Supporting Information

Electrocyclization of arylvinyl β-hydroxyacetonitrile to substituted cyanomethyl indene derivatives

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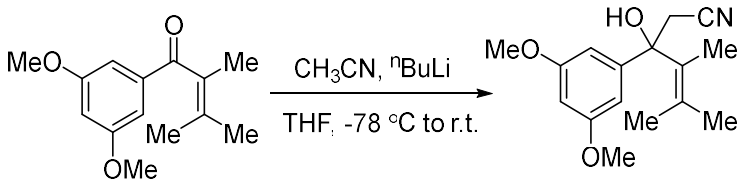
1. General Information:

All reagents and solvents were of analytical purity and used as received. Column chromatography was performed using silica gel (100-200 or 230– 400 mesh). Thin-layer chromatography (TLC) was performed on pre-coated silica gel-60 F254 (0.5 mm) glass plates and visualized by exposure to UV light (254 nm) or staining the plates in methanolic anisaldehyde-sulphuric acid-acetic acid solutions and charring on a hot plate. IR spectra were recorded as neat over the range 600–4000 cm^{-1}. Mass spectra were recorded on a Micro Mass VG-7070H mass spectrometer for ESI and are given in mass units (*m/z*). The ^{1}H and ^{13}C NMR spectra of purified products were recorded in $CDCl_3$ solvent on 500 MHz, 400 MHz, 300 MHz, 125 MHz, 100 MHz, and 75 MHz spectrometers, respectively, at ambient temperature. Data were reported as chemical shifts in ppm with respect to the residual solvent signal $CDCl_3$ (^{1}H NMR: δ = 7.24 ppm; ^{13}C NMR: δ = 77.16 ppm). The abbreviations used for Peak multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd =doublet of doublet, dq = doublet of quartets, brs = broad singlet, and m = multiplet.

2. Experimental Procedures:

Synthesis of 3-(3,5-dimethoxyphenyl)-3-hydroxy-4,5-dimethylhex-4-enenitrile(7a):

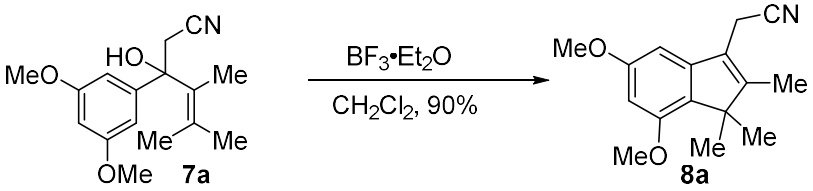


S1 **7a**

Take a 50 mL vacuum-dried round-bottom flask with acetonitrile (1.78 mL, 34.14 mmole, 2 equiv) with THF (53 mL), cool to -78°C, and add ^{n}BuLi (1.6 M, 16 mL, 25.6 mmol, 1.5 equiv), and stirred for half an hour at the same temperature. Then, 1-(3,5-dimethoxyphenyl)-2,3-dimethylbut-2-en-1-one (**S1**)[20d,f] (4 g, 17.07 mmol, 1 equiv) was cannulated into the reaction mixture in dry THF (18 mL), and the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with saturated NH_4Cl solution. The reaction mixture was extracted with EtOAc (100 mL), washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude product was purified by flash chromatography with 20% EtOAc/hexane as eluent to furnish the desired product **7a** (4.5 g, 96% yield, colourless).

R_f= 0.5 (15% EtOAc/ hexane); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.56 (d, *J* = 2.2 Hz, 1H), 6.37 (t, *J* = 2.2 Hz, 1H), 3.79 (s, 6H), 2.91 (ABq, J = 16.3 Hz, 2H), δ 2.56 (brs, 1H), 1.95 (s, 3H), 1.75 (s, 3H), 1.58 (s, 3H); **^{13}C {^{1}H} NMR(101 MHz, $CDCl_3$):** δ 160.8, 148.1, 133.2, 130.9, 118.0, 103.7, 98.9, 77.5, 55.4, 33.3, 23.1, 22.8, 17.6; **IR (Neat): ν_{max}** 3470, 3000, 2924, 2854, 2252, 1593, 1457,14251289, 1203, 1152, 1011, 923, 841, 767, 700; **HRMS (ESI-TOF):** *m/z* $(M + Na)^+$ calcd for $C_{16}H_{21}NO_3Na$ 298.1419; found: 298.1403.

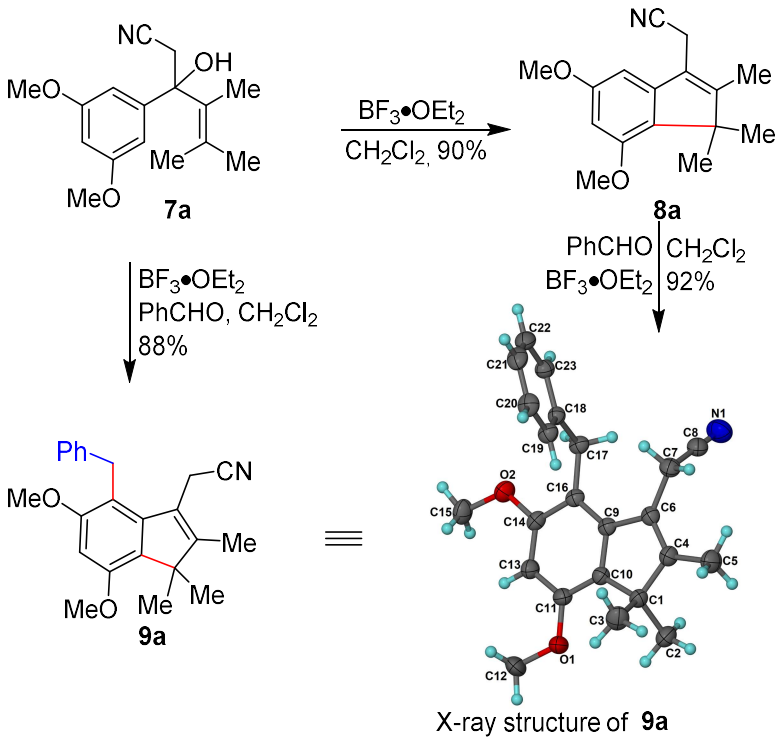
2-(5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl) acetonitrile (8a):



Compound **7a** (500 mg, 1.8 mmol, 1.0 equiv) was taken in a round-bottom flask under a nitrogen atmosphere, and to this was added CH_2Cl_2 (18 mL). Then, BF_3•Et_2O (230 µL, 1.8 mmol, 1.0 equiv) was added at room temperature. After completion of the reaction (confirmed by TLC), it was quenched by adding a saturated $NaHCO_3$ solution until the pH became neutral.

The reaction mixture was then extracted with EtOAc (100 mL), and the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified using silica gel column chromatography (EtOAc/Hexanes) to obtain **8a** (420 mg, 90% yield) as a colorless liquid.

R_f= 0.6 (15% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.50 (d, *J* = 2.0 Hz, 1H), 6.34 (d, *J* = 2.0 Hz, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 3.48 (d, *J* = 0.6 Hz, 2H), 1.93 (s, 3H), 1.28 (s, 6H); **^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$):** δ 160.7, 155.9, 154.5, 143.4, 130.7, 121.9, 117.3, 95.9, 95.8, 55.7, 55.2, 50.5, 21.2, 14.0, 9.8; **IR (Neat):** ν_{max} 2959, 2928, 2864, 2840, 2249, 1590, 1485, 1458, 1354, 1200, 1153, 1091, 1043, 933, 863, 825, 700; **HRMS (ESI-TOF):** *m/z* $(M + H)^+$ calcd for $C_{16}H_{20}NO_3$ 258.1494; found: 258.1472.



Synthesis of 9a from 8a

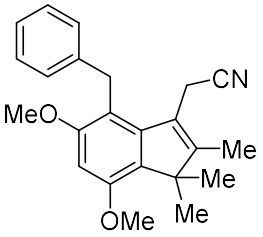
To a stirred solution of **8a** (100 mg, 0.389 mmol, 1 equiv) and benzaldehyde (82.5 mg, 0.778 mmol, 2.0 equiv) in dry CH_2Cl_2 (3.89 mL), BF_3 •OEt_2 (0.24 mL, 1.945 mmol, 5.0 equiv) was added at rt and stirred at the same temperature under an inert atmosphere. After completing the starting material, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by using

silica gel column chromatography (EtOAc/hexanes) to give the desired product **9a** (124 mg, 0.357 mmol) with 92% yield.

Synthesis of 9a from 7a

To a stirred solution of **7a** (60 mg, 0.22 mmol, 1 equiv) and benzaldehyde (58 mg, 0.54 mmol, 2.5 equiv) in dry CH_2Cl_2 (2.2 mL) was added BF_3•OEt_2 (0.21 mL, 1.6 mmol, 7.5 equiv) at rt and stirred at the same temperature under an inert atmosphere. After completing the starting material, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/hexanes) to give the desired product **9a**.

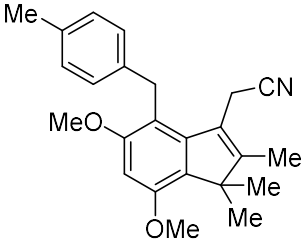
2-(4-Benzyl-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9a):



Yield: 66 mg (88%), crystalline white solid; m.p.: 140.5-143.5 °C; $\mathbf{R_f}$ = 0.5 (10% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.26–7.22 (m, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 2H), 6.40 (s, 1H), 4.34 (s, 2H), 3.91 (s, 3H), 3.80 (s, 3H), 3.30 (s, 2H), 1.86 (s, 3H), 1.29 (s, 6H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.6, 156.2, 154.2, 142.1, 131.4, 128.6, 127.6, 125.8, 123.1, 118.2, 112.7, 92.9, 56.4, 55.3, 49.5, 30.3, 21.3, 15.8, 9.9; **IR (Neat):** ν_{max} 2957, 2923, 2852, 2247, 1736, 1599, 1483, 1453, 1353, 1293, 1196, 1134, 1074, 1025, 947, 860, 700; **HRMS (ESI):** *m/z* $(M + Na)^+$ calcd for $C_{23}H_{25}NO_2Na$ 370.1783; found: 370.1758.

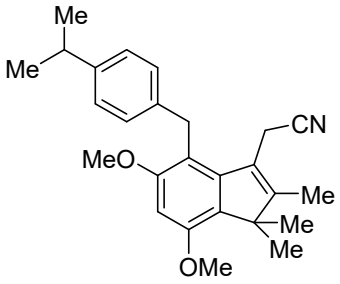
Compounds 9b to 9v were synthesized using the synthetic procedure for 9a from 7a.

2-(5,7-Dimethoxy-1,1,2-trimethyl-4-(4-methylbenzyl)-1*H*-inden-3-yl)acetonitrile(9b):



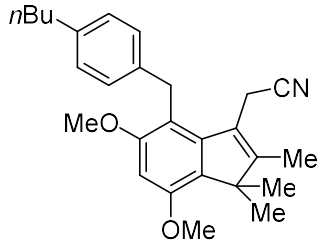
Yield: 63 mg (80%), yellowish oil, $\mathbf{R_f}$ = 0.4 (15% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.06 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 1H), 4.30 (s, 2H), 3.90 (s, 3H), 3.80 (s, 3H), 3.32 (s, 2H), 2.29 (s, 3H), 1.86 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.6, 156.1, 154.1, 142.0, 138.9, 135.2, 131.4, 129.3, 127.5, 123.2, 118.2, 112.9, 92.9, 56.4, 55.3, 49.5, 29.9, 21.4, 20.9, 15.8, 9.9; **IR (Neat):** ν_{max} 2958, 2924, 2853, 2247, 1683, 1626, 1597, 1456, 1353, 1293, 1285, 1215, 1175, 1074, 1025, 939, 790; **HRMS (ESI):** *m/z* $(M + H)^+$calcd for $C_{24}H_{28}NO_2$ 362.2120; found: 362.2103.

2-(4-(4-Isopropylbenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9c):



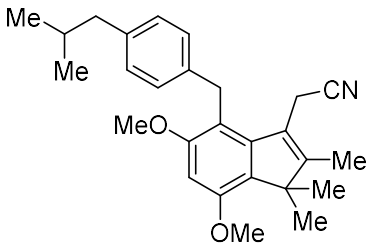
Yield: 59 mg (70%), yellowish oil, $\mathbf{R_f}$ = 0.5 (10% EtOAc/ hexane; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.11 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.41 (s, 1H), 4.31 (s, 3H), 3.91 (s, 3H), 3.80 (s, 2H), 3.33 (s, 3H), 2.90-2.81 (m, 1H), 1.87 (s, 3H), 1.29 (s, 6H), 1.23 (s, 3H), 1.21 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.6, 156.0, 154.1, 146.3, 142.0, 139.3, 131.4, 127.5, 126.6, 123.2, 118.2, 113.1, 92.9, 56.4, 55.3, 49.5, 33.7, 29.9, 24.1, 21.4, 15.8, 9.9; **IR (Neat):** ν_{max} 2958, 2927, 2868, 2248,1620, 1589, 1511, 1483, 1454, 1380, 1285, 1217, 1158, 1073, 1025, 932, 809, 757; **HRMS (ESI):** *m/z* $(M + Na)^+$ calcd for $C_{26}H_{31}NO_2Na$ 412.2252; found: 412.2273

2-(4-(4-Butylbenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile(9d):



Yield: 69 mg (79%), yellowish oil, $\mathbf{R_f}$= 0.5 (10% EtOAc/ hexane; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.06 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.41 (s, 1H), 4.30 (s, 2H), 3.91 (s, 3H), 3.80 (s, 3H), 3.32 (s, 2H), 2.59–2.52 (m, 2H), 1.86 (s, 3H), 1.61–1.52 (m, 2H), 1.38-1.31 (m, 2H), 1.29 (s, 6H), 0.92 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 158.6, 156.0, 154.1, 142.1, 140.3, 139.2, 131.4, 128.6, 127.4, 123.2, 118.2, 113.1, 92.9, 56.4, 55.3, 49.5, 35.2, 33.7, 29.9, 22.5, 21.4, 15.8, 14.0, 9.9; **IR (Neat):** ν_{max} 2957, 2923, 2827, 2246, 1738, 1672, 1594, 1454, 1351, 1290, 1205, 1130, 1081, 1025, 936, 811; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{27}H_{34}NO_2$ 404.2590; found: 404.2568.

2-(4-(4-Isobutylbenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9e):

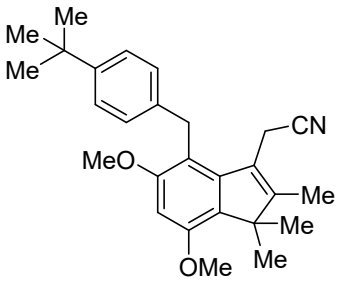


Yield: 67 mg (76%), yellowish oil, $\mathbf{R_f}$ = 0.5 (10% EtOAc/ hexane; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.01 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.40 (s, 1H), 4.30 (s, 2H), 3.90 (s, 3H), 3.80 (s, 3H), 3.31 (s, 2H), 2.40 (d, *J* = 7.2 Hz, 2H), 1.86 (s, 3H), 1.86–1.78 (m, 1H), 1.28 (s, 6H), 0.89 (s, 3H), 0.87 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.6, 156.1, 154.1, 142.1, 139.2, 139.1, 131.4, 129.4, 127.3, 123.2, 118.2, 113.1, 93.0, 56.5, 55.3, 49.5, 45.0, 30.2, 29.9, 22.4, 21.4, 15.7, 9.9; **IR (Neat):** ν_{max} 2956, 2923, 2851, 2247, 1596,

1509, 1457, 1353, 1285, 1264, 1217, 1196, 1174, 1096, 1074, 1025, 954, 932, 835, 809, 772; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{27}H_{34}NO_2$ 404.2590; found: 404.2570.

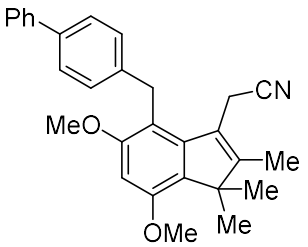
2-(4-(4-(Tert-butyl)benzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9f):

Yield: 60 mg (68%), colourless, $\mathbf{R_f}$= 0.5 (10% EtOAc/ hexane; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.40 (s, 1H), 4.30 (s, 2H), 3.90 (s, 3H), 3.80 (s, 3H), 3.33 (s, 2H), 1.86 (s, 3H), 1.29 (s, 6H), 1.28 (s, 9H); **^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$):** δ 158.6, 156.0, 154.1, 148.5, 142.0, 138.9, 131.4, 127.2, 125.5, 123.3, 118.2, 113.1, 93.0, 56.4, 55.3, 49.5, 34.3, 31.4, 29.8, 21.4, 15.8, 9.9; **IR (Neat):** ν_{max} 2926, 2924, 2857, 2246, 1723, 1673, 1595, 1453, 1355, 1286, 1205, 1129, 1081, 1025, 936, 814, 716; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{27}H_{34}NO_2$ 404.2590; found: 404.2570.

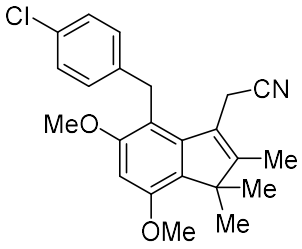


2-(4-([1,1'-Biphenyl]-4-ylmethyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9g):

Yield: 66 mg (71%), gummy, $\mathbf{R_f}$= 0.6 (10% EtOAc/ hexane; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.58–7.53 (m, 2H), 7.52–7.44 (m, 2H), 7.46–7.37 (m, 2H), 7.35–7.28 (m, 1H), 7.15 (d, *J*– 8.4 Hz, 2H), 6.43 (s, 1H), 4.39 (s, 2H), 3.92 (s, 3H), 3.83 (s, 3H), 3.36 (s, 2H), 1.88 (s, 3H), 1.31 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.6, 156.3, 154.2, 142.1, 141.2, 141.0, 138.8, 131.5, 128.7, 128.0, 127.4, 127.0, 126.9, 123.1, 118.2, 112.7, 92.9, 56.4, 55.3, 49.6, 30.0, 21.4, 15.9, 9.9; **IR (Neat):** ν_{max} 2958, 2926, 2853, 2247, 1677, 1599, 1486, 1454, 1353, 1293, 1238, 1196, 1176, 1134, 1074, 1024, 936, 864, 812, 758, 698; **HRMS (ESI):** *m/z* $(M + Na)^+$ calcd for $C_{29}H_{29}NO_2Na$ 446.2096; found: 446.2078.



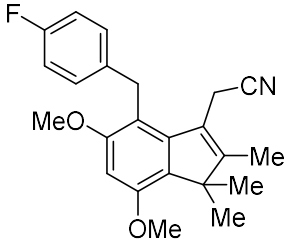
2-(4-(4-Chlorobenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9h):



Yield: 70 mg (84%), colourless oil, $\mathbf{R_f}$ = 0.5 (15% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.21 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.40 (s, 1H), 4.30 (s, 2H), 3.91 (s, 3H), 3.79 (s, 3H), 3.29 (s, 2H), 1.87 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.5, 156.6, 154.3, 141.9, 140.6, 131.5, 131.4, 128.9, 128.7, 122.9, 118.1, 112.2, 92.9, 56.4, 55.3,

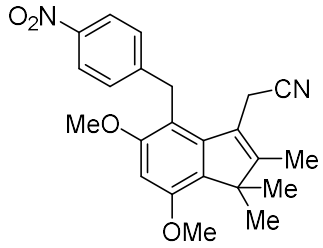
49.6, 29.8, 21.3, 15.8, 9.9; **IR (Neat):** ν_{max} 2958, 2925, 2853, 2247, 1591, 1486, 1453, 1352, 1284, 1284, 1195, 1175, 1133, 1091, 1072, 918, 863, 757, 716; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{23}H_{25}NO_2Cl$ 382.1574; found: 382.1547.

2-(4-(4-Fluorobenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9i):



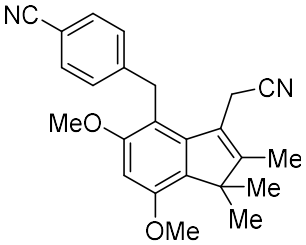
Yield: 65 mg (81%), gummy, $\mathbf{R_f}$ = 0.6 (15% EtOAc/ hexane); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.06–6.98 (m, 2H), 6.98–6.88 (m, 2H), 6.40 (s, 1H), 4.29 (s, 2H), 3.91 (s, 3H), 3.80 (s, 3H), 3.30 (s, 2H), 1.87 (s, 3H), 1.29 (s, 6H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 161.2 (d, *J* = 243.6 Hz), 158.5, 156.5, 154.3, 141.9, 137.6 (d, *J* = 2.5 Hz), 131.5, 128.9 (d, *J* = 7.7 Hz), 122.9, 118.1, 115.3 (d, *J* = 21.1 Hz), 112.6, 92.9, 56.4, 55.3, 49.6, 29.6, 21.3, 15.8, 9.9; **IR (Neat):** ν_{max} 2959, 2927, 2248, 1626, 1598, 1483, 1455, 1353, 1285, 1217, 1156, 1134, 1025, 973, 917, 813, 770; **HRMS (ESI):** *m/z* $(M + Na)^+$calcd for $C_{23}H_{24}NO_2FNa$ 388.1689; found: 388.1664.

2-(5,7-Dimethoxy-1,1,2-trimethyl-4-(4-nitrobenzyl)-1*H*-inden-3-yl)acetonitrile (9j):



Yield: 79 mg (92%), white foam, $\mathbf{R_f}$ = 0.5 (20% EtOAc/ hexane); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.41 (s, 1H), 4.42 (s, 2H), 3.92 (s, 3H), 3.79 (s, 3H), 3.27 (s, 2H), 1.88 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.5, 157.1, 154.6, 150.1, 146.4, 141.8, 131.5, 128.5, 123.8, 122.5, 117.8, 110.9, 92.8, 56.2, 55.3, 49.6, 30.7, 21.3, 15.9, 10.0; **IR (Neat):** ν_{max} 2959, 2925, 2853, 2247, 1597, 1518, 1485, 1455, 1343, 1293, 1238, 1217, 1196, 1134, 1109, 1072, 1023, 937, 918, 859, 758; **HRMS (ESI):** *m/z* $(M + Na)^+$ calcd for $C_{23}H_{25}N_2O_4Na$ 393.1814; found: 393.1793.

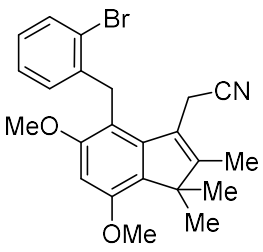
4-((3-(Cyanomethyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-4-yl)methyl)benzonitrile (9k):



Yield: 78 mg (96%), yellowish oil, $\mathbf{R_f}$ = 0.5 (25% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.40 (s, 1H), 4.38 (s, 2H), 3.91 (s, 3H), 3.78 (s, 3H), 3.26 (s, 2H), 1.88 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 158.5, 157.0, 154.6, 147.9, 141.9, 132.4, 131.5, 128.5, 122.5, 119.1, 117.8, 111.0, 109.7, 92.8, 56.2, 55.3, 49.6, 30.8, 21.3, 15.9, 10.0;

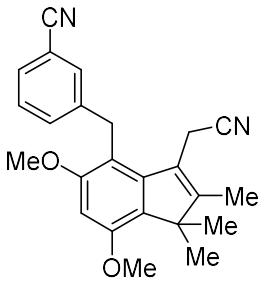
IR (Neat): ν_{max} 2957, 2924, 2853, 2225, 1602, 1589, 1482, 1454, 1352, 1284, 1217, 1195, 1094, 1022, 935, 809, 772; **HRMS (ESI):** m/z (M + H)+ calcd for $C_{24}H_{25}O_2N_2$ 373.1911; found: 373.1902.

2-(4-(2-Bromobenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl) acetonitrile (9l):



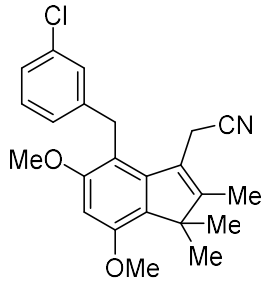
Yield: 83 mg (89%), yellowish oil, $\mathbf{R_f}$ = 0.6 (15% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.10 (td, *J* = 7.8, 1.4 Hz, 1H), 7.04 (td, *J* = 7.8, 1.8 Hz, 1H), 6.63 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.41 (s, 1H), 4.32 (s, 2H), 3.92 (s, 3H), 3.79 (s, 3H), 3.20 (s, 2H), 1.87 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 158.7, 156.6, 154.4, 141.9, 140.9, 132.6, 131.6, 129.1, 127.6, 127.5, 124.5, 122.9, 117.7, 111.6, 92.9, 56.4, 55.3, 49.6, 31.3, 21.3, 15.5, 9.9; **IR (Neat):** ν_{max} 2958, 2928, 2849, 2247, 1598, 1462, 1451, 1353, 1321, 1294, 1218, 1180, 1136, 1073, 1021, 939, 868, 749; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{23}H_{25}NO_2Br$ 426.1069; found: 426.1040.

3-((3-(Cyanomethyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-4-yl)methyl)benzonitrile (9m):



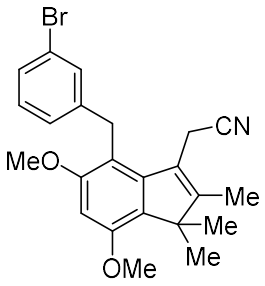
Yield: 75 mg (92%), yellowish oil, $\mathbf{R_f}$ = 0.4 (20% EtOAc/ hexane); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.49–7.42 (m, 1H), 7.42-7.38 (m, 1H), 7.38–7.32 (m, 1H), 7.26–7.24 (m, 1H), 6.40 (s, 1H), 4.34 (s, 2H), 3.92 (s, 3H), 3.79 (s, 3H), 3.27 (s, 2H), 1.89 (s, 3H), 1.30 (s, 6H); **^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):** δ 158.5, 157.0, 154.6, 143.7, 141.8, 132.4, 131.5, 131.2, 129.7, 129.3, 122.5, 119.2, 117.8, 112.6, 110.9, 92.9, 56.2, 55.3, 49.6, 30.2, 21.3, 15.9, 10.0; **IR (Neat):** ν_{max} 2959, 2928, 2841, 2228, 1625, 1598, 1482, 1454, 1353, 1285, 1217, 1196, 1134, 1073, 1024, 918, 855, 784, 687; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{24}H_{25}O_2N_2$ 373.1911; found: 373.1903.

2-(4-(3-Chlorobenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9n):



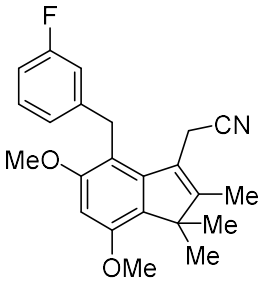
Yield: 69 mg (83%), Yellowish oil, $\mathbf{R_f}$ = 0.5 (20% EtOAc/ hexane); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.15–7.09 (m, 1H), 7.05 (td, *J* = 7.9, 1.3 Hz, 1H), 6.68–6.61 (m, 1H), 6.41 (s, 1H), 4.34 (s, 2H), 3.91 (s, 3H), 3.79 (s, 3H), 3.21 (s, 2H), 1.87 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.7, 156.6, 154.4, 142.0, 139.2, 133.8, 131.6, 129.3, 128.9, 127.2, 126.9, 122.9, 117.8, 111.4, 92.9, 56.4, 55.3, 49.6, 28.4, 21.3, 15.4, 9.9; **IR (Neat):** ν_{max} 2958, 2925, 2853, 2247, 1598, 1590, 1468, 1451, 1353, 1294, 1197, 1122, 1074, 1048, 1048, 1025, 952, 868, 751; **HRMS (ESI):** *m/z* $(M + Na)^+$ calcd for $C_{23}H_{24}NO_2ClNa$ 404.1393; found: 404.1371.

2-(4-(3-Bromobenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9o):



Yield: 80 mg (86%), yellowish oil, $\mathbf{R_f}$ = 0.6 (20% EtOAc/ hexane); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.30–7.27 (m, 1H), 7.19 (s, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.03–6.99 (m, 1H), 6.40 (s, 1H), 4.30 (s, 2H), 3.91 (s, 3H), 3.79 (s, 3H), 3.29 (s, 2H), 1.87 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):** δ 158.5, 156.6, 154.4, 144.6, 141.9, 131.5, 130.6, 130.1, 129.0, 126.3, 122.9, 122.8, 118.0, 111.7, 92.9, 56.3, 55.3, 49.6, 30.2, 21.3, 15.9, 9.9; **IR (Neat):** ν_{max} 2959, 2922, 2851, 2248, 1698, 1591, 1571, 1466, 1435, 1382, 1353, 1293, 1216, 1190, 1122, 1065, 1025, 944, 877, 853, 705, 672; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{23}H_{25}NO_2Br$ 426.1063; found: 426.1071.

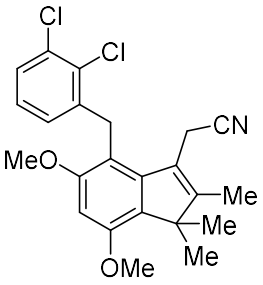
2-(4-(3-Fluorobenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9p):



Yield: 58 mg (73%), yellowish oil, $\mathbf{R_f}$ = 0.4 (20% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.25–7.18 (m, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.86–6.81 (m, 1H), 6.73–6.67 (m, 1H), 6.40 (s, 1H), 4.33 (s, 2H), 3.91 (s, 3H), 3.80 (s, 3H), 3.29 (s, 2H), 1.87 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 163.2 (d, *J* = 245.5 Hz), 158.5, 156.5, 154.4, 144.9 (d, *J* = 6.8 Hz), 141.9, 131.5, 129.9 (d, *J* = 8.3 Hz), 123.3, 122.9, 118.0, 114.5 (d, *J* = 21.5 Hz), 112.7 (d, *J* = 21.4 Hz), 111.9, 92.9, 56.3, 55.3, 49.6, 30.1, 21.3, 15.8, 9.9; **IR (Neat):** ν_{max} 2960, 2926, 2851, 2248, 1613, 1588, 1485, 1453, 1438, 1353, 1294, 1217, 1179, 1137, 1073, 1025, 946, 810, 742; **HRMS (ESI):** *m/z* $(M + Na)^+$calcd for $C_{23}H_{24}NO_2FNa$ 388.1686; found: 388.1661.

2-(4-(2,3-Dichlorobenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9q):

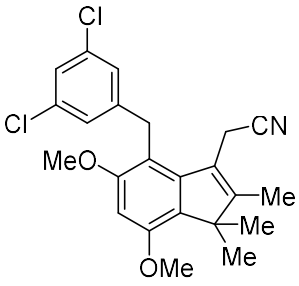
Yield: 77 mg (85%), Off white solid, m.p.: 189.5-192.5 °C; $\mathbf{R_f}$ = 0.5 (15% EtOAc/ hexane);



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.28 (m, 1H), 6.99 (t, *J* = 7.9 Hz, 1H), 6.57–6.55 (m, 1H), 6.41 (s, 1H), 4.36 (s, 2H), 3.92 (s, 3H), 3.78 (s, 3H), 3.20 (s, 2H), 1.88 (s, 3H), 1.30 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.6, 156.8, 154.5, 142.0, 141.7, 133.0, 131.9, 131.6, 128.0, 127.2, 127.1, 122.8, 117.6, 110.9, 92.8, 56.3, 55.3, 49.6, 29.5, 21.3, 15.6, 9.9; **IR (Neat):** ν_{max} 2959, 2921, 2851, 2248, 1625, 1588, 1486, 1453, 1418, 1353, 1294, 1240, 1217, 1197, 1174, 1154, 1123, 1096, 1073, 1024, 943, 874, 756, 738, 720, 667; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{23}H_{24}NO_2Cl_2$ 416.1184; found: 416.1158.

2-(4-(3,5-Dichlorobenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9r):

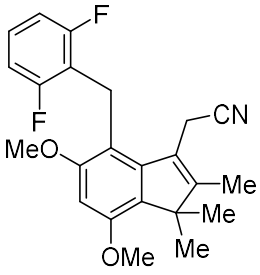
Yield: 78 mg (86%), yellowish oil, $\mathbf{R_f}$ = 0.4 (10% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):**



δ 7.16 (t, *J* = 1.9 Hz, 1H), 6.95–6.92 (m, 2H), 6.39 (s, 1H), 4.27 (s, 2H), 3.91 (s, 3H), 3.80 (s, 3H), 3.30 (s, 2H), 1.89 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.5, 156.9, 154.6, 145.7, 141.9, 135.0, 131.5, 126.2, 122.6, 117.9, 110.8, 92.8, 56.2, 55.3, 49.6, 30.1, 21.3, 15.9, 10.0; **IR (Neat):** ν_{max} 2958, 2923, 2853, 2248, 1565, 1454, 1428, 1353, 1293, 1267, 1216, 1197, 1135, 1123, 1097, 1074, 944, 849, 798; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{23}H_{24}NO_2Cl_2$ 416.1184; found: 416.1157.

2-(4-(2,6-Difluorobenzyl)-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetonitrile (9s):

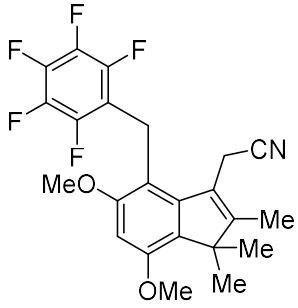
Yield: 52 mg (62%), yellowish white solid, m.p.: 160.5-163.5 °C; $\mathbf{R_f}$ = 0.4 (10% EtOAc/ hexane);



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.03 (m, 1H), 6.77 (t, *J* = 8.2 Hz, 2H), 6.27 (s, 1H), 4.20 (s, 2H), 3.84 (s, 3H), 3.77 (s, 2H), 3.69 (s, 3H), 1.94 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 162.7 (d, *J* = 8.2 Hz), 160.8 (d, *J* = 8.7 Hz), 158.7, 156.1, 154.1, 141.1, 130.9, 127.1 (t, *J* = 10.4 Hz), 123.3, 118.0, 112.6, 111.1 (d, *J* = 6.3 Hz), 111.0 (d, *J* = 6.2 Hz), 92.8, 55.9, 55.2, 49.3, 21.4, 20.2, 16.6, 10.0; **IR (Neat):** ν_{max} 2957, 2922, 2852, 2248, 1714, 1678, 1588, 1466, 1437, 1354, 1286, 1216, 1135, 1097, 1072, 1026, 1001, 806, 777; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{23}H_{24}NO_2F_2$ 384.1775; found: 384.1757.

2-(5,7-Dimethoxy-1,1,2-trimethyl-4-((perfluorophenyl)methyl)-1*H*-inden-3-yl)acetonitrile (9t):

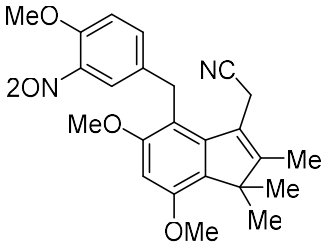
Yield: 56 mg (58%), yellowish solid, m.p.: 150.5-153.5 °C; $\mathbf{R}_f$ = 0.5 (10% EtOAc/ hexane);



^{1}H NMR (300 MHz, $CDCl_3$): δ 6.27 (s, 1H), 4.22 (s, 2H), 3.86 (s, 3H), 3.75 (s, 2H), 3.73 (s, 3H), 1.96 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.5, 156.9, 154.5, 146.7 (m), 144.2 (m), 140.9, 140.6-138.3 (m), 136.1 (m), 134.0 (m), 131.1, 122.7, 117.8, 114.8 (m), 110.6, 92.5, 55.7, 55.2, 49.4, 21.3, 20.4, 16.8, 10.1. **IR (Neat):** ν_{max} 2960, 2923, 2850, 2249, 1684, 1599, 1590, 1519, 1499, 1455, 1437, 1354, 1294, 1285, 1217, 1200, 1117, 1098, 1072, 1025, 996, 954, 809, 756; **HRMS (ESI):** *m/z* calcd for $C_{23}H_{21}O_2NF_5$ $(M + H)^+$: 438.1487, found: 438.1478.

2-(5,7-Dimethoxy-4-(4-methoxy-3-nitrobenzyl)-1,1,2-trimethyl-1*H*-inden-3yl)acetonitrile (9u):

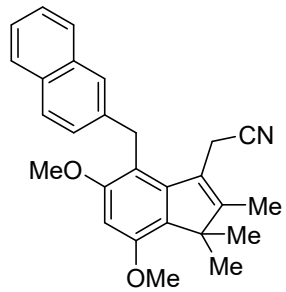
Yield: 82 mg (88%), White solid, m.p.: 173.5-177.5 °C; $\mathbf{R}_f$ = 0.5 (20% EtOAc/ hexane); **^{1}H**



NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 2.2 Hz, 1H), 7.30 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.39 (s, 1H), 4.28 (s, 2H), 3.91 (s, 6H), 3.79 (s, 3H), 3.32 (s, 2H), 1.89 (s, 3H), 1.29 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.5, 156.9, 154.5, 151.1, 141.8, 139.8, 134.6, 133.3, 131.5, 124.5, 122.6, 117.9, 113.7, 111.3, 92.9, 56.6, 56.2, 55.3, 49.6, 29.3, 21.3, 15.9, 10.0; **IR (Neat):** ν_{max} 2956, 2925, 2852, 2247, 1598, 1529, 1457, 1438, 1352, 1279, 1217, 1197, 1180, 1134, 1072, 1022, 942, 858, 809, 758, 677; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{24}H_{27}NO_5$ 423.1920; found: 423.1901.

2-(5,7-Dimethoxy-1,1,2-trimethyl-4-(naphthalen-2-ylmethyl)-1*H*-inden-3-yl)acetonitrile

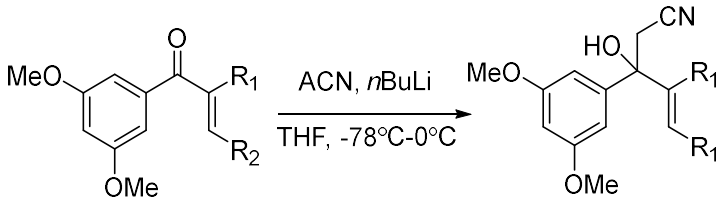
(9v): Yield: 64 mg (73%), gummy, $\mathbf{R}_f$ = 0.5 (10% EtOAc/ hexane); **^{1}H NMR (400 MHz,**



$CDCl_3$): δ 8.36 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.67–7.61 (m, 1H), 7.59–7.53 (m, 1H), 7.29–7.22 (m, 1H), 6.73 (dd, *J* = 7.1, 0.9 Hz, 1H), 6.46 (s, 1H), 4.75 (s, 2H), 3.94 (s, 3H), 3.77 (s, 3H), 3.06 (s, 2H), 1.84 (s, 3H), 1.33 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.7, 156.3, 154.3, 142.4, 137.6, 133.7, 131.8, 131.6, 128.7, 126.6, 126.4, 125.8, 125.7,

124.4, 123.4, 123.2, 118.2, 111.9, 93.0, 56.4, 55.3, 49.6, 27.4, 21.4, 15.3, 9.9; **IR (Neat):** ν_{max} 2957, 2922, 2855, 2246, 1731, 1593, 1453, 1351, 1290, 1230, 1202, 1132, 1080, 1024, 943, 788, 761; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{27}H_{28}NO_2$ 398.2120; found: 398.2101.

General method for preparation of β-hydroxy nitrile substrate (7b-7f):

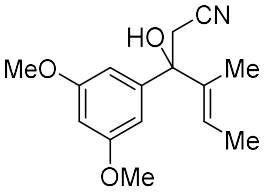


7b-7f

Place a 50 mL vacuum-dried round-bottom flask containing acetonitrile (2.0 equiv) and THF in an ice bath, cool to -78°C, and add n-BuLi (1.6 M in THF, 1.5 equiv). The pink-coloured solution is stirred for 30 minutes at the same temperature. Then, aryl vinyl ketone (1.0 equiv) was cannulated to the reaction mixture in dry THF, and the reaction was monitored by TLC. After the reaction was completed, it was quenched with a saturated NH_4Cl solution. The reaction mixture was extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude product was purified by flash chromatography using 20% EtOAc in hexane as the eluent, yielding the desired products (**7b-7f**).

(E)-3-(3,5-Dimethoxyphenyl)-3-hydroxy-4-methylhex-4-enenitrile (7b):

Yield: 0.54 g (91%), gummy, $\mathbf{R_f}$ = 0.5 (30 % EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):**



δ 6.55 (d, *J* = 2.2 Hz, 2H), 6.39 (t, *J* = 2.2 Hz, 1H), 5.84–5.77 (m, 1H), 3.79 (s, 6H), 2.97 (ABq, *J* = 16.5 Hz, 1H), 2.38 (brs, 1H), 1.74–1.70 (m, 3H), 1.53–1.52 (m, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 160.9, 145.1, 136.8, 121.5, 117.3, 103.8, 99.2, 77.6, 55.4, 30.9, 13.5, 12.6; **IR (Neat):** ν_{max} 3456, 2956, 2921, 2851, 2337, 1602, 1588, 1484, 1436, 1377, 1272, 1196, 1149, 1093, 1077, 1025, 937, 809, 757, 730, 698; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{15}H_{20}NO_3$ 262.1438; found: 262.1436.

(*E*)-3-(3,5-Dimethoxyphenyl)-3-hydroxy-4-methylhept-4-enenitrile (7c):

Yield: 0.53 g (90%), colourless oil, $\mathbf{R_f}$ = 0.4 (30 % EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.55 (d, *J* = 2.2 Hz, 2H), 6.39 (t, *J* = 2.2 Hz, 1H), 5.71 (qt, *J* = 7.2, 1.2 Hz, 1H), 3.79 (s, 6H), 2.97 (ABq, *J* = 16.5 Hz, 1H), 2.44 (brs, 1H), 2.13 (p, *J* = 7.2 Hz, 2H), 1.52 (d, *J* = 1.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 160.9, 145.1, 135.4, 129.0, 117.4, 103.8, 99.4, 77.5, 55.4, 31.0, 21.3, 13.8, 12.8; **IR (Neat):** ν_{max} 3461, 2960, 2871, 2839, 2251, 1593, 1457, 1424, 1378, 1290, 1203, 1152, 1057, 1042, 923, 840, 772, 699; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{16}H_{22}NO_3$ 276.1618; found: 276.1614.

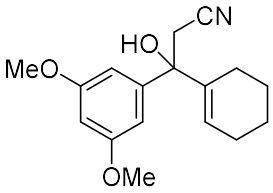
(*E*)-3-(3,5-Dimethoxyphenyl)-4-ethyl-3-hydroxyoct-4-enenitrile(7d):

Yield: 0.440 g (77%), yellowish oil, $\mathbf{R_f}$ = 0.5 (30 % EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.56 (d, *J* = 2.2 Hz, 2H), 6.38 (t, *J* = 2.2 Hz, 1H), 5.65 (t, *J* = 7.2 Hz, 1H), 3.78 (s, 6H), 2.97 (ABq, *J* = 16.1 Hz, 1H), 2.33 (brs, 1H), 2.13 (q, *J* = 7.2 Hz, 2H), 2.09–1.98 (m, 1H), 1.93–1.83 (m, 1H), 1.54–1.44 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 160.8, 145.3, 141.9, 127.9, 117.4, 103.9, 99.4, 78.1, 55.4, 31.5, 29.9, 22.8, 21.0, 14.9, 13.9; **IR (Neat):** ν_{max} 3462, 2962, 2872, 2854, 2257, 1596, 1460, 1425, 1338, 1290, 1204, 1154, 1056, 993, 924, 842, 770, 618, 581, 568, 555; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{18}H_{26}NO_3$ 304.1907; found: 304.1899.

(E)-3-(3,5-dimethoxyphenyl)-3-hydroxy-4-methyl-5-phenylpent-4-enenitrile (7e):

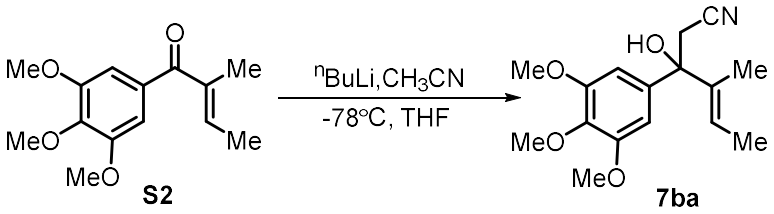
Yield: 0.61g (88%), colourless oil, $\mathbf{R_f}$ = 0.5 (25 % EtOAc/hexane); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.39–7.21 (m, 5H), 6.83 (s, 1H), 6.62 (d, *J* = 2.2 Hz, 2H), 6.41 (t, *J* = 2.2 Hz, 1H), 3.78 (s, 6H), δ 3.14 (d, *J* = 16.5 Hz, 1H), 3.06 (d, *J* = 16.5 Hz, 1H), 2.81 (brs, 1H), 1.72 (d, *J* = 1.2 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 161.0, 144.8, 138.8, 136.9, 129.2, 128.3, 127.1, 126.7, 117.3, 103.9, 99.6, 77.8, 55.5, 30.8, 14.7; **IR (Neat):** ν_{max} 3452, 2958, 2925, 2583, 2253, 1594, 1457, 1425, 1337, 1291, 1203, 1153, 1058, 1043, 922, 840, 753, 697; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{20}H_{22}NO_3$ 324.1613; found: 324.1609

3-(Cyclohex-1-en-1-yl)-3-(3,5-dimethoxyphenyl)-3-hydroxypropanenitrile (7f):



Yield: 0.46 g (80%), colourless oil, $\mathbf{R_f}$ = 0.5 (25 % EtOAc/ hexane);**^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.56 (d, *J* = 2.2 Hz, 2H), 6.39 (t, *J* = 2.2 Hz, 1H), 5.98–5.94 (m, 1H), 3.79 (s, 6H), δ 2.95 (ABq, *J* = 16.5 Hz, 1H), 2.46 (brs, 1H), 2.24–2.10 (m, 2H), 2.02–1.89 (m, 1H), 1.78–1.68 (m, 1H), 1.67–1.49 (m, 4H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 160.9, 145.3, 138.8, 124.2, 117.5, 103.8, 99.3, 77.2, 55.4, 30.9, 25.2, 24.3, 22.6, 21.9; **IR (Neat)**: ν_{max} 3469, 2929, 2855, 2838, 2255, 1595, 1458, 1425, 1337, 1291, 1203, 1153, 1056, 1022, 921, 839, 771, 698; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{17}H_{22}NO_3$ 288.1613; found: 288.1608.

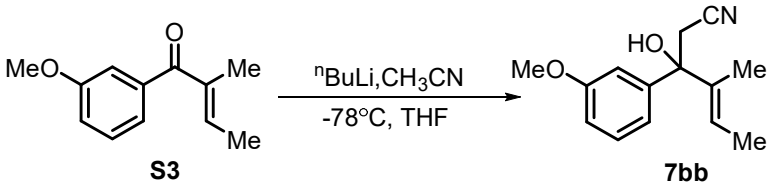
(*E*)-3-Hydroxy-4-methyl-3-(3,4,5-trimethoxyphenyl)hex-4-enenitrile (7ba):



Take a 50 mL vacuum-dried round-bottom flask with acetonitrile (0.419 mL, 2.0 mmol, 2.0 equiv) with THF (3 mL), cool to -78°C, and add ^{n}BuLi (4 mL, 6.0 mmol, 1.5 equiv), a pink colour solution is stirred for half an hour at the same temperature. Then, aryvinyl ketone **S2**[20h] (1 g, 4.0 mmol, 1.0 equiv) was cannulated into the reaction mixture in dry THF (8 mL), and the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with saturated NH_4Cl solution. The reaction mixture was extracted with EtOAc (100 mL), washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude product was purified by flash chromatography to furnish the desired product **7ba**.

Yield: 980 mg (84%), yellowish oil, $\mathbf{R_f}$ = 0.4 (30% EtOAc/ hexane);**^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.61 (s, 2H), 5.84– 5.74 (m, 1H), 3.85 (s, 6H), 3.84 (s, 3H), 3.00 AB q, *J* = 16.5 Hz, 2H), 2.38 (br, 1H), 1.74 (dd, *J* = 6.7, 0.9 Hz, 3H), 1.54 (d, *J* = 0.9 Hz, 3H); **^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)** δ 153.21, 138.13, 137.61, 136.99, 121.77, 117.41, 102.82, 77.77, 60.86, 56.26, 31.20, 13.66, 12.79; **IR (Neat): ν_{max}** 3457, 2959, 2922, 2850, 2253, 1590, 1504, 1504, 1455, 1380, 1322, 1234, 1184, 1126, 1061, 1003, 842, 811, 770, 732; **HRMS (ESI-TOF):** *m/z* $(M + H)^+$ calcd for $C_{16}H_{22}NO_4$ 292.1548; found: 292.1540.

(*E*)-3-Hydroxy-3-(3-methoxyphenyl)-4-methylhex-4-enenitrile (7bb):

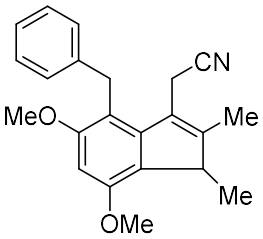


Take a 50 mL vacuum-dried round-bottom flask with acetonitrile (0.548 mL, 2.0 mmol, 2.0 equiv) with THF (3 mL), cool to -78°C, and add ^{n}BuLi (5.23 mL, 7.85 mmol, 1.5 equiv), a pink colour solution is stirred for half an hour at the same temperature. Then, aryvinyl ketone **S3** (1g, 5.2 mmol, 1.0 equiv) was cannulated into the reaction mixture in dry THF (1 mL), and the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with saturated NH_4Cl solution. The reaction mixture was extracted with EtOAc (100 mL), washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude product was purified by flash chromatography to furnish the desired product **7bb**.

Yield:1.070 g (88%), coloureless oil, $\mathbf{R_f}$ = 0.5 (25% EtOAc/ hexane); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 – 7.25 (m, 1H), 7.02 – 6.92 (m, 1H), 6.83 (ddd, *J*, 1H), 5.85– 5.79 (m, 1H), 3.81 (s, 3H), 3.02 (AB q, *J* = 16.5 Hz, 2H), 2.41 (br, 1H), 1.72 (dd, *J* = 6.7, 1.0 Hz, 3H), 1.56 – 1.47 (m, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 159.8, 144.2, 136.9, 129.6, 121.6, 117.6, 117.4, 112.9, 111.7, 77.6, 55.3, 30.9, 13.6, 12.7; **IR (Neat): ν_{max}** 3456, 2953, 2924, 2852, 2255, 1601, 1584, 1487, 1432, 1317, 1250, 1148, 1040, 996, 783, 699; **HRMS (ESI-TOF):** *m/z* $(M + H)^+$ calcd for $C_{14}H_{18}NO_2$ 232.1335; found: 232.1329.

Compounds 9ba to 9fa were synthesized using the synthetic procedure for 9a from 7a.

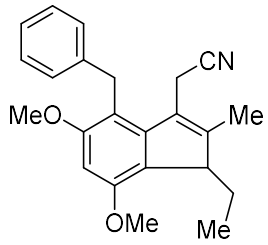
2-(4-benzyl-5,7-dimethoxy-1,2-dimethyl-1*H*-inden-3-yl) acetonitrile (9ba)



Yield: 67 mg (87%), colourless oil, $\mathbf{R_f}$ = 0.5 (15 % EtOAc/hexane);**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.27–7.21 (m, 2H), 7.15 (t, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.42 (s, 1H), δ 4.37 (d, *J* = 17.3 Hz, 1H), 4.32 (d, *J* = 17.3 Hz, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.34–3.26 (m, 3H), 1.98 (s, 3H), 1.31 (d, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 158.7, 154.1, 151.6, 143.3, 141.9, 128.5, 127.5, 127.1, 125.7, 124.9, 118.0, 112.8, 92.8, 56.4, 55.3, 45.2, 30.1, 15.6, 14.4, 12.4; **IR (Neat):** ν_{max} 2996, 2961, 2923, 2853, 2255, 1594, 1457, 1425, 1380, 1291, 1203, 1058, 1042, 923, 842, 759, 700; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{22}H_{24}NO_2$ 334.1799; found: 334.1807.

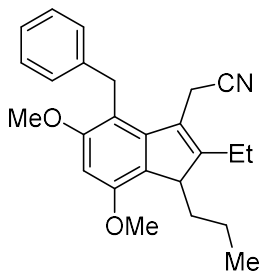
2-(4-Benzyl-1-ethyl-5,7-dimethoxy-2-methyl-1*H*-inden-3-yl) acetonitrile (9ca):

Yield: 65 mg (86%), Colourless oil, $\mathbf{R_f}$ = 0.6 (15 % EtOAc/hexane); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.25–7.20 (m, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.06–7.02 (m, 2H), 6.41 (s, 1H), 4.37 (d, *J* = 17.3 Hz, 1H), 4.33 (d, *J* = 17.3 Hz, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.44 (t, *J* = 4.2 Hz, 1H), 3.32 (s, 2H), 2.43–2.31 (m, 1H), 1.95 (s, 3H), 1.89–1.80 (m, 1H), 0.34 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.7, 154.1, 149.5, 144.4, 142.1, 128.6, 127.5, 126.6, 125.8, 124.6, 118.1, 112.7, 92.7, 56.5, 55.4, 50.5, 30.1, 20.4, 15.6, 12.6, 7.3; **IR (Neat):** ν_{max} 2957, 2923, 2852, 2247, 1602, 1589, 1462, 1457, 1339, 1311, 1272, 1197, 1093, 1078, 1026, 757, 732, 699, 600; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{23}H_{25}NO_2$ 370.1778; found: 370.1782



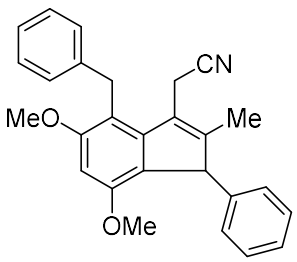
2-(4-Benzyl-2-ethyl-5,7-dimethoxy-1-propyl-1*H*-inden-3-yl)acetonitrile (9da):

Yield: 62 mg (83%), Colourless oil, $\mathbf{R_f}$ = 0.5 (25 % EtOAc/hexane); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.26–7.20 (m, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 6.9 Hz, 2H), 6.42 (s, 1H), 4.35 (s, 2H), 3.90 (s, 3H), 3.80 (s, 3H), 3.59 (t, *J* = 4.3 Hz, 1H), 3.32 (s, 2H), 2.51–2.37 (m, 1H), 2.36–2.17 (m, 2H), 1.82–1.67 (m, 1H), 1.12 (t, *J* = 7.6 Hz, 3H), 0.79–0.69 (m, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.7, 155.7, 154.2, 144.2, 142.1, 128.6, 127.6, 125.8, 125.7, 125.4, 118.3, 112.9, 92.8, 56.5, 55.4, 47.4, 30.2, 29.9, 20.0, 16.6, 15.4, 14.5, 14.0; **IR (Neat)**: ν_{max} 2999, 2926, 2861, 2250, 1599, 1481, 1461, 1363, 1307, 1211, 1109, 1033, 937, 812, 767, 733, 639, 609; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{25}H_{30}NO_2$ 376.2271; found: 376.2264.



2-(4-benzyl-5,7-dimethoxy-2-methyl-1-phenyl-1*H*-inden-3-yl) acetonitrile (9ea):

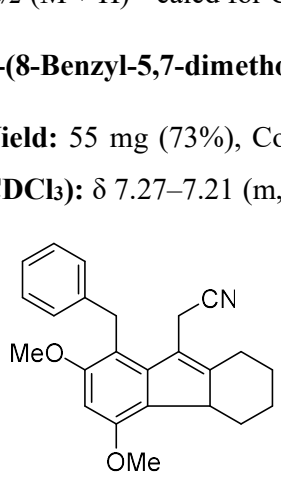
Yield: 59 mg (80%), Colourless oil, $\mathbf{R_f}$ = 0.5 (10 % EtOAc/hexane); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.28–7.24 (m, 1H), 7.24–7.20 (m, 2H), 7.20–7.16 (m, 2H), 7.16–7.13 (m, 2H), 7.09 (t, *J* = 7.0 Hz, 1H), 7.02–6.97 (m, 2H), 6.76 (s, 1H), 4.42 (s, 1H), 4.03 (d, *J* = 14.7 Hz, 1H), 3.93 (d, *J* = 14.7 Hz, 1H), 3.87 (s, 3H), 3.56 (s, 2H), 3.23 (s, 3H), 1.85 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 158.8, 154.9, 148.1, 143.8, 141.7, 138.7, 129.7, 128.7, 128.3, 128.0, 127.0, 125.3, 124.9, 119.8, 117.0, 97.6, 60.1, 57.8, 56.0, 29.3, 14.1, 12.6; **IR (Neat):** ν_{max} 3061, 2999, 2956, 2922, 2552,



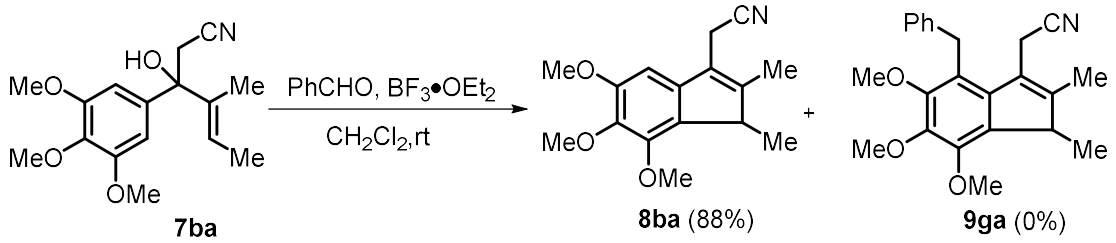
2250, 1493, 1462, 1416, 1359, 1272, 1210, 1157, 1108, 1049, 913, 752, 699; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{27}H_{26}NO_2$ 396.1979; found: 396.1975.

2-(8-Benzyl-5,7-dimethoxy-2,3,4,4a-tetrahydro-1*H*-fluoren-9-yl) acetonitrile (9fa).

Yield: 55 mg (73%), Colourless oil, $\mathbf{R_f}$ = 0.6 (10 % EtOAc/hexane); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.27–7.21 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 6.42 (s, 1H), 4.37 (ABq, *J* = 17.2 Hz, 2H), 3.89 (s, 3H), 3.81 (s, 3H), 3.36 (d, *J* = 17.8 Hz, 1H), 3.32 (d, *J* = 17.8 Hz, 1H), 3.12 (dd, *J* = 12.2, 5.2 Hz, 1H), 2.87–2.75 (m, 1H), 2.71 (d, *J* = 13.5 Hz, 1H), 2.22 (td, *J* = 13.5, 5.2 Hz, 1H), 2.07–1.94 (m, 1H), 1.82 (d, *J* = 13.5 Hz, 1H), 1.55–1.50 (m, 1H), 1.25–1.16 (m, 1H), 0.90–0.77 (m, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 158.7, 154.4, 153.8, 143.8, 142.1, 128.6, 127.6, 126.2, 125.8, 121.8, 118.4, 113.2, 92.7, 56.5, 55.4, 48.1, 31.8, 30.3, 27.9, 26.8, 25.3, 15.2; **IR (Neat):** ν_{max} 2997, 2925, 2852, 2349, 1588, 1454, 1437, 1315, 1299, 1216, 1157, 1061, 1035, 950, 754, 730, 698; **HRMS (ESI)** *m/z*: $(M + H)^+$ calcd for $C_{24}H_{26}NO_2$ 360.1983; found: 360.1979.

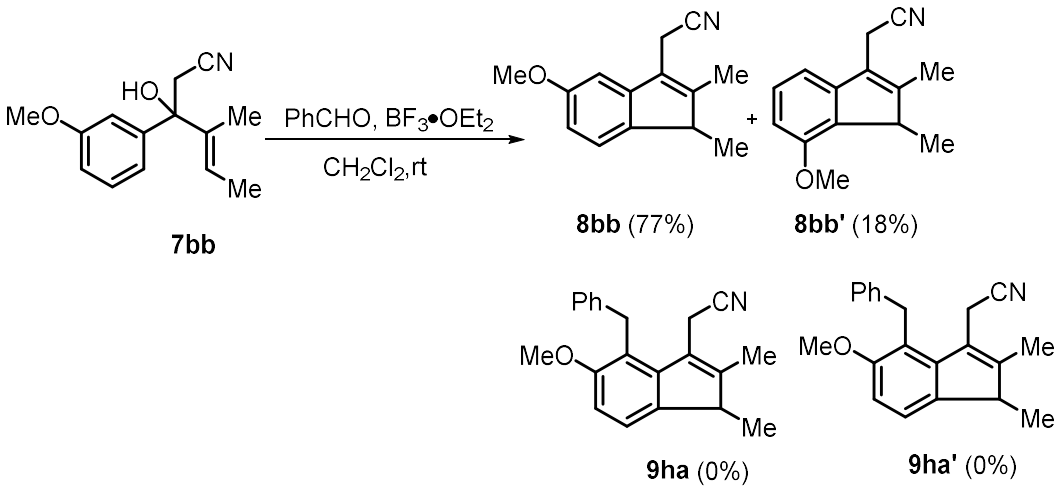


2-(5,6,7-Trimethoxy-1,2-dimethyl-1*H*-inden-3-yl)acetonitrile (8ba):



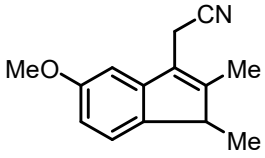
To a stirred solution of **7ba** (100 mg, 0.34 mmol, 1 equiv) and benzaldehyde (92 mg, 0.86 mmol, 2.5 equiv) in dry CH_2Cl_2 (3.4 mL) was added BF_3•OEt_2 (0.314 mL, 2.55 mmol, 7.5 equiv) at rt and stirred at the same temperature under an inert atmosphere. After completing the starting material, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/hexanes) to obtain isolated **8ba** (82 mg, 88%) as a colorless oil. $\mathbf{R_f}$ = 0.5 (20% EtOAc/ hexane); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.66 (s, 1H), 3.97 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H), 3.49 (s, 2H), 3.36 (q, *J* = 7.4 Hz, 1H), 2.03 (s, 3H), 1.33 (d, *J* = 7.5 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 153.5, 149.9, 148.6, 140.0, 138.5, 131.1, 123.5, 117.2, 98.2, 61.1, 60.7, 56.4, 46.3, 14.6, 14.0, 12.3; **IR (Neat):** $\mathbf{\nu_{max}}$ 2963, 2933, 2851, 2249, 1604, 1581, 1469, 1434, 1367, 1288, 1247, 1197, 1117, 1089, 1035, 1009, 940, 921, 863, 659.

Synthesis of 8bb and 8bb' from 7bb:

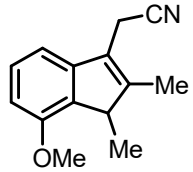


To a stirred solution of **7bb** (100 mg, 0.43 mmol, 1 equiv) and benzaldehyde (114 mg, 1.06 mmol, 2.5 equiv) in dry CH_2Cl_2 (4.3 mL) was added BF_3•OEt_2 (0.4 mL, 3.25 mmol, 7.5 equiv) at rt and stirred at the same temperature under an inert atmosphere. After completing the starting material, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/hexanes) to obtain isolated **8bb** (71 mg, 77%) and **8bb'**(16 mg, 18%) as a colorless oils**.**

2-(5-Methoxy-1,2-dimethyl-1*H*-inden-3-yl)acetonitrile (8bb): R_f = 0.5 (20% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (d, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 2.3 Hz, 1H), 6.75 (dd, *J* = 8.1, 2.3 Hz, 1H), 3.85 (s, 3H), 3.51 (s, 2H), 3.23 (q, *J* = 7.5 Hz, 1H), 2.06 (s, 3H), 1.27 (d, *J* = 7.5 Hz, 3H);**^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 159.2, 149.6, 144.0, 139.9, 124.0, 123.1, 117.1, 110.3, 104.2, 55.6, 46.7, 15.7, 13.9, 12.5; **IR (Neat): ν_{max}** 2963, 2928, 2870, 2248, 1607, 1584, 1481, 1434, 1370, 1288, 1235, 1198, 1174, 1063, 1034, 910, 854, 813, 717, 649; **HRMS (ESI-TOF):** *m/z* $(M + H)^+$ calcd for $C_{14}H_{16}NO$ 214.1228; found: 214.1221.

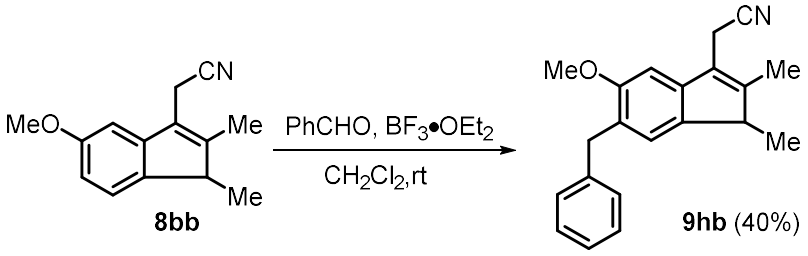


2-(7-Methoxy-1,2-dimethyl-1*H*-inden-3-yl)acetonitrile (8bb'): R_f = 0.6 (20% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 3.51 (s, 2H), 3.37 (q, *J* = 7.4 Hz, 1H), 2.05 (s, 3H), S1.34 (d, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 155.5, 148.8, 144.4, 133.8, 128.4, 123.7, 117.3, 111.1, 107.8, 55.3, 46.4, 14.04, 13.9, 12.2; **IR (Neat): ν_{max}** 2958, 2923, 2855, 2240, 1595, 1455, 1434,



1349, 1286, 1209, 1133, 1092, 1061, 942, 806, 734, 700; **HRMS (ESI-TOF):** *m/z* $(M + H)^+$ calcd for $C_{14}H_{16}NO$ 214.1228; found: 214.1221.

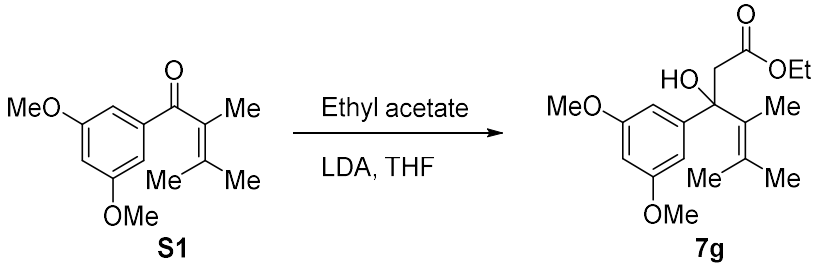
2-(6-Benzyl-5-methoxy-1,2-dimethyl-1*H*-inden-3-yl)acetonitrile (9hb):



To a stirred solution of **8bb** (50 mg, 0.23 mmol, 1 equiv) and benzaldehyde (48.9 mg, 0.46 mmol, 2.0 equiv) in dry CH_2Cl_2 (2.3 mL) was added BF_3•OEt_2 (0.56 mL, 4.60 mmol, 20.0 equiv) at rt and stirred at the same temperature under an inert atmosphere for 3days. The reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/hexanes) to recovered starting material and required product **9hb** (28 mg, 40%).

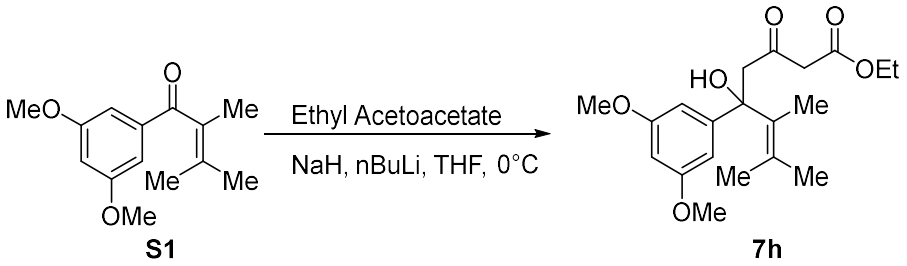
R_f = 0.5 (10% EtOAc/hexanes); **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.30 – 7.25 (m, 1H), 7.24 – 7.13 (m, 4H), 7.08 (s, 1H), 6.86 (s, 1H),4.06 (d, *J* = 15.1 Hz, 1H), 3.95 (d, *J* = 15.1 Hz, 1H), 3.87 (s, 3H), 3.52 (s, 2H), 3.17 (q, J = 7.5 Hz, 1H), 2.03 (s, 3H), 1.23 (d, J = 7.5 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.83, 148.49, 141.93, 141.49, 139.62, 128.86, 128.27, 126.27, 125.73, 124.51, 123.95, 117.24, 101.14, 55.85, 46.87, 36.10, 15.61, 14.02, 12.39. **IR (Neat):** **ν_{max}** 2960, 2923, 2852, 2209, 1602, 1452, 1432, 1349, 1244, 11, 1133, 1092, 1061, 942, 806, 734, 700; **HRMS (ESI-TOF):** *m/z* $(M + H)^+$ calcd for $C_{21}H_{22}NO$ 304.1698; found: 304.1690.

Ethyl 3-(3,5-dimethoxyphenyl)-3-hydroxy-4,5-dimethylhex-4-enoate (7g):



Compound **7g** was prepared according to the literature procedures, and its spectral data showed good agreement with the literature data.[20a]

Ethyl 5-(3,5-dimethoxyphenyl)-5-hydroxy-6,7-dimethyl-3-oxooct-6-enoate (7h):

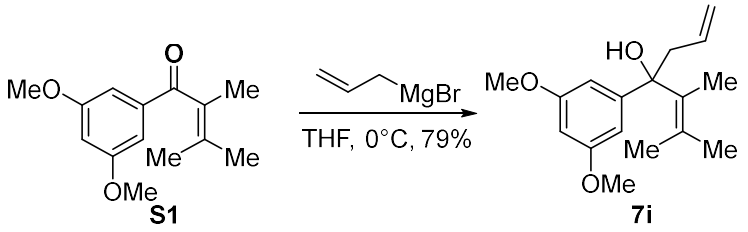


S1 **7h**

To an oven-dried round-bottom flask equipped with a stirring bar, under a nitrogen atmosphere, is added a suspension of NaH (60% suspension, 171 mg, 4.27 mmol, 2 equiv) in dry THF (6 mL) at 0 °C. Then ethyl acetoacetate (417 mg, 3.20 mmol, 1.5 equiv.) was added dropwise and stirred for 10 minutes, after which n-BuLi (1.6 M, 4.27 mmol, 2 equiv.) was added dropwise at the same temperature, and the reaction mixture was stirred for a further 15 minutes at this temperature. After that, aryl vinyl ketone **S1** (500 mg, 2.13 mmol, 1 equiv) was cannulated to the reaction mixture in dry THF (2 mL), the reaction was monitored by TLC, quenched with aq NH_4Cl solution, extracted with EtOAc (3 × 10 mL), and washed with saturated brine solution, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography using EtOAc/hexane as the eluent, yielding 645 mg (83%) over **7 h**.

R_f = 0.5 (30% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.54–6.50 (m, 2H), 6.32 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.11 (brs, 1H), 3.77 (s, 3H), 3.77 (s, 3H), 3.41–3.37 (m, 2H), 3.32 (d, *J* = 17.5 Hz, 1H), 3.03 (d, *J* = 17.5 Hz, 1H), 1.74 (s, 3H), 1.69 (s, 3H), 1.62 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 201.0, 167.3, 160.8, 155.9, 154.7, 145.0, 131.0, 125.7, 96.2, 95.7, 61.5, 55.7, 55.3, 50.4, 47.6, 41.0, 21.5, 14.2, 9.9; **IR (Neat):** ν_{max} 2958, 2924, 2852, 1744, 1714, 1591, 1484, 1461, 1427, 1354, 1315, 1259, 1205, 1152, 1091, 1041, 934, 825, 772; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{20}H_{29}O_6$ 365.1959; found: 365.1950.

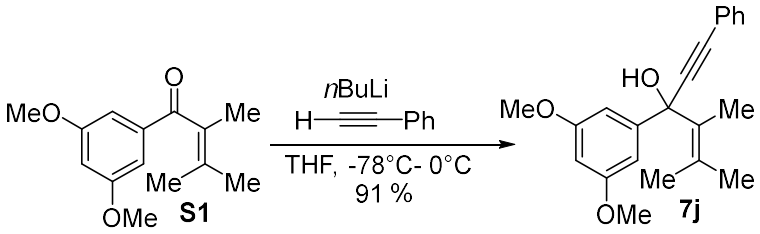
4-(3,5-Dimethoxyphenyl)-5,6-dimethylhepta-1,5-dien-4-ol (7i):



To a solution of aryl vinyl ketone **S1** (500 mg, 2.13 mmol, 1 equiv) in THF (9 mL) at 0 °C was added allylmagnesium bromide (1.0 M in THF, 2.56 mL, 2.56 mmol, 1.2 equiv) dropwise. The reaction mixture was stirred at 0 °C for 30 minutes. The reaction mixture was then warmed to room temperature and stirred overnight. A saturated aqueous NH_4Cl solution (5 mL) was added to quench the reaction, and the reaction mixture was extracted with EtOAc (40 mL). The combined organic layers were washed with brine (20mL), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography to give the title divinyl alcohol **7i** (470 mg, 79 % yield) as a pale-yellow oil.

R_f = 0.4 (20% EtOAc/ hexane); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 6.57 (d, *J* = 2.3 Hz, 1H), 6.33 (t, *J* = 2.3 Hz, 1H), 5.79–5.67 (m, 1H), 5.19–5.12 (m, 2H), 3.78 (s, 6H), 2.83 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.69 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.23 (brs, 1H), 1.83–1.80 (m, 3H), 1.70 (s, 3H), 1.64 (q, *J* = 1.4 Hz, 2H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 160.4, 150.6, 134.3, 132.2, 130.3, 119.4, 104.2, 97.9, 78.4, 55.3, 46.8, 23.3, 22.7, 17.7; **IR (Neat):** ν_{max} 3079, 2997, 2956, 2927, 2854, 1591, 1455, 1423, 1351, 1288, 1204, 1153, 1065, 993, 929, 907, 833, 772, 706; **HRMS (ESI):** *m/z* $(M - H)^+$ calcd for $C_{17}H_{23}O_3$ 275.1642; found: 275.1639.

3-(3,5-Dimethoxyphenyl)-4,5-dimethyl-1-phenylhex-4-en-1-yn-3-ol (7j):

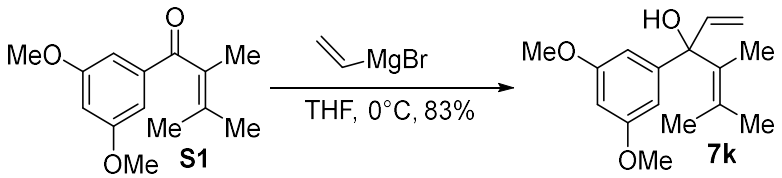


^{n}BuLi (1.33 mL, 1.6 M, 2.13 mmol, 1 equiv) was added to a stirred solution of phenylacetylene (218 mg, 2.13 mmol, 1 equiv) in THF (5 mL) at −78 °C. After 30 min, the reaction was allowed to warm to 0 °C and held there for 2 h. The mixture was cooled to −78 °C, and aryl vinyl ketone **S1** (500 mg, 2.13 mmol, 1 equiv) in THF (3.0 mL) was added dropwise by cannula, forming a white precipitate. After 30 min, the reaction was allowed to warm to 0 °C, at which

point the precipitate redissolved. The reaction was quenched with H_2O (4 mL), and the layers were separated. The aqueous phase was neutralized with 1 M HCl (aq) and was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with H_2O (5 mL) and brine (5 mL), dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (50 g silica, 20:1 hexanes/EtOAc) gave 650 mg (91%) of the desired alcohol **7j** as a yellowish oil.

R_f= 0.5 (20% EtOAc/ hexane); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.48–7.41 (m, 2H), 7.33–7.29 (m, 3H), 6.85 (d, *J* = 2.3 Hz, 1H), 6.40 (t, *J* = 2.3 Hz, 1H), 3.81 (s, 6H), 2.45 (brs, 1H), 1.92–1.89 (m, 3H), 1.80 (q, *J* = 1.4 Hz, 3H), 1.77 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 160.7, 147.9, 131.6, 130.4, 130.3, 128.3, 128.3, 122.9, 104.6, 99.3, 92.2, 85.9, 75.3, 55.4, 23.2, 22.7, 17.2; **IR (Neat):** ν_{max} 3051, 2954 2923, 2852, 1594, 1459, 1424, 1344, 1288, 1249, 1203, 1154, 1059, 1011, 923, 840, 756, 691, 669; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{22}H_{25}O_3$ 337.1798; found: 337.1795.

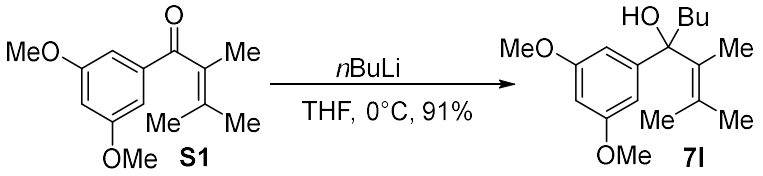
3-(3,5-Dimethoxyphenyl)-4,5-dimethylhexa-1,4-dien-3-ol (7k):



To a solution of aryl vinyl ketone **S1** (500 mg, 2.13 mmol, 1 equiv) in THF (9 mL) at 0 °C was added vinylmagnesium bromide (1.0 M in THF, 2.56 mL, 2.56 mmol, 1.2 equiv) dropwise. The reaction mixture was stirred at 0 °C for 30 minutes. The reaction mixture was then warmed to room temperature and stirred overnight. A saturated aqueous NH_4Cl solution (5 mL) was added to quench the reaction, and the reaction mixture was extracted with EtOAc (40 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography to give the required product **7k** (470 mg, 79 % yield) as a pale-yellow oil.

R_f= 0.5 (15% EtOAc/hexane); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 6.56 (d, *J* = 2.3 Hz, 2H), 6.34 (t, *J* = 2.3 Hz, 1H), 6.22 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.28 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.13 (dd, *J* = 10.6, 1.5 Hz, 1H), 3.77 (s, 6H), 1.91 (brs, 1H), 1.77–1.75 (m, 3H), 1.73–1.71 (m, 3H), 1.51 (q, *J* = 1.4 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 160.7, 149.7, 143.2, 132.0, 129.7, 111.8, 104.5, 98.5, 80.3, 55.3, 23.0, 22.8, 17.4; **IR (Neat):** ν_{max} 3524, 2999, 2923, 2853, 1594, 1459, 1424, 1339, 1287, 1204, 1153, 1065, 1001, 920, 841, 775, 700; **HRMS (ESI):** *m/z* calcd for $C_{16}H_{21}O_3$ $(M - H)^+$: 261.1485, found: 261.1486

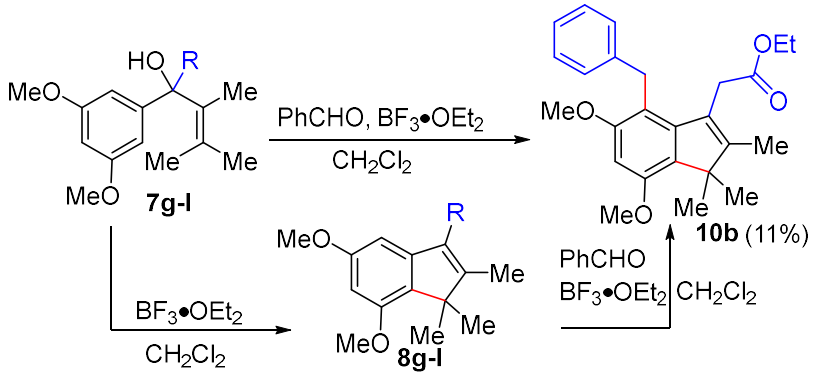
4-(3,5-Dimethoxyphenyl)-2,3-dimethyloct-2-en-4-ol (7l):



Aryl vinyl ketone **S1** (500 mg, 2.13 mmol, 1 equiv) in THF (10 mL) was cooled to 0 °C. n-BuLi (1.6 M in THF, 2.66 mL, 4.26 mmol, 2.0 equiv) was added dropwise, and the mixture was stirred at 0 °C for 2 h. The reaction mixture was then warmed to rt and stirred overnight. The reaction was quenched by adding a saturated aqueous NH4Cl solution, followed by extraction with EtOAc. The phases were then separated, the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography to yield the required product **7l** (470 mg, 79% yield) as a pale-yellow oil.

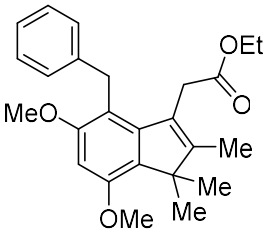
R_f = 0.5 (20% EtOAc/ hexane); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 6.56 (d, *J* = 2.3 Hz, 2H), 6.32 (t, *J* = 2.3 Hz, 1H), 3.78 (s, 6H), 2.05–1.97 (m, 1H), 1.91–1.84 (m, 1H), 1.80–1.77 (m, 3H), 1.69 (s, 3H), 1.59 (q, *J* = 1.4 Hz, 3H), 1.36–1.18 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 160.4, 151.4, 133.2, 129.5, 104.2, 97.7, 79.7, 55.3, 41.9, 26.1, 23.3, 23.2, 22.6, 17.6, 14.2; **IR (Neat):** ν_{max} 2931, 2869, 2837, 1594, 1456, 1423, 1344, 1303, 1203, 1152, 1061, 1028, 994, 924, 844, 833, 754, 702; **HRMS (ESI):** *m/z* $(M + Na)^+$ calcd for $C_{18}H_{28}O_3Na$ 315.1936; found: 315.1934.

Scheme 2: General procedure for synthesis of 10:



To a stirred solution of **7g** (1 equiv) and benzaldehyde (2.5 equiv) in dry CH_2Cl_2 (2.2 mL), BF_3 •OEt_2 (7.5 equiv) was added at rt and stirred at the same temperature under an inert atmosphere. After completing the starting material, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/hexanes) to give the desired product **10b** (13 mg, 11% yield), as a colorless oil, along with **8g** (37 mg, 79% yield)

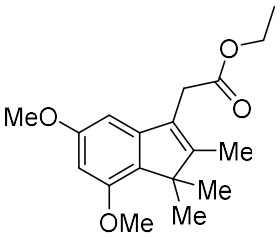
Ethyl 2-(4-benzyl-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl) acetate (10b):



R_f = 0.5 (10% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.22 (t, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.37 (s, 1H), 4.23 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.76 (s, 3H), 3.38 (s, 2H), 1.82 (s, 3H), 1.29 (s, 6H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):** δ 171.6, 158.4, 155.2, 153.9, 143.6, 142.5, 131.7, 128.2, 127.9, 126.8, 125.3, 113.2, 92.5, 60.6, 56.3, 55.3, 49.1, 32.8, 30.0, 21.6, 14.2, 9.9; **IR (Neat):** ν_{max} 2954, 2924, 2856, 1732, 1595, 1454, 1354, 1287, 1245, 1203, 1167, 1081, 1028, 943, 807, 734, 699; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{25}H_{31}O_4$ 395.2246, found: 395.2242.

Compounds 8g-l were synthesized using the synthetic procedure for 8a from 7a.

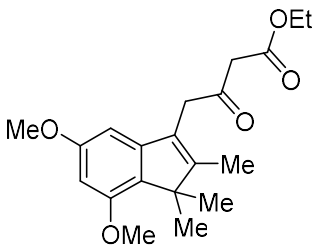
Ethyl 2-(5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetate (8g):



Yield: 85 mg (90 %), colourless oil, $\mathbf{R_f}$ = 0.5 (15% EtOAc/ hexane); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.49 (d, *J* = 2.0 Hz, 1H), 6.29 (d, *J* = 2.0 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.83 (s, 3H), 3.44 (s, 2H), 1.90 (s, 3H), 1.27 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 171.2, 160.4, 155.6, 153.5, 145.4, 130.9, 126.1, 96.3, 95.2, 60.7, 55.5, 55.2, 50.1, 31.8, 21.5, 14.2, 9.8; **IR (Neat):** ν_{max} 2958, 2928, 2866, 1736, 1591, 1484, 1428, 1354, 1283, 1205, 1152, 1092, 1072, 1040, 934, 825, 685; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{18}H_{25}O$ 305.1753, found: 305.1735.

Ethyl 4-(5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)-3-oxobutanoate (8h):

Yield: 84 mg (88%), colourless oil, $\mathbf{R_f}$ = 0.5 (20% EtOAc/ hexane); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.37 (d, *J* = 2.0 Hz, 1H), 6.29 (d, *J* = 2.0 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.62 (s, 2H), 3.37 (s, 2H), 1.89 (s, 3H), 1.28 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 204.3, 166.6, 160.6, 149.6, 131.7, 131.1, 103.7, 98.3, 78.5, 61.5, 55.3, 54.4, 50.3, 23.2, 22.8, 18.2, 14.1; **IR (Neat):** ν_{max} 2957, 2920, 2850, 1738, 1710, 1592, 1456, 1425, 1306, 1288, 1203, 1151, 1061, 1027, 936, 924, 837, 755, 732, 697; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{20}H_{27}O_5$ 347.1858, found: 347.1835.

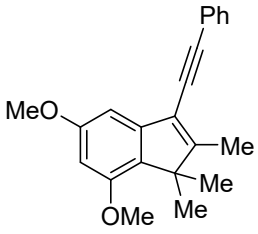


3-Allyl-5,7-dimethoxy-1,1,2-trimethyl-1*H*-indene (8i):

Yield: 86 mg (92%), colourless oil, $\mathbf{R_f}$ = 0.6 (5% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.42 (d, *J* = 2.0 Hz, 1H), 6.27 (d, *J* = 2.0 Hz, 1H), 5.95–5.82 (m, 1H), 5.08–4.95 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.19 (d, *J* = 5.9 Hz, 2H), 1.83 (s, 3H), 1.27 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 160.3, 155.6, 151.3, 146.1, 135.7, 131.2, 130.3, 115.1, 96.6, 94.8, 55.5, 55.2, 49.9, 29.5, 21.7, 9.4; **IR (Neat):** ν_{max} 2956, 2924, 2853, 2837, 1589, 1483, 1457, 1426, 1352, 1241, 1200, 1149, 1090, 1065, 1043, 991, 933, 909, 821, 711, 677; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{17}H_{23}O_2$ 259.1698, found: 259.1672.

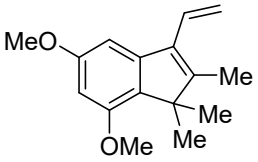
5,7-Dimethoxy-1,1,2-trimethyl-3-(phenylethynyl)-1*H*-indene (8j):

Yield: 85 mg (90%), white solid; m.p.: 120.5-123.5°C, $\mathbf{R_f}$= 0.5 (5% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60–7.55 (m, 2H), 7.39–7.33 (m, 3H), 6.68 (d, *J* = 2.1 Hz, 1H), 6.33 (d, *J* = 2.1 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 2.13 (s, 3H), 1.33 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 162.5, 160.6, 155.7, 143.9, 131.7, 130.2, 128.4, 128.1, 123.7, 117.8, 96.9, 95.9, 94.5, 83.4, 55.7, 55.2, 50.5, 21.6, 11.8; **IR (Neat):** ν_{max} 3031, 2959, 2925, 2850, 1594, 1486, 1460, 1428, 1352, 1299, 1219, 1199, 1151, 1125, 1091, 1066, 1041, 1013, 934, 755, 690, 634; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{22}H_{23}O_2$ 319.1698, found: 319.1682.



5,7-Dimethoxy-1,1,2-trimethyl-3-vinyl-1*H*-indene (8k):

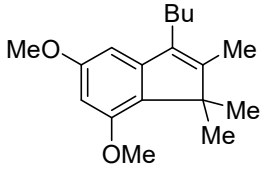
Yield: 90 mg (96%), yellowish oil, $\mathbf{R_f}$ = 0.6 (15% EtOAc/ hexane); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.70 (d, *J* = 2.0 Hz, 1H), 6.69–6.65 (m, 1H), 6.31 (d, *J* = 2.0 Hz, 1H), 5.63 (dd, *J* = 18.0, 1.7 Hz, 1H), 5.39 (dd, *J* = 11.6, 1.7 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 1.95 (s, 3H), 1.28 (s, 6H); **^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$):** δ 160.3, 155.8, 154.0, 144.4, 131.3, 131.0, 130.0, 116.4, 97.5, 95.2, 55.6, 55.2, 50.0, 21.5, 10.3.



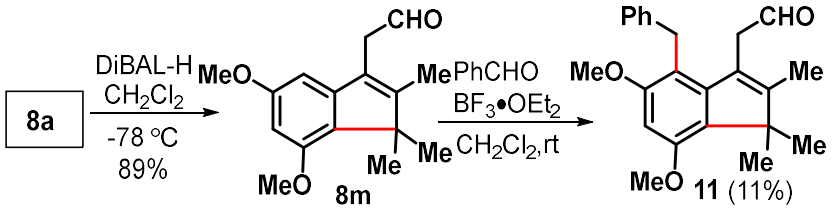
The spectral data of **8k** showed good agreement with the literature.[20a]

3-butyl-5,7-dimethoxy-1,1,2-trimethyl-1*H*-indene(8l):

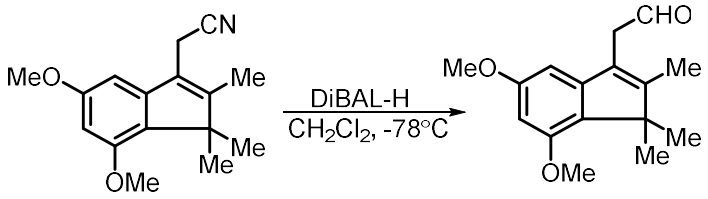
Yield: 89 mg (95%), yellowish oil, $\mathbf{R_f}$= 0.6 (10% EtOAc/ hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.43 (d, *J* = 2.0 Hz, 1H), 6.27 (d, *J* = 2.0 Hz, 1H), 3.84 (s, 6H), 2.43 (t, *J* = 7.3 Hz, 2H), 1.82 (s, 3H), 1.52–1.46 (m, 2H), 1.40–1.30 (m, 2H), 1.25 (s, 6H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 160.3, 155.6, 149.9, 146.5, 133.2, 131.3, 96.5, 94.5, 55.5, 55.2, 49.7, 31.1, 24.9, 22.6, 21.7, 14.1, 9.5; **IR (Neat):** ν_{max} 2956, 2925, 2854, 1591, 1483, 1352, 1282, 1206, 1151, 1066, 1044, 935, 834, 798, 677; **HRMS (ESI):** *m/z* $(M + H)^+$ calcd for $C_{18}H_{27}O_2$ 275.2011, found: 275.2021.



Synthesis of compound 11 from 8a *via* 8m:



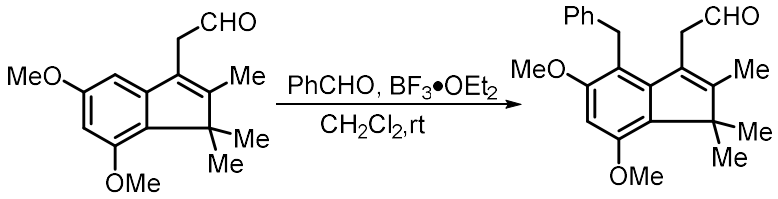
2-(5,7-dimethoxy-1,1,2-trimethyl-1H-inden-3-yl)acetaldehyde (8m):



To a solution of nitrile compound **8a** (80 mg, 0.23 mmol) in dry CH_2Cl_2 (2 mL) was added a 1 M solution of DIBAL-H in toluene (0.23 mL, 0.23 mmol) dropwise at -78 °C and stirred at -78 °C for 2 h under argon. The reaction mixture was quenched with MeOH, poured into saturated Rochelle's salt solution, and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified (8% EtOAc/hexanes) to give aldehyde **8m** as a yellowish oil (71 mg, 89%).

R_f =0.5 (20% EtOAc/hexanes);**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.59 (t, *J* = 2.7 Hz, 1H), 6.36 (d, *J* = 2.0 Hz, 1H), 6.31 (d, *J* = 2.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.49 (d, *J* = 2.5 Hz, 2H), 1.89 (s, 3H), 1.30 (s, 6H);**^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 199.1, 160.6, 155.9, 155.1, 145.1, 130.9, 123.7, 95.9, 95.5, 55.6, 55.2, 50.4, 40.9, 21.6, 9.9; **IR (Neat): ν_{max}** 2958, 2923, 2851, 1725, 1591, 1484, 1353, 1288, 1241, 1206, 1152, 1042, 934, 824, 761, 730; **HRMS (ESI-TOF):** *m/z* $(M + H)^+$ calcd for $C_{16}H_{21}NO_3$ 261.1486; found: 261.1480.

2-(4-Benzyl-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetaldehyde (11):[21]



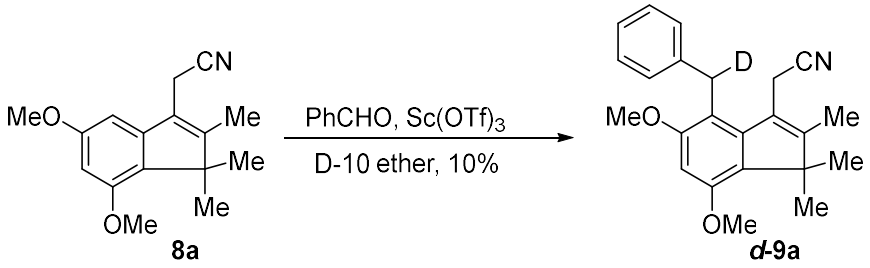
To a stirred solution of **8m** (60 mg, 0.23 mmol, 1 equiv) and benzaldehyde (48.9 mg, 0.46 mmol, 2.0 equiv) in dry CH_2Cl_2 (2.3 mL) was added BF_3•OEt_2 (0.14 mL, 1.15 mmol, 5.0 equiv) at rt and stirred at the same temperature under an inert atmosphere. After completing the

starting material, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/hexanes) to give the desired product **11** (5 mg, 6%), colourless liquid with recovered starting material.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.18 – 7.09 (m, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.39 (s, 1H), 4.18 (s, 1H), 3.90 (s, 1H), 3.77 (s, 1H), 3.45 (s, 1H), 1.80 (s, 1H), 1.31 (s, 1H);**^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 199.8, 158.5, 156.6, 154.1, 143.3, 141.9, 131.8, 128.4, 127.9, 125.6, 124.8, 113.0, 92.7, 56.4, 55.3, 49.4, 42.3, 30.2, 21.7, 10.0.

The spectral data of **11** showed good agreement with the literature.[20a]

General Procedure for Synthesis of Indenyl Acetonitrile (*d*-9a).

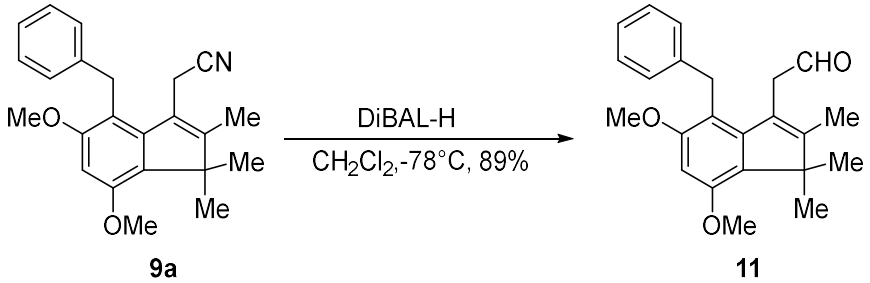


To a stirred solution of **8a** (1 equiv) and benzaldehyde (2.0 equiv) in dry CH_2Cl_2 (2.2 mL), BF_3 •OEt_2 (5.0 equiv) was added at rt and stirred at the same temperature under an inert atmosphere. After completing the starting material, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/hexanes) to give the desired product ***d*-9a**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 7.3 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 2H), 6.40 (s, 1H), 4.35–4.30 (m, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 3.30 (s, 2H), 1.86 (s, 2H), 1.28 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 158.6, 156.2, 154.2, 142.0, 131.4, 128.6, 127.6, 125.8, 123.1, 118.2, 112.7, 92.9, 56.4, 55.3, 49.5, 31.9, 29.8 (m), 21.3, 15.8, 9.9; **IR (Neat):** ν_{max} 2956, 2925, 2853, 2246, 1740, 1635, 1601, 1482, 1354, 1286, 1181, 1123, 1075, 1042, 990, 798, 755; **HRMS (ESI):** *m/z* calcd for C_{23} H_{25} D N O_2 $(M + H)^+$: 349.2026, found: 349.2034

Derivatizations of Products

2-(4-Benzyl-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl) acetaldehyde (11):



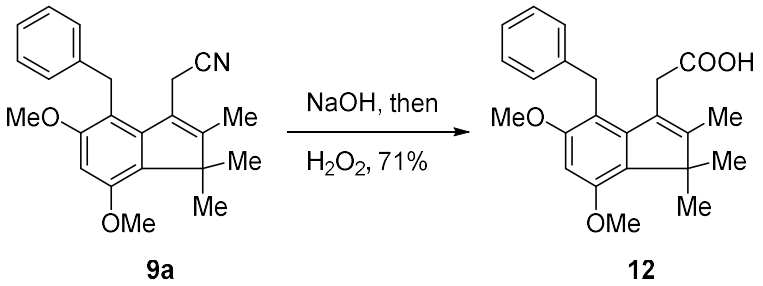
9a **11**

To a solution of nitrile compound **9a** (80 mg, 0.23 mmol) in dry CH_2Cl_2 (2 mL) was added a 1 M solution of DIBAL-H in toluene (0.23 mL, 0.23 mmol) dropwise at -78 °C and stirred at -78 °C for 2 h under argon.[20] The reaction mixture was quenched with MeOH, poured into saturated Rochelle's salt solution, and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified (8% EtOAc/hexanes) to give aldehyde **11** as a yellowish oil (71 mg, 89%).

R_f = 0.5 (10% EtOAc/hexanes); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.38 (t, *J* = 2.2 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.39 (s, 1H), 4.18 (s, 2H), 3.90 (s, 3H), 3.77 (s, 3H), 3.44 (d, *J* = 2.2 Hz, 2H), 1.80 (s, 3H), 1.31 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ 199.7, 158.5, 156.6, 154.1, 143.3, 141.9, 131.9, 128.4, 127.9, 125.6, 124.9, 113.0, 92.7, 56.4, 55.3, 49.4, 42.3, 30.1, 21.7, 10.0.

The spectral data of **11** showed good agreement with the literature.[20a]

2-(4-Benzyl-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)acetic acid (12):



9a **12**

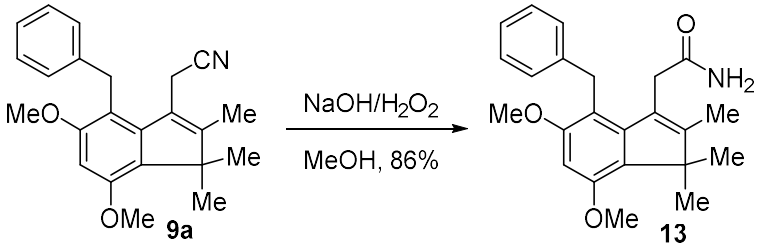
A mixture of nitrile compound **9a** (104 mg, 0.300 mmol) and NaOH (600 mg, 15 mmol) was dissolved in EtOH (2 mL) and H_2O (8 mL). The reaction mixture was heated to 110 °C and kept for 5 h.[21] The resulting mixture was then acidified with 1M H_2SO_4 and extracted with ethyl acetate (60 mL). The combined organic layer was washed with brine, dried over Na_2SO_4,

filtered, and concentrated. The crude material was purified by flash column chromatography (silica gel, 30% EtOAc/hexane) to yield the carboxylic compound **12** as a colourless oil (78 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (t, *J* = 7.5 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.30 (s, 1H), 4.16 (s, 2H), 3.82 (s, 3H), 3.70 (s, 3H), 3.34 (s, 2H), 1.75 (s, 3H), 1.22 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)**: δ 177.5, 158.5, 155.7, 154.0, 143.3, 142.3, 131.7, 128.3, 127.9, 126.2, 125.4, 113.2, 92.7, 56.4, 55.3, 49.2, 32.5, 30.1, 21.5, 9.9;

The spectral data of **12** showed good agreement with the literature.[20a]

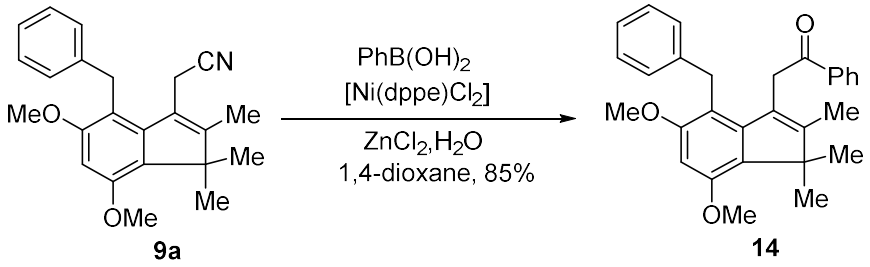
2-(4-Benzyl-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl) acetamide (13):



To a solution of **9a** (137 mg, 0.39 mmol) in MeOH (4 mL) was added a 30% hydrogen peroxide solution (125 µl, 1.58 mmol). The pH was adjusted to 8.0 by adding 2M sodium hydroxide. After 3 h, 30% hydrogen peroxide solution (125 µl, 1.58 mmol) was added to the reaction.[22] The reaction mixture was stirred for an additional 3 h. The solvent was removed in vacuo, and the residue was extracted with ethyl acetate (20 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude material was purified by flash column chromatography (silica gel, 40% EtOAc/hexane) to give **13** (125 mg, 0.342 mmol) in 86% yield as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.40 (s, 1H), 5.56 (d, *J* = 8.5 Hz, 2H), 4.16 (s, 2H), 3.91 (s, 3H), 3.78 (s, 3H), 3.34 (s, 2H), 1.83 (s, 3H), 1.31 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 173.5, 158.6, 156.0, 154.1, 142.6, 142.0, 131.7, 128.3, 128.2, 127.9, 125.5, 113.7, 92.8, 56.3, 55.3, 49.4, 34.9, 30.2, 21.6, 9.8; **IR (Neat):** ν_{max} 3468, 3367, 2958, 2931, 2837, 1672, 1587, 1435, 1352, 1288, 1215, 1176, 1135, 1094, 1074, 1025, 947, 860, 801, 752, 699; **HRMS (ESI):** *m/z* calcd for $C_{23}H_{28}O_3N$ $(M + H)^+$: 366.2063, found: 366.2059.

2-(4-Benzyl-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)-1-phenylethan-1-one (14):

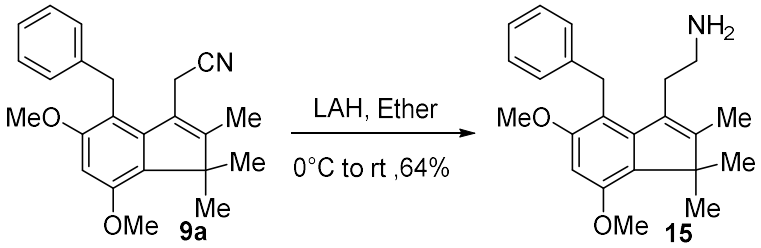


A suspension of **9a** (173 mg, 0.500 mmol), phenylboronic acid (124.0 mg, 1.017 mmol), [Ni(dppe)Cl_2] (14.7 mg, 0.0278 mmol), $ZnCl_2$ (104.0 mg, 0.763 mmol), and H_2O (10 ul, 0.555 mmol) in 1,4-dioxane (1 mL) was stirred at 80 °C for 12 h under a nitrogen atmosphere.[22] The mixture was filtered through a short Celite pad, which was then washed with dichloromethane (10 mL x 3). The filtrate was concentrated, and the residue was purified by flash column chromatography (silica gel; 10% EtOAc/hexane) to give **14** (181 mg, 0.425 mmol) in 85% yield as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85–7.79 (m, 2H), 7.61–7.53 (m, 1H), 7.47–7.38 (m, 2H), 7.21–7.06 (m, 3H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.37 (s, 1H), 4.00 (s, 2H), 3.94 (s, 2H), 3.90 (s, 3H), 3.74 (s, 3H), 1.73 (s, 3H), 1.34 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)**: δ 197.2, 158.5, 155.0, 154.1, 144.1, 142.3, 136.8, 133.0, 131.9, 128.5, 128.3, 128.2, 127.8, 127.0, 125.5, 112.5, 92.5, 56.4, 55.3, 49.3, 37.4, 30.2, 21.8, 9.8.

The spectral data of **14** showed good agreement with the literature.[20e]

2-(4-Benzyl-5,7-dimethoxy-1,1,2-trimethyl-1*H*-inden-3-yl)ethan-1-amine (15):



A solution of nitrile **9a** (30 mg, 0.09 mmol, 1.0 equiv) in dry ether (0.3 mL) to $LiAlH_4$ (6.3 mg, 0.18 mmol, 2.0 equiv) in ether (0.6 mL) was added at 0 °C under an argon atmosphere. The mixture was stirred for 1 h at the same temperature. Then, the reaction was stirred at rt until TLC confirmed the disappearance of the nitrile. The mixture was carefully quenched with 1 M NaOH, then ethyl acetate (10 mL) was added. The mixture was filtered through celite, the

filtrate was concentrated, and the residue was purified by flash column chromatography (silica gel; 10% MeOH/$CHCl_3$) to give **15** (20 mg, 0.425 mmol) in 64% yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.24 – 7.16 (m, 2H), 7.14 – 7.03 (m, 3H), 6.36 (s, 1H), 4.22 (s, 2H), 3.89 (s, 3H), 3.76 (s, 3H), 2.82 – 2.72 (m, 2H), 2.71 – 2.62 (m, 2H), 1.85 (s, 3H), 1.26 (s, 6H), 1.25 (br, 2H);**^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 158.6, 154.8, 154.1, 143.2, 142.3, 132.2, 130.0, 128.4, 128.1, 125.6, 113.5, 92.6, 56.4, 55.4, 49.1, 40.5, 30.5, 27.7, 21.8, 9.9; **IR (Neat): ν_{max}** 3342, 2955, 2923, 2853, 1601, 1587, 1352, 1288, 1216, 1197, 1136, 1093, 1061, 943, 799, 775, 672; **HRMS (ESI):** *m/z* calcd for $C_{23}H_{29}O_2N$ $(M + H)^+$: 352.2256, found: 352.2270.

3. X-ray Crystallography Information of 9a

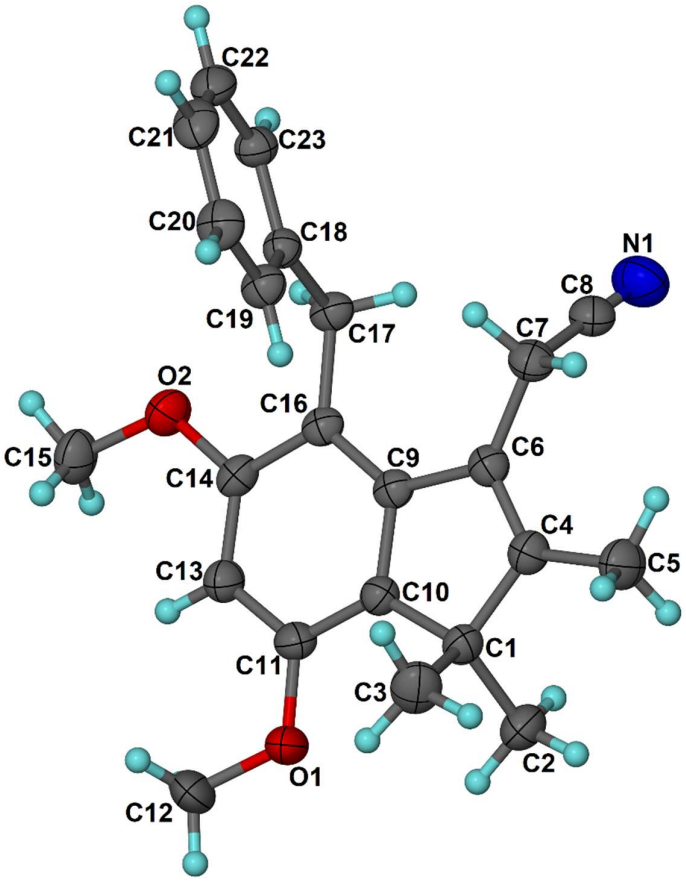


Figure caption: ORTEP diagram of compound **9a** with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level, and H atoms are shown as small spheres of arbitrary radius.

Crystal data for 9a: $C_{23}H_{25}NO_2$, M = 347.44, Monoclinic, Space group $P2_1/c$ (No.14), a = 13.1788(6)Å, b = 8.0426(4)Å, c = 19.5290(9)Å, α = 90°, β = 108.991(2)°, γ = 90°, V = 1957.25(16)Å^3, Z = 4, D_c = 1.179 g/cm^3, F_{000} = 744, Bruker D8 QUEST PHOTON III C7 HPAD detector, Mo-Kα radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 55°, μ = 0.075 mm^{-1}, 24408 reflections collected, 4476 unique (R_{int} = 0.0469), 240 parameters, *R1* = 0.0482, *wR2* = 0.1161, *R* indices based on 2434 reflections with I > 2σ(I) (refinement on F^2), Final *GooF* = 1.013, largest difference hole and peak = -0.155 and 0.180 e.Å^{-3}. **CCDC deposition number 2541948** contains the supplementary crystallographic data for this paper, which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

Data collection and Structure solution details:

X-ray data for the compounds were collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 Å) and a PHOTON-III C7 HPAD detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[24] The structure was solved using an intrinsic phasing method[24] and further refined with the SHELXL[25-27] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms]. **CCDC deposition number 2541948** contains the supplementary crystallographic data for this paper, which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

4. Reference

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20d. N. Satish, G. Sudhakar, *Synlett,* 2021, **32**, 605-610.

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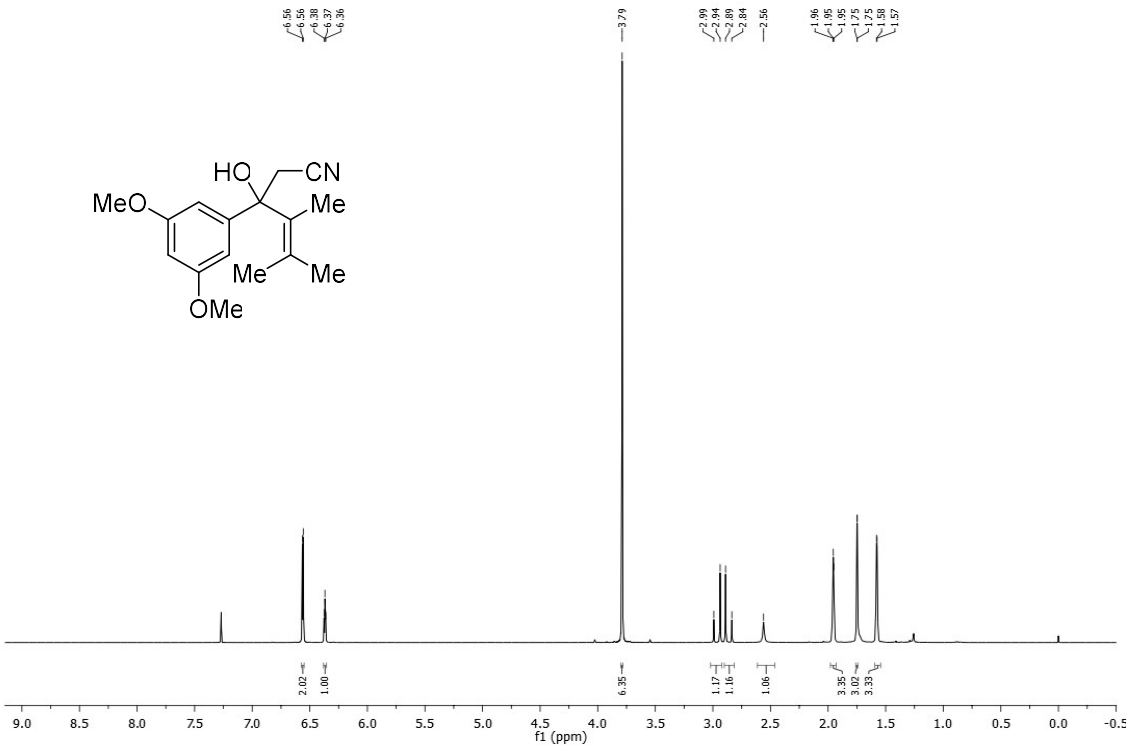
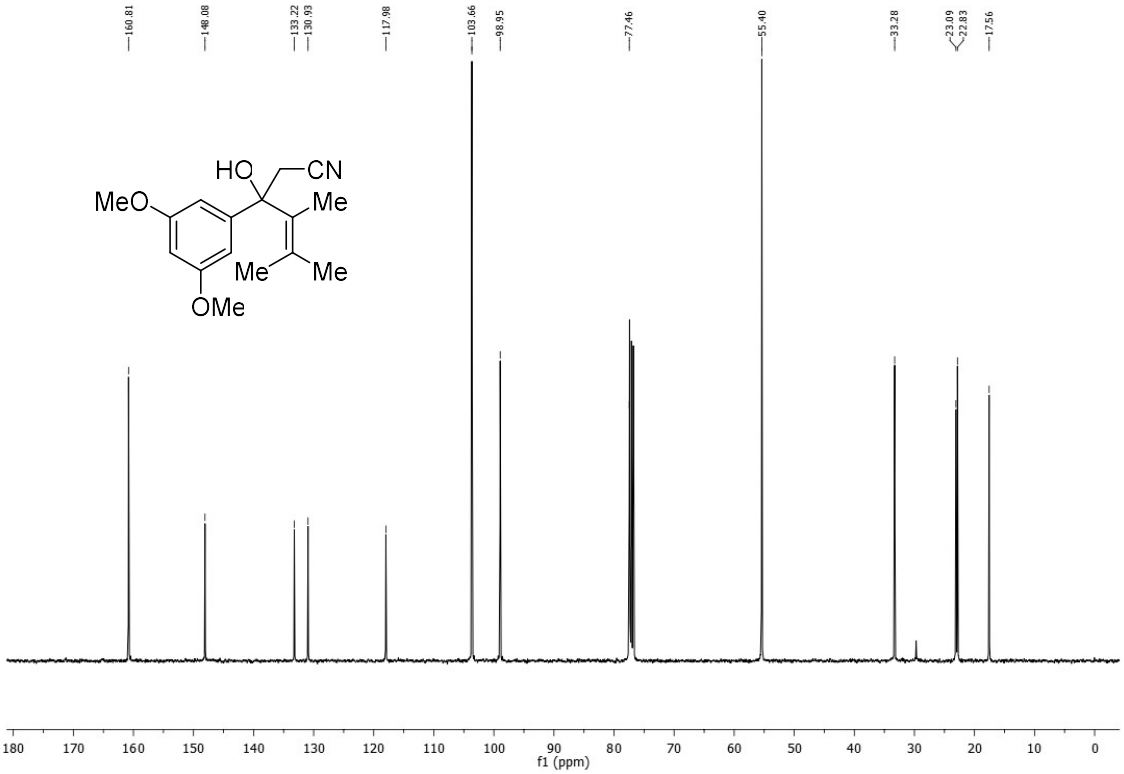
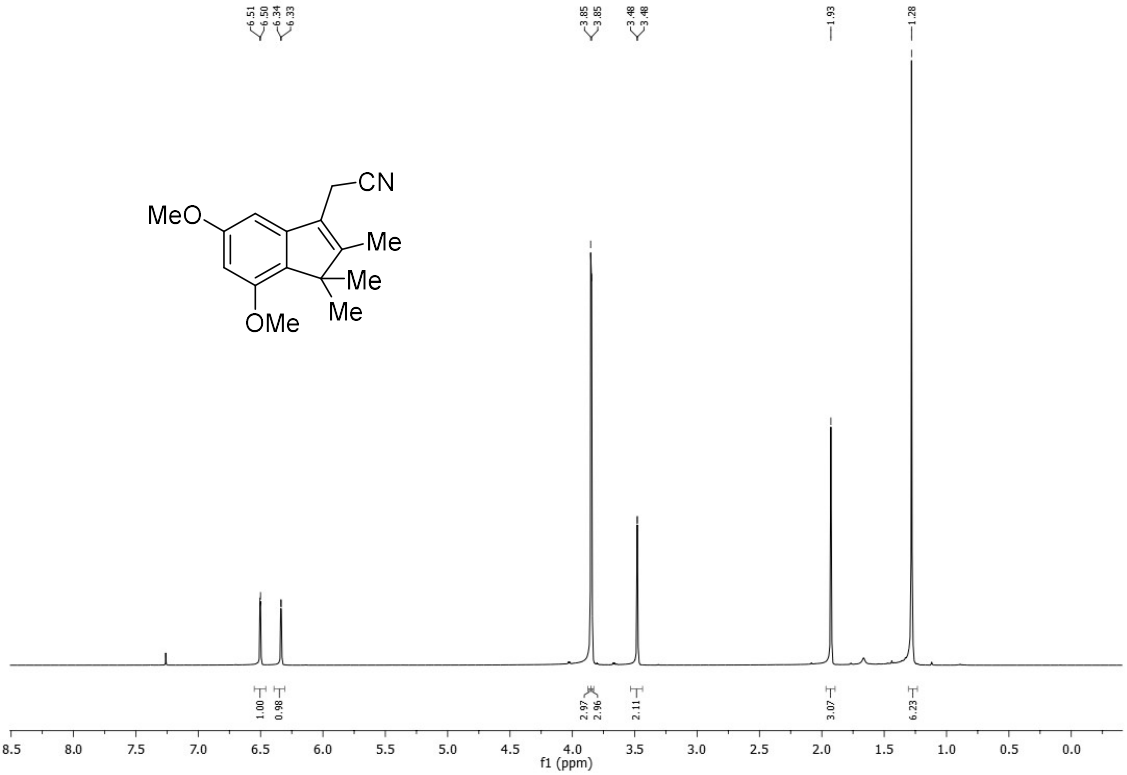
5. NMR Spectra of all new compounds



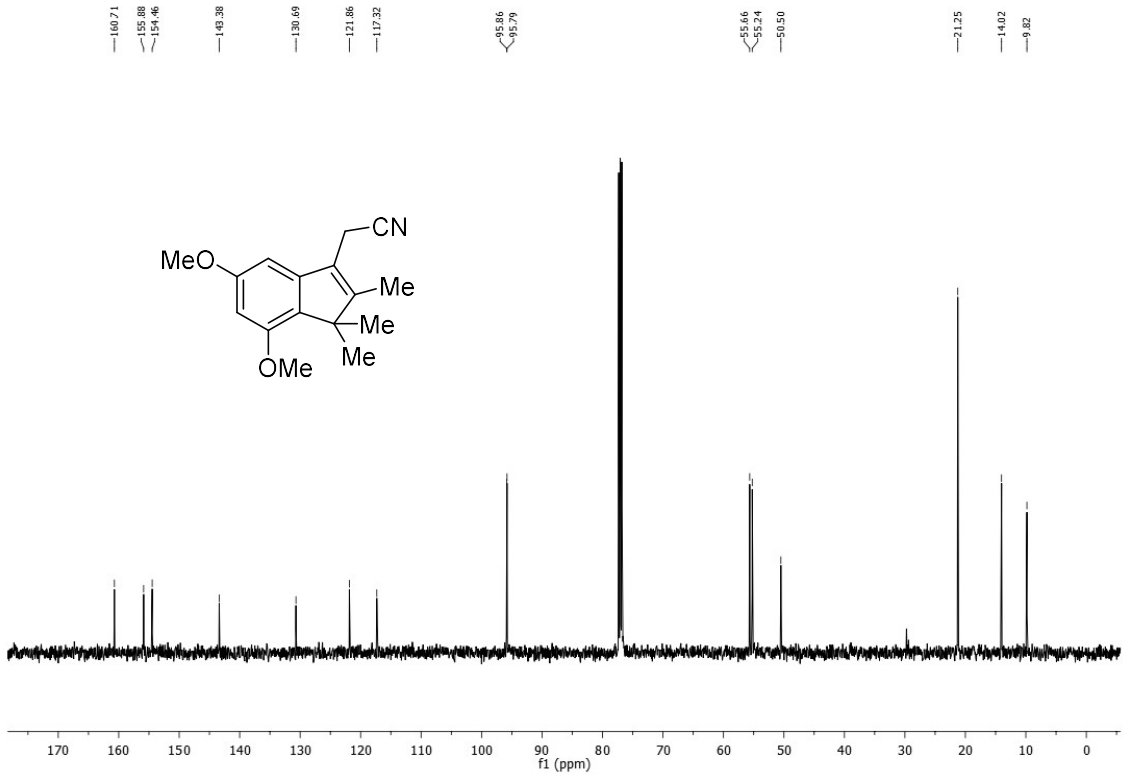
^{1}H NMR (300 MHz, $CDCl_3$) of compound **7a**.



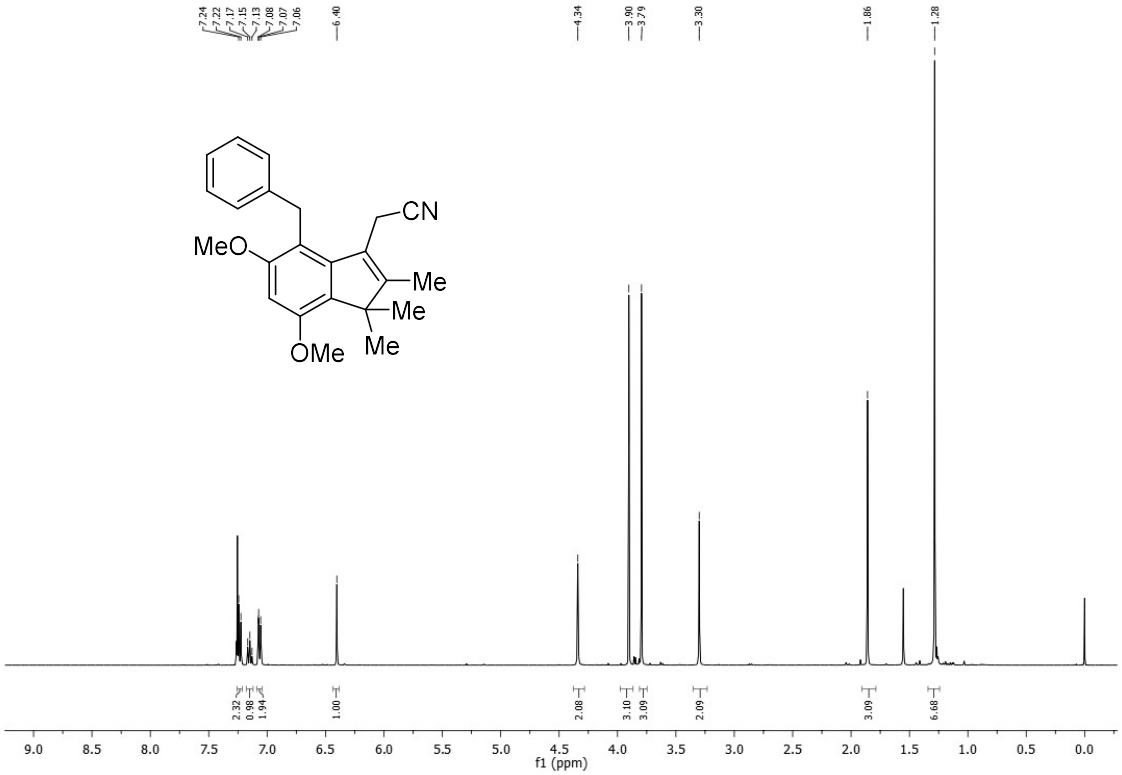
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound **7a**.



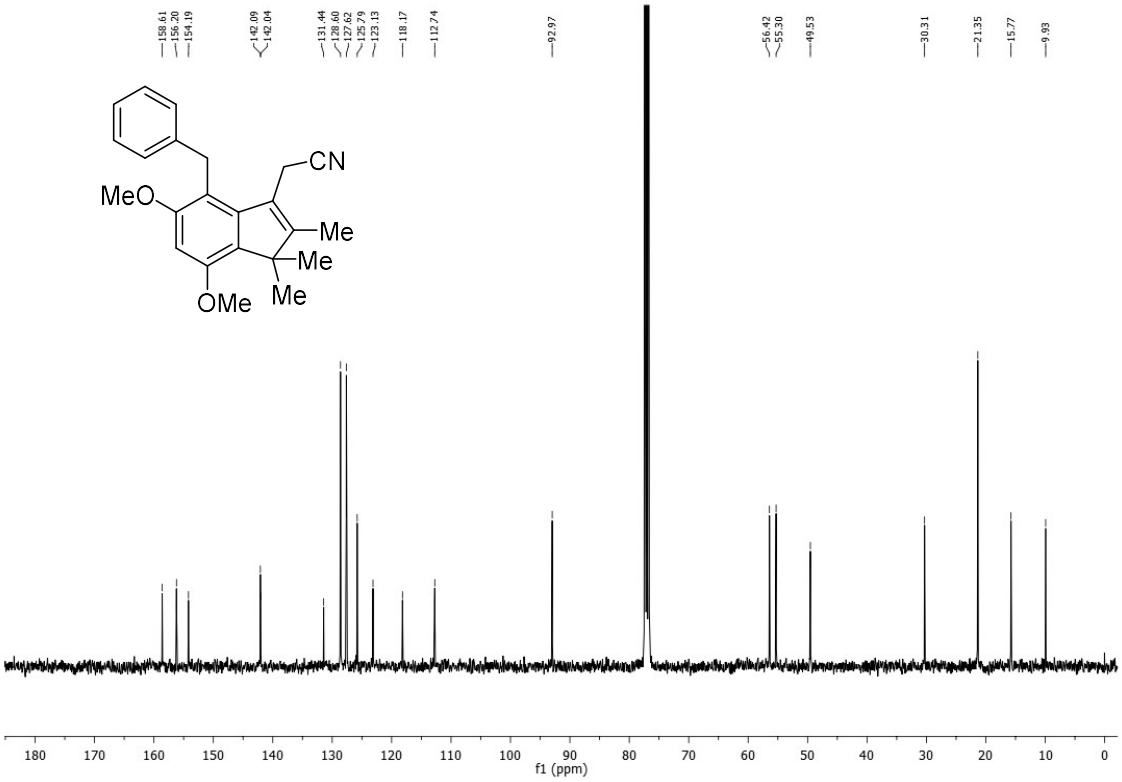
^{1}H NMR (400 MHz, $CDCl_3$) for compound **8a**.



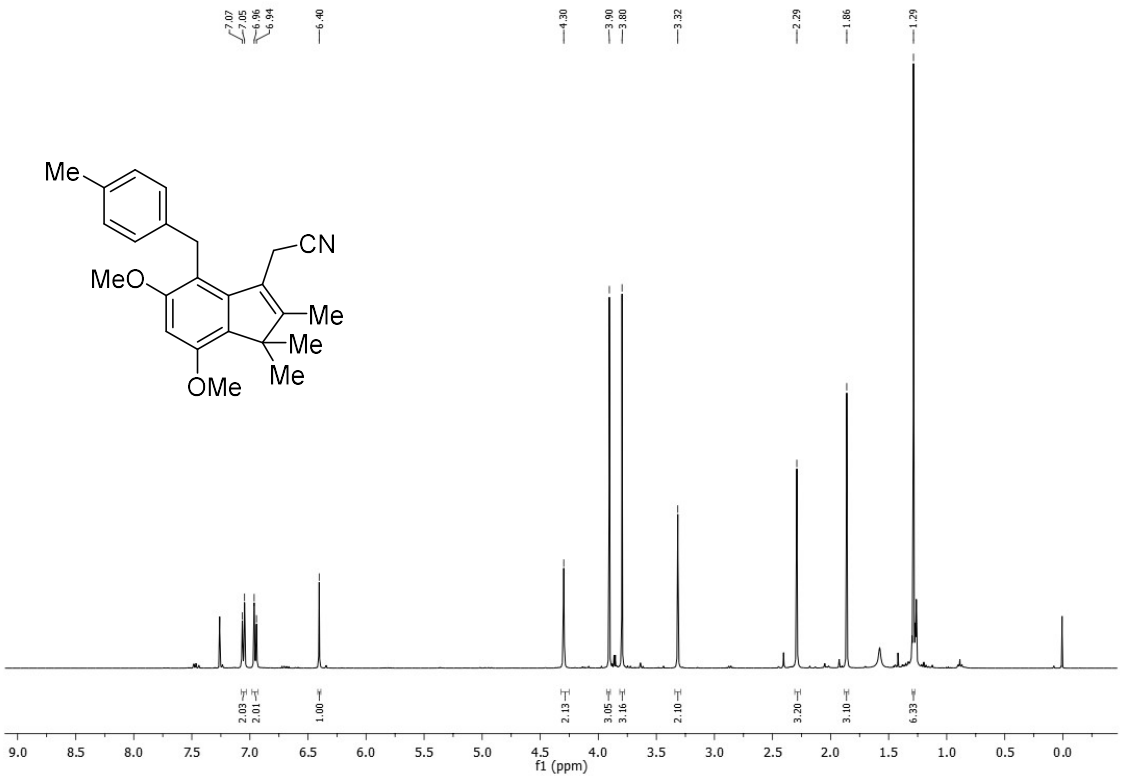
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) for compound **8a**.



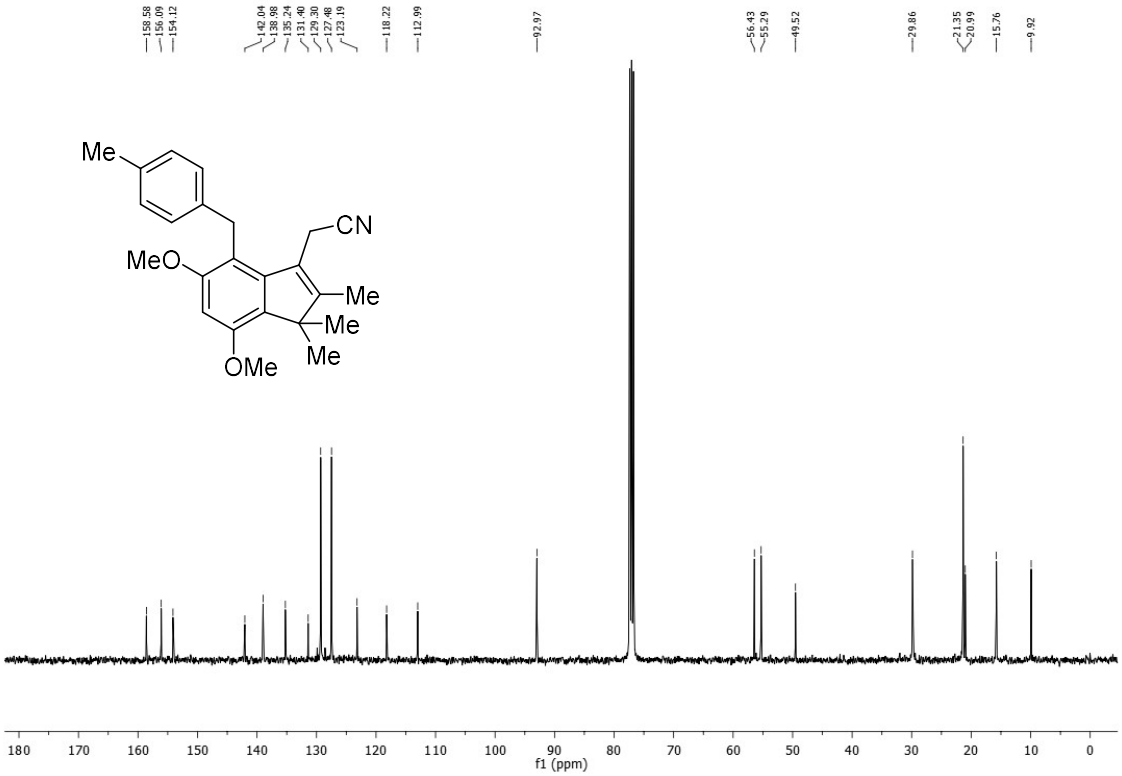
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9a**.



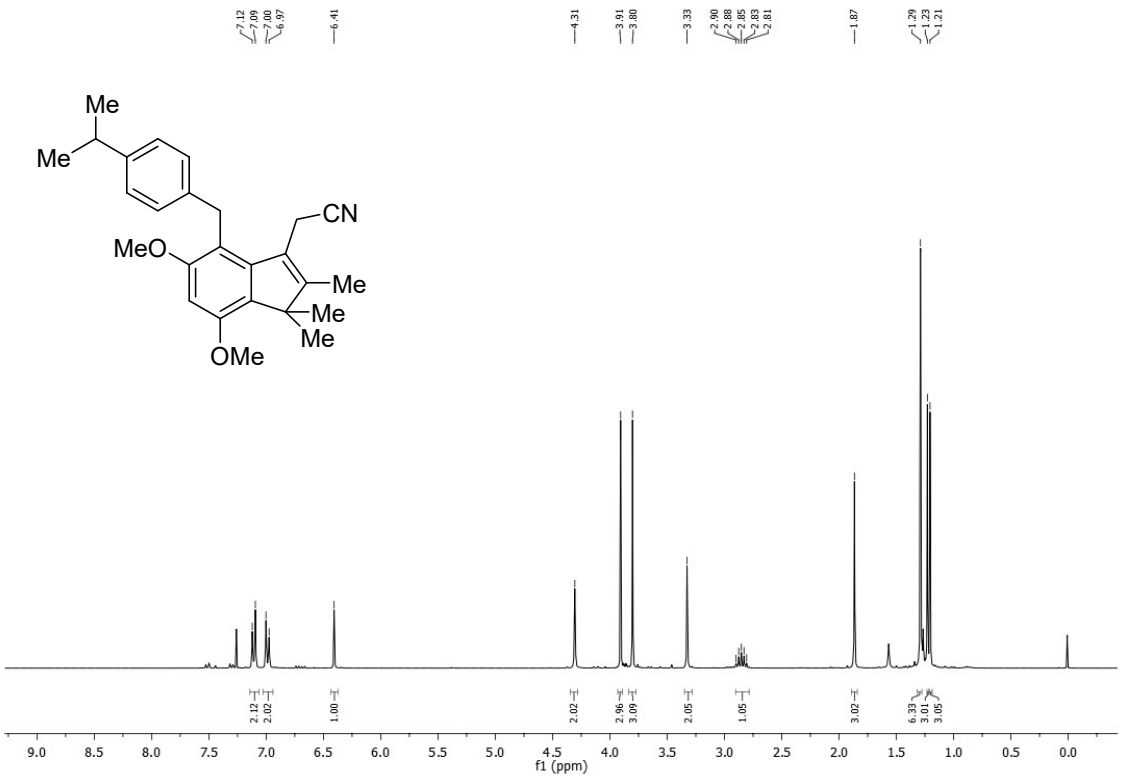
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9a**.



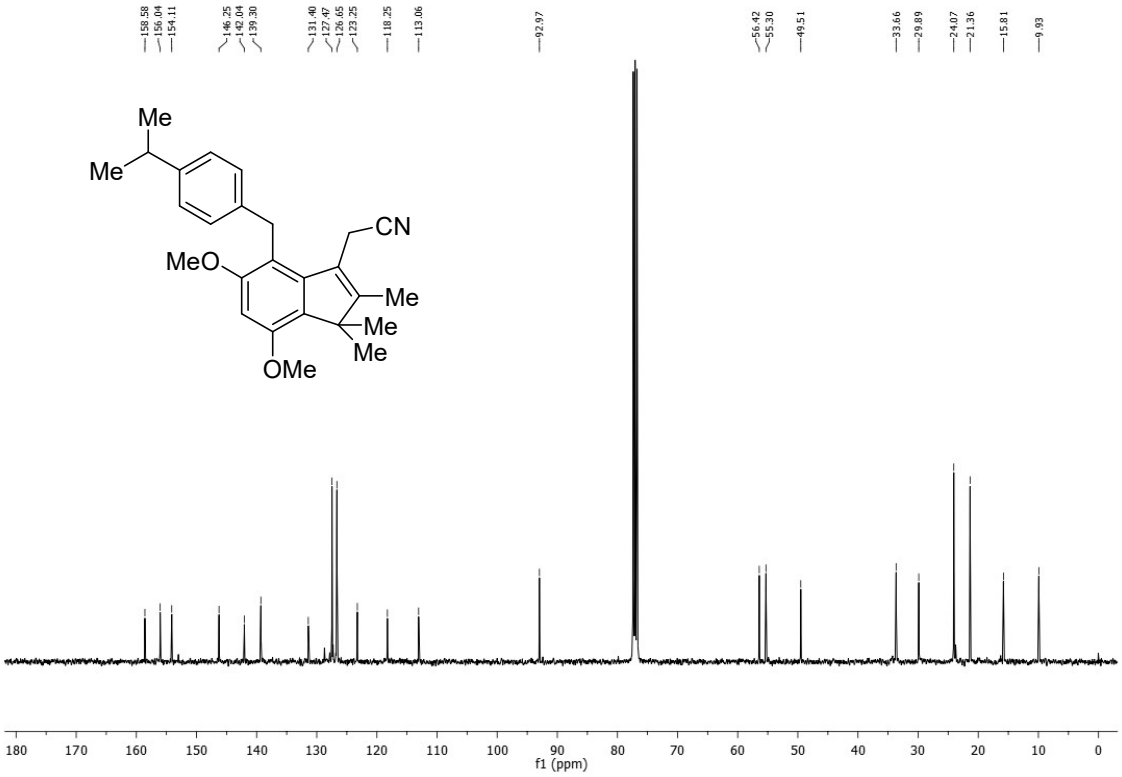
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9b**.



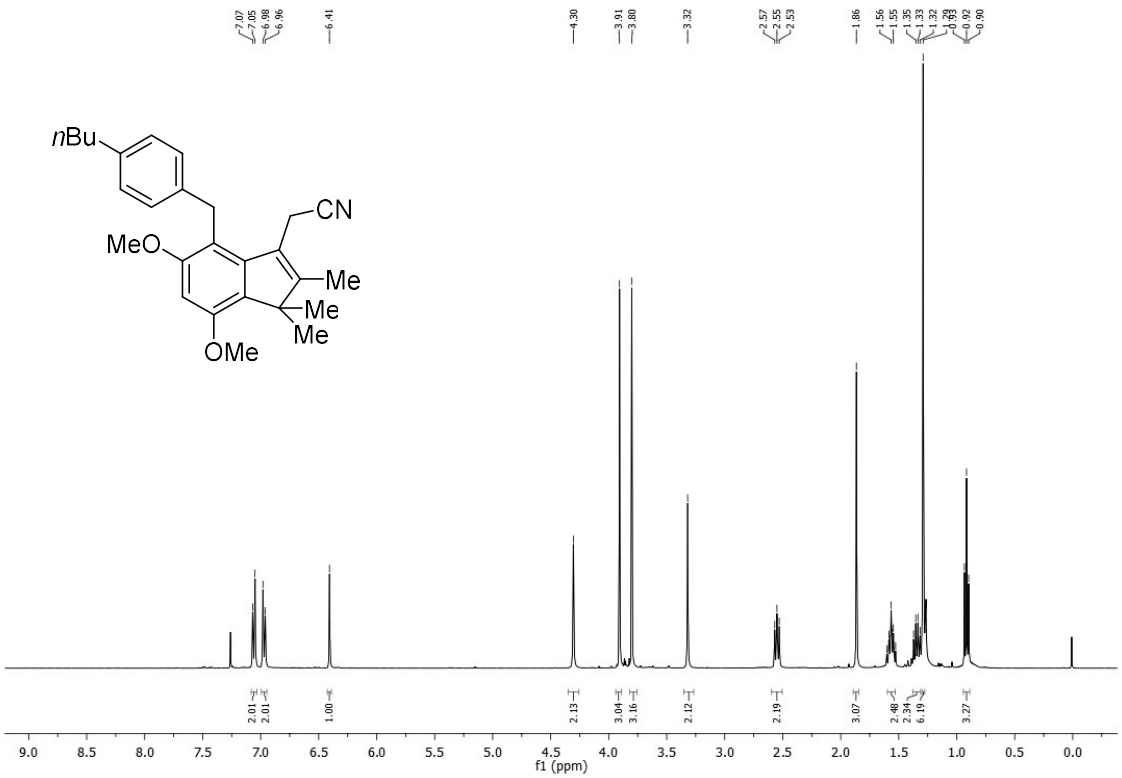
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound **9b**.



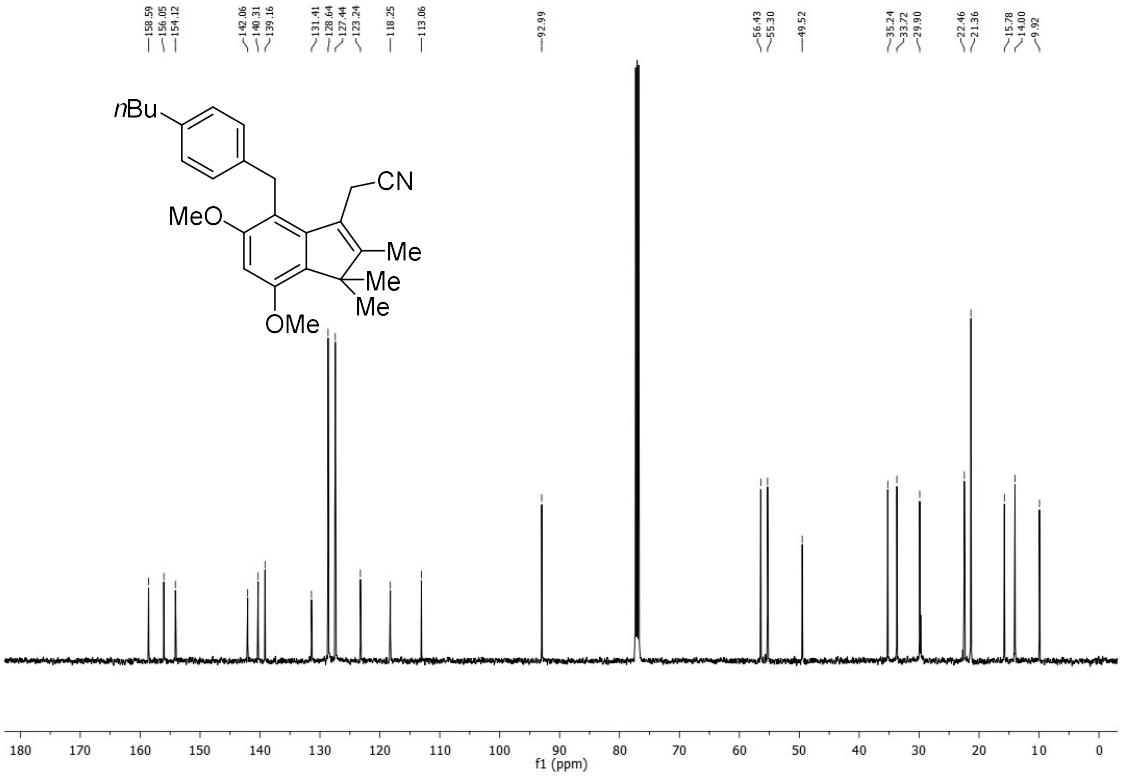
^{1}H NMR (000 MHz, $CDCl_3$) for compound **9c**.



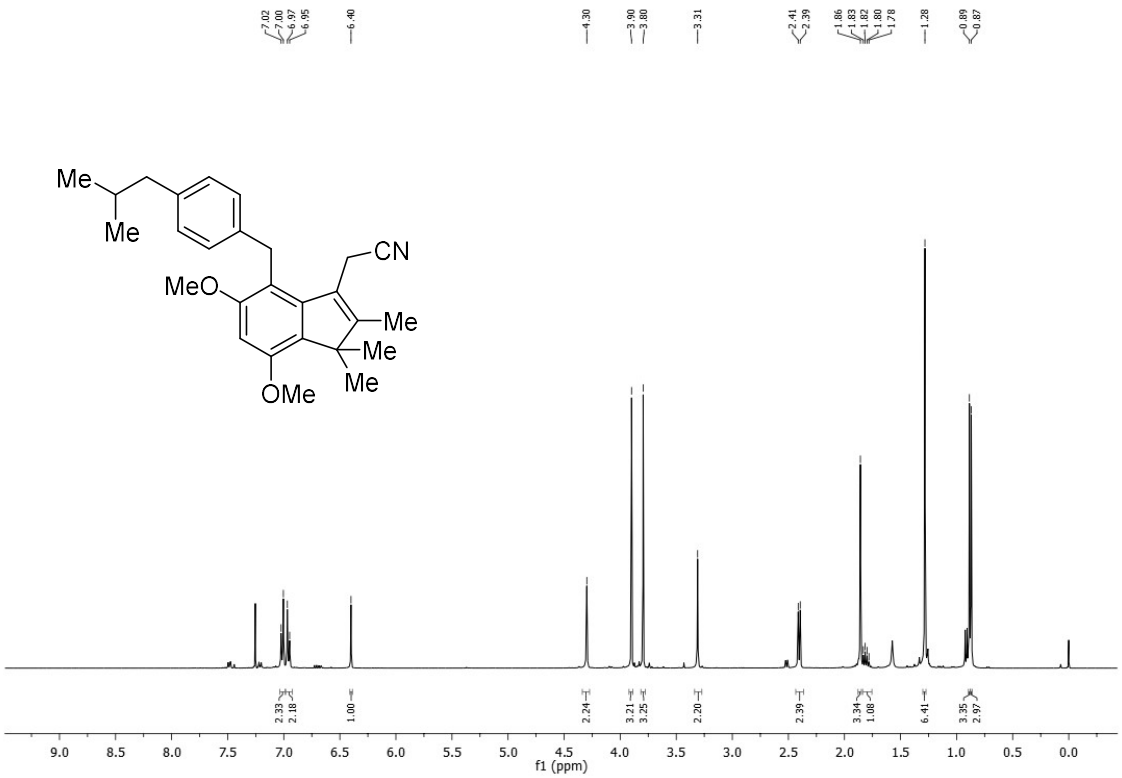
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9c**.



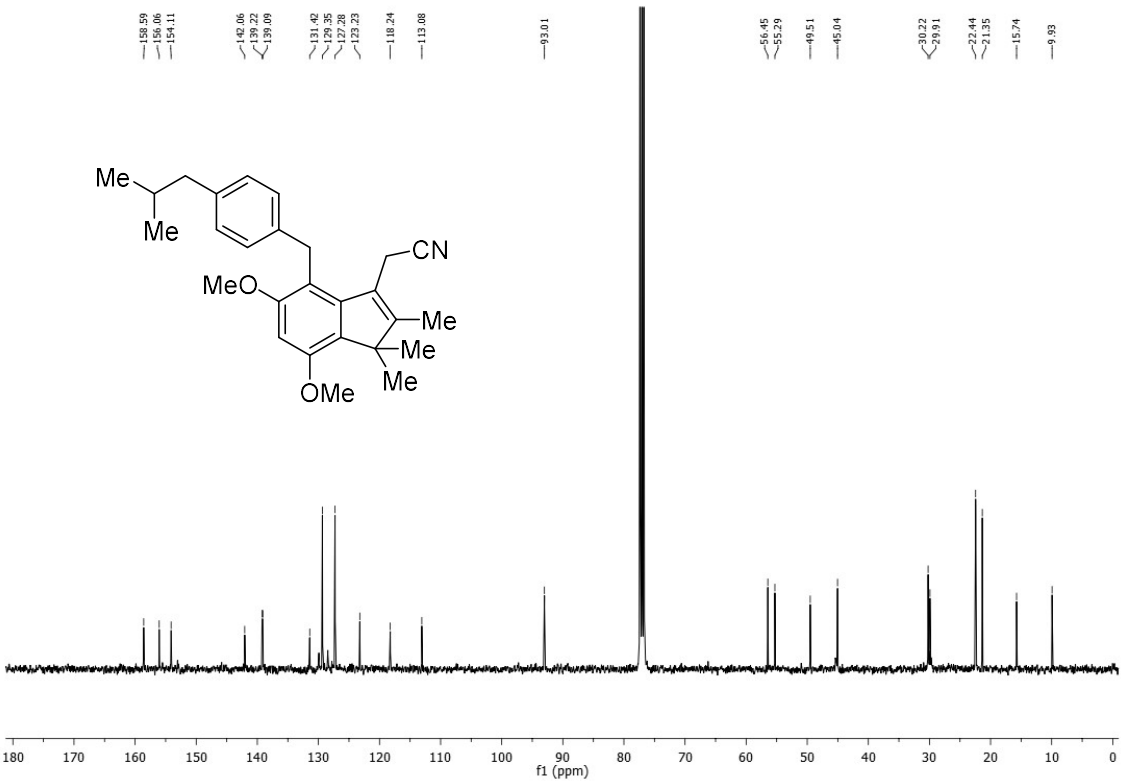
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9d**.



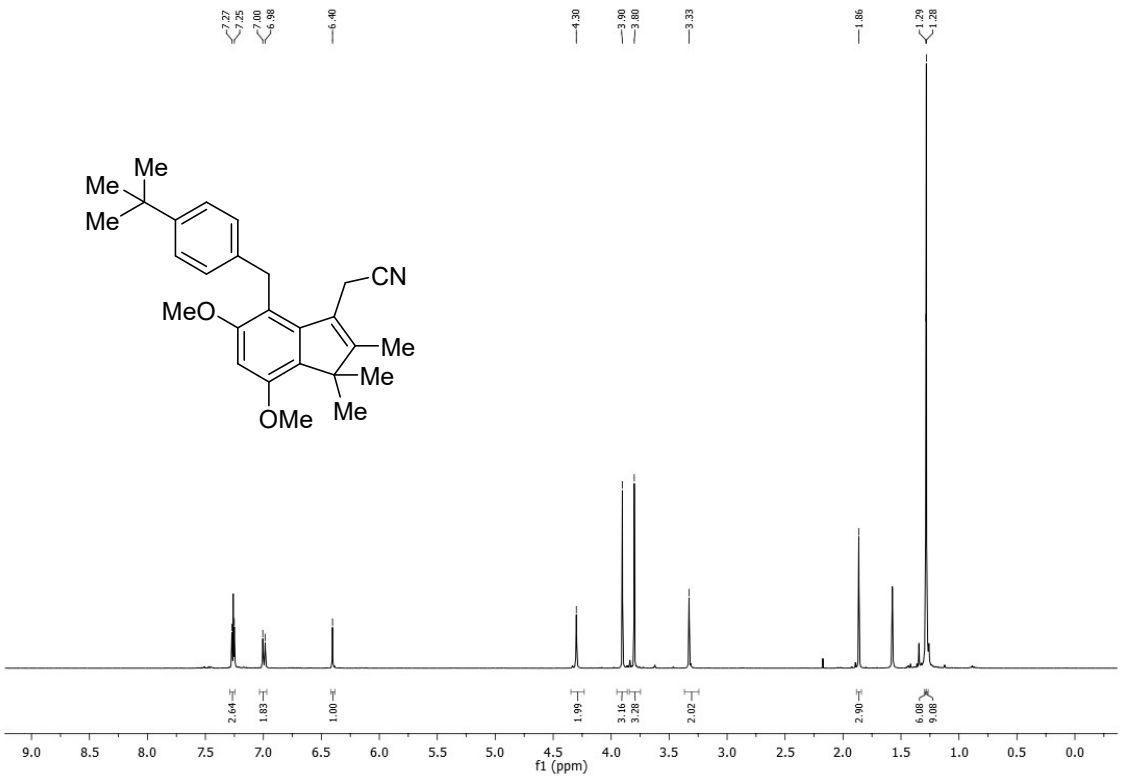
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for compound **9d**.



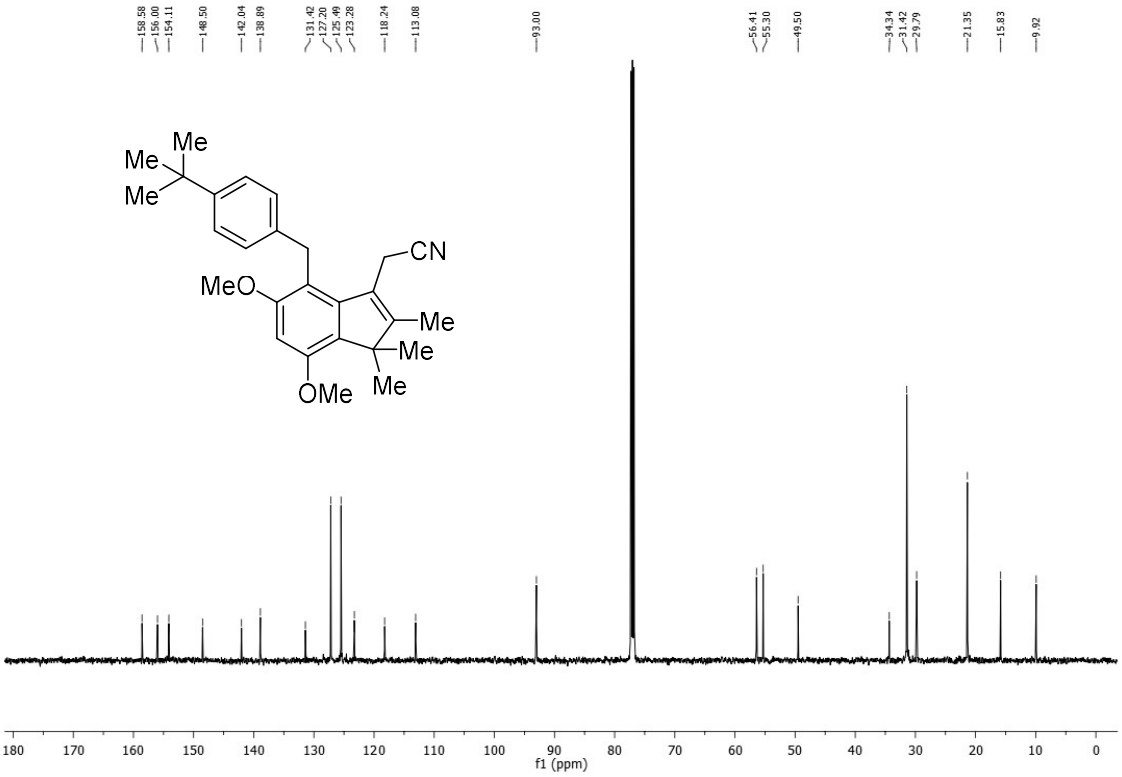
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9e**.



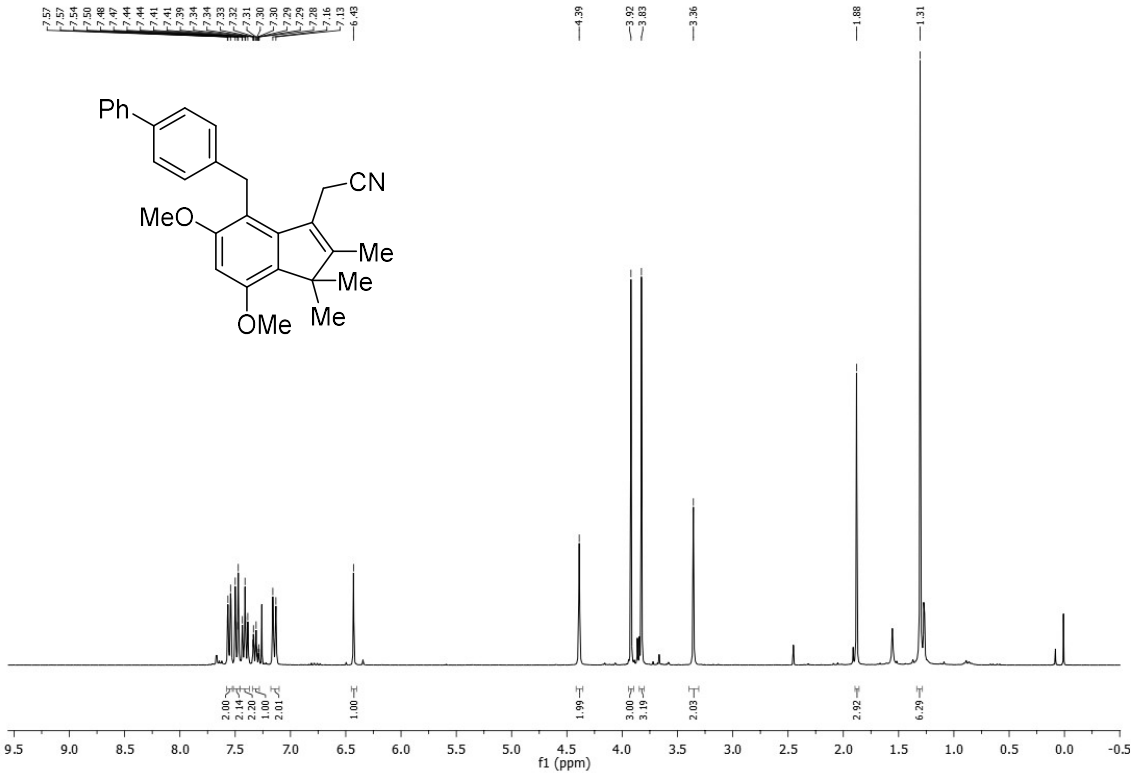
^{13}C NMR (126 MHz, $CDCl_3$) for compound **9e**.



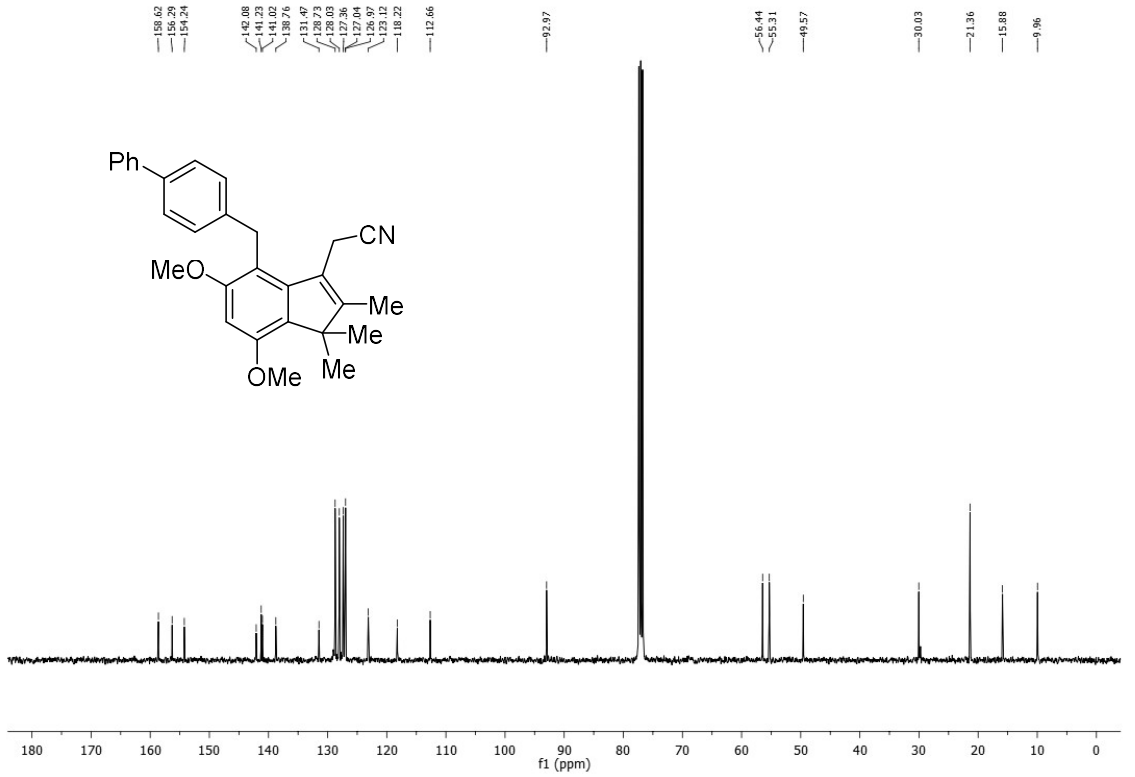
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9f**.



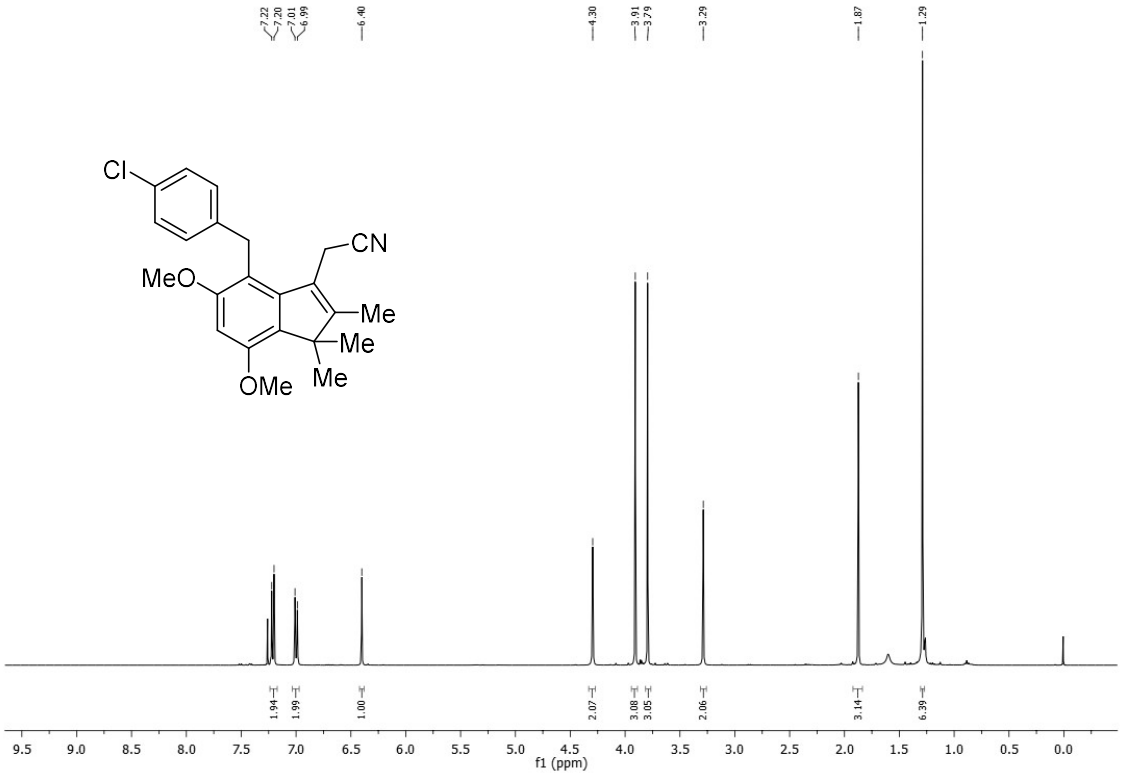
^{13}C{1H} NMR (126 MHz, $CDCl_3$) for compound **9f**.



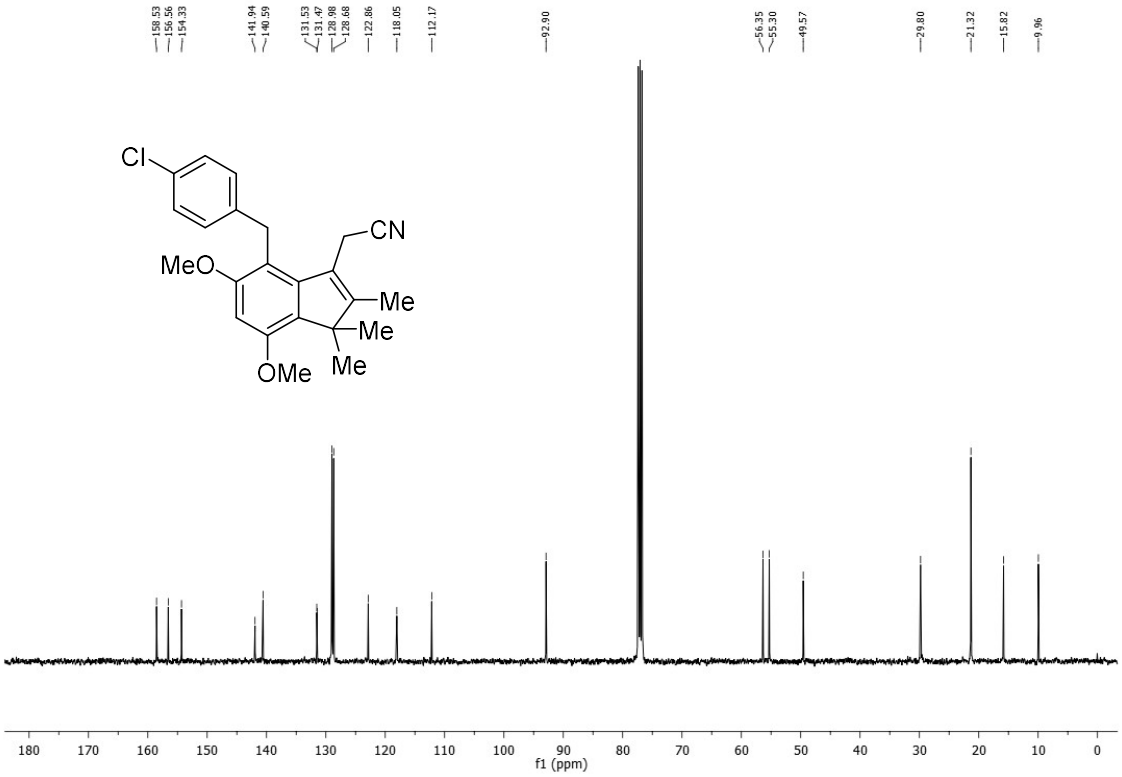
^{1}H NMR (300 MHz, $CDCl_3$) for compound **9h**.



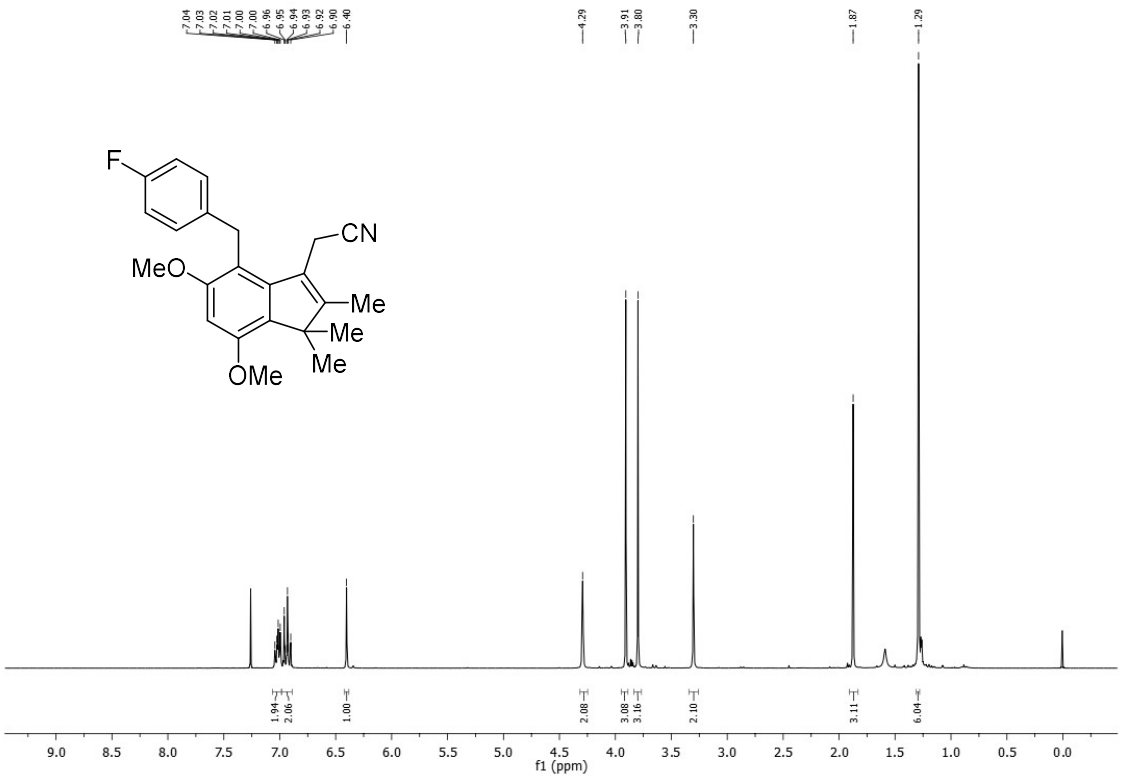
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9g**.



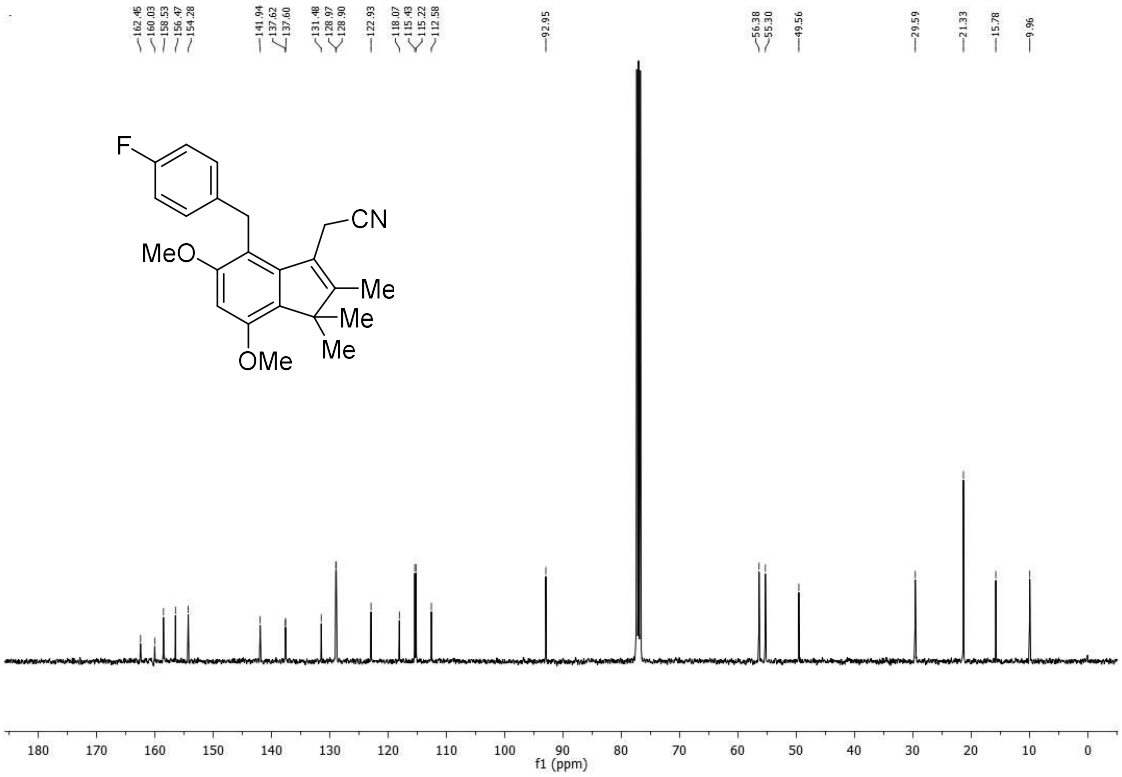
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9h**.



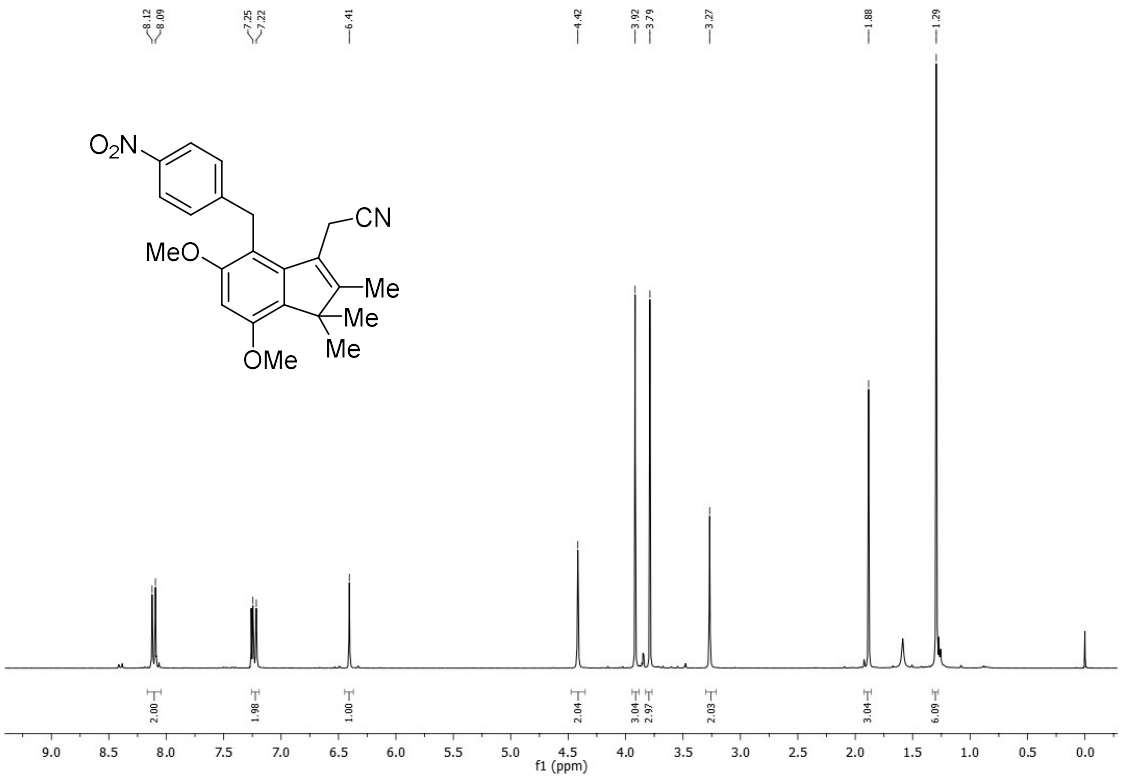
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound **9h**.



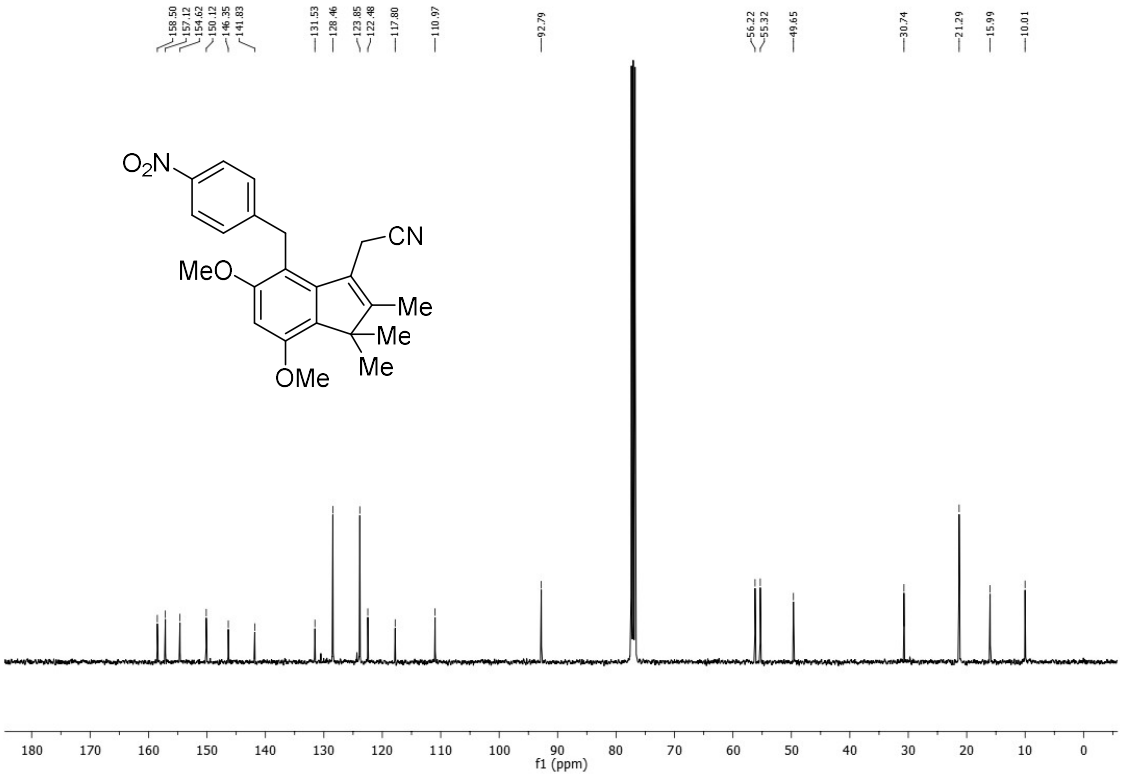
^{1}H NMR (300 MHz, $CDCl_3$) for compound **9i**.



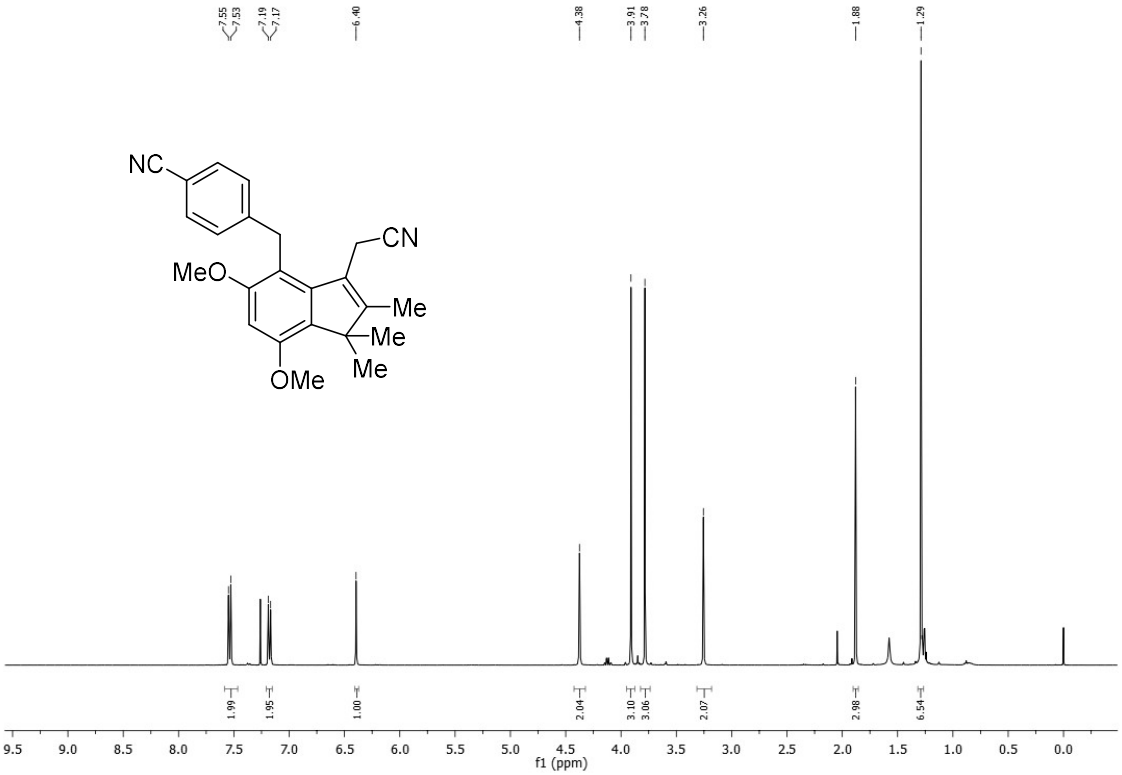
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9i**.



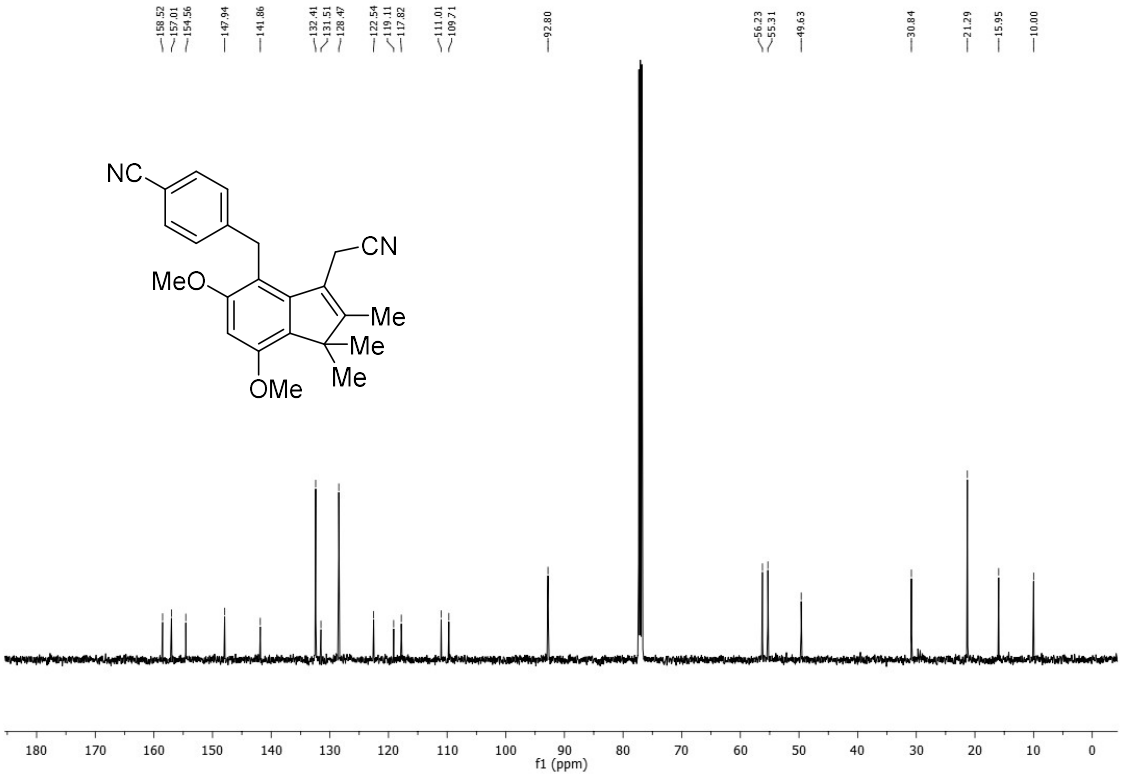
^{1}H NMR (300 MHz, $CDCl_3$) for compound **9j**.



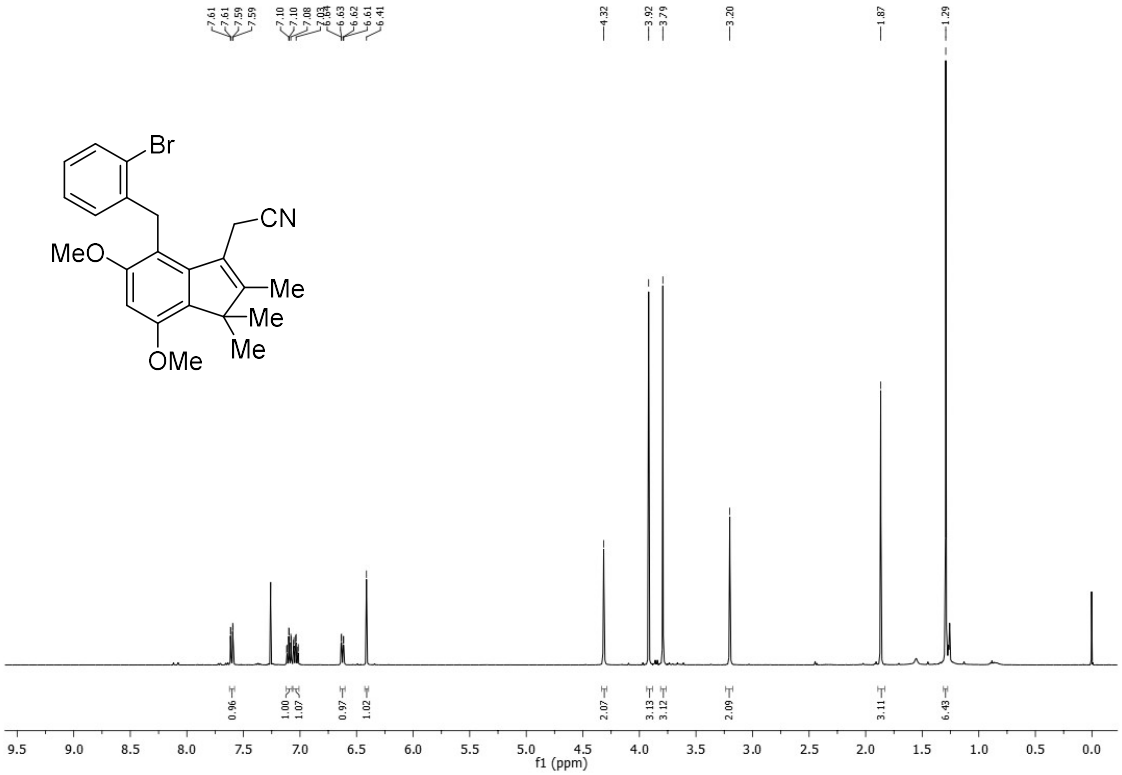
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound **9j**.



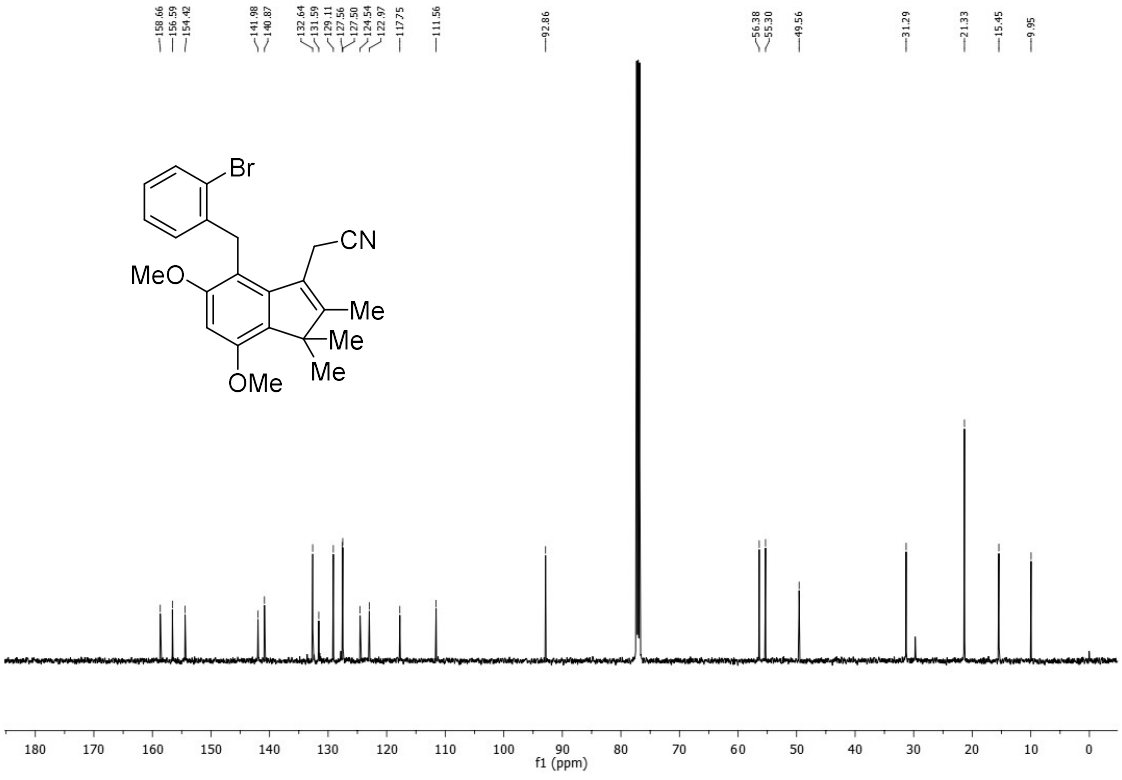
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9k**.



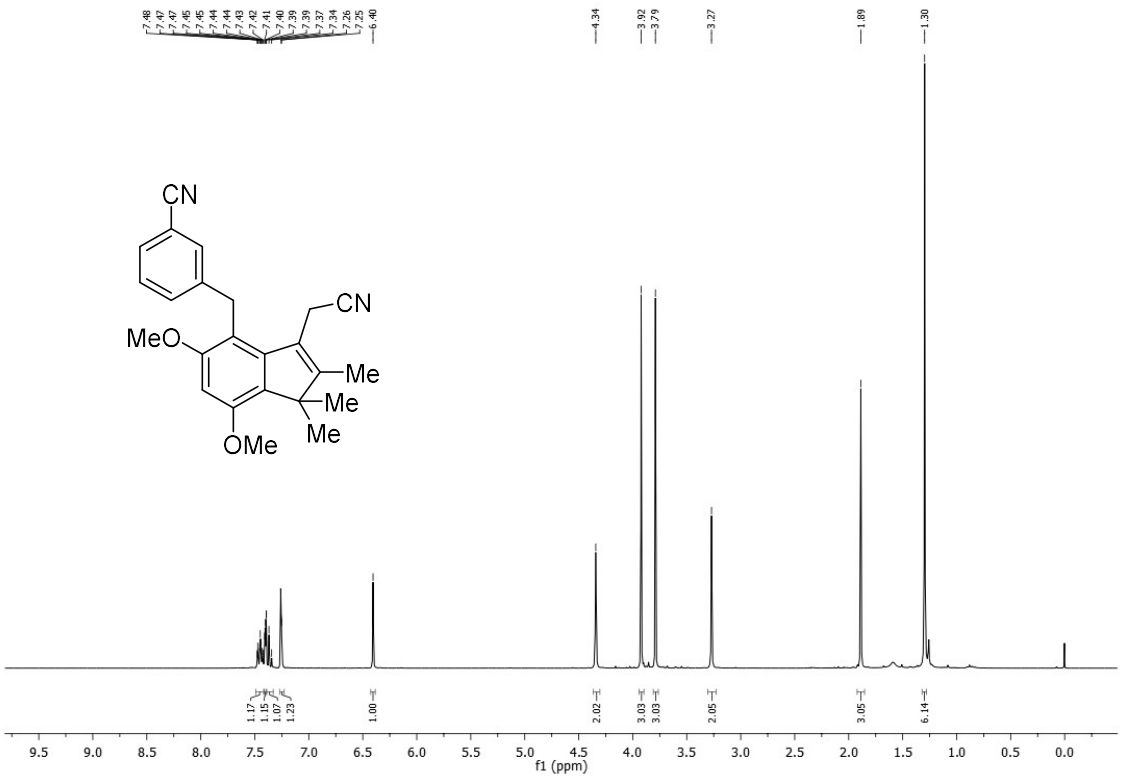
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) for compound **9k**.



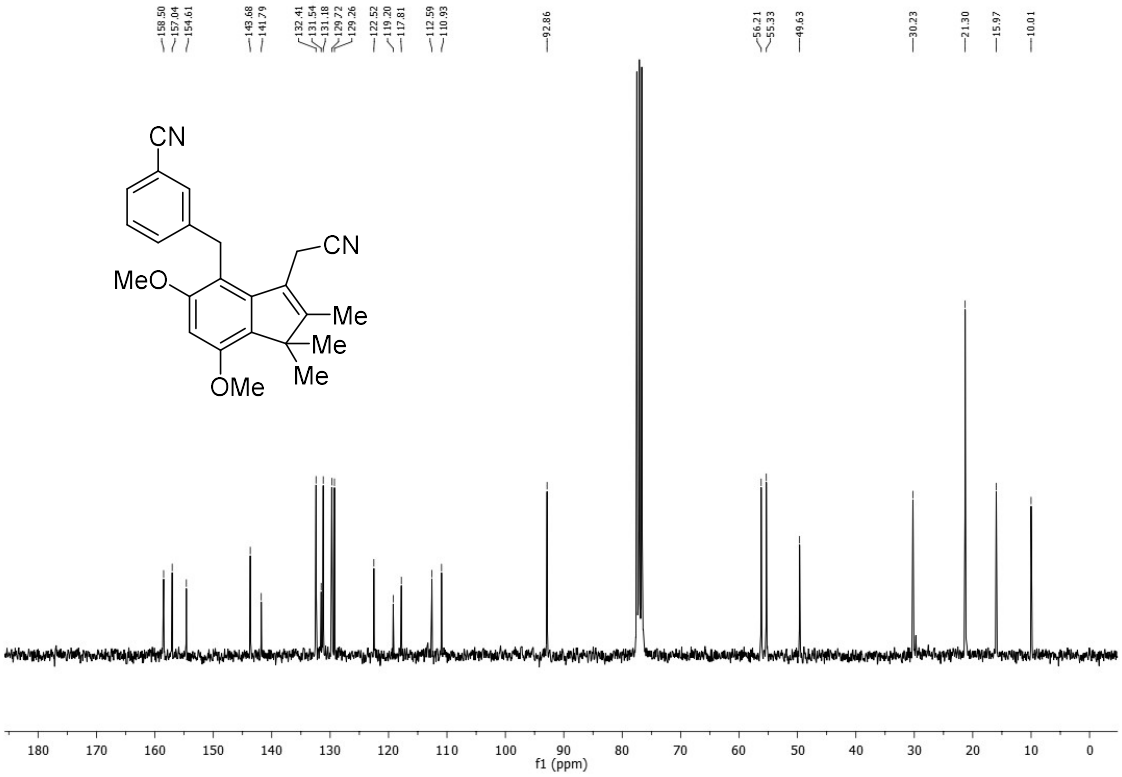
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9l**.



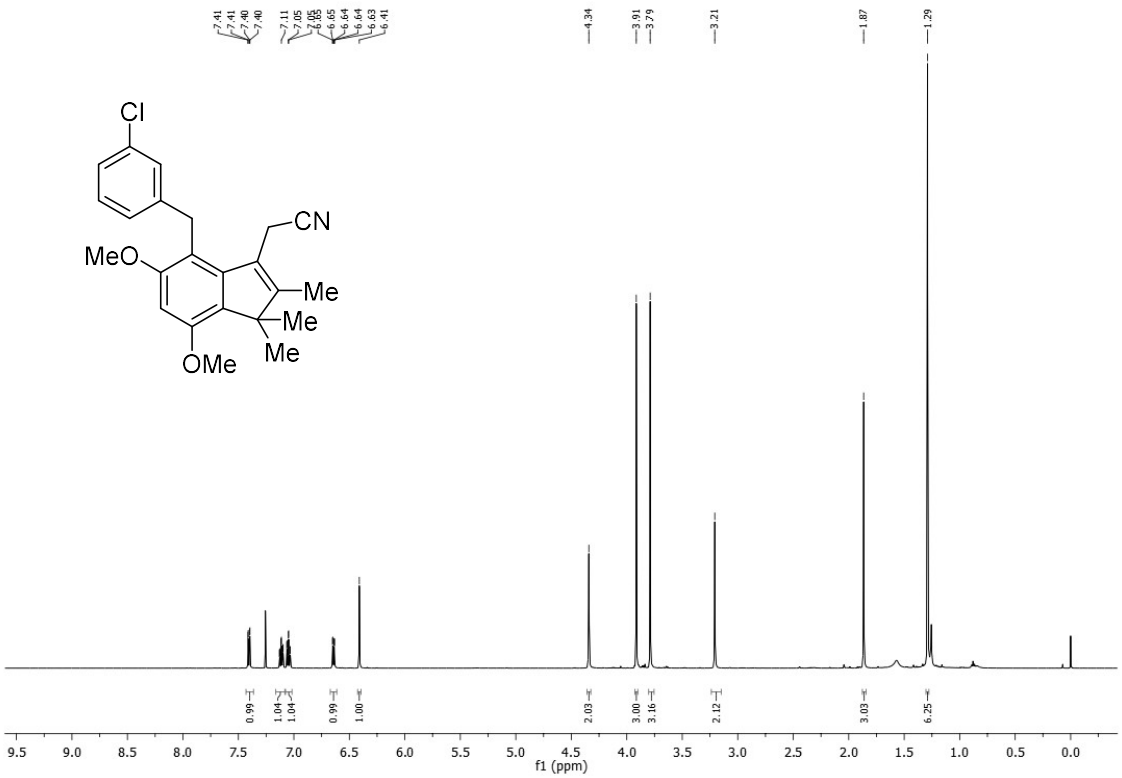
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for compound **9l**.



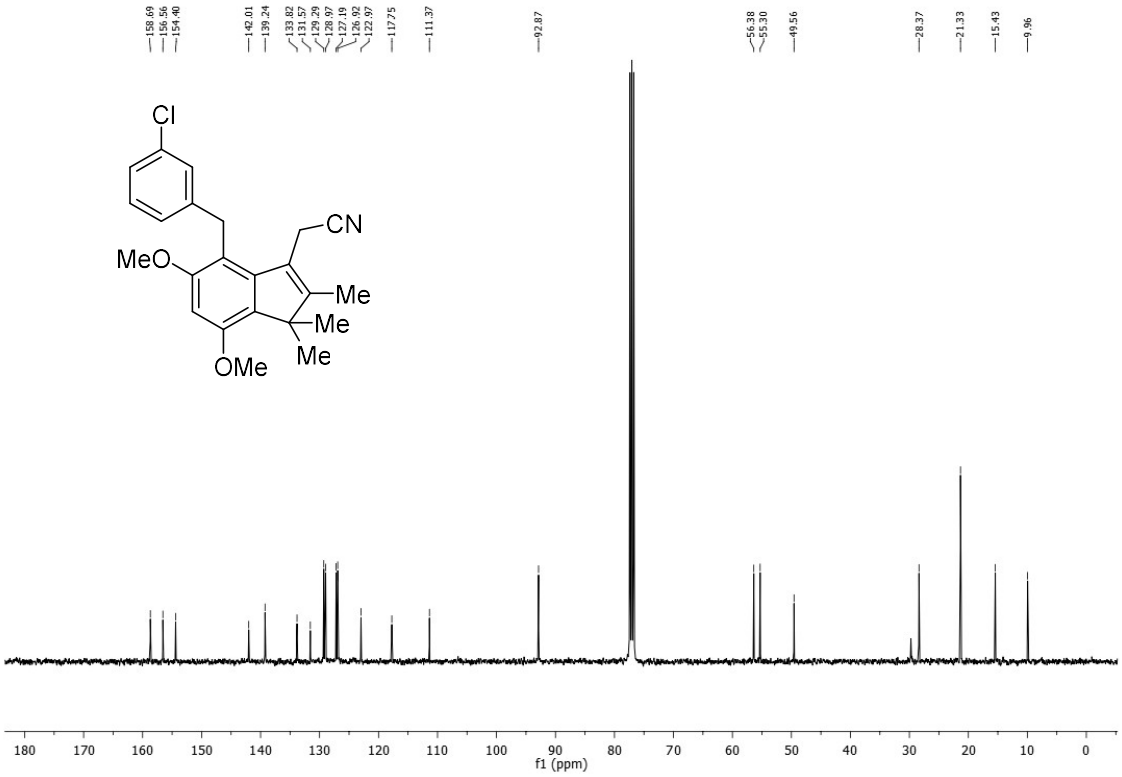
^{1}H NMR (300 MHz, $CDCl_3$) for compound **9m**.



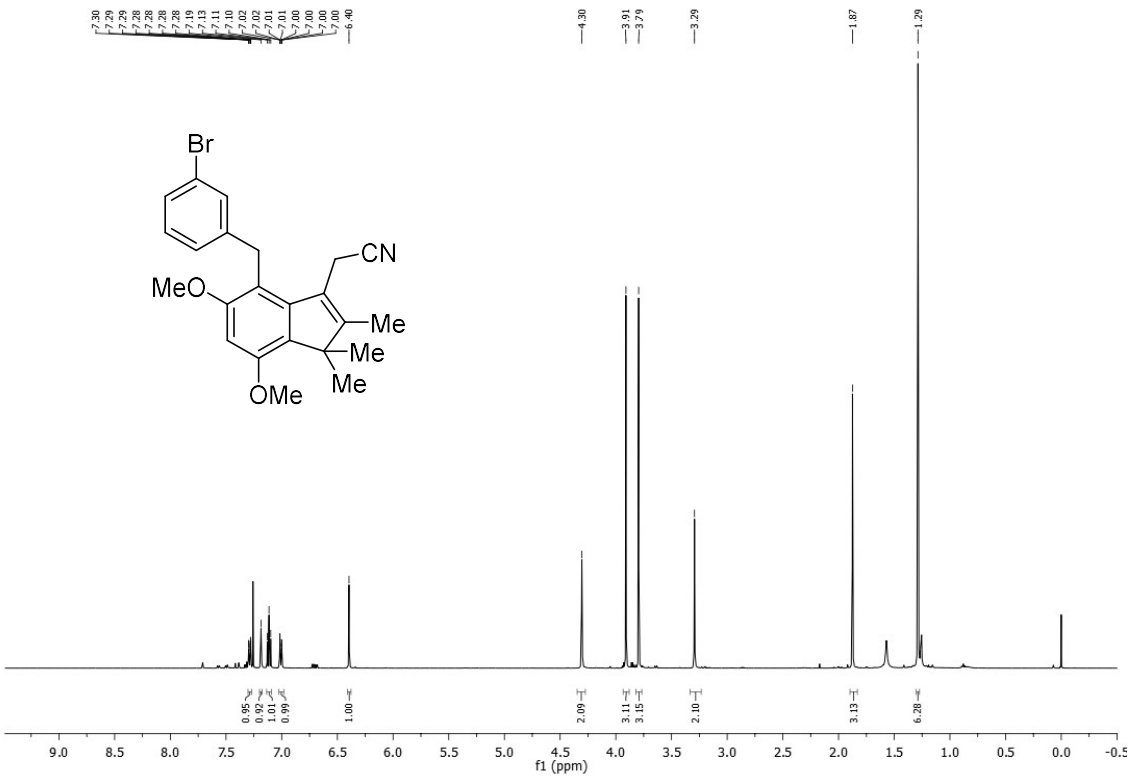
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) for compound **9m**.



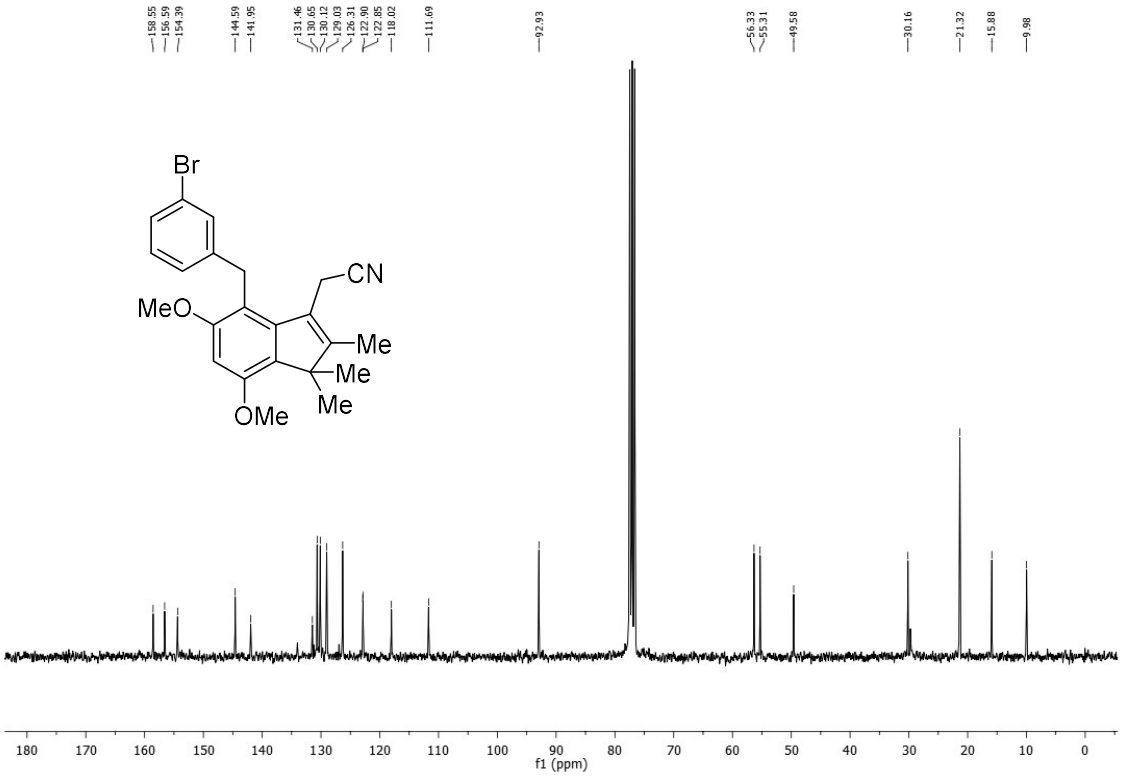
^{1}H NMR (500 MHz, $CDCl_3$) for compound **9n**.



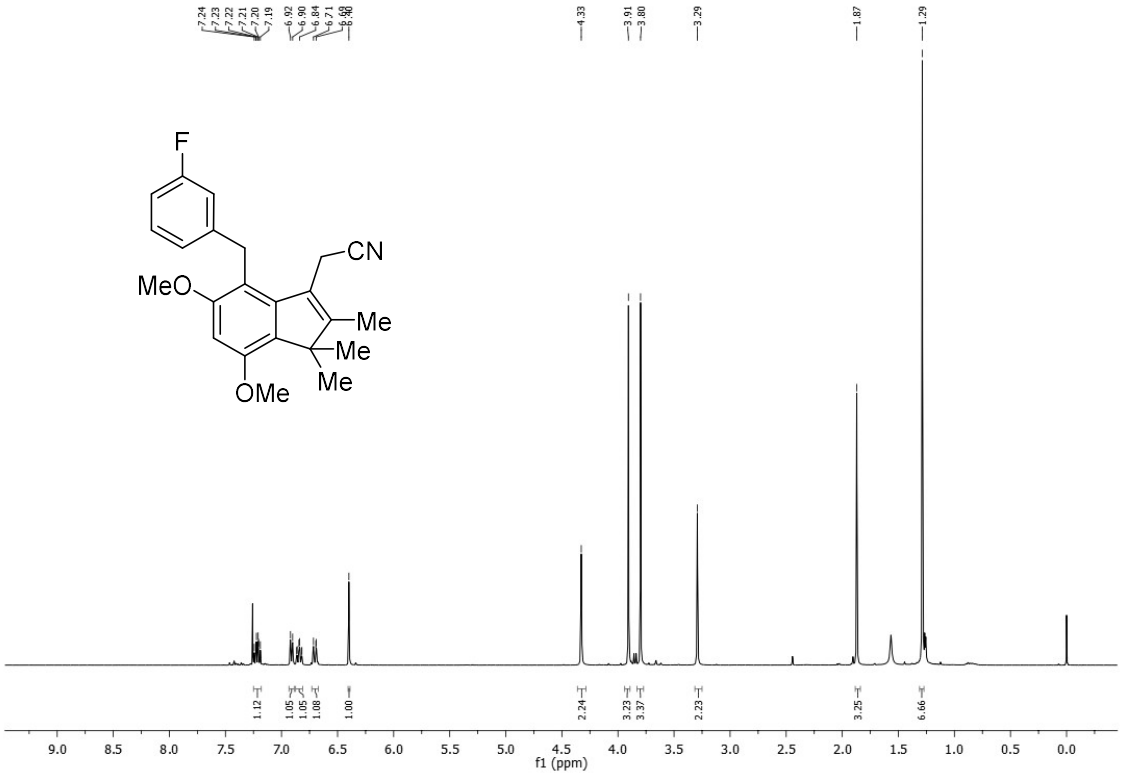
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9n**.



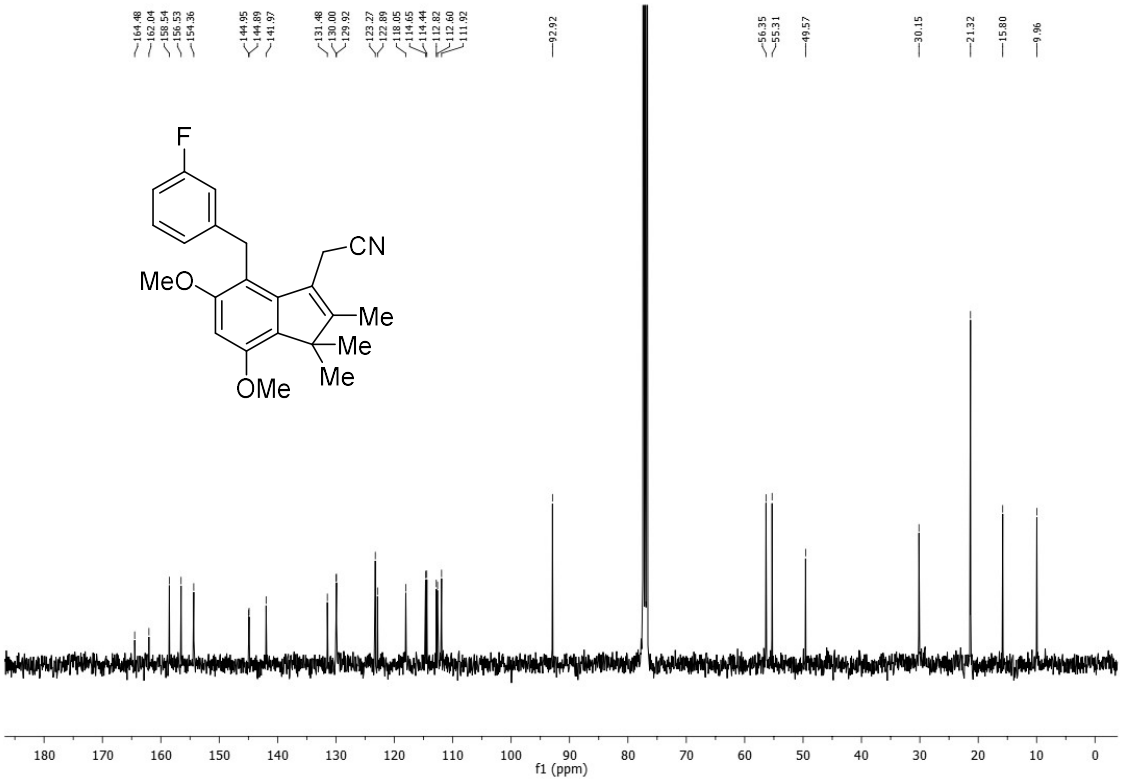
^{1}H NMR (500 MHz, $CDCl_3$) for compound **9o**.



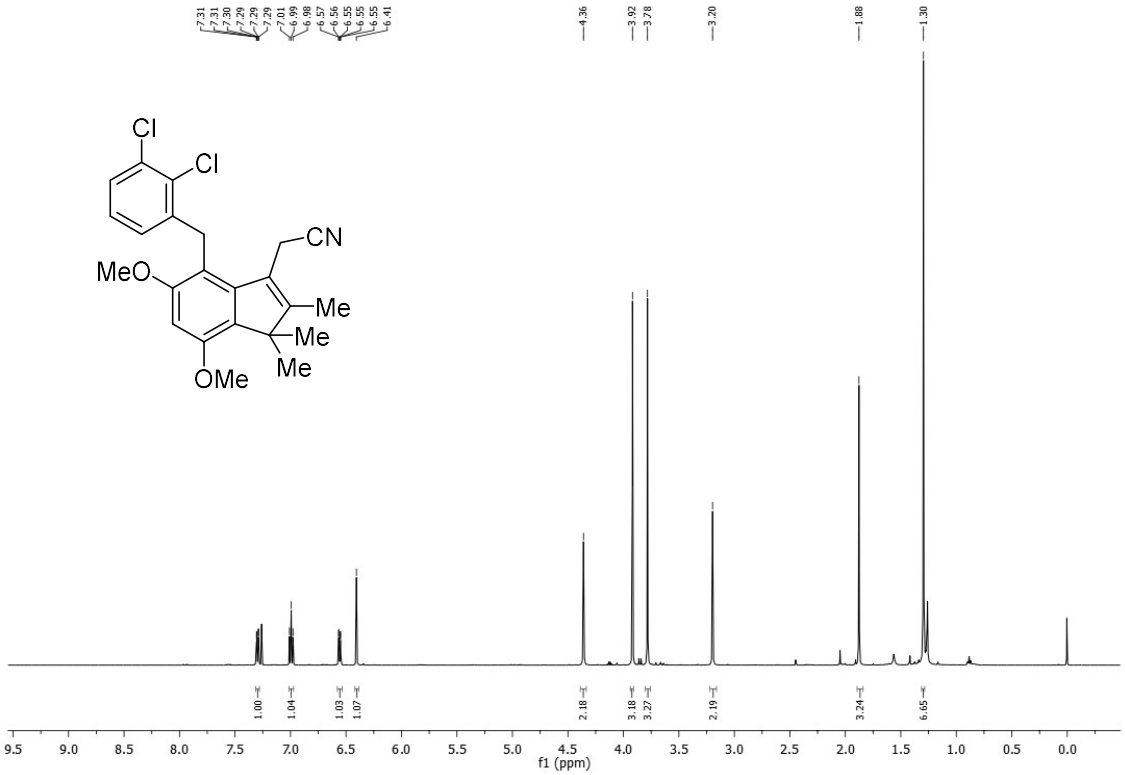
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) for compound **9o**.



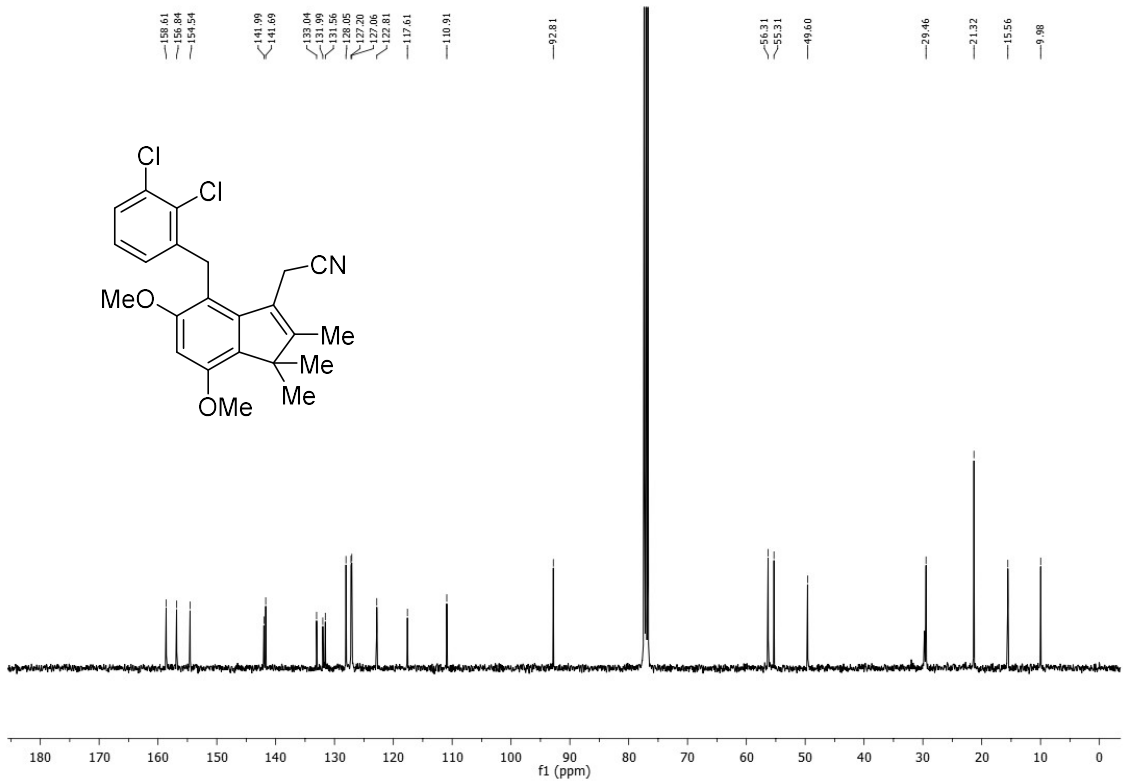
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9p**.



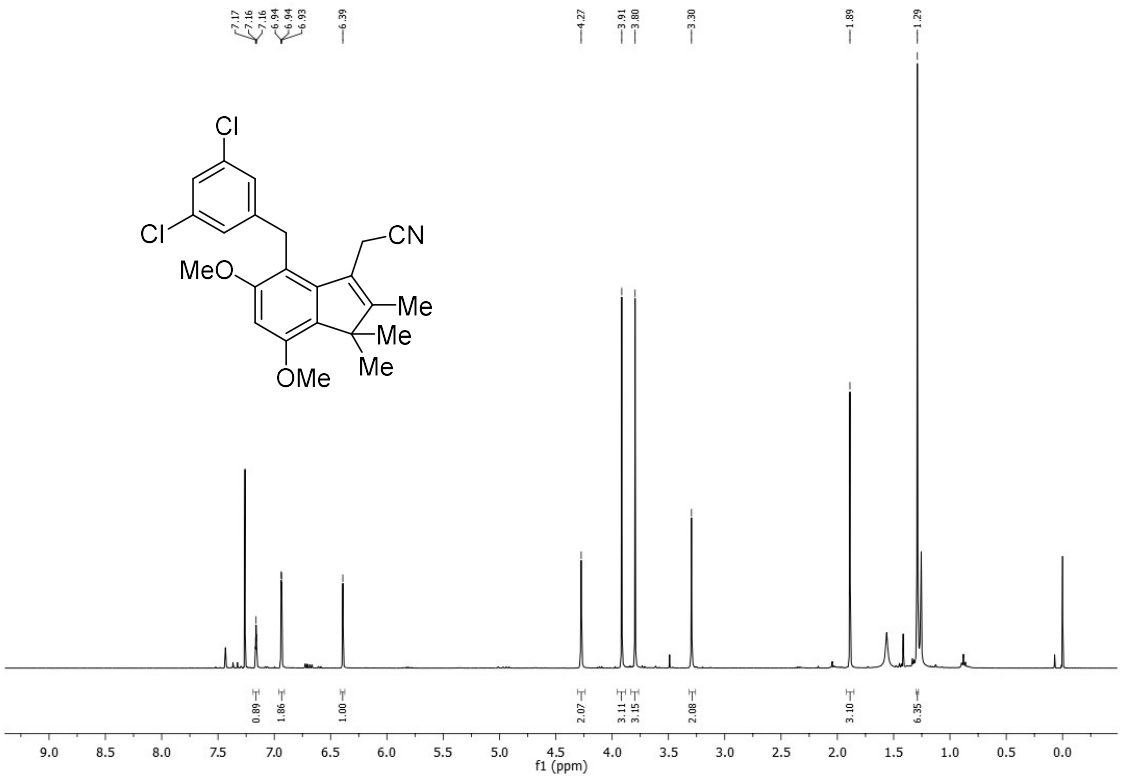
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound **9p**.



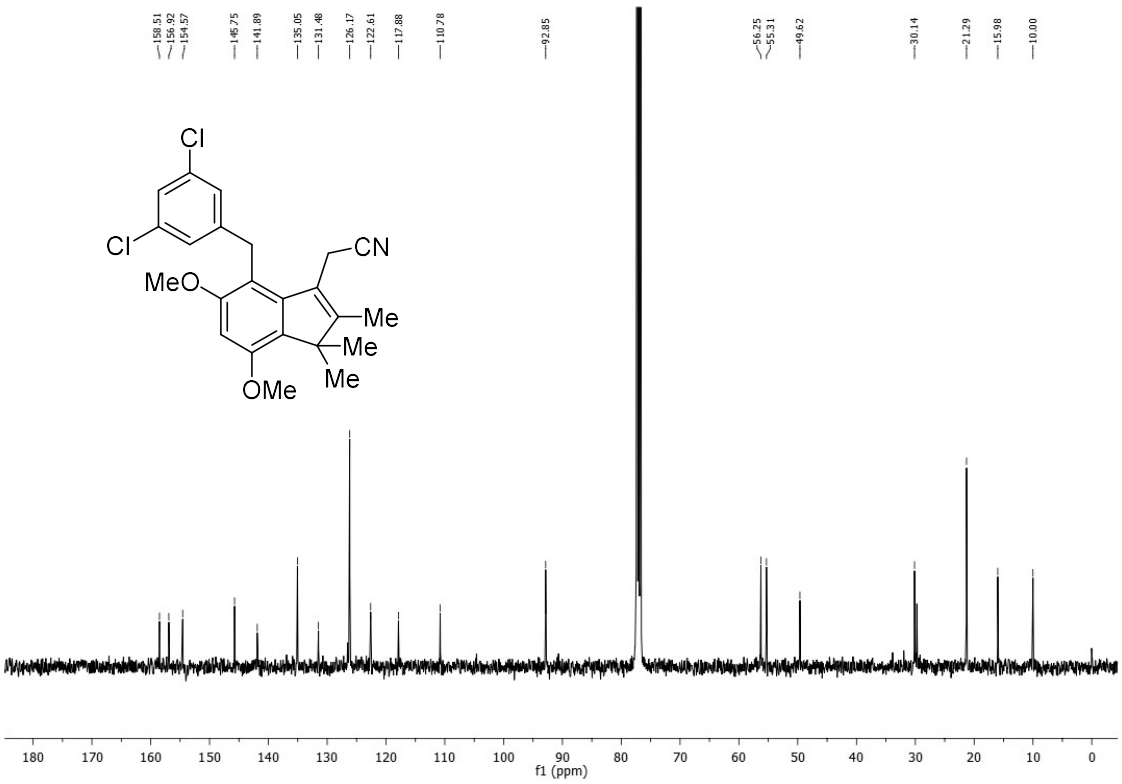
^{1}H NMR (500 MHz, $CDCl_3$) for compound **9q**.



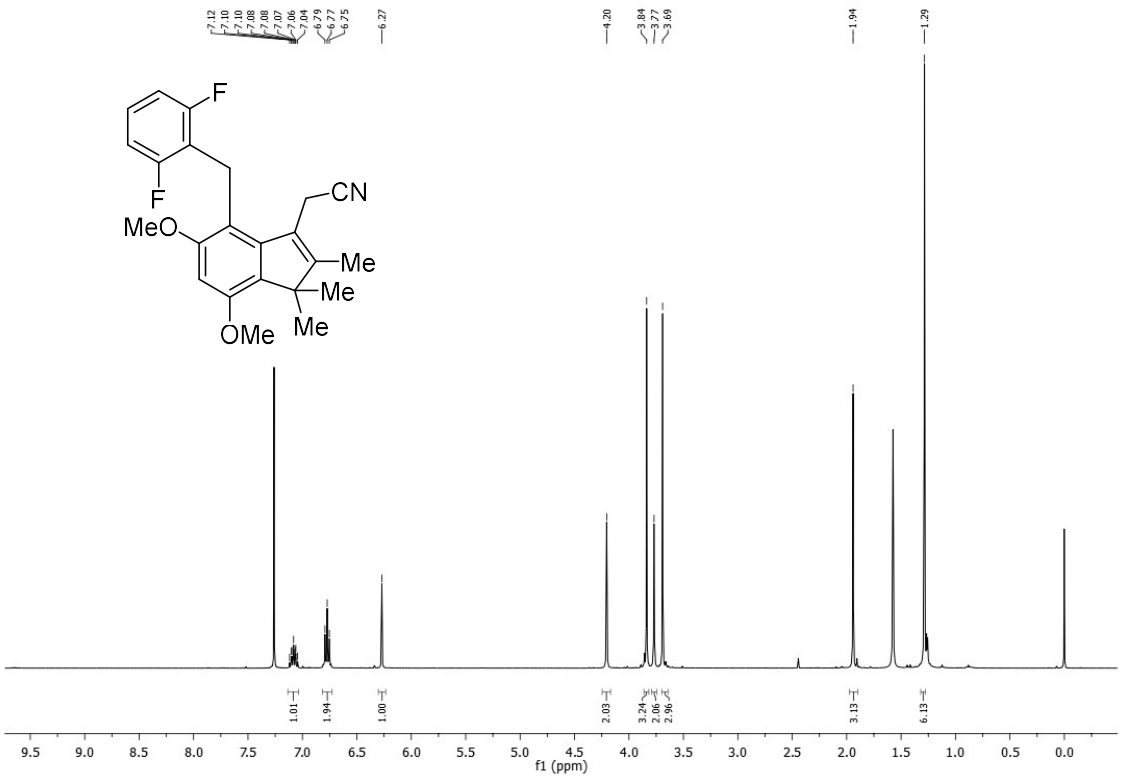
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9q**.



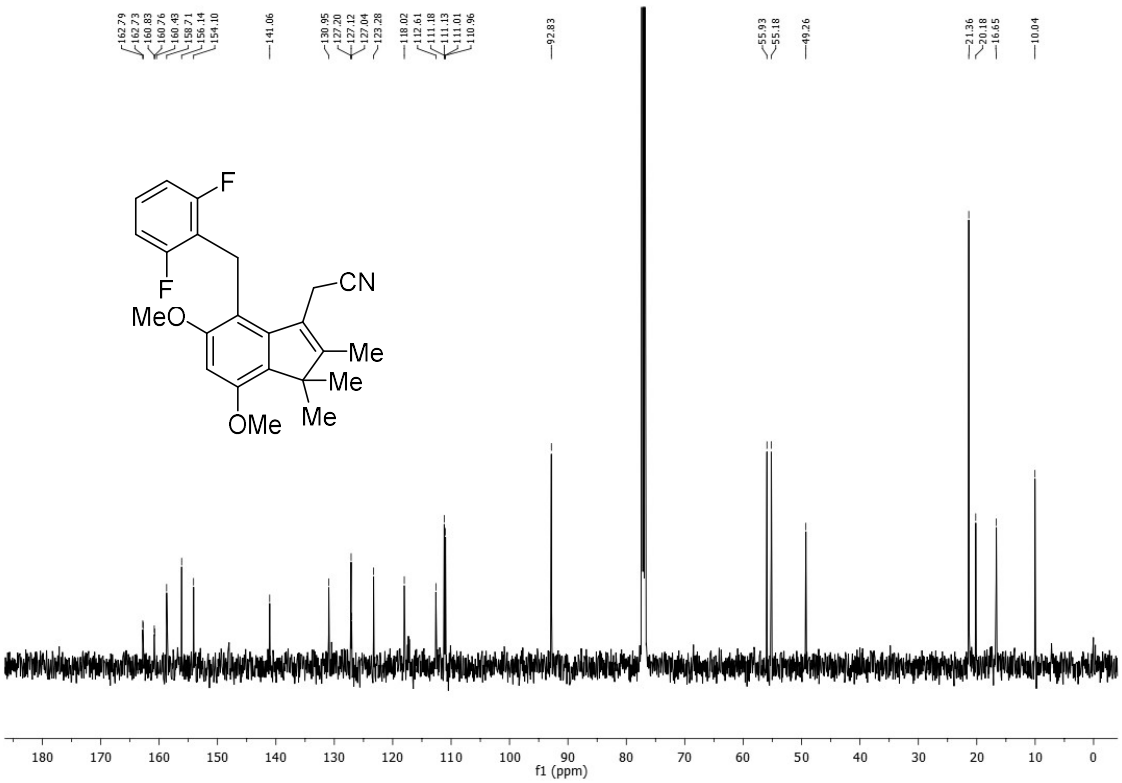
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9r**.



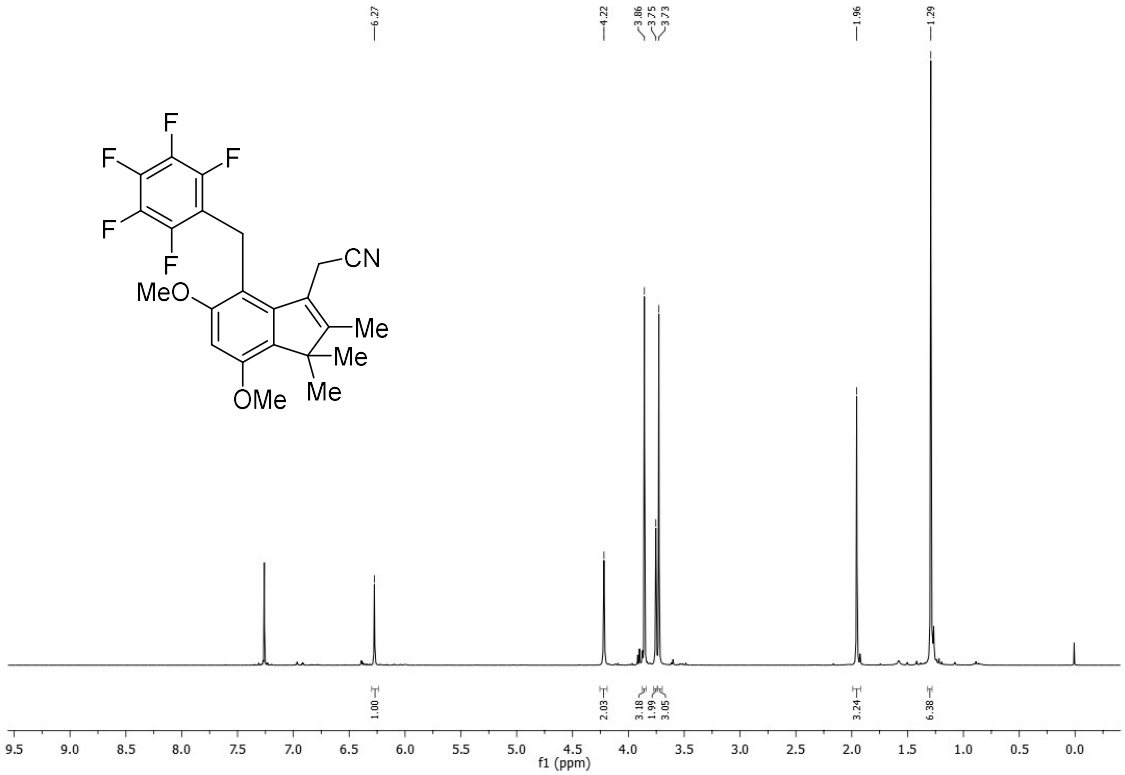
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound **9r**.



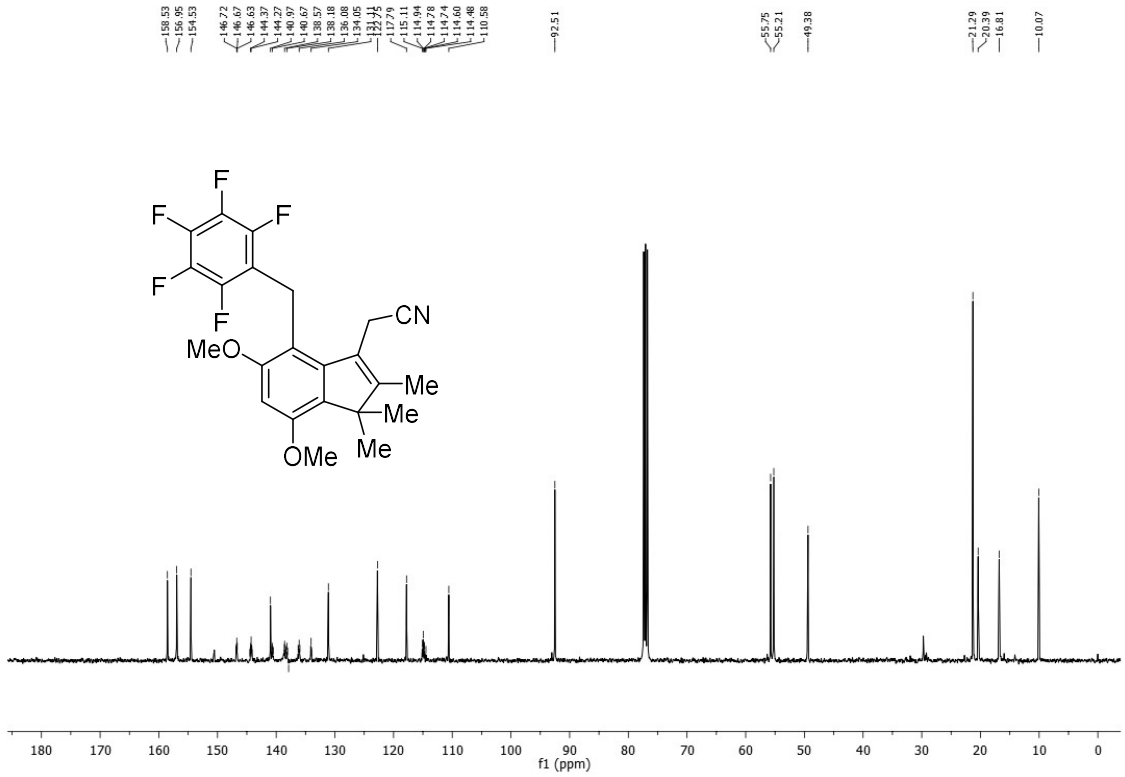
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9s**.



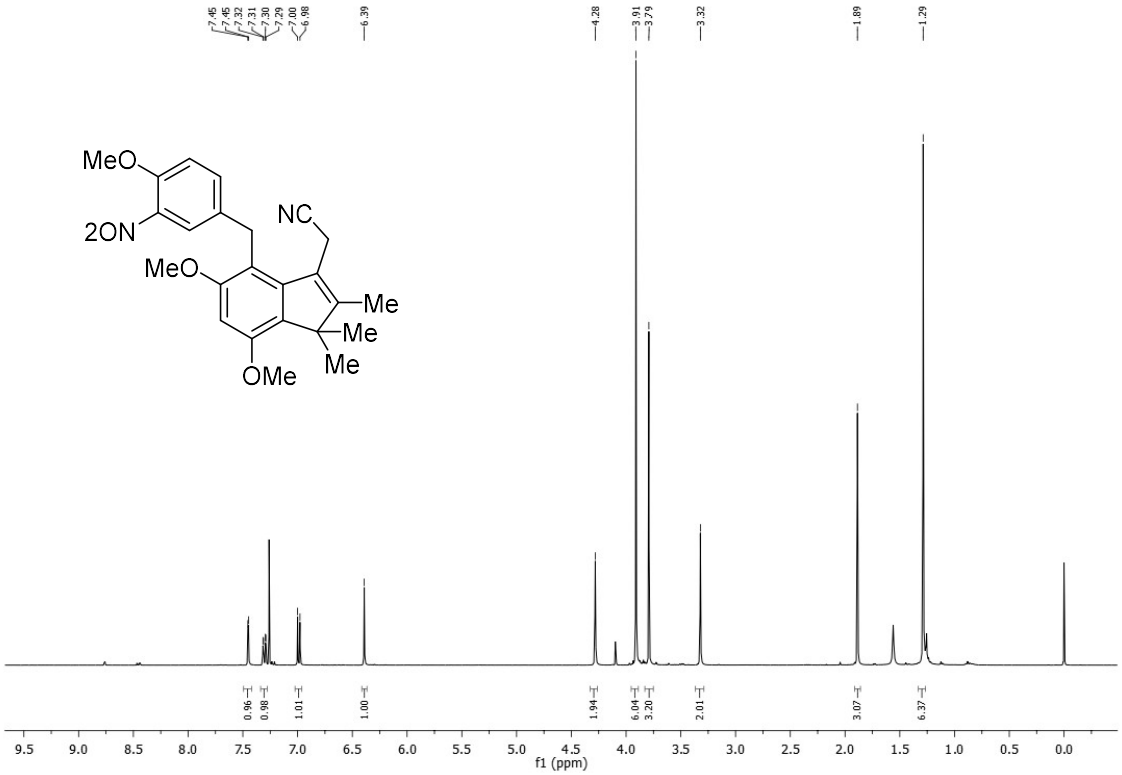
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for compound **9s**.



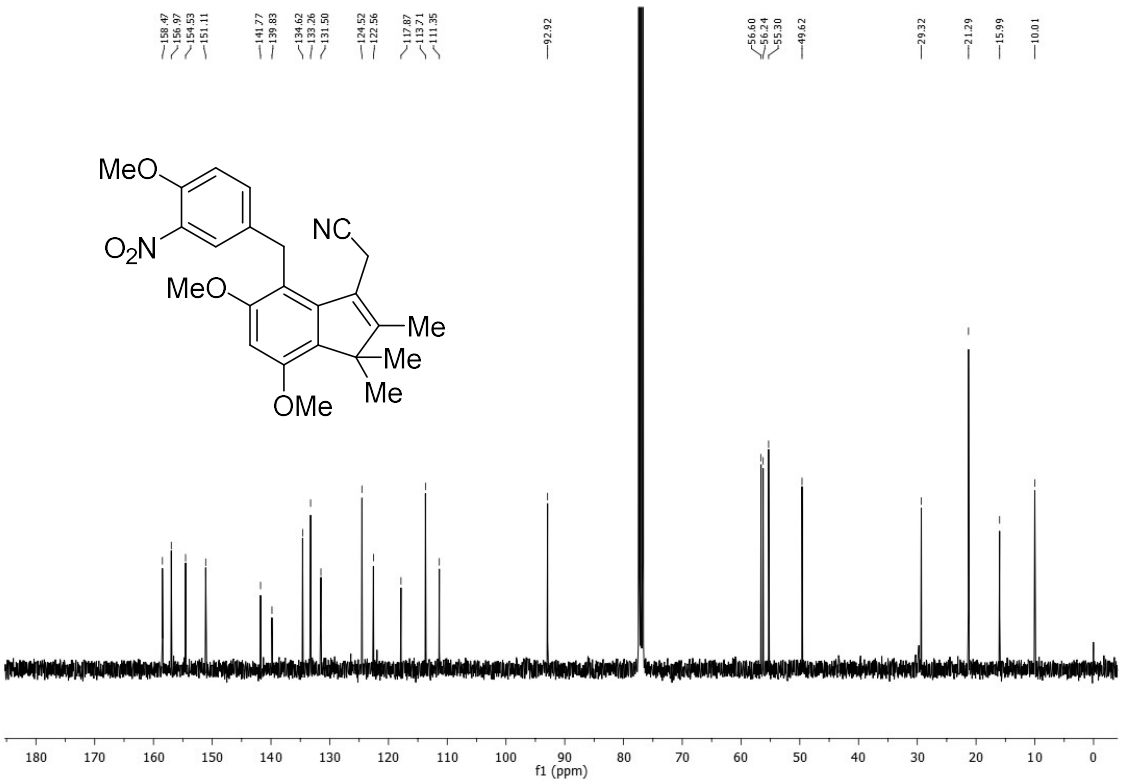
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9t**.



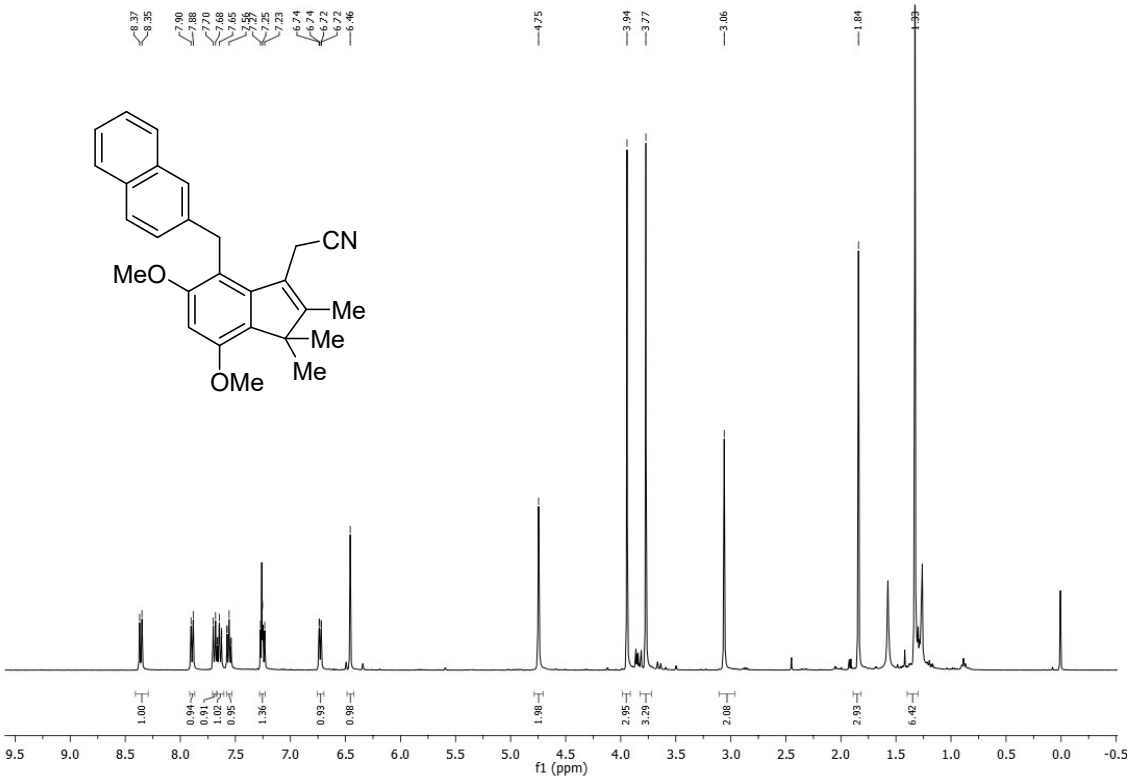
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound **9t**.



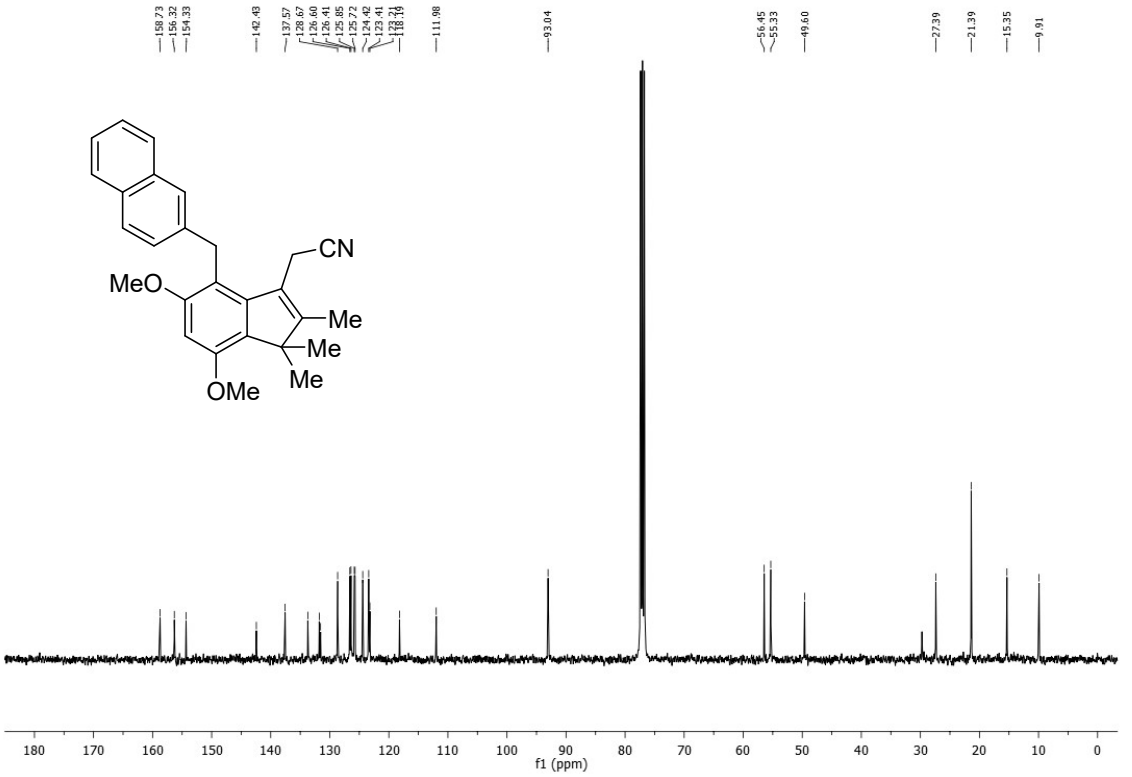
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9u**.



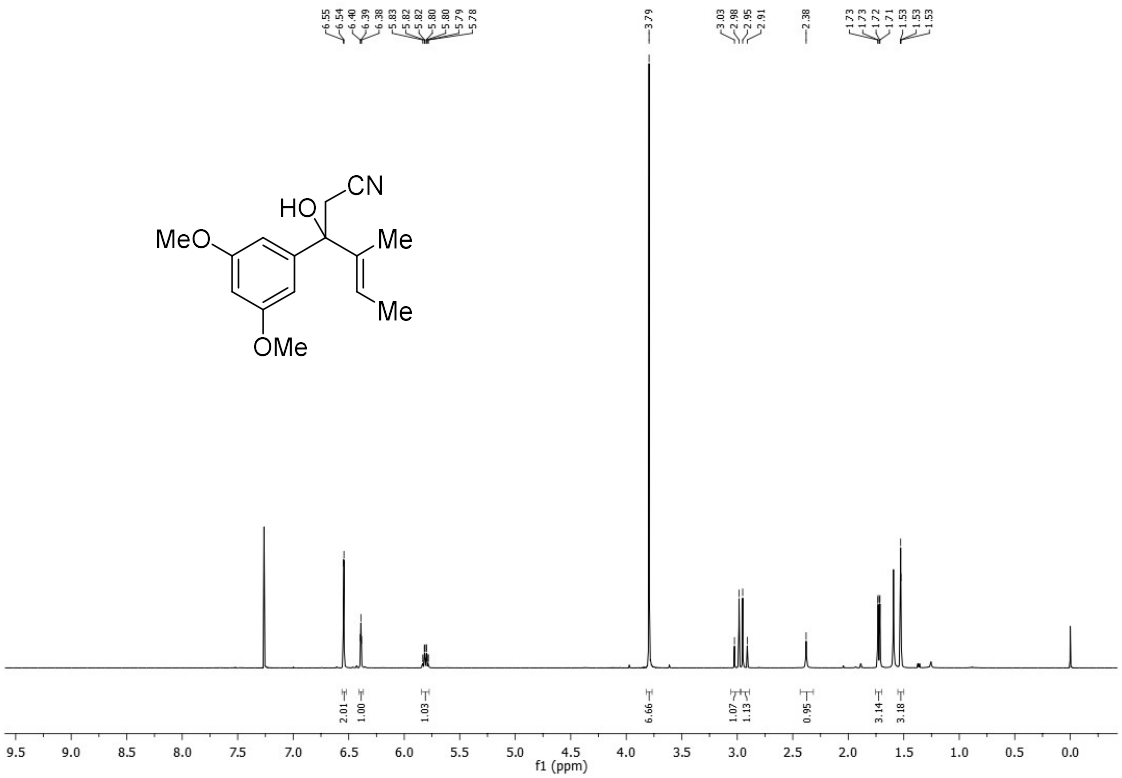
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9u**.



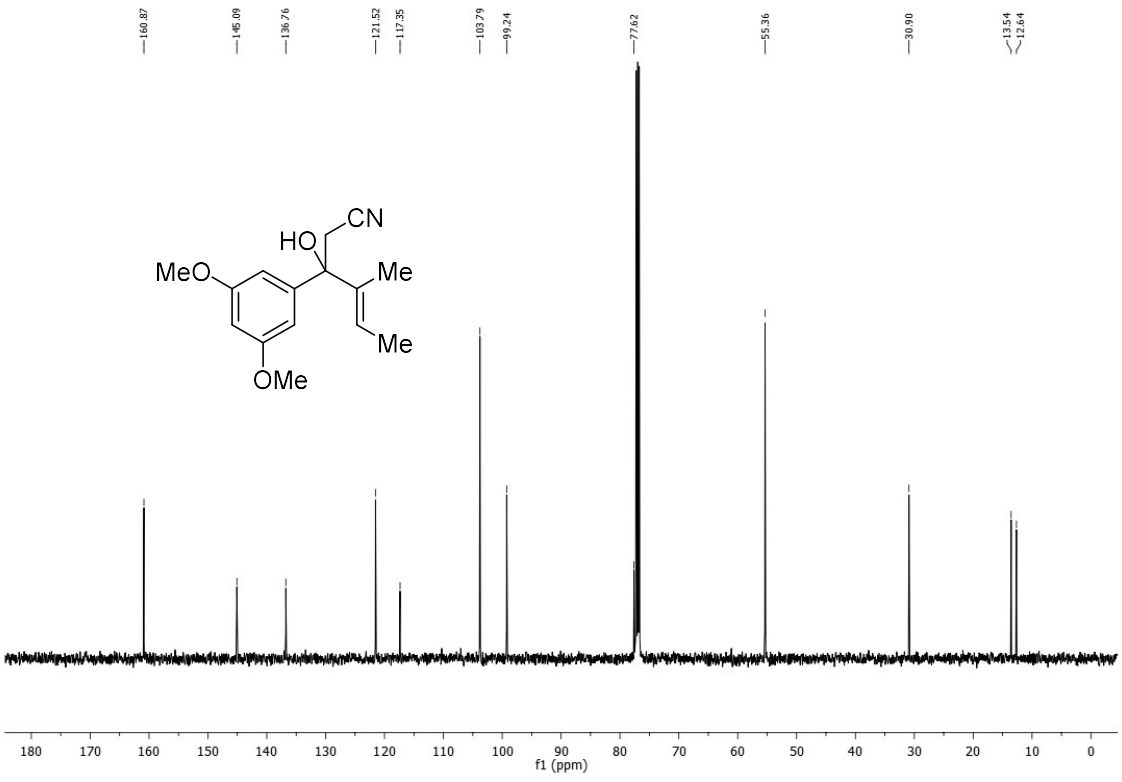
^{1}H NMR (400 MHz, $CDCl_3$) for compound **9v**.



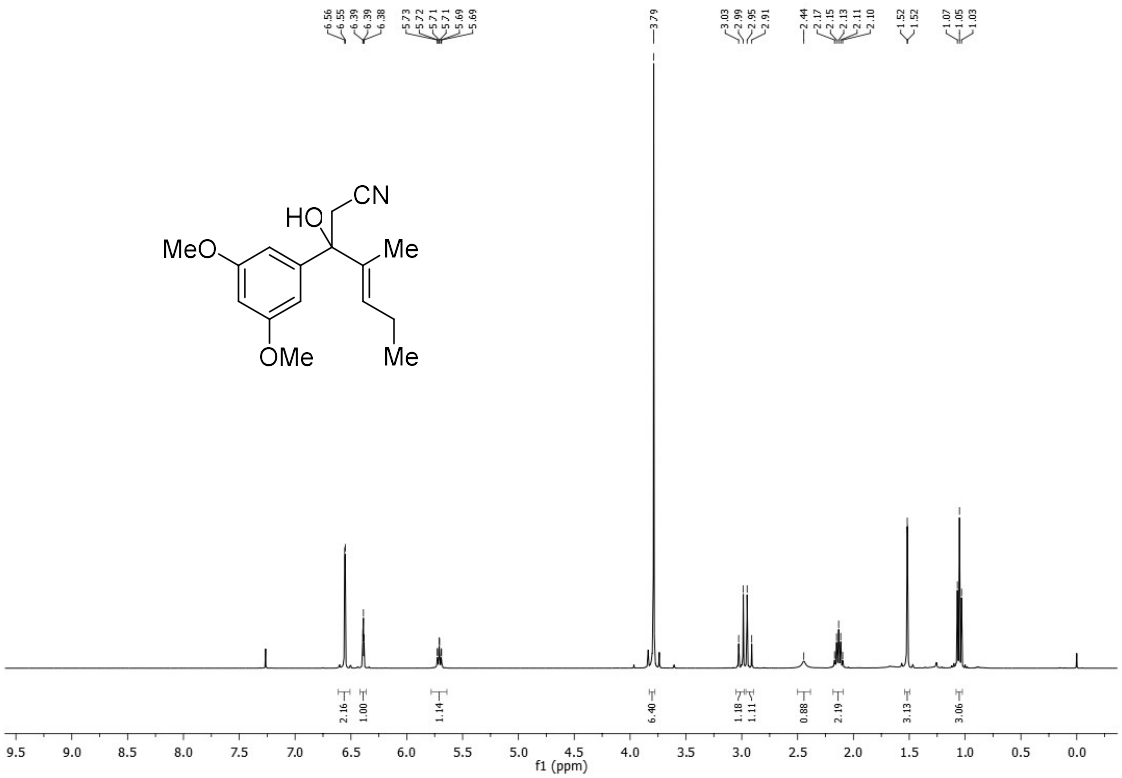
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9v**.



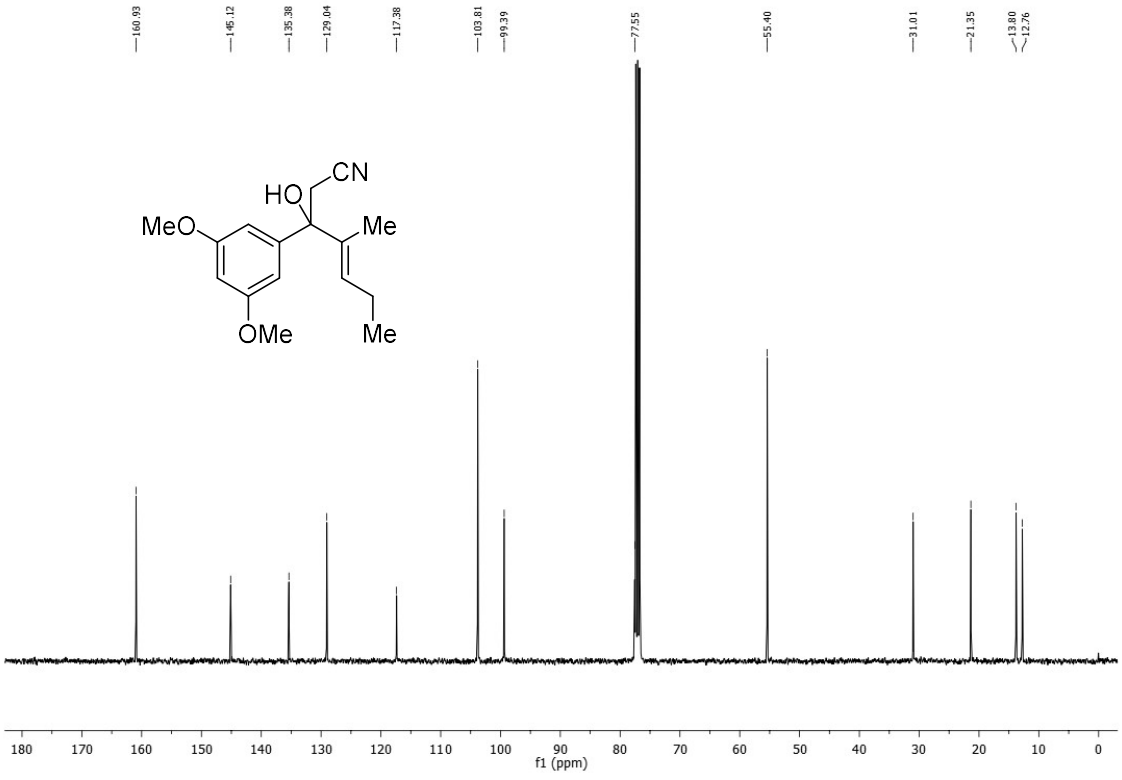
^{1}H NMR (400 MHz, $CDCl_3$) for compound **7b**.



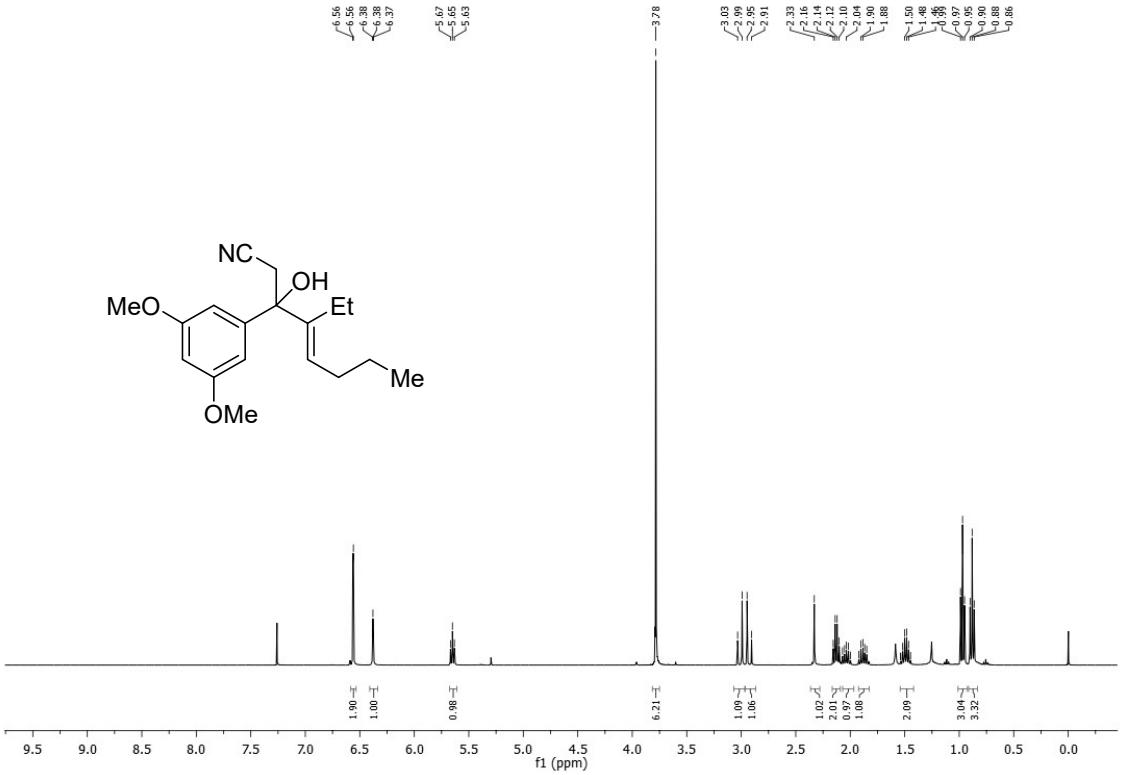
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for compound **7b**.



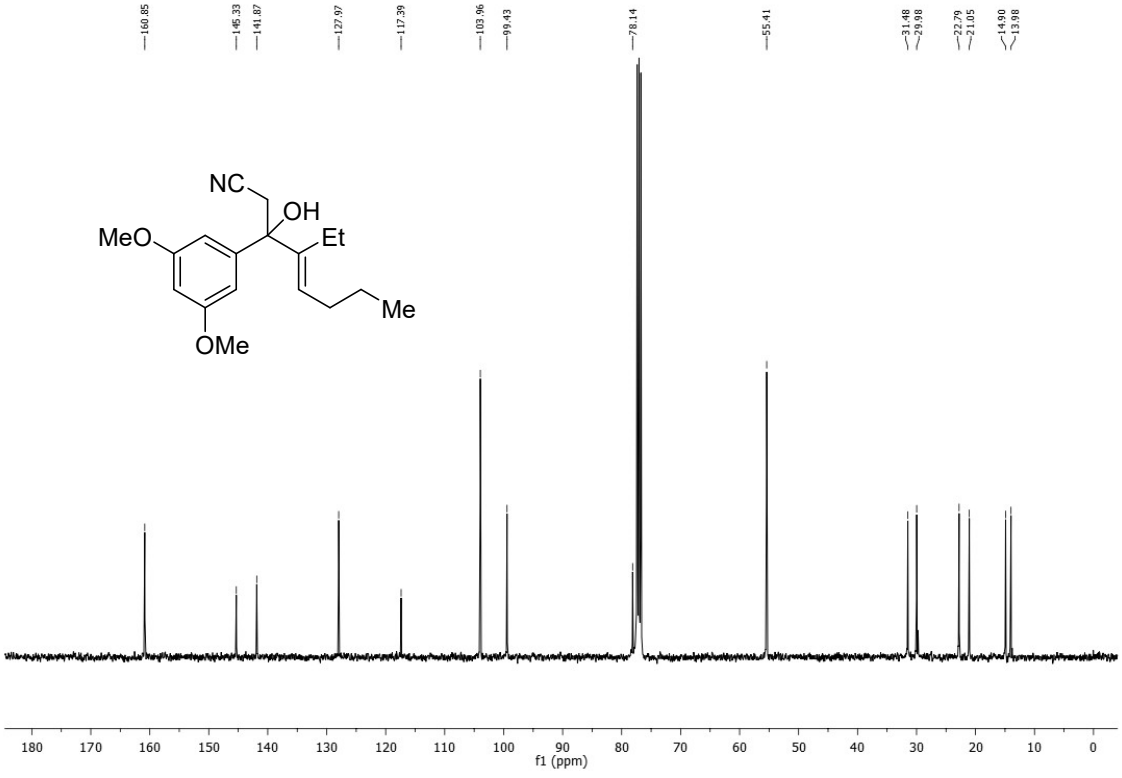
^{1}H NMR (400 MHz, $CDCl_3$) for compound **7c**.



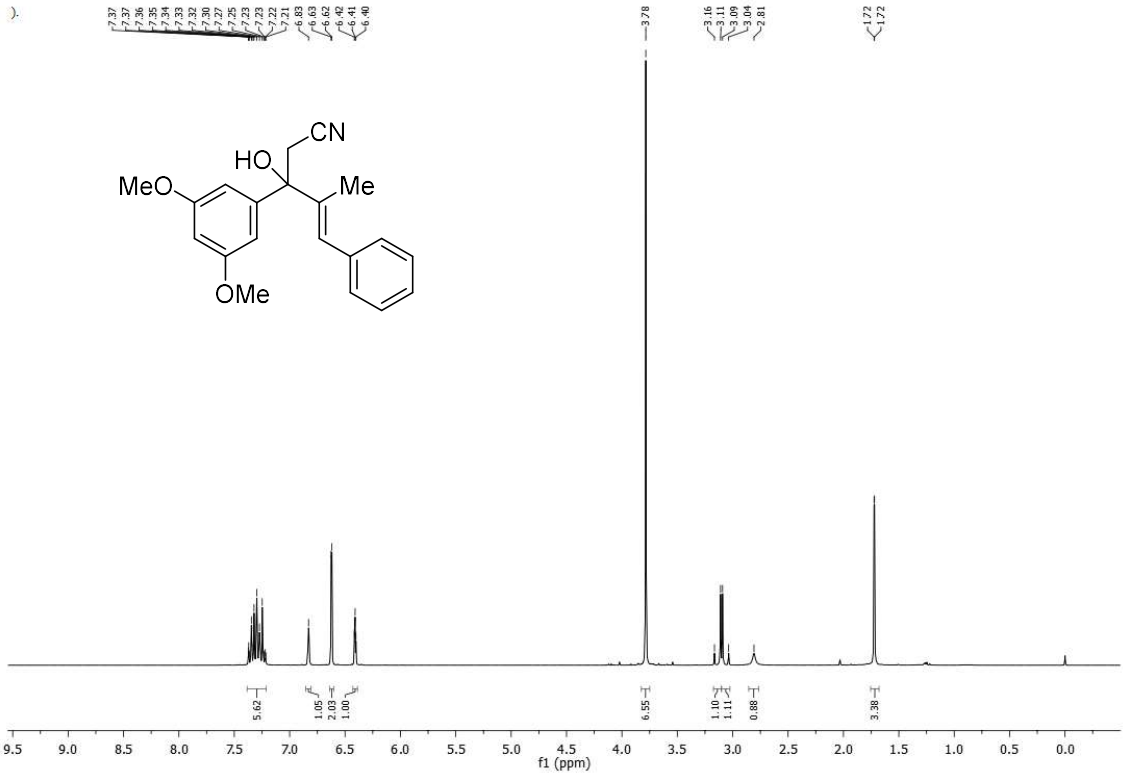
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **7c**.



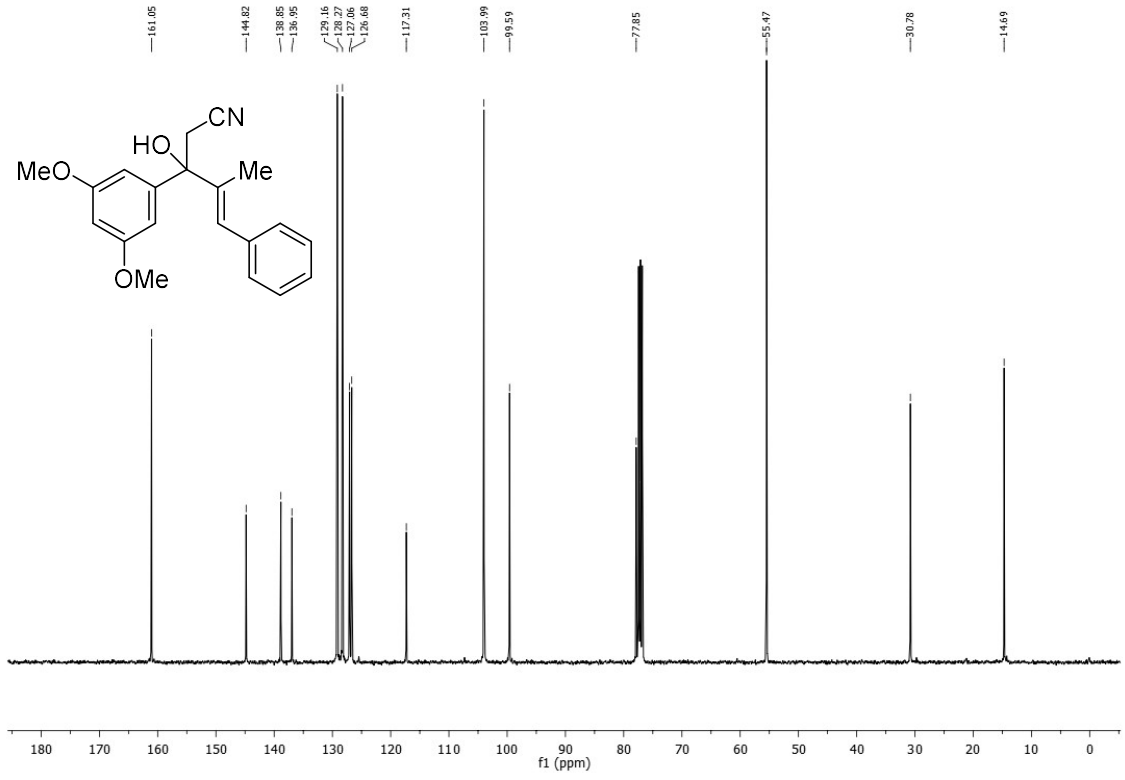
^{1}H NMR (400 MHz, $CDCl_3$) for compound **7d**.



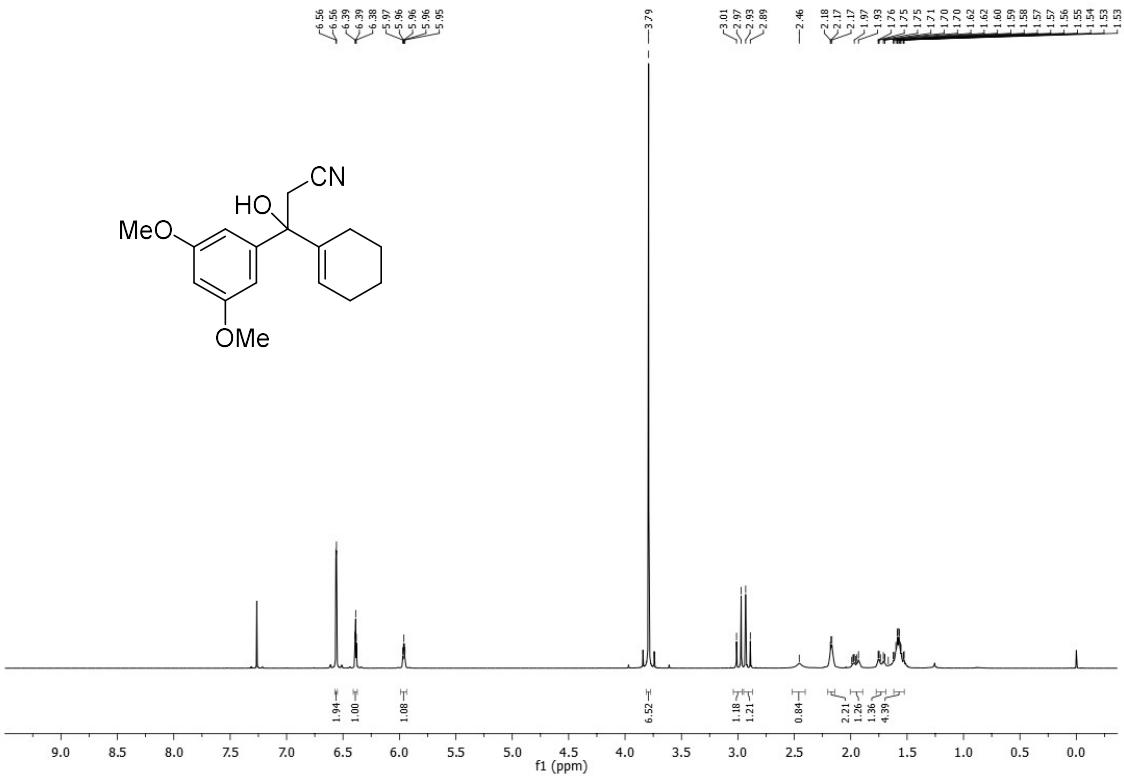
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **7d**.



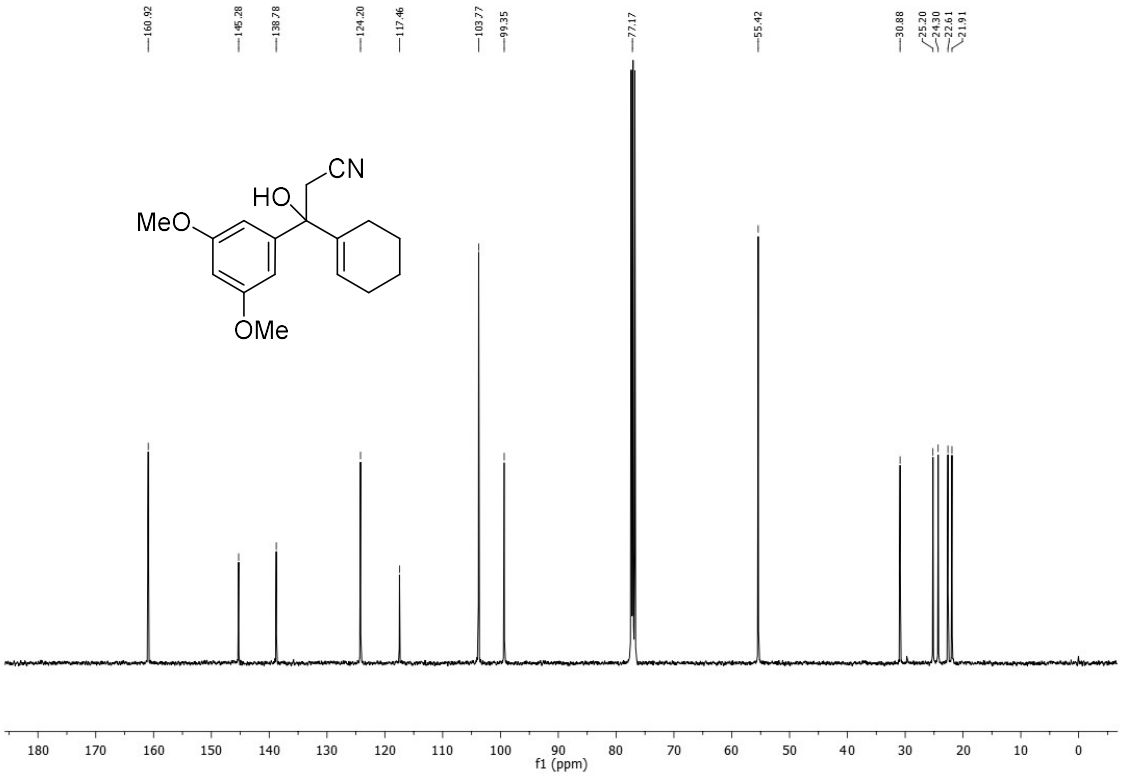
^{1}H NMR (300 MHz, $CDCl_3$) for compound **7e**.



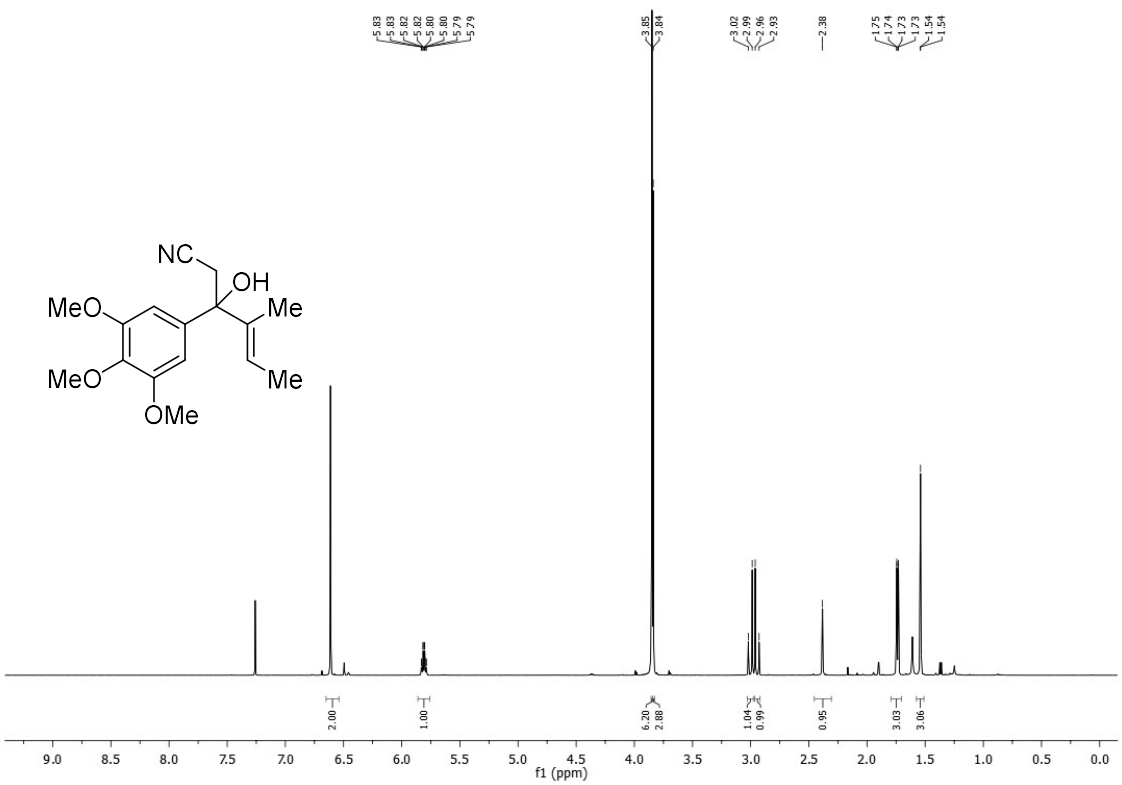
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **7e**.



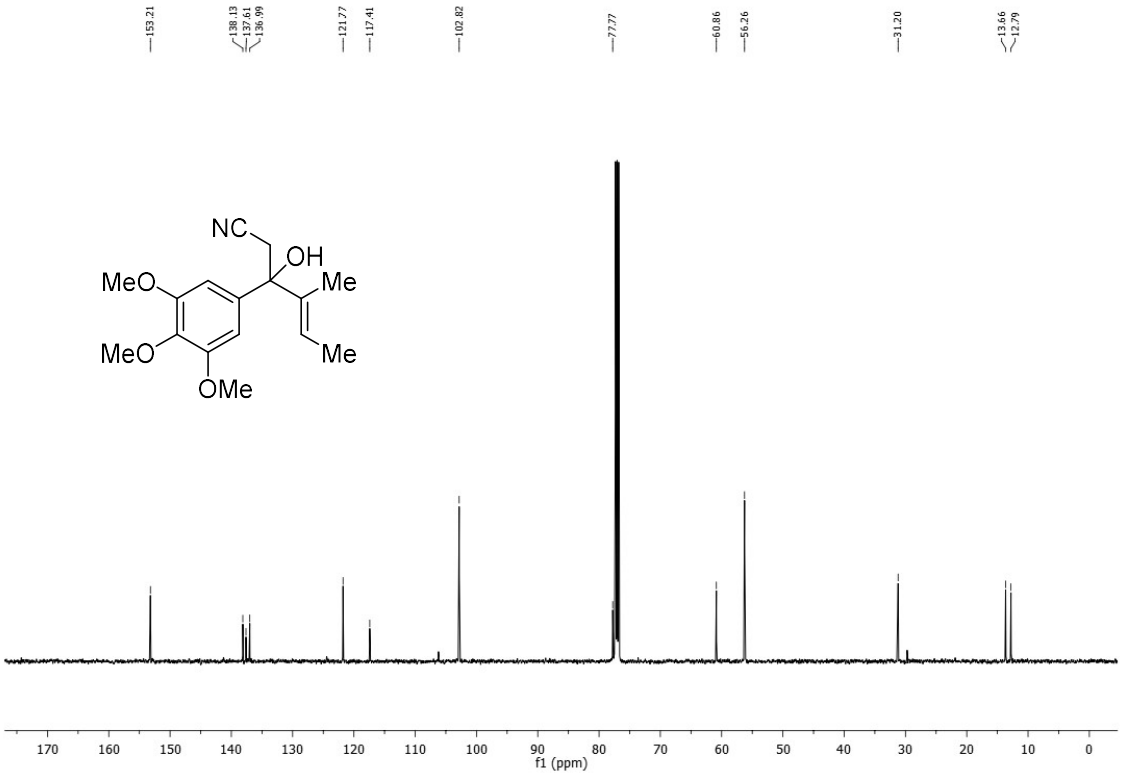
^{1}H NMR (400 MHz, $CDCl_3$) for compound **7f**.



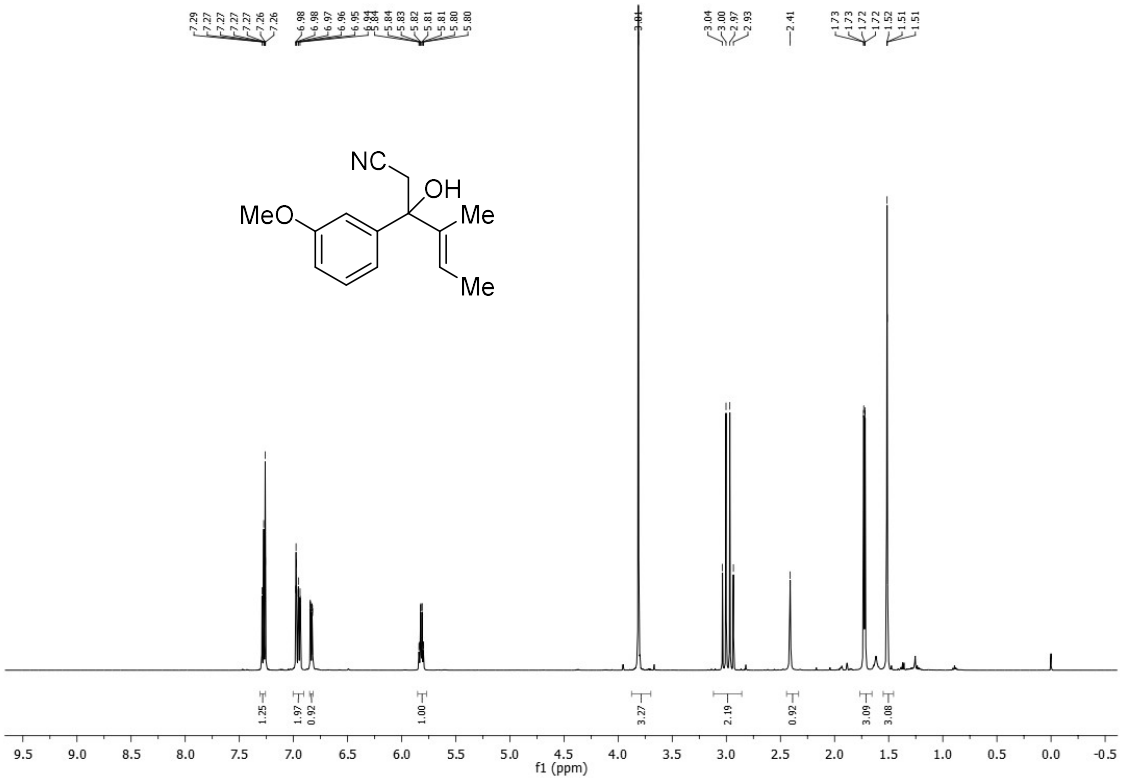
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **7f**.



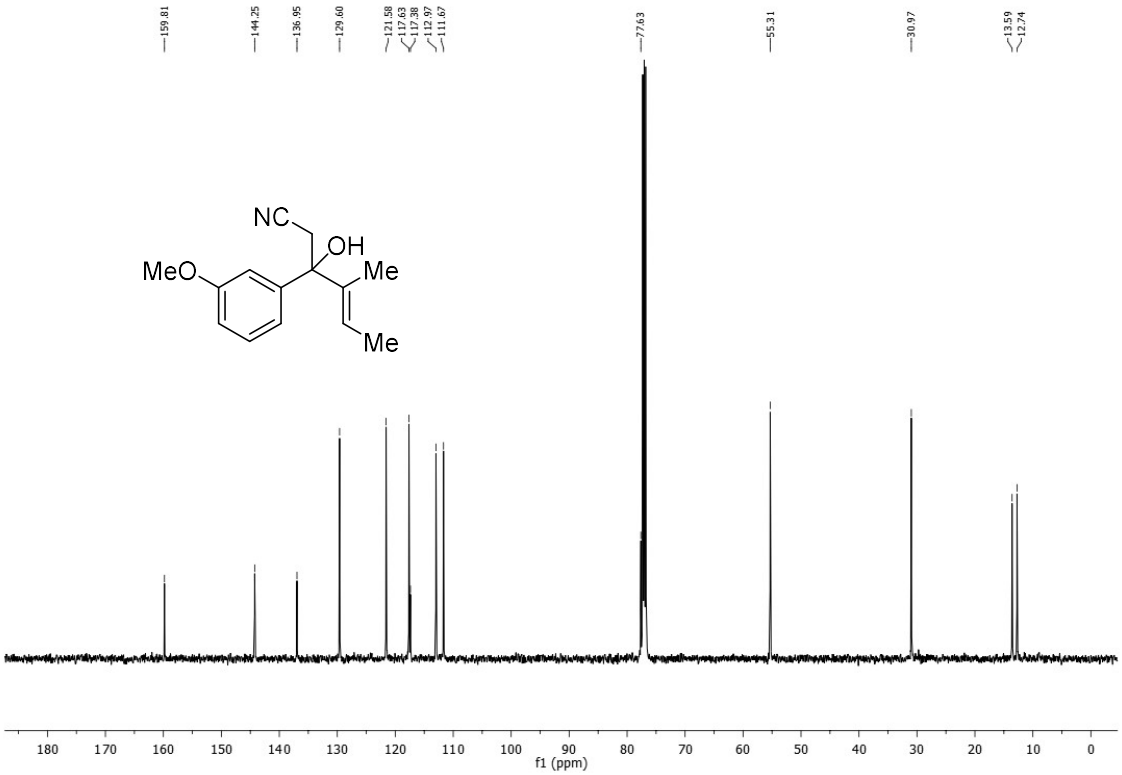
^{1}H NMR (500 MHz, $CDCl_3$) for compound **7ba**.



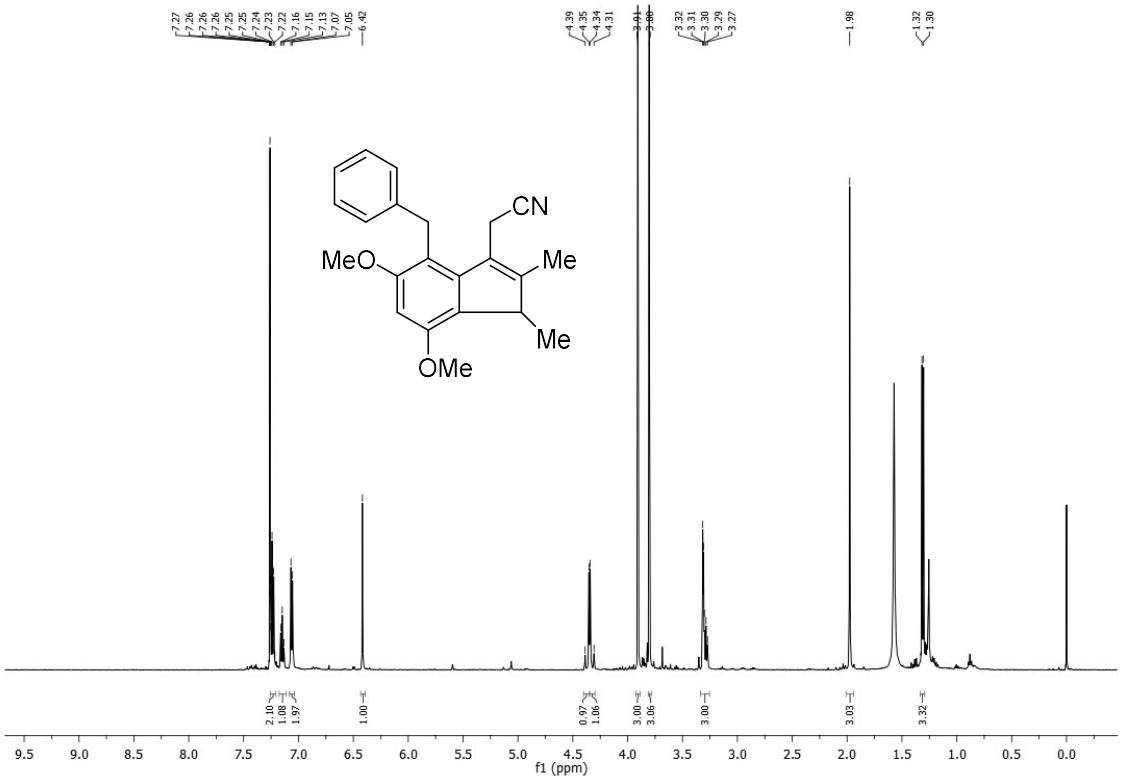
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) for compound **7ba.**



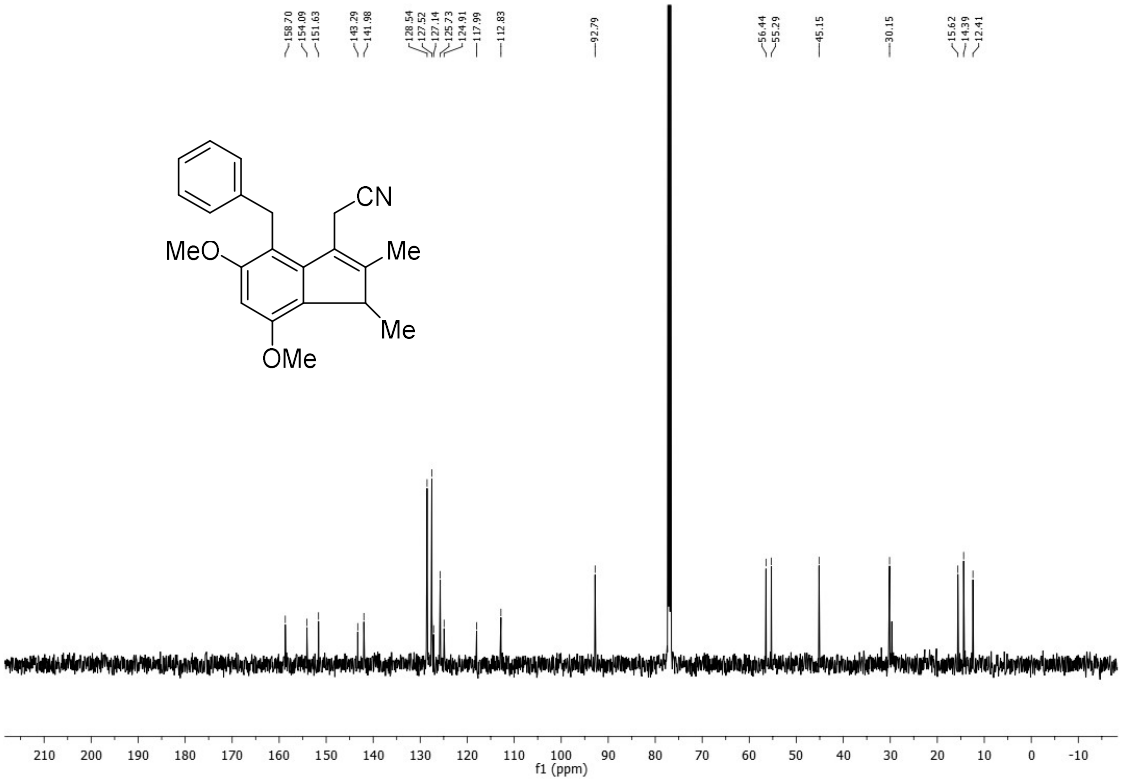
^{1}H NMR (500 MHz, $CDCl_3$) for compound **7bb**.



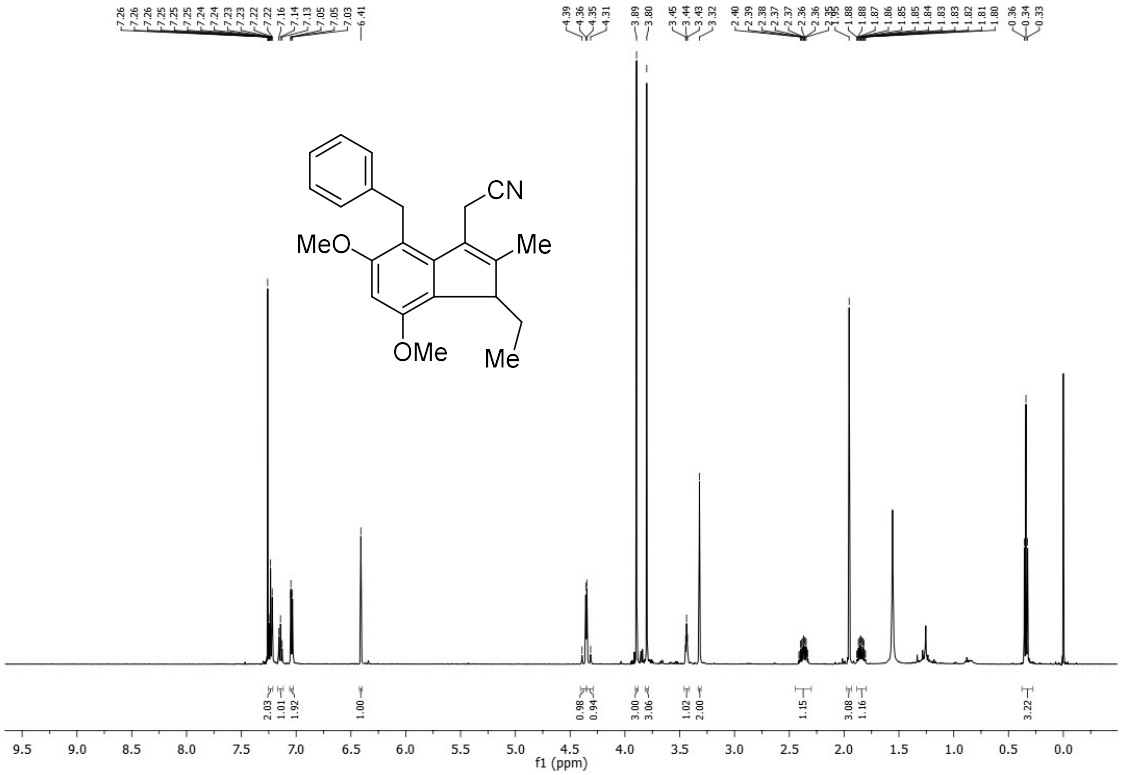
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) for compound **7bb**.



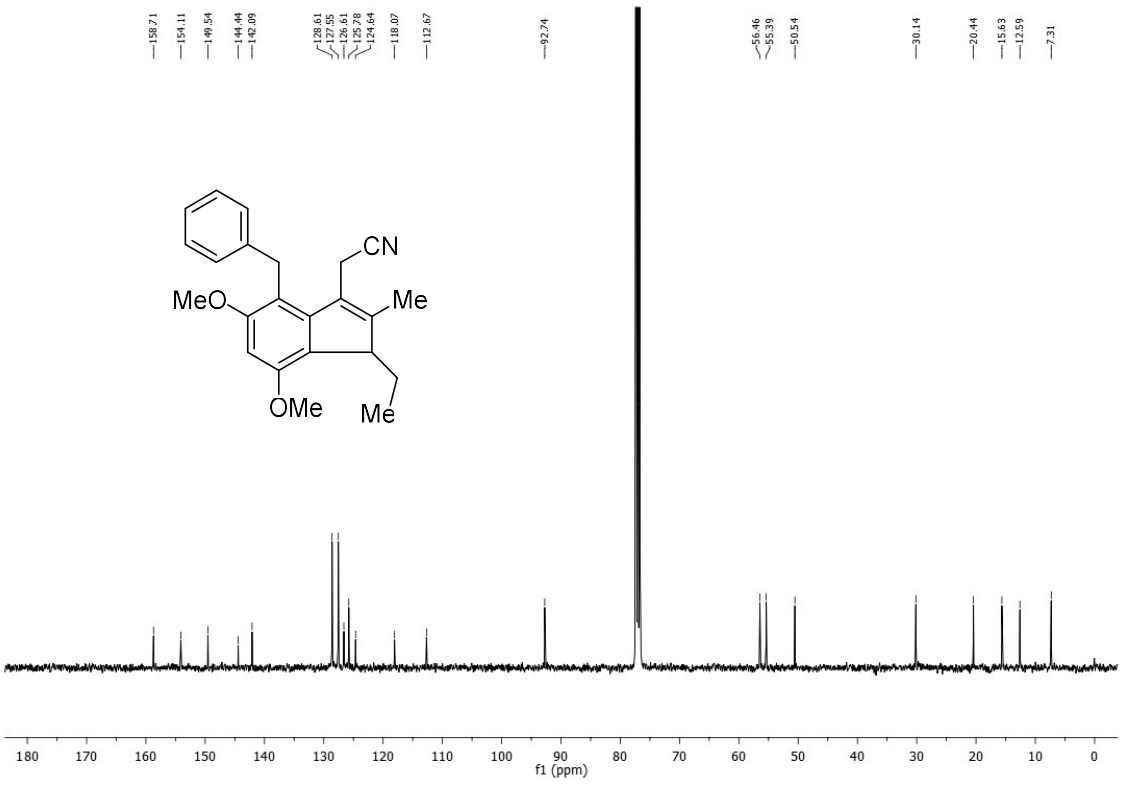
^{1}H NMR (500 MHz, $CDCl_3$) for compound **9ba**.



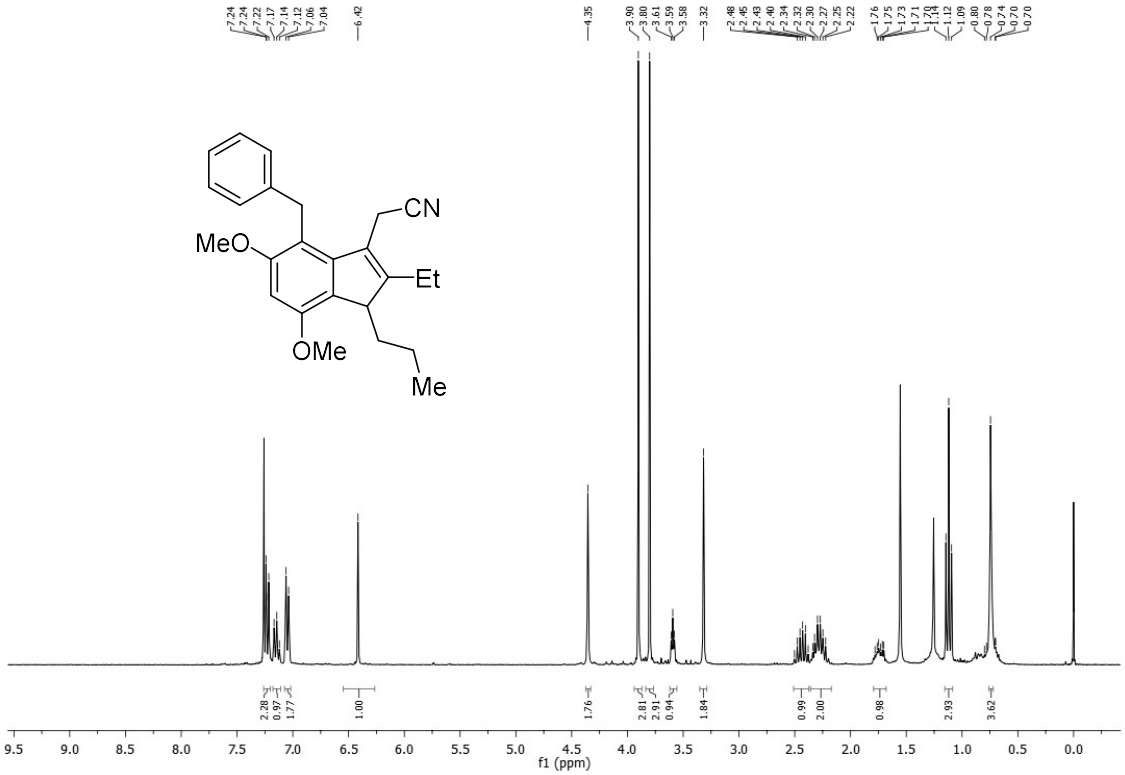
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for compound **9ba**.



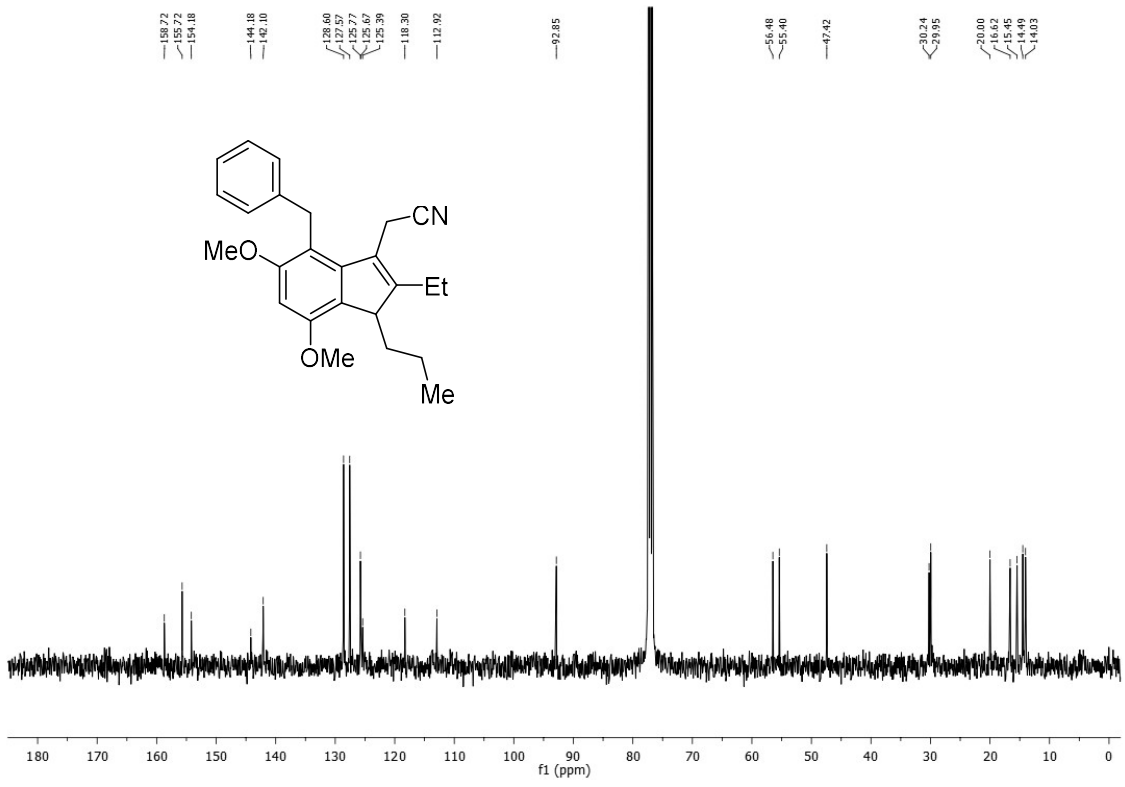
^{1}H NMR (500 MHz, $CDCl_3$) for compound **9ca**.



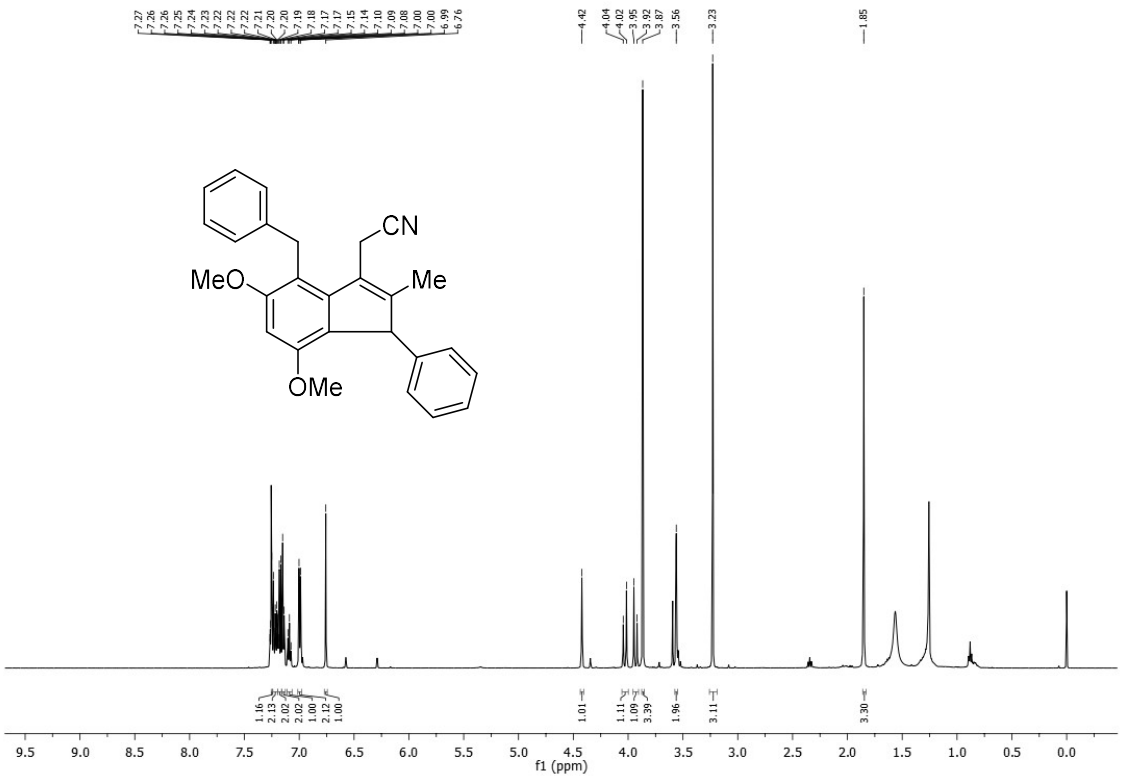
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9ca**.



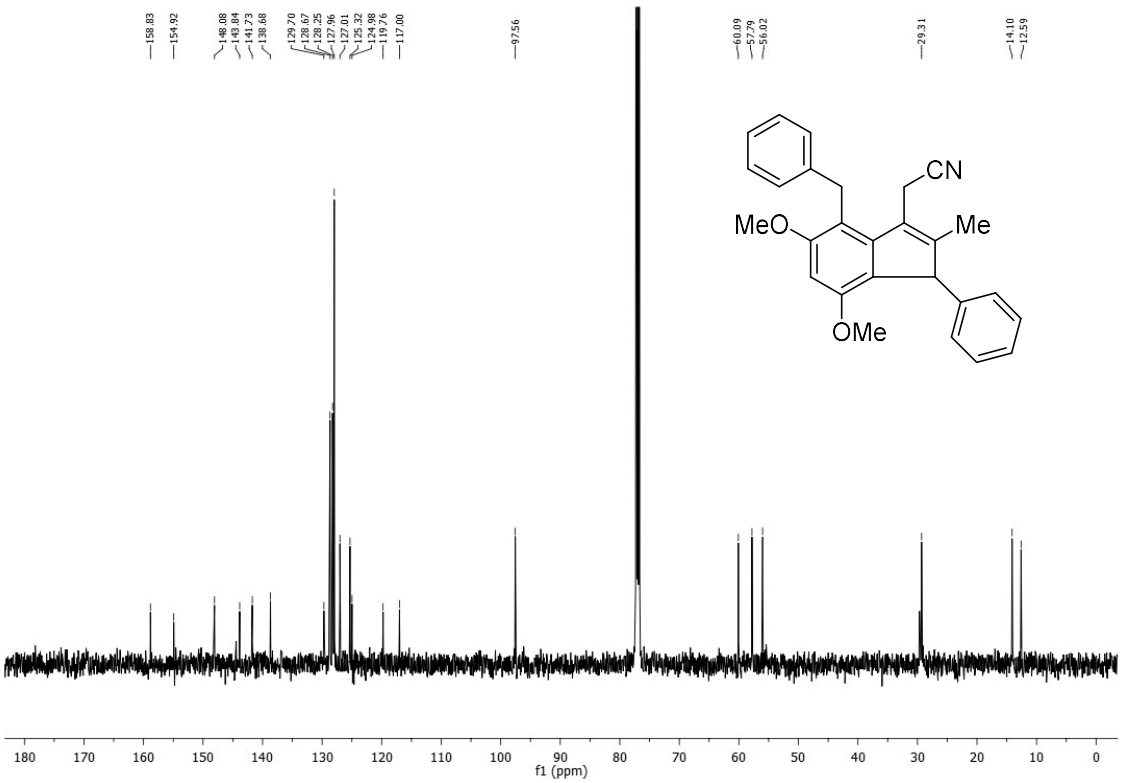
^{1}H NMR (300 MHz, $CDCl_3$) for compound **9da**.



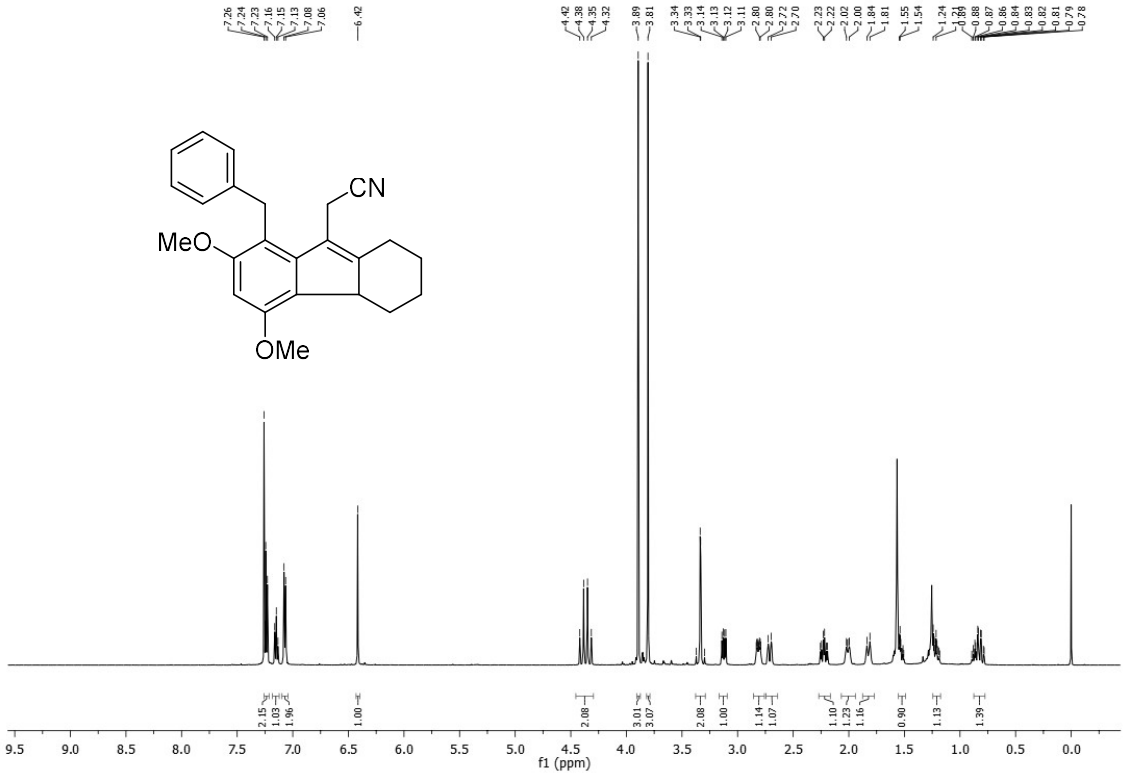
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9da**.



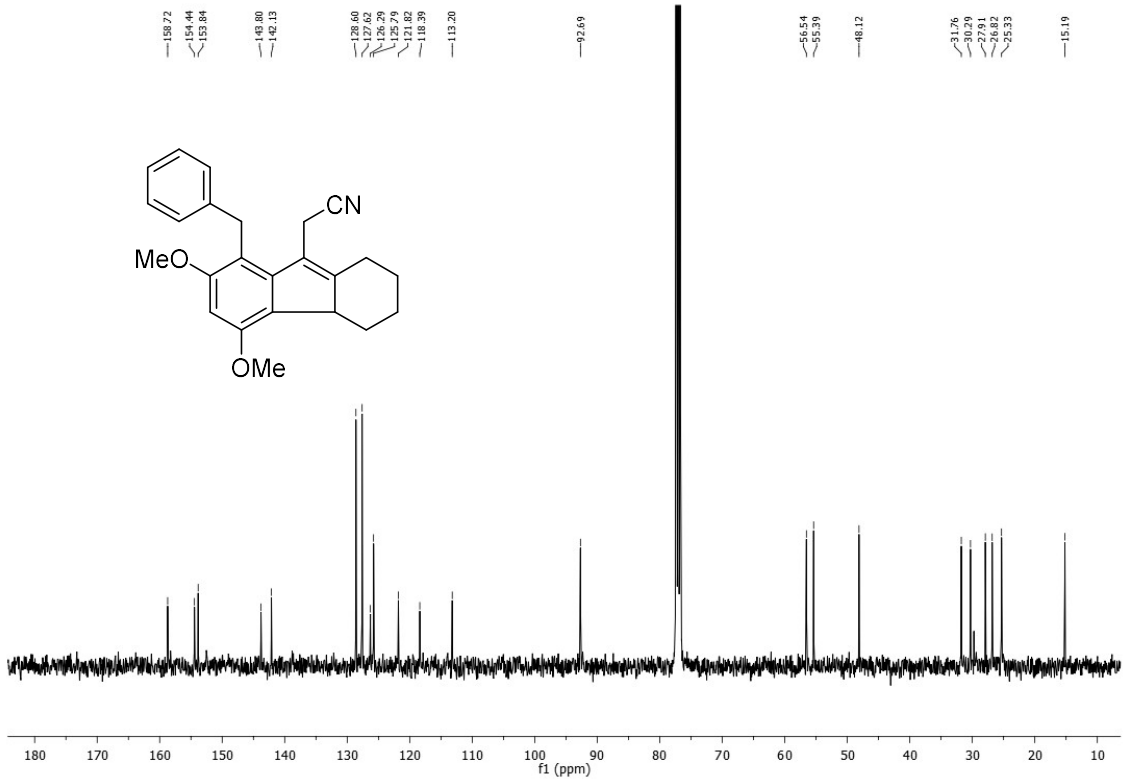
^{1}H NMR (500 MHz, $CDCl_3$) for compound **9ea**.



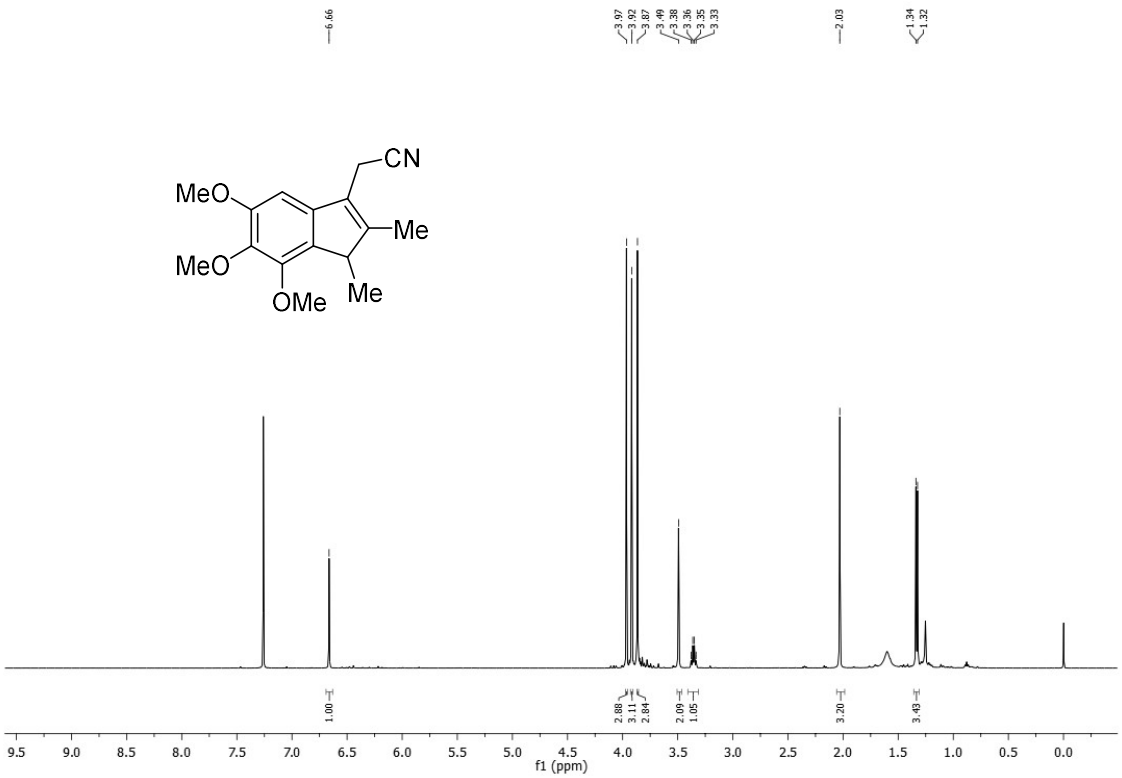
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for compound **9ea**.



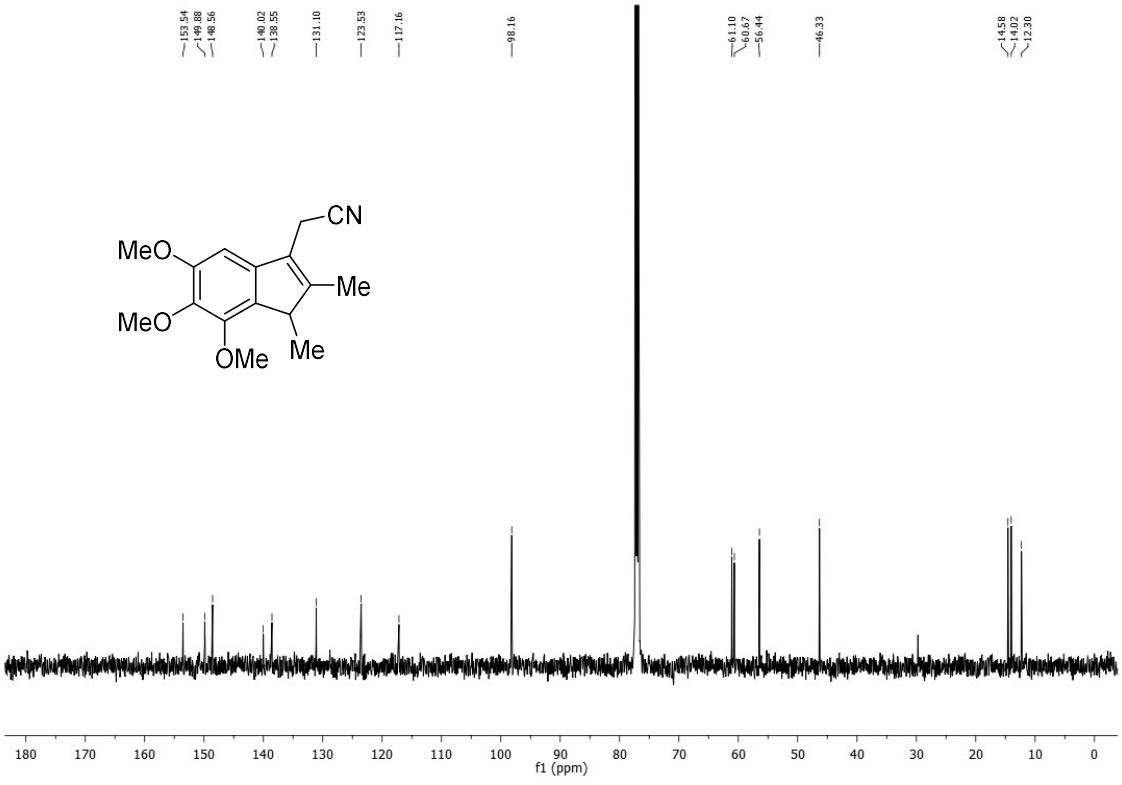
^{1}H NMR (500 MHz, $CDCl_3$) for compound **9fa**.



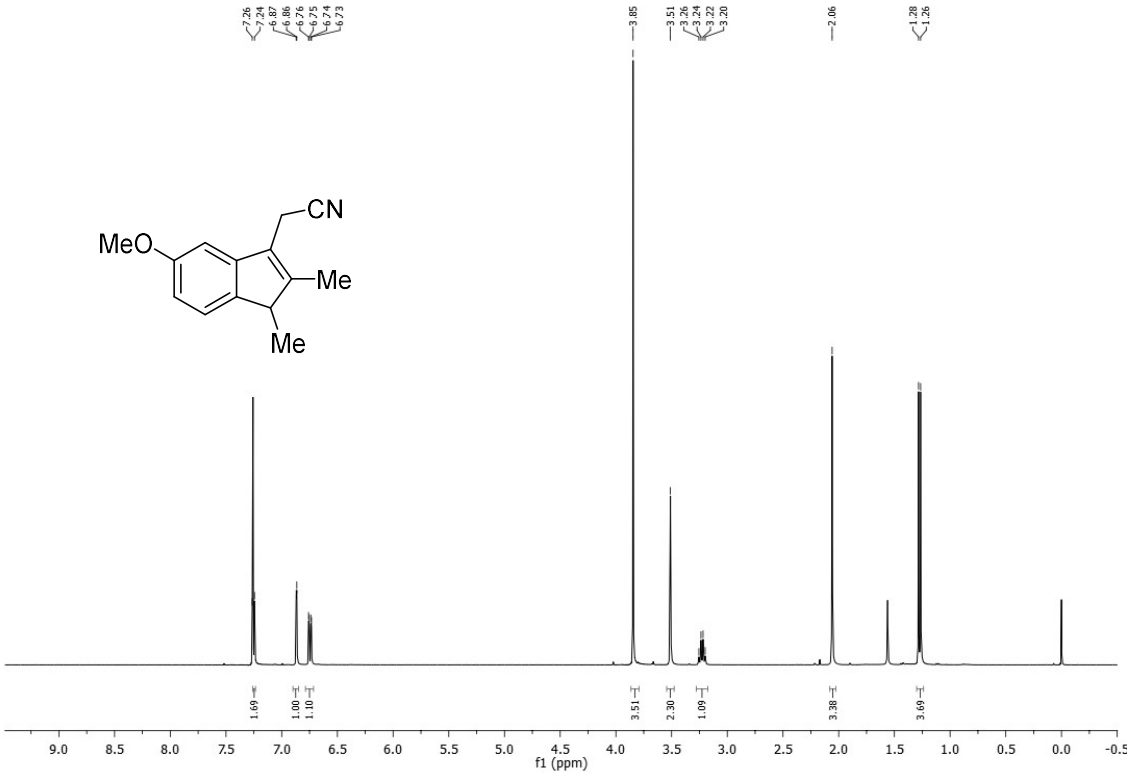
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **9fa**.



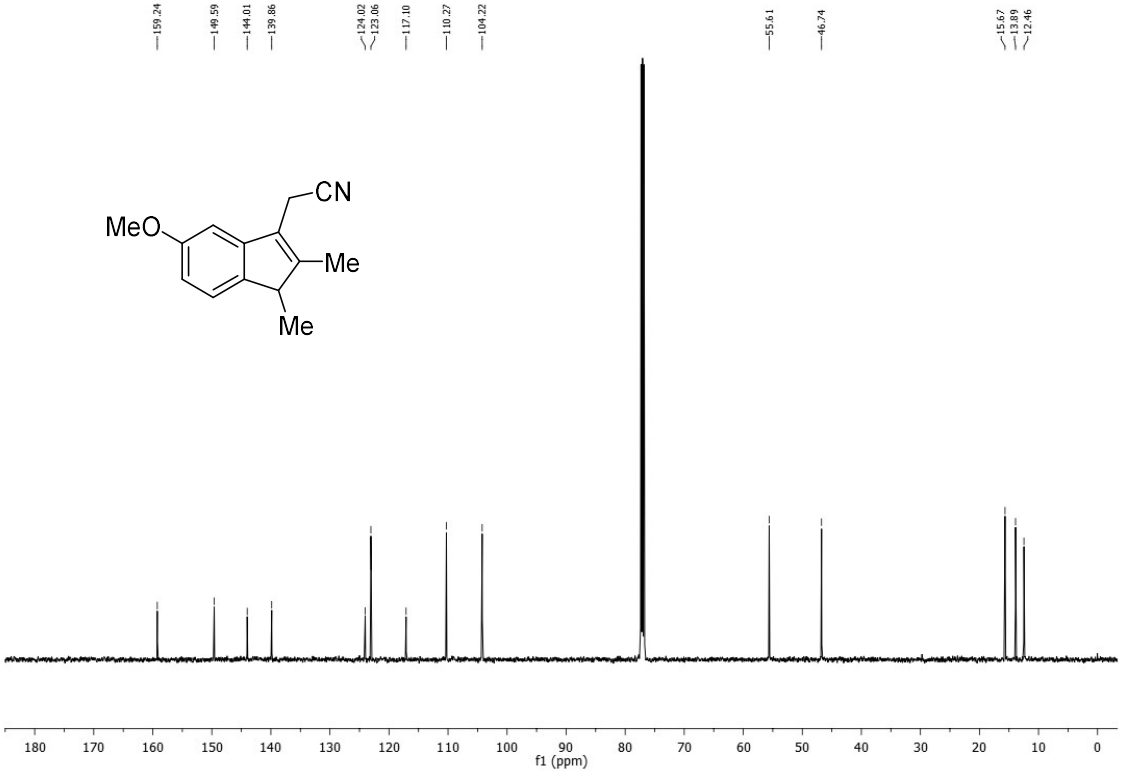
^{1}H NMR (500 MHz, $CDCl_3$) for compound **8ba**.



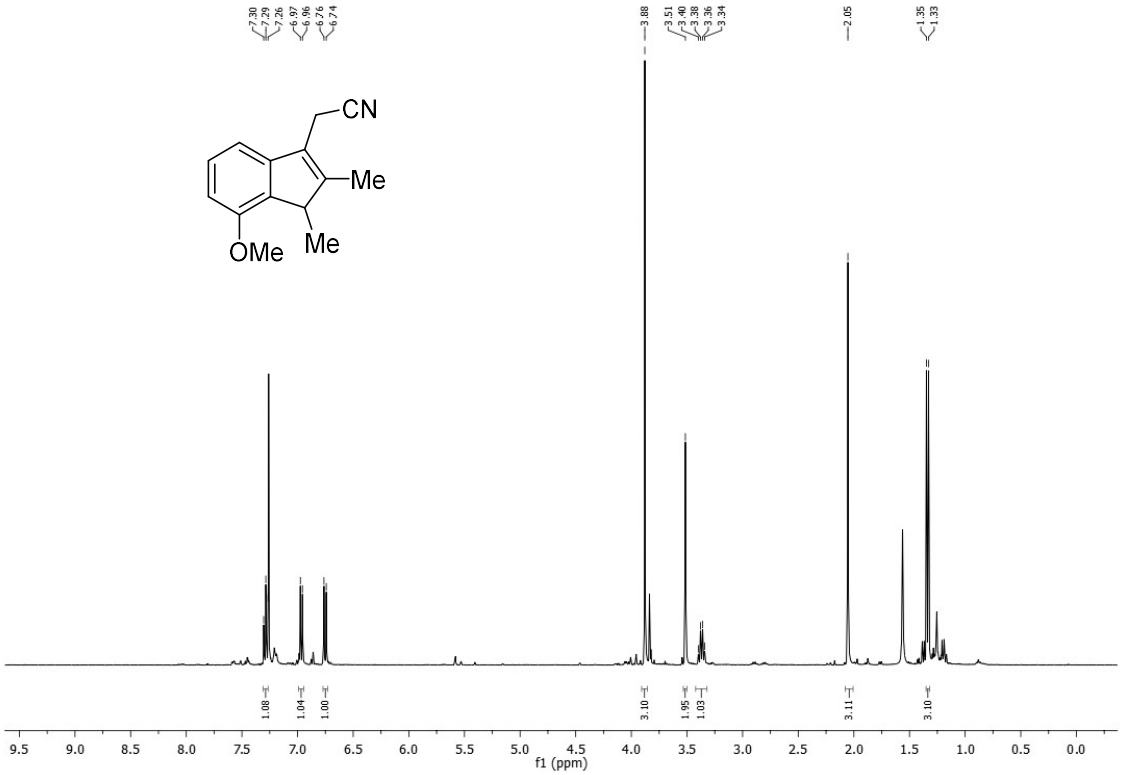
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) for compound **8ba**.



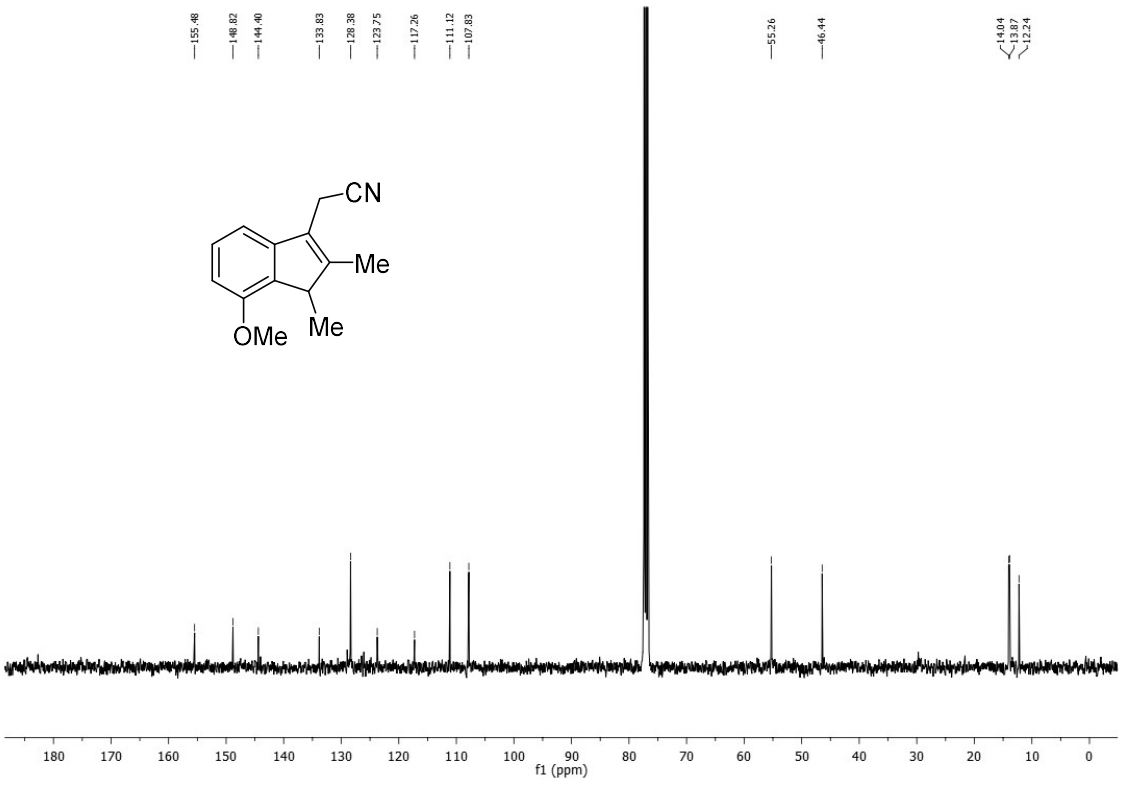
^{1}H NMR (400 MHz, $CDCl_3$) for compound **8bb**.



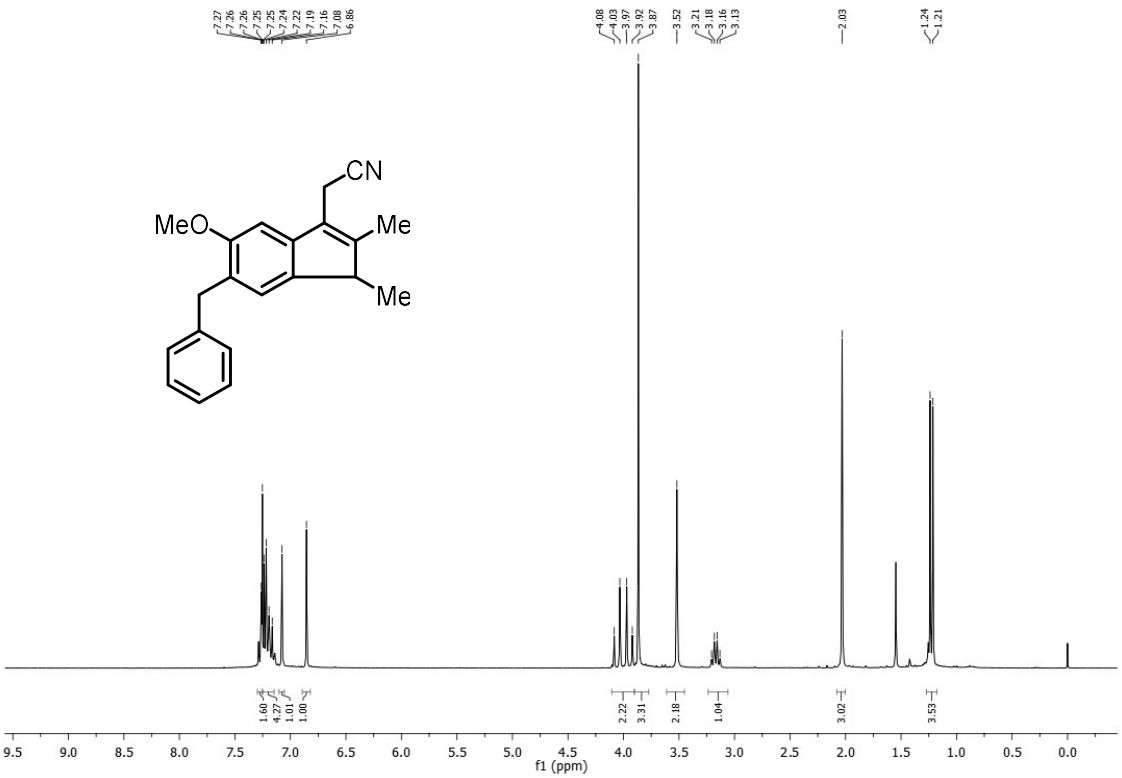
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) for compound **8bb**.



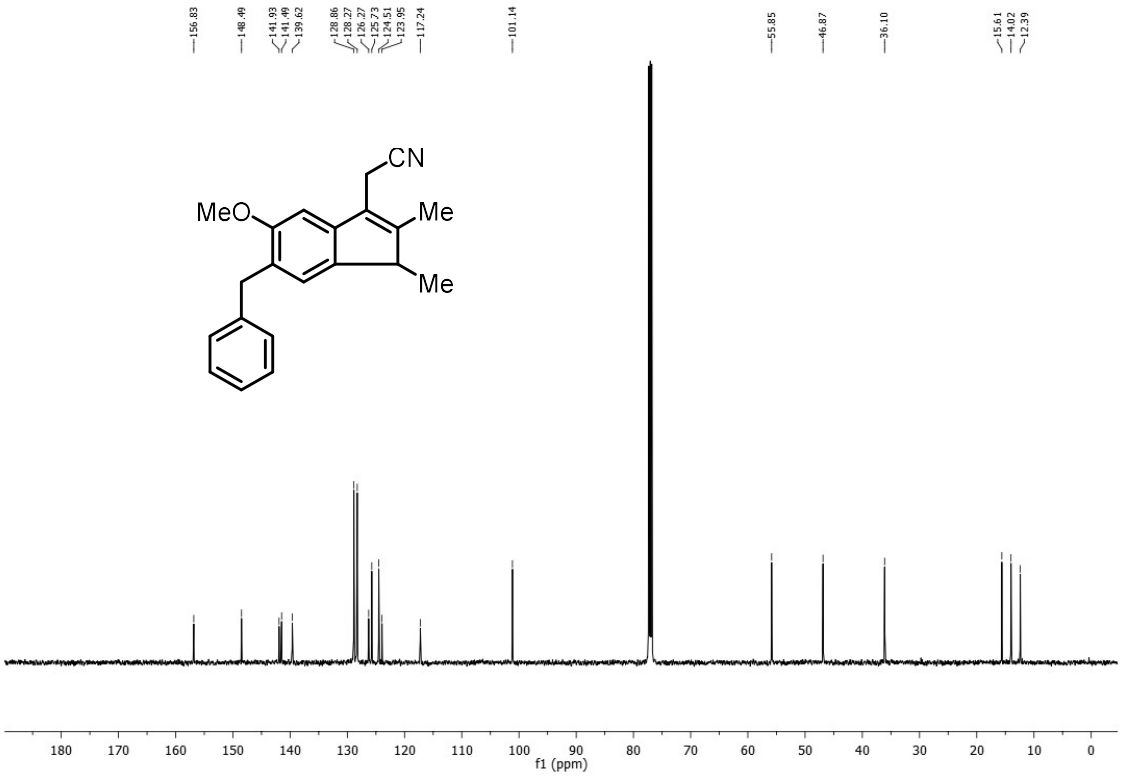
^{1}H NMR (400 MHz, $CDCl_3$) for compound **8bb'**.



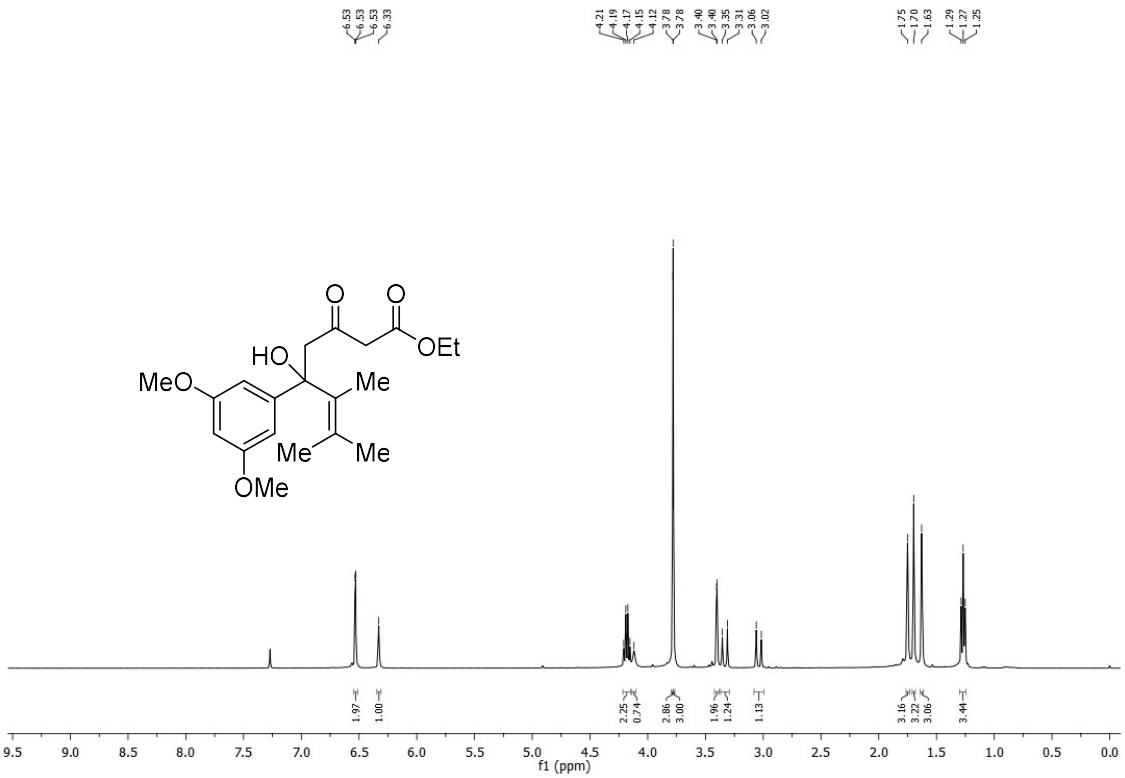
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **8bb'**.



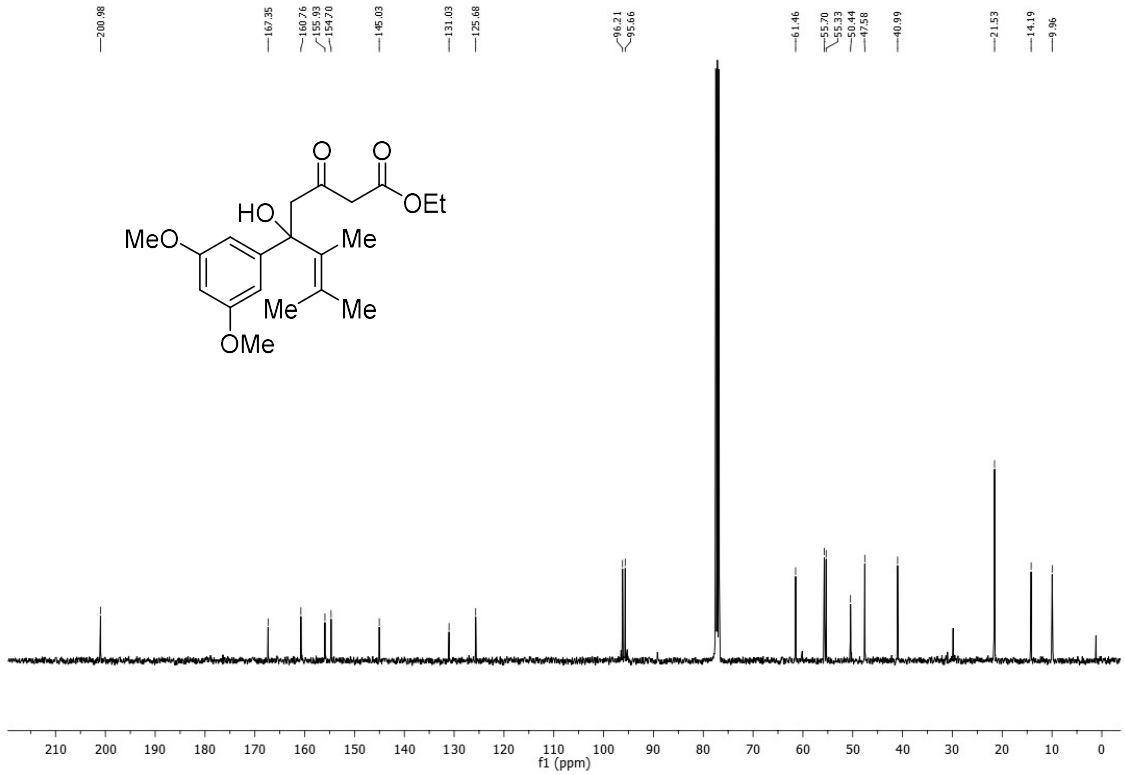
^{1}H NMR (300 MHz, $CDCl_3$) for compound **9hb**.



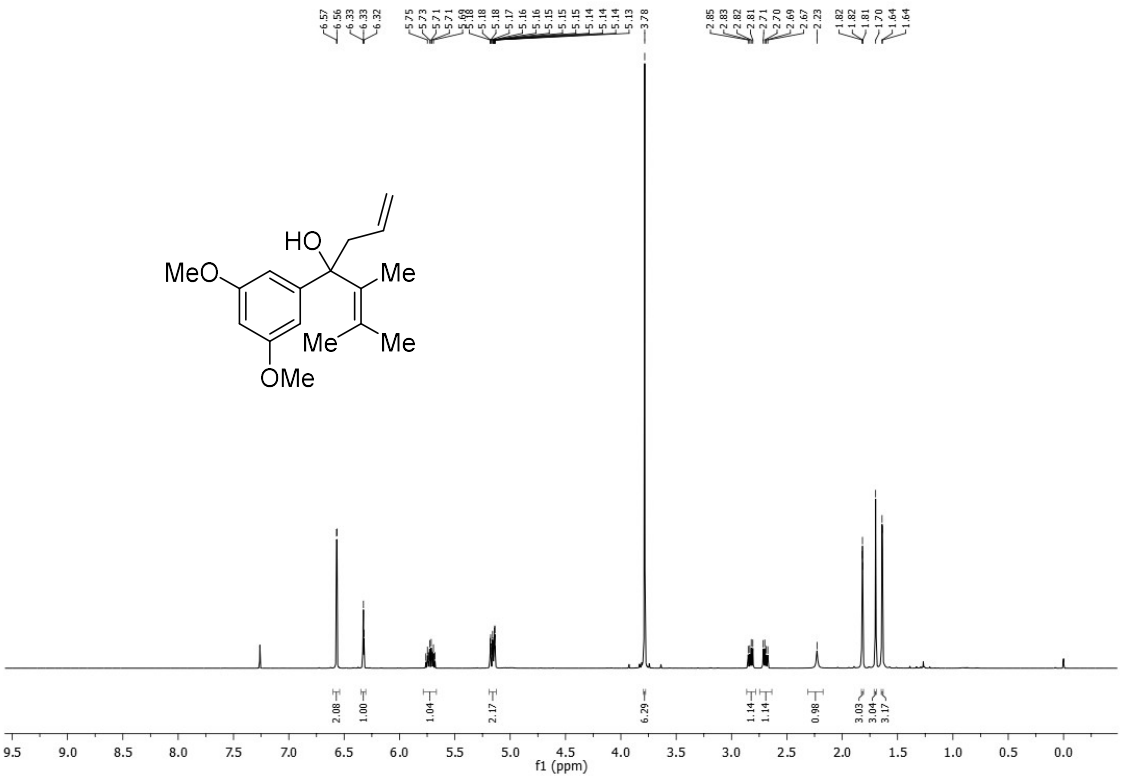
^{13}C NMR (126 MHz, $CDCl_3$) for compound **9hb**.



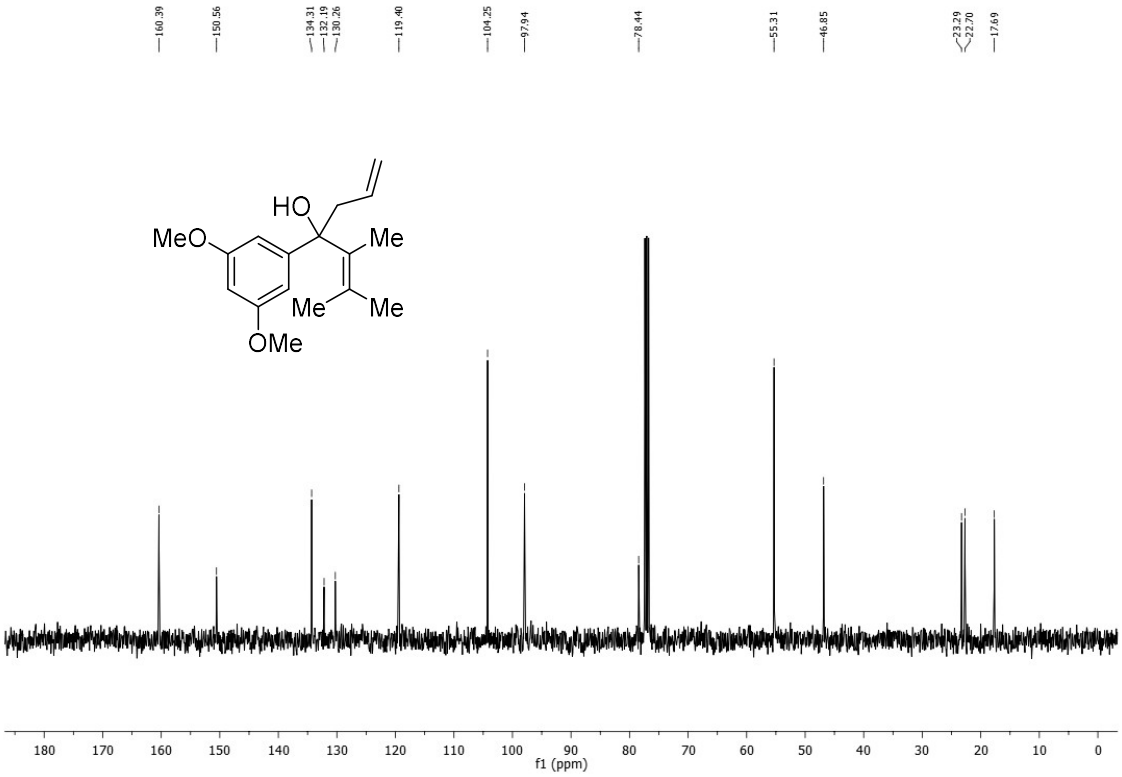
^{1}H NMR (400 MHz, $CDCl_3$) for compound **7h**.



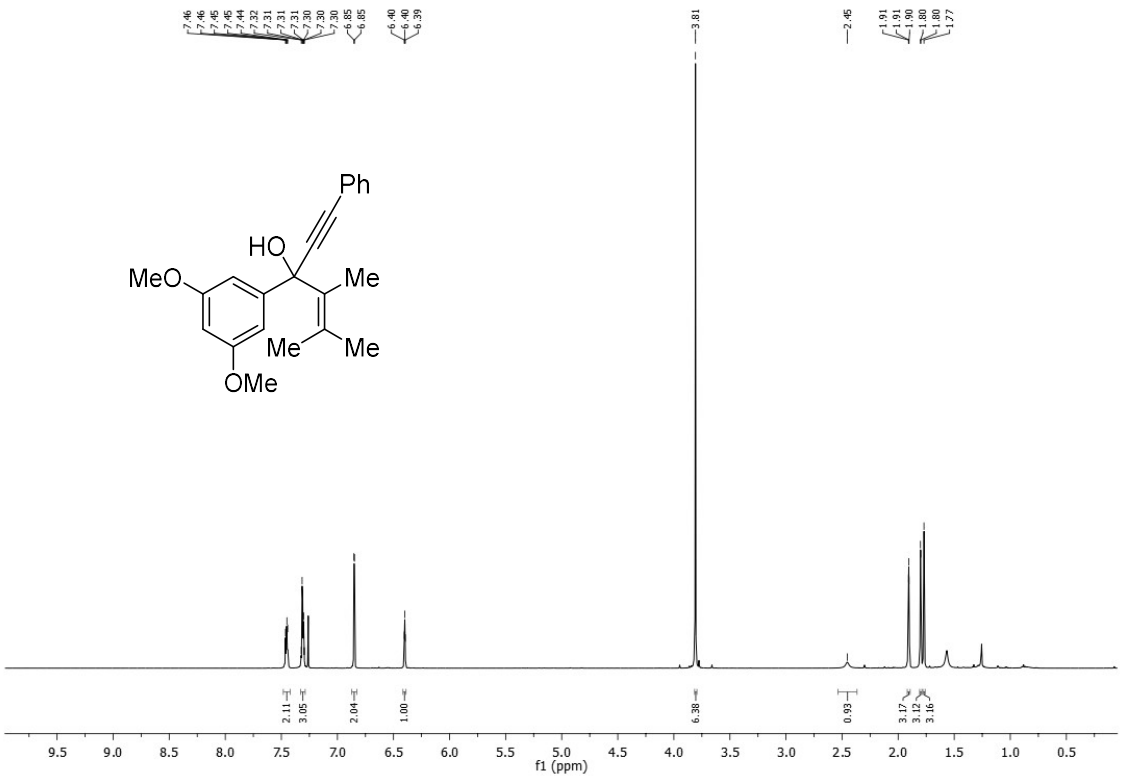
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound**7h**.



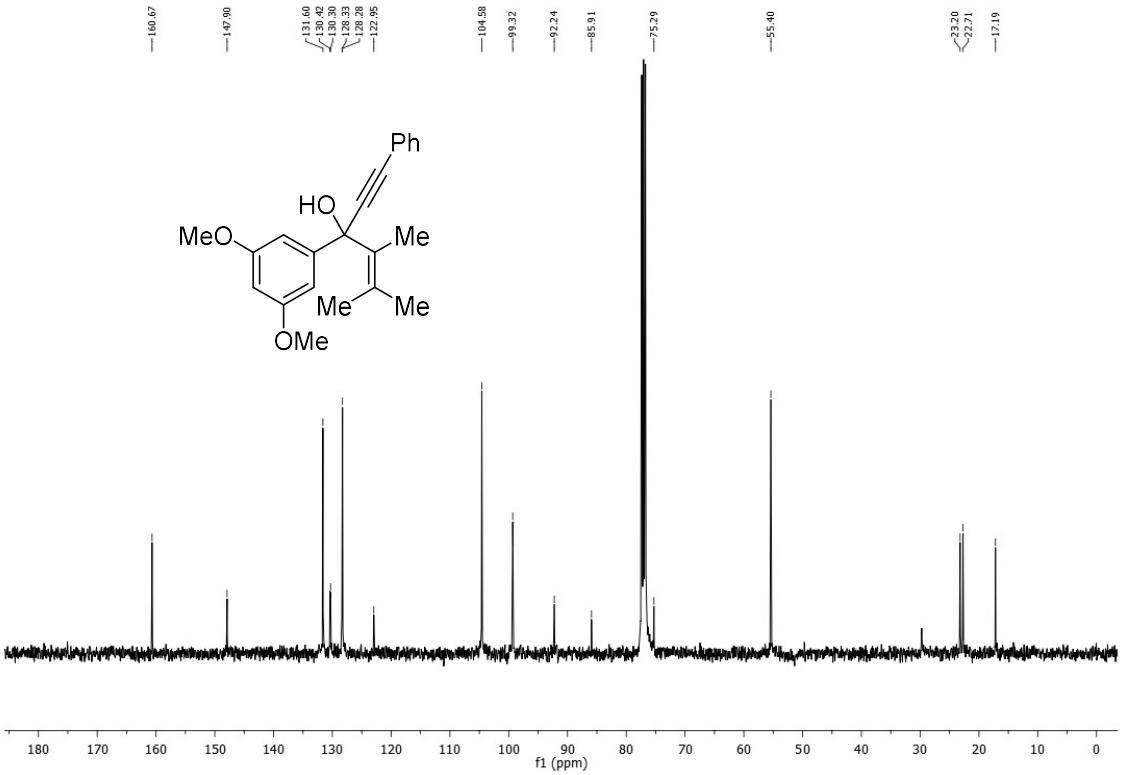
^{1}H NMR (500 MHz, $CDCl_3$) for compound **7i**.



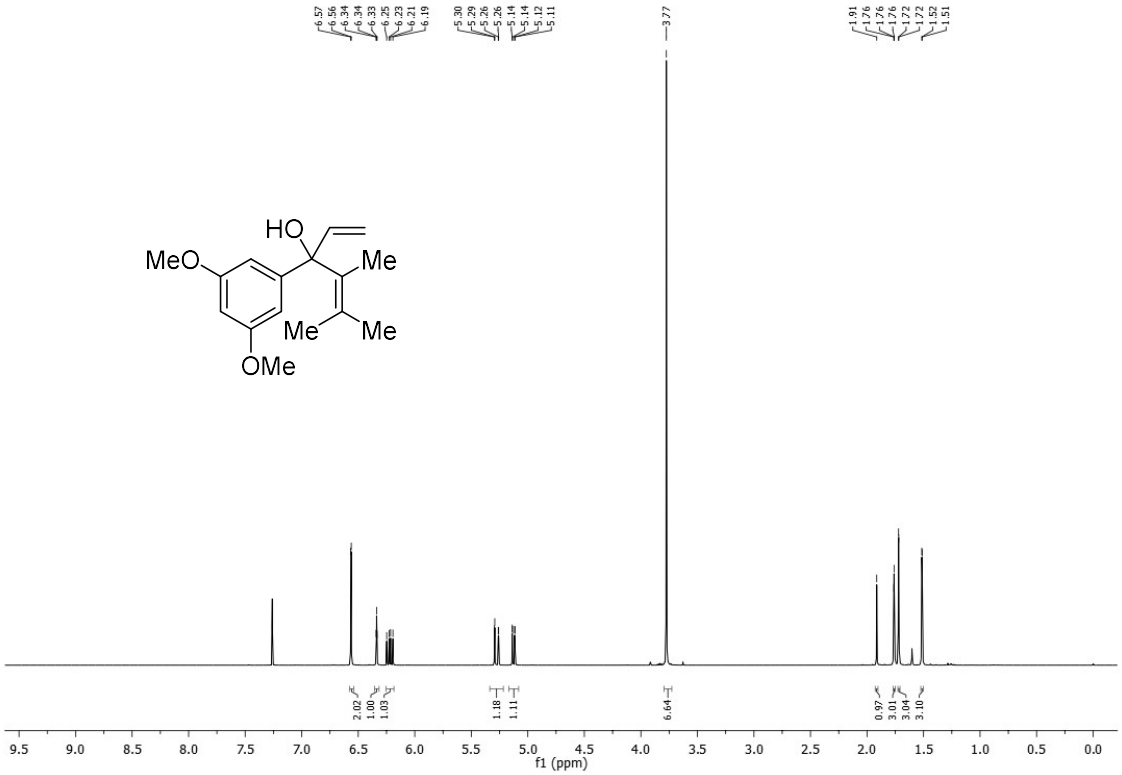
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **7i**.



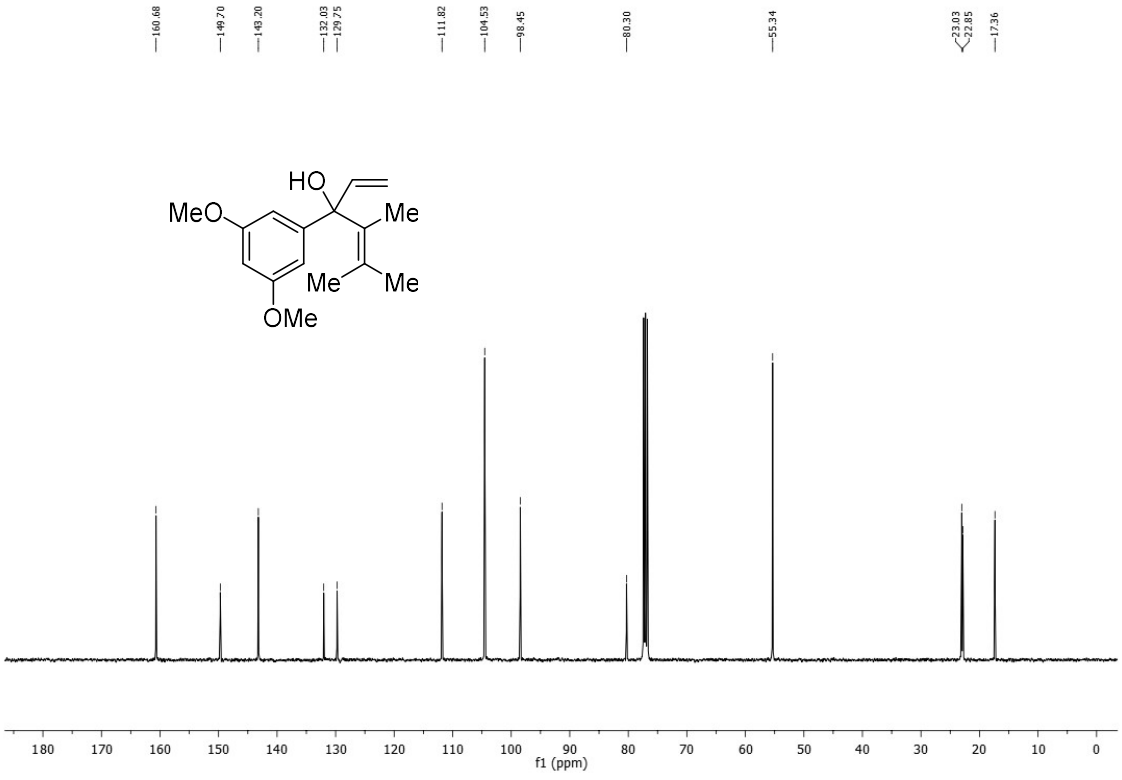
^{1}H NMR (500 MHz, $CDCl_3$) for compound **7j**.



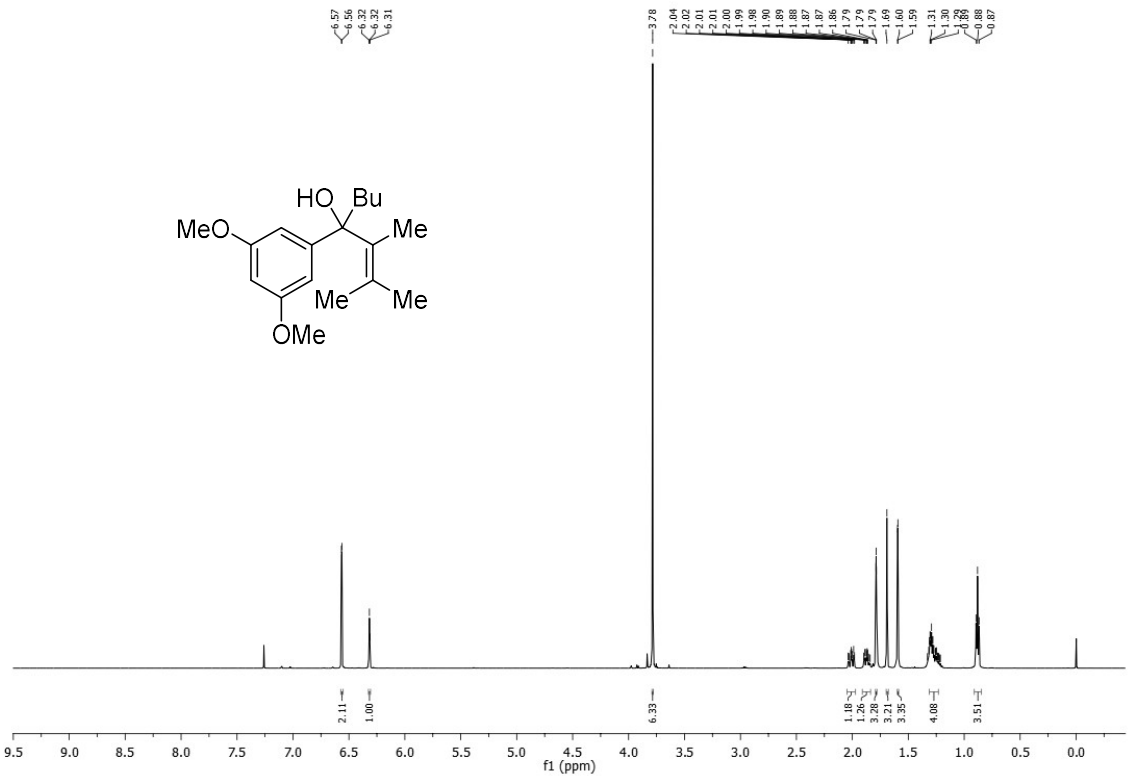
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **7j**.



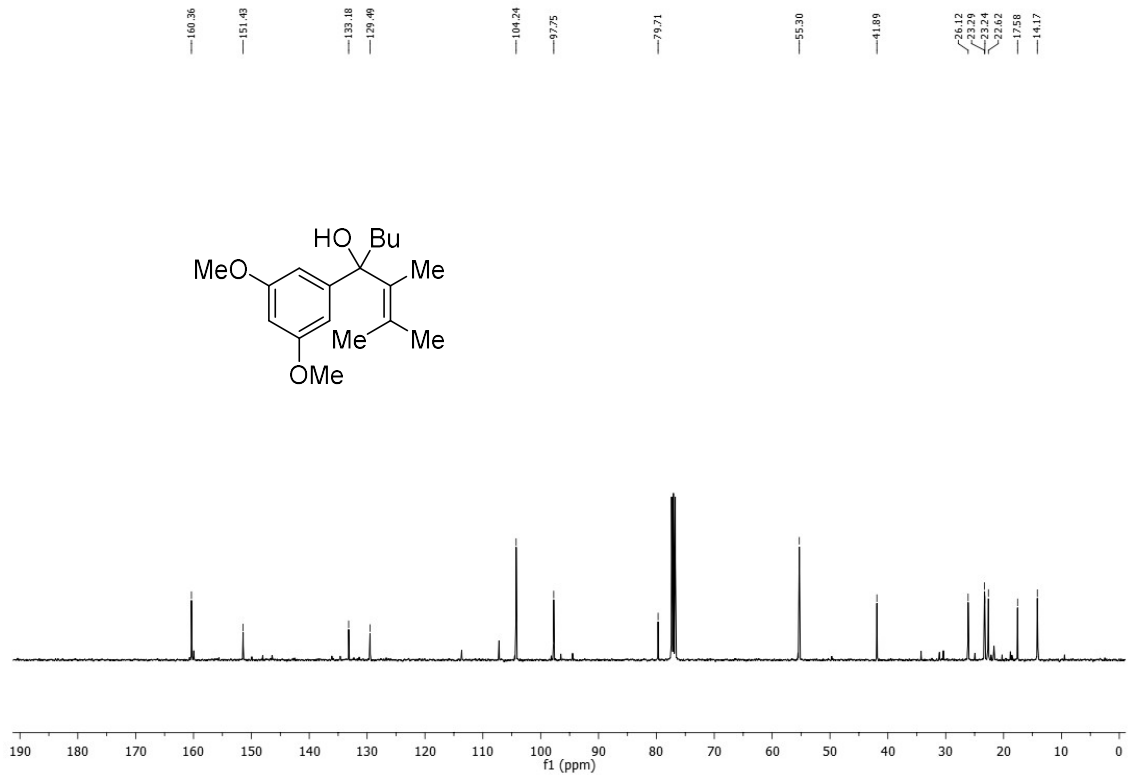
^{1}H NMR (500 MHz, $CDCl_3$) for compound **7k**.



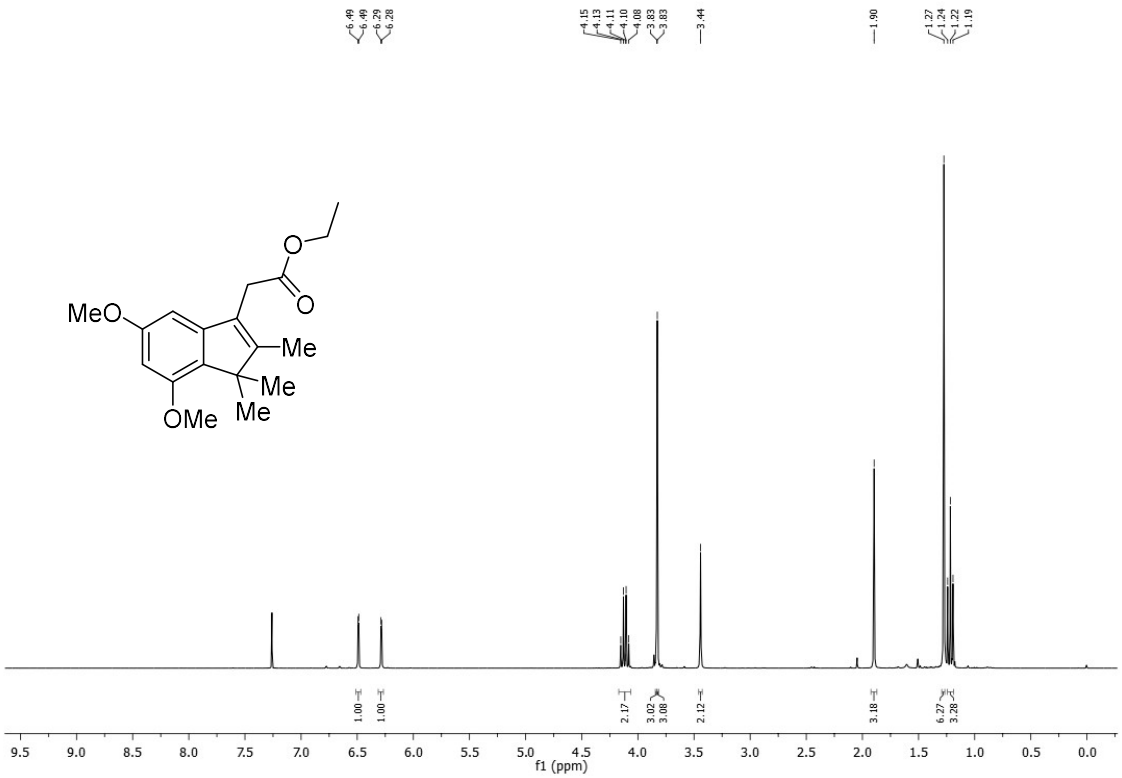
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound **7k**.



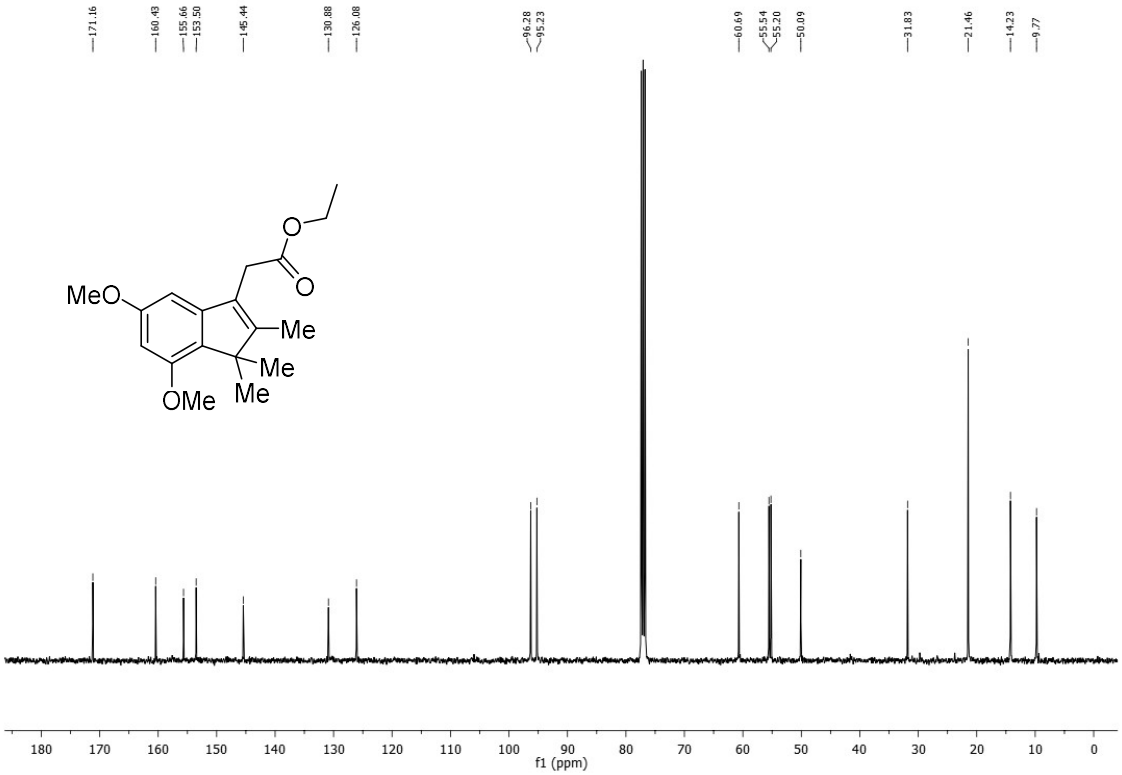
^{1}H NMR (500 MHz, $CDCl_3$) for compound **7l**.



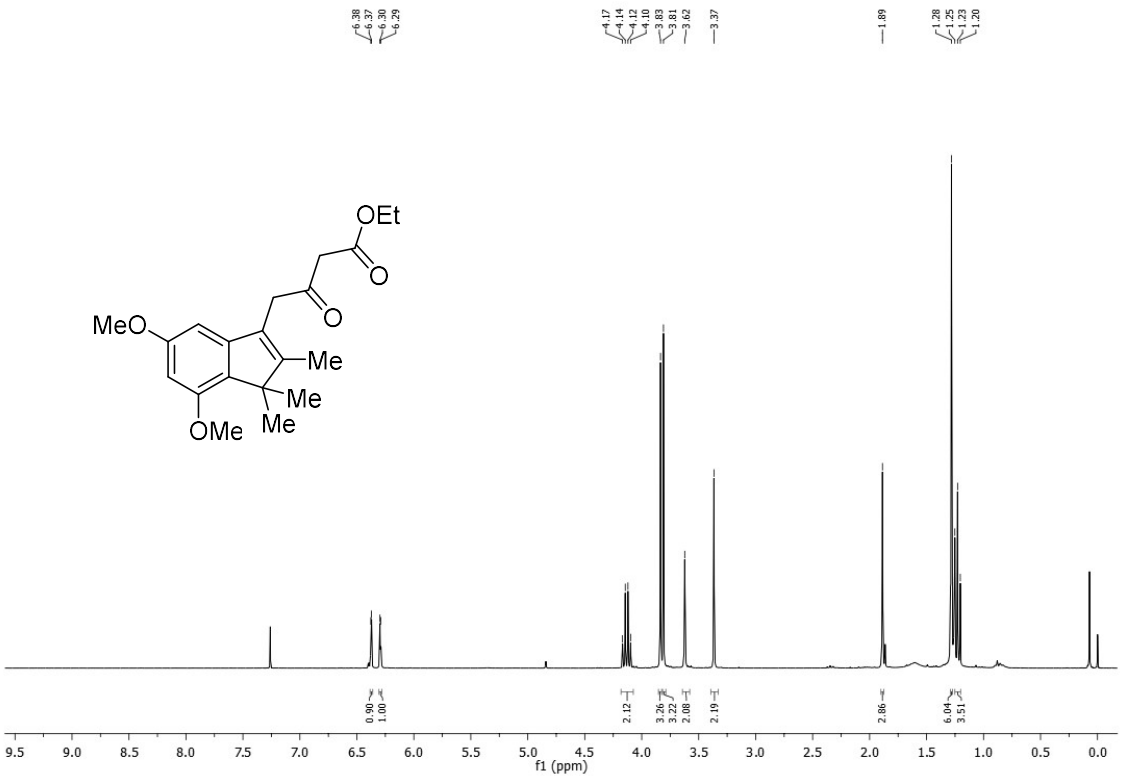
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **7l**.



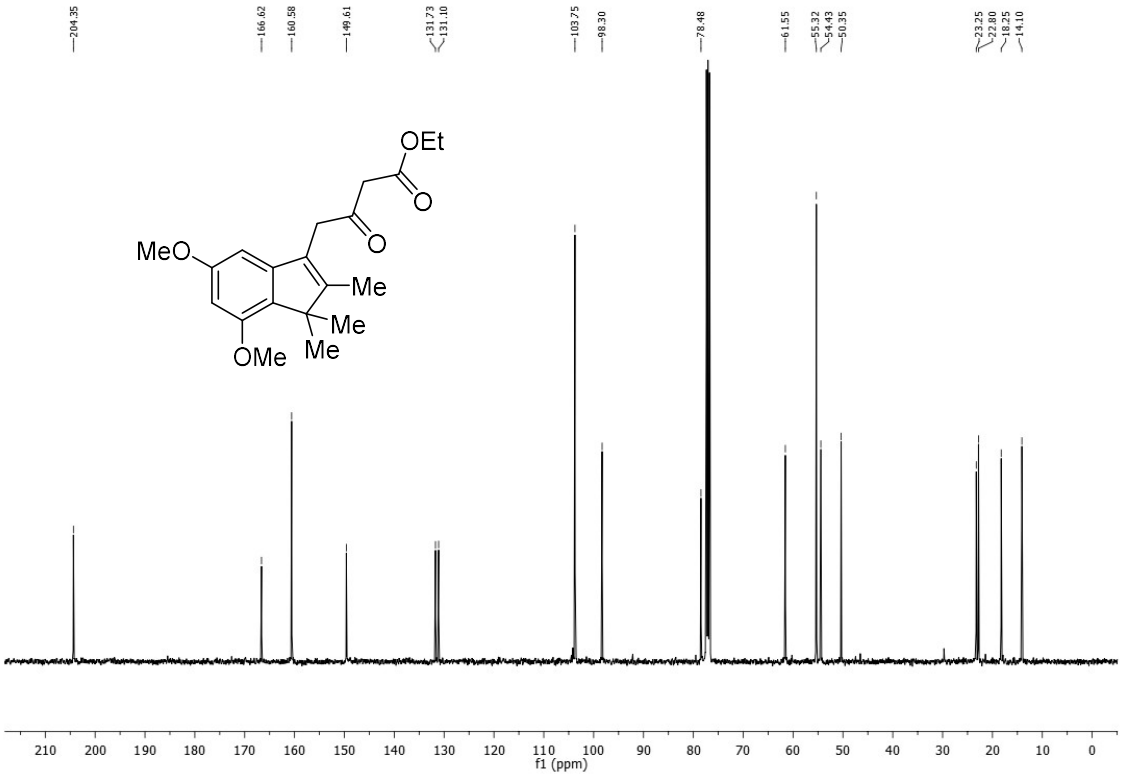
^{1}H NMR (300 MHz, $CDCl_3$) for compound **8g**.



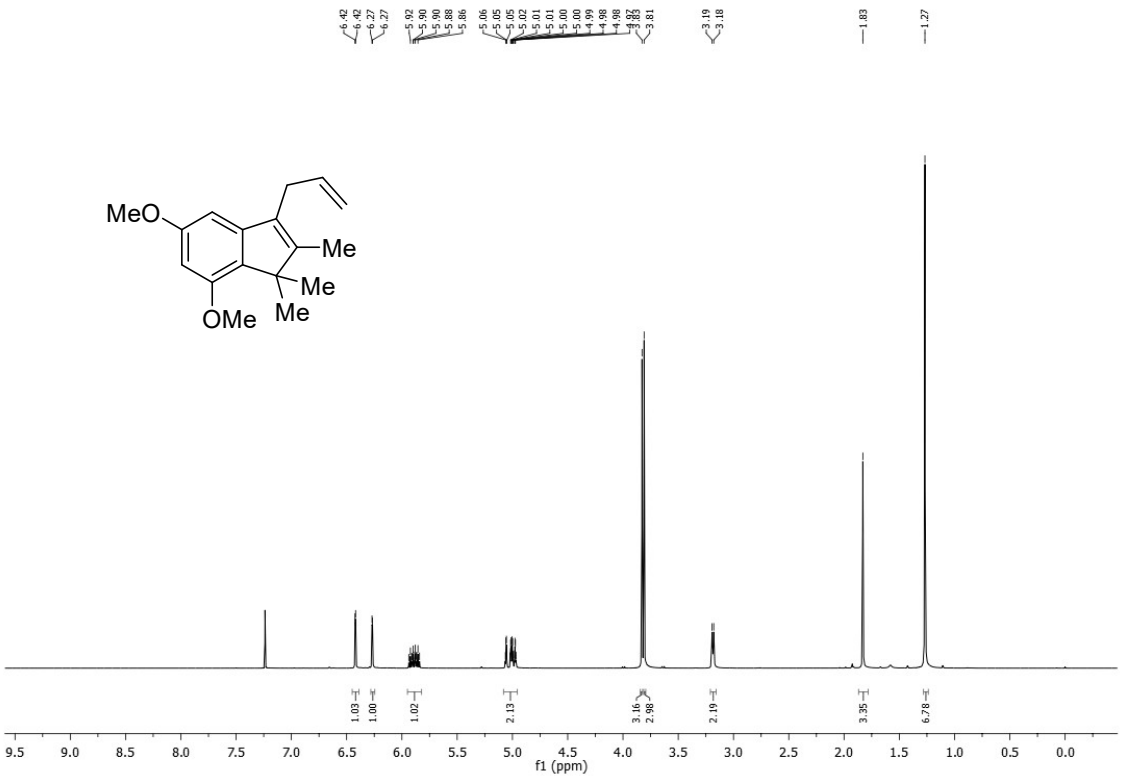
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound **8g**.



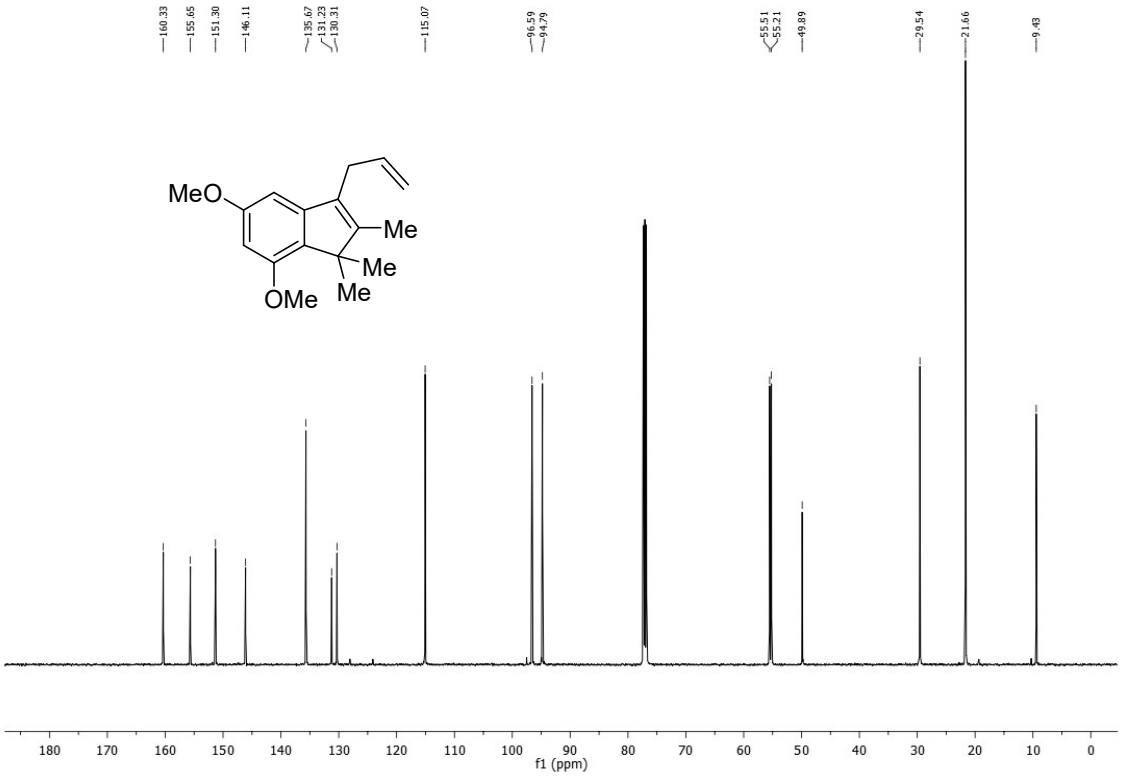
^{1}HNMR (300 MHz, $CDCl_3$) for compound **8h**.



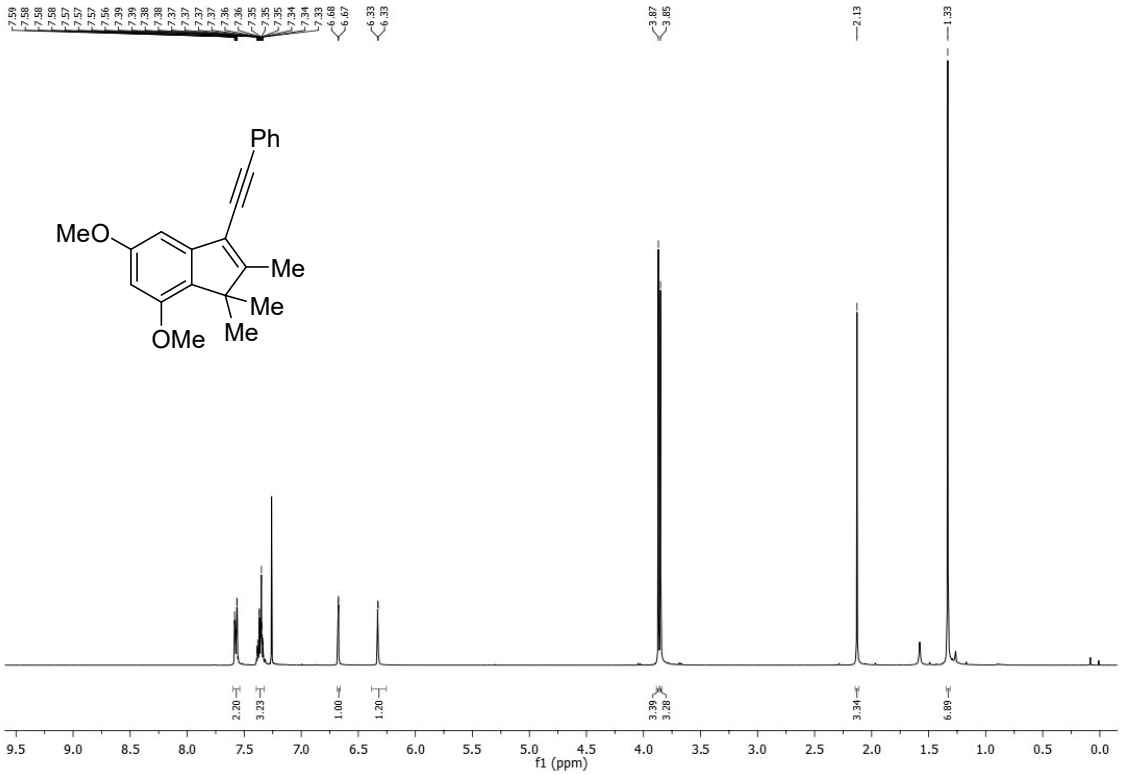
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) for compound **8h.**



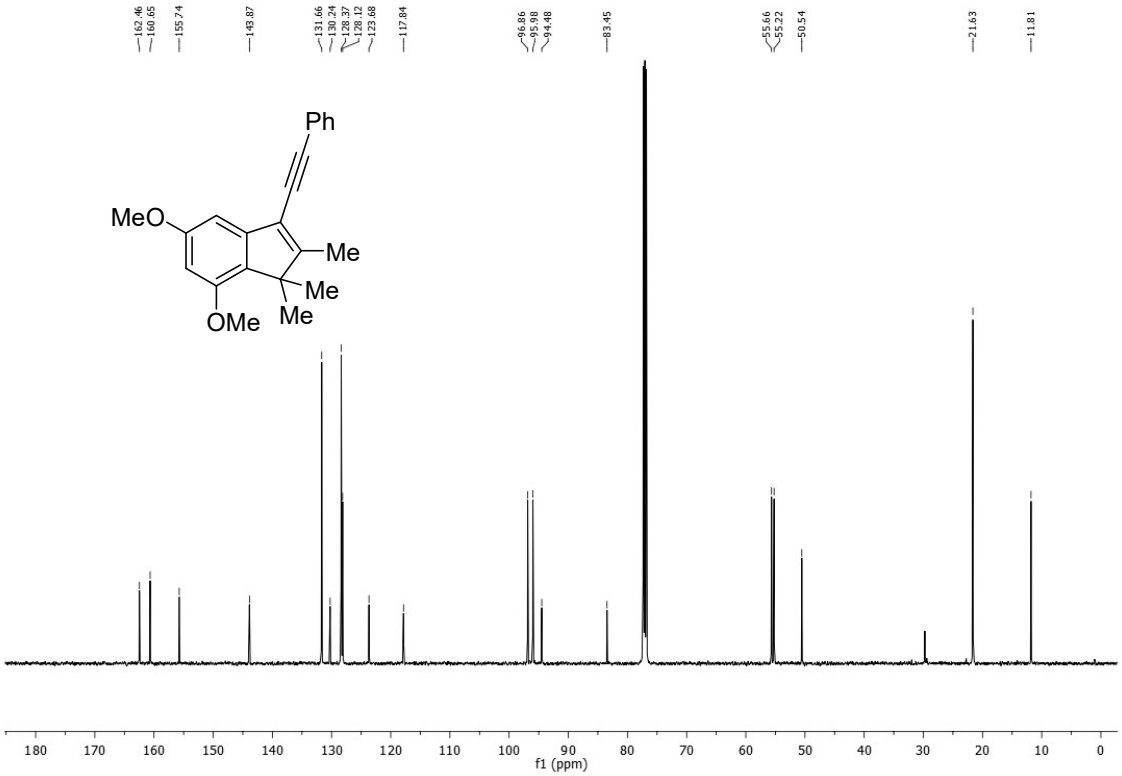
^{1}H NMR (400 MHz, $CDCl_3$) for compound **8i**.



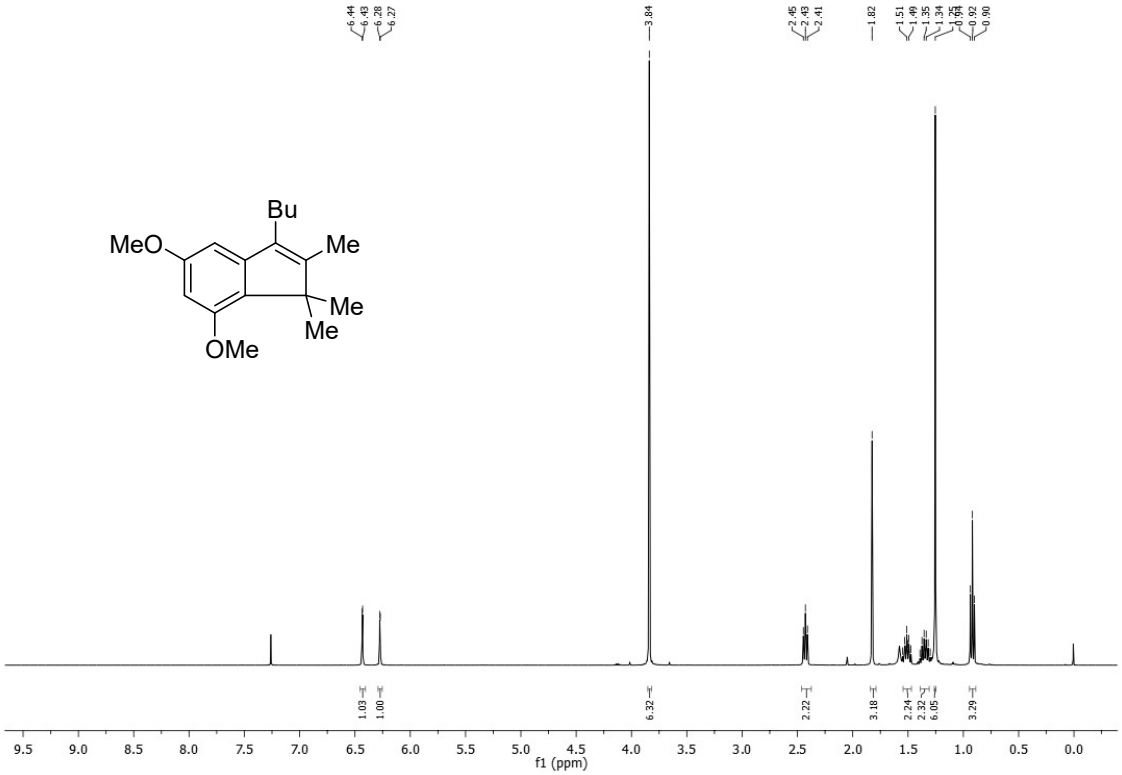
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for compound **8i.**



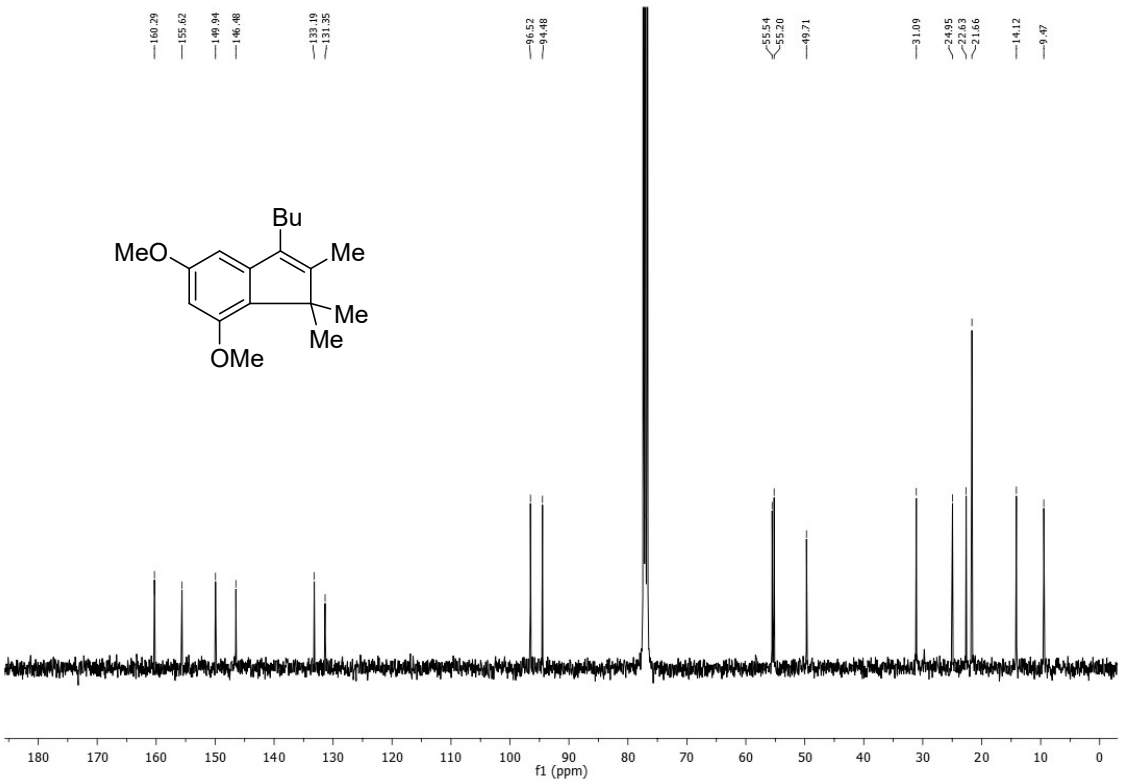
^{1}H NMR (400 MHz, $CDCl_3$) for compound **8j**.



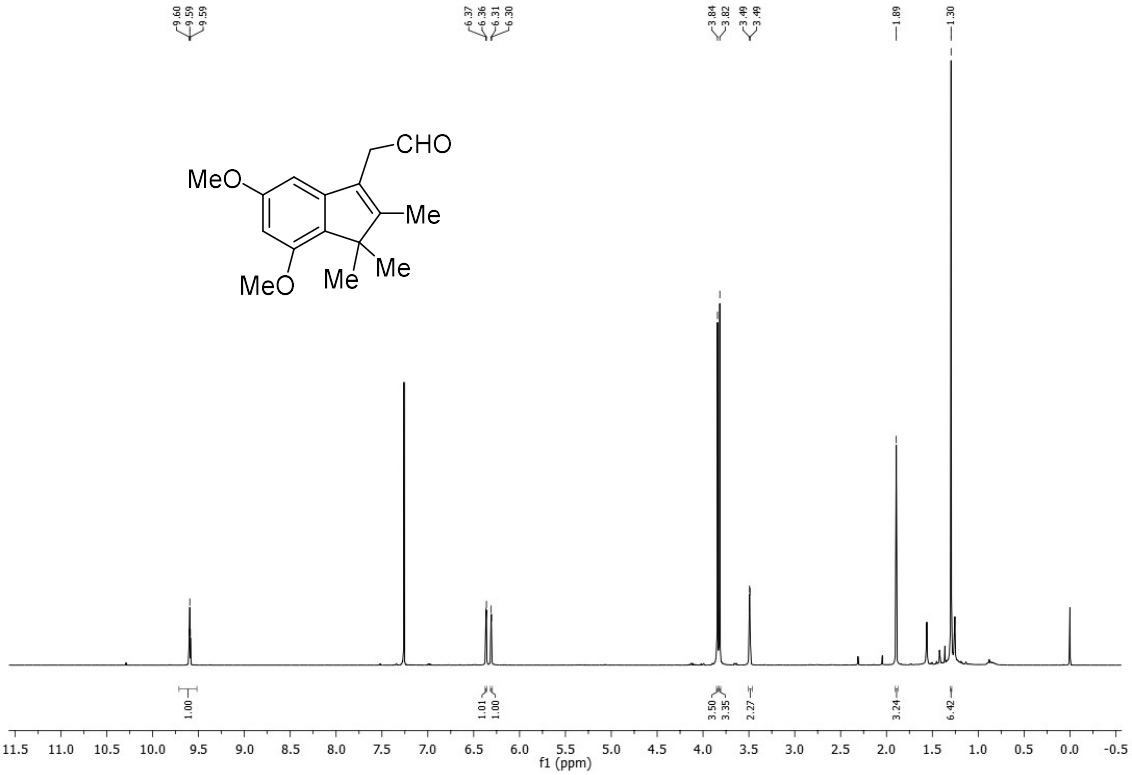
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for compound **8j.**



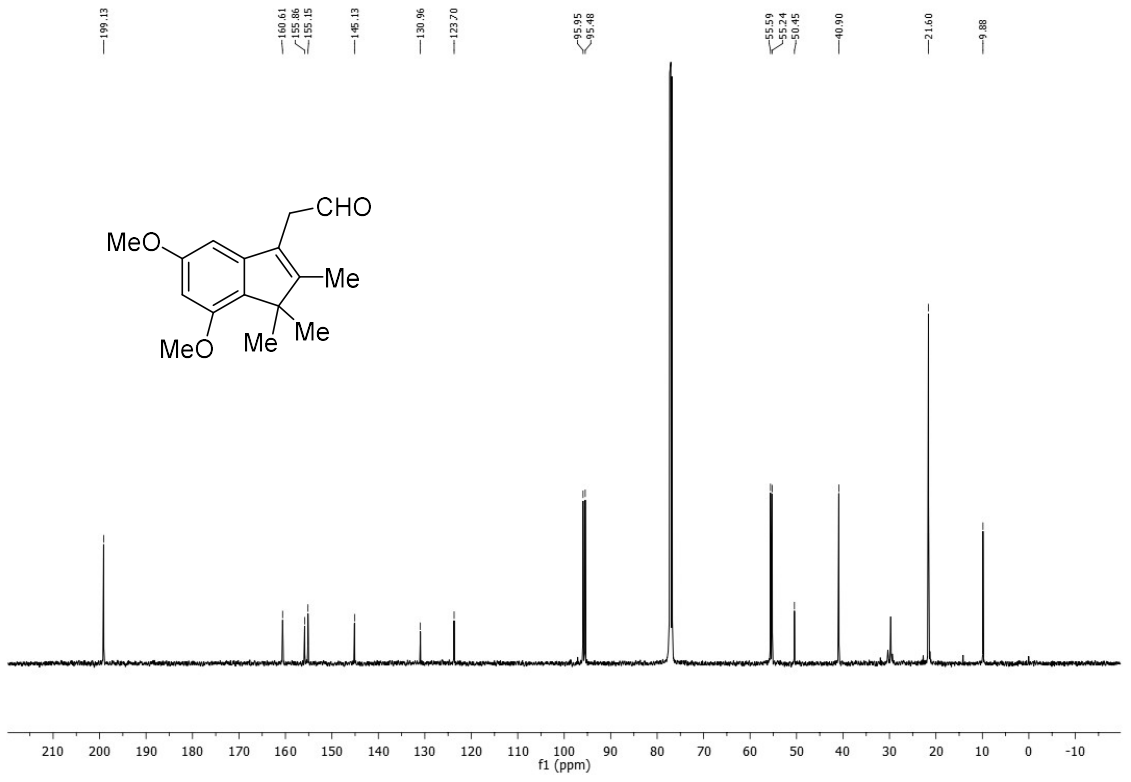
^{1}HNMR (400 MHz, $CDCl_3$) for compound **8l**.



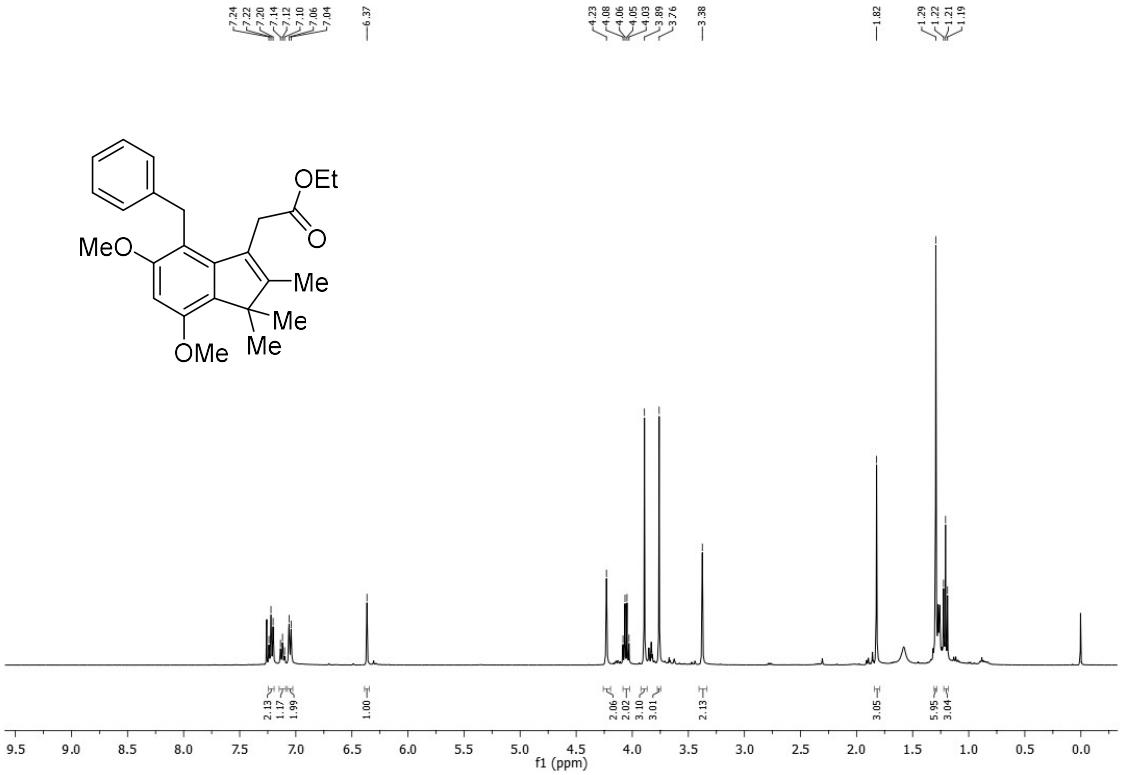
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for compound **8l.**



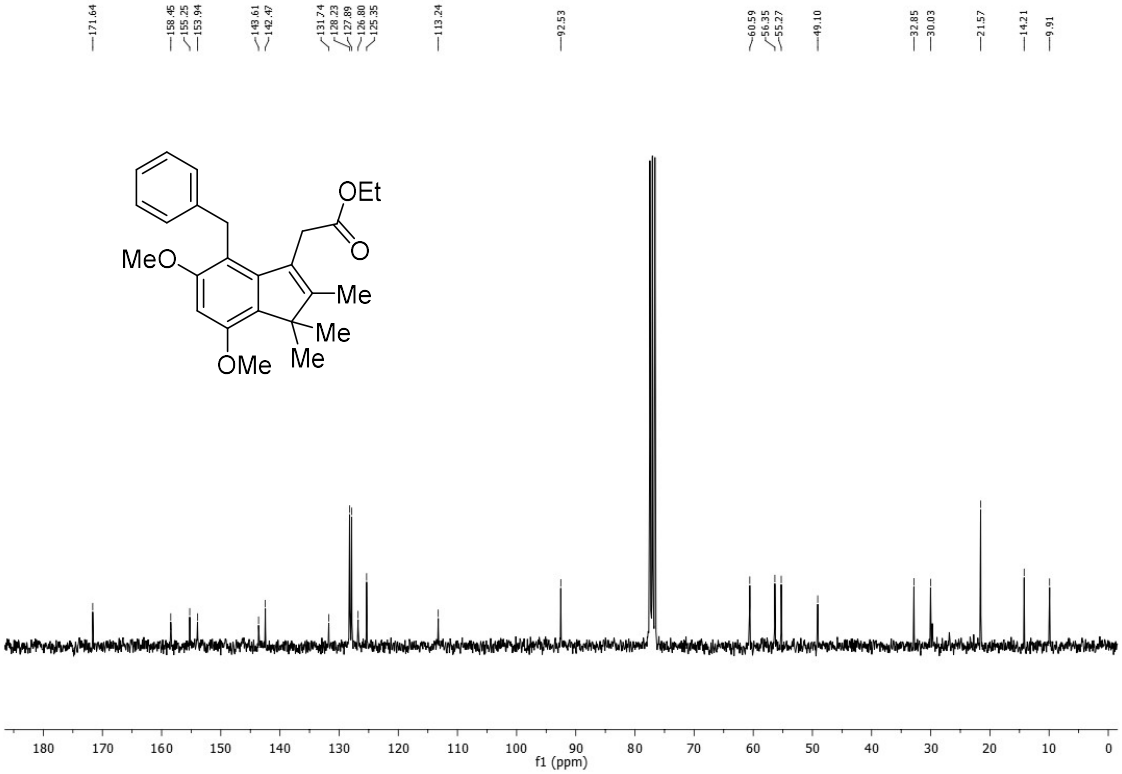
^{1}H NMR (400 MHz, $CDCl_3$) for compound **8m**



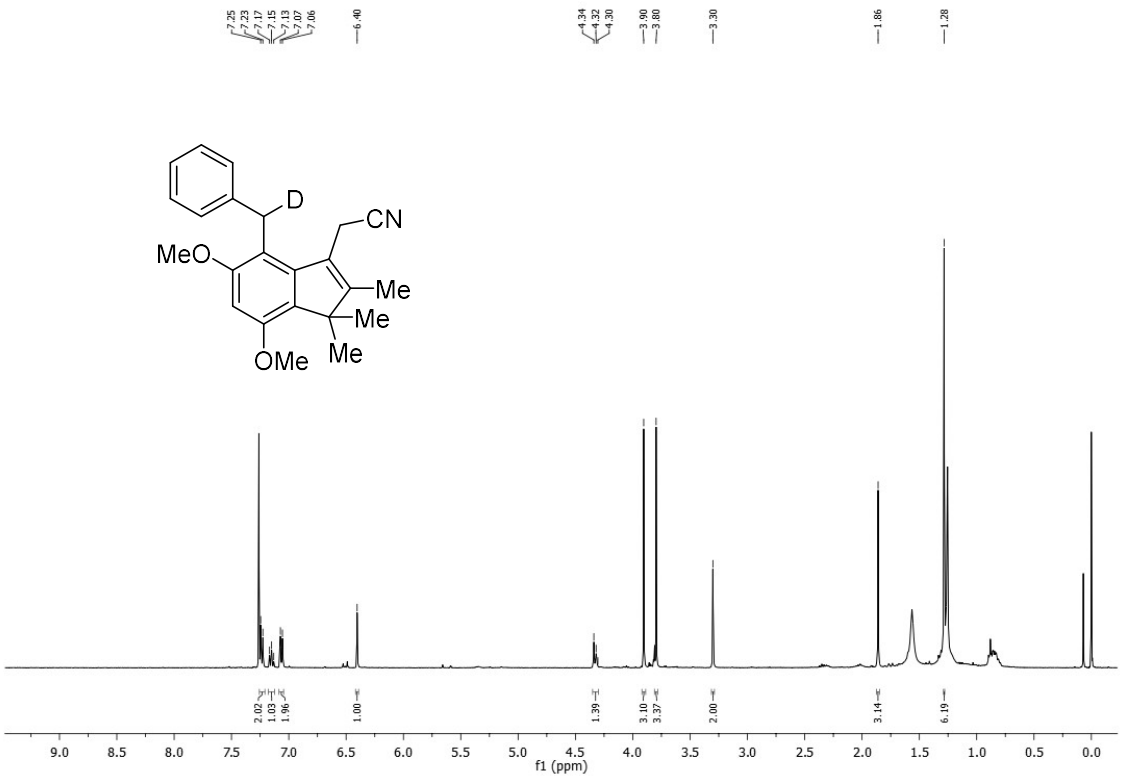
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) for compound **8m**



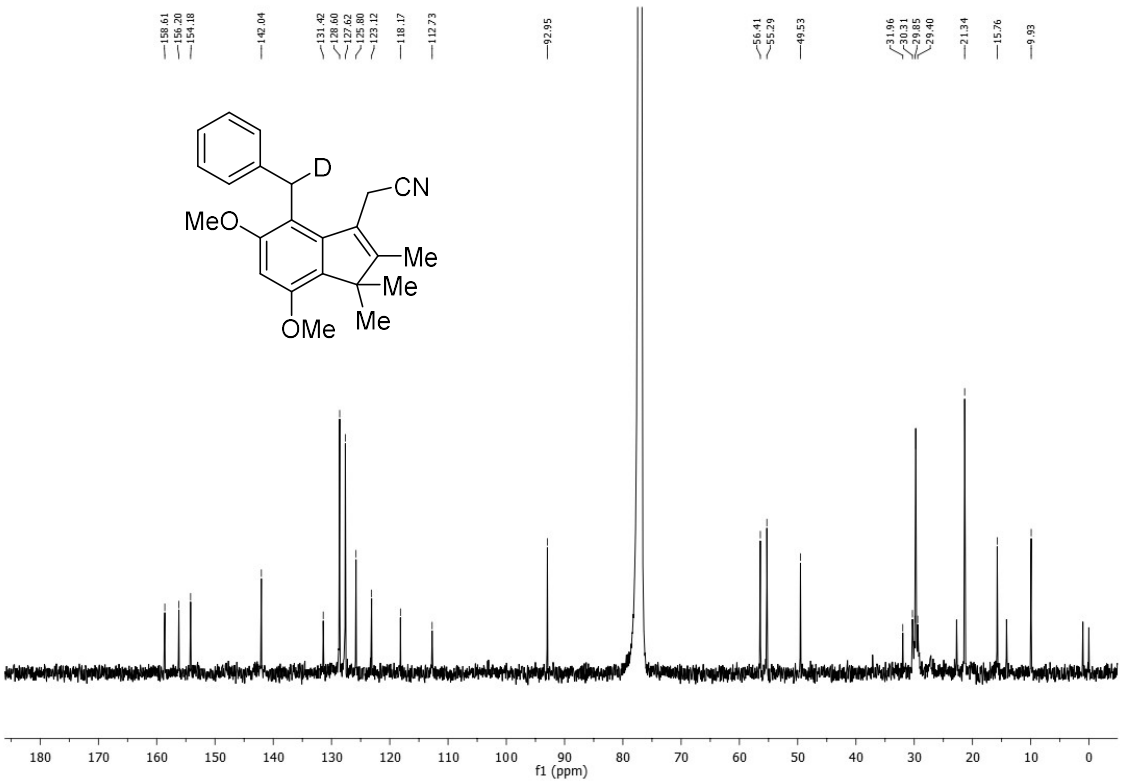
^{1}H NMR (400 MHz, $CDCl_3$) for compound **10b**.



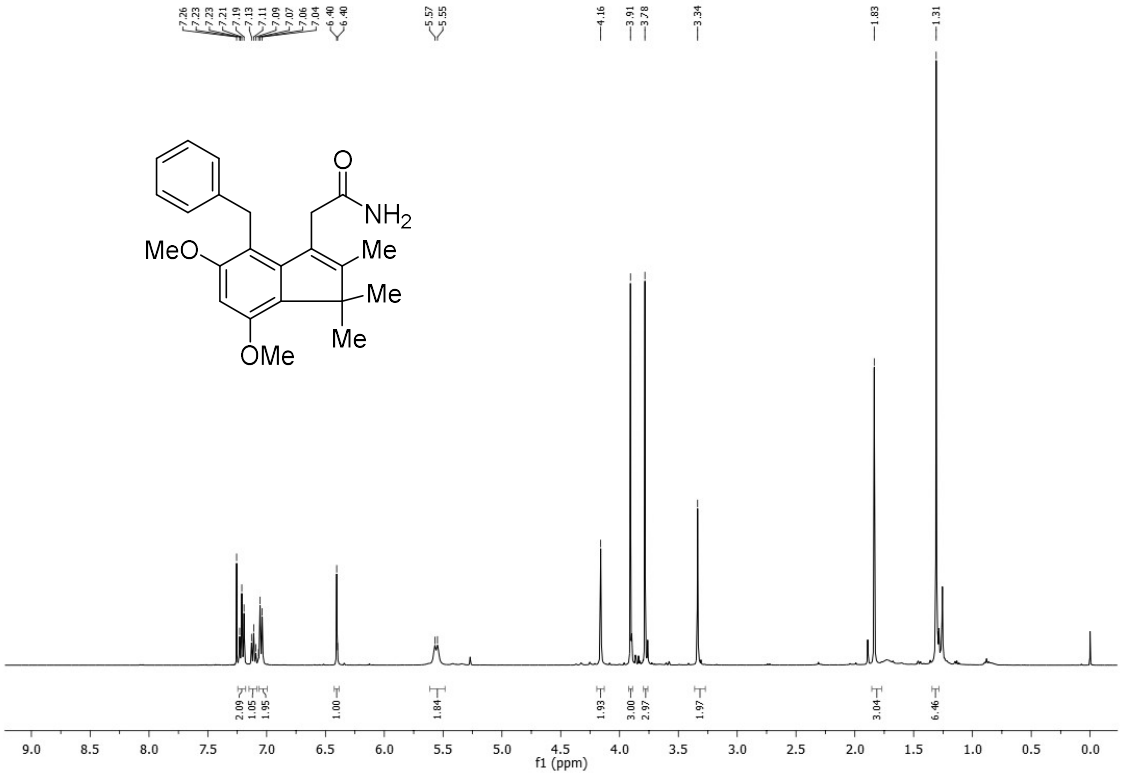
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) for compound **10b.**



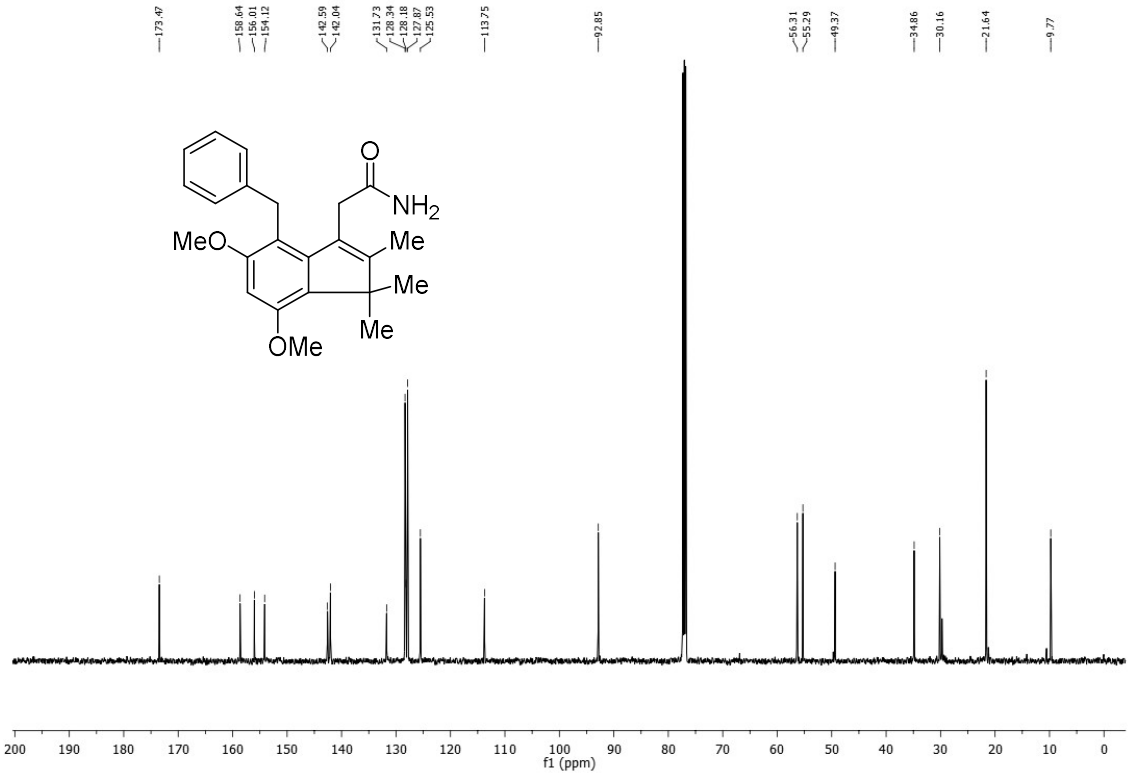
^{1}H NMR (400 MHz, $CDCl_3$) for compound ***d*-9a** .



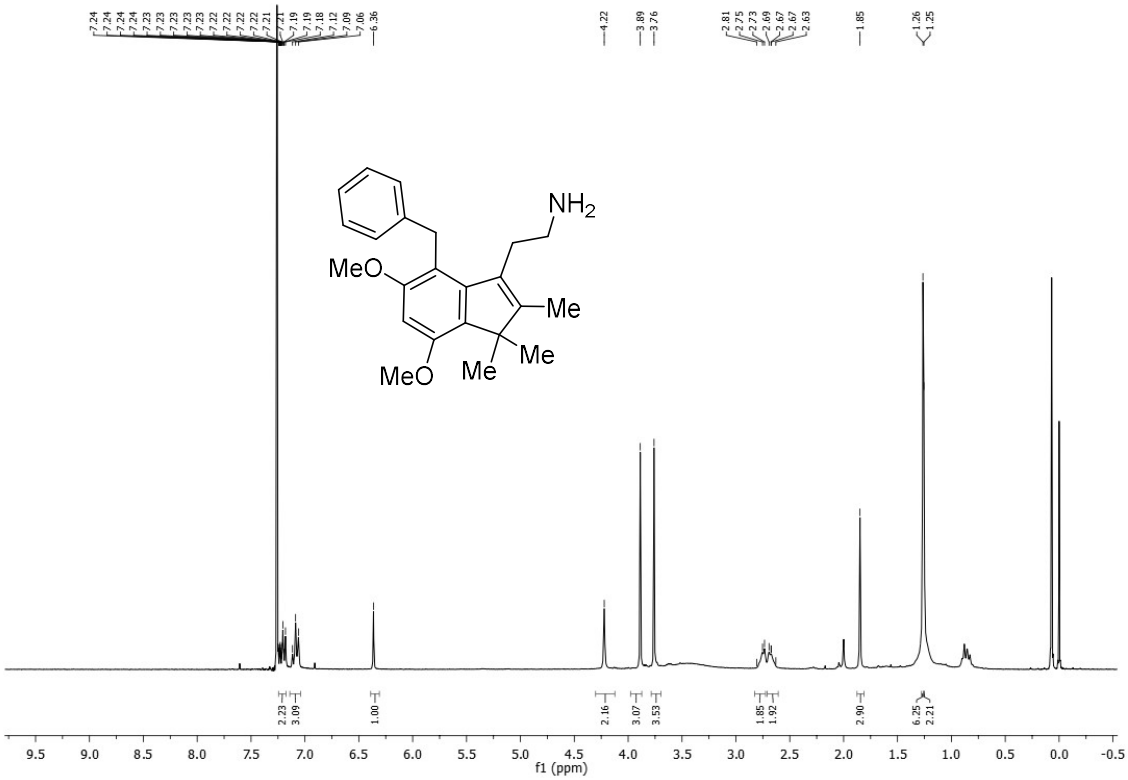
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) for compound ***d*-9a**.



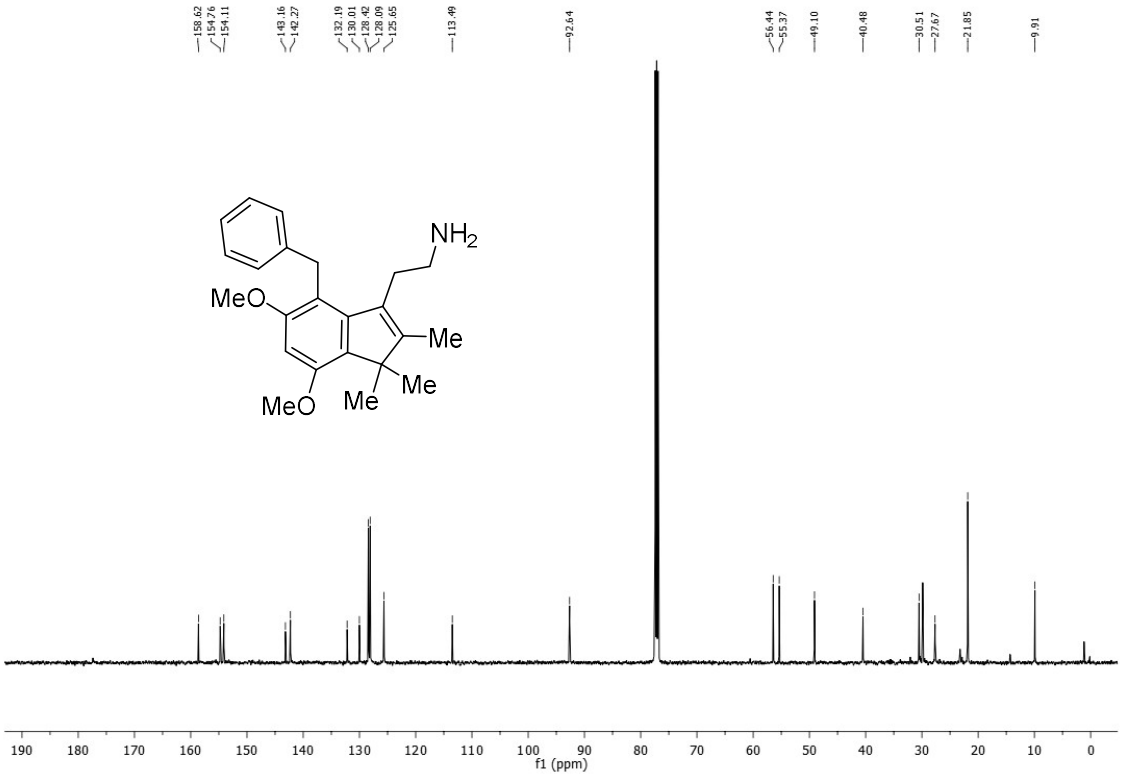
^{1}HNMR (400 MHz, $CDCl_3$) for compound **13**.



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) for compound **13.**



^{1}HNMR (300 MHz, $CDCl_3$) for compound **15**.



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for compound **15.**