Supporting Information

Palladium-Catalyzed Oxidative Cross-Coupling of Indoles with Azole-4-carboxylates: An approach to the Synthesis of Pimprinine

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1. General Information

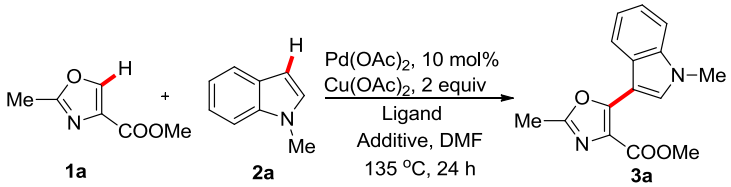
Reagents and Solvents: Pd^{II} catalysts, oxidants and additives were commercially available. azole-4-carboxylate substrates were synthesized from corresponding aldehydes or nitriles by our recently disclosed methods. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA or DCM/MeOH, they are listed as volume/volume ratios.

Data collection: Melting point (m.p.) was measured on a microscopic melting point apparatus. ^{1}H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300MHz) spectrometer using d_6-DMSO and $CDCl_3$ as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard (d_6-DMSO: δ = 2.5 ppm; $CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard (d_6-DMSO: δ = 39.52±0.06 ppm; $CDCl_3$: δ = 77.0 ppm). Infrared spectra (IR) were recorded on a Thermo Scientific iS10 FT/IR spectrometer; absorptions are reported in reciprocal centimeters. High Resolution Mass measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Unless otherwise indicated, all reagents and solvents were obtained from commercial suppliers and used as received.

2. Optimization of Reaction Conditions

Table S1. Screening of Reaction Conditions[a]



Entry	Additive (2 equiv)	Ligand (10 mol %)	Temp/Time (^{o}C/h)	Yield (%)
1	Na_2HPO_4	-	135/24	10
2	2-methylpyridine	-	135/24	47
3	2-acetylpyridine	-	135/24	trace
4	4-acetylpyridine	-	135/24	78
5	3,5-Dichloropyridine	-	135/24	39
6	quinoline	-	135/24	53
7	DMAP	-	135/24	35
8	DABCO	-	135/24	trace
9	DBU	-	135/24	22
10	morpholine	-	135/24	11
11	Et_3N	-	135/24	trace
12	3-acetylpyridine	DPPB	135/24	74
13	3-acetylpyridine	$P(^{n}Bu)_3{\cdot}HBF_4$	135/24	80
14	3-acetylpyridine	X-Phos	135/24	81
15	3-acetylpyridine	Xantphos	135/24	81
16	3-acetylpyridine	Boc-lle-OH	135/24	74
17	3-acetylpyridine	2,2'-Bipy	135/24	30
18	3-acetylpyridine	-	135/12	68
19	3-acetylpyridine	-	135/16	73
20	3-acetylpyridine	-	135/20	74

[a]reaction condition: **1a** (0.5 mmol, 1 equiv); **2a** (1.0 mmol, 2 equiv); $Pd(OAc)_2$ (0.05 mmol), $Cu(OAc)_2$ (1.0 mmol), additive (1.0 mmol) and ligand (0.05 mmol) in DMF (2 mL) at 135 ^{o}C for 24 hours.

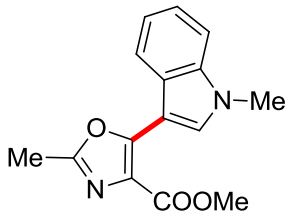
3. Palladium-Catalyzed oxidative Cross-Coupling between Indoles and Azole-4-carboxylates.

3.1 General Procedure

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$ (1.0 mmol), 3-acetylpyridine (1.0 mmol), indoles (1.0 mmol), azole-4-carboxylates (0.5 mmol), and DMF (2 mL) under argon. After stirring at 135 ^oC for 24 hours, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (20 mL), filtered through a Celite pad, and washed with CH_2Cl_2 (10-20 mL). The organic extracts were concentrated, and the resulting residue was purified by column chromatography on silica gel to afford the desired products.

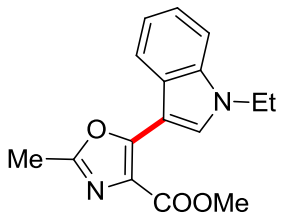
3.2 Characterization of the heteroarylated Products (3a-3r; 4a-4t)

Methyl 2-methyl-5-(1-methyl-1H-indol-3-yl)oxazole-4-carboxylate (3a)



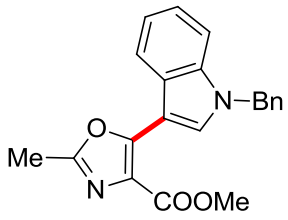
This compound was obtained as a brown solid (221 mg, 82% yield): mp 133-135 ℃; ^1H NMR (300 MHz, d_6-DMSO) δ 8.56 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.28 (dt, *J* = 14.5, 7.0 Hz, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 163.1, 157.8, 154.1, 136.9, 133.6, 125.5, 122.9, 122.5, 121.5, 121.3, 111.0, 101.9, 51.8, 33.5, 13.7; IR (KBr) 3144, 3050, 2938, 1705, 1612, 1578, 1522, 1435, 1395, 1334, 1308, 1216, 1102 ,1079, 915, 780, 742 cm^{-1}; HRMS (ESI^+): calcd for $C_{15}H_{14}N_2NaO_3$ $[M+Na]^+$ 293.0897, found 293.0898.

Methyl 5-(1-ethyl-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3b)



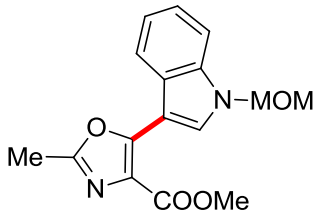
This compound was obtained as a grey solid (272 mg, 96% yield): mp 109-109.5 ℃; ^1H NMR (300 MHz, d_6-DMSO) δ 8.65 (s, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.17 (m, 2H), 4.31 (quart, *J* = 6.9 Hz, 2H), 3.86 (s, 3H), 2.53 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 163.1, 157.9, 154.1, 135.9, 132.0, 125.7, 122.9, 122.5, 121.5, 111.0, 102.1, 51.8, 41.4, 15.6, 13.7; IR (KBr) 3156, 3144, 2973, 2937, 1705, 1603, 1578, 1522, 1437, 1405, 1305, 1209, 1097, 1083, 1061, 912, 806, 785, 748 cm^{-1}; HRMS (ESI^+): calcd for $C_{16}H_{16}N_2NaO_3$ $[M+Na]^+$ 307.1053, found 307.1051.

Methyl 5-(1-benzyl-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3c)



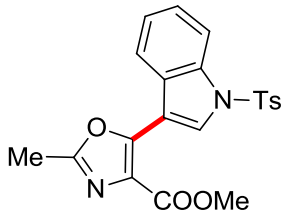
This compound was obtained as a pale yellow solid (325 mg, 94% yield): mp 166-167 ℃; ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.73 (s, 1H), 8.16 – 8.04 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.31 – 7.20 (m, 5H), 5.58 (s, 2H), 3.83 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 163.1, 158.2, 153.8, 137.8, 136.3, 133.0, 129.2, 128.1, 127.6, 125.8, 123.3, 122.9, 121.7, 121.5, 111.6, 102.6, 51.9, 50.0, 13.7; IR (KBr) 3126, 3056, 2938, 1699, 1606, 1569, 1434, 1395, 1337, 1304, 1209, 1167, 1099, 1065, 1024, 914, 812, 786, 734, 709, 635 cm^{-1}; HRMS (ESI^{+}): calcd for $C_{21}H_{18}N_2NaO_3$ $[M+Na]^+$ 369.1210, found 369.1211.

Methyl 5-(1-(methoxymethyl)-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3d)



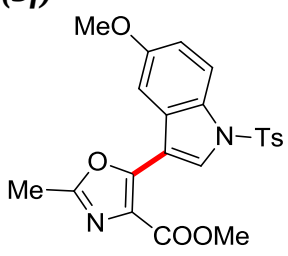
This compound was obtained as a brown solid (252 mg, 84% yield): mp 129.5-130 ℃; ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.68 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.20 (quint, *J* = 7.5 Hz, 2H), 5.64 (s, 2H), 3.83 (s, 3H), 3.21 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 163.0, 158.4, 153.5, 136.4, 132.9, 126.1, 123.5, 123.4, 122.1, 121.5, 111.6, 103.2, 77.5, 55.9, 51.9, 13.7; IR (KBr) 3138, 2991, 2949, 2920, 1706, 1604, 1580, 1436, 1395, 1340, 1302, 1213, 1186, 1130, 1101, 1071, 913, 750, 668 cm^{-1}; HRMS (ESI^{+}): calcd for $C_{16}H_{16}N_2NaO_4$ $[M+Na]^+$ 323.1002, found 323.1003.

Methyl 2-methyl-5-(1-tosyl-1H-indol-3-yl)oxazole-4-carboxylate (3e)



This compound was obtained as a pale yellow solid (201 mg, 49% yield): mp 200-201 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.27 (quint, *J* = 8.0Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 3.97 (s, 3H), 2.59 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5, 159.3, 151.5, 145.4, 134.8, 134.5, 130.1, 129.6, 127.7, 127.1, 126.2, 125.4, 124.1, 121.8, 113.6, 108.9, 52.2, 21.6, 13.8; IR (KBr) 3150, 3050, 2991, 2955, 1712, 1602, 1591, 1444, 1363, 1218, 1175, 1096, 814, 761, 750, 687, 658, 587, 577, 570, 537 cm^{-1}; HRMS (ESI^{+}): calcd for $C_{21}H_{18}N_2NaO_5S$ $[M+Na]^+$ 433.0829, found 433.0825.

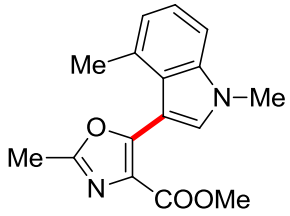
Methyl 5-(5-methoxy-1-tosyl-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3f)



This compound was obtained as a pale yellow solid (238 mg, 54% yield): mp 157-158 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.92 (d, *J* = 9.1 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.47 (s, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.98 (dd, *J* = 9.1, 2.3 Hz, 1H), 3.99 (s, 3H), 3.86 (s, 3H), 2.60 (s, 3H), 2.32 (s,

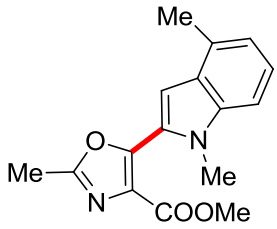
3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5, 159.1, 156.9, 151.5, 145.3, 134.8, 130.3, 130.0, 129.3, 128.7, 127.0, 126.0, 114.3, 113.7, 108.9, 104.9, 55.7, 52.2, 21.5, 13.8; IR (KBr) 3161, 3014, 2949, 2926, 1709, 1608, 1595, 1469, 1370, 1337, 1137, 1083, 1031, 959, 845, 804, 788, 676, 597, 583, 552, 539 cm^{-1}; HRMS (ESI^+): calcd for $C_{22}H_{20}N_2NaO_6S$ $[M+Na]^+$ 463.0934, found 463.0932.

Methyl 5-(1,4-dimethyl-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3g)



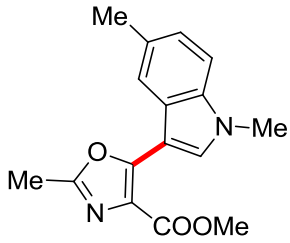
This compound was obtained as a white solid (114 mg, 40% yield): mp 139.5-140 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (m, 1H), 7.24 – 7.15 (m, 2H), 6.99 (d, *J* = 5.8 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 2.54 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 159.3, 153.0, 137.1, 132.8, 130.7, 126.4, 125.6, 122.7, 122.7, 107.6, 101.1, 51.9, 33.4, 20.6, 14.0; IR (KBr) 3103, 2955, 2921, 2849, 1720, 1626, 1592, 1522, 1441, 1390, 1350, 1267, 1224, 1200, 1177, 1162, 1065, 965, 847, 812, 787, 762, 671 cm^{-1}; HRMS (ESI^+): calcd for $C_{16}H_{16}N_2NaO_3$ $[M+ Na]^+$ 307.1053, found 307.1055.

Methyl 5-(1,4-dimethyl-1H-indol-2-yl)-2-methyloxazole-4-carboxylate (3g')



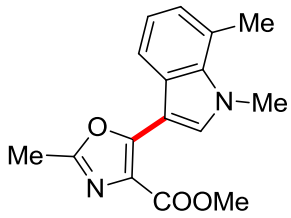
This compound was obtained as a white solid (134 mg, 47% yield): mp 102-103 ℃; ^{1}H NMR (300 MHz, d_6-DMSO) δ 11.50 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 2.6 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.15 – 7.07 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 158.2, 147.3, 136.3, 123.8, 122.8, 122.0, 119.9, 119.4, 119.2, 112.0, 103.9, 13.5; IR (KBr) 3149, 3002, 2943, 2843, 1709, 1605, 1563, 1448, 1352, 1286, 1211, 1188, 1094, 1030, 956, 827, 772, 738, 665 cm^{-1}; HRMS (ESI^+): calcd for $C_{16}H_{17}N_2O_3$ $[M+H]^+$ 285.1234, found 285.1233.

Methyl 5-(1,5-dimethyl-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3h)



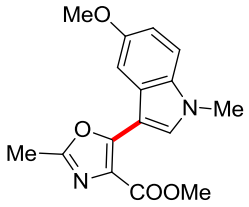
This compound was obtained as a pale yellow solid (242 mg, 85% yield): mp 141-141.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.93 (s, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 3.94 (s, 3H), 3.83 (s, 3H), 2.61 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 157.5, 155.1, 135.3, 133.6, 130.8, 126.0, 124.4, 122.2, 121.1, 109.5, 102.1, 51.8, 33.4, 21.7, 13.9; IR (KBr) 3134, 3038, 2955, 2926, 1696, 1607, 1566, 1526, 1472, 1422, 1396, 1320, 1207, 1148, 1102, 1074, 1055, 853, 801, 785, 665, 618 cm^{-1}; HRMS (ESI^+): calcd for $C_{16}H_{16}N_2NaO_3$ $[M+Na]^+$ 307.1053, found 307.1052.

Methyl 5-(1,7-dimethyl-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3i)



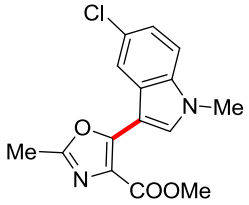
This compound was obtained as a light brown solid (242 mg, 85% yield): mp 184.5-185 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.1 Hz, 1H), 4.09 (s, 3H), 3.95 (s, 3H), 2.76 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 157.5, 154.8, 135.5, 135.1, 126.9, 125.6, 122.5, 121.7, 121.4, 119.5, 102.2, 51.8, 37.6, 19.7, 13.8; IR (KBr) 3139, 3085, 3018, 2943, 1707, 1611, 1574, 1452, 1434, 1382, 1319, 1309, 1207, 1111, 1089, 1039, 945, 874, 786, 753 cm^{-1}; HRMS (ESI^+): calcd for $C_{16}H_{16}N_2NaO_3$ $[M+Na]^+$ 307.1053, found 307.1054.

Methyl 5-(5-methoxy-1-methyl-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3j)



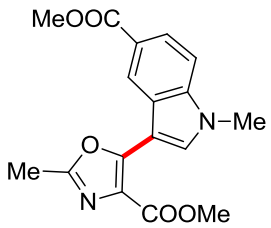
This compound was obtained as a light brown solid (261 mg, 87% yield): mp 179.5-180 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.20 (d, *J* = 8.9 Hz, 1H), 6.93 (dd, *J* = 8.9, 2.3 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.77 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 157.2, 155.3, 155.0, 133.9, 132.1, 126.4, 122.0, 112.2, 110.4, 104.1, 102.1, 55.9, 51.8, 33.5, 13.8; IR (KBr) 3144, 3028, 2957, 2923, 1697, 1618, 1606, 1522, 1440, 1413, 1324, 1225, 1207, 1142, 1126, 1097, 1033, 859, 839, 805, 786 cm^{-1}; HRMS (ESI^+): calcd for $C_{16}H_{16}N_2NaO_4$ $[M+Na]^+$ 323.1002, found 323.1001.

Methyl 5-(5-chloro-1-methyl-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3k)



This compound was obtained as a yellow solid (246 mg, 81% yield): mp 196-197 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.03 (s, 1H), 7.27 – 7.15 (m, 2H), 3.95 (s, 3H), 3.79 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 157.7, 154.0, 135.1, 134.3, 127.1, 126.5, 123.0, 122.6, 120.9, 110.7, 102.3, 51.9, 33.5, 13.8; IR (KBr) 3138, 3079, 2955, 2938, 1697, 1614, 1573, 1524, 1469, 1395, 1321, 1024, 1082, 922, 805, 786, 662, 618, 591 cm^{-1}; HRMS (ESI^+): calcd for $C_{15}H_{13}ClNaN_2O_3$ $[M+Na]^+$ 327.0507, found 327.0506.

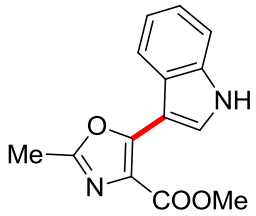
Methyl 5-(5-(methoxycarbonyl)-1-methyl-1H-indol-3-yl)-2-methyloxazole -4-carboxylate (3l)



This compound was obtained as a yellow solid (141 mg, 86% yield): mp 169-171 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.66 (s, 1H), 7.97 (dd, *J* = 8.7, 1.3 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 3.96 (d, *J* = 2.1 Hz, 6H), 3.83 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 162.7, 157.6, 153.3, 138.6, 134.0, 124.7, 124.2, 123.8, 123.5, 122.6, 108.9, 103.3, 51.5, 51.4, 33.0, 13.3; IR (KBr) 3475, 3415, 3233, 2944, 1701, 1638, 1618, 1572, 1397, 1326, 1215, 1099, 1071, 768, 609 cm^{-1}; HRMS (ESI^+): calcd

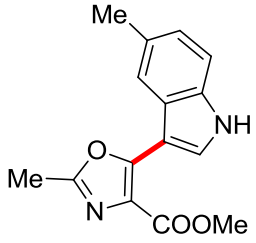
for $C_{17}H_{16}N_2NaO_5$ $[M+Na]^+$ 351.0957, found 351.0963.

Methyl 5-(1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3m)



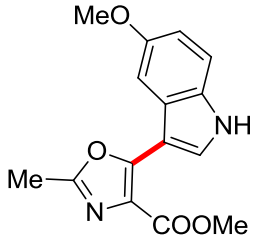
This compound was obtained as a brown solid (195 mg, 76% yield): mp 251-251.5 ℃; ^{1}H NMR (300 MHz, d_6-DMSO) δ 11.93 (s, 1H), 8.65 (d, *J* = 2.5 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.13 (m, 2H), 3.85 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 163.1, 157.9, 154.5, 136.4, 130.0, 125.2, 122.9, 122.6, 121.3, 121.1, 112.7, 102.8, 51.8, 13.7; IR (KBr) 3132, 3091, 3032, 2973, 2914, 2873, 1708, 1610, 1584, 1433, 1285, 1206, 927, 780,7 44 cm^{-1}; HRMS (ESI^+): calcd for $C_{14}H_{12}N_2NaO_3$ $[M+Na]^+$ 279.0740, found 279.0739.

Methyl 2-methyl-5-(5-methyl-1H-indol-3-yl)oxazole-4-carboxylate (3n)



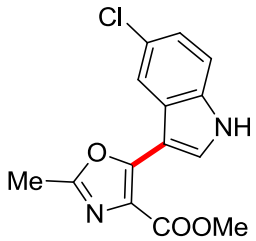
This compound was obtained as a light grey solid (151 mg, 56% yield): mp 260-260.5 ℃; ^{1}H NMR (300 MHz, d_6-DMSO) δ 11.79 (s, 1H), 8.58 (s, 1H), 7.85 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 3.83 (s, 3H), 2.55 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 163.2, 157.8, 154.7, 134.8, 130.1, 130.0, 125.5, 124.5, 122.4, 120.6, 112.4, 102.3, 51.8, 21.9, 13.8; IR (KBr) 3149, 3026, 2949, 2926, 1701, 1610, 1577, 1434, 1288, 1248, 915 ,794, 777, 615 cm^{-1}; HRMS (ESI^+): calcd for $C_{15}H_{14}N_2NaO_3$ $[M + Na]^+$ 293.0897, found 293.0895.

Methyl 5-(5-methoxy-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3o)



This compound was obtained as a brown solid (166 mg, 58% yield): mp 264-265 ℃; ^{1}H NMR (300 MHz, d_6-DMSO) δ 11.72 (s, 1H), 8.53 (s, 1H), 7.49 (s, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 3.80 (s, 6H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 163.2, 157.7, 155.1, 154.6, 131.5, 130.5, 125.8, 122.3, 113.4, 112.6, 103.4, 102.6, 55.8, 51.8, 13.7; IR (KBr) 3257, 3179, 3002, 2949, 2890, 2825, 1713, 1695, 1581, 1480, 1454, 1440, 1369, 1291, 1214, 1200, 1129, 1118, 1100, 1074, 1021, 915, 841, 803, 779, 629 cm^{-1}; HRMS (ESI^+): calcd for $C_{15}H_{14}N_2NaO_4$ $[M+Na]^+$ 309.0846, found 309.0845.

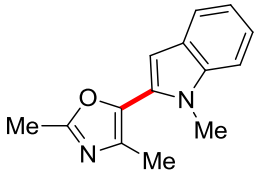
Methyl 5-(5-chloro-1H-indol-3-yl)-2-methyloxazole-4-carboxylate (3p)



This compound was obtained as a brown solid (215 mg, 74% yield): mp 259.5-260 ℃; ^{1}H NMR (300 MHz, d_6-DMSO) δ 12.08 (s, 1H), 8.66 (s, 1H), 8.00 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 163.0, 158.0, 153.7, 134.9, 131.3, 126.2, 125.9, 122.9, 120.1, 114.2, 102.7, 51.8, 13.7; IR (KBr) 3146, 3020, 2932, 1710, 1608, 1583, 1458, 1438, 1287, 1207, 1145, 1133, 1091, 980, 933, 893, 782, 612, 579 cm^{-1}; HRMS (ESI^+): calcd for $C_{14}H_{11}ClN_2NaO_3$[M+Na]$^+$

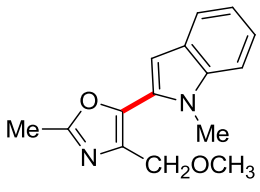
313.0350, found 313.0348.

2, 4-dimethyl-5-(1-methyl-1H-indol-2-yl)oxazole (3q)



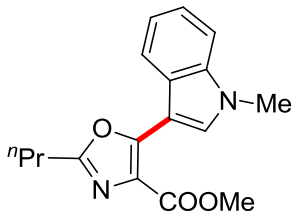
This compound was obtained as yellow oil (25 mg, 22% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.27 (t, *J* = 6.7 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.61 (s, 1H), 3.77 (s, 3H), 2.51 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 140.0, 138.0, 135.5, 127.8, 127.6, 122.5, 120.8, 120.0, 109.5, 103.5, 31.2, 14.1, 12.4; IR (KBr) 2924, 1578, 1464, 1275, 1262, 1204, 1095, 764, 750 cm^{-1}; HRMS (ESI$^+$): calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1184, found 227.1191.

4-(methoxymethyl)-2-methyl-5-(1-methyl-1H-indol-2-yl)oxazole (3r)



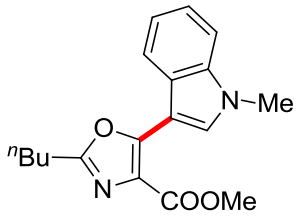
This compound was obtained as yellow soild (58 mg, 45% yield): mp 110-112^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.71 (s, 1H), 4.42 (s, 2H), 3.79 (s, 3H), 3.45 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 141.6, 138.4, 135.8, 127.4, 126.7, 122.9, 121.1, 120.2, 109.6, 104.8, 65.9, 58.6, 31.2, 14.1; IR (KBr) 3414, 3149, 2926, 1638, 1617, 1584, 1401, 1304, 1257, 1194, 1079, 950, 801, 753 cm^{-1}; HRMS (ESI$^+$): calcd for $C_{15}H_{16}NaN_2O_2$ $[M+Na]^+$ 279.1109, found 279.1113.

Methyl 5-(1-methyl-1H-indol-3-yl)-2-propyloxazole-4-carboxylate (4a)



This compound was obtained as a light brown solid (224 mg, 75% yield): mp 84.5-85.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.15 (d, *J* = 7.2 Hz, 1H), 7.39 – 7.22 (m, 3H), 3.95 (s, 3H), 3.84 (s, 3H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.00 – 1.83 (sext, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 161.0, 154.7, 136.8, 133.5, 125.8, 122.8, 122.4, 121.4, 121.3, 109.8, 102.8, 51.8, 33.4, 30.0, 20.7, 13.8; IR (KBr) 3145, 3044, 2965, 2946, 1697, 1576, 1569, 1442, 1393, 1334, 1224, 1210, 1141, 916, 788, 735, 576 cm^{-1}; HRMS (ESI$^+$): calcd for $C_{17}H_{19}N_2O_3$ $[M+H]^+$ 299.1390, found 299.1389.

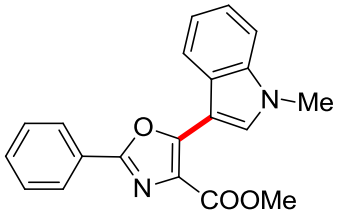
Methyl 5-(1-methyl-1H-indol-3-yl)-2-butyloxazole-4-carboxylate (4b)



This compound was obtained as a light brown solid (184 mg, 59% yield): mp 80-80.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.15 (d, *J* = 7.1 Hz, 1H), 7.39 – 7.21 (m, 3H), 3.95 (s, 3H), 3.84 (s, 3H), 2.90 (t, *J* = 7.6 Hz, 2H), 1.95 – 1.79 (quint, *J* = 7.5Hz, 2H), 1.55 – 1.37 (sext, *J* = 7.2 Hz,2H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 161.2, 154.7, 136.9, 133.5, 125.9, 122.8, 122.4, 121.4, 121.3, 109.8, 102.8, 51.9, 33.4, 29.2, 27.8, 22.3, 13.7; IR (KBr) 3150, 2961, 2926, 2896, 1691, 1637, 1601, 1475,

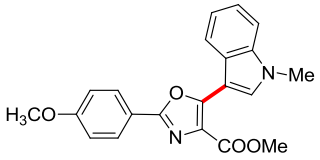
1400, 1226, 1097, 1078, 930, 791, 747 cm^{-1}; HRMS (ESI^+): calcd for $C_{18}H_{21}N_2O_3$ $[M + H]^+$ 313.1547, found 313.1549.

Methyl 5-(1-methyl-1H-indol-3-yl)-2-phenyloxazole-4-carboxylate (4c)



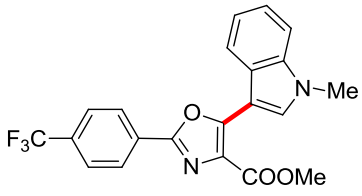
This compound was obtained as a light yellow solid (276 mg, 83% yield): mp 208-209 ℃; ^1H NMR (300 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.34 – 8.22 (m, 1H), 8.22 – 8.11 (m, 2H), 7.50 (d, *J* = 6.8 Hz, 3H), 7.39 – 7.28 (m, 3H), 4.00 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 157.7, 154.9, 136.9, 134.1, 130.5, 128.8, 126.8, 126.5, 125.8, 123.0, 121.60, 121.4, 109.9, 102.7, 52.1, 33.4; IR (KBr) 3132, 3050, 2979, 2943,1701, 1577, 1568, 1445, 1392, 1333, 1221, 1133, 1109, 1073, 1045, 912, 786, 736, 704, 686 cm^{-1}; HRMS (ESI^+): calcd for $C_{20}H_{16}N_2NaO_3$ $[M+Na]^+$ 355.1053, found 355.1054.

Methyl 2-(4-methoxyphenyl)-5-(1-methyl-1H-indol-3-yl)oxazole-4-carboxylae (4d)



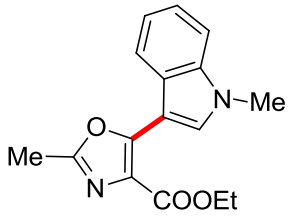
This compound was obtained as a light yellow solid (261 mg, 72% yield): mp 159-160 ℃; ^1H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.23 (dd, *J* = 5.8, 2.5 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.99 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 161.0, 157.8, 154.7, 136.8, 133.5, 128.2, 125.8, 123.6, 122.9, 122.4, 121.5, 121.3, 114.2, 109.8, 102.8, 51.8, 33.4, 30.0, 20.7, 13.8; IR (KBr) 3138, 2943, 2837, 1701, 1616, 1578, 1503, 1445, 1421, 1248, 1170, 1103, 1087, 1030, 915, 831, 740, 629 cm^{-1}; HRMS (ESI^+): calcd for $C_{21}H_{18}NaN_2O_4$ $[M+Na]^+$ 385.1159, found 385.1156.

Methyl 5-(1-methyl-1H-indol-3-yl)-2-(4-(trifluoromethyl)phenyl)oxazole-4-carboxylate (4e)



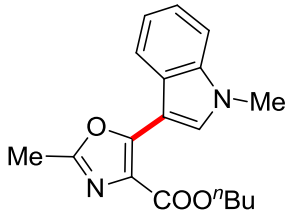
This compound was obtained as a white solid (288 mg, 70% yield): mp 215-216 ℃; ^1H NMR (300 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.26 (dd, *J* = 12.8, 5.8 Hz, 3H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.31 (m, 3H), 4.02 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 156.2, 155.5, 136.9, 134.5, 129.9, 126.6, 125.9, 125.9, 125.8, 125.8, 123.1, 121.8, 121.2, 110.1, 102.4, 52.2, 33.5; IR (KBr) 3132, 3014, 2949, 1697, 1617, 1569, 1438, 1336, 1300, 1227, 1175, 1124, 1088, 1069, 1014, 917, 847, 785, 705, 576 cm^{-1}; HRMS (ESI^+): calcd for $C_{21}H_{15}F_3N_2NaO_3$ $[M+Na]^+$ 423.0927, found 423.0926.

Ethyl 2-methyl-5-(1-methyl-1H-indol-3-yl)oxazole-4-carboxylate (4f)



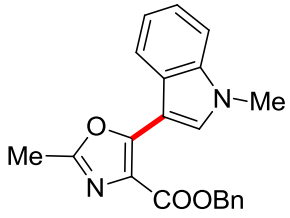
This compound was obtained as a yellow solid (239 mg, 84% yield): mp 115-116 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.15 (d, *J* = 7.3 Hz, 1H), 7.44 – 7.15 (m, 3H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 2.59 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 157.5, 154.7, 136.8, 133.5, 125.8, 122.8, 121.5, 121.2, 109.8, 102.6, 60.8, 33.3, 14.6, 13.8; IR(KBr) 3144, 3126, 3050, 2976, 2932, 1690, 1617, 1566, 1426, 1331, 1307, 1204, 1101, 1080, 928, 850, 784, 735, 668, 576 cm^{-1}; HRMS (ESI^+): calcd for $C_{16}H_{16}N_2NaO_3$ $[M+Na]^+$ 307.1053, found 307.1056.

Butyl 2-methyl-5-(1-methyl-1H-indol-3-yl)oxazole-4-carboxylate (4g)



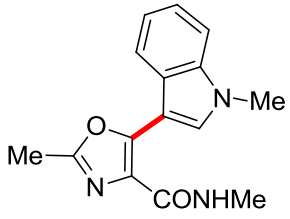
This compound was obtained as a light yellow solid (228 mg, 73% yield): mp 76.5-77 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.21 – 8.09 (m, 1H), 7.36 – 7.22 (m, 3H), 4.37 (t, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 2.58 (s, 3H), 1.91 – 1.73 (quint, *J* = 7.4 Hz, 2H), 1.55 – 1.38 (sext, *J* = 7.8 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 157.5, 154.7, 136.8, 133.4, 125.9, 122.8, 122.7, 121.5, 121.2, 109.8, 102.7, 64.7, 33.3, 30.9, 19.2, 13.9, 13.8; IR (KBr) 3144, 3038, 2955, 2920, 2867, 1700, 1606, 1525, 1425, 1332, 1216, 1101, 1015, 933, 862, 786, 727, 662 cm^{-1}; HRMS (ESI^+): calcd for $C_{18}H_{21}N_2O_3$ $[M+H]^+$ 313.1547, found 313.1545.

Benzyl 2-methyl-5-(1-methyl-1H-indol-3-yl)oxazole-4-carboxylate (4h)



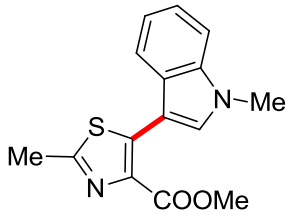
This compound was obtained as a light yellow solid (235 mg, 68% yield): mp 116-117.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.11 (d, *J* = 7.3 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.42 – 7.14 (m, 6H), 5.41 (s, 2H), 3.69 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7, 157.6, 154.9, 136.8, 136.3, 133.6, 128.6, 128.5, 128.2, 125.9, 122.8, 122.6, 121.5, 121.3, 109.8, 102.6, 66.4, 33.2, 13.8; IR (KBr) 3144, 2955, 1700, 1605, 1577, 1447, 1427, 1332, 1213, 1100, 1078, 1015, 918, 780, 753, 733, 697 cm^{-1}; HRMS (ESI^+): calcd for $C_{21}H_{19}N_2O_3$ $[M+H]^+$ 369.1210, found 369.1208.

N, 2-dimethyl-5-(1-methyl-1H-indol-3-yl)oxazole-4-carboxamide (4i)



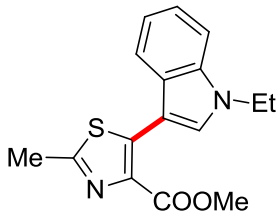
This compound was obtained as a light yellow solid (215 mg, 80% yield): mp 140-140.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.14 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.19 (m, 3H), 7.09 (s, 1H), 3.78 (s, 3H), 2.97 (d, *J* = 5.0 Hz, 3H), 2.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 156.5, 151.1, 136.8, 133.4, 125.8, 125.2, 122.4, 121.3, 120.8, 109.7, 102.8, 33.2, 25.7, 13.7; IR (KBr) 3419, 3126, 2961, 2926, 1654, 1604, 1508, 1391, 1219, 1207, 1093, 912, 815, 740, 562 cm^{-1}; HRMS (ESI^+): calcd for $C_{15}H_{15}N_3NaO_2$ $[M+Na]^+$ 292.1056, found 292.1054.

Methyl 2-methyl-5-(1-methyl-1H-indol-3-yl)thiazole-4-carboxylate (4j)



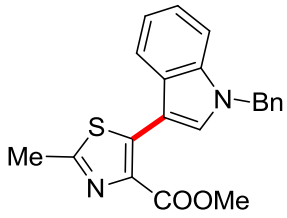
This compound was obtained as a yellow oil (180 mg, 63% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.26 (ddd, *J* = 14.8, 11.9, 6.8 Hz, 2H), 3.91 (s, 3H), 3.83 (s, 3H), 2.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 162.0, 141.4, 137.7, 136.8, 131.8, 127.2, 122.5, 120.7, 119.7, 109.8, 104.2, 52.2, 33.2, 19.2; IR (KBr) 3138, 3050, 2989, 2922, 2849, 1707, 1552, 1498, 1477, 1431, 1399, 1381, 1329, 1216, 1198, 1171, 1079, 909, 786, 746, 606 cm^{-1}; HRMS (ESI^+): calcd for $C_{15}H_{15}N_2O_2S$ $[M + H]^+$ 287.0849, found 287.0848.

Methyl 5-(1-ethyl-1H-indol-3-yl)-2-methylthiazole-4-carboxylate (4k)



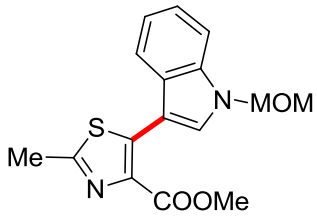
This compound was obtained as a white solid (177 mg, 59% yield): mp 110-110.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.16 (m, 2H), 4.22 (q, *J* = 7.3 Hz, 2H), 3.88 (s, 3H), 2.75 (s, 3H), 1.51 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 161.9, 141.5, 137.8, 135.8, 130.3, 127.4, 122.3, 120.6, 119.9, 109.9, 104.3, 52.2, 41.4, 19.2, 15.3; IR (KBr) 3131, 3044, 2997, 2976, 1700, 1546, 1474, 1459, 1397, 1327, 1300, 1208, 1156, 1137, 1094, 993, 903, 839, 777, 740, 727 cm^{-1}; HRMS (ESI^+): calcd for $C_{16}H_{17}N_2O_2S$ $[M + H]^+$ 301.1005, found 301.1007.

Methyl 5-(1-benzyl-1H-indol-3-yl)-2-methylthiazole-4-carboxylate (4l)



This compound was obtained as a light yellow oil (221 mg, 61% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.79 (dd, *J* = 6.3, 2.7 Hz, 1H), 7.27 (dt, *J* = 10.6, 5.8 Hz, 4H), 7.22 – 7.08 (m, 4H), 5.30 (s, 2H), 3.83 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 162.2, 141.0, 138.2, 136.7, 136.3, 131.3, 128.9, 127.9, 127.5, 126.9, 122.7, 120.9, 119.9, 110.4, 104.9, 52.2, 50.5, 19.2; IR (KBr) 3005, 2989, 2921, 2850, 1716, 1552, 1495, 1469, 1392, 1301, 1275, 1260, 1204, 1174, 998, 909, 747, 699 cm^{-1}; HRMS (ESI^+): calcd for $C_{21}H_{19}N_2O_2S$ $[M + H]^+$ 363.1162, found 363.1159.

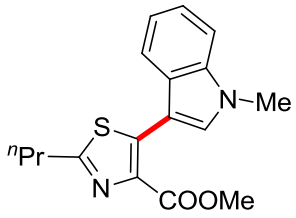
Methyl 5-(1-(methoxymethyl)-1H-indol-3-yl)-2-methylthiazole-4-carboxylate (4m)



This compound was obtained as a grey soild (199 mg, 63% yield): mp 101-102 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.20 (m, 2H), 5.49 (s, 2H), 3.87 (s, 3H), 3.30 (s, 3H), 2.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 162.6, 140.4, 138.6, 136.2, 130.9, 127.9, 123.1, 121.4, 119.8, 110.6, 105.6, 77.8, 56.1, 52.2, 19.2; IR(KBr) 3120, 2997, 2943, 2920, 1699, 1548, 1494, 1460, 1389, 1327, 1298, 1192, 1178, 1160, 1134, 1033, 995, 908, 741, 656, 630,

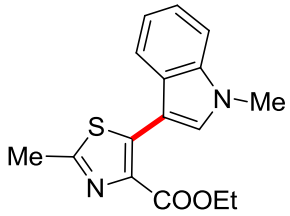
567 cm^{-1}; HRMS (ESI^+): calcd for $C_{16}H_{17}N_2O_3S$ $[M + H]^+$ 317.0954, found 317.0952.

Methyl 5-(1-methyl-1H-indol-3-yl)-2-propylthiazole-4-carboxylate (4n)



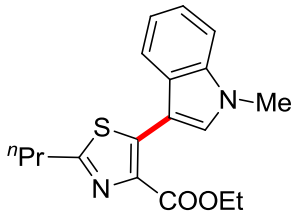
This compound was obtained as a yellow solid (179 mg, 57% yield): mp 78-79 ℃; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.17 (m, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 3.09 – 2.94 (t, *J* = 7.7 Hz, 2H), 1.93 – 1.79 (sext, *J* = 7.7 Hz, 7.3Hz ,2H), 1.06 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 163.2, 140.9, 137.7, 136.8, 131.8, 127.2, 122.4, 120.6, 119.8, 109.8, 104.4, 52.2, 35.5, 33.2, 23.6, 13.8; IR (KBr) 3143, 3061, 2953, 2926, 2861, 1716, 1602, 1497, 1478, 1458, 1380, 1326, 1303, 1202, 1177, 1132, 1012, 912, 833, 788, 744, 600 cm^{-1}; HRMS (ESI^+): calcd for $C_{17}H_{19}N_2O_2S$ $[M + H]^+$ 315.1162, found 315.1159.

Ethyl 2-methyl-5-(1-methyl-1H-indol-3-yl)thiazole-4-carboxylate (4o)



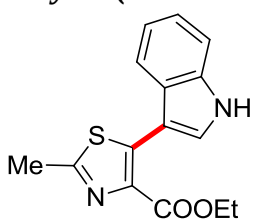
This compound was obtained as a yellow oil (261 mg, 87% yield); ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.34 (s, 1H), 7.30 – 7.23 (dt, 1H), 7.23 – 7.15 (dt, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.74 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6, 162.1, 140.8, 138.8, 136.8, 131.6, 127.3, 122.4, 120.6, 119.8, 109.8, 104.4, 61.1, 33.1, 19.3, 14.3; IR (KBr) 2979, 2921, 2850, 1713, 1632, 1477, 1423, 1380, 1299,1 275, 1260, 1215, 1183, 1080, 906, 764, 749 cm^{-1}; HRMS (ESI^+): calcd for $C_{16}H_{17}N_2O_2S$ $[M + H]^+$ 301.1005, found 301.1006.

Ethyl 5-(1-methyl-1H-indol-3-yl)-2-propylthiazole-4-carboxylate (4p)



This compound was obtained as a yellow solid (233 mg, 71% yield): mp 59.5-60 ℃; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (t, *J* = 3.8 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.24 – 7.16 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.10 – 2.93 (t,*J* = 7.8 Hz, 2H), 1.84 (sext, *J* = 7.8 Hz, 7.4 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 162.8, 140.2, 138.4, 136.8, 131.5, 127.3, 122.4, 120.5, 119.8, 109.7, 104.6, 61.1, 35.5, 33.1, 23.6, 14.3, 13.8; IR (KBr) 3138, 3050, 2959, 2926, 2896, 1712, 1605, 1540, 1496, 1381, 1324, 1196, 1132, 1122, 1081, 912, 780, 737, 641, 428 cm^{-1}; HRMS (ESI^+): calcd for $C_{18}H_{21}N_2O_2S$ $[M+H]^+$ 329.1318, found 329.1317.

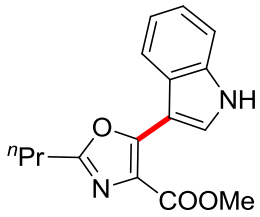
Ethyl 5-(1H-indol-3-yl)-2-methylthiazole-4-carboxylate (4q)



This compound was obtained as a grey solid (143 mg, 50% yield): mp 136-137.5 ℃; ^1H NMR (300 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.76 (d, *J* = 2.5 Hz, 1H), 7.74 – 7.57 (m, 1H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.31 – 7.13 (m, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

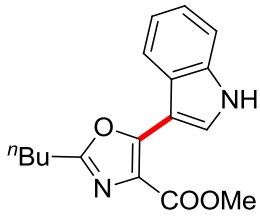
162.8, 162.7, 140.8, 138.9, 135.9, 127.1, 126.6, 122.6, 120.7, 119.5, 111.8, 105.6, 61.3, 19.2, 14.2; IR (KBr) 3203, 3182, 3109, 2978, 2920, 1740, 1716, 1532, 1456, 1320, 1279, 1241, 1197, 1137, 1121, 1095, 1034, 926, 783, 740, 615, 594cm^{-1}; HRMS (ESI^{+}): calcd for $C_{15}H_{15}N_2O_2S$ $[M+H]^+$ 287.0849, found 287.0847.

Methyl 5-(1H-indol-3-yl)-2-propyloxazole-4-carboxylate (4r)



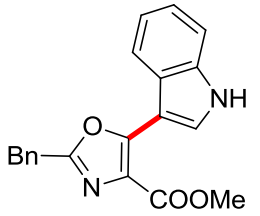
This compound was obtained as a yellow solid (88 mg, 62% yield): mp 172-174 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.82 (d, *J* = 2.8 Hz, 1H), 8.18 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.42 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.35 – 7.18 (m, 2H), 3.94 (s, 3H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.00 – 1.84 (sext, *J* = 7.4 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 161.4, 154.9, 136.0, 129.6, 125.2, 123.1, 122.6, 121.4, 121.2, 111.8, 104.0, 51.9, 30.0, 20.6, 13.8; IR (KBr) 3461, 3139, 3098, 2967, 2923, 1708, 1603, 1584, 1372, 1289, 1245, 1209, 1135, 1084, 930, 781, 743 cm^{-1}; HRMS (ESI^{+}): calcd for $C_{16}H_{15}N_2O_3$ $[M-H]^-$ 283.1083, found 283.1090.

Methyl 5-(1H-indol-3-yl)-2-butyloxazole-4-carboxylate (4s)



This compound was obtained as a yellow solid (75 mg, 50% yield): mp 144-146 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.81 (d, *J* = 2.8 Hz, 1H), 8.27 – 8.11 (m, 1H), 7.52 – 7.38 (m, 1H), 7.34 – 7.22 (m, 2H), 3.95 (s, 3H), 2.92 (t, *J* = 7.6 Hz, 2H), 1.96 – 1.82 (quint, *J* = 7.6, 7.4 Hz, 2H), 1.54 – 1.40 (sex, *J* = 7.4, 7.3 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 161.5, 154.7, 135.9, 129.4, 125.2, 123.1, 122.9, 121.5, 121.2, 111.7, 104.2, 51.9, 29.2, 27.8, 22.3, 13.7; IR (KBr) 2956, 2924, 1708, 1638, 1618, 1460, 1433, 1400, 1374, 1284, 1210, 1136, 1086, 927, 780, 744, 615 cm^{-1}; HRMS (ESI^{+}): calcd for $C_{17}H_{17}N_2O_3$ $[M-H]^-$ 297.1239, found 297.1247.

Methyl 5-(1H-indol-3-yl) 2-benzyloxazole-4-carboxylate (4t)

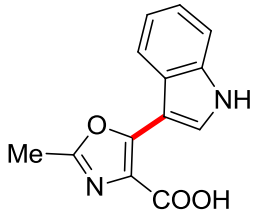


This compound was obtained as a yellow solid (69 mg, 42% yield): mp 192-194 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.76 (d, *J* = 2.6 Hz, 1H), 7.97 (d, *J* = 7.0 Hz, 1H), 7.35 (dt, *J* = 12.0, 7.4 Hz, 5H), 7.29 – 7.15 (m, 3H), 4.21 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 159.4, 155.3, 135.9, 135.0, 129.7, 128.9, 128.9, 127.3, 125.1, 123.1, 122.8, 121.5, 121.2, 111.7, 103.9, 52.0, 34.6; IR (KBr) 3412，3151，2949，1705, 1594，1562，1426, 1374，1277， 1205, 1129，1080，1012, 965，927, 784, 741, 742, 695 cm^{-1}; HRMS (ESI^{+}): calcd for $C_{20}H_{15}N_2O_3$ $[M-H]^-$ 331.1083, found 331.1092.

4. General Procedure for Synthesis of Pimprinine and WS-30581 A

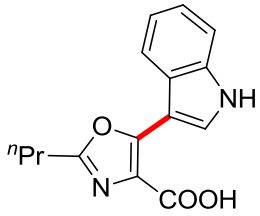
To the solution of methyl 5-(1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (256 mg, 1.0 mmol) in EtOH (5 mL) was added a solution of NaOH (112 mg, 2.0 mmol) in water (1 mL). The resulting mixture was stirred at 80 ^{o}C overnight. The mixture was concentrated in vacuo and acidified with 1 M HCl to precipitate the carboxylic acid. Then vacuum filtration and dry to give a pale yellow solid **5a** (240 mg, 99% yield) which was used for the next step without further purification.

5-(1H-indol-3-yl)-2-methyloxazole-4-carboxylic acid (5a)



This compound was obtained as a pale yellow solid (240 mg, 99% yield): mp 210-211 ℃; ^{1}H NMR (300 MHz, d_6-DMSO) δ 11.86 (s, 1H), 8.63 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.0 Hz, 1H), 7.29 – 7.08 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 165.2, 157.2, 152.4, 136.5, 130.0, 126.3, 125.4, 122.5, 121.1, 120.8, 112.7, 103.5, 13.9; IR(KBr) 3186, 2973, 1682, 1606, 1583, 1400, 1268, 1215, 1135, 1082, 948, 736, 618 cm^{-1}; HRMS (ESI^{+}): calcd for $C_{13}H_{11}N_2O_3$ $[M + H]^{+}$ 243.0764, found 243.0766.

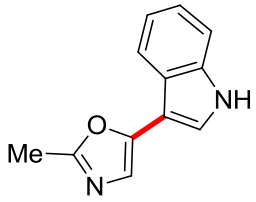
5-(1H-indol-3-yl)-2-propyloxazole-4-carboxylic acid (5b)



This compound was obtained as a grey solid (265 mg, 98% yield): mp 228-230 ℃; ^{1}H NMR (300 MHz, d_6-DMSO) δ 12.06 (s, 1H), 8.68 (d, *J* = 2.3 Hz, 1H), 8.09 (d, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.14 (m, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 1.94 – 1.76 (sex, *J* = 7.3 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, d_6-DMSO) δ 164.3, 160.7, 153.9, 136.4, 130.1, 125.3, 123.4, 122.8, 121.2, 120.9, 112.8, 103.0, 29.5, 20.4, 13.9; IR(KBr) 3554, 3455, 3381, 3157, 2964, 2874, 1664, 1560, 1486, 1459, 1409, 1358, 1329, 1271, 1240, 1116, 1095, 951, 761, 743, 712 cm^{-1}; MS-ES: *m/z*: 269.1[M-H]$^{-}$; HRMS (ESI^{+}): calcd for $C_{15}H_{14}N_2O_3Na$ $[M+Na]^{+}$ 293.0902, found 293.0910.

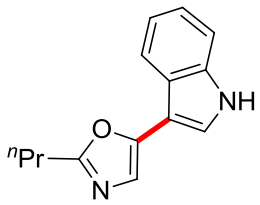
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with Ag_2CO_3 (20 mol %), PivOH (50 mol %), **5a or 5b** (0.5 mmol), and DMSO (1 mL). After stirring at 120 ^{o}C for 12 hours, the reaction mixture was cooled to room temperature, diluted with EtOAc (20 mL), filtered through a Celite pad, and wash with EtOAc (10-20 mL). The organic extracts were concentrated, and the resulting residue was purified by column chromatography on silica gel to afford the desired product **6a or 6b**.

5-(1H-indol-3-yl)-2-methyloxazole (Pimprinine, 6a)



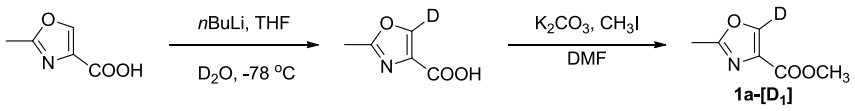
This compound was obtained as a pale yellow solid (54 mg, 55% yield): mp 200-201 ℃; ^{1}H NMR (300 MHz, d_6-DMSO) δ 11.50 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 2.6 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.15 – 7.07 (m, 1H), 2.46 (s, 3H).; ^{13}C NMR (75 MHz, d_6-DMSO) δ 158.2, 147.3, 136.3, 123.8, 122.8, 122.0, 119.9, 119.4, 119.2, 112.0, 103.9, 13.5; IR(KBr) 3133, 3109, 2930, 2896, 1638, 1585, 1453, 1360, 1248, 1123, 1027, 771, 735 cm^{-1}; HRMS (ESI^{+}): calcd for $C_{12}H_{11}N_2O$ $[M+H]^{+}$ 199.0866, found 199.0867.

5-(1H-indol-3-yl)-2-propyloxazole (WS-30581 A, 6b)

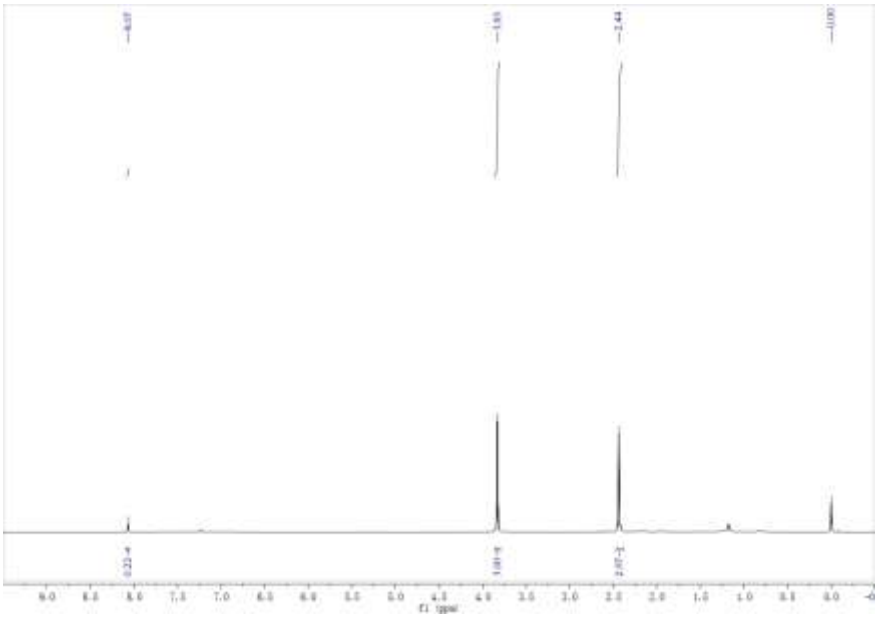


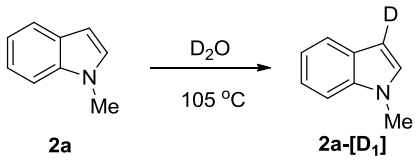
This compound was obtained as a pale yellow solid (59mg, 52% yield): mp 96-98 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 2.5 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.33 – 7.27 (m, 1H), 7.26 – 7.21 (m, 1H), 7.17 (s, 1H), 2.84 (t, *J* = 7.5 Hz, 2H), 1.88 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 147.7, 136.5, 124.2, 122.9, 122.0, 120.7, 119.9, 119.4, 111.8, 105.6, 77.6, 77.2, 76.7, 30.2, 20.7, 13.8; IR(KBr) 3414, 3129, 2932, 2875, 1636, 1571, 1448, 1251, 1119, 1003, 778, 736, 638 cm^{-1}; HRMS (ESI^{+}): calcd for $C_{14}H_{13}N_2O$ $[M-H]^{-}$ 225.1028, found 225.1034.

5. KIE experiment



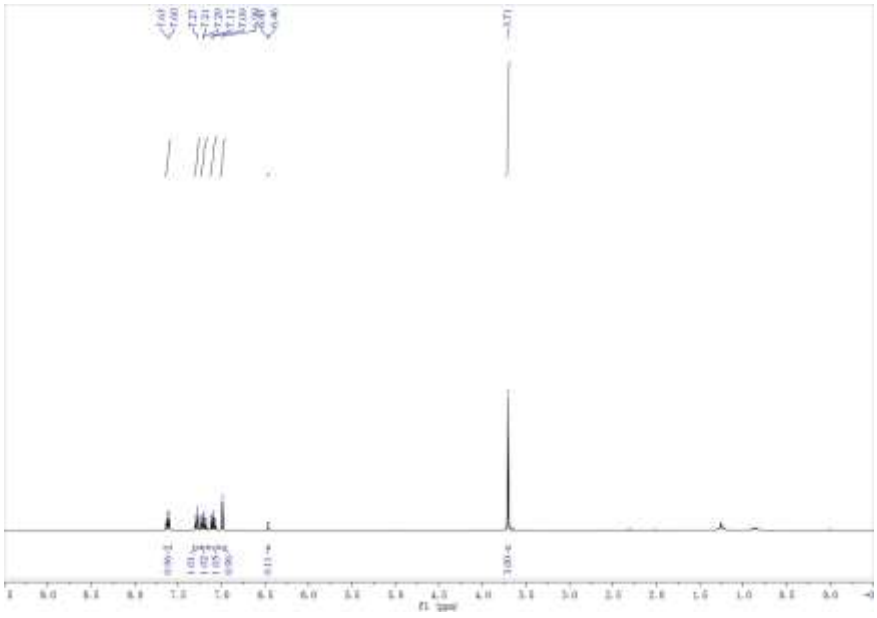
Preparation of 5-deutero-2-methyloxazole-4-carboxylate (1a-[D_1]): A stirred solution of 2-methyloxazole-4-carboxylic acid (5 mmol) in dry THF (10 mL) under argon was cooled to -78 °C and 12 mmol *n*BuLi in hexane was added dropwise. The solution was quenched with D_2O (1.0 mL) after 30 minutes. The mixture was concentrated in vacuo and acidified with 1 M HCl to precipitate the carboxylic acid (4 mmol). The 5-deutero-2-methyloxazole-4-carboxylic acid was suspended in DMF, K_2CO_3 (8 mmol) and CH_3I (8 mmol) were added for 2 hours. The suspension was extracted with ethyl acetate and washed with water three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The resulting residue was purified by column chromatography on silica gel to afford the desired product as a white soild in 65% yield. The product was 80% enriched with deuterium in the 3-position, as determined by ^{1}H NMR.

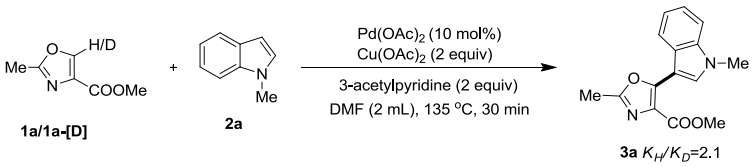




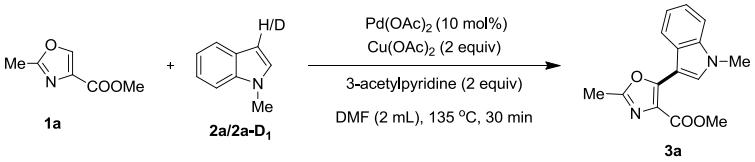
2a **2a-[D_1]**

Preparation of 3-deutero-1-methylindole: A flame-dried Schlenk test tube with a magnetic stirring bar was charged with N-methyl indole (500 mg) and D_2O (1 mL) under argon. After stirring at 105 ^oC for 12 hours, the reaction mixture was cooled to the room temperature, it is extracted with hexanes, and dried over Na_2SO_4. The solvent is removed and the final product was purified by distillation from molecular sieves. The product was 90% enriched with deuterium in the 3-position, as determined by ^1H NMR.





A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 1-methylindole (0.8 mmol), 2-methyloxazole-4-carboxylate **1a** (0.2 mmol) and 5-deutero-2-methyloxazole-4-carboxylate **1a-[D_1]** (0.2 mmol). After stirring at 135 ^{o}C for 30 minutes, the reaction mixture was cooled to the room temperature, diluted with CH_2Cl_2 (20 mL), filtered through a Celite pad, and washed with CH_2Cl_2 (10-20 mL). The organic extracts were concentrated. The yield of **3a** was determined by ^{1}H NMR.

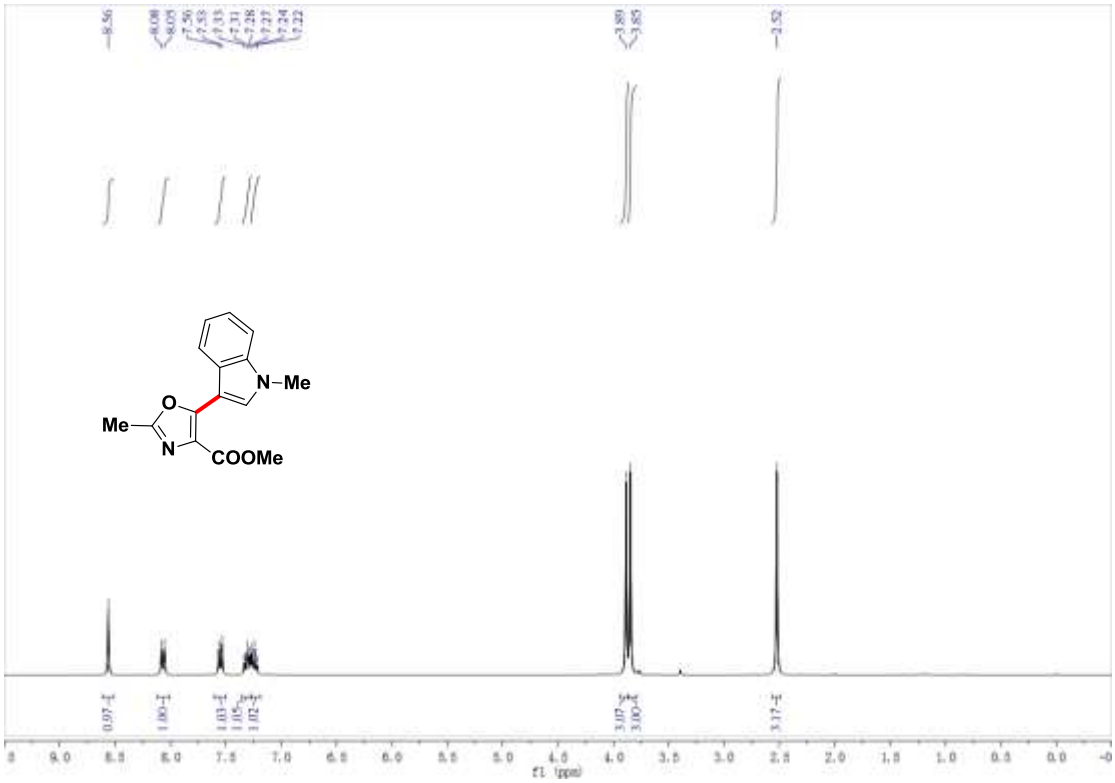


A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-methyloxazole-4-carboxylate **1a** (0.5 mmol), 1-methylindole **2a** (0.5 mmol) and 3-deutero-1-methylindole **2a-[D_1]** (0.5 mmol). After stirring at 135 ^{o}C for 30 minutes, the reaction mixture was cooled to the room temperature, diluted with CH_2Cl_2 (20 mL), filtered through a Celite pad, and washed with CH_2Cl_2 (10-20 mL). The organic extracts were concentrated. The yield of **3a** was determined by ^{1}H NMR.

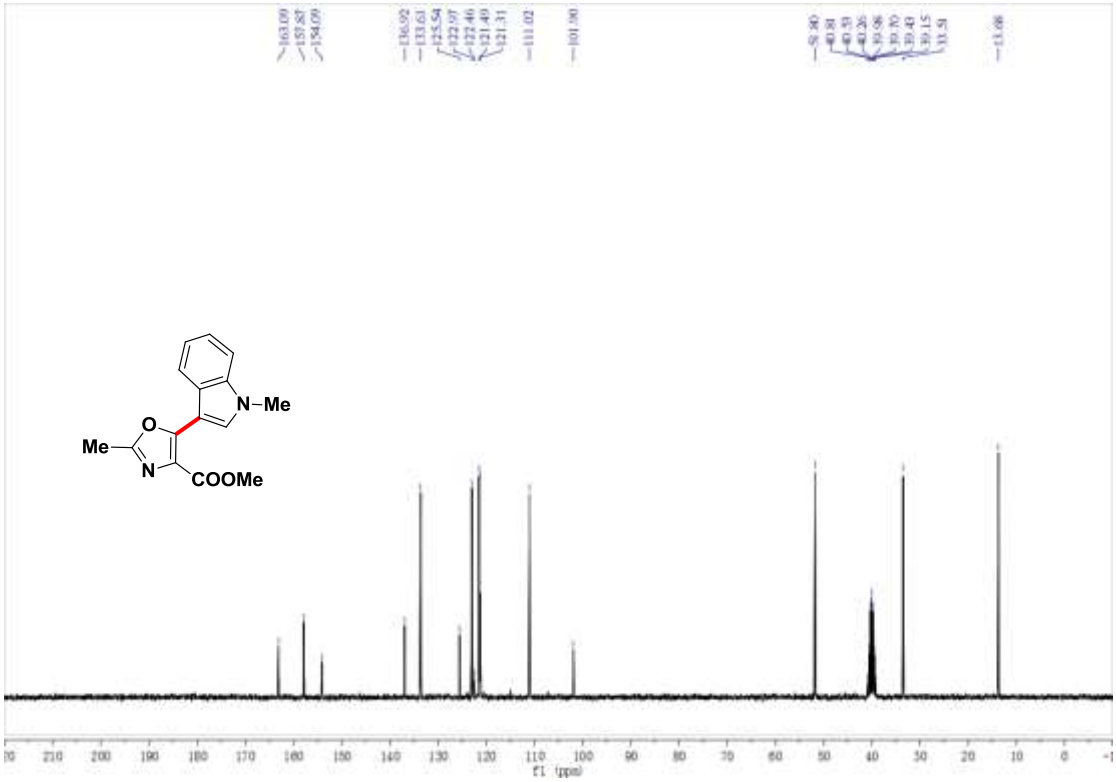
6.^{1}H NMR and ^{13}C NMR Spectra

Methyl 2-methyl-5-(1-methyl-1*H*-indol-3-yl)oxazole-4-carboxylate (3a)

^{1}H NMR (300 MHz, d_6-DMSO)

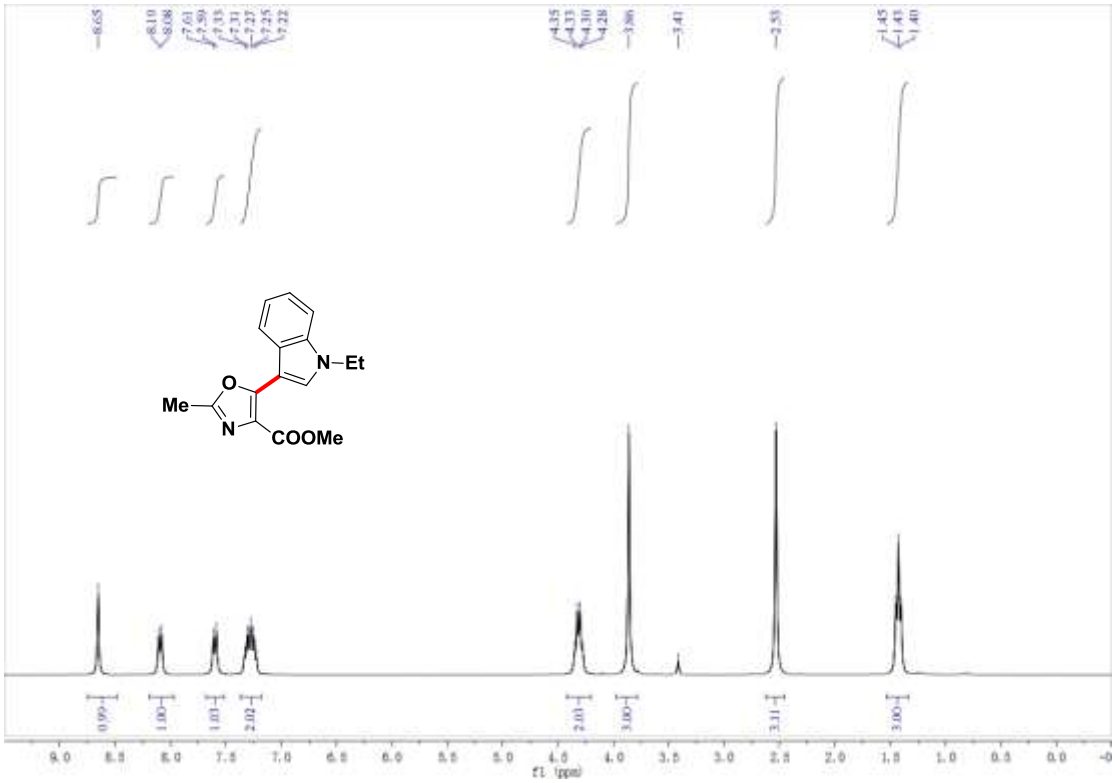


^{13}C NMR (75 MHz, d_6-DMSO)

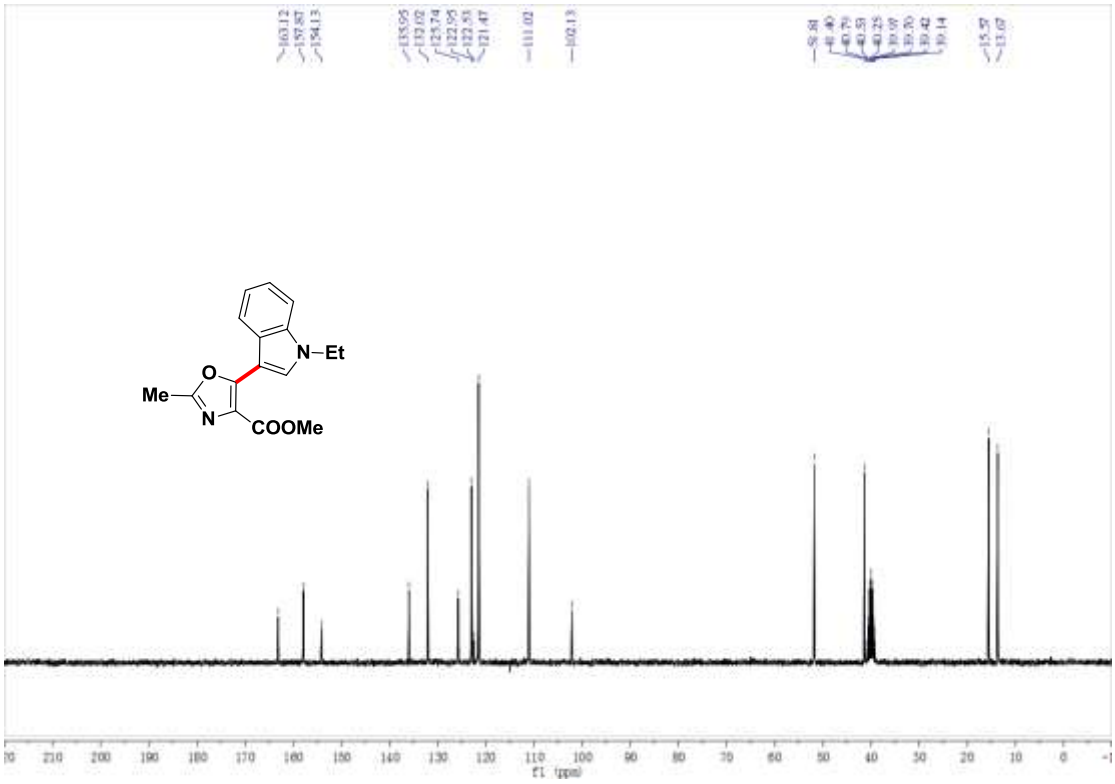


Methyl 5-(1-ethyl-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3b)

^{1}H NMR (300 MHz, d_6-DMSO)

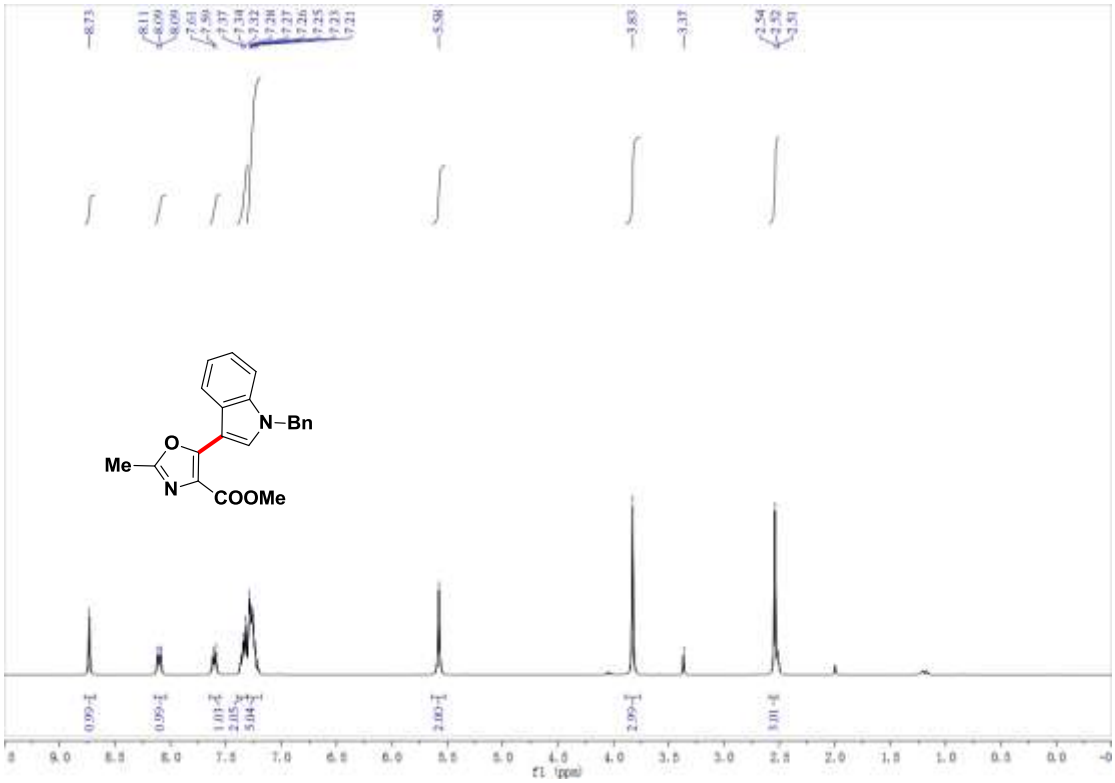


^{13}C NMR (75 MHz, d_6-DMSO)

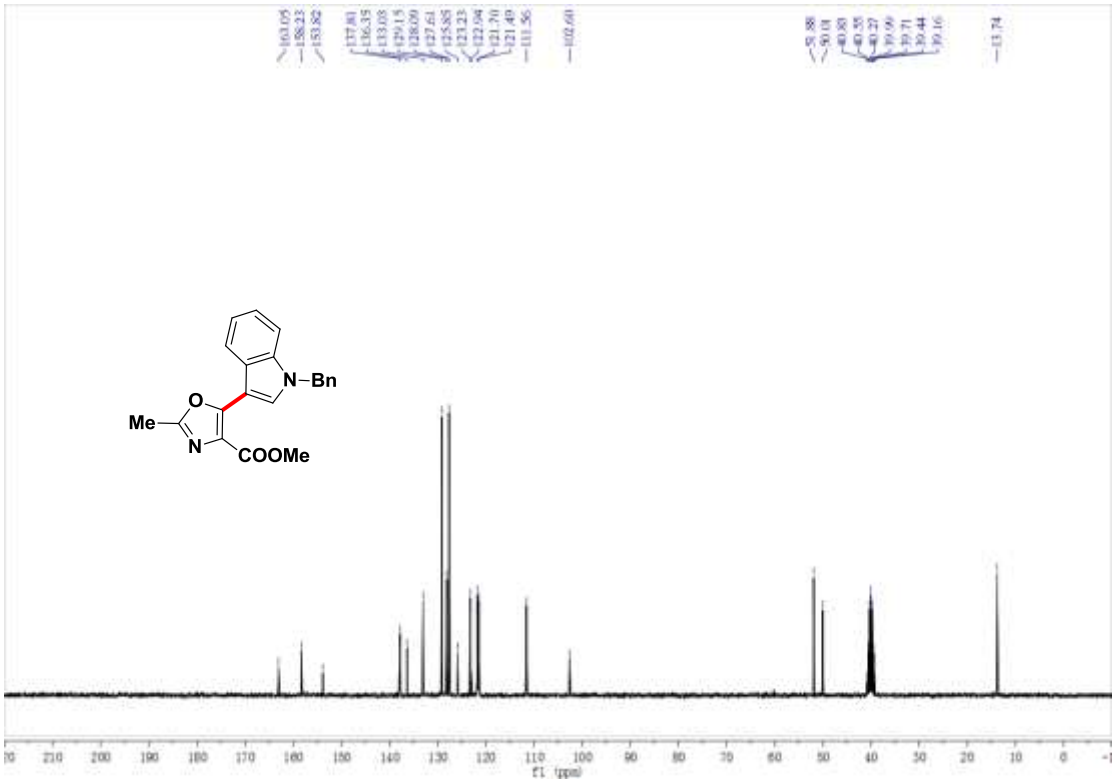


Methyl 5-(1-benzyl-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3c)

^{1}H NMR (300 MHz, d_6-DMSO)

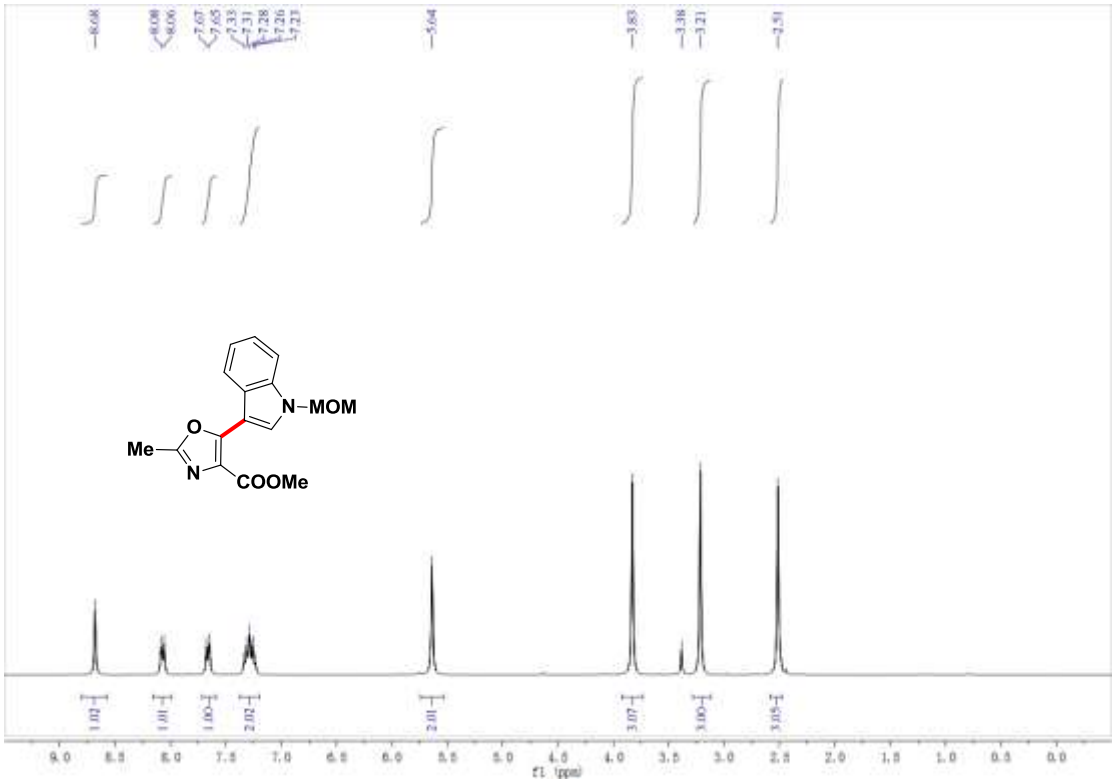


^{13}C NMR (75 MHz, d_6-DMSO)

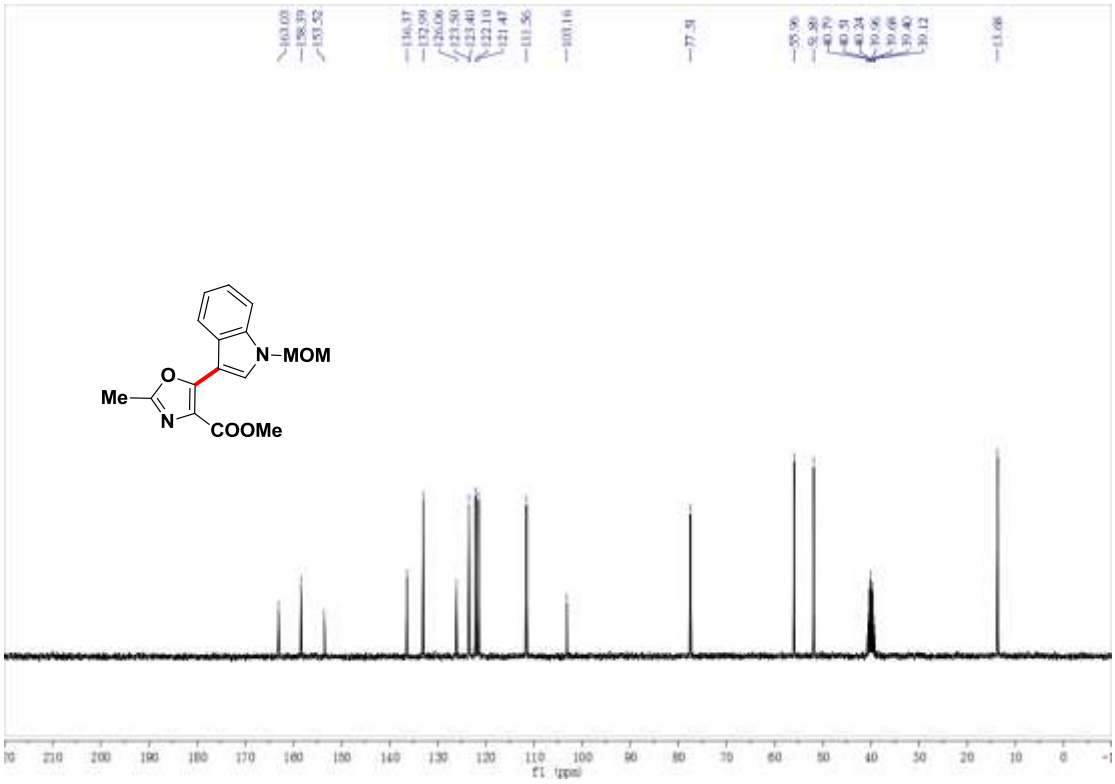


Methyl 5-(1-(methoxymethyl)-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3d)

^{1}H NMR (300 MHz, d_6-DMSO)

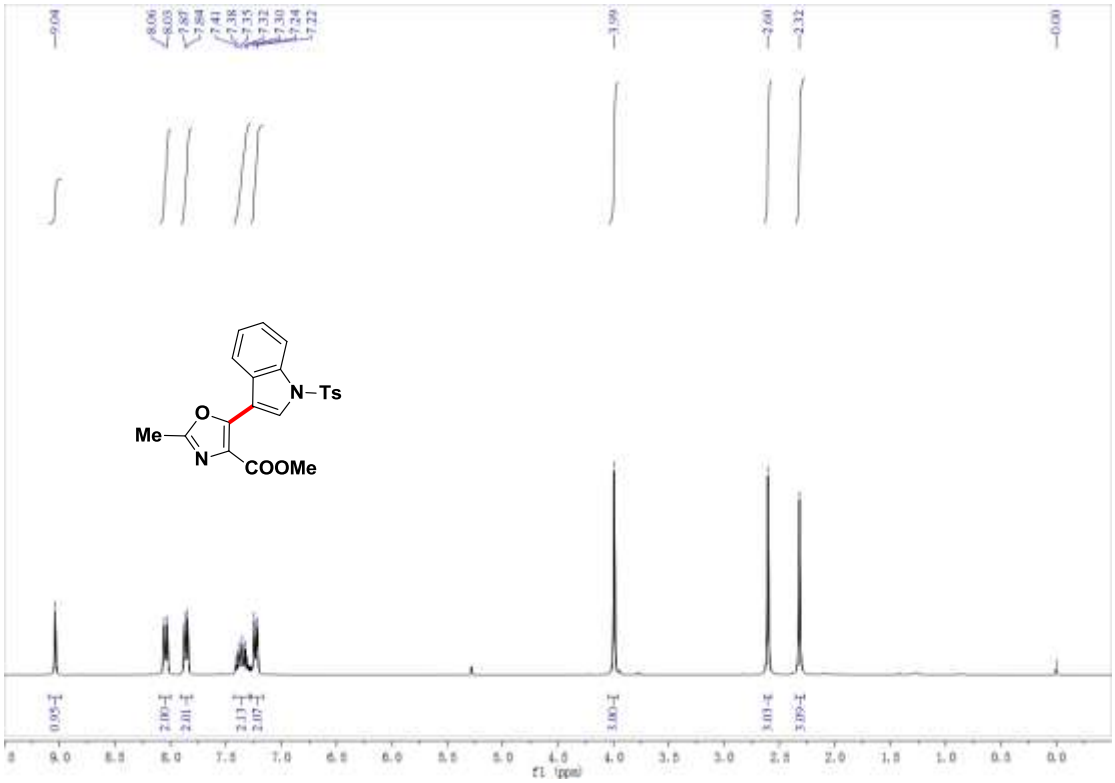


^{13}C NMR (75 MHz, d_6-DMSO)

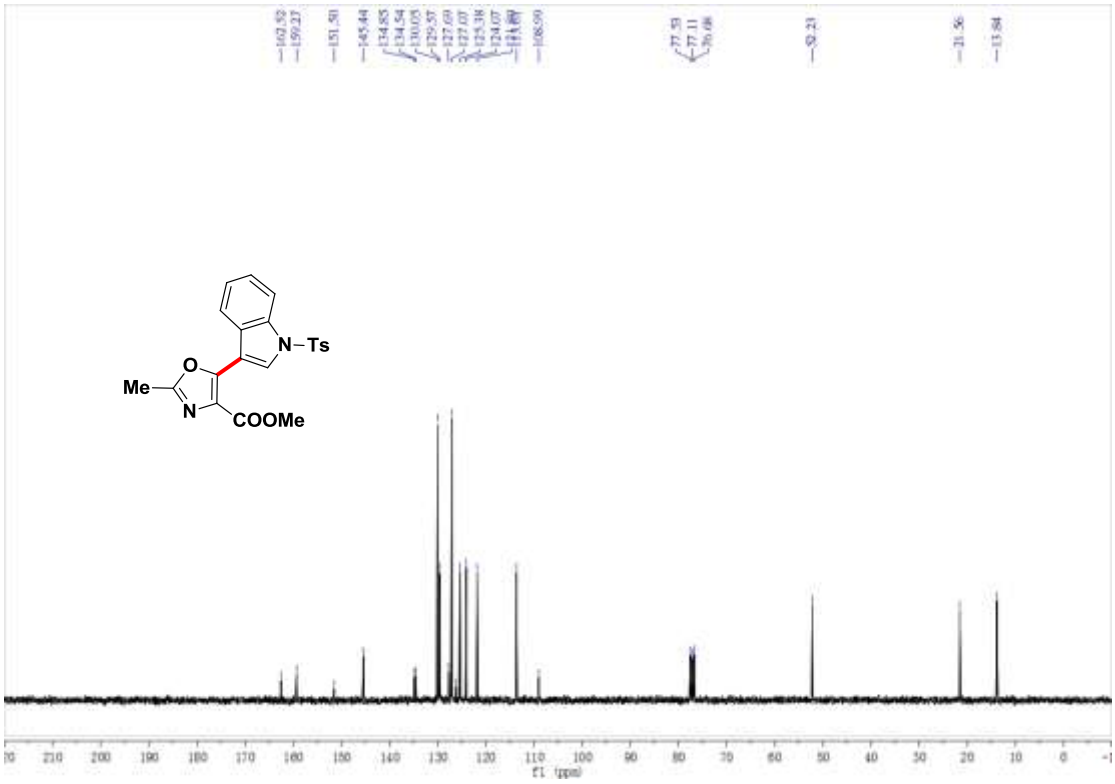


Methyl 2-methyl-5-(1-tosyl-1*H*-indol-3-yl)oxazole-4-carboxylate (3e)

^{1}H NMR (300 MHz, $CDCl_3$)

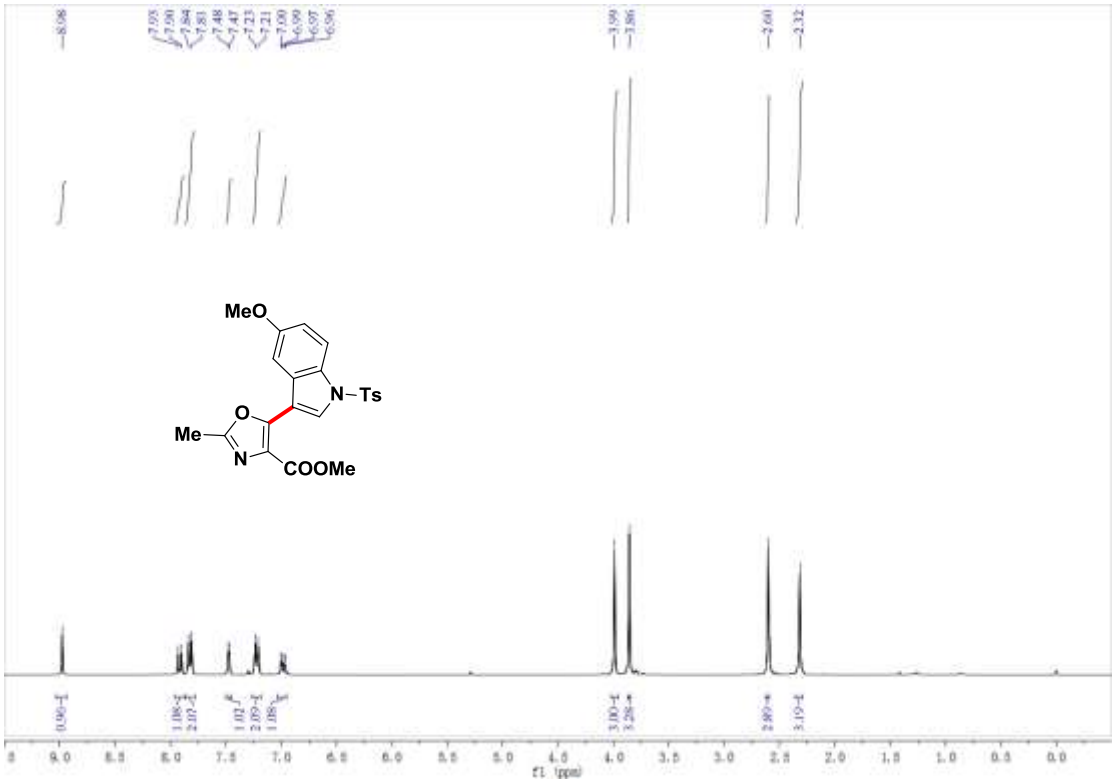


^{13}C NMR (75 MHz, $CDCl_3$)

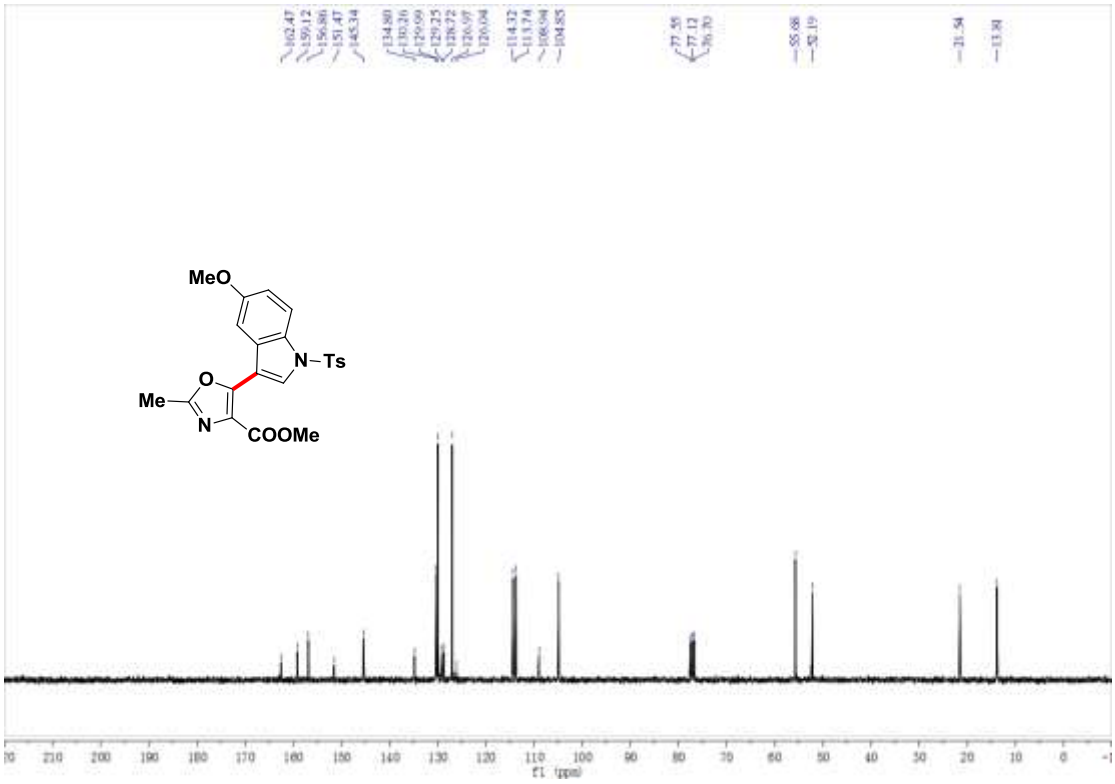


Methyl 5-(5-methoxy-1-tosyl-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3f)

^{1}H NMR (300 MHz, $CDCl_3$)

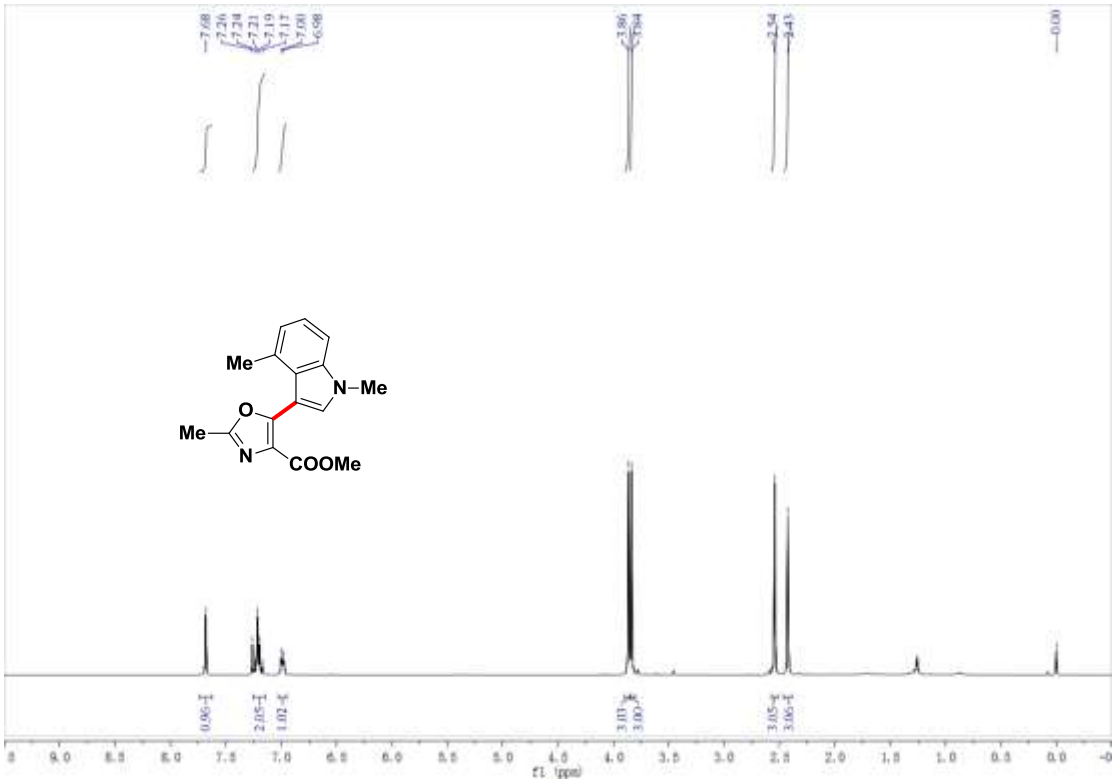


^{13}C NMR (75 MHz, $CDCl_3$)

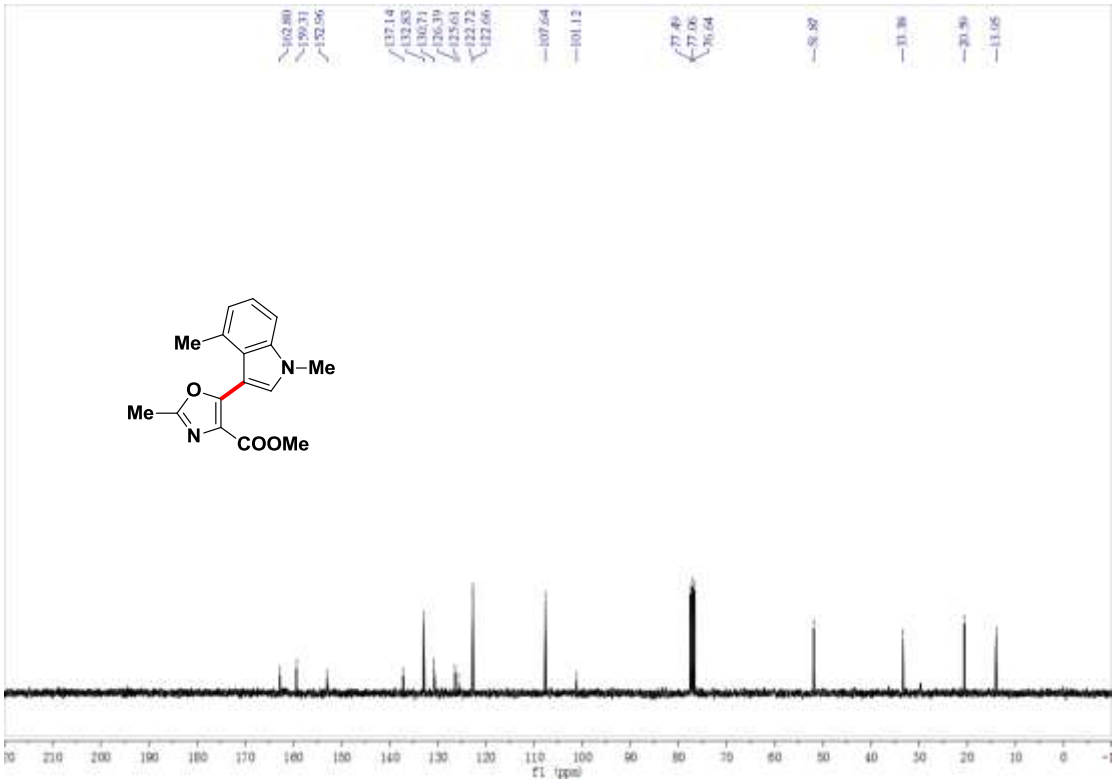


Methyl 5-(1,4-dimethyl-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3g)

^{1}H NMR (300 MHz, $CDCl_3$)

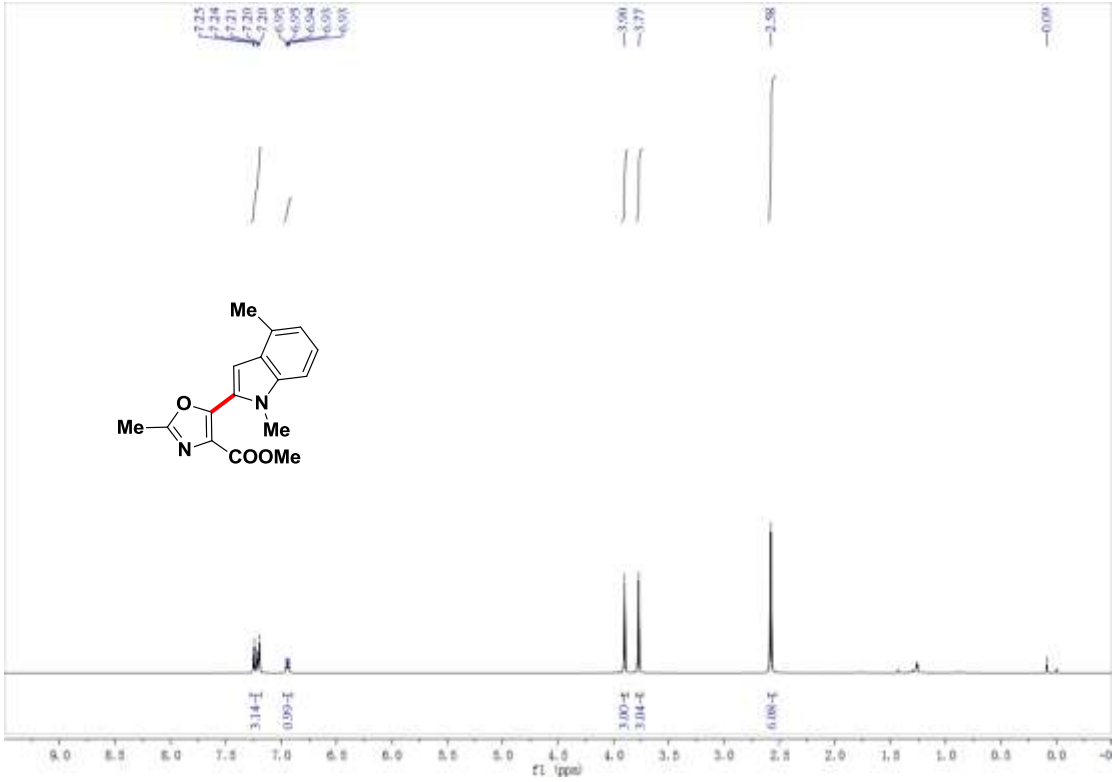


^{13}C NMR (75 MHz, $CDCl_3$)

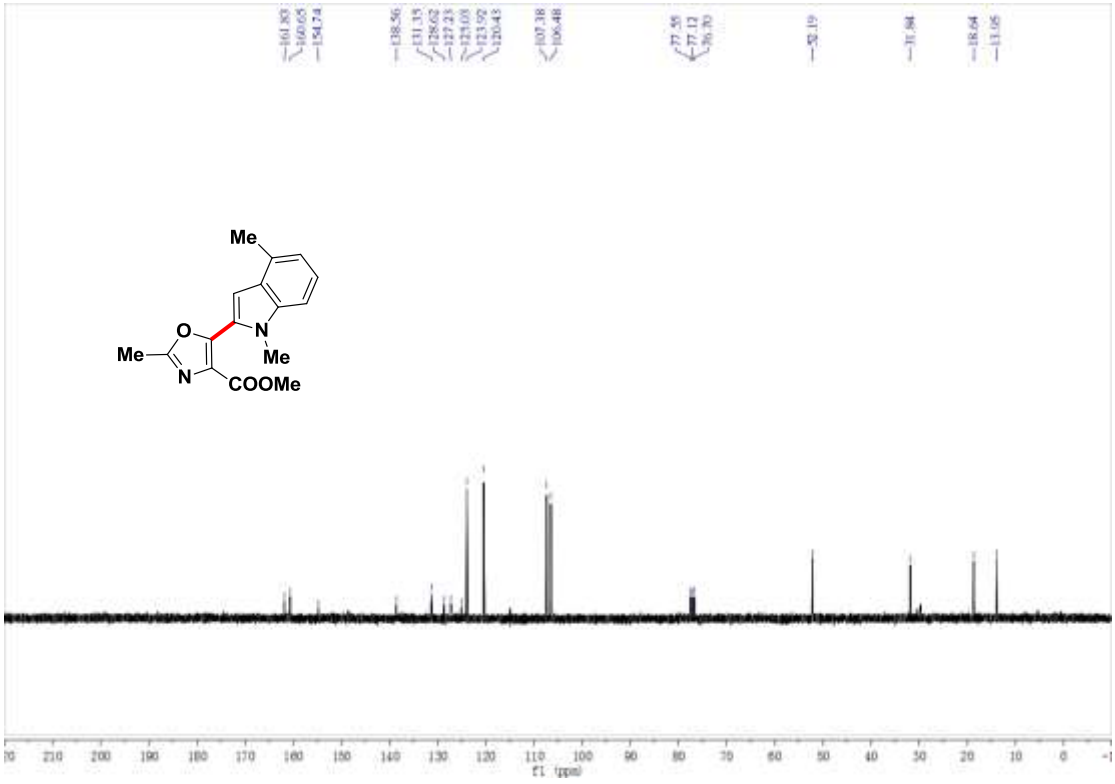


Methyl 5-(1, 4-dimethyl-1*H*-indol-2-yl)-2-methyloxazole-4-carboxylate (3g')

^{1}H NMR (300 MHz, $CDCl_3$)

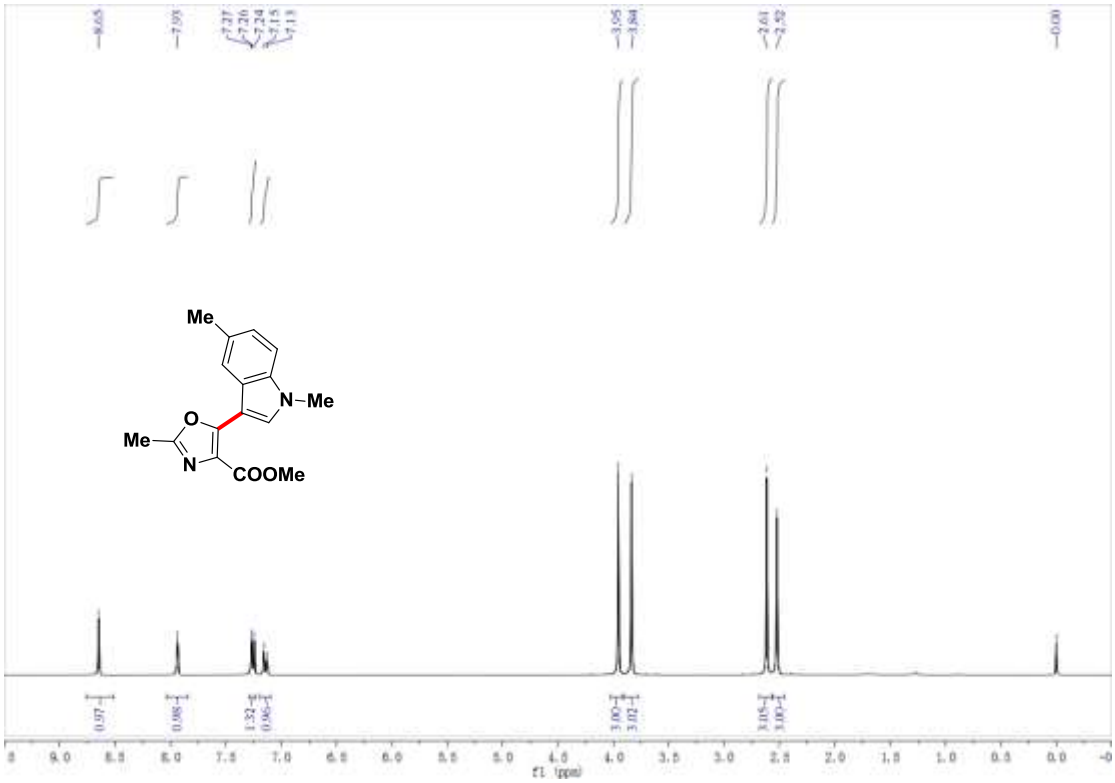


^{13}C NMR (75 MHz, $CDCl_3$)

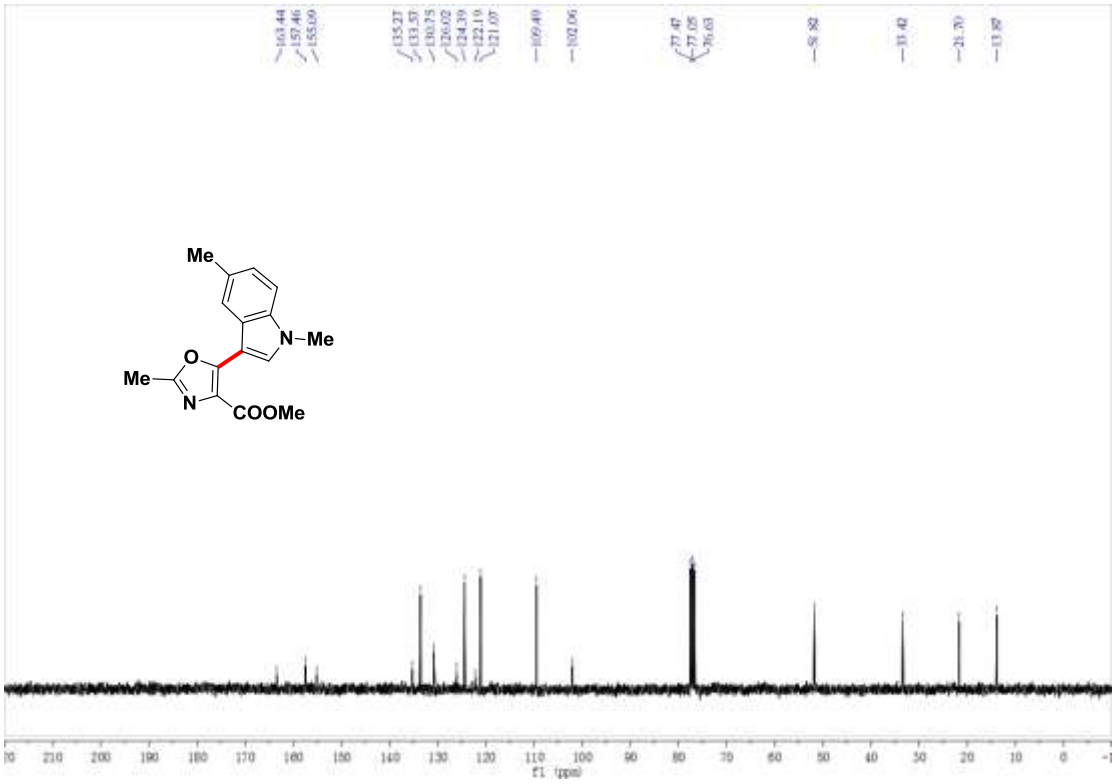


Methyl 5-(1, 5-dimethyl-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3h)

^{1}H NMR (300 MHz, $CDCl_3$)

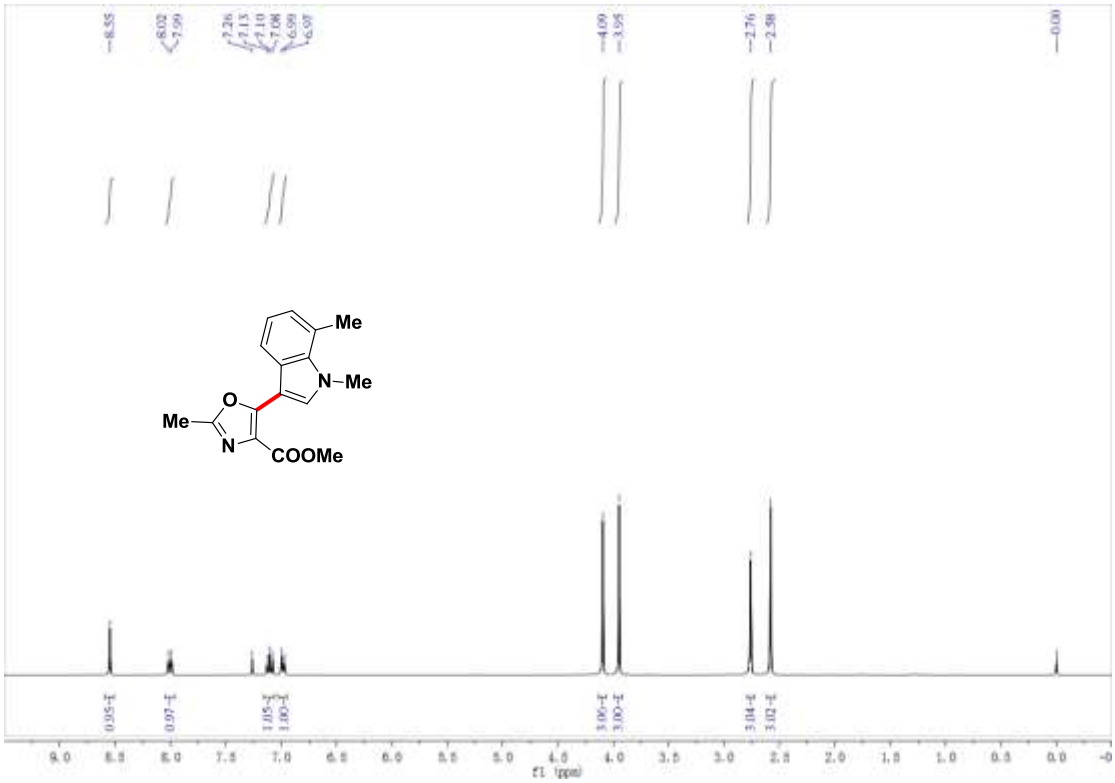


^{13}C NMR (75 MHz, $CDCl_3$)

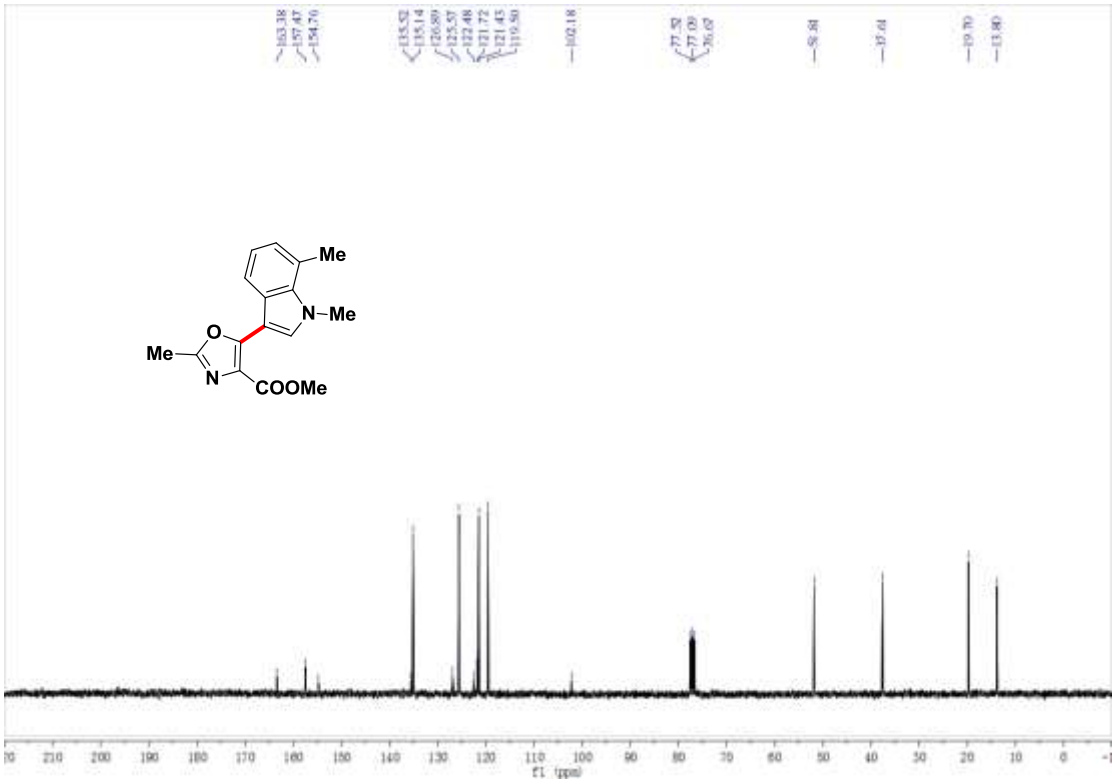


Methyl 5-(1, 7-dimethyl-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3i)

^{1}H NMR (300 MHz, $CDCl_3$)

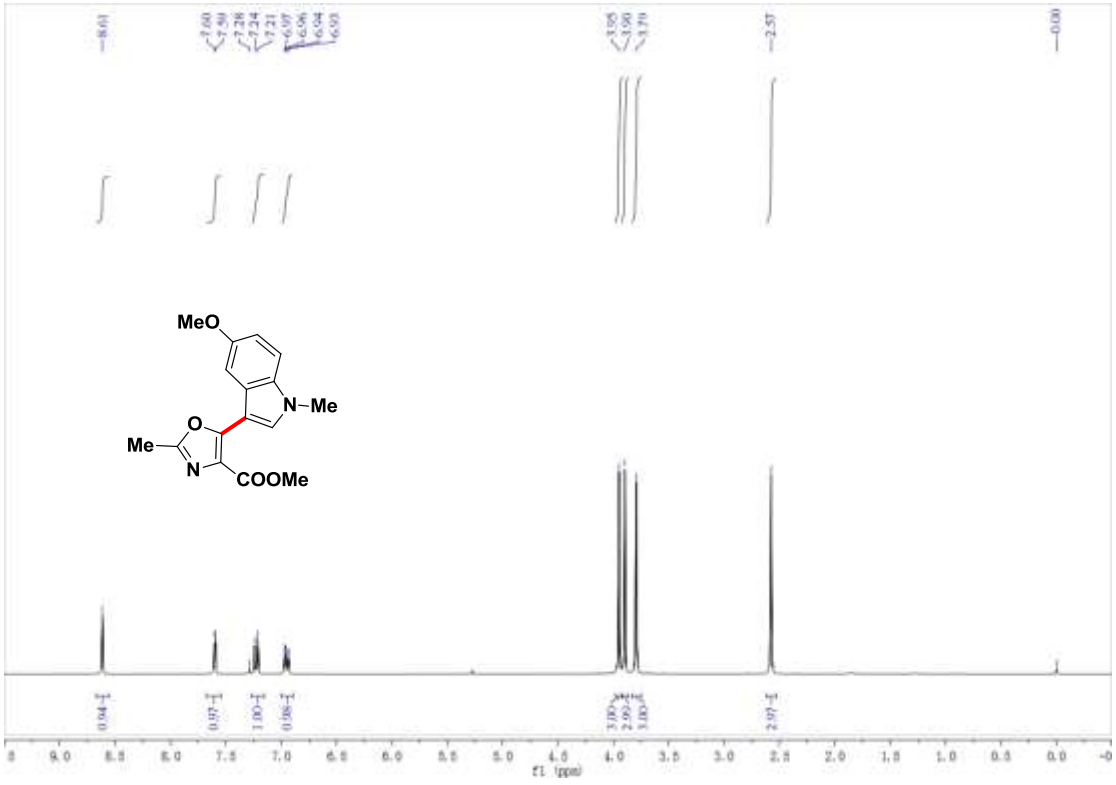


^{13}C NMR (75 MHz, $CDCl_3$)

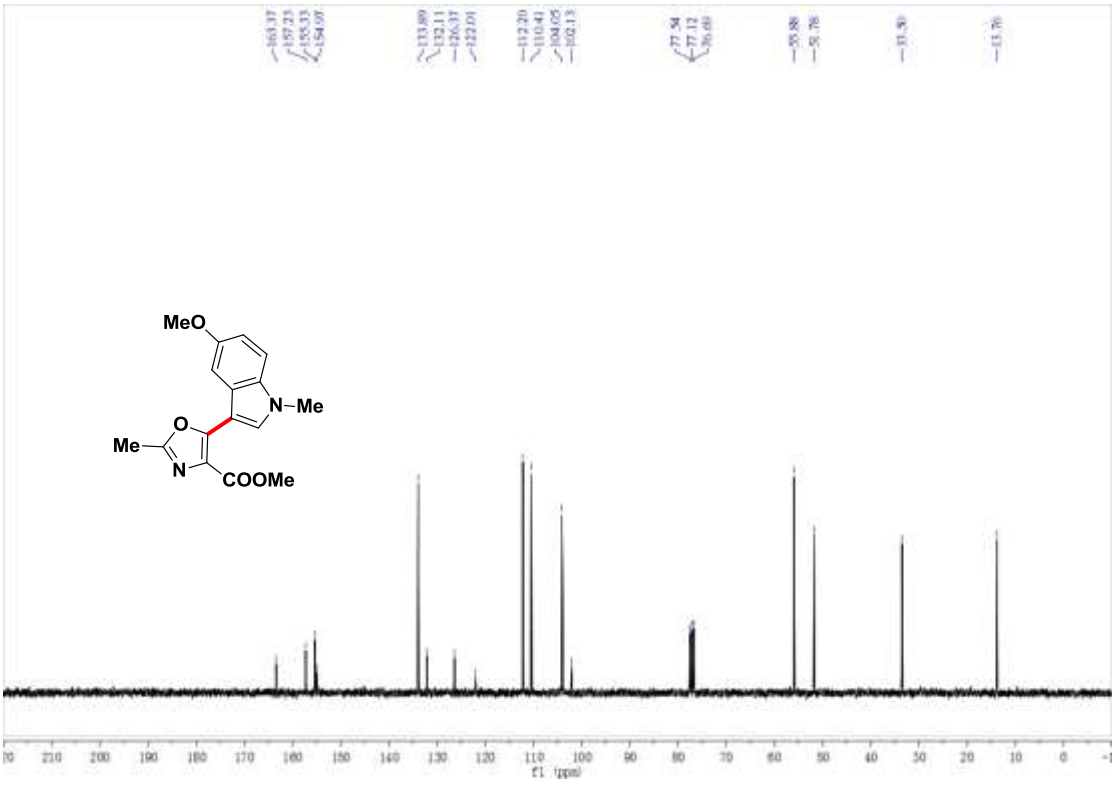


Methyl 5-(5-methoxy-1-methyl-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3j)

^{1}H NMR (300 MHz, $CDCl_3$)

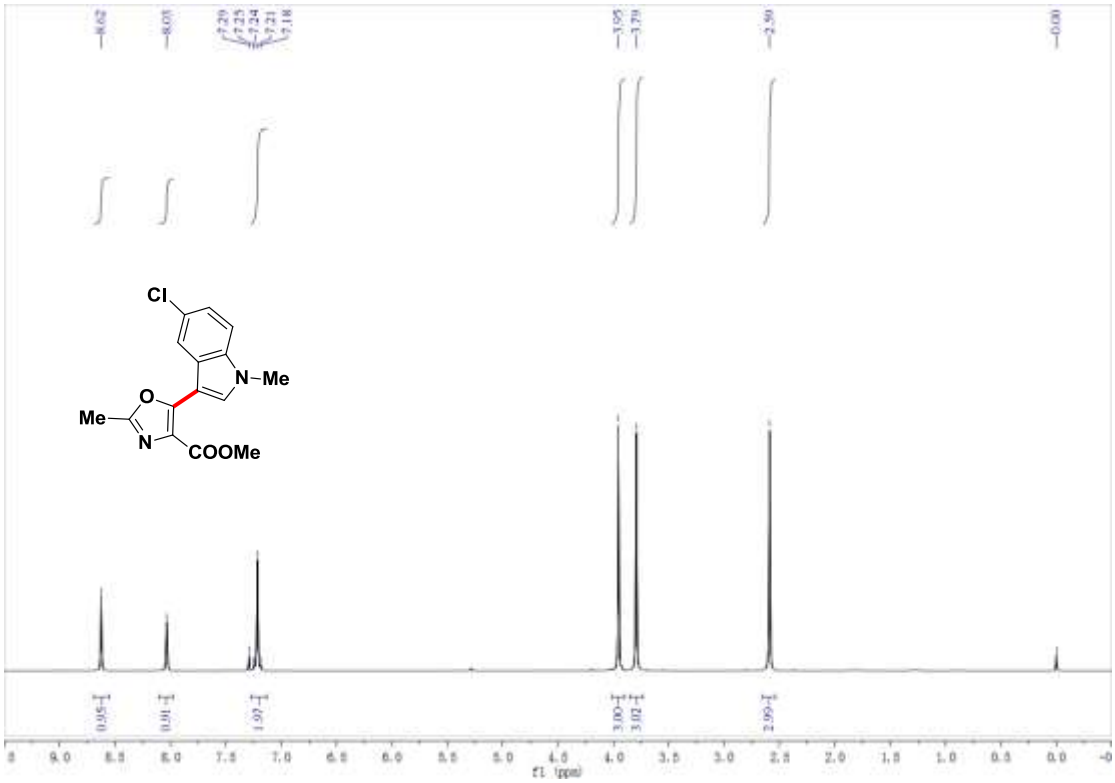


^{13}C NMR (75 MHz, $CDCl_3$)

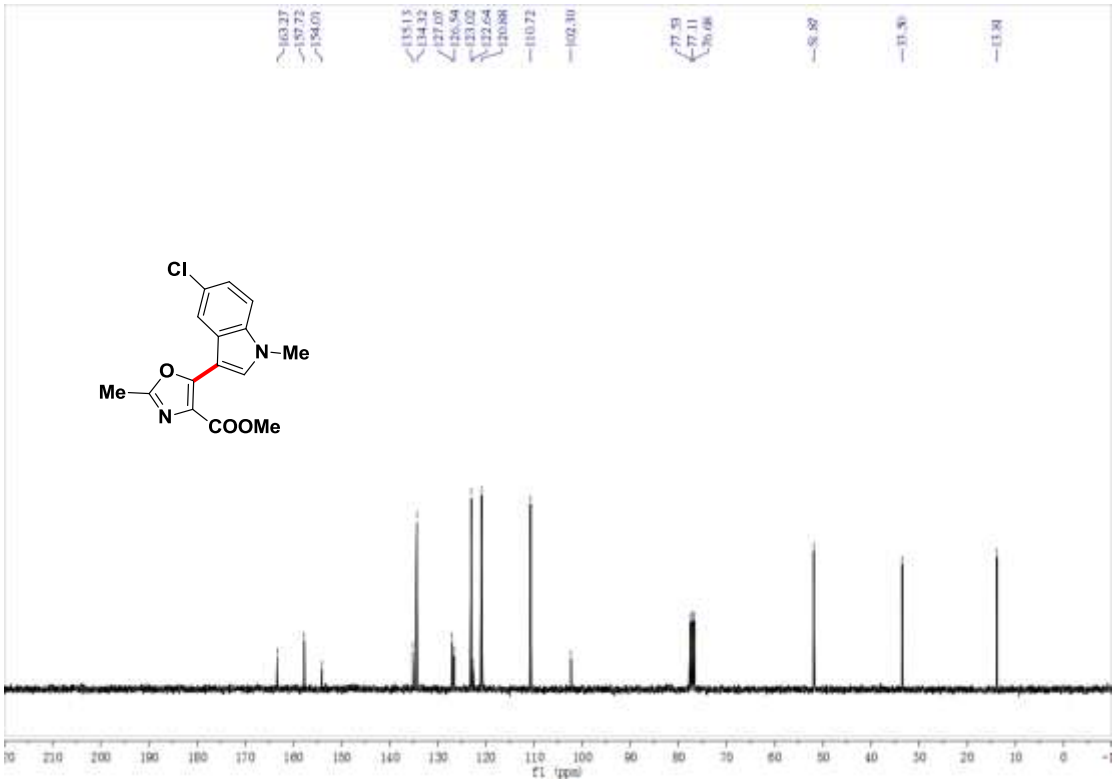


Methyl 5-(5-chloro-1-methyl-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3k)

^{1}H NMR (300 MHz, $CDCl_3$)

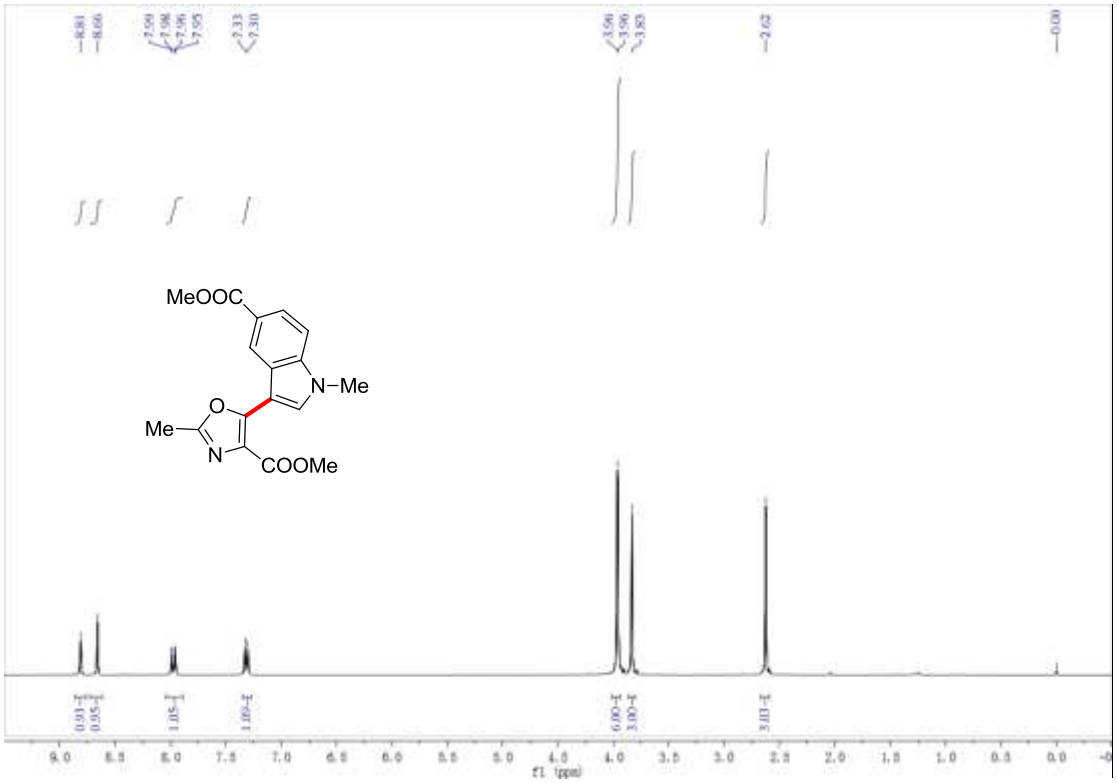


^{13}C NMR (75 MHz, $CDCl_3$)

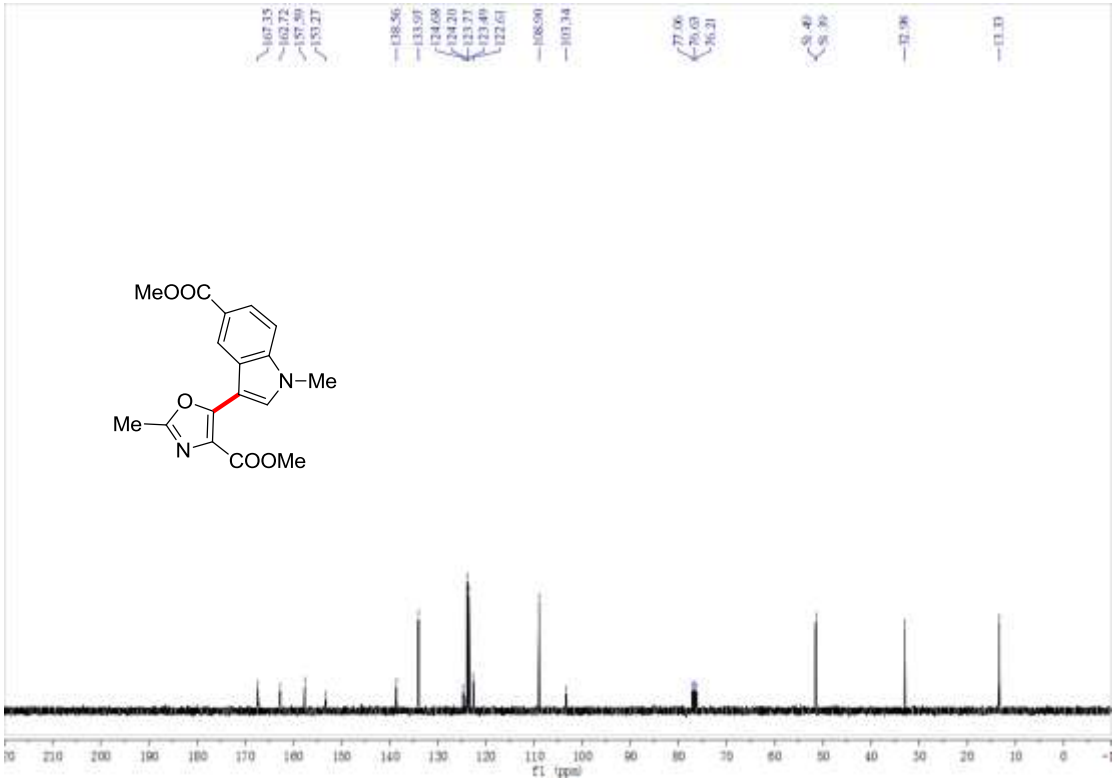


Methyl 5-(5-(methoxycarbonyl)-1-methyl-1*H*-indol-3-yl)-2-methyloxazole -4-carboxylate (3l)

^{1}H NMR (300 MHz, $CDCl_3$)

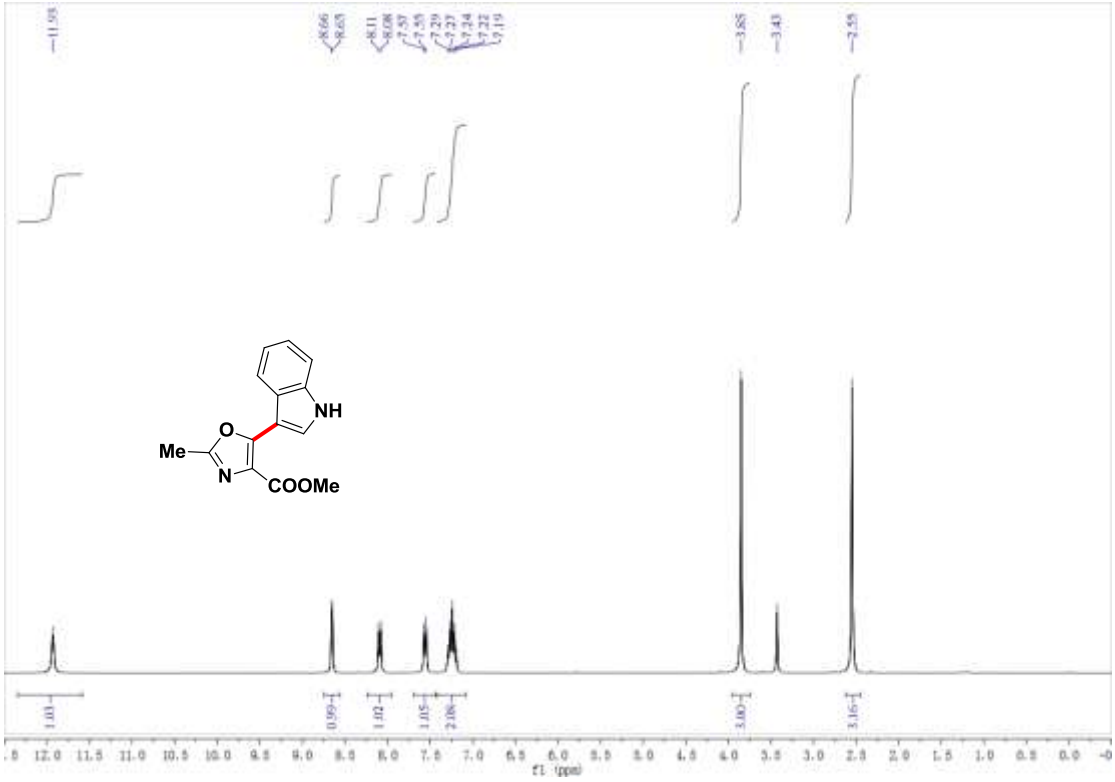


^{13}C NMR (75 MHz, $CDCl_3$)

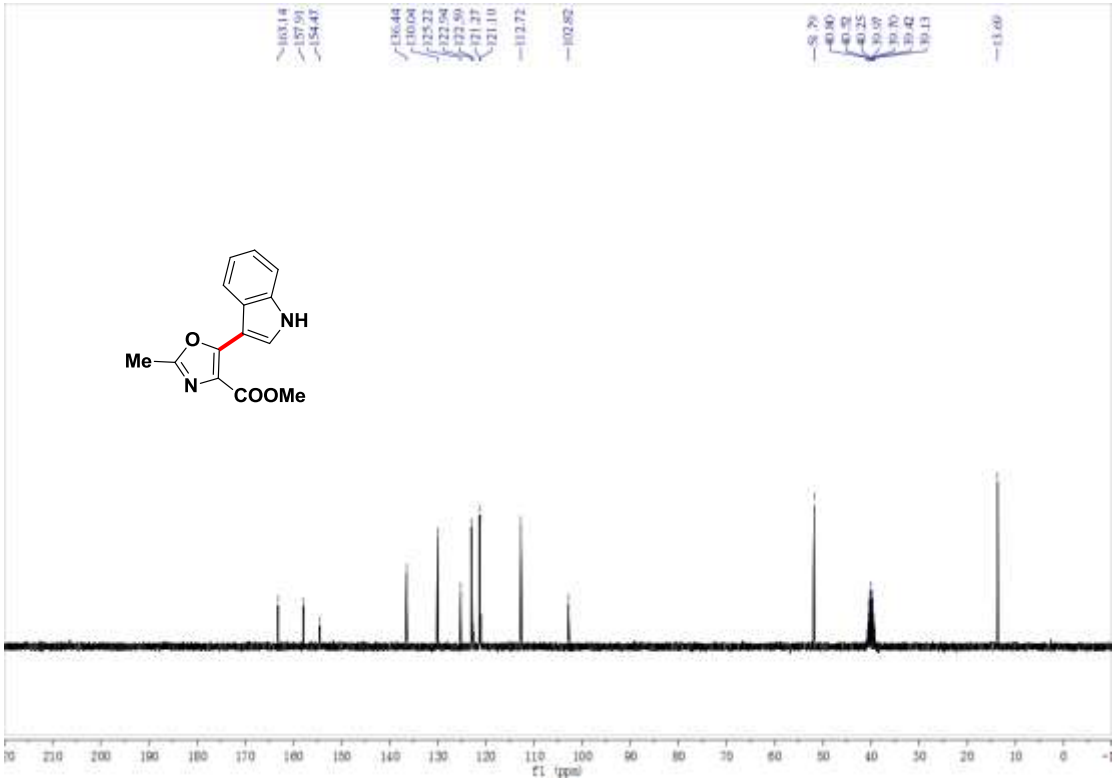


Methyl 5-(1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3m)

^{1}H NMR (300 MHz, d_6-DMSO)

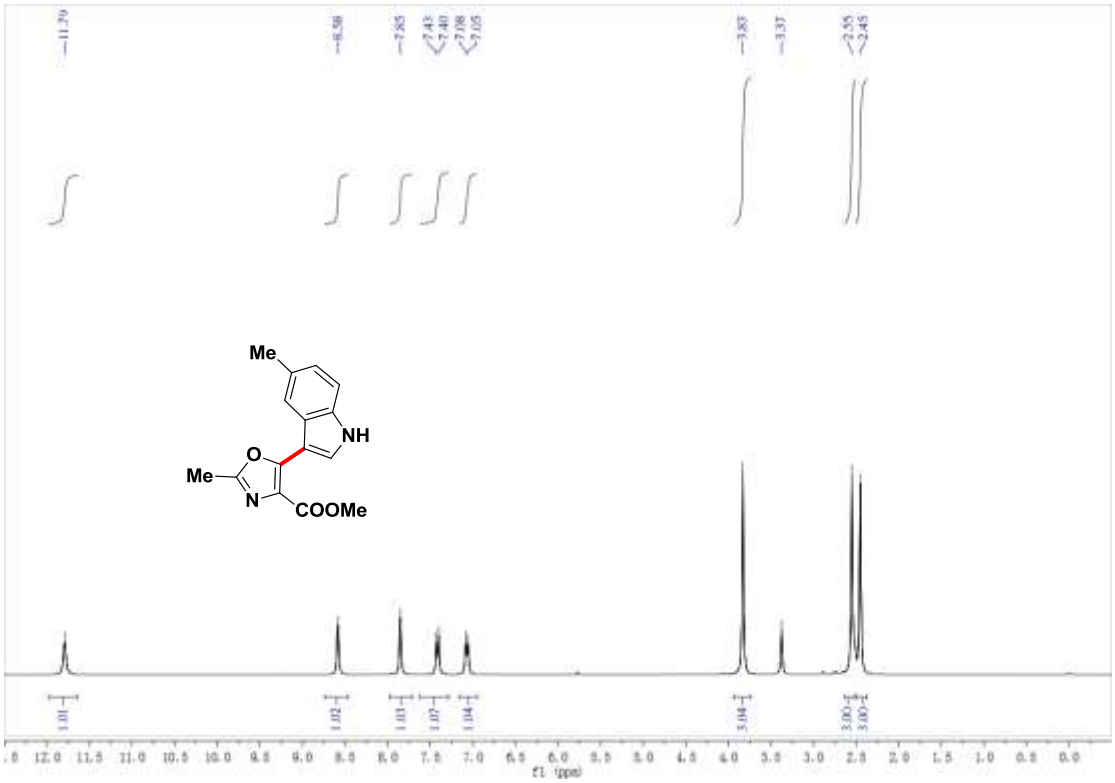


^{13}C NMR (75 MHz, d_6-DMSO)

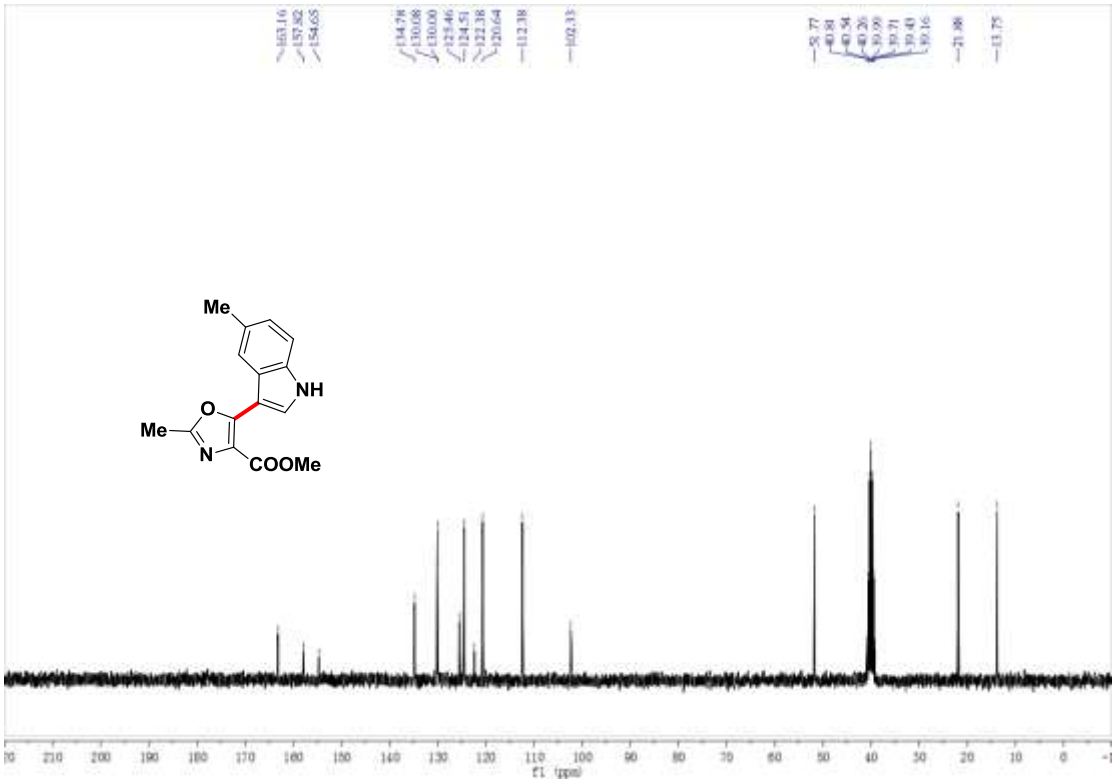


Methyl 2-methyl-5-(5-methyl-1*H*-indol-3-yl)oxazole-4-carboxylate (3n)

^{1}H NMR (300 MHz, d_6-DMSO)

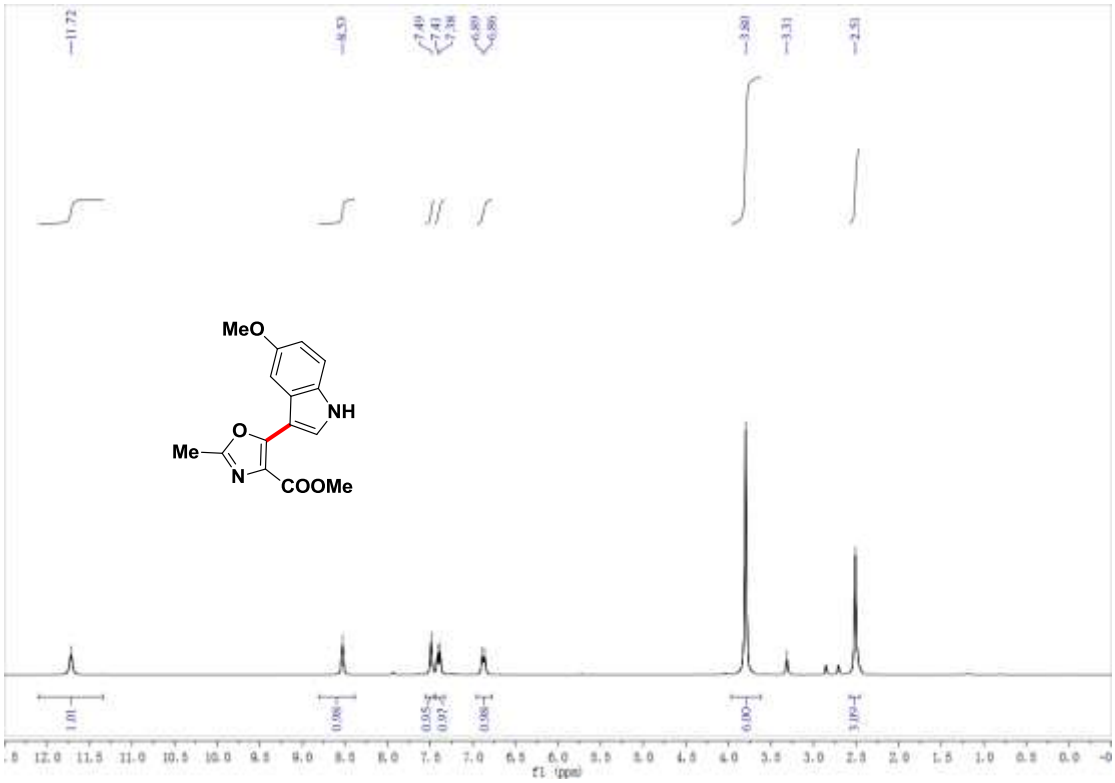


^{13}C NMR (75 MHz, d_6-DMSO)

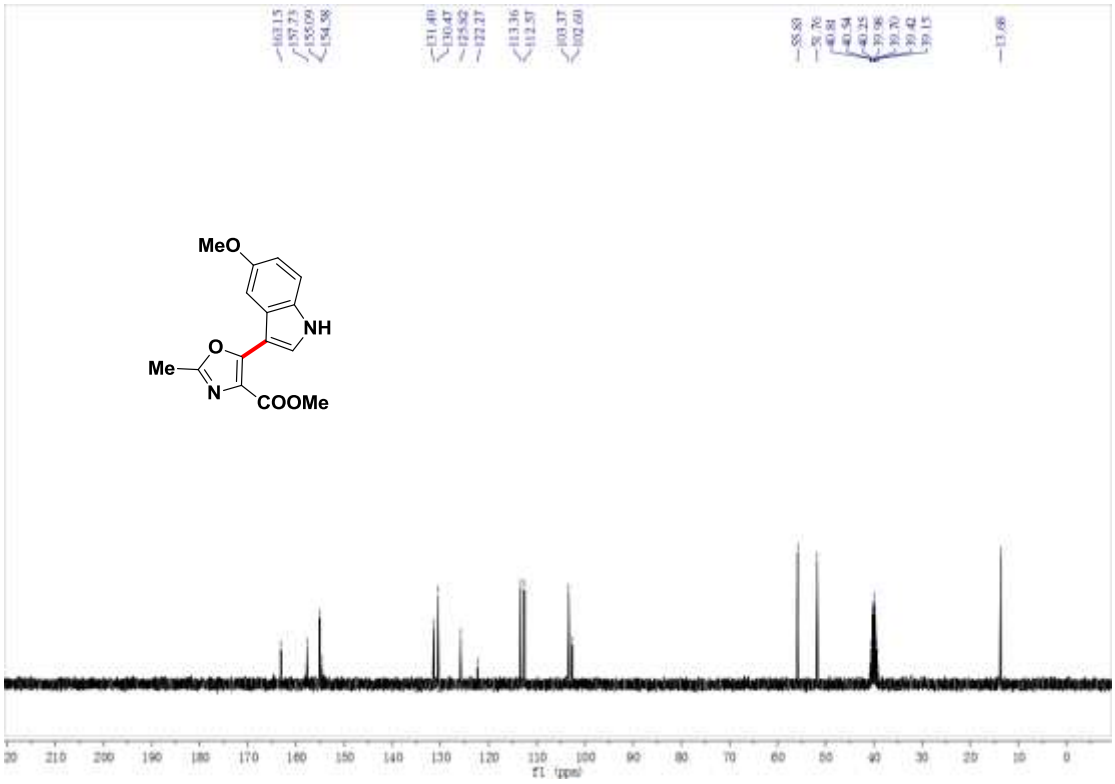


Methyl 5-(5-methoxy-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3o)

^{1}H NMR (300 MHz, d_6-DMSO)

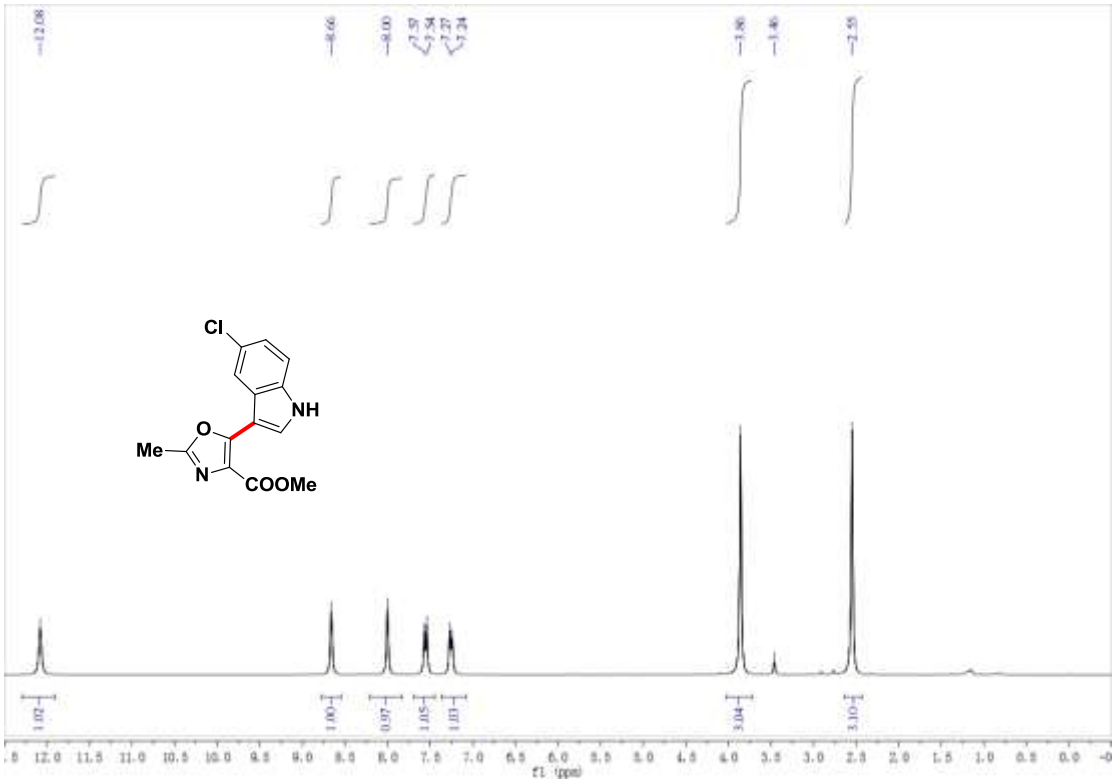


^{13}C NMR (75 MHz, d_6-DMSO)

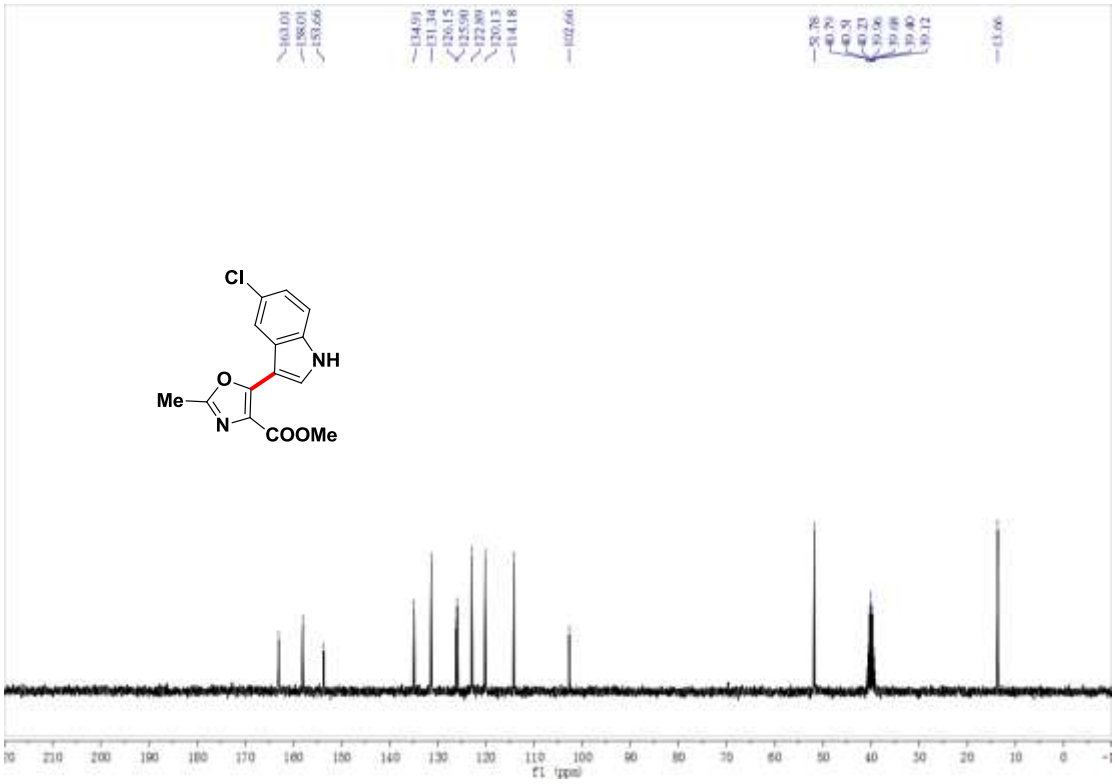


Methyl 5-(5-chloro-1*H*-indol-3-yl)-2-methyloxazole-4-carboxylate (3p)

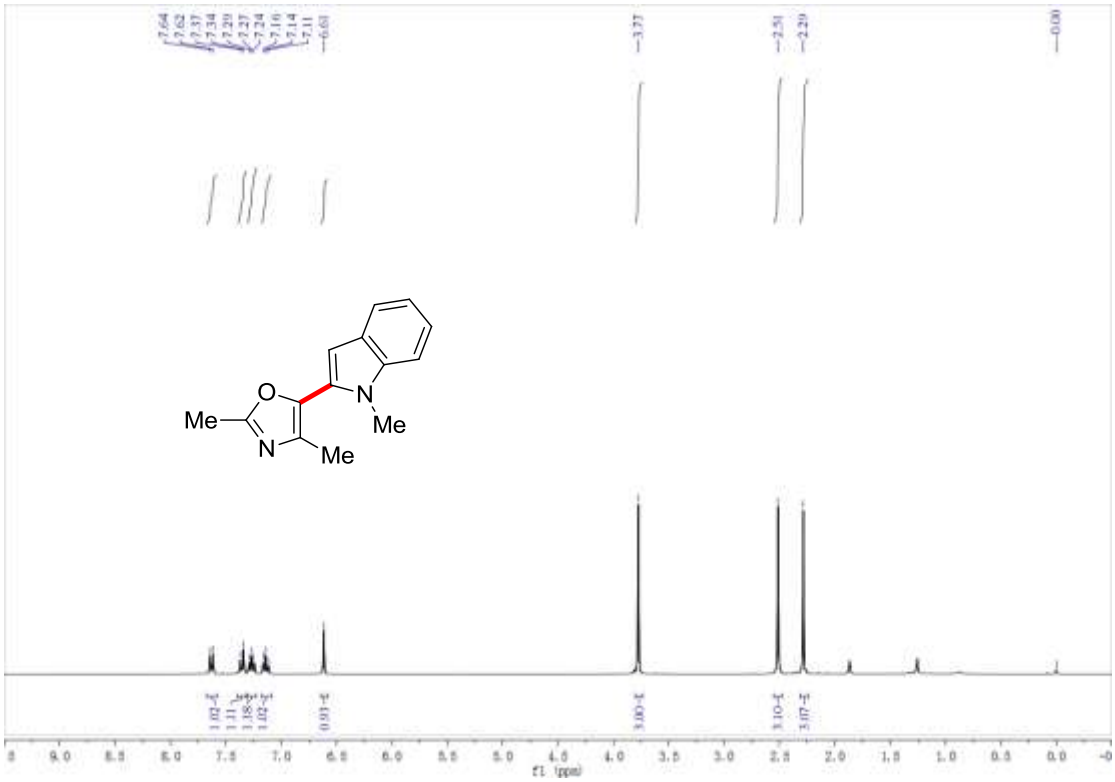
^{1}H NMR (300 MHz, d_6-DMSO)

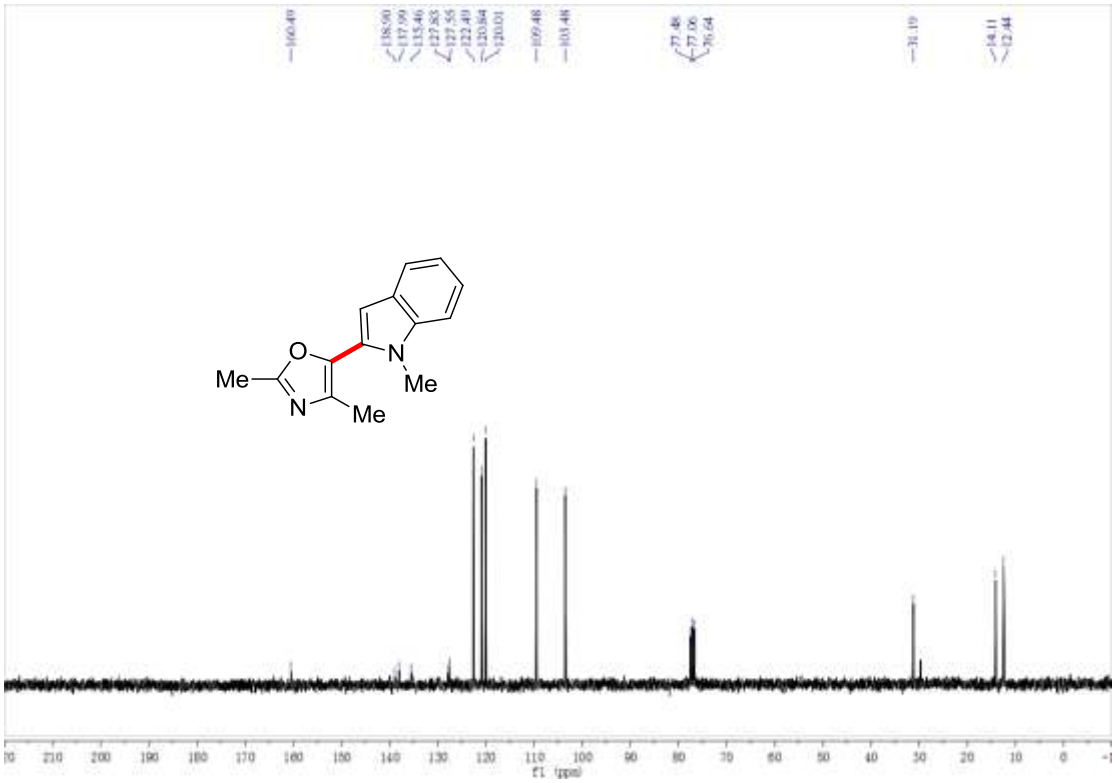


^{13}C NMR (75 MHz, d_6-DMSO)

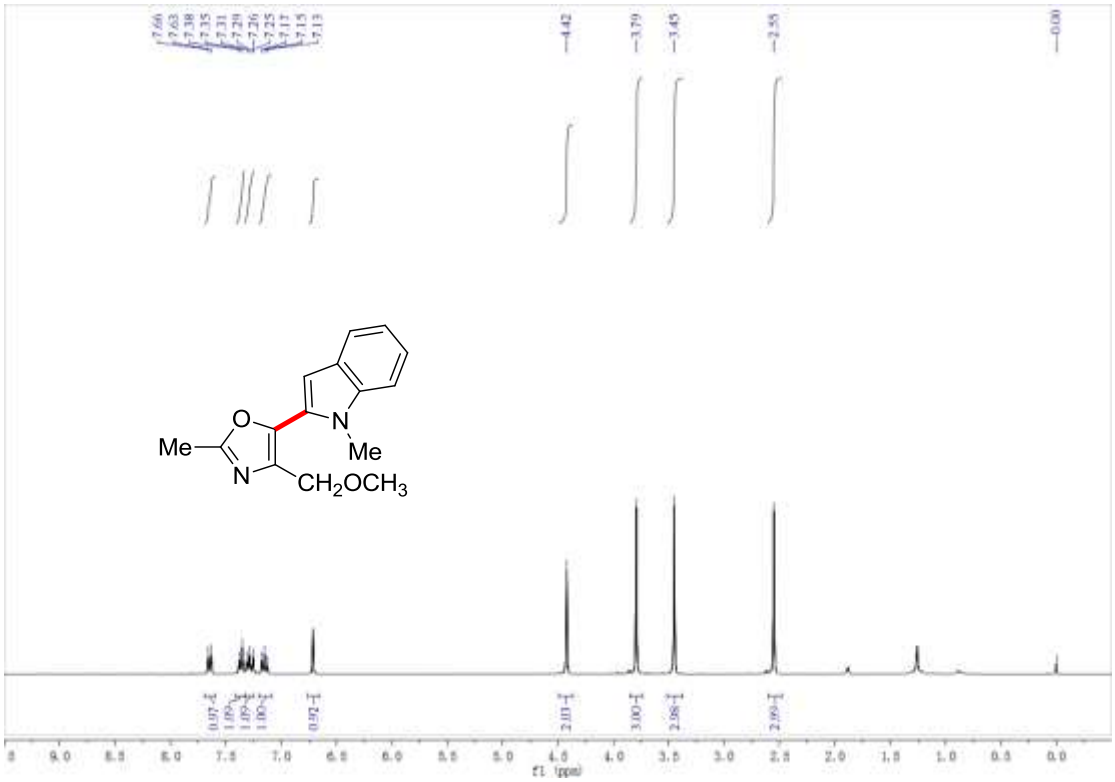


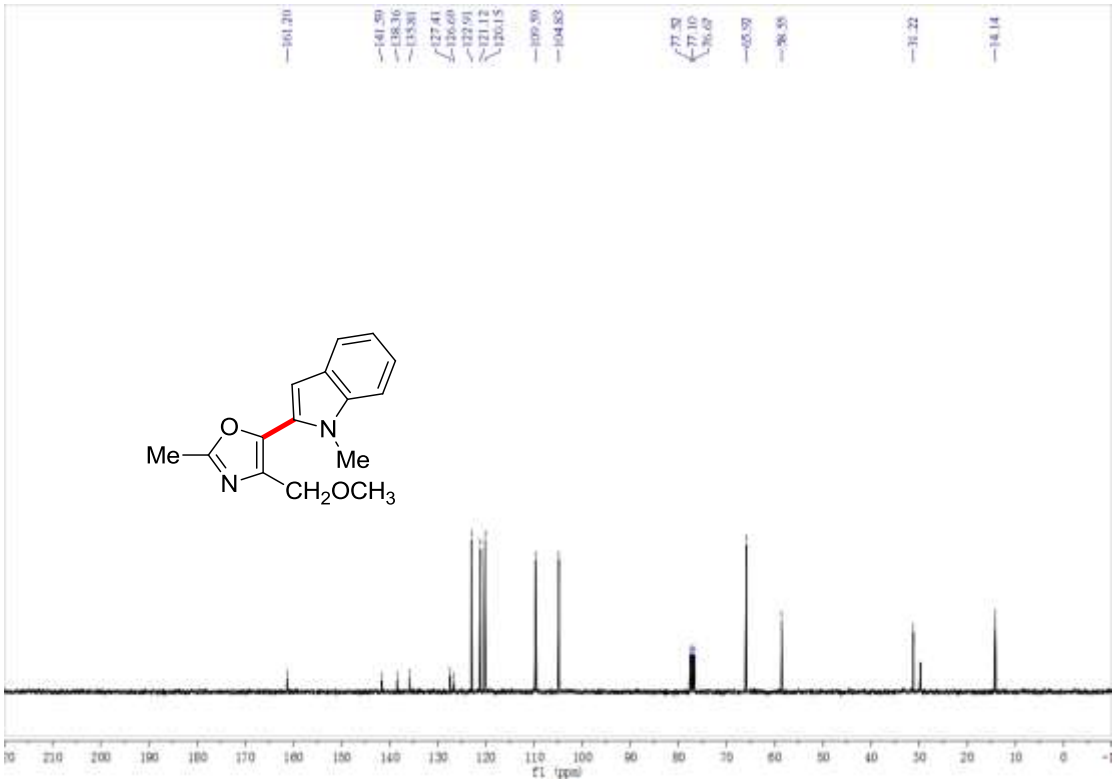
2, 4-dimethyl-5-(1-methyl-1*H*-indol-2-yl)oxazole (3q)





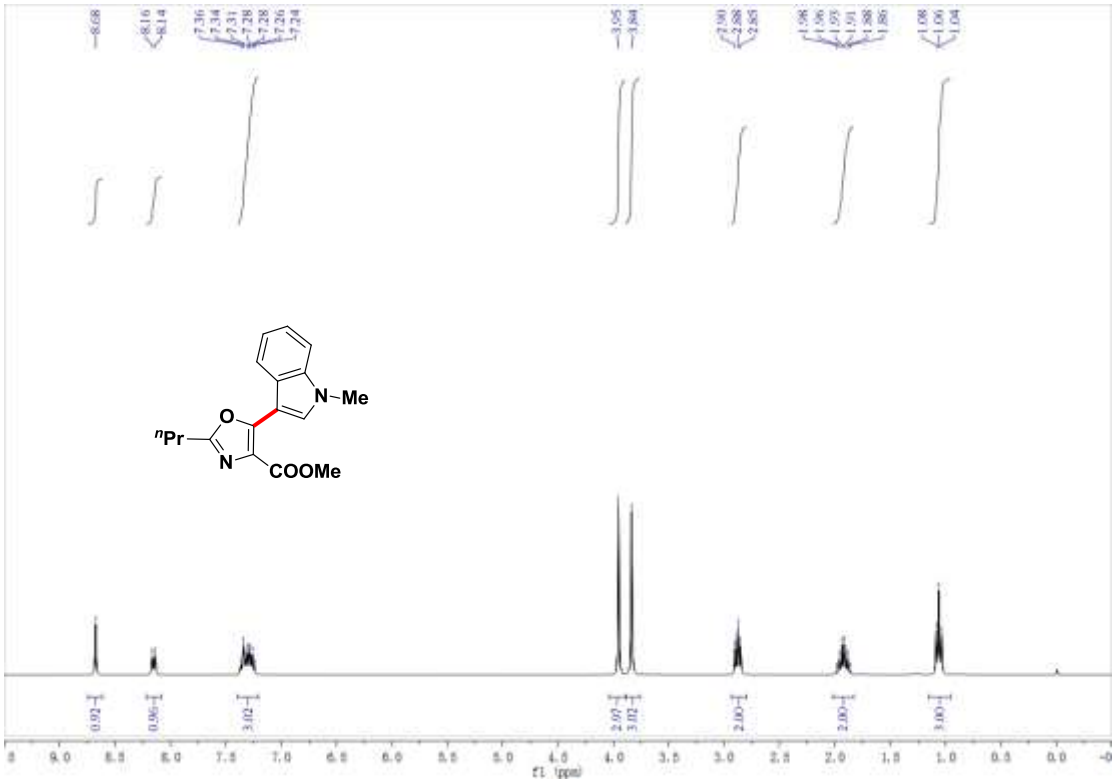
4-(methoxymethyl)-2-methyl-5-(1-methyl-1H-indol-2-yl)oxazole (3r)



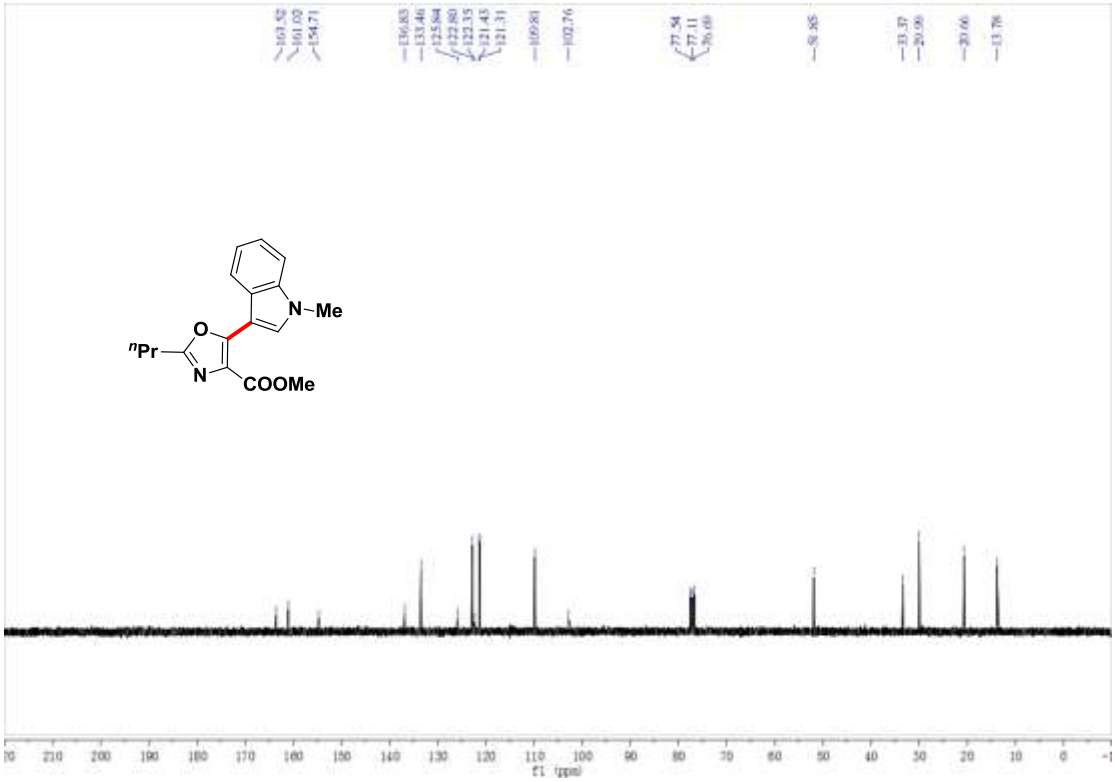


Methyl 5-(1-methyl-1*H*-indol-3-yl)-2-propyloxazole-4-carboxylate (4a)

^{1}H NMR (300 MHz, $CDCl_3$)

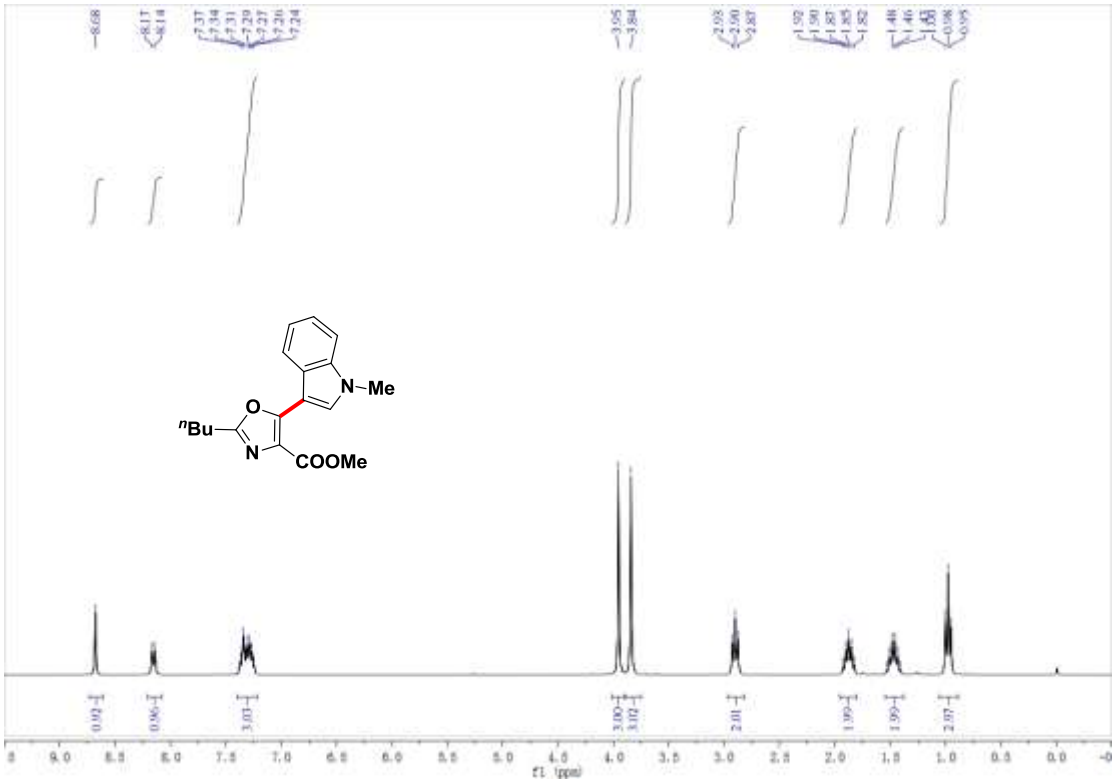


^{13}C NMR (75 MHz, $CDCl_3$)

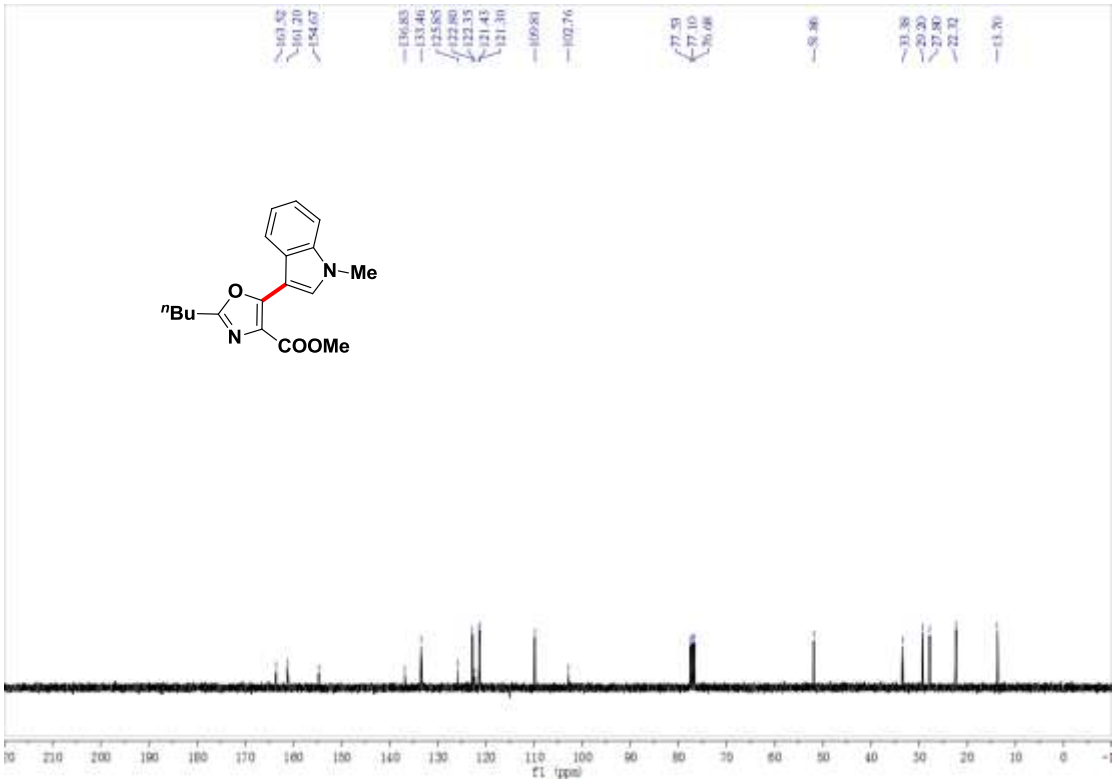


Methyl 5-(1-methyl-1*H*-indol-3-yl)-2-butyloxazole-4-carboxylate (4b)

^{1}H NMR (300 MHz, $CDCl_3$)

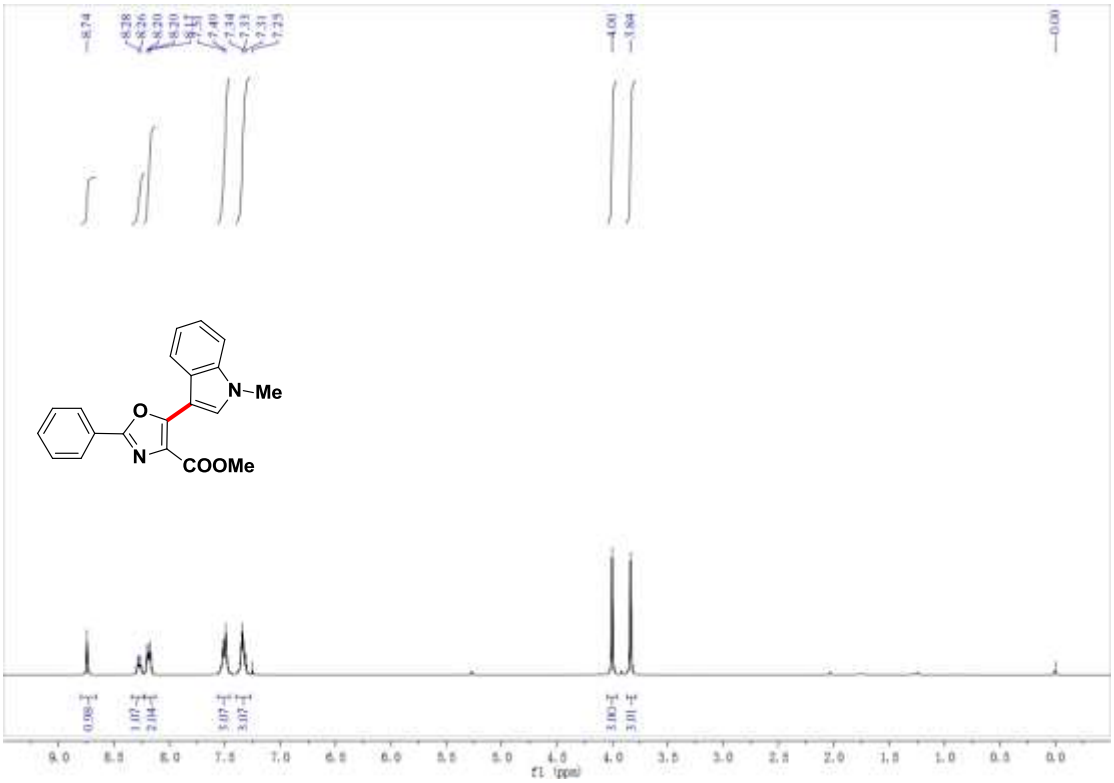


^{13}C NMR (75 MHz, $CDCl_3$)

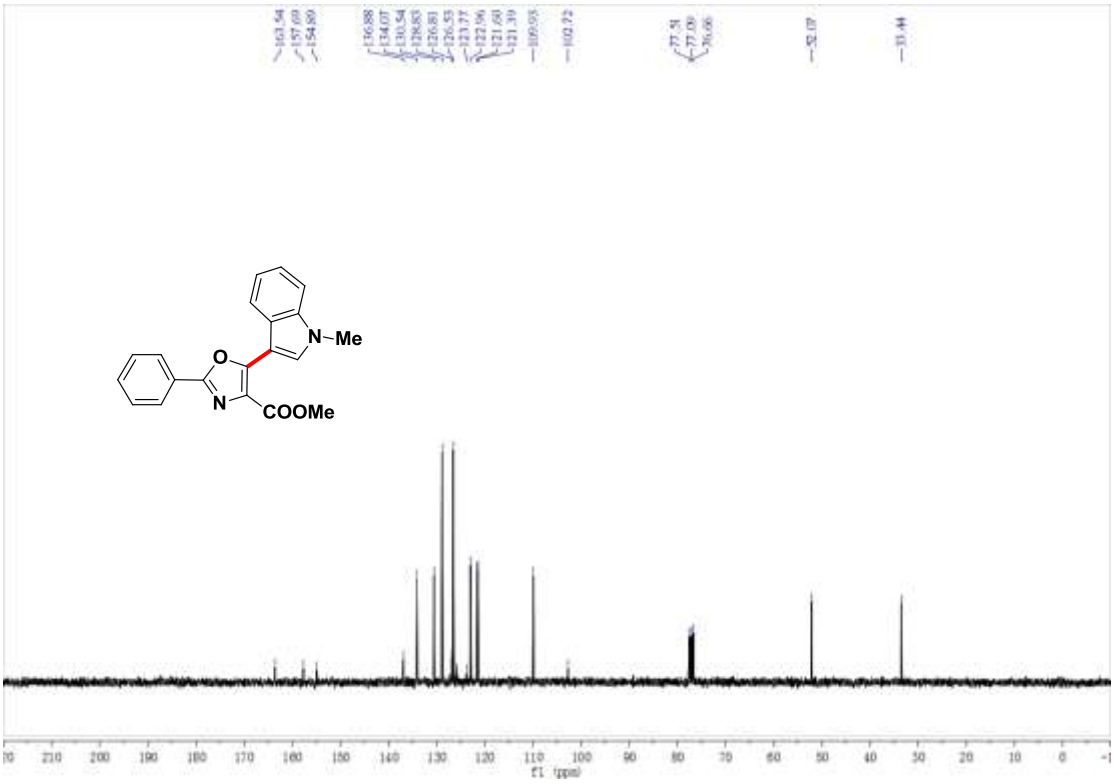


Methyl 5-(1-methyl-1*H*-indol-3-yl)-2-phenyloxazole-4-carboxylate (4c)

^{1}H NMR (300 MHz, $CDCl_3$)

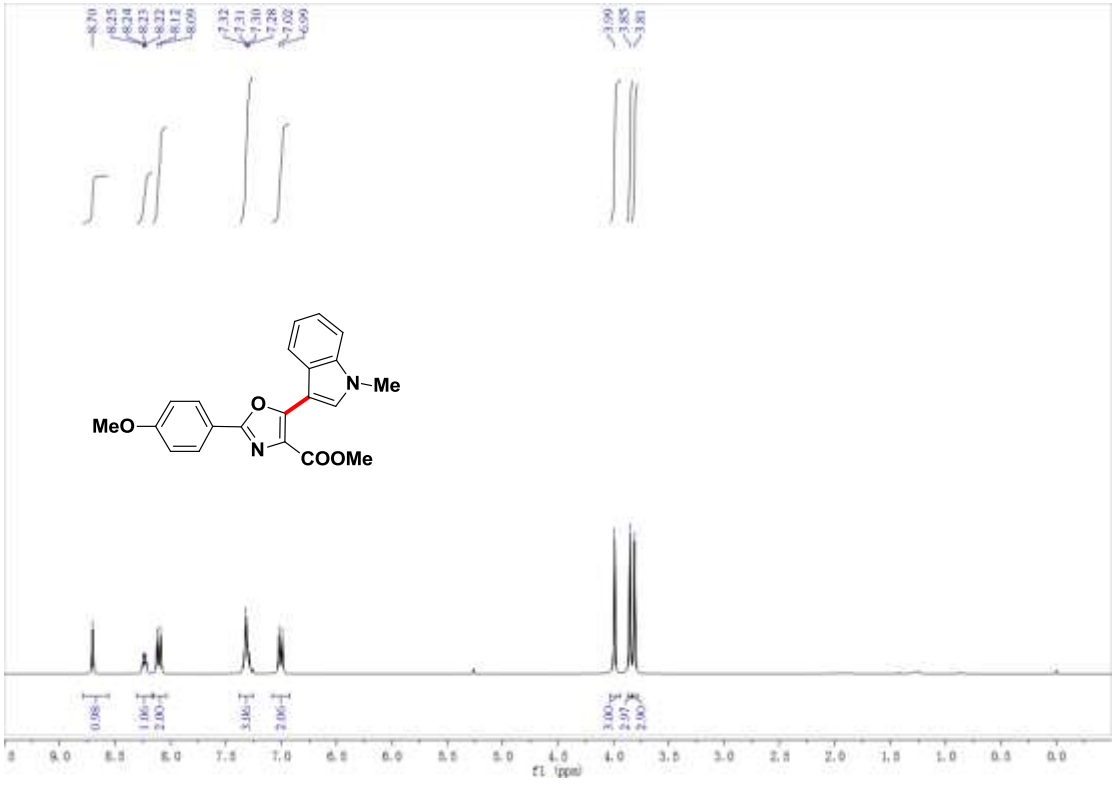


^{13}C NMR (75 MHz, $CDCl_3$)

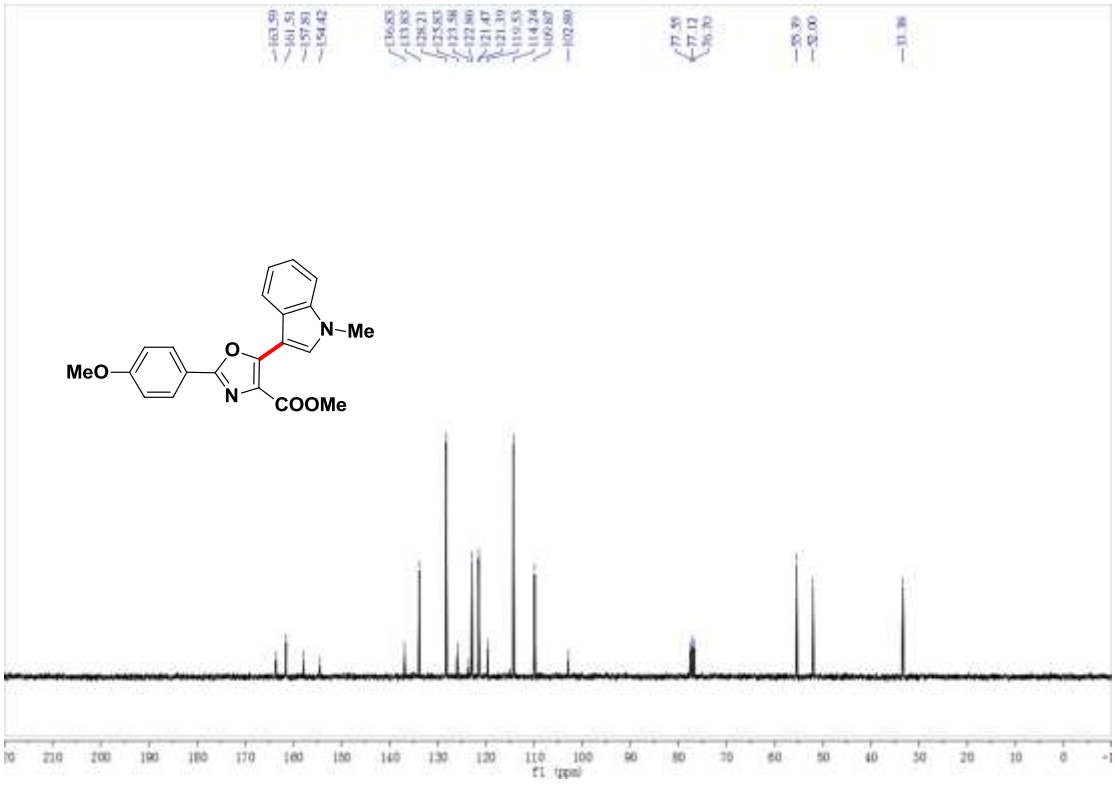


Methyl 2-(4-methoxyphenyl)-5-(1-methyl-1*H*-indol-3-yl)oxazole-4-carboxylate (4d)

^{1}H NMR (300 MHz, $CDCl_3$)

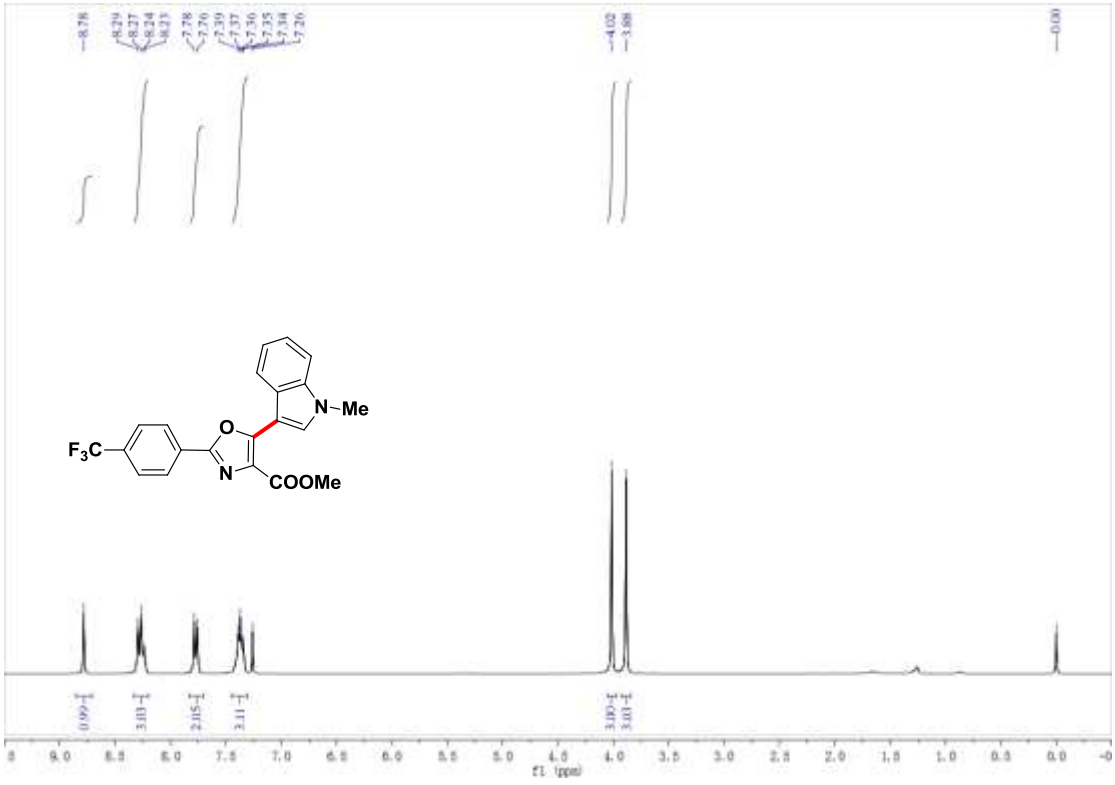


^{13}C NMR (75 MHz, $CDCl_3$)

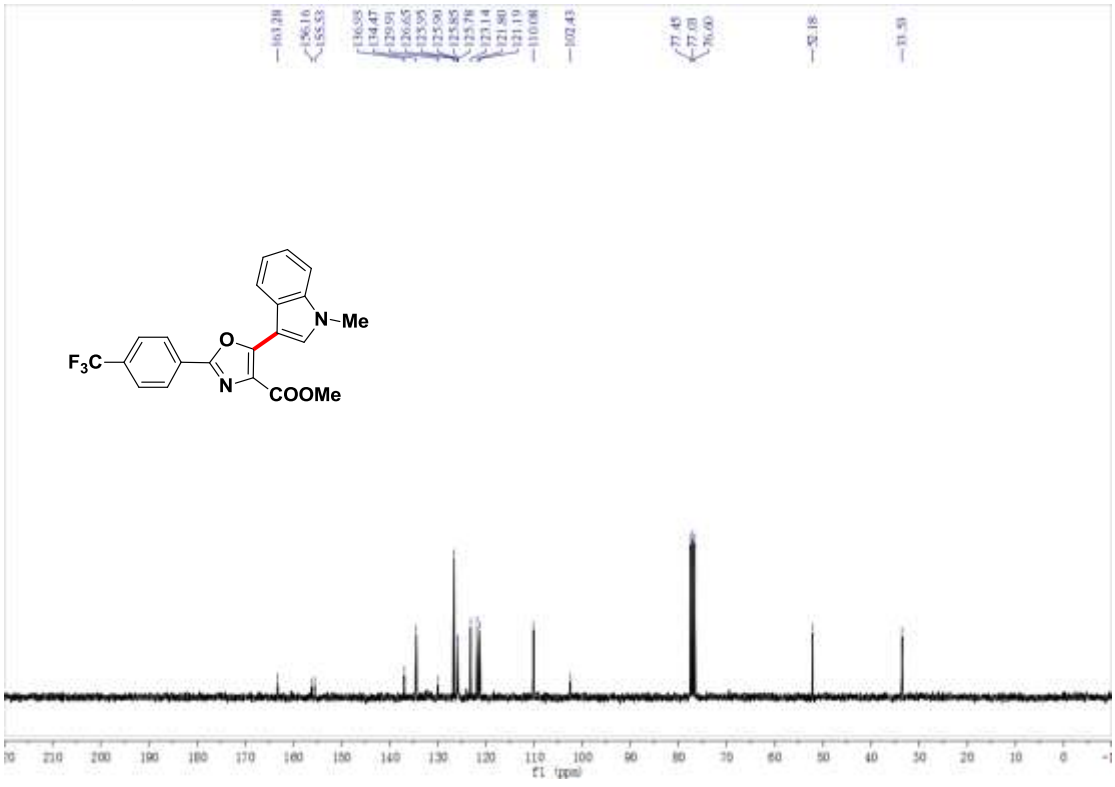


Methyl 5-(1-methyl-1*H*-indol-3-yl)-2-(4-(trifluoromethyl)phenyl)oxazole-4-carboxylate (4e)

^{1}H NMR (300 MHz, $CDCl_3$)

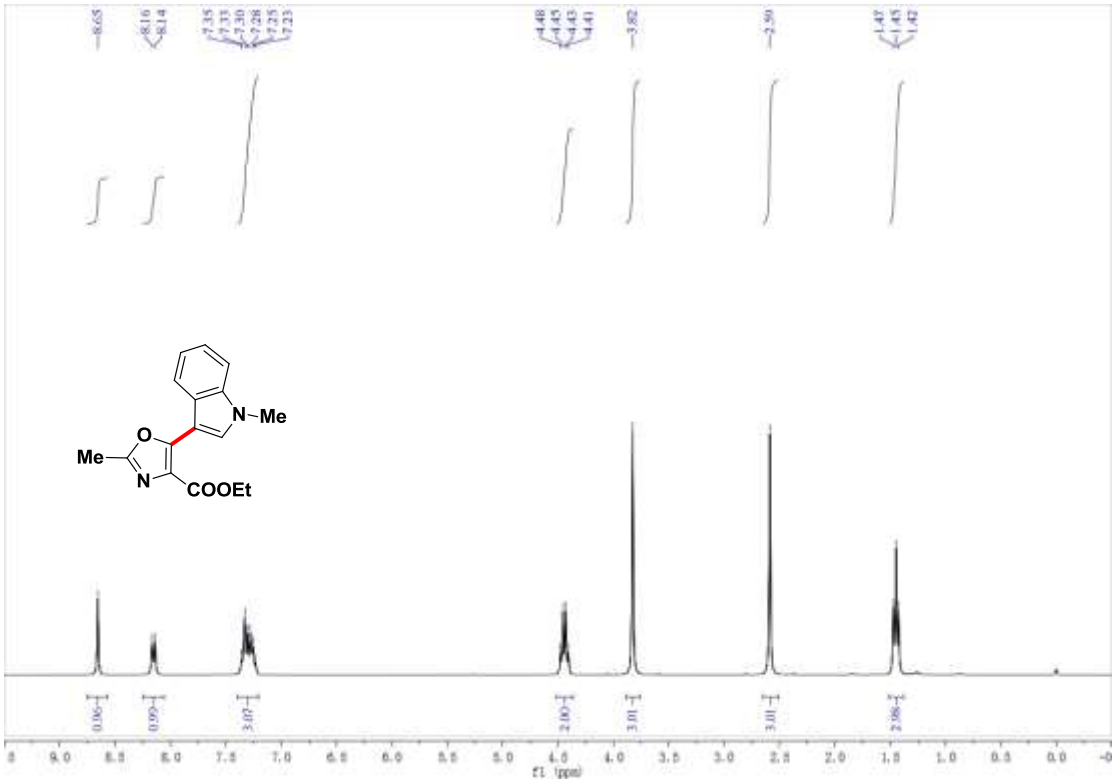


^{13}C NMR (75 MHz, $CDCl_3$)

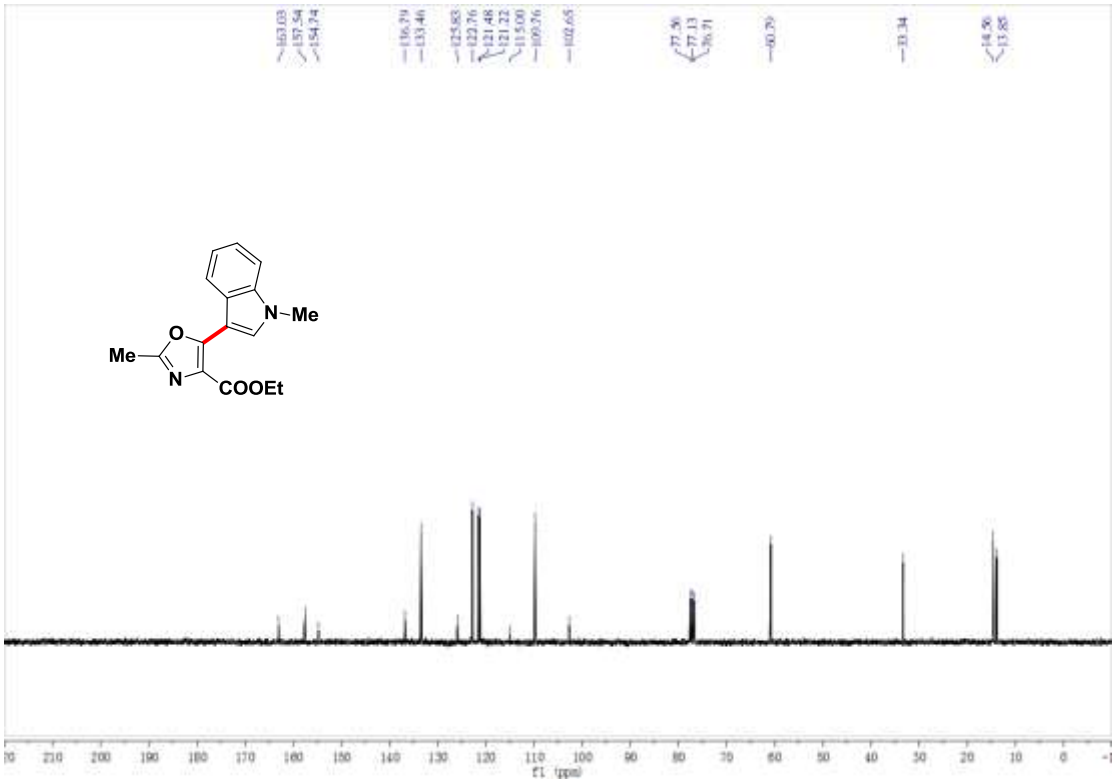


Ethyl 2-methyl-5-(1-methyl-1*H*-indol-3-yl)oxazole-4-carboxylate (4f)

^{1}H NMR (300 MHz, $CDCl_3$)

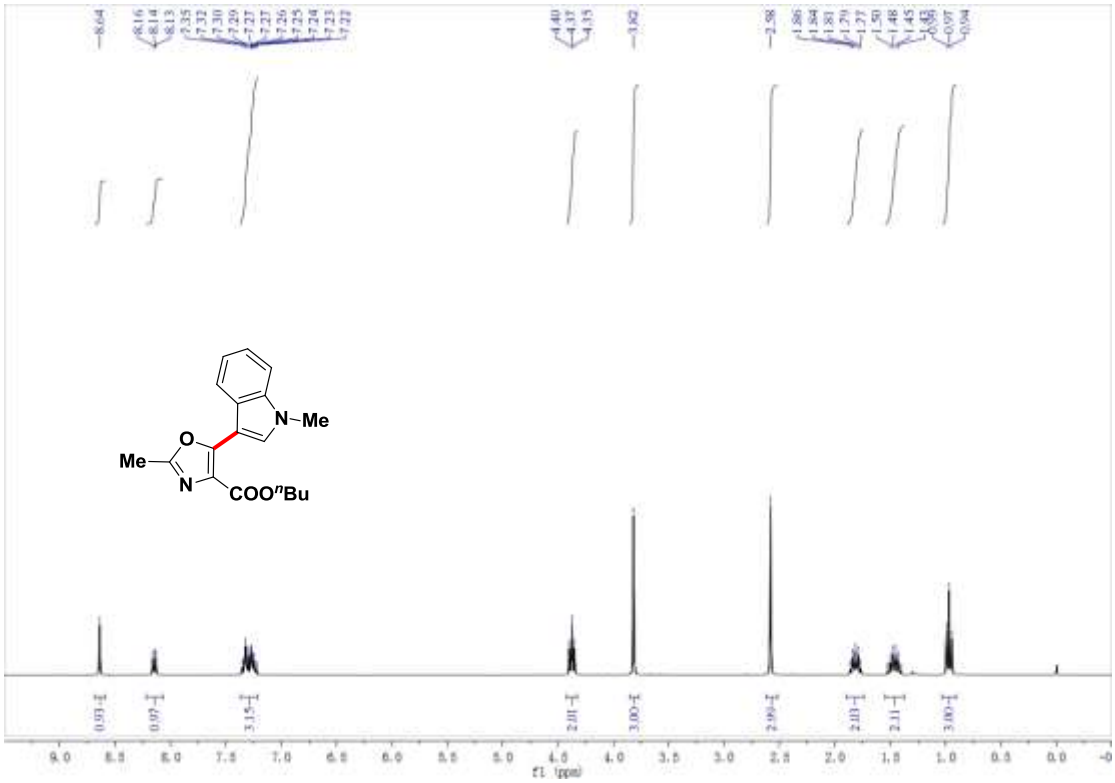


^{13}C NMR (75 MHz, $CDCl_3$)

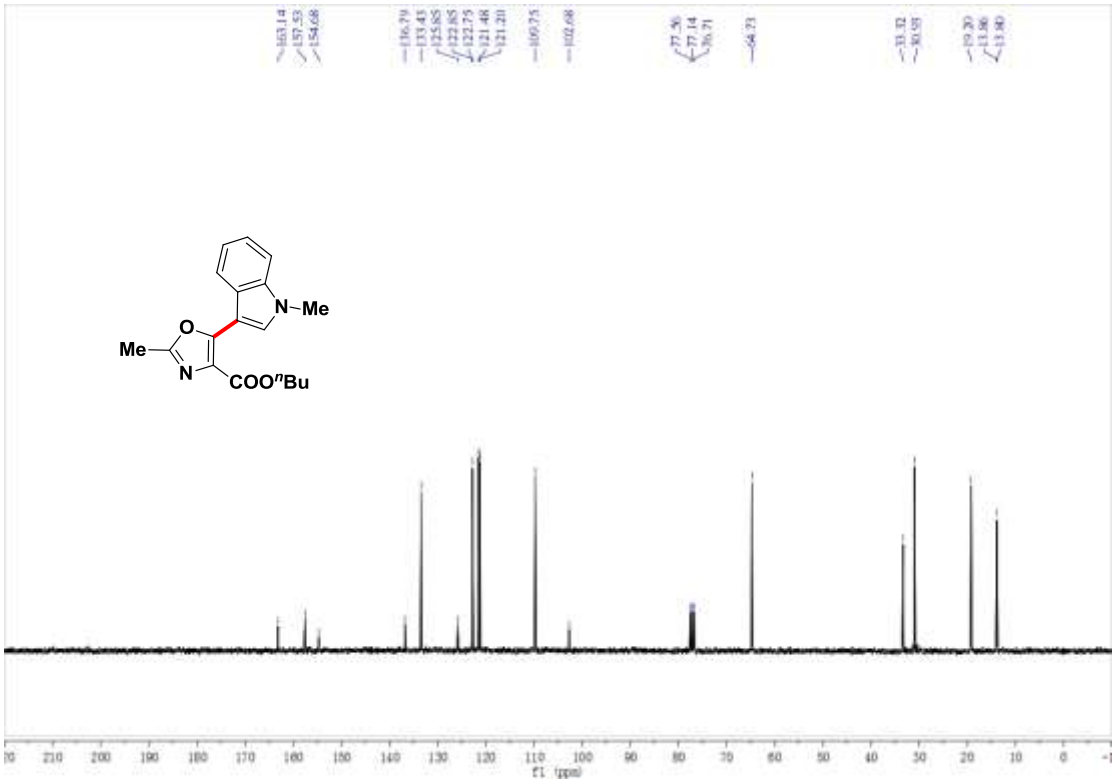


Butyl 2-methyl-5-(1-methyl-1*H*-indol-3-yl)oxazole-4-carboxylate (4g)

^{1}H NMR (300 MHz, $CDCl_3$)

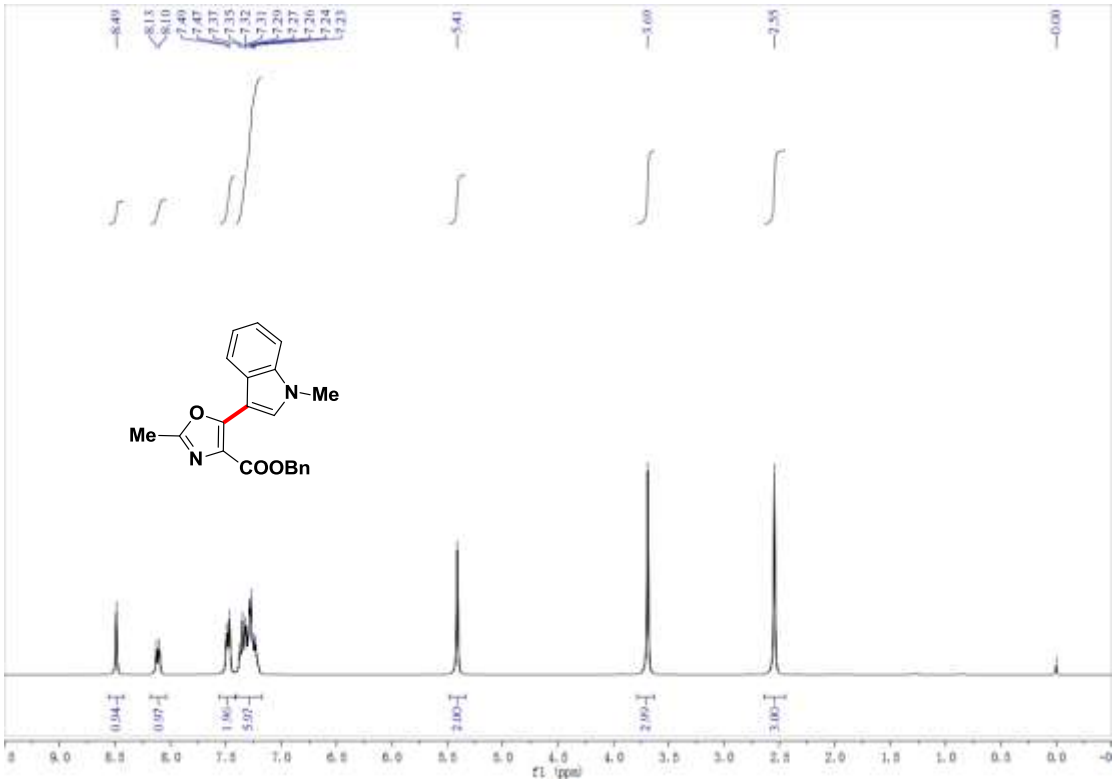


^{13}C NMR (75 MHz, $CDCl_3$)

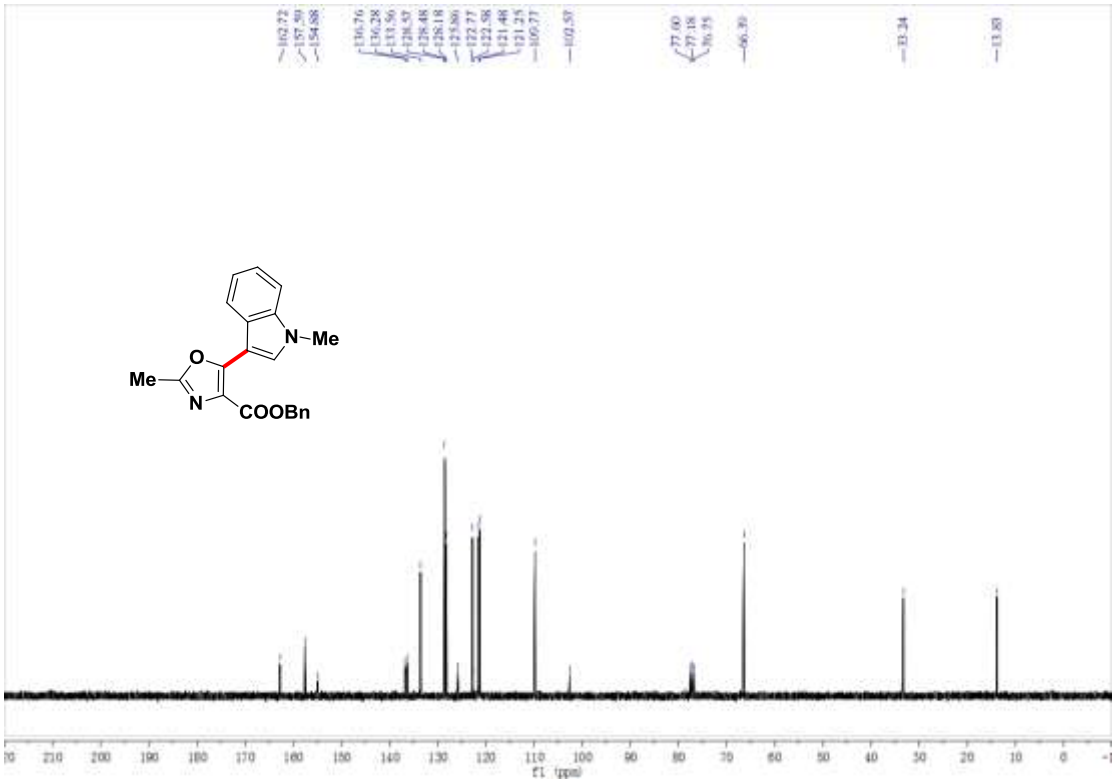


Benzyl 2-methyl-5-(1-methyl-1*H*-indol-3-yl)oxazole-4-carboxylate (4h)

^{1}H NMR (300 MHz, $CDCl_3$)

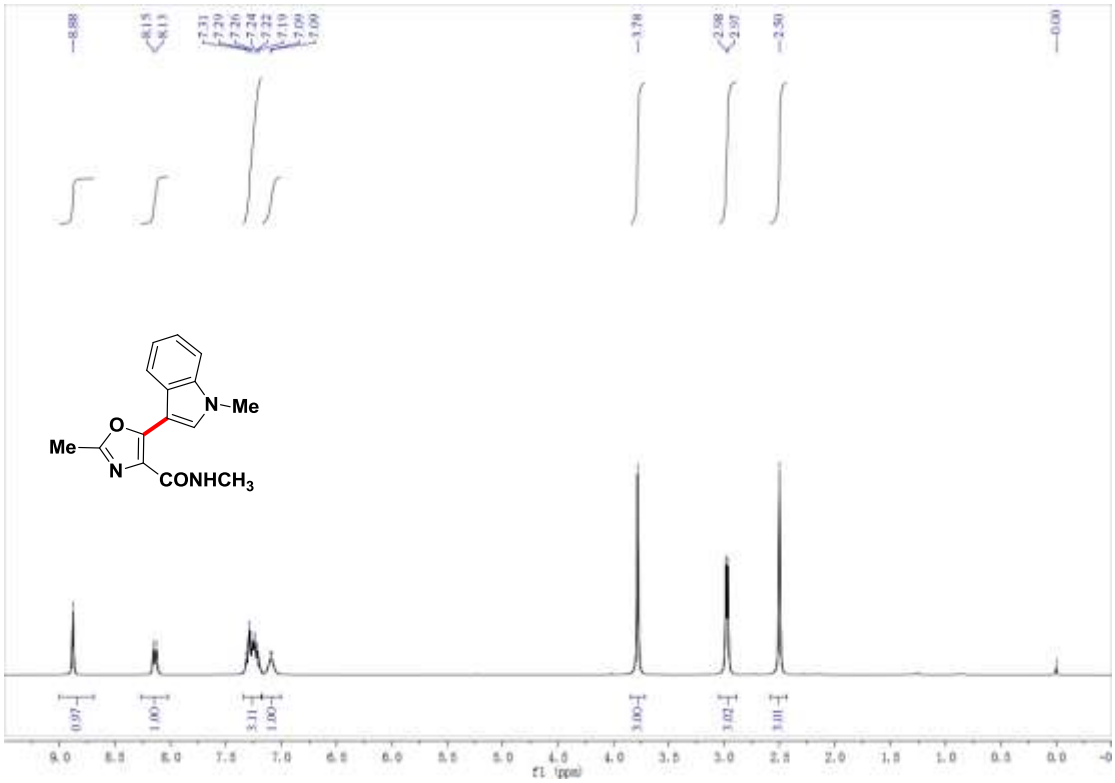


^{13}C NMR (75 MHz, $CDCl_3$)

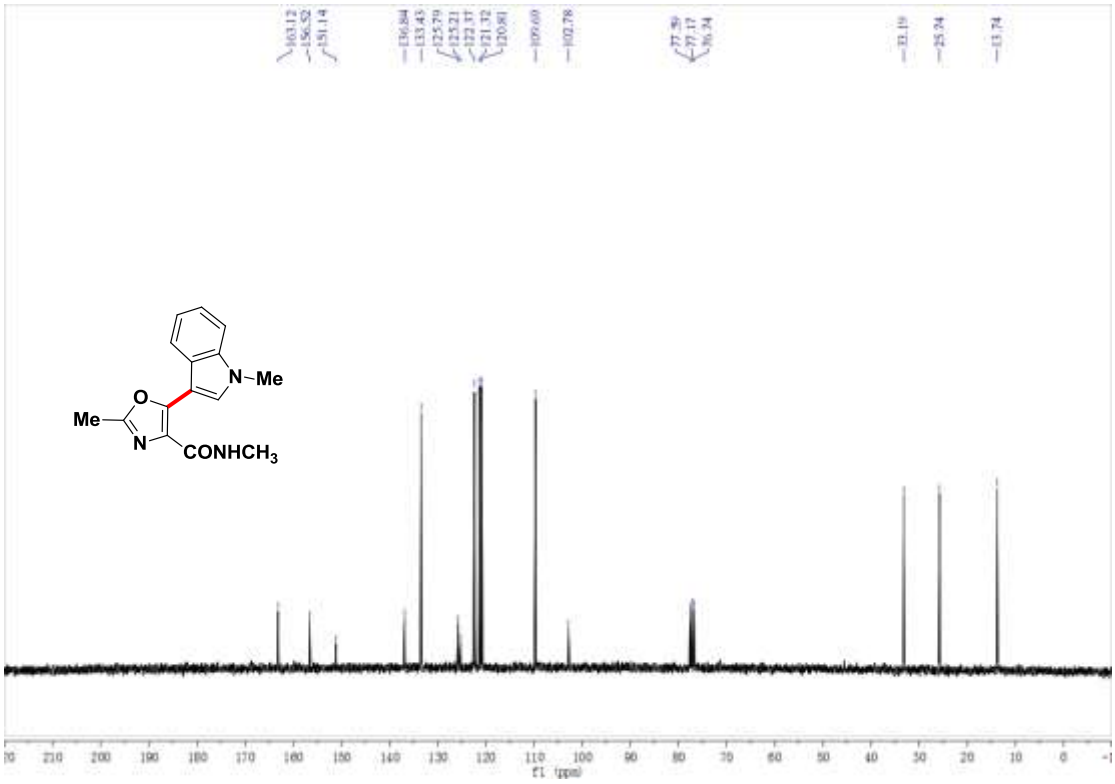


N,2-dimethyl-5-(1-methyl-1*H*-indol-3-yl)oxazole-4-carboxamide (4i)

^{1}H NMR (300 MHz, $CDCl_3$)

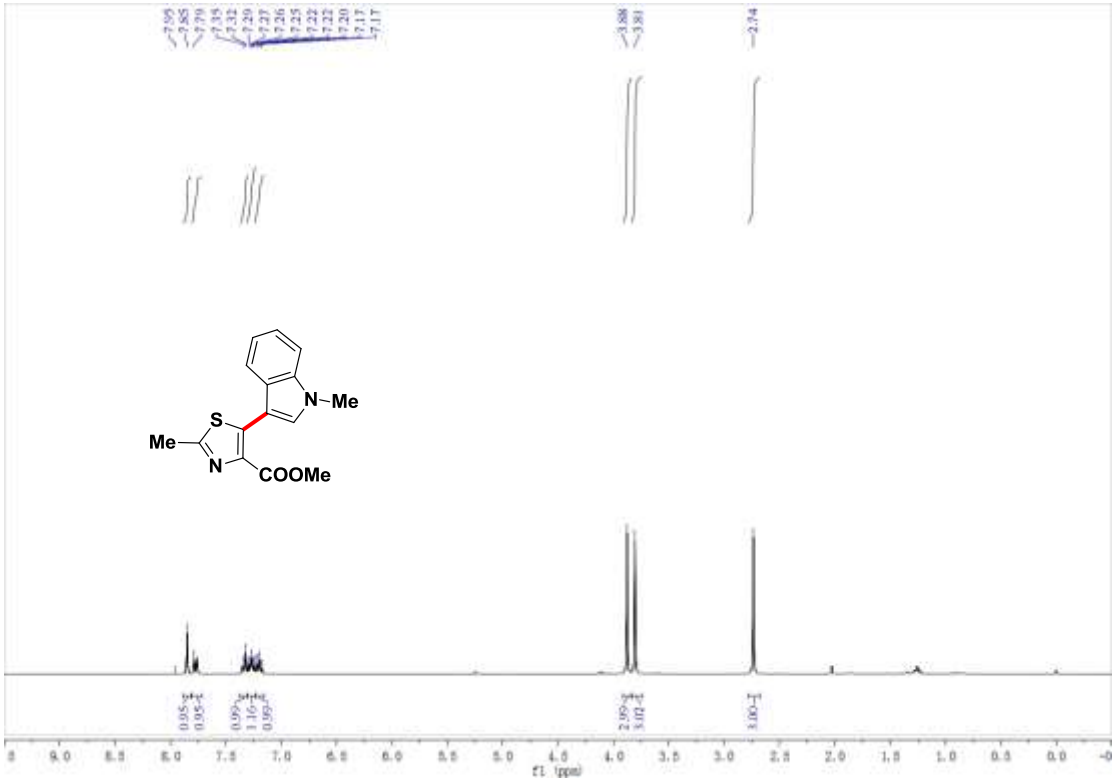


^{13}C NMR (75 MHz, $CDCl_3$)

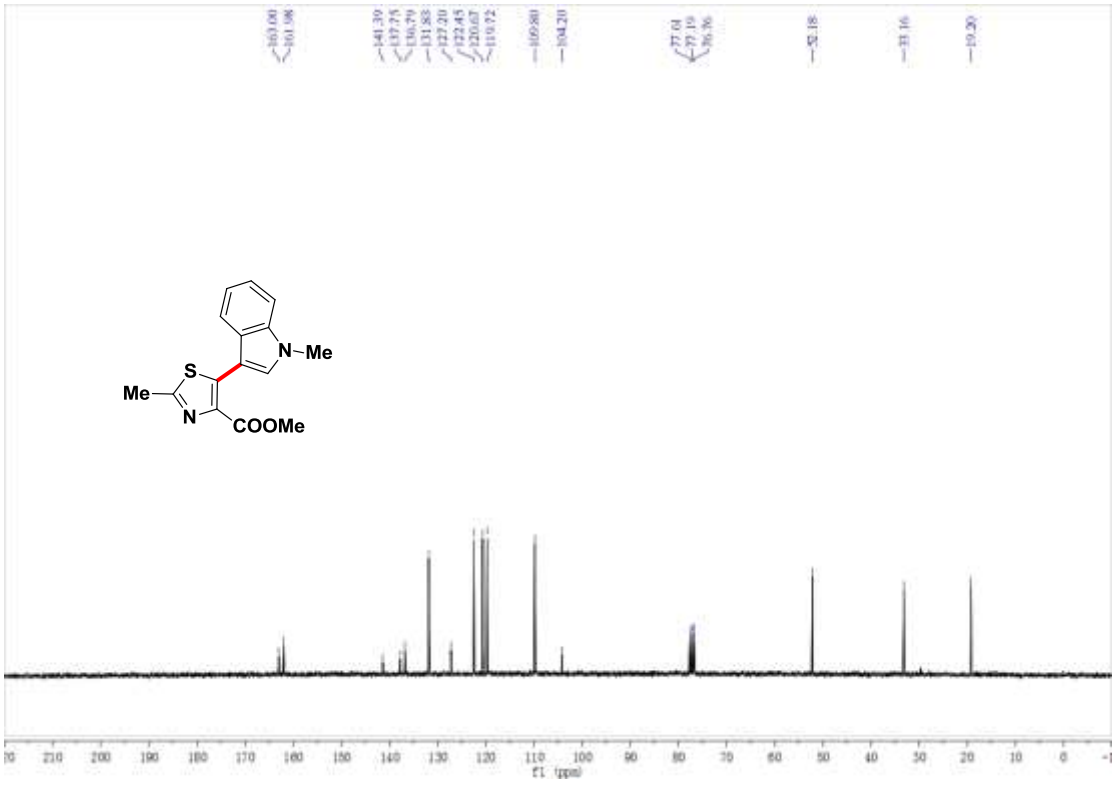


Methyl 2-methyl-5-(1-methyl-1*H*-indol-3-yl)thiazole-4-carboxylate (4j)

^{1}H NMR (300 MHz, $CDCl_3$)

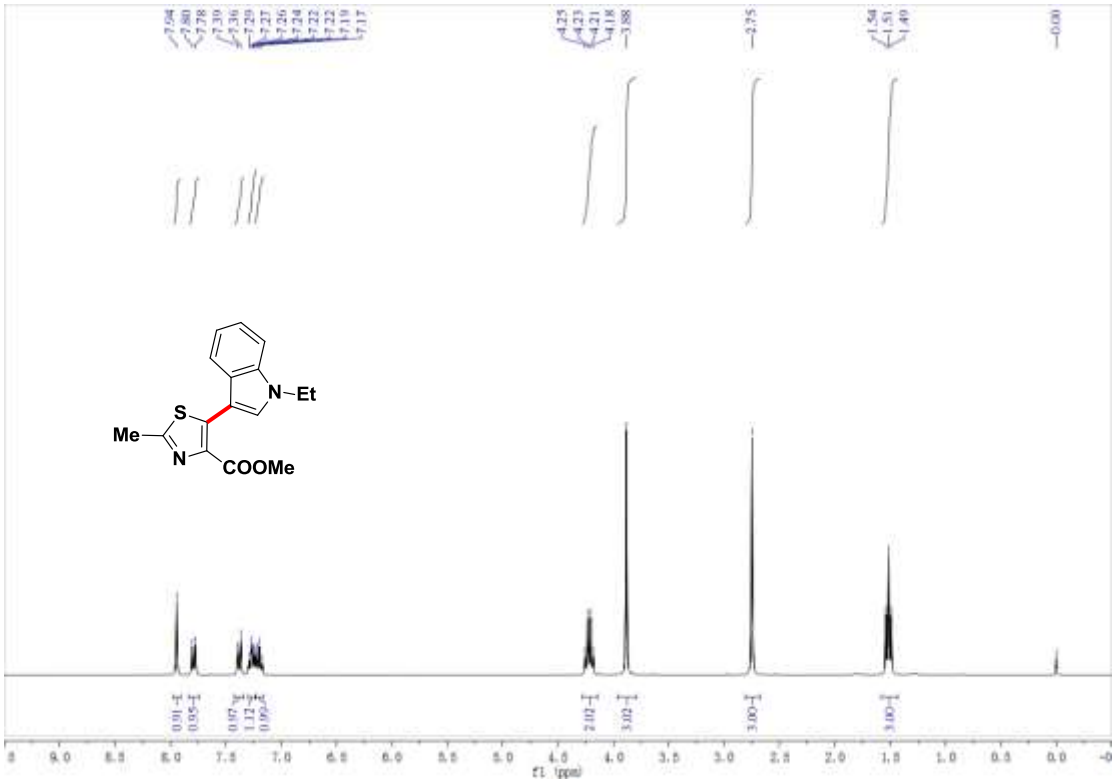


^{13}C NMR (75 MHz, $CDCl_3$)

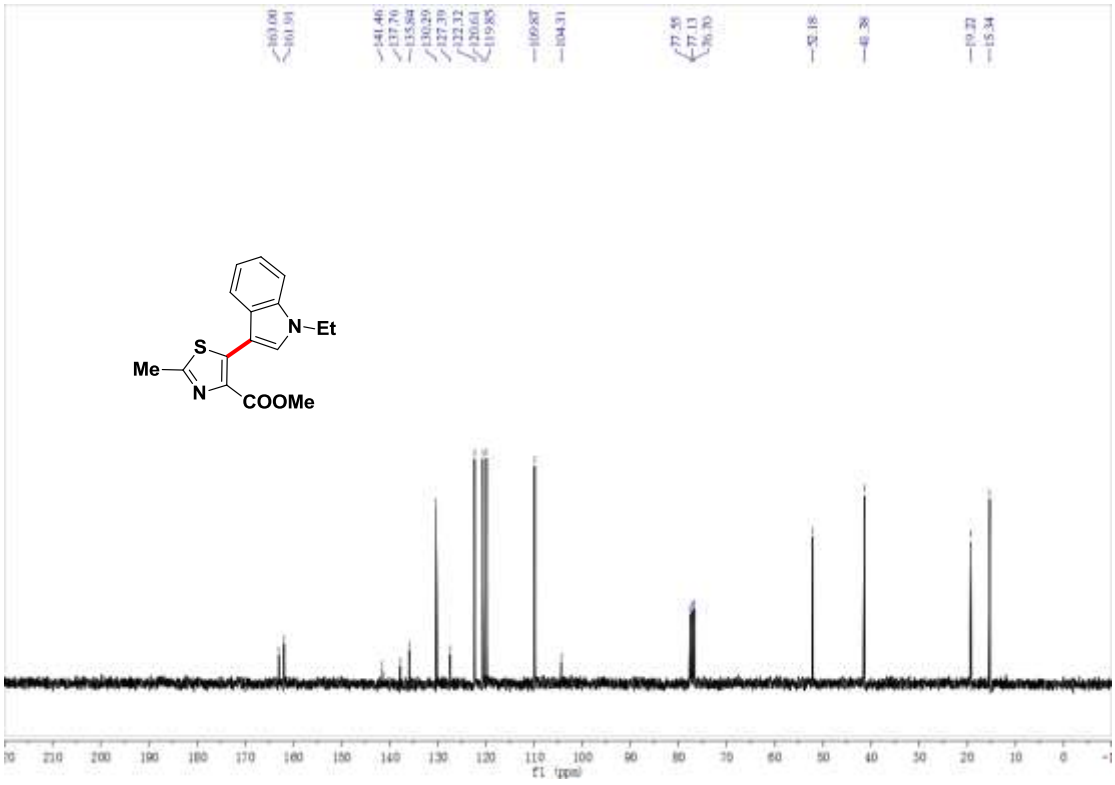


Methyl 5-(1-ethyl-1*H*-indol-3-yl)-2-methylthiazole-4-carboxylate (4k)

^{1}H NMR (300 MHz, $CDCl_3$)

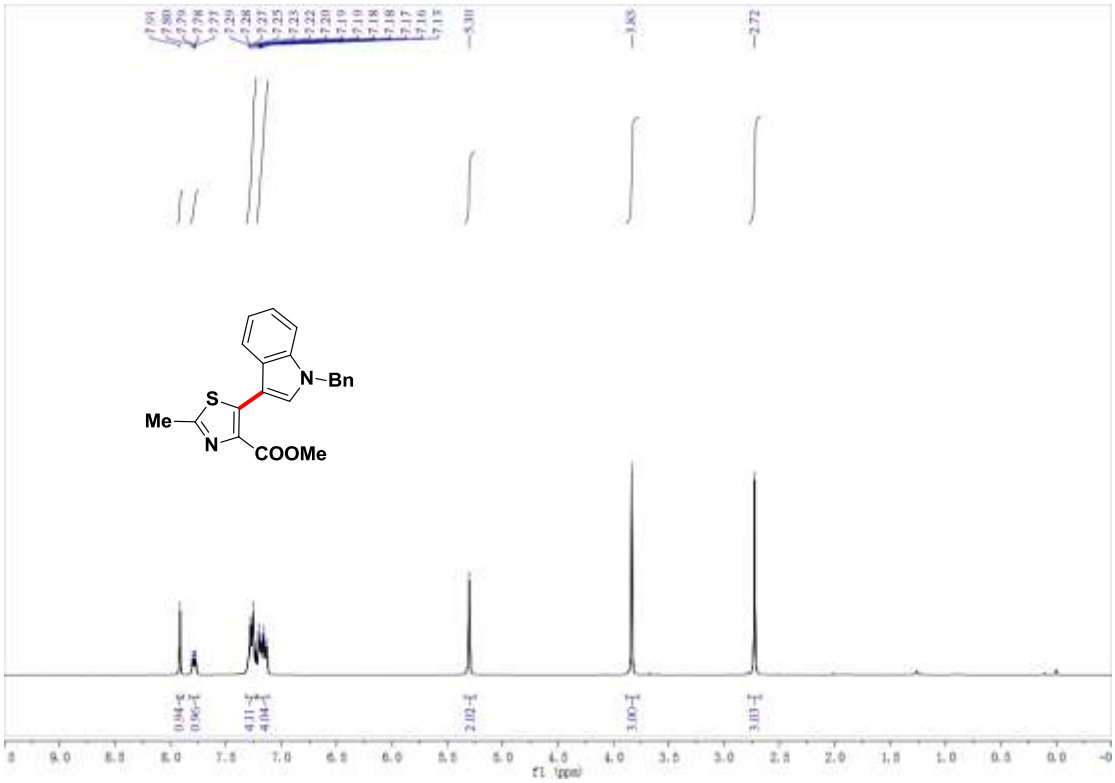


^{13}C NMR (75 MHz, $CDCl_3$)

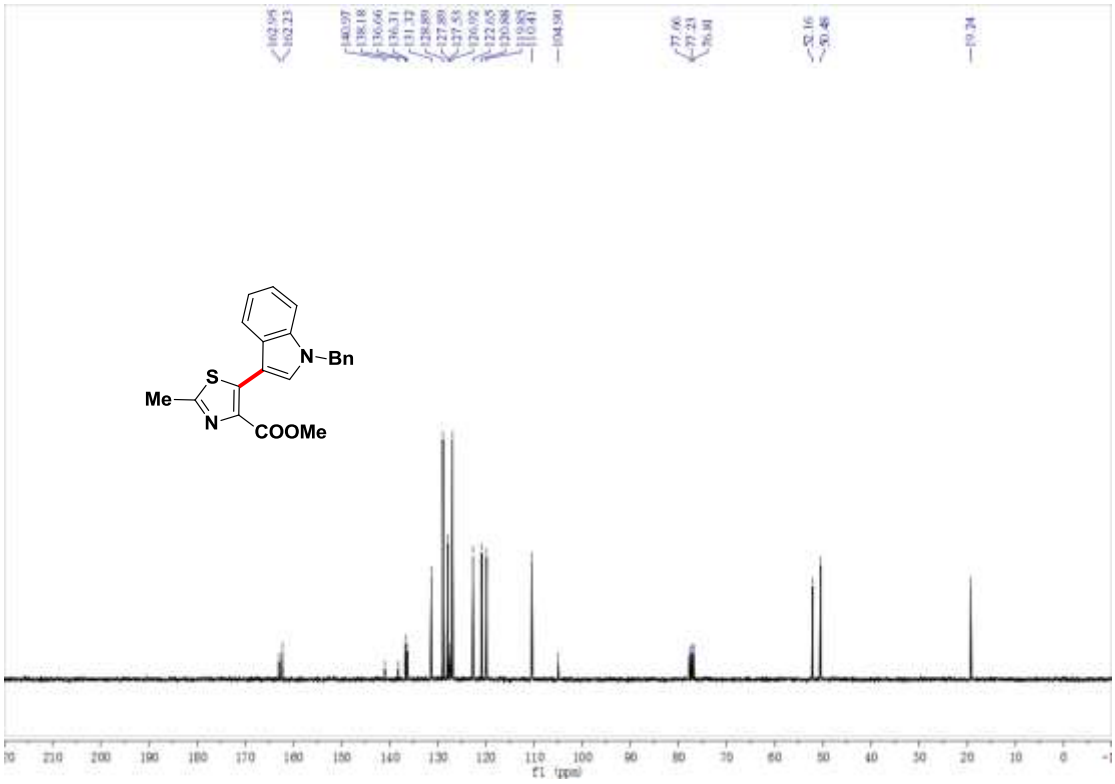


Methyl 5-(1-benzyl-1*H*-indol-3-yl)-2-methylthiazole-4-carboxylate (4l)

^{1}H NMR (300 MHz, $CDCl_3$)

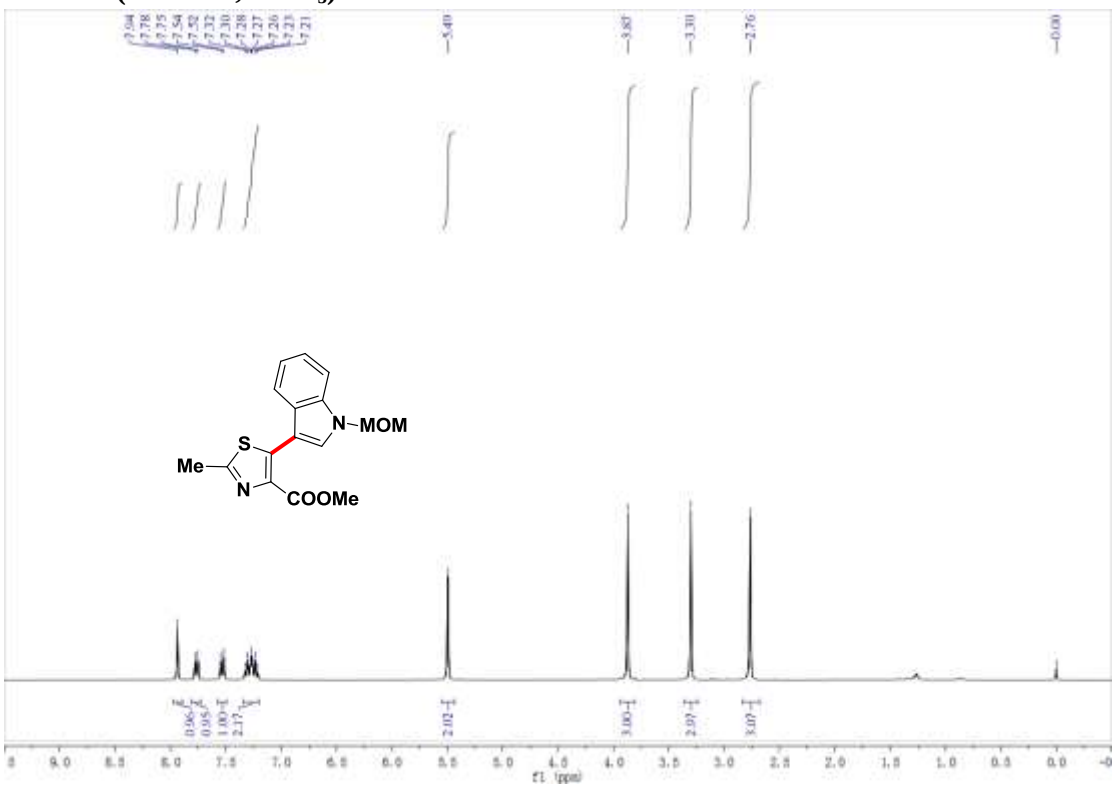


^{13}C NMR (75 MHz, $CDCl_3$)

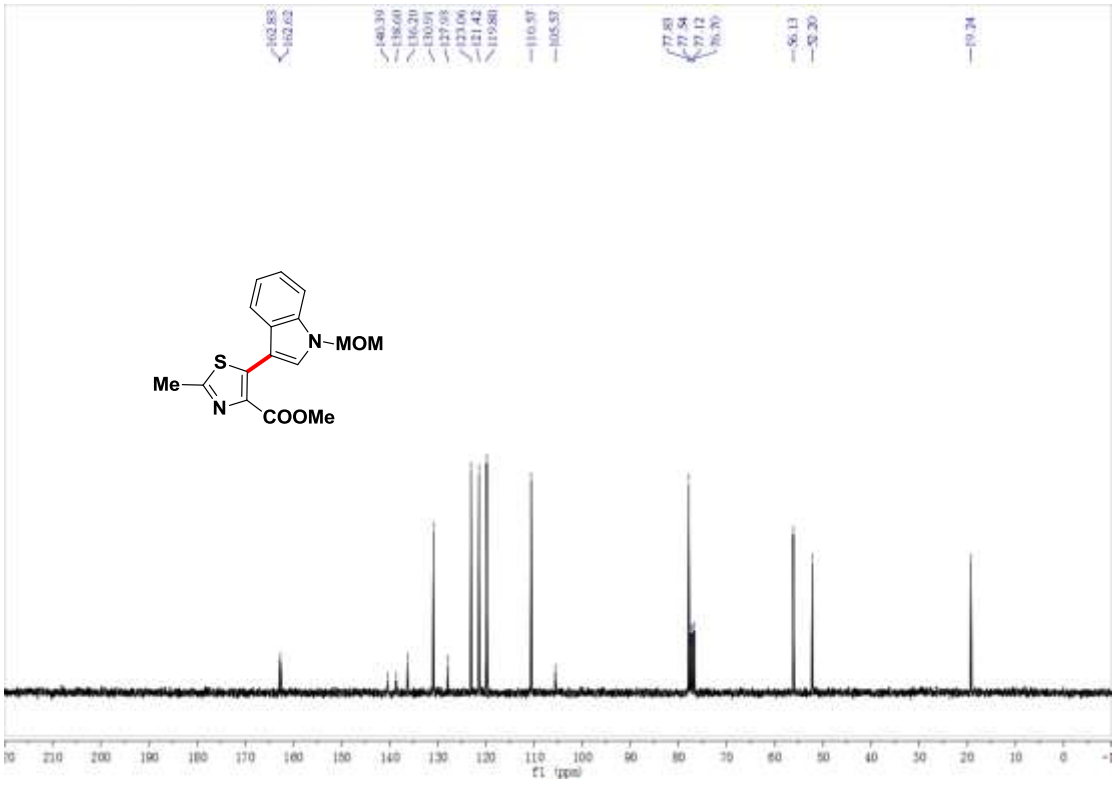


Methyl 5-(1-(methoxymethyl)-1*H*-indol-3-yl)-2-methylthiazole-4-carboxylate (4m)

^{1}H NMR (300 MHz, $CDCl_3$)

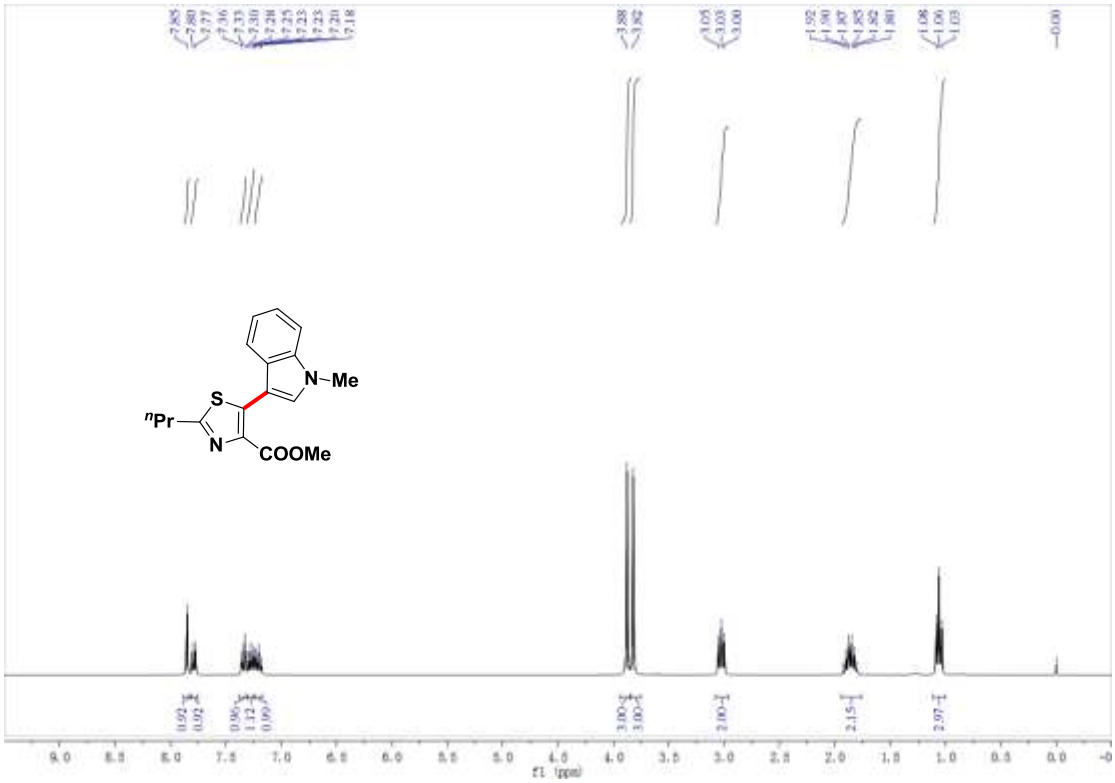


^{13}C NMR (75 MHz, $CDCl_3$)

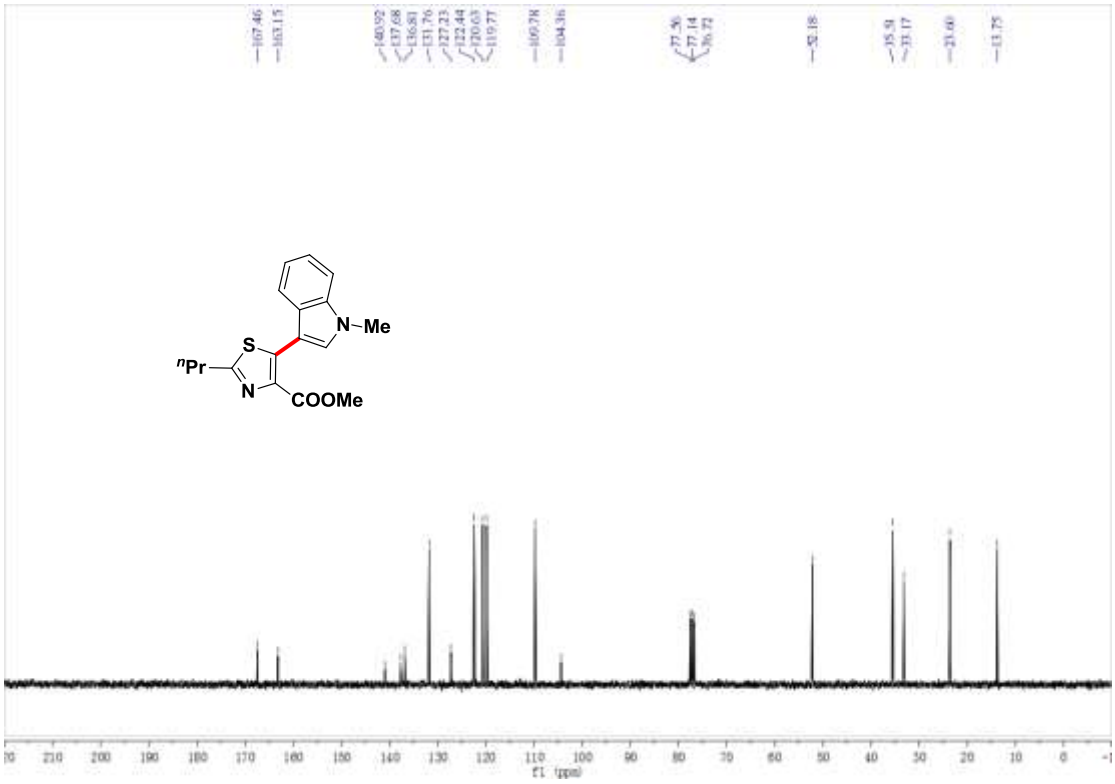


Methyl 5-(1-methyl-1*H*-indol-3-yl)-2-propylthiazole-4-carboxylate (4n)

^{1}H NMR (300 MHz, $CDCl_3$)

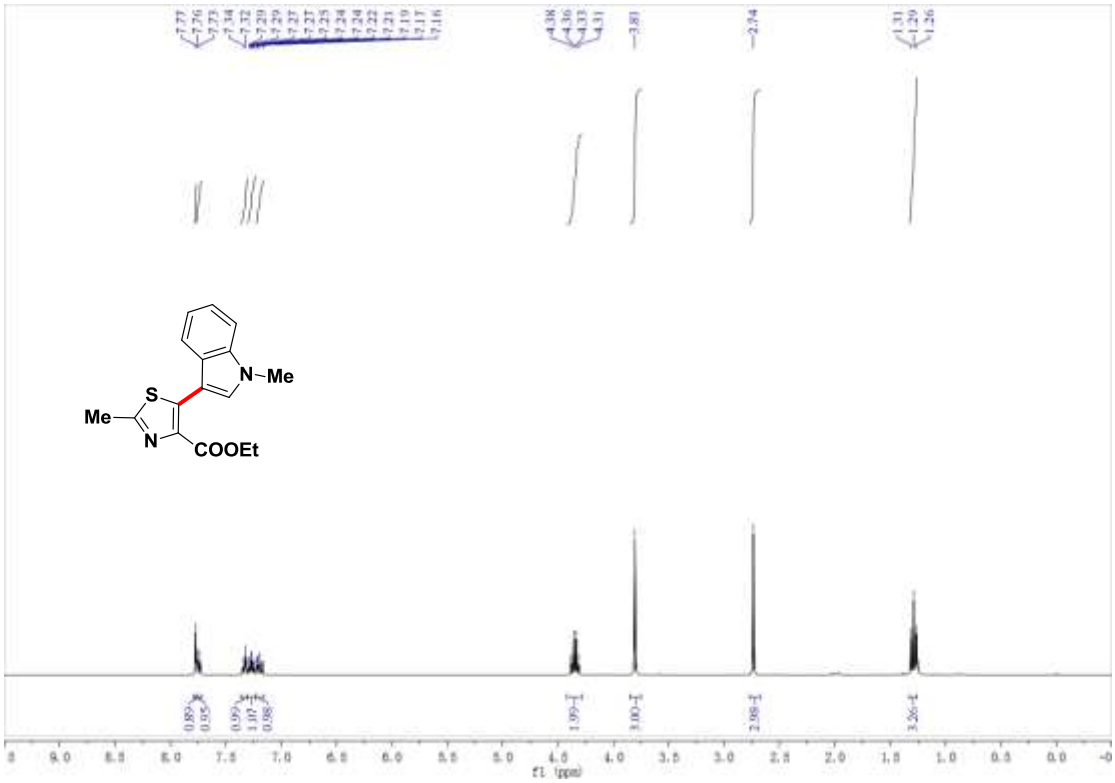


^{13}C NMR (75 MHz, $CDCl_3$)

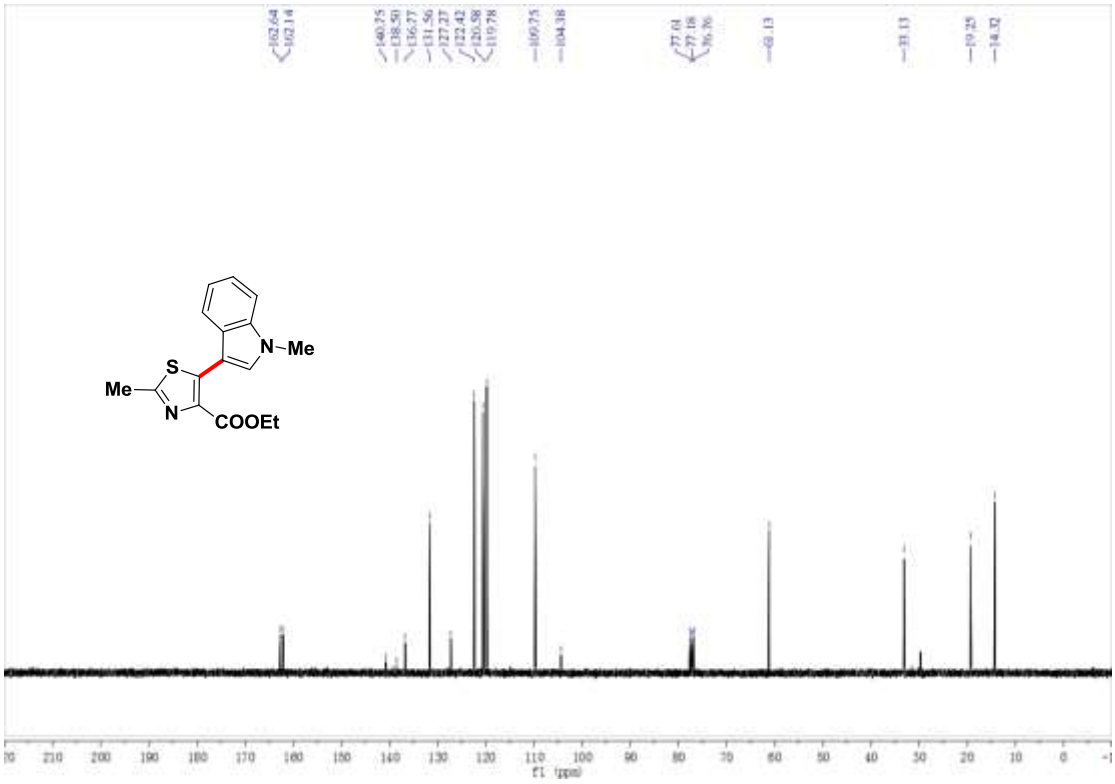


Ethyl 2-methyl-5-(1-methyl-1*H*-indol-3-yl)thiazole-4-carboxylate (4o)

^{1}H NMR (300 MHz, $CDCl_3$)

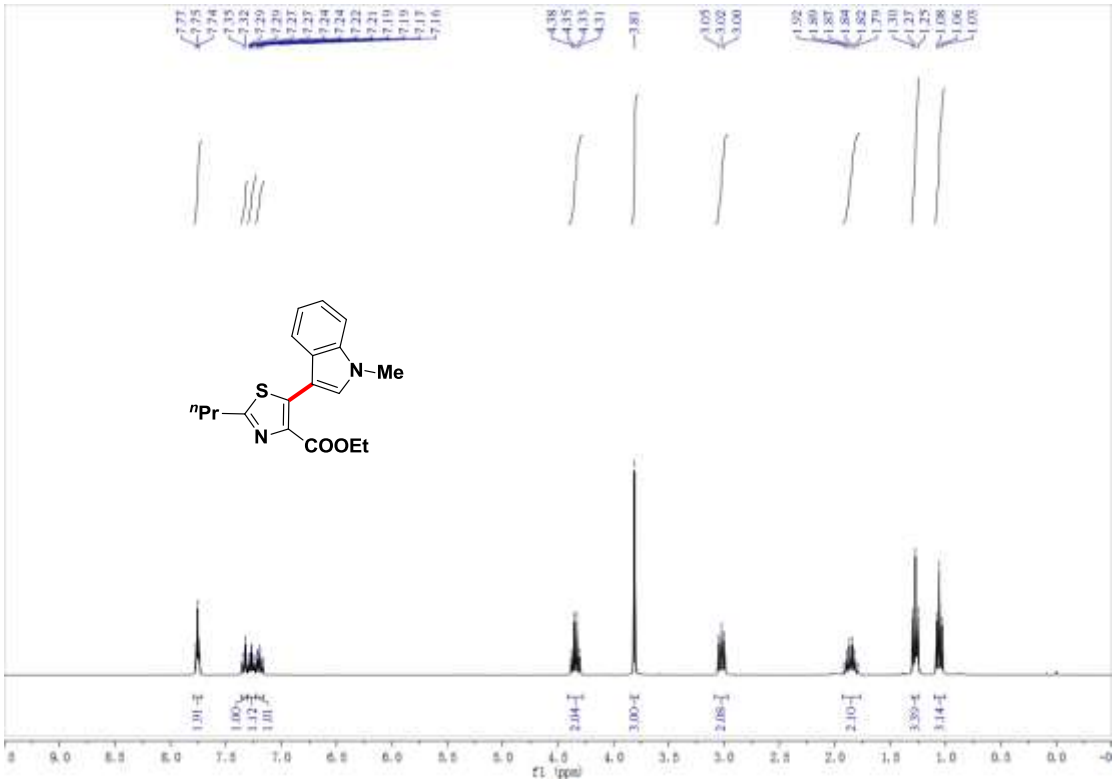


^{13}C NMR (75 MHz, $CDCl_3$)

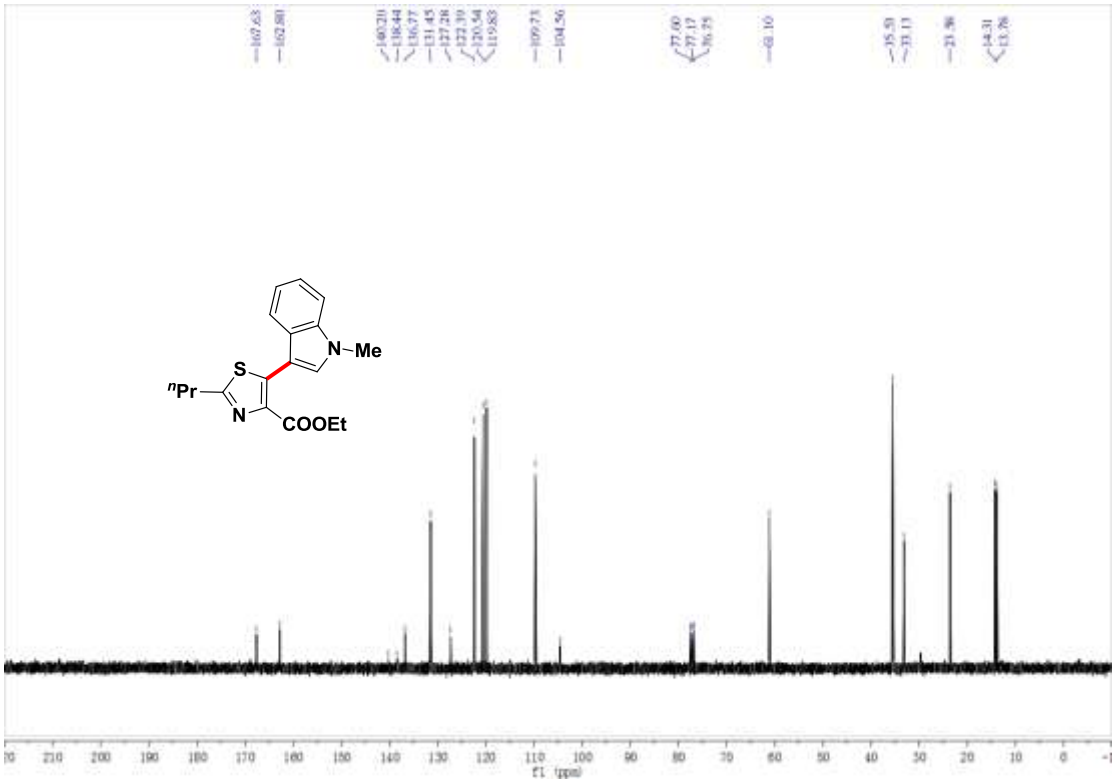


Ethyl 5-(1-methyl-1*H*-indol-3-yl)-2-propylthiazole-4-carboxylate (4p)

^{1}H NMR (300 MHz, $CDCl_3$)

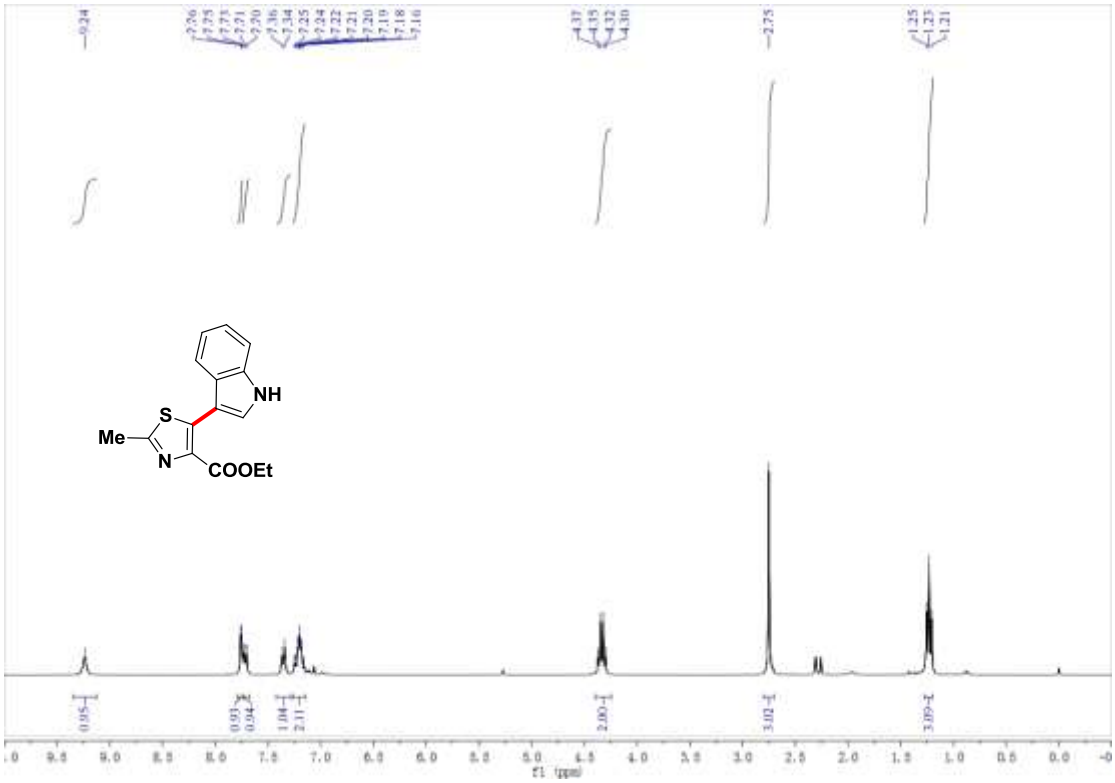


^{13}C NMR (75 MHz, $CDCl_3$)

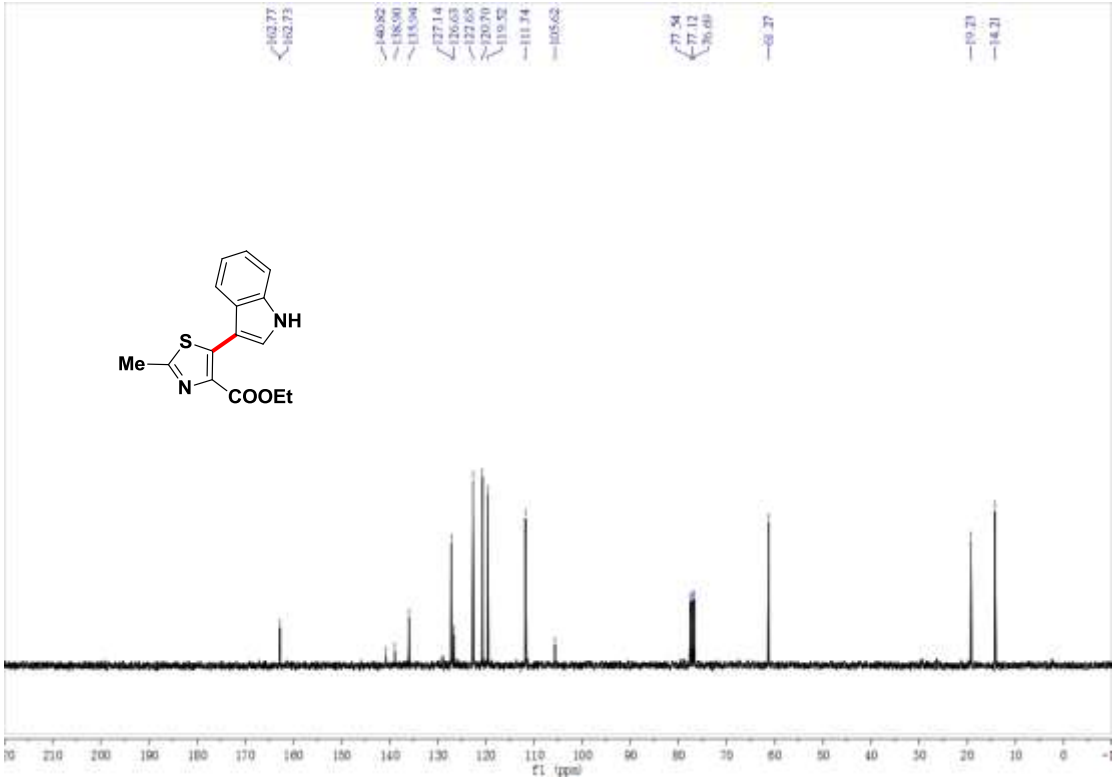


Ethyl 5-(1*H*-indol-3-yl)-2-methylthiazole-4-carboxylate (4q)

^{1}H NMR (300 MHz, $CDCl_3$)

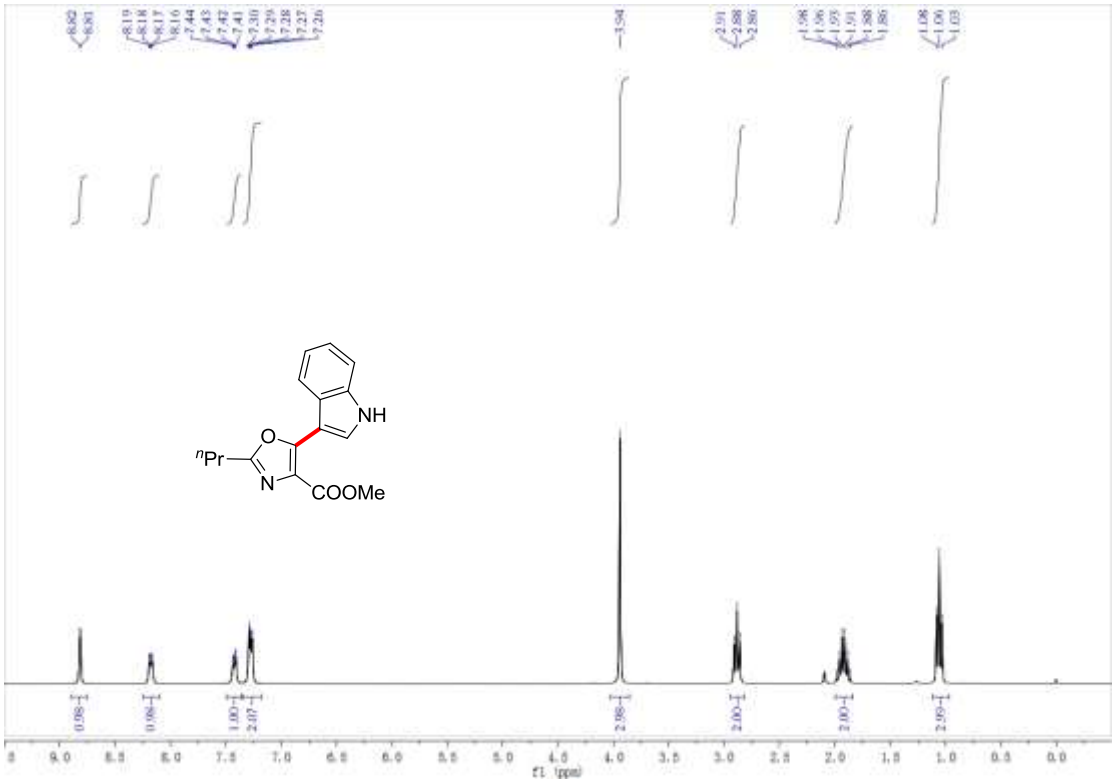


^{13}C NMR (75 MHz, $CDCl_3$)

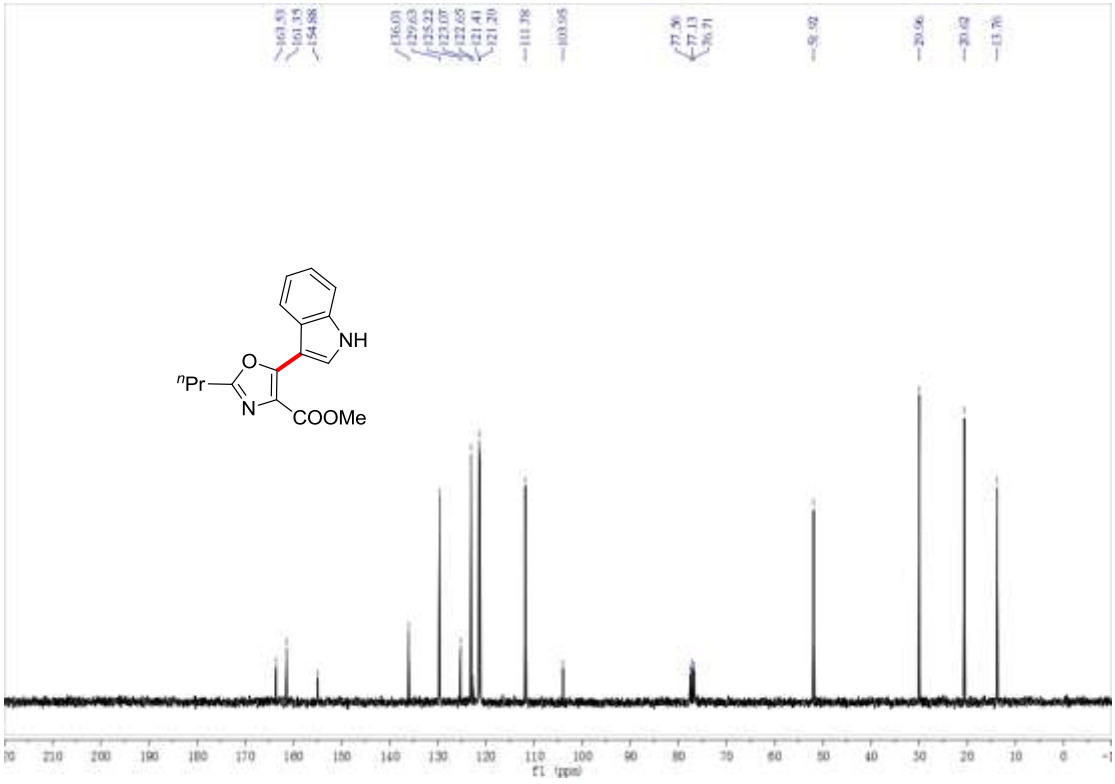


Methyl 5-(1H-indol-3-yl)-2-propyloxazole-4-carboxylate (4r)

^{1}H NMR (300 MHz, $CDCl_3$)

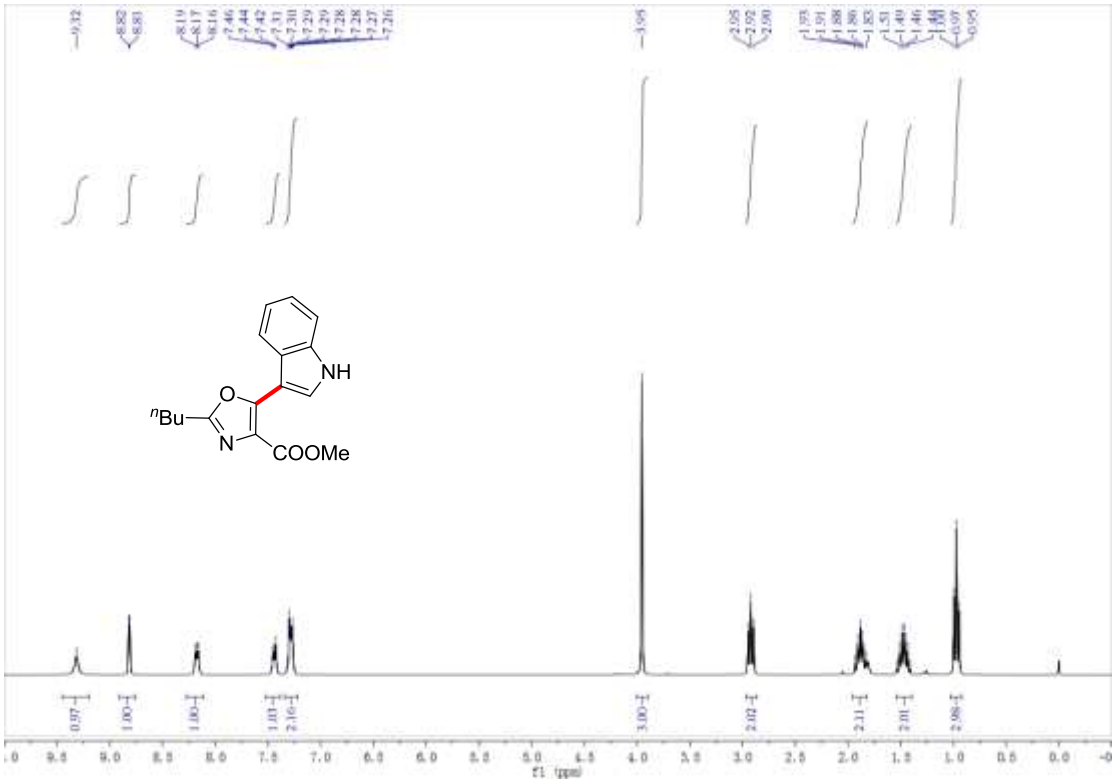


^{13}C NMR (75 MHz, $CDCl_3$)

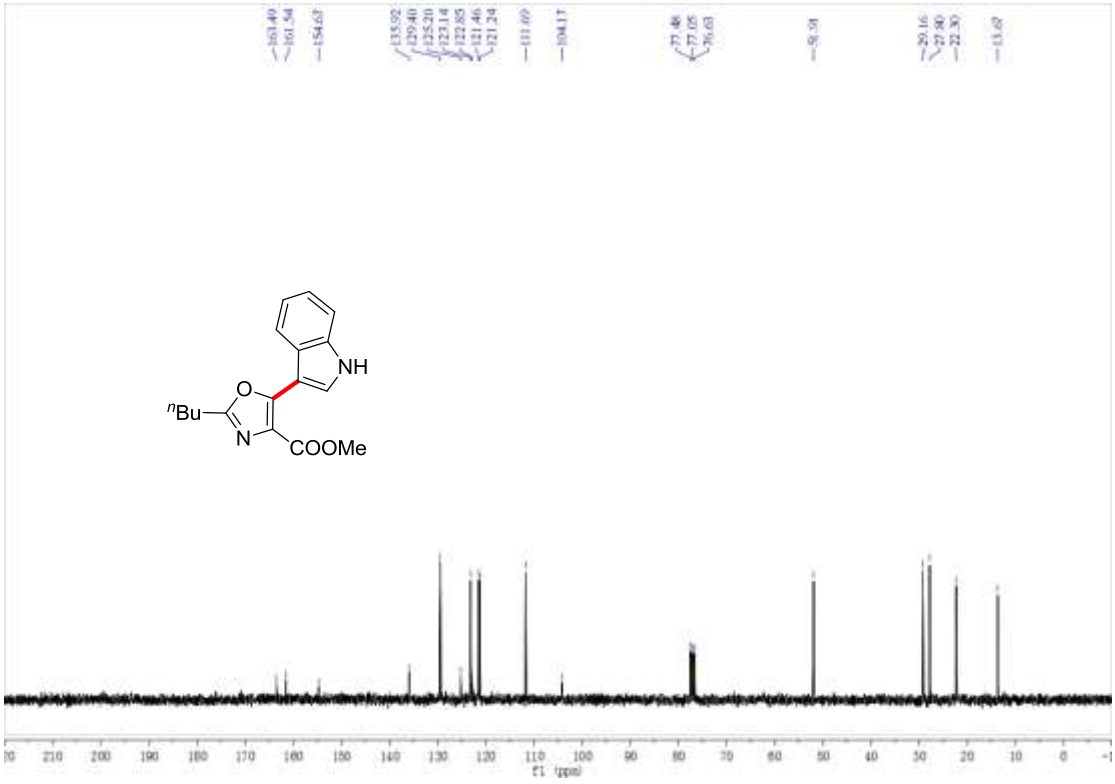


Methyl 5-(1H-indol-3-yl)-2-butyloxazole-4-carboxylate (4s)

^{1}H NMR (300 MHz, $CDCl_3$)

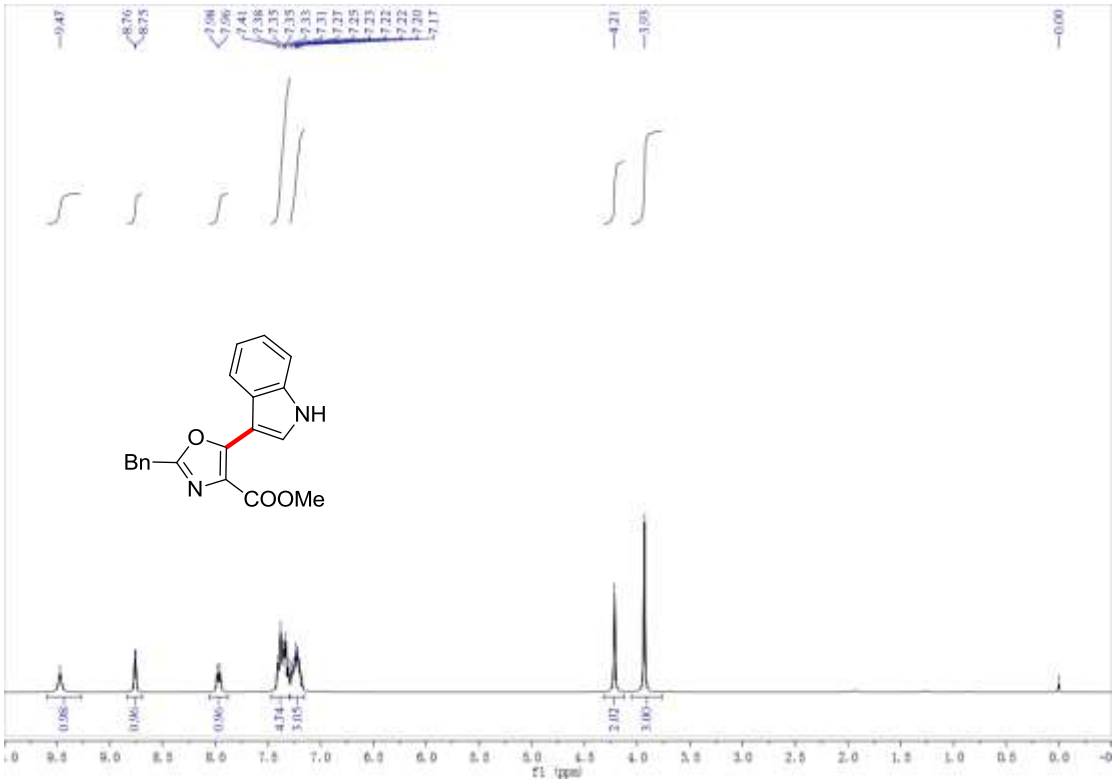


^{13}C NMR (75 MHz, $CDCl_3$)

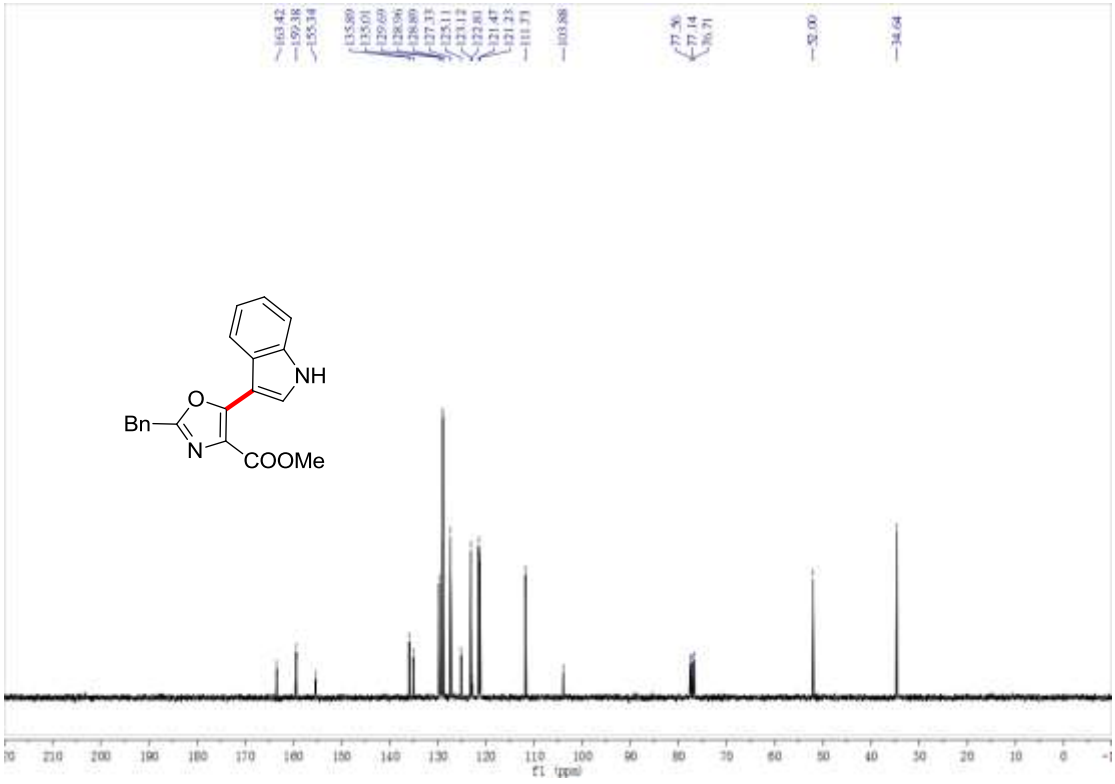


Methyl 5-(1H-indol-3-yl) 2-benzyloxazole-4-carboxylate (4t)

^{1}H NMR (300 MHz, $CDCl_3$)

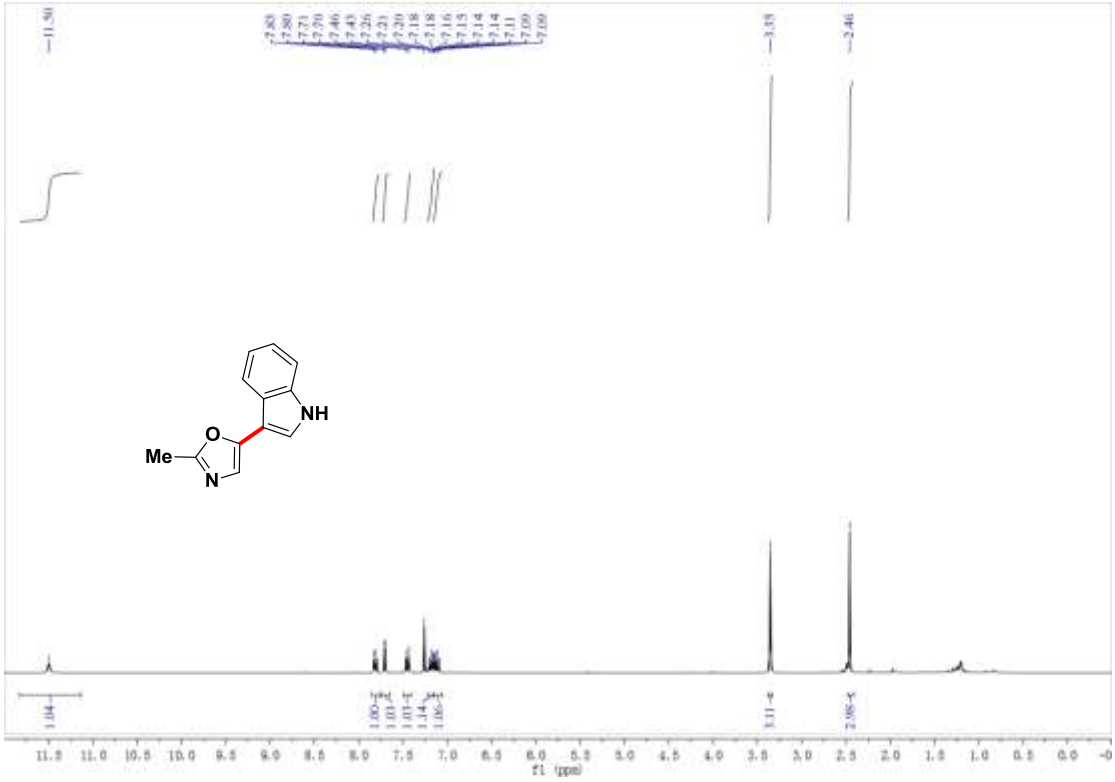


^{13}C NMR (75 MHz, $CDCl_3$)

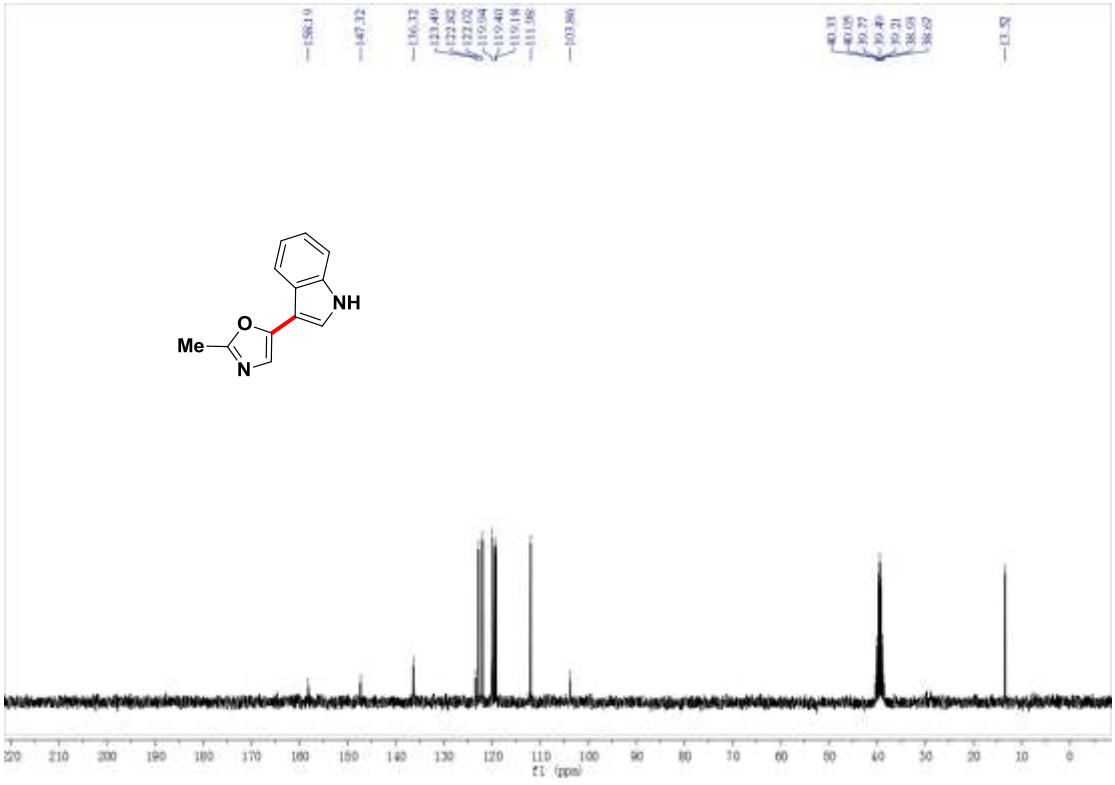


5-(1*H*-indol-3-yl)-2-methyloxazole (Pimprinine)

^{1}H NMR (300 MHz, d_6-DMSO)

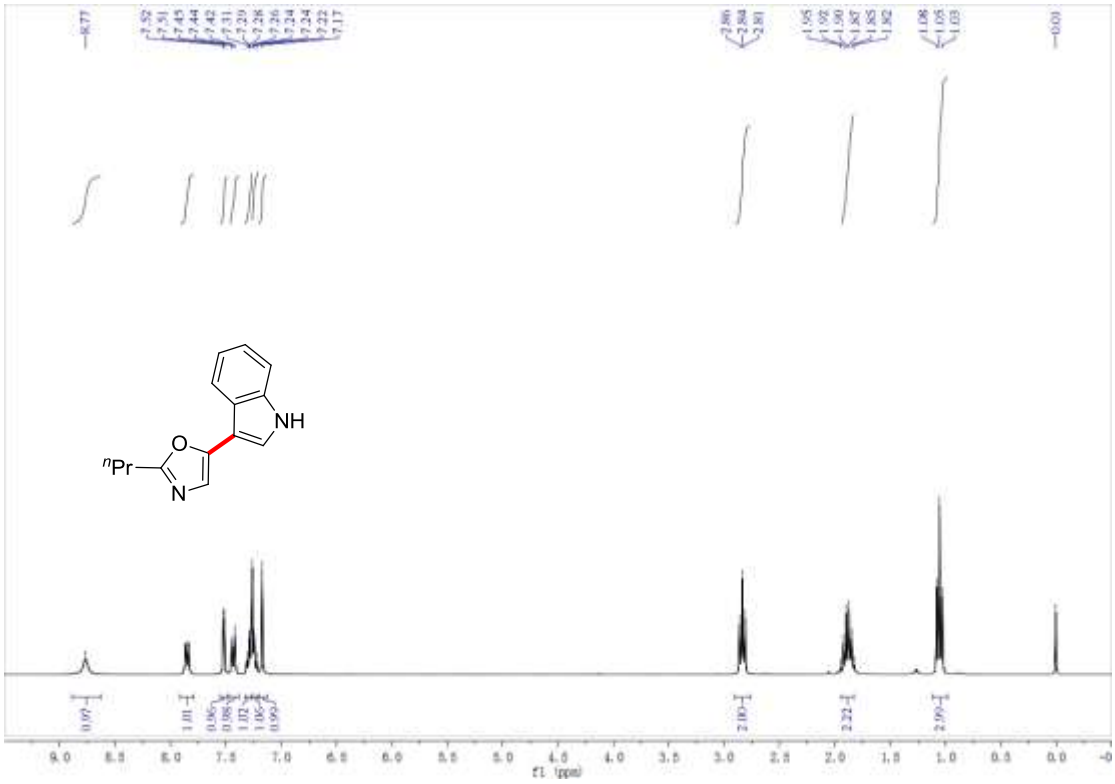


^{13}C NMR (75 MHz, d_6-DMSO)



5-(1H-indol-3-yl)-2-propyloxazole (WS-30581 A)

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)