Ruthenium-Catalyzed Direct C3 Alkylation of Indoles with *α,β*-Unsaturated Ketones

Shuai-Shuai Li,[a,b,c] Hui Lin,[c] Xiao-Mei Zhang,[a] and Lin Dong*[c]

[a] S.-S. Li, Prof. Dr. X.-M. Zhang
Key Laboratory for Asymmetric Synthesis and Chiraltechnology of Sichuan Province,
Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China

[b] S.-S. Li
Graduate School of the Chinese Academy of Sciences,
Beijing 100049, China

[c] S.-S. Li, H. Lin, Prof. Dr. L. Dong
Key Laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry, West China School of Pharmacy,
Sichuan University, Chengdu 610041, China
E-mail: dongl@scu.edu.cn

Supporting Information

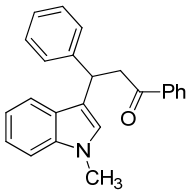
Table of Contents

1. General Methods

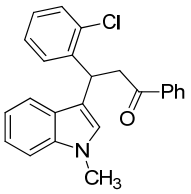
NMR data were obtained for ^{1}H at 300 MHz or 400 MHz, and for ^{13}C at 75 MHz or 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ or DMSO-d_6 solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether. CH_2Cl_2, $CHCl_2CHCl_2$ were distilled over CaH_2. All indoles were commercially available and *N*-methyl indoles were prepared according to the literature procedures.[1] All *α,β*-unsaturated ketones were prepared according to the literature procedures.[2]

2. **General Procedure for Synthesis of 3-alkyl indole derivatives and Characterization Data**

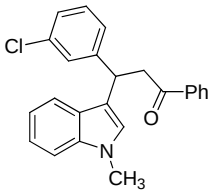
N-CH_3 indole **1a** (6.6 mg, 0.05 mmol), chalcone **2a** (12.1 mg, 0.058 mmol), $RuCl_2(PPh_3)_3$ (1.4 mg, 3 mol %) and $AgSbF_6$ (3.44 mg, 20 mol %) were stirred in DCM (1.0 mL) at room temperature for 4 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:50) to give the product **3aa** as a white solid (16.3 mg, 96%).



3-(1-methyl-1*H*-indol-3-yl)-1,3-diphenylpropan-1-one (**3aa**). 4 h, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.58-7.54 (m, 1H), 7.49-7.43 (m, 3H), 7.40-7.39 (m, 2H), 7.31-7.27 (m, 3H), 7.23-7.17 (m, 2H), 7.06-7.03 (m, 1H), 6.87 (s, 1H), 5.10 (t, J = 7.2 Hz, 1H), 3.81 (ddd, J = 6.4, 20.4, 24.4 Hz, 2H), 3.73 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 144.4, 137.3, 137.1, 132.9, 128.5, 128.4, 128.0, 127.8, 126.9, 126.2, 121.6, 119.5, 118.8, 117.7, 109.2, 45.3, 38.0, 32.6 ppm. ESI HRMS: calcd. for $C_{24}H_{21}NO$+Na 362.1521, found 362.1515.

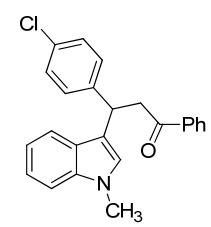


3-(2-Chloro-phenyl)-3-(1-methyl-1*H*-indol-3-yl)-1-phenyl-propan-1-one (**3ab**). 8 h, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.55-7.52 (m, 1H), 7.44-7.41 (m, 3H), 7.39-7.37 (m, 1H), 7.25-7.23 (m, 2H), 7.18-7.15 (m, 1H), 7.11-7.09 (m, 2H), 7.02-6.98 (m, 1H), 6.85 (s, 1H), 5.53 (t, *J* = 7.2 Hz, 1H), 3.73 (ddd, *J* = 8.4, 20.8, 44.4 Hz, 2H), 3.70 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 141.7, 137.2, 136.8, 133.5, 133.0, 129.7, 128.9, 128.6, 128.1, 127.5, 127.0, 126.9, 126.6, 121.7, 119.5, 118.9, 116.1, 109.2, 44.3, 34.7, 32.7 ppm. ESI HRMS: calcd. for $C_{24}H_{20}ClNO$+Na 396.1131 found $C_{24}H_{20}{}^{35}ClNNaO$ 396.1133, $C_{24}H_{20}{}^{37}ClNNaO$ 398.1105.

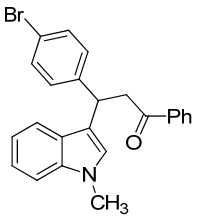


3-[1-(3-Chloro-phenyl)-3-phenyl-but-3-enyl]-1-methyl-1*H*-indole (**3ac**). 10 h, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.58-7.54 (m, 1H), 7.47-7.44 (m, 3H), 7.36 (s, 1H), 7.29-7.25 (m, 2H), 7.24-7.14 (m, 3H), 7.07-7.04 (m, 1H), 6.87 (s, 1H),

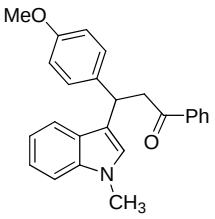
5.07 (t, J = 7.2 Hz, 1H), 3.78 (ddd, J = 6.8 , 20, 33.6 Hz, 2H), 3.73 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 146.6, 137.3, 136.9, 134.1, 133.1, 129.6, 128.6, 128.0, 127.9, 126.7, 126.4, 126.1, 121.8, 119.3, 118.9, 117.0, 109.2, 44.9, 37.7, 32.7 ppm. ESI HRMS: calcd. for $C_{24}H_{20}ClNO$+Na 396.1131 found $C_{24}H_{20}{}^{35}ClNNaO$ 396.1142, $C_{24}H_{20}{}^{37}ClNNaO$ 398.1096.



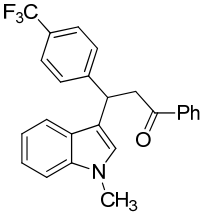
3-(4-Chloro-phenyl)-3-(1-methyl-1*H*-indol-3-yl)-1-phenyl-propan-1-one (**3ad**). 8 h, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.2 Hz, 2H), 7.56-7.52 (m, 1H), 7.45-7.39 (m, 3H), 7.29-7.24 (m, 3H), 7.21-7.17 (m, 3H), 7.04-7.00 (m, 1H), 6.82 (s, 1H), 5.03 (t, J = 7.2 Hz, 1H), 3.74 (ddd, J = 6.4, 20, 29.6 Hz, 2H), 3.73 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 142.9, 137.3, 136.9, 133.1, 131.8, 129.1, 128.6, 128.5, 128.0, 126.7, 126.1, 121.8, 119.1, 119.0, 117.3, 109.3, 45.0, 37.4, 32.7 ppm. ESI HRMS: calcd. for $C_{24}H_{20}ClNO$+Na 396.1131 found $C_{24}H_{20}{}^{35}ClNNaO$ 396.1140, $C_{24}H_{20}{}^{37}ClNNaO$ 398.1090.



3-(4-Bromo-phenyl)-3-(1-methyl-1*H*-indol-3-yl)-1-phenyl-propan-1-one (**3ae**). 10 h, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.6 Hz, 2H), 7.55-7.51 (m, 1H), 7.44-7.39 (m, 3H), 7.36-7.34 (m, 2H), 7.26-7.16 (m, 4H), 7.03-7.00 (m, 1H), 6.81 (s, 1H), 5.01 (t, J = 7.2 Hz, 1H), 3.75 (ddd, J = 10.8, 22.2, 31.8 Hz, 2H), 3.70 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 143.4, 137.3, 136.9, 133.1, 131.4, 129.6, 128.6, 128.0, 126.7, 126.1, 121.8, 119.9, 119.4, 118.9, 117.2, 109.3, 44.9, 37.4, 32.7 ppm. ESI HRMS: calcd. for $C_{24}H_{20}BrNO$+Na 440.0626, found $C_{24}H_{20}{}^{79}BrNNaO$ 440.0615, $C_{24}H_{20}{}^{81}BrNNaO$ 442.0593.

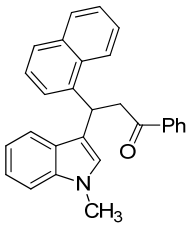


3-(4-Methoxy-phenyl)-3-(1-methyl-1*H*-indol-3-yl)-1-phenyl-propan-1-one (**3af**). 10 h, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.6 Hz, 2H), 7.53-7.50 (m, 1H), 7.44-7.39 (m, 3H), 7.27-7.23 (m, 3H), 7.18-7.15 (m, 1H), 7.02-6.98 (m, 1H), 6.81-6.77 (m, 3H), 5.00 (t, J = 7.2 Hz, 1H), 3.75 (ddd, J = 6.8, 25.2, 33.2 Hz, 2H), 3.73 (s, 3H), 3.68 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 157.8, 137.3, 137.0, 136.4, 132.9, 128.7, 128.5, 128.0, 126.9, 126.1, 121.6, 119.6, 118.7, 118.1, 113.7, 109.1, 55.1, 45.4, 37.3, 32.6 ppm. ESI HRMS: calcd. for $C_{25}H_{23}NO_2$+Na 392.1626, found 392.1627.

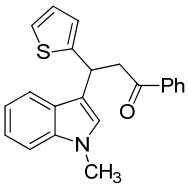


3-(1-Methyl-1*H*-indol-3-yl)-1-phenyl-3-(4-trifluoromethyl-phenyl)-propan-1-one (**3ag**). 12 h, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.6 Hz, 2H), 7.56-7.40 (m, 8H), 7.28-7.26 (m, 1H), 7.23-7.18 (m, 1H), 7.05-7.01 (m, 1H), 6.84 (s, 1H), 5.12 (t, J = 7.2 Hz, 1H), 3.79 (ddd, J = 6.4, 20.4, 26 Hz, 2H), 3.72 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 148.5, 137.3, 136.8, 133.2, 128.6, 128.1, 128.0, 126.7, 126.2, 125.4, 125.3, 125.3, 121.2, 119.3,

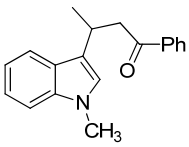
119.0, 116.9, 109.3, 44.8, 37.8, 32.7 ppm. ESI HRMS: calcd. for $C_{25}H_{20}F_3NO$+Na 430.1395, found 430.1401.



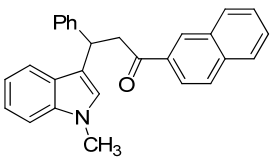
3-(1-Methyl-1*H*-indol-3-yl)-3-naphthalen-1-yl-1-phenyl-propan-1-one (**3ah**). 10 h, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.85-7.35 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.54-7.38 (m, 8H), 7.35-7.31 (m, 1H), 7.24-7.21 (m, 1H), 7.19-7.15 (m, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 5.94 (t, *J* = 6.8 Hz, 1H), 3.88 (ddd, *J* = 7.6, 21.4, 61.8 Hz, 2H), 3.62 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 140.0, 137.3, 137.0, 134.0, 133.0, 131.4, 128.8, 128.5, 128.0, 127.0, 126.9, 126.1, 125.4, 125.3, 124.2, 123.6, 121.6, 119.5, 118.8, 117.5, 109.2, 44.9, 33.0, 32.6 ppm. ESI HRMS: calcd. for $C_{28}H_{23}NO$+Na 412.1677, found 412.1675.



3-(1-Methyl-1*H*-indol-3-yl)-1-phenyl-3-thiophen-2-yl-propan-1-one (**3ai**). 18 h, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.59-7.54 (m, 2H), 7.47-7.43 (m, 2H), 7.31-7.21 (m, 2H), 7.12-7.07 (m, 2H), 6.96-6.95 (m, 2H), 6.91-6.89 (m, 1H), 5.39 (t, *J* = 7.2 Hz, 1H), 3.86 (ddd, *J* = 7.6, 17.6, 21.2 Hz, 2H), 3.73 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 148.9, 137.2, 136.9, 133.0, 128.5, 128.0, 126.5, 126.4, 126.3, 124.1, 123.3, 121.7, 119.5, 118.9, 117.4, 109.3, 46.2, 33.3, 32.7 ppm. ESI HRMS: calcd. For $C_{22}H_{19}NOS$+Na 368.1085, found 368.1093.

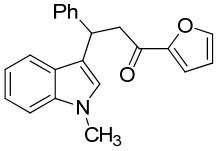


3-(1-Methyl-1*H*-indol-3-yl)-1-phenyl-butan-1-one (**3aj**). 10 h, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.67-7.65 (m, 1H), 7.55-7.51 (m, 1H), 7.45-7.41 (m, 2H), 7.29-7.27 (m, 1H), 7.24-7.20 (m, 1H), 7.12-7.08 (m, 1H), 6.88 (s, 1H), 3.81 (m, 1H), 3.73 (s, 3H), 3.34 (ddd, *J* = 5.2, 18.8, 89.4 Hz, 2H), 1.43 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 137.3, 137.2, 132.9, 128.5, 128.1, 126.6, 125.0, 121.5, 120.0, 119.3, 118.6, 109.3, 46.6, 32.6, 29.7, 27.0, 21.1 ppm. ESI HRMS: calcd. for $C_{19}H_{19}NO$+Na 300.1364, found 300.1366.

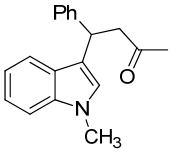


3-(1-Methyl-1*H*-indol-3-yl)-1-naphthalen-2-yl-3-phenyl-propan-1-one (**3ak**). 12 h, 96% yield; ^{1}H NMR (400 MHz, DMSO): δ 8.79 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.97-7.95 (m, 3H), 7.68-7.60 (m, 2H), 7.49-7.43 (m, 3H), 7.35-7.33 (m, 2H), 7.25-7.21 (m, 2H), 7.11-7.08 (m, 2H), 6.96-6.92 (m, 1H), 4.94 (t, *J* = 7.2 Hz, 1H), 4.01 (ddd, *J* = 7.2, 20.8, 32.8 Hz, 2H), 3.71 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 198.3, 145.4, 136.9, 135.2, 134.3, 132.4, 130.3, 129.8, 128.8, 128.4, 128.3, 128.0, 127.8, 127.1, 126.9, 126.5, 126.1, 123.8, 121.4, 119.2, 118.6, 117.7,

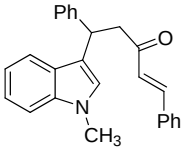
109.8, 44.5, 37.7, 32.5 ppm. ESI HRMS: calcd. for $C_{28}H_{23}NO$+Na 412.1677, found 412.1667.



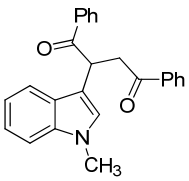
1-Furan-2-yl-3-(1-methyl-1*H*-indol-3-yl)-3-phenyl-propan-1-one (**3al**). 10 h, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.45-7.43 (m, 1H), 7.36-7.34 (m, 2H), 7.26-7.23 (m, 3H), 7.18-7.12 (m, 2H), 7.11-7.10 (m, 1H), 7.02-6.98 (m, 1H), 6.87 (s, 1H), 6.46-6.45 (m, 1H), 5.03 (t, *J* = 7.6 Hz, 1H), 3.70 (s, 3H), 3.63 (ddd, *J* = 7.6, 19.6, 28.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.6, 152.9, 146.2, 144.1, 137.2, 128.3, 127.8, 126.9, 126.2, 121.6, 119.6, 118.8, 117.4, 117.0, 112.2, 109.1, 45.0, 38.1, 32.6 ppm. ESI HRMS: calcd. for $C_{22}H_{19}NO_2$+Na 352.1313, found 352.1307.



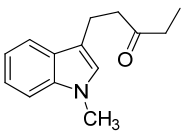
4-(1-Methyl-1*H*-indol-3-yl)-4-phenyl-butan-2-one (**3am**). 8 h, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.46 (m, 1H), 7.36-7.34 (m, 2H), 7.32-7.26 (m, 3H), 7.23-7.18 (m, 2H), 7.07-7.03 (m, 1H), 6.86 (s, 1H), 4.86 (t, *J* = 7.6 Hz, 1H), 3.74 (s, 3H), 3.23 (ddd, *J* = 7.2, 19.6, 32 Hz, 2H), 2.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 144.1, 137.2, 128.4, 127.6, 126.8, 126.3, 126.1, 121.7, 119.4, 118.8, 117.2, 109.2, 50.4, 38.3, 32.6, 30.3 ppm. ESI HRMS: calcd. for $C_{19}H_{19}NO$+Na 300.1364, found 300.1360.



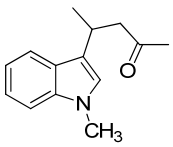
5-(1-Methyl-1*H*-indol-3-yl)-1,5-diphenyl-pent-1-en-3-one (**3an**). 8 h, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.52-7.48 (m, 3H), 7.42-7.40 (m, 5H), 7.33-7.28 (m, 3H), 726-7.19 (m, 2H), 7.09-7.05 (m, 1H), 6.91 (s, 1H), 6.76-6.72 (m, 1H), 5.02 (t, *J* = 7.2 Hz, 1H), 3.74 (s, 3H), 3.50 (ddd, *J* = 6.8, 19.2, 37.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 144.2, 142.6, 137.2, 134.4, 130.4, 128.8, 128.4, 128.2, 127.7, 126.9, 126.2, 126.1, 121.6, 119.6, 118.8, 117.5, 109.2, 47.5, 38.4, 32.6 ppm. ESI HRMS: calcd. for $C_{26}H_{23}NO$+Na 388.1677, found 388.1676.



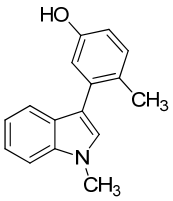
2-(1-Methyl-1*H*-indol-3-yl)-1,4-diphenyl-butane-1,4-dione (**3ao**). 6 h, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.05 (m, 2H), 7.98-7.96 (m, 2H), 7.78-7.76 (m, 1H), 7.54-7.50 (m, 1H), 746-7.39 (m, 3H), 7.37-7.33 (m, 2H), 7.28-7.22 (m, 2H), 7.18-7.15 (m, 1H), 6.88 (s, 1H), 5.59 (dd, *J* = 3.6, 10.4 Hz, 1H), 4.24 (dd, *J* = 10.4, 18.4 Hz, 1H), 3.42 (dd, *J* = 3.2, 18 Hz, 1H), 3.66 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 198.6, 137.1, 136.5, 136.4, 133.1, 132.6, 128.7, 128.5, 128.4, 128.1, 127.4, 126.4, 122.0, 119.5, 118.7, 111.4, 109.5, 43.1, 39.4, 32.7 ppm. ESI HRMS: calcd. for $C_{25}H_{21}NO_2$+Na 390.1470, found 390.1465.



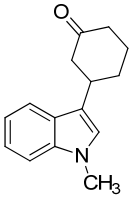
1-(1-Methyl-1*H*-indol-3-yl)-pentan-3-one (**3ap**). 8 h, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.28-7.19 (m, 2H), 7.12-7.08 (m, 1H), 6.82 (s, 1H), 3.70 (s, 3H), 3.03 (t, *J* = 7.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.39 (q, *J* = 7.2 Hz, 2H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.3, 136.9, 127.5, 126.3, 121.5, 118.7, 118.6, 113.7, 109.1, 42.9, 35.9, 32.5, 19.2, 7.7 ppm. ESI HRMS: calcd. for $C_{14}H_{17}NO$+Na 238.1208, found 238.1210.



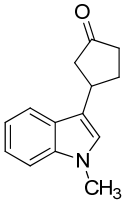
4-(1-Methyl-1*H*-indol-3-yl)-pentan-2-one (**3aq**). 8 h, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.62 (m, 1H), 7.29-7.27 (m, 1H), 7.24-7.20 (m, 1H), 7.12-7.09 (m, 1H), 6.82 (s, 1H), 3.72 (s, 3H), 3.65-3.60 (m, 1H), 2.81 (ddd, *J* = 6.0, 19, 86.6 Hz, 2H), 2.09 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.6, 137.1, 126.5, 124.9, 121.5, 119.4, 119.1, 118.6, 109.3, 51.6, 32.5, 30.3, 26.9, 21.4 ppm. ESI HRMS: calcd. for $C_{14}H_{17}NO$+Na 238.1208, found 238.1205.



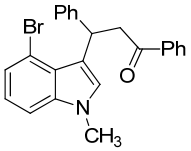
4-Methyl-3-(1-methyl-1*H*-indol-3-yl)-phenol (**3ar**). 12 h, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.52-7.50 (m, 1H), 7.43-7.38 (m, 1H), 7.32-7.26 (m, 2H), 7.16 (s, 1H), 7.05-7.04 (m, 1H), 6.89-6.86 (m, 1H), 5.23 (s, 1H), 3.93 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 136.6, 135.6, 131.3, 128.6, 127.6, 127.3, 121.7, 120.2, 119.4, 117.4, 115.6, 113.4, 109.3, 32.8, 19.8 ppm. ESI HRMS: calcd. for $C_{16}H_{15}NO$+Na 260.1051, found 260.1048.



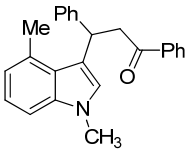
3-(1*H*-Indol-3-yl)-cyclohexanone (**3as**). 4 h, 33% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.32-7.30 (m, 1H), 7.27-7.23 (m, 1H), 7.14-7.11 (m, 1H), 6.84 (s, 1H), 3.76 (s, 3H), 3.49-3.44 (m, 1H), 2.82-2.81 (m, 1H), 2.66-2.60 (m, 1H), 2.50-2.37 (m, 2H), 2.27-2.24 (m, 1H), 2.09-2.02 (m, 1H), 1.99-1.93 (m, 1H), 1.88-1.82 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 170.6, 137.0, 126.4, 125.2, 121.7, 119.0, 118.8, 118.1, 109.3, 48.1, 41.5, 35.8, 32.6, 31.8, 24.8 ppm. ESI HRMS: calcd. for $C_{15}H_{17}NO$+Na 250.1208, found 250.1196.



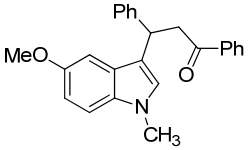
3-(1-methyl-1*H*-indol-3-yl)cyclopentanone (**3at**). 4 h, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.28-7.26 (m, 1H), 7.22-7.19 (m, 1H), 7.10-7.06 (m, 1H), 6.78 (s, 1H), 3.70 (s, 3H), 3.66-3.64 (m, 1H), 2.73-2.66 (m, 1H), 2.49-2.44 (m, 1H), 2.43-2.34 (m, 2H), 2.31-2.22 (m, 1H), 2.12-2.04 (m, 1H) ppm; ^{13}C NMR (75 MHz, DMSO): δ 218.3, 136.9, 126.8, 125.6, 121.2, 118.9, 118.4, 116.5, 109.7, 44.9, 37.9, 33.1, 32.3, 29.7 ppm. ESI HRMS: calcd. For $C_{14}H_{15}NO$+Na 236.1051, found 236.1042.



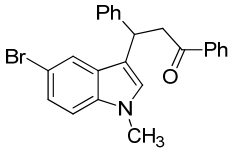
3-(4-Bromo-1-methyl-1*H*-indol-3-yl)-1,3-diphenyl-propan-1-one (**3ba**). 10 h, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.56-7.53 (m, 1H), 7.46-7.42 (m, 2H), 7.39-7.37 (m, 2H), 7.32-7.25 (m, 3H), 7.22-7.20 (m, 2H), 7.05-7.00 (m, 1H), 6.74 (s, 1H), 5.82 (t, *J* = 7.2 Hz, 1H), 3.82 (ddd, *J* = 5.6, 20.4, 27.2 Hz, 2H), 3.67 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 144.3, 138.5, 137.0, 132.9, 128.5, 128.3, 128.1, 128.0, 126.1, 124.8, 123.8, 122.4, 118.8, 114.3, 108.5, 46.7, 36.9, 32.9 ppm. ESI HRMS: calcd. for $C_{24}H_{20}BrNO$+Na 440.0626, found $C_{24}H_{20}{}^{79}BrNNaO$ 440.0620, $C_{24}H_{20}{}^{81}BrNNaO$ 442.0612.



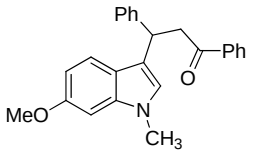
3-(1,4-Dimethyl-1*H*-indol-3-yl)-1,3-diphenyl-propan-1-one (**3ca**). 8 h, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.59-7.55 (m, 1H), 7.48-7.45 (m, 2H), 7.31-7.25 (m, 4H), 7.19-7.14 (m, 1H), 7.12-7.08 (m, 2H), 6.86 (s, 1H), 6.79 (d, *J* = 6.4 Hz, 1H), 5.45 (t, *J* = 7.2 Hz, 1H), 3.74 (ddd, *J* = 6.8, 24.6, 33 Hz, 2H), 3.72 (s, 3H), 2.57 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 145.4, 137.6, 137.1, 133.0, 131.2, 128.6, 128.4, 128.0, 127.9, 126.5, 126.1, 125.8, 121.7, 120.8, 118.1, 107.0, 47.1, 38.6, 32.8, 20.7 ppm. ESI HRMS: calcd. for $C_{25}H_{23}NO$+Na 376.1677, found 376.1680.



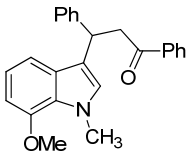
3-(5-Methoxy-1-methyl-1*H*-indol-3-yl)-1,3-diphenyl-propan-1-one (**3da**). 8 h, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.41-7.39 (m, 2H), 7.31-7.26 (m, 2H), 7.21-7.15 (m, 2H), 6.89-6.83 (m, 3H), 5.05 (t, *J* = 7.2 Hz, 1H), 3.81 (ddd, *J* = 6.8, 20.2, 29.2 Hz, 2H), 3.77 (s, 3H), 3.69 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 153.5, 144.3, 137.0, 132.9, 132.6, 128.5, 128.4, 128.0, 127.7, 127.2, 126.7, 126.2, 117.2, 111.7, 109.9, 101.4, 55.8, 45.2, 37.9, 32.8 ppm. ESI HRMS: calcd. for $C_{25}H_{23}NO_2$+Na 392.1626, found 392.1633.



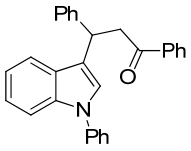
3-(5-Bromo-1-methyl-1*H*-indol-3-yl)-1,3-diphenyl-propan-1-one (**3ea**). 8 h, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.54-7.50 (m, 2H), 7.43-7.39 (m, 2H), 7.33-7.31 (m, 2H), 7.27-7.22 (m, 2H), 7.20-7.16 (m, 2H), 7.08-7.05 (m, 1H), 6.83 (s, 1H), 4.98 (t, *J* = 7.6 Hz, 1H), 3.72 (ddd, *J* = 7.2, 20.4, 27.6 Hz, 2H), 3.63 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 143.9, 136.9, 135.9, 133.0, 128.5, 128.4, 128.0, 127.6, 127.3, 126.4, 124.4, 121.9, 117.3, 112.2, 110.7, 45.2, 37.8, 32.8 ppm. ESI HRMS: calcd. for $C_{24}H_{20}BrNO$+Na 440.0626 found $C_{24}H_{20}{}^{79}BrNNaO$ 440.0626, $C_{24}H_{20}{}^{81}BrNNaO$ 442.0608.



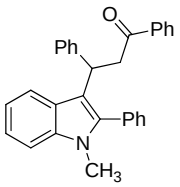
3-(6-Methoxy-1-methyl-1*H*-indol-3-yl)-1,3-diphenyl-propan-1-one (**3fa**). 8 h, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.53-7.49 (m, 1H), 7.42-7.38 (m, 2H), 7.35-7.33 (m, 2H), 7.28-7.22 (m, 3H), 7.16-7.12 (m, 1H), 6.71-6.65 (m, 3H), 5.00 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 3.74 (ddd, *J* = 6.8, 20.2, 27.4 Hz, 2H), 3.62 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 156.3, 144.4, 138.0, 137.0, 132.9, 128.5, 128.4, 128.0, 127.7, 126.2, 125.0, 121.4, 120.2, 117.7, 108.6, 92.73, 55.60, 45.3, 38.1, 32.6 ppm. ESI HRMS: calcd. for $C_{25}H_{23}NO_2$+Na 392.1626 found 392.1621.



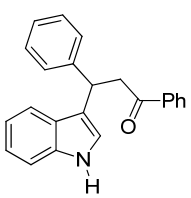
3-(7-Methoxy-1-methyl-1*H*-indol-3-yl)-1,3-diphenyl-propan-1-one (**3ga**). 8 h, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.49-7.45 (m, 2H), 7.37-7.34 (m, 4H), 7.24-7.19 (m, 3H), 7.14-7.07 (m, 2H), 7.00-6.96 (m, 1H), 5.12 (t, *J* = 7.2 Hz, 1H), 3.93 (ddd, *J* = 7.6, 17.2, 20 Hz, 2H), 3.58 (s, 3H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0, 144.4, 137.1, 136.8, 133.6, 132.8, 128.4, 128.2, 128.0, 127.5, 126.4, 125.8, 120.2, 119.1, 118.7, 112.9, 108.7, 43.7, 37.0, 29.4, 10.5 ppm. ESI HRMS: calcd. for $C_{25}H_{23}NO_2$+Na 392.1626 found 392.1619.



1,3-diphenyl-3-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**3ha**). 20 h, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.58-7.54 (m, 3H), 7.53-7.44 (m, 8H), 7.37-7.30 (m, 3H), 7.26-7.20 (m, 3H), 7.13-7.09 (m, 1H), 5.18 (t, *J* = 7.2 Hz, 1H), 3.86 (ddd, *J* = 6.4, 20.4, 22.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 143.9, 139.7, 137.0, 136.3, 132.9, 129.5, 128.5, 128.4, 128.0, 127.8, 126.4, 126.2, 125.2, 124.1, 122.6, 120.3, 120.0, 119.8, 110.5, 45.1, 38.0 ppm. ESI HRMS: calcd. for $C_{29}H_{23}NO$+Na 424.1677, found 424.1674.

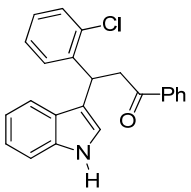


3-(1-Methyl-2-phenyl-1*H*-indol-3-yl)-1,3-diphenyl-propan-1-one (**3ia**). 14 h, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.6Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.54-7.48 (m, 4H), 7.41-7.36 (m, 7H), 7.30-7.25 (m, 3H), 7.20-7.14 (m, 2H), 5.07 (t, *J* = 7.2 Hz, 1H), 3.92 (ddd, *J* = 7.2, 15.6, 20.4 Hz, 2H), 3.56 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 144.6, 138.3, 137.3, 136.8, 132.7, 131.8, 130.8, 128.3, 128.2, 128.0, 127.5, 126.4, 125.7, 121.4, 120.1, 119.2, 114.6, 109.5, 44.2, 37.5, 30.6 ppm. ESI HRMS: calcd. for $C_{30}H_{25}NO$+Na 438.1834 found 438.1833.

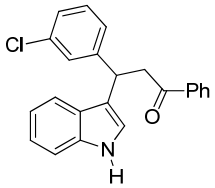


3-(1*H*-Indol-3-yl)-1,3-diphenyl-propan-1-one (**5aa**). 12 h, 90% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.9 (s, 1H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.63-7.61 (m, 1H), 7.54-7.50 (m, 2H), 7.46-7.42 (m, 3H), 7.38-7.33 (m, 2H), 7.26-7.22 (m, 2H), 7.13-7.12 (m, 1H), 7.06-7.03 (m,

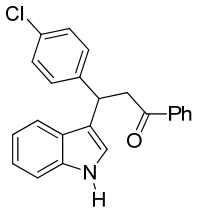
1H), 6.93-6.90 (m, 1H), 4.90 (t, *J* = 6.4 Hz, 1H), 3.90 (ddd, *J* = 6.8, 20, 40.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 214.7, 198.6, 145.5, 137.1, 136.6, 133.3, 128.9, 128.3, 128.0, 126.6, 126.0, 122.1, 121.2, 118.9, 118.5, 118.2, 111.6, 44.5, 37.9 ppm. ESI HRMS: calcd. for $C_{23}H_{19}NO$+Na 348.1364, found 348.1365.



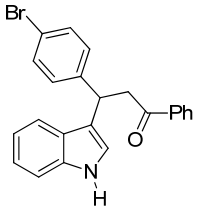
3-(2-Chloro-phenyl)-3-(1*H*-indol-3-yl)-1-phenyl-propan-1-one (**5ab**). 12 h, 93% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.93 (s, 1H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.65-7.62 (m, 1H), 7.54-7.50 (m, 2H), 7.46-7.42 (m, 3H), 7.34-7.30 (m, 2H), 7.23-7.15 (m, 2H), 7.07-7.03 (m, 1H), 6.94-6.91 (m, 1H), 5.38 (t, *J* = 7.2 Hz, 1H), 4.02 (dd, *J* = 7.2, 16.8 Hz, 1H), 3.72 (dd, J = 6.4, 17.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 203.1, 147.4, 141.8, 141.4, 138.3, 137.7, 134.5, 134.4, 133.8, 133.2, 132.7, 132.3, 131.5, 127.8, 127.7, 126.3, 123.6, 121.8, 116.6, 48.8, 39.9 ppm. ESI HRMS: calcd. for $C_{23}H_{18}ClNO$+Na 382.0975, found $C_{23}H_{18}{}^{35}ClNNaO$ 382.0960, $C_{23}H_{18}{}^{37}ClNNaO$ 384.0944.



3-(3-Chloro-phenyl)-3-(1*H*-indol-3-yl)-1-phenyl-propan-1-one (**5ac**). 12 h, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.58-7.55 (m, 1H), 7.47-7.43 (m, 3H), 7.35-7.30 (m, 2H), 7.28-7.26 (m, 1H), 7.21-7.14 (m, 3H), 7.08-7.04 (m, 1H), 6.95-6.94 (m, 1H), 5.07 (t, *J* = 7.2 Hz, 1H), 3.77 (ddd, *J* = 6.4, 20.4, 44.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 146.4, 136.8, 136.5, 134.1, 133.2, 129.6, 128.6, 128.0, 127.9, 126.5, 126.3, 126.1, 122.2, 121.4, 119.5, 119.2, 118.4, 111.2, 44.8, 37.8 ppm. ESI HRMS: calcd. for $C_{23}H_{18}ClNO$+Na 382.0975, found $C_{23}H_{18}{}^{35}ClNNaO$ 382.0967, $C_{23}H_{18}{}^{37}ClNNaO$ 384.0947.

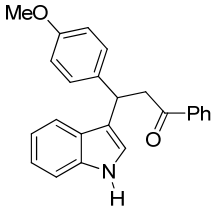


3-(4-chlorophenyl)-3-(1*H*-indol-3-yl)-1-phenylpropan-1-one (**5ad**). 12 h, 87% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.91 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 2H), 7.63-7.60 (m, 1H), 7.52-7.48 (m, 2H), 7.44-7.42 (m, 3H), 7.38 (s, 1H), 7.33-7.31 (m, 1H), 7.28-7.26 (m, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 4.89 (t, *J* = 7.2 Hz, 1H), 3.89 (ddd, *J* = 6.8, 20.8, 35.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 198.4, 144.5, 137.0, 136.6, 133.4, 130.5, 129.9, 128.9, 128.3, 128.2, 126.4, 122.2, 121.3, 118.8, 118.6, 117.8, 111.6, 44.2, 37.2 ppm. ESI HRMS: calcd. for $C_{23}H_{18}ClNO$+Na 382.0975, found $C_{23}H_{18}{}^{35}ClNNaO$ 382.0967, $C_{23}H_{18}{}^{37}ClNNaO$ 384.0940.

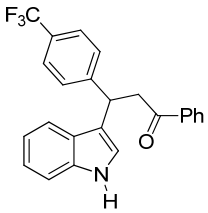


3-(4-Bromo-phenyl)-3-(1*H*-indol-3-yl)-1-phenyl-propan-1-one (**5ae**). 14 h, 90% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.91 (s, 1H), 8.02-8.00 (m, 2H), 7.63-7.60 (m, 1H), 7.52-7.48 (m, 2H), 7.43-7.31 (m, 7H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.2Hz, 1H), 4.87

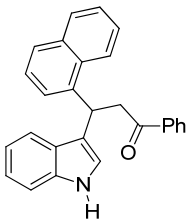
(t, J = 5.6 Hz, 1H), 3.88 (ddd, J = 6.4, 20.4, 33.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 198.4, 145.0, 137.0, 136.6, 133.4, 131.1, 130.3, 128.9, 128.3, 126.4, 122.2, 121.3, 119.0, 118.8, 118.6, 117.8, 111.6, 44.2, 37.2 ppm. ESI HRMS: calcd. for $C_{23}H_{18}BrNO$+Na 426.0469, found $C_{23}H_{18}{}^{79}BrNNaO$ 426.0483, $C_{23}H_{18}{}^{81}BrNNaO$ 428.3361.



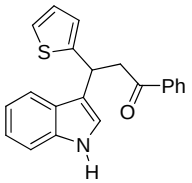
3-(1*H*-indol-3-yl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (**5af**). 26 h, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.91 (d, J = 7.6 Hz, 2H), 7.51-7.49 (m, 1H), 7.42-7.48 (m, 3H), 7.27-7.22 (m, 3H), 7.13-7.09 (m, 1H), 7.01-6.98 (m, 1H), 6.90 (s, 1H), 6.77 (d, J = 8.4 Hz, 2H), 5.00 (t, J = 7.2 Hz, 1H), 3.71 (ddd, J = 6.4, 20, 30 Hz, 2H), 3.70 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 157.8, 137.0, 136.6, 136.3, 133.0, 128.7, 128.5, 128.0, 126.5, 122.0, 121.3, 119.5, 119.4, 119.2, 113.7, 111.1, 55.1, 45.3, 37.4 ppm. ESI HRMS: calcd. for $C_{24}H_{21}NO_2$+Na 378.1470, found 378.1466.



3-(1H-indol-3-yl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**5ag**). 26 h, 70% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.96 (s, 1H), 8.04 (d, J = 7.6 Hz, 2H), 7.67-7.65 (m, 3H), 7.62-7.58 (m, 2H), 7.54-7.50 (m, 2H), 7.48-7.43 (m, 2H), 7.34-7.32 (m, 1H), 7.06-7.03 (m, 1H), 6.94-6.90 (m, 1H), 4.99 (s, 1H), 3.97 (ddd, J = 6.8, 21.2, 24.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 198.3, 150.4, 136.9, 136.5, 133.4, 128.9, 128.8, 128.3, 126.4, 125.2, 125.2, 122.4, 121.3, 118.7, 118.7, 117.4, 111.6, 44.0, 37.6 ppm. ESI HRMS: calcd. for $C_{24}H_{18}F_3NO$+Na 416.1238, found 416.1240.

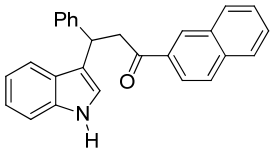


3-(1*H*-Indol-3-yl)-3-naphthalen-1-yl-1-phenyl-propan-1-one (**5ah**). 12 h, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35-8.33 (m, 1H), 7.97-7.95 (m, 2H), 7.90-7.87 (m, 2H), 7.75-7.73 (m, 1H), 7.58-7.54 (m, 1H), 7.50-7.44 (m, 5H), 7.42-7.33 (m, 2H), 7.29-7.26 (m, 1H), 7.17-7.14 (m, 1H), 7.04-7.00 (m, 1H), 6.77-6.76 (m, 1H), 5.97 (t, J = 6.8 Hz, 1H), 3.89 (ddd, J = 8.0, 21.2, 77.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 139.9, 137.0, 136.6 ,134.0, 133.1, 131.4, 128.8, 128.6, 128.0, 127.0, 126.6, 126.1, 125.5, 125.3, 124.3, 123.6, 122.2, 122.0, 119.4, 119.3, 118.9, 111.1, 44.6, 33.2 ppm. ESI HRMS: calcd. for $C_{27}H_{21}NO$+Na 398.1521, found 398.1530.

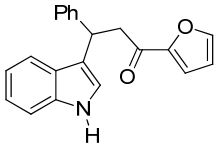


3-(1*H*-indol-3-yl)-1-phenyl-3-(thiophen-2-yl)propan-1-one (**5ai**). 48 h, 40% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.92 (s, 1H), 8.02 (d, J = 7.2Hz, 2H), 7.64-7.60 (m, 1H), 7.51 (t, J = 7.2 Hz, 3H), 7.35-7.33 (m, 2H), 7.23-7.22 (m, 1H), 7.08-7.04 (m, 1H), 7.00-6.99 (m, 1H), 6.95 (t, J = 7.2 Hz, 1H), 6.88-6.86 (m, 1H), 5.20 (t, J = 7.2 Hz, 1H), 3.92 (d, J = 7.2 Hz, 2H) ppm; ^{13}C NMR

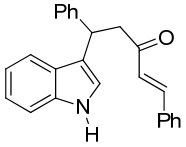
(100 MHz, DMSO): δ 198.2, 149.9, 136.9, 136.6, 133.4, 128.9, 128.3, 126.7, 126.3, 124.1, 123.8, 122.4, 121.3, 118.9, 118.7, 117.9, 111.7, 45.4, 32.9 ppm. ESI HRMS: calcd. for $C_{21}H_{17}NOS$+Na 354.0929, found 354.0930.



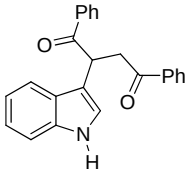
3-(1*H*-Indol-3-yl)-1-naphthalen-2-yl-3-phenyl-propan-1-one (**5ak**). 11 h, 80% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.89 (s, 1H), 8.81 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.98-7.07 (m, 3H), 7.68-7.60 (m, 2H), 7.47-7.45 (m, 3H), 7.39 (m, 1H), 7.34-7.32 (m, 1H), 7.24 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2Hz, 1H), 7.06-7.02 (m, 1H), 6.93-6.89 (m, 1H), 4.97 (t, *J* = 7.2Hz, 1H), 4.02 (ddd, *J* = 7.2, 20.8, 66.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 198.5, 145.5, 136.6, 135.2, 134.4, 132.4, 130.3, 129.8, 128.8, 128.4, 128.3, 128.0, 127.8, 127.1, 126.6, 126.0, 123.8, 122.1, 121.2, 118.9, 118.5, 118.2, 111.6, 44.4, 38.0 ppm. ESI HRMS: calcd. for $C_{27}H_{21}NO$+Na 398.1521, found 398.1511.



1-Furan-2-yl-3-(1*H*-indol-3-yl)-3-phenyl-propan-1-one (**5al**). 16 h, 73% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.88 (s, 1H), 7.95 (s, 1H), 7.60-7.59 (m, 1H), 7.43-7.38 (m, 3H), 7.33-7.30 (m, 2H), 7.24-7.20 (m, 2H), 7.12-7.08 (m, 1H), 7.04-7.00 (m, 1H), 6.91-6.88 (m, 1H), 6.69-6.68 (m, 1H), 4.85 (s, 1H), 3.64 (ddd, *J* = 6.4, 19.6, 60 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 186.9, 152.4, 148.1, 148.0, 145.1, 136.5, 128.4, 127.9, 126.5, 126.1, 122.1, 122.1, 121.3, 119.3, 118.9, 118.6, 117.8, 112.7, 112.7, 111.6, 44.2, 38.0 ppm. ESI HRMS: calcd. for $C_{21}H_{17}NO_2$+Na 338.1157, found 338.1157.

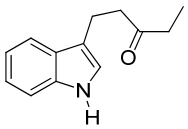


5-(1*H*-Indol-3-yl)-1,5-diphenyl-pent-1-en-3-one (**5an**). 12 h, 62% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.88 (s, 1H), 7.69-7.67 (m ,2H), 7.63 (s, 1H), 7.43-7.38 (m, 6H), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 2H), 7.13-7.09 (m, 1H), 7.05-7.01 (m, 1H), 6.96 (s, 1H), 6.92-6.88 (m, 1H), 4.84 (t, *J* = 7.6 Hz, 1H), 3.52 (ddd, *J* = 7.6, 20, 66.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 198.7, 145.4, 142.4, 136.6, 134.7, 130.6, 129.1, 128.6, 128.3, 127.9, 126.9, 126.6, 126.0, 122.1, 121.2, 118.9, 118.4, 118.0, 111.6, 46.5, 38.0 ppm. ESI HRMS: calcd. for $C_{25}H_{21}NO$+Na 374.1521, found 374.1514.

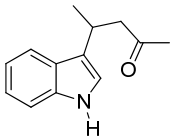


2-(1*H*-Indol-3-yl)-1,4-diphenyl-butane-1,4-dione (**5ao**). 12 h, 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 8.04-8.02 (m, 2H), 7.95-7.93 (m, 2H), 7.77-7.75 (m, 1H), 7.53-7.49 (m, 1H), 7.43-7.37 (m, 3H), 7.32-7.27 (m, 3H), 7.22-7.14 (m, 2H), 6.92 (s, 1H), 5.58 (dd, *J* = 3.2, 10.4 Hz, 1H), 4.24 (dd, *J* = 10.4, 18.4 Hz, 1H) 3.40 (dd, J = 3.6, 18.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 198.8, 136.4, 136.4, 133.2, 132.7, 128.7, 128.5, 128.4, 128.1, 125.9, 122.8, 122.4, 119.9, 118.6, 112.9, 111.5, 42.8, 39.6 ppm. ESI HRMS: calcd. for $C_{24}H_{19}NO_2$+Na 376.1313,

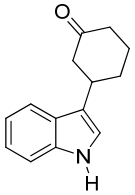
found 376.1311.



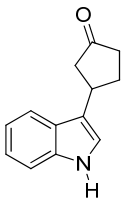
1-(1*H*-Indol-3-yl)-pentan-3-one (**5ap**). 12 h, 91% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.77 (s, 1H), 7.53-7.51 (m, 1H), 7.35-7.33 (m, 1H), 7.09-7.05 (m, 2H), 6.99-6.96 (m, 1H), 2.90 (t, *J* = 7.2Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.45 (q, *J* = 7.2 Hz, 2H), 0.93 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 210.9, 136.5, 127.2, 122.4, 121.2, 118.5, 118.4, 113.8, 111.5, 42.4, 35.2, 19.3, 7.8 ppm. ESI HRMS: calcd. for $C_{13}H_{15}NO$+Na 224.1051, found 224.1044.



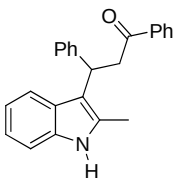
4-(1*H*-Indol-3-yl)-pentan-2-one (**5aq**). 12 h, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.33-7.32 (m, 1H), 7.20-7.16 (m, 1H), 7.13-7.09 (m, 1H), 6.93 (s, 1H), 3.66-3.60 (m, 1H), 2.81 (ddd, *J* = 6.0, 18.8, 86.4 Hz, 2H), 2.08 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.8, 136.4, 126.2, 121.9, 120.8, 120.1, 119.1, 119.0, 111.3, 51.4, 30.4, 26.9, 21.2 ppm. ESI HRMS: calcd. for $C_{13}H_{15}NO$+Na 224.1051, found 224.1042.



3-(1*H*-Indol-3-yl)-cyclohexanone (**5as**). 16 h, 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.27-7.22 (m, 1H), 7.18-7.14 (m, 1H), 6.98 (s, 1H), 3.51-3.44 (m, 1H), 2.86-2.81 (m, 1H), 2.69-2.63 (m, 1H), 2.53-2.39 (m, 2H), 2.31-2.27 (m, 1H), 2.11-1.95 (m, 2H), 1.91-1.81 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.0, 136.4, 126.0, 122.1, 120.3, 119.5, 119.3, 118.9, 111.3, 48.0, 41.5, 35.9, 31.6, 24.8 ppm. ESI HRMS: calcd. for $C_{14}H_{15}NO$+Na 236.1051, found 236.1043.

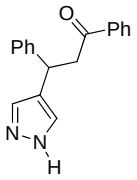


3-(1*H*-Indol-3-yl)-cyclopentanone (**5at**). 16 h, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.64-7.62 (m, 1H), 7.38-7.36 (m, 1H), 7.24-7.20 (m, 1H), 7.16-7.20 (m, 1H), 6.96-6.95 (m, 1H), 3.75-3.67 (m, 1H), 2.79-2.72 (m, 1H), 2.56-2.50 (m, 1H), 2.50-2.41 (m, 2H), 2.40-2.27 (m, 1H), 2.17-2.08 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 219.6, 136.6, 126.5, 122.2, 119.9, 119.4, 119.0, 118.4, 111.3, 45.2, 38.1, 33.6, 29.8 ppm. ESI HRMS: calcd. for $C_{13}H_{13}NO$+Na 222.0895, found 222.0892.

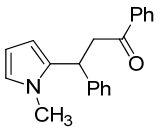


3-(2-Methyl-1*H*-indol-3-yl)-1,3-diphenyl-propan-1-one (**5ba**). 16 h, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.75 (s, 1H), 7.50-7.46 (m, 2H), 7.38-7.34 (m, 4H), 7.25-7.18 (m, 3H), 7.15-7.11 (m, 1H), 7.06-7.03 (m, 1H), 7.00-6.96 (m, 1H), 5.08 (t, *J* = 6.8 Hz, 1H), 3.92 (ddd, *J* = 7.6, 24.8, 26 Hz, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 144.2, 137.1, 135.4, 132.9, 131.7, 128.4, 128.2, 128.0, 127.5, 127.4, 125.8, 120.6, 119.1, 119.1, 113.5, 110.4,

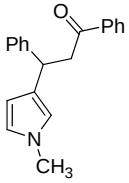
43.5, 36.7, 12.1 ppm. ESI HRMS: calcd. for $C_{24}H_{21}NO$+Na 362.1521, found 362.1508.



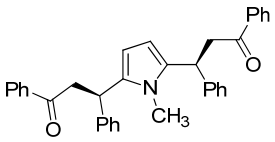
1,3-Diphenyl-3-(1*H*-pyrazol-4-yl)-propan-1-one (**5ca**). 10 h, 30% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.57-7.49 (m, 3H), 7.45-7.42 (m, 2H), 7.33-7.32 (m, 4H), 7.30-7.25 (m, 1H), 6.23 (s, 1H), 5.2 (dd, J = 5.2, 8.4 Hz, 1H), 4.49 (q, *J* = 8.8 Hz, 1H) 3.64 (dd, J = 4.8, 17.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 140.7, 139.2, 136.4, 133.3, 129.7, 128.8, 128.6, 128.2, 127.9, 126.6, 105.5, 60.7, 44.1 ppm. ESI HRMS: calcd. for $C_{18}H_{16}N_2O$+Na 299.1160, found 299.1154.



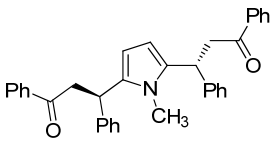
3-(1-methyl-1H-pyrrol-2-yl)-1,3-diphenylpropan-1-one (**7a**). 8 h, 33% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.57-7.55 (m, 1H), 7.46-7.42 (m, 2H), 7.28-7.17 (m, 5H), 6.54 (s, 1H), 6.08 (s, 2H), 4.81 (t, *J* = 7.2 Hz, 1H), 3.80 (dd, *J* = 7.2, 17.2 Hz, 1H), 3.50 (dd, *J* = 7.2, 17.2 Hz, 1H), 3.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 143.2, 137.0, 134.3, 133.0, 128.6, 128.5, 128.0, 127.9, 126.4, 121.9, 106.3, 105.6, 45.5, 38.2, 33.9 ppm. ESI HRMS: calcd. for $C_{20}H_{19}NO$+Na 312.1364, found 312.1365.



3-(1-methyl-1H-pyrrol-3-yl)-1,3-diphenylpropan-1-one (**7b**). 8 h, 6% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.55-7.51 (m, 1H), 7.45-7.41 (m, 2H), 7.32-7.30 (m, 3H), 7.28-7.26 (m, 1H), 7.18-7.14 (m, 1H), 6.48 (s, 1H), 6.32 (s, 1H), 5.97 (s, 1H), 4.69 (t, *J* = 7.2 Hz, 1H), 3.62 (ddd, *J* = 7.2, 20.3, 34.4 Hz, 2H), 2.56 (s, 3H) ppm. ESI HRMS: calcd. for $C_{20}H_{19}NO$+Na 312.1364, found 312.1364.



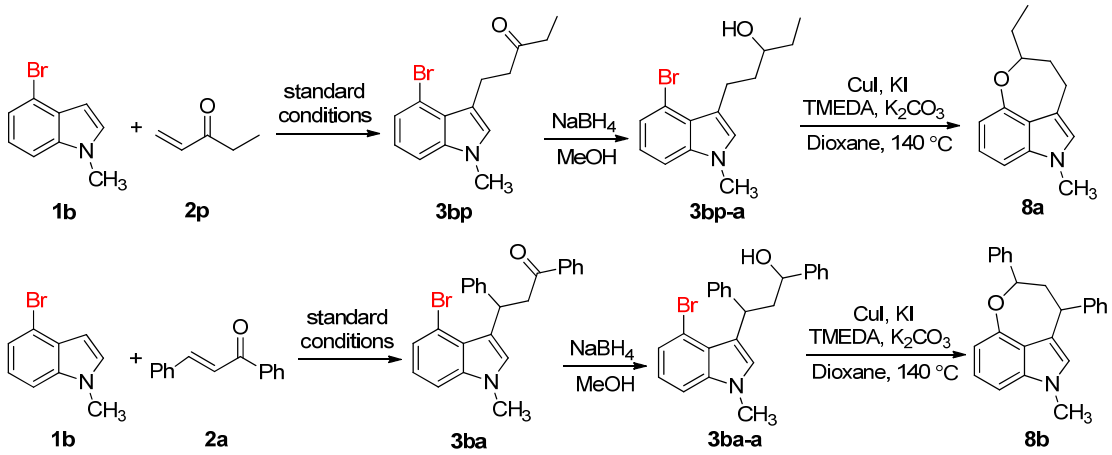
(3R,3'S)-3,3'-(1-methyl-1H-pyrrole-2,5-diyl)bis(1,3-diphenylpropan-1-one) (**7c**). 8 h, 16% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.2 Hz, 4H), 7.55-7.52 (m, 2H), 7.44-7.41 (m, 4H), 7.27-7.23 (m, 4H), 7.18-7.14 (m, 6H), 6.04 (s, 2H), 4.71 (t, *J* = 7.2 Hz, 2H), 3.61 (ddd, *J* = 6.4, 20.4, 91.6 Hz, 4H), 3.05 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 143.3, 137.1, 134.4, 132.9, 128.5, 128.4, 127.9, 127.8, 126.4, 104.2, 45.4, 38.6, 30.6 ppm. ESI HRMS: calcd. for $C_{35}H_{31}NO_2$+Na 520.2252, found 520.2250.



(3R,3'R)-3,3'-(1-methyl-1H-pyrrole-2,5-diyl)bis(1,3-diphenylpropan-1-one) (**7d**). 8 h, 17% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.90 (m, 4H), 7.55-7.52 (m, 2H), 7.44-7.41 (m, 4H), 7.26-7.15 (m, 4H), 7.11-7.09 (m, 6H), 6.00 (s, 2H), 4.75 (t, *J* = 7.2 Hz, 2H), 3.75 (dd, *J* = 7.2, 17.2 Hz, 2H), 3.43 (dd, *J* = 7.2, 17.2 Hz, 2H), 2.99 (s, 3H) ppm; ^{13}C NMR

(75 MHz, DMSO): δ 197.8, 143.7, 136.7, 134.2, 133.2, 128.7, 128.2, 128.0, 127.7, 126.1, 104.2, 44.6, 37.9, 30.2 ppm. ESI HRMS: calcd. for $C_{35}H_{31}NO_2$+Na 520.2252, found 520.2258.

3. Synthetic Applications and Characterization Data

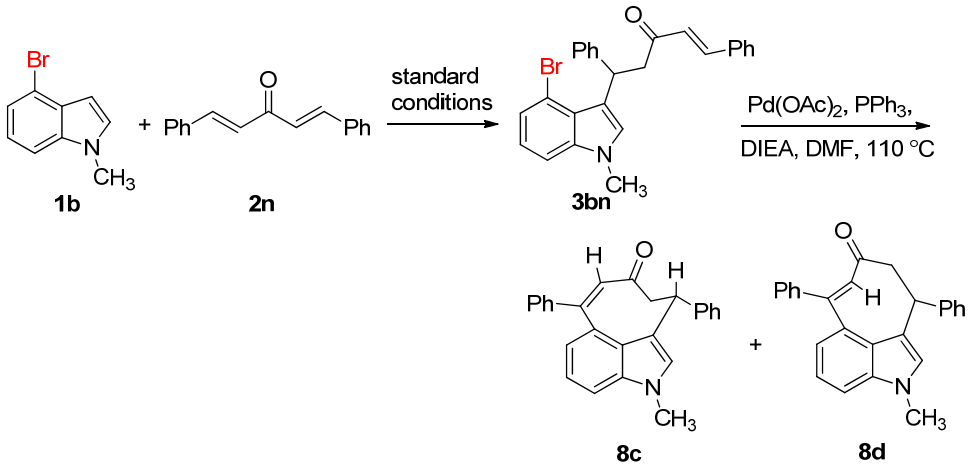


General Procedure for Synthesis of Compound 8a:

(1) **1b** (20.9 mg, 0.1 mmol) and **2p** (9.2 mg, 0.11 mmol) worked under standard conditions to produce **3bp** (60% yield). To the MeOH (1.5 mL) solution of **3bp** (17.6 mg, 0.06 mmol) at r.t. was added $NaBH_4$ (2.3 mg, 0.06 mmol). The resulting mixture was further stirred at room temperature for 2 h, then quenched with water. The aqueous layer was extracted further with ethyl acetate three times; then the combined organic layer was washed with brine and dried over Na_2SO_4. Then the organic layer was concentration in vacuo. In this step, **3bp** would convert to **3bp-a** completely.

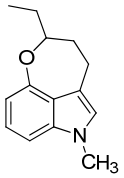
(2) To a mixture of **3bp-a** (17.7 mg, 0.06 mmol), K_2CO_3 (16.6 mg, 0.12 mmol), KI (19.8 mg, 0.12 mmol) and CuI (2.9 mg, 0.015 mmol) in anhydrous dioxane (0.8 mL), in a dry flask under nitrogen atmosphere, was added TMEDA (3.5 mg, 0.03 mmol), and the reaction mixture was stirred at 140 °C for 48 h. Then the mixture quenched with water. The aqueous layer was extracted further with ethyl acetate three times; then the combined organic layer was washed with brine and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate: petroleum ether = 1: 200) to give compound **8a** (80% conversion) as white solid.[3]

The general procedure for synthesis of compound **8b** was same as compound **8a**.

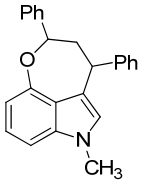


General Procedure for Synthesis of Compound 8c and 8d:

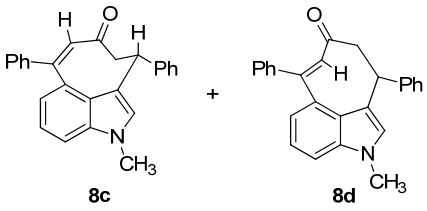
1b (20.9 mg, 0.1 mmol) and **2n** (25.7 mg, 0.11 mmol) worked under standard conditions to produce **3bn** (58% yield). To the DMF (1.0 mL) solution of **3bn** (27 mg, 0.058 mmol) was added $Pd(OAc)_2$ (1.9 mg, 0.0087 mmol), PPh_3 (7.6mg, 0.029mmol), DIEA (15 mg, 0.116 mmol). The mixture was stirred at 100 °C under Ar atmosphere for 18 h. Then the mixture quenched with water. The aqueous layer was extracted further with ethyl acetate three times; then the combined organic layer was washed with brine and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate: petroleum ether = 1: 50) to give compound **8c** (57.3% yield) and **8d** (28.7% yield) as yellow solid.[4]



2-ethyl-6-methyl-2,3,4,6-tetrahydrooxepino[4,3,2-*cd*]indole (**8a**). 48 h, 80% conversion; ^{1}H NMR (300 MHz, DMSO): δ 7.00 (s, 1H), 6.99-6.89 (m, 2H), 6.45-6.42 (m, 1H), 3.96-3.92 (m, 1H), 3.68 (s, 3H), 3.03-2.98 (m, 1H), 2.75-2.74 (m, 1H), 2.15-2.10 (m, 1H), 1.86-1.69 (m, 3H), 1.05-0.99 (m, 3H) ppm; ^{13}C NMR (75 MHz, DMSO): δ 152.0, 138.8, 124.6, 121.6, 117.4, 112.0, 105.0, 101.9, 83.7, 34.9, 32.4, 29.4, 24.6, 10.0 ppm. ESI HRMS: calcd. for $C_{14}H_{18}NO$+H 216.1388, found 216.1386.



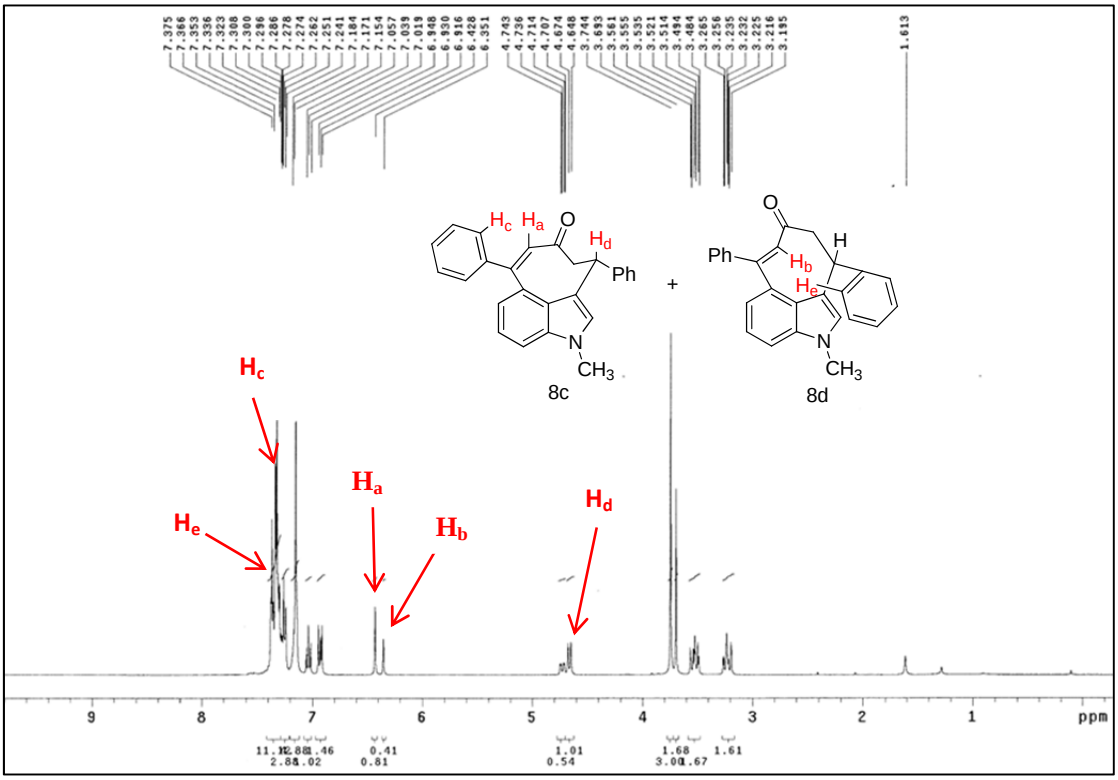
6-methyl-2,4-diphenyl-2,3,4,6-tetrahydrooxepino[4,3,2-*cd*]indole (**8b**). 48 h, 72% conversion; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.24 (m, 4H), 7.23-7.17 (m, 4H), 7.15-7.13 (m, 1H), 7.11-7.09 (m, 2H), 6.96-6.94 (m, 1H), 6.72-6.70 (m, 2H), 5.44 (d, J = 7.2 Hz, 1H), 4.72 (t, J = 4.0 Hz, 1H), 3.74 (s, 3H), 3.01 (ddd, J = 4.4, 9.8, 13 Hz, 1H), 2.60 (dd, J = 4.0, 14.8 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.5, 146.7, 143.6, 139.2, 128.3, 126.9, 126.1, 125.4, 122.6, 118.2, 115.1, 106.3, 102.0, 78.8, 46.6, 40.6, 33.0 ppm. ESI HRMS: calcd. for $C_{24}H_{22}NO$+H 340.1701, found 340.1700.

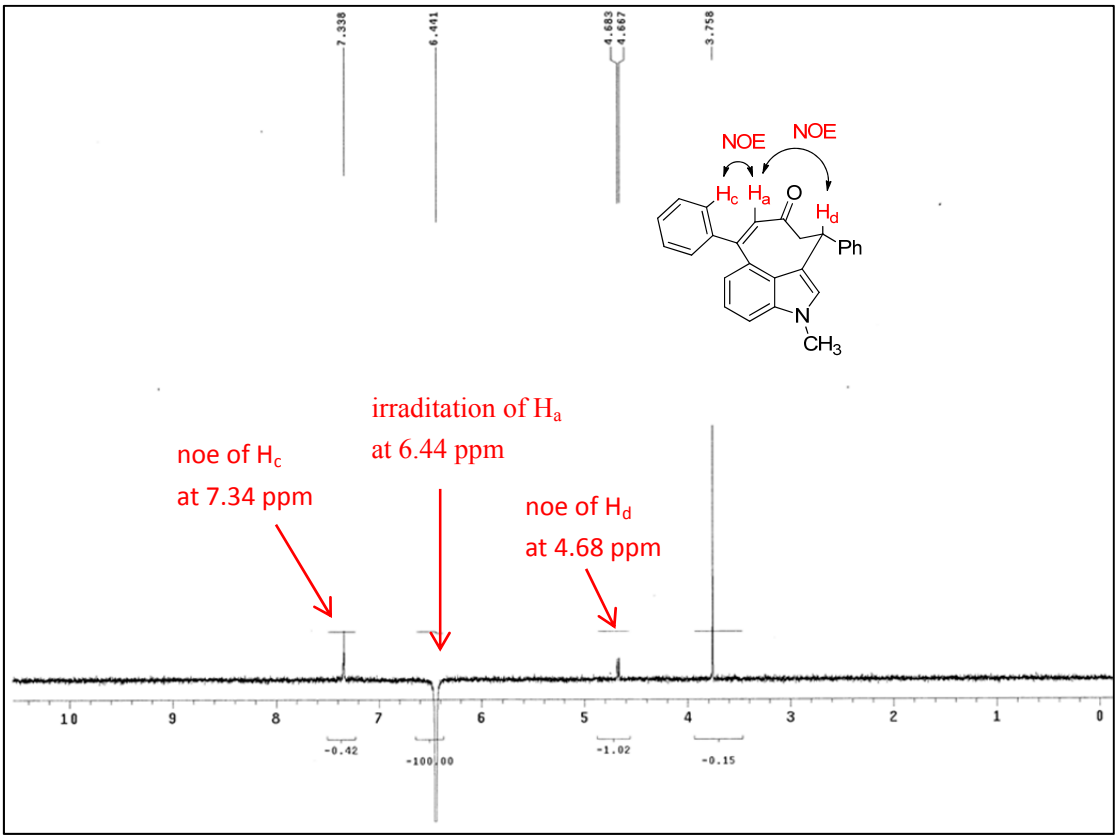


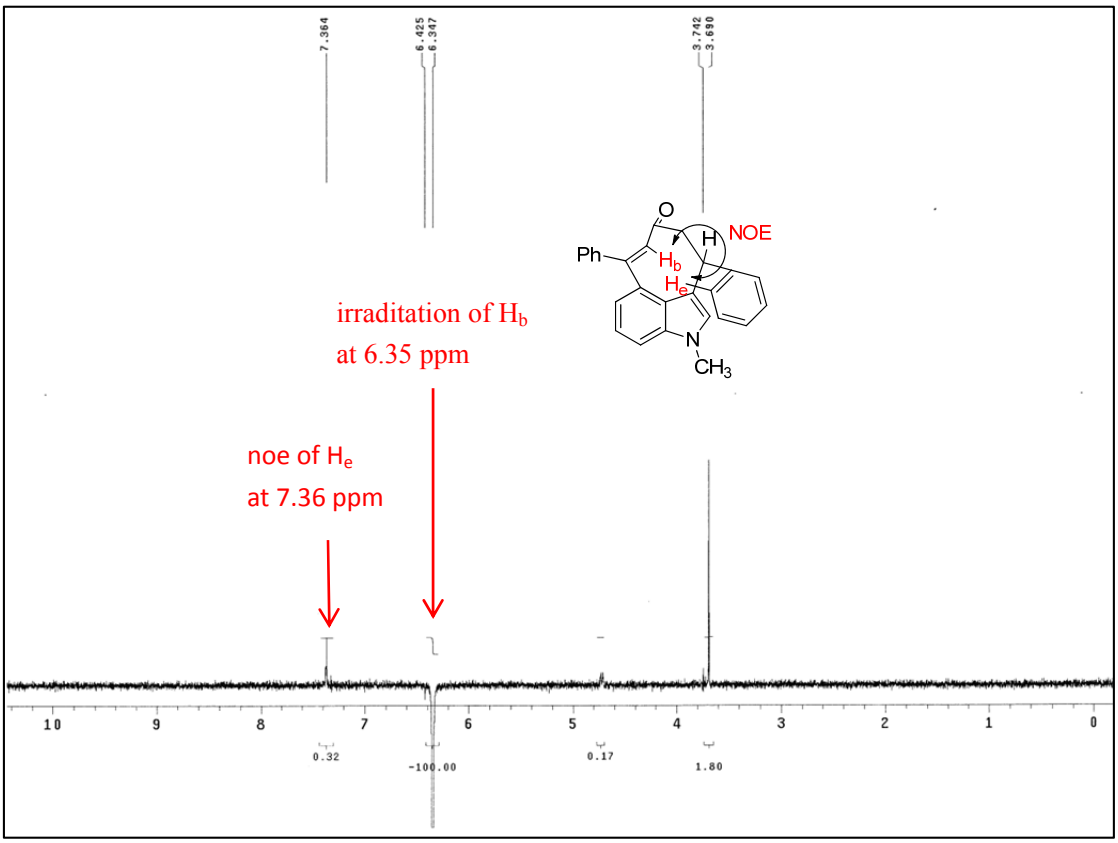
(*Z*)-1-methyl-3,7-diphenyl-3,4-dihydrocycloocta[*cd*]indol-5(1*H*)-one (**8c**) & (*E*)-1-methyl-3,7-diphenyl-3,4-dihydrocycloocta[*cd*]indol-5(1*H*)-one (**8d**), (**8c** : **8d** = 2 : 1). 18 h, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.29 (m, 8H, **8c** and 3H, **8d**), 7.28-7.24 (m, 2H, **8c** and 1H, **8d**), 7.18-7.15 (m, 3H, **8c** and 2H, **8d**), 7.06-7.02 (m, 1H, **8c**), 6.95-6.92 (m, 1H, **8d**), 6.43 (s, 1H, **8c**), 6.35 (s, 1H, **8d**), 4.74-4.71 (m, 1H, **8d**), 4.66 (d, J = 10.4 Hz, 1H, **8c**), 3.74 (s, 3H, **8c**), 3.69 (s, 2H, **8d**), 3.56-3.48 (m, 2H, **8c**), 3.26-3.20 (m, H, **8d**) ppm. ESI HRMS (**8c**): calcd. for $C_{26}H_{21}NO$+Na 386.1521, found 386.1521.

Structure Determination

The structure of compound **8c** and compound **8d** were determined by NOE




7.338
6.441
4.683
4.667
3.758
NOE
NOE
Hc Ha
O
Hd
Ph
N
CH3
irraditation of Ha
at 6.44 ppm
noe of Hc
at 7.34 ppm
noe of Hd
at 4.68 ppm
10 9 8 7 6 5 4 3 2 1 0
-0.42
-100.00
-1.02
-0.15


7.364
6.425
6.347
3.742
3.690
O
NOE
H
Ph
Hb
He
N
CH3
irraditation of Hb
at 6.35 ppm
noe of He
at 7.36 ppm
10 9 8 7 6 5 4 3 2 1 0
0.32
-100.00
0.17
1.80

Reference

[1] J. M. Fraile, K. L. Jeune, J. A. Mayoral, N. Ravasio, F. Zaccheria, *Org. Biomol. Chem.*, **2013**, *11*, 4327.

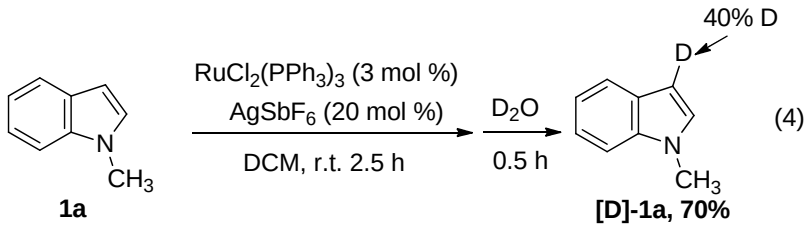
[2] L.-J Zhang, X.-X Xu, Q.-R Shao, L. Pan, Q. Liu, *Org. Biomol. Chem.*, **2013**, *11*, 7393; F. D. Therkelsen, A. L. Hansen, E. B. Pedersen, C. Nielsen, *Org. Biomol. Chem.*, **2003**, *1*, 2908.

[3] a) M. Mari, F. Bartoccini, G. Piersanti, *J. Org. Chem.* **2013**, *78*, 7727; b) R. J. Rafferty, R. M. Williams, *J. Org. Chem.* **2012**, *77*, 519.

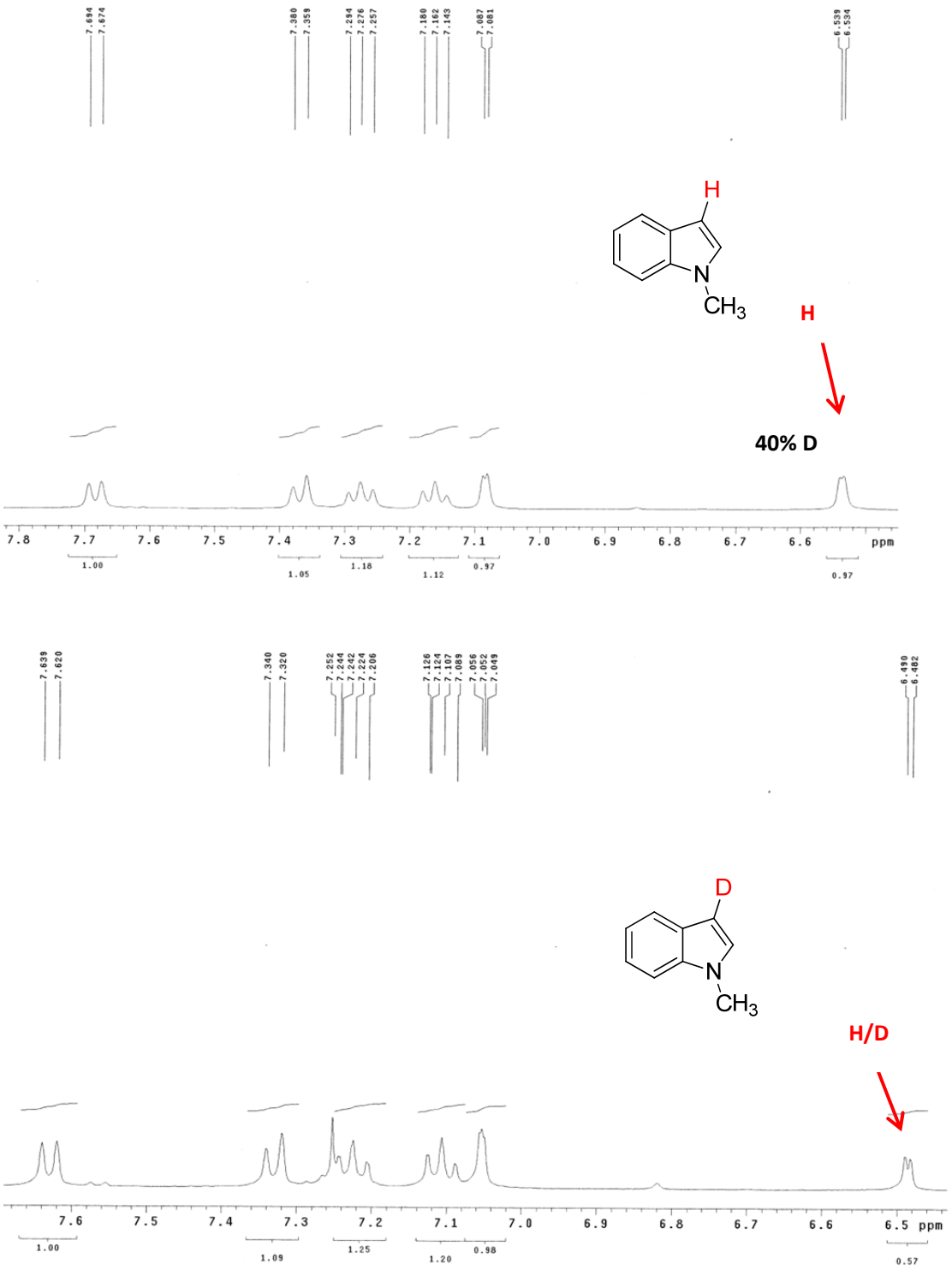
[4] a) S. Fujita, T. Tanaka, Y. Akiyama, K. Asai, J. Hao, F. Zhao, and M. Araia, *Adv. Synth. Catal.* **2008**, *350*, 1615; b) A. Mansour, M. Portnoy, *Tetrahedron Lett.* **2003**, *44*, 2195; c) H.- J. Li, L. Wang, *Eur. J. Org. Chem*. **2006**, 5099.

4. Mechanism Study

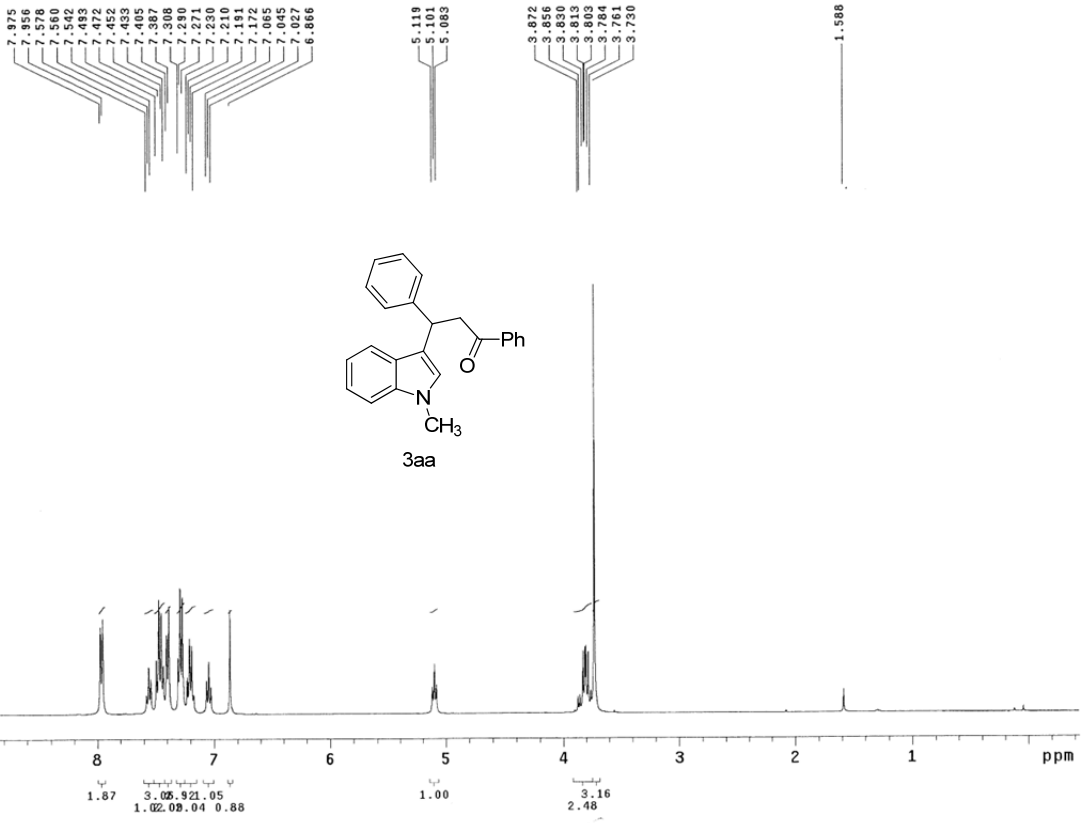
Deuterium-labeling experiments were carried out to study the mechanism of this alkylation reaction. **1a** was stirred in the absence of alkynes for 2.5 h, then D_2O was added and stirred for 0.5 h. ^{1}HNMR indicated the possibility of the reaction pathway via C-H activation.



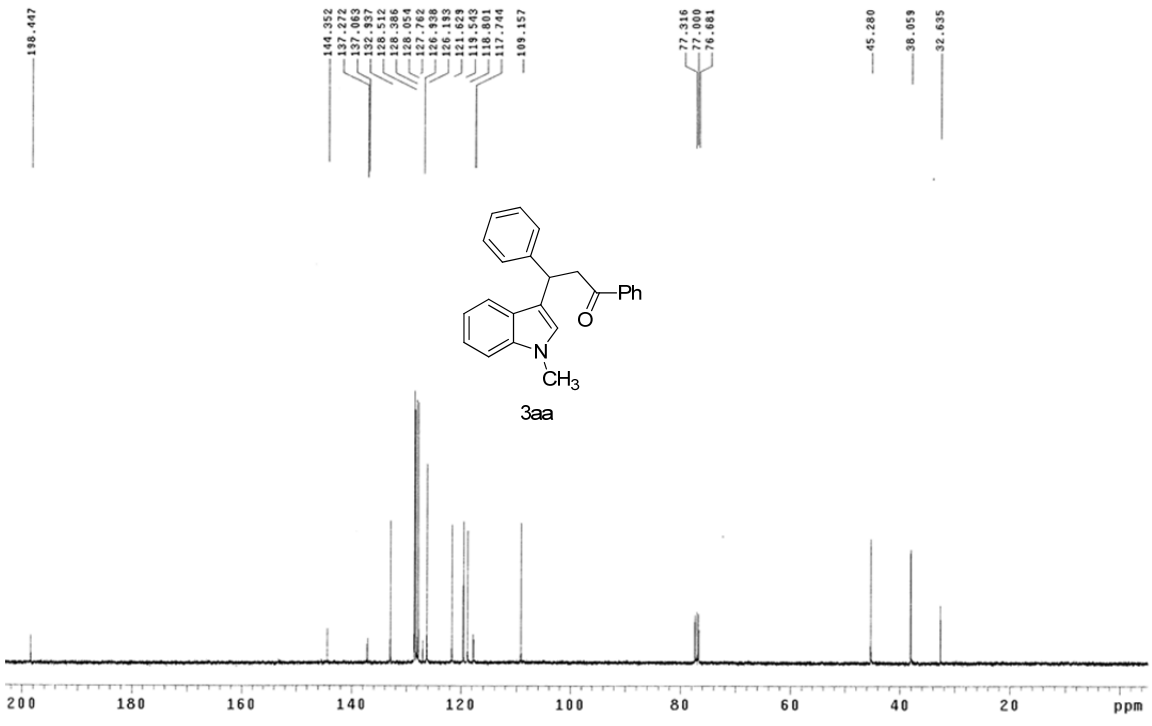
(4)



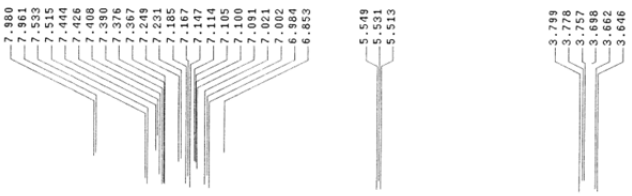
5. NMR Spectra of 3-alkyl indole

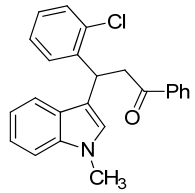

7.975
7.956
7.578
7.560
7.542
7.493
7.472
7.452
7.433
7.405
7.387
7.308
7.290
7.271
7.230
7.210
7.191
7.172
7.065
7.045
7.027
6.866
5.119
5.101
5.083
3.872
3.856
3.830
3.813
3.803
3.784
3.761
3.730
1.588
Ph
O
N
CH3
9
8
7
6
5
4
3
2
1
ppm
1.87
1.00
3.16
2.48

3aa

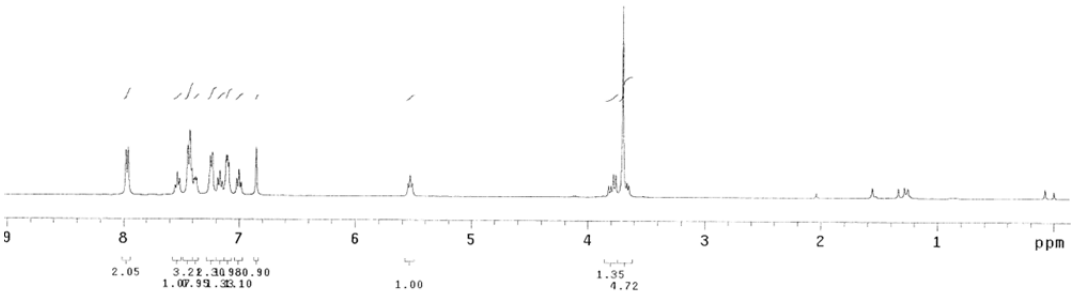

198.447
144.352
137.272
137.063
132.937
128.512
128.386
128.054
127.762
126.198
125.853
121.623
119.543
118.801
117.744
109.157
77.316
77.000
76.681
45.280
38.059
32.635
Ph
O
N
CH3
200
180
160
140
120
100
80
60
40
20
ppm

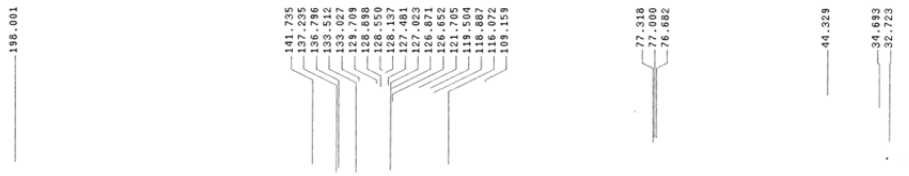
3aa

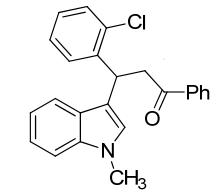

7.980
7.961
7.533
7.515
7.444
7.426
7.408
7.390
7.376
7.367
7.249
7.231
7.185
7.167
7.147
7.114
7.105
7.100
7.091
7.021
7.002
6.984
6.853
5.549
5.531
5.513
3.799
3.778
3.757
3.698
3.662
3.646


Cl
Ph
O
N
CH3

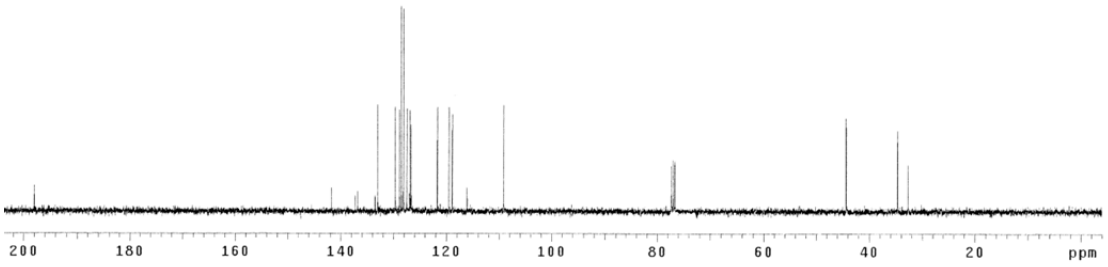
3ab

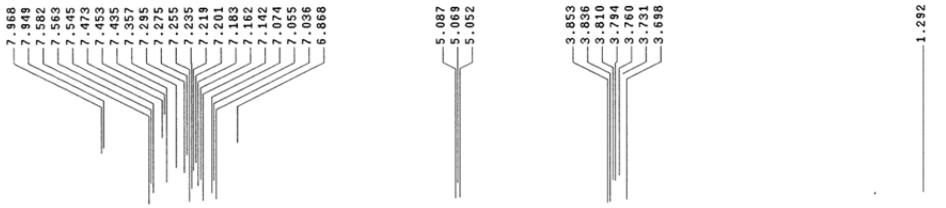

9
8
7
6
5
4
3
2
1
ppm
2.05
1.00
1.35
4.72

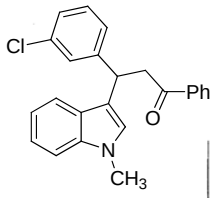

198.001
141.735
137.235
136.796
133.512
133.027
129.709
128.898
128.550
128.137
127.481
127.023
126.871
126.652
121.705
119.504
118.887
116.072
109.159
77.318
77.000
76.682
44.329
34.693
32.723


Cl
Ph
O
N
CH3

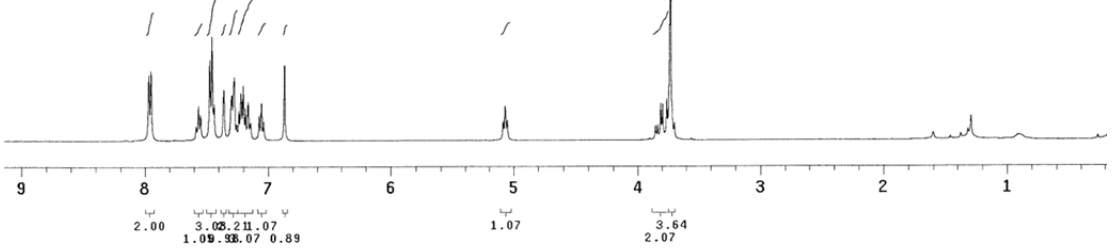
3ab

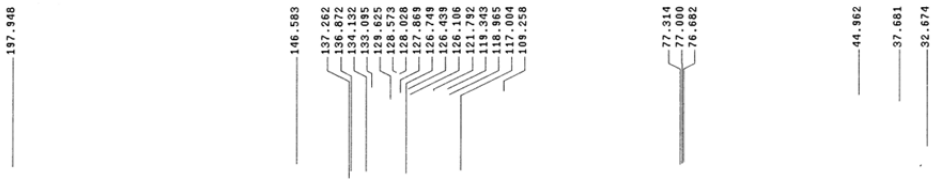

200
180
160
140
120
100
80
60
40
20
ppm

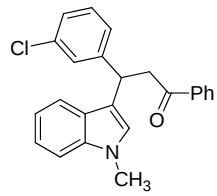

7.968
7.949
7.582
7.563
7.545
7.473
7.453
7.435
7.357
7.295
7.275
7.255
7.235
7.219
7.201
7.183
7.162
7.142
7.074
7.055
7.036
6.868
5.087
5.069
5.052
3.853
3.836
3.810
3.794
3.760
3.731
3.698
1.292


Cl
Ph
O
N
CH3

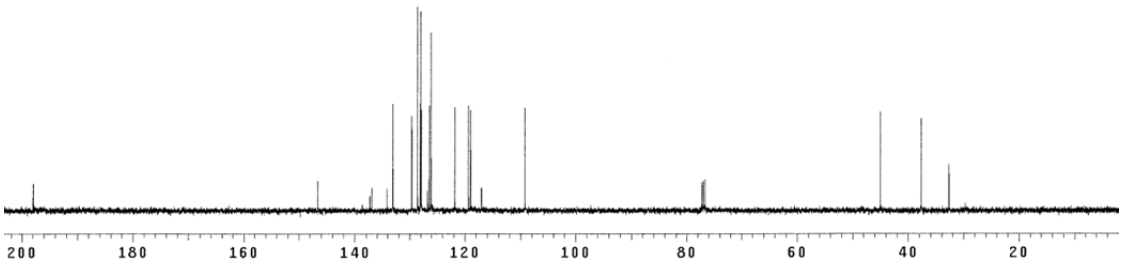
3ac

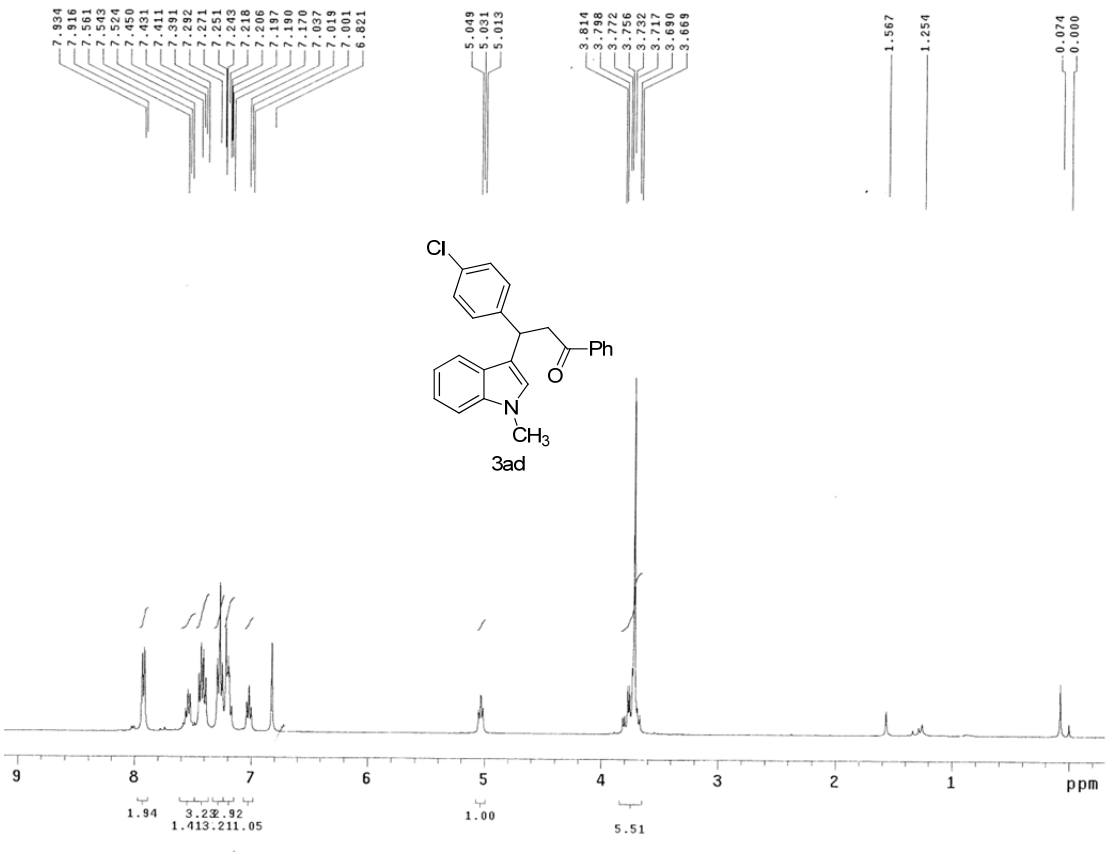

9
8
7
6
5
4
3
2
1
2.00
1.07
3.64
2.07

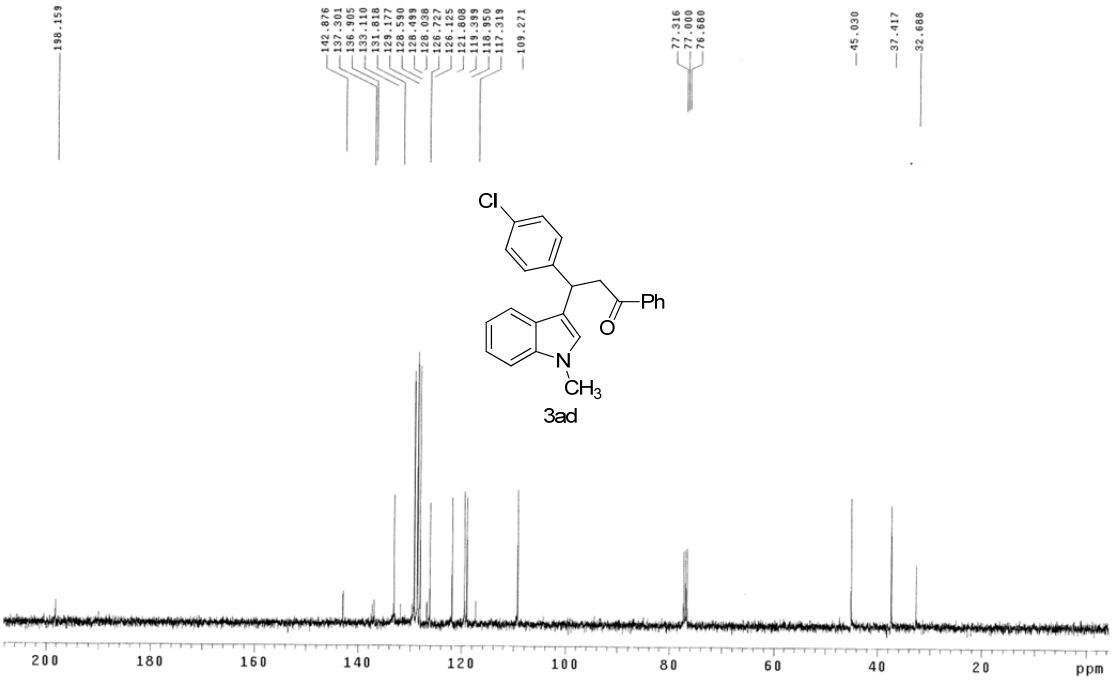

197.948
146.583
137.262
136.872
134.132
133.095
129.625
128.573
128.028
127.668
127.248
126.439
126.106
121.792
119.343
118.965
117.004
109.258
77.314
77.000
76.682
44.962
37.681
32.674

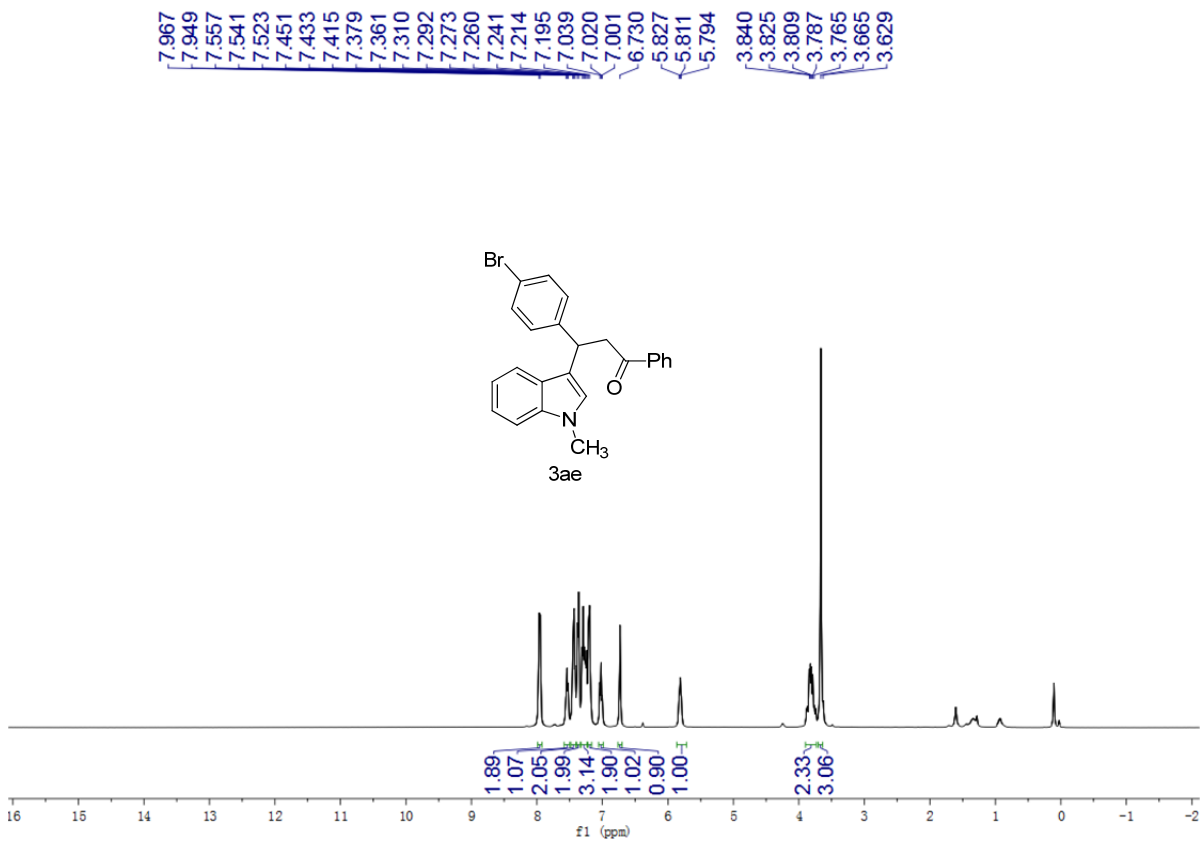

Cl
Ph
O
N
CH3

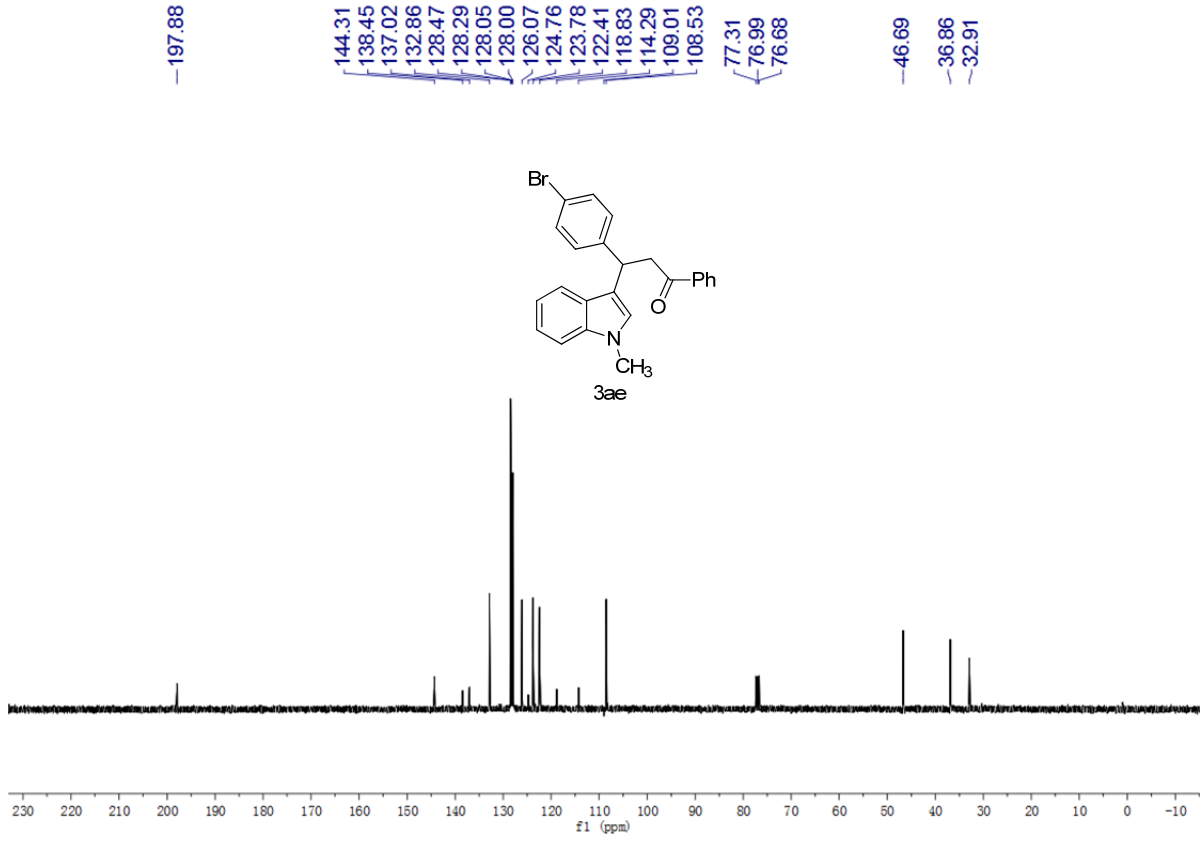
3ac

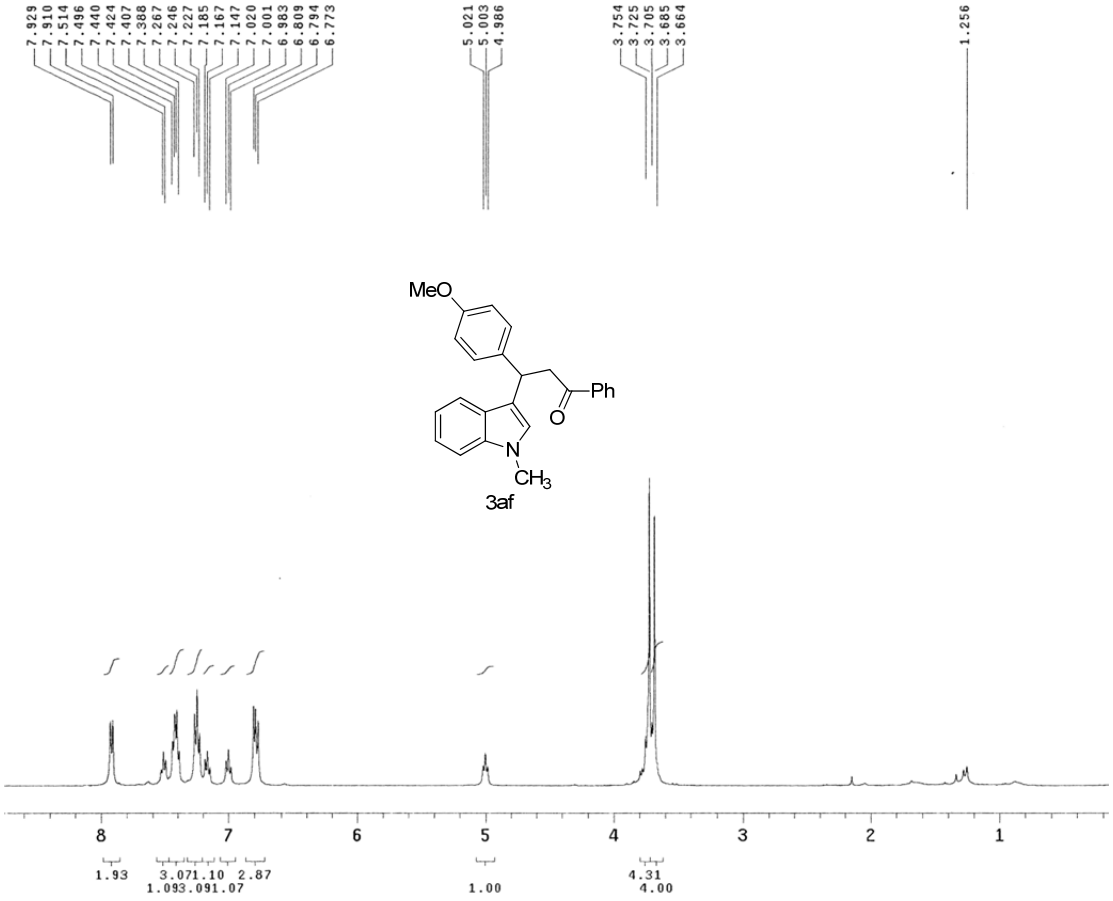

200
180
160
140
120
100
80
60
40
20

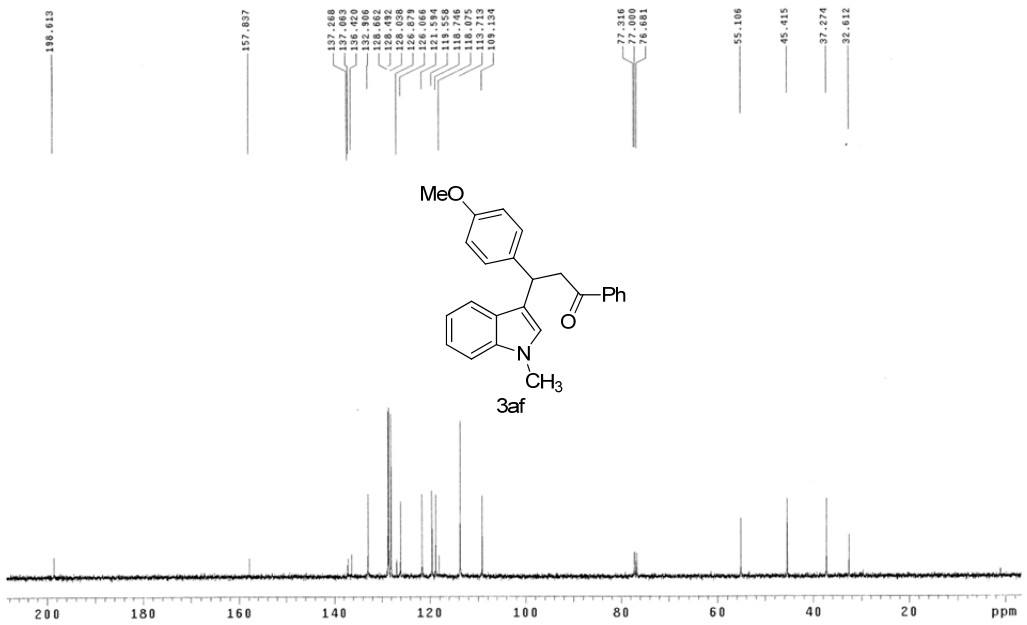

7.934
7.916
7.561
7.543
7.524
7.450
7.431
7.411
7.391
7.292
7.271
7.251
7.243
7.218
7.206
7.197
7.190
7.170
7.037
7.019
7.001
6.821
5.049
5.031
5.013
3.814
3.798
3.772
3.756
3.732
3.717
3.690
3.669
1.567
1.254
0.074
0.000
Cl
Ph
O
N
CH3
3ad
9
8
7
6
5
4
3
2
1
ppm
1.94
3.23
2.92
1.41
3.21
1.05
1.00
5.51

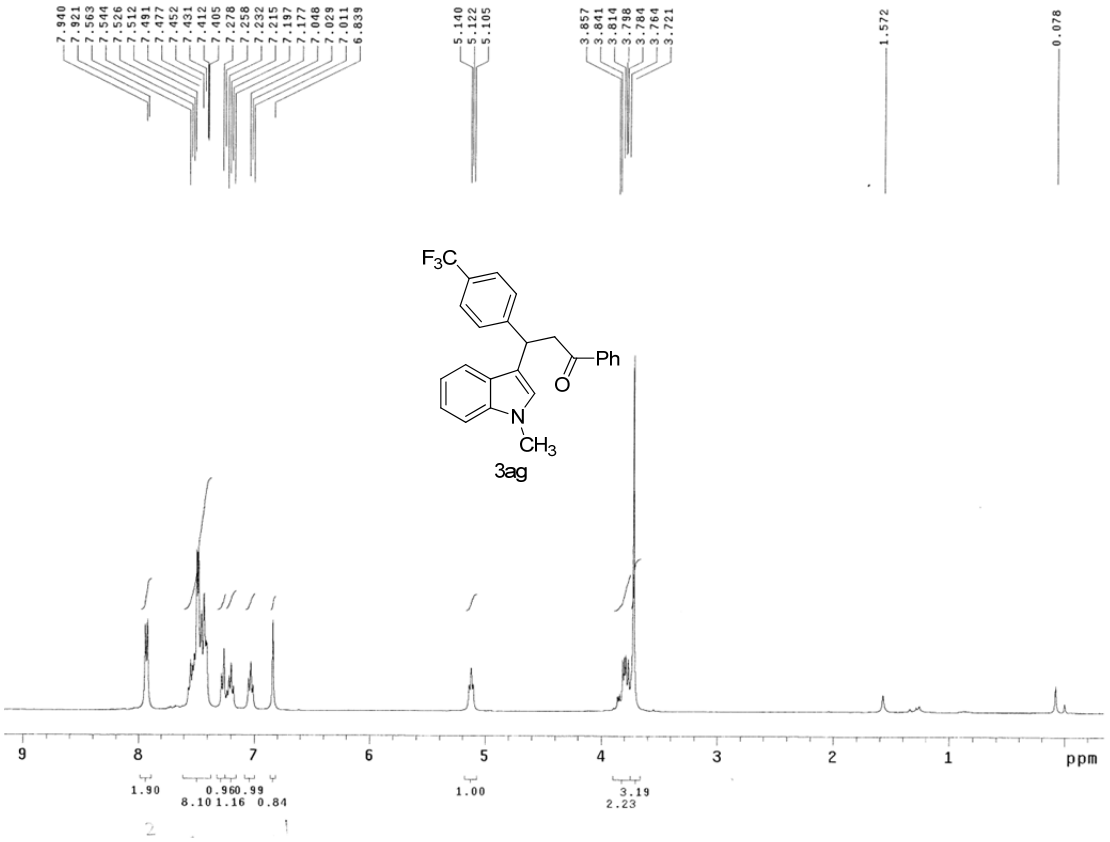

198.159
142.876
137.301
136.905
133.110
131.818
129.177
128.590
128.499
128.038
126.727
126.125
121.608
119.399
118.950
117.319
109.271
77.316
77.000
76.680
45.030
37.417
32.688
Cl
Ph
O
N
CH3
3ad
200
180
160
140
120
100
80
60
40
20
ppm

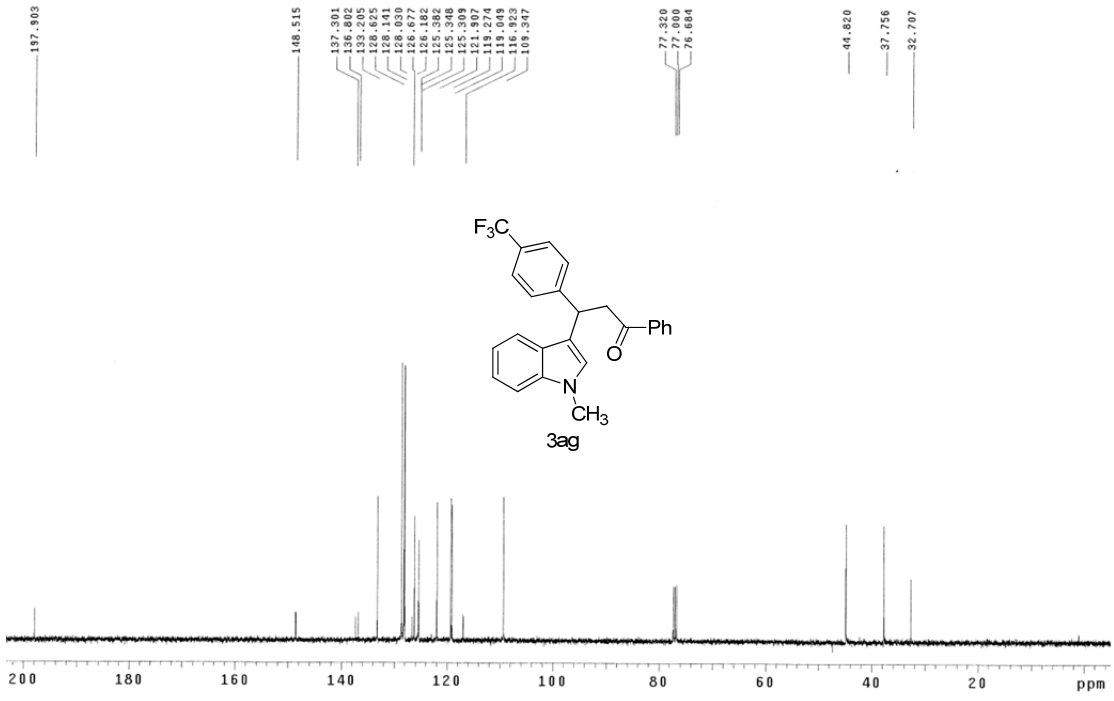

7.967
7.949
7.557
7.541
7.523
7.451
7.433
7.415
7.379
7.361
7.310
7.292
7.273
7.260
7.241
7.214
7.195
7.039
7.020
7.001
6.730
5.827
5.811
5.794
3.840
3.825
3.809
3.787
3.765
3.665
3.629
Br
Ph
O
N
CH3
3ae
1.89
1.07
2.05
1.99
3.14
1.90
1.02
0.90
1.00
2.33
3.06
f1 (ppm)

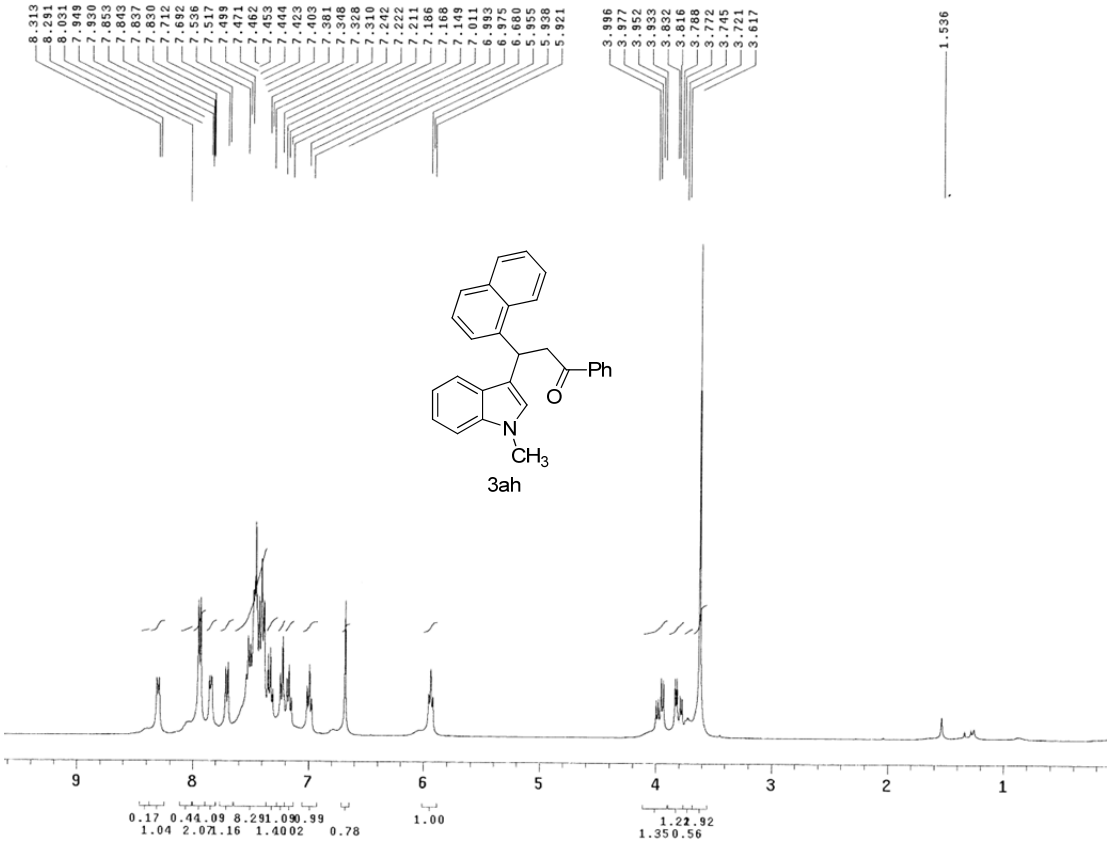

197.88
144.31
138.45
137.02
132.86
128.47
128.29
128.05
128.00
126.07
124.76
123.78
122.41
118.83
114.29
109.01
108.53
77.31
76.99
76.68
46.69
36.86
32.91
Br
Ph
O
N
CH3
3ae
f1 (ppm)

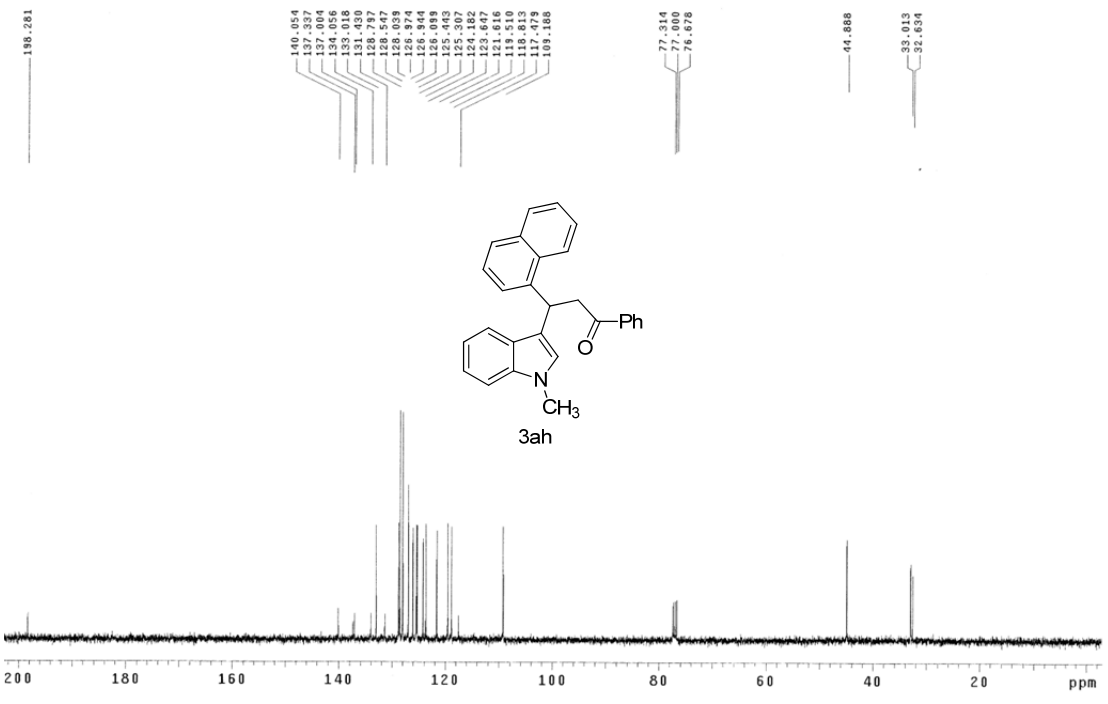

7.929
7.910
7.514
7.496
7.440
7.424
7.407
7.388
7.267
7.246
7.227
7.185
7.167
7.147
7.020
7.001
6.983
6.809
6.794
6.773
5.021
5.003
4.986
3.754
3.725
3.705
3.685
3.664
1.256
MeO
Ph
O
N
CH3
3af
8
7
6
5
4
3
2
1
1.93
3.071.10
2.87
1.093.091.07
1.00
4.31
4.00

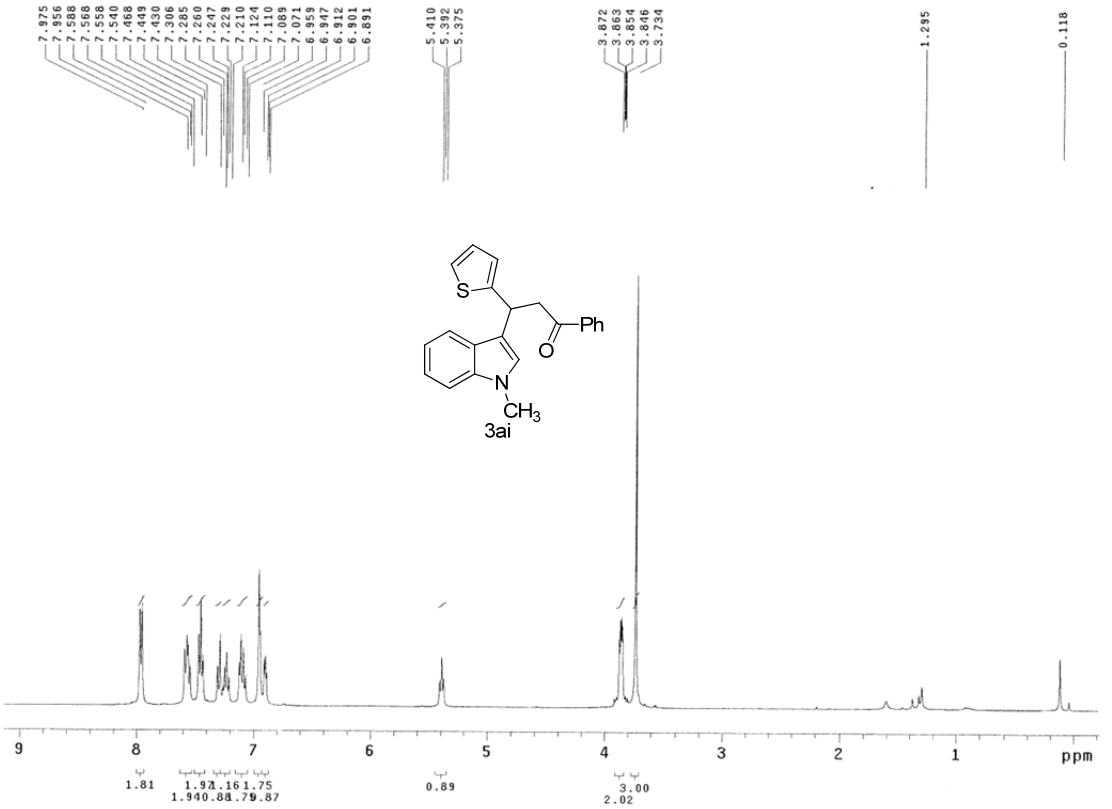

198.613
157.837
137.268
137.063
136.420
132.886
128.662
128.492
128.038
126.079
125.666
121.594
119.558
118.746
118.075
113.733
109.134
77.316
77.000
76.681
55.106
45.415
37.274
32.612
MeO
Ph
O
N
CH3
3af
200
180
160
140
120
100
80
60
40
20
ppm

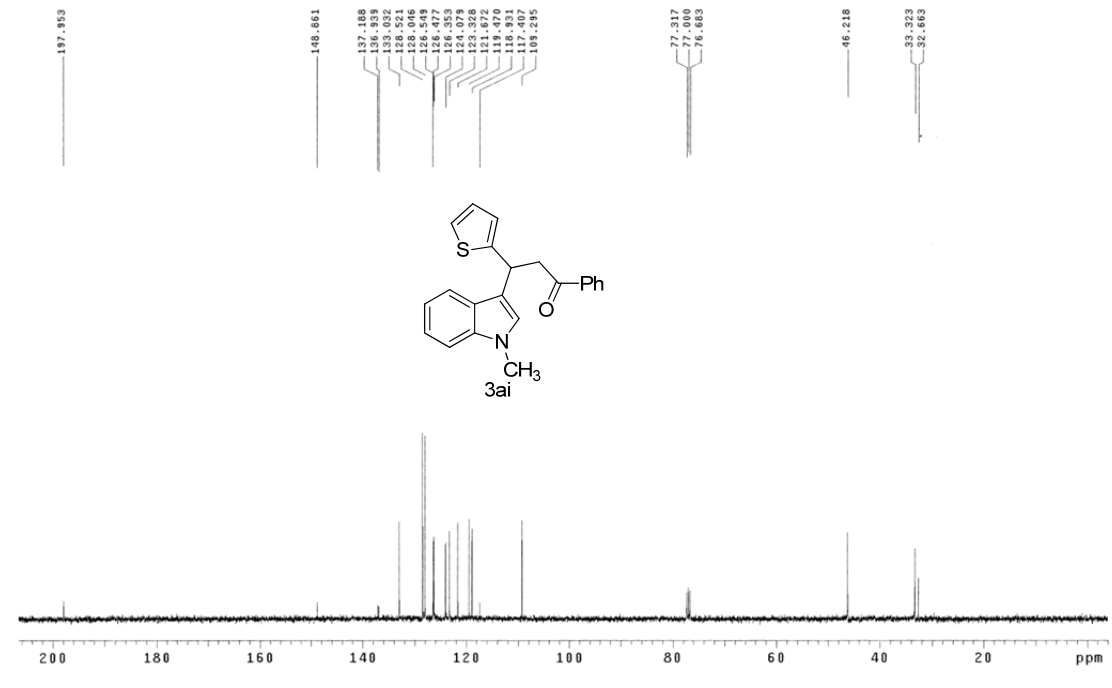

7.840
7.821
7.563
7.544
7.526
7.512
7.491
7.477
7.452
7.431
7.412
7.405
7.278
7.258
7.232
7.215
7.197
7.177
7.048
7.029
7.011
6.839
5.140
5.122
5.105
3.857
3.841
3.814
3.798
3.784
3.764
3.721
1.572
0.078
F3C
Ph
O
N
CH3
3ag
9
8
7
6
5
4
3
2
1
ppm
1.90
0.96
0.99
8.10
1.16
0.84
1.00
3.19
2.23

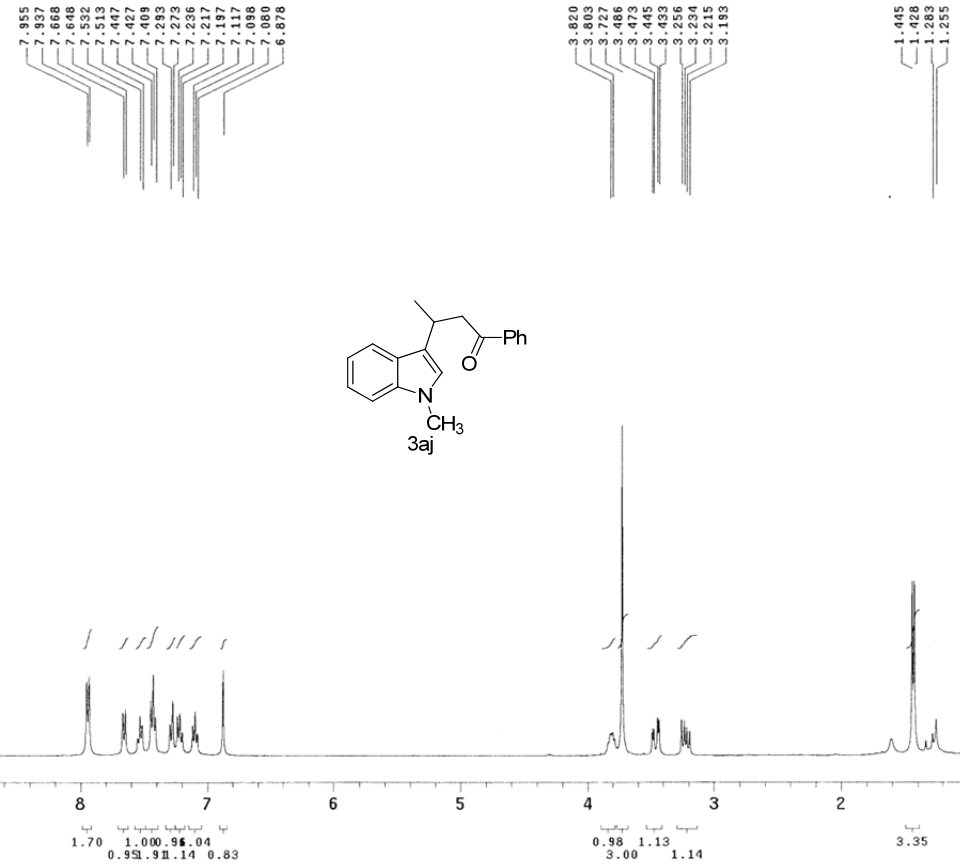

197.903
148.515
137.301
136.802
133.205
128.625
128.141
128.030
126.677
125.382
125.348
125.309
121.907
119.274
119.049
116.923
109.347
77.320
77.000
76.684
44.820
37.756
32.707
F3C
Ph
O
N
CH3
3ag
200
180
160
140
120
100
80
60
40
20
ppm

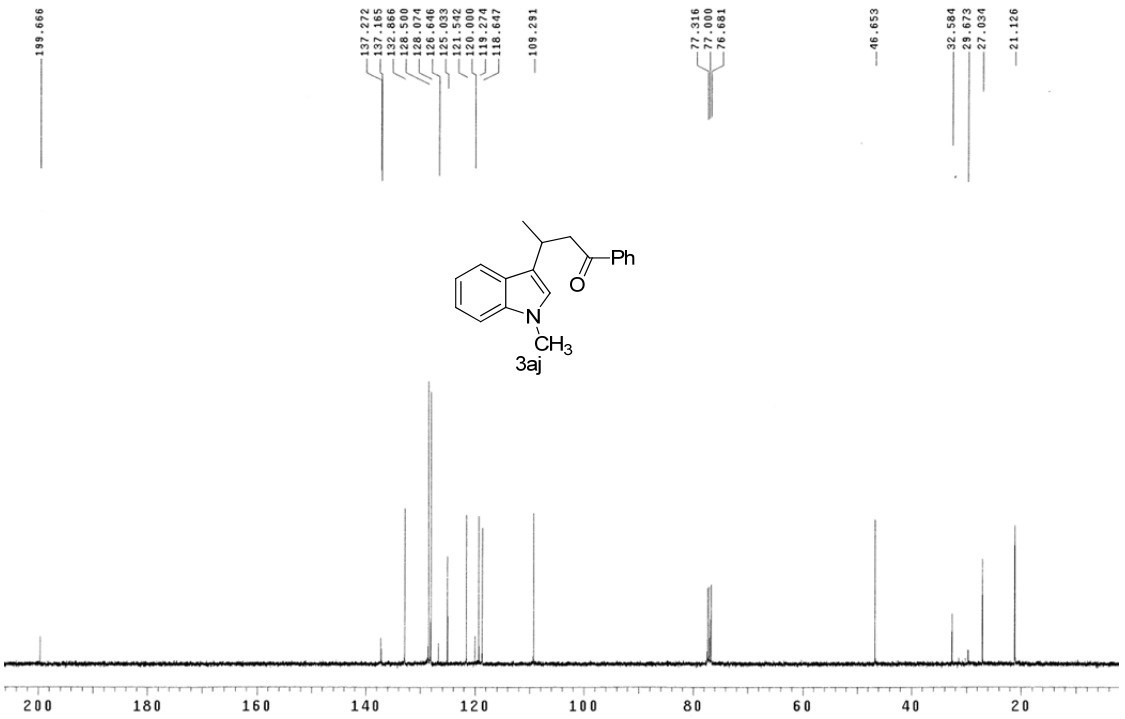

8.313
8.291
8.031
7.949
7.930
7.853
7.843
7.837
7.830
7.712
7.692
7.536
7.517
7.498
7.471
7.462
7.453
7.444
7.423
7.403
7.381
7.348
7.328
7.310
7.242
7.222
7.211
7.186
7.168
7.149
7.011
6.993
6.975
6.680
6.955
5.938
5.921
3.996
3.977
3.952
3.933
3.832
3.816
3.788
3.772
3.745
3.721
3.617
1.536
Ph
O
N
CH3
3ah
9
8
7
6
5
4
3
2
1
0.17 0.44 4.09 8.29 1.09 0.99
1.04 2.07 1.16 1.40 0.78
1.00
1.22 2.92
1.35 0.56

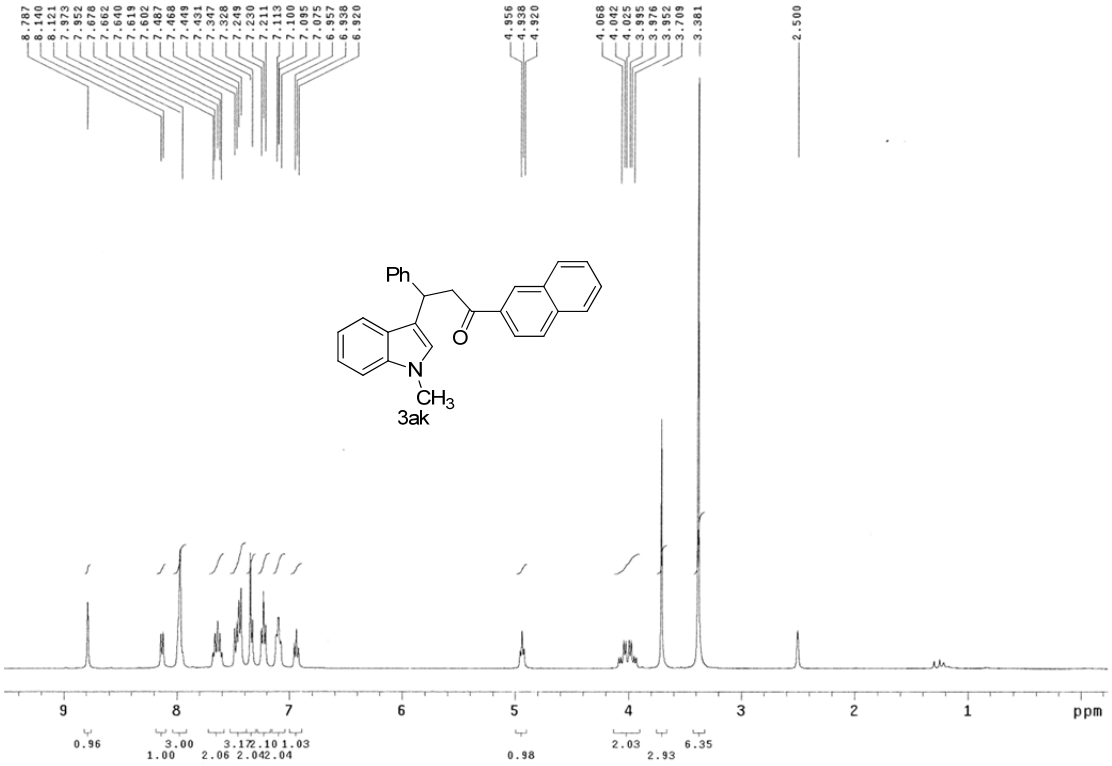

198.281
140.054
137.337
137.004
134.056
133.018
131.430
128.797
128.547
128.039
127.874
126.344
126.099
125.443
125.307
124.182
123.647
121.616
119.510
118.613
111.273
101.186
77.314
77.000
76.678
44.888
33.013
32.634
Ph
O
N
CH3
3ah
200
180
160
140
120
100
80
60
40
20
ppm

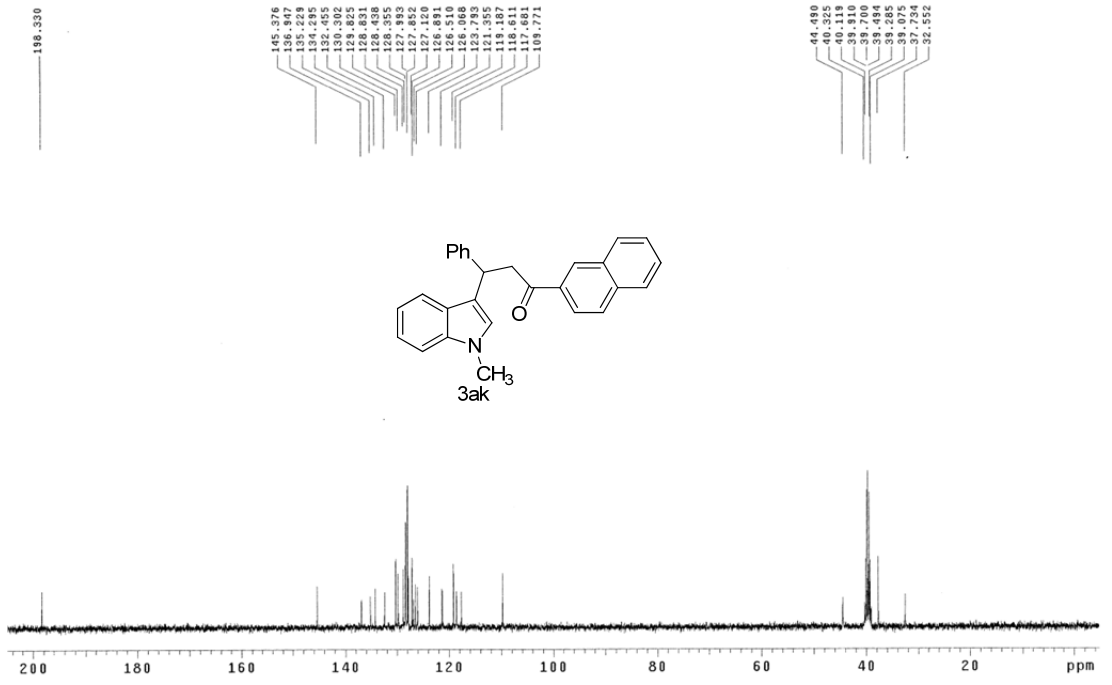

7.975
7.956
7.588
7.568
7.558
7.540
7.468
7.449
7.430
7.306
7.285
7.260
7.247
7.229
7.210
7.124
7.110
7.089
7.071
6.959
6.947
6.912
6.901
6.891
5.410
5.392
5.375
3.872
3.863
3.854
3.846
3.734
1.295
0.118
S
Ph
O
N
CH3
3ai
9
8
7
6
5
4
3
2
1
ppm
1.81
1.97
1.94
1.16
0.88
1.75
1.79
9.87
0.89
3.00
2.02

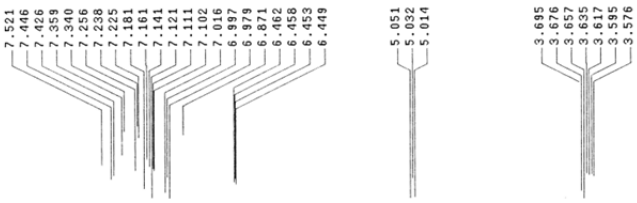

197.953
140.861
137.188
130.839
130.032
128.521
128.046
126.549
126.477
126.353
124.079
123.398
121.672
119.476
118.931
117.407
109.295
77.317
77.000
76.683
46.218
33.323
32.663
S
Ph
O
N
CH3
3ai
200
180
160
140
120
100
80
60
40
20
ppm

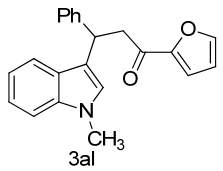

7.955
7.937
7.668
7.648
7.532
7.513
7.447
7.427
7.409
7.293
7.273
7.236
7.217
7.197
7.117
7.098
7.080
6.878
3.820
3.803
3.727
3.486
3.473
3.445
3.433
3.256
3.234
3.215
3.193
1.445
1.428
1.283
1.255
Ph
O
N
CH3
3aj
8
7
6
5
4
3
2
1
1.70
1.00
0.95
1.91
0.96
1.14
1.04
0.83
0.98
3.00
1.13
1.14
3.35


199.666
137.272
137.165
132.866
128.500
128.074
126.646
125.033
121.542
120.000
119.274
118.647
109.291
77.316
77.000
76.681
46.653
32.584
29.673
27.034
21.126
Ph
O
N
CH3
3aj
200
180
160
140
120
100
80
60
40
20

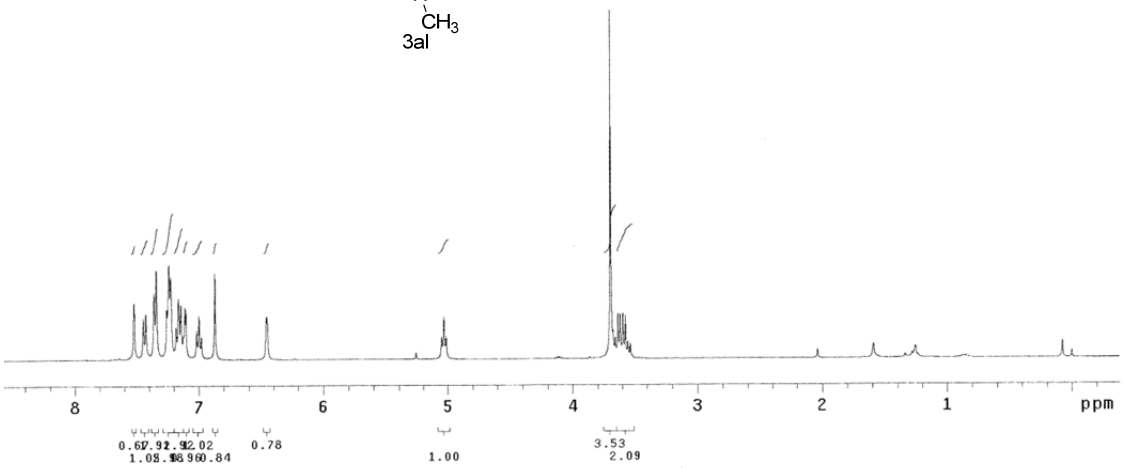

8.787
8.140
8.121
7.973
7.952
7.678
7.662
7.640
7.619
7.602
7.487
7.468
7.446
7.431
7.347
7.328
7.249
7.230
7.211
7.113
7.100
7.095
7.075
6.957
6.938
6.920
4.956
4.938
4.920
4.068
4.042
4.025
3.995
3.976
3.952
3.709
3.381
2.500
Ph
O
N
CH3
3ak
9
8
7
6
5
4
3
2
1
ppm
0.96
3.00
1.00
3.17
2.06
2.10
2.04
1.03
0.98
2.03
2.93
6.35

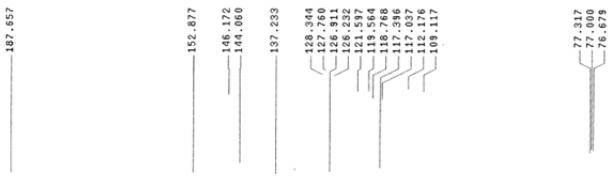

198.330
145.376
136.947
135.229
134.295
132.455
132.302
129.825
128.831
128.438
128.355
127.993
127.852
127.120
126.811
126.510
126.068
123.793
121.355
119.187
118.611
117.681
109.771
44.490
40.325
40.119
39.910
39.700
39.494
39.285
39.075
37.734
32.552
Ph
O
N
CH3
3ak
200
180
160
140
120
100
80
60
40
20
ppm

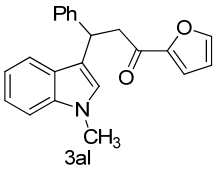

7.521
7.446
7.426
7.359
7.340
7.256
7.238
7.225
7.181
7.161
7.141
7.121
7.111
7.102
7.016
6.997
6.979
6.871
6.462
6.458
6.453
6.449
5.051
5.032
5.014
3.695
3.676
3.657
3.635
3.617
3.595
3.576


Ph
O
O
N
CH3

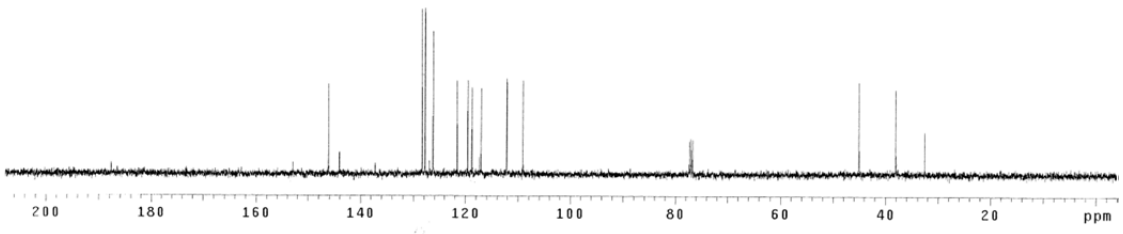
3al

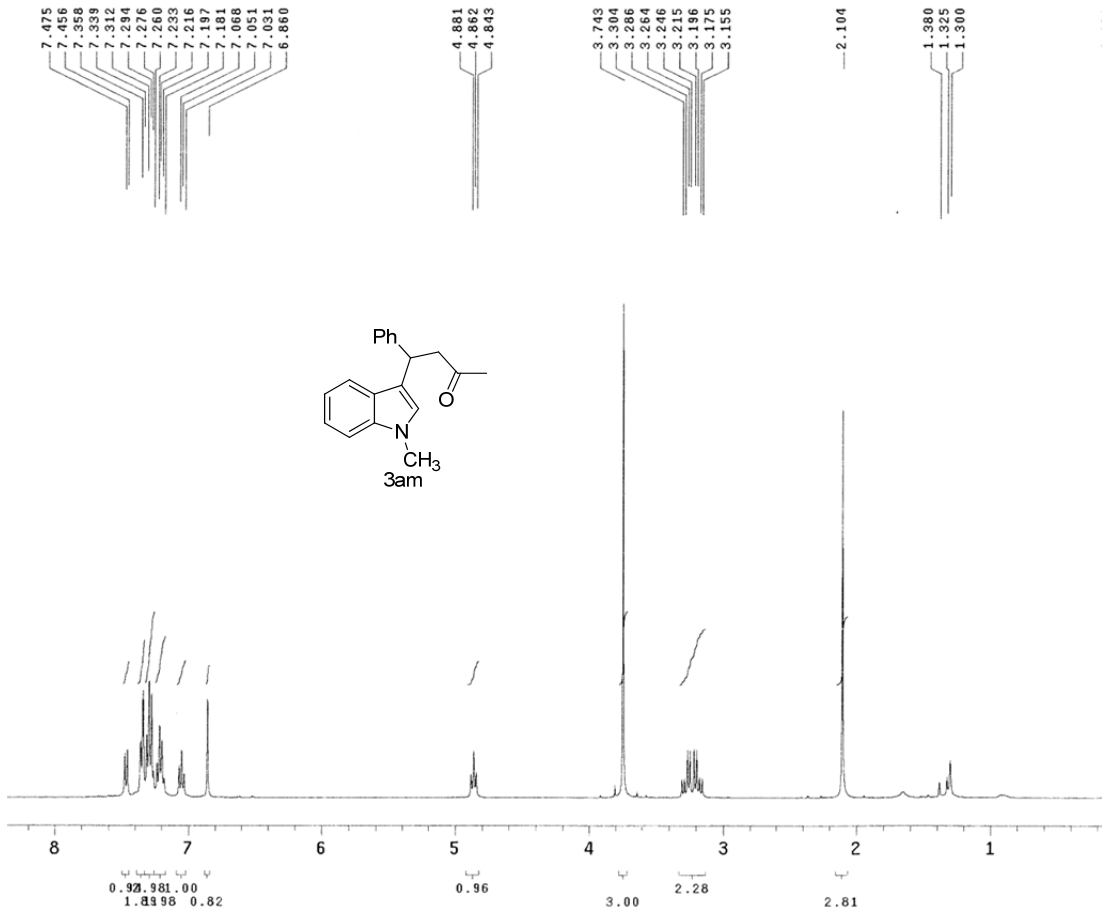

8
7
6
5
4
3
2
1
ppm
0.67
1.08
1.92
1.89
2.02
0.84
0.78
1.00
3.53
2.09

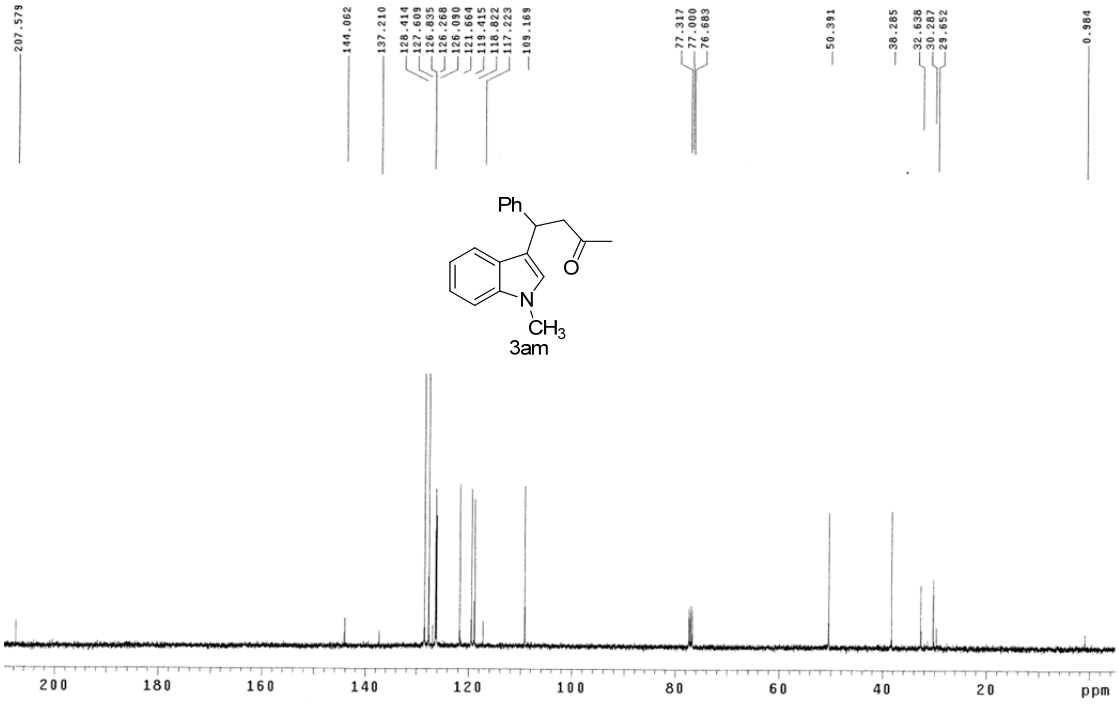

187.657
152.877
146.172
144.060
137.233
128.344
127.760
126.911
126.232
121.597
119.564
118.768
117.396
117.037
112.176
109.117
77.317
77.000
76.679
45.052
38.086
32.641


Ph
O
O
N
CH3

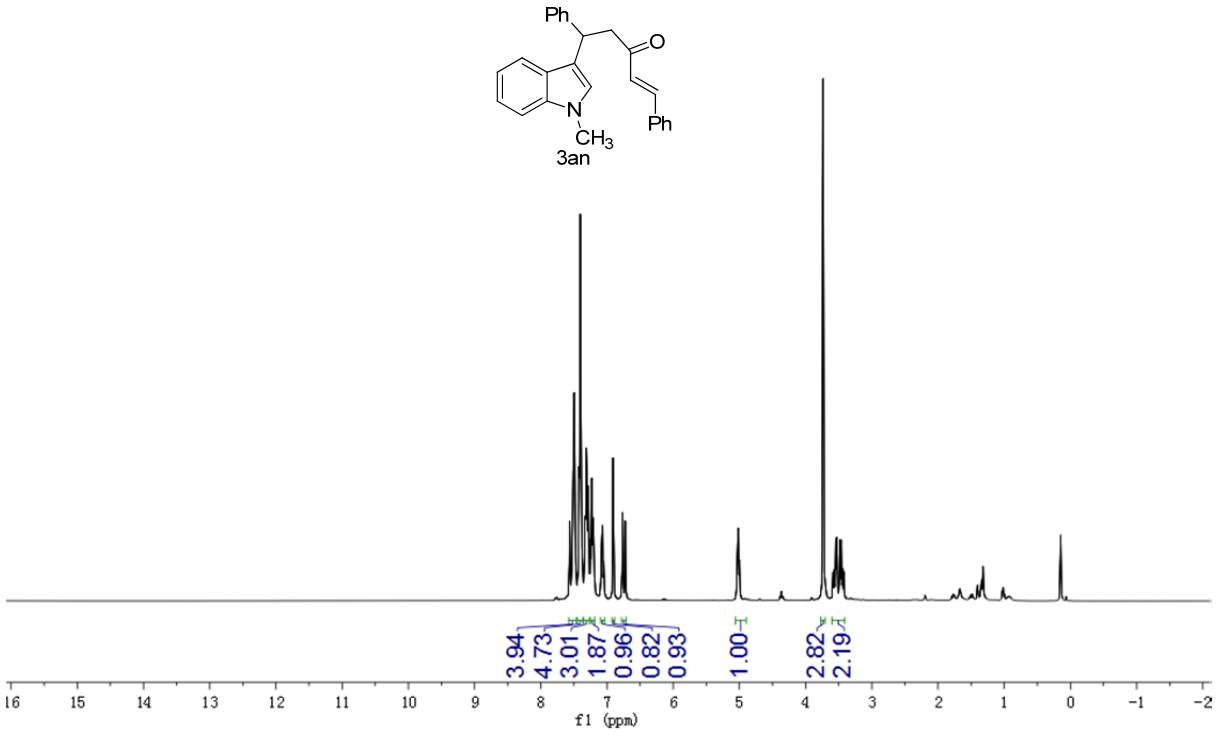
3al


200
180
160
140
120
100
80
60
40
20
ppm

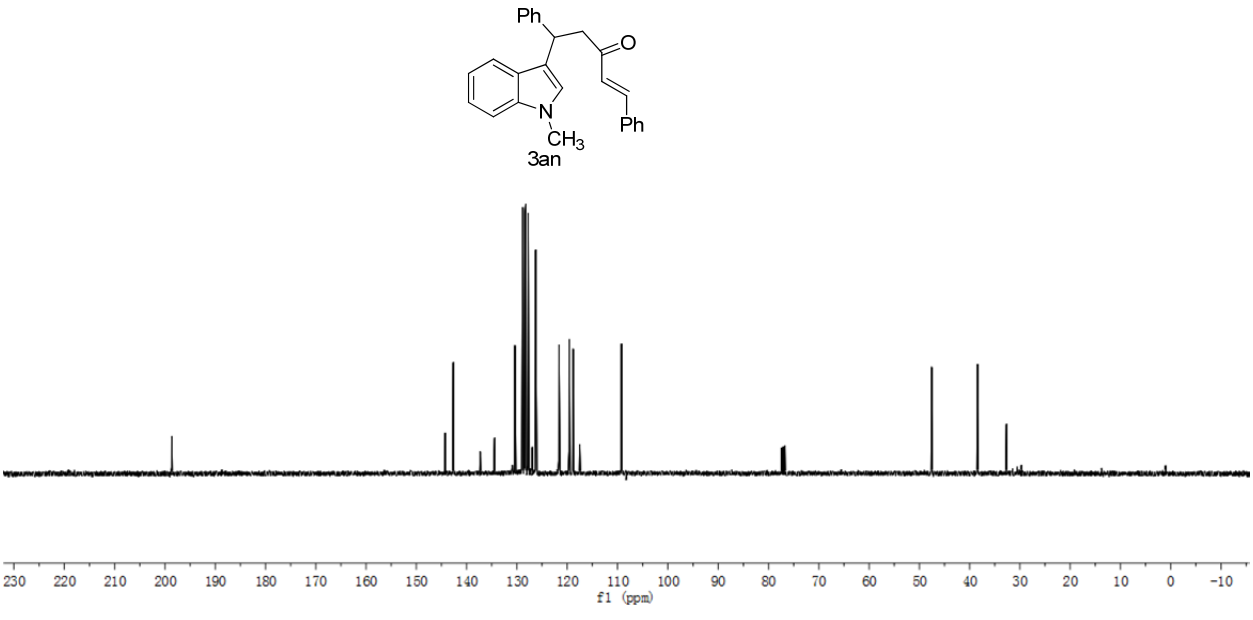

7.475
7.456
7.358
7.339
7.312
7.294
7.276
7.260
7.233
7.216
7.197
7.181
7.068
7.051
7.031
6.860
4.881
4.862
4.843
3.743
3.304
3.286
3.264
3.246
3.215
3.196
3.175
3.155
2.104
1.380
1.325
1.300
Ph
O
N
CH3
3am
8
7
6
5
4
3
2
1
0.96
3.00
2.28
2.81

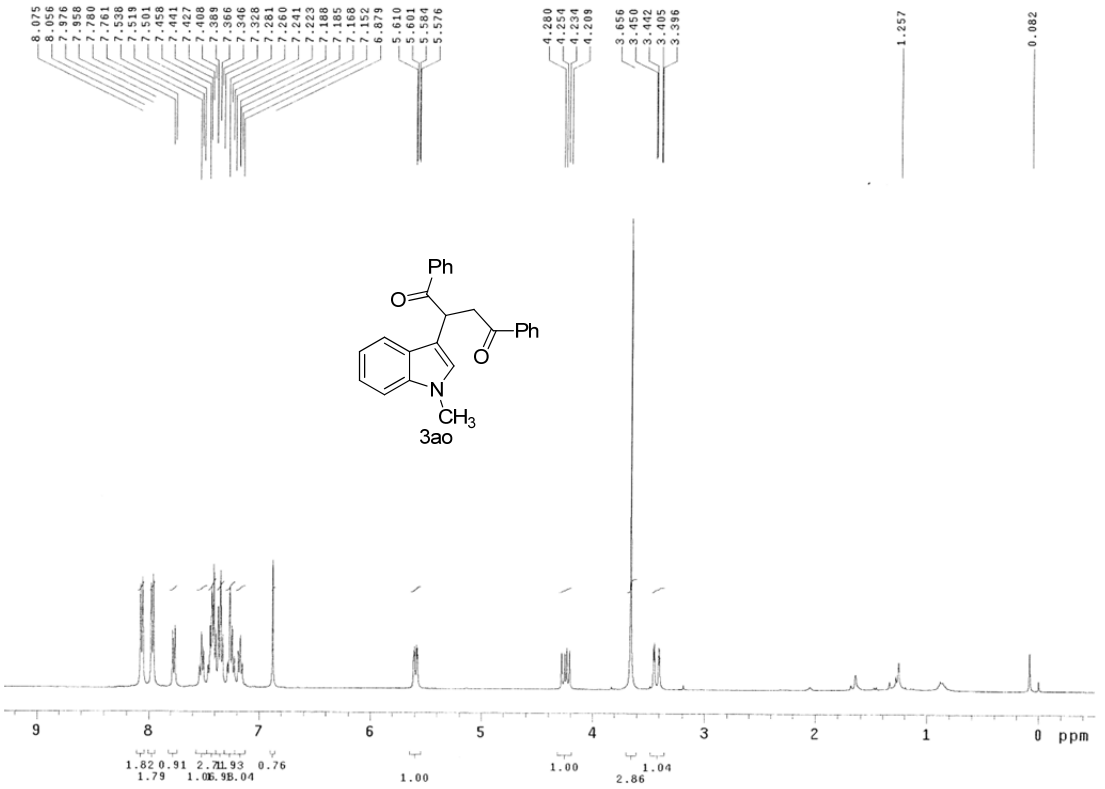

207.579
144.062
137.210
128.414
127.609
126.835
126.268
126.090
121.664
119.415
118.822
117.223
109.169
77.317
77.000
76.683
50.391
38.285
32.638
30.287
29.652
0.984
Ph
O
N
CH3
3am
200
180
160
140
120
100
80
60
40
20
ppm

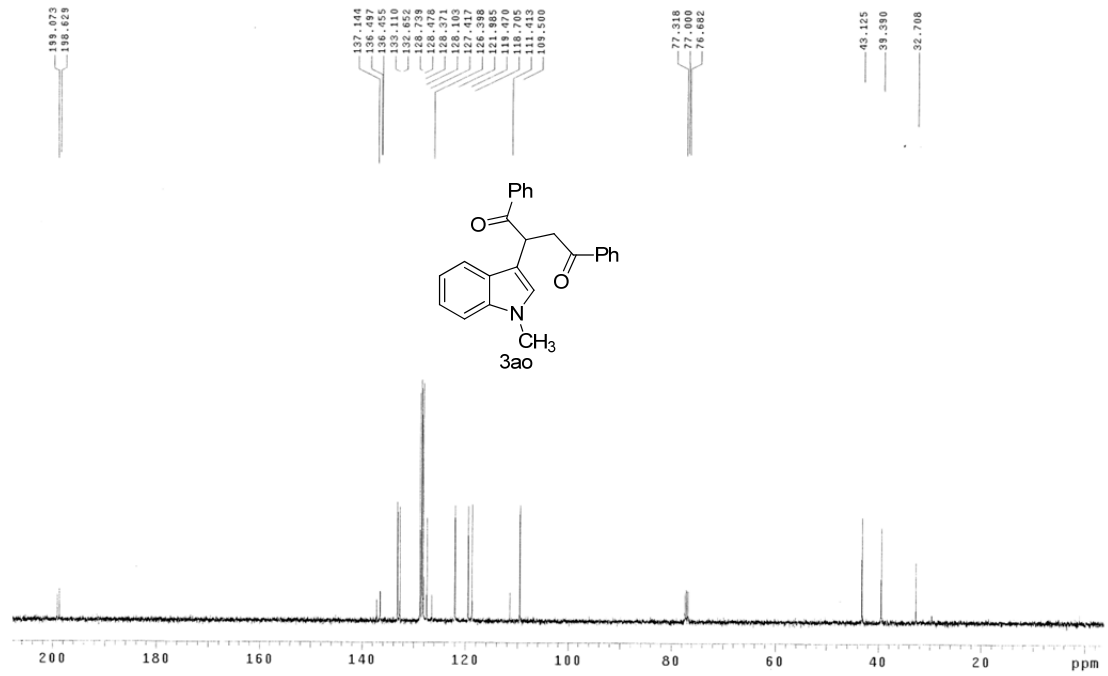

7.562
7.520
7.511
7.494
7.422
7.404
7.333
7.315
7.299
7.282
7.260
7.246
7.228
7.210
7.194
7.086
7.068
7.050
6.907
6.765
6.725
5.036
5.018
5.000
3.736
3.584
3.567
3.545
3.527
3.483
3.463
3.443
3.424

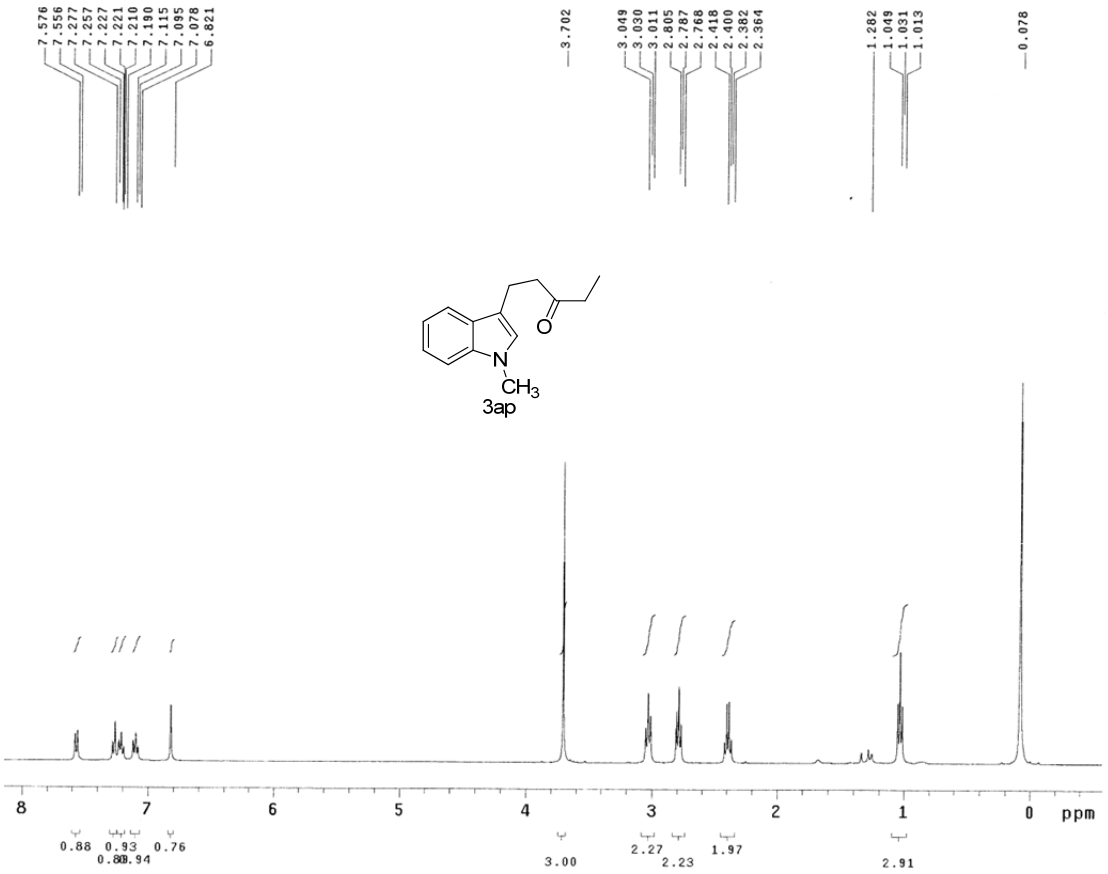

Ph
O
N
CH3
Ph
3an
3.94
4.73
3.01
1.87
0.96
0.82
0.93
1.00
2.82
2.19
f1 (ppm)

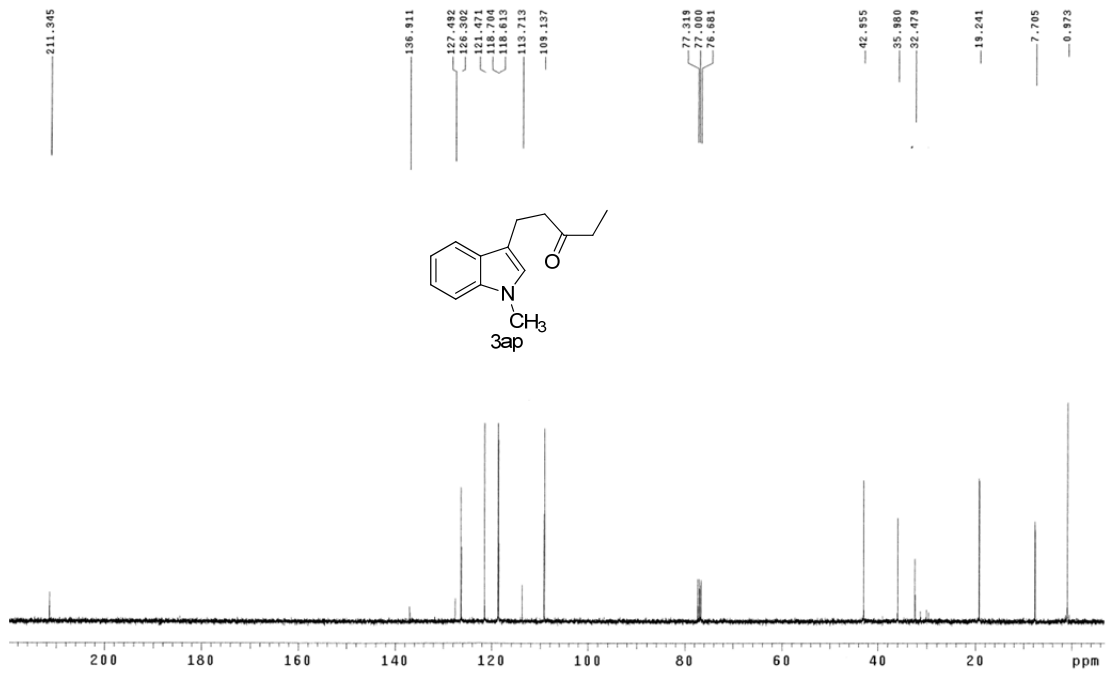

198.62
144.25
142.65
137.30
134.43
130.90
130.41
128.86
128.41
128.24
127.77
126.95
126.26
126.19
121.65
119.61
118.83
117.52
109.20
77.37
77.05
76.74
47.55
38.44
32.66

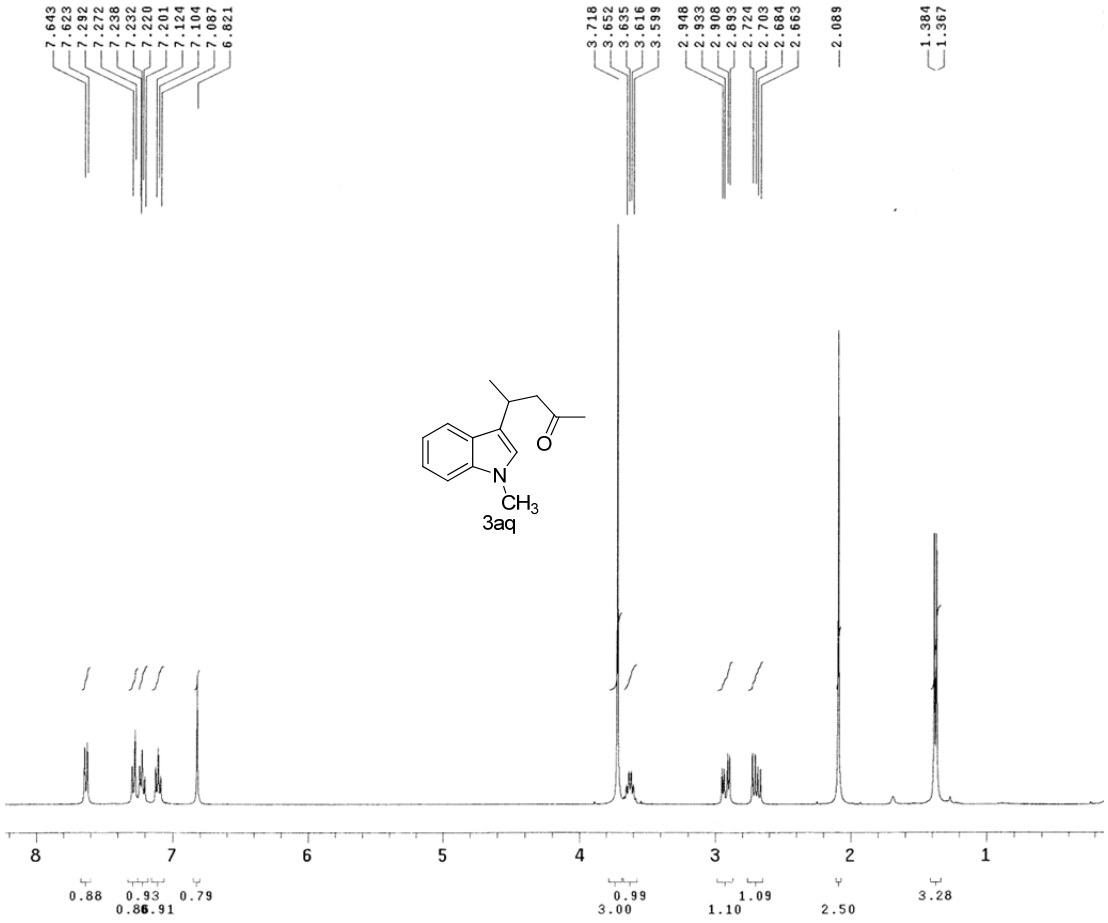

Ph
O
N
CH3
Ph
3an
f1 (ppm)

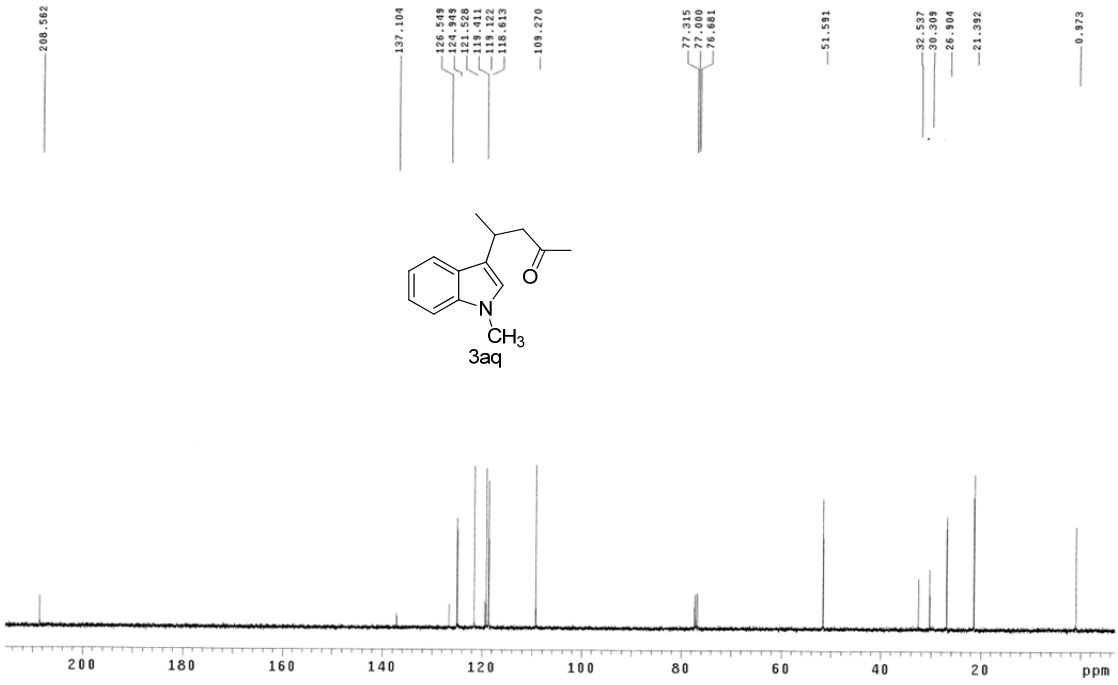

8.075
8.056
7.976
7.958
7.780
7.761
7.538
7.519
7.501
7.458
7.441
7.427
7.408
7.389
7.366
7.346
7.328
7.281
7.260
7.241
7.223
7.188
7.185
7.168
7.152
6.879
5.610
5.601
5.584
5.576
4.280
4.254
4.234
4.209
3.656
3.450
3.442
3.405
3.396
1.257
0.082
Ph
O
Ph
O
N
CH3
3ao
9
8
7
6
5
4
3
2
1
0 ppm
1.82 0.91 2.71 1.93 0.76
1.79 1.00 6.98.04
1.00
1.00
1.04
2.86

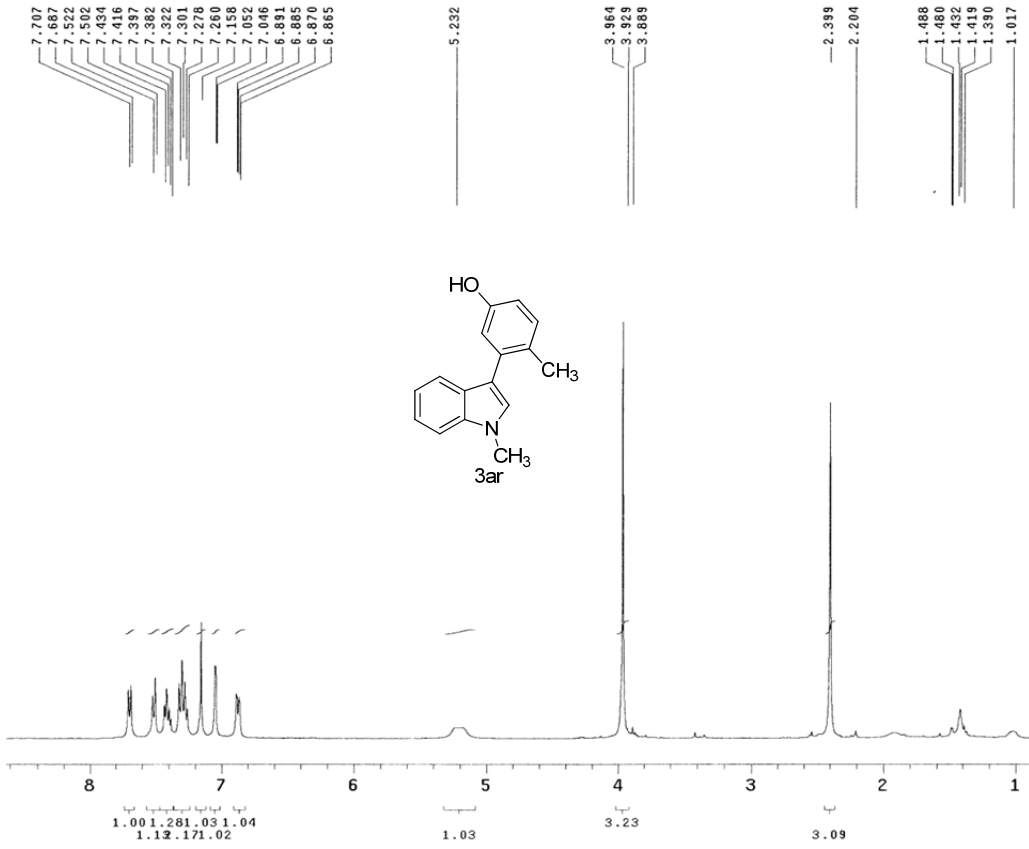

199.073
198.629
137.144
136.497
136.455
132.110
132.652
128.739
128.476
128.371
128.103
127.417
126.398
121.895
119.470
118.705
111.413
109.500
77.318
77.000
76.682
43.125
39.390
32.708
Ph
O
Ph
O
N
CH3
3ao
200
180
160
140
120
100
80
60
40
20
ppm

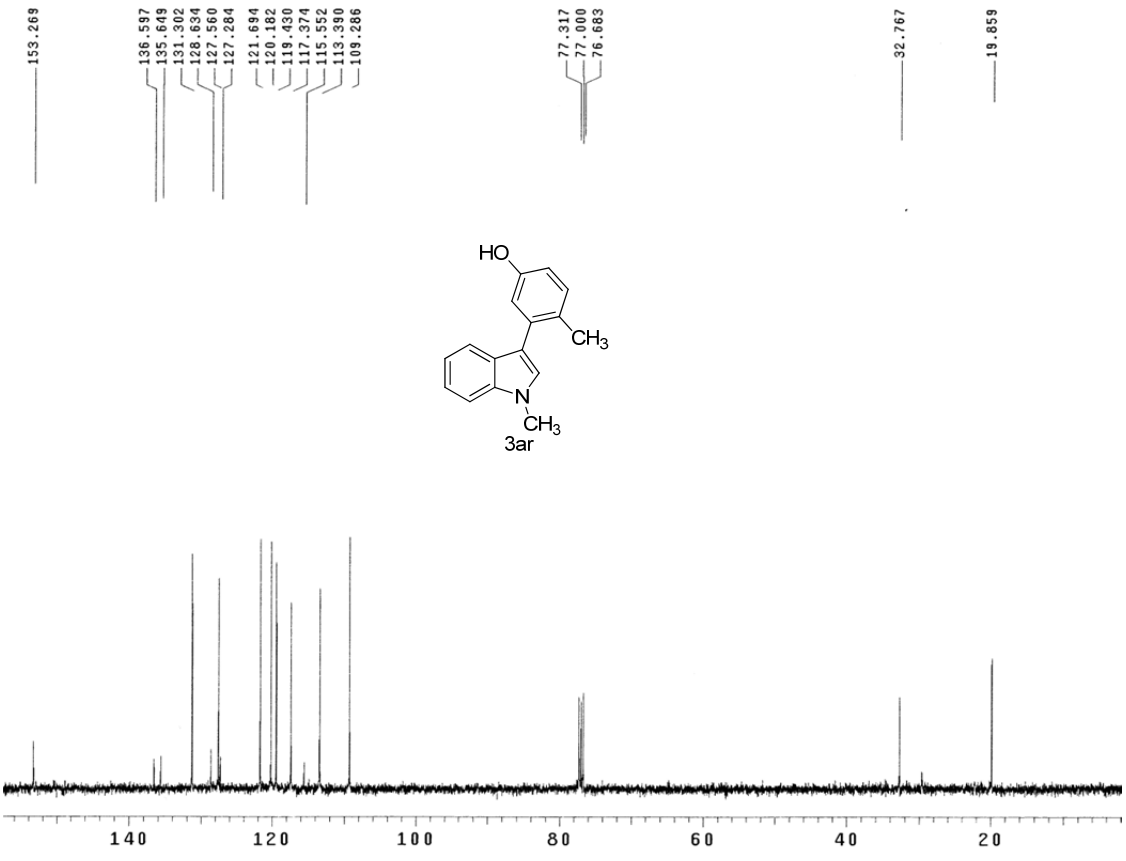

7.576
7.556
7.277
7.257
7.227
7.221
7.210
7.190
7.115
7.095
7.078
6.821
3.702
3.049
3.030
3.011
2.805
2.787
2.768
2.418
2.400
2.382
2.364
1.282
1.049
1.031
1.013
0.078
O
N
CH3
3ap
8
7
6
5
4
3
2
1
0
ppm
0.88
0.93
0.76
0.80
0.94
3.00
2.27
2.23
1.97
2.91

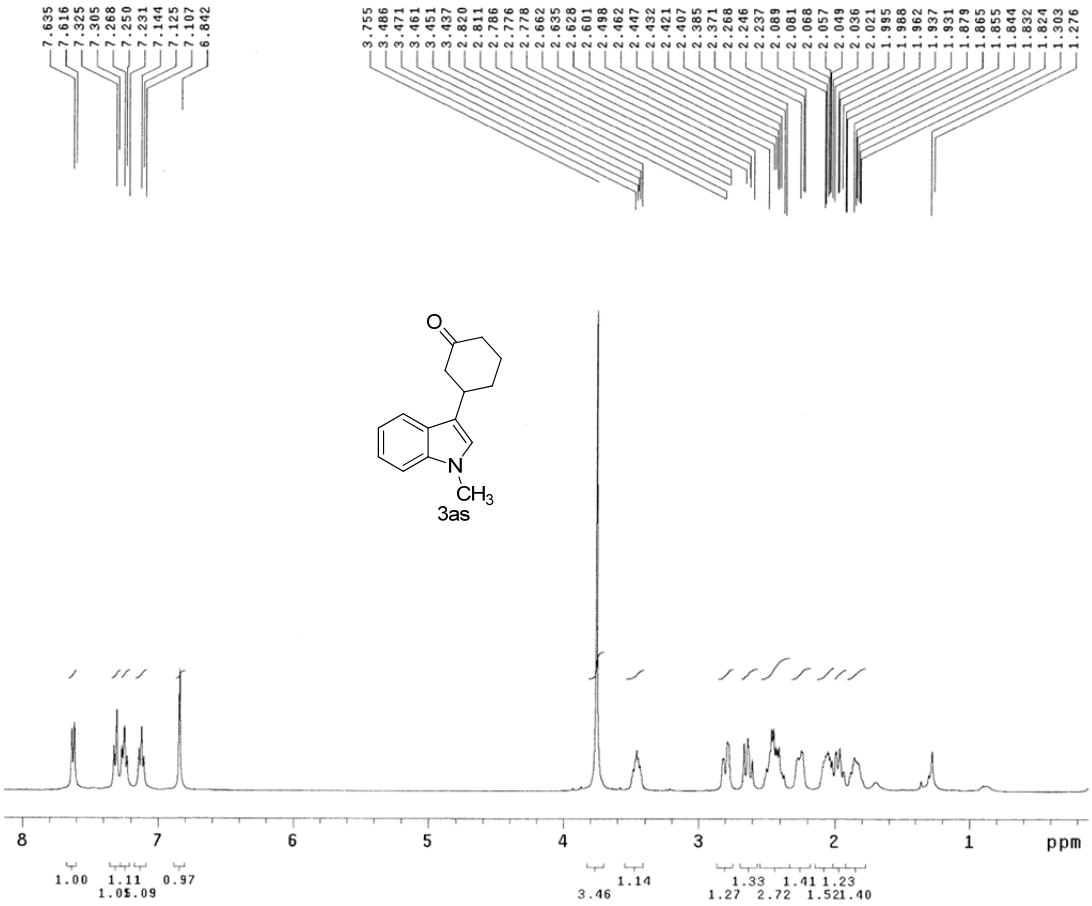

211.345
136.911
127.492
126.302
121.471
118.704
118.613
113.713
109.137
77.319
77.000
76.681
42.555
35.980
32.479
19.241
7.705
0.973
O
N
CH3
3ap
200
180
160
140
120
100
80
60
40
20
ppm

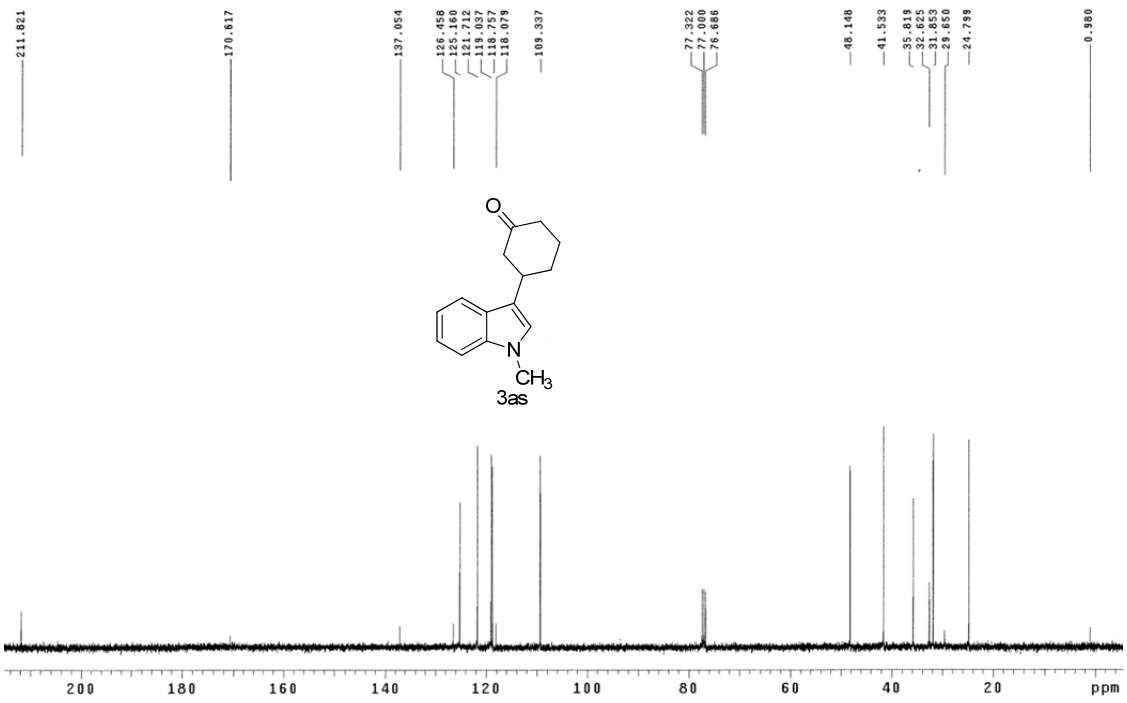

7.643
7.623
7.292
7.272
7.238
7.232
7.220
7.201
7.124
7.104
7.087
6.821
3.718
3.652
3.635
3.616
3.599
2.948
2.933
2.908
2.893
2.724
2.703
2.684
2.663
2.089
1.384
1.367
O
N
CH3
3aq
8
7
6
5
4
3
2
1
0.88
0.93
0.86
0.91
0.79
0.99
3.00
1.09
1.10
2.50
3.28

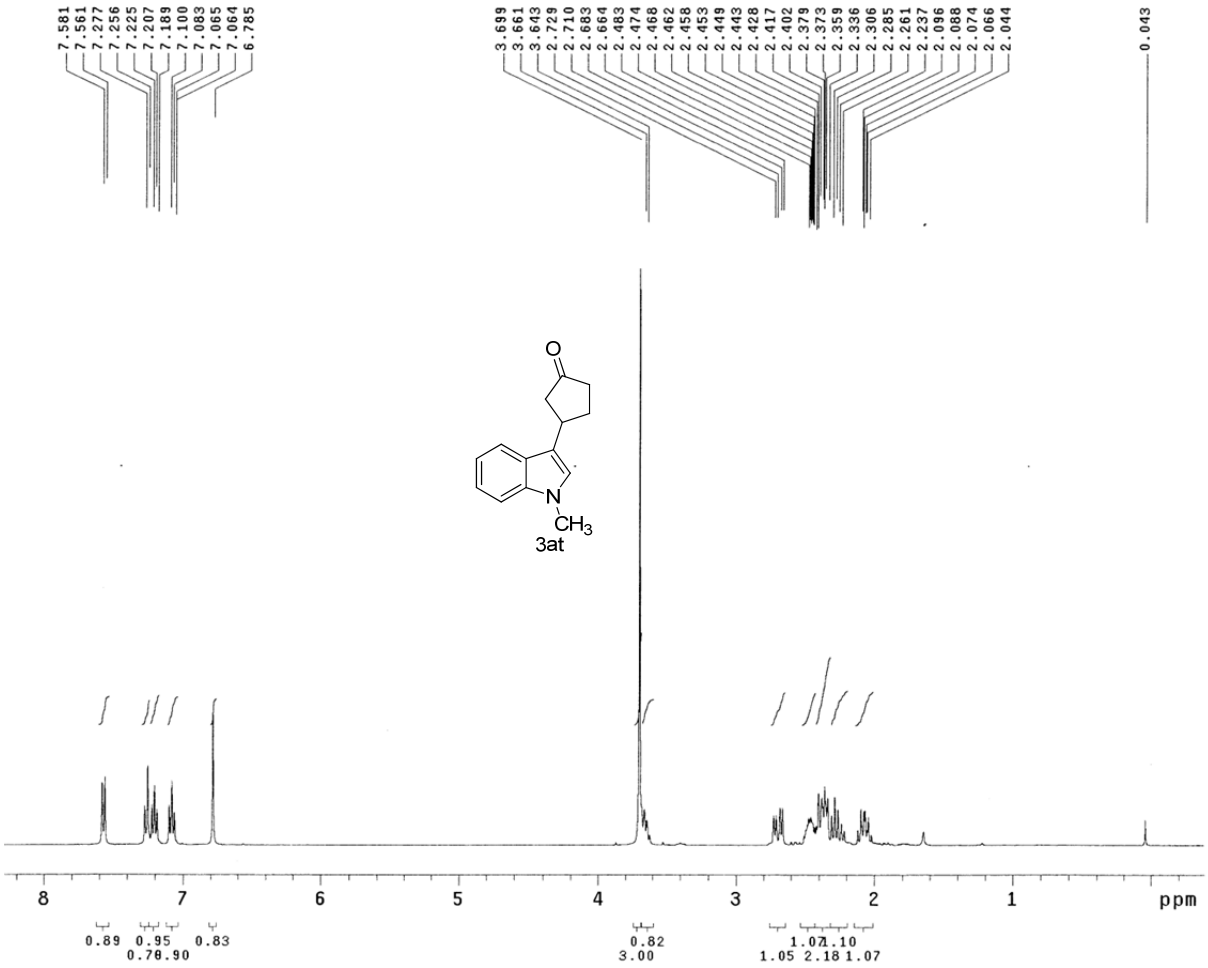

208.562
137.104
126.548
124.648
121.528
119.411
119.122
118.613
109.270
77.315
77.000
76.681
51.591
32.537
30.309
26.904
21.392
0.973
O
N
CH3
3aq
200
180
160
140
120
100
80
60
40
20
ppm

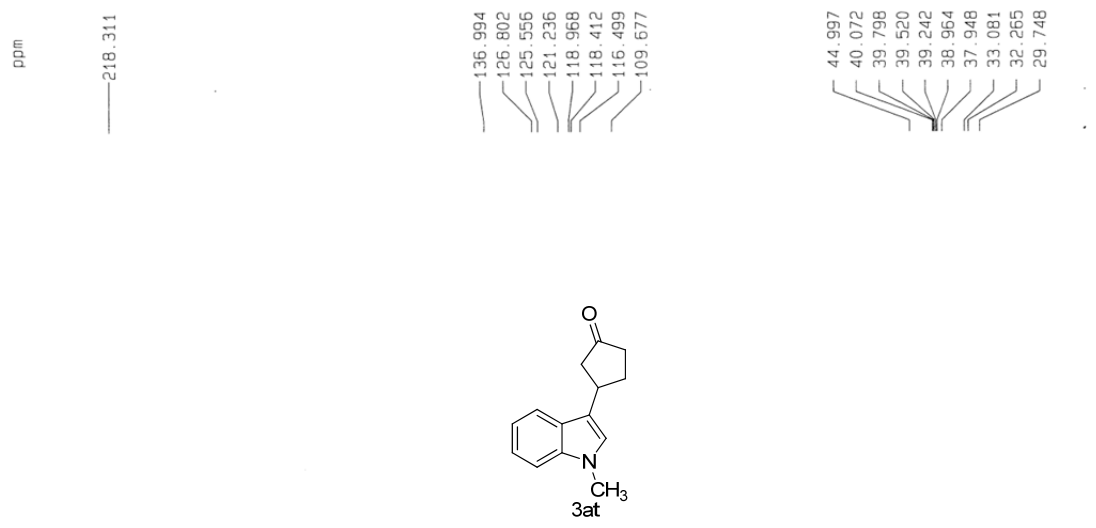

7.707
7.687
7.522
7.502
7.434
7.416
7.397
7.382
7.322
7.301
7.278
7.260
7.158
7.052
7.046
6.891
6.885
6.870
6.865
5.232
3.964
3.929
3.889
2.399
2.204
1.488
1.480
1.432
1.419
1.330
1.017
HO
CH3
N
CH3
3ar
8
7
6
5
4
3
2
1
1.00
1.28
1.03
1.04
1.12
2.17
1.02
1.03
3.23
3.09

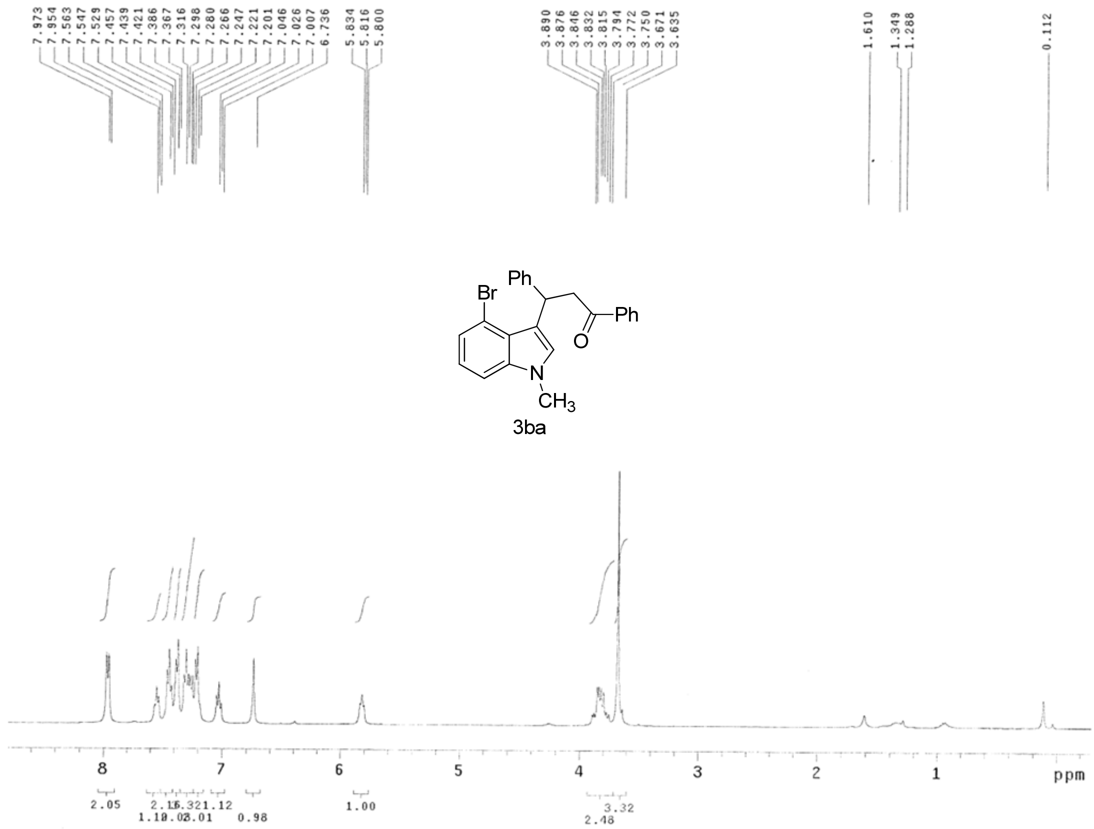

153.269
136.597
135.649
131.302
128.634
127.560
127.284
121.694
120.182
119.430
117.374
115.552
113.390
109.286
77.317
77.000
76.683
32.767
19.859
HO
CH3
N
CH3
3ar
140
120
100
80
60
40
20

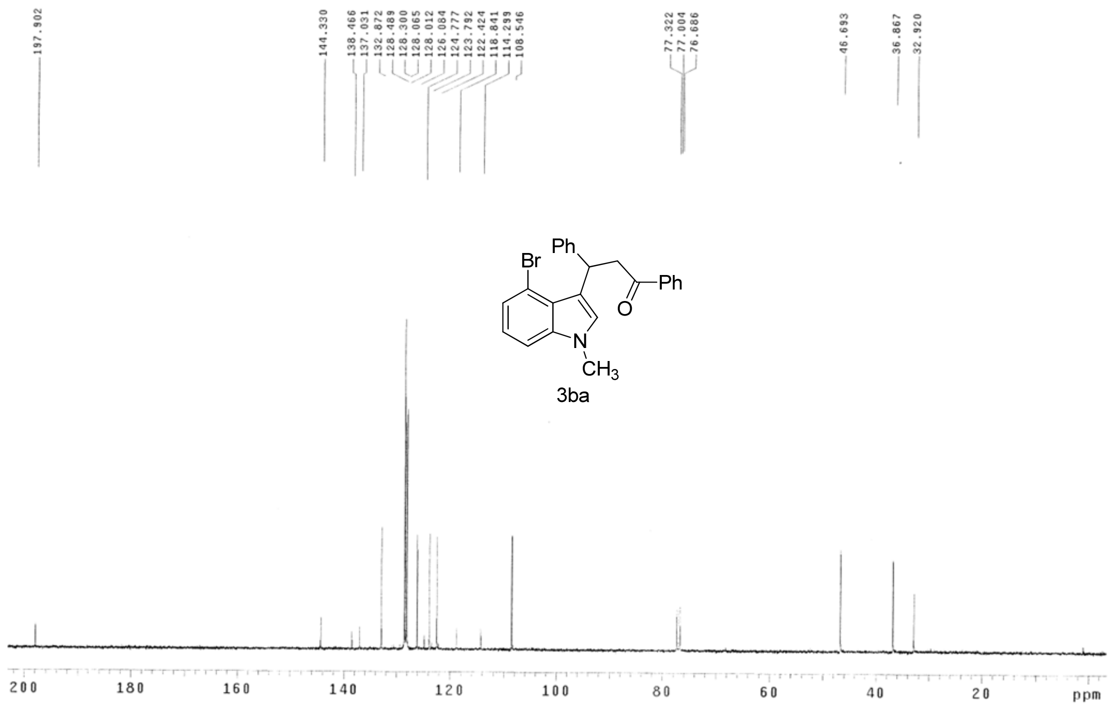

7.635
7.616
7.325
7.305
7.268
7.250
7.231
7.144
7.125
7.107
6.842
3.755
3.486
3.471
3.461
3.451
3.437
2.820
2.811
2.786
2.776
2.778
2.662
2.635
2.628
2.601
2.498
2.462
2.447
2.432
2.421
2.407
2.385
2.371
2.268
2.246
2.237
2.089
2.081
2.068
2.057
2.049
2.036
2.021
1.995
1.988
1.962
1.937
1.931
1.879
1.865
1.855
1.844
1.832
1.824
1.303
1.276
O
N
CH3
3as
8
7
6
5
4
3
2
1
ppm
1.00
1.11
0.97
1.05
1.09
3.46
1.14
1.33
1.41
1.23
1.27
2.72
1.52
1.40

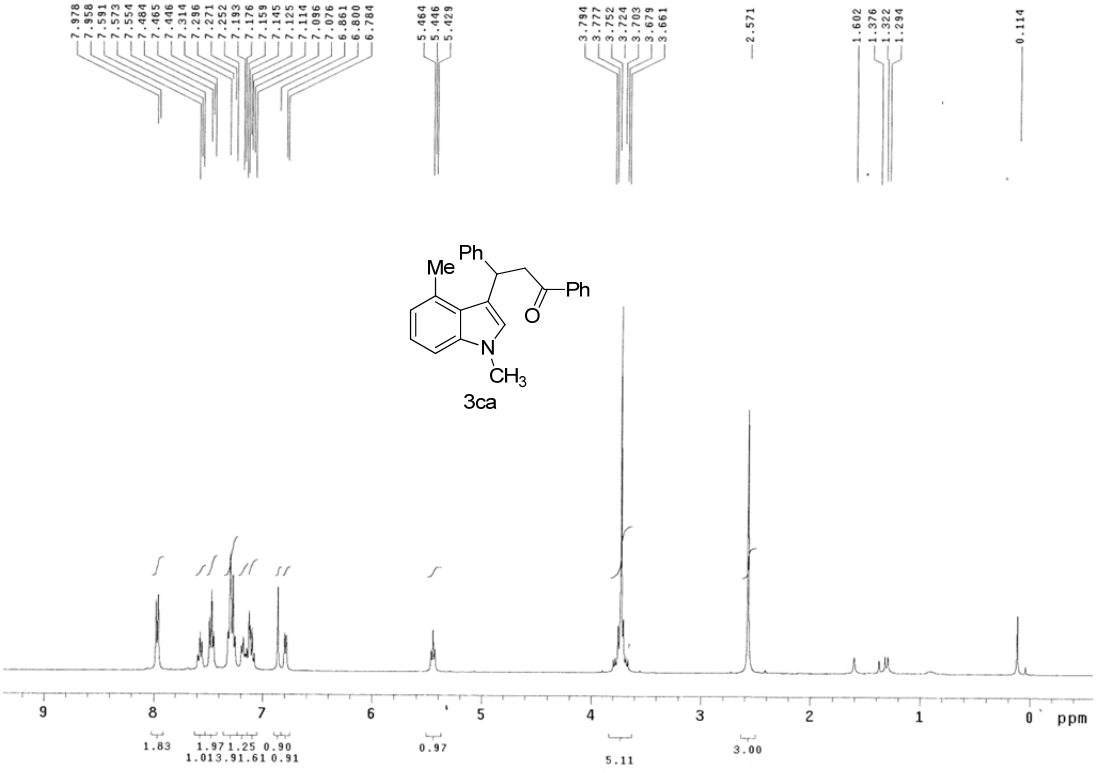

211.821
170.617
137.054
126.458
125.160
121.712
119.037
118.757
118.079
109.337
77.322
77.000
76.686
48.148
41.533
35.819
32.625
31.853
29.650
24.799
0.980
O
N
CH3
3as
200
180
160
140
120
100
80
60
40
20
ppm

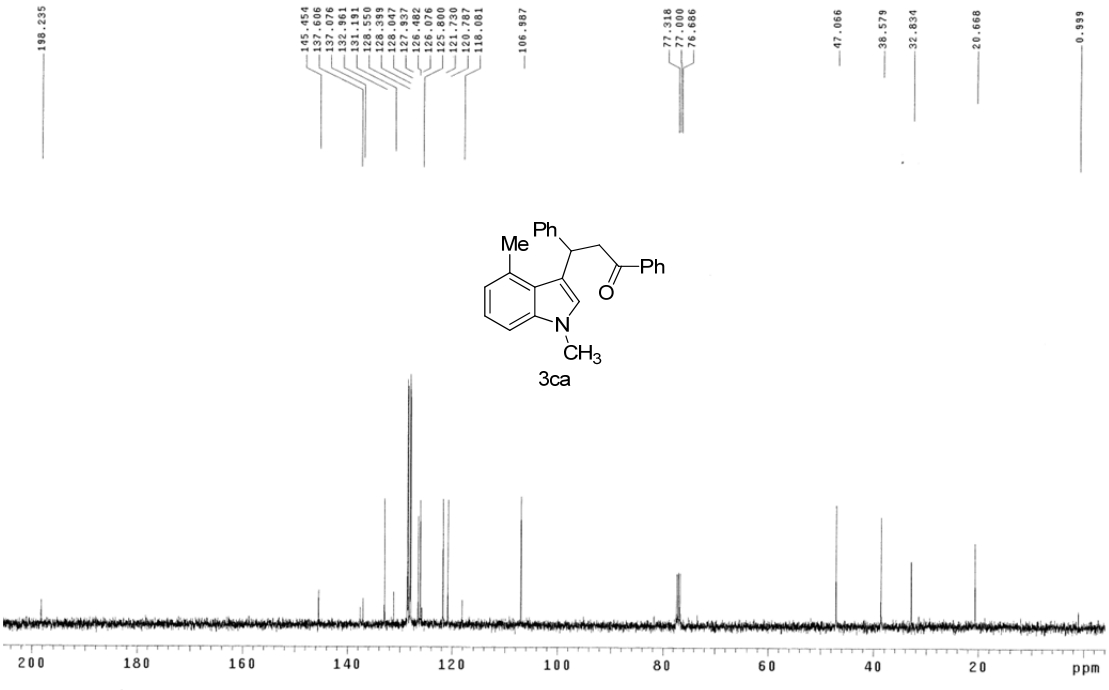

7.581
7.561
7.277
7.256
7.225
7.207
7.189
7.100
7.083
7.065
7.064
6.785
3.689
3.661
3.643
2.729
2.710
2.683
2.664
2.483
2.474
2.468
2.462
2.458
2.453
2.449
2.443
2.428
2.417
2.402
2.379
2.373
2.359
2.336
2.306
2.285
2.261
2.237
2.096
2.088
2.074
2.066
2.044
0.043
O
N
CH3
3at
8
7
6
5
4
3
2
1
ppm
0.89
0.95
0.83
0.78
0.90
0.82
3.00
1.07
1.10
1.05
2.18
1.07

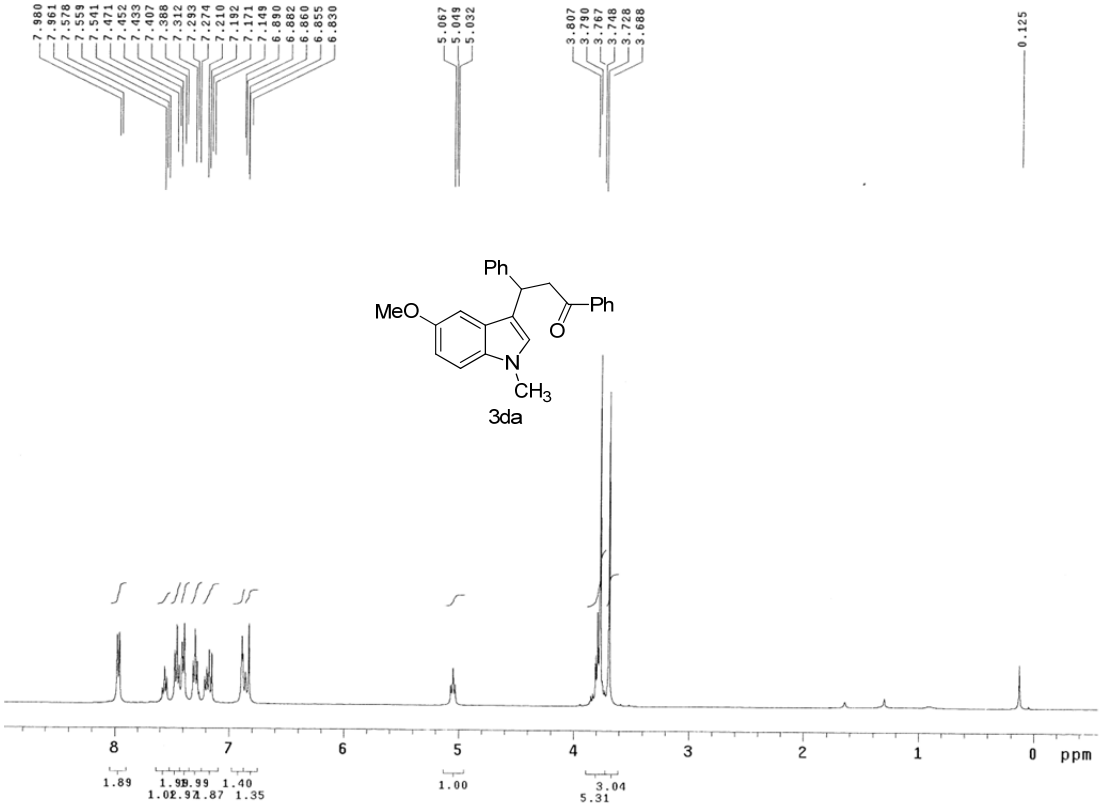

ppm
218.311
136.994
126.802
125.556
121.236
118.968
118.412
116.499
109.677
44.997
40.072
39.798
39.520
39.242
38.964
37.948
33.081
32.265
29.748
O
N
CH3
3at
ppm
200
150
100
50
0

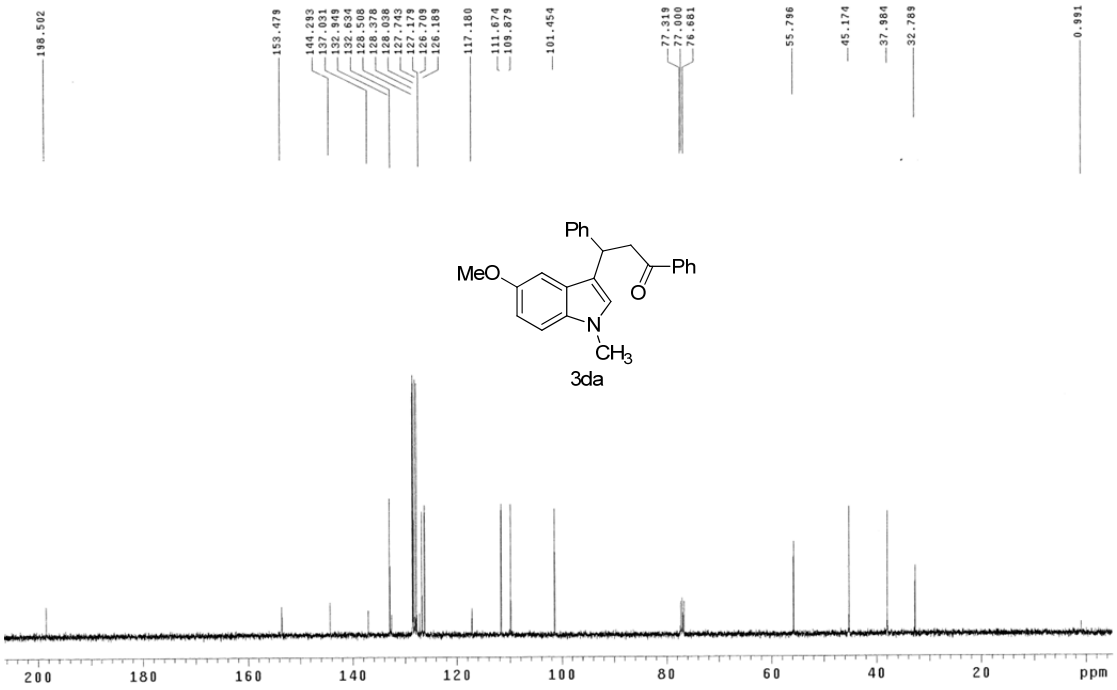

7.973 7.954 7.563 7.547 7.529 7.457 7.439 7.421 7.386 7.367 7.316 7.298 7.280 7.266 7.247 7.221 7.201 7.046 7.026 7.007 6.736
5.834 5.816 5.800
3.890 3.876 3.846 3.832 3.815 3.794 3.772 3.750 3.671 3.635
1.610 1.349 1.288
0.112
Br
Ph
Ph
O
N
CH3
3ba
8 7 6 5 4 3 2 1 ppm
2.05 1.00 0.98 3.32 2.48

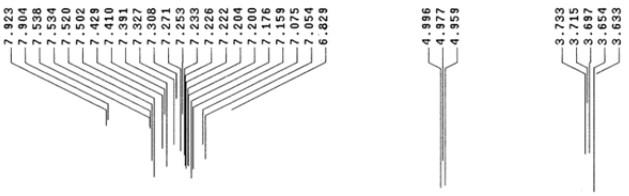

197.902
144.330 138.466 137.031 132.872 128.489 128.300 128.065 128.012 126.084 124.777 123.792 122.424 118.841 114.299 108.546
77.322 77.004 76.686
46.693 36.867 32.920
Br
Ph
Ph
O
N
CH3
3ba
200 180 160 140 120 100 80 60 40 20 ppm

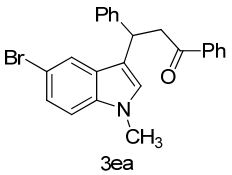

7.978
7.956
7.591
7.573
7.554
7.484
7.465
7.446
7.314
7.296
7.271
7.252
7.193
7.176
7.159
7.145
7.125
7.114
7.096
7.076
6.861
6.800
6.784
5.464
5.446
5.429
3.794
3.777
3.752
3.724
3.703
3.679
3.661
2.571
1.602
1.376
1.322
1.294
0.114
Me
Ph
Ph
O
N
CH3
3ca
9
8
7
6
5
4
3
2
1
0
ppm
1.83
1.97
1.25
0.90
1.01
3.91
1.61
0.91
0.97
5.11
3.00


198.235
145.454
137.606
137.076
132.961
131.191
128.550
128.369
128.047
127.337
126.482
126.076
125.800
121.730
120.787
110.081
106.987
77.318
77.000
76.686
47.066
38.579
32.834
20.668
0.999
Me
Ph
Ph
O
N
CH3
3ca
200
180
160
140
120
100
80
60
40
20
ppm

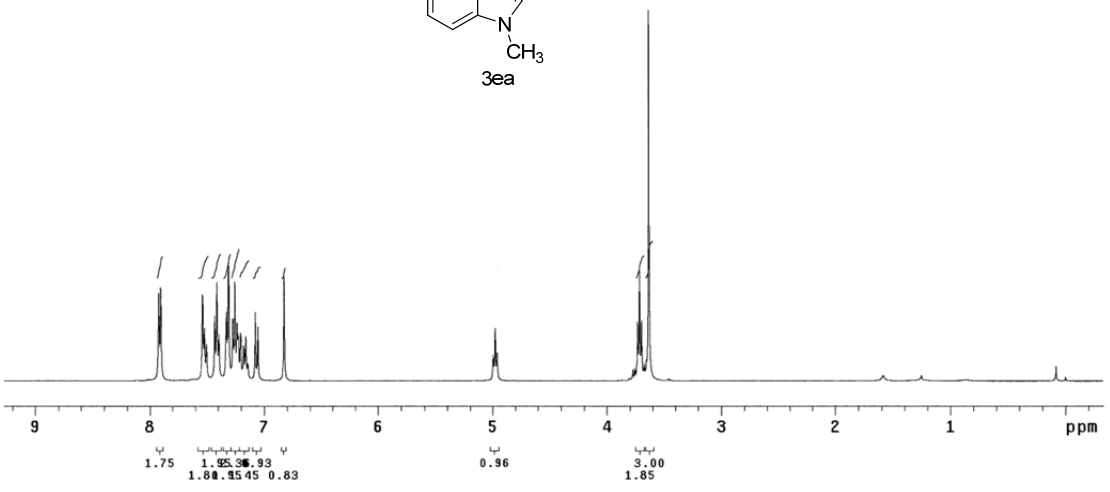

7.980
7.961
7.578
7.559
7.541
7.471
7.452
7.433
7.407
7.388
7.312
7.293
7.274
7.210
7.192
7.171
7.149
6.890
6.882
6.860
6.855
6.830
5.067
5.049
5.032
3.807
3.790
3.767
3.748
3.728
3.688
0.125
Ph
MeO
O
Ph
N
CH3
3da
8
7
6
5
4
3
2
1
0
ppm
1.89
1.00
3.04
5.31

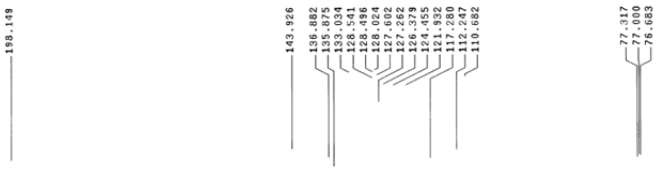

198.502
153.479
144.293
137.031
132.949
132.634
128.508
128.378
128.038
127.743
127.278
126.709
126.183
117.180
111.674
109.879
101.454
77.319
77.000
76.681
55.796
45.174
37.984
32.789
0.991
Ph
MeO
O
Ph
N
CH3
3da
200
180
160
140
120
100
80
60
40
20
ppm

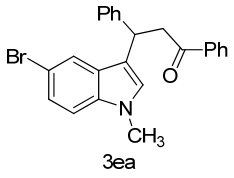

7.923
7.904
7.538
7.534
7.520
7.502
7.429
7.410
7.391
7.327
7.308
7.271
7.253
7.233
7.226
7.222
7.204
7.200
7.176
7.159
7.075
7.054
6.829
4.986
4.977
4.959
3.733
3.715
3.697
3.654
3.633


Ph
Br
Ph
O
N
CH3

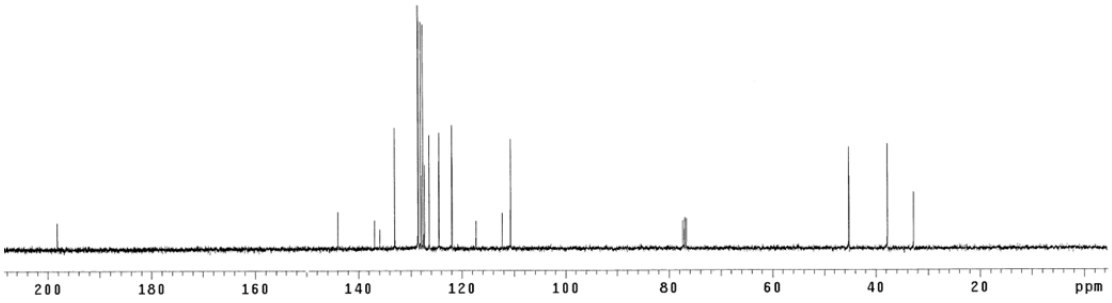
3ea

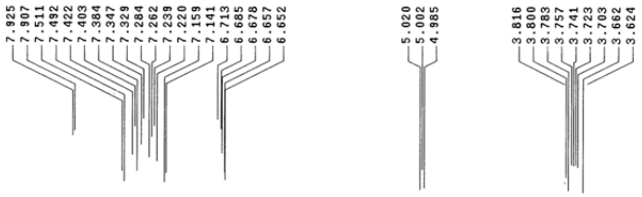

9
8
7
6
5
4
3
2
1
ppm
1.75
0.96
3.00
1.85

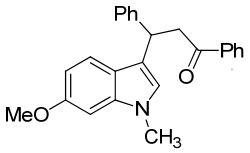

198.149
143.926
136.082
135.075
133.034
128.541
128.496
128.024
127.602
127.262
126.379
124.455
121.932
117.280
112.267
110.682
77.317
77.000
76.683
45.208
37.760
32.789


Ph
Br
Ph
O
N
CH3

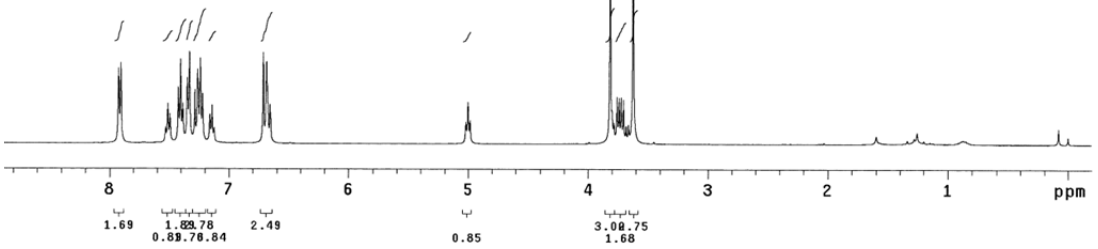
3ea

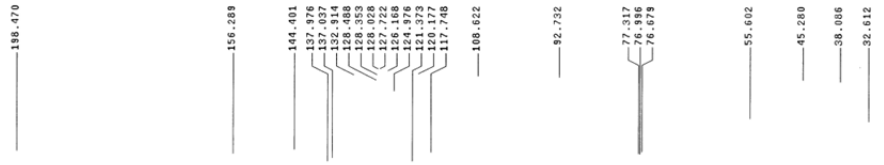

200
180
160
140
120
100
80
60
40
20
ppm

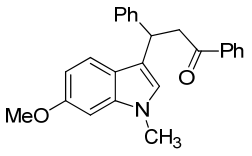

7.925
7.907
7.511
7.492
7.422
7.403
7.384
7.347
7.329
7.284
7.262
7.239
7.220
7.159
7.141
6.713
6.685
6.678
6.657
6.652
5.020
5.002
4.985
3.816
3.800
3.783
3.757
3.741
3.723
3.703
3.662
3.624


Ph
Ph
O
MeO
N
CH3

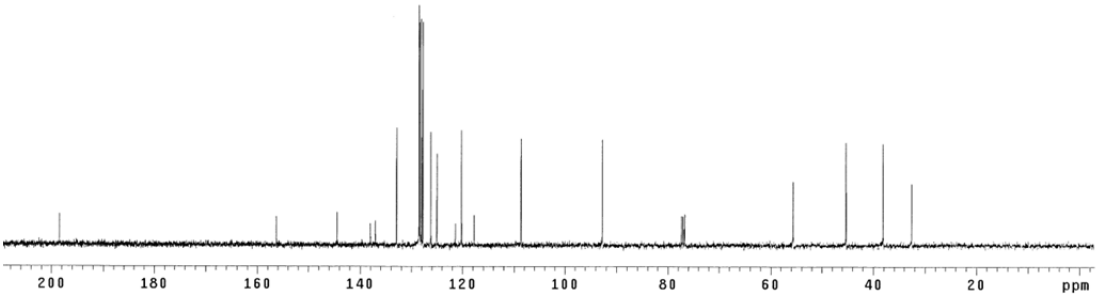
3fa

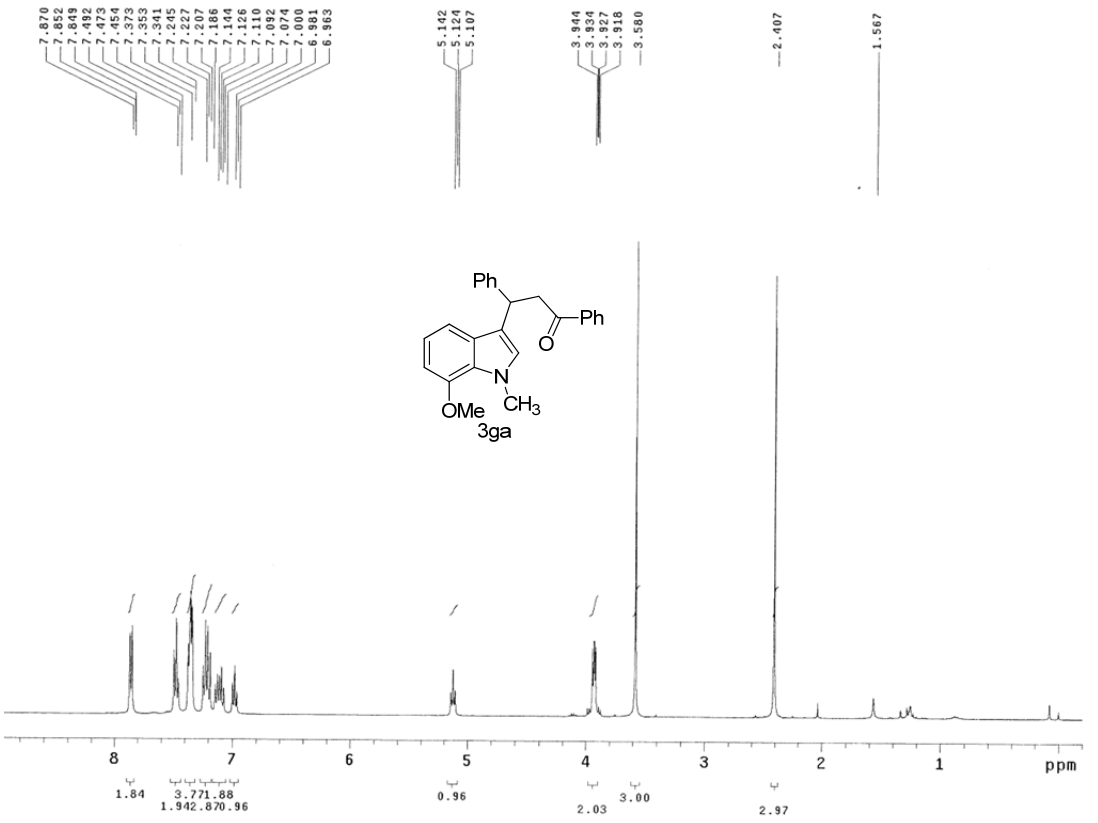

8
7
6
5
4
3
2
1
ppm
1.69
2.49
0.85
1.68

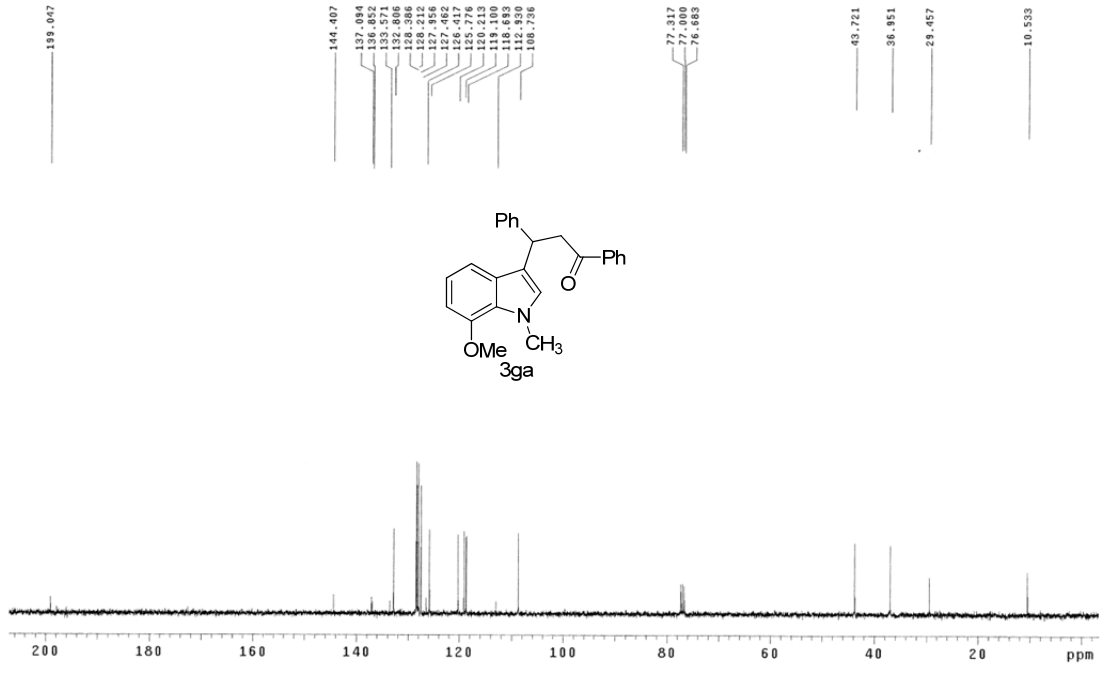

198.470
156.289
144.401
137.976
137.037
132.914
128.488
128.353
128.022
127.722
126.168
124.976
121.373
120.177
117.748
108.622
92.732
77.317
76.996
76.679
55.602
45.280
38.086
32.612

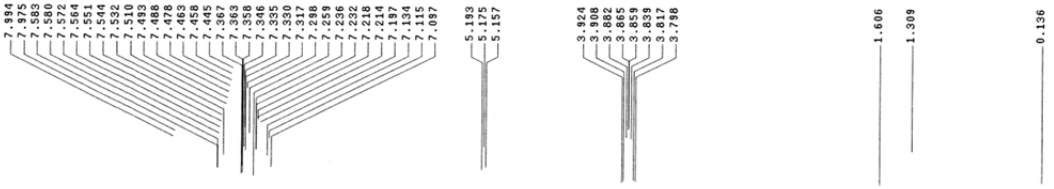

Ph
Ph
O
MeO
N
CH3

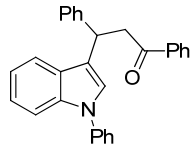
3fa


200
180
160
140
120
100
80
60
40
20
ppm

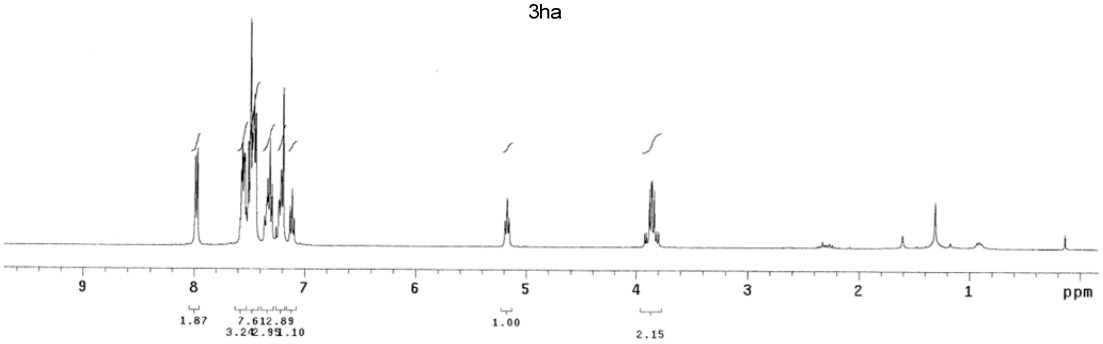

7.870
7.852
7.849
7.492
7.473
7.454
7.373
7.353
7.341
7.245
7.227
7.207
7.186
7.144
7.126
7.110
7.092
7.074
7.000
6.981
6.963
5.142
5.124
5.107
3.944
3.934
3.927
3.918
3.580
2.407
1.567
Ph
Ph
O
N
CH3
OMe
3ga
8
7
6
5
4
3
2
1
ppm
1.84
3.771.88
1.942.870.96
0.96
2.03
3.00
2.97

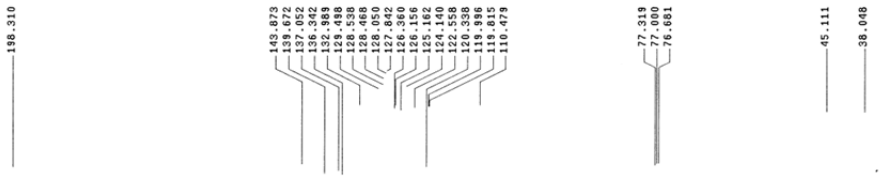

199.047
144.407
137.094
136.852
133.571
132.806
128.386
128.212
127.956
127.462
126.417
125.776
120.213
119.100
118.693
112.930
108.736
77.317
77.000
76.683
43.721
36.951
29.457
10.533
Ph
Ph
O
N
CH3
OMe
3ga
200
180
160
140
120
100
80
60
40
20
ppm

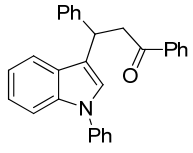

7.394
7.375
7.583
7.580
7.572
7.564
7.551
7.544
7.532
7.510
7.493
7.488
7.478
7.463
7.458
7.445
7.367
7.363
7.358
7.346
7.335
7.330
7.317
7.298
7.259
7.236
7.232
7.218
7.214
7.197
7.134
7.115
7.097
5.193
5.175
5.157
3.924
3.908
3.882
3.865
3.859
3.839
3.817
3.798
1.606
1.309
0.136


Ph
Ph
O
N
Ph

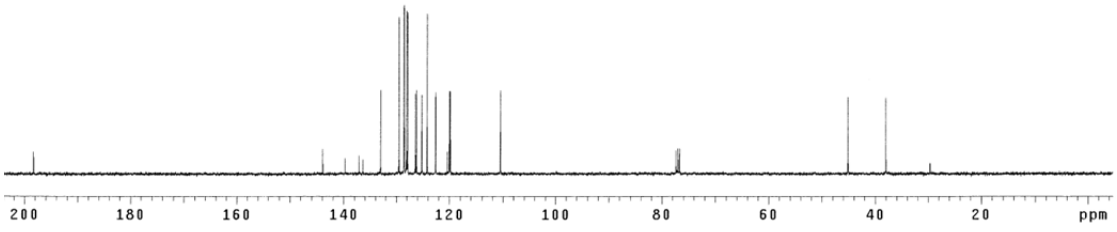
3ha

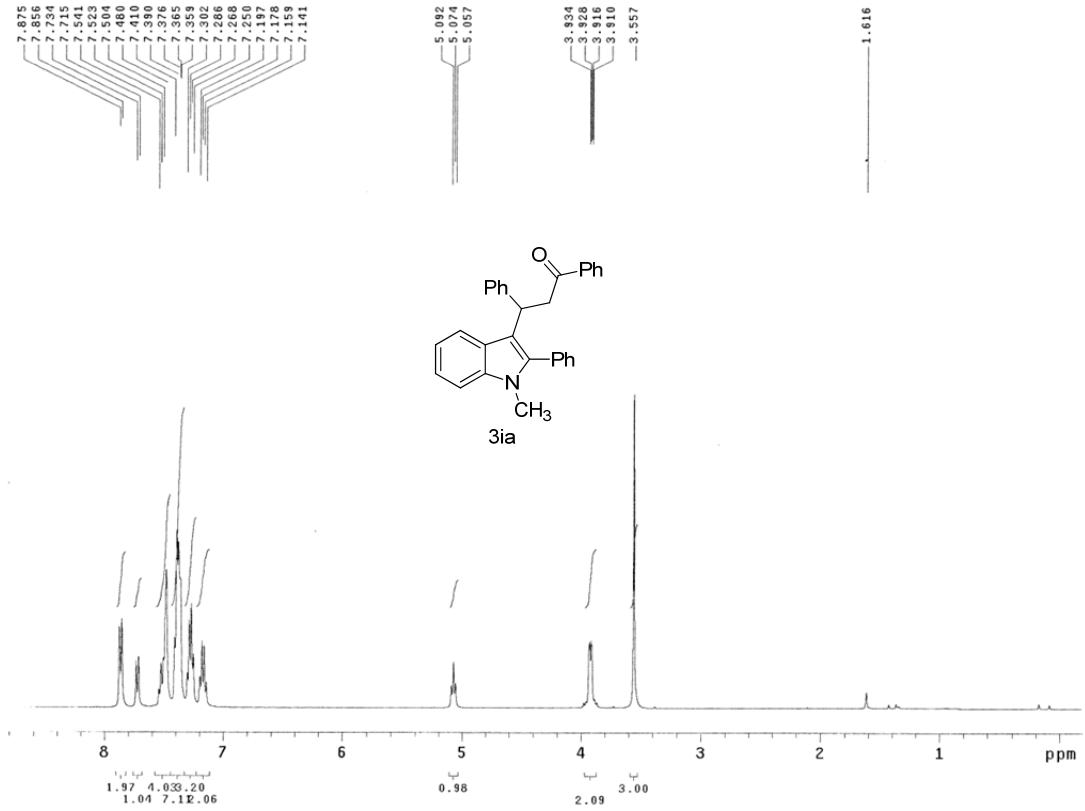

9
8
7
6
5
4
3
2
1
ppm
1.87
7.61
2.89
3.24
2.95
1.10
1.00
2.15

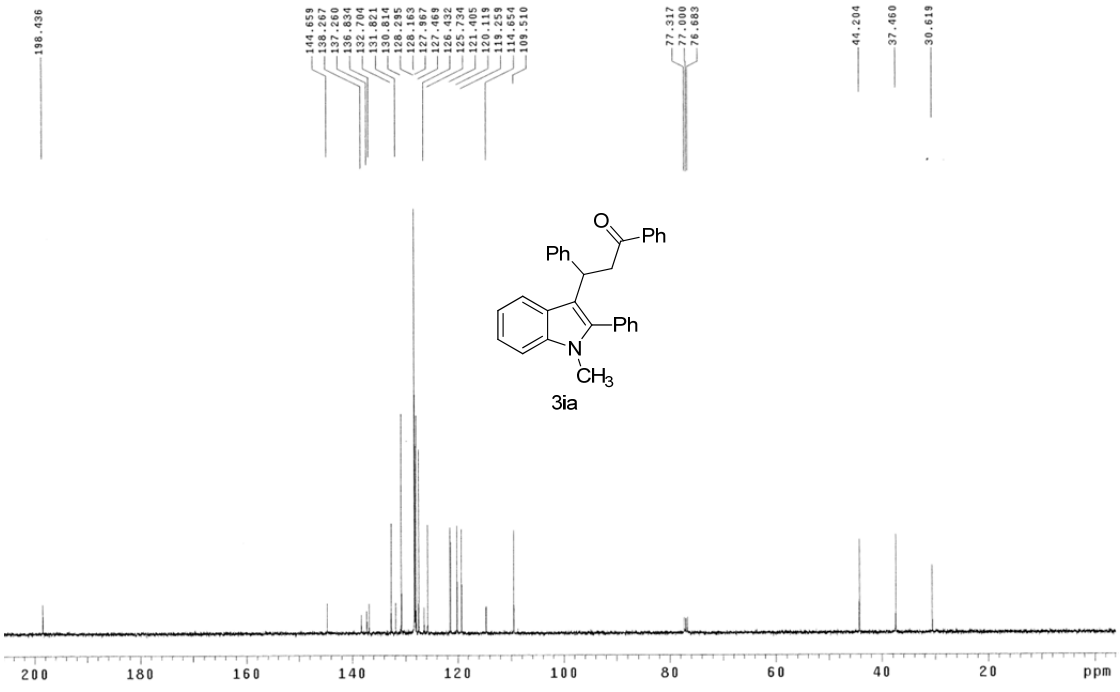

198.310
143.873
139.672
137.052
136.342
132.989
129.498
128.538
128.466
128.050
127.802
126.360
126.156
125.162
124.140
122.558
120.338
119.996
119.015
110.479
77.319
77.000
76.681
45.111
38.048

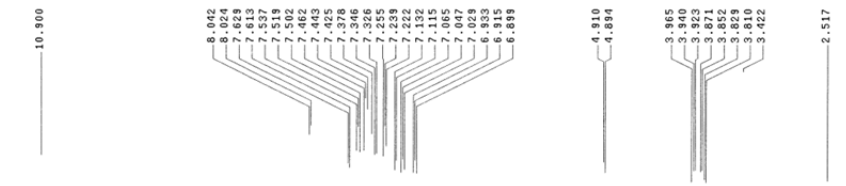

Ph
Ph
O
N
Ph

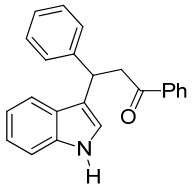
3ha


200
180
160
140
120
100
80
60
40
20
ppm

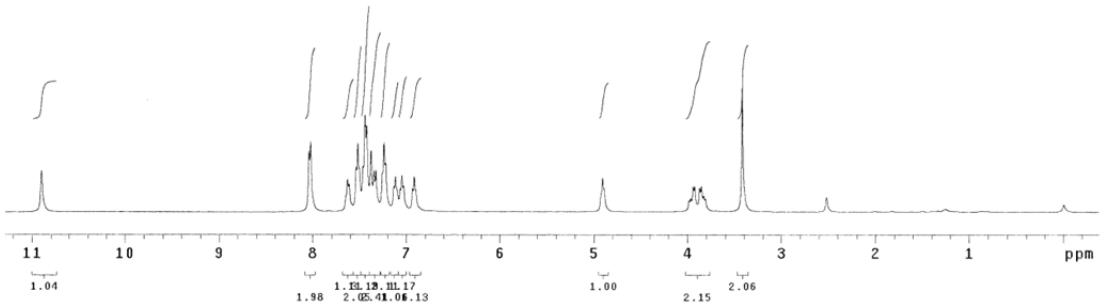

7.875
7.856
7.734
7.715
7.541
7.523
7.504
7.480
7.410
7.390
7.376
7.365
7.359
7.302
7.286
7.268
7.250
7.197
7.178
7.159
7.141
5.092
5.074
5.057
3.834
3.828
3.816
3.810
3.557
1.616
O
Ph
Ph
Ph
N
CH3
3ia
8
7
6
5
4
3
2
1
ppm
1.97
4.03
3.20
1.04
7.11
2.06
0.98
2.09
3.00

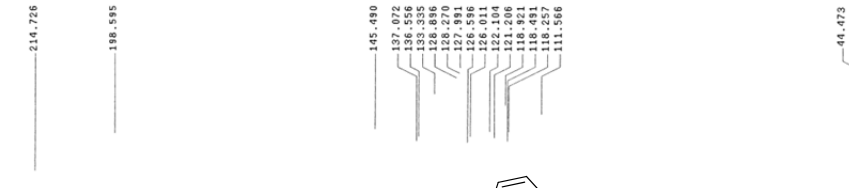

198.436
144.659
138.267
137.260
136.834
132.704
131.821
130.814
128.295
128.155
127.967
127.469
126.432
125.734
121.405
120.119
119.259
114.654
109.510
77.317
77.000
76.683
44.204
37.460
30.618
O
Ph
Ph
Ph
N
CH3
3ia
200
180
160
140
120
100
80
60
40
20
ppm

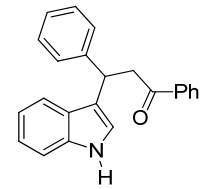

10.300
8.042
8.024
7.623
7.603
7.537
7.519
7.502
7.462
7.443
7.425
7.378
7.346
7.326
7.255
7.239
7.222
7.192
7.115
7.065
7.047
7.029
6.333
6.315
6.299
4.910
4.894
3.865
3.340
3.323
3.871
3.852
3.829
3.810
3.422
2.517


Ph
O
N
H

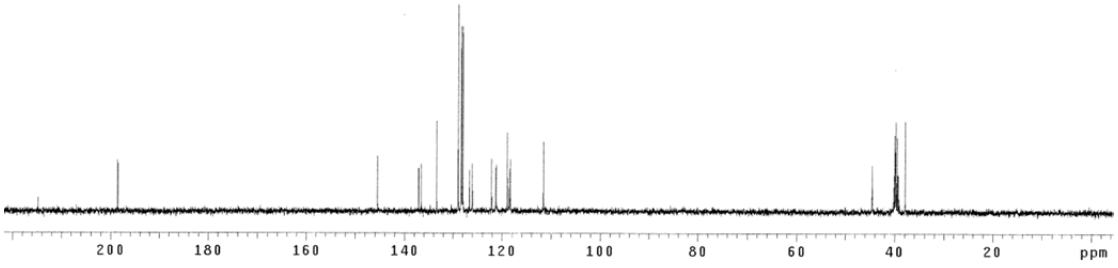
5aa

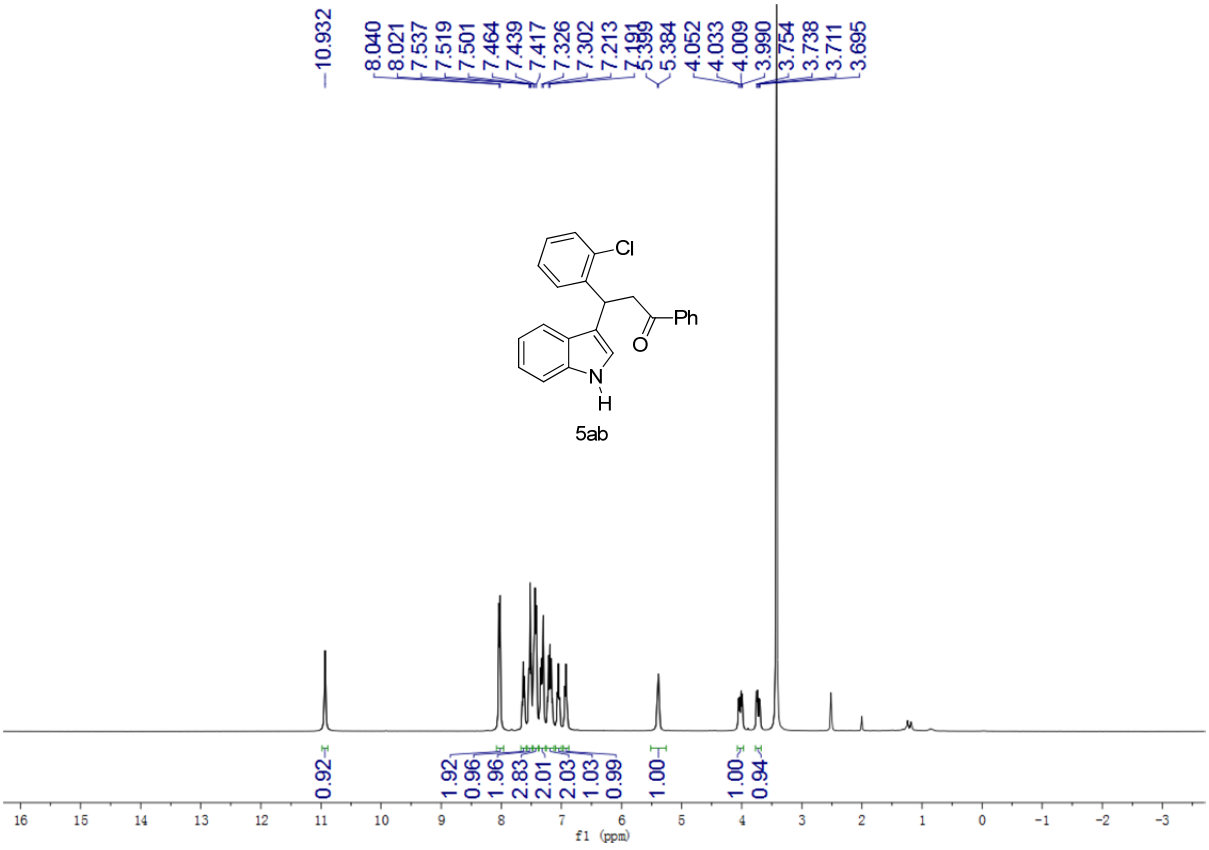

11
10
9
8
7
6
5
4
3
2
1
ppm
1.04
1.98
1.00
2.15
2.06

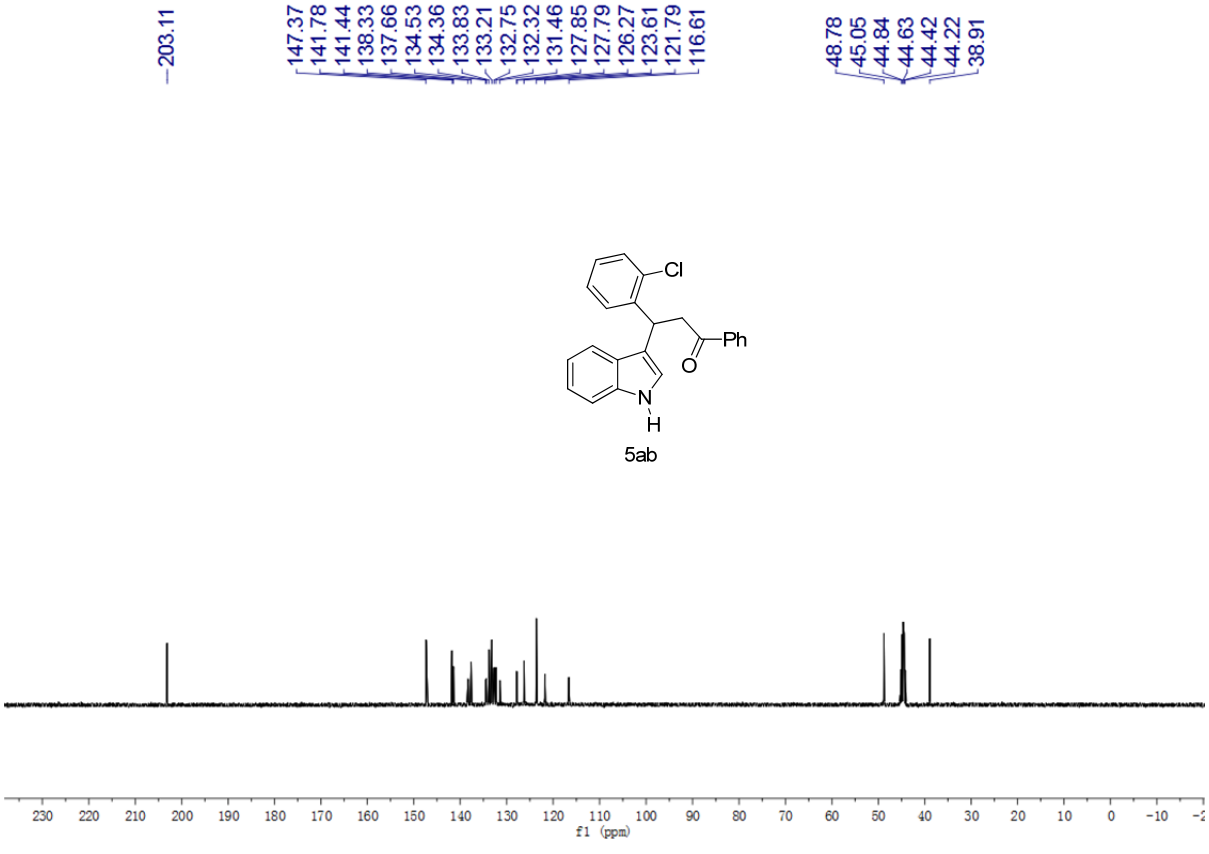

214.726
198.595
145.490
137.072
136.556
133.335
128.886
128.270
127.991
126.596
126.011
122.104
121.206
118.921
118.491
118.257
111.566
44.473
40.125
39.917
39.706
39.499
39.291
39.076
37.866

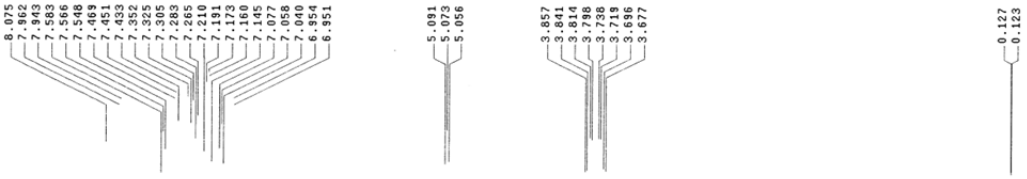

Ph
O
N
H

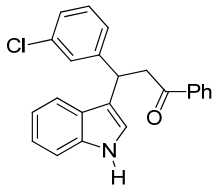
5aa


200
180
160
140
120
100
80
60
40
20
ppm

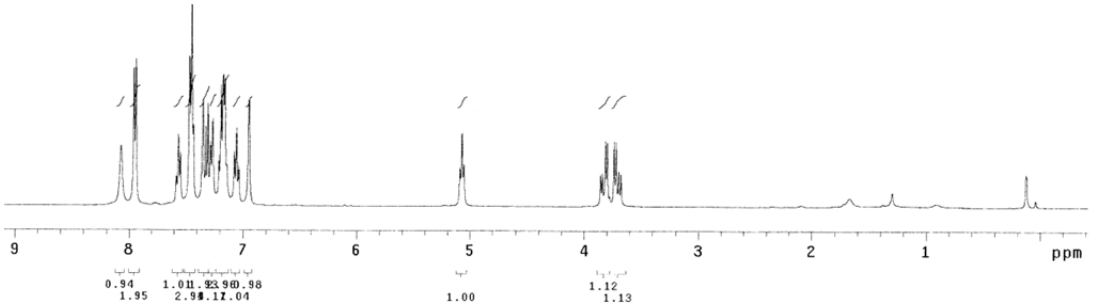

10.932
8.040
8.021
7.537
7.519
7.501
7.464
7.439
7.417
7.326
7.302
7.213
5.384
4.052
4.033
4.009
3.990
3.754
3.738
3.711
3.695
Cl
Ph
O
N
H
5ab
0.92
1.92
0.96
1.96
2.83
2.01
2.03
1.03
0.99
1.00
1.00
0.94
f1 (ppm)

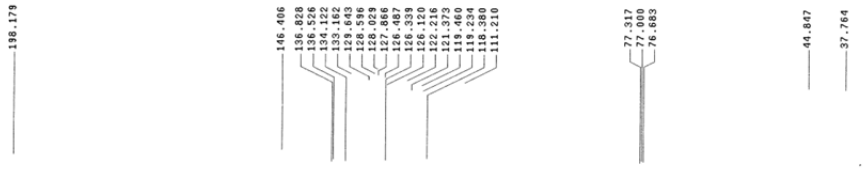

203.11
147.37
141.78
141.44
138.33
137.66
134.53
134.36
133.83
133.21
132.75
132.32
131.46
127.85
127.79
126.27
123.61
121.79
116.61
48.78
45.05
44.84
44.63
44.42
44.22
38.91
Cl
Ph
O
N
H
5ab
f1 (ppm)

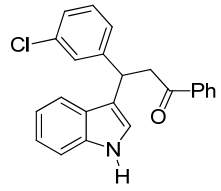

8.075
7.962
7.943
7.583
7.566
7.548
7.469
7.451
7.433
7.352
7.325
7.305
7.283
7.265
7.210
7.191
7.173
7.160
7.145
7.077
7.058
7.040
6.954
6.951
5.091
5.073
5.056
3.857
3.841
3.814
3.798
3.738
3.719
3.696
3.677
0.127
0.123


Cl
Ph
O
N
H

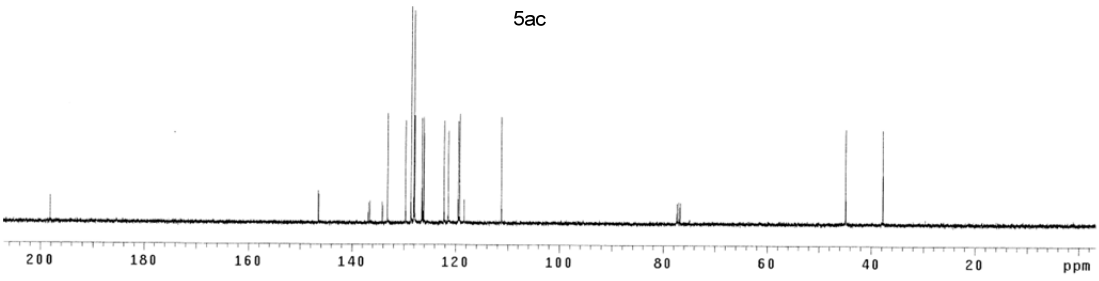
5ac

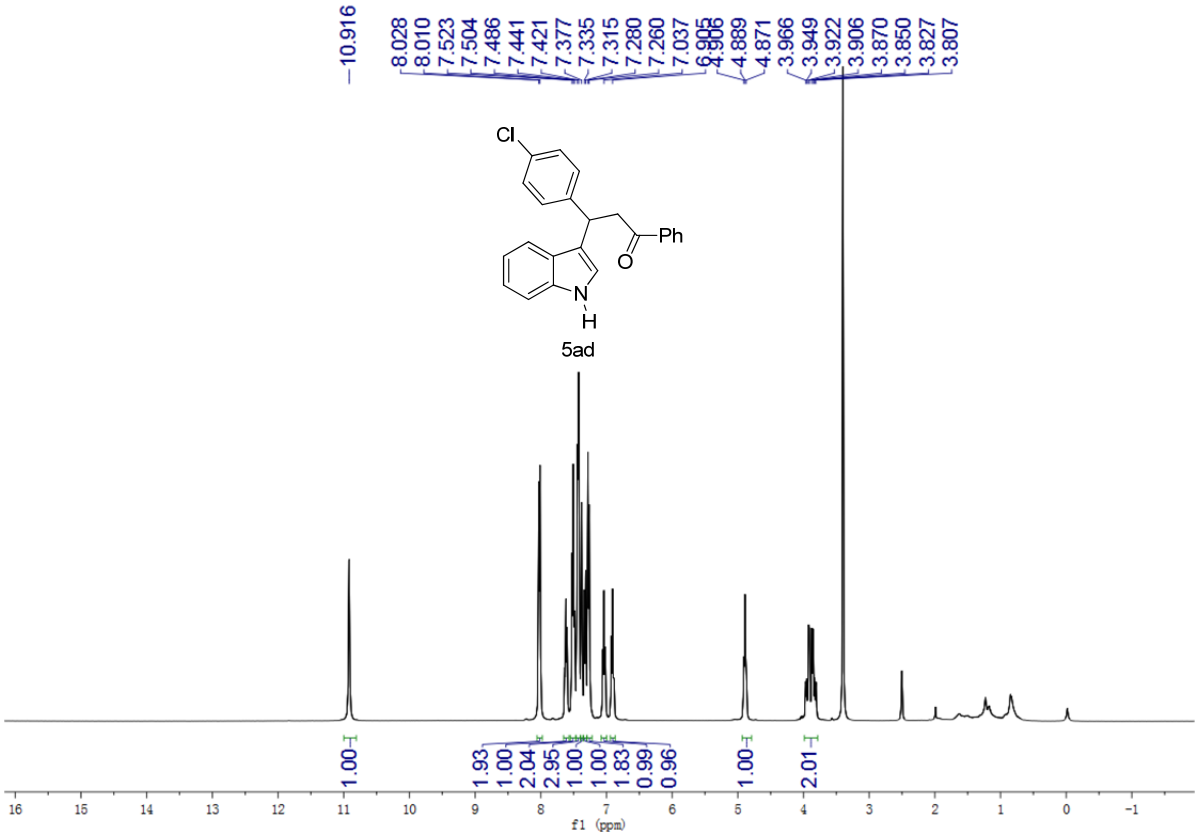

9
8
7
6
5
4
3
2
1
ppm
0.94
1.95
1.00
1.12
1.13

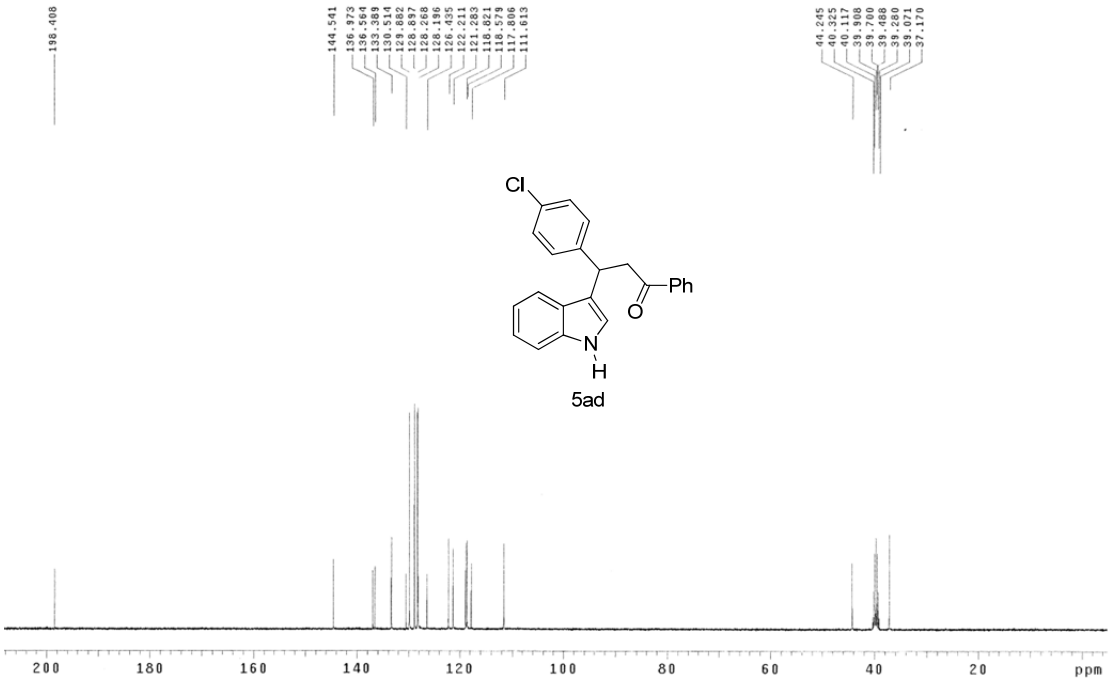

198.179
146.406
136.828
136.526
134.122
133.162
130.643
128.595
128.029
127.866
126.487
126.339
126.120
122.216
121.373
119.460
119.234
118.380
111.210
77.317
77.000
76.683
44.847
37.764

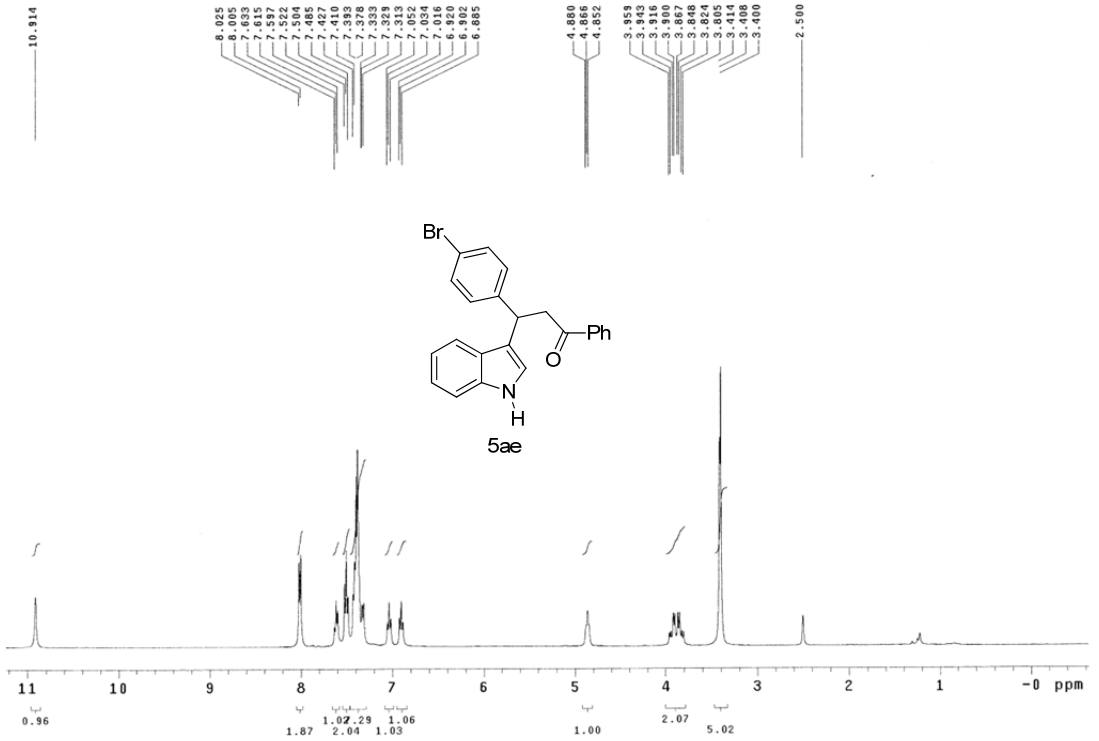

Cl
Ph
O
N
H

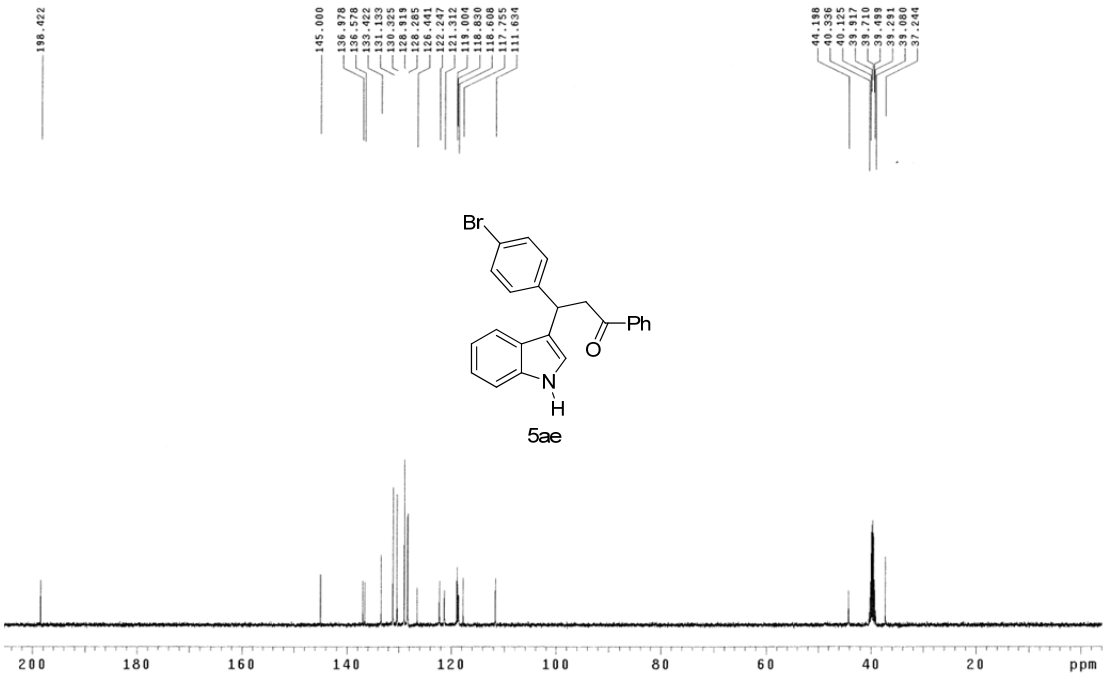
5ac

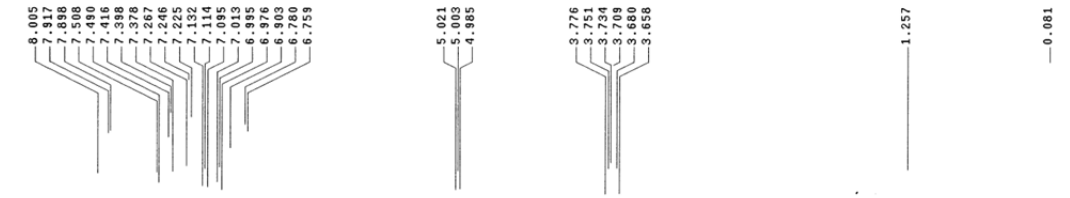

200
180
160
140
120
100
80
60
40
20
ppm

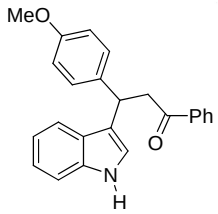

10.916
8.028
8.010
7.523
7.504
7.486
7.441
7.421
7.377
7.335
7.315
7.280
7.260
7.037
6.905
4.906
4.889
4.871
3.966
3.949
3.922
3.906
3.870
3.850
3.827
3.807
Cl
Ph
O
N
H
5ad
1.00
1.93
1.00
2.04
2.95
1.00
1.00
1.83
0.99
0.96
1.00
2.01
f1 (ppm)


198.408
144.541
136.973
136.564
133.389
130.514
129.082
128.897
128.268
128.156
126.435
122.211
121.283
118.021
118.579
117.806
111.613
44.245
40.325
40.117
39.908
39.700
39.488
39.280
39.071
37.170
Cl
Ph
O
N
H
5ad
ppm

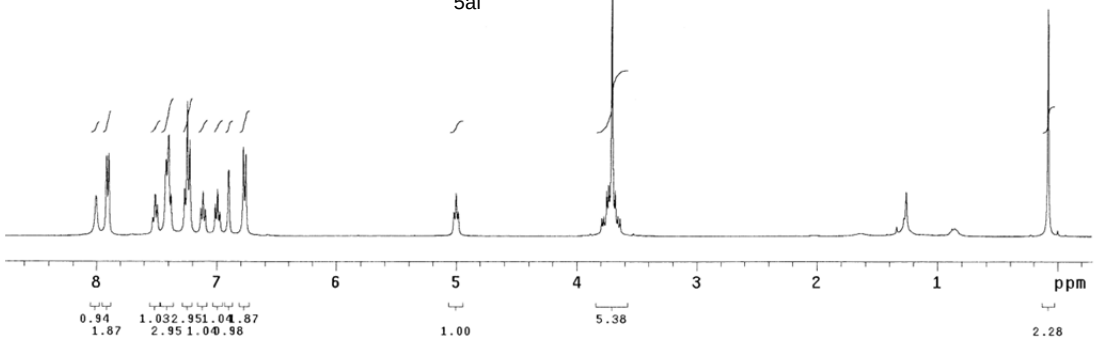

10.914
8.025
8.005
7.615
7.597
7.522
7.504
7.485
7.427
7.410
7.393
7.378
7.333
7.328
7.311
7.313
7.052
7.034
7.016
6.920
6.902
6.885
4.880
4.866
4.852
3.959
3.943
3.916
3.900
3.867
3.848
3.824
3.805
3.414
3.408
3.400
2.500
Br
Ph
O
N
H
5ae
11
10
9
8
7
6
5
4
3
2
1
-0 ppm
0.96
1.87
1.02
2.04
2.29
1.03
1.06
1.00
2.07
5.02

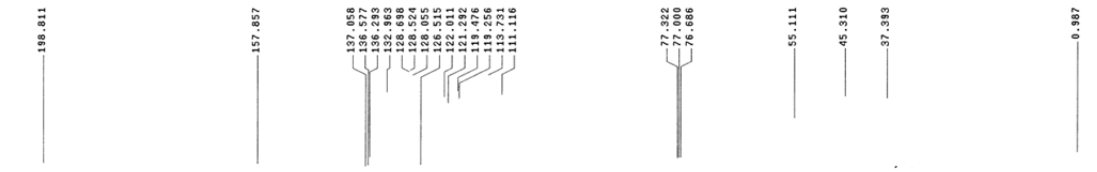

198.422
145.000
136.978
136.578
133.422
131.133
130.335
128.819
128.285
126.441
122.247
121.312
119.004
118.830
118.608
117.795
111.634
44.188
40.336
40.125
39.917
39.710
39.499
39.291
39.080
37.244
Br
Ph
O
N
H
5ae
200
180
160
140
120
100
80
60
40
20
ppm

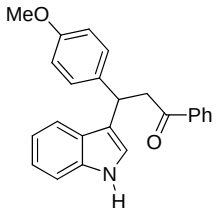

8.005
7.917
7.898
7.508
7.490
7.416
7.398
7.378
7.267
7.246
7.225
7.132
7.114
7.095
7.013
6.995
6.976
6.903
6.780
6.759
5.021
5.003
4.985
3.776
3.751
3.734
3.709
3.680
3.658
1.257
0.081


MeO
Ph
O
N
H

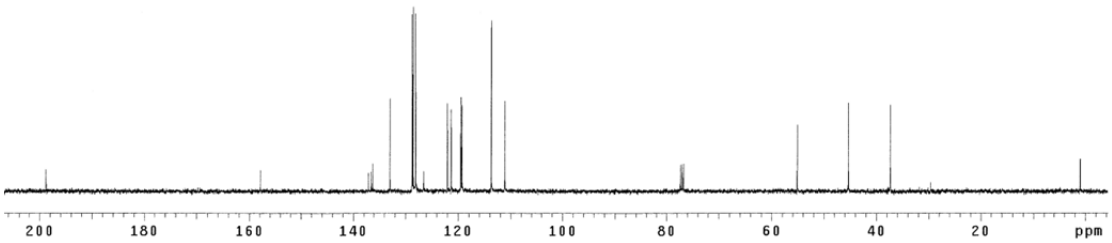
5af

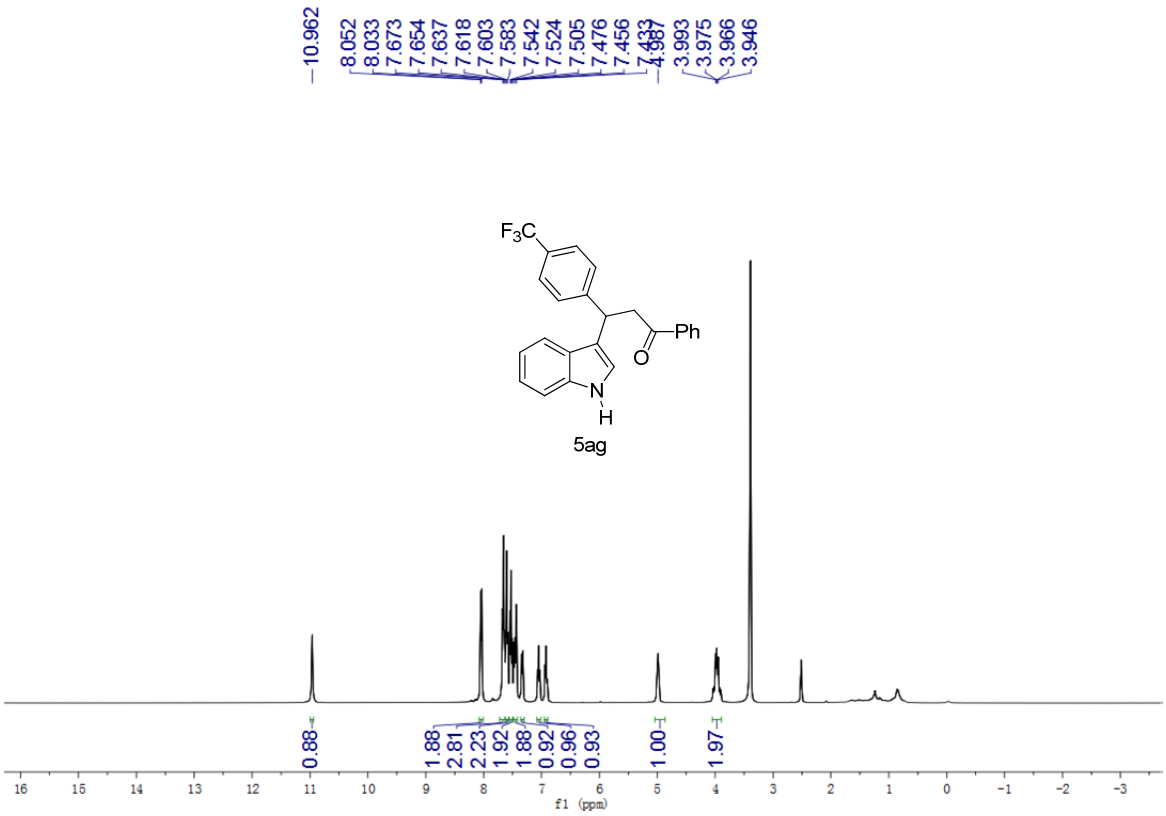

8
7
6
5
4
3
2
1
ppm
0.94
1.87
1.03
2.95
1.04
1.04
0.98
1.87
1.00
5.38
2.28

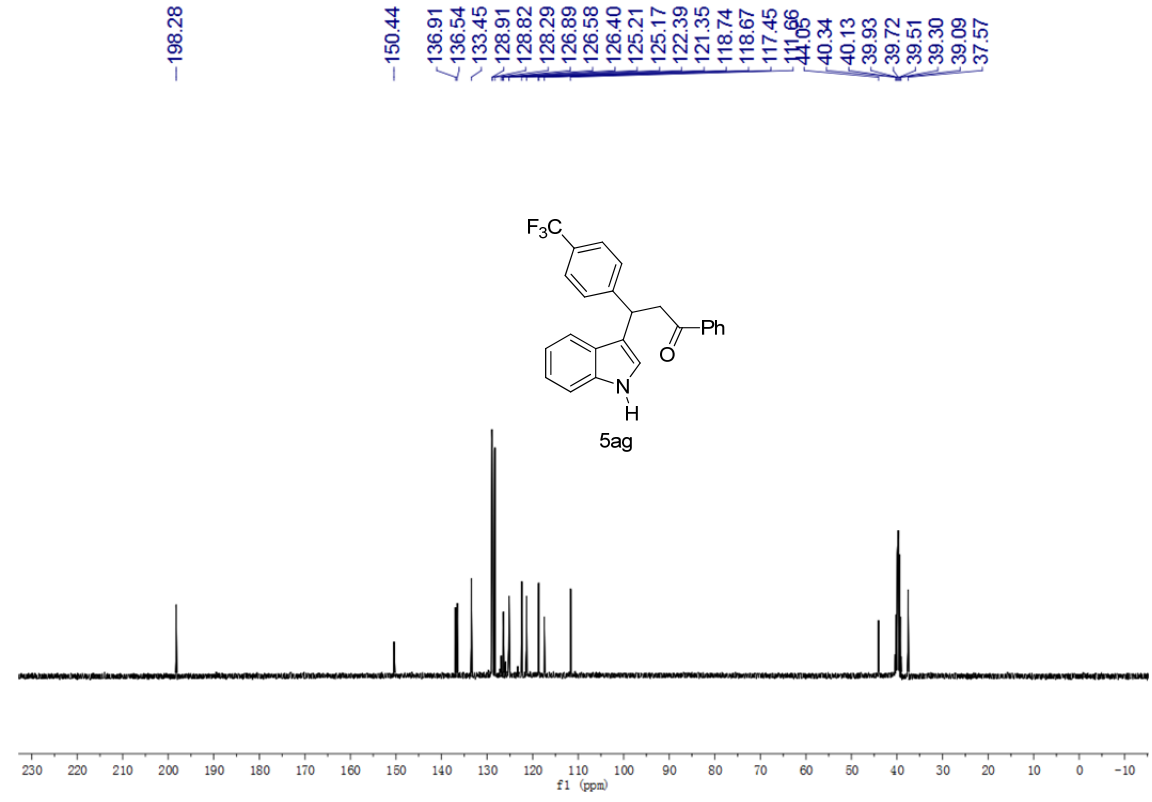

198.811
157.857
137.058
136.577
136.253
132.963
128.698
128.524
128.055
126.515
122.011
121.292
119.476
119.256
113.731
111.116
77.322
77.000
76.686
55.111
45.310
37.393
0.987

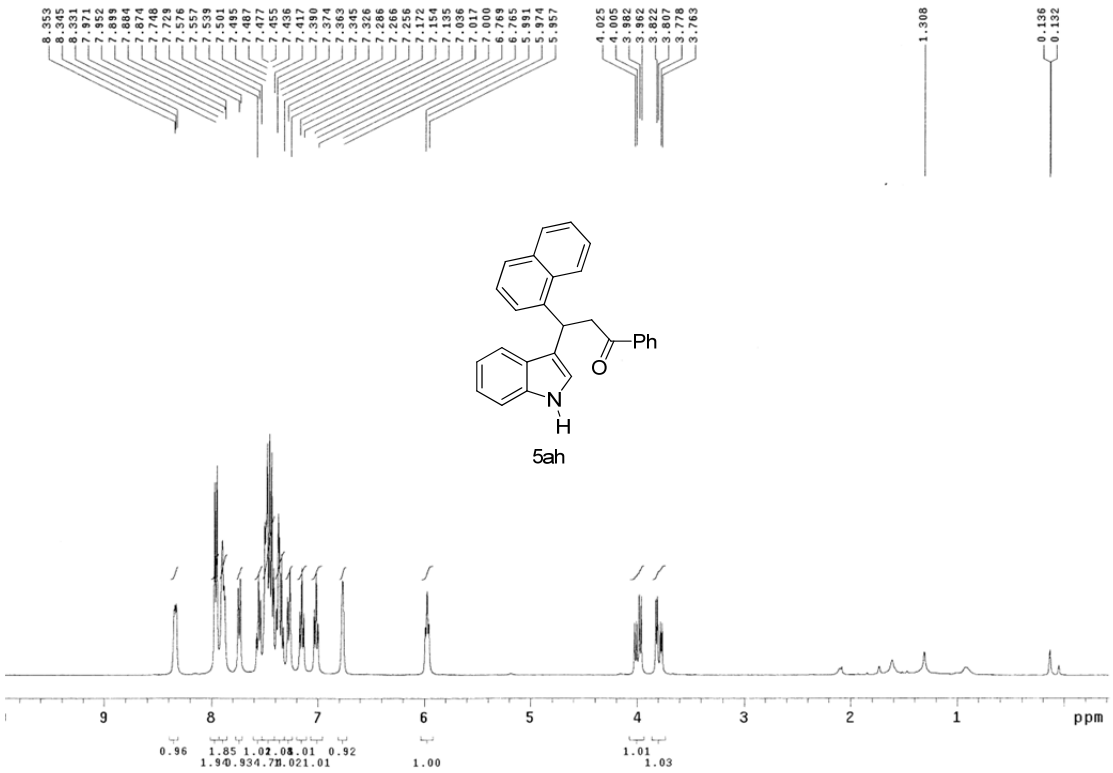

MeO
Ph
O
N
H

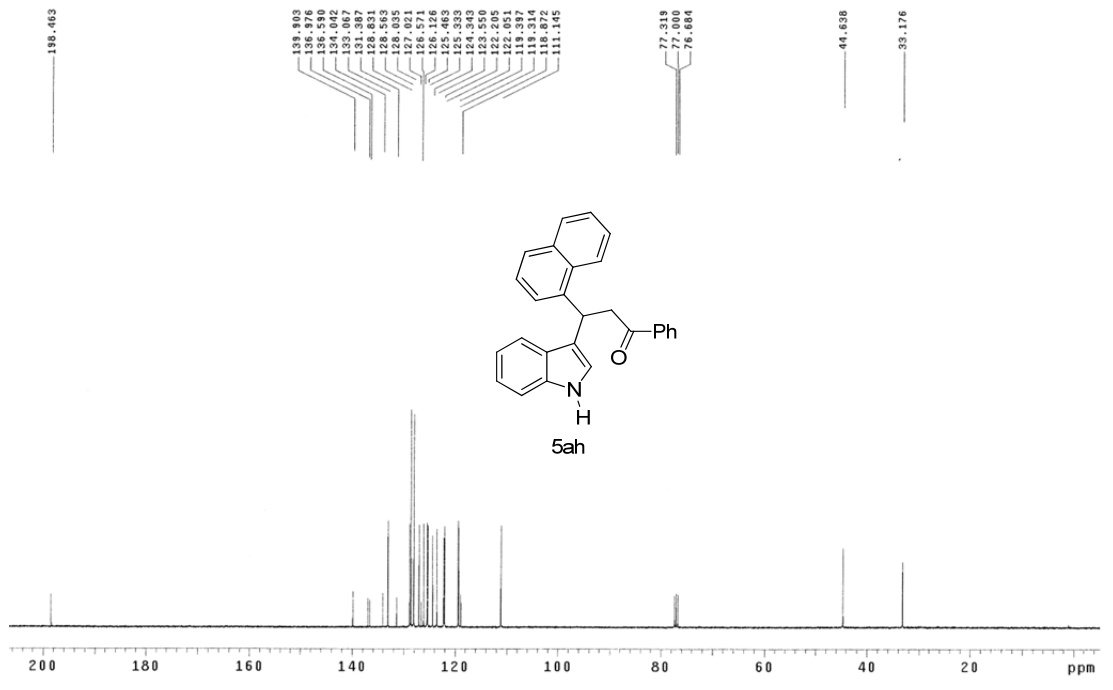
5af

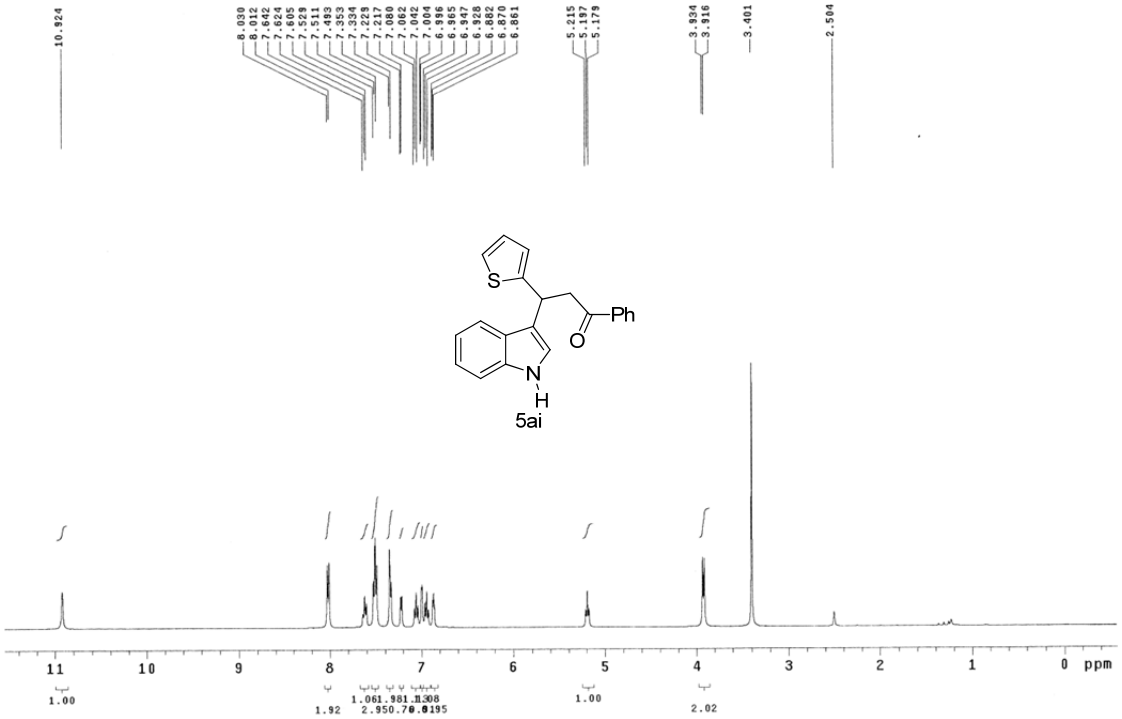

200
180
160
140
120
100
80
60
40
20
ppm

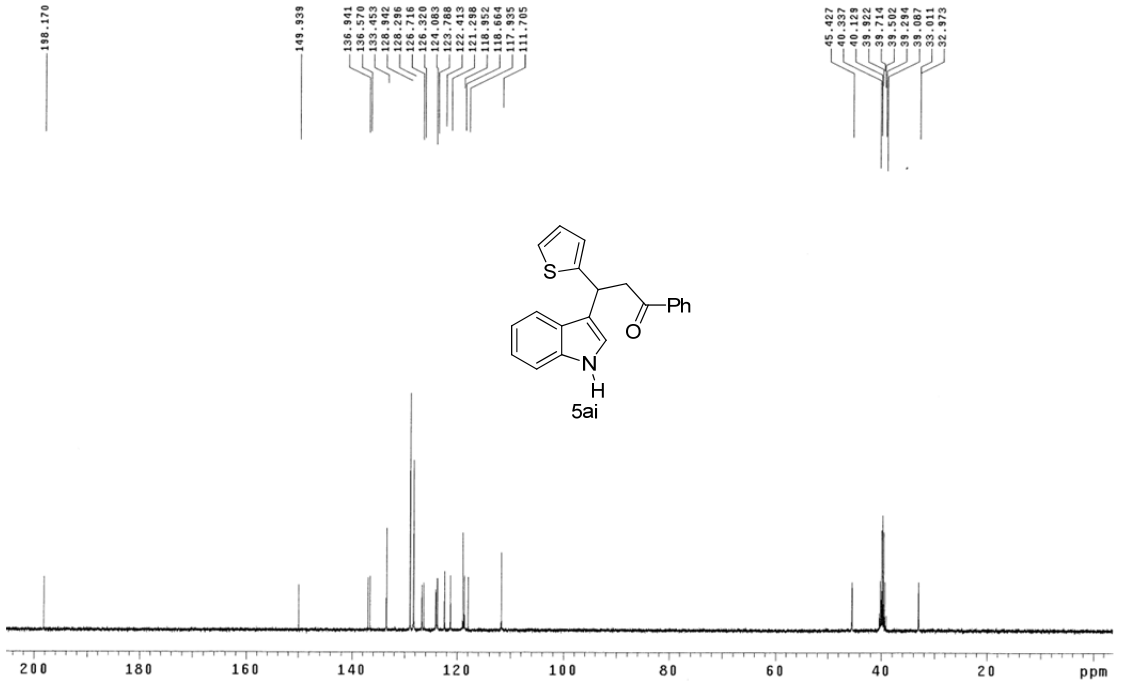

10.962
8.052
8.033
7.673
7.654
7.637
7.618
7.603
7.583
7.542
7.524
7.505
7.476
7.456
7.433
4.987
3.993
3.975
3.966
3.946
F3C
Ph
O
N
H
5ag
0.88
1.88
2.81
2.23
1.92
1.88
0.92
0.96
0.93
1.00
1.97
f1 (ppm)

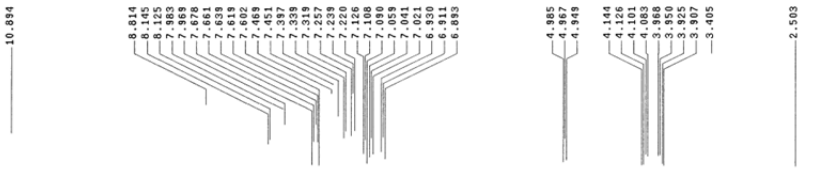

198.28
150.44
136.91
136.54
133.45
128.91
128.82
128.29
126.89
126.58
126.40
125.21
125.17
122.39
121.35
118.74
118.67
117.45
111.66
111.05
40.34
40.13
39.93
39.72
39.51
39.30
39.09
37.57
F3C
Ph
O
N
H
5ag
f1 (ppm)

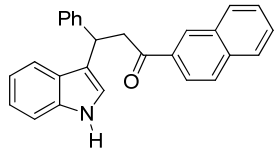

8.353
8.345
8.331
7.971
7.952
7.899
7.884
7.874
7.748
7.729
7.576
7.557
7.539
7.501
7.495
7.487
7.477
7.455
7.436
7.417
7.390
7.374
7.363
7.345
7.326
7.286
7.266
7.256
7.172
7.154
7.135
7.036
7.017
7.000
6.769
6.765
5.931
5.774
5.957
4.025
4.005
3.982
3.962
3.822
3.807
3.778
3.763
1.308
0.136
0.132
Ph
O
N
H
5ah
9
8
7
6
5
4
3
2
1
ppm
0.96
1.85
1.02
2.08
1.01
0.92
1.94
0.93
4.78
1.02
1.01
1.00
1.01
1.03


198.463
139.903
136.976
136.590
134.042
133.067
131.387
129.831
128.563
128.035
127.021
126.571
126.126
125.463
125.333
124.948
123.550
122.205
122.051
119.397
119.314
118.872
111.145
77.319
77.000
76.684
44.638
33.176
Ph
O
N
H
5ah
200
180
160
140
120
100
80
60
40
20
ppm

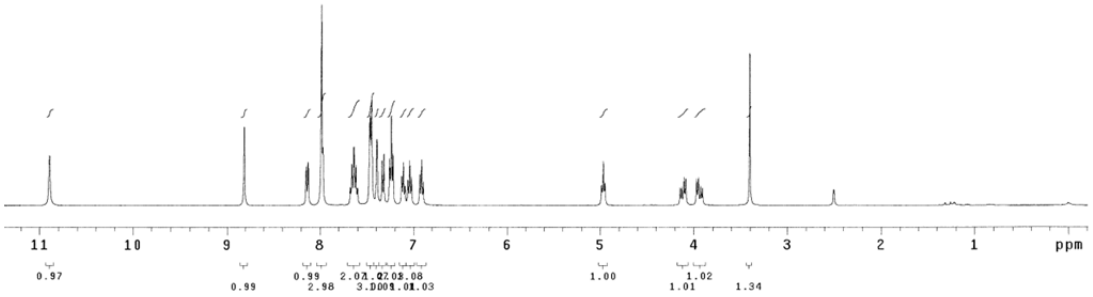

10.924
8.030
8.012
7.642
7.624
7.605
7.529
7.511
7.493
7.353
7.334
7.229
7.217
7.080
7.062
7.042
7.004
6.986
6.965
6.947
6.928
6.882
6.870
6.861
5.215
5.197
5.179
3.934
3.916
3.401
2.504
S
Ph
O
N
H
5ai
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.92
1.061.981.1308
2.950.70.0195
1.00
2.02

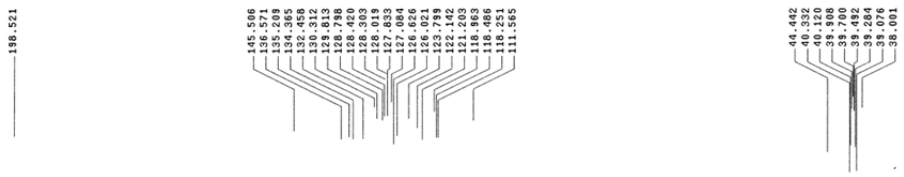

180.170
149.939
136.941
136.570
133.453
128.942
128.236
126.715
126.320
124.083
123.788
122.413
121.288
118.952
118.604
117.935
111.765
45.427
40.337
40.129
39.922
39.714
39.502
39.294
39.087
33.011
32.973
S
Ph
O
N
H
5ai
200
180
160
140
120
100
80
60
40
20
ppm

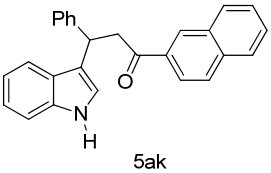



Ph
O
N
H

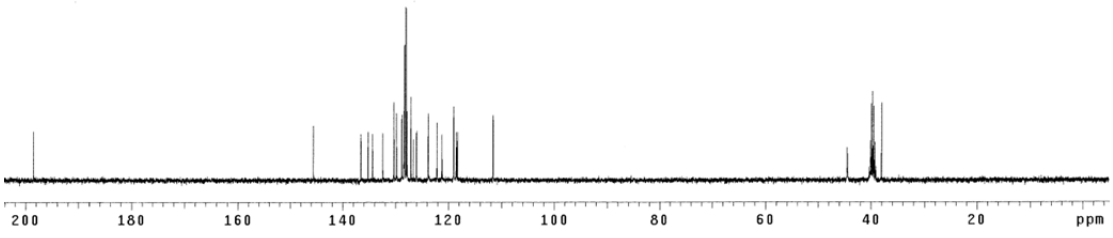
5ak

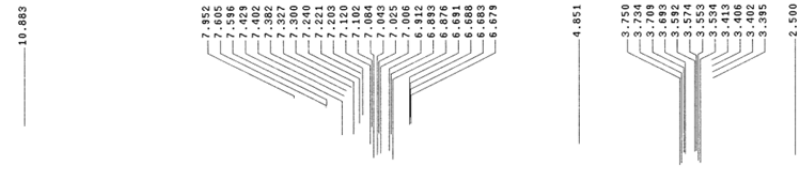

11
10
9
8
7
6
5
4
3
2
1
ppm
0.97
0.99
0.99
2.98
1.00
1.02
1.01
1.34




Ph
O
N
H

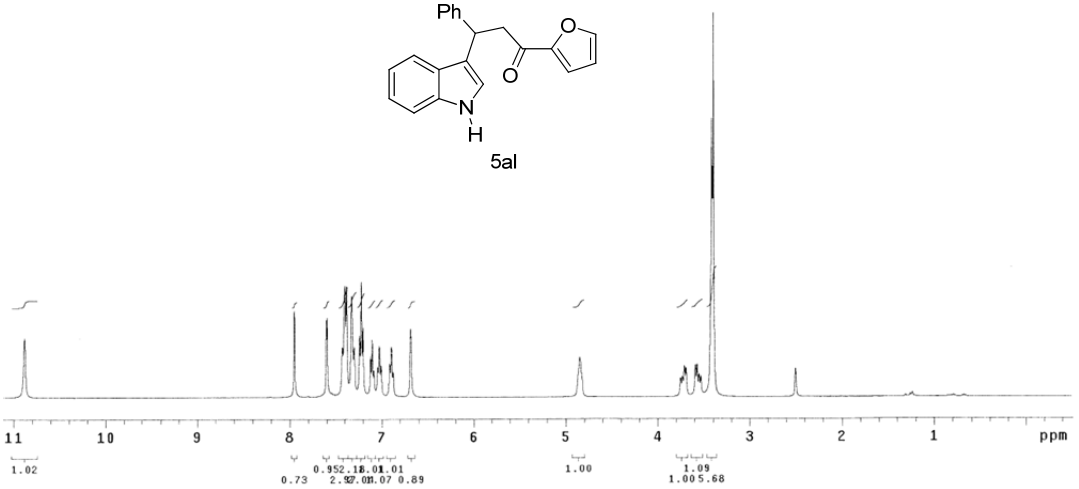
5ak

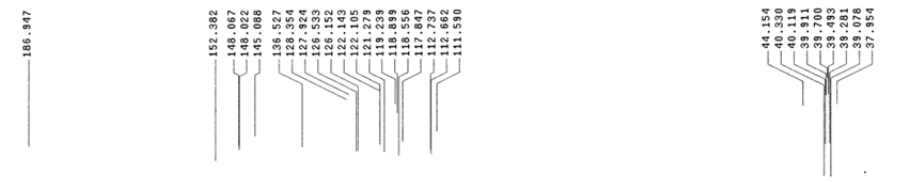

200
180
160
140
120
100
80
60
40
20
ppm

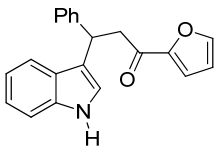

10.883
7.952
7.605
7.596
7.429
7.402
7.382
7.327
7.300
7.240
7.221
7.203
7.120
7.102
7.084
7.043
7.025
6.916
6.912
6.893
6.876
6.691
6.688
6.683
6.679
4.851
3.750
3.734
3.709
3.693
3.592
3.574
3.553
3.536
3.413
3.406
3.402
3.395
2.500

Ph
O
O
N
H

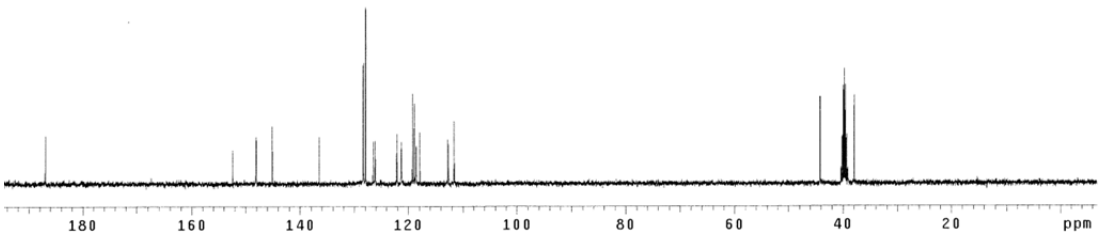
5al

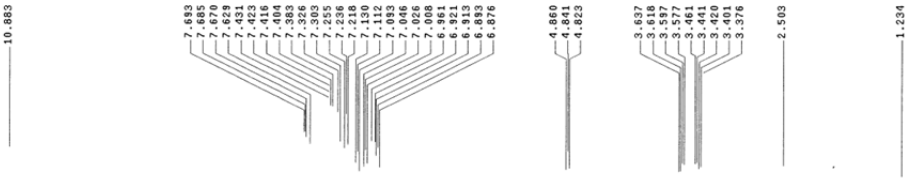

11
10
9
8
7
6
5
4
3
2
1
ppm
1.02
0.73
0.95
2.57
2.18
8.01
7.08
1.01
0.07
0.89
1.00
1.09
1.00
5.68

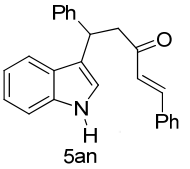

186.947
152.382
148.067
148.022
145.088
136.527
128.354
127.924
126.533
126.152
122.143
122.105
121.279
119.239
118.889
118.556
117.047
112.737
112.662
111.590
44.154
40.330
40.119
39.911
39.700
39.493
39.281
39.078
37.954


Ph
O
O
N
H

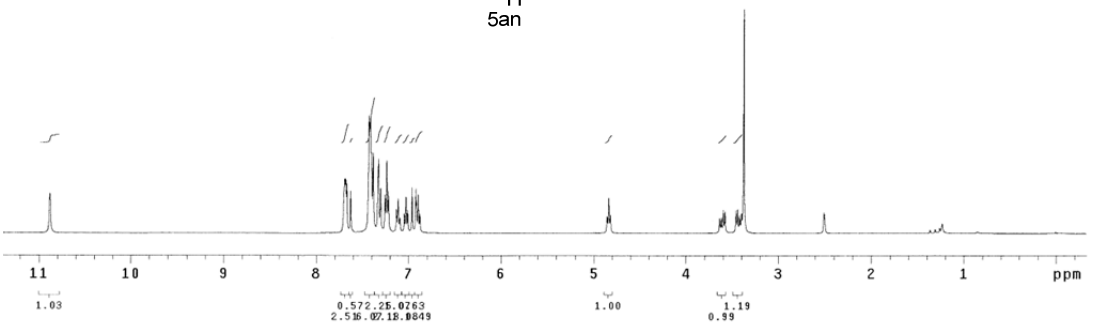
5al

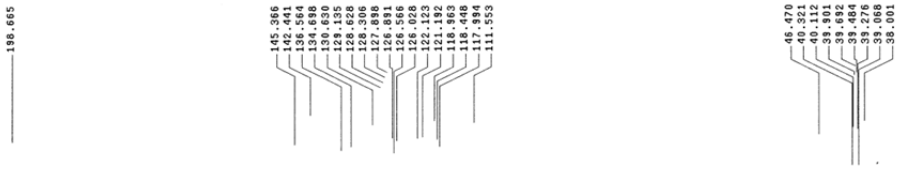

180
160
140
120
100
80
60
40
20
ppm

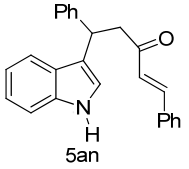

10.883
7.693
7.685
7.670
7.629
7.431
7.423
7.416
7.404
7.383
7.326
7.303
7.255
7.236
7.218
7.130
7.112
7.093
7.046
7.026
7.008
6.961
6.921
6.913
6.893
6.876
4.860
4.841
4.823
3.637
3.616
3.597
3.577
3.461
3.441
3.420
3.401
3.376
2.503
1.234


Ph
O
N
H
Ph

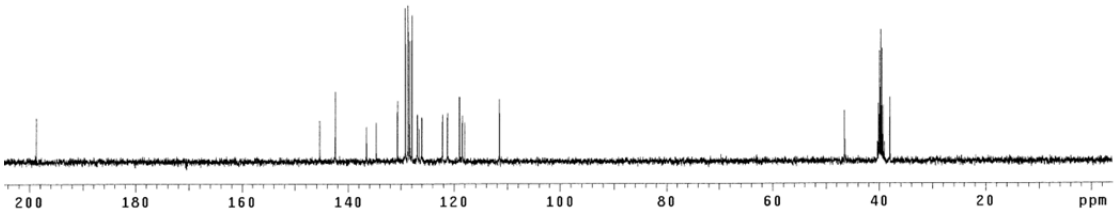
5an

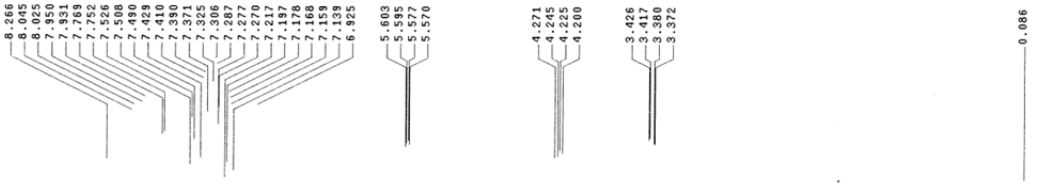

11
10
9
8
7
6
5
4
3
2
1
ppm
1.03
0.57
2.51
25.07
63
16.07
2.18
1.00
1.19
0.99

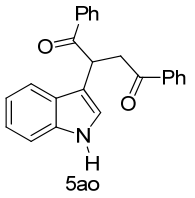

198.665
145.366
142.441
136.564
134.698
130.630
129.135
128.628
128.306
127.898
126.891
126.556
126.028
122.123
121.192
118.963
118.448
117.994
111.553
46.470
40.321
40.112
39.901
39.692
39.484
39.276
39.068
38.001


Ph
O
N
H
Ph

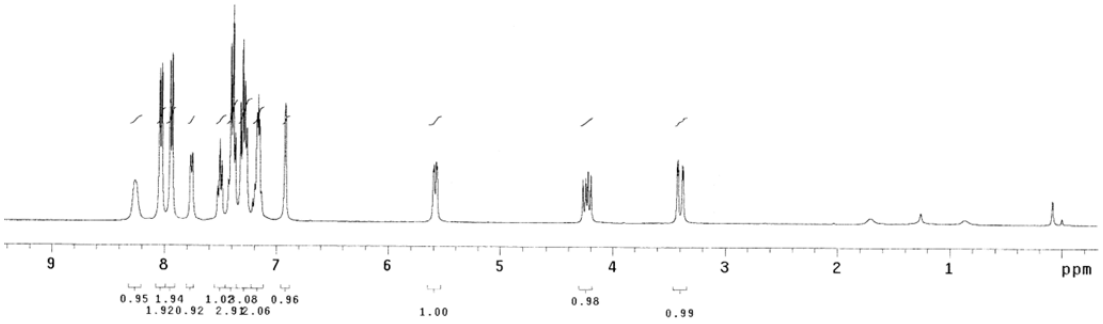
5an

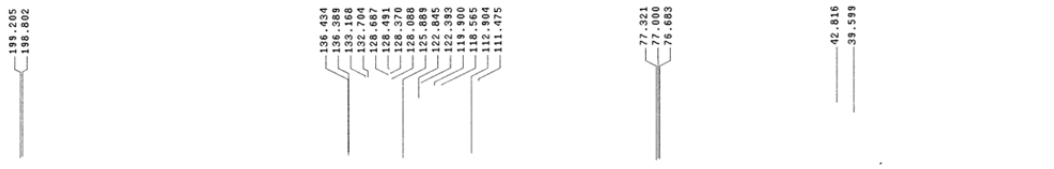

200
180
160
140
120
100
80
60
40
20
ppm

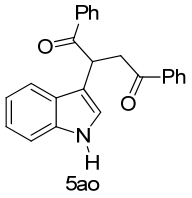

8.266
8.045
8.025
7.950
7.931
7.769
7.752
7.526
7.508
7.490
7.429
7.410
7.390
7.371
7.325
7.306
7.287
7.277
7.270
7.217
7.197
7.178
7.168
7.159
7.138
6.925
5.603
5.595
5.577
5.570
4.271
4.245
4.225
4.200
3.426
3.417
3.380
3.372
0.086


Ph
O
Ph
O
N
H

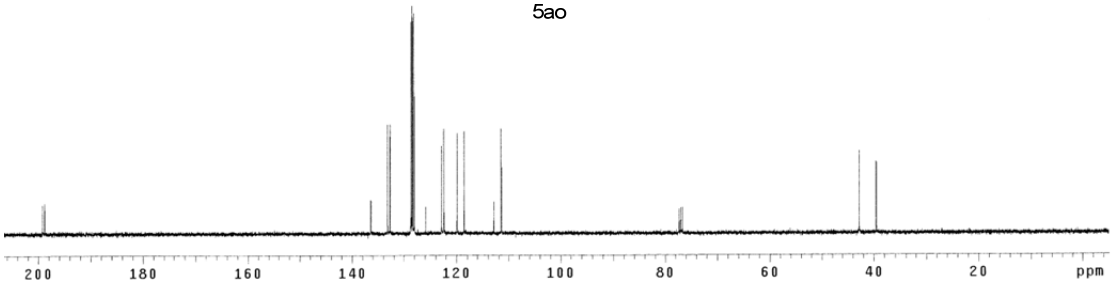
5ao

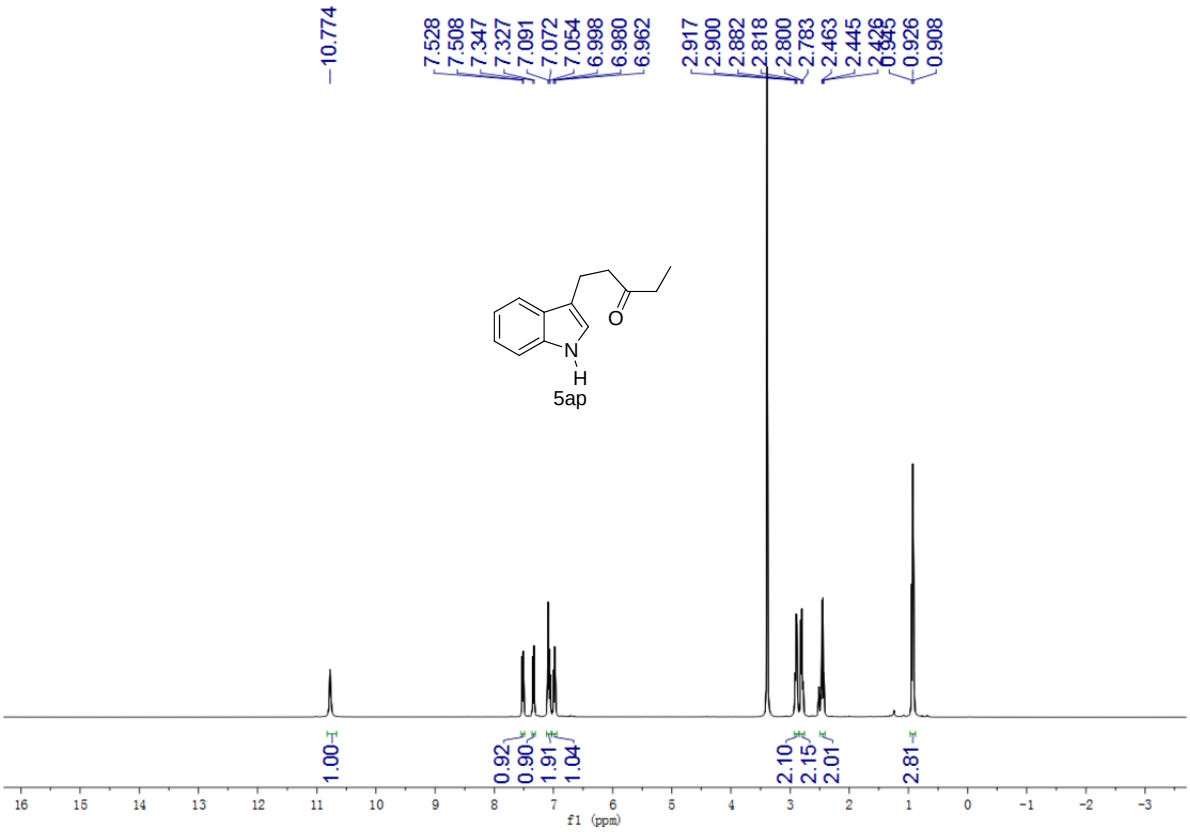

9
8
7
6
5
4
3
2
1
ppm
0.95 1.94 1.92 0.92 1.02 2.91 2.08 2.06 0.96
1.00
0.98
0.99

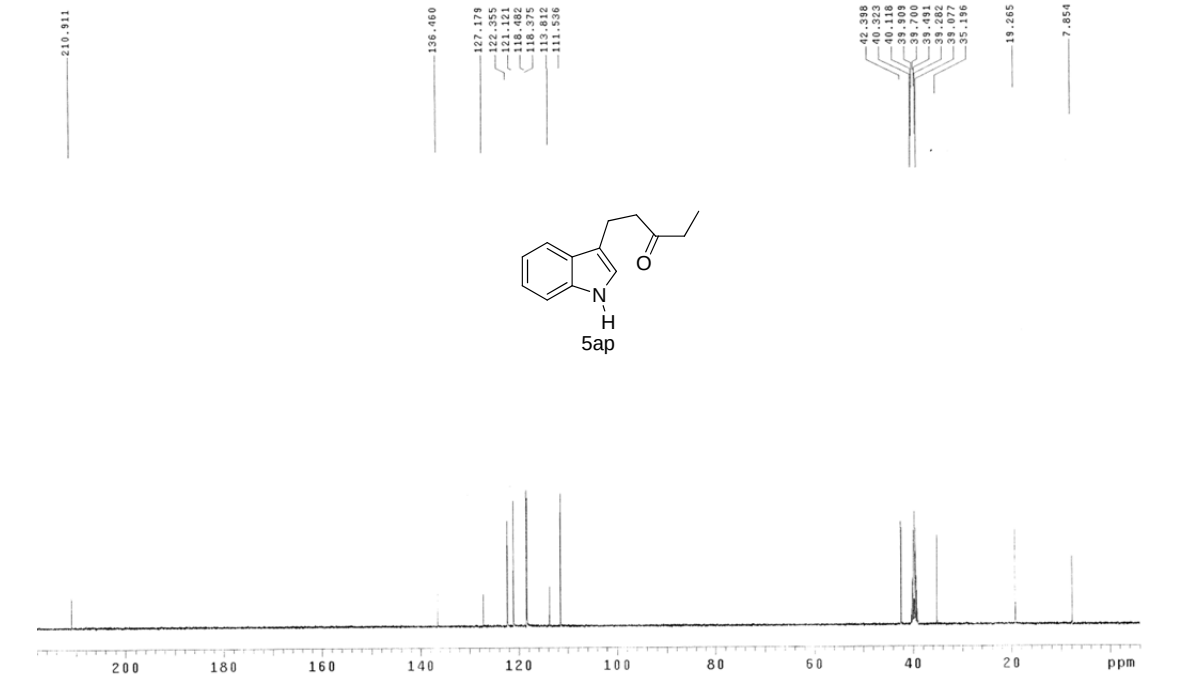

199.205
198.802
136.434
136.389
133.168
132.704
132.687
128.491
128.370
128.088
125.889
122.845
122.393
119.900
118.655
112.904
111.475
77.321
77.000
76.683
42.816
39.599

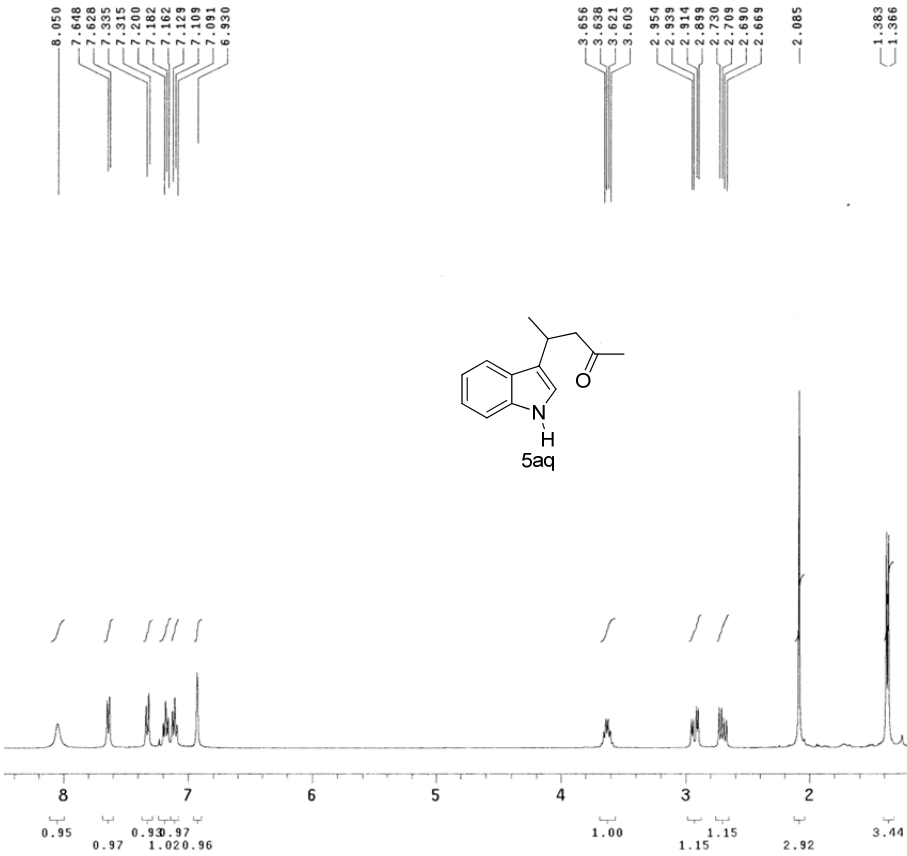

Ph
O
Ph
O
N
H

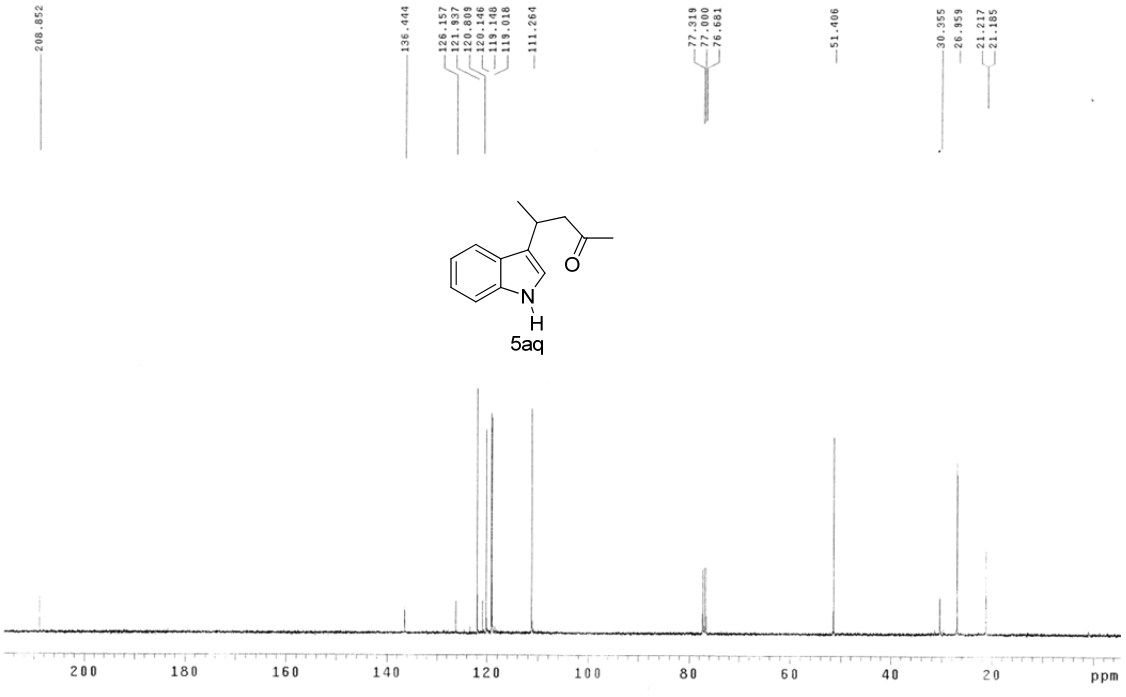
5ao

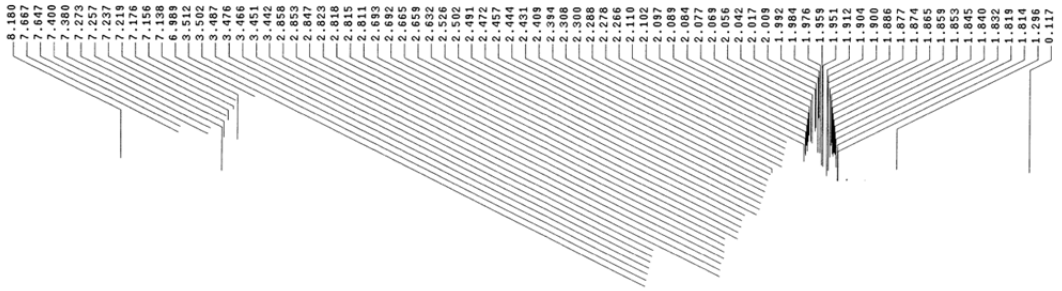

200
180
160
140
120
100
80
60
40
20
ppm

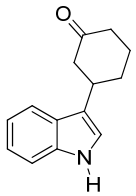

10.774
7.528
7.508
7.347
7.327
7.091
7.072
7.054
6.998
6.980
6.962
2.917
2.900
2.882
2.818
2.800
2.783
2.463
2.445
0.926
0.908
O
N
H
5ap
1.00
0.92
0.90
1.91
1.04
2.10
2.15
2.01
2.81
f1 (ppm)


210.911
136.460
127.179
122.355
121.121
118.482
118.375
113.612
111.536
42.388
40.323
40.118
39.909
39.700
39.491
39.282
39.077
35.196
19.265
7.854
O
N
H
5ap
200
180
160
140
120
100
80
60
40
20
ppm

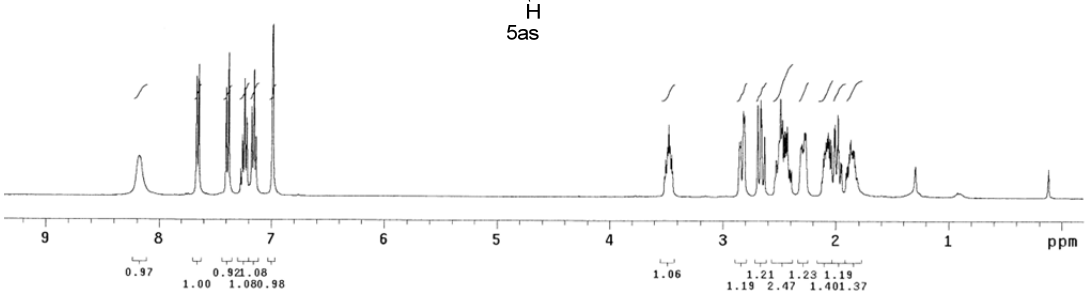

8.050
7.648
7.628
7.335
7.315
7.200
7.182
7.162
7.129
7.109
7.091
6.930
3.656
3.638
3.621
3.603
2.954
2.939
2.914
2.889
2.730
2.709
2.690
2.669
2.085
1.383
1.366
O
N
H
5aq
8
7
6
5
4
3
2
1
ppm
0.95
0.97
0.93
1.02
0.97
0.96
1.00
1.15
1.15
2.92
3.44

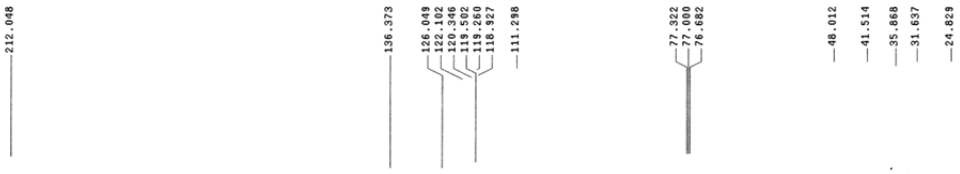

208.852
136.444
126.157
121.937
120.808
120.146
119.148
119.018
111.264
77.318
77.000
76.681
51.406
30.355
26.959
21.217
21.185
O
N
H
5aq
200
180
160
140
120
100
80
60
40
20
ppm

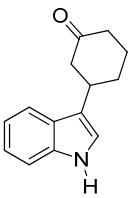

8.180
7.667
7.647
7.400
7.380
7.273
7.257
7.237
7.219
7.176
7.156
7.138
6.989
3.512
3.502
3.487
3.476
3.466
3.451
3.442
2.858
2.853
2.847
2.823
2.816
2.815
2.811
2.693
2.682
2.655
2.632
2.526
2.502
2.491
2.472
2.457
2.444
2.431
2.409
2.394
2.308
2.300
2.288
2.278
2.266
2.110
2.102
2.097
2.089
2.084
2.077
2.069
2.056
2.042
2.017
2.009
1.992
1.984
1.976
1.959
1.951
1.912
1.904
1.900
1.886
1.877
1.874
1.865
1.859
1.853
1.845
1.840
1.832
1.819
1.814
1.296
0.117


O
N
H

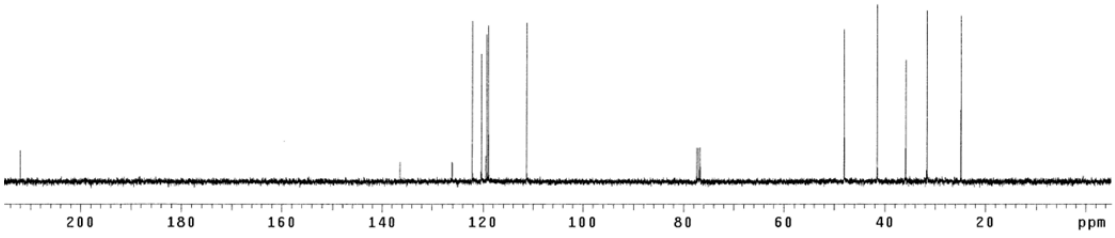
5as

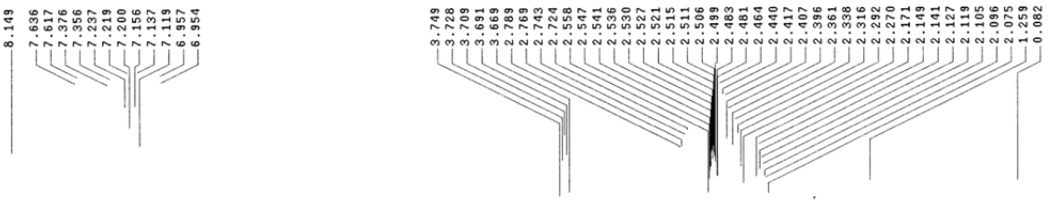

9
8
7
6
5
4
3
2
1
ppm
0.97
0.921.08
1.00 1.080.98
1.06
1.21 1.23 1.19
1.19 2.47 1.401.37

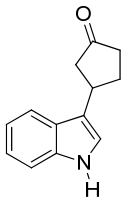

212.048
136.373
126.049
122.102
120.346
119.502
119.260
118.927
111.298
77.322
77.000
76.682
48.012
41.514
35.868
31.637
24.829


O
N
H

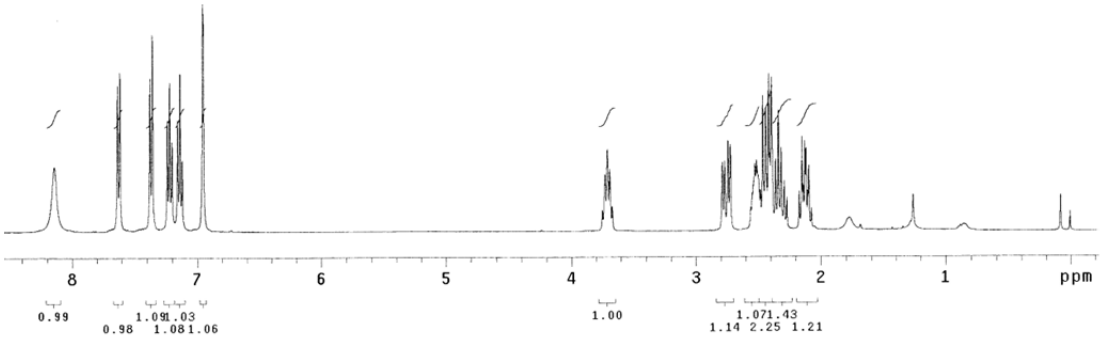
5as

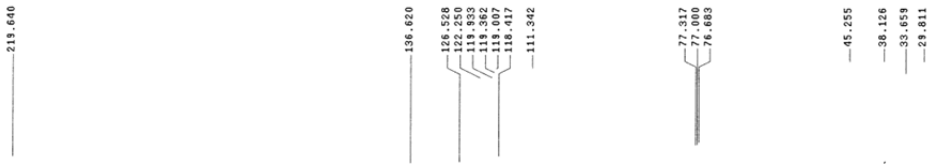

200
180
160
140
120
100
80
60
40
20
ppm

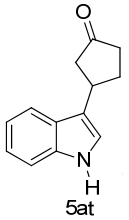

8.149
7.636
7.617
7.376
7.356
7.237
7.219
7.200
7.156
7.137
7.119
6.957
6.954
3.749
3.728
3.709
3.691
3.669
2.789
2.769
2.743
2.724
2.558
2.547
2.541
2.536
2.530
2.527
2.521
2.515
2.511
2.506
2.499
2.483
2.481
2.464
2.440
2.417
2.407
2.396
2.361
2.338
2.316
2.292
2.270
2.171
2.149
2.141
2.127
2.119
2.105
2.096
2.075
1.259
0.082


O
N
H

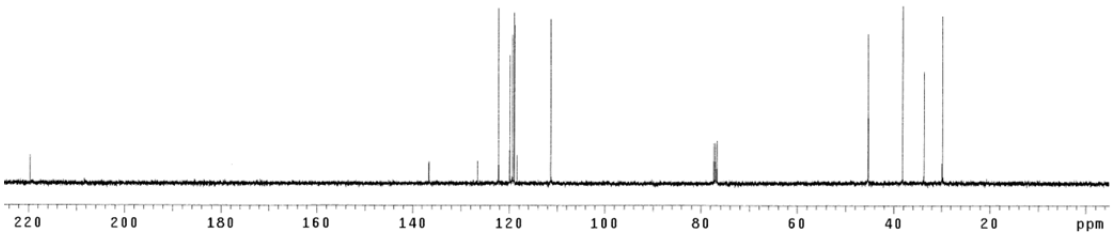
5at

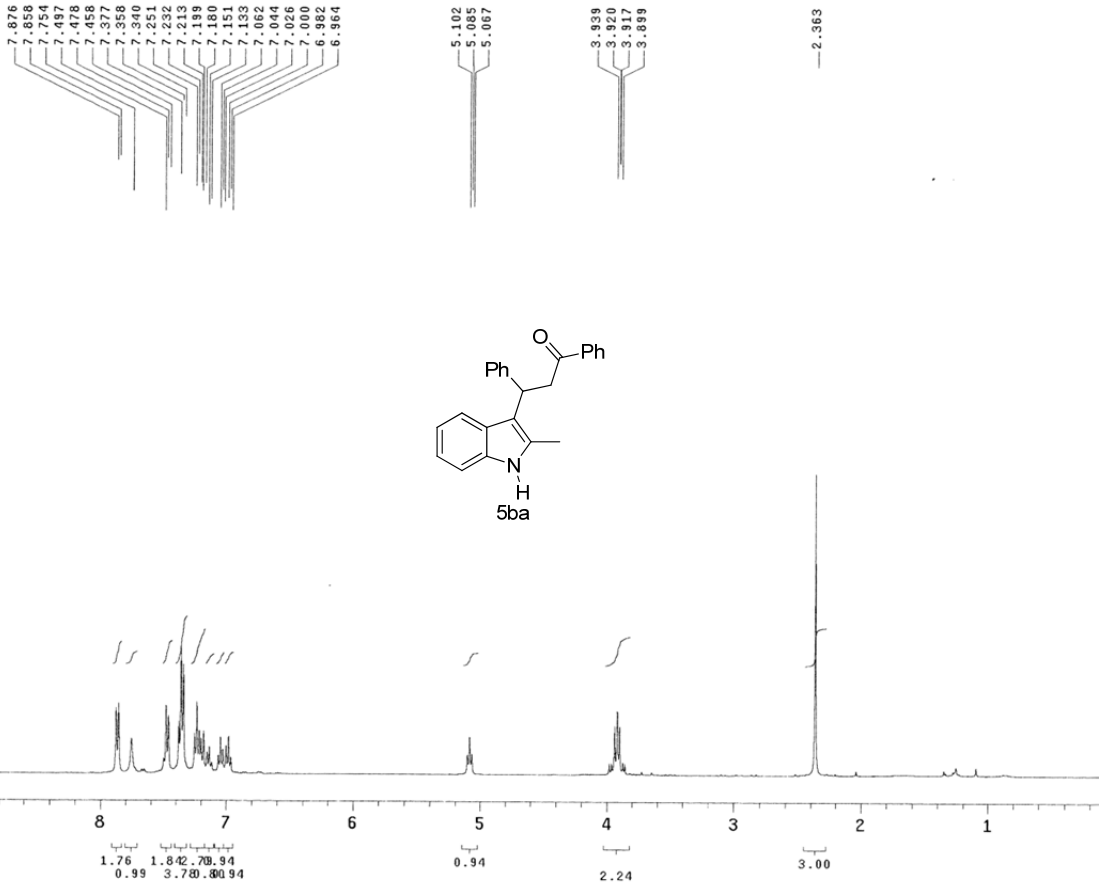

8
7
6
5
4
3
2
1
ppm
0.99
1.09
1.03
0.98
1.08
1.06
1.00
1.07
1.43
1.14
2.25
1.21

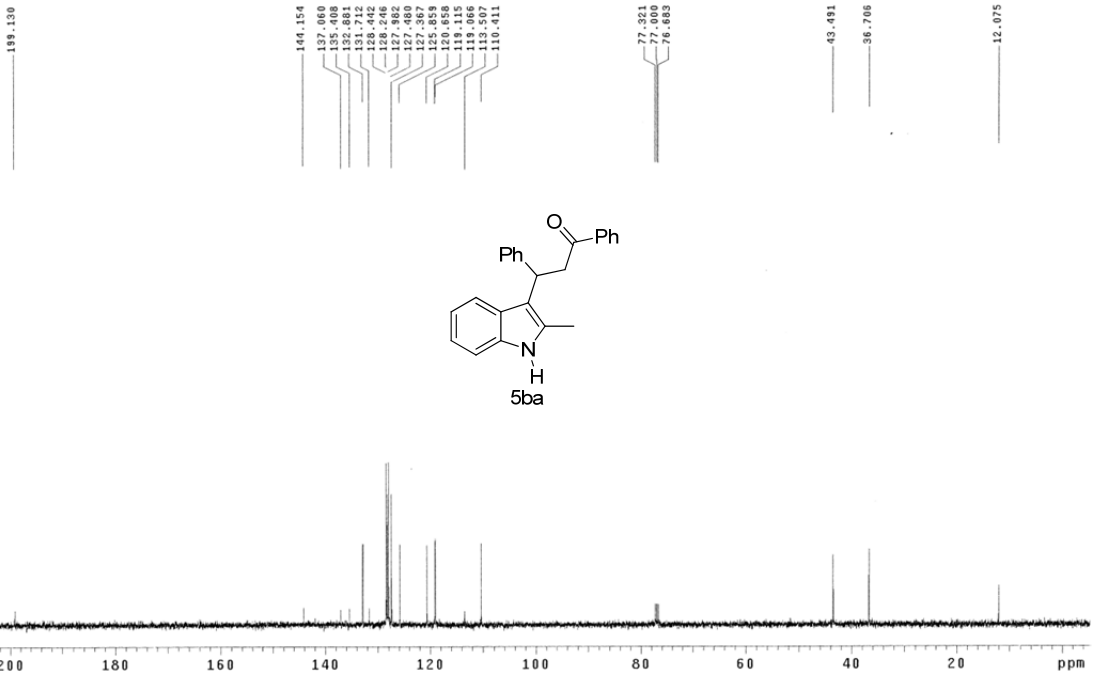

219.640
136.620
126.528
122.250
119.933
119.362
119.007
118.417
111.342
77.317
77.000
76.683
45.255
38.126
33.659
29.811

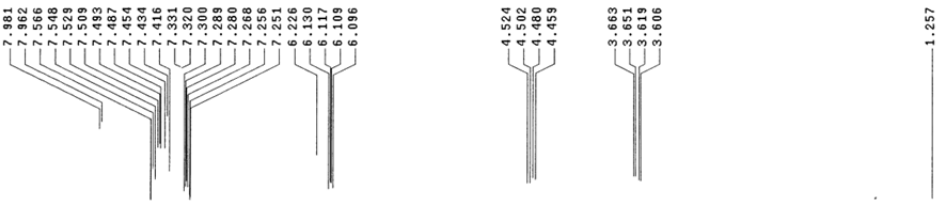

O
N
H

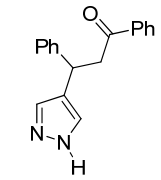
5at


220
200
180
160
140
120
100
80
60
40
20
ppm

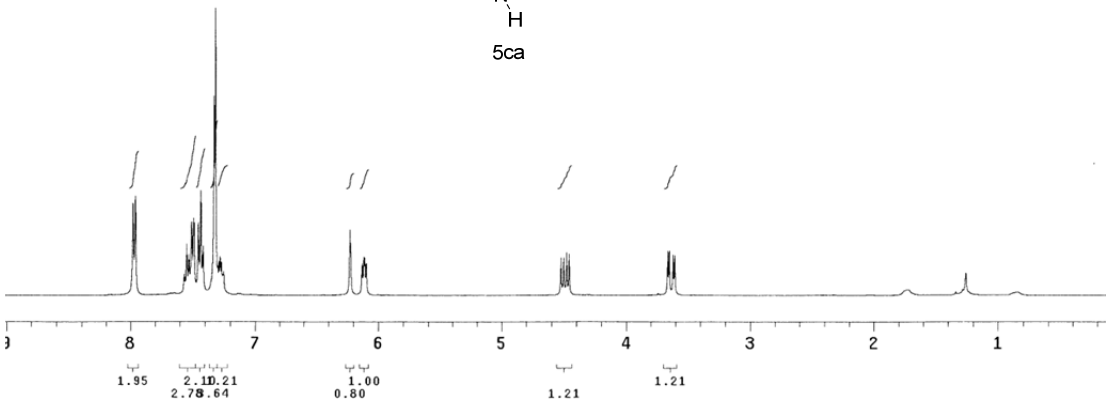

7.876
7.858
7.754
7.497
7.478
7.458
7.377
7.358
7.340
7.251
7.232
7.213
7.199
7.180
7.151
7.133
7.062
7.044
7.026
7.000
6.982
6.964
5.102
5.085
5.067
3.939
3.920
3.917
3.899
2.363
O
Ph
Ph
N
H
5ba
8
7
6
5
4
3
2
1
1.76
0.99
1.84
3.78
2.70
0.80
0.94
0.94
0.94
2.24
3.00


199.130
144.154
137.060
135.408
135.081
131.712
128.442
128.246
127.982
127.480
127.367
125.859
120.658
120.115
119.066
113.507
110.411
77.321
77.000
76.683
43.491
36.706
12.075
O
Ph
Ph
N
H
5ba
200
180
160
140
120
100
80
60
40
20
ppm

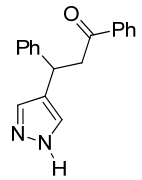

7.981
7.962
7.566
7.548
7.529
7.509
7.493
7.487
7.454
7.434
7.416
7.331
7.320
7.300
7.289
7.280
7.268
7.256
7.251
6.226
6.130
6.117
6.109
6.096
4.524
4.502
4.480
4.459
3.663
3.651
3.619
3.606
1.257


O
Ph
Ph
N
N
H

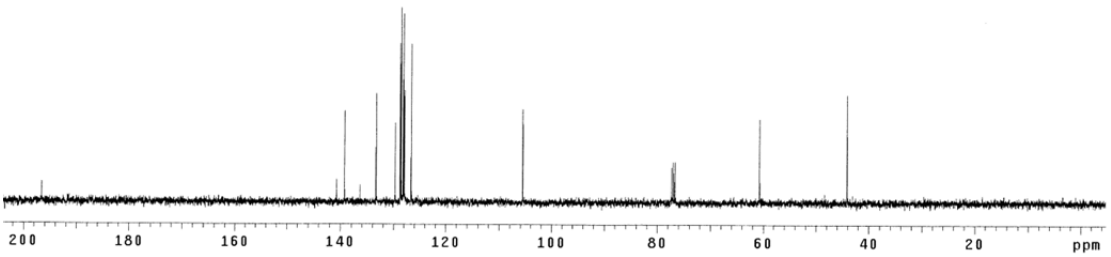
5ca

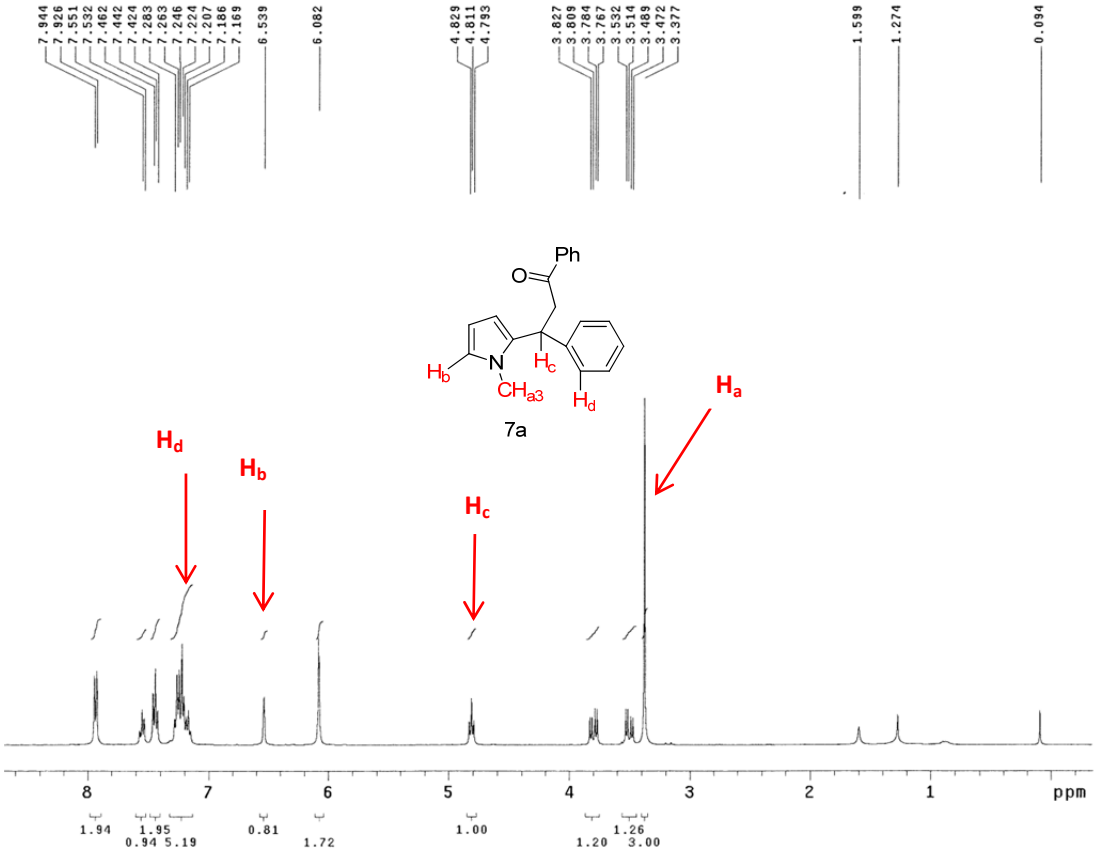

8
7
6
5
4
3
2
1
1.95
2.11
0.21
2.78
3.64
1.00
0.80
1.21
1.21

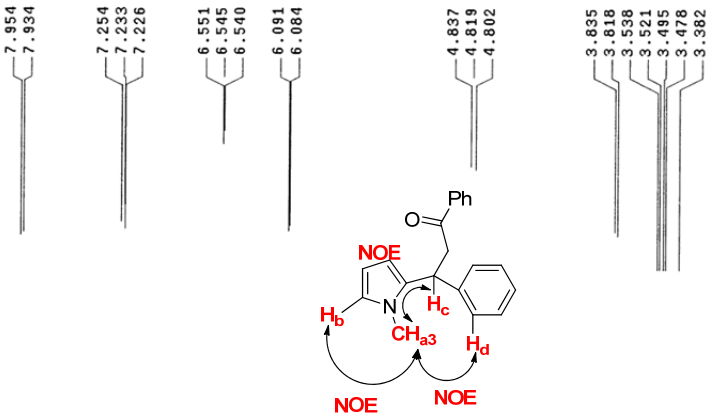

196.555
140.679
139.230
136.441
133.349
129.727
128.755
128.573
128.151
127.953
126.639
105.542
77.322
77.000
76.686
60.723
44.133

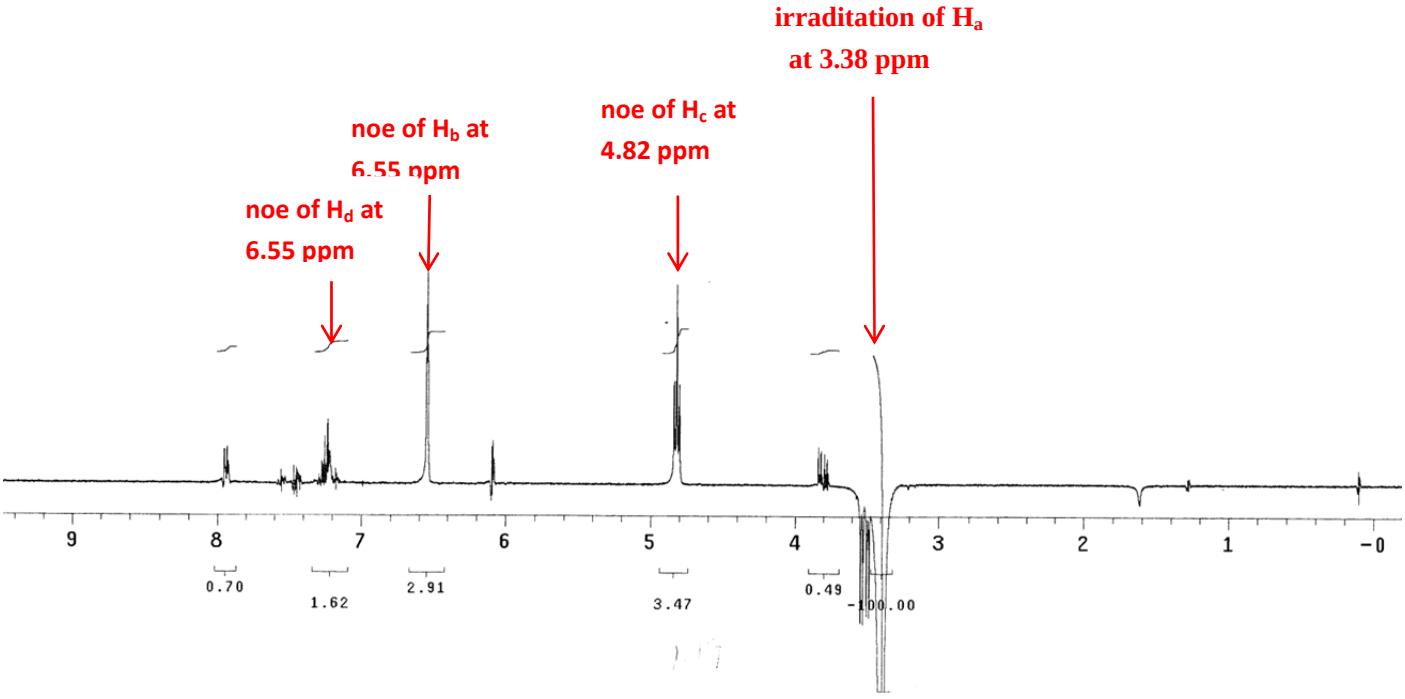

O
Ph
Ph
N
N
H

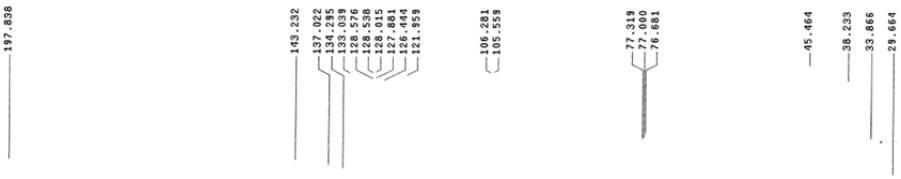
5ca

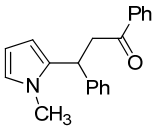

200
180
160
140
120
100
80
60
40
20
ppm


7.944
7.926
7.551
7.532
7.462
7.442
7.424
7.283
7.263
7.246
7.224
7.207
7.186
7.169
6.539
6.082
4.829
4.811
4.793
3.827
3.809
3.784
3.767
3.532
3.514
3.489
3.472
3.377
1.599
1.274
0.094
Ph
O
N
Hb
Hc
CHa3
Hd
7a
Hd
Hb
Hc
Ha
8
7
6
5
4
3
2
1
ppm
1.94
1.95
0.94
5.19
0.81
1.72
1.00
1.20
1.26
3.00

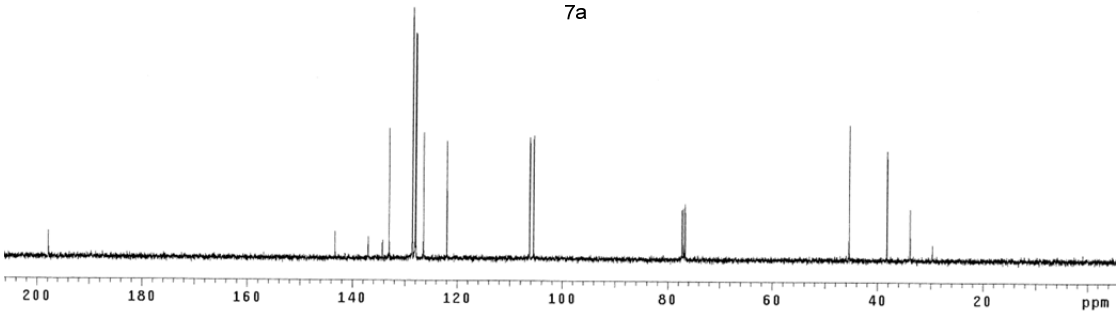

7.954
7.934
7.254
7.233
7.226
6.551
6.545
6.540
6.091
6.084
4.837
4.819
4.802
3.835
3.818
3.538
3.521
3.495
3.478
3.382
Ph
O
NOE
N
H_b
H_c
CH_{a3}
H_d
NOE
NOE

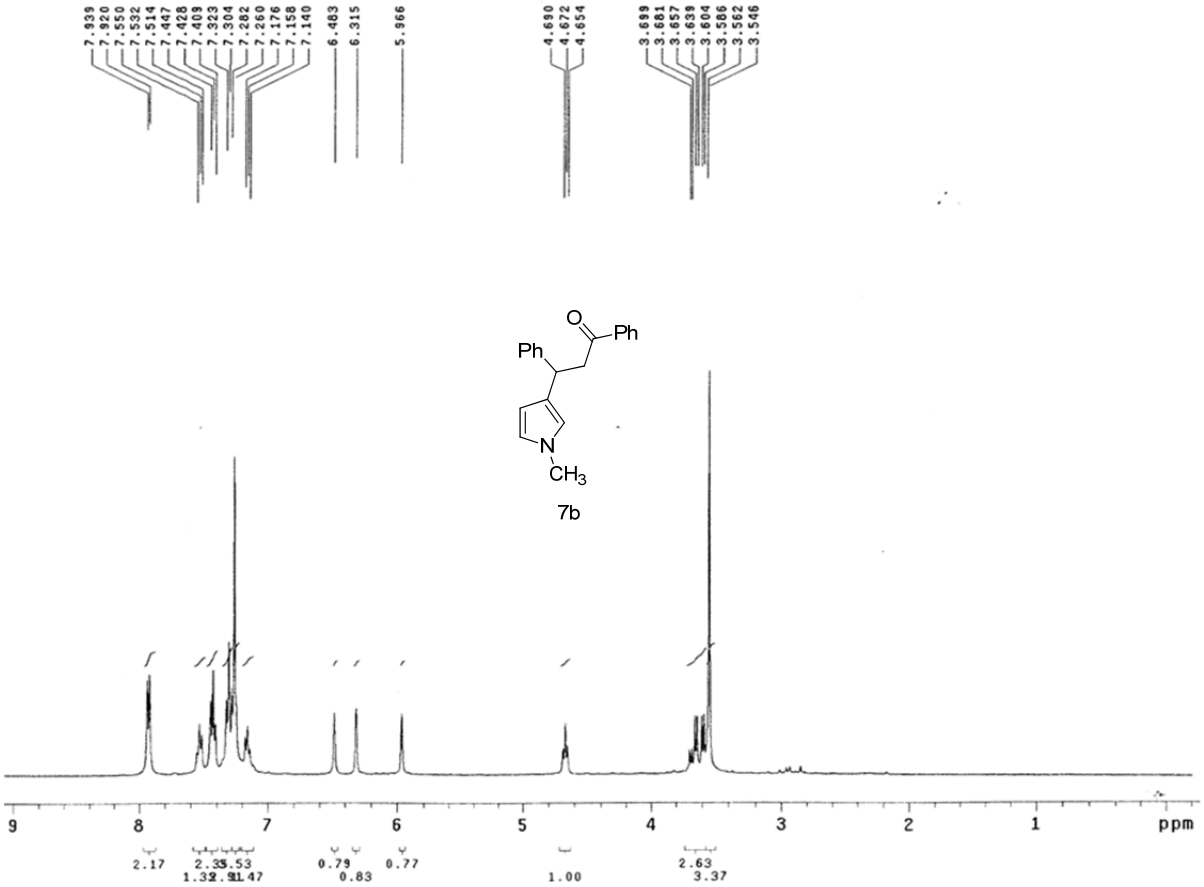

irraditation of H_a
at 3.38 ppm
noe of H_c at
4.82 ppm
noe of H_b at
6.55 ppm
noe of H_d at
6.55 ppm
9
8
7
6
5
4
3
2
1
-0
0.70
1.62
2.91
3.47
0.49
-100.00


197.838
143.232
137.022
134.295
133.039
128.576
128.538
128.015
127.681
126.444
121.959
106.281
105.559
77.319
77.000
76.681
45.464
38.233
33.866
29.664

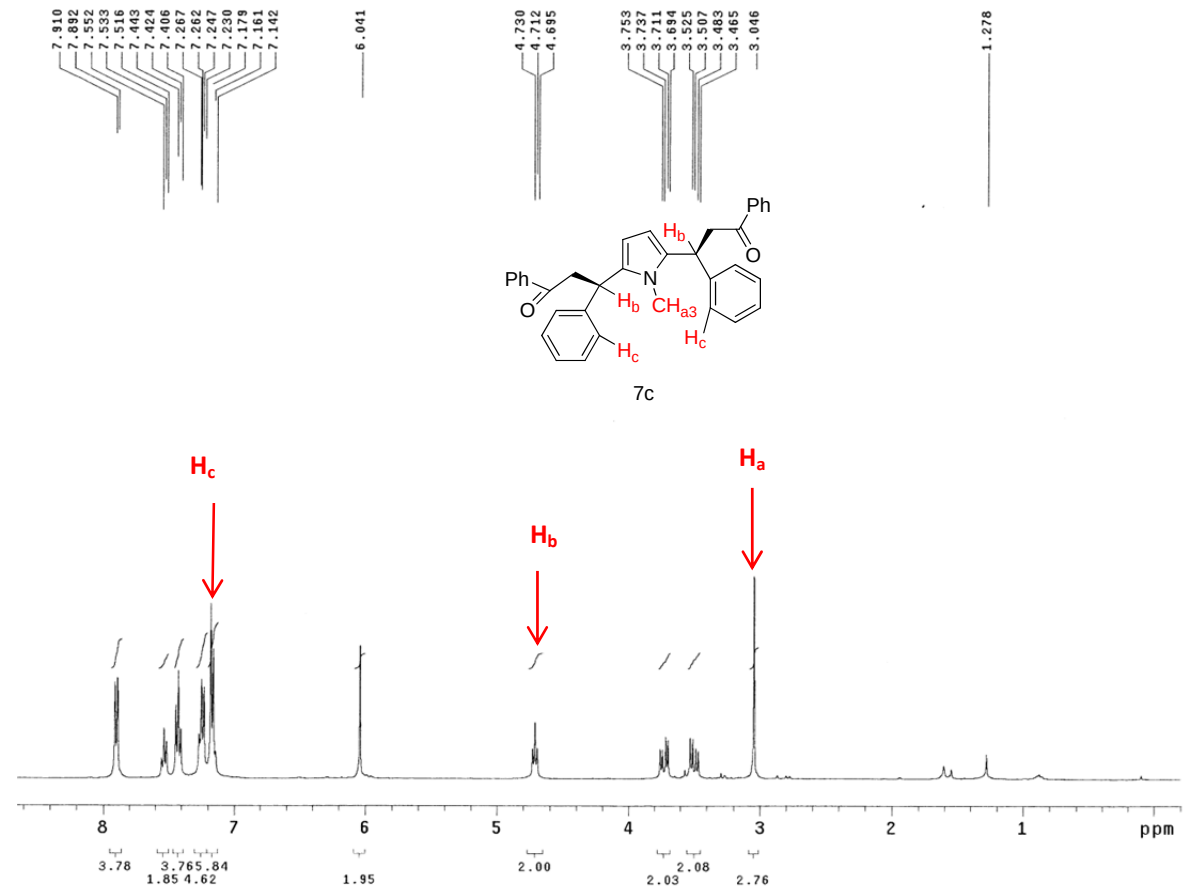

Ph
O
N
Ph
CH_3

7a

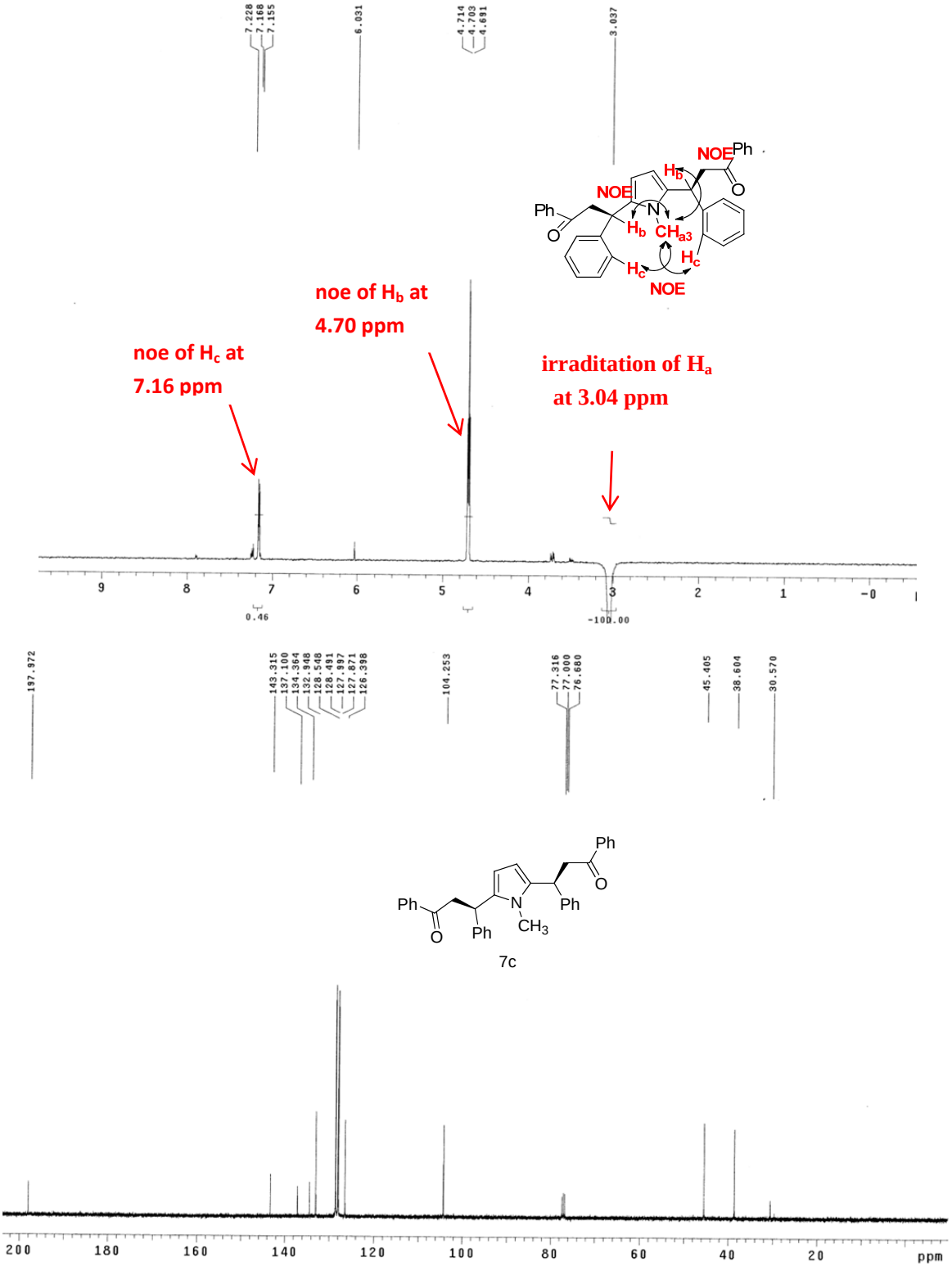

200
180
160
140
120
100
80
60
40
20
ppm


7.939
7.920
7.550
7.532
7.514
7.447
7.428
7.409
7.323
7.304
7.282
7.260
7.176
7.158
7.140
6.483
6.315
5.966
4.690
4.672
4.654
3.699
3.681
3.657
3.639
3.604
3.586
3.562
3.546
O
Ph
Ph
N
CH3
9
8
7
6
5
4
3
2
1
ppm
2.17
2.35
3.53
1.32
2.91
1.47
0.79
0.83
0.77
1.00
2.63
3.37

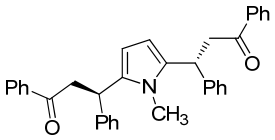
7b


7.910
7.892
7.552
7.533
7.516
7.443
7.424
7.406
7.267
7.262
7.247
7.230
7.179
7.161
7.142
6.041
4.730
4.712
4.695
3.753
3.737
3.711
3.694
3.525
3.507
3.483
3.465
3.046
1.278
Ph
Hb
O
Ph
O
N
Hb
CHa3
Hc
Hc
Hc
Hb
Ha
8
7
6
5
4
3
2
1
ppm
3.78
3.76
5.84
1.85
4.62
1.95
2.00
2.08
2.03
2.76

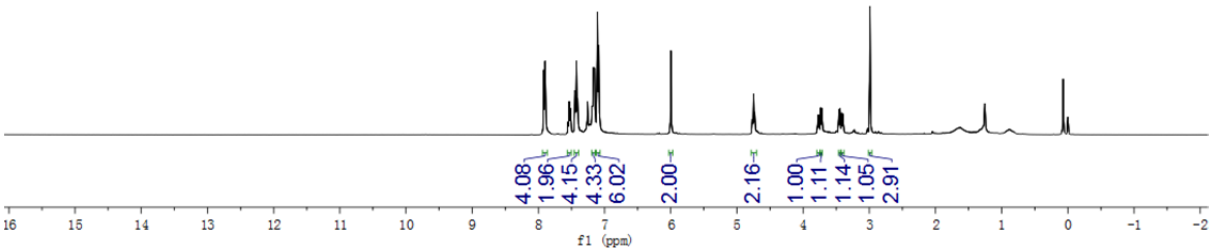
7c

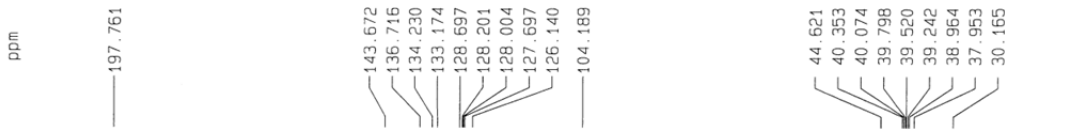

7.228
7.168
7.155
6.031
4.714
4.703
4.691
3.037
NOE
Ph
Hb
NOE
Ph
O
N
Hb
CHa3
Hc
Hc
NOE
noe of Hb at
4.70 ppm
noe of Hc at
7.16 ppm
irraditation of Ha
at 3.04 ppm
9
8
7
6
5
4
3
2
1
-0
0.46
-100.00
197.872
143.315
137.100
134.364
132.948
128.548
128.491
127.997
127.871
126.398
104.253
77.316
77.000
76.680
45.405
38.604
30.570
Ph
O
Ph
N
CH3
Ph
Ph
O
Ph
7c
200
180
160
140
120
100
80
60
40
20
ppm

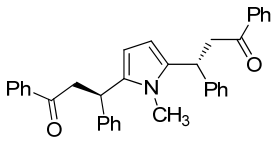

7.919
7.899
7.552
7.534
7.516
7.444
7.426
7.407
7.257
7.189
7.170
7.152
7.107
7.089
5.998
4.766
4.748
4.731
3.777
3.759
3.734
3.717
3.459
3.442
3.417
3.399
2.990


Ph
O
Ph
N
CH3
Ph
O
Ph

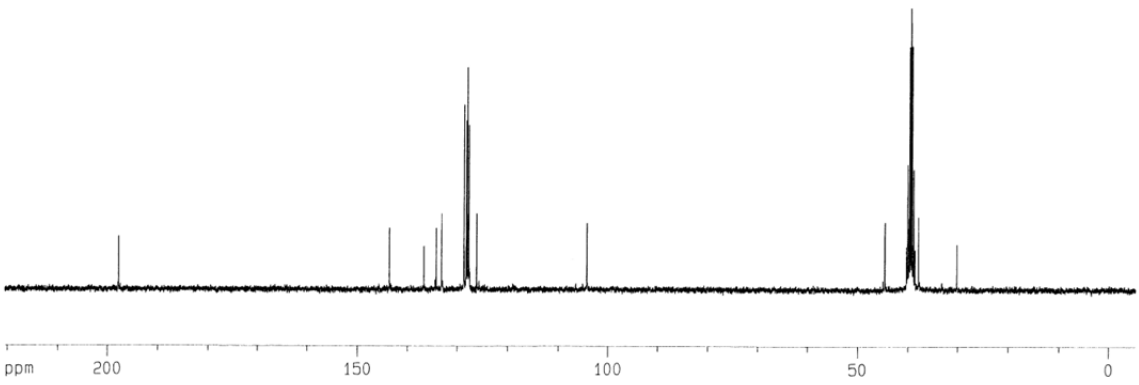
7d

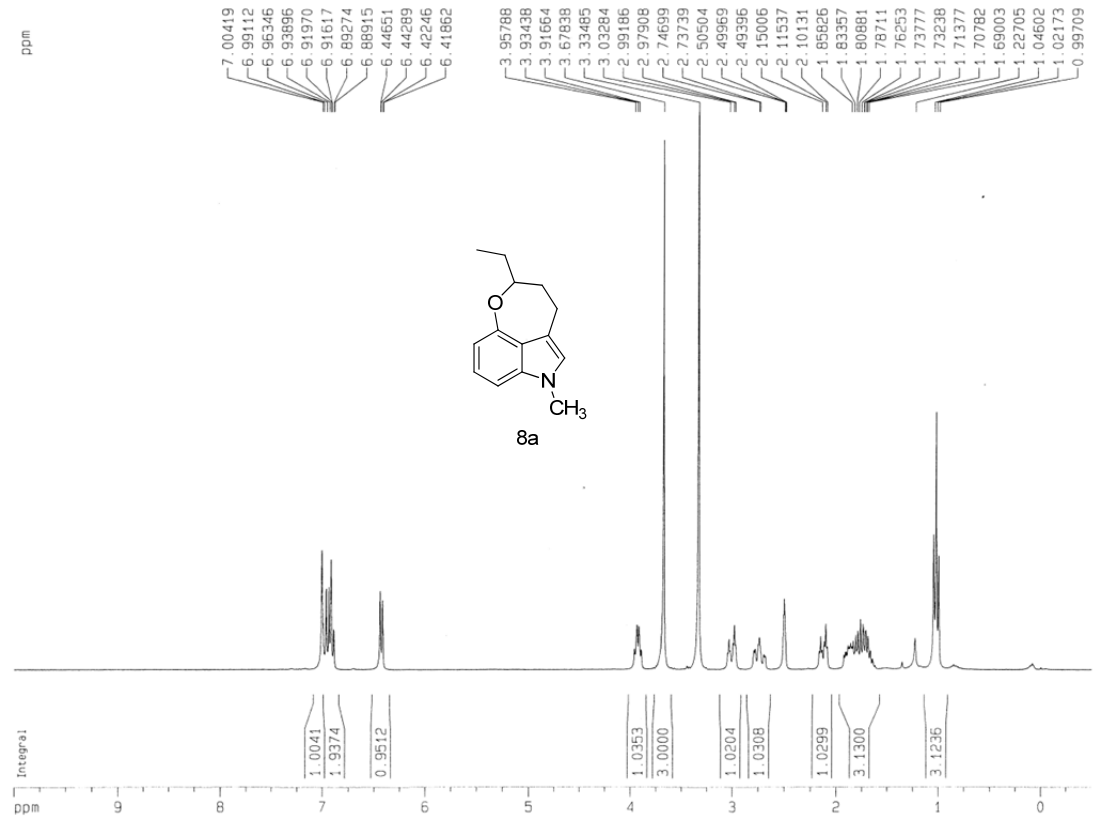

4.08
1.96
4.15
4.33
6.02
2.00
2.16
1.00
1.11
1.14
1.05
2.91
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

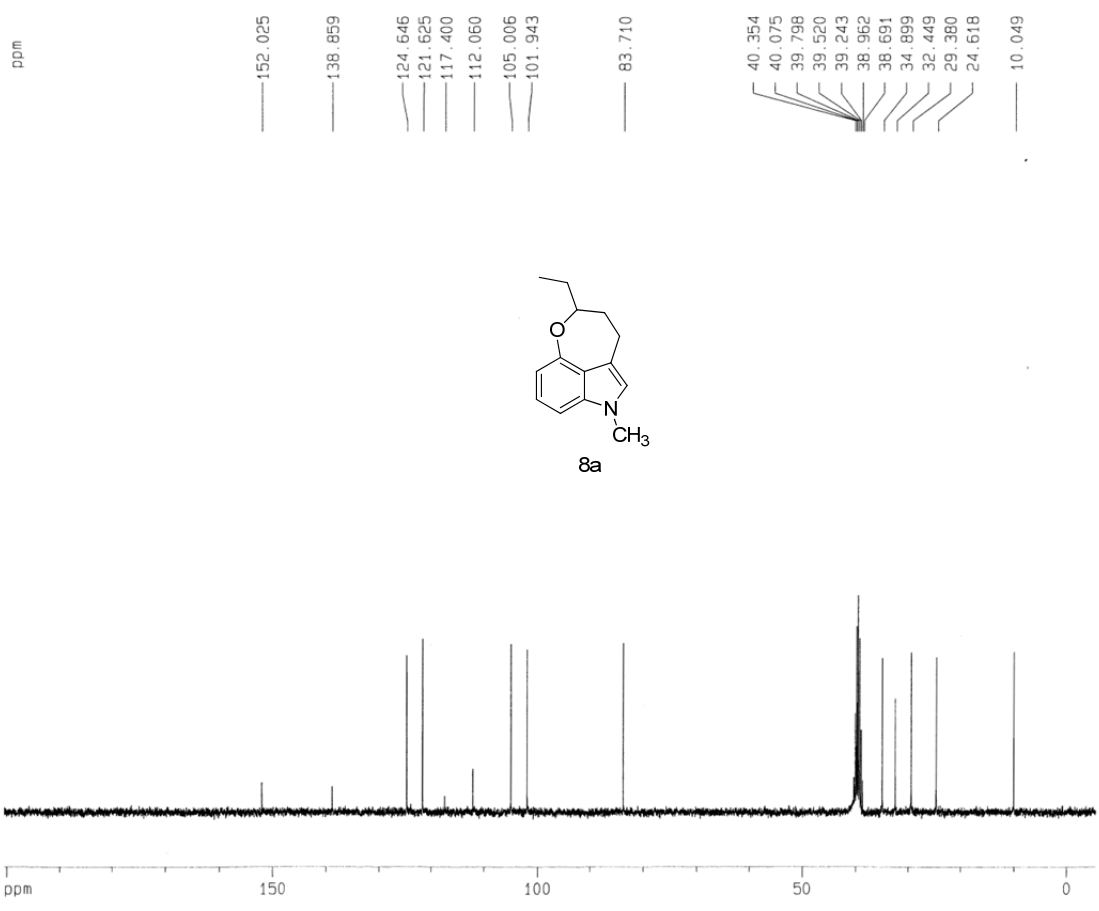

ppm
197.761
143.672
136.716
134.230
133.174
128.697
128.201
128.004
127.697
126.140
104.189
44.621
40.353
40.074
39.798
39.520
39.242
38.964
37.953
30.165

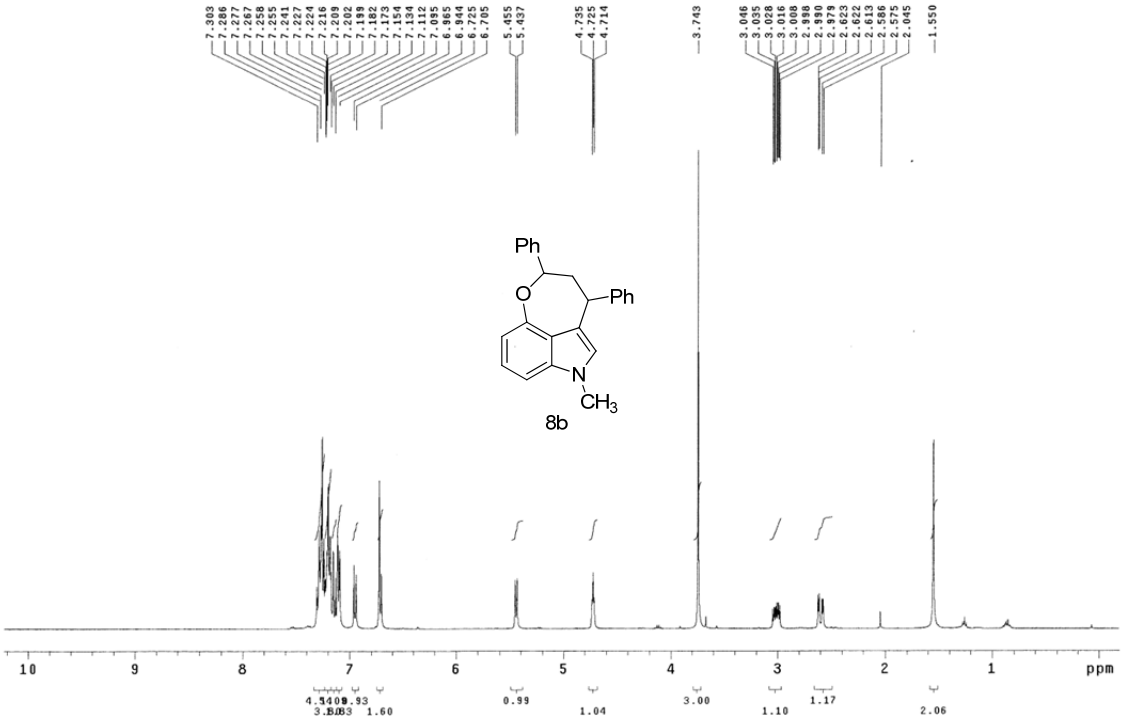

Ph
O
Ph
N
CH3
Ph
O
Ph

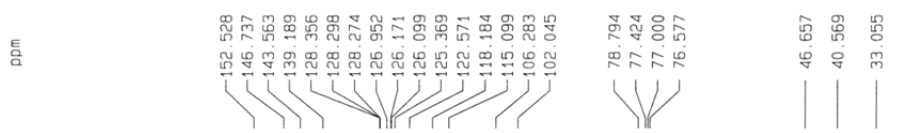
7d

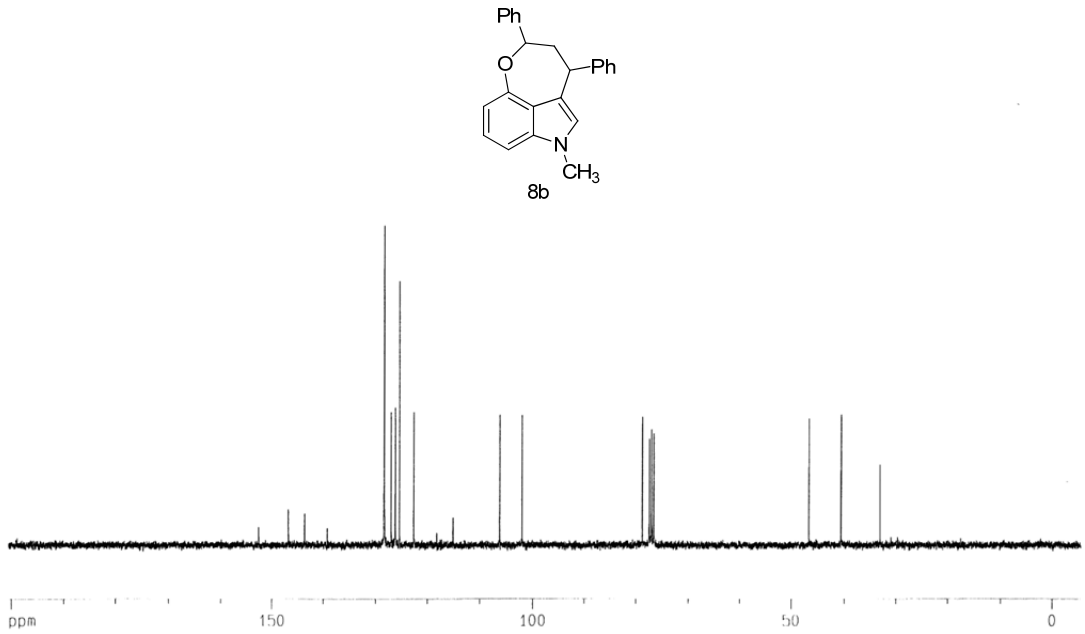

ppm
200
150
100
50
0

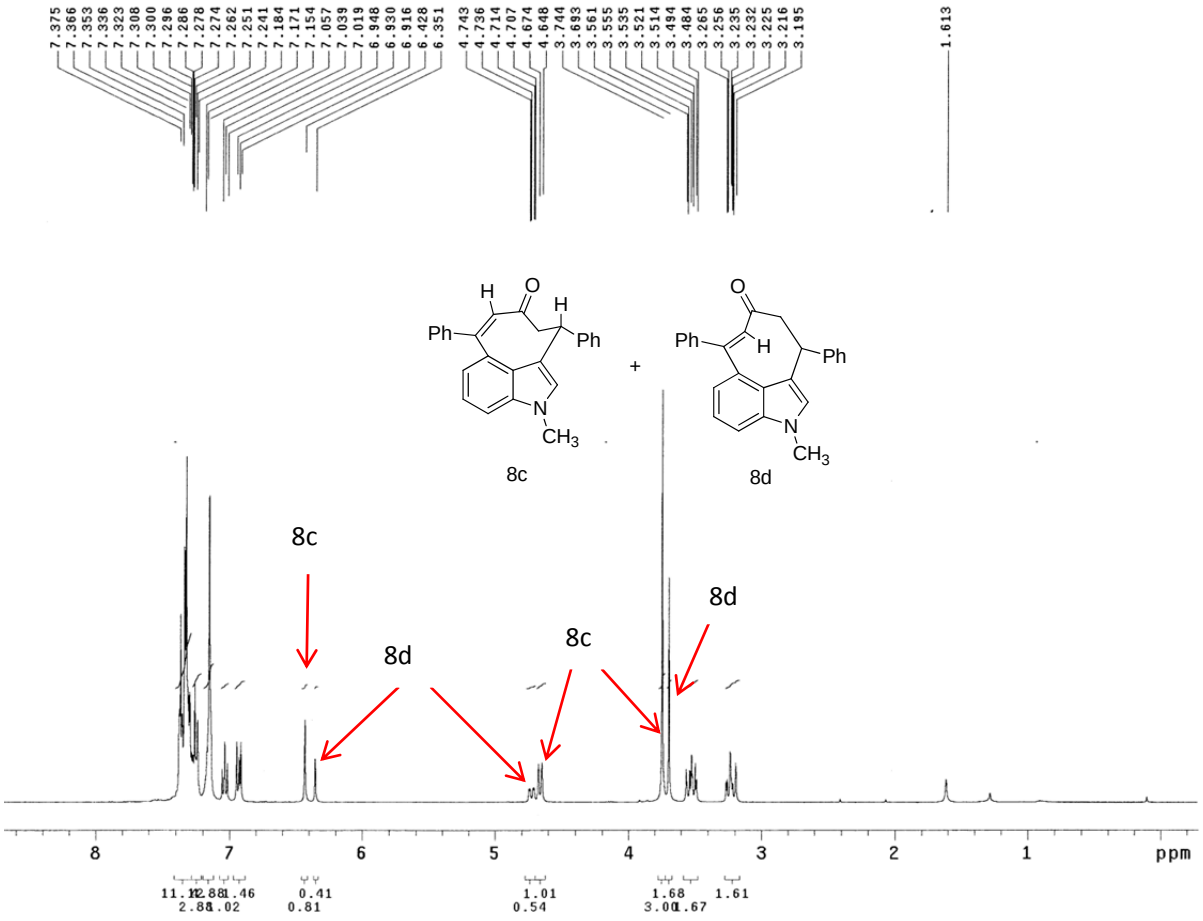

ppm
7.00419
6.99112
6.96346
6.93896
6.91970
6.91617
6.89274
6.88915
6.44651
6.44289
6.42246
6.41862
3.95788
3.93438
3.91664
3.67838
3.33485
3.03284
2.99186
2.97908
2.74699
2.73739
2.50504
2.49969
2.49396
2.15006
2.11537
2.10131
1.85826
1.83357
1.80881
1.78711
1.76253
1.73777
1.73238
1.71377
1.70782
1.69003
1.22705
1.04602
1.02173
0.99709
O
N
CH3
8a
Integral
1.0041
1.9374
0.9512
1.0353
3.0000
1.0204
1.0308
1.0299
3.1300
3.1236
ppm
9
8
7
6
5
4
3
2
1
0


ppm
152.025
138.859
124.646
121.625
117.400
112.060
105.006
101.943
83.710
40.354
40.075
39.798
39.520
39.243
38.962
38.691
34.899
32.449
29.380
24.618
10.049
O
N
CH3
8a
ppm
150
100
50
0


7.303
7.286
7.277
7.267
7.258
7.255
7.241
7.227
7.224
7.216
7.209
7.202
7.199
7.182
7.173
7.154
7.134
7.112
7.095
6.965
6.944
6.725
6.705
5.455
5.437
4.735
4.725
4.714
3.743
3.046
3.035
3.028
3.016
3.008
2.998
2.990
2.979
2.623
2.622
2.613
2.586
2.575
2.045
1.550
Ph
O
Ph
N
CH3
8b
10
9
8
7
6
5
4
3
2
1
ppm
0.99
1.04
3.00
1.10
1.17
2.06
1.60


ppm
152.528
146.737
143.563
139.189
128.356
128.298
128.274
126.952
126.171
126.099
125.369
122.571
118.184
115.099
106.283
102.045
78.794
77.424
77.000
76.577
46.657
40.569
33.055


Ph
O
Ph
N
CH3
8b
ppm
150
100
50
0


7.375
7.366
7.353
7.336
7.323
7.308
7.300
7.296
7.286
7.278
7.274
7.262
7.251
7.241
7.184
7.171
7.154
7.057
7.039
7.019
6.948
6.930
6.916
6.428
6.351
4.743
4.736
4.714
4.707
4.674
4.648
3.744
3.693
3.561
3.555
3.535
3.521
3.514
3.494
3.484
3.265
3.256
3.235
3.232
3.225
3.216
3.195
1.613
H
O
H
Ph
Ph
N
CH3
8c
+
O
Ph
H
Ph
N
CH3
8d
8c
8d
8c
8d
8
7
6
5
4
3
2
1
ppm
11.12
2.88
2.88
1.46
2.88
1.02
0.41
0.81
1.01
0.54
1.68
3.00
1.67
1.61