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Graphical Abstract

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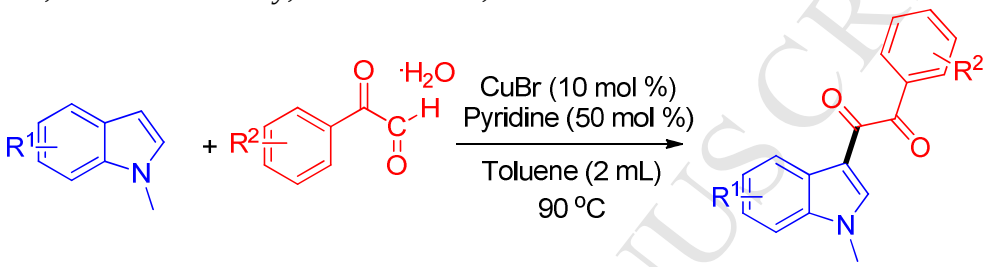

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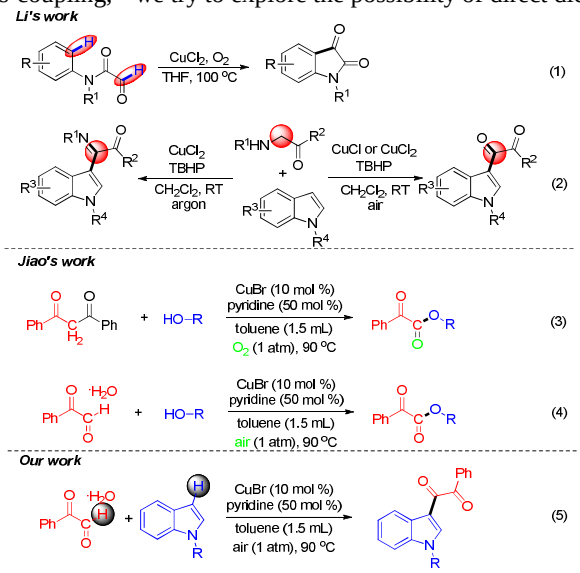
ABSTRACT

An efficient and practical protocol for copper-catalyzed aerobic oxidative dicarbonylation of indoles using α-carbonyl aldehydes to construct C-3 indole-substituted 1,2-diketones is developed. Various C-3 indole-substituted 1,2-diketones were observed in good to excellent yields under mild reaction conditions. This transformation used air as an ideal oxidant and produced water as the only by-product.

1. Introduction

Indole skeleton is widespread in bioactive synthetic and natural products,[1] and occupies a privileged position in medicinally relevant compounds,[2] hence the direct indole functionalization reactions are deemed important.[3] Heteroaryl 1,2-diketones are a class of versatile and powerful building blocks in organic synthesis, which are ideal for the preparation of heterocyclic compounds possessing pharmacological properties.[4] Therefore, exploring new methods for the direct dicarbonylation of nonactivated indoles will be much meaningful.[5]

In 2004, Li developed a strategy for constructing functional molecules by only using two different C-H bonds under oxidative conditions, which was termed cross-dehydrogenative coupling (CDC).[6] Over the past decade, copper catalyzed aerobic oxidative cross dehydrogenative coupling (CDC) has gained impressive progress, which is regarded as an efficient tool in synthetic methodology.[7] In 2010, Li and co-workers described a novel copper-catalyzed intramolecular C-H oxidation/acylation protocol for constructing substituted indoline-2,3-diones with good functional groups tolerance (Scheme 1, eq. 1),[8] as such reaction only used two C-H bonds under oxidative conditions. Recently, they reported a novel intermolecular reaction of α-amino carbonyls with indoles, which could selectively furnish 2-(1*H*-indol-3-yl)-2-imino-carbonyls and 2-(1*H*-indol-3-yl)-2-oxocar-bonyls *via* copper catalyzed C-H oxidative/cross-coupling (Scheme 1, eq. 2).[5e] More recently, Jiao's group reported a Cu-catalyzed aerobic oxidative esterification reaction of 1,3-diones to construct α-ketoesters by C-C bond cleavage and oxidative C-H bond functionalization (Scheme 1, eq. 3).[9] Moreover, they explored a more efficient and practical strategy for construction of α-ketoesters through Cu-catalyzed aerobic oxidative dehydrogenative coupling of α-carbonyl aldehydes with alcohols (Scheme 1, eq. 4).[10] This transformation used air as an ideal oxidant and produced water as the only by-product. In light of our sustained efforts to perfrom Cu-catalyzed aerobic oxidative cross-coupling,[11] we try to explore the possibility of direct dicar-



Scheme 1 Copper-catalyzed cross-dehydrogenative coupling.

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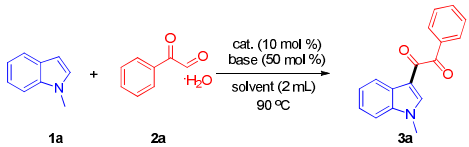
bonylation of non-activated indoles using α-carbonyl aldehydes under mild conditions (Scheme 1, eq. 5). Recently, Wu and co-workers established a molecular iodine mediated direct oxidative cross-coupling of indoles with methyl ketones for the dicarbonylation of indoles.[5f] Meanwhile, Vishwakarma, Ahmed and co-workers developed a novel aminocatalytic cross-coupling approach to construt C-3 indole-substituted 1,2-diketones via iminium ions.[5g]

2. Results and discussion

Our study was initiated by treating 1-methyl-1*H*-indole **1a** with phenylglyoxal monohydrate **2a** in the presence of pyridine (0.5 equiv) and CuBr (0.1 equiv) at 90 °C for 6 hours. To our delight, 1-(1-methyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione **3a** was formed in 82% LC-yield (75% isolated yield). Then, we screened different catalysts, solvents, reaction temperature, as well as additives (details see Supporting Information). As presented in Table 1, a range of copper salts, such as CuCl, CuI, Cu_2O, $CuCl_2$, $CuBr_2$ and $Cu(OAc)_2{\cdot}H_2O$ could promote the reaction smoothly and afford the desired product in 75% to 81% LC-yields (Table 1, entries 2-7). We then proceed on to screen the effect of different bases, whereby, good yields were achieved when using either organic bases (Table 1, entries 8-12) or inorganic bases (Table 1, entries 12-14). However, the yields obtained were all lower than using pyridine. When the reaction were carried out in other different solvents (Table 1, entries 15-18) such as CH_3CN and 1,4-dioxane, lower yields were obtained. Only trace amount of **3a** was detected when DCE and DMSO were examined instead of toluene.

Table 1

Screening of reaction conditions.[a]



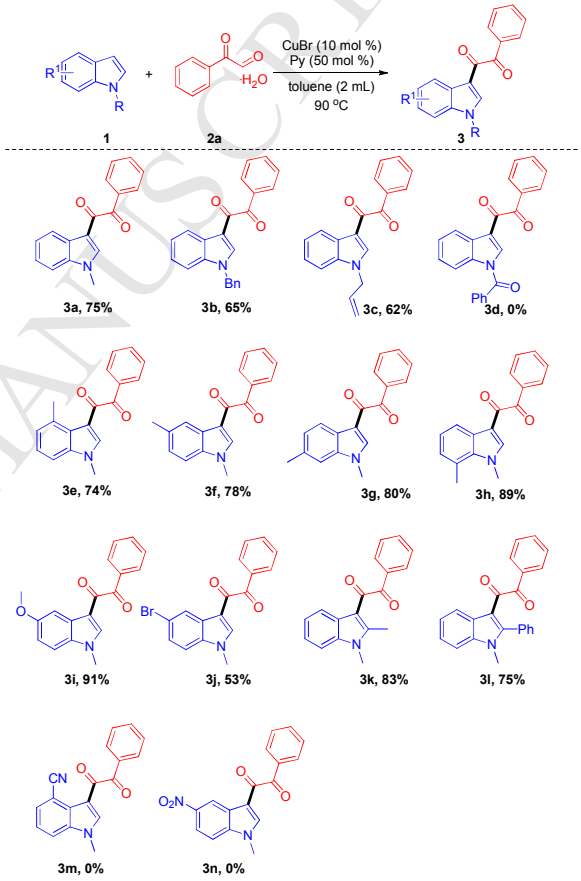
Entry	Cat. (0.1 equiv)	Base (0.5 equiv)	Solvent (2 mL)	Yield[b] (LC-MS)
1	CuBr	Pyridine	Toluene	82 (75)[c]
2	CuCl	Pyridine	Toluene	81
3	CuI	Pyridine	Toluene	81
4	Cu_2O	Pyridine	Toluene	75
5	$CuCl_2$	Pyridine	Toluene	76
6	$CuBr_2$	Pyridine	Toluene	76
7	$Cu(OAc)_2{\cdot}H_2O$	Pyridine	Toluene	75
8	CuBr	Et_3N	Toluene	67
9	CuBr	DABCO	Toluene	79
10	CuBr	Pyrrolidine	Toluene	72
11	CuBr	Piperidine	Toluene	78
12	CuBr	Et_2NH	Toluene	75
13	CuBr	Na_2CO_3	Toluene	73
14	CuBr	$NaHCO_3$	Toluene	75
15	CuBr	Pyridine	CH_3CN	36
16	CuBr	Pyridine	1,4-dioxane	20
17	CuBr	Pyridine	DCE	Trace
18	CuBr	Pyridine	DMSO	Trace

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), cat. (0.05 mmol), Pyridine (0.25 mmol), solvent (2 mL) at 90 °C. [b]The yields were determined by LC analysis using biphenyl as the internal standard. [c]Isolated yields.

With the optimized conditions in hand, the substrate scope was explored at 90 °C for 6 h under atmospheric air using 10 mol% of CuBr as the promoter, pyridine as the base, and toluene (2 mL) as the solvent. As presented in Table 2, A range of indoles could be converted to the corresponding indoleyl 1,2-diketones smoothly. The dicarbonylation of indoles with different *N*-protective groups could react smoothly to afford the desired products **3b** and **3c** in 65% and 62% yield, respectively. However, *N*-benzoyl indole**1d** with electron-withdrawing moieties could not transform to the corresponding product for the decreased electron density. All 4-methyl-, 5-methyl-, 6-methyl- or 7-methyl-substituted indole substrates could proceed smoothly to furnish the desired products in moderate to good yield (**3e**-**3h**). Notably, **3i** could be isolated in 91% yield when 5-methoxy-indole was subjected to the reaction with **2a**. Particularly, the reactions of 2-substitued indole such as 2-methyl- or 2-phenyl-indole with **2a** gave the dicarbonylation products **3k** and **3l** in 83% and 75% yield, respectively, which was hard to be obtained by other reported methods. However, the reaction of indole with strong electron-withdrawing substituent group failed to give the desired product due to the decreased electron density.

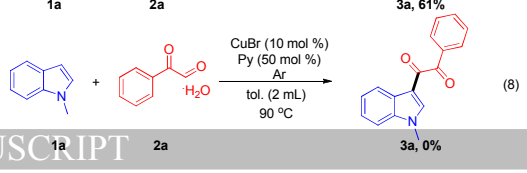
Table 2

The reaction of various indoles with α-carbonyl aldehyde[a]



[a]Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), CuBr (0.05 mmol), Pyridine (0.25 mmol), toluene (2 mL) at 90 °C, 6 h.

Next, various α-carbonyl aldehydes were applied to the reaction with **1a** under the optimal reaction conditions and the results were listed in Table 3. The *para*-position substituted with methyl, methoxy, isopropyl or t-butyl gave the desired products **4a-d** in moderate yields (70% to 75% yields). Moreover, halo-substituted α-carbonyl aldehydes were also tolerant in this transformation, affording halo-substituted products (**4e-i**) in moderate to good yields. The structure of **4g** was also further confirmed by X-ray crystallography (Details see supporting information). [12] Substituents at the *meta* and *ortho* position of the aromatic ring reduced the yields for the steric effect. It is noteworthy that naphthyl substituted and heteroaryl substituted α-carbonyl aldehydes survived well, generating **4j**, **4k** and **4l** in 68%, 75% and 82% yield, respectively. Meanwhile, α-carbonyl aldehydes carbonyl aldehydes with electron-deficient groups (trifluoromethyl group) also worked well to afford **4m** in 77% yield. However, strong electron-withdrawing substituted

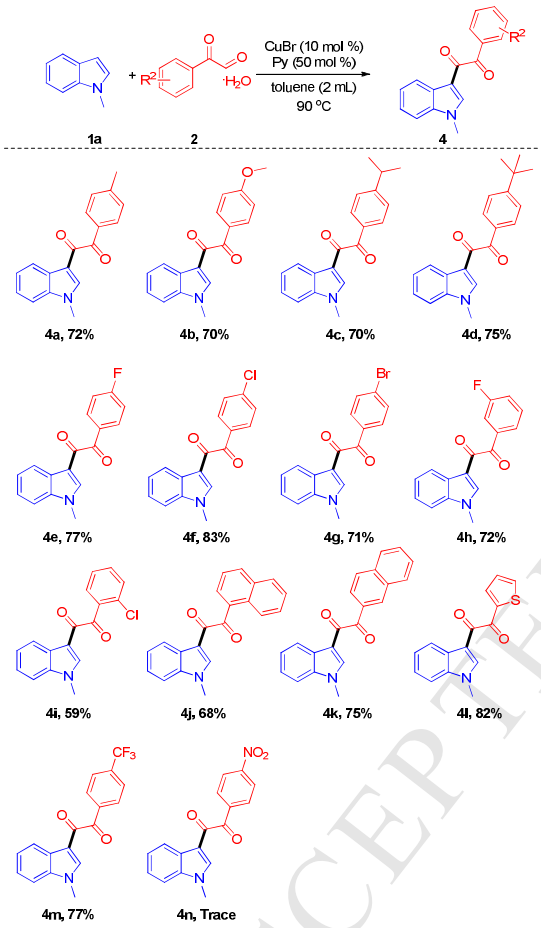


α-carbonyl aldehydes carbonyl aldehyde led to the desired product **4n** in trace yield.

We then carried out some control reactions so as to understand the mechanim of this transformation (Scheme 2). No desired product **3a** was formed when the reaction was proceeded in the absence of CuBr (Scheme 2, eq. 6). The reaction also proceeded and gave the desired product in 61% isolated yield under the modified conditions without pyridine (Scheme 2, eq. 7). These experiments indicate that copper salt is essential for the reaction and pyridine is as an additive to increase the yield. Furthermore, the reaction in the atmosphere of Ar was also investigated, which failed to give **3a** (Scheme 2, eq. 8). This result indicated that air is an important oxidant for the reaction to work.

Table 3

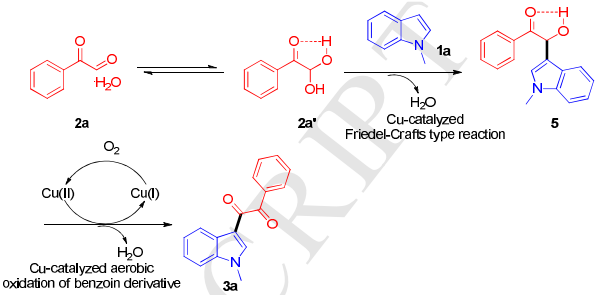
The reaction of indole with various α-carbonyl aldehydes [a]



[a]Reaction conditions: **1a** (0.5 mmol), **2** (0.5 mmol), CuBr (0.05 mmol), Pyridine (0.25 mmol), toluene (2 mL) at 90 °C, 6 h.

Scheme 2 Some control experiments.

Based on our above results and the reported works,[10] a plausible reaction mechanism for the Cu-catalyzed dicarbonylation reaction is presented in Scheme 3. Indole **1a** react with 2,2-dihydroxy-1-phenylethanone **2a′** generated from 2-oxo-2-phenylacetaldehyde hydrate to give the benzoin intermediate **5** via a copper catalyzed Friedel-Crafts type reaction[13] and followed by a copper-catalyzed aerobic oxidation of the benzoin intermediate **5** to deliver the final product **3a**.[14]



Scheme 3 A plausible mechanism.

3. Conclusion

In conclusion, we have developed a Cu-catalyzed aerobic oxidative dicarbonylation of indoles and α-carbonyl aldehydes under mild conditions. The reaction can serve as an efficient and practical protocol for the synthesis of various indole-substituted 1,2-diketones in moderate to excellent yield with a broad substrate scopes. This transformation used air as an ideal oxidant and produce water as the only by-product, which is environmentally friendly. Further investigations to understand the mechanism of this reaction and their applications in other organic reactions are ongoing in our laboratory.

4. Experimental Section

4.1. General

Melting points were recorded on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a Varian FT-1000 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) spectrumeter using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. High resolution mass spectra were obtained using BRUKER micrOTOF-Q III instrument with ESI source.

4.2. Typical procedure for the construction of 3a:

The substrate 1-methyl-1*H*-indole (**1a**, 0.5 mmol, 0.0655 g), phenylglyoxal monohydrate (**2a**, 0.5 mmol, 0.0760 g), CuBr (0.05 mmol, 0.0072 g, 10 mol%), and Pyridine (0.25 mmol, 0.0198 g) were added to a 10 mL Schlenk tube, followed by addition of Toluene (2.0 mL). The mixture was stirred at 90 ℃ as monitored by TLC. The solution was then quenched by H_2O and extracted with EtOAc, the combined organic layers were dried over Na_2SO_4, filtered, and evaporated under vaccum. The residue was purified by column chromatography on silica gel (eluent: light petroleum ether : ethyl acetate, V : V = 5 : 1) to afford the desired product 1-(1-methyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione **3a**.

4.2.1. 1-(1-methyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3a): Yellow Solid, mp: 92-93 °C; **IR** (neat, ν, cm-1): 1674, 1618, 1523, 1446cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) 8.53 – 8.43 (m, 1H), 8.09 (d, J = 7.5 Hz, 2H), 7.77 (s, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.40 – 7.33 (m, 3H), 3.77 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.34, 187.20, 139.15, 137.25, 133.85, 132.98, 129.82, 128.29, 125.84, 123.75, 123.01, 122.11, 112.33, 109.62, 33.28; **HRMS (ESI)** *m/z*: Found: 286.0838. Calcd for $C_{17}H_{13}NO_2$: $(M+Na)^+$ 286.0838.

4.2.2. 1-(1-benzyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3b): Yellow Solid, mp: 79-80 °C; **IR** (neat, ν, cm-1): 1667, 1616, 1595, 1577, 1517cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 7.3 Hz, 2H), 7.78 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.24 (ddd, *J* = 8.0, 6.0, 2.2 Hz, 1H), 7.16 (dd, *J* = 9.9, 4.0 Hz, 5H), 7.02 – 6.98 (m, 2H), 5.16 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.12, 187.25, 138.53, 136.79, 134.72, 133.88, 132.97, 129.91, 128.62, 128.31, 127.89, 126.57, 126.19, 123.89, 123.14, 122.29, 112.85, 110.29, 50.68; **HRMS (ESI)** *m/z*: Found: 362.1150. Calcd for $C_{23}H_{17}NO_2$: $(M+Na)^+$ 362.1151.

4.2.3. 1-(1-allyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3c): Yellow Solid, mp: 66-67 °C; **IR** (neat, ν, cm-1): 1670, 1611, 1577, 1521, 1450cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 9.6 Hz, 1H), 8.06 – 7.97 (m, 2H), 7.74 (s, 1H), 7.51 (t, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.22 (m, 3H), 5.86 (ddd, *J* = 15.9, 10.7, 5.6 Hz, 1H), 5.13 (dd, *J* = 39.8, 13.7 Hz, 2H), 4.62 (d, *J* = 5.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.20, 187.25, 138.13, 136.65, 133.86, 132.96, 130.97, 129.96, 129.86, 129.62, 128.29, 127.96, 126.05, 123.75, 123.06, 122.25, 118.81, 112.67, 110.08, 49.25, 0.60; **HRMS (ESI)** *m/z*: Found: 312.0995; Calcd for $C_{19}H_{15}NO_2$: $(M+Na)^+$ 312.0995.

4.2.4. 1-(1,4-dimethyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3e): Yellow Solid, mp: 102-103 °C; **IR** (neat, ν, cm-1): 1669, 1632, 1575, 1495, 1451cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.3 Hz, 2H), 7.75 (s, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.30 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 2H), 3.81 (s, 3H), 3.08 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.56, 187.38, 141.03, 138.31, 133.78, 133.48, 133.16, 129.69, 128.33, 124.81, 124.65, 124.08, 113.64, 107.00, 33.41, 22.79; **HRMS (ESI)** *m/z*: Found: 300.0991. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

4.2.5. 1-(1,5-dimethyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3f): Yellow Solid, mp: 87-88 °C; **IR** (neat, ν, cm-1): 1661, 1632, 1595, 1448cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.03 – 7.98 (m, 2H), 7.65 (s, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.18 – 7.16 (m, 1H), 7.11 (d, *J* = 9.7 Hz, 1H), 3.70 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.37, 187.14, 139.09, 135.64, 133.78, 133.04, 132.87, 129.83, 128.24, 126.10, 125.24, 121.95, 111.98, 109.20, 33.32, 21.07; **HRMS (ESI)** *m/z*: Found: 300.0996. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

4.2.6. 1-(1,6-dimethyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3g): Yellow Solid, mp: 120-121 °C; **IR** (neat, ν, cm-1): 1668, 1612, 1594, 1573, 1503, 1450cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.1 Hz, 1H), 8.09 (d, *J* = 7.3 Hz, 2H), 7.71 (s, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.15 (s, 1H), 3.75 (s, 3H), 2.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.40, 187.12, 138.78, 137.68, 133.86, 133.79, 133.04, 129.81, 128.26, 124.65, 123.56, 121.74, 112.34, 109.60, 33.20, 21.42; **HRMS (ESI)** *m/z*: Found: 300.0990. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

4.2.7. 1-(1,7-dimethyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3h): Yellow Solid, mp: 129-130 °C; **IR** (neat, ν, cm-1): 1665, 1620, 1596, 1450cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.9 Hz, 1H), 8.14 (d, *J* = 7.4 Hz, 2H), 7.72 (s, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.29 (dd, *J* = 12.8, 5.3 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 4.06 (s, 3H), 2.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.33, 187.08, 140.70, 135.94, 133.79, 133.03, 129.82, 128.26, 126.98, 126.55, 123.21, 121.52, 120.19, 111.82, 37.52, 18.98; **HRMS (ESI)** *m/z*: Found: 300.0992. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

4.2.8. 1-(5-methoxy-1-methyl-1*H*-indol-3-yl)-2-phenyle-thane-1,2-dione (3i): Yellow Solid, mp: 147-148 °C; **IR** (neat, ν, cm-1): 1672, 1616, 1580, 1449cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.4 Hz, 2H), 8.02 (d, *J* = 1.8 Hz, 1H), 7.77 (s, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 1H), 7.04 (dd, *J* = 8.9, 2.3 Hz, 1H), 3.98 (s, 3H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.34, 187.04, 156.66, 138.94, 133.79, 133.04, 132.12, 129.81, 128.26, 126.82, 114.05, 112.07, 110.44, 103.46, 55.37, 33.46; **HRMS (ESI)** *m/z*: Found: 316.0948. Calcd for $C_{18}H_{15}NO_3$: $(M+Na)^+$ 316.0944.

4.2.9. 1-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-phenyle-thane-1,2-dione (3j): Yellow Solid, mp: 192-193 °C; **IR** (neat, ν, cm-1): 1659, 1636, 1595, 1579, 1450cm^{-1}; **^{1}H NMR** (400 MHz, DMSO-d_6) δδ 8.38 (s, 1H), 8.31 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.62 (dd, *J* = 15.4, 8.1 Hz, 3H), 7.54 (dd, *J* = 8.7, 1.4 Hz, 1H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 193.55, 187.78, 142.10, 136.53, 134.84, 132.67, 129.78, 129.16, 127.12, 126.45, 123.39, 116.10, 113.55, 110.75, 33.63; **HRMS (ESI)** *m/z*: Found: 363.9946. Calcd for $C_{17}H_{12}BrNO_2$: $(M+Na)^+$ 363.9944.

4.2.10. 1-(1,2-dimethyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3k): Yellow Solid, mp: 147-148 °C; **IR** (neat, ν, cm-1): 1670, 1597, 1578, 1510, 1415cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.4 Hz, 2H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.27 (m, 3H), 3.73 (s, 3H), 2.70 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.01, 189.57, 147.18, 136.57, 133.97, 132.88, 129.56, 128.52, 125.63, 122.59, 122.56, 120.30, 110.07, 109.21, 29.33, 12.27; **HRMS (ESI)** *m/z*: Found: 300.0993. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

4.2.11. 1-(1-methyl-2-phenyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3l): Yellow Solid, mp: 119-120 °C; **IR** (neat, ν, cm-1): 1673, 1610, 1577, 1464, 1435cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.5 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.47 (s, 3H), 7.34 (dd, *J* = 13.6, 6.3 Hz, 3H), 7.25 – 7.08 (m, 4H), 3.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.37, 190.65, 149.38, 136.72, 133.18, 133.07, 130.58, 129.29, 128.86, 128.54, 127.78, 127.50, 126.03, 123.71, 123.23, 122.19, 112.08, 109.53, 30.54; **HRMS (ESI)** *m/z*: Found: 362.1155. Calcd for $C_{23}H_{17}NO_2$: $(M+Na)^+$ 362.1151.

4.2.12. 1-(1-methyl-1*H*-indol-3-yl)-2-(p-tolyl)ethane-1,2-dione (4a): Yellow Solid, mp: 95-96 °C; **IR** (neat, ν, cm-1): 1672, 1613, 1605, 1577, 1463cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 – 8.42 (m, 1H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.77 (s, 1H), 7.40 – 7.35 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.09, 187.49, 145.01, 139.03, 137.23, 130.50, 129.95, 129.01, 125.87, 123.68, 122.95, 122.17, 112.42, 109.53, 33.27, 21.41; **HRMS (ESI)** *m/z*: Found: 300.0992. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

4.2.13. 1-(4-methoxyphenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4b): Yellow Solid, mp: 116-117 °C; **IR** (neat, ν, cm-1): 1661, 1599, 1573, 1460cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.5 Hz, 1H), 8.08 (d, *J* = 8.6 Hz, 2H), 7.78 (s, 1H), 7.36 (s, 3H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.05, 187.71, 164.08, 139.05, 137.21, 132.27, 125.95, 125.90, 123.63, 122.91, 122.14, 113.59, 112.46, 109.52, 55.12, 33.25; **HRMS (ESI)** *m/z*: Found: 316.0947. Calcd for $C_{18}H_{15}NO_3$: $(M+Na)^+$ 316.0944.

4.2.14. 1-(4-isopropylphenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4c): Yellow Solid, mp: 116-117 °C; **IR**

(neat, ν, cm-1): 1666, 1631, 1600, 1465cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.08 (s, 2H), 7.83 (s, 1H), 7.42 (s, 5H), 3.86 (s, 3H), 3.03 (s, 1H), 1.33 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.12, 187.53, 155.65, 139.04, 137.23, 130.85, 130.12, 126.45, 125.88, 123.68, 122.94, 122.18, 112.43, 109.53, 33.98, 33.27, 23.13; **HRMS (ESI)** *m/z*: Found: 328.1305. Calcd for $C_{20}H_{19}NO_2$: $(M+Na)^+$ 328.1308.

4.2.15. 1-(4-(tert-butyl)phenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4d): Yellow Solid, mp: 180-181 °C; **IR** (neat, ν, cm-1): 1669, 1628, 1600, 1522, 1463cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 4.7 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.67 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.26 (s, 3H), 3.69 (s, 3H), 1.24 (s, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.11, 187.49, 157.84, 139.04, 137.23, 130.42, 129.81, 125.89, 125.30, 123.68, 122.94, 122.19, 112.43, 109.53, 34.84, 33.27, 30.56; **HRMS (ESI)** *m/z*: Found: 342.1463. Calcd for $C_{21}H_{21}NO_2$: $(M+Na)^+$ 342.1465.

4.2.16. 1-(4-fluorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4e): Yellow Solid, mp: 112-113 °C; **IR** (neat, ν, cm-1): 1665, 1611, 1593, 1504cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.14 (s, 2H), 7.82 (s, 1H), 7.38 (s, 3H), 7.15 (t, *J* = 8.0 Hz, 2H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.50, 186.55, 166 (d, *J* = 255.4), 139.20, 137.24, 132.7 (d, *J* = 9.6), 129.4 (d, *J* = 2.6) 125.89, 123.81, 123.09, 122.14, 115.5 (d, J = 21.9), 112.26, 109.59, 33.32; **HRMS (ESI)** *m/z*: Found: 304.0747. Calcd for $C_{17}H_{12}FNO_2$: $(M+Na)^+$ 304.0744.

4.2.17. 1-(4-chlorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4f): Yellow Solid, mp: 157-158 °C; **IR** (neat, ν, cm-1): 1670, 1618, 1583, 1459cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 – 8.42 (m, 1H), 8.08 – 8.01 (m, 2H), 7.81 (s, 1H), 7.49 – 7.42 (m, 2H), 7.42 – 7.35 (m, 3H), 3.81 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.78, 186.24, 140.36, 139.24, 137.24, 131.38, 131.22, 128.61, 125.89, 123.84, 123.13, 122.15, 112.21, 109.61, 33.34; **HRMS (ESI)** *m/z*: Found: 320.0441. Calcd for $C_{17}H_{12}ClO_2$: $(M+Na)^+$ 320.0449.

4.2.18. 1-(4-bromophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4g): Yellow Solid, mp: 165-166 °C; **IR** (neat, ν, cm-1): 1662, 1624, 1583, 1467cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 – 8.41 (m, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.81 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.39 (dd, *J* = 6.7, 3.3 Hz, 3H), 3.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.97, 186.16, 139.24, 137.24, 131.79, 131.60, 131.28, 129.25, 125.89, 123.85, 123.14, 122.16, 112.21, 109.60, 33.35; **HRMS (ESI)** *m/z*: Found: 363.9931. Calcd for $C_{17}H_{12}BrNO_2$: $(M+Na)^+$ 363.9944.

4.2.19. 1-(3-fluorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4h): Yellow Solid, mp: 121-122 °C; **IR** (neat, ν, cm-1): 1672, 1619, 1523cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.94 (d, *J* = 6.8 Hz, 1H), 7.87 (s, 2H), 7.51 (d, *J* = 5.5 Hz, 1H), 7.44 (s, 3H), 7.38 (d, *J* = 6.8 Hz, 1H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.72, 186.02, 162.3 (d, *J* = 247), 139.22, 137.26, 135.0 (d, *J* = 6.5), 130.0 (d, *J* = 7.5), 125.9 (d, *J* = 2.8), 125.85, 123.87, 123.15, 122.18, 120.8 (d, *J* = 21.3), 116.1 (d, *J* = 22.5), 112.19, 109.60, 33.34; **HRMS (ESI)** *m/z*: Found: 304.0745. Calcd for $C_{17}H_{12}FNO_2$: $(M+Na)^+$ 304.0744.

4.2.20. 1-(2-chlorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4i): Yellow Solid, mp: 163-164 °C; **IR** (neat, ν, cm-1): 1687, 1611, 1588, 1518cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 – 8.39 (m, 1H), 8.04 (s, 1H), 7.78 (d, *J* = 6.8 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 1H), 7.44 – 7.36 (m, 5H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.52, 184.44, 139.10, 137.14, 134.85, 132.88, 132.76, 131.37, 129.88, 126.52, 126.36, 123.68, 122.98, 122.24, 111.53, 109.51, 33.38; **HRMS (ESI)** *m/z*: Found: 320.0454. Calcd for $C_{17}H_{12}ClO_2$: $(M+Na)^+$ 320.0449.

4.2.21. 1-(1-methyl-1*H*-indol-3-yl)-2-(naphthalen-1-yl)ethane-1,2-dione (4j): Yellow Solid, mp: 102-103 °C; **IR** (neat, ν, cm-1): 1649, 1638, 1525, 1469cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.54 (d, *J* = 6.4 Hz, 1H), 8.17 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.93 (dd, *J* = 8.4, 3.0 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.83 (s, 1H), 7.62 (t, *J* = 7.1 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.44 – 7.37 (m, 3H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.40, 187.33, 139.18, 137.28, 135.70, 133.23, 131.96, 130.25, 129.51, 128.71, 128.30, 127.38, 126.45, 125.93, 123.92, 123.77, 123.06, 122.24, 112.54, 109.58, 33.30; **HRMS (ESI)** *m/z*: Found: 336.0993. Calcd for $C_{21}H_{15}NO_2$: $(M+Na)^+$ 336.0995.

4.2.22. 1-(1-methyl-1*H*-indol-3-yl)-2-(naphthalen-2-yl)ethane-1,2-dione (4k): Yellow Solid, mp: 106-107 °C; **IR** (neat, ν, cm-1): 1637, 1595, 1524, 1468cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), δ 8.64 (s, 1H), 8.54 (d, *J* = 6.8 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.83 (s, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 9.5, 2.6 Hz, 3H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.40, 187.33, 139.18, 137.28, 135.69, 133.22, 131.95, 130.25, 129.51, 128.71, 128.30, 127.38, 126.46, 125.93, 123.92, 123.77, 123.06, 122.24, 112.54, 109.58, 33.30; **HRMS (ESI)** *m/z*: Found: 336.0999. Calcd for $C_{21}H_{15}NO_2$: $(M+Na)^+$ 336.0995.

4.2.23. 1-(1-methyl-1*H*-indol-3-yl)-2-(thiophen-2-yl)ethane-1,2-dione (4l): Yellow Solid, mp: 93-94 °C; **IR** (neat, ν, cm-1): 1642, 1610, 1578, 1520, 1463cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 6.0, 1.6 Hz, 1H), 7.97 (d, *J* = 5.8 Hz, 2H), 7.69 – 7.61 (m, 1H), 7.24 (ddd, *J* = 10.6, 7.7, 4.3 Hz, 3H), 7.07 – 7.00 (m, 1H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.11, 184.11, 139.92, 138.87, 137.00, 136.25, 136.24, 127.94, 126.41, 123.67, 123.02, 122.14, 111.52, 109.61, 33.30; **HRMS (ESI)** *m/z*: Found: 292.0401. Calcd for $C_{15}H_{11}NO_2S$: $(M+Na)^+$ 292.0403.

4.2.24. 1-(1-methyl-1*H*-indol-3-yl)-2-(4-(trifluoromethyl)-phenyl)ethane-1,2-dione (4m): Yellow Solid, mp: 153-154 °C; **IR** (neat, ν, cm-1): 1680, 1614, 1579, 1491cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.0 Hz, 1H), 8.22 (d, *J* = 8.1 Hz, 2H), 7.86 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 10.0 Hz, 3H), 3.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.70, 185.53, 139.34, 137.27, 135.85, 134.7 (q, *J* = 32.5), 130.17, 125.91, 125.2 (q, *J* = 3.7), 123.95, 123.24, 123.0 (q, *J* = 271.3), 122.17, 112.13, 109.64, 33.36; **HRMS (ESI)** *m/z*: Found: 354.0712. Calcd for $C_{18}H_{12}F_3NO_2$: $(M+Na)^+$ 354.0712.

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12. Compounds **3g** was determined by X-ray crystallography. See the Supporting Information for full details. CCDC 1041632 (**3g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.
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Supporting Information for

Copper-Catalyzed Aerobic Oxidative Dicarbonylation of Indoles Utilizing α-Carbonyl Aldehydes

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Experimental Section

General

Melting points were recorded on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a Varian FT-1000 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) spectrumeter using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. High resolution mass spectra were obtained using BRUKER micrOTOF-Q III instrument with ESI source.

Typical procedure for the construction of 3a:

The substrate 1-methyl-1*H*-indole (**1a**, 0.5 mmol, 0.0655 g), phenylglyoxal monohydrate (**2a**, 0.5 mmol, 0.0760 g), CuBr (0.05 mmol, 0.0072 g, 10 mol%), and Pyridine (0.25 mmol, 0.0198 g) were added to a 10 mL Schlenk tube, followed by addition of Toluene (2.0 mL). The mixture was stirred at 90 ℃ as monitored by TLC. The solution was then quenched by H_2O and extracted with EtOAc, the combined organic layers were dried over Na_2SO_4, filtered, and evaporated under vaccum. The residue was purified by column chromatography on silica gel (eluent: light petroleum ether : ethyl acetate, *V* : *V* = 5 : 1) to afford the desired product 1-(1-methyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione **3a**.

Table S1: The reactions of **1a** and **2a** catalyzed by different catalysts .

entry	cat. (equiv)	base (equiv)	solvent (mL)	temp (℃)	yield (LC-MS)
1	CuBr (0.1)	Py (0.5)	Tol. (2)	90	82
2	CuCl (0.1)	Py (0.5)	Tol. (2)	90	81
3	CuI (0.1)	Py (0.5)	Tol. (2)	90	81
4	Cu_2O (0.1)	Py (0.5)	Tol. (2)	90	75
5	$CuCl_2$ (0.1)	Py (0.5)	Tol. (2)	90	76
6	$CuBr_2$ (0.1)	Py (0.5)	Tol. (2)	90	76
7	$Cu(OAc)_2 \cdot H_2O$ (0.1)	Py (0.5)	Tol. (2)	90	75
8	$CuSO_4 \cdot H_2O$ (0.1)	Py (0.5)	Tol. (2)	90	75

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), cat. (0.05 mmol), Pyridine (0.25 mmol), solvent (2 mL) at 90 ℃, 6 h. [b]The yields were determined by LC analysis using biphenyl as the internal standard.

Table S2: The reactions of **1a** and **2a** catalyzed by different solvents .

entry	cat. (equiv)	base (equiv)	solvent (mL)	temp (℃)	yield (LC-MS)
1	CuBr (0.1)	Py (0.5)	Tol. (2)	90	82
2	CuBr (0.1)	Py (0.5)	CH_3CN (2)	80	36
3	CuBr (0.1)	Py (0.5)	CH_3NO_2 (2)	80	38
4	CuBr (0.1)	Py (0.5)	DMSO (2)	90	Trace
5	CuBr (0.1)	Py (0.5)	DCE (2)	90	Trace
6	CuBr (0.1)	Py (0.5)	1,4-dioxane (2)	90	20
7	CuBr (0.1)	Py (0.5)	EtOH (2)	80	Trace

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), cat. (0.05 mmol), Pyridine (0.25 mmol), solvent (2 mL) at 90 ℃, 6 h. [b]The yields were determined by LC analysis using biphenyl as the internal standard.

Table S3: The reactions of **1a** and **2a** catalyzed by different base .

entry	cat. (equiv)	base (equiv)	solvent (mL)	temp (℃)	yield (LC-MS)
1	CuBr (0.1)	Py (0.5)	Tol. (2)	90	82
2	CuBr (0.1)	Et_3N (0.5)	Tol. (2)	90	67
3	CuBr (0.1)	DABCO (0.5)	Tol. (2)	90	79
4	CuBr (0.1)	Pyrrolidine (0.5)	Tol. (2)	90	72
5	CuBr (0.1)	Piperidine (0.5)	Tol. (2)	90	78
6	CuBr (0.1)	Et_2NH (0.5)	Tol. (2)	90	75
7	CuBr (0.1)	Na_2CO_3 (0.5)	Tol. (2)	90	73
8	CuBr (0.1)	$NaHCO_3$ (0.5)	Tol. (2)	90	75

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), cat. (0.05 mmol), base (0.25 mmol), tol. (2 mL) at 90 ℃, 6 h. [b]The yields were determined by LC analysis using biphenyl as the internal standard.

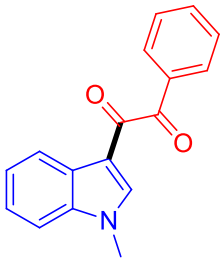
Table S6: The reactions of **1a** and **2a** with different time.

entry	cat. (equiv)	base (equiv)	Time (h)	solvent (mL)	temp (℃)	yield (LC-MS)
1	CuBr (0.1)	Py (0.5)	4	Tol. (2)	90	74
2	CuBr (0.1)	Py (0.5)	5	Tol. (2)	90	74
3	CuBr (0.1)	Py (0.5)	6	Tol. (2)	90	82
4	CuBr (0.1)	Py (0.5)	7	Tol. (2)	90	76
5	CuBr (0.1)	Py (0.5)	8	Tol. (2)	90	76

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), cat. (0.05 mmol), base (0.25 mmol), tol. (2 mL) at 90 ℃. [b]The yields were determined by LC analysis using biphenyl as the internal standard.

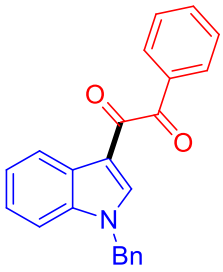
Characterization Data of Compounds:

1-(1-methyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3a)



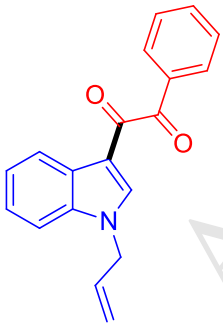
Yellow Solid, mp: 92-93 °C;
IR (neat, ν, cm-1): 1674, 1618, 1523, 1446cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) 8.53 – 8.43 (m, 1H), 8.09 (d, *J* = 7.5 Hz, 2H), 7.77 (s, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.33 (m, 3H), 3.77 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.34, 187.20, 139.15, 137.25, 133.85, 132.98, 129.82, 128.29, 125.84, 123.75, 123.01, 122.11, 112.33, 109.62, 33.28;
HRMS (ESI) *m/z*: Found: 286.0838. Calcd for $C_{17}H_{13}NO_2$: $(M+Na)^+$ 286.0838.

1-(1-benzyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3b)



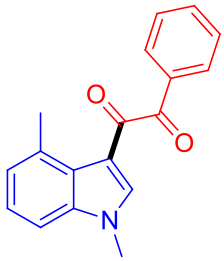
Yellow Solid, mp: 79-80 °C;
IR (neat, ν, cm-1): 1667, 1616, 1595, 1577, 1517cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 7.3 Hz, 2H), 7.78 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.24 (ddd, *J* = 8.0, 6.0, 2.2 Hz, 1H), 7.16 (dd, *J* = 9.9, 4.0 Hz, 5H), 7.02 – 6.98 (m, 2H), 5.16 (s, 2H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.12, 187.25, 138.53, 136.79, 134.72, 133.88, 132.97, 129.91, 128.62, 128.31, 127.89, 126.57, 126.19, 123.89, 123.14, 122.29, 112.85, 110.29, 50.68;
HRMS (ESI) *m/z*: Found: 362.1150. Calcd for $C_{23}H_{17}NO_2$: $(M+Na)^+$ 362.1151.

1-(1-allyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3c)



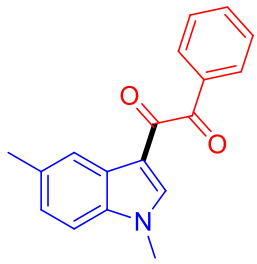
Yellow Solid, mp: 66-67 °C;
IR (neat, ν, cm-1): 1670, 1611, 1577, 1521, 1450cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 9.6 Hz, 1H), 8.06 – 7.97 (m, 2H), 7.74 (s, 1H), 7.51 (t, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.22 (m, 3H), 5.86 (ddd, *J* = 15.9, 10.7, 5.6 Hz, 1H), 5.13 (dd, *J* = 39.8, 13.7 Hz, 2H), 4.62 (d, *J* = 5.6 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.20, 187.25, 138.13, 136.65, 133.86, 132.96, 130.97, 129.96, 129.86, 129.62, 128.29, 127.96, 126.05, 123.75, 123.06, 122.25, 118.81, 112.67, 110.08, 49.25, 0.60;
HRMS (ESI) *m/z*: Found: 312.0995; Calcd for $C_{19}H_{15}NO_2$: $(M+Na)^+$ 312.0995.

1-(1,4-dimethyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3e)



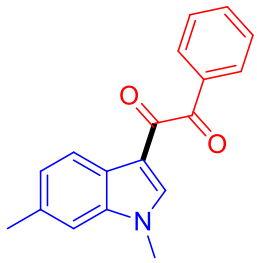
Yellow Solid, mp: 102-103 °C;
IR (neat, ν, cm-1): 1669, 1632, 1575, 1495, 1451cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.3 Hz, 2H), 7.75 (s, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.30 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 2H), 3.81 (s, 3H), 3.08 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 194.56, 187.38, 141.03, 138.31, 133.78, 133.48, 133.16, 129.69, 128.33, 124.81, 124.65, 124.08, 113.64, 107.00, 33.41, 22.79;
HRMS (ESI) *m/z*: Found: 300.0991. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

1-(1,5-dimethyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3f)



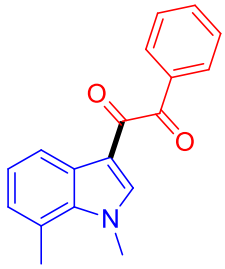
Yellow Solid, mp: 87-88 °C;
IR (neat, ν, cm-1): 1661, 1632, 1595, 1448cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.03 – 7.98 (m, 2H), 7.65 (s, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.18 – 7.16 (m, 1H), 7.11 (d, *J* = 9.7 Hz, 1H), 3.70 (s, 3H), 2.44 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.37, 187.14, 139.09, 135.64, 133.78, 133.04, 132.87, 129.83, 128.24, 126.10, 125.24, 121.95, 111.98, 109.20, 33.32, 21.07;
HRMS (ESI) *m/z*: Found: 300.0996. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

1-(1,6-dimethyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3g)



Yellow Solid, mp: 120-121 °C;
IR (neat, ν, cm-1): 1668, 1612, 1594, 1573, 1503, 1450cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.1 Hz, 1H), 8.09 (d, *J* = 7.3 Hz, 2H), 7.71 (s, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.15 (s, 1H), 3.75 (s, 3H), 2.52 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.40, 187.12, 138.78, 137.68, 133.86, 133.79, 133.04, 129.81, 128.26, 124.65, 123.56, 121.74, 112.34, 109.60, 33.20, 21.42;
HRMS (ESI) *m/z*: Found: 300.0990. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

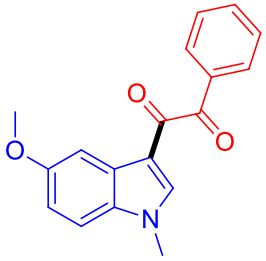
1-(1,7-dimethyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3h)



Yellow Solid, mp: 129-130 °C;
IR (neat, ν, cm-1): 1665, 1620, 1596, 1450cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.9 Hz, 1H), 8.14 (d, *J* = 7.4 Hz, 2H), 7.72 (s, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.29 (dd, *J* = 12.8, 5.3 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 4.06 (s, 3H), 2.77 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.33, 187.08, 140.70, 135.94, 133.79,

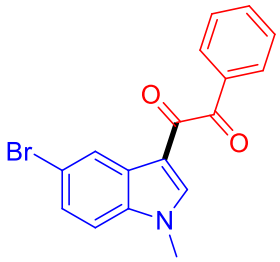
133.03, 129.82, 128.26, 126.98, 126.55, 123.21, 121.52, 120.19, 111.82, 37.52, 18.98;
HRMS (ESI) *m/z*: Found: 300.0992. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

1-(5-methoxy-1-methyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3i)



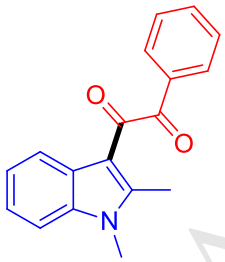
Yellow Solid, mp: 147-148 °C;
IR (neat, ν, cm-1): 1672, 1616, 1580, 1449cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.4 Hz, 2H), 8.02 (d, *J* = 1.8 Hz, 1H), 7.77 (s, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 1H), 7.04 (dd, *J* = 8.9, 2.3 Hz, 1H), 3.98 (s, 3H), 3.82 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.34, 187.04, 156.66, 138.94, 133.79, 133.04, 132.12, 129.81, 128.26, 126.82, 114.05, 112.07, 110.44, 103.46, 55.37, 33.46;
HRMS (ESI) *m/z*: Found: 316.0948. Calcd for $C_{18}H_{15}NO_3$: $(M+Na)^+$ 316.0944.

1-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3j)



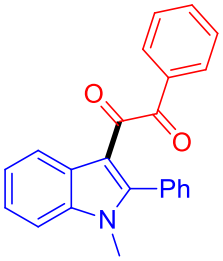
Yellow Solid, mp: 192-193 °C;
IR (neat, ν, cm-1): 1659, 1636, 1595, 1579, 1450cm^{-1};
^{1}H NMR (400 MHz, DMSO-d_6) δδ 8.38 (s, 1H), 8.31 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.62 (dd, *J* = 15.4, 8.1 Hz, 3H), 7.54 (dd, *J* = 8.7, 1.4 Hz, 1H), 3.88 (s, 3H);
^{13}C NMR (100 MHz, DMSO-d_6) δ 193.55, 187.78, 142.10, 136.53, 134.84, 132.67, 129.78, 129.16, 127.12, 126.45, 123.39, 116.10, 113.55, 110.75, 33.63;
HRMS (ESI) *m/z*: Found: 363.9946. Calcd for $C_{17}H_{12}BrNO_2$: $(M+Na)^+$ 363.9944.

1-(1,2-dimethyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3k)



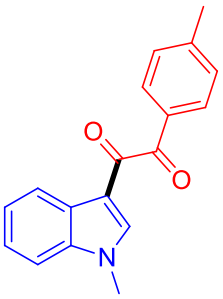
Yellow Solid, mp: 147-148 °C;
IR (neat, ν, cm-1): 1670, 1597, 1578, 1510, 1415cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.4 Hz, 2H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.27 (m, 3H), 3.73 (s, 3H), 2.70 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.01, 189.57, 147.18, 136.57, 133.97, 132.88, 129.56, 128.52, 125.63, 122.59, 122.56, 120.30, 110.07, 109.21, 29.33, 12.27;
HRMS (ESI) *m/z*: Found: 300.0993. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

1-(1-methyl-2-phenyl-1*H*-indol-3-yl)-2-phenylethane-1,2-dione (3l)



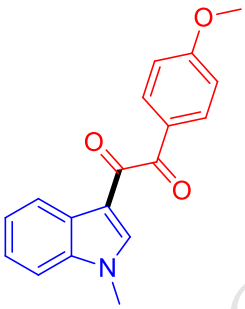
Yellow Solid, mp: 119-120 ºC;
IR (neat, ν, cm-1): 1673, 1610, 1577, 1464, 1435cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.5 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.47 (s, 3H), 7.34 (dd, *J* = 13.6, 6.3 Hz, 3H), 7.25 – 7.08 (m, 4H), 3.57 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.37, 190.65, 149.38, 136.72, 133.18, 133.07, 130.58, 129.29, 128.86, 128.54, 127.78, 127.50, 126.03, 123.71, 123.23, 122.19, 112.08, 109.53, 30.54;
HRMS (ESI) *m/z*: Found: 362.1155. Calcd for $C_{23}H_{17}NO_2$: $(M+Na)^+$ 362.1151.

1-(1-methyl-1*H*-indol-3-yl)-2-(p-tolyl)ethane-1,2-dione (4a)



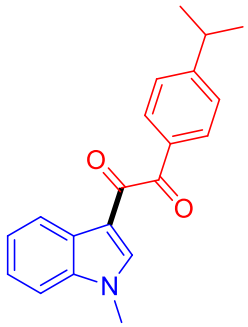
Yellow Solid, mp: 95-96 ºC;
IR (neat, ν, cm-1): 1672, 1613, 1605, 1577, 1463cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.42 (m, 1H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.77 (s, 1H), 7.40 – 7.35 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 2.42 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.09, 187.49, 145.01, 139.03, 137.23, 130.50, 129.95, 129.01, 125.87, 123.68, 122.95, 122.17, 112.42, 109.53, 33.27, 21.41;
HRMS (ESI) *m/z*: Found: 300.0992. Calcd for $C_{18}H_{15}NO_2$: $(M+Na)^+$ 300.0995.

1-(4-methoxyphenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4b)



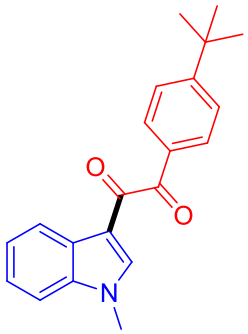
Yellow Solid, mp: 116-117 ºC;
IR (neat, ν, cm-1): 1661, 1599, 1573, 1460cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.5 Hz, 1H), 8.08 (d, *J* = 8.6 Hz, 2H), 7.78 (s, 1H), 7.36 (s, 3H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.05, 187.71, 164.08, 139.05, 137.21, 132.27, 125.95, 125.90, 123.63, 122.91, 122.14, 113.59, 112.46, 109.52, 55.12, 33.25;
HRMS (ESI) *m/z*: Found: 316.0947. Calcd for $C_{18}H_{15}NO_3$: $(M+Na)^+$ 316.0944.

1-(4-isopropylphenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4c)



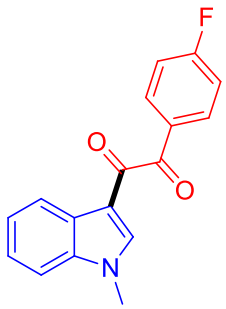
Yellow Solid, mp: 116-117 °C;
IR (neat, ν, cm-1): 1666, 1631, 1600, 1465cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.08 (s, 2H), 7.83 (s, 1H), 7.42 (s, 5H), 3.86 (s, 3H), 3.03 (s, 1H), 1.33 (s, 6H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.12, 187.53, 155.65, 139.04, 137.23, 130.85, 130.12, 126.45, 125.88, 123.68, 122.94, 122.18, 112.43, 109.53, 33.98, 33.27, 23.13;
HRMS (ESI) *m/z*: Found: 328.1305. Calcd for $C_{20}H_{19}NO_2$: $(M+Na)^+$ 328.1308.

1-(4-(tert-butyl)phenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4d)



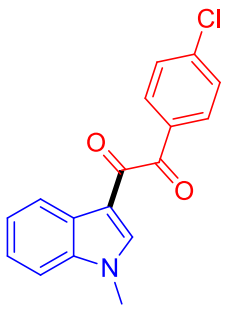
Yellow Solid, mp: 180-181 °C;
IR (neat, ν, cm-1): 1669, 1628, 1600, 1522, 1463cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 4.7 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.67 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.26 (s, 3H), 3.69 (s, 3H), 1.24 (s, 10H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.11, 187.49, 157.84, 139.04, 137.23, 130.42, 129.81, 125.89, 125.30, 123.68, 122.94, 122.19, 112.43, 109.53, 34.84, 33.27, 30.56;
HRMS (ESI) *m/z*: Found: 342.1463. Calcd for $C_{21}H_{21}NO_2$: $(M+Na)^+$ 342.1465.

1-(4-fluorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4e)



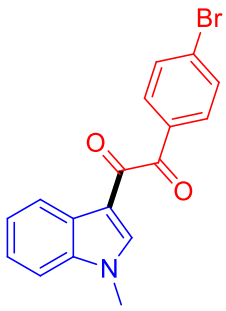
Yellow Solid, mp: 112-113 °C;
IR (neat, ν, cm-1): 1665, 1611, 1593, 1504cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.14 (s, 2H), 7.82 (s, 1H), 7.38 (s, 3H), 7.15 (t, *J* = 8.0 Hz, 2H), 3.82 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.50, 186.55, 166 (d, *J* = 255.4), 139.20, 137.24, 132.7 (d, *J* = 9.6), 129.4 (d, *J* = 2.6) 125.89, 123.81, 123.09, 122.14, 115.5 (d, J = 21.9), 112.26, 109.59, 33.32;
HRMS (ESI) *m/z*: Found: 304.0747. Calcd for $C_{17}H_{12}FNO_2$: $(M+Na)^+$ 304.0744.

1-(4-chlorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4f)



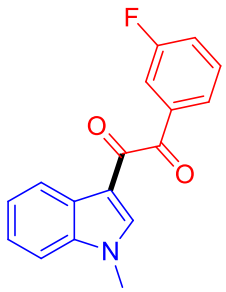
Yellow Solid, mp: 157-158 ºC;
IR (neat, ν, cm-1): 1670, 1618, 1583, 1459cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.42 (m, 1H), 8.08 – 8.01 (m, 2H), 7.81 (s, 1H), 7.49 – 7.42 (m, 2H), 7.42 – 7.35 (m, 3H), 3.81 (s, 3H).;
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.78, 186.24, 140.36, 139.24, 137.24, 131.38, 131.22, 128.61, 125.89, 123.84, 123.13, 122.15, 112.21, 109.61, 33.34;
HRMS (ESI) *m/z*: Found: 320.0441. Calcd for $C_{17}H_{12}ClO_2$: $(M+Na)^+$ 320.0449.

1-(4-bromophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4g)



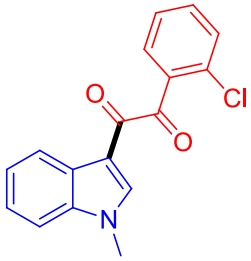
Yellow Solid, mp: 165-166 ºC;
IR (neat, ν, cm-1): 1662, 1624, 1583, 1467cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.41 (m, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.81 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.39 (dd, *J* = 6.7, 3.3 Hz, 3H), 3.81 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.97, 186.16, 139.24, 137.24, 131.79, 131.60, 131.28, 129.25, 125.89, 123.85, 123.14, 122.16, 112.21, 109.60, 33.35;
HRMS (ESI) *m/z*: Found: 363.9931. Calcd for $C_{17}H_{12}BrNO_2$: $(M+Na)^+$ 363.9944.

1-(3-fluorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4h)



Yellow Solid, mp: 121-122 ºC;
IR (neat, ν, cm-1): 1672, 1619, 1523cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.94 (d, *J* = 6.8 Hz, 1H), 7.87 (s, 2H), 7.51 (d, *J* = 5.5 Hz, 1H), 7.44 (s, 3H), 7.38 (d, *J* = 6.8 Hz, 1H), 3.88 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.72, 186.02, 162.3 (d, *J* = 247), 139.22, 137.26, 135.0 (d, *J* = 6.5), 130.0 (d, *J* = 7.5), 125.9 (d, *J* = 2.8), 125.85, 123.87, 123.15, 122.18, 120.8 (d, *J* = 21.3), 116.1 (d, *J* = 22.5), 112.19, 109.60, 33.34;
HRMS (ESI) *m/z*: Found: 304.0745. Calcd for $C_{17}H_{12}FNO_2$: $(M+Na)^+$ 304.0744.

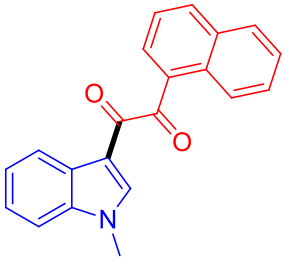
1-(2-chlorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethane-1,2-dione (4i)



Yellow Solid, mp: 163-164 ºC;
IR (neat, ν, cm-1): 1687, 1611, 1588, 1518cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 – 8.39 (m, 1H), 8.04 (s, 1H), 7.78 (d, *J* = 6.8 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 1H), 7.44 – 7.36 (m, 5H), 3.88 (s, 3H);

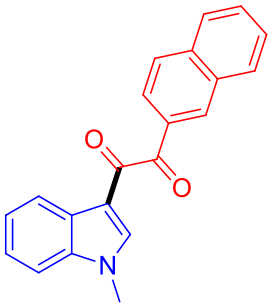
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.52, 184.44, 139.10, 137.14, 134.85, 132.88, 132.76, 131.37, 129.88, 126.52, 126.36, 123.68, 122.98, 122.24, 111.53, 109.51, 33.38;
HRMS (ESI) *m/z*: Found: 320.0454. Calcd for $C_{17}H_{12}ClO_2$: $(M+Na)^+$ 320.0449.

1-(1-methyl-1*H*-indol-3-yl)-2-(naphthalen-1-yl)ethane-1,2-dione (4j)



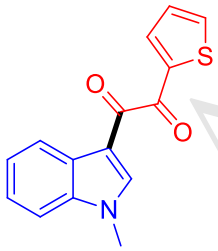
Yellow Solid, mp: 102-103 °C;
IR (neat, ν, cm-1): 1649, 1638, 1525, 1469cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.54 (d, *J* = 6.4 Hz, 1H), 8.17 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.93 (dd, *J* = 8.4, 3.0 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.83 (s, 1H), 7.62 (t, *J* = 7.1 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.44 – 7.37 (m, 3H), 3.80 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.40, 187.33, 139.18, 137.28, 135.70, 133.23, 131.96, 130.25, 129.51, 128.71, 128.30, 127.38, 126.45, 125.93, 123.92, 123.77, 123.06, 122.24, 112.54, 109.58, 33.30;
HRMS (ESI) *m/z*: Found: 336.0993. Calcd for $C_{21}H_{15}NO_2$: $(M+Na)^+$ 336.0995.

1-(1-methyl-1*H*-indol-3-yl)-2-(naphthalen-2-yl)ethane-1,2-dione (4k)



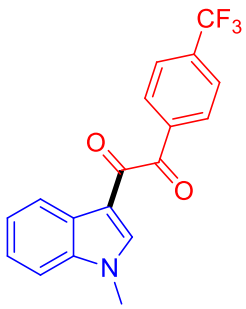
Yellow Solid, mp: 106-107 °C;
IR (neat, ν, cm-1): 1637, 1595, 1524, 1468cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), δ 8.64 (s, 1H), 8.54 (d, *J* = 6.8 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.83 (s, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 9.5, 2.6 Hz, 3H), 3.80 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 193.40, 187.33, 139.18, 137.28, 135.69, 133.22, 131.95, 130.25, 129.51, 128.71, 128.30, 127.38, 126.46, 125.93, 123.92, 123.77, 123.06, 122.24, 112.54, 109.58, 33.30;
HRMS (ESI) *m/z*: Found: 336.0999. Calcd for $C_{21}H_{15}NO_2$: $(M+Na)^+$ 336.0995.

1-(1-methyl-1*H*-indol-3-yl)-2-(thiophen-2-yl)ethane-1,2-dione (4l)



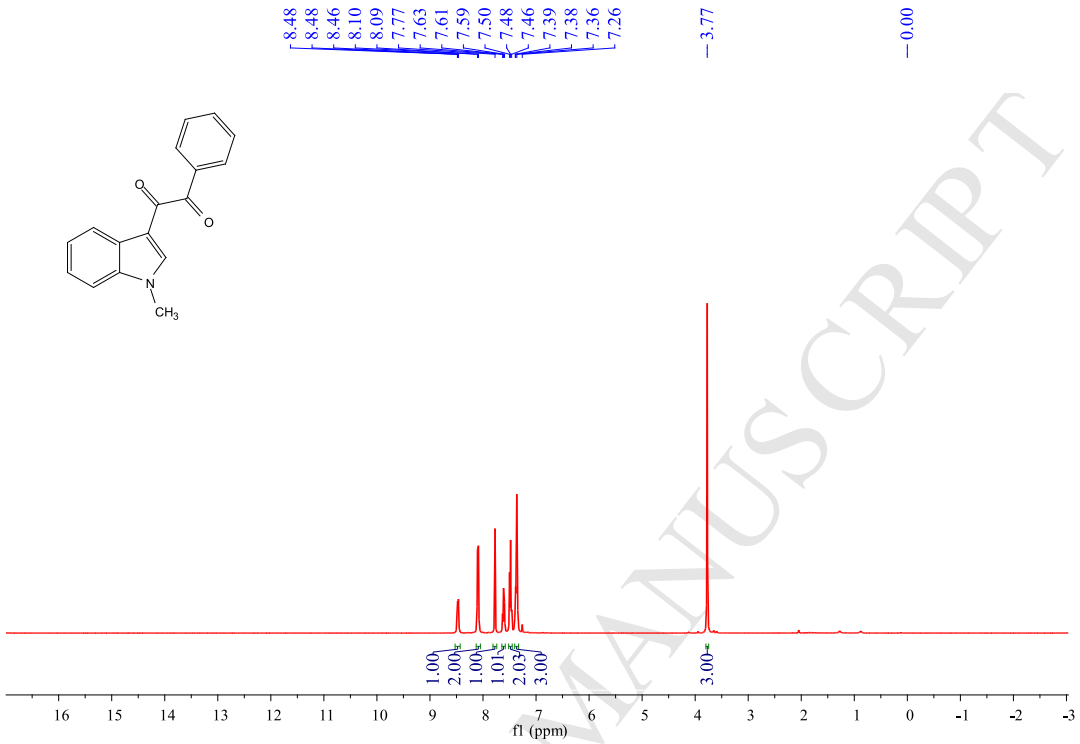
Yellow Solid, mp: 93-94 °C;
IR (neat, ν, cm-1): 1642, 1610, 1578, 1520, 1463cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 6.0, 1.6 Hz, 1H), 7.97 (d, *J* = 5.8 Hz, 2H), 7.69 – 7.61 (m, 1H), 7.24 (ddd, *J* = 10.6, 7.7, 4.3 Hz, 3H), 7.07 – 7.00 (m, 1H), 3.66 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 184.11, 184.11, 139.92, 138.87, 137.00, 136.25, 136.24, 127.94, 126.41, 123.67, 123.02, 122.14, 111.52, 109.61, 33.30;
HRMS (ESI) *m/z*: Found: 292.0401. Calcd for $C_{15}H_{11}NO_2S$: $(M+Na)^+$ 292.0403.

1-(1-methyl-1*H*-indol-3-yl)-2-(4-(trifluoromethyl)phenyl)ethane-1,2-dione (4m)

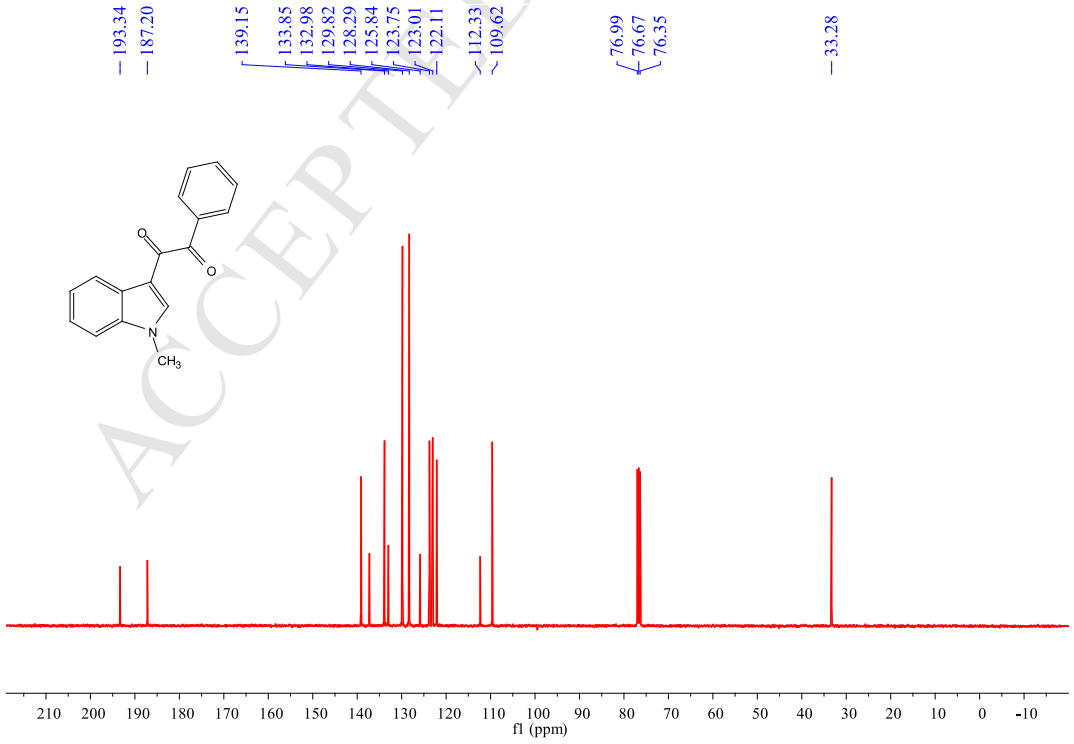


Yellow Solid, mp: 153-154 ºC;
IR (neat, ν, cm-1): 1680, 1614, 1579, 1491cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.0 Hz, 1H), 8.22 (d, *J* = 8.1 Hz, 2H), 7.86 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 10.0 Hz, 3H), 3.84 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.70, 185.53, 139.34, 137.27, 135.85, 134.7 (q, *J* = 32.5), 130.17, 125.91, 125.2 (q, *J* = 3.7), 123.95, 123.24, 123.0 (q, *J* = 271.3), 122.17, 112.13, 109.64, 33.36;
HRMS (ESI) *m/z*: Found: 354.0712. Calcd for $C_{18}H_{12}F_3NO_2$: $(M+Na)^+$ 354.0712.

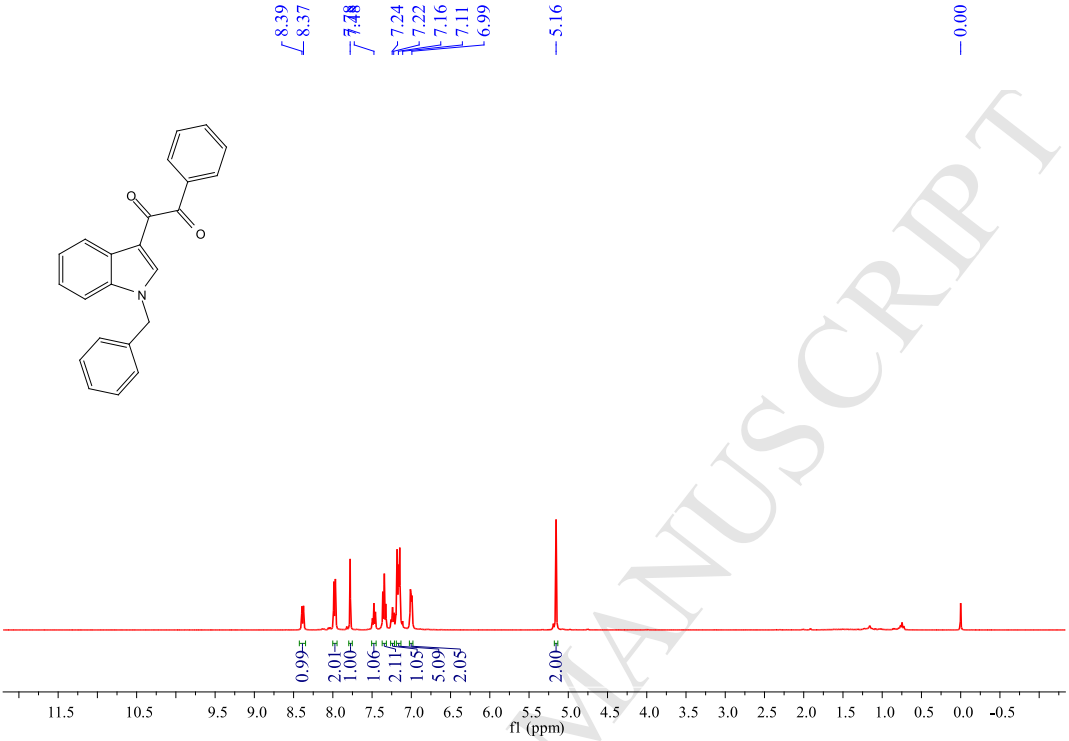
Copies of ^{1}H and ^{13}C NMR Spectra for Compounds



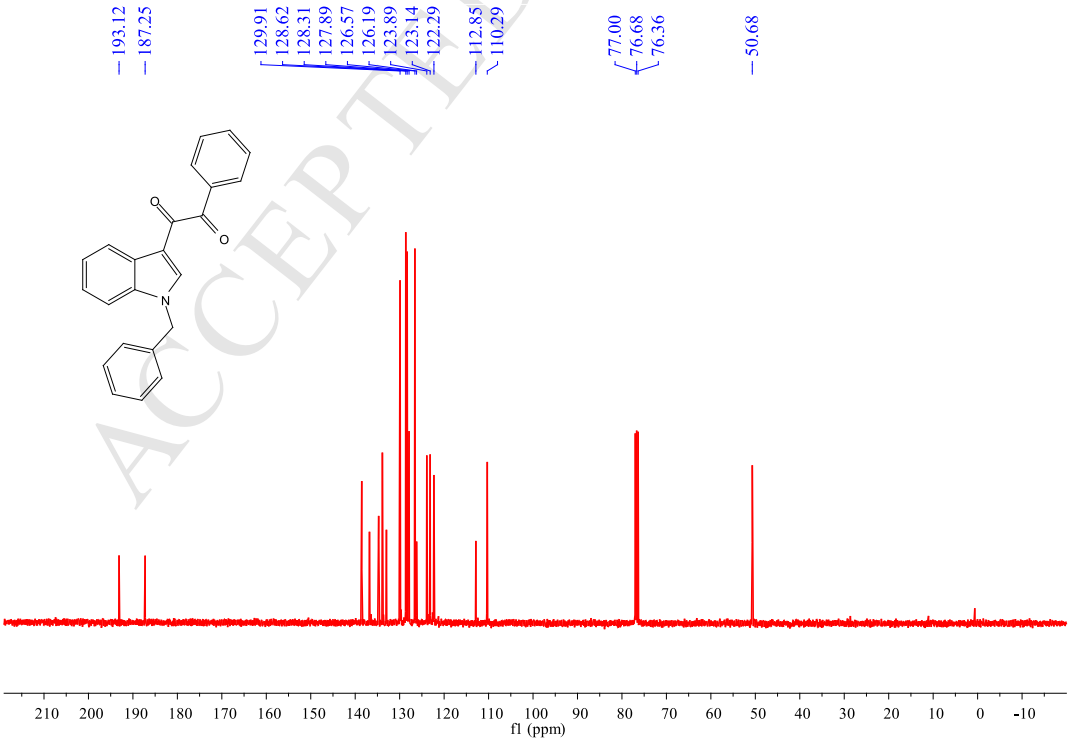
^{1}H NMR Spectrum of Compound 3a



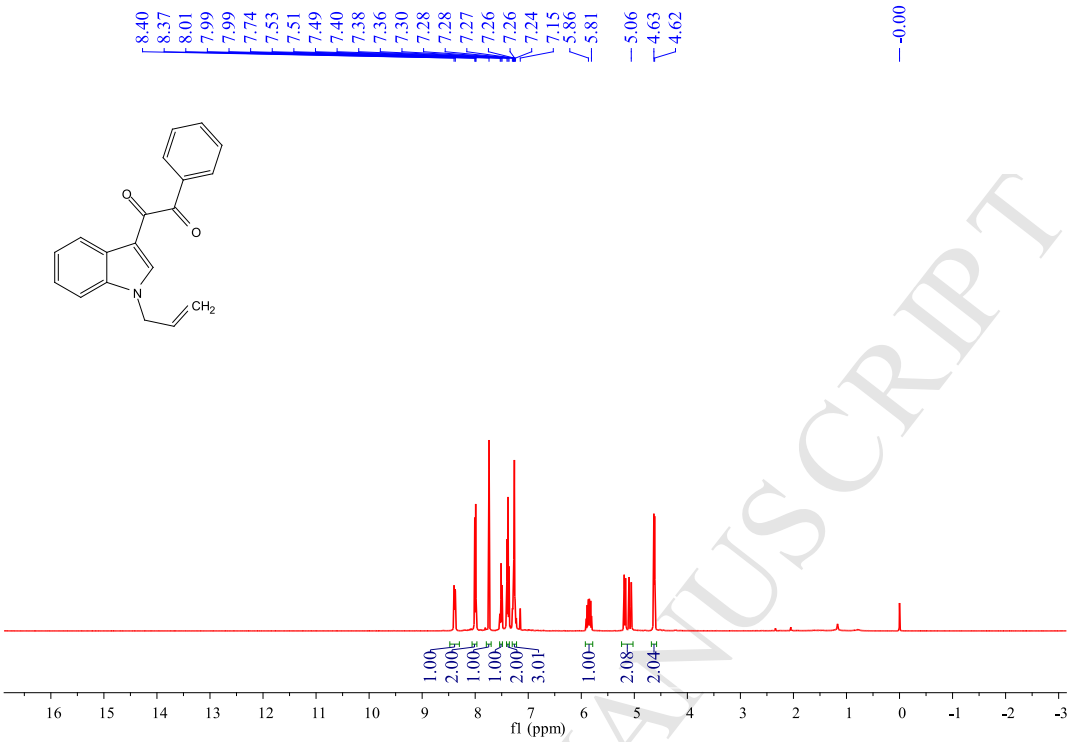
^{13}C NMR Spectrum of Compound 3a



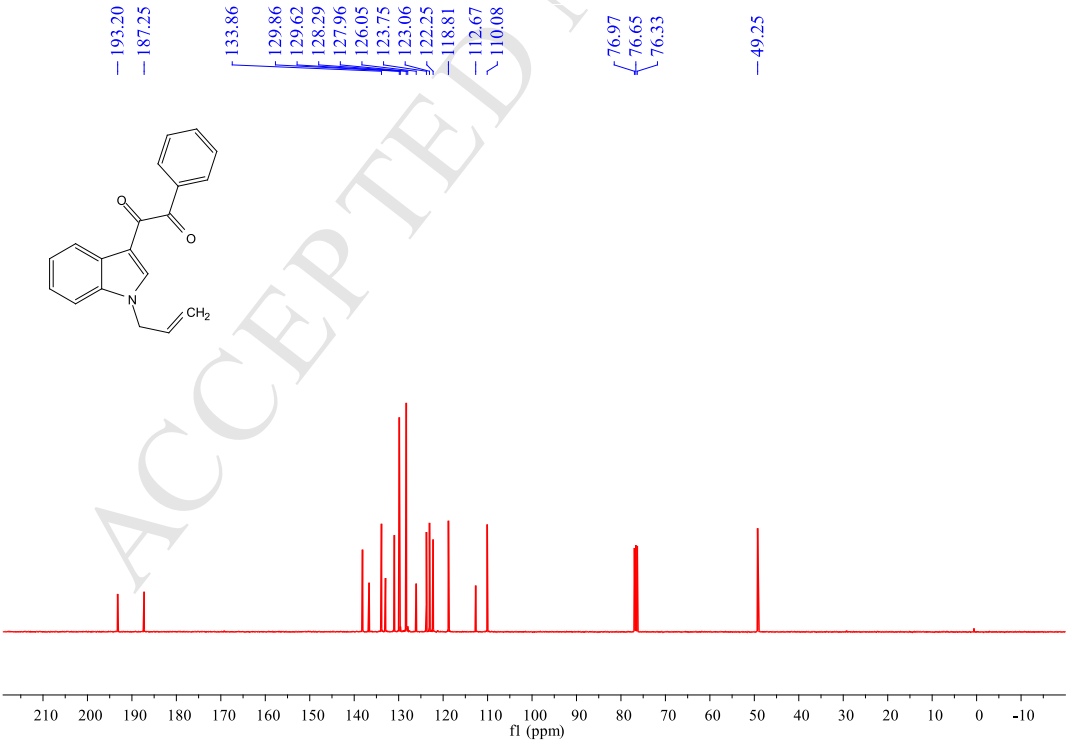
^{1}H NMR Spectrum of Compound 3b



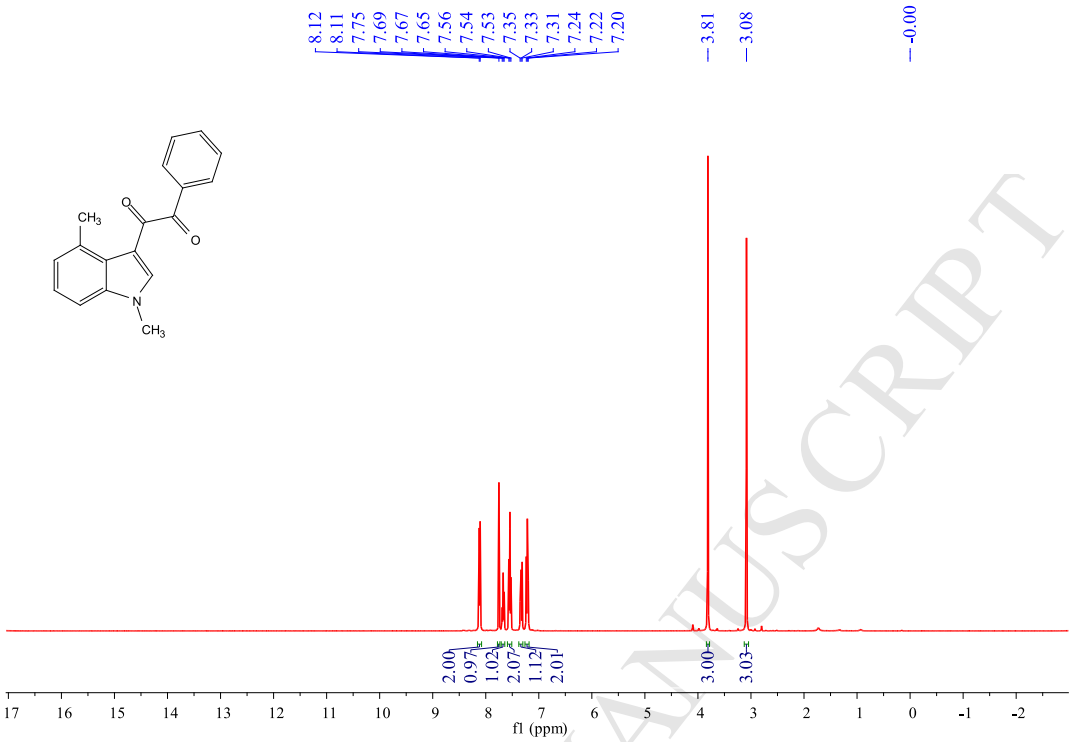
^{13}C NMR Spectrum of Compound 3b



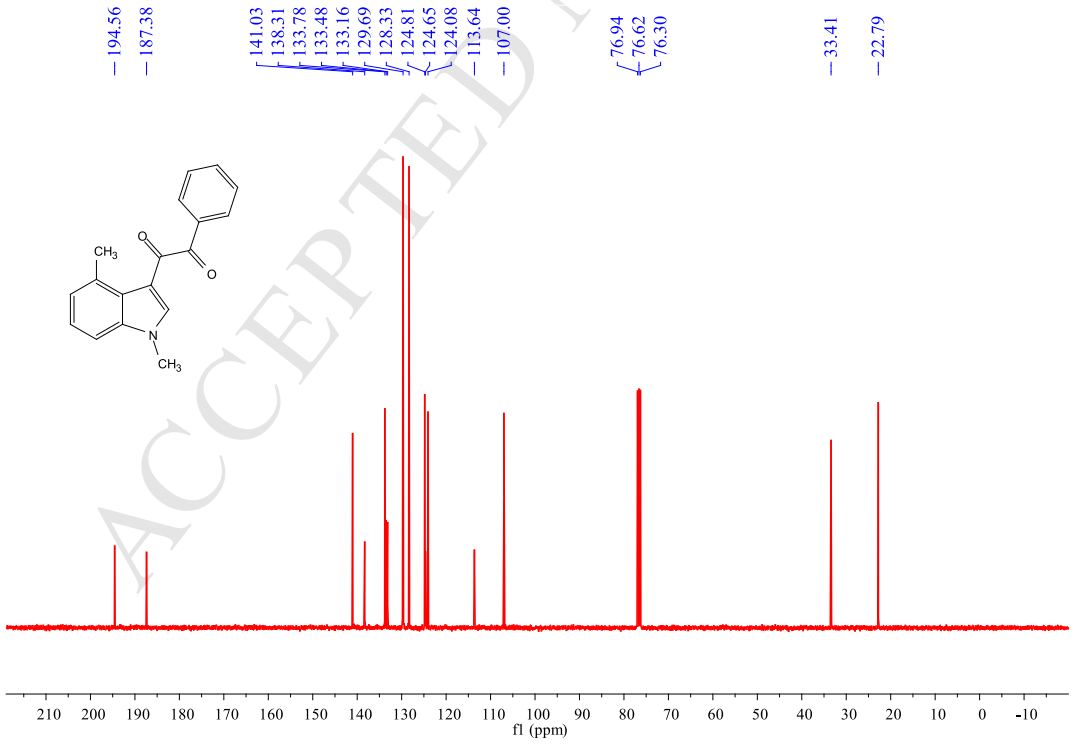
^{1}H NMR Spectrum of Compound 3c



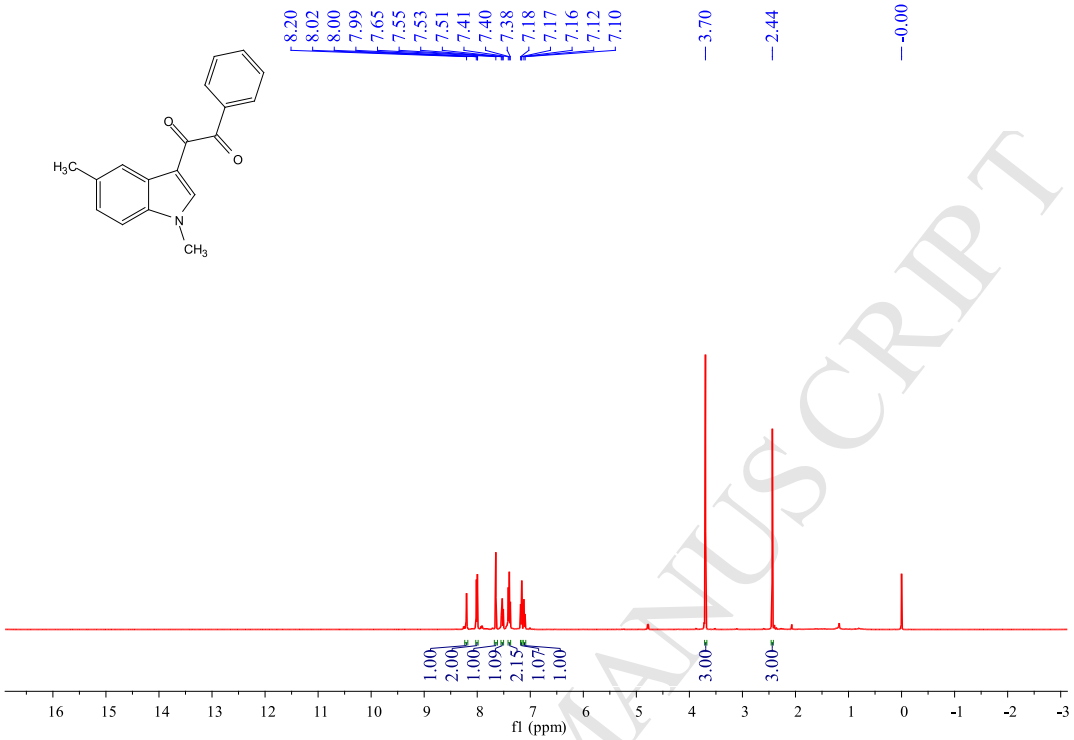
^{13}C NMR Spectrum of Compound 3c



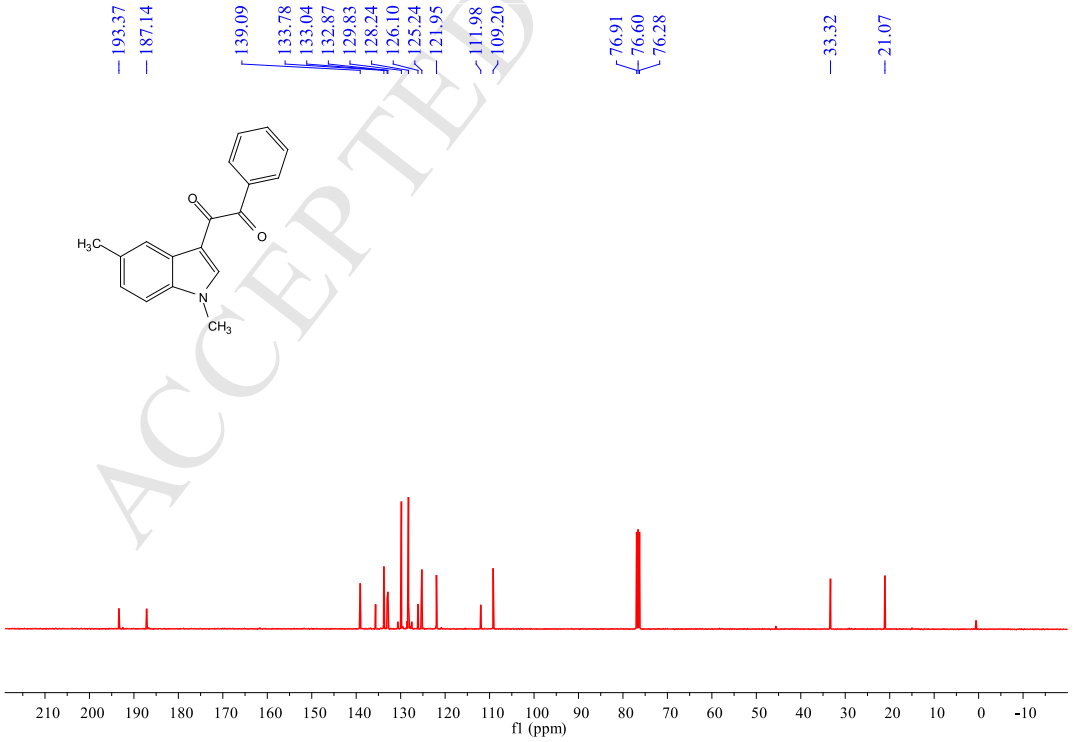
^{1}H NMR Spectrum of Compound 3e



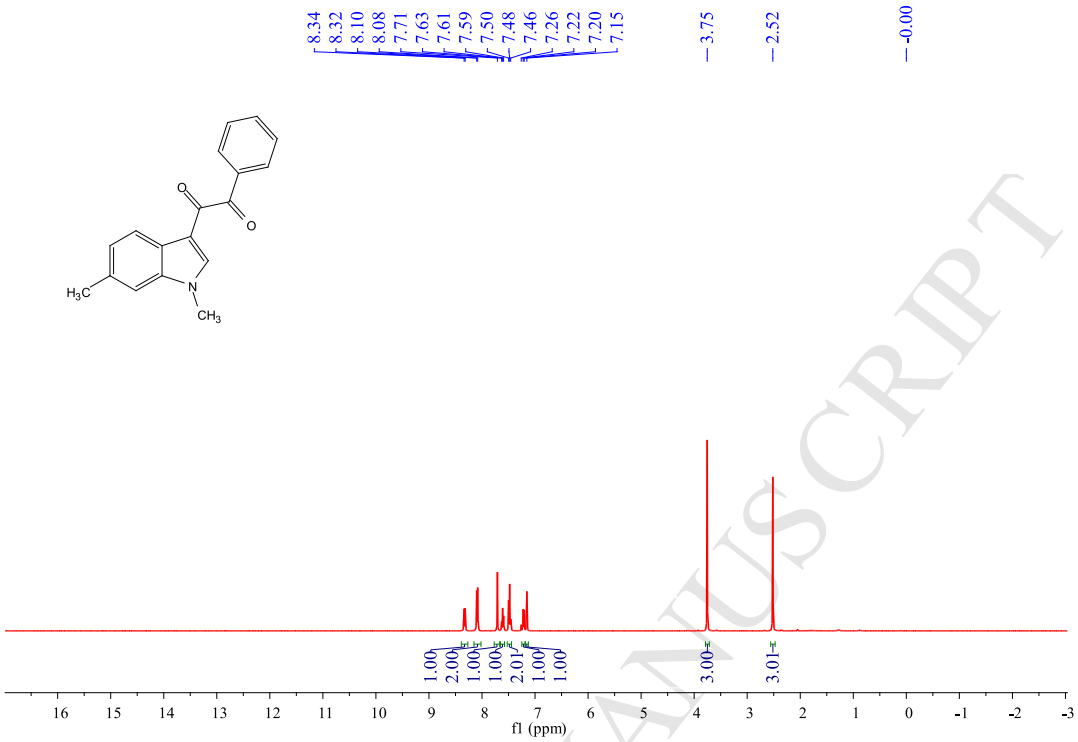
^{13}C NMR Spectrum of Compound 3e



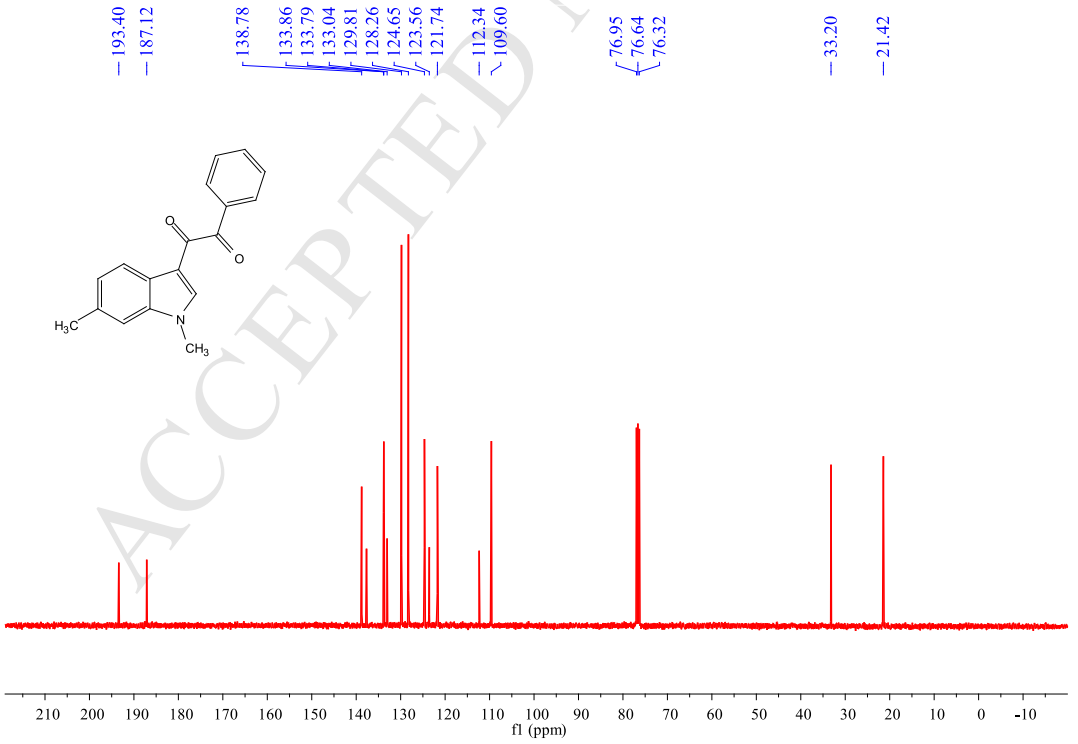
^{1}H NMR Spectrum of Compound 3f



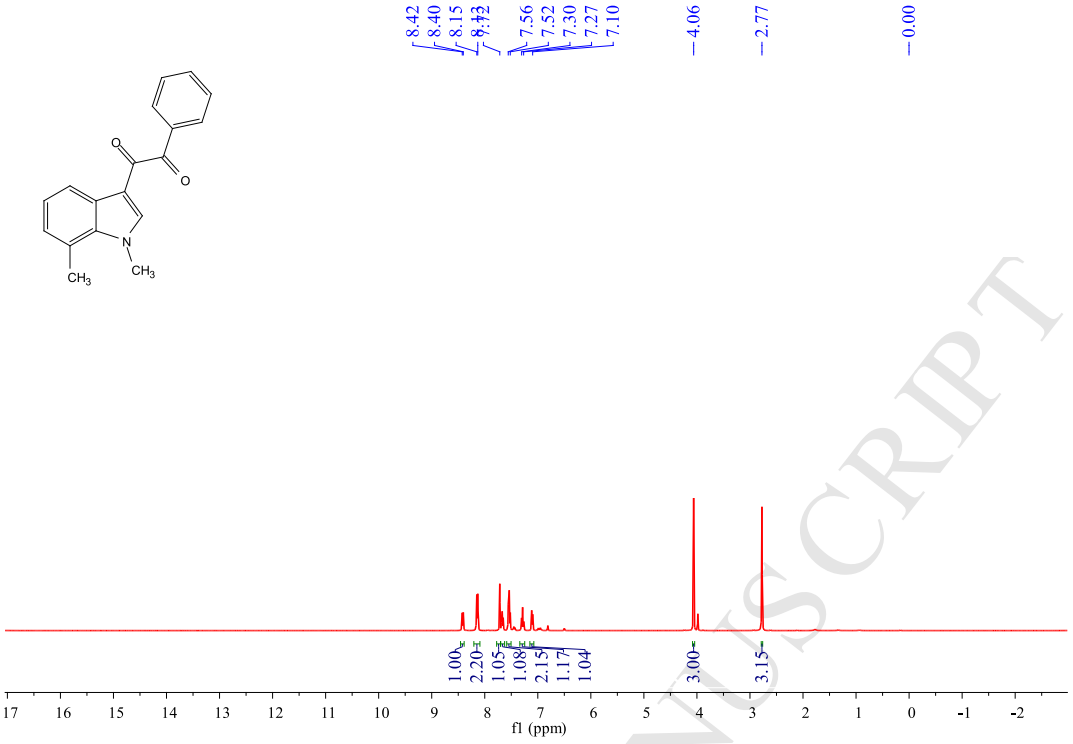
^{13}C NMR Spectrum of Compound 3f



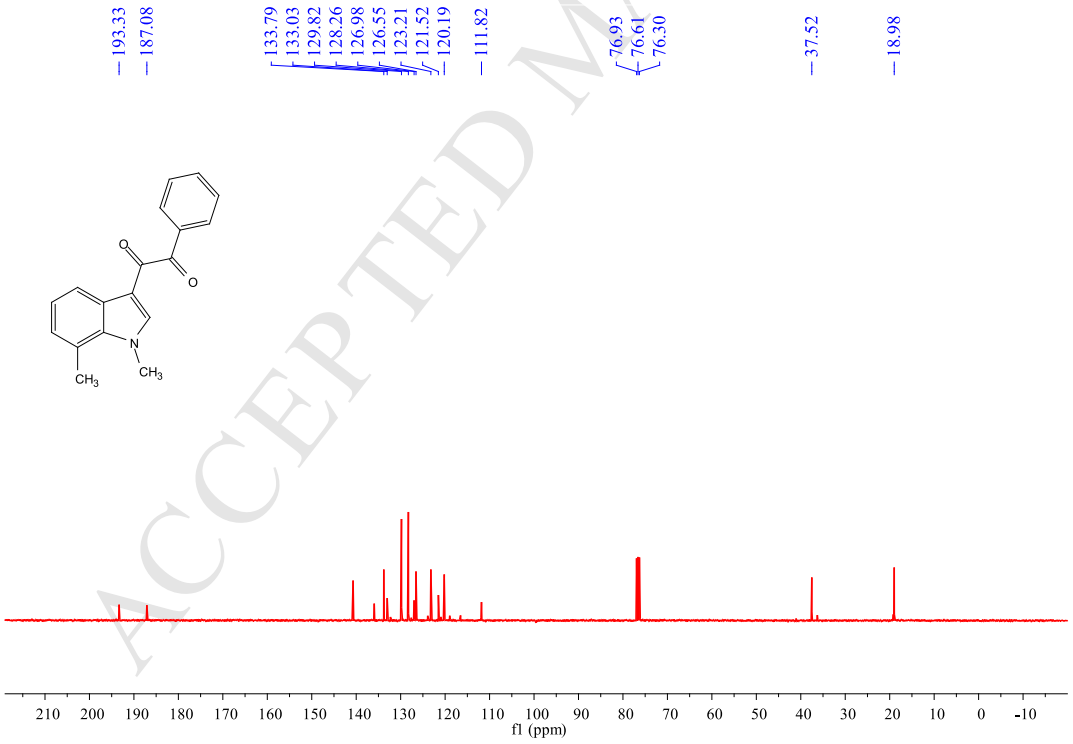
^{1}H NMR Spectrum of Compound 3g



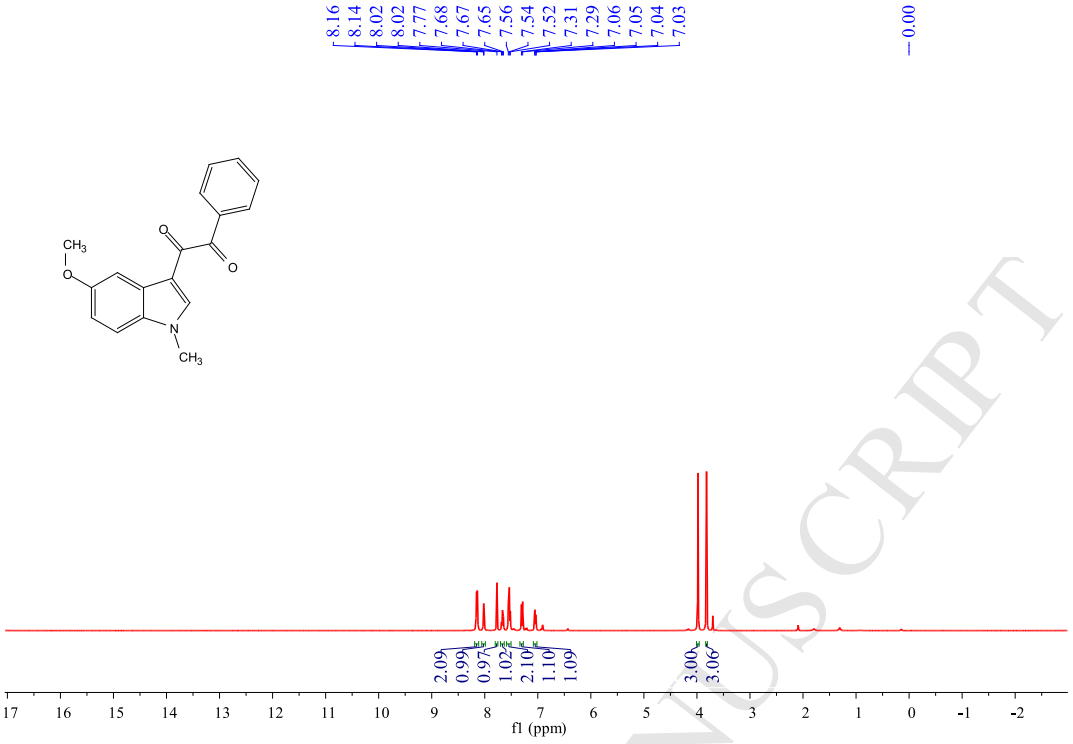
^{13}C NMR Spectrum of Compound 3g



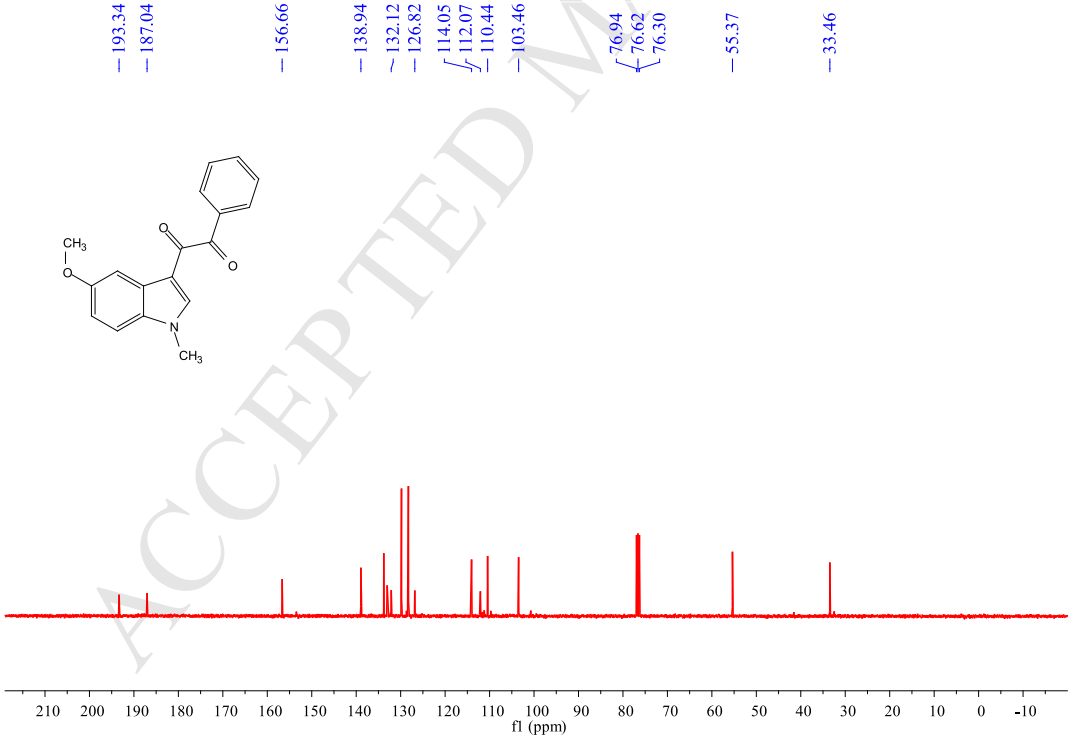
^{1}H NMR Spectrum of Compound 3h



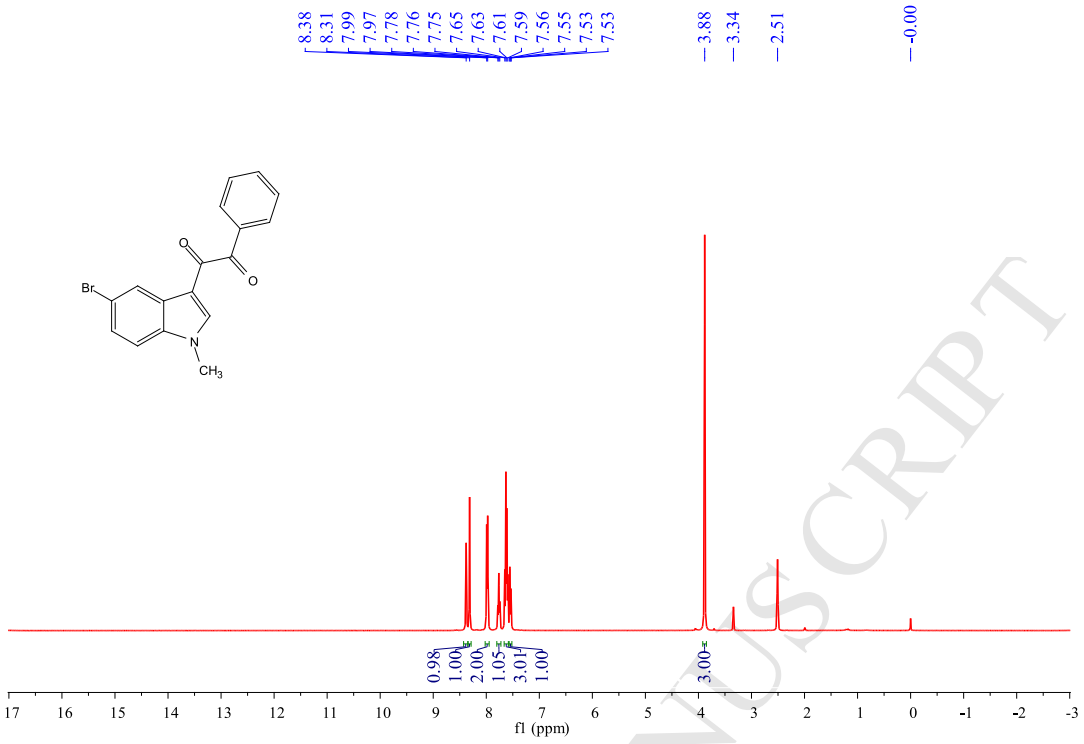
^{13}C NMR Spectrum of Compound 3h



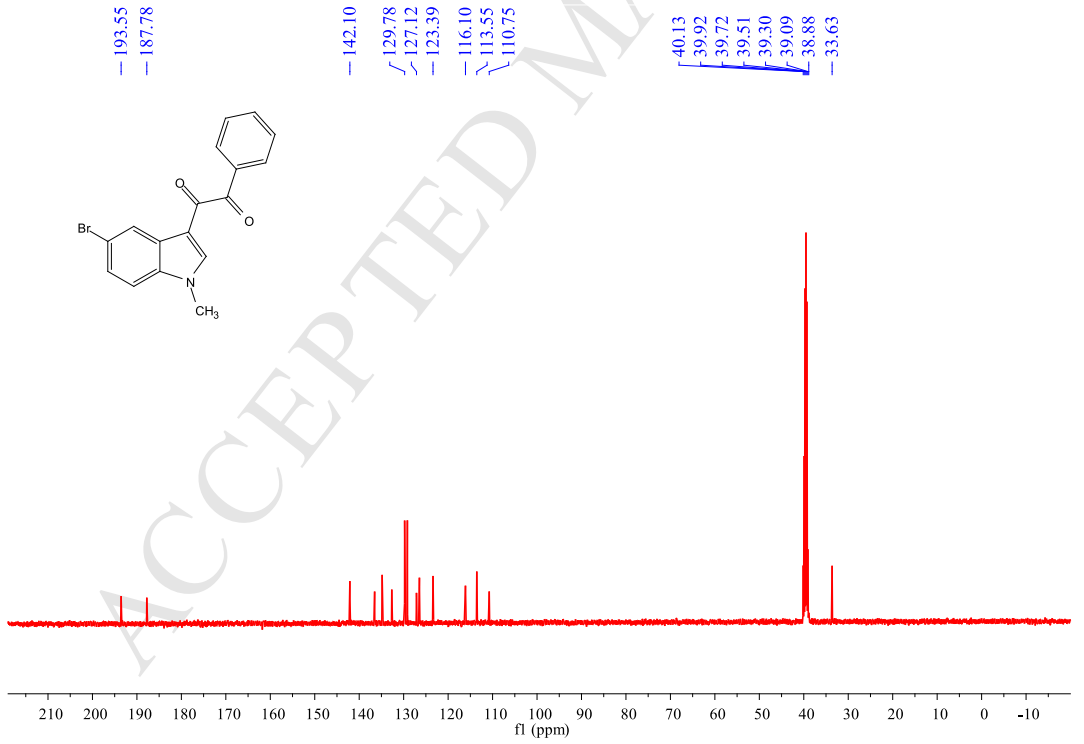
^{1}H NMR Spectrum of Compound 3i



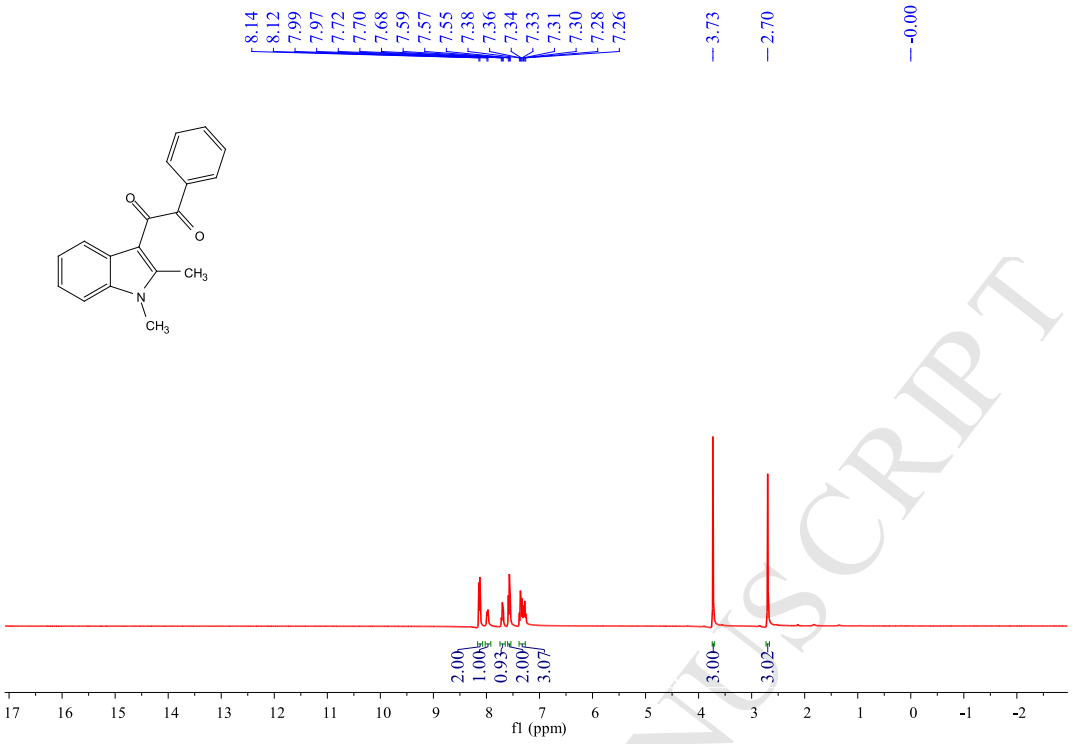
^{13}C NMR Spectrum of Compound 3i



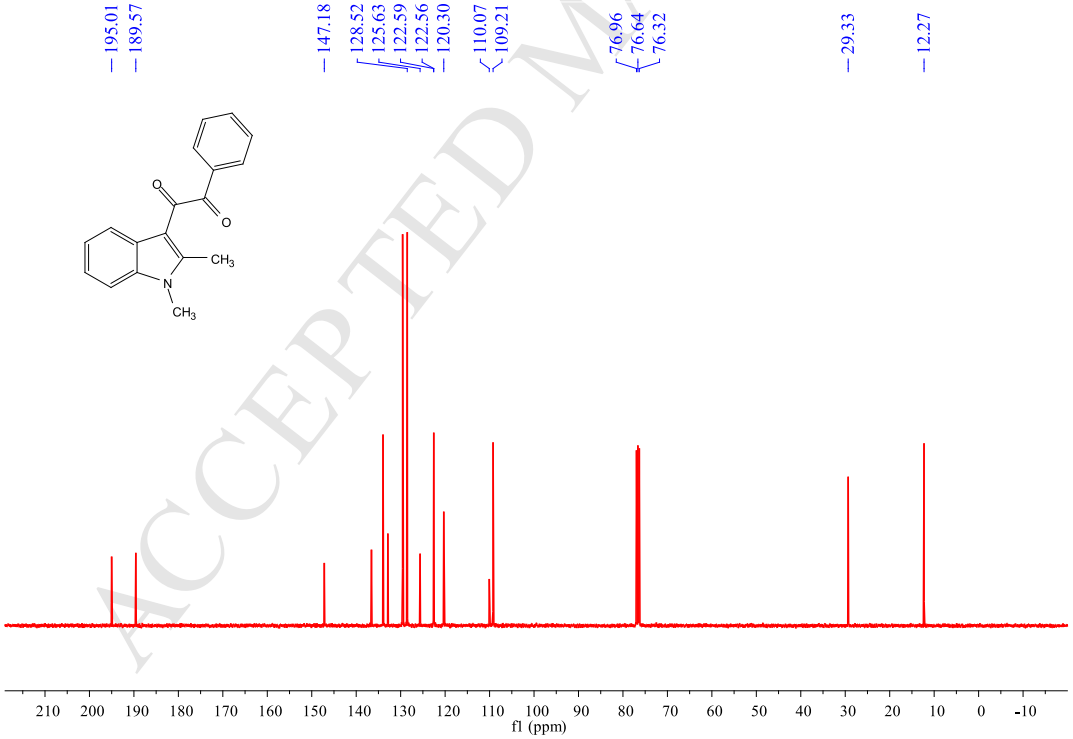
^{1}H NMR Spectrum of Compound 3j



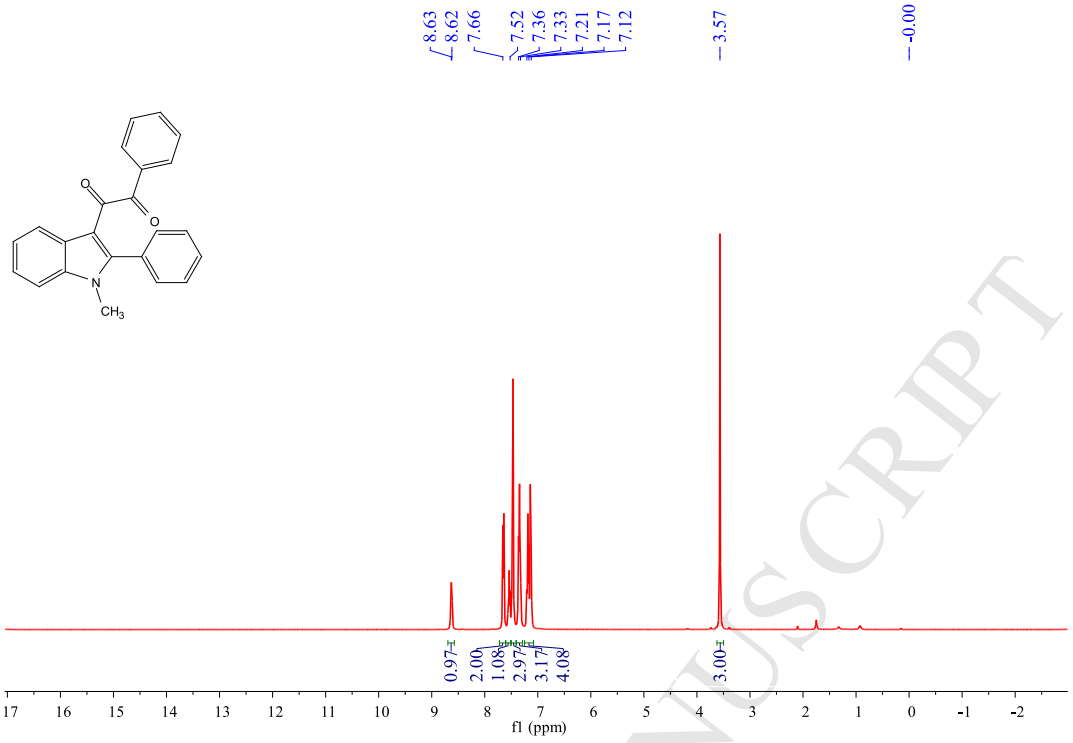
^{13}C NMR Spectrum of Compound 3j



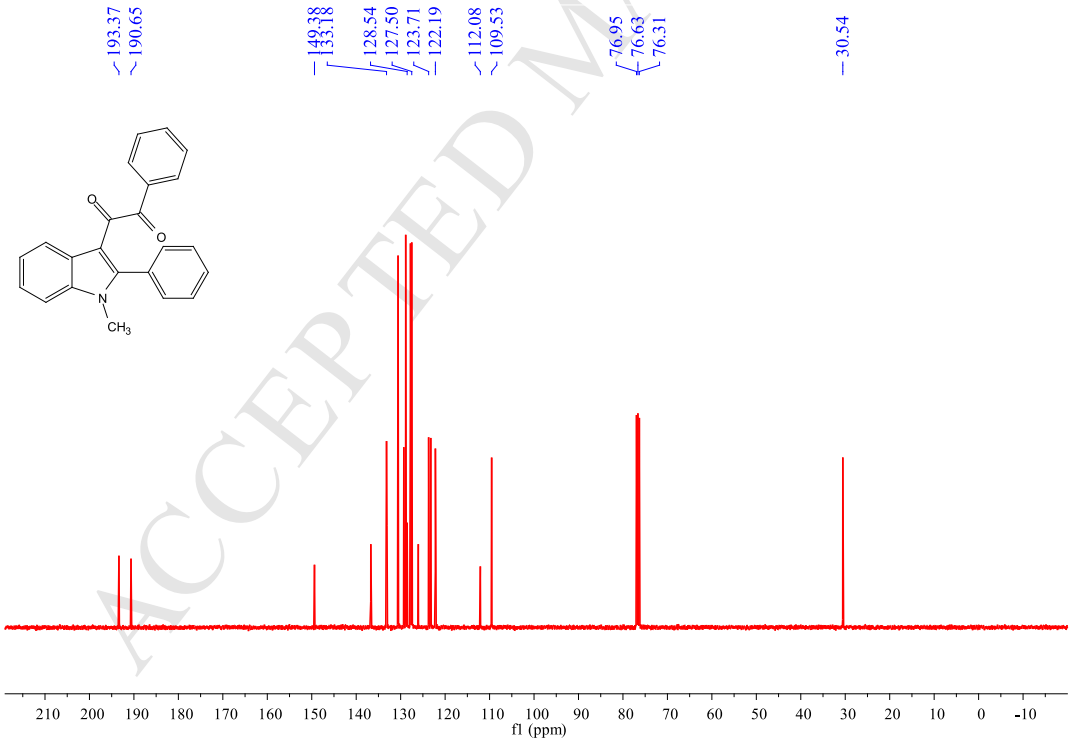
^{1}H NMR Spectrum of Compound 3k



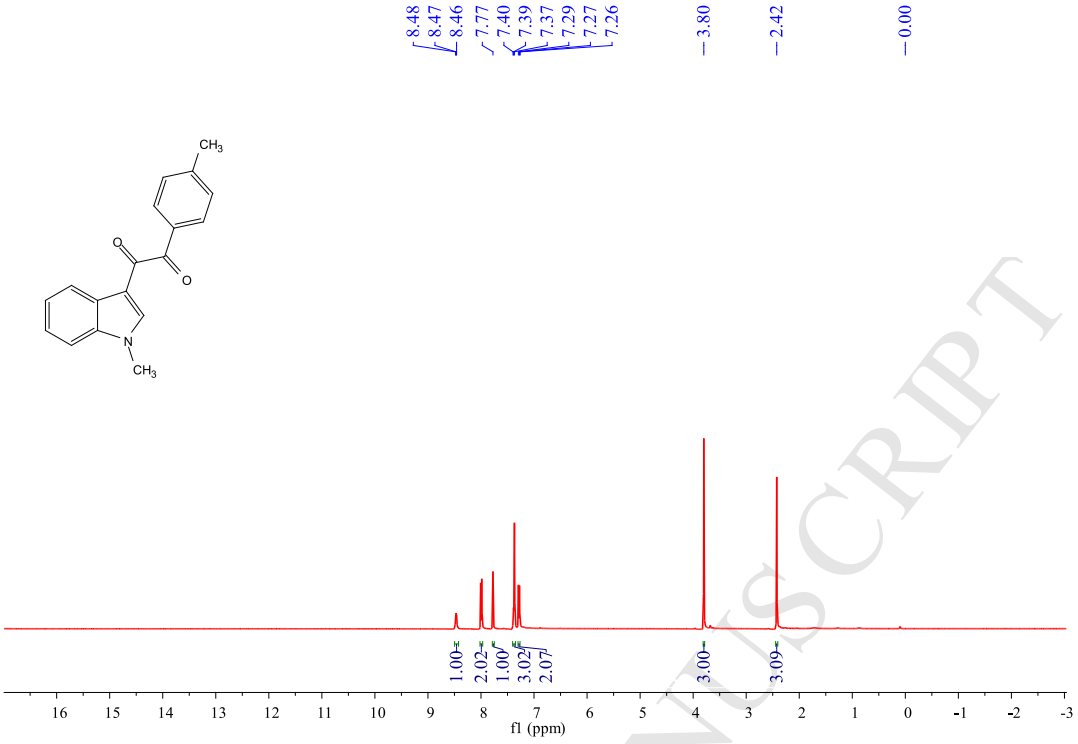
^{13}C NMR Spectrum of Compound 3k



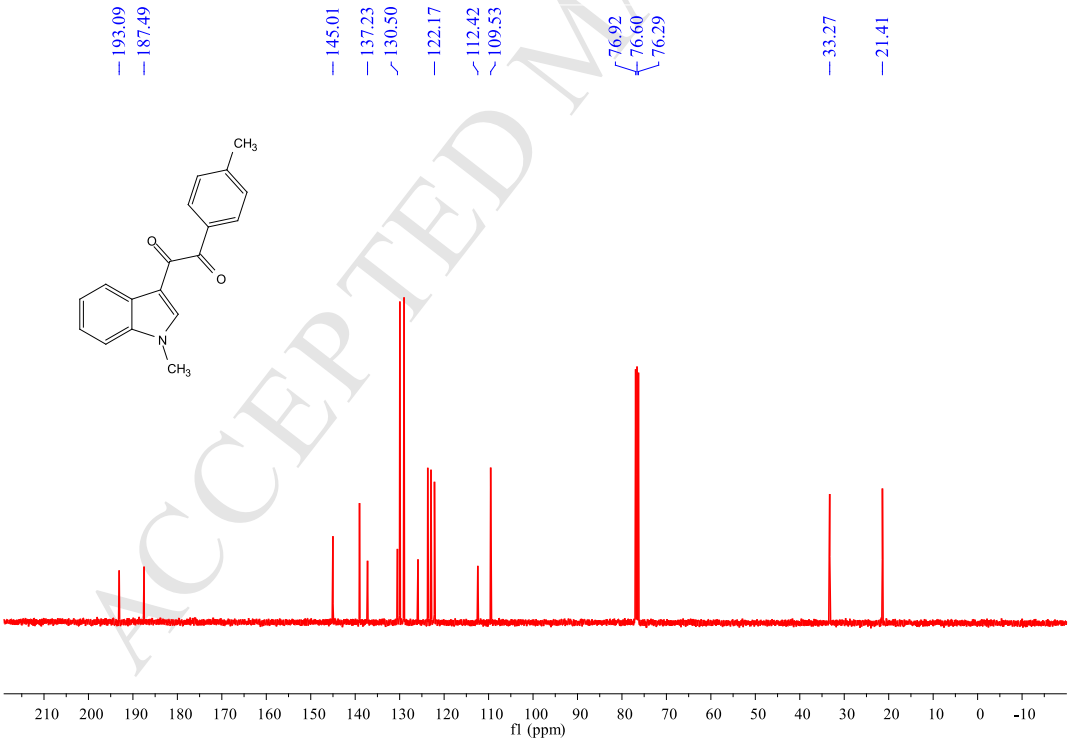
^{1}H NMR Spectrum of Compound 3l



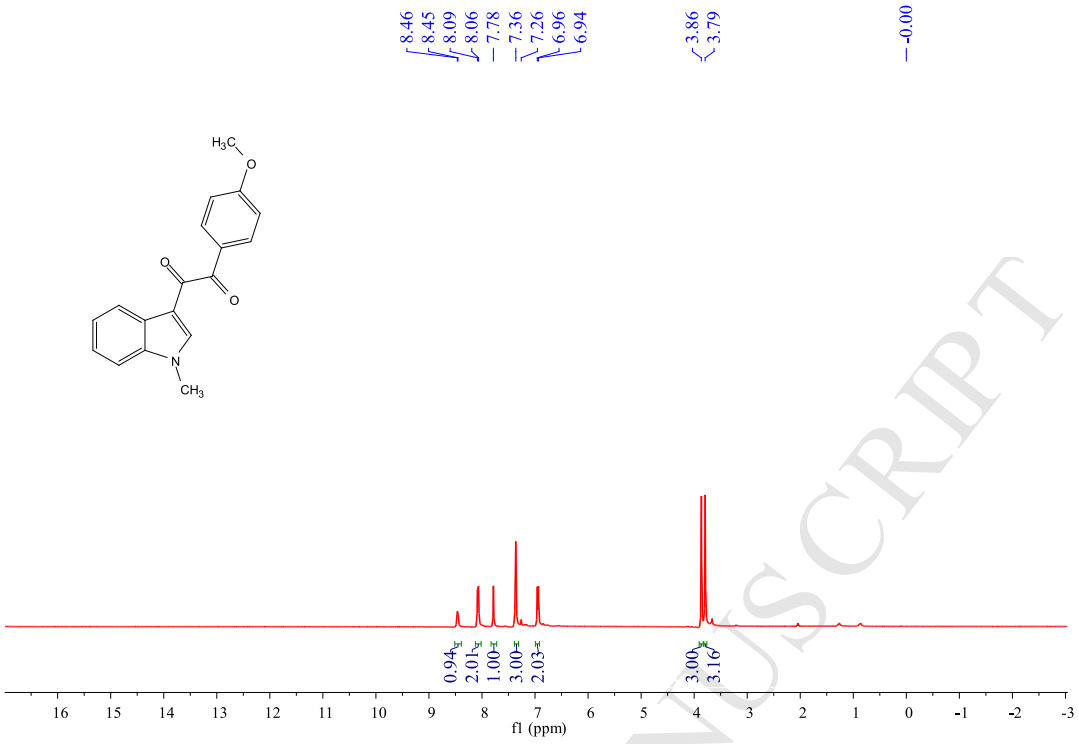
^{13}C NMR Spectrum of Compound 3l



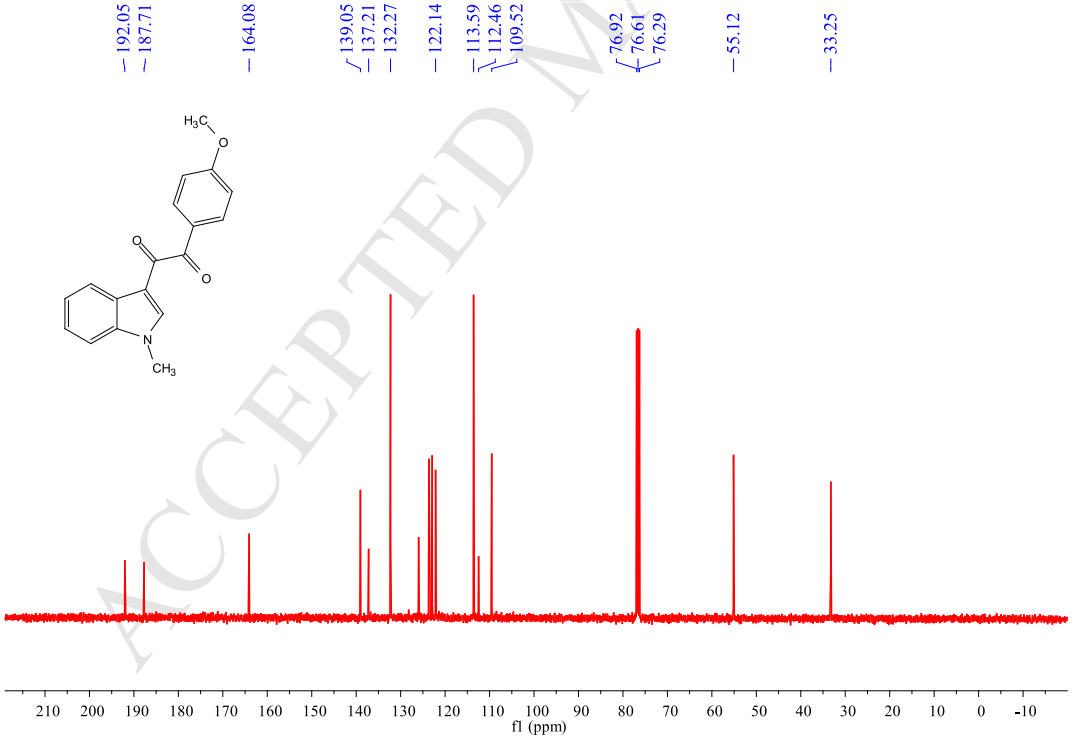
^{1}H NMR Spectrum of Compound 4a



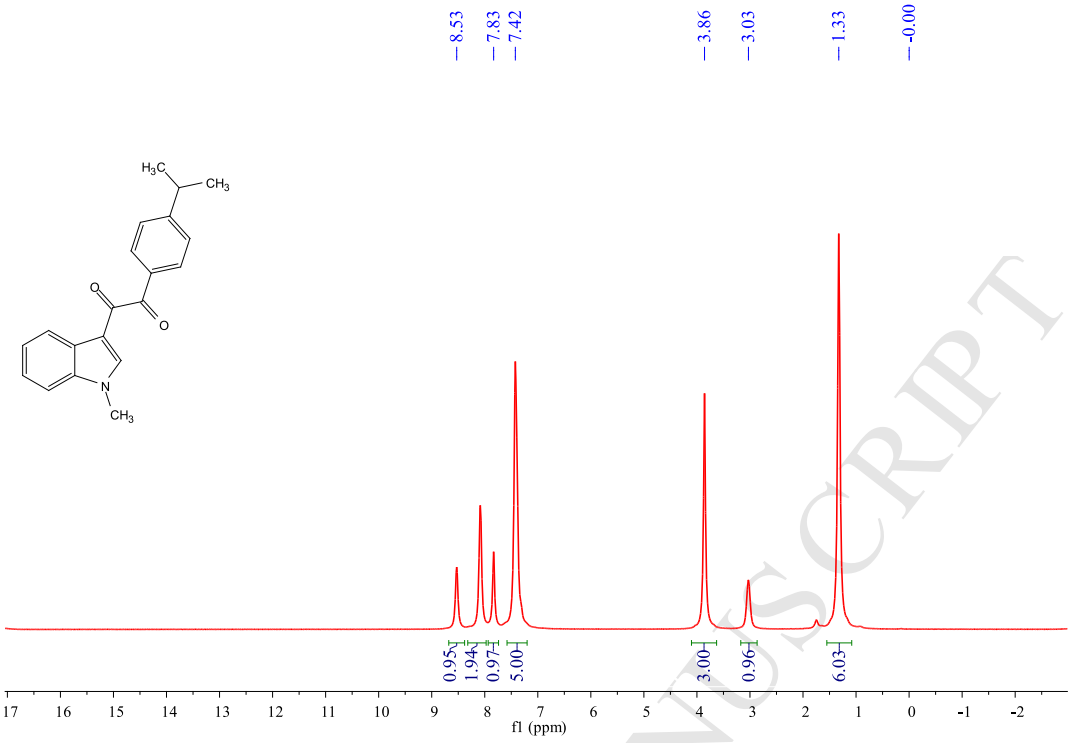
^{13}C NMR Spectrum of Compound 4a



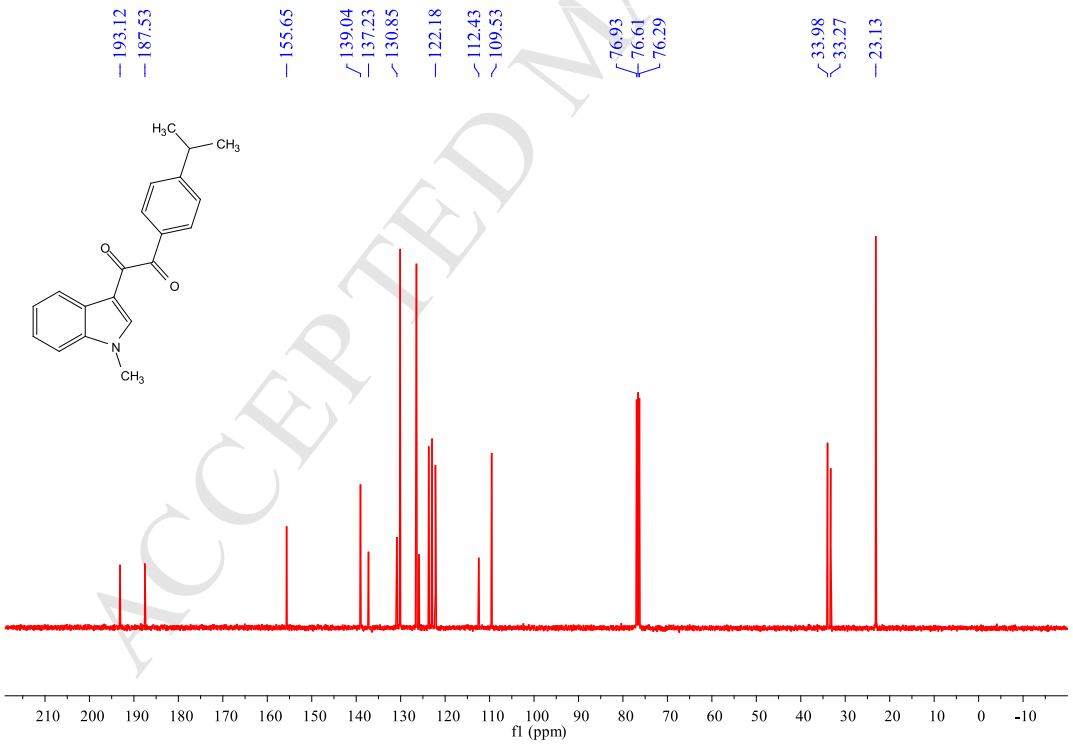
^{1}H NMR Spectrum of Compound 4b



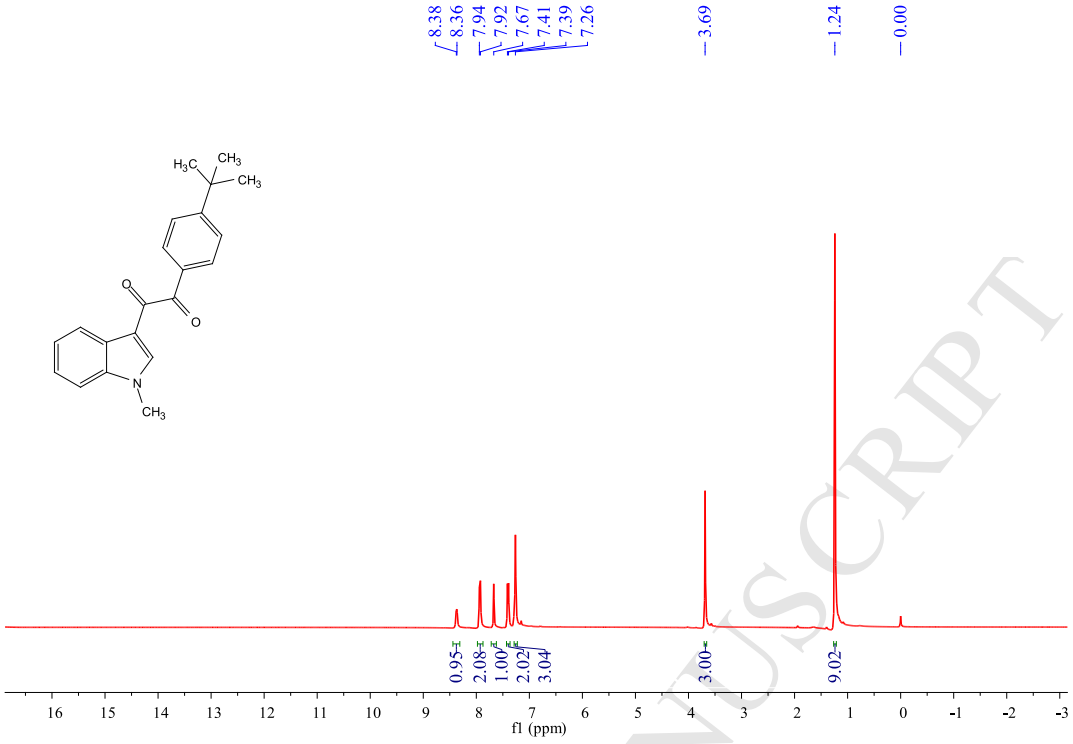
^{13}C NMR Spectrum of Compound 4b



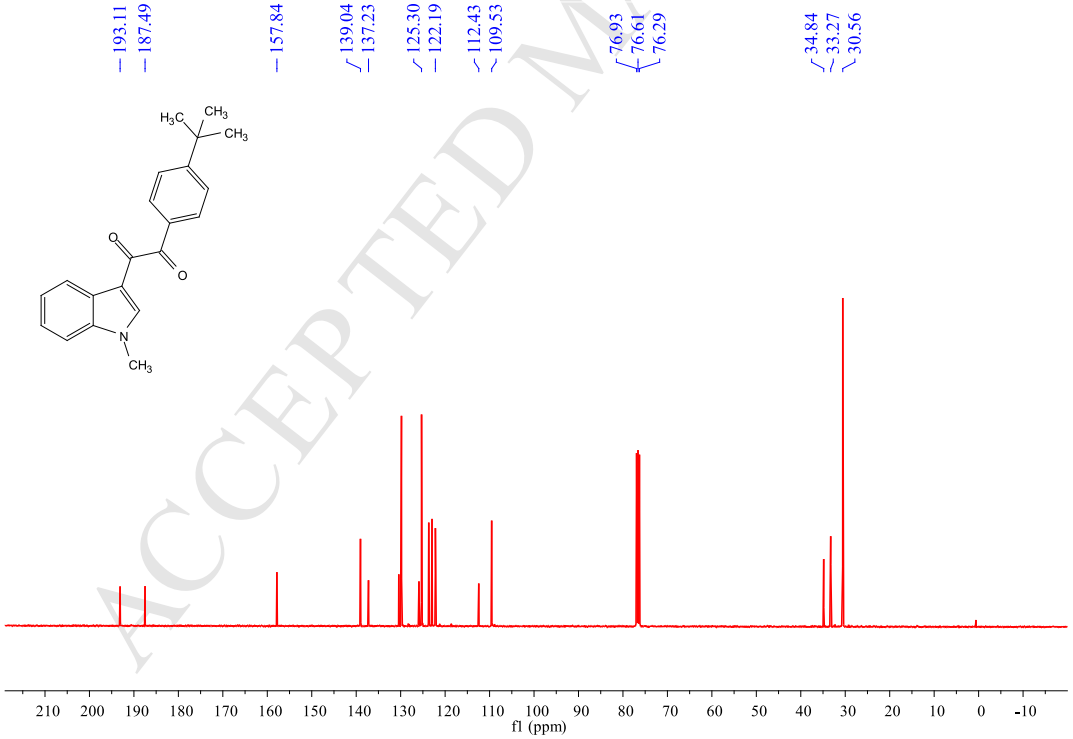
^{1}H NMR Spectrum of Compound 4c



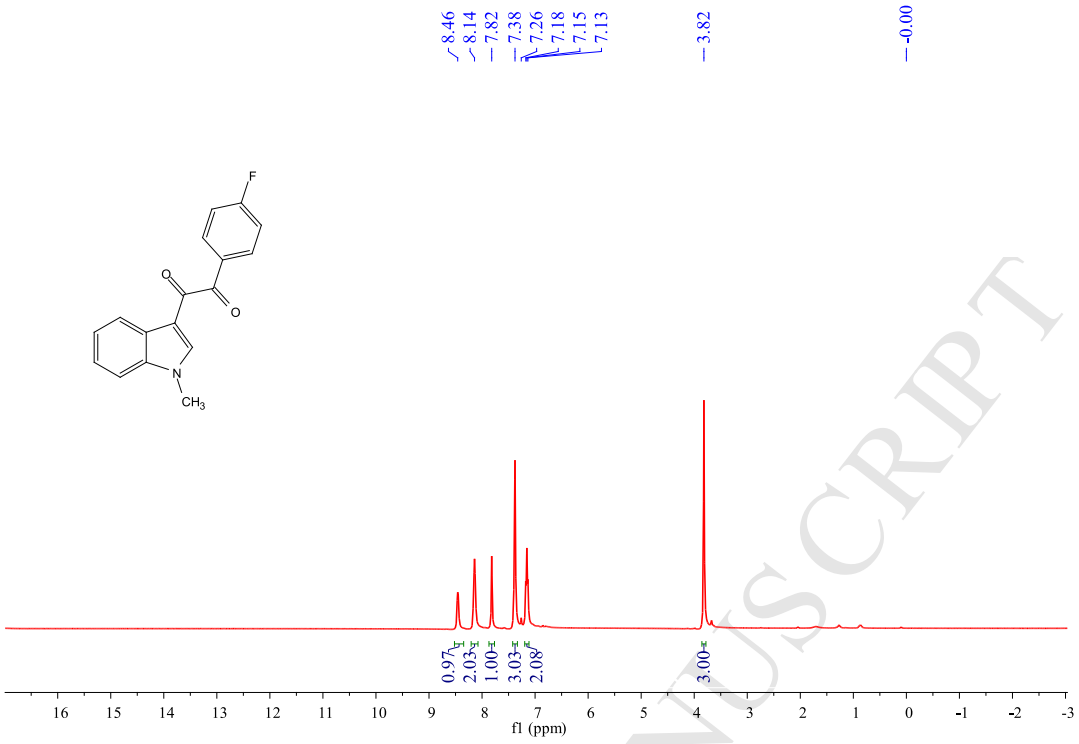
^{13}C NMR Spectrum of Compound 4c



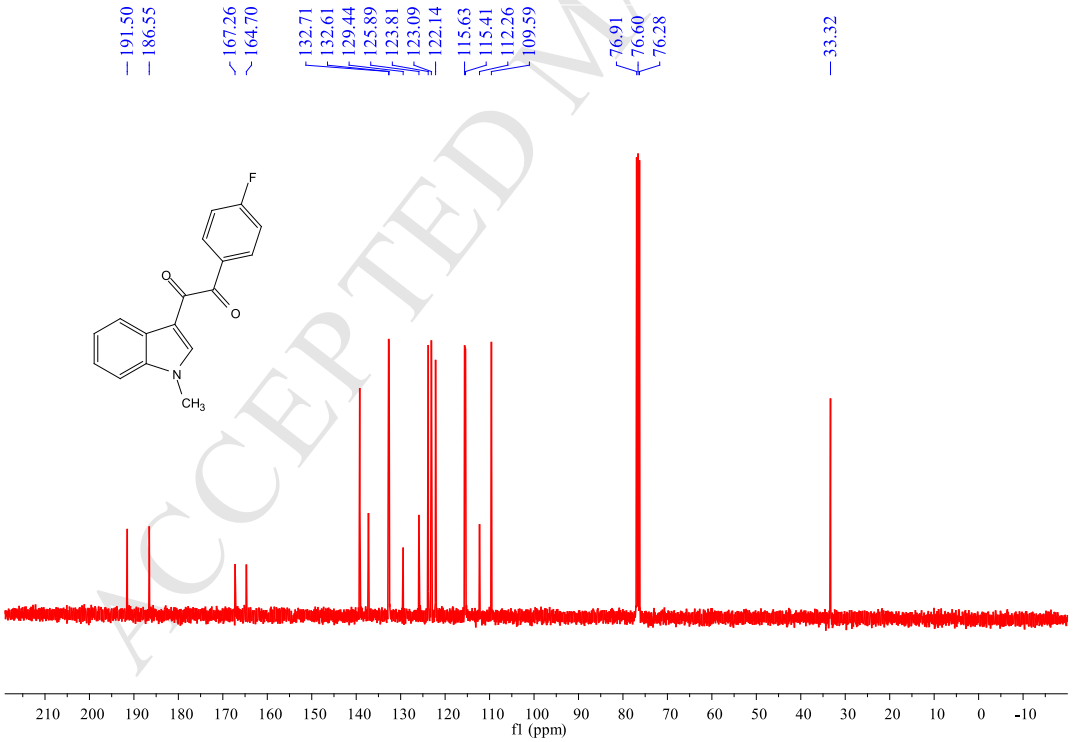
^{1}H NMR Spectrum of Compound 4d



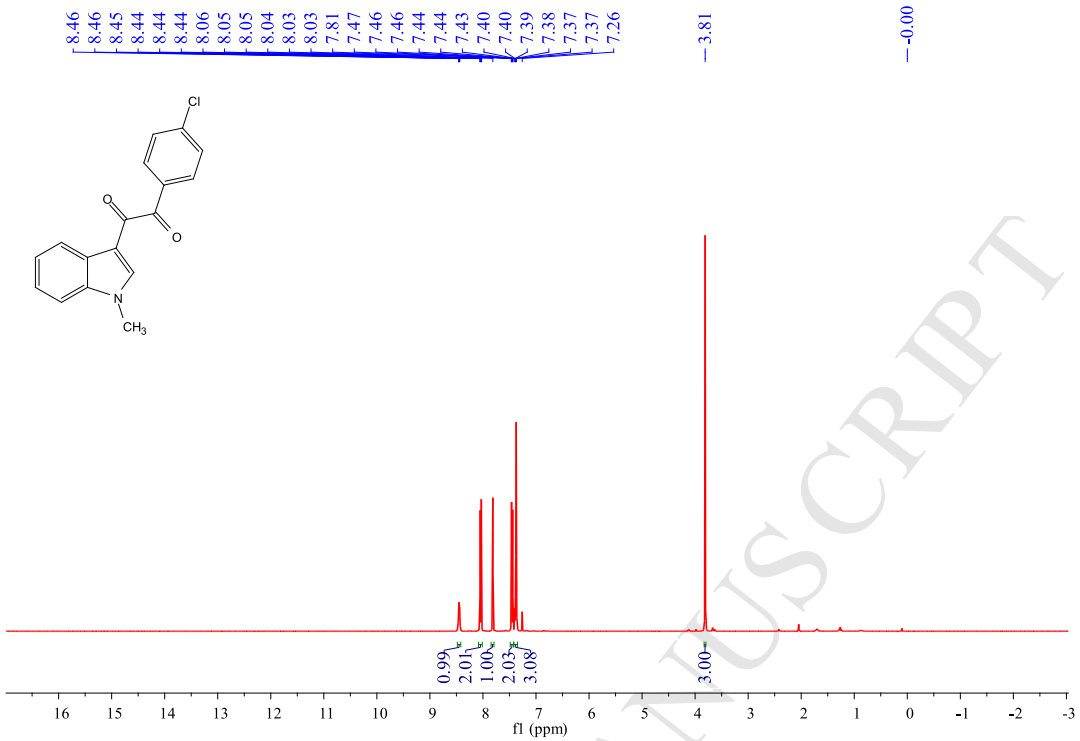
^{13}C NMR Spectrum of Compound 4d



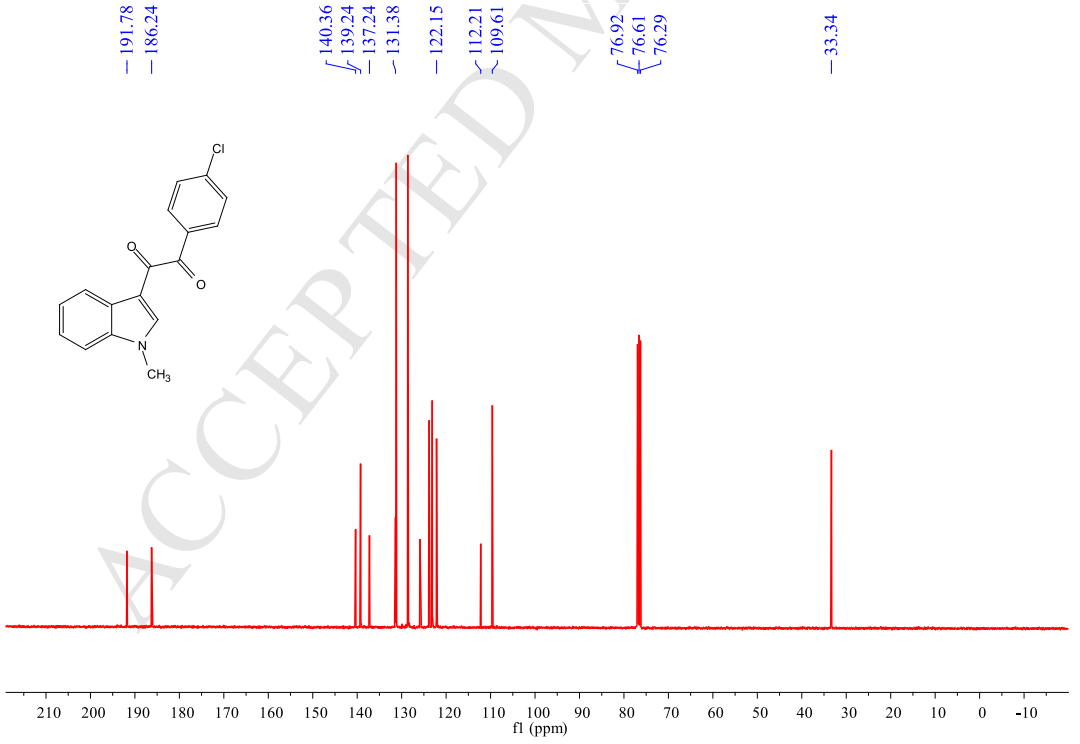
^{1}H NMR Spectrum of Compound 4e



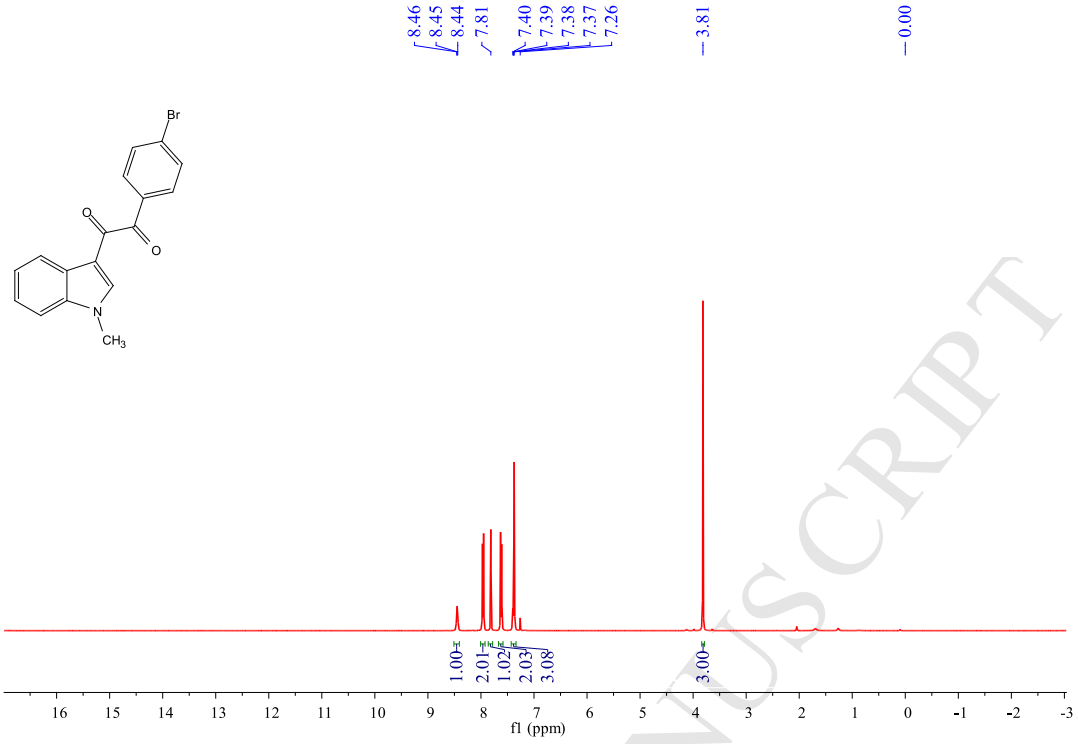
^{13}C NMR Spectrum of Compound 4e



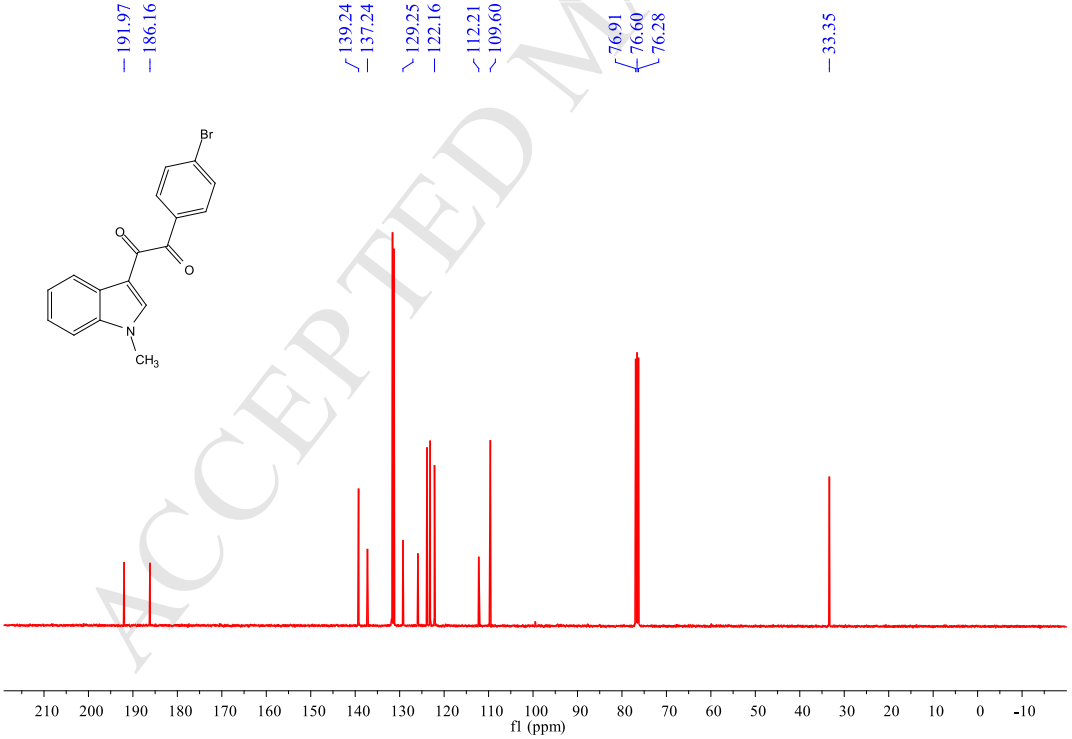
^{1}H NMR Spectrum of Compound 4f



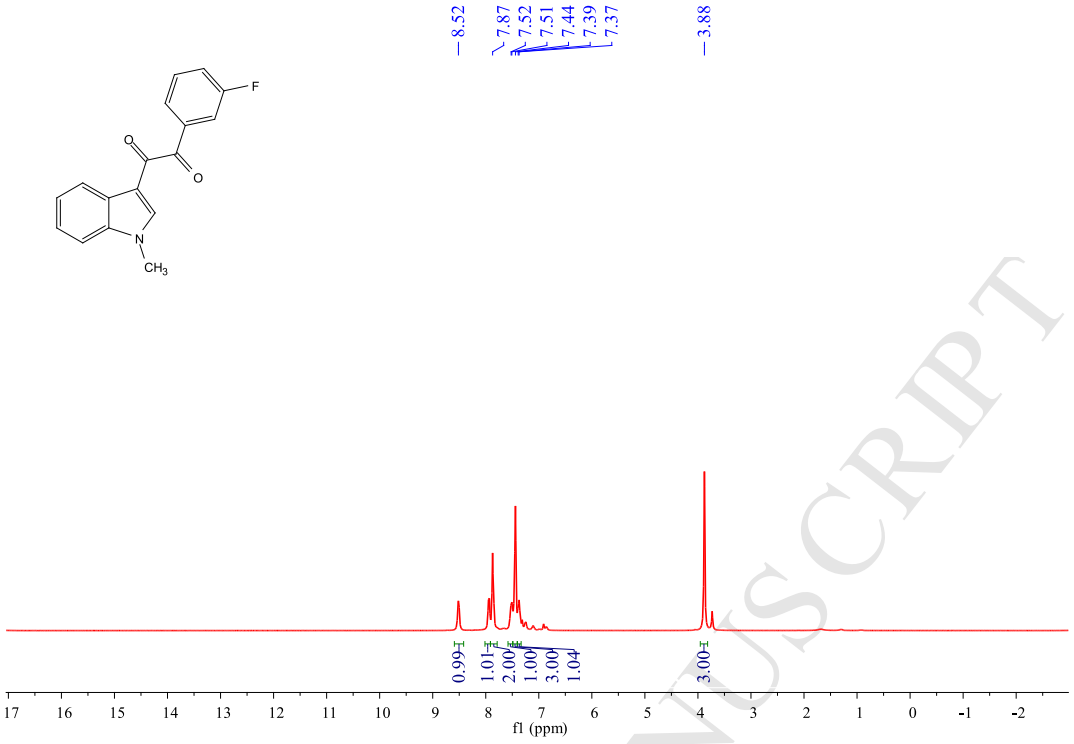
^{13}C NMR Spectrum of Compound 4f



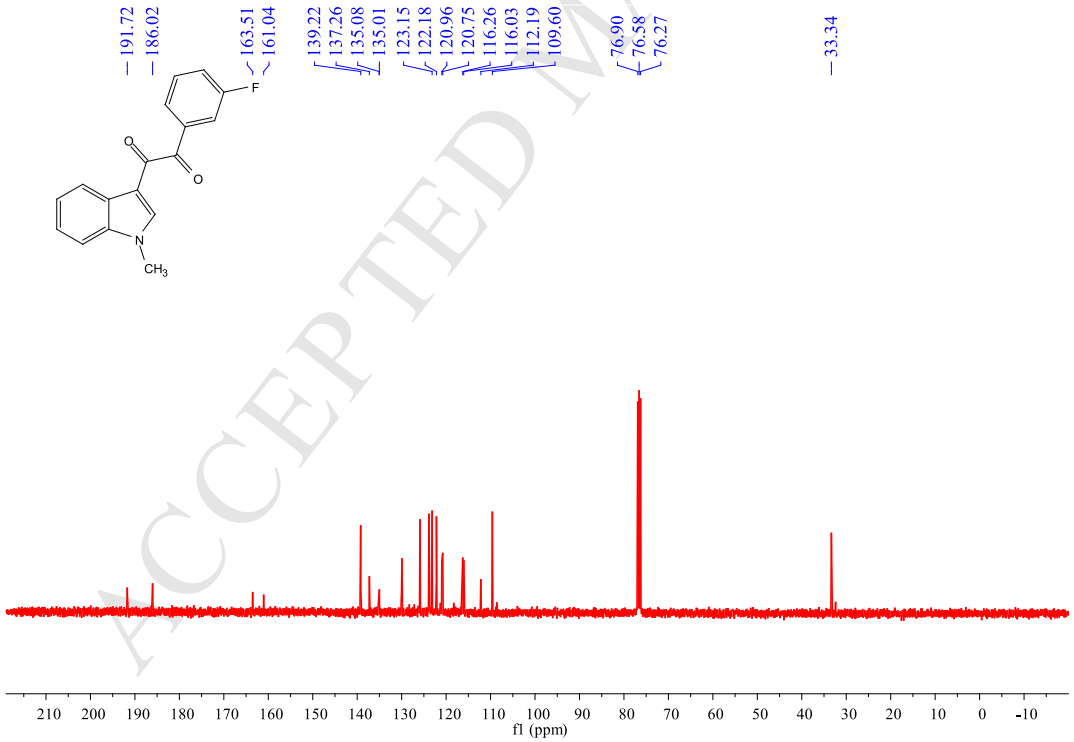
^{1}H NMR Spectrum of Compound 4g



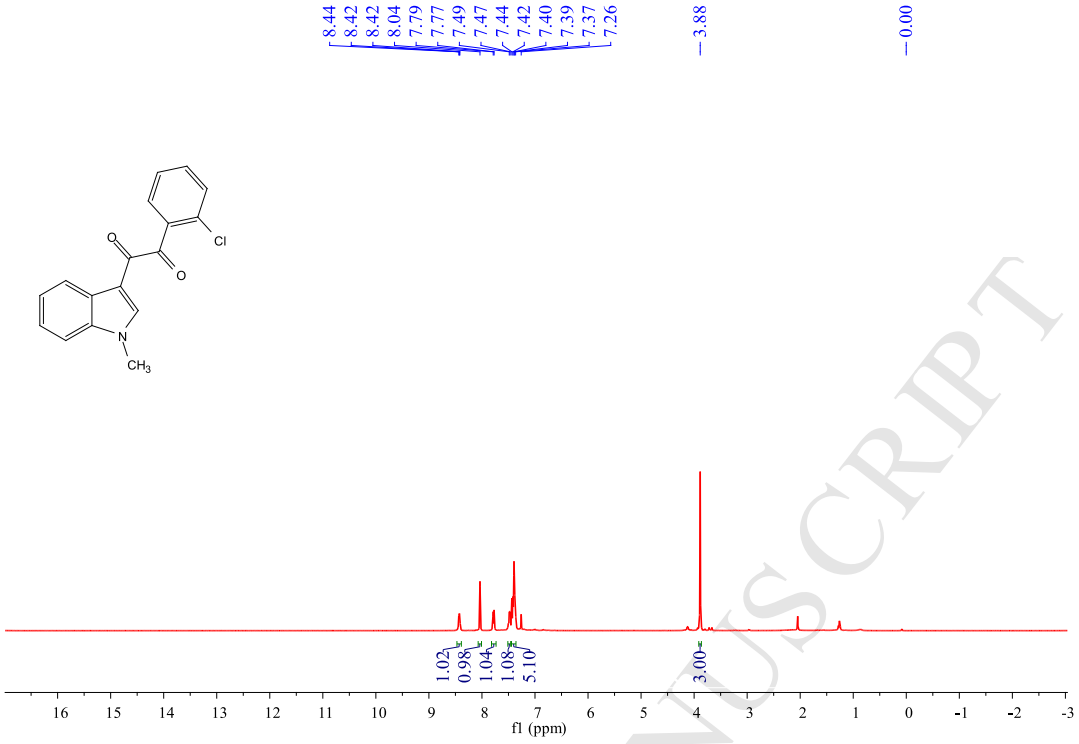
^{13}C NMR Spectrum of Compound 4g



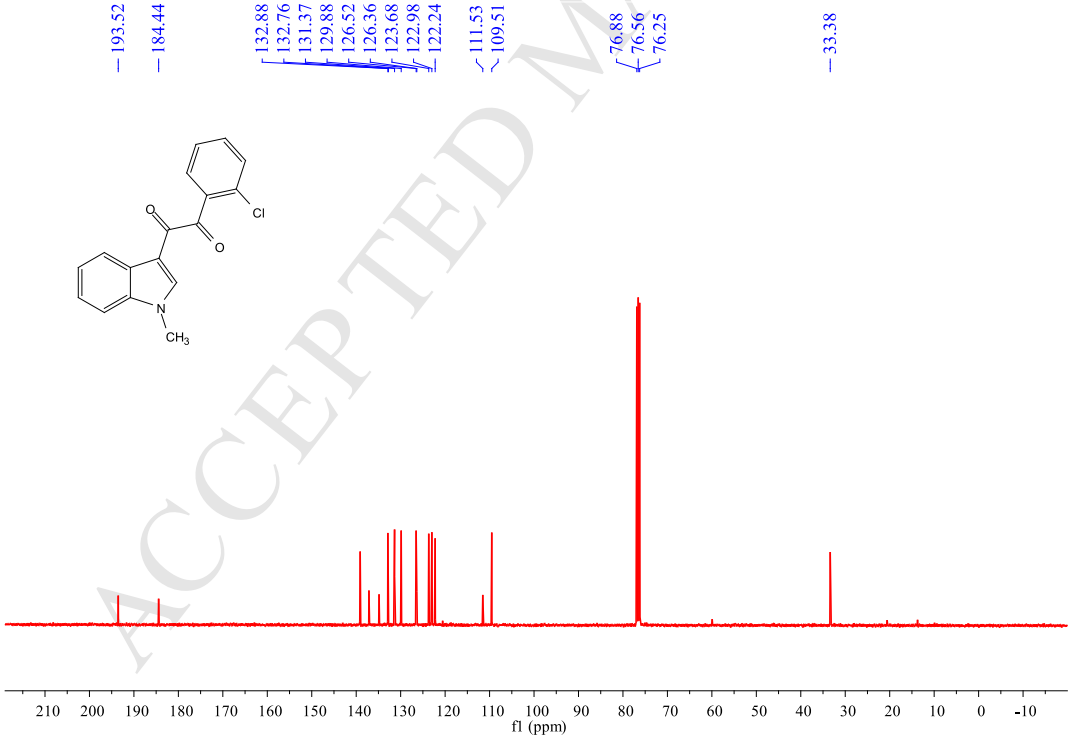
^{1}H NMR Spectrum of Compound 4h



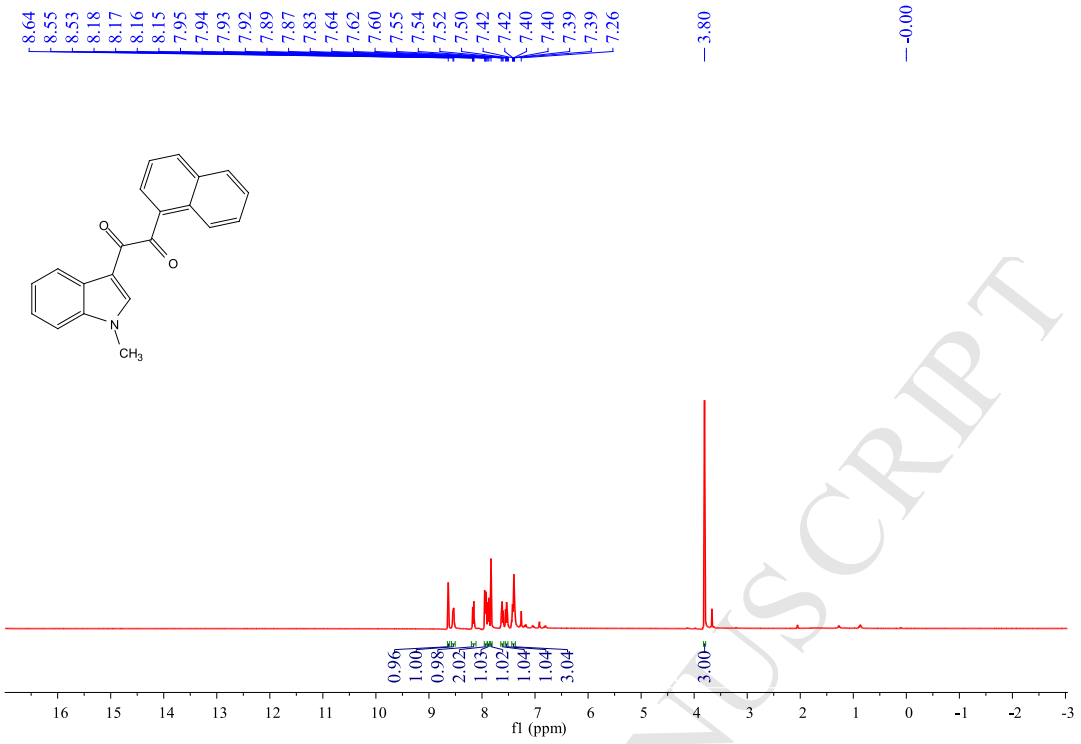
^{13}C NMR Spectrum of Compound 4h



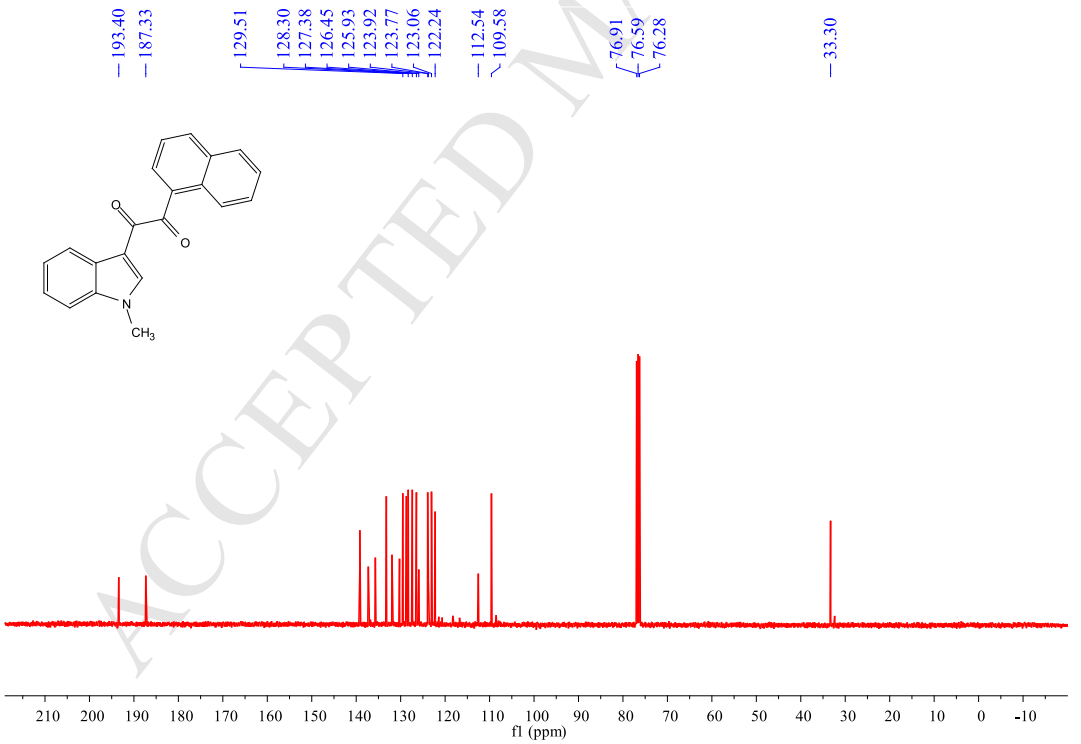
^{1}H NMR Spectrum of Compound 4i



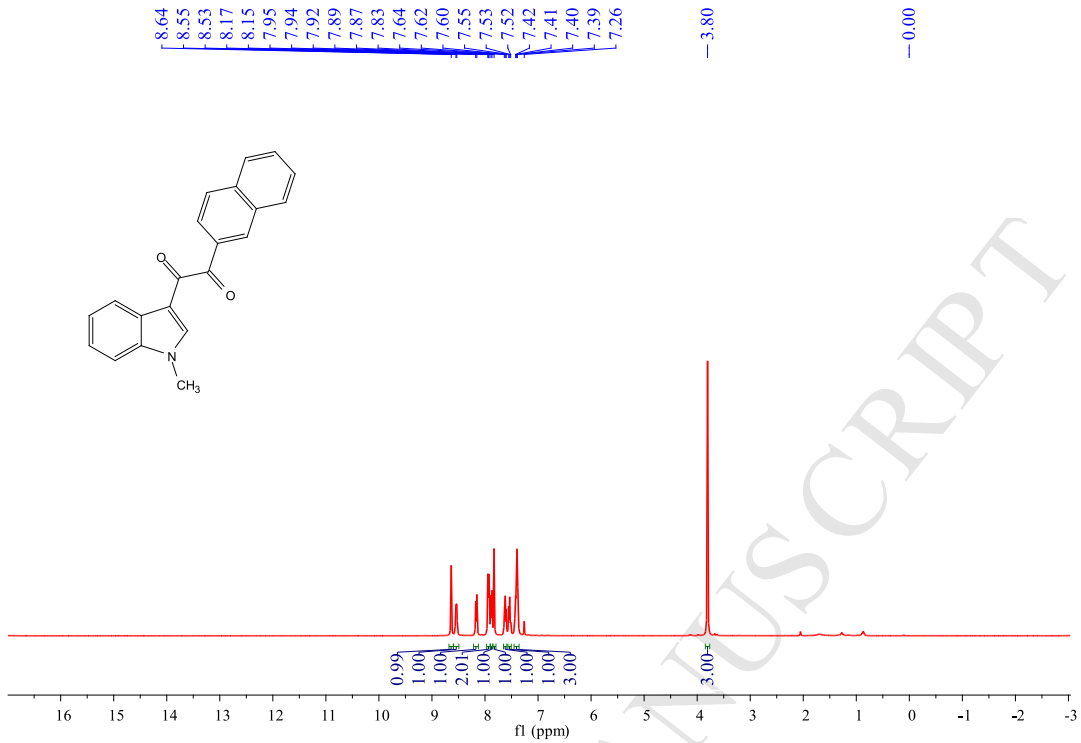
^{13}C NMR Spectrum of Compound 4i



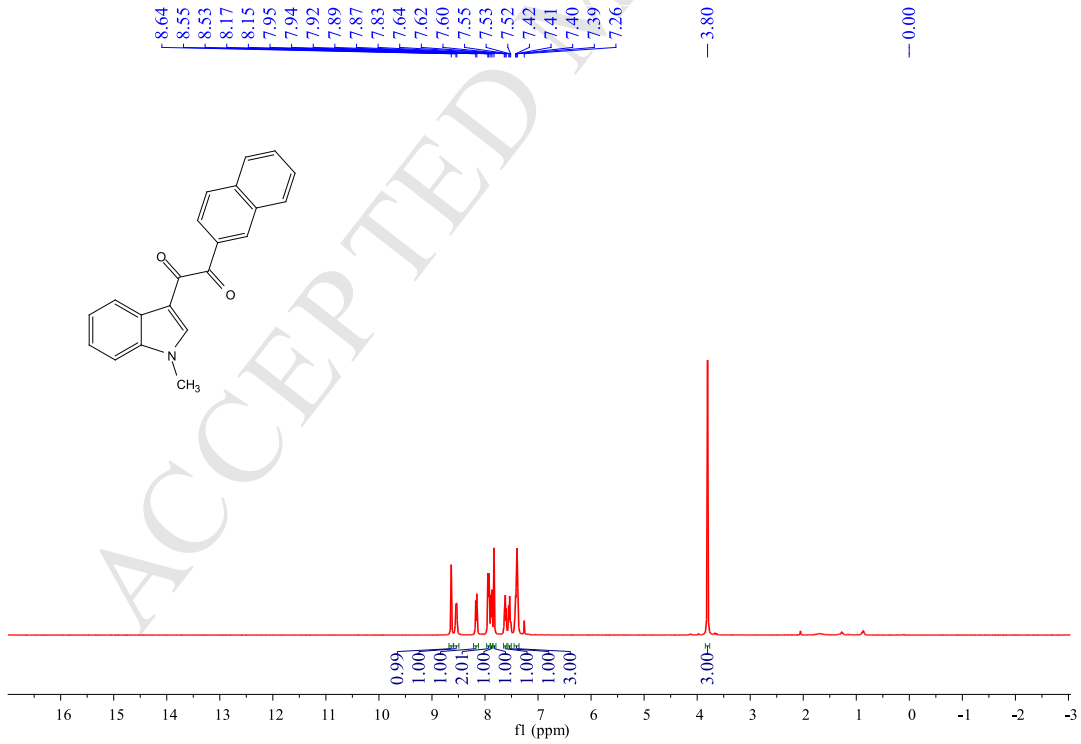
^{1}H NMR Spectrum of Compound 4j



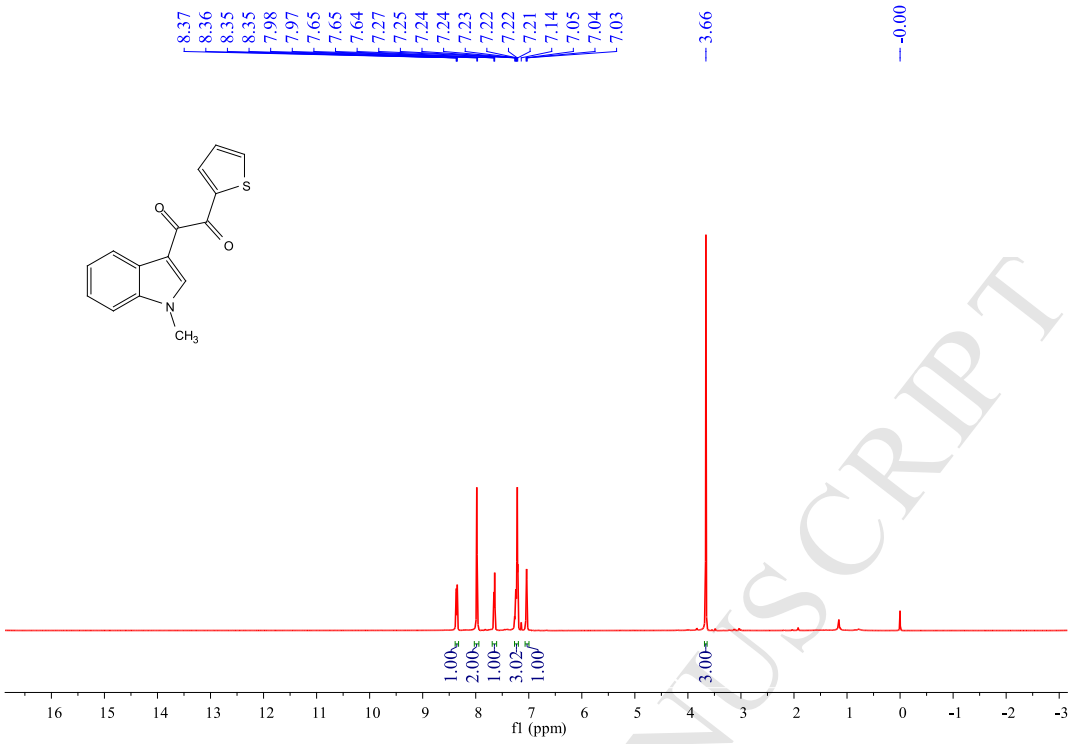
^{13}C NMR Spectrum of Compound 4j



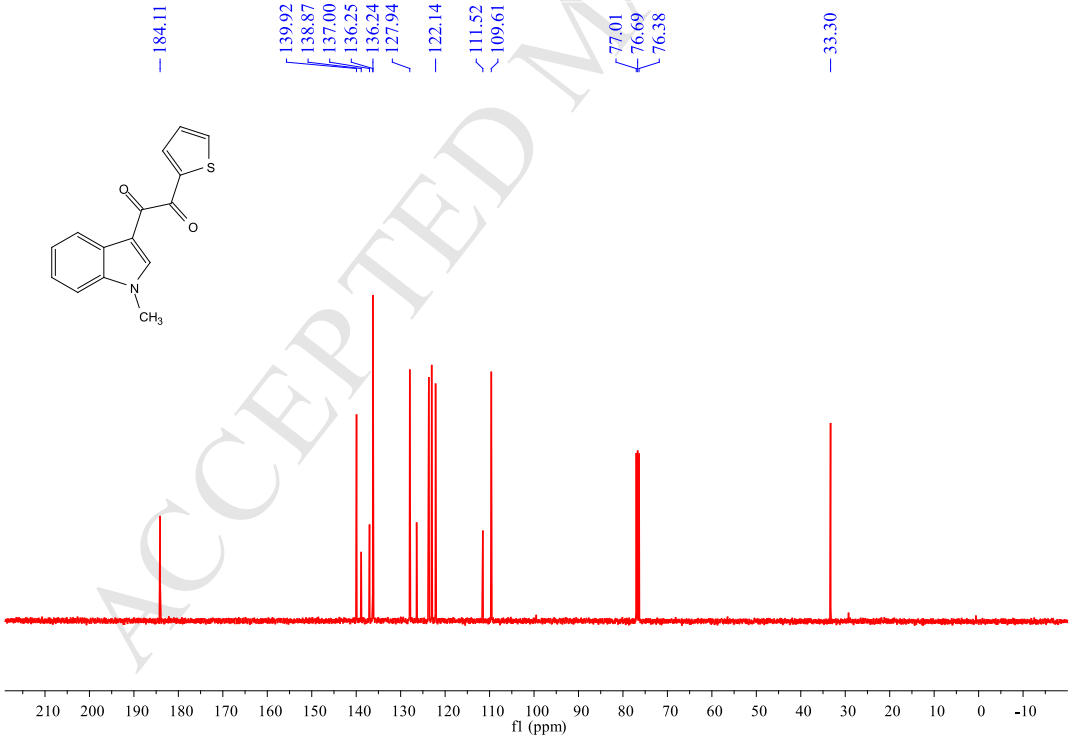
^{1}H NMR Spectrum of Compound 4k



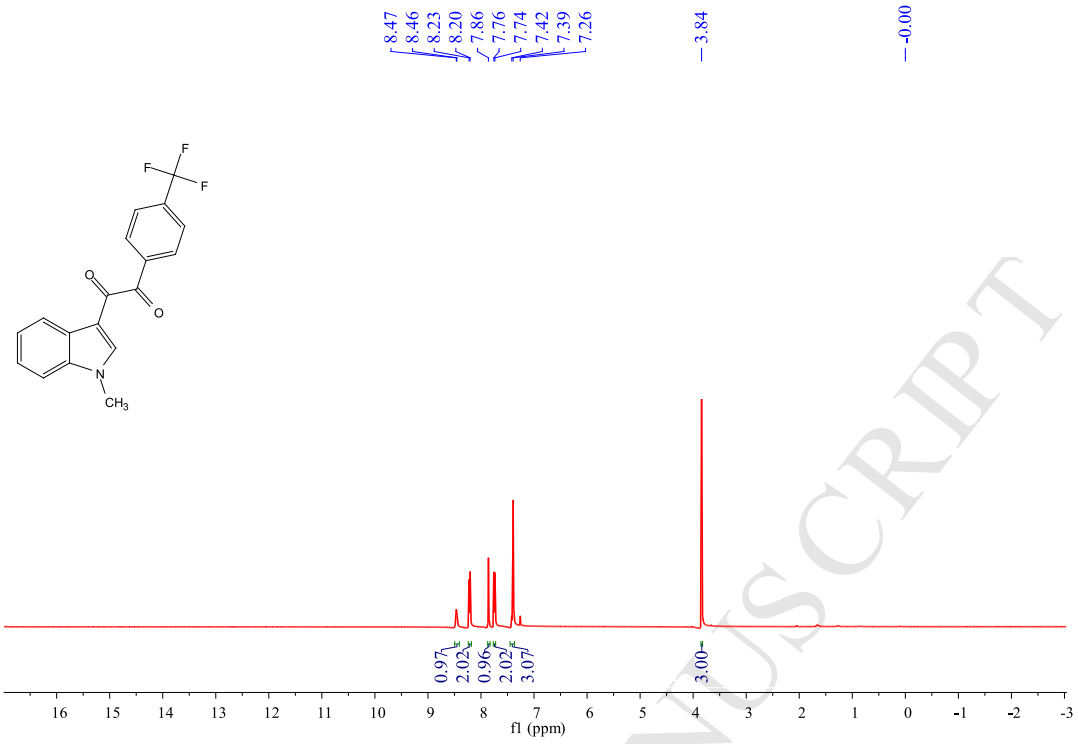
^{13}C NMR Spectrum of Compound 4k



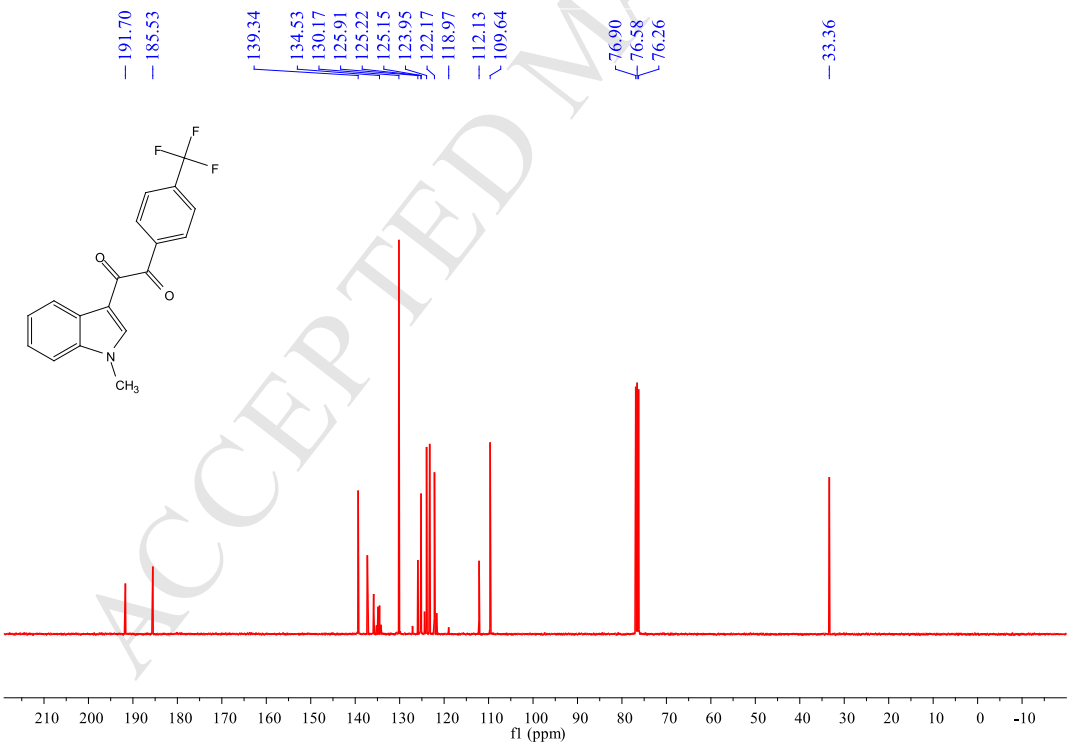
^{1}H NMR Spectrum of Compound 4l



^{13}C NMR Spectrum of Compound 4l



^{1}H NMR Spectrum of Compound 4m



^{13}C NMR Spectrum of Compound 4m