Lanthanide amide-catalyzed one-pot functionalization of isatins: synthesis of spiro[cyclopropan-1,3′-oxindoles] and 2-oxoindolin-3-yl phosphates

Cheng Peng, Jiaojiao Zhai, Mingqiang Xue,* Fan Xu*

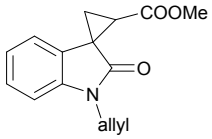
College of Chemistry, Chemical Engineering and Materials Science,
Soochow University, Suzhou 215123, P. R. China

xufan@suda.edu.cn xuemq@sina.com

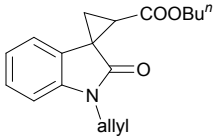
SUPPLEMENTARY INFORMATION

TABLE OF CONTENTS

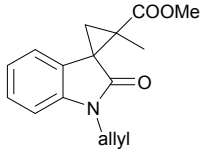
Characterization Data



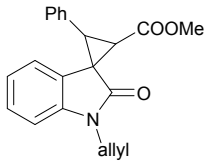
Methyl 1'-allyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4a). colorless oil (117 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 6.8 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 6.8 Hz, 1H), 5.89–5.80 (m, 1H), 5.26–5.20 (m, 2H), 4.39 (d, *J* = 5.2 Hz, 2H), 3.74 (s, 3H), 2.67 (t, *J* = 8.4 Hz, 1H), 2.40 (dd, *J* = 8.0, 4.8 Hz, 1H), 1.83 (dd, *J* = 8.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 167.5, 142.8, 131.5, 128.8, 127.7, 122.3, 118.6, 117.5, 109.1, 52.4, 42.7, 33.2, 32.2, 21.1; IR *v* 3003, 2951, 1741, 1706, 1644, 1614, 1489, 1467, 1434, 1381, 1010, 749 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{16}NO_3$ $[M + H]^+$ 258.1125, found 258.1124.



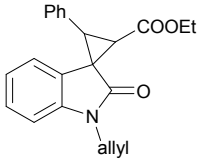
Butyl 1'-allyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4b). colorless oil (132 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.89–5.79 (m, 1H), 5.25–5.20 (m, 2H), 4.45–4.33 (m, 2H), 4.21–4.05 (m, 2H), 2.66 (t, *J* = 8.4 Hz, 1H), 2.39 (dd, *J* = 8.0, 4.8 Hz, 1H), 1.82 (dd, *J* = 8.4, 4.8 Hz, 1H), 1.64–1.57 (m, 2H), 1.40–1.31 (m, 2H). 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 167.2, 142.9, 131.6, 129.0, 127.7, 122.2, 118.6, 117.5, 109.1, 65.4, 42.7, 33.5, 32.2, 30.6, 21.1, 19.2, 13.8; IR *v* 2956, 2931, 2871, 1727, 1708, 1644, 1615, 1489, 1467, 1434, 1379, 1018, 760 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{22}NO_3$ $[M + H]^+$ 300.1594, found 300.1601.



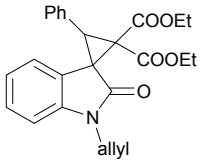
Methyl 1'-allyl-2-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4c). white solid (125 mg, 92% yield), m.p. 90–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.89–5.79 (m, 1H), 5.25–5.19 (m, 2H), 4.44–4.30 (m, 2H), 3.73 (s, 3H), 2.48 (d, *J* = 5.2 Hz, 1H), 1.61 (s, 3H), 1.60 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 171.3, 143.7, 131.5, 127.4, 126.1, 121.7, 121.5, 117.2, 109.0, 52.3, 42.5, 38.4, 36.2, 26.9, 16.9; IR *v* 3063, 2951, 1737, 1706, 1648, 1610, 1465, 1436, 1381, 1020, 744 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{18}NO_3$ $[M + H]^+$ 272.1281, found 272.1268.



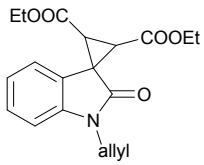
Methyl 1'-allyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-2-carboxylate (4d). yellow solid (100 mg, 60% yield), m.p. 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 3H), 7.19–7.12 (m, 3H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 5.98 (d, *J* = 7.6 Hz, 1H), 5.93–5.84 (m, 1H), 5.26–5.22 (m, 2H), 4.49–4.37 (m, 2H), 3.95 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 3.09 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 167.6, 143.1, 133.2, 131.5, 129.6, 128.6, 127.8, 127.4, 125.5, 121.7, 121.2, 117.4, 108.9, 52.5, 42.7, 38.0, 37.9, 37.0; IR *v* 2981, 2944, 1737, 1706, 1643, 1614, 1489, 1454, 1432, 1381, 1202, 741 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{20}NO_3$ $[M + H]^+$ 334.1438, found 334.1434.



Ethyl 1'-allyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-2-carboxylate (4e). yellow solid (123 mg, 71% yield), m.p. 124–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 3H), 7.20–7.12 (m, 3H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 5.99 (d, *J* = 8.0 Hz, 1H), 5.93–5.84 (m, 1H), 5.25–5.21 (m, 2H), 4.51–4.35 (m, 2H), 4.30–4.21 (m, 2H), 3.94 (d, *J* = 8.0 Hz, 1H), 3.08 (d, *J* = 8.4 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 167.2, 143.2, 133.3, 131.6, 129.7, 128.6, 127.9, 127.4, 125.7, 121.7, 121.2, 117.3, 108.9, 61.5, 42.7, 38.0, 37.9, 37.3, 14.3; IR *v* 3008, 2975, 2922, 1725, 1702, 1644, 1614, 1491, 1453, 1436, 1202, 1011, 748 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{22}NO_3$ $[M + H]^+$ 348.1594, found 348.1603.

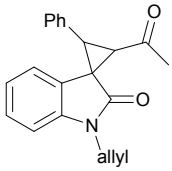


Diethyl 1'-allyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-2,2-dicarboxylate (4f). colorless oil (98.5 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.23 (m, 4H), 7.11–7.09 (m, 2H), 6.92–6.84 (m, 3H), 5.93–5.84 (m, 1H), 5.30–5.23 (m, 2H), 4.62–4.56 (m, 1H), 4.32–4.03 (m, 6H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 166.2, 164.7, 144.1, 131.3, 130.8, 130.0, 128.8, 128.2, 128.1, 127.8, 121.7, 121.3, 117.5, 108.8, 62.1, 62.0, 49.5, 42.8, 42.0, 39.5, 14.1, 14.0; IR *v* 3060, 2982, 2921, 1715, 1611, 1489, 1468, 1446, 1026, 751 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{26}NO_5$ $[M + H]^+$ 420.1811, found 420.1816.

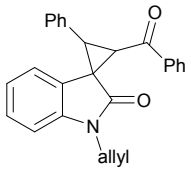


Diethyl 1'-allyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (4g, *trans*). white solid (94.4 mg, 55% yield), m.p. 75–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 5.89–5.80 (m, 1H), 5.25–5.21 (m, 2H), 4.46–4.32 (m, 2H), 4.26–4.07 (m, 4H), 3.30 (d, *J* = 7.6 Hz, 1H), 3.28 (d, *J* = 8.0 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 167.3, 165.9, 143.6, 131.3, 128.4, 124.5, 122.8, 122.5, 117.7, 109.2, 61.8, 61.7, 42.8, 37.5, 35.5, 35.5, 14.2; IR *v* 3011, 2989, 2936, 1721, 1706, 1613, 1490, 1438, 1380, 1198, 757 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{22}NO_5$ $[M + H]^+$ 344.1492, found 344.1489.

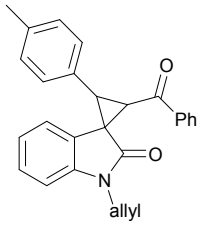
Diethyl 1'-allyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (4g', *cis*). yellow solid (30.9 mg, 18% yield), m.p. 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.2 Hz, 1H), 5.90–5.81 (m, 1H), 5.27–5.20 (m, 2H), 4.41–4.39 (m, 2H), 4.28–4.20 (m, 4H), 2.86 (s, 2H), 1.28 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 164.8, 143.1, 131.6, 128.4, 127.9, 122.2, 118.5, 117.5, 109.1, 61.7, 42.8, 35.3, 34.3, 14.1; IR *v* 2983, 2937, 1716, 1613, 1490, 1468, 1204, 752 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{22}NO_5$ $[M + H]^+$ 344.1492, found 344.1490.



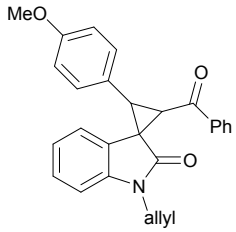
2-Acetyl-1'-allyl-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-one (4h). yellow oil (98.4 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 3H), 7.18–7.13 (m, 3H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.01 (d, *J* = 7.2 Hz, 1H), 5.93–5.83 (m, 1H), 5.26–5.21 (m, 2H), 4.50–4.36 (m, 2H), 3.98 (d, *J* = 8.4 Hz, 1H), 3.12 (d, *J* = 8.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 172.8, 143.1, 133.4, 131.5, 129.7, 128.6, 127.9, 127.5, 125.7, 121.9, 121.2, 117.6, 109.0, 44.6, 42.7, 39.4, 38.7, 30.3; IR *v* 2959, 2920, 1712, 1643, 1610, 1433, 1378, 1191, 1013, 760, 699 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{20}NO_2$ $[M + H]^+$ 318.1489, found 318.1498.



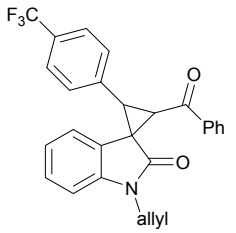
1'-Allyl-2-benzoyl-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-one (4i). yellow solid (173 mg, 91% yield), m.p. 179–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.37–7.31 (m, 5H), 7.26–7.19 (m, 3H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.17 (d, *J* = 7.6 Hz, 1H), 5.70–5.61 (m, 1H), 5.08–5.01 (m, 2H), 4.44–4.19 (m, 2H), 4.16 (d, *J* = 8.4 Hz, 1H), 3.64 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 172.3, 143.4, 136.6, 133.8, 133.4, 131.5, 129.9, 128.8, 128.7, 128.4, 127.9, 127.7, 125.5, 122.0, 121.3, 117.3, 109.1, 42.6, 41.8, 39.5, 37.6; IR *v* 3056, 2959, 2922, 1701, 1680, 1649, 1597, 1455, 1434, 1214, 1015, 766, 753, 698 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{22}NO_2$ $[M + H]^+$ 380.1645, found 380.1655.



1'-Allyl-2-benzoyl-3-(p-tolyl)spiro[cyclopropane-1,3'-indolin]-2'-one (4j). yellow solid (185 mg, 94% yield), m.p. 136–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.35–7.31 (m, 2H), 7.24–7.18 (m, 2H), 7.11–7.09 (m, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.22 (d, *J* =7.2 Hz, 1H), 5.69–5.60 (m, 1H), 5.08–5.00 (m, 2H), 4.43–4.15 (m, 2H), 4.12 (d, *J* = 8.4 Hz, 1H), 3.63 (d, *J* = 8.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 172.2, 143.4, 138.3, 136.6, 133.6, 133.4, 131.5, 130.5, 128.7, 128.6, 128.4, 128.3, 127.6, 126.9, 125.6, 121.9, 121.3, 117.3, 109.1, 42.5, 41.8, 39.5, 37.6, 21.5; IR *v* 3054, 3002, 2922, 1700, 1680, 1612, 1489, 1448, 1432, 1377, 1213, 1019, 759, 748 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{24}NO_2$ $[M + H]^+$ 394.1807, found 394.1818.

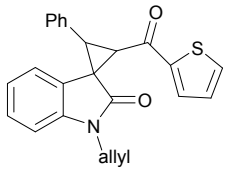


1'-Allyl-2-benzoyl-3-(4-methoxyphenyl)spiro[cyclopropane-1,3'-indolin]-2'-one (4k). yellow solid (195 mg, 95% yield), m.p. 180–181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.32–7.18 (m, 6H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.83–6.76 (m, 3H), 6.16 (d, *J* = 7.2 Hz, 1H), 5.73–5.63 (m, 1H), 5.10–5.04 (m, 2H), 4.44–4.16 (m, 2H), 4.13 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.60 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 172.3, 163.8, 143.4, 134.0, 131.6, 130.7, 129.9, 129.8, 128.6, 127.9, 127.6, 125.6, 121.9, 121.2, 117.3, 114.0, 109.1, 55.6, 42.6, 41.8, 39.4, 37.7; IR *v* 3060, 2920, 2850, 1711, 1673, 1603, 1509, 1488, 1452, 1254, 1024, 1014, 826, 747, 734, 698 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{24}NO_3$ $[M + H]^+$ 410.1756, found 410.1766.

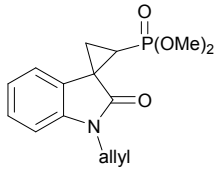


1'-Allyl-2-benzoyl-3-(4-(trifluoromethyl)phenyl)spiro[cyclopropane-1,3'-indolin]-2'-one (4l). white solid (159 mg, 71% yield), m.p. 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.39–7.32 (m, 4H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.17 (d, *J* = 7.6 Hz, 1H), 5.69–5.60 (m, 1H), 5.08–5.00 (m, 2H), 4.43–4.18 (m, 2H), 4.15 (d, *J* = 7.6 Hz, 1H), 3.67 (d, *J* = 8.4 Hz, 1H); ^{13}C

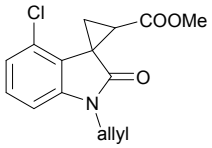
NMR (100 MHz, $CDCl_3$) δ 191.3, 171.8, 143.4, 138.0, 136.3, 133.6, 131.2, 130.3, 130.1 (d, *J* = 32 Hz), 128.8, 128.3, 128.1, 125.6 (d, *J* = 4 Hz), 125.4, 123.5 (d, *J* = 263 Hz), 122.7, 121.1, 117.4, 109.4, 42.6, 41.6, 39.3, 36.8; IR *v* 3059, 2990, 1707, 1686, 1599, 1488, 1449, 1440, 1383, 1355, 1225, 1016, 847, 749, 740, 691 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{21}F_3NO_2$ $[M + H]^+$ 448.1524, found 448.1532.



1'-Allyl-2-phenyl-3-(thiophene-2-carbonyl)spiro[cyclopropane-1,3'-indolin]-2'-one (4m). yellow solid (181 mg, 94% yield), m.p. 185–186 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.44 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.32–7.31 (m, 3H), 7.26–7.24 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 5.2, 4.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 7.2 Hz, 1H), 5.76–5.67 (m, 1H), 5.14–5.07 (m, 2H), 4.46–4.21 (m, 2H), 4.14 (d, *J* = 8.4 Hz, 1H), 3.61 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 172.2, 143.8, 143.3, 134.0, 133.6, 132.2, 131.5, 129.8, 128.7, 128.1, 127.9, 127.7, 125.5, 122.0, 121.2, 117.4, 109.1, 42.7, 42.3, 37.4, 37.7; IR *v* 2965, 1697, 1666, 1609, 1432, 1377, 1213, 1019, 759, 751, 706 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{20}NO_2S$ $[M + H]^+$ 386.1215, found 386.1229.

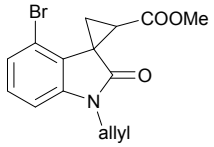


Dimethyl (1'-allyl-2'-oxospiro[cyclopropane-1,3'-indolin]-2-yl)phosphonate (4n). yellow oil (101 mg, 66% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.92–5.82 (m, 1H), 5.27–5.21 (m, 2H), 4.49–4.36 (m, 2H), 3.83 (d, *J* = 10.8 Hz, 3H), 3.77 (d, *J* = 11.2 Hz, 3H), 2.30–2.24 (m, 1H), 1.99–1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2 (d, *J* = 6.5 Hz), 142.9, 131.5, 128.7, 127.9, 122.3, 118.5, 117.5, 109.1, 53.4 (d, *J* = 6.3 Hz) , 53.1 (d, *J* = 6.4 Hz), 42.8, 31.7 (d, *J* = 4.4 Hz), 25.6 (d, *J* = 194 Hz), 22.5 (d, *J* = 5.5 Hz); IR *v* 3057, 2955, 2852, 1716, 1490, 1380, 1245, 1026, 829, 752 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{19}NO_4P$ $[M + H]^+$ 308.1052, found 308.1065.

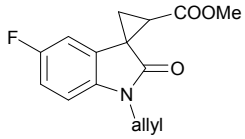


Methyl 1'-allyl-4'-chloro-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4o). yellow solid (105 mg, 72% yield), m.p. 101–103 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.87–5.77 (m, 1H), 5.23–5.19 (m, 2H), 4.38–4.36 (m, 2H), 3.74 (s, 3H), 3.48 (t, *J* = 8.4 Hz, 1H), 2.53 (dd, *J* = 8.8, 4.8 Hz, 1H), 2.21 (dd, *J* = 8.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 168.1, 144.8, 131.2, 128.6, 127.8,

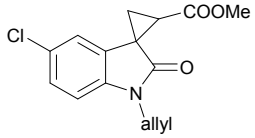
123.7, 123.4, 117.7, 107.8, 52.5, 42.9, 33.0, 29.3, 17.9; IR *v* 2999, 2953, 1736, 1711, 1607, 1451, 1389, 1013, 780 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{15}ClNO_3$ $[M + H]^+$ 292.0740, found 292.0749.



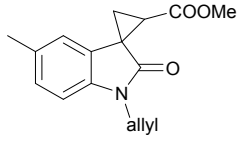
Methyl 1'-allyl-4'-bromo-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4p). yellow solid (134 mg, 80% yield), m.p. 111–113 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.13–7.07 (m, 2H), 6.84 (dd, *J* = 7.2, 2.0 Hz, 1H), 5.86–5.77 (m, 1H), 5.23–5.18 (m, 2H), 4.38–4.36 (m, 2H), 3.74 (s, 3H), 3.56 (t, *J* = 8.4 Hz, 1H), 2.60 (dd, *J* = 9.2, 4.8 Hz, 1H), 2.16 (dd, *J* = 8.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 168.2, 145.1, 131.2, 128.9, 126.6, 125.0, 117.8, 115.6, 108.4, 52.5, 42.8, 33.6, 29.2, 17.9; IR *v* 2998, 2951, 1734, 1710, 1604, 1577, 1447, 1387, 1053, 1008, 777 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{15}BrNO_3$ $[M + H]^+$ 336.0235, found 336.0233.



Methyl 1'-allyl-5'-fluoro-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4q). yellow oil (124 mg, 90% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 6.97–6.92 (m, 1H), 6.80 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.62 (dd, *J* = 8.0, 2.4 Hz, 1H), 5.88–5.78 (m, 1H), 5.24–5.21 (m, 2H), 4.38–4.37 (m, 2H), 3.75 (s, 3H), 2.67 (t, *J* = 8.4 Hz, 1H), 2.42 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.83 (dd, *J* = 8.4, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 167.2, 159.2 (d, *J* = 239 Hz), 138.8 (d, *J* =1.8 Hz), 131.4, 130.5 (d, *J* = 8.7 Hz), 117.7, 113.9 (d, *J* = 23.3 Hz), 109.7 (d, *J* = 8.1 Hz), 106.9 (d, *J* = 25.5 Hz), 52.5, 42.9, 33.5, 32.5 (d, *J* = 2.2 Hz), 21.4; IR *v* 2952, 1701, 1489, 1435, 1173, 1013, 804 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{15}FNO_3$ $[M + H]^+$ 276.1036, found 276.1040.

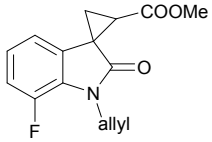


Methyl 1'-allyl-5'-chloro-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4r). white solid (134 mg, 92% yield), m.p. 92–93 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 1H), 6.84–6.79 (m, 2H), 5.87–5.77 (m, 1H), 5.24–5.19 (m, 2H), 4.38–4.36 (m, 2H), 3.74 (s, 3H), 2.68 (t, *J* = 8.4 Hz, 1H), 2.42 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.85 (dd, *J* = 8.4, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 167.0, 141.3, 131.1, 130.5, 127.6, 127.5, 119.2, 117.7, 109.9, 52.4, 42.7, 33.4, 32.0, 21.3; IR *v* 3085, 2952, 1741, 1710, 1614, 1486, 1436, 1390, 1046, 1011, 807 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{15}ClNO_3$ $[M + H]^+$ 292.0735, found 292.0746.

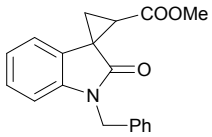


Methyl 1'-allyl-5'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4s). yellow

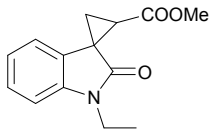
oil (117 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 5.88–5.78 (m, 1H), 5.24–5.18 (m, 2H), 4.37–4.35 (m, 2H), 3.73 (s, 3H), 2.64 (t, *J* = 8.4 Hz, 1H), 2.38 (dd, *J* = 8.0, 5.2 Hz, 1H), 2.32 (s, 3H), 1.80 (dd, *J* = 8.8, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 167.6, 140.5, 131.9, 131.7, 128.9, 128.0, 119.4, 117.5, 108.9, 52.4, 42.8, 33.2, 32.3, 21.2, 21.1; IR *v* 2951, 2862, 1742, 1705, 1644, 1599, 1494, 1435, 1390, 1011, 870, 806 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{18}NO_3$ $[M + H]^+$ 272.1287, found 272.1297.



Methyl 1'-allyl-7'-fluoro-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4t). yellow oil (118 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02–6.94 (m, 2H), 6.64 (d, *J* = 6.8 Hz, 1H), 5.96–5.87 (m, 1H), 5.22–5.15 (m, 2H), 4.52–4.50 (m, 2H), 3.74 (s, 3H), 2.68 (t, *J* = 8.4 Hz, 1H), 2.42 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.85 (dd, *J* = 8.4, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 167.1, 147.4 (d, *J* = 243 Hz), 132.3, 131.8 (d, *J* = 4.1 Hz), 129.4 (d, *J* = 9.4 Hz), 122.9 (d, *J* = 6.6 Hz), 117.0, 115.8 (d, *J* = 19.6 Hz), 114.5 (d, *J* = 3.1 Hz), 52.5, 44.2 (d, *J* = 4.7 Hz), 33.9, 32.4 (d, *J* = 2.9 Hz), 21.7; IR *v* 3086, 2986, 2953, 1716, 1634, 1597, 1435, 1377, 1206, 1177, 1022, 778 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{15}FNO_3$ $[M + H]^+$ 276.1036, found 276.1039.

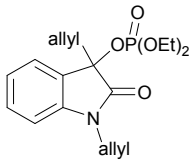


Methyl 1'-benzyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4u). yellow solid (135 mg, 88% yield), m.p. 101–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 5H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 4.95 (s, 2H), 3.76 (s, 3H), 2.69 (t, *J* = 8.4 Hz, 1H), 2.44 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.85 (dd, *J* = 8.4, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 167.6, 142.8, 136.0, 128.9, 128.8, 127.8, 127.7, 127.5, 122.4, 118.7, 109.3, 52.6, 44.2, 33.5, 32.4, 21.1; IR *v* 3060, 2950, 1742, 1707, 1489, 1453, 1435, 1384, 1011, 727, 696 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{18}NO_3$ $[M + H]^+$ 308.1281, found 308.1282.

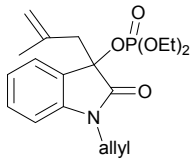


Methyl 1'-ethyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2-carboxylate (4v). yellow solid (99.3 mg, 81% yield), m.p. 56–57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 3.84–3.78 (m, 2H), 3.75 (s, 3H), 2.65 (t, *J* = 8.4 Hz, 1H), 2.38 (dd, *J* = 8.0, 4.8 Hz, 1H), 1.80 (dd, *J* = 8.4, 4.8 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 167.7, 142.8, 129.1, 127.8, 122.1, 118.7, 108.4,

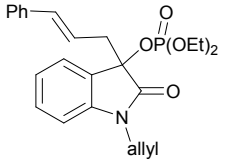
52.4, 35.2, 33.0, 32.4, 21.1, 12.9; IR *v* 3059, 2984, 2943, 1724, 1491, 1457, 1437, 1374, 1012, 749 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{16}NO_3$ $[M + H]^+$ 246.1130, found 246.1137.



1,3-Diallyl-2-oxoindolin-3-yl diethyl phosphate (7a). yellow oil (168 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.87–5.78 (m, 1H), 5.58–5.46 (m, 1H), 5.33–5.20 (m, 2H), 5.09–5.04 (m, 2H), 4.41 (dd, *J* = 16.4, 5.6 Hz, 1H), 4.26 (dd, *J* = 16.4, 5.2 Hz, 1H), 4.07–3.83 (m, 4H), 2.94 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.72 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.24–1.19 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5 (d, *J* = 2.1 Hz), 143.0, 131.2, 130.3, 129.4, 126.4, 124.9, 122.4, 120.8, 117.6, 109.4, 80.6 (d, *J* = 6.8 Hz), 63.9 (d, *J* = 6.0 Hz), 63.8 (d, *J* = 5.6 Hz). 42.5, 42.2 (d, *J* = 10.0 Hz), 15.9 (d, *J* = 6.8 Hz), 15.8 (d, *J* = 5.9 Hz); IR *v* 2983, 1725, 1644, 1613, 1489, 1367, 1266, 1022, 819, 757 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{25}NO_5P$ $[M + H]^+$ 366.1465, found 366.1469.

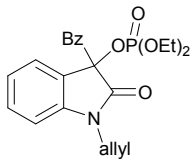


1-Allyl-3-(2-methylallyl)-2-oxoindolin-3-yl diethyl phosphate (7b). yellow oil (157 mg, 83% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.86–5.77 (m, 1H), 5.32–5.20 (m, 2H), 4.77–4.60 (m, 2H), 4.46–4.40 (m, 1H), 4.25–4.20 (m, 1H), 4.06–3.81 (m, 4H), 2.90 (d, *J* = 12.8 Hz, 1H), 2.78 (d, *J* = 12.8 Hz, 1H), 1.49 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4 (d, *J* = 2.3 Hz), 143.1, 137.5, 131.0, 130.2, 126.3, 125.2, 122.0, 117.4, 117.0, 109.2, 81.1 (d, *J* = 7.0 Hz), 63.6 (d, *J* = 5.9 Hz), 63.6 (d, *J* = 5.5 Hz), 44.9 (d, *J* = 9.9 Hz), 42.4, 23.7, 15.7 (d, *J* = 6.5 Hz), 15.6 (d, *J* = 6.4 Hz); IR *v* 2983, 1729, 1645, 1613, 1489, 1363, 1268, 1022, 816, 752 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{27}NO_5P$ $[M + H]^+$ 380.1621, found 380.1622.

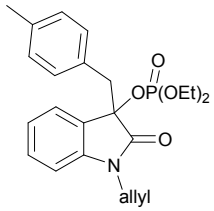


1-Allyl-3-cinnamyl-2-oxoindolin-3-yl diethyl phosphate (7c). yellow oil (214 mg, 97% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.26–7.18 (m, 5H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 5.91–5.84 (m, 1H), 5.77–5.68 (m, 1H), 5.23–5.19 (m, 1H), 5.07–5.05 (m, 1H), 4.40 (dd, *J* = 16.4, 5.2 Hz, 1H), 4.21 (dd, *J* = 16.4, 5.2 Hz, 1H), 4.08–3.84 (m, 4H), 3.10 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.85 (dd, *J* = 13.2, 8.8 Hz, 1H), 1.24–1.19 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3 (d, *J* = 2.0 Hz), 142.7, 136.5, 135.4, 130.7, 130.1, 128.2, 127.3, 126.2, 125.9, 124.7, 122.2, 120.4, 117.3, 109.2, 80.7 (d, *J*

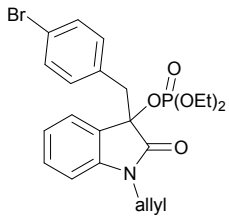
= 6.8 Hz), 63.7 (d, *J* = 5.9 Hz), 63.6 (d, *J* = 5.5 Hz), 42.2, 41.2 (d, *J* = 10.1 Hz), 15.7 (d, *J* = 5.9 Hz), 15.6 (d, *J* = 6.0 Hz); IR *v* 2985, 1727, 1643, 1612, 1487, 1362, 1265, 1024, 815, 754, 744, 690 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{28}NNaO_5P$ $[M + Na]^+$ 464.1603, found 464.1597.



1-Allyl-3-benzyl-2-oxoindolin-3-yl diethyl phosphate (7d). yellow oil (204 mg, 98% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.13–7.02 (m, 4H), 6.90–6.88 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 5.50–5.41 (m, 1H), 4.98 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.78 (dd, *J* = 17.2, 0.8 Hz, 1H), 4.29 (dd, *J* = 16.8, 4.8 Hz, 1H), 4.10–3.84 (m, 5H), 3.49 (d, *J* = 12.8 Hz, 1H), 3.29 (d, *J* = 12.4 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1 (d, *J* = 2.0 Hz), 142.8, 132.4, 130.4, 130.3, 130.1, 127.5, 126.8, 125.7, 124.9, 121.9, 116.9, 109.1, 81.6 (d, *J* = 6.9 Hz), 63.6 (d, *J* = 5.9 Hz), 63.6 (d, *J* = 5.6 Hz), 43.6 (d, *J* = 10.4 Hz), 42.0, 15.7, 15.6; IR *v* 2983, 1727, 1645, 1613, 1489, 1455, 1365, 1268, 1023, 804, 751, 731, 699 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{27}NO_5P$ $[M + H]^+$ 416.1621, found 416.1622.

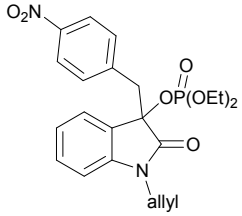


1-Allyl-3-(4-methylbenzyl)-2-oxoindolin-3-yl diethyl phosphate (7e). colorless oil (212 mg, 99% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 5.51–5.42 (m, 1H), 4.98–4.95 (m, 1H), 4.76–4.72 (m, 1H), 4.30 (dd, *J* = 16.8, 4.8 Hz, 1H), 4.09–3.84 (m, 5H), 3.46 (d, *J* = 12.8 Hz, 1H), 3.25 (d, *J* = 12.8 Hz, 1H), 2.22 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 142.8, 136.3, 130.4, 130.2, 130.0, 129.2, 128.2, 125.8, 124.9, 121.8, 116.7, 109.0, 81.6 (d, *J* = 6.7 Hz), 63.5 (d, *J* = 3.9 Hz), 63.5 (d, *J* = 4.3 Hz), 43.2 (d, *J* = 10.2 Hz), 41.9, 20.7, 15.7 (d, *J* = 5.7 Hz), 15.6 (d, *J* = 6.8 Hz); IR *v* 2983, 1725, 1645, 1611, 1487, 1363, 1269, 1016, 838, 808, 759 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{28}NNaO_5P$ $[M + Na]^+$ 452.1597, found 452.1580.

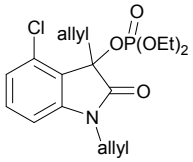


1-Allyl-3-(4-bromobenzyl)-2-oxoindolin-3-yl diethyl phosphate (7f). yellow oil (235 mg, 95% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 1H), 7.28–7.25 (m, 1H), 7.22 (d, *J* = 8.0

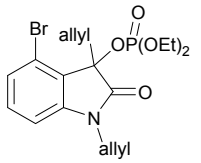
Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.54–5.45 (m, 1H), 5.05–5.03 (m, 1H), 4.82–4.78 (m, 1H), 4.29 (dd, *J* = 16.4, 5.2 Hz, 1H), 4.09–3.84 (m, 5H), 3.44 (d, *J* = 12.8 Hz, 1H), 3.24 (d, *J* = 12.8 Hz, 1H), 1.25–1.20 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7 (d, *J* = 2.1 Hz), 142.7, 132.0, 131.5, 130.5, 130.2, 130.1, 125.3, 124.7, 121.9, 120.9, 116.9, 109.1, 81.1 (d, *J* = 6.6 Hz), 63.5 (d, *J* = 5.9 Hz), 63.5 (d, *J* = 5.6 Hz), 42.8 (d, *J* = 10.3 Hz), 41.9, 15.6 (d, *J* = 6.9 Hz), 15.5 (d, *J* = 6.7 Hz); IR *v* 2985, 1724, 1643, 1612, 1485, 1440, 1360, 1263, 1030, 980, 814, 763, 730 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{26}BrNO_5P$ $[M + H]^+$ 494.0726, found 494.0737.



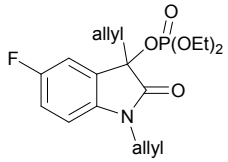
1-Allyl-3-(4-nitrobenzyl)-2-oxoindolin-3-yl diethyl phosphate (7g). yellow oil (207 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 5.50–5.40 (m, 1H), 4.91–4.89 (m, 1H), 4.82–4.77 (m, 1H), 4.14 (dd, *J* = 16.4, 4.8 Hz, 1H), 4.02–3.73 (m, 5H), 3.49 (d, *J* = 12.4 Hz, 1H), 3.29 (d, *J* = 12.8 Hz, 1H), 1.12 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5 (d, *J* = 2.1 Hz), 146.7, 142.5, 140.3, 131.3, 130.4, 130.2, 124.9, 124.7, 122.4, 122.1, 117.0, 109.2, 80.7 (d, *J* = 6.4 Hz), 63.6 (d, *J* = 5.0 Hz), 63.6 (d, *J* = 5.1 Hz), 43.1 (d, *J* = 10.4 Hz), 42.0, 15.5 (d, *J* = 6.9 Hz), 15.4 (d, *J* = 6.7 Hz); IR *v* 2984, 1723, 1644, 1612, 1515, 1486, 1441, 1364, 1341, 1276, 1012, 855, 820, 747 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{26}N_2O_7P$ $[M + H]^+$ 461.1472, found 461.1479.



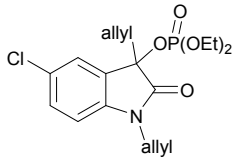
1,3-Diallyl-4-chloro-2-oxoindolin-3-yl diethyl phosphate (7h). yellow oil (162 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.85–5.76 (m, 1H), 5.32–5.20 (m, 3H), 5.12–5.07 (m, 1H), 4.96–4.93 (m, 1H), 4.42 (dd, *J* = 16.4, 5.2 Hz, 1H), 4.26–3.83 (m, 5H), 3.32 (dd, *J* = 12.8, 7.2 Hz, 1H), 2.95 (dd, *J* = 12.8, 7.6 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 145.2, 131.6, 131.4, 130.9, 128.7, 123.5, 122.9, 120.9, 117.7, 108.0, 80.9 (d, *J* = 7.0 Hz), 63.9 (d, *J* = 5.9 Hz), 63.9 (d, *J* = 5.5 Hz), 42.7, 39.0 (d, *J* = 11.4 Hz), 15.8 (d, *J* = 7.3 Hz), 15.7 (d, *J* = 7.8 Hz); IR *v* 2983, 1733, 1643, 1607, 1589, 1478, 1458, 1371, 1266, 1023, 986, 818, 778 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{23}ClNNaO_5P$ $[M + Na]^+$ 422.0900, found 422.0899.



1,3-Diallyl-4-bromo-2-oxoindolin-3-yl diethyl phosphate (7i). yellow oil (191 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.13 (m, 2H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.85–5.76 (m, 1H), 5.32–5.19 (m, 3H), 5.13–5.08 (m, 1H), 4.96–4.93 (m, 1H), 4.42 (dd, *J* = 16.4, 5.2 Hz, 1H), 4.26–4.13 (m, 3H), 4.01–3.86 (m, 2H), 3.41 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.92 (dd, *J* = 12.8, 7.6 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5 (d, *J* = 0.9 Hz), 145.2, 131.4, 130.6, 128.5, 126.4, 124.4, 120.7, 119.4, 117.5, 108.3, 81.3 (d, *J* = 6.9 Hz), 63.7 (d, *J* = 6.0 Hz), 63.6 (d, *J* = 5.7 Hz), 42.4, 38.6 (d, *J* = 11.3 Hz), 15.7 (d, *J* = 4.3 Hz), 15.6 (d, *J* = 4.7 Hz); IR *v* 2982, 1734, 1643, 1605, 1582, 1476, 1454, 1369, 1266, 1023, 986, 816, 778 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{23}BrNNaO_5P$ $[M + Na]^+$ 466.0395, found 466.0389.

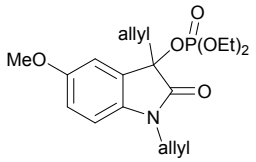


1,3-Diallyl-5-fluoro-2-oxoindolin-3-yl diethyl phosphate (7j). white solid (171 mg, 89% yield), m.p. 60–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.6 Hz, 1H), 7.04–6.99 (m, 1H), 6.75 (dd, *J* = 8.4, 4.0 Hz, 1H), 5.86–5.76 (m, 1H), 5.57–5.47 (m, 1H), 5.33–5.22 (m, 2H), 5.11–5.07 (m, 2H), 4.39 (dd, *J* = 16.4, 4.8 Hz, 1H), 4.26 (dd, *J* = 16.4, 3.6 Hz, 1H), 4.13–3.87 (m, 4H), 2.91 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.69 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 158.5 (d, *J* = 239.9 Hz), 138.7, 130.7, 128.8, 127.7 (d, *J* = 8.0 Hz), 120.8, 117.5, 116.2 (d, *J* = 23.4 Hz), 112.6 (d, *J* = 23.8 Hz), 109.9 (d, *J* = 7.1 Hz), 80.1 (d, *J* = 6.5 Hz), 63.7, 63.6, 42.3, 41.9 (d, *J* = 10.4 Hz), 15.6, 15.5; IR *v* 2983, 1725, 1646, 1487, 1456, 1360, 1266, 1243, 1024, 881, 818, 778 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{23}FNNaO_5P$ $[M + Na]^+$ 406.1196, found 406.1201.

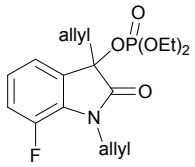


1,3-Diallyl-5-chloro-2-oxoindolin-3-yl diethyl phosphate (7k). yellow solid (188 mg, 94% yield), m.p. 49–50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.85–5.76 (m, 1H), 5.57–5.46 (m, 1H), 5.32–5.21 (m, 2H), 5.12–5.08 (m, 2H), 4.38 (dd, *J* = 16.4, 5.2 Hz, 1H), 4.25 (dd, *J* = 16.4, 5.2 Hz, 1H), 4.14–3.84 (m, 4H), 2.90 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.69 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1 (d, *J* = 0.9 Hz), 141.5, 130.7, 130.0, 128.9, 128.0, 127.6, 125.1, 121.2, 117.8, 110.5, 80.1 (d, *J* = 6.6 Hz), 63.9, 63.8, 42.6, 42.0 (d, *J* = 10.7 Hz), 15.8, 15.8; IR *v* 2984, 1724, 1644, 1613, 1483, 1371, 1263, 1100, 1025, 884, 826, 777 cm^{-1}; HRMS (ESI)

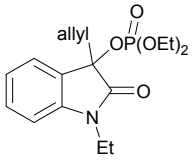
calcd. for $C_{18}H_{23}ClNNaO_5P$ [M + Na]$^+$ 422.0900, found 422.0901.



1,3-Diallyl-5-methoxy-2-oxoindolin-3-yl diethyl phosphate (7l). yellow oil (105 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 2.8 Hz, 1H), 6.77–6.74 (m, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 5.79–5.70 (m, 1H), 5.50–5.39 (m, 1H), 5.25–5.12 (m, 2H), 5.03–4.98 (m, 2H), 4.31 (dd, *J* = 16.4, 5.2 Hz, 1H), 4.16 (dd, *J* = 16.4, 5.2 Hz, 1H), 4.02–3.80 (m, 4H), 3.72 (s, 3H), 2.85 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.64 (dd, *J* = 13.2, 8.0 Hz, 1H), 1.18–1.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3 (d, *J* = 2.0 Hz), 155.8, 136.4, 131.4, 129.5, 127.8, 120.9, 117.7, 114.7, 112.2, 109.9, 81.0 (d, *J* = 6.9 Hz), 64.0, 63.9, 55.9, 42.7, 42.3 (d, *J* = 10.0 Hz), 16.0 (d, *J* = 4.2 Hz), 15.9 (d, *J* = 4.7 Hz); IR *v* 2983, 1725, 1642, 1603, 1493, 1363, 1271, 1023, 1005, 809, 778 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{26}NNaO_6P$ [M + Na]$^+$ 418.1395, found 418.1400.

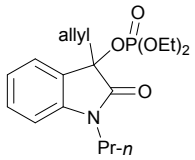


1,3-Diallyl-7-fluoro-2-oxoindolin-3-yl diethyl phosphate (7m). yellow oil (144 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 1H), 7.09–6.99 (m, 2H), 5.96–5.86 (m, 1H), 5.54–5.44 (m, 1H), 5.34–5.30 (m, 1H), 5.19–5.17 (m, 1H), 5.08–5.04 (m, 2H), 4.51–4.40 (m, 2H), 4.10–3.85 (m, 4H), 2.90 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.72 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.26–1.21 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2 (d, *J* = 1.4 Hz), 147.2 (d, *J* = 243.6 Hz), 132.0, 129.5 (d, *J* = 15.2 Hz), 129.5 (d, *J* = 3.2 Hz), 129.0, 123.1 (d, *J* = 6.1 Hz), 121.1, 120.6, 118.3 (d, *J* = 19.5 Hz), 117.2, 80.4 (d, *J* = 4.7 Hz), 63.9, 63.8, 44.1 (d, *J* = 4.8 Hz), 42.4 (d, *J* = 10.1 Hz), 15.8 (d, *J* = 6.9 Hz), 15.7 (d, *J* = 6.6 Hz); IR *v* 2984, 1736, 1631, 1600, 1488, 1267, 1249, 1021, 812, 762 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{23}FNNaO_5P$ [M + Na]$^+$ 406.1196, found 406.1195.

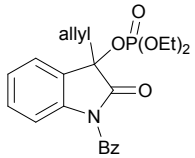


3-Allyl-1-ethyl-2-oxoindolin-3-yl diethyl phosphate (7n). yellow solid (159 mg, 90% yield), m.p. 48.5–49.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.53–5.43 (m, 1H), 5.07–5.01 (m, 2H), 4.05–3.66 (m, 6H), 2.91 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.70 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.28–1.18 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2 (d, *J* = 1.9 Hz), 142.8, 130.3, 129.4, 126.6, 125.1, 122.1, 120.6, 108.4, 80.5 (d, *J* = 6.9 Hz), 63.8 (d, *J* = 5.5 Hz), 63.7 (d, *J* = 6.4 Hz), 42.1 (d, *J* = 9.9 Hz), 34.7, 15.9 (d, *J* = 6.8 Hz), 15.8 (d, *J* = 6.6 Hz), 12.2; IR *v* 2979, 1723, 1640, 1613, 1490, 1366, 1261, 1006, 797, 757 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{25}NO_5P$ [M + H]$^+$ 354.1465, found

354.1466.

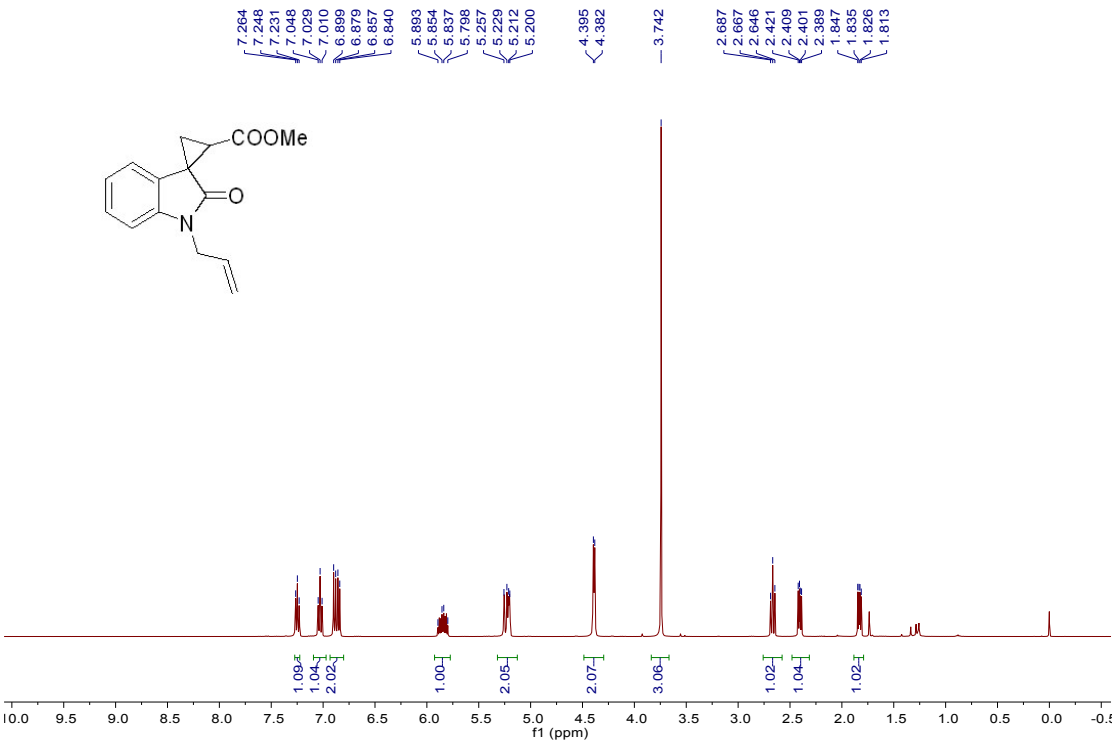


3-Allyl-2-oxo-1-propylindolin-3-yl diethyl phosphate (7o). yellow oil (171 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.55–5.45 (m, 1H), 5.08–5.03 (m, 2H), 4.03–3.54 (m, 6H), 2.93 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.70 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.72–1.67 (m, 2H), 1.24–1.19 (m, 6H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0 (d, *J* = 2.1 Hz), 142.8, 129.8, 128.9, 125.9, 124.4, 121.5, 119.9, 108.1, 79.9 (d, *J* = 6.7 Hz), 63.1 (d, *J* = 5.8 Hz), 63.0 (d, *J* = 5.3 Hz), 41.6 (d, *J* = 10.0 Hz), 41.2, 20.0, 15.3 (d, *J* = 7.1 Hz), 15.2 (d, *J* = 6.9 Hz), 10.8; IR *v* 2978, 1727, 1641, 1613, 1489, 1367, 1268, 1023, 817, 751 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{26}NNaO_5P$ [M + Na]$^+$ 390.1446, found 390.1440.

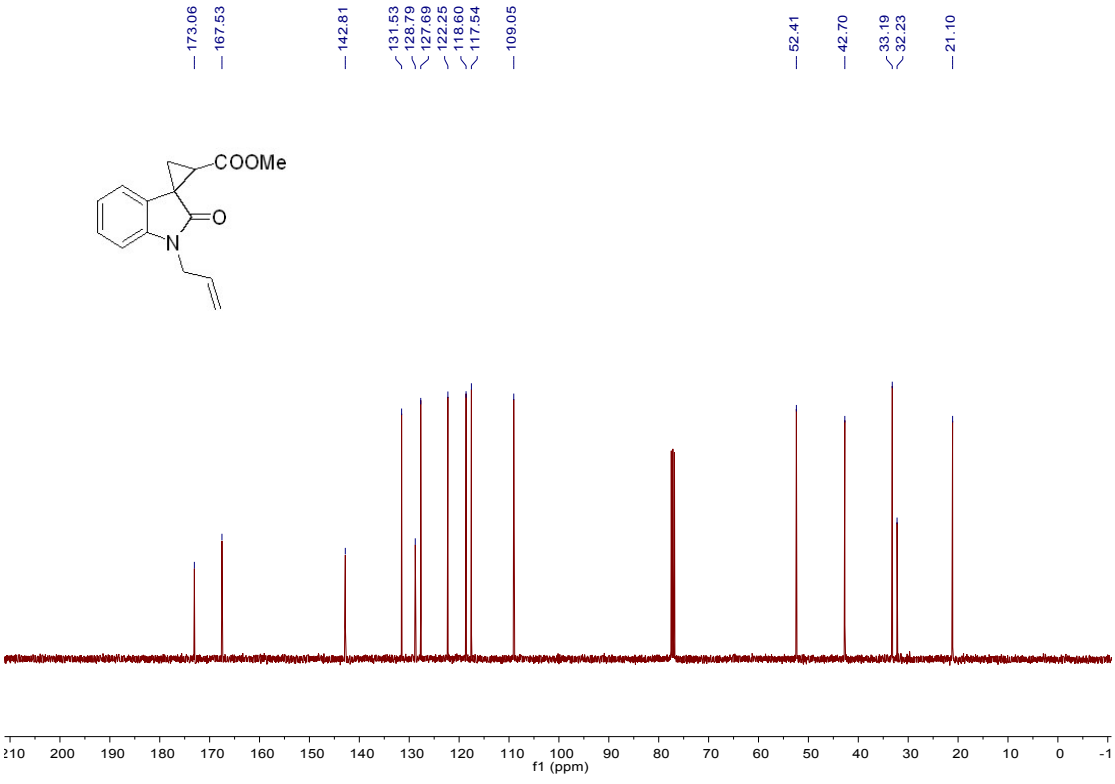


3-Allyl-1-benzyl-2-oxoindolin-3-yl diethyl phosphate (7p). yellow oil (147 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 1H), 7.36–7.19 (m, 6H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 5.56–5.45 (m, 1H), 5.12–5.04 (m, 3H), 4.76 (d, *J* = 15.6 Hz, 1H), 4.05–3.86 (m, 4H), 2.98 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.78 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6 (d, *J* = 2.1 Hz), 142.7, 135.3, 130.1, 129.3, 128.4, 127.3, 127.2, 126.2, 124.8, 122.3, 120.7, 109.3, 80.5 (d, *J* = 6.9 Hz), 63.6 (d, *J* = 6.4 Hz), 63.6 (d, *J* = 5.8 Hz), 43.9, 42.1 (d, *J* = 10.1 Hz), 15.7 (d, *J* = 6.7 Hz), 15.6 (d, *J* = 6.6 Hz); IR *v* 2982, 1729, 1641, 1613, 1488, 1455, 1364, 1267, 1017, 818, 751, 735, 697 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{26}NNaO_5P$ [M + Na]$^+$ 438.1441, found 438.1452.

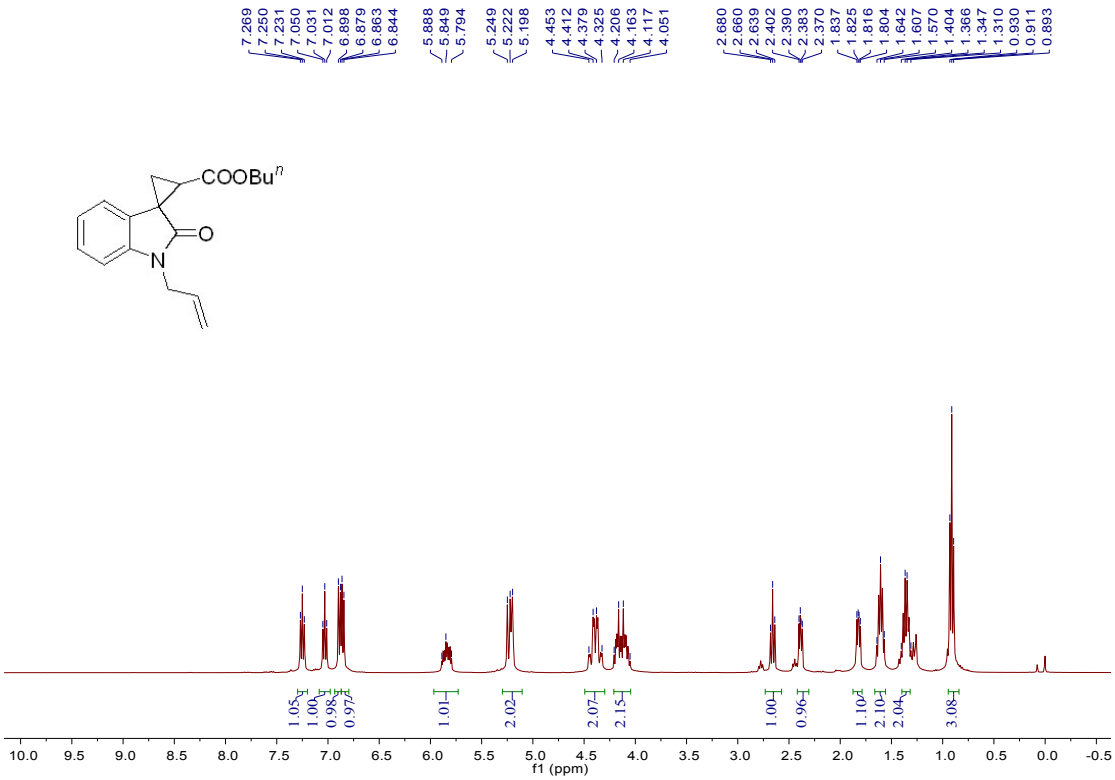
Copies of ^{1}H NMR and ^{13}C NMR Spectra



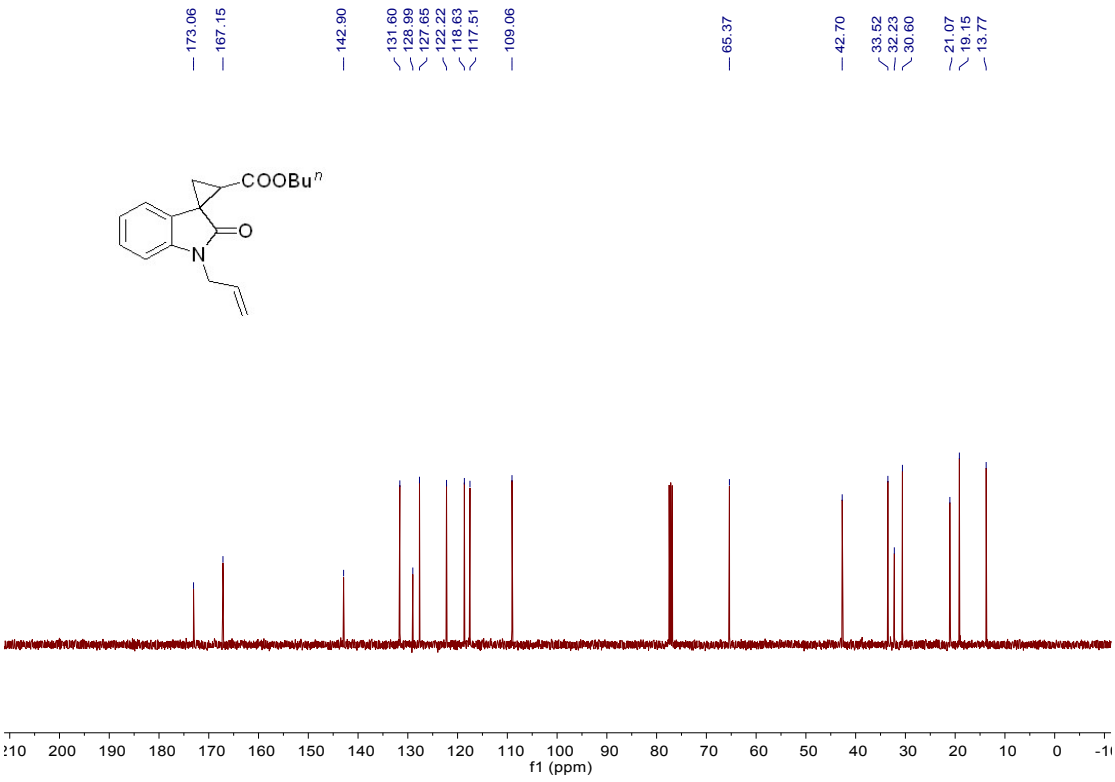
^{1}H NMR spectrum of **4a**



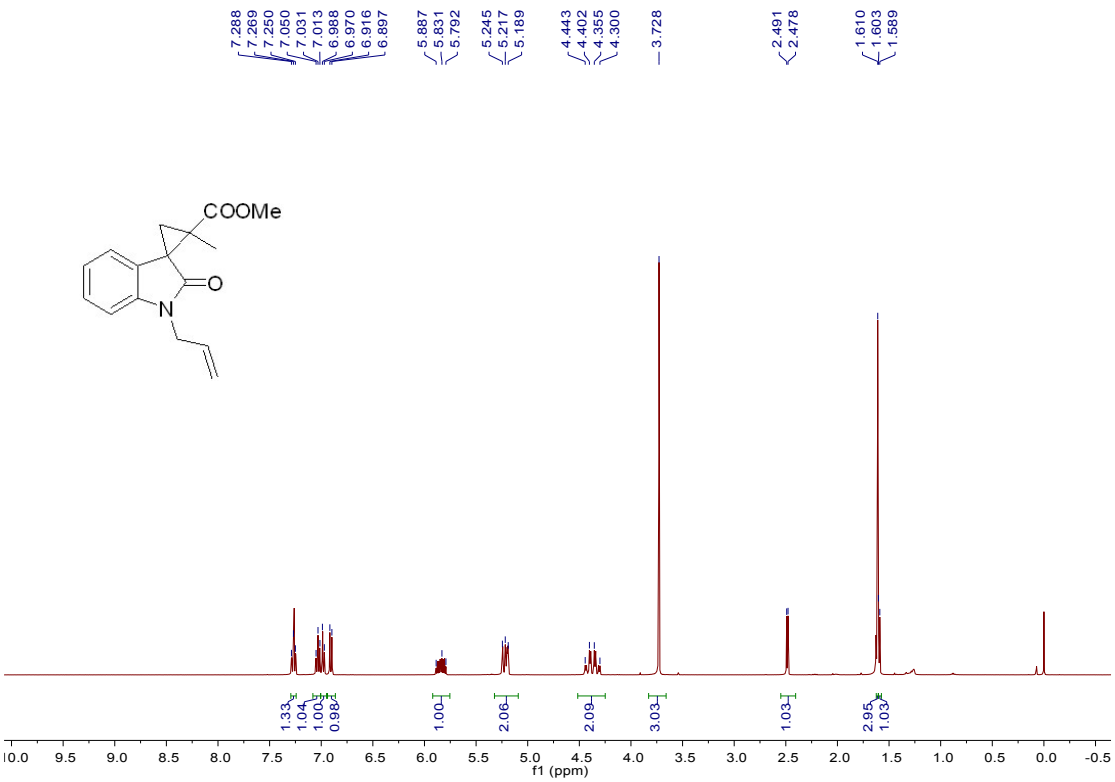
^{13}C NMR spectrum of **4a**



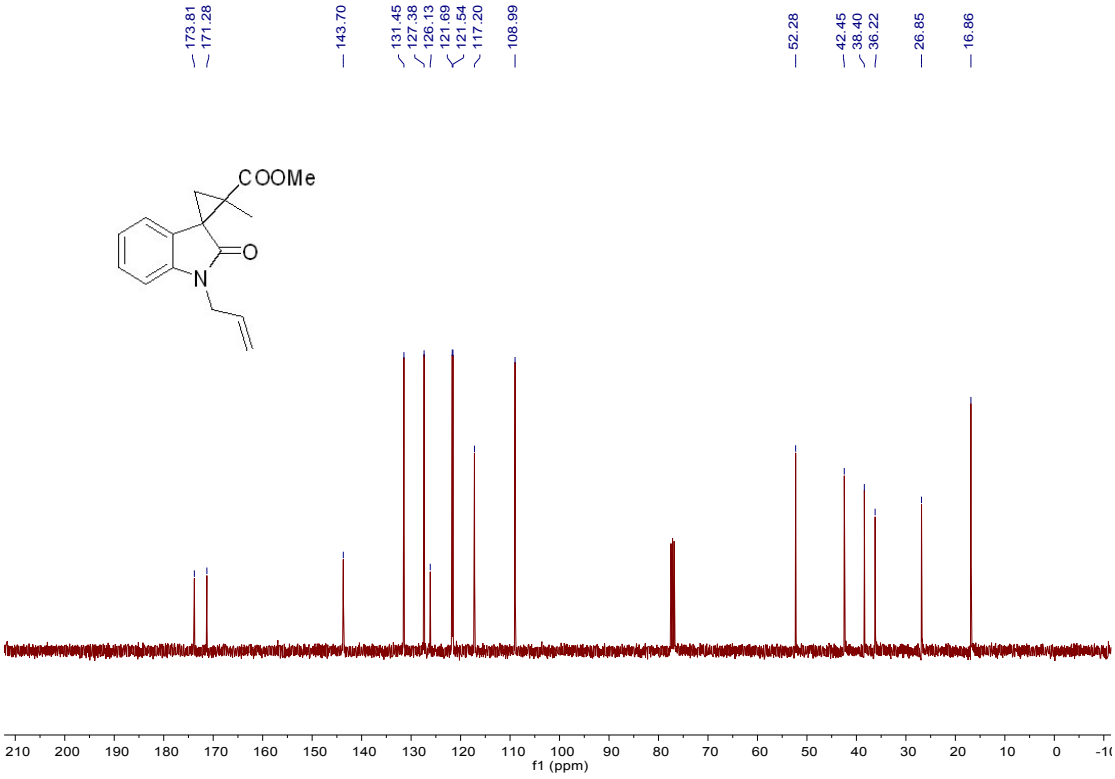
^{1}H NMR spectrum of **4b**



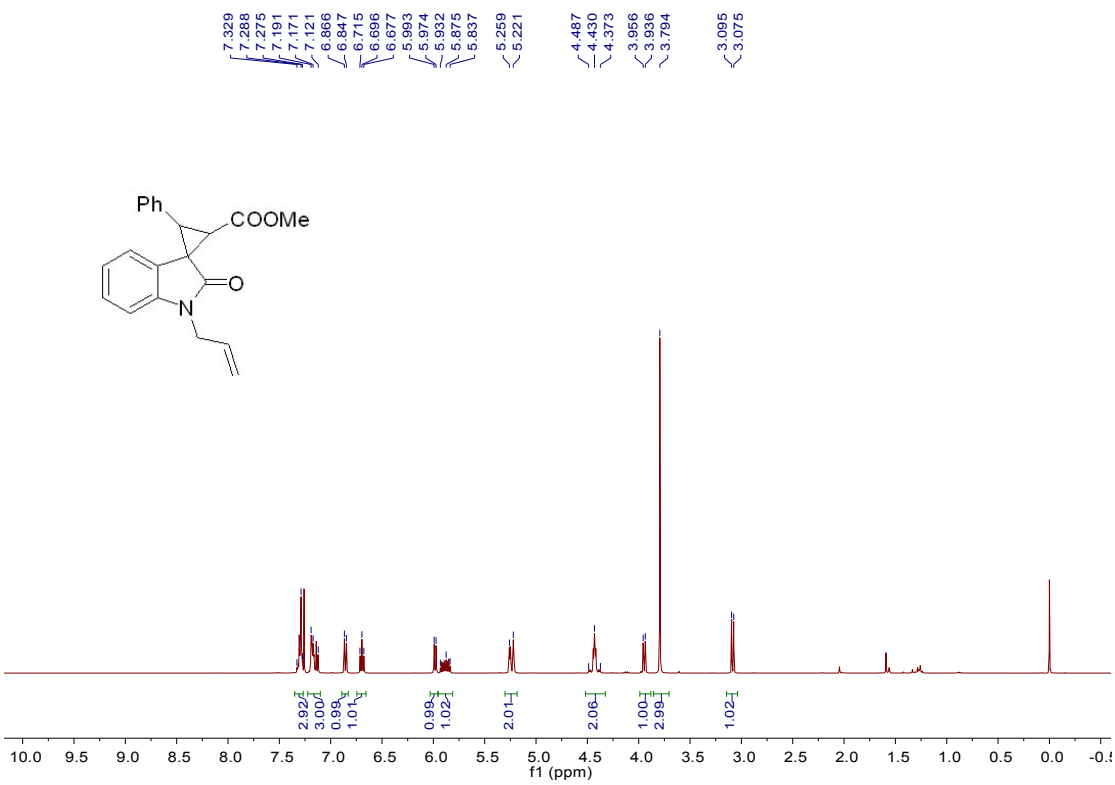
^{13}C NMR spectrum of **4b**



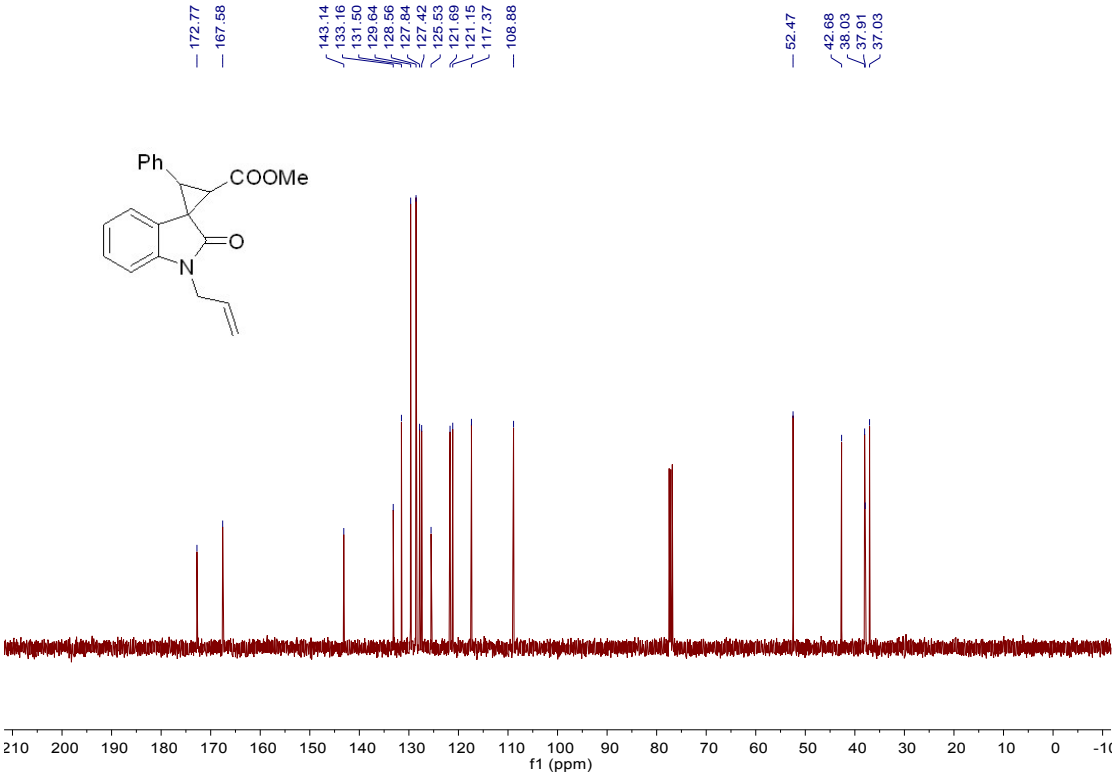
^{1}H NMR spectrum of **4c**



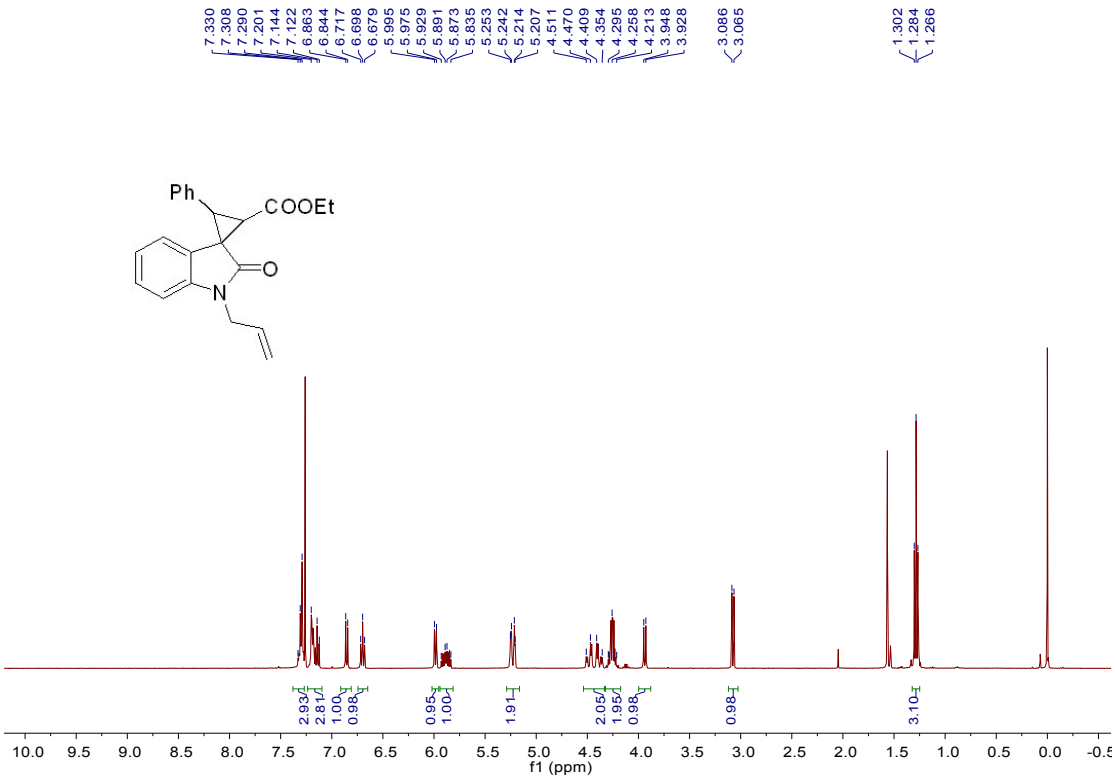
^{13}C NMR spectrum of **4c**



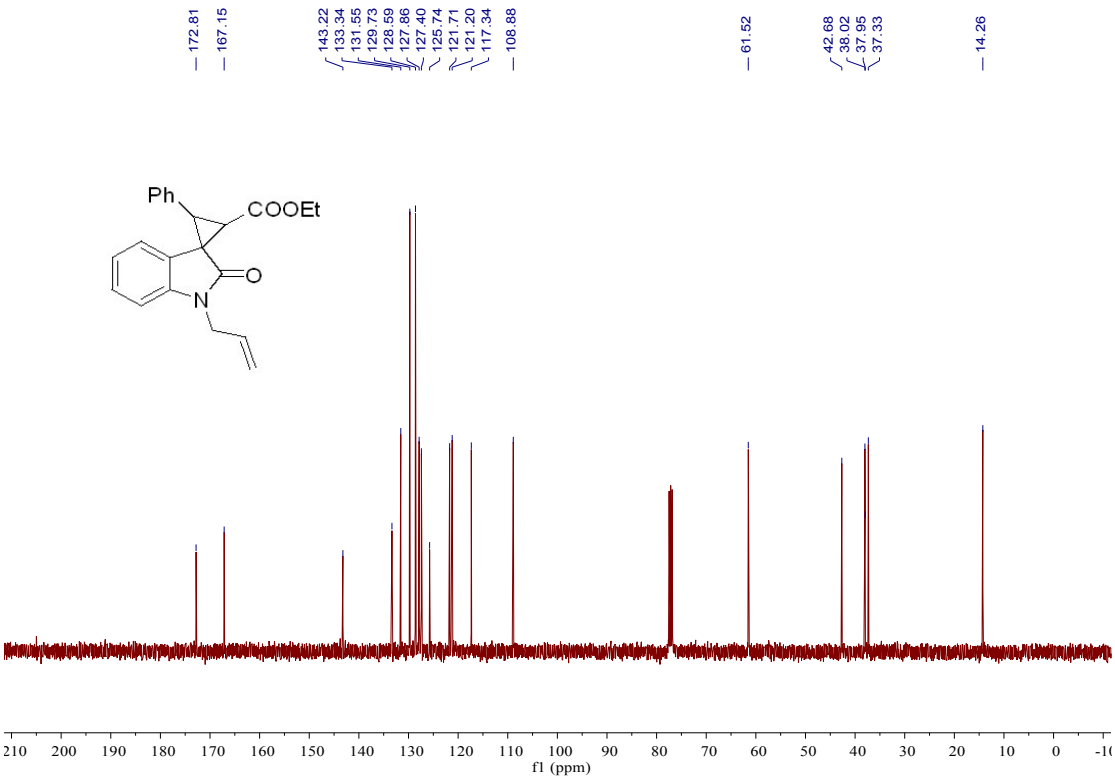
^{1}H NMR spectrum of **4d**



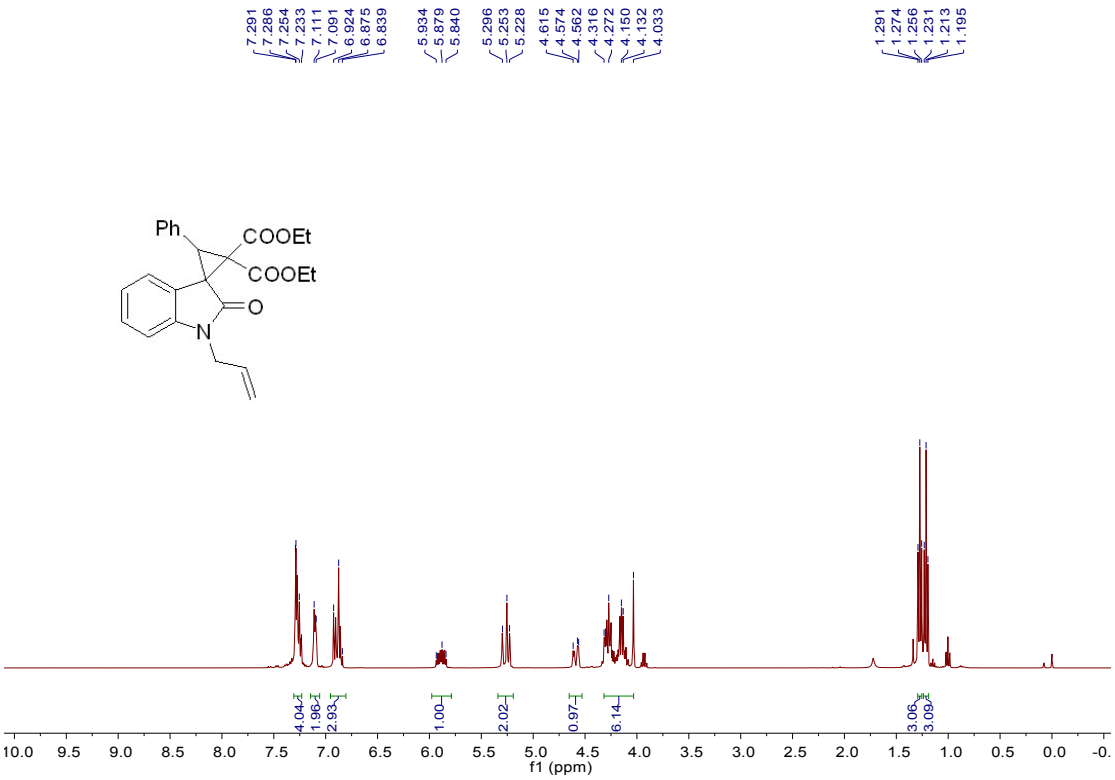
^{13}C NMR spectrum of **4d**



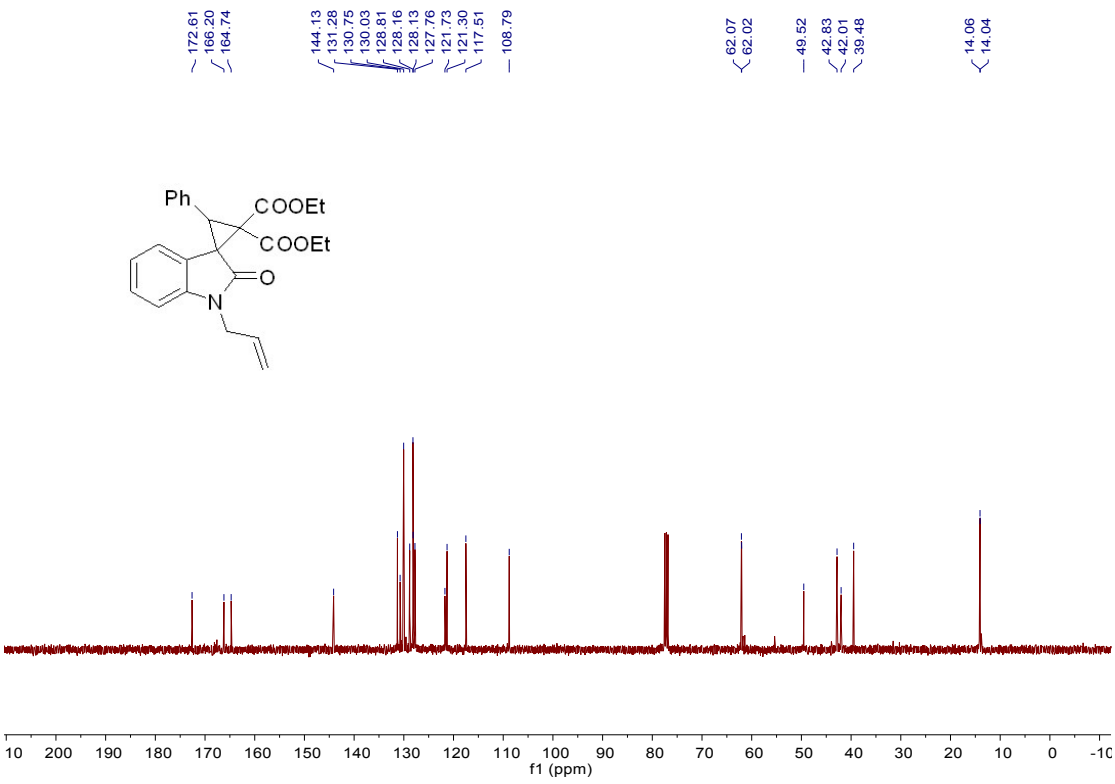
^{1}H NMR spectrum of **4e**



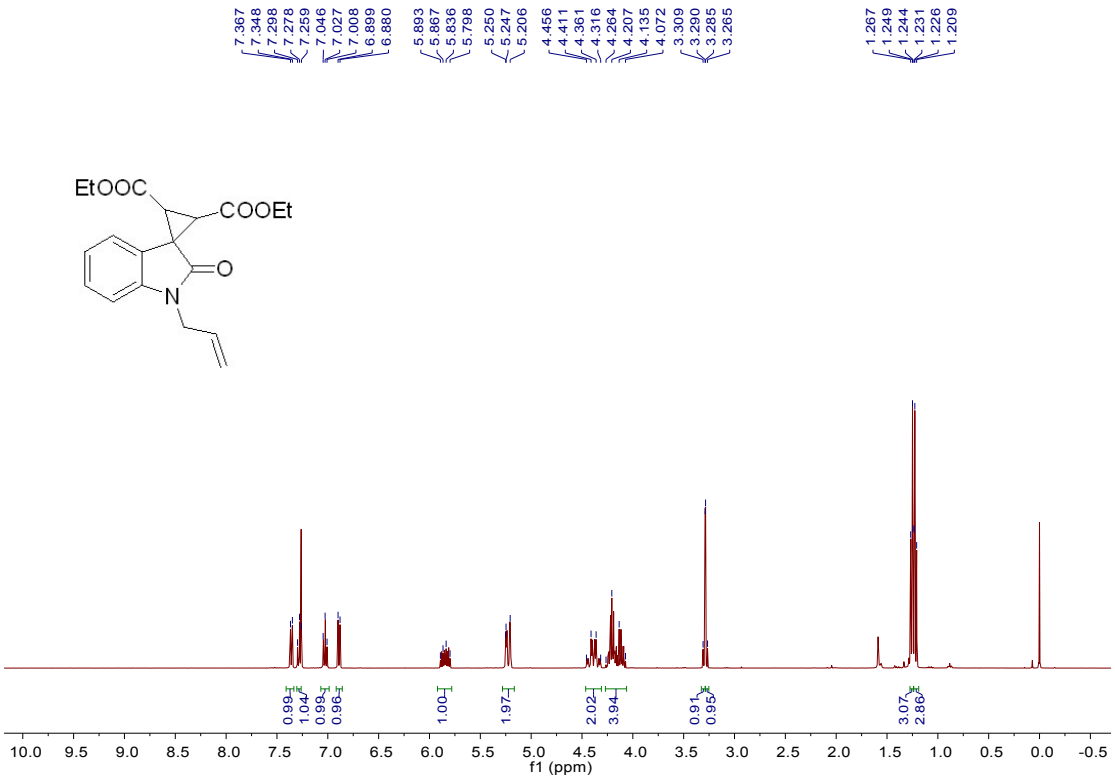
^{13}C NMR spectrum of **4e**



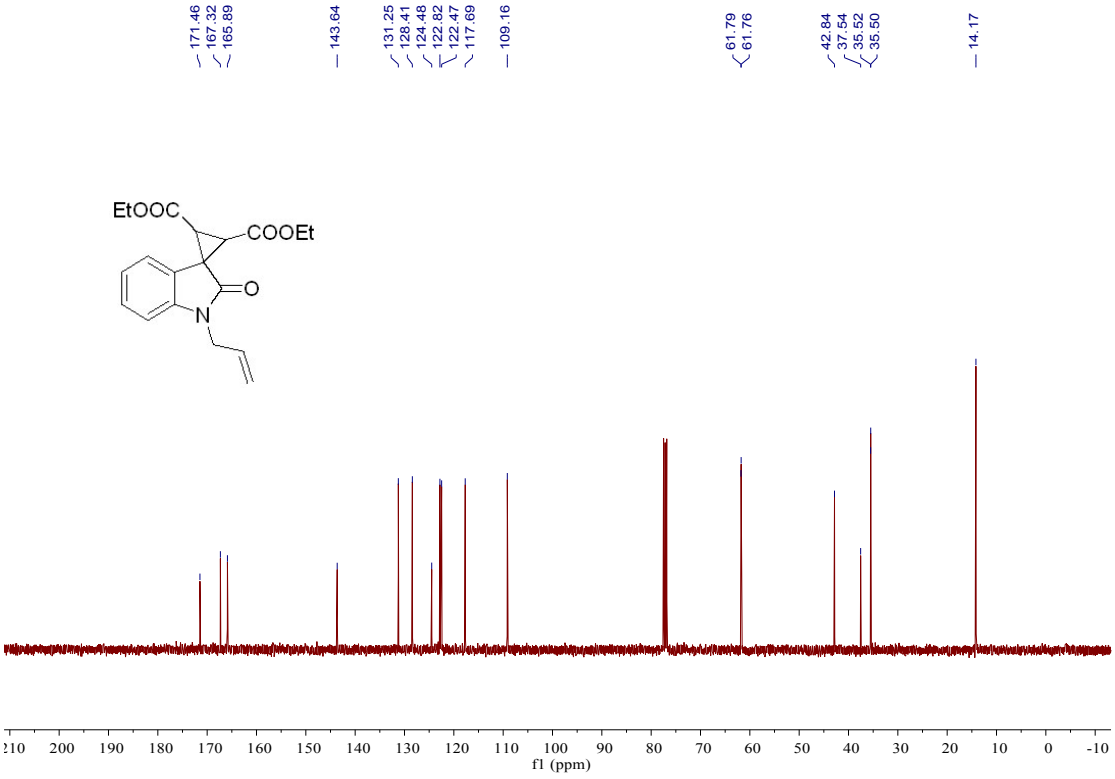
^{1}H NMR spectrum of **4f**



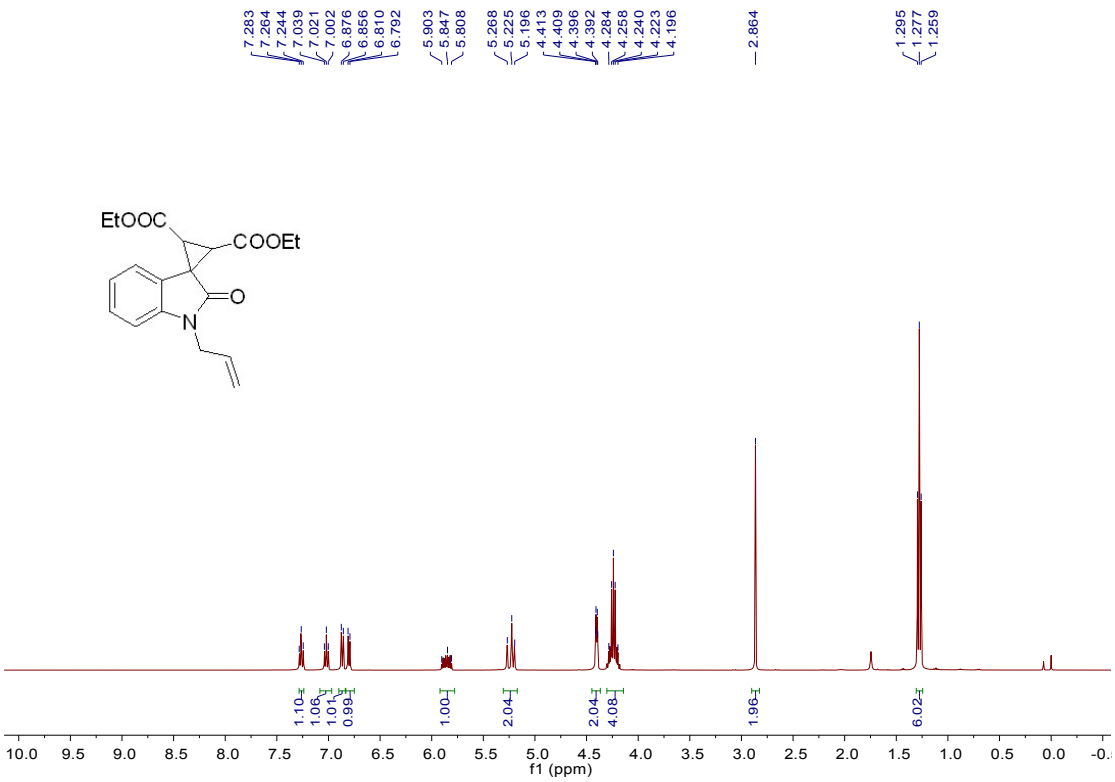
^{13}C NMR spectrum of **4f**



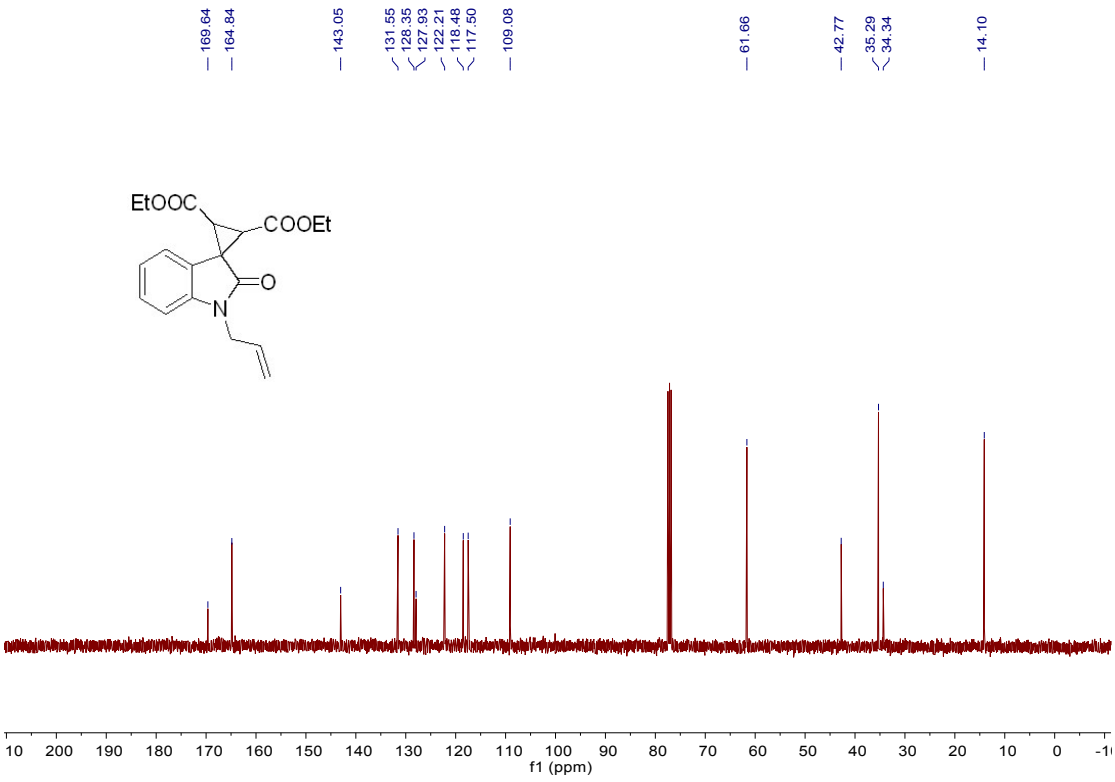
^{1}H NMR spectrum of **4g**



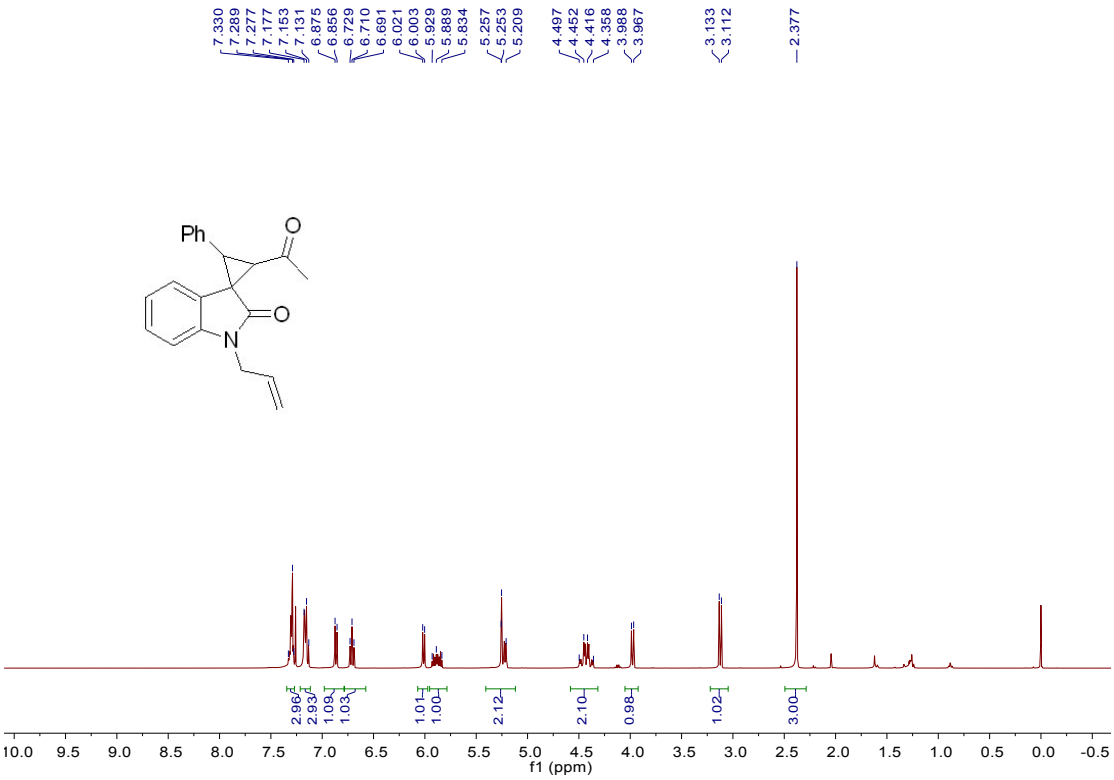
^{13}C NMR spectrum of **4g**



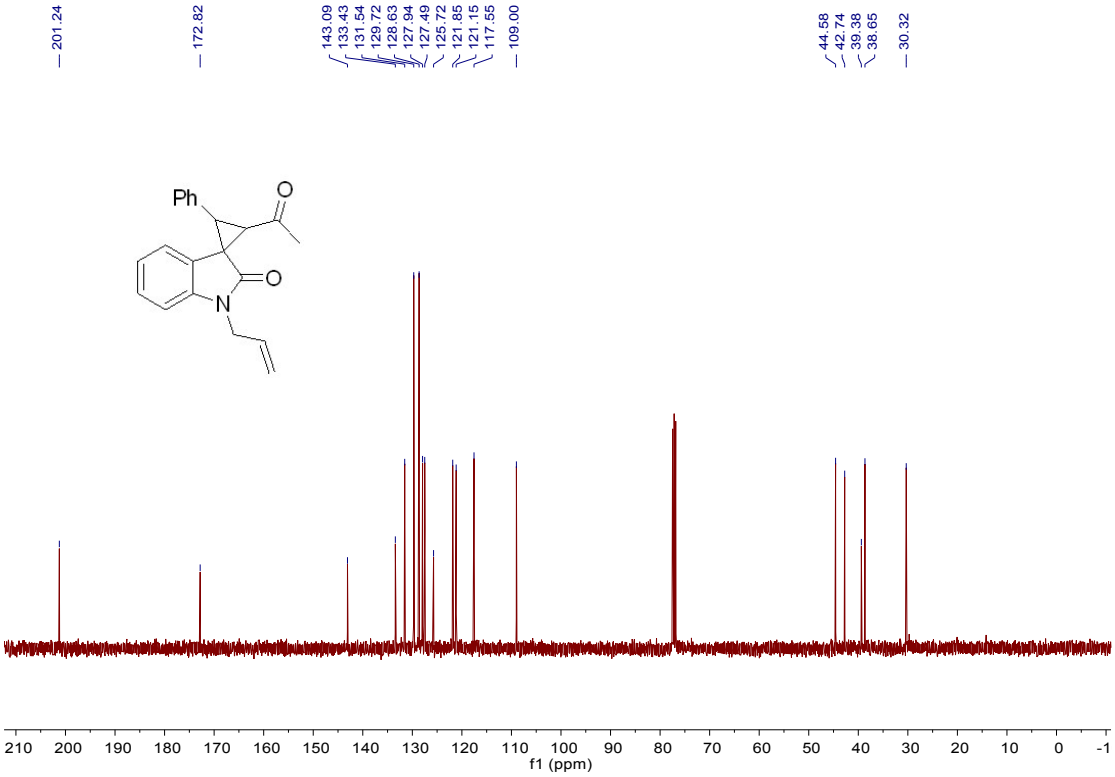
^{1}H NMR spectrum of **4g'**



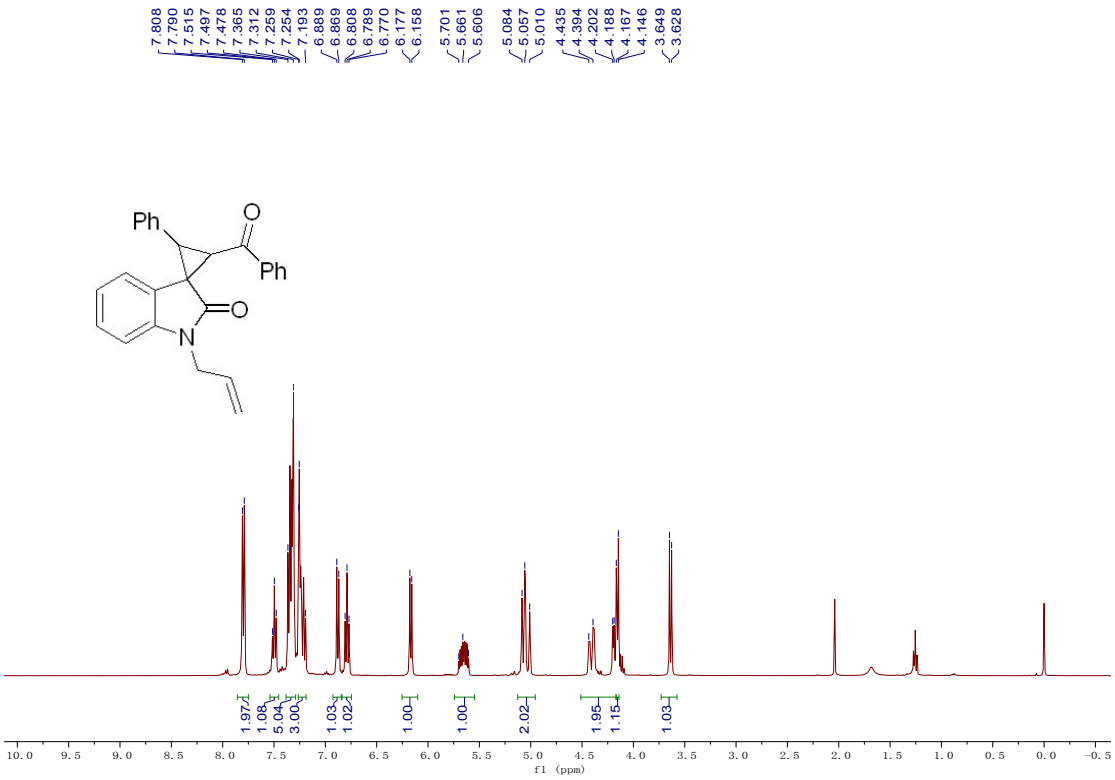
^{13}C NMR spectrum of **4g'**



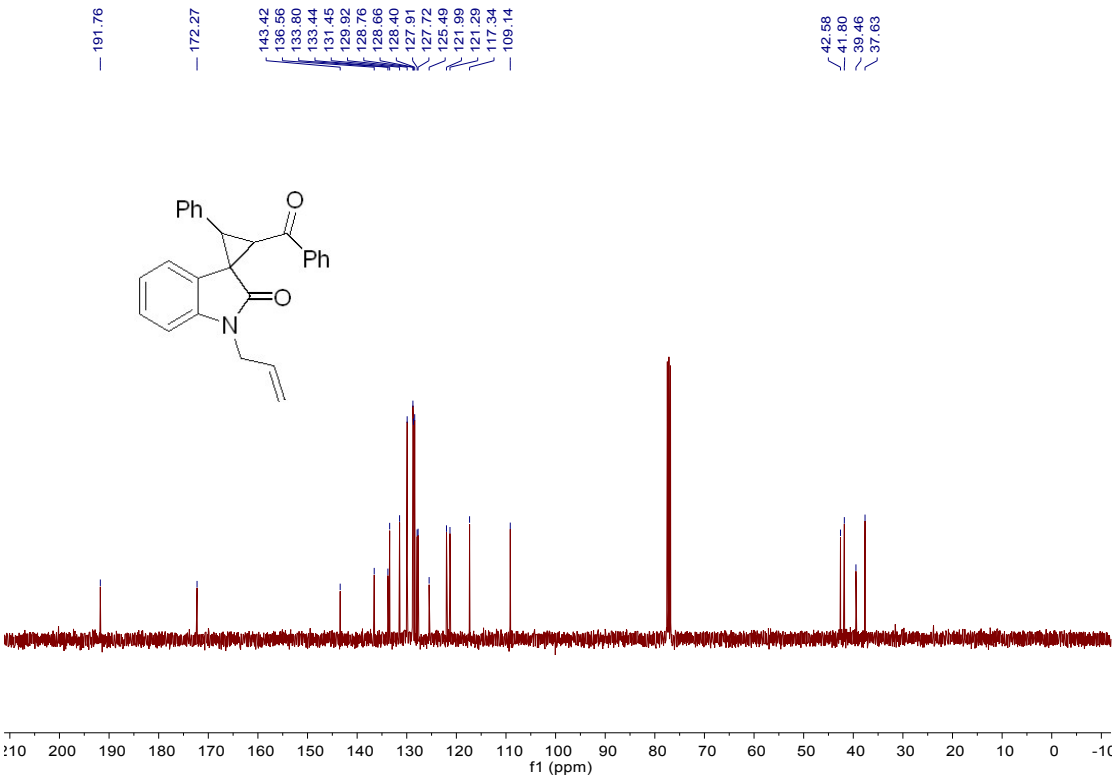
^{1}H NMR spectrum of **4h**



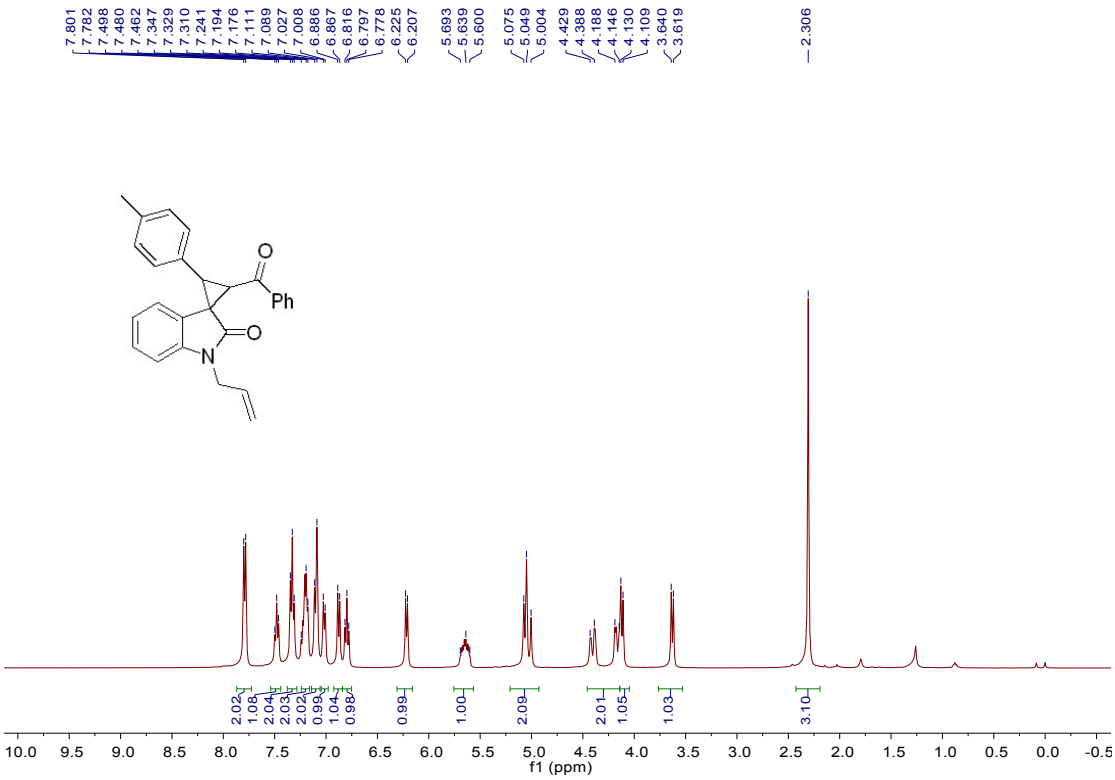
^{13}C NMR spectrum of **4h**



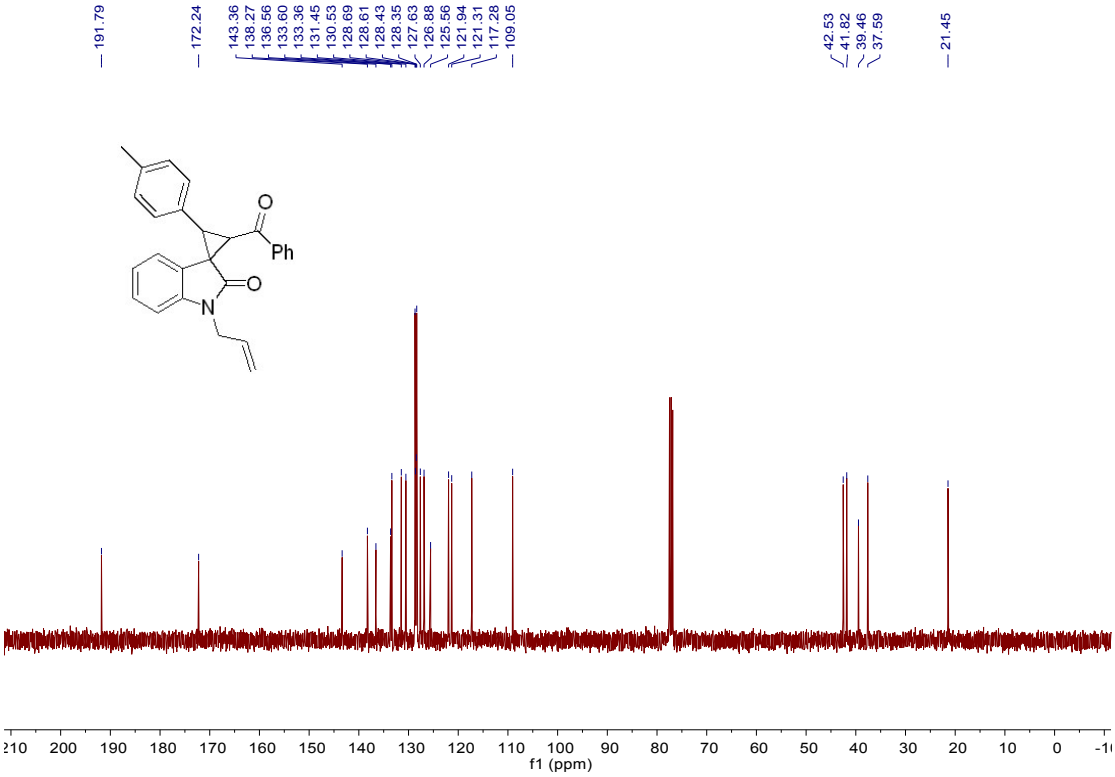
^{1}H NMR spectrum of **4i**



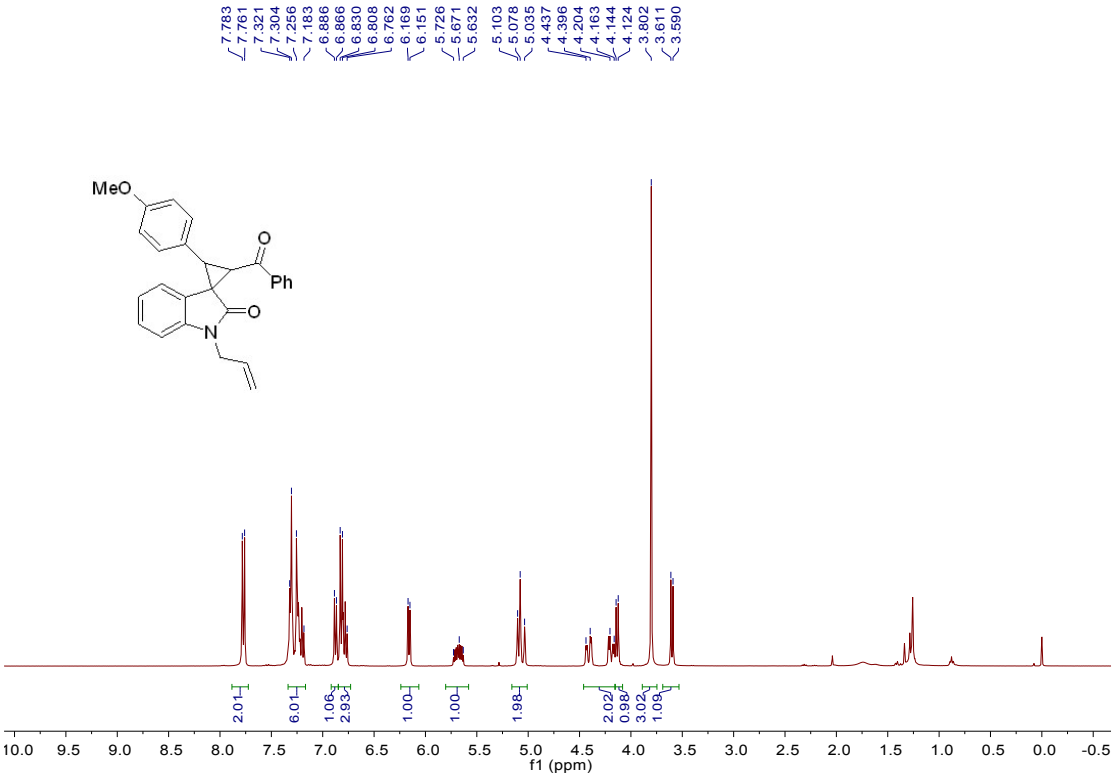
^{13}C NMR spectrum of **4i**



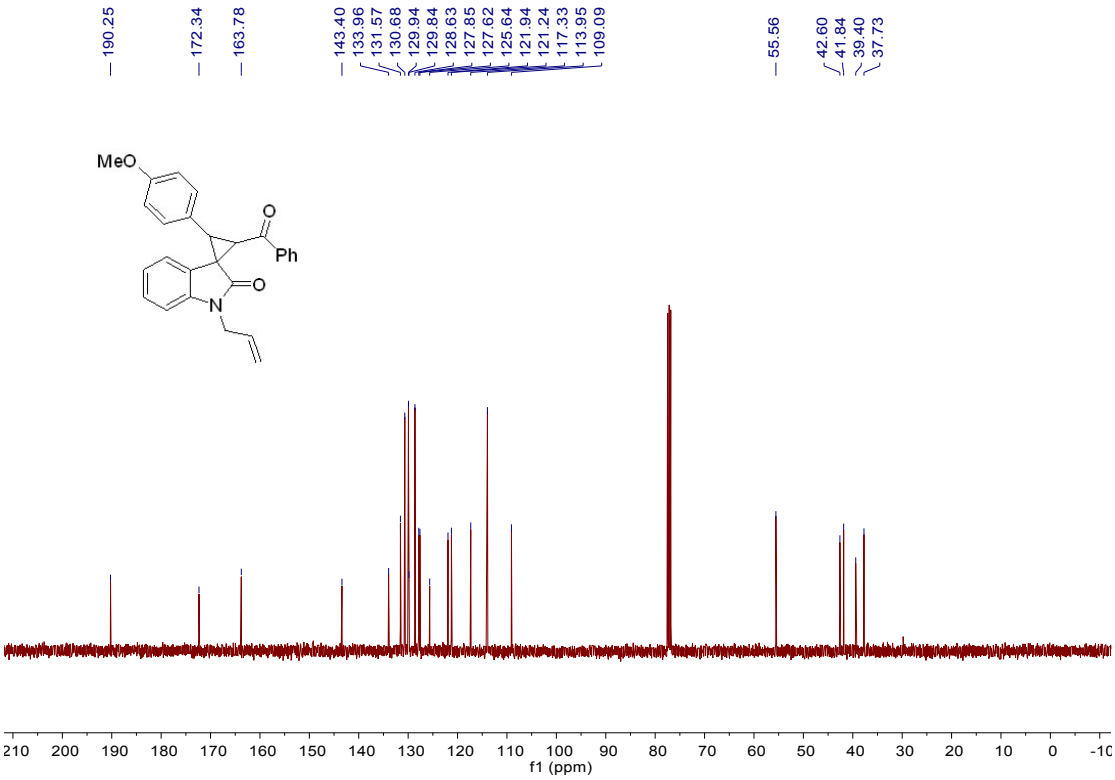
^{1}H NMR spectrum of **4j**



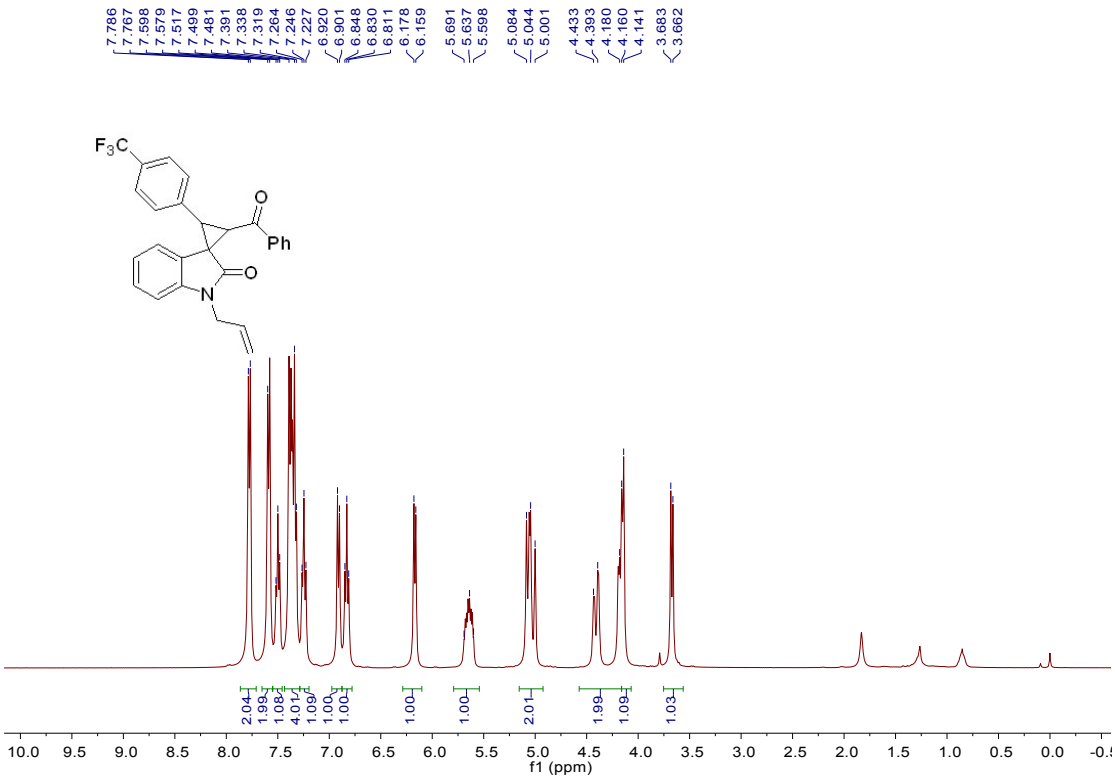
^{13}C NMR spectrum of **4j**



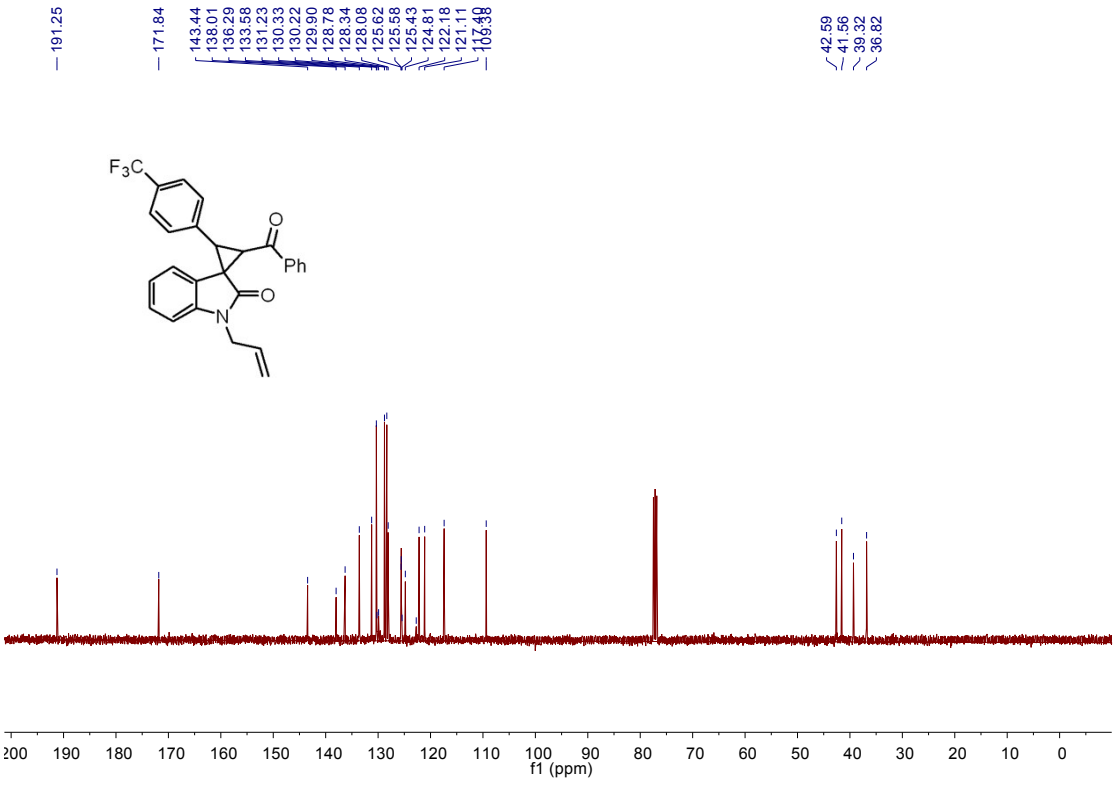
^{1}H NMR spectrum of **4k**



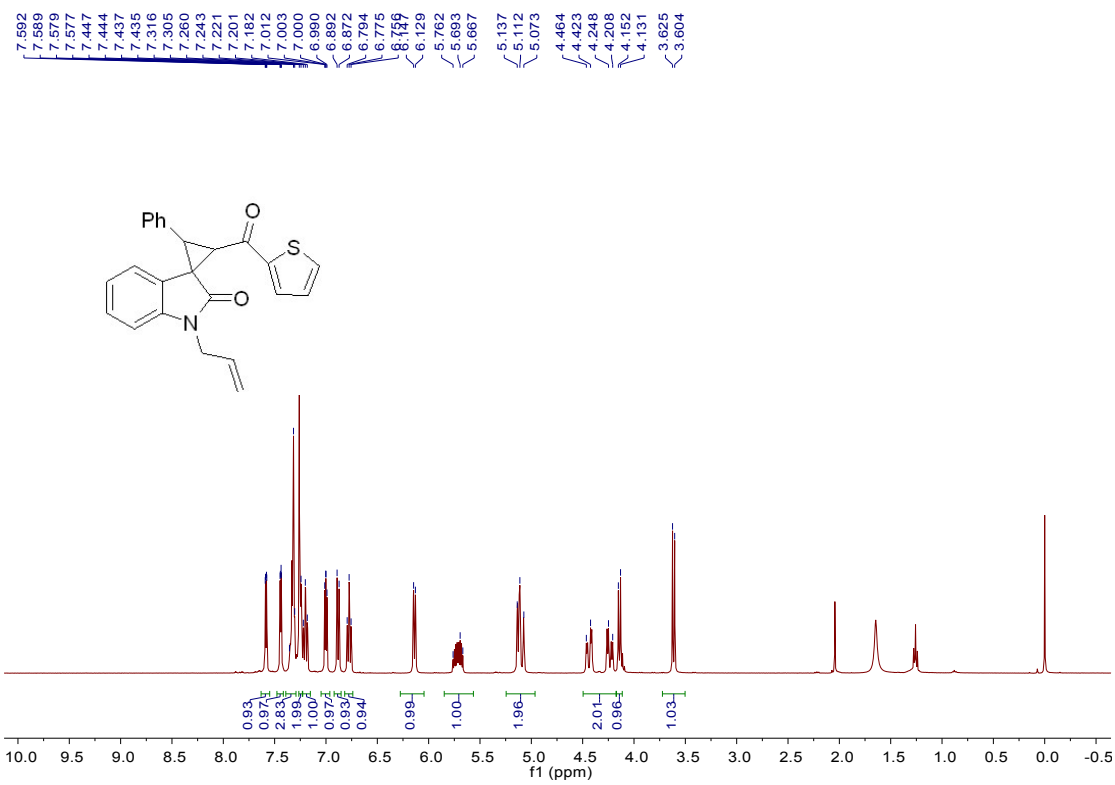
^{13}C NMR spectrum of **4k**



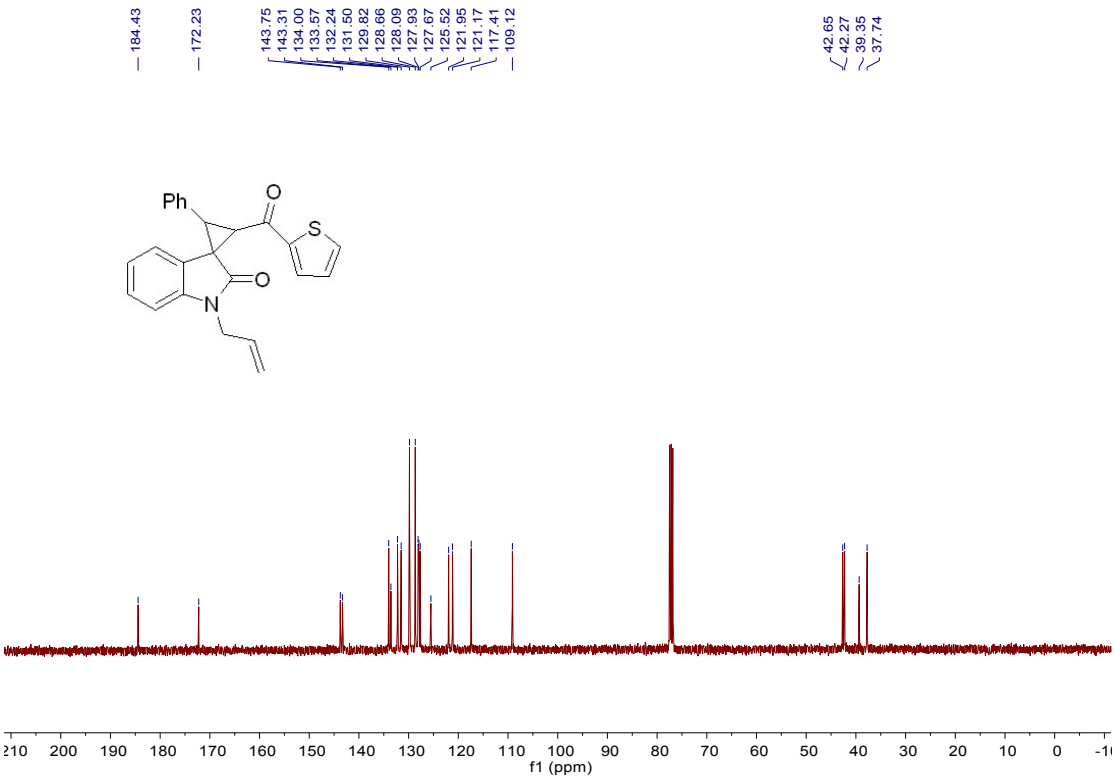
^{1}H NMR spectrum of **4l**



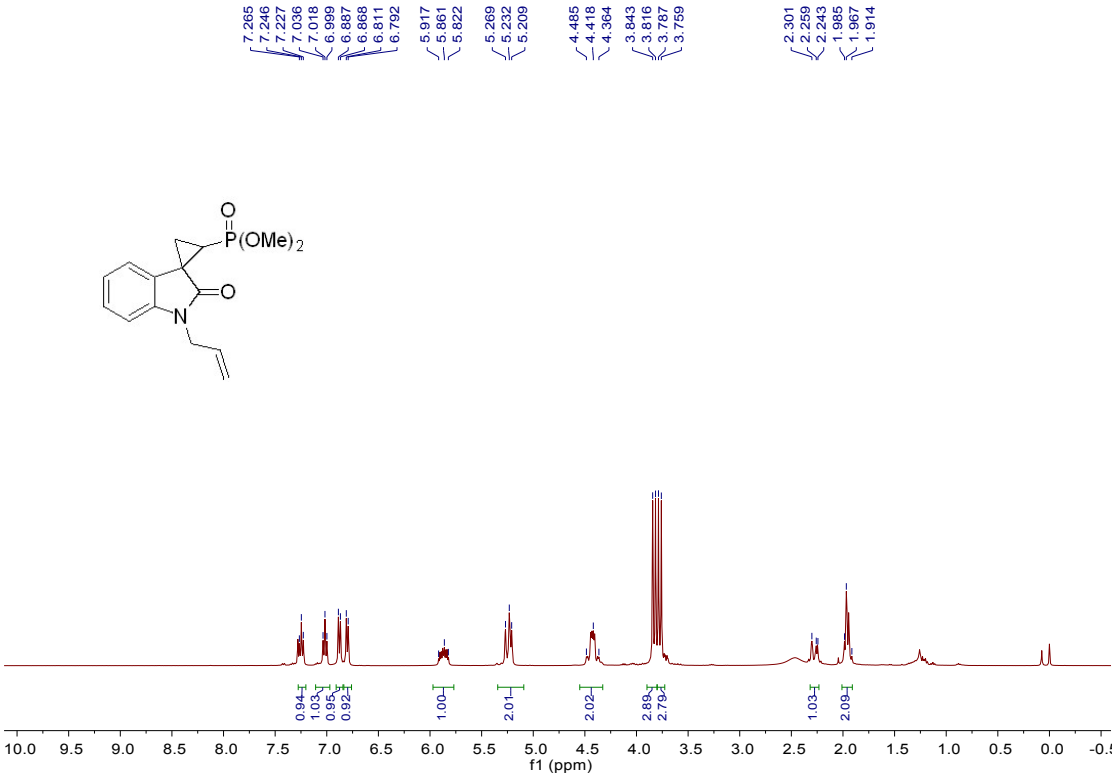
^{13}C NMR spectrum of **4l**



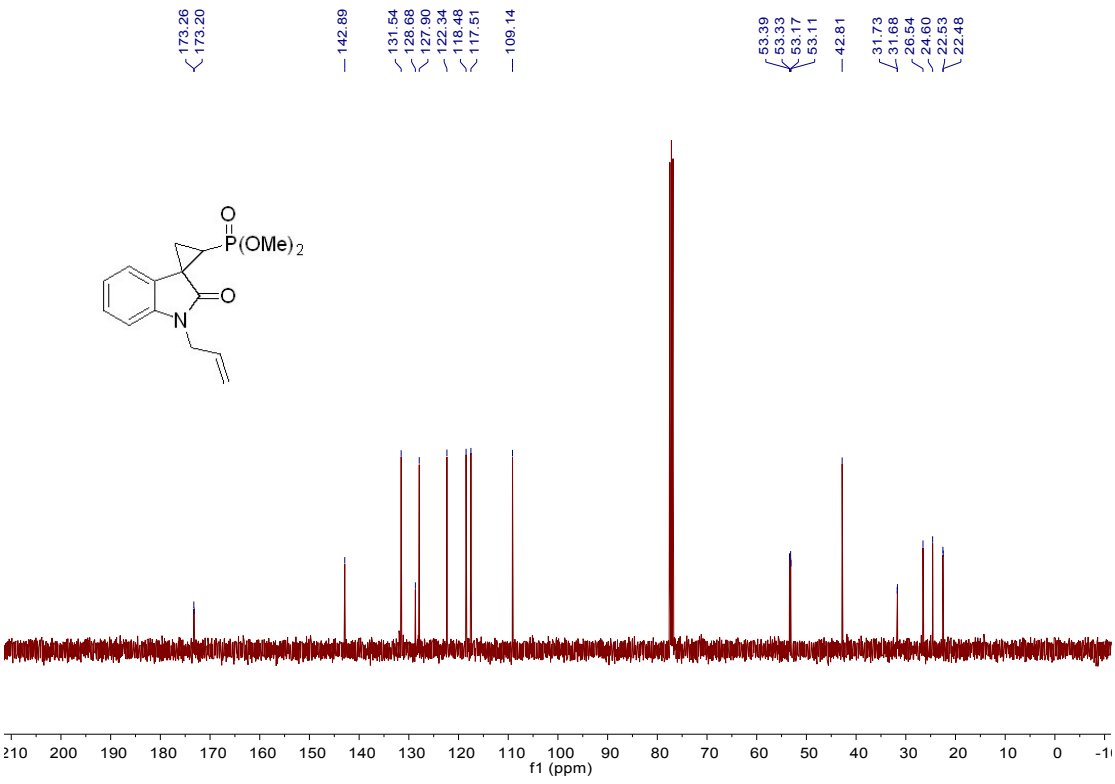
^{1}H NMR spectrum of **4m**



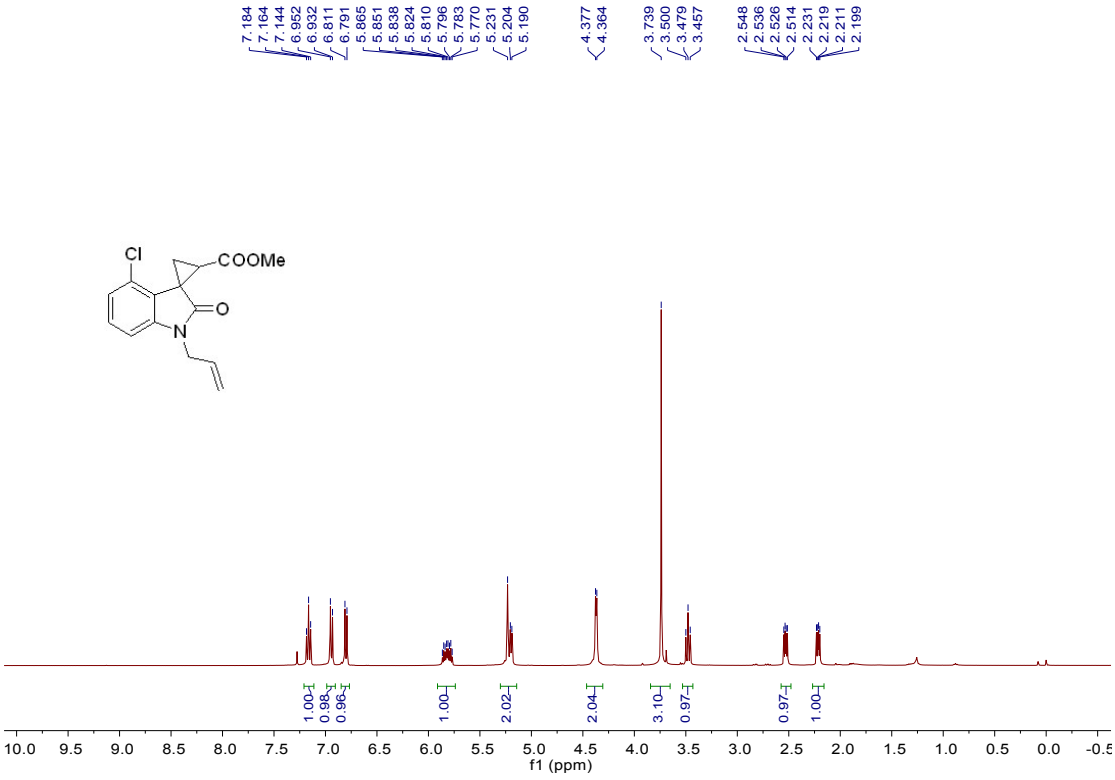
^{13}C NMR spectrum of **4m**



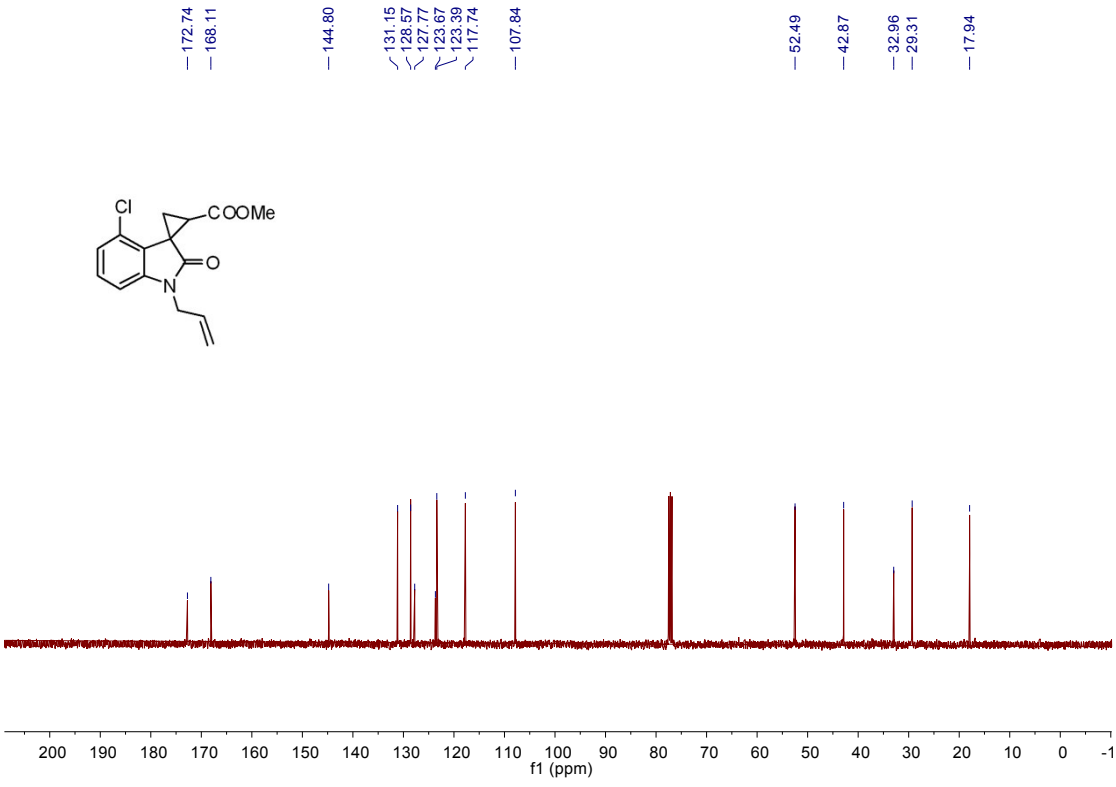
^{1}H NMR spectrum of **4n**



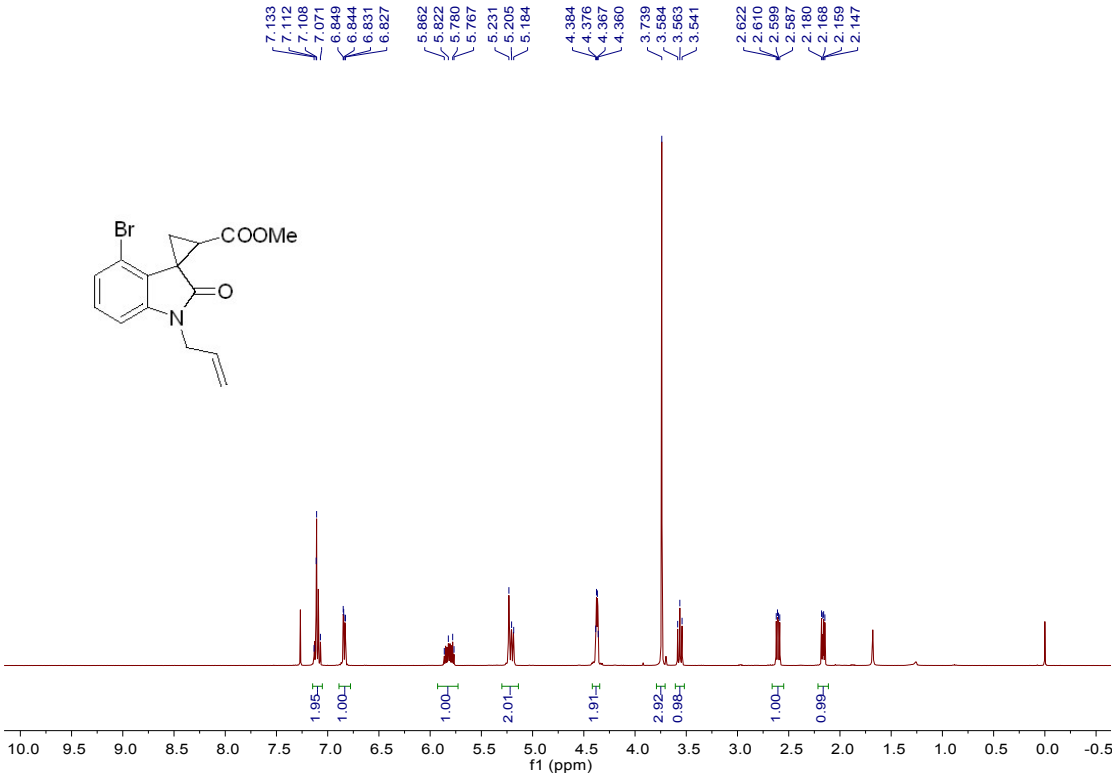
^{13}C NMR spectrum of **4n**



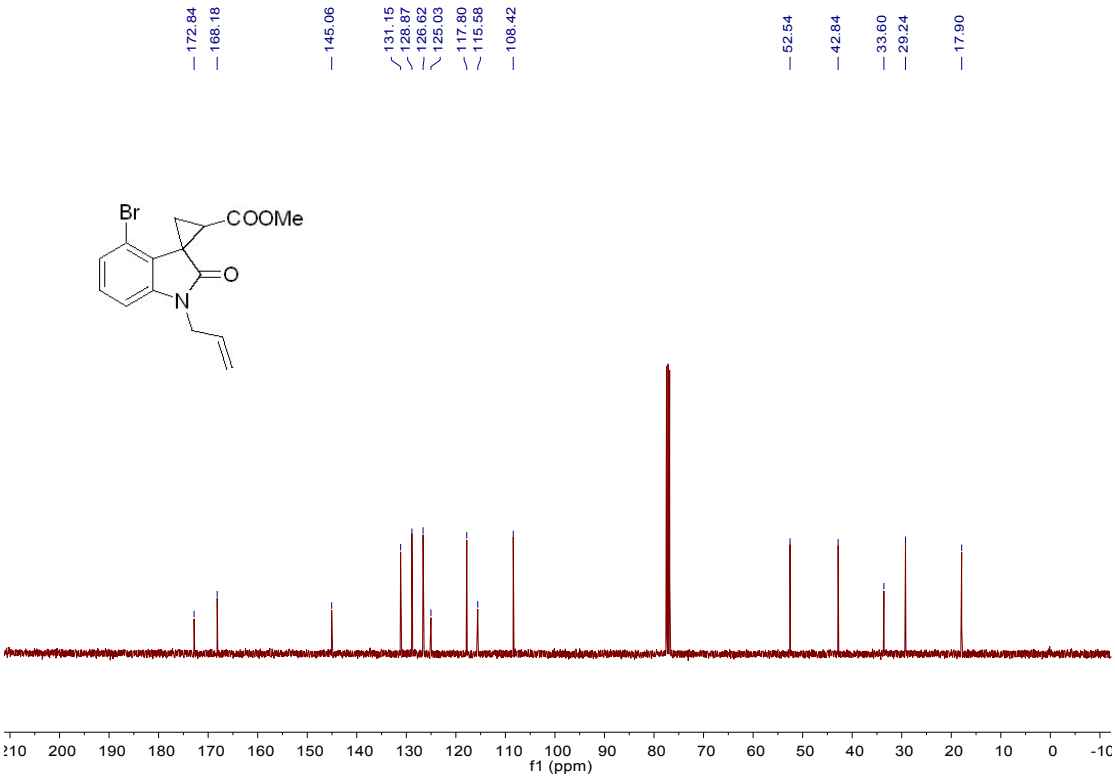
^{1}H NMR spectrum of **4o**



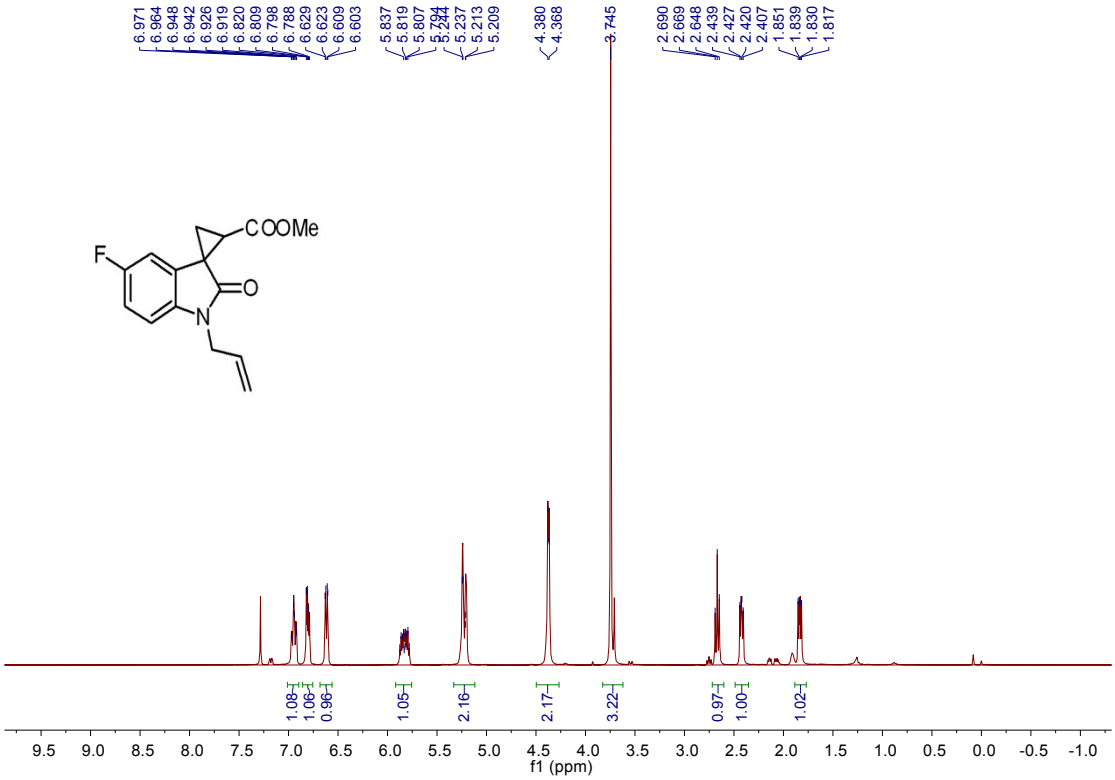
^{13}C NMR spectrum of **4o**



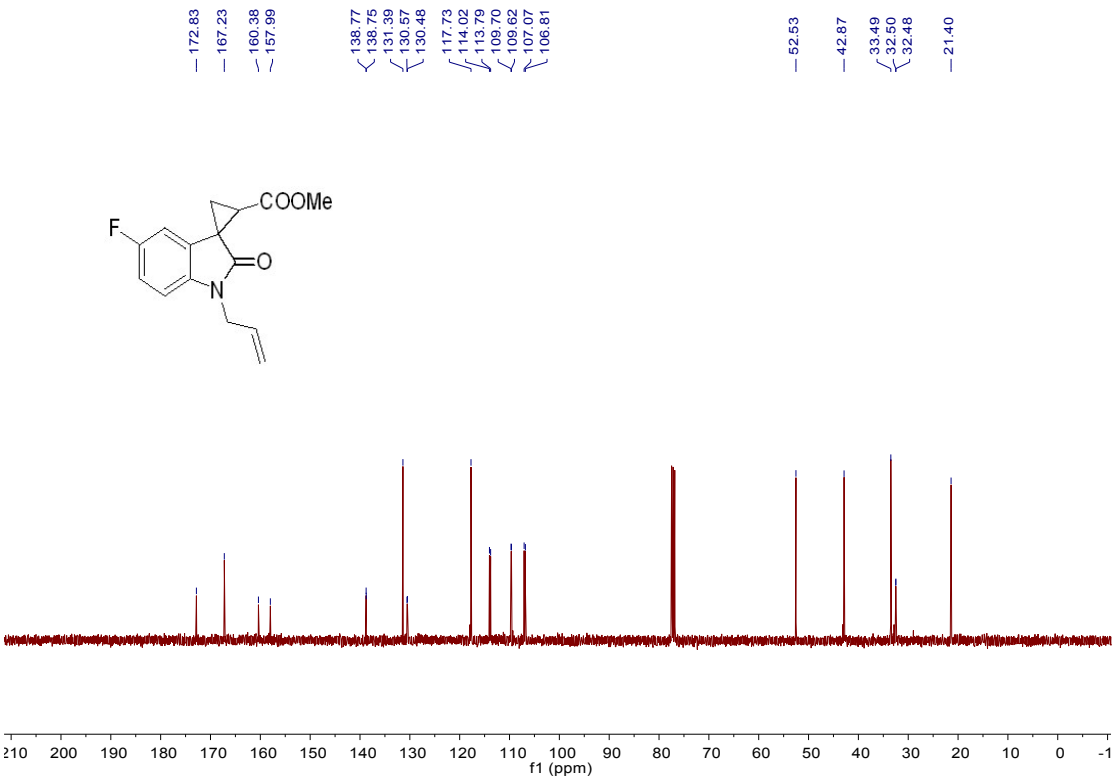
^{1}H NMR spectrum of **4p**



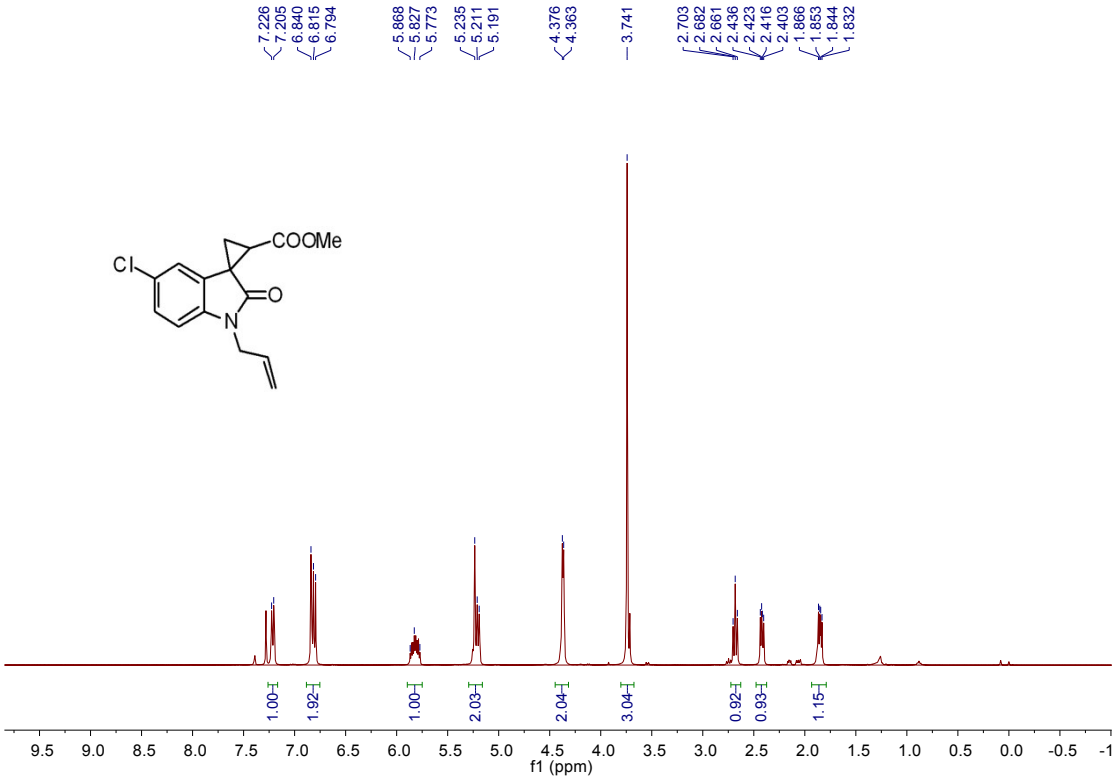
^{13}C NMR spectrum of **4p**



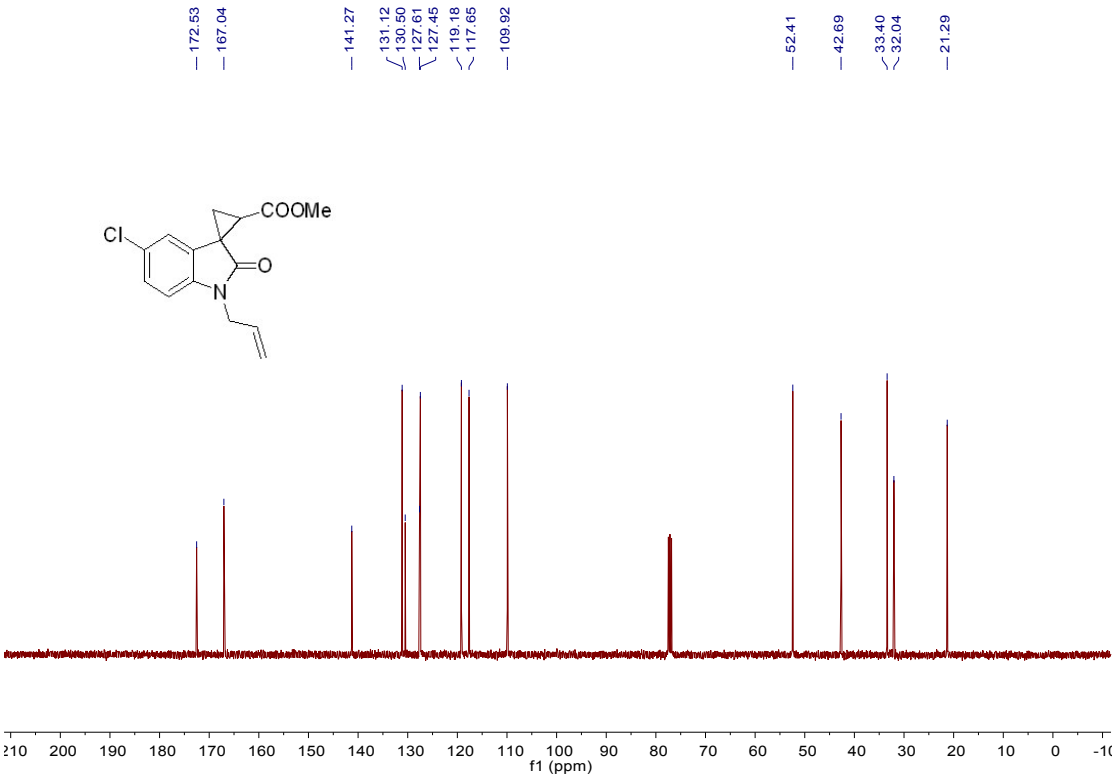
^{1}H NMR spectrum of **4q**



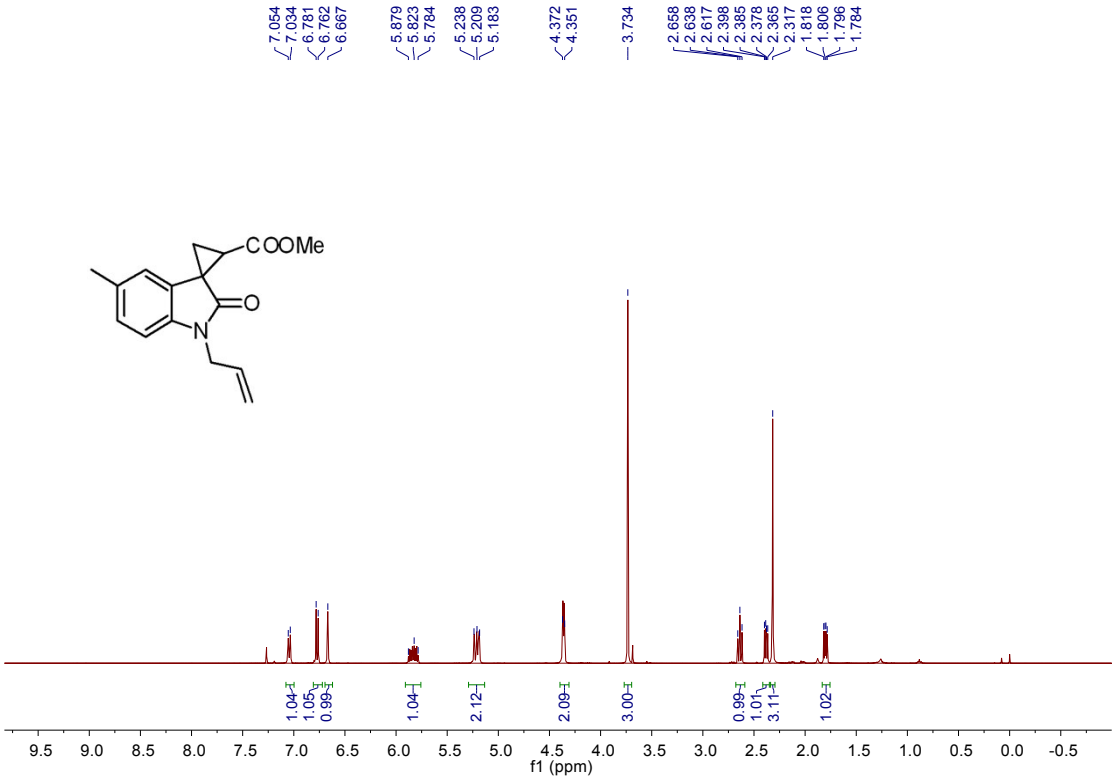
^{13}C NMR spectrum of **4q**



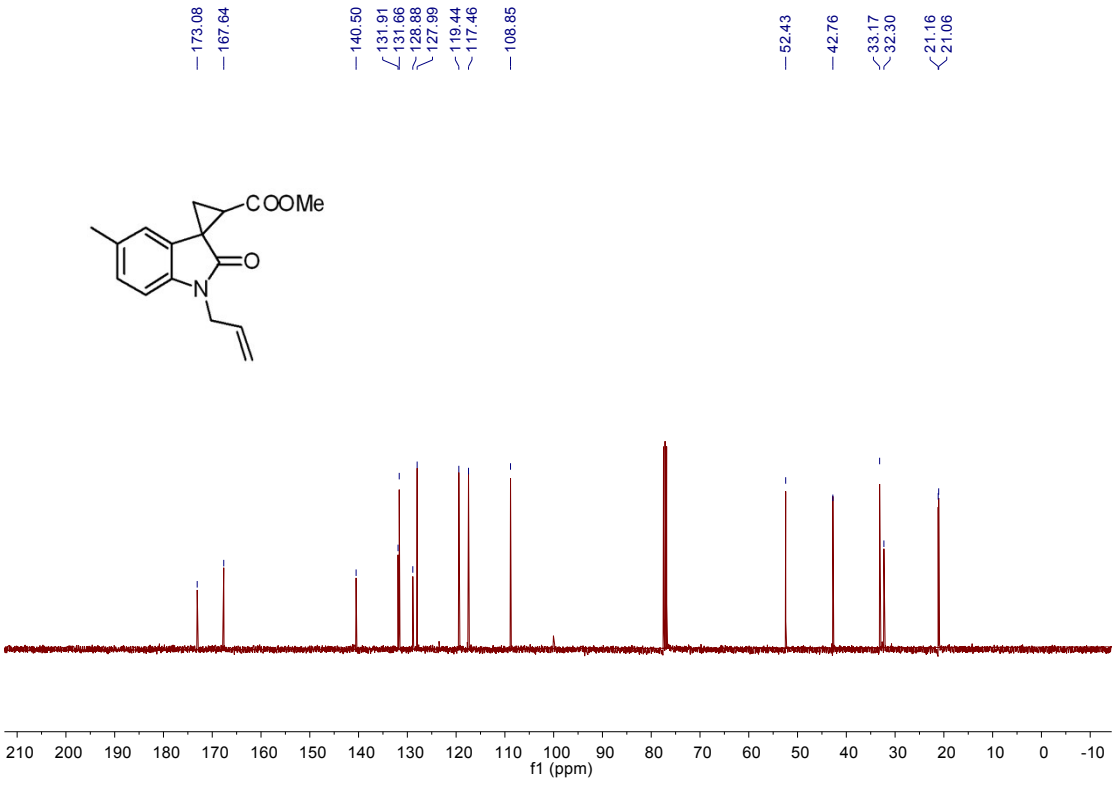
^{1}H NMR spectrum of **4r**



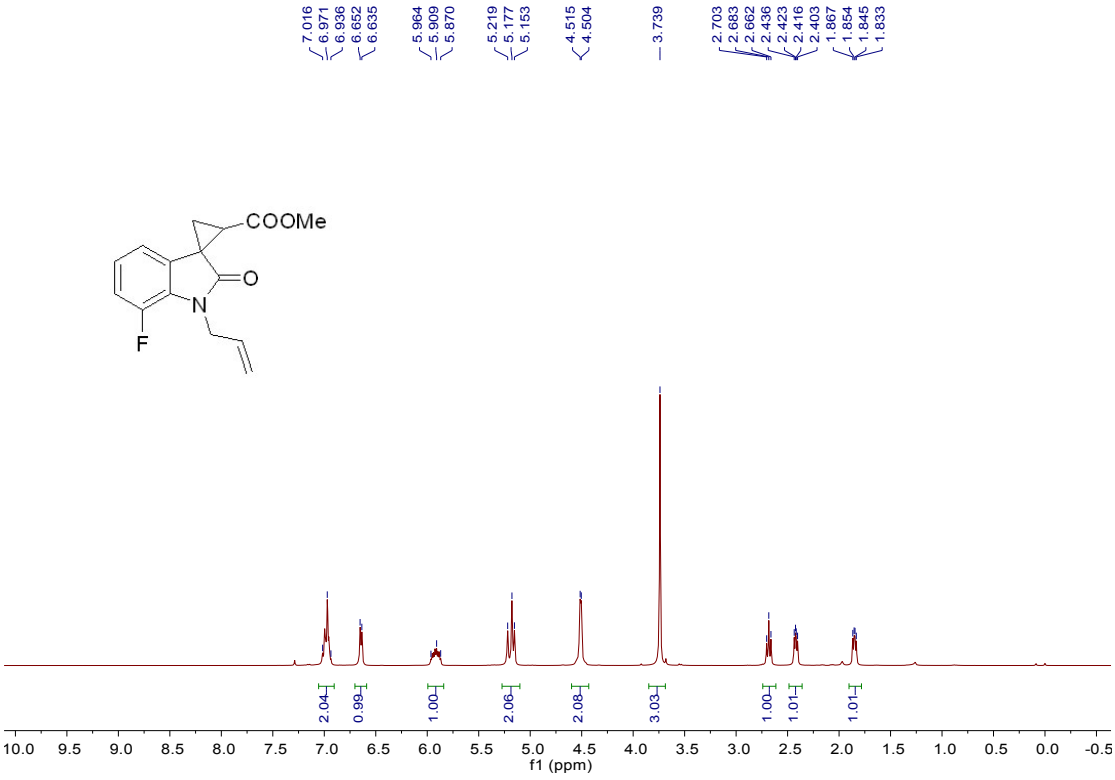
^{13}C NMR spectrum of **4r**



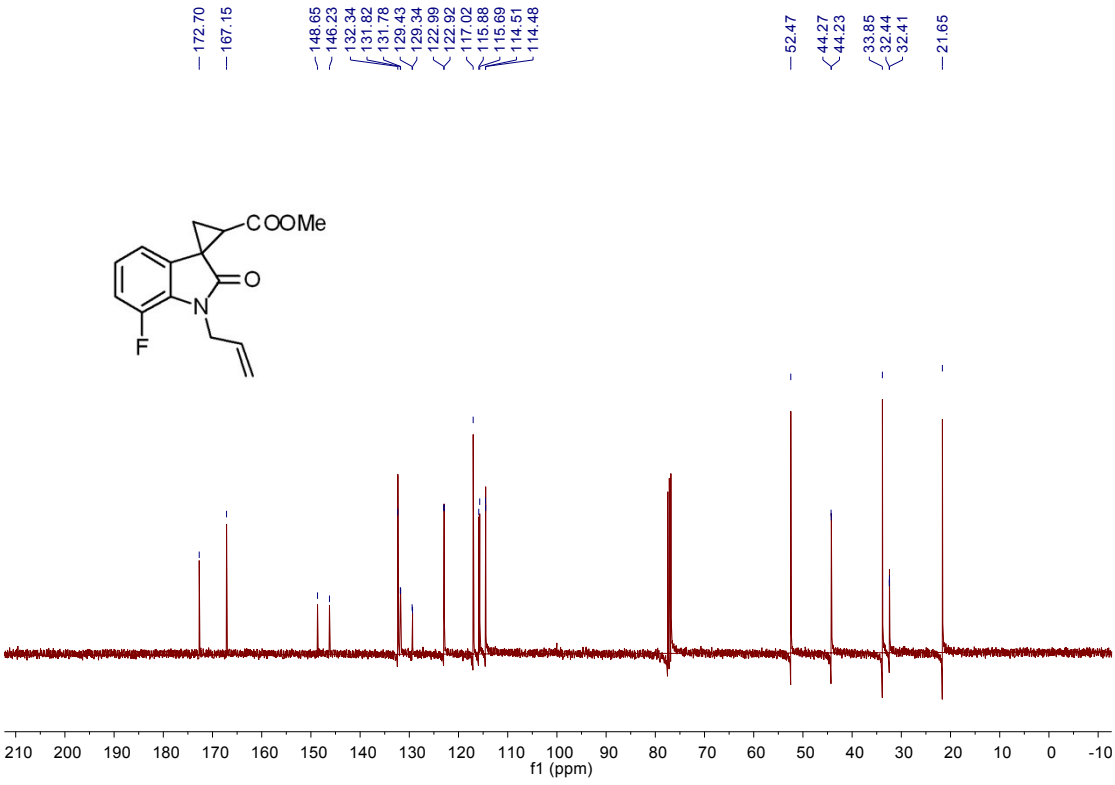
^{1}H NMR spectrum of **4s**



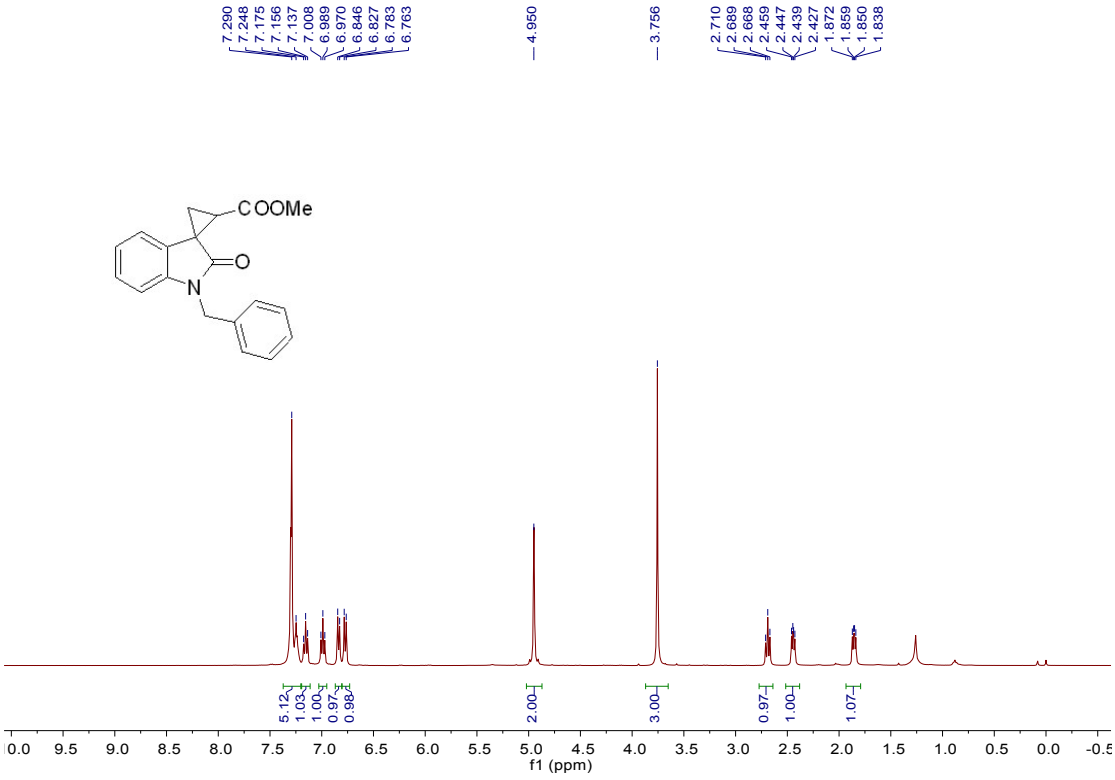
^{13}C NMR spectrum of **4s**



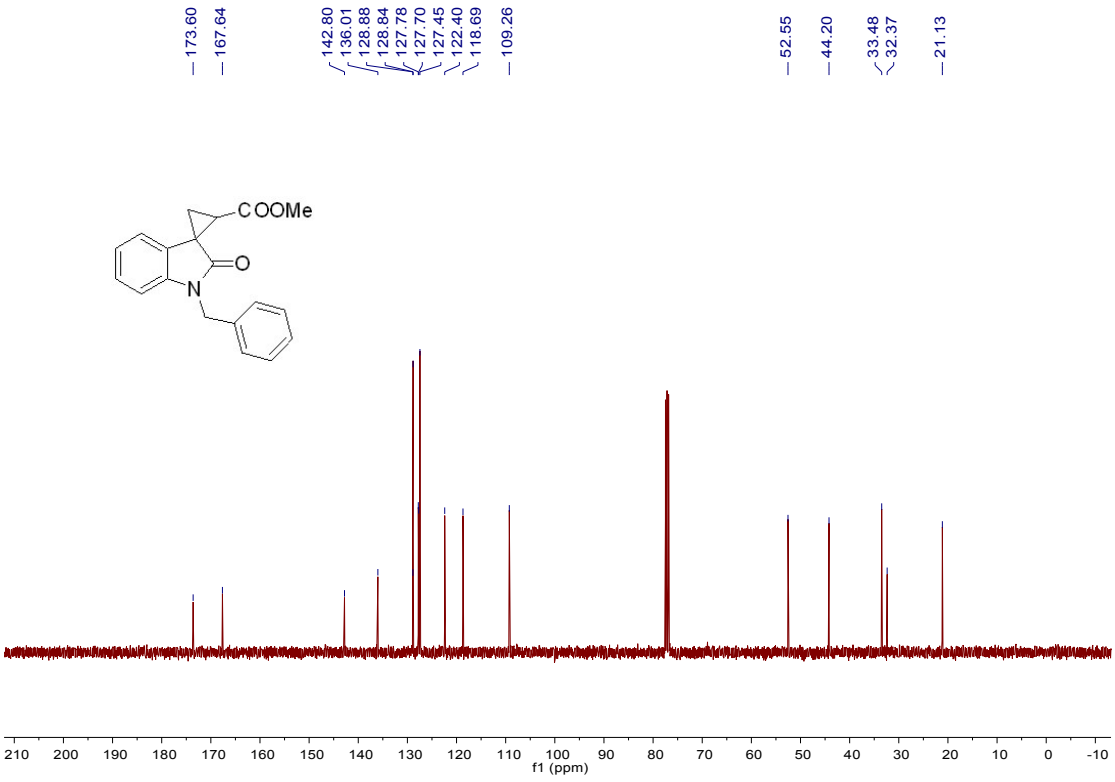
^{1}H NMR spectrum of **4t**



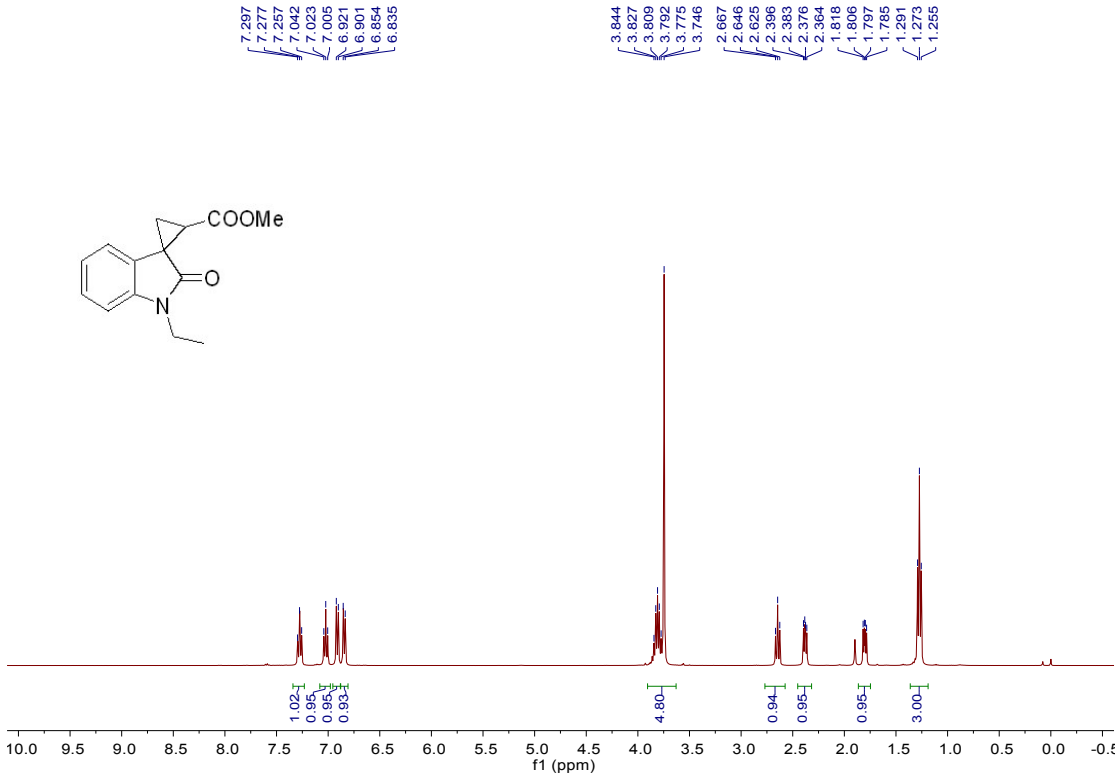
^{13}C NMR spectrum of **4t**



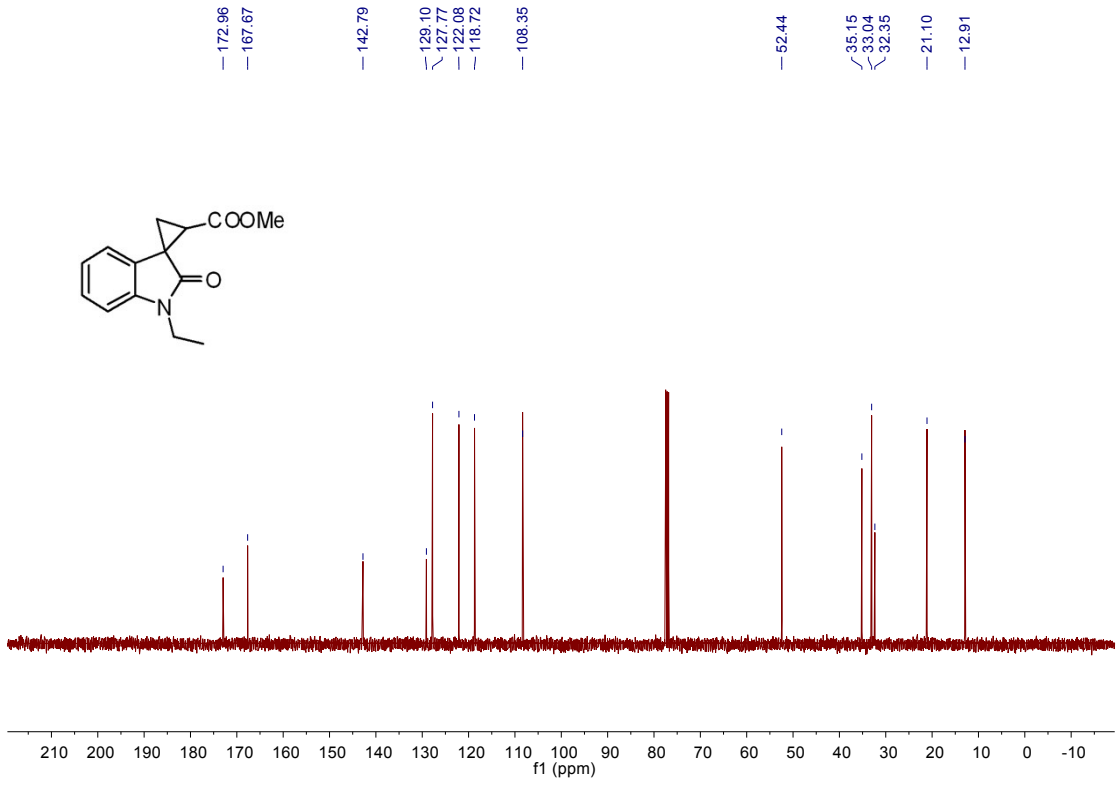
^{1}H NMR spectrum of **4u**



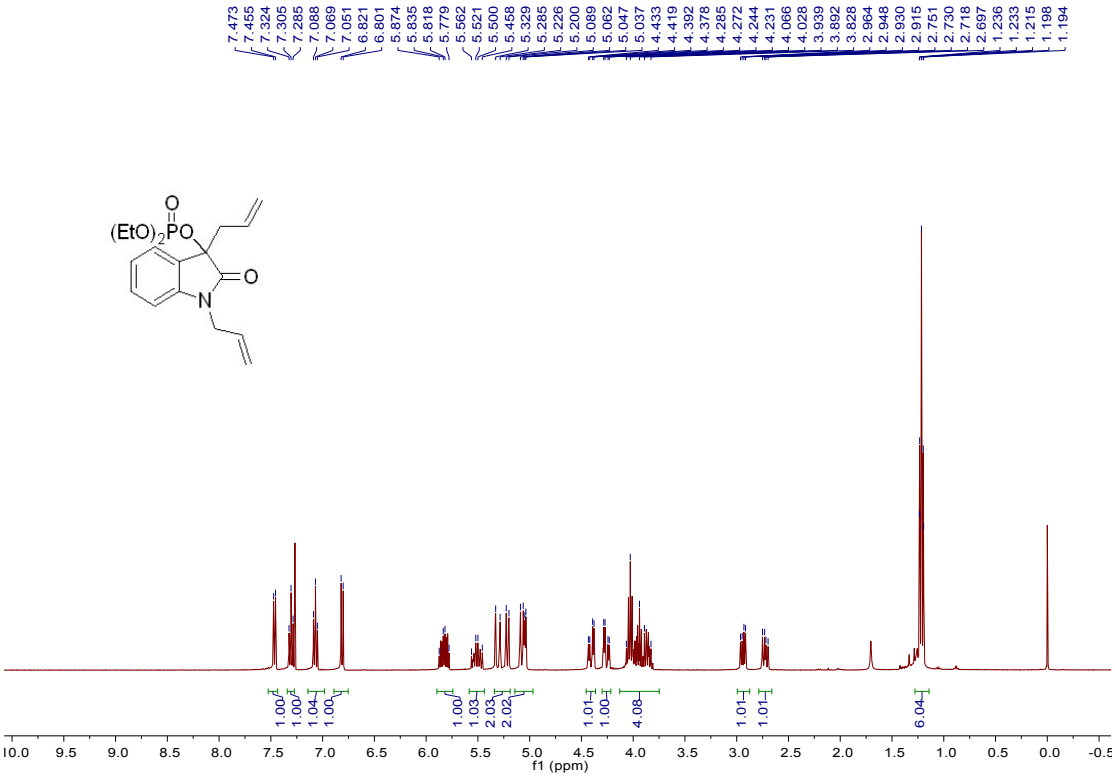
^{13}C NMR spectrum of **4u**



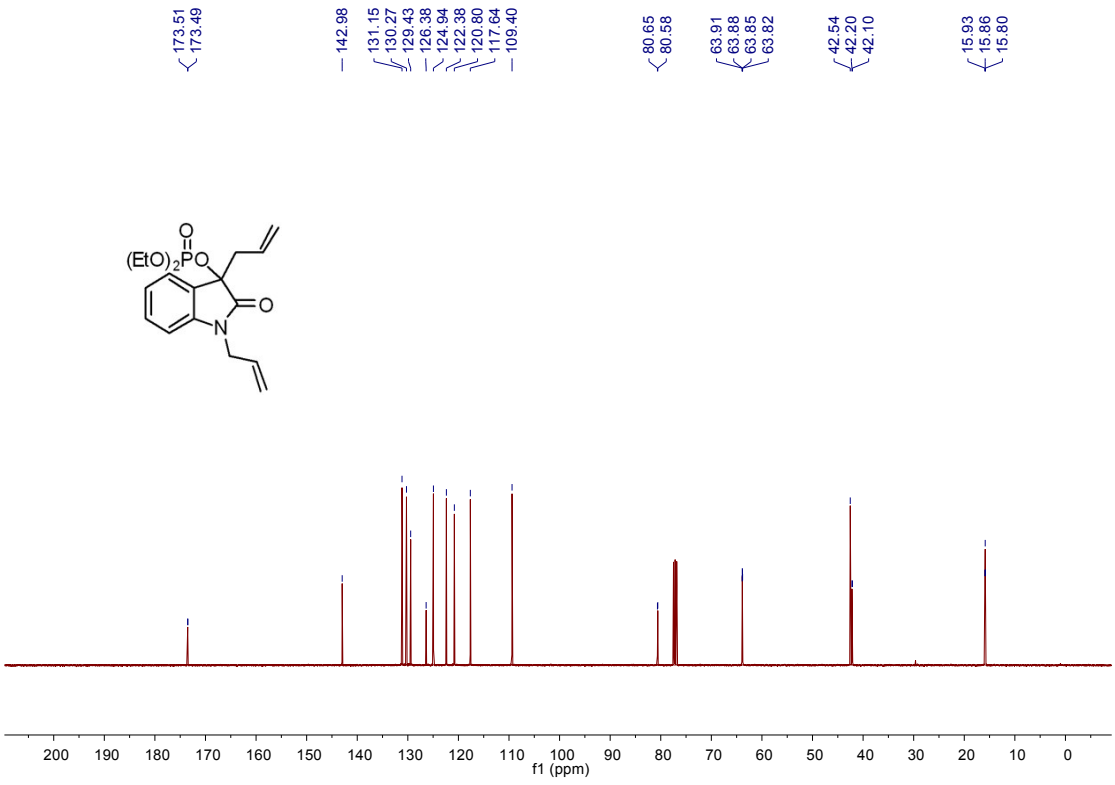
^{1}H NMR spectrum of **4v**



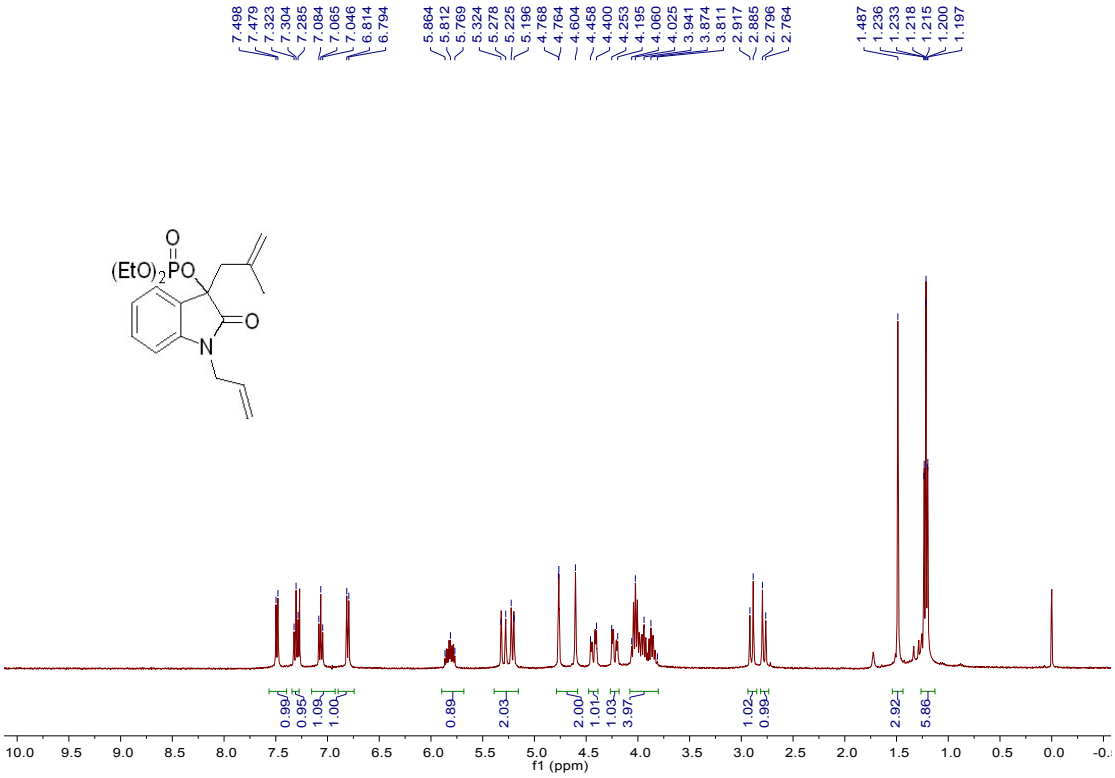
^{13}C NMR spectrum of **4v**



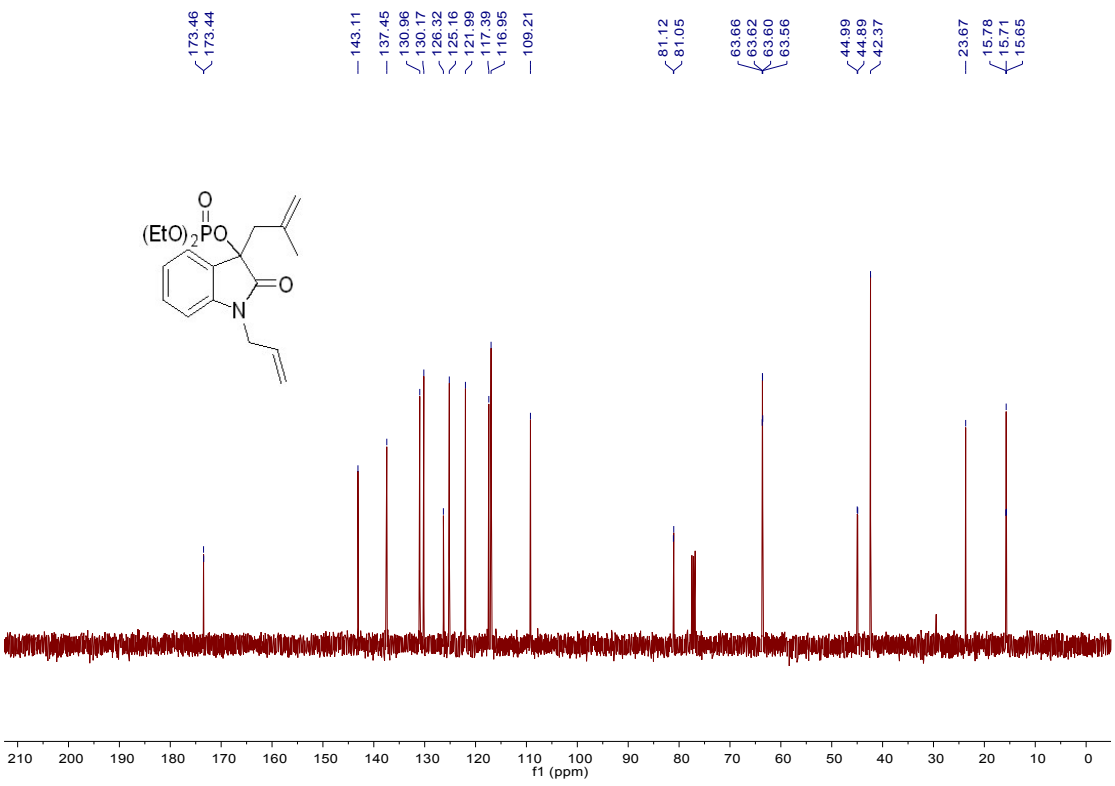
^{1}H NMR spectrum of **7a**



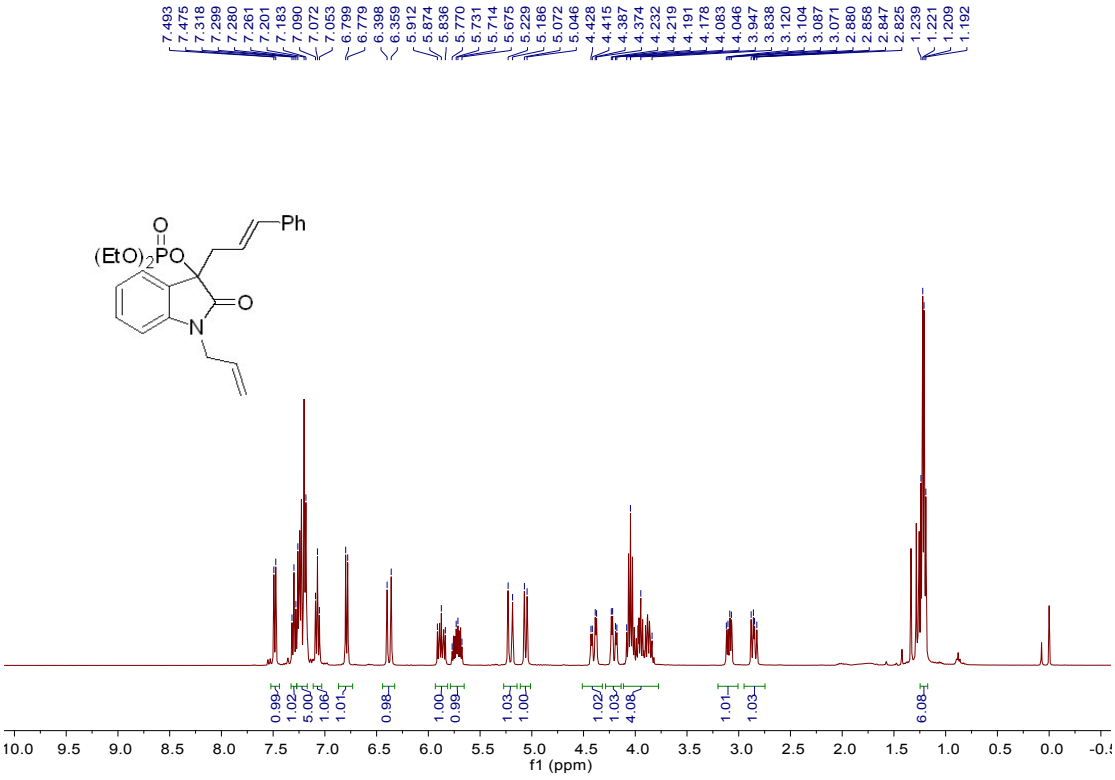
^{13}C NMR spectrum of **7a**



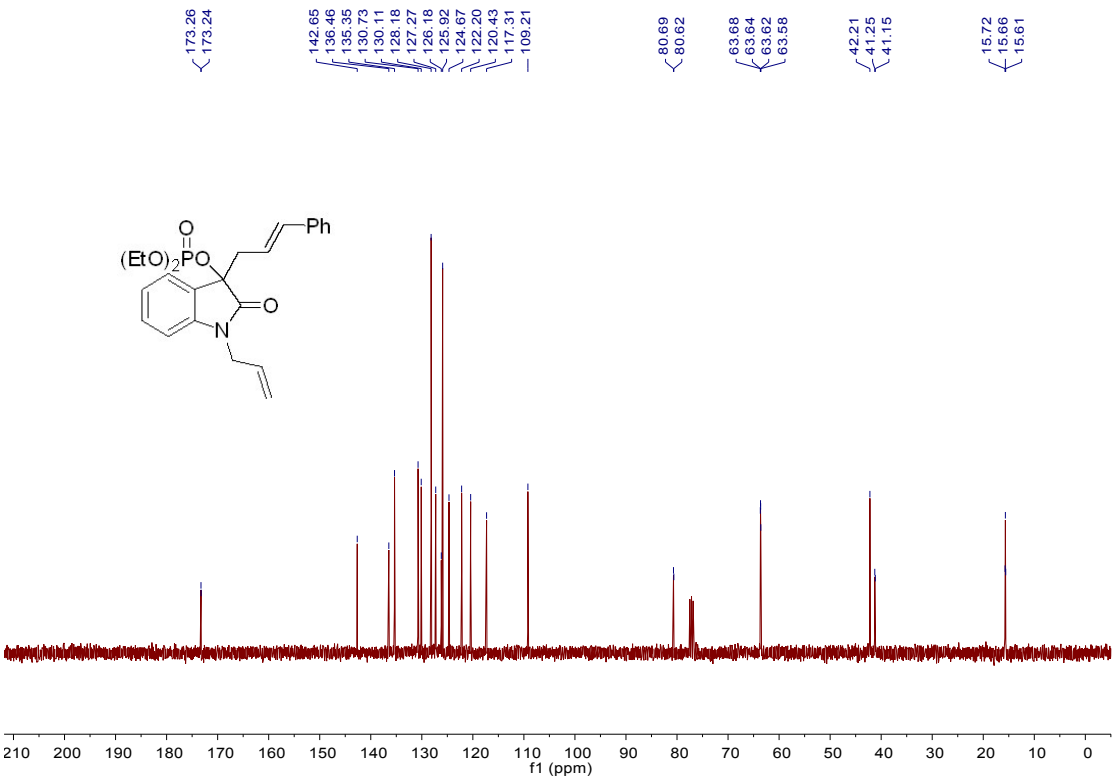
^{1}H NMR spectrum of **7b**



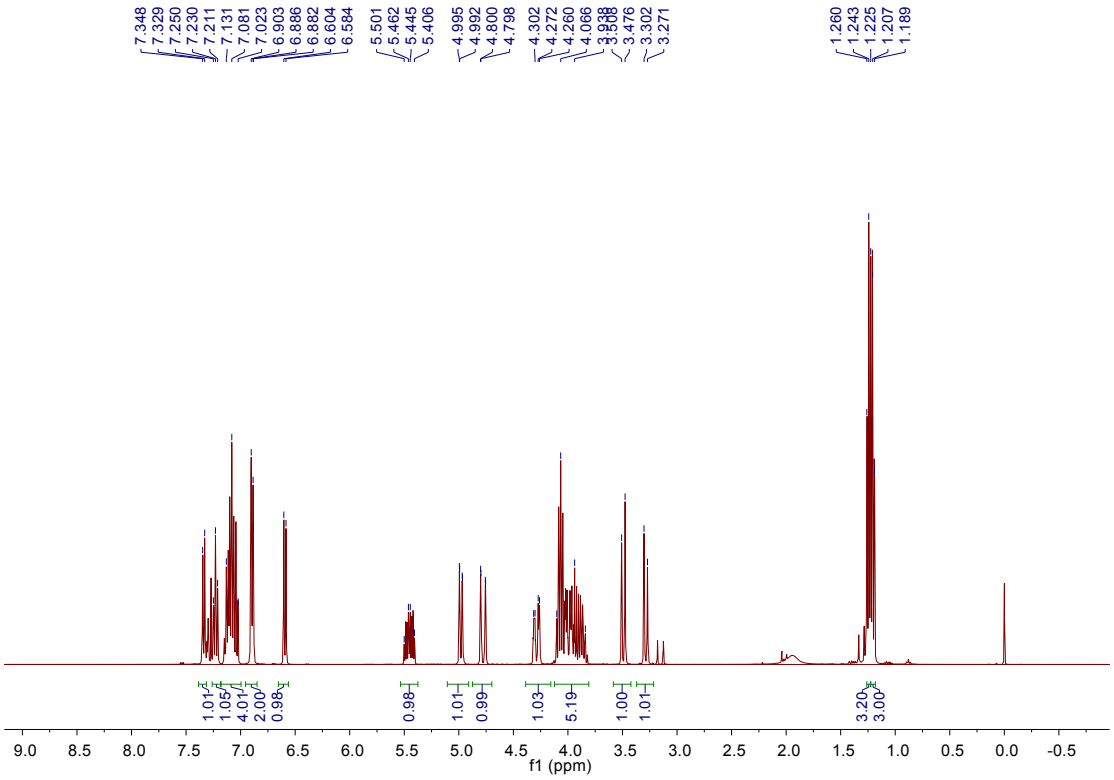
^{13}C NMR spectrum of **7b**



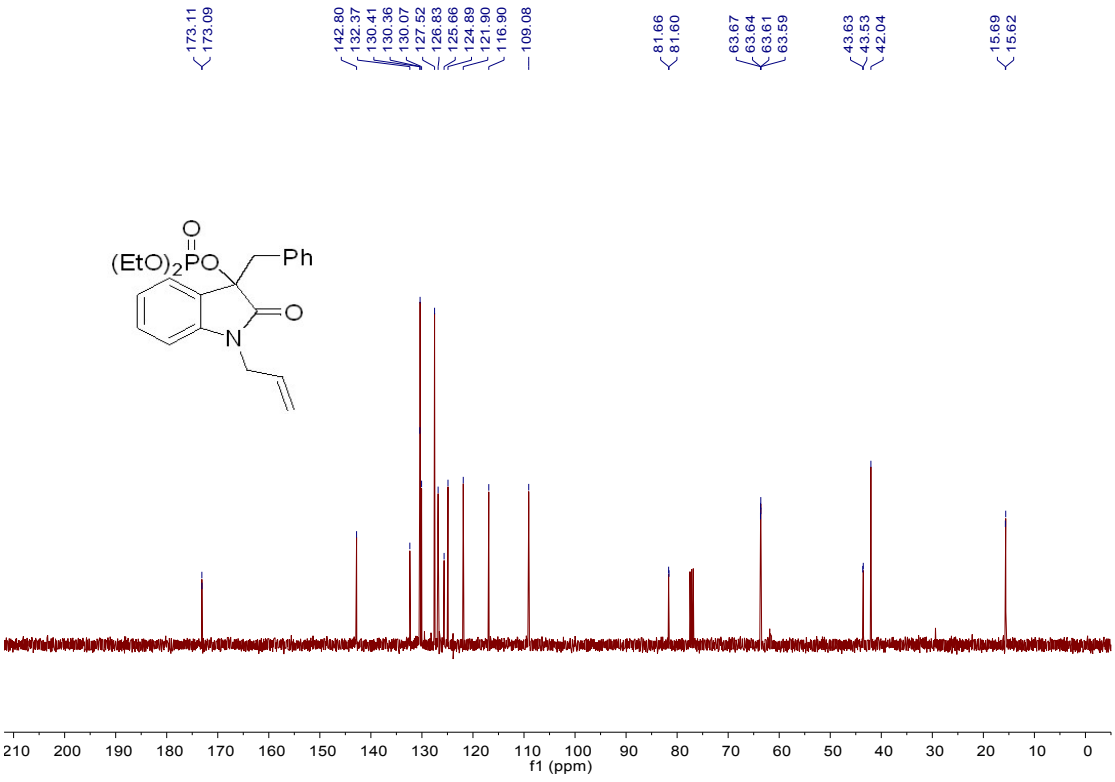
^{1}H NMR spectrum of **7c**



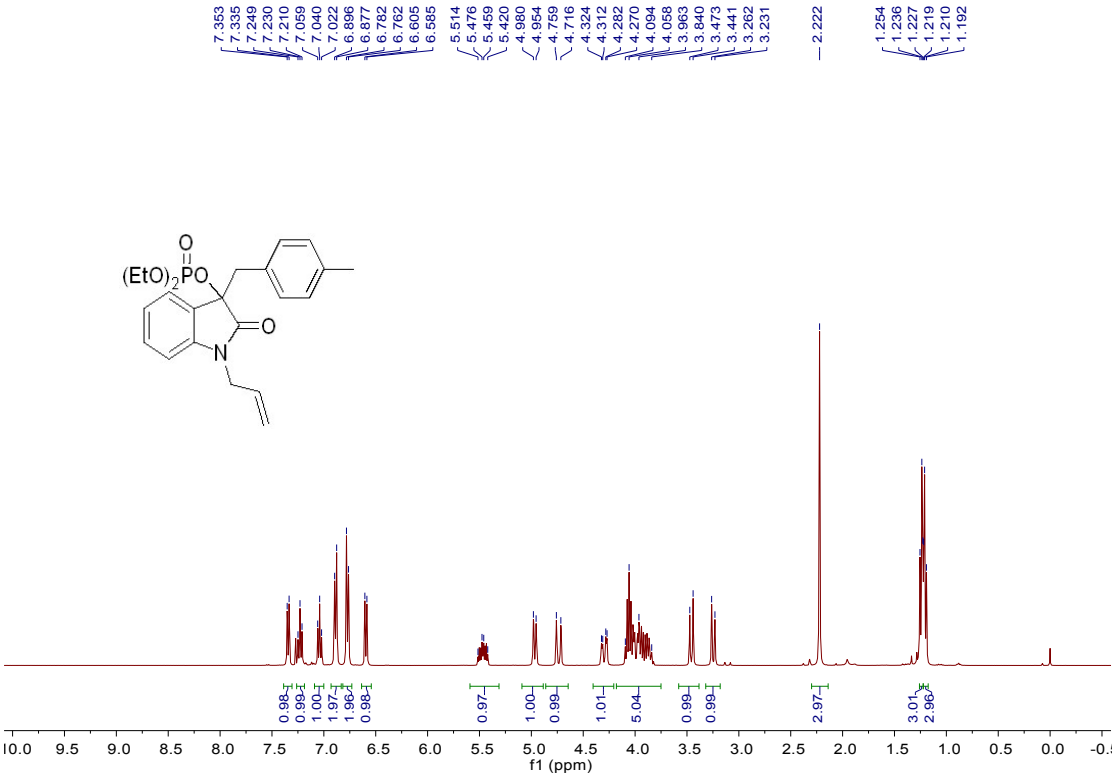
^{13}C NMR spectrum of **7c**



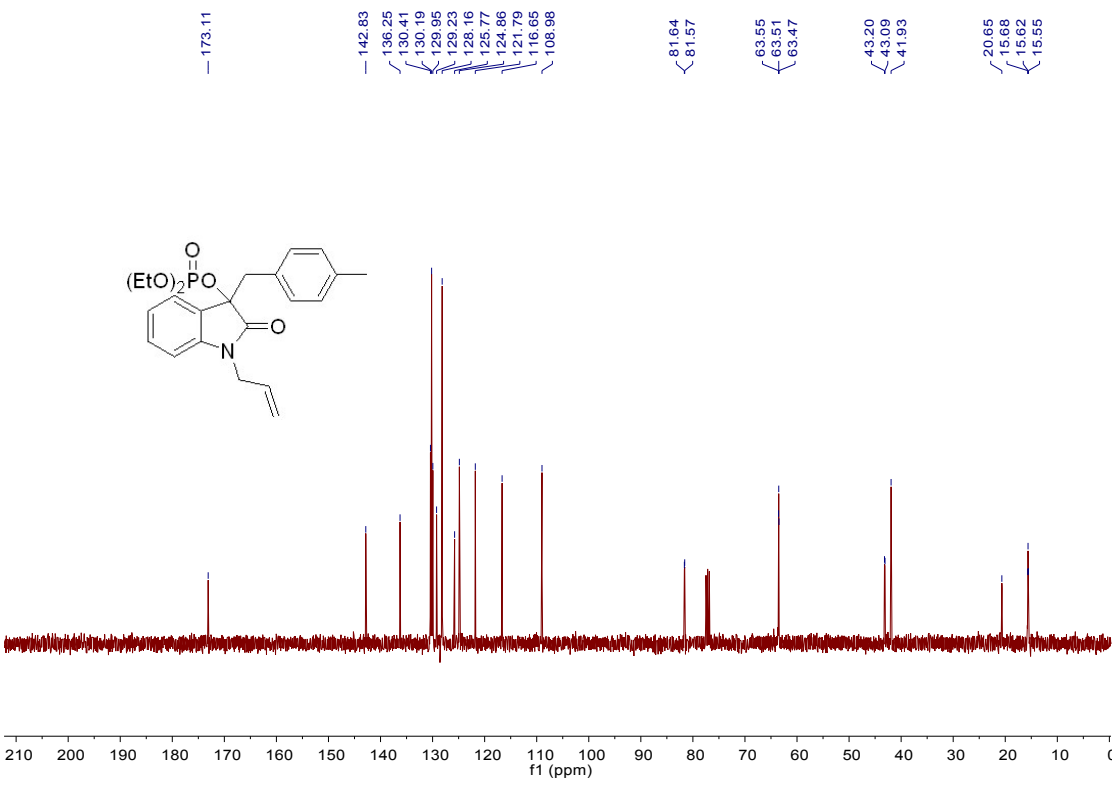
^{1}H NMR spectrum of **7d**



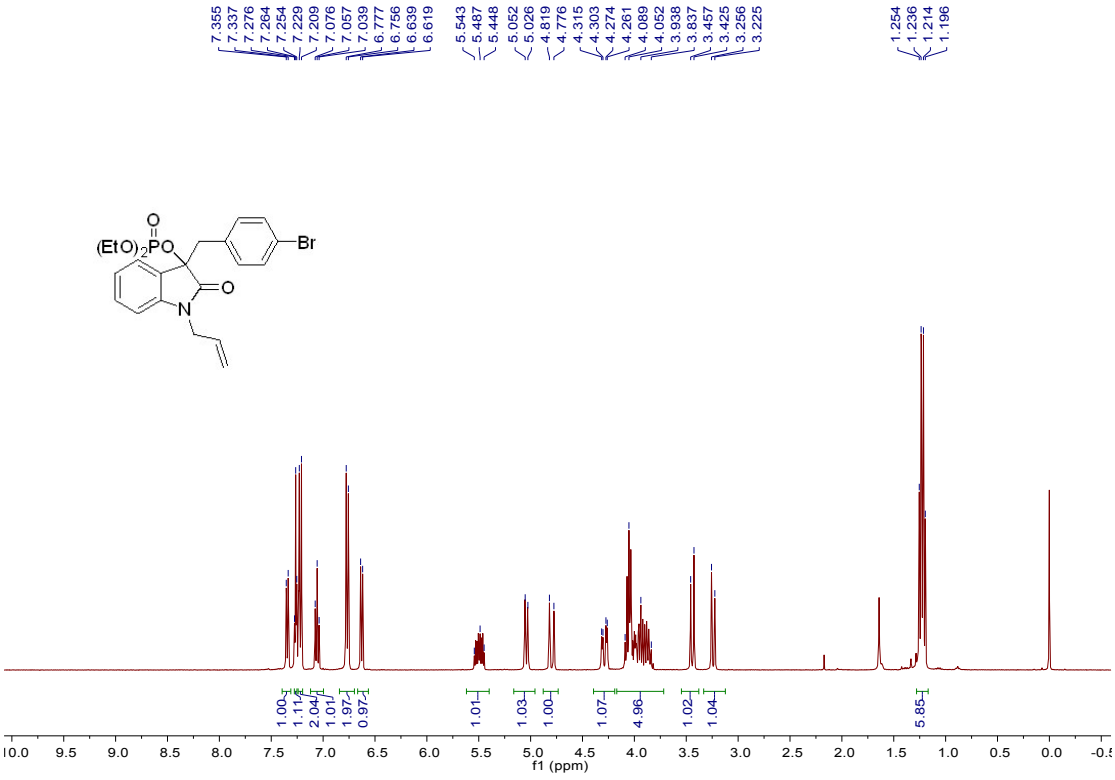
^{13}C NMR spectrum of **7d**



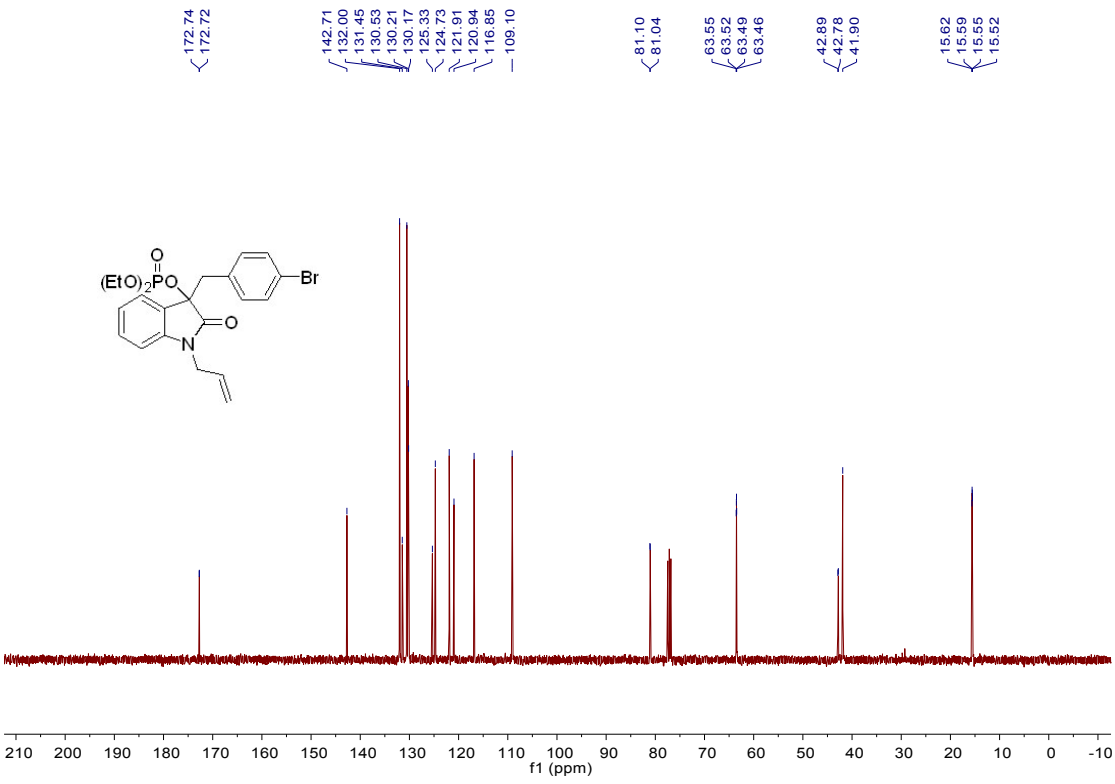
^{1}H NMR spectrum of **7e**



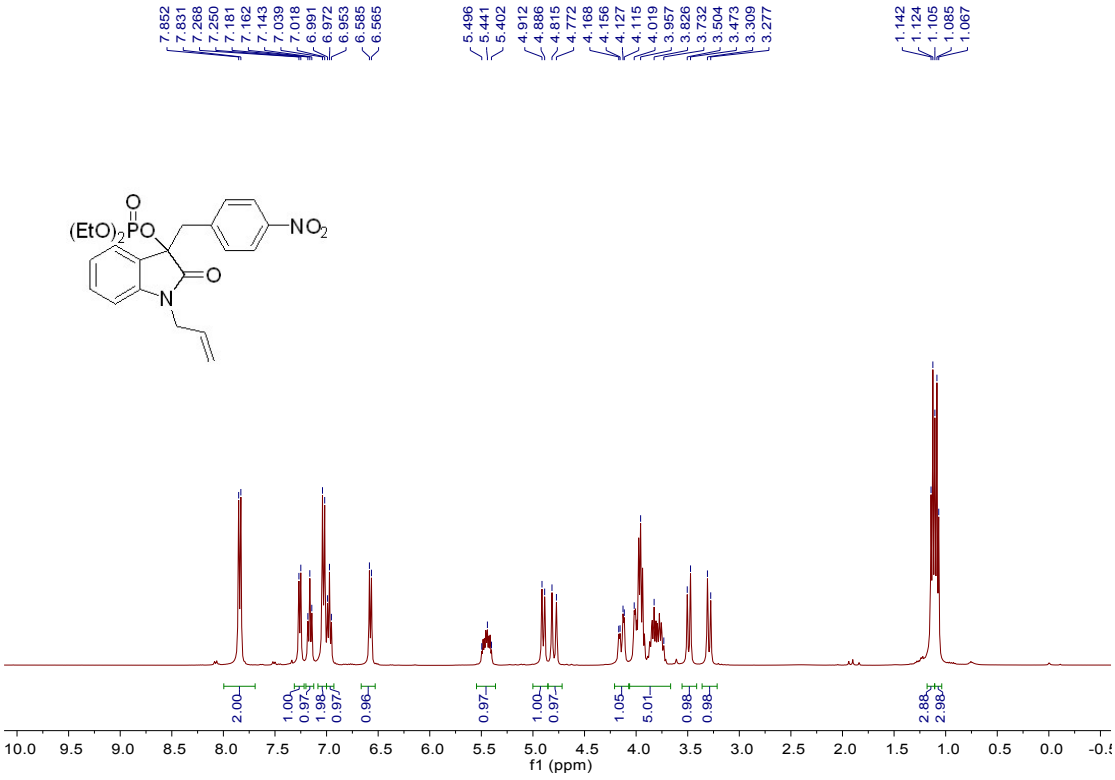
^{13}C NMR spectrum of **7e**



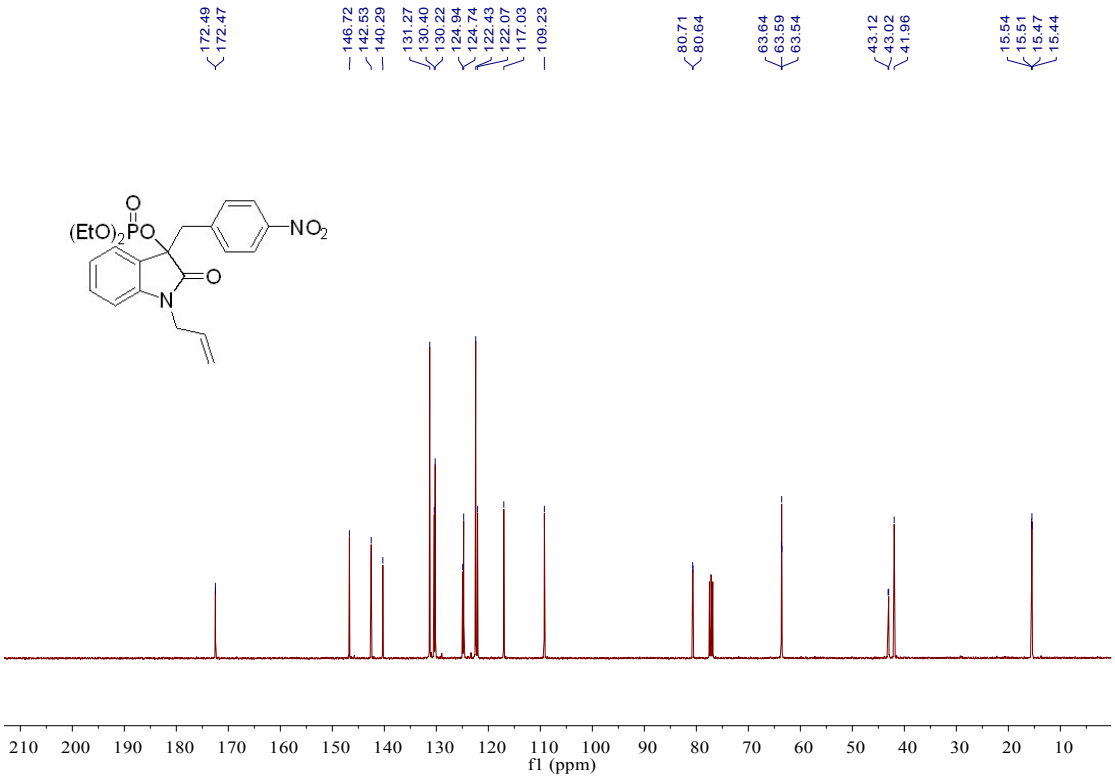
^{1}H NMR spectrum of **7f**



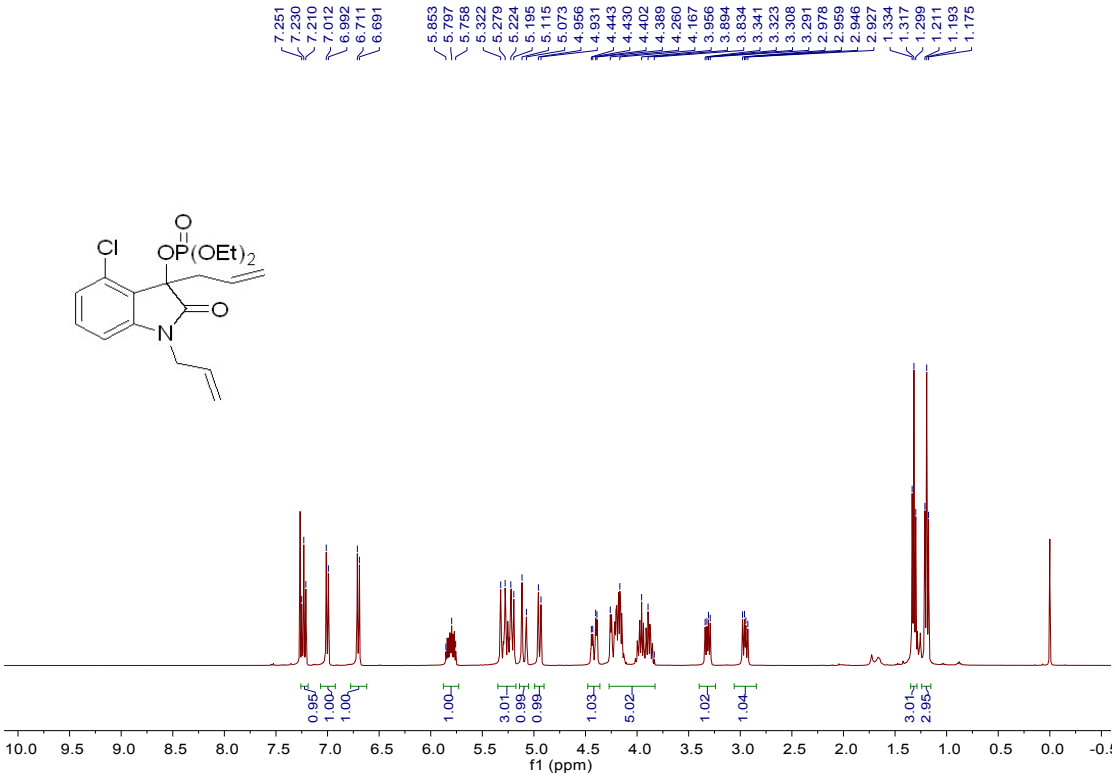
^{13}C NMR spectrum of **7f**



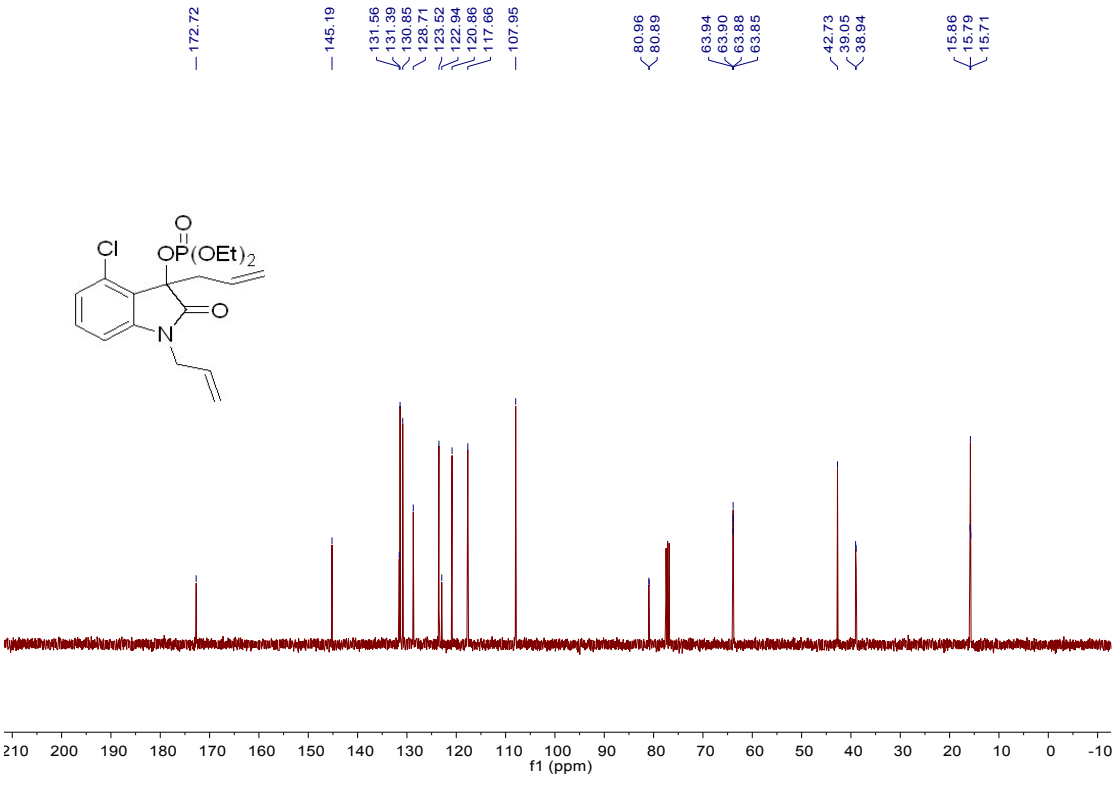
^{1}H NMR spectrum of **7g**



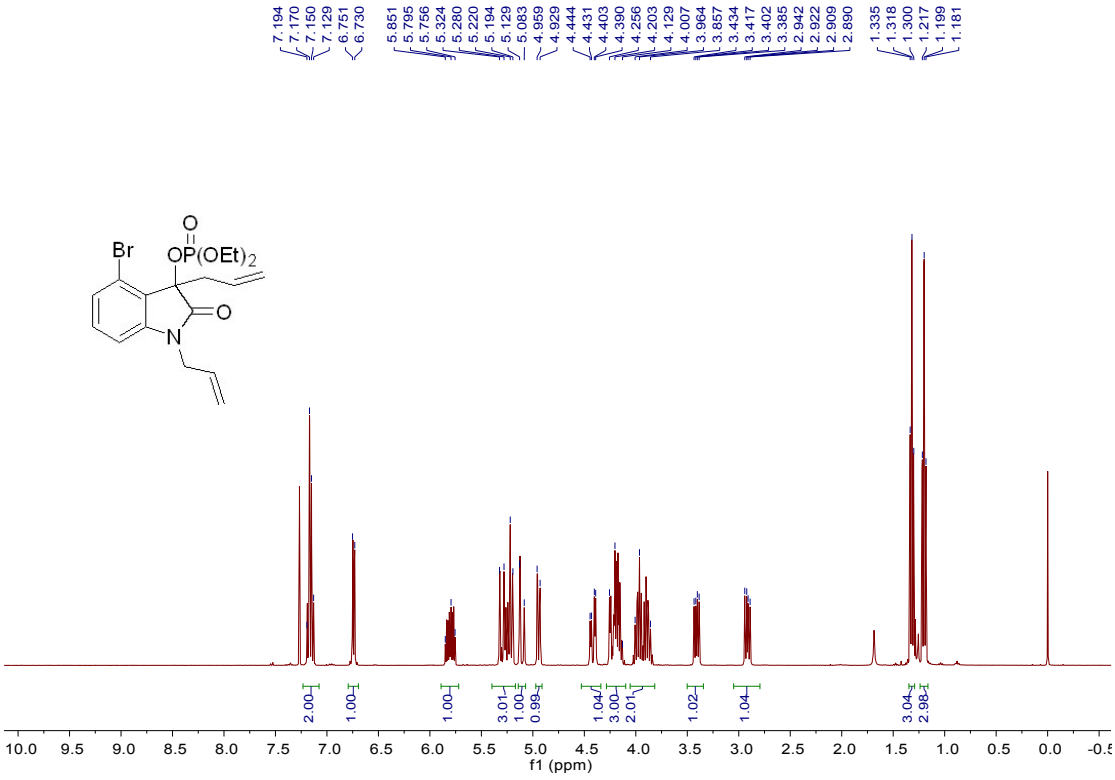
^{13}C NMR spectrum of **7g**



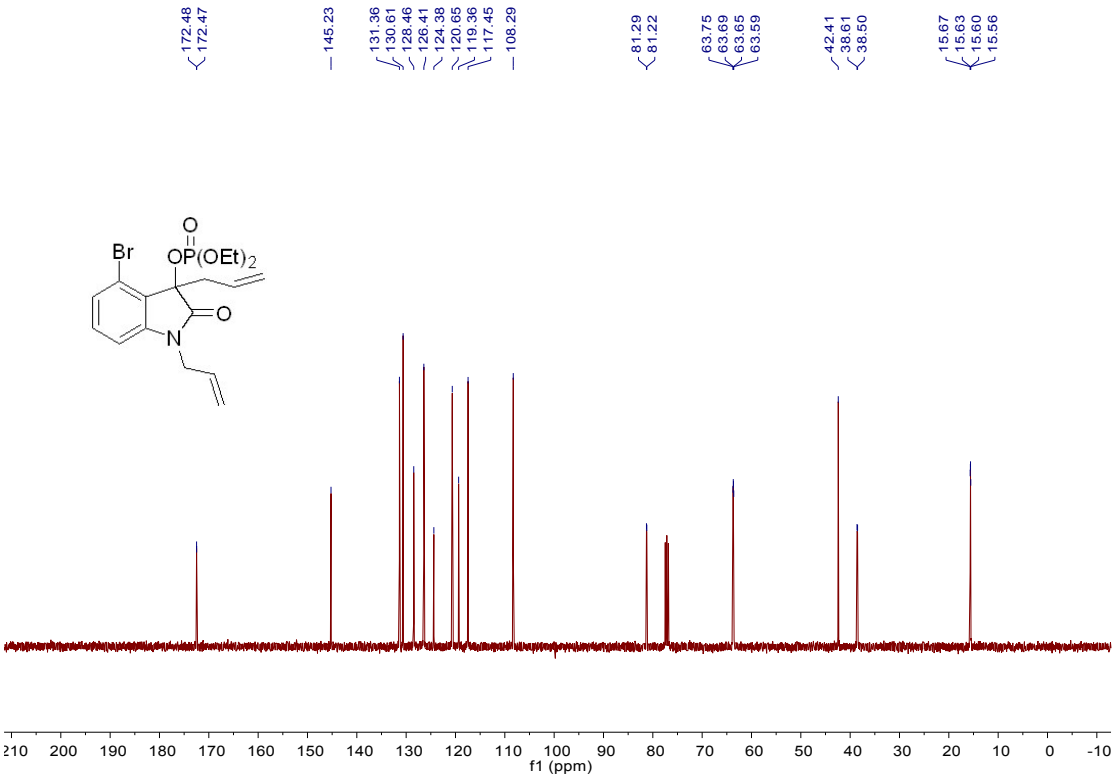
^{1}H NMR spectrum of **7h**



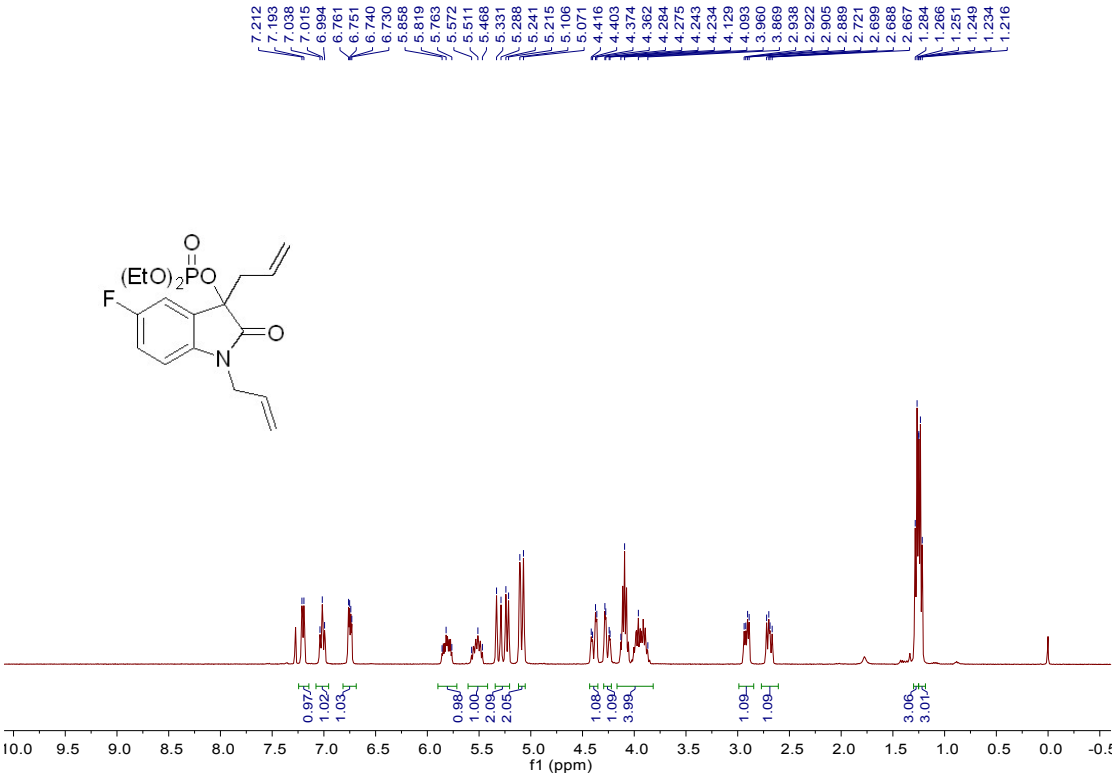
^{13}C NMR spectrum of **7h**



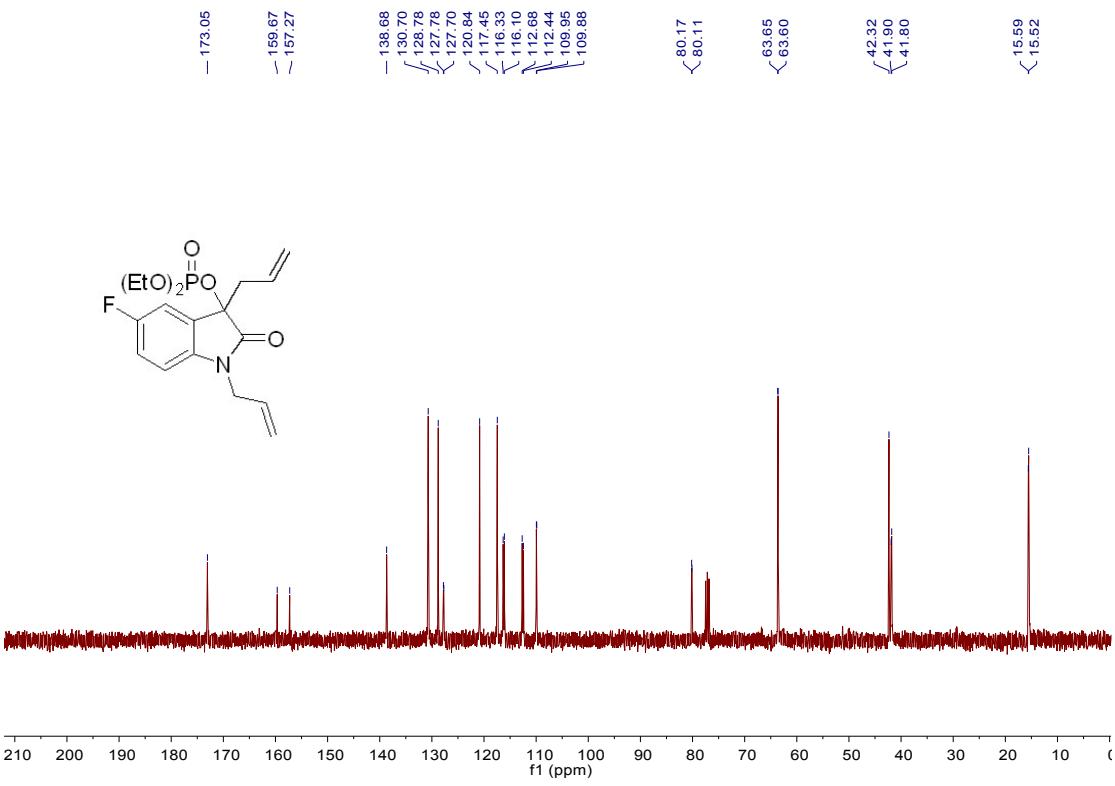
^{1}H NMR spectrum of **7i**



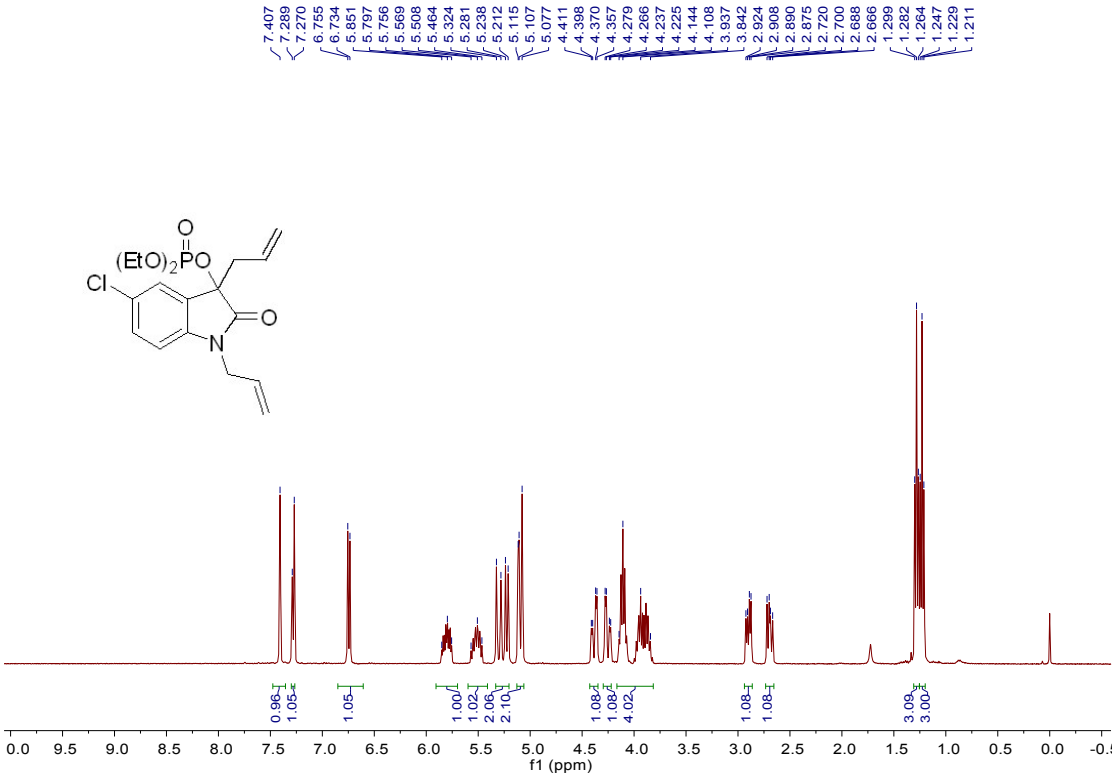
^{13}C NMR spectrum of **7i**



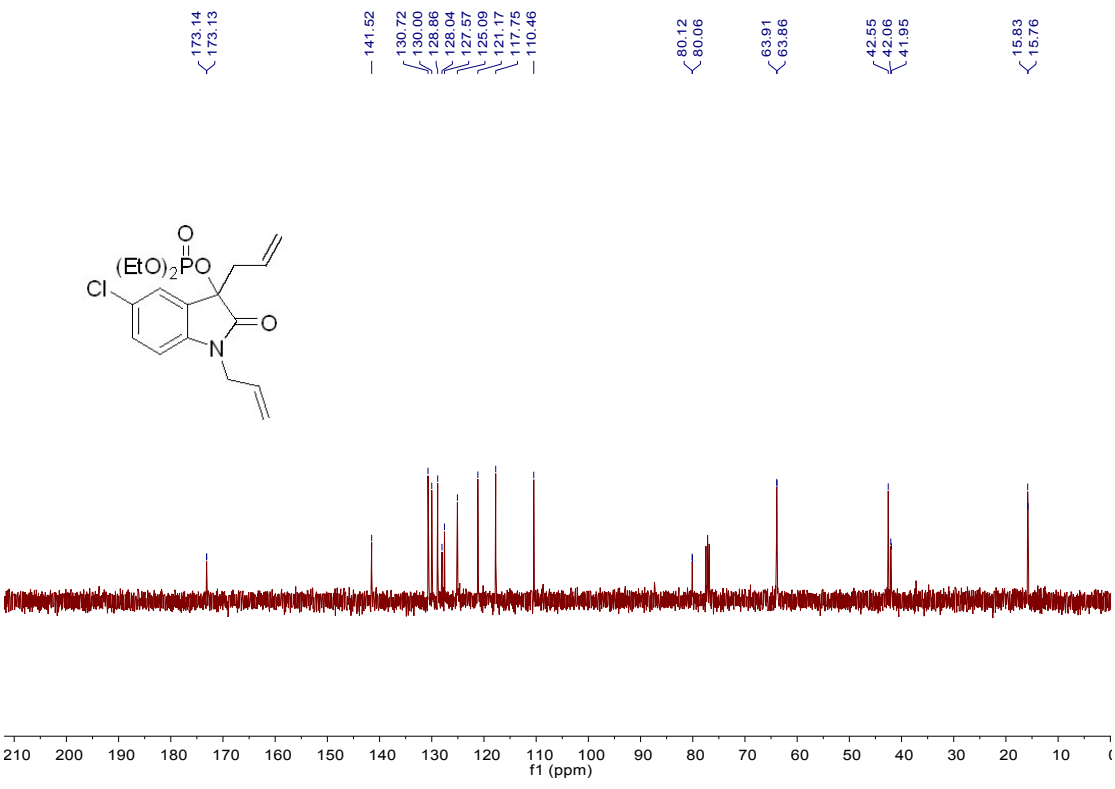
^{1}H NMR spectrum of **7j**



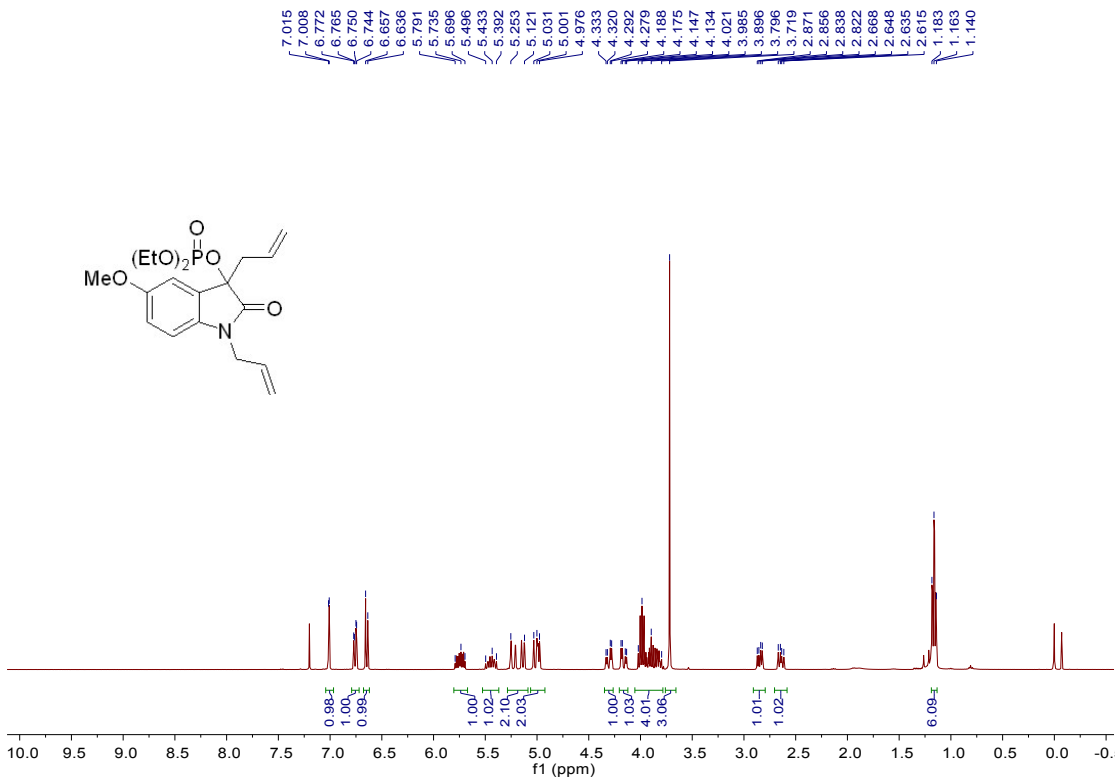
^{13}C NMR spectrum of **7j**



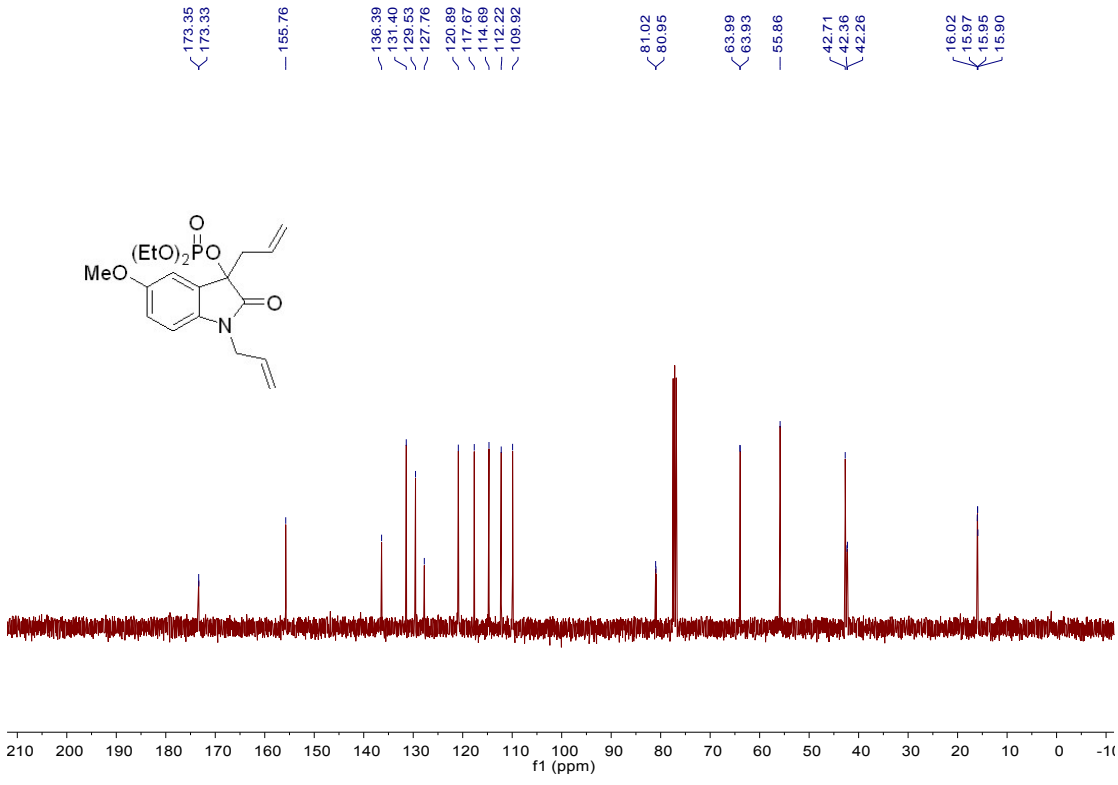
^{1}H NMR spectrum of **7k**



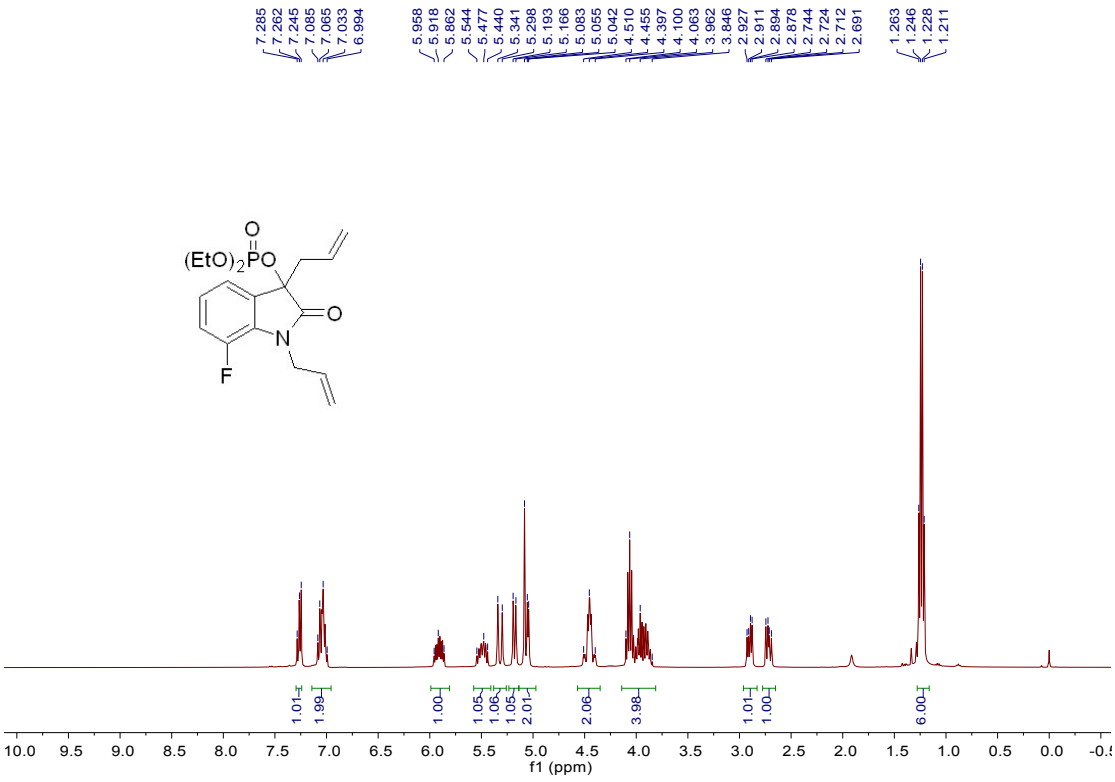
^{13}C NMR spectrum of **7k**



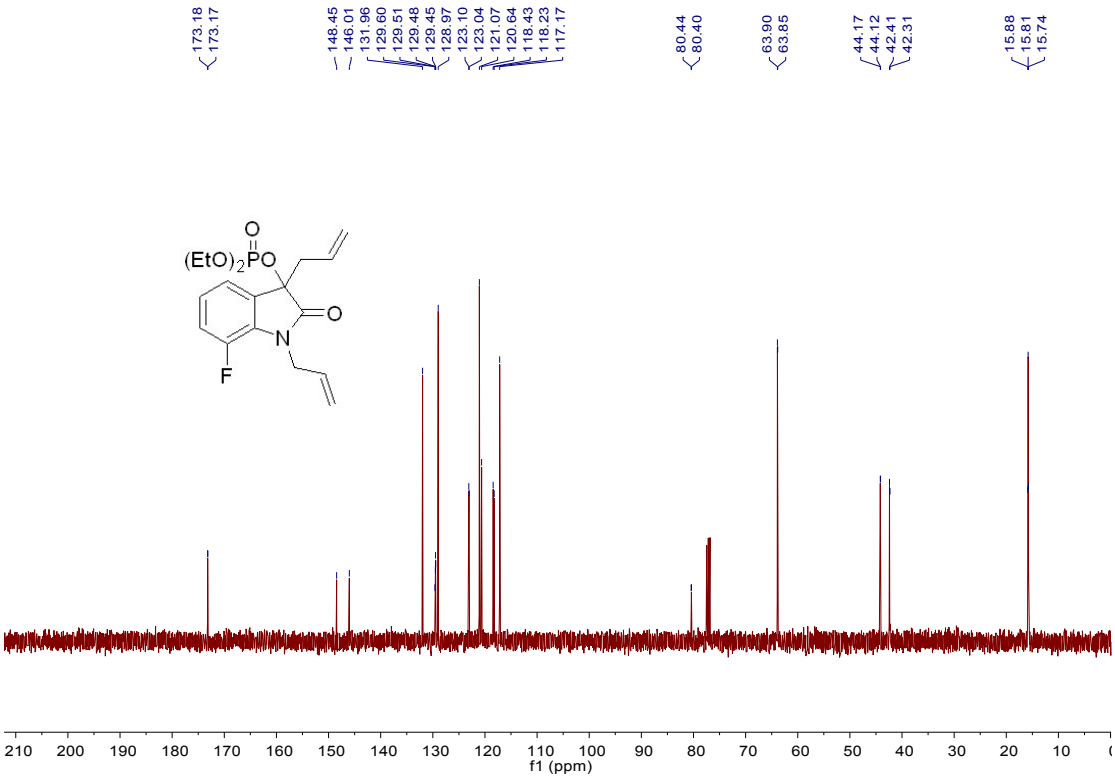
^{1}H NMR spectrum of **7l**



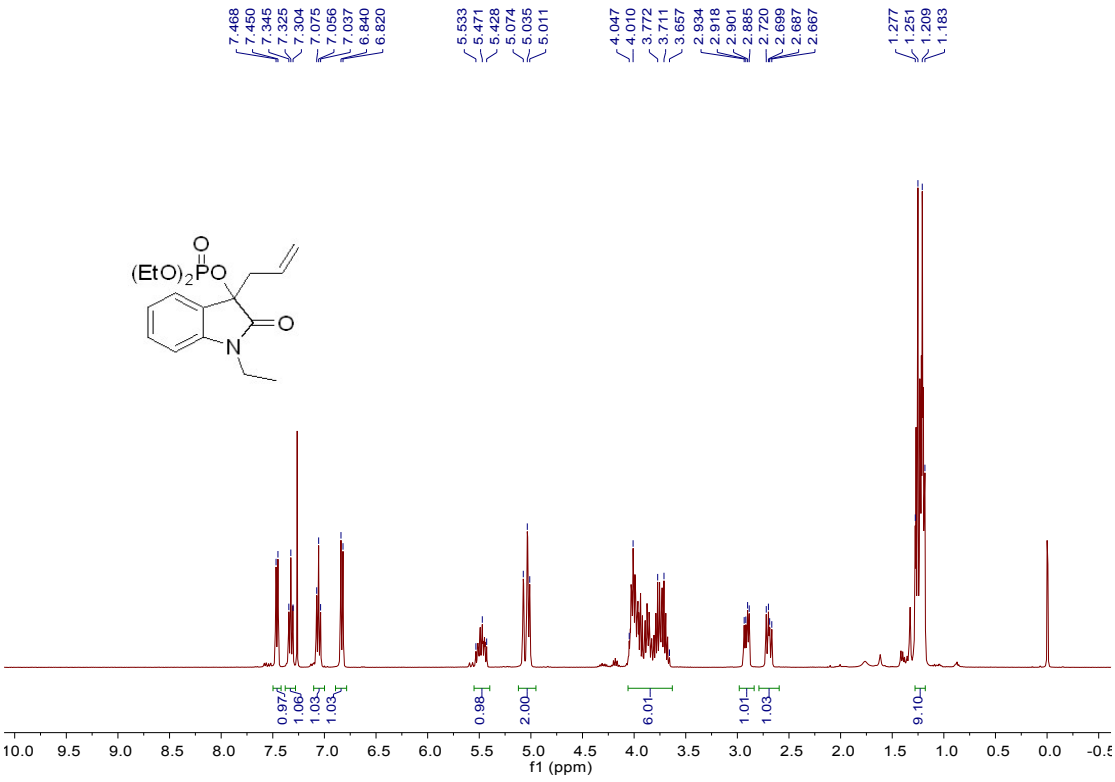
^{13}C NMR spectrum of **7l**



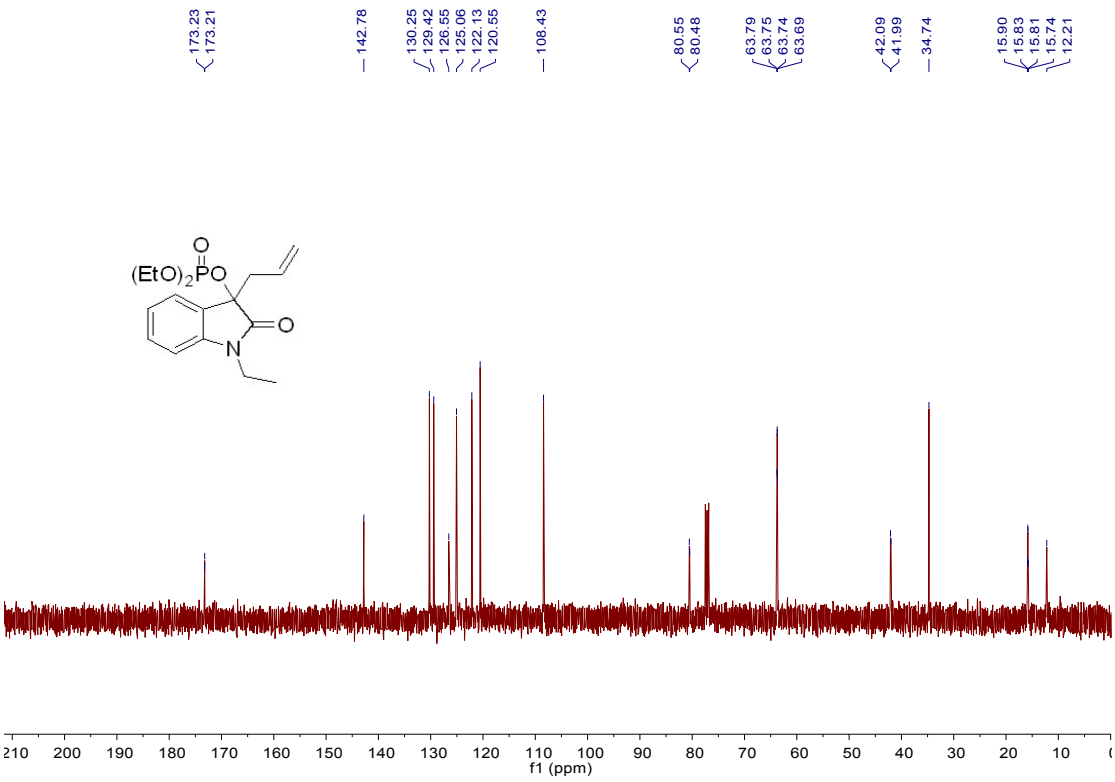
^{1}H NMR spectrum of **7m**



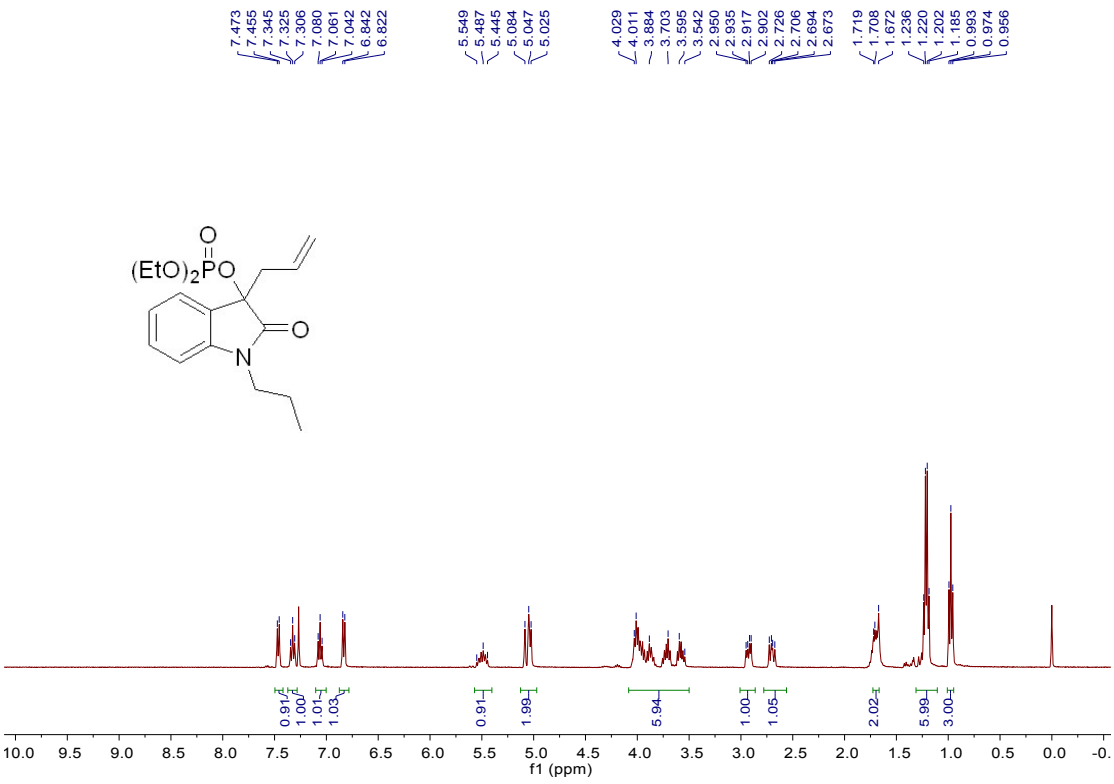
^{13}C NMR spectrum of **7m**



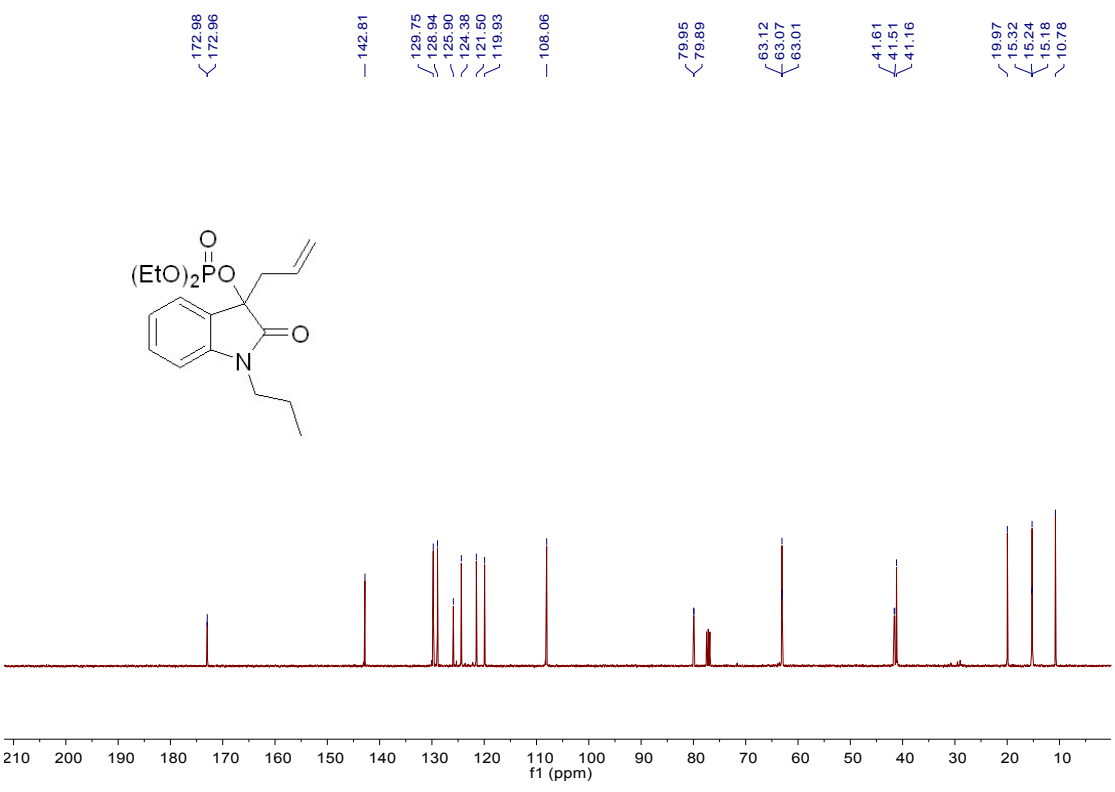
^{1}H NMR spectrum of **7n**



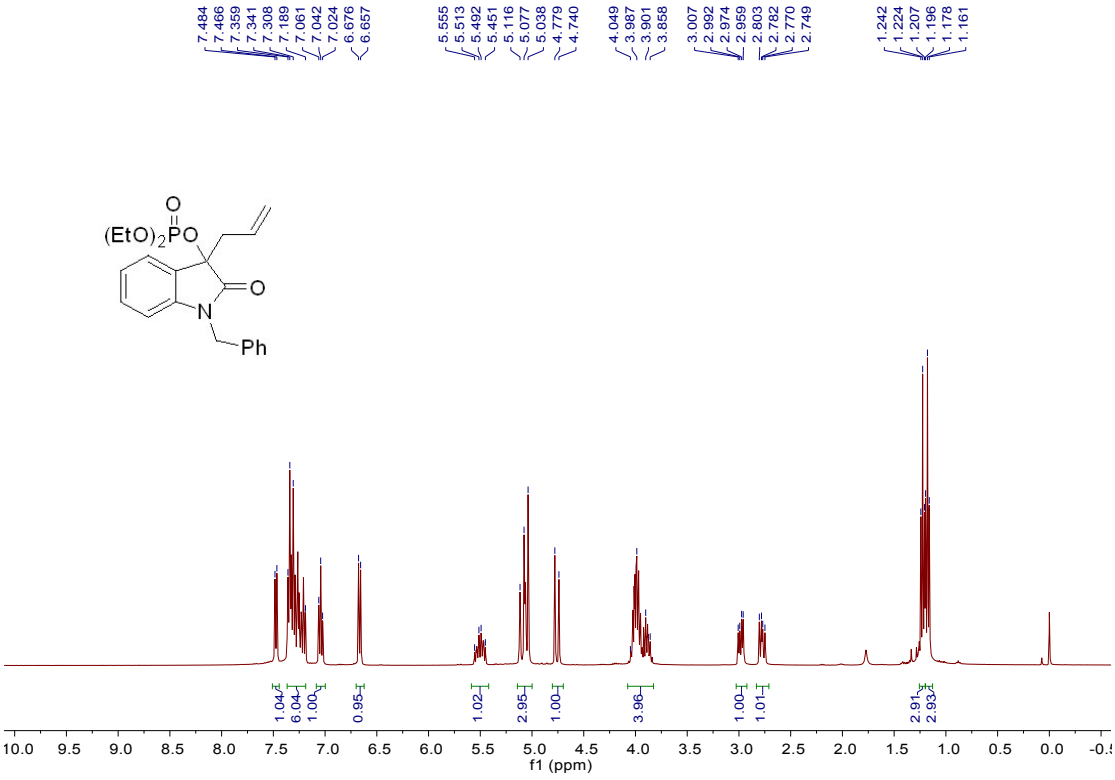
^{13}C NMR spectrum of **7n**



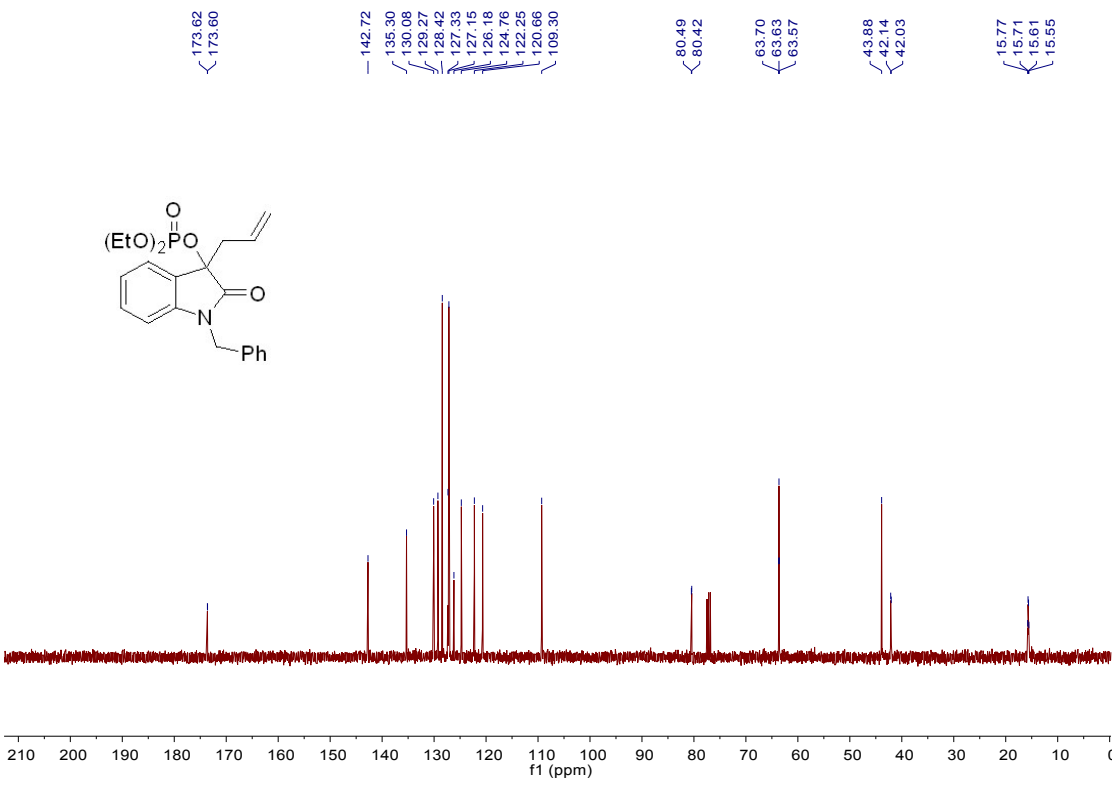
^{1}H NMR spectrum of **7o**



^{13}C NMR spectrum of **7o**



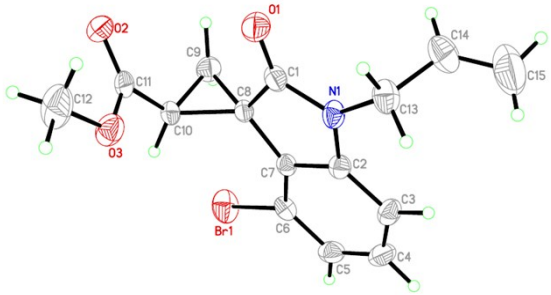
^{1}H NMR spectrum of **7p**



^{13}C NMR spectrum of **7p**

X-ray structures of 4p and 4r

4p:



4r: