Supporting Information

TBAI-catalyzed C-H bond activation to construct $C_{(sp3)}$-O bond in water: the synthesis of indole-3-carboxylic-α-esters under metal-free conditions

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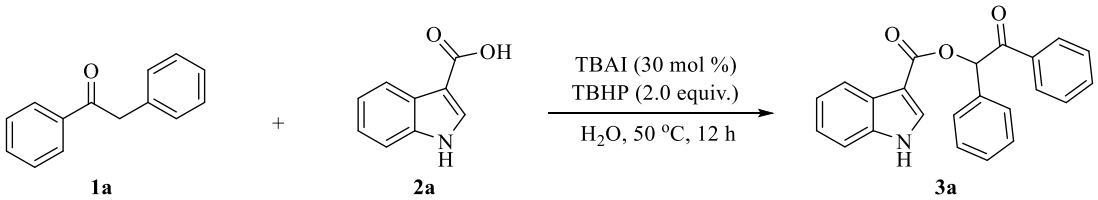
1. General methods

All reactions were performed in flame-dried glassware in an atmosphere, unless otherwise noted. Column chromatographic purification of products was carried out by using silica gel (200~300 mesh). The commercial reagents were used without further purification. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$/DMSO-*d*$_6$ (containing 0.03% TMS) solution. ^{1}H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. ^{1}H NMR spectra were recorded with DMSO-d_6 (δ = 2.50 ppm) as internal reference; ^{13}C NMR spectra were recorded with DMSO-d_6 (δ = 39.52 ppm) as internal reference. High-resolution mass spectra (HRMS) were performed on an electrospray ionization (ESI) Fourier transform mass spectrometer (FTMS, Thermo Q-Exactive Focus). Single crystal X-ray diffraction data were collected in an Rigaku XtaLAB Synergy.

2. Synthesis of products 3-17

Example (3a):

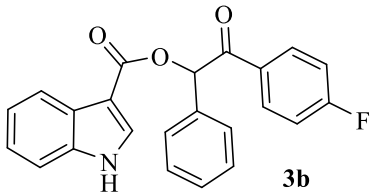


1a **2a** **3a**

Benzyl phenyl ketone **1a** (39.2 mg, 0.2 mmol), indole-3-carboxylic acid **2a** (48.3 mg, 0.3 mmol), TBAI (22.2 mg, 0.06 mmol), and H_2O (2 mL) were placed in an Schlenk tube, then TBHP (70% in water, 55.0 uL, 0.4 mmol) was added into the above mixture under air condition. After the completion of the addition, the reaction mixture was allowed to react at 50 °C (oil bath) for 12 h. Subsequently, the reaction mixture was cooled to room temperature, and then extracted with ethyl acetate. The organic layer was dried with anhydrous Na_2SO_4. After removal of the ethyl acetate under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 5:1-3:1) to afford 2-oxo-1,2-diphenylethyl-1*H*-indole-3-carboxylate **3a** (white solid, 58.8 mg, 83% yield).

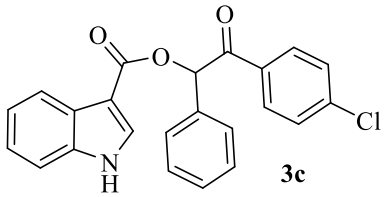
2-Oxo-1,2-diphenylethyl-1*H*-indole-3-carboxylate (**3a**). Following the general procedure, the crude product was purified using silica gel column chromatography

(petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3a** (white solid, 58.8 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.17-8.12 (m, 1H), 8.08-8.02 (m, 2H), 7.93-7.89 (m, 1H), 7.63-7.57 (m, 2H), 7.56-7.50 (m, 1H), 7.45-7.33 (m, 6H), 7.25-7.16 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 164.3, 136.1, 134.8, 134.2, 133.5, 132.0, 129.1, 129.1, 128.9, 128.7, 125.8, 123.2, 122.2, 121.5, 111.6, 107.6, 76.8. HRMS (ESI, m/z) calcd. for $C_{23}H_{17}NO_3Na$ $[M+Na]^+$ calc.: 378.1101; found: 378.1103.



3b

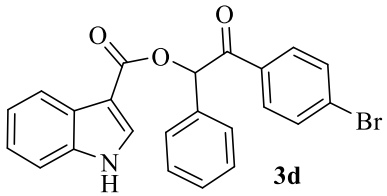
2-(4-Fluorophenyl)-2-oxo-1-phenylethyl-1*H*-indole-3-carboxylate (**3b**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3b** (brown solid, 108.0 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.15-8.10 (m, 1H), 8.09-8.04 (m, 2H), 7.88 (d, J = 3.2 Hz, 1H), 7.59-7.55 (m, 2H), 7.43-7.31 (m, 4H), 7.23-7.17 (m, 2H), 7.12-7.05 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 165.9 ($J_{C\text{-}F}$ = 254.0 Hz), 164.3, 136.1, 134.0, 132.1, 131.6 ($J_{C\text{-}F}$ = 10.0 Hz), 131.1 ($J_{C\text{-}F}$ = 3.0 Hz), 129.3, 129.2, 128.6, 125.8, 123.2, 122.2, 121.4, 115.9 ($J_{C\text{-}F}$ = 22.0 Hz), 111.7, 107.3, 76.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.7. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}FNO_3Na$ $[M+Na]^+$ calc.: 396.1006; found: 396.1003.



3c

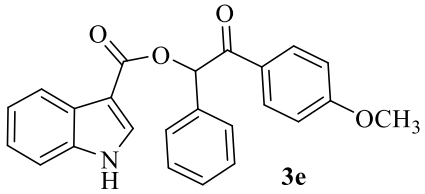
2-(4-Chlorophenyl)-2-oxo-1-phenylethyl-*1*H-indole-3-carboxylate (**3c**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3c** (yellow solid, 62.6 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.14 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 1H), 7.99-7.95 (m, 2H), 7.92 (d, J = 3.2 Hz, 1H), 7.59-7.56 (m, 2H), 7.41-7.35 (m, 6H), 7.24-7.21 (m, 2H), 7.09 (s, 1H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 193.7, 164.3, 139.9, 136.1, 133.9, 133.1, 132.0, 129.3, 129.2, 129.0, 128.6, 125.8, 123.3, 122.2, 121.4, 111.6, 107.5, 76.8. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}ClNO_3Na$ $[M+Na]^+$ calc.: 412.0711; found: 412.0716.



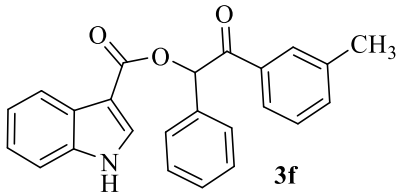
3d

2-(4-Bromophenyl)-2-oxo-1-phenylethyl-*1*H-indole-3-carboxylate (**3d**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3d** (brown solid, 104.1 mg, 60% yield); ^1H NMR (400 MHz, DMSO-d_6) δ 12.09 (s, 1H), 8.19 (d, *J* = 3.2 Hz, 1H), 8.08-8.04 (m, 2H), 7.94 (d, *J* = 7.2 Hz, 1H), 7.77-7.73 (m, 2H), 7.69-7.65 (m, 2H), 7.53-7.49 (m, 1H), 7.47-7.36 (m, 3H), 7.32 (s, 1H), 7.24-7.14 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.8, 163.7, 136.5, 133.8, 133.5, 133.2, 132.1, 130.7, 129.2, 129.1, 128.7, 128.1, 125.6, 122.6, 121.1, 120.3, 112.6, 105.5, 76.0. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}BrNO_3Na$ $[M+Na]^+$ calc.: 456.0206; found: 456.0209.



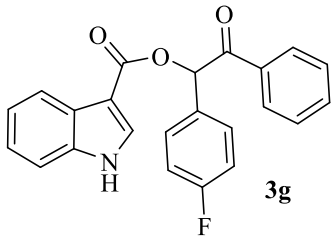
3e

2-(4-Methoxyphenyl)-2-oxo-1-phenylethyl-1*H*-indole-3-carboxylate (**3e**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3e** (brown solid, 55.8 mg, 36% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.19-8.16 (m, 1H), 8.07-8.02 (m, 2H), 7.95 (d, *J* = 2.8 Hz, 1H), 7.62-7.58 (m, 2H), 7.42-7.34 (m, 4H), 7.25-7.20 (m, 2H), 7.15 (s, 1H), 6.92-6.88 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 164.2, 163.8, 136.1, 134.8, 131.9, 131.3, 129.0, 129.0, 128.6, 127.7, 125.9, 123.2, 122.2, 121.6, 113.9, 111.5, 107.8, 76.5. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_4Na$ $[M+Na]^+$ calc.: 408.1206; found: 408.1210.



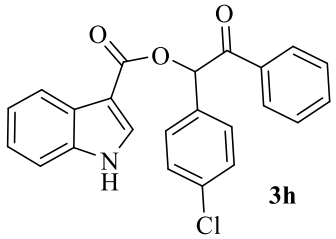
3f

2-Oxo-1-phenyl-2-(*m*-tolyl)ethyl-1*H*-indole-3-carboxylate (**3f**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3f** (brown solid, 85.8, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.14-8.11 (m, 1H), 7.87-7.83 (m, 3H), 7.60-7.56(m, 2H), 7.39- 7.30 (m, 6H), 7.20-7.16 (m, 3H), 2.35 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 164.4, 138.6, 136.1, 134.8, 134.4, 134.2, 132.2, 129.4, 129.1, 129.1, 128.6, 128.5, 126.1, 125.8, 123.1, 122.1, 121.3, 111.7, 107.3, 76.7, 21.3. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_3Na$ $[M+Na]^+$ calc.: 392.1257; found: 392.1260.



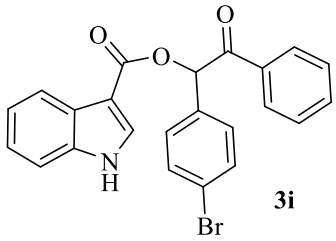
3g

1-(4-Fluorophenyl)-2-oxo-2-phenylethyl-1*H*-indole-3-carboxylate (**3g**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3g** (white solid, 118.6 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.14-8.10 (m, 1H), 8.04-8.01 (m, 2H), 7.87 (d, J = 2.8 Hz, 1H), 7.59-7.52 (m, 3H), 7.46-7.41 (m, 2H), 7.36-7.33 (m, 1H), 7.24-7.19 (m, 2H), 7.16 (s, 1H), 7.10-7.05 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 164.2, 163.1 ($J_{C\text{-}F}$ = 247.0 Hz), 136.1, 134.6, 133.7, 132.1, 130.6 ($J_{C\text{-}F}$ = 9.0 Hz), 130.1 ($J_{C\text{-}F}$ = 3.0 Hz), 128.9, 128.8, 125.8, 123.2, 122.2, 121.3, 116.2 ($J_{C\text{-}F}$ = 22.0 Hz), 111.7, 107.3, 75.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.8. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}FNO_3Na$ $[M+Na]^+$ calc.: 396.1006; found: 396.1009.



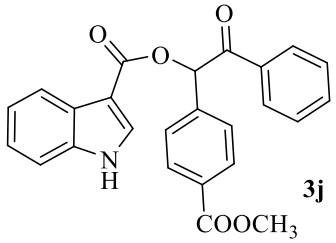
3h

1-(4-Chlorophenyl)-2-oxo-2-phenylethyl-1*H*-indole-3-carboxylate (**3h**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3h** (white solid, 57.9 mg, 37% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.10 (s, 1H), 8.20 (d, *J* = 3.2 Hz, 1H), 8.15-8.12 (m, 2H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.74-7.69 (m, 2H), 7.68-7.62 (m, 1H), 7.60-7.50 (m, 5H), 7.39 (s, 1H), 7.24-7.15 (m, 2H).^{13}C NMR (100 MHz, DMSO-d_6) δ 194.2, 163.5, 136.5, 134.1, 134.0, 133.9, 133.4, 133.2, 130.5, 129.1, 129.0, 128.7, 125.6, 122.6, 121.5, 120.3, 112.5, 105.4, 75.2. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}ClNO_3Na$ $[M+Na]^+$ calc.: 412.0711; found: 412.0716.



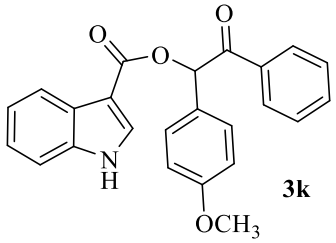
3i

1-(4-Bromophenyl)-2-oxo-2-phenylethyl-1*H*-indole-3-carboxylate (**3i**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3i** (brown solid, 57.2 mg, 33% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.15-8.11 (m, 1H), 8.04-8.00 (m, 2H), 7.91 (d, *J* = 3.2 Hz, 1H), 7.56-7.50 (m, 3H), 7.48-7.41 (m, 4H), 7.39-7.35 (m, 1H), 7.25-7.22 (m, 2H), 7.13 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 164.1, 136.1, 134.6, 133.7, 133.3, 132.3, 132.1, 130.2, 128.9, 128.8, 125.8, 123.5, 123.3, 122.3, 121.4, 111.6, 107.4, 75.9. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}BrNO_3Na$ $[M+Na]^+$ calc.: 456.0206; found: 456.0208.



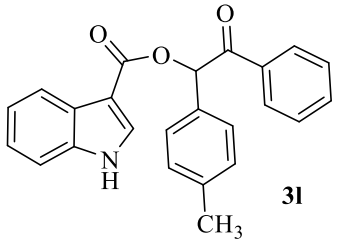
3j

1-(4-(Methoxycarbonyl)phenyl)-2-oxo-2-phenylethyl-1*H*-indole-3-carboxylate (**3j**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3j** (brown solid, 78.9 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.17-8.13 (m, 1H), 8.07 -8.00 (m, 4H), 7.97 (d, *J* = 2.8 Hz, 1H), 7.69-7.66 (m, 2H), 7.57-7.52 (m, 1H), 7.46-7.38 (m, 3H), 7.25-7.23 (m, 2H), 7.20 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 166.5, 164.0, 139.1, 136.1, 134.7, 133.7, 132.0, 130.7, 130.3, 128.9, 128.8, 128.5, 125.8, 123.4, 122.3, 121.4, 111.6, 107.5, 76.2, 52.3. HRMS (ESI, m/z) calcd. for $C_{25}H_{19}NO_5Na$ $[M+Na]^+$ calc.: 436.1155; found: 436.1160.



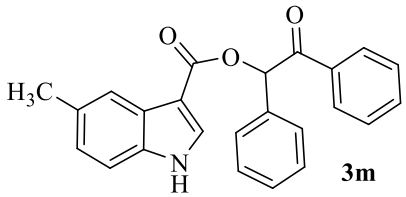
3k

1-(4-Methoxyphenyl)-2-oxo-2-phenylethyl-1*H*-indole-3-carboxylate (**3k**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3k** (brown solid, 81.2 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.14-8.11 (m, 1H), 8.05-8.01 (m, 2H), 7.85 (d, *J* = 2.8 Hz, 1H), 7.54-7.48 (m, 3H), 7.44-7.39 (m, 2H), 7.35-7.32 (m, 1H), 7.22-7.17 (m, 2H), 7.13 (s, 1H), 6.93-6.88 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 164.5, 160.2, 136.1, 134.8, 133.5, 132.1, 130.2, 128.9, 128.7, 126.1, 125.8, 123.1, 122.1, 121.4, 114.5, 111.7, 107.5, 76.4, 55.3. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_4Na$ $[M+Na]^+$ calc.: 408.1206; found: 408.1209.



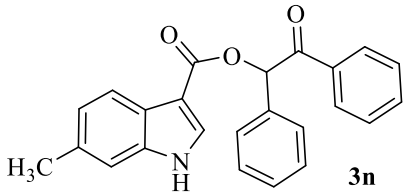
3l

2-Oxo-2-phenyl-1-(*p*-tolyl)ethyl-1*H*-indole-3-carboxylate (**3l**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3l** (brown solid, 99.0 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.14-8.11 (m, 1H), 8.06-8.02 (m, 2H), 7.84 (d, J = 3.2 Hz, 1H), 7.54-7.46(m, 3H), 7.44-7.39 (m, 2H), 7.34-7.31 (m, 1H), 7.21-7.17(m, 4H), 7.14 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 164.4, 139.2, 136.1, 134.8, 133.5, 132.1, 131.1, 129.8, 128.9, 128.7, 125.8, 123.1, 122.1, 121.4, 111.7, 107.4, 76.7, 21.2. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_3Na$ $[M+Na]^+$ calc.: 392.1257; found: 392.1263.



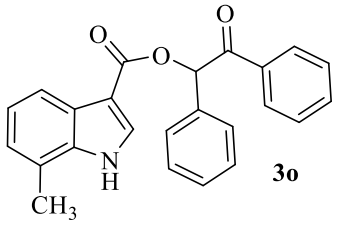
3m

2-Oxo-1,2-diphenylethyl-5-methyl-1*H*-indole-3-carboxylate (**3m**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3m** (brown solid, 104.8 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.07-8.03 (m, 2H), 7.96 (s, 1H), 7.90 (d, J = 3.2 Hz, 1H), 7.62-7.58 (m, 2H), 7.56-7.51 (m, 1H), 7.46-7.35 (m, 5H), 7.26-7.25 (m, 1H), 7.15 (s, 1H), 7.05 (dd, J_1= 8.6 Hz, J_2= 1.6 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 164.3, 134.9, 134.4, 134.3, 133.5, 131.8, 131.7, 129.1, 129.0, 128.9, 128.7, 128.7, 126.2, 124.8, 121.2, 111.2, 107.0, 76.7, 21.5. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_3Na$ $[M+Na]^+$ calc.: 392.1257; found: 392.1256.



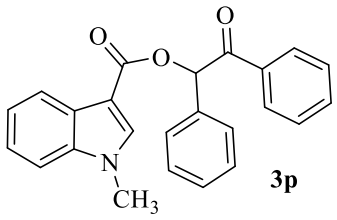
3n

2-Oxo-1,2-diphenylethyl-6-methyl-1*H*-indole-3-carboxylate (**3n**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3n** (brown solid, 88.1 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.06-8.00 (m, 3H), 7.86 (d, J = 3.2 Hz, 1H), 7.61-7.57 (m, 2H), 7.55-7.50 (m, 1H), 7.45-7.35 (m, 5H), 7.16-7.15 (m, 2H), 7.06 (dd, J_1 = 8.0 Hz, J_2 =1.2 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 164.3, 136.5, 134.9, 133.4, 133.2, 131.4, 129.1, 129.1, 128.9, 128.7, 128.7, 124.0, 123.7, 121.1, 111.4, 107.6, 76.7, 21.6. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_3Na$ $[M+Na]^+$ calc.: 392.1257; found: 392.1255.



3o

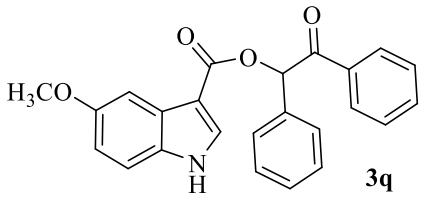
2-Oxo-1,2-diphenylethyl-7-methyl-1*H*-indole-3-carboxylate (**3o**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3o** (white solid, 84.8 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.06-8.02 (m, 2H), 7.96 (d, J = 7.2 Hz, 1H), 7.91 (d, J =2.8 Hz, 1H), 7.61-7.57 (m, 2H), 7.55-7.49 (m, 1H), 7.44-7.34 (m, 5H), 7.17 (s, 1H), 7.12-7-07 (m, 1H), 6.97 (d, J = 7.2 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 164.4, 135.7, 134.9, 134.2, 133.5, 131.7, 129.1, 129.1, 128.9, 128.7, 125.4, 123.7, 122.3, 120.8, 119.0, 107.8, 76.8, 16.4. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_3Na$ $[M+Na]^+$ calc.: 392.1257; found: 392.1259.



3p

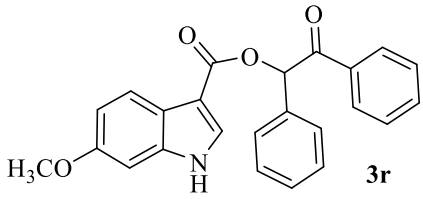
2-Oxo-1,2-diphenylethyl-1-methyl-1*H*-indole-3-carboxylate (**3p**). Following the general procedure, the crude product was purified using silica gel column

chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3p** (brown solid, 101.1 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.17 (m, 1H), 8.05-8.01(m, 2H), 7.87 (s, 1H), 7.62-7.59 (m, 2H), 7.54-7.48 (m, 1H), 7.43-7.37 (m, 4H), 7.37-7.31 (m, 2H),7.35-7.23 (m, 2H) 7.16 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 164.0, 137.2, 135.9, 135.0, 134.4, 133.3, 129.0, 128.9, 128.7, 128.6, 126.8, 122.9, 122.1, 121.7, 109.8, 105.9, 76.7, 33.4. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_3Na$ $[M+Na]^+$ calc.: 392.1257; found: 392.1262.



3q

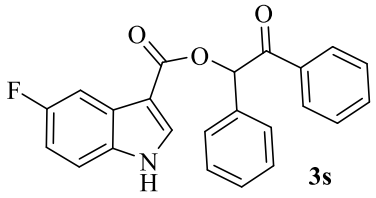
2-Oxo-1,2-diphenylethyl-5-methoxy-1*H*-indole-3-carboxylate (**3q**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3q** (brown solid, 86.7 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.06-8,03 (m, 2H), 7.84 (d, J = 3.2 Hz, 1H), 7.61-7.58 (m, 3H), 7.56-7.50 (m, 1H), 7.45-7.34 (m, 5H), 7.22 (d, J = 8.8 Hz, 1H), 7.14 (s, 1H), 6.83 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 164.3, 155.8, 134.8, 134.2, 133.6, 132.1, 130.9, 129.2, 129.1, 128.9, 128.7, 128.7, 126.7, 113.9, 112.4, 107.2, 102.4, 76.7, 55.5. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_4Na$ $[M+Na]^+$ calc.: 408.1206; found: 408.1209.



3r

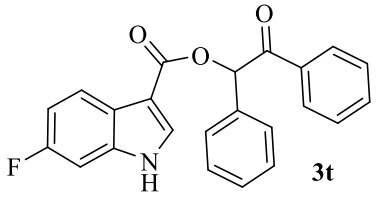
2-Oxo-1,2-diphenylethyl-6-methoxy-1*H*-indole-3-carboxylate (**3r**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3r** (brown solid, 84.5 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.05-8.01 (m, 2H), 7.95 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 2.8 Hz, 1H), 7.59-7.56 (m, 2H), 7.53-7.48 (m, 1H), 7.43-7.33 (m, 5H), 7.14 (s, 1H), 6.83 (dd, J_1 = 8.8 Hz, J_2 =

2.0 Hz, 1H), 6.77 (d, J = 2.4 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 164.4, 156.9, 137.0, 134.8, 134.2, 133.6, 131.1, 129.1, 129.1, 128.9, 128.7, 128.6, 121.9, 119.9, 111.9, 107.3, 95.0, 76.7, 55.5. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_4Na$ $[M+Na]^+$ calc.: 408.1206; found: 468.1209.



3s

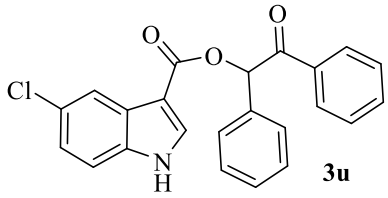
2-Oxo-1,2-diphenylethyl-5-fluoro-1*H*-indole-3-carboxylate (**3s**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3s** (white solid, 99.2 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.06-8.02 (m, 2H), 7.86 (d, J = 3.2 Hz, 1H), 7.69 (dd, J_1 = 9.6 Hz, J_2 = 2.4 Hz, 1H), 7.59-7.51 (m, 3H), 7.46-7.36 (m, 5H), 7.26-7.22 (m, 1H), 7.15 (s, 1H), 6.94-6-88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 164.0, 159.2 ($J_{C\text{-}F}$ = 236.0 Hz), 134.7, 134.0, 133.7, 133.2, 132.5, 129.3, 129.2, 128.9, 128.8, 128.7, 126.5 ($J_{C\text{-}F}$ = 11.0 Hz), 112.5 ($J_{C\text{-}F}$ = 10.0 Hz), 111.7 ($J_{C\text{-}F}$ = 26.0 Hz), 107.6 ($J_{C\text{-}F}$ = 4.0 Hz), 106.7 ($J_{C\text{-}F}$ = 25.0 Hz), 76.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.1. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}FNO_3Na$ $[M+Na]^+$ calc.: 396.1006; found: 396.1011.



3t

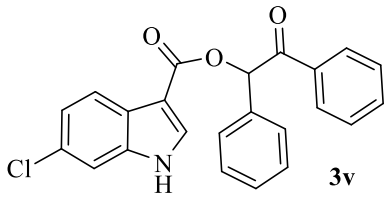
2-Oxo-1,2-diphenylethyl-6-fluoro-1*H*-indole-3-carboxylate (**3t**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3t** (brown solid, 123.9 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.06-8.03 (m, 2H), 7.96 (dd, J_1 = 8.8 Hz, J_2 = 5.6 Hz, 1H), 7.79 (d, J = 3.2 Hz, 1H), 7.59-7.56 (m, 2H), 7.55-7.52 (m, 1H), 7.46-7.36 (m, 5H), 7.16 (s, 1H), 7.00 (dd, J_1 = 9.2 Hz, J_2 = 2.0 Hz, 1H), 6.94-6.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 164.1, 160.2 ($J_{C\text{-}F}$ = 238.0 Hz), 136.2 ($J_{C\text{-}F}$ = 12.0 Hz), 134.7, 133.9, 133.7, 132.4 ($J_{C\text{-}F}$

= 3.0 Hz), 129.3, 129.2, 128.9, 128.8, 128.7, 122.2 ($J_{C\text{-}F}$ = 9.0 Hz), 122.1 ($J_{C\text{-}F}$ = 1.0 Hz), 110.7 ($J_{C\text{-}F}$ = 24.0 Hz), 107.4, 98.1 ($J_{C\text{-}F}$ = 26.0 Hz), 76.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.3. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}FNO_3Na$ $[M+Na]^+$ calc.: 396.1006; found: 396.1011.



3u

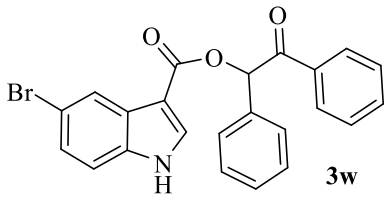
2-Oxo-1,2-diphenylethyl-5-chloro-1*H*-indole-3-carboxylate (**3u**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3u** (white solid, 105.1 mg, 67% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.27 (s, 1H), 8.27 (s, 1H), 8.15-8.11 (m, 2H), 7.91 (d, J = 2.0 Hz, 1H), 7.71-7.67 (m, 2H),7.66-7.62 (m, 1H), 7.55 (s, 1H), 7.53-7.50 (m, 2H), 7.47-7.38 (m, 3H), 7.36 (s, 1H), 7.24 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.2, 163.3, 135.0, 134.8, 134.2, 134.0, 133.9, 129.2, 129.1, 129.0, 128.8, 128.7, 126.8, 126.3, 122.7, 119.6, 114.3, 105.4, 76.3. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}ClNO_3Na$ $[M+Na]^+$ calc.: 412.0711; found: 412.0716.



3v

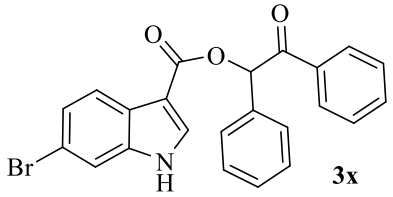
2-Oxo-1,2-diphenylethyl-6-chloro-1*H*-indole-3-carboxylate (**3v**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3v** (brown solid, 73.2 mg, 47% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.17 (s, 1H), 8.23 (d, J = 2.8 Hz, 1H), 8.14-8.10 (m, 2H), 7.92 (d, J = 8.4 Hz, 1H), 7.70-7.67(m, 2H), 7.66-7.61 (m, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.55-7.50 (m, 2H), 7.46-7.37 (m, 3H), 7.34 (s, 1H), 7.21 (dd, J_1 =8.4 Hz J_2 =2.0 Hz 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.2, 163.3, 136.9, 134.3, 134.2, 134.0, 133.8, 129.1, 129.0, 128.9, 128.7, 128.6, 127.2, 124.4, 121.9, 121.6, 112.2, 105.8, 76.3. HRMS (ESI, m/z) calcd. for

$C_{23}H_{16}ClNO_3Na$ $[M+Na]^+$ calc.: 412.0711; found: 412.0716.



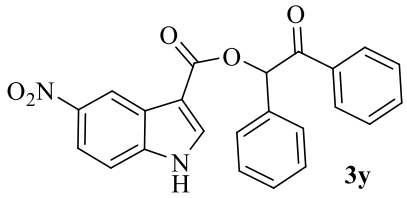
3w

2-Oxo-1,2-diphenylethyl-5-bromo-1*H*-indole-3-carboxylate (**3w**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3w** (white solid, 83.0 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.21 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 3.2 Hz, 1H), 7.61-7.54 (m, 3H), 7.47-7.36 (m, 5H), 7.31-7.28 (m, 1H), 7.24-7.20 (m, 1H), 7.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 163.8, 134.7, 133.9, 133.7, 132.6, 129.3, 129.2, 129.0, 128.8, 128.7, 127.4, 126.2, 124.1, 115.7, 113.0, 107.0, 76.9. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}BrNO_3Na$ $[M+Na]^+$ calc.: 456.0206; found: 456.0202.



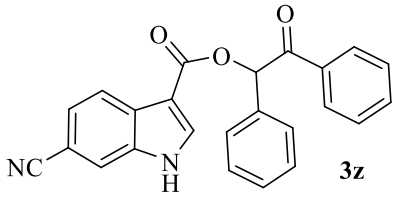
3x

2-Oxo-1,2-diphenylethyl-6-bromo-1*H*-indole-3-carboxylate (**3x**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3x** (brown solid, 61.2 mg, 35% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.17 (s, 1H), 8.21 (d, *J* = 2.4 Hz, 1H), 8.14-8.10 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.71-7.66 (m, 3H), 7.65-7.62 (m, 1H), 7.55-7.50 (m, 2H), 7.46-7.37 (m, 3H), 7.34-7.31 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.2, 163.3, 137.4, 134.2, 134.2, 134.0, 133.8, 129.0, 128.9, 128.7, 128.7, 124.7, 124.5, 122.0, 115.2, 105.8, 76.3. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}BrNO_3Na$ $[M+Na]^+$ calc.: 456.0206; found: 456.0211.



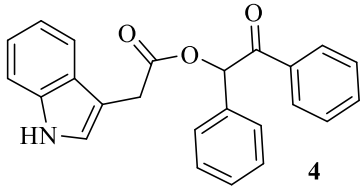
3y

2-Oxo-1,2-diphenylethyl-5-nitro-1*H*-indole-3-carboxylate (**3y**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3y** (yellow solid, 40.8 mg, 25% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.71 (s, 1H), 8.86 (d, *J* = 2.0 Hz, 1H), 8.48 (d, *J* = 2.0 Hz, 1H), 8.16-8.10 (m, 3H), 7.74-7.69 (m, 3H), 7.68-7.63 (m, 1H), 7.57-7.51 (m, 2H), 7.48-7.40 (m, 4H).^{13}C NMR (100 MHz, DMSO-d_6) δ 194.1, 162.9, 142.6, 139.7, 137.0, 134.1, 134.0, 133.8, 129.3, 129.1, 129.0, 128.8, 128.7, 125.1, 118.0, 116.9, 113.4, 107.7, 76.6. HRMS (ESI, m/z) calcd. for $C_{23}H_{16}N_2O_5Na$ $[M+Na]^+$ calc.: 423.0951; found: 423.0956.



3z

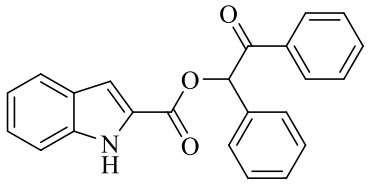
2-Oxo-1,2-diphenylethyl-6-cyano-1*H*-indole-3-carboxylate (**3z**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **3z** (white solid, 55.4 mg, 36% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.08-8.05 (m, 2H), 7.98-7.94 (m, 2H), 7.67-7.65 (m, 1H), 7.61-7.56 (m, 3H), 7.49-7.40 (m, 5H), 7.30 (dd, J_1 = 8.0 Hz J_2 =1.2 Hz, 1H), 7.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 163.4, 135.0, 134.9, 134.5, 134.1, 133.5, 129.6, 129.4, 129.0, 128.9, 128.7, 124.8, 122.0, 119.9, 116.7, 107.9, 105.8, 77.2. HRMS (ESI, m/z) calcd. for $C_{24}H_{16}N_2O_3Na$ $[M+Na]^+$ calc.: 403.1053; found: 403.1059.



4

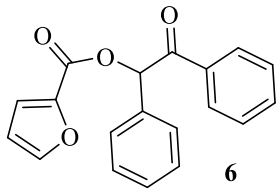
2-Oxo-1,2-diphenylethyl-2-(1*H*-indol-3-yl)acetate (**4**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **4** (yellow liquid, 91.2 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.92-7.89 (m, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.51-7.44 (m, 3H), 7.38-7.29 (m, 6H), 7.19-7.14 (m, 2H),

7.12-7.07 (m, 1H), 6.89 (s, 1H), 4.00-3.89 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 171.5, 136.0, 134.6, 133.5, 133.4, 129.3, 129.1, 128.8, 128.6, 128.6, 127.2, 123.3, 122.1, 119.6, 118.8, 111.1, 107.8, 77.9, 30.9. HRMS (ESI, m/z) calcd. for $C_{24}H_{19}NO_3Na$ $[M+Na]^+$ calc.: 392.1257; found: 392.1263.



5

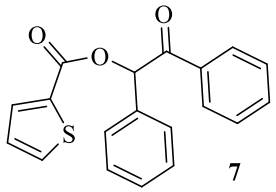
2-Oxo-1,2-diphenylethyl-1*H*-indole-2-carboxylate (**5**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **5** (white solid, 111.4 mg, 78% yield, *dr* = 2.0:1.0); ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 9.14 (s, 1H), 8.01-7.97 (m, 2H), 7.66 (dd, J_1 = 8.2 Hz, J_2 = 0.8 Hz, 1H), 7.57 (d, J = 1.6 Hz, 1H), 7.52-7.49 (m, 1H), 7.42-7.37 (m, 7H), 7.32-7.29 (m, 2H), 7.14-7.09 (m, 2H); (minor isomer) δ 9.52 (s, 0.50H), 8.01-7.97 (m, 1.59H), 7.63 (dd, J_1 = 7.4 Hz, J_2 = 2.0 Hz, 1H), 7.59 (d, J = 2.0 Hz, 1H), 7.54-7.51 (m, 1H), 7.37-7.33 (m, 3.52 H), 7.28-7.25 (m, 1H), 7.21-7.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 193.4, 161.1, 137.1, 134.5, 133.6, 133.5, 129.5, 129.2, 128.9, 128.8, 128.7, 127.4, 126.3, 125.7, 122.7, 120.8, 112.0, 110.2, 77.9; (minor isomer) δ 193.2, 159.9, 136.5, 134.4, 133.7, 133.2, 131.4, 129.6, 129.2, 129.1, 128.9, 128.7, 126.9, 123.5, 121.7, 112.2, 78.1. HRMS (ESI, m/z) calcd. for $C_{23}H_{17}NO_3Na$ $[M+Na]^+$ calc.: 378.1101; found: 378.1098.



6

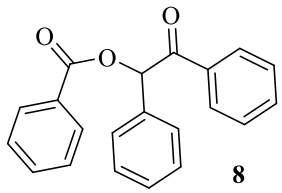
2-Oxo-1,2-diphenylethyl-furan-2-carboxylate (**6**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **6** (white solid, 63.3 mg, 52% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10-8.07 (m, 2H), 8.03-8.01 (m, 1H),

7.66-7.60 (m, 3H), 7.54-7.49 (m, 2H), 7.45-7.38 (m, 4H), 7.36 (s, 1H), 6.73 (dd, J_1 = 3.4 Hz, J_2 = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.4, 157.2, 148.2, 143.2, 134.0, 133.8, 133.2, 129.4, 129.1, 129.0, 128.8, 128.7, 119.4, 112.6, 77.3. HRMS (ESI, m/z) calcd. for $C_{19}H_{14}O_4Na$ $[M+Na]^+$ calc.: 329.0784; found: 329.0789.



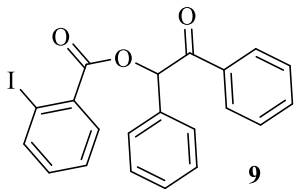
7

2-Oxo-1,2-diphenylethyl-thiophene-2-carboxylate (**7**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **7** (white solid, 109.5 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.97 (m, 2H), 7.89 (dd, J_1 = 3.6 Hz, J_2 =1.2 Hz, 1H), 7.59 (dd, J_1 = 5.2 Hz, J_2 =1.2 Hz, 1H), 7.57-7.54 (m, 2H), 7.53-7.50 (m, 1H), 7.44-7.35 (m, 5H), 7.12-7.09 (m, 1H), 7.05 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 161.6, 134.6, 134.3, 133.5, 133.2, 132.7, 129.3, 129.1, 128.9, 128.7, 128.6, 127.8, 78.0. HRMS (ESI, m/z) calcd. for $C_{19}H_{14}O_3SNa$ $[M+Na]^+$ calc.: 345.0556; found: 345.0561.



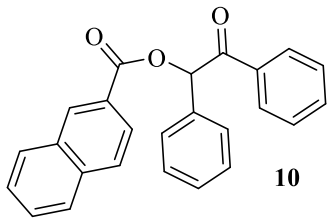
8

2-Oxo-1,2-diphenylethyl benzoate (**8**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **8** (white solid, 67.6 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.11 (m, 2H), 8.02-7.99 (m, 2H), 7.60-7.54 (m, 3H), 7.53-7.50 (m, 1H), 7.46-7.41 (m, 4H), 7.40-7.35 (m, 3H), 7.10 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 166.0, 134.7, 133.7, 133.5, 133.4, 130.0, 129.4, 129.3, 129.1, 128.8, 128.7, 128.4, 77.9. HRMS (ESI, m/z) calcd. for $C_{21}H_{16}O_3Na$ $[M+Na]^+$ calc.: 339.0992; found: 339.0990.



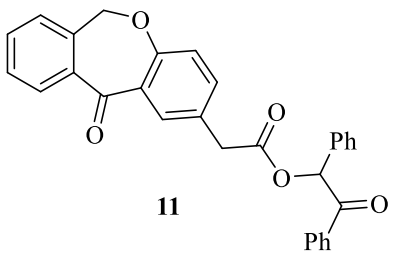
9

2-Oxo-1,2-diphenylethyl-2-iodobenzoate (**9**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **9** (white solid, 130.3 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 8.01-7.97 (m, 3H), 7.58-7.54 (m, 2H), 7.54-7.50 (m, 1H), 7.44-7.35 (m, 6H), 7.19-7.14 (m, 1H), 7.13 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 165.7, 141.4, 134.5, 133.8, 133.6, 133.3, 133.1, 131.8, 129.5, 129.2, 128.9, 128.8, 128.7, 128.0, 94.5, 78.5. HRMS (ESI, m/z) calcd. for $C_{21}H_{15}IO_3Na$ $[M+Na]^+$ calc.: 464.9958; found: 464.9966.



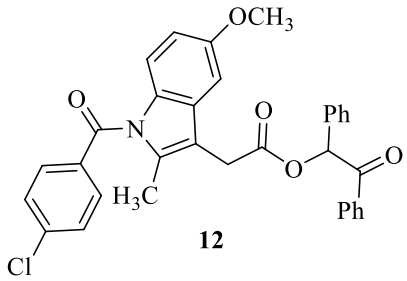
10

2-Oxo-1,2-diphenylethyl-2-naphthoate (**10**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **10** (yellow solid, 133.1 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.12 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 8.05-8.01 (m, 2H), 7.95 (d, J = 8.4 Hz, 1H), 7.89-7.85 (m, 2H), 7.64-7.61 (m, 2H), 7.60-7.56 (m, 1H), 7.55-7.51 (m, 2H), 7.45-7.42 (m, 3H), 7.41-7.38 (m, 2H), 7.16 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 166.2, 135.7, 134.7, 133.8, 133.5, 132.4, 131.7, 129.4, 129.3, 129.2, 128.9, 128.8, 128.7, 128.4, 128.2, 127.8, 126.6, 126.5, 125.4, 78.0. HRMS (ESI, m/z) calcd. for $C_{25}H_{18}O_3Na$ $[M+Na]^+$ calc.: 389.1148; found: 389.1153.



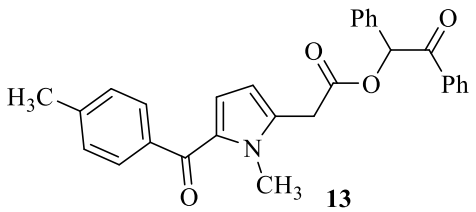
11

2-Oxo-1,2-diphenylethyl-2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (**11**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **11** (white solid, 126.9 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.92-7.86 (m, 3H), 7.57-7.52 (m, 1H), 7.51-7.46 (m, 5H), 7.39-7.34 (m, 6H), 7.02 (d, J = 8.8 Hz, 1H), 6.87 (s, 1H), 5.17 (s, 2H), 3.88-3.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 190.8, 171.0, 160.5, 140.4, 136.5, 135.5, 134.5, 133.5, 133.3, 132.7, 132.6, 129.5, 129.3, 129.2, 129.1, 128.8, 128.6, 127.8, 127.2, 125.0, 121.1, 78.1, 73.6, 39.6. HRMS (ESI, m/z) calcd. for $C_{30}H_{22}O_5Na$ $[M+Na]^+$ calc.: 485.1359; found: 485.1362.



12

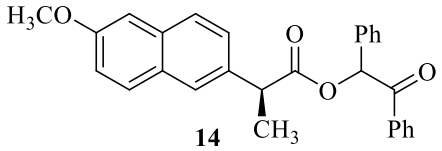
2-Oxo-1,2-diphenylethyl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (**12**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **12** (brown oil, 170.2 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.62-7.59 (m, 2H), 7.47-7.39 (m, 5H), 7.35-7.30 (m, 5H), 7.01-7.00 (m, 1H), 6.94-6.91 (m, 1H), 6.87 (s, 1H), 6.66 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 3.84 (s, 2H), 3.78 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 170.2, 168.2, 156.0, 139.0, 135.8, 134.3, 133.8, 133.4, 133.3, 131.1, 130.6, 130.4, 129.2, 129.0, 128.9, 128.6, 128.5, 128.4, 114.8, 112.1, 112.0, 100.9, 78.1, 55.5, 29.8, 13.3. HRMS (ESI, m/z) calcd. for $C_{33}H_{26}ClNO_5Na$ $[M+Na]^+$ calc.: 574.1392; found: 574.1397.



13

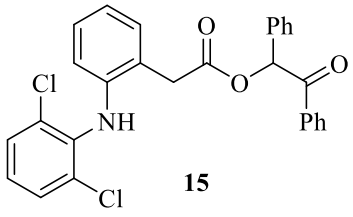
2-Oxo-1,2-diphenylethyl-2-(1-methyl-5-(4-methylbenzoyl)-1*H*-pyrrol-2-yl)acetate

(**13**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **13** (brown oil, 103.8 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.50-7.44 (m, 3H), 7.38-7.32 (m, 5H), 7.23-7.20 (m, 2H), 6.90 (s, 1H), 6.66 (d, *J* = 4.0 Hz, 1H), 6.15 (d, *J* = 4.4 Hz, 1H), 3.94-3.82 (m, 5H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 185.7, 168.9, 141.7, 137.2, 134.3, 133.8, 133.5, 133.0, 131.3, 129.4, 129.3, 129.1, 128.7, 128.6, 128.5, 122.1, 109.6, 78.4, 33.1, 32.4, 21.4. HRMS (ESI, m/z) calcd. for $C_{29}H_{25}NO_4Na$ $[M+Na]^+$ calc.: 474.1676; found: 474.1684.



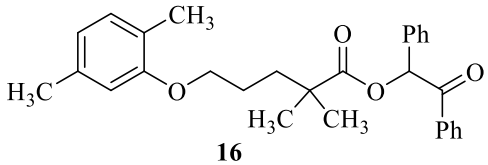
14

2-Oxo-1,2-diphenylethyl-(2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (**14**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **14** (yellow oil, 99.0 mg, 58% yield, *dr* = 1.0:1.0); isomer 1 + isomer 2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 2H, isomer 1), 7.84-7.81 (m, 2H, isomer 2), 7.70-7.63 (m, 3H, isomer 1 + 3H, isomer 2), 7.47-7.20 (m, 9H, isomer 1 + 9H, isomer 2), 7.14-7.07 (m, 2H, isomer 1 + 2H, isomer 2), 6.82-6.80 (m, 1H, isomer 1 + 1H, isomer 2), 4.13-3.98 (m, 1H, isomer 1 + 1H, isomer 2), 3.87(s, 1H, isomer 1), 3.85 (s, 1H, isomer 2), 1.66-1.60 (m, 3H, isomer 1 + 3H, isomer 2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 193.7, 174.2, 173.9, 157.5, 135.1, 134.9, 134.6, 134.5, 133.7, 133.6, 133.5, 133.4, 133.2, 129.3, 129.2, 129.0, 129.0, 128.9, 128.9, 128.8, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.0, 127.0, 126.4, 126.3, 126.1, 126.1, 118.8, 118.7, 105.5, 105.4, 77.9, 77.7, 55.2, 55.1, 45.1, 45.0, 18.7, 18.4. HRMS (ESI, m/z) calcd. for $C_{28}H_{24}O_4Na$ $[M+Na]^+$ calc.: 447.1567; found: 447.1573.



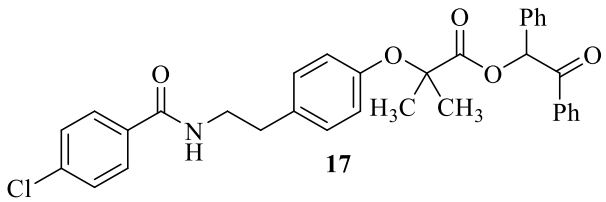
15

2-Oxo-1,2-diphenylethyl-2-(2-((2,6-dichlorophenyl)amino)phenyl)acetate (15). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **15** (yellow oil, 136.5 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.46-7.40 (m, 3H), 7.34-7.30 (m, 5H), 7.28-7.23 (m, 3H), 7.11-7.07 (m, 1H), 6.96-6.87(m, 3H), 6.64 (s, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 4.06-3.93 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 171.7, 142.7, 137.9, 134.3, 133.4, 133.2, 130.9, 129.3, 129.3, 129.1, 128.7, 128.7, 128.6, 128.5, 128.0, 124.4, 123.8, 122.2, 118.7, 78.3, 38.0. HRMS (ESI, m/z) calcd. for $C_{28}H_{21}Cl_2NO_3Na$ $[M+Na]^+$ calc.: 512.0791; found: 512.0798.



16

2-Oxo-1,2-diphenylethyl-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (16). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **16** (yellow oil, 149.0 mg, 84% yield, *dr* = 2.0:1.0); ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.50-7.44 (m, 3H), 7.39-7.29 (m, 5H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.79 (s, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 3.91 (s, 2H), 2.29 (s, 3H), 2.14(s, 3H), 1.88-1.74 (m, 4H), 1.31 (s, 3H), 1.29 (s, 3H); (minor isomer) δ 7.97 (d, *J* = 7.6 Hz, 1H), 7.65-7.60 (m, 0.47H), 7.50-7.44 (m, 1H), 2.29 (s, 0.17H), 2.14 (s, 0.15H), 1.88-1.74 (m, 0.25H), 1.31 (s, 0.17H), 1.29 (s, 0.94H). ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 194.2, 177.3, 156.9, 136.3, 134.8, 133.6, 133.3, 130.2, 129.8, 128.9, 128.7, 128.5, 123.5, 120.5, 111.9, 77.3, 67.9, 42.0, 37.0, 25.1, 25.0, 24.9, 21.3, 15.7; (minor isomer) δ 194.5, 134.8, 132.9, 129.0, 129.0, 128.2. HRMS (ESI, m/z) calcd. for $C_{29}H_{32}O_4Na$ $[M+Na]^+$ calc.: 467.2193; found: 467.2199.



17

2-Oxo-1,2-diphenylethyl-2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate (**17**). Following the general procedure, the crude product was purified using silica gel column chromatography (petroleum ether / ethyl acetate = 5:1-3:1) to produce the desired product **17** (yellow oil, 150.1 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.51-7.46 (m, 1H), 7.42-7.35 (m, 4H), 7.34-7.25 (m, 5H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.89-6.86 (m, 3H), 6.56-6.46 (m, 1H), 3.58 (q, *J* = 6.8 Hz, 2H), 2.80 (t, *J* = 6.8 Hz, 2H), 1.68 (s, 3H),1.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 173.6, 166.4, 153.8, 137.3, 134.4, 133.5, 133.0, 132.9, 132.5, 129.3, 129.3, 129.0, 128.7, 128.6, 128.5, 128.3, 128.2, 119.9, 79.1, 78.1, 41.2, 34.6, 25.9, 24.9. HRMS (ESI, m/z) calcd. for $C_{33}H_{30}ClNO_5Na$ $[M+Na]^+$ calc.: 578.1705; found: 578.1710.

3. Gram-scale synthesis of 3a

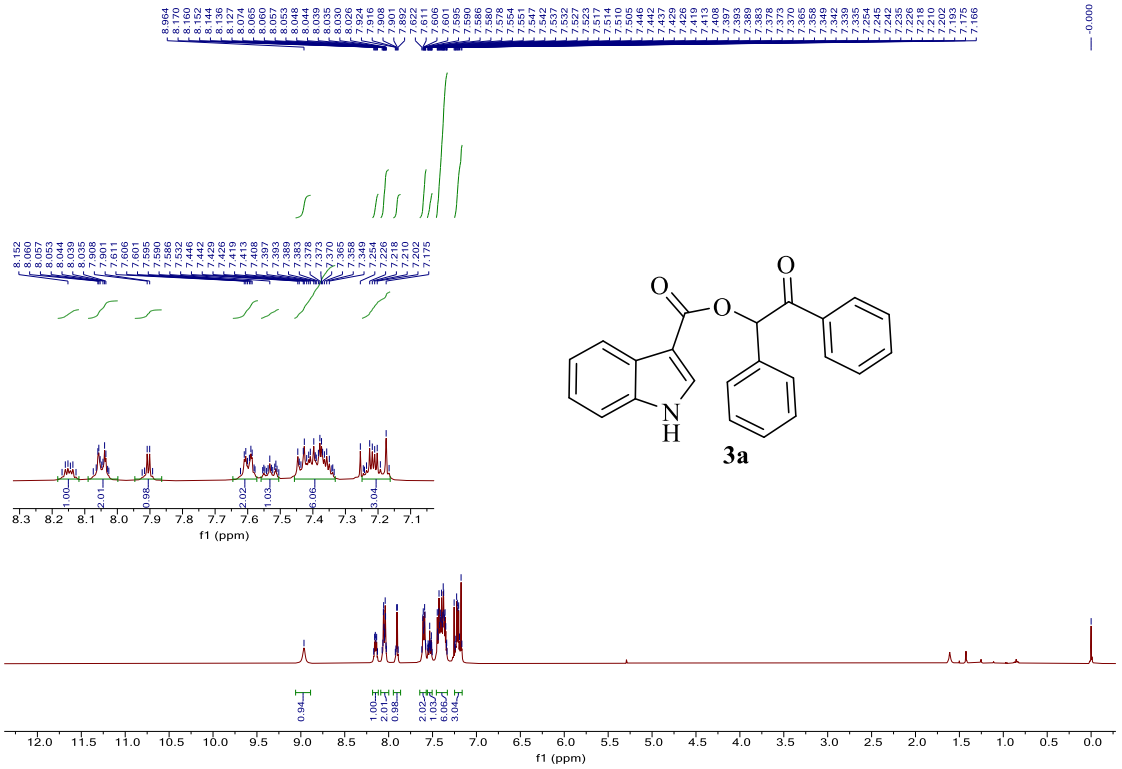
Benzyl phenyl ketone **1a** (0.785 g, 4 mmol), indole-3-carboxylic acid **2a** (0.967 g, 6 mmol), TBAI (0.443 g, 1.2 mmol) and H_2O (20 mL) were placed in an Schlenk tube, then TBHP (70% in water, 1.1 mL, 8 mmol) was added into the above mixture under air condition. After the completion of the addition, the reaction mixture was allowed to react at 50 °C (oil bath) for 12 h. Subsequently, the reaction mixture was cooled to room temperature, and then extracted with ethyl acetate. The organic layer was dried with anhydrous Na_2SO_4. After removal of the ethyl acetate under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 5:1-3:1) to afford 2-oxo-1,2-diphenylethyl-1*H*-indole-3-carboxylate **3a** (white solid, 1.13 g, 79% yield).

4. Crystal Preparation Methods of 3a

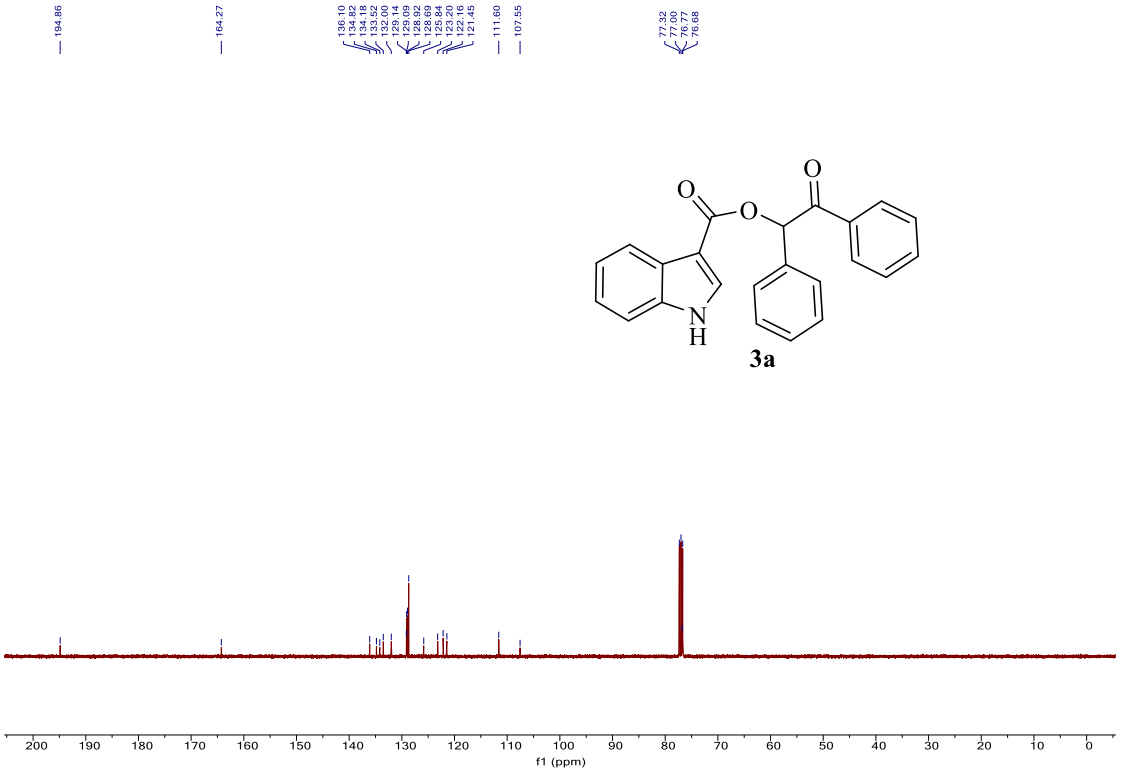
In a 50 mL round bottom flask, 50 mg of **3a** was dissolved in 3 mL DCM. Subsequently, 3 mL petroleum ether was added to the flask. The prepared solution was well shaken and kept at room temperature until crystals had precipitated out. The crystals were carefully picked out for single crystal X-ray diffraction.

5. ^{1}H NMR and ^{13}C NMR Spectra of Products 3-17

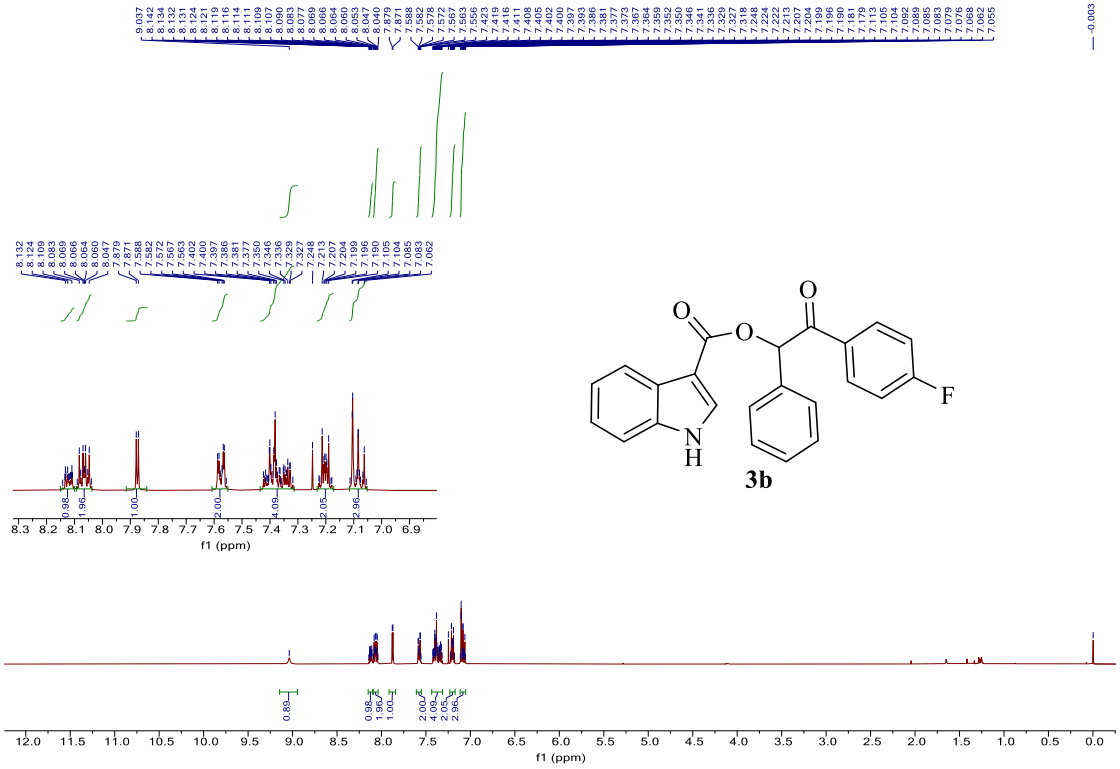
The ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



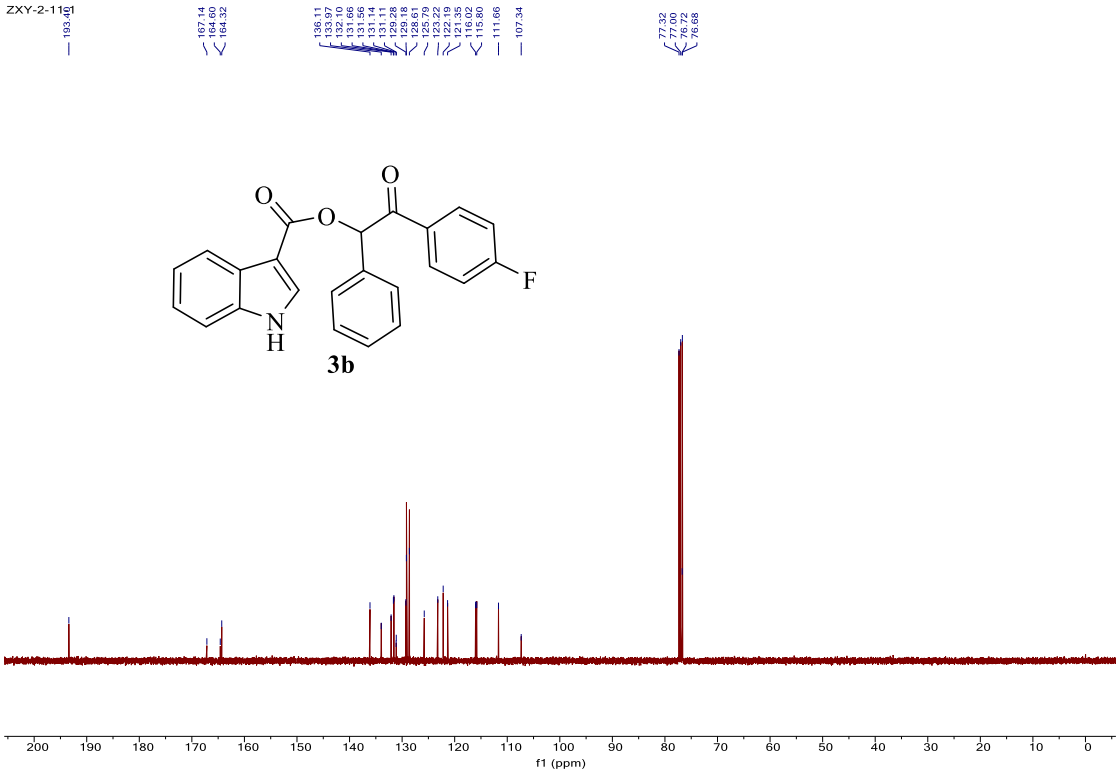
The ^{13}C{^{1}H} NMR spectrum of **3a** (100 MHz, $CDCl_3$)



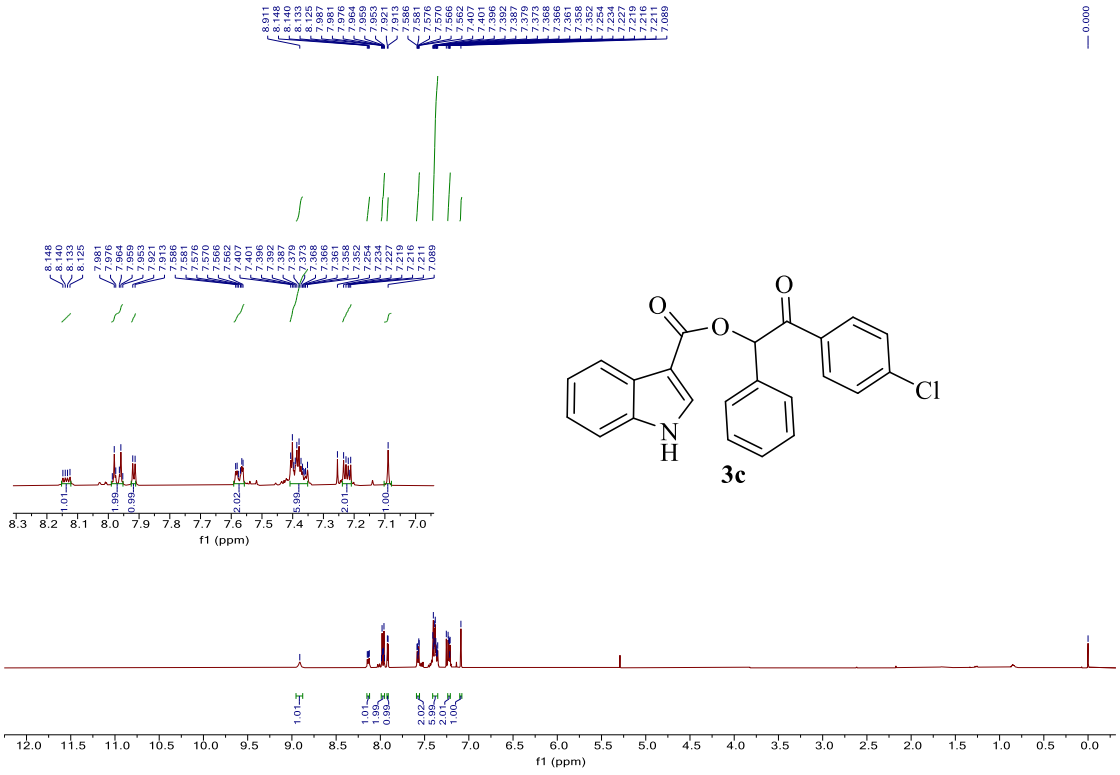
The ^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



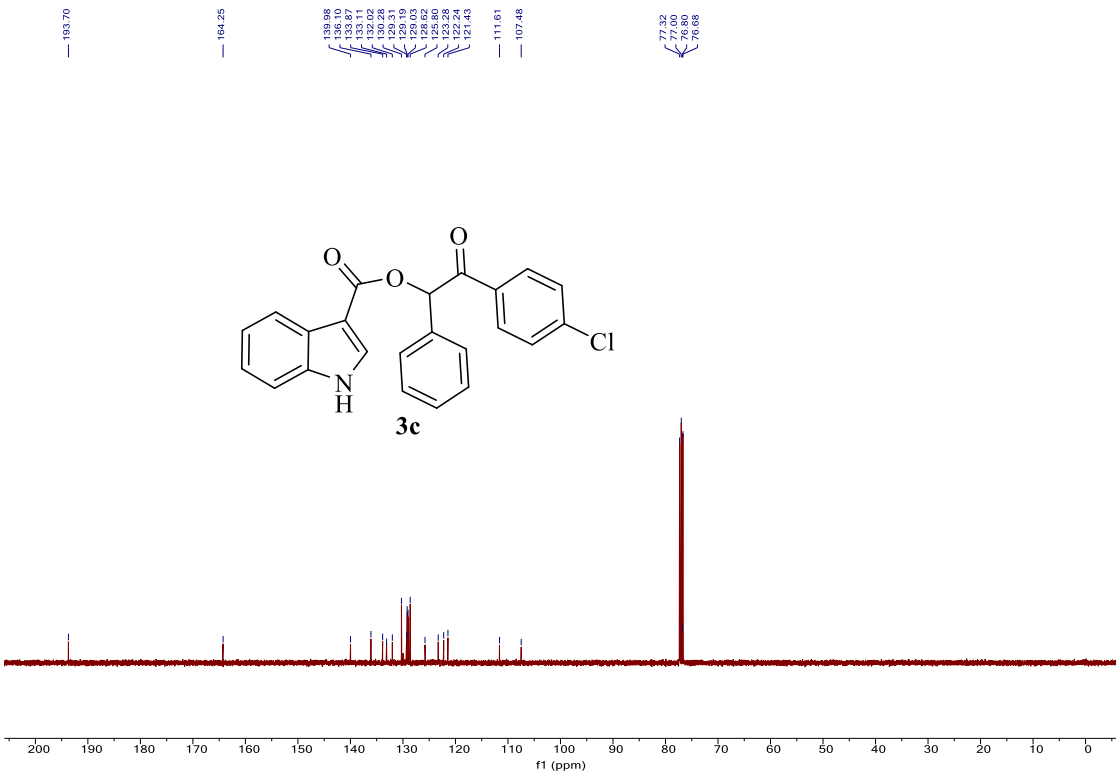
The $^{13}C\{^{1}H\}$ NMR spectrum of **3b** (100 MHz, $CDCl_3$)



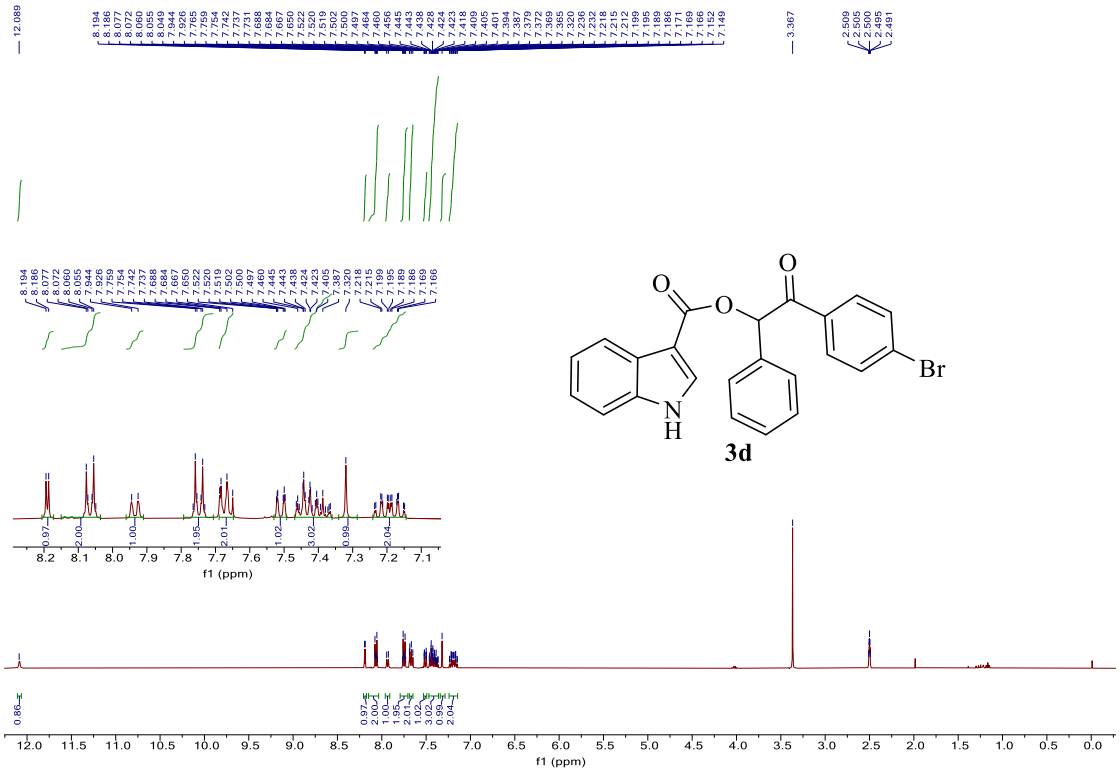
The ^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)



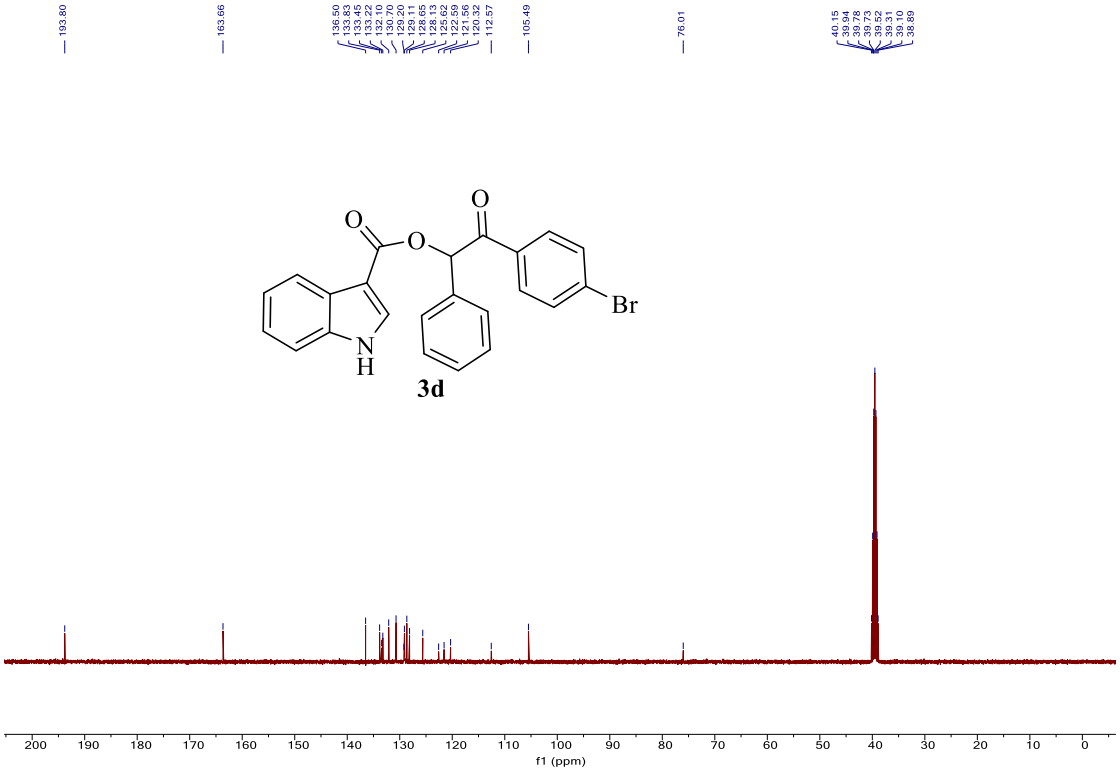
The $^{13}C\{^{1}H\}$ NMR spectrum of **3c** (100 MHz, $CDCl_3$)



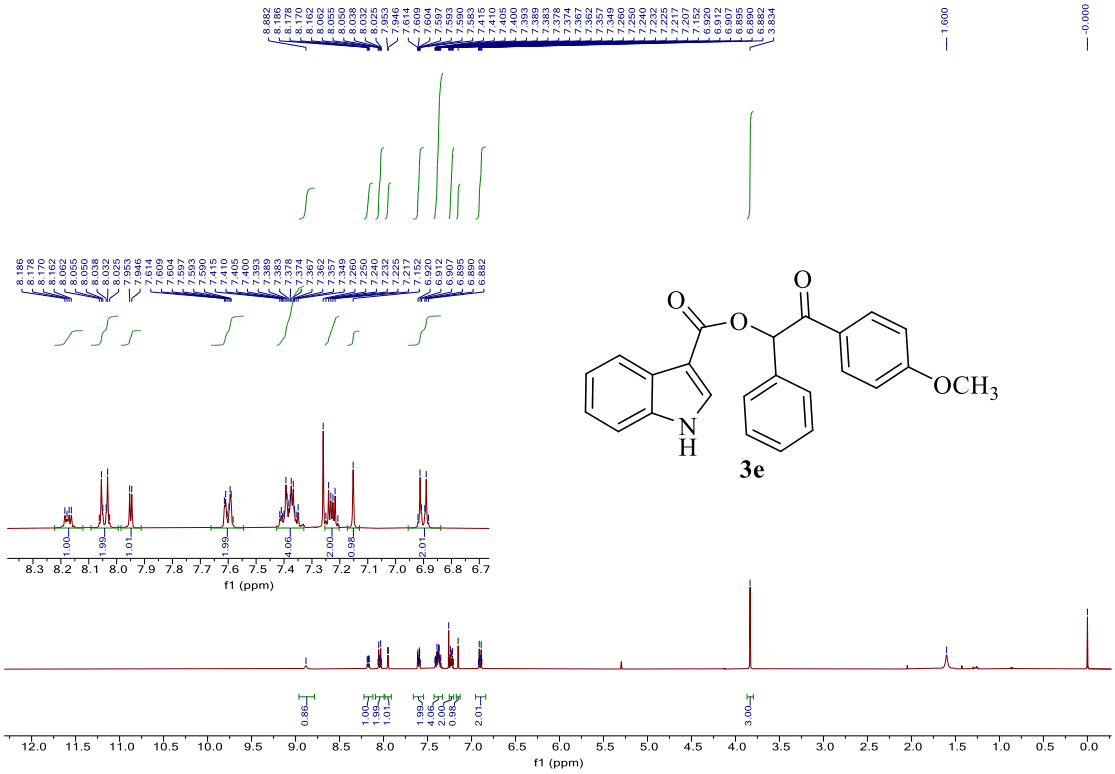
The ^{1}H NMR spectrum of **3d** (400 MHz, DMSO-d_6)



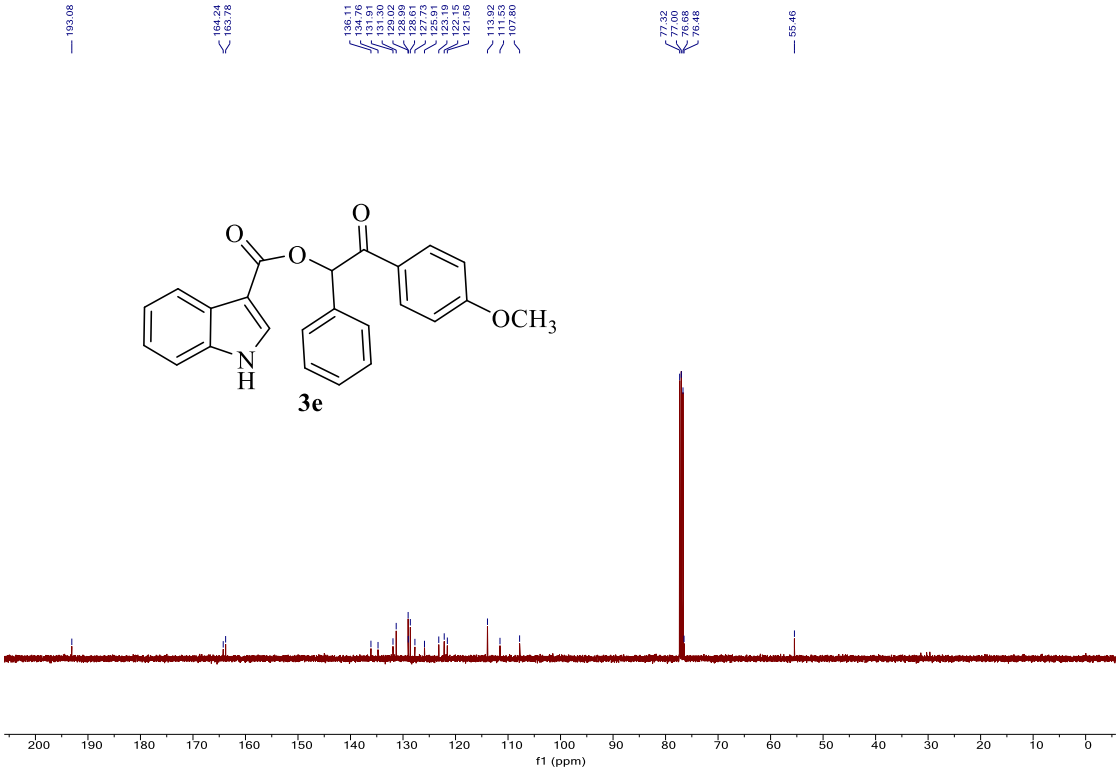
The $^{13}C\{^{1}H\}$ NMR spectrum of **3d** (100 MHz, DMSO-d_6)



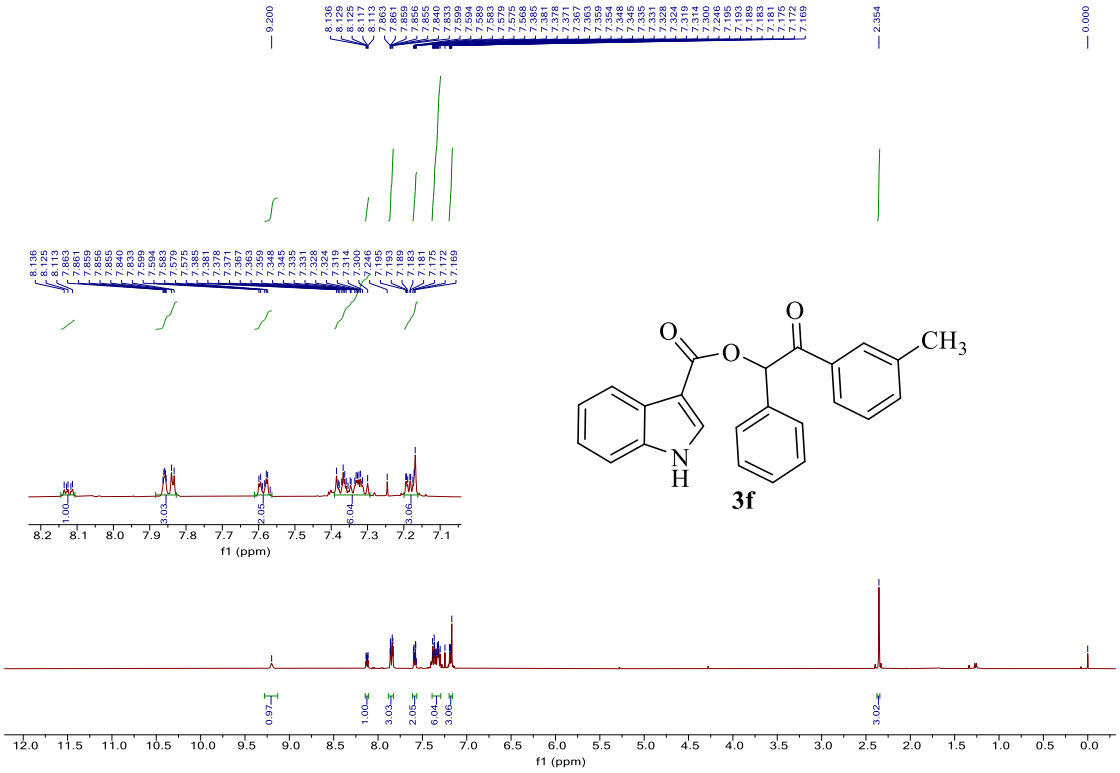
The ^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)



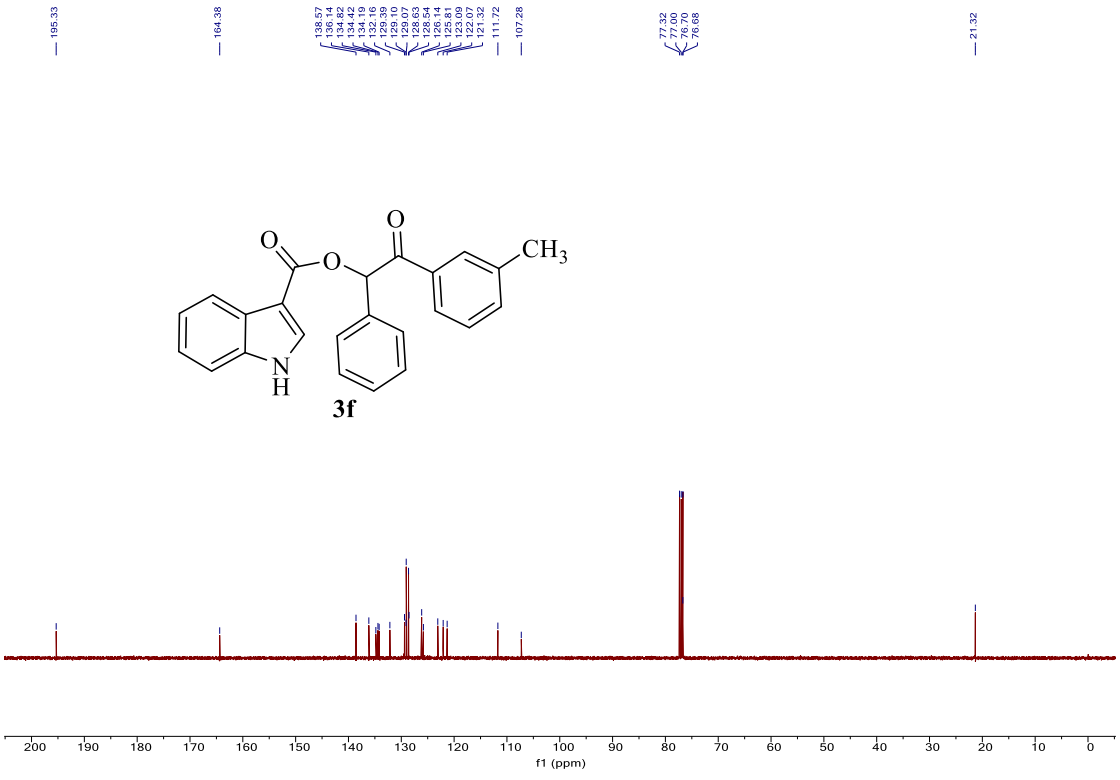
The $^{13}C\{^{1}H\}$ NMR spectrum of **3e** (100 MHz, $CDCl_3$)



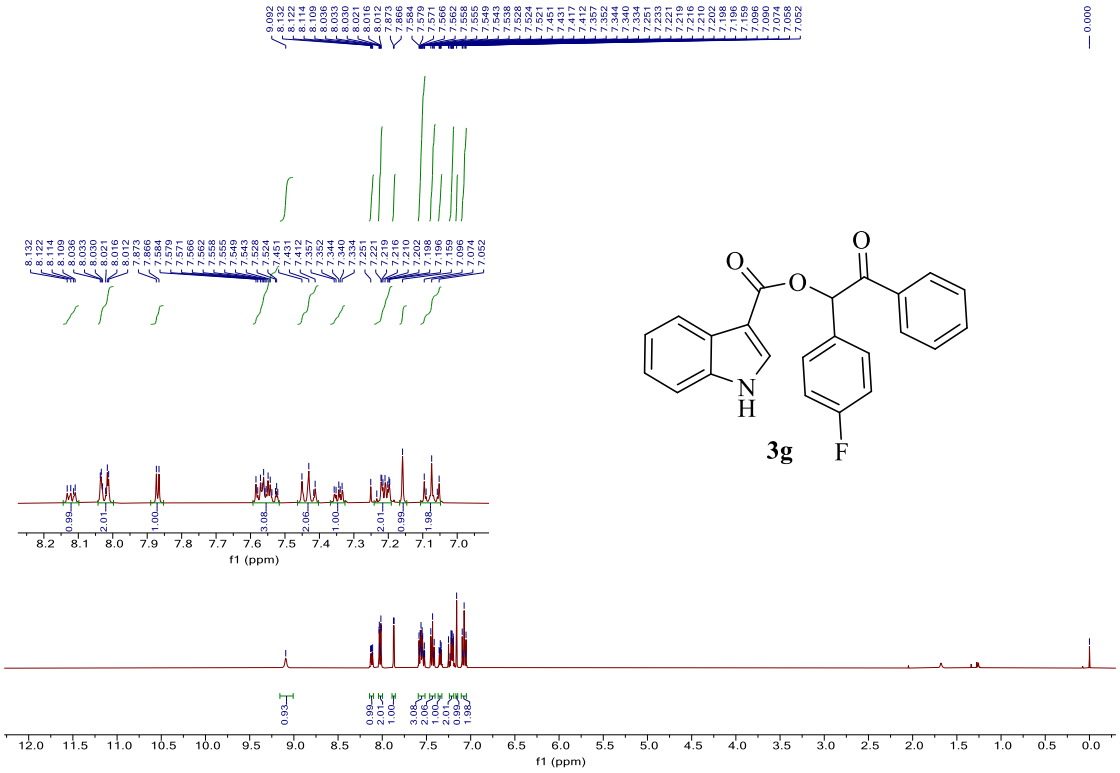
The ^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



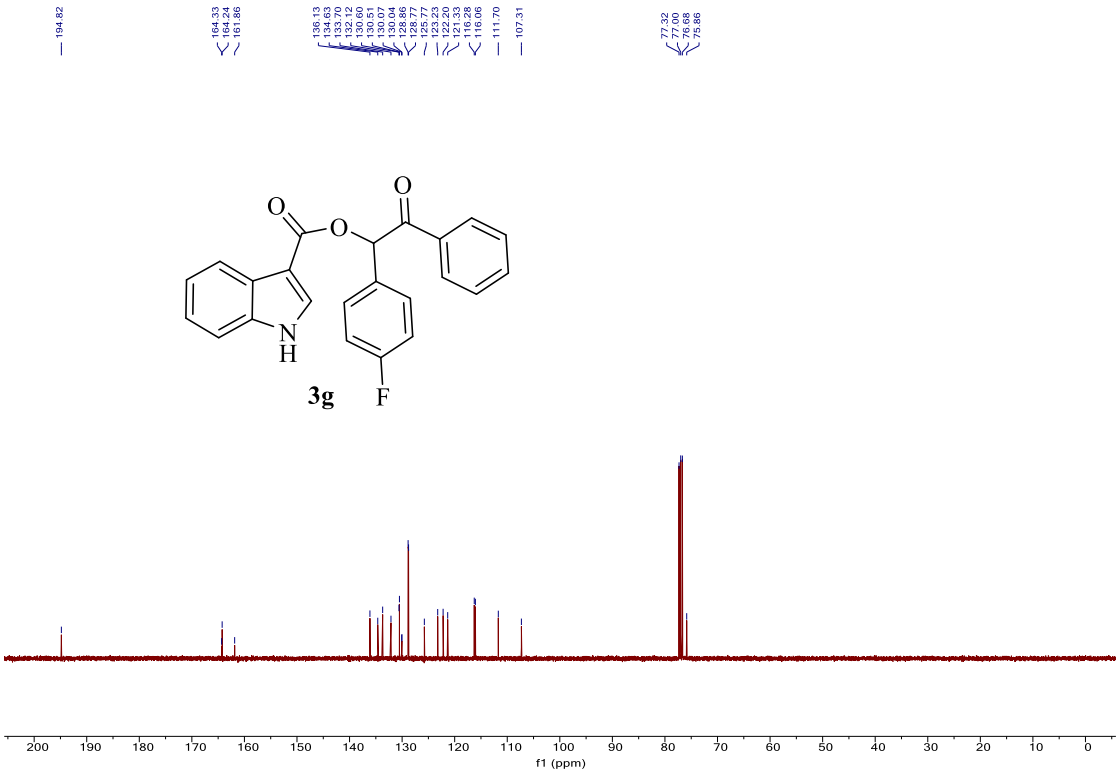
The $^{13}C\{^{1}H\}$ NMR spectrum of **3f** (100 MHz, $CDCl_3$)



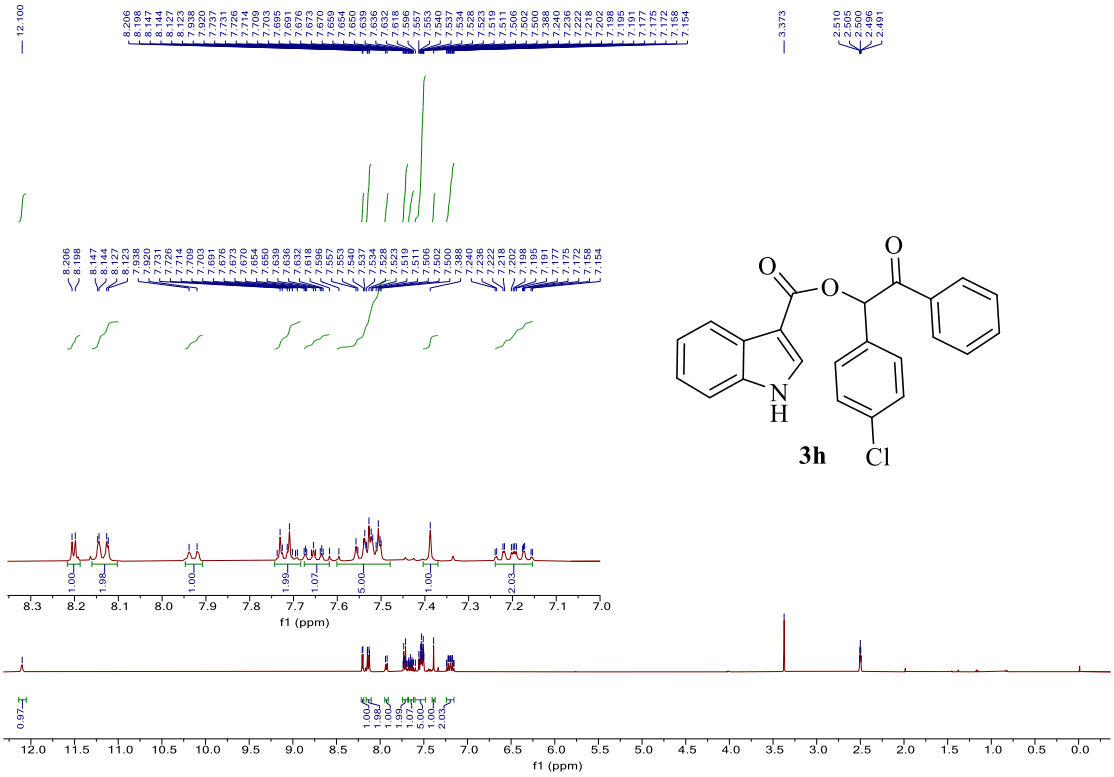
The ^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



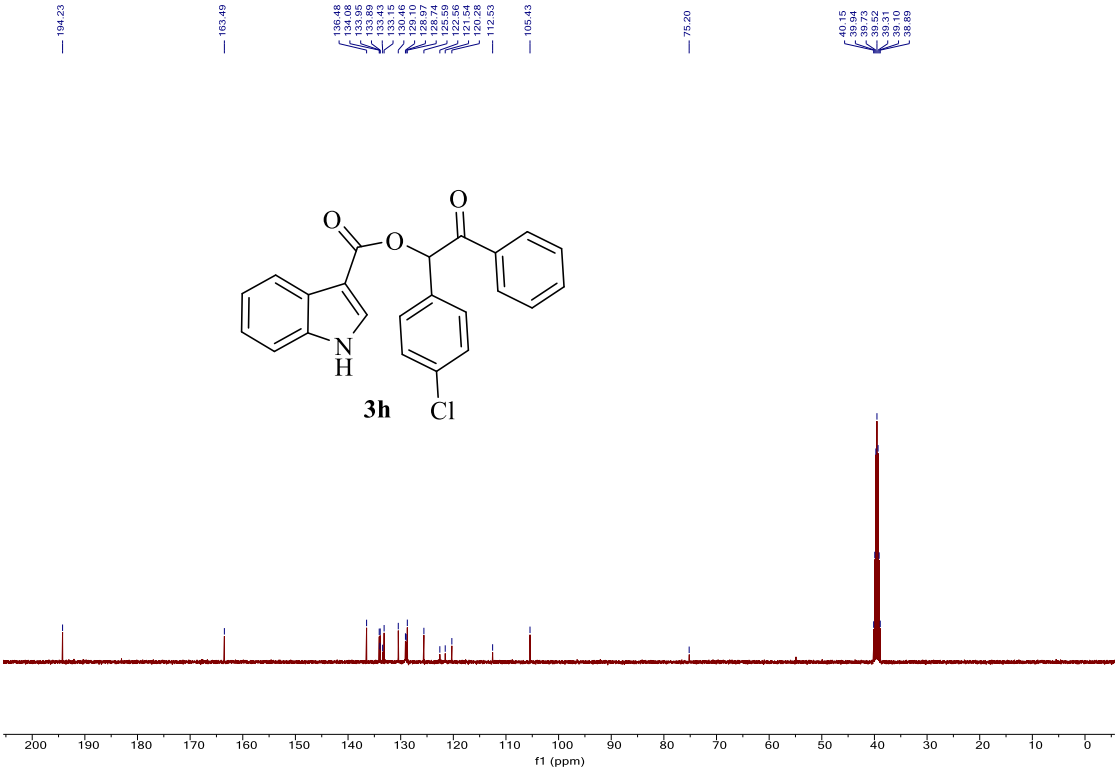
The $^{13}C\{^{1}H\}$ NMR spectrum of **3g** (100 MHz, $CDCl_3$)



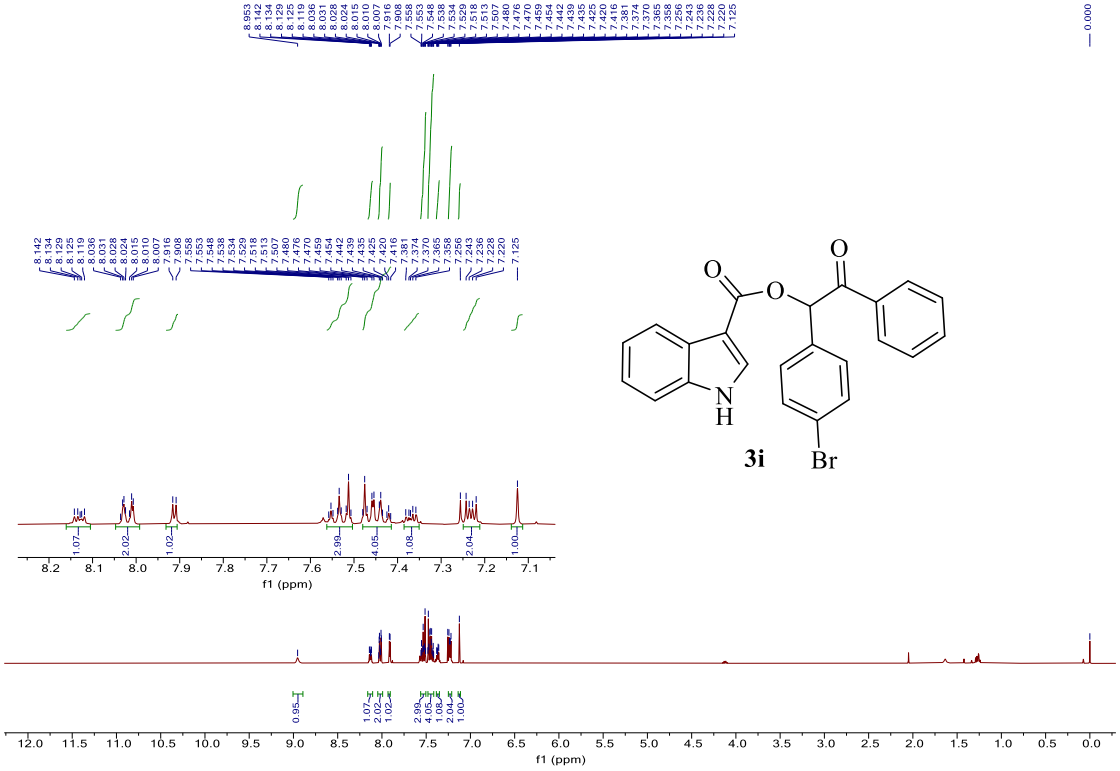
The ^{1}H NMR spectrum of **3h** (400 MHz, DMSO-d_6)



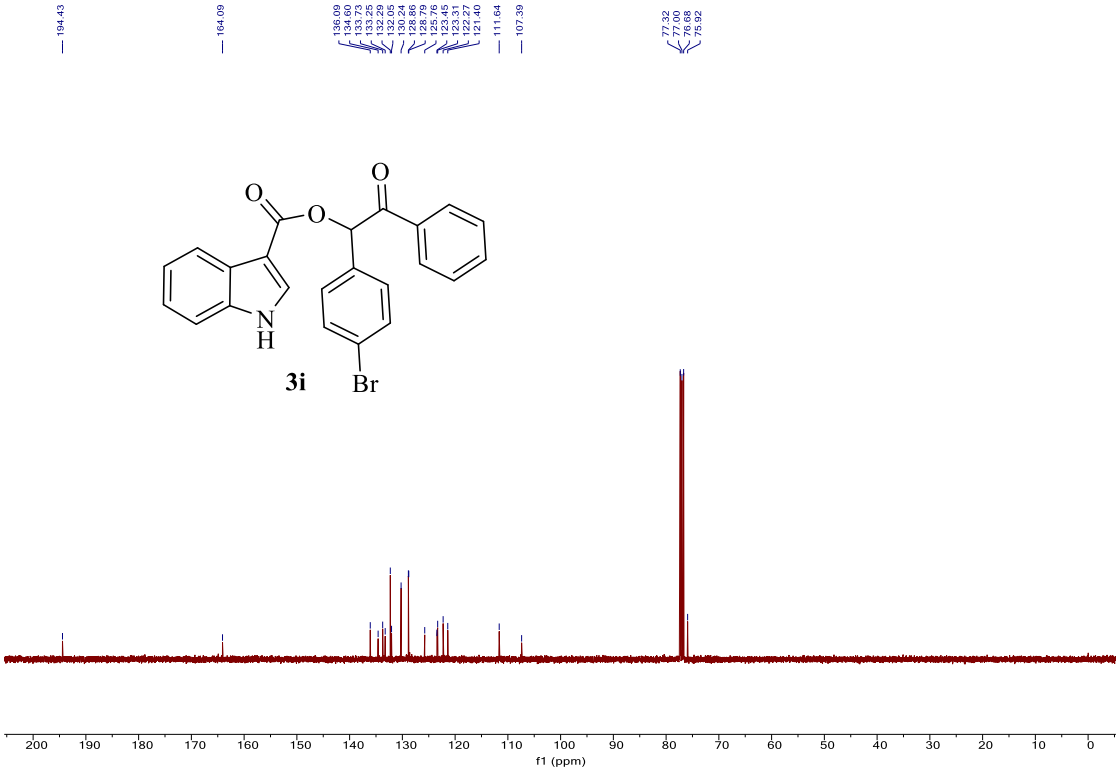
The $^{13}C\{^{1}H\}$ NMR spectrum of **3h** (100 MHz, DMSO-d_6)



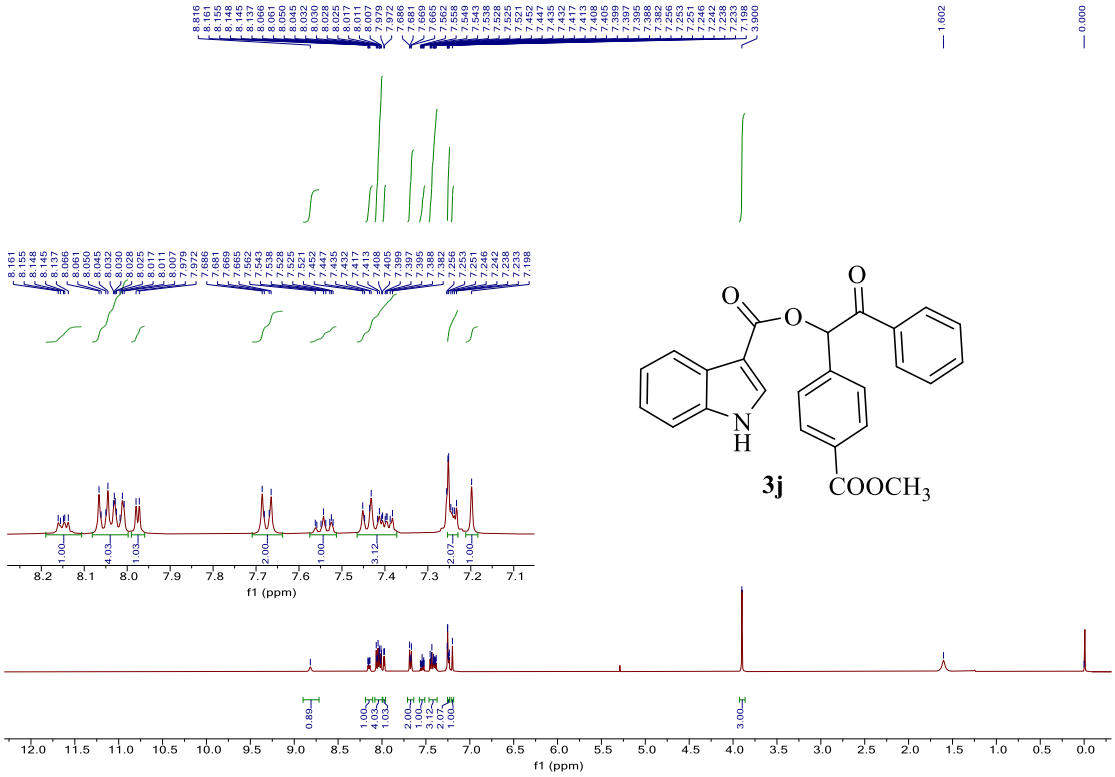
The ^{1}H NMR spectrum of **3i** MHz, $CDCl_3$)



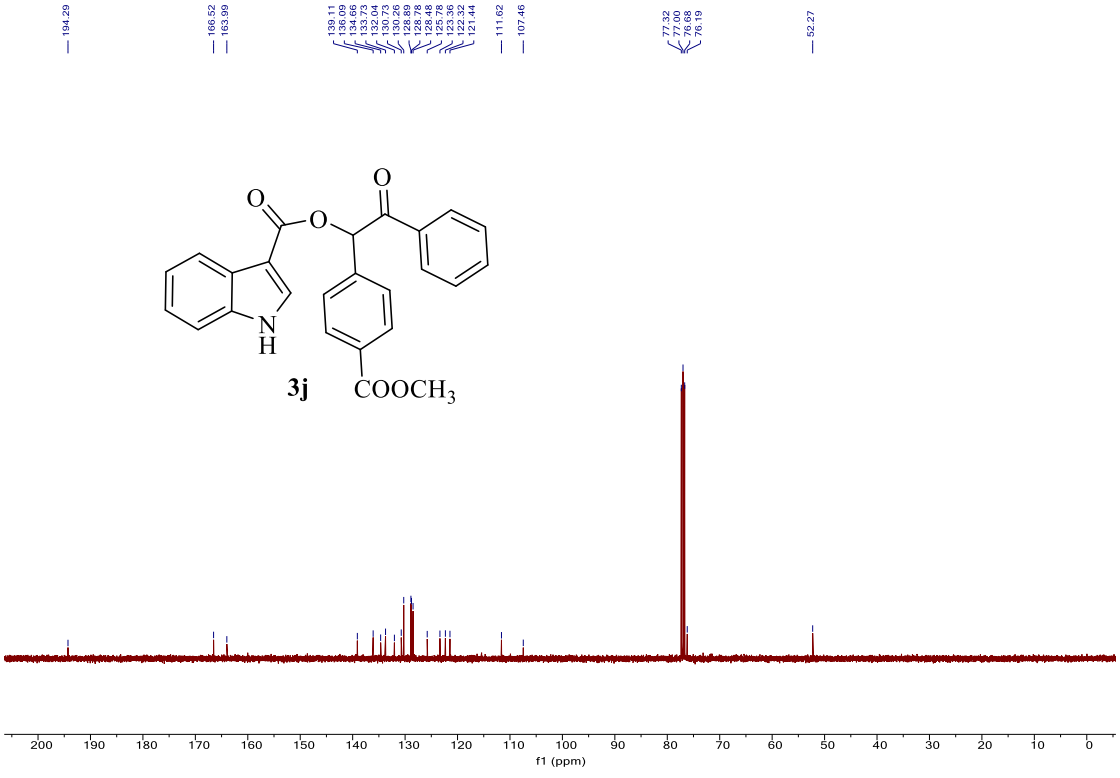
The $^{13}C\{^{1}H\}$ NMR spectrum of **3i** (100 MHz, $CDCl_3$)



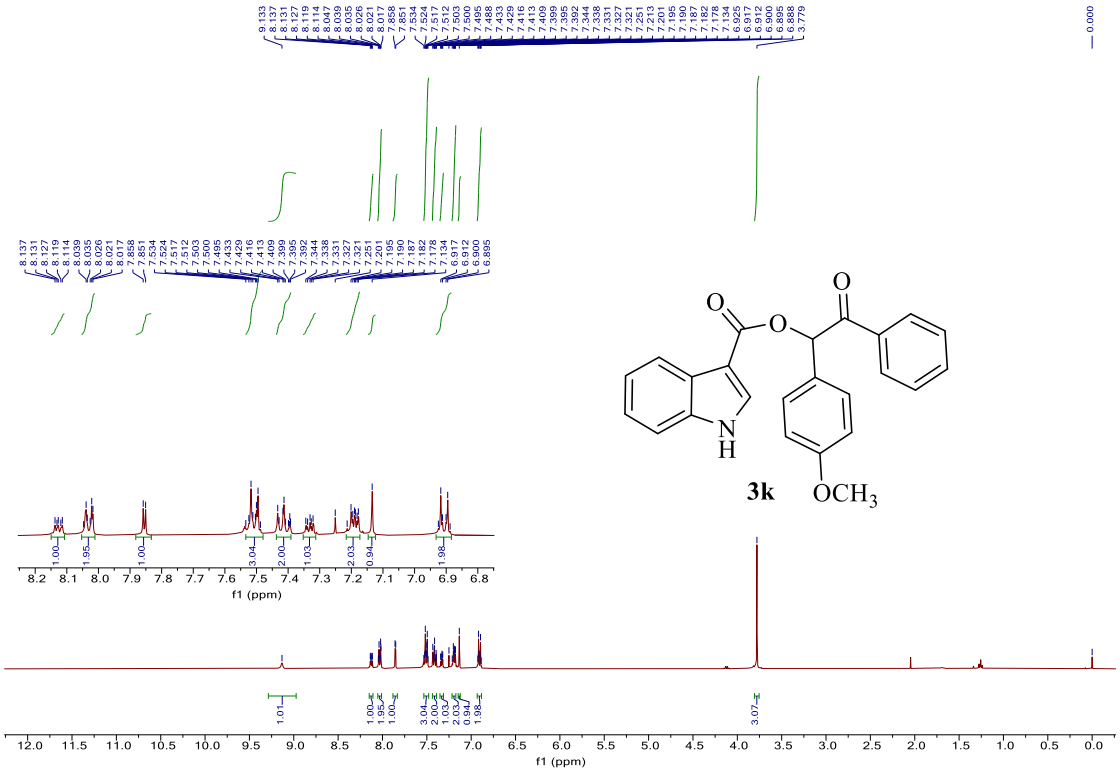
The ^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)



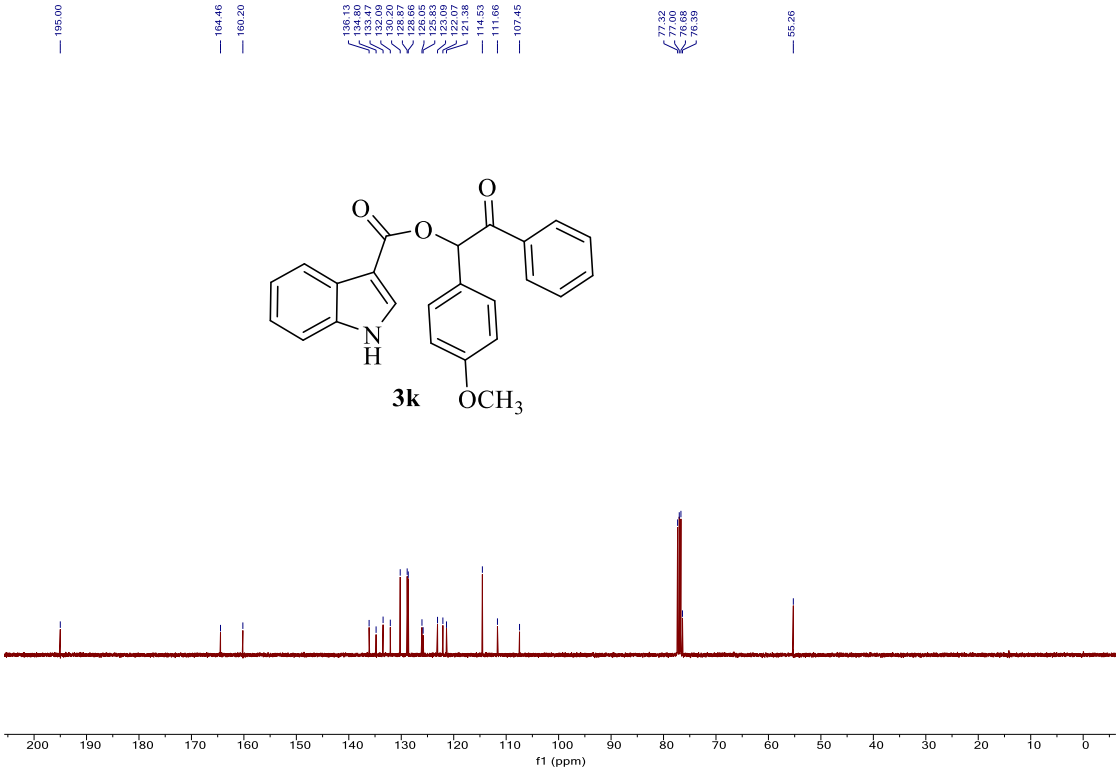
The $^{13}C\{^{1}H\}$ NMR spectrum of **3j** (100 MHz, $CDCl_3$)



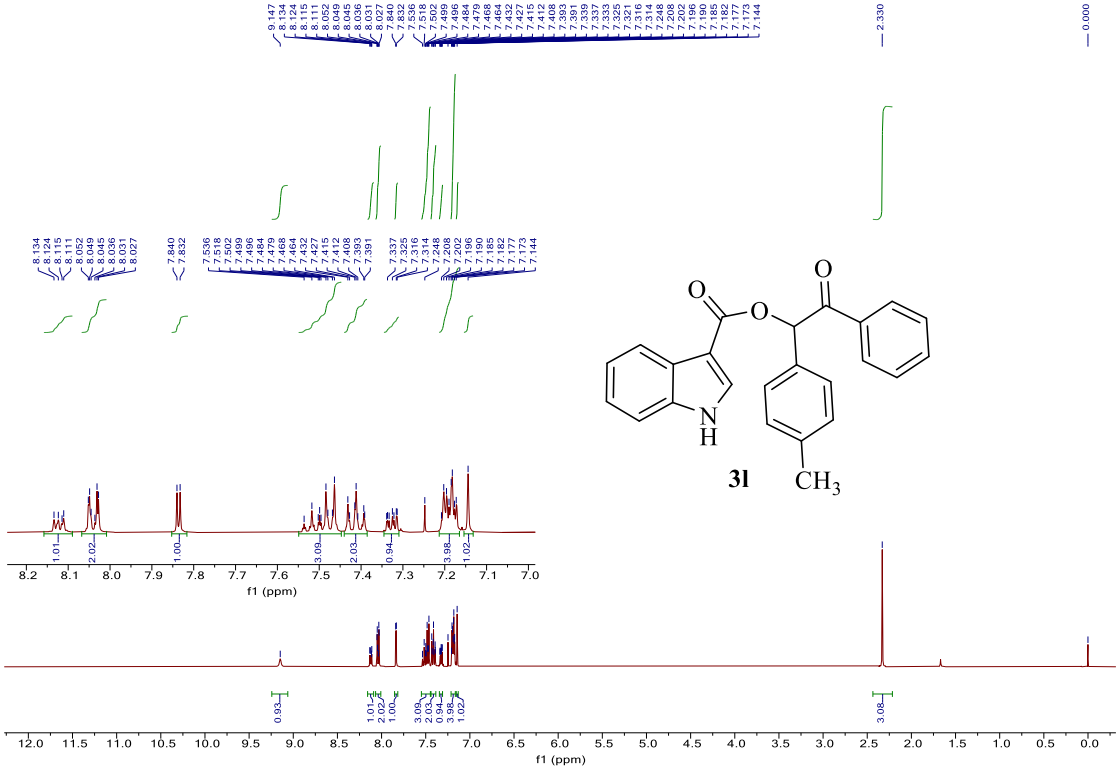
The ^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



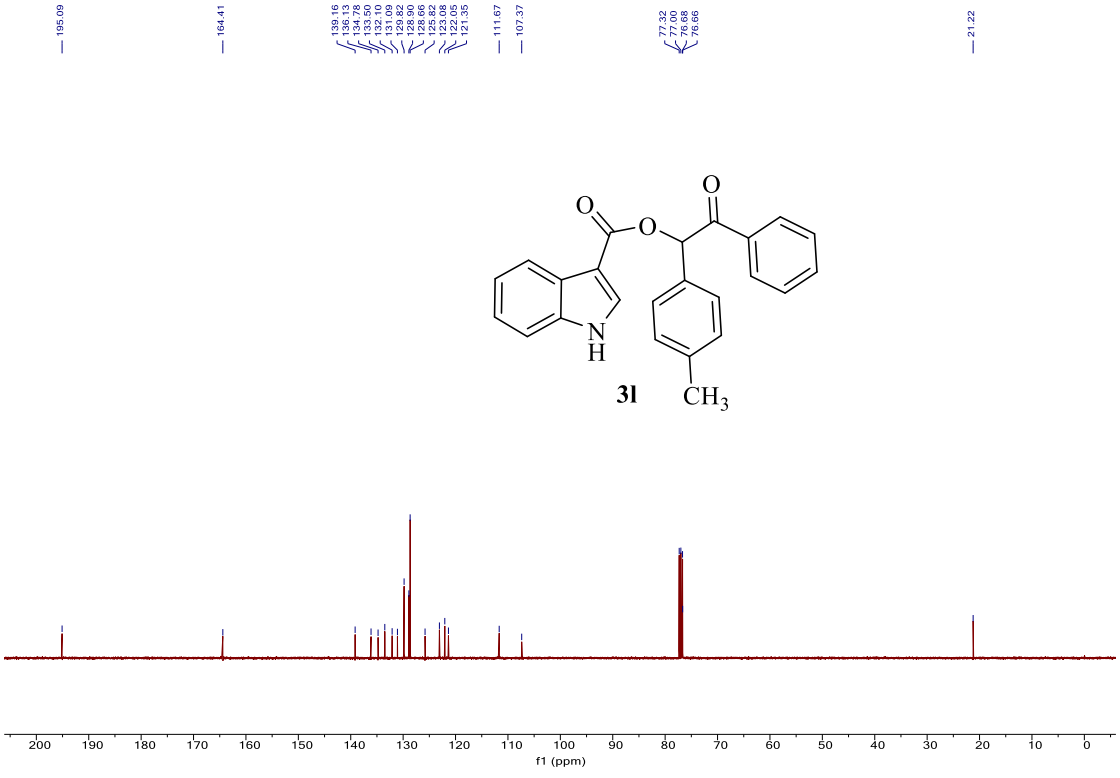
The $^{13}C\{^{1}H\}$ NMR spectrum of **3k** (100 MHz, $CDCl_3$)



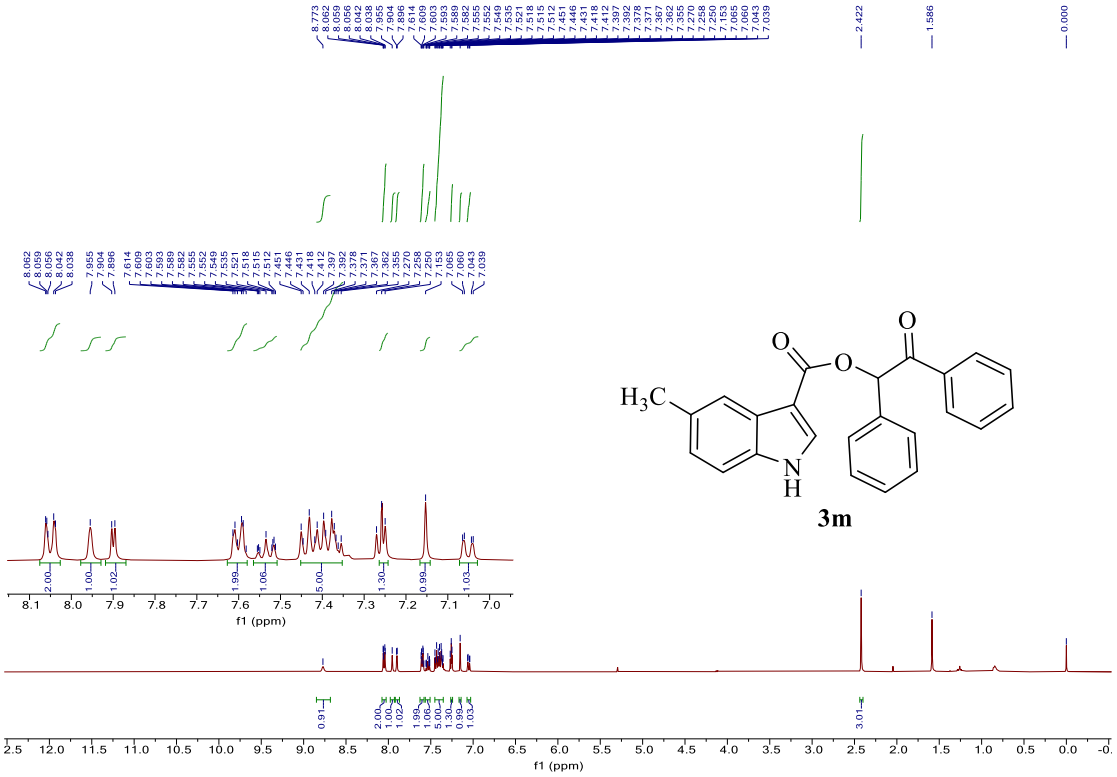
The ^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



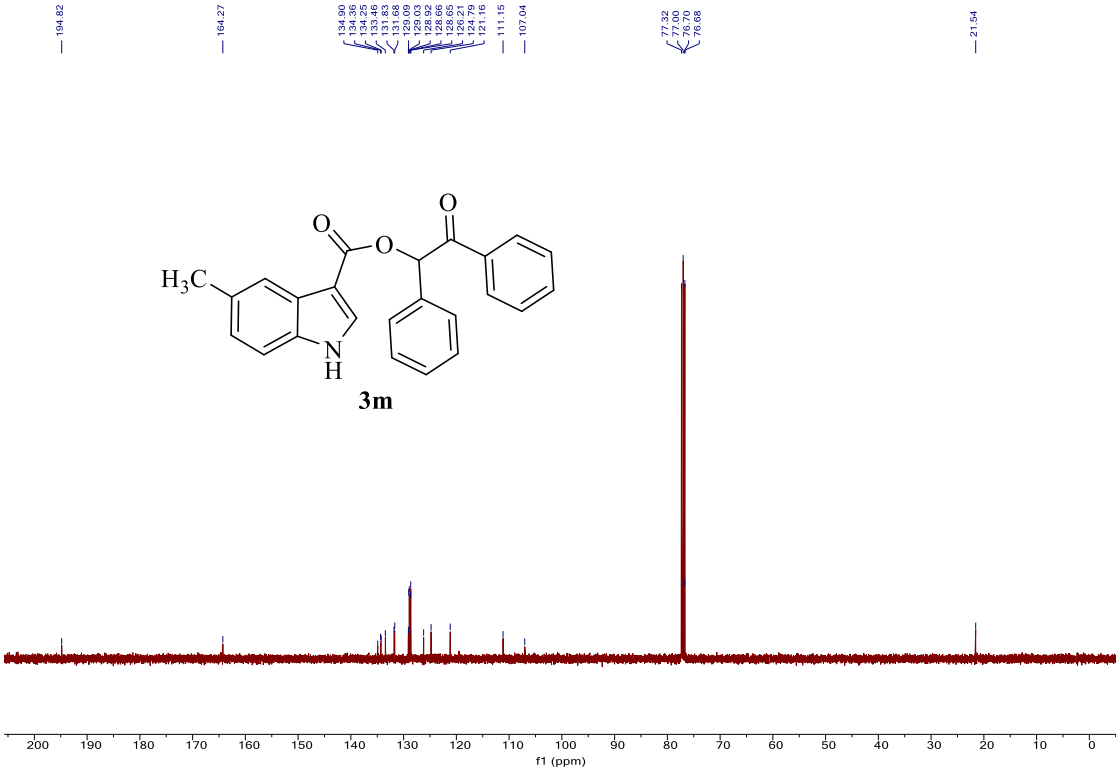
The $^{13}C\{^{1}H\}$ NMR spectrum of **3l** (100 MHz, $CDCl_3$)



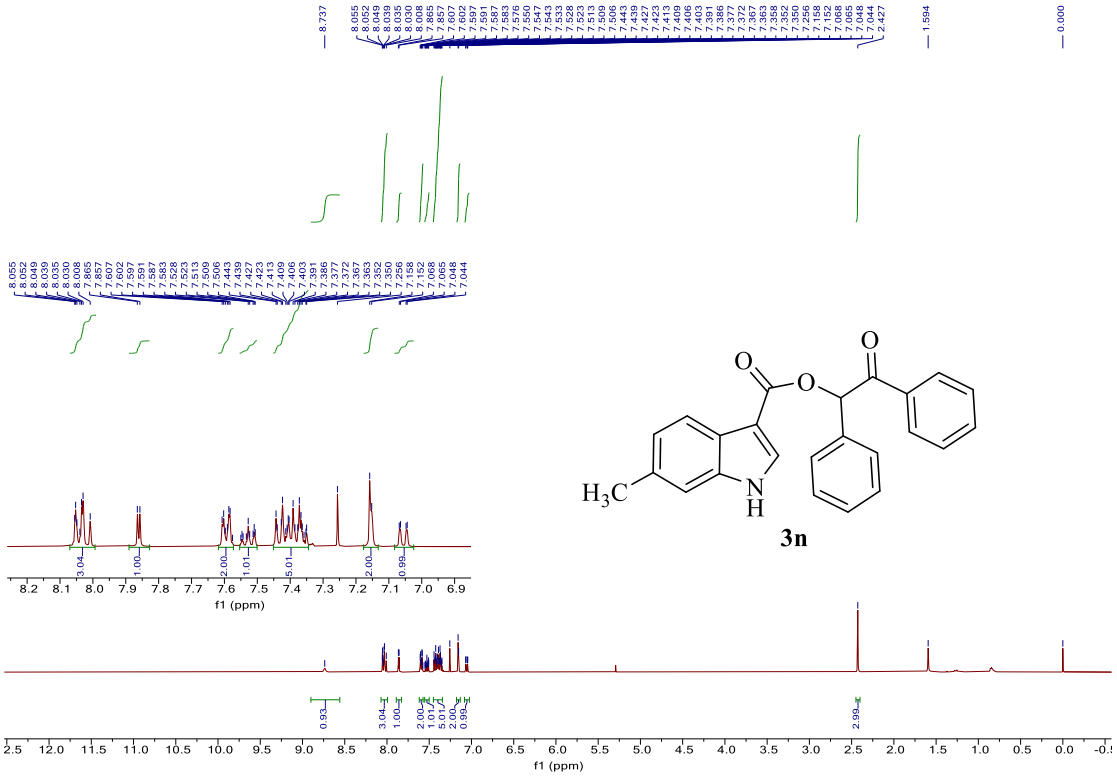
The ^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



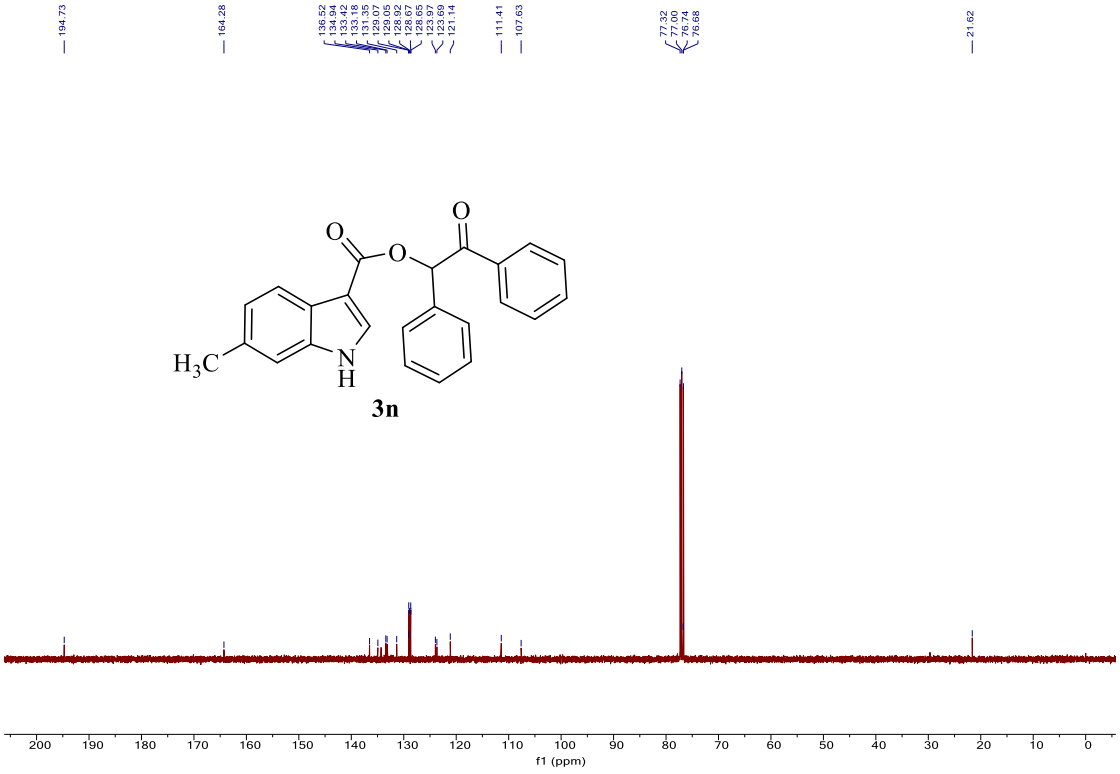
The $^{13}C\{^{1}H\}$ NMR spectrum of **3m** (100 MHz, $CDCl_3$)



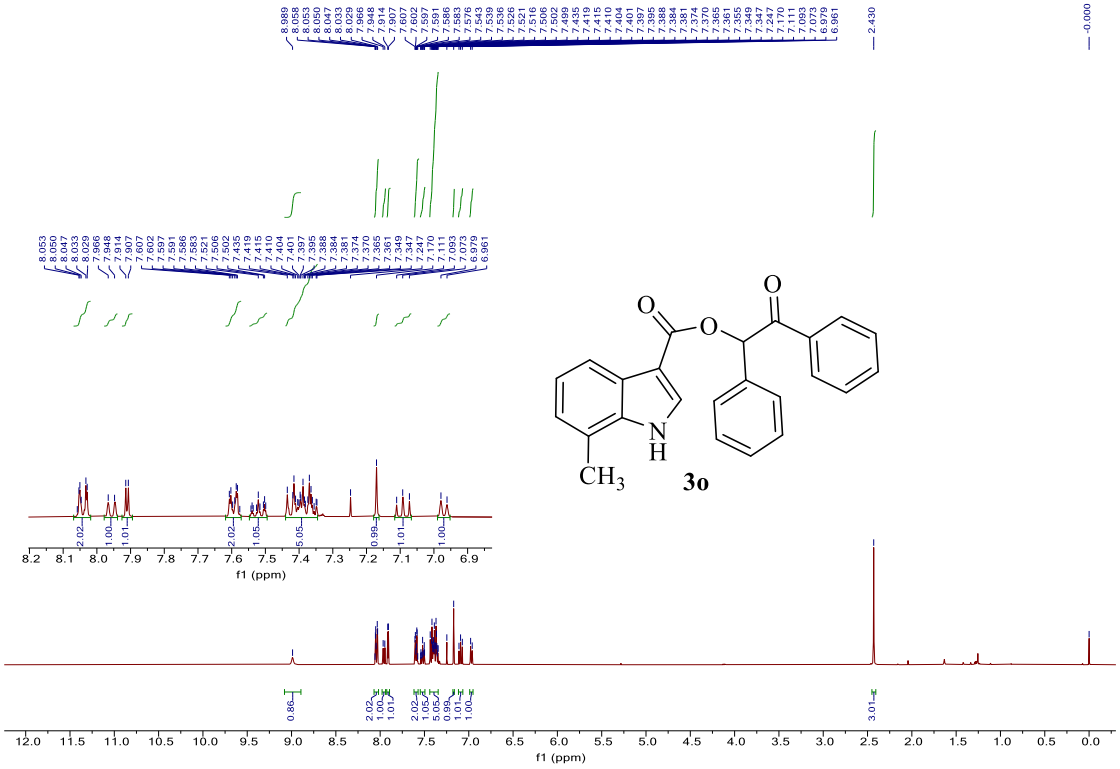
The ^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)



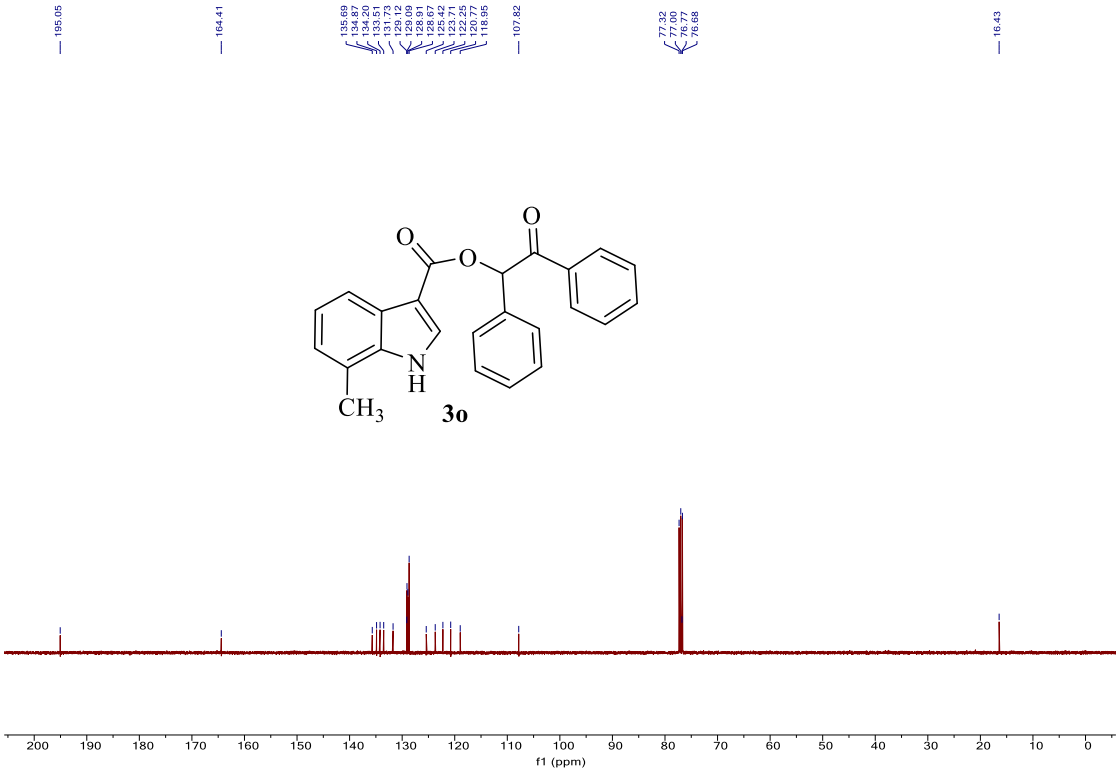
The $^{13}C\{^{1}H\}$ NMR spectrum of **3n** (100 MHz, $CDCl_3$)



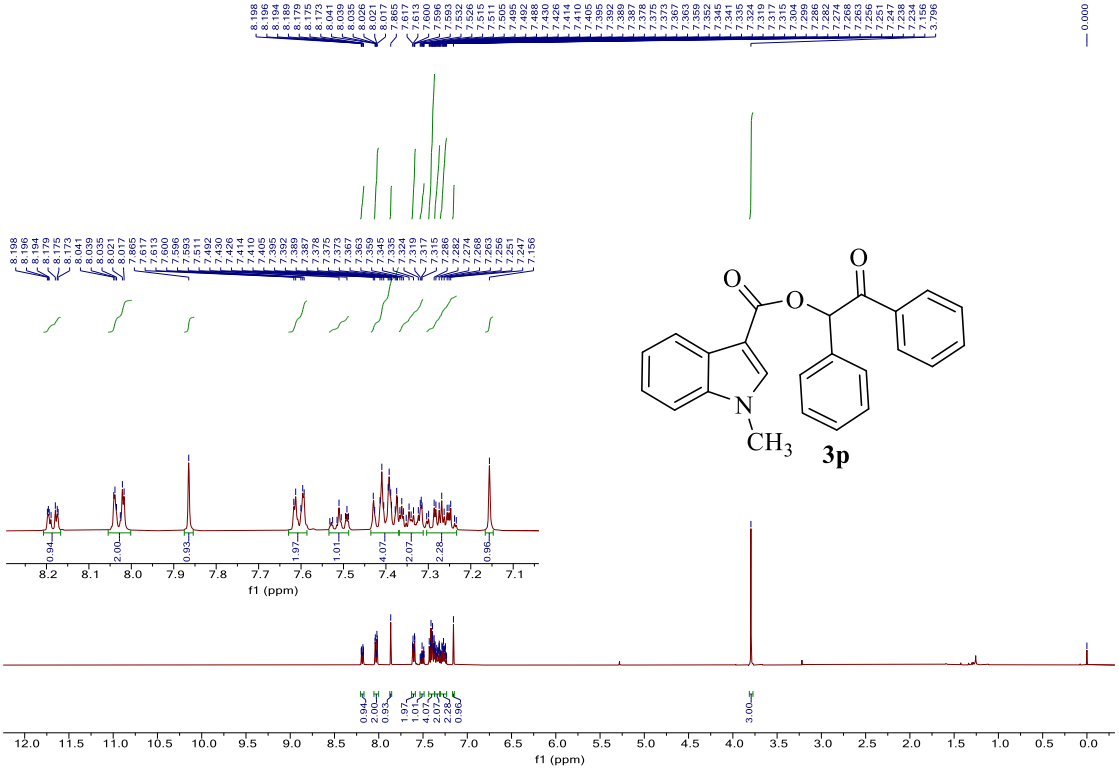
The ^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)



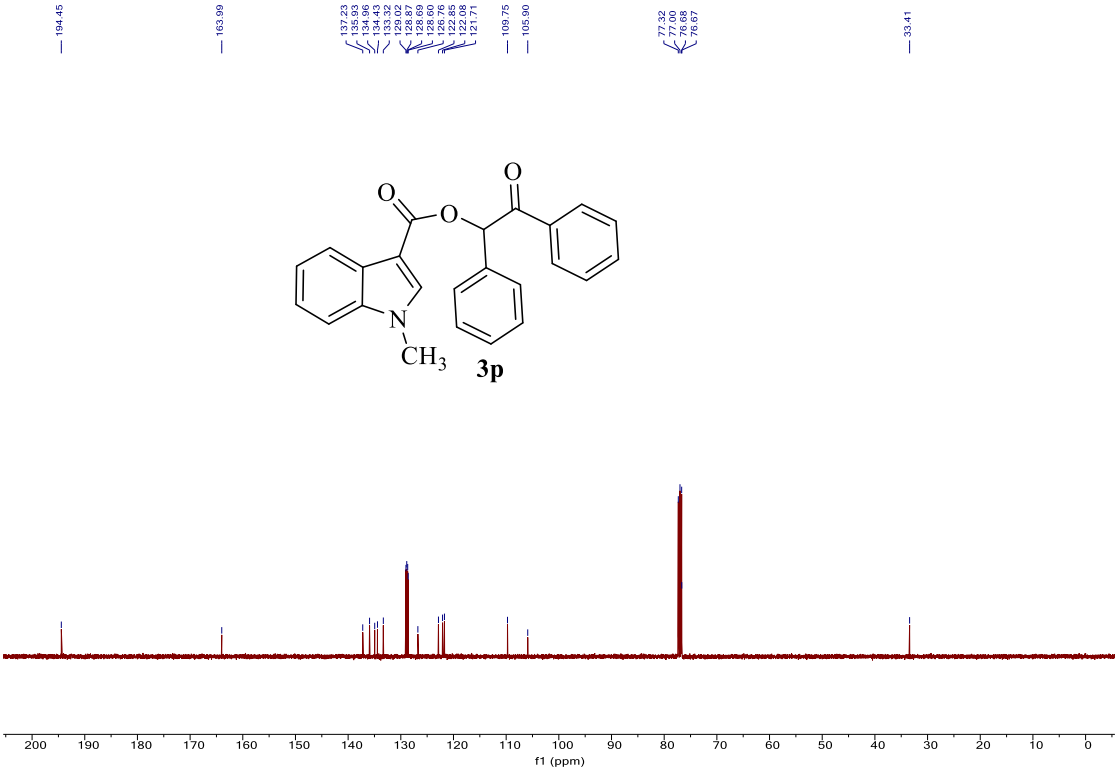
The $^{13}C\{^{1}H\}$ NMR spectrum of **3o** (100 MHz, $CDCl_3$)



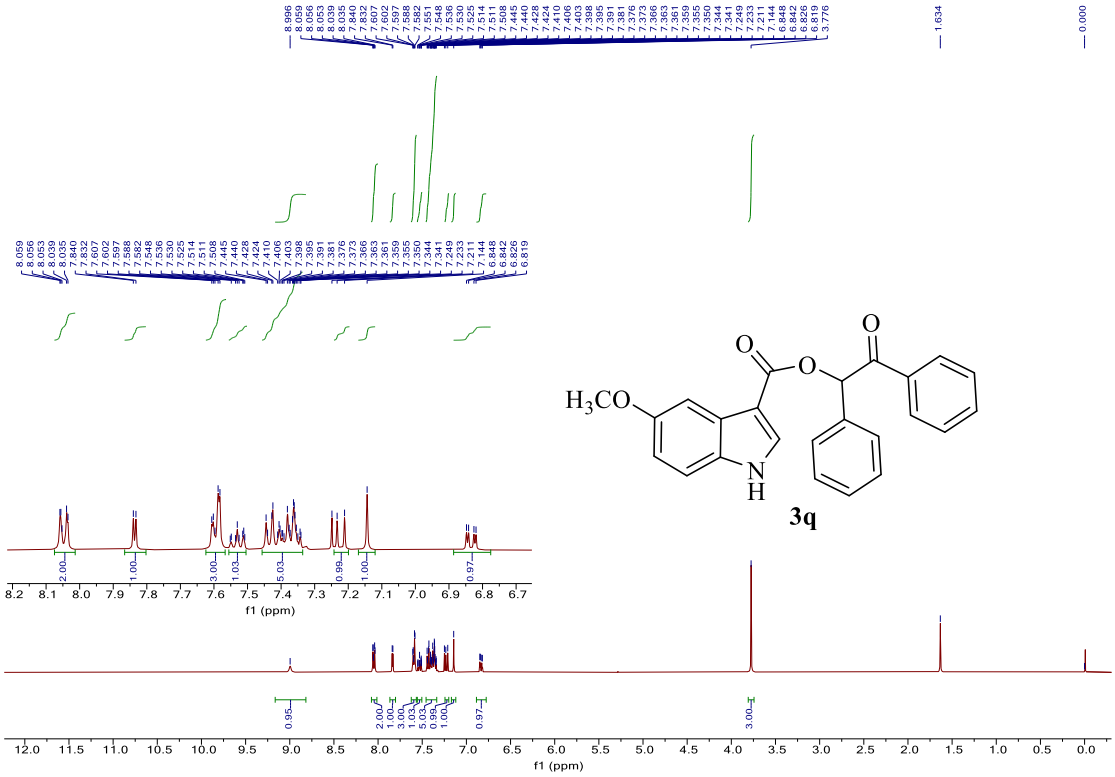
The ^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)



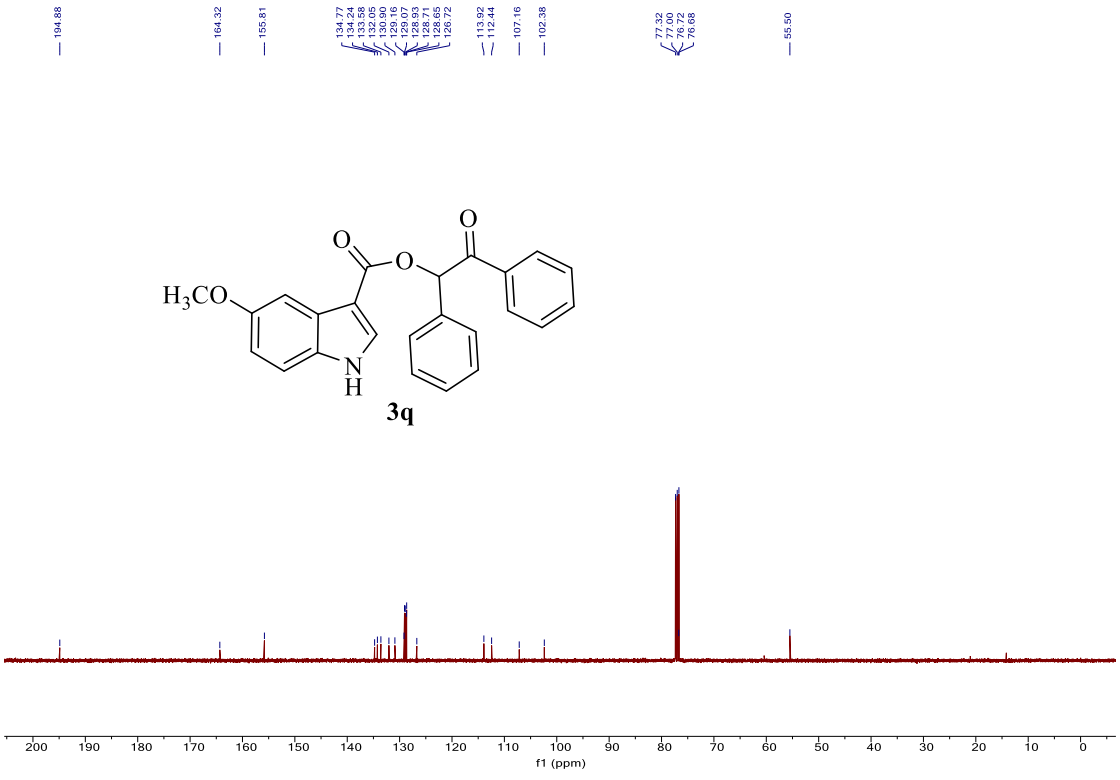
The $^{13}C\{^{1}H\}$ NMR spectrum of **3p** (100 MHz, $CDCl_3$)



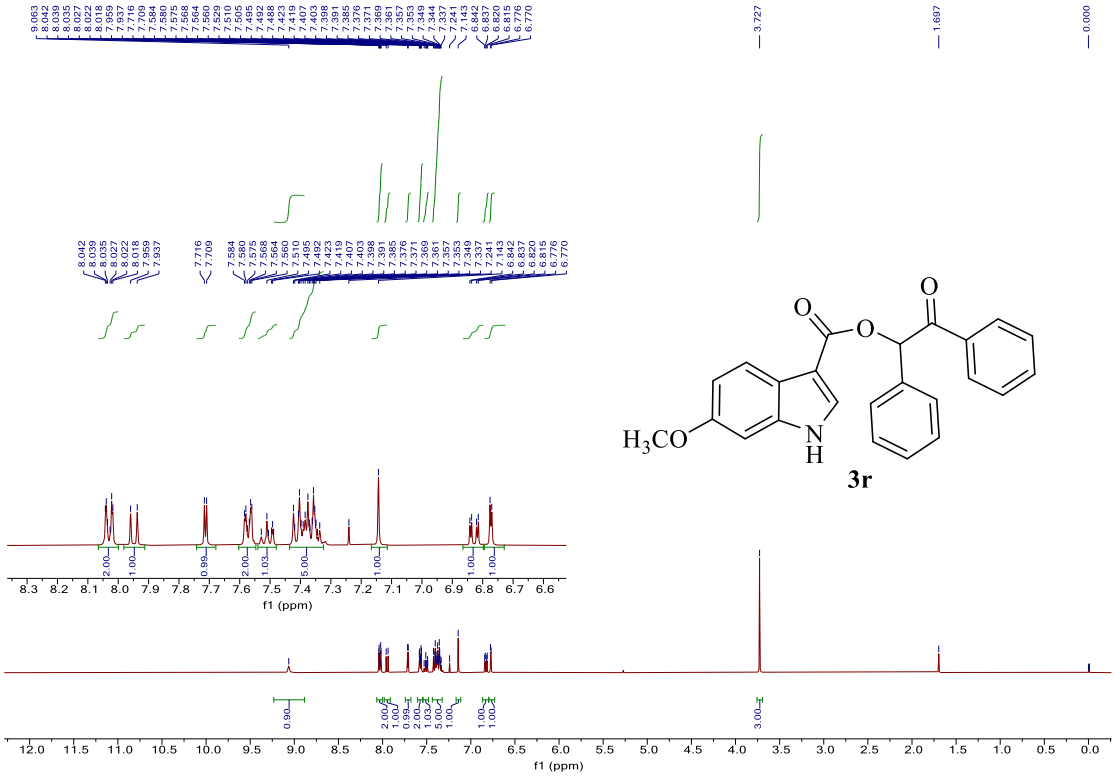
The ^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)



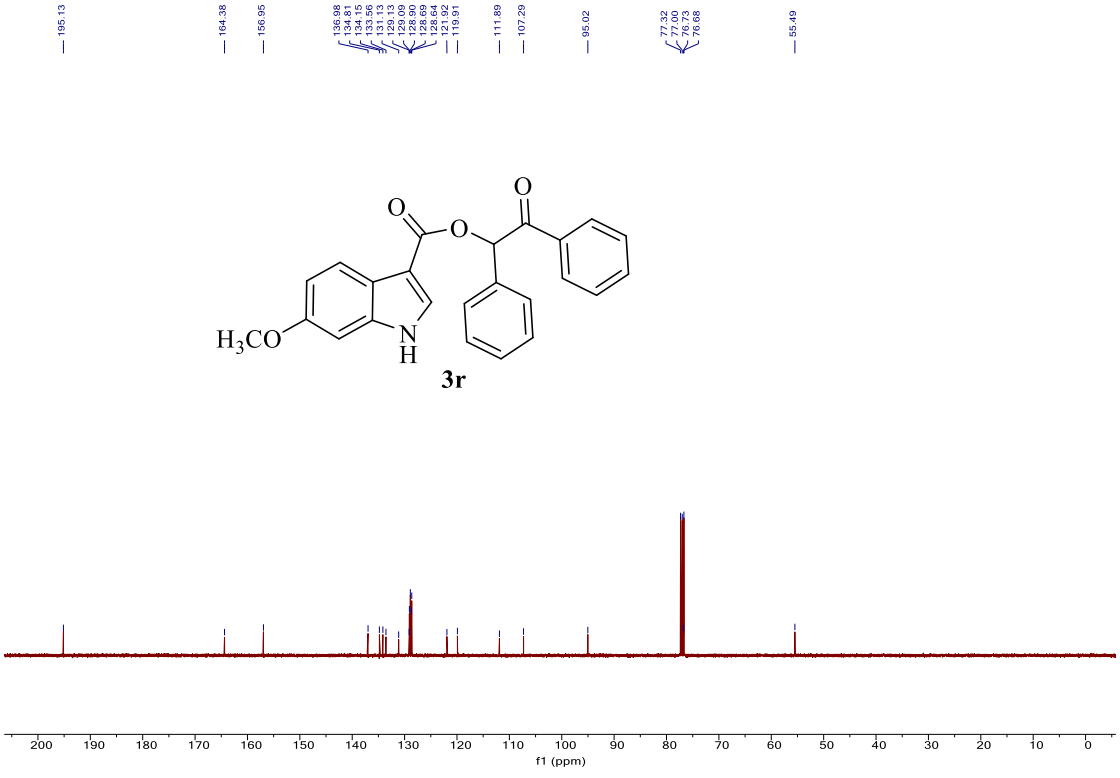
The $^{13}C\{^{1}H\}$ NMR spectrum of **3q** (100 MHz, $CDCl_3$)



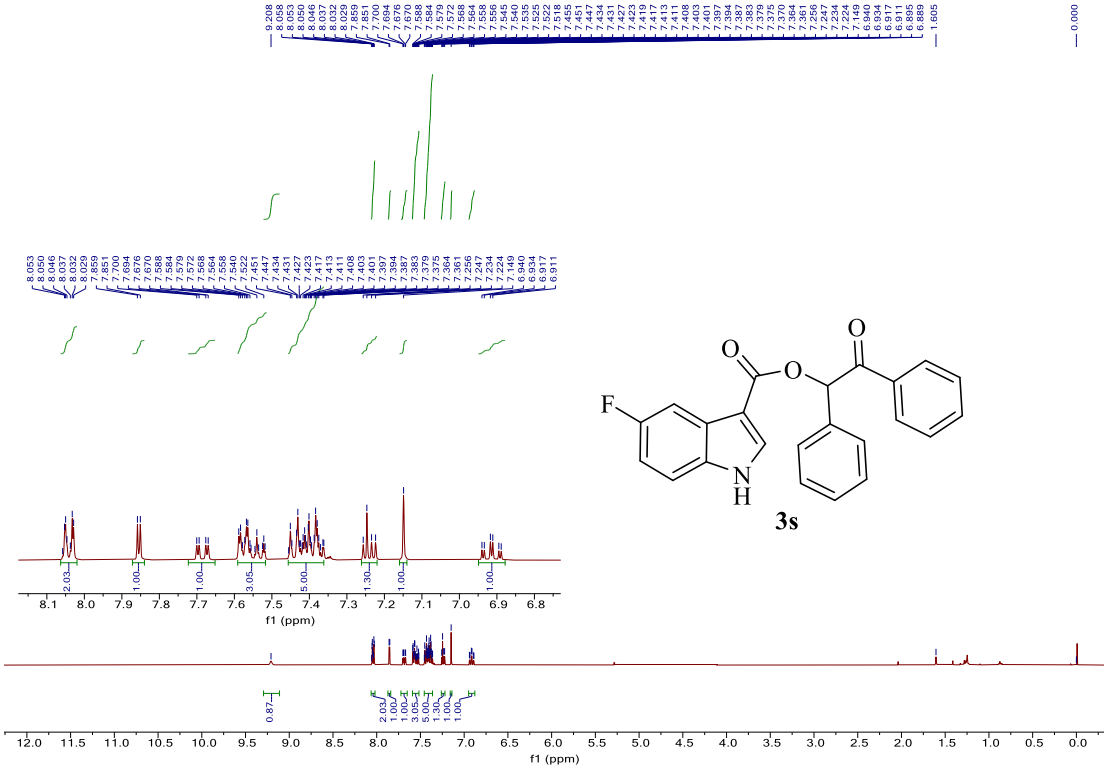
The ^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$)



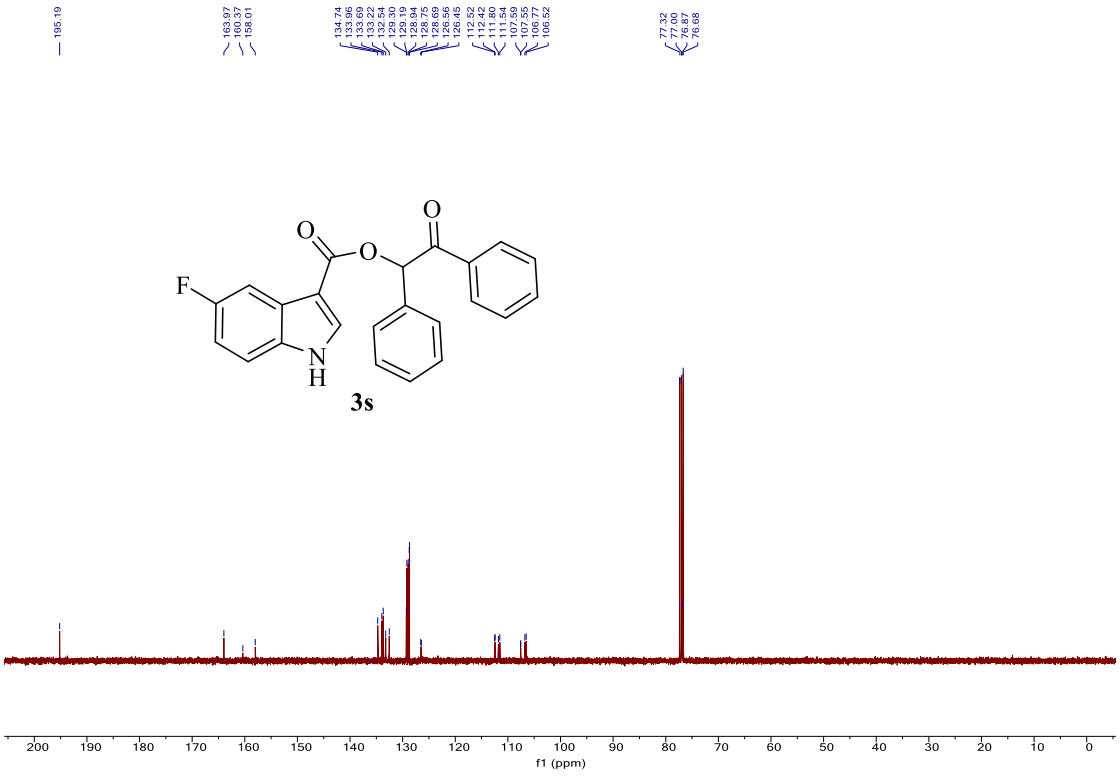
The $^{13}C\{^{1}H\}$ NMR spectrum of **3r** (100 MHz, $CDCl_3$)



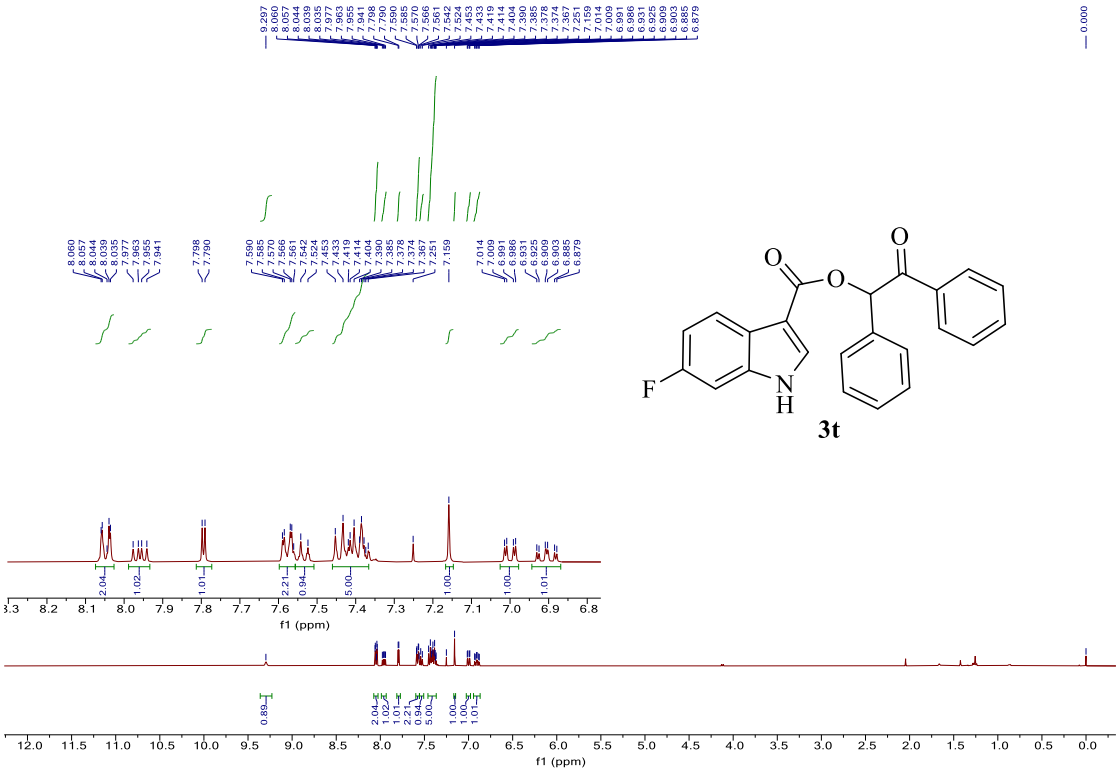
The ^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$)



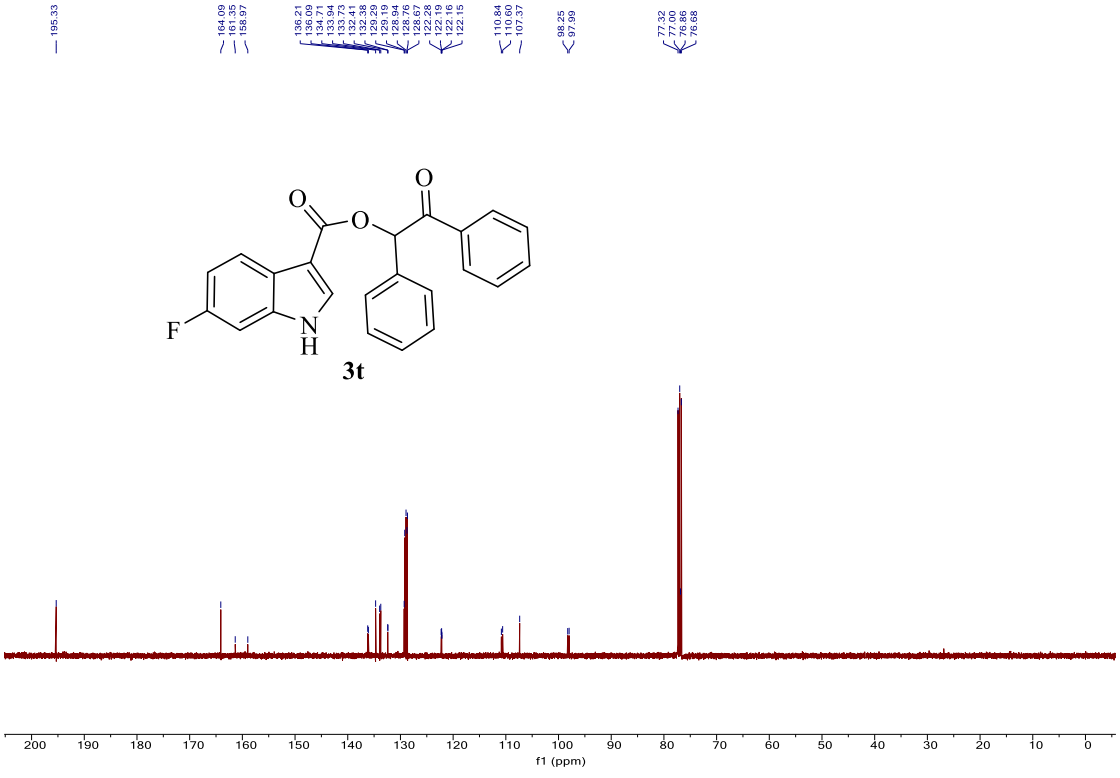
The $^{13}C\{^{1}H\}$ NMR spectrum of **3s** (100 MHz, $CDCl_3$)



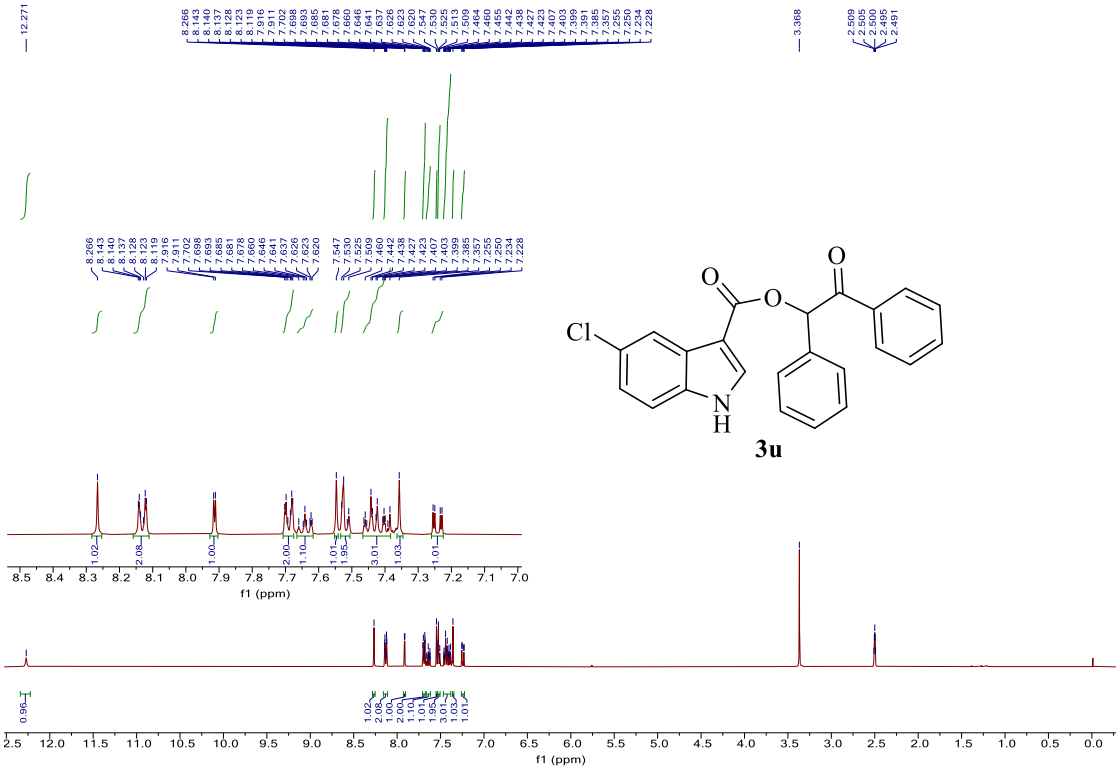
The ^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$)



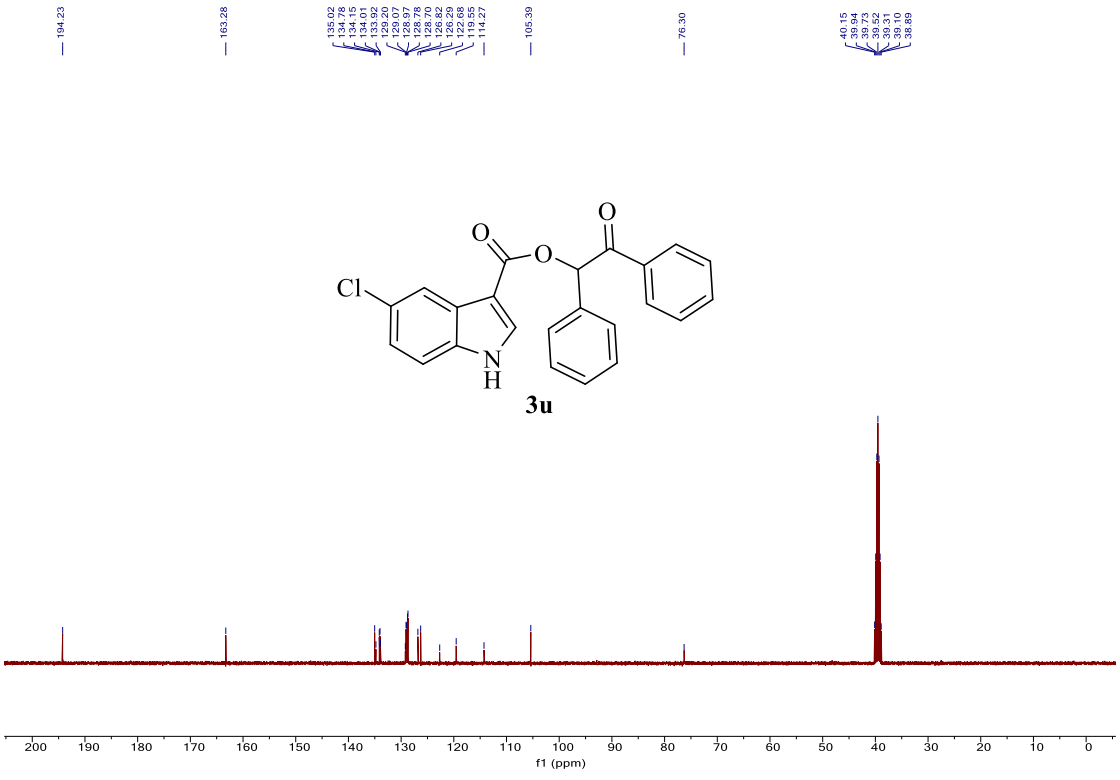
The $^{13}C\{^{1}H\}$ NMR spectrum of **3t** (100 MHz, $CDCl_3$)



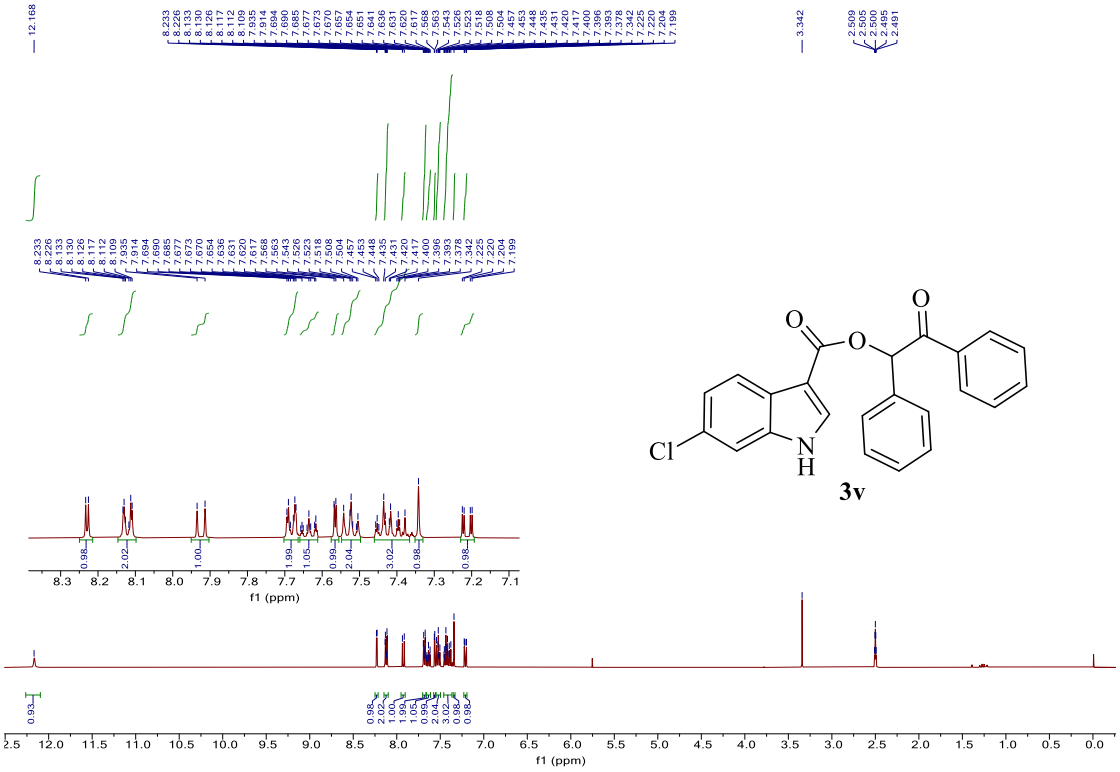
The ^{1}H NMR spectrum of **3u** (400 MHz, DMSO-d_6)



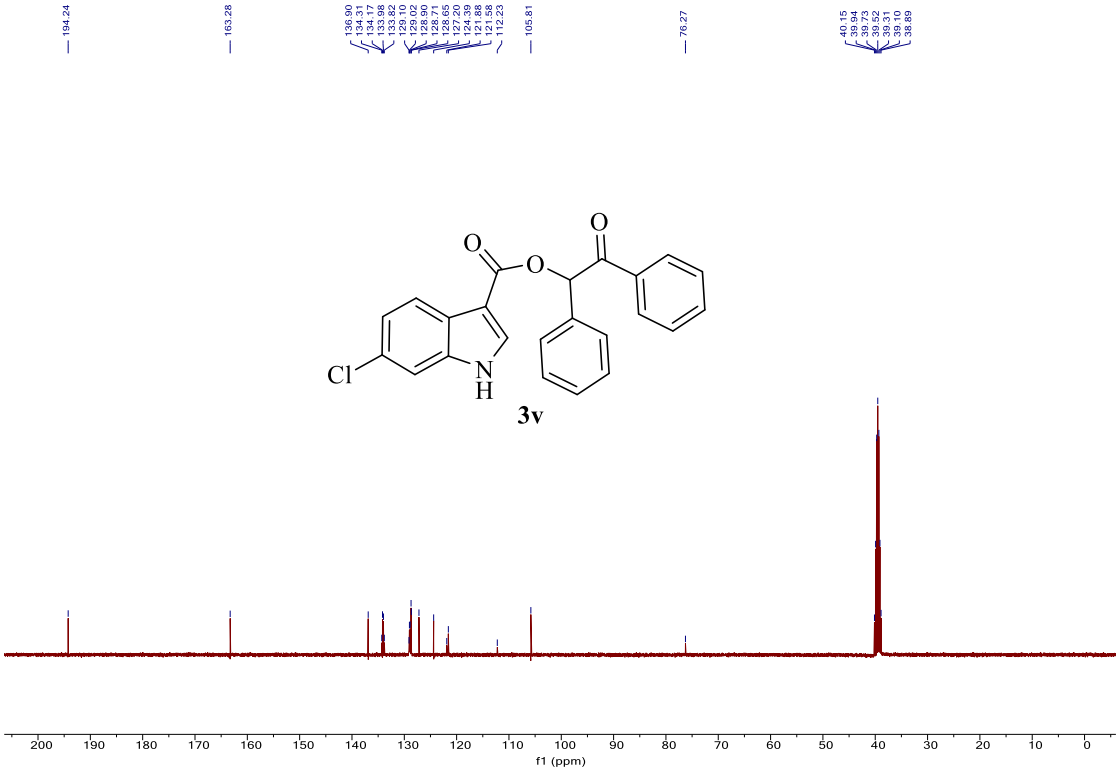
The $^{13}C\{^{1}H\}$ NMR spectrum of **3u** (100 MHz, DMSO-d_6)



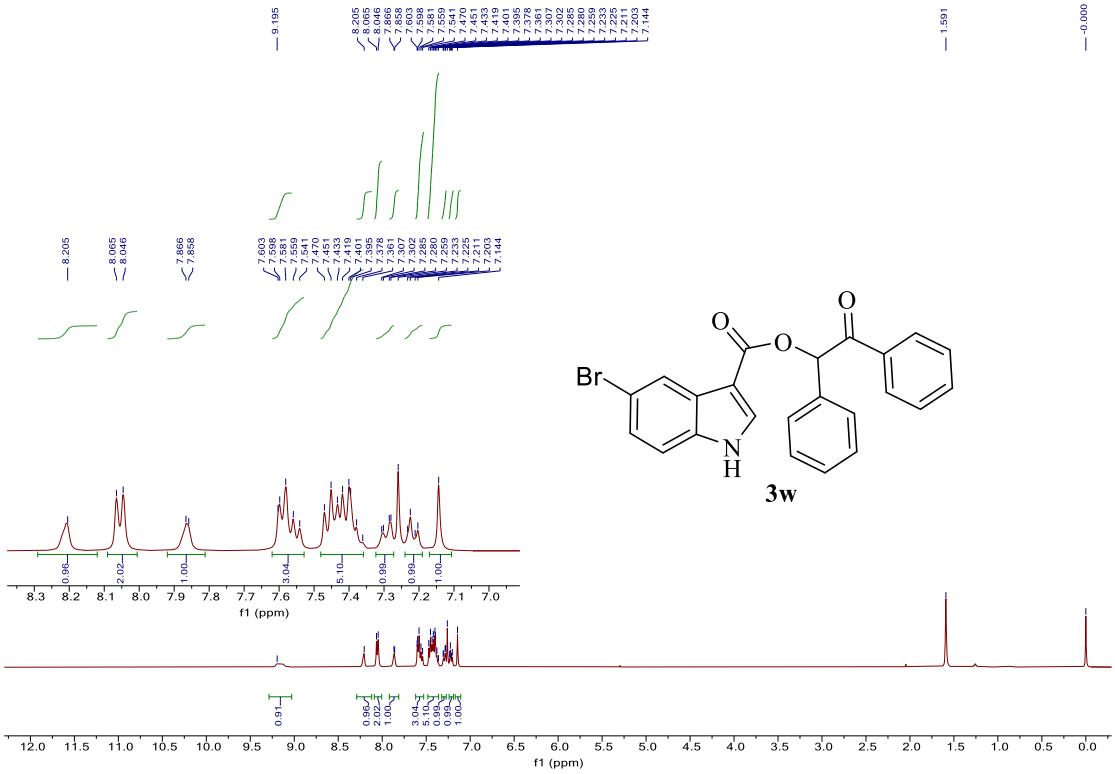
The ^{1}H NMR spectrum of **3v** (400 MHz, DMSO-d_6)



The $^{13}C\{^{1}H\}$ NMR spectrum of **3v** (100 MHz, DMSO-d_6)

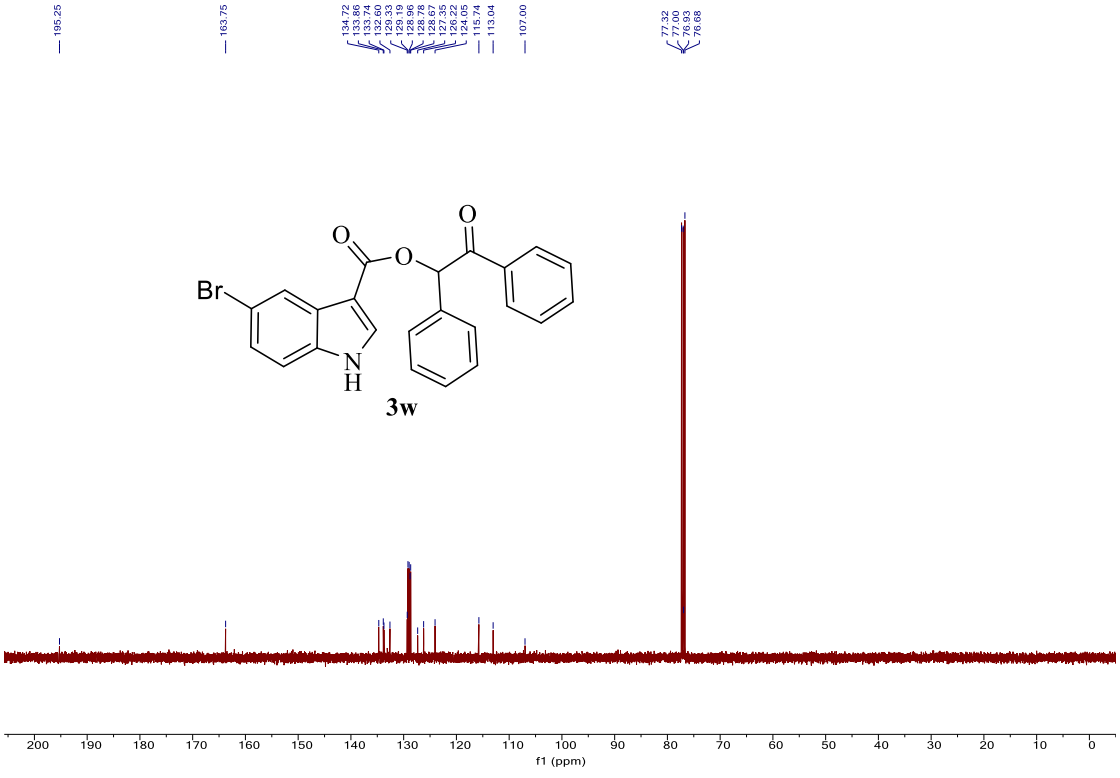


The ^{1}H NMR spectrum of **3w** (400 MHz, $CDCl_3$)



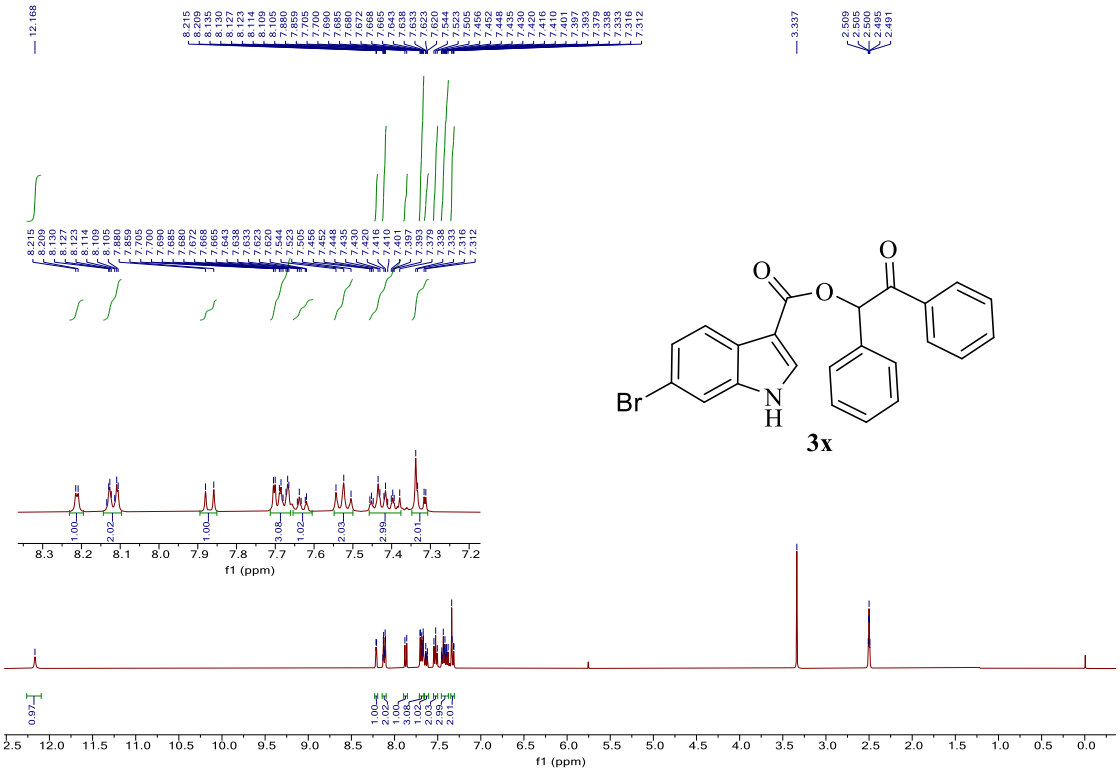
3w

The $^{13}C\{^{1}H\}$ NMR spectrum of **3w** (100 MHz, $CDCl_3$)

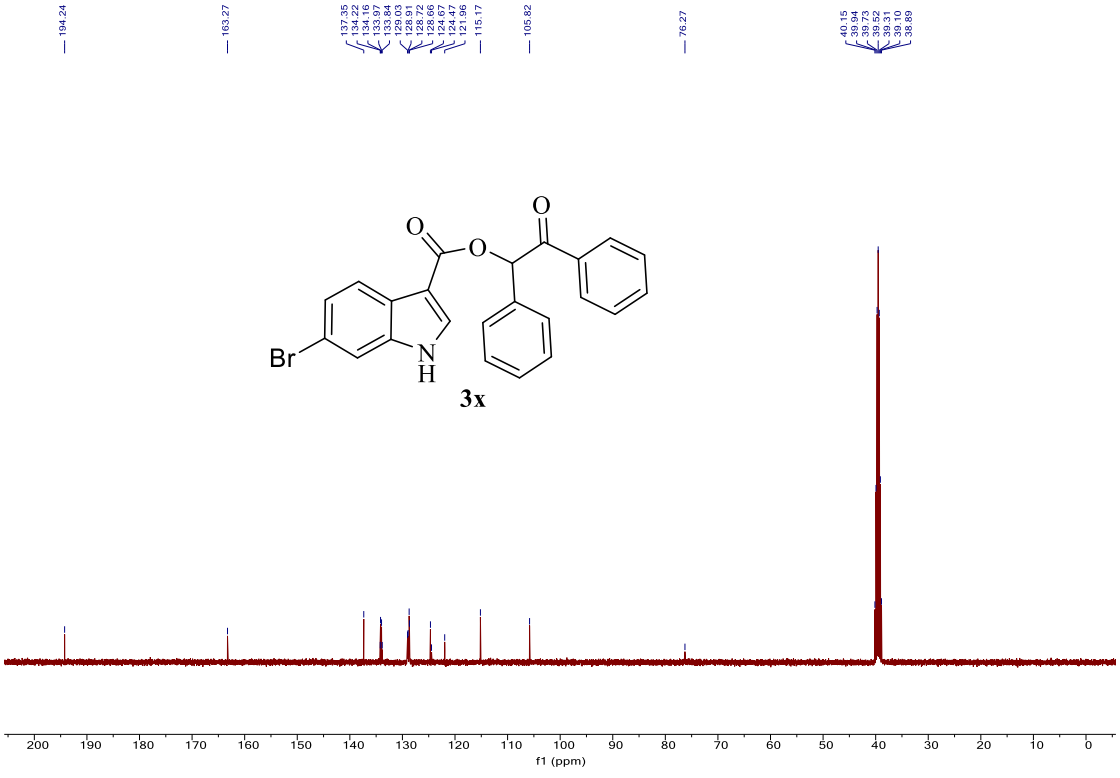


3w

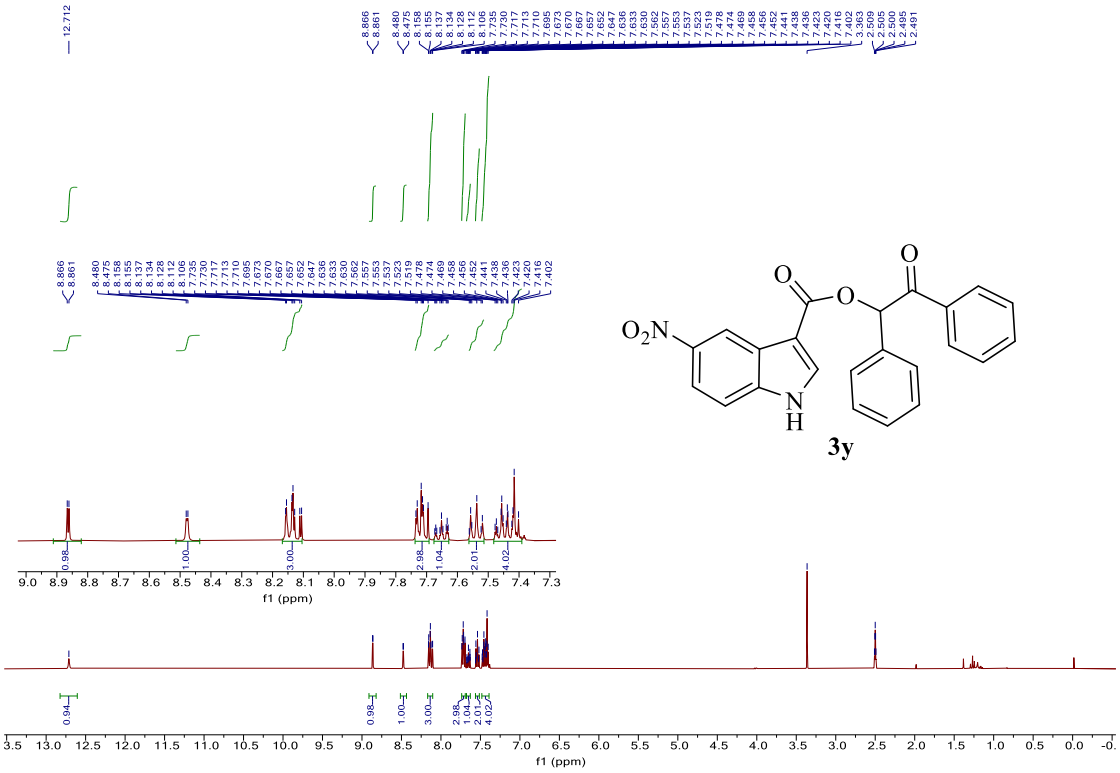
The ^{1}H NMR spectrum of **3x** (400 MHz, DMSO-d_6)



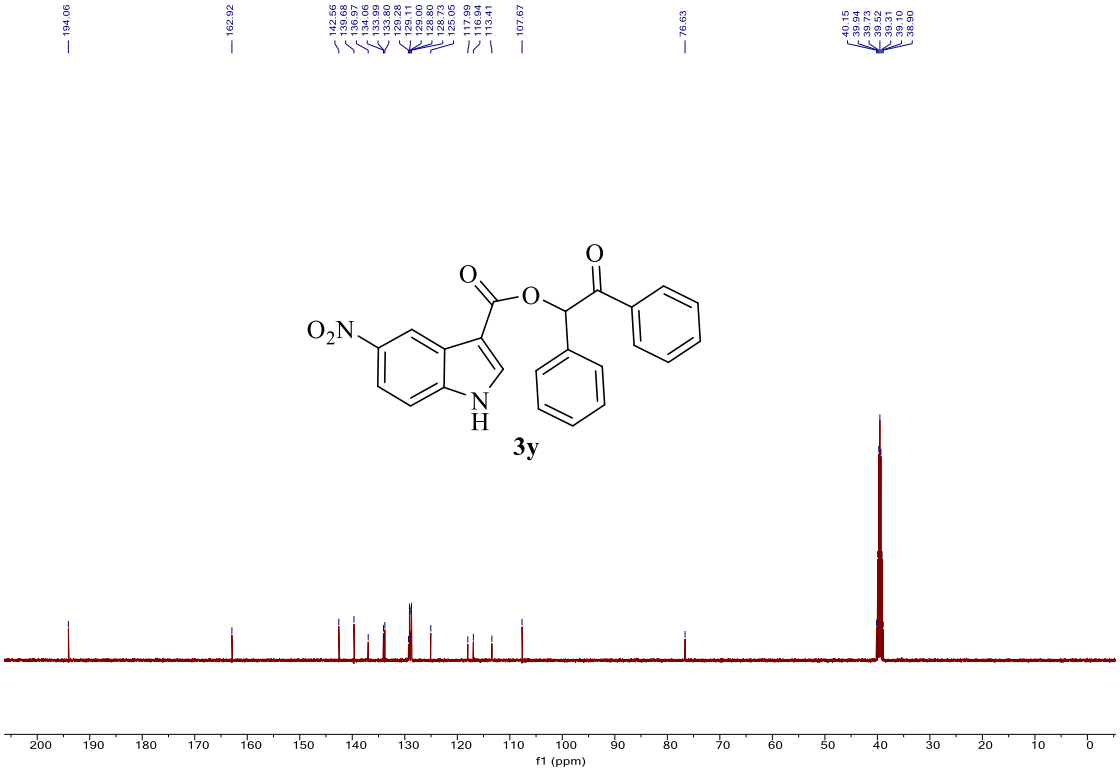
The $^{13}C\{^{1}H\}$ NMR spectrum of **3x** (100 MHz, DMSO-d_6)



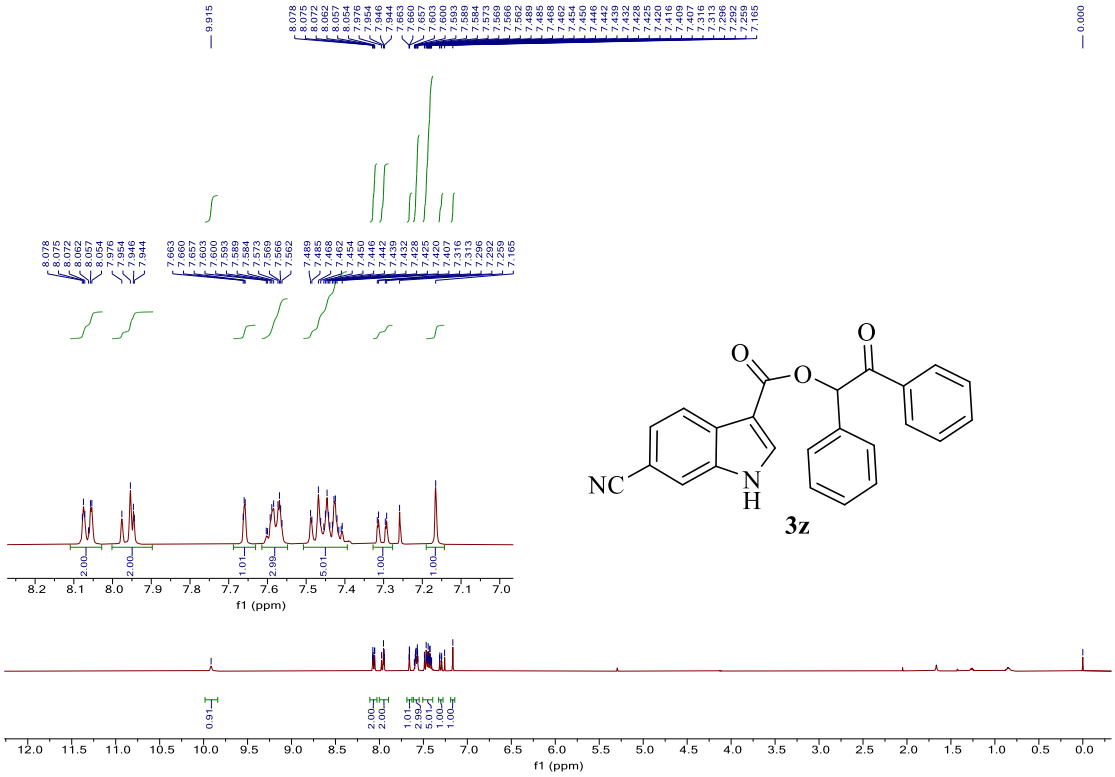
The ^{1}H NMR spectrum of **3y** (400 MHz, DMSO-d_6)



The $^{13}C\{^{1}H\}$ NMR spectrum of **3y** (100 MHz, DMSO-d_6)

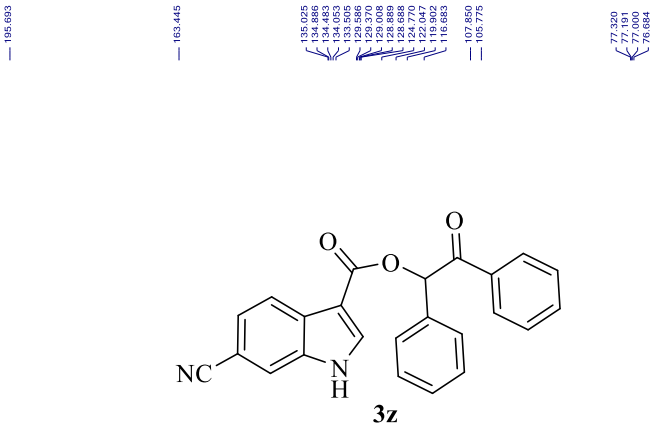


The ^{1}H NMR spectrum of **3z** (400 MHz, $CDCl_3$)



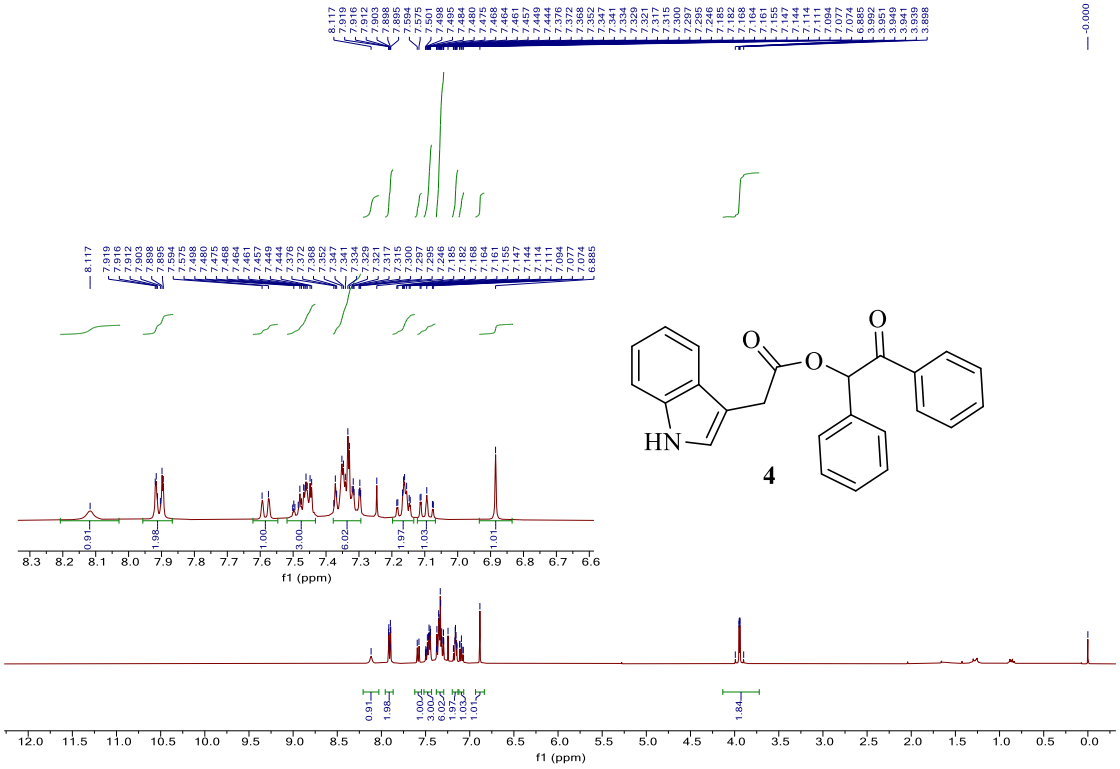
3z

The $^{13}C\{^{1}H\}$ NMR spectrum of **3z** (100 MHz, $CDCl_3$)

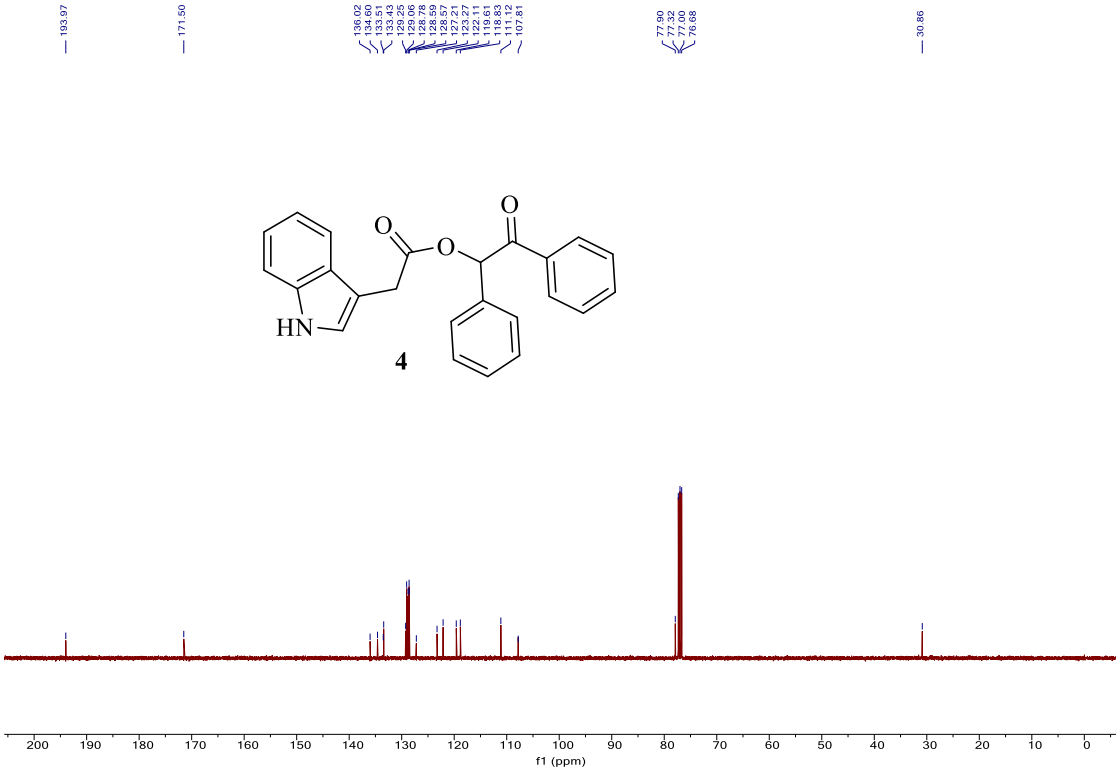


3z

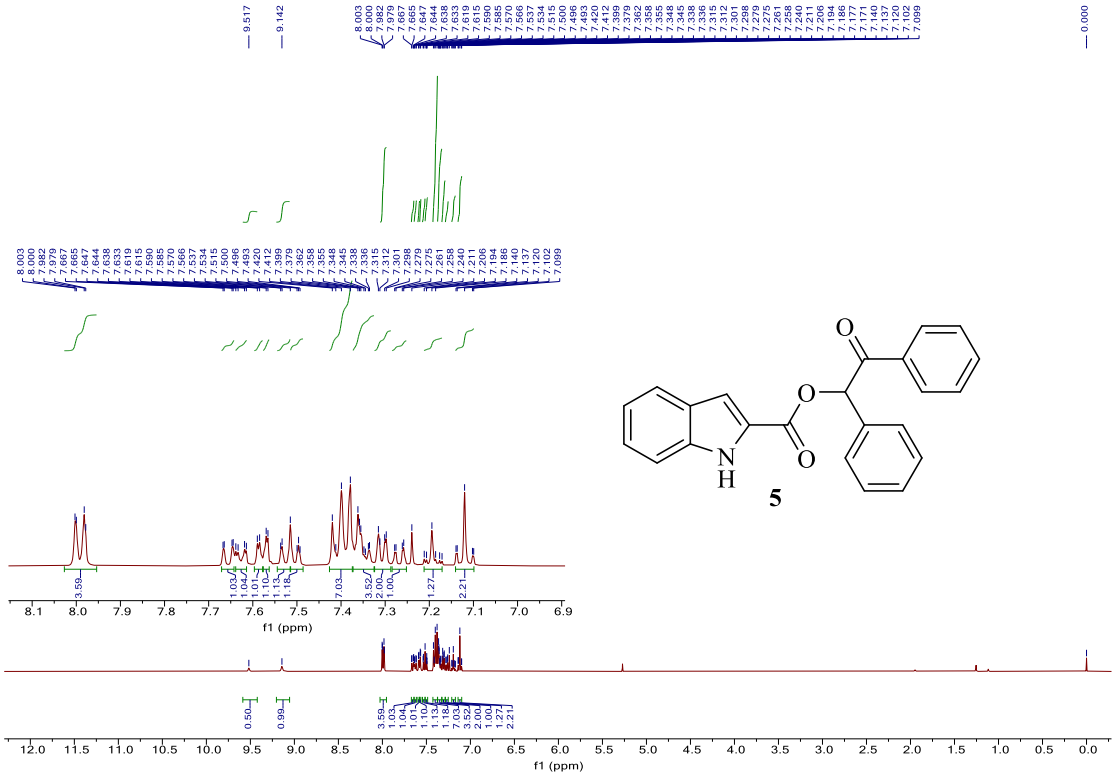
The ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$)



The $^{13}C\{^{1}H\}$ NMR spectrum of **4** (100 MHz, $CDCl_3$)

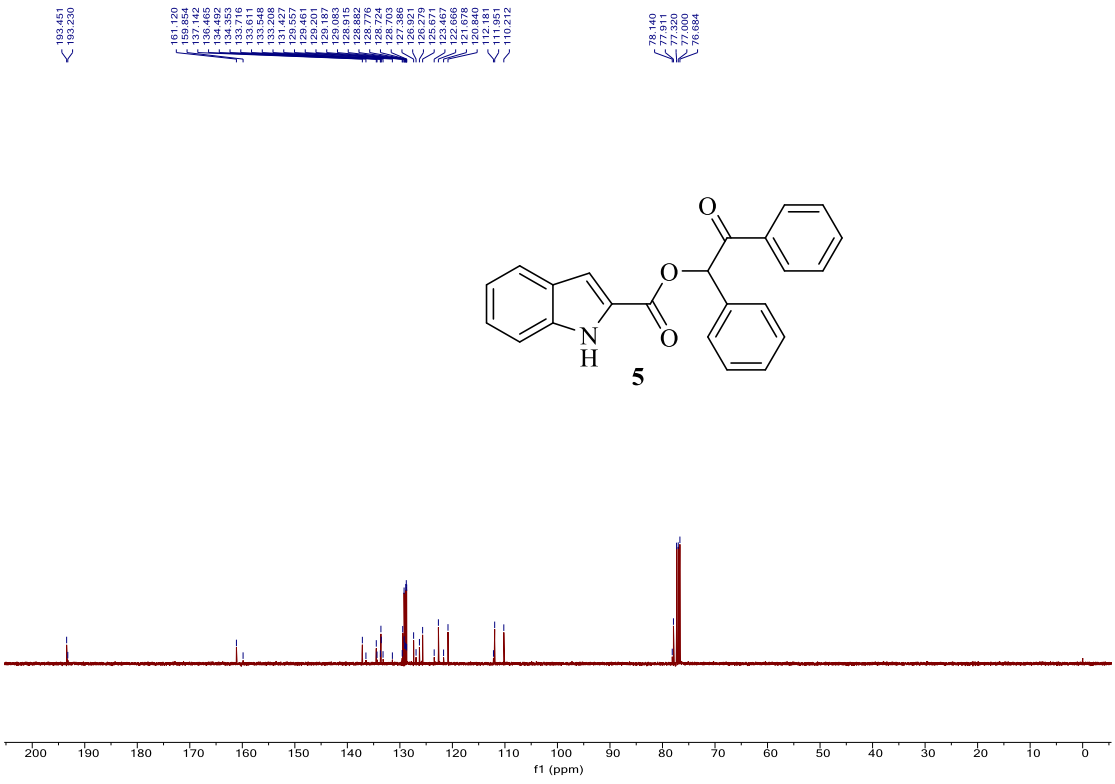


The ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)



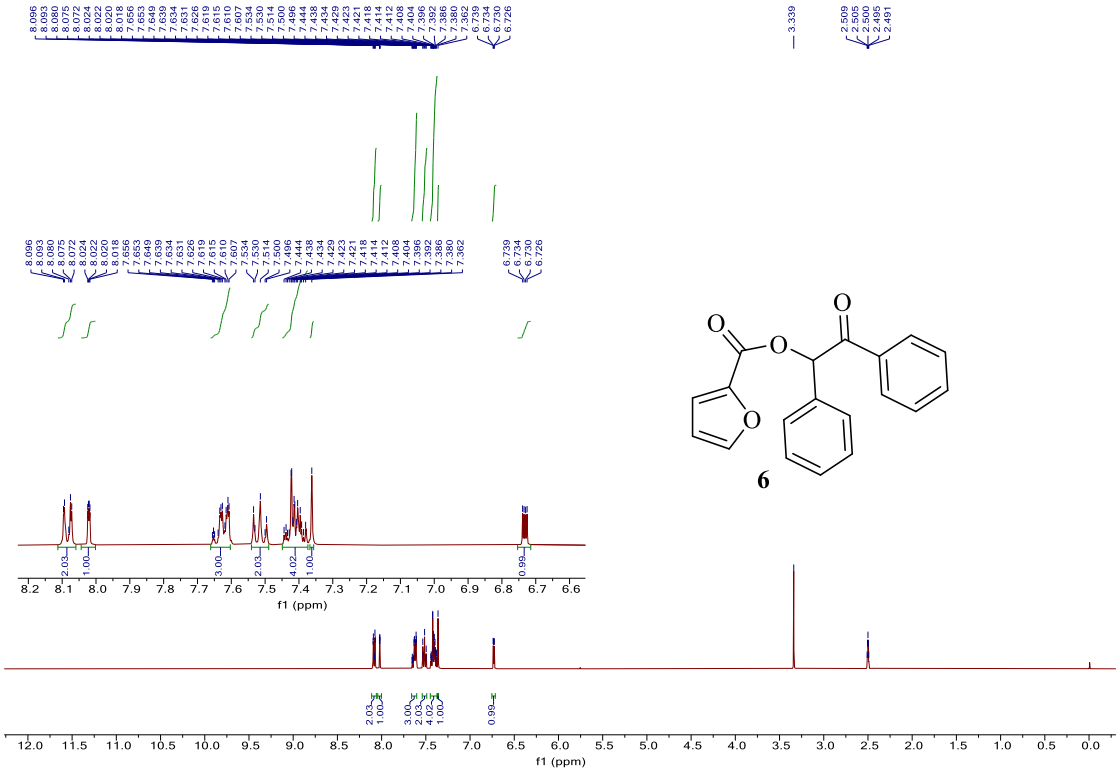
5

The $^{13}C\{^{1}H\}$ NMR spectrum of **5** (100 MHz, $CDCl_3$)



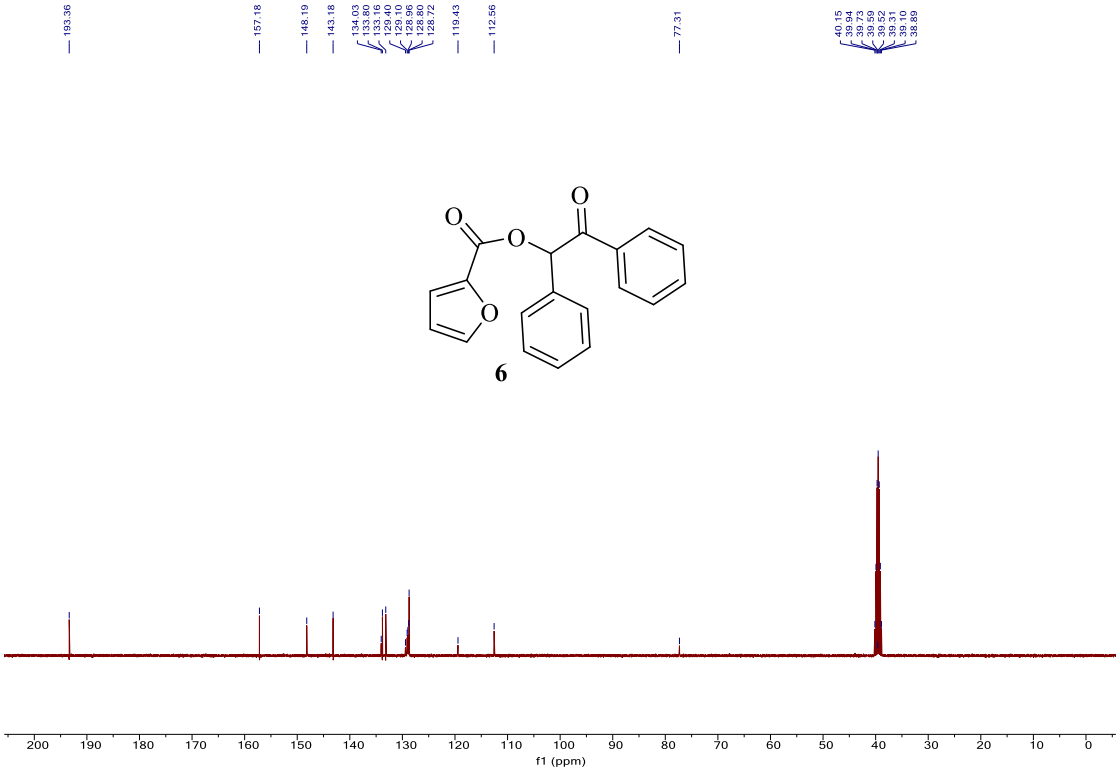
5

The ^{1}H NMR spectrum of **6** (400 MHz, DMSO-d_6)



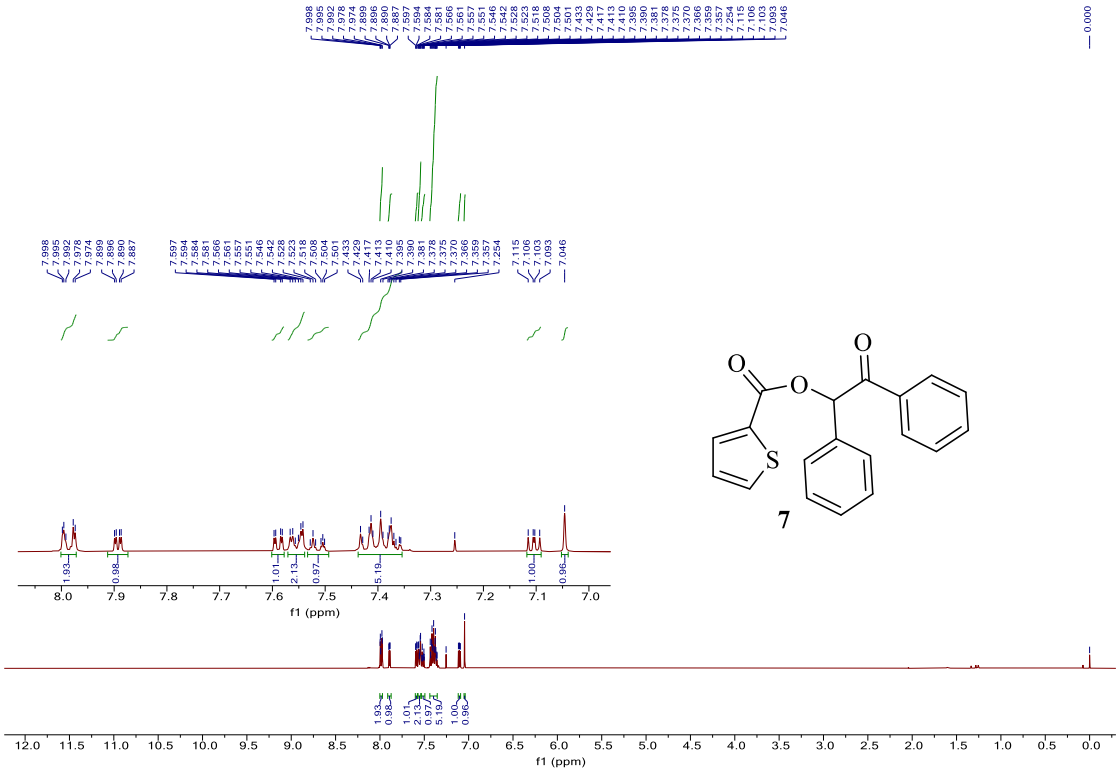
6

The $^{13}C\{^{1}H\}$ NMR spectrum of **6** (100 MHz, DMSO-d_6)

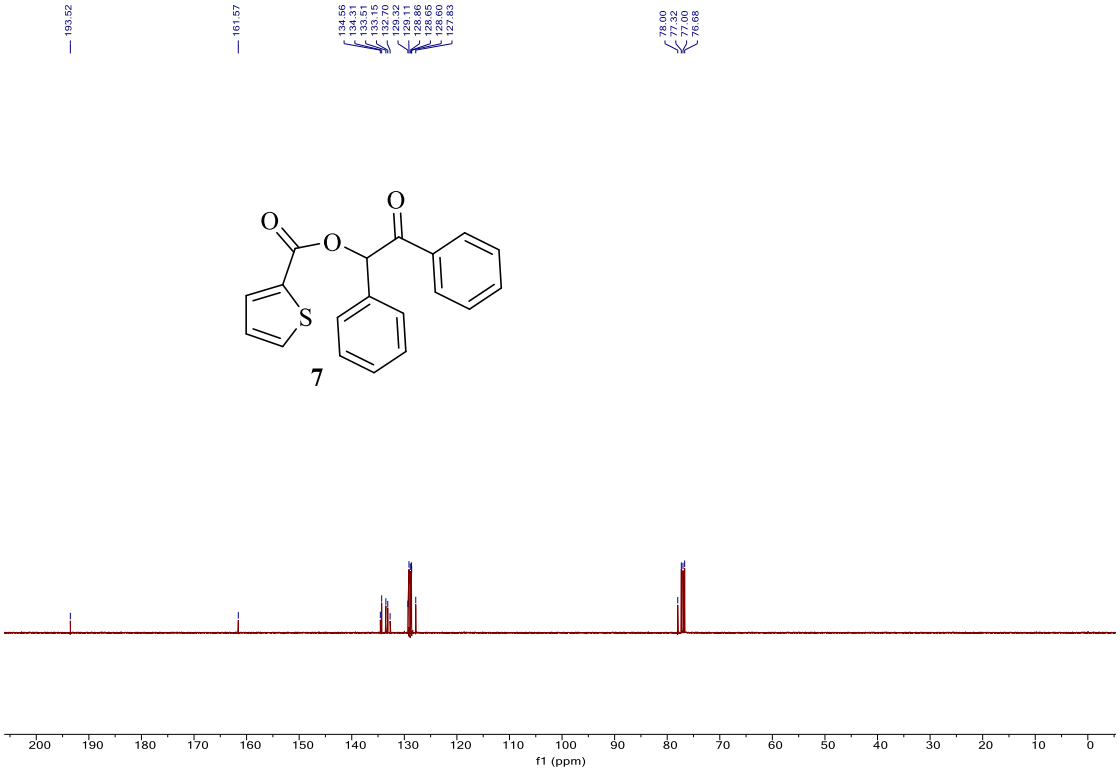


6

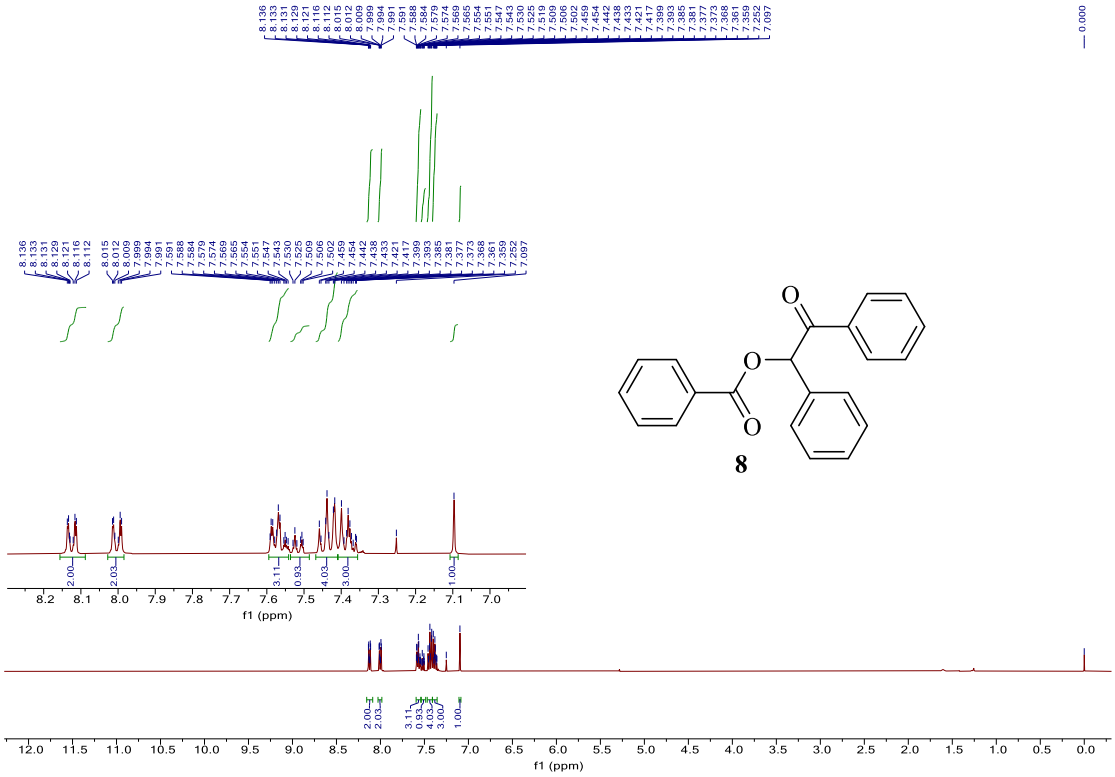
The ^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)



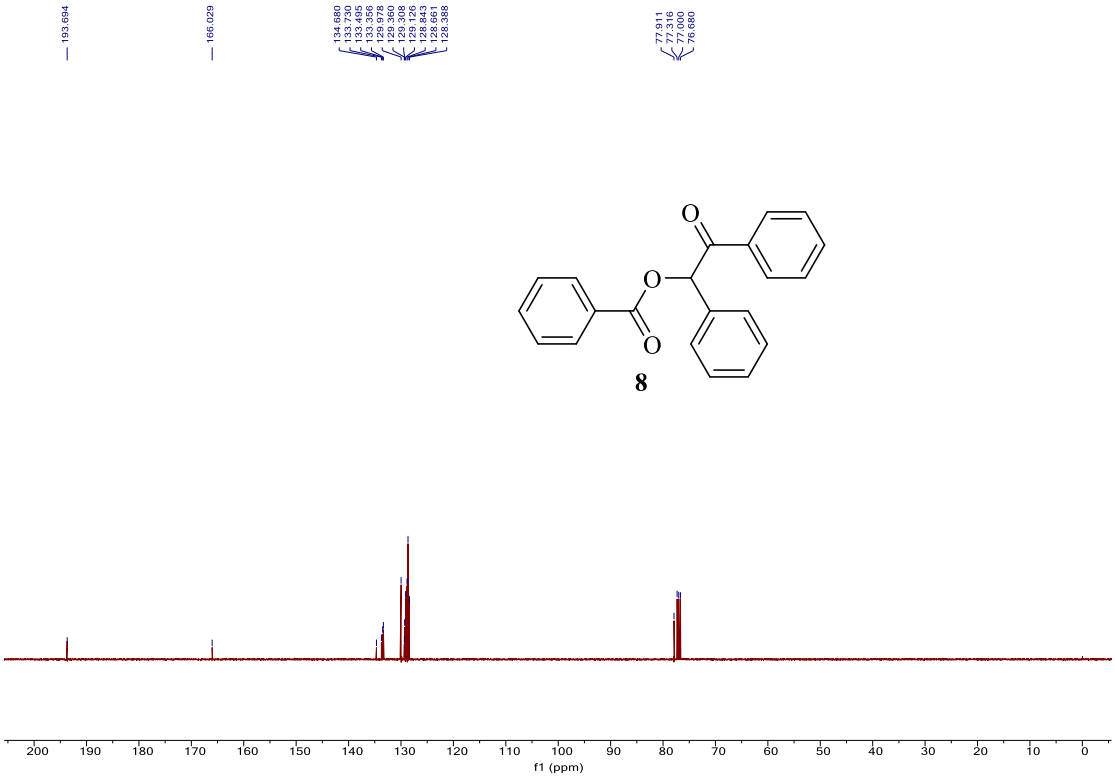
The $^{13}C\{^{1}H\}$ NMR spectrum of **7** (100 MHz, $CDCl_3$)



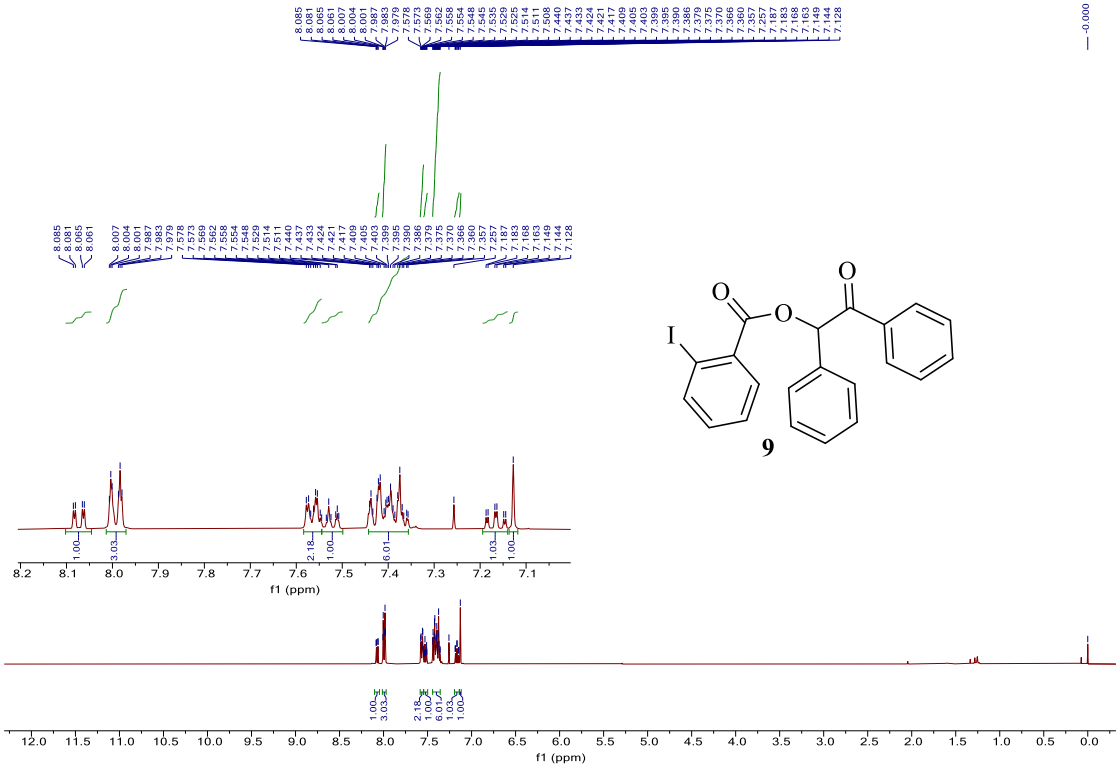
The ^{1}H NMR spectrum of **8** (400 MHz, $CDCl_3$)



The $^{13}C\{^{1}H\}$ NMR spectrum of **8** (100 MHz, $CDCl_3$)

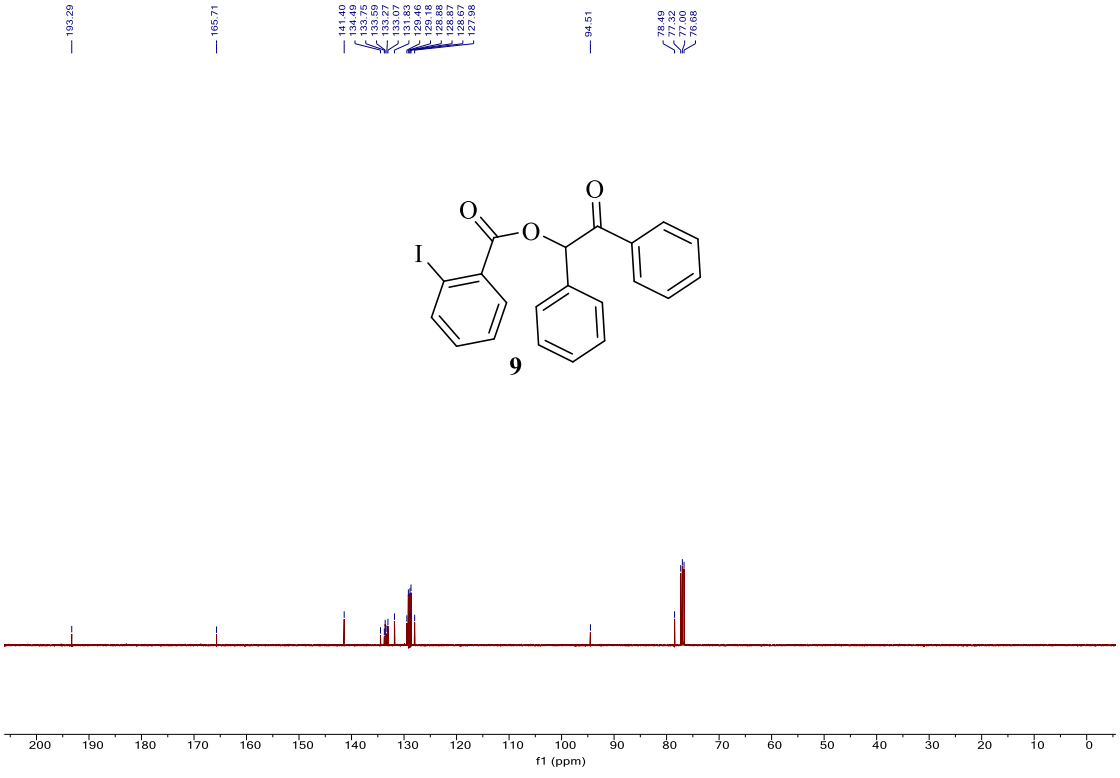


The ^{1}H NMR spectrum of **9** (400 MHz, $CDCl_3$)



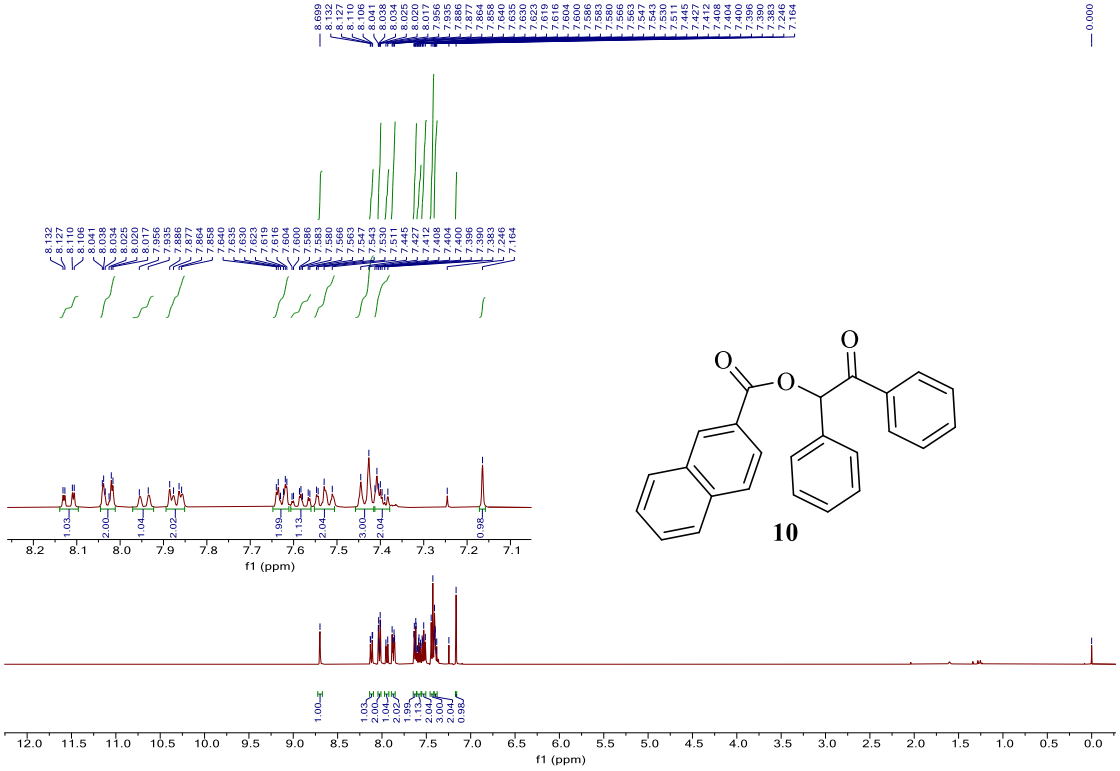
9

The $^{13}C\{^{1}H\}$ NMR spectrum of **9** (100 MHz, $CDCl_3$)

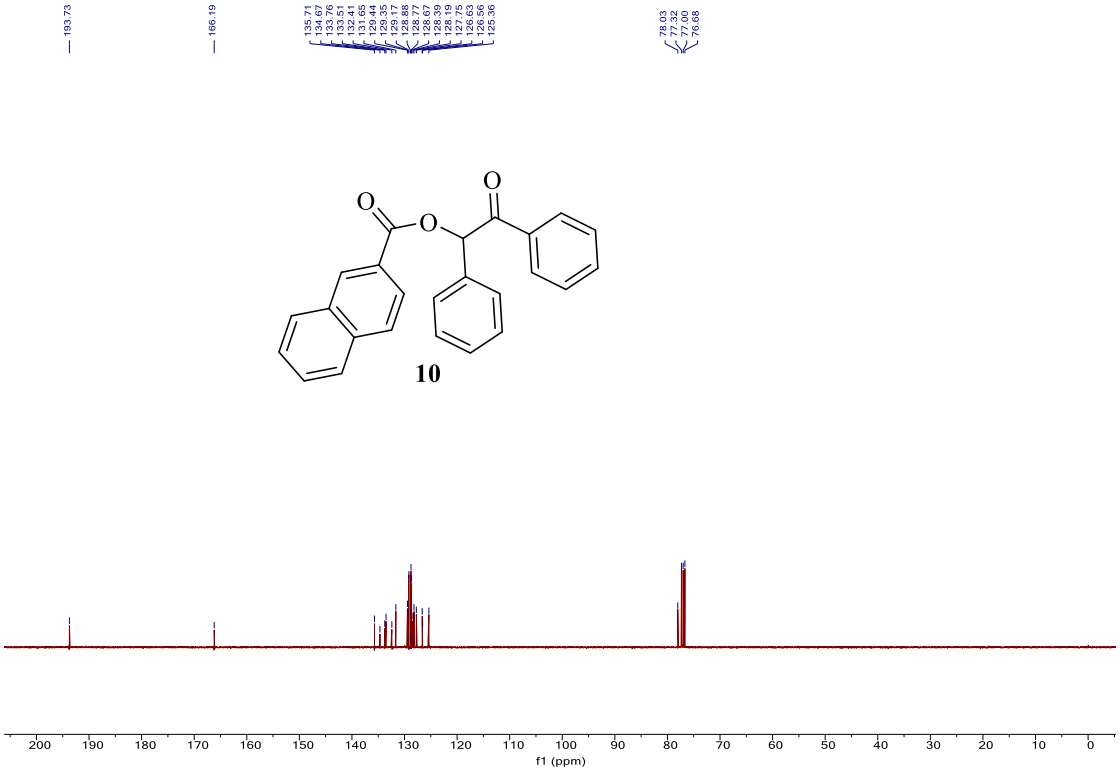


9

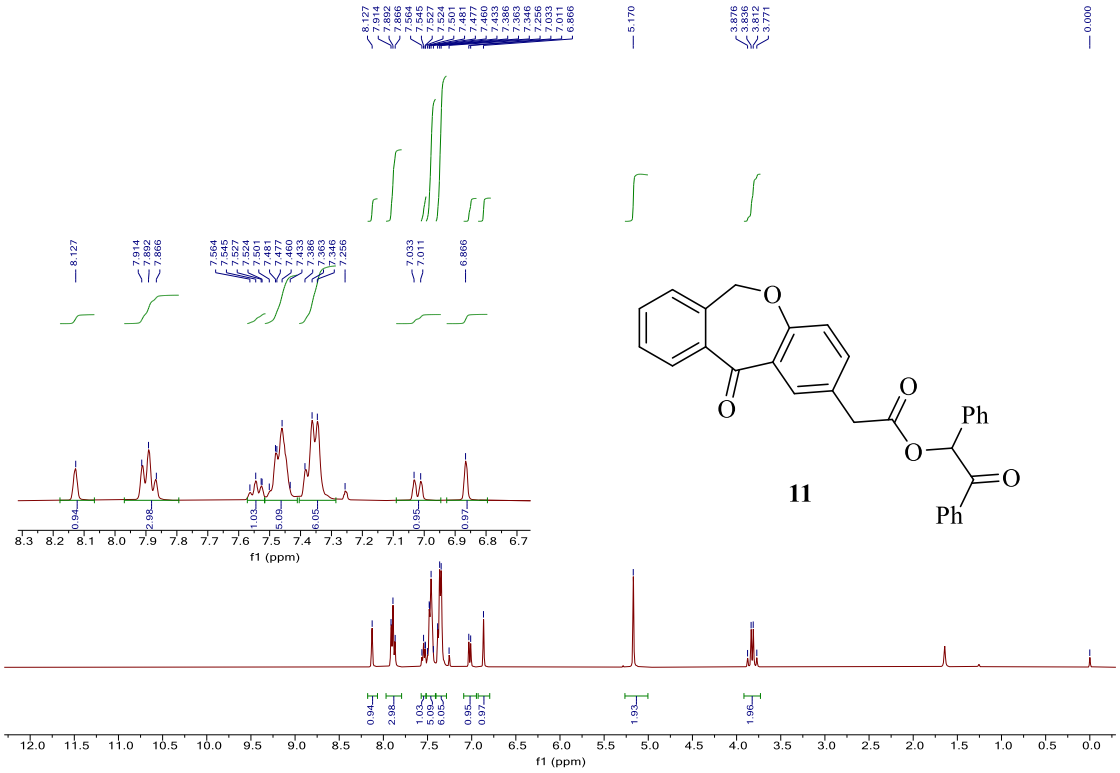
The ^{1}H NMR spectrum of **10** (400 MHz, $CDCl_3$)



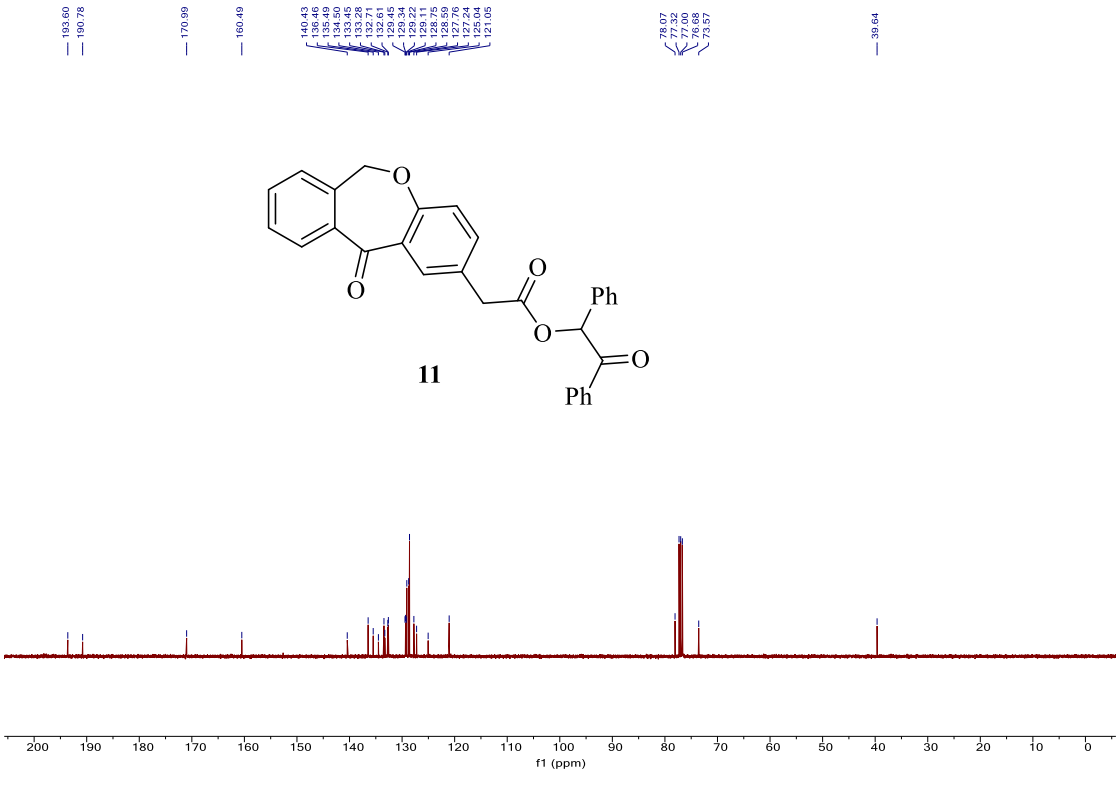
The $^{13}C\{^{1}H\}$ NMR spectrum of **10** (100 MHz, $CDCl_3$)



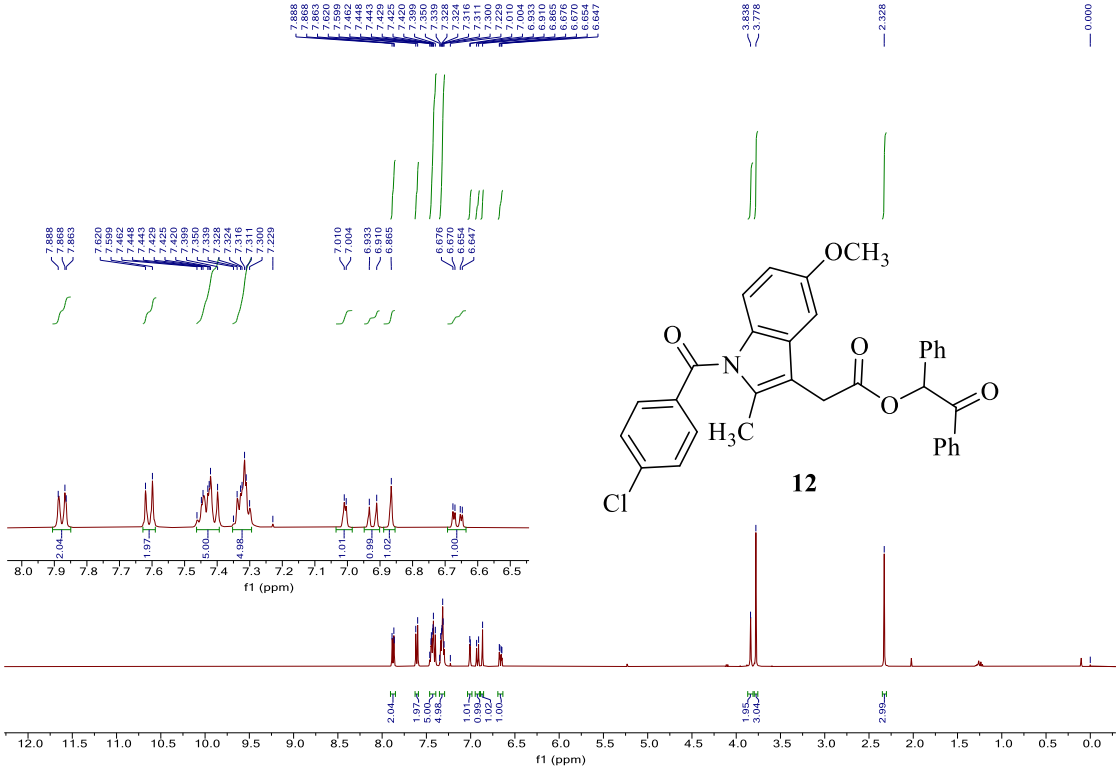
The ^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$)



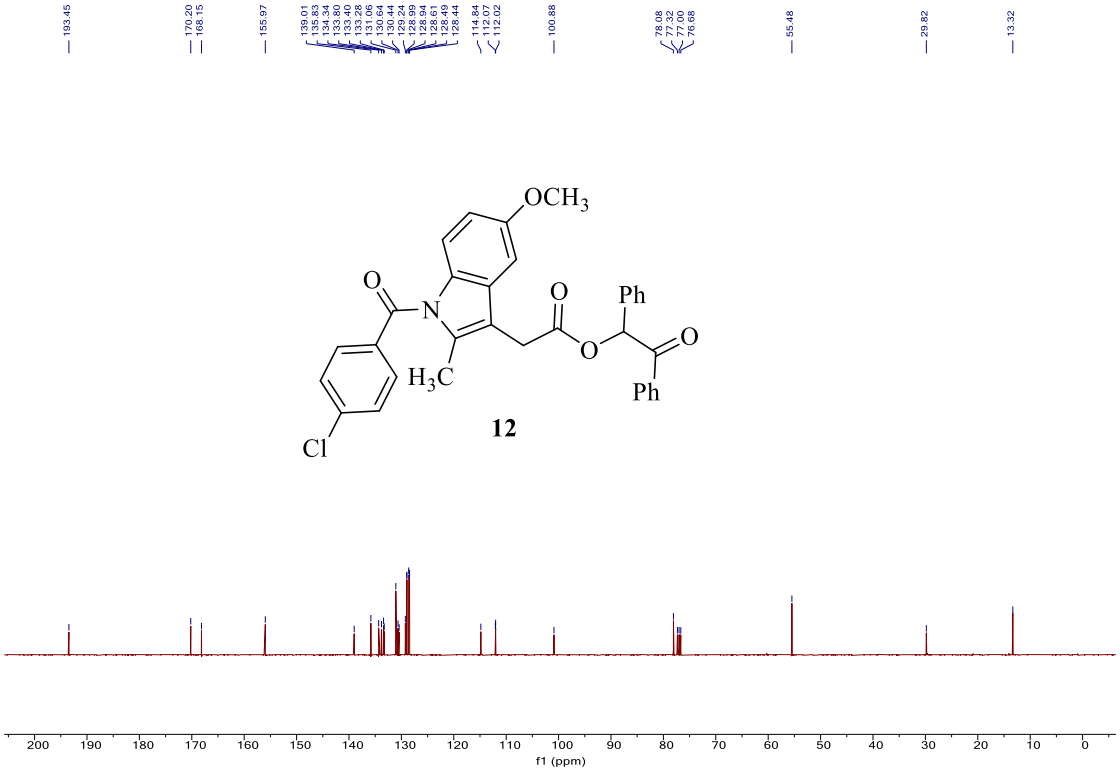
The $^{13}C\{^{1}H\}$ NMR spectrum of **11** (100 MHz, $CDCl_3$)



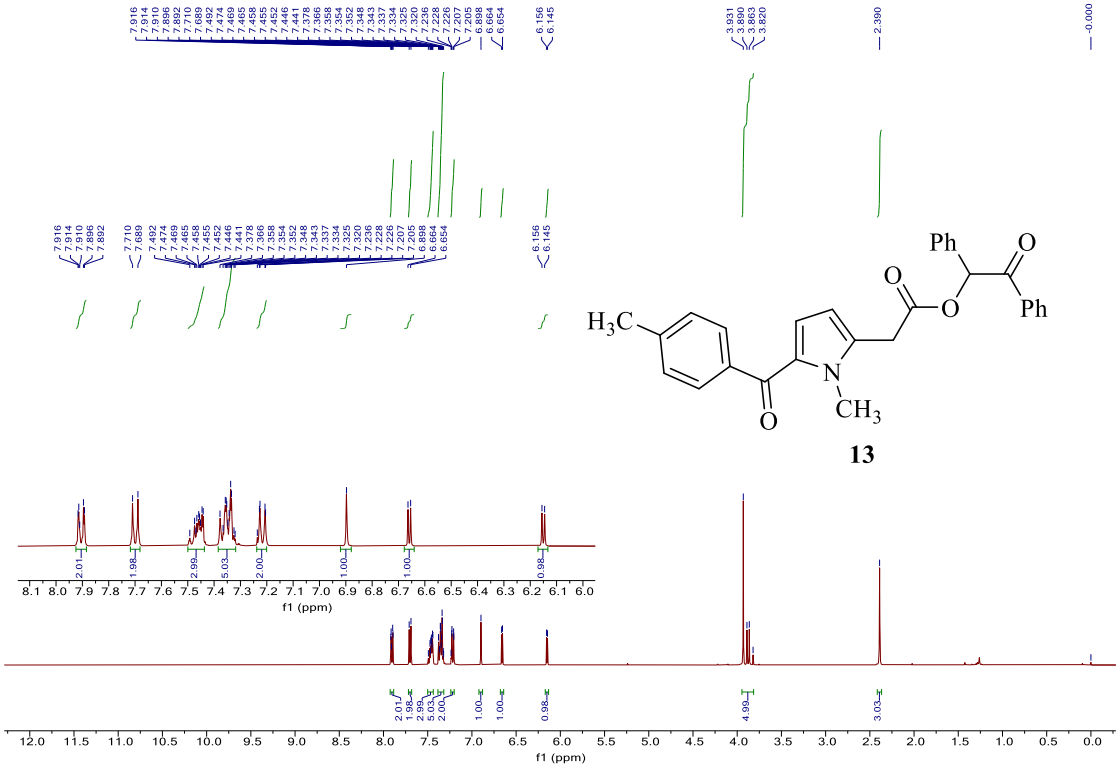
The ^{1}H NMR spectrum of **12** (400 MHz, $CDCl_3$)



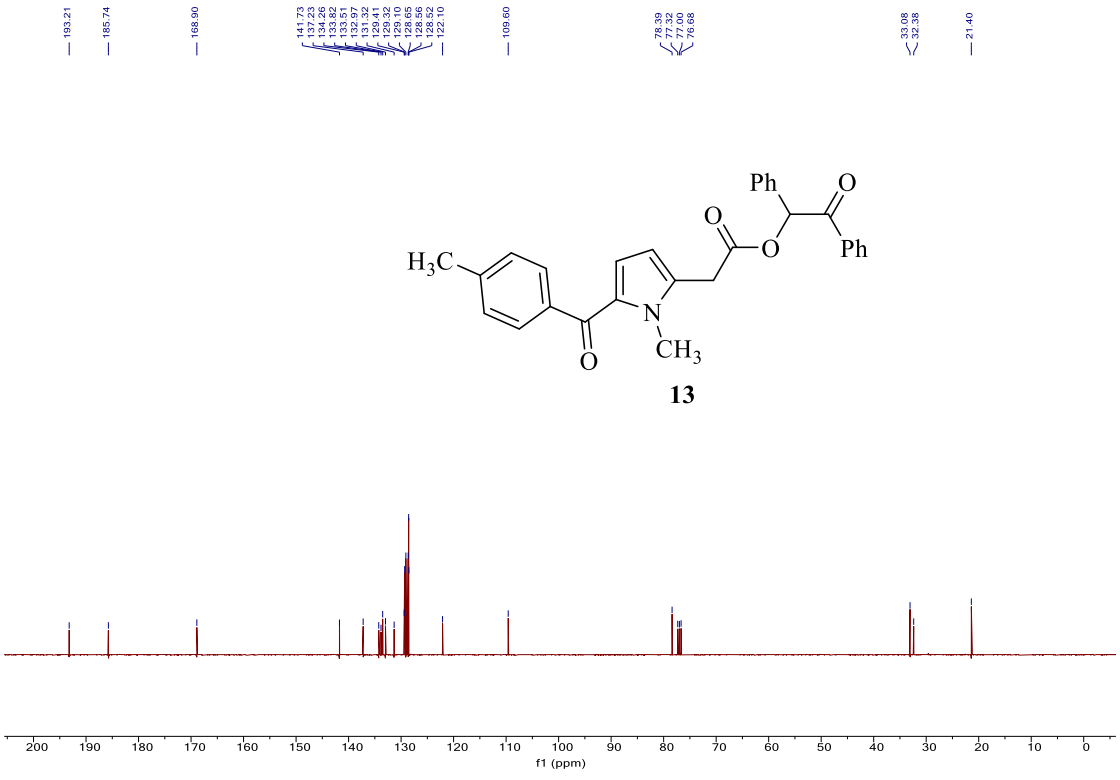
The $^{13}C\{^{1}H\}$ NMR spectrum of **12** (100 MHz, $CDCl_3$)



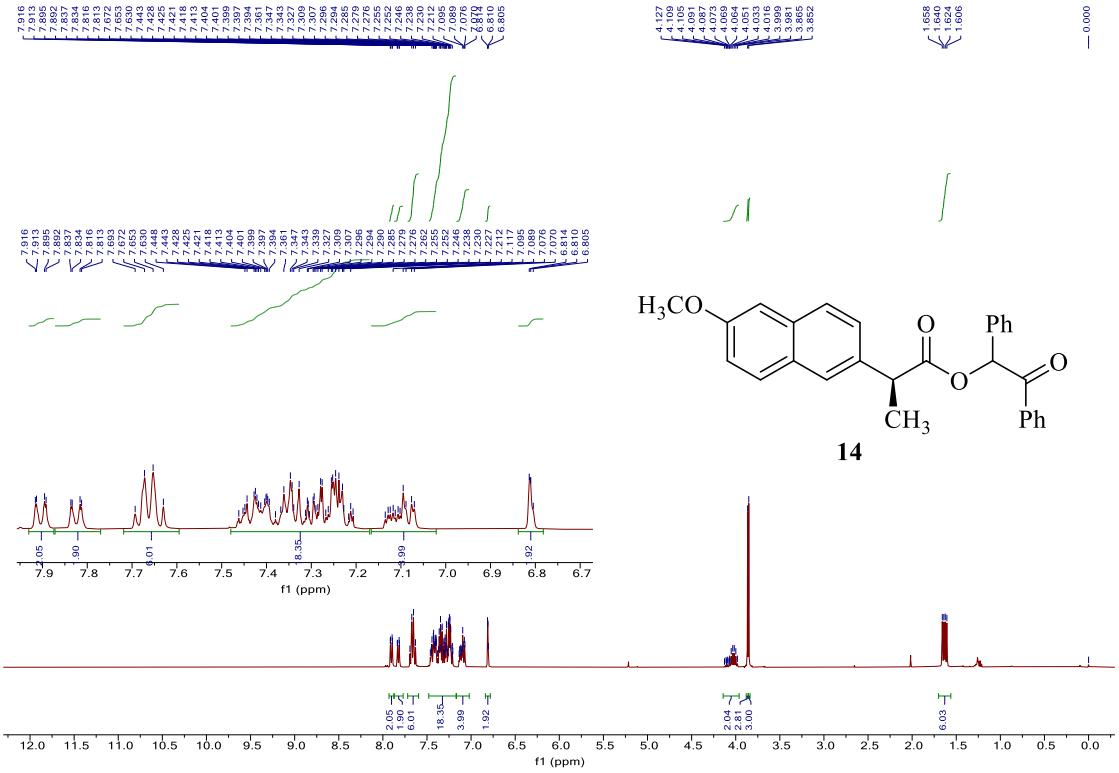
The ^{1}H NMR spectrum of **13** (400 MHz, $CDCl_3$)



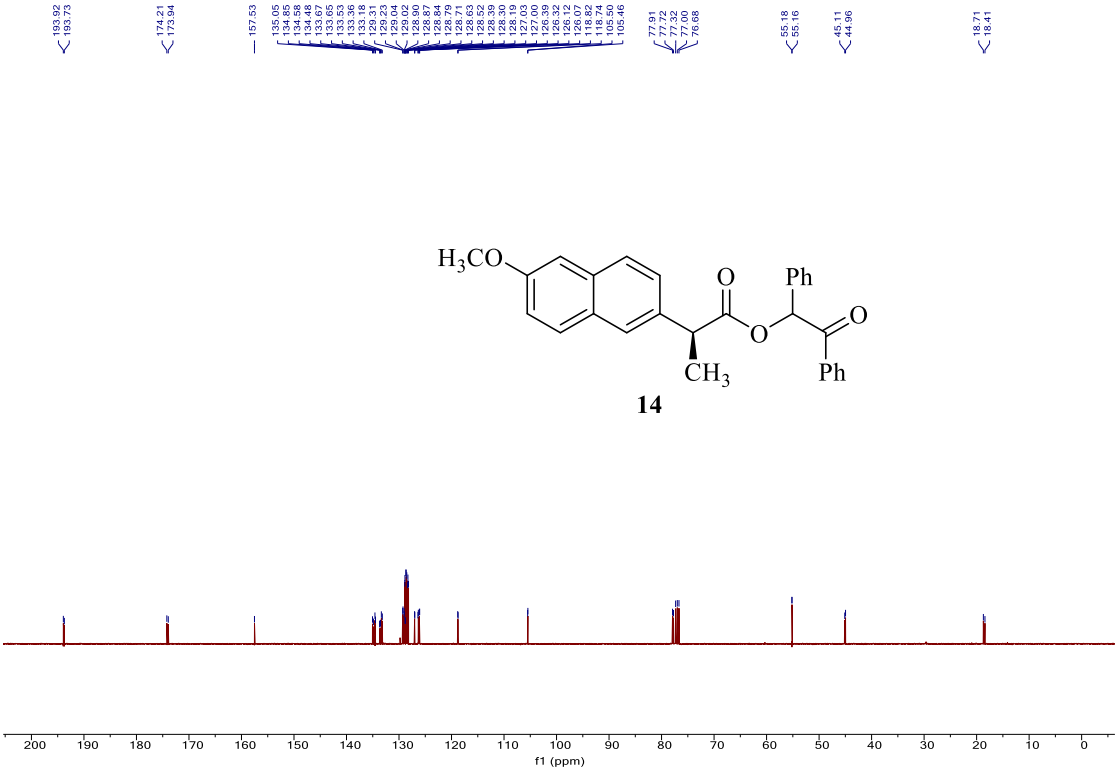
The $^{13}C\{^{1}H\}$ NMR spectrum of **13** (100 MHz, $CDCl_3$)



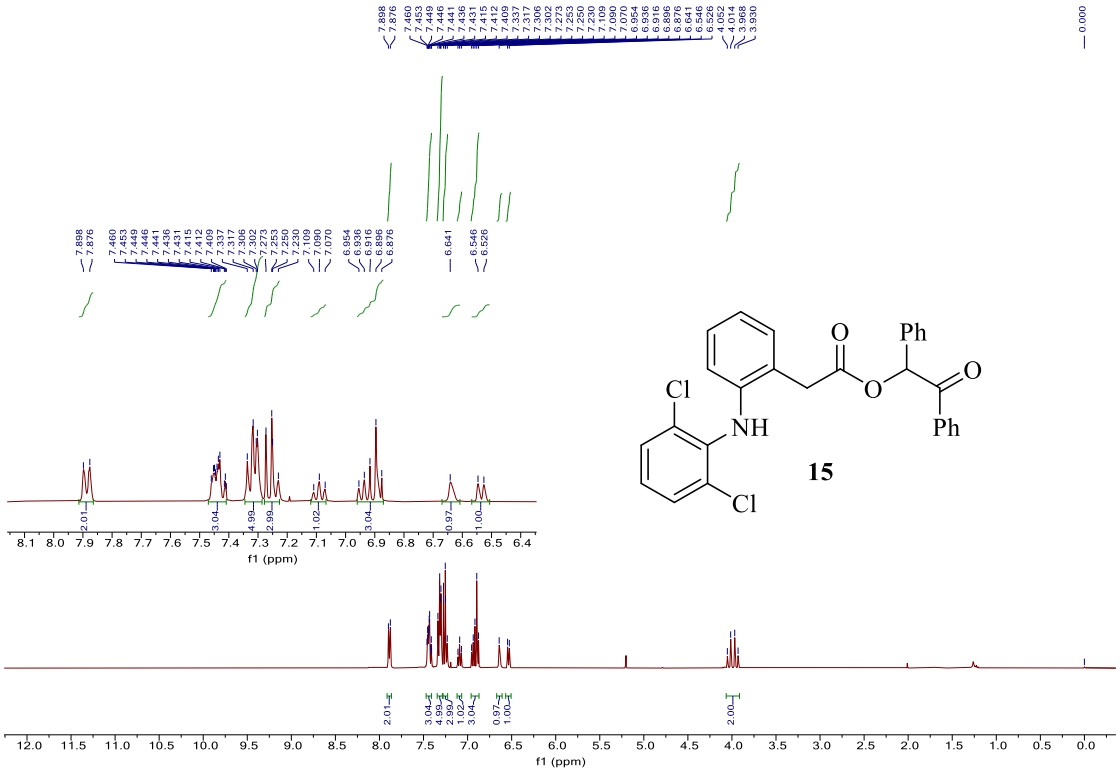
The ^{1}H NMR spectrum of **14** (400 MHz, $CDCl_3$)



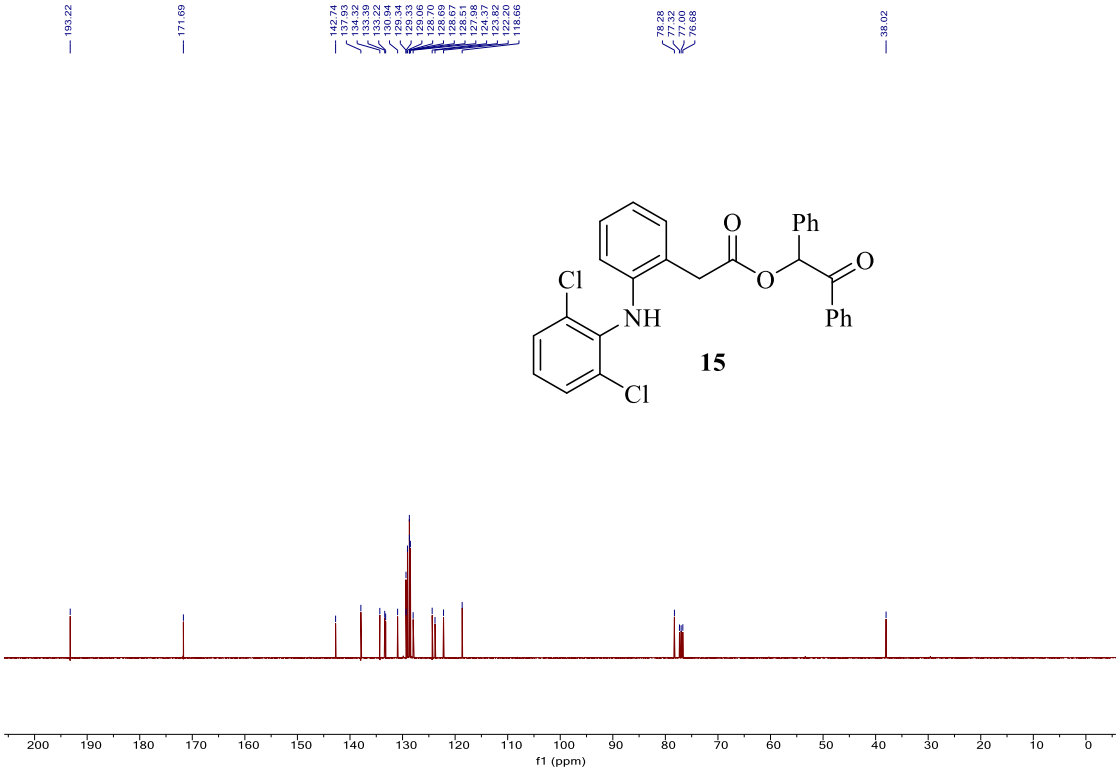
The $^{13}C\{^{1}H\}$ NMR spectrum of **14** (100 MHz, $CDCl_3$)



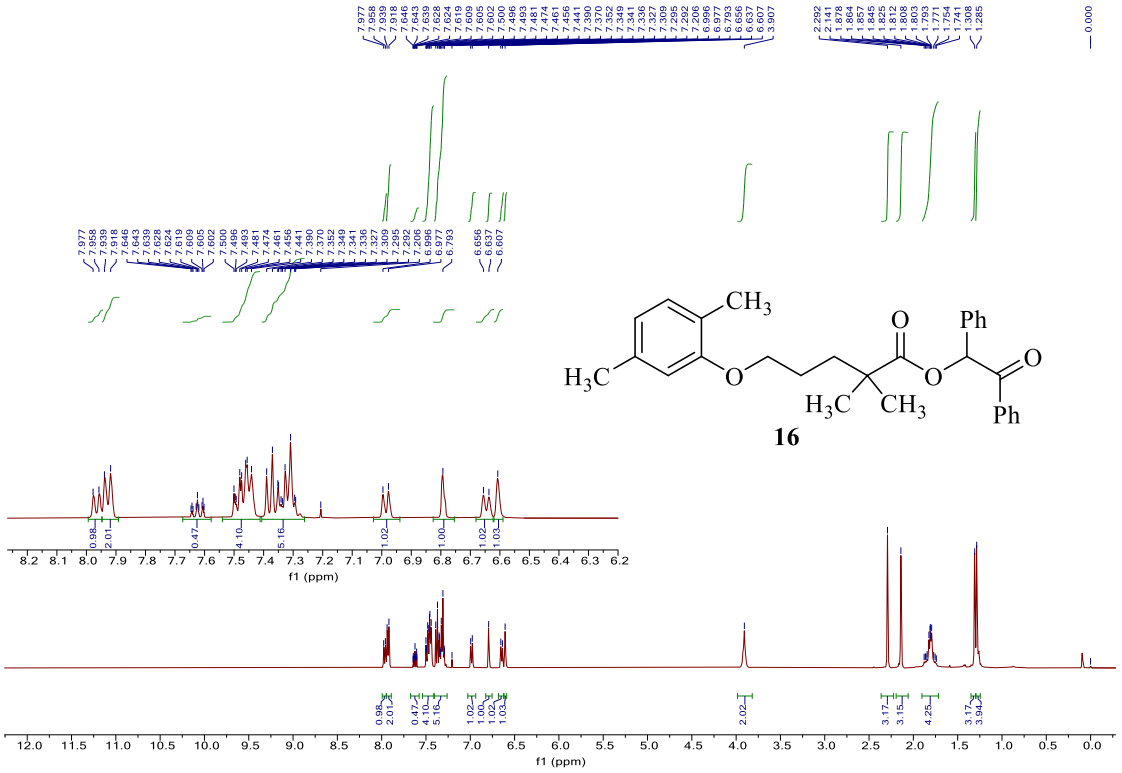
The ^{1}H NMR spectrum of **15** (400 MHz, $CDCl_3$)



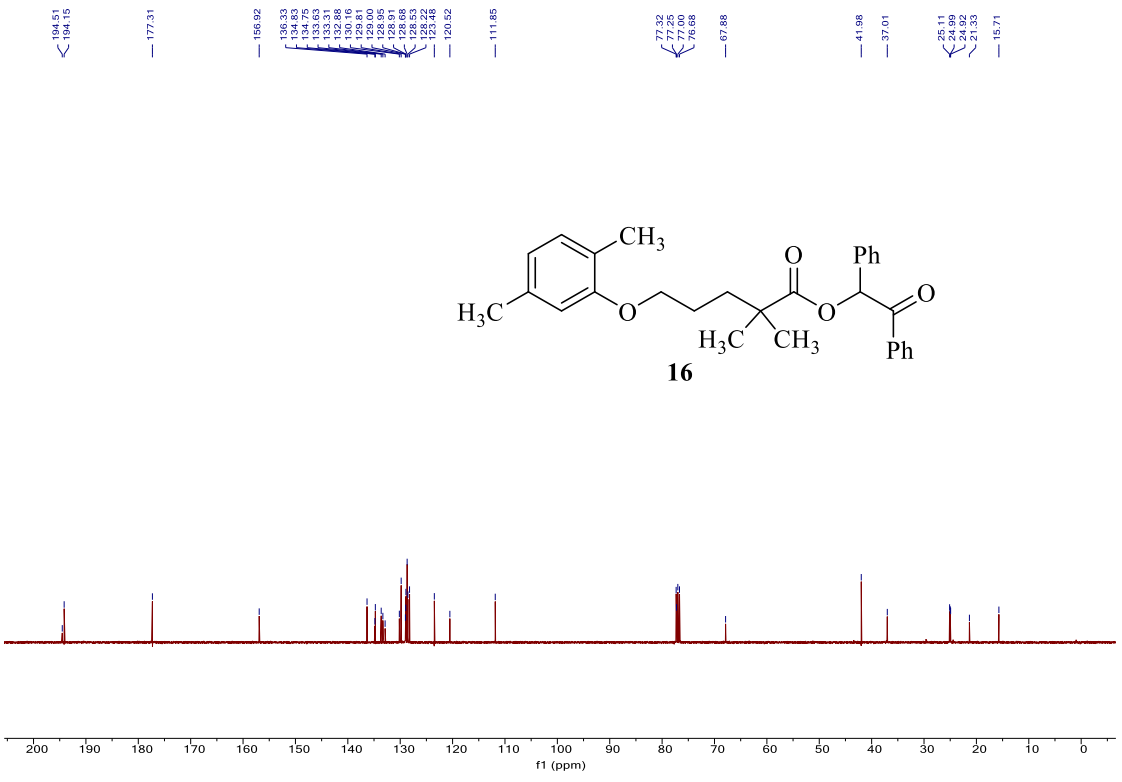
The $^{13}C\{^{1}H\}$ NMR spectrum of **15** (100 MHz, $CDCl_3$)



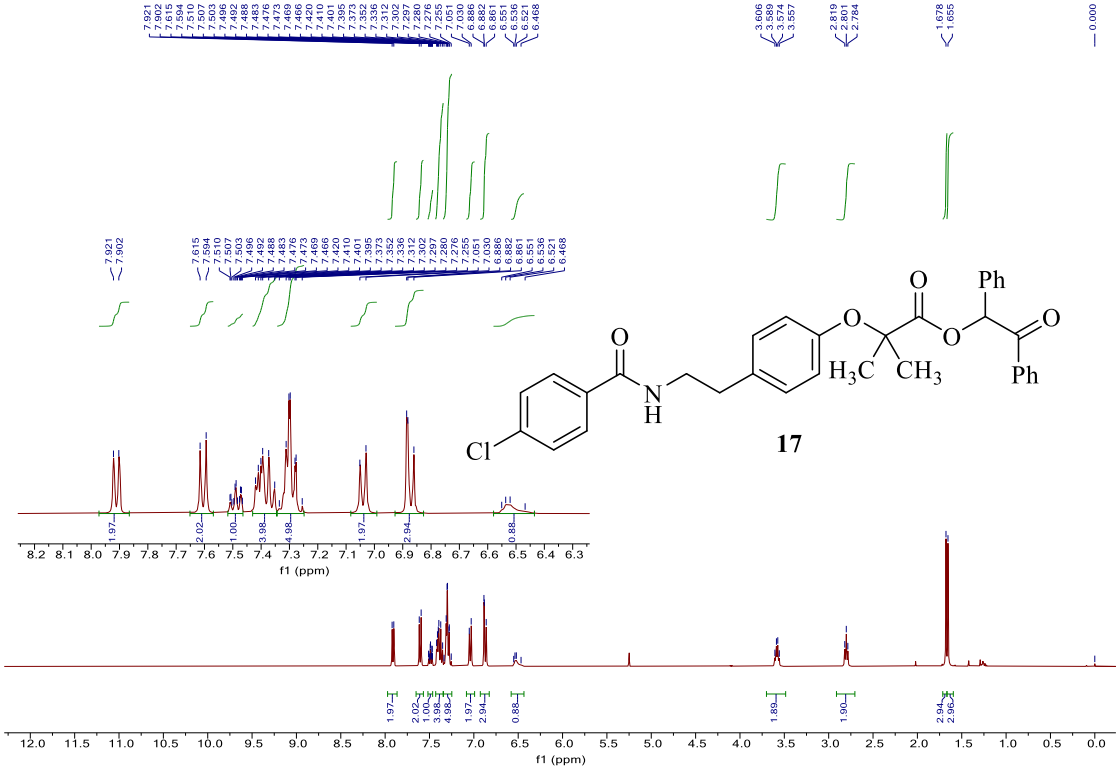
The ^{1}H NMR spectrum of **16** (400 MHz, $CDCl_3$)



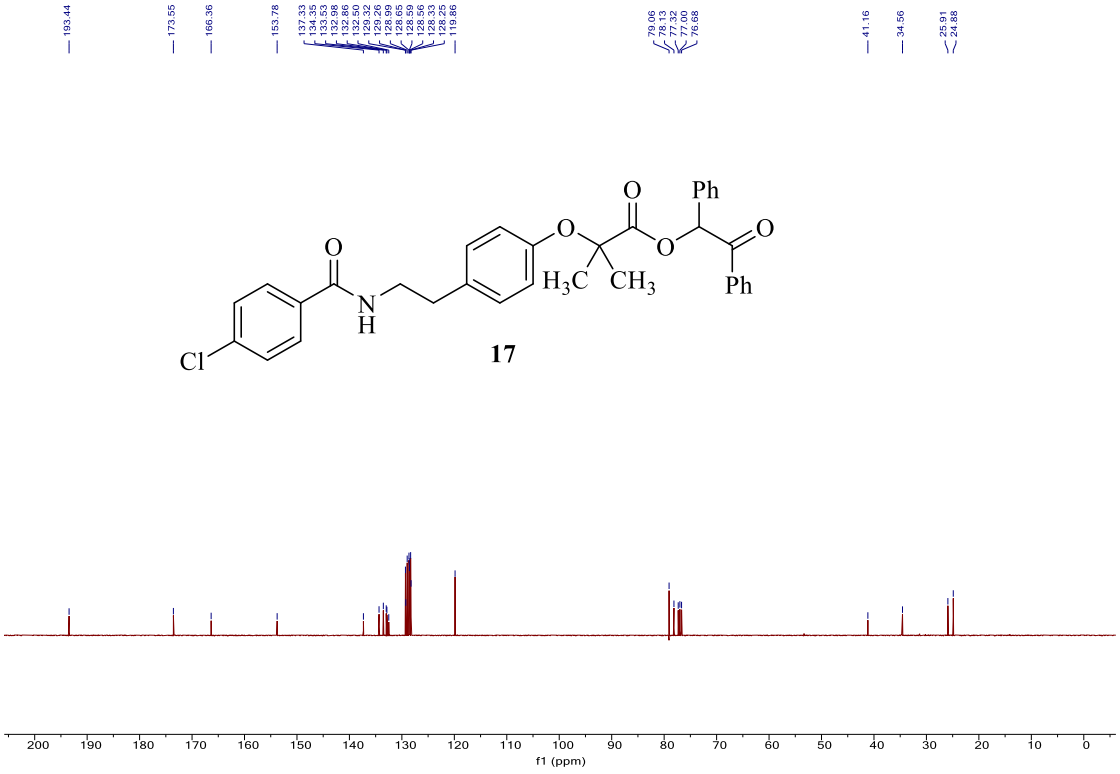
The $^{13}C\{^{1}H\}$ NMR spectrum of **16** (100 MHz, $CDCl_3$)



The ^{1}H NMR spectrum of **17** (400 MHz, $CDCl_3$)

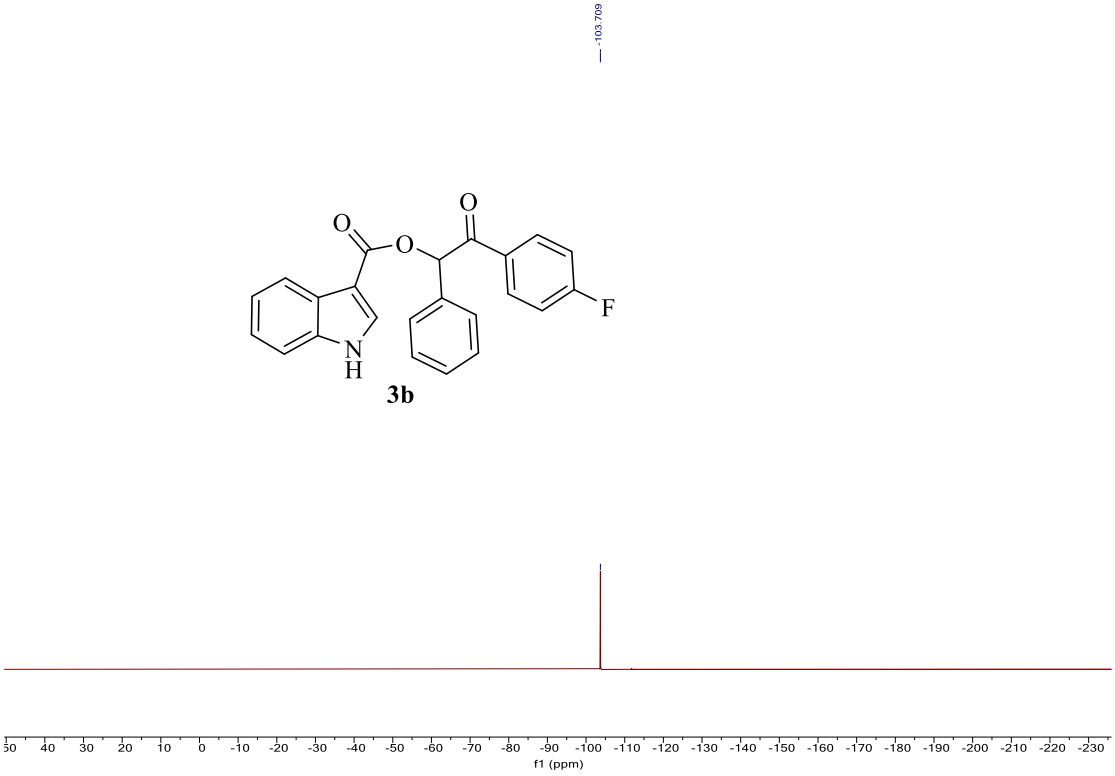


The $^{13}C\{^{1}H\}$ NMR spectrum of **17** (100 MHz, $CDCl_3$)

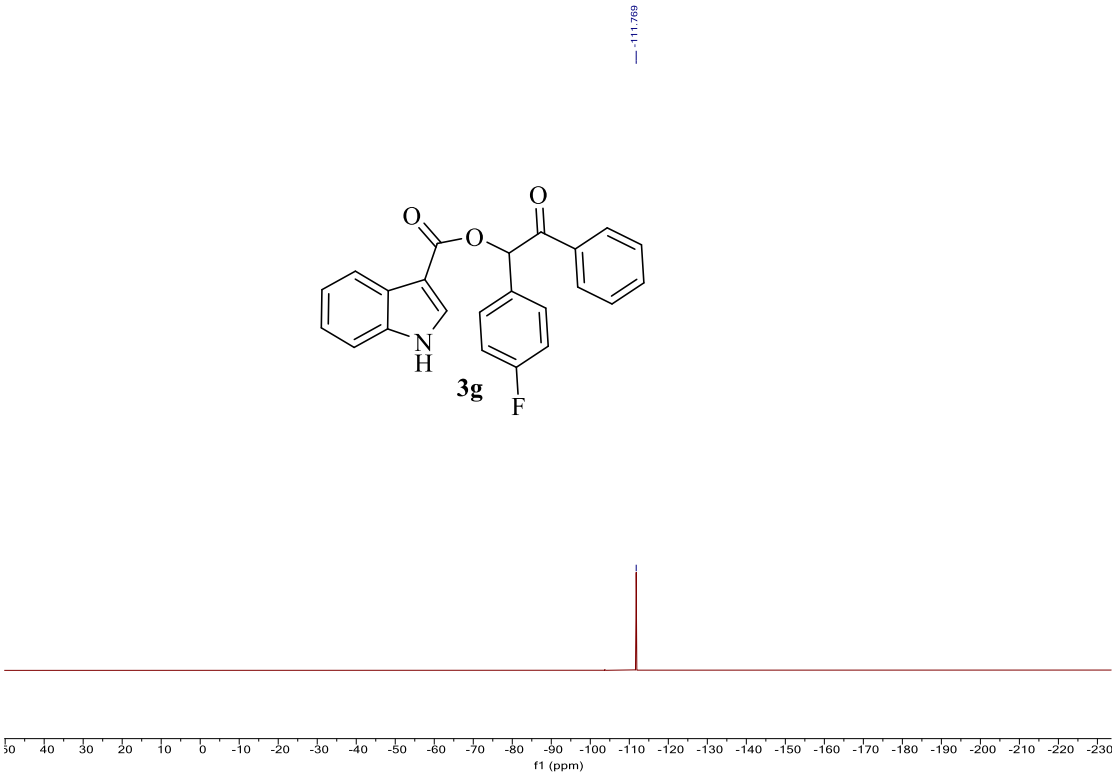


6. ^{19}F NMR Spectra of Products 3b, 3g, 3s, 3t

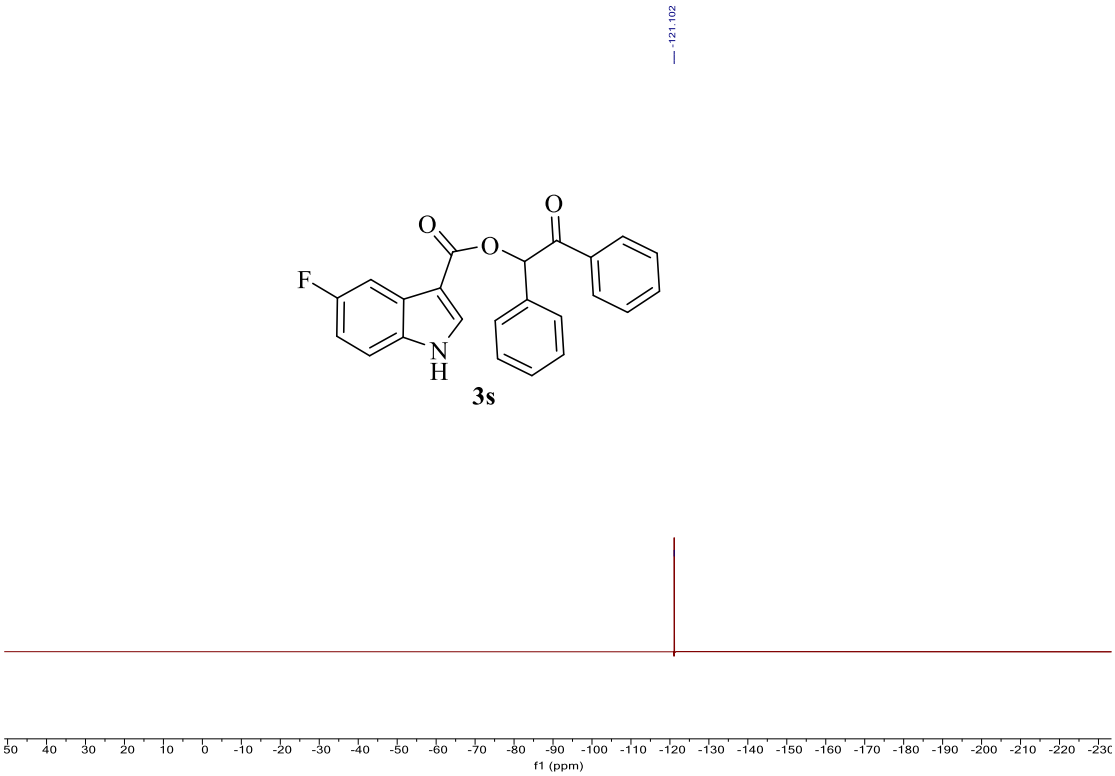
The ^{19}F NMR spectrum of **3b** (376 MHz, $CDCl_3$)



The ^{19}F NMR spectrum of **3g** (376 MHz, $CDCl_3$)

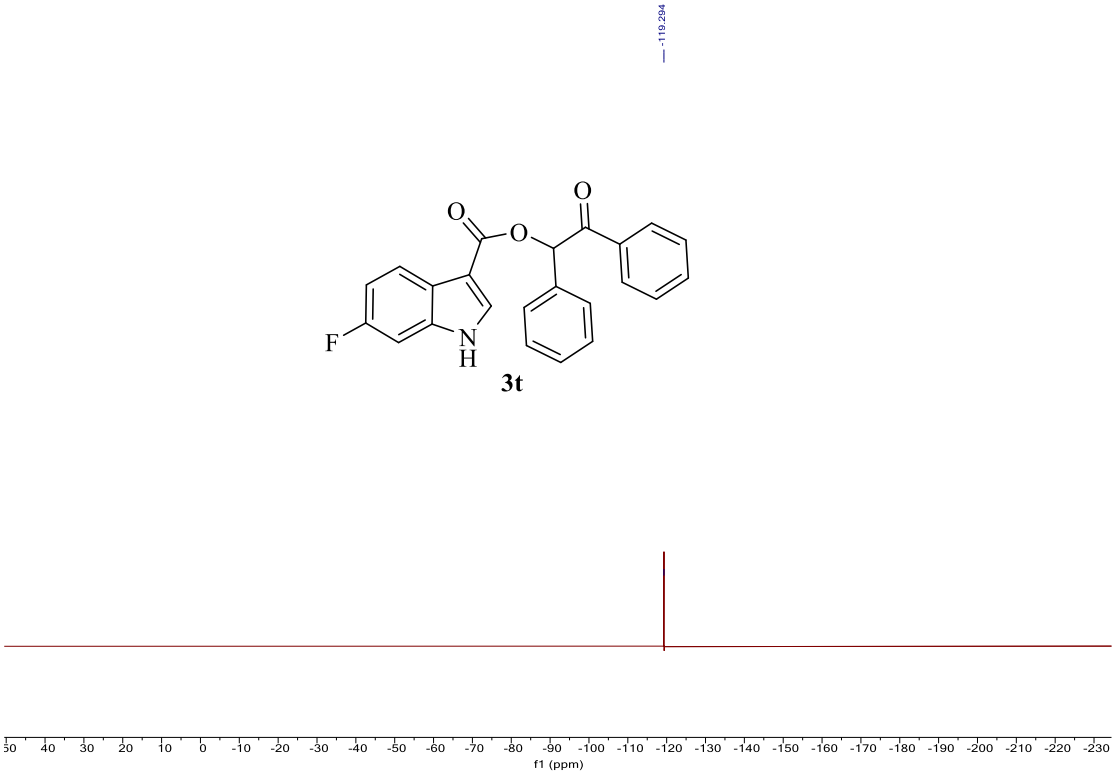


The ^{19}F NMR spectrum of **3s** (376 MHz, $CDCl_3$)



3s

The ^{19}F NMR spectrum of **3t** (376 MHz, $CDCl_3$)

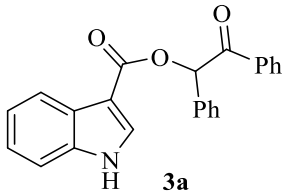


3t

7. X-ray crystallography of compounds 3a

2-Oxo-1,2-diphenylethyl-1*H*-indole-3-carboxylate (3a, zz)

(Ortep ellipsoids are depicted at the 50% level)



3a

Table 1. Crystal data and structure refinement for **3a**

Identification code	**3a**
Empirical formula	$C_{23}H_{17}NO_3$
Formula weight	355.39
Temperature	273 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.222 (3) Å α = 92.926 (9)°. b = 10.291 (3) Å β = 110.642 (9)°. c = 12.395 (4) Å γ = 98.522 (9)°.
Volume	1081.8 (6) $Å^3$
Z, Calculated density	2, 1.221 g/cm^3
Absorption coefficient	0.199 mm^{-1}
F(000)	414.0
Crystal size	0.08 x 0.06 x 0.03
Theta range for data collection	2.014 to 25.330°.
Index ranges	-11<=h<=11, -12<=k<=12, -14<=l<=14
Reflections collected / Independent reflections	28182/3922 [R(int) = 0.0334]
Completeness to theta = 25.242°	99.5 %
Absorption correction	Multi-Scan
Max. and min. transmission	0.745 and 0.715
Data / restraints / parameters	3922 / 29 / 284
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0614, wR2 = 0.1751
R indices (all data)	R1 = 0.0754, wR2 = 0.1918
Largest diff. peak and hole	0.405 and -0.218 $e.Å^{-3}$

Datablock zz - ellipsoid plot