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Synthesis

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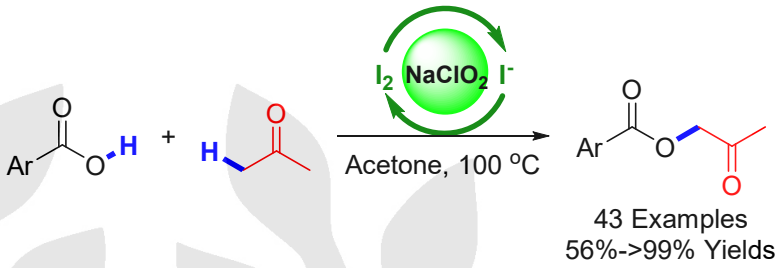

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Abstract Iodine catalyzed oxidative C(sp^3)-H acyloxylation of acetone with carboxylic acids has been developed. The method employs an iodide as catalyst and sodium chlorite as oxidant. Substituted benzoic acids, naphthoic acids and hetero-aromatic carboxylic acids can be used, and 2-oxopropyl carboxylates are obtained with good to excellent yields.

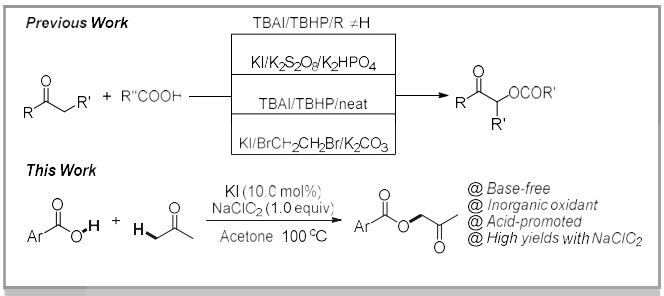
Key words iodine; oxidative C-H functionalization; acetone; carboxylic acids; carboxylates

Halogen chemistry has aroused the interest of many chemists including halogen bond[1] and hypervalent iodine compounds.[2] Iodine shows different properties and reactivity from the light main-group elements. In contrast to heavy metals, iodine and its salts are able to be used as environmentally benign and relatively inexpensive reagents or catalysts.

Iodine donors mediated cyclization of 2-alkynyl-1-methylene azide aromatics,[3] enynes[4], enamines[5], anilines with methyl ketones,[6] aryl methyl ketoxime acetates with triethylamineand,[7] aryl methylketones with 4-hydroxycoumarins,[8] and C-C/C-O bond-forming of 1,3-dienes with malonate esters[9] had been developed for the synthesis of valuable cyclic products. Not only that, many cyclization also had been conducted by iodine catalyst to give good results, such as domino Michael addition-intramolecular cyclization,[10] dehydrative-cycloisomerization of pent-4-yne-1,2-diols,[11] C-N and C-C bonds formation,[12] Nazarov or *iso*-Nazarov cyclization,[13] hydroamination[14] or deamination[15] of styrene, ring opening of 1-aryltetrahydro-β-carbolines,[16] intramolecular carbonyl-olefin metathesis.[17] In multi-component cascade systems, iodine catalyzed cyclization for the synthesis of benzothiazoles,[18] pyrazolones,[19] 2-phenylnaphtho[2,1-*d*]selenazoles[20] were reported as well.

Iodine, an effective catalyst, was widely applied to the functionalization of cyclic compounds. It showed good catalytic activity in sulfenylation of indoles[21] and pyrazolones,[22] selenylation of 2*H*-indazole,[23] C-3 benzylation[24] and consecutive diazenylation/amination[25] of indoles, diazenylation of *N*-heterocyclic compounds,[26] C-N bond-forming of heterocyclic thiols and thiones,[27] arylation of substituted 1,4-naphthoquinones,[28] rearrangement of 3-aminoindazoles.[29] Iodine catalyzed system was a good choice for oxidative transformation. For instance, iodine-catalyzed oxidative annulation,[30] functionalization of aliphatic C-H bonds,[31] oxidative dehydrogenation coupling of amines,[32] deprotective oxidation to access α,β-unsaturated ketones and aldehydes[33] and convergent aerobic dehydro-aromatization[34] were realized successfully.

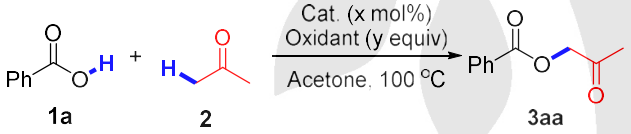
Carboxylate is a common structural motif in natural products, pharmaceuticals and fine chemicals.[35] Few protocols have been developed for the synthesis of 2-oxopropyl carboxylates,[36] and the iodine catalyzed or mediated systems have been unfolded.[37] In which, iodine catalyzed (with TBHP or $K_2S_2O_8$ as oxidant) and 1,2-dibromoethane/KI mediated acyloxylation of ketones had been developed (**Scheme 1**). The approaches that allow for the direct and efficient preparation of 2-oxopropyl carboxylates from readily available precursors will be highly desired.[38] However, the simple and convenient catalysis system is necessary to be explored for the synthesis of 2-oxopropyl carboxylates. Herein, an iodine catalyzed oxidative C-H functionalization of acetone with carboxylic acids to 2-oxopropyl carboxylates was developed with simple reaction conditions.



Scheme 1 Iodine catalysis system for the synthesis of 2-oxopropyl carboxylates

At the outset, we envisaged that iodine catalyst could play an important role in C-H functionalization of acetone. For a proof of the concept, we commenced our study for the oxidative functionalization of benzoic acid (**1a**) and acetone (**2**) with iodine (5.0 mol%) as catalyst in the presence of $K_2S_2O_8$, hydrogen peroxide (H_2O_2), air or oxygen (O_2) at 100 °C. But the results were far from satisfaction (Table 1, entries 1-3). Pleasingly, the product 2-oxopropyl benzoate (**3aa**) was isolated with 39% yield in acetone when *tert*-butyl peroxide (TBHP, 3.0 equiv) was chosen as oxidant (entry 4). The higher yields were obtained when $NaIO_4$ and $NaClO_2$ were used as oxidant (entries 5 and 6). Subsequently, the chloride, bromide and iodide were tested (entries 8-13); among which, KI gave the same result (entry 14). With KI (10.0 mol%) as catalyst, the oxidants were optimized again (entries 15-19) and >99% yields were observed with 1.0 equivalent of $NaIO_4$ or $NaClO_2$. Moreover, the decreased temperature led to lower yield (86%, entry 20). In view of the molar mass of oxidant, we preferred the optimized reaction conditions: KI (10.0 mol%)/$NaClO_2$ (1.0 equiv)/100 °C.

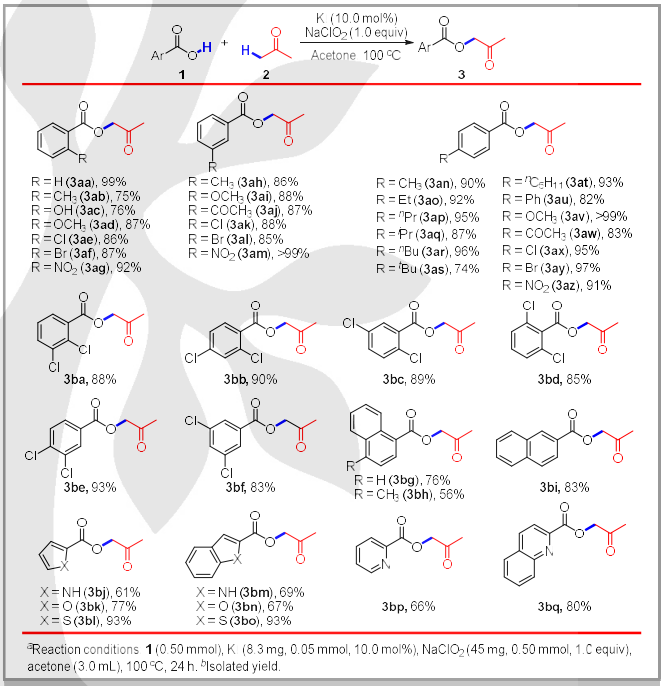
Table 1 Conditions optimization[a]



entry	Cat. (x)	Oxidant (y)	Yield (%)[b]
1	I_2 (5.0)	$K_2S_2O_8$ (1.0)	--
2	I_2 (5.0)	H_2O_2 (3.0)	trace
3	I_2 (5.0)	Air or O_2 (1 atm)	trace
4	I_2 (5.0)	TBHP (3.0)	39
5	I_2 (5.0)	$NaIO_4$ (1.0)	>99
6	I_2 (5.0)	$NaClO_2$ (1.0)	99
7	--	$NaIO_4$ (1.0)	--
8	NaCl (10.0)	$NaIO_4$ (1.0)	--
9	$ZnCl_2$ (10.0)	$NaIO_4$ (1.0)	68
10	CuCl (10.0)	$NaIO_4$ (1.0)	trace
11	CuBr (10.0)	$NaIO_4$ (1.0)	30
12	CuI (10.0)	$NaIO_4$ (1.0)	trace
13	ZnI_2 (10.0)	$NaIO_4$ (1.0)	71
14	KI (10.0)	$NaIO_4$ (1.0)	>99
15	KI (10.0)	$K_2S_2O_8$ (1.0)	--
16	KI (10.0)	$NaClO_2$ (1.0)	>99
17	KI (10.0)	TBHP (3.0)	82
18	KI (10.0)	H_2O_2 (3.0)	77
19	KI (10.0)	Air or O_2 (1 atm)	--
20[d]	KI (10.0)	$NaClO_2$ (1.0)	86

[a]Reaction conditions: **1a** (61 mg, 0.50 mmol), cat. (x mol%), oxidant (y equiv), acetone (3.0 mL), 100 °C, 24 h. [b]Isolated yield. [c]Carried out at 80 °C.

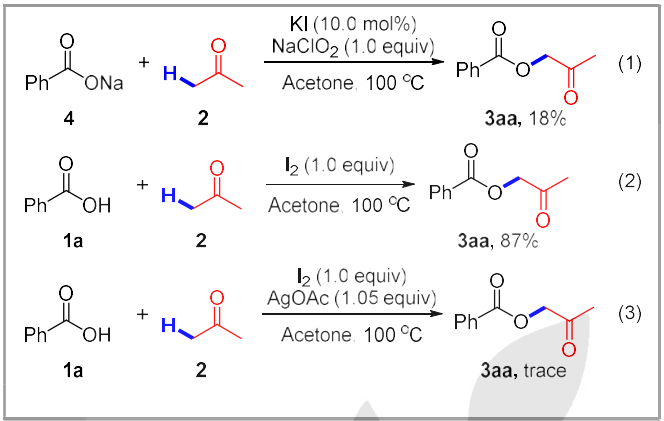
Under the optimized reaction conditions detailed in entry 16 of Table 1, a variety of carboxylic acids were subjected to the KI catalyzed oxidative functionalization of acetone, as shown in **Scheme 2**. For the substrates with different substituent, alkyl, alkoxyl, hydroxyl, chloro, bromo, nitro or phenyl groups on the 2-, 3- or 5- of benzoic acid, the good to excellent isolated yields (74->99% yields) of **3aa**-**3az** were attained. For 2,3-, 2,4- 2,5-, 2,6-, 3,4- or 3,5-dichloro substituted benzoic acids, 83%-93% yields of the corresponding 2-oxopropyl benzoates (**3ba**-**3bf**) were obtained. Similarly, the expected products **3bg**, **3bh** and **3bi** were prepared in 76%, 56% and 83% yields, respectively, from their precursors. The reactions of hetero-aryl carboxylic acids also furnished the products **3bj**-**3bq** in 61%-93% yields. The reaction was conducted in pentan-2-one, hexan-2-one, pentan-3-one, cyclohexanone, cyclopentanone and acetophenone. Very little mixed products were observed. The low reactivity and selectivity might be caused by various C-H active sites of other ketones.



[a]Reaction conditions: **1** (0.50 mmol), KI (8.3 mg, 0.05 mmol, 10.0 mol%), $NaClO_2$ (45 mg, 0.50 mmol, 1.0 equiv), acetone (3.0 mL), 100 °C, 24 h. [b]Isolated yield.

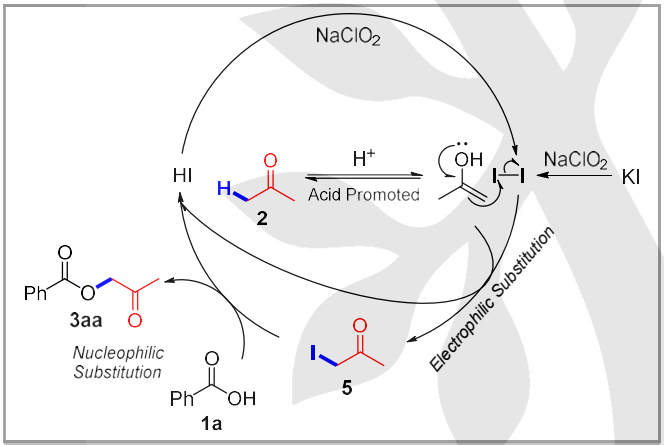
Scheme 2 Screen on the scope of carboxylic acids[a]

In order to investigate the mechanism of iodine catalyzed C-H functionalization of acetone with carboxylic acids, the control experiments had been carried out, as shown in **Scheme 3**. When sodium benzoate **4** was used to replace carboxylic acid **1**, only 18% **3aa** was isolated (equation 1). This result indicated that the reaction might be enhanced under acidic condition. Iodine (1.0 equiv) was put into the reaction system without other oxidants and 87% **3aa** was obtained (equation 2); however, the reaction was inhibited by AgOAc (1.05 equiv, equation 3). It was further confirmed that element iodine was the active catalyst.



Scheme 3 Control experiments

According to the above results and iodine catalyzed dehydrogenation of ketones and aldehydes,[29b] the mechanism had been proposed. (**Scheme 4**). We assumed the process could be initialized by electrophilic substitution of acetone with iodine to afford **5** with the promotion of carboxylic acid. Then nucleophilic substitution of iodoacetone with benzoic acid could occur to provide the product **3**. Then the active catalyst iodine was regenerated by oxidation of $NaClO_2$ or $NaIO_4$.



Scheme 4 Proposed mechanism

In summary, iodine catalyzed oxidative C-H functionalization of acetone with carboxylic acids has been successfully achieved with good to excellent yields. The present study provides an efficient route to prepare 2-oxopropyl carboxylates. The principle will provide a strategy for the functionalization of C-H bonds and further study is in process.

All reagents and solvents were of pure analytical grade. Thin layer chromatography (TLC) was performed on HSGF254 silica gel, pre-coated on glass-backed plates coated with 0.2 mm silica and revealed with either a UV lamp (λ_{max} = 254 nm). The products were purified by flash column chromatography on silica gel 200-300 mesh. ^1H and ^{13}C NMR spectra were recorded on a 600 MHz spectrometer (^1H 600 MHz, ^{13}C 151 MHz) using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are in δ (ppm) relative to TMS. The coupling constants (J) are in Hz.

The Typical Procedure for the synthesis of 3aa-3bq:

A mixture of aryl carboxylic acid **1** (0.50 mmol), KI (8.3 mg, 0.05 mmol, 10.0 mol%) and $NaClO_2$ (45 mg, 0.50 mmol, 1.0 equiv) in acetone (3 mL) was added into a Schlenk flask (25 mL) and stirred at 100 °C. After the reaction was finished, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate 10:1 to 3:1) to provide 2-oxopropyl carboxylates **3**.

2-oxopropyl benzoate (3aa)

Yield: 99%, 88.2 mg, colorless oil; R_f 0.41 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.60–7.57 (m, 1H), 7.47–7.44 (m, 2H), 4.87 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.8, 165.8, 133.5, 129.9, 129.2, 128.5, 68.7, 26.2; IR (neat) 3058, 2935, 1729, 1273, 1114, 908, 711 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_{10}O_3Na$: 201.0528 $[M+Na]^+$; found: 201.0534.

2-oxopropyl 2-methylbenzoate (3ab)

Yield: 75%, 72.2 mg, colorless oil; R_f 0.42 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.1, 1.2 Hz, 1H), 7.44–7.41 (m, 1H), 7.30–7.24 (m, 2H), 4.86 (s, 2H), 2.62 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.8, 166.6, 140.7, 132.5, 131.8, 130.9, 128.6, 125.8, 68.6, 26.2, 21.7; IR (neat) 3053, 2939, 1731, 1270, 1112, 905, 714 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_3Na$: 215.0684 $[M+Na]^+$; found: 215.0689.

2-oxopropyl 2-hydroxybenzoate (3ac)

Yield: 76%, 73.7 mg, white solid, m.p. 85–87 °C; R_f 0.39 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.94 (dd, J = 8.0, 1.6 Hz, 1H), 7.54–7.47 (m, 1H), 7.05–6.99 (m, 1H), 6.96–6.90 (m, 1H), 4.92 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.9, 169.2, 161.8, 136.3, 130.1, 119.4, 117.7, 111.7, 68.7, 26.1; IR (KBr) 3231, 3060, 2931, 1727, 1270, 1116, 909, 704 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_{10}O_4Na$: 217.0477 $[M+Na]^+$; found: 217.0473.

2-oxopropyl 2-methoxybenzoate (3ad)

Yield: 87%, 90.1 mg, colorless oil; R_f 0.36 (2:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.92–7.85 (m, 1H), 7.52–7.43 (m, 1H), 6.99–6.94 (m, 2H), 4.80 (s, 2H), 3.87 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.4, 165.2, 159.6, 134.2, 132.0, 120.2, 118.7, 112.1, 68.6, 55.9, 26.3; IR (neat) 3065, 2937, 1736, 1276, 1235, 1114, 903, 716 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_4Na$: 231.0633 $[M+Na]^+$; found: 231.0630.

2-oxopropyl 2-chlorobenzoate (3ae)

Yield: 86%, 91.2 mg, colorless oil; R_f 0.37 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.98–7.91 (m, 1H), 7.50–7.40 (m, 2H), 7.36–7.29 (m, 1H), 4.88 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 164.7, 134.0, 133.1, 131.9, 131.2, 128.9, 126.7, 68.9, 26.2; IR (neat) 3060, 2931, 1727, 1271, 1119, 1084, 907, 714 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9ClO_3Na$: 235.0138 $[M+Na]^+$; found: 235.0143.

2-oxopropyl 2-bromobenzoate (3af)

Yield: 87%, 111.6 mg, colorless oil; R_f 0.38 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.6, 1.8 Hz, 1H), 7.66 (dd, J = 7.8, 1.0 Hz, 1H), 7.40–7.31 (m, 2H), 4.88 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.2, 165.2, 134.5, 133.1, 131.8, 130.9, 127.3, 122.0, 69.0, 26.2; IR (neat) 3056, 2933, 1728, 1270, 1113, 1068, 907, 712 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9BrO_3Na$: 278.9633 $[M+Na]^+$; found: 278.9639.

2-oxopropyl 2-nitrobenzoate (3ag)

Yield: 92%, 102.9 mg, colorless oil; R_f 0.33 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.0, 1.0 Hz, 1H), 7.87 (dd, J = 7.6, 1.4 Hz, 1H), 7.73–7.65 (m, 2H), 4.90 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.7, 164.7, 148.0, 133.17, 132.21, 130.3, 126.7, 124.0, 69.5, 26.2; IR (neat) 3062, 2930, 1728, 1541, 1274, 1116, 910, 709 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9O_5Na$: 246.0378 [M+Na]$^+$; found: 246.0383.

2-oxopropyl 3-methylbenzoate (3ah)

Yield: 86%, 82.9 mg, colorless oil; R_f 0.46 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99–7.83 (m, 2H), 7.46–7.31 (m, 2H), 4.87 (s, 2H), 2.41 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.9, 166.0, 138.3, 134.2, 130.4, 129.1, 128.4, 127.0, 68.7, 26.2, 21.2; IR (neat) 3057, 2936, 1726, 1278, 1117, 906, 713 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_3Na$: 215.0684 [M+Na]$^+$; found: 215.0689.

2-oxopropyl 3-methoxybenzoate (3ai)

Yield: 88%, 91.6 mg, colorless oil; R_f 0.42 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72–7.65 (m, 1H), 7.59 (d, J = 1.4 Hz, 1H), 7.38–7.33 (m, 1H), 7.15–7.09 (m, 1H), 4.86 (s, 2H), 3.83 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.8, 165.7, 159.6, 130.5, 129.5, 122.2, 119.9, 114.3, 68.8, 55.4, 26.1; IR (neat) 3053, 2937, 1725, 1276, 1120, 907, 710 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_4Na$: 231.0633 [M+Na]$^+$; found: 231.0637.

2-oxopropyl 3-acetylbenzoate (3aj)

Yield: 87%, 95.5 mg, colorless oil; R_f 0.36 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, J = 3.0 Hz, 1H), 8.28–8.08 (m, 2H), 7.54–7.51 (m, 1H), 4.89 (s, 2H), 2.59 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 197.0, 165.0, 137.3, 134.1, 132.8, 129.8, 129.7, 129.0, 68.9, 26.6, 26.1; IR (neat) 3056, 2931, 1742, 1724, 1278, 1110, 909, 708 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{12}O_4Na$: 243.0633 [M+Na]$^+$; found: 243.0630.

2-oxopropyl 3-chlorobenzoate (3ak)

Yield: 88%, 93.1 mg, colorless oil; R_f 0.37 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (t, J = 1.7 Hz, 1H), 8.01–7.96 (m, 1H), 7.58–7.56 (m, 1H), 7.41 (t, J = 7.9 Hz, 1H), 4.90 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 164.7, 134.7, 133.5, 130.9, 129.9, 129.9, 128.0, 68.9, 26.1; IR (neat) 3060, 2935, 1728, 1279, 1082, 1117, 907, 712 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9ClO_3Na$: 235.0138 [M+Na]$^+$; found: 235.0131.

2-oxopropyl 3-bromobenzoate (3al)

Yield: 85%, 109.3 mg, colorless oil; R_f 0.36 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (t, J = 1.7 Hz, 1H), 8.02–7.99 (m, 1H), 7.71–7.70 m, 1H), 7.34 (t, J = 7.9 Hz, 1H), 4.89 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 164.5, 136.4, 132.8, 131.1, 130.1, 128.5, 122.5, 68.9, 26.1; IR (neat) 3058, 2934, 1726, 1274, 1115, 1077, 907, 711 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9BrO_3Na$: 278.9633 [M+Na]$^+$; found: 278.9638.

2-oxopropyl 3-nitrobenzoate (3am)

Yield: >99%, 111.3 mg, white solid, m.p. 101–103 °C; R_f 0.37 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.8 9 (s, 1H), 8.45–8.39 (m, 2H), 7.69 (t, J = 8.0 Hz, 1H), 4.98 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.4, 163.8, 148.3, 135.5, 131.0, 129.8, 127.8, 124.8, 69.2, 26.1; IR (KBr) 3059, 2934, 1729, 1352, 1272, 1113, 906, 713 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9NO_5Na$: 246.0378 [M+Na]$^+$; found: 246.0388.

2-oxopropyl 4-methylbenzoate (3an)

Yield: 90%, 85.9 mg, colorless oil; R_f 0.42 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.87 (s, 2H), 2.43 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 144.3, 129.9, 129.2, 126.4, 68.6, 26.2, 21.7; IR (neat) 3058, 2930, 1730, 1275, 1118, 907, 795, 710 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_3Na$: 215.0684 [M+Na]$^+$; found: 215.0697.

2-oxopropyl 4-ethylbenzoate (3ao)

Yield: 92%, 94.5 mg, colorless oil; R_f 0.36 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.31–7.26 (m, 2H), 4.86 (s, 2H), 2.71 (q, J = 7.6 Hz, 2H), 2.22 (s, 3H), 1.26 (t, J = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 150.4, 130.0, 128.0, 126.7, 68.6, 29.0, 26.2, 15.2; IR (neat) 3059, 2937, 1730, 1276, 1113, 908, 709 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{14}O_3Na$: 229.0841 [M+Na]$^+$; found: 229.0828.

2-oxopropyl 4-propylbenzoate (3ap)

Yield: 95%, 104.1 mg, colorless oil; R_f 0.41 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.86 (s, 2H), 2.65 (t, J = 7.6 Hz, 2H), 2.23 (d, J = 1.8 Hz, 3H), 1.70–1.63 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 148.9, 129.9, 128.6, 126.7, 68.6, 38.1, 26.2, 24.2, 13.7; IR (neat) 3062, 2939, 1725, 1271, 1115, 908, 712 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{16}O_3Na$: 243.0997 [M+Na]$^+$; found: 243.1011.

2-oxopropyl 4-isopropylbenzoate (3aq)

Yield: 87%, 95.6 mg, colorless oil; R_f 0.41 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.87 (s, 2H), 3.00–2.96 (m, 1H), 2.23 (s, 3H), 1.28 (d, J = 7.0 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 155.0, 130.1, 126.8, 126.6, 68.6, 34.3, 26.2, 23.7; IR (neat) 3064, 2932, 1733, 1268, 1126, 916, 708 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{16}O_3Na$: 243.0997 [M+Na]$^+$; found: 243.1008.

2-oxopropyl 4-butylbenzoate (3ar)

Yield: 96%, 112.1 mg, colorless oil; R_f 0.41 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 4.85 (s, 2H), 2.69–2.64 (m, 2H), 2.22 (s, 3H), 1.64–1.58 (m, 2H), 1.39–1.32 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 149.1, 129.9, 128.6, 126.6, 68.6, 35.7, 33.2, 26.2, 22.3, 13.9; IR (neat) 3062, 2940, 1725, 1278, 1123, 917, 705 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{18}O_3Na$: 257.1154 [M+Na]$^+$; found: 257.1137.

2-oxopropyl 4-(*tert*-butyl)benzoate (3as)

Yield: 74%, 86.2 mg, colorless oil; R_f 0.38 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 4.87 (s, 2H), 2.23 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 157.2, 129.8, 126.4, 125.5, 68.6, 35.1, 31.1, 26.2; IR (neat) 3052, 2931, 1724, 1275, 1124, 923, 715 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{18}O_3Na$: 257.1154 [M+Na]$^+$; found: 257.1170.

2-oxopropyl 4-pentylbenzoate (3at)

Yield: 93%, 115.7 mg, colorless oil; R_f 0.41 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.86 (s, 2H), 2.67 (t, J = 7.7 Hz, 2H), 2.28–2.19 (m, 3H), 1.68–1.61 (m, 2H), 1.37–1.30 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9,

149.2, 130.0, 128.6, 126.6, 68.6, 36.0, 31.4, 30.8, 26.2, 22.5, 14.0; IR (neat) 3057, 2932, 1728, 1276, 1120, 918, 712 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{20}O_3Na$: 271.1310 $[M+Na]^+$; found: 271.1327.

2-oxopropyl [1,1'-biphenyl]-4-carboxylate (3au)

Yield: 82%, 103.7 mg, white solid, m.p. 56–58 °C; R_f 0.31 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 8.21–8.18 (m, 2H), 7.73–7.70 (m, 2H), 7.66 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 4.93 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.9, 165.8, 146.2, 139.9, 130.5, 129.0, 128.3, 127.9, 127.3, 127.2, 68.8, 26.3; IR (KBr) 3060, 2941, 1728, 1269, 1108, 914, 707 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{14}O_3Na$: 277.0841 $[M+Na]^+$; found: 277.0832.

2-oxopropyl 4-methoxybenzoate (3av)

Yield: >99%, 103.9 mg, colorless oil; R_f 0.42 (2:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.85 (s, 2H), 3.88 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.3, 165.6, 163.8, 132.0, 121.5, 113.8, 68.6, 55.5, 26.2; IR (neat) 3059, 2931, 1732, 1276, 1110, 913, 707 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_4Na$: 231.0633 $[M+Na]^+$; found: 231.0621.

2-oxopropyl 4-acetylbenzoate (3aw)

Yield: 83%, 91.2 mg, white solid, m.p. 81–83 °C; R_f 0.30 (2:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H), 4.92 (s, 2H), 2.65 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 197.5, 165.0, 140.6, 132.9, 130.1, 128.3, 68.9, 26.9, 26.2; IR (KBr) 3057, 2931, 1736, 1721, 1271, 1112, 913, 708 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{12}O_4Na$: 243.0633 $[M+Na]^+$; found: 243.0649.

2-oxopropyl 4-chlorobenzoate (3ax)

Yield: 95% (24 h), 100.5 mg, colorless oil; R_f 0.40 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 4.88 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 165.0, 139.9, 131.3, 128.9, 127.7, 68.8, 26.1; IR (neat) 3057, 2938, 1728, 1274, 1115, 1082, 910, 712 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{17}ClO_3Na$: 235.0138 $[M+Na]^+$; found: 235.0145.

2-oxopropyl 4-bromobenzoate (3ay)

Yield: 97%, 124.9 mg, colorless oil; R_f 0.31 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.99–7.92 (m, 2H), 7.65–7.58 (m, 2H), 4.89 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 165.1, 131.9, 131.4, 128.7, 128.1, 68.8, 26.2; IR (neat) 3056, 2937, 1728, 1272, 1111, 1073, 910, 716 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9BrO_3Na$: 278.9633 $[M+Na]^+$; found: 278.9626.

2-oxopropyl 4-nitrobenzoate (3az)

Yield: 91%, 101.6 mg, white solid, m.p. 87-89 °C; R_f 0.43 (2:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 8.32–8.26 (m, 4H), 4.97 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.3, 164.0, 150.8, 134.6, 131.1, 123.6, 69.2, 26.1; IR (KBr) 3062, 2937, 1721, 1361, 1270, 1107, 912, 709 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9NO_5Na$: 246.0378 $[M+Na]^+$; found: 246.0360.

2-oxopropyl 2,3-dichlorobenzoate (3ba)

Yield: 88%, 109.0 mg, colorless oil; R_f 0.33 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 4.91 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 164.4, 134.7, 133.6, 131.9, 131.7, 129.6, 127.3, 69.1, 26.2; IR (neat) 3064, 2931, 1727, 1273, 1107, 1088, 917, 713 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9761.

2-oxopropyl 2,4-dichlorobenzoate (3bb)

Yield: 90%, 111.4 mg, colorless oil; R_f 0.32 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.52–7.46 (m, 1H), 7.34–7.32 (m, 1H), 4.90 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 163.8, 138.9, 135.3, 133.0, 131.1, 127.2, 127.1, 69.0, 26.2; IR (neat) 3065, 2940, 1733, 1279, 1122, 1087, 915, 712 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9765.

2-oxopropyl 2,5-dichlorobenzoate (3bc)

Yield: 89%, 109.3 mg, colorless oil; R_f 0.37 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.4 Hz, 1H), 7.45–7.40 (m, 2H), 4.91 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.6, 163.5, 133.1, 132.7, 132.5, 132.4, 131.7, 130.1, 69.1, 26.2; IR (neat) 3064, 2936, 1730, 1275, 1116, 1089, 910, 713 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9732.

2-oxopropyl 2,6-dichlorobenzoate (3bd)

Yield: 85%, 104.3 mg, colorless oil; R_f 0.36 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.36–7.30 (m, 3H), 4.90 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 164.1, 132.5, 132.1, 131.4, 128.0, 69.5, 26.6; IR (neat) 3061, 2937, 1731, 1274, 1115, 1087, 912, 711 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9735.

2-oxopropyl 3,4-dichlorobenzoate (3be)

Yield: 93%, 115.1 mg, white solid, m.p. 59–61 °C; R_f 0.38 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.9 Hz, 1H), 7.91 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 4.91 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 164.0, 138.1, 133.1, 131.8, 130.7, 129.0, 128.9, 69.0, 26.1; IR (KBr) 3057, 2939, 1730, 1275, 1114, 1081, 912, 710 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9730.

2-oxopropyl 3,5-dichlorobenzoate (3bf)

Yield: 83%, 102.2 mg, white solid, m.p. 63–65 °C; R_f 0.45 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.59 (s, 1H), 4.92 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.5, 163.6, 135.4, 133.3, 132.0, 128.3, 69.1, 26.1; IR (KBr) IR (neat) 3056, 2937, 1728, 1272, 1113, 1082, 907, 710 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9762.

2-oxopropyl 1-naphthoate (3bg)

Yield: 76%, 86.3 mg, colorless oil; R_f 0.36 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 8.98 (d, *J* = 8.7 Hz, 1H), 8.32 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.65–7.64 (m, 1H), 7.57–7.51 (m, 2H), 4.97 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.8, 166.7, 133.9, 133.8, 130.7, 128.6, 128.0, 126.4, 126.1, 125.8, 124.6, 68.8, 26.2; IR (neat) 3057, 2935, 1728, 1272, 1108, 906, 708 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{12}O_3Na$: 251.0684 $[M+Na]^+$; found: 251.0671.

2-oxopropyl 4-methyl-1-naphthoate (3bh)

Yield: 56%, 67.3 mg, colorless oil; R_f 0.38 (5:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 9.02 (d, *J* = 8.5 Hz, 1H), 8.24 (d, *J* =

7.4 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.64–7.59 (m, 2H), 7.39 (d, *J* = 7.4 Hz, 1H), 4.97 (s, 2H), 2.77 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 166.7, 141.1, 132.9, 131.5, 130.6, 127.6, 126.3, 126.2, 125.6, 124.5, 124.3, 68.7, 26.3, 20.2; IR (neat) 3057, 2934, 1731, 1278, 1109, 909, 713 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{14}O_3Na$: 265.0841 [M+Na]$^+$; found: 265.0828.

2-oxopropyl 2-naphthoate (3bi)

Yield: 83%, 94.8 mg, colorless oil; R_f 0.34 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.11 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.93–7.88 (m, 2H), 7.65–7.54 (m, 2H), 4.96 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.9, 166.0, 135.8, 132.5, 131.6, 129.5, 128.6, 128.4, 127.8, 126.8, 126.4, 125.3, 68.9, 26.3; IR (neat) 3060, 2934, 1734, 1275, 1109, 914, 708 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{12}O_3Na$: 251.0684 [M+Na]$^+$; found: 251.0695.

2-oxopropyl 1*H*-pyrrole-2-carboxylate (3bj)

Yield: 61%, 50.7 mg, colorless oil; R_f 0.40 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.11–6.98 (m, 2H), 6.30 (d, *J* = 1.2 Hz, 1H), 4.83 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.5, 160.3, 124.0, 121.5, 116.5, 110.7, 68.2, 26.2; IR (neat) 2974, 2937, 1713, 1605, 1466, 1374, 1273, 1151, 1087, 1055, 979, 852, 756, 736 cm^{-1}; HRMS (EI) Calcd for $C_8H_9NO_3Na$: 190.0480 [M+Na]$^+$; found: 190.0463.

2-oxopropyl furan-2-carboxylate (3bk)

Yield: 77%, 64.7 mg, colorless oil; R_f 0.71 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65–7.58 (m, 1H), 7.29–7.25 (m, 1H), 6.56–6.51 (m, 1H), 4.85 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 157.7, 146.9, 143.7, 119.1, 112.1, 68.3, 26.1; IR (neat) 3058, 2935, 1729, 1273, 1114, 908, 711 cm^{-1}; HRMS (EI) Calcd for $C_8H_8O_4Na$: 191.0320 [M+Na]$^+$; found: 191.0333.

2-oxopropyl thiophene-2-carboxylate (3bl)

Yield: 93%, 85.5 mg, colorless oil; R_f 0.76 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.62 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.13 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.84 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.7, 161.4, 134.4, 133.3, 132.4, 128.0, 68.7, 26.2; IR (neat) 3050, 2941, 1727, 1278, 1123, 916, 718 cm^{-1}; HRMS (EI) Calcd for $C_8H_8O_3SNa$: 207.0092 [M+Na]$^+$; found: 207.0109.

2-oxopropyl 1H-indole-2-carboxylate (3bm)

Yield: 69%, 75.2 mg, white solid, m.p. 107–109 °C; R_f 0.32 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, DMSO) δ 11.98 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 1.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 5.04 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (151 MHz, DMSO) δ 202.3, 161.0, 138.0, 127.2, 126.9, 125.4, 122.6, 120.8, 113.1, 108.9, 69.0, 26.4; IR (KBr) 2980, 2934, 1715, 1611, 1452, 1380, 1295, 1279, 1058, 975, 735 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{11}NO_3Na$: 240.0637 [M+Na]$^+$; found: 240.0625.

2-oxopropyl benzofuran-2-carboxylate (3bn)

Yield: 67%, 73.4 mg, light yellow oil; R_f 0.46 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.65 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.50-7.46 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 4.95 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.9, 158.7, 156.0, 144.5, 128.1, 126.8, 124.0, 123.0, 115.1, 112.4, 68.7, 26.1; IR (neat) 3048, 2924, 1725, 1270, 1118, 921, 709 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{10}O_4Na$: 241.0477 [M+Na]$^+$; found: 241.0470.

2-oxopropyl benzo[*b*]thiophene-2-carboxylate (3bo)

Yield: 93%, 109.2 mg, white solid, m.p. 76–78 °C; R_f 0.47 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.90 (dd, *J* = 11.2, 8.2 Hz, 2H), 7.51–7.42 (m, 2H), 4.91 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 162.0, 142.5, 138.6, 132.2, 131.6, 127.3, 125.7, 125.1, 122.8, 69.0, 26.2; IR (KBr) 2978, 2931, 1740, 1718, 1604, 1465, 1372, 1298, 1273, 1155, 1090, 908, 737 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{10}O_3SNa$: 257.0248 [M+Na]$^+$; found: 257.0235.

2-oxopropyl picolinate (3bp)

Yield: 66%, 58.8 mg, colorless oil; R_f 0.26 (1:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83–8.75 (m, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.89–7.86 (m, 1H), 7.58–7.47 (m, 1H), 4.98 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 164.4, 150.0, 147.1, 137.2, 127.4, 125.6, 69.3, 26.1; IR (neat) 3064, 2930, 1735, 1278, 1120, 980, 720 cm^{-1}; HRMS (EI) Calcd for $C_9H_9NO_3Na$: 202.0480 [M+Na]$^+$; found: 202.0457.

2-oxopropyl quinoline-2-carboxylate (3bq)

Yield: 80%, 91.9 mg, colorless oil; R_f 0.37 (1:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 8.4, 3.7 Hz, 2H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.85–7.77 (m, 1H), 7.67 (dd, *J* = 11.1, 3.9 Hz, 1H), 5.06 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.9, 164.7, 147.6, 147.1, 137.4, 130.8, 130.4, 129.5, 128.9, 127.6, 121.3, 69.5, 26.1; IR (neat) 3061, 2938, 1735, 1276, 1124, 978, 721 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{11}NO_3Na$: 252.0637 [M+Na]$^+$; found: 252.0656.

Acknowledgment

The work was supported by the Foundation of Guizhou Educational Committee (Grant No. qianjiaohe KY zi [2019] 081) and the Natural Science Foundation of Guizhou Province (Grant No. qiankehejichu [2018] number 1141)

Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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Supporting Information

Oxidative C-H Acyloxylation of Acetone with Carboxylic Acids under Iodine Catalysis

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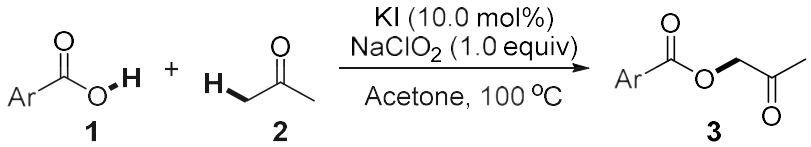
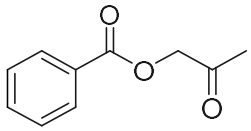
1. General and Materials.

All reagents and solvents were of pure analytical grade. Thin layer chromatography (TLC) was performed on HSGF254 silica gel, pre-coated on glass-backed plates coated with 0.2 mm silica and revealed with either a UV lamp (λ_{max} = 254 nm). The products were purified by flash column chromatography on silica gel 200-300 mesh. ^{1}H and ^{13}C NMR spectra were recorded on a 600 MHz spectrometer (^{1}H 600 MHz, ^{13}C 151 MHz) using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are in δ (ppm) relative to TMS. The coupling constants (J) are in Hz.

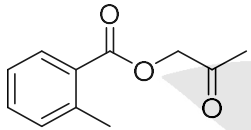
2. The Typical Procedure for Iodine Catalyzed C-H Acyloxylation of Acetone



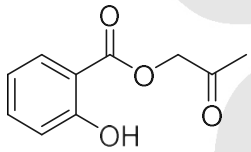
The Typical Procedure for Iodine Catalyzed C-H Acyloxylation of Acetone: A mixture of aryl carboxylic acid **1** (0.50 mmol), KI (8.3 mg, 0.05 mmol, 10.0 mol%) and $NaClO_2$ (45 mg, 0.50 mmol, 1.0 equiv) in acetone (3 mL) was added into a Schlenk flask (25 mL) and stirred at 100 °C. After the reaction was finished, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate 10:1 to 3:1) to provide 2-oxopropyl carboxylates **3**.



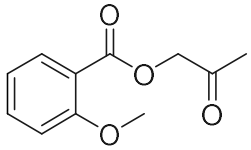
2-oxopropyl benzoate (3aa): Yield: 99%, 88.2 mg, colorless oil; R_f 0.41 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.60−7.57 (m, 1H), 7.47−7.44 (m, 2H), 4.87 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.8, 165.8, 133.5, 129.9, 129.2, 128.5, 68.7, 26.2; IR (neat) 3058, 2935, 1729, 1273, 1114, 908, 711 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_{10}O_3Na$: 201.0528 $[M+Na]^+$; found: 201.0534.



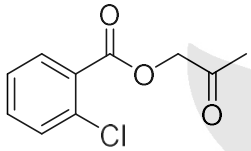
2-oxopropyl 2-methylbenzoate (3ab): Yield: 75%, 72.2 mg, colorless oil; R_f 0.42 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.1, 1.2 Hz, 1H), 7.44−7.41 (m, 1H), 7.30−7.24 (m, 2H), 4.86 (s, 2H), 2.62 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.8, 166.6, 140.7, 132.5, 131.8, 130.9, 128.6, 125.8, 68.6, 26.2, 21.7; IR (neat) 3053, 2939, 1731, 1270, 1112, 905, 714 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_3Na$: 215.0684 $[M+Na]^+$; found: 215.0689.



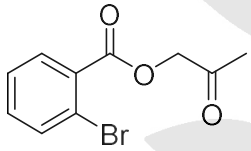
2-oxopropyl 2-hydroxybenzoate (3ac): Yield: 76%, 73.7 mg, white solid, m.p. 85−87 °C; R_f 0.39 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.94 (dd, J = 8.0, 1.6 Hz, 1H), 7.54−7.47 (m, 1H), 7.05−6.99 (m, 1H), 6.96−6.90 (m, 1H), 4.92 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.9, 169.2, 161.8, 136.3, 130.1, 119.4, 117.7, 111.7, 68.7, 26.1; IR (KBr) 3231, 3060, 2931, 1727, 1270, 1116, 909, 704 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_{10}O_4Na$: 217.0477 $[M+Na]^+$; found: 217.0473.



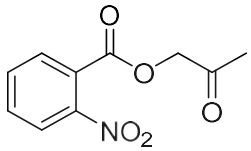
2-oxopropyl 2-methoxybenzoate (3ad): Yield: 87%, 90.1 mg, colorless oil; R_f 0.36 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92−7.85 (m, 1H), 7.52−7.43 (m, 1H), 6.99−6.94 (m, 2H), 4.80 (s, 2H), 3.87 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.4, 165.2, 159.6, 134.2, 132.0, 120.2, 118.7, 112.1, 68.6, 55.9, 26.3; IR (neat) 3065, 2937, 1736, 1276, 1235, 1114, 903, 716 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_4Na$: 231.0633 $[M+Na]^+$; found: 231.0630.



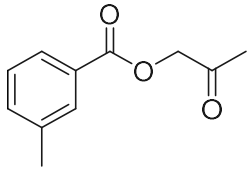
2-oxopropyl 2-chlorobenzoate (3ae): Yield: 86%, 91.2 mg, colorless oil; R_f 0.37 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98−7.91 (m, 1H), 7.50−7.40 (m, 2H), 7.36−7.29 (m, 1H), 4.88 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 164.7, 134.0, 133.1, 131.9, 131.2, 128.9, 126.7, 68.9, 26.2; IR (neat) 3060, 2931, 1727, 1271, 1119, 1084, 907, 714 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9ClO_3Na$: 235.0138 $[M+Na]^+$; found: 235.0143.



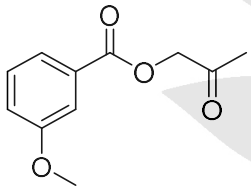
2-oxopropyl 2-bromobenzoate (3af): Yield: 87%, 111.6 mg, colorless oil; R_f 0.38 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.6, 1.8 Hz, 1H), 7.66 (dd, J = 7.8, 1.0 Hz, 1H), 7.40−7.31 (m, 2H), 4.88 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.2, 165.2, 134.5, 133.1, 131.8, 130.9, 127.3, 122.0, 69.0, 26.2; IR (neat) 3056, 2933, 1728, 1270, 1113, 1068, 907, 712 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9BrO_3Na$: 278.9633 $[M+Na]^+$; found: 278.9639.



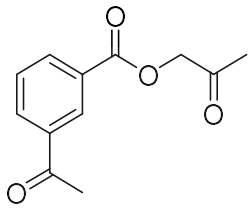
2-oxopropyl 2-nitrobenzoate (3ag): Yield: 92%, 102.9 mg, colorless oil; R_f 0.33 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.0, 1.0 Hz, 1H), 7.87 (dd, J = 7.6, 1.4 Hz, 1H), 7.73−7.65 (m, 2H), 4.90 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.7, 164.7, 148.0, 133.17, 132.21, 130.3, 126.7, 124.0, 69.5, 26.2; IR (neat) 3062, 2930, 1728, 1541, 1274, 1116, 910, 709 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9O_5Na$: 246.0378 $[M+Na]^+$; found: 246.0383.



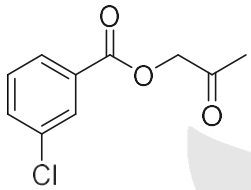
2-oxopropyl 3-methylbenzoate (3ah): Yield: 86%, 82.9 mg, colorless oil; R_f 0.46 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99−7.83 (m, 2H), 7.46-7.31 (m, 2H), 4.87 (s, 2H), 2.41 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.9, 166.0, 138.3, 134.2, 130.4, 129.1, 128.4, 127.0, 68.7, 26.2, 21.2; IR (neat) 3057, 2936, 1726, 1278, 1117, 906, 713 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_3Na$: 215.0684 $[M+Na]^+$; found: 215.0689.



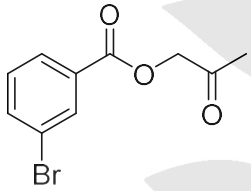
2-oxopropyl 3-methoxybenzoate (3ai): Yield: 88%, 91.6 mg, colorless oil; R_f 0.42 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72−7.65 (m, 1H), 7.59 (d, J = 1.4 Hz, 1H), 7.38−7.33 (m, 1H), 7.15−7.09 (m, 1H), 4.86 (s, 2H), 3.83 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.8, 165.7, 159.6, 130.5, 129.5, 122.2, 119.9, 114.3, 68.8, 55.4, 26.1; IR (neat) 3053, 2937, 1725, 1276, 1120, 907, 710 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_4Na$: 231.0633 $[M+Na]^+$; found: 231.0637.



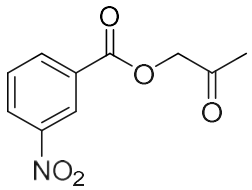
2-oxopropyl 3-acetylbenzoate (3aj): Yield: 87%, 95.5 mg, colorless oil; R_f 0.36 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, J = 3.0 Hz, 1H), 8.28-8.08 (m, 2H), 7.54−7.51 (m, 1H), 4.89 (s, 2H), 2.59 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 197.0, 165.0, 137.3, 134.1, 132.8, 129.8, 129.7, 129.0, 68.9, 26.6, 26.1; IR (neat) 3056, 2931, 1742, 1724, 1278, 1110, 909, 708 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{12}O_4Na$: 243.0633 $[M+Na]^+$; found: 243.0630.



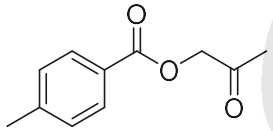
2-oxopropyl 3-chlorobenzoate (3ak): Yield: 88%, 93.1 mg, colorless oil; R_f 0.37 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (t, J = 1.7 Hz, 1H), 8.01−7.96 (m, 1H), 7.58−7.56 (m, 1H), 7.41 (t, J = 7.9 Hz, 1H), 4.90 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 164.7, 134.7, 133.5, 130.9, 129.9, 129.9, 128.0, 68.9, 26.1; IR (neat) 3060, 2935, 1728, 1279, 1082, 1117, 907, 712 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9ClO_3Na$: 235.0138 $[M+Na]^+$; found: 235.0131.



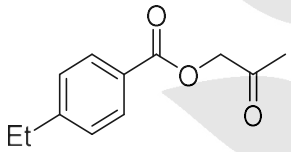
2-oxopropyl 3-bromobenzoate (3al): Yield: 85%, 109.3 mg, colorless oil; R_f 0.36 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (t, J = 1.7 Hz, 1H), 8.02−7.99 (m, 1H), 7.71−7.70 m, 1H), 7.34 (t, J = 7.9 Hz, 1H), 4.89 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 164.5, 136.4, 132.8, 131.1, 130.1, 128.5, 122.5, 68.9, 26.1; IR (neat) 3058, 2934, 1726, 1274, 1115, 1077, 907, 711 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9BrO_3Na$: 278.9633 $[M+Na]^+$; found: 278.9638.



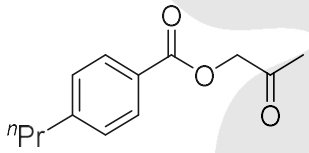
2-oxopropyl 3-nitrobenzoate (3am): Yield: >99%, 111.3 mg, white solid, m.p. 101−103 °C; R_f 0.37 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.45−8.39 (m, 2H), 7.69 (t, J = 8.0 Hz, 1H), 4.98 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.4, 163.8, 148.3, 135.5, 131.0, 129.8, 127.8, 124.8, 69.2, 26.1; IR (KBr) 3059, 2934, 1729, 1352, 1272, 1113, 906, 713 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9NO_5Na$: 246.0378 $[M+Na]^+$; found: 246.0388.



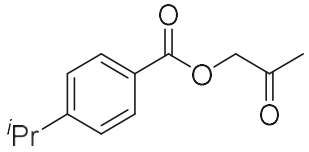
2-oxopropyl 4-methylbenzoate (3an): Yield: 90%, 85.9 mg, colorless oil; R_f 0.42 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.87 (s, 2H), 2.43 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 144.3, 129.9, 129.2, 126.4, 68.6, 26.2, 21.7; IR (neat) 3058, 2930, 1730, 1275, 1118, 907, 795, 710 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_3Na$: 215.0684 $[M+Na]^+$; found: 215.0697.



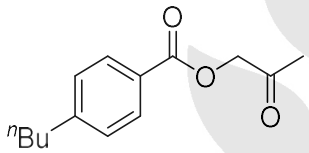
2-oxopropyl 4-ethylbenzoate (3ao): Yield: 92%, 94.5 mg, colorless oil; R_f 0.36 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.31−7.26 (m, 2H), 4.86 (s, 2H), 2.71 (q, J = 7.6 Hz, 2H), 2.22 (s, 3H), 1.26 (t, J = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 150.4, 130.0, 128.0, 126.7, 68.6, 29.0, 26.2, 15.2; IR (neat) 3059, 2937, 1730, 1276, 1113, 908, 709 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{14}O_3Na$: 229.0841 $[M+Na]^+$; found: 229.0828.



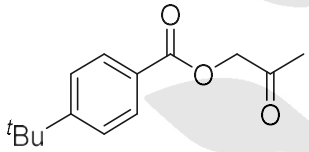
2-oxopropyl 4-propylbenzoate (3ap): Yield: 95%, 104.1 mg, colorless oil; R_f 0.41 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.86 (s, 2H), 2.65 (t, J = 7.6 Hz, 2H), 2.23 (d, J = 1.8 Hz, 3H), 1.70−1.63 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 148.9, 129.9, 128.6, 126.7, 68.6, 38.1, 26.2, 24.2, 13.7; IR (neat) 3062, 2939, 1725, 1271, 1115, 908, 712 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{16}O_3Na$: 243.0997 $[M+Na]^+$; found: 243.1011.



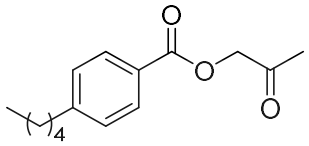
2-oxopropyl 4-isopropylbenzoate (3aq): Yield: 87%, 95.6 mg, colorless oil; R_f 0.41 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.87 (s, 2H), 3.00−2.96 (m, 1H), 2.23 (s, 3H), 1.28 (d, J = 7.0 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 155.0, 130.1, 126.8, 126.6, 68.6, 34.3, 26.2, 23.7; IR (neat) 3064, 2932, 1733, 1268, 1126, 916, 708 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{16}O_3Na$: 243.0997 $[M+Na]^+$; found: 243.1008.



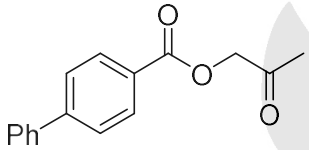
2-oxopropyl 4-butylbenzoate (3ar): Yield: 96%, 112.1 mg, colorless oil; R_f 0.41 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 4.85 (s, 2H), 2.69−2.64 (m, 2H), 2.22 (s, 3H), 1.64−1.58 (m, 2H), 1.39−1.32 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 149.1, 129.9, 128.6, 126.6, 68.6, 35.7, 33.2, 26.2, 22.3, 13.9; IR (neat) 3062, 2940, 1725, 1278, 1123, 917, 705 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{18}O_3Na$: 257.1154 $[M+Na]^+$; found: 257.1137.



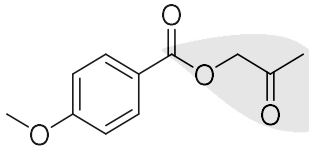
2-oxopropyl 4-(*tert*-butyl)benzoate (3as): Yield: 74%, 86.2 mg, colorless oil; R_f 0.38 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 4.87 (s, 2H), 2.23 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 157.2, 129.8, 126.4, 125.5, 68.6, 35.1, 31.1, 26.2; IR (neat) 3052, 2931, 1724, 1275, 1124, 923, 715 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{18}O_3Na$: 257.1154 $[M+Na]^+$; found: 257.1170.



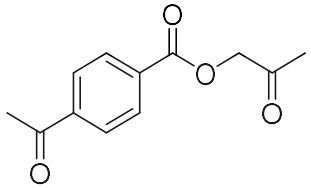
2-oxopropyl 4-pentylbenzoate (3at): Yield: 93%, 115.7 mg, colorless oil; R_f 0.41 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.86 (s, 2H), 2.67 (t, J = 7.7 Hz, 2H), 2.28−2.19 (m, 3H), 1.68−1.61 (m, 2H), 1.37−1.30 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 165.9, 149.2, 130.0, 128.6, 126.6, 68.6, 36.0, 31.4, 30.8, 26.2, 22.5, 14.0; IR (neat) 3057, 2932, 1728, 1276, 1120, 918, 712 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{20}O_3Na$: 271.1310 $[M+Na]^+$; found: 271.1327.



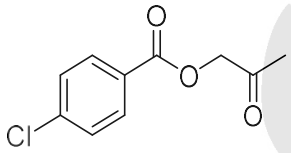
2-oxopropyl [1,1'-biphenyl]-4-carboxylate (3au): Yield: 82%, 103.7 mg, white solid, m.p. 56−58 °C; R_f 0.31 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21−8.18 (m, 2H), 7.73−7.70 (m, 2H), 7.66 (dd, J = 8.1, 1.0 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 4.93 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.9, 165.8, 146.2, 139.9, 130.5, 129.0, 128.3, 127.9, 127.3, 127.2, 68.8, 26.3; IR (KBr) 3060, 2941, 1728, 1269, 1108, 914, 707 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{14}O_3Na$: 277.0841 $[M+Na]^+$; found: 277.0832.



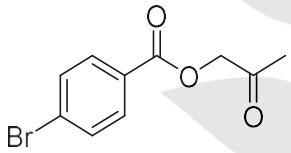
2-oxopropyl 4-methoxybenzoate (3av): Yield: >99%, 103.9 mg, colorless oil; R_f 0.42 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 4.85 (s, 2H), 3.88 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.3, 165.6, 163.8, 132.0, 121.5, 113.8, 68.6, 55.5, 26.2; IR (neat) 3059, 2931, 1732, 1276, 1110, 913, 707 cm^{-1}; HRMS (EI) Calcd for $C_{11}H_{12}O_4Na$: 231.0633 $[M+Na]^+$; found: 231.0621.



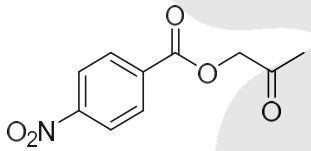
2-oxopropyl 4-acetylbenzoate (3aw): Yield: 83%, 91.2 mg, white solid, m.p. 81−83 °C; R_f 0.30 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 8.5 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H), 4.92 (s, 2H), 2.65 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.1, 197.5, 165.0, 140.6, 132.9, 130.1, 128.3, 68.9, 26.9, 26.2; IR (KBr) 3057, 2931, 1736, 1721, 1271, 1112, 913, 708 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{12}O_4Na$: 243.0633 $[M+Na]^+$; found: 243.0649.



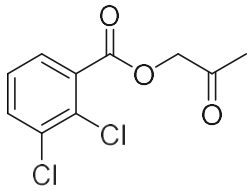
2-oxopropyl 4-chlorobenzoate (3ax): Yield: 95% (24 h), 100.5 mg, colorless oil; R_f 0.40 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 4.88 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 165.0, 139.9, 131.3, 128.9, 127.7, 68.8, 26.1; IR (neat) 3057, 2938, 1728, 1274, 1115, 1082, 910, 712 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{17}ClO_3Na$: 235.0138 $[M+Na]^+$; found: 235.0145.



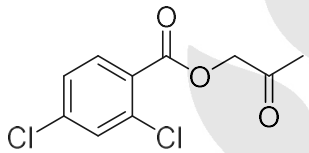
2-oxopropyl 4-bromobenzoate (3ay): Yield: 97%, 124.9 mg, colorless oil; R_f 0.31 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99−7.92 (m, 2H), 7.65−7.58 (m, 2H), 4.89 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 165.1, 131.9, 131.4, 128.7, 128.1, 68.8, 26.2; IR (neat) 3056, 2937, 1728, 1272, 1111, 1073, 910, 716 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9BrO_3Na$: 278.9633 $[M+Na]^+$; found: 278.9626.



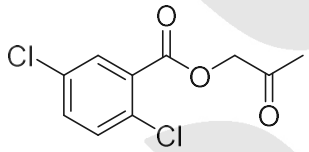
2-oxopropyl 4-nitrobenzoate (3az): Yield: 91%, 101.6 mg, white solid, m.p. 87−89 °C; R_f 0.43 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32−8.26 (m, 4H), 4.97 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.3, 164.0, 150.8, 134.6, 131.1, 123.6, 69.2, 26.1; IR (KBr) 3062, 2937, 1721, 1361, 1270, 1107, 912, 709 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_9NO_5Na$: 246.0378 $[M+Na]^+$; found: 246.0360.



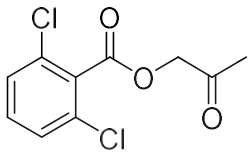
2-oxopropyl 2,3-dichlorobenzoate (3ba): Yield: 88%, 109.0 mg, colorless oil; R_f 0.33 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.8, 1.5 Hz, 1H), 7.62 (dd, J = 8.0, 1.5 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H), 4.91 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 164.4, 134.7, 133.6, 131.9, 131.7, 129.6, 127.3, 69.1, 26.2; IR (neat) 3064, 2931, 1727, 1273, 1107, 1088, 917, 713 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9761.



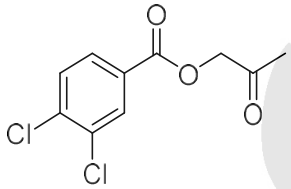
2-oxopropyl 2,4-dichlorobenzoate (3bb): Yield: 90%, 111.4 mg, colorless oil; R_f 0.32 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.4, 1.5 Hz, 1H), 7.52−7.46 (m, 1H), 7.34−7.32 (m, 1H), 4.90 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 163.8, 138.9, 135.3, 133.0, 131.1, 127.2, 127.1, 69.0, 26.2; IR (neat) 3065, 2940, 1733, 1279, 1122, 1087, 915, 712 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9765.



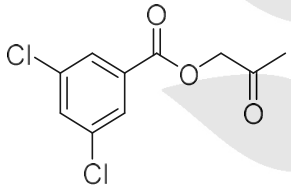
2-oxopropyl 2,5-dichlorobenzoate (3bc): Yield: 89%, 109.3 mg, colorless oil; R_f 0.37 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 1.4 Hz, 1H), 7.45−7.40 (m, 2H), 4.91 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.6, 163.5, 133.1, 132.7, 132.5, 132.4, 131.7, 130.1, 69.1, 26.2; IR (neat) 3064, 2936, 1730, 1275, 1116, 1089, 910, 713 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9732.



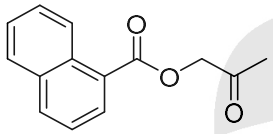
2-oxopropyl 2,6-dichlorobenzoate (3bd): Yield: 85%, 104.3 mg, colorless oil; R_f 0.36 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.30 (m, 3H), 4.90 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 164.1, 132.5, 132.1, 131.4, 128.0, 69.5, 26.6; IR (neat) 3061, 2937, 1731, 1274, 1115, 1087, 912, 711 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9735.



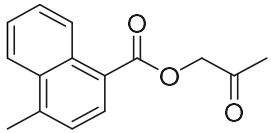
2-oxopropyl 3,4-dichlorobenzoate (3be): Yield: 93%, 115.1 mg, white solid, m.p. 59−61 °C; R_f 0.38 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 1.9 Hz, 1H), 7.91 (dd, J = 8.4, 2.0 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 4.91 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 164.0, 138.1, 133.1, 131.8, 130.7, 129.0, 128.9, 69.0, 26.1; IR (KBr) 3057, 2939, 1730, 1275, 1114, 1081, 912, 710 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9730.



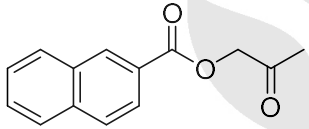
2-oxopropyl 3,5-dichlorobenzoate (3bf): Yield: 83%, 102.2 mg, white solid, m.p. 63−65 °C; R_f 0.45 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.59 (s, 1H), 4.92 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.5, 163.6, 135.4, 133.3, 132.0, 128.3, 69.1, 26.1; IR (KBr) IR (neat) 3056, 2937, 1728, 1272, 1113, 1082, 907, 710 cm^{-1}; HRMS (EI) Calcd for $C_{10}H_8Cl_2O_3Na$: 268.9748 $[M+Na]^+$; found: 268.9762.



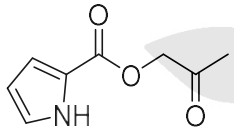
2-oxopropyl 1-naphthoate (3bg): Yield: 76%, 86.3 mg, colorless oil; R_f 0.36 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.98 (d, J = 8.7 Hz, 1H), 8.32 (dd, J = 7.3, 1.2 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.65−7.64 (m, 1H), 7.57−7.51 (m, 2H), 4.97 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.8, 166.7, 133.9, 133.8, 130.7, 128.6, 128.0, 126.4, 126.1, 125.8, 124.6, 68.8, 26.2; IR (neat) 3057, 2935, 1728, 1272, 1108, 906, 708 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{12}O_3Na$: 251.0684 $[M+Na]^+$; found: 251.0671.



2-oxopropyl 4-methyl-1-naphthoate (3bh): Yield: 56%, 67.3 mg, colorless oil; R_f 0.38 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.02 (d, J = 8.5 Hz, 1H), 8.24 (d, J = 7.4 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H), 7.64−7.59 (m, 2H), 7.39 (d, J = 7.4 Hz, 1H), 4.97 (s, 2H), 2.77 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.1, 166.7, 141.1, 132.9, 131.5, 130.6, 127.6, 126.3, 126.2, 125.6, 124.5, 124.3, 68.7, 26.3, 20.2; IR (neat) 3057, 2934, 1731, 1278, 1109, 909, 713 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_{14}O_3Na$: 265.0841 $[M+Na]^+$; found: 265.0828.

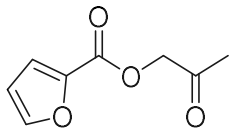


2-oxopropyl 2-naphthoate (3bi): Yield: 83%, 94.8 mg, colorless oil; R_f 0.34 (5:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.11 (dd, J = 8.6, 1.6 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.93−7.88 (m, 2H), 7.65−7.54 (m, 2H), 4.96 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.9, 166.0, 135.8, 132.5, 131.6, 129.5, 128.6, 128.4, 127.8, 126.8, 126.4, 125.3, 68.9, 26.3; IR (neat) 3060, 2934, 1734, 1275, 1109, 914, 708 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{12}O_3Na$: 251.0684 $[M+Na]^+$; found: 251.0695.

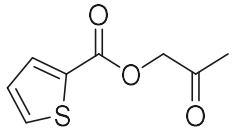


2-oxopropyl 1*H*-pyrrole-2-carboxylate (3bj): Yield: 61%, 50.7 mg, colorless oil; R_f 0.40 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.11-6.98 (m, 2H), 6.30 (d, J = 1.2 Hz, 1H), 4.83 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.5, 160.3, 124.0, 121.5, 116.5, 110.7, 68.2, 26.2; IR (neat) 2974, 2937, 1713,

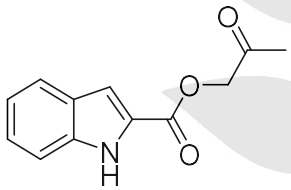
1605, 1466, 1374, 1273, 1151, 1087, 1055, 979, 852, 756, 736 cm^{-1}; HRMS (EI) Calcd for $C_8H_9NO_3Na$: 190.0480 $[M+Na]^+$; found: 190.0463.



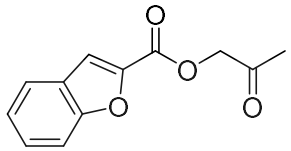
2-oxopropyl furan-2-carboxylate (3bk): Yield: 77%, 64.7 mg, colorless oil; R_f 0.71 (2:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.65−7.58 (m, 1H), 7.29−7.25 (m, 1H), 6.56−6.51 (m, 1H), 4.85 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 157.7, 146.9, 143.7, 119.1, 112.1, 68.3, 26.1; IR (neat) 3058, 2935, 1729, 1273, 1114, 908, 711 cm^{-1}; HRMS (EI) Calcd for $C_8H_8O_4Na$: 191.0320 $[M+Na]^+$; found: 191.0333.



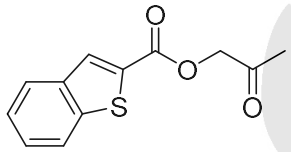
2-oxopropyl thiophene-2-carboxylate (3bl): Yield: 93%, 85.5 mg, colorless oil; R_f 0.76 (2:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, J = 3.8, 1.2 Hz, 1H), 7.62 (dd, J = 5.0, 1.2 Hz, 1H), 7.13 (dd, J = 4.9, 3.8 Hz, 1H), 4.84 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.7, 161.4, 134.4, 133.3, 132.4, 128.0, 68.7, 26.2; IR (neat) 3050, 2941, 1727, 1278, 1123, 916, 718 cm^{-1}; HRMS (EI) Calcd for $C_8H_8O_3SNa$: 207.0092 $[M+Na]^+$; found: 207.0109.



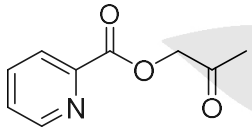
2-oxopropyl 1H-indole-2-carboxylate (3bm): Yield: 69%, 75.2 mg, white solid, m.p. 107−109 °C; R_f 0.32 (2:1 *n*-hexane/EtOAc). ^1H NMR (600 MHz, DMSO) δ 11.98 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 1.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 5.04 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (151 MHz, DMSO) δ 202.3, 161.0, 138.0, 127.2, 126.9, 125.4, 122.6, 120.8, 113.1, 108.9, 69.0, 26.4; IR (KBr) 2980, 2934, 1715, 1611, 1452, 1380, 1295, 1279, 1058, 975, 735 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{11}NO_3Na$: 240.0637 $[M+Na]^+$; found: 240.0625.



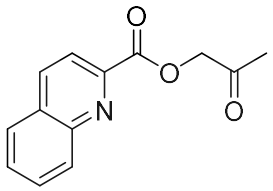
2-oxopropyl benzofuran-2-carboxylate (3bn): Yield: 67%, 73.4 mg, light yellow oil; R_f 0.46 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 7.9 Hz, 1H), 7.65 (s, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.50−7.46 (m, 1H), 7.33 (t, J = 7.5 Hz, 1H), 4.95 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.9, 158.7, 156.0, 144.5, 128.1, 126.8, 124.0, 123.0, 115.1, 112.4, 68.7, 26.1; IR (neat) 3048, 2924, 1725, 1270, 1118, 921, 709 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{10}O_4Na$: 241.0477 $[M+Na]^+$; found: 241.0470.



2-oxopropyl benzo[*b*]thiophene-2-carboxylate (3bo): Yield: 93%, 109.2 mg, white solid, m.p. 76−78 °C; R_f 0.47 (2:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.90 (dd, J = 11.2, 8.2 Hz, 2H), 7.51−7.42 (m, 2H), 4.91 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 162.0, 142.5, 138.6, 132.2, 131.6, 127.3, 125.7, 125.1, 122.8, 69.0, 26.2; IR (KBr) 2978, 2931, 1740, 1718, 1604, 1465, 1372, 1298, 1273, 1155, 1090, 908, 737 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{10}O_3SNa$: 257.0248 $[M+Na]^+$; found: 257.0235.



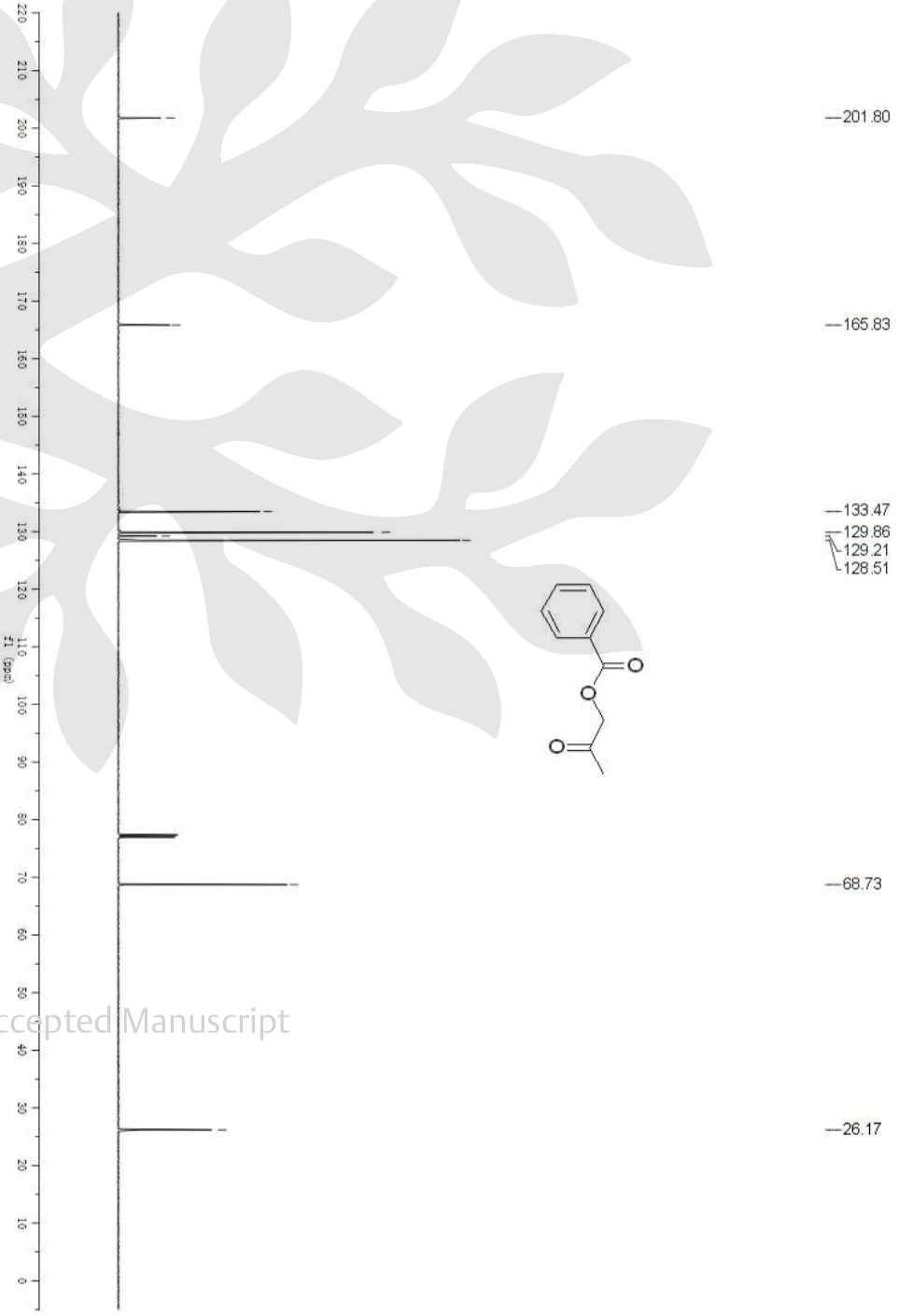
2-oxopropyl picolinate (3bp): Yield: 66%, 58.8 mg, colorless oil; R_f 0.26 (1:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83−8.75 (m, 1H), 8.18 (d, J = 7.8 Hz, 1H), 7.89−7.86 (m, 1H), 7.58−7.47 (m, 1H), 4.98 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 164.4, 150.0, 147.1, 137.2, 127.4, 125.6, 69.3, 26.1; IR (neat) 3064, 2930, 1735, 1278, 1120, 980, 720 cm^{-1}; HRMS (EI) Calcd for $C_9H_9NO_3Na$: 202.0480 $[M+Na]^+$; found: 202.0457.



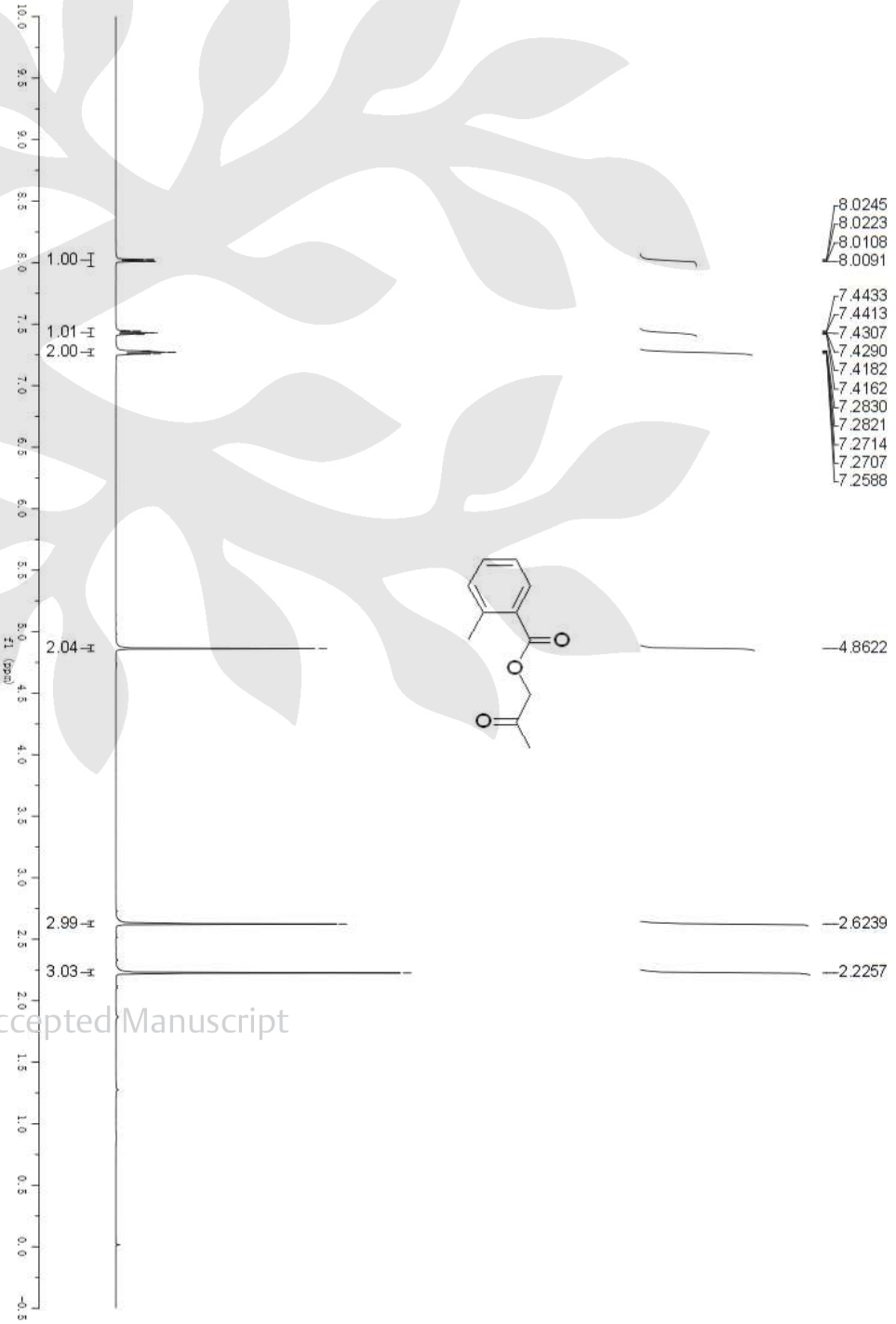
2-oxopropyl quinoline-2-carboxylate (3bq): Yield: 80%, 91.9 mg, colorless oil; R_f 0.37 (1:1 *n*-hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (dd, J = 8.4, 3.7 Hz, 2H), 8.23 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.85−7.77 (m, 1H), 7.67 (dd, J = 11.1, 3.9 Hz, 1H), 5.06 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.9, 164.7, 147.6, 147.1, 137.4, 130.8, 130.4, 129.5, 128.9, 127.6, 121.3, 69.5, 26.1; IR (neat) 3061, 2938, 1735, 1276, 1124, 978, 721 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{11}NO_3Na$: 252.0637 $[M+Na]^+$; found: 252.0656.

3. Copy of NMR for the 2-Oxopropyl Carboxylates

^{1}H NMR of 3aa

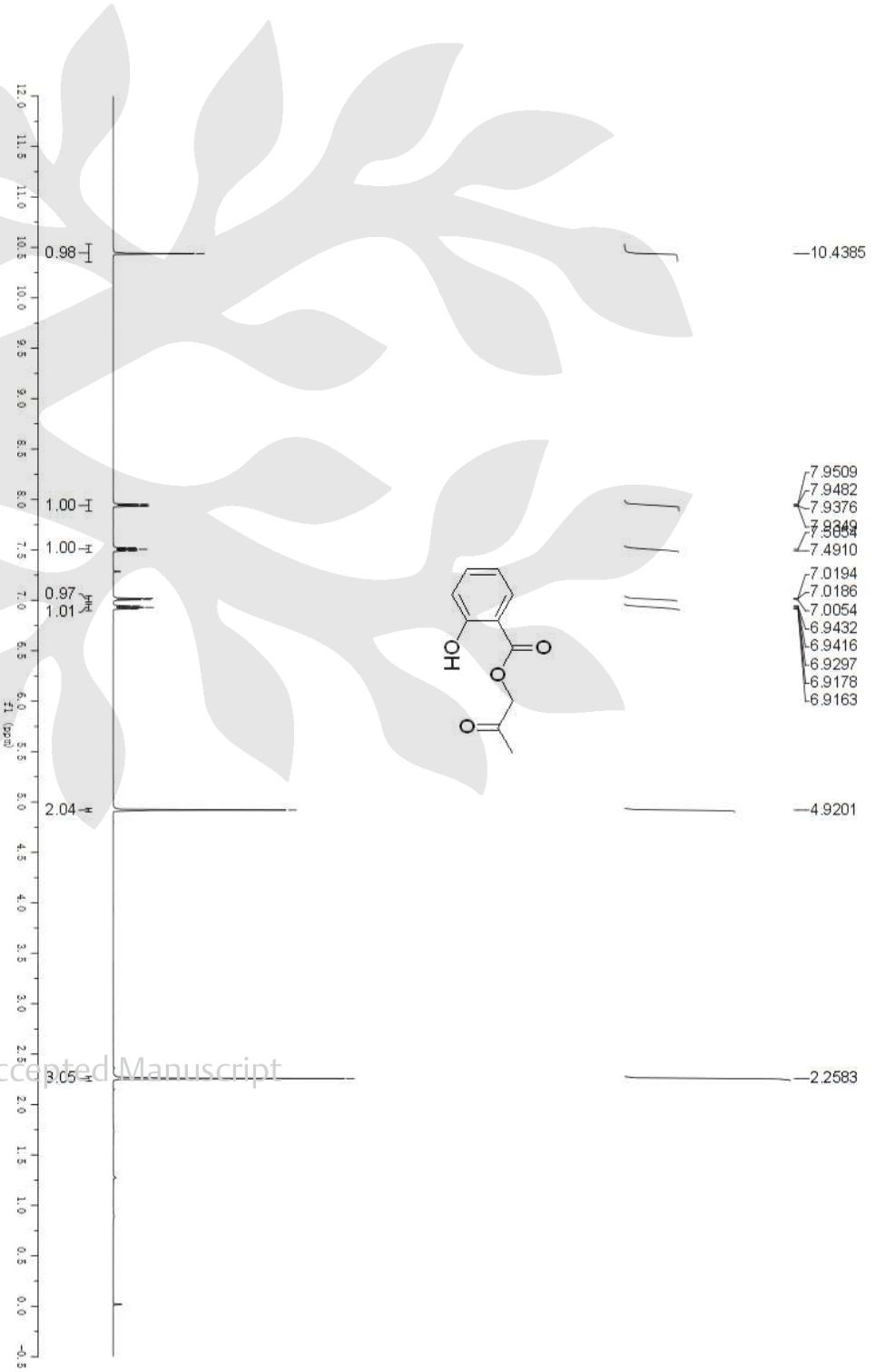


^{13}C NMR of 3aa



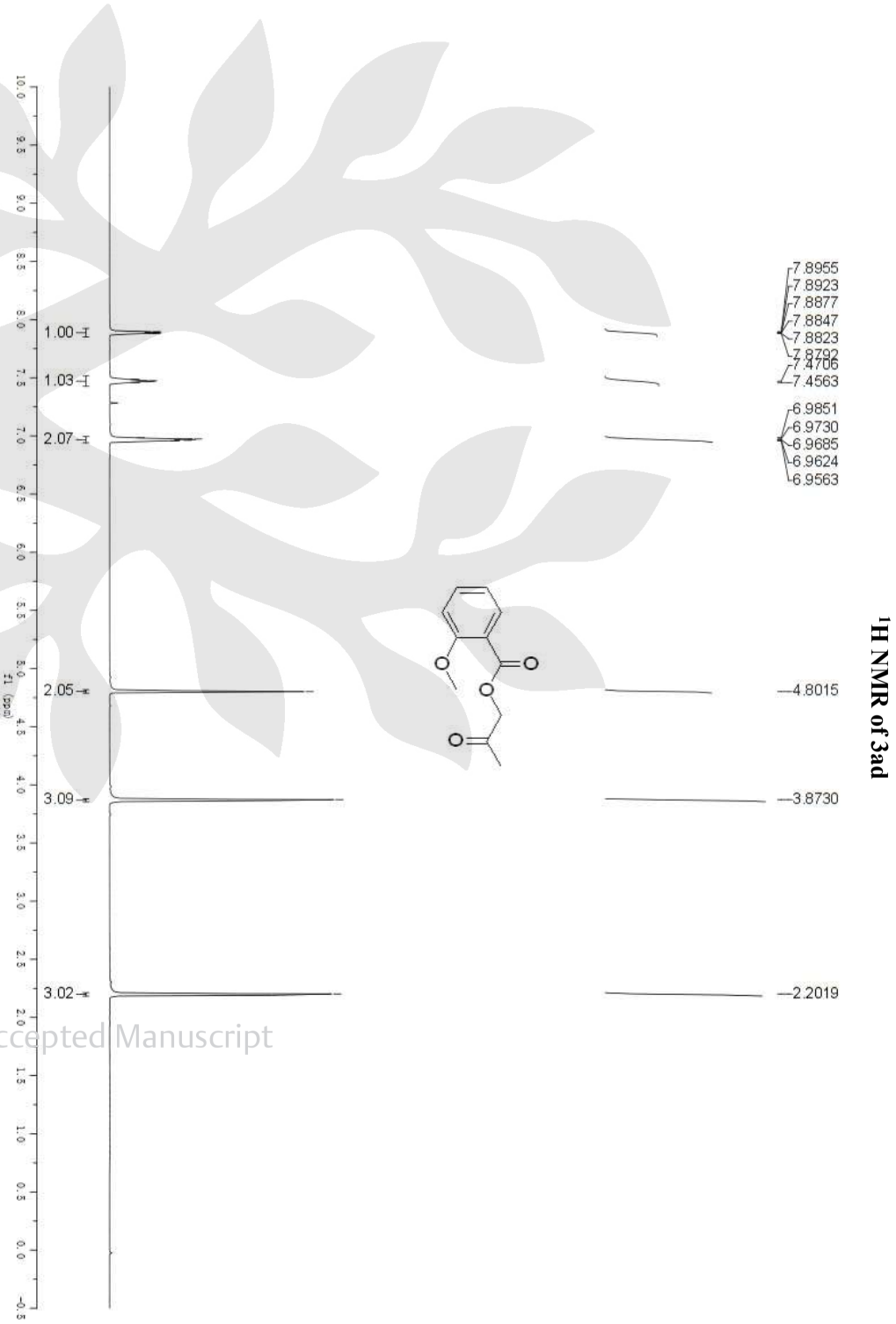
^{1}H NMR of 3ab

^{13}C NMR of 3ab

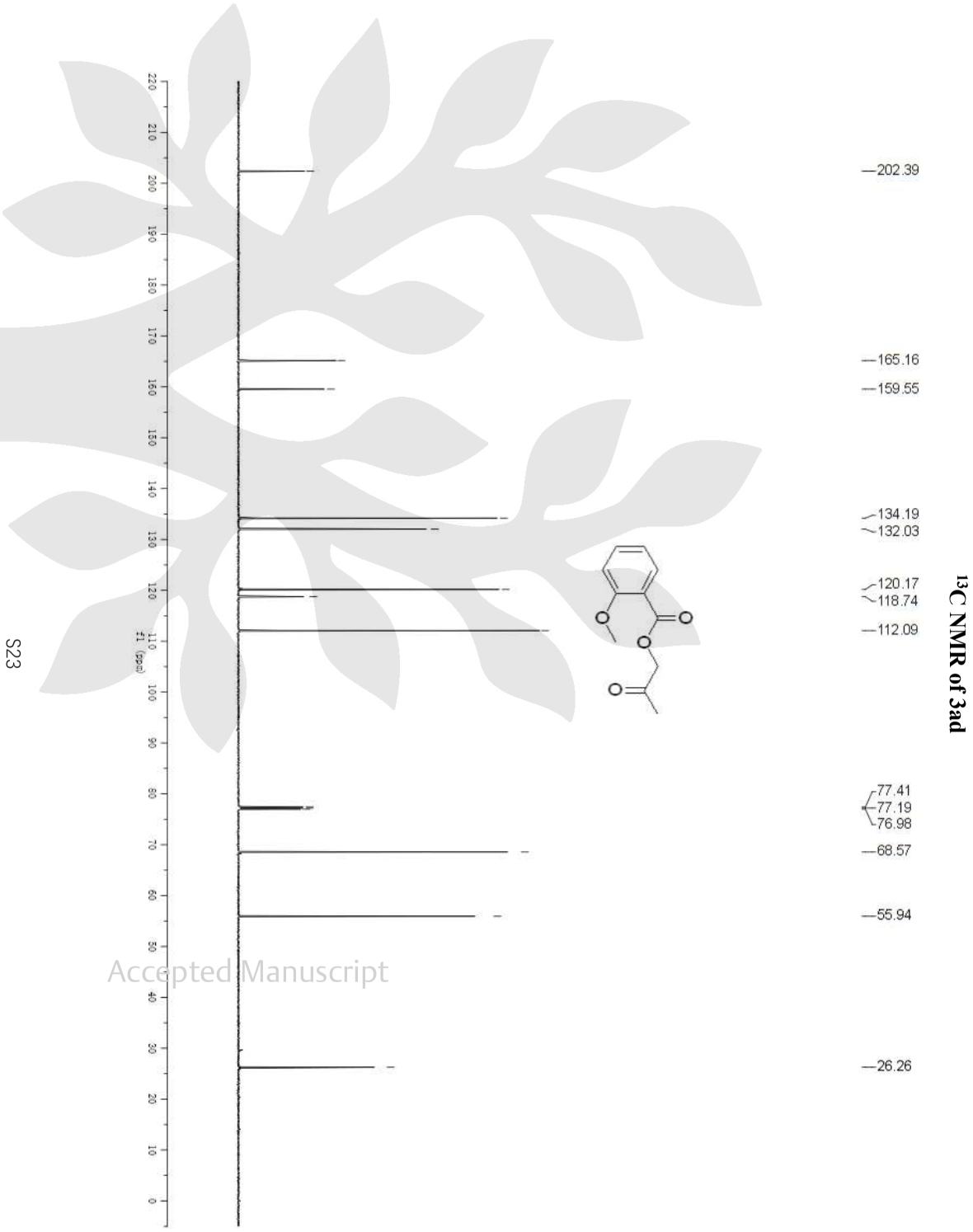


^{1}H NMR of 3ac

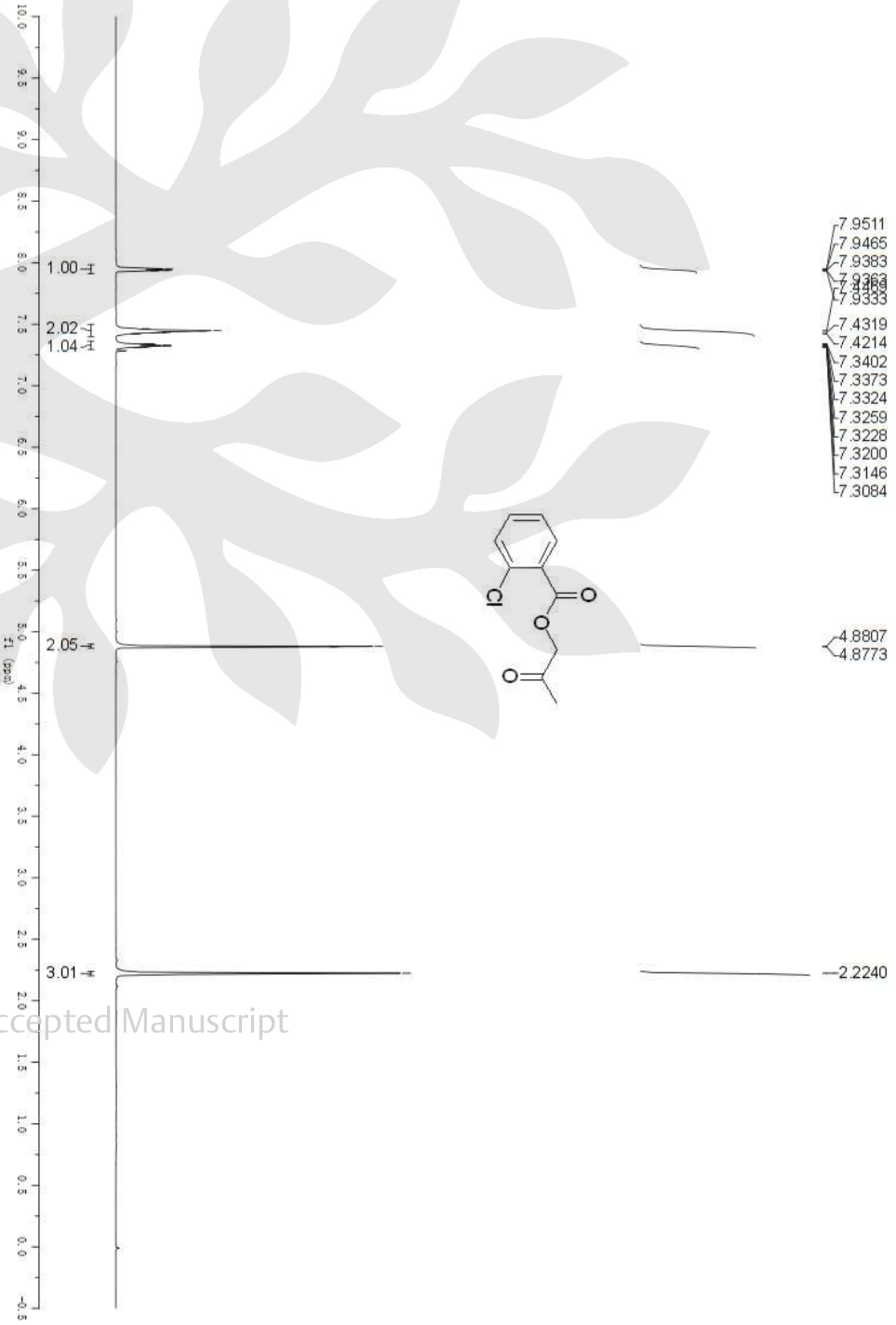
^{13}C NMR of 3ac



^{1}H NMR of 3ad

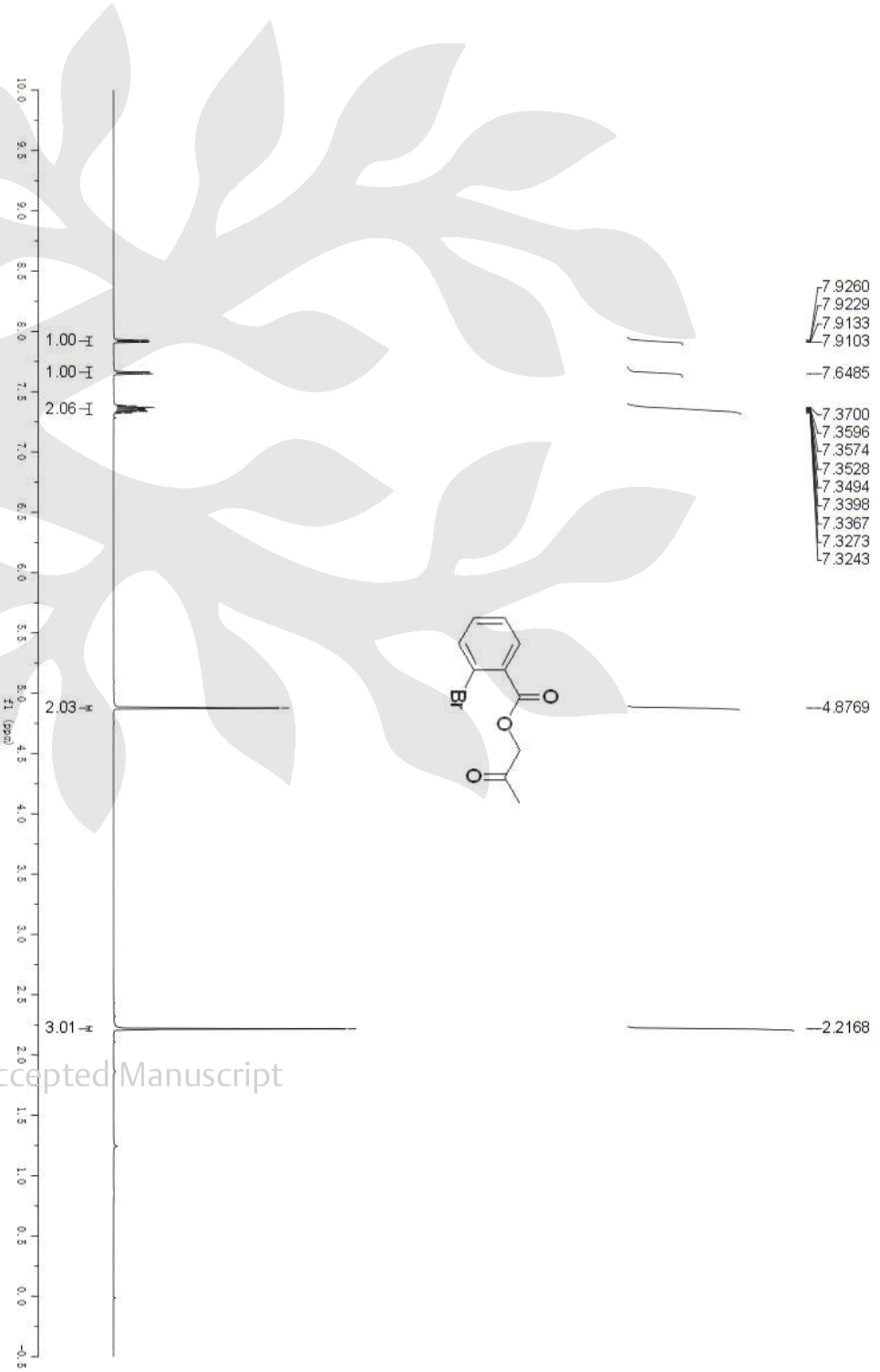


^{13}C NMR of 3ad



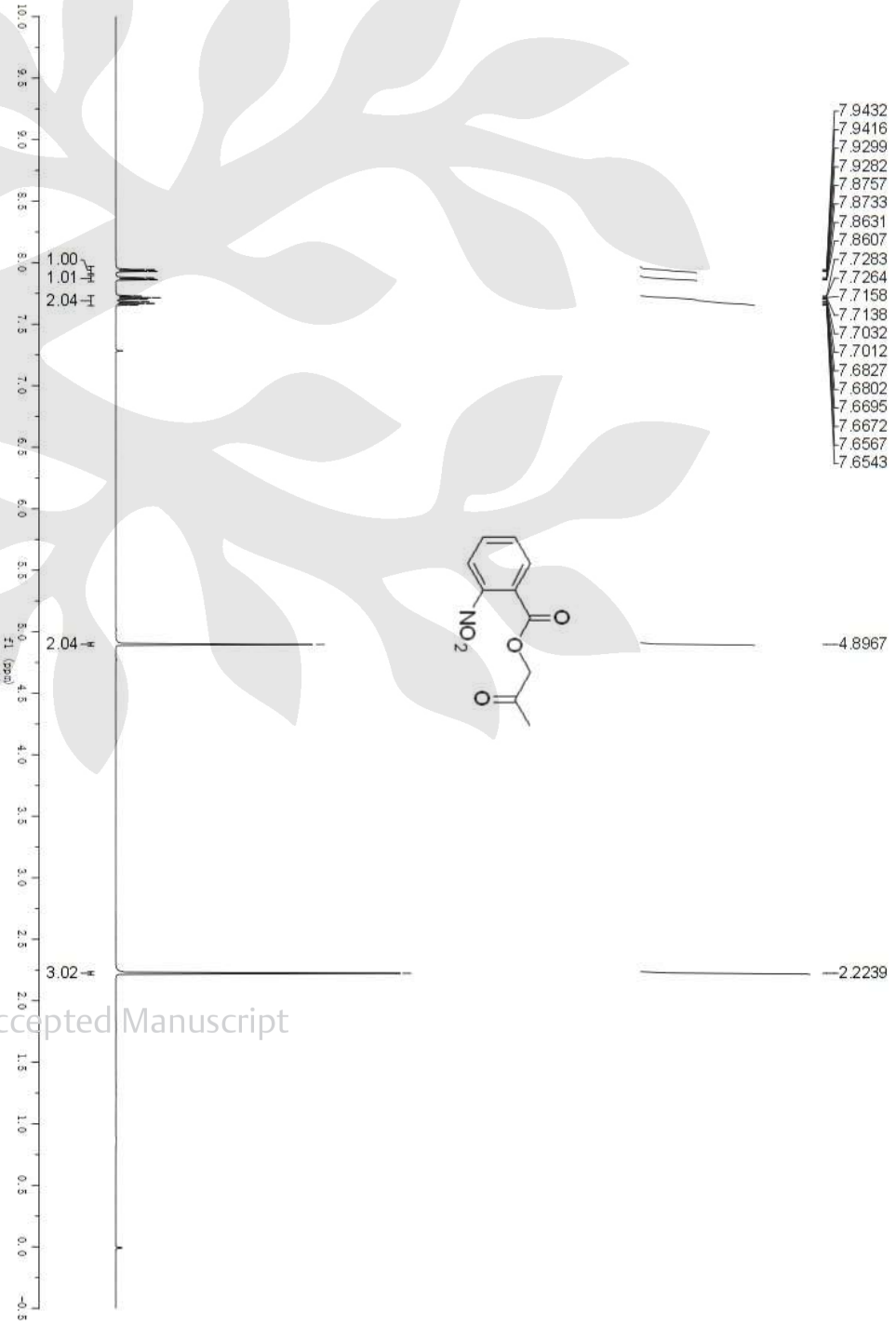
^{1}H NMR of 3ae

^{13}C NMR of 3ae

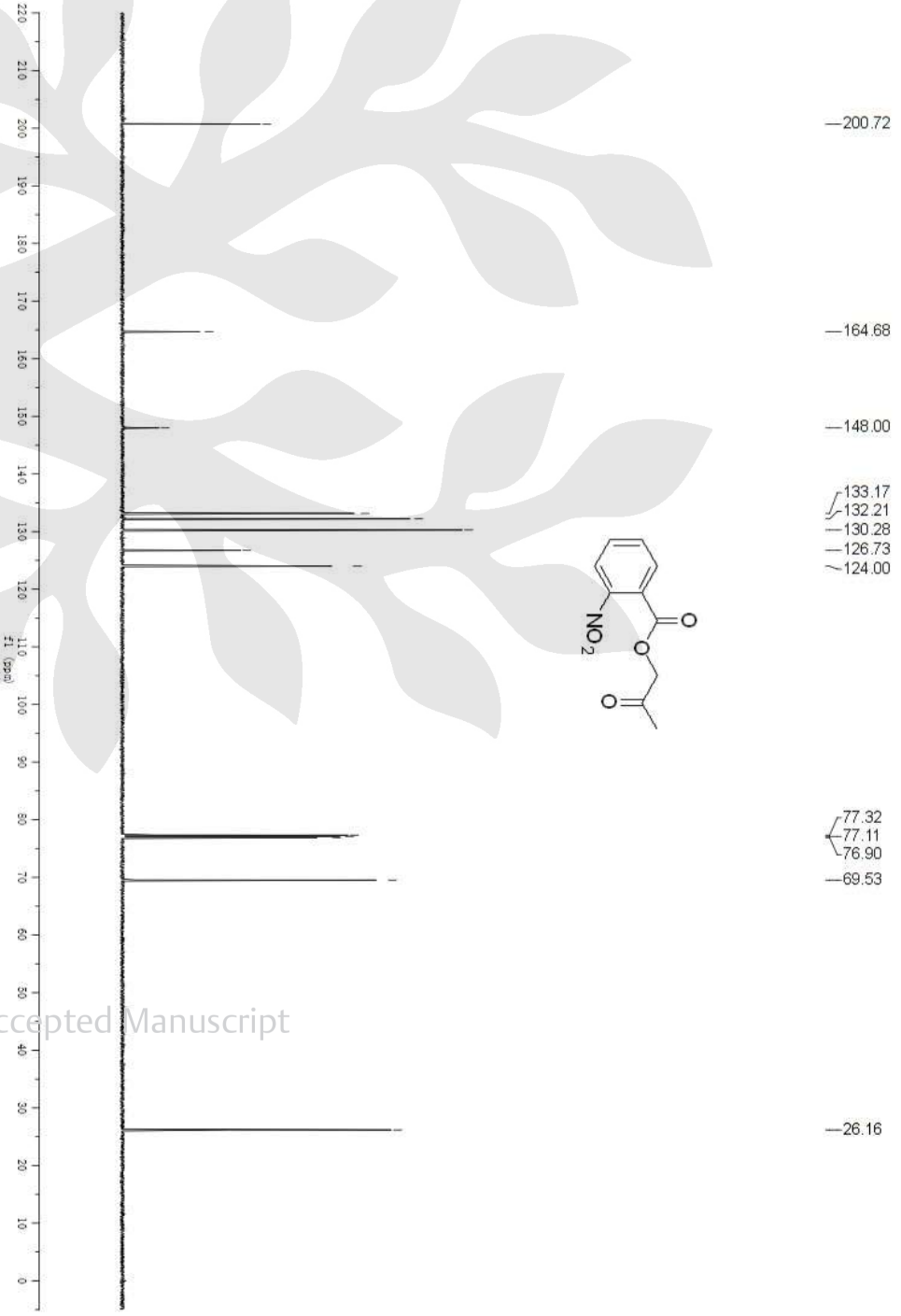


^{1}H NMR of 3af

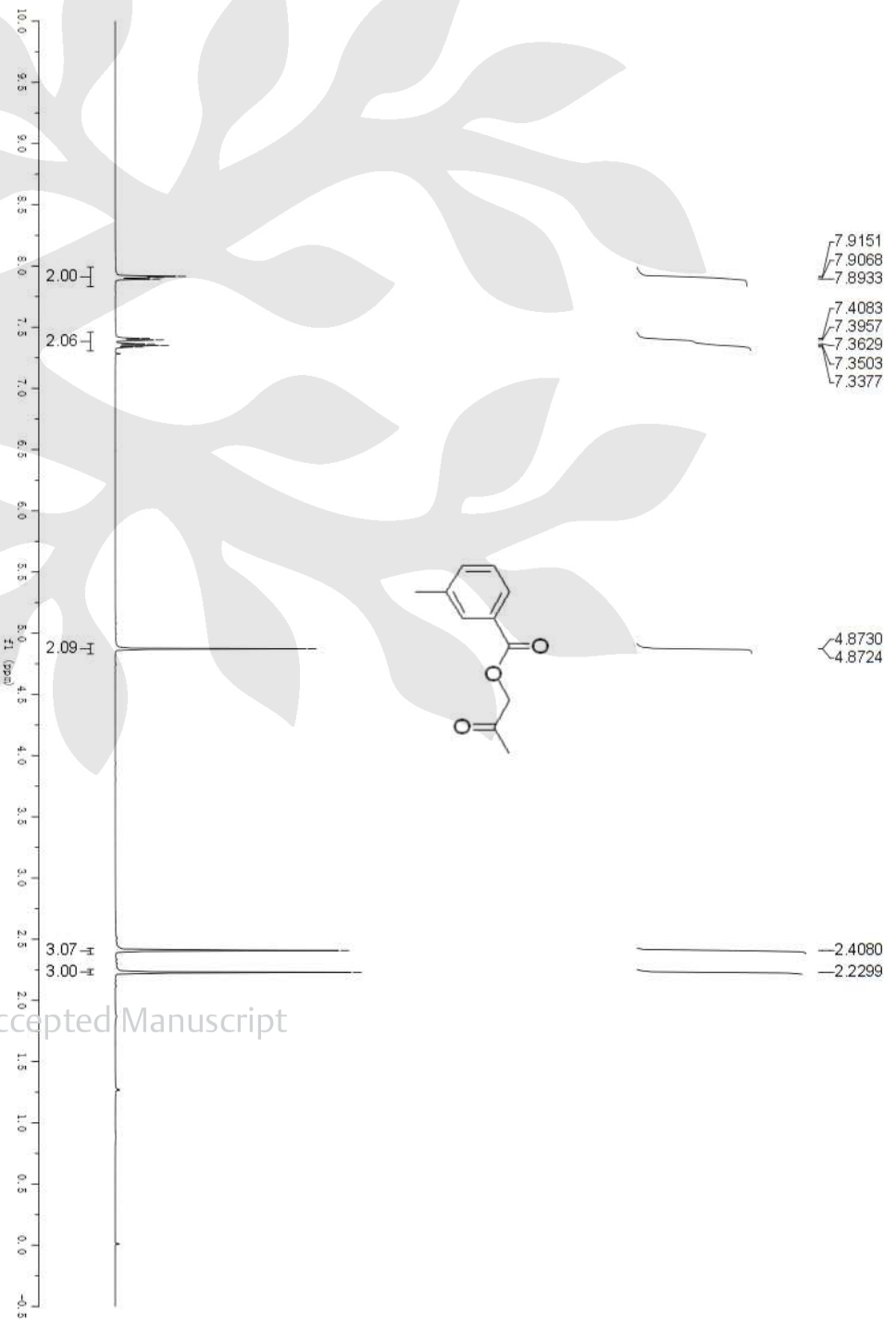
^{13}C NMR of 3af



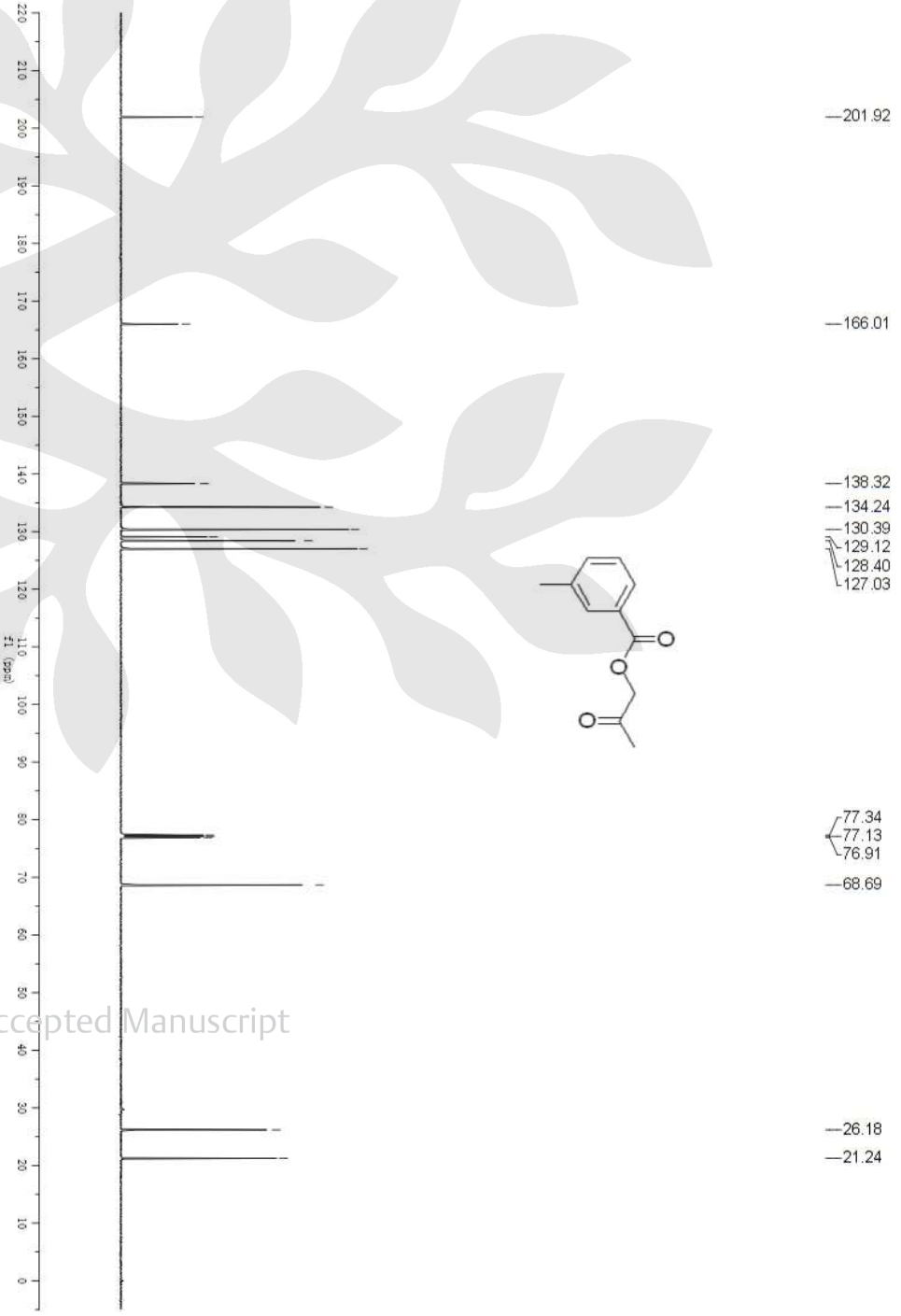
^{1}H NMR of 3ag



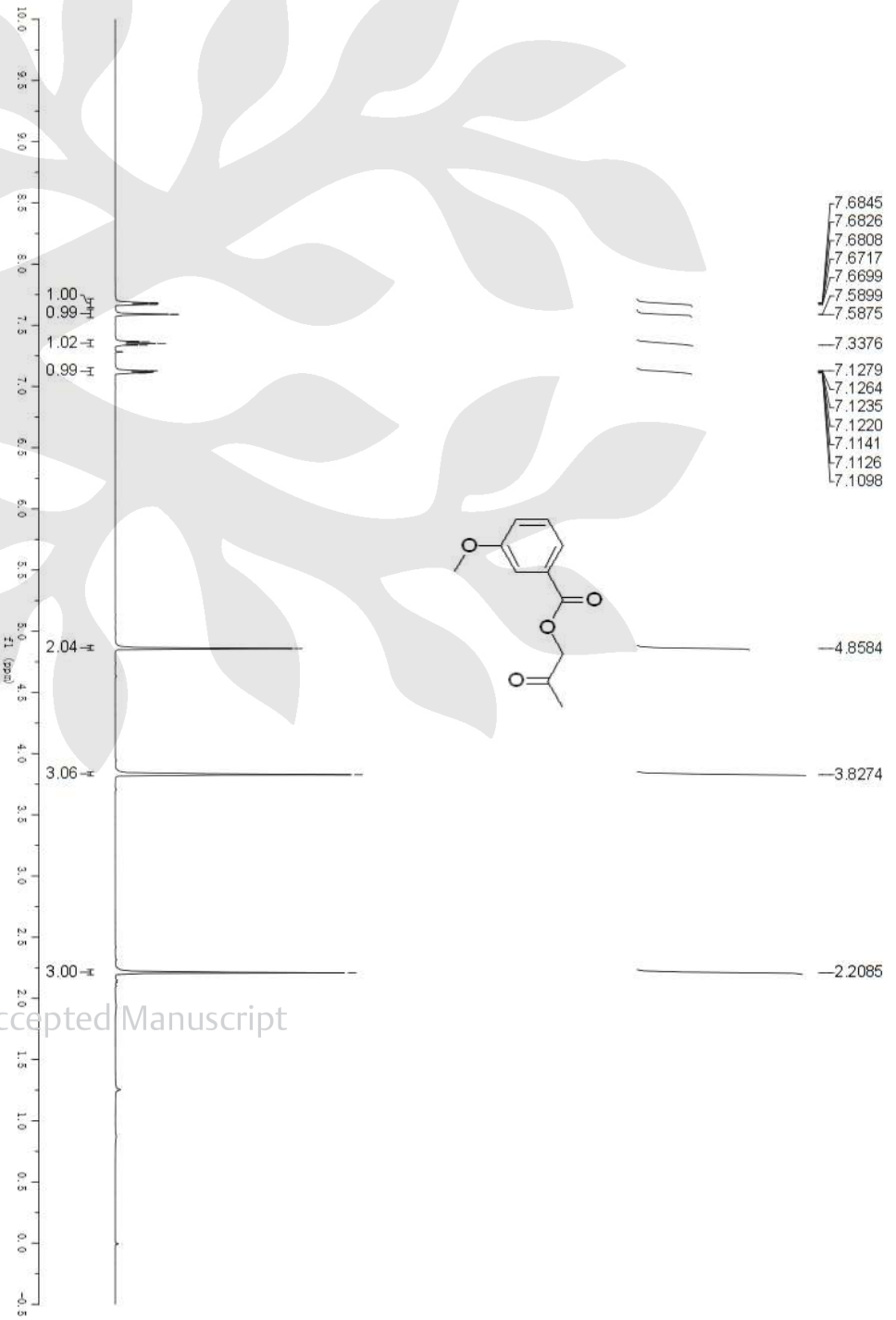
^{13}C NMR of 3ag



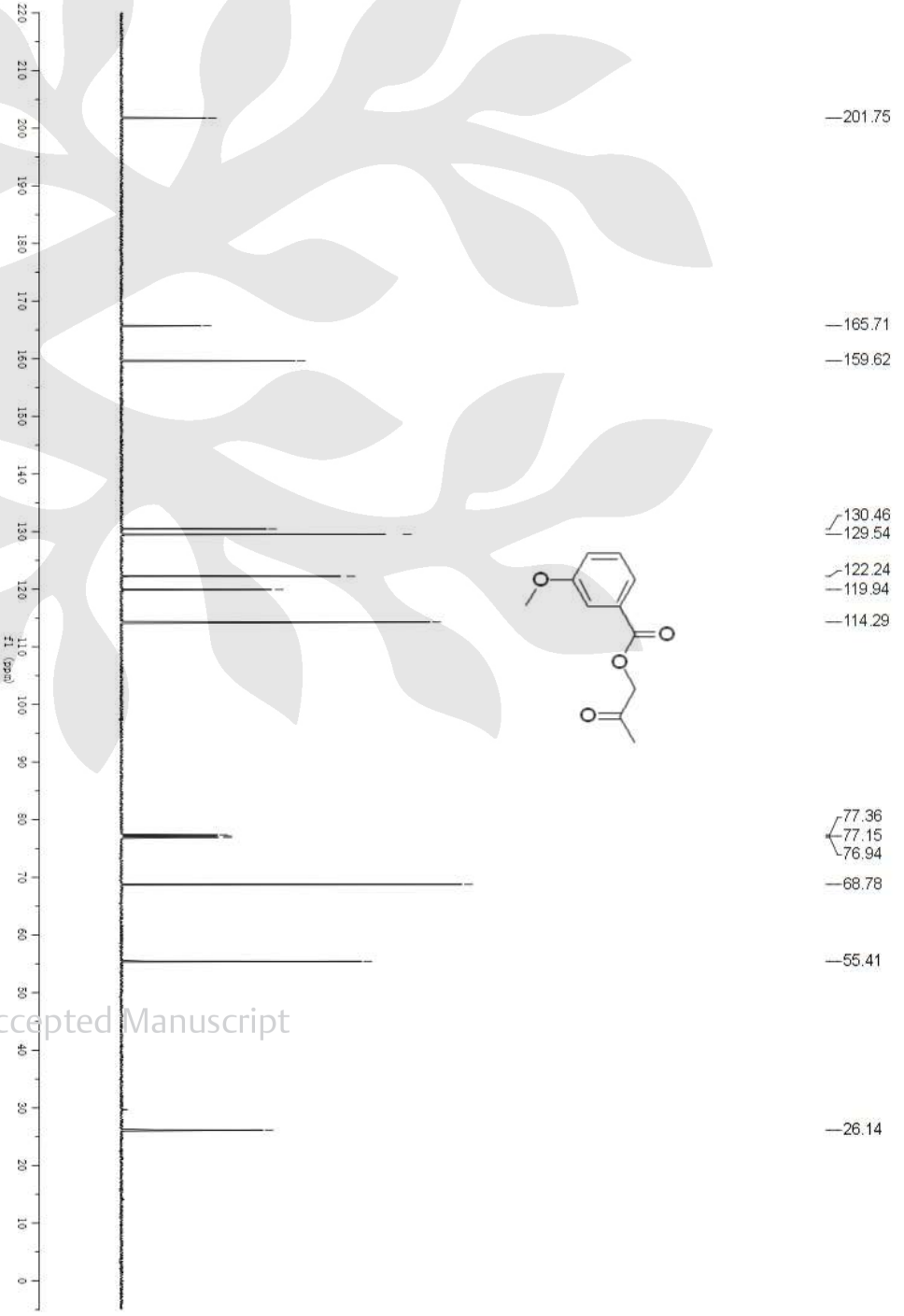
^{1}H NMR of 3ah



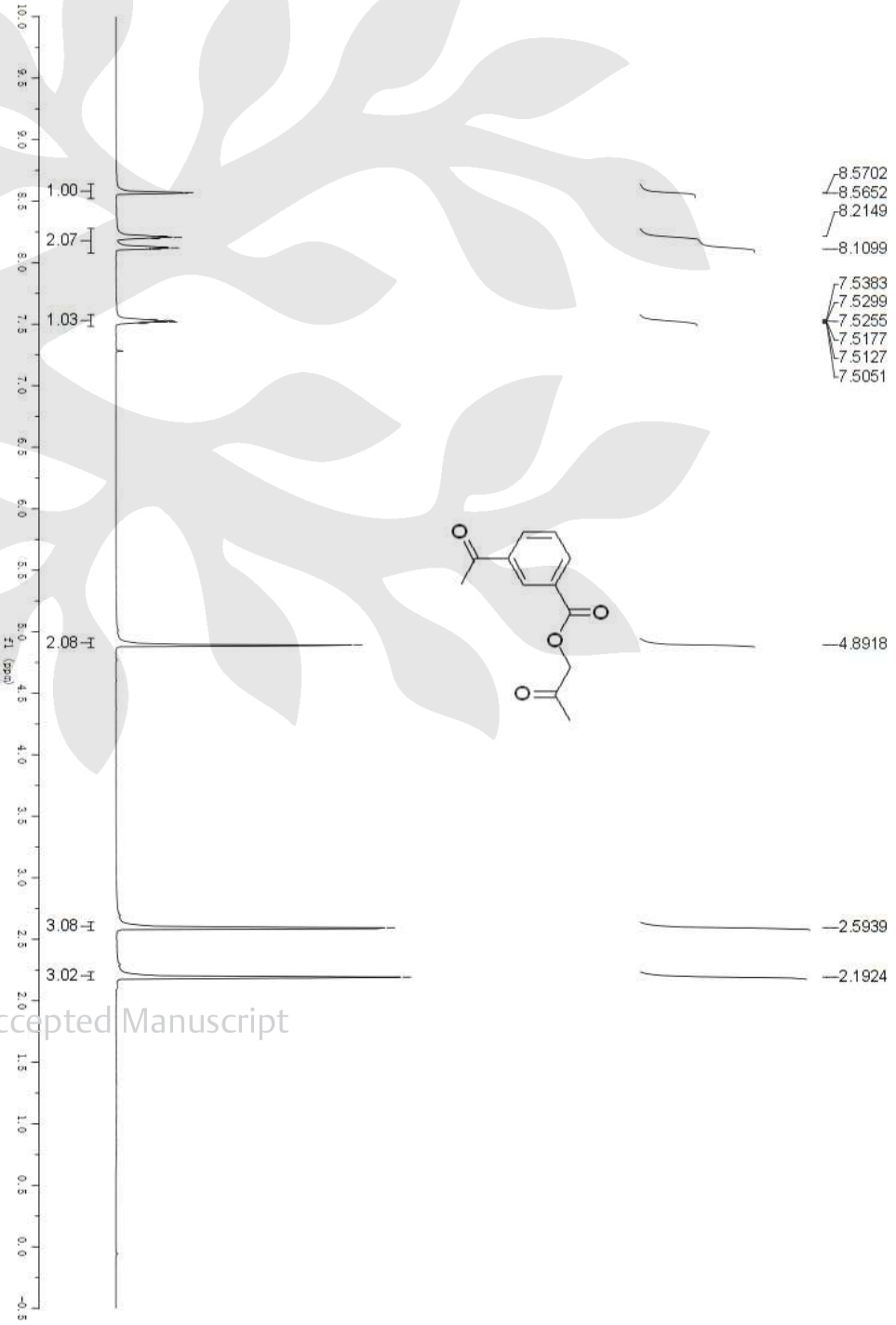
^{13}C NMR of 3ah



^{1}H NMR of 3ai

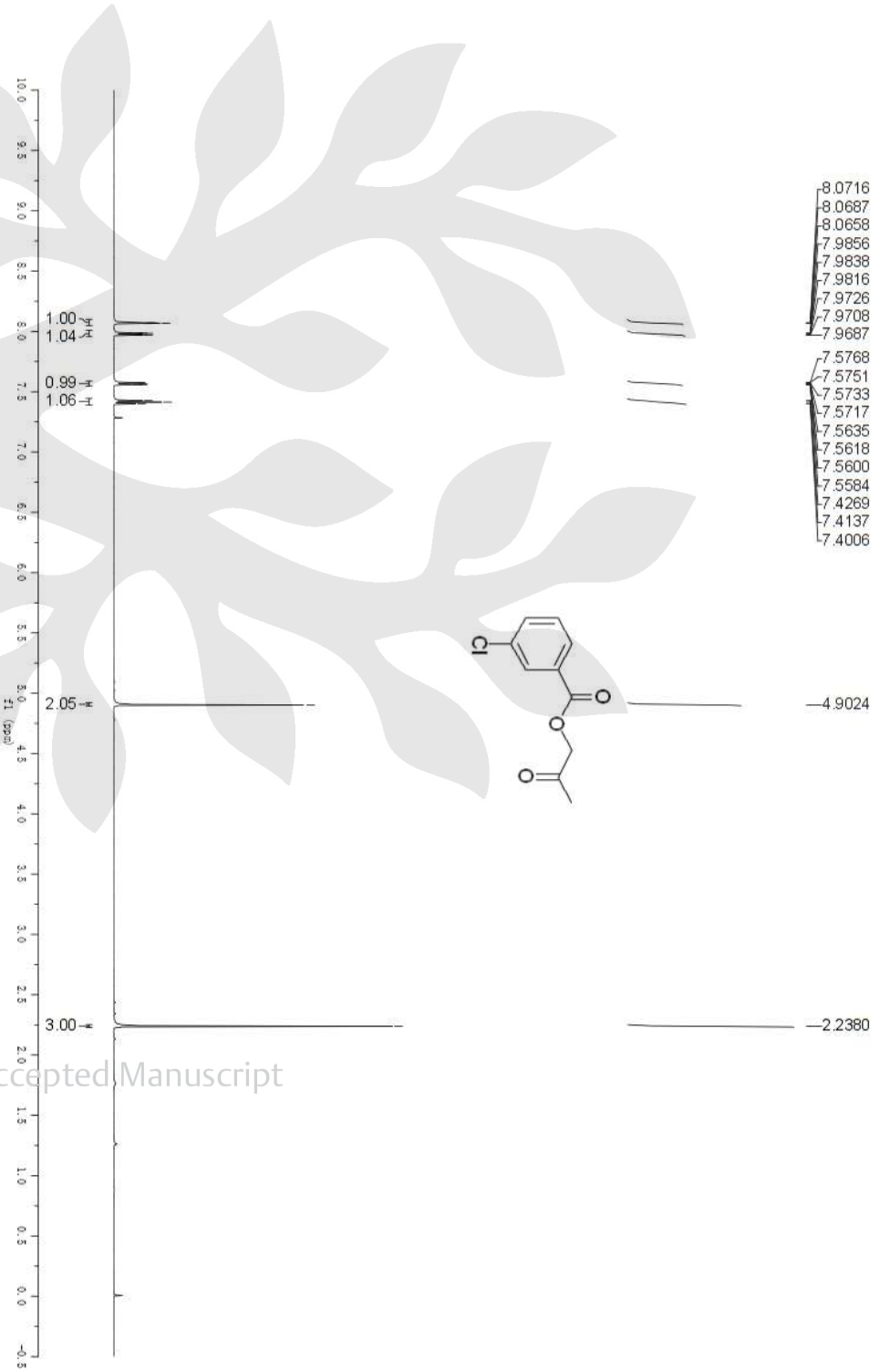


^{13}C NMR of 3ai



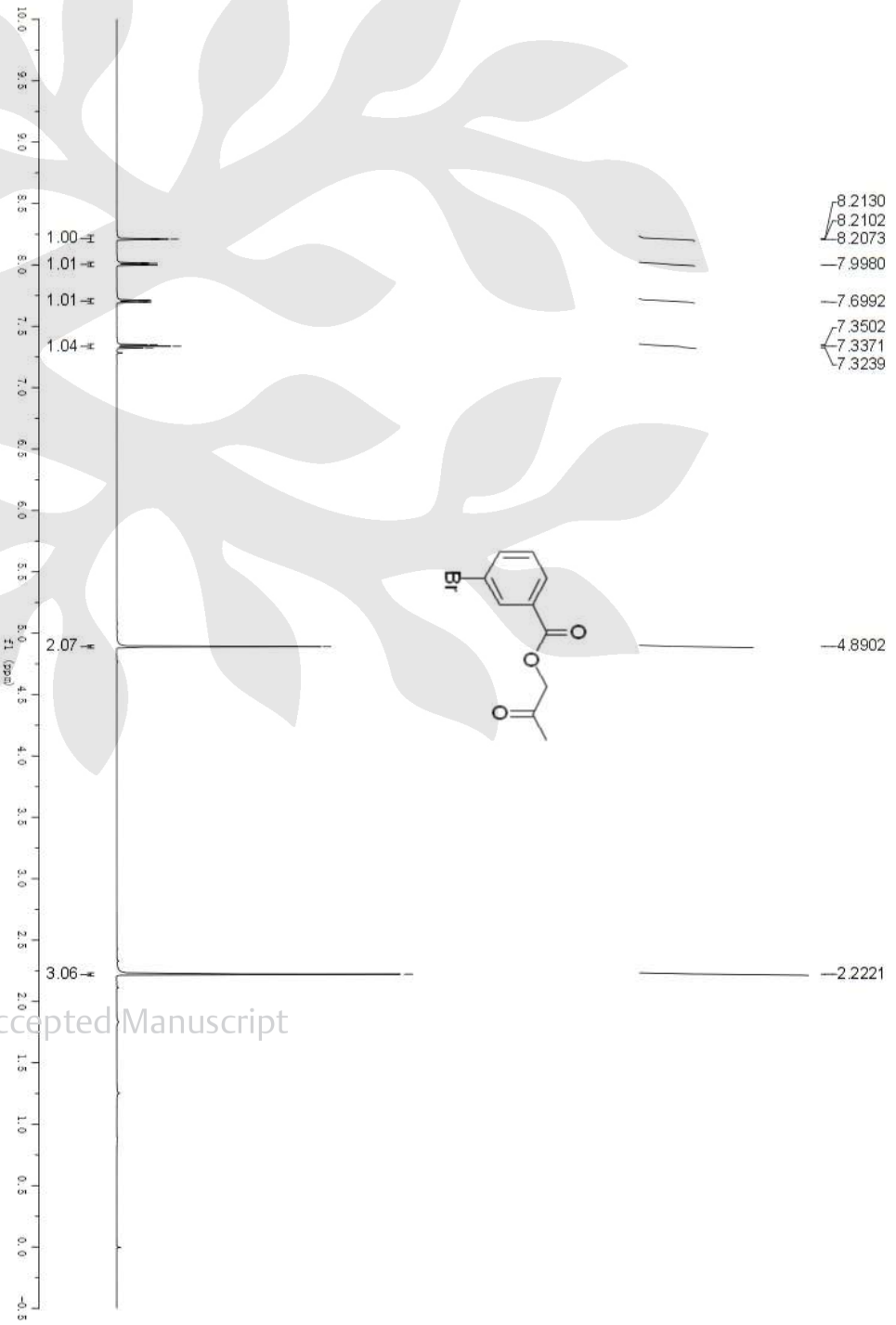
^{1}H NMR of 3aj

^{13}C NMR of 3aj



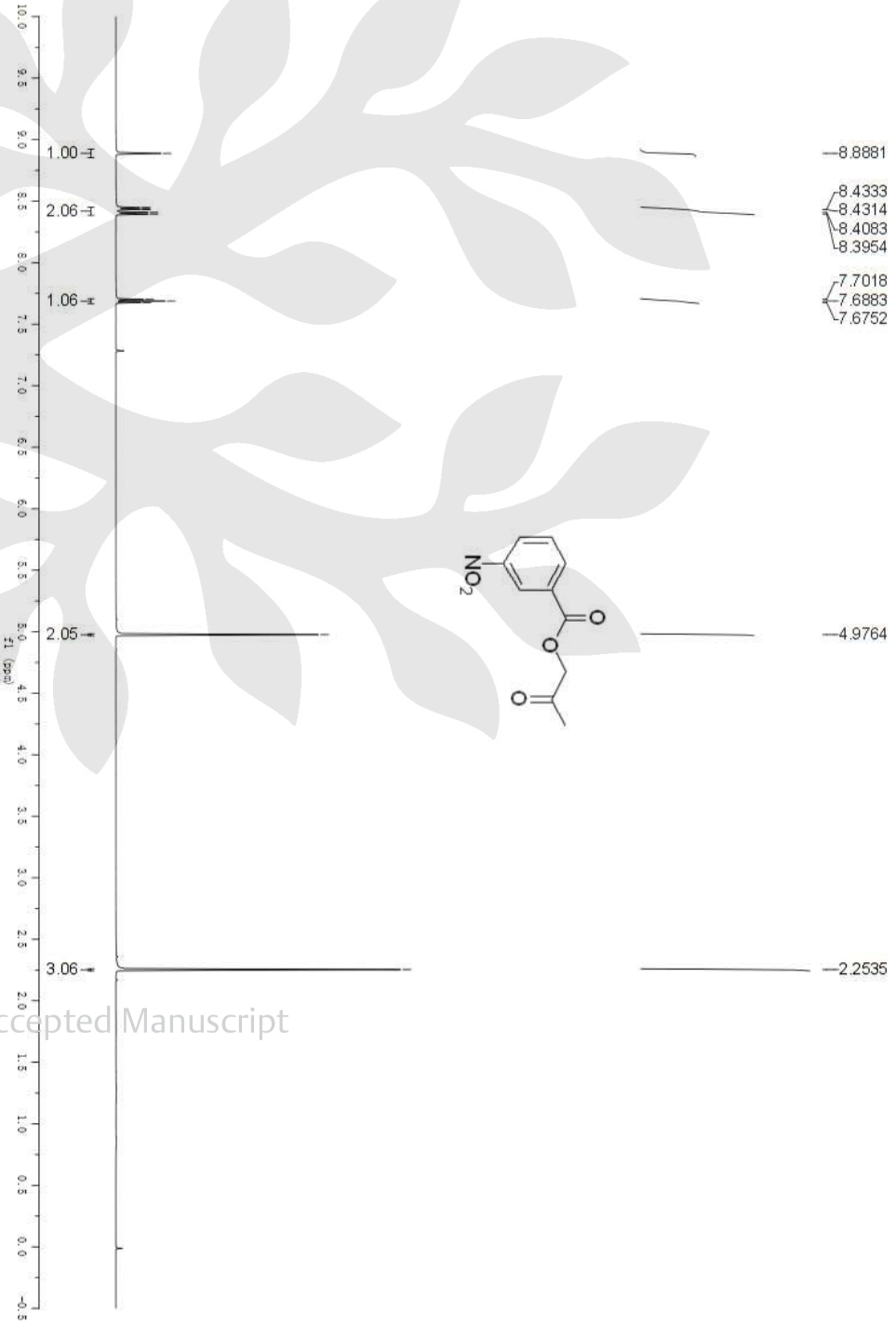
^{1}H NMR of 3ak

^{13}C NMR of 3ak

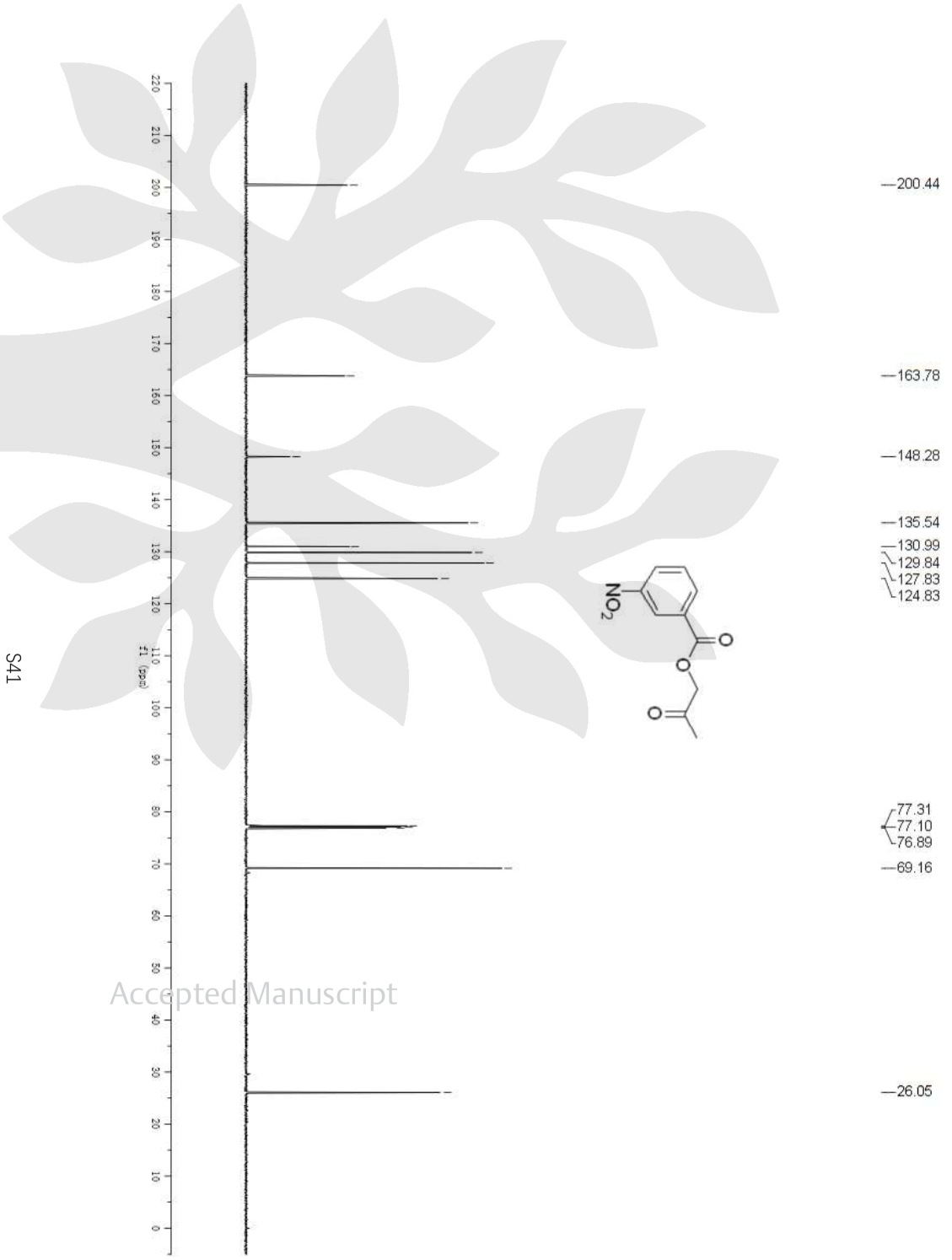


^{1}H NMR of 3al

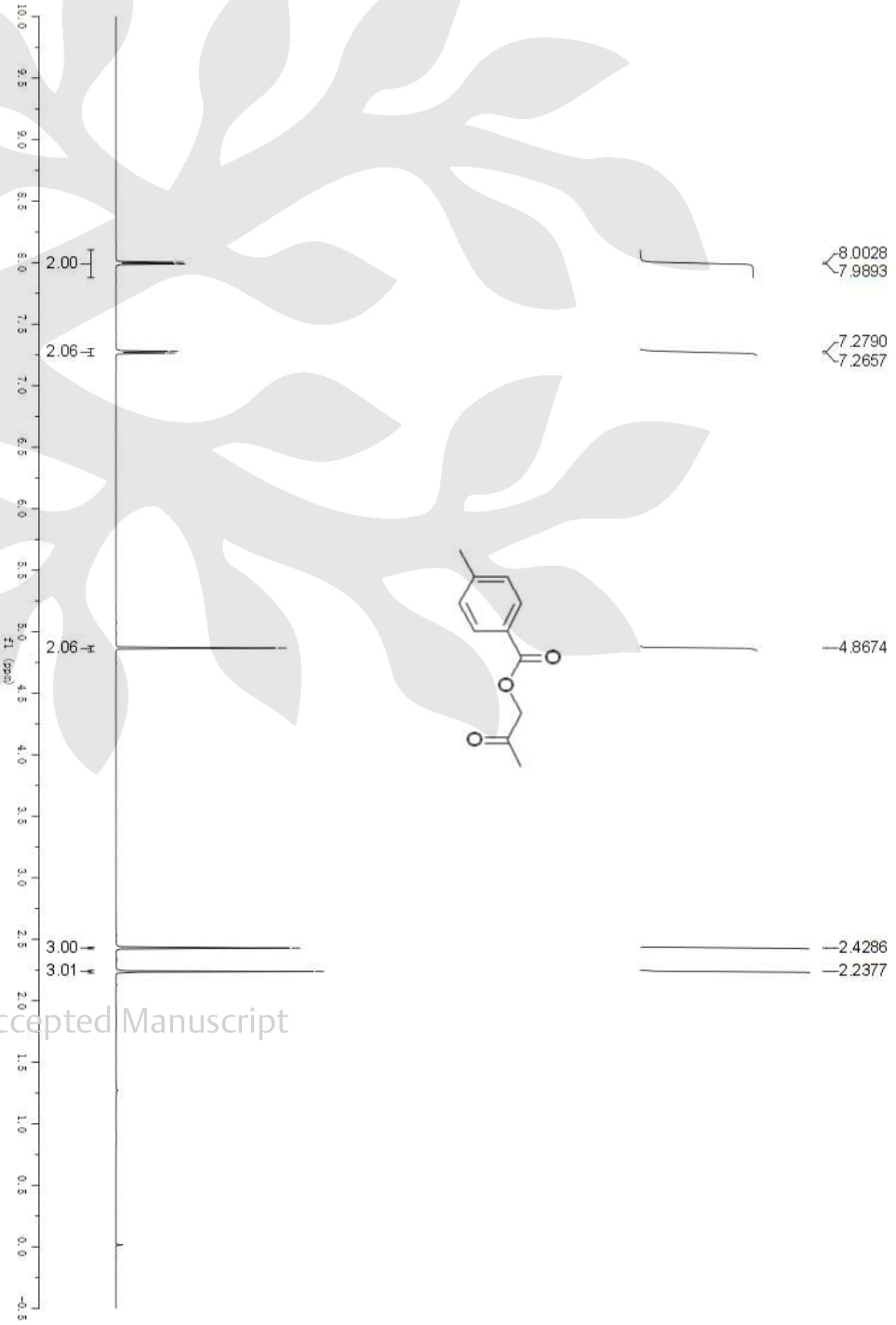
^{13}C NMR of 3al



^{1}H NMR of 3am

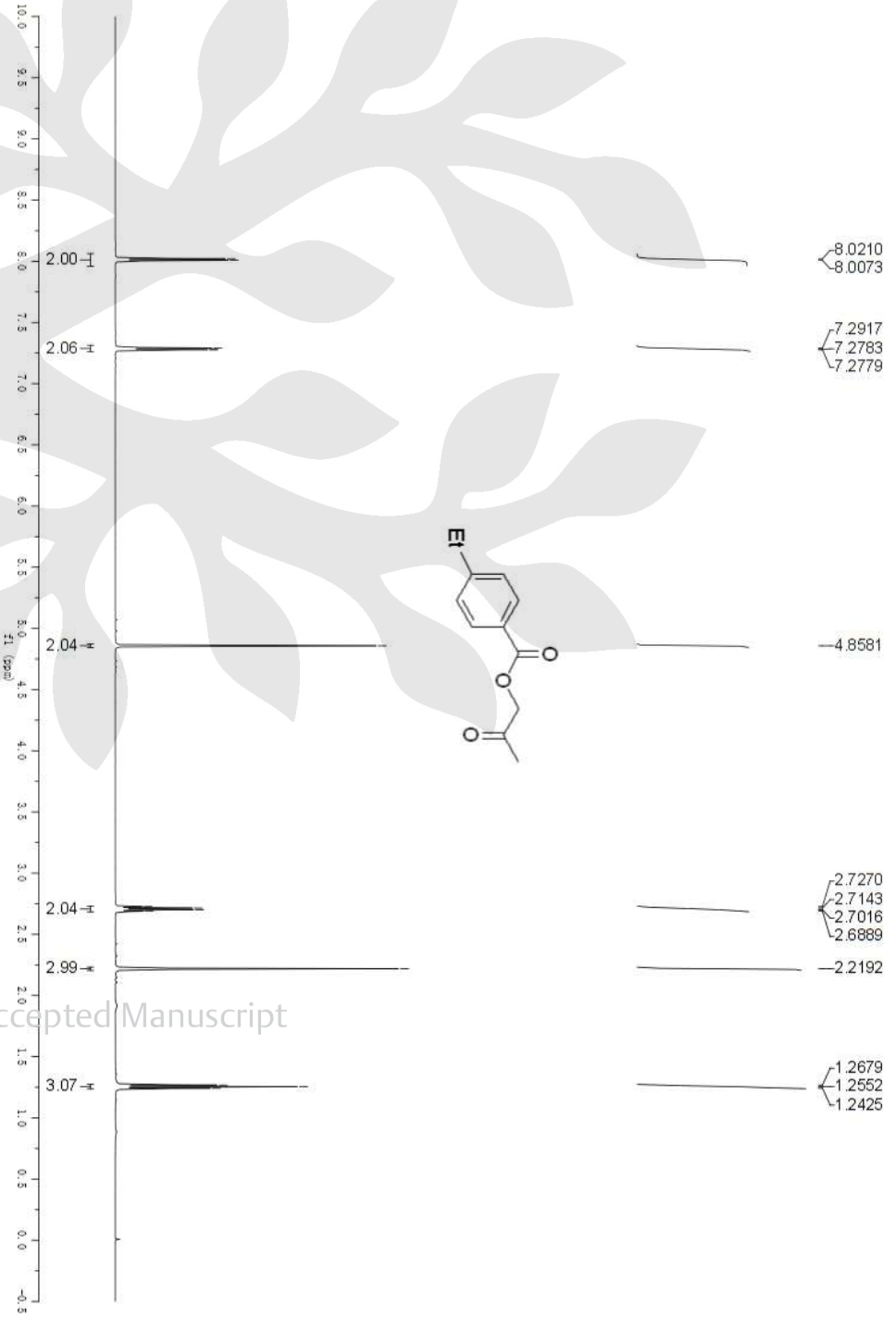


^{13}C NMR of 3am



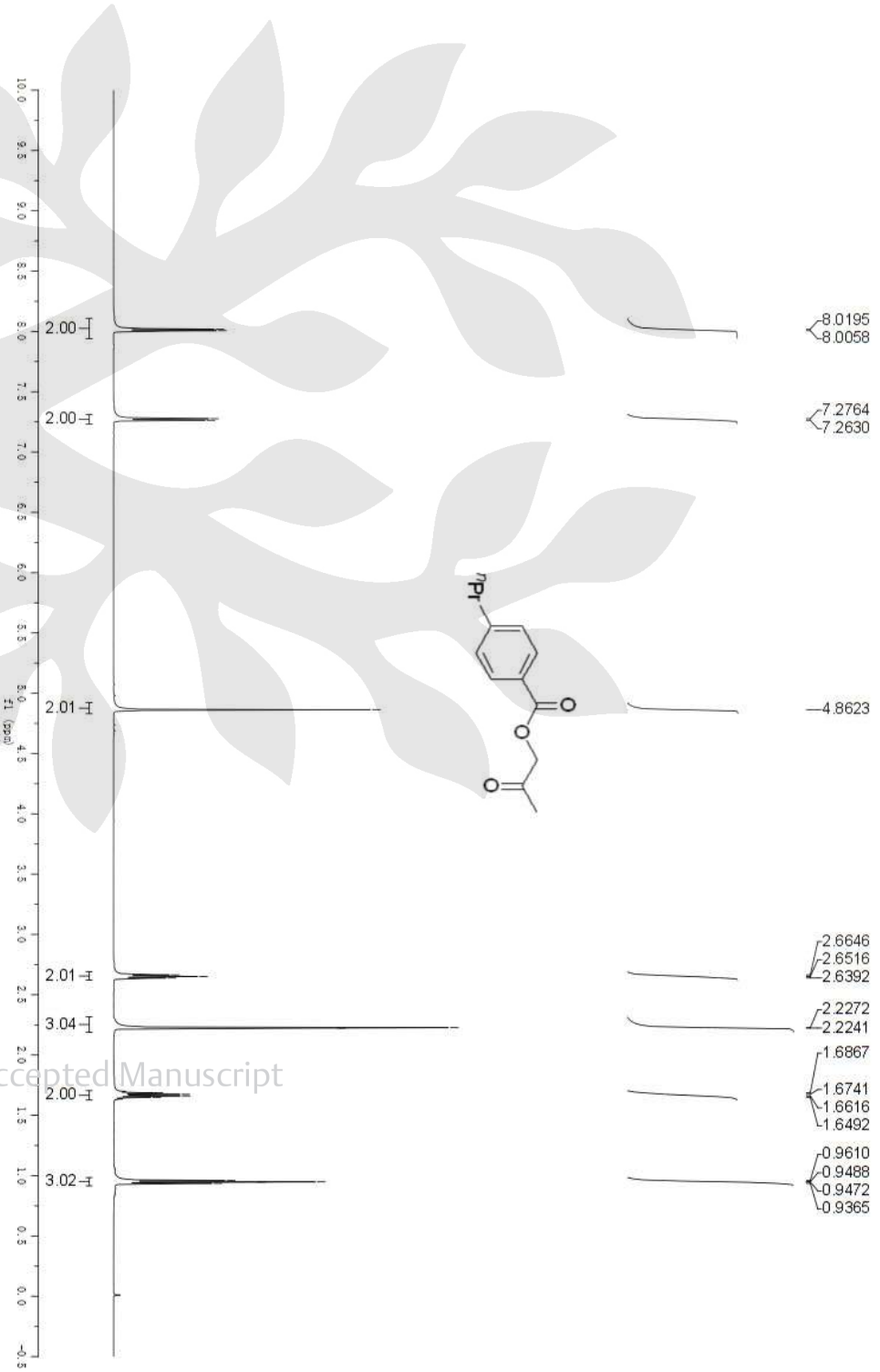
^{1}H NMR of 3an

^{13}C NMR of 3an



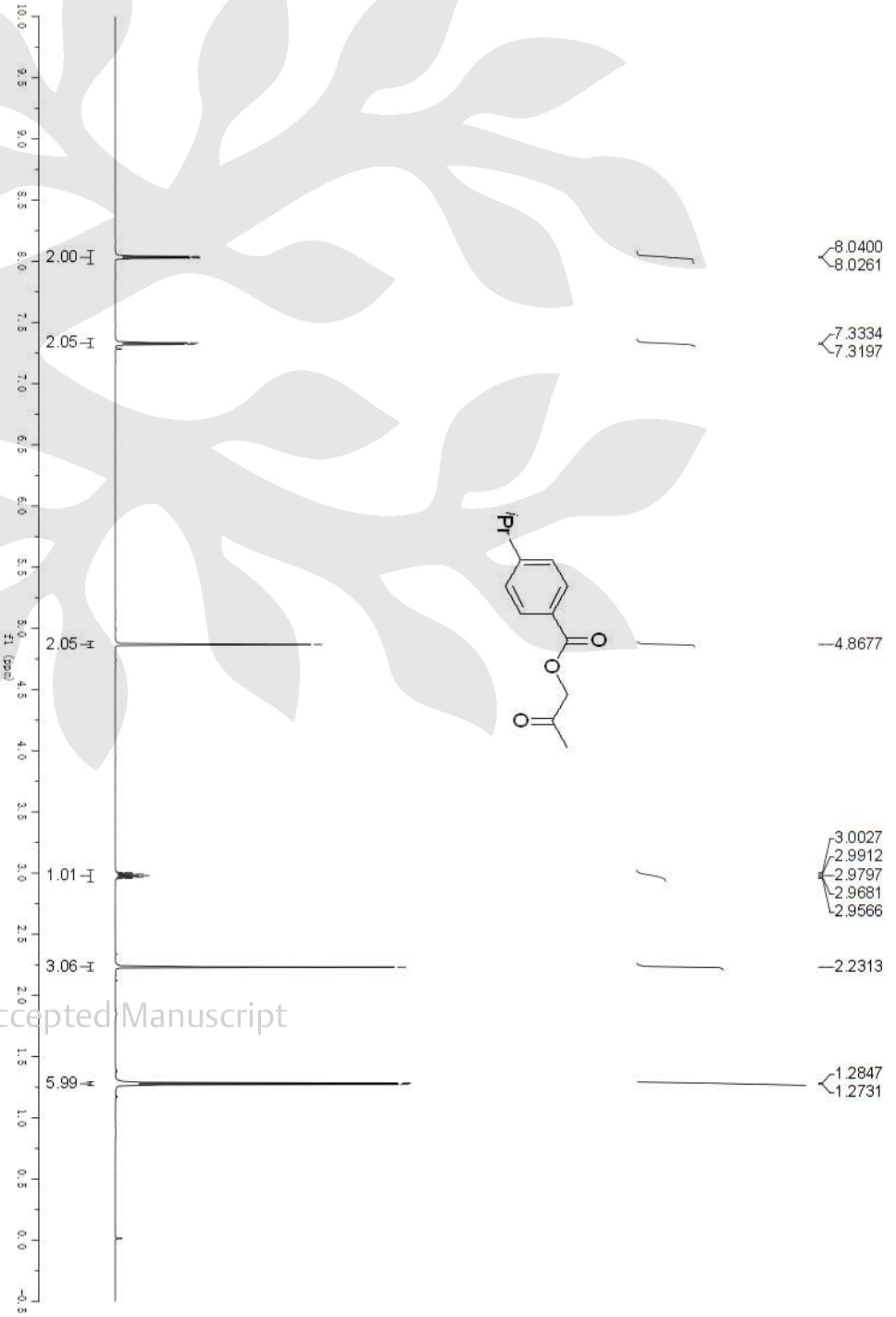
^{1}H NMR of 3ao

^{13}C NMR of 3ao



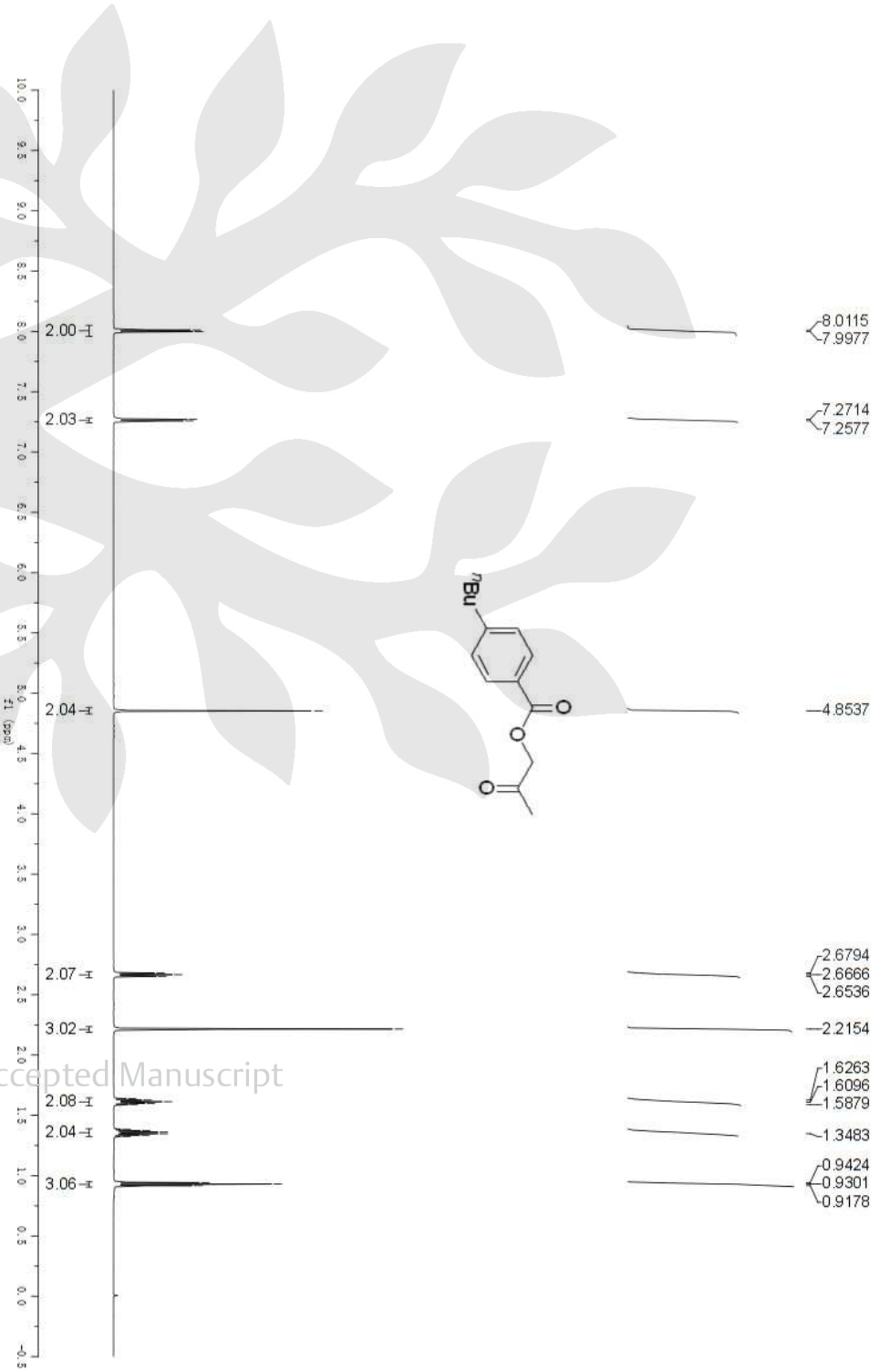
^{1}H NMR of 3ap

^{13}C NMR of 3ap



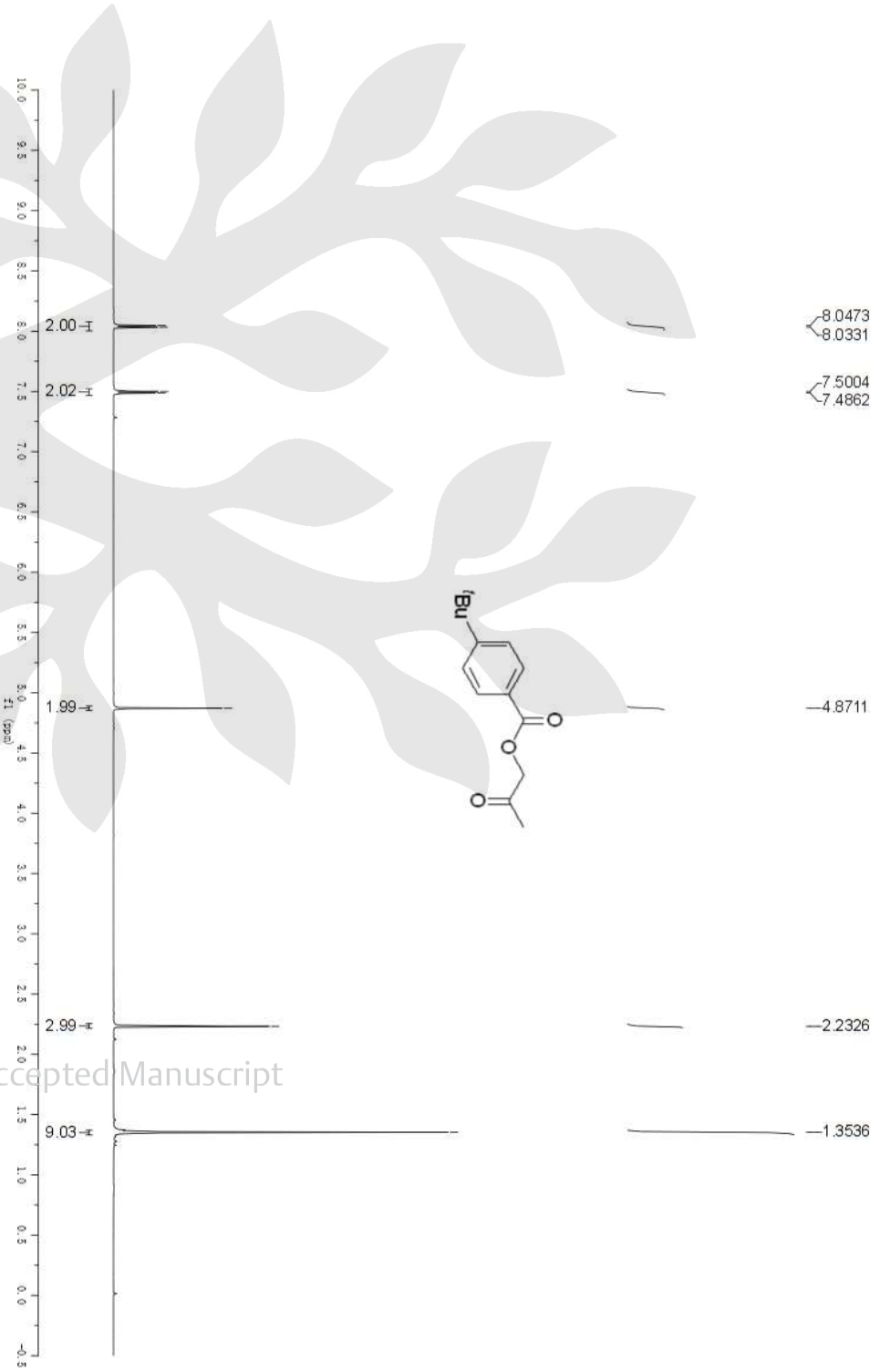
^{1}H NMR of 3aq

^{13}C NMR of 3aq



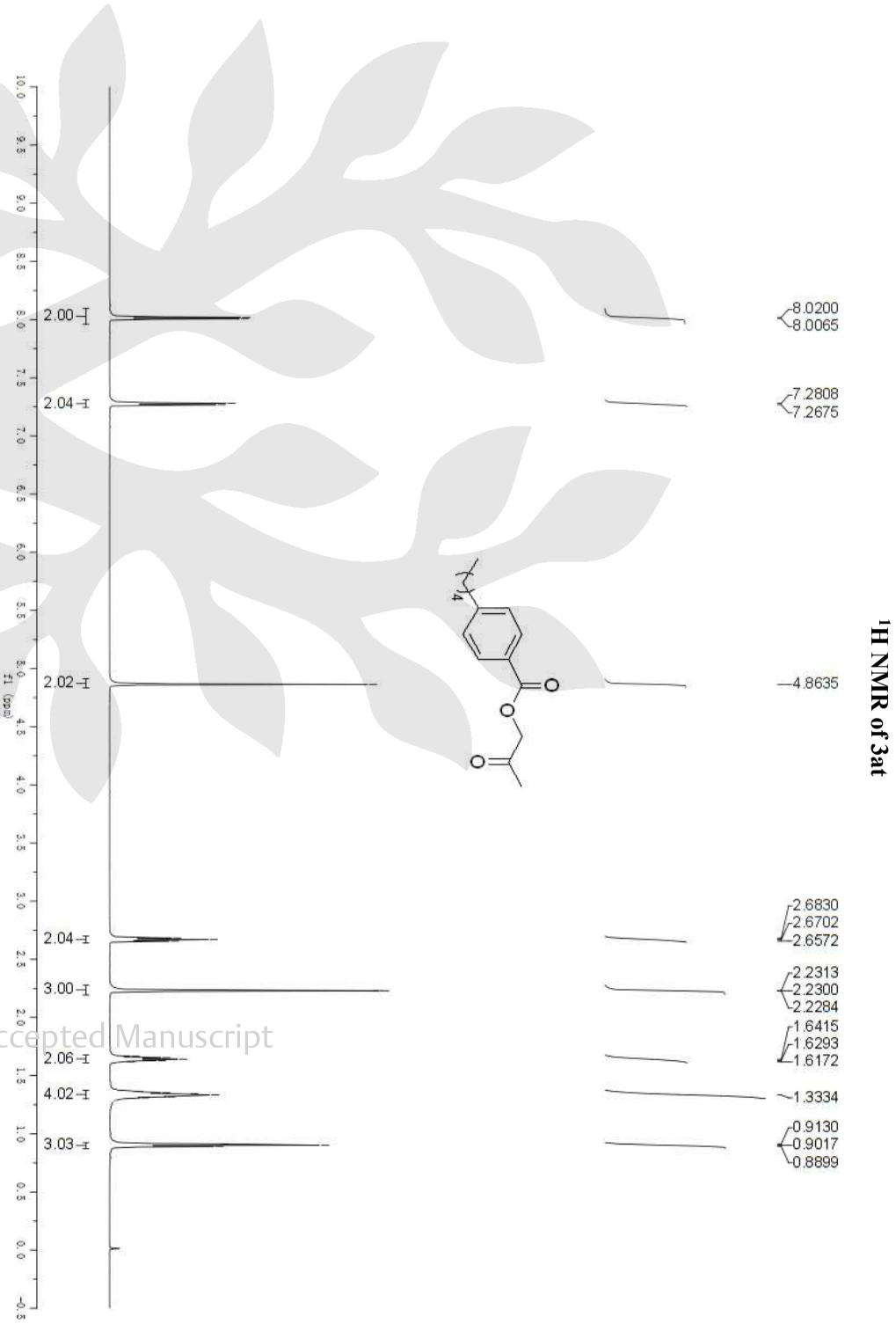
^{1}H NMR of 3ar

^{13}C NMR of 3ar

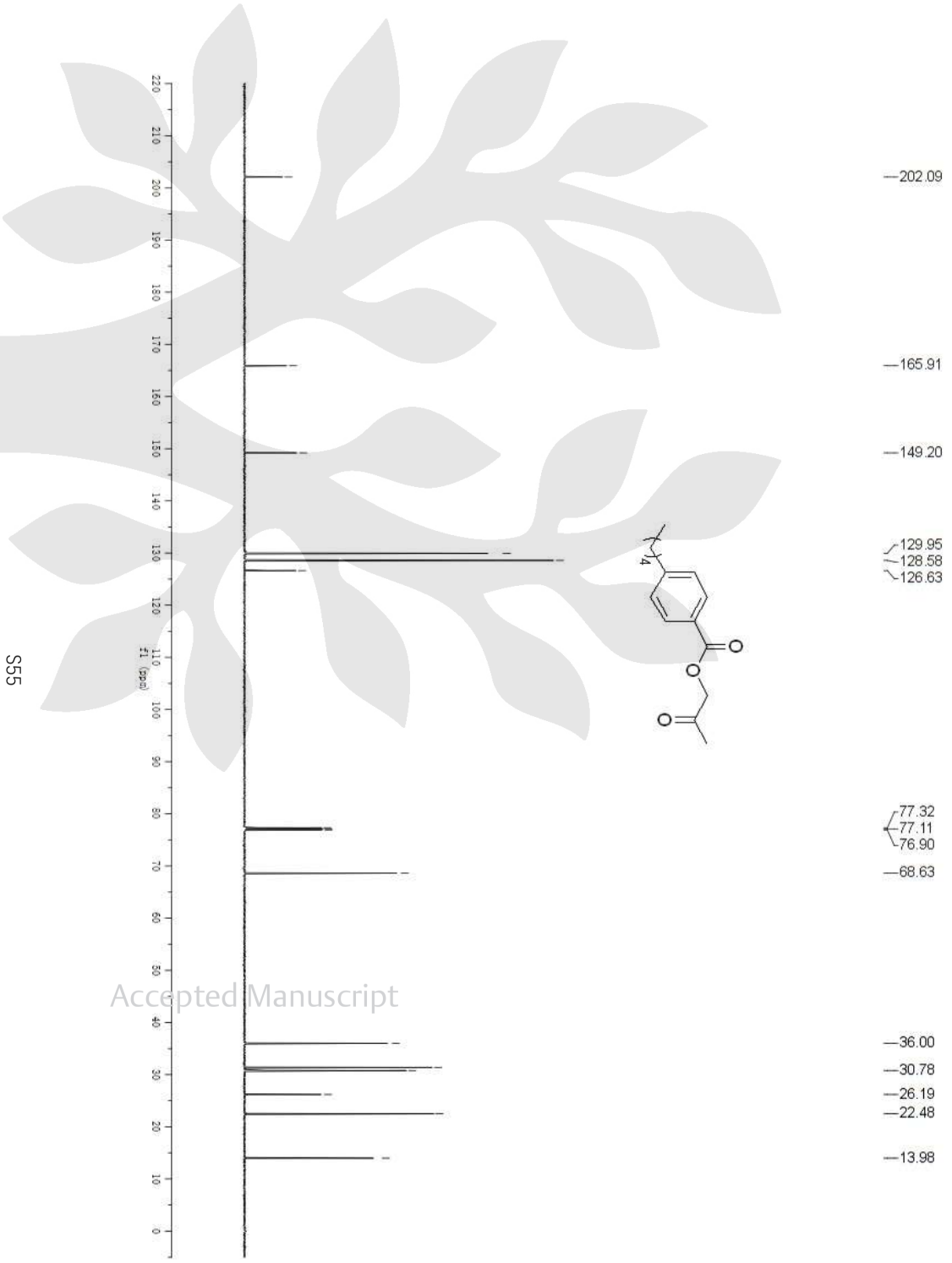


^{1}H NMR of 3as

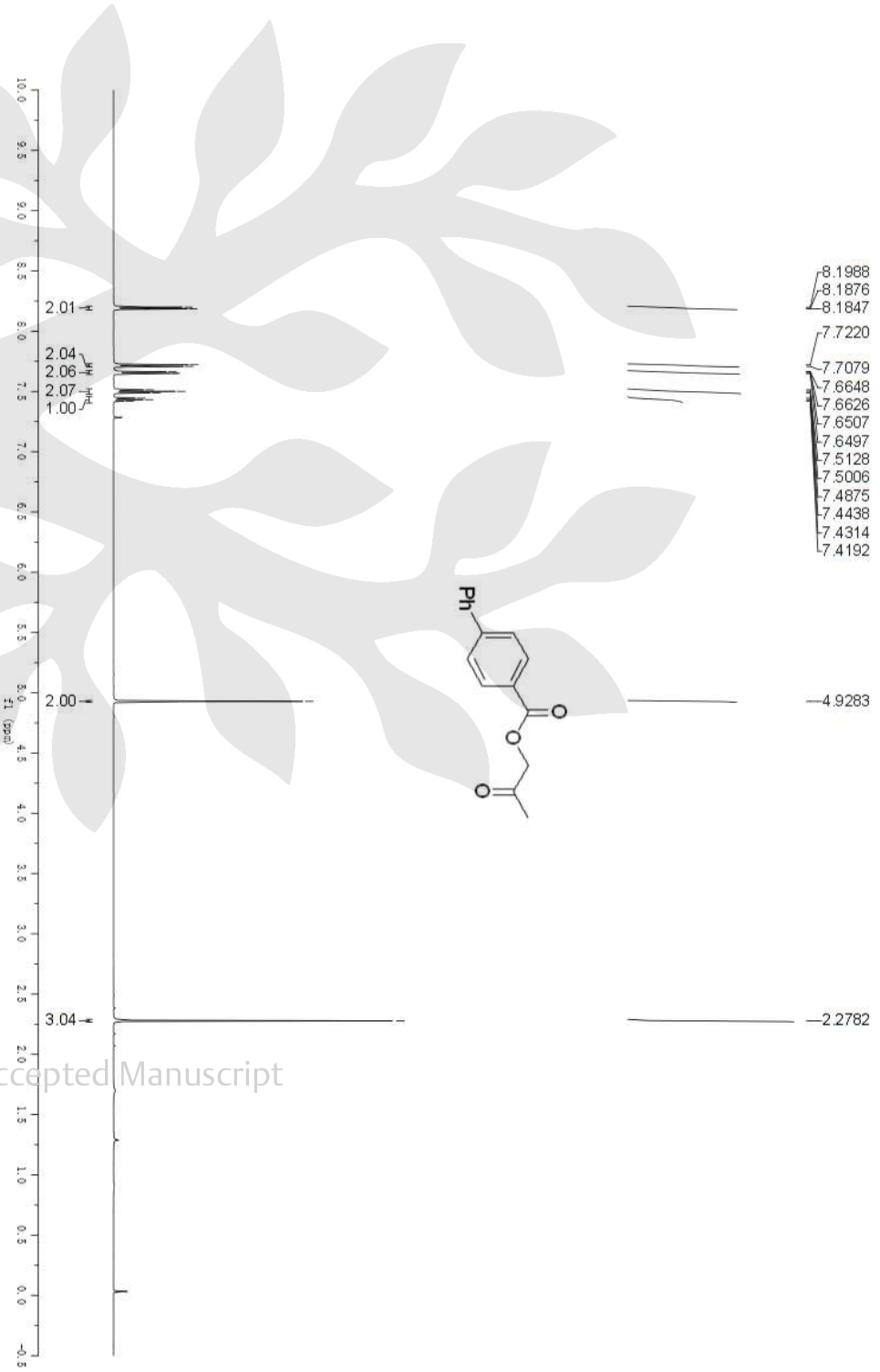
^{13}C NMR of 3as



^{1}H NMR of 3at

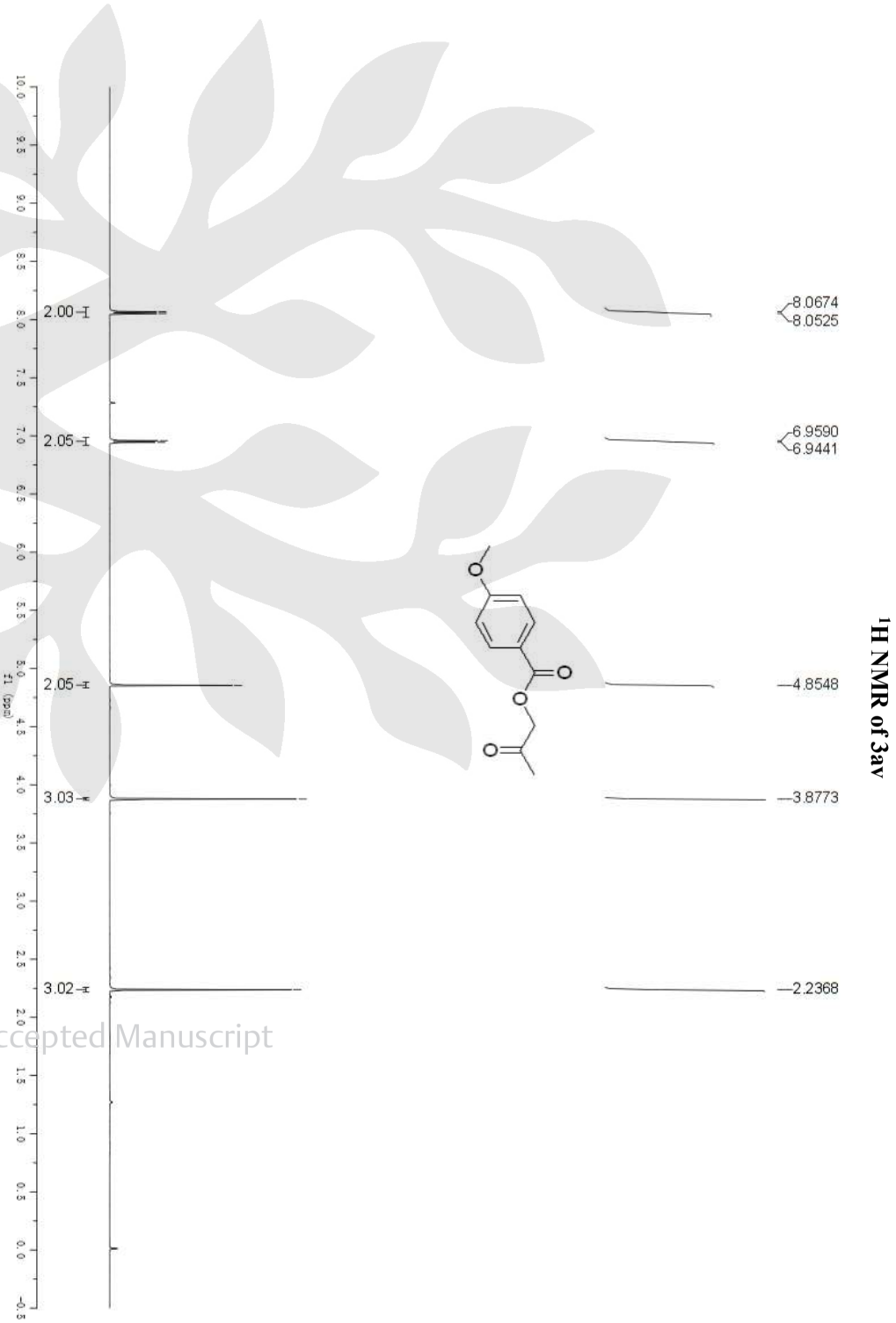


^{13}C NMR of 3at



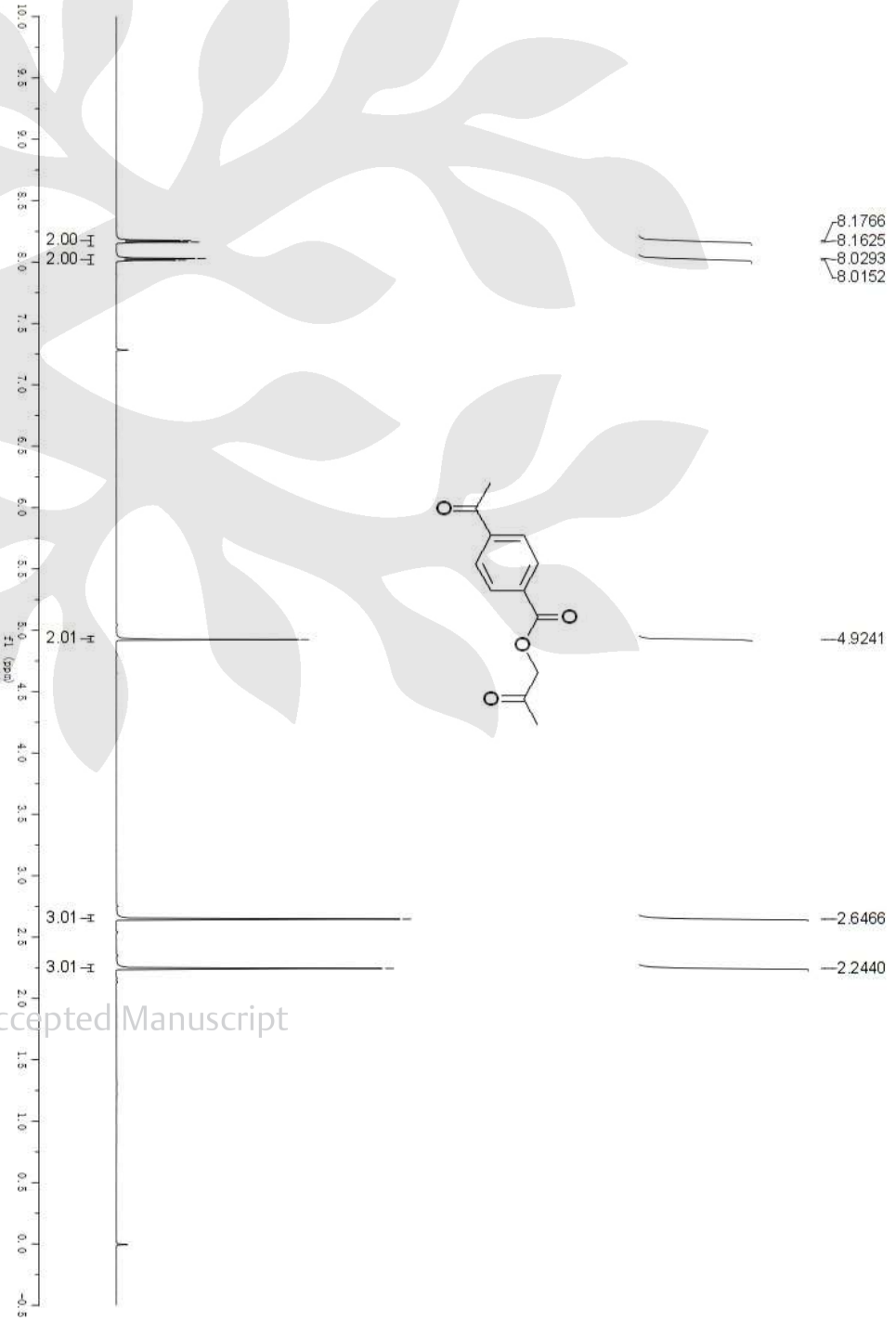
^{1}H NMR of 3au

^{13}C NMR of 3au



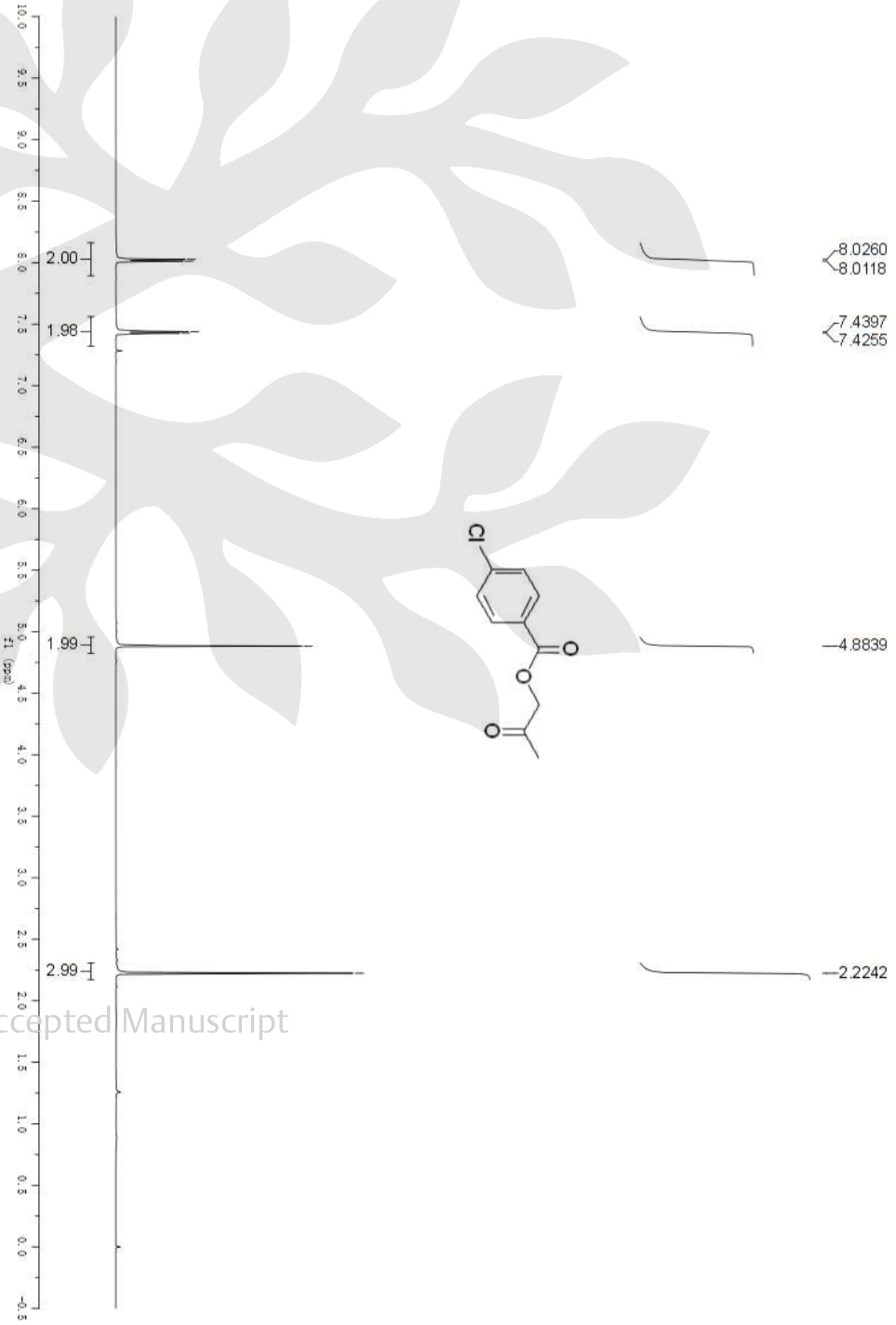
^{1}H NMR of 3av

^{13}C NMR of 3av



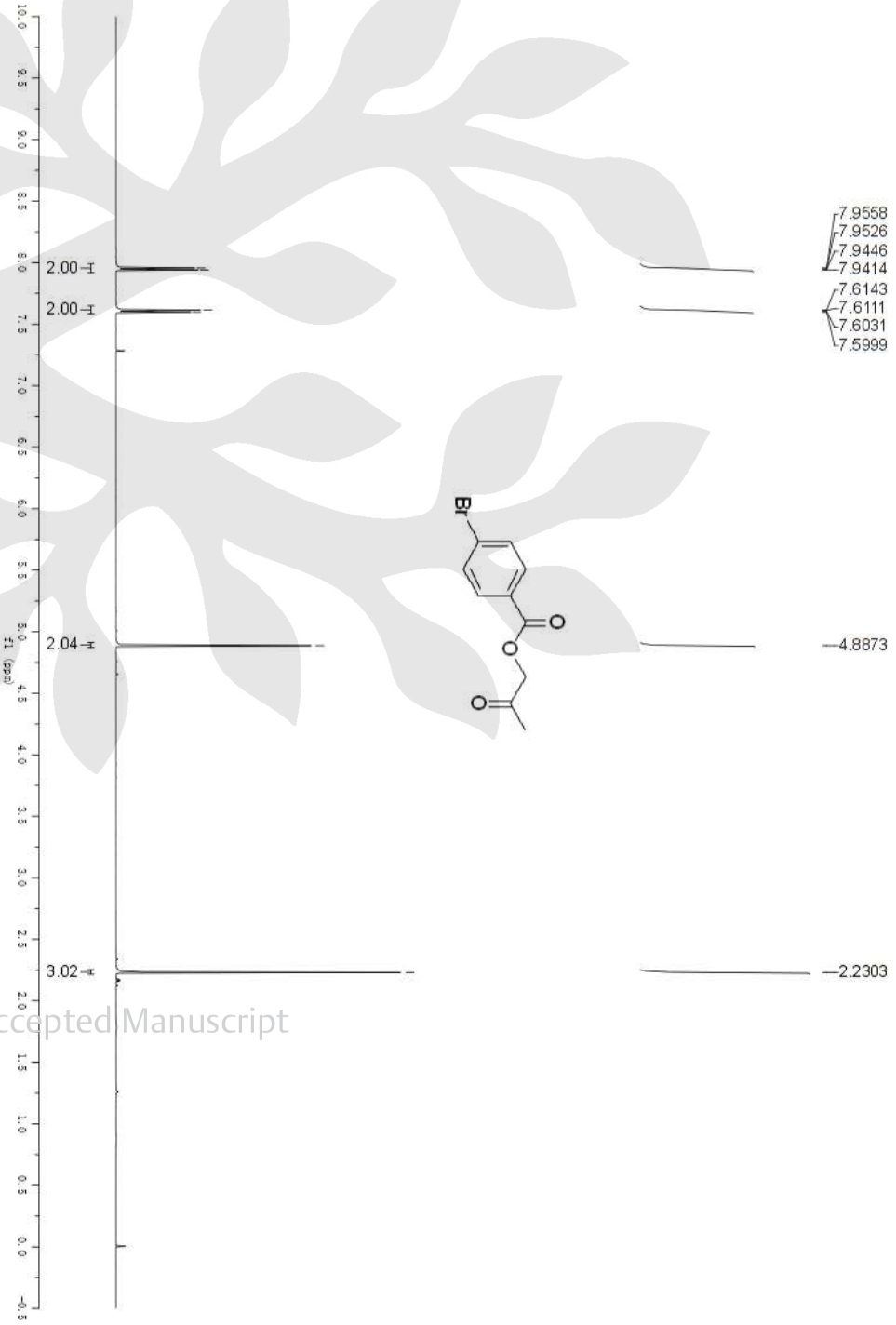
^{1}H NMR of 3aw

^{13}C NMR of 3aw



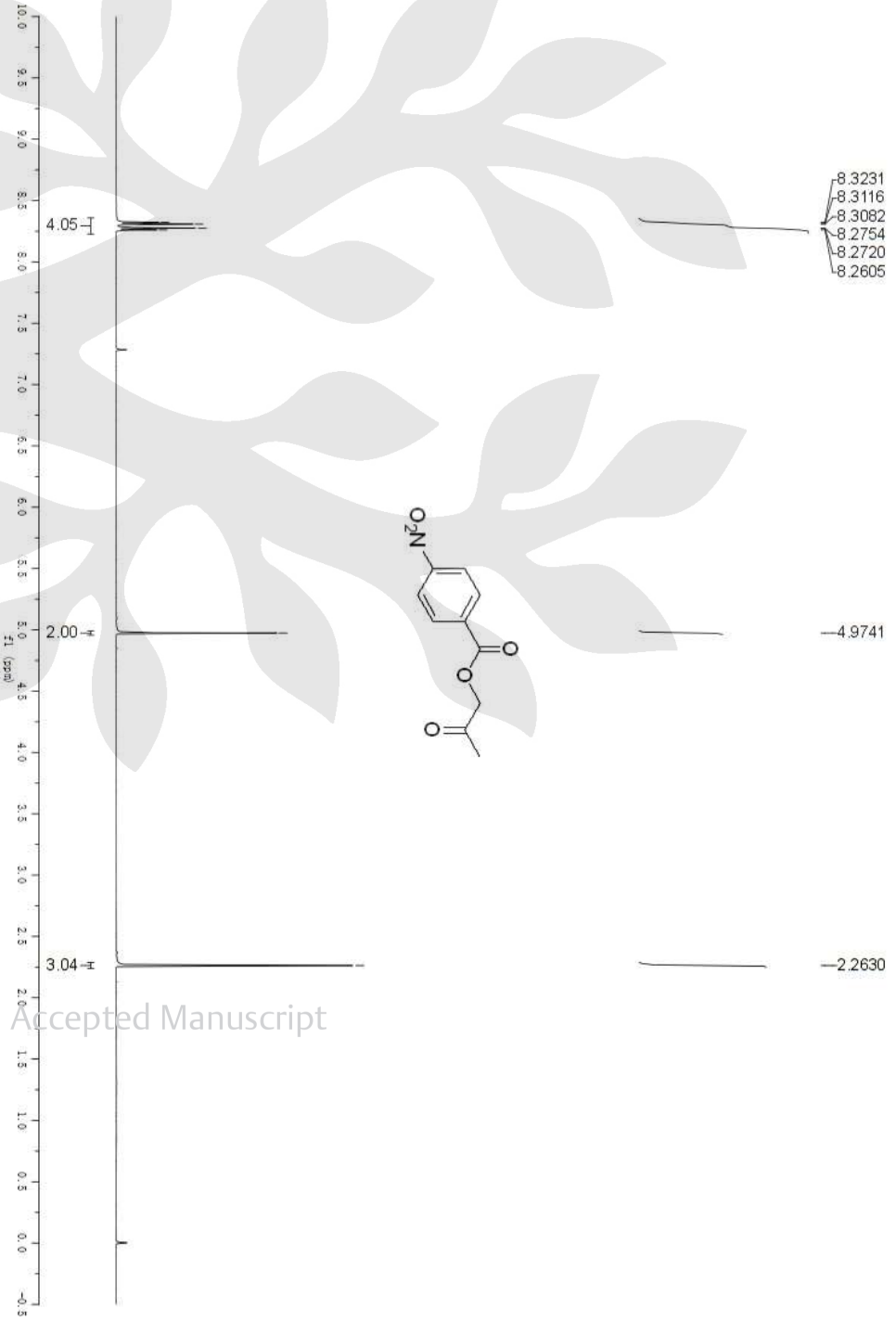
^{1}H NMR of 3ax

^{13}C NMR of 3ax



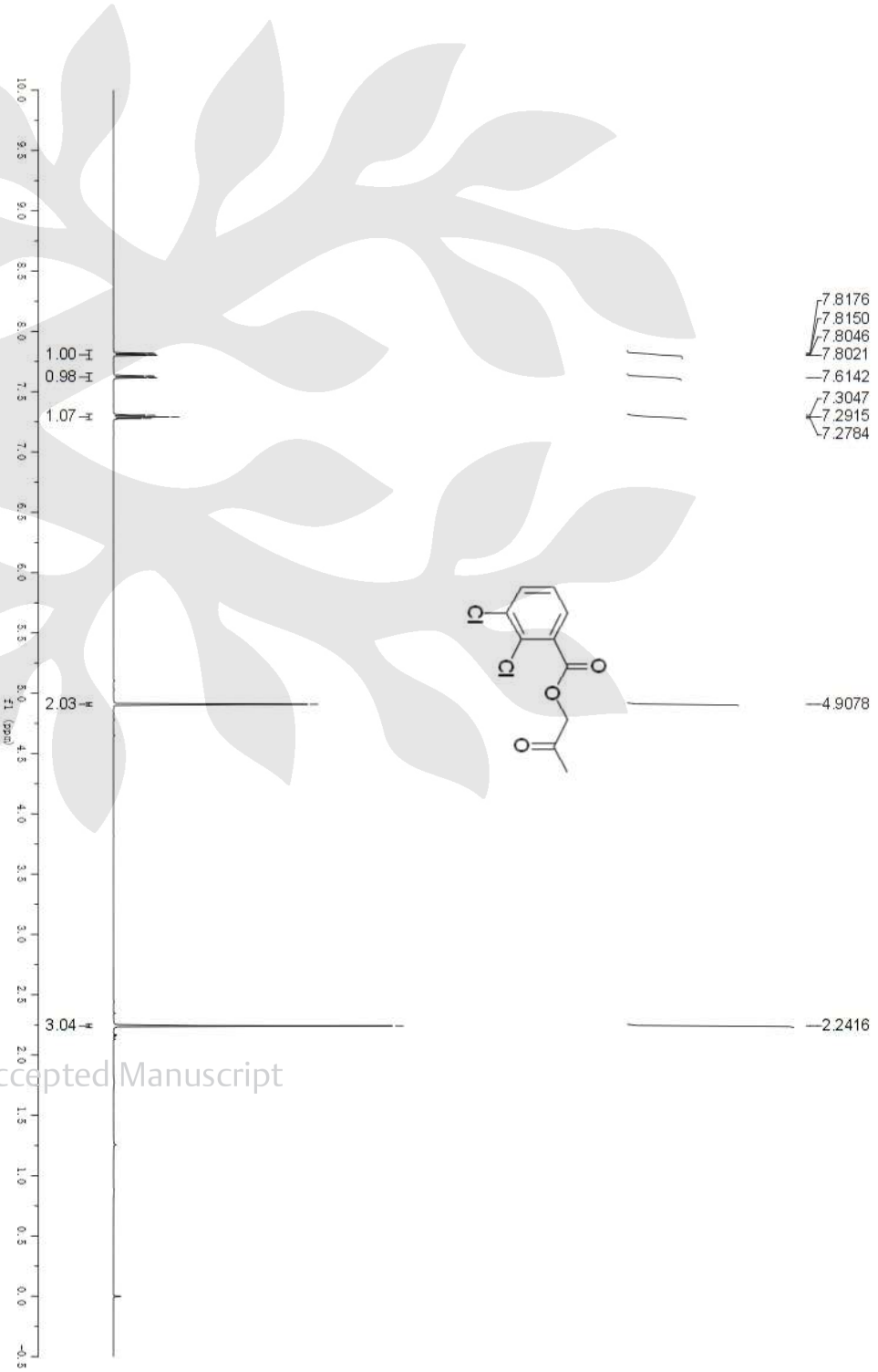
^{1}H NMR of 3ay

^{13}C NMR of 3ay

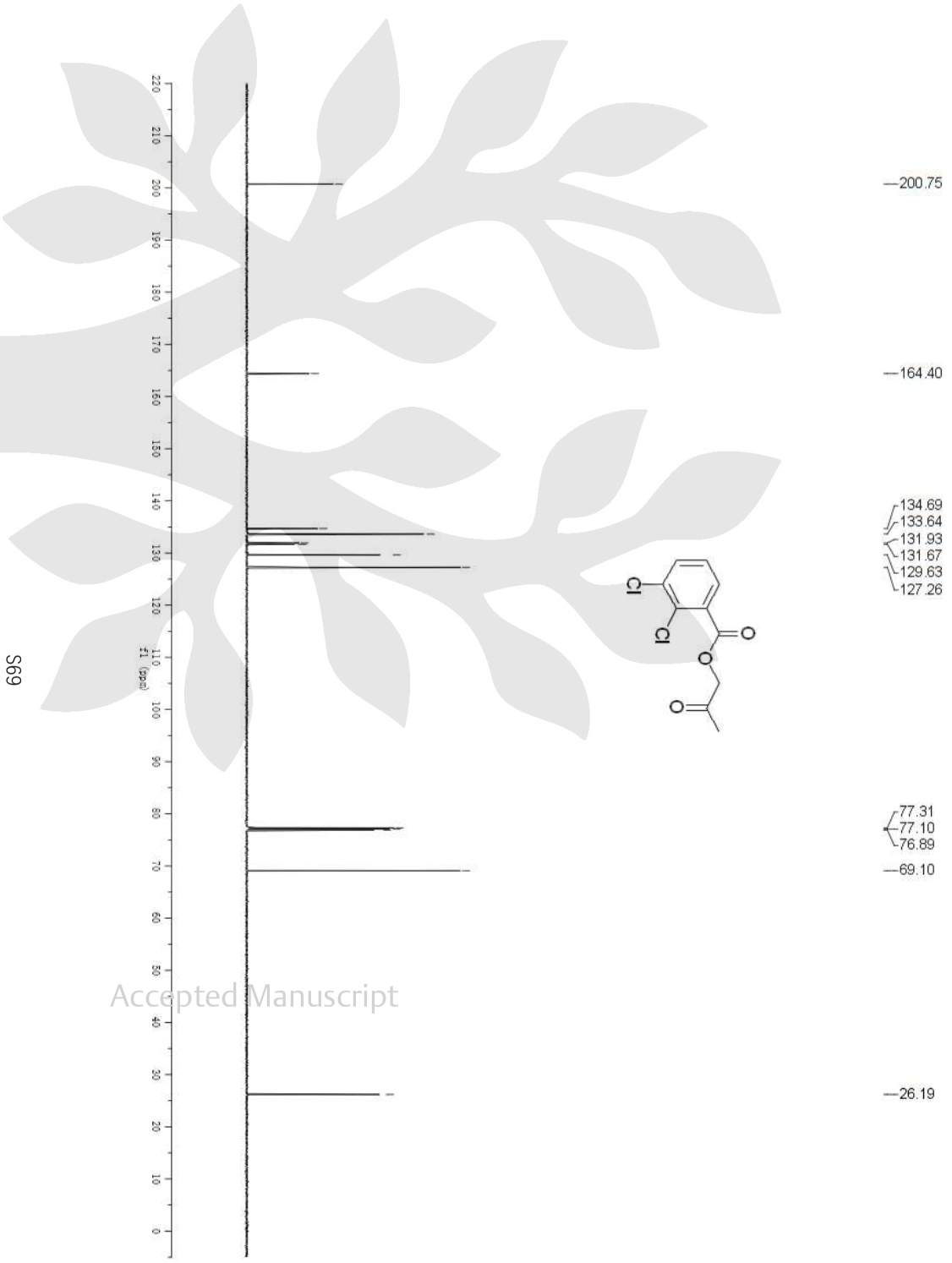


^{1}H NMR of 3az

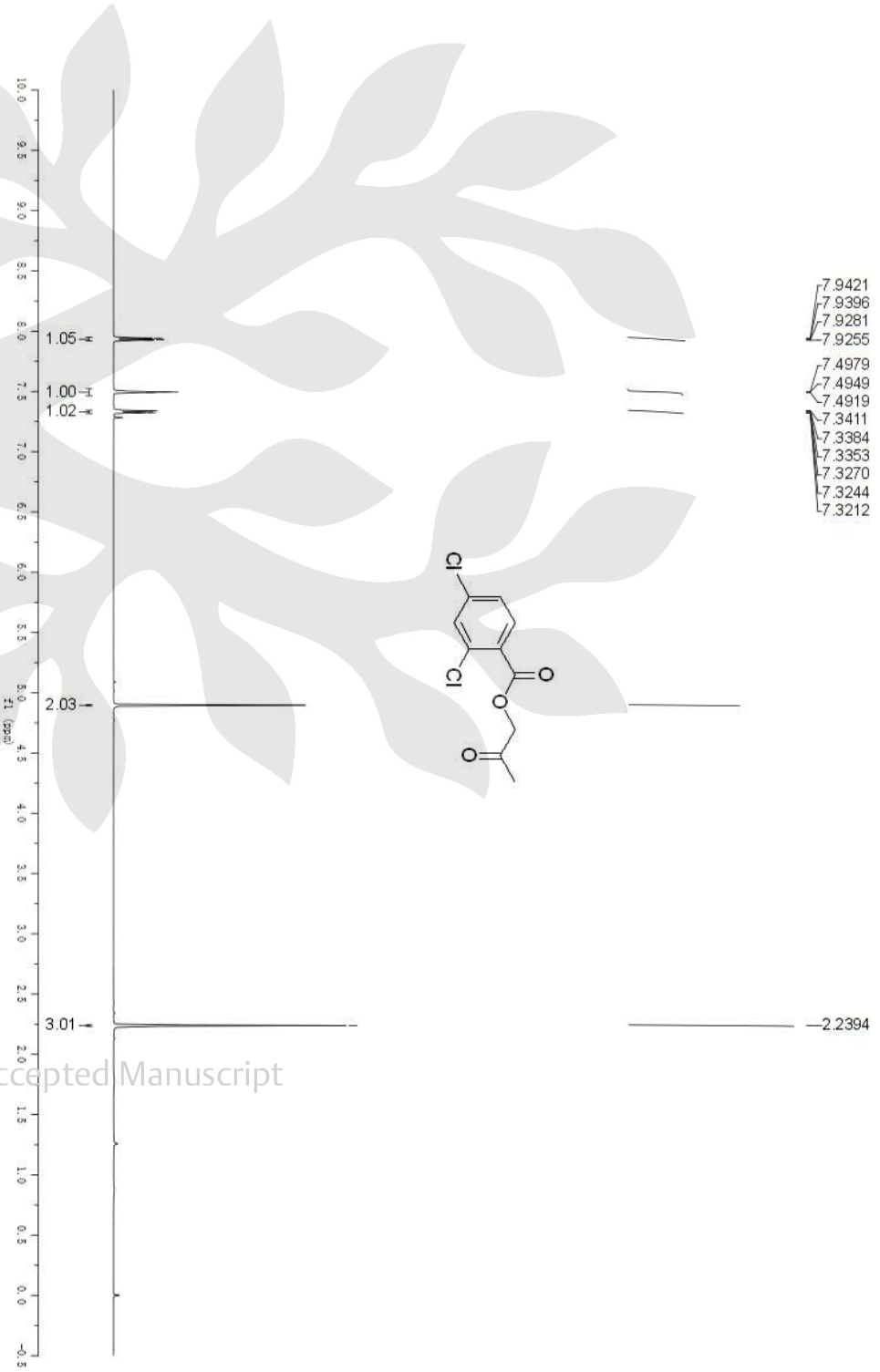
^{13}C NMR of 3az



^{1}H NMR of 3ba

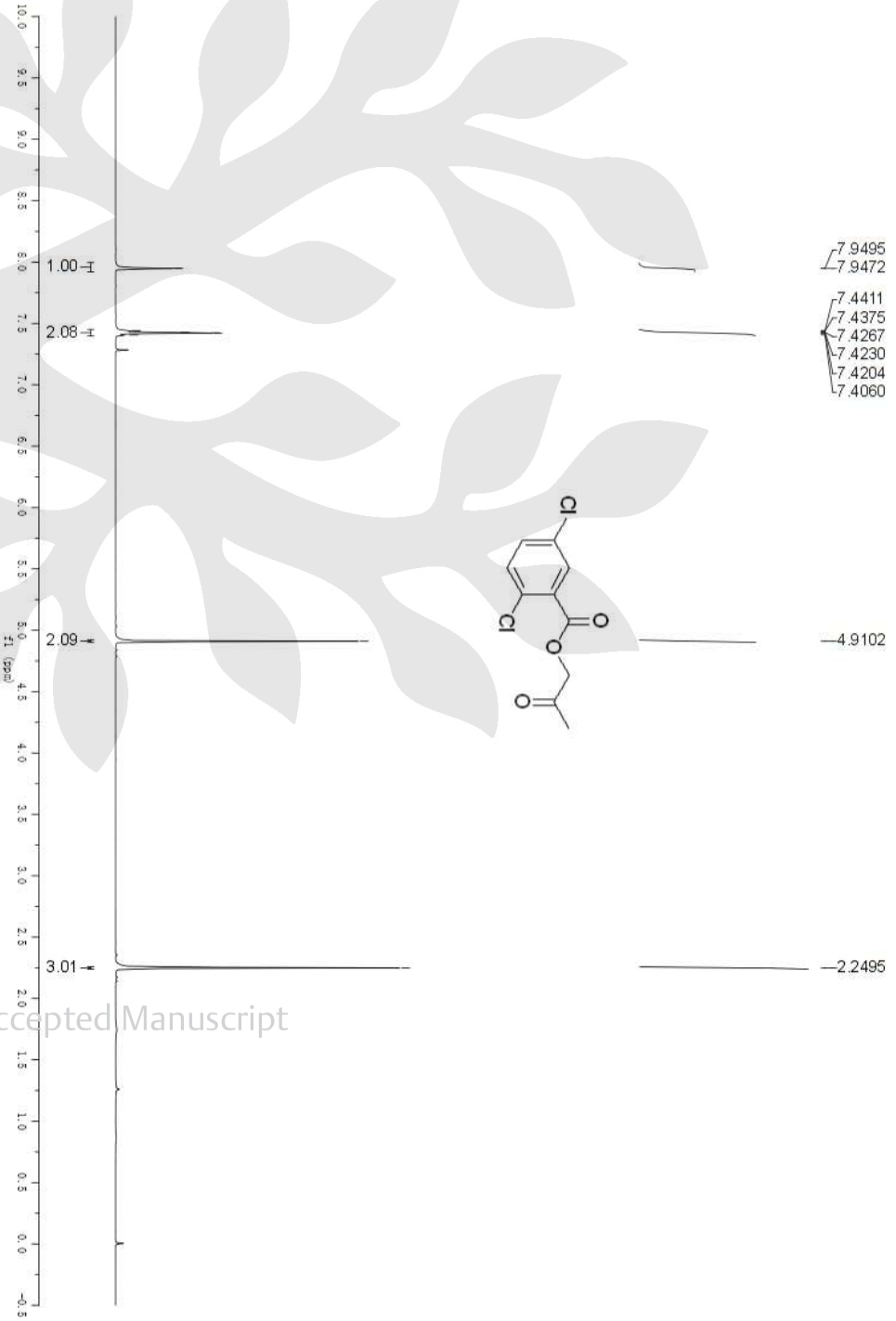


^{13}C NMR of 3ba



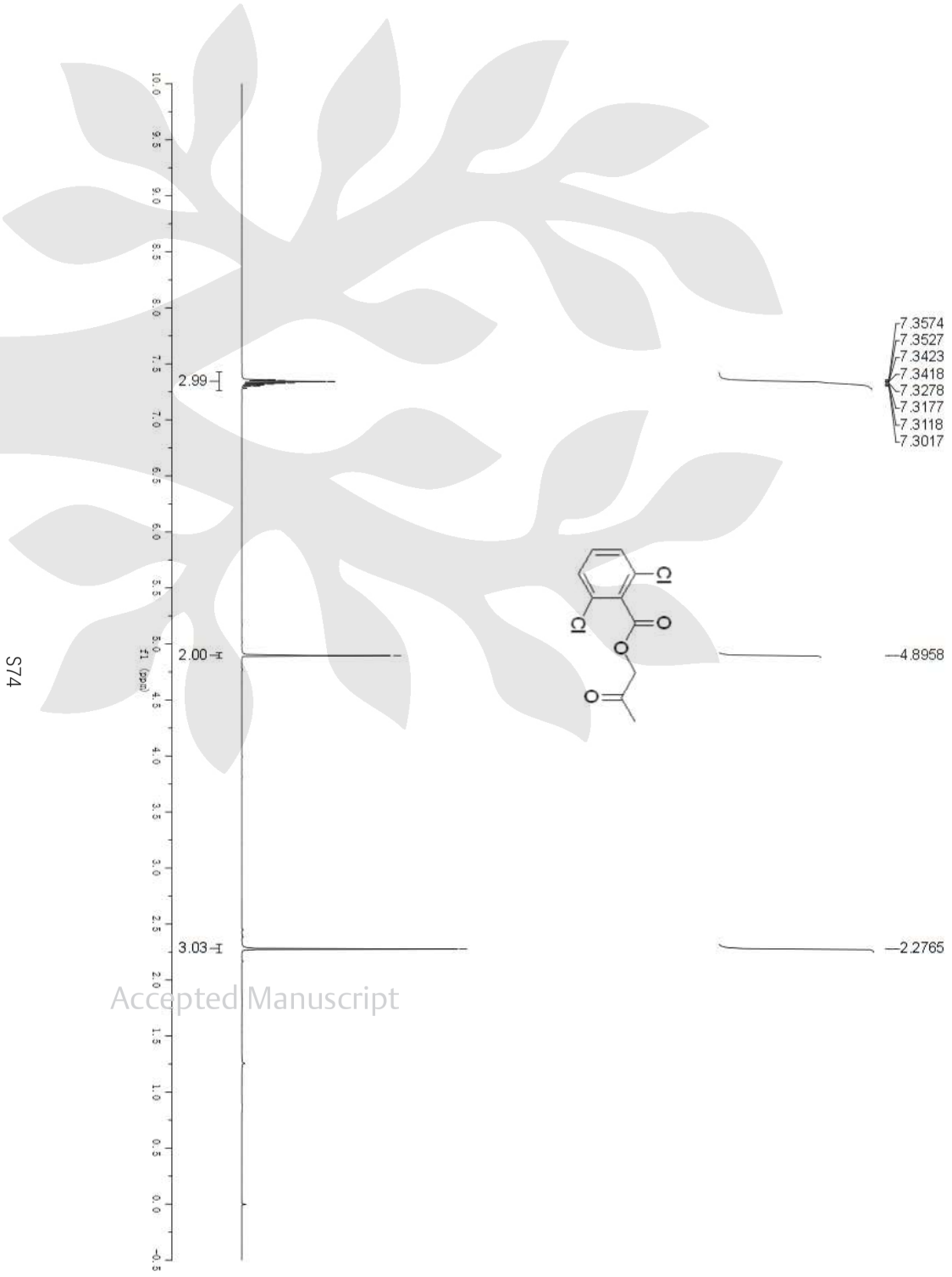
^{1}H NMR of 3bb

^{13}C NMR of 3bb



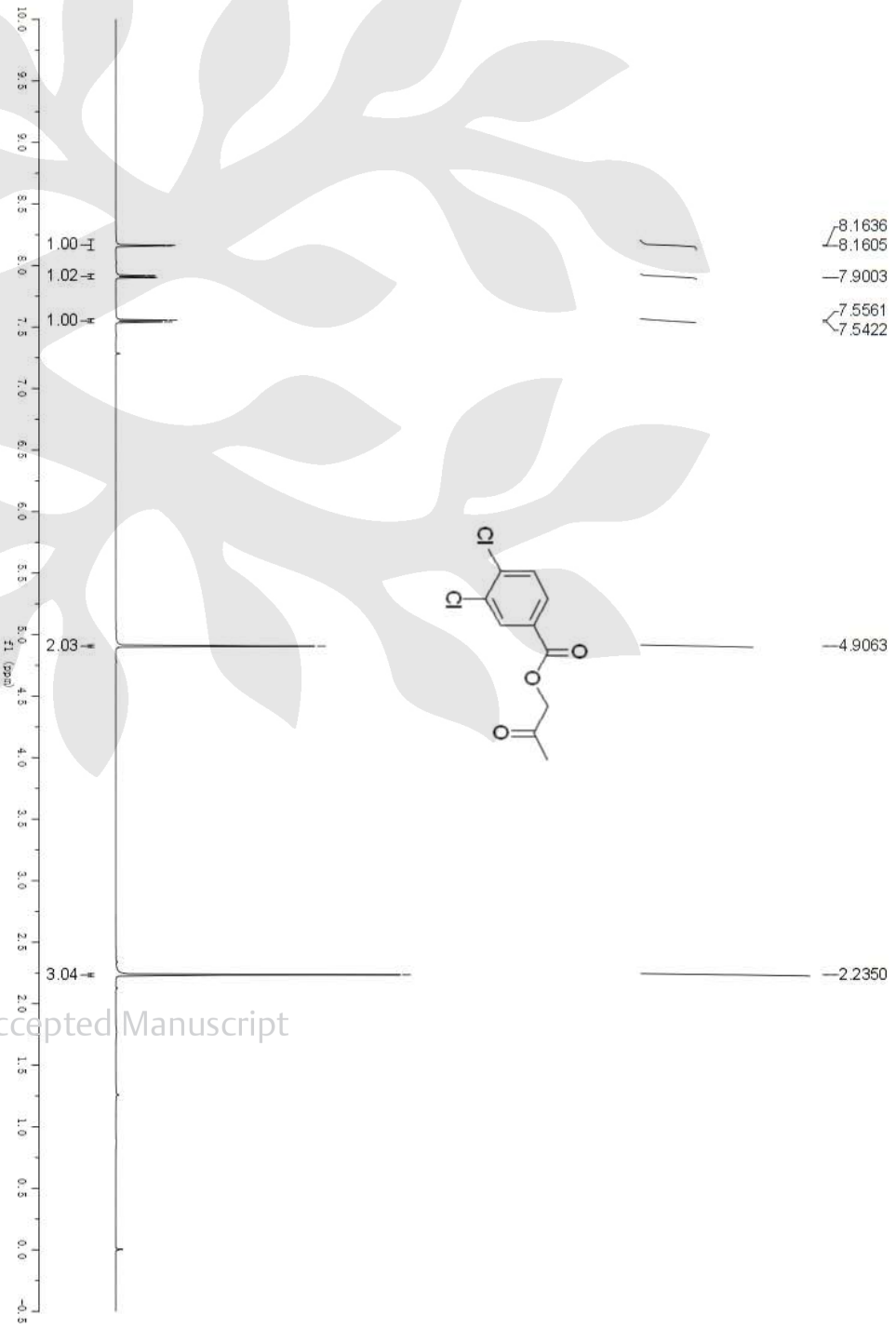
^{1}H NMR of 3bc

^{13}C NMR of 3bc



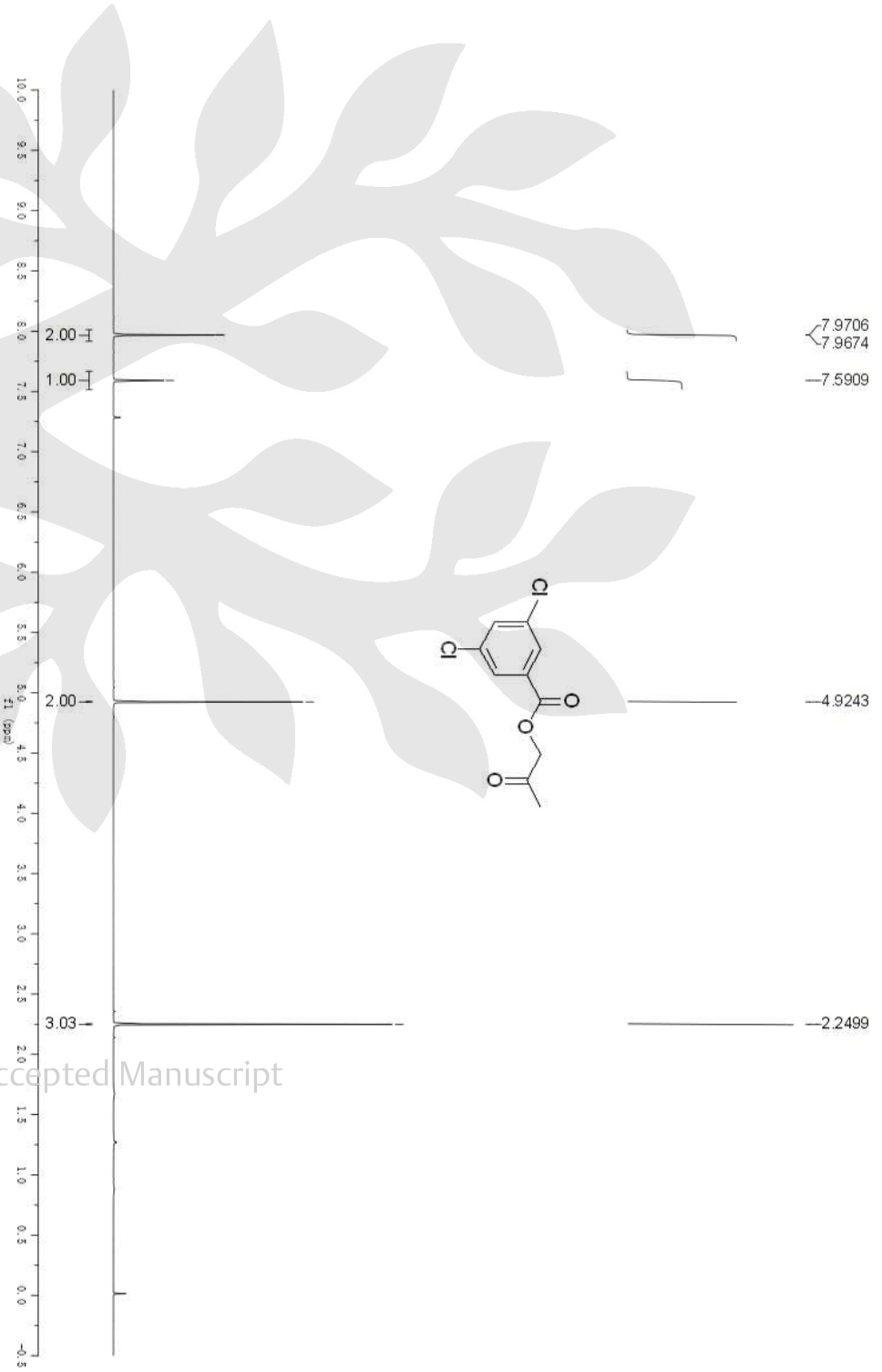
^{1}H NMR of 3bd

^{13}C NMR of 3bd



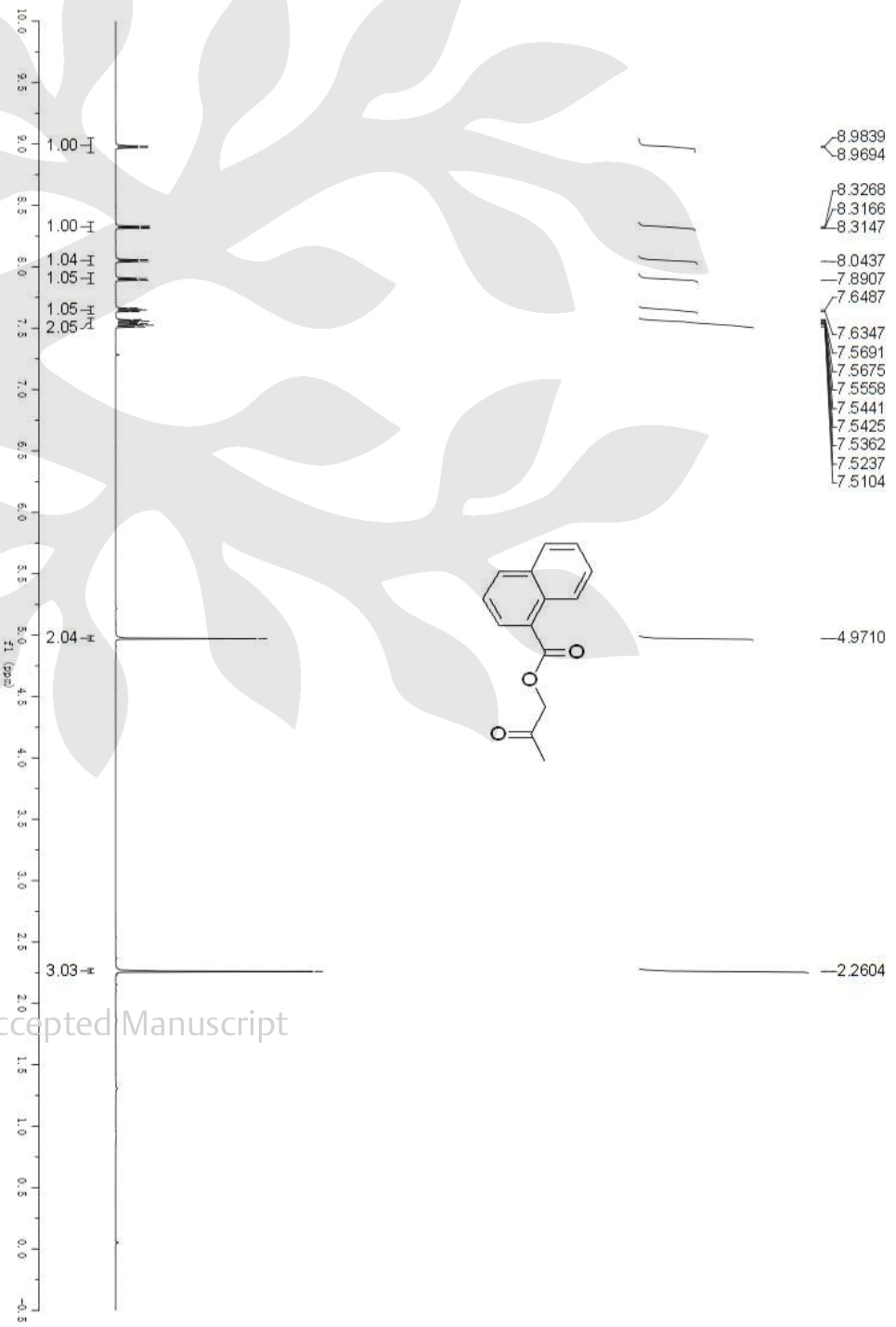
^{1}H NMR of 3be

^{13}C NMR of 3be



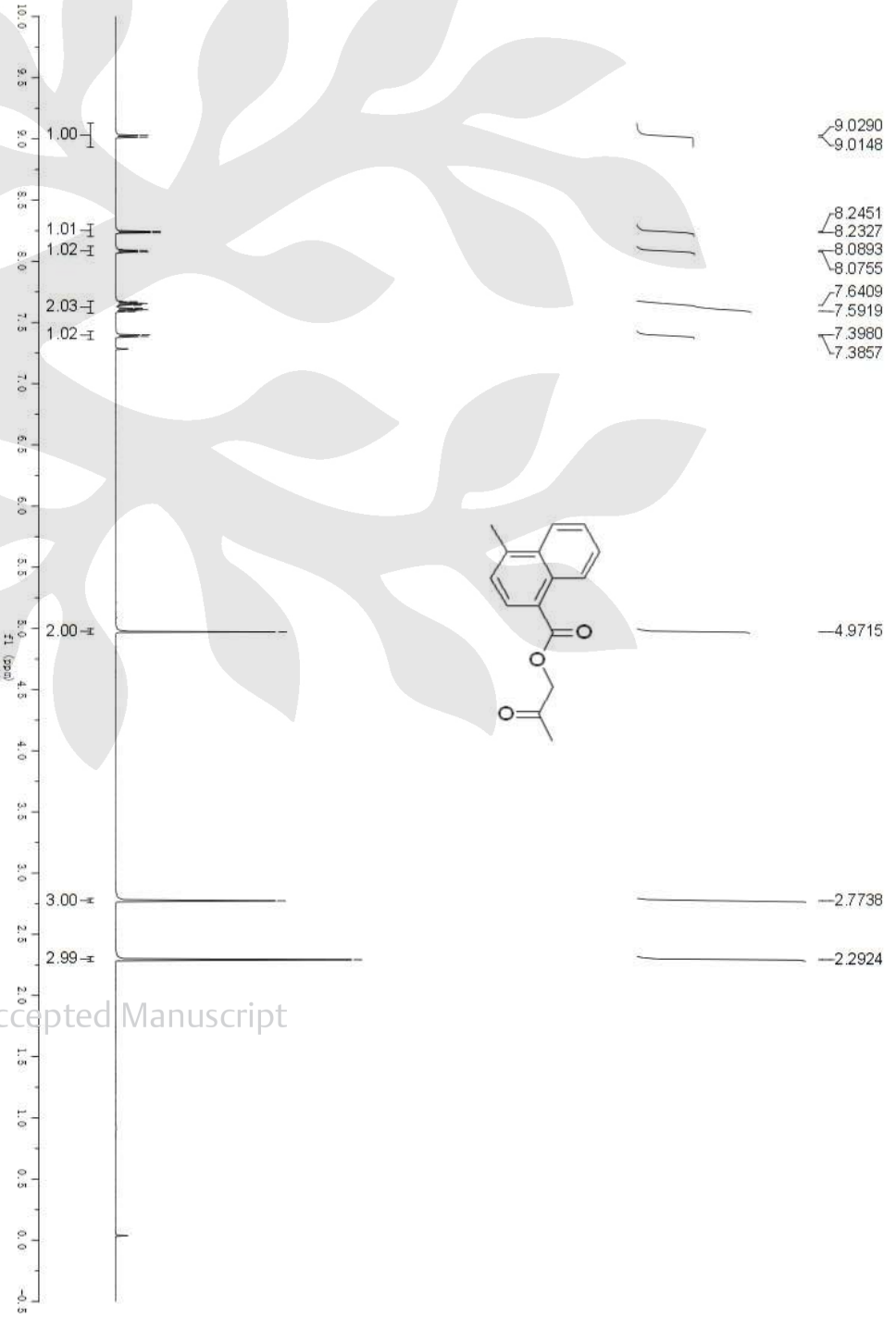
^{1}H NMR of 3bf

^{13}C NMR of 3bf

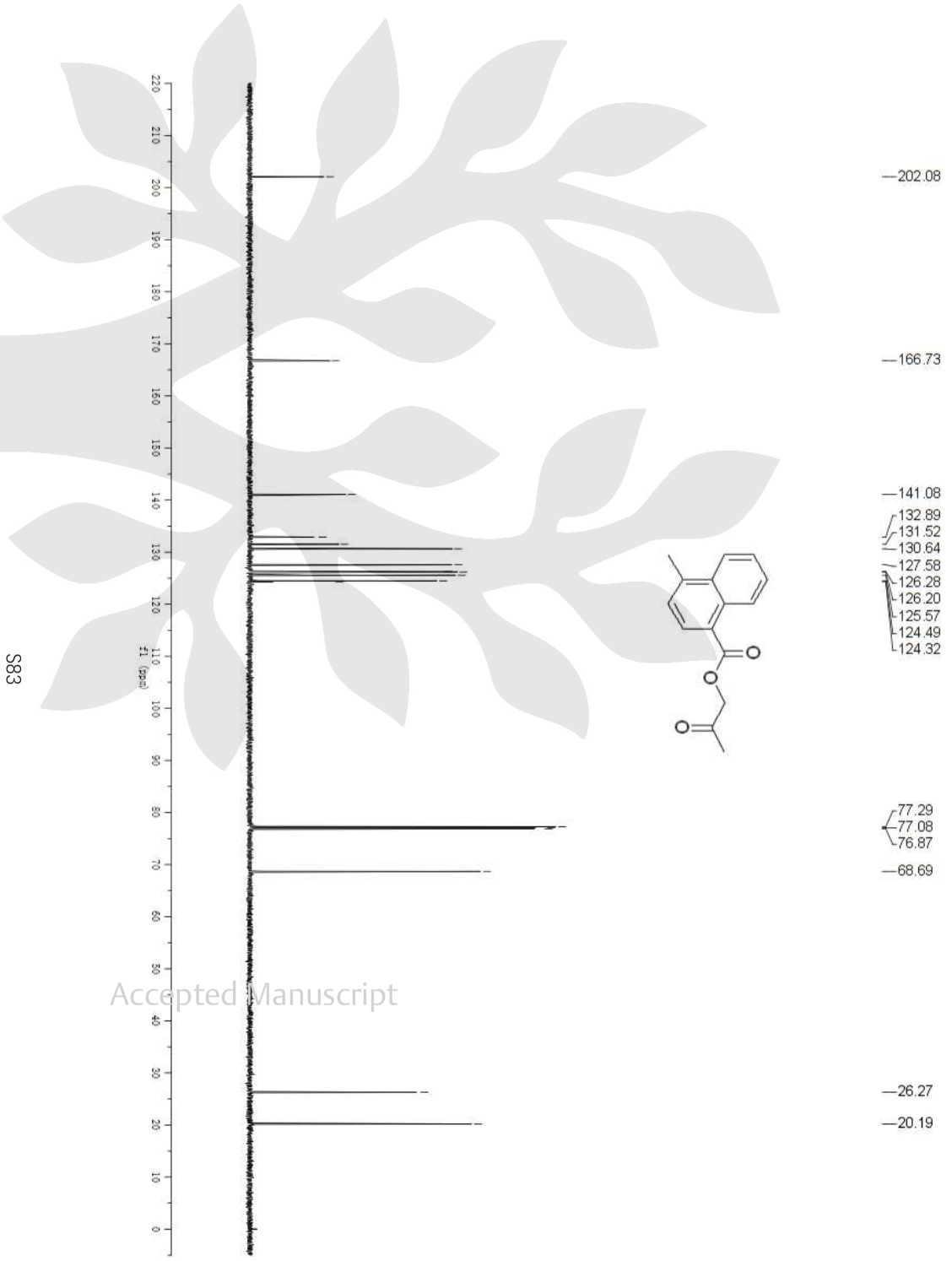


^{1}H NMR of 3bg

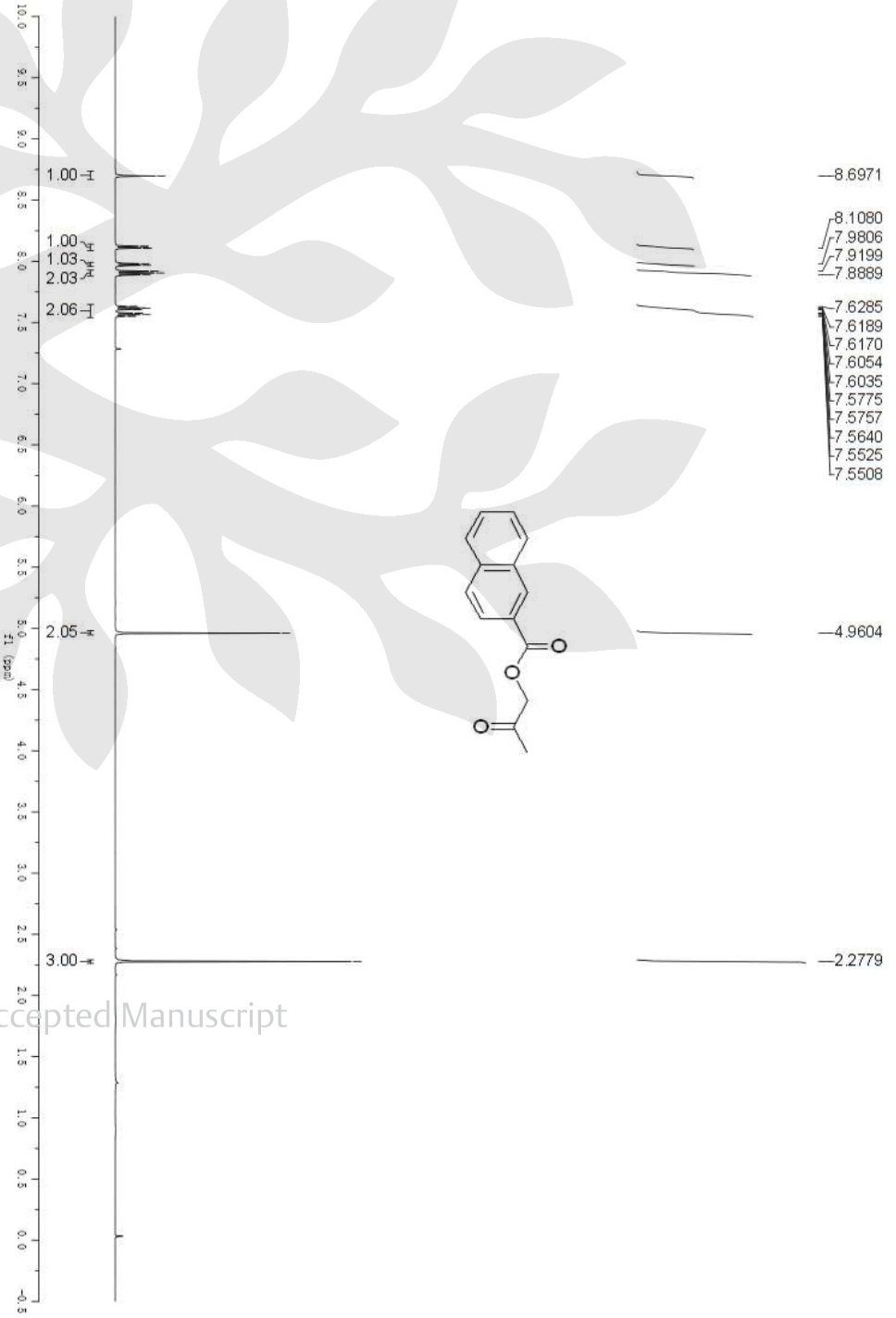
^{13}C NMR of 3bg



^{1}H NMR of 3bh

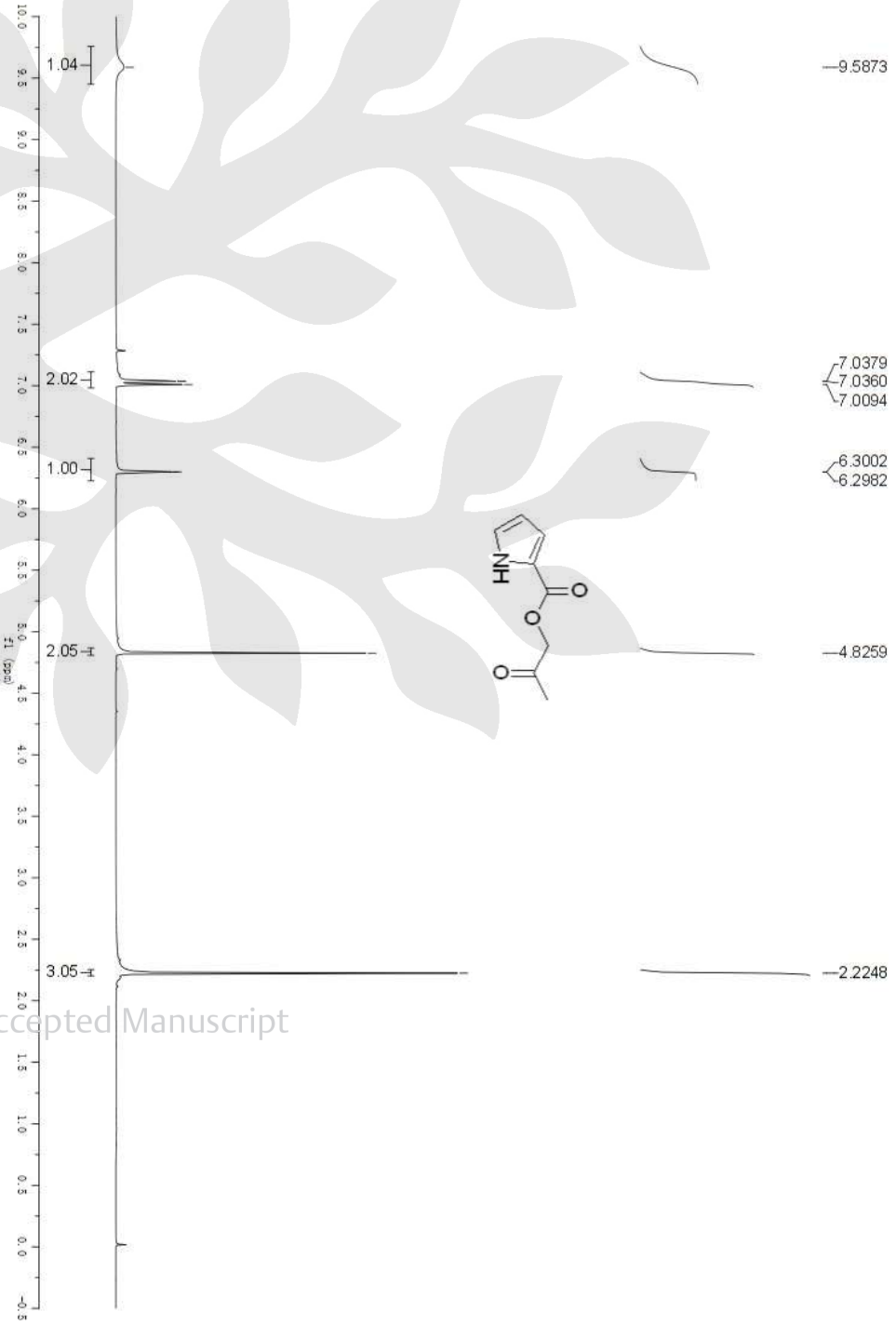


^{13}C NMR of 3bh

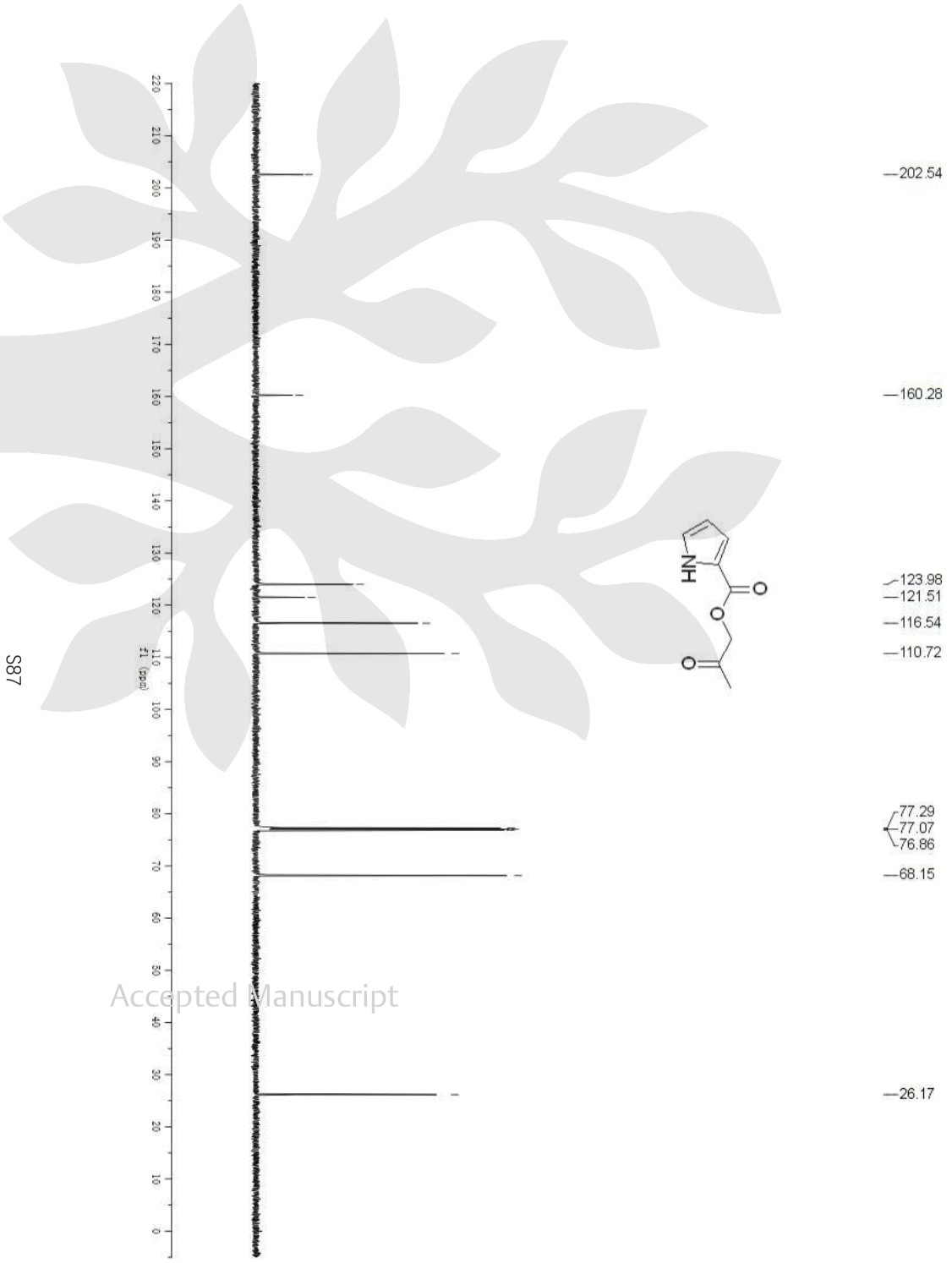


^{1}H NMR of 3bi

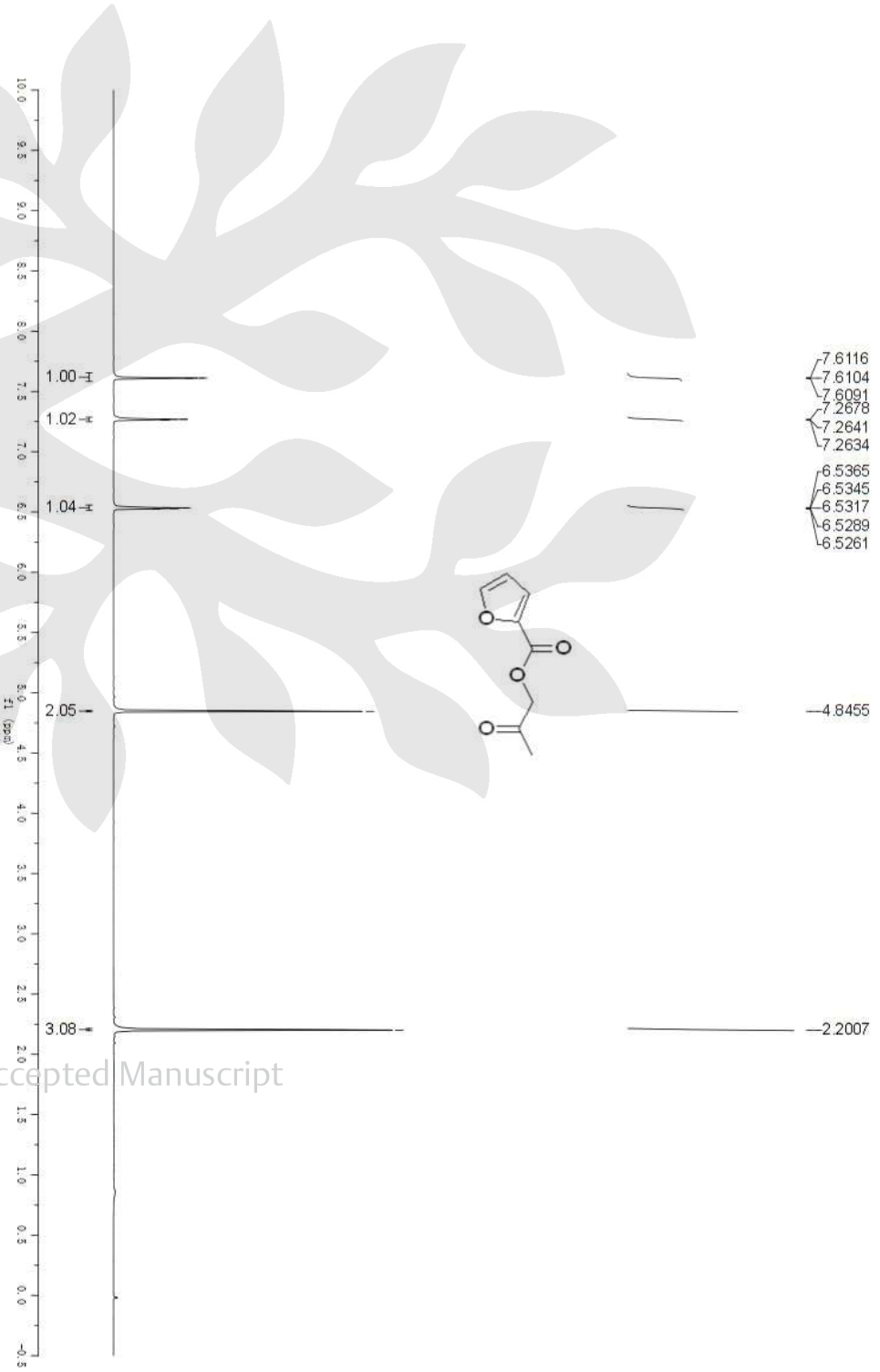
^{13}C NMR of 3bi



^{1}H NMR of 3bj

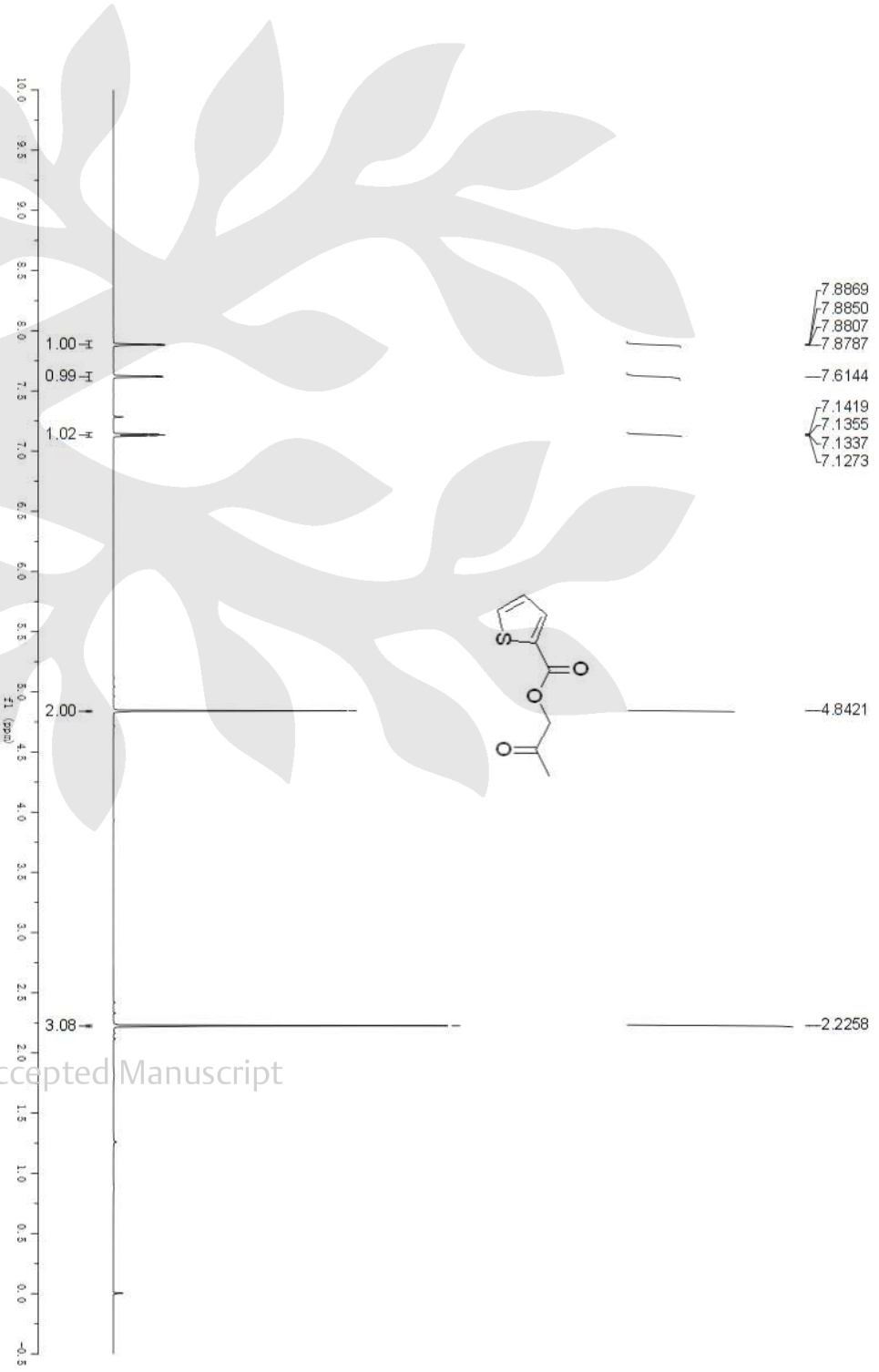


^{13}C NMR of 3bj

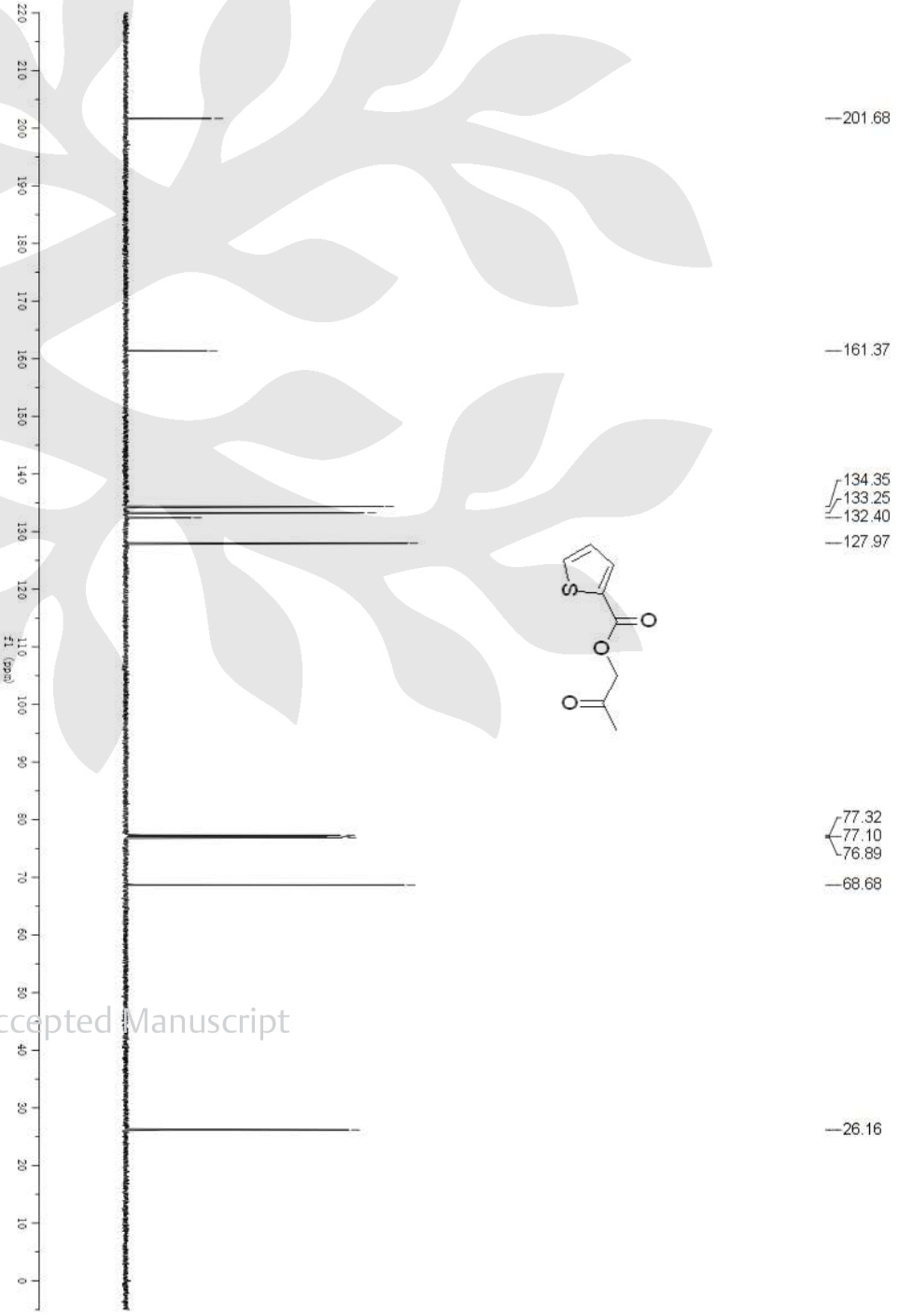


^{1}H NMR of 3bk

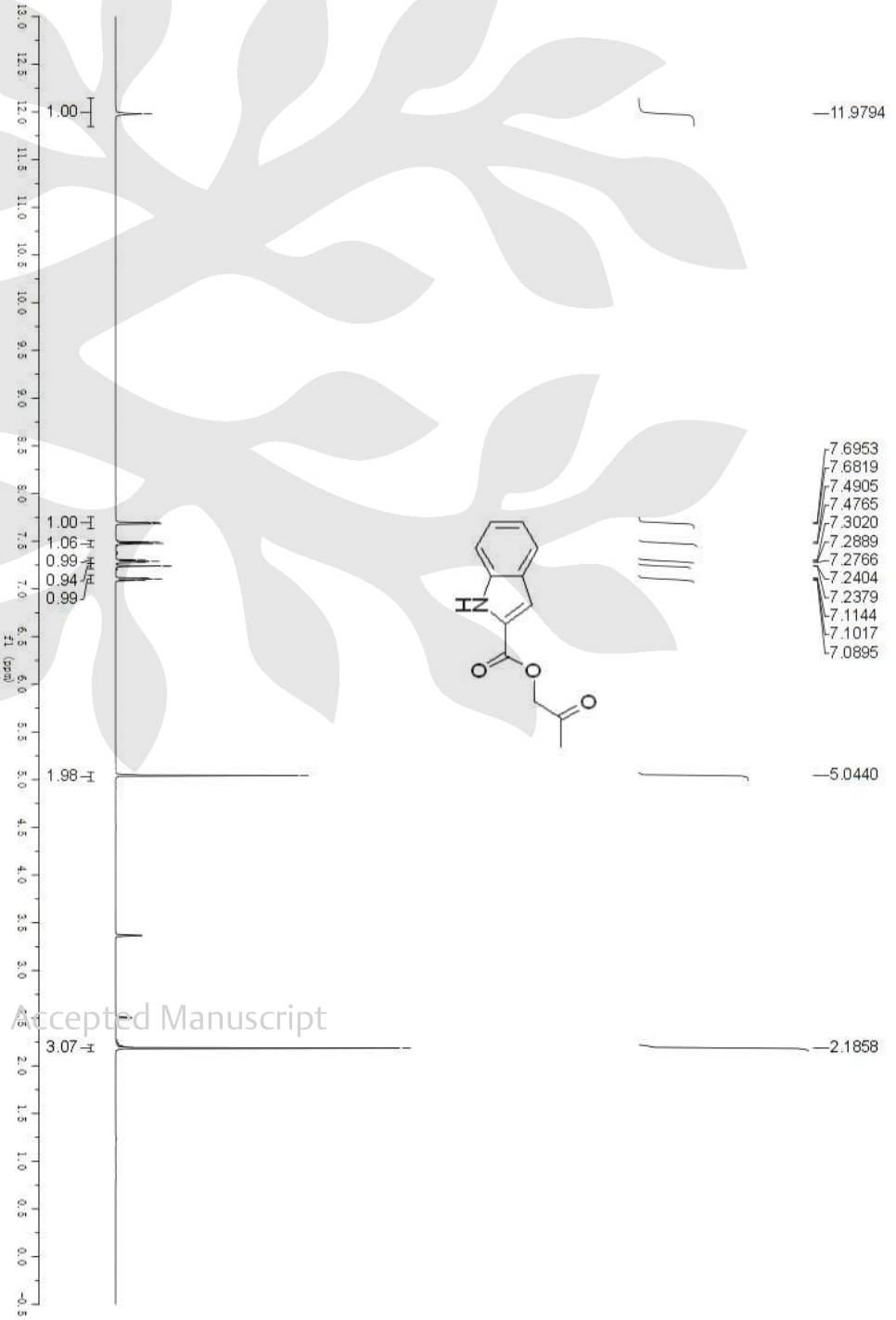
^{13}C NMR of 3bk



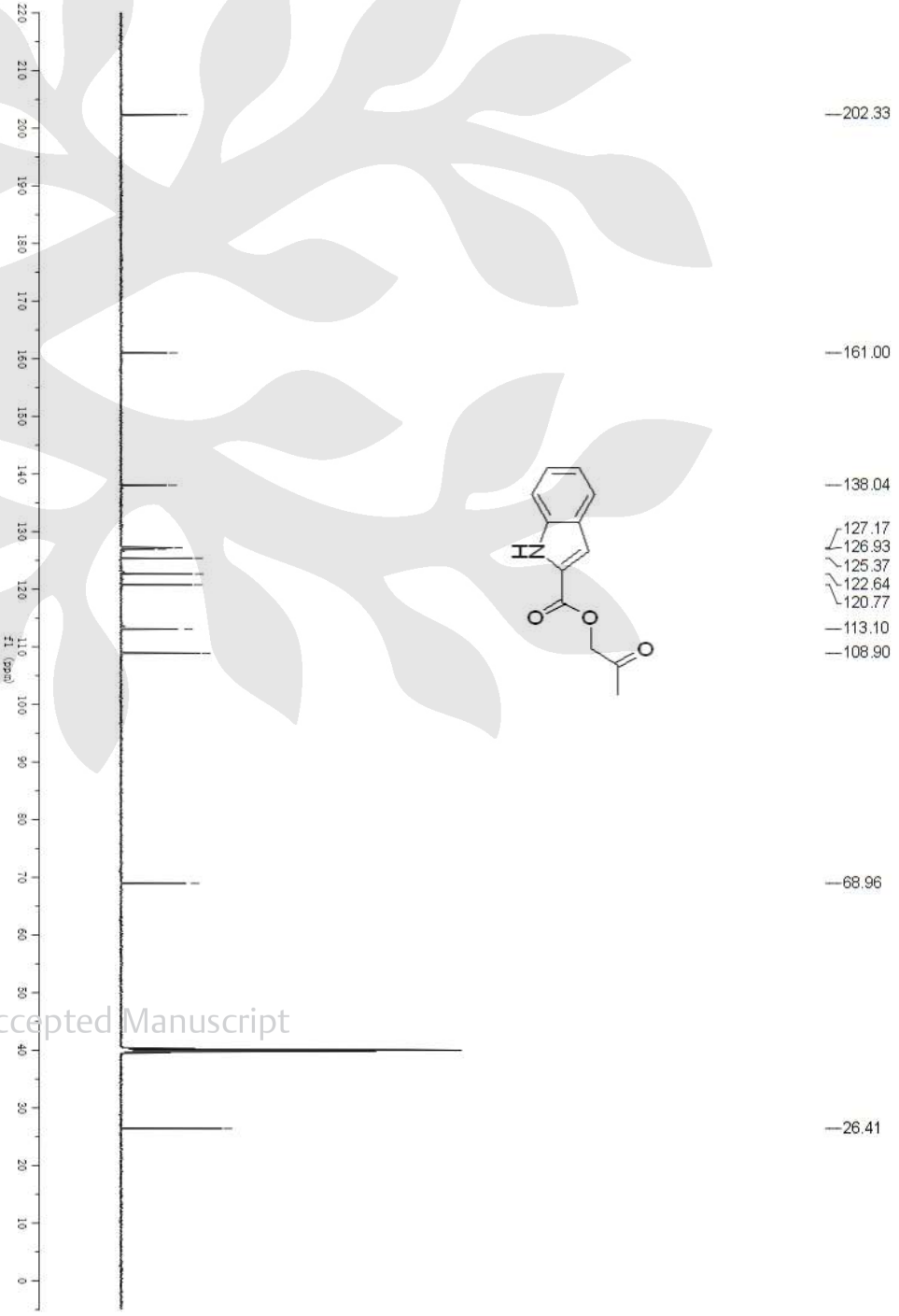
^{1}H NMR of 3bl



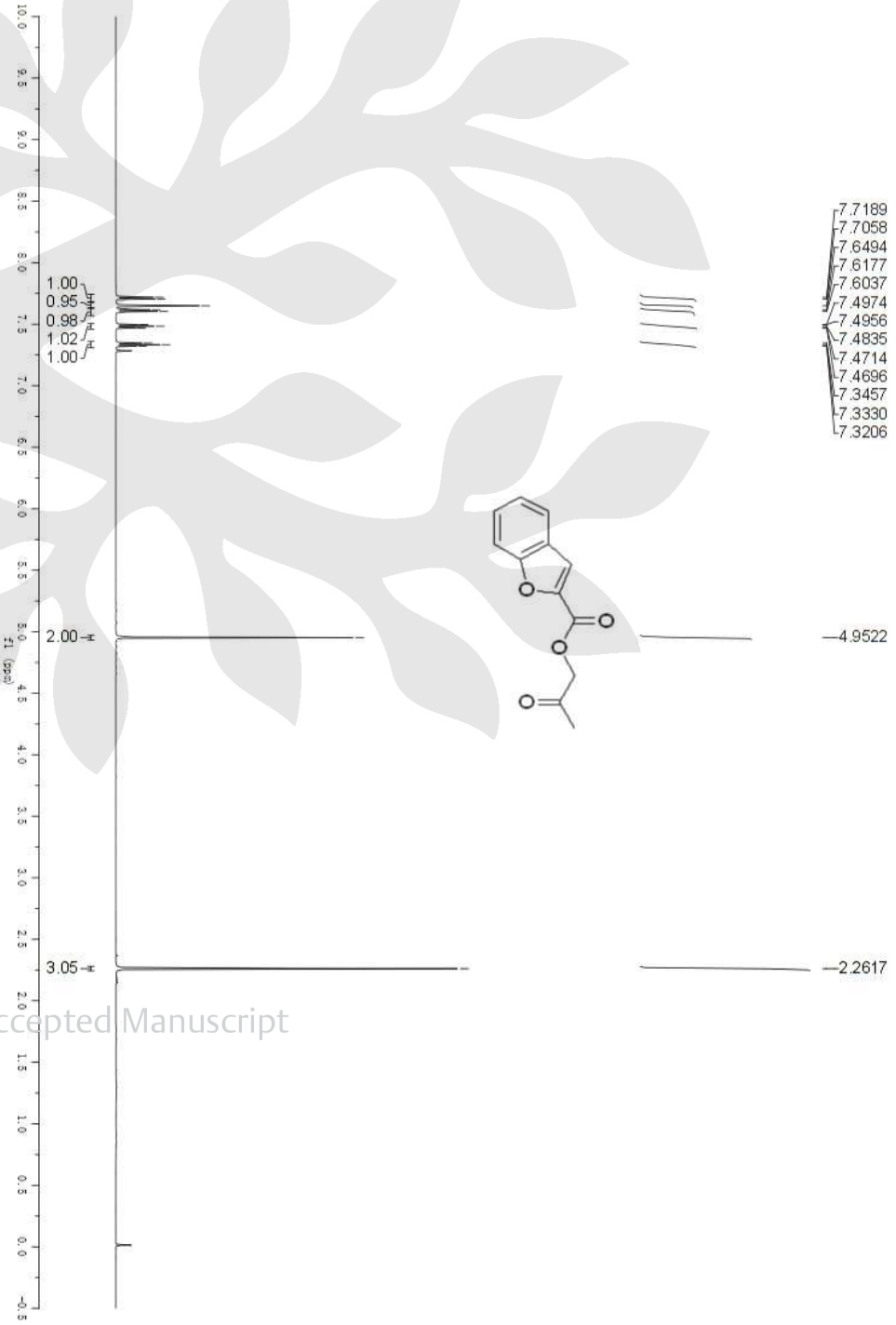
^{13}C NMR of 3bl



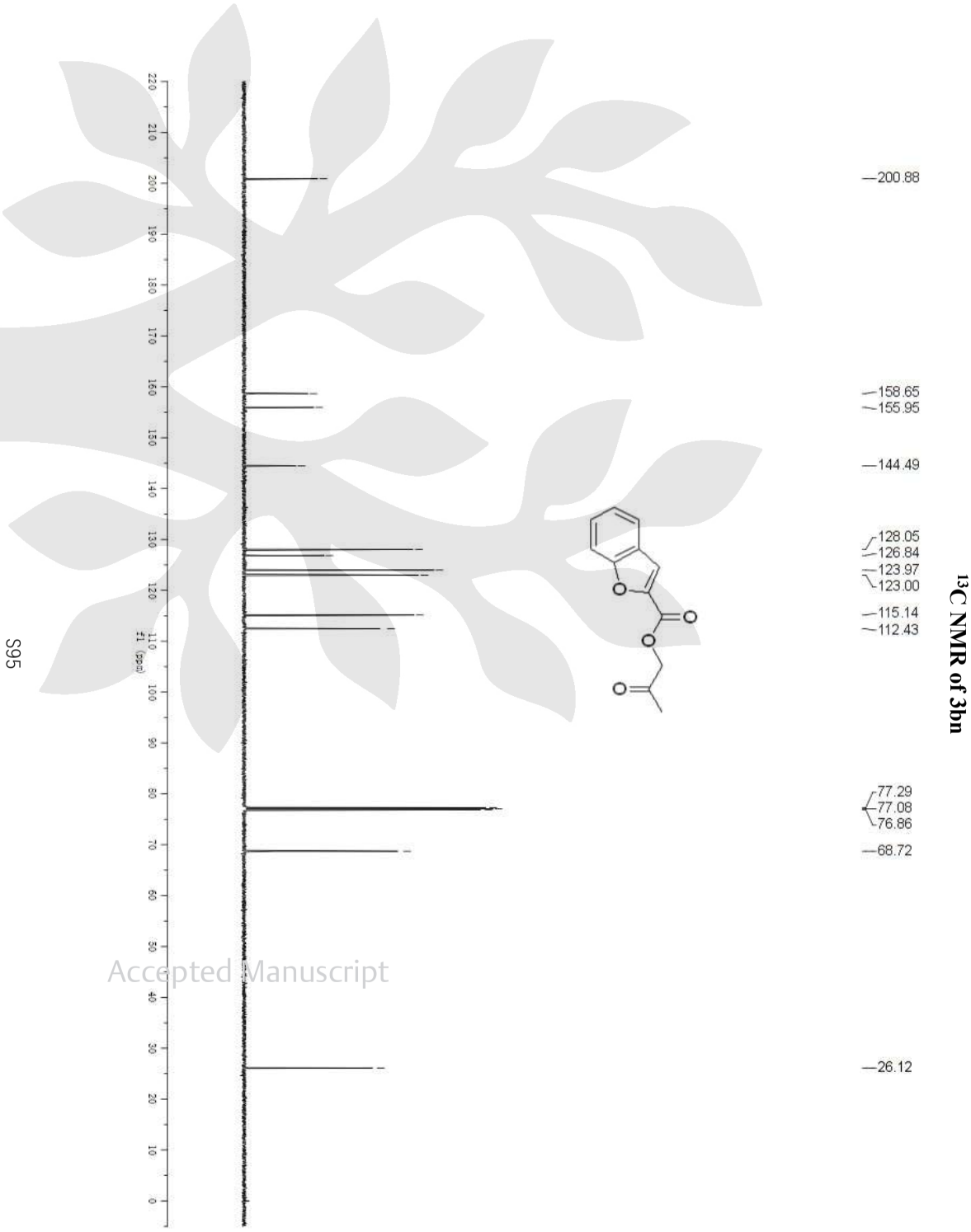
^{1}H NMR of 3bm



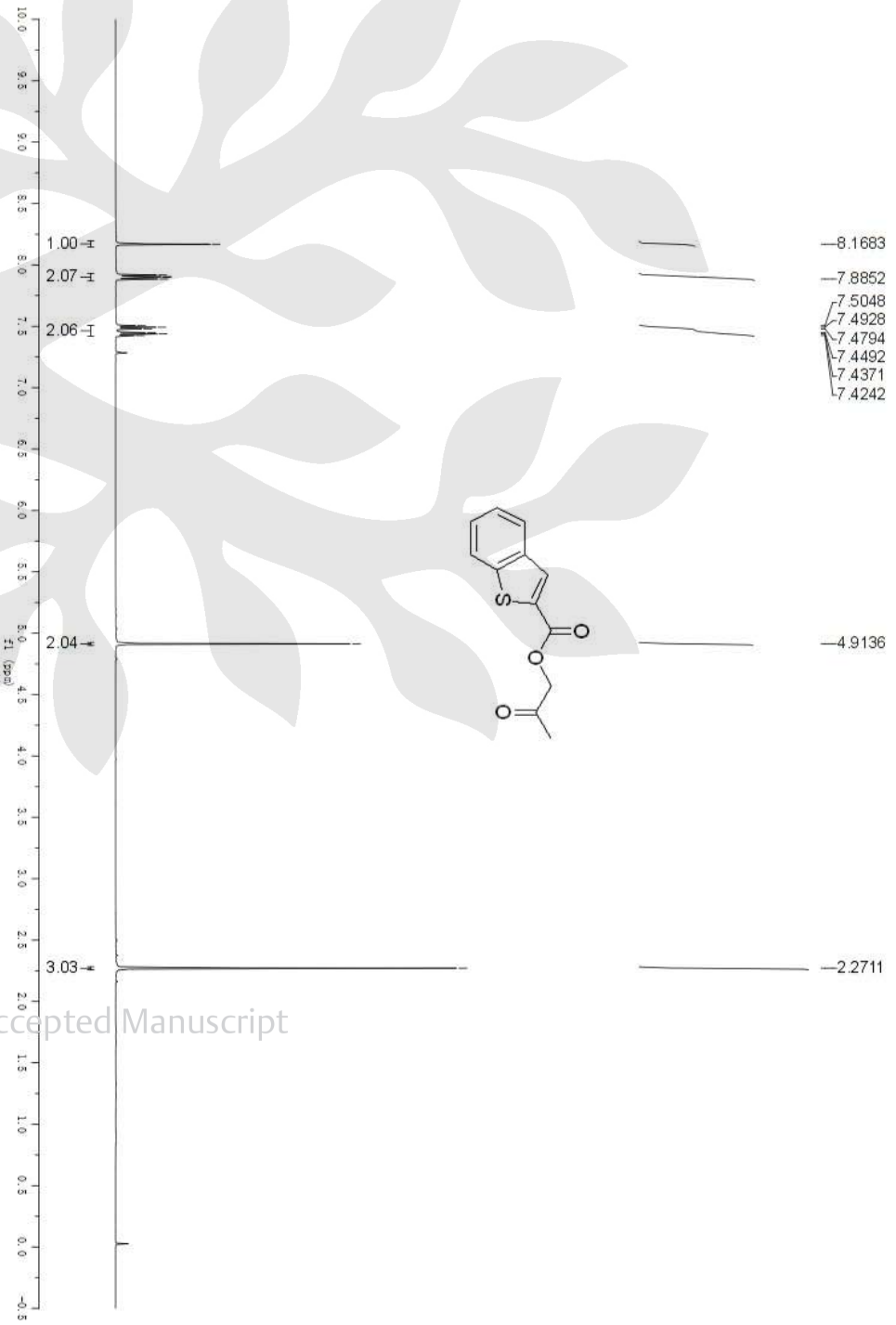
^{13}C NMR of 3bm



^{1}H NMR of 3bn

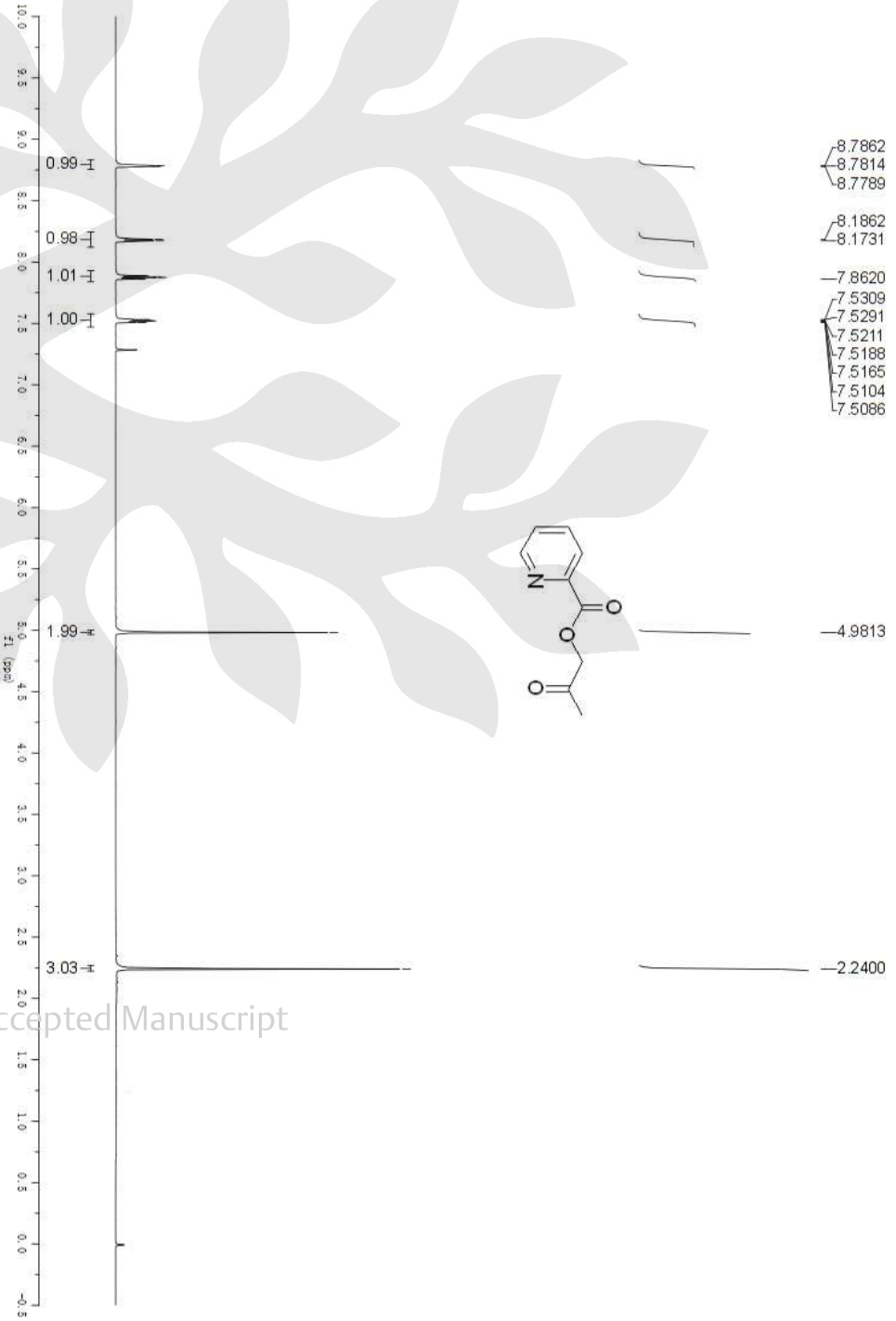


^{13}C NMR of 3bn



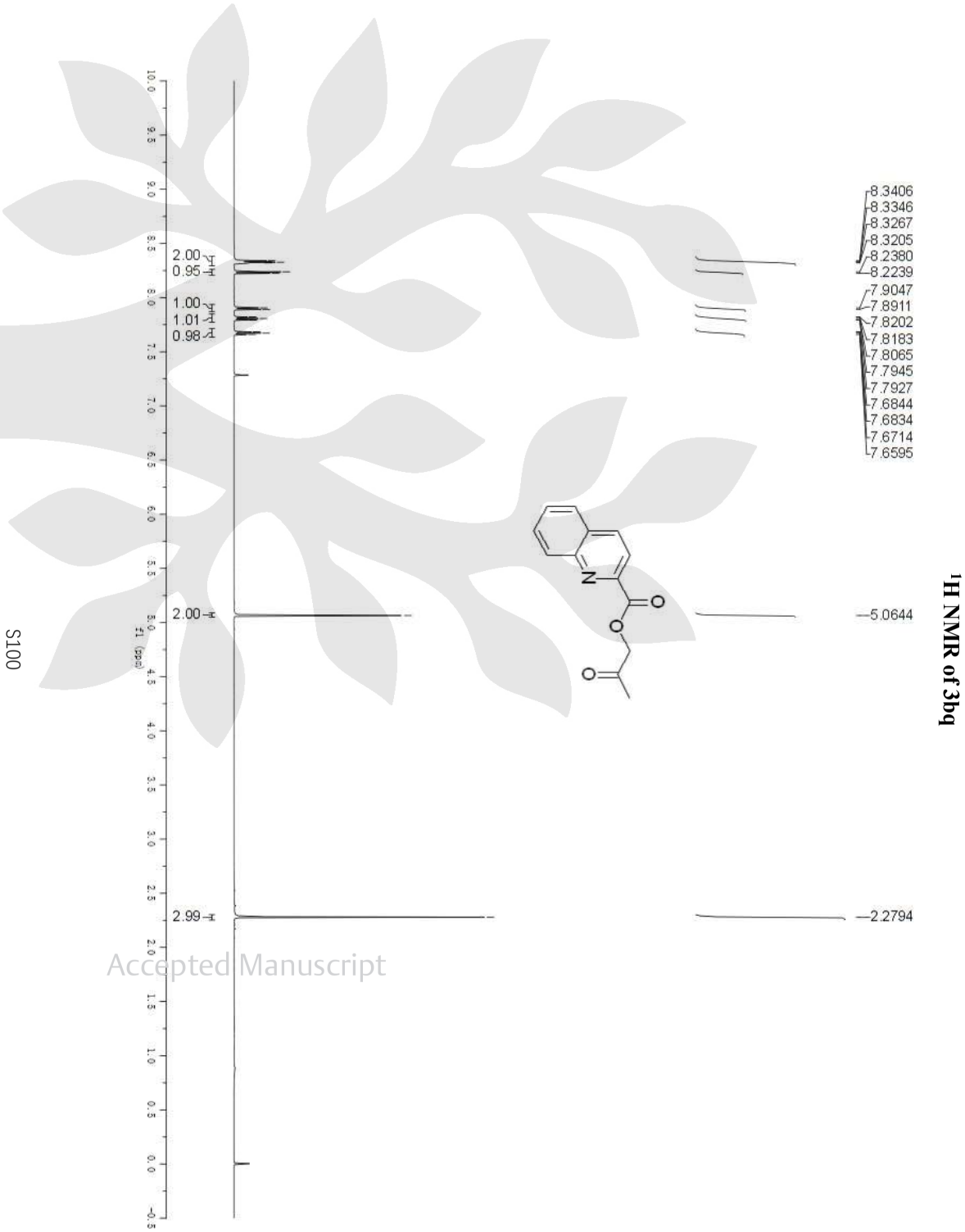
^{1}H NMR of 3bo

^{13}C NMR of 3bo

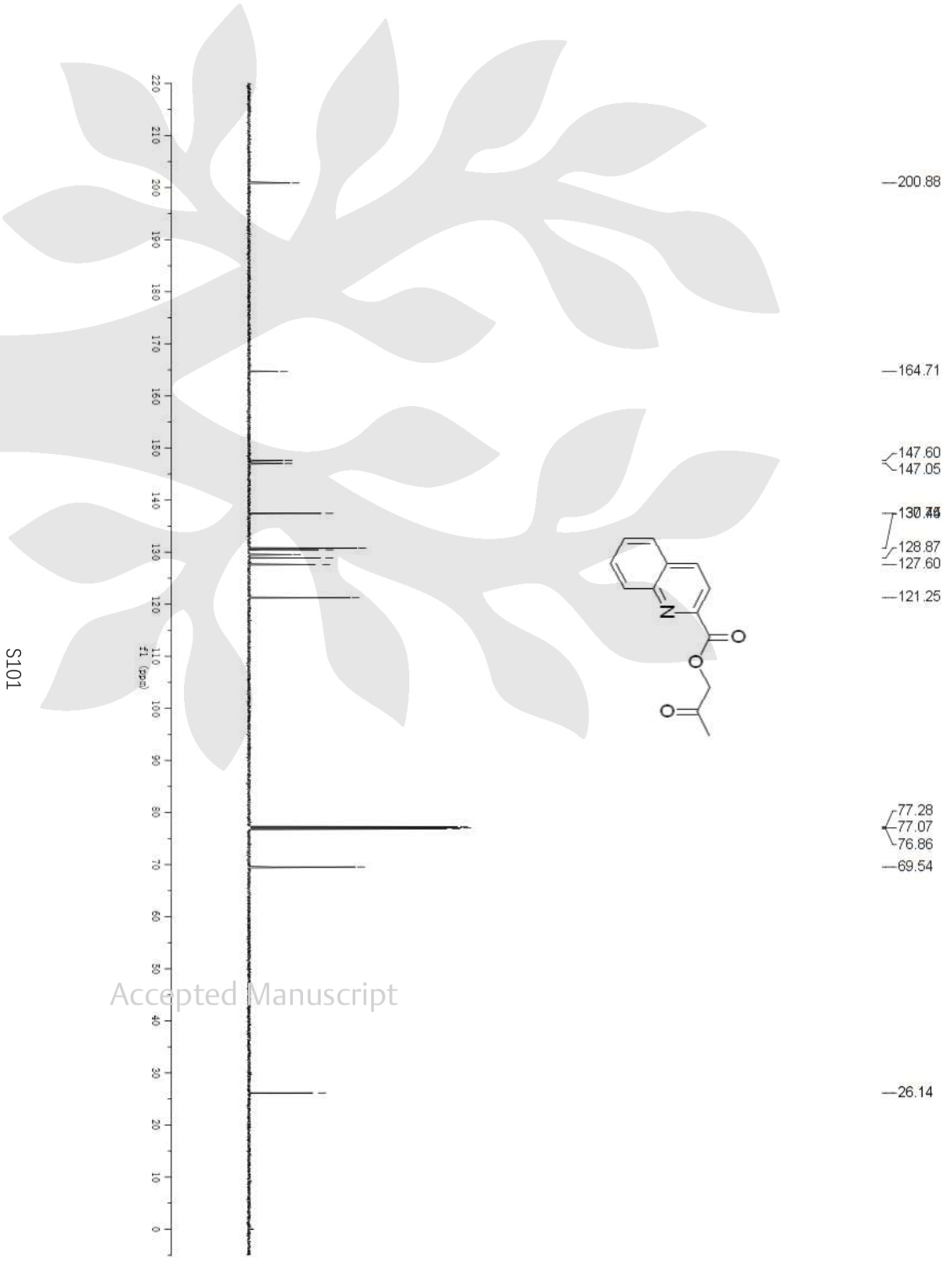


^{1}H NMR of 3bp

^{13}C NMR of 3bp



^{1}H NMR of 3bq



^{13}C NMR of 3bq