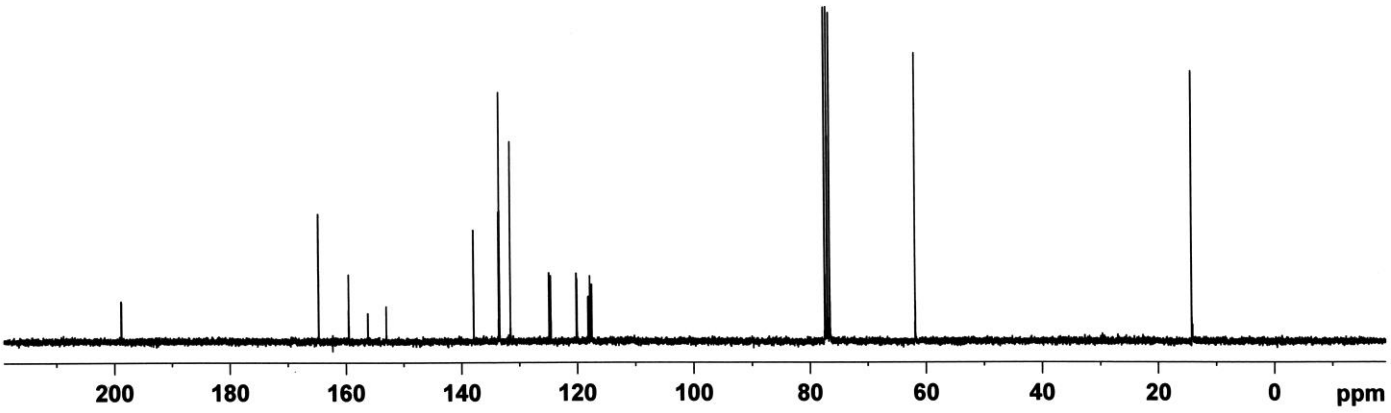
300 MHz, $CDCl_3$



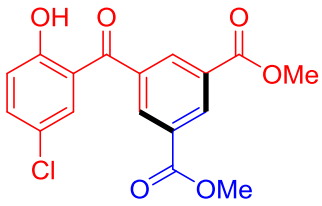
^{13}C NMR of Compound **14g**



75 MHz, $CDCl_3$

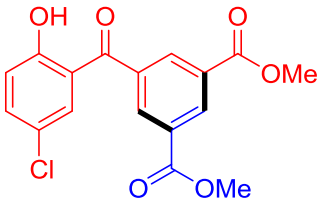


^{1}H NMR of Compound **14h**

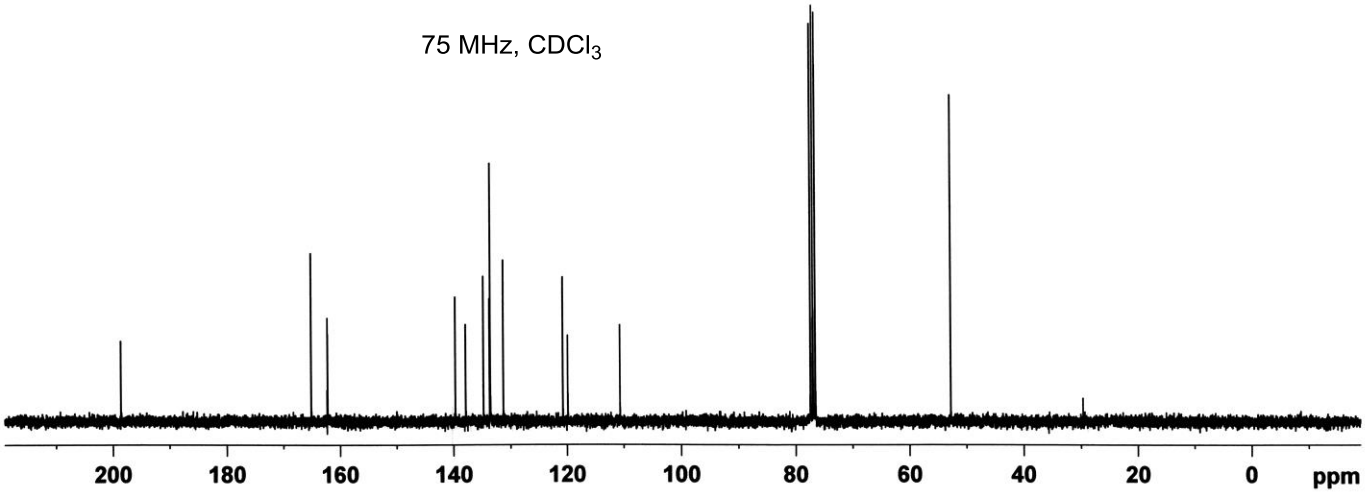


300 MHz, $CDCl_3$

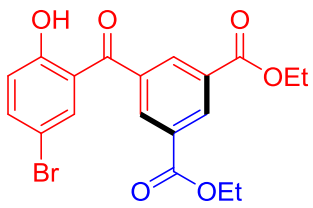
^{13}C NMR of Compound **14h**



75 MHz, $CDCl_3$

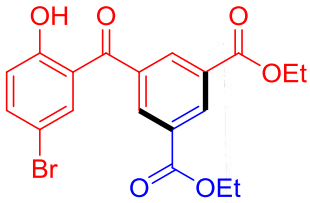


^{1}H NMR of Compound **14i**

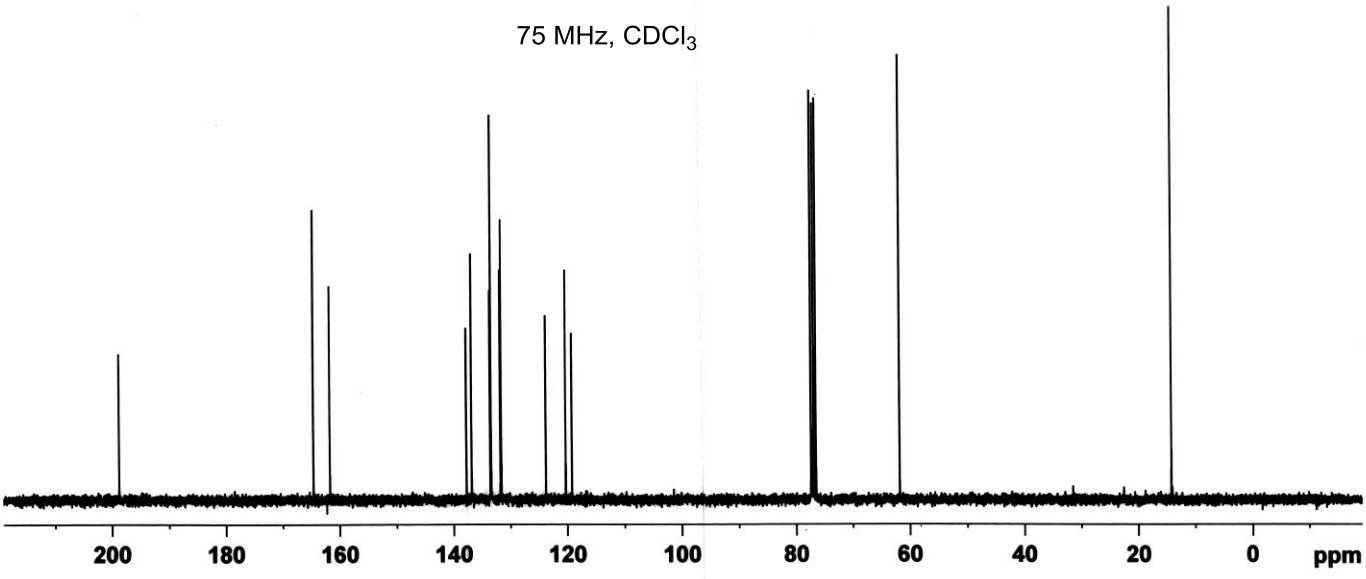


300 MHz, $CDCl_3$

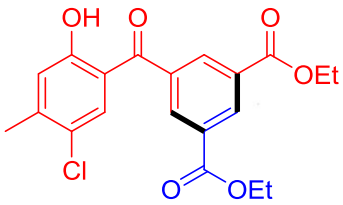
^{13}C NMR of Compound **14i**



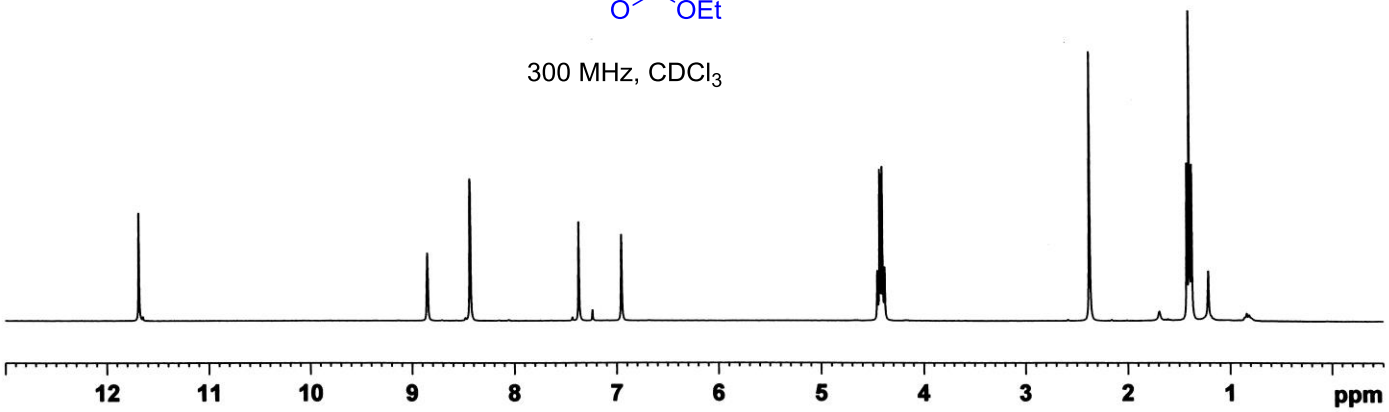
75 MHz, $CDCl_3$



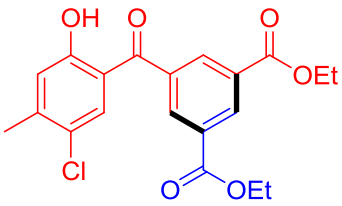
^{1}H NMR of Compound **14j**



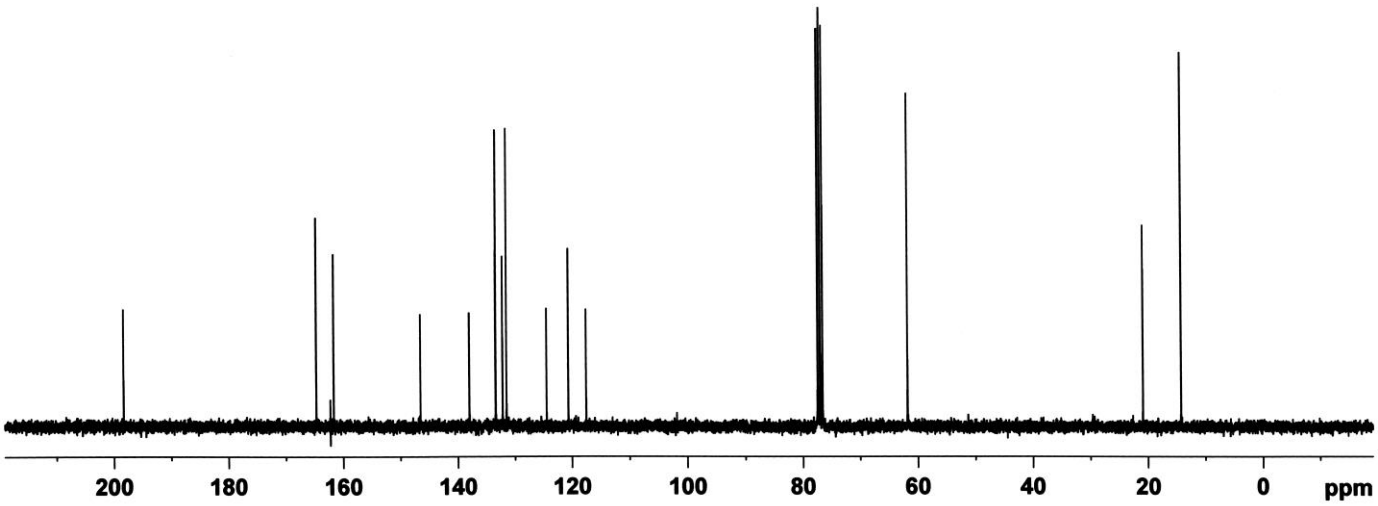
300 MHz, $CDCl_3$



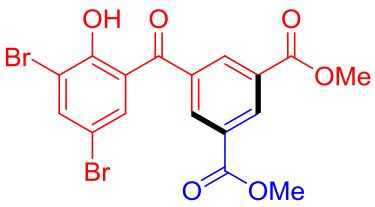
^{13}C NMR of Compound **14j**



75 MHz, $CDCl_3$

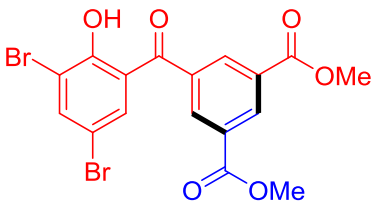


^{1}H NMR of Compound **14k**

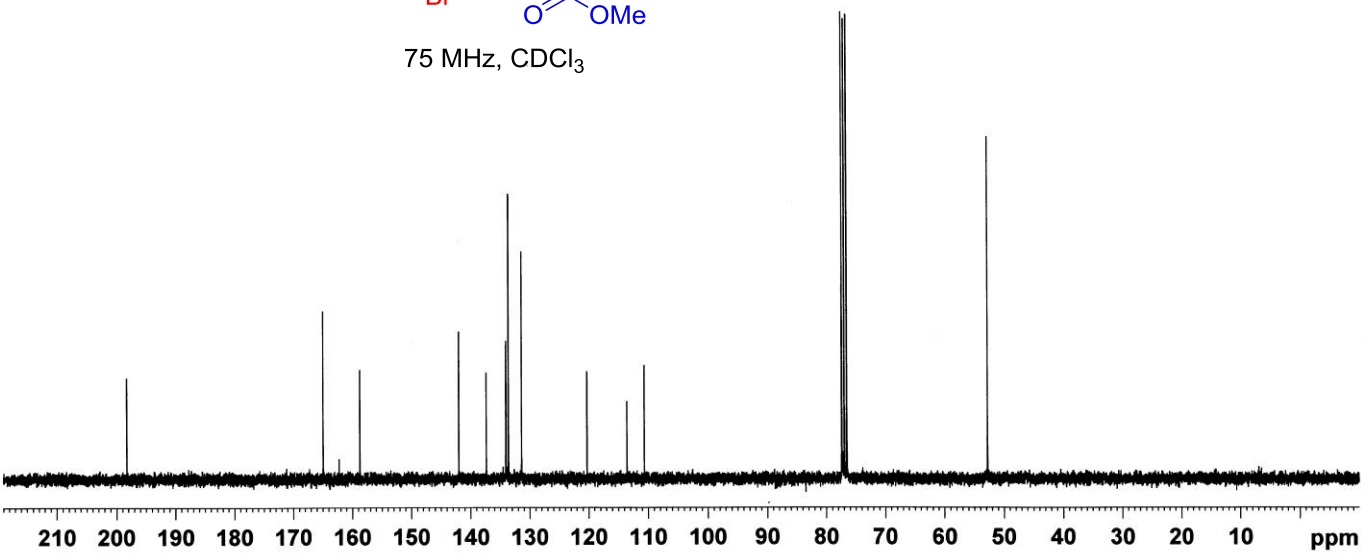


300 MHz, $CDCl_3$

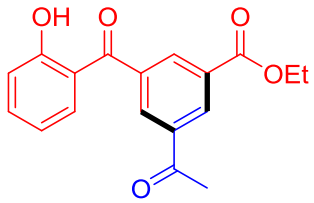
^{13}C NMR of Compound **14k**



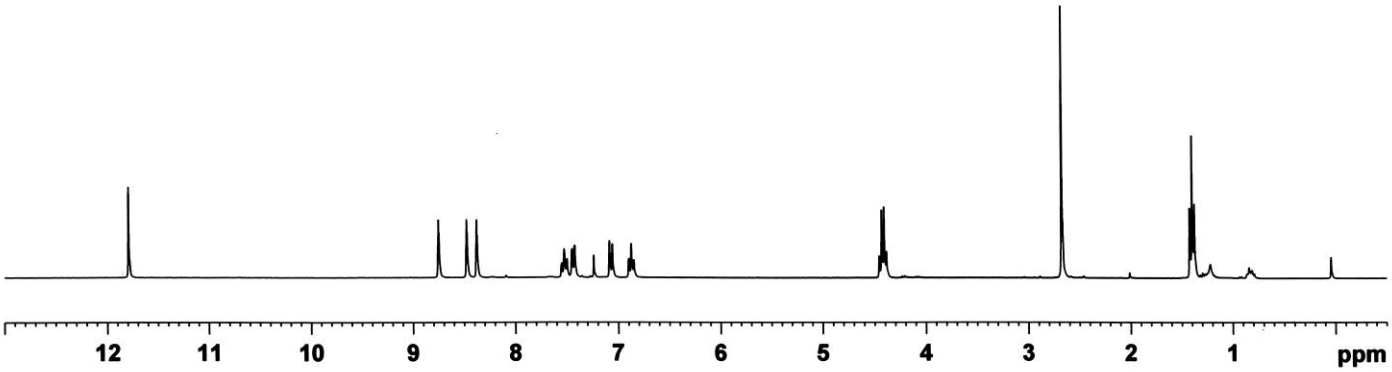
75 MHz, $CDCl_3$



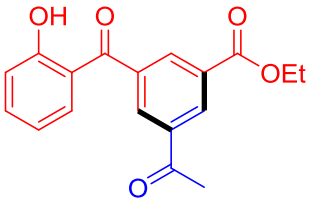
^{1}H NMR of Compound **14l**



300 MHz, $CDCl_3$

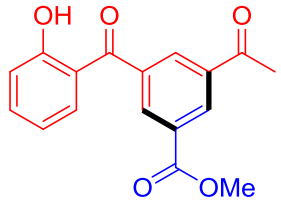


^{13}C NMR of Compound **14l**

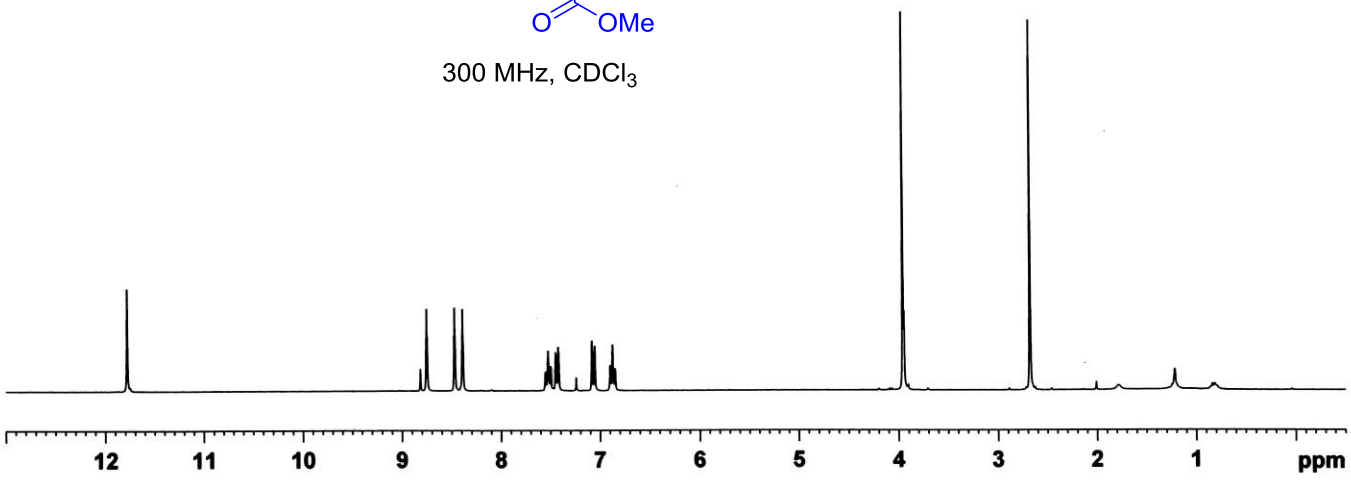


75 MHz, $CDCl_3$

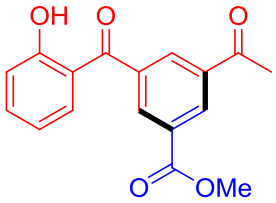
^{1}H NMR of Compound **14m**



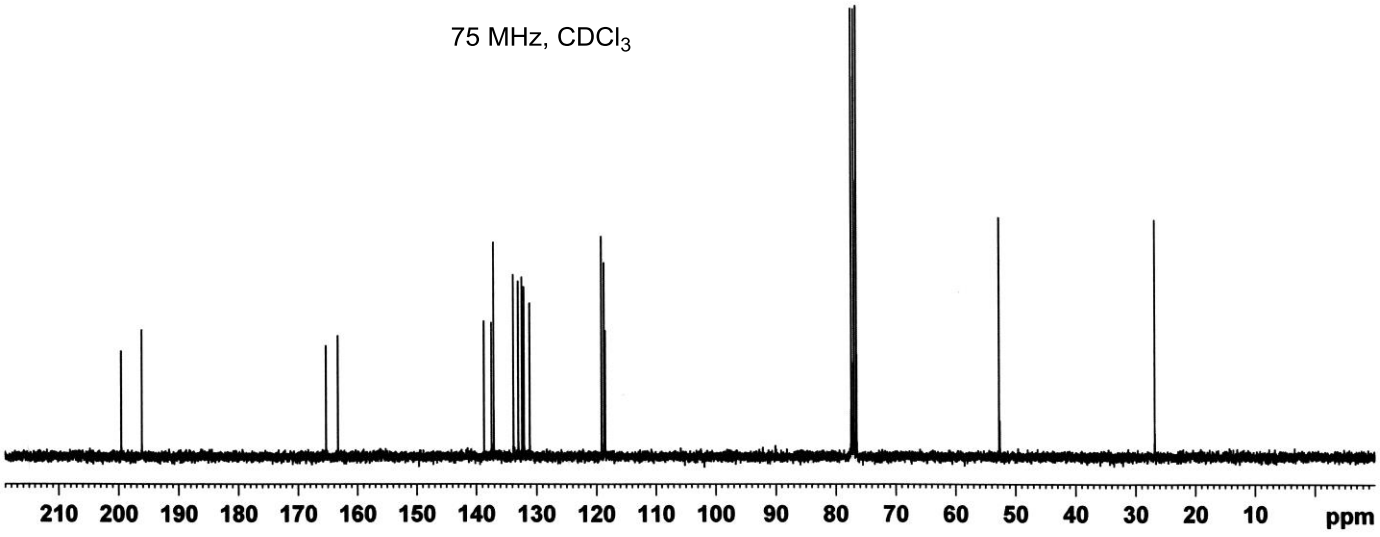
300 MHz, $CDCl_3$



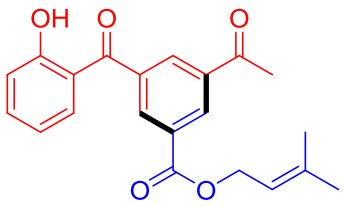
^{13}C NMR of Compound **14m**



75 MHz, $CDCl_3$

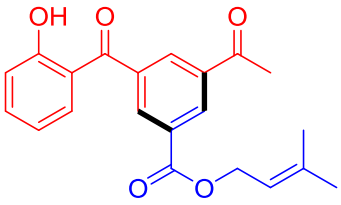


^{1}H NMR of Compound **14n**



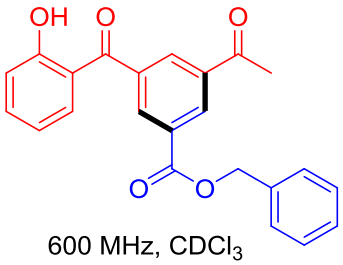
600 MHz, $CDCl_3$

^{13}C NMR of Compound **14n**

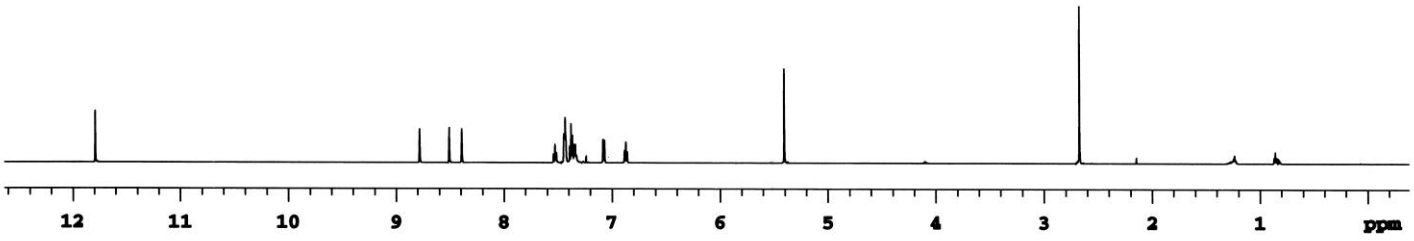


150 MHz, $CDCl_3$

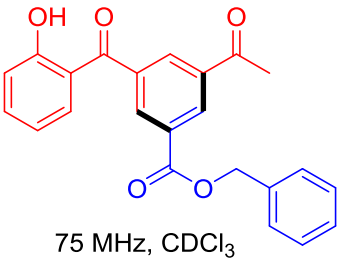
^{1}H NMR of Compound **14o**



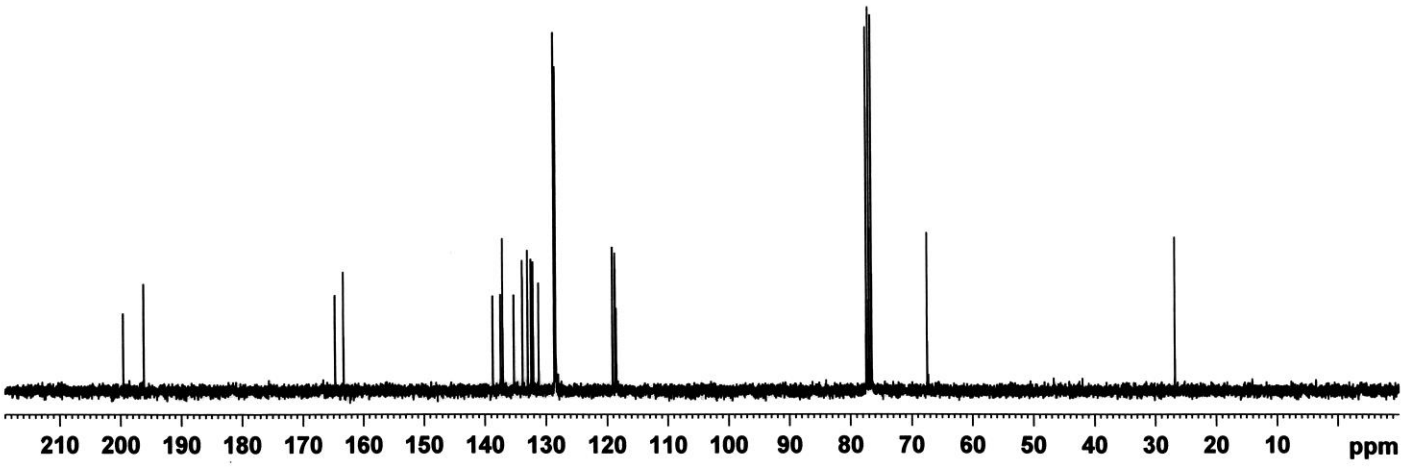
600 MHz, $CDCl_3$



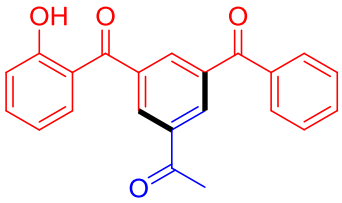
^{13}C NMR of Compound **14o**



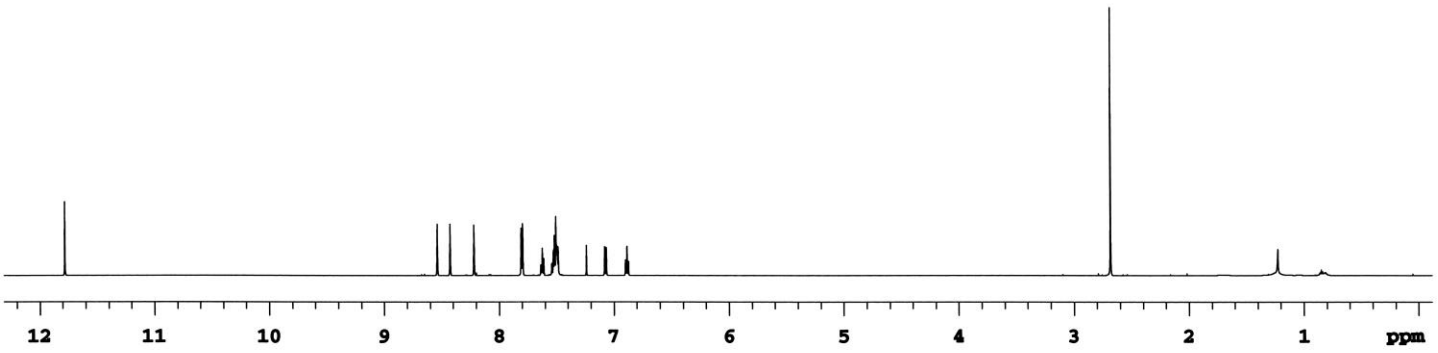
75 MHz, $CDCl_3$



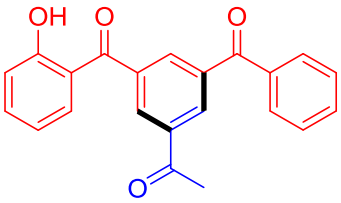
^{1}H NMR of Compound **14p**



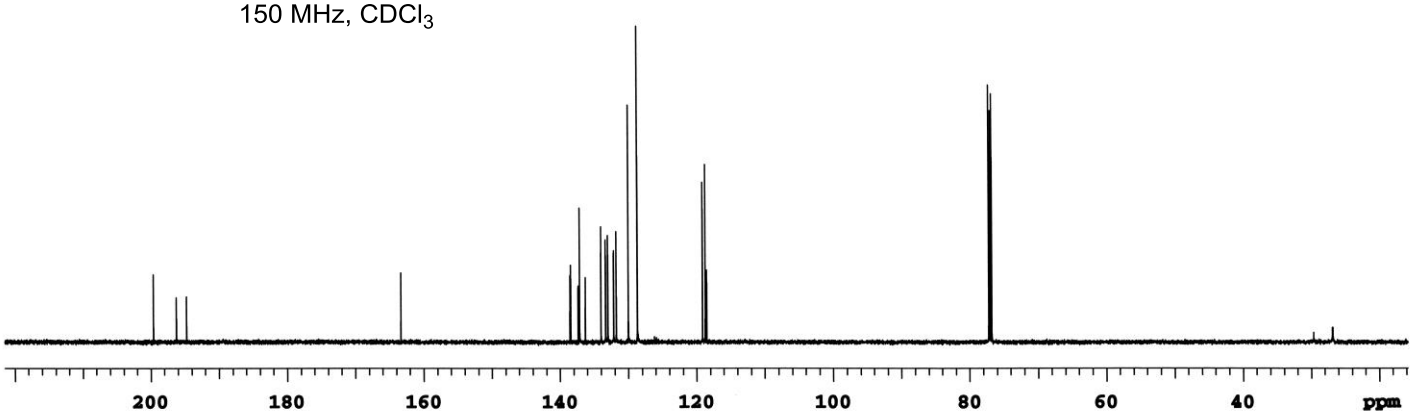
600 MHz, $CDCl_3$



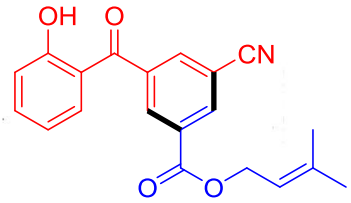
^{13}C NMR of Compound **14p**



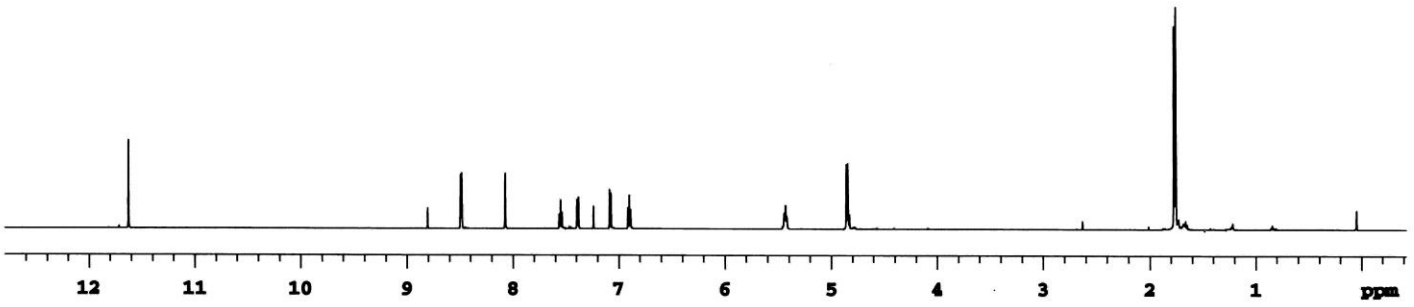
150 MHz, $CDCl_3$



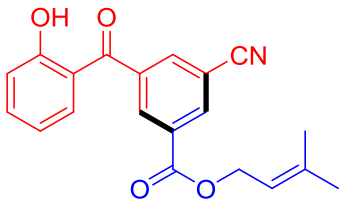
^{1}H NMR of Compound **14q**



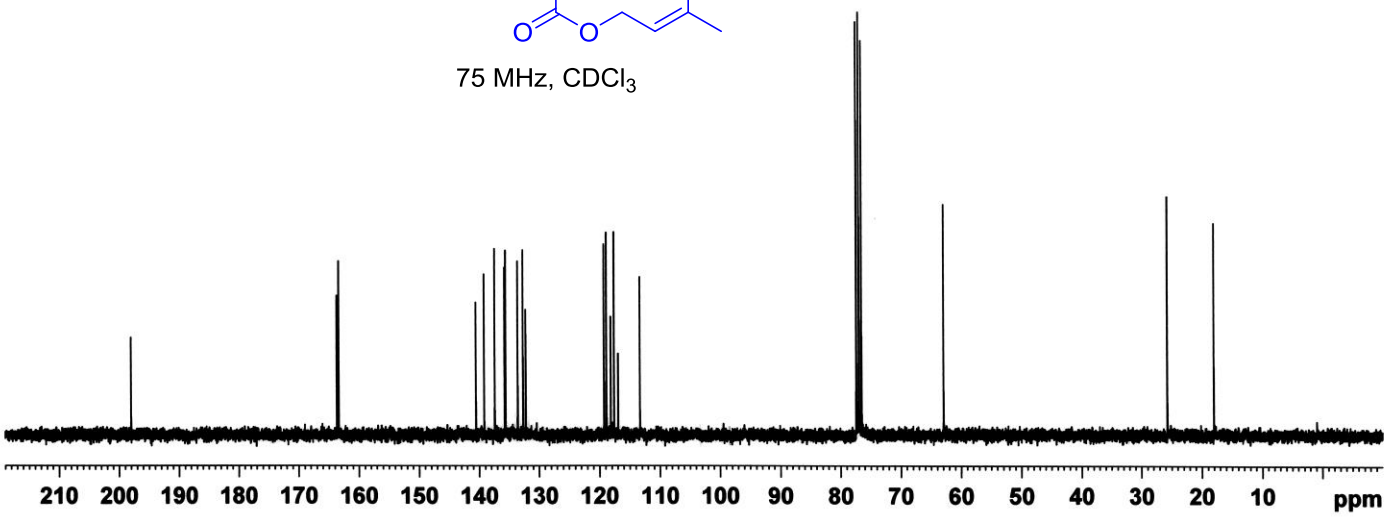
600 MHz, $CDCl_3$



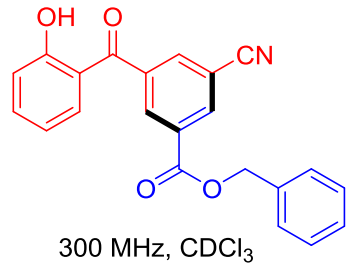
^{13}C NMR of Compound **14q**



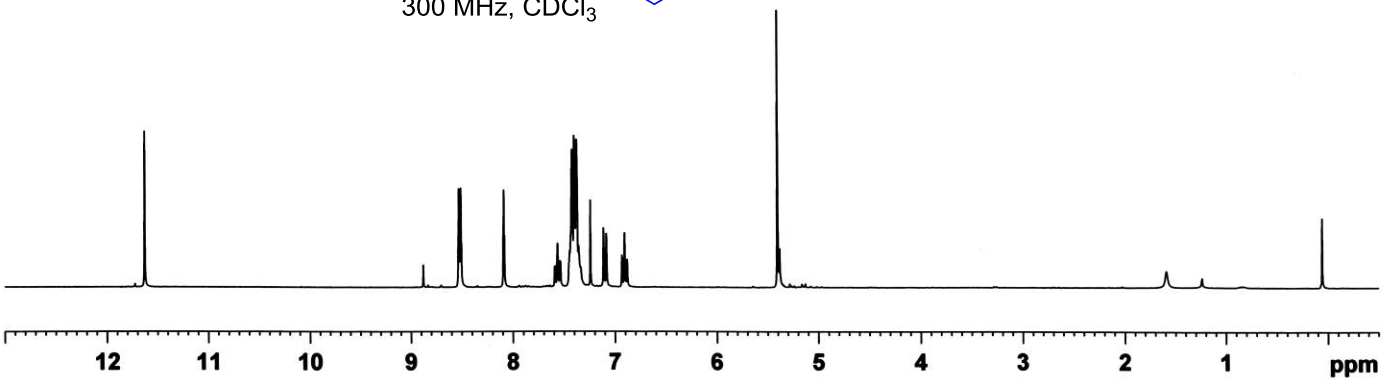
75 MHz, $CDCl_3$



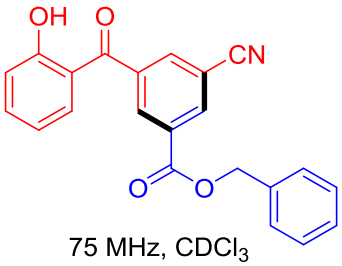
^{1}H NMR of Compound **14r**



300 MHz, $CDCl_3$



^{13}C NMR of Compound **14r**



75 MHz, $CDCl_3$