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Graphical Abstract

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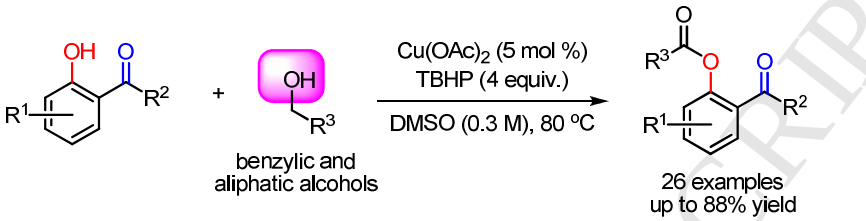

Cu(II)-catalyzed oxidative esterification of 2-carbonyl substituted phenols from the alcohol oxidation level

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Keywords: Alcohols; Aryl Benzoate; Cooper; Esterification; Phenols.

Abstract

A copper-catalyzed oxidative esterification of 2-carbonyl substituted phenols from the alcohol oxidation level is described. This protocol represents direct access to a range of 2-carbonylated aryl benzoate derivatives, which are important building blocks in the synthesis of natural and pharmacological compounds.

1. Introduction

Esterification is one of the vital chemical reactions that have been extensively used in the chemical and pharmaceutical industries.[1] The general strategies usually involve the activation of the carboxylic acid as an acyl halide, anhydride, or activated ester followed by nucleophilic substitution with alcohols.[2] Although various research groups have exploited and developed several methods to the formation of esters, oxidative esterification has received increasing attention from the atom economic point of view, and has become an economical alternative to traditional ester formation. Recent efforts have been made towards the oxidative coupling between aldehydes and alcohols.[3] A variety of conditions have been executed such as those using a stoichiometric oxidant, *N*-heterocyclic carbene activation, and transition metal-mediated processes.[4]

An attractive alternative is the direct formation of esters from the alcohol oxidation level, which represent a step forward toward green, economic, and sustainable processes. Alcohols are available at low cost in great structural diversity, and are easy to handle and to store. Also, alcohols can be readily oxidized into aldehydes under metal catalysis.[5] Scheidt described a tandem oxidation of allylic and benzylic alcohols to esters using *N*-heterocyclic carbenes as catalysts, which required large amounts of

MnO_2 as the oxidant.[6] Very recently, Lei et al. developed a palladium-catalyzed aerobic esterification of benzylic alcohols with methanol and long-chain aliphatic alcohols.[7] Also, Beller and coworkers developed a palladium/NHC-catalyzed oxidative esterification of benzylic alcohols.[8] Though a significant progress has been made toward oxidative processes for the formation of simple esters, no much attention has been paid to the synthesis of aryl benzoate derivatives, which serve as an important building blocks in the synthesis of natural and pharmacological compounds.[9] Traditional methods for synthesizing these compounds include esterification of phenols,[10] trans-esterifications[11] and Baeyer-Villiger oxidation reactions.[12] These reactions were often required strong acidic or basic conditions, which limit the scope of functional groups. Recently, Chen[13] and Pan[14] described palladium/NHC and ruthenium/NHC-catalayzed oxidative esterification of phenols with benzylic alcohols to afford aryl benzoate derivatives. However there is no report for the oxidative esterification of 2-carbonyl substituted phenols from the alcohol oxidation level. In particular, 2-carbonyl substituted aryl and alkylbenzoates are found to be important precursor for biologically active moieties such as flavanols and benzopyrans.[15]

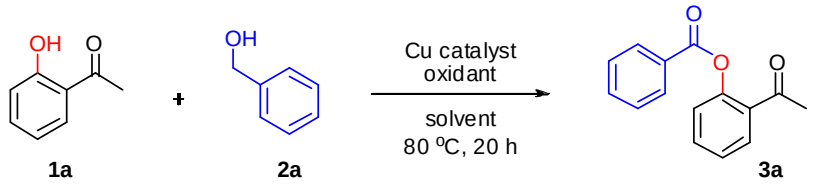
As part of an ongoing research program directed towards the development of transition metal-catalyzed oxidative acylation reactions,[16] we became interested in developing an efficient route to synthesize 2-carbonyl substituted benzoates from the alcohol oxidation level. Herein we present the copper-catalyzed esterification of 2-carbonyl substituted phenols with benzylic and aliphatic alcohols using *tert*-butyl hydroperoxide (TBHP) as a convenient oxidant.

2. Results and discussion

Our investigation was initiated by reacting phenol derivative (**1a**) with benzyl alcohol (**2a**) and the selected results are summarized in Table 1. To our delight, in the presence of 5 mol % of $Cu(OAc)_2 \cdot H_2O$ and 4 equiv. of *tert*-butyl hydroperoxide (TBHP) in DCE at 80 ^oC for 20 h, **1a** can be coupled with **2a** to provide our desired ester **3a** in 32% yield (Table 1, entry 1). Exclusion of either $Cu(OAc)_2 \cdot H_2O$ or TBHP resulted in no observation of the desired product **3a**. After screening of a range of copper catalysts, $Cu(OAc)_2$ was found to exhibit the highest reactivity (Table 1, entries 2–6). Further screening of solvents under otherwise identical conditions revealed that DMSO was found to be the most effective solvent in this coupling reaction, whereas other solvents such as DMF, MeCN, toluene, NMP and CH_2Cl_2 were less effective (Table 1, entries 7–12). Intrestingly, this process provided the coupling product **3a** under either aqueous conditions or neat conditions, albeit in moderate yields (Table 1, entries 13 and 14). Screening of oxidants showed that TBHP was superior to other oxidants such as $K_2S_2O_8$, Ag_2O and *tert*-butyl peroxybenzoate (TBPB) (Table 1, entries 15–17). Decreasing amount of oxidant results in a slightly

decreased reactivity (Table 1, entry 18).

Table 1. Selected optimization of reaction conditions.[a]



1a **2a** **3a**

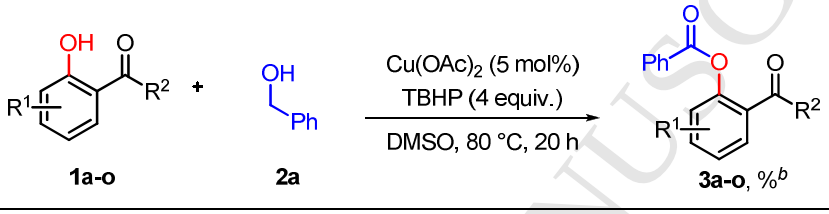
Entry	Catalyst	Oxidant	Solvent	Yield (%)[b]
1	$Cu(OAc)_2·H_2O$	TBHP	DCE	32
2	$CuCl_2·2H_2O$	TBHP	DCE	20
3	$Cu(OTf)_2$	TBHP	DCE	trace
4	CuI	TBHP	DCE	15
5	$CuBr_2$	TBHP	DCE	28
6	$Cu(OAc)_2$	TBHP	DCE	38
7	$Cu(OAc)_2$	TBHP	DMF	33
8	$Cu(OAc)_2$	TBHP	MeCN	23
9	$Cu(OAc)_2$	TBHP	toluene	18
10	$Cu(OAc)_2$	TBHP	NMP	trace
11	$Cu(OAc)_2$	TBHP	CH_2Cl_2	trace
12	**$Cu(OAc)_2$**	**TBHP**	**DMSO**	**70**
13	$Cu(OAc)_2$	TBHP	H_2O	56
14	$Cu(OAc)_2$	TBHP		44
15	$Cu(OAc)_2$	$K_2S_2O_8$	DMSO	trace
16	$Cu(OAc)_2$	Ag_2O	DMSO	trace
17[c]	$Cu(OAc)_2$	TBPB	DMSO	30
18[d]	$Cu(OAc)_2$	TBHP	DMSO	64

[a] *Reaction conditions*: **1a** (0.3 mmol), **2a** (0.4 mmol), Cu catalyst (5 mol %), *tert*-butyl hydroperoxide (TBHP, 70% in water) (4 equiv.), solvent (1 mL) at 80 °C for 20 h in pressure tubes. [b] Isolated yield by flash column chromatography. [c] TBPB = *tert*-butyl peroxybenzoate. [d] TBHP (3 equiv.).

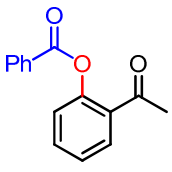
With the optimal reaction conditions in hand, a broad range of 2-carbonyl substituted phenols were subjected to esterification with benzyl alcohol (**2a**), as shown in Table 2. The coupling of 2-hydroxyacetophenones **1b**–**1e** with electron-donating and withdrawing groups (OMe, Me, F and Br)

underwent smoothly the esterification reaction to afford the corresponding products **3b**–**3e** in moderate to good yields. The yields were slightly increased when 2-hydroxybenzophenones **1f**–**1h** were used instead of 2-hydroxyacetophenones. Further investigation revealed that 2-hydroxybenzoates **1i**–**1l** also provided our desirable products in moderate yields. Various benzoates containing methyl, ethyl, phenyl and benzyl were well tolerated under these conditions. In addition, *ortho*-hydroxy acetonaphthones **1m** and **1n** were also found to undergo esterification. Further, we examined the effect of other directing groups instead of carbonyl group at the *ortho*-position of phenol. Gratifingly, compound **1o** with benzothiazole moiety underwent esterification to give **3o** in 57% yield.

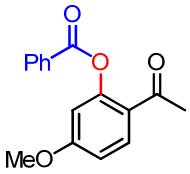
Table 2. Scope of 2-carbonyl substituted phenols[a]



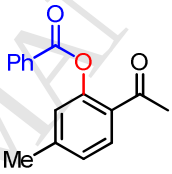
1a-o **2a** **3a-o**, %[b]



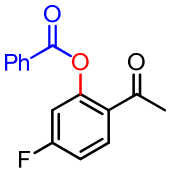
3a, 70%



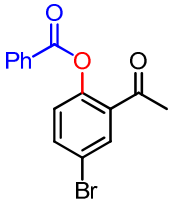
3b, 80%



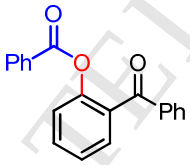
3c, 55%



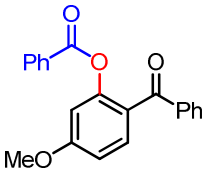
3d, 47%



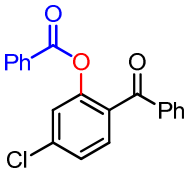
3e, 44%



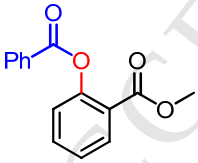
3f, 72%



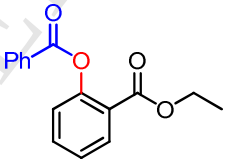
3g, 88%



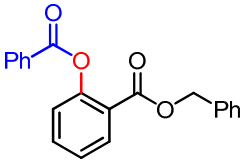
3h, 52%



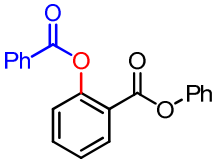
3i, 48%



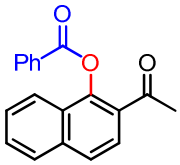
3j, 51%



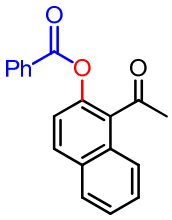
3k, 65%



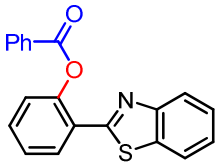
3l, 46%



3m, 46%



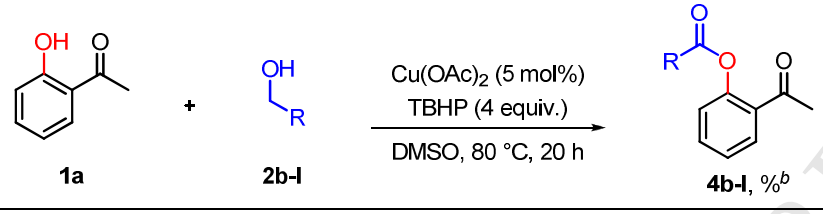
3n, 35%



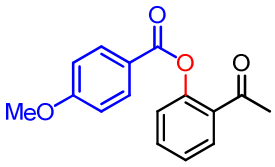
3o, 57%

[a] *Reaction conditions*: **1a**–**o** (0.3 mmol), **2a** (0.6 mmol), $Cu(OAc)_2$ (5 mol %), TBHP (4 equiv.), DMSO (1 mL) at 80 °C for 20 h. [b] Isolated yield by flash column chromatography.

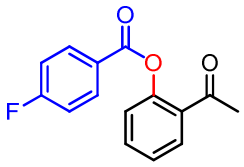
Table 3. Scope of alcohols[a]



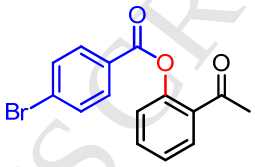
1a + **2b-l** → **4b-l**, %[b]



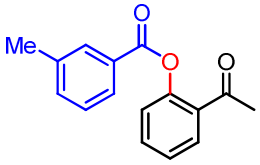
4b, 67%



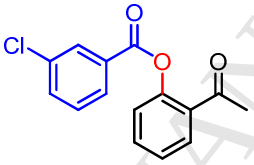
4c, 56%



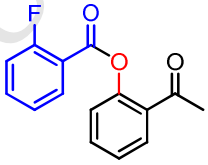
4d, 45%



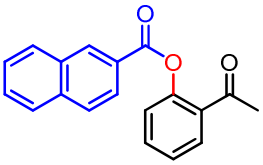
4e, 56%



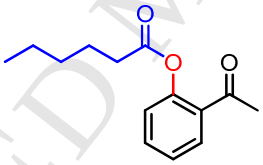
4f, 42%



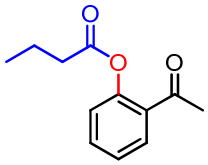
4g, 40%



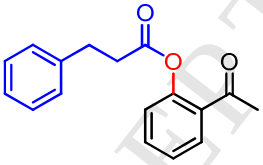
4h, 58%



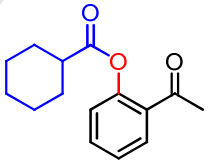
4i, 50%



4j, 44%



4k, 39%



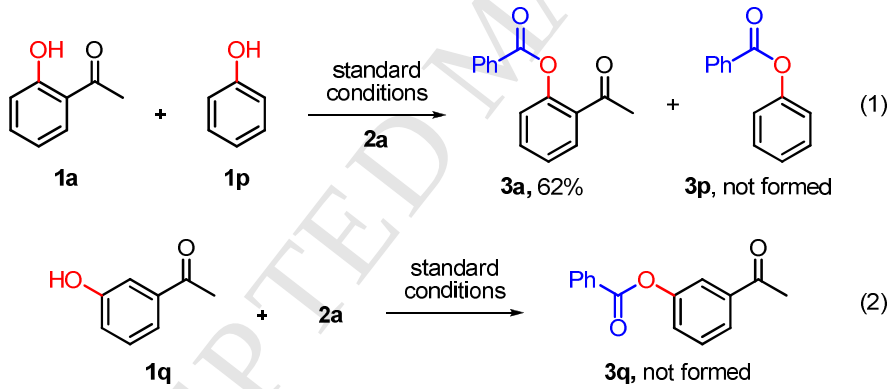
4l, 41%

[a] *Reaction conditions*: **1a** (0.3 mmol), **2b**–**l** (0.6 mmol), $Cu(OAc)_2$ (5 mol %), TBHP (4 equiv.), DMSO (1 mL) at 80 °C for 20 h. [b] Isolated yield by flash column chromatography.

To further explore the substrate scope and limitations, a range of alcohol **2b**–**2l** was screened to couple with 2-hydroxyacetophenone (**1a**) under the optimal reaction conditions, as shown in Table 3. The coupling of **1a** and benzylic alcohols **2b**–**2g** with electron-rich and electron-deficient groups (OMe, Me, F,

Br and Cl), regardless of substituent position on the aromatic ring, was found to participate in the acylation reaction to afford the corresponding products **4b**–**4g** in moderate to good yields. However, electron-withdrawing groups such as NO_2 and COOMe at the *para*-position did not deliver the corresponding ester products under the optimal reaction conditions. In addition, 2-naphthalenemethanol (**2h**) smoothly underwent this coupling reaction to generate the product **4h** in 58% yield. To our delight, this reaction is not limited to benzylic alcohols. Aliphatic alcohols such as 1-hexanol, 1-butanol, 3-phenylpropanol and cyclohexylmethanol also participated in the oxidative esterification as the acylating agents to afford the corresponding products **4i**–**4l** in moderate yields.

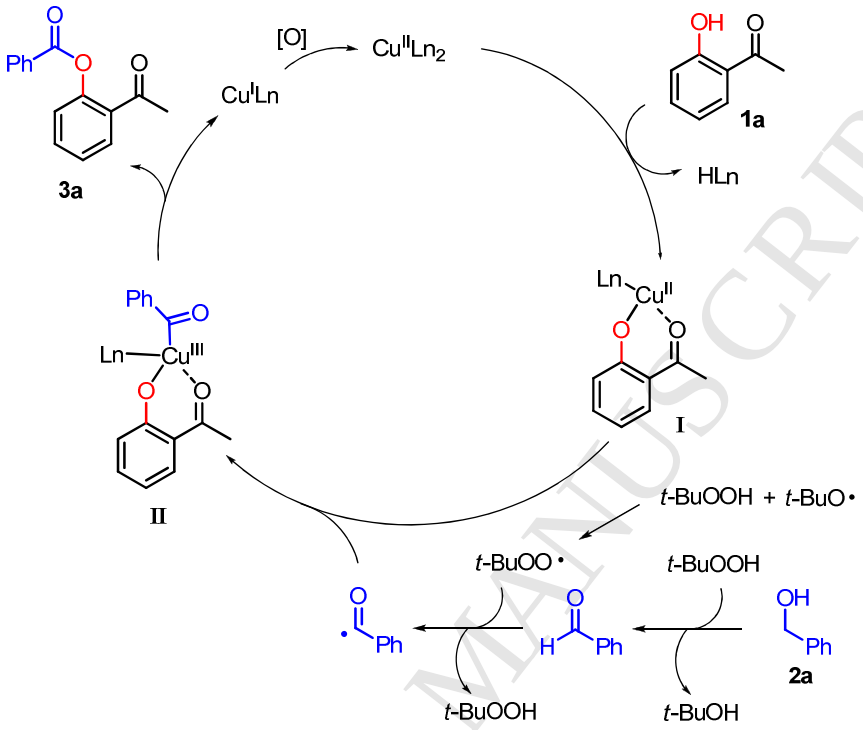
To examine the influence of *ortho*-carbonyl group of this process, competition experiment was performed between 2-hydroxyacetophenone (**1a**) and phenol (**1p**) under the standard conditions (Scheme 1, eq. 1). Interestingly, no esterification of **1p** was observed. In addition, we performed oxidative benzoylation of 3-hydroxyacetophenone (**1q**) with **2a** leading to no observation of the corresponding product **3q** under the standard conditions (Scheme 1, eq. 2). Thus, the lack of ester formation of phenols **1p** and **1q** suggest that the substrates binding to copper metal in a bidentate fashion could be one of the key factors for the formation of ester.



Scheme 1. Mechanistic investigation.

A plausible reaction pathway is illustrated in Scheme 2. First, Cu(II) catalyst forms complex **I** with 2-hydroxyacetophenone (**1a**) and at the same time the alcohol **2a** was oxidized to aldehyde by TBHP and the *t*-BuO$^{\cdot}$ radical reacts with TBHP to generate *t*-BuOO$^{\cdot}$ radical,[17] which can abstract H atom from the aldehyde to give a reactive acyl radical.[18] The newly formed benzoyl radical can react with complex **I** by single electron transfer to produce Cu(III) complex **II**, which can undergo reductive elimination to afford the product **3a** and Cu(I) catalyst. Finally, Cu(I) catalyst is oxidized to Cu(II) by TBHP.[19] Alternatively,

Cu(II) complex **I** can undergo nucleophilic addition with aldehyde to deliver a copper hemiacetal intermediate, which on further H-abstraction followed by a single electron transfer to lead the desired product and Cu(I) catalyst.[20]



Scheme 2. Proposed mechanistic pathway.

3. Conclusion

In conclusion, we described a highly efficient method for the copper-catalyzed oxidative esterification of 2-carbonyl substituted phenols from the alcohol oxidation level. These transformations have been applied to a wide range of substrates. Also this protocol allows us to generate 2-carbonyl substituted aryl and alkylbenzoates which constitute important functionallity for biologically active moieties.

4. Experimental

4.1. General methods: Commercially available reagents were used without additional purification,

unless otherwise stated. Sealed tubes (13 × 100 mm^2) were purchased from Fischer Scientific and dried in oven for overnight and cooled under a stream of nitrogen prior to use. Thin layer chromatography was carried out using plates coated with Kieselgel $60F_{254}$ (Merck). For flash column chromatography, E. Merck Kieselgel 60 (230-400 mesh) was used. Nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded on a Bruker Unity 400 MHz and 700 MHz spectrometer for $CDCl_3$ solutions and chemical shifts are reported as parts per million (ppm) relative to, respectively, residual $CHCl_3$ δ_H (7.24 ppm) and $CDCl_3$ δ_C (77.2 ppm) as internal standards. Resonance patterns are reported with the notations s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). In addition, the notation br is used to indicate a broad signal. Coupling constants (*J*) are reported in hertz (Hz). IR spectra were recorded on a Varian 2000 Infrared spectrophotometer and are reported as cm^{-1}. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer.

4.2. Typical procedure for the esterification of 2-carbonyl substtuted phenols: To an oven-dried sealed tube charged with 2-hydroxyacetophenone (**1a**) (40.8 mg, 0.3 mmol, 1.0 equiv.), $Cu(OAc)_2$ (2.7 mg, 0.015 mmol, 5 mol %), and TBHP (70% in water) (0.16 mL, 1.2 mmol, 4.0 equiv.) in DMSO (1 mL, 0.3 M) was added benzyl alcohol (**2a**) (65.4 mg, 0.6 mmol, 2 equiv.). The reaction mixture was allowed to stir at 80 ºC for 20 h. After cooling at room temperature, the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: *n*-hexanes/EtOAc = 40:1) provided **3a** (50.5 mg) in 70% yield

4.2.1. 2-Acetylphenyl benzoate (3a): yellow oil; R_f = 0.60 (*n*-hexanes/EtOAc = 6:1); ^1H NMR (700 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.4, 165.1, 149.3, 133.7, 133.3, 131.2, 130.3, 129.1, 128.6, 126.1, 123.8, 29.7; IR (KBr) υ 2925, 1732, 1638, 1620, 1481, 1448, 1357, 1264, 1202, 1177, 1061, 956 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{12}O_3$ $[M]^+$ 240.0786, found 240.0785.

4.2.2. 2-Acetyl-5-methoxyphenyl benzoate (3b): colorless sticky solid; R_f = 0.40 (*n*-hexanes/EtOAc = 6:1); ^1H NMR (700 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 1H), 7.05 (s, 1H), 3.82 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 195.5, 165.0, 163.6, 151.5, 133.6, 132.3, 130.2, 129.2, 128.5, 123.3, 111.8, 109.1, 55.6, 29.3; IR (KBr) υ 2925, 1738, 1682, 1607, 1568, 1499, 1452, 1357, 1264, 1164, 1175, 1137, 1068, 1024, 964 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{14}O_4$ $[M]^+$ 270.0892, found 270.0890.

4.2.3. 2-Acetyl-5-methylphenyl benzoate (3c): yellow oil; R_f = 0.50 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 2.49 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 196.9, 165.2, 149.5, 144.8, 133.6, 130.4, 130.2, 129.3, 128.6, 128.2, 126.9, 124.3, 29.6, 21.3; IR (KBr) υ 2923, 1738, 1682, 1615, 1451, 1357, 1266, 1229, 1143, 1062, 1024, 967 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{14}O_3$ $[M]^+$ 254.0943, found 254.0945.

4.2.4. 2-Acetyl-5-fluorophenyl benzoate (3d): colorless oil; R_f = 0.55 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 2H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 8.1 Hz, 2H), 7.06–7.05 (m, 1H), 6.97 (d, *J* = 8.8 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 195.8, 164.9 (d, $J_{C–F}$ = 255.9 Hz), 164.7, 151.1 (d, $J_{C–F}$ = 11.3 Hz), 134.0, 132.3 (d, $J_{C–F}$ = 10.5 Hz), 130.3, 128.8, 128.7, 127.6 (d, $J_{C–F}$ = 3.0 Hz), 113.4 (d, $J_{C–F}$ = 21.2 Hz), 111.8 (d, $J_{C–F}$ = 24.4 Hz), 29.7; IR (KBr) υ 2923, 1746, 1688, 1603, 1452, 1357, 1263, 1149, 1023, 976 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{11}FO_3$ $[M]^+$ 258.0692, found 258.0695.

4.2.5. 2-Acetyl-4-bromophenyl benzoate (3e): light yellow sticky solid; R_f = 0.50 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 2H), 7.94 (s, 1H), 7.66–7.64 (m, 1H), 7.51 (t, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 196.0, 164.7, 148.2, 136.0, 134.0, 132.9, 132.8, 130.2, 128.7, 125.6, 119.3, 29.7; IR (KBr) υ 2917, 1742, 1694, 1600, 1472, 1356, 1260, 1202, 1055, 1023, 957 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{11}BrO_3$ $[M]^+$ 317.9892, found 317.9890.

4.2.6. 2-Benzoylphenyl benzoate (3f): light yellow oil; R_f = 0.55 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.60–7.57 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.37–7.31 (m, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 194.7, 164.5, 148.7, 137.4, 133.4, 132.8, 132.1, 131.7, 130.3, 129.9, 129.6, 128.7, 128.3, 128.2, 125.7, 123.2; IR (KBr) υ 2917, 1738, 1666, 1600, 1449, 1293, 1262, 1202, 1104, 1059, 1023, 928 cm^{-1}; HRMS (EI) Calcd for $C_{20}H_{14}O_3$ $[M]^+$ 302.0943, found 302.0940.

4.2.6. 2-Benzoyl-5-methoxyphenyl benzoate (3g): colorless sticky solid; R_f = 0.45 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.34–7.31 (m, 4H), 6.87–6.85 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 194.1, 164.5, 162.9, 150.8, 138.3, 133.4, 132.5, 132.3, 129.9, 129.4, 128.7, 128.2, 128.1, 123.9, 111.4, 108.8, 55.6; IR (KBr) υ 2932, 1738, 1660, 1608, 1448, 1317, 1272,

1158, 1111, 1024, 949 cm^{-1}; HRMS (EI) Calcd for $C_{21}H_{16}O_4$ $[M]^+$ 332.1049, found 332.1051.

4.2.7. 2-Benzoyl-5-chlorophenyl benzoate (3h): colorless sticky solid; R_f = 0.50 (*n*-hexanes/EtOAc = 6:1); ^1H NMR (700 MHz, $CDCl_3$) δ 7.76 (t, *J* = 8.4 Hz, 4H), 7.75–7.73 (m, 2H), 7.51–7.44 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 193.3, 164.3, 147.1, 136.8, 133.6, 133.3, 133.2, 131.9, 131.3, 130.0, 129.9, 129.6, 128.5, 128.4, 128.3, 124.6; IR (KBr) υ 2923, 1745, 1668, 1598, 1472, 1398, 1260, 1205, 1177, 1113, 1055, 1023, 948 cm^{-1}; HRMS (EI) Calcd for $C_{20}H_{13}ClO_3$ $[M]^+$ 336.0553, found 336.0547.

4.2.8. Methyl 2-(benzoyloxy)benzoate (3i): light yellow oil; R_f = 0.48 (*n*-hexanes/EtOAc = 6:1); ^1H NMR (700 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 2H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.63–7.58 (m, 2H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.3, 165.0, 150.7, 133.8, 133.5, 131.9, 130.2, 129.4, 128.5, 126.0, 123.9, 123.4, 52.1; IR (KBr) υ 2953, 1731, 1606, 1451, 1299, 1265, 1205, 1126, 1082, 1061, 1024, 965 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{12}O_4$ $[M]^+$ 256.0736, found 256.0734.

4.2.9. Ethyl 2-(benzoyloxy)benzoate (3j): colorless sticky solid; R_f = 0.45 (*n*-hexanes/EtOAc = 6:1); ^1H NMR (700 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.63–7.56 (m, 2H), 7.50 (t, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.07 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.2, 164.7, 150.5, 133.6, 133.5, 131.9, 130.2, 129.4, 128.5, 126.0, 123.9, 123.8, 61.1, 13.8; IR (KBr) υ 2982, 1742, 1720, 1606, 1451, 1295, 1266, 1204, 1125, 1061, 1023 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{14}O_4$ $[M]^+$ 270.0892, found 270.0892.

4.2.10. Benzyl 2-(benzoyloxy)benzoate (3k): colorless sticky solid; R_f = 0.50 (*n*-hexanes/EtOAc = 6:1); ^1H NMR (700 MHz, $CDCl_3$) δ 8.12–8.09 (m, 3H), 7.60–7.58 (m, 2H), 7.44 (t, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.22–7.20 (m, 6H), 5.18 (s, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.2, 164.5, 150.7, 135.2, 133.8, 133.4, 132.0, 130.2, 129.3, 128.5, 128.4, 128.3, 128.1, 126.0, 123.9, 123.6, 67.1; IR (KBr) υ 2923, 1739, 1731, 1606, 1451, 1291, 1266, 1204, 1122, 1078, 1061, 1023, 957 cm^{-1}; HRMS (EI) Calcd for $C_{21}H_{16}O_4$ $[M]^+$ 332.1049, found 332.1045.

4.2.11. Phenyl 2-(benzoyloxy)benzoate (3l): white solid; mp 68–71 ^oC; R_f = 0.40 (*n*-hexanes/EtOAc = 6:1); ^1H NMR (700 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.8 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 2H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46–7.41 (m, 3H), 7.32–7.29 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.2, 162.9, 151.1, 150.4, 134.4, 133.5, 132.2, 130.3, 129.3,

129.2, 128.4, 126.2, 125.8, 124.1, 123.0, 121.5; IR (KBr) υ 2921, 1742, 1605, 1484, 1451, 1265, 1206, 1192, 1112, 1078, 1058, 1023 cm^{-1}; HRMS (EI) Calcd for $C_{20}H_{14}O_4$ $[M]^+$ 318.0892, found 318.0883.

4.2.12. 2-Acetylnaphthalen-1-yl benzoate (3m): colorless oil; R_f = 0.45 (*n*-hexanes/EtOAc = 5:1); ^1H NMR (700 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 8.6 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.60–7.56 (m, 3H), 7.53–7.50 (m, 1H), 2.62 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.6, 165.0, 146.6, 136.3, 134.0, 130.4, 128.9, 128.8, 128.5, 127.9, 127.4, 127.3, 127.0, 126.1, 125.1, 122.9, 30.1; IR (KBr) υ 2917, 1742, 1683, 1626, 1598, 1451, 1358, 1259, 1177, 1082, 1068, 1021 cm^{-1}; HRMS (EI) Calcd for $C_{19}H_{14}O_3$ $[M]^+$ 290.0943, found 290.0936.

4.2.13. 1-Acetylnaphthalen-2-yl benzoate (3n): light yellow sticky solid; R_f = 0.48 (*n*-hexanes/EtOAc = 5:1); ^1H NMR (700 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 8.4 Hz, 1H), 7.55–7.50 (m, 4H), 7.38 (d, *J* = 8.8 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 202.8, 164.8, 144.9, 134.0, 131.6, 130.9, 130.4, 130.3, 129.8, 128.8, 128.7, 128.4, 127.6, 126.1, 124.4, 121.4, 32.5; IR (KBr) υ 2922, 1739, 1702, 1595, 1491, 1351, 1260, 1208, 1177, 1080, 1062, 1022 cm^{-1}; HRMS (EI) Calcd for $C_{19}H_{14}O_3$ $[M]^+$ 290.0943, found 290.0943.

4.2.14. 2-(Benzo[d]thiazol-2-yl)phenyl benzoate (3o): light yellow solid; mp 144–147 ^oC; R_f = 0.40 (*n*-hexanes/EtOAc = 5:1); ^1H NMR (700 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.8 Hz, 1H), 8.31 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.56–7.53 (m, 3H), 7.44–7.40 (m, 2H), 7.33–7.31 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.0, 162.2, 152.8, 148.5, 135.3, 133.7, 131.4, 130.6, 130.2, 129.4, 128.6, 126.4, 126.3, 126.1, 125.1, 123.8, 123.2, 121.3; IR (KBr) υ 2917, 1742, 1601, 1482, 1449, 1314, 1259, 1191, 1176, 1104, 1054, 1022, 966 cm^{-1}; HRMS (EI) Calcd for $C_{20}H_{13}NO_2S$ $[M]^+$ 331.0667, found 331.0659.

4.2.15. 2-Acetylphenyl 4-methoxybenzoate (4b): colorless sticky solid; R_f = 0.45 (*n*-hexanes/EtOAc = 6:1); ^1H NMR (700 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.6, 164.7, 164.0, 149.4, 133.2, 132.4, 131.4, 130.0, 125.9, 123.9, 121.4, 113.9, 55.4, 29.8; IR (KBr) υ 2923, 1724, 1684, 1608, 1579, 1482, 1450, 1258, 1199, 1166, 1071, 1022, 963 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{14}O_4$ $[M]^+$ 270.0892, found 270.0895.

4.2.16. 2-Acetylphenyl 4-fluorobenzoate (4c): yellow sticky solid; R_f = 0.55 (*n*-hexanes/EtOAc = 6:1);

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22–8.20 (m, 2H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.21–7.16 (m, 3H), 2.52 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.4, 166.2 (d, $J_{C–F}$ = 255.1 Hz), 164.1, 149.1, 133.4, 132.9 (d, $J_{C–F}$ = 9.6 Hz), 131.0, 130.3, 126.2, 125.5 (d, $J_{C–F}$ = 3.2 Hz), 123.8, 115.9 (d, $J_{C–F}$ = 22.1 Hz), 29.5; IR (KBr) υ 2924, 1739, 1688, 1630, 1507, 1448, 1357, 1265, 1199, 1154, 1069, 1013, 956 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{11}FO_3$ $[M]^+$ 258.0692, found 258.0692.

4.2.17. 2-Acetylphenyl 4-bromobenzoate (4d): yellow solid; mp 121–124 ^{o}C; R_f = 0.50 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.3, 164.5, 149.0, 133.4, 132.0, 131.7, 130.8, 130.3, 129.0, 128.2, 126.2, 123.8, 29.4; IR (KBr) υ 2917, 1739, 1687, 1603, 1589, 1486, 1357, 1264, 1199, 1173, 1071, 1010, 956 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{11}BrO_3$ $[M]^+$ 317.9892, found 317.9888.

4.2.18. 2-Acetylphenyl 3-methylbenzoate (4e): colorless oil; R_f = 0.45 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.00–7.99 (m, 2H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.44–7.43 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 2.52 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.5, 165.2, 149.4, 138.5, 134.6, 133.3, 131.3, 130.7, 130.2, 129.1, 128.5, 127.4, 126.1, 123.8, 29.7, 21.2; IR (KBr) υ 2922, 1738, 1688, 1603, 1447, 1357, 1273, 1182, 1117, 1062, 956 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{14}O_3$ $[M]^+$ 254.0943, found 254.0945.

4.2.19. 2-Acetylphenyl 2-naphthoate (4f): yellow oil; R_f = 0.40 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.63–7.55 (m, 3H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.5, 165.3, 149.4, 135.8, 133.4, 132.4, 132.1, 131.3, 130.2, 129.5, 128.7, 128.5, 127.8, 126.8, 126.3, 126.1, 125.3, 123.9, 29.7; IR (KBr) υ 2923, 1732, 1688, 1603, 1447, 1356, 1281, 1188, 1127, 1072, 950 cm^{-1}; HRMS (EI) Calcd for $C_{19}H_{14}O_3$ $[M]^+$ 290.0943, found 290.0936.

4.2.20. 2-Acetylphenyl 3-chlorobenzoate (4g): yellow oil; R_f = 0.48 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.60–7.56 (m, 2H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.3, 164.0, 149.0, 134.8, 133.7, 133.5, 131.0, 130.8, 130.4, 130.2, 129.9, 128.3, 126.3, 123.8, 29.4; IR (KBr) υ 2924, 1742, 1687, 1604, 1576, 1447, 1357, 1282, 1249, 1199, 1118, 1071, 957 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{11}ClO_3$ $[M]^+$ 274.0397, found 274.0394.

4.2.21. 2-Acetylphenyl 2-fluorobenzoate (4h): yellow sticky solid; R_f = 0.50 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.13 (t, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.58–7.55 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.23–7.18 (m, 2H), 2.54 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.3, 162.6 (d, $J_{C–F}$ = 3.3 Hz), 162.3 (d, $J_{C–F}$ = 261.5 Hz), 148.9, 135.4 (d, $J_{C–F}$ = 9.4 Hz), 133.4, 132.7, 130.9, 130.3, 126.2, 124.2 (d, $J_{C–F}$ = 3.9 Hz), 123.9, 117.8 (d, $J_{C–F}$ = 9.3 Hz), 117.2 (d, $J_{C–F}$ = 22.0 Hz) 24.9; IR (KBr) υ 2917, 1748, 1686, 1613, 1488, 1448, 1357, 1291, 1243, 1197, 1126, 1052, 954 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{11}FO_3$ $[M]^+$ 258.0692, found 258.0690.

4.2.22. 2-Acetylphenyl hexanoate (4i): colorless oil; R_f = 0.44 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.52 (s, 3H), 1.73–1.78 (m, 2H), 1.39–1.35 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.6, 172.2, 149.0, 133.2, 130.9, 130.1, 125.8, 123.7, 34.2, 31.2, 29.4, 24.1, 22.3, 13.8; IR (KBr) υ 2931, 1765, 1689, 1604, 1448, 1357, 1250, 1201, 1138, 1098, 956 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{18}O_3$ $[M]^+$ 234.1256, found 234.1255.

4.2.23. 2-Acetylphenyl butyrate (4j): colorless oil; R_f = 0.55 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 2.57 (t, *J* = 7.4 Hz, 2H), 2.52 (s, 3H), 1.76–1.80 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.6, 172.0, 149.0, 133.3, 130.9, 130.1, 125.8, 123.7, 36.1, 29.4, 18.0, 13.6; IR (KBr) υ 2968, 1760, 1694, 1630, 1447, 1358, 1282, 1251, 1140, 1072, 956 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{14}O_3$ $[M]^+$ 206.0943, found 206.0942.

4.2.24. 2-Acetylphenyl 3-phenylpropanoate (4k): colorless sticky solid; R_f = 0.40 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.31–7.28 (m, 3H), 7.27–7.25 (m, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.08 (t, *J* = 7.5 Hz, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.5, 171.3, 148.9, 140.1, 133.3, 130.7, 130.2, 128.5, 128.3, 126.3, 126.0, 123.7, 35.9, 30.5, 29.3; IR (KBr) υ 2925, 1760, 1688, 1603, 1448, 1357, 1283, 1251, 1198, 1129, 1072, 956 cm^{-1}; HRMS (EI) Calcd for $C_{17}H_{16}O_3$ $[M]^+$ 268.1099, found 268.1106.

4.2.25. 2-Acetylphenyl cyclohexanecarboxylate (4l): colorless oil; R_f = 0.50 (*n*-hexanes/EtOAc = 6:1); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 2.52 (s, 3H), 2.10–2.08 (m, 2H), 1.82–1.79 (m, 2H), 1.68–1.66 (m, 1H), 1.58–1.54 (m, 2H), 1.36–1.23 (m, 4H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 197.8, 174.3, 149.1, 133.2, 131.2, 129.9,

125.8, 123.7, 43.2, 29.5, 28.7, 25.6, 25.3; IR (KBr) υ 2932, 1756, 1689, 1603, 1482, 1448, 1356, 1283, 1250, 1190, 1149, 1116, 1015, 956 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{18}O_3$ $[M]^+$ 246.1256, found 246.1254..

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Supplementary data

Supplementary data available: ^1H NMR and ^{13}C NMR copies of all compounds. Supplementary data associated with this article can be found in the online version, at http://

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Supplementary Data

Cu(II)-catalyzed oxidative esterification of 2-carbonyl substituted phenols from the alcohol oxidation level

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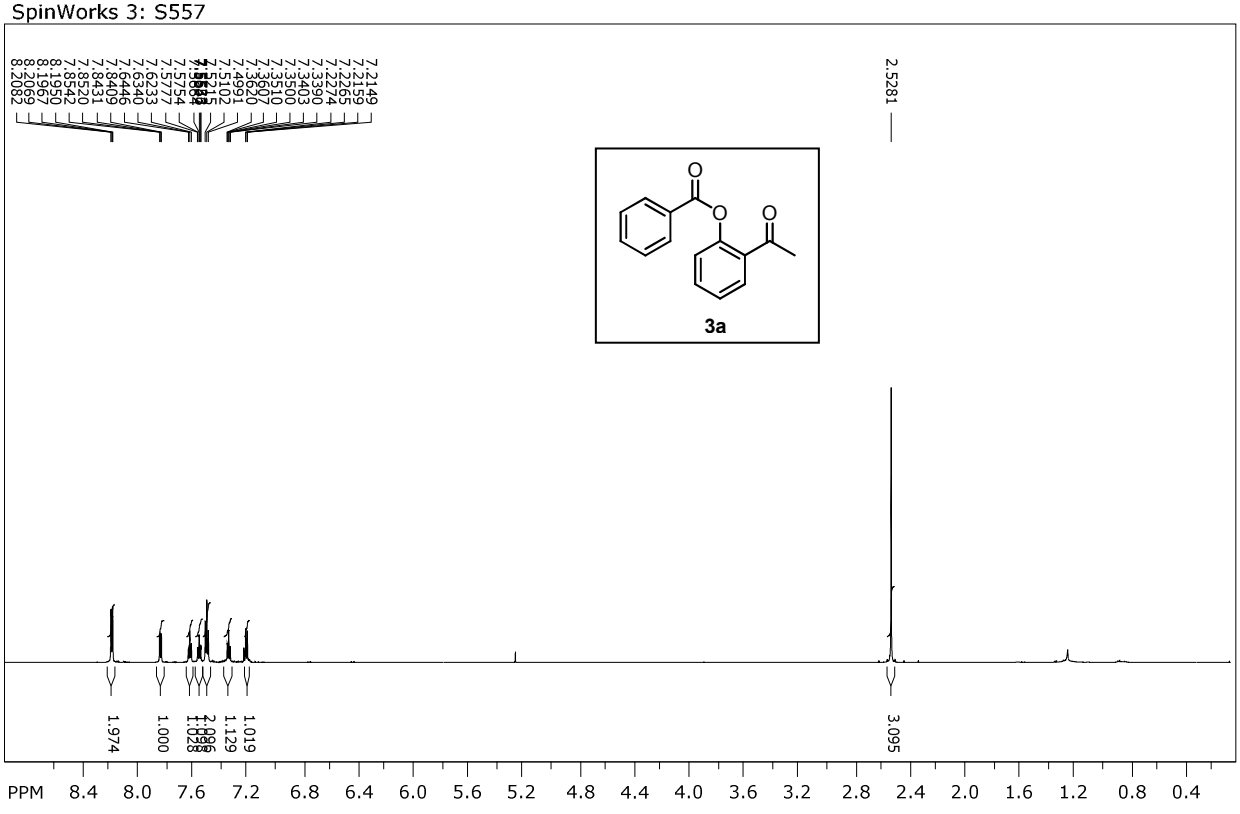

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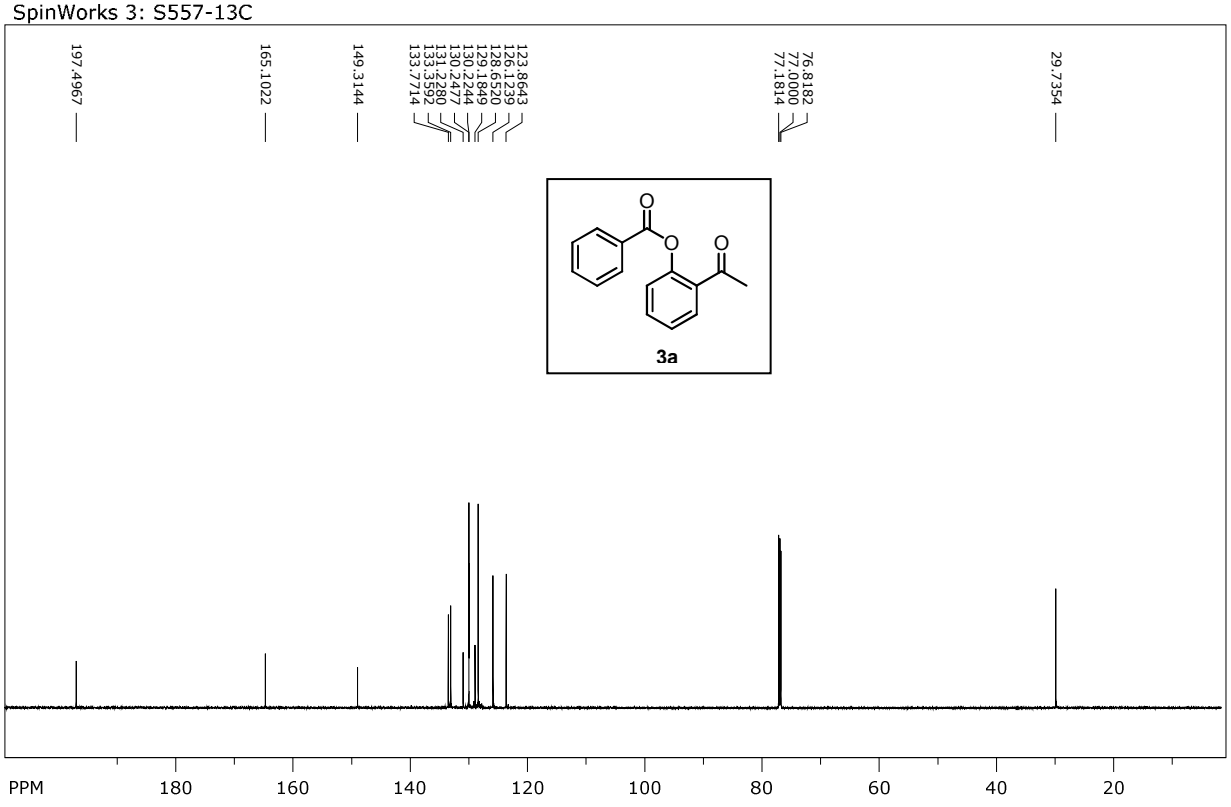

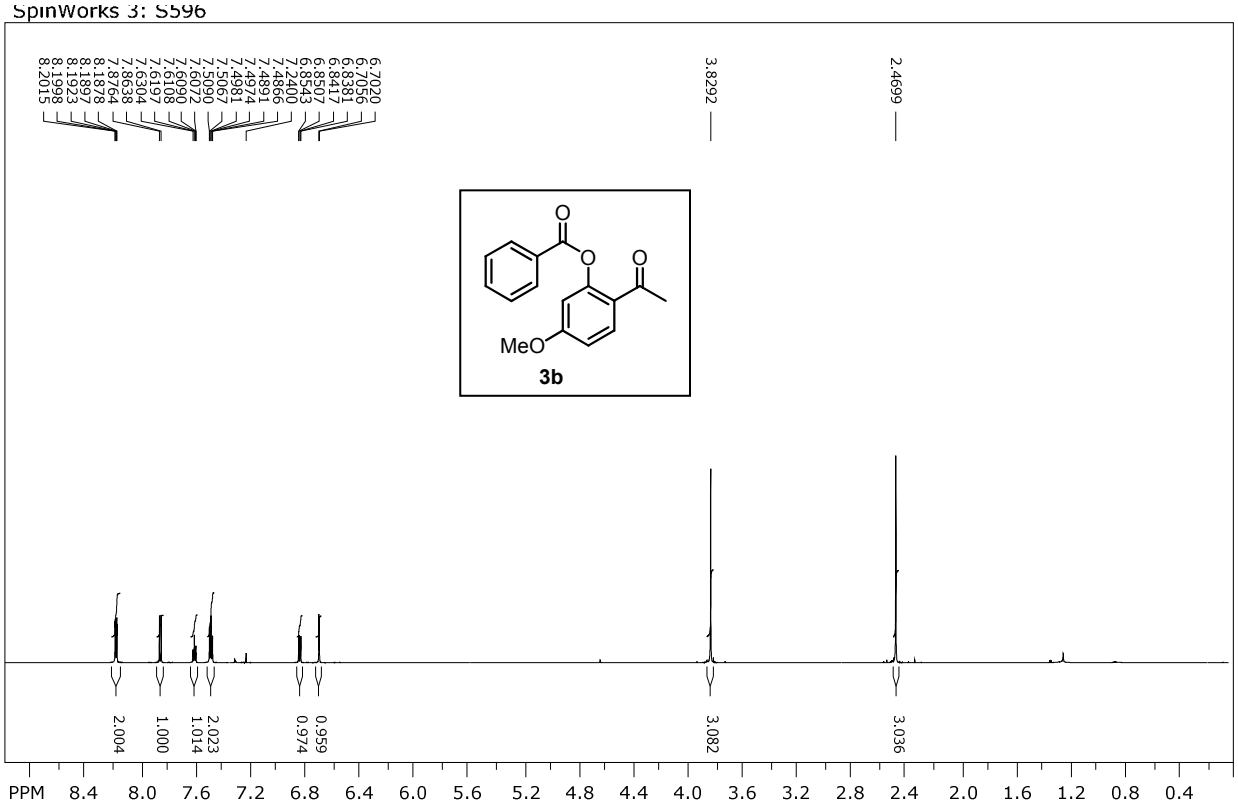
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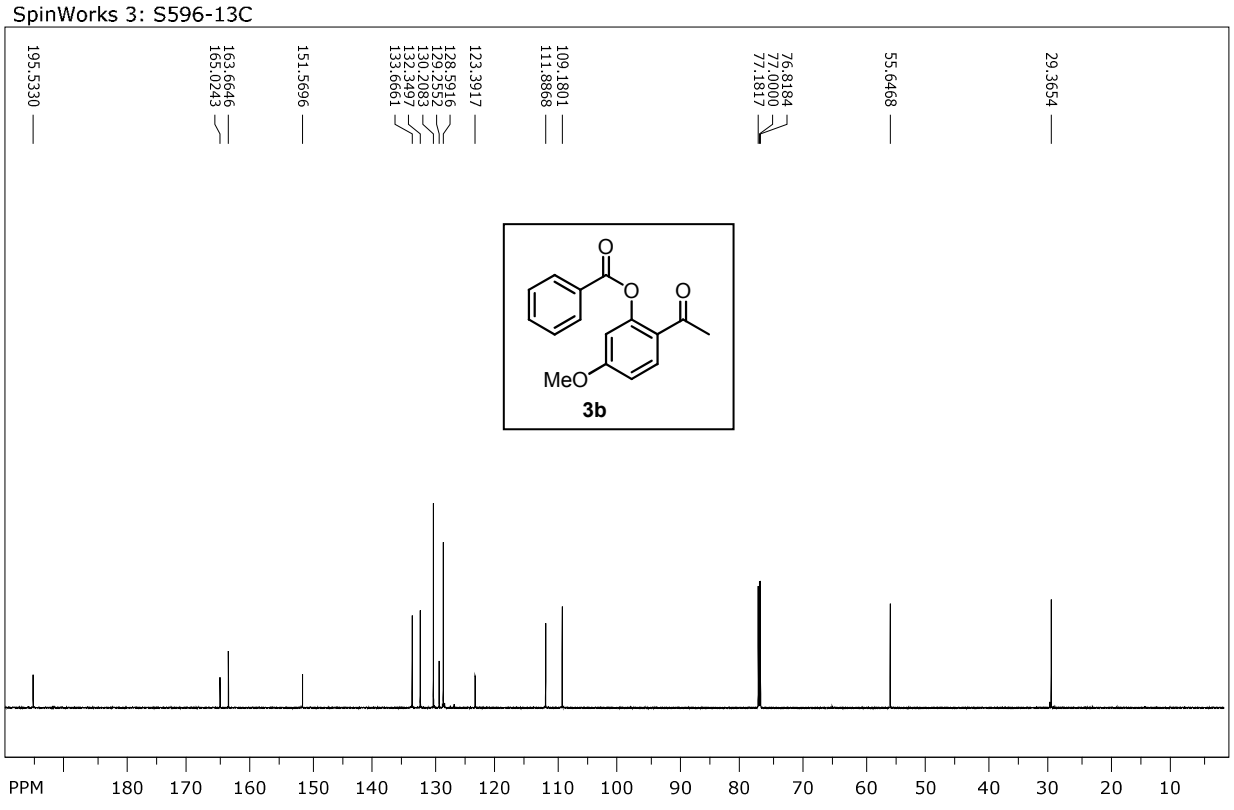
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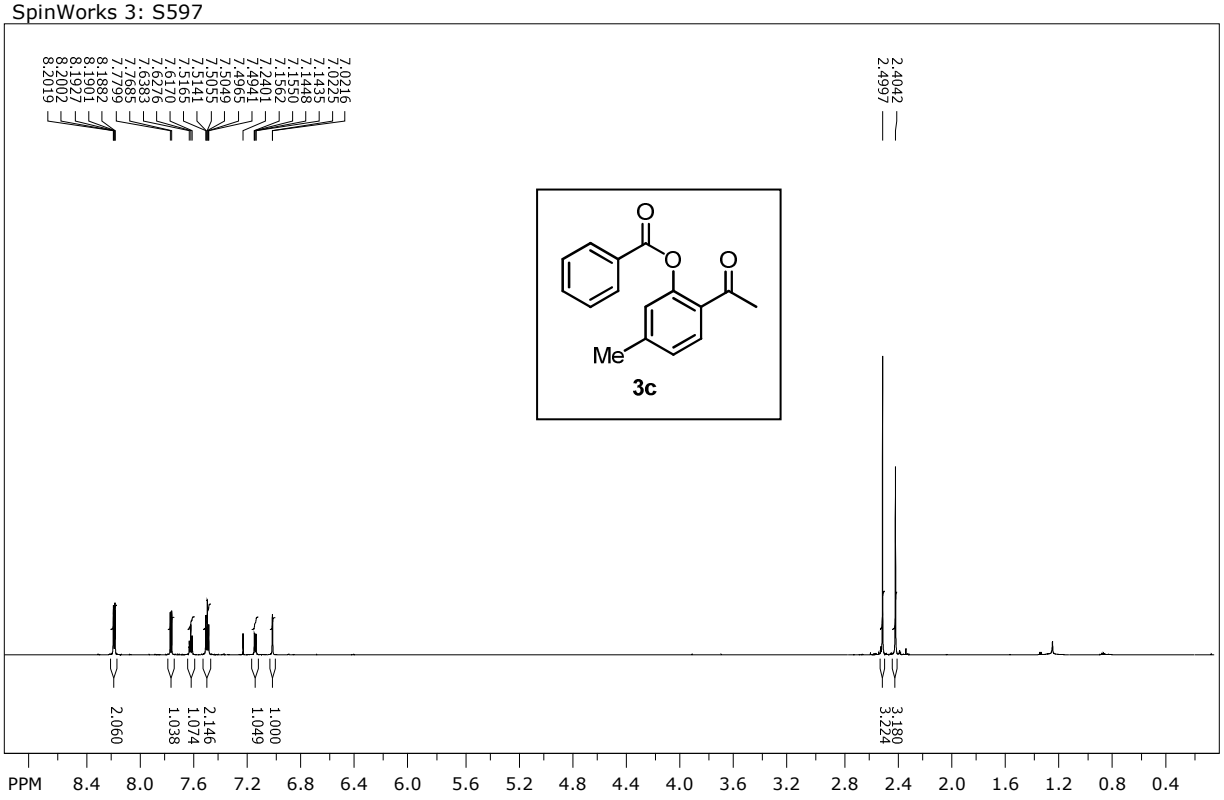

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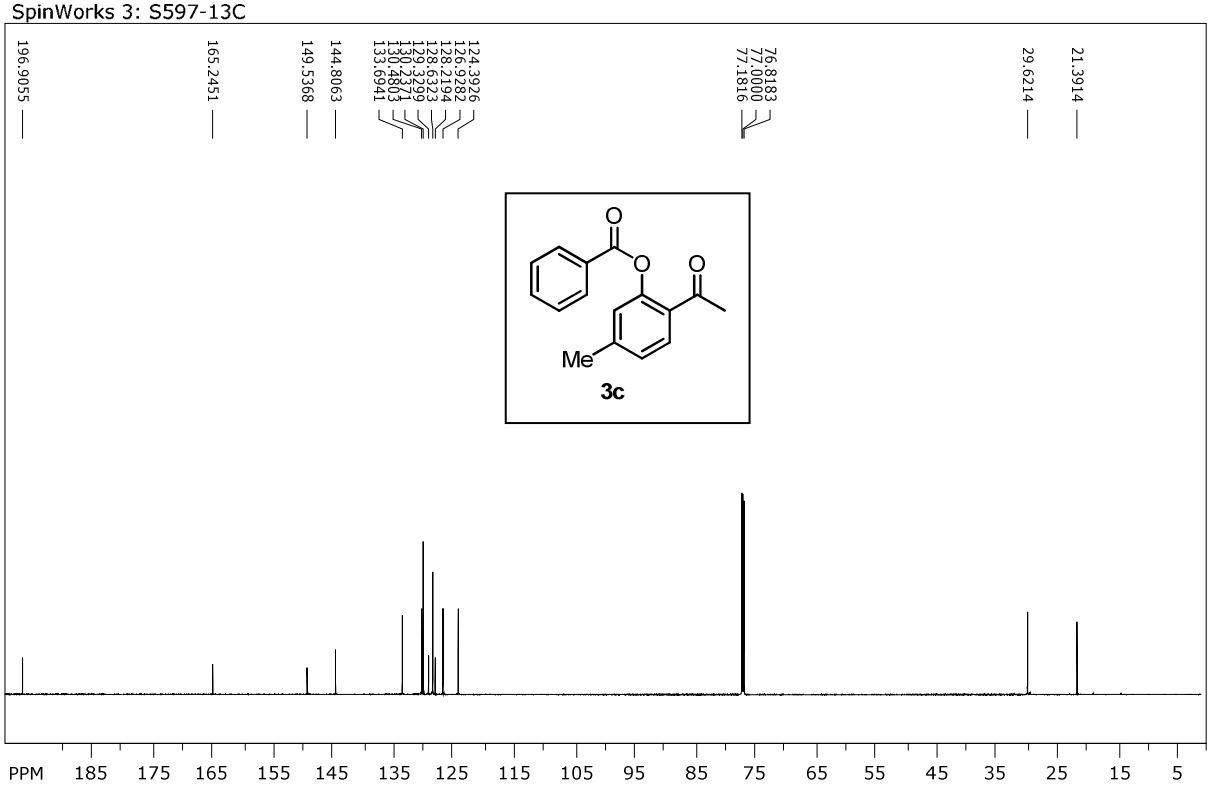

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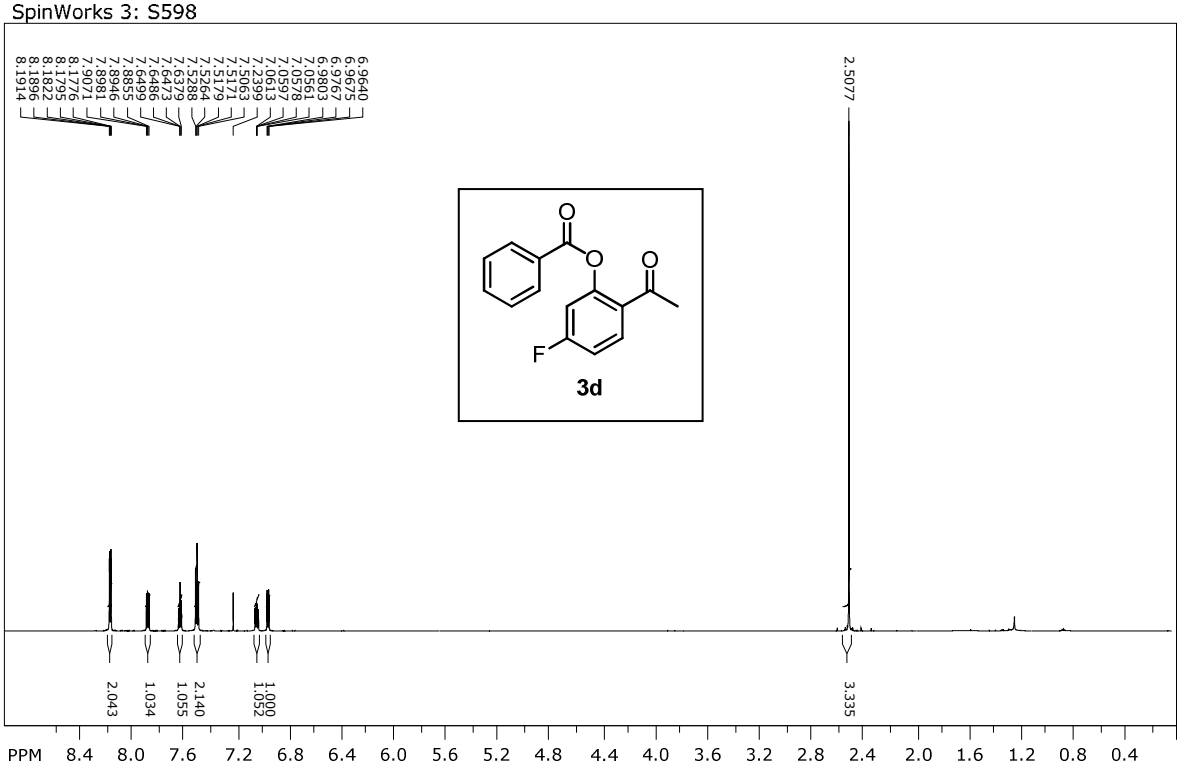

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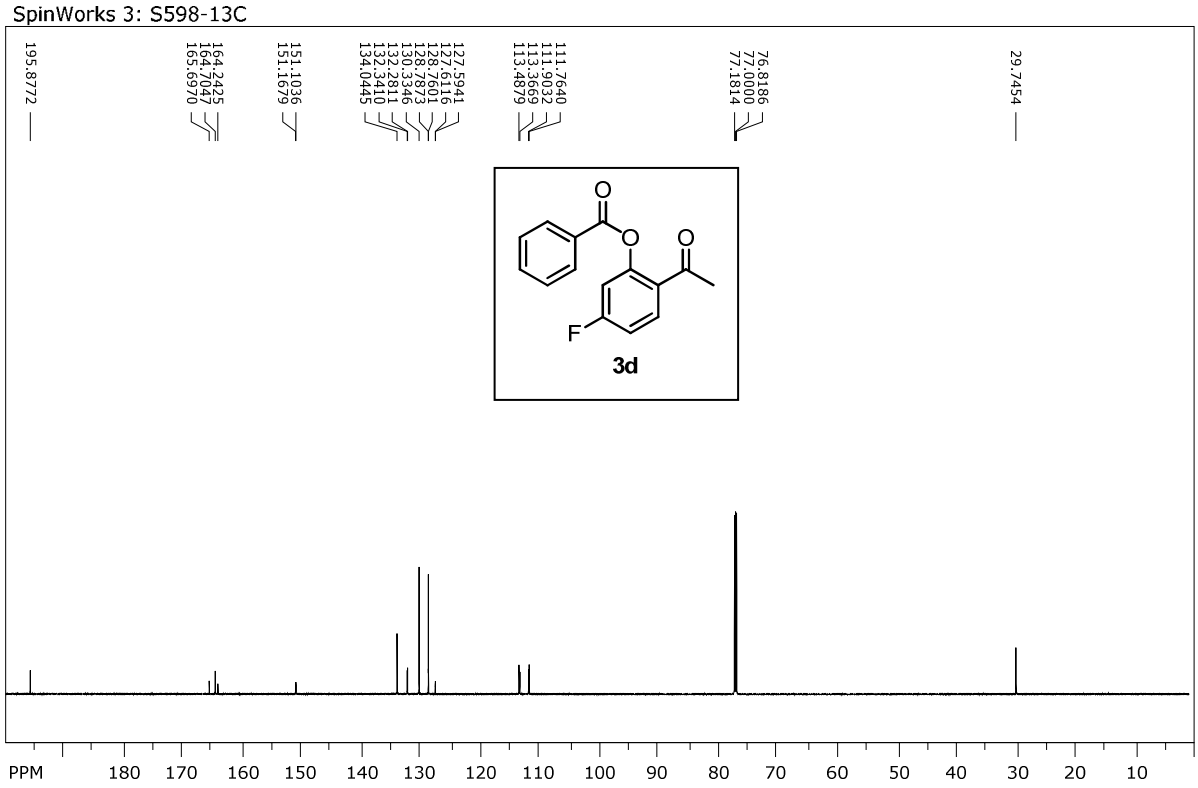

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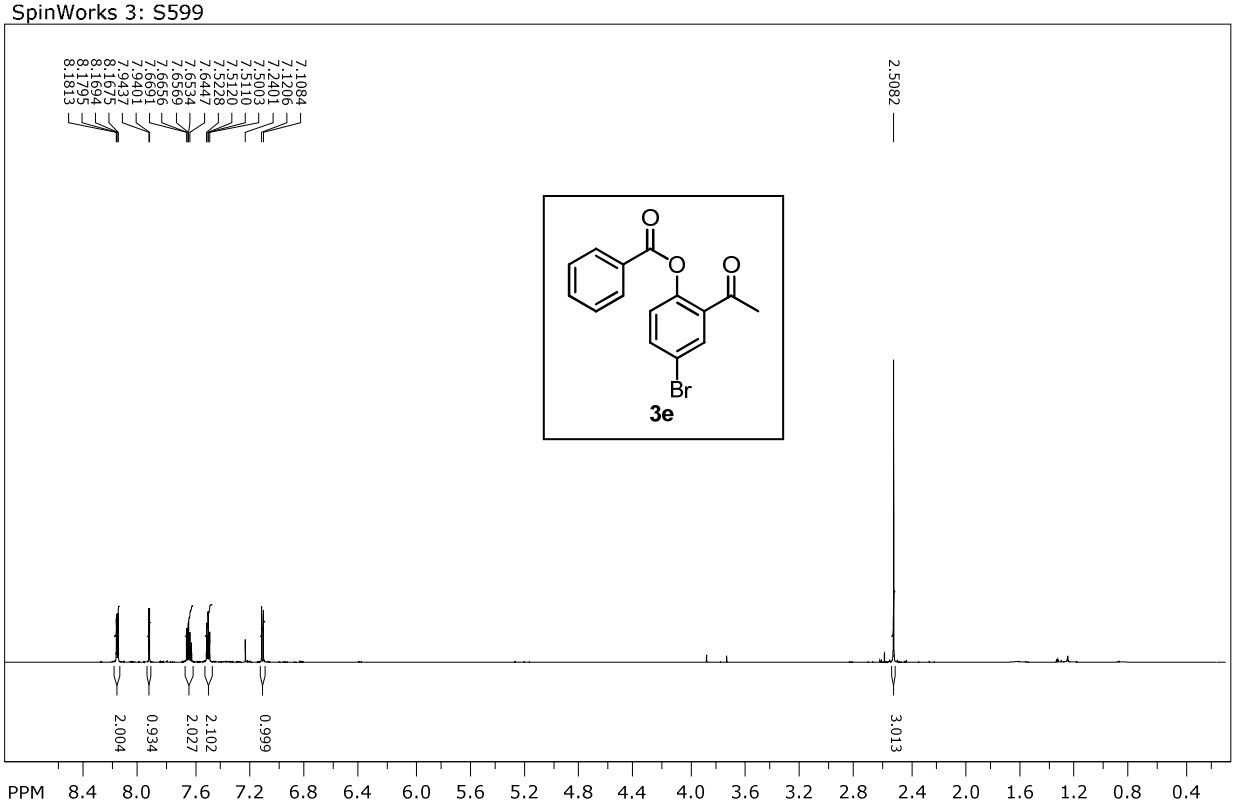

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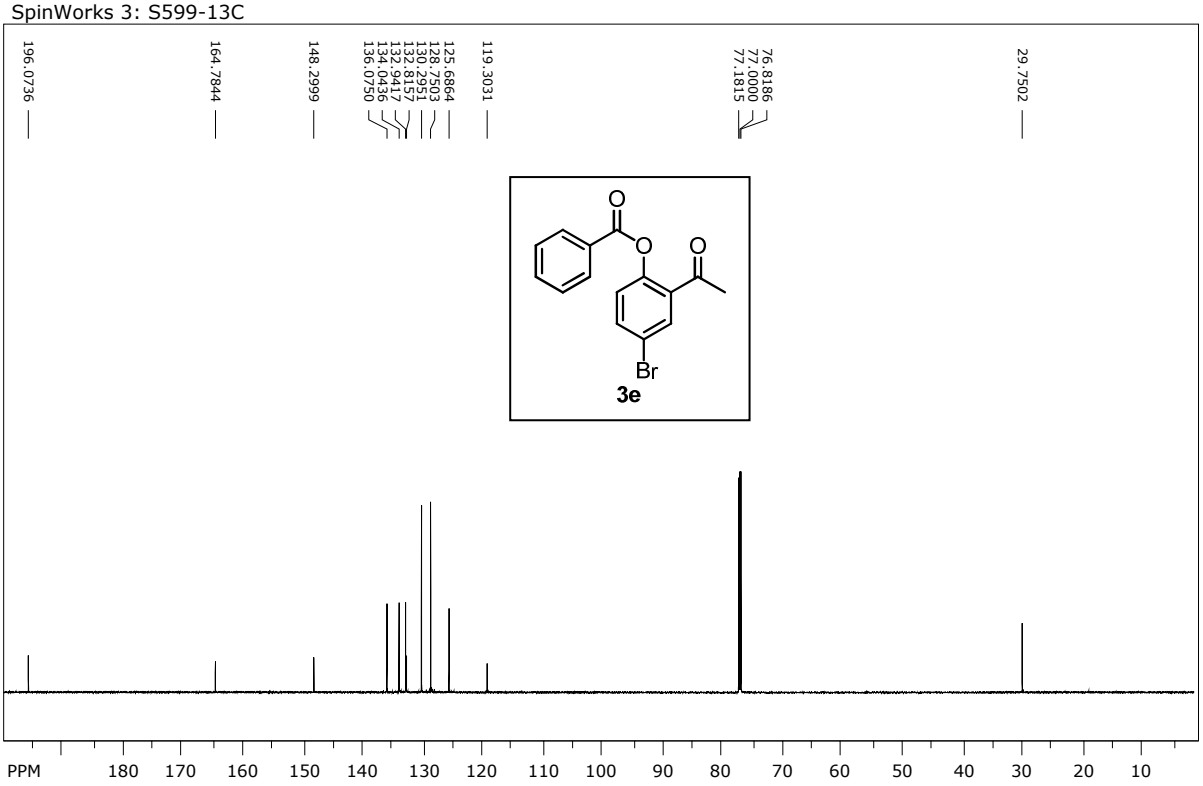

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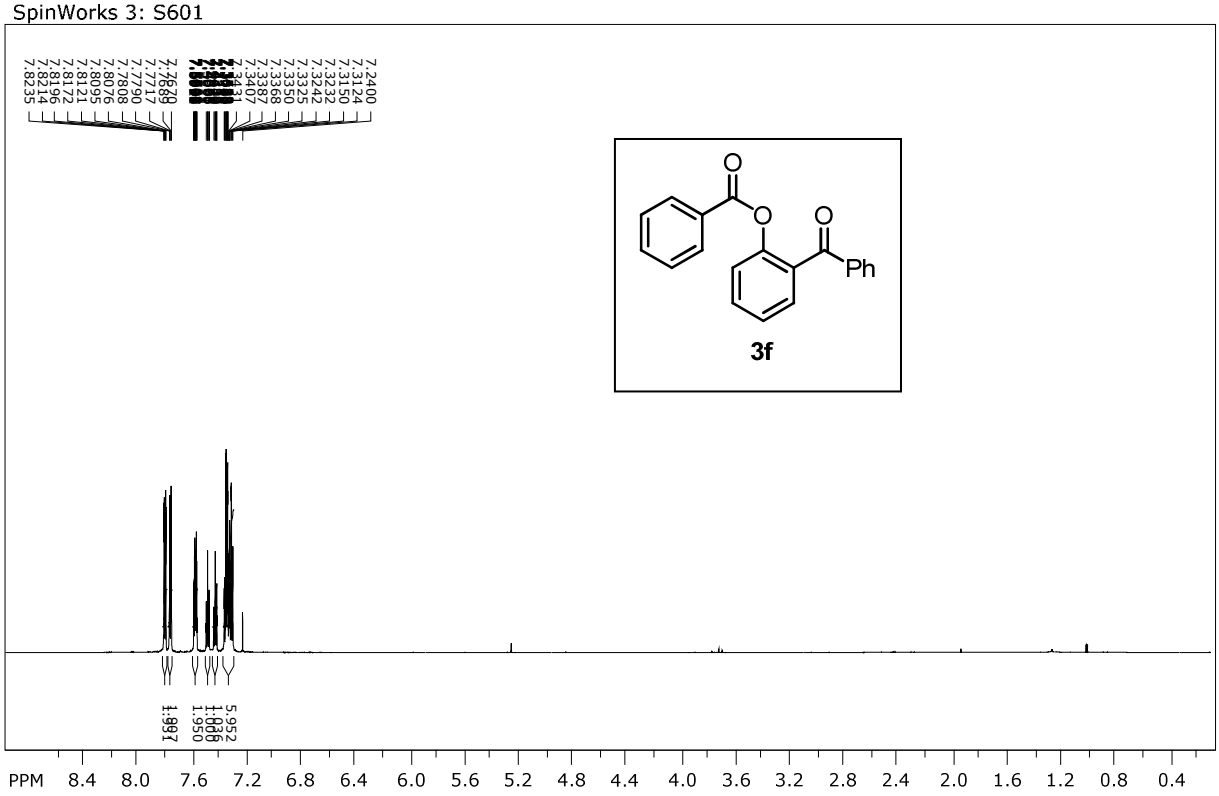

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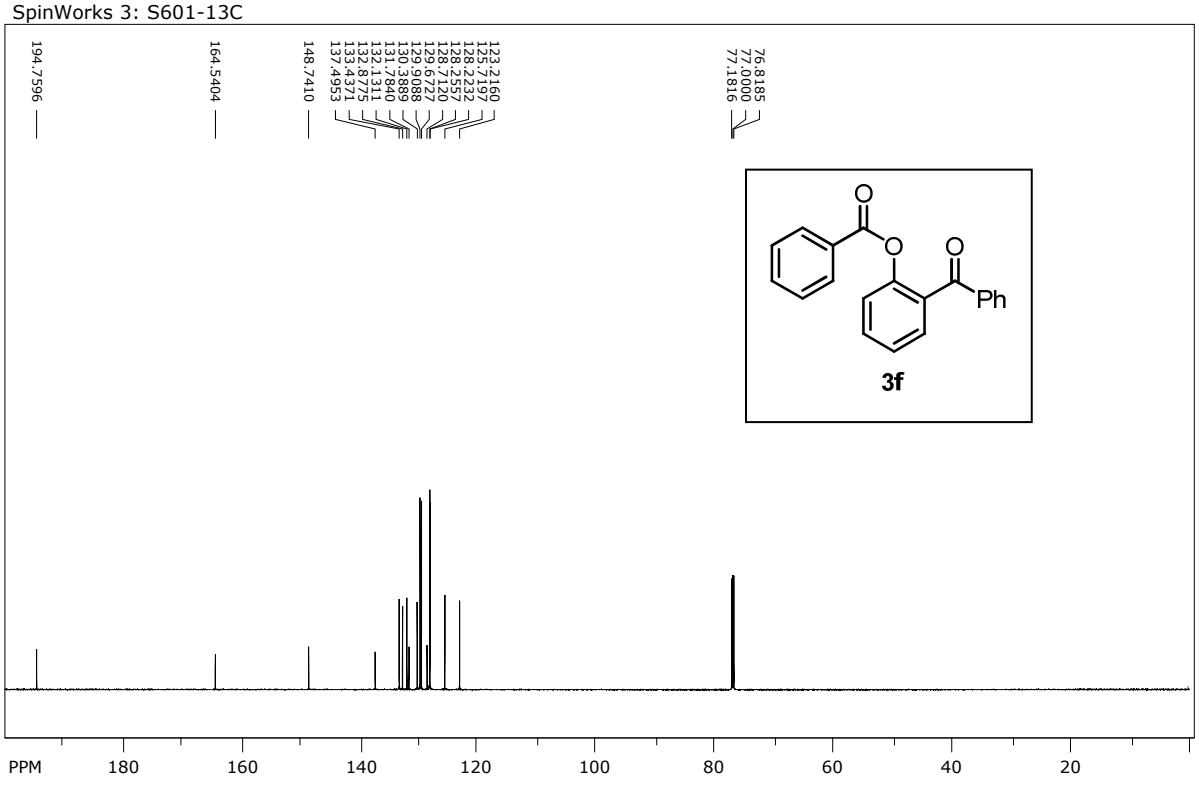

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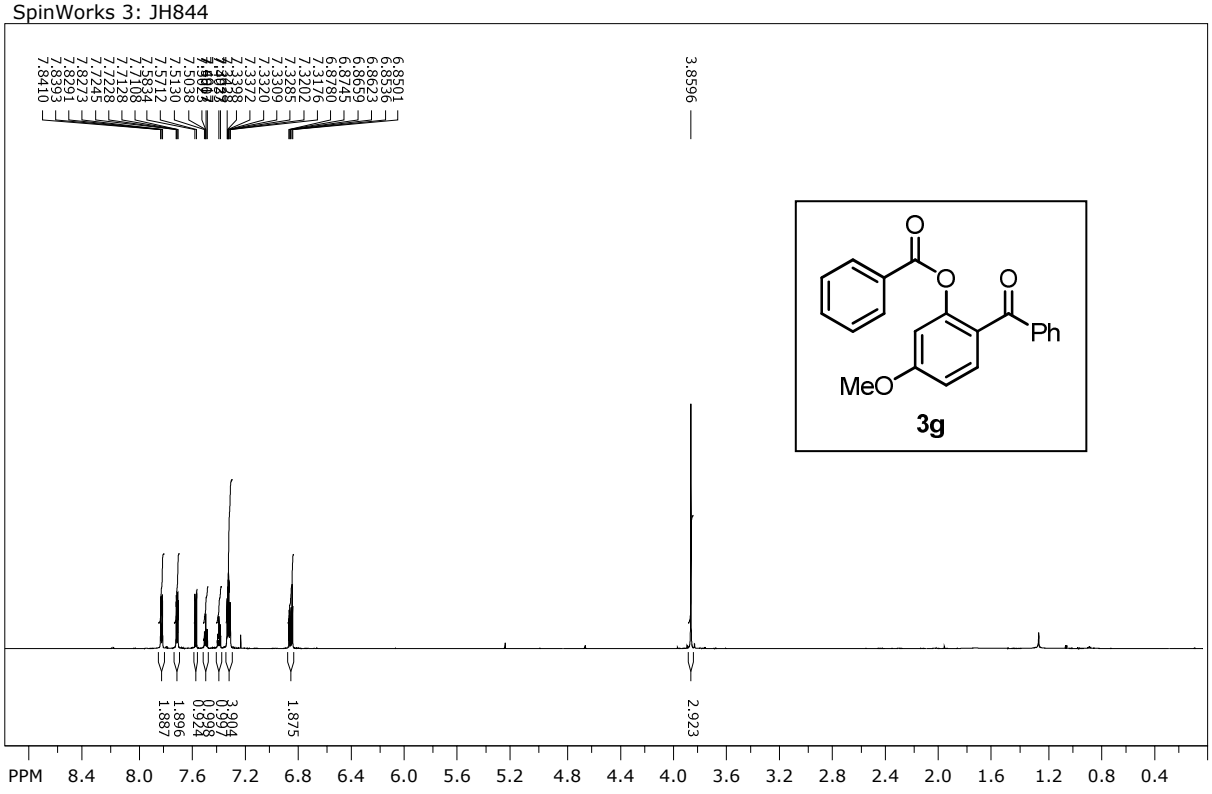

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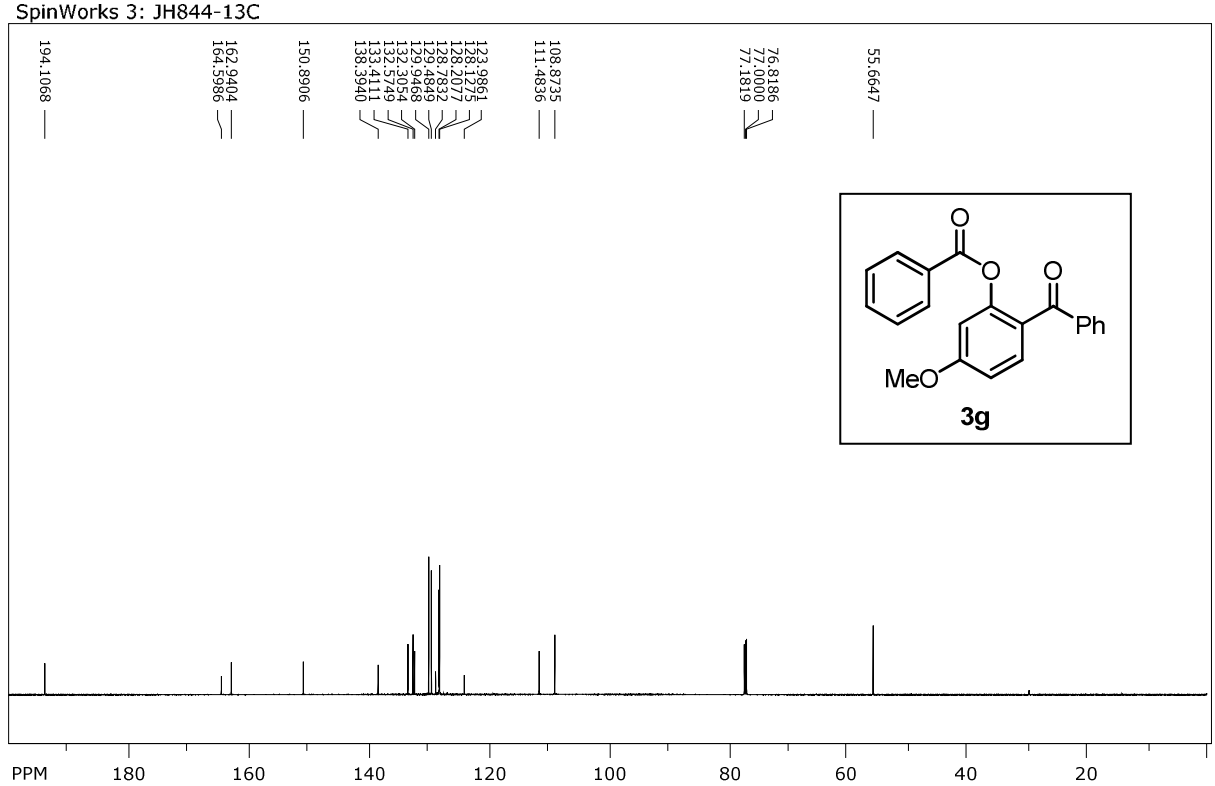

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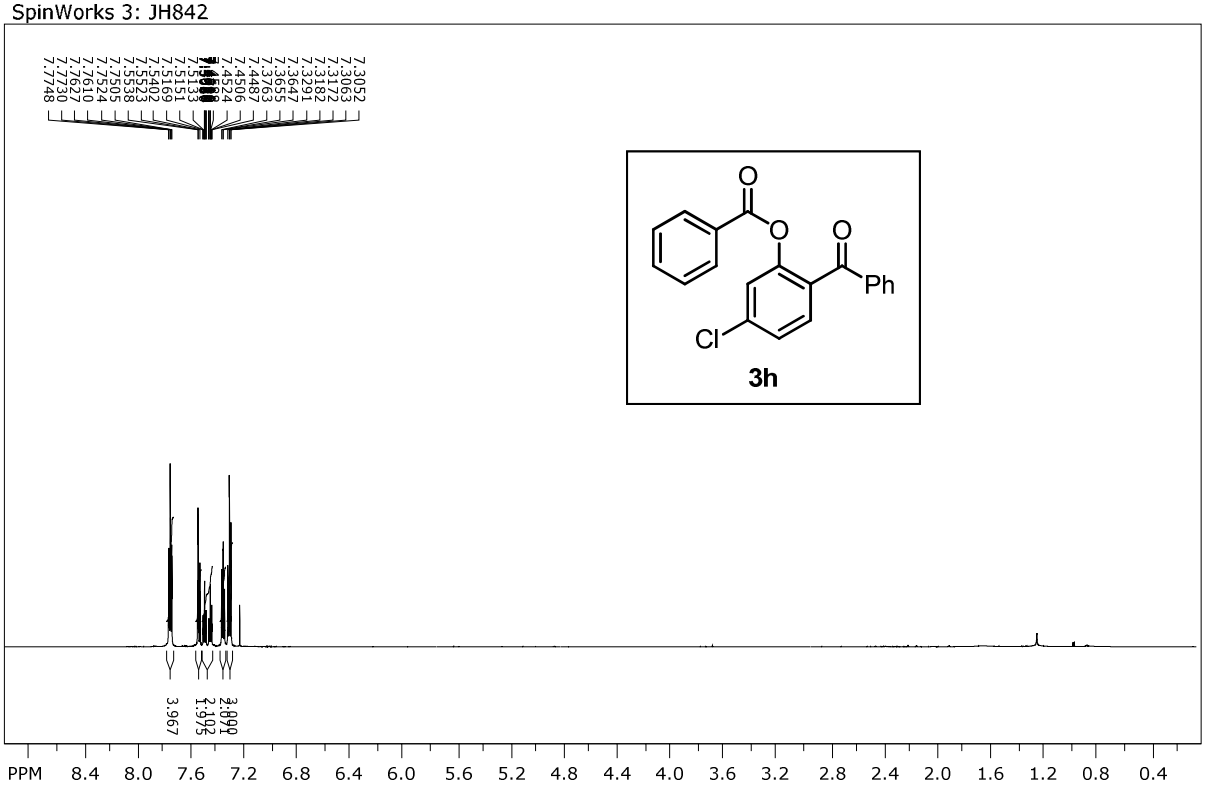

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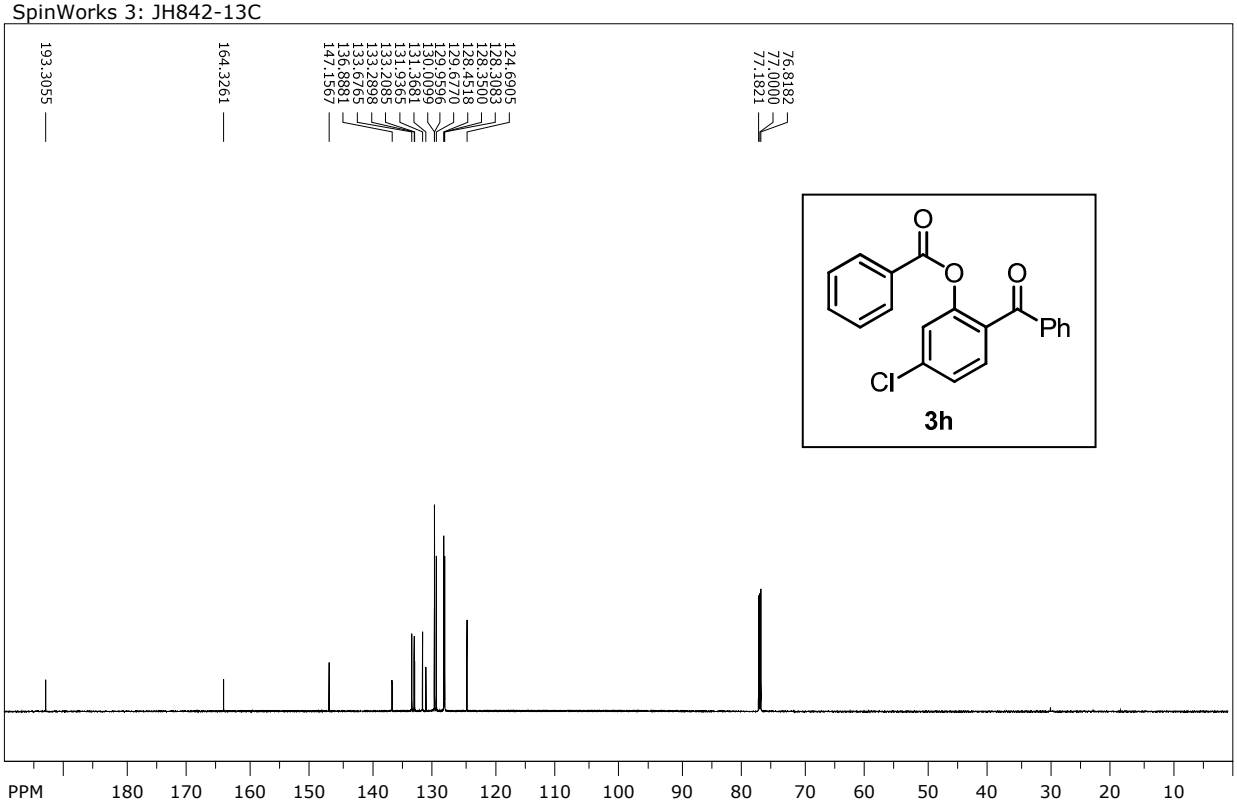

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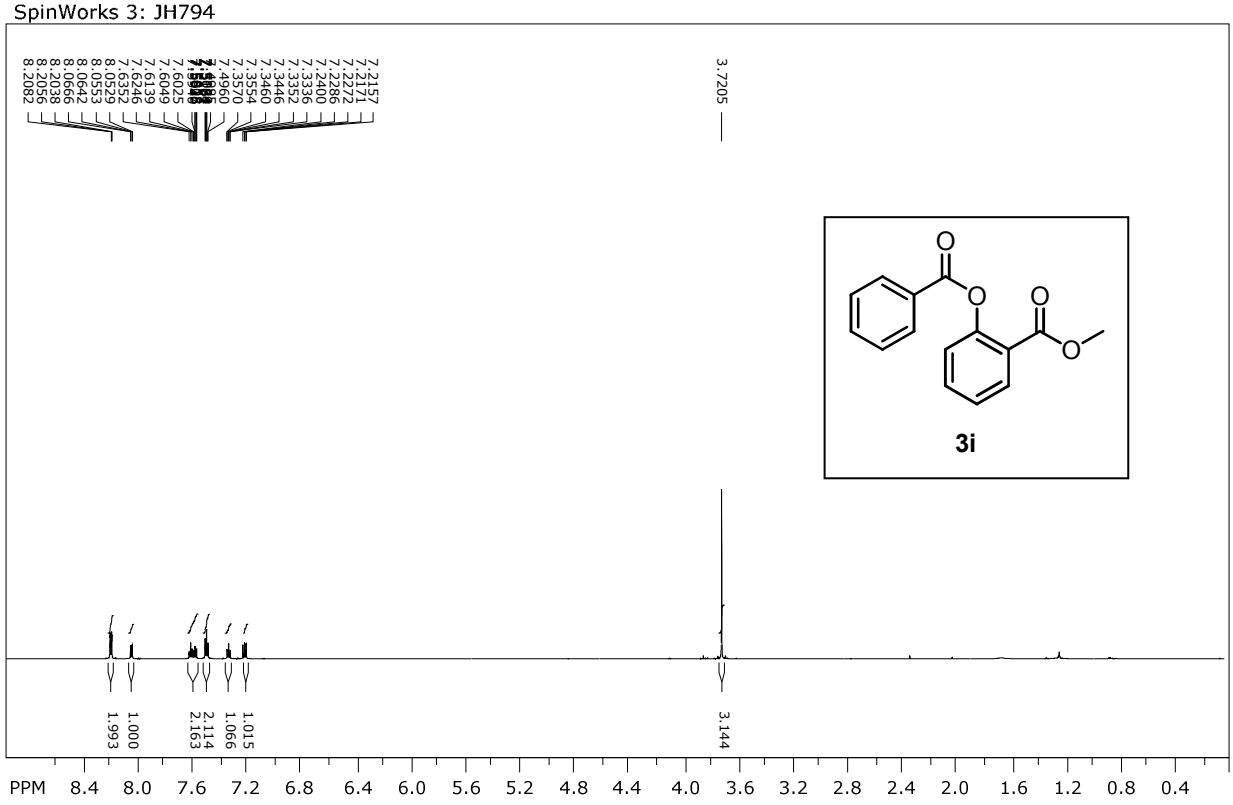

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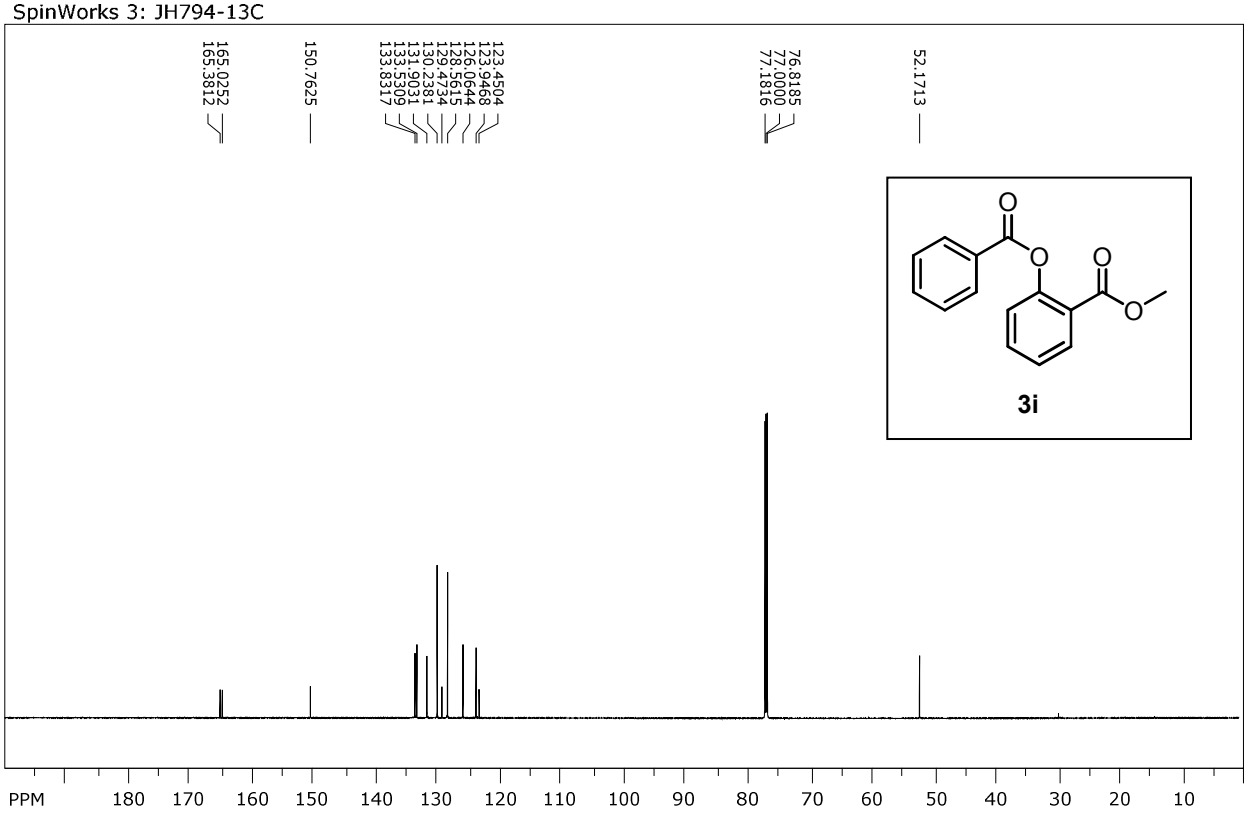
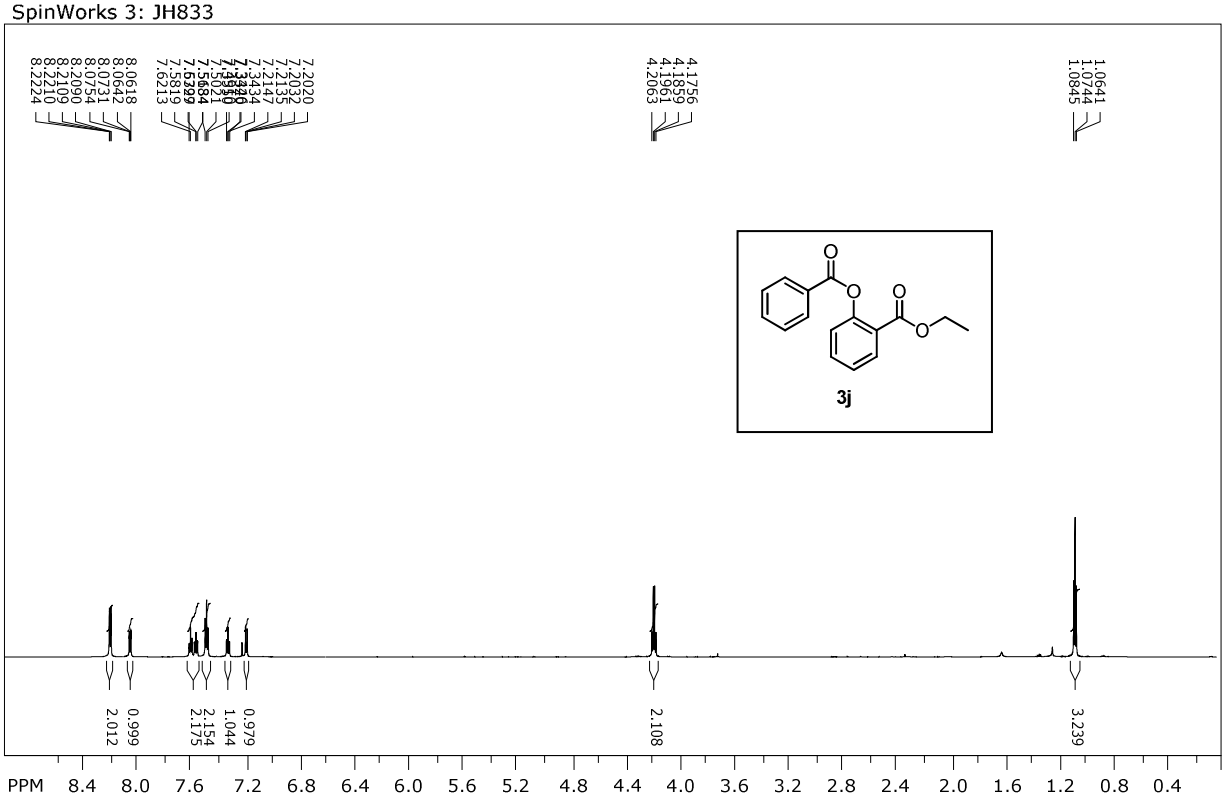
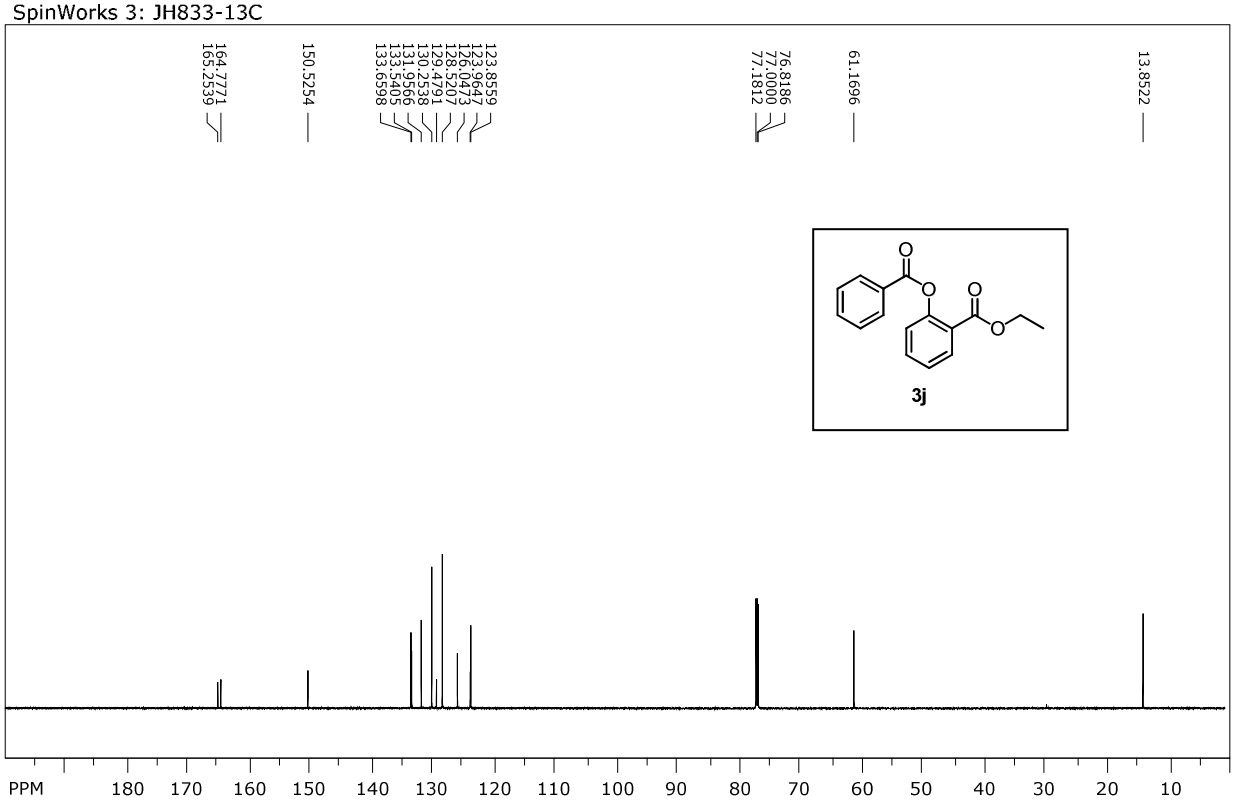
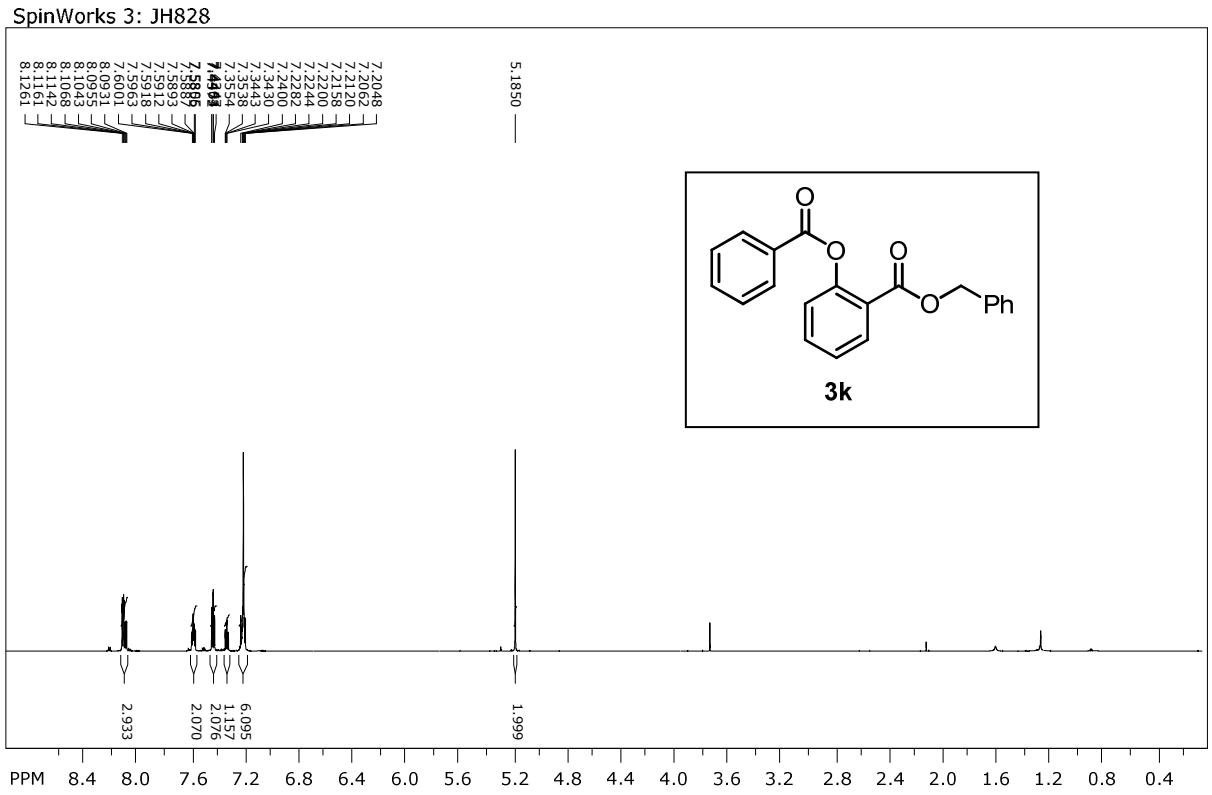


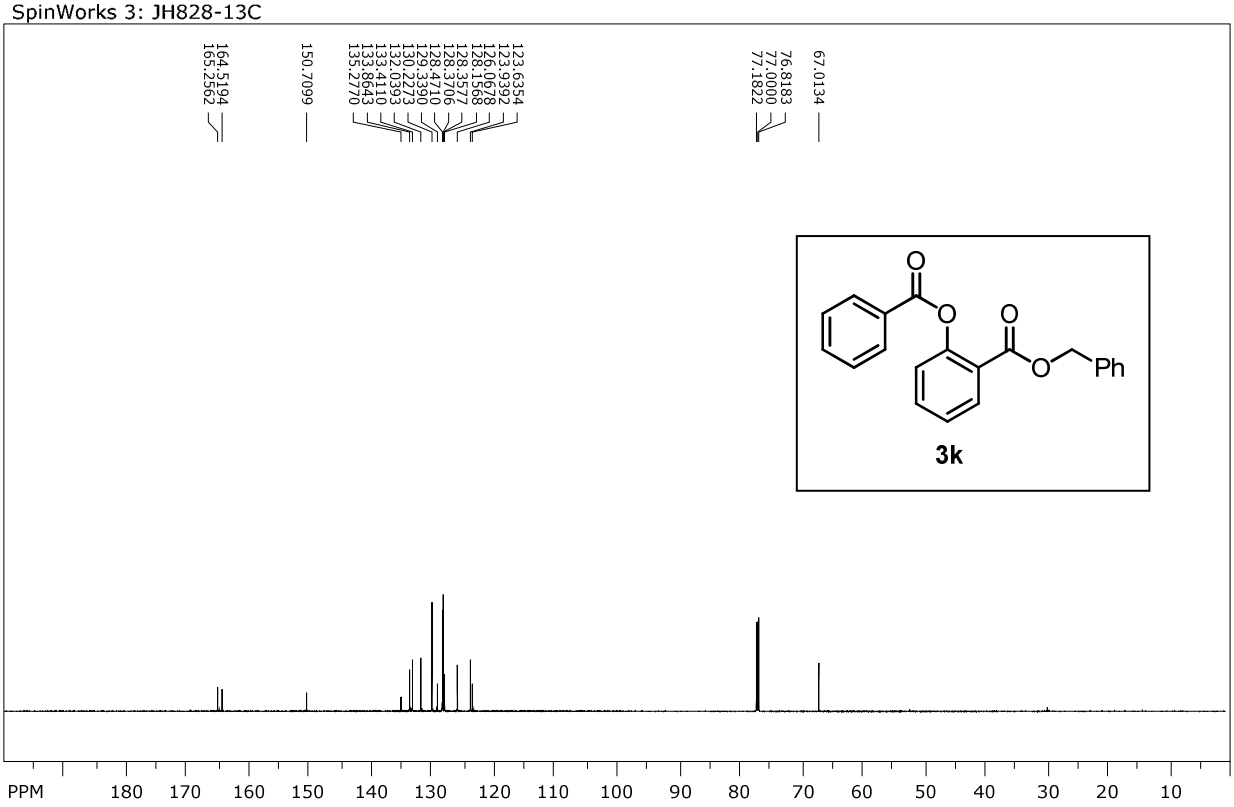
SpinWorks 3: JH833



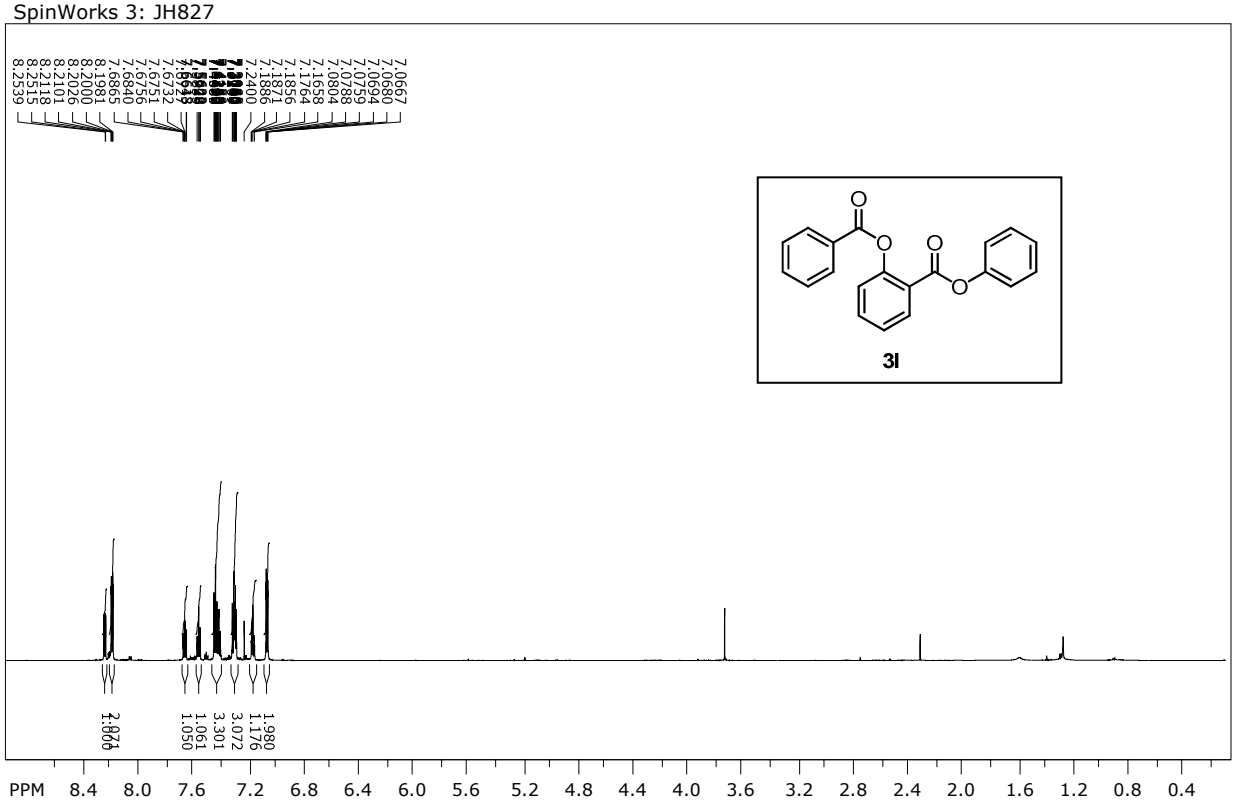
SpinWorks 3: JH833-13C



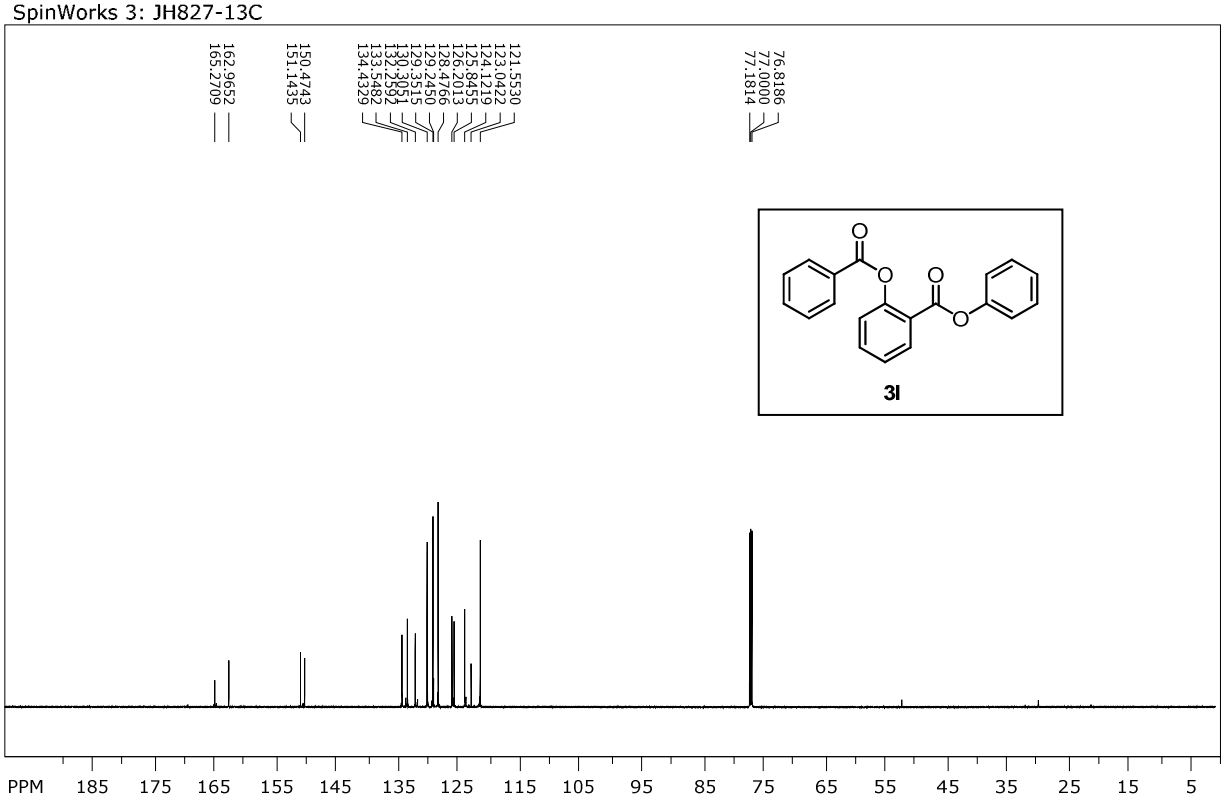

SpinWorks 3: JH828
8.1261
8.1161
8.1142
8.1068
8.1043
8.0955
8.0931
7.6001
7.5963
7.5918
7.5912
7.5887
7.5885
7.3554
7.3543
7.3430
7.2400
7.2282
7.2244
7.2200
7.2158
7.2120
7.2062
7.2048
5.1850
O
O
O
O
Ph
3k
2.933
2.070
1.157
2.076
6.095
1.999
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4

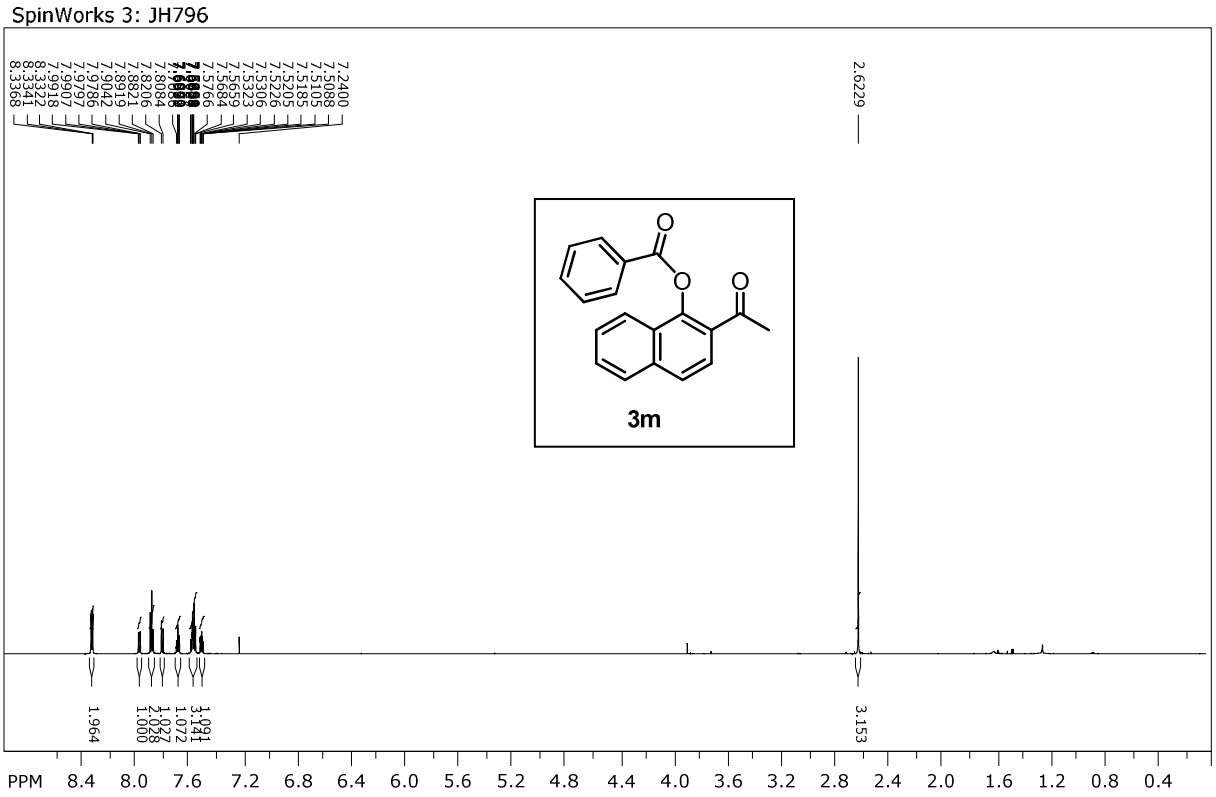

SpinWorks 3: JH828-13C
164.5194
165.2562
150.7099
135.2770
133.8643
133.4110
132.0393
130.2273
129.3390
128.4710
128.3706
128.3577
128.1568
126.0678
123.9392
123.6354
76.8183
77.0000
77.1822
67.0134
O
O
O
O
Ph
3k
PPM 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

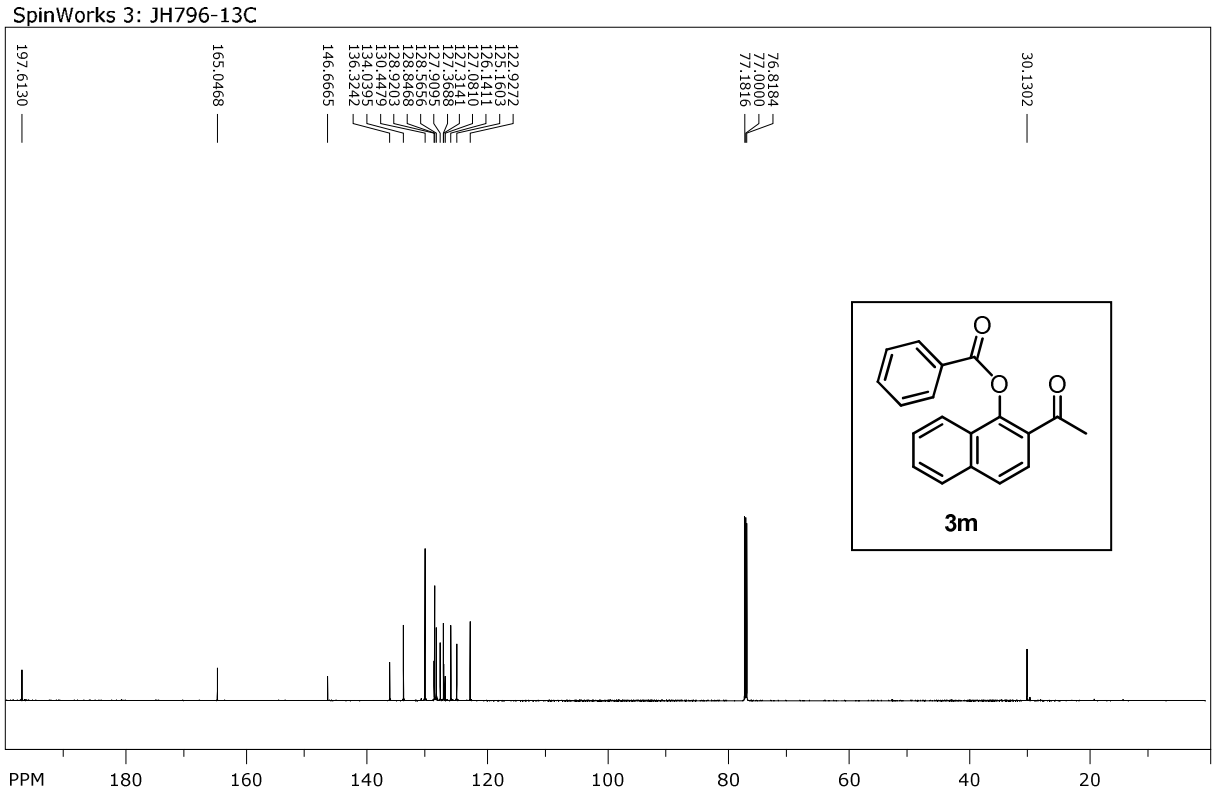
SpinWorks 3: JH827



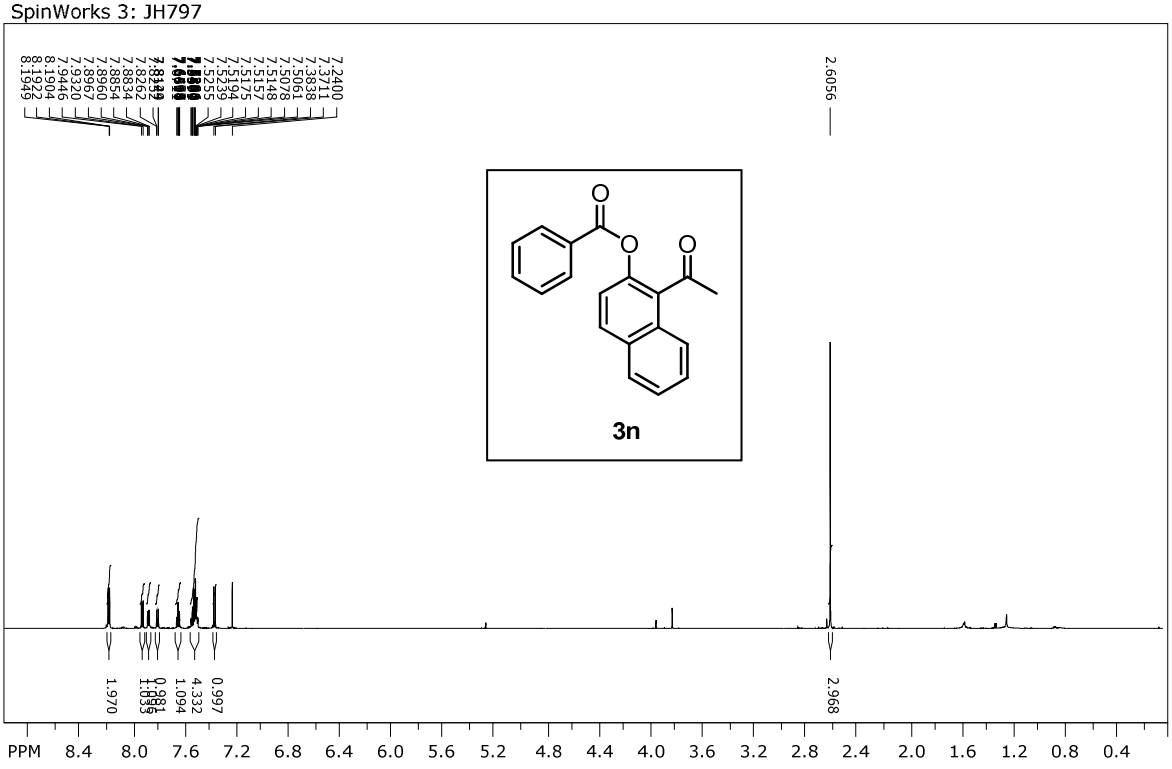
SpinWorks 3: JH827-13C



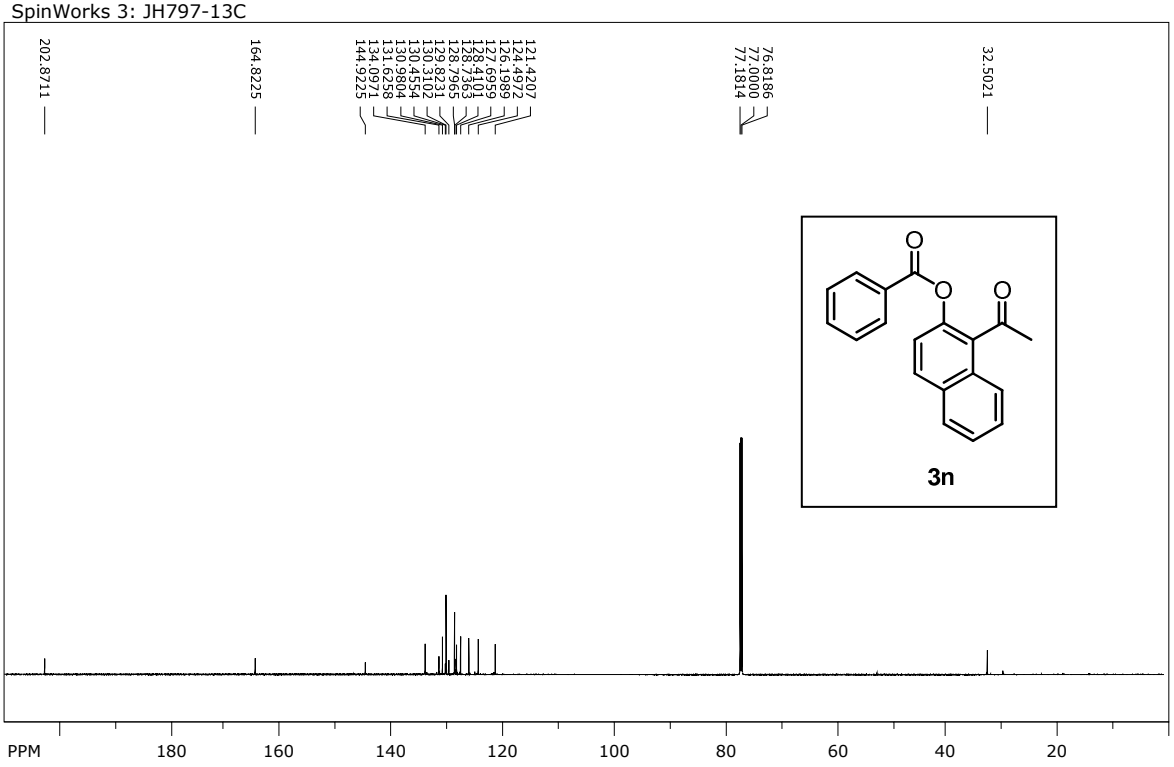

SpinWorks 3: JH796
8.3368
8.3341
8.3322
7.9918
7.9907
7.9797
7.9786
7.9042
7.8919
7.8821
7.8206
7.8084
7.5766
7.5684
7.5659
7.5323
7.5306
7.5226
7.5205
7.5185
7.5105
7.5088
7.2400
2.6229
3m
1.964
2.028
1.000
1.027
1.072
3.141
1.091
3.153
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4


SpinWorks 3: JH796-13C
197.6130
165.0468
146.6665
136.3242
134.0395
130.4479
128.9203
128.8468
128.5656
127.3688
127.3441
127.0810
126.1411
125.1603
122.9272
77.1816
77.0000
76.8184
30.1302
3m
PPM 180 160 140 120 100 80 60 40 20

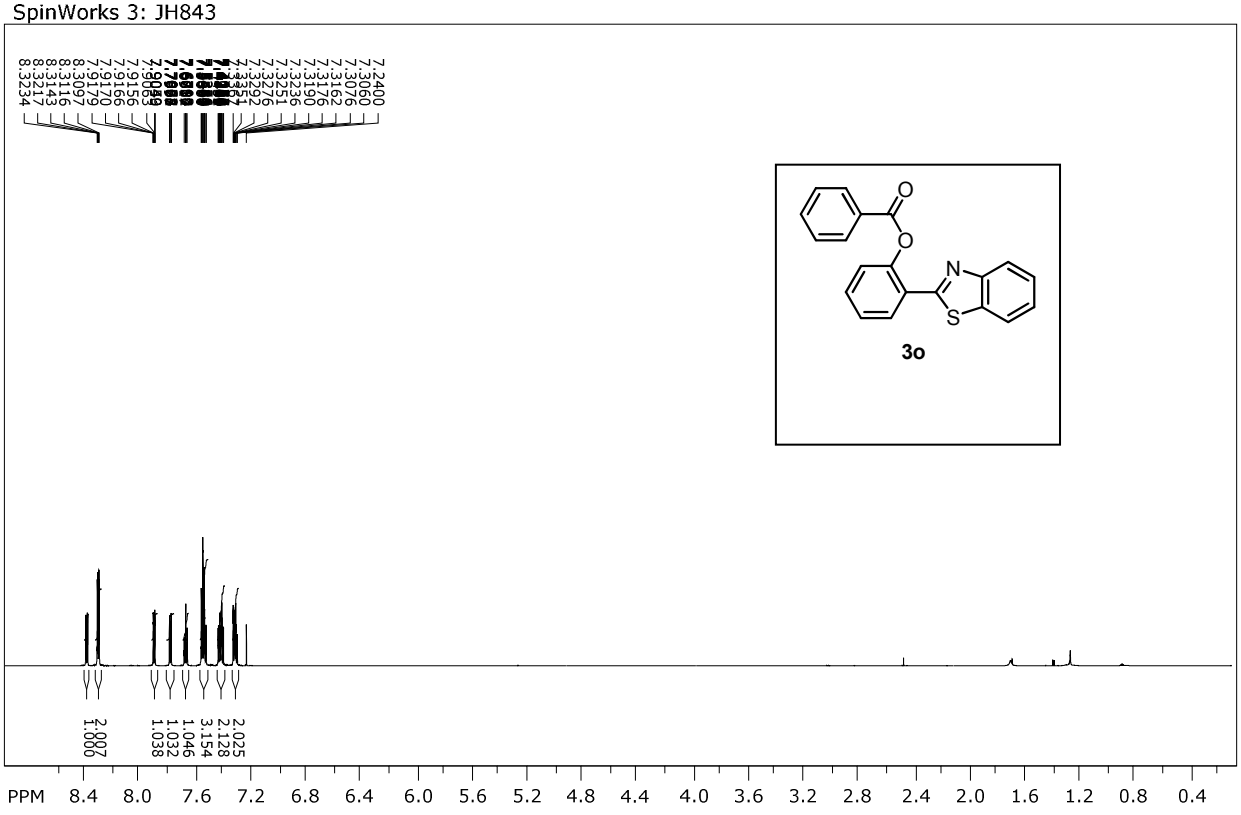
SpinWorks 3: JH797



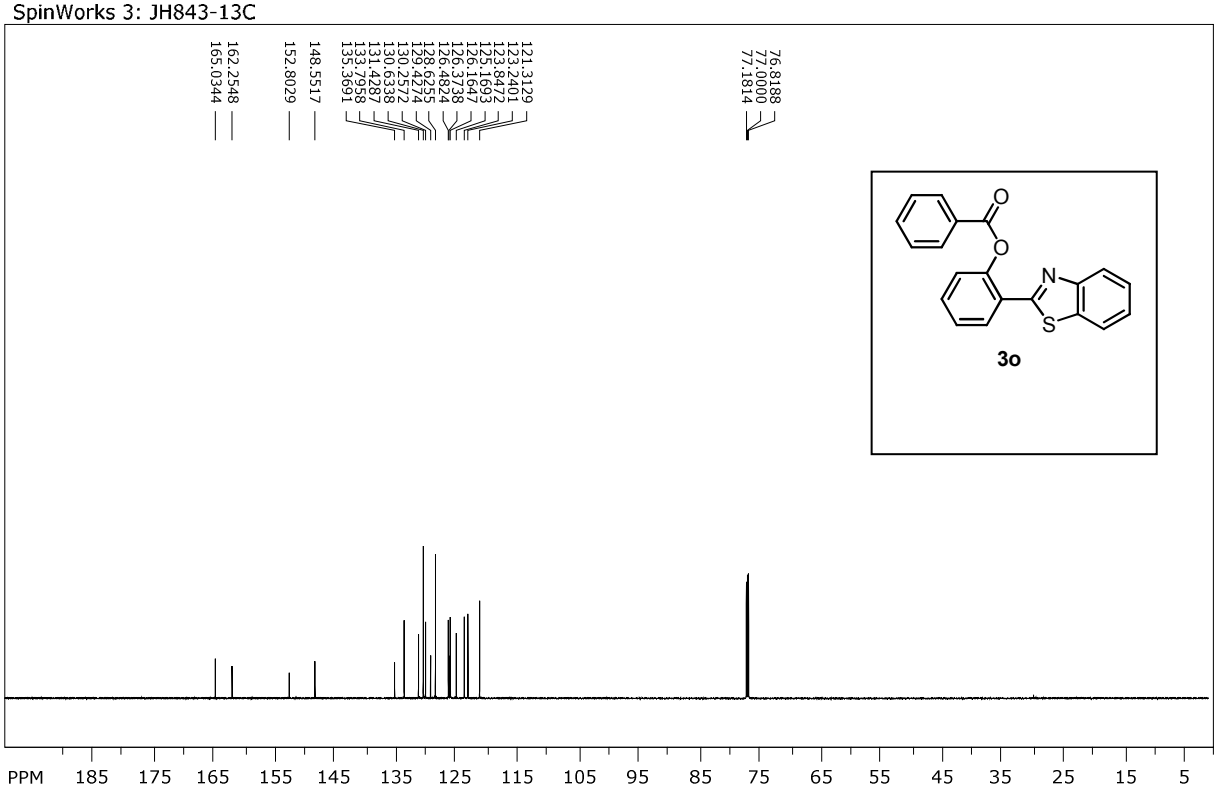
SpinWorks 3: JH797-13C



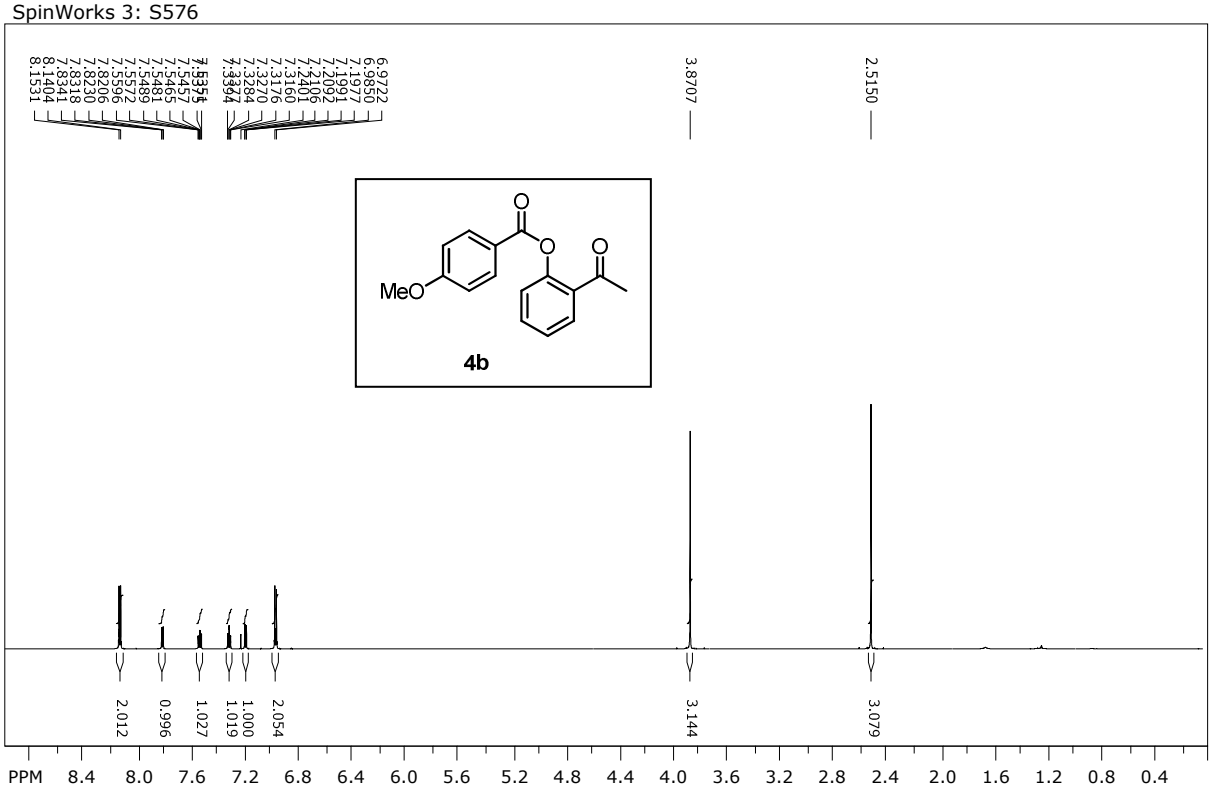
SpinWorks 3: JH843



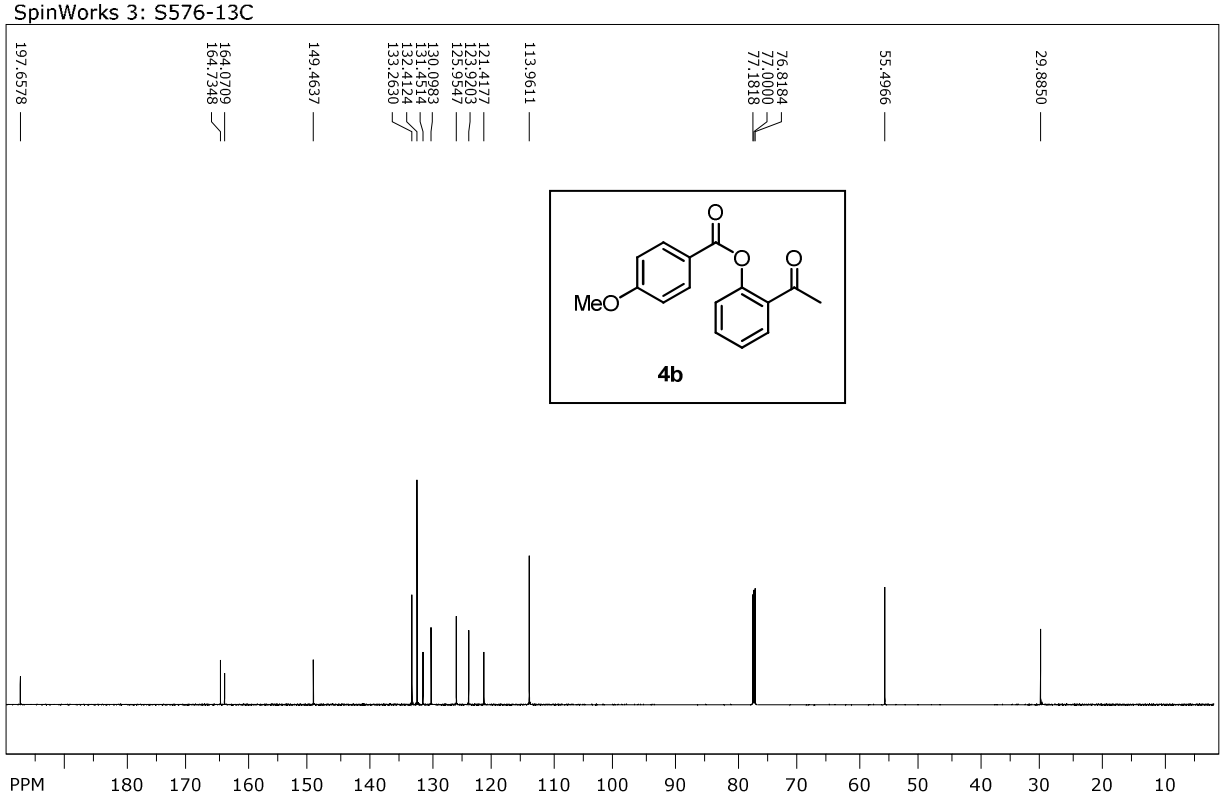
SpinWorks 3: JH843-13C



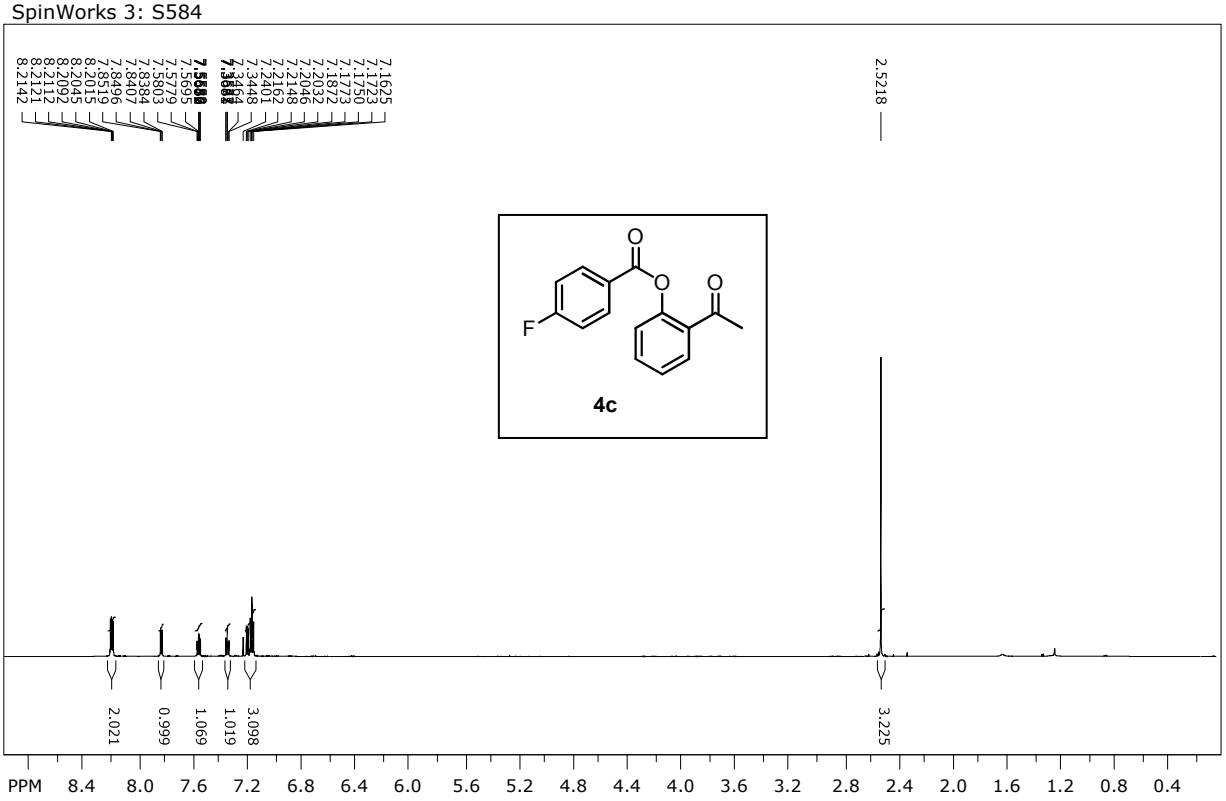
SpinWorks 3: S576



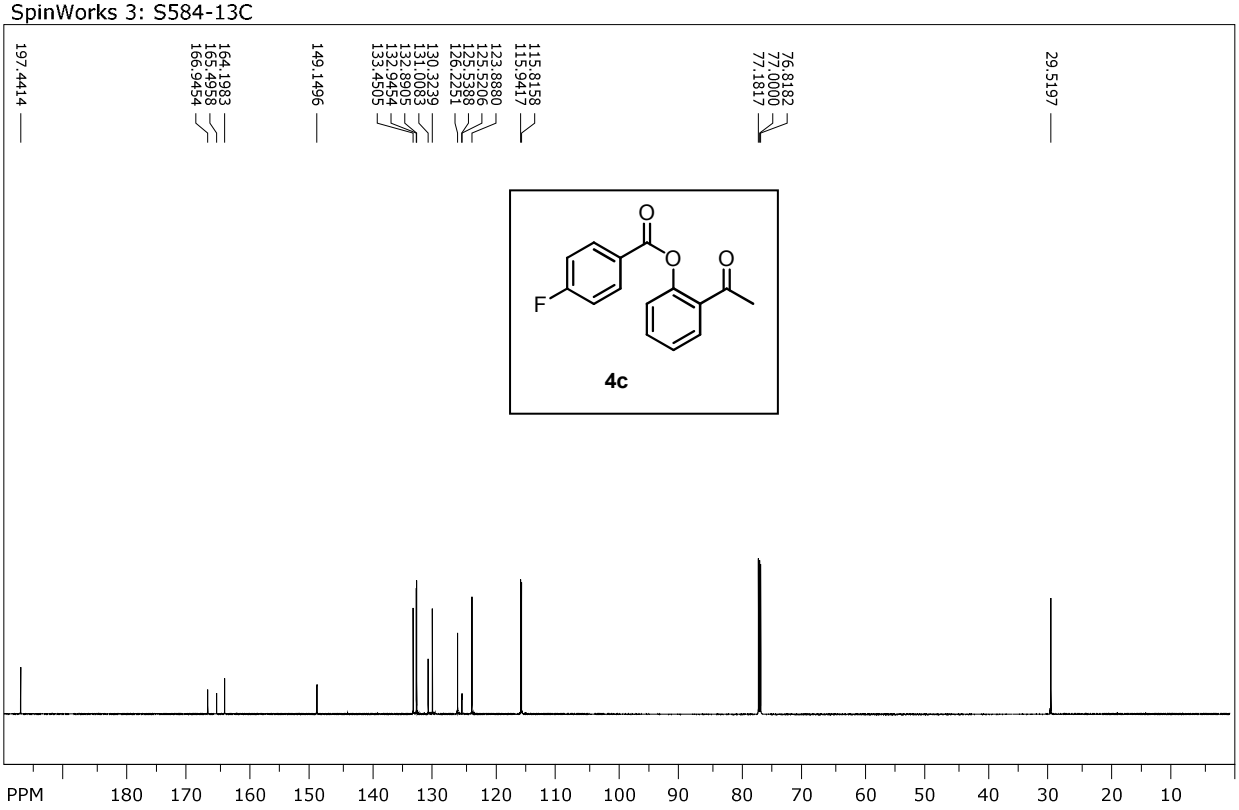
SpinWorks 3: S576-13C



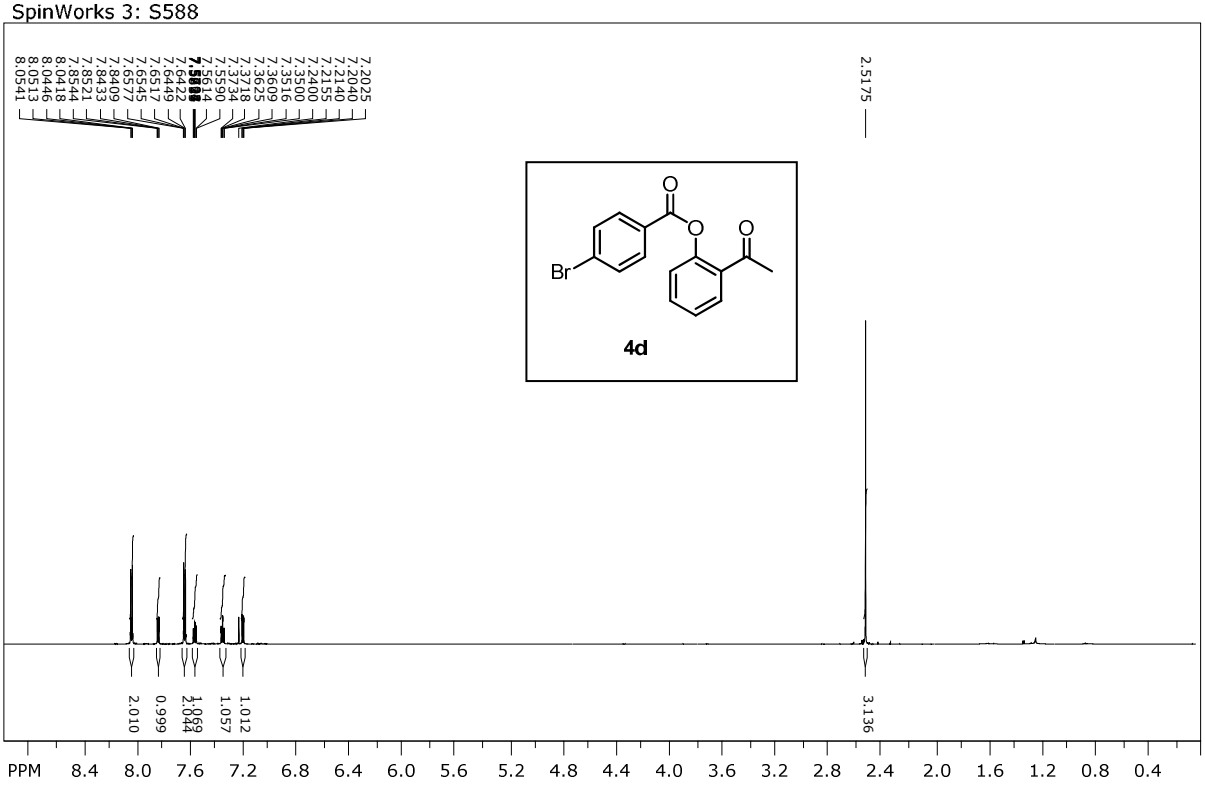
SpinWorks 3: S584



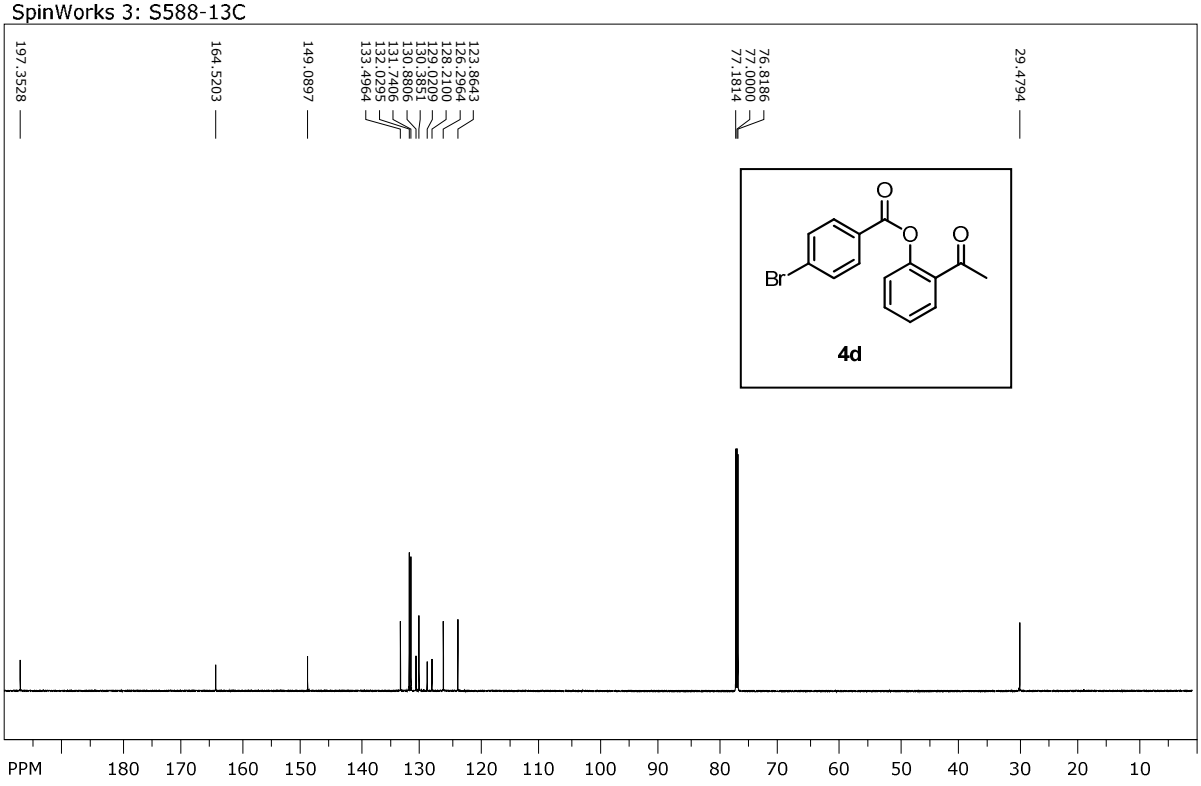
SpinWorks 3: S584-13C

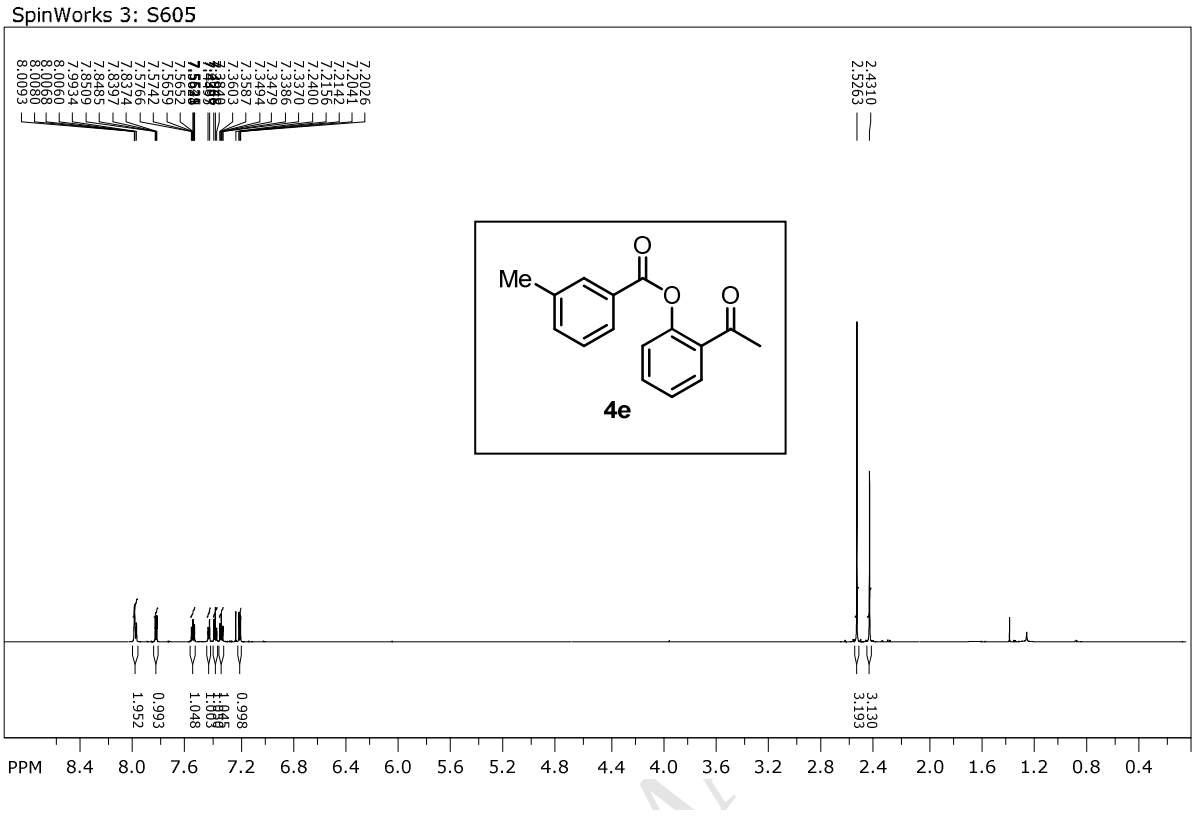


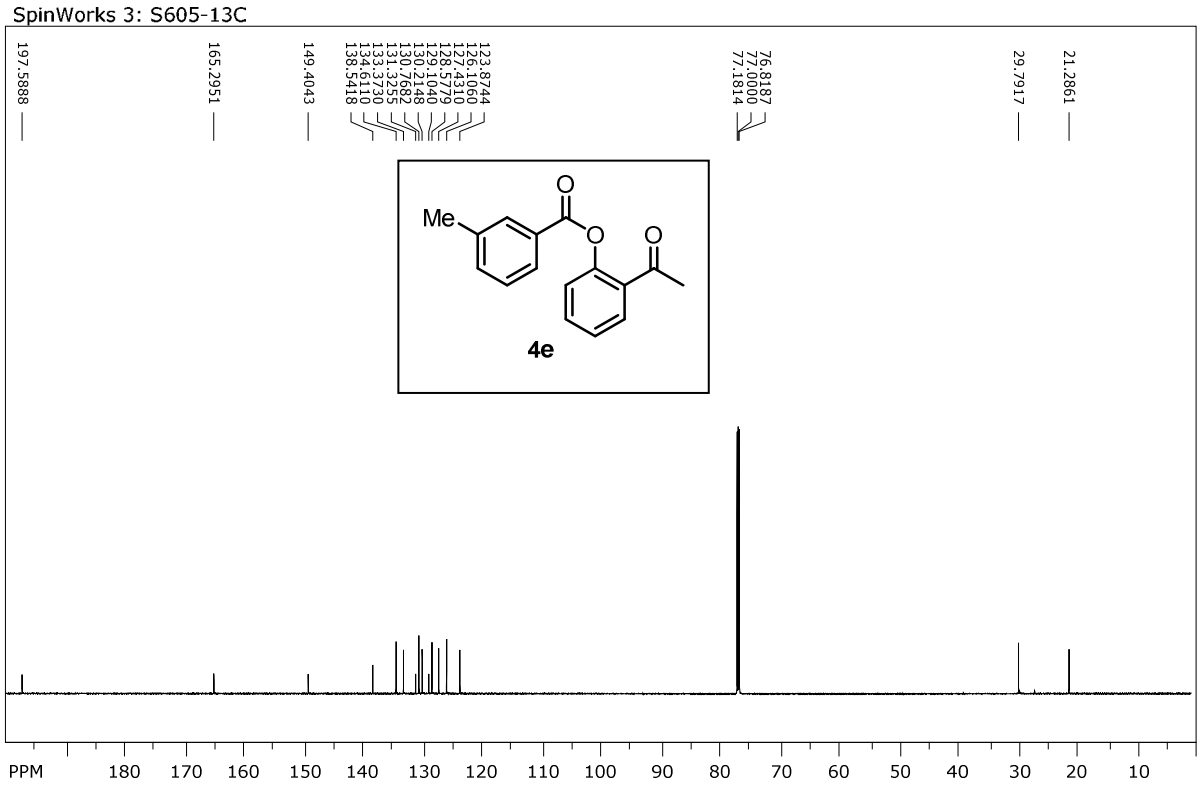
SpinWorks 3: S588

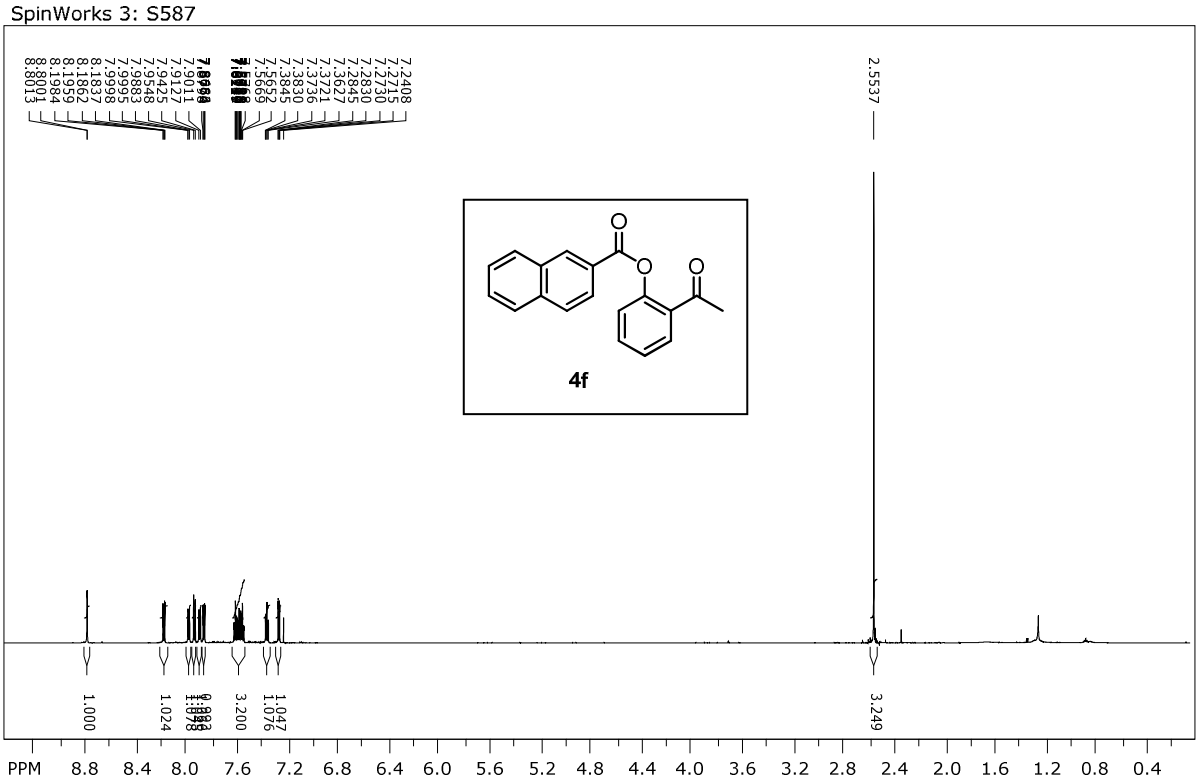


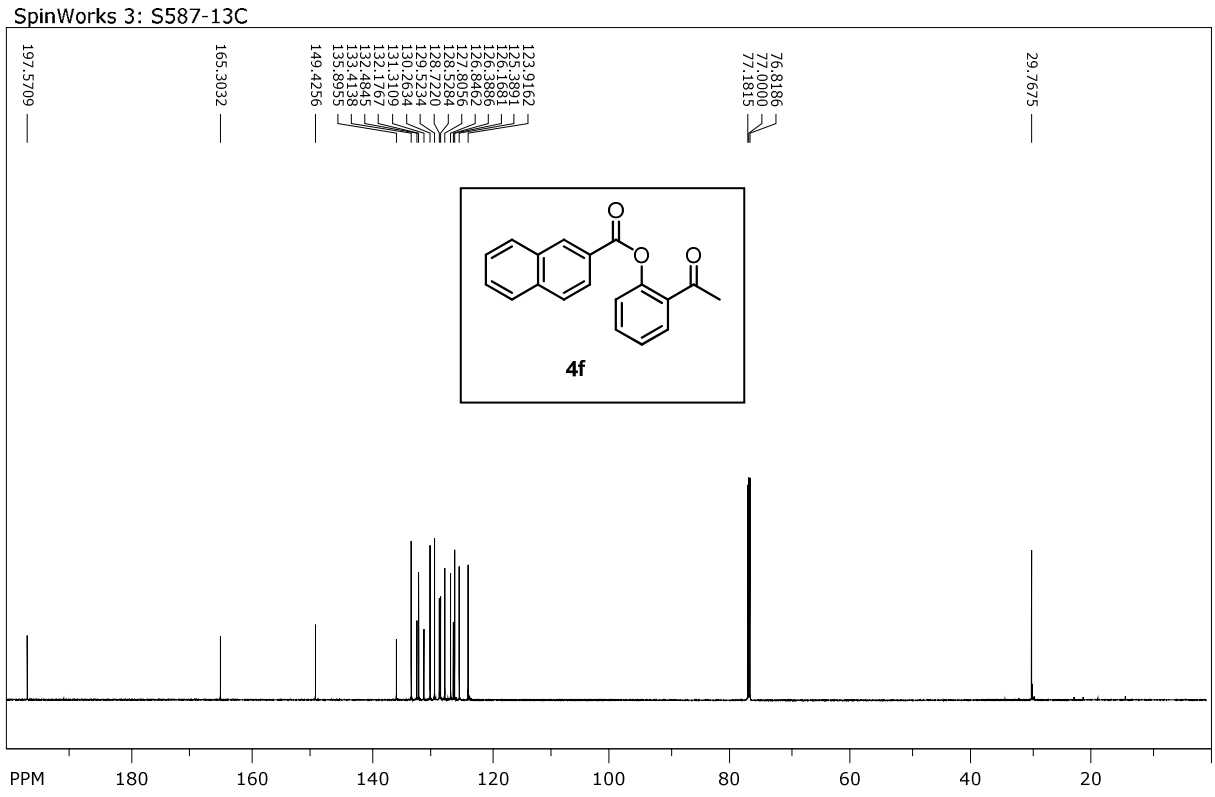
SpinWorks 3: S588-13C



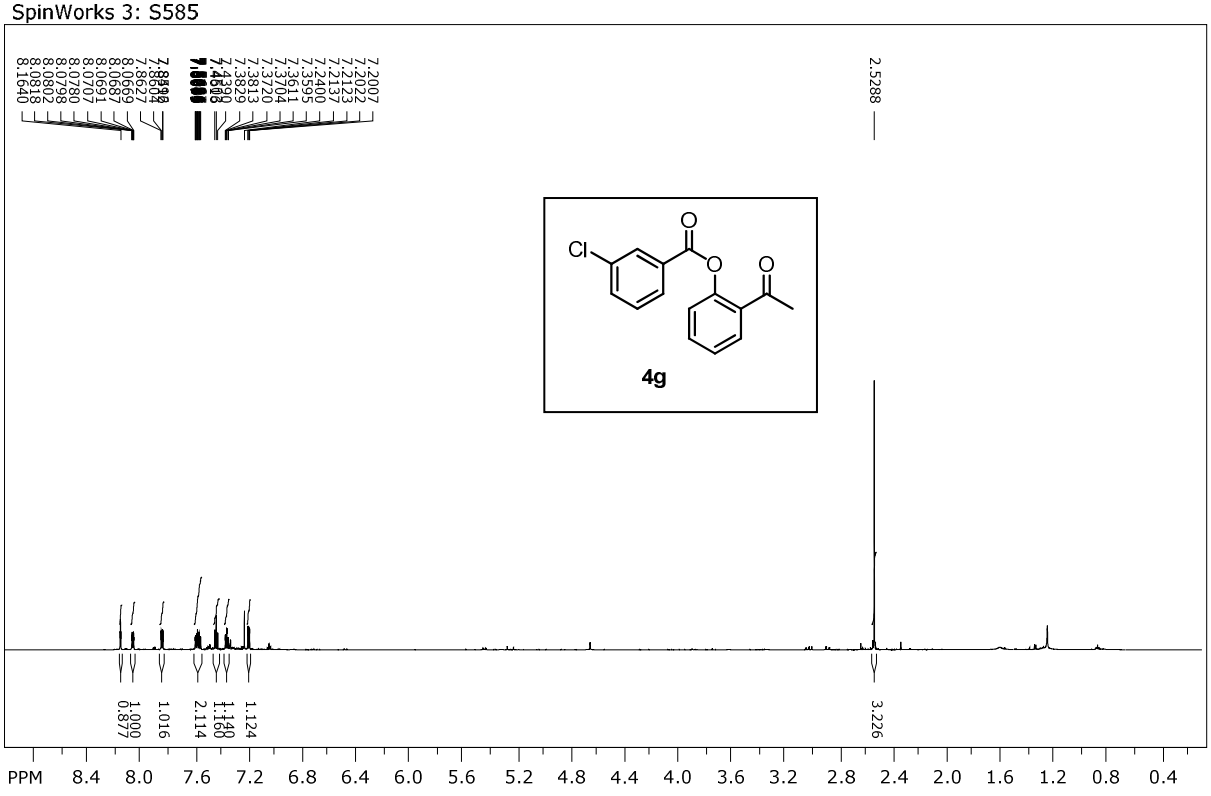

SpinWorks 3: S605
Me
O
O
O
4e
PPM


SpinWorks 3: S605-13C
Me
O
O
O
4e
PPM

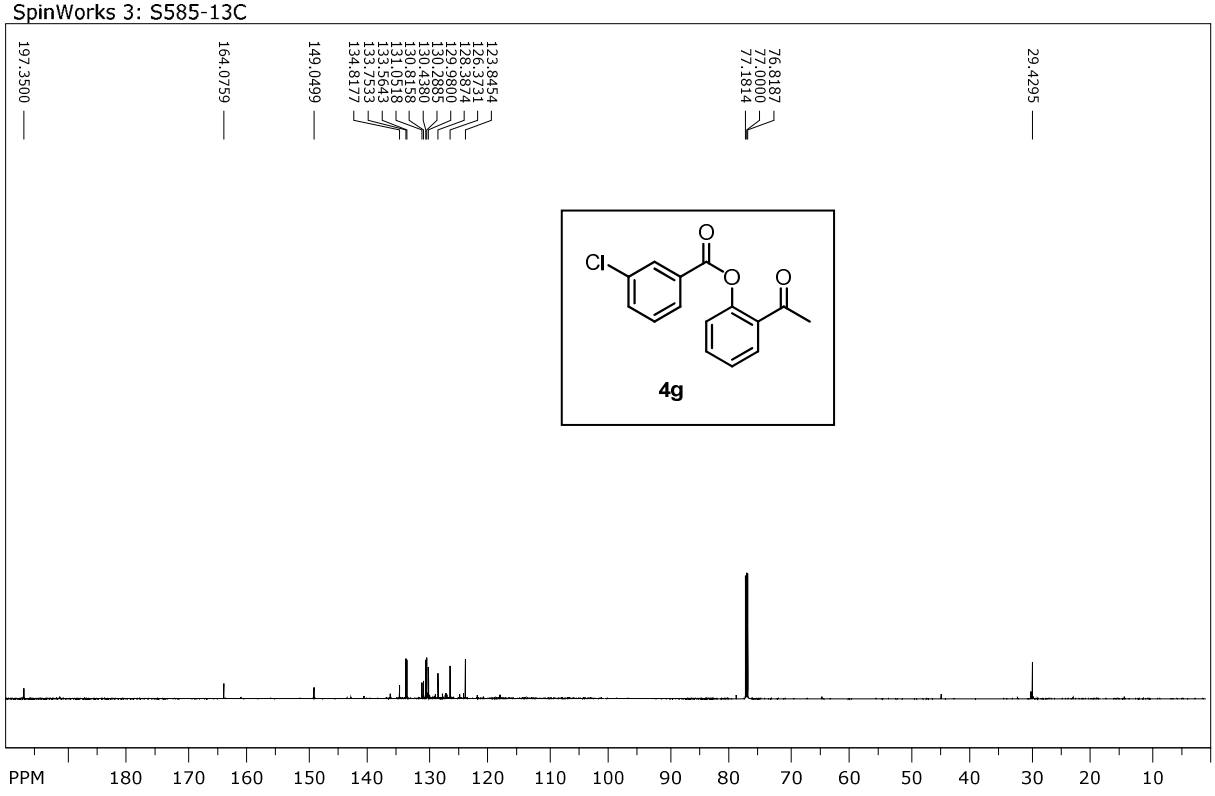

SpinWorks 3: S587
8.8013
8.8001
8.1994
8.1859
8.1852
8.1837
7.9995
7.9883
7.9548
7.9425
7.9127
7.9011
7.5669
7.5552
7.3845
7.3830
7.3736
7.3721
7.3627
7.2845
7.2830
7.2730
7.2715
7.2408
2.5537
4f
1.000
1.024
3.200
1.047
1.076
3.249
PPM
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4


SpinWorks 3: S587-13C
197.5709
165.3032
149.4256
135.8955
133.4138
132.4845
132.1767
131.3109
130.2634
129.5234
128.7220
128.5284
127.8056
126.8462
126.3886
126.1681
125.3891
123.9162
77.1815
77.0000
76.8186
29.7675
4f
PPM
180
160
140
120
100
80
60
40
20

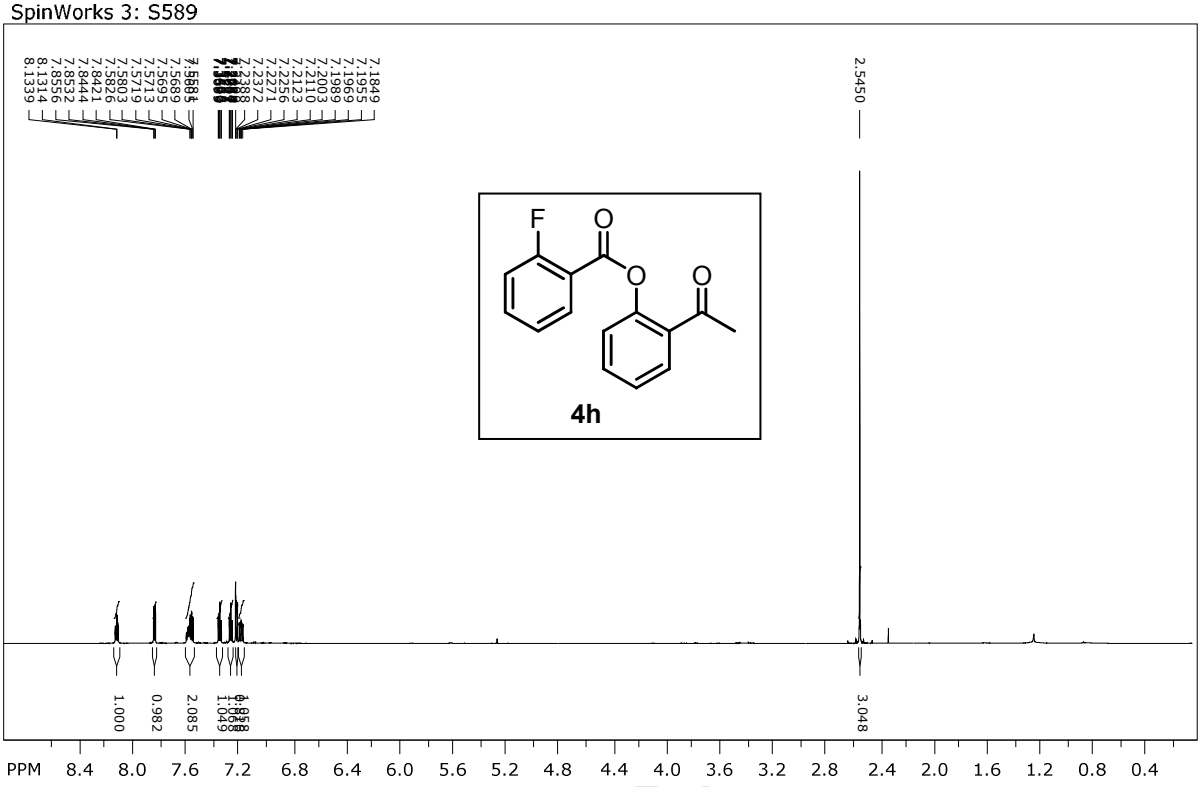
SpinWorks 3: S585



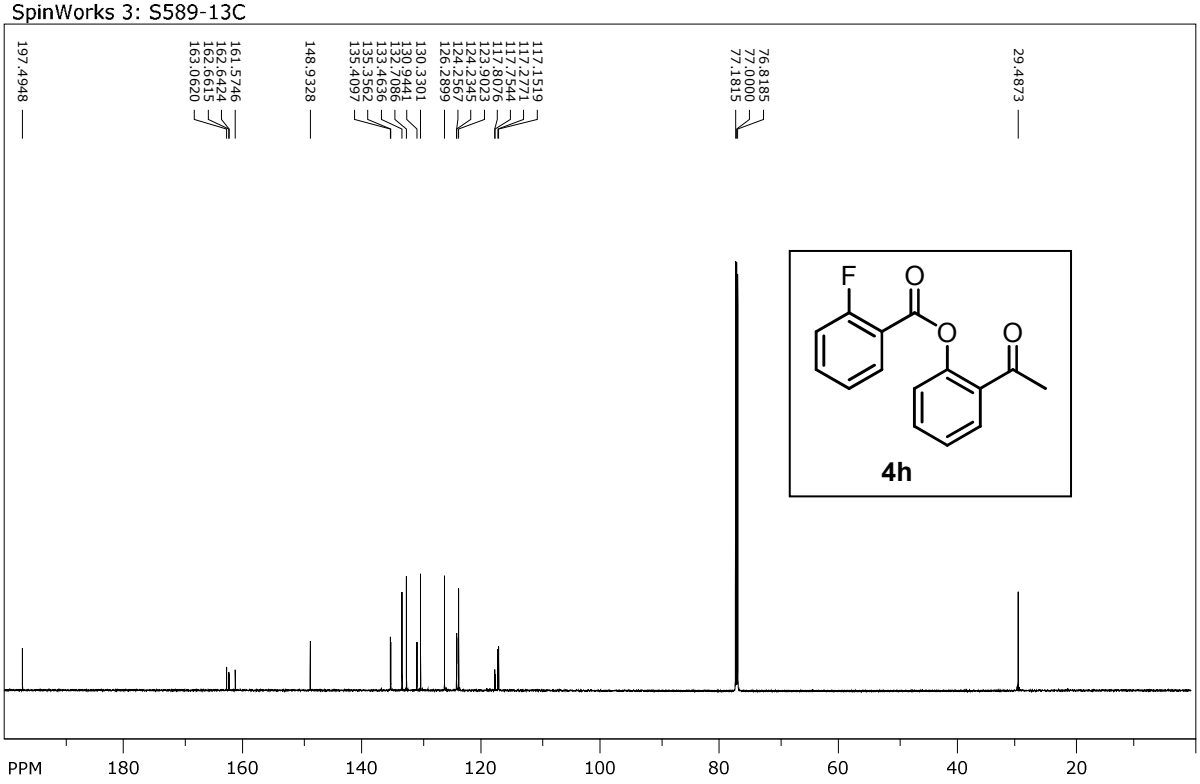
SpinWorks 3: S585-13C



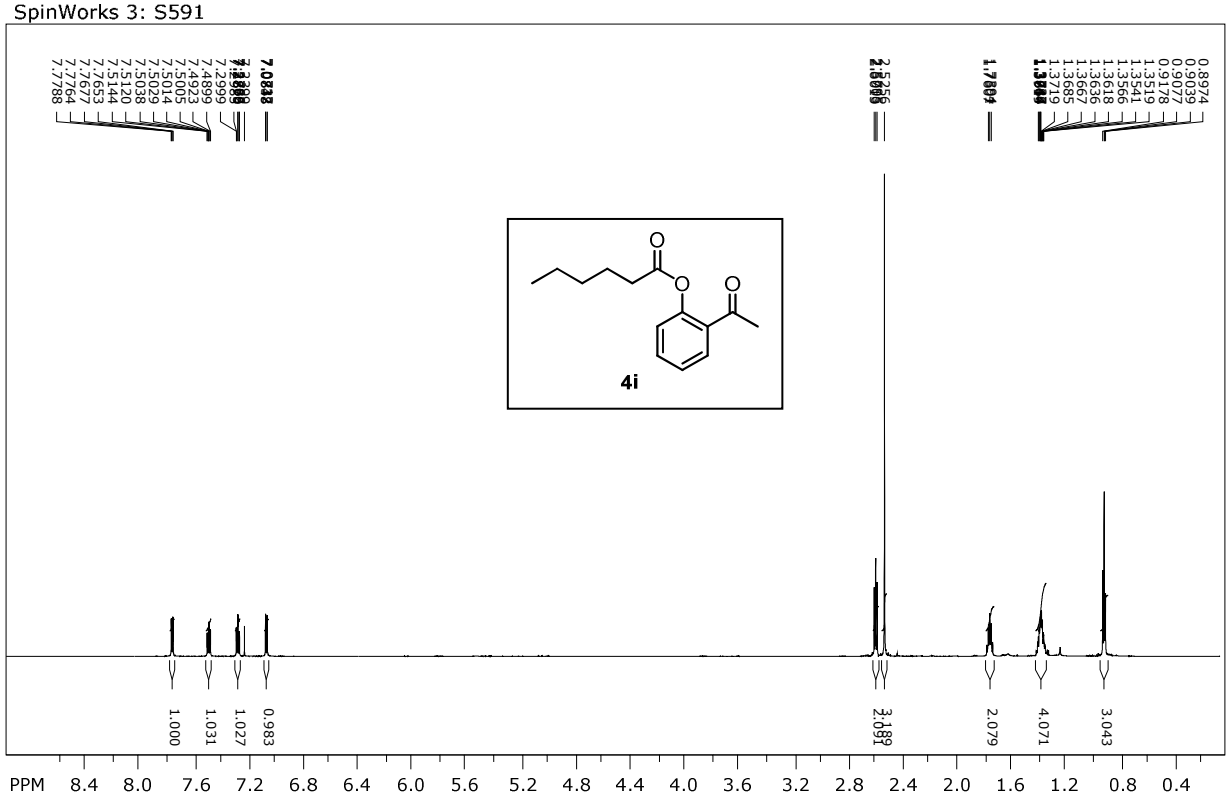
SpinWorks 3: S589



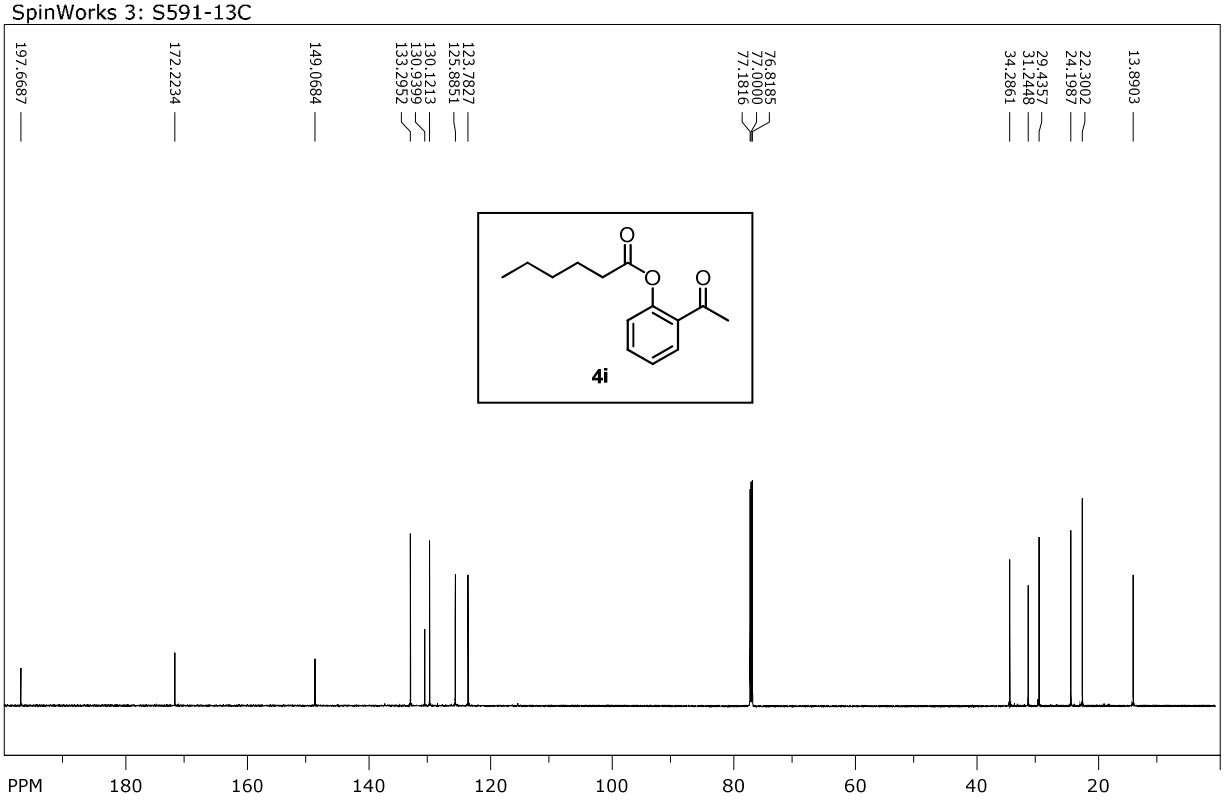
SpinWorks 3: S589-13C



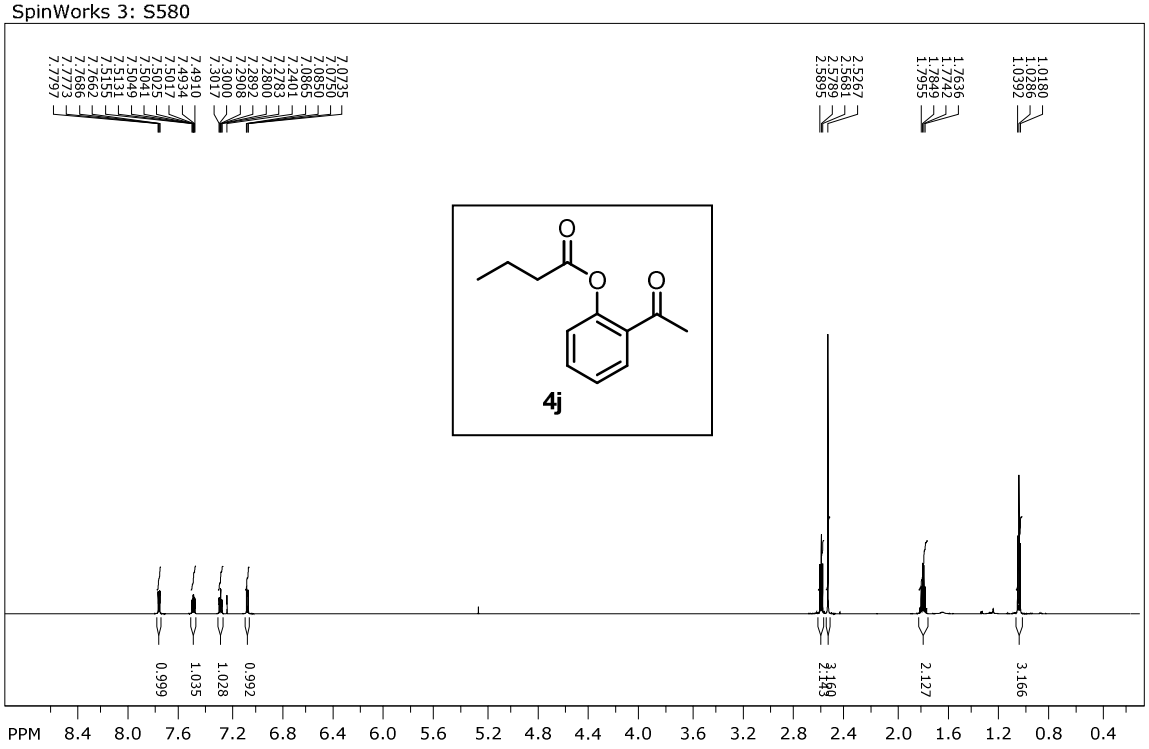
SpinWorks 3: S591



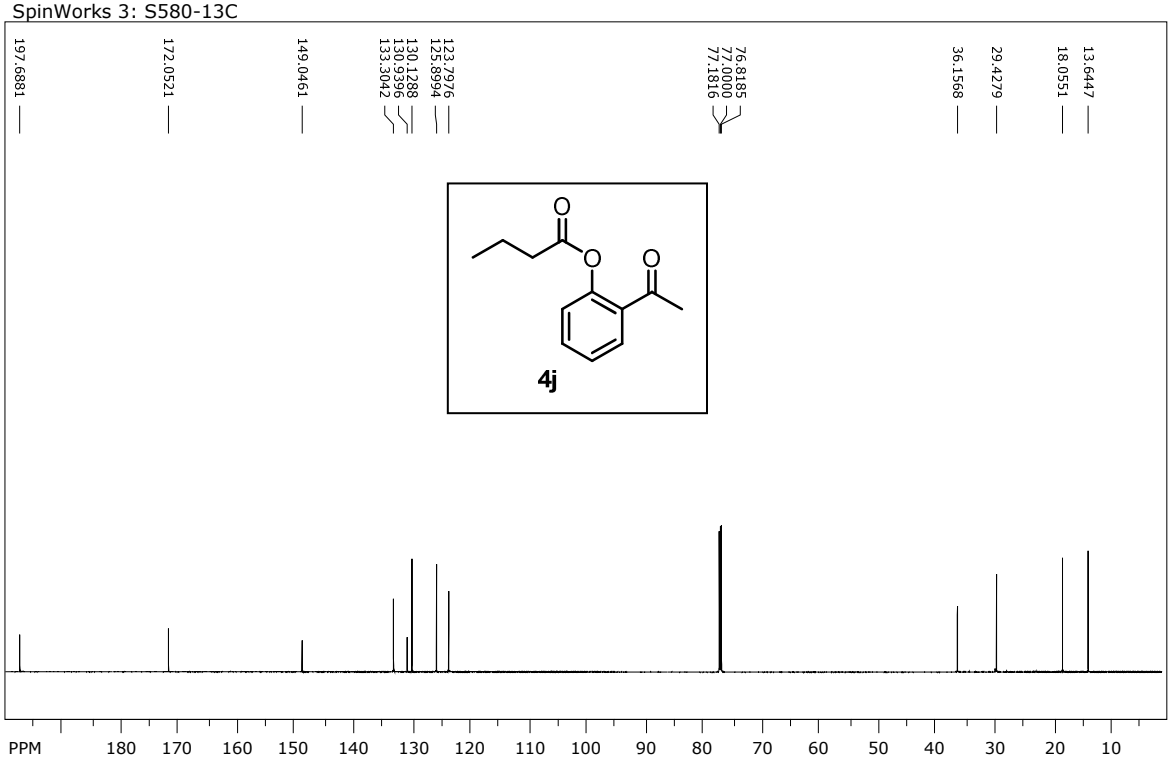
SpinWorks 3: S591-13C



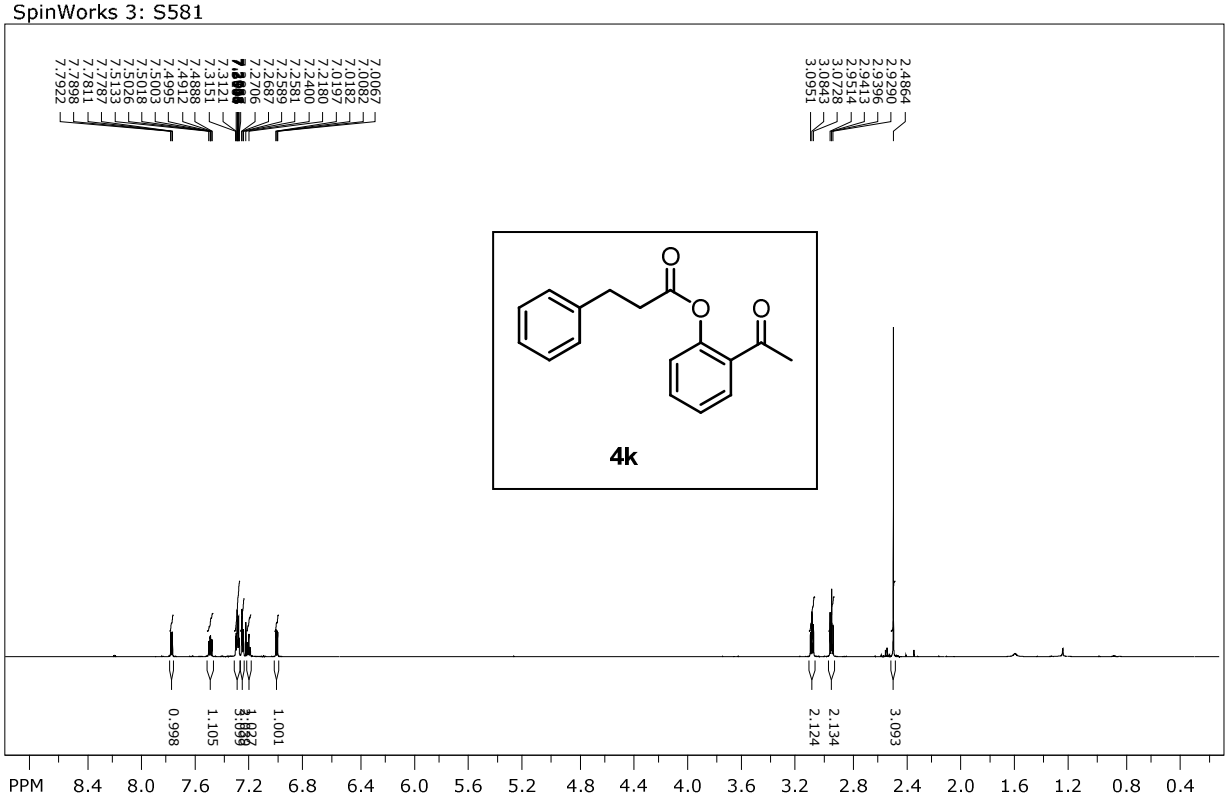
SpinWorks 3: S580



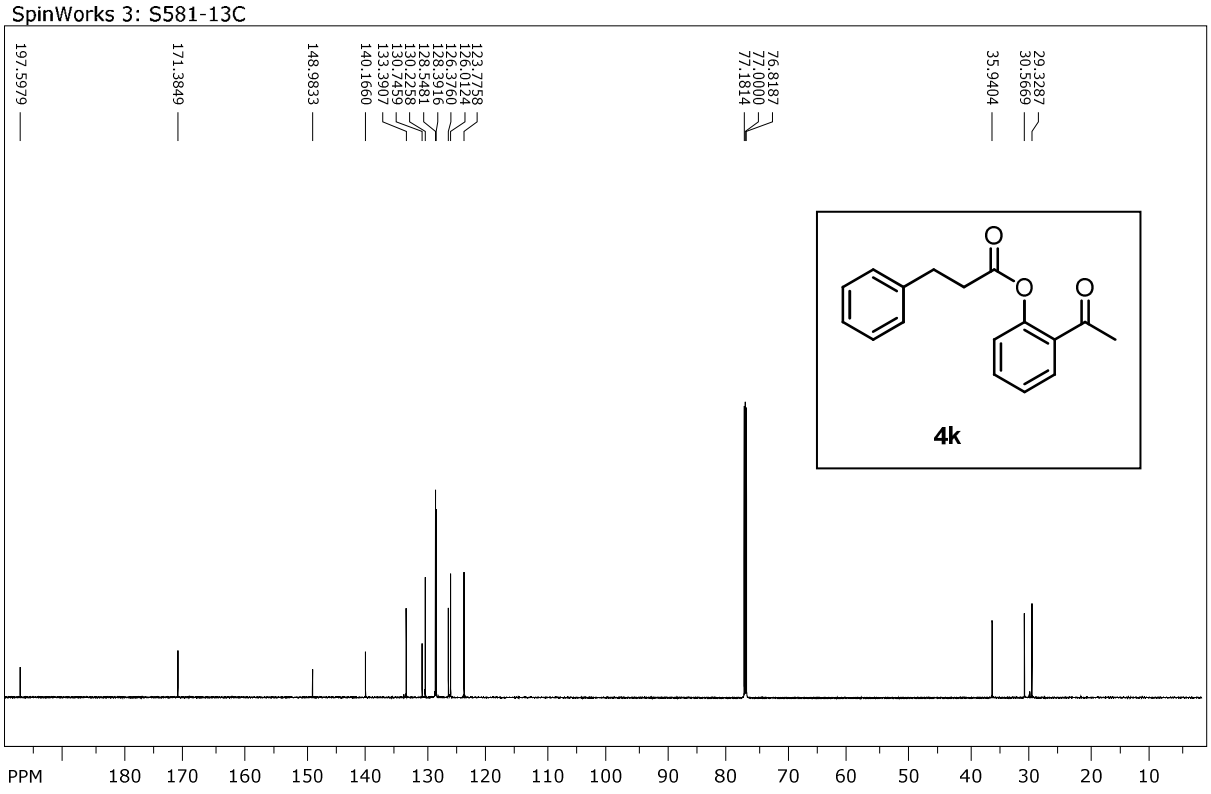
SpinWorks 3: S580-13C



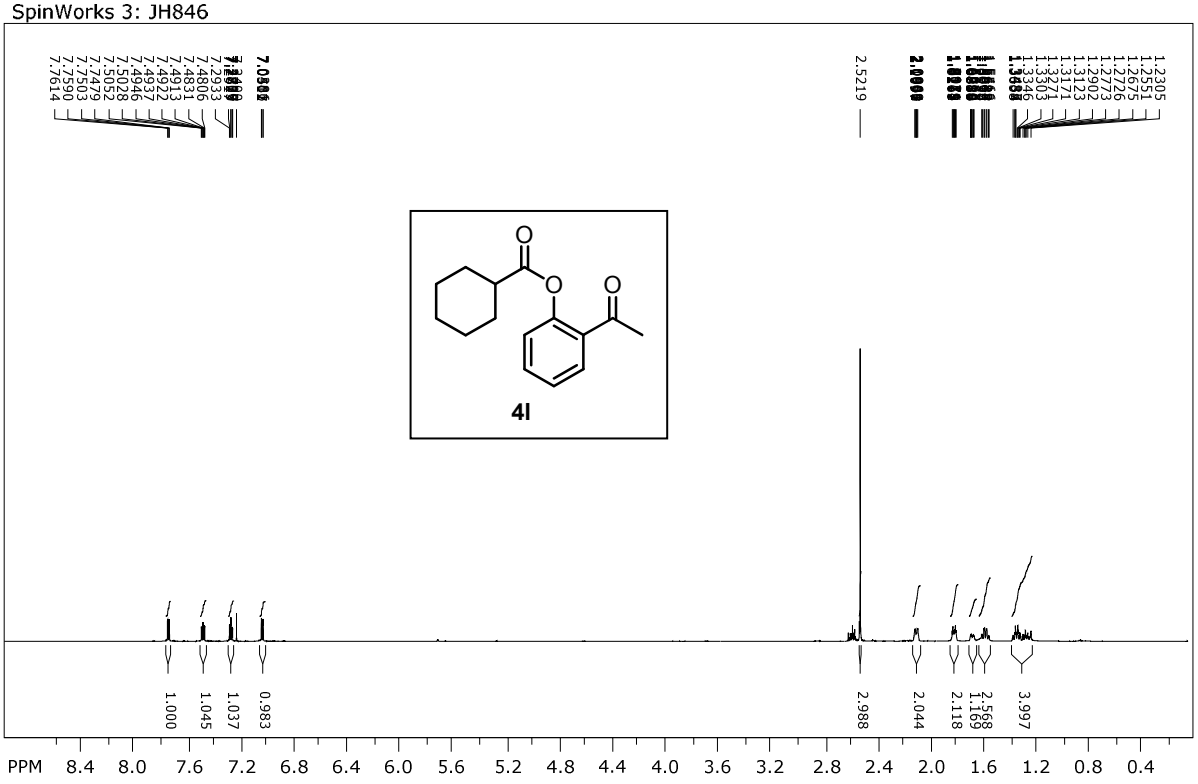
SpinWorks 3: S581



SpinWorks 3: S581-13C



SpinWorks 3: JH846



SpinWorks 3: JH846-13C