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Graphical Abstract

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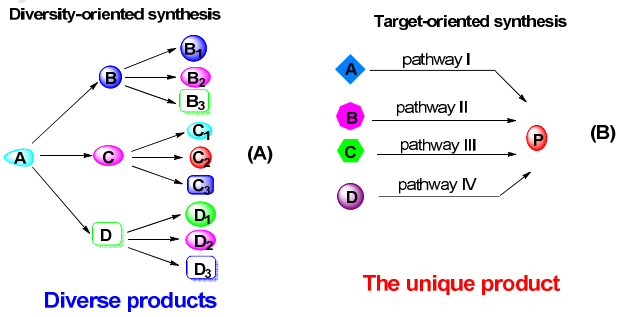
ABSTRACT

Target-oriented synthetic protocol was presented for the synthesis of 1,4-enediones. The approach can efficiently construct 1,4-enediones through different reaction pathways from multiform substrates α-halo aromatic ketones, 2-hydroxy-aromatic ketones and methyl carbinols. In this reaction, CuI was found to be the most efficient catalyst. Multiform substrates were also found to perform well to afford the products in a one-pot fashion.

1. Introduction

In recently years, many novel and versatile synthetic strategies have been proposed and utilized to obtain miscellaneous and sophisticated molecular structures. [1-6] In particular, diversity-oriented synthesis (DOS), which aims to generate a collection of structurally diverse small molecules from a given synthetic scheme, has been widely used in drug precursors screening and drug-discovery programmes.[1a-d] The process is well-known for converting simple starting materials into diverse molecules in a divergent manner (Scheme 1A). As an alternative to the divergent synthetic method, the target-oriented synthesis is also very important in synthetic chemistry and pharmaceutical chemistry (Scheme 1B).[1e-f] It is highly advantageous for chemists to have two or more distinct pathways for accessing the same target product during the process of natural products total synthesis or target-oriented synthesis. When considering the demands of actual synthesis, the development of miscellaneous protocols would be of high value in synthetic chemistry, as it would allow for changes in substrates and provide flexibility in synthetic plans.



Scheme 1 Diversity-oriented synthesis and target-oriented synthesis.

The 1,4-enedione is an important framework that is widely present in natural products and medicinal compounds.[7] By virtue of their multifunctional composition, 1,4-enediones can also serve as versatile precursors for the synthesis of furans, thiophenes, pyrroles and pyridazines.[8] In addition, they can perform many other useful transformations, such as Diels-Alder cyclization and Michael addition.[9] Although there have been many useful advancements in this area,[10] further research into

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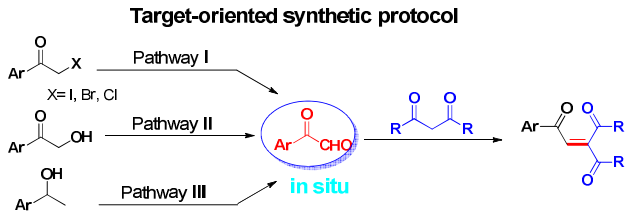
diverse methods to construct 1,4-enediones from simple and readily available starting materials remains highly desirable.



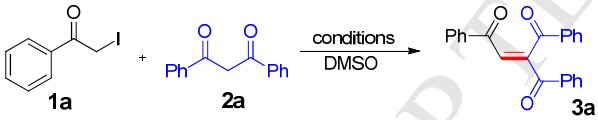
Scheme 2 Target-oriented synthetic protocol to access 1,4-enediones.

We herein report a target-oriented synthetic protocol to synthesize 1,4-enediones from 1,3-dicarbonyl compounds with α-halo aromatic ketones, 2-hydroxy-aromatic ketones and methyl carbinols (Scheme 2). In the process, different substrates α-halo aromatic ketones, 2-hydroxy-aromatic ketones and methyl carbinols were converted in situ through different reaction pathways into the same intermediate arylglyoxal, which was then utilized by 1,3-dicarbonyl compounds to afford 1,4-enediones.

2. Results and discussion

Initially, the reaction conditions were fully optimized with phenacyl iodine **(1a)** and dibenzoylmethane (**2a)** as model substrates. The reaction of **1a** with **2a** performed smoothly to afford the desired product with 72% yield in the presence of CuO in DMSO at 80 ℃. However, the same reaction in the absence of CuO provided a moderate yield (Entry 2). Thus, a series of catalysts, such as $Cu(OAc)_2$, CuI, CuBr, CuCl, $CuCl_2$, $CuBr_2$, $CuSO_4$ and $Cu(acac)_2$ were screened for the reaction (Table 1, Entries 3–10). Among them, CuI was found the most efficient catalyst for the transformation (Table 1, Entry 4). In addition, $CuSO_4$ and $Cu(OAc)_2$ also provided good results (Entries 3 and 9). The other catalysts provided only low to moderate yields. The influence of temperature was then investigated, the results shown that the reaction worked fine in the range of 80–100 ℃(Table 1, Entries 4, 11–12).

Table 1 Optimization of the reaction conditions [a]

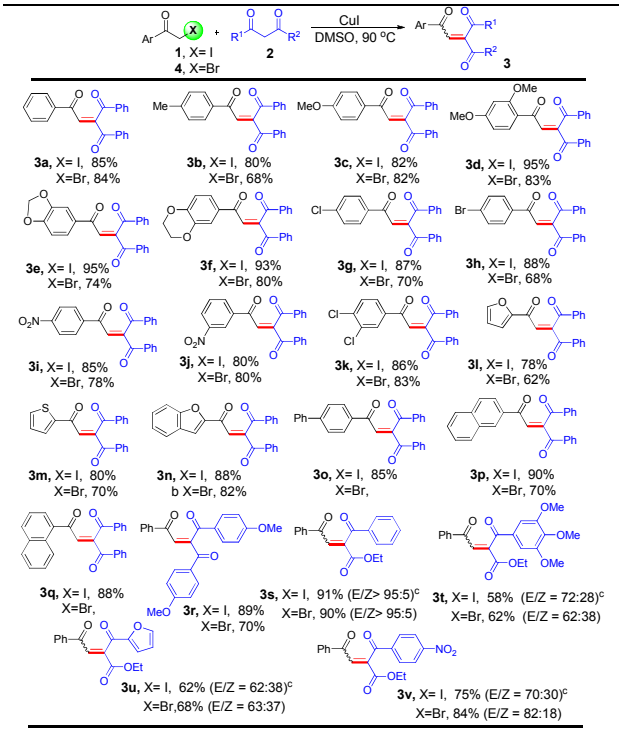


Entry	Catalyst /equiv	T / ℃	Time / h	Yield / % [b]
1	CuO (0.5)	80	12	72
2	-	80	24	52
3	$Cu(OAc)_2$ (0.5)	80	12	80
4	CuI (0.5)	80	6	84
5	CuBr (0.5)	80	12	65
6	CuCl (0.5)	80	12	68
7	$CuCl_2$ (0.5)	80	12	60
8	$CuBr_2$ (0.5)	80	12	45
9	$CuSO_4$ (0.5)	80	12	78
10	$Cu(acac)_2$ (0.5)	80	12	<10
11	CuI (0.5)	90	4	84
12	CuI (0.5)	100	4	84
13	CuI (0.5)	25	24	0

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol) in DMSO (3–5 mL). [b] Isolated yield.

The scope of the substrates was examined under the optimized conditions (Table 2); various substituted α-iodide aryl methyl ketones were thus employed in the transformation.[16] To our delight, all of the α-iodide aryl methyl ketones **1** proceeded smoothly to afford the desired products in moderate to high yields (Table 2, **3a**–**3v**, 58–95%). The electronic and steric properties of the substrates were seen to have little influence on the reaction efficiency. Both mono-substituted and multi-substituted α-iodide aryl methyl ketones **1** were employed in the reaction to provide the corresponding products in high yields (Table 2, 86-95%, **3d**–**3f** and **3k**). Notably, the substrates with heterocycle, such as furanyl (**1l**), thiophenyl (**1m**) and benzofuryl (**1n**) also reacted to furnish the corresponding products **3l-3n** in good yields (78–88%). Meanwhile, the substrates with 2-naphthyl (**1p**) and 1-naphthyl (**1q**) also reacted with **2a** to obtain satisfying results (**3p** and **3q**, 90% and 88% yields). The scope of substrate **2** was subsequently examined. The reaction was seen to tolerate substituted dibenzoylmethane **2b** to provide the expected product **3r** in 89% yield. Various β-keto esters were also employed for the reaction. Electron-neutral (H), electron-deficient (NO_2) and heterocycle (furanyl) containing β-keto esters provided satisfying results (**3s**, **3u**–**3v**, 62–91% yields). However, the strong electron-donating groups (3,4,5-OMe_3) attached to the phenyl of β-keto ester produced 58% yield (Table 2, **3t**). In these cases, the reaction afforded a mixture of *E*/*Z* isomers. α-Bromo aryl methyl ketones were also examined for the transformation (Table 2).[17] Regardless of their electronic or steric properties, all of the α-bromo aryl methyl ketones performed smoothly to afford their corresponding products **3a**–**3v** in good yields under the optimized conditions (62–90%; Table 2). The diversity of β-keto esters was also investigated for the reaction. All of the corresponding products were obtained in 62–90% yields (Table 2, **3s**–**3v**). Interestingly, the reactivity of α-bromo aryl methyl ketones was found to be very similar to that of α-iodide aryl methyl ketones.

Table 2. The scope of α-iodide/α-bromo aromatic ketones and 1,3-dicarbonyl compounds [a,b]



[a] The reaction was carried out with 1.0 equiv of **1** or **4**, 1.0

equiv of **2**, 50 mol% CuI in DMSO at 90 ℃ for 2–10 h. [b] Isolated yields. [c] *E:Z* ratio of compounds **3s**–**3v** determined by ^{1}H NMR.

In addition to α-iodide and α-bromo aryl methyl ketones, more challenging α-chloro aryl methyl ketones **5** were also examined (Table 3). To our delight, both electron-donating and electron-withdrawing groups attached to the phenyl rings of **5** could smoothly react with **2a** and **2b** to afford the corresponding products in moderate to good yields (Table 3, 56–93%). It was therefore determined that the overall reaction efficiency was not influenced by the electronic or steric properties of **5**. Yet, when the substrates ethyl benzoylacetate **2c** and ethyl 4-nitrobenzoylacetate **2f** were used as nucleophiles, only very low yields were obtained (**3s** and **3v**). Subsequently, some additives were added. The reaction efficiency showed no improvement with the addition of NaI, KI and TBAI. However, the yields were greatly improved when 1 equivalent of I_2 was added to the reaction system (Table 4, **3s** and **3v**).

Table 3 The scope of α-chloro aromatic ketones and 1,3-dicarbonyl compounds [a]

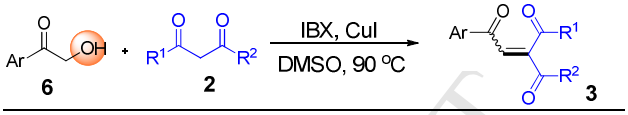
5 **2** **3**

Entry	Ar	2	3	Yield / % [b]
1	C_6H_5 (**5a**)		**3a**	85
2	4-Me-C_6H_4 (**5b**)		**3b**	88
3	4-Cl-C_6H_4 (**5g**)		**3g**	78
4	4-Br-C_6H_4 (**5h**)		**3h**	93
5	4-NO_2-C_6H_4 (**5i**)	**2a**	**3i**	90
6	3-NO_2-C_6H_4 (**5j**)		**3j**	92
7	2-naphthyl (**5p**)		**3p**	90
8	C_6H_5 (**5a**)	**2b**	**3r**	63
9[b]	C_6H_5 (**5a**)	**2c**	**3s**	15 (85)[c] *E/Z* > 95:5 [d]
10[b]	C_6H_5 (**5a**)	**2f**	**3v**	<10 (56)[c] *E/Z* = 65:35 [d]

[a] The reaction was carried out with 1.0 equiv of **5**, 1.0 equiv of **2**, 50 mol% CuI in DMSO at 90 ℃. [b] Isolated yields. [c] The reaction was carried out with 1.0 equiv of **5**, 1.0 equiv of **2**, 1.0 equiv of I_2, and 50 mol% CuI in DMSO at 90 ℃. [d] *E:Z* ratio of compounds **3s** and **3v** determined by ^{1}H NMR.

The substrates were subsequently extended to 2-hydroxy-aromatic ketones **6** (Table 4). On the basis of previous reports, we found that 2-hydroxy-aromatic ketones in the presence of IBX were easily transformed into 2-aryl-2-oxoacetaldehyde, which was then captured by dibenzoylmethane **2a** to afford the desired products in good yields. In addition, the scope of 2-hydroxy-aromatic ketones and 1,3-diketones was examined in the presence of IBX (0.8 equiv) and CuI (0.5 equiv). Electron-neutral (H, Me), electron-donating (OMe) and electron-withdrawing (Br, NO_2) groups attached to the phenyl ring of **6** were found tolerable in the reaction to produce yields of 60–75% (Table 4, **3a–3c**, **3h** and **3i**). Nucleophiles 1,3-bis(4-methoxyphenyl)propane-1,3-dione **2b** and ethyl benzoylacetate **2c** also reacted with 2-hydroxy-aromatic ketones to obtain the corresponding products in 60% and 68% yields, respectively (Table 4, **3r** and **3s**).

Table 4 The scope of 2-hydroxy-aromatic ketones and 1,3-dicarbonyl compounds [a]

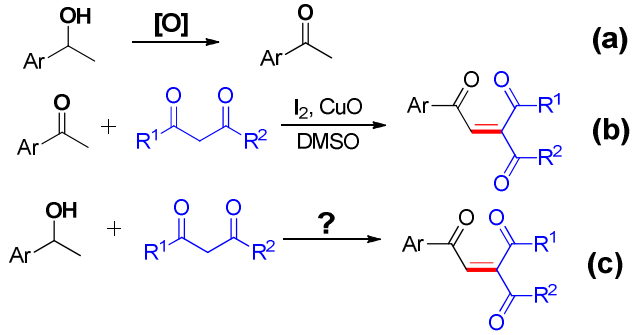


6 **2** **3**

Entry	Ar	2	3	Yield / % [b]
1	C_6H_5 (**6a**)		**3a**	72
2	4-Me-C_6H_4 (**6b**)		**3b**	65
3	4-OMe-C_6H_4 (**6c**)	**2a**	**3c**	73
4	4-Cl-C_6H_4 (**6g**)		**3g**	74
5	4-Br-C_6H_4 (**6h**)		**3h**	75
6	C_6H_4 (**6a**)	**2b**	**3r**	60
7	C_6H_5 (**6a**)	**2c**	**3s**	68 (*E/Z* > 95:5) [c]

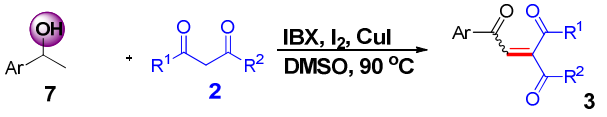
[a] The reaction was carried out with 1.0 equiv of **6**, 1.0 equiv of **2**, 0.8 equiv of IBX, 50 mol% CuI in DMSO at 90 ℃. [b] Isolated yields. [c] *E:Z* ratio of compounds **3s** determined by ^{1}H NMR.

Methyl carbinols **7** are widely known for their ability to oxidize into methyl ketones **8** in the presence of oxidant (Scheme 3a).[12] In our previous studies, we found that methyl ketones could easily react with 1,3-diketones to afford the desired 1,4-enediones (Scheme 3b).[11] We therefore wanted to examine the possibility of affording 1,4-enediones from methyl carbinols and 1,3-diketones (Scheme 3c). After many optimized processes, it was found that methyl carbinols **8** could react with 1,3-diketones **2** to obtain the desired 1,4-enediones **3** in the presence of IBX (0.75 equiv), I_2 (1.0 equiv) and CuI (0.5 equiv) in DMSO at 90 ℃. With the optimized conditions in hand, the generality, electronic and steric properties of the substrates **7** were evaluated. Both the electron-donating and electron-withdrawing groups attached to the phenyl rings of **7** could obtain the corresponding products **3a-3h** (Table 5, 58-85% yields). The steric influence was not obvious in the reaction. The substrates 1,3-bis(4-methoxyphenyl)propane-1,3-dione **2b** and ethyl benzoylacetate **2c** were also found suitable for the transformation, obtaining the corresponding products in 48% and 63% yields, respectively (Table 5, **3r** and **3s**).



Scheme 3 Synthesis of 1,4-enediones from methyl carbinols and 1,3-dicarbonyl compounds in one-pot

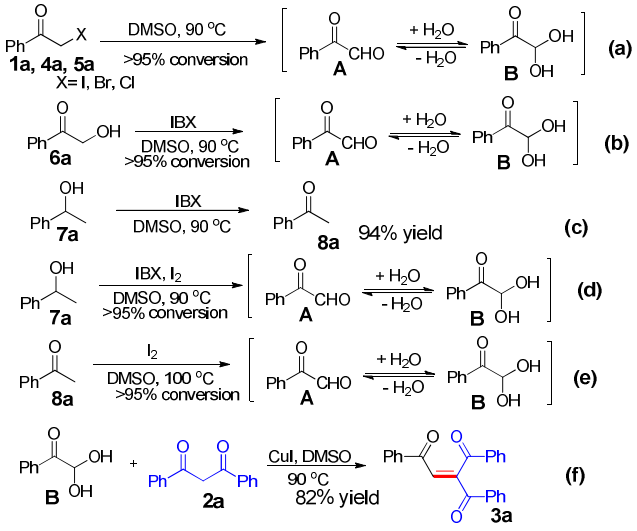
Table 5 The scope of methyl carbinols and 1,3-dicarbonyl compounds [a]



Entry	Ar	2	3	Yield / % [b]
1	C_6H_5 (**7a**)		**3a**	84
2	4-Me-C_6H_4 (**7b**)		**3b**	85
3	4-OMe-C_6H_4 (**7c**)	**2a**	**3c**	65
4	2-OMe-C_6H_4 (**7w**)		**3w**	60
5	4-Br-C_6H_4 (**7h**)		**3h**	58
6	C_6H_4 (**7a**)	**2b**	**3r**	48
7	C_6H_5 (**7a**)	**2c**	**3s**	63 (*E*/*Z* = 90:10) [c]

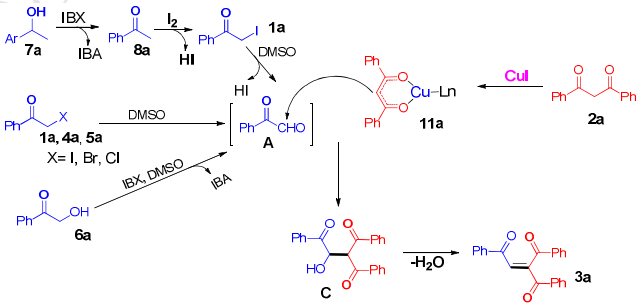
[a] The reaction was carried out with **7** (1.0 equiv), **2** (1.0 equiv), IBX (0.75 equiv), I_2 (1.0 equiv) and 50 mol% CuI in DMSO at 90 ℃. [b] Isolated yields. [c] *E*:*Z* ratio of compounds **3s** determined by ^{1}H NMR.

As shown in Scheme 4, various control experiments were performed. It was found that α-halo methyl ketones (**1a**, **4a**, **5a**) could be converted to the same product phenylglyoxal (**A**) with excellent conversion in DMSO at 90 ℃ (Scheme 4a). 2-Hydroxy-1-phenylethanone **6a** was also oxidized to afford phenylglyoxal (**A**) by IBX in DMSO (Scheme 4b).[13] IBX was shown to efficiently oxidize 1-phenylethanol **7a** to furnish acetophenone **8a** in a quantitative 94% yield (Scheme 4c). With the addition of IBX and I_2 to 1-phenylethanol **7a**, the product phenylglyoxal **A** was produced (Scheme 4d).[13] Moreover, I_2 and DMSO oxidized acetophenone **8a** to produce phenylglyoxal **A** in quantitative conversion at 100 ℃ (Scheme 4e).[14] The reaction of hydrated phenylglyoxal **B** with dibenzoylmethane **2a** also performed efficiently with a good yield of 82% (Scheme 4f).



Scheme 4 Control experiments.

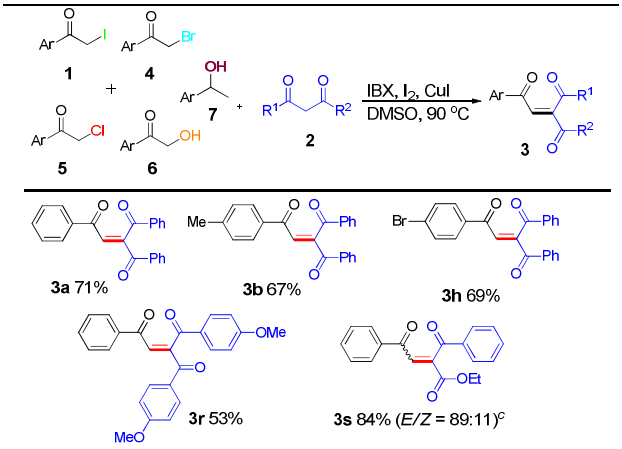
Based on the above results, we proposed a possible mechanism for the present reactions (Scheme 5). Initially, carbinol **7a** was oxidized by IBX to afford acetophenone **8a**, which was followed by iodination and Kornblum oxidation to provide phenylglyoxal (**A**). α-Halo aryl methyl ketones (**1a**, **4a** and **5a**) and 2-hydroxy-1-phenylethanone (**6a**) were oxidized by either IBX or DMSO to afford phenylglyoxal (**A**). Meanwhile, dibenzoylmethane (**2a**) was activated by CuI to form intermediate **11a**.[15] Activated intermediate **11a** subsequently reacted with phenylglyoxal (**A**) to obtain intermediate **C**. Finally, intermediate **C** underwent dehydration to afford the desired product 1,4-enedione **3a**.



Scheme 3 The proposed mechanism for the transformation.

With the aforementioned successful results in hand, we attempted to integrate the miscellaneous reactions (Table 2–5) into one pot, thus providing a successful novel model of domino reaction. To our delight, the reaction could efficiently perform in the conditions of IBX (1.5 equiv), I_2 (0.8 equiv), CuI (2.5 equiv) in DMSO at 90 ℃. The scope of the substrates was also examined (Table 6); it was found that both the electron-donating and electron-withdrawing groups attached to the phenyl rings of substrates **1**, **4**, **5**, **6** and **7** could afford the corresponding 1,4-enediones (Table 6, **3a**–**3b**, **3h**). Nucleophiles 1,3-diketones **2b**–**2c** were also tolerated in the reaction to obtain the corresponding products in 53% and 84% yields, respectively (**3r** and **3s**). The results demonstrate that an efficient integrated domino synthetic strategy is feasible under suitable conditions.

Table 6 Multiform substrates performed in a one-pot fashion. [a,b]



[a] The reaction was carried out with **1** (1.0 equiv), **4** (1.0 equiv), **5** (1.0 equiv), **6** (1.0 equiv), **7** (1.0 equiv), **2** (5.0 equiv), CuI (2.5 equiv), I_2 (0.8 equiv) and IBX (1.5 equiv) in DMSO at 90 ℃. [b] Isolated yields. [c] *E*:*Z* ratio of compounds **3s** determined by ^{1}H NMR.

3. Conclusion

In conclusion, a target-oriented synthetic protocol has been developed for the construction of 1,4-enediones. In this reaction, multiform substrates α-halo aromatic ketones, 2-hydroxy-aromatic ketones and methyl carbinols could react with 1,3-dicarbonyl compounds to afford 1,4-enediones through different pathways. CuI was identified as a powerful catalyst for the reaction. The reaction was advantageous due to its simple and readily available starting materials, inexpensive catalyst and wide substrate scope; it should therefore prove highly valuable in organic chemistry.

4. Experimental

4.1. General method

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh).

IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. NMR spectra were recorded on a Varian Mercury 400 or 600 MHz spectrometer Chemical shifts are reported in ppm ($CDCl_3$ δ 7.26 for ^{1}H NMR and 77.0 for ^{13}C NMR, ppm), relative to the internal standard of tetramethylsilane (TMS), multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz). HRMS were obtained on a Bruker Apex-Ultra 7.0T FTMS equipped with an electrospray source (ESI) or Atmospheric-pressure chemical ionization (APCI).

4.2.1 General procedure for preparation of 3 from 1, 4 and 5 (3a as an example):

A sealed tube was charged with α-iodide aromatic ketone **1a** (123 mg, 0.5 mmol), dibenzoylmethane **2a** (112 mg, 0.5 mmol), and CuI (47.6 mg, 0.25 mmol) at room temperature, and then solvent DMSO (3 mL) was added. The resulting mixture was stirred at 90 ℃, after disappearance of the reactant (monitored by TLC), then added 50mL water to the mixture, extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield the desired product **3a** as a yellow solid.

4.2.2 General procedure for preparation of 3 from 2-hydroxy-aromatic ketones 6 (3a as an example):

A sealed tube was charged with 2-hydroxy aromatic ketone **6a** (136 mg, 1.0 mmol), dibenzoylmethane **2a** (224 mg, 1.0 mmol), IBX (224 mg) and CuI (95 mg, 0.5 mmol) at room temperature, and then solvent DMSO (3 mL) was added. The resulting mixture was stirred at 90 ℃, after disappearance of the reactant (monitored by TLC), then added 50mL water to the mixture, extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield the desired product **3a** in 72% yield.

4.2.3 General procedure for preparation of 3 from Methyl carbinols 7 (3a as an example):

A sealed tube was charged with methyl carbinol **7a** (122 mg, 1.0 mmol), dibenzoylmethane **2a** (224 mg, 1.0 mmol), IBX (210 mg, 0.75 mmol) and CuI (95 mg, 0.5 mmol) at room temperature, and then solvent DMSO (3 mL) was added. The resulting mixture was stirred at 90 ℃, after disappearance of the reactant (monitored by TLC), then added 50mL water to the mixture, extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield the desired product **3a** in 84% yield.

4.3. Spectroscopic data

4.3.1 2-Benzoyl-1,4-diphenylbut-2-ene-1,4-dione **(3a):** yellow solid, mp 101–103 ℃ (lit[11] mp 101–102 ℃); IR (KBr): 3443, 3056, 1685, 1641, 1594, 1444, 1360, 1266, 1212, 1006 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.6 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 4H), 7.42-7.54 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =193.9, 193.8, 188.6, 152.7, 136.2, 135.8, 135.6, 134.1, 133.7, 130.9, 130.2, 129.1, 128.9, 128.8, 128.74, 128.68; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{16}NaO_3$: 363.0992; found: 363.0987.

4.3.2 2-Benzoyl-1-phenyl-4-(p-tolyl)but-2-ene-1,4-dione **(3b):** yellow solid, mp 109–111 ℃; IR (KBr): 3459, 3059, 1666, 1646, 1597, 1448, 1377, 1317, 1268, 1232, 1209, 1180, 1125, 1103, 1019 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.6 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.50-7.58 (m, 5H), 7.42-7.48 (m, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 192.9, 188.0, 152.3, 145.3, 135.7, 135.5, 134.0, 133.7, 133.6, 131.0, 130.2, 129.6, 129.0, 128.9, 128.8, 128.7, 21.7; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{24}H_{19}O_3$: 355.1329; found: 355.1329.

4.3.3 2-Benzoyl-4-(4-methoxyphenyl)-1-phenylbut-2-ene-1,4-dione **(3c):** yellow solid, mp 125–127 ℃; IR (KBr): 3058, 2938, 1662, 1643, 1594, 1569, 1512, 1447, 1426, 1372, 1318, 1275, 1228, 1172, 1123, 1009 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 5.2 Hz, 2H), 7.99 (d, *J* = 5.2 Hz, 2H), 7.88 (d, *J* = 6.0 Hz, 2H), 7.64 (t, *J* = 4.8 Hz, 1H), 7.51-70.54 (m, 4H), 7.44 (t, *J* = 5.2 Hz, 2H), 6.91 (d, *J* = 6.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 193.0, 186.8, 164.3, 151.9, 134.0, 133.5, 131.3, 130.2, 129.3, 129.0, 128.8, 128.6, 114.1, 55.5; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{24}H_{19}O_4$: 371.1278;

found: 371.1278.

4.3.4 2-Benzoyl-4-(2,4-dimethoxyphenyl)-1-phenylbut-2-ene-1,4-dione **(3d):** yellow solid, mp 121–123 ℃; IR (KBr): 3097, 1683, 1667, 1642, 1612, 1596, 1597, 1529, 1520, 1482, 1445, 1352, 1315, 1293, 1276, 1225, 1168, 1100, 1019, 1000 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (t, J = 8.0 Hz, 4H), 7.63 (d, J = 15.2 HZ, 1H), 7.60 (s, 2H), 7.48-7.52 (m, 3H), 7.42 (t, J = 8.0 Hz, 2H), 6.45 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 6.39 (t, J = 2.4 Hz, 1H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.5, 193.8, 187.6, 165.6, 161.1, 147.7, 133.4, 133.2, 129.9, 128.9, 128.4, 119.8, 105.9, 98.0, 55.6, 55.5; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{25}H_{21}O_5$: 401.1384; found: 401.1383.

4.3.5 4-(Benzo[d][1,3]dioxol-5-yl)-2-benzoyl-1-phenylbut-2-ene-1,4-dione **(3e):** yellow solid, mp 125–127 ℃; IR (KBr): 3066, 1683, 1660, 1640, 1592, 1515, 1488, 1330, 1290, 1270, 1176, 1119, 1105 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.53 (d, J = 7.6 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.2 Hz, 3H), 7.33 (s, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 192.9, 186.4, 152.8, 152.0, 148.5, 134.0, 133.6, 131.2, 130.2, 129.0, 128.8, 128.7, 125.8, 108.1, 108.0; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{24}H_{17}O_5$: 385.1071; found: 385.1071.

4.3.6 2-Benzoyl-4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1-phenylbut-2-ene-1,4-dione **(3f):** yellow solid, mp 131–133 ℃; IR (KBr): 3444, 3063, 2991, 1683, 1658, 1641, 1591, 1510, 1446, 1434, 1330, 1291, 1264, 1238, 1176, 1143, 1103, 1064, 1031, 1002 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.61-7.63 (m, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 8.4 Hz, 2H), 7.43 (s, 1H), 7.41 (s, 2H), 7.88 (t, J = 9.6 Hz, 1H), 4.20-4.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 193.0, 186.6, 151.9, 149.0, 143.6, 135.8, 135.6, 134.0, 133.5, 131.1, 130.0, 129.0, 128.8, 128.6, 123.1, 121.7, 118.2, 117.5, 64.7, 63.9; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{25}H_{19}O_5$: 371.1278; found: 371.1278.

4.3.7 2-Benzoyl-4-(4-chlorophenyl)-1-phenylbut-2-ene-1,4-dione **(3g):** yellow solid, mp 96–98 ℃; IR (KBr): 3059, 1665, 1645, 1586, 1490, 1448, 1406, 1317, 1305, 1264, 1228, 1175, 1119, 1093, 1025, 1013 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.52-7.57 (m, 3H), 7.40-7.48 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 192.5, 187.4, 153.2, 140.7, 135.6, 135.3, 134.4, 134.2, 133.8, 130.2, 130.1, 129.2, 129.1, 128.8, 128.7, 128.4; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{23}H_{16}O_3Cl$: 375.0782; found: 375.0784.

4.3.8 2-Benzoyl-4-(4-bromophenyl)-1-phenylbut-2-ene-1,4-dione **(3h):** yellow solid, mp 108–110 ℃; IR (KBr): 3058, 1665, 1645, 1595, 1518, 1487, 1448, 1403, 1374, 1317, 1263, 1227, 1175, 1118, 1102, 1072, 1025, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.51-7.56 (m, 3H), 7.43-7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 192.5, 187.7, 153.3, 135.6, 135.3, 134.8, 134.2, 133.8, 132.2, 130.2, 129.6, 129.0, 128.8, 128.7; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{23}H_{16}O_3Br$: 419.0277; found: 419.0278.

4.3.9 2-Benzoyl-4-(4-nitrophenyl)-1-phenylbut-2-ene-1,4-dione **(3i):** yellow solid, mp 90–93 ℃; IR (KBr): 3106, 3060, 2926, 2853, 1812, 1670, 1656, 1596, 1578, 1523, 1449, 1407, 1343, 1318, 1247, 1218, 1178, 1110, 1098, 1073, 1032, 1024, 1007 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, J = 8.4 Hz, 2H), 8.03-8.05 (br, 4H), 7.97 (d, J = 8.4 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.50-7.57 (m, 3H), 7.48 (s, 1H), 7.45 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.2, 192.1, 187.5, 154.4, 150.5, 140.4, 135.3, 135.0, 134.4, 134.0, 130.2, 129.7, 129.6, 129.1, 128.9, 128.8, 124.0; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{23}H_{16}O_5N$: 386.1023; found: 386.1024.

4.3.10 2-Benzoyl-4-(3-nitrophenyl)-1-phenylbut-2-ene-1,4-dione **(3j):** yellow solid, mp 125–127 ℃; IR (KBr): 3448, 3095, 1682, 1641, 1597, 1525, 1481, 1444, 1352, 1265, 1225, 1100, 1020 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 6.8 Hz, 1H), 8.06 (d, J = 7.2 Hz, 2H), 7.98 (d, J = 7.2 Hz, 2H), 7.51-7.67 (m, 2H), 7.45-7.49 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.2, 192.1, 186.9, 154.6, 148.4, 137.3, 135.4, 135.1, 134.4, 134.1, 134.0, 130.2, 129.5, 129.1, 128.9, 128.8, 128.4, 128.1, 123.4; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{23}H_{16}O_5N$: 386.1023; found: 386.1022.

4.3.11 2-Benzoyl-4-(3,4-dichlorophenyl)-1-phenylbut-2-ene-1,4-dione **(3k):** yellow solid, mp 123–125 ℃; IR (KBr): 3091, 3062, 1656, 1595, 1579, 1449, 1392, 1338, 1248, 1213, 1177, 1073, 1045, 1027 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 7.6 Hz, 2H), 7.97 (d, J = 7.6 Hz, 2H), 7.93 (d, J = 2.0 Hz, 1H), 7.69 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.49-7.57 (m, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 192.3, 186.6, 153.9, 138.7, 135.6, 135.4, 135.2, 134.3, 133.8, 133.6, 130.9, 130.5, 130.2, 129.6, 129.0, 128.8, 128.7, 127.6; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{23}H_{15}Cl_2O_3$: 409.0393; found: 409.0393.

4.3.12 2-Benzoyl-4-(furan-2-yl)-1-phenylbut-2-ene-1,4-dione **(3l):** yellow solid, mp 106–107 ℃; IR (KBr): 3451, 3153, 3124, 3095, 3062, 2924, 1675, 1650, 1602, 1578, 1557, 1460, 1449, 1398, 1366, 1316, 1292, 1261, 1229, 1173, 1157, 1106, 1080, 1052, 1014 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.59 (s, 1H), 7.52-7.56 (m, 3H), 7.45 (t, J = 7.2 Hz, 2H), 7.38 (s, 1H), 7.25 (t, J = 4.0 Hz, 1H), 7.54-7.55 (dd, J_1 = 1.6 Hz, J_2 = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 192.7, 175.7, 152.7, 152.4, 147.7, 134.0, 130.2, 128.9, 128.7, 128.6, 119.3, 113.2; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{21}H_{15}O_4$: 331.0965; found: 331.0965.

4.3.13 2-Benzoyl-1-phenyl-4-(thiophen-2-yl)but-2-ene-1,4-dione **(3m):** yellow solid, mp 104–106 ℃; IR (KBr): 3451, 3115, 1652, 1594, 1517, 1451, 1413, 1358, 1319, 1273, 1243, 1223, 1176, 1090, 1072, 1022 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.6 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 4.0 Hz, 1H), 7.69 (d, J = 4.0 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.49-7.51 (m, 3H), 7.46 (t, J = 7.6 Hz, 2H),7.36 (s, 1H), 7.11 (t, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 192.5, 180.1, 152.7, 143.7, 136.2, 135.6, 135.3, 134.1, 133.6, 133.5, 130.2, 129.6, 129.0, 128.7, 128.6; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{21}H_{15}O_3S$: 347.0736; found: 347.0737.

4.3.14 4-(Benzofuran-2-yl)-2-benzoyl-1-phenylbut-2-ene-1,4-dione **(3n):** yellow solid, mp 105–107 ℃; IR (KBr): 3457, 3057, 1653, 1595, 1550, 1450, 1375, 1340, 1278, 1255, 1227, 1166, 1138, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.42-7.55 (m, 9H), 7.29 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 192.5, 177.8, 155.9, 153.4, 152.2, 135.6, 135.3, 134.1, 133.6, 130.3, 129.1, 129.0,

128.8, 128.7, 128.6, 124.2, 123.5, 115.1, 112.4; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{25}H_{17}O_4$: 381.1121; found: 381.1122.

4.3.15 4-([1,1'-Biphenyl]-4-yl)-2-benzoyl-1-phenylbut-2-ene-1,4-dione **(3o):** yellow solid, mp 111–113 ℃; IR (KBr): 3453, 1657, 1597, 1556, 1448, 1407, 1367, 1314, 1264, 1225, 1185, 1118, 1028, 1004 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.63-7.66 (m, 3H), 7.55-7.61 (m, 3H), 7.49-7.53 (m, 3H), 7.38-7.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 192.8, 188.0, 152.5, 146.7, 139.3, 135.8, 135.6, 134.9, 134.0, 133.6, 130.9, 130.2, 129.3, 129.0, 128.9, 128.8, 128.6, 128.5, 127.4, 127.2; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{29}H_{21}O_3$: 417.1485; found: 417.1485.

4.3.16 2-Benzoyl-4-(naphthalen-2-yl)-1-phenylbut-2-ene-1,4-dione **(3p):** yellow solid, mp 51–53 ℃; IR (KBr): 3455, 3058, 1652, 1626, 1595, 1578, 1468, 1448, 1359, 1343, 1317, 1279, 1219, 1178, 1125, 1073, 1001 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.39(s, 1H), 8.08 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 7.2 Hz, 2H), 7.85-7.90 (m, 2H), 7.79-7.82 (m, 2H), 7.68 (s, 1H), 7.54-7.61 (m, 2H), 7.50 (br, 4H), 7.40 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 192.8, 188.2, 152.5, 135.7, 135.8, 135.4, 134.0, 133.6, 132.1, 130.1, 129.6, 129.1, 129.0, 128.7, 128.6, 127.7, 127.0, 123.6; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{27}H_{19}O_3$: 391.1329; found: 391.1328.

4.3.17 2-Benzoyl-4-(naphthalen-1-yl)-1-phenylbut-2-ene-1,4-dione **(3q):** yellow solid, mp 97–99 ℃; IR (KBr): 3452, 3045, 1672, 1641, 1594, 1576, 1506, 1449, 1355, 1277, 1260, 1240, 1223, 1181, 1116, 1099 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, J = 7.2 Hz, 1H), 8.08 (d, J = 7.2 Hz, 2H), 8.00 (t, J = 8.0 Hz, 3H), 7.92 (d, J = 7.2 Hz, 1H), 7.82-7.85 (m, 1H), 7.63 (t, J = 7.2 Hz, 1H), 7.51-7.54 (m, 5H), 7.40-7.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 193.0, 191.5, 151.4, 135.9, 135.6, 134.7, 134.2, 134.0, 133.8, 133.7, 133.6, 130.1, 129.9, 129.0, 128.8, 128.4; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{27}H_{19}O_3$: 391.1329; found: 391.1329.

4.3.18 2-(4-Methoxybenzoyl)-1-(4-methoxyphenyl)-4-phenylbut-2-ene-1,4-dione **(3r):** yellow oil, IR (KBr): 3443, 3056, 1685, 1641, 1594, 1529, 1520, 1444, 1360, 1266, 1212, 1006 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.4 Hz, 2H), 7.99 (t, J = 8.4 Hz, 2H),7.90 (d, J = 8.4 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H), 7.41 (s, 1H), 6.97 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.2, 191.1, 188.6, 164.5, 164.0, 154.3, 136.4, 133.8, 133.0, 132.8, 131.7, 131.5, 128.9, 128.7, 128.6, 128.3, 114.1, 114.0, 113.9, 113.9, 55.5, 55.3; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{25}H_{21}O_5$: 401.1384; found: 401.1384.

4.3.19 Ethyl 2-benzoyl-4-oxo-4-phenylbut-2-enoate **(3s):**lit[11] yellow oil, ^1H NMR (600 MHz, $CDCl_3$): δ = 8.15 (s, 1H), 7.95 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 7.2 Hz, 2H), 7.55-7.60 (m, 2H), 7.46 (q, J = 11.4 Hz, 4H), 4.27 (q, J = 10.8 Hz, 2H), 1.21 (t, J = 10.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (*E/Z*): δ = 193.3, 188.3, 163.6, 144.8, 136.1, 135.8, 134.2, 133.5, 128.9, 128.8, 128.7, 128.5, 128.4, 62.4, 31.9; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{19}H_{17}O_4$: 309.1121; found: 309.1121.

4.3.20 Ethyl 4-oxo-4-phenyl-2-(3,4,5-trimethoxybenzoyl)but-2-enoate **(3t):** lit[11] yellow oil,^1H NMR (600 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.97 (d, J = 12.0 Hz, 2H), 7.62 (t, J = 10.8 Hz, 1H), 7.49 (t, J = 11.4 Hz, 2H), 7.15 (s, 2H), 4.31 (q, J = 10.8 Hz, 2H), 3.85-3.91 (m, 9H), 1.26 (t, J = 10.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (*E/Z*): δ = 191.9, 191.1, 190.1, 188.5, 164.1, 163.7, 153.2, 144.2, 140.4, 136.1, 135.7, 134.2, 130.9, 130.7, 128.9, 128.7, 107.1, 107.0, 106.0, 105.8, 62.4, 56.2, 56.1, 56.0, 14.0, 13.8; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{22}H_{23}O_7$: 399.1438; found: 399.1439.

4.3.21 Ethyl 2-(furan-2-carbonyl)-4-oxo-4-phenylbut-2-enoate **(3u):** lit[11] yellow oil, ^1H NMR (600 MHz, $CDCl_3$): δ = 8.07 (s, 1H), 7.95 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.55 (s, 1H), 7.49 (q, J = 7.8 Hz, 2H), 7.20 (d, J = 3.0 Hz, 1H), 6.55 (s, 1H), 4.31 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (*E/Z*): δ = 188.7, 180.6, 163.3, 152.0, 147.9, 142.5, 136.1, 134.7, 134.2, 128.8, 118.2, 112.9, 112.5, 62.4, 13.9; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{17}H_{15}O_5$: 299.0914; found: 299.0914.

4.3.22 Ethyl 2-(4-nitrobenzoyl)-4-oxo-4-phenylbut-2-enoate **(3v):** yellow solid, mp 96–97 ℃ (lit[4] mp 97-98 ℃); ^1H NMR (600 MHz, $CDCl_3$): δ = 8.32 (d, J = 8.4 Hz, 2H), 8.21 (s, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.2 Hz, 2H), 4.31 (q, J = 7.8 Hz, 2H), 1.24 (t, J = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (*E/Z*): δ = 192.0, 188.1, 163.0, 144.1, 140.2, 135.7, 134.6, 133.9, 129.4, 129.2, 128.8, 124.0, 123.9, 62.7, 13.9, 13.8; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{15}NNaO_6$: 376.0792; found: 376.0801.

4.3.23 2-Benzoyl-4-(2-methoxyphenyl)-1-phenylbut-2-ene-1,4-dione **(3w):** White solid, mp 95–98 ℃; IR (KBr): 3445, 3055, 2940, 1662, 1645, 1594, 1569, 1515, 1447, 1426, 1375, 1318, 1275, 1228, 1172, 1123, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ =8.05 (d, J = 7.2 Hz, 2H), 8.00 (d, J = 7.2 Hz, 2H), 7.58-7.63 (m, 2H), 7.52 (t, J = 7.6 Hz, 4H), 7.45 (q, J = 7.2 Hz, 3H), 6.94 (q, J = 7.2 Hz, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.3, 193.6, 189.9, 159.1, 148.4, 136.3, 136.1, 136.0, 135.0, 133.7, 133.4, 131.1, 130.1, 129.1, 128.6, 121.0, 111.6, 55.7; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{24}H_{19}O_4$: 371.1278; found: 371.1278.

Acknowledgments

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References and notes

1. Selective examples for diversity-oriented synthesis: (a) Burke, M. D.; Schreiber, S. L. *Angew. Chem. Int. Ed.* **2003**, *43*, 46–58. (b) Kumagai, N.; Muncipinto, G.; Schreiber, S. L. *Angew. Chem. Int. Ed.* **2006**, *46*, 3635–3638; (c) Galloway, W. R. J. D.; Isidro-Llobet, A.; Spring, D. R. *Nat. Commun*., **2010**, *1*, 80; (d) O' Connor, C. J.; Beckmann, H. S. G. Spring, D. R. *Chem. Soc. Rev*., **2012**, *41*, 4444–4456; (e) Schreiber, S. L. *Science*, **2000**, *287*, 1964–1969; (f) Burke1, M. D.; Lalic, G. *Chemistry & Biology*, **2002**, *9*, 535-541.
2. Selective examples for synergistic catalysis: (a) Strater, N.; Lipscomb, W. N.; Klabunde, T., Krebs, B. *Angew. Chem. Int. Ed.* **1996**, *35*, 2024–2055; (b) Sawamura, M.; Sudoh, M.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3309–310; (c) Ibrahem, I.; Córdova, A.; *Angew. Chem. Int. Ed*. **2006**, *45*, 1952–1956; (d) Sammis, G. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2003**, *125*, 4442–4443; (e) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett*. **1975**, *16*, 4467–4470; (f) Kang, F. A.; Lanter, J. C.; Cai, C.; Sui, Z.; Murray, W. V. *Chem. Commun*. **2010**, *46*, 1347–1349 ; (g) Allen, A. E.; MacMillan, D. W. C. *Chem. Sci*. **2012**, *3*, 633–658.
3. Selective examples for auto-tandem catalysis: (a) Fogg, D. E.; dos Santos, E. N. *Coord. Chem. Rev*. **2004**, *248*, 2365–2379; (b) Wasilke, J. C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001–1020; (c) Shindoh, N.; Takemoto, Y.; Takasu, K. *Chem.-Eur. J.* **2009**, *15*, 12168–12179.

4. The self-sorting domino reactions: (a) Yin, G. D.; Zhou, B. H.; Meng, X. G.; Wu, A. X.; Pan, Y. J. *Org. Lett.* **2006**, *8*, 2245–2248; (b) Gao, M.; Yin, G. D.; Wang, Z. H.; Wu, Y. D.; Guo, C.; Pan, Y. J.; Wu, A. X. *Tetrahedron* **2009**, *65*, 6047–6049.
5. For reviews on multicomponent reactions, see: (a) Zhu, J. P.; Bienaymé, H. Eds.; *Multicomponent Reactions*; Wiley-VCH: Weinheim, 2005. (b) Ramón, D. J.; Yus, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 1602–1634.
6. Byproduct catalyzed domino reactions, see: (a) Alaimo, P. J.; O'Brien, R.; Johnson, A. W.; Slauson, S. R.; O'Brien, J. M.; Tyson, E. L.; Marshall, A.-L.; Ottinger, C. E.; Chacon, J. G.; Wallace, L.; Paulino, C. Y.; Connell, S. *Org. Lett.* **2008**, *10*, 5111–5114; (b) Cao, J. J.; Zhou, F.; Zhou, J. *Angew. Chem. Int. Ed*. **2010**, *49*, 4976–4980; (c) Yang, B. L.; Weng, Z. T.; Yang, S. J.; Tian, S. K. *Chem.-Eur. J.* **2010**, *16*, 718–723; (d) Gao, M.; Yang, Y.; Wu, Y. D.; Deng, C.; Shu, W. M.; Zhang, D. X.; Cao, L. P.; She, N. F.; Wu, A. X. *Org. Lett*. **2010**, *12*, 4026–4029; (e) Zhu, Y. P.; Gao, Q. H.; Lian, M.; Yuan, J. J.; Liu, M. C.; Zhao, Q.; Yang, Y.; Wu, A. X. *Chem. Commun*. **2011**, *47*, 12700–12702;
7. (a) Salvá, J.; Faulkner, D. J.; *J. Org. Chem.* **1990**, *55*, 1941–1943. (b) Nguyen, C.; Teo, J. L.; Matsuda, A.; Eguchi, M.; Chi, E. Y.; Henderson, W. R.; Kahn, M. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 1169–1173; (c) Yu, J. Q.; Corey, E. J. *J. Am. Chem. Soc*. **2003**, *125*, 3232–3233; (d) Fouad, M.; Edrada, R. A.; Ebel, R.; Wray, V.; Müller, W. E. G.; Lin, W. H.; Proksch, P. *J. Nat. Prod.* **2006**, *69*, 211–218.
8. (a) Eicher, T.; Hauptmann, S.; Speicher, A.; *The Chemistry of Heterocycles*; Wiley-VCH: Weinheim, 2003. (b) Yin, G. D.; Wang, Z. H.; Chen, A. H.; Gao, M.; Wu, A. X.; Pan, Y. J. *J. Org. Chem*. **2008**, *73*, 3377–3383; (c) Yang, Y.; Gao, M.; Wu, L. M.; Deng, C.; Zhang, D. X.; Gao, Y.; Zhu, Y. P.; Wu, A. X. *Tetrahedron* **2011**, *67*, 5142–5149.
9. (a) Danishefsky, S.; Kahn, M. *Tetrahedron Lett*. **1981**, *22*, 489–492; (b) Ballini, R.; Bosica, G. *Tetrahedron*, **1995**, *51*, 4213–4222; (c) Allen, J. G.; Danishefsky, S. J.; *J. Am. Chem. Soc.* **2001**, *123*, 351–352; (d) DeMartino, M. P.; Chen, K.; Baran, P. S. *J. Am. Chem. Soc.* **2008**, *130*, 11546–11560.
10. (a) Schaefer, J. P. *J. Am. Chem. Soc*. **1962**, *84*, 713–716; (b) Vassilikogiannakis, G.; Margaros, I.; Montagnon, T. *Org. Lett.* **2004**, *6*, 2039–2042; (c) Prakash, O.; Batra, A.; Chaudhri, V.; Prakash, R. *Tetrahedron Lett.* **2005**, *46*, 2877–2878; (d) Crone, B.; Kirsch, S. F. *Chem. Commun*. **2006**, 764–766; (e) Wasnaire, P.; de Merode, T.; Markó, I. E. *Chem. Commun*. **2007**, 4755–4757.
11. Gao, M.; Yang, Y.; Wu, Y. D.; Deng, C.; Cao, L. P.; Meng X. G.; Wu, A. X. *Org. Lett.* **2010**, *12*, 1856–1859.
12. (a) Taylor, R. J. K.; Reid, M.; Foot, J. Raw, S. A. *Acc. Chem. Res*. **2005**, *38*, 851–869; (b) Ozanne, A.; Pouységu, L.; Depernet, D.; Francüois, B.; Quideau, S. *Org. Lett*. **2003**, *5*, 2903–2906; (c) Surendra, K.; Krishnaveni, N. S.; Reddy, M. A.; Nageswar, Y. V. D.; Rao, K. R. J. *Org. Chem*. **2003**, *68*, 2058–2059; (d) Bartlett, S. L.; Beaudry, C. M. *J. Org. Chem*. **2011**, *76*, 9852–9855.
13. Zhu, Y. P.; Jia, F. C.; Liu, M. C.; Wu, A. X. *Org. Lett.* **2012**, *14*, 4414–4417.
14. Zhu, Y. P.; Lian, M.; Jia, F. C.; Liu, M. C.; Yuan, J. J.; Gao, Q. H.; Wu, A. X. *Chem. Commun*. **2012**, *48*, 9086–9088.
15. (a) Ma, D. W.; Cai, Q. *Acc. Chem. Res.* **2008**, *41*, 1450–1460; (b) Yan, R. L.; Luo, J.; Wang, C. X.; Ma, C. W.; Huang, G. S.; Liang, Y. M. *J. Org. Chem.* **2010**, *75*, 5395–5397; (c) Deng, C.-L.; Song, R.-J.; Guo, S.-M.; Wang, Z.-Q.; Li, J.-H. *Org. Lett.* **2007**, *9*, 5111-5114; (d) Deng, C.-L.; Zou, T.; Wang, Z.-Q.; Song, R.-J.; Li, J.-H. *J. Org. Chem.* **2008**, *74*, 412-414; (e) Cao, H.; Jiang, H.-F.; Huang, H.-W.; Zhao, J.-W. *Org. Biomol. Chem.* **2011**, *9*, 7313-7317; (f) Cai, S. J.; Wang, F.; Xi, C. J. *J. Org. Chem*. **2012**, *77*, 2331–2336; (g) Xie, Z.; Zhu, X.; Guan, Y.; Zhu, D.; Hu, H.; Lin, C.; Pan, Y.; Jiang, J.; Wang, L. *Org. Biomol. Chem.* **2013**, *11*, 1390-1398.
16. General procedure for preparation of substrates **1** see: Yin, G. D.; Gao, M.; She, N. F.; Hu, S. L.; Wu, A. X.; Pan, Y. J. *Synthesis* **2007**, 3113–3116.
17. General procedure for preparation of **4** and **5** see: Lee, J. C.; Bae, Y. H.; Chang, S.-K. *Bull. Korean. Chem. Soc.* **2003**, *24*, 407–408.

Supporting Information available

Target-oriented synthesis: miscellaneous synthetic routes to access 1,4-enediones through the coupling of 1,3-dicarbonyl compounds with multiform substrates

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1. General

Unless otherwise noted, all 1,3-dicarbonyl compounds (**2a-f**), 2-hydroxy-aromatic ketones **6**, methyl carbinols **7,** and other reagents were obtained from commercial suppliers and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh).

IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. NMR spectra were recorded on a Varian Mercury 400 or 600 MHz spectrometer Chemical shifts are reported in ppm ($CDCl_3$: δ 7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR), relative to the internal standard of tetramethylsilane (TMS), multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz). HRMS were obtained on a Bruker Apex-Ultra 7.0T FTMS equipped with an electro-spray source (ESI) or Atmospheric-pressure chemical ionization (APCI). Melting points were determined using XT-4 apparatus and not corrected.

2. Synthesis of 3a-3w

2.1 General procedure for preparation of 3 from 1, 4 and 5 (3a as an example):

General procedure: A sealed tube was charged with α-iodide aromatic ketone **1a** (123 mg, 0.5 mmol), dibenzoylmethane **2a** (112 mg, 0.5 mmol), and CuI (47.6 mg, 0.25 mmol) at room temperature, and then dried solvent DMSO (3 mL) was added. The resulting mixture was stirred at 90 ℃, after disappearance of the reactant (monitored by TLC), then added 50mL water to the mixture, extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1) to yield the desired product **3a** as a yellow solid (85% yield).

2.2 General procedure for preparation of from 2-hydroxy-aromatic ketones 6 (3a as an example):

General procedure: A sealed tube was charged with 2-hydroxy aromatic ketone **6a** (136 mg, 1.0 mmol), dibenzoylmethane **2a** (224 mg, 1.0 mmol), IBX (224 mg) and CuI (95 mg, 0.5 mmol) at room temperature, and then solvent DMSO (3 mL) was added. The resulting mixture was stirred at 90 ℃, after disappearance of the reactant (monitored by TLC), then added 50mL water to the mixture, extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield the desired product **3a** in 72% yield.

2.3 General procedure for preparation of 3 from Methyl carbinols 7 (3a as an example):

General procedure: A sealed tube was charged with methyl carbinol **7a** (122 mg, 1.0 mmol), dibenzoylmethane **2a** (224 mg, 1.0 mmol), IBX (210 mg, 0.75 mmol) and CuI (95 mg, 0.5 mmol) at room temperature, and then solvent DMSO (3 mL) was added. The resulting mixture

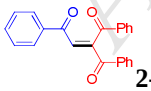
was stirred at 90 ℃, after disappearance of the reactant (monitored by TLC), then added 50mL water to the mixture, extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield the desired product **3a** in 84% yield.

2.4 Synthesis of starting material 1(1a as an example):[1] Finely powdered CuO (0.8 g, 10.0 mmol) and I_2 (2.53 g, 10.0 mmol) were added to a solution of aryl methyl ketone **9a** (1.2 g, 10.0 mmol) in anhydrous MeOH (20 mL). The mixture was refluxed for 1-2.5 h. After disappearance of aryl methyl ketone **9a** (monitored by TLC), the mixture was filtered and the solvent was removed under reduced pressure. The residue was poured into 10% $Na_2S_2O_3$ solution (50 mL), the mixture was extracted with EtOAc (3 × 50 mL), and the organic layer was dried (Na_2SO_4). Removal of the solvent and purification of the residue by column chromatography gave the desired product **1a** in 96% yield.

2.5 Synthesis of starting material 4 (4a as an example):[2] N-Bromobutanimide (NBS, 356 mg, 2.0 mmol) and 4-Methylbenzenesulfonic acid (PTSA, 344 mg, 2.0 mmol) were added to a well-stirred solution of aryl methyl ketone **8a** (240 mg, 2.0 mmol) in anhydrous MeCN (15 mL). The mixture was stirred at room temperature for 1 h, and then refluxed for another 1-2.5 h. After disappearance of aryl methyl ketone **8a** (monitored by TLC), the solvent was removed under reduced pressure, then added 50mL water to the mixture, extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield the desired product **4a** as a white solid in 90% yield.

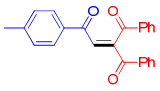
2.6 Synthesis of starting material 5 (5a as an example):[2] : N-Chlorosuccinimide (NCS, 266 mg, 2.0 mmol) and 4-Methylbenzenesulfonic acid (PTSA, 344 mg, 2.0 mmol) were added to a well-stirred solution of aryl methyl ketone **8a** (240 mg, 2.0 mmol) in anhydrous MeCN (15 mL). The mixture was stirred at room temperature for 1 h, and then refluxed for another 1-2.5 h. After disappearance of aryl methyl ketone **8a** (monitored by TLC), the solvent was removed under reduced pressure, then added 50mL water to the mixture, extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield the desired product **5a** as a white solid in 85% yield.

3. Spectral data of compound 3a-3w.

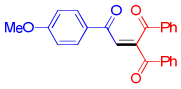


2-benzoyl-1,4-diphenylbut-2-ene-1,4-dione (3a): yellow solid, mp 101–103℃ (lit[3] mp 101–102 ℃); IR (KBr): 3443, 3056, 1685, 1641, 1594, 1444, 1360, 1266, 1212, 1006 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.6 Hz, 2H), 7.99 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.58 (t, J = 7.2 Hz, 4H), 7.42-7.54 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =193.9, 193.8, 188.6, 152.7, 136.2, 135.8, 135.6, 134.1, 133.7, 130.9, 130.2, 129.1,

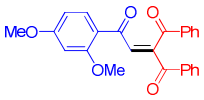
128.9, 128.8, 128.74, 128.68; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{16}NaO_3$: 363.0992; found: 363.0987.



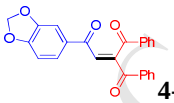
2-benzoyl-1-phenyl-4-(p-tolyl)but-2-ene-1,4-dione (3b): yellow solid, mp 109–111℃; IR (KBr): 3459, 3059, 1666, 1646, 1597, 1448, 1377, 1317, 1268, 1232, 1209, 1180, 1125, 1103, 1019 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.50-7.58 (m, 5H), 7.42-7.48 (m, 2H), 7.24 (d, J = 7.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 192.9, 188.0, 152.3, 145.3, 135.7, 135.5, 134.0, 133.7, 133.6, 131.0, 130.2, 129.6, 129.0, 128.9, 128.8, 128.7, 21.7; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{24}H_{19}O_3$: 355.1329; found: 355.1329.



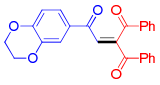
2-benzoyl-4-(4-methoxyphenyl)-1-phenylbut-2-ene-1,4-dione (3c): yellow solid, mp 125–127 ℃; IR (KBr): 3058, 2938, 1662, 1643, 1594, 1569, 1512, 1447, 1426, 1372, 1318, 1275, 1228, 1172, 1123, 1009 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 5.2 Hz, 2H), 7.99 (d, J = 5.2 Hz, 2H), 7.88 (d, J = 6.0 Hz, 2H), 7.64 (t, J = 4.8 Hz, 1H), 7.51-70.54 (m, 4H), 7.44 (t, J = 5.2 Hz, 2H), 6.91 (d, J = 6.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 193.0, 186.8, 164.3, 151.9, 134.0, 133.5, 131.3, 130.2, 129.3, 129.0, 128.8, 128.6, 114.1, 55.5; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{24}H_{19}O_4$: 371.1278; found: 371.1278.



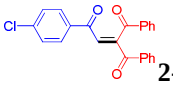
2-benzoyl-4-(2,4-dimethoxyphenyl)-1-phenylbut-2-ene-1,4-dione (3d): yellow solid, mp 121–123 ℃; IR (KBr): 3097, 1683, 1667, 1642, 1612, 1596, 1597, 1529, 1520, 1482, 1445, 1352, 1315, 1293, 1276, 1225, 1168, 1100, 1019, 1000 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (t, J = 8.0 Hz, 4H), 7.63 (d, J = 15.2 HZ, 1H), 7.60 (s, 2H), 7.48-7.52 (m, 3H), 7.42 (t, J = 8.0 Hz, 2H), 6.45 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 6.39 (t, J = 2.4 Hz, 1H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.5, 193.8, 187.6, 165.6, 161.1, 147.7, 133.4, 133.2, 129.9, 128.9, 128.4, 119.8, 105.9, 98.0, 55.6, 55.5; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{25}H_{21}O_5$: 401.1384; found: 401.1383.



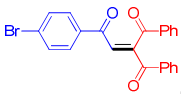
4-(benzo[d][1,3]dioxol-5-yl)-2-benzoyl-1-phenylbut-2-ene-1,4-dione (3e): yellow solid, mp 125–127 ℃; IR (KBr): 3066, 1683, 1660, 1640, 1592, 1515, 1488, 1330, 1290, 1270, 1176, 1119, 1105 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.53 (d, J = 7.6 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.2 Hz, 3H), 7.33 (s, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 192.9, 186.4, 152.8, 152.0, 148.5, 134.0, 133.6, 131.2, 130.2, 129.0, 128.8, 128.7, 125.8, 108.1, 108.0; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{24}H_{17}O_5$: 385.1071; found: 385.1071.



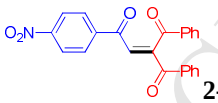
2-benzoyl-4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1-phenylbut-2-ene-1,4-dione (3f): yellow solid, mp 131–133 ℃; IR (KBr): 3444, 3063, 2991, 1683, 1658, 1641, 1591, 1510, 1446, 1434, 1330, 1291, 1264, 1238, 1176, 1143, 1103, 1064, 1031, 1002 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.61-7.63 (m, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 8.4 Hz, 2H), 7.43 (s, 1H), 7.41 (s, 2H), 7.88 (t, J = 9.6 Hz, 1H), 4.20-4.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 193.0, 186.6, 151.9, 149.0, 143.6, 135.8, 135.6, 134.0, 133.5, 131.1, 130.0, 129.0, 128.8, 128.6, 123.1, 121.7, 118.2, 117.5, 64.7, 63.9; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{25}H_{19}O_5$: 371.1278; found: 371.1278.



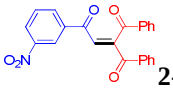
2-benzoyl-4-(4-chlorophenyl)-1-phenylbut-2-ene-1,4-dione (3g): yellow solid, mp 96–98 ℃; IR (KBr): 3059, 1665, 1645, 1586, 1490, 1448, 1406, 1317, 1305, 1264, 1228, 1175, 1119, 1093, 1025, 1013 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.52-7.57 (m, 3H), 7.40-7.48 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 192.5, 187.4, 153.2, 140.7, 135.6, 135.3, 134.4, 134.2, 133.8, 130.2, 130.1, 129.2, 129.1, 128.8, 128.7, 128.4; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{23}H_{16}O_3Cl$: 375.0782; found: 375.0784.



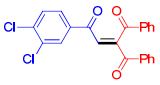
2-benzoyl-4-(4-bromophenyl)-1-phenylbut-2-ene-1,4-dione (3h): yellow solid, mp 108–110℃; IR (KBr): 3058, 1665, 1645, 1595, 1518, 1487, 1448, 1403, 1374, 1317, 1263, 1227, 1175, 1118, 1102, 1072, 1025, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.51-7.56 (m, 3H), 7.43-7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 192.5, 187.7, 153.3, 135.6, 135.3, 134.8, 134.2, 133.8, 132.2, 130.2, 129.6, 129.0, 128.8, 128.7; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{23}H_{16}O_3Br$: 419.0277; found: 419.0278.



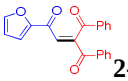
2-benzoyl-4-(4-nitrophenyl)-1-phenylbut-2-ene-1,4-dione (3i): yellow solid, mp 90–93 ℃; IR (KBr): 3106, 3060, 2926, 2853, 1812, 1670, 1656, 1596, 1578, 1523, 1449, 1407, 1343, 1318, 1247, 1218, 1178, 1110, 1098, 1073, 1032, 1024, 1007 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, J = 8.4 Hz, 2H), 8.03-8.05 (br, 4H), 7.97 (d, J = 8.4 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.50-7.57 (m, 3H), 7.48 (s, 1H), 7.45 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.2, 192.1, 187.5, 154.4, 150.5, 140.4, 135.3, 135.0, 134.4, 134.0, 130.2, 129.7, 129.6, 129.1, 128.9, 128.8, 124.0; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{23}H_{16}O_5N$: 386.1023; found: 386.1024.



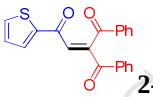
2-benzoyl-4-(3-nitrophenyl)-1-phenylbut-2-ene-1,4-dione (3j): yellow solid, mp 125–127 ℃; IR (KBr): 3448, 3095, 1682, 1641, 1597, 1525, 1481, 1444, 1352, 1265, 1225, 1100, 1020 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 6.8 Hz, 1H), 8.06 (d, J = 7.2 Hz, 2H), 7.98 (d, J = 7.2 Hz, 2H), 7.51-7.67 (m, 2H), 7.45-7.49 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.2, 192.1, 186.9, 154.6, 148.4, 137.3, 135.4, 135.1, 134.4, 134.1, 134.0, 130.2, 129.5, 129.1, 128.9, 128.8, 128.4, 128.1, 123.4; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{23}H_{16}O_5N$: 386.1023; found: 386.1022.



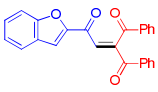
2-benzoyl-4-(3,4-dichlorophenyl)-1-phenylbut-2-ene-1,4-dione (3k): yellow solid, mp 123–125 ℃; IR (KBr): 3091, 3062, 1656, 1595, 1579, 1449, 1392, 1338, 1248, 1213, 1177, 1073, 1045, 1027 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 7.6 Hz, 2H), 7.97 (d, J = 7.6 Hz, 2H), 7.93 (d, J = 2.0 Hz, 1H), 7.69 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.49-7.57 (m, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 192.3, 186.6, 153.9, 138.7, 135.6, 135.4, 135.2, 134.3, 133.8, 133.6, 130.9, 130.5, 130.2, 129.6, 129.0, 128.8, 128.7, 127.6; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{23}H_{15}Cl_2O_3$: 409.0393; found: 409.0393.



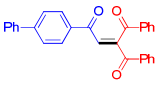
2-benzoyl-4-(furan-2-yl)-1-phenylbut-2-ene-1,4-dione (3l): yellow solid, mp 106–107 ℃; IR (KBr): 3451, 3153, 3124, 3095, 3062, 2924, 1675, 1650, 1602, 1578, 1557, 1460, 1449, 1398, 1366, 1316, 1292, 1261, 1229, 1173, 1157, 1106, 1080, 1052, 1014 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.59 (s, 1H), 7.52-7.56 (m, 3H), 7.45 (t, J = 7.2 Hz, 2H), 7.38 (s, 1H), 7.25 (t, J = 4.0 Hz, 1H), 7.54-7.55 (dd, J_1 = 1.6 Hz, J_2 = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 192.7, 175.7, 152.7, 152.4, 147.7, 134.0, 130.2, 128.9, 128.7, 128.6, 119.3, 113.2; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{21}H_{15}O_4$: 331.0965; found: 331.0965.



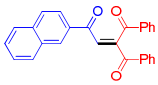
2-benzoyl-1-phenyl-4-(thiophen-2-yl)but-2-ene-1,4-dione (3m): yellow solid, mp 104–106 ℃; IR (KBr): 3451, 3115, 1652, 1594, 1517, 1451, 1413, 1358, 1319, 1273, 1243, 1223, 1176, 1090, 1072, 1022 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.6 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 4.0 Hz, 1H), 7.69 (d, J = 4.0 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.49-7.51 (m, 3H), 7.46 (t, J = 7.6 Hz, 2H),7.36 (s, 1H), 7.11 (t, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 192.5, 180.1, 152.7, 143.7, 136.2, 135.6, 135.3, 134.1, 133.6, 133.5, 130.2, 129.6, 129.0, 128.7, 128.6; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{21}H_{15}O_3S$: 347.0736; found: 347.0737.



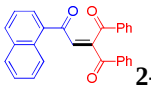
4-(benzofuran-2-yl)-2-benzoyl-1-phenylbut-2-ene-1,4-dione (3n): yellow solid, mp 105–107 ℃; IR (KBr): 3457, 3057, 1653, 1595, 1550, 1450, 1375, 1340, 1278, 1255, 1227, 1166, 1138, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.42-7.55 (m, 9H), 7.29 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 192.5, 177.8, 155.9, 153.4, 152.2, 135.6, 135.3, 134.1, 133.6, 130.3, 129.1, 129.0, 128.8, 128.7, 128.6, 124.2, 123.5, 115.1, 112.4; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{25}H_{17}O_4$: 381.1121; found: 381.1122.



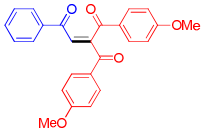
4-([1,1'-biphenyl]-4-yl)-2-benzoyl-1-phenylbut-2-ene-1,4-dione (3o): yellow solid, mp 111–113 ℃; IR (KBr): 3453, 1657, 1597, 1556, 1448, 1407, 1367, 1314, 1264, 1225, 1185, 1118, 1028, 1004 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.63-7.66 (m, 3H), 7.55-7.61 (m, 3H), 7.49-7.53 (m, 3H), 7.38-7.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 192.8, 188.0, 152.5, 146.7, 139.3, 135.8, 135.6, 134.9, 134.0, 133.6, 130.9, 130.2, 129.3, 129.0, 128.9, 128.8, 128.6, 128.5, 127.4, 127.2; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{29}H_{21}O_3$: 417.1485; found: 417.1485.



2-benzoyl-4-(naphthalen-2-yl)-1-phenylbut-2-ene-1,4-dione (3p): yellow solid, mp 51–53 □; IR (KBr): 3455, 3058, 1652, 1626, 1595, 1578, 1468, 1448, 1359, 1343, 1317, 1279, 1219, 1178, 1125, 1073, 1001 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.39(s, 1H), 8.08 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 7.2 Hz, 2H), 7.85-7.90 (m, 2H), 7.79-7.82 (m, 2H), 7.68 (s, 1H), 7.54-7.61 (m, 2H), 7.50 (br, 4H), 7.40 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 192.8, 188.2, 152.5, 135.7, 135.8, 135.4, 134.0, 133.6, 132.1, 130.1, 129.6, 129.1, 129.0, 128.7, 128.6, 127.7, 127.0, 123.6; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{27}H_{19}O_3$: 391.1329; found: 391.1328.

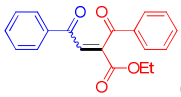


2-benzoyl-4-(naphthalen-1-yl)-1-phenylbut-2-ene-1,4-dione (3q): yellow solid, mp 97–99 ℃; IR (KBr): 3452, 3045, 1672, 1641, 1594, 1576, 1506, 1449, 1355, 1277, 1260, 1240, 1223, 1181, 1116, 1099 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, J = 7.2 Hz, 1H), 8.08 (d, J = 7.2 Hz, 2H), 8.00 (t, J = 8.0 Hz, 3H), 7.92 (d, J = 7.2 Hz, 1H), 7.82-7.85 (m, 1H), 7.63 (t, J = 7.2 Hz, 1H), 7.51-7.54 (m, 5H), 7.40-7.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 193.0, 191.5, 151.4, 135.9, 135.6, 134.7, 134.2, 134.0, 133.8, 133.7, 133.6, 130.1, 129.9, 129.0, 128.8, 128.4; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{27}H_{19}O_3$: 391.1329; found: 391.1329.

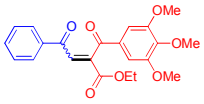


2-(4-methoxybenzoyl)-1-(4-methoxyphenyl)-4-phenylbut-2-ene-1,4-dione (3r): yellow oil, IR (KBr): 3443, 3056, 1685, 1641, 1594, 1529, 1520, 1444, 1360, 1266, 1212, 1006 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.4 Hz, 2H), 7.99 (t, J = 8.4 Hz, 2H),7.90

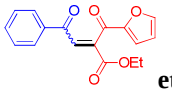
(d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.41 (s, 1H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.2, 191.1, 188.6, 164.5, 164.0, 154.3, 136.4, 133.8, 133.0, 132.8, 131.7, 131.5, 128.9, 128.7, 128.6, 128.3, 114.1, 114.0, 113.9, 113.9, 55.5, 55.3; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{25}H_{21}O_5$: 401.1384; found: 401.1384.



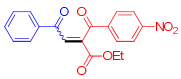
ethyl 2-benzoyl-4-oxo-4-phenylbut-2-enoate (3s):lit[4] yellow oil, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.15 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 7.2 Hz, 2H), 7.55-7.60 (m, 2H), 7.46 (q, *J* = 11.4 Hz, 4H), 4.27 (q, *J* = 10.8 Hz, 2H), 1.21 (t, *J* = 10.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (*E/Z*): δ = 193.3, 188.3, 163.6, 144.8, 136.1, 135.8, 134.2, 133.5, 128.9, 128.8, 128.7, 128.5, 128.4, 62.4, 31.9; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{19}H_{17}O_4$: 309.1121; found: 309.1121.



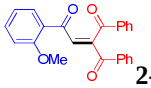
ethyl 4-oxo-4-phenyl-2-(3,4,5-trimethoxybenzoyl)but-2-enoate (3t): lit[4] yellow oil, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.97 (d, *J* = 12.0 Hz, 2H), 7.62 (t, *J* = 10.8 Hz, 1H), 7.49 (t, *J* = 11.4 Hz, 2H), 7.15 (s, 2H), 4.31 (q, *J* = 10.8 Hz, 2H), 3.85-3.91 (m, 9H), 1.26 (t, *J* = 10.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (*E/Z*): δ = 191.9, 191.1, 190.1, 188.5, 164.1, 163.7, 153.2, 144.2, 140.4, 136.1, 135.7, 134.2, 130.9, 130.7, 128.9, 128.7, 107.1, 107.0, 106.0, 105.8, 62.4, 56.2, 56.1, 56.0, 14.0, 13.8; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{22}H_{23}O_7$: 399.1438; found: 399.1439.



ethyl 2-(furan-2-carbonyl)-4-oxo-4-phenylbut-2-enoate (3u): lit[4] yellow oil, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.55 (s, 1H), 7.49 (q, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 3.0 Hz, 1H), 6.55 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (*E/Z*): δ = 188.7, 180.6, 163.3, 152.0, 147.9, 142.5, 136.1, 134.7, 134.2, 128.8, 118.2, 112.9, 112.5, 62.4, 13.9; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{17}H_{15}O_5$: 299.0914; found: 299.0914.



ethyl 2-(4-nitrobenzoyl)-4-oxo-4-phenylbut-2-enoate (3v): yellow solid, mp 96–97 ℃ (lit[4] mp 97-98 ℃); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.4 Hz, 2H), 8.21 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 4.31 (q, *J* = 7.8 Hz, 2H), 1.24 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (*E/Z*): δ = 192.0, 188.1, 163.0, 144.1, 140.2, 135.7, 134.6, 133.9, 129.4, 129.2, 128.8, 124.0, 123.9, 62.7, 13.9, 13.8; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{15}NNaO_6$: 376.0792; found: 376.0801.



2-benzoyl-4-(2-methoxyphenyl)-1-phenylbut-2-ene-1,4-dione (3w): White solid, mp 95–98 □; IR (KBr): 3445, 3055, 2940, 1662, 1645, 1594, 1569, 1515, 1447, 1426, 1375, 1318, 1275, 1228, 1172, 1123, 1010 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.05 (d, *J* = 7.2 Hz, 2H), 8.00 (d, *J* = 7.2 Hz, 2H), 7.58-7.63 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 4H), 7.45 (q, *J* = 7.2 Hz, 3H), 6.94 (q, *J*

= 7.2 Hz, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.3, 193.6, 189.9, 159.1, 148.4, 136.3, 136.1, 136.0, 135.0, 133.7, 133.4, 131.1, 130.1, 129.1, 128.6, 121.0, 111.6, 55.7; HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{24}H_{19}O_4$: 371.1278; found: 371.1278.

4. Reference

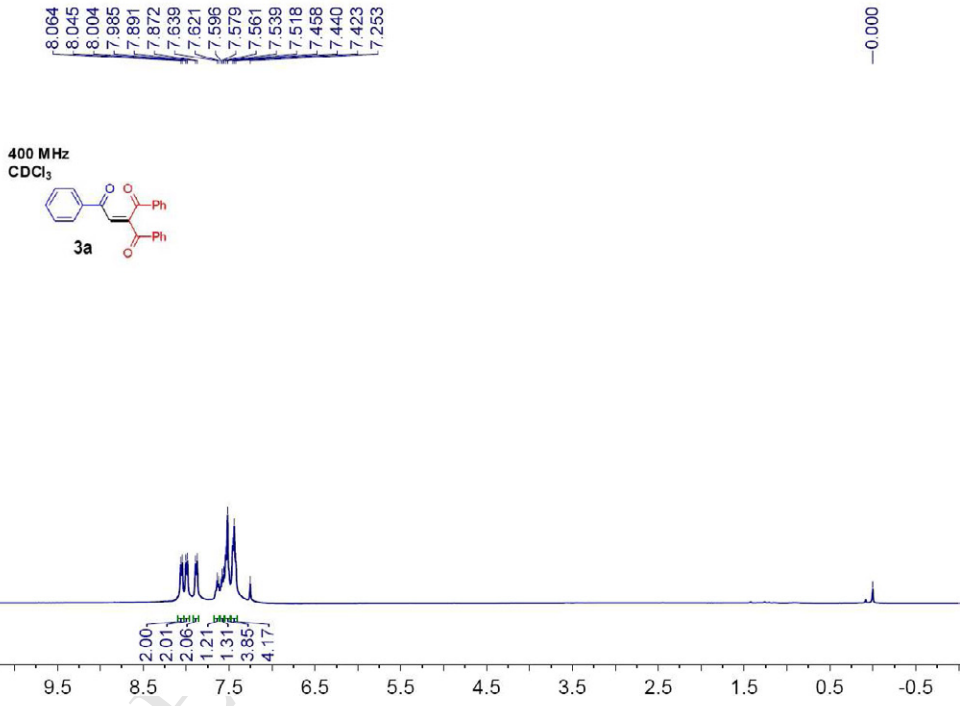
(1) Yin, G. D.; Gao, M.; She, N. F.; Hu, S. L.; Wu, A. X.; Pan, Y. J. *Synthesis* **2007**, 3113.

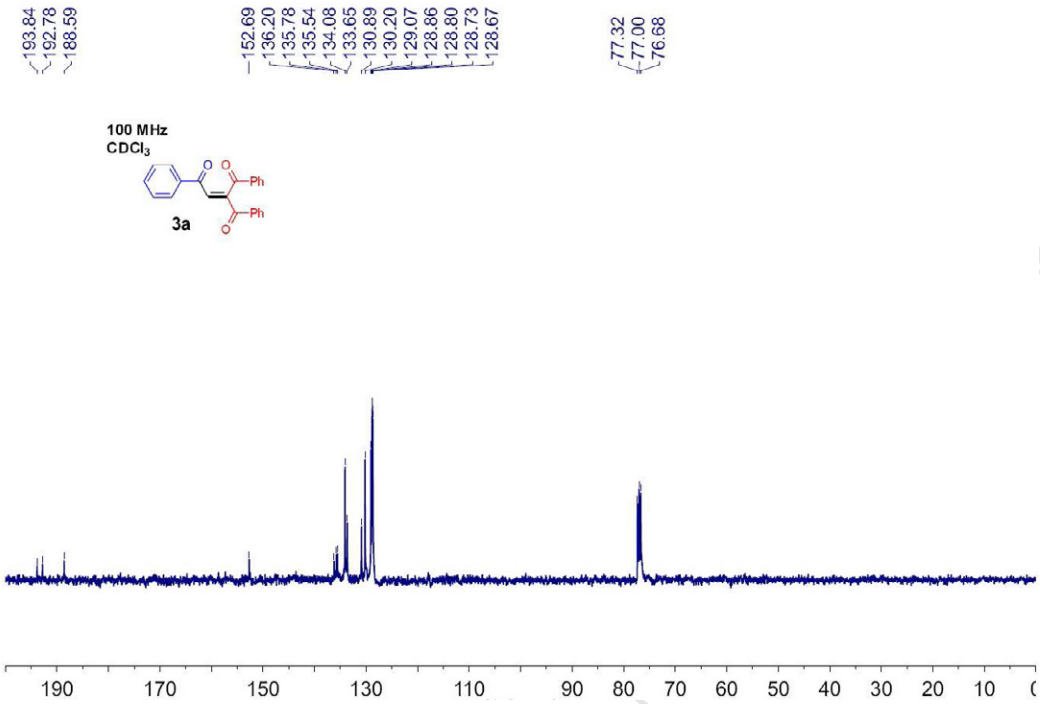
(2) Lee. J. C.; Bae, Y. H.; Chang, S.-K. *Bull. Korean. Chem. Soc.* **2003**, *24*, 407.

(3) Dien, C.-K.; Lutz, R. E. *J. Am. Chem. Soc.* **1956**, *78*, 1987.

(4) Gao, M.; Yang, Y.; Wu, Y. D.; Deng, C.; Cao, L. P.; Meng, X. G.; Wu, A. X. *Org. Lett.* **2010**, *12*, 1856.

5. Appendix: spectral copies of ^{1}H NMR, and ^{13}C NMR

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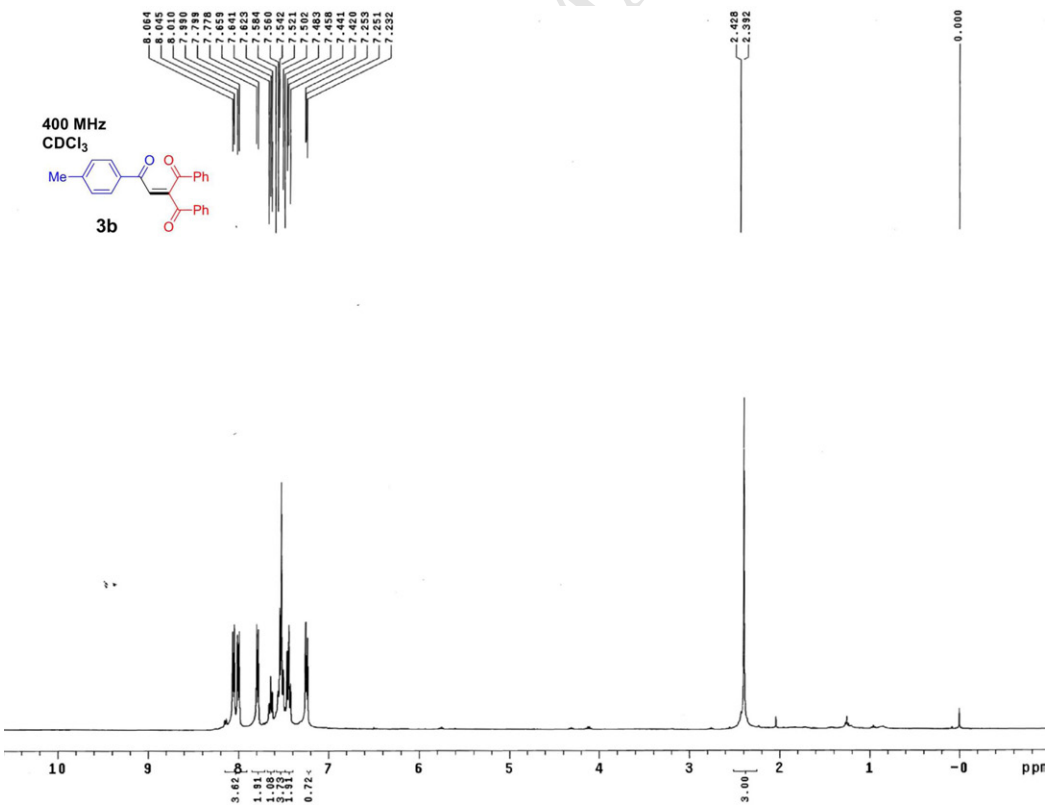
188.59
152.69
136.20
135.78
135.54
134.08
133.65
130.89
130.20
129.07
128.86
128.80
128.73
128.67
77.32
77.00
76.68
100 MHz
CDCl3
Ph
Ph
3a
190
170
150
130
110
90
80
70
60
50
40
30
20
10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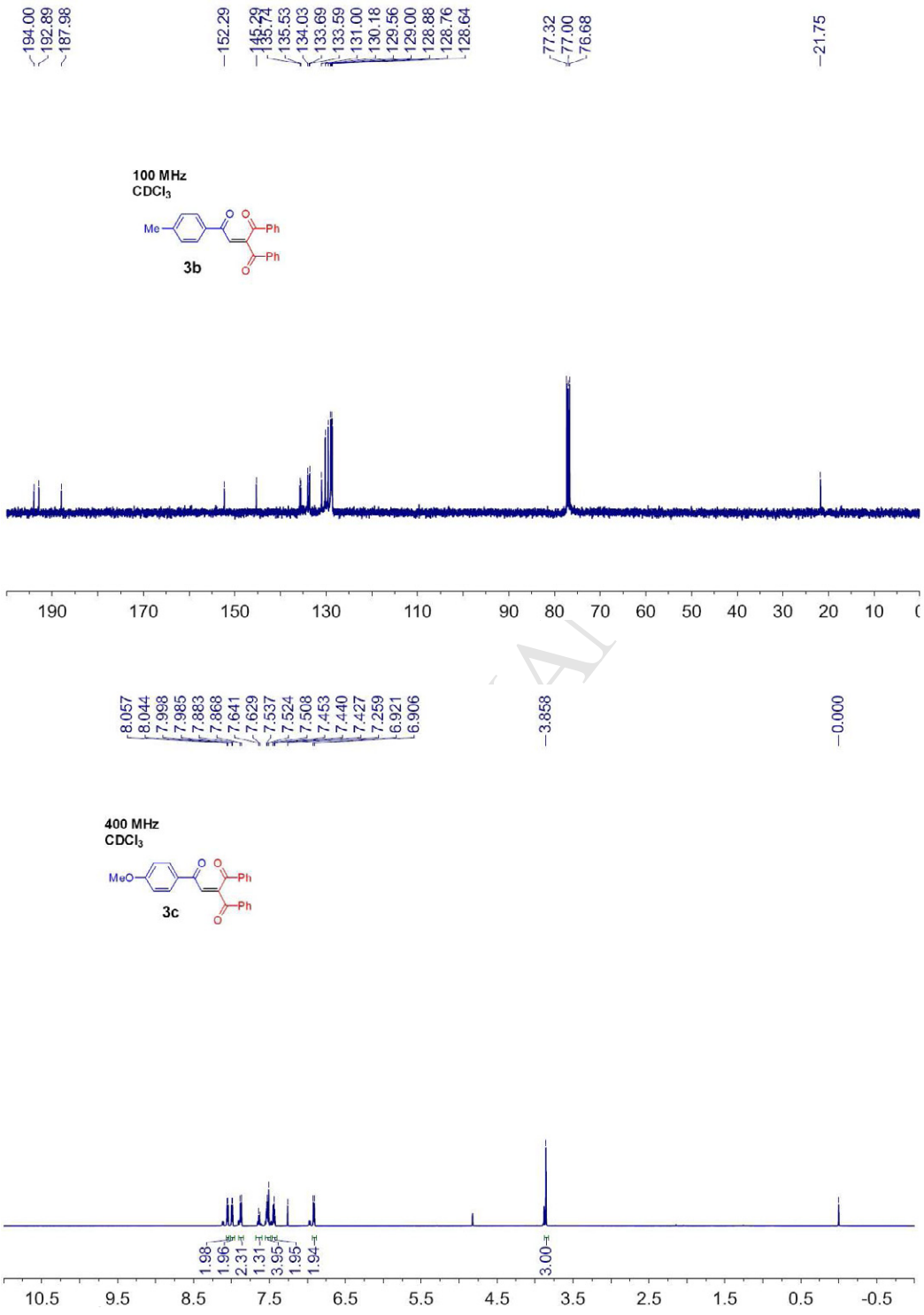
8.045
7.799
7.778
7.659
7.641
7.623
7.564
7.542
7.521
7.502
7.483
7.458
7.441
7.423
7.253
7.251
7.232
2.428
2.392
0.000
400 MHz
CDCl3
Me
Ph
Ph
3b
10
9
8
7
6
5
4
3
2
1
-0
ppm
3.62
1.84
1.08
3.03
1.91
0.72
3.00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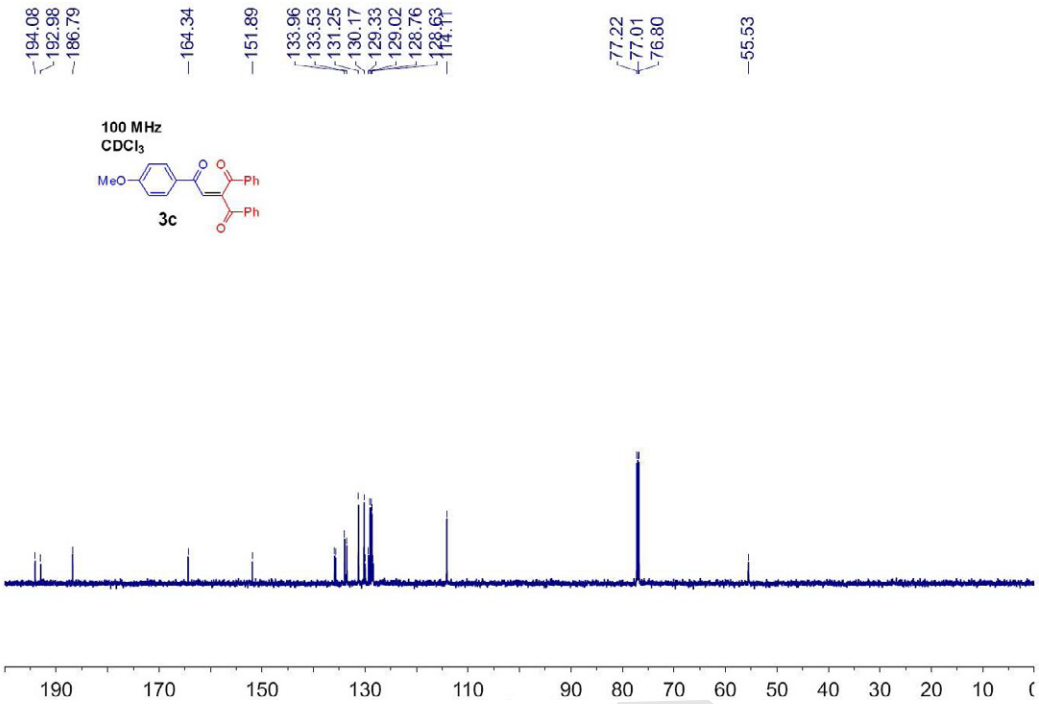
134.03
133.69
133.59
131.00
130.18
129.56
129.00
128.88
128.76
128.64
77.32
77.00
76.68
21.75
100 MHz
CDCl3
Me
Ph
Ph
3b
190
170
150
130
110
90
80
70
60
50
40
30
20
10
8.057
8.044
7.998
7.985
7.883
7.868
7.641
7.629
7.537
7.524
7.508
7.453
7.440
7.427
7.259
6.921
6.906
3.858
0.000
400 MHz
CDCl3
MeO
Ph
Ph
3c
1.98
1.96
2.31
1.31
3.95
1.93
1.94
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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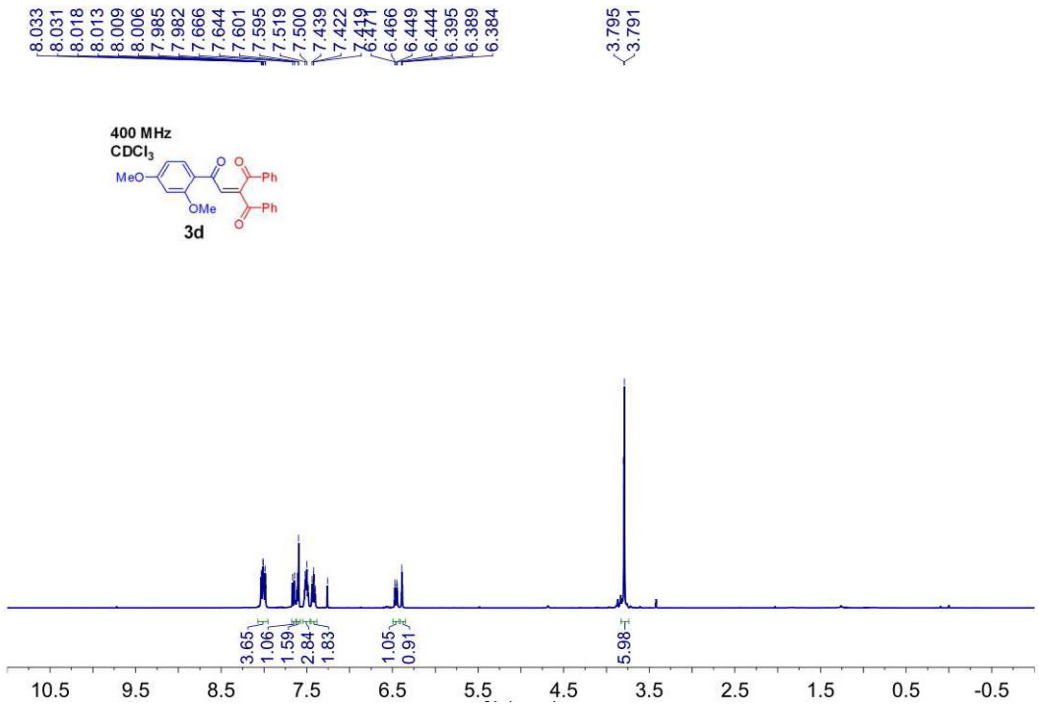
186.79
164.34
151.89
133.96
133.53
131.25
130.17
129.33
129.02
128.76
77.22
77.01
76.80
55.53
100 MHz
CDCl3
MeO
Ph
Ph
3c
190
170
150
130
110
90
80
70
60
50
40
30
20
10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8.018
8.013
8.009
8.006
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7.982
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7.644
7.601
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7.519
7.500
7.439
7.422
6.466
6.449
6.444
6.395
6.389
6.384
3.795
3.791
400 MHz
CDCl3
MeO
OMe
Ph
Ph
3d
3.65
1.06
1.59
2.84
1.83
1.05
0.91
5.98
10.5
9.5
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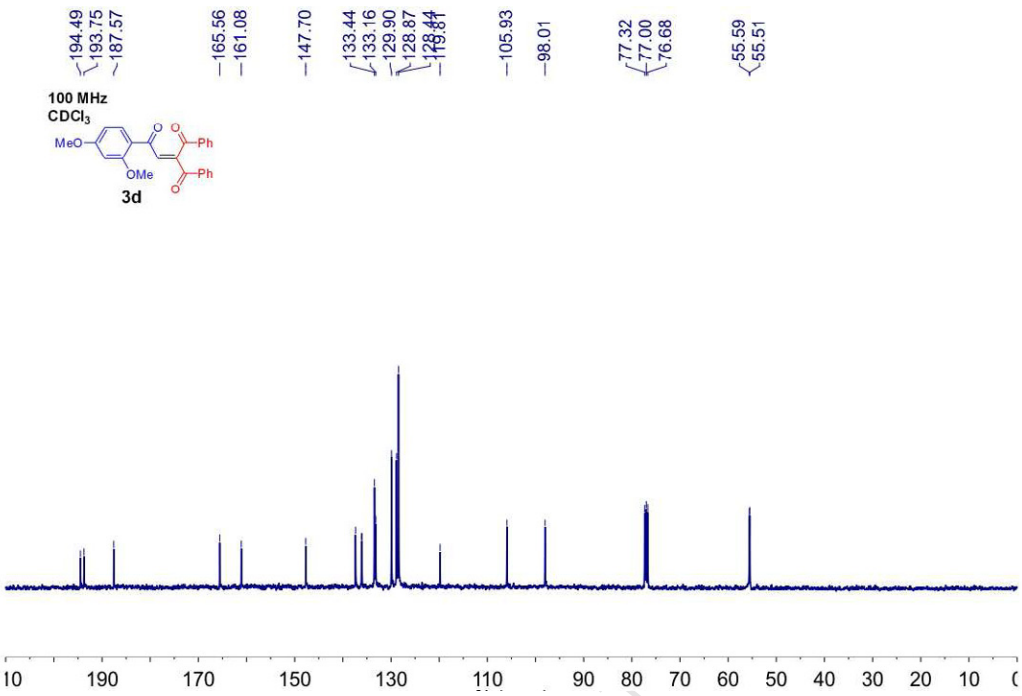
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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77.32
77.00
76.68
55.59
55.51
100 MHz
CDCl3
MeO
OMe
Ph
Ph
3d
10
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170
150
130
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80
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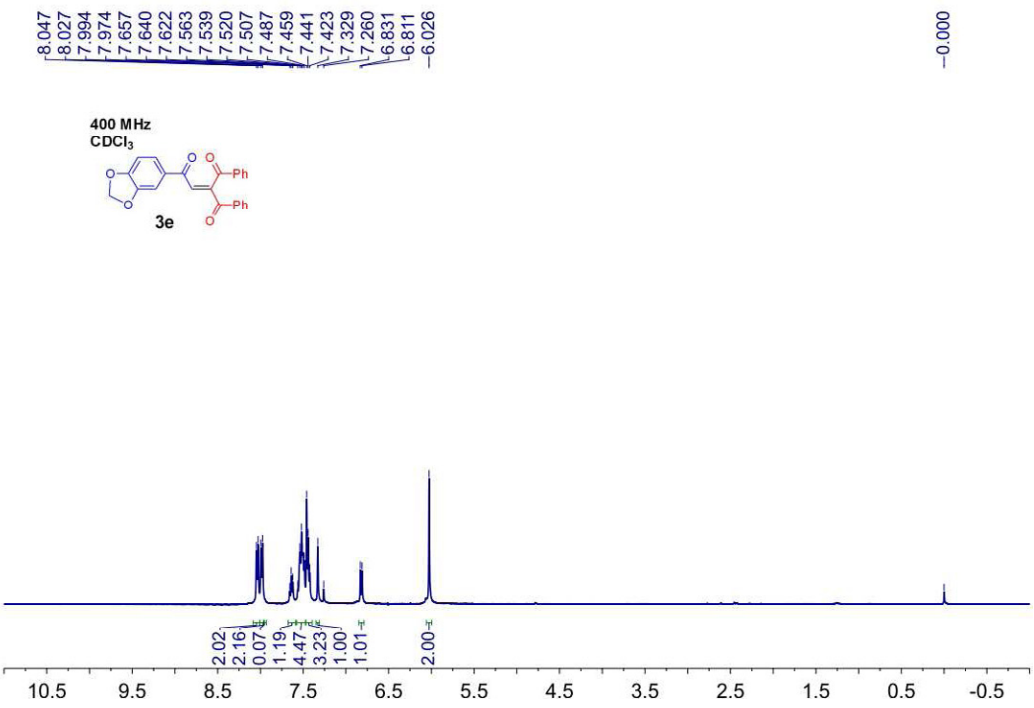
50
40
30
20
10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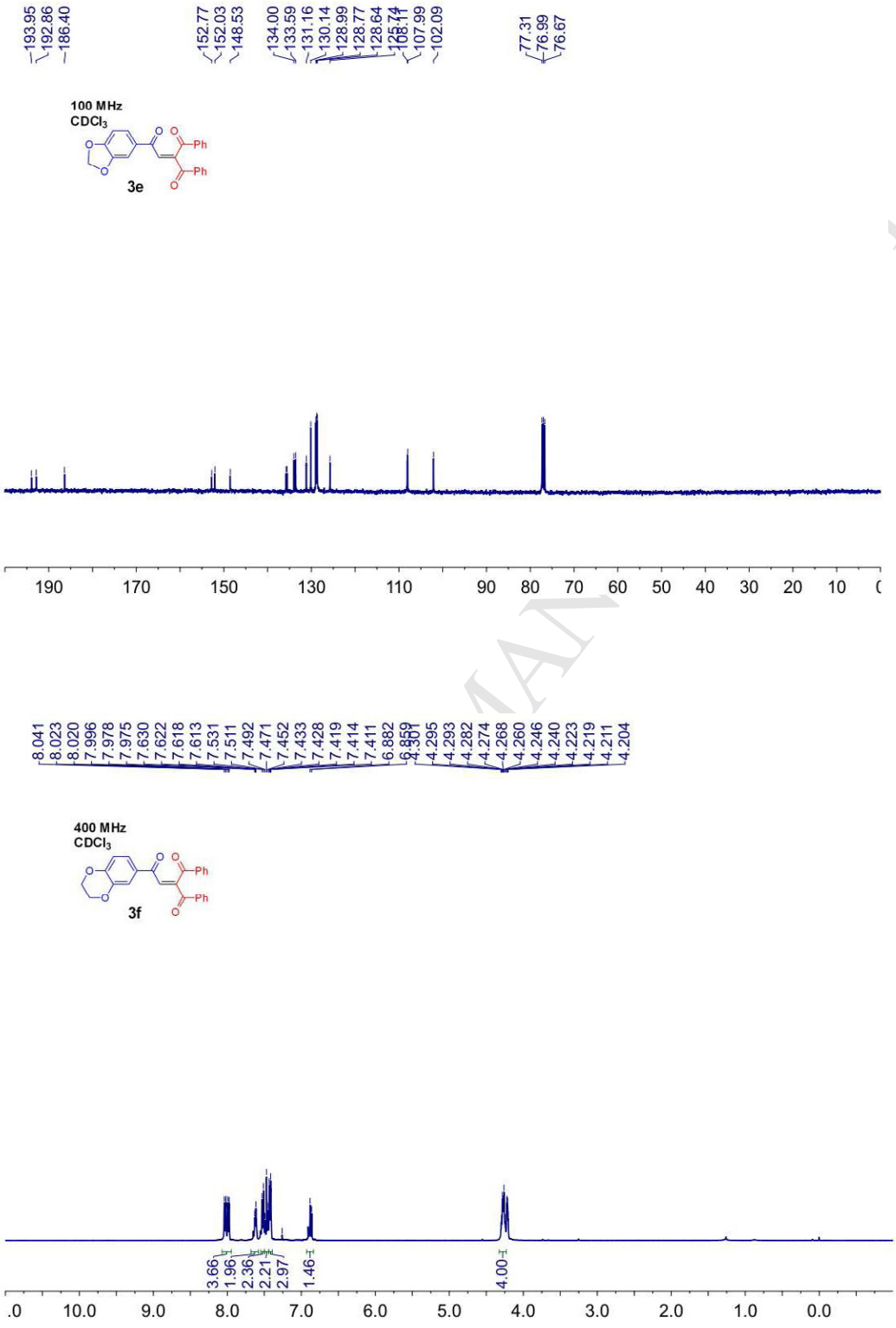
7.563
7.539
7.520
7.507
7.487
7.459
7.441
7.423
7.329
7.260
6.831
6.811
6.026
0.000
400 MHz
CDCl3
Ph
Ph
3e
2.02
2.16
0.07
1.19
4.47
3.23
1.00
1.01
2.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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128.64
107.99
102.09
77.31
76.99
76.67
100 MHz
CDCl3
Ph
Ph
3e
190
170
150
130
110
90
80
70
60
50
40
30
20
10
8.041
8.023
8.020
7.996
7.978
7.975
7.630
7.622
7.618
7.613
7.531
7.511
7.492
7.471
7.452
7.433
7.428
7.419
7.414
7.411
6.882
4.295
4.293
4.282
4.274
4.268
4.260
4.246
4.240
4.223
4.219
4.211
4.204
400 MHz
CDCl3
Ph
Ph
3f
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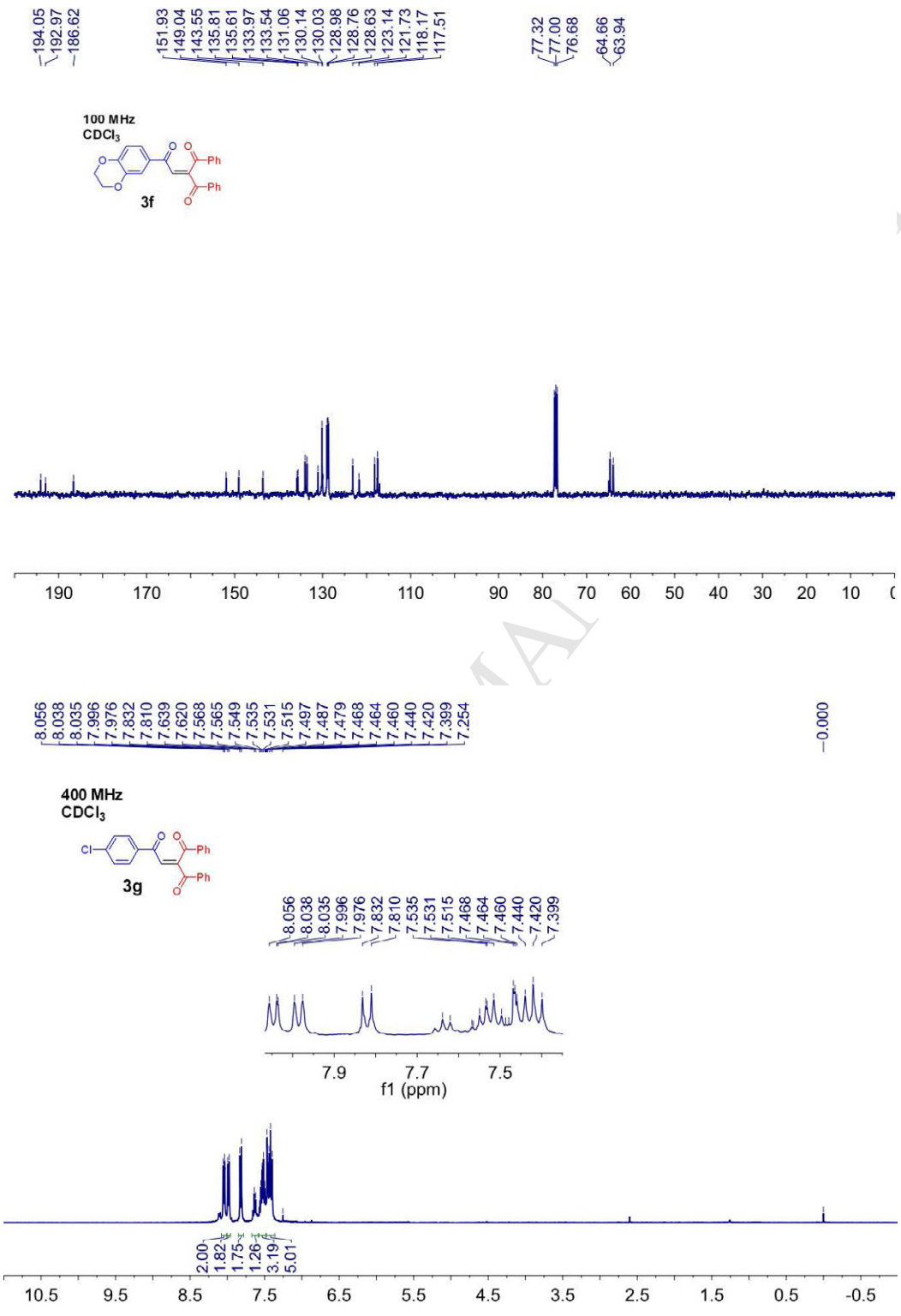
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130.03
128.98
128.76
128.63
123.14
121.73
118.17
117.51
77.32
77.00
76.68
64.66
63.94
100 MHz
CDCl3
Ph
Ph
3f
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170
150
130
110
90
80
70
60
50
40
30
20
10
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8.038
8.035
7.996
7.976
7.832
7.810
7.639
7.620
7.568
7.565
7.549
7.535
7.531
7.515
7.497
7.487
7.479
7.468
7.464
7.460
7.440
7.420
7.399
7.254
0.000
400 MHz
CDCl3
Cl
Ph
Ph
3g
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8.038
8.035
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7.832
7.810
7.535
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7.515
7.468
7.464
7.460
7.440
7.420
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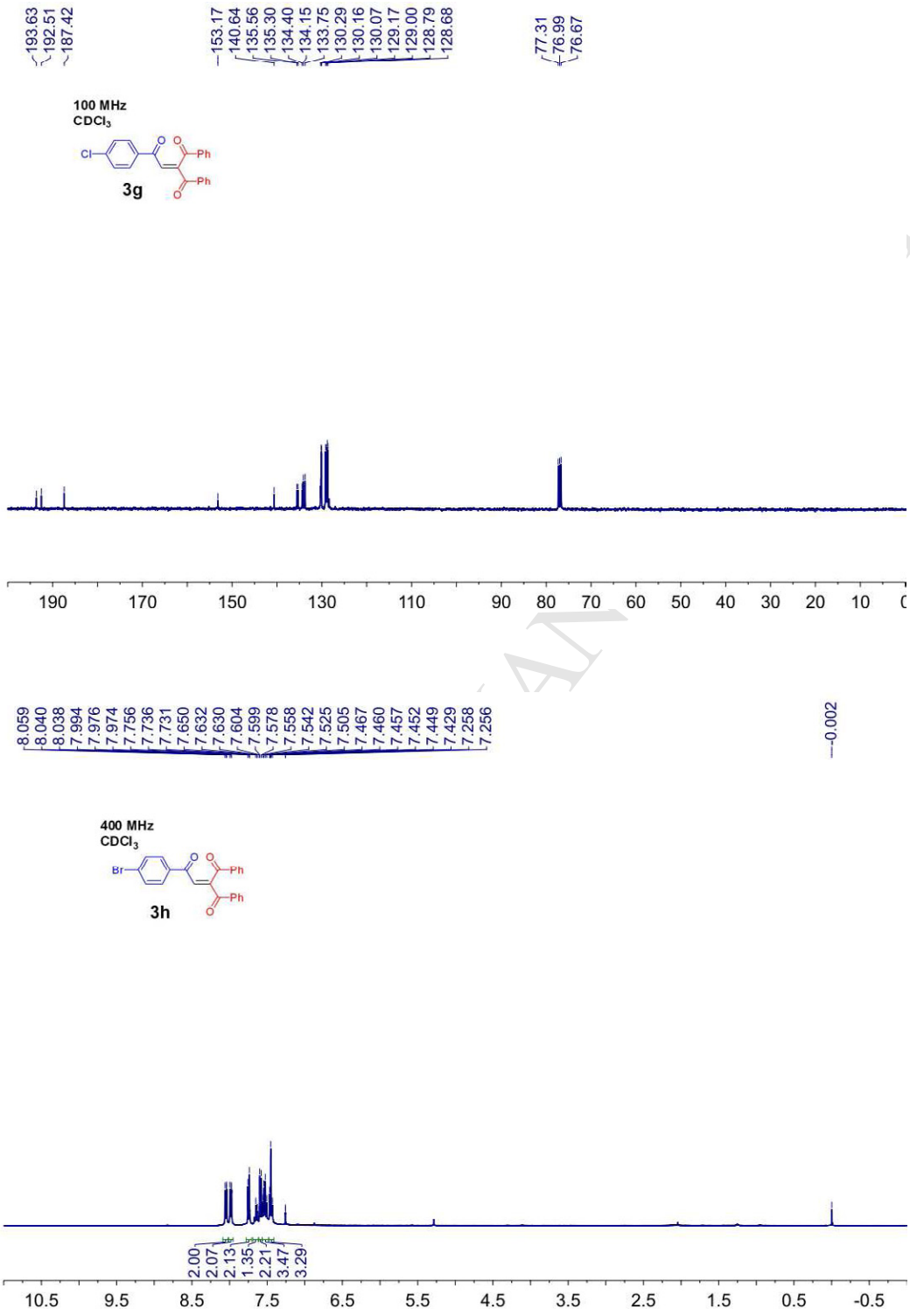
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128.68
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76.67
100 MHz
CDCl3
Cl
O
O
Ph
Ph
O
3g
190
170
150
130
110
90
80
70
60
50
40
30
20
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400 MHz
CDCl3
Br
O
O
Ph
Ph
O
3h
2.00
2.07
2.13
1.35
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3.47
3.29
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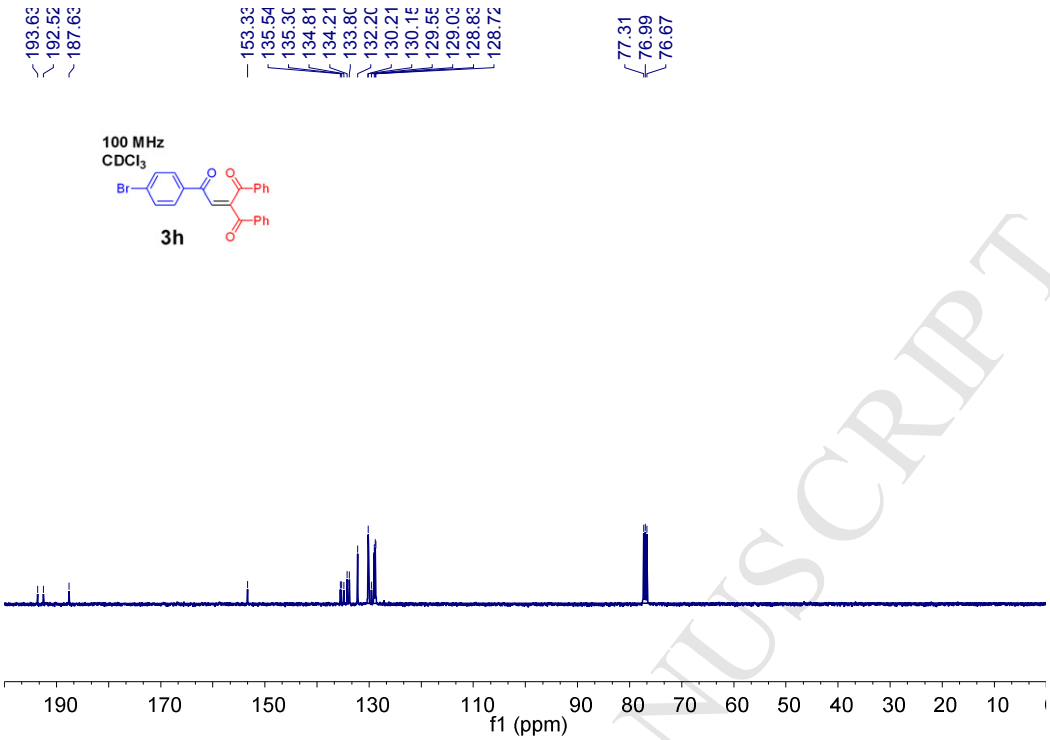
-0.5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129.03
128.83
128.72
77.31
76.99
76.67
100 MHz
CDCl3
Br
O
O
Ph
Ph
O
3h
190
170
150
130
110
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80
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60
50
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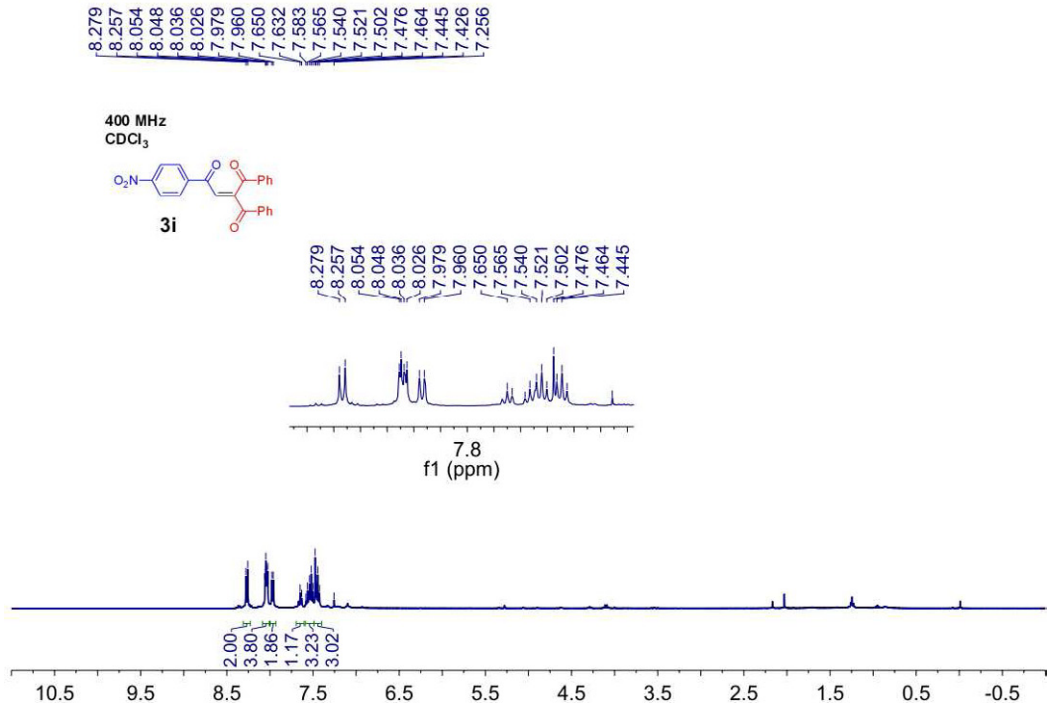
30
20
10
f1 (ppm)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400 MHz
CDCl3
O2N
O
O
Ph
Ph
O
3i
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f1 (ppm)
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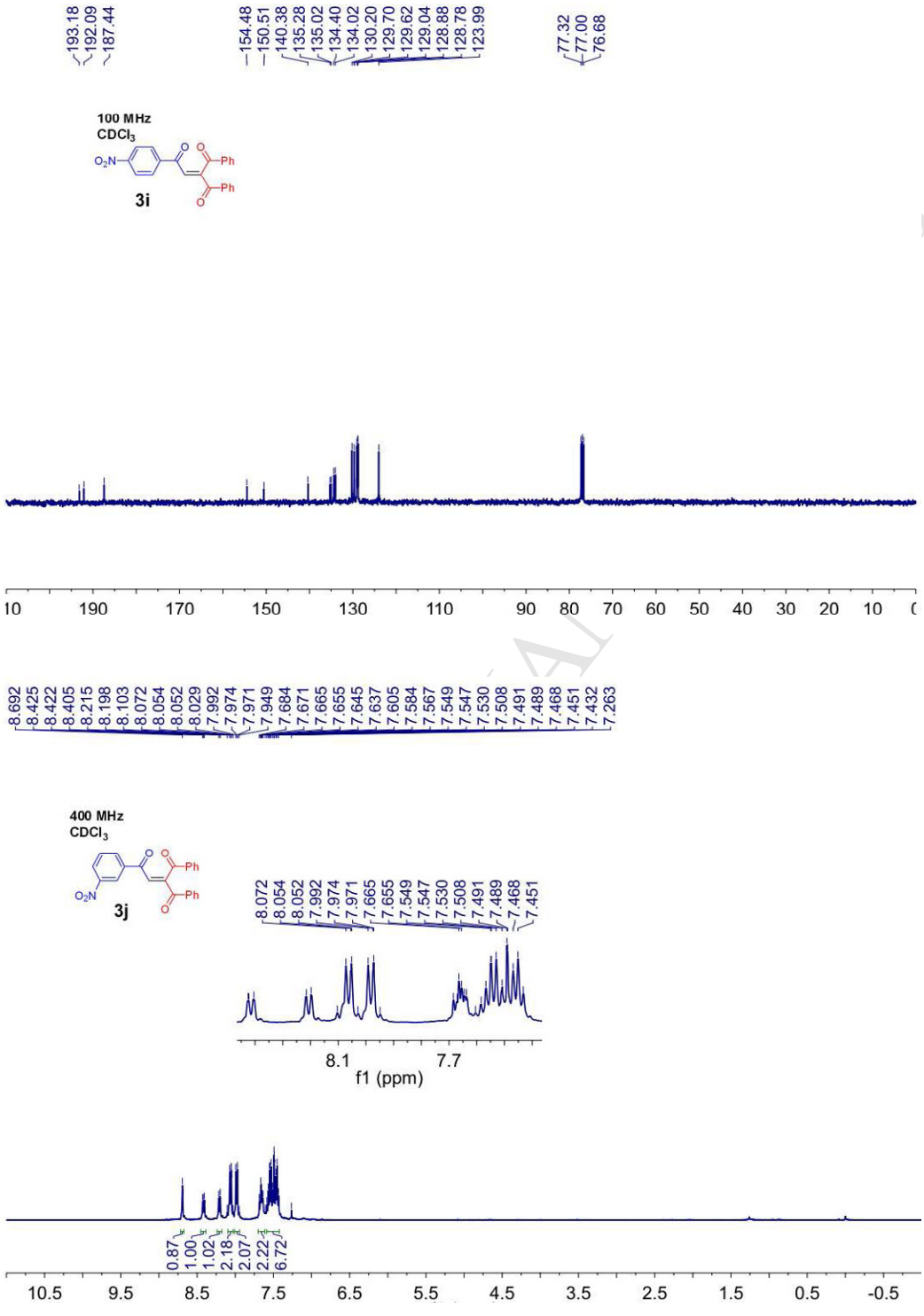
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100 MHz
CDCl3
O2N
Ph
Ph
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7.549
7.547
7.530
7.508
7.491
7.489
7.468
7.451
7.432
7.263
400 MHz
CDCl3
3j
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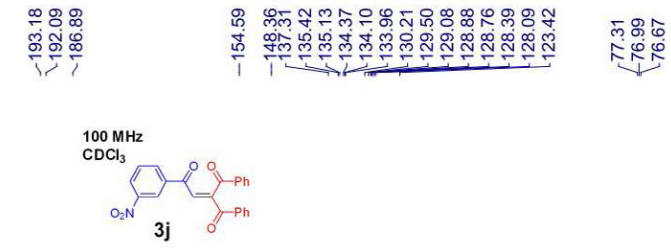
6.72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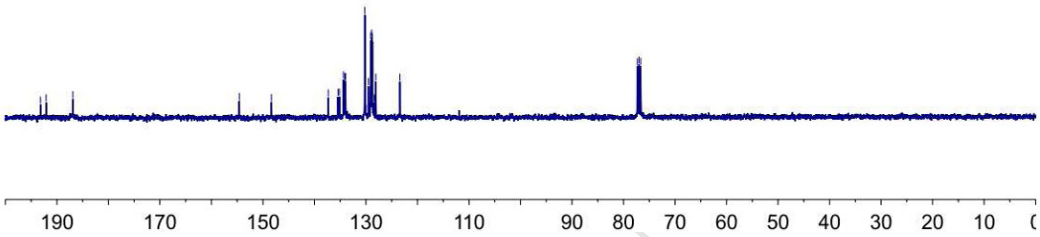
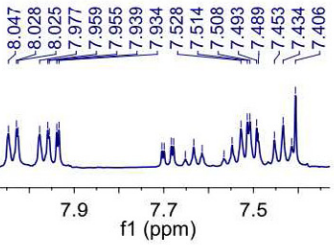
129.50
129.08
128.88
128.76
128.39
128.09
123.42
77.31
76.99
76.67

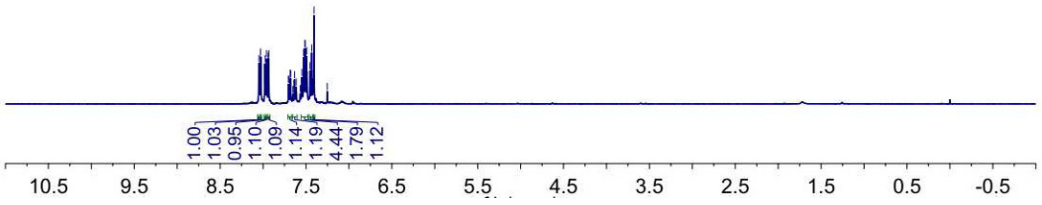
100 MHz
CDCl3
Ph
Ph
O2N
3j

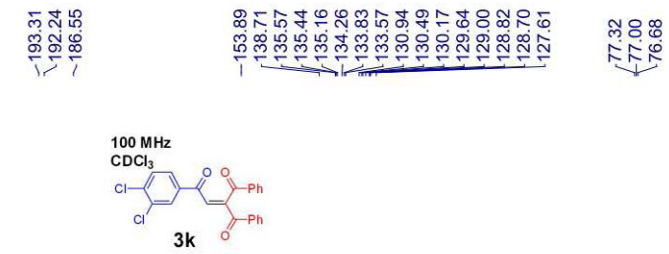

190
170
150
130
110
90
80
70
60
50
40
30
20
10

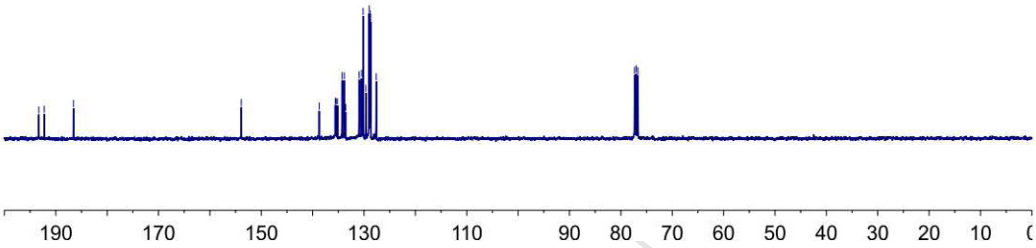

8.047
8.028
8.025
7.977
7.959
7.955
7.939
7.934
7.704
7.699
7.683
7.678
7.652
7.633
7.615
7.566
7.547
7.528
7.514
7.508
7.493
7.489
7.453
7.434
7.415
7.406
7.252


400 MHz
CDCl3
Cl
Cl
Ph
Ph
3k

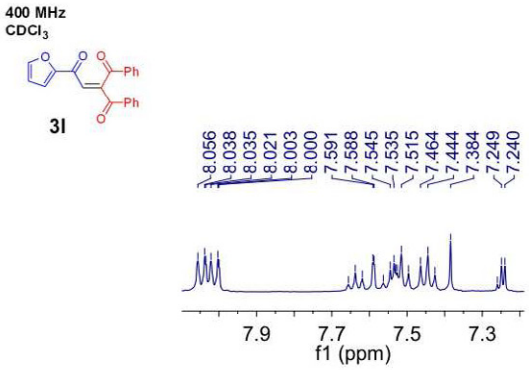

8.047
8.028
8.025
7.977
7.959
7.955
7.939
7.934
7.528
7.514
7.508
7.493
7.489
7.453
7.434
7.406
7.9
7.7
7.5
f1 (ppm)

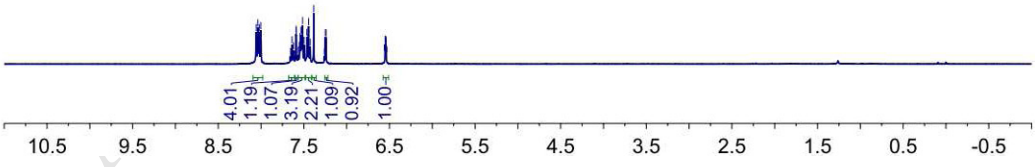

1.00
1.03
0.95
1.10
1.09
1.14
1.19
4.44
1.79
1.12
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

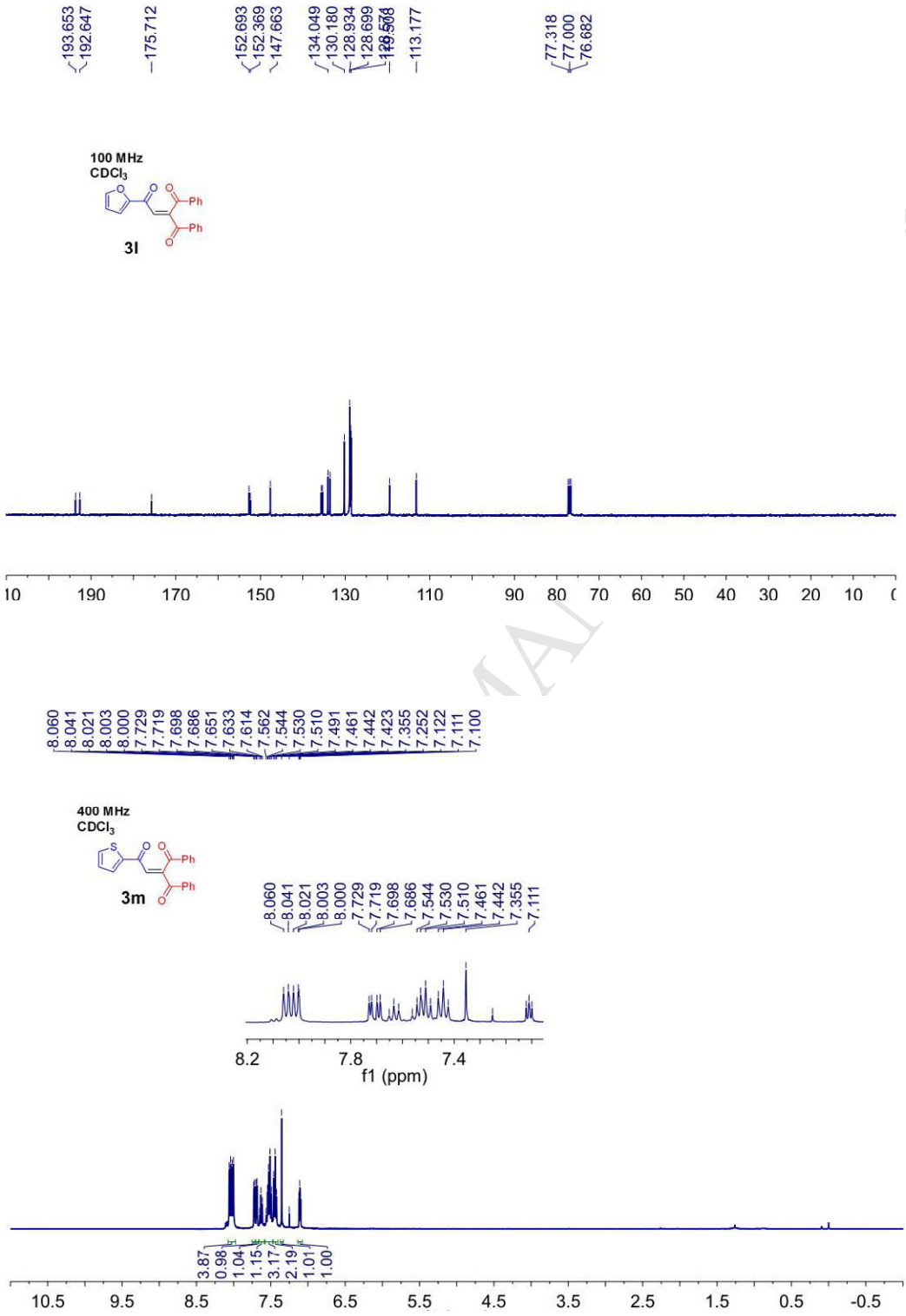

193.31
192.24
186.55
153.89
138.71
135.57
135.44
135.16
134.26
133.83
133.57
130.94
130.49
130.17
129.64
129.00
128.82
128.70
127.61
77.32
77.00
76.68
100 MHz
CDCl3
Cl
Cl
O
O
Ph
Ph
O
3k


190
170
150
130
110
90
80
70
60
50
40
30
20
10

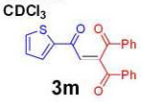

8.056
8.038
8.035
8.021
8.003
8.000
7.591
7.588
7.545
7.535
7.530
7.515
7.464
7.444
7.384
7.249
7.240
6.550
6.546
6.541
6.537


400 MHz
CDCl3
O
O
Ph
Ph
O
3l
8.056
8.038
8.035
8.021
8.003
8.000
7.591
7.588
7.545
7.535
7.515
7.464
7.444
7.384
7.249
7.240
7.9
7.7
7.5
7.3
f1 (ppm)

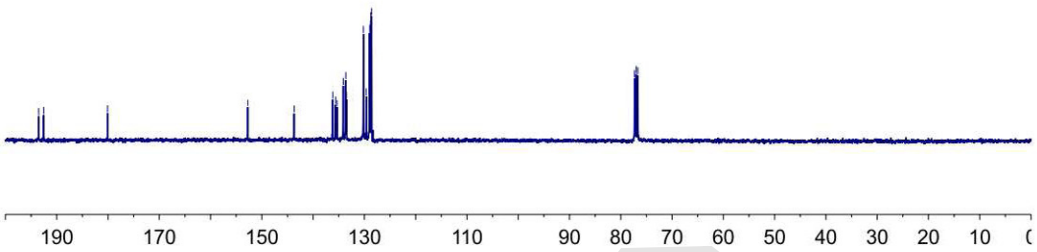

4.01
1.19
1.07
3.19
2.21
1.09
0.92
1.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


193.653
192.647
175.712
152.693
152.369
147.663
134.049
130.180
128.934
128.699
113.177
77.318
77.000
76.682
100 MHz
CDCl3
Ph
Ph
3l
8.060
8.041
8.021
8.003
8.000
7.729
7.719
7.698
7.686
7.651
7.633
7.614
7.562
7.544
7.530
7.510
7.491
7.461
7.442
7.423
7.355
7.252
7.122
7.111
7.100
400 MHz
CDCl3
Ph
Ph
3m
8.060
8.041
8.021
8.003
8.000
7.729
7.719
7.698
7.686
7.544
7.530
7.510
7.461
7.442
7.355
7.111
8.2
7.8
7.4
f1 (ppm)
3.87
0.98
1.04
1.15
3.17
2.19
1.01
1.00

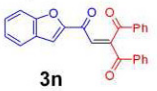
100 MHz
$CDCl_3$



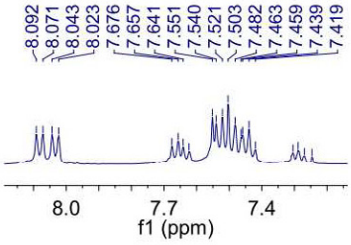
3m

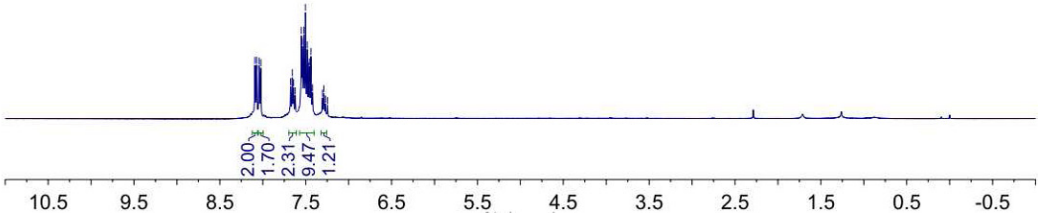


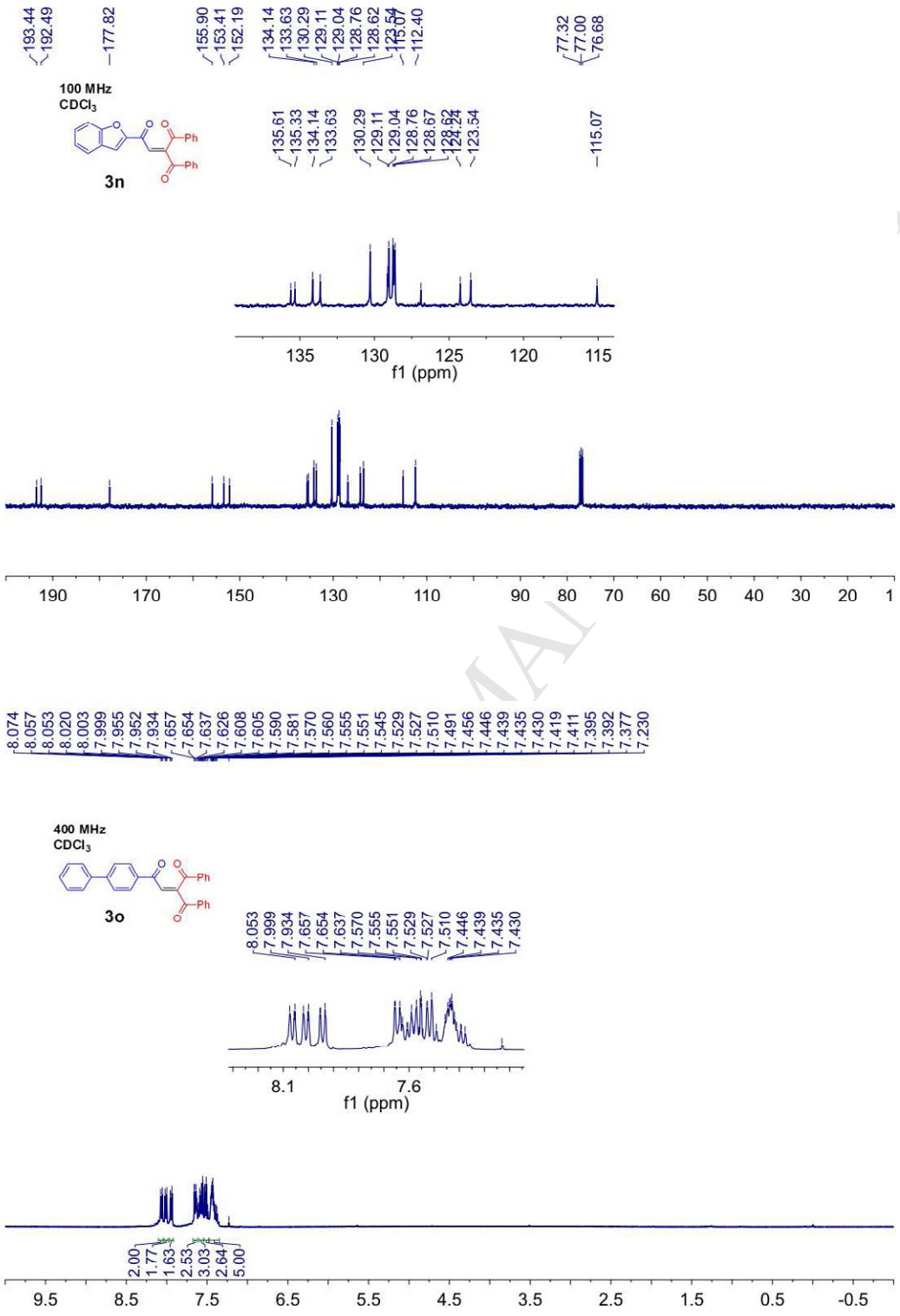
400 MHz
$CDCl_3$

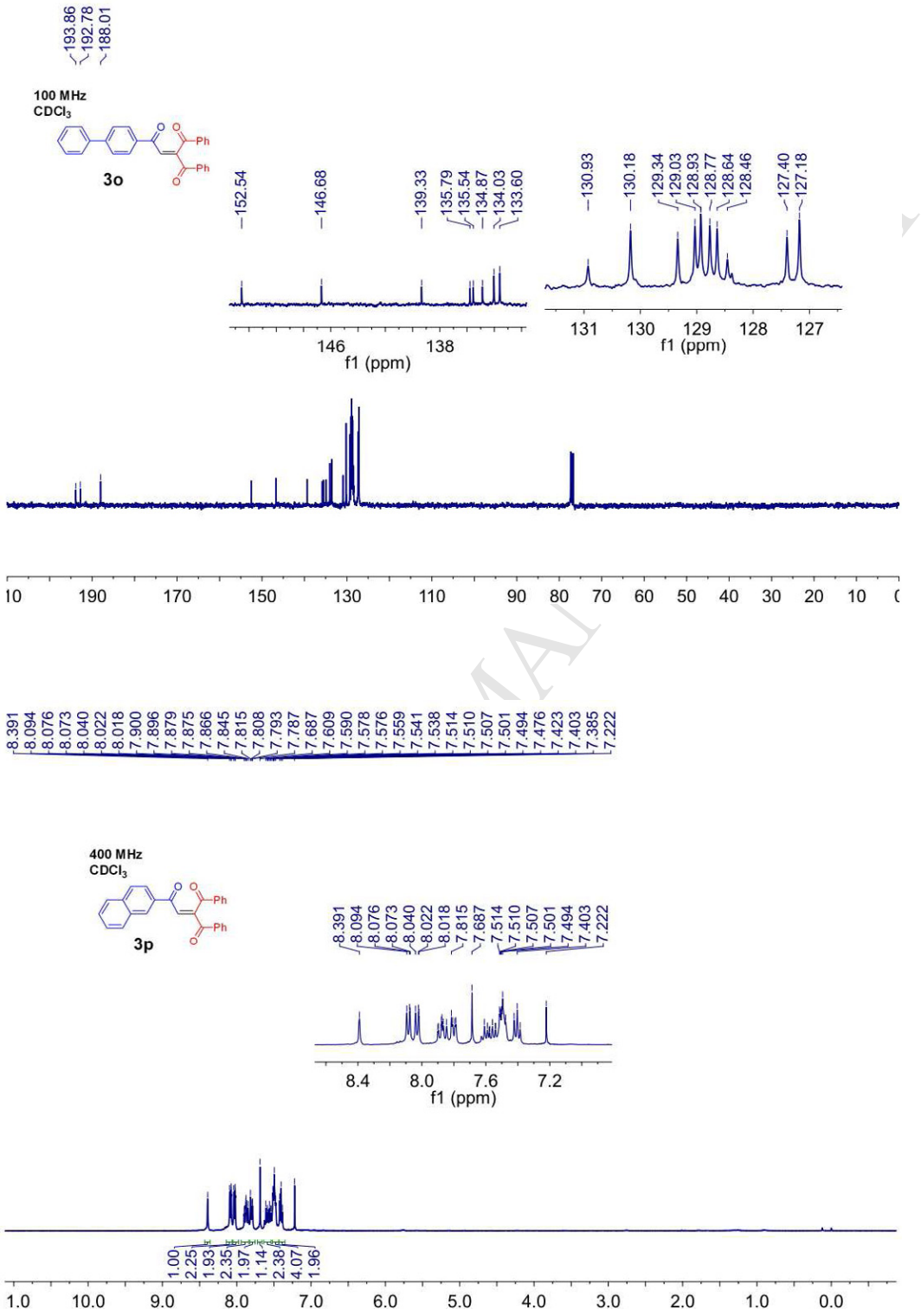


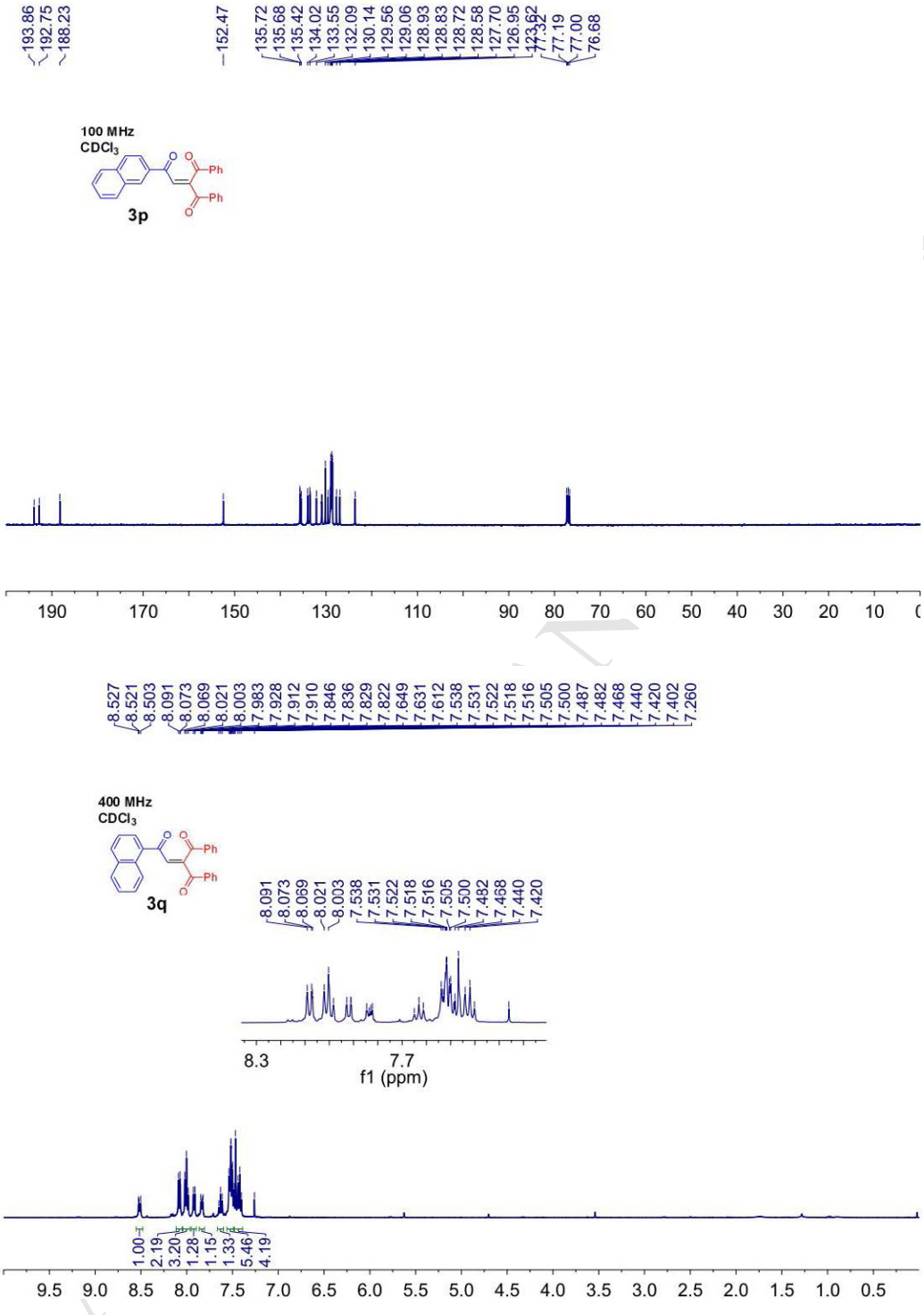
3n

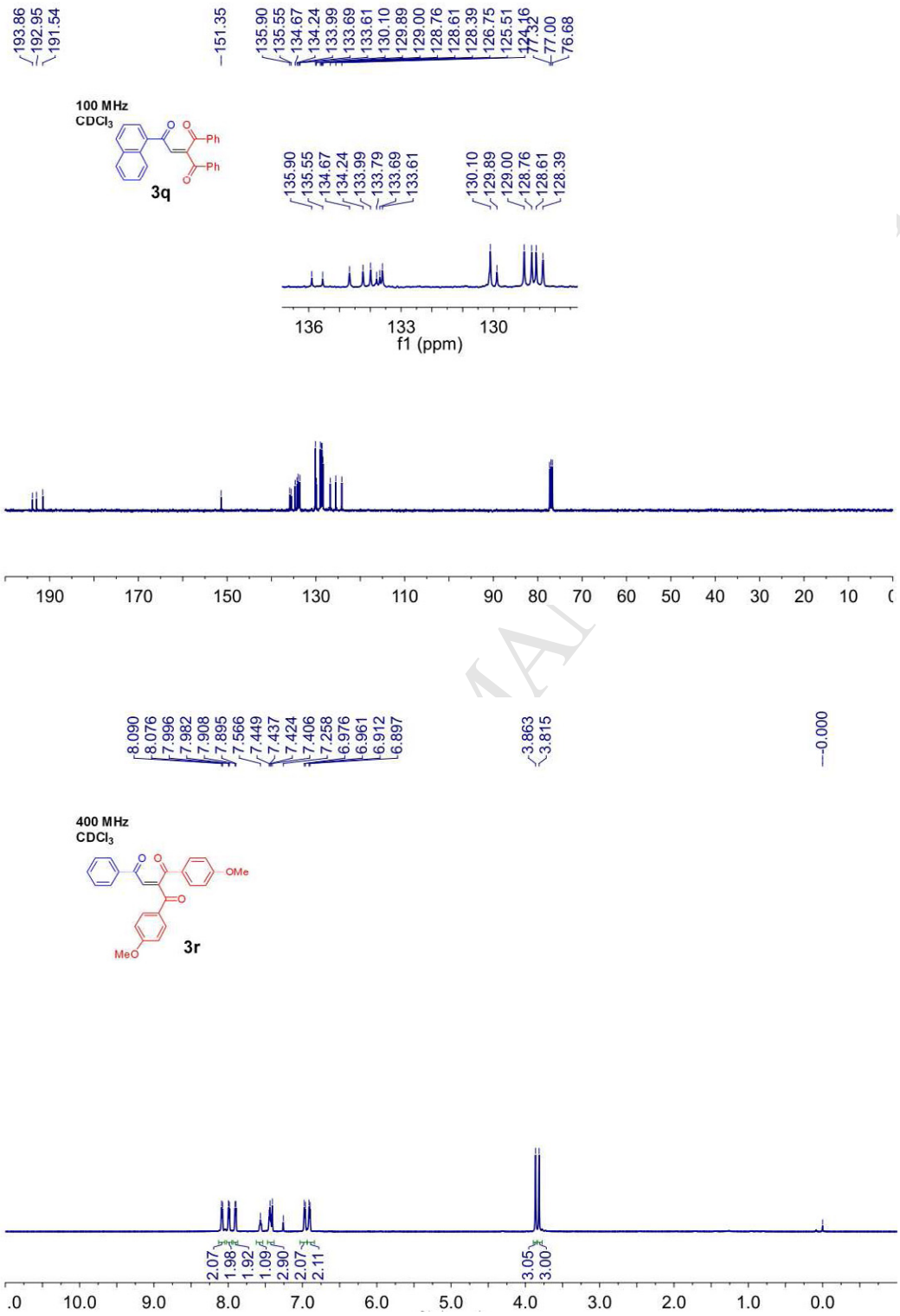


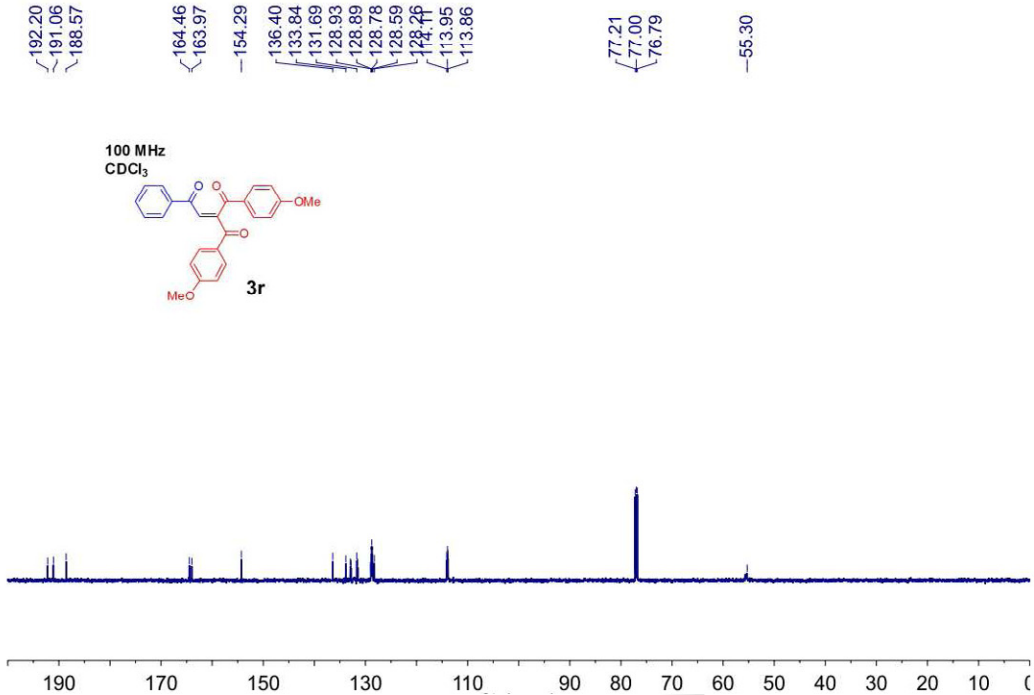


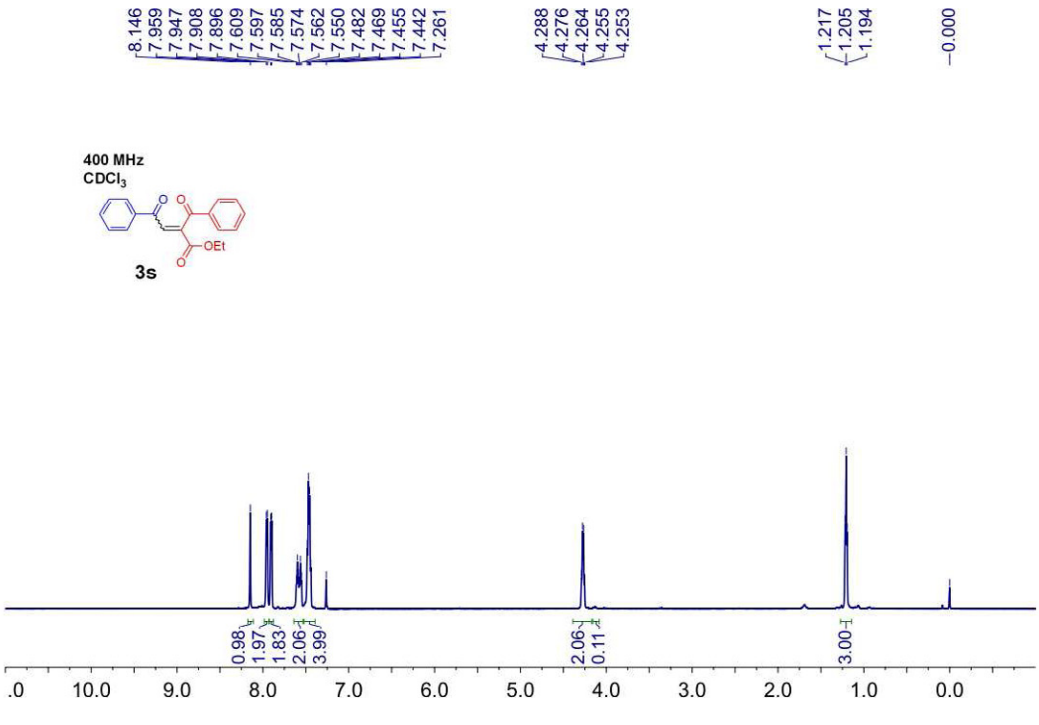

193.44
192.49
177.82
155.90
153.41
152.19
134.14
133.63
130.29
129.11
129.04
128.76
128.62
123.54
115.07
112.40
77.32
77.00
76.68
100 MHz
CDCl3
Ph
Ph
3n
135.61
135.33
134.14
133.63
130.29
129.11
129.04
128.76
128.67
123.54
115.07
135
130
125
120
115
f1 (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
1
8.074
8.057
8.053
8.020
8.003
7.999
7.955
7.952
7.934
7.657
7.654
7.637
7.626
7.608
7.605
7.590
7.581
7.570
7.560
7.555
7.551
7.545
7.529
7.527
7.510
7.491
7.456
7.446
7.439
7.435
7.430
7.419
7.411
7.395
7.392
7.377
7.230
400 MHz
CDCl3
Ph
Ph
3o
8.053
7.999
7.934
7.657
7.654
7.637
7.570
7.555
7.551
7.529
7.527
7.510
7.446
7.439
7.435
7.430
8.1
7.6
f1 (ppm)
2.00
1.77
1.63
2.53
3.03
2.64
5.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

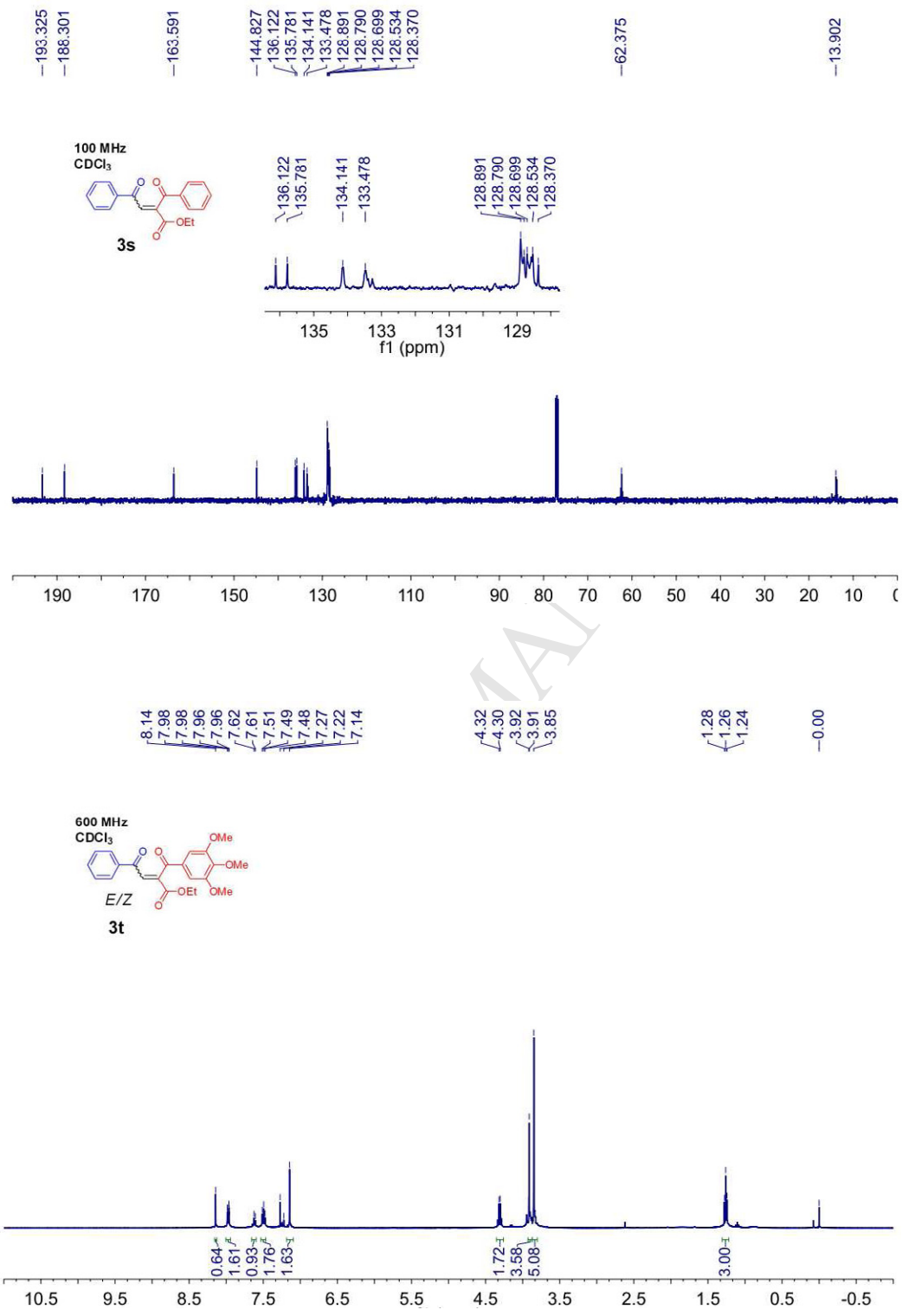

193.86
192.78
188.01
100 MHz
CDCl3
Ph
Ph
3o
152.54
146.68
139.33
135.79
135.54
134.87
134.03
133.60
130.93
130.18
129.34
129.03
128.93
128.77
128.64
128.46
127.40
127.18
146
138
131
130
129
128
127
f1 (ppm)
8.391
8.094
8.076
8.073
8.040
8.022
8.018
7.900
7.896
7.879
7.875
7.866
7.845
7.815
7.808
7.793
7.787
7.687
7.609
7.590
7.578
7.576
7.559
7.541
7.538
7.514
7.510
7.507
7.501
7.494
7.476
7.423
7.403
7.385
7.222
400 MHz
CDCl3
Ph
Ph
3p
8.4
8.0
7.6
7.2
f1 (ppm)
1.00
2.25
1.93
2.35
1.97
1.14
2.38
4.07
1.96

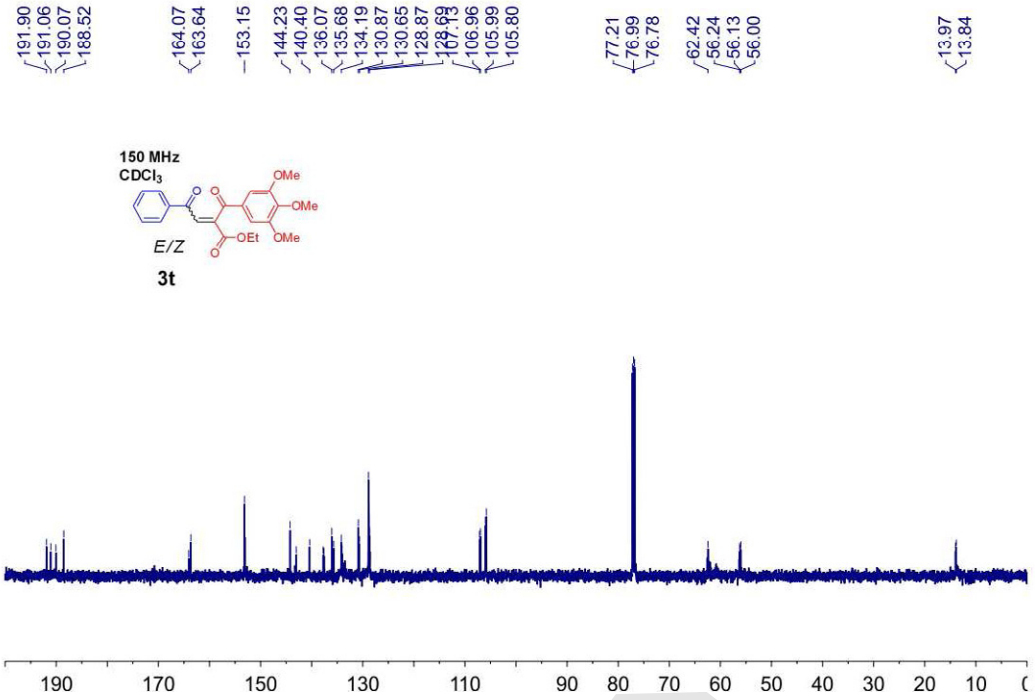

193.86
192.75
188.23
152.47
135.72
135.68
135.42
134.02
133.55
132.09
130.14
129.56
129.06
128.93
128.83
128.72
128.58
127.70
126.95
123.62
77.32
77.19
77.00
76.68
100 MHz
CDCl3
Ph
Ph
3p
190
170
150
130
110
90
80
70
60
50
40
30
20
10
8.527
8.521
8.503
8.091
8.073
8.069
8.021
8.003
7.983
7.928
7.912
7.910
7.846
7.836
7.829
7.822
7.649
7.631
7.612
7.538
7.531
7.522
7.518
7.516
7.505
7.500
7.487
7.482
7.468
7.440
7.420
7.402
7.260
400 MHz
CDCl3
Ph
Ph
3q
8.091
8.073
8.069
8.021
8.003
7.538
7.531
7.522
7.518
7.516
7.505
7.500
7.482
7.468
7.440
7.420
8.3
7.7
f1 (ppm)
1.00
2.19
3.20
1.28
1.15
1.33
5.46
4.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

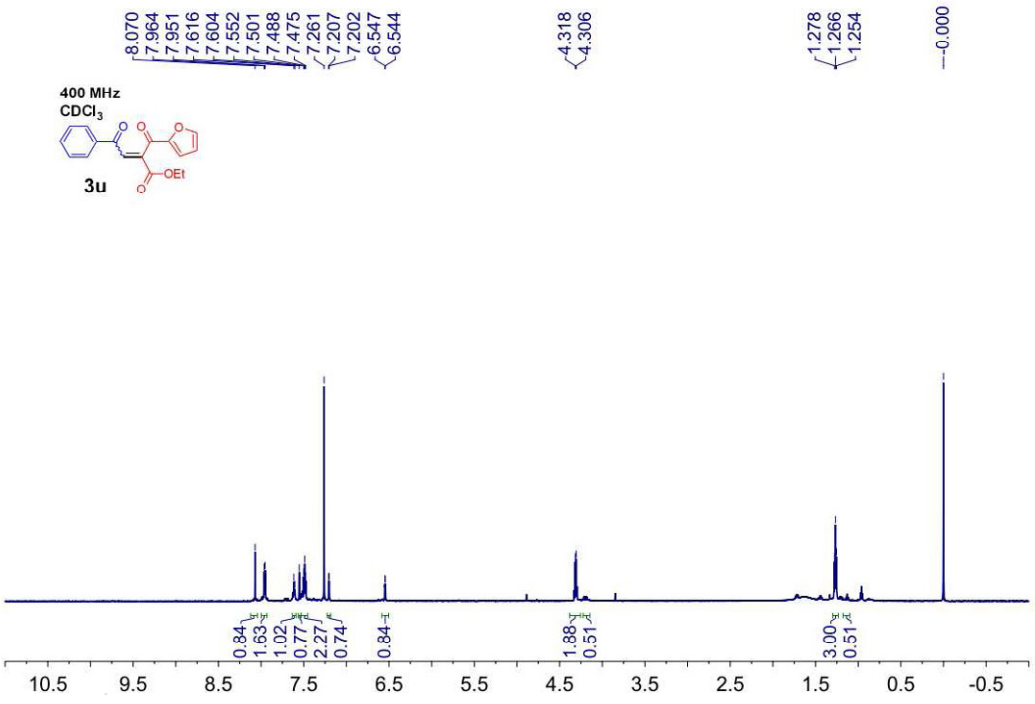

193.86
192.95
191.54
151.35
135.90
135.55
134.67
134.24
133.99
133.69
133.61
130.10
129.89
129.00
128.76
128.61
128.39
126.75
125.51
124.16
77.00
76.68
100 MHz
CDCl3
Ph
Ph
3q
136
133
130
f1 (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
8.090
8.076
7.996
7.982
7.908
7.895
7.566
7.449
7.437
7.424
7.406
7.258
6.976
6.961
6.912
6.897
3.863
3.815
0.000
400 MHz
CDCl3
OMe
MeO
3r
2.07
1.98
1.92
1.09
2.90
2.07
2.11
3.05
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

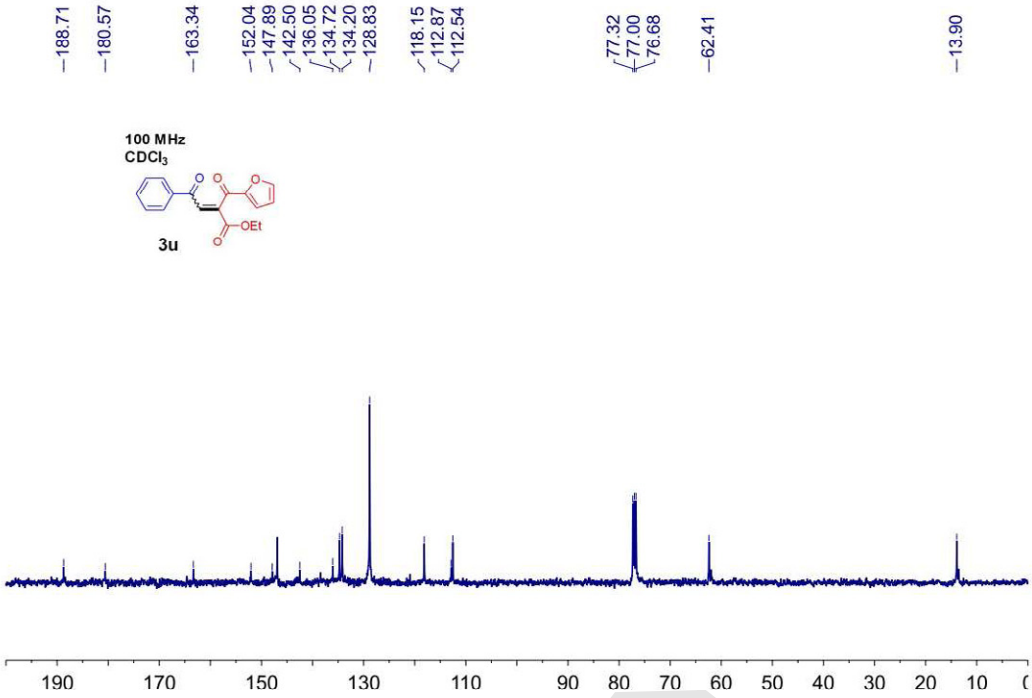

192.20
191.06
188.57
164.46
163.97
154.29
136.40
133.84
131.69
128.93
128.89
128.78
128.59
128.26
114.11
113.95
113.86
77.21
77.00
76.79
55.30
100 MHz
CDCl3
OMe
MeO
3r
190
170
150
130
110
90
80
70
60
50
40
30
20
10

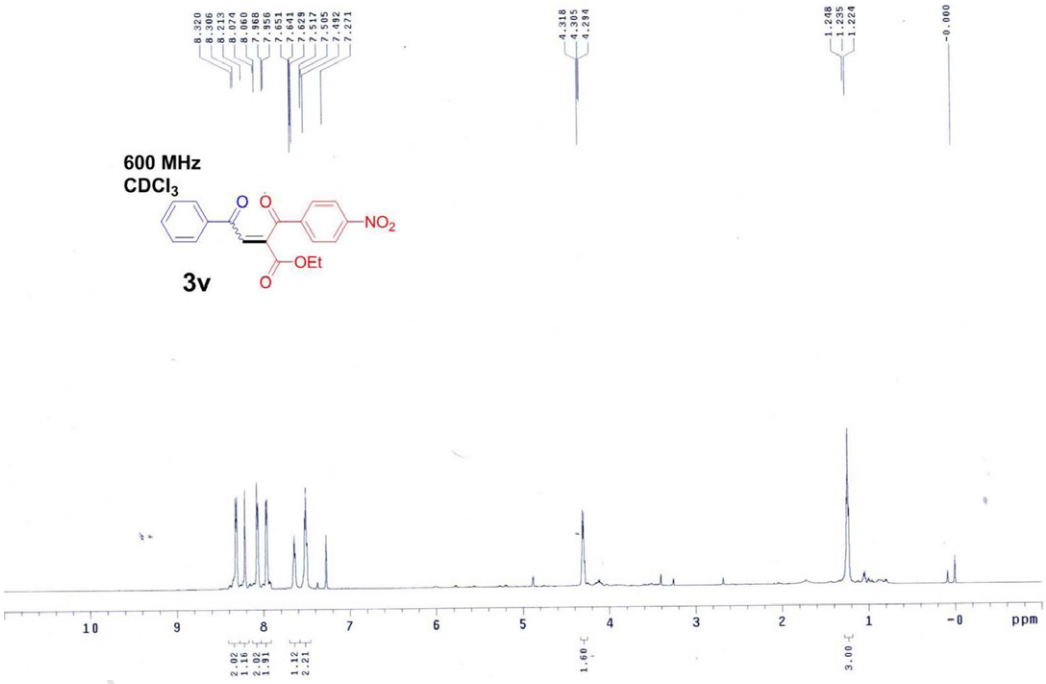

8.146
7.959
7.947
7.908
7.896
7.609
7.597
7.585
7.574
7.562
7.550
7.482
7.469
7.455
7.442
7.261
4.288
4.276
4.264
4.255
4.253
1.217
1.205
1.194
0.000
400 MHz
CDCl3
OEt
3s
0.98
1.97
1.83
2.06
3.99
2.06
0.11
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

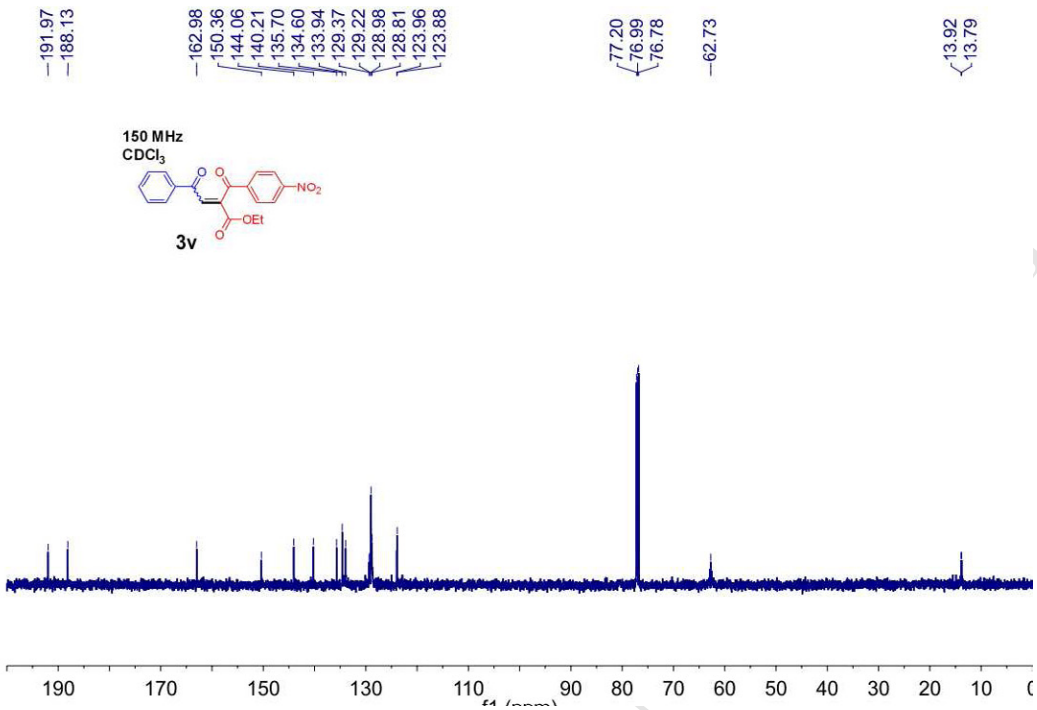

193.325
188.301
163.591
144.827
136.122
135.781
134.141
133.478
128.891
128.790
128.699
128.534
128.370
62.375
13.902
100 MHz
CDCl3
OEt
3s
136.122
135.781
134.141
133.478
128.891
128.790
128.699
128.534
128.370
135
133
131
129
f1 (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
8.14
7.98
7.98
7.96
7.96
7.62
7.61
7.51
7.49
7.48
7.27
7.22
7.14
4.32
4.30
3.92
3.91
3.85
1.28
1.26
1.24
0.00
600 MHz
CDCl3
OMe
OMe
OEt
OMe
E/Z
3t
0.64
1.61
0.93
1.76
1.63
1.72
3.58
5.08
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

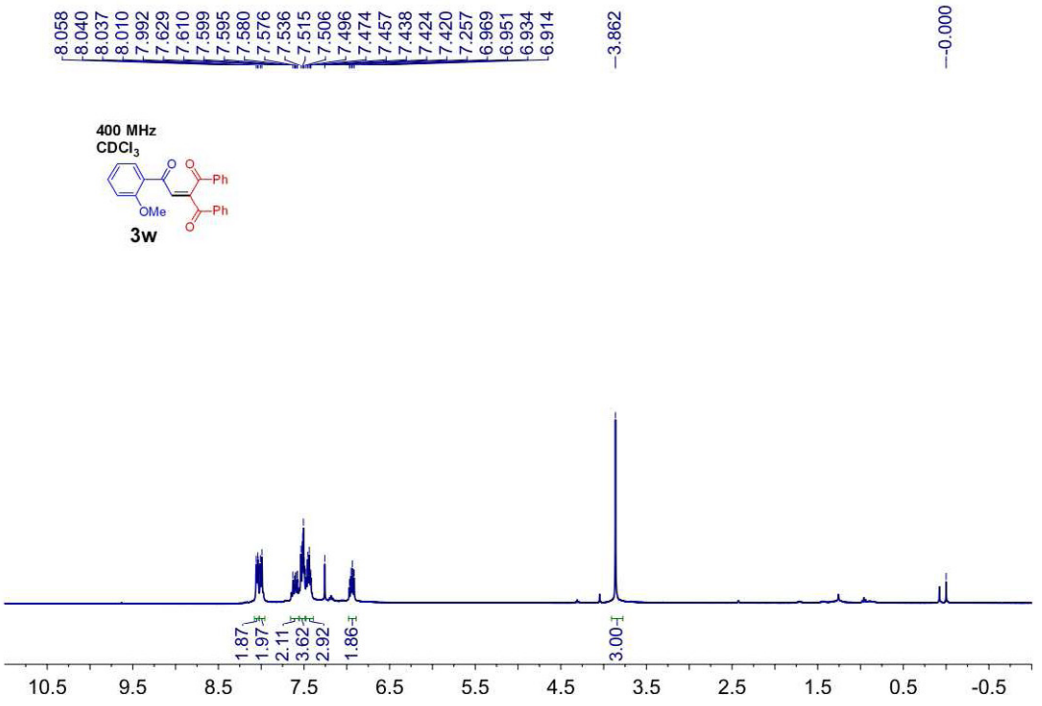

191.90
191.06
190.07
188.52
164.07
163.64
153.15
144.23
140.40
136.07
135.68
134.19
130.87
130.65
128.87
106.96
105.99
105.80
77.21
76.99
76.78
62.42
56.24
56.13
56.00
13.97
13.84
150 MHz
CDCl3
OMe
OMe
OEt
OMe
E/Z
3t
190
170
150
130
110
90
80
70
60
50
40
30
20
10


8.070
7.964
7.951
7.616
7.604
7.552
7.501
7.488
7.475
7.261
7.207
7.202
6.547
6.544
4.318
4.306
1.278
1.266
1.254
0.000
400 MHz
CDCl3
OEt
3u
0.84
1.63
1.02
0.77
2.27
0.74
0.84
1.38
0.51
3.00
0.51
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


188.71
180.57
163.34
152.04
147.89
142.50
136.05
134.72
134.20
128.83
118.15
112.87
112.54
77.32
77.00
76.68
62.41
13.90
100 MHz
CDCl3
OEt
3u
190
170
150
130
110
90
80
70
60
50
40
30
20
10


8.320
8.306
8.213
8.074
8.060
7.666
7.656
7.651
7.641
7.629
7.517
7.505
7.492
7.271
4.318
4.305
4.294
1.248
1.235
1.224
-0.000
600 MHz
CDCl3
NO2
OEt
3v
10
9
8
7
6
5
4
3
2
1
-0
ppm
2.02
1.16
1.02
2.91
1.12
2.21
1.60
3.00


191.97
188.13
162.98
150.36
144.06
140.21
135.70
134.60
133.94
129.37
129.22
128.98
128.81
123.96
123.88
77.20
76.99
76.78
62.73
13.92
13.79
150 MHz
CDCl3
NO2
OEt
3v
190
170
150
130
110
90
80
70
60
50
40
30
20
10


8.058
8.040
8.037
8.010
7.992
7.629
7.610
7.599
7.595
7.580
7.576
7.536
7.515
7.506
7.496
7.474
7.457
7.438
7.424
7.420
7.257
6.969
6.951
6.934
6.914
3.862
0.000
400 MHz
CDCl3
Ph
Ph
OMe
3w
1.87
1.97
2.11
3.62
2.92
1.86
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5