Supplementary Material (ESI) for Chemical Communications

Synthesis of 3-Hydroxyoxindoles by Pd-catalysed Intramolecular Nucleophilic Addition of Arylhalides to α-Ketoamides

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CONTENTS:

General:

Solvents were purified by filtration on Al_2O_3 drying columns using the Solvtek© system or by distillation over Na and benzophenone. Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated under vacuum prior to use. ^{1}H- and ^{13}C-NMR spectra were

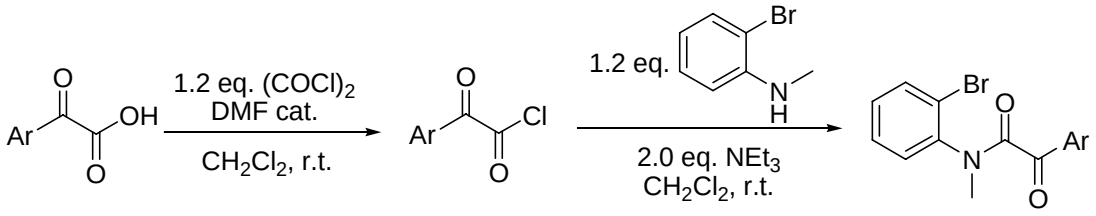
recorded on Bruker AMX-400 or AMX-300 FT spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million (ppm) downfield of tetramethylsilane. Coupling constants *J* are quoted in Hz. Infrared spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer. Electrospray ionization (ESI) HRMS analyses were measured on a VG analytical 7070E instrument. Melting points were determined on a Büchi 510 and are uncorrected.

1. Synthesis of the substrates:

Aryl α-ketoacids were obtained by saponification of the corresponding ketoesters. The latter were prepared from arylbromides and diethyl oxalate according to Saito *et al.*[1] *N*-methyl *ortho*-bromide aniline was prepared according to *Barluenga et al.*[2]

Substrates **1a-h**, **1m** and **1n** were prepared according to the general procedure A, and **1i-o** prepared according to the general procedure B.

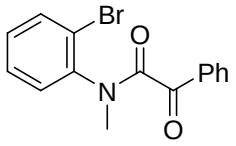
General procedure A:



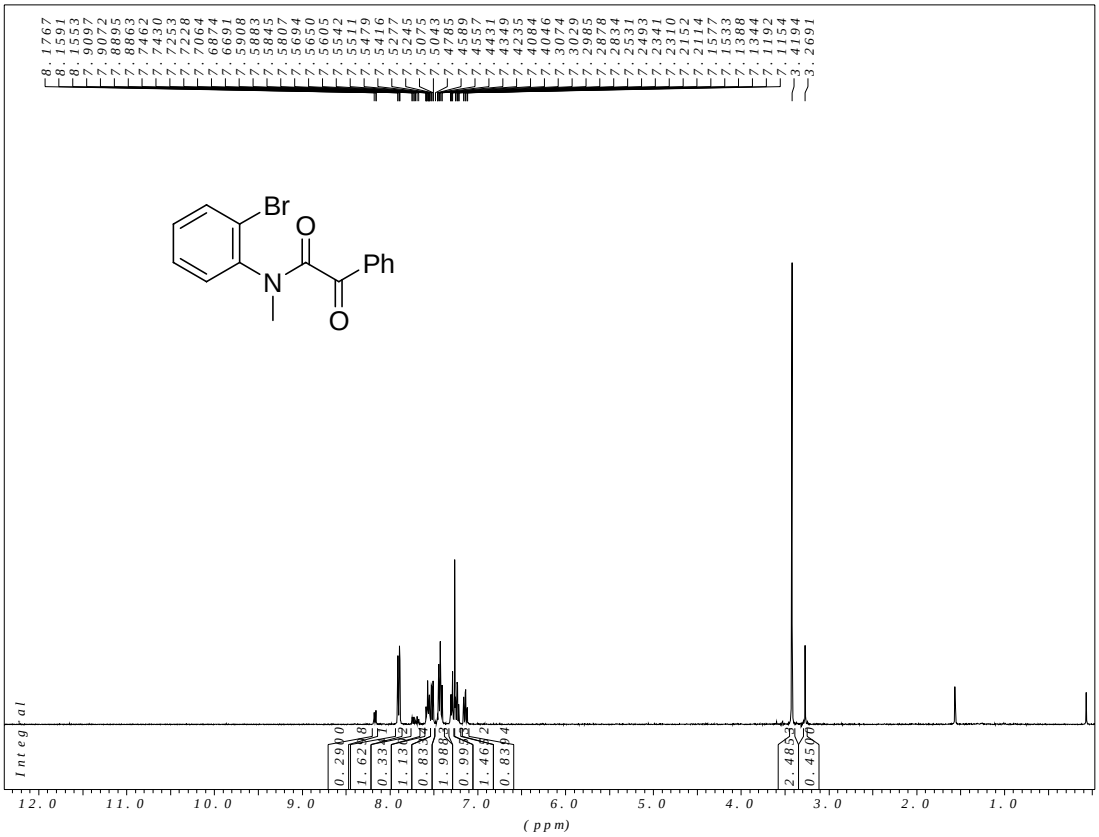
To a solution of the aryl α-ketoacid (1.0 eq., 0.5 M) in CH_2Cl_2 was added oxalyl chloride (1.2 eq.) at room temperature (r.t.) followed by addition of a drop of DMF as catalyst. The mixture was stirred at this temperature gas evolution seized. After removing all volatiles under vacuum, the residue was dissolved in CH_2Cl_2 (0.5 M) and cooled to 0 ^oC followed by addition of *N*-methyl aniline (1.2 eq.) and NEt_3 (2.0 eq.). This mixture was allowed to warm to r.t. and stirred overnight. After dilution with ether, the organic phase was washed in succession with 1N HCl, water and brine. Drying over $MgSO_4$, concentration and chromatographic purification yielded the products **1a-h**,**m,n**.

[1] T. Shimada, Y. Kobayashi and K. Saigo, *Tetrahedron Asymmetry*, 2006, **15**, 3807-3813.
[2] F. J. Fananas, A. Granados, R. Sanz, J. S. Ignacio and J. Barluenga, *Chem. Eur. J.*, 2001, **7**, 2896-2907.

N-(2-bromophenyl)-*N*-methyl-2-oxo-2-phenylacetamide (**1a**):



White solid. 83% yield, m.p. 72-73.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (s, 0.5H), 3.41 (s, 2.5H), 7.13 (td, 0.84H, *J* = 1.8, 7.6 Hz), 7.23 (td, 1.5H, *J* = 1.5, 7.6 Hz), 7.28 (d, 0.7H, *J* = 1.8 Hz), 7.30 (d, 0.3H, *J* = 1.8 Hz), 7.40-7.47 (m, 2.0H), 7.52 (dd, 0.84H, *J* = 1.3, 8.1 Hz), 7.54-7.59 (m, 1.13H), 7.66-7.74 (m, 0.33H), 7.90 (dd, 1.65H, *J* = 1.0, 8.0 Hz), 8.17 (dd, 0.30H, *J* = 1.0, 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.3, 37.7, 121.8, 122.8, 128.3, 128.4, 128.91, 128.97, 129.4, 129.6, 129.8, 129.9, 130.1, 130.9, 132.7, 133.6, 134.2, 134.8, 139.6, 139.9, 166.5, 189.9, 191.0. ν_{max}/cm^{-1}: 1651, 1597, 1572, 1510, 1478, 1257, 1243 1171. HRMS: *m/z* (ESI+) calculated for $C_{15}H_{13}BrNO_2$ ($[M+H]^+$): 318.0124, found: 318.0128.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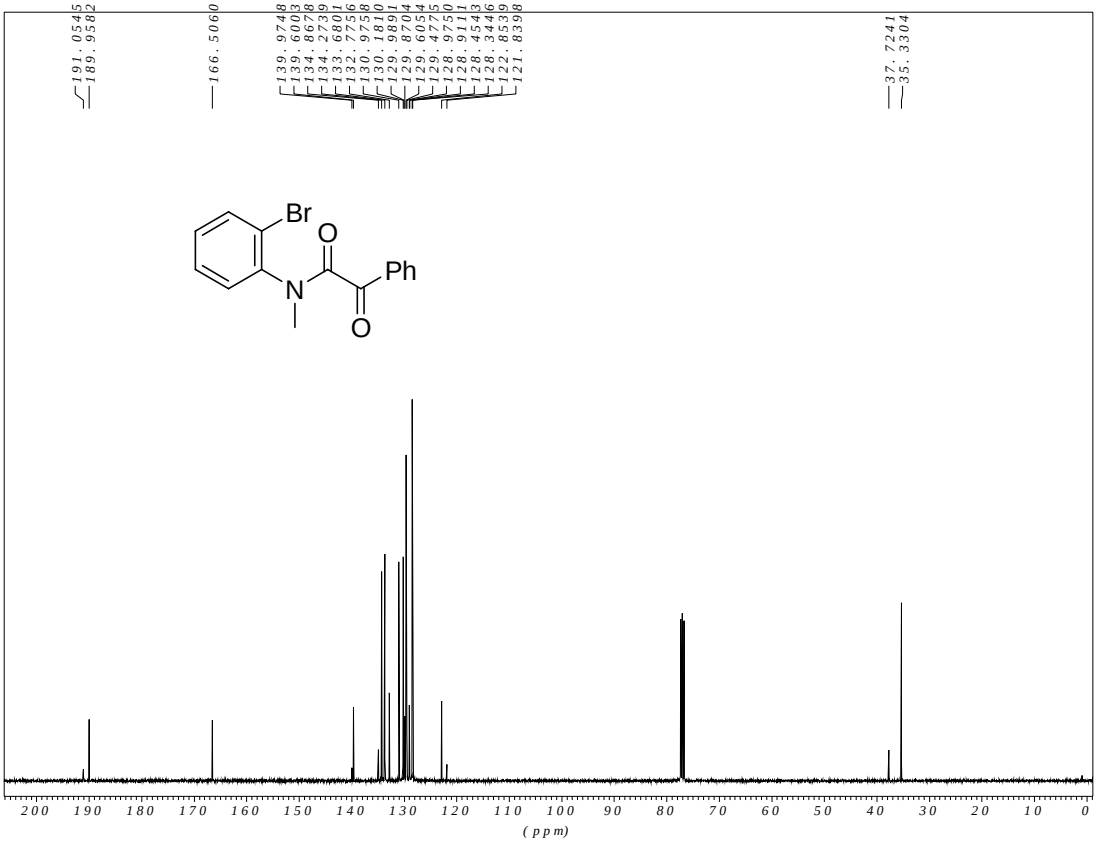
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(ppm)

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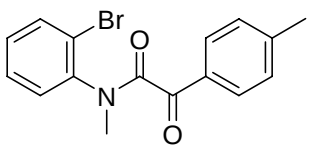

White solid. 73% yield, m.p. 132.5-133 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 2.5H), 2.46 (s, 0.5H), 3.25 (s, 0.5H), 3.41 (s, 2.5H), 7.13 (td, 0.9H, *J* = 1.8, 7.8 Hz), 7.21-7.25 (m, 2.5H), 7.29 (td, 1.1H, *J* = 1.5, 7.6 Hz), 7.36 (d, 0.35H, *J* = 8.1 Hz), 7.40-7.47 (m, 0.35H), 7.52 (dd, 0.8H, *J* = 1.2, 7.6 Hz), 7.73 (dd, 0.2H, *J* = 1.2, 7.6 Hz), 7.80 (d, 1.7H, *J* = 8.1 Hz), 8.06 (d, 0.3H, *J* = 8.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 21.9, 35.3, 37.7, 121.9, 122.9, 128.3, 128.9, 129.2, 129.6, 129.7, 129.8, 129.9, 130.0, 130.1, 130.45, 130.49, 131.0, 133.7, 139.8, 140.1, 145.4, 145.7, 146.2, 166.7, 189.6, 190.8. ν_{max}/cm^{-1}: 1738, 1654, 1604, 1478, 1381, 1236. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{15}BrNO_2$ ($[M+H]^+$): 332.0280, found: 332.0290.

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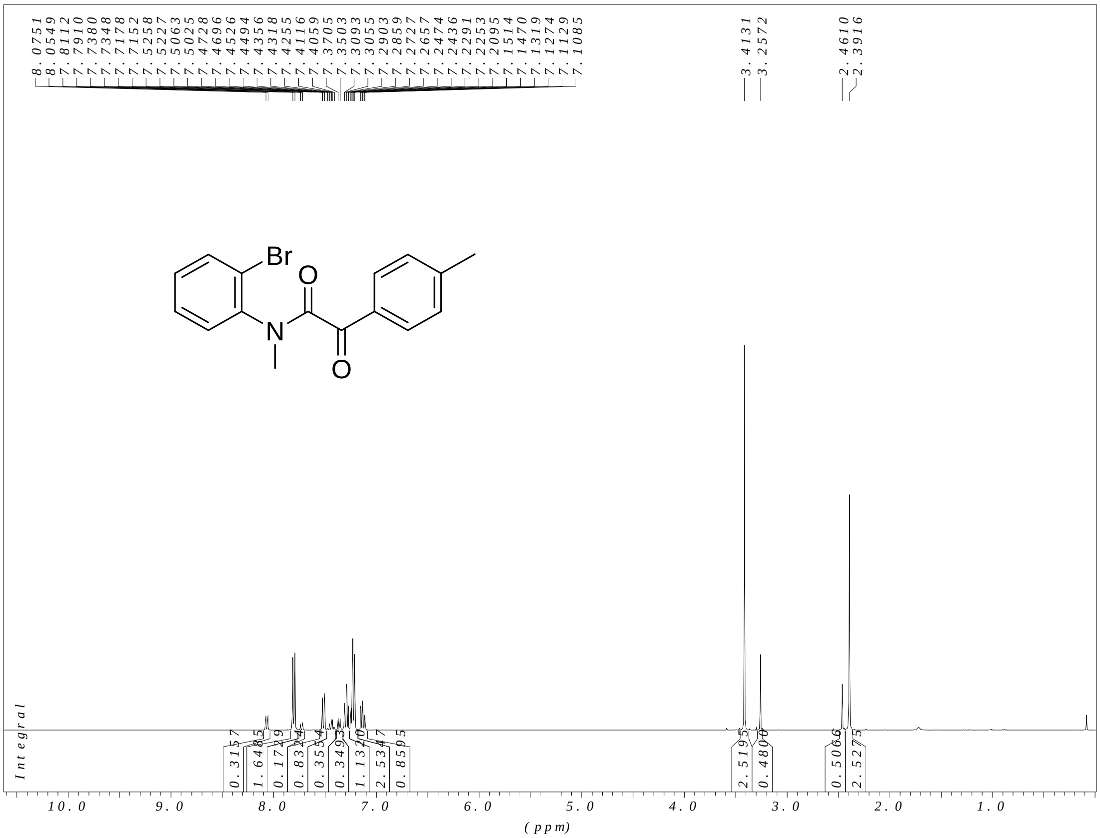
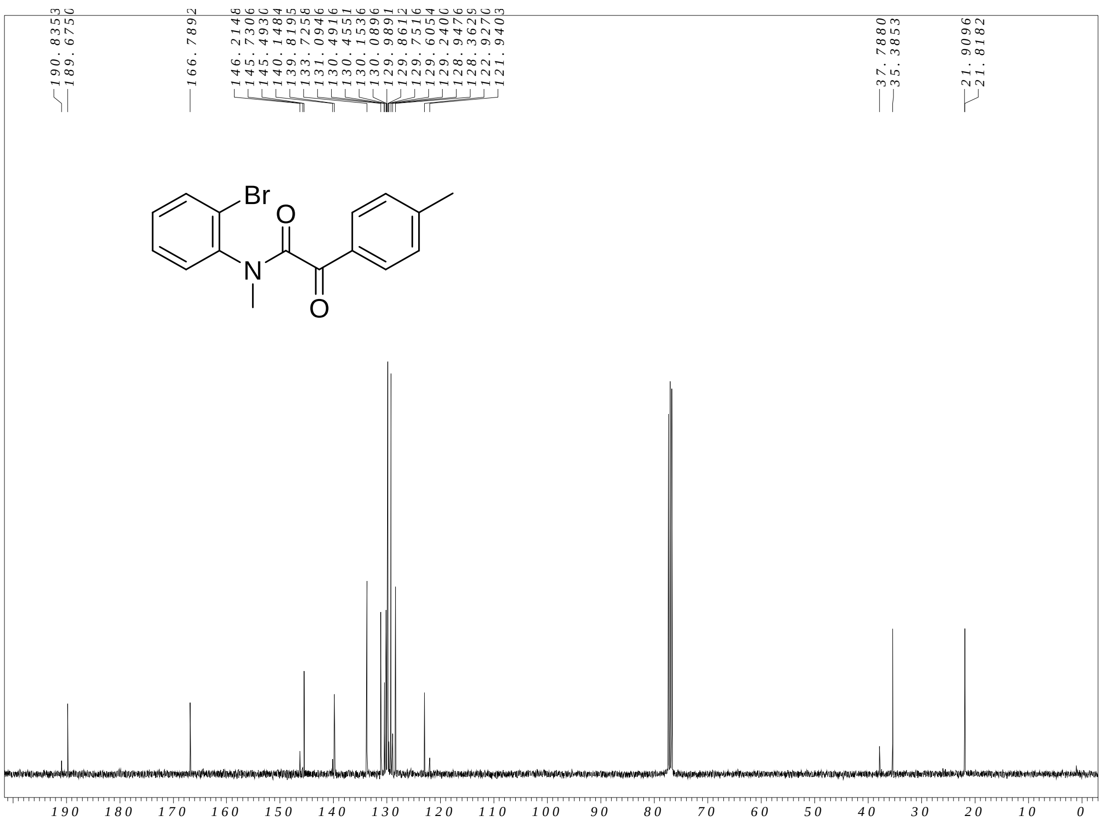
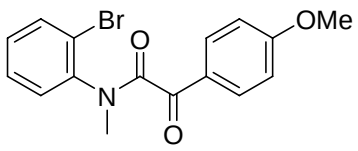
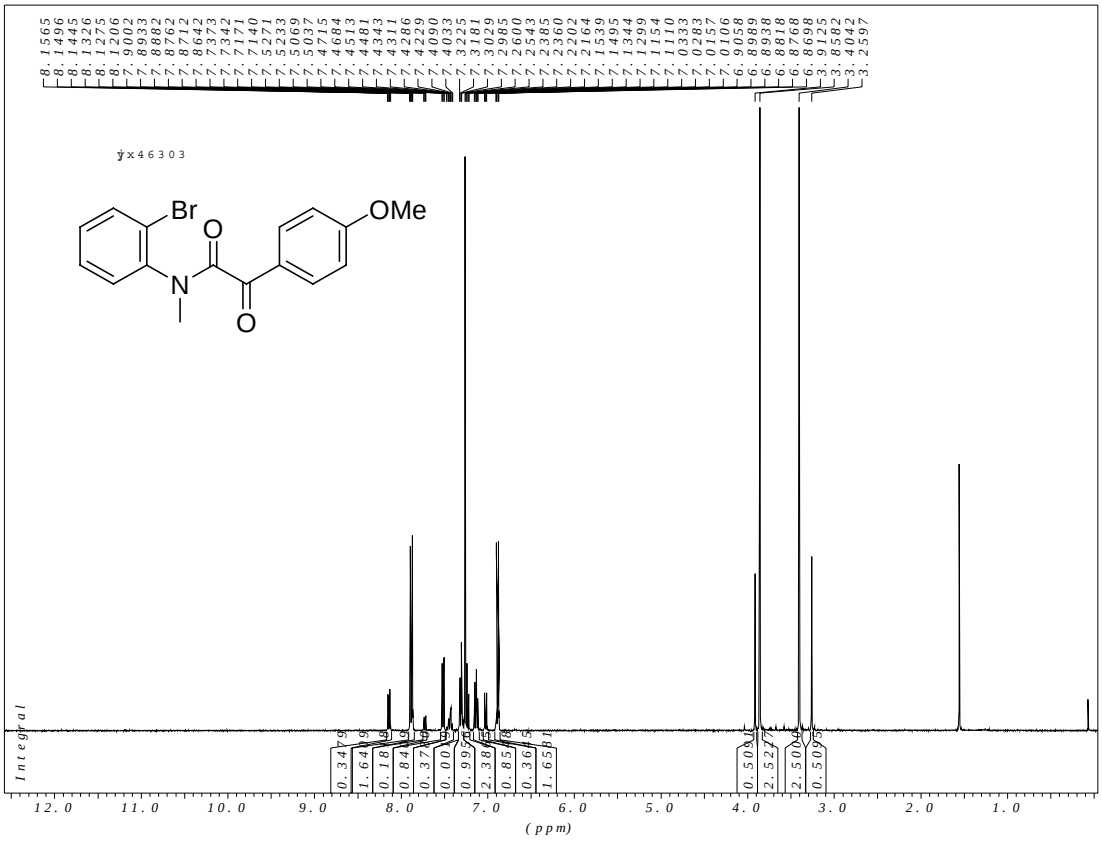




N-(2-bromophenyl)-2-(4-methoxyphenyl)-*N*-methyl-2-oxoacetamide (**1c**):



White solid. 71% yield, m.p. 80-81°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25 (s, 0.5H), 3.40 (s, 2.5H), 3.85 (s, 2.5H), 3.91 (s, 0.5H), 6.89 (dt, 1.66H, *J* = 2.8, 8.8 Hz), 7.02 (dt, 0.36H, *J* = 2.0, 9.1 Hz), 7.13 (td, 0.85H, *J* = 1.8, 7.8 Hz), 7.23 (td, 1.2H, *J* = 1.0, 7.3 Hz), 7.28-7.32 (m, 1H), 7.40-7.47 (m, 0.38H), 7.52 (dd, 0.84H, *J* = 1.5, 8.1 Hz), 7.73 (dd, 0.18H, *J* = 1.5, 8.1 Hz), 7.88 (dt, 1.64H, *J* = 2.8, 8.8 Hz), 8.14 (dt, 0.35H, *J* = 2.8, 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.2, 37.7, 113.7, 114.2, 121.8, 122.7, 125.8, 128.2, 128.8, 129.4, 129.8, 130.0, 130.9, 132.0, 132.3, 133.5, 139.7, 140.1, 164.3, 164.8, 166.8, 188.5, 189.6. ν_{max}/cm^{-1}: 1736, 1649, 1595, 1571, 1509, 1476, 1255, 1241, 1169. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{15}BrNO_3$ ($[M+H]^+$): 348.0229, found: 348.0222.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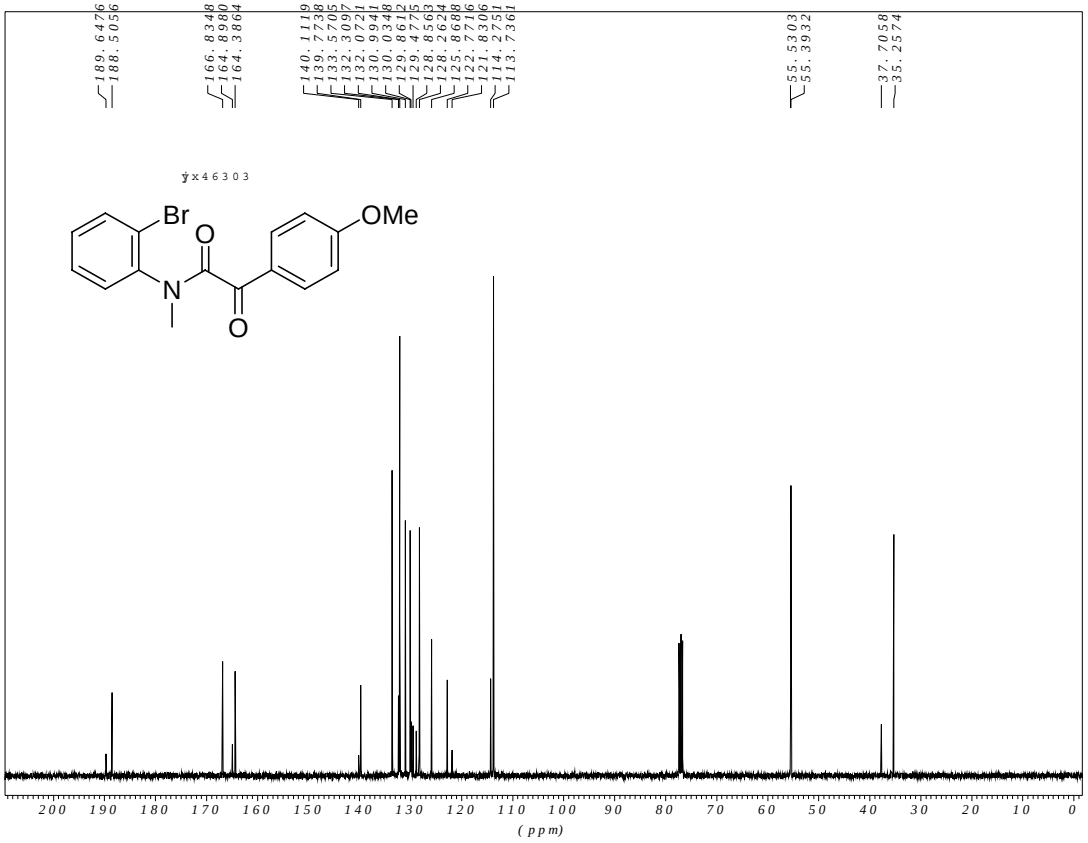
(ppm)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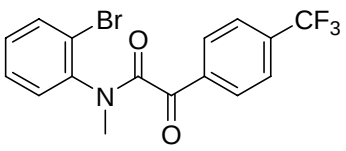
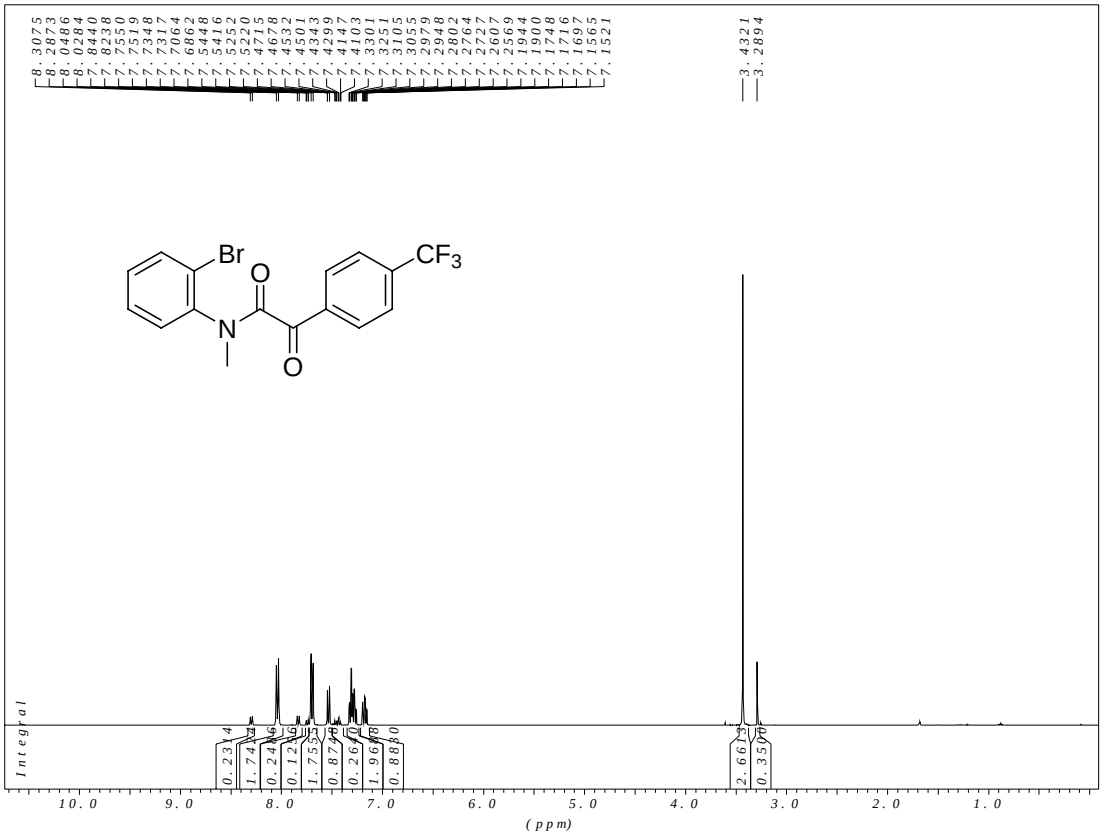
(ppm)

N-(2-bromophenyl)-*N*-methyl-2-oxo-2-(4-(trifluoromethyl)phenyl)acetamide (**1d**):



White solid. 73% yield, m.p. 102.5-104°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.28 (s, 0.35H), 3.43 (s, 2.65H), 7.17 (td, 0.88H, *J* = 1.8, 7.8 Hz), 7.26-7.33 (m, 2.0H), 7.41-7.47 (m, 0.26H), 7.53 (dd, 0.87H, *J* = 1.3, 7.8 Hz), 7.70 (d, 1.75H, *J* = 8.1 Hz), 7.74 (dd, 0.13H, *J* = 1.3, 7.8 Hz), 7.83 (d, 0.25H, *J* = 8.1 Hz), 8.04 (d, 1.75H, *J* = 8.1 Hz), 8.30 (d, 0.25H, *J* = 8.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.5, 37.8, 119.2, 121.7, 121.9, 122.7, 124.7, 125.4, 125.53, 125.56, 125.6, 126.01, 126.05, 126.08, 127.4, 128.6, 129.0, 129.4, 130.0, 130.2, 130.3, 130.4, 130.9, 133.8, 134.7, 135.0, 135.4, 135.50, 135.58, 135.6, 135.7, 139.5, 139.8, 165.6, 188.5, 189.7. ν_{max}/cm^{-1}: 1738, 1688, 1653, 1582, 1477, 1322. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{12}BrF_3NO_2$ ($[M+H]^+$): 385.9998, found: 385.9992.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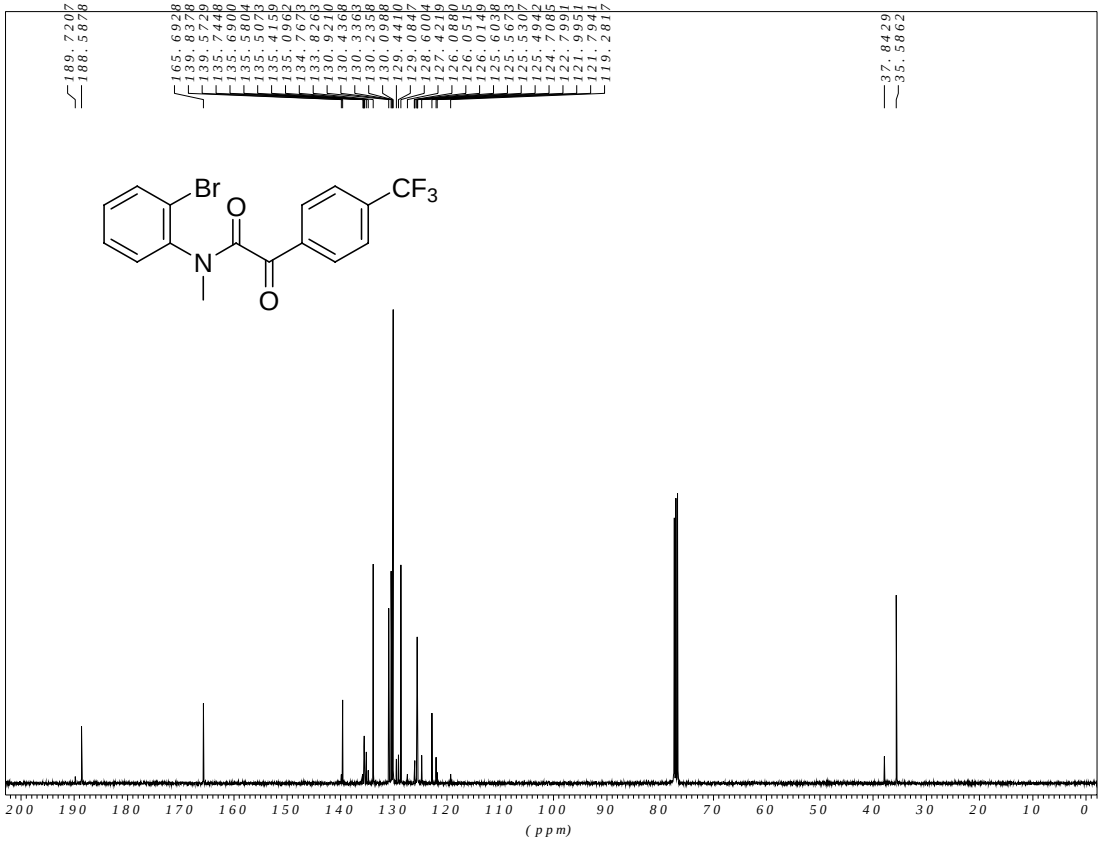
(ppm)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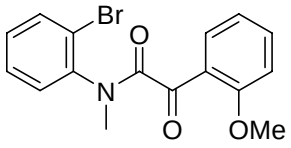
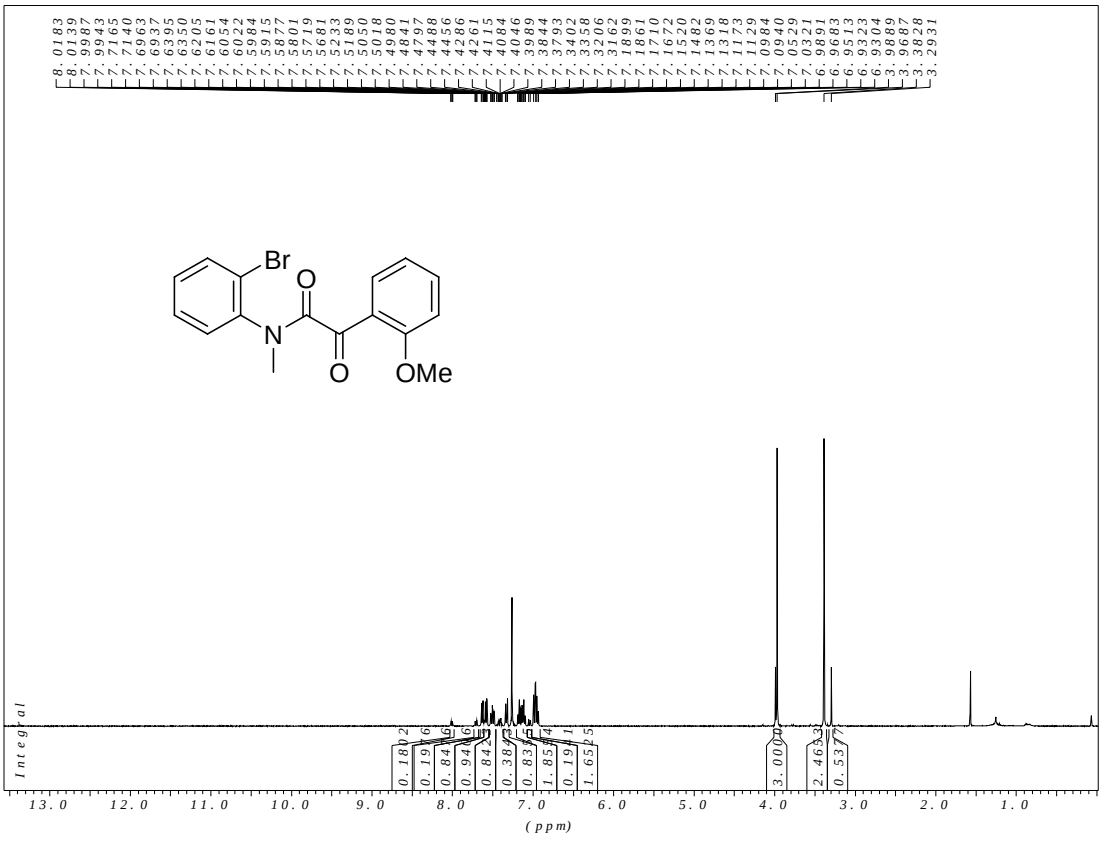
(ppm)

N-(2-bromophenyl)-2-(2-methoxyphenyl)-*N*-methyl-2-oxoacetamide (**1e**):



White solid. 74% yield, m.p. 96.5-98^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.29 (s, 0.5H), 3.38 (s, 2.5H), 3.96 (s, 2.5H), 3.98 (s, 0.5H), 6.96 (dd, 1.65H, *J* = 8.3, 15.1 Hz), 7.04 (d, 0.19H, *J* = 8.3 Hz), 7.09-7.19 (m, 1.86H), 7.33 (dd, 0.84H, *J* = 1.8, 7.8 Hz), 7.37-7.45 (m, 0.38H), 7.47-7.52 (m, 0.84H), 7.58 (dd, 0.84H, *J* = 1.5, 6.3 Hz), 7.63 (dd, 0.84H, *J* = 1.8, 7.6 Hz), 7.71 (dd, 0.2H, *J* = 1.0, 8.1 Hz), 8.01 (dd, 0.18H, *J* = 1.8, 7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.2, 37.5, 56.2, 56.3, 112.2, 112.3, 121.0, 121.2, 121.9, 123.22, 123.28, 123.7, 128.3, 128.5, 129.4, 129.5, 129.80, 129.82, 130.7, 131.2, 133.8, 135.5, 136.1, 140.4, 140.5, 159.5, 160.3, 167.2, 167.7, 189.0, 190.0. ν_{max}/cm^{-1}: 1738, 1652, 1596, 1581, 1480, 1284. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{15}BrNO_3$ ($[M+H]^+$): 348.0229, found: 348.0224.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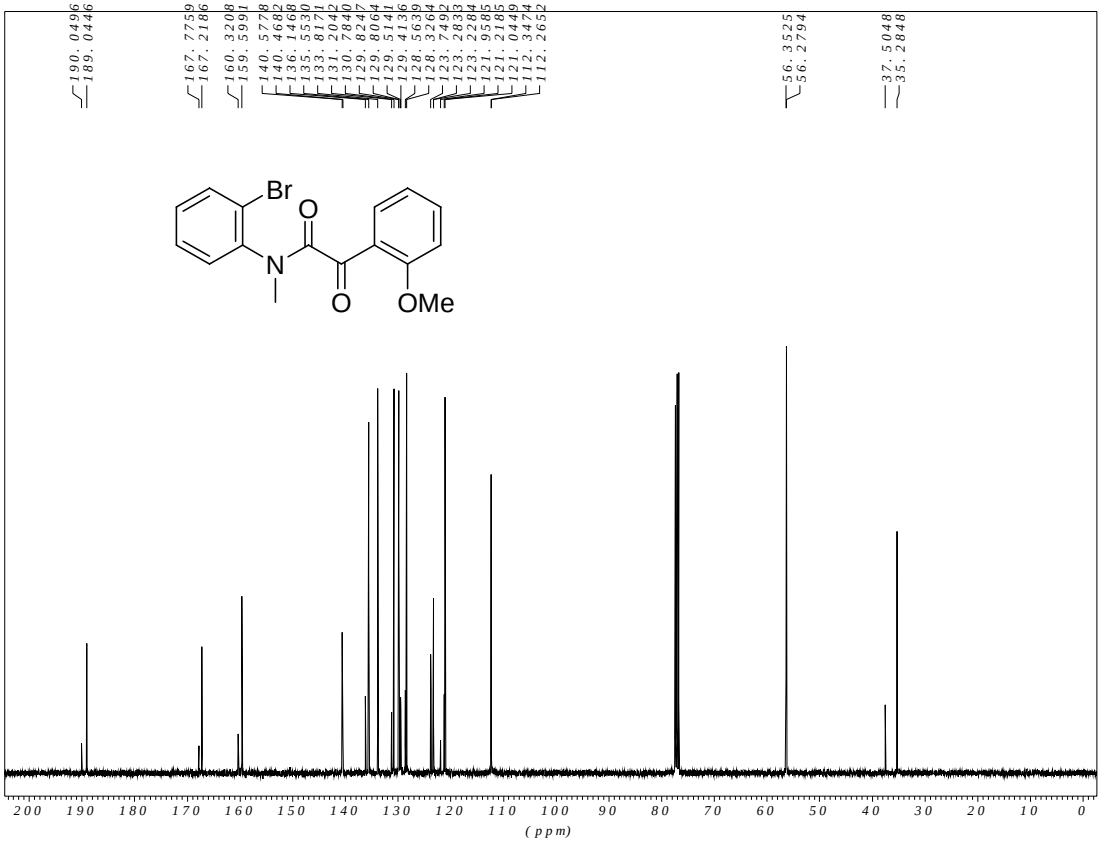
(ppm)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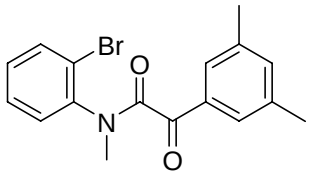
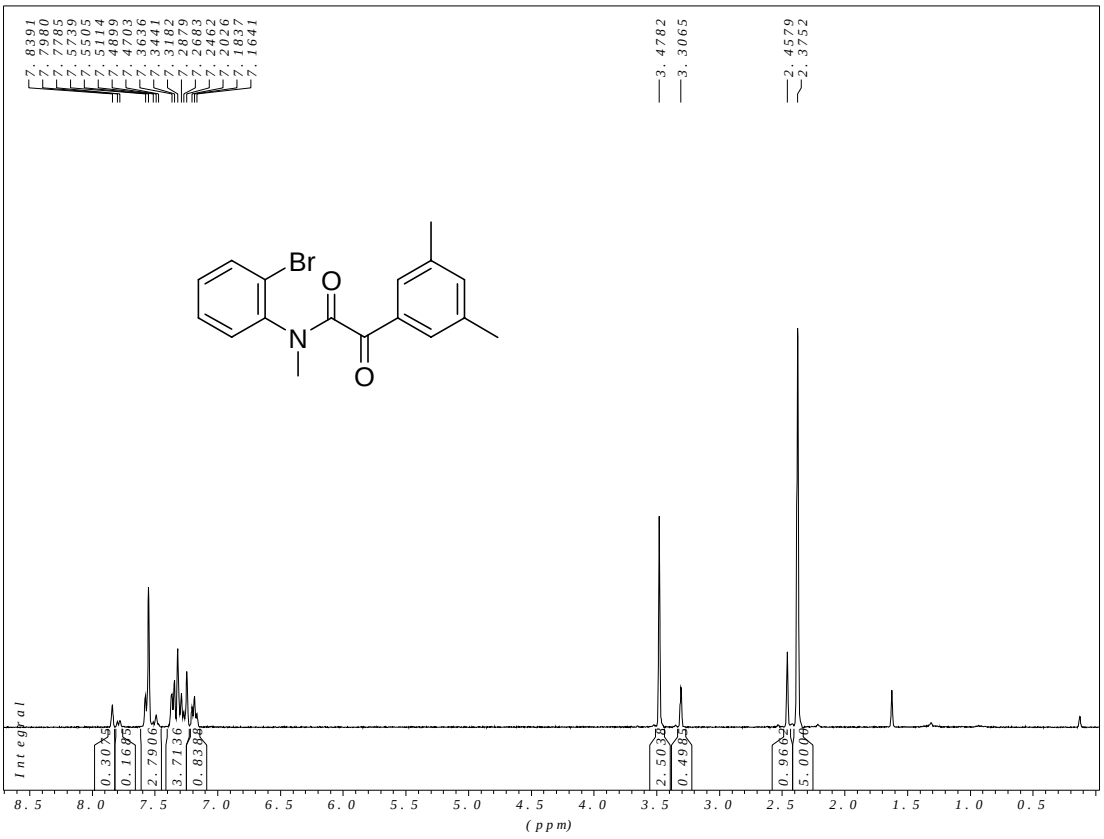
(ppm)

N-(2-bromophenyl)-2-(3,5-dimethylphenyl)-*N*-methyl-2-oxoacetamide (**1f**):



White solid. 68% yield, m.p. 105-106^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 5H), 2.45 (s, 1H), 3.30 (s, 0.5H), 3.47 (s, 2.5H), 7.18 (t, 0.84H, *J* = 7.6 Hz), 7.24-7.36 (m, 3.7H), 7.47-7.57 (m, 2.8H), 7.79 (d, 0.17H, *J* = 7.8 Hz), 7.84 (s, 0.3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.00, 21.05, 35.3, 37.7, 121.8, 122.8, 127.3, 127.6, 128.3, 128.9, 129.6, 129.9, 130.1, 131.1, 132.7, 132.8, 133.7, 136.1, 136.6, 138.1, 138.7, 139.6, 140.0, 166.8, 166.9, 190.5, 191.5. ν_{max}/cm^{-1}: 1738, 1677, 1651, 1598, 1583, 1476, 1380, 1292. HRMS: *m/z* (ESI+) calculated for $C_{17}H_{17}BrNO_2$ ($[M+H]^+$): 346.0437, found: 346.0434.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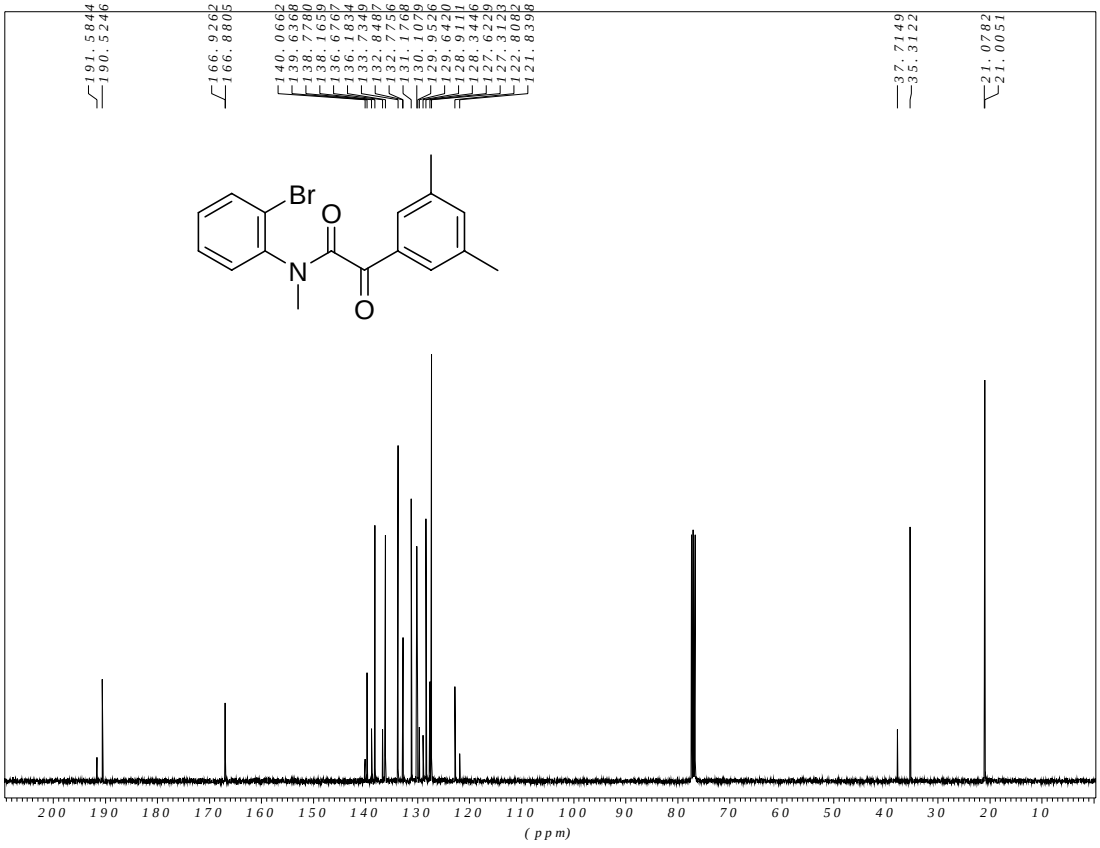
(ppm)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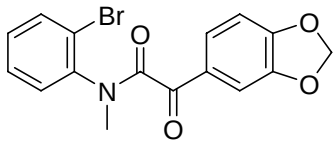
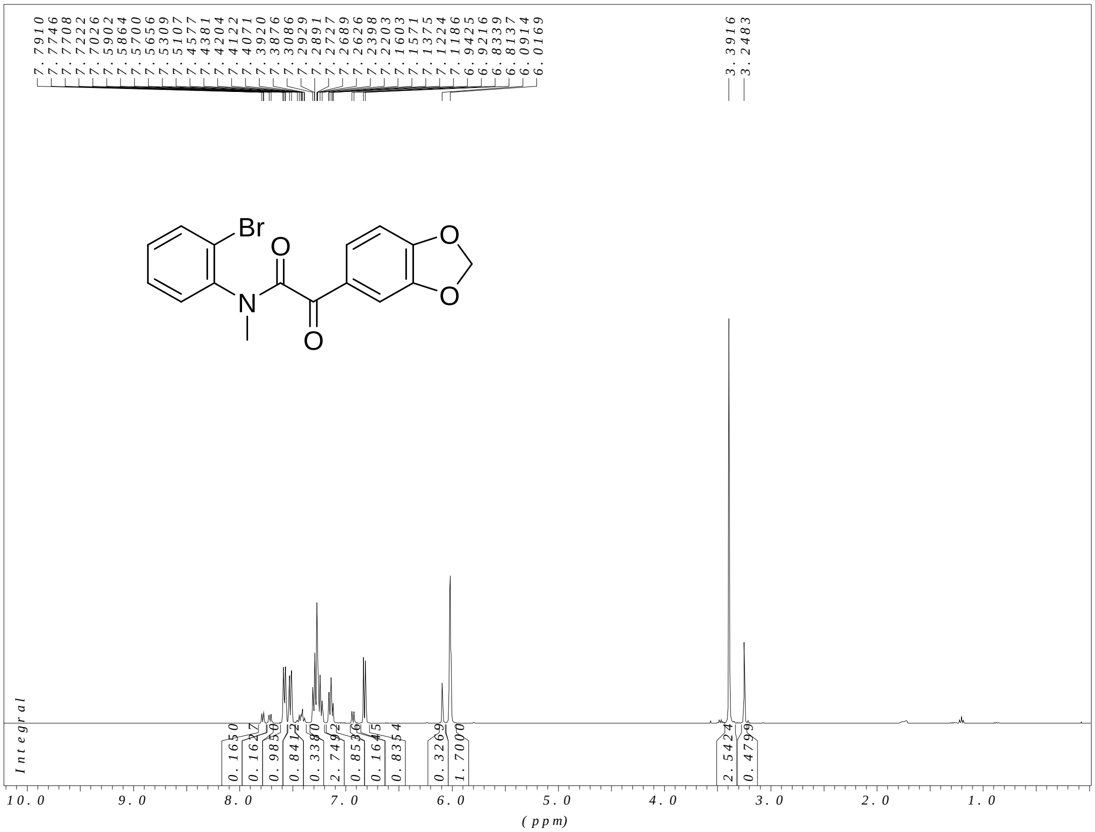
35.3122
21.0782
21.0051
Br
O
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

2-(Benzo[1,3]dioxol-5-yl)-*N*-(2-bromophenyl)-*N*-methyl-2-oxoacetamide (**1g**):



White solid. 79% yield, m.p. 89-90^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.24 (s, 0.5H), 3.39 (s, 2.5H), 6.01 (s, 1.7H), 6.09 (s, 0.3H), 6.83 (d, 0.84H, *J* = 8.1 Hz), 6.93 (d, 0.16H, *J* = 8.1 Hz), 7.13 (t, 0.85H, *J* = 7.6 Hz), 7.22-7.31 (m, 2.8H), 7.38-7.46 (m, 0.34H), 7.52 (d, 0.84H, *J* = 8.1 Hz), 7.58 (dd, 0.84H, *J* = 1.5, 8.1 Hz), 7.71 (d, 0.16H, *J* = 8.1 Hz), 7.78 (dd, 0.17H, *J* = 1.5, 8.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.4, 37.8, 102.0, 102.1, 107.9, 108.2, 108.42, 108.46, 121.9, 122.8, 127.5, 127.70, 127.76, 127.8, 128.3, 128.9, 129.5, 129.9, 130.1, 131.1, 133.7, 139.8, 140.1, 148.1, 148.5, 152.9, 153.4, 166.6, 188.2, 189.3. ν_{max}/cm^{-1}: 1737, 1648, 1601, 1478, 1442, 1248. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{13}BrNO_4$ ($[M+H]^+$): 362.0022, found: 362.0012.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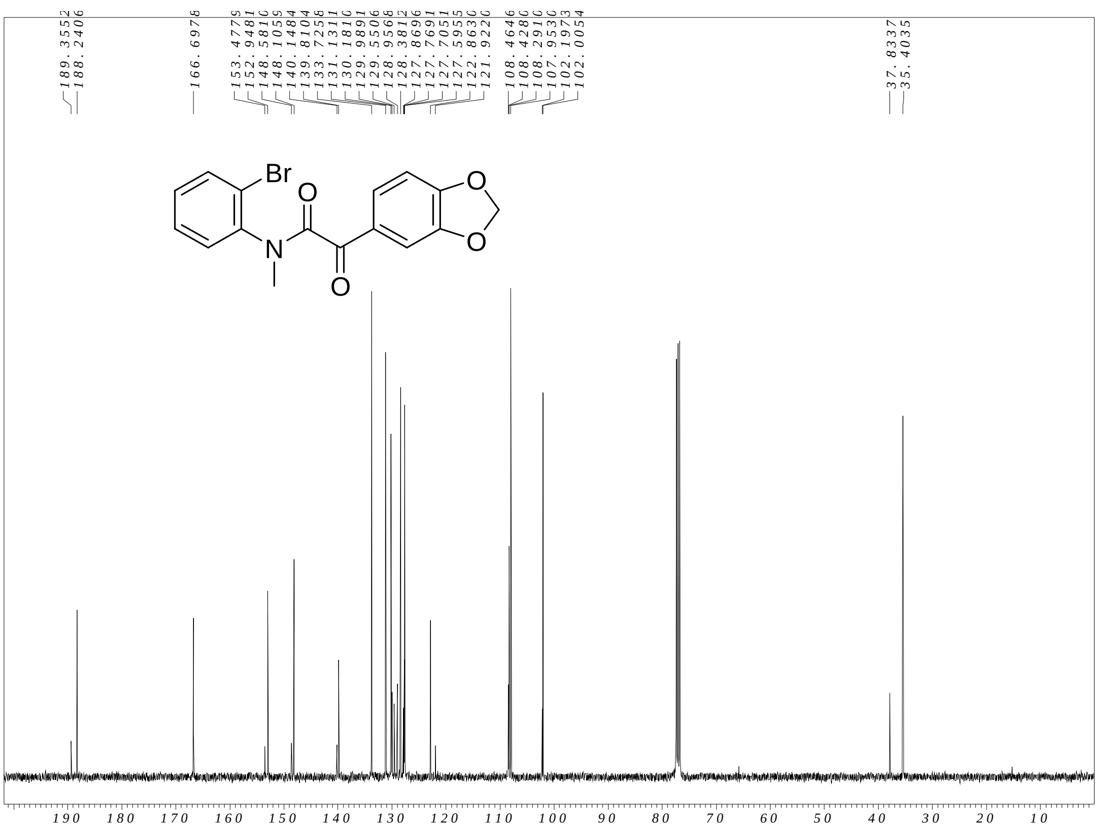
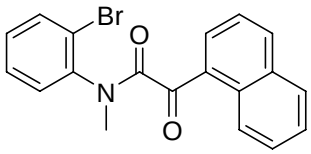
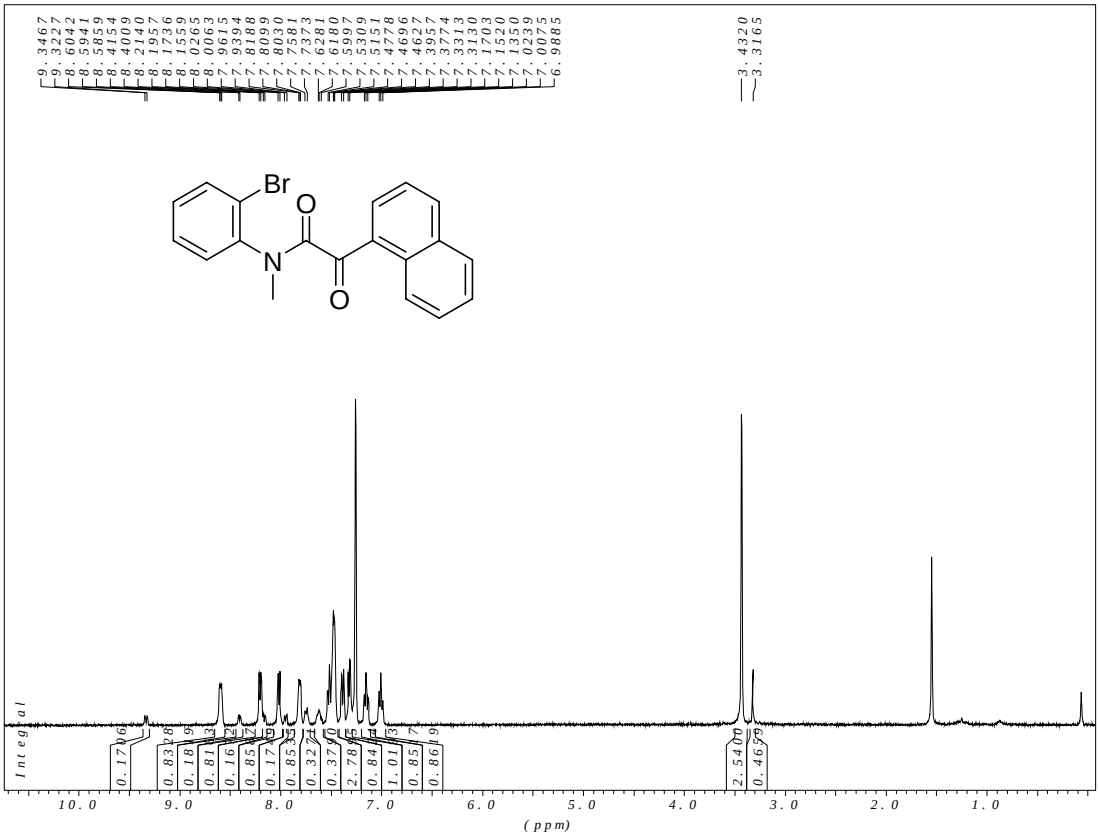
7.3920
7.3876
7.3086
7.2929
7.2891
7.2727
7.2689
7.2626
7.2398
7.2203
7.1603
7.1571
7.1375
7.1224
7.1186
6.9425
6.9216
6.8339
6.8137
6.0914
6.0169
3.3916
3.2483
Br
O
N
O
O
O
Integral
0.1650
0.1627
0.9850
0.8412
0.3380
2.7492
0.8536
0.1645
0.8354
0.3269
1.7000
2.5424
0.4799
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)

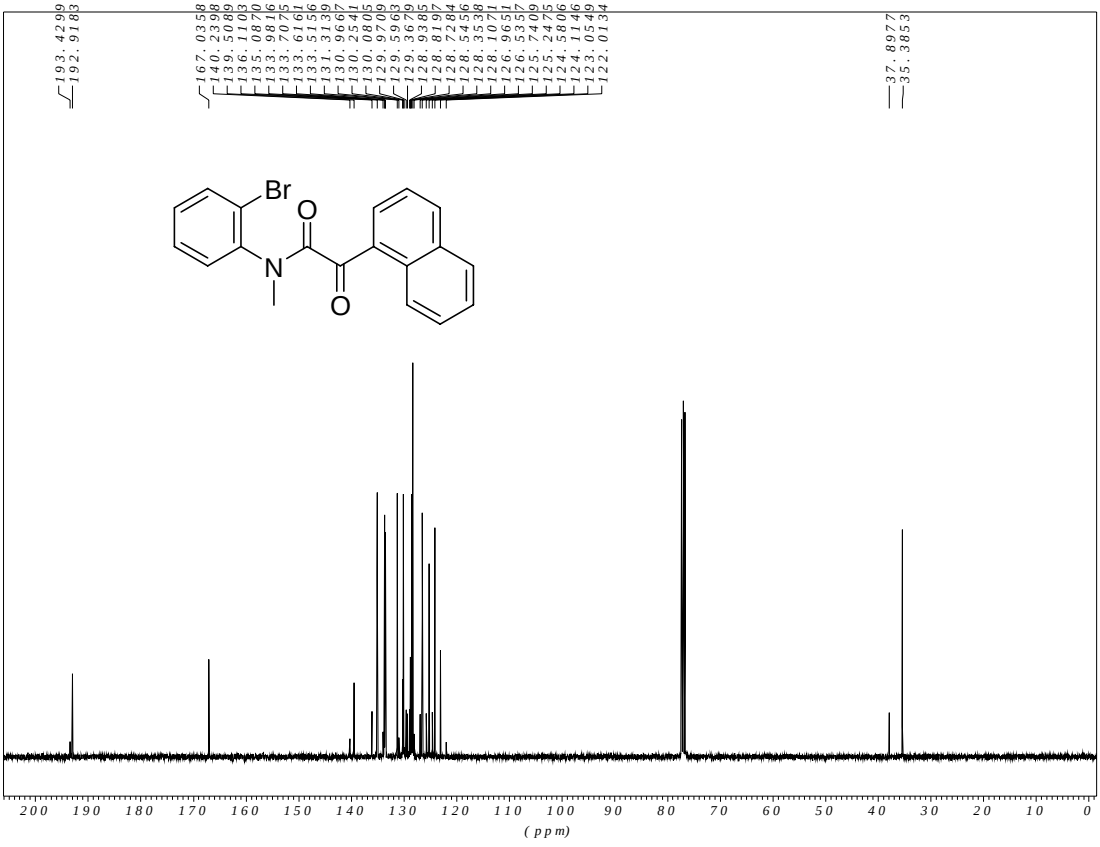

189.3552
188.2406
166.6976
153.4775
152.9481
148.5810
148.1059
140.1484
139.8104
133.7258
131.1311
130.1816
129.9891
129.5506
128.9568
128.3812
127.8696
127.7691
127.7051
127.5955
122.8630
121.9220
108.4646
108.4286
108.2916
107.9536
102.1973
102.0054
37.8337
35.4035
Br
O
N
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

N-(2-bromophenyl)-*N*-methyl-2-(naphthalen-1-yl)-2-oxoacetamide (**1h**):

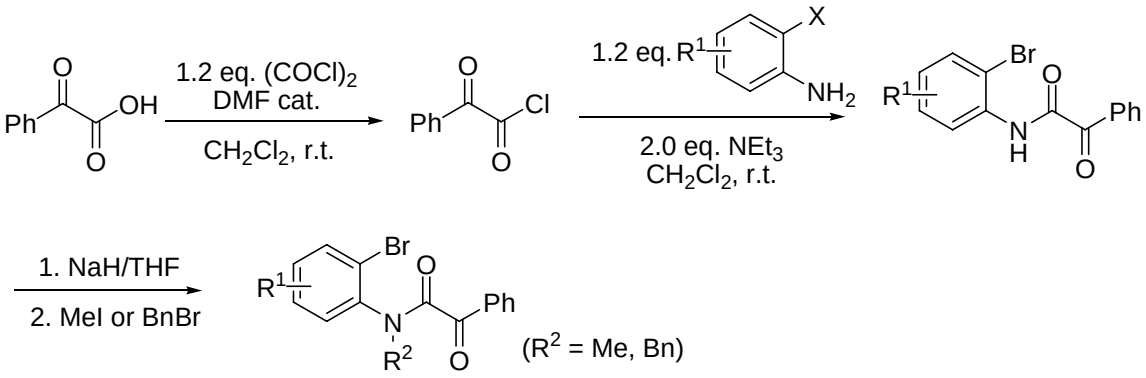


White solid. 60% yield, m.p. 103.5-105^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.31 (s, 0.47H), 3.43 (s, 2.54H), 7.00 (t, 0.86H, *J* = 6.6 Hz), 7.15 (t, 0.85H, *J* = 7.3 Hz), 7.32 (d, 1H, *J* = 7.3 Hz), 7.39 (d, 0.84H, *J* = 7.3 Hz), 7.46-7.53 (m, 2.8H), 7.59-7.63 (m, 0.38H), 7.75 (d, 0.33H, *J* = 8.3 Hz), 7.81 (t, 0.85H, *J* = 3.6 Hz), 7.95 (d, 0.17H, *J* = 8.8 Hz), 8.02 (d, 0.86H, *J* = 8.1 Hz), 8.16 (d, 0.17H, *J* = 7.1 Hz), 8.20 (d, 0.82H, *J* = 7.3 Hz), 8.41 (d, 0.18H, *J* = 5.8 Hz), 8.59 (t, 0.83H, *J* = 4.0 Hz), 9.33 (d, 0.17H, *J* = 9.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.3, 37.8, 122.0, 123.0, 124.1, 124.5, 125.2, 125.7, 126.5, 126.9, 128.1, 128.3, 128.5, 128.7, 128.8, 128.9, 129.3, 129.5, 129.9, 130.0, 130.2, 130.9, 131.3, 133.5, 133.6, 133.7, 133.9, 135.0, 136.1, 139.5, 140.2, 167.0, 192.9, 193.4. ν_{max}/cm^{-1}: 1738, 1649, 1572, 1508, 1475, 1380, 1231. HRMS: *m/z* (ESI+) calculated for $C_{19}H_{15}BrNO_2$ ($[M+H]^+$): 368.0280, found: 368.0280.


Br
O
N
O
(ppm)


Br
O
N
O
(ppm)

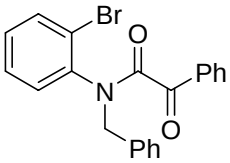
General Procedure B:



The first two steps are the same as general procedure A.

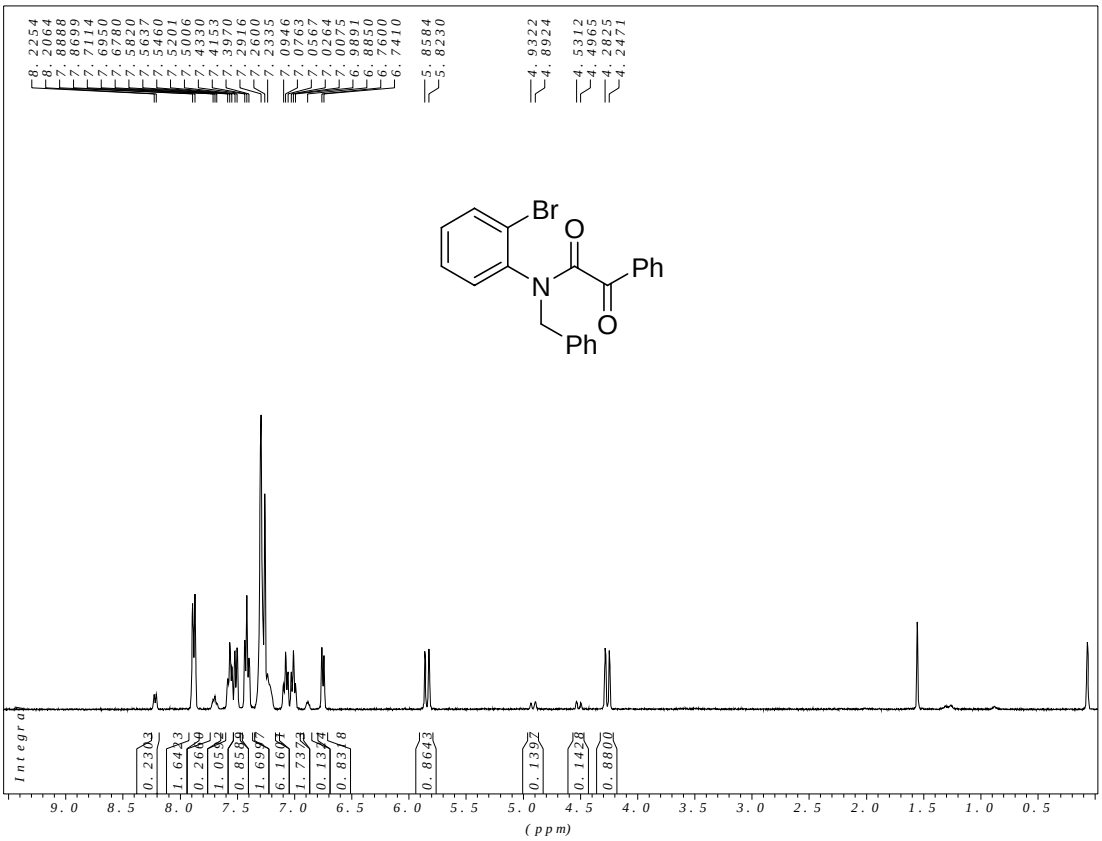
Methylation and benzylation of N-H amides: To a suspension of 1.1 eq. NaH in THF was added the N-H amide (1.0 eq., 0.5 M) at 0 ^{o}C. The reaction was stirred for 1 h at r.t., cooled to 0 ^{o}C and treated with MeI or BnBr (1.1 eq., respectively). After warm up to r.t. and stirring for 20 h, the reaction was quenched with sat. NH_4Cl and diluted with ether. The organic phase was washed in succession with water and brine. Drying over $MgSO_4$, concentration and chromatographic purification yielded the products **1i-o**.

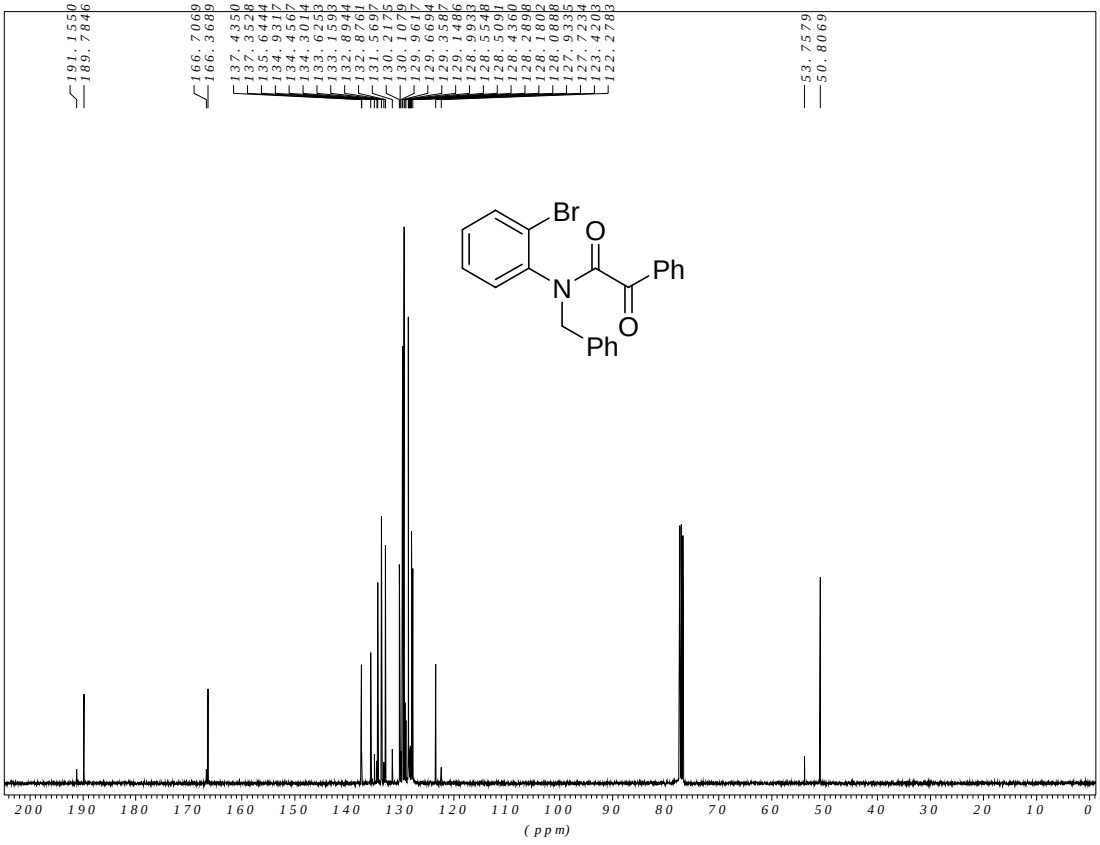
N-benzyl-*N*-(2-bromophenyl)-2-oxo-2-phenylacetamide (**1i**):



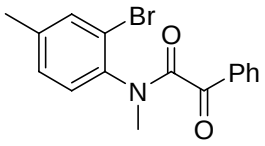
White solid. 70% yield, m.p. 121-121.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27 (d, 0.88H, *J* = 14.2 Hz), 4.52 (d, 0.12H, *J* = 14.2 Hz), 4.91 (d, 0.12H, *J* = 14.4 Hz), 5.84 (d, 0.88H, *J* = 14.4 Hz), 6.75 (d, 0.83H, *J* = 7.6 Hz), 6.88 (s, 0.12H), 7.01 (t, 0.87H, *J* = 7.3 Hz), 7.08 (t, 0.87H, *J* = 7.3 Hz), 7.19-7.29 (m, 6H), 7.42 (t, 1.7H, *J* = 7.1 Hz), 7.51 (d, 0.86H, *J* = 7.8 Hz), 7.56 (t, 1.1H, *J* = 7.3 Hz), 7.69 (t, 0.3H, *J* = 6.8 Hz), 7.88 (d, 1.7H, *J* = 1.0, 7.6 Hz), 8.22 (d, 0.3H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.8, 53.7,

122.2, 123.4, 127.7, 127.9, 128.0, 128.1, 128.2, 128.4, 128.50, 128.55, 128.9, 129.1, 129.3, 129.6, 129.9, 130.1, 130.2, 131.5, 132.87, 132.89, 133.1, 133.6, 134.3, 134.4, 134.9, 135.6, 137.3, 137.4, 166.3, 166.7, 189.7, 191.1. ν_{max}/cm^{-1}: 1678, 1651, 1595, 1581, 1474, 1229. HRMS: *m/z* (ESI+) calculated for $C_{21}H_{17}BrNO_2$ ($[M+H]^+$): 394.0437, found: 394.0453.

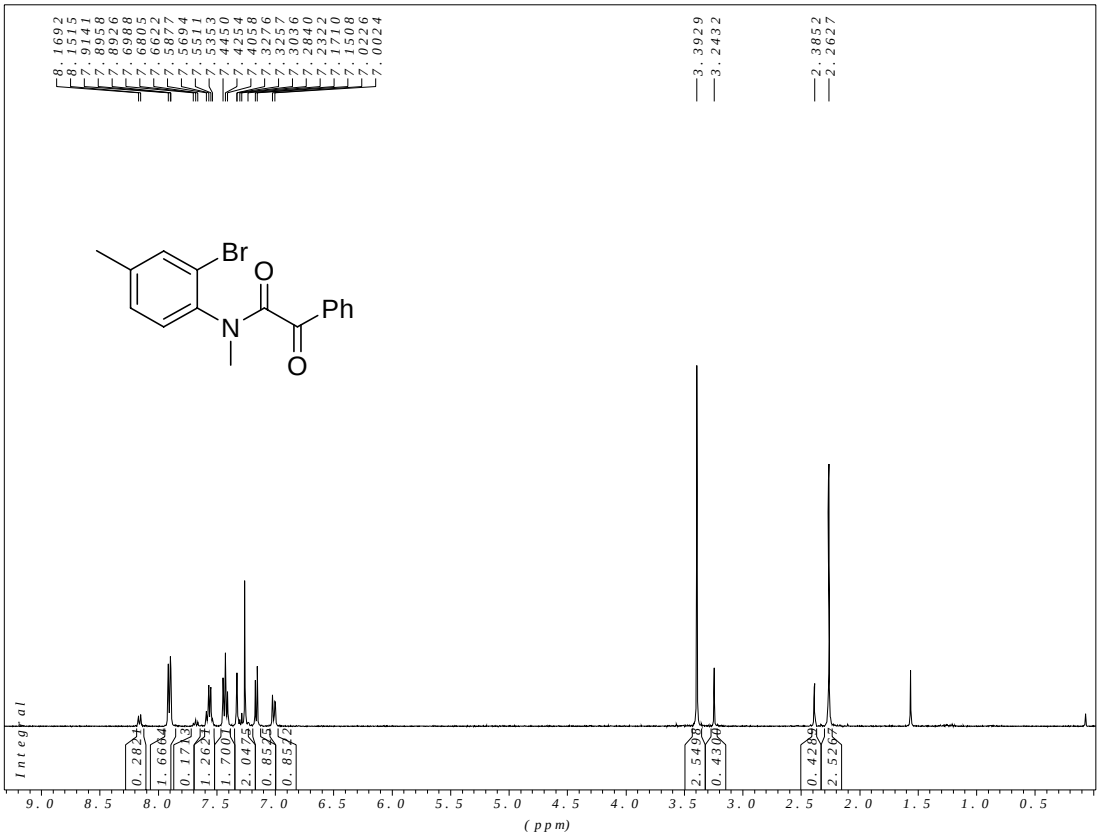

8.2254
8.2064
7.8889
7.8679
7.6514
7.6350
7.6180
7.5637
7.5460
7.5201
7.5006
7.4330
7.4153
7.3970
7.2916
7.2600
7.2335
7.0946
7.0763
7.0567
7.0374
6.9891
6.8850
6.7600
6.7410
5.8584
5.8230
4.9322
4.8924
4.5312
4.4965
4.2825
4.2471
Br
O
Ph
N
O
Ph
Integral
0.2303
1.6433
0.2604
1.0558
0.8598
1.6997
6.1607
1.7372
0.1314
0.8378
0.8643
0.1397
0.1428
0.8800
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

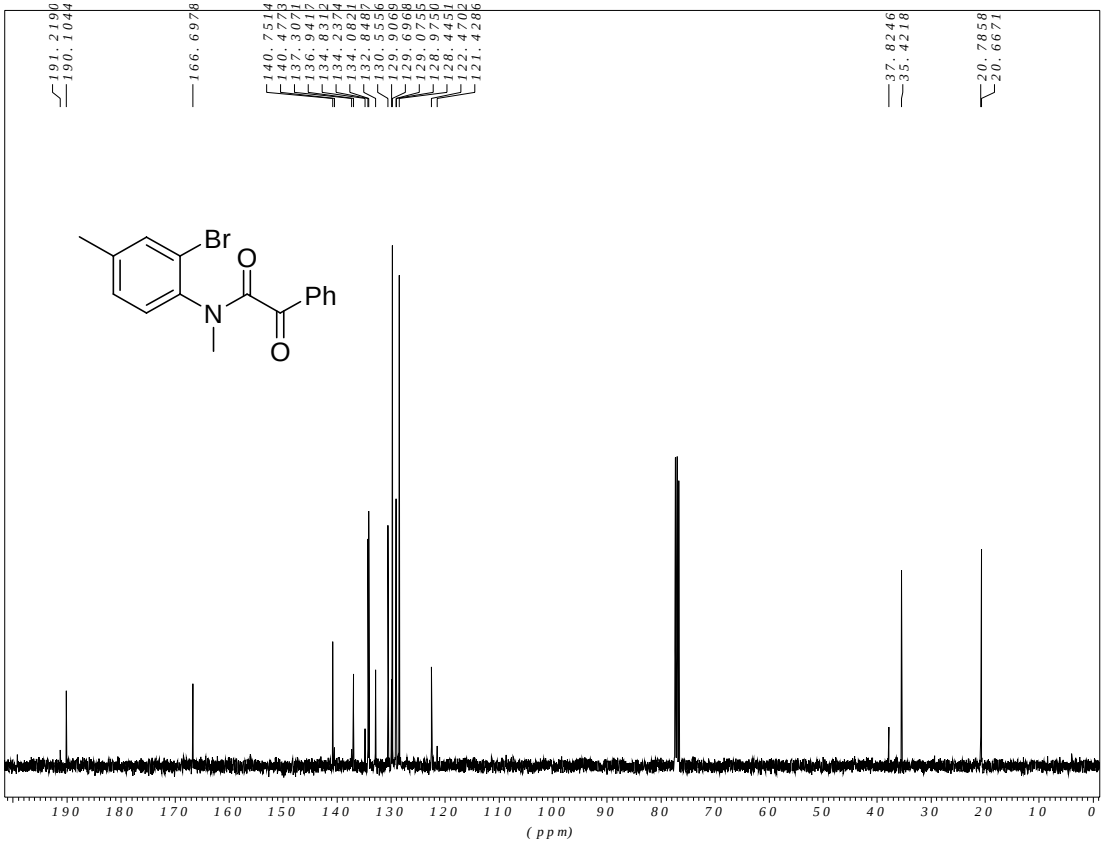

191.1550
189.7846
166.7069
166.3689
137.4350
137.3528
135.6444
134.9317
134.4567
134.3014
133.6253
133.1593
132.8944
132.8761
131.5697
130.2175
130.1079
129.9617
129.6694
129.3587
129.1486
128.9933
128.5548
128.5091
128.4360
128.2898
128.1802
128.0888
127.9335
127.7234
123.4203
122.2783
53.7579
50.8069
Br
O
Ph
N
O
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

N-(2-bromo-4-methylphenyl)-*N*-methyl-2-oxo-2-phenylacetamide (**1j**):



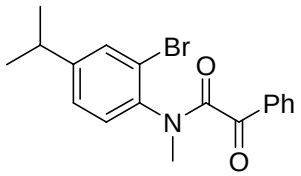
White solid. 59% yield, m.p. 95-95.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 2.53H), 2.36 (s, 0.43H), 3.24 (s, 0.43H), 3.39 (s, 2.55H), 7.01 (d, 0.85H, *J* = 8.1 Hz), 7.16 (d, 0.85H, *J* = 8.1 Hz), 7.23-7.33 (m, 1H), 7.42 (t, 1.7H, *J* = 7.8 Hz), 7.56 (dd, 1.26H, *J* = 7.3, 14.6 Hz), 7.68 (t, 0.17H, *J* = 7.3 Hz), 7.91 (d, 1.67H, *J* = 7.3 Hz), 8.16 (d, 0.28H, *J* = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 20.7, 35.4, 37.8, 121.4, 122.4, 128.4, 128.9, 129.0, 129.6, 129.9, 130.5, 132.8, 134.0, 134.2, 134.8, 136.9, 137.3, 140.4, 140.7, 166.6, 190.1, 191.2. ν_{max}/cm^{-1}: 1678, 1650, 1595, 1582, 1493, 1449, 1385, 1232. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{15}BrNO_2$ ($[M+H]^+$): 332.0280, found: 332.0290.


8.1692
8.1515
7.9441
7.8956
7.8808
7.6805
7.6622
7.5877
7.5694
7.5511
7.5353
7.4450
7.4254
7.4058
7.3276
7.3257
7.3036
7.2840
7.2322
7.1710
7.1508
7.0226
7.0024
3.3929
3.2432
2.3052
2.2627
Br
O
N
Ph
O
Integral
0.2821
1.6604
0.1763
1.2621
1.7001
2.0475
0.8575
0.8572
2.5498
0.4390
0.4209
2.5267
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

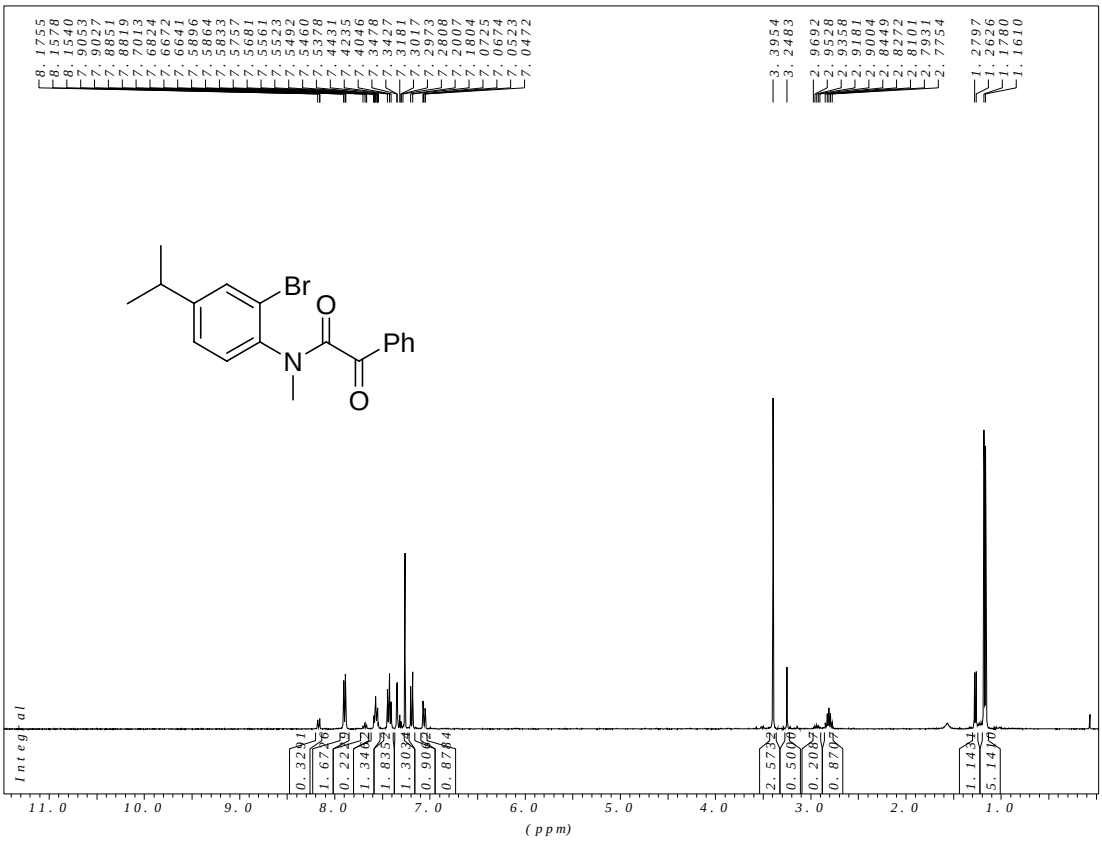

191.2190
190.1044
166.6978
140.7514
140.4773
137.3071
136.9417
134.8312
134.2374
134.0821
132.8487
130.5556
129.9069
129.6968
129.0755
128.9750
128.4451
122.4702
121.4286
37.8246
35.4218
20.7858
20.6671
Br
O
N
Ph
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

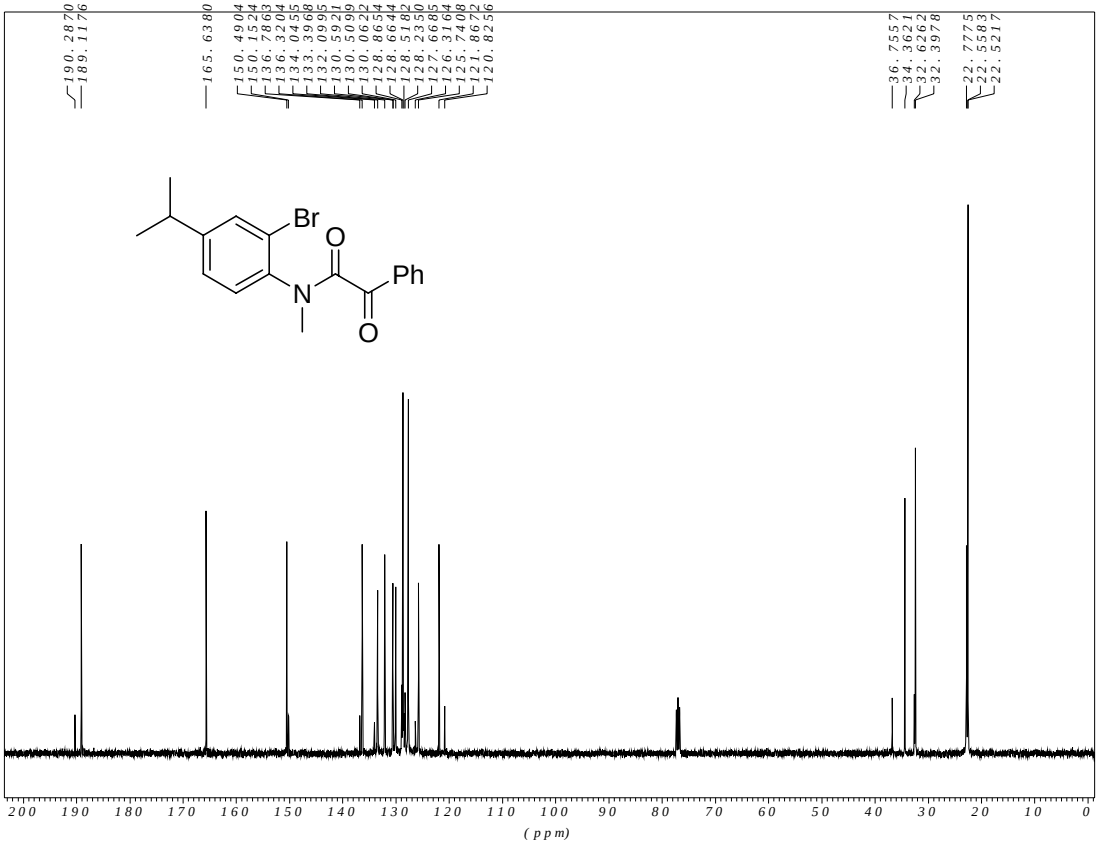
:

N-(2-bromo-4-isopropylphenyl)-*N*-methyl-2-oxo-2-phenylacetamide (**1k**):

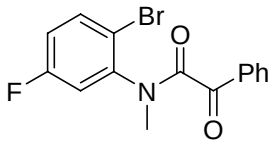


Yellow oil. 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (d, 5H, *J* = 6.8 Hz), 1.27 (d, 1H, *J* = 6.8 Hz), 2.77-2.84 (m, 0.8H), 2.90-2.97 (m, 0.2H), 3.24 (s, 0.5H), 3.39 (s, 2.5H), 7.06 (dd, 0.88H, *J* = 2.0, 8.1 Hz), 7.19 (d, 0.9H, *J* = 8.1 Hz), 7.28-7.35 (m, 1.3H), 7.42 (t, 1.84H, *J* = 7.8 Hz), 7.53-7.59 (m, 1.35H), 7.68 (t, 0.22H, *J* = 7.6 Hz), 7.89 (dd, 1.67H, *J* = 1.0, 8.1 Hz), 8.16 (dd, 0.33H, *J* = 1.0, 8.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.52, 22.55, 22.7, 32.3, 32.6, 34.3, 36.7, 120.8, 121.8, 125.7, 126.3, 127.6, 128.2, 128.5, 128.6, 128.8, 130.0, 130.50, 130.59, 132.0, 133.3, 134.0, 136.3, 136.7, 150.1, 150.4, 165.6, 189.1, 190.2. ν_{max}/cm^{-1}: 1712, 1679, 1652, 1596, 1491, 1449, 1386, 1232. HRMS: *m/z* (ESI+) calculated for $C_{18}H_{19}BrNO_2$ ($[M+H]^+$): 360.0593, found: 360.0612.

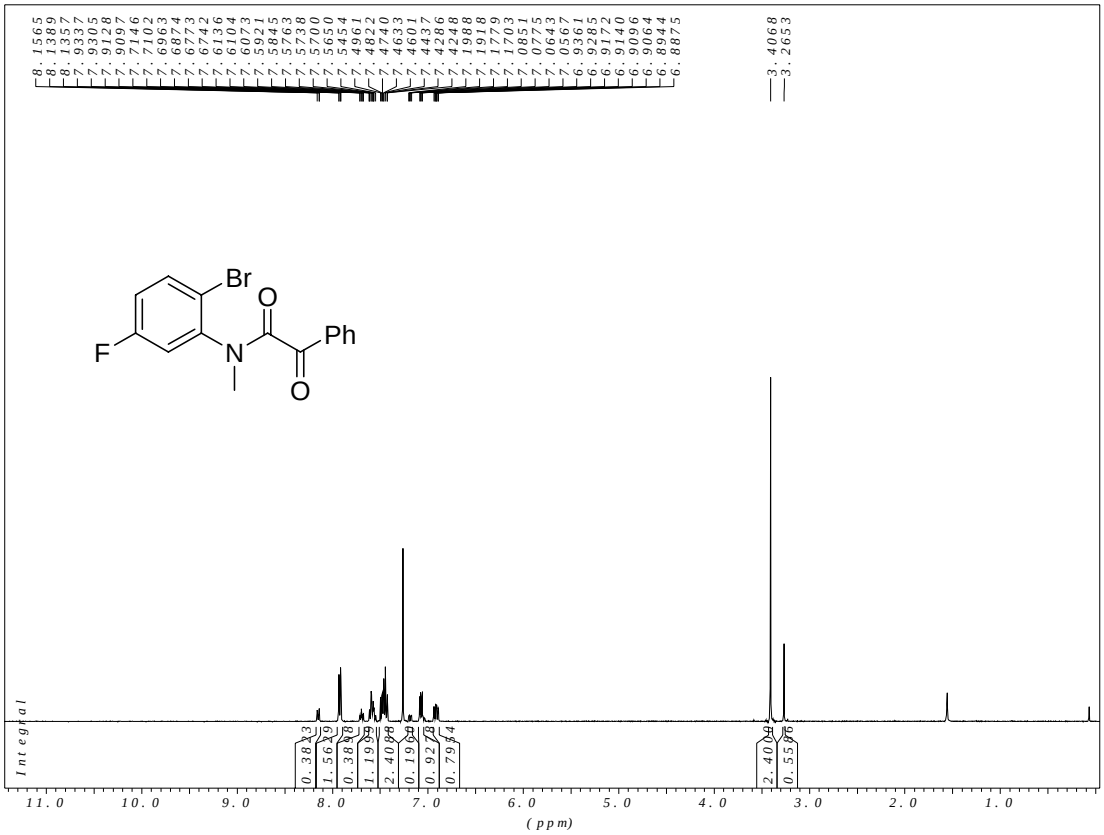

Br
O
N
Ph
O
(ppm)

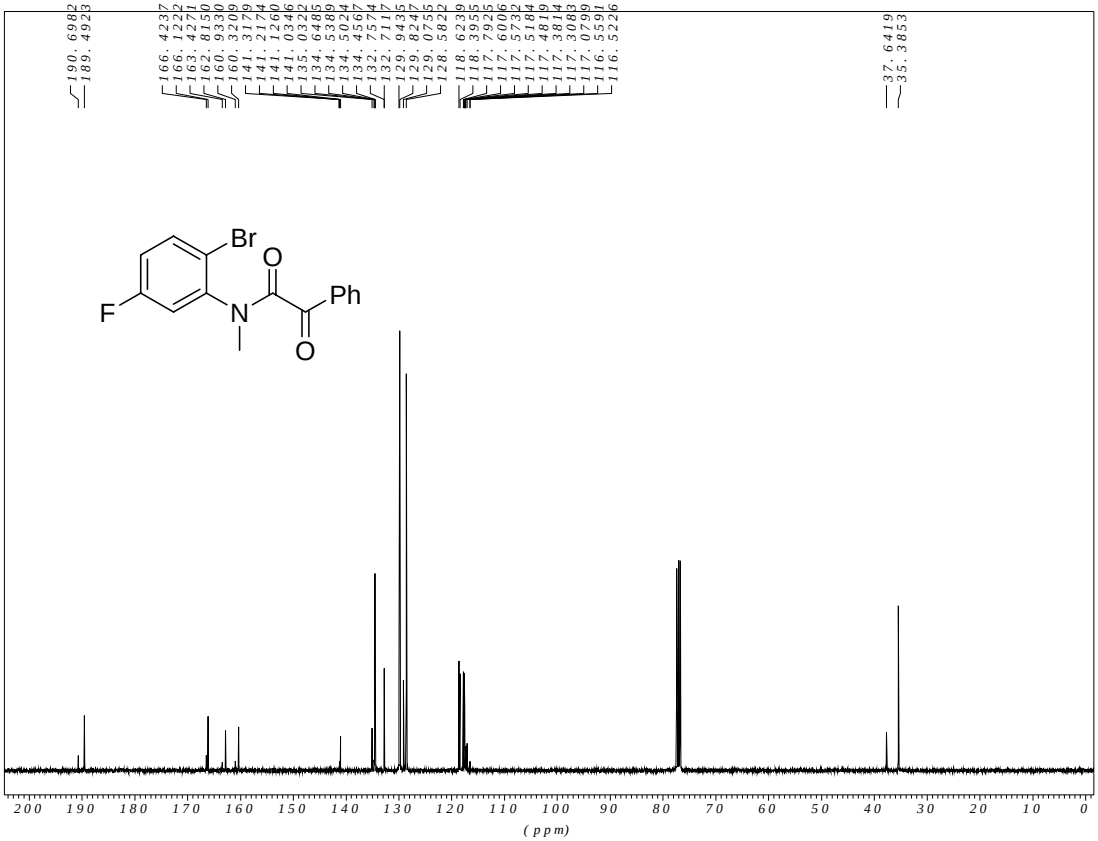

Br
O
N
Ph
O
(ppm)

N-(2-bromo-5-fluorophenyl)-*N*-methyl-2-oxo-2-phenylacetamide (**1l**):

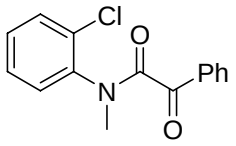


White solid. 74% yield, m.p. 94-95°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (s, 0.6H), 3.40 (s, 2.4H), 6.88-6.94 (m, 0.8H), 7.07 (dd, 0.9H, *J* = 3.0, 8.3 Hz), 7.18 (dd, 0.2H, *J* = 2.8, 8.4 Hz), 7.42-7.50 (m, 2.4H), 7.54-7.61 (m, 1.2H), 7.67-7.71 (m, 0.4H), 7.92 (dd, 1.6H, *J* = 1.3, 8.4 Hz), 8.14 (dd, 0.4H, *J* = 1.3, 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.3, 37.6, 116.52, 116.55, 117.0, 117.30, 117.38, 117.4, 117.51, 117.57, 117.6, 117.7, 118.3, 118.6, 128.5, 129.0, 129.8, 129.9, 132.71, 132.75, 134.4, 134.50, 134.53, 134.6, 135.0, 141.0, 141.1, 141.2, 141.3, 160.3, 160.9, 163.4, 166.1, 166.4, 189.4, 190.6. ν_{max}/cm^{-1}: 1678, 1653, 1594, 1579, 1471, 1450, 1420, 1380, 1232. HRMS: *m/z* (ESI+) calculated for $C_{15}H_{12}BrFNO_2$ ($[M+H]^+$): 336.0029, found: 336.0015.

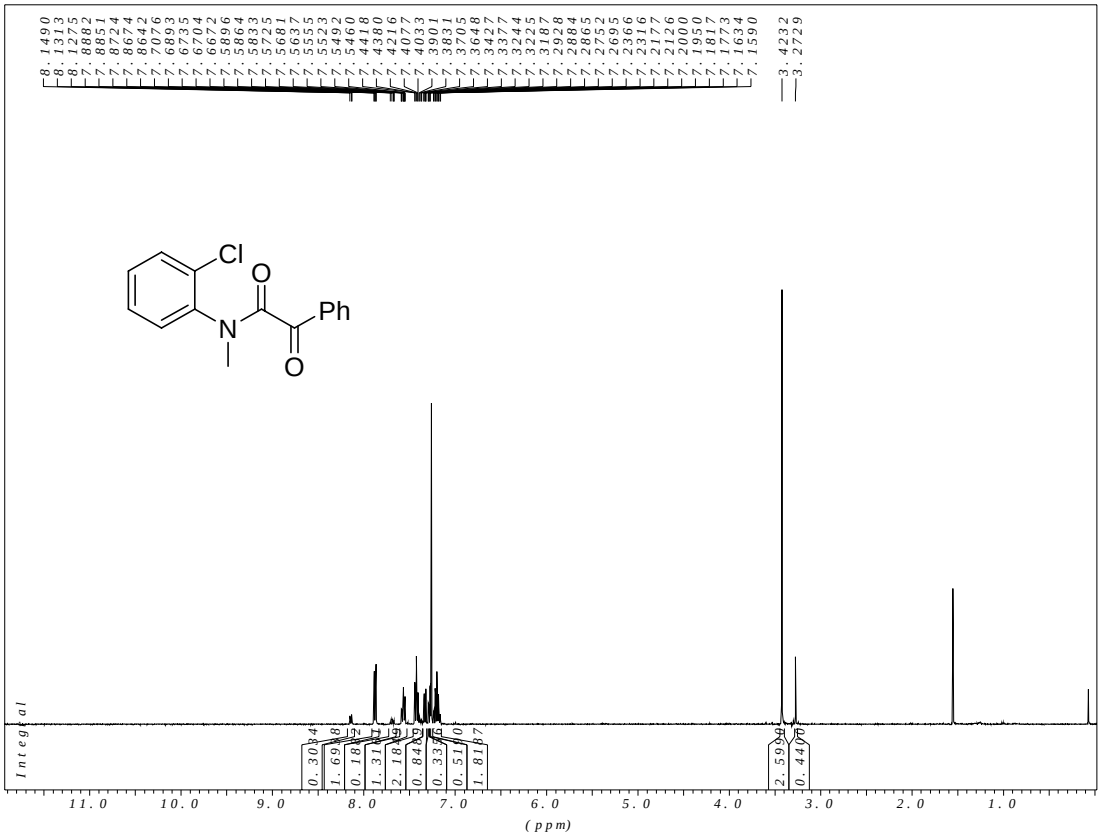

Br
O
F
N
Ph
O
Integral
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)

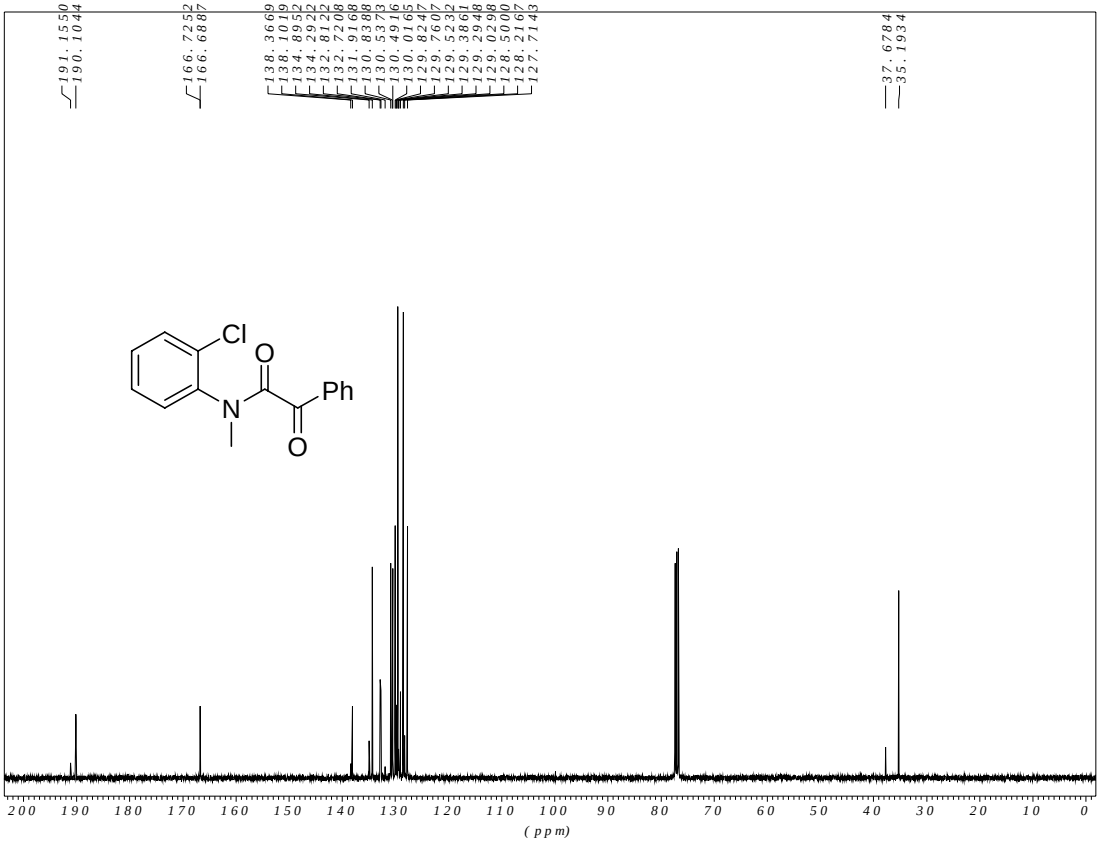

Br
O
F
N
Ph
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

N-(2-chlorophenyl)-*N*-methyl-2-oxo-2-phenylacetamide (**1m**):

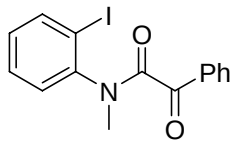


White solid. 68% yield, m.p. 89-81^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.27 (s, 0.4H), 3.42 (s, 2.6H), 7.15-7.24 (m, 1.82H), 7.27 (d, 0.6H, *J* = 2.3 Hz), 7.29 (d, 0.4H, *J* = 2.5 Hz), 7.33 (dd, 0.85H, *J* = 2.0, 8.1 Hz), 7.36-7.44 (m, 2.2H), 7.54-7.59 (m, 1.3H), 7.66-7.71 (m, 0.2H), 7.88 (dd, 1,7H, *J* = 1.2, 8.3 Hz), 8.14 (dd, 0.3H, *J* = 1.2, 8.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.1, 37.6, 127.7, 128.2, 128.5, 129.0, 129.2, 129.3, 129.5, 129.7, 129.8, 130.0, 130.4, 130.5, 130.8, 131.9, 132.7, 132.8, 134.2, 134.8, 138.1, 138.3, 166.6, 166.7, 190.1, 191.1. ν_{max}/cm^{-1}: 1678, 1651, 1596, 1586, 1482, 1449, 1387, 1234. HRMS: *m/z* (ESI+) calculated for $C_{15}H_{13}ClNO_2$ ($[M+H]^+$): 274.0629, found: 274.0636.

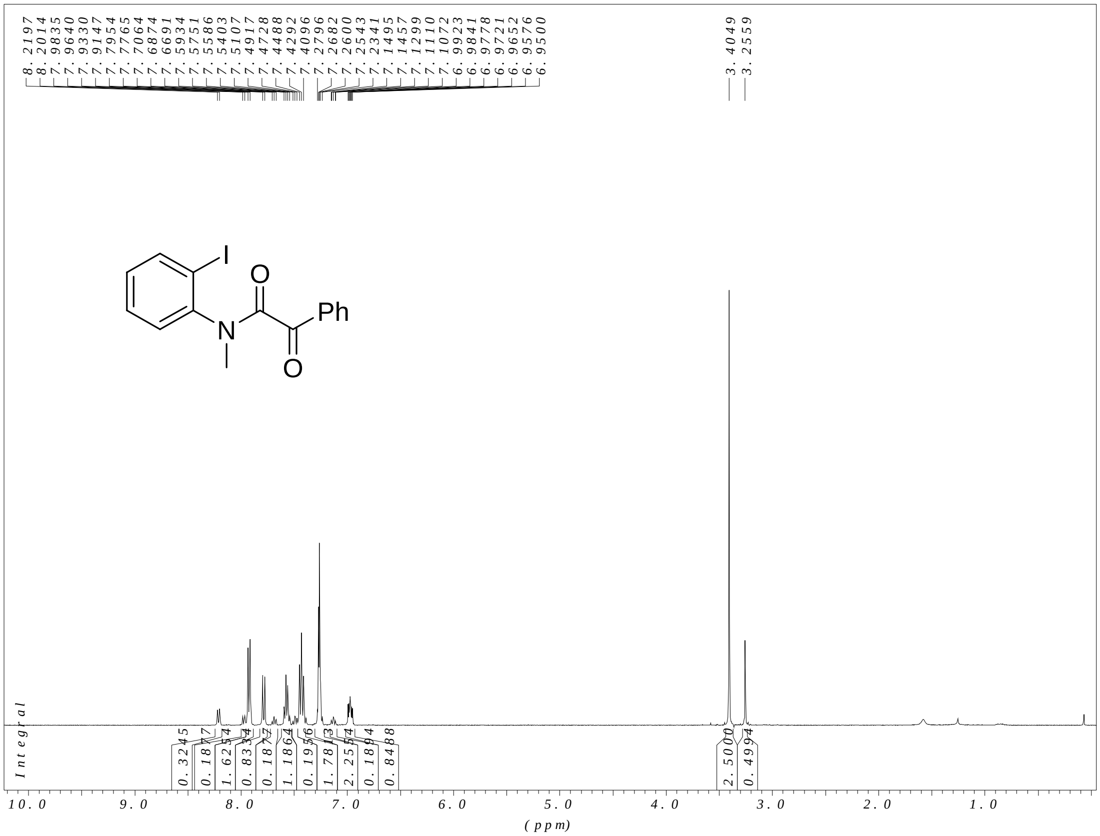

Cl
O
N
Ph
O
Integral
(ppm)

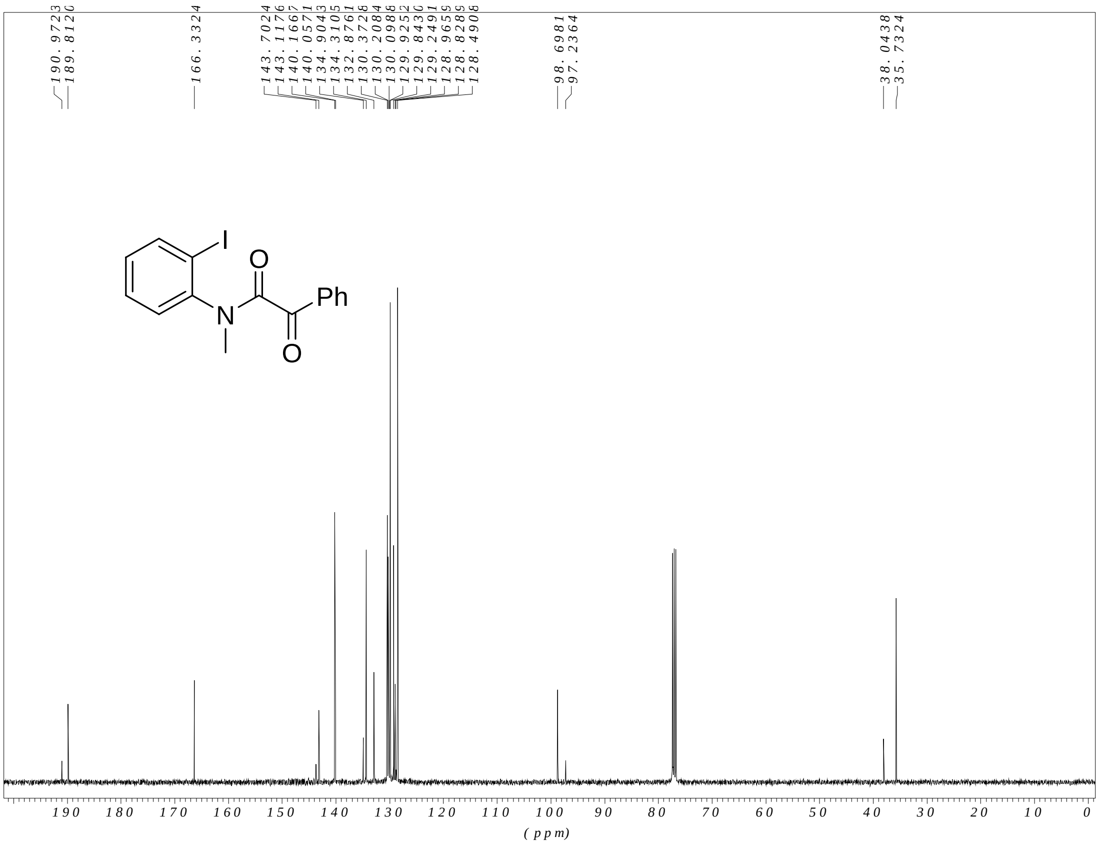

Cl
O
N
Ph
O
(ppm)

N-(2-iodophenyl)-*N*-methyl-2-oxo-2-phenylacetamide (**1n**):

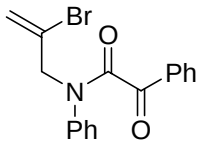


Yellow solid. 39% yield, m.p. 63.5-65.5^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25 (s, 0.5H), 3.40 (s, 2.5H), 6.95-6.99 (m, 0.85H), 7.12 (t, 0.2H, *J* = 7.8 Hz), 7.23-7.28 (m, 2H), 7.42 (t, 1.8H, *J* = 7.8 Hz), 7.49 (t, 0.2H, *J* = 7.6 Hz), 7.57 (dd, 1.2H, *J* = 7.3, 13.9 Hz), 7.68 (t, 0.2H, *J* = 7.6 Hz), 7.78 (d, 0.8H, *J* = 7.6 Hz), 7.92 (d, 1.6H, *J* = 7.3 Hz), 7.97 (d, 0.2H, *J* = 7.8 Hz), 8.21 (d, 0.3H, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.7, 38.0, 97.2, 98.6, 128.4, 128.8, 128.9, 129.2, 129.8, 129.9, 130.0, 130.2, 130.3, 132.8, 134.3, 134.9, 140.0, 140.1, 143.1, 143.7, 166.3, 189.8, 190.9. ν_{max}/cm^{-1}: 1677, 1646, 1595, 1577, 1470, 1449, 1385, 1231. HRMS: *m/z* (ESI+) calculated for $C_{15}H_{13}INO_2$ ($[M+H]^+$): 365.9985, found: 365.9974.

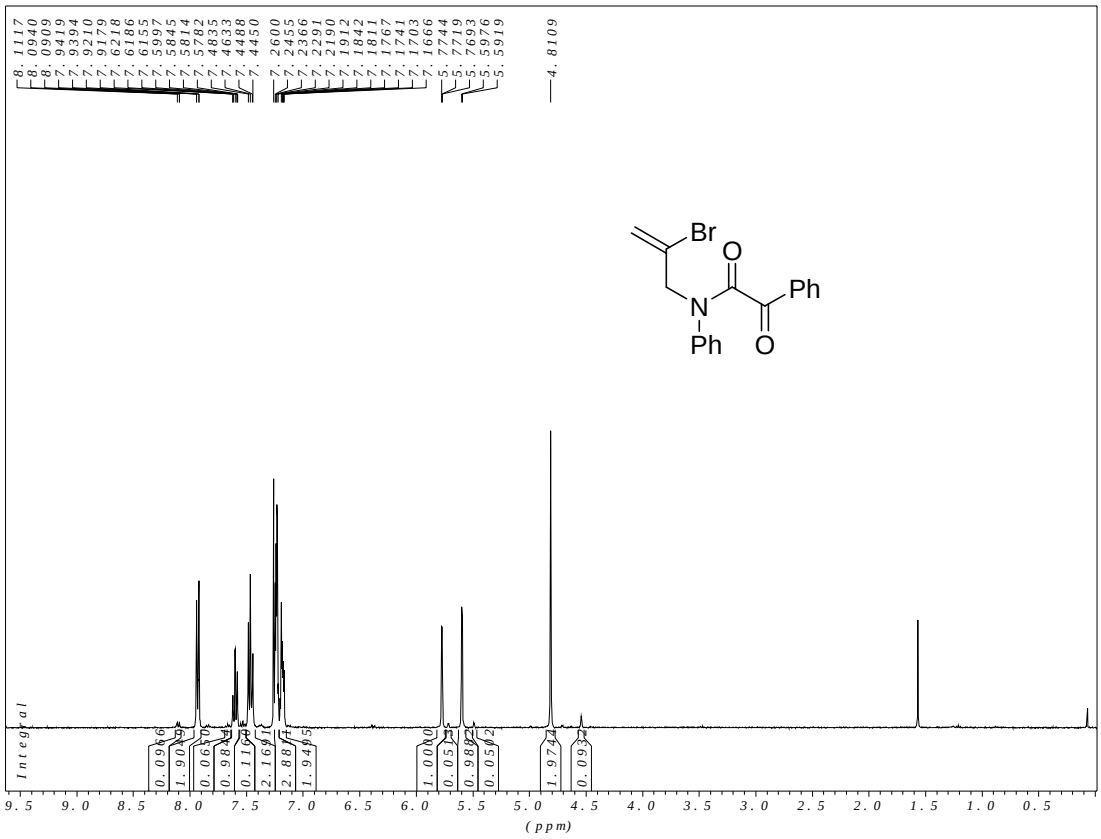

8.2197
8.2014
7.9835
7.9640
7.9330
7.9147
7.7954
7.7765
7.7064
7.6874
7.6691
7.5934
7.5751
7.5586
7.5403
7.5107
7.4917
7.4728
7.4488
7.4292
7.4096
7.2796
7.2682
7.2600
7.2543
7.2341
7.1495
7.1457
7.1299
7.1110
7.1072
6.9923
6.9841
6.9778
6.9721
6.9652
6.9576
6.9500
3.4049
3.2559
I
O
N
Ph
O
Integral
0.3245
0.1877
1.6254
0.8334
0.1877
1.1864
0.1956
1.7813
2.2554
0.1894
0.8488
2.5000
0.4994
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)

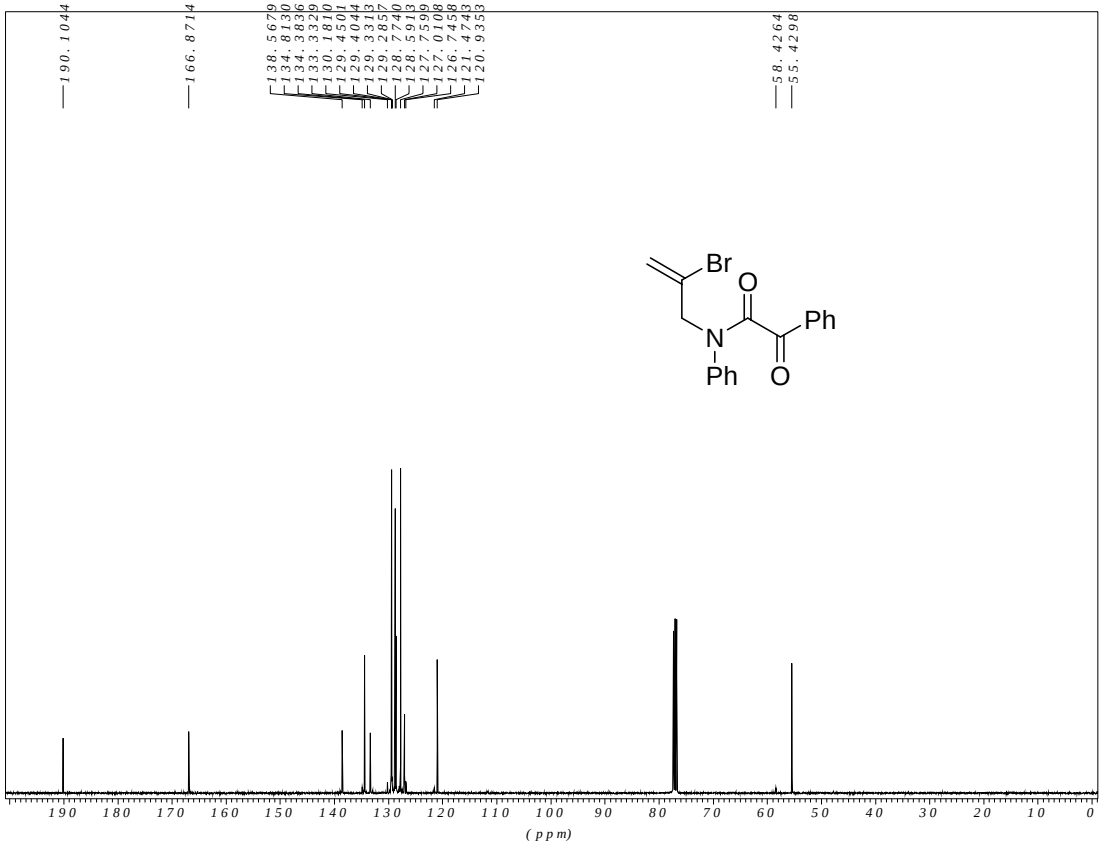

190.9723
189.8120
166.3324
143.7024
143.1176
140.1667
140.0571
134.9043
134.3105
132.8761
130.3726
130.2084
130.0988
129.9252
129.8430
129.2491
128.9659
128.8289
128.4908
98.6981
97.2364
38.0438
35.7324
I
O
N
Ph
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

N-(2-bromoallyl)-2-oxo-*N*,2-diphenylacetamide (**1o**):



White solid. 65% yield, m.p. 84.5-85.5°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.81 (s, 2H), 5.59 (d, 1H, *J* = 2.3 Hz), 5.77 (t, 1H, *J* =1.0 Hz), 7.16-7.19 (m, 2H), 7.21-7.25 (m, 3H), 7.46 (t, 2H, *J* = 8.1 Hz), 7.57-7.62 (m, 1H), 7.93 (dd, 2H, *J* = 1.0, 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 58.4, 120.9, 121.4, 126.7, 127.0, 127.7, 128.5, 128.7, 129.2, 129.3, 129.40, 129.45, 130.1, 133.3, 134.3, 134.8, 138.5, 166.8, 190.1. ν_{max}/cm^{-1}: 1679, 1650, 1594, 1493, 1450, 1394, 1236, 1213. HRMS: *m/z* (ESI+) calculated for $C_{17}H_{15}BrNO_2$ ($[M+H]^+$): 344.0280, found: 344.0286.

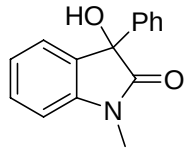

8.1117
8.0940
8.0909
7.9419
7.9394
7.9210
7.9179
7.6218
7.6186
7.6155
7.5997
7.5845
7.5814
7.5782
7.4635
7.4633
7.4488
7.4450
7.2600
7.2455
7.2366
7.2291
7.2190
7.1912
7.1842
7.1811
7.1767
7.1741
7.1703
7.1666
5.7744
5.7719
5.7693
5.5976
5.5919
4.8109
Br
O
Ph
N
Ph
O
Integral
0.0966
1.9000
0.0610
0.9801
0.1102
2.1691
2.8874
1.9495
1.0000
0.0522
0.9802
0.0502
1.9734
0.0932
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


190.1044
166.8714
138.5679
134.8130
134.3836
133.3329
130.1810
129.4501
129.4044
129.3313
129.2857
128.7740
128.5913
127.5599
127.1108
126.4458
121.4243
120.9353
58.4264
55.4298
Br
O
Ph
N
Ph
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

2. Palladium-catalysed intramolecular addition of arylbromides to α-ketoamides:

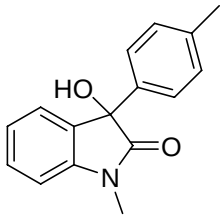
A dry Schlenk tube was charged with $Pd(dba)_2$ (11.6 mg, 0.02 mmol), P*t*Bu_3·HBF_4 (11.5 mg, 0.04 mmol) and K_3PO_4·H_2O (185 mg, 0.8 mmol) under N_2. Toluene (4 mL) was added and the mixture was stirred at 80 ^oC for 1.0 h before addition of a solution of the ketoamide (0.4 mmol) in 4 mL toluene and *n*BuOH (59 mg, 0.8 mmol). The reaction mixture was stirred at 80 ^oC for the indicated time. Flash chromatography afforded the product oxindoles.

3-Hydroxy-1-methyl-3-phenyloxindole (**2a**):[3]



^1H NMR (400 MHz, $CDCl_3$): δ 3.14 (s, 1H), 3.26 (s, 3H), 6.91 (d, 1H, *J* = 7.6 Hz), 7.09 (t, 1H, *J* = 7.6 Hz), 7.28-7.40 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.3, 77.9, 108.5, 123.4, 124.8, 125.3, 128.0, 128.3, 129.6, 131.7, 140.0, 143.2, 177.6.

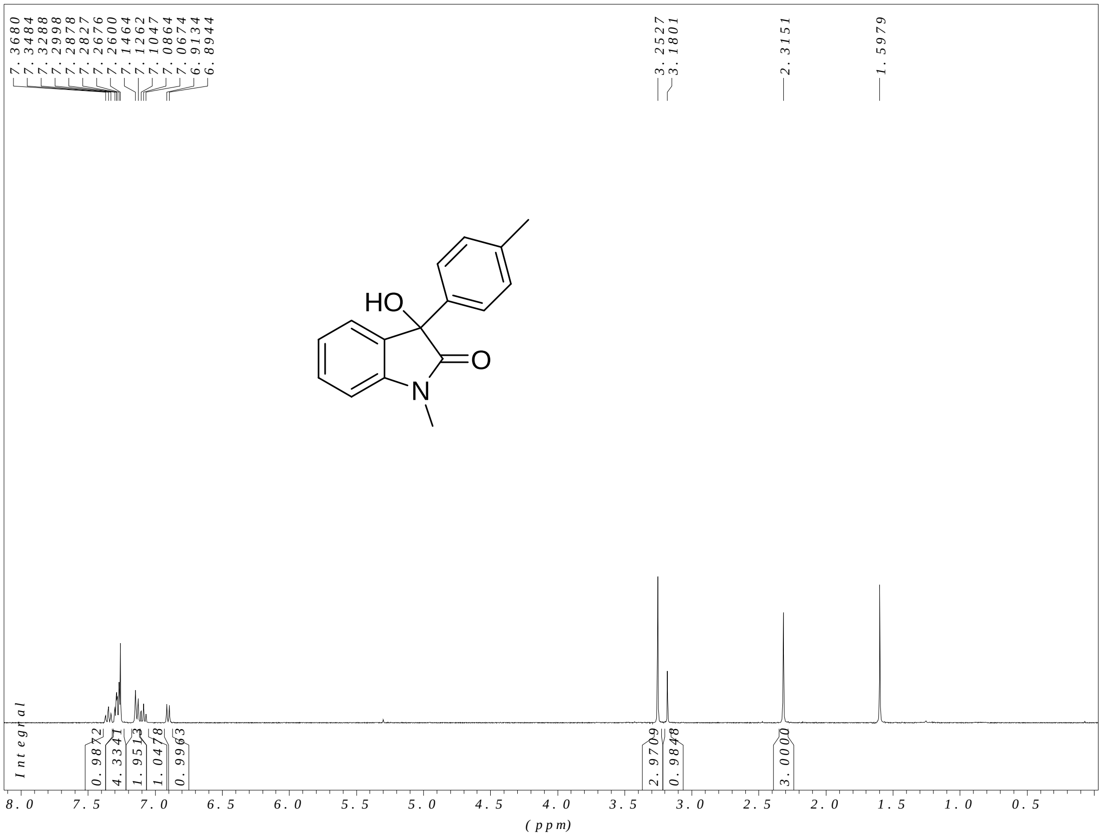
3-Hydroxy-1-methyl-3-p-tolyloxindole (**2b**):

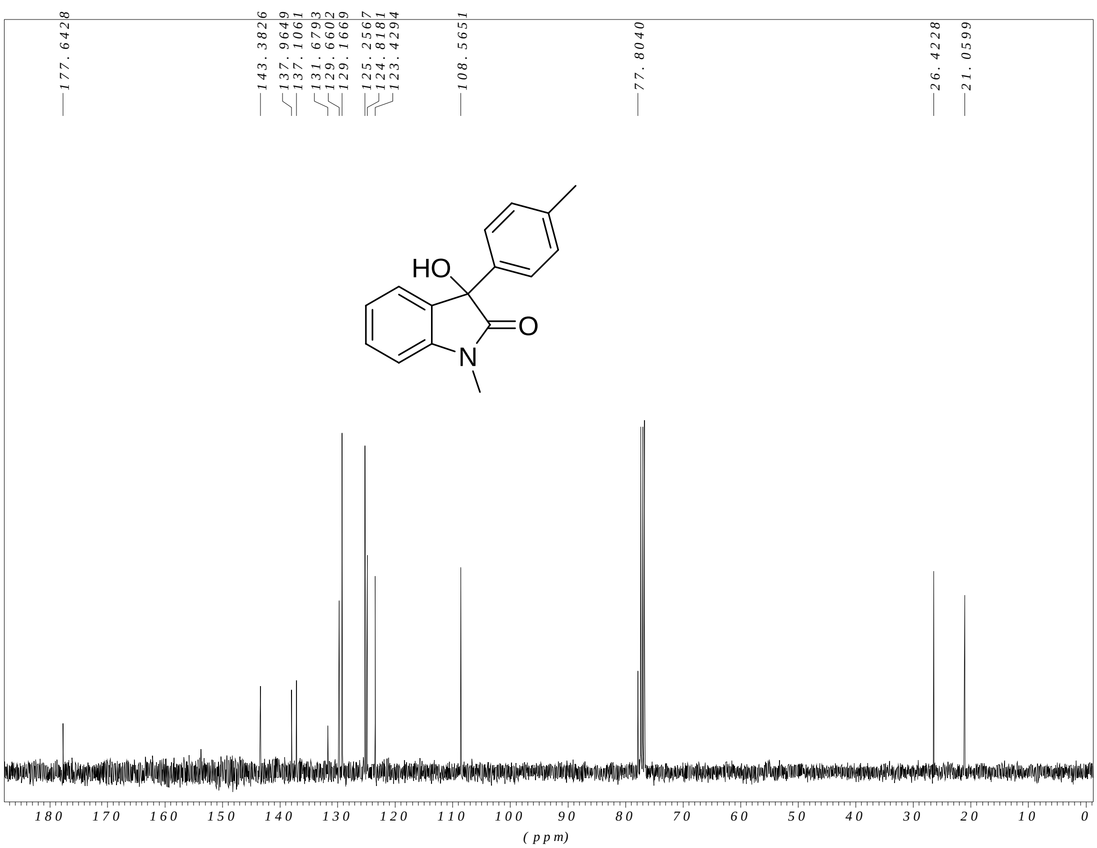


White solid. m.p. 191.4-192.9 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 3.18 (s, 1H), 3.25 (s, 3H), 6.90 (d, 1H, *J* = 7.6 Hz), 7.08 (t, 1H, *J* = 7.3 Hz), 7.14 (d, 2H, *J* = 8.1 Hz), 7.26-7.30 (m, 3H), 7.34 (t, 1H, *J* = 7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$):

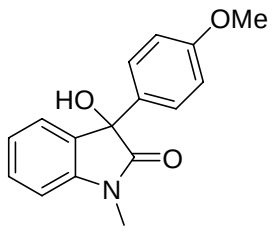
[3] S. Kafka, J. Kosmrlj and A. Klasek, *J. Org, Chem.*, 2001, **66**, 6394-6399.

δ 21.0, 26.4, 77.8, 108.5, 123.4, 124.8, 125.2, 129.1, 129.6, 131.6, 137.1, 137.9, 143.3, 177.6. ν_{max}/cm^{-1}: 3378, 1702, 1611, 1492, 1469, 1370, 1348, 1095. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{16}NO_2$ ($[M+H]^+$): 254.1175, found: 254.1184.



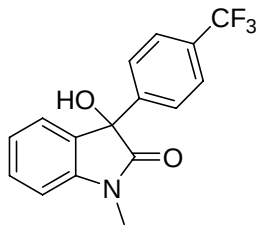


3-Hydroxy-3-(4-methoxyphenyl)-1-methyloxindole (**2c**):[4]



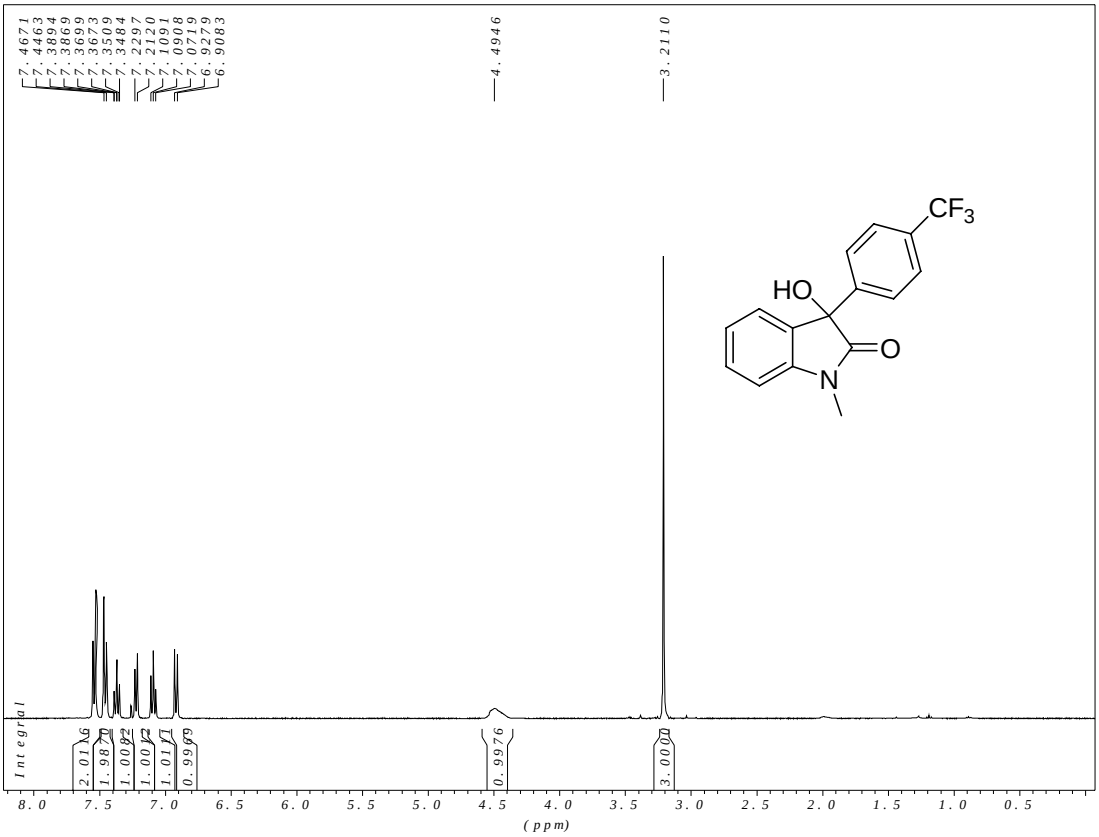
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.06 (d, 1H, *J* = 0.8 Hz), 3.24 (s, 3H), 3.77 (s, 3H), 6.86 (dt, 2H, *J* = 3.0, 8.8 Hz), 6.90 (d, 1H, *J* = 7.6 Hz), 7.10 (td, 1H, *J* = 0.8, 7.6 Hz), 7.30-7.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.3, 55.1, 77.5, 108.5, 113.7, 123.3, 124.8, 126.8, 129.5, 131.7, 132.1, 143.3, 159.3, 177.7.

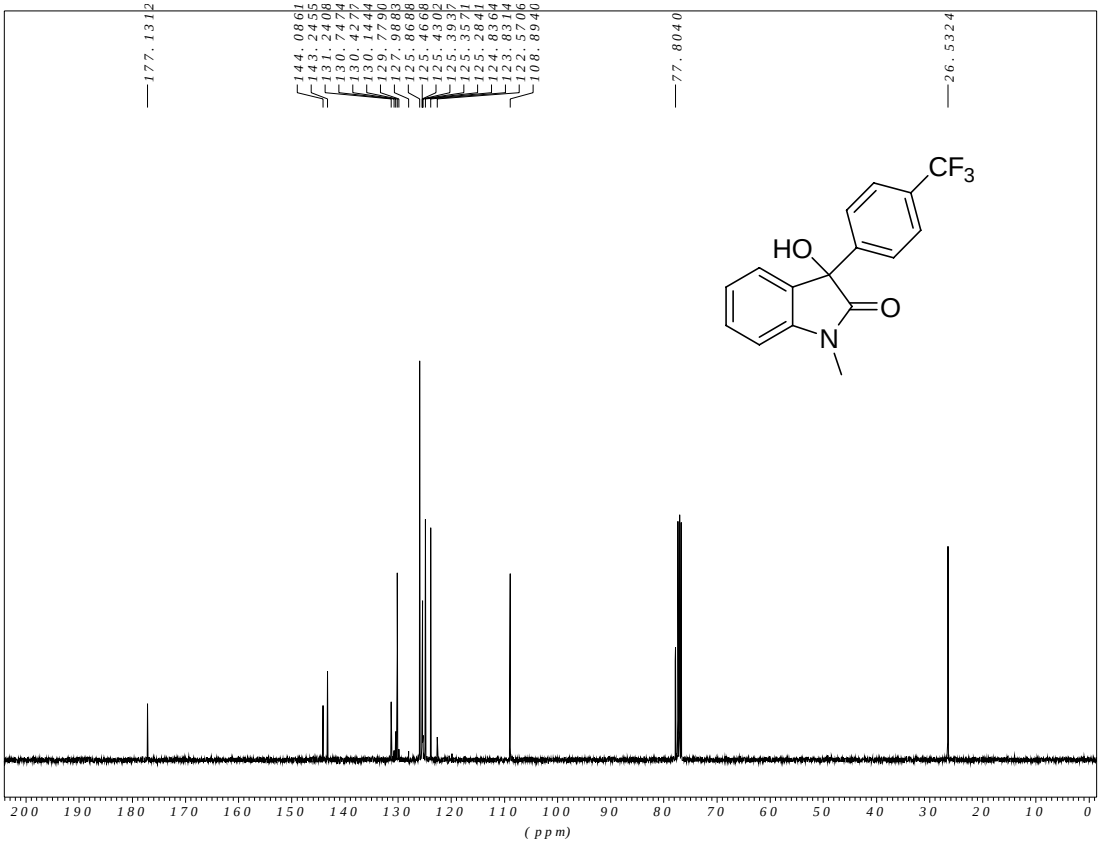
3-Hydroxy-1-methyl-3-(4-(trifluoromethyl)phenyl)oxindole (**2d**):



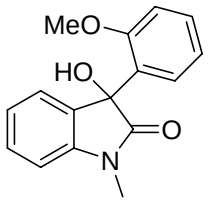
White solid. m.p. 148-149.1 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.21 (s, 3H), 4.49 (s, 1H), 6.92 (d, 1H, *J* = 7.8 Hz), 7.09 (t, 1H, *J* = 7.3 Hz), 7.22 (d, 1H, *J* = 7.1 Hz), 7.36 (td, 1H, *J* = 1.0, 7.8 Hz), 7.46 (d, 2H, *J* = 8.3 Hz), 7.53 (d, 2H, *J* = 8.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.5, 77.8, 108.8, 122.5, 123.8, 124.8, 125.2, 125.35, 125.39, 125.43, 125.46, 125.8, 127.9, 129.7, 130.1, 130.4, 130.7, 131.2, 143.2, 144.0, 177.1. ν_{max}/cm^{-1}: 3378, 1707, 1614, 1493, 1471, 1325, 1123, 1068. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{13}NO_2F_3$ ($[M+H]^+$): 308.0892, found: 308.0910.

[4] M. J. Durbin and M. C. Willis, *Org. Lett.*, 2008, **10**, 1413-1415.

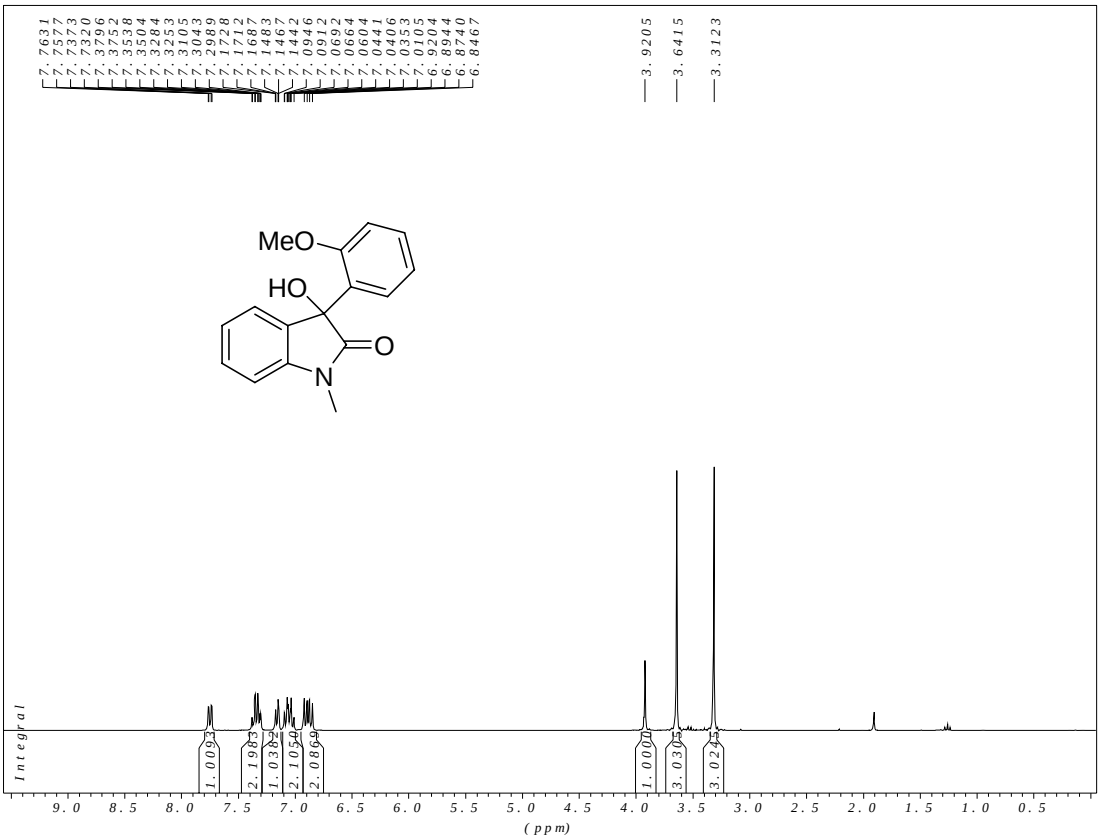

7.4671
7.4463
7.3894
7.3869
7.3699
7.3673
7.3509
7.3484
7.2297
7.2120
7.1091
7.0908
7.0719
6.9279
6.9083
4.4946
3.2110
CF3
HO
O
N
Integral
2.0116
1.9871
1.0092
1.0012
1.0117
0.9999
0.9976
3.0000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

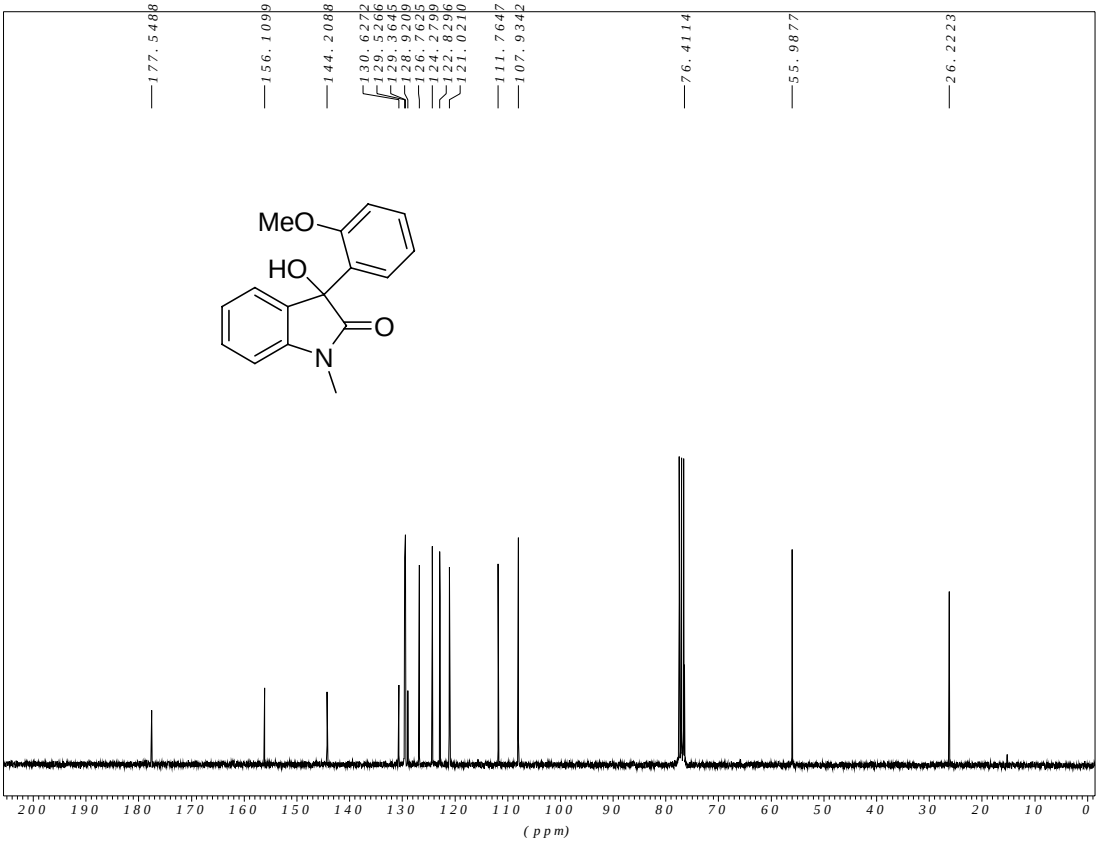

177.1312
144.0861
143.2455
131.2408
130.7474
130.4277
130.1444
129.7790
127.9883
125.8688
125.4668
125.4302
125.3937
125.3571
125.2841
124.8364
123.8314
122.5706
108.8940
77.8040
26.5324
CF3
HO
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

3-Hydroxy-3-(2-methoxyphenyl)-1-methyloxindole (**2e**):

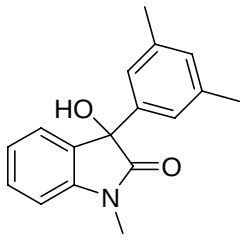


White solid. m.p. 210.5-211.5^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.31 (s, 3H), 3.64 (s, 3H), 3.92 (s, 1H), 6.88 (dd, 2H, *J* = 7.8, 13.9 Hz), 7.01-7.10 (m, 2H), 7.16 (dt, 1H, *J* = 0.5, 7.4 Hz), 7.29-7.38 (m, 2H), 7.75 (dd, 1H, *J* = 1.6, 7.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 55.9, 76.4, 107.9, 111.7, 121.0, 122.8, 124.2, 126.7, 128.9, 129.3, 129.5, 130.6, 144.2, 156.1, 177.5. ν_{max}/cm^{-1}: 3342, 1701, 1614, 1490, 1469, 1374, 1357, 1251, 1091. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{16}NO_3$ ($[M+H]^+$): 254.1124, found: 254.1128.

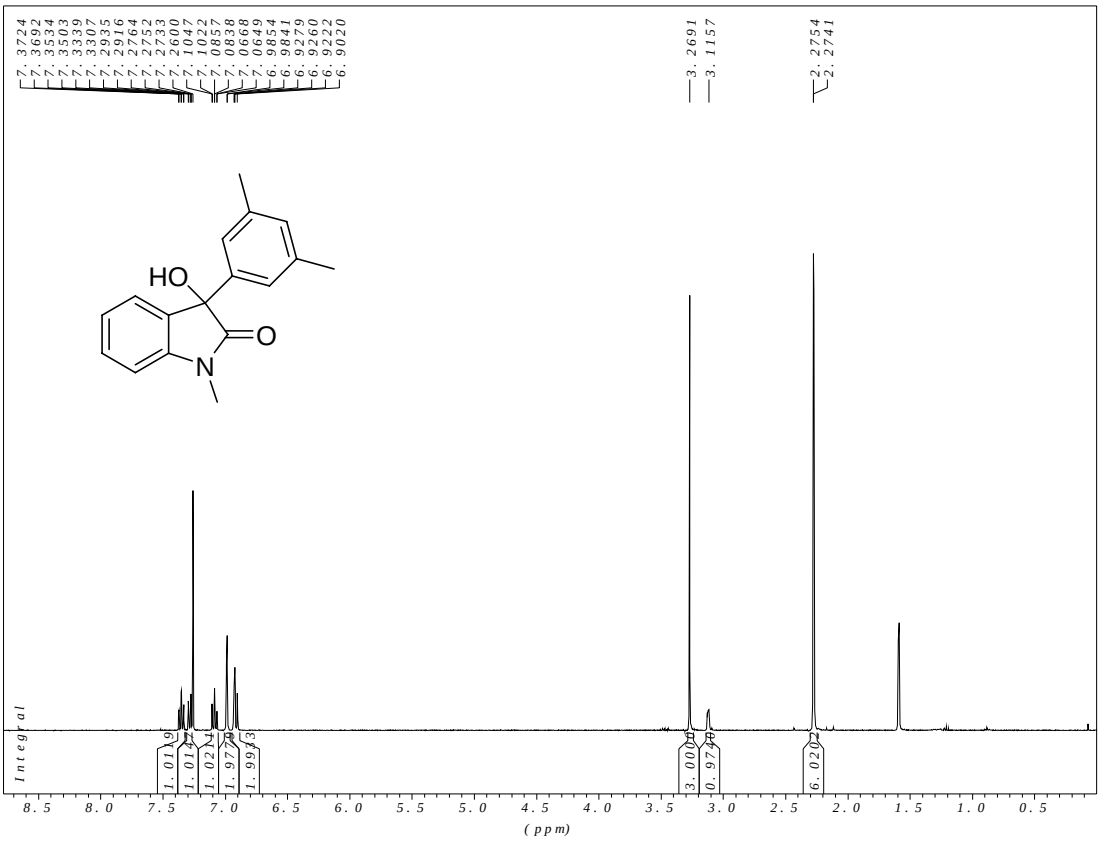

7.7631
7.7373
7.7320
7.3796
7.3752
7.3538
7.3504
7.3384
7.3253
7.3105
7.3043
7.2989
7.1728
7.1712
7.1687
7.1483
7.1467
7.1442
7.0946
7.0912
7.0692
7.0664
7.0604
7.0441
7.0406
7.0353
7.0105
6.9204
6.8944
6.8740
6.8467
3.9205
3.6415
3.3123
MeO
HO
O
N
Integral
1.0093
2.1983
1.0302
2.1054
2.0869
1.0000
3.0315
3.0215
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

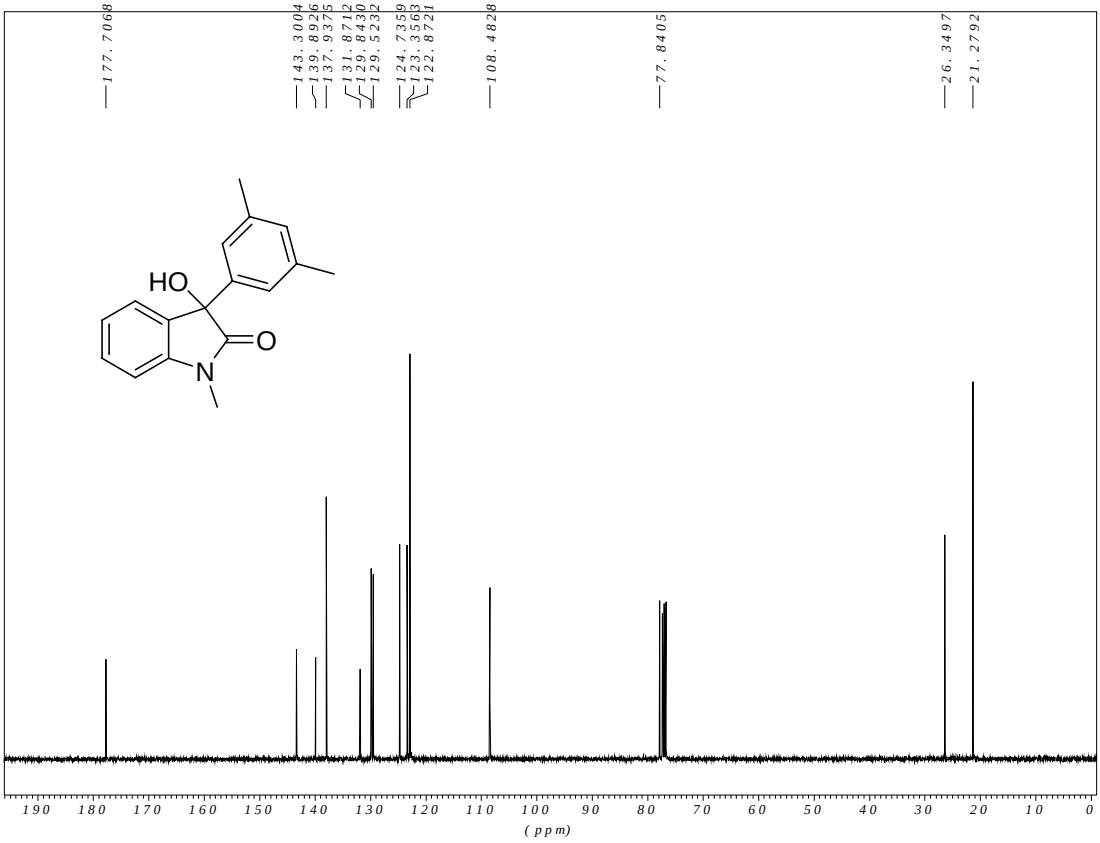

177.5488
156.1099
144.2088
130.6272
129.5266
129.3645
128.9209
126.7625
124.2799
122.8296
121.0210
111.7647
107.9342
76.4114
55.9877
26.2223
MeO
HO
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

3-(3,5-Dimethylphenyl)-3-hydroxy-1-methyloxindole (**2f**):

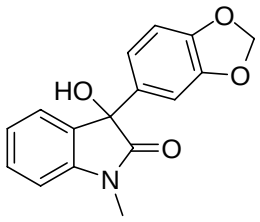


White solid. m.p. 135-136.5°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (d, 6H, *J* = 0.5 Hz), 3.11 (s, 1H), 3.26 (s, 3H), 6.90 (s, 1H), 6.92 (t, 1H, *J* = 0.8 Hz), 6.98 (s, 2H), 7.08 (td, 1H, *J* = 1.0, 7.6 Hz), 7.28 (dd, 1H, *J* = 0.8, 7.3 Hz), 7.35 (td, 1H, *J* = 1.3, 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 26.3, 77.8, 108.4, 122.8, 123.3, 124.7, 129.5, 129.8, 131.8, 137.9, 139.8, 143.3, 177.7. ν_{max}/cm^{-1}: 3388, 2918, 1706, 1613, 1493, 1470, 1372, 1350, 1101. HRMS: *m/z* (ESI+) calculated for $C_{17}H_{18}NO_2$ ($[M+H]^+$): 268.1332, found: 268.1352.

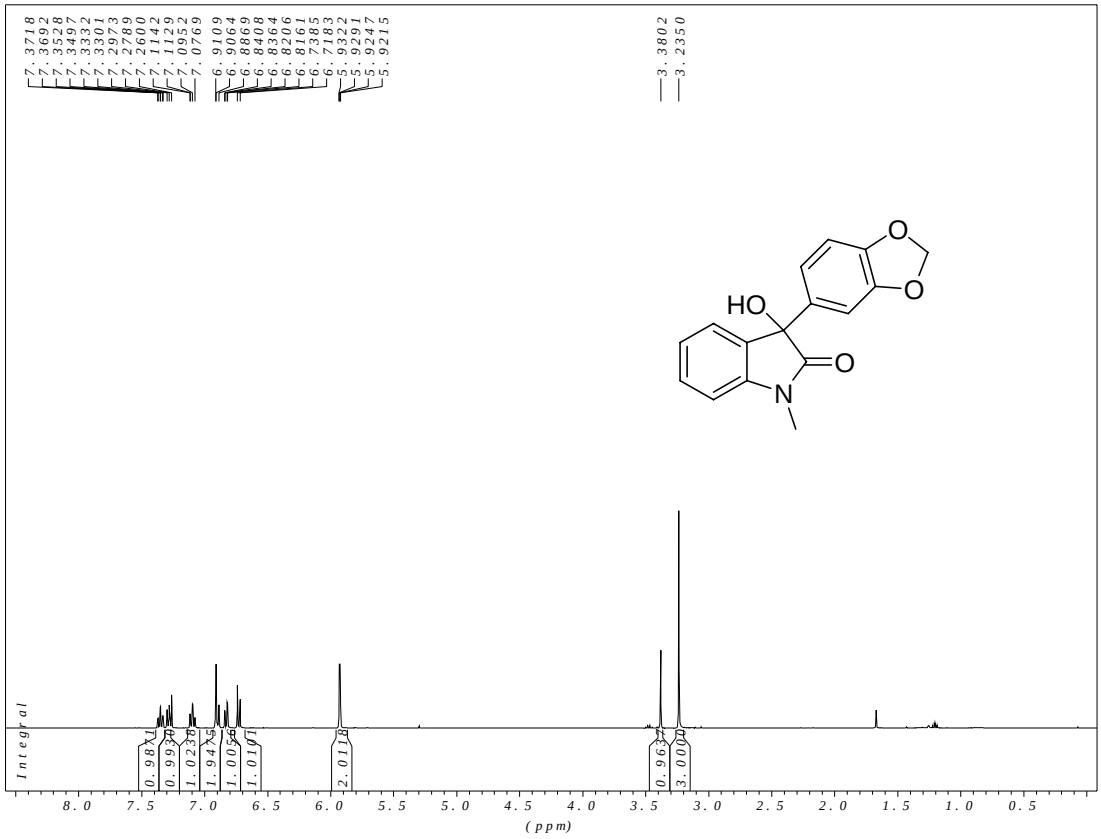

7.3724
7.3692
7.3534
7.3503
7.3339
7.3307
7.2935
7.2916
7.2764
7.2752
7.2733
7.2600
7.1047
7.1022
7.0857
7.0838
7.0668
7.0649
6.9854
6.9841
6.9279
6.9260
6.9222
6.9020
3.2691
3.1157
2.2754
2.2741
HO
O
N
Integral
1.0119
1.0142
1.0271
1.9778
1.9943
3.0000
0.9738
6.0227
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

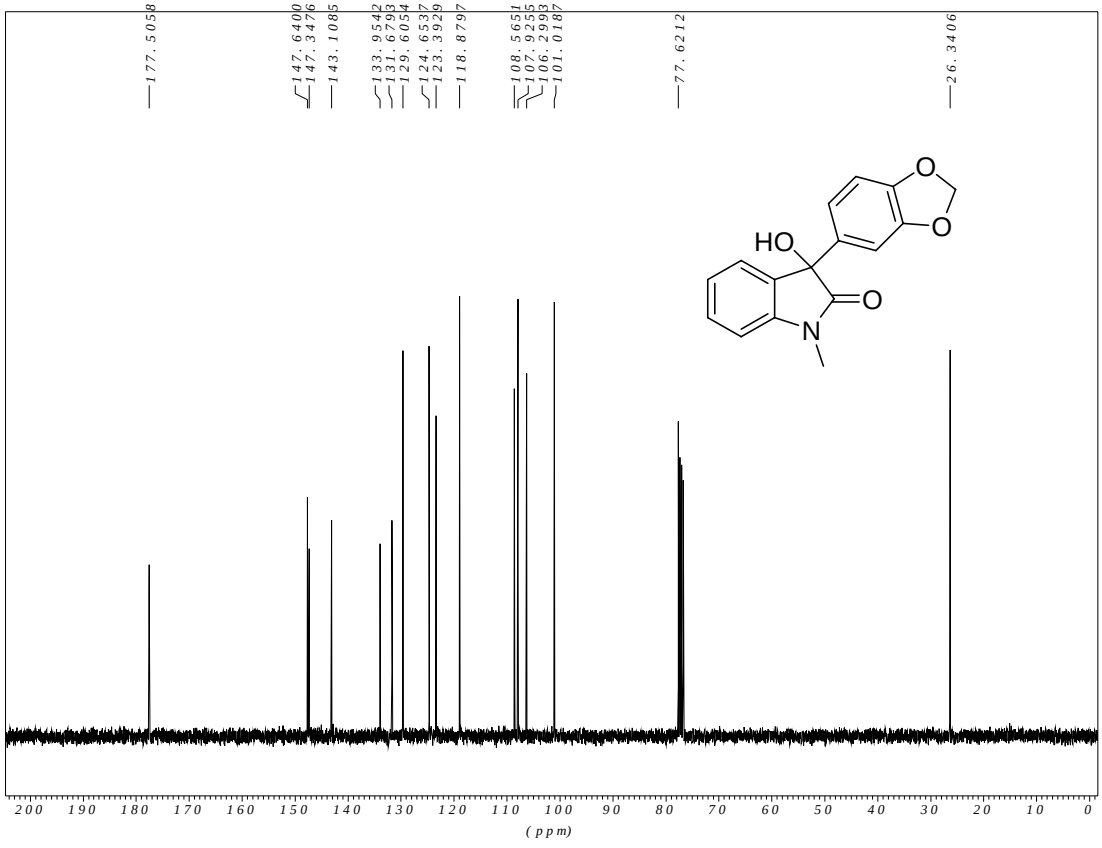

177.7068
143.3004
139.8926
137.9375
131.8712
129.8430
129.5232
124.7359
123.3563
122.8721
108.4828
77.8405
26.3497
21.2792
HO
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

3-(Benzo[*d*][1,3]dioxol-5-yl)-3-hydroxy-1-methyloxindole (**2g**):

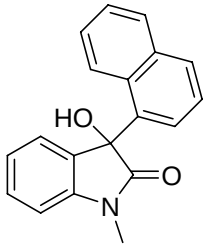


White solid. m.p. 149 -143.5°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (s, 3H), 3.38 (s, 1H), 5.92 (dd, 2H, *J* = 1.2, 3.0 Hz), 6.73 (d, 1H, *J* = 8.1 Hz), 6.83 (dd, 1H, *J* = 1.8, 6.8 Hz), 6.88 (s, 1H), 6.91 (d, 1H, *J* = 1.8 Hz), 7.09 (t, 1H, *J* = 7.3 Hz), 7.29 (d, 1H, *J* = 8.1 Hz), 7.35 (td, 1H, *J* = 1.0, 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.3, 77.6, 101.0, 106.2, 107.9, 108.5, 118.8, 123.3, 124.6, 129.6, 131.6, 133.9, 143.1, 147.3, 147.6, 177.5. ν_{max}/cm^{-1}: 3381, 2892, 1702, 1611, 1502, 1487, 1470, 1373, 1347, 1243, 1093, 1035. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{14}NO_4$ ($[M+H]^+$): 284.0917, found: 284.0930.

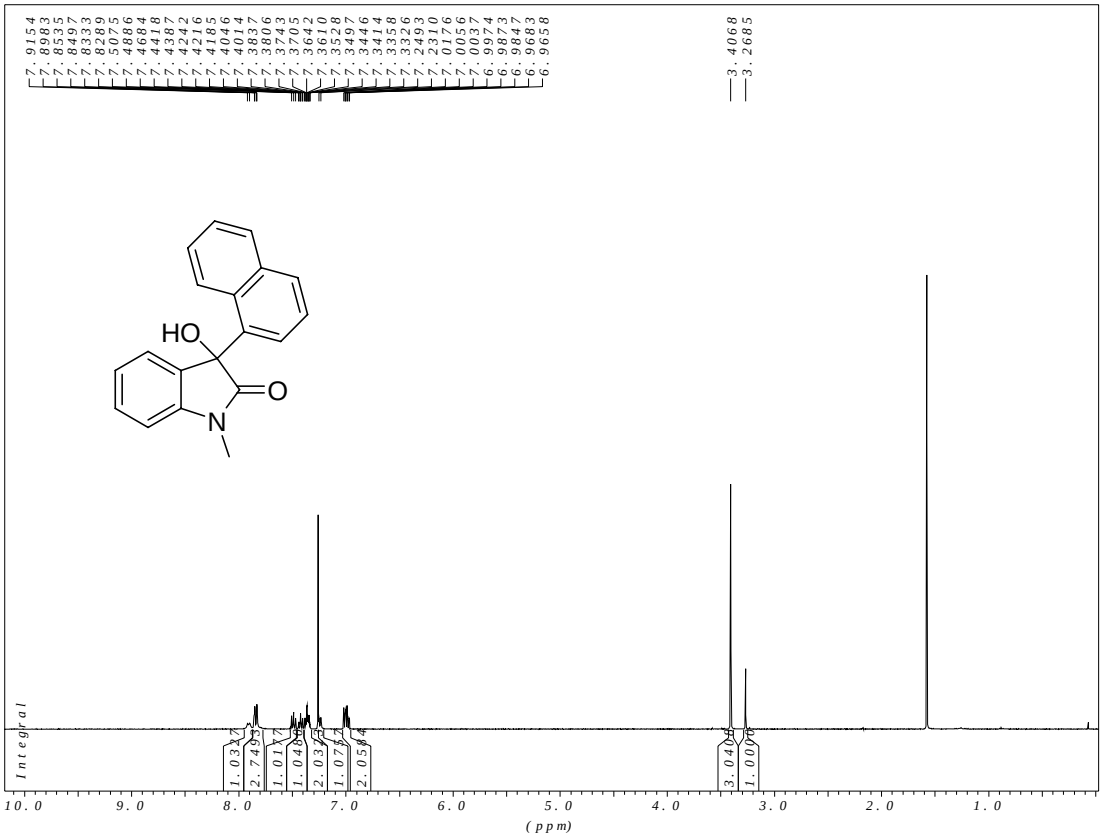

7.3718
7.3692
7.3528
7.3497
7.3332
7.3301
7.2973
7.2789
7.2600
7.1142
7.1129
7.0952
7.0769
6.9109
6.9064
6.8869
6.8408
6.8364
6.8206
6.8161
6.7385
6.7183
5.9322
5.9291
5.9247
5.9215
3.3802
3.2350
HO
O
O
O
N
Integral
0.9814
0.9930
1.0238
1.9475
1.0056
1.0107
2.0118
0.9627
3.0000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

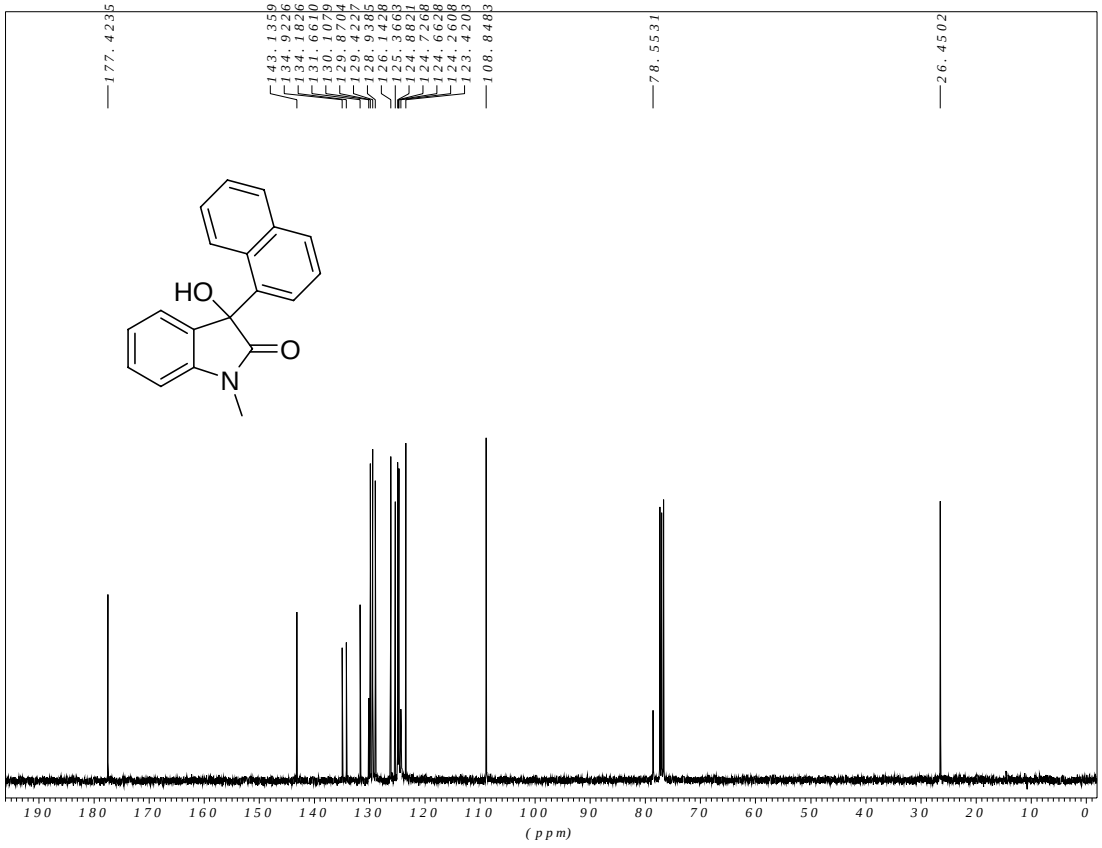

177.5058
147.6400
147.3476
143.1085
133.9542
131.6793
129.6054
124.6537
123.3929
118.8797
108.5651
107.9255
106.2993
101.0187
77.6212
26.3406
HO
O
O
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

3-Hydroxy-1-methyl-3-(naphthalen-1-yl)oxindole (**2h**):

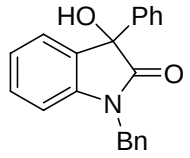


White solid. m.p. 157.5-158.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (s, 1H), 3.40 (s, 3H), 6.96-7.01 (m, 2H), 7.24 (d, 1H, *J* = 7.3 Hz), 7.33-7.38 (m, 2H), 7.40-7.44 (m, 1H), 7.48 (t, 1H, *J* = 7.6 Hz), 7.84 (dd, 3H, *J* = 1.5, 8.0 Hz), 7.91 (d, 1H, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.4, 78.5, 108.8, 123.4, 124.2, 124.6, 124.7, 124.8, 125.3, 126.1, 128.9, 129.4, 130.1, 131.6, 134.1, 134.9, 143.1, 177.4. ν_{max}/cm^{-1}: 3354, 3052, 1700, 1611, 1491, 1469, 1369, 1341, 1085. HRMS: *m/z* (ESI+) calculated for $C_{19}H_{16}NO_2$ ($[M+H]^+$): 290.1175, found: 290.1178.


7.9154
7.8983
7.8535
7.8497
7.8333
7.8289
7.5075
7.4886
7.4684
7.4418
7.4387
7.4242
7.4216
7.4185
7.4046
7.4014
7.3837
7.3806
7.3743
7.3705
7.3642
7.3610
7.3528
7.3497
7.3446
7.3414
7.3358
7.3326
7.2493
7.2310
7.0176
7.0056
7.0037
6.9974
6.9873
6.9847
6.9683
6.9658
3.4068
3.2685
HO
O
N
Integral
1.0317
2.7455
1.0117
1.0400
2.0372
1.0713
2.0584
3.0400
1.0000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)

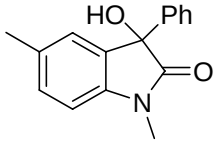

177.4235
143.1359
134.9226
134.1826
131.6610
130.1079
129.8704
129.4227
128.9385
126.1428
125.3663
124.8821
124.2268
124.6628
124.6608
123.4203
108.8483
78.5531
26.4502
HO
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

1-Benzyl-3-hydroxy-3-phenyloxindole (**2i**):

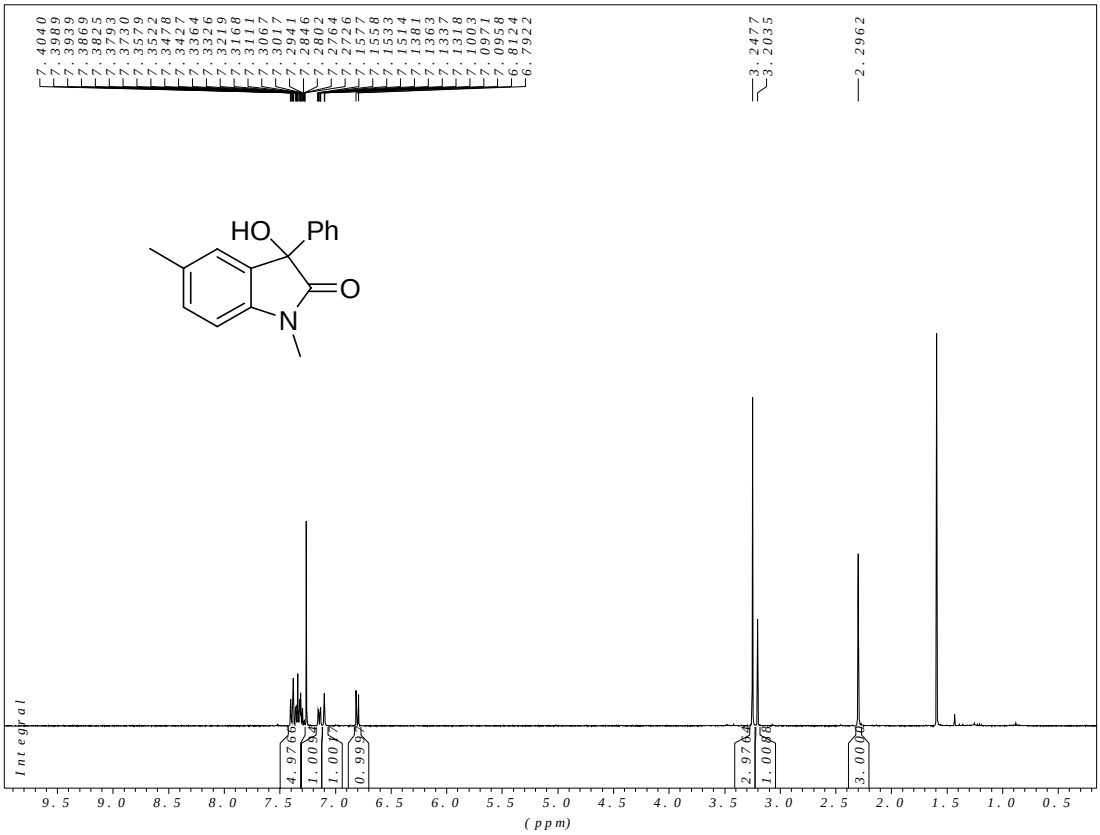


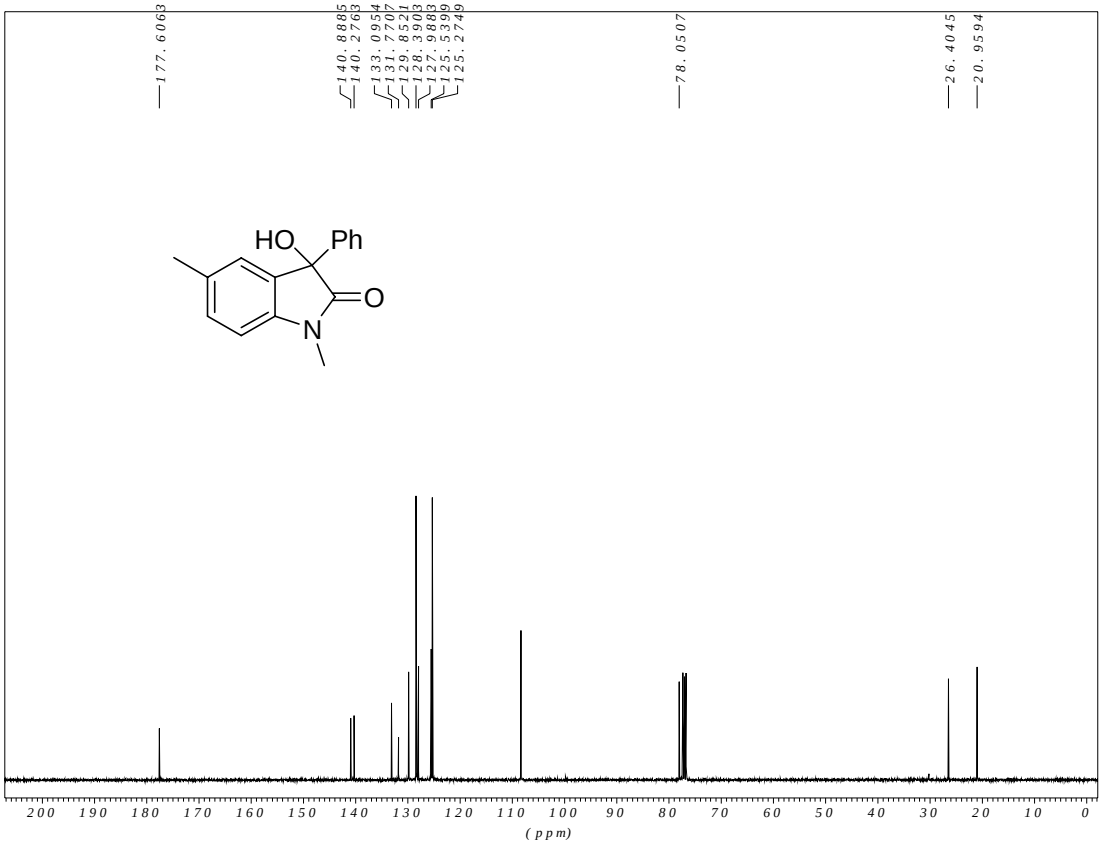
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.16 (s, 1H), 4.85 (d, 1H, *J* = 15.6 Hz), 5.06 (d, 1H, *J* = 15.8 Hz), 6.79 (d, 1H, *J* = 7.8 Hz), 7.04 (td, 1H, *J* = 0.8, 7.6 Hz), 7.23-7.38 (m, 10H), 7.40-7.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.8, 77.9, 109.6, 123.4, 124.9, 125.3, 127.1, 127.6, 128.1, 128.4, 128.7, 129.5, 131.8, 135.3, 140.1, 142.4, 177.7.

3-Hydroxy-1,5-dimethyl-3-phenyloxindole (**2j**):

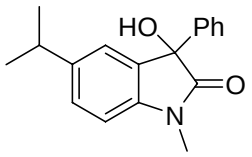


White solid. m.p. 124.4-125.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 3.20 (s, 1H), 3.24 (s, 3H), 6.80 (d, 1H, *J* = 8.1 Hz), 7.10 (dd, 1H, *J* = 0.5, 1.3 Hz), 7.14 (d, 1H, *J* = 7.8 Hz), 7.27-7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 26.4, 78.0, 125.2, 125.5, 127.9, 128.3, 129.8, 131.7, 133.0, 140.2, 140.8, 177.6. ν_{max}/cm^{-1}: 3351, 1687, 1621, 1602, 1495, 1091. HRMS: *m/z* (ESI+) calculated for $C_{16}H_{16}NO_2$ ($[M+H]^+$): 254.1175, found: 254.1186.

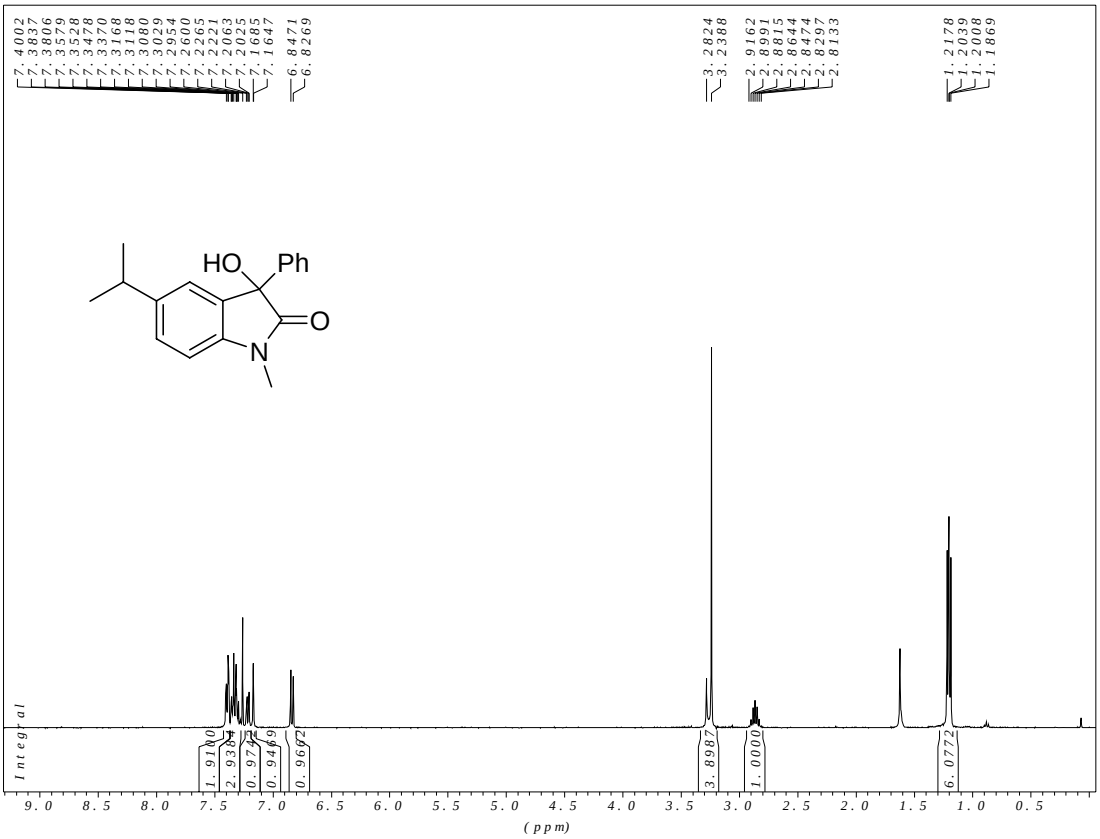

7.4040
7.3989
7.3939
7.3869
7.3825
7.3793
7.3730
7.3579
7.3522
7.3478
7.3427
7.3364
7.3326
7.3219
7.3168
7.3111
7.3067
7.3017
7.2941
7.2846
7.2802
7.2764
7.2726
7.1577
7.1558
7.1533
7.1514
7.1381
7.1363
7.1337
7.1318
7.1003
7.0971
7.0958
6.8124
6.7922
3.2477
3.2035
2.2962
HO
Ph
O
N
Integral
4.9766
1.0054
1.0077
0.9992
2.9764
1.0078
3.0000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

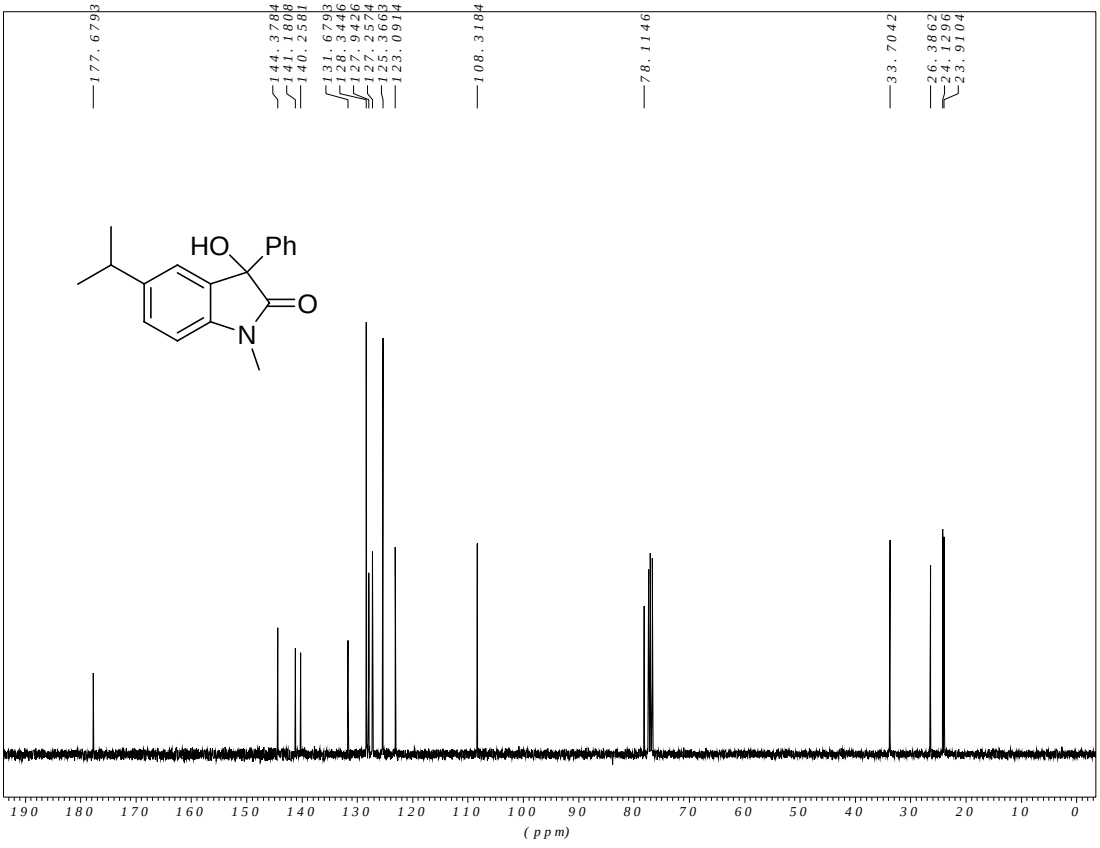

177.6063
140.8885
140.2763
133.0954
131.7707
129.8521
128.3903
127.9883
125.5399
125.2749
78.0507
26.4045
20.9594
HO
Ph
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

3-Hydroxy-5-isopropyl-1-methyl-3-phenyloxindole (**2k**):

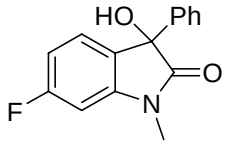


White solid. m.p. 153-155^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (d, 3H, *J* = 5.6 Hz), 1.21 (d, 3H, *J* = 5.6 Hz), 2.81-2.92 (m, 1H), 3.23 (s, 3H), 3.28 (s, 1H), 6.83 (d, 1H, *J* = 8.1 Hz), 7.16 (d, 1H, *J* = 1.5 Hz), 7.21 (dd, 1H, *J* = 1.8, 8.1 Hz), 7.29-7.36 (m, 3H), 7.39 (dd, 2H, *J* = 1.8, 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9, 24.1, 26.3, 33.7, 78.1, 108.3, 123.0, 125.3, 127.2, 127.9, 128.3, 131.6, 140.2, 141.1, 144.3, 177.6. ν_{max}/cm^{-1}: 3385, 2959, 1702, 1620, 1605, 1495, 1367, 1101. HRMS: *m/z* (ESI+) calculated for $C_{18}H_{20}NO_2$ ($[M+H]^+$): 282.1488, found: 282.1493.

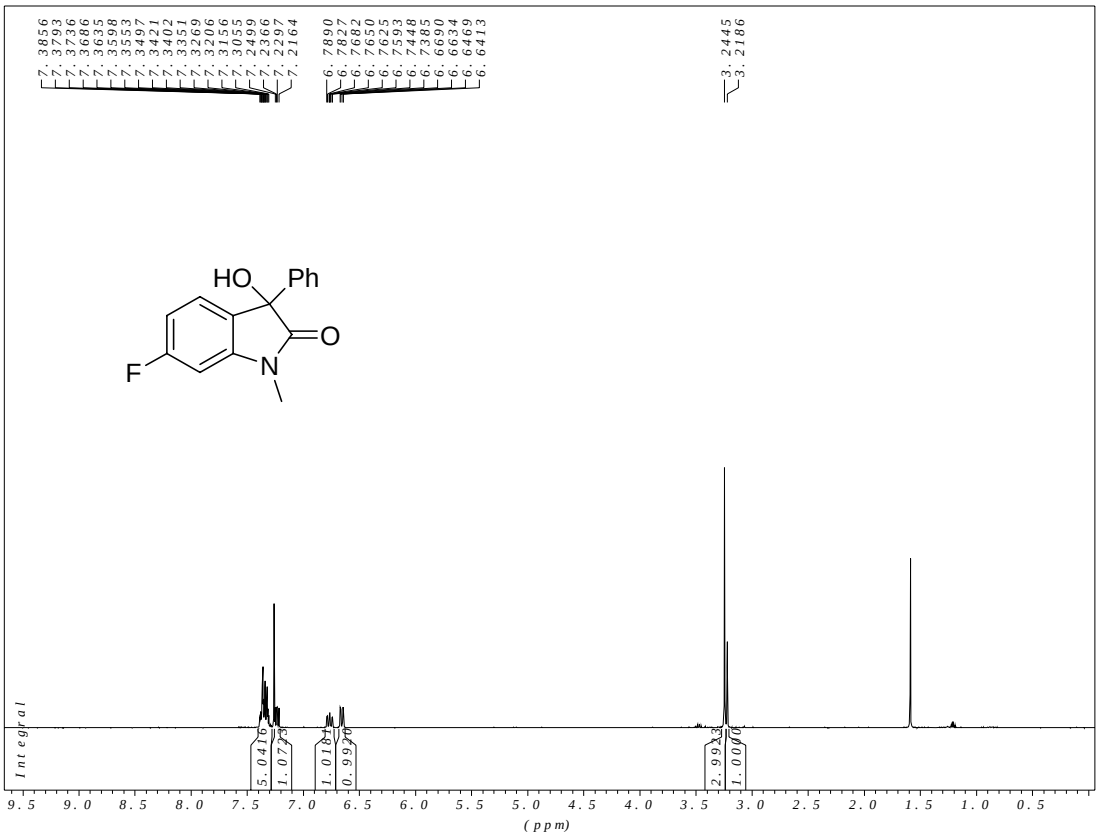

7.4002
7.3837
7.3806
7.3579
7.3528
7.3478
7.3370
7.3168
7.3118
7.3080
7.3029
7.2954
7.2600
7.2265
7.2221
7.2063
7.2025
7.1685
7.1647
6.8471
6.8269
3.2824
3.2388
2.9162
2.8991
2.8815
2.8644
2.8474
2.8297
2.8133
1.2178
1.2039
1.2008
1.1869
HO
Ph
O
N
Integral
1.9110
2.9361
0.9734
0.9469
0.9692
3.8987
1.0000
6.0772
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

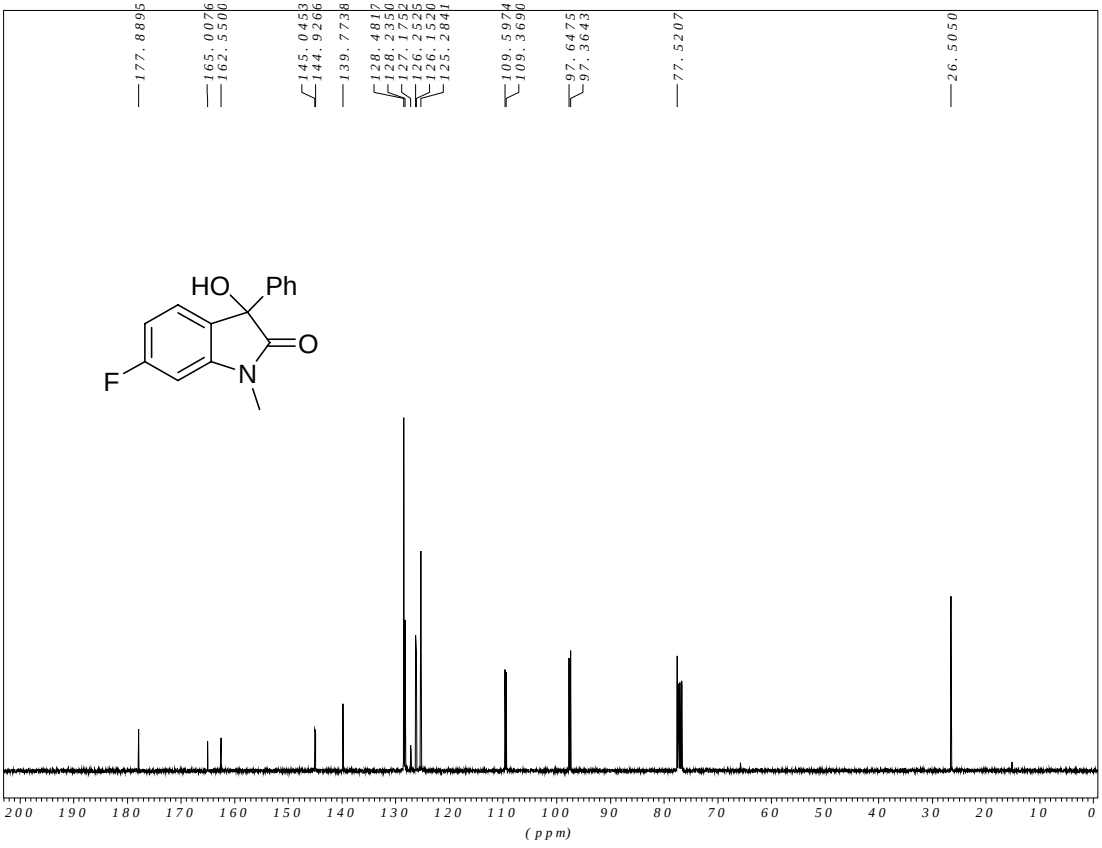

177.6793
144.3784
141.1808
140.2581
131.6793
128.3446
127.9426
127.2574
125.3663
123.0914
108.3184
78.1146
33.7042
26.3862
24.1296
23.9104
HO
Ph
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

6-Fluoro-3-hydroxy-1-methyl-3-phenyloxindole (**2l**):

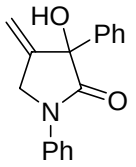


White solid. m.p. 156-157°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.21 (s, 1H), 3.24 (s, 3H), 6.65 (dd, 1H, *J* = 2.2, 6.8 Hz), 6.73-6.79 (m, 1H), 7.23 (dd, 1H, *J* = 5.3, 8.1 Hz), 7.30-7.39 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.5, 77.5, 97.3, 97.6, 109.3, 109.5, 125.2, 126.1, 126.2, 127.1, 128.2, 128.4, 139.7, 144.9, 145.0, 162.5, 165.0, 177.8. ν_{max}/cm^{-1}: 3353, 3073, 1707, 1613, 1504, 1453, 1361, 1081, 1072. HRMS: *m/z* (ESI+) calculated for $C_{15}H_{12}O_2NFNa$ ($[M+Na]^+$): 280.0744, found: 280.0739.

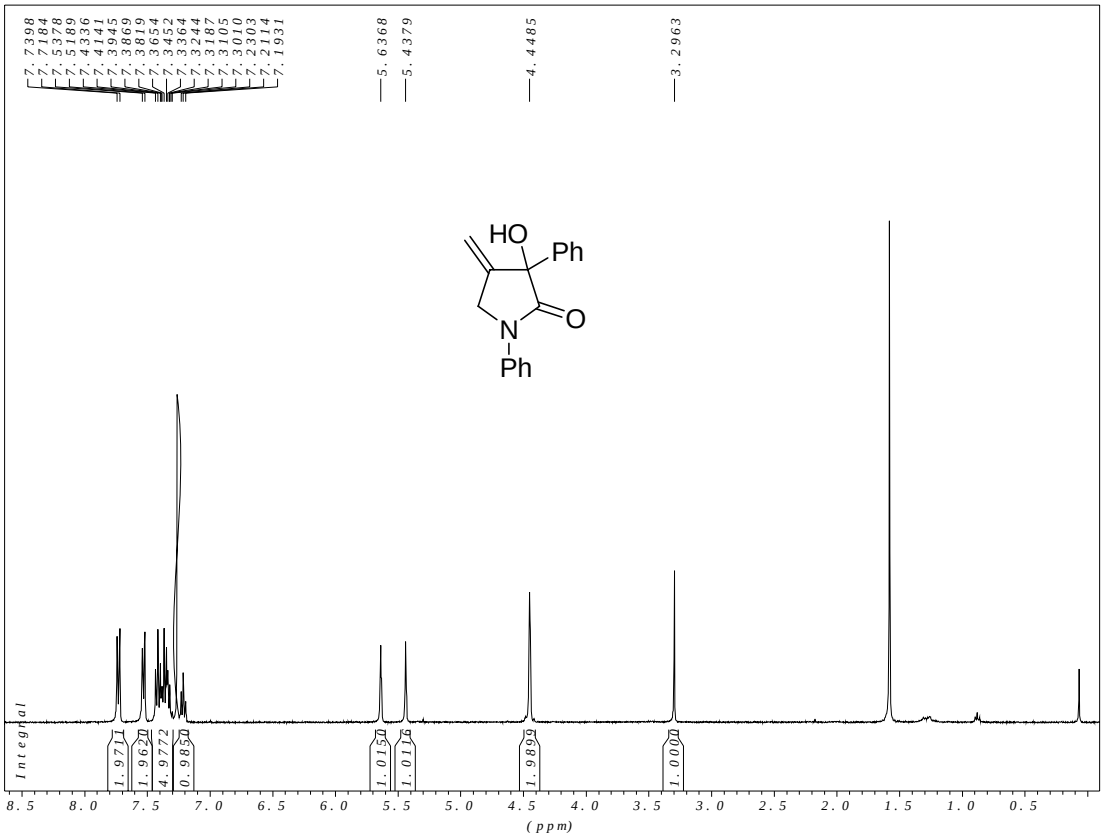

HO
Ph
O
F
N
(ppm)

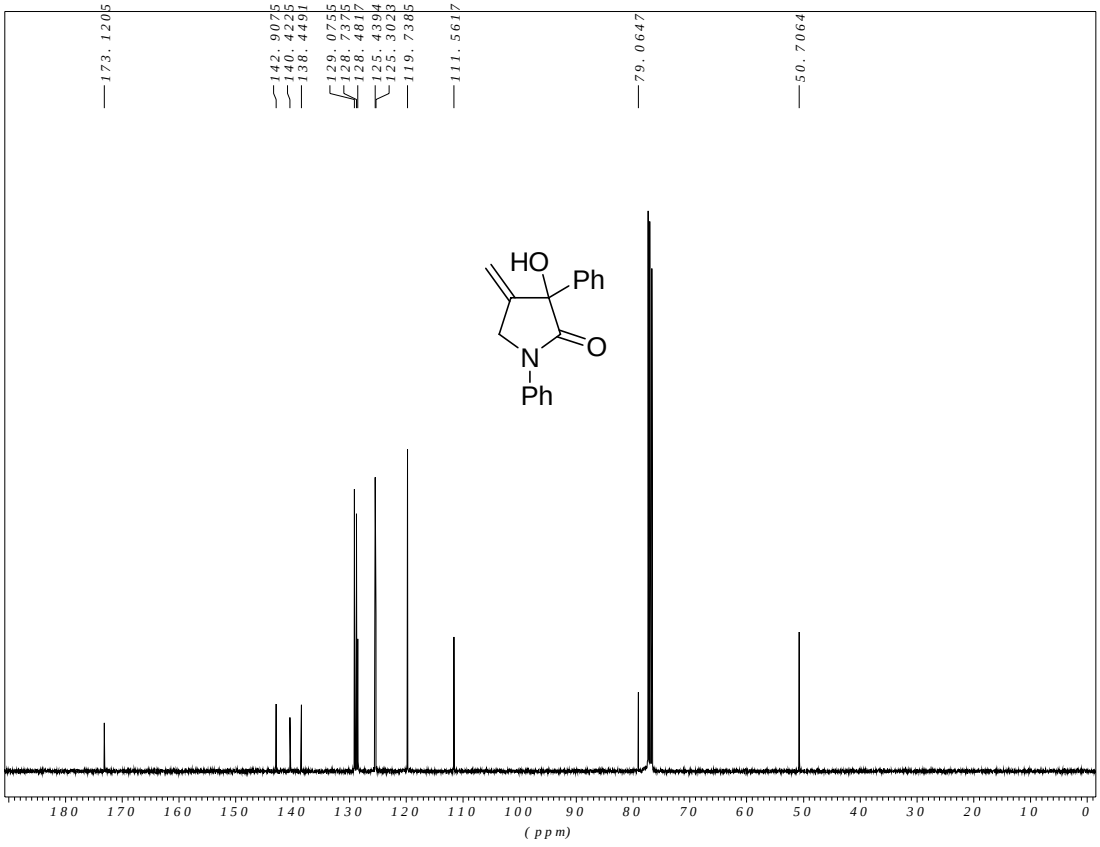

HO
Ph
O
F
N
(ppm)

3-Hydroxy-4-methylene-1,3-diphenylpyrrolidinone (**2m**):



White solid. m.p. 133-134^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.29 (s, 1H), 4.44 (s, 2H), 5.43 (s, 1H), 5.63 (s, 1H), 7.21 (t, 1H, *J* = 7.6 Hz), 7.30-7.43 (m, 5H), 7.53 (d, 2H, *J* = 7.6 Hz), 7.73 (d, 2H, *J* = 8.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.7, 79.0, 111.5, 119.7, 125.3, 125.4, 128.4, 128.7, 129.0, 138.4, 140.4, 142.9, 173.1. ν_{max}/cm^{-1}: 3385, 2924, 1695, 1671, 1597, 1493, 1392, 1275. HRMS: *m/z* (ESI+) calculated for $C_{17}H_{16}NO_2$ ($[M+H]^+$): 266.1175, found: 266.1179.


7.7398
7.7184
7.5378
7.5189
7.4336
7.4141
7.3945
7.3869
7.3819
7.3654
7.3452
7.3364
7.3244
7.3187
7.3105
7.3010
7.2303
7.2114
7.1931
5.6368
5.4379
4.4485
3.2963
HO
Ph
O
N
Ph
Integral
1.9711
1.9621
4.9772
0.9850
1.0150
1.0115
1.9899
1.0000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


173.1205
142.9075
140.4225
138.4491
129.0755
128.7375
128.4817
125.4394
125.3023
119.7385
111.5617
79.0647
50.7064
HO
Ph
O
N
Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)