Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Aroyl Chlorides as Novel Acyl Radical Precursors via Visible-Light Photoredox Catalysis

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Contents

1. General information

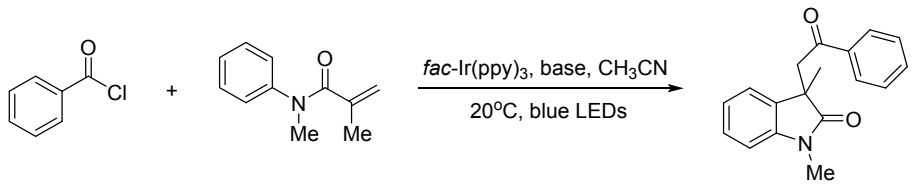
All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200−300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in deuterochloroform ($CDCl_3$) as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. IR spectra were recorded using Nicolet NEXUS 670 FT-IR instrument and are reported in wave numbers (cm^{-1}). HRMS were performed on a Bruker Apex II mass instrument (ESI).

Compounds **2a-o**, **5a** and **5b** were synthetized according to the literature procedure.[1, 2, 3, 4]

DIPEA = ethyldiisopropylamine; DABCO = triethylenediamine; DBU = 1,8-diazabicyclo[5.4.0] undec-7-ene; DMAP = 4-dimethylaminopyridine; DMF = N,N-dimethylformamide; EA = ethyl acetate; THF = tetrahydrofuran; DCM = dichloromethane; DCE = 1,2-dichloroethane.

2. Optimization studies

Table 1. Base Screening [a,b]

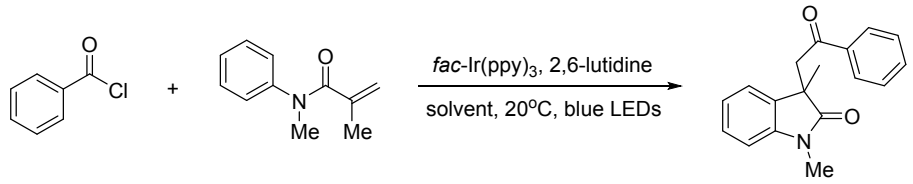


1a **2a** **3a**

Entry	Base	Yield (%)
1	2,6-lutidine	68
2	Et_3N	48
3	DIPEA	36
4	DABCO	32
5	DBU	0
6	DMAP	0
7	pyridine	0
8	2-picoline	61
9	3-picoline	0
10	4-picoline	0
11	2,4,6- collidine	38
12	Na_2HPO_4	59
13	Na_2CO_3	43
14	Cs_2CO_3	0

[a] Unless otherwise noted, reaction conditions are as follows: **2a** (0.1 mmol), **1a** (2 equiv.), *fac*-$Ir(ppy)_3$ (0.001 mmol), base (2 equiv.), CH_3CN (2 mL), 25 W blue LED strip, 20 °C, 12 h, under N_2 atmosphere. [b] Isolated yield.

Table 2. Solvent Screening [a,b]

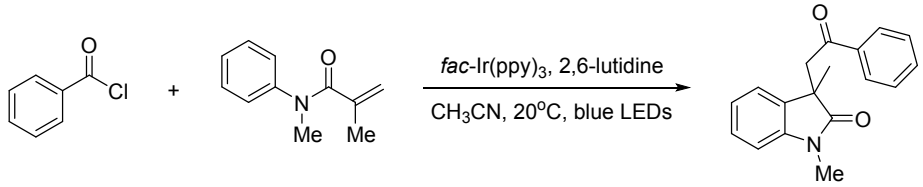


1a **2a** **3a**

Entry	Solvent	Yield (%)
1	CH_3CN	68
2	DMF	55
3	EA	58
4	acetone	62
5	THF	51
6	DCM	49
7	DCE	55
8	toluene	46

[a] Unless otherwise noted, reaction conditions are as follows: **2a** (0.1 mmol), **1a** (2 equiv.), *fac*-Ir(ppy)$_3$ (0.001 mmol), 2,6-lutidine (2 equiv.), solvent (2 mL), 25 W blue LED strip, 20 °C, 12 h, under N_2 atmosphere. [b] Isolated yield.

Table 3. Material ratio in the reaction system [a,b]

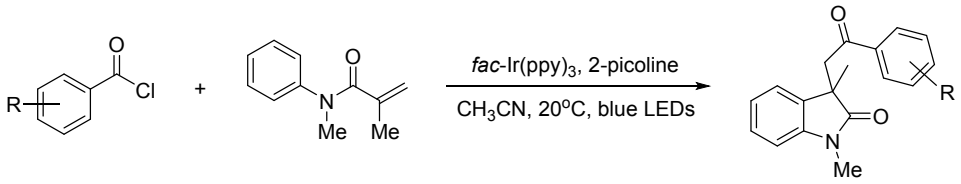


1a **2a** **3a**

Entry	1a:2a:Base	Yield (%)
1	2:1:2	68
2	1:1:1	32
3	2:1:1	34
4	2:1:2.5	70
5[c]	2:1:2.5	89
6[c,d]	2:1:2.5	95

[a] Unless otherwise noted, reaction conditions are as follows: **2a** (0.1 mmol), **1a** (2 equiv.), *fac*-Ir(ppy)$_3$ (0.001 mmol), 2,6-lutidine (2 equiv.), CH_3CN (2 mL), 25 W blue LED strip, 20 °C, 12 h, under N_2 atmosphere. [b] Isolated yield. [c] photocatalyst (0.002 mmol). [d] solvent (4 mL).

Table 4. Screening of 2-picoline [a,b]



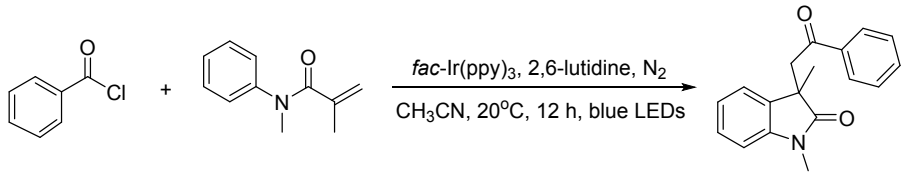
1a **2a** **3a**

Entry	R	Yield (%)
1	H	61 (68)[c]
2	2-Me	56 (29)[c]
3	4-Me	72 (76)[c]
4	2-Cl	64 (73)[c]

[a] Unless otherwise noted, reaction conditions are as follows: **2a** (0.1 mmol), **1a** (2 equiv.), *fac*-$Ir(ppy)_3$ (0.001 mmol), 2-picoline (2 equiv.), CH_3CN (2 mL), 25 W blue LED strip, 20 °C, 12 h, under N_2 atmosphere. [b] Isolated yield. [c] Yields in the presence of 2,6-lutidine are in the brackets.

3. General Procedures

3.1 Typical procedure for the photocatalytic reaction

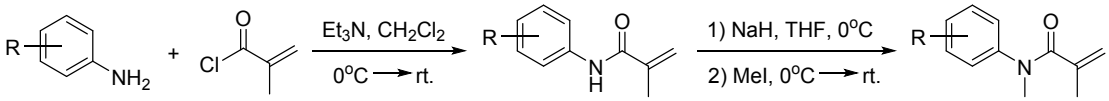


1a **2a** **3a**

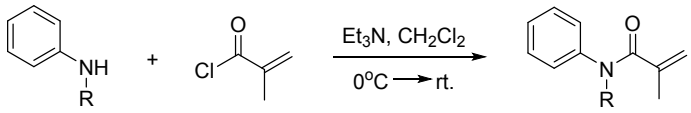
Photocatalyst *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and N-methyl-N-phenylmethacrylamide **2a** (17.5 mg, 0.1 mmol) were added into a 10 mL vial dried before. The vial was added a Teflon coated magnetic stirring bar, anhydrous CH_3CN (4 mL), 2,6-lutidine (35 μL, 0.25 mmol) and benzoyl chloride **1a** (29 μL, 0.2 mmol). Then the vial was sealed and degassed by three cycles of freeze-pump-thaw to exchange the internal atmosphere with nitrogen. The above reaction system was stirred vigorously in the irradiation apparatus equipped with a 25 W blue LED strip at 20 °C. After the starting material was completely consumed as monitored by TLC, the reaction mixture was concentrated under reduced pressure. The resulting crude mixture was washed with water and ethyl acetate, and the organic phase was dried over anhydrous Na_2SO_4. The Na_2SO_4 was then filtered, and the crude mixture was purified by flash column chromatography on silica gel to furnish the desired product **3a** as described.

3.2 Preparation of amides

Method A:



Method B:



Method A:

Aniline (10.00 mmol, 1.0 equiv.) was dissolved in DCM (30 mL). Et_3N (12.00 mmol, 1.2 equiv) was added to the reaction flask at 0 °C. Acid chloride (12.00 mmol, 1.2 equiv.) was added slowly to the mixture and the reaction was monitored by TLC. After completion of the reaction, aqueous $NaHCO_3$ (25 mL) was added. The crude product was extracted with DCM (3 x 50 mL). The combined organic layers were washed with 1M HCl (3 x 20 mL) and brine (3 x 20 mL) and dried over Na_2SO_4. Solvent was removed in *vacuo*. The crude product was purified by flash column chromatography.

Purified amide (8.00 mmol, 1.0 equiv.) was dissolved in THF (50 mL) at 0 °C. NaH (10.40 mmol, 1.3 equiv.) was added in three portions and the mixture was stirred for further 15 min. CH_3I (32.00 mmol, 4.0 equiv.) was added slowly and the reaction mixture was stirred until completion as monitored by TLC. THF was removed in *vacuo*. Water (30 mL) was added to the mixture and the

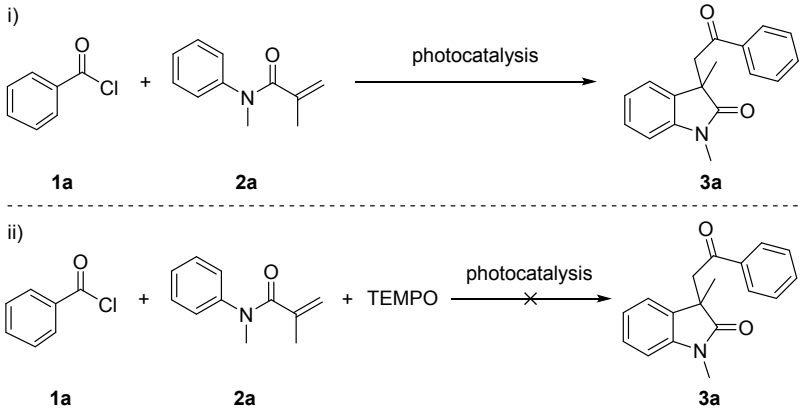
crude product was extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine (3 x 20 mL) and dried over Na_2SO_4. Solvent was removed in *vacuo*. The crude product was purified by flash column chromatography to obtain the final product.

Method B:

N-methylaniline (10.00 mmol, 1.0 equiv.) was dissolved in DCM (30 mL). Et_3N (12.00 mmol, 1.2 equiv) was added to the reaction flask at 0 ^oC. Acid chloride (12.00 mmol, 1.2 equiv.) was added slowly to the mixture and the reaction was monitored by TLC. After completion of the reaction, aqueous $NaHCO_3$ (25 mL) was added. The crude product was extracted with DCM (3 x 50 mL). The combined organic layers were washed with 1M HCl (3 x 20 mL) and brine (3 x 20 mL), and then dried over Na_2SO_4. Solvent was removed in *vacuo*. The crude product was purified by flash column chromatography to obtain the final product.

All spectral data of amides are in agreement with literature values.[2]

3.3 Control experiment



Reaction **i** was performed following the typical procedure as control experiment and reaction **ii** was added the TEMPO (0.25 mmol, 2.5 equiv.) before the vial was sealed and degassed. After 12 hours, the two reaction mixtures were purified by flash column chromatography on silica gel. The results showed that reaction in the presence of TEMPO cannot afford any product **3a**. Since TEMPO is usually served as radical trapping agent to block radical reactions, the existence of acyl radicals is confirmed.

4. Cyclic Voltammetry Experiments

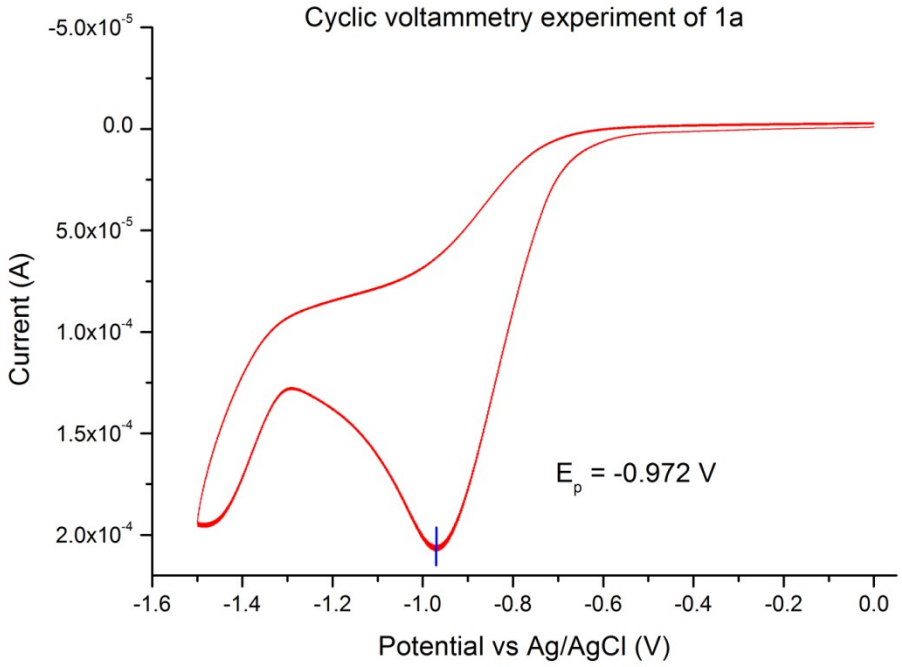


Figure 1. Reduction potential measurement of benzoyl chloride **1a**

Determination of the reduction potential[5] of **1a** was performed by cyclic voltammetry using a CHI660D potentiostation. The electrochemical measurements were made using a polished glassy carbon electrode (Ø = 2 mm) as the working electrode, platinum mesh as counter electrode and a double junction Ag/AgCl (0.1 M $AgNO_3$) as reference electrode. Measurements of **1a** (0.01M) were performed in 0.1 M of Bu_4NBF_4/CH_3CN with a sweep rate of 100 mV/s under anhydrous and anaerobic conditions.

The reduction potential of benzoyl chloride **1a** is -1.14 V vs SCE according to the literature value[6]. Converting reduction potential measured with Ag/AgCl to the one with saturated calomel electrode (SCE) needs reducing 45.9 mV. So the experiment result (E_p = -1.018 V vs SCE) is within the measurement uncertainty (±150 mV).

The result suggested that the excited photocatalyst $*Ir^{III}(ppy)_3$ ($E_{1/2}^{IV/*III}$ = -1.73 V vs SCE in CH_3CN) is sufficient to reduce the benzoyl chloride **1a** (E_p = -0.972 V vs Ag/AgCl) to generate the acyl radical intermediate.

5. Luminescence Quenching Experiments

Emission intensities were recorded using a Perkin Elmer LS55 spectrofluorimeter. All *fac*-$Ir(ppy)_3$ solutions were excited at 375 nm and the emission intensity at 520 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of *fac*-$Ir(ppy)_3$ and different concentration (0.005~0.025 M) of benzoyl chloride **1a**, *N*-methyl-*N*-phenylmethacrylamide **2a** and 2,6-lutidine in anhydrous CH_3CN in 10 mm path length quartz cuvette was collected.

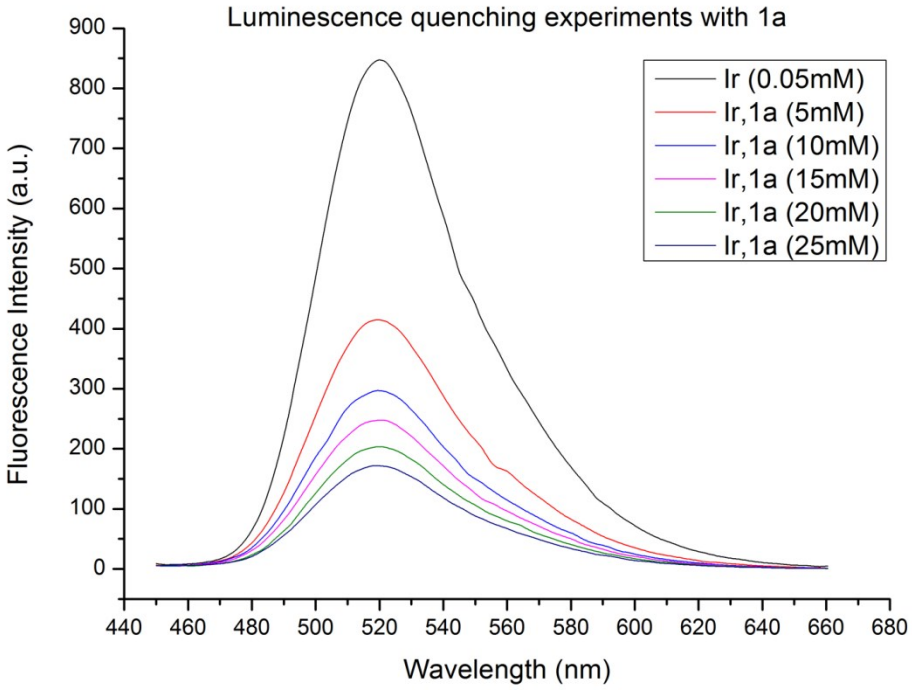


Figure 2. Luminescence quenching experiments of *fac*-Ir(ppy)$_3$ with **1a**

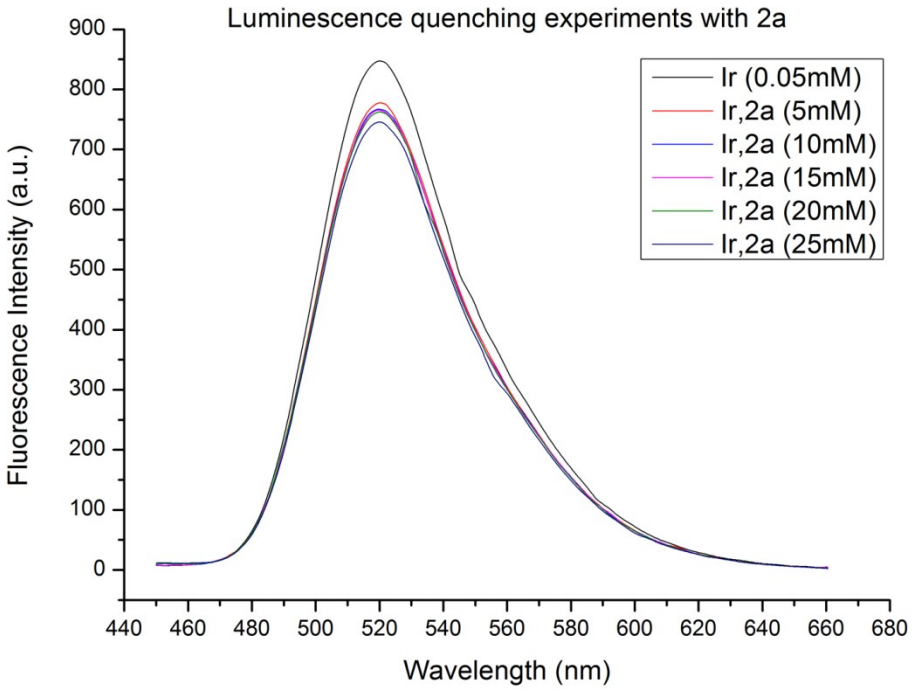


Figure 3. Luminescence quenching experiments of *fac*-Ir(ppy)$_3$ with **2a**

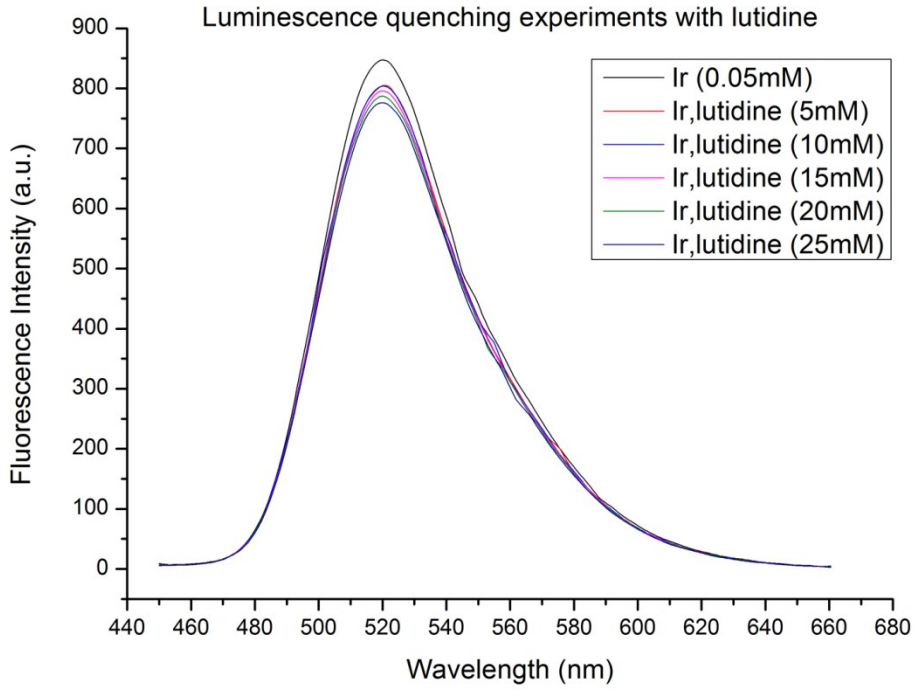


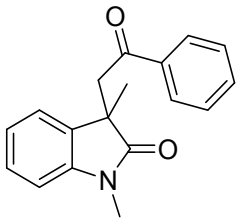
Figure 4. Luminescence quenching experiments of *fac*-Ir(ppy)$_3$ with 2,6-lutidine

As shown in Figure 2, the emission intensity of the excited photocatalyst *fac*-Ir(ppy)$_3$ is decreased in the presence of benzoyl chloride **1a**. From Figure 3 and Figure 4, we know that 2,6-lutidine and *N*-methyl-*N*-phenylmethacrylamide **2a** are unable to quench the excited photocatalyst. So benzoyl chloride **1a** is the only molecular entity in the reaction mixture severed as the oxidative quencher of the excited photocatalyst.

6. Reference

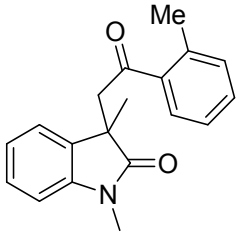
(1) C.-C. Li and S.-D. Yang, *Org. Lett.,* 2015, **17**, 2142.
(2) L.-W. Zheng, H.-L. Huang, C. Yang and W.-J. Xia, *Org. Lett.,* 2015, **17***,* 1034.
(3) Z. He, M. Bae, J. Wu and T. F. Jamison, *Angew. Chem., Int. Ed.,* 2014, **53**, 14451.
(4) F. Gao, C. Yang, G.-L. L.-W. Gao, Zheng and W.-J. Xia, *Org. Lett.,* 2015, **17**, 3478.
(5) D. Occhialini, K. Daasbjerg and H. Lund, *Acta. Chem. Scand.,* 1993, **47**, 1100.
(6) X.-Q. Hu, X.-T. Qi, J.-R. Chen, Q.-Q. Zhao, Q. Wei, Y. Lan and W.-J. Xiao, *Nat. Commun.,* 2016*,* **7**, 11188.
(7) G. Bergonzini, C. Cassani and C.-J. Wallentin, *Angew. Chem., Int. Ed.,* 2015, **54**, 14066.

7. Characterization of Products



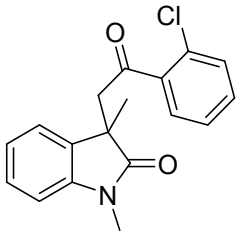
1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3a)

Colorless oil; 26.6 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.84-7.82 (m, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.25 (td, J_t = 7.6 Hz, J_d = 0.9 Hz, 1H), 7.14 (d, J = 7.1 Hz, 1H), 6.97 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.72 (d, J = 17.9 Hz, 1H), 3.65 (d, J = 17.9 Hz, 1H), 3.31 (s, 3H), 1.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.1, 180.5, 143.8, 136.4, 133.7, 133.1, 128.4, 127.9, 127.8, 122.1, 121.7, 108.1, 46.0, 45.2, 26.4, 24.9. **IR** (KBr): 3431, 3057, 2965, 2925, 1711, 1689, 1614, 1470, 1449, 1378, 1350, 1248, 1215, 1125, 753, 690 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{18}NO_2$ $[M+H]^+$ calcd 280.1332, found 280.1330.



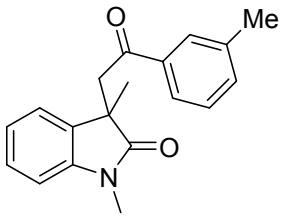
1,3-dimethyl-3-(2-oxo-2-(o-tolyl)ethyl)indolin-2-one (3b)

Colorless oil; 16.5 mg, 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.51-7.48 (m, 1H), 7.32-7.23 (m, 2H), 7.20 (d, J = 7.6 Hz, 1H), 7.16 (dd, J_d = 7.4 Hz, J_d = 0.7 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 6.99 (td, J_t = 7.4 Hz, J_d = 0.9 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.61 (d, J = 17.0 Hz, 1H), 3.51 (d, J = 17.0 Hz, 1H), 3.21 (s, 3H), 2.10 (s, 3H), 1.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 200.7, 180.3, 143.8, 137.8, 133.4, 131.6, 131.1, 128.2, 127.9, 126.5, 125.4, 122.2, 122.1, 108.1, 49.1, 45.8, 26.4, 24.9, 20.5. **IR** (KBr): 3436, 3063, 2965, 2927, 1783, 1719, 1652, 1626, 1595, 1494, 1457, 1367, 1201, 1124, 996, 769, 742, 700 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{20}NO_2$ $[M+H]^+$ calcd 294.1489, found 280.1488.



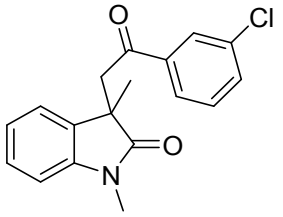
3-(2-(2-chlorophenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3c)

Colorless oil; 22.8 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.3-7.24 (m, 3H), 7.23-7.15 (m, 3H), 7.00 (td, J_t = 7.2 Hz, J_d = 0.8 Hz, 1H), 6.86 (d, J = 7.6 Hz, 1H), 3.68 (d, J = 17.6 Hz, 1H), 3.60 (d, J = 17.6 Hz, 1H), 3.26 (s, 3H), 1.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 199.4, 180.0, 143.8, 138.7, 133.0, 131.7, 130.8, 130.3, 129.0, 128.0, 126.8, 122.2, 108.2, 50.1, 45.8, 26.4, 24.7. **IR** (KBr): 3449, 3057, 2966, 2927, 1710, 1690, 1614, 1494, 1471, 1379, 1350, 1267, 1250, 1126, 941, 754, 737 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{17}ClNO_2$ $[M+H]^+$ calcd 314.0942, found 314.0944.



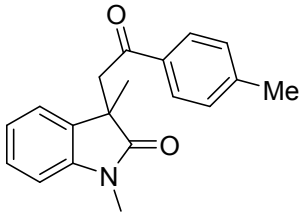
1,3-dimethyl-3-(2-oxo-2-(m-tolyl)ethyl)indolin-2-one (3d)

Colorless oil; 22.8 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.64-7.63 (m, 2H), 7.34-7.32 (m, 1H), 7.30-7.28 (m, 1H), 7.25 (td, J_t = 7.6 Hz, J_d = 0.8 Hz, 1H), 7.13 (d, J = 7.0 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.71 (d, J = 17.9 Hz, 1H), 3.63 (d, J = 17.9 Hz, 1H), 3.31 (s, 3H), 2.35(s, 3H), 1.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.3, 180.6, 143.9, 138.3, 136.4, 133.9, 133.8, 129.2, 128.5, 128.3, 127.8, 126.9, 126.5, 125.2, 122.1, 121.7, 108.1, 46.1, 45.3, 26.4, 24.9, 21.2. **IR** (KBr): 3473, 3055, 2967, 2926, 1713, 1687, 1614, 1494, 1471, 1379, 1349, 1252, 1125, 914, 776, 754, 734 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{20}NO_2$ $[M+H]^+$ calcd 294.1489, found 280.1491.



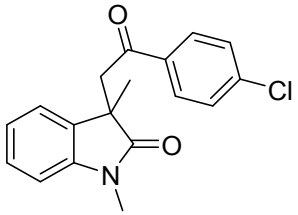
3-(2-(3-chlorophenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3e)

Colorless oil; 20.8 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.79 (t, J = 2.0 Hz, 1H), 7.71 (dt, J_d = 8.0 Hz, J_t = 1.2 Hz, 1H), 7.50-7.47 (m, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.26 (td, J_t = 8.4 Hz, J_d = 1.2 Hz, 1H), 7.13 (dd, J_d = 7.2 Hz, J_d = 0.8 Hz, 1H), 6.98 (td, J_t = 7.6 Hz, J_d = 0.8 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 3.67 (d, J = 18.0 Hz, 1H), 3.61 (d, J = 18.0 Hz, 1H), 3.31 (s, 3H), 1.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 194.9, 180.3, 143.8, 137.8, 134.8, 133.4, 133.1, 129.8, 128.1, 127.9, 126.0, 122.2, 108.2, 46.1, 45.2, 26.4, 24.8. **IR** (KBr): 3432, 3058, 2971, 2927, 1709, 1691, 1615, 1495, 1471, 1380, 1351, 1265, 1210, 1125, 909, 766, 736, 702 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{17}ClNO_2$ $[M+H]^+$ calcd 314.0942, found 314.0942.



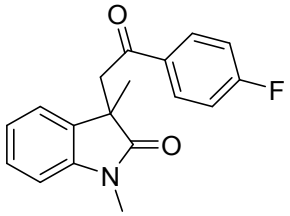
1,3-dimethyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3f)

Colorless oil; 22.2 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.74-7.72 (m, 2H), 7.24 (td, J_t = 7.6 Hz, J_d = 1.2 Hz, 1H), 7.19-7.17 (m, 2H), 7.13 (d, J = 6.8 Hz, 1H), 6.98-6.94 (m, 1H), 6.89 (d, J = 7.6 Hz, 1H), 3.70 (d, J = 18.0 Hz, 1H), 3.61 (d, J = 18.0 Hz, 1H), 3.31 (s, 3H), 2.37 (s, 3H), 1.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 195.7, 180.6, 143.9, 143.8, 133.9, 133.8, 129.1, 128.0, 127.8, 122.1, 121.7, 108.1, 45.9, 45.3, 26.4, 24.9, 21.6. **IR** (KBr): 3456, 3055, 2966, 2926, 1712, 1686, 1613, 1494, 1471, 1379, 1350, 1249, 1183, 1125, 818, 754, 736 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{20}NO_2$ $[M+H]^+$ calcd 294.1489, found 280.1491.



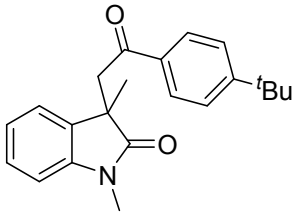
3-(2-(4-chlorophenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3g)

Colorless oil; 19.1 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.78-7.75 (m, 2H), 7.38-7.35 (m, 2H), 7.26 (td, J_t = 7.6 Hz, J_d = 1.2 Hz, 1H), 7.13 (dd, J_d = 7.2 Hz, J_d = 0.8 Hz, 1H), 6.98 (td, J_t = 7.6 Hz, J_d = 0.8 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 3.66 (d, J = 18.0 Hz, 1H), 3.61 (d, J = 18.0 Hz, 1H), 3.30 (s, 3H), 1.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 194.9, 180.4, 143.8, 139.6, 134.6, 133.5, 129.4, 128.8, 127.9, 122.2, 121.7, 108.2, 45.9, 45.2, 26.4, 24.9. **IR** (KBr): 3407, 3056, 2966, 2926, 1711, 1690, 1614, 1587, 1494, 1471, 1379, 1351, 1250, 1213, 1126, 1092, 837, 754, 741 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{17}ClNO_2$ $[M+H]^+$ calcd 314.0942, found 314.0942.



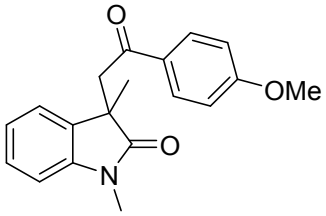
3-(2-(4-fluorophenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3h)

Colorless oil; 19.4 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.88-7.83 (m, 2H), 7.26 (td, J_t = 8.0 Hz, J_d = 1.2 Hz, 1H), 7.14-7.12 (m, 2H), 7.09-7.03 (m, 1H), 6.98 (td, J_t = 7.6 Hz, J_d = 0.8 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 3.67 (d, J = 17.6 Hz, 1H), 3.62 (d, J = 17.6 Hz, 1H), 3.31 (s, 3H), 1.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 194.5, 180.5, 165.7 (d, J = 254 Hz), 143.8, 133.6, 132.9, 132.8 (d, J = 3 Hz), 130.7, 130.6, 127.9, 122.2, 121.7, 115.6 (d, J = 22 Hz), 108.2, 45.9, 45.3, 26.4, 24.9. **IR** (KBr): 3443, 3059, 2968, 2927, 1711, 1690, 1614, 1598, 1495, 1471, 1380, 1351, 1228, 1157, 1126, 840, 754, 737 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{17}FNO_2$ $[M+H]^+$ calcd 298.1238, found 298.1239.



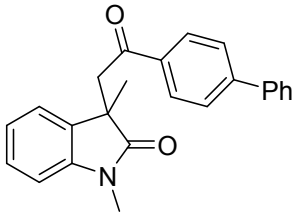
3-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3i)

Colorless oil; 27.5 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.78-7.76 (m, 2H), 7.41-7.39 (m, 2H), 7.24 (td, J_t = 7.6 Hz, J_d = 1.2 Hz, 1H), 7.13-7.11 (m, 1H), 6.96 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.71 (d, J = 18.0 Hz, 1H), 3.62 (d, J = 18.0 Hz, 1H), 3.31 (s, 3H), 1.43 (s, 3H), 1.30 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): 195.7, 180.6, 156.8, 143.8, 133.8, 133.8, 127.8, 127.7, 125.4, 122.0, 121.7, 108.1, 45.9, 45.2, 35.0, 31.0, 26.4, 24.9. **IR** (KBr): 3429, 3056, 2965, 2927, 1711, 1689, 1608, 1494, 1471, 1380, 1351, 1249, 1181, 1125, 846, 753, 741 cm^{-1}. **HRMS** (ESI) for $C_{22}H_{26}NO_2$ $[M+H]^+$ calcd 336.1958, found 336.1960.



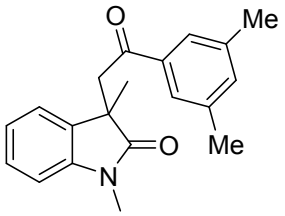
3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3j)

Colorless oil; 22.3 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.84-7.80 (m, 2H), 7.27-7.23 (m, 1H), 7.14-7.12 (m, 1H), 6.96 (td, J_t = 7.6 Hz, J_d = 0.9 Hz, 1H), 6.90-6.84(m, 3H), 3.83 (s, 3H), 3.68 (d, J = 17.7 Hz, 1H), 3.60 (d, J = 17.7 Hz, 1H), 3.31 (s, 3H), 1.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 194.6, 180.7, 163.5, 143.8, 133.9, 130.2, 129.5, 127.7, 122.1, 121.7, 113.6, 108.1, 55.4, 45.6, 45.3, 26.4, 24.9. **IR** (KBr): 3412, 3056, 2966, 2929, 2248, 1708, 1681, 1602, 1495, 1470, 1379, 1351, 1250, 1171, 1125, 910, 839, 754, 743 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{20}NO_3$ $[M+H]^+$ calcd 310.1473, found 310.1475.



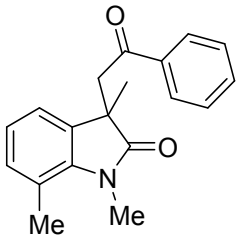
3-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3k)

Colorless oil; 18.4 mg, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.91-7.89 (m, 2H), 7.62-7.57 (m, 4H), 7.47-7.43 (m, 2H), 7.40-7.36 (m, 1H), 7.28-7.23 (m, 1H), 7.15 (dd, J_d = 7.2 Hz, J_d = 0.4 Hz, 1H), 6.98 (td, J_t = 7.6 Hz, J_d = 0.8 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 3.75 (d, J = 17.8 Hz, 1H), 3.68 (d, J = 17.8 Hz, 1H), 3.32 (s, 3H), 1.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 195.7, 180.6, 145.8, 143.8, 139.7, 135.1, 133.7, 128.9, 128.6, 128.2, 127.8, 127.2, 127.1, 122.2, 121.8, 108.2, 46.4, 45.3, 26.5, 24.9. **IR** (KBr): 3416, 3056, 2966, 2926, 1712, 1686, 1613, 1494, 1471, 1379, 1351, 1250, 1220, 1125, 1006, 847, 764, 753, 736, 699 cm^{-1}. **HRMS** (ESI) for $C_{24}H_{22}NO_2$ $[M+H]^+$ calcd 356.1645, found 356.1646.



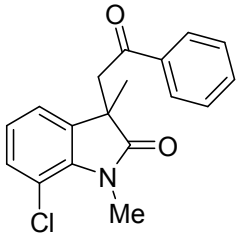
3-(2-(3,5-dimethylphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3l)

Colorless oil; 25.9 mg, 83% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.44 (s, 2H), 7.26-7.22 (m, 1H), 7.14-7.12 (m, 2H), 6.96 (td, J_t = 7.6 Hz, J_d = 0.6 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.70 (d, J = 17.9 Hz, 1H), 3.60 (d, J = 17.9 Hz, 1H), 3.31 (s, 3H), 2.31 (s, 6H), 1.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.4, 180.6, 143.9, 138.1, 136.4, 134.7, 133.8, 127.7, 125.7, 122.1, 121.7, 108.0, 46.1, 45.2, 26.4, 24.8, 21.1. **IR** (KBr): 3450, 3054, 2966, 2924, 1713, 1688, 1614, 1495, 1471, 1380, 1350, 1249, 1183, 1125, 855, 754, 741 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{20}NO_2$ $[M+H]^+$ calcd 308.1645, found 308.1643.



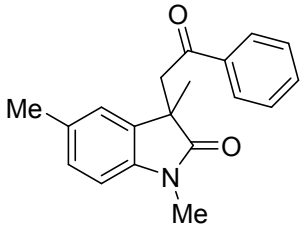
1,3,7-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3m)

Colorless oil; 16.2 mg, 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.84-7.82 (m, 2H), 7.53-7.49 (m, 1H), 7.39 (t, J = 7.5 Hz, 2H), 6.95 (t, J = 7.6 Hz, 2H), 6.85 (t, J = 7.5 Hz, 1H), 3.69 (d, J = 17.9 Hz, 1H), 3.64 (d, J = 17.9 Hz, 1H), 3.58 (s, 3H), 2.62 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.2, 181.4, 141.6, 136.4, 134.4, 133.1, 128.4, 127.9, 122.0, 119.7, 119.5, 46.3, 44.6, 29.8, 25.5, 19.1. **IR** (KBr): 3449, 3058, 2970, 2927, 1710, 1690, 1601, 1461, 1449, 1373, 1244, 1217, 1127, 778, 747, 712, 691 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{20}NO_2$ $[M+H]^+$ calcd 294.1489, found 294.1488.



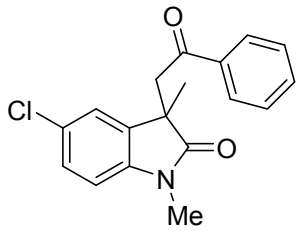
7-chloro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3n)

Colorless oil; 23.3 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.84-7.82 (m, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.16 (dd, J_d = 8.2 Hz, J_d = 0.9 Hz, 1H), 6.98 (dd, J_d = 7.2 Hz, J_d = 0.8 Hz, 1H), 6.87 (t, J = 8.0 Hz, 1H), 3.69 (s, 2H), 3.68 (s, 3H), 1.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 195.9, 180.9, 139.8, 136.7, 136.1, 133.3, 130.2, 128.5, 127.9, 122.9, 120.0, 115.6, 46.4, 45.0, 29.8, 25.3. **IR** (KBr): 3421, 3063, 2969, 2927, 1718, 1689, 1609, 1468, 1450, 1367, 1352, 1217, 1125, 1065, 774, 754, 736, 690 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{17}ClNO_2$ $[M+H]^+$ calcd 314.0942, found 314.0943.



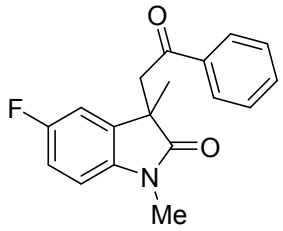
1,3,5-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3o)

Colorless oil; 25.4 mg, 87% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.85-7.83 (m, 2H), 7.53-7.49 (m, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.04 (dd, J_d = 7.9 Hz, J_d = 0.8 Hz, 2H), 6.95 (s, 1H), 6.78 (d, J = 7.8 Hz, 1H), 3.69 (d, J = 17.9 Hz, 1H), 3.63 (d, J = 17.9 Hz, 1H), 3.29 (s, 3H), 2.27 (s, 3H), 1.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.1, 180.5, 141.4, 136.4, 133.7, 133.1, 131.5, 128.4, 128.0, 128.0, 122.7, 107.8, 46.0, 45.3, 26.4, 25.0, 21.1. **IR** (KBr): 3409, 3059, 2966, 2925, 1711, 1690, 1621, 1600, 1502, 1449, 1352, 1247, 1217, 875, 807, 762, 690 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{20}NO_2$ $[M+H]^+$ calcd 294.1489, found 294.1491.



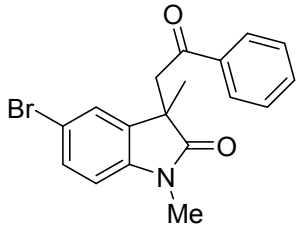
5-chloro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3p)

Colorless oil; 25.6 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.85-7.83 (m, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.9 Hz, 2H), 7.23 (dd, J_d = 8.4 Hz, J_d = 2.0 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 3.69 (s, 2H), 3.30 (s, 3H), 1.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 195.8, 180.1, 142.5, 136.1, 135.6, 133.4, 128.6, 128.0, 127.7, 127.5, 122.3, 109.0, 46.1, 45.4, 26.6, 24.8. **IR** (KBr): 3443, 3061, 2970, 2928, 1718, 1690, 1611, 1492, 1450, 1349, 1245, 1216, 1130, 1048, 878, 811, 740, 690 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{17}ClNO_2$ $[M+H]^+$ calcd 314.0942, found 314.0941.



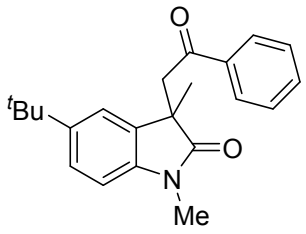
5-fluoro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3q)

Colorless oil; 24.2 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.85-7.83 (m, 2H), 7.55-7.51 (m, 1H), 7.40 (t, J = 7.9 Hz, 2H), 6.97-6.92 (m, 1H), 6.90 (dd, J_d = 7.9 Hz, J_d = 2.5 Hz, 1H), 6.81 (dd, J_d = 8.5 Hz, J_d = 4.2 Hz, 1H), 3.67 (s, 2H), 3.30 (s, 3H), 1.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 195.9, 180.2, 159.1 (d, J = 238 Hz), 139.8, 136.2, 135.4 (d, J = 8.0 Hz), 133.3, 130.1, 128.5, 113.8 (d, J = 23 Hz), 110.1 (d, J = 24 Hz), 108.5 (d, J = 8 Hz), 45.9, 45.7, 26.6, 24.8. **IR** (KBr): 3420, 3062, 2969, 2929, 1713, 1690, 1618, 1498, 1469, 1449, 1353, 1281, 1245, 1218, 1118, 877, 810, 763, 690 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{17}FNO_2$ $[M+H]^+$ calcd 298.1238, found 298.1236.



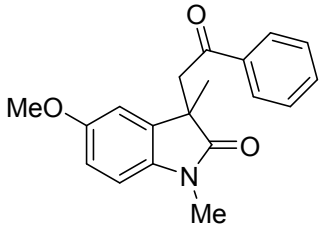
5-bromo-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3r)

Colorless oil; 29.2 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.84-7.82 (m, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.9 Hz, 2H), 7.38 (dd, J_d = 8.2 Hz, J_d = 1.9 Hz, 1H), 7.23 (d, J = 1.9 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 3.69 (s, 2H), 3.30 (s, 3H), 1.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 195.8, 180.0, 143.0, 136.1, 136.0, 133.4, 130.6, 128.6, 128.0, 125.0, 114.8, 109.6, 46.1, 45.4, 26.5, 24.9. **IR** (KBr): 3422, 3060, 2968, 2927, 1717, 1689, 1608, 1490, 1449, 1347, 1244, 1216, 1130, 1117, 1048, 878, 809, 738, 690 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{17}BrNO_2$ $[M+H]^+$ calcd 358.0437, found 358.0439.



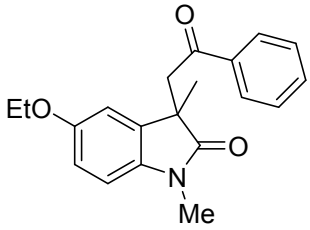
5-(tert-butyl)-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3s)

Colorless oil; 27.1 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.83-7.81 (m, 2H), 7.52-7.48 (m, 1H), 7.38 (t, J = 7.4 Hz, 2H), 7.26 (dd, J_d = 8.1 Hz, J_d = 1.9 Hz, 1H), 7.17 (d, J = 1.8 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 3.69 (d, J = 17.5 Hz, 1H), 3.60 (d, J = 17.5 Hz, 1H), 3.28 (s, 3H), 1.45 (s, 3H), 1.24 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.4, 180.6, 145.3, 141.3, 136.6, 133.2, 133.0, 129.0, 128.4, 127.9, 127.6, 124.4, 119.2, 107.4, 45.9, 45.7, 34.4, 31.5, 26.4, 24.8. **IR** (KBr): 3282, 3061, 2961, 2929, 1713, 1692, 1621, 1598, 1500, 1449, 1367, 1351, 1255, 1215, 1119, 871, 814, 747, 691 cm^{-1}. **HRMS** (ESI) for $C_{22}H_{26}NO_2$ $[M+H]^+$ calcd 336.1958, found 336.1956.



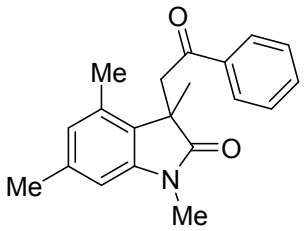
5-methoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3t)

Colorless oil; 27.9 mg, 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.85-7.83 (m, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 6.81-6.76 (m, 3H), 3.73 (s, 3H), 3.69 (d, J = 18.4 Hz, 1H), 3.64 (d, J = 18.4 Hz, 1H), 3.29 (s, 3H), 1.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 195.8, 180.1, 142.5, 136.1, 135.6, 133.4, 128.6, 128.0, 127.7, 127.5, 122.3, 109.0, 46.1, 45.4, 26.6, 24.8. **IR** (KBr): 3402, 3060, 2965, 2929, 1708, 1690, 1599, 1500, 1470, 1449, 1353, 1292, 1221, 1127, 1041, 871, 806, 761, 690 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{20}NO_3$ $[M+H]^+$ calcd 310.1438, found 310.1439.



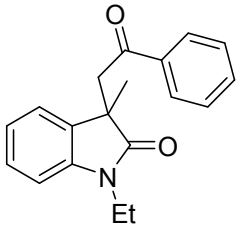
5-ethoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3u)

Colorless oil; 27.2 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.84-7.82 (m, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 6.80-6.75 (m, 3H), 3.94 (q, J = 7.0 Hz, 2H), 3.68 (d, J = 18.0 Hz, 1H), 3.63 (d, J = 18.0 Hz, 1H), 3.28 (s, 3H), 1.43 (s, 3H), 1.35 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.0, 180.2, 155.1, 137.4, 136.4, 135.1, 133.1, 128.5, 128.0, 122.1, 110.6, 108.3, 64.0, 46.0, 45.7, 26.5, 24.9, 14.9. **IR** (KBr): 3404, 3061, 2975, 2927, 1709, 1691, 1600, 1501, 1449, 1354, 1294, 1245, 1220, 1114, 1046, 870, 803, 763, 691 cm^{-1}. **HRMS** (ESI) for $C_{20}H_{22}NO_3$ $[M+H]^+$ calcd 324.1594, found 324.1596.



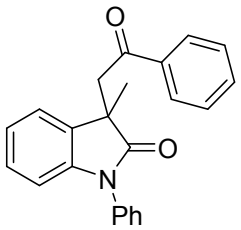
1,3,4,6-tetramethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3v)

Colorless oil; 24.6 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.82-7.80 (m, 2H), 7.50 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 6.56 (d, J = 4.0 Hz, 2H), 3.92 (d, J = 17.8 Hz, 1H), 3.67 (d, J = 17.8 Hz, 1H), 3.25 (s, 3H), 2.32 (s, 3H), 2.25 (s, 3H), 1.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.4, 180.7, 144.2, 137.5, 136.2, 133.0, 132.4, 129.0, 128.4, 127.9, 127.6, 127.4, 125.3, 107.0, 45.8, 45.0, 26.4, 23.0, 21.5, 18.1. **IR** (KBr): 3408, 3058, 2967, 2927, 1713, 1692, 1621, 1598, 1501, 1467, 1449, 1342, 1240, 1213, 1061, 914, 833, 730, 690 cm^{-1}. **HRMS** (ESI) for $C_{20}H_{22}NO_2$ $[M+H]^+$ calcd 308.1645, found 308.1644.



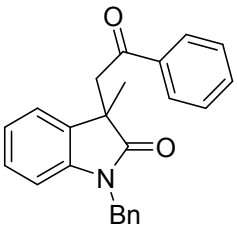
1-ethyl-3-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3w)

Colorless oil; 27.0 mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.84-7.82 (m, 2H), 7.50 (tt, J_t = 7.2 Hz, J_t = 1.2 Hz, 1H), 7.40-7.36 (m, 2H), 7.23 (td, J_t = 7.6 Hz, J_d = 1.2 Hz, 1H), 7.13 (dd, J_d = 7.3 Hz, J_d = 0.8 Hz, 1H), 6.96 (td, J_t = 7.5 Hz, J_d = 0.8 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 3.93-3.77 (m, 2H), 3.71 (d, J = 17.8 Hz, 1H), 3.64 (d, J = 17.8 Hz, 1H), 1.43 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.0, 180.1, 142.9, 136.5, 134.0, 133.1, 128.4, 128.0, 127.7, 121.9, 121.9, 108.3, 45.9, 45.2, 34.7, 25.0, 12.3. **IR** (KBr): 3402, 3057, 2973, 2930, 1710, 1691, 1613, 1490, 1468, 1449, 1377, 1353, 1217, 1132, 756, 741, 690 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{20}NO_2$ $[M+H]^+$ calcd 294.1489, found 294.1491.



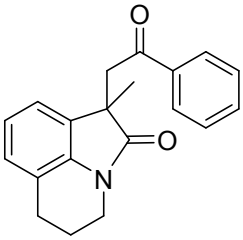
3-methyl-3-(2-oxo-2-phenylethyl)-1-phenylindolin-2-one (3x)

Colorless oil; 25.2 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.88-7.86 (m, 2H), 7.58-7.50 (m, 5H), 7.42-7.38 (m, 3H), 7.18-7.14 (m, 2H), 7.01-6.97 (m, 1H), 6.85-6.83 (m, 1H), 3.82 (d, J = 17.9 Hz, 1H), 3.75 (d, J = 17.9 Hz, 1H), 1.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.0, 180.1, 144.1, 136.3, 135.1, 133.5, 133.2, 129.5, 128.5, 128.0, 127.9, 127.7, 127.0, 122.5, 121.8, 109.4, 46.7, 45.3, 25.3. **IR** (KBr): 3356, 3060, 2967, 2925, 1720, 1688, 1612, 1597, 1502, 1466, 1449, 1378, 1216, 1174, 757, 738, 693 cm^{-1}. **HRMS** (ESI) for $C_{23}H_{20}NO_2$ $[M+H]^+$ calcd 342.1489, found 342.1488.



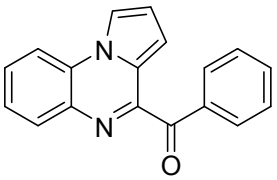
1-benzyl-3-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3y)

Colorless oil; 33.5 mg, 94% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.89-7.87 (m, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.43-7.40 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 6.9 Hz, 1H), 7.15-7.10 (m, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.09 (d, *J* = 15.8 Hz, 1H), 4.96 (d, *J* = 15.8 Hz, 1H), 3.78 (d, *J* = 17.8 Hz, 1H), 3.72 (d, *J* = 17.8 Hz, 1H), 1.50 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 195.9, 180.6, 142.9, 136.4, 136.3, 133.8, 133.2, 128.7, 128.5, 128.0, 127.7, 127.4, 127.2, 122.2, 121.7, 109.3, 45.8, 45.4, 44.0, 25.5. **IR** (KBr): 3338, 3059, 2967, 2925, 1711, 1690, 1612, 1599, 1489, 1467, 1450, 1354, 1216, 1179, 753, 739, 692 cm^{-1}. **HRMS** (ESI) for $C_{24}H_{22}NO_2$ $[M+H]^+$ calcd 356.1645, found 356.1644.



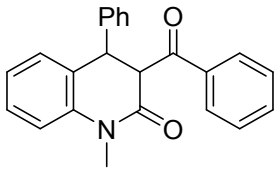
1-methyl-1-(2-oxo-2-phenylethyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (3ab)

Colorless oil; 29.2 mg, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.84-7.82 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 3.81-3.77 (m, 2H), 3.68 (d, *J* = 17.8 Hz, 1H), 3.60 (d, *J* = 17.8 Hz, 1H), 2.88-2.75 (m, 2H), 2.14-2.00 (m, 2H), 1.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.3, 179.4, 139.6, 136.5, 133.0, 132.2, 128.4, 127.9, 126.7, 121.6, 120.1, 119.9, 46.6, 45.9, 38.9, 24.7, 24.5, 21.2. **IR** (KBr): 3403, 3055, 2964, 2926, 1707, 1690, 1627, 1601, 1483, 1448, 1354, 1217, 1167, 774, 750, 734, 691 cm^{-1}. **HRMS** (ESI) for $C_{20}H_{20}NO_2$ $[M+H]^+$ calcd 306.1489, found 306.1488.



phenyl(pyrrolo[1,2-a]quinoxalin-4-yl)methanone (6a)

Yellowish oil; 20.9 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 8.18-8.16 (m, 2H), 8.02-8.00 (m, 2H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.64-7.57 (m, 2H), 7.51-7.46 (m, 3H), 7.21 (dd, J_d = 4.0 Hz, J_d = 1.0 Hz, 1H), 6.94 (dd, J_d = 4.0 Hz, J_d = 2.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 192.3, 149.9, 135.8, 134.7, 133.5, 131.1, 131.0, 130.3, 129.4, 128.3, 127.9, 125.4, 124.3, 114.9, 114.7, 113.8, 108.9. **IR** (KBr): 3163, 1666, 1460, 1426, 1374, 1308, 1254, 1202, 1037, 1448, 977, 873, 758, 730, 682 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{13}N_2O$ $[M+H]^+$ calcd 273.1022, found 273.1021.

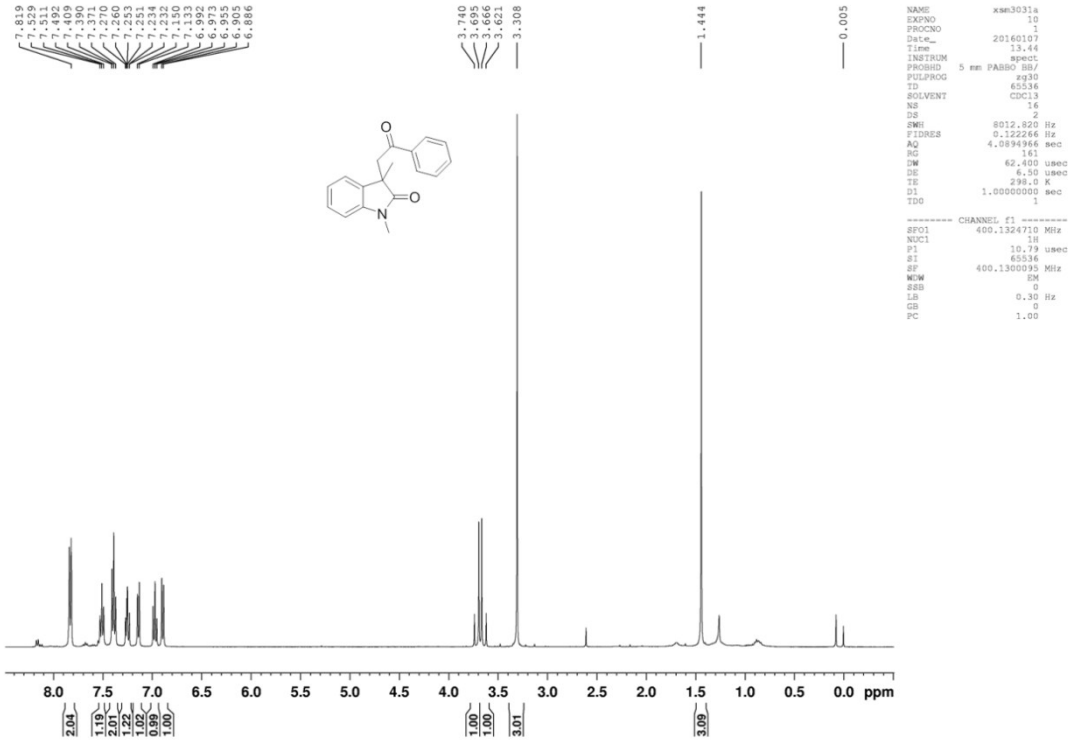


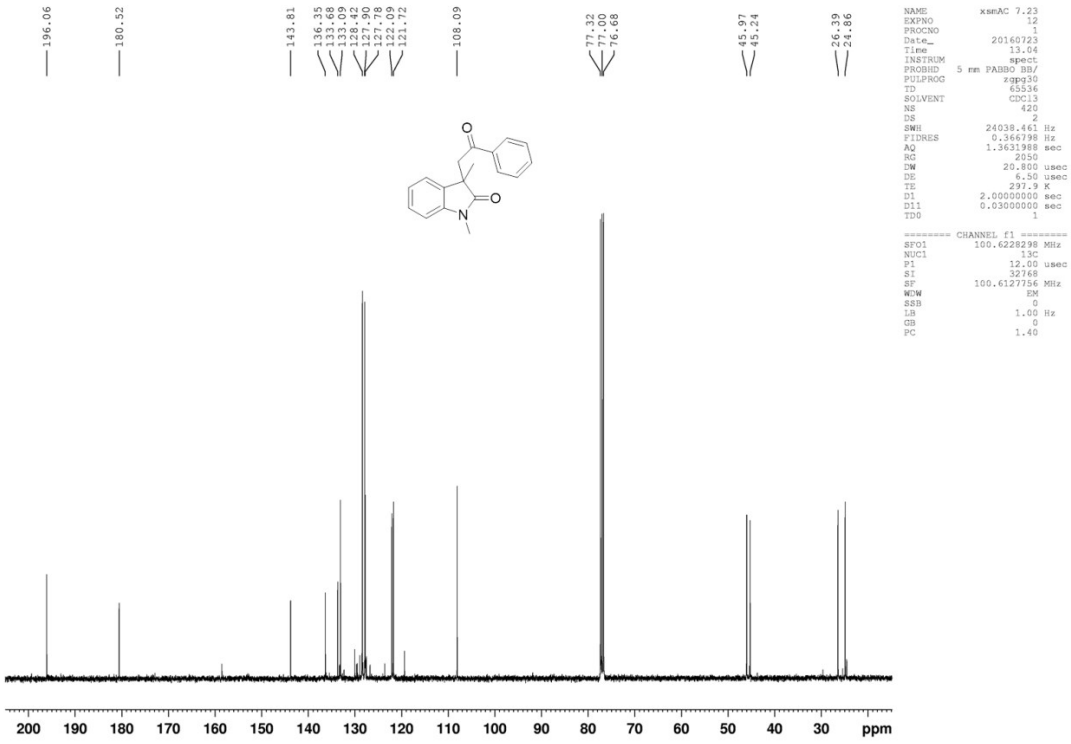
3-benzoyl-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (6b)

Colorless oil; 12.7 mg, 37% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.91-7.89 (m, 2H), 7.54 (tt, J_t = 7.4 Hz, J_t = 1.2 Hz, 1H), 7.43 (t, J = 7.9 Hz, 2H), 7.34-7.27 (m, 3H), 7.24-7.17 (m, 3H), 7.10 (d, J = 7.6 Hz, 1H), 7.00 (td, J_t = 7.5 Hz, J_d = 1.0 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 4.93 (d, J = 7.8 Hz, 1H), 4.71 (d, J = 7.8 Hz, 1H), 3.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 195.6, 166.7, 140.0, 139.5, 136.7, 133.3, 129.0, 128.7, 128.6, 128.0, 127.4, 127.3, 123.5, 114.9, 55.9, 44.9, 29.9. **IR** (KBr): 3445, 3062, 3029, 2929, 1690, 1661, 1596, 1495, 1449, 1366, 1289, 1217, 1125, 757, 732, 698 cm^{-1}. **HRMS** (ESI) for $C_{23}H_{20}NO_2$ $[M+H]^+$ calcd 342.1489, found 342.1487.

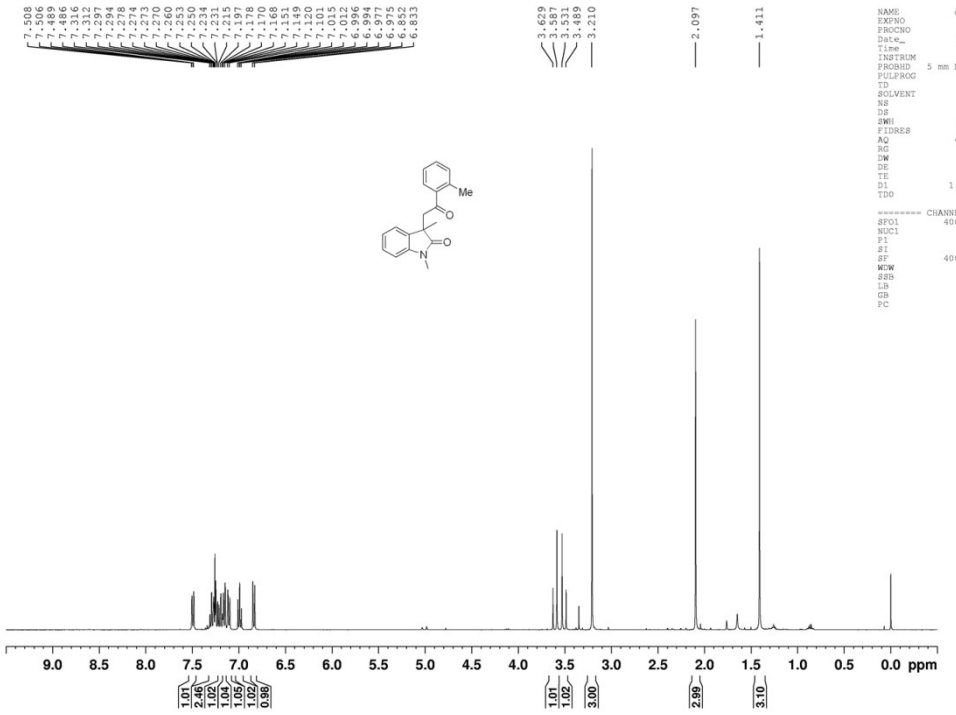
8. NMR Spectra

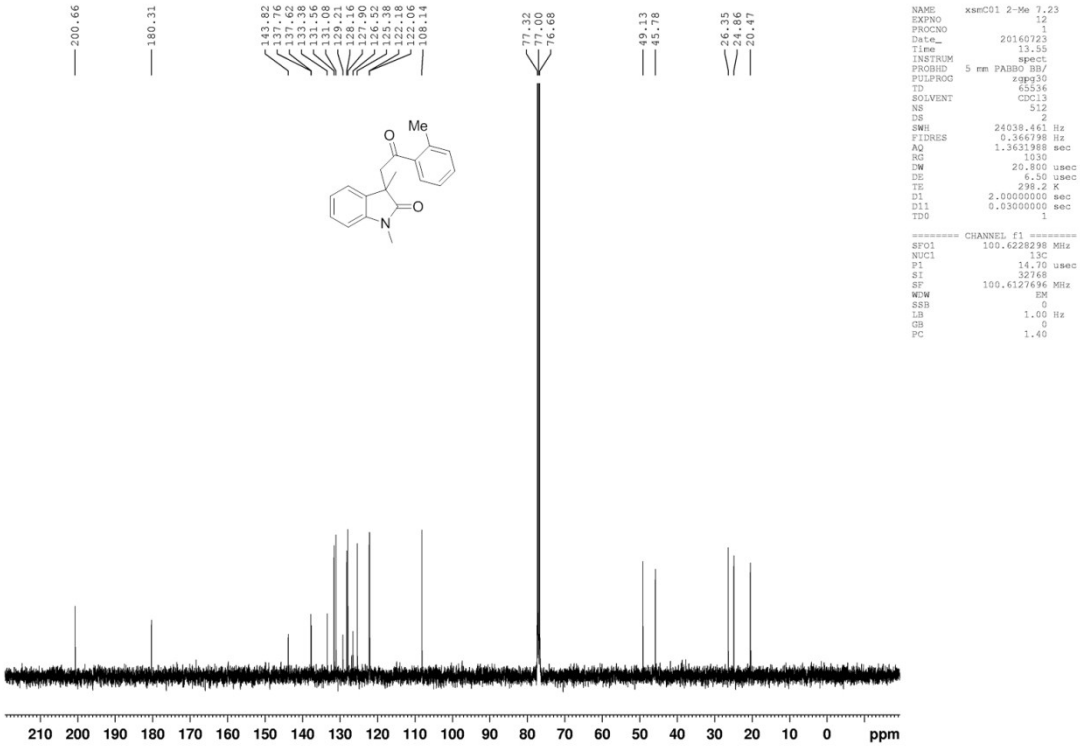
1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3a)



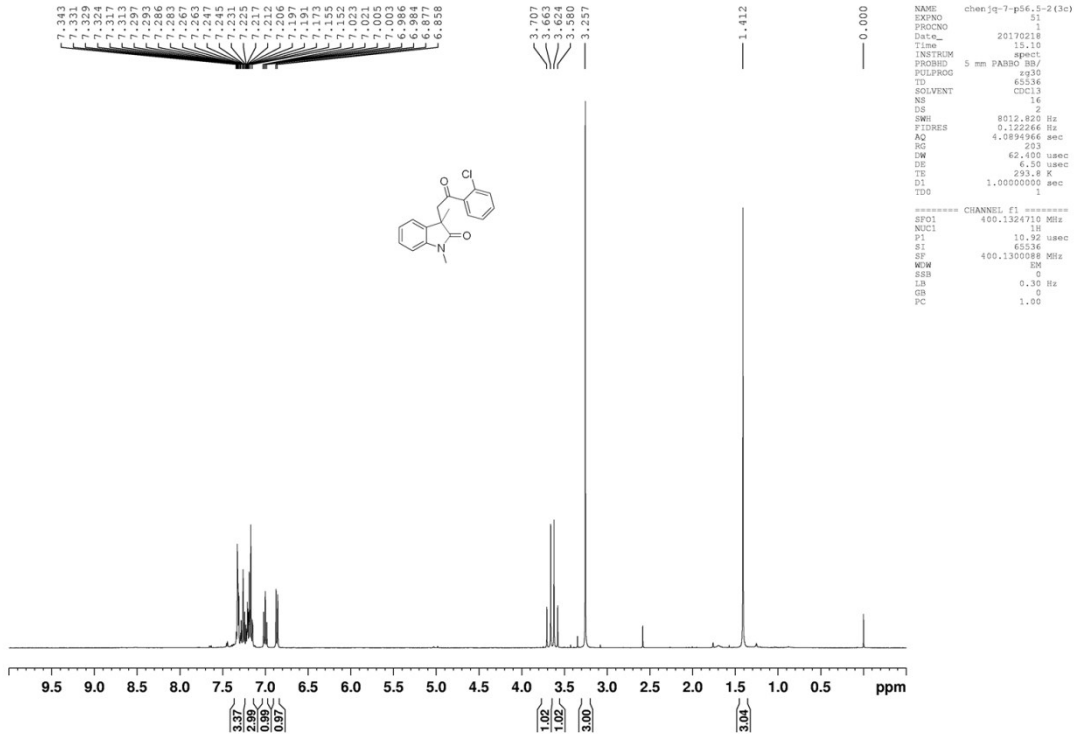


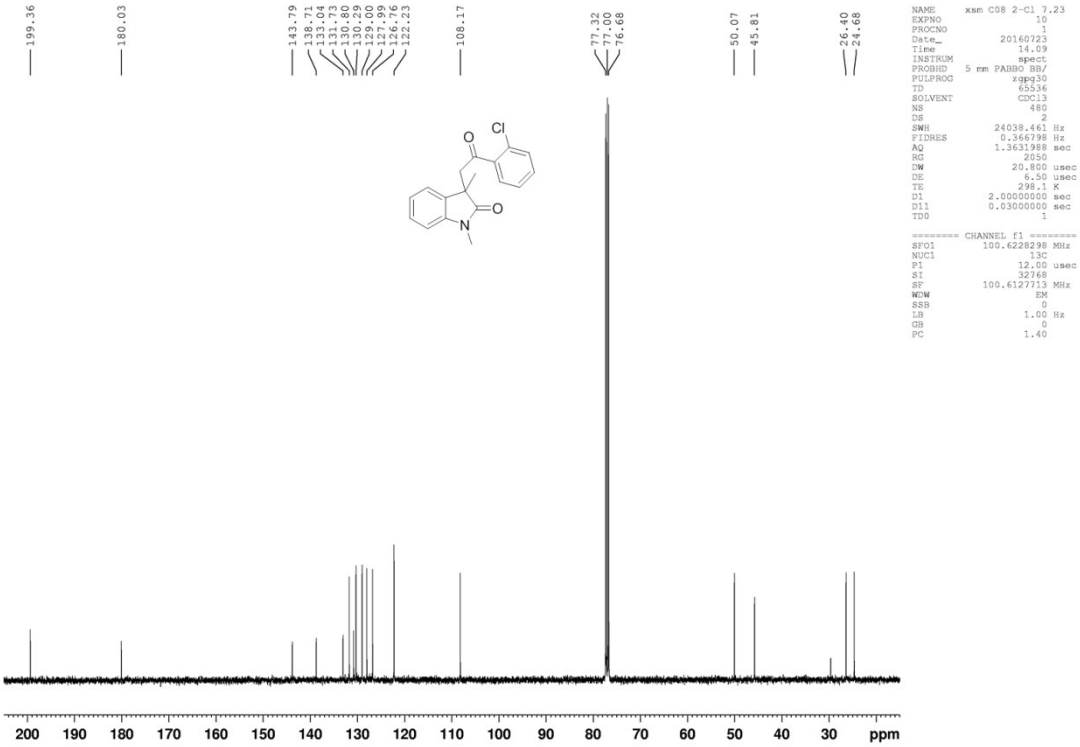
1,3-dimethyl-3-(2-oxo-2-(o-tolyl)ethyl)indolin-2-one (3b)



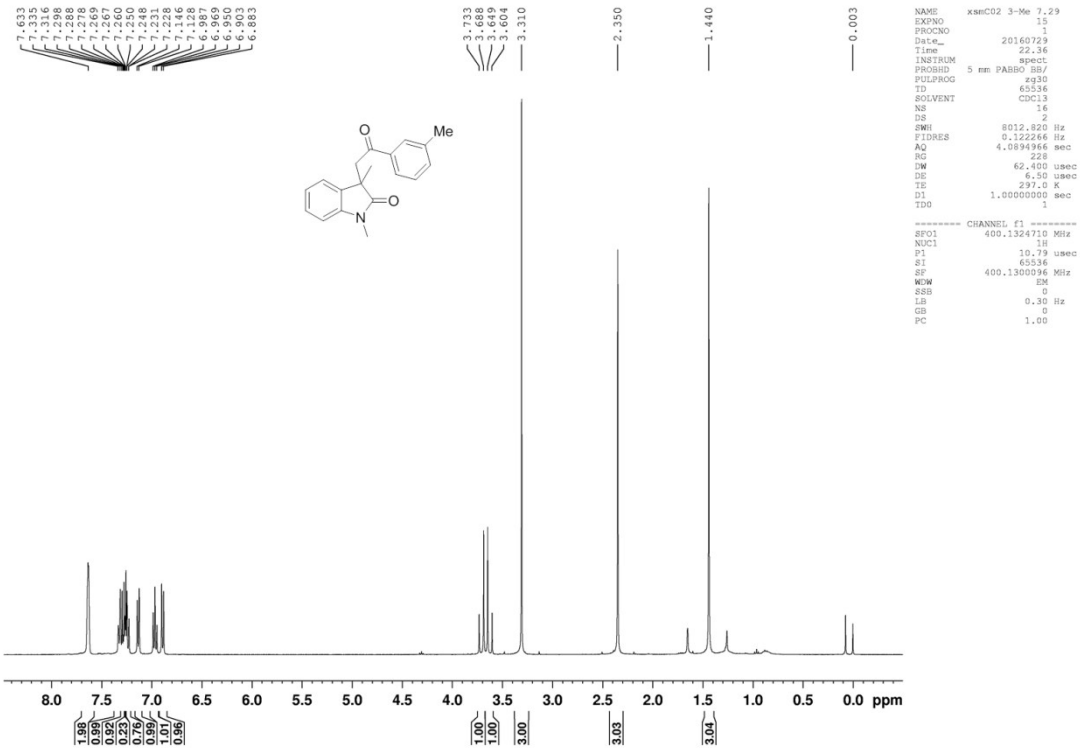


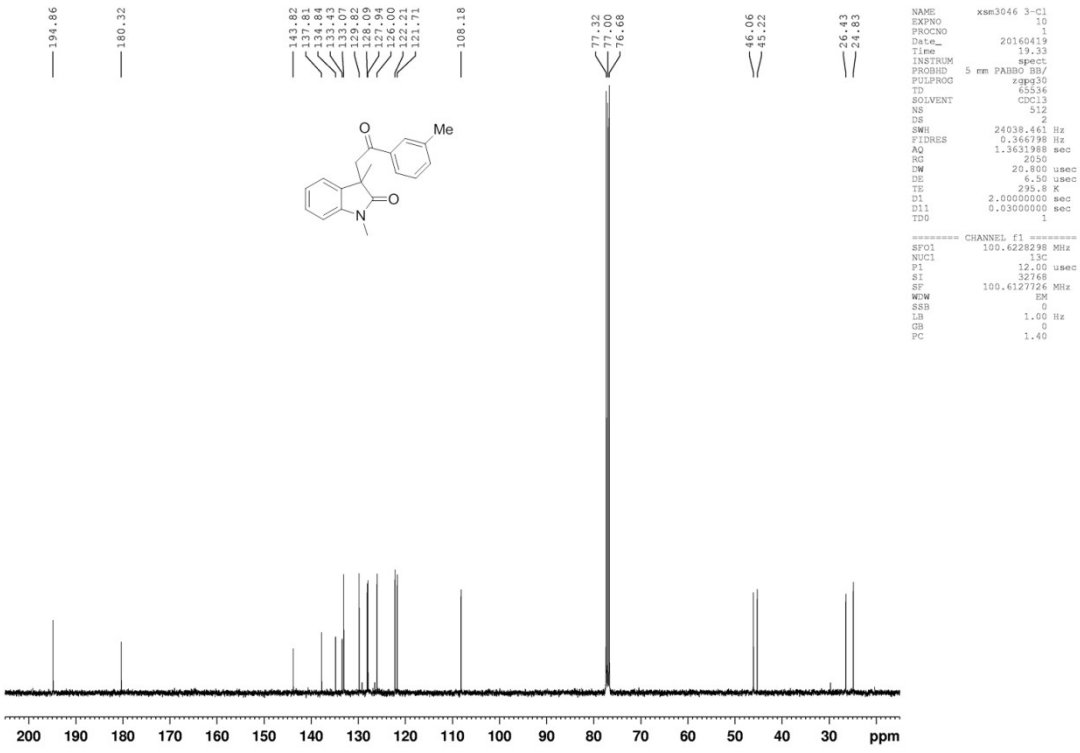
3-(2-(2-chlorophenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3c)



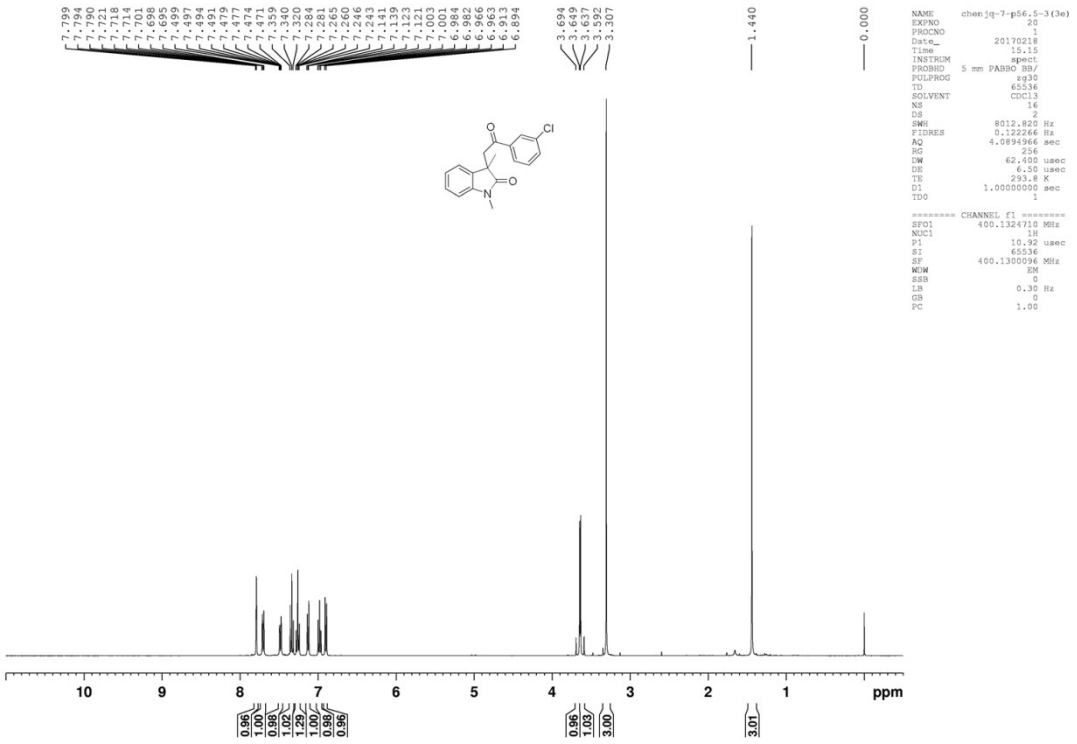


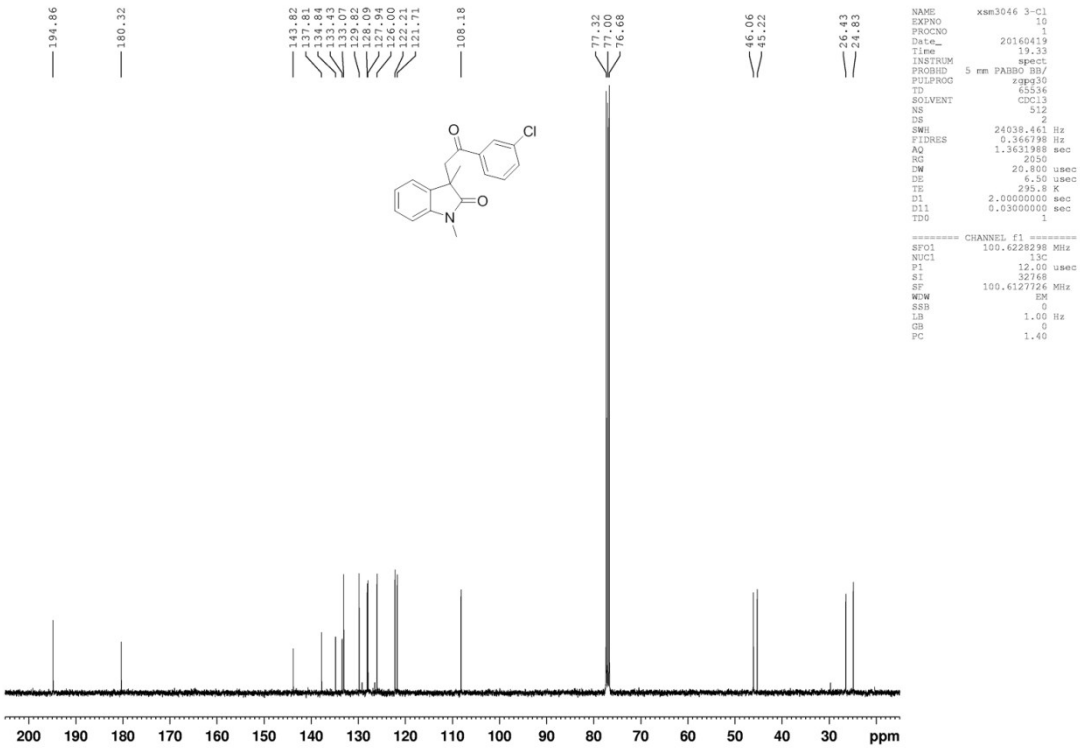
1,3-dimethyl-3-(2-oxo-2-(m-tolyl)ethyl)indolin-2-one (3d)



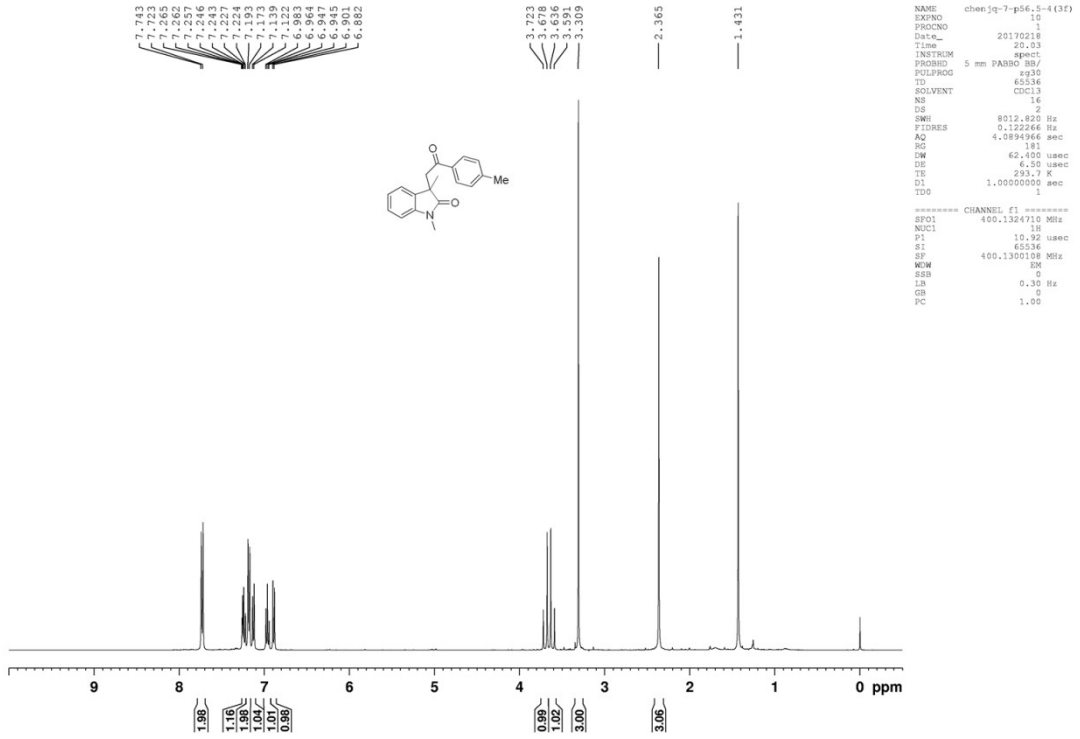


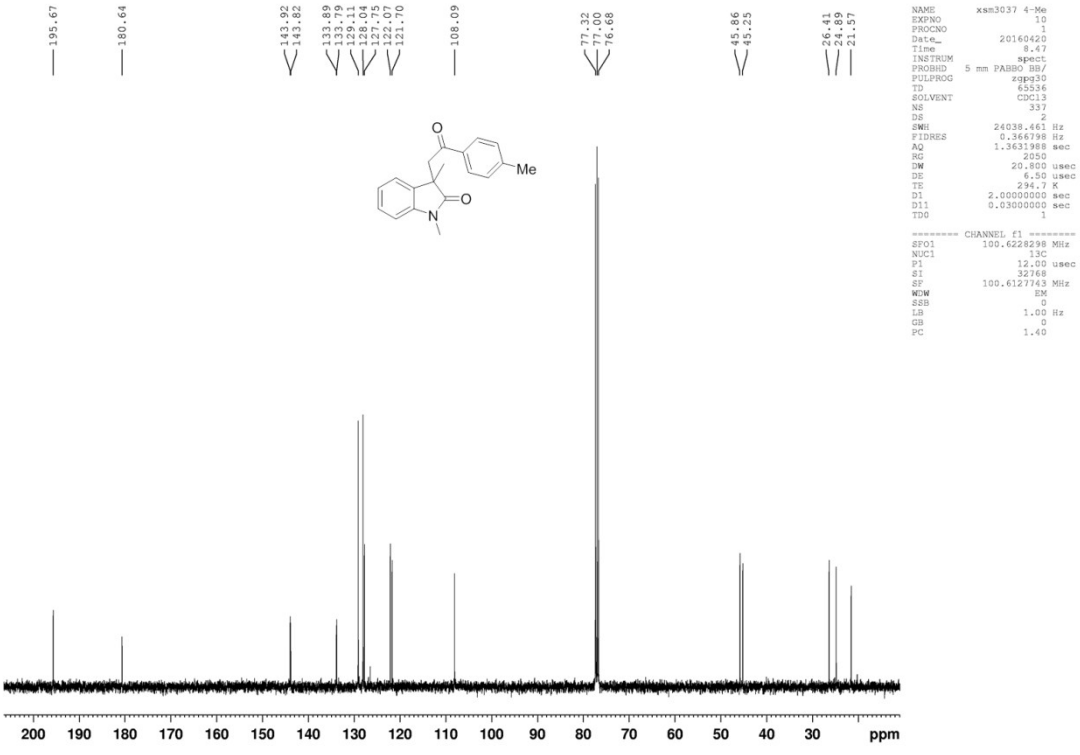
3-(2-(3-chlorophenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3e)



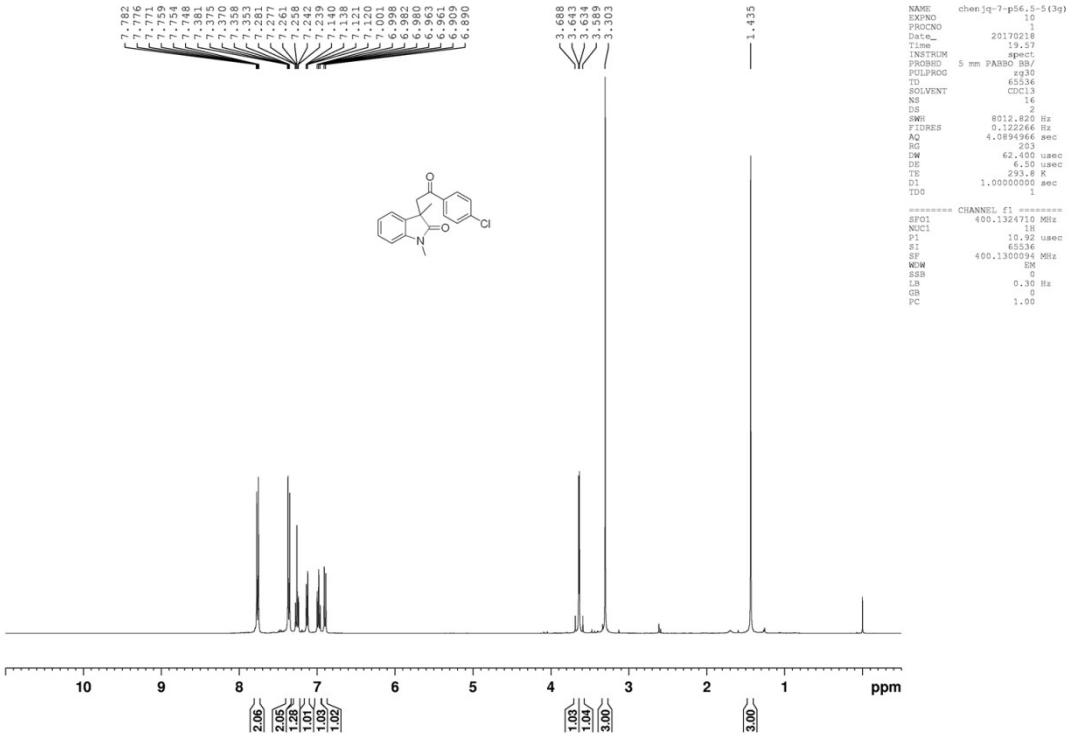


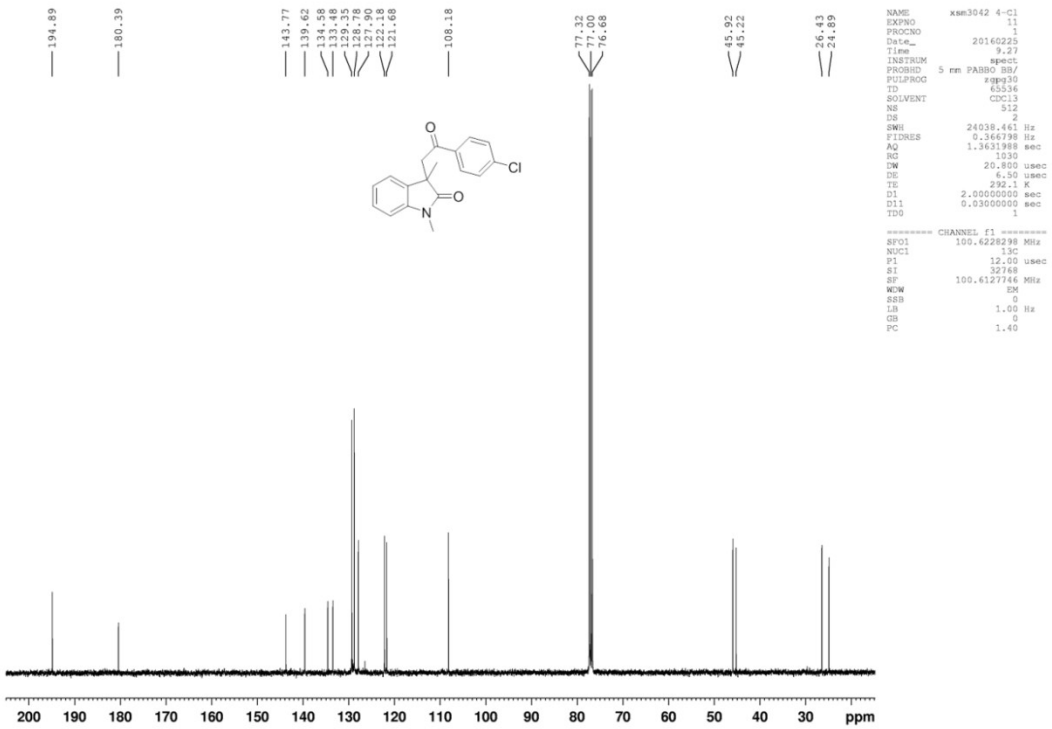
1,3-dimethyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3f)



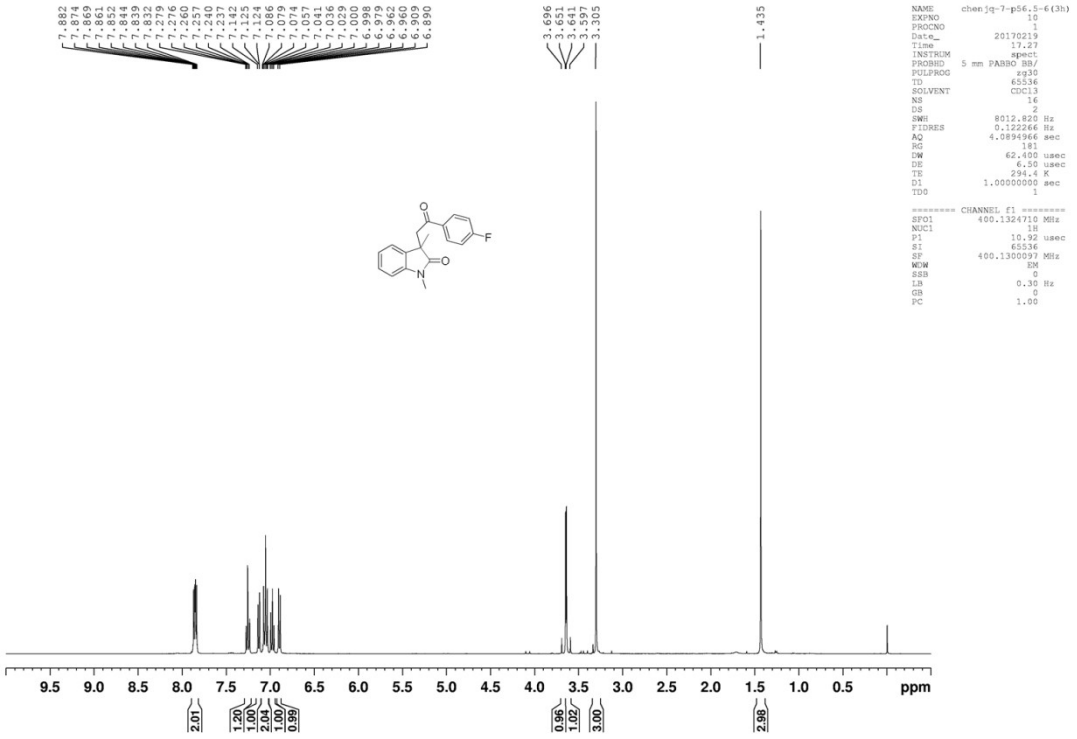


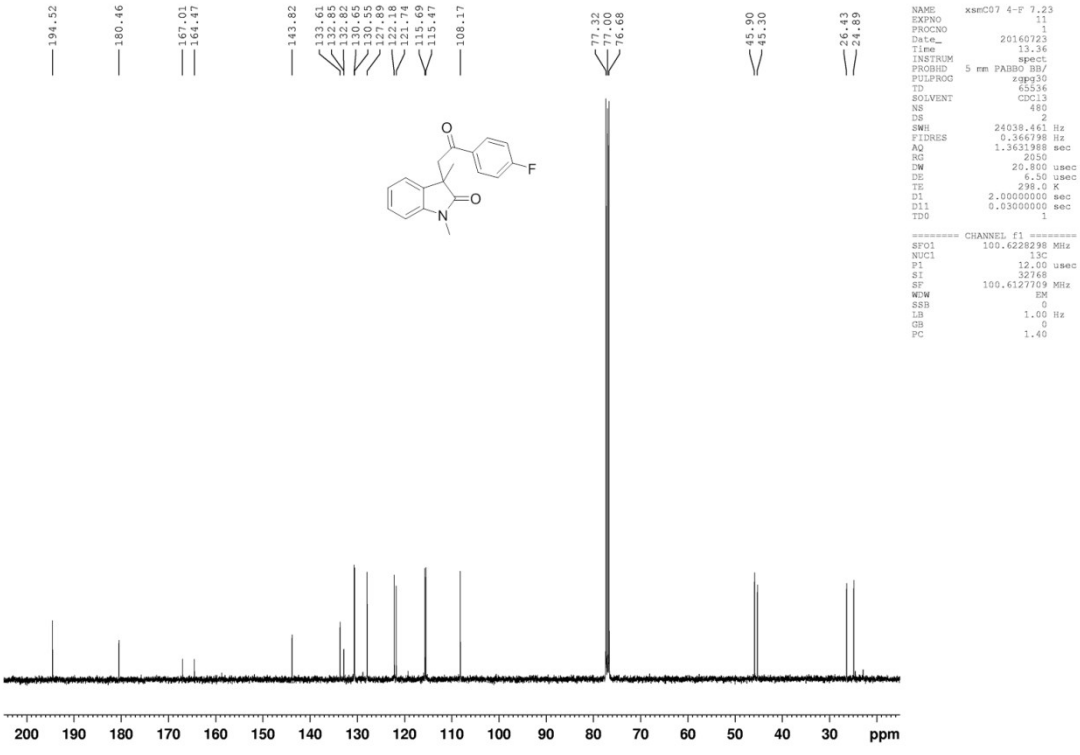
3-(2-(4-chlorophenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3g)



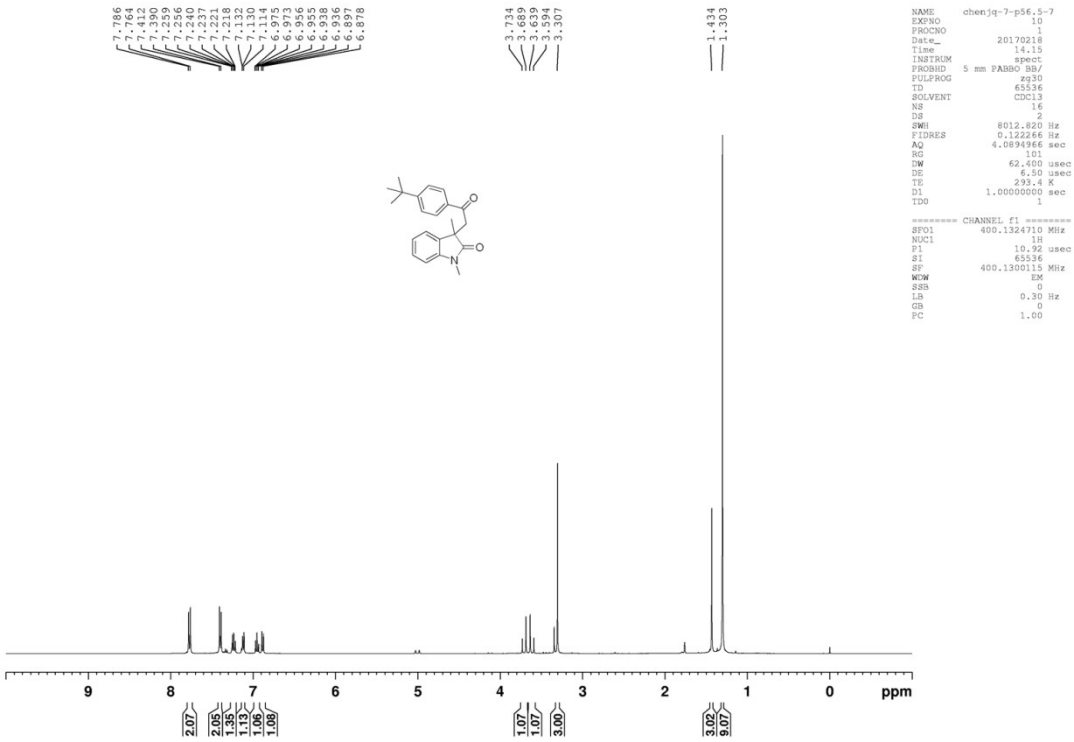


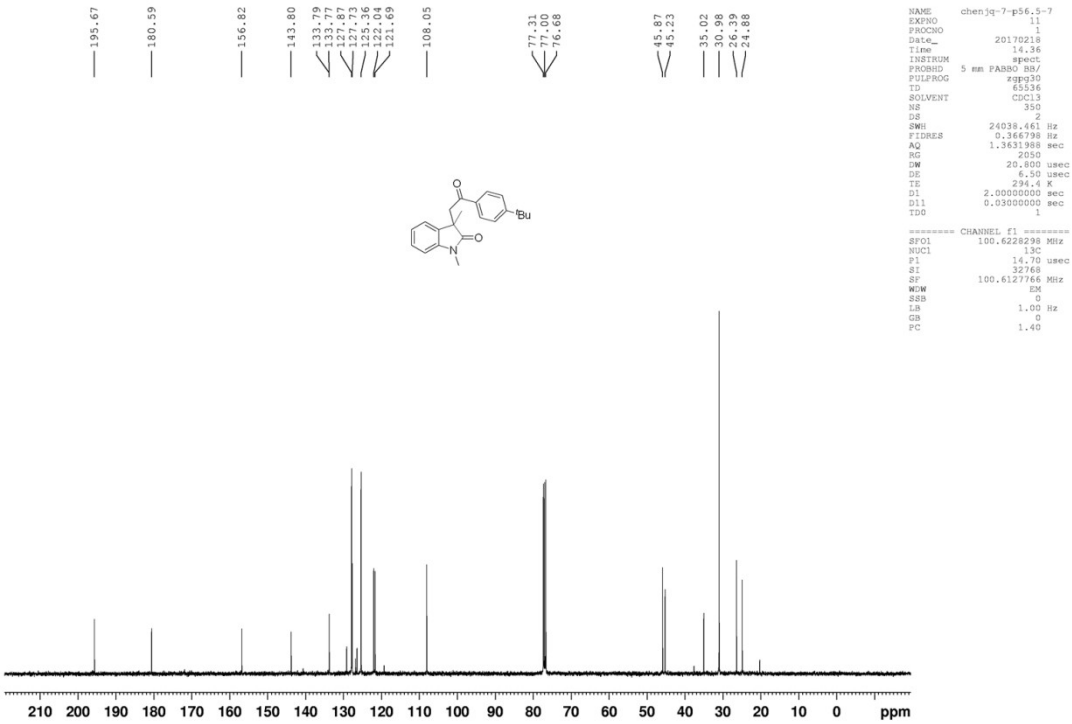
3-(2-(4-fluorophenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3h)



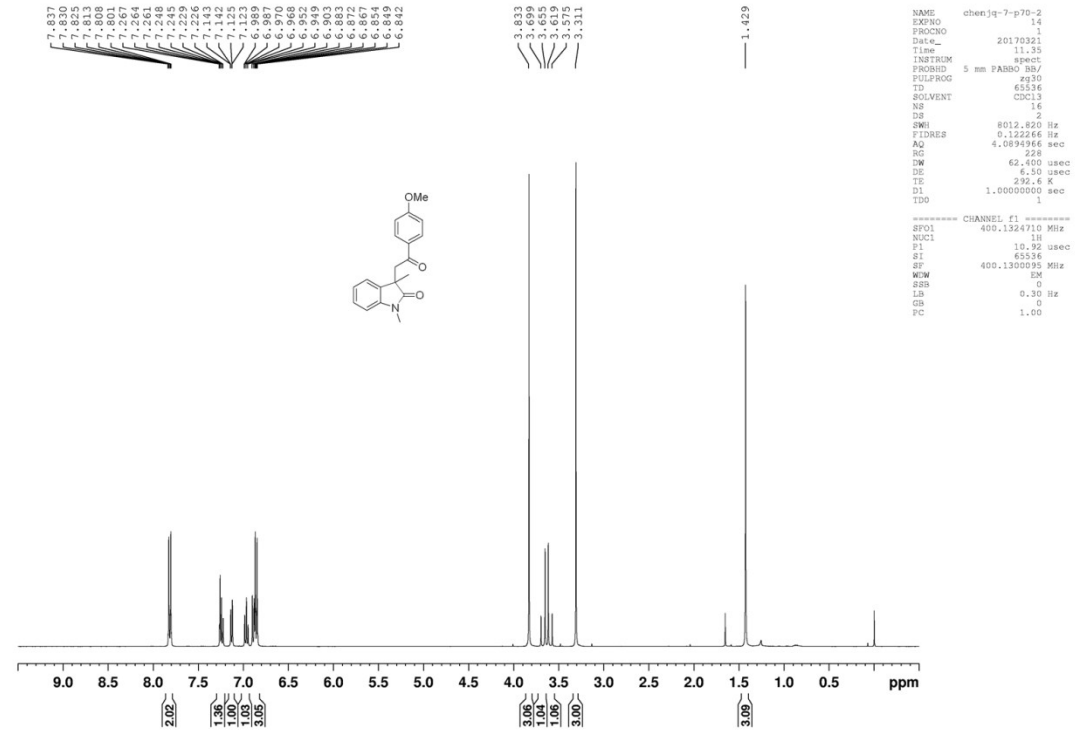


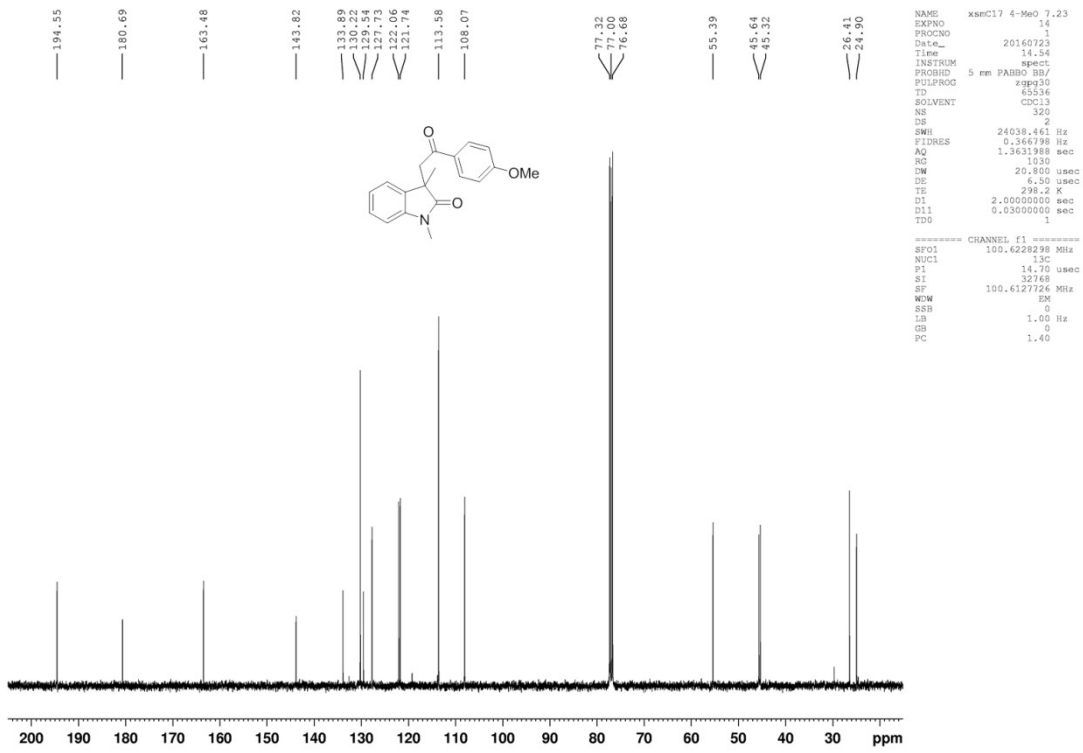
3-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3i)



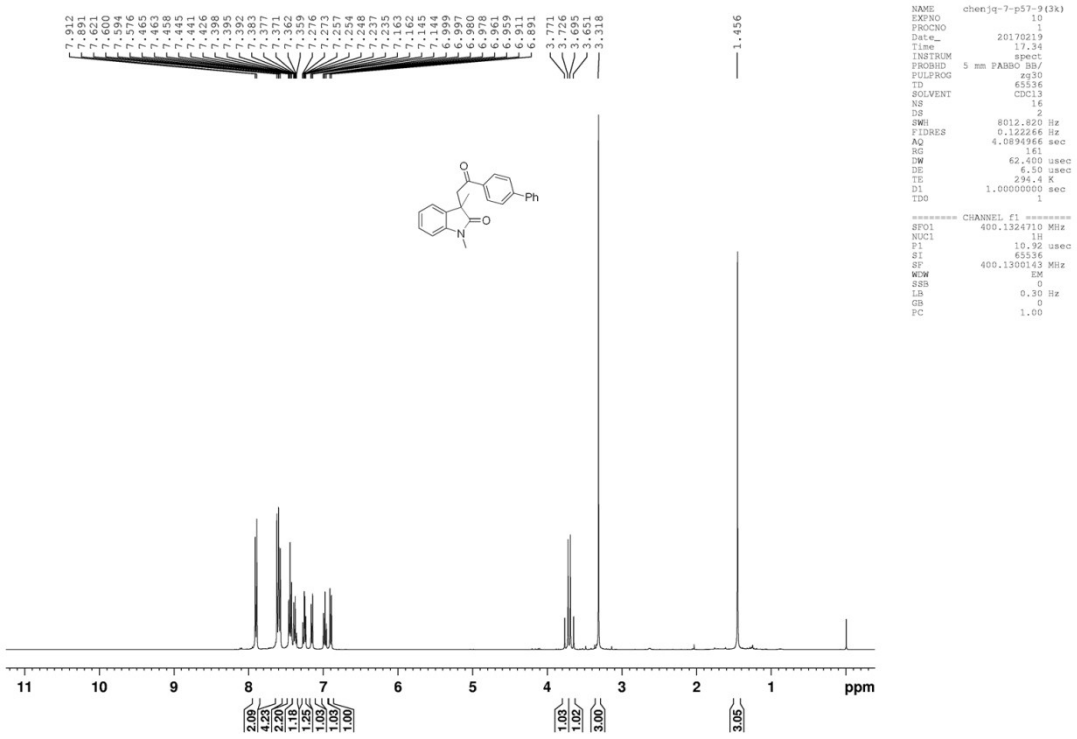


3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3j)





3-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3k)

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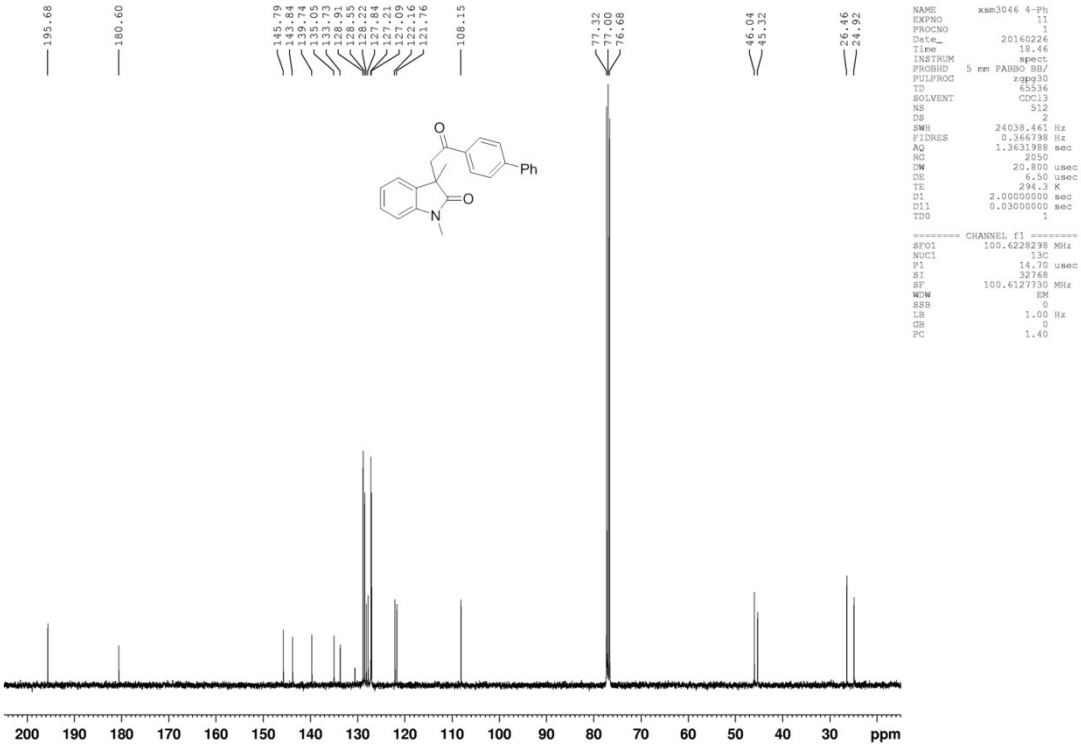
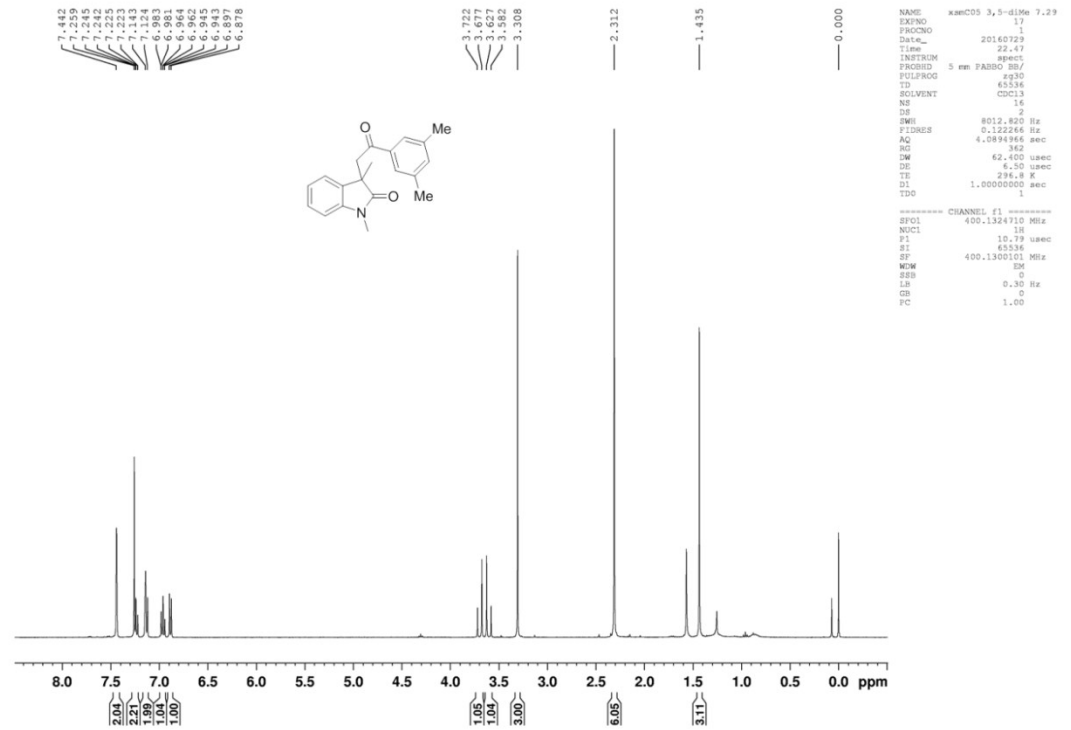
P1                     10.92 usec
SI                       65536
SF              400.1300143 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

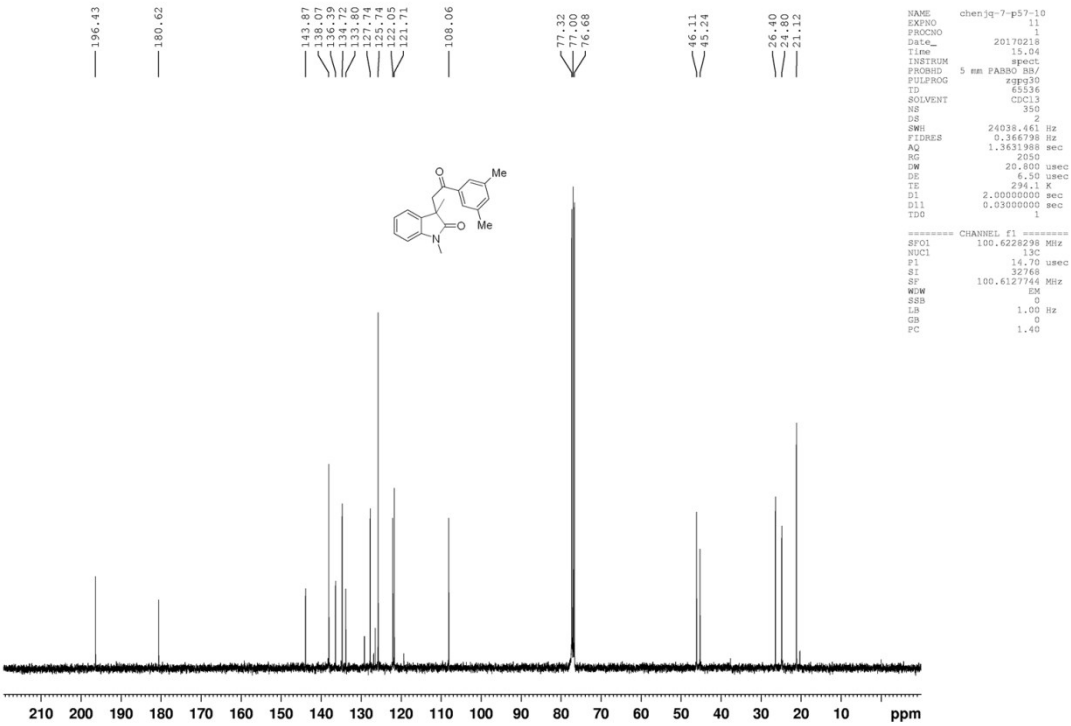



```
NAME          xsm3046 4-Ph
EXPNO                        11
PROCNO                        1
Date_                  20160226
Time                      18.46
INSTRUM                   spect
PROBHD   5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          512
DS                            2
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         2050
DW                     20.800 usec
DE                      6.50 usec
TE                     294.3 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                           1

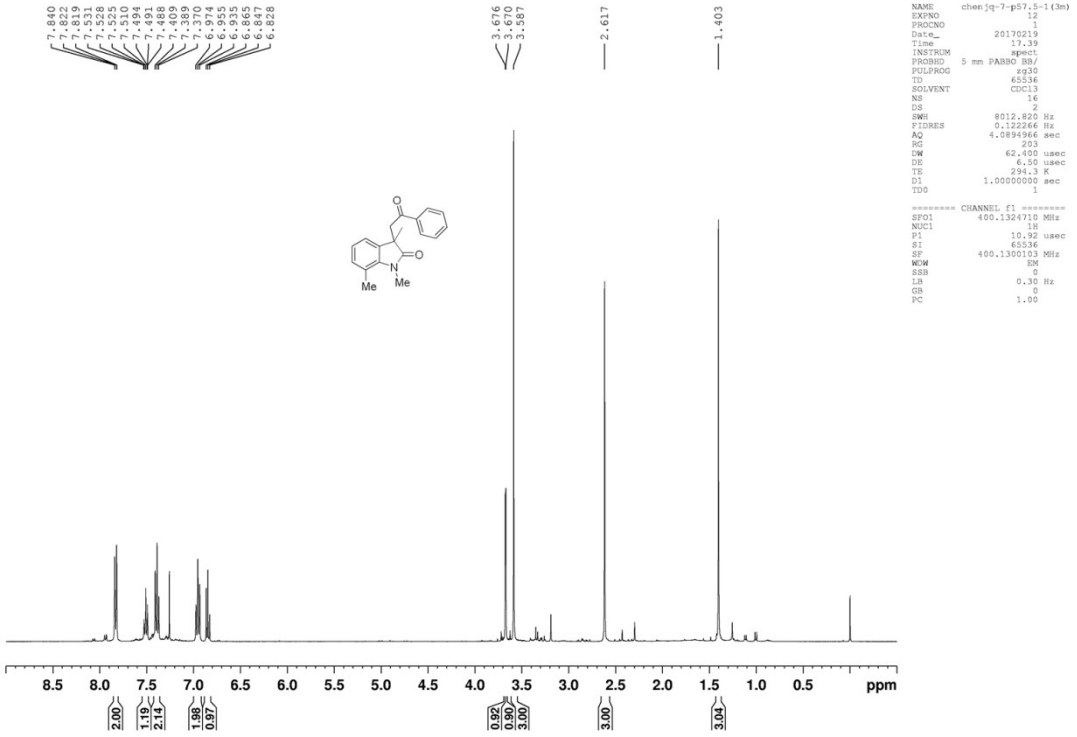
======== CHANNEL f1 ========
SFO1            100.6228298 MHz
NUC1                      13C
P1                     14.70 usec
SI                       32768
SF              100.6127730 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

3-(2-(3,5-dimethylphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3l)



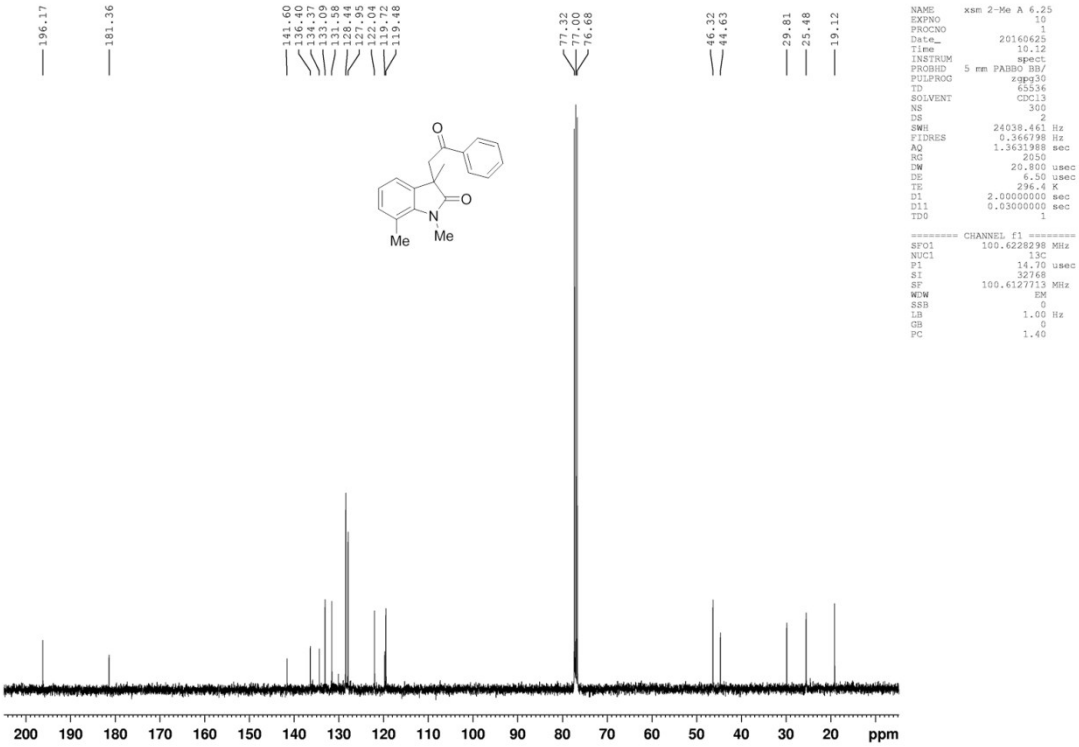


1,3,7-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3m)




```
NAME          chenjq-7-p57.5-1(3m)
EXPNO                          12
PROCNO                          1
Date_                    20170219
Time                        17.39
INSTRUM                     spect
PROBHD     5 mm PABBO BB/
PULPROG                      zg30
TD                          65536
SOLVENT                     CDCl3
NS                             16
DS                              2
SWH                      8012.820 Hz
FIDRES                   0.122266 Hz
AQ                       4.0894966 sec
RG                            203
DW                         62.400 usec
DE                          6.50 usec
TE                         294.3 K
D1                    1.00000000 sec
TD0                             1

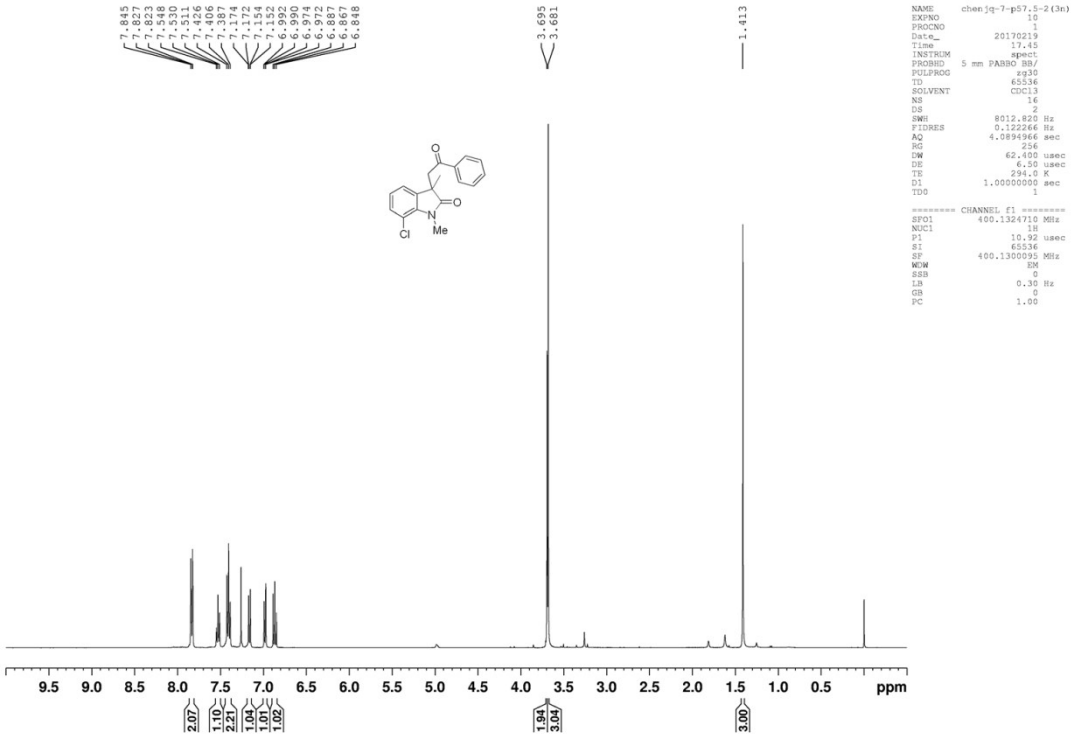
======== CHANNEL f1 ========
SFO1                   400.1324710 MHz
NUC1                           1H
P1                          10.92 usec
SI                          65536
SF                     400.1300103 MHz
WDW                            EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
```




```
NAME          xsm 2-Me A 6.25
EXPNO                          10
PROCNO                          1
Date_                    20160625
Time                        10.12
INSTRUM                     spect
PROBHD     5 mm PABBO BB/
PULPROG                   zgpg30
TD                          65536
SOLVENT                     CDCl3
NS                            300
DS                              2
SWH                     24038.461 Hz
FIDRES                   0.366798 Hz
AQ                       1.3631988 sec
RG                           2050
DW                         20.800 usec
DE                          6.50 usec
TE                         296.4 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                             1

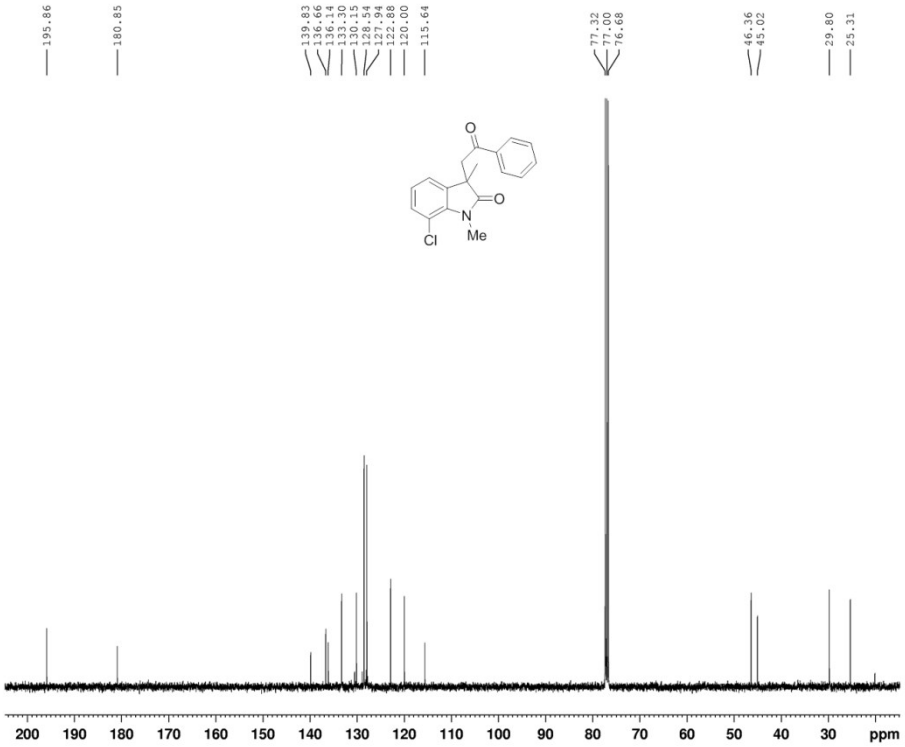
======== CHANNEL f1 ========
SFO1                   100.6228298 MHz
NUC1                           13C
P1                          14.70 usec
SI                          32768
SF                     100.6127713 MHz
WDW                            EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40
```

7-chloro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3n)




```
NAME          chenjq-7-p57.5-2(3n)
EXPNO                          10
PROCNO                          1
Date_                    20170219
Time                        17.45
INSTRUM                     spect
PROBHD     5 mm PABBO BB/
PULPROG                      zg30
TD                          65536
SOLVENT                     CDCl3
NS                             16
DS                              2
SWH                      8012.820 Hz
FIDRES                   0.122266 Hz
AQ                       4.0894966 sec
RG                            256
DW                         62.400 usec
DE                          6.50 usec
TE                         294.0 K
D1                    1.00000000 sec
TD0                             1

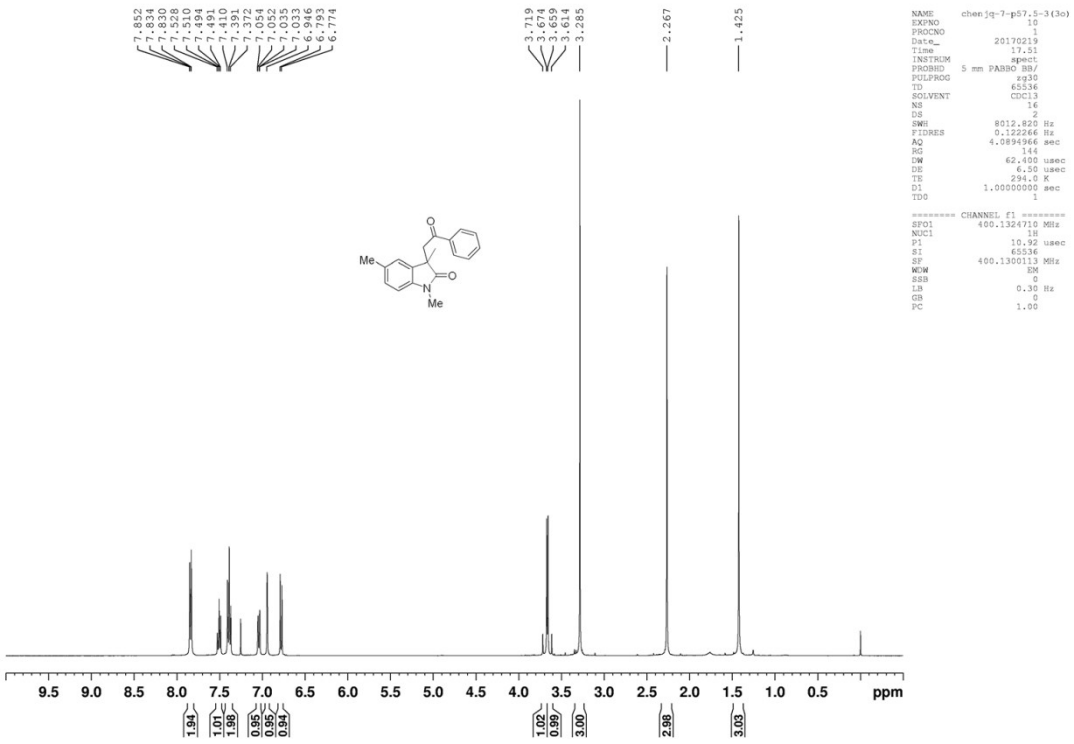
======== CHANNEL f1 ========
SFO1                   400.1324710 MHz
NUC1                           1H
P1                          10.92 usec
SI                          65536
SF                     400.1300095 MHz
WDW                            EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
```

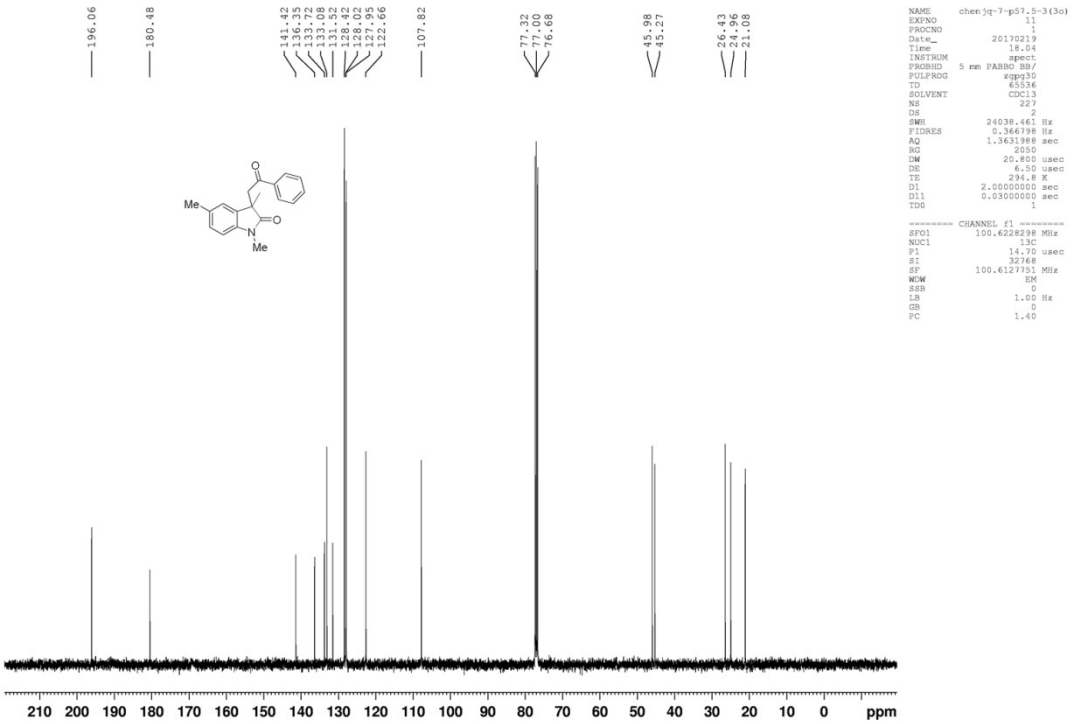



```
NAME          xsm 2-Cl A 6.29
EXPNO                          10
PROCNO                          1
Date_                    20160630
Time                        14.45
INSTRUM                     spect
PROBHD     5 mm PABBO BB/
PULPROG                   zgpg30
TD                          65536
SOLVENT                     CDCl3
NS                            512
DS                              2
SWH                     24038.461 Hz
FIDRES                   0.366798 Hz
AQ                       1.3631988 sec
RG                           2050
DW                         20.800 usec
DE                          6.50 usec
TE                         297.1 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                             1

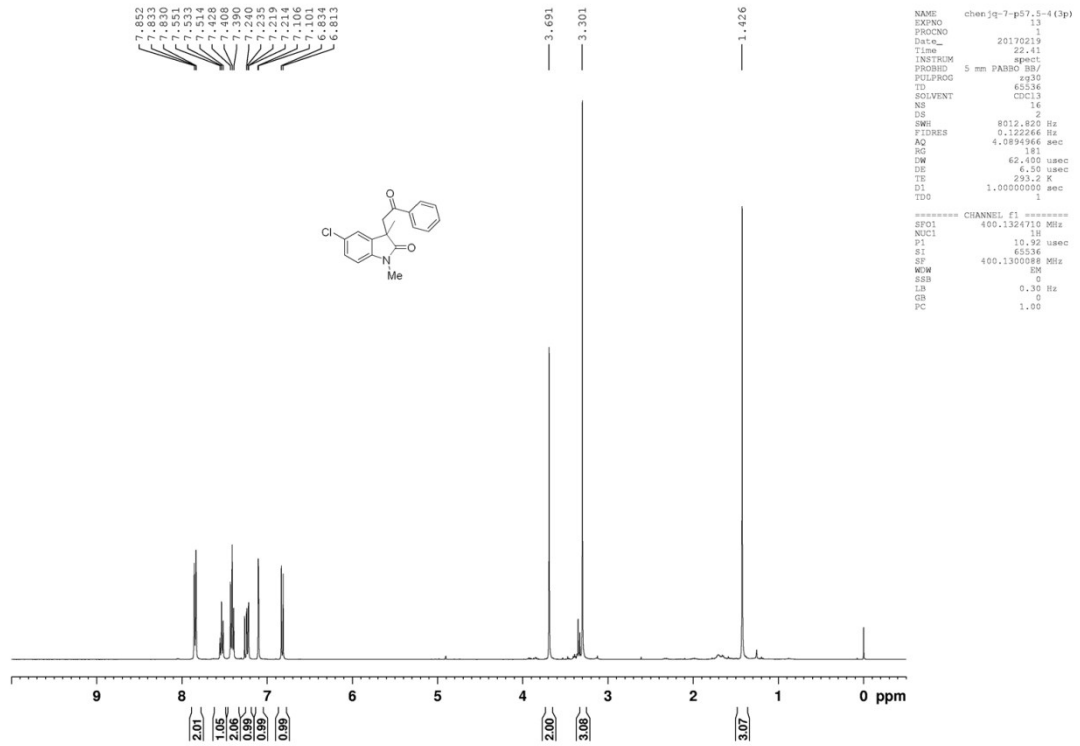
======== CHANNEL f1 ========
SFO1                   100.6228298 MHz
NUC1                           13C
P1                          14.70 usec
SI                          32768
SF                     100.6127708 MHz
WDW                            EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40
```

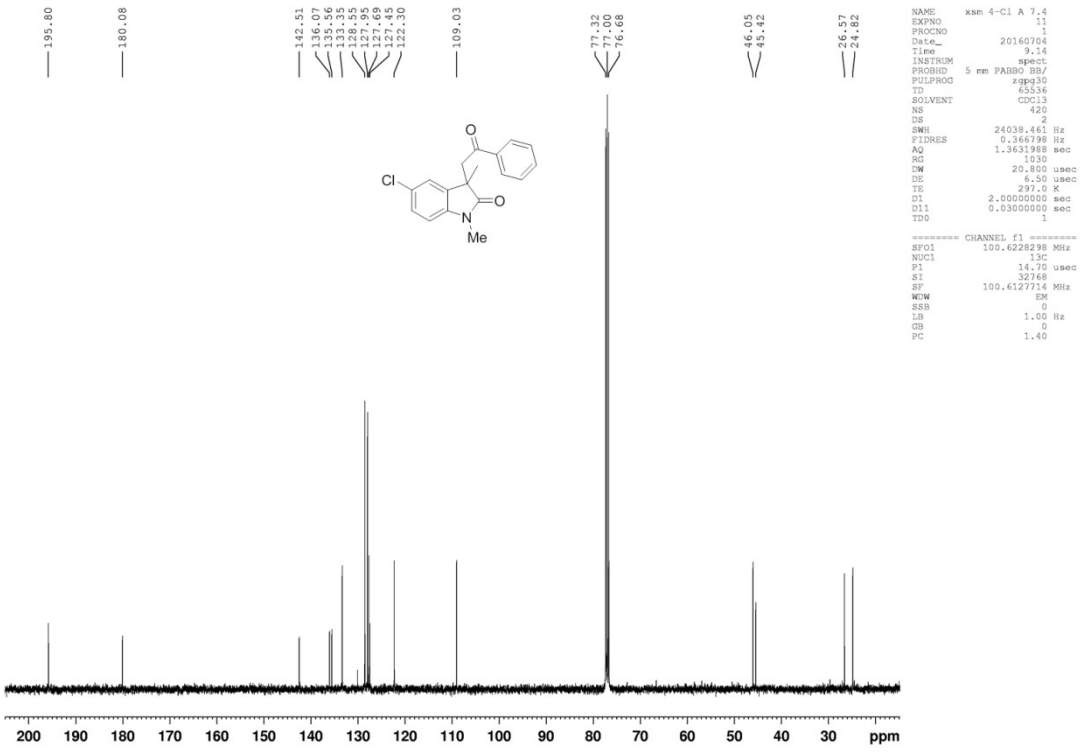
1,3,5-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3o)



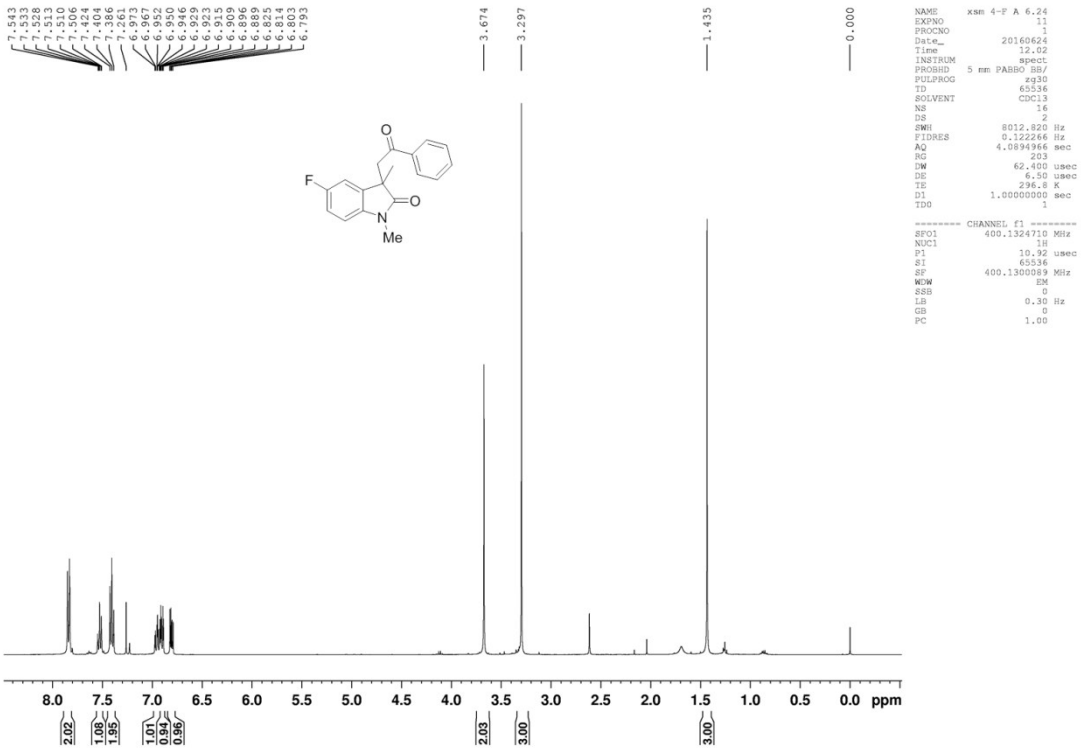


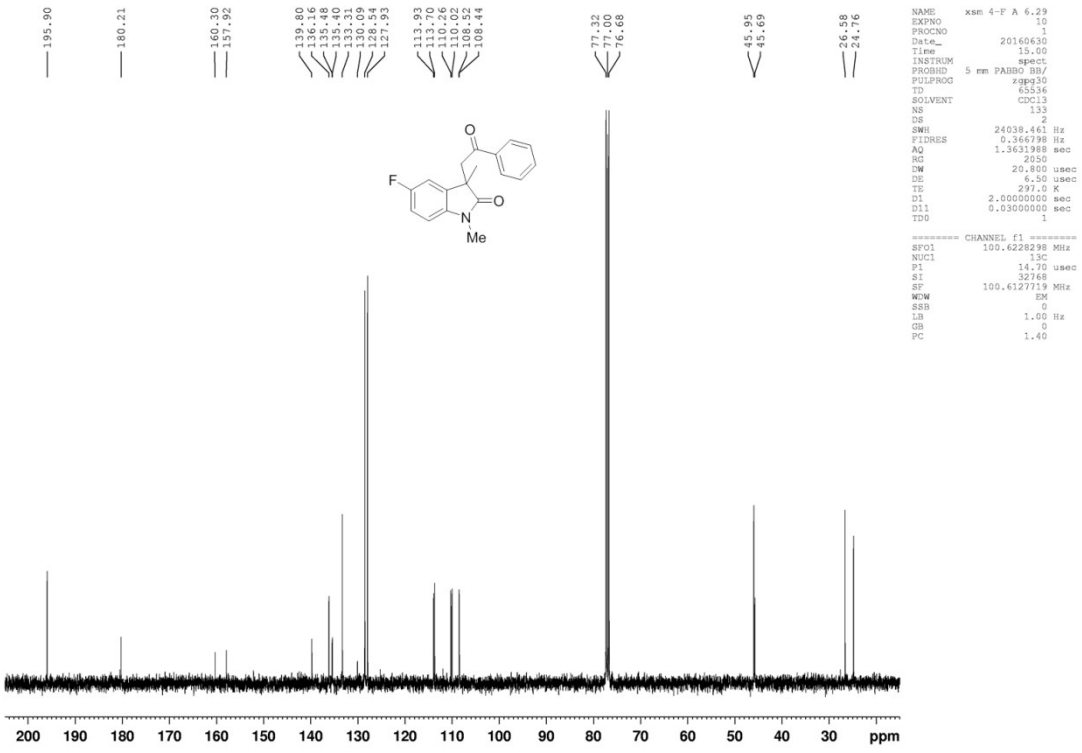
5-chloro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3p)



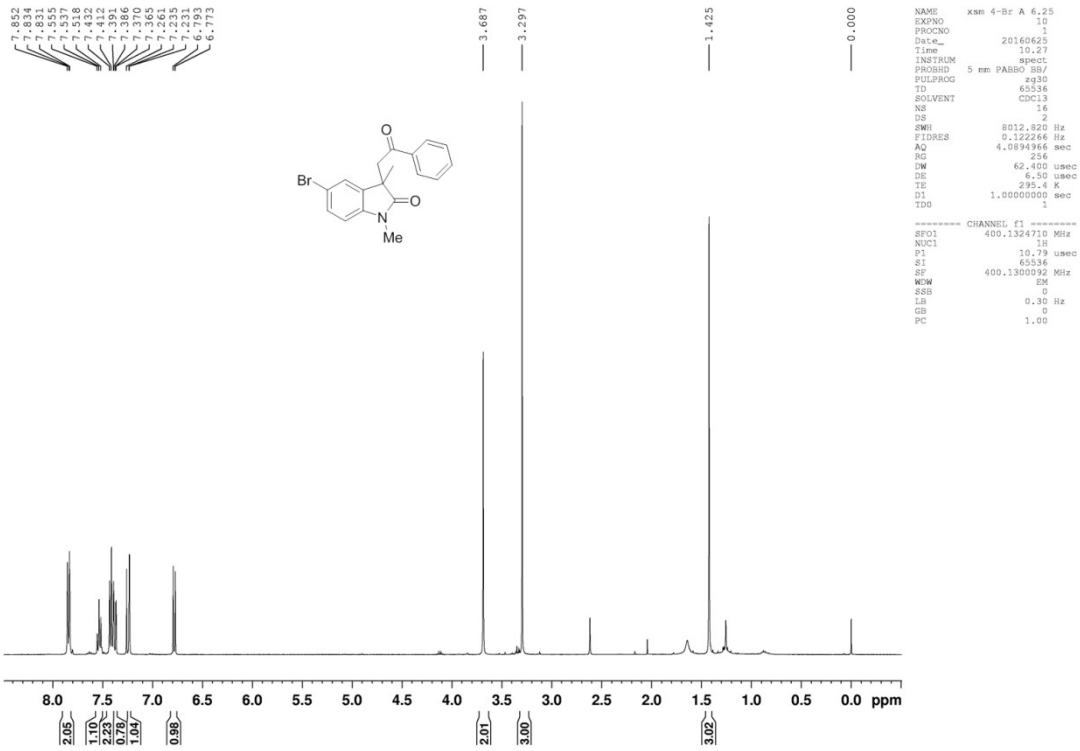


5-fluoro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3q)



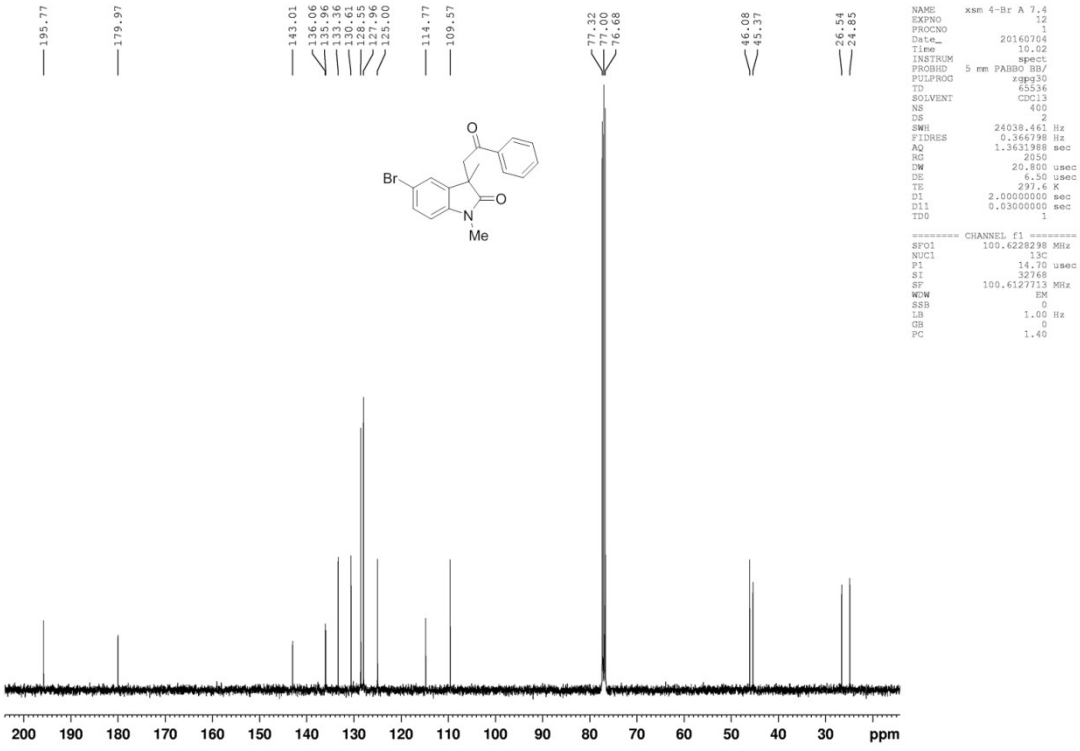


5-bromo-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3r)




```
NAME        xsm 4-Br A 6.25
EXPNO               10
PROCNO               1
Date_         20160625
Time             10.27
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES           0.122266 Hz
AQ            4.0894966 sec
RG                 256
DW               62.400 usec
DE                6.50 usec
TE               295.4 K
D1            1.00000000 sec
TD0                  1

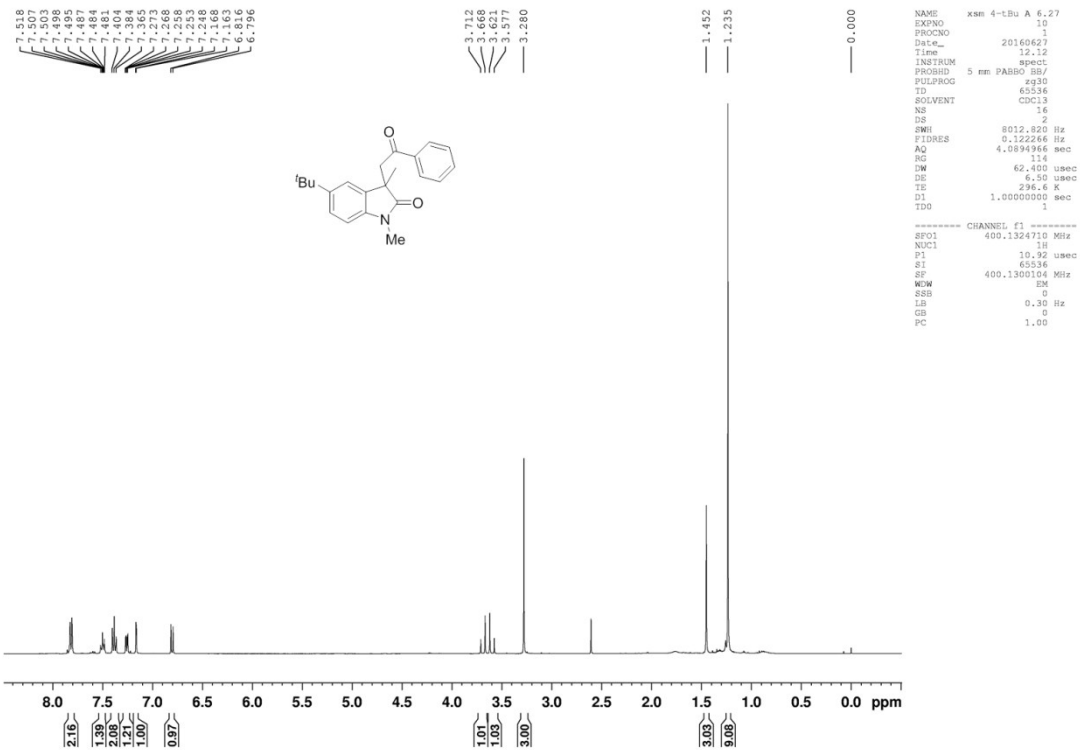
======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1               1H
P1               10.79 usec
SI              65536
SF          400.1300092 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

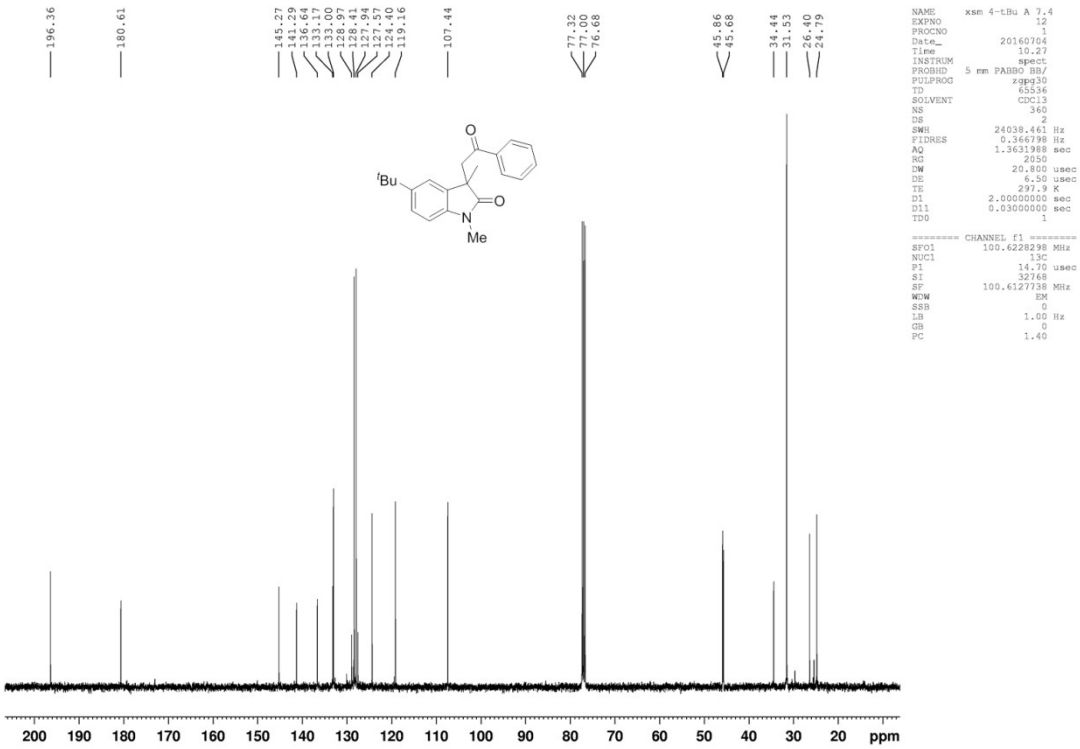



```
NAME        xsm 4-Br A 7.4
EXPNO               12
PROCNO               1
Date_         20160704
Time             10.02
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG       zgpg30
TD              65536
SOLVENT         CDCl3
NS                 400
DS                   2
SWH          24038.461 Hz
FIDRES           0.366798 Hz
AQ            1.3631988 sec
RG                2050
DW               20.800 usec
DE                6.50 usec
TE               297.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

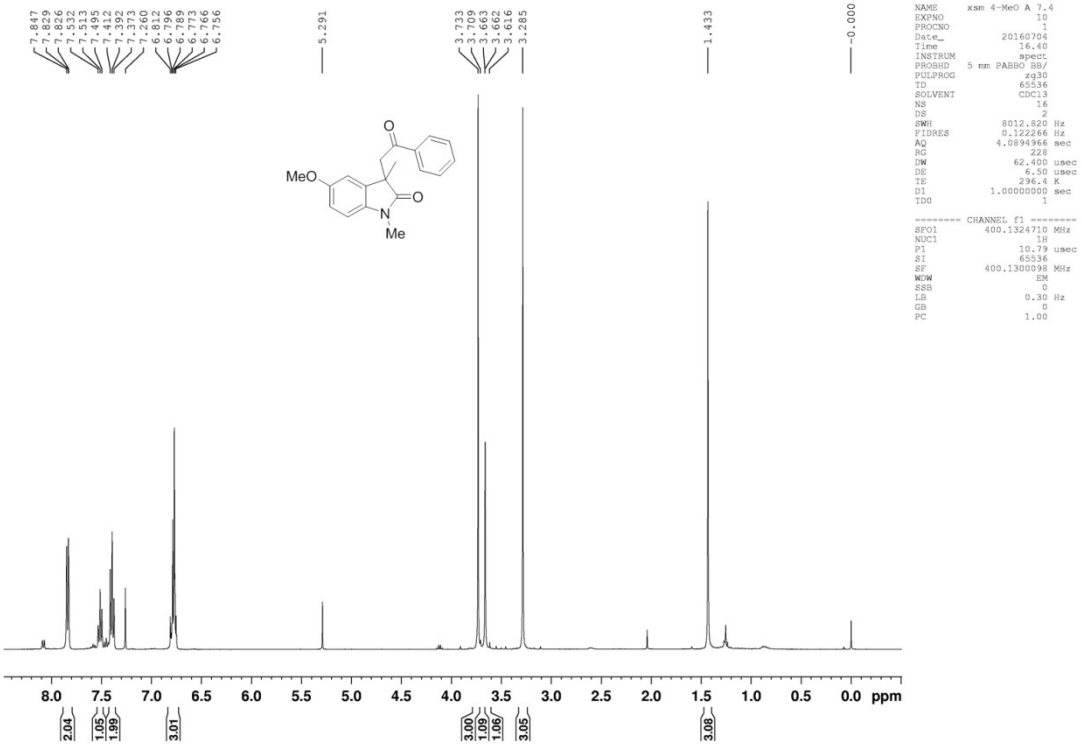
======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1               13C
P1               14.70 usec
SI              32768
SF          100.6127713 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

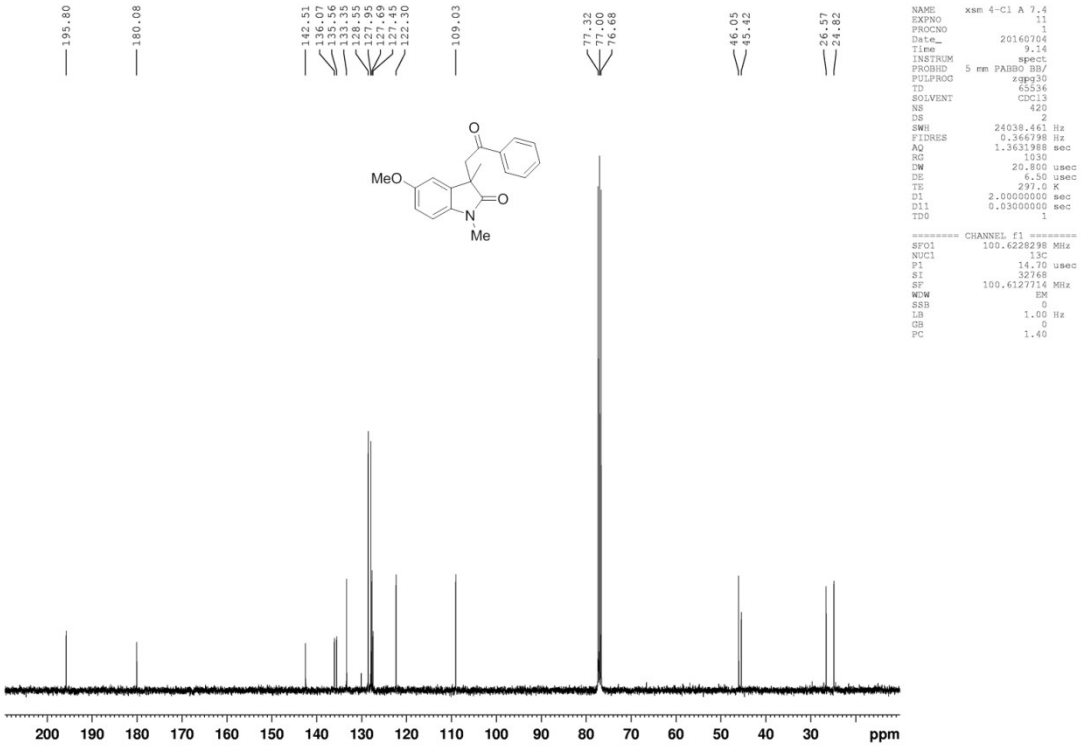
5-(tert-butyl)-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3s)



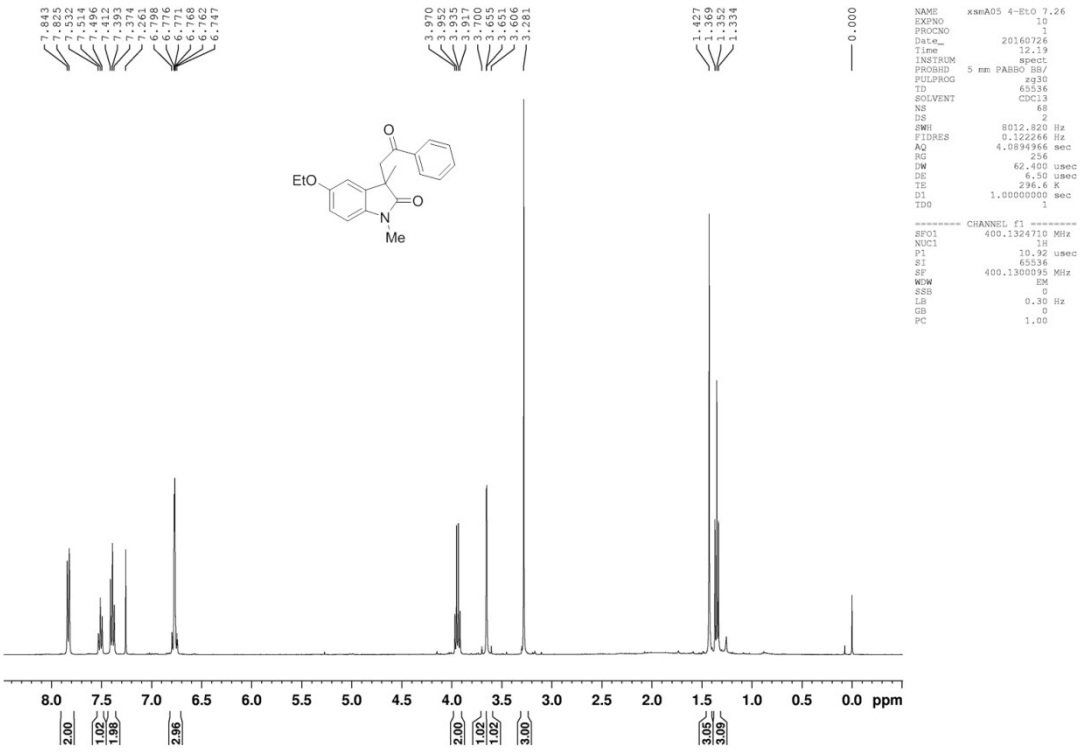


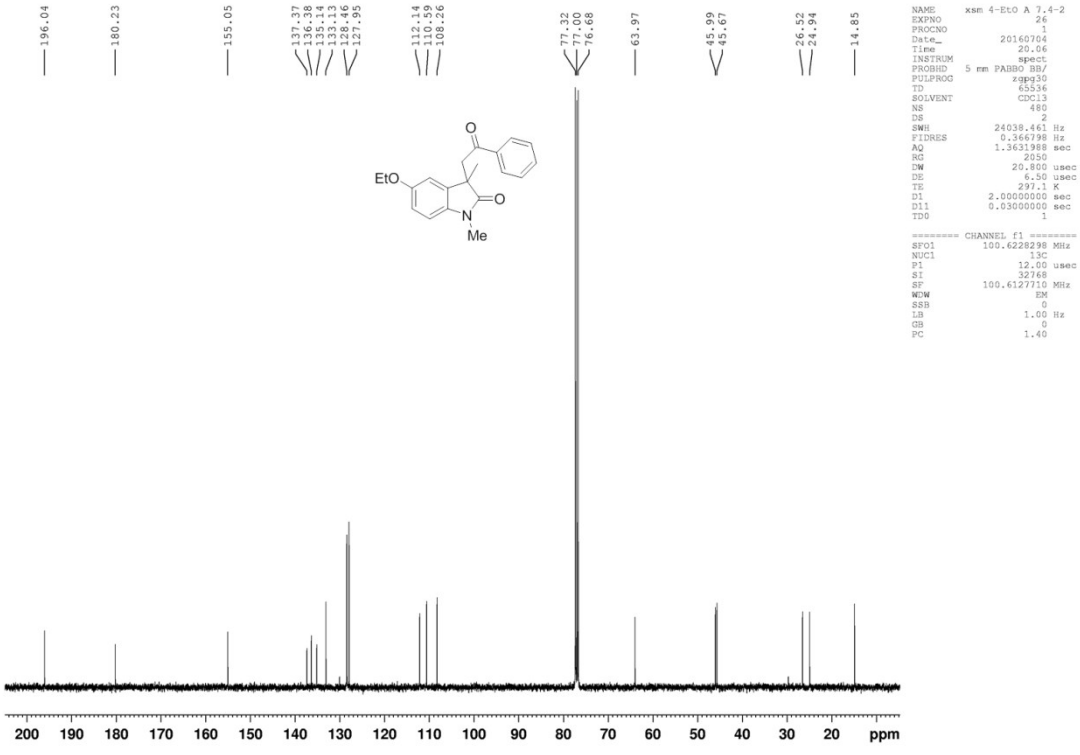
5-methoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3t)



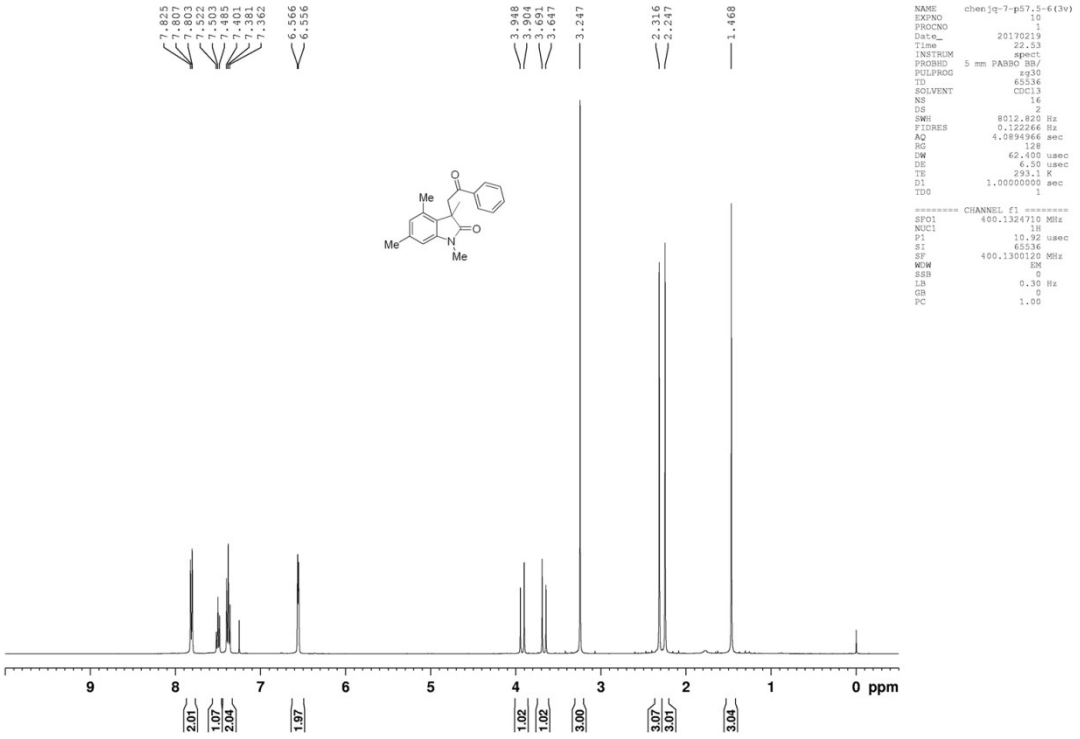


5-ethoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3u)



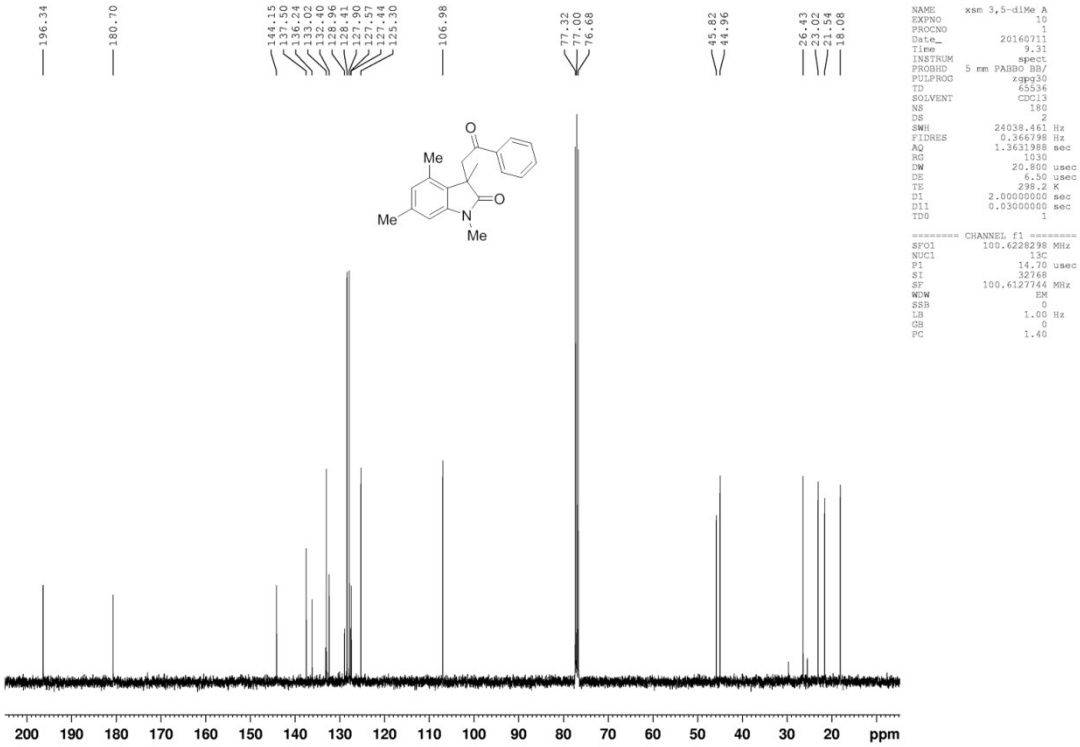


1,3,4,6-tetramethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3v)




```
NAME          chenjq-7-p57.5-6(3v)
EXPNO                          10
PROCNO                          1
Date_                    20170219
Time                        22.53
INSTRUM                     spect
PROBHD     5 mm PABBO BB/
PULPROG                      zg30
TD                          65536
SOLVENT                     CDCl3
NS                             16
DS                              2
SWH                      8012.820 Hz
FIDRES                   0.122266 Hz
AQ                       4.0894966 sec
RG                            128
DW                         62.400 usec
DE                          6.50 usec
TE                         293.1 K
D1                    1.00000000 sec
TD0                             1

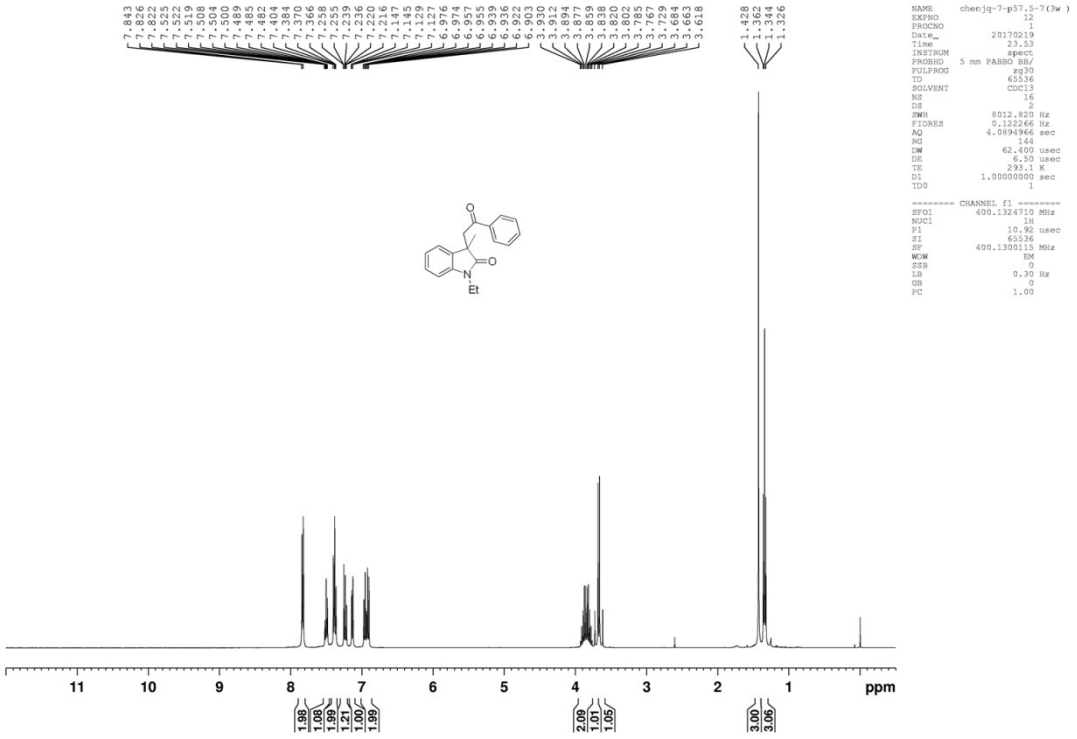
======== CHANNEL f1 ========
SFO1                   400.1324710 MHz
NUC1                           1H
P1                         10.92 usec
SI                          65536
SF                     400.1300120 MHz
WDW                            EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
```




```
NAME          xsm 3,5-diMe A
EXPNO                          10
PROCNO                          1
Date_                    20160711
Time                         9.31
INSTRUM                     spect
PROBHD     5 mm PABBO BB/
PULPROG                   zgpg30
TD                          65536
SOLVENT                     CDCl3
NS                            180
DS                              2
SWH                     24038.461 Hz
FIDRES                   0.366798 Hz
AQ                       1.3631988 sec
RG                           1030
DW                         20.800 usec
DE                          6.50 usec
TE                         298.2 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                             1

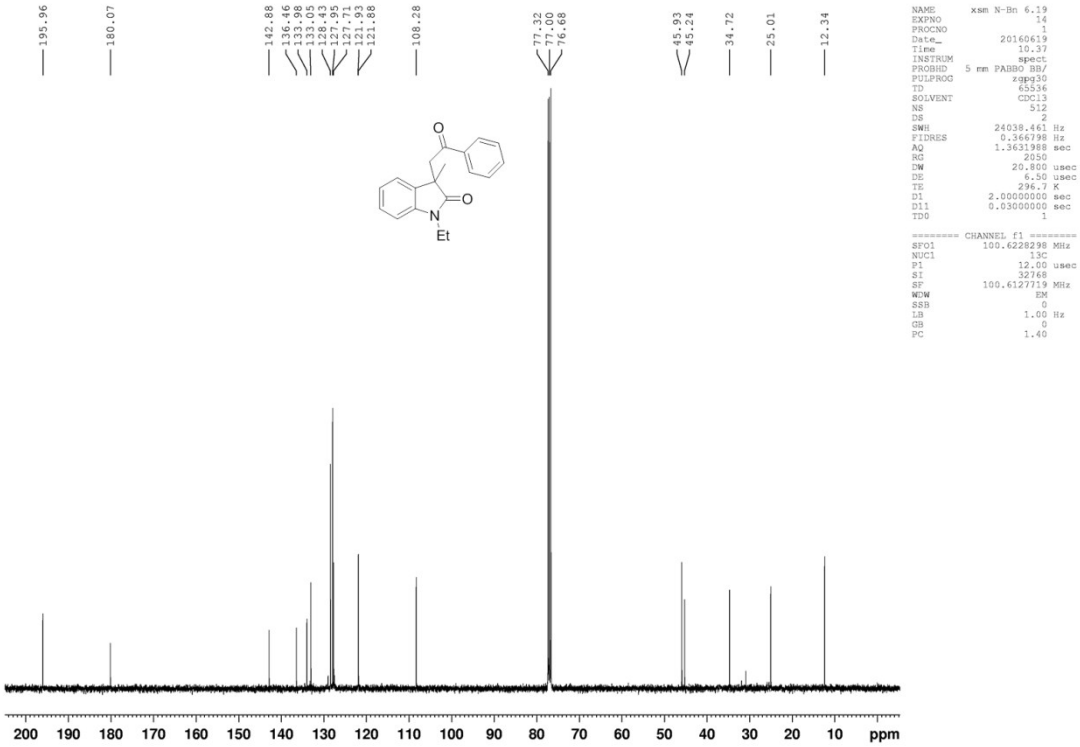
======== CHANNEL f1 ========
SFO1                   100.6228298 MHz
NUC1                           13C
P1                         14.70 usec
SI                          32768
SF                     100.6127744 MHz
WDW                            EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40
```

1-ethyl-3-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3w)




```
NAME          chenjq-7-p57.5-7(3w )
EXPNO                           12
PROCNO                           1
Date_                     20170219
Time                         23.53
INSTRUM                      spect
PROBHD     5 mm PABBO BB/
PULPROG                      zg30
TD                          65536
SOLVENT                     CDCl3
NS                              16
DS                               2
SWH                       8012.820 Hz
FIDRES                    0.122266 Hz
AQ                        4.0894966 sec
RG                             144
DW                        62.400 usec
DE                         6.50 usec
TE                           293.1 K
D1                    1.00000000 sec
TD0                              1

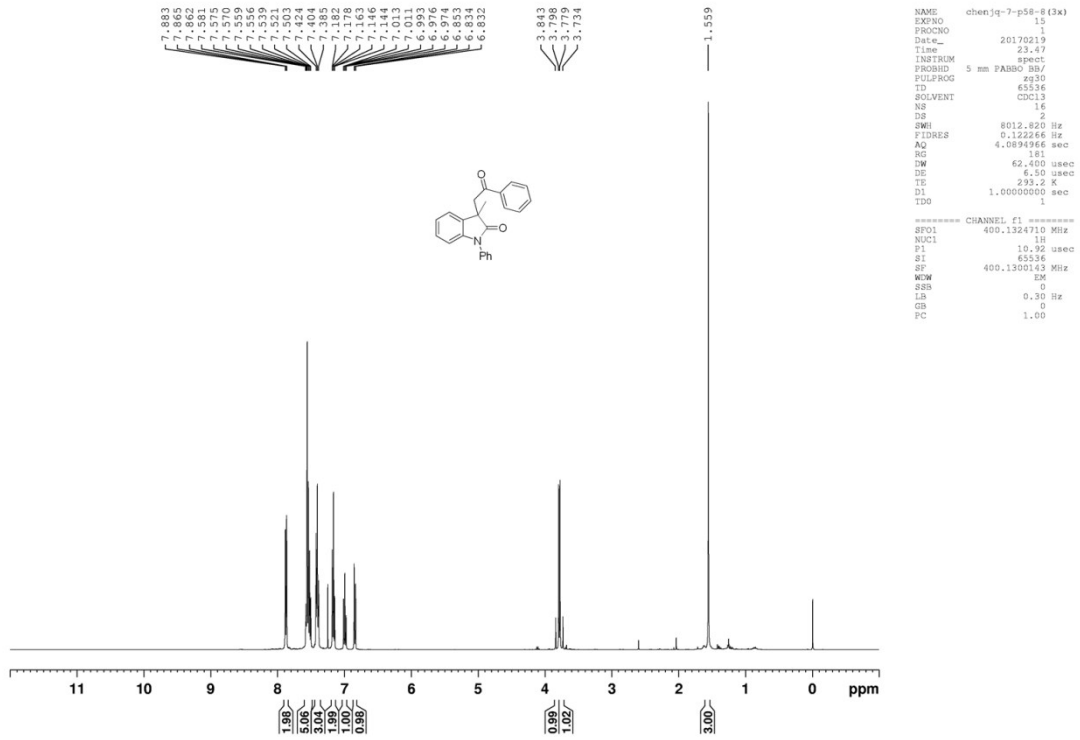
======== CHANNEL f1 ========
SFO1                  400.1324710 MHz
NUC1                          1H
P1                        10.92 usec
SI                           65536
SF                    400.1300115 MHz
WDW                             EM
SSB                              0
LB                            0.30 Hz
GB                               0
PC                            1.00
```




```
NAME          xsm N-Bn 6.19
EXPNO                           14
PROCNO                           1
Date_                     20160619
Time                         10.37
INSTRUM                      spect
PROBHD     5 mm PABBO BB/
PULPROG                   zgpg30
TD                          65536
SOLVENT                     CDCl3
NS                             512
DS                               2
SWH                      24038.461 Hz
FIDRES                    0.366798 Hz
AQ                        1.3631988 sec
RG                            2050
DW                        20.800 usec
DE                         6.50 usec
TE                           296.7 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                              1

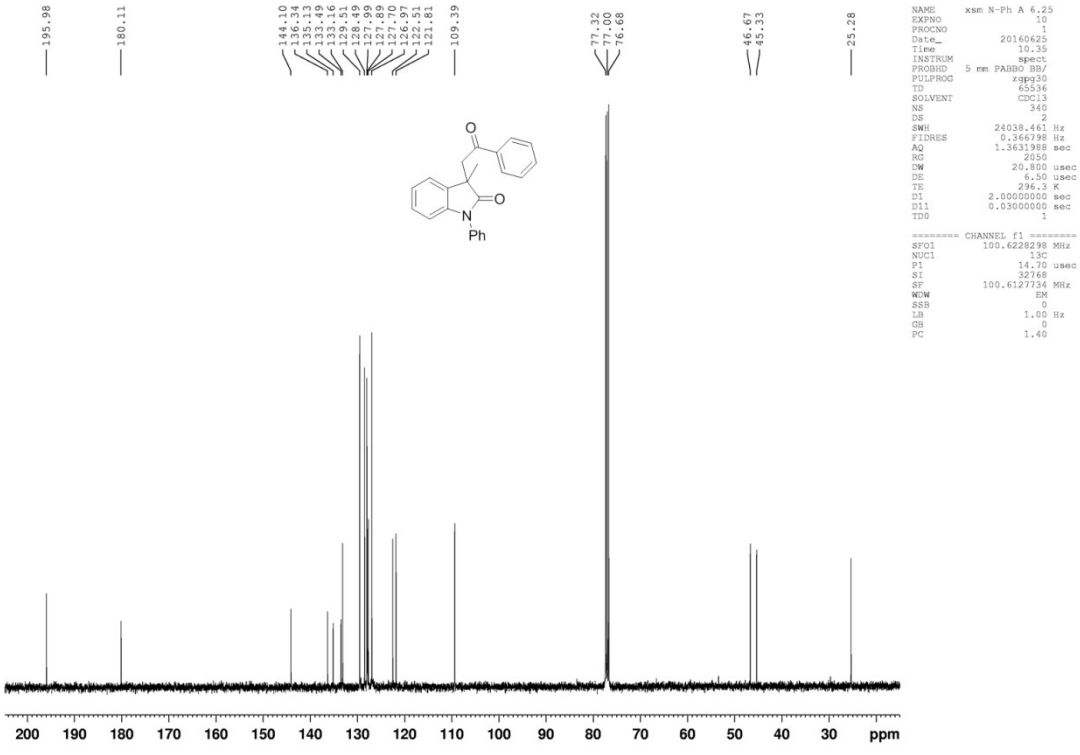
======== CHANNEL f1 ========
SFO1                  100.6228298 MHz
NUC1                          13C
P1                        12.00 usec
SI                           32768
SF                    100.6127719 MHz
WDW                             EM
SSB                              0
LB                            1.00 Hz
GB                               0
PC                            1.40
```

3-methyl-3-(2-oxo-2-phenylethyl)-1-phenylindolin-2-one (3x)




```
NAME          chenjq-7-p58-8(3x)
EXPNO                        15
PROCNO                        1
Date_                  20170219
Time                      23.47
INSTRUM                    spect
PROBHD   5 mm PABBO BB/
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                         181
DW                      62.400 usec
DE                       6.50 usec
TE                      293.2 K
D1                    1.00000000 sec
TD0                           1

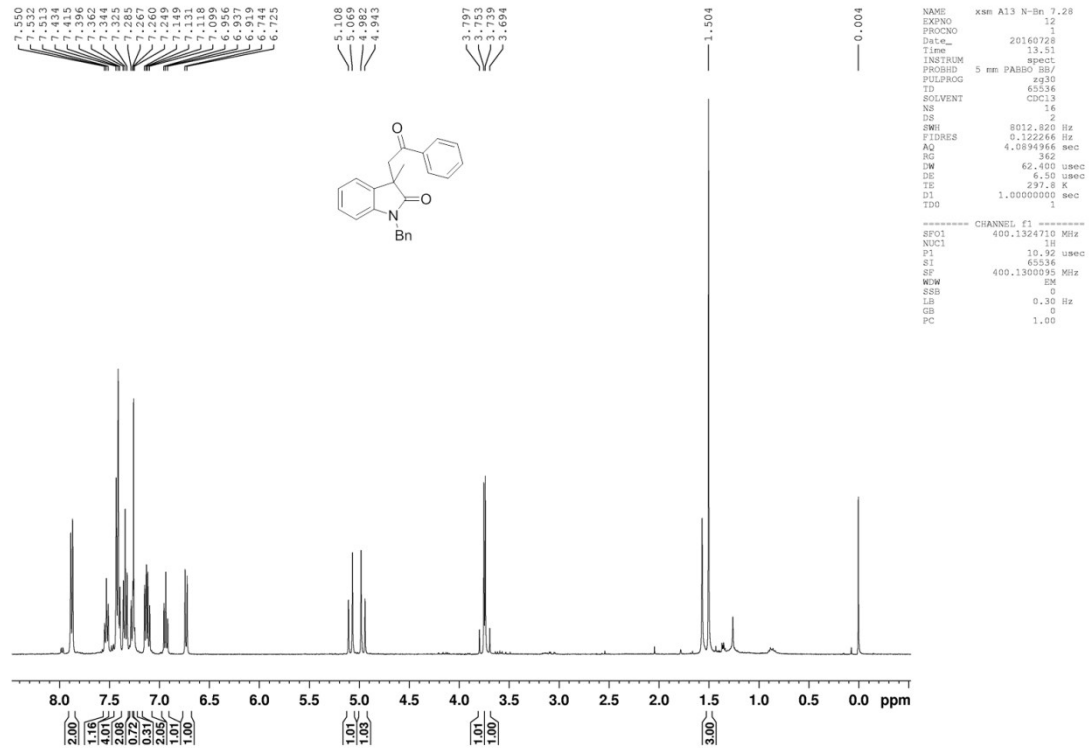
======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                       1H
P1                      10.92 usec
SI                       65536
SF              400.1300143 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

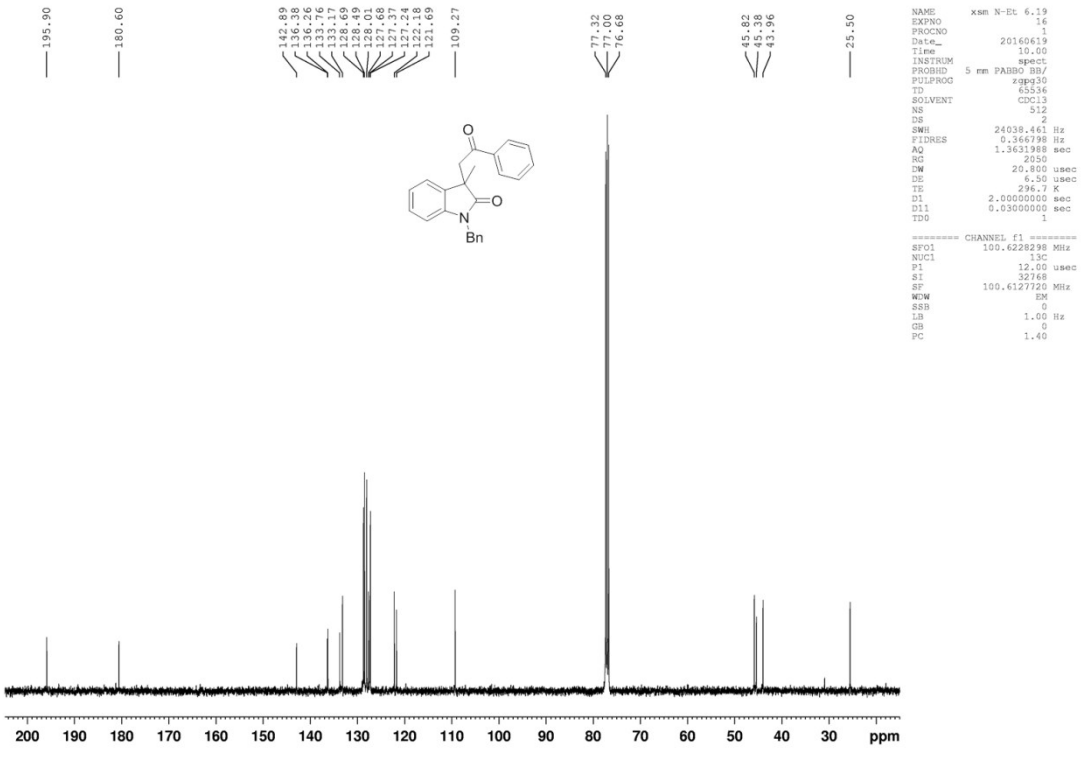



```
NAME          xsm N-Ph A 6.25
EXPNO                        10
PROCNO                        1
Date_                  20160625
Time                      10.35
INSTRUM                    spect
PROBHD   5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         340
DS                           2
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                        2050
DW                      20.800 usec
DE                       6.50 usec
TE                      296.3 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                           1

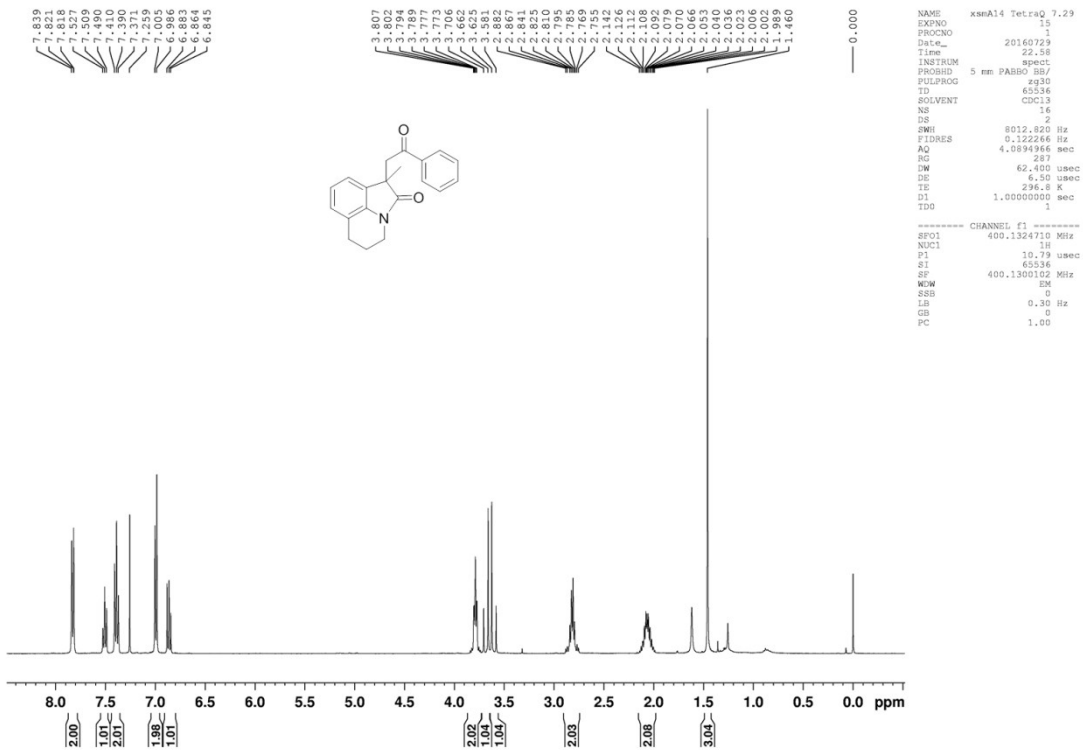
======== CHANNEL f1 ========
SFO1            100.6228298 MHz
NUC1                      13C
P1                      14.70 usec
SI                       32768
SF              100.6127734 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

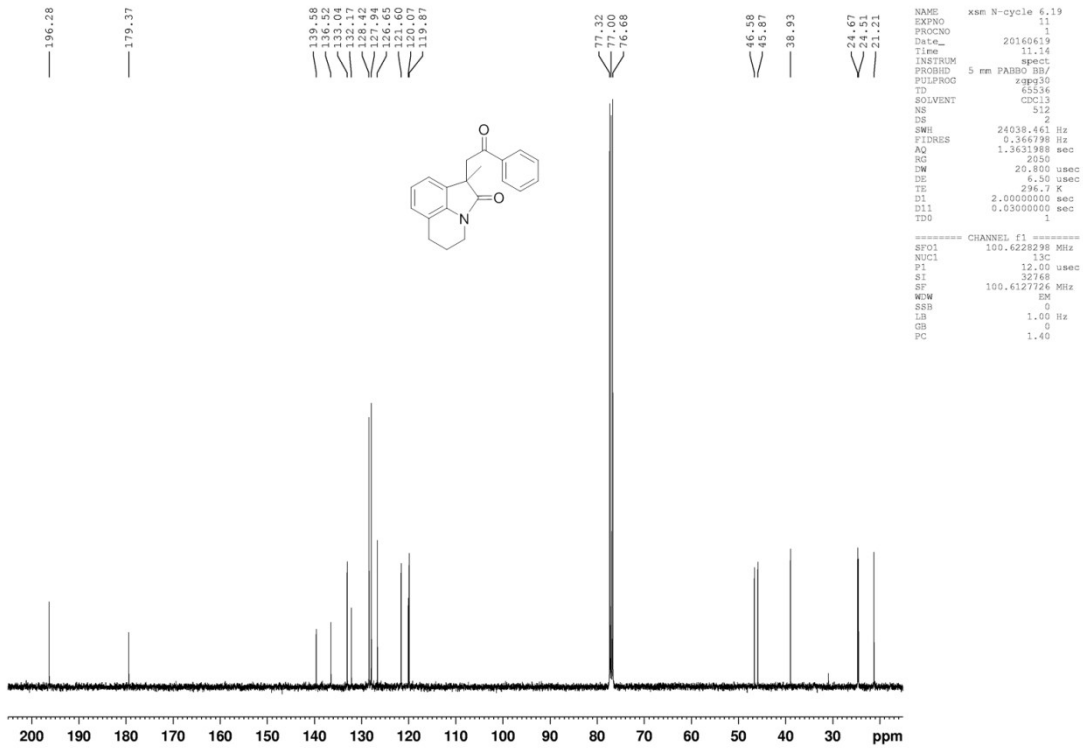
1-benzyl-3-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3y)



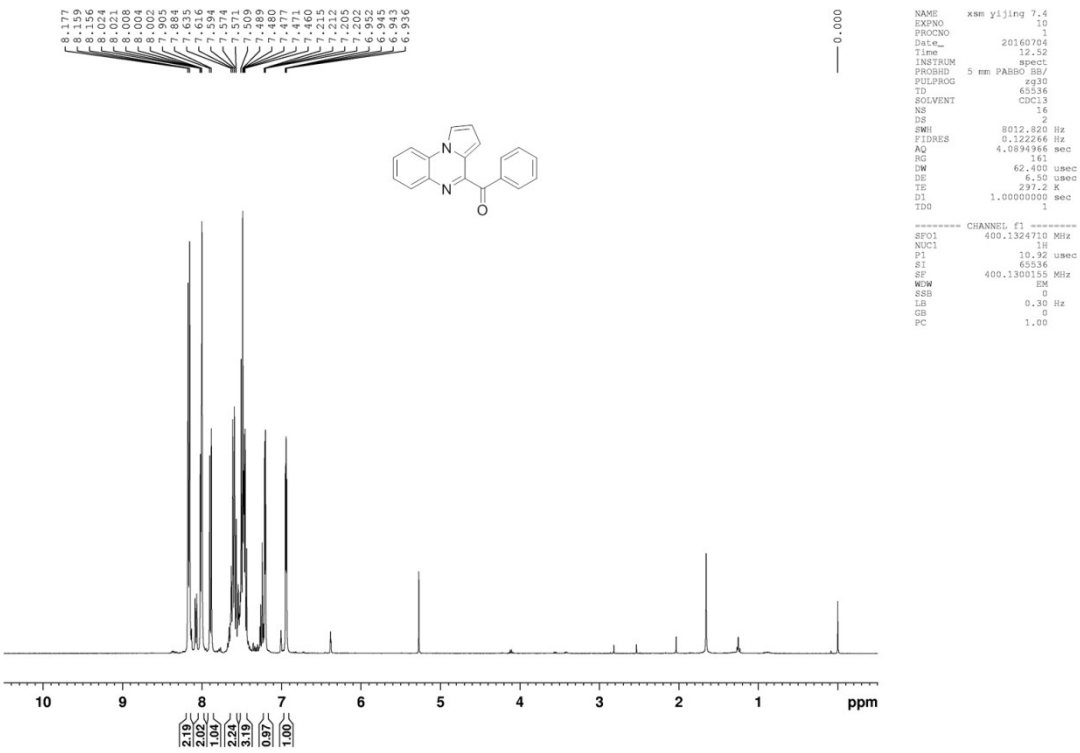


1-methyl-1-(2-oxo-2-phenylethyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (3ab)



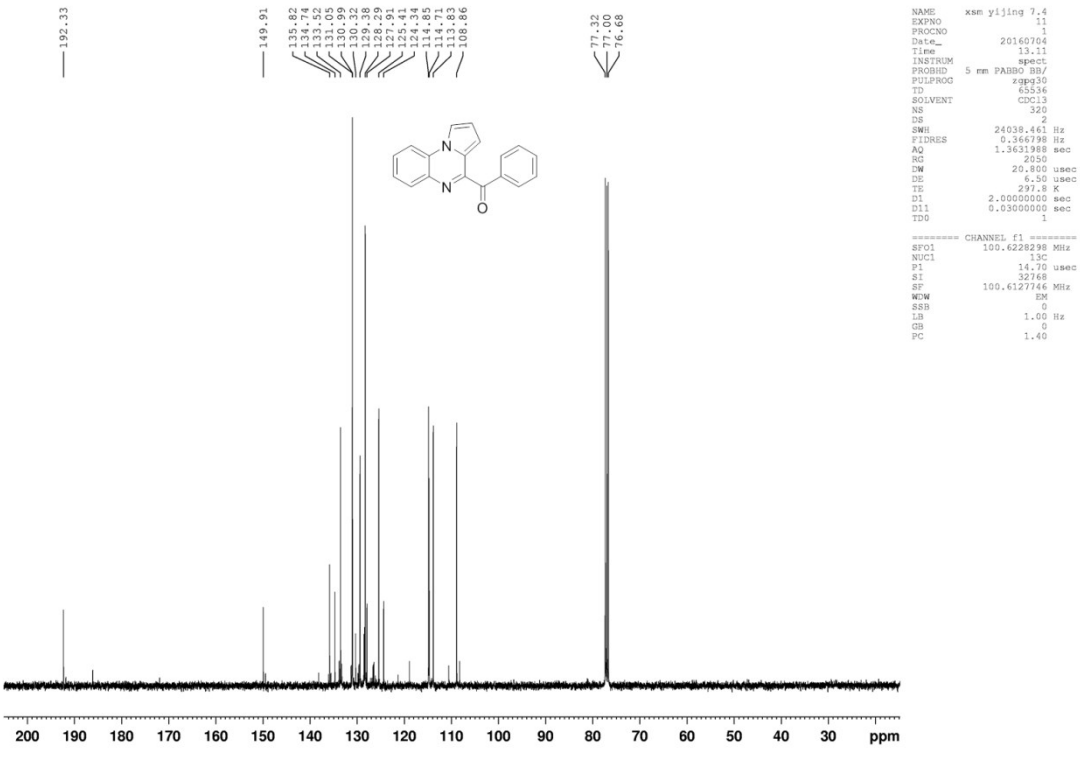


phenyl(pyrrolo[1,2-a]quinoxalin-4-yl)methanone (6a)




```
NAME        xsm yijing 7.4
EXPNO               10
PROCNO               1
Date_         20160704
Time             12.52
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES           0.122266 Hz
AQ            4.0894966 sec
RG                 161
DW               62.400 usec
DE                6.50 usec
TE               297.2 K
D1            1.00000000 sec
TD0                  1

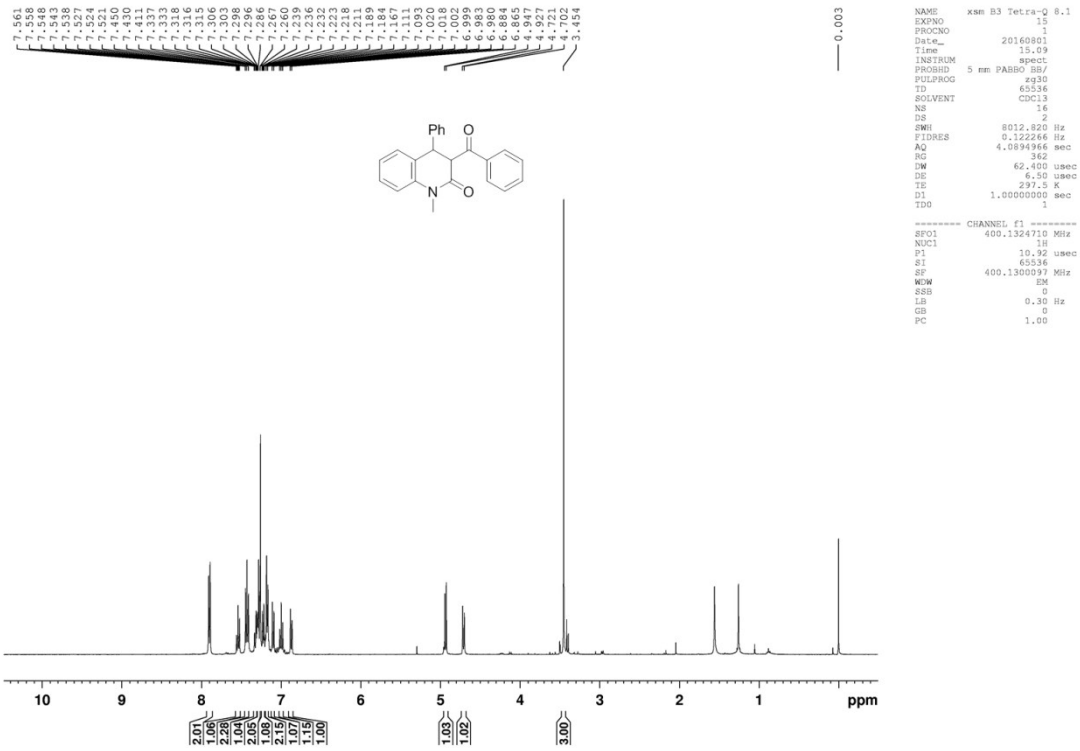
======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1               1H
P1               10.92 usec
SI              65536
SF          400.1300155 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```




```
NAME        xsm yijing 7.4
EXPNO               11
PROCNO               1
Date_         20160704
Time             13.11
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 320
DS                   2
SWH          24038.461 Hz
FIDRES           0.366798 Hz
AQ            1.3631988 sec
RG                2050
DW               20.800 usec
DE                6.50 usec
TE               297.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

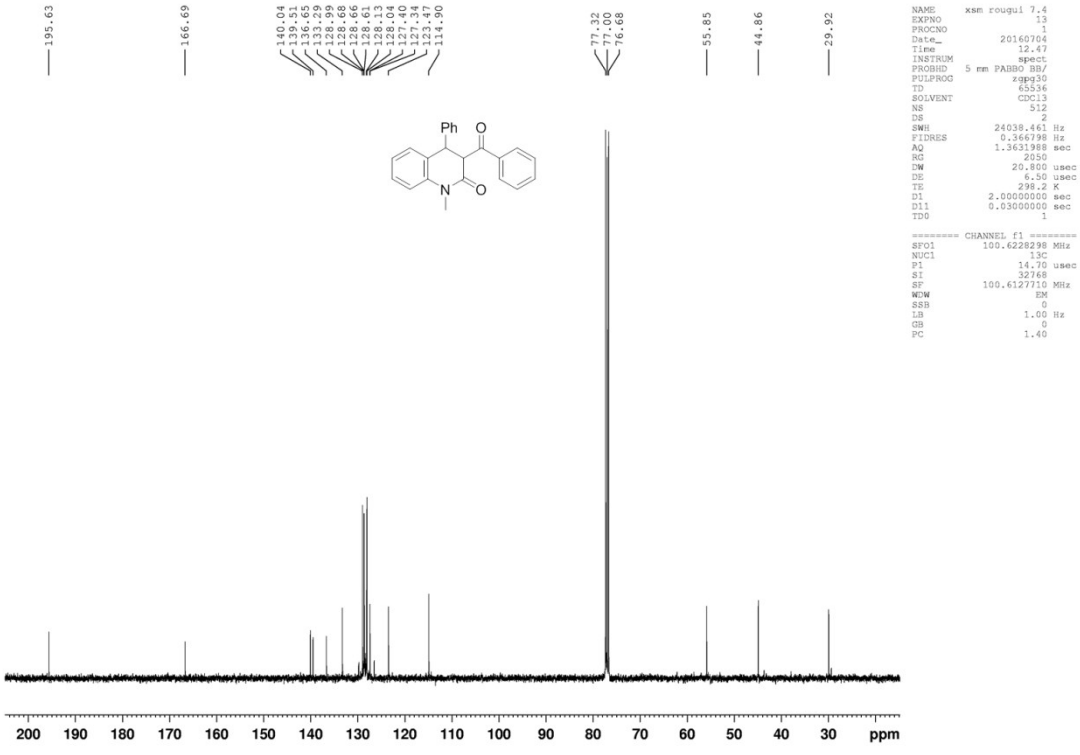
======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1               13C
P1               14.70 usec
SI              32768
SF          100.6127746 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

3-benzoyl-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (6b)




```
NAME        xsm B3 Tetra-Q 8.1
EXPNO                 15
PROCNO                 1
Date_           20160801
Time               15.09
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                   362
DW                62.400 usec
DE                 6.50 usec
TE                 297.5 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                   1H
P1                 10.92 usec
SI                 65536
SF              400.1300097 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




```
NAME        xsm rouqui 7.4
EXPNO                 13
PROCNO                 1
Date_           20160704
Time               12.47
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     2
SWH            24038.461 Hz
FIDRES             0.366798 Hz
AQ              1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                 298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1            100.6228298 MHz
NUC1                   13C
P1                 14.70 usec
SI                 32768
SF              100.6127710 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```