Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Radicals-Carbenes Coupling Reactions: Mn-Catalyzed Syn-thesis of Indoles from Tertiary Amines and Diazo Compounds

Huihuang Li, Yanwei Zhao, Liang Ma, Meihua Ma, Jun Jiang, and Xiaobing Wan*

Table of Contents

General Information

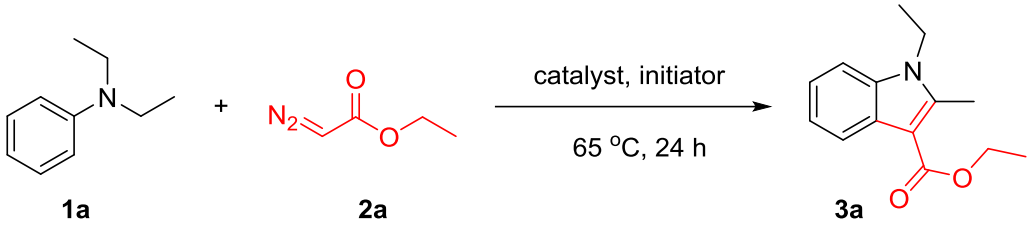
All manipulations were carried out under air atmosphere. Column chromatography was generally performed on basic aluminum oxide (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H NMR (400MHz) and ^{13}C NMR (100MHz) data were recorded with $CDCl_3$ as solvent at room temperature unless specified otherwise. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) or DMSO (δ = 40.00 ppm) as internal reference. IR, MS and HRMS were performed by the State-authorized Analytical Center in Soochow University.

General procedures for reactions

$Mn(OAc)_2$•$4H_2O$ (0.025 mmol), 4,4'-Azobis(4-cyanovaleric acid) (ACVA) (0.63 mmol) were added to a 20 mL test tube with a stirring bar. DMF/EtOH=3:1 (2.0 mL), N,N-Diethylaniline (**1a**) (0.25 mmol, 1.0 eq), diazoacetic ester (0.75 mmol) were added via syringe. The reaction mixture was heated in an oil bath at 65 °C for 24 h under air. The reaction mixture was then poured in brine solution (15 mL) and extracted with diethyl ether (3x20 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by basic aluminum oxide column chromatography using petroleum ether/ ethylacetate to give the desired products.

Optimization of the Reaction Conditions

Table S1. Optimization of the Reaction Conditions.[a]



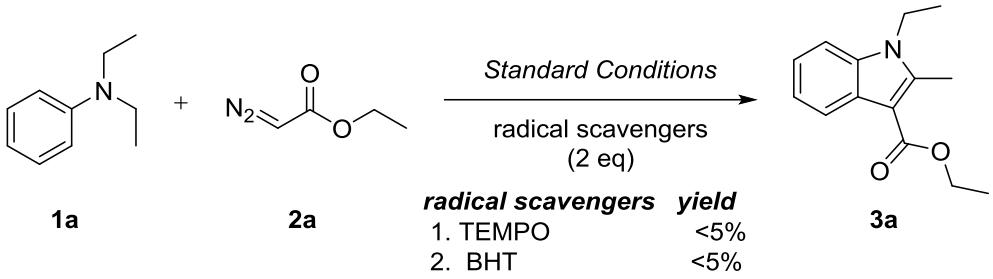
1a **2a** **3a**

Entry	Catalyst	Initiator	Solvent	Yield[b]
1	$Mn(OAc)_2$▪$4H_2O$	ACVA[c]	DMF/EtOH (3:1)	81%
2	$Mn(OAc)_2$▪$4H_2O$	AIBN[d]	DMF/EtOH (3:1)	36%
3	$Mn(OAc)_2$▪$4H_2O$	AMBN[e]	DMF/EtOH (3:1)	51%
4	$Mn(OAc)_2$▪$4H_2O$	AMVN[f]	DMF/EtOH (3:1)	39%
5	$Mn(OAc)_2$▪$4H_2O$	MAIB[g]	DMF/EtOH (3:1)	63%
6	$Mn(OAc)_2$▪$4H_2O$	AAPH[h]	DMF/EtOH (3:1)	trace
7	$Mn(OAc)_2$▪$4H_2O$	DTBP	DMF/EtOH (3:1)	trace
8	$Mn(OAc)_2$▪$4H_2O$	TBHP	DMF/EtOH (3:1)	10%
9	$Mn(OAc)_2$▪$4H_2O$	TBN	DMF/EtOH (3:1)	trace
10	$Mn(OAc)_2$▪$4H_2O$	-	DMF/EtOH (3:1)	trace
11	-	ACVA	DMF/EtOH (3:1)	35%
12	MnC_2O_4▪$2H_2O$	ACVA	DMF/EtOH (3:1)	65%
13	$Mn(OAc)_3$▪$2H_2O$	ACVA	DMF/EtOH (3:1)	71%
14	$MnBr_2$	ACVA	DMF/EtOH (3:1)	63%
15	CuO	ACVA	DMF/EtOH (3:1)	62%
16	$Co(OAc)_2$▪$4H_2O$	ACVA	DMF/EtOH (3:1)	53%
17	AgOAc	ACVA	DMF/EtOH (3:1)	27%
18	$Rh_2(OAc)_4$	ACVA	DMF/EtOH (3:1)	trace
19	Ferrocene	ACVA	DMF/EtOH (3:1)	5%
20	$Pd(OAc)_2$	ACVA	DMF/EtOH (3:1)	15%
21	$Mn(OAc)_2$▪$4H_2O$	ACVA	DMF	66%
22	$Mn(OAc)_2$▪$4H_2O$	ACVA	DCE	12%
23	$Mn(OAc)_2$▪$4H_2O$	ACVA	EtOH	24%
24	$Mn(OAc)_2$▪$4H_2O$	ACVA	THF	15%
25	$Mn(OAc)_2$▪$4H_2O$	ACVA	MeCN	<5%
26	$Mn(OAc)_2$▪$4H_2O$	ACVA	Toluene	<5%
27[i]	$Mn(OAc)_2$▪$4H_2O$	ACVA	DMF/EtOH (3:1)	trace

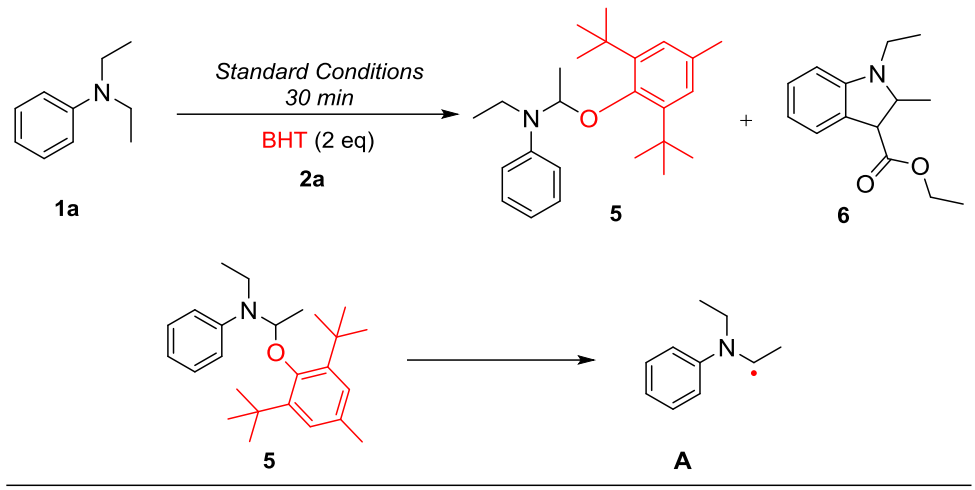
[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.75 mmol), catalyst (10 mol%) and initiator (2.5 equiv.) in 2.0 mL of solvent was stirred at 65 °C for 24 h under air. [b] Isolated yields. [c] ACVA = cis-4,4'-azobis(4-cyanovaleric acid). [d] AIBN = 2,2'-dicyano-2,2'-azopropane. [e] AMBN = 2,2'-azodi-(2-methylbutyronitrile). [f] AMVN = 2,2'-azobis(2,4-dimethyl)valeronitrile. [g] MAIB= dimethyl 2,2'-azobis(isobutyrate). [h] AAPH = 2,2'-azobis(2-methylpropionamidine) dihydrochloride. [i] argon atmosphere.

Mechanistic studies

(a) Radical scavengers

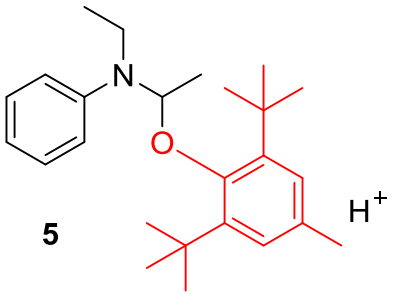


(b) Trapping of radical intermediates by BHT[a].



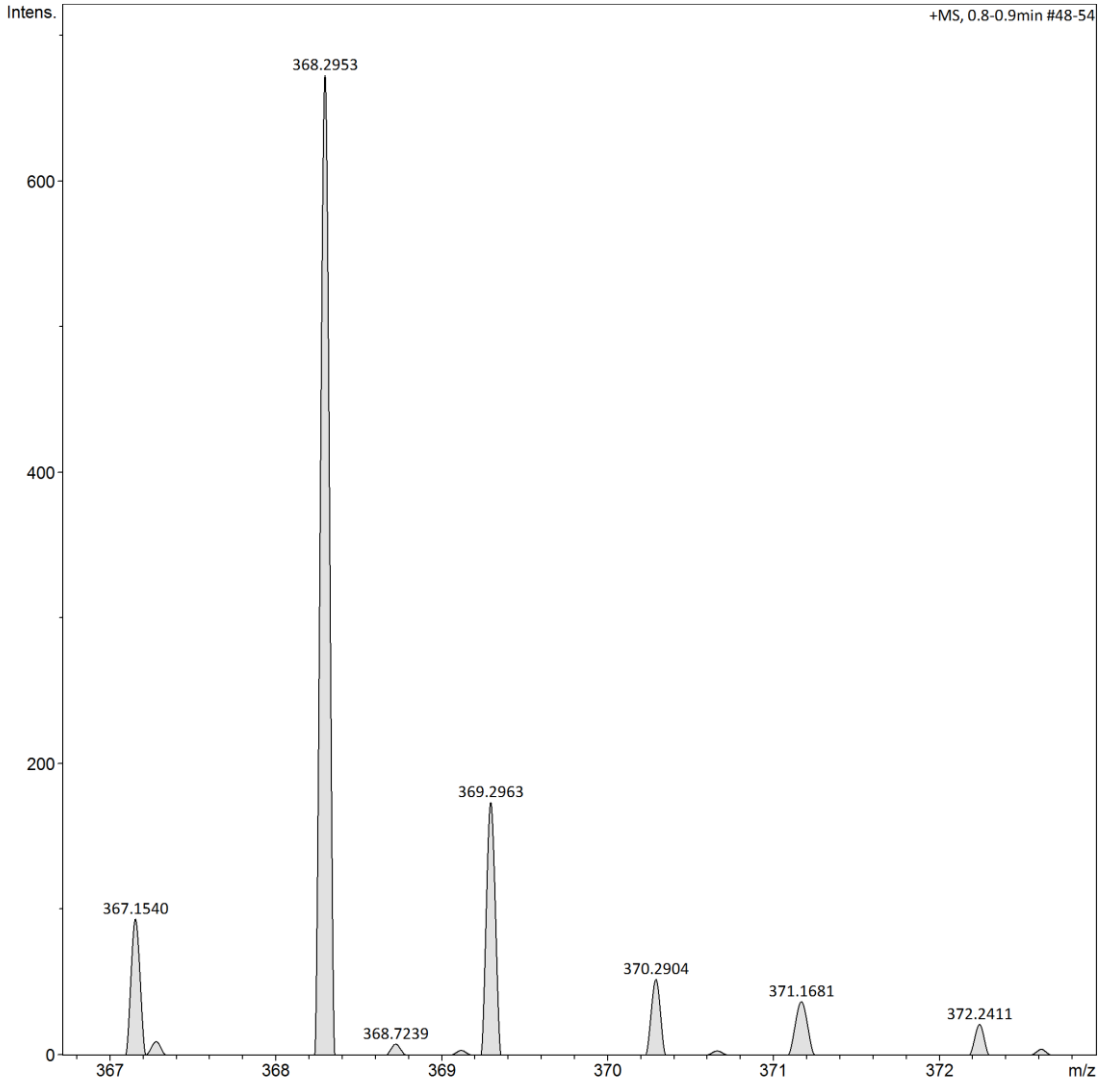
[a] BHT was added after the standard system being stirred for 15 minutes, the reaction was stopped after another 30 minutes.

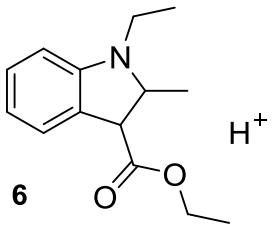
Adduct Detected by HRMS



5

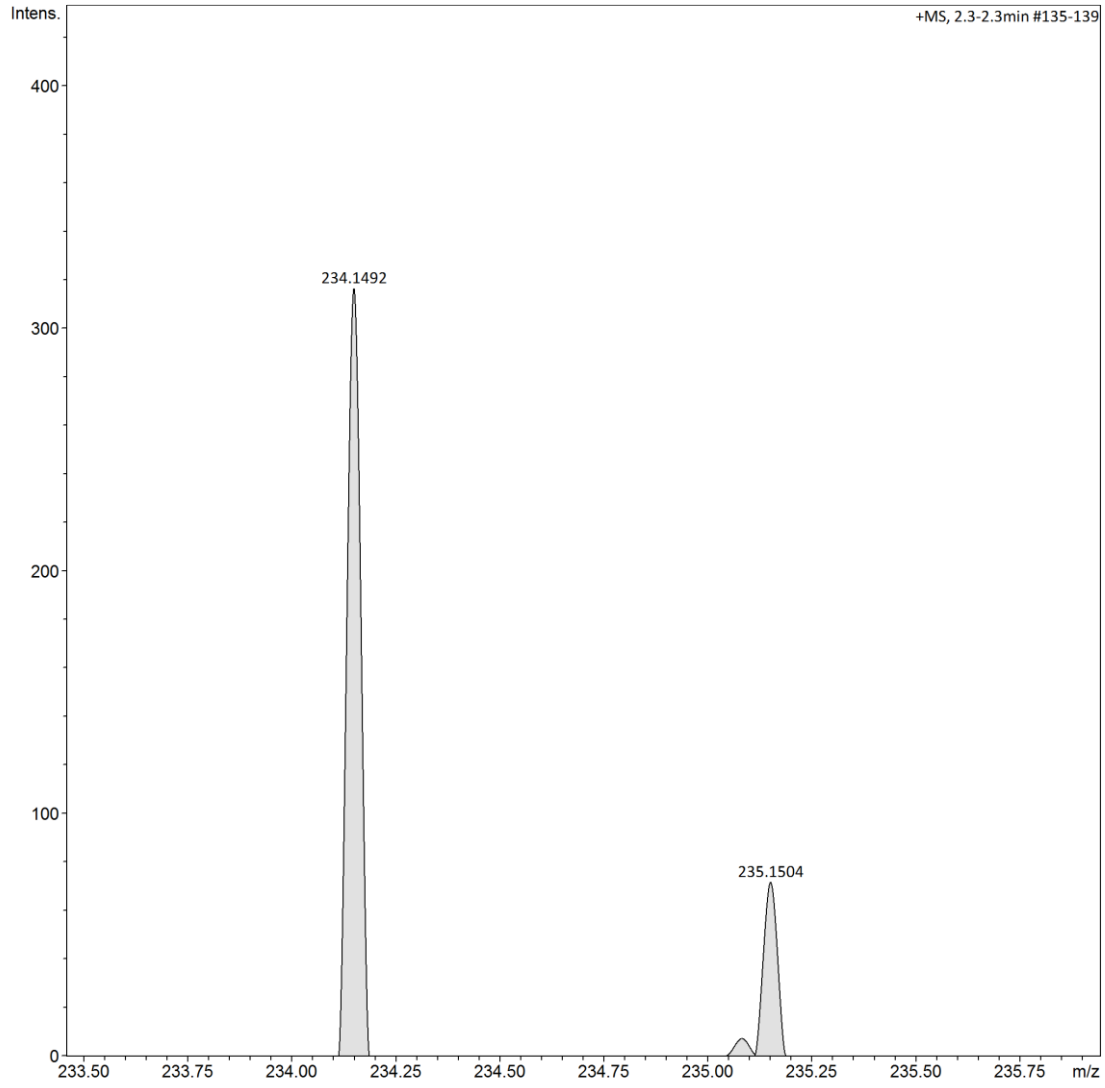
Exact Mass: 368.2948



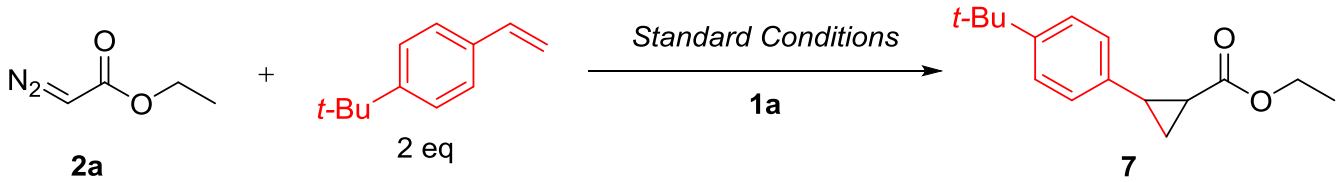


6

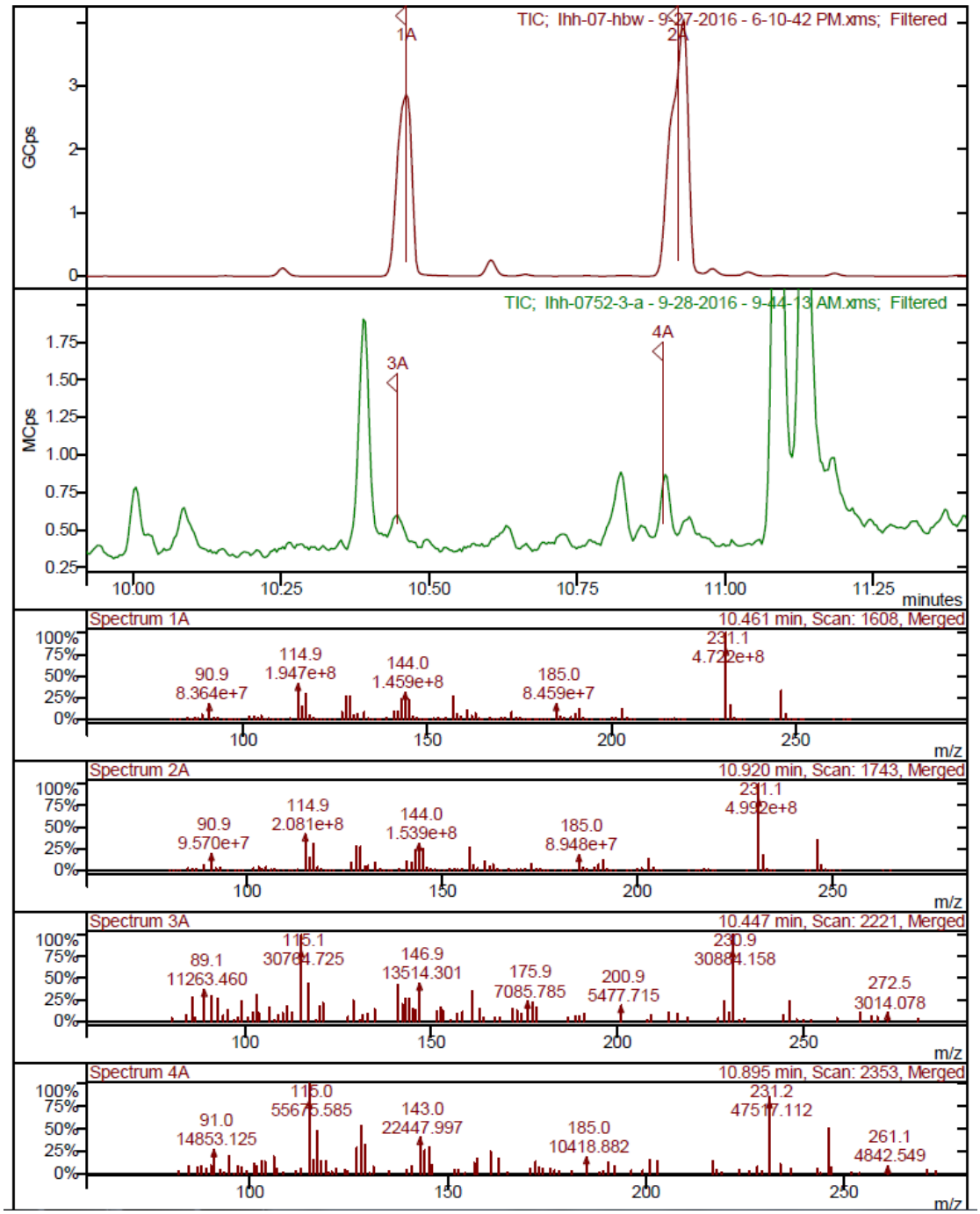
Exact Mass: 234.1489



(c) Cyclopropanation experiment



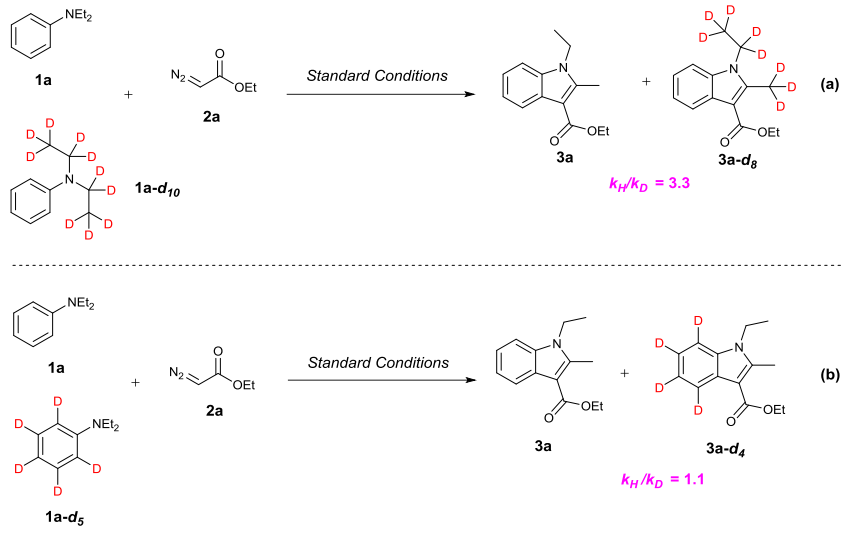
2a **7**

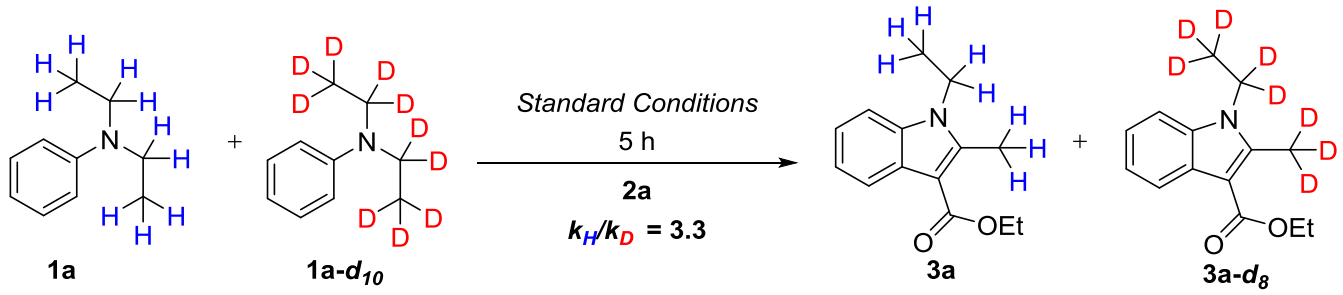


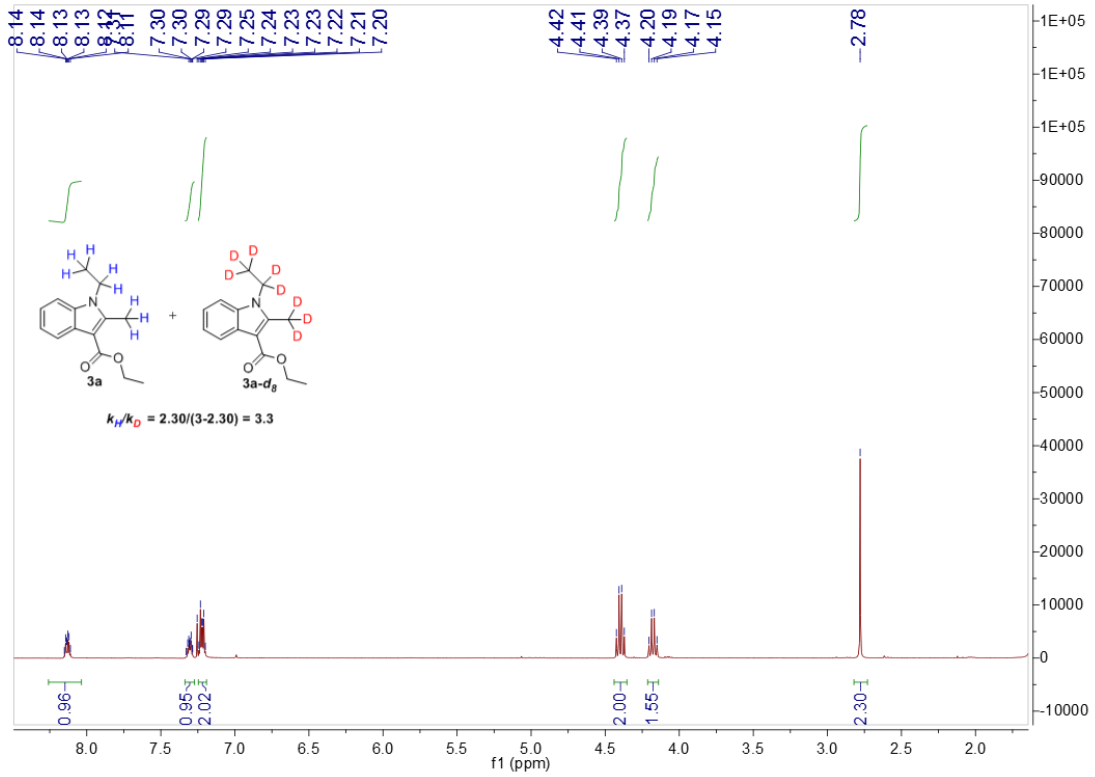
(d) Kinetic isotope study

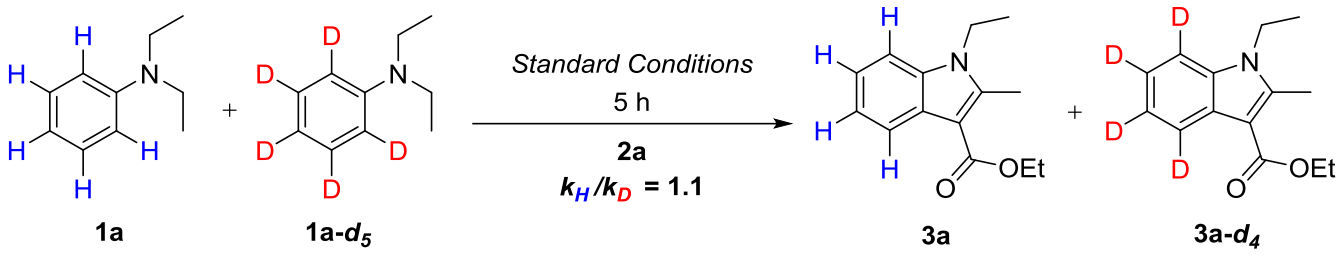
$Mn(OAc)_2$•$4H_2O$ (0.025 mmol), 4,4'-Azobis(4-cyanovaleric acid) (ACVA) (0.63mmol) were added to a 20mL test tube with a stirring bar. DMF/EtOH=3:1 (2.0 mL), N,N-Diethylaniline (**1a**) (0.25mmol, 1.0eq), **1a-*d*$_5$** *or* **1a-*d*$_8$** (0.25mmol, 1.0eq) diazoacetic ester (0.75 mmol) were added via syringe. The reaction mixture was heated in an oil bath at 65 ℃ for 5 h under air. The reaction mixture was then poured in brine solution (15 mL) and extracted with diethyl ether (3x20 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by basic aluminum oxide column chromatography using petroleum ether/ ethylacetate to give the desired product. The KIE value was estimated to be 1.1 or 3.3 by ^{1}H NMR analysis.

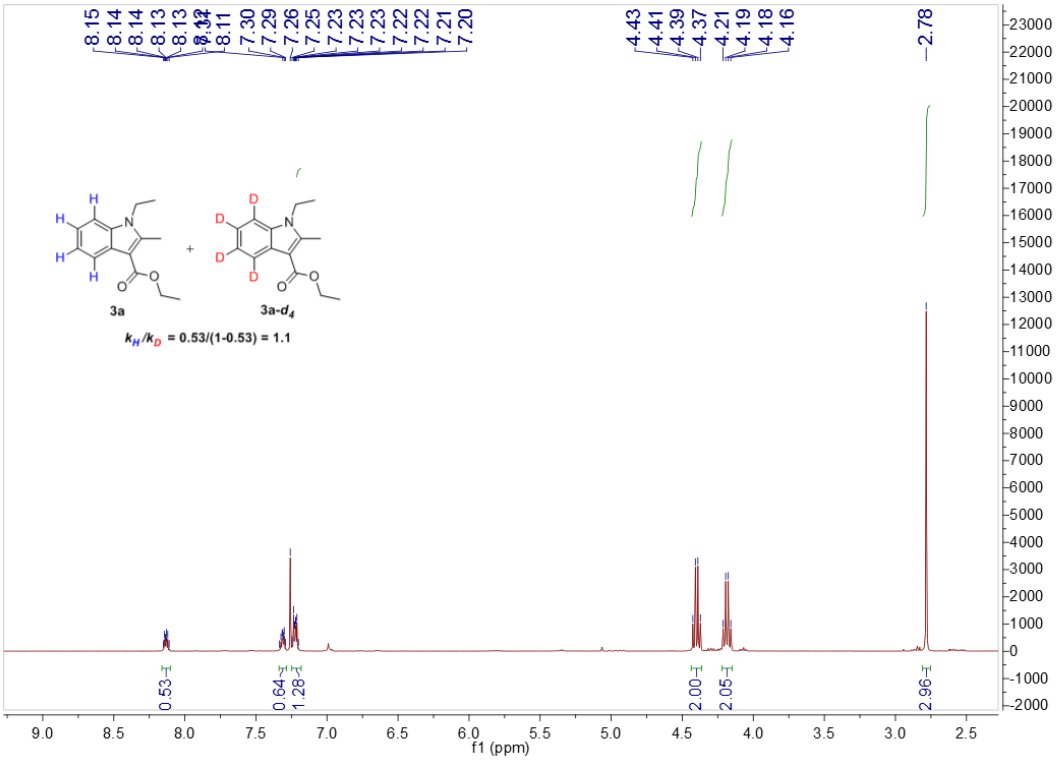
Scheme S1. Kinetic Isotope Effect Study.





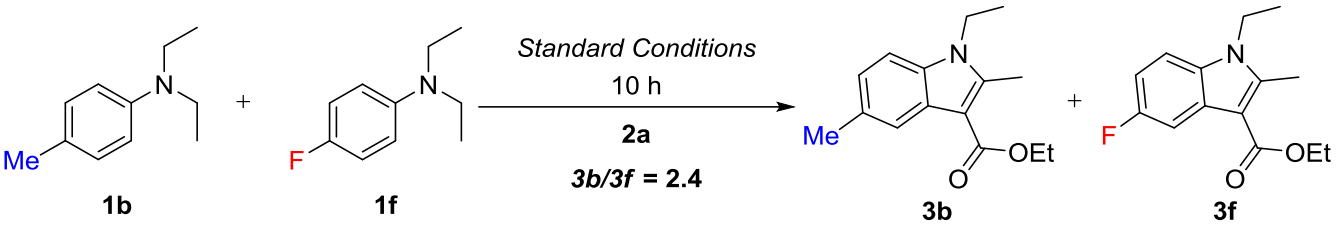


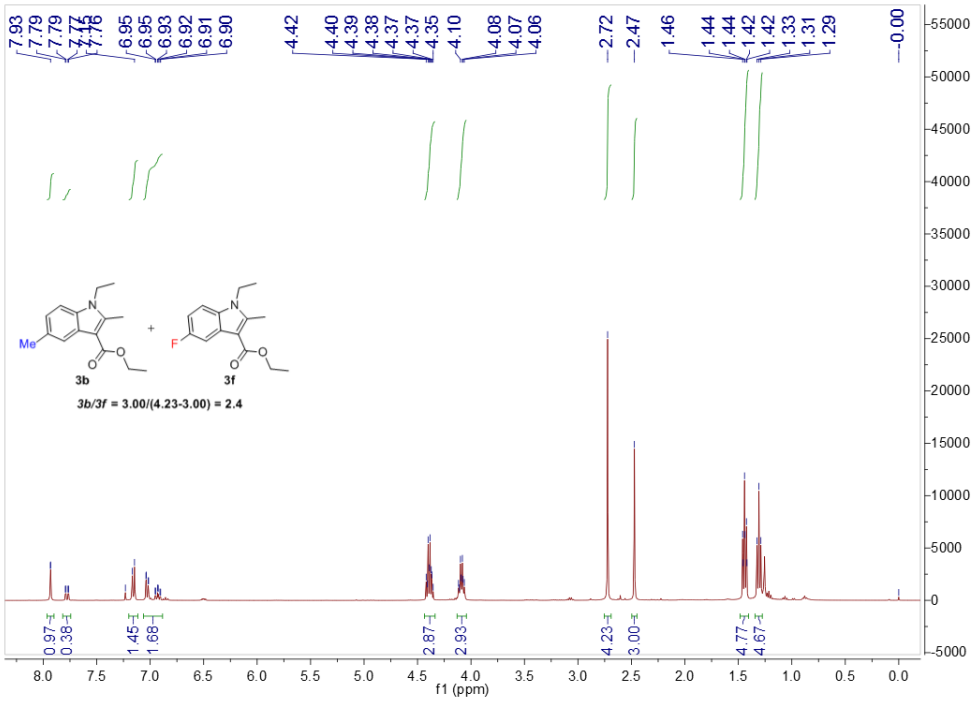




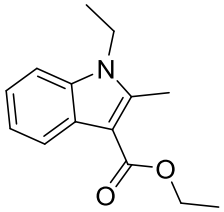
(e) Competition experiment

$Mn(OAc)_2$•$4H_2O$ (0.025 mmol), 4,4'-Azobis(4-cyanovaleric acid) (ACVA) (0.63mmol) were added to a 20mL test tube with a stirring bar. DMF/EtOH=3:1 (2.0 mL), **1b** (0.25mmol, 1.0eq), **1f** (0.25mmol, 1.0eq) diazoacetic ester (0.75 mmol) were added via syringe. The reaction mixture was heated in an oil bath at 65 °C for 10 h under air. The reaction mixture was then poured in brine solution (15 mL) and extracted with diethyl ether (3x20 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by basic aluminum oxide column chromatography using petroleum ether/ ethylacetate to give the desired product. The KIE value was estimated to be 2.4 by ^{1}H NMR analysis.


Me
F
N
Standard Conditions
10 h
2a
3b/3f = 2.4
OEt
O
1b
1f
3b
3f

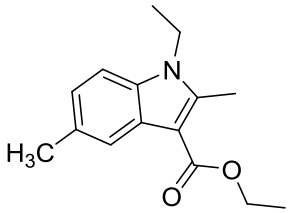

3b/3f = 3.00/(4.23-3.00) = 2.4
f1 (ppm)

Compound Characterizations



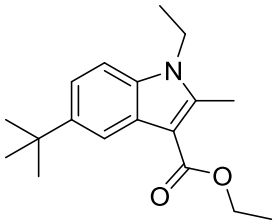
ethyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (3a)

petroleum ether/ ethylacetate = 20:1, yellow oil, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 1H), 7.26 (m, 1H), 7.20 (m, 2H), 4.39 (q, J = 8.0 Hz, 2H), 4.10 (q, J = 8.0 Hz, 2H), 2.73 (s, 3H), 1.44 (t, J = 8.0 Hz, 3H), 1.31 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 144.3, 135.3, 126.7, 121.8, 121.4, 121.4, 59.2, 37.7, 14.6, 11.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{17}NO_2$+H^+: 232.1332, Found: 232.1340; IR (neat, cm-1): υ 2984, 1673, 1538, 1412, 1210, 1158, 1105, 783, 752, 737.



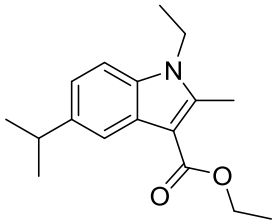
ethyl 1-ethyl-2,5-dimethyl-1H-indole-3-carboxylate (3b)

petroleum ether/ ethylacetate = 20:1, yellow oil, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.16 (m, 1H), 7.03 (m, 1H), 4.39 (q, J = 8.0Hz, 2H), 4.10 (q, J = 8.0 Hz, 2H), 2.73 (s, 3H), 2.47 (s, 3H), 1.44 (t, J = 8.0 Hz, 3H), 1.31 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 144.2, 133.7, 130.8,127.0, 123.3, 121.3, 108.7, 103.5, 59.2, 37.8, 21.7, 14.7, 14.6, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{19}NO_2$+H^+: 246.1489, Found: 246.1494; IR (neat, cm-1): υ 2978, 1685, 1537, 1416, 1256, 1152, 1106, 1054, 782, 703.



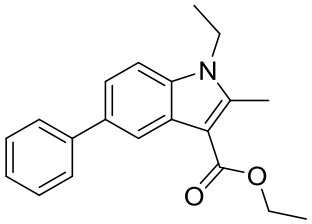
ethyl 5-(tert-butyl)-1-ethyl-2-methyl-1H-indole-3-carboxylate (3c)

petroleum ether/ ethylacetate = 20:1, yellow oil, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (m, 1H), 7.30 (m, 1H), 7.21 (m, 1H), 4.39 (q, J = 8.0 Hz, 2H), 4.10 (q, J = 8.0 Hz, 2H), 2.73 (s, 3H), 1.46 (t, J = 8.0 Hz, 3H), 1.41 (s, 9H), 1.32 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 144.4, 144.3, 133.5, 126.6, 119.9, 117.5, 108.5, 103.79, 59.1, 37.7, 34.6, 31.8, 14.8, 14.5, 11.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{25}NO_2$+H^+: 288.1958, Found: 288.1969; IR (neat, cm-1): υ 2690, 1681, 1538, 1415, 1168, 1153, 1118, 1097, 827, 800.



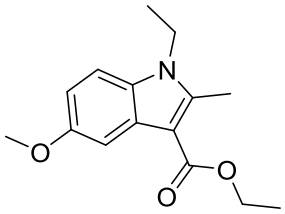
ethyl 1-ethyl-5-isopropyl-2-methyl-1H-indole-3-carboxylate (3d)

petroleum ether/ ethylacetate = 20:1, yellow oil, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (m, 1H), 7.21 (m, 1H), 7.11 (m, 1H), 4.40 (q, J = 8.0 Hz, 2H), 4.11 (q, J = 8.0 Hz, 2H), 3.04 (m, 1H), 2.73 (s, 3H), 1.45 (t, J = 8.0 Hz, 3H), 1.40 – 1.20 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 144.2, 142.2, 133.9, 126.9, 120.8, 118.6, 108.8, 103.6, 59.2, 37.7, 34.3, 24.5, 14.7, 14.5, 11.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{23}NO_2$+H^+: 274.1802, Found: 274.1808; IR (neat, cm-1): υ 2958, 1686, 1537, 1416, 1156, 1107, 1052, 890, 784, 752.



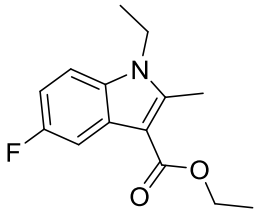
ethyl 1-ethyl-2-methyl-5-phenyl-1H-indole-3-carboxylate (3e)

petroleum ether/ ethylacetate = 20:1, yellow solid, 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (m, 1H), 7.68 (m, 2H), 7.45 (m, 3H), 7.33 (m, 2H), 4.41 (q, J = 8.0 Hz, 2H), 4.19 (q, J = 8.0 Hz, 2H), 2.79 (s, 3H), 1.45 (t, J = 8.0 Hz, 3H), 1.38 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 145.0, 142.4, 135.0, 134.9, 128.6, 127.4, 127.3, 126.4, 121.6, 120.2, 109.3 104.4, 59.4, 38.0, 149, 14.6, 11.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{21}NO_2$+H^+: 308.1645, Found: 308.1665; IR (neat, cm-1): υ 2978, 1686, 1467, 1438, 1377, 1155, 1108, 893, 761, 699.



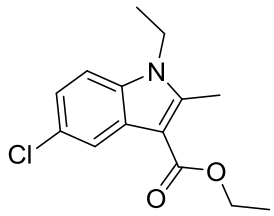
ethyl 1-ethyl-5-methoxy-2-methyl-1H-indole-3-carboxylate (3f)

petroleum ether/ ethylacetate = 20:1, yellow solid, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (m, 1H), 7.18 (m, 1H), 6.86 (m, 1H), 4.39 (q, J = 8.0 Hz, 2H), 4.13 (q, J = 8.0 Hz, 2H), 3.88 (s, 3H), 2.74 (s, 3H), 1.45 (t, J = 8.0 Hz, 3H), 1.34 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 155.5, 144.4, 130.4, 127.6, 111.6, 109.7, 103.7, 59.2, 55.7, 38.0, 14.9, 14.6, 11.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{19}NO_3$+H^+: 262.1438, Found: 262.1448; IR (neat, cm-1): υ 2985, 1684, 1527, 1483, 1417, 1199, 1169, 1107, 849, 783.



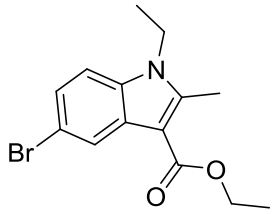
ethyl 1-ethyl-5-fluoro-2-methyl-1H-indole-3-carboxylate (3g)

petroleum ether/ ethylacetate = 20:1, yellow oil, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 1H), 7.19 (m, 1H), 6.94 (m, 1H), 4.39 (q, J = 8.0 Hz, 2H), 4.13 (q, J = 8.0 Hz, 2H), 2.75 (s, 3H), 1.45 (t, J = 8.0 Hz, 3H), 1.34 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 160.2, 157.8, 145.7, 131.8, 127.4, 127.3, 110.0, 109.7, 109.6, 109.5, 107.0, 106.7, 104.1, 104.0, 59.4, 38.0, 14.7, 14.5, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{16}FNO_2$+H^+: 250.1238, Found: 250.1248; IR (neat, cm-1): υ 2981, 1686, 1536, 1462, 1418, 1168, 1104, 1053, 866, 778.



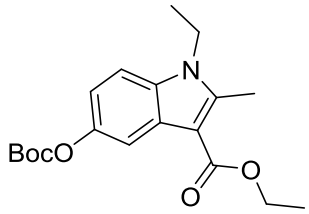
ethyl 5-chloro-1-ethyl-2-methyl-1H-indole-3-carboxylate (3h)

petroleum ether/ ethylacetate = 20:1, yellow solid, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (m, 1H), 7.15 (m, 2H), 4.39 (q, J = 8.0 Hz, 2H), 4.11 (q, J = 8.0 Hz, 2H), 2.73 (s, 3H), 1.45 (t, J = 8.0 Hz, 3H), 1.32 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 145.5, 133.7, 127.8, 127.3, 122.1, 121.0, 101.0, 103.8, 59.5, 38.0, 14.7, 14.6, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{16}ClNO_2$+H^+: 266.0942, Found: 266.0953; IR (neat, cm-1): υ 2924, 1688, 1538, 1416, 1210, 1155, 1108, 1068, 779, 690.



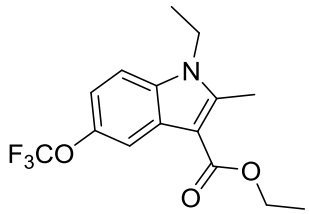
ethyl 5-bromo-1-ethyl-2-methyl-1H-indole-3-carboxylate (3i)

petroleum ether/ ethylacetate = 20:1, yellow solid, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (m, 1H), 7.27 (m, 1H), 7.11 (m, 1H), 4.39 (q, J = 8.0 Hz, 2H), 4.09 (q, J = 8.0 Hz, 2H), 2.73 (s, 3H), 1.44 (t, J = 8.0 Hz, 3H), 1.32 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 145.3, 134.0, 128.3, 124.7, 124.0, 115.0, 110.4, 103.7, 59.5, 38.0, 14.7, 14.6, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{16}BrNO_2$+H^+: 310.0437, Found: 310.0446; IR (neat, cm-1): υ 2977, 1689, 1561, 1449, 1122, 1156, 1109,1063, 779, 745.



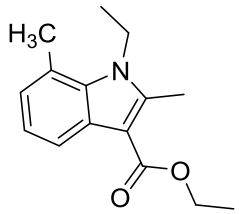
ethyl 5-((tert-butoxycarbonyl)oxy)-1-ethyl-2-methyl-1H-indole-3-carboxylate (3j)

petroleum ether/ ethylacetate = 15:1, yellow solid, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (m, 1H), 7.22 (m, 1H), 7.02 (m, 1H), 4.38 (q, J = 8.0 Hz, 2H), 4.09 (q, J = 8.0 Hz, 2H), 2.73 (s, 3H), 1.57 (s, 9H), 1.43 (t, J = 8.0 Hz, 3H), 1.30 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 152.7, 146.2, 145.4, 133.0, 127.1, 115.7, 113.7, 109.3, 104.2, 83.0, 59.3, 37.9, 27.6, 14.7, 14.5, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{25}NO_5$+H^+: 348.1805, Found: 348.1811; IR (neat, cm-1): υ 2980, 1753, 1691, 1619, 1370, 1278, 1244, 1141, 1107, 803.



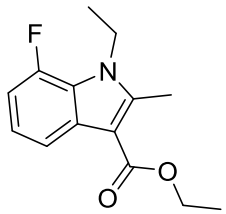
ethyl 1-ethyl-2-methyl-5-(trifluoromethoxy)-1H-indole-3-carboxylate (3k)

petroleum ether/ ethylacetate = 20:1, yellow oil, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 1H), δ 7.24 (m, 1H)., 7.08 (m, 1.5 Hz, 1H), 4.39 (q, J = 8.0 Hz, 2H), 4.14 (q, J = 8.0 Hz, 2H), 2.75 (s, 3H), 1.45 (t, J = 8.0 Hz, 3H), 1.34 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 146.0, 144.4, 133.6, 127.2, 122.1, 119.5, 115.6, 114.1, 109.6, 104.4, 59.6, 38.1, 14.7, 14.5, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{16}F_3NO_3+H^+$: 316.1155, Found: 316.1157; IR (neat, cm-1): υ 2983, 1692, 1418, 1247, 1212, 1148, 1107, 1054, 780, 746.



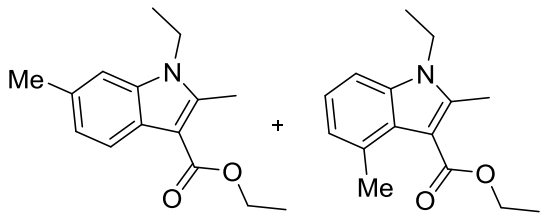
ethyl 1-ethyl-2,7-dimethyl-1H-indole-3-carboxylate (3l)

petroleum ether/ ethylacetate = 20:1, yellow solid, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (m, 1H), 7.08 (m, 1H), 6.93 (m, 1H), 4.38 (q, J = 8.0 Hz, 2H), 4.33 (q, J = 8.0 Hz, 2H), 2.75 (s, 3H), 2.71 (s, 3H), 1.44 (t, J = 8.0 Hz, 3H), 1.33 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 144.8, 134.2, 127.6, 125.5, 121.3, 120.0, 119.5, 104.34, 59.3, 39.3, 20.1, 16.7, 14.6, 11.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{19}NO_2+H^+$: 246.1489, Found: 246.1497; IR (neat, cm-1): υ 2923, 1674, 1539, 1414, 1231, 1112, 1074, 917, 792, 746.



ethyl 1-ethyl-7-fluoro-2-methyl-1H-indole-3-carboxylate (3m)

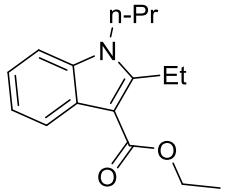
petroleum ether/ ethylacetate = 20:1, yellow solid, 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (m, 1H), 7.08 (m, 1H), 6.88 (m, 1H), 4.39 (q, J = 8.0 Hz, 2H), 4.32 (q, J = 8.0 Hz, 2H), 2.75 (s, 3H), 1.44 (t, J = 8.0 Hz, 3H), 1.38 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 150.5, 148.1, 145.4, 130.4, 130.4, 123.2, 123.2, 121.5, 121.5, 117.2, 117.2 107.9, 107.7, 104.9, 59.5, 40.3, 40.3, 16.0, 15.9, 14.5, 11.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{16}FNO_2+H^+$: 250.1238, Found: 250.1263; IR (neat, cm-1): υ 2925, 1685, 1444, 1375, 1251, 1229, 1024, 929, 795, 731.



ethyl 1-ethyl-2,6-dimethyl-1H-indole-3-carboxylate (3na)

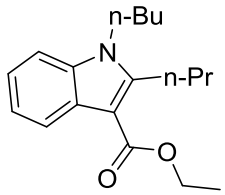
ethyl 1-ethyl-2,4-dimethyl-1H-indole-3-carboxylate (3nb)

petroleum ether/ ethylacetate = 20:1, yellow oil, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J=8.0, 1H), 7.16–7.01 (m, 6H), 6.96 (m, 2H), 4.45–4.31 (m, 6H), 4.19–4.04 (m, 6H), 2.74 (s, 3H), 2.66 (s, 6H), 2.63 (s, 6H), 2.48 (s, 3H), 1.48–1.38 (m, 9H), 1.33 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 166.3, 143.9, 141.7, 135.7, 135.7, 131.6, 131.1, 124.9, 124.5, 123.5, 123.1, 121.9, 121.2, 109.1, 106.8, 106.0, 103.8, 59.9, 59.2, 37.9, 37.7, 22.1, 21.7, 14.8, 14.7, 14.6, 14.4, 11.6, 11.5; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{19}NO_2+H^+$: 246.1489, Found: 246.1488; IR (neat, cm-1): υ 2978, 1687, 1415, 1207, 1150, 1101, 1066, 811, 762, 739.



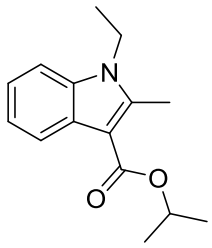
ethyl 2-ethyl-1-propyl-1H-indole-3-carboxylate (3n)

petroleum ether/ ethylacetate = 20:1, yellow oil, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (m, 1H), 7.29 (m, 1H), 7.21 (m, 2H), 4.40 (q, J = 8.0 Hz, 2H), 4.06 (m, 2H), 3.20 (q, J = 8.0 Hz, 2H), 1.81 (m, 2H), 1.44 (t, J = 8.0 Hz, 3H), 1.28 (t, J = 8.0 Hz, 3H), 0.98 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 150.5, 135.7, 126.8, 121.8, 121.5, 121.5, 109.5, 102.96, 59.2, 44.6, 23.3, 18.9, 14.5, 13.2, 11.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{21}NO_2+H^+$: 260.1645, Found: 260.1643; IR (neat, cm-1): υ 2977, 1681, 1530, 1461, 1210, 1160, 1136, 1108, 788, 742.



ethyl 1-butyl-2-propyl-1H-indole-3-carboxylate (3o)

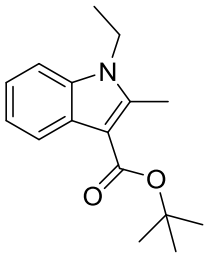
petroleum ether/ ethylacetate = 20:1, yellow oil, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (m, 1H), 7.29 (m, 1H), 7.22 (m, 2H), 4.39 (q, J = 8.0 Hz, 2H), 4.09 (m, 2H), 3.15 (m, 2H), 1.71 (m, 4H), 1.44 (t, J = 8.0 Hz, 3H), 1.06 (t, J = 8.0 Hz, 3H), 0.96 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 149.1, 135.7, 126.9, 121.8, 121.6, 121.5, 109.5, 103.42, 59.2, 43.0, 32.1, 27.5, 23.1, 20.2, 14.5, 14.4, 13.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{25}NO_2+H^+$: 288.1958, Found: 288.1965; IR (neat, cm-1): υ 2960, 1687,1531, 1461, 1421, 1220, 1136, 1106, 789, 739.



isopropyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4a)

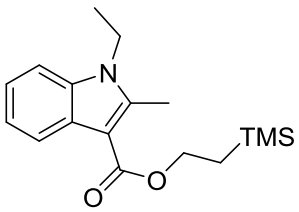
petroleum ether/ ethylacetate = 20:1, yellow oil, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (m, 1H), 7.29 (m, 1H), 7.22 (m, 2H), 5.30 (m, 1H), 4.15 (q, J = 8.0 Hz, 2H), 2.77 (s, 3H), 1.42 (d, J = 8.0 Hz, 6H), 1.34 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 144.3, 135.3, 126.8, 121.8, 121.6, 121.4, 109.0, 104.3, 66.5, 37.8, 22.3, 14.8, 11.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{19}NO_2+H^+$:

246.1489, Found: 246.1491; IR (neat, cm-1): υ 2977, 1683, 1538, 1414, 1157, 1136, 1097, 995, 832, 751.



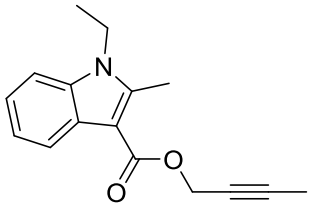
tert-butyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4b)

petroleum ether/ ethylacetate = 20:1, yellow oil, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (m, 1H), 7.27 (m, 1H), 7.20 (m, 2H), 4.13 (q, J = 8.0 Hz, 2H), 2.74 (s, 3H), 1.66 (s, 9H), 1.32 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 144.0, 135.2, 126.8, 121.7, 121.4, 121.3, 108.9, 105.24, 79.6, 37.7, 28.7, 14.8, 11.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{21}NO_2$+H^+: 260.1645, Found: 260.1657; IR (neat, cm-1): υ 2975, 1683, 1538, 1413, 1218, 1146, 1105, 994, 765, 752.



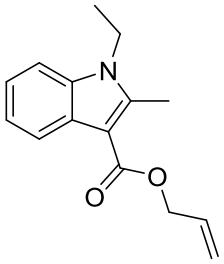
2-(trimethylsilyl)ethyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4c)

petroleum ether/ ethylacetate = 20:1, yellow oil, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (m, 1H), 7.30 (m, 1H), 7.22 (m, 2H), 2.77 (s, 3H), 1.35 (t, J = 8.0 Hz, 3H), 1.22 (m, 2H), 0.09 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 144.4, 135.4, 126.8, 121.8, 121.6, 121.4, 109.0, 104.14, 61.5, 37.8, 17.8, 14.8, 11.6, -1.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{25}NO_2Si$+H^+: 304.1727, Found: 304.1730; IR (neat, cm-1): υ 2952, 1686, 1538, 1415, 1212, 1154, 1103, 1054, 835, 751.



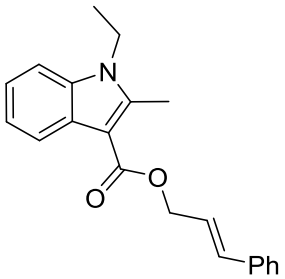
but-2-yn-1-yl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4d)

petroleum ether/ ethylacetate = 20:1, yellow solid, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (m, 1H), 7.30 (m, 1H), 7.24 (m, 2H), 4.92 (q, J = 2.4 Hz, 2H), 4.17 (q, J = 8.0 Hz, 2H), 2.78 (s, 3H), 1.88 (t, J = 2.4 Hz, 3H), 1.36 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 145.0, 135.4, 126.7, 122.0, 121.7, 121.7, 109.0, 103.40, 82.3, 76.7, 74.2, 51.6, 37.9, 14.8, 11.7, 3.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{17}NO_2$+H^+: 256.1332, Found: 256.1347; IR (neat, cm-1): υ 2953, 1688, 1428, 1379, 1343, 1146, 1102, 1003, 784, 753.



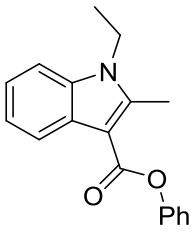
allyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4e)

petroleum ether/ ethylacetate = 20:1, yellow oil, 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (m, 1H), 7.30 (m, 1H), 7.23 (m, 2H), 6.15 (m, 1H), 5.43 (m, 1H), 5.27 (m, 1H), 4.87 (m, 2H), 4.17 (q, J = 8.0 Hz, 2H), 2.78 (s, 3H), 1.36 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 144.7, 135.34, 133.2, 126.7, 122.0, 121.6, 121.6, 117.5, 109.1, 103.7, 64.1, 37.9, 14.8, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{17}NO_2$+H^+: 244.1332, Found: 244.1336; IR (neat, cm-1): υ 2928, 1687, 1536, 1413, 1210, 1149, 1102, 994, 783, 751.



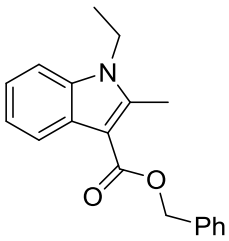
cinnamyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4f)

petroleum ether/ ethylacetate = 20:1, yellow oil, 37% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (m, 1H), 7.42 (m, 2H), 7.27 (m, 6H), 6.75 (m, 1H), 6.47 (m, 1H), 5.01 (m, 2H), 4.13 (q, J = 8.0 Hz, 2H), 2.76 (s, 3H), 1.33 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 144.7, 136.5, 135.3, 133.3, 128.5, 127.8, 126.7, 126.55, 124.4, 121.9, 121.6, 121.6, 109.1, 103.7, 64.0, 37.8, 14.7, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{21}H_{21}NO_2$+H^+: 320.1645, Found: 320.1647; IR (neat, cm-1): υ 2978, 1685, 1536, 1414, 1210, 1100, 1044, 965, 739, 692.



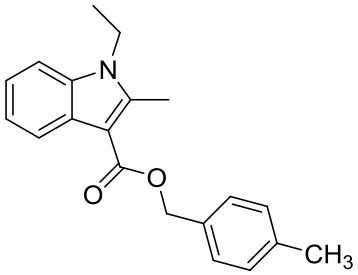
phenyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4g)

petroleum ether/ ethylacetate = 20:1, yellow solid, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (m, 1H), 7.43 (m, 2H), 7.35 (m, 1H), 7.26 (m, 5H), 4.21 (q, J = 8.0 Hz, 2H), 2.82 (s, 3H), 1.39 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 151.0, 146.0, 135.5, 129.3, 126.7, 125.4, 122.3, 122.0, 121.7, 109.3, 103.1, 38.0, 14.8, 11.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{17}NO_2$+H^+: 280.1332, Found: 280.1333; IR (neat, cm-1): υ 2985, 1710, 1530, 1408, 1186, 1091, 985, 750, 692.



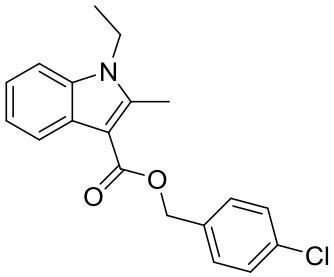
benzyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4h)

petroleum ether/ ethylacetate = 20:1, yellow solid, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 1H), 7.48 (m, 2H), 7.37 (m, 2H), 7.31 (m, 1H), 7.27 (m, 1H), 7.19 (m, 2H), 5.40 (s, 2H), 4.12 (q, J = 8.0 Hz, 2H), 2.75 (s, 3H), 1.32 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 144.8, 137.0, 135.3, 128.5, 127.9, 127.8, 126.7, 121.9, 121.6, 121.5, 109.0, 103.6, 65.2, 37.8, 14.7, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{19}NO_2$+H^+: 294.1489, Found: 294.1500; IR (neat, cm-1): υ 2978, 1686, 1536, 1414, 1210, 1148, 1100, 1000, 738, 697.



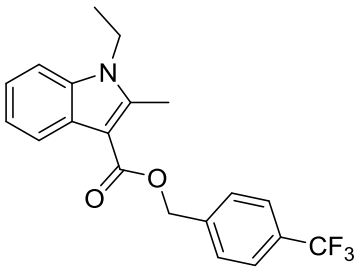
4-methylbenzyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4i)

petroleum ether/ ethylacetate = 20:1, yellow oil, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (m, 1H), 7.37 (m, 2H), 7.25 (m, 1H), 7.18 (m, 4H), 5.36 (s, 2H), 4.09 (q, J = 8.0 Hz, 2H), 2.73 (s, 3H), 2.34 (s, 3H), 1.30 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 164.8, 145.0, 137.1, 135.2, 134.0, 129.0, 128.0, 126.2, 121.8, 121.3, 120.6, 109.9, 102.5, 64.4, 37.5, 20.7, 14.5, 11.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{21}NO_2$+H^+: 308.1645, Found: 308.1641; IR (neat, cm-1): υ 2922, 1686, 1536, 1414, 1182, 1149, 1100, 997, 782, 751.



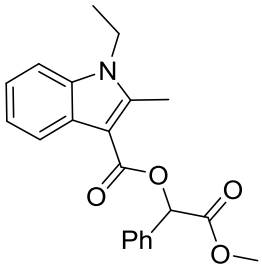
4-chlorobenzyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4j)

petroleum ether/ ethylacetate = 20:1, yellow solid, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (m, 1H), 7.41 (m, 2H), 7.33 (m, 2H), 7.28 (m, 1H), 7.21 (m, 2H), 5.35 (s, 2H), 4.13 (q, J = 8.0 Hz, 2H), 2.75 (s, 3H), 1.33 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 145.0, 135.6, 135.4, 133.6, 129.4, 128.7, 126.6, 122.0, 121.7, 121.4, 109.1, 103.4, 64.4 37.8, 14.7, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{18}ClNO_2$+H^+: 328.1099, Found: 328.1108; IR (neat, cm-1): υ 2922, 1685, 1536, 1416, 1208, 1151, 1105, 1044, 813, 737.



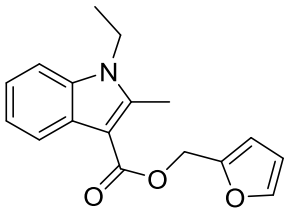
4-(trifluoromethyl)benzyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4k)

petroleum ether/ ethylacetate = 20:1, yellow solid, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 1H), 7.61 (m, 4H), 7.31 (m, 1H), 7.22 (m, 2H), 5.45 (s, 2H), 4.16 (q, J = 8.0 Hz, 2H), 2.77 (s, 3H), 1.35 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 145.2, 141.2, 141.2, 135.4, 127.9, 126.7, 125.5, 125.5, 125.5, 125.4, 122.1, 121.8, 121.4, 109.2, 103.3, 64.2, 37.9, 14.7, 11.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{18}F_3NO_2$+H^+: 362.1362, Found: 362.1356; IR (neat, cm-1): υ 2923, 1681, 1529, 1326, 1281, 1151, 1103, 1065, 816, 718.



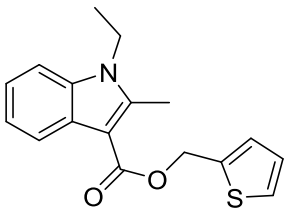
2-methoxy-2-oxo-1-phenylethyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4l)

petroleum ether/ ethylacetate = 15:1, yellow oil, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (m, 1H), 7.63 (m, 2H), 7.42 (m, 3H), 7.31 (m, 1H), 7.22 (m, 2H), 6.26 (s, 1H), 4.17 (q, J = 8.0 Hz, 2H), 3.76 (s, 3H), 2.78 (s, 3H), 1.35 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 164.9, 145.5, 135.5, 134.8, 129.0, 128.8, 127.8, 126.8, 122.1, 121.9, 121.7, 109.1, 103.0, 74.0, 52.5, 37.9, 14.8, 11.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{21}H_{21}NO_4$+H^+: 352.1543, Found: 352.1548; IR (neat, cm-1): υ 3359, 2919, 2850, 1670, 1415, 1209, 1147, 1097, 781, 696.



furan-2-ylmethyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4m)

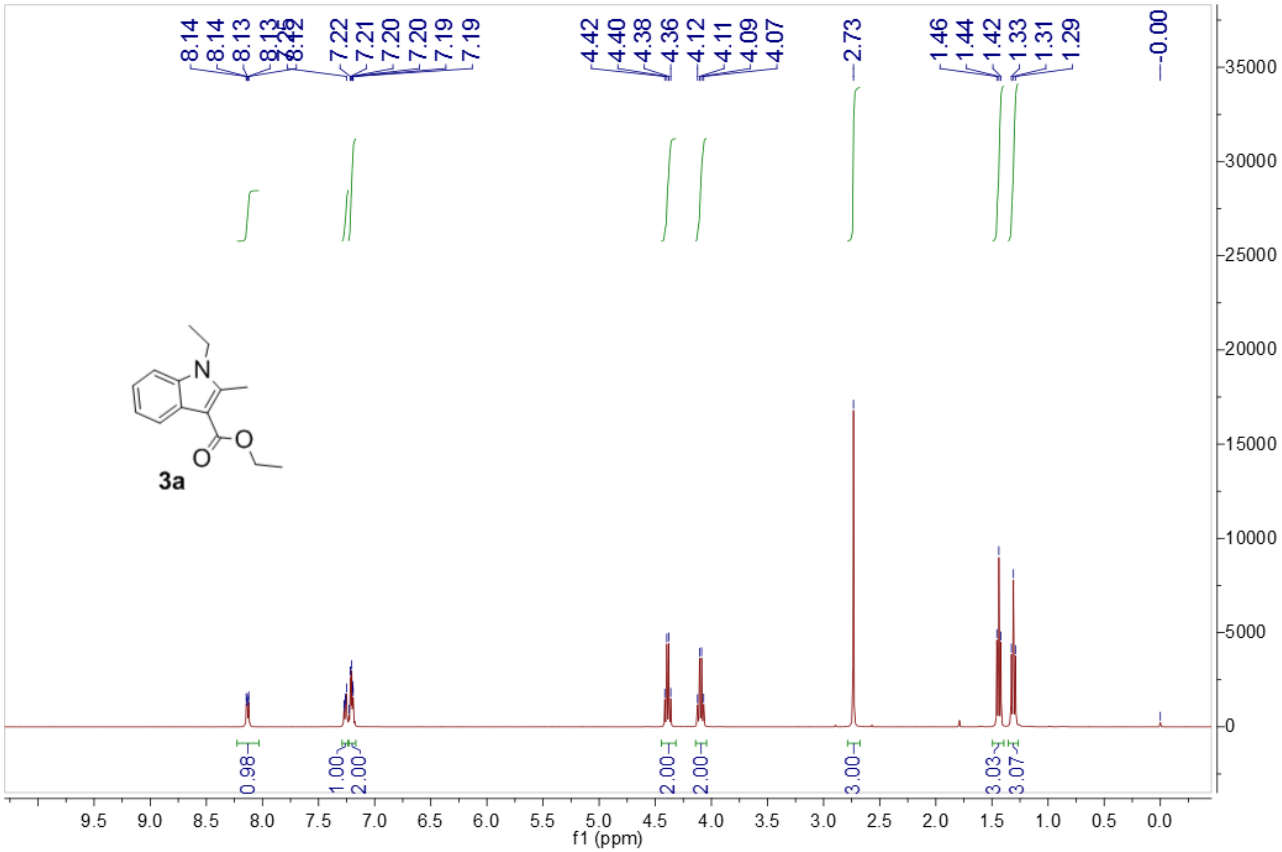
petroleum ether/ ethylacetate = 20:1, yellow solid, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (m, 1H), 7.45 (m, 1H), 7.29 (m, 1H), 7.20 (m, 2H), 6.48 (m, 1H), 6.38 (m, 1.9 Hz, 1H), 5.34 (s, 2H), 4.16 (q, J = 8.0 Hz, 2H), 2.76 (s, 3H), 1.34 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 150.5, 144.9, 142.9, 135.4, 126.7, 122.0, 121.7, 121.6, 110.4, 109.9, 109.0, 103.5, 57.1, 37.9, 14.8, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{17}NO_3$+H^+: 284.1281, Found: 284.1289; IR (neat, cm-1): υ 2966, 1688, 1530, 1428, 1210, 1154, 1103, 994, 782, 749.

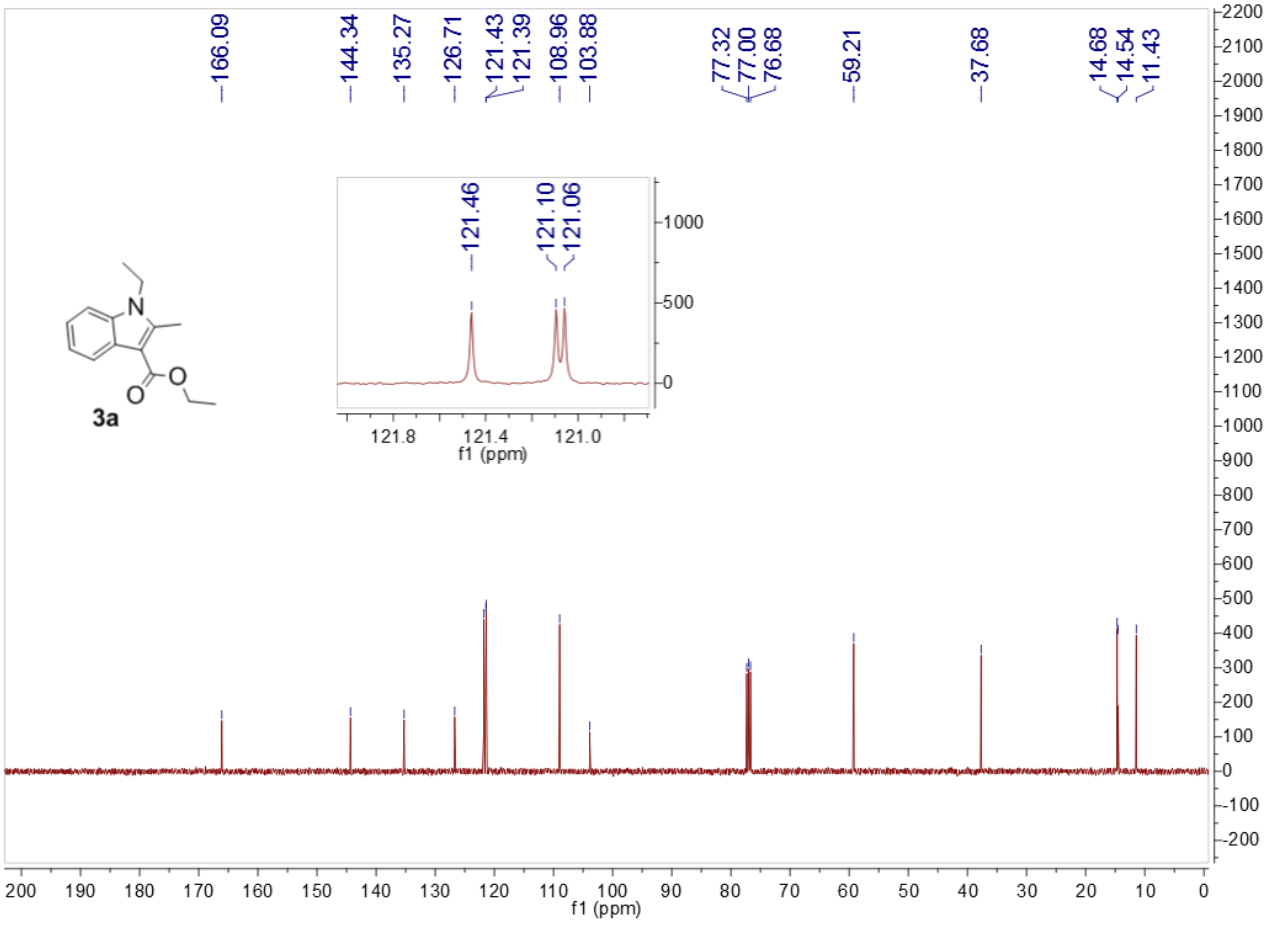


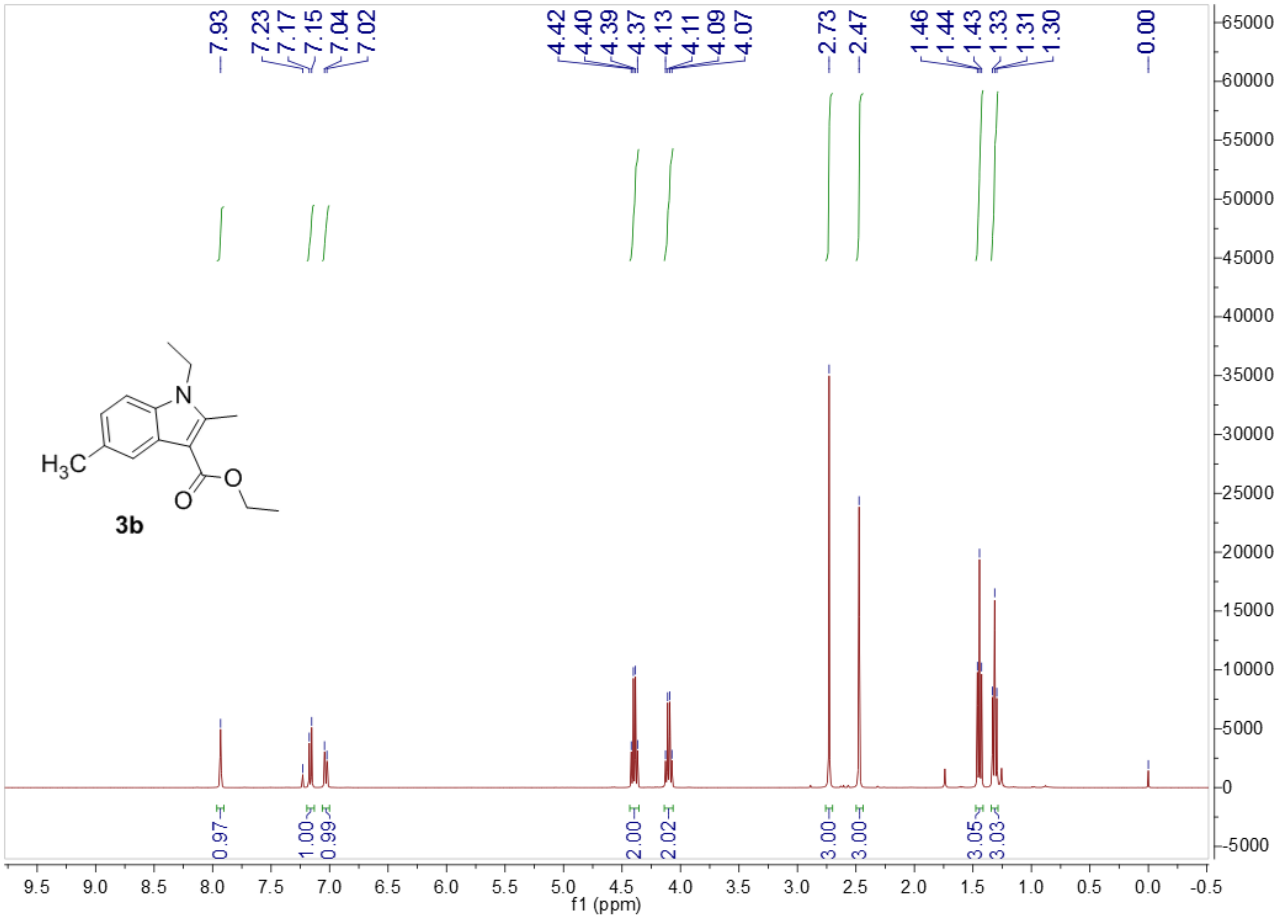
thiophen-2-ylmethyl 1-ethyl-2-methyl-1H-indole-3-carboxylate (4n)

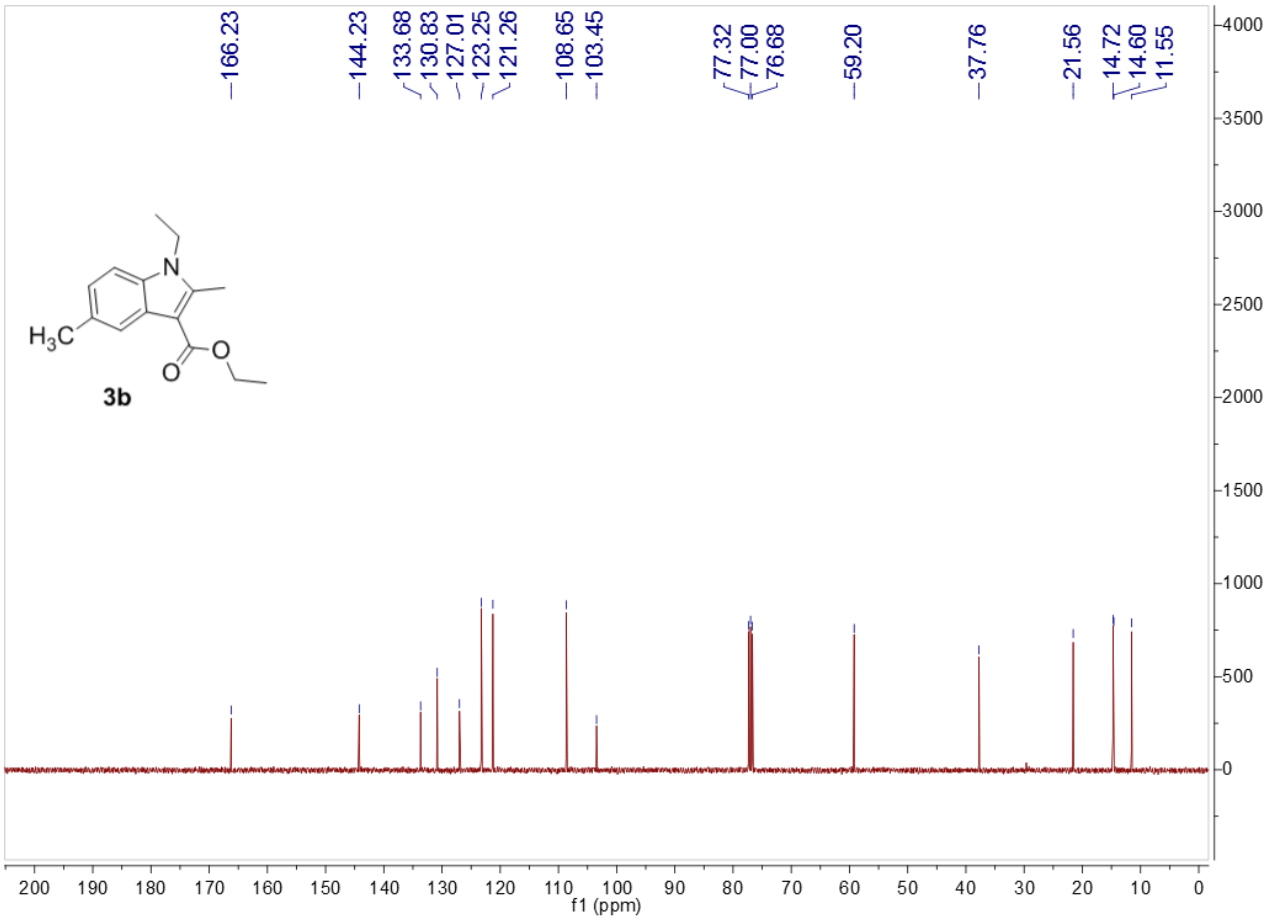
petroleum ether/ ethylacetate = 20:1, yellow solid, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 1H), 7.30 (m, 1H), 7.24 (m, 1H), 7.20 (m, 2H), 7.16 (m, 1H), 5.53 (s, 2H), 4.09 (q, J = 8.0 Hz, 2H), 2.73 (s, 3H), 1.30 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 144.9, 139.2, 135.3, 127.4, 126.7, 126.6, 126.3, 121.9, 121.6, 121.5, 109.0, 103.4, 59.7, 37.8, 14.7, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{17}NO_2S+H^+$: 300.1053, Found: 300.1064; IR (neat, cm-1): υ 2921, 1685, 1531, 1428, 1154, 1134, 1084, 1018, 745, 726.

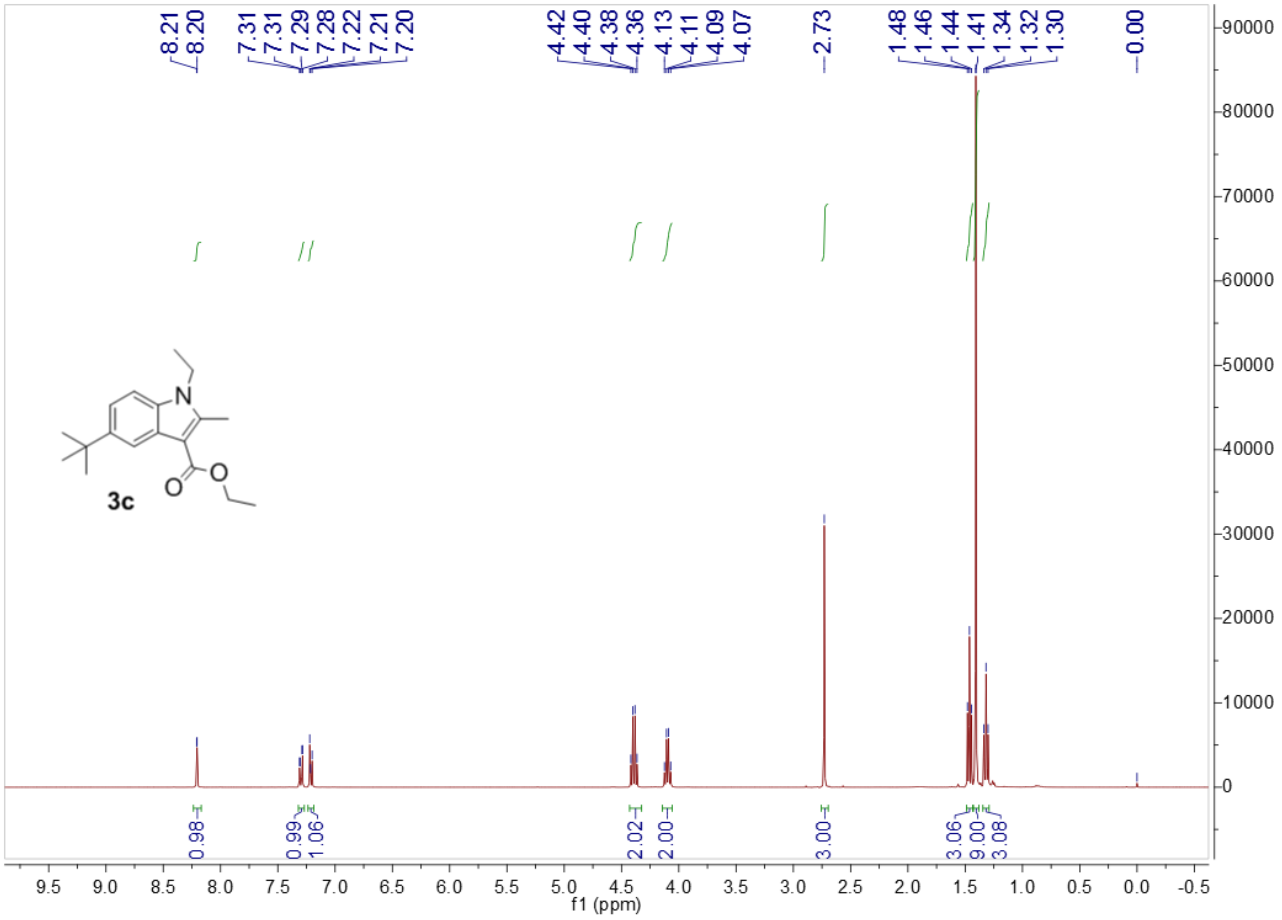
Spectroscopic data for products

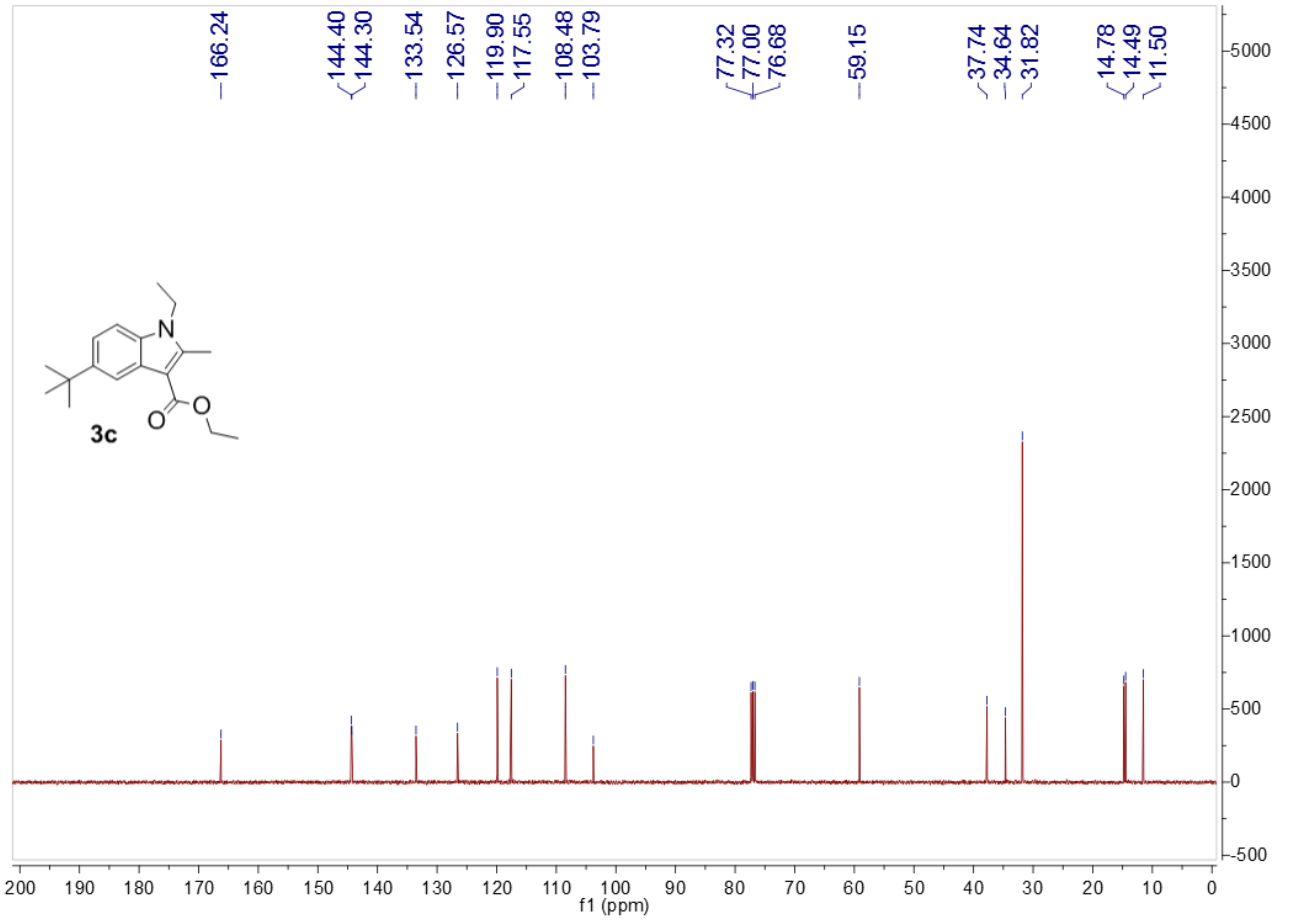


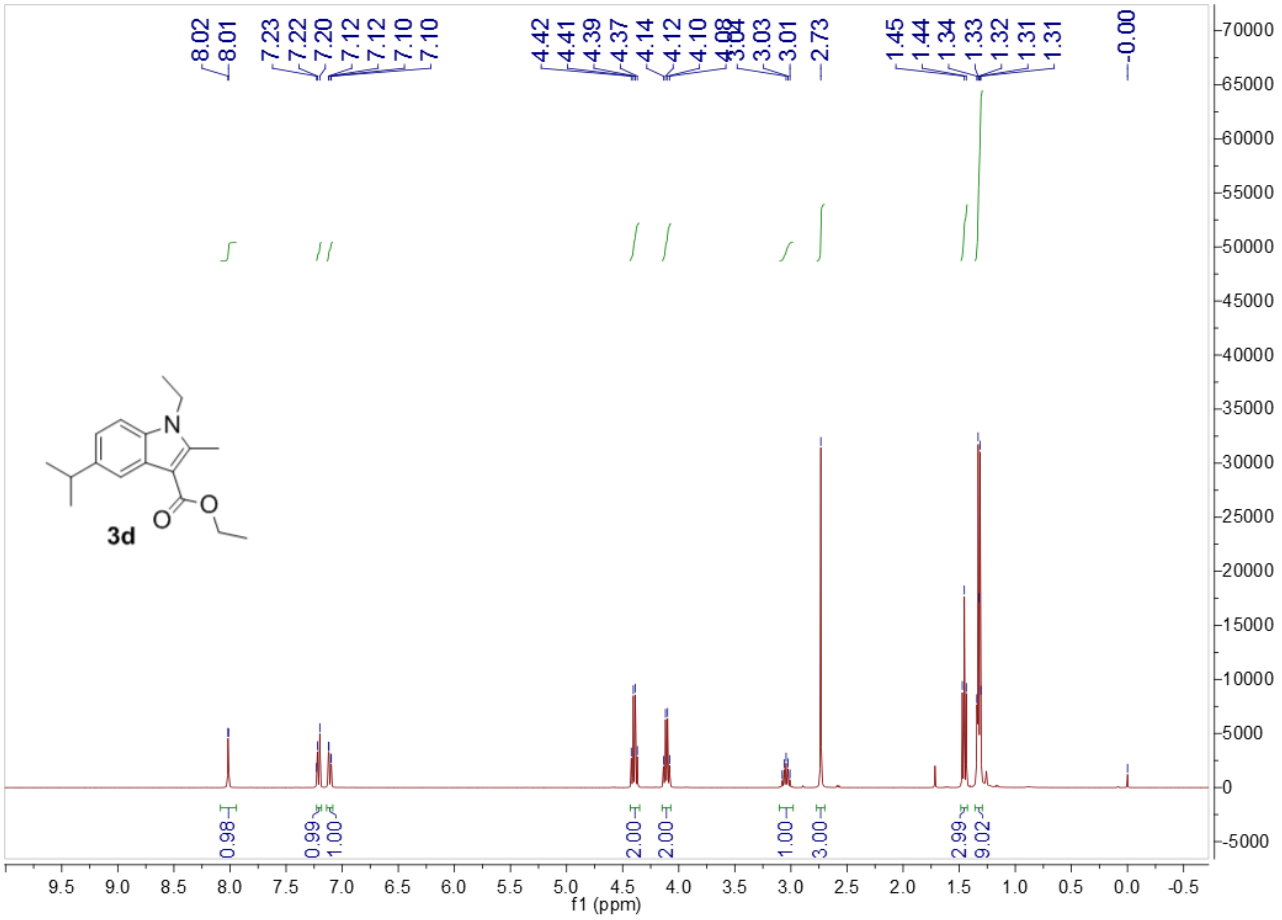


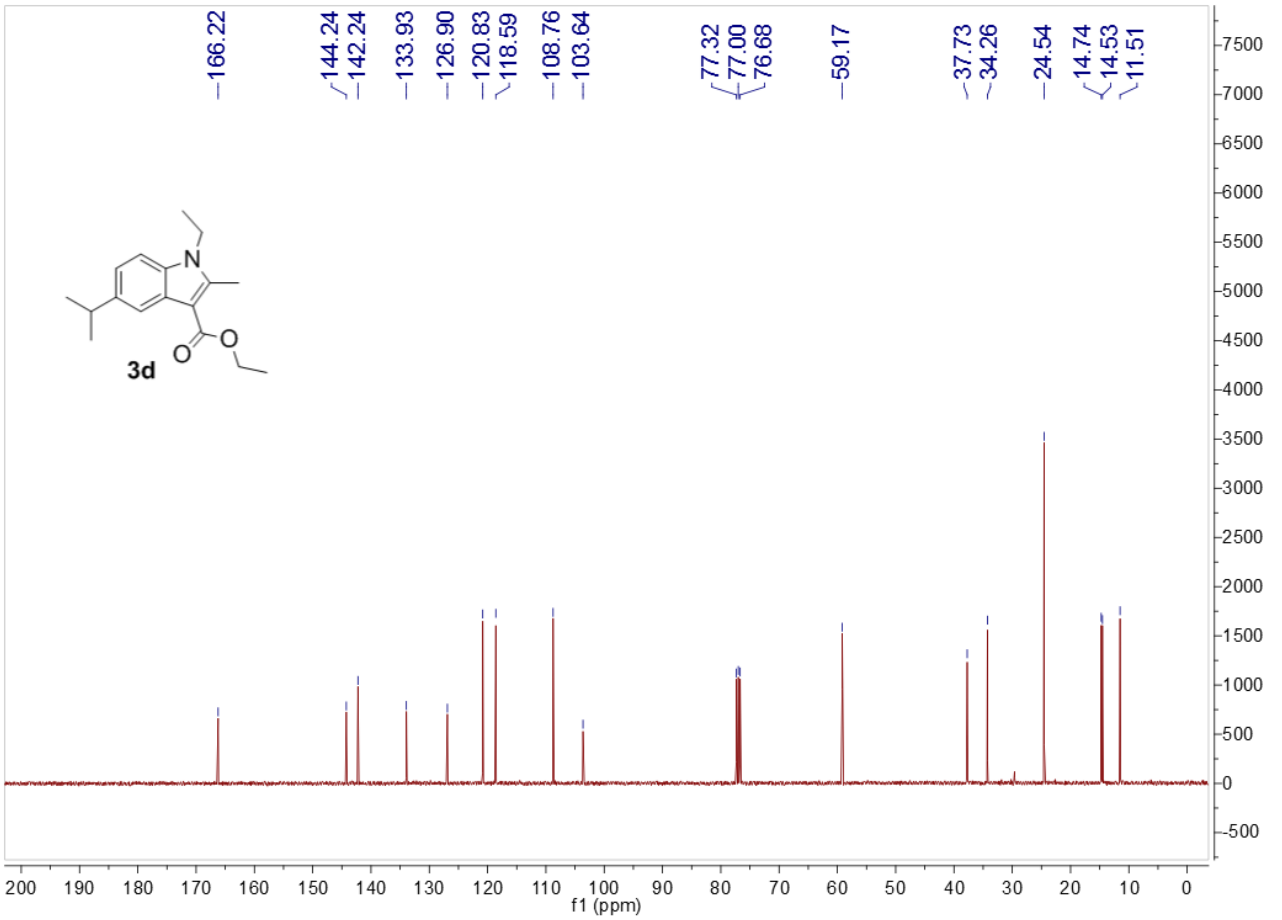

7.93
7.23
7.17
7.15
7.04
7.02
4.42
4.40
4.39
4.37
4.13
4.11
4.09
4.07
2.73
2.47
1.46
1.44
1.43
1.33
1.31
1.30
0.00
0.97
1.00
0.99
2.00
2.02
3.00
3.00
3.05
3.03
f1 (ppm)
3b

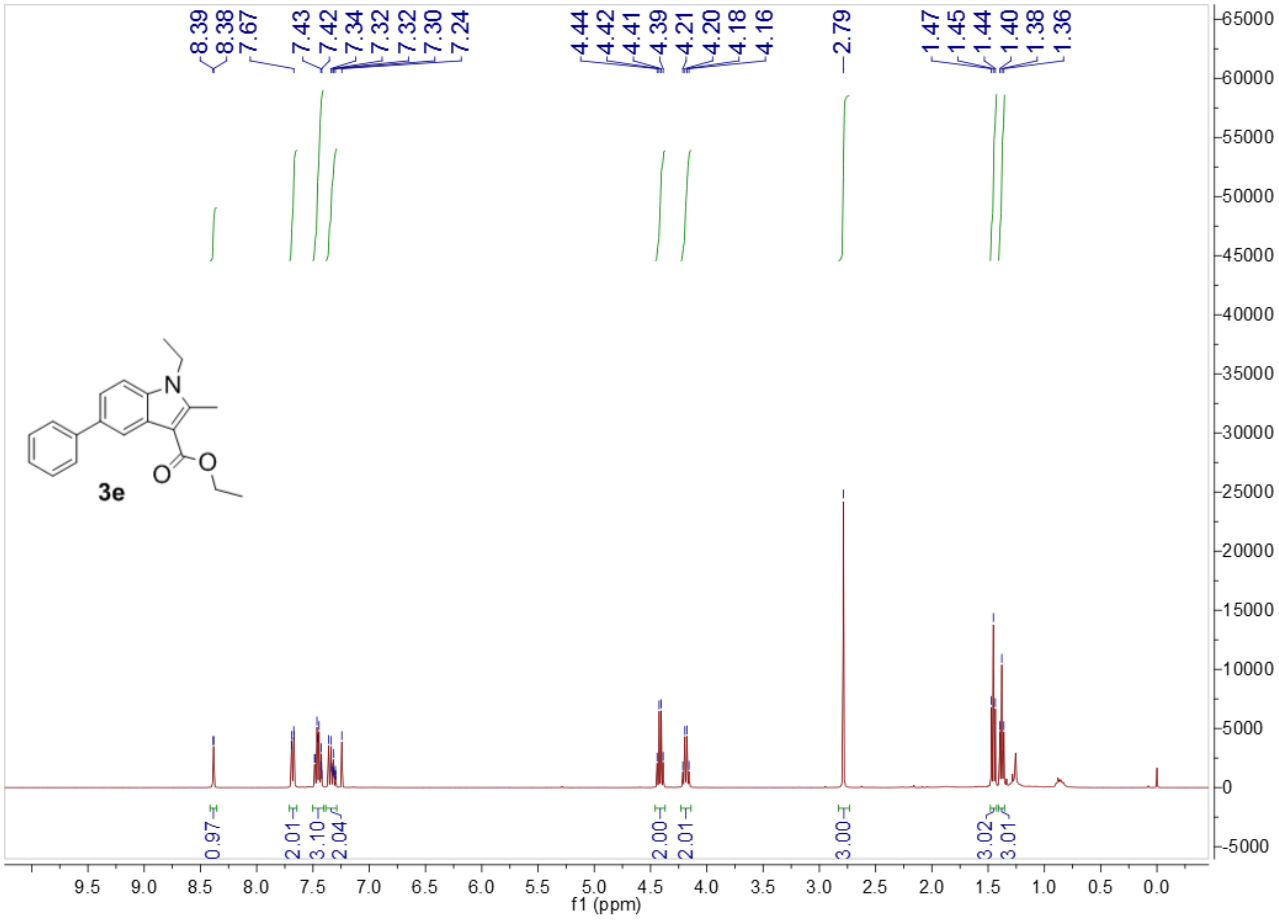

166.23
144.23
133.68
130.83
127.01
123.25
121.26
108.65
103.45
77.32
77.00
76.68
59.20
37.76
21.56
14.72
14.60
11.55
f1 (ppm)
3b

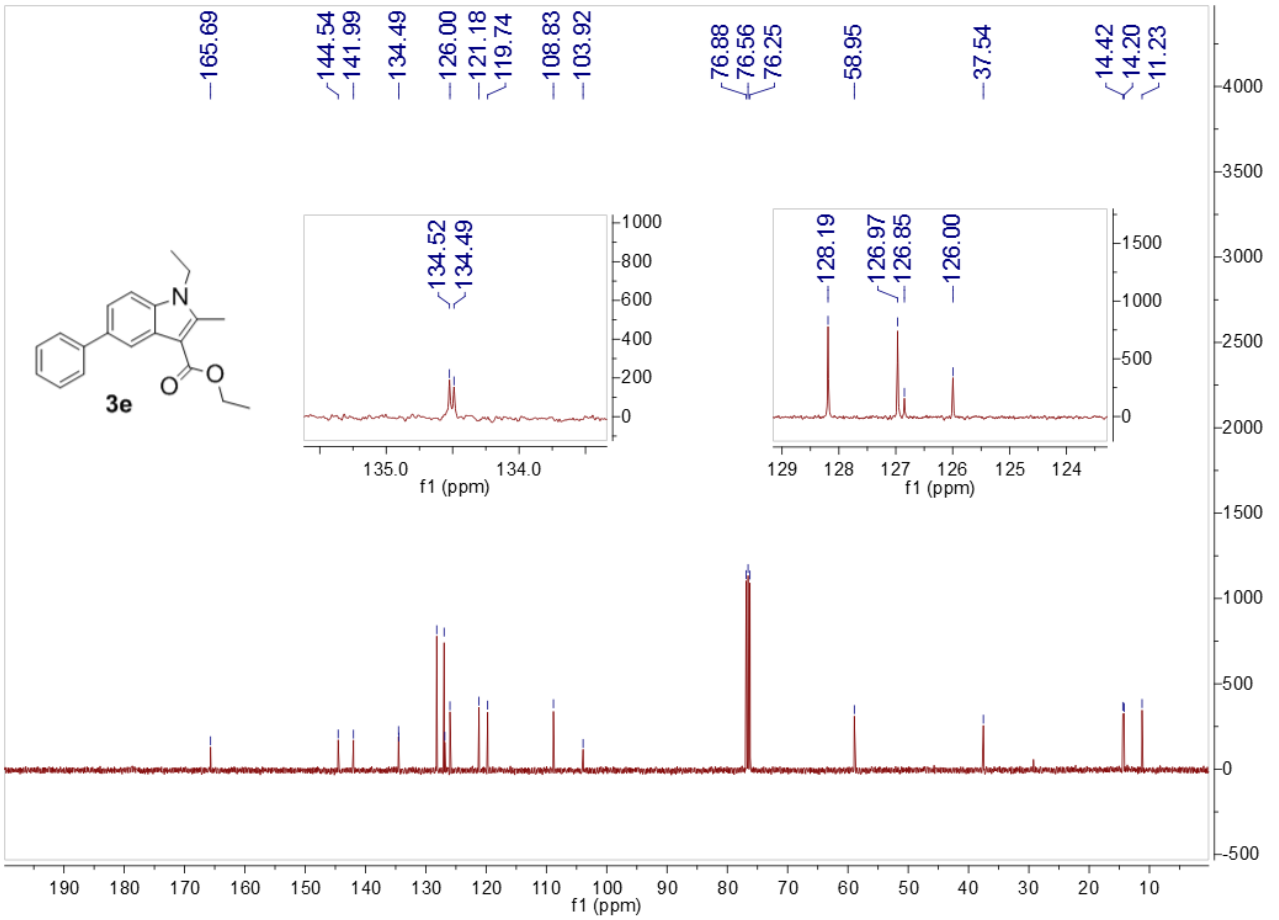

8.21
8.20
7.31
7.31
7.29
7.28
7.22
7.21
7.20
4.42
4.40
4.38
4.36
4.13
4.11
4.09
4.07
2.73
1.48
1.46
1.44
1.41
1.34
1.32
1.30
0.00
0.98
0.99
1.06
2.02
2.00
3.00
3.06
9.00
3.08
f1 (ppm)
3c

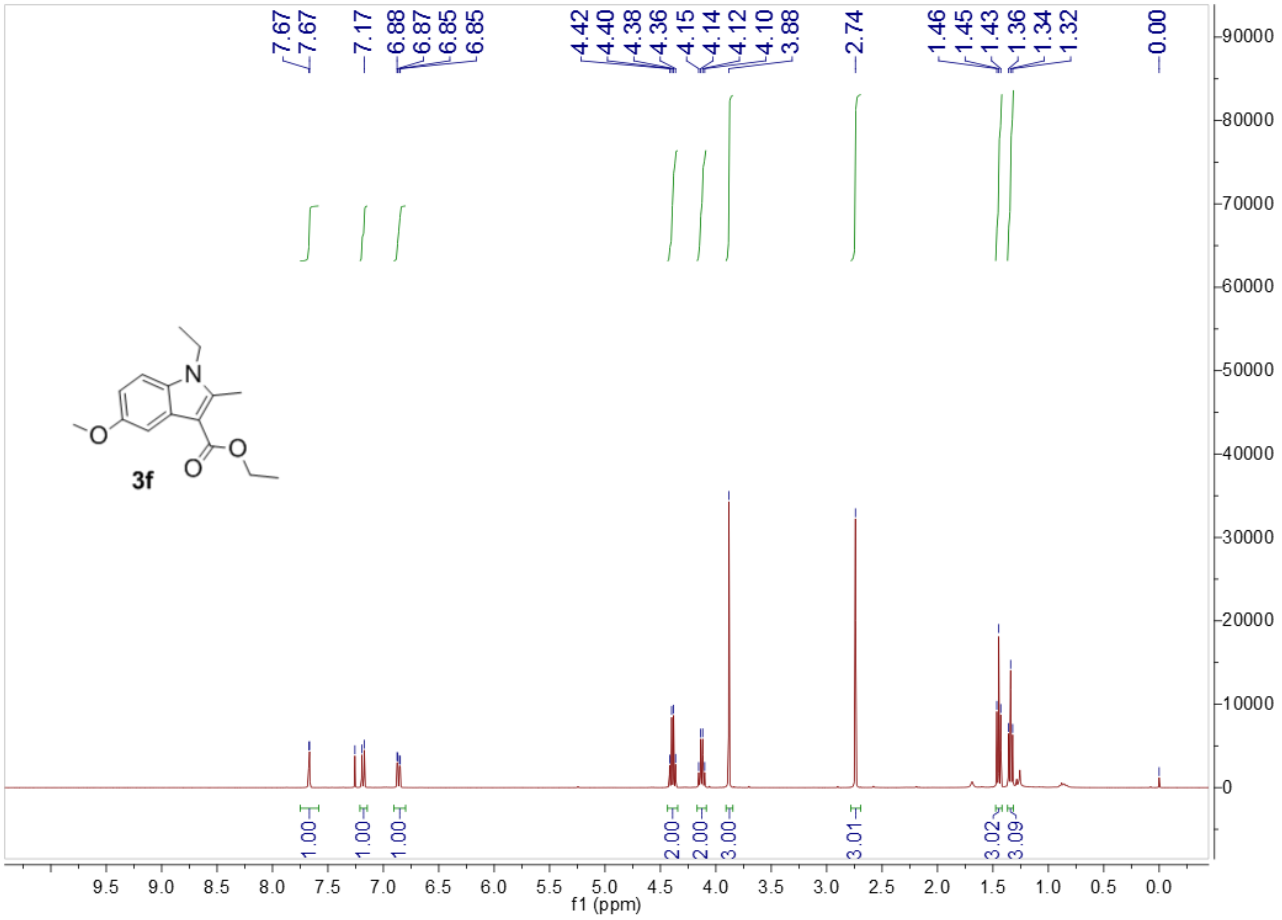

166.24
144.40
144.30
133.54
126.57
119.90
117.55
108.48
103.79
77.32
77.00
76.68
59.15
37.74
34.64
31.82
14.78
14.49
11.50
f1 (ppm)
3c

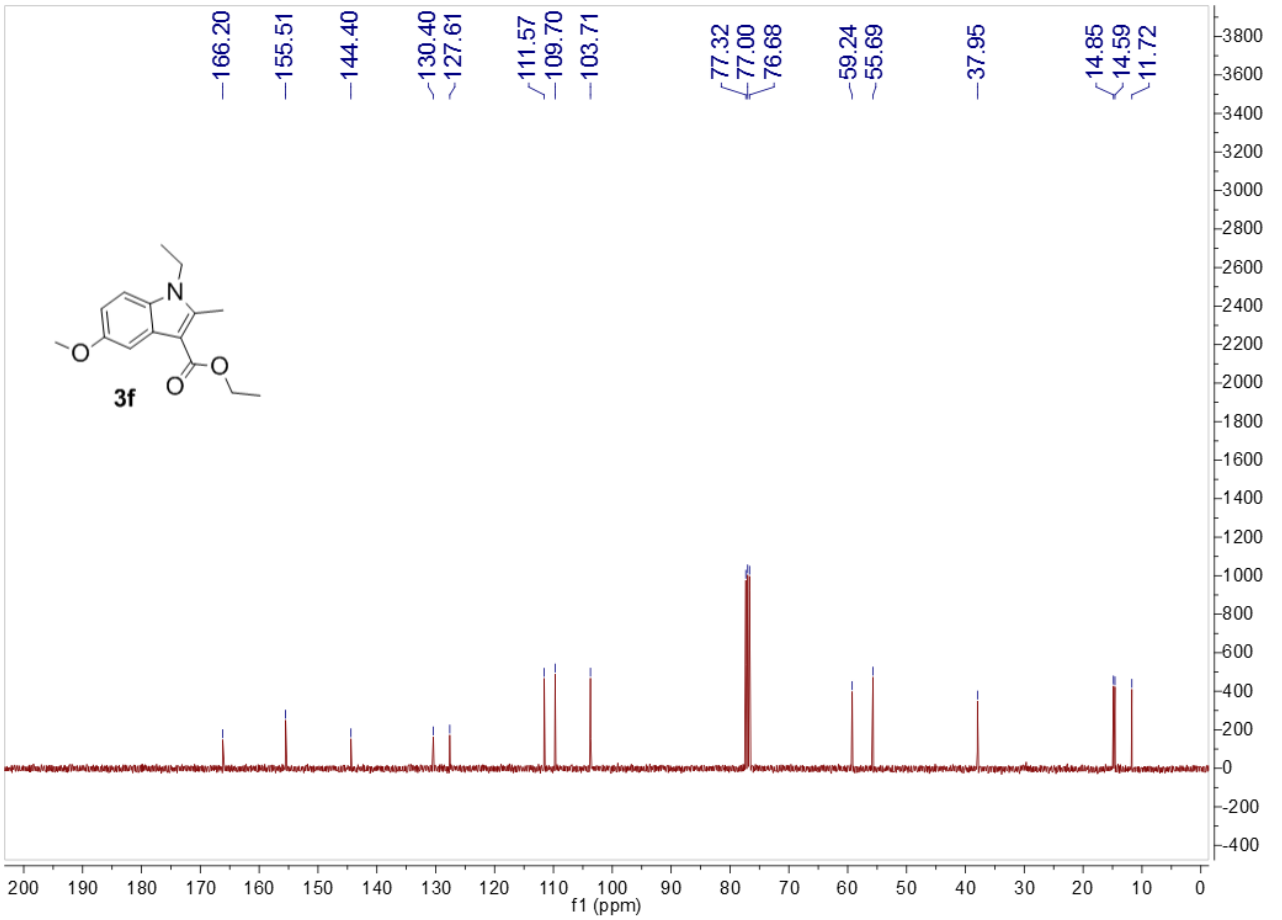

8.02
8.01
7.23
7.22
7.20
7.12
7.12
7.10
7.10
4.42
4.41
4.39
4.37
4.14
4.12
4.10
3.03
3.01
2.73
1.45
1.44
1.34
1.33
1.32
1.31
1.31
-0.00
0.98
0.99
1.00
2.00
2.00
1.00
3.00
2.99
9.02
3d
f1 (ppm)

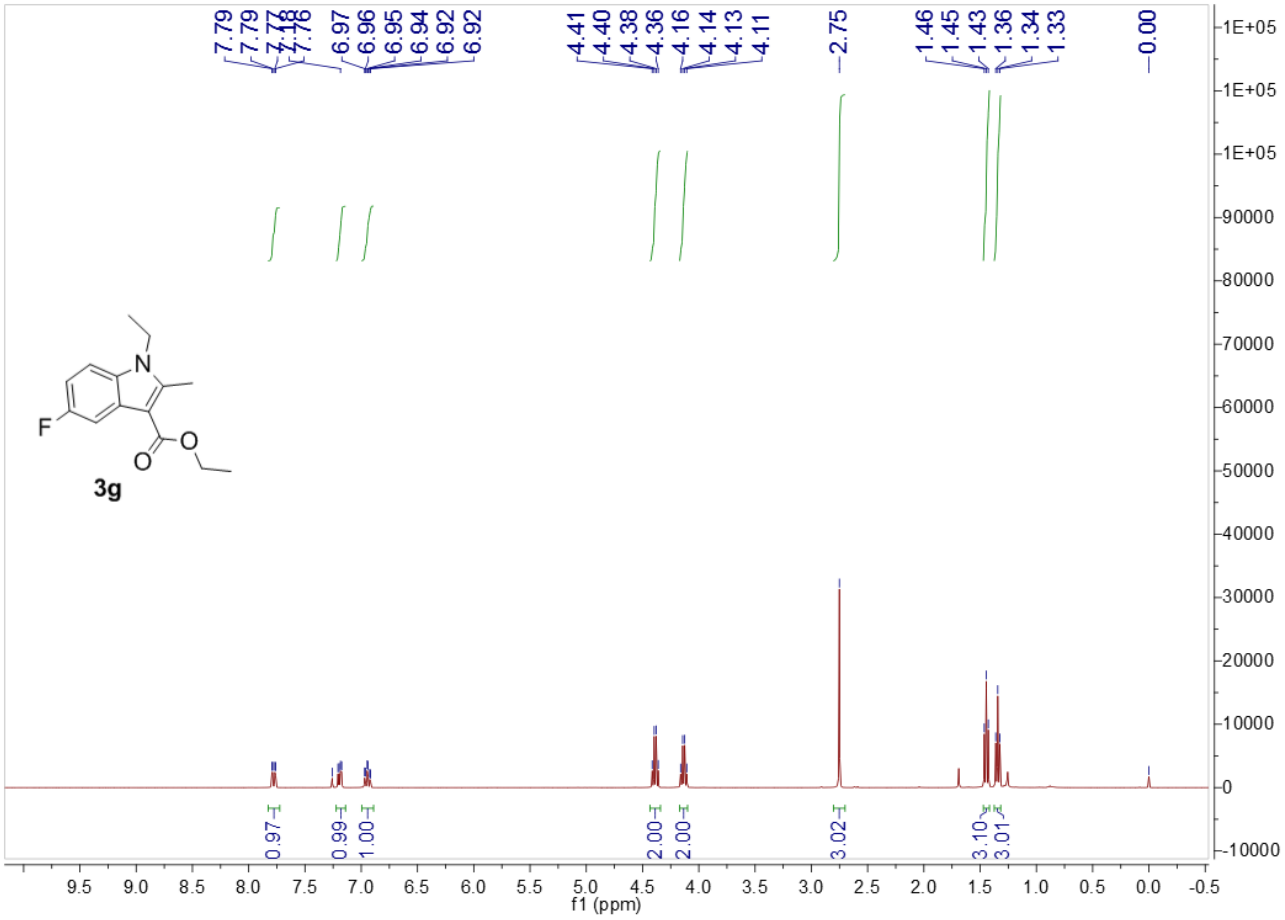

166.22
144.24
142.24
133.93
126.90
120.83
118.59
108.76
103.64
77.32
77.00
76.68
59.17
37.73
34.26
24.54
14.74
14.53
11.51
3d
f1 (ppm)

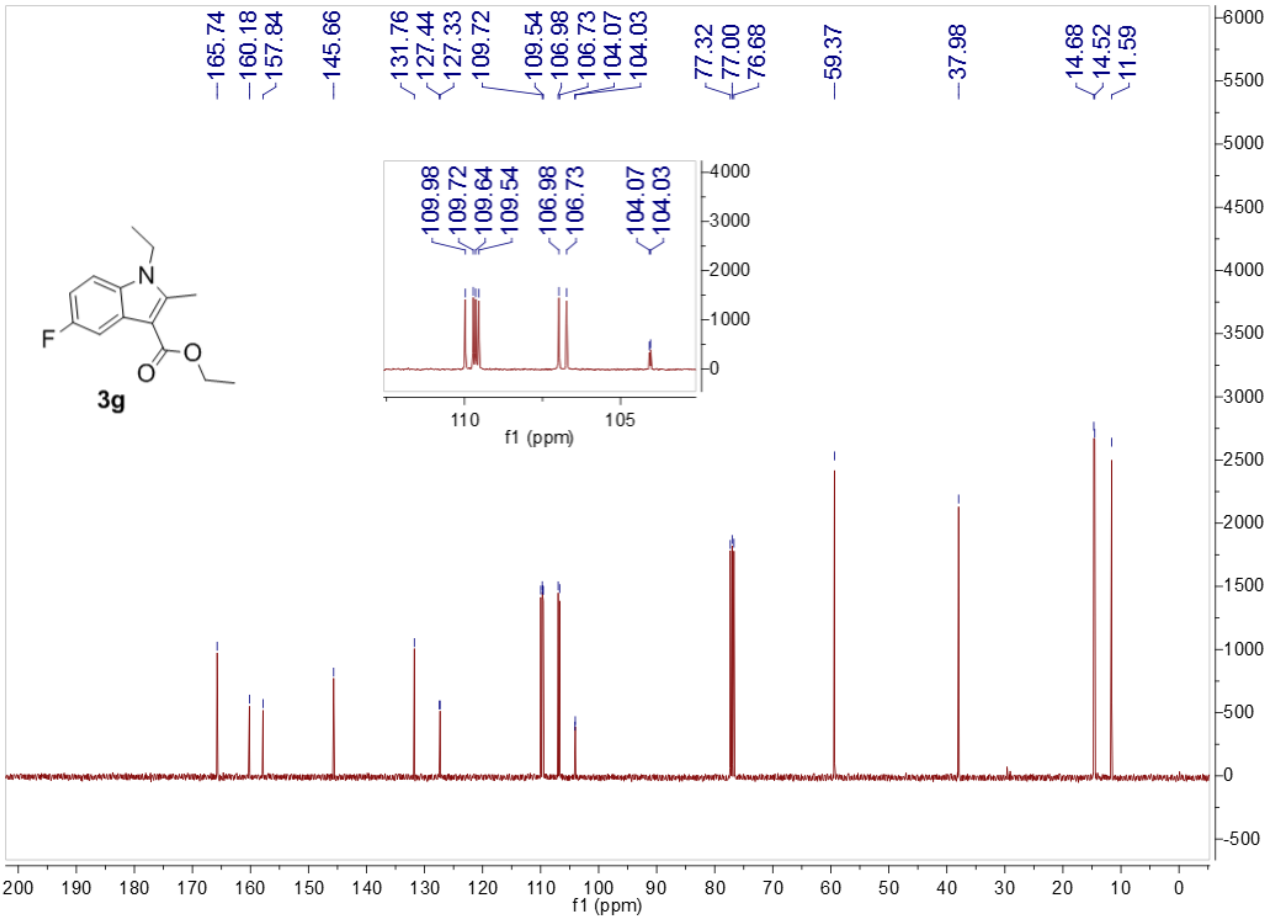

8.39
8.38
7.67
7.43
7.42
7.34
7.32
7.32
7.30
7.24
4.44
4.42
4.41
4.39
4.21
4.20
4.18
4.16
2.79
1.47
1.45
1.44
1.40
1.38
1.36
3e
0.97
2.01
3.10
2.04
2.00
2.01
3.00
3.02
3.01
f1 (ppm)

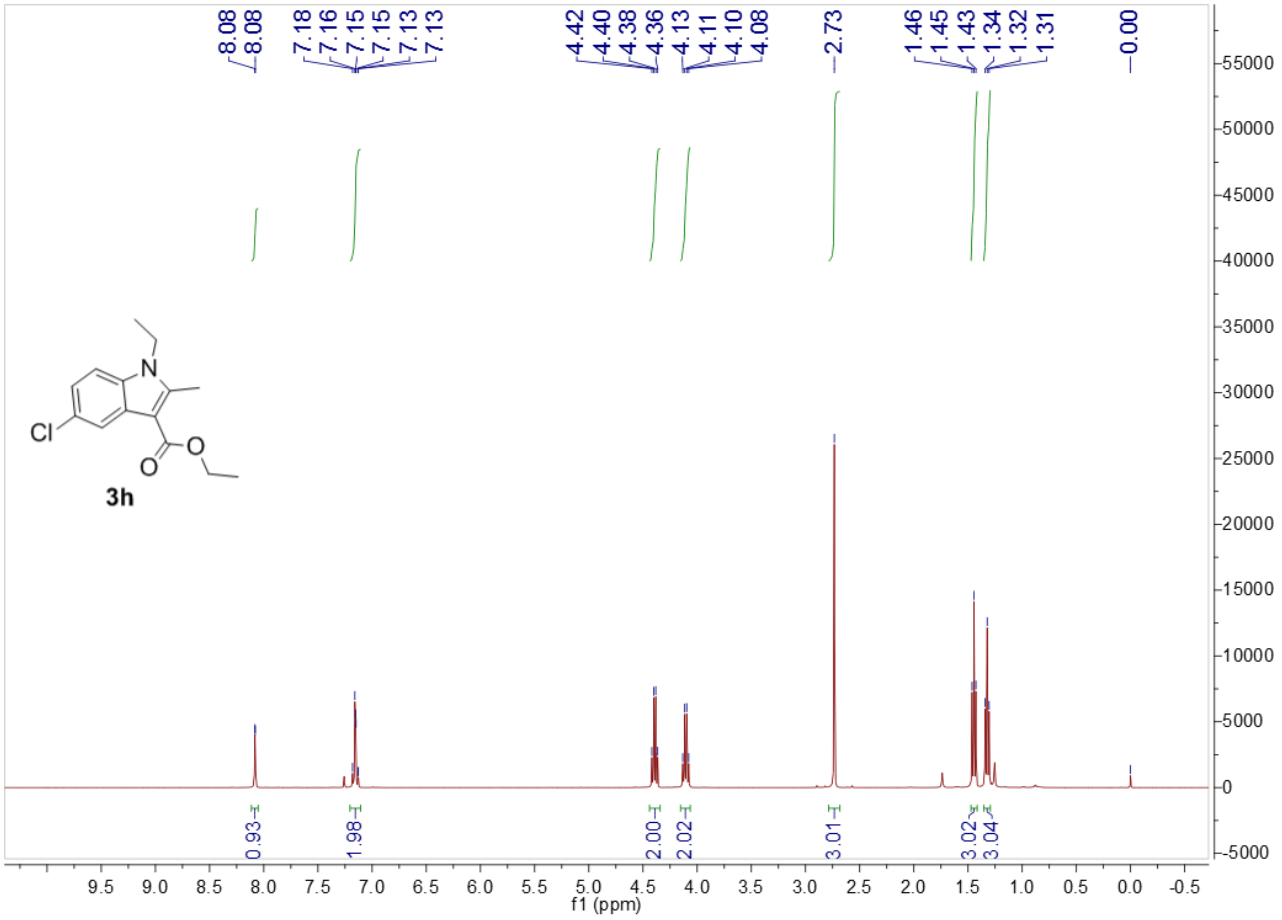

165.69
144.54
141.99
134.49
126.00
121.18
119.74
108.83
103.92
76.88
76.56
76.25
58.95
37.54
14.42
14.20
11.23
134.52
134.49
128.19
126.97
126.85
126.00
3e
f1 (ppm)

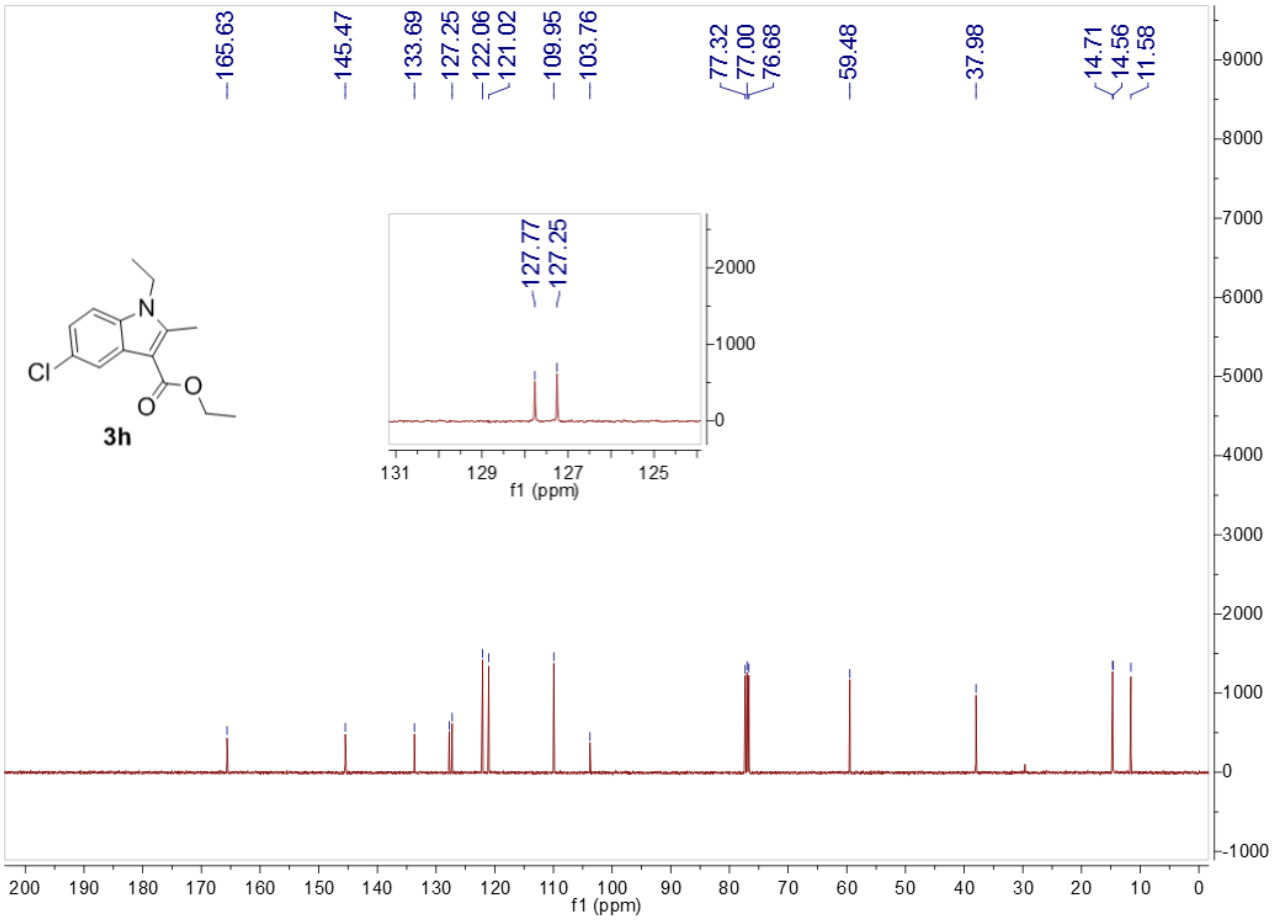

7.67
7.67
7.17
6.88
6.87
6.85
6.85
4.42
4.40
4.38
4.36
4.15
4.14
4.12
4.10
3.88
2.74
1.46
1.45
1.43
1.36
1.34
1.32
0.00
3f
1.00
1.00
1.00
2.00
2.00
3.00
3.01
3.02
3.09
f1 (ppm)

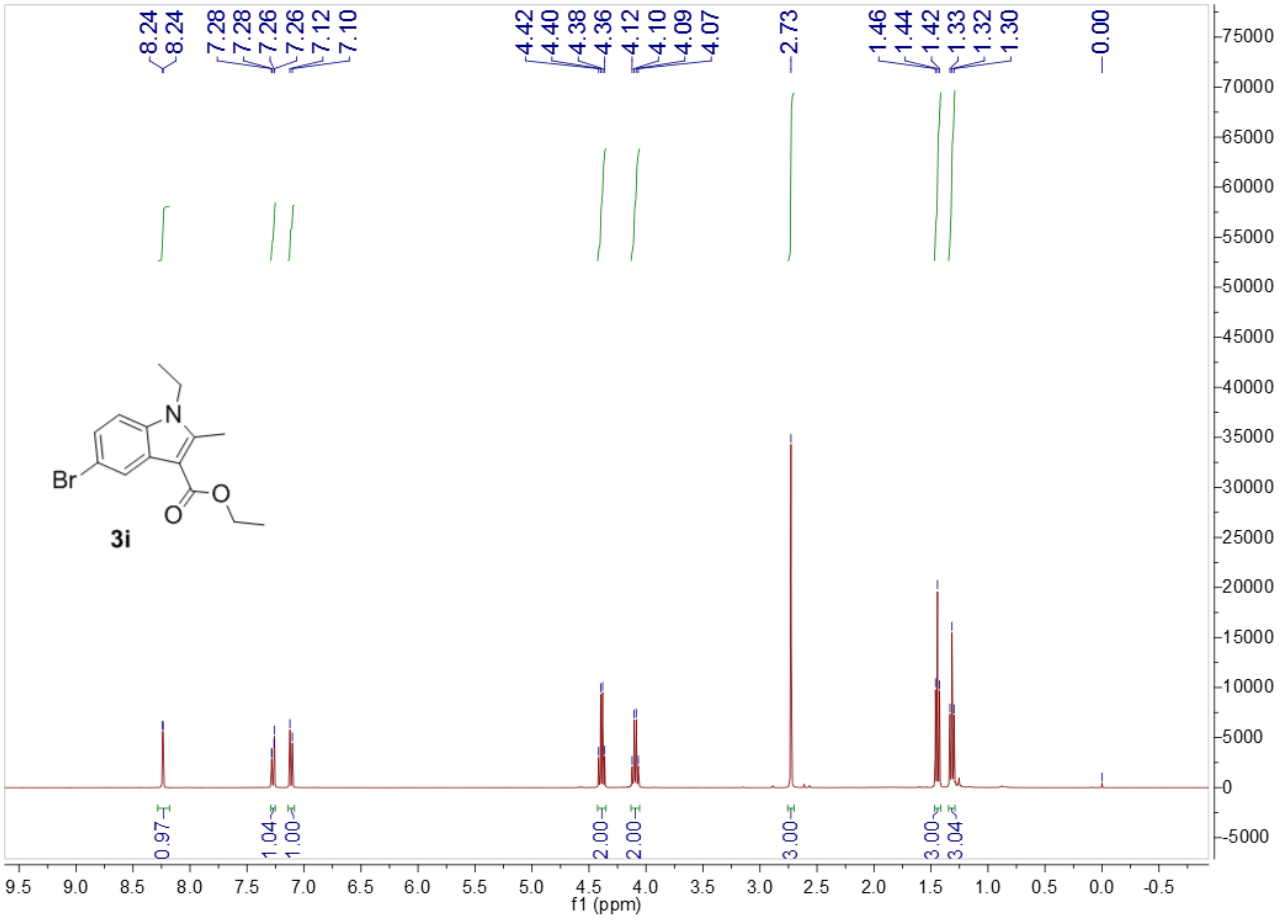

166.20
155.51
144.40
130.40
127.61
111.57
109.70
103.71
77.32
77.00
76.68
59.24
55.69
37.95
14.85
14.59
11.72
3f
f1 (ppm)

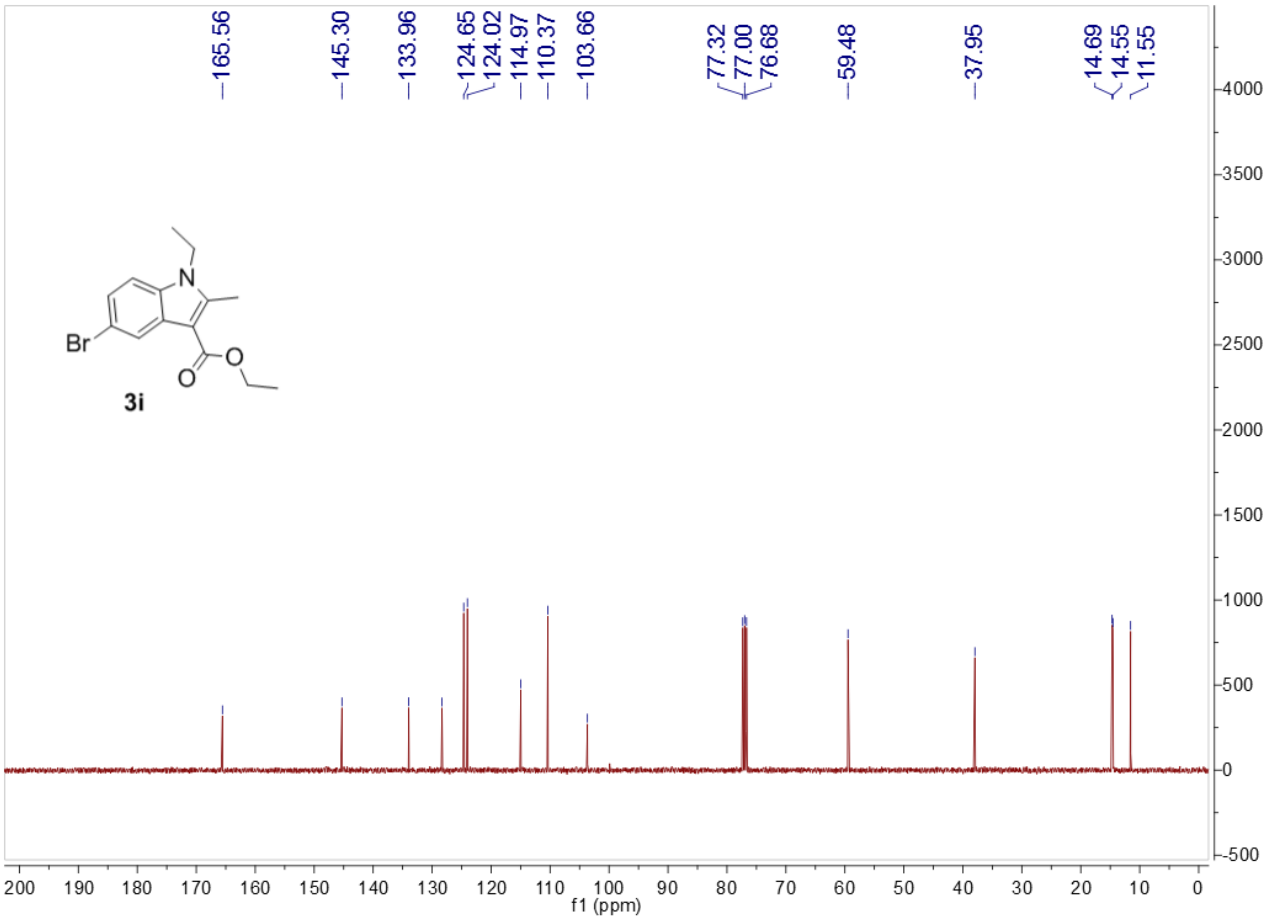

7.79
7.79
7.77
7.76
6.97
6.96
6.95
6.94
6.92
6.92
4.41
4.40
4.38
4.36
4.16
4.14
4.13
4.11
2.75
1.46
1.45
1.43
1.36
1.34
1.33
0.00
0.97
0.99
1.00
2.00
2.00
3.02
3.10
3.01
f1 (ppm)
3g

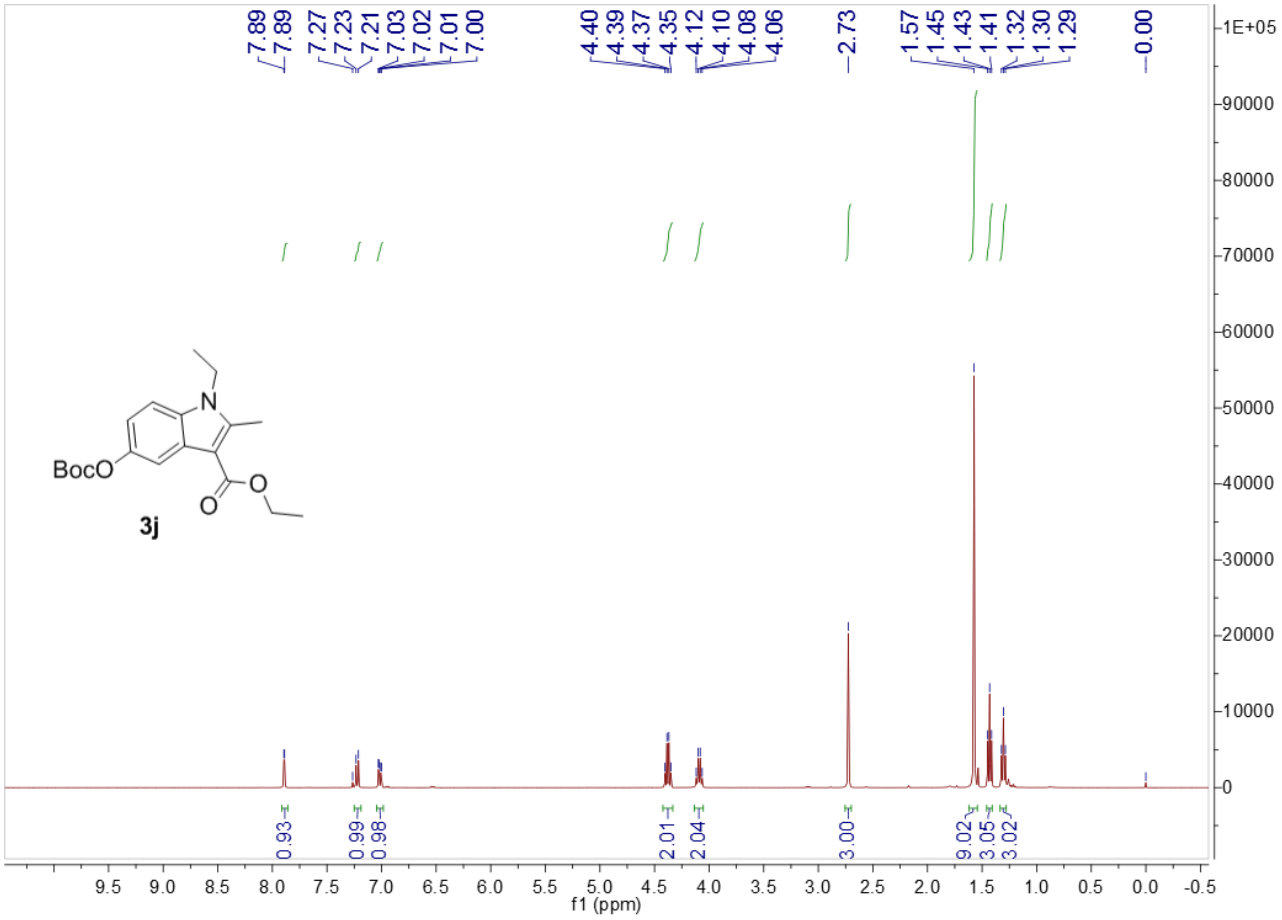

165.74
160.18
157.84
145.66
131.76
127.44
127.33
109.72
109.54
106.98
106.73
104.07
104.03
77.32
77.00
76.68
59.37
37.98
14.68
14.52
11.59
109.98
109.72
109.64
109.54
106.98
106.73
104.07
104.03
f1 (ppm)
f1 (ppm)
3g

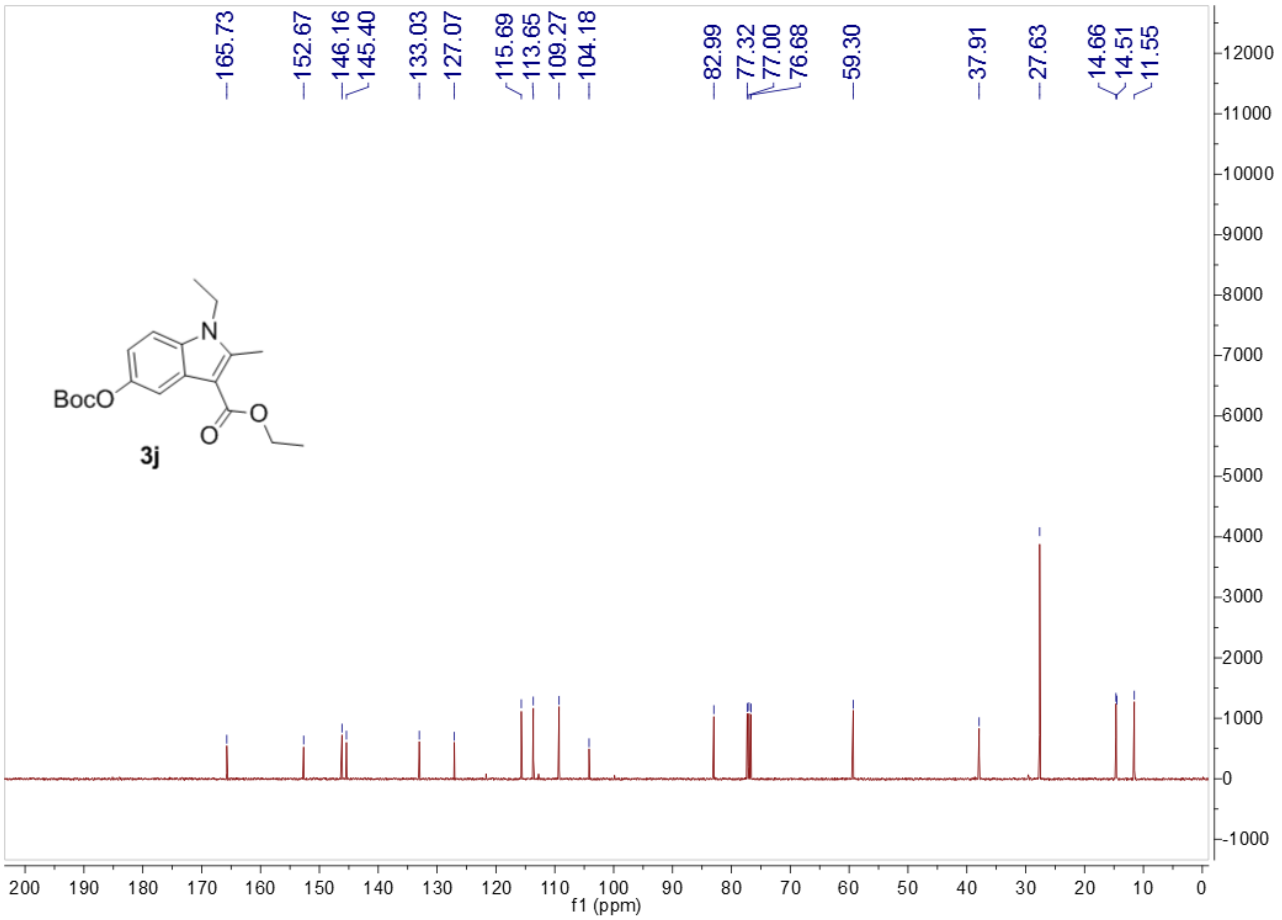

8.08
8.08
7.18
7.16
7.15
7.15
7.13
7.13
4.42
4.40
4.38
4.36
4.13
4.11
4.10
4.08
2.73
1.46
1.45
1.43
1.34
1.32
1.31
0.00
0.93
1.98
2.00
2.02
3.01
3.02
3.04
f1 (ppm)
Cl
N
O
O
3h

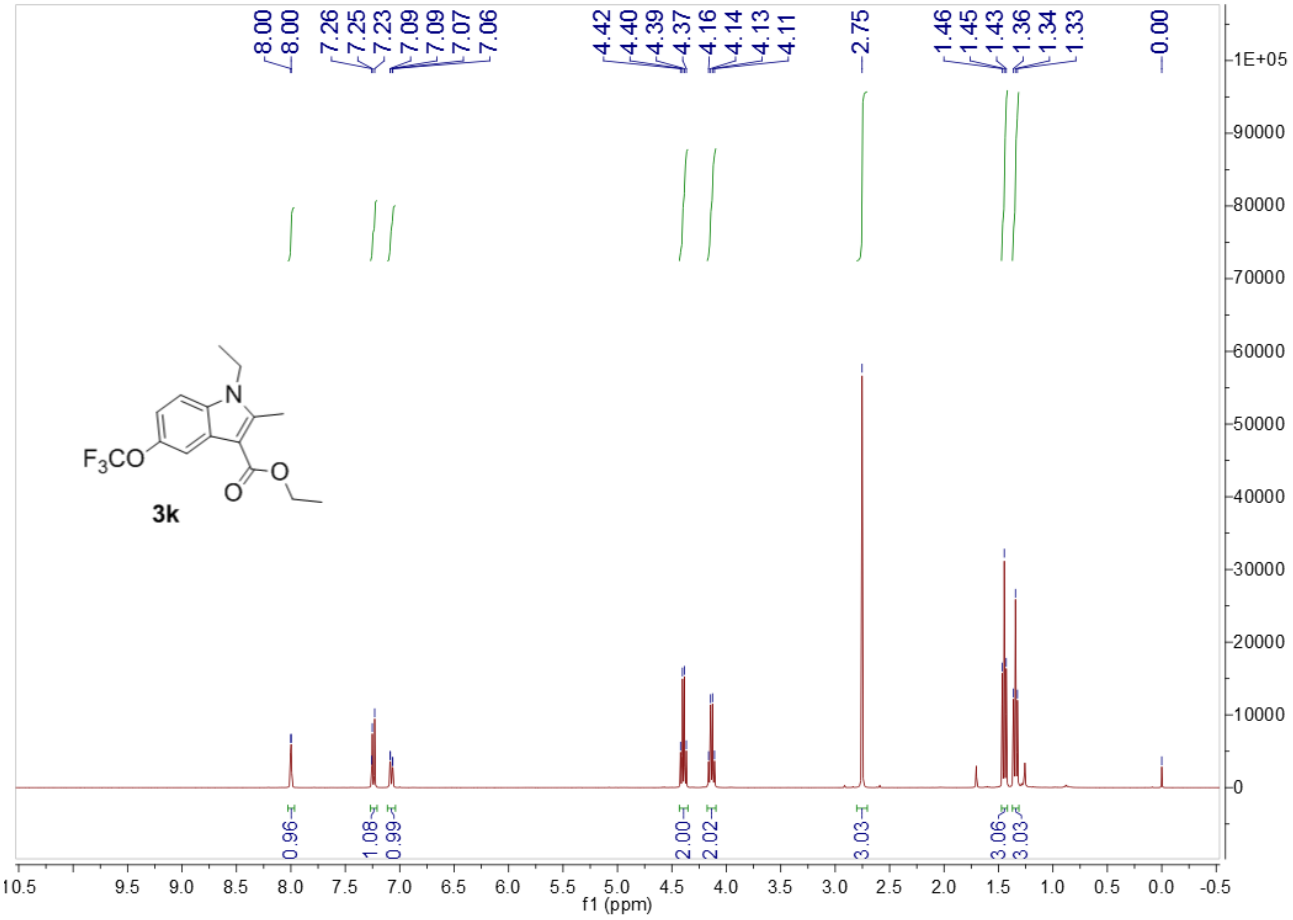

165.63
145.47
133.69
127.25
122.06
121.02
109.95
103.76
77.32
77.00
76.68
59.48
37.98
14.71
14.56
11.58
127.77
127.25
f1 (ppm)
Cl
N
O
O
3h

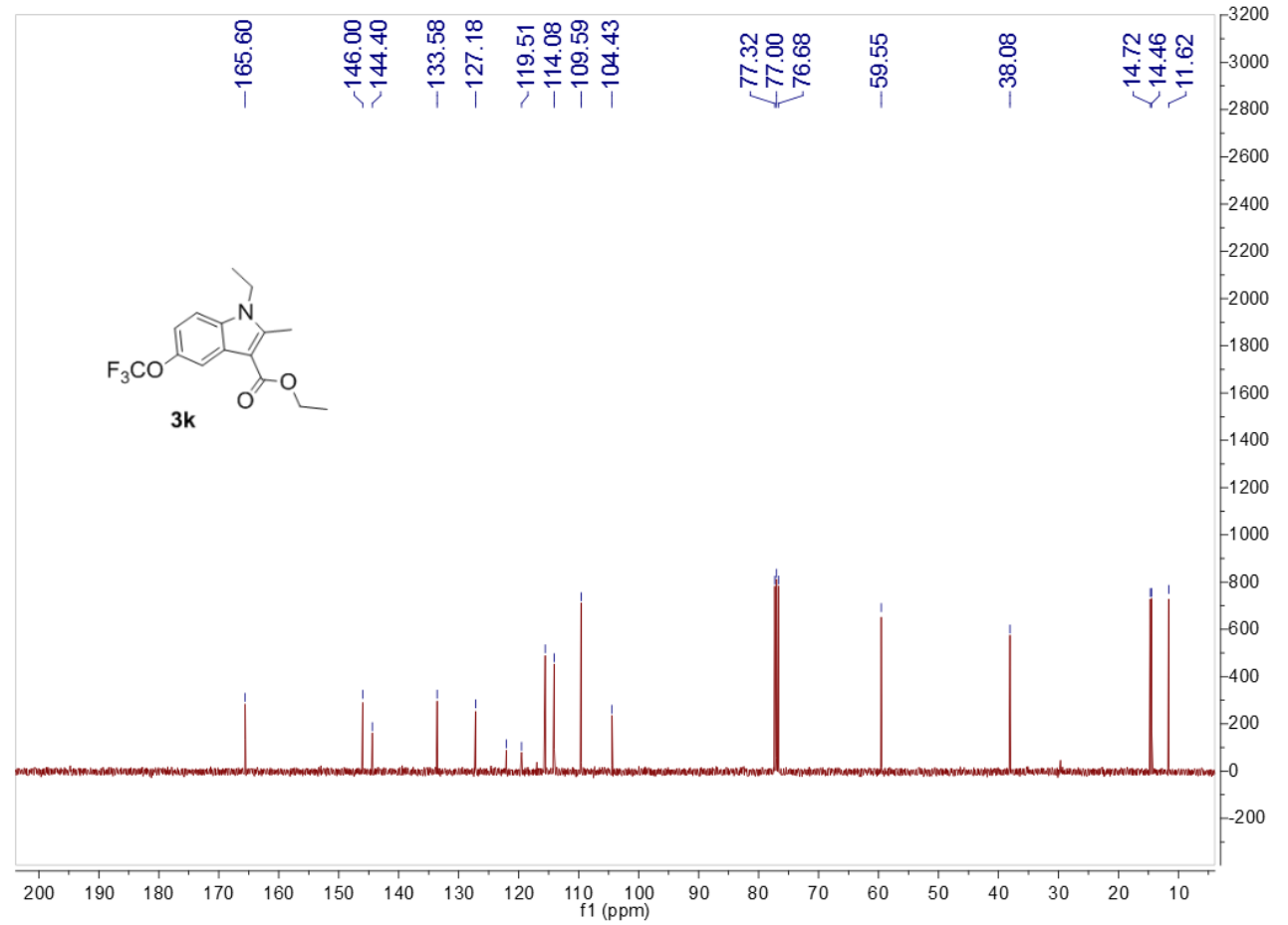

8.24
8.24
7.28
7.28
7.26
7.26
7.12
7.10
4.42
4.40
4.38
4.36
4.12
4.10
4.09
4.07
2.73
1.46
1.44
1.42
1.33
1.32
1.30
0.00
Br
N
O
O
3i
0.97
1.04
1.00
2.00
2.00
3.00
3.00
3.04
f1 (ppm)

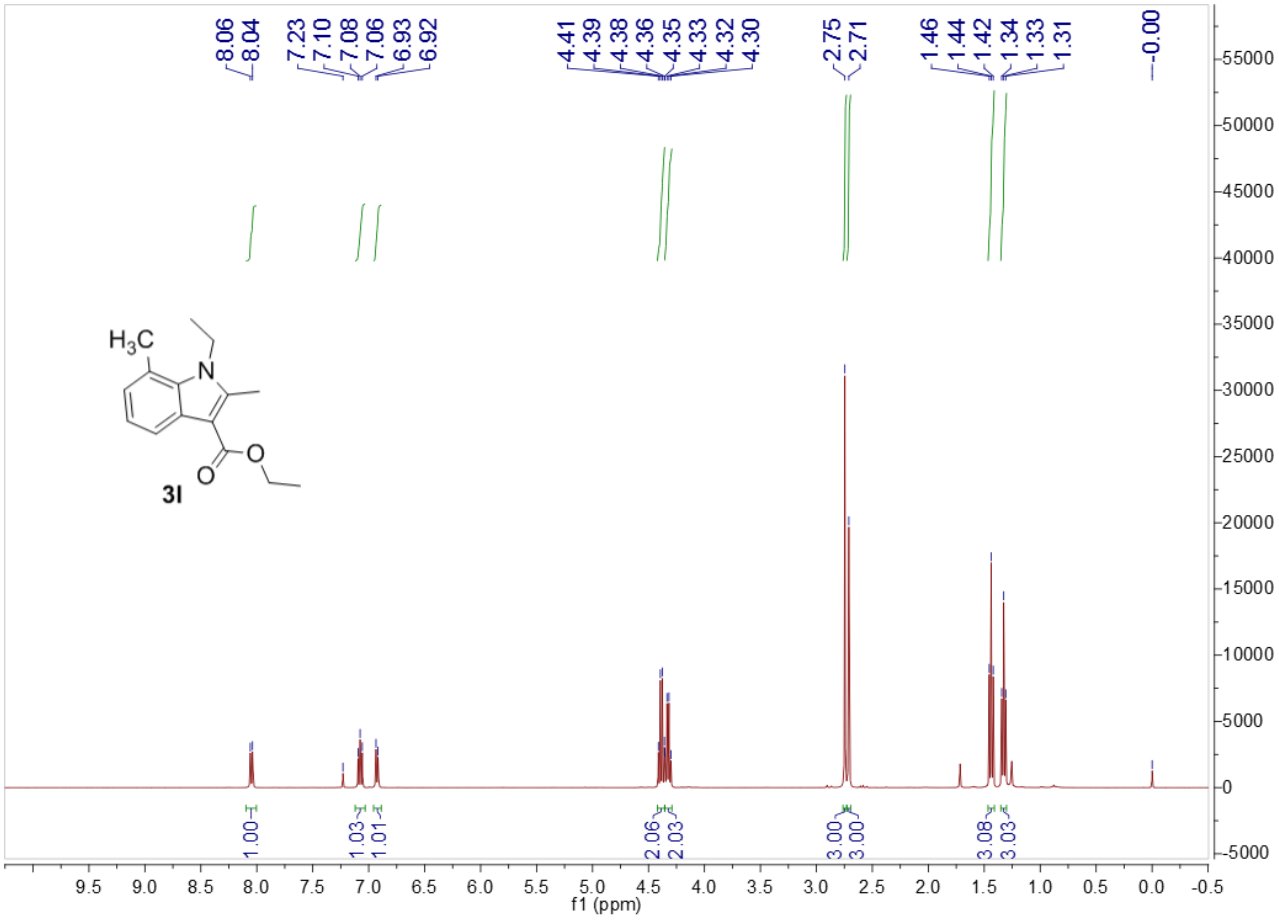

165.56
145.30
133.96
124.65
124.02
114.97
110.37
103.66
77.32
77.00
76.68
59.48
37.95
14.69
14.55
11.55
Br
N
O
O
3i
f1 (ppm)

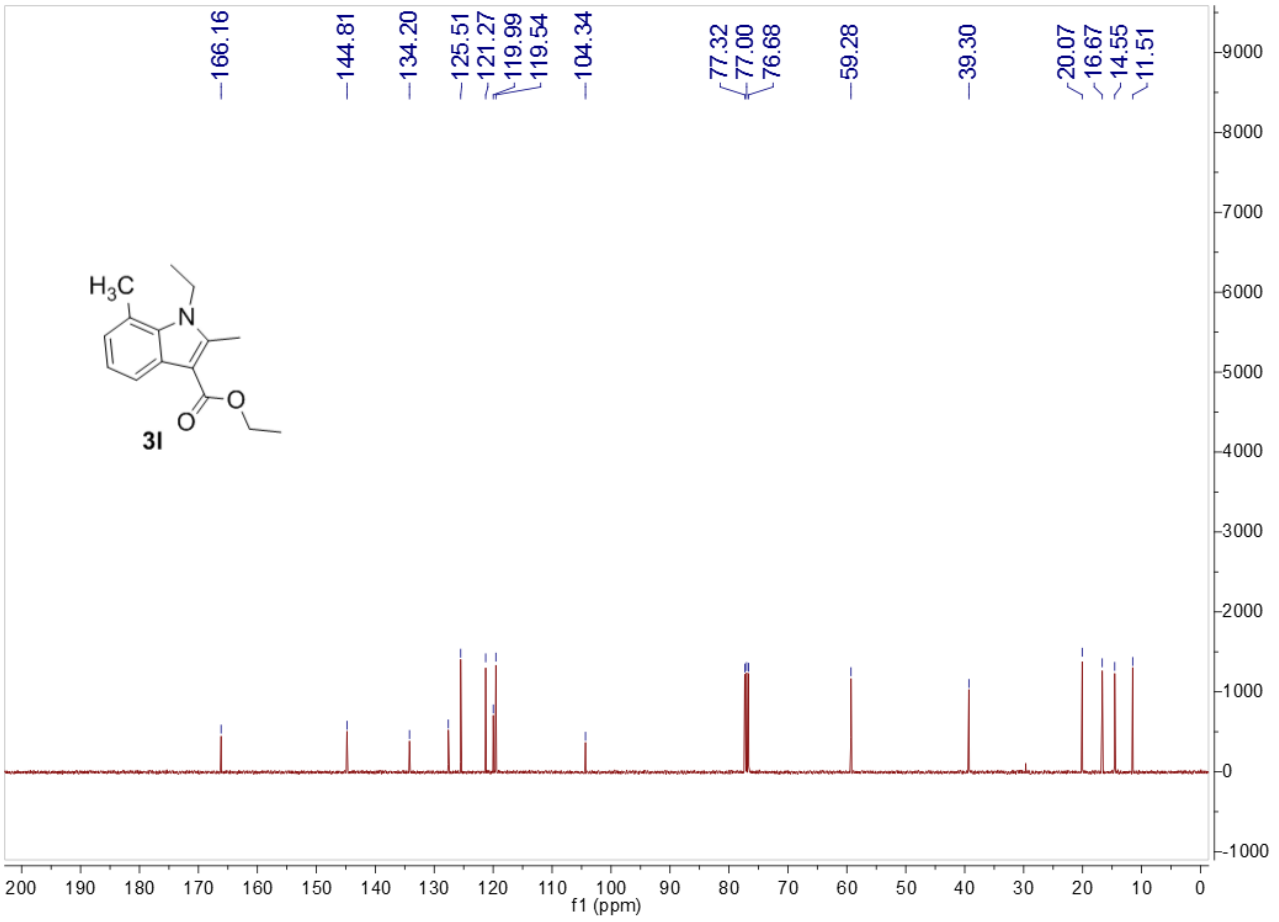

7.89
7.89
7.27
7.23
7.21
7.03
7.02
7.01
7.00
4.40
4.39
4.37
4.35
4.12
4.10
4.08
4.06
2.73
1.57
1.45
1.43
1.41
1.32
1.30
1.29
0.00
BocO
N
O
O
3j
0.93
0.99
0.98
2.01
2.04
3.00
9.02
3.05
3.02
f1 (ppm)

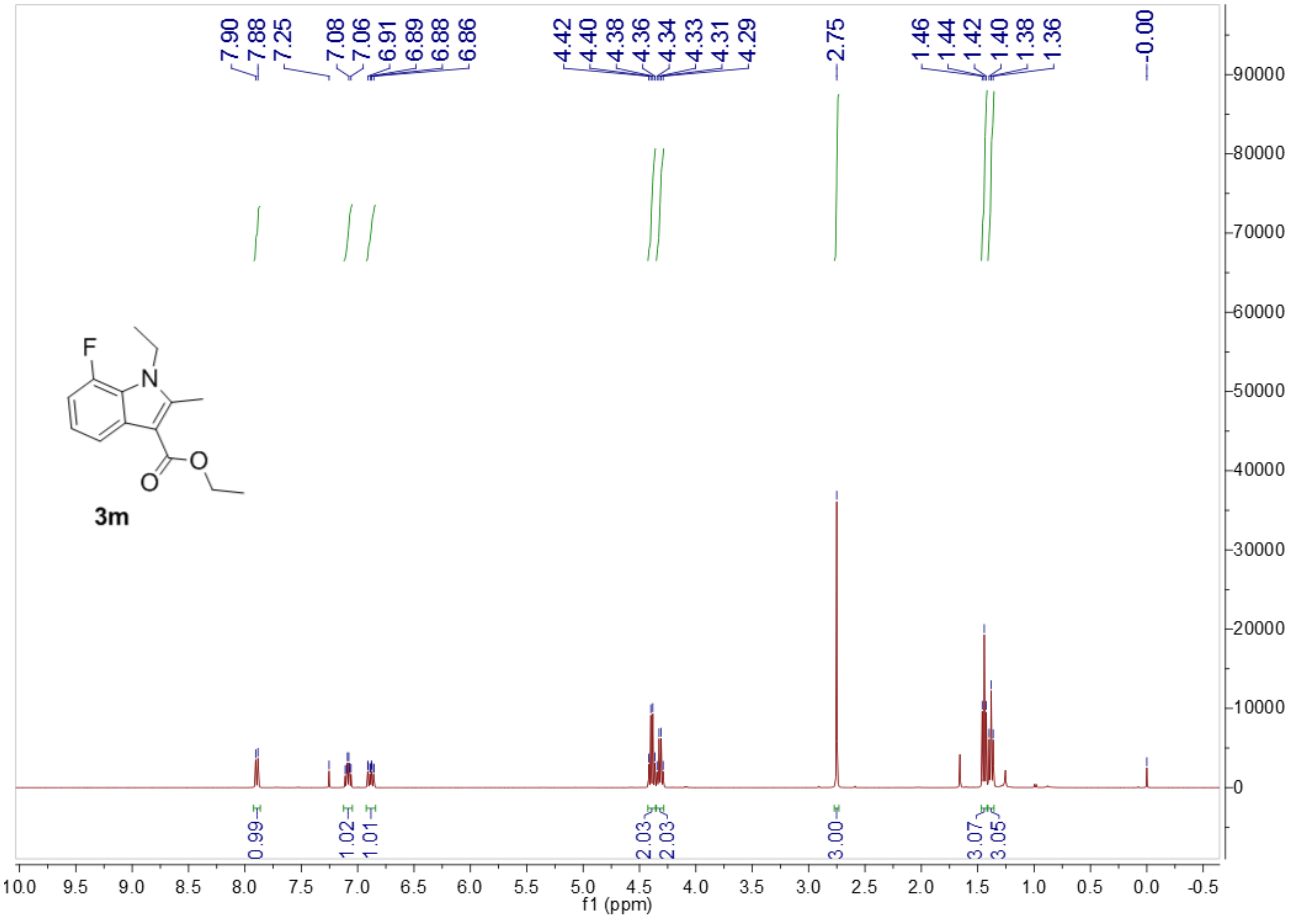

165.73
152.67
146.16
145.40
133.03
127.07
115.69
113.65
109.27
104.18
82.99
77.32
77.00
76.68
59.30
37.91
27.63
14.66
14.51
11.55
BocO
N
O
O
3j
f1 (ppm)

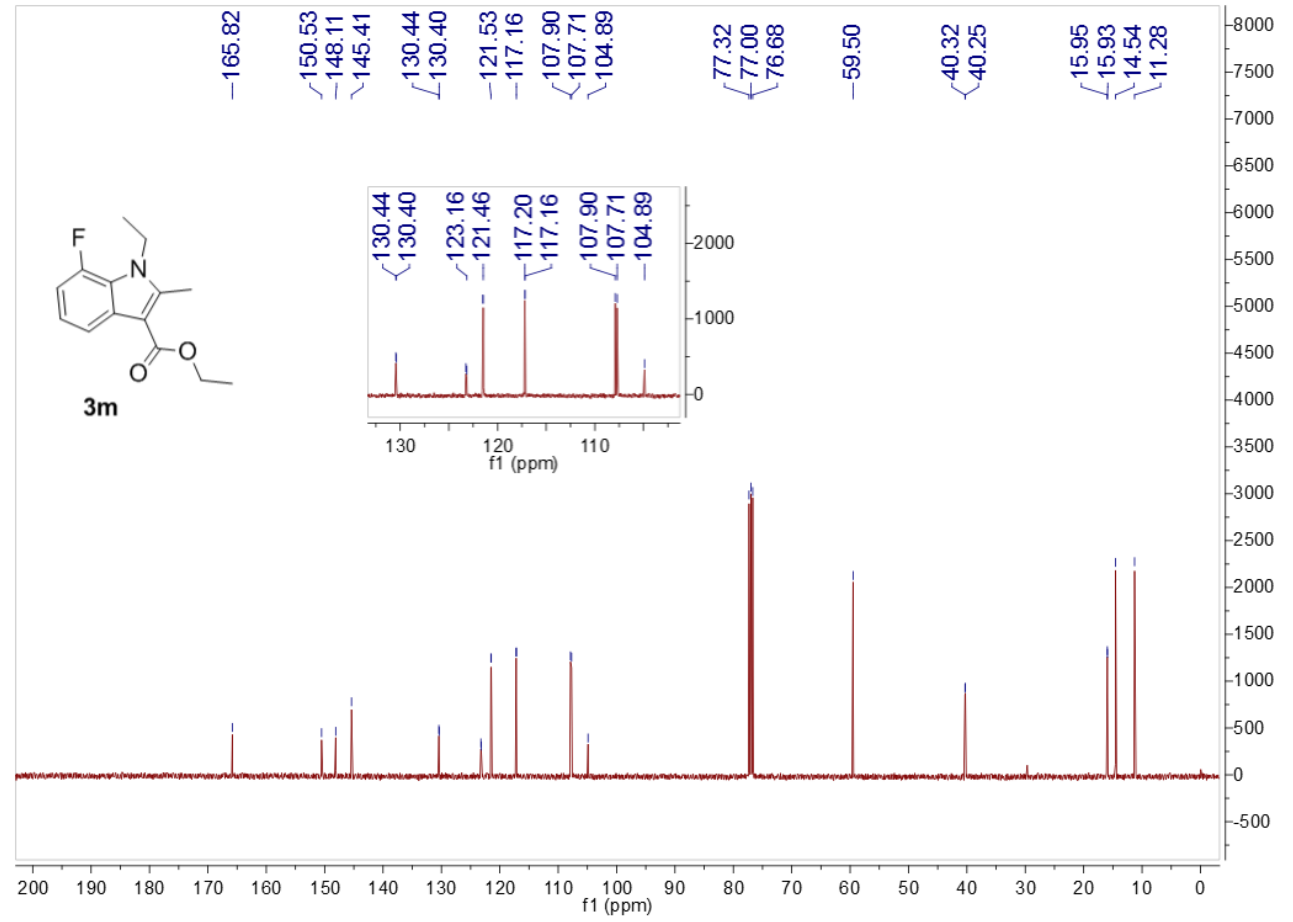

8.00
8.00
7.26
7.25
7.23
7.09
7.09
7.07
7.06
4.42
4.40
4.39
4.37
4.16
4.14
4.13
4.11
2.75
1.46
1.45
1.43
1.36
1.34
1.33
0.00
F3CO
N
O
O
3k
0.96
1.08
0.99
2.00
2.02
3.03
3.06
3.03
f1 (ppm)

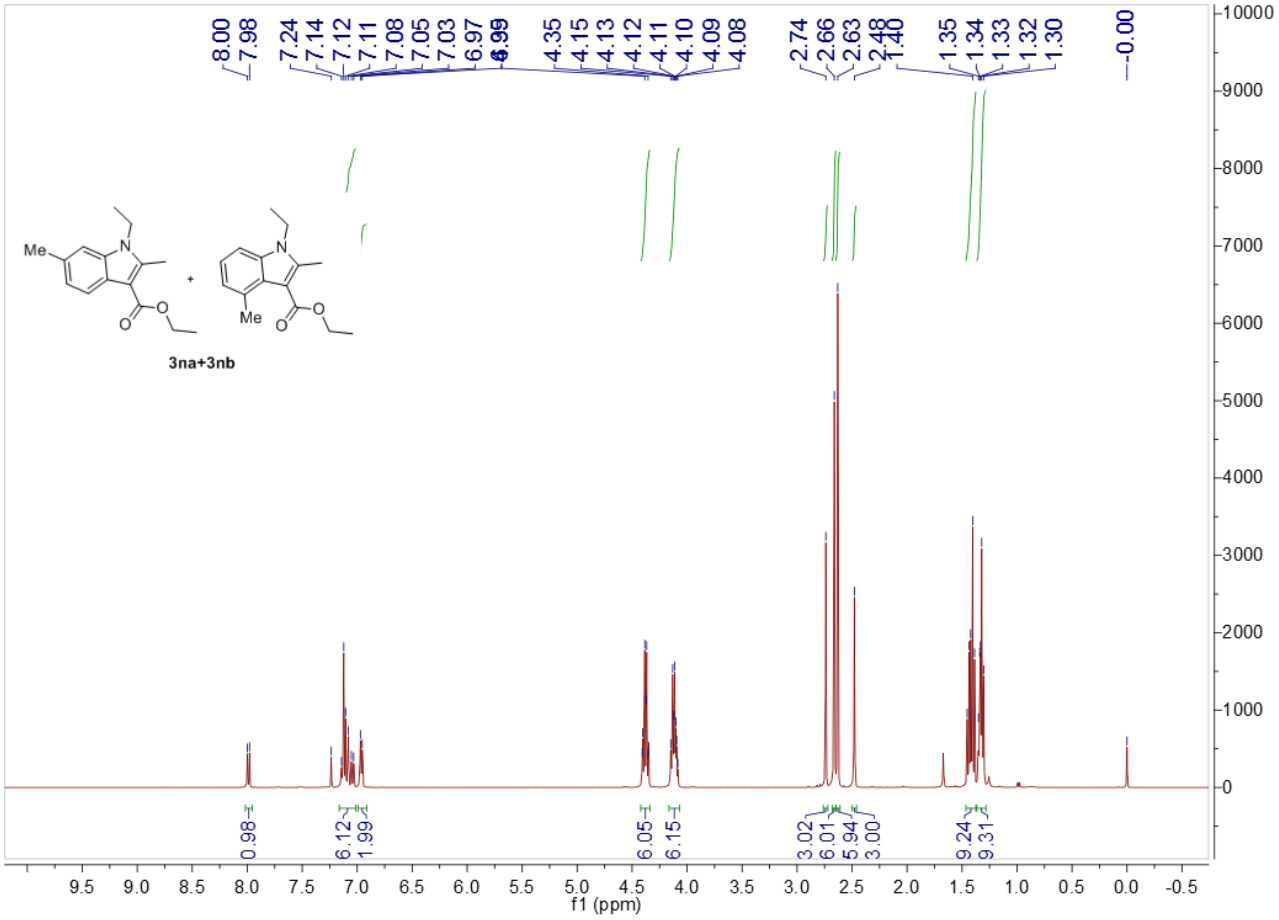

165.60
146.00
144.40
133.58
127.18
119.51
114.08
109.59
104.43
77.32
77.00
76.68
59.55
38.08
14.72
14.46
11.62
F3CO
N
O
O
3k
f1 (ppm)

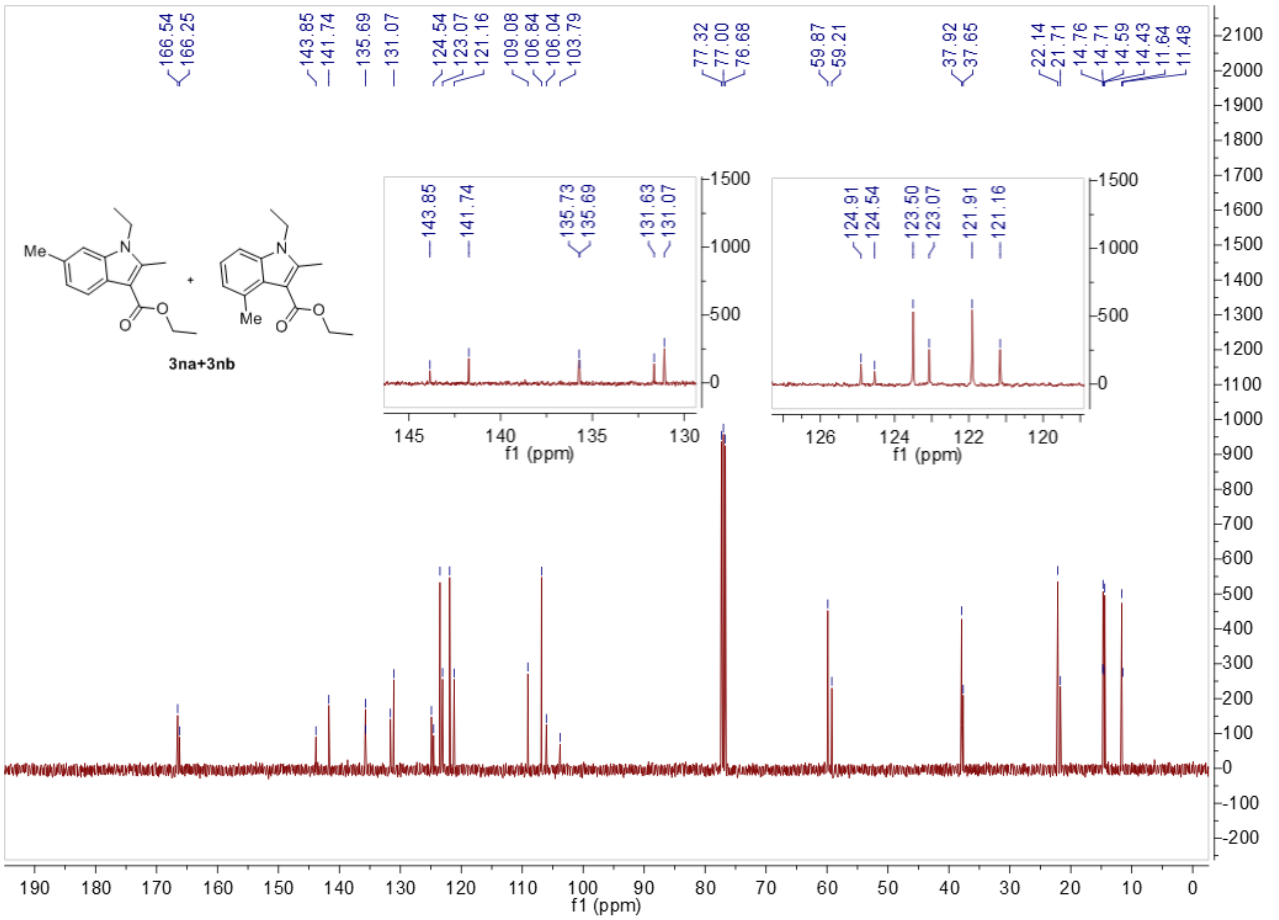

8.06
8.04
7.23
7.10
7.08
7.06
6.93
6.92
4.41
4.39
4.38
4.36
4.35
4.33
4.32
4.30
2.75
2.71
1.46
1.44
1.42
1.34
1.33
1.31
-0.00
1.00
1.03
1.01
2.06
2.03
3.00
3.00
3.08
3.03
H3C
N
O
O
3l
f1 (ppm)

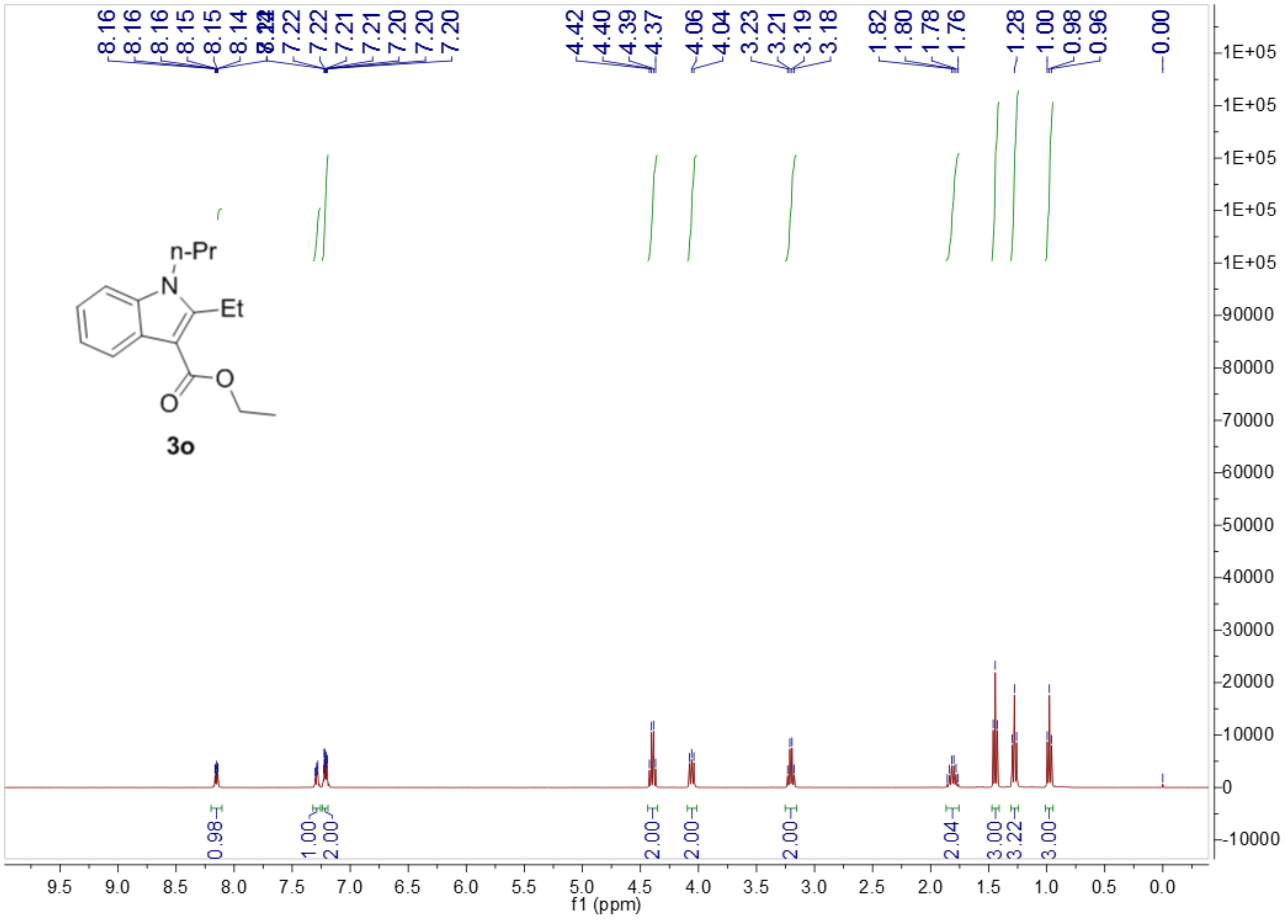

166.16
144.81
134.20
125.51
121.27
119.99
119.54
104.34
77.32
77.00
76.68
59.28
39.30
20.07
16.67
14.55
11.51
H3C
N
O
O
3l
f1 (ppm)

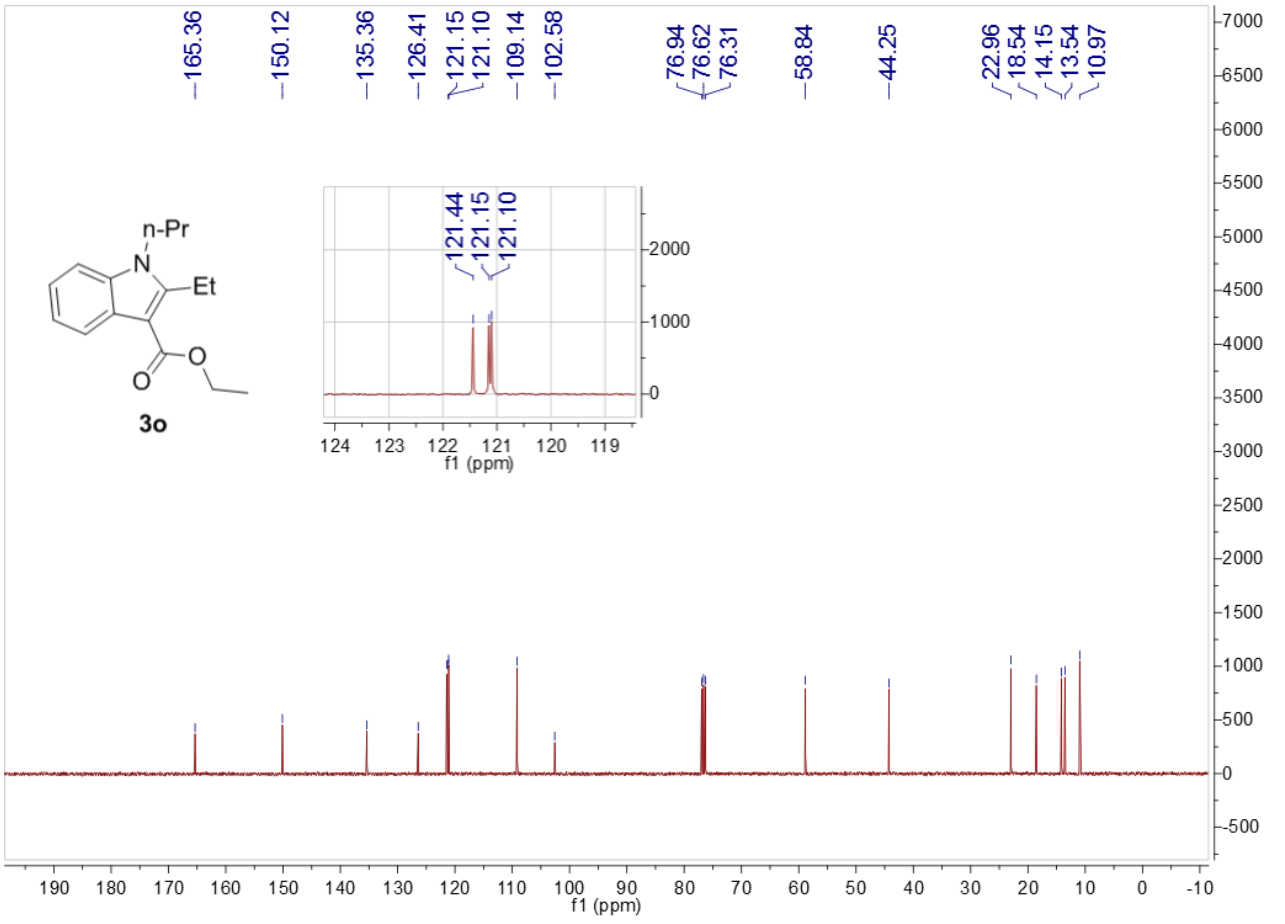

7.90
7.88
7.25
7.08
7.06
6.91
6.89
6.88
6.86
4.42
4.40
4.38
4.36
4.34
4.33
4.31
4.29
2.75
1.46
1.44
1.42
1.40
1.38
1.36
0.00
F
N
O
O
3m
0.99
1.02
1.01
2.03
2.03
3.00
3.07
3.05
f1 (ppm)

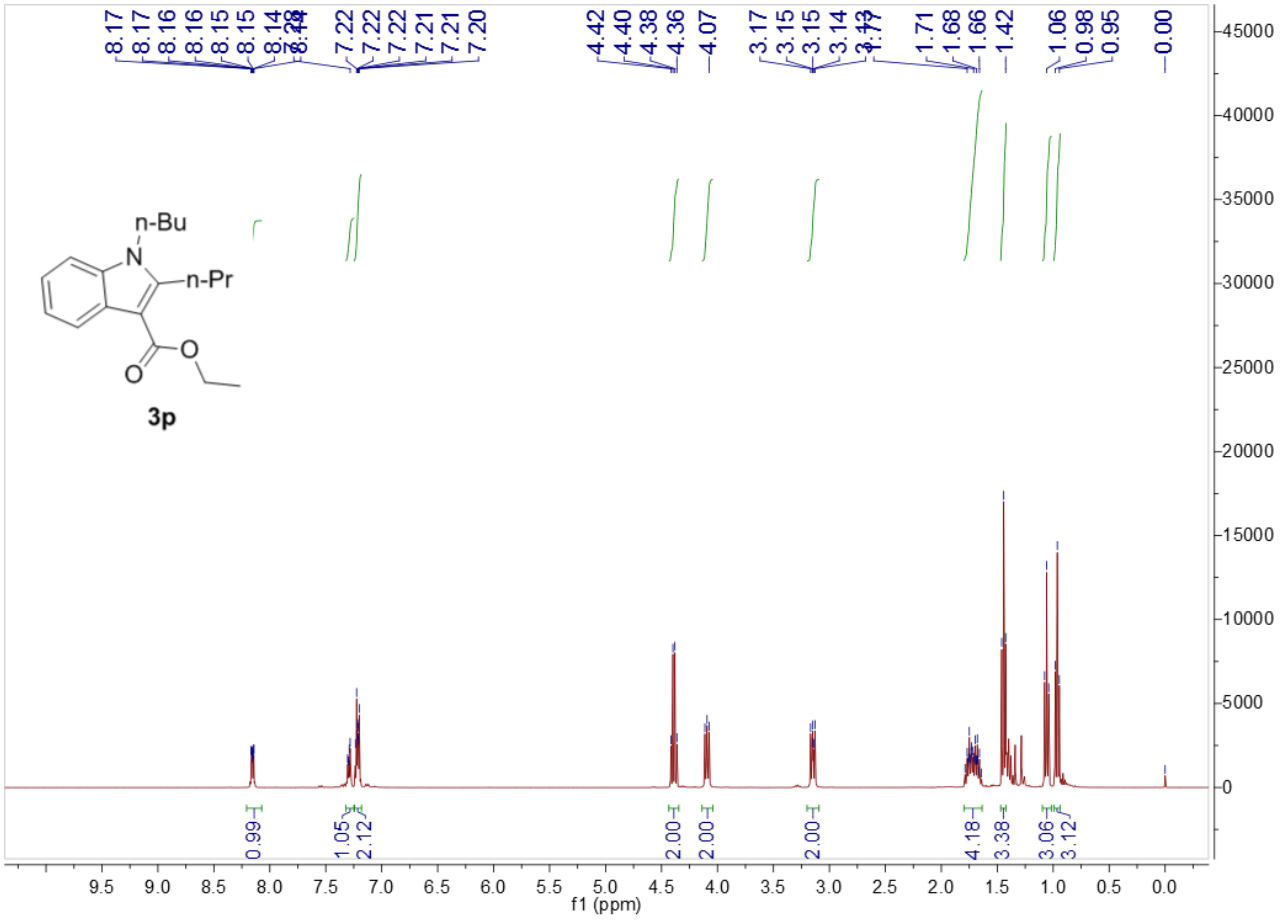

165.82
150.53
148.11
145.41
130.44
130.40
121.53
117.16
107.90
107.71
104.89
77.32
77.00
76.68
59.50
40.32
40.25
15.95
15.93
14.54
11.28
F
N
O
O
3m
130.44
130.40
123.16
121.46
117.20
117.16
107.90
107.71
104.89
f1 (ppm)

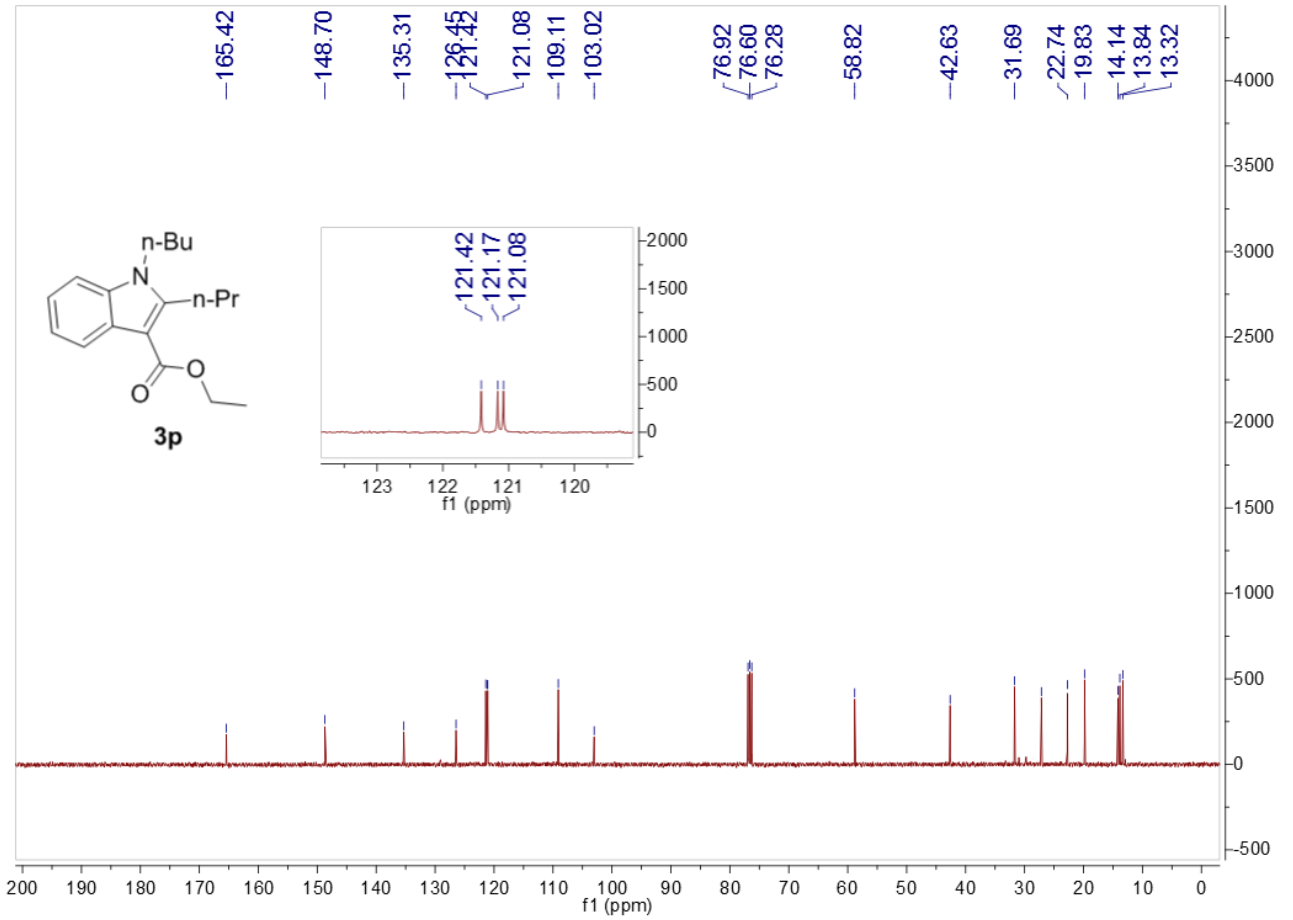

8.00
7.98
7.24
7.14
7.12
7.11
7.08
7.05
7.03
6.97
4.35
4.15
4.13
4.12
4.11
4.10
4.09
4.08
2.74
2.66
2.63
2.48
1.40
1.35
1.34
1.33
1.32
1.30
-0.00
Me
Me
3na+3nb
0.98
6.12
1.99
6.05
6.15
3.02
6.01
5.94
3.00
9.24
9.31
f1 (ppm)

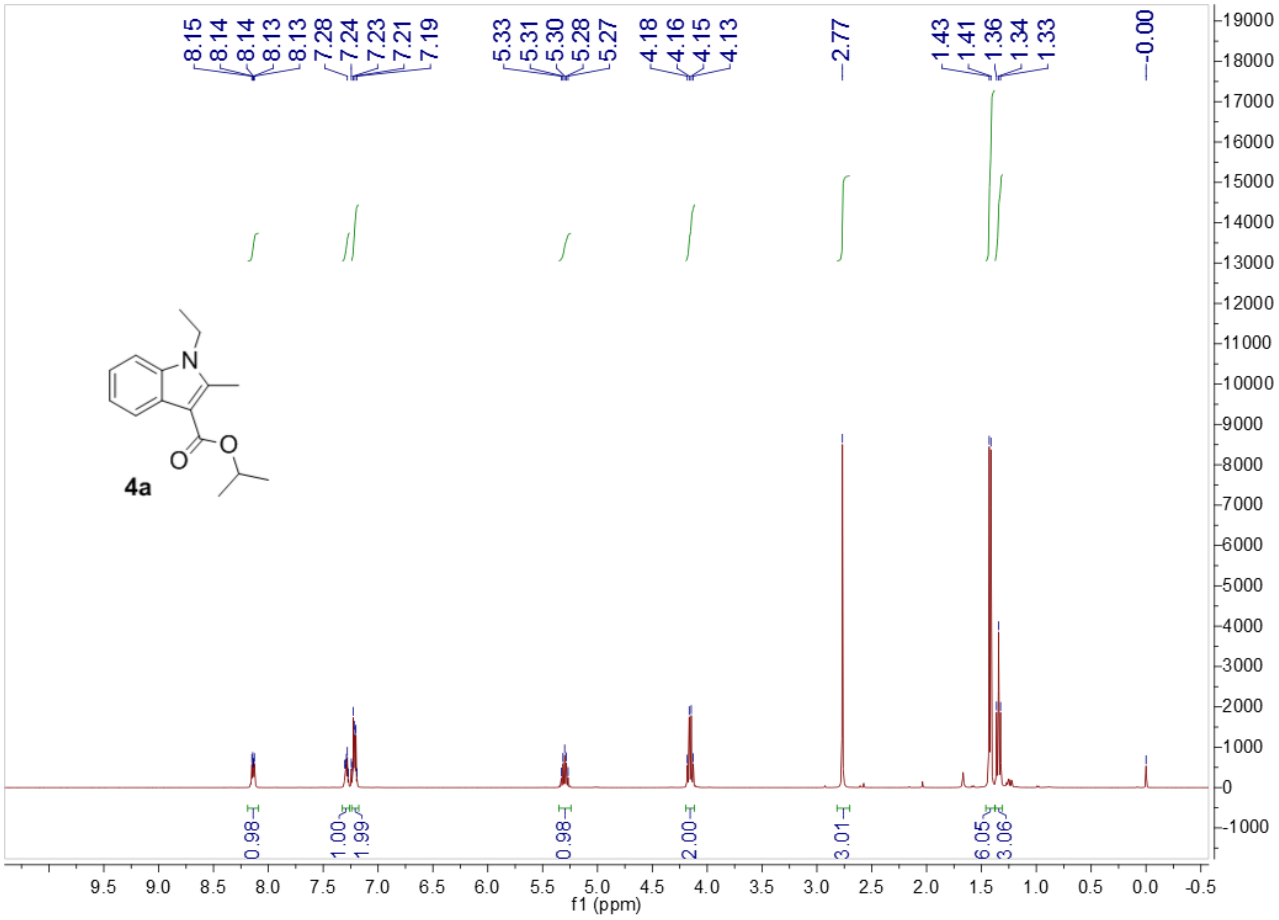

166.54
166.25
143.85
141.74
135.69
131.07
124.54
123.07
121.16
109.08
106.84
106.04
103.79
77.32
77.00
76.68
59.87
59.21
37.92
37.65
22.14
21.71
14.76
14.71
14.59
14.43
11.64
11.48
Me
Me
3na+3nb
143.85
141.74
135.73
135.69
131.63
131.07
124.91
124.54
123.50
123.07
121.91
121.16
f1 (ppm)
f1 (ppm)

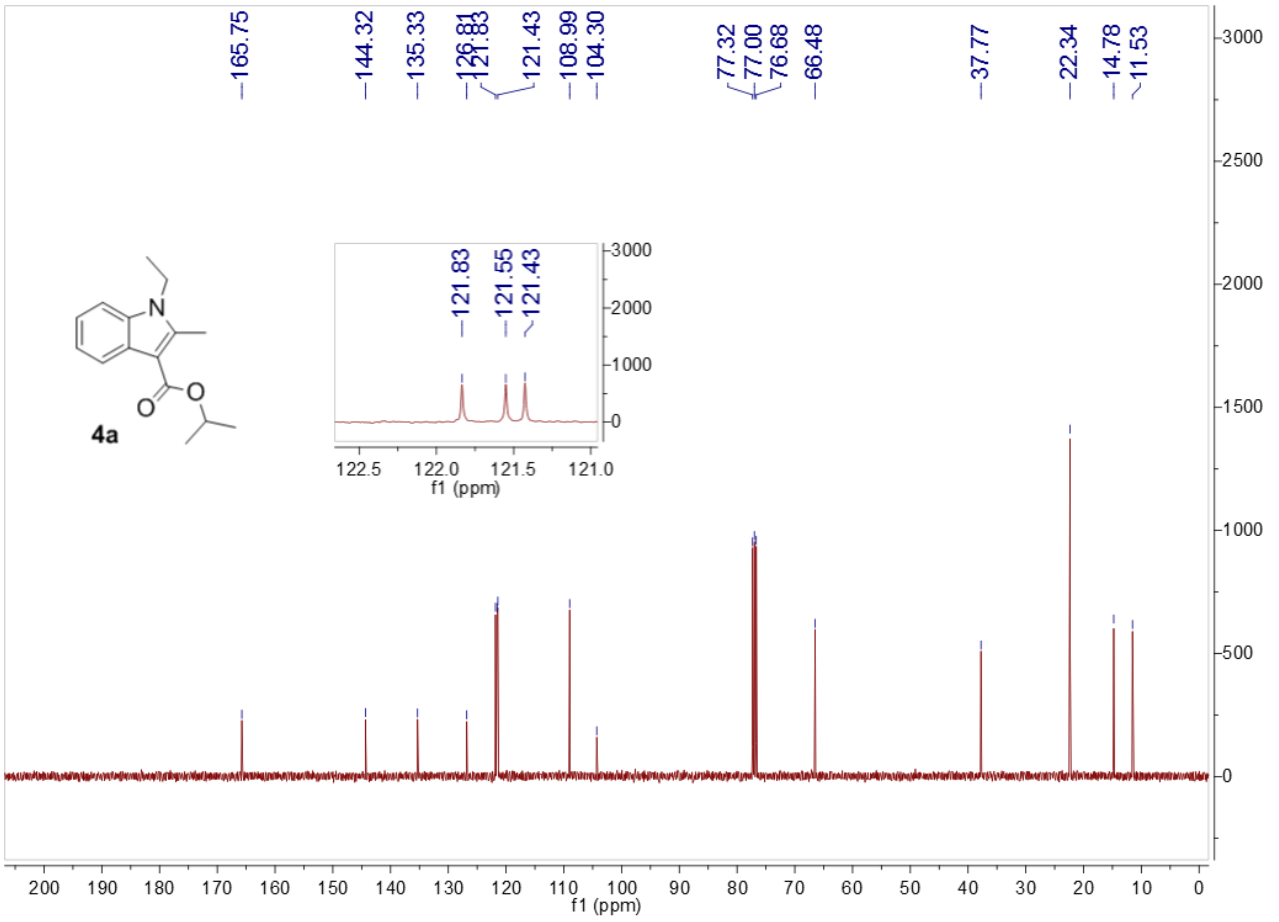

8.16
8.16
8.16
8.15
8.15
8.14
7.22
7.22
7.21
7.21
7.20
7.20
7.20
4.42
4.40
4.39
4.37
4.06
4.04
3.23
3.21
3.19
3.18
1.82
1.80
1.78
1.76
1.28
1.00
0.98
0.96
0.00
n-Pr
N
Et
O
O
3o
0.98
1.00
2.00
2.00
2.00
2.00
2.04
3.00
3.22
3.00
f1 (ppm)

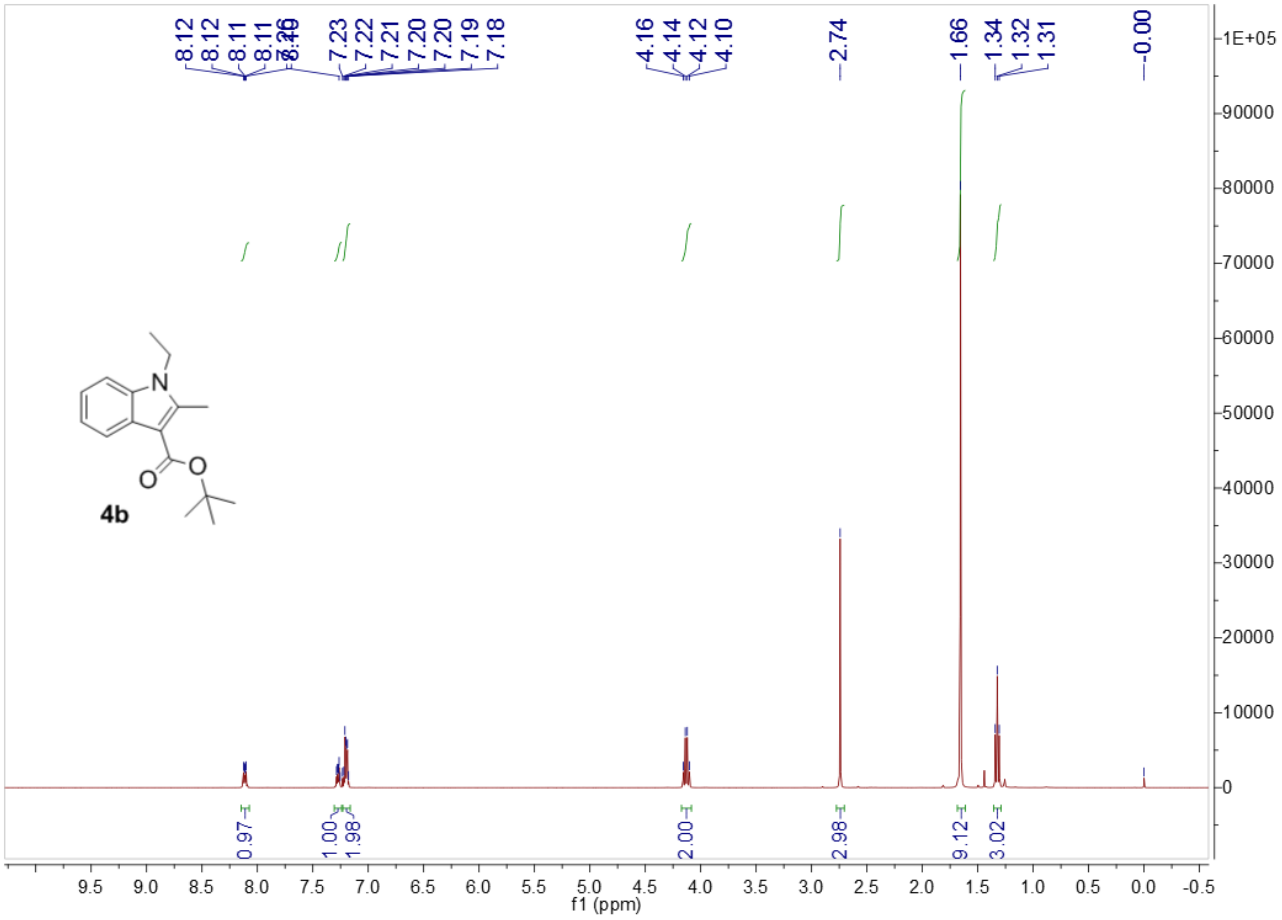

165.36
150.12
135.36
126.41
121.15
121.10
109.14
102.58
76.94
76.62
76.31
58.84
44.25
22.96
18.54
14.15
13.54
10.97
n-Pr
N
Et
O
O
3o
121.44
121.15
121.10
f1 (ppm)
f1 (ppm)

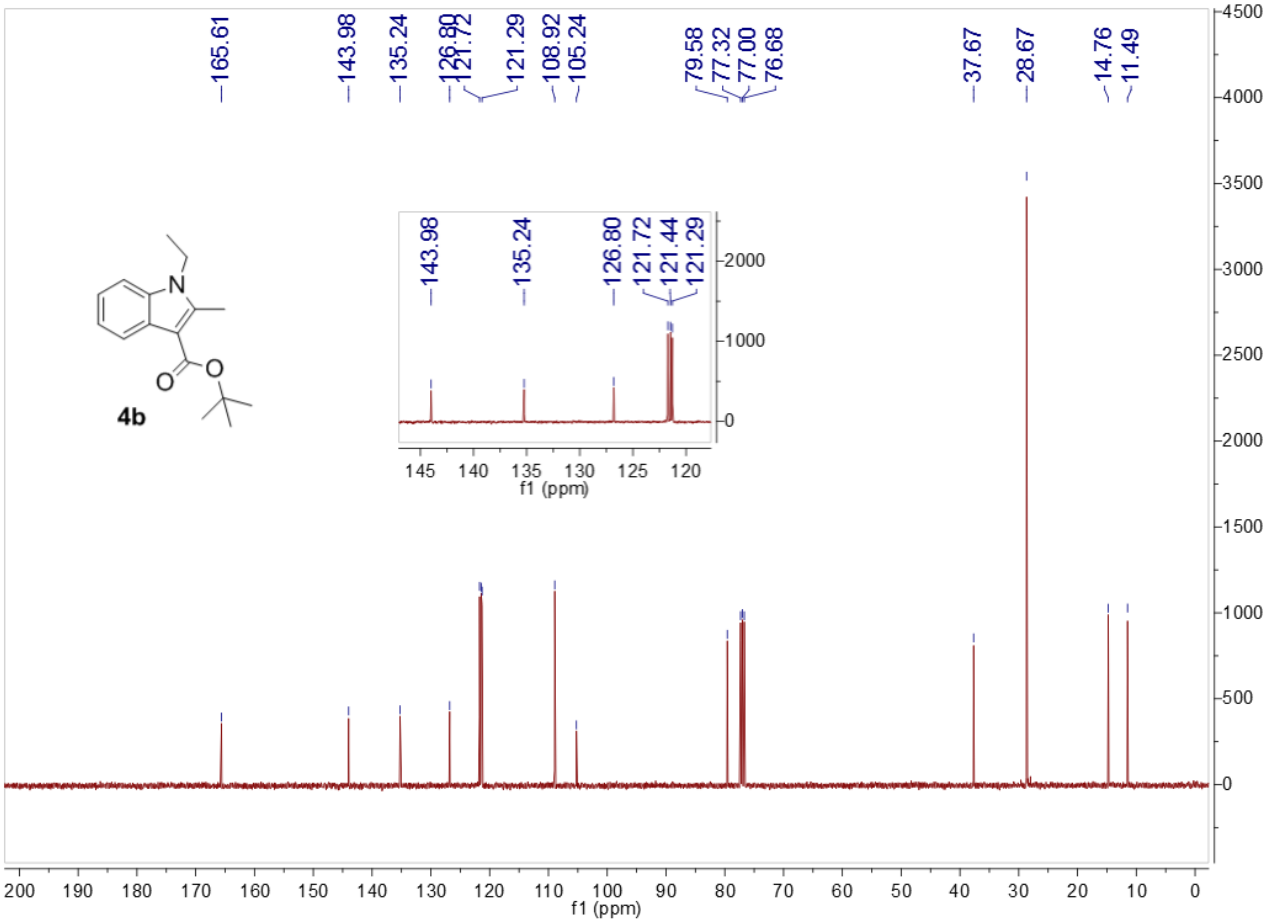

8.17
8.17
8.16
8.16
8.15
8.15
8.14
7.22
7.22
7.22
7.21
7.21
7.20
4.42
4.40
4.38
4.36
4.07
3.17
3.15
3.15
3.14
1.71
1.68
1.66
1.42
1.06
0.98
0.95
0.00
n-Bu
N
n-Pr
O
O
3p
0.99
1.05
2.12
2.00
2.00
2.00
4.18
3.38
3.06
3.12
f1 (ppm)

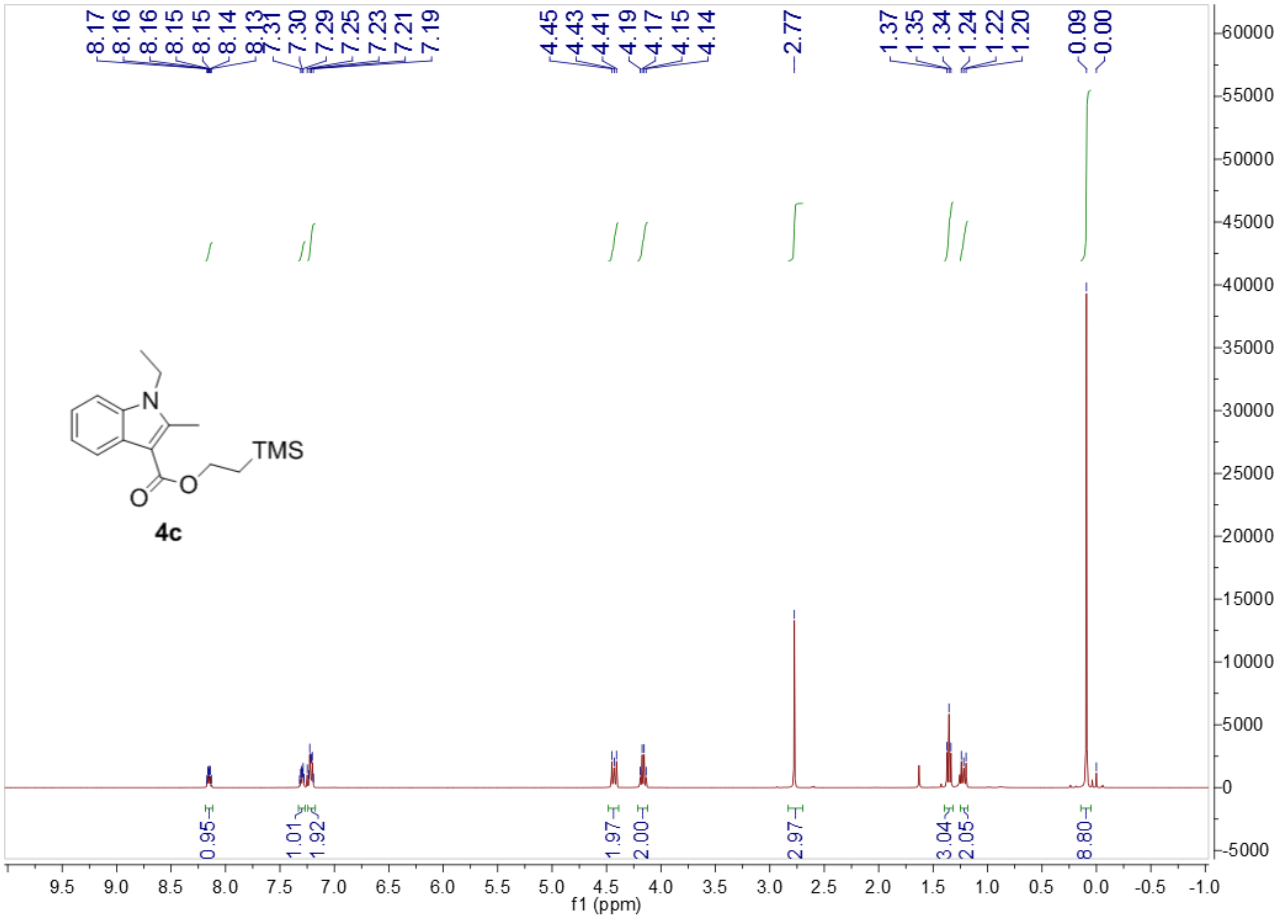

165.42
148.70
135.31
126.45
121.42
121.08
109.11
103.02
76.92
76.60
76.28
58.82
42.63
31.69
22.74
19.83
14.14
13.84
13.32
n-Bu
N
n-Pr
O
O
3p
121.42
121.17
121.08
f1 (ppm)

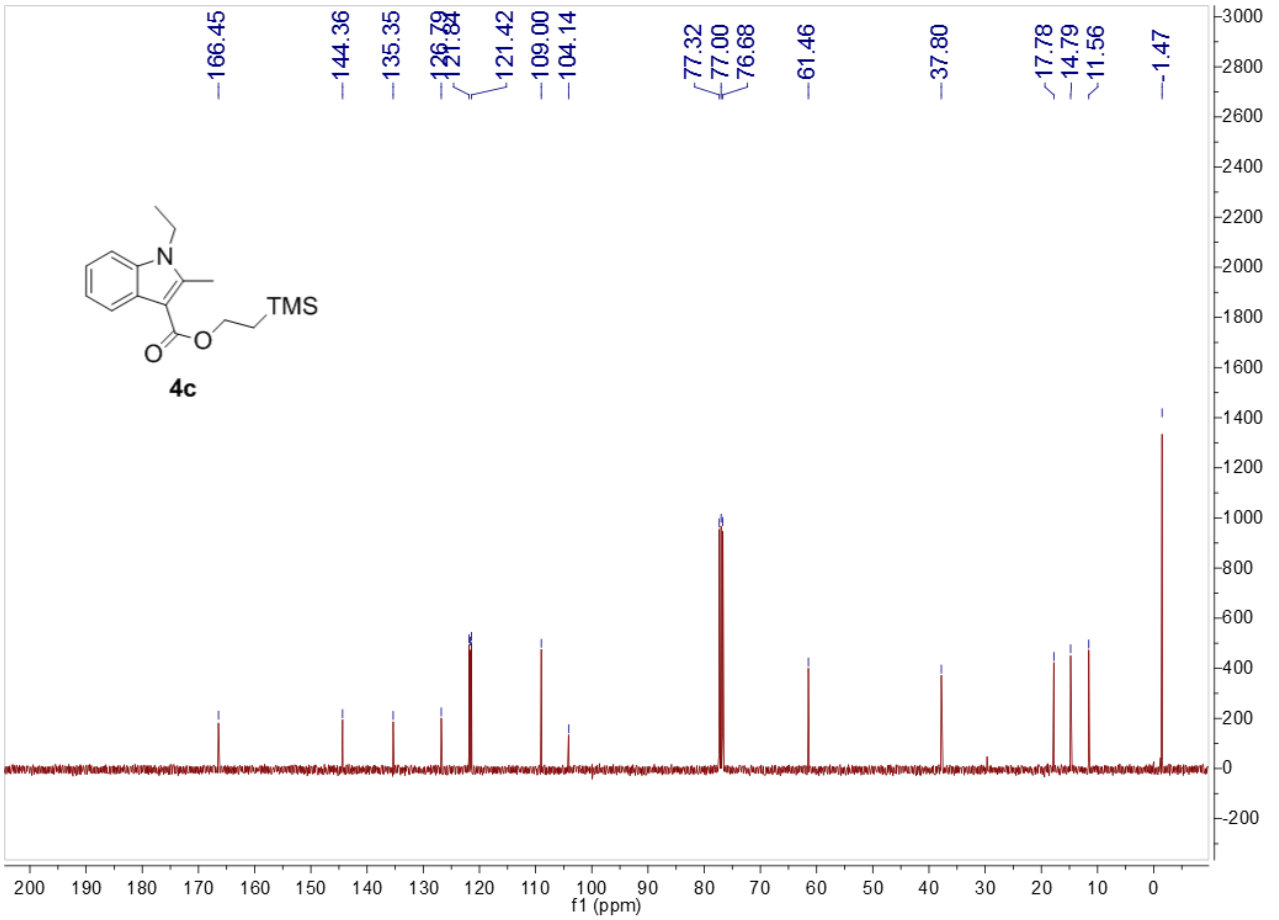

8.15
8.14
8.14
8.13
8.13
7.28
7.24
7.23
7.21
7.19
5.33
5.31
5.30
5.28
5.27
4.18
4.16
4.15
4.13
2.77
1.43
1.41
1.36
1.34
1.33
0.00
0.98
1.00
1.99
0.98
2.00
3.01
6.05
3.06
f1 (ppm)
4a

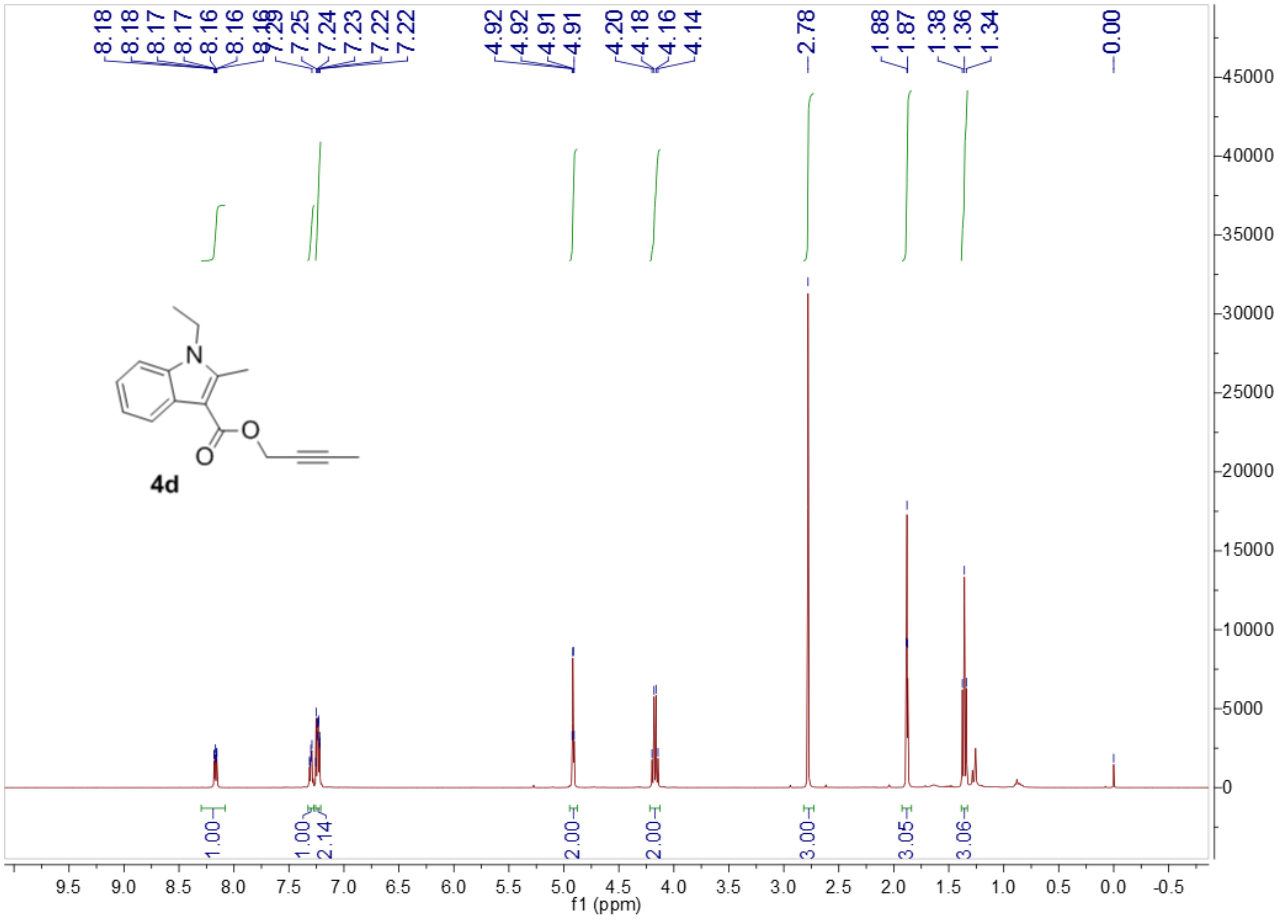

165.75
144.32
135.33
126.81
121.83
121.43
108.99
104.30
77.32
77.00
76.68
66.48
37.77
22.34
14.78
11.53
121.83
121.55
121.43
f1 (ppm)
4a

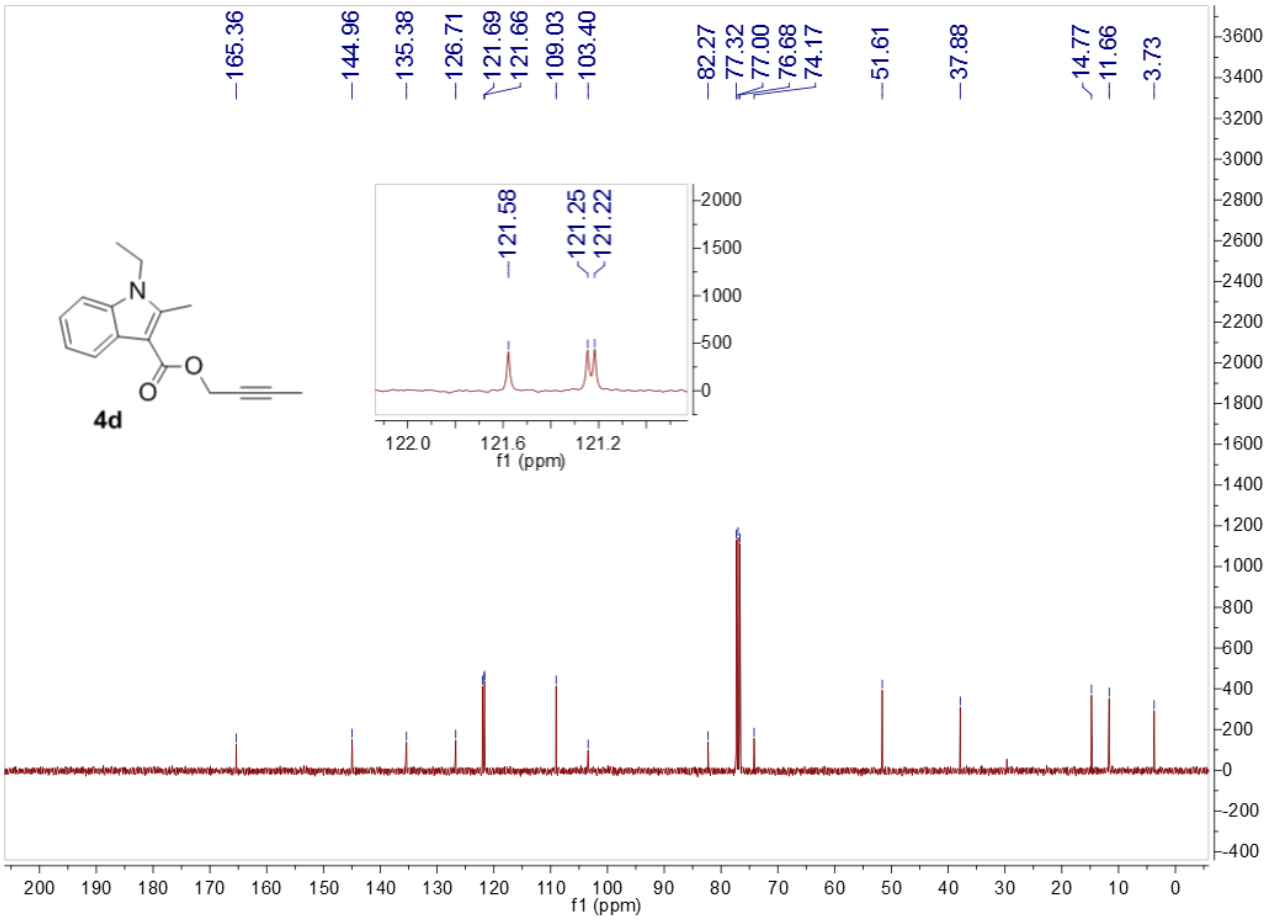

8.12
8.12
8.11
8.11
7.23
7.22
7.21
7.20
7.20
7.19
7.18
4.16
4.14
4.12
4.10
2.74
1.66
1.34
1.32
1.31
0.00
0.97
1.00
1.98
2.00
2.98
9.12
3.02
4b
f1 (ppm)

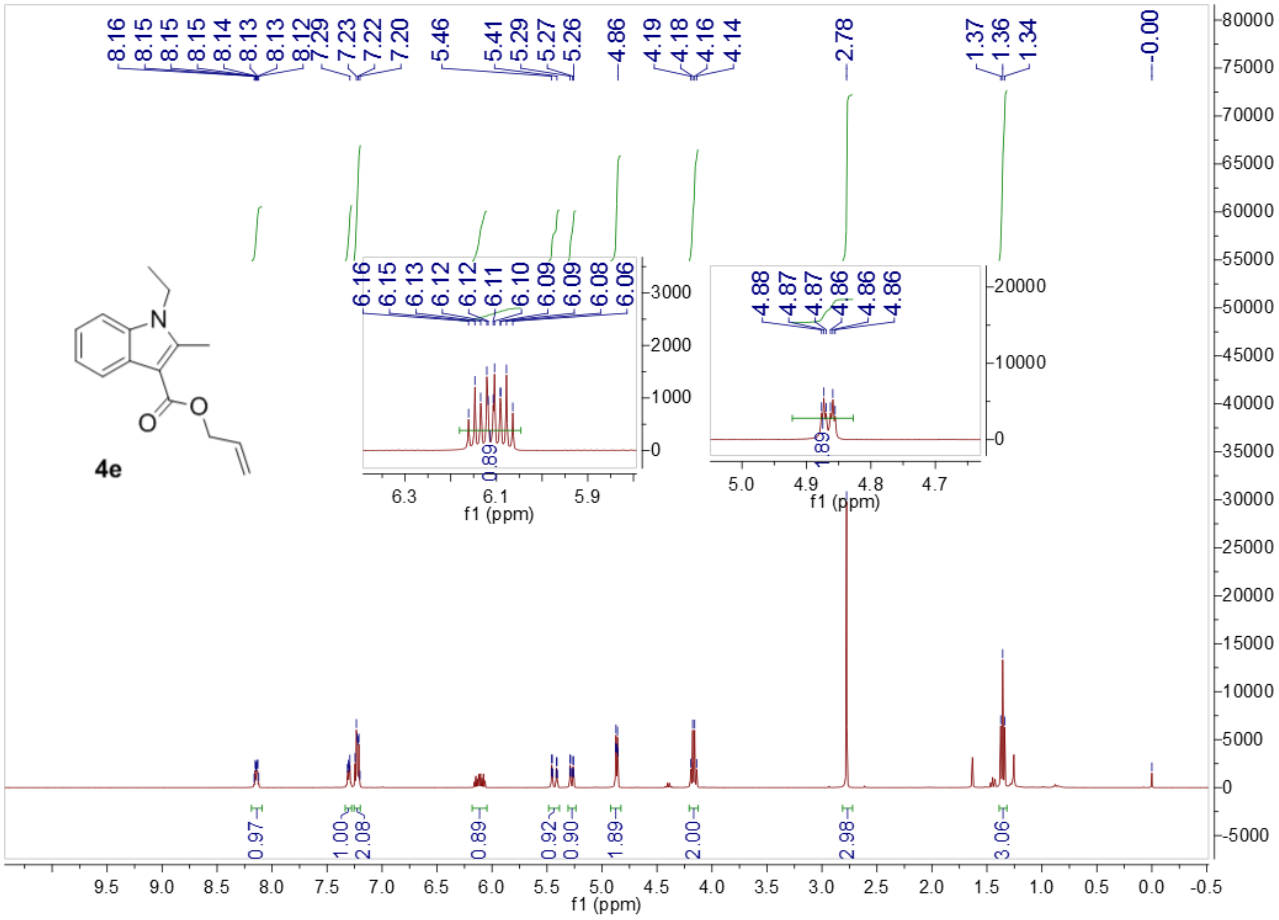

165.61
143.98
135.24
126.80
121.72
121.29
108.92
105.24
79.58
77.32
77.00
76.68
37.67
28.67
14.76
11.49
4b
f1 (ppm)

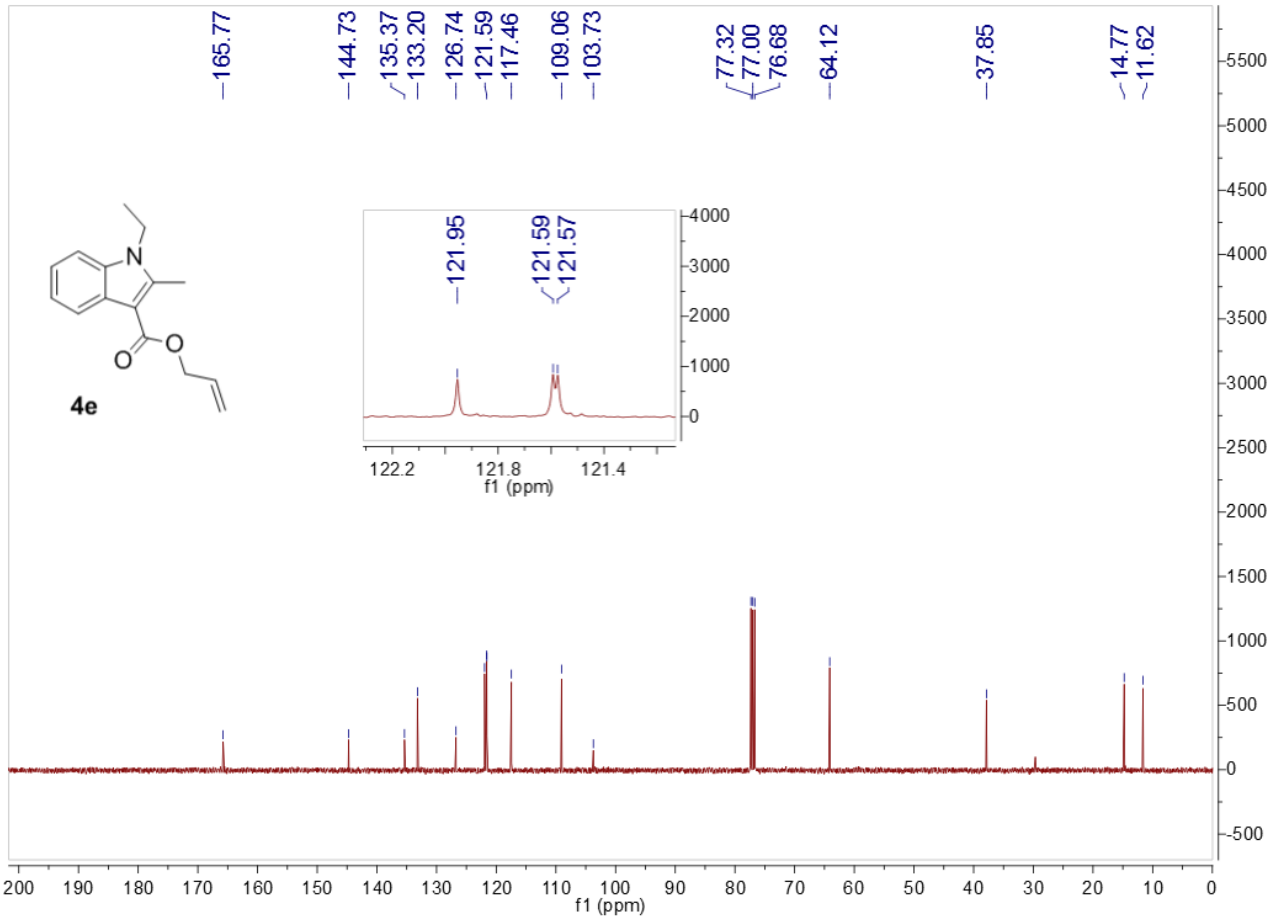

8.17
8.16
8.16
8.15
8.15
8.14
8.13
7.31
7.30
7.29
7.25
7.23
7.21
7.19
4.45
4.43
4.41
4.19
4.17
4.15
4.14
2.77
1.37
1.35
1.34
1.24
1.22
1.20
0.09
0.00
TMS
4c
0.95
1.01
1.92
1.97
2.00
2.97
3.04
2.05
8.80
f1 (ppm)

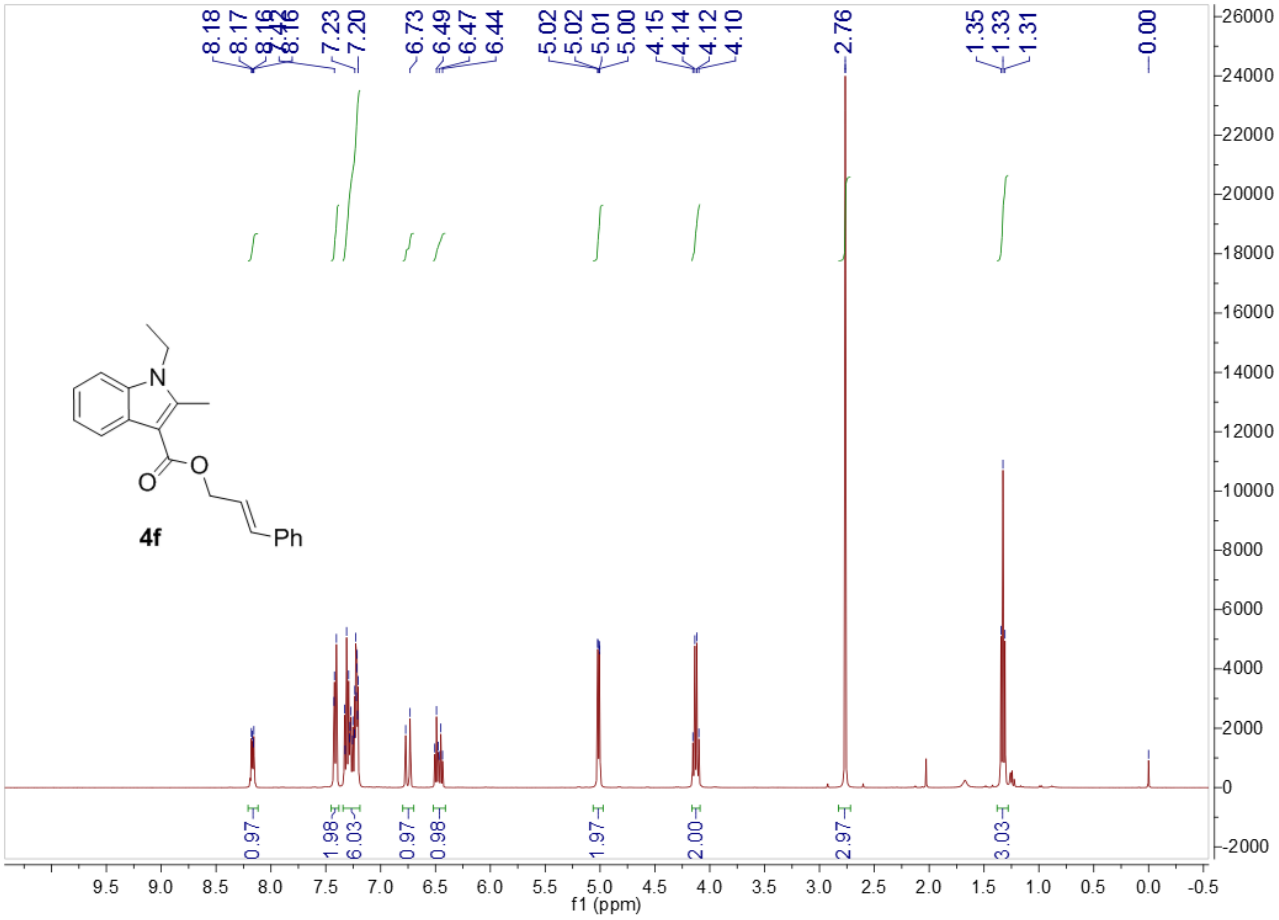

166.45
144.36
135.35
126.79
121.84
121.42
109.00
104.14
77.32
77.00
76.68
61.46
37.80
17.78
14.79
11.56
1.47
TMS
4c
f1 (ppm)

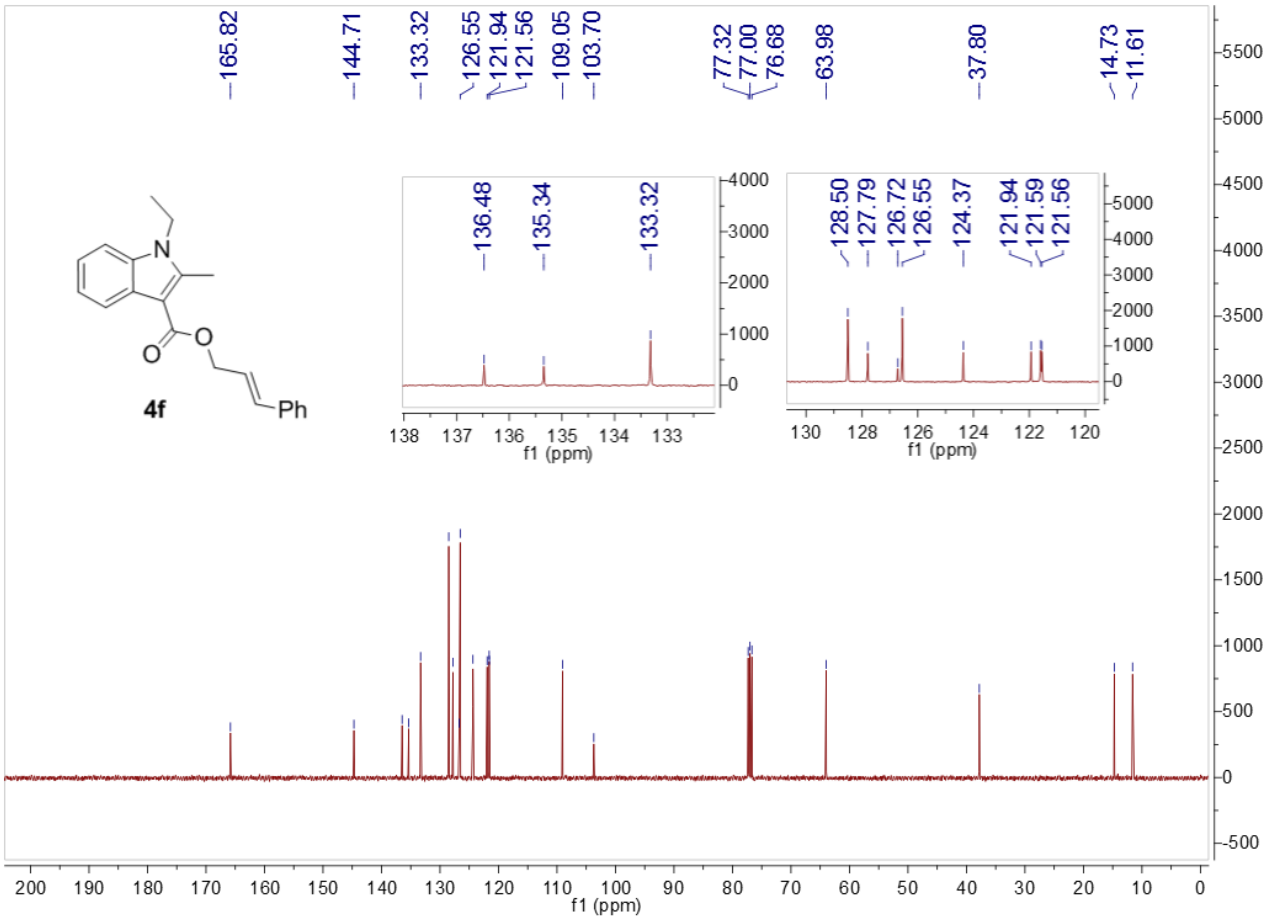

8.18
8.18
8.17
8.17
8.16
8.16
7.25
7.24
7.23
7.22
7.22
4.92
4.92
4.91
4.91
4.20
4.18
4.16
4.14
2.78
1.88
1.87
1.38
1.36
1.34
0.00
4d
1.00
1.00
2.14
2.00
2.00
3.00
3.05
3.06
f1 (ppm)

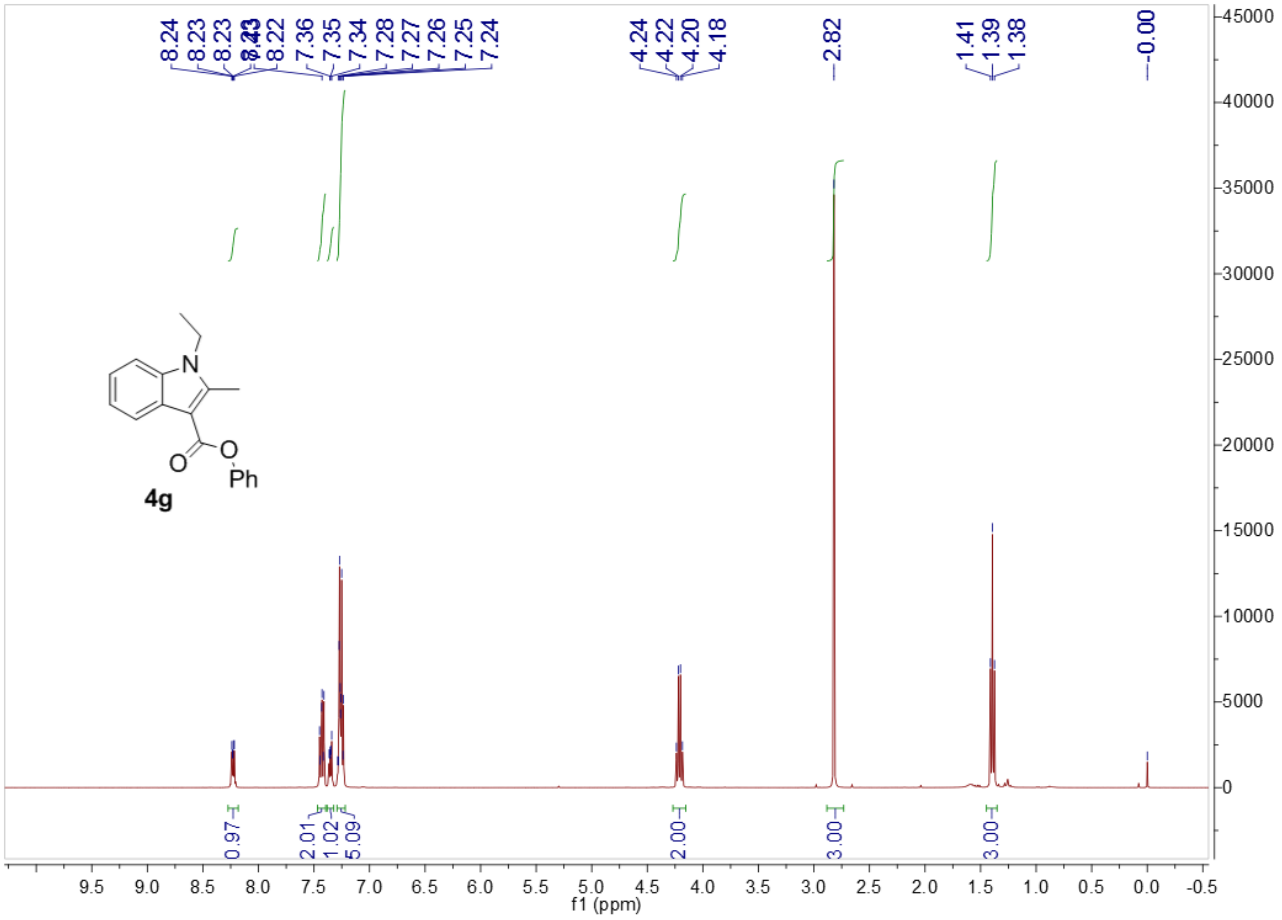

165.36
144.96
135.38
126.71
121.69
121.66
109.03
103.40
82.27
77.32
77.00
76.68
74.17
51.61
37.88
14.77
11.66
3.73
121.58
121.25
121.22
4d
122.0
121.6
121.2
f1 (ppm)
f1 (ppm)

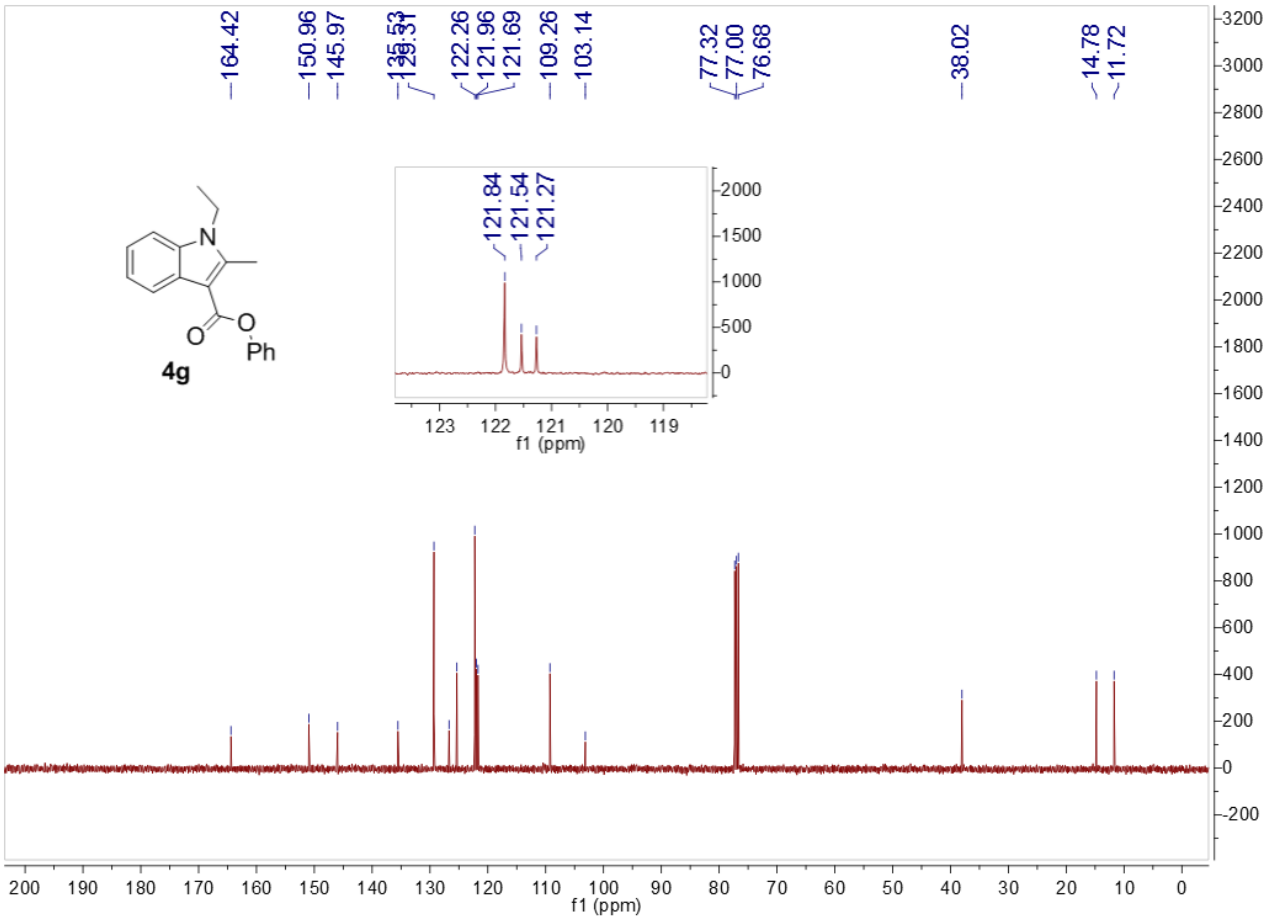

8.16
8.15
8.15
8.15
8.14
8.13
8.13
8.12
7.29
7.23
7.22
7.20
5.46
5.41
5.29
5.27
5.26
4.86
4.19
4.18
4.16
4.14
2.78
1.37
1.36
1.34
0.00
6.16
6.15
6.13
6.12
6.12
6.11
6.10
6.09
6.09
6.08
6.06
4.88
4.87
4.87
4.86
4.86
4.86
4e
f1 (ppm)
f1 (ppm)
0.97
1.00
2.08
0.89
0.92
0.90
1.89
2.00
2.98
3.06
f1 (ppm)

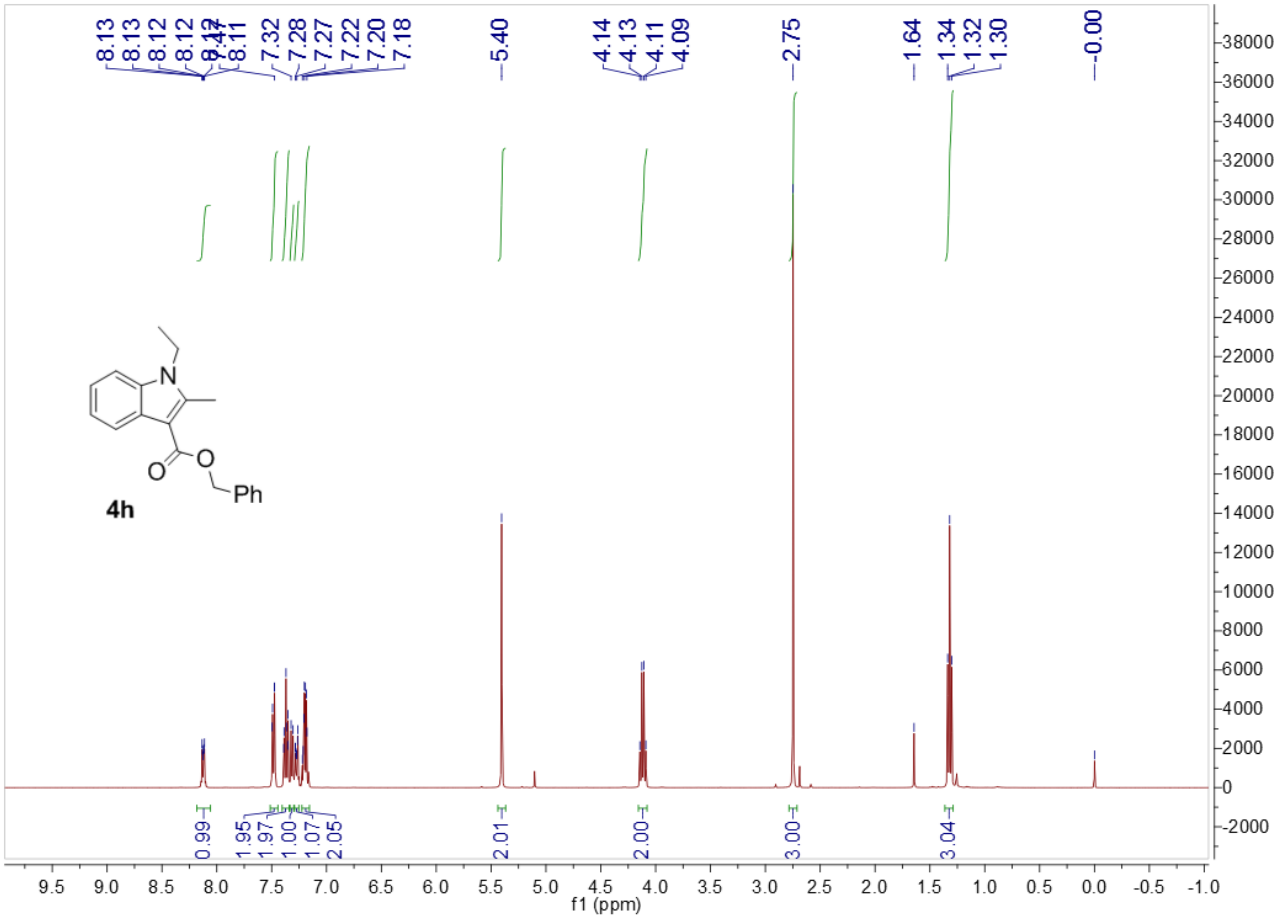

165.77
144.73
135.37
133.20
126.74
121.59
117.46
109.06
103.73
77.32
77.00
76.68
64.12
37.85
14.77
11.62
121.95
121.59
121.57
4e
f1 (ppm)
f1 (ppm)

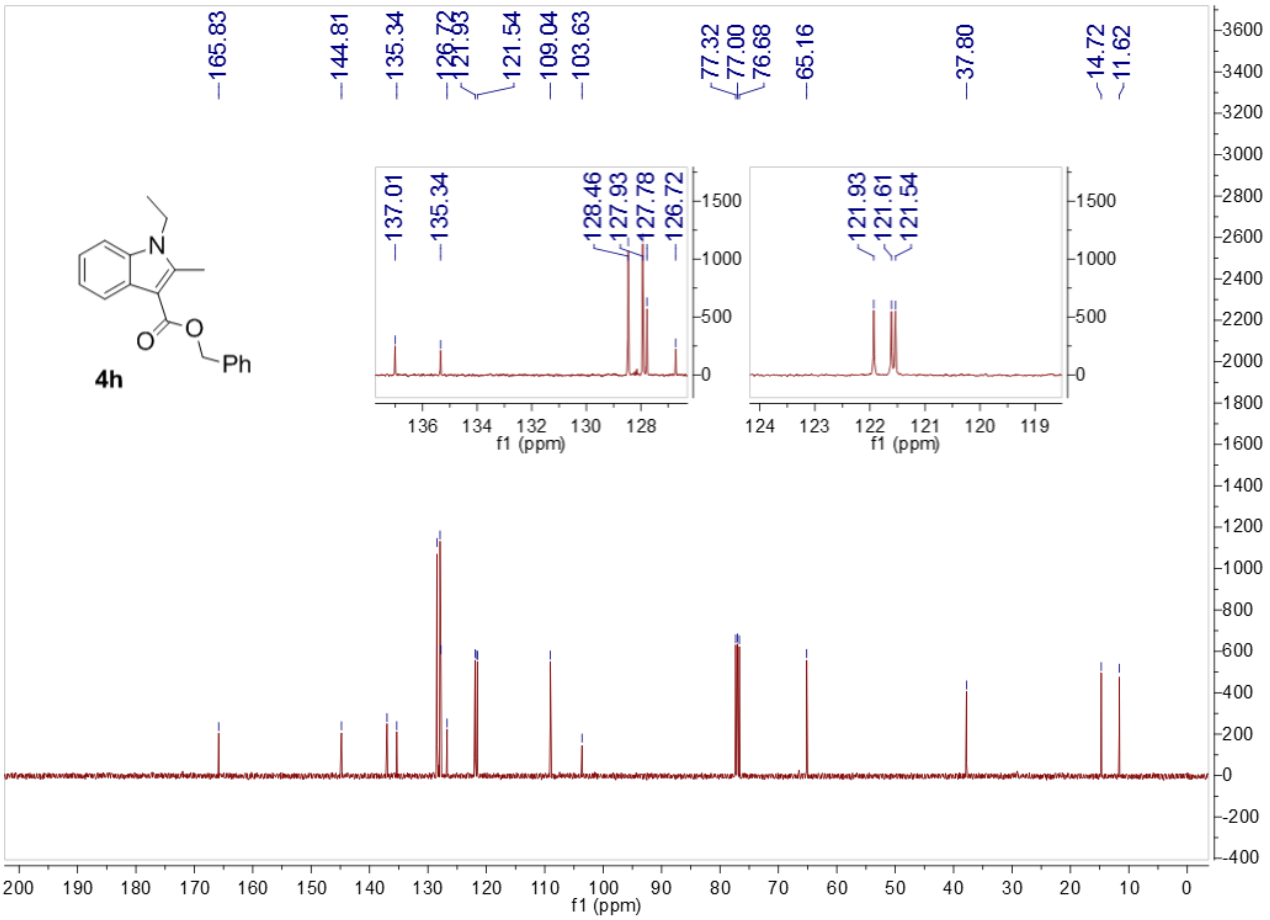

8.18
8.17
8.16
8.16
7.46
7.23
7.20
6.73
6.49
6.47
6.44
5.02
5.02
5.01
5.00
4.15
4.14
4.12
4.10
2.76
1.35
1.33
1.31
0.00
0.97
1.98
6.03
0.97
0.98
1.97
2.00
2.97
3.03
f1 (ppm)
4f
Ph

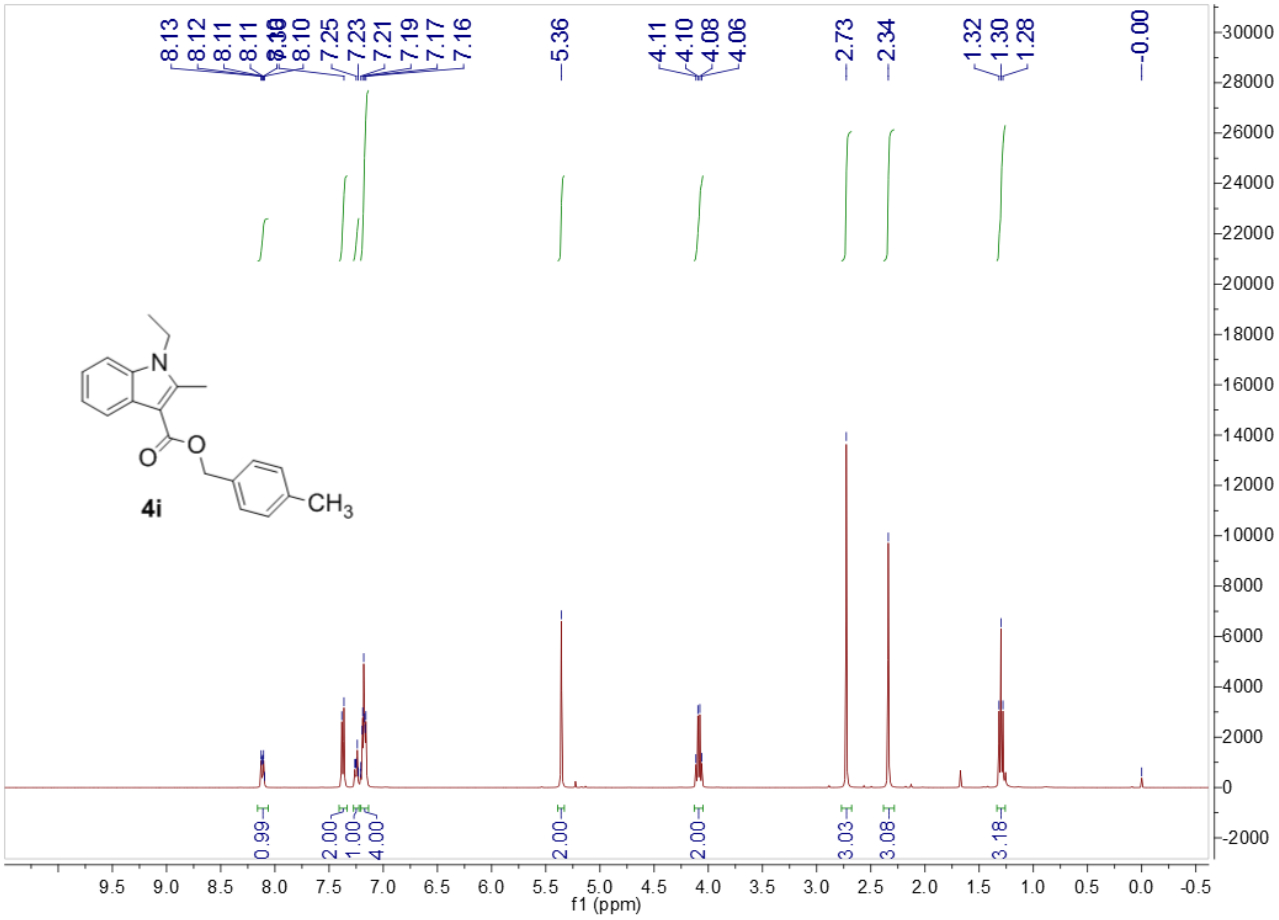

165.82
144.71
133.32
126.55
121.94
121.56
109.05
103.70
77.32
77.00
76.68
63.98
37.80
14.73
11.61
136.48
135.34
133.32
128.50
127.79
126.72
126.55
124.37
121.94
121.59
121.56
f1 (ppm)
4f
Ph

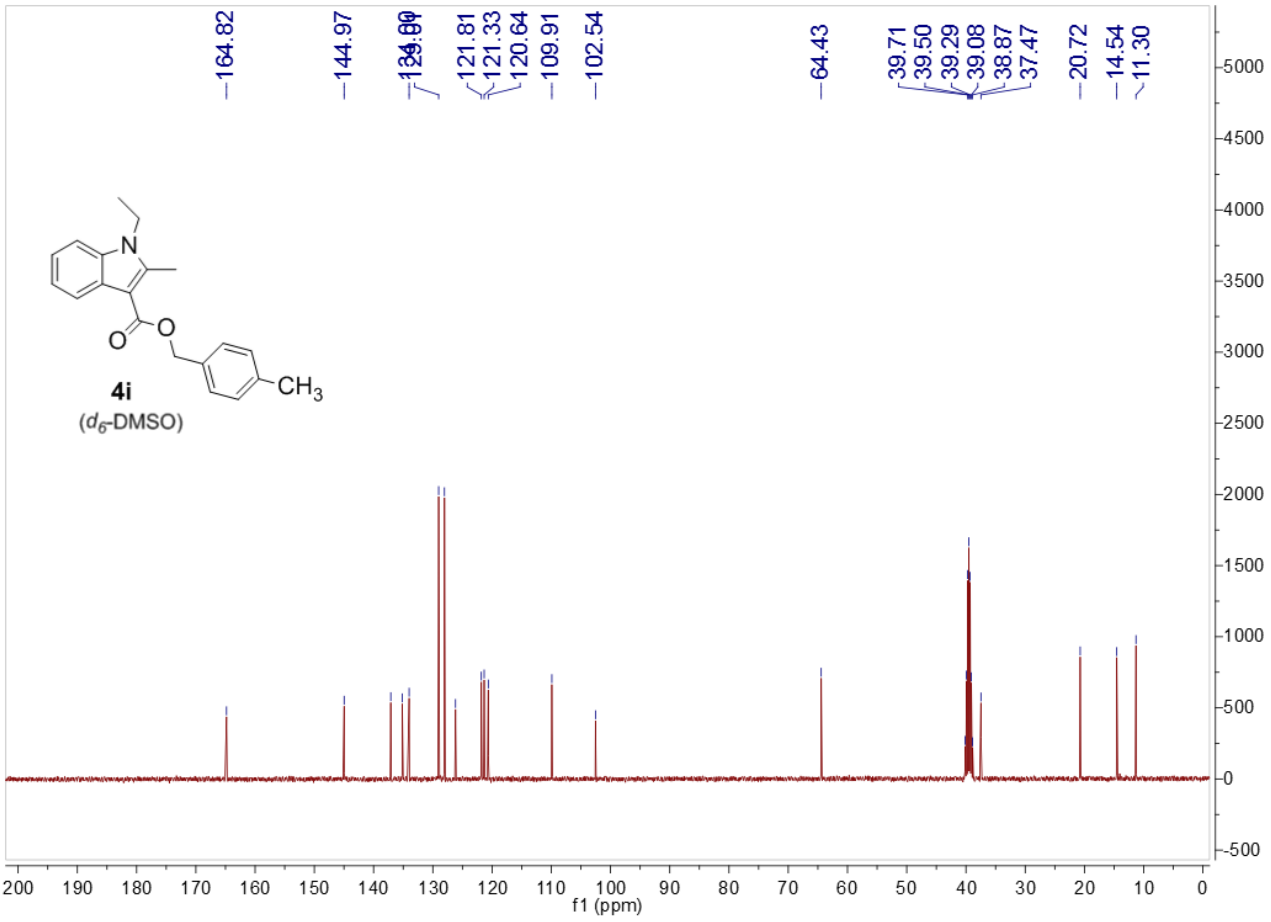

8.24
8.23
8.23
8.22
7.36
7.35
7.34
7.28
7.27
7.26
7.25
7.24
4.24
4.22
4.20
4.18
2.82
1.41
1.39
1.38
0.00
0.97
2.01
1.02
5.09
2.00
3.00
3.00
f1 (ppm)
4g

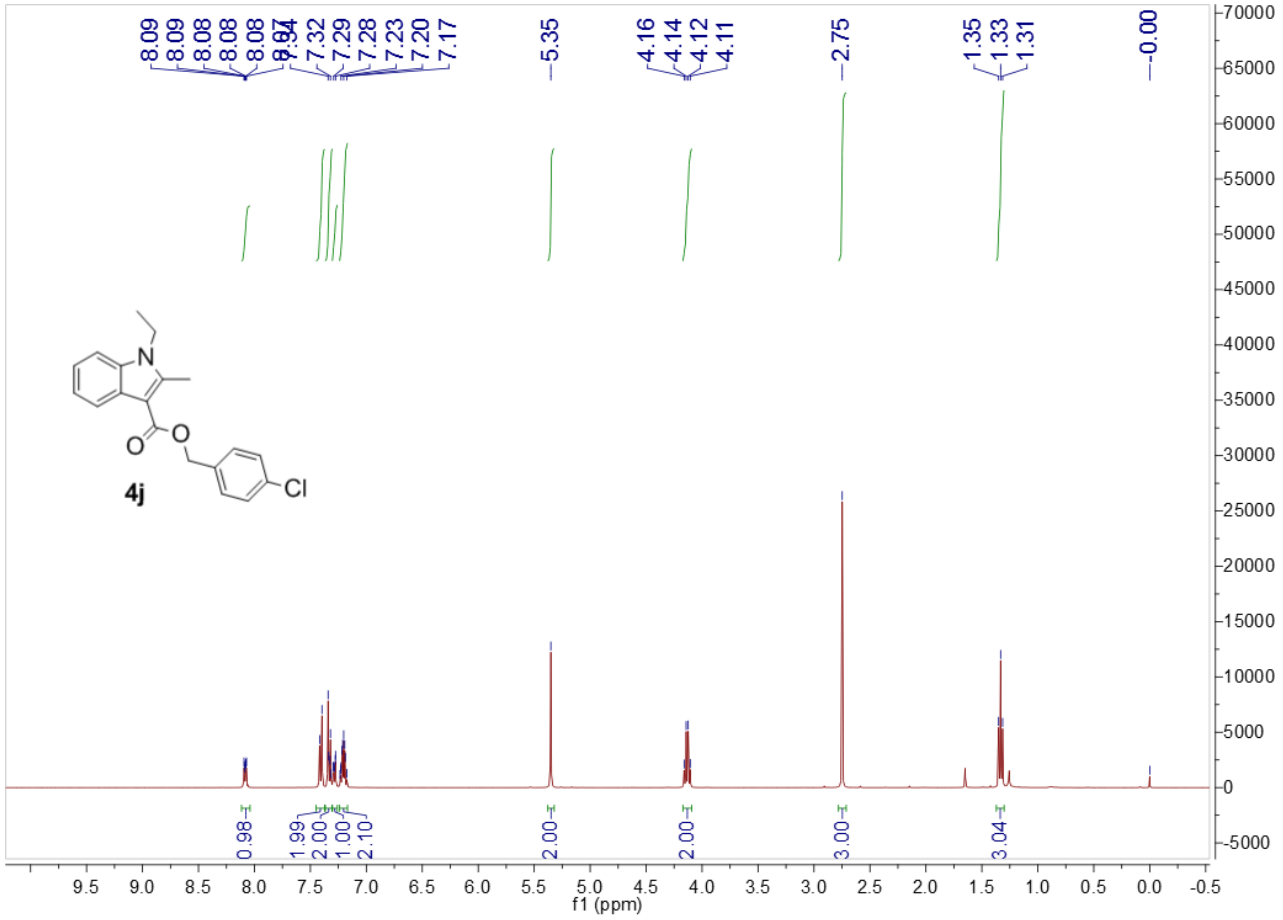

164.42
150.96
145.97
135.53
129.31
122.26
121.96
121.69
109.26
103.14
77.32
77.00
76.68
38.02
14.78
11.72
121.84
121.54
121.27
f1 (ppm)
4g

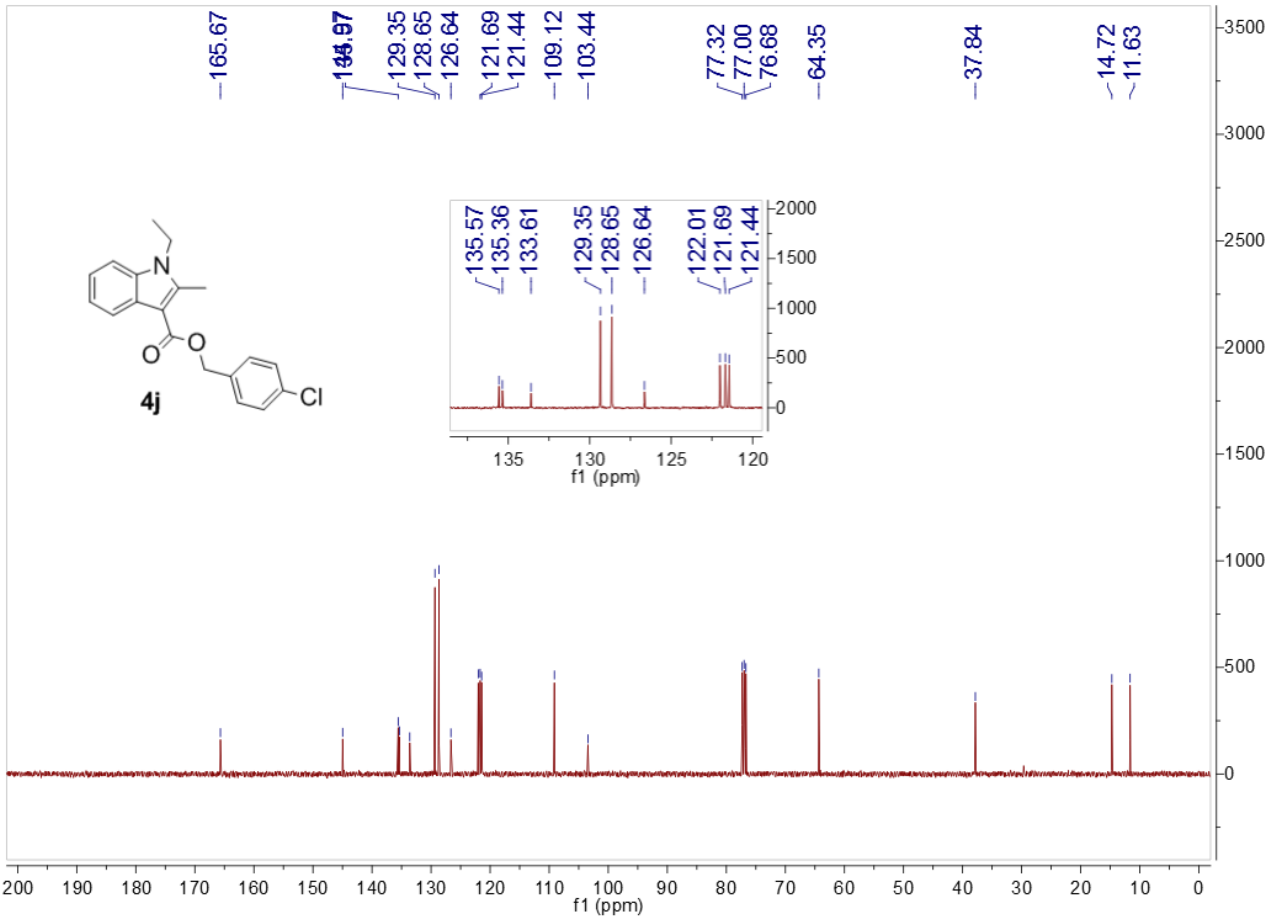

8.13
8.13
8.12
8.12
8.11
7.32
7.28
7.27
7.22
7.20
7.18
5.40
4.14
4.13
4.11
4.09
2.75
1.64
1.34
1.32
1.30
0.00
0.99
1.95
1.97
1.00
1.07
2.05
2.01
2.00
3.00
3.04
f1 (ppm)
4h

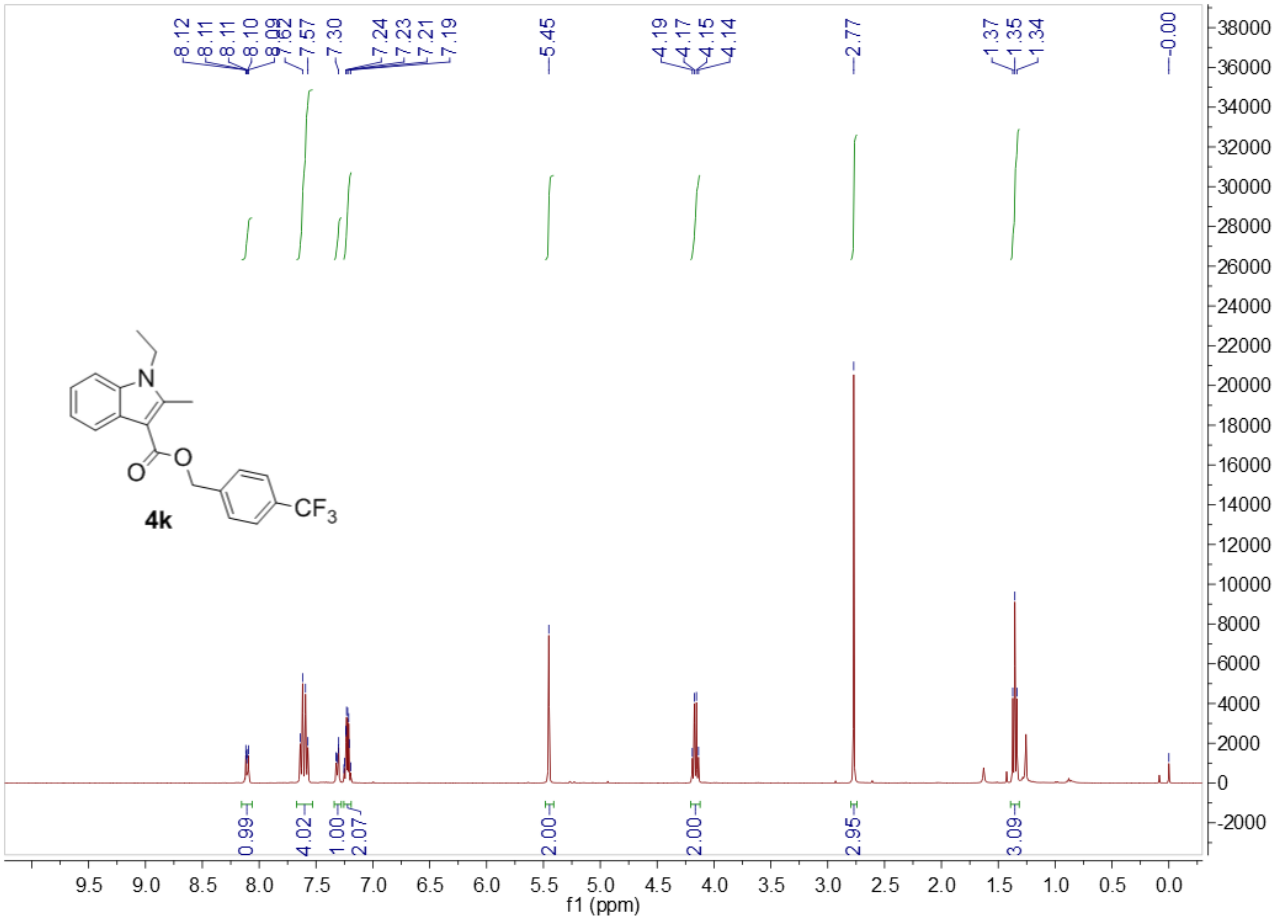

165.83
144.81
135.34
126.72
121.93
121.54
109.04
103.63
77.32
77.00
76.68
65.16
37.80
14.72
11.62
137.01
135.34
128.46
127.93
127.78
126.72
121.93
121.61
121.54
f1 (ppm)
f1 (ppm)
f1 (ppm)
4h

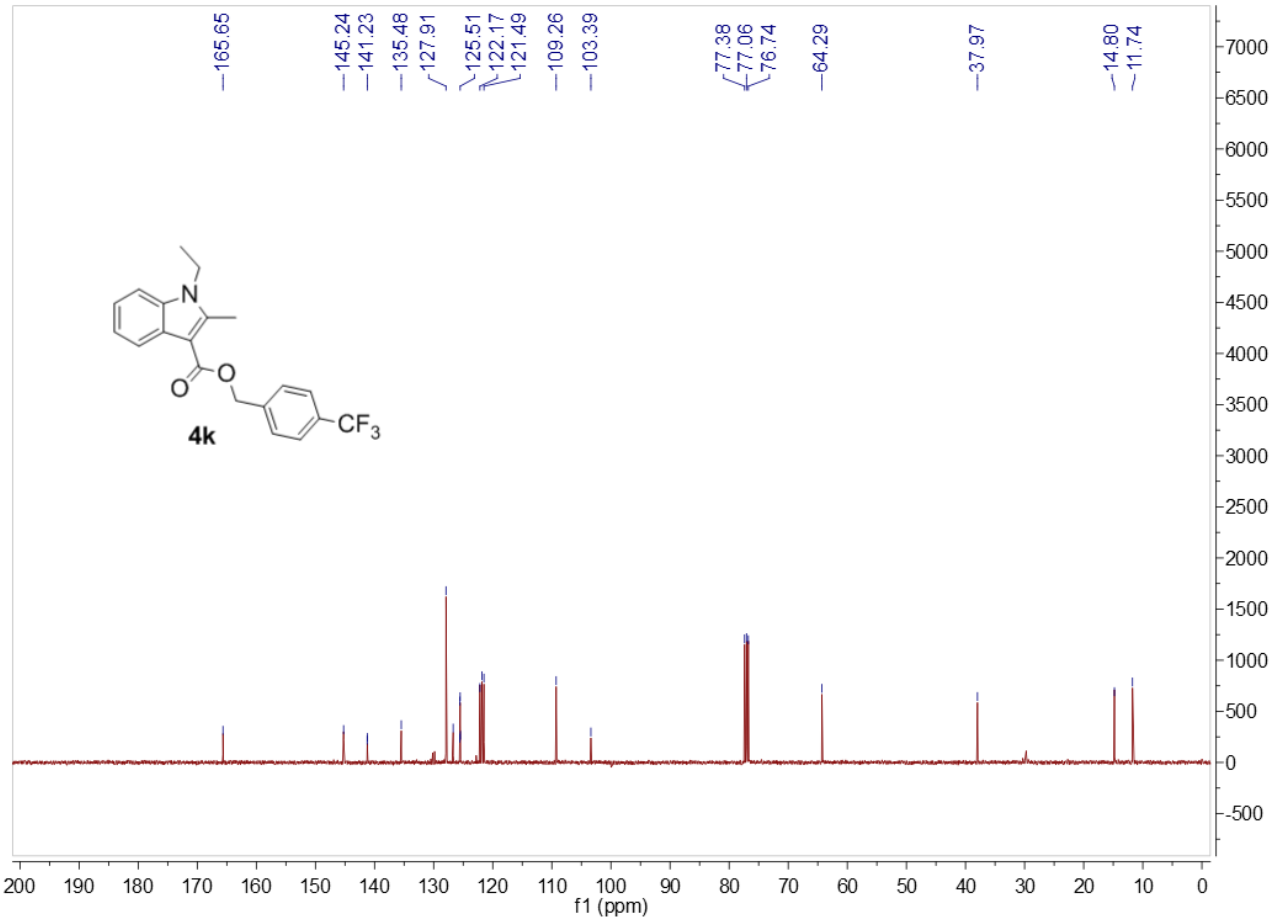

8.13
8.12
8.11
8.11
8.10
7.25
7.23
7.21
7.19
7.17
7.16
5.36
4.11
4.10
4.08
4.06
2.73
2.34
1.32
1.30
1.28
-0.00
0.99
2.00
1.00
4.00
2.00
2.00
3.03
3.08
3.18
f1 (ppm)
4i

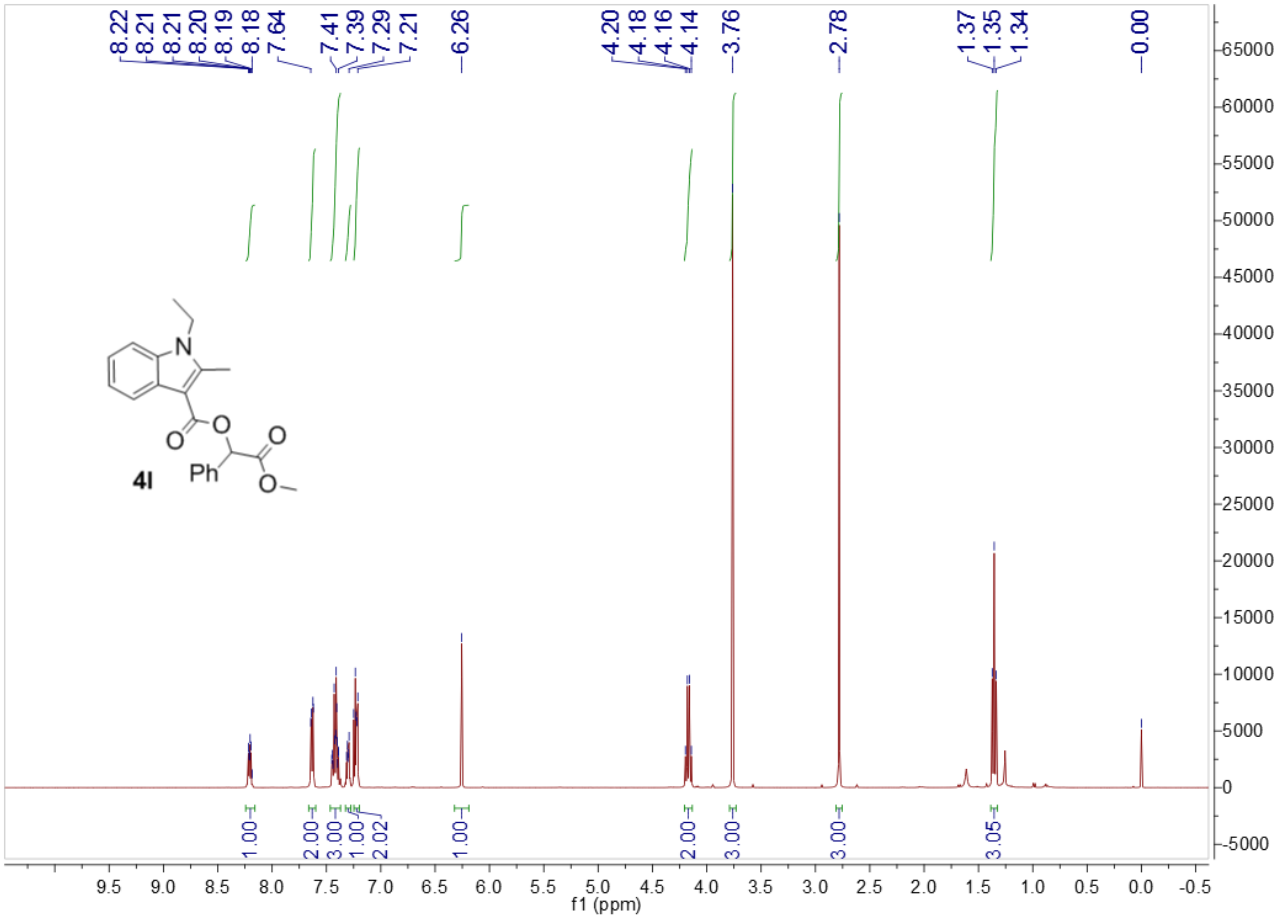

164.82
144.97
121.81
121.33
120.64
109.91
102.54
64.43
39.71
39.50
39.29
39.08
38.87
37.47
20.72
14.54
11.30
f1 (ppm)
4i
(d_6-DMSO)

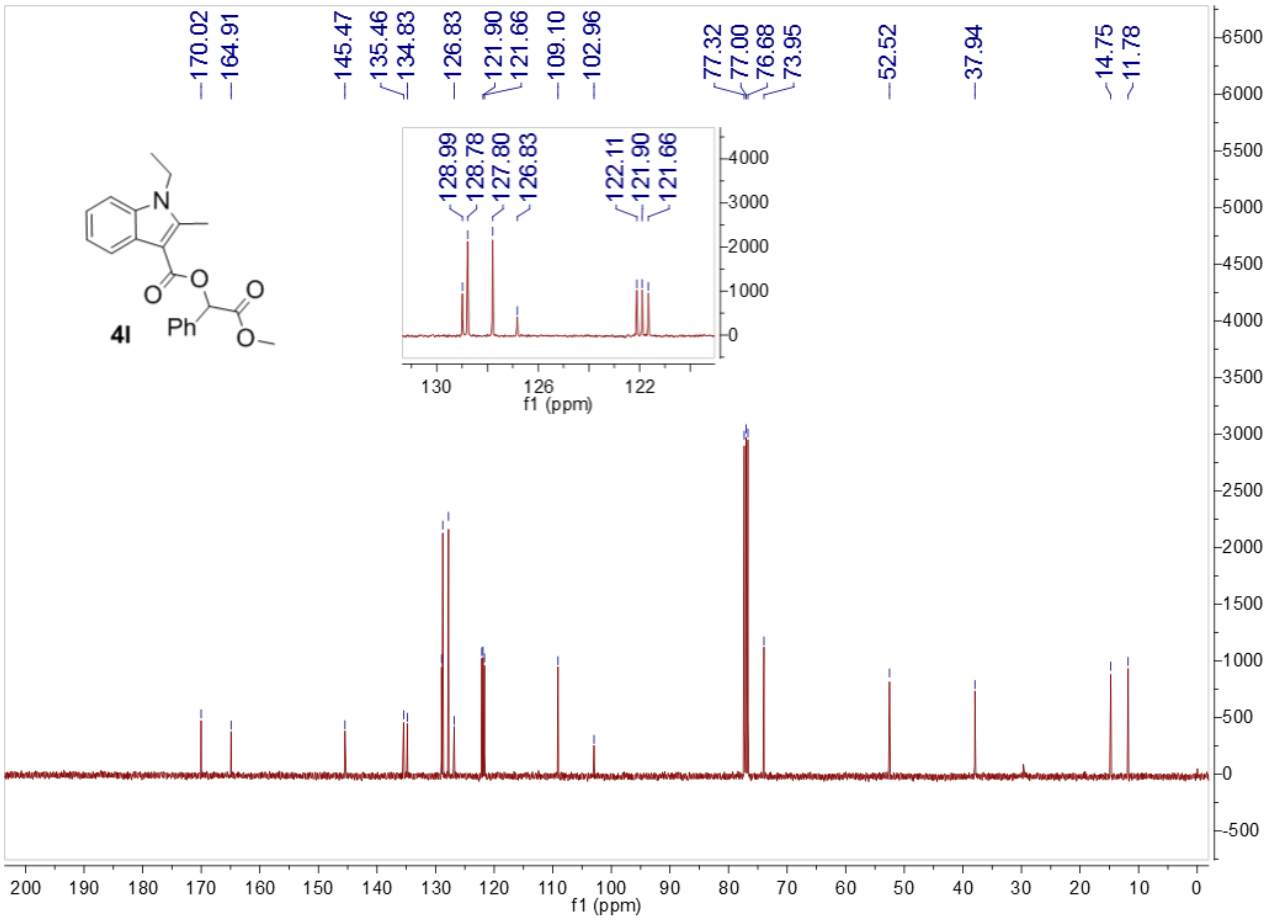

8.09
8.09
8.08
8.08
8.08
7.32
7.29
7.28
7.23
7.20
7.17
5.35
4.16
4.14
4.12
4.11
2.75
1.35
1.33
1.31
0.00
4j
Cl
0.98
1.99
2.00
1.00
2.10
2.00
2.00
3.00
3.04
f1 (ppm)

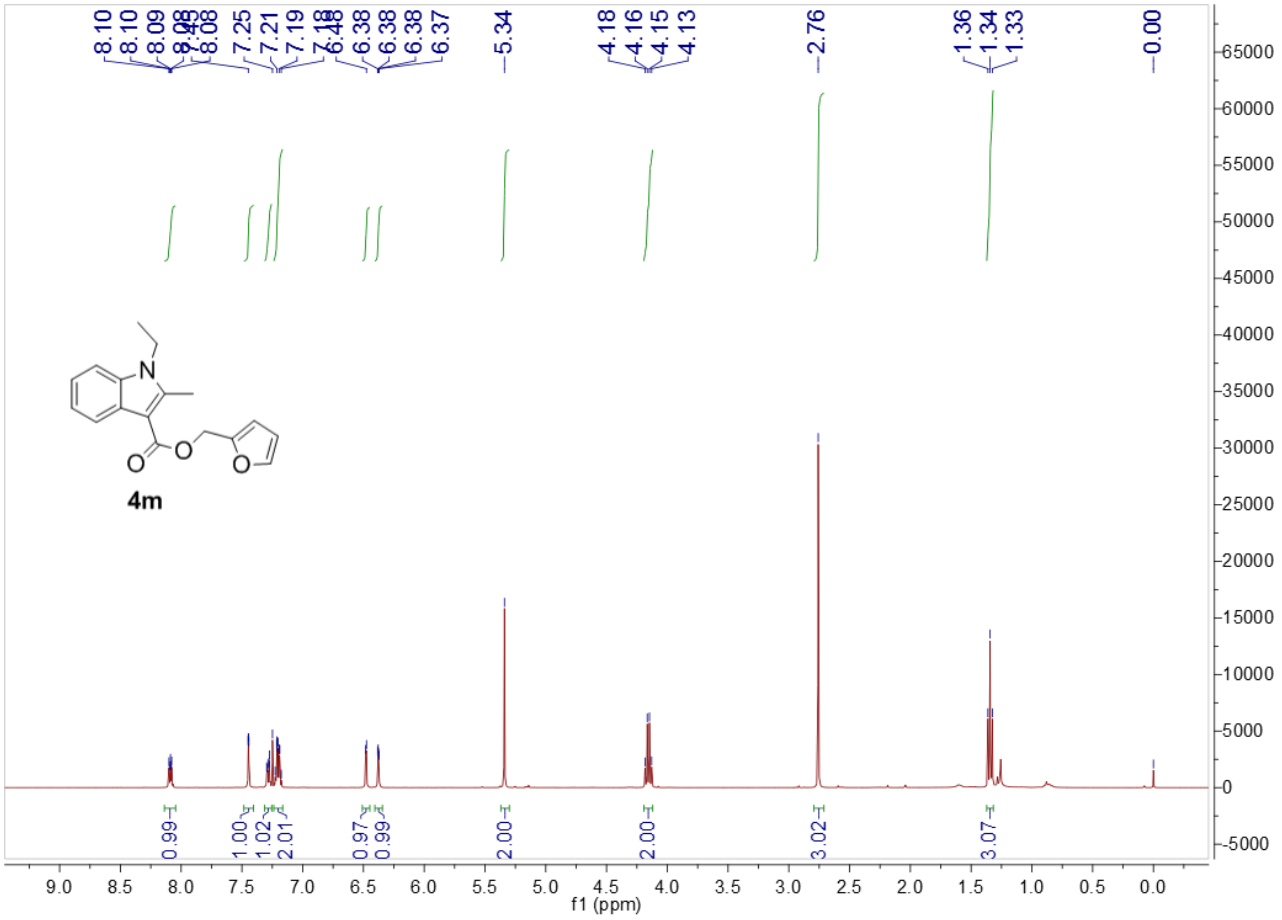

165.67
129.35
128.65
126.64
121.69
121.44
109.12
103.44
77.32
77.00
76.68
64.35
37.84
14.72
11.63
135.57
135.36
133.61
129.35
128.65
126.64
122.01
121.69
121.44
4j
Cl
f1 (ppm)

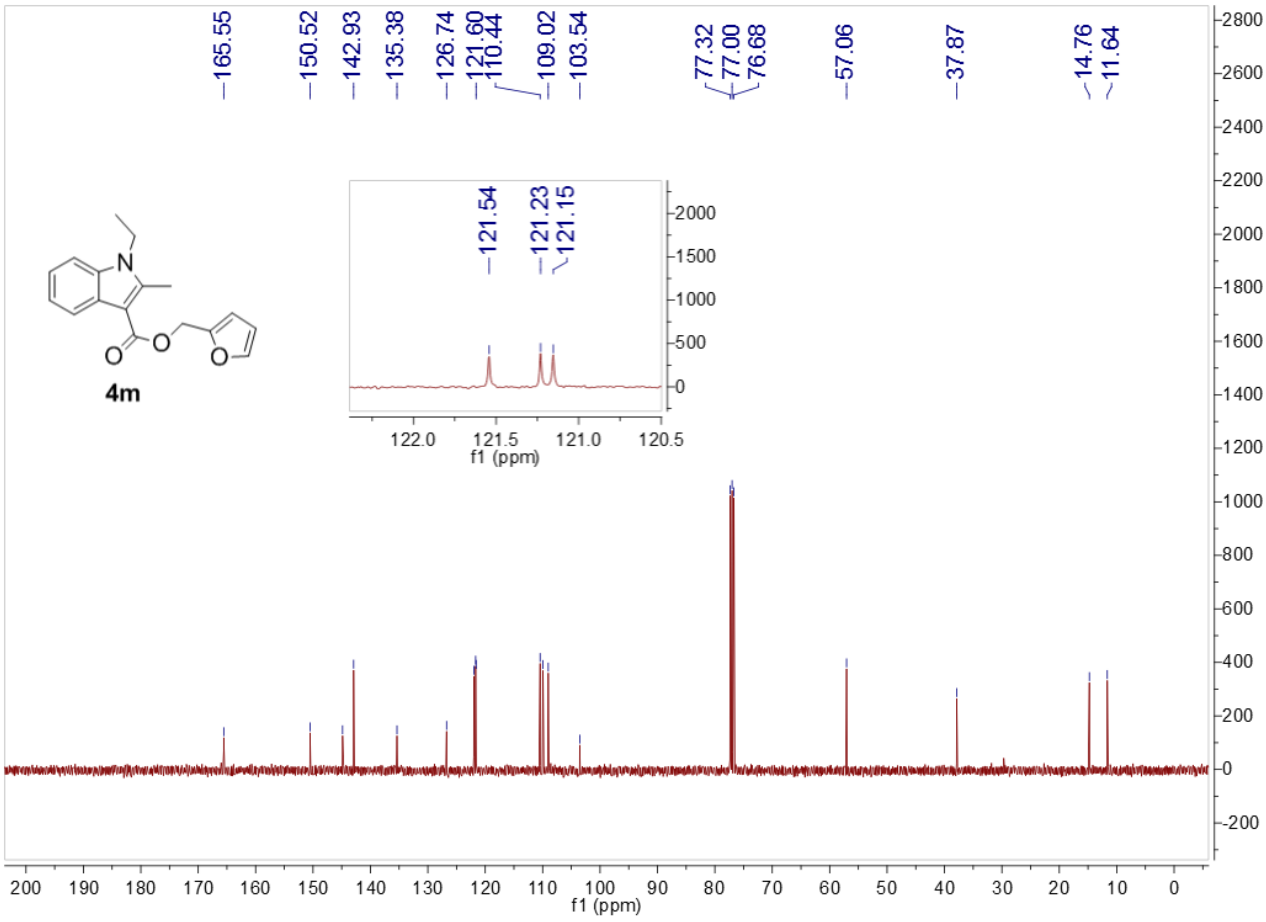

8.12
8.11
8.11
8.10
7.57
7.30
7.24
7.23
7.21
7.19
5.45
4.19
4.17
4.15
4.14
2.77
1.37
1.35
1.34
0.00
0.99
4.02
1.00
2.07
2.00
2.00
2.95
3.09
f1 (ppm)
4k

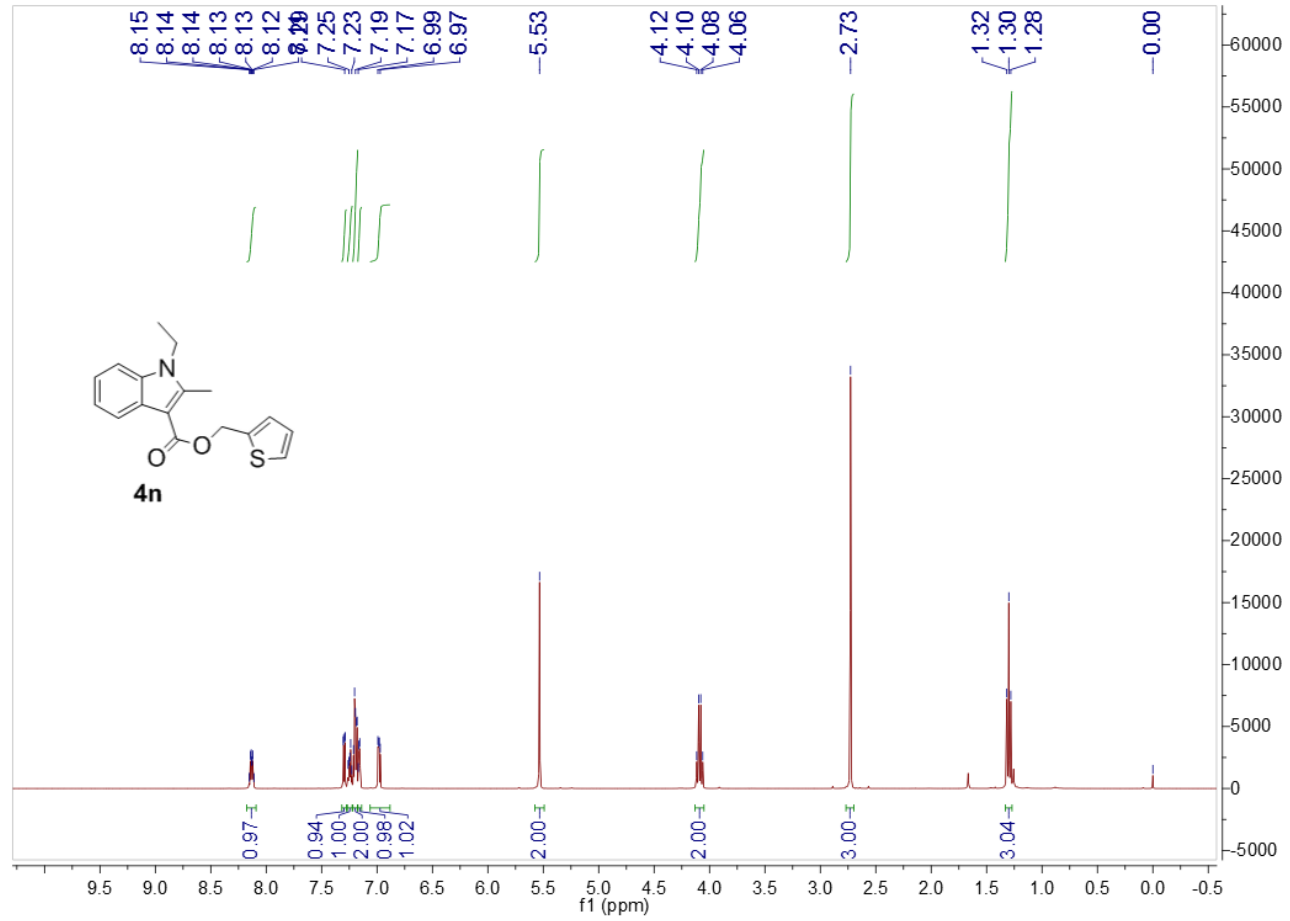

165.65
145.24
141.23
135.48
127.91
125.51
122.17
121.49
109.26
103.39
77.38
77.06
76.74
64.29
37.97
14.80
11.74
f1 (ppm)
4k

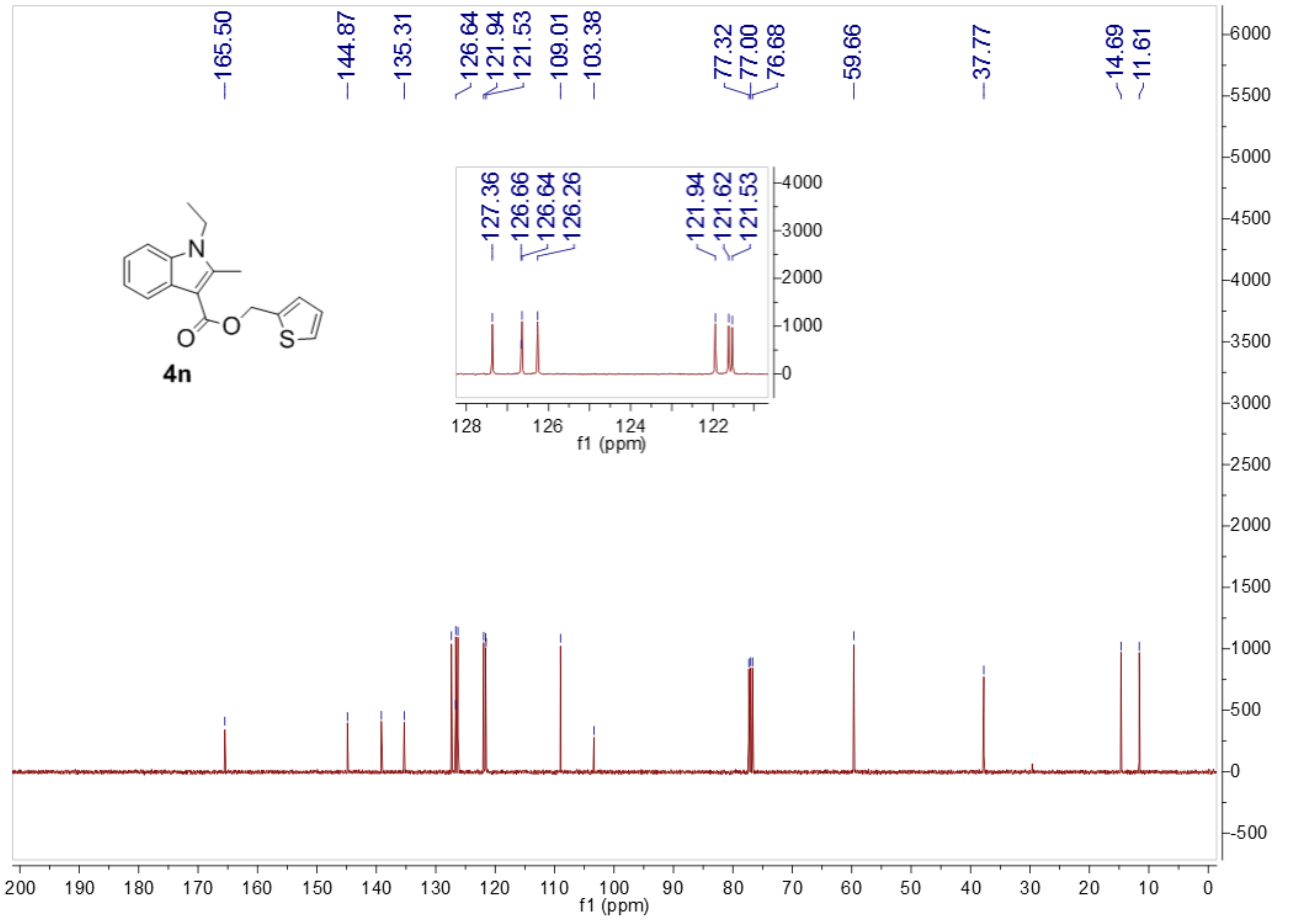

8.22
8.21
8.21
8.20
8.19
8.18
7.64
7.41
7.39
7.29
7.21
6.26
4.20
4.18
4.16
4.14
3.76
2.78
1.37
1.35
1.34
0.00
4l
Ph
1.00
2.00
3.00
1.00
2.02
1.00
2.00
3.00
3.00
3.05
f1 (ppm)


170.02
164.91
145.47
135.46
134.83
126.83
121.90
121.66
109.10
102.96
77.32
77.00
76.68
73.95
52.52
37.94
14.75
11.78
128.99
128.78
127.80
126.83
122.11
121.90
121.66
4l
Ph
f1 (ppm)
f1 (ppm)


8.10
8.10
8.09
8.08
7.25
7.21
7.19
7.18
6.38
6.38
6.38
6.37
5.34
4.18
4.16
4.15
4.13
2.76
1.36
1.34
1.33
0.00
4m
0.99
1.00
1.02
2.01
0.97
0.99
2.00
2.00
3.02
3.07
f1 (ppm)


165.55
150.52
142.93
135.38
126.74
121.60
110.44
109.02
103.54
77.32
77.00
76.68
57.06
37.87
14.76
11.64
121.54
121.23
121.15
4m
f1 (ppm)


8.15
8.14
8.14
8.13
8.13
8.12
7.25
7.23
7.19
7.17
6.99
6.97
5.53
4.12
4.10
4.08
4.06
2.73
1.32
1.30
1.28
0.00
4n
0.97
0.94
1.00
2.00
0.98
1.02
2.00
2.00
3.00
3.04
f1 (ppm)


165.50
144.87
135.31
126.64
121.94
121.53
109.01
103.38
77.32
77.00
76.68
59.66
37.77
14.69
11.61
127.36
126.66
126.64
126.26
121.94
121.62
121.53
4n
f1 (ppm)
f1 (ppm)

XRD data of the compound 4g

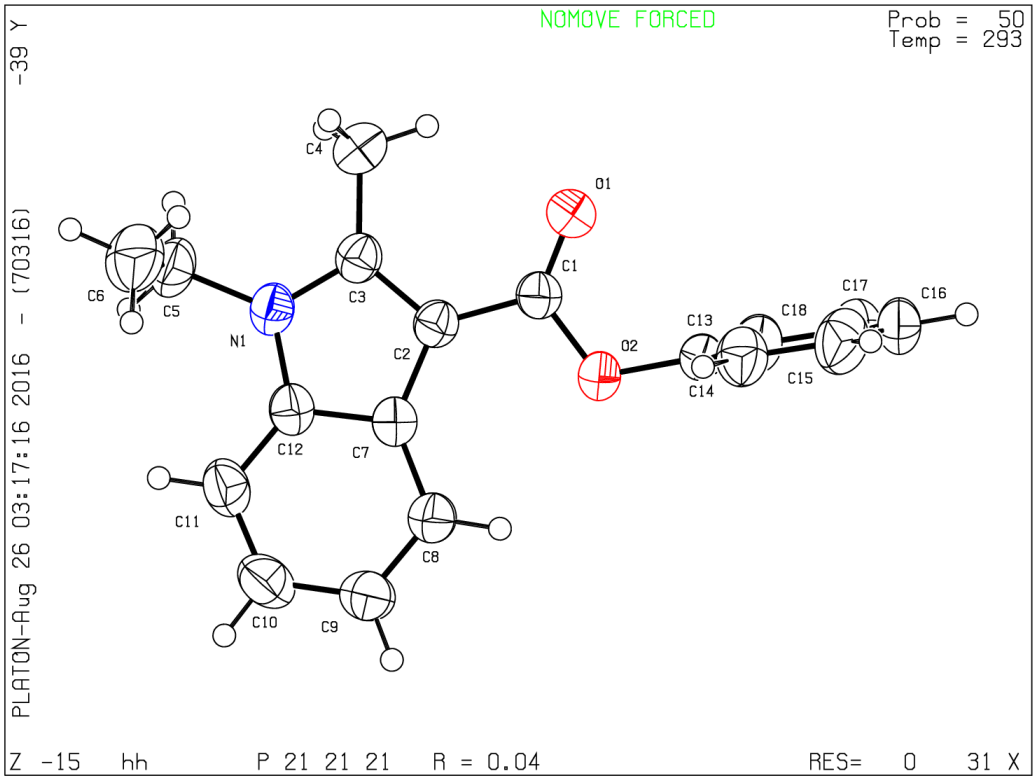


Figure S1. ORTEP structural drawing of **4g**. (CCDC: 1501144)

Table S2. Crystallography data for **4g**.

complex	**4g**
Empirical formula	$C_{18}H_{17}NO_2$
Formula weight(g mol^{-1})	279.33
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
space group	P 21 21 21
Unit cell dimensions	a = 7.2650(3) Å b = 8.2770(5) Å c = 24.8418(14) Å α = 90° β = 90° γ = 90°
Volume ($Å^3$)	1493.80(14)
Z	4
ρ(g cm^{-3})	1.242
F(000)	592

Crystal size(mm^3)	0.75 x 0.65 x 0.30
Theta range for data collection	2.92 ° to 25.00 °
Limiting indices	-7<=h<=8 -9<=k<=9 -29<=l<=26
Reflections collected / unique	5363 / 2503
Data / restraints / parameters	2503 / 0 /192
GOF	1.048
R1,*wR2*[I > 2σ(I)]	*R1* = 0.0398 *wR2* = 0.0870
R1,*wR2*(all data)	*R1* = 0.0516 *wR2* = 0.0925
Largest diff. peak and hole(e $Å^3$)	0.130 and -0.193

Table S3. Bond lengths [Å] and angles [°] for **4g**.

O(2)-C(1) 1.367(2)	O(2)-C(13) 1.410(2)	N(1)-C(3) 1.363(2)	N(1)-C(12) 1.390(3)
N(1)-C(5) 1.460(2)	C(7)-C(8) 1.404(3)	C(7)-C(12) 1.407(2)	C(7)-C(2) 1.442(2)
C(2)-C(3) 1.380(3)	C(2)-C(1) 1.453(3)	C(12)-C(11) 1.381(3)	C(3)-C(4) 1.488(3)
O(1)-C(1) 1.197(2)	C(8)-C(9) 1.375(3)	C(13)-C(14) 1.361(3)	C(13)-C(18) 1.369(3)
C(5)-C(6) 1.510(3)	C(11)-C(10) 1.378(3)	C(14)-C(15) 1.373(3)	C(9)-C(10) 1.388(3)
C(18)-C(17) 1.371(3)	C(15)-C(16) 1.385(3)	C(16)-C(17) 1.371(3)	C(1)-O(2)-C(13) 116.18(14)
C(3)-N(1)-C(12) 109.34(14)	C(3)-N(1)-C(5) 126.62(17)	C(12)-N(1)-C(5) 123.48(16)	C(8)-C(7)-C(12) 118.19(17)
C(8)-C(7)-C(2) 135.74(17)	C(12)-C(7)-C(2) 106.06(16)	C(3)-C(2)-C(7) 107.51(16)	C(3)-C(2)-C(1) 124.37(17)
C(7)-C(2)-C(1) 128.05(17)	C(11)-C(12)-N(1) 129.21(18)	C(11)-C(12)-C(7) 122.84(18)	N(1)-C(12)-C(7) 107.95(15)
N(1)-C(3)-C(2) 109.12(16)	N(1)-C(3)-C(4) 121.03(17)	C(2)-C(3)-C(4) 129.82(17)	O(1)-C(1)-O(2) 121.54(17)
O(1)-C(1)-C(2) 127.13(18)	O(2)-C(1)-C(2) 111.31(16)	C(9)-C(8)-C(7) 118.98(19)	C(14)-C(13)-C(18) 121.62(19)
C(14)-C(13)-O(2) 119.20(17)	C(18)-C(13)-O(2) 119.12(18)	N(1)-C(5)-C(6) 112.18(17)	C(10)-C(11)-C(12) 117.32(19)
C(13)-C(14)-C(15) 119.28(19)	C(8)-C(9)-C(10) 121.3(2)	C(11)-C(10)-C(9) 121.3(2)	C(13)-C(18)-C(17) 119.0(2)
C(14)-C(15)-C(16) 120.0(2)	C(17)-C(16)-C(15) 119.6(2)	C(16)-C(17)-C(18) 120.5(2)	