Visible-Light-Promoted Cascade Alkene Trifluoromethylation and Dearomatization of Indole Derivatives *via* Intermolecular Charge Transfer

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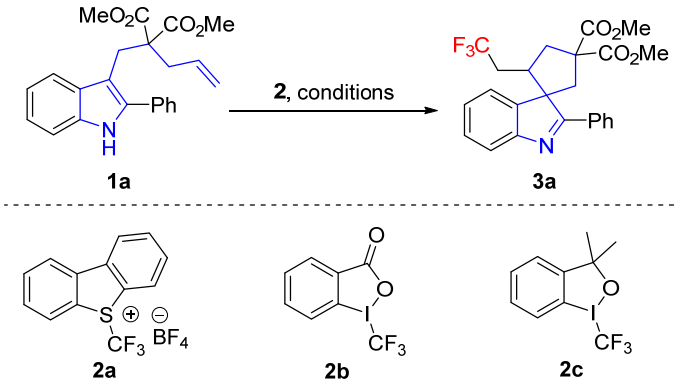
1. General methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on an Agilent instrument (400 MHz and 100 MHz, respectively) or an Agilent instrument (600 MHz and 150 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{19}F NMR spectra were recorded on an Agilent instrument (376 MHz) and referenced relative to $CFCl_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). UV/vis absorption spectra were recorded on a Thermo Nanodrop 2000c UV/Vis spectrometer.

Substrates **1a-1w** were synthesized according to the literature procedures.[1] Reagents **2a**, **2b** and **2c** are commercially available from Alfa Aesar, and were used without further purification.

2. Detailed screening of reaction conditions

Table 1. Optimization of the reaction conditions[a]



entry	**2**	solvent	base	t (h)	yield (%)[b]
1	**2a**	DMF	-	48	43
2	**2a**	CH_3CN	-	24	72
3	**2a**	MeOH	-	48	56
4	**2a**	$CHCl_3$	-	2	78
5	**2a**	DCM	-	2	80
6	**2a**	DCE	-	2	83
7	**2a**	1,4-dioxane	-	24	57
8	**2a**	Et_2O	-	24	n.d.
9	**2a**	toluene	-	24	n.d.
10	**2a**	DCE	K_2HPO_4	15	75
11	**2a**	DCE	K_2CO_3	15	77
12	**2a**	DCE	Cs_2CO_3	24	75
13	**2a**	DCE	^{t}BuOK	48	52[c]
14	**2a**	DCE	Et_3N	48	59[c]
15	**2b**	DCE	-	24	n.d.[c]
16	**2c**	DCE	-	24	54[c]
17[d]	**2a**	DCE	-	4	77
18[e]	**2a**	DCE	-	15	77
19[f]	**2a**	DCE	-	24	n.d.
20[g]	**2a**	DCE	-	24	n.d.

[a]General conditions: **1a** (0.05 mmol), **2** (0.075 mmol), and base (0.075 mmol) in solvent (0.5 mL, 0.1 M) were stirred at room temperature under visible light. Unless otherwise noted, 24W blue LEDs were used as the light source. The product was observed in the form of two diastereoisomers and the dr value was determined as 1.3:1 by ^{19}F NMR. [b]Isolated yield. [c]NMR yield determined by ^{19}F NMR with $PhCF_3$

as the internal standard. [d]Light source: 23W CFL. [e]DCE (0.25 mL, 0.2 M). [f]Open to air. [g]In dark. n.d. = not detected.

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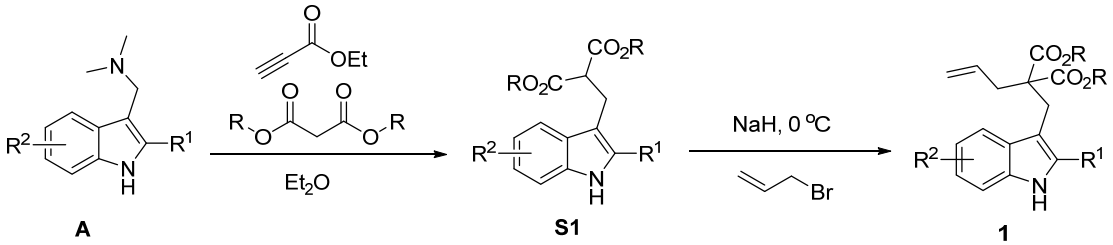
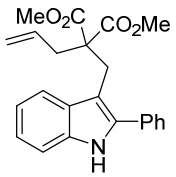
3. Reaction details and characterization data

General procedure for the synthesis of substrates (1a-1w):

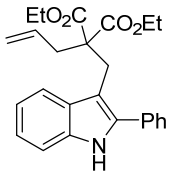


In a round bottom flask, **A** (21 mmol) was dissolved into reagent grade Et_2O. After the addition of dialkyl malonate (23 mmol), ethylpropriolate (2.3 mL, 23 mmol) was added at once. After the reaction was complete (monitored by TLC), it was quenched with water. The aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organics were washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/Acetone = 12/1) to afford the desired product **S1**.

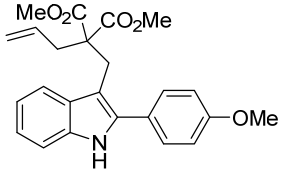
To a solution of the above **S1** (2 g, 5.7 mmol, 1.0 equiv) in THF was added NaH (272 mg, 6.8 mmol), followed by the dropwise addition of allyl bromide (0.6 mL, 6.8 mmol) under ice bath. Then the reaction was allowed to warm to room temperature. After the reaction was complete (monitored by TLC), it was quenched with water. The mixture was extracted with EtOAc (3 x 30 mL). The organic layer was washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 12/1) to afford the desired product **1**.



1a, red solid, 3.2 g, 60% yield, m.p. = 129.3-131.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.34-7.33 (m, 2H), 7.24 (br, 3H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.12-7.07 (m, 2H), 5.37-5.27 (m, 1H), 4.79 (d, *J* = 10.4 Hz, 1H), 4.74 (d, *J* = 17.2 Hz, 1H), 3.69 (s, 2H), 3.34 (s, 6H), 2.34 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 137.0, 135.5, 133.4, 132.7, 129.4, 128.8, 128.7, 127.7, 121.8, 119.3, 119.1, 118.1, 110.9, 105.8, 59.4, 51.9, 36.8, 27.0. IR (thin film): ν_{max} (cm^{-1}) = 3412, 3052, 2956, 2926, 1722, 1688, 1643, 1489, 1438, 1347, 1293, 1240, 1201, 1024, 911, 862, 808, 738, 696. HRMS (ESI) calcd for $C_{23}H_{27}N_2O_4$ $[M+NH_4]^+$: 395.1965. Found: 395.1960.

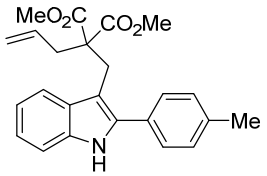


1b, white solid, 0.9 g, 75% yield, m.p. = 109.8-111.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.41-7.31 (m, 3H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.16-7.07 (m, 2H), 5.39-5.29 (m, 1H), 4.80 (d, *J* = 10.4 Hz, 1H), 4.76 (d, *J* = 16.8 Hz, 1H), 3.99-3.91 (m, 2H), 3.79-3.71 (m, 2H), 3.68 (s, 2H), 2.35 (d, *J* = 7.1 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 137.1, 135.6, 133.6, 132.8, 129.6, 129.0, 128.9, 127.9, 122.0, 119.5, 119.4, 118.1, 110.8, 106.5, 60.9, 59.1, 36.8, 26.9, 13.8. IR (thin film): ν_{max} (cm^{-1}) = 3386, 2984, 2924, 1744, 1718, 1640, 1473, 1443, 1368, 1345, 1328, 1228, 1200, 1067, 1041, 915, 862, 767, 745, 702. HRMS (ESI) calcd for $C_{25}H_{28}NO_4$ $[M+H]^+$: 406.2013. Found: 406.2007.

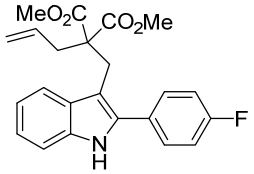


1c, white solid, 0.3 g, 76% yield, m.p. = 148.9-150.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz,

1H), 7.14-7.07 (m, 2H), 6.83 (d, J = 8.4 Hz, 2H), 5.42-5.31 (m, 1H), 4.83 (d, J = 11.2 Hz, 1H), 4.81 (d, J = 17.2 Hz, 1H), 3.77 (s, 3H), 3.67 (s, 2H), 3.42 (s, 6H), 2.36 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 159.2, 137.0, 135.4, 132.9, 130.1, 129.5, 125.8, 121.7, 119.3, 119.1, 118.1, 114.2, 110.8, 105.6, 59.4, 55.3, 52.0, 36.9, 27.2. IR (thin film): ν_{max} (cm^{-1}) = 3410, 2953, 2834, 1753, 1727, 1608, 1502, 1459, 1437, 1343, 1307, 1287, 1247, 1205, 1183, 1027, 920, 862, 835, 750, 691, 643. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_5$ $[M+NH_4]^+$: 425.2071. Found: 425.2066.

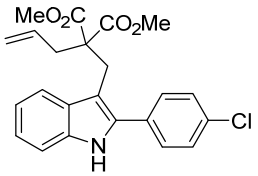


1d, white solid, 1.1 g, 71% yield, m.p. = 107.5-108.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.10-7.05 (m, 3H), 6.99 (d, J = 8.0 Hz, 2H), 5.38-5.28 (m, 1H), 4.77 (d, J = 12.0 Hz, 1H), 4.74 (d, J = 19.2 Hz, 1H), 3.66 (s, 2H), 3.31 (s, 6H), 2.33 (d, J = 6.8 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 137.2, 137.0, 135.4, 132.7, 130.3, 129.3, 129.1, 128.5, 121.4, 119.0, 118.9, 117.8, 110.8, 105.2, 59.3, 51.7, 36.7, 27.0, 20.8. IR (thin film): ν_{max} (cm^{-1}) = 3415, 3029, 2954, 1728, 1642, 1502, 1457, 1343, 1288, 1234, 1204, 1144, 950, 919, 879, 862, 827, 744, 689. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_4$ $[M+NH_4]^+$: 409.2122. Found: 409.2114.

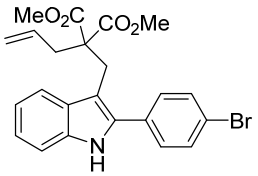


1e, white solid, 1.0 g, 50% yield, m.p. = 113.0-114.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (br, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.44-7.43 (m, 2H), 7.29 (br, 1H), 7.19-7.08 (m, 4H), 5.40-5.29 (m, 1H), 4.86 (d, J = 10.4 Hz, 1H), 4.80 (d, J =17.2 Hz, 1H), 3.67 (s, 2H), 3.45 (s, 6H), 2.35 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 162.3 (d, J = 246.0 Hz), 136.0, 135.5, 132.4, 130.7 (d, J = 7.0 Hz), 129.5 (d, J = 3.0 Hz), 129.3, 122.1, 119.5, 119.2, 118.3, 115.7 (d, J = 21.0 Hz), 111.0, 106.0, 59.4, 52.0, 36.9, 27.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.1 - -113.2 (m, 1H). IR (thin film): ν_{max} (cm^{-1}) = 3415, 3377, 2953, 1719, 1604, 1556,

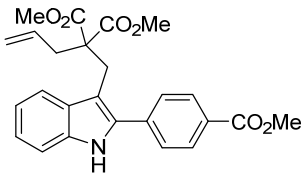
1499, 1457, 1436, 1344, 1205, 1156, 1122, 962, 926, 864, 841, 742, 699. HRMS (ESI) calcd for $C_{23}H_{26}FN_2O_4$ $[M+NH_4]^+$: 413.1871. Found: 413.1868.



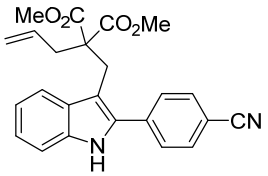
1f, yellow solid, 1.0 g, 63% yield, m.p. = 131.2-132.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.55 (d, *J* = 6.8 Hz, 1H), 7.26-7.21 (m, 5H), 7.15-7.11 (m, 2H), 5.40-5.34 (m, 1H), 4.86 (d, *J* = 10.0 Hz, 1H), 4.79 (d, *J* = 16.8 Hz, 1H), 3.65 (s, 2H), 3.41 (s, 6H), 2.33 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 135.64, 135.59, 133.8, 132.5, 131.9, 130.1, 129.4, 129.0, 122.3, 119.7, 119.4, 118.4, 111.0, 106.5, 59.4, 52.0, 37.0, 27.1. IR (thin film): ν_{max} (cm^{-1}) = 3411, 3368, 3007, 1720, 1642, 1484, 1455, 1434, 1344, 1290, 1234, 1206, 1142, 1091, 1013, 927, 880, 749, 740. HRMS (ESI) calcd for $C_{23}H_{26}ClN_2O_4$ $[M+NH_4]^+$: 429.1576. Found: 429.1574.



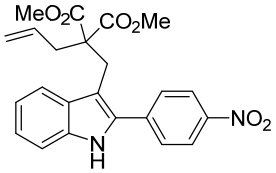
1g, yellow solid, 0.4 g, 53% yield, m.p. = 139.7-140.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.23 (br, 3H), 7.17-7.11 (m, 2H), 5.41-5.35 (m, 1H), 4.87 (d, *J* = 10.0 Hz, 1H), 4.80 (d, *J* = 16.8 Hz, 1H), 3.65 (s, 2H), 3.41 (s, 6H), 2.34 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 135.6, 132.5, 132.3, 131.9, 130.4, 129.4, 122.4, 121.9, 119.7, 119.4, 118.4, 111.0, 106.6, 59.3, 52.1, 37.0, 27.1. IR (thin film): ν_{max} (cm^{-1}) = 3416, 3374, 3007, 1720, 1642, 1484, 1455, 1435, 1343, 1291, 1254, 1232, 1205, 1122, 1100, 1070, 924, 880, 833, 743, 712. HRMS (ESI) calcd for $C_{23}H_{26}BrN_2O_4$ $[M+NH_4]^+$: 473.1070. Found: 473.1068.



1h, yellow solid, 1.6 g, 75% yield, m.p. = 131.5-132.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.23-7.21 (m, 1H), 7.15-7.05 (m, 2H), 5.42-5.32 (m, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 4.76 (d, *J* = 17.2 Hz, 1H), 3.87 (s, 3H), 3.70 (s, 2H), 3.35 (s, 6H), 2.32 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 166.5, 138.0, 135.8, 135.4, 132.3, 129.7, 129.2, 128.6, 128.4, 122.3, 119.4, 119.3, 118.2, 111.0, 106.9, 59.2, 52.0, 51.8, 36.8, 27.1. IR (thin film): ν_{max} (cm^{-1}) = 3365, 2951, 1747, 1721, 1637, 1566, 1430, 1403, 1344, 1277, 1253, 1209, 1205, 1176, 1152, 1113, 929, 743, 699. HRMS (ESI) calcd for $C_{25}H_{29}N_2O_6$ $[M+NH_4]^+$: 453.2020. Found: 453.2014

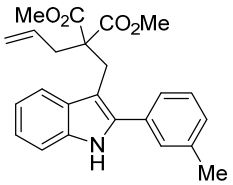


1i, yellow solid, 0.2 g, 51% yield, m.p. = 164.8-166.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.26-7.13 (m, 3H), 5.43-5.32 (m, 1H), 4.88 (d, *J* = 10.0 Hz, 1H), 4.81 (d, *J* = 16.8, 1H), 3.68 (s, 2H), 3.42 (s, 6H), 2.33 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 138.1, 136.0, 134.6, 132.4, 132.1, 129.3, 129.2, 123.0, 120.0, 119.7, 118.6, 118.5, 111.2, 110.9, 107.9, 59.3, 52.1, 37.0, 27.1. IR (thin film): ν_{max} (cm^{-1}) = 3371, 3020, 2227, 1748, 1711, 1637, 1605, 1496, 1436, 1347, 1291, 1269, 1210, 1176, 990, 963, 945, 920, 845, 743, 645. HRMS (ESI) calcd for $C_{24}H_{26}N_3O_4$ $[M+NH_4]^+$: 420.1918. Found: 420.1916.

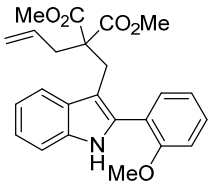


1j, yellow solid, 0.2 g, 47% yield, m.p. = 148.0-150.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.29-7.26 (m, 1H), 7.22-7.15 (m, 2H), 5.45-5.35 (m, 1H), 4.87 (d, *J* = 10.0 Hz, 1H), 4.81 (d, *J* = 16.8 Hz, 1H), 3.72 (s, 2H), 3.43 (s, 6H), 2.35 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $cdcl_3$) δ 171.4, 146.7, 140.0, 136.1, 134.2, 132.1, 129.32, 129.28, 124.0, 123.3, 120.1, 119.8, 118.7, 111.3, 108.6, 59.3, 52.2, 37.2, 27.3. IR (thin film): ν_{max} (cm^{-1}) = 3373, 3020, 2950, 1748, 1709, 1637, 1596, 1543, 1513, 1339, 1267,

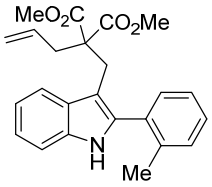
1209, 1152, 1109, 851, 744, 686, 618. HRMS (ESI) calcd for $C_{23}H_{26}N_3O_6$ $[M+NH_4]^+$: 440.1816. Found: 440.1819.



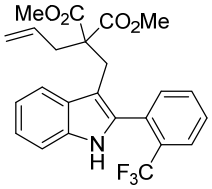
1k, white solid, 0.9 g, 70% yield, m.p. = 114.2-115.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.23 (s, 1H), 7.14 (t, *J* = 5.6 Hz, 3H), 7.10-7.05 (m, 3H), 5.36-5.26 (m, 1H), 4.78 (d, *J* = 10.0 Hz, 1H), 4.72 (d, *J* = 16.8 Hz, 1H), 3.67 (s, 2H), 3.33 (s, 6H), 2.33 (d, *J* = 7.2 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 138.2, 137.0, 135.4, 133.3, 132.6, 129.29, 129.27, 128.6, 128.4, 125.8, 121.7, 119.1, 119.0, 117.9, 110.8, 105.6, 59.3, 51.8, 36.7, 26.9, 21.1. IR (thin film): ν_{max} (cm^{-1}) = 3409, 3051, 2952, 1725, 1606, 1585, 1485, 1457, 1437, 1344, 1291, 1239, 1198, 1051, 948, 913, 879, 845, 792, 740, 705, 690. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_4$ $[M+NH_4]^+$: 409.2122. Found: 409.2114.



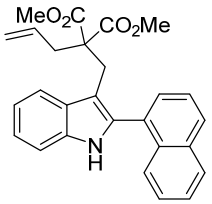
1l, white solid, 1.7 g, 60% yield, m.p. = 159.0-160.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.09-6.99 (m, 3H), 5.26-5.15 (m, 1H), 4.77-4.72 (m, 2H), 3.84 (s, 3H), 3.63 (s, 2H), 3.46 (s, 6H), 2.34 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 157.2, 135.4, 133.7, 133.0, 131.9, 129.8, 128.9, 122.0, 121.9, 121.0, 119.2, 119.1, 117.8, 111.4, 110.6, 107.6, 59.4, 55.6, 52.0, 36.6, 27.4. IR (thin film): ν_{max} (cm^{-1}) = 3371, 3053, 2948, 1734, 1711, 1492, 1462, 1433, 1284, 1254, 1232, 1211, 1177, 1117, 1052, 921, 883, 861, 778, 767, 747, 666, 608. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_5$ $[M+NH_4]^+$: 425.2071. Found: 425.2062.



1m, white solid, 0.9 g, 70% yield, m.p. = 130.7-131.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.26-7.22 (m, 3H), 7.21-7.15 (m, 2H), 7.13-7.04 (m, 2H), 5.11-5.01 (m, 1H), 4.72 (d, *J* = 10.4 Hz, 1H), 4.64 (d, *J* = 16.8 Hz, 1H), 3.46 (s, 2H), 3.38 (s, 6H), 2.29 (d, *J* = 7.2 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 137.4, 136.6, 135.4, 132.5, 132.4, 131.1, 130.4, 128.7, 128.5, 125.8, 121.6, 119.1, 119.0, 118.1, 110.6, 106.7, 59.1, 51.9, 36.5, 27.0, 19.8. IR (thin film): ν_{max} (cm^{-1}) = 3362, 3055, 2951, 1728, 1704, 1486, 1456, 1430, 1286, 1244, 1210, 1104, 1068, 951, 918, 820, 787, 772, 749, 712, 666, 622. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_4$ $[M+NH_4]^+$: 409.2122. Found: 409.2111.

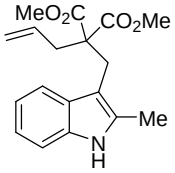


1n, yellow solid, 0.6 g, 83% yield, m.p. = 117.2-118.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.54-7.44 (m, 4H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 5.13-5.00 (m, 1H), 4.71 (d, *J* = 10.0 Hz, 1H), 4.71 (d, *J* = 16.8 Hz, 1H), 3.52 (s, 2H), 3.40 (s, 6H), 2.34 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 135.4, 133.6, 133.4, 132.3, 131.7, 131.3, 129.4 (q, *J* = 300.0 Hz), 128.6, 128.4, 126.6, 126.5, 125.1, 122.4, 122.3, 119.34, 119.29, 118.0, 59.0, 51.9, 36.8, 27.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.48. IR (thin film): ν_{max} (cm^{-1}) = 3413, 3057, 2953, 1752, 1723, 1491, 1460, 1435, 1369, 1343, 1312, 1263, 1221, 1121, 1076, 990, 941, 927, 915, 789, 767, 737, 706, 688. HRMS (ESI) calcd for $C_{24}H_{26}F_3N_2O_4$ $[M+NH_4]^+$: 463.1839. Found: 463.1832.

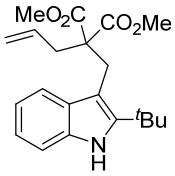


1o, yellow solid, 0.4 g, 84% yield, m.p. = 220.5-221.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.91 (t, *J* = 6.8 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.60-7.47 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.23-7.14 (m, 2H), 4.94-4.83 (m, 1H), 4.56 (d, *J* = 10.4 Hz, 1H), 4.45 (d, *J* = 16.8 Hz, 1H), 3.69-3.47 (m, 2H), 3.41 (s, 3H), 3.27 (s, 3H), 2.26 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4,

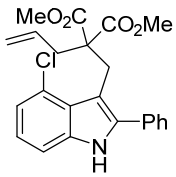
135.6, 135.2, 133.5, 132.1, 131.9, 130.6, 128.8, 128.7, 128.6, 128.1, 126.7, 126.0, 125.7, 125.1, 121.9, 119.3, 119.1, 117.8, 110.8, 107.9, 59.1, 51.8, 36.5, 27.3. IR (thin film): ν_{max} (cm^{-1}) = 3402, 3054, 2953, 1749, 1725, 1505, 1455, 1430, 1395, 1291, 1236, 1202, 1053, 1012, 942, 922, 865, 813, 783, 739, 702. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_4$ $[M+NH_4]^+$: 445.2122. Found: 445.2119.



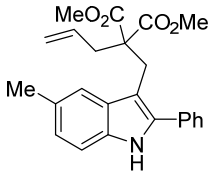
1p, white solid, 1.9 g, 70% yield, m.p. = 88.7-89.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.19-7.17 (m, 1H), 7.11-7.06 (m, 2H), 5.98-5.91 (m, 1H), 5.18-5.13 (m, 2H), 3.66 (s, 6H), 3.45 (s, 2H), 2.69 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 135.1, 133.4, 133.2, 129.1, 120.9, 119.0, 118.6, 118.3, 110.1, 105.6, 59.6, 52.2, 37.9, 28.5, 12.2. IR (thin film): ν_{max} (cm^{-1}) = 3392, 3013, 2955, 1748, 1720, 1492, 1433, 1342, 1326, 1236, 1206, 1148, 1062, 1039, 1012, 995, 965, 933, 900, 875, 785, 749, 691, 653. HRMS (ESI) calcd for $C_{18}H_{25}N_2O_4$ $[M+NH_4]^+$: 333.1809. Found: 333.1805.



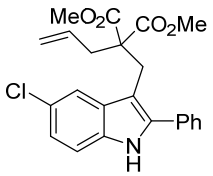
1q, brown oil, 1.4 g, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 6.4 Hz, 1H), 7.08-6.99 (m, 2H), 5.90-5.79 (m, 1H), 5.06-5.00 (m, 2H), 3.80 (s, 2H), 3.56 (s, 6H), 2.64 (d, *J* = 6.8 Hz, 2H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 143.6, 134.1, 133.8, 129.7, 120.9, 119.0, 118.7, 117.9, 109.9, 104.8, 59.2, 52.0, 39.7, 33.3, 31.0, 29.6. IR (thin film): ν_{max} (cm^{-1}) = 3419, 3076, 2953, 1721, 1639, 1460, 1432, 1341, 1301, 1240, 1212, 1133, 1089, 1039, 919, 865, 742, 707, 666. HRMS (ESI) calcd for $C_{21}H_{31}N_2O_4$ $[M+NH_4]^+$: 375.2278. Found: 375.2271.



1r, white solid, 0.3 g, 63% yield, m.p. = 136.8-137.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.34 (br, 2H), 7.26 (br, 3H), 7.14-7.07 (m, 2H), 7.01 (d, *J* = 7.2 Hz, 1H), 5.50-5.44 (m, 1H), 4.78 (d, *J* = 12.4 Hz, 1H), 4.74 (d, *J* = 19.2 Hz, 1H), 4.12 (s, 2H), 3.24 (s, 6H), 2.39 (d, *J* = 4.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 138.3, 137.0, 133.5, 132.9, 129.1, 128.9, 128.7, 128.1, 125.9, 122.1, 121.5, 117.6, 110.0, 105.9, 59.7, 51.6, 37.5, 27.3. IR (thin film): ν_{max} (cm^{-1}) = 3376, 3062, 2947, 1749, 1722, 1640, 1485, 1433, 1333, 1298, 1242, 1222, 1199, 1158, 991, 965, 943, 919, 768, 739. HRMS (ESI) calcd for $C_{23}H_{23}ClNO_4$ $[M+H]^+$: 412.1310. Found: 412.1304.

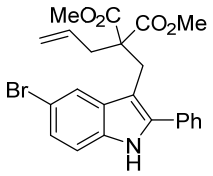


1s, white solid, 0.7 g, 54% yield, m.p. = 134.5-136.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 6.0 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 5.34-5.24 (m, 1H), 4.79 (d, *J* = 10.0 Hz, 1H), 4.75 (d, *J* = 16.8 Hz, 1H), 3.67 (s, 2H), 3.42 (s, 6H), 2.44 (s, 3H), 2.33 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 137.2, 133.9, 133.7, 132.8, 129.8, 128.90, 128.87, 128.5, 127.9, 123.7, 119.1, 118.1, 110.5, 105.8, 59.4, 51.9, 36.8, 27.1, 21.5. IR (thin film): ν_{max} (cm^{-1}) = 3414, 3378, 3028, 1751, 1722, 1479, 1436, 1323, 1292, 1201, 1149, 1098, 1072, 926, 800, 768, 726, 700, 611. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_4$ $[M+NH_4]^+$: 409.2122. Found: 409.2114.

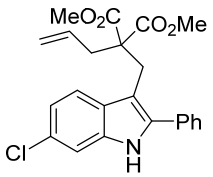


1t, white solid, 0.4 g, 60% yield, m.p. = 152.4-153.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.51 (s, 1H), 7.38 (br, 5H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.21-5.13 (m, 1H), 4.79 (d, *J* = 10.0 Hz, 1H), 4.71 (d, *J* = 16.8 Hz, 1H), 3.62 (s,

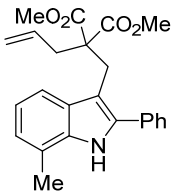
2H), 3.48 (s, 6H), 2.28 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 138.6, 133.8, 132.9, 132.3, 130.4, 129.0, 128.9, 128.3, 125.2, 122.3, 118.8, 118.5, 112.0, 105.9, 59.2, 52.1, 36.8, 26.8. IR (thin film): ν_{max} (cm^{-1}) = 3374, 3060, 2950, 1751, 1724, 1465, 1442, 1297, 1283, 1203, 1164, 920, 904, 881, 870, 793, 756, 695, 651. HRMS (ESI) calcd for $C_{23}H_{26}ClN_2O_4$ $[M+NH_4]^+$: 429.1576. Found: 429.1567.



1u, white solid, 0.5 g, 40% yield, m.p. = 163.4-164.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.67 (d, J = 1.6 Hz, 1H), 7.41-7.36 (m, 5H), 7.23-7.20 (m, 1H), 7.13 (d, J = 8.8 Hz, 1H), 5.22-5.11 (m, 1H), 4.78 (d, J = 10.0 Hz, 1H), 4.71 (d, J = 17.2 Hz, 1H), 3.61 (s, 2H), 3.50 (s, 6H), 2.28 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 138.4, 134.1, 132.8, 132.2, 131.0, 129.0, 128.9, 128.3, 124.8, 121.9, 118.5, 112.7, 112.4, 105.8, 59.2, 52.2, 36.7, 26.8. IR (thin film): ν_{max} (cm^{-1}) = 3373, 3064, 2949, 1757, 1724, 1465, 1433, 1312, 1285, 1252, 1199, 1163, 1137, 963, 926, 898, 867, 787, 764, 677, 658. HRMS (ESI) calcd for $C_{23}H_{26}BrN_2O_4$ $[M+NH_4]^+$: 473.1070. Found: 473.1072.

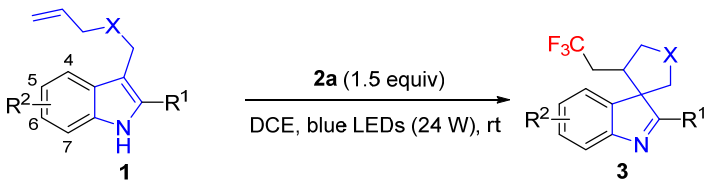


1v, white solid, 0.2 g, 71% yield, m.p. = 163.8-165.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.34-7.32 (m, 5H), 7.19 (s, 1H), 7.05 (d, J = 8.8 Hz, 1H), 5.32-5.22 (m, 1H), 4.81 (d, J = 10.0 Hz, 1H), 4.74 (d, J = 17.2 Hz, 1H), 3.64 (s, 2H), 3.39 (s, 6H), 2.31 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 137.7, 135.8, 133.0, 132.3, 128.9, 128.8, 128.1, 128.0, 127.6, 120.13, 120.05, 118.4, 110.8, 106.1, 59.3, 52.1, 36.9, 26.9. IR (thin film): ν_{max} (cm^{-1}) = 3385, 3081, 2952, 1748, 1724, 1439, 1415, 1342, 1295, 1200, 1138, 988, 943, 916, 871, 854, 820, 763, 698. HRMS (ESI) calcd for $C_{23}H_{26}ClN_2O_4$ $[M+NH_4]^+$: 429.1576. Found: 429.1574.

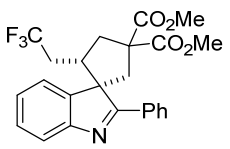


1w, white solid, 1.0 g, 50% yield, m.p. = 54.8-56.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.45-7.33 (m, 4H), 7.04-6.95 (m, 2H), 5.37-5.26 (m, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 4.76 (d, *J* = 18.0 Hz, 1H), 3.68 (s, 2H), 3.39 (s, 6H), 2.43 (s, 3H), 2.33 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 136.8, 135.1, 133.7, 132.9, 129.1, 129.0, 128.9, 128.0, 122.7, 119.9, 119.8, 118.1, 117.2, 106.9, 59.4, 51.9, 36.9, 27.3, 16.5. IR (thin film): ν_{max} (cm^{-1}) = 3368, 3023, 2950, 1721, 1639, 1604, 1489, 1435, 1342, 1291, 1255, 1205, 1122, 1070, 993, 919, 860, 774, 746, 699. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_4$ $[M+NH_4]^+$: 409.2122. Found: 409.2113.

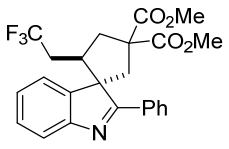
General procedure for visible-light promoted intramolecular dearomatization of indole derivatives.



A flame-dried sealed tube were added indole derivative **1a** (75.5 mg, 0.2 mmol) and Umemoto's reagent (102 mg, 0.3 mmol) and DCE (2.0 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from 24 W blue LEDs. The mixture was stirred at room temperature for the indicated time (monitored by TLC) under argon atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. The diastereomeric ratio was determined by ^{19}F NMR of the crude reaction mixture. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 40/1) to afford the desired products **3**. The analytical data of the products are summarized below, and the data of minor diastereomer were indicated by *.

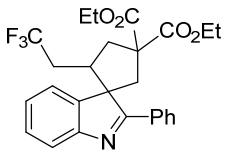


major isomer



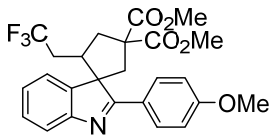
minor isomer

3a, 89.0 mg, 83% yield, 1.3/1 dr. For the major isomer, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.20 (m, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.52-7.50 (m, 3H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.58 (d, *J* = 15.6 Hz, 1H), 3.33-3.18 (m, 1H), 2.92 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.79 (t, *J* = 13.6 Hz, 1H), 2.69 (d, *J* = 15.6 Hz, 1H), 1.46-1.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 173.0, 171.8, 153.5, 142.5, 131.9, 130.9, 128.74, 128.69, 128.1, 126.32, 126.28 (q, *J* = 275.0 Hz), 122.5, 121.4, 67.1, 59.4, 53.4, 53.2, 41.6, 40.4, 39.6, 33.3 (q, *J* = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 (t, *J* = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3005, 2955, 1730, 1522, 1436, 1393, 1346, 1253, 1172, 1127, 1043, 995, 963, 936, 879, 839, 752, 694, 650, 631. HRMS (ESI) calcd for $C_{24}H_{23}F_3NO_4$ $[M+H]^+$: 446.1574. Found: 446.1564. For the minor isomer, white solid, m.p. = 164.8-165.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.51-7.44 (m, 4H), 7.39 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.35-7.31 (m, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.43 (d, *J* = 16.0 Hz, 1H), 3.07-2.94 (m, 2H), 2.75 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.42 (t, *J* = 13.6 Hz, 1H), 1.84-1.70 (m, 1H), 1.49-1.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 172.8, 171.2, 153.0, 144.1, 135.6, 130.7, 128.9, 128.6, 128.2, 127.2, 126.0 (q, *J* = 275.0 Hz), 121.6, 120.8, 66.6, 60.2, 53.4, 53.2, 43.3, 40.2, 39.7, 32.9 (q, *J* = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (t, *J* = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3020, 2922, 2850, 1751, 1724, 1523, 1492, 1459, 1441, 1397, 1350, 1154, 1100, 1057, 1039, 1025, 788, 769, 755, 726, 699. HRMS (ESI) calcd for $C_{24}H_{23}F_3NO_4$ $[M+H]^+$: 446.1574. Found: 446.1566.

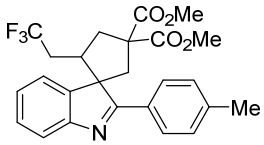


3b, colorless oil, 66.5 mg, 70% yield, 1.4/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.20 (m, 2H), 7.90 (d, *J* = 6.8 Hz, 2H*), 7.70 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H*), 7.51-7.24 (m, 6H), 4.40-4.23 (m, 4H), 3.56 (d, *J* = 15.6 Hz, 1H), 3.43 (d, *J* = 16.0 Hz, 1H*), 3.26-2.39 (m, 4H), 1.83-1.27 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 178.3, 172.5, 172.3, 171.4, 170.8, 153.6, 153.1, 144.3, 142.7, 135.7, 132.1,

130.9, 130.7, 128.8, 128.7, 128.7, 128.5, 128.3, 128.2, 127.1, 126.4 (q, J = 275.0 Hz) 126.3, 126.1* (q, J = 275.0 Hz), 122.6, 121.6, 121.4, 120.8, 67.2, 66.6, 62.3, 62.24, 62.15, 62.1, 60.4, 59.6, 43.3, 41.7, 40.3, 40.1, 39.6, 33.3 (q, J = 29.0 Hz), 32.9* (q, J = 29.0 Hz) 14.03, 14.00. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 (t, J = 11.3 Hz), -65.2* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3064, 2981, 2927, 1726, 1521, 1464, 1443, 1392, 1253, 1181, 1128, 1040, 1015, 860, 840, 752, 695, 650. HRMS (ESI) calcd for $C_{26}H_{27}F_3NO_4$ $[M+H]^+$: 474.1887. Found: 474.1879.

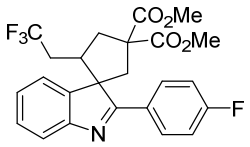


3c, yellow oil, 60.0 mg, 63% yield, 1.3/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H*), 7.66 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H*), 7.42-7.20 (m, 3H), 7.02 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H*), 3.90 (br, 6H*), 3.89 (br, 6H), 3.85 (s, 3H*), 3.82 (s, 3H), 3.58 (d, J = 15.6 Hz, 1H), 3.40 (d, J = 16.0 Hz, 1H*), 3.26-2.49 (m, 4H), 1.80-1.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 177.4, 173.3, 172.7, 171.9, 171.5, 161.8, 161.6, 153.7, 153.1, 144.5, 142.5, 130.0, 128.7, 128.5, 127.7, 126.7, 126.4 (q, J = 275.0 Hz), 126.1* (q, J = 275.0 Hz), 125.8, 124.4, 122.4, 121.5, 121.0, 120.4, 114.2, 114.1, 66.8, 66.1, 60.5, 59.4, 55.4, 53.6, 53.4, 53.3, 43.4, 42.1, 40.9, 40.7, 39.7, 39.6, 33.3 (q, J = 29.0 Hz), 33.1* (q, J = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 (t, J = 11.3 Hz), -65.1* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3006, 2995, 2843, 1730, 1604, 1578, 1508, 1462, 1436, 1418, 1252, 1176, 1128, 1037, 994, 881, 837, 752, 661. HRMS (ESI) calcd for $C_{25}H_{25}F_3NO_5$ $[M+H]^+$: 476.1679. Found: 476.1672.

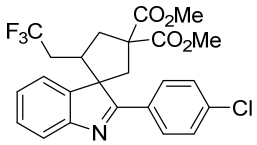


3d, yellow oil, 61.5 mg, 67% yield, 1.2/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H*), 7.68 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H*), 7.44-7.22 (m, 5H), 3.894 (s, 3H*), 3.886 (s, 3H), 3.84 (s, 3H*), 3.82 (s, 3H), 3.56 (d, J = 15.6 Hz, 1H), 3.41 (d, J = 16.0 Hz, 1H*), 3.30-2.45 (m, 4H), 2.42 (br, 3H), 1.81-1.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 178.0, 173.0, 172.8, 171.9, 171.3, 153.7, 153.1, 144.3, 142.6, 141.5, 141.2, 132.7, 129.6, 129.5, 129.1, 128.7,

128.5, 128.2, 128.1, 127.0, 126.3 (q, J = 275.0 Hz), 126.1, 126.095* (q, J = 275.0 Hz), 122.5, 121.6, 121.3, 120.6, 67.0, 66.4, 60.4, 59.5, 53.5, 53.4, 53.3, 53.2, 43.3, 41.9, 40.6, 40.4, 39.6, 33.3 (q, J = 29.0 Hz), 29.7, 21.5, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 (t, J = 11.3 Hz), -65.1* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3030, 2954, 1731, 1609, 1512, 1456, 1435, 1394, 1351, 1254, 1190, 1172, 1127, 1041, 995, 963, 839, 823, 752. HRMS (ESI) calcd for $C_{25}H_{25}F_3NO_4$ $[M+H]^+$: 460.1730. Found: 460.1722.

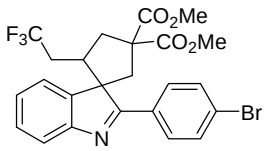


3e, yellow oil, 68.5 mg, 74% yield, 1.4/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.28 (m, 2H), 7.97-7.93 (m, 2H*), 7.69 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H*), 7.43-7.15 (m, 5H), 3.90 (s, 3H*), 3.89 (s, 3H), 3.84 (s, 3H*), 3.82 (s, 3H), 3.57 (d, J = 15.6 Hz, 1H), 3.38 (d, J = 16.0 Hz, 1H*), 3.22-2.39 (m, 4H), 1.76-1.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 176.9, 173.2, 172.6, 171.8, 171.3, 165.6, 165.4, 163.1, 162.9, 153.4, 152.9, 144.2, 142.5, 131.71, 131.68, 130.5, 130.4, 128.8, 128.7, 128.18, 128.15, 127.3, 126.4, 126.3 (q, J = 275.0 Hz), 126.0* (q, J = 275.0 Hz), 122.5, 121.6, 121.4, 120.8, 116.2, 116.0, 115.9, 115.8, 67.0, 66.4, 60.3, 59.3, 53.6, 53.4, 53.3, 43.4, 41.7, 40.6, 40.4, 39.8, 39.7, 33.3 (q, J = 29.0 Hz), 33.0 (q, J = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.7 (t, J = 11.3 Hz, 3F), -65.2* (t, J = 11.3 Hz, 3F), -108.4 - -108.5 (m, 1F), -108.7 - -108.8* (m, 1F). IR (thin film): ν_{max} (cm^{-1}) = 3006, 2958, 1750, 1730, 1597, 1506, 1437, 1399, 1351, 1261, 1199, 1172, 1157, 1126, 994, 962, 939, 884, 767, 640. HRMS (ESI) calcd for $C_{24}H_{22}F_4NO_4$ $[M+H]^+$: 464.1479. Found: 464.1471.

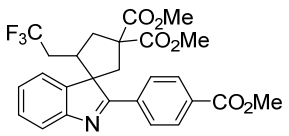


3f, yellow oil, 77.0 mg, 80% yield, 1.3/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H*), 7.69 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 7.2 Hz, 1H*), 7.50-7.25 (m, 5H), 3.90 (s, 3H*), 3.89 (s, 3H), 3.84 (s, 3H*), 3.82 (s, 3H), 3.55 (d, J = 15.6 Hz, 1H), 3.37 (d, J = 16.0 Hz, 1H*), 3.21-2.39 (m, 4H), 1.76-1.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 176.8, 173.1, 172.6, 171.8, 171.3, 153.6,

152.8, 144.3, 142.6, 137.3, 137.1, 133.8, 130.3, 129.7, 129.5, 129.2, 129.1, 128.8, 128.7, 127.4, 126.6, 126.2 (q, *J* = 276.0 Hz), 125.9* (q, *J* = 276.0 Hz), 122.5, 121.6, 120.9, 67.0, 66.4, 60.3, 59.3, 53.6, 53.4, 53.3, 43.4, 41.7 40.5 40.3, 39.8, 39.7, 33.3 (q, *J* = 29.0 Hz), 33.0* (q, *J* = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 (t, *J* = 11.3 Hz), -65.2* (t, *J* = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3008, 2955, 1730, 1592, 1519, 1492, 1460, 1435, 1398, 1351, 1255, 1200, 1128, 1095, 1013, 994, 836, 751, 722. HRMS (ESI) calcd for $C_{24}H_{22}ClF_3NO_4$ $[M+H]^+$: 480.1184. Found: 480.1175.

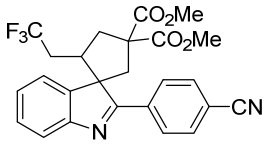


3g, yellow oil, 91.0 mg, 86% yield, 1.3/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H*), 7.70-7.61 (m, 3H), 7.43-7.25 (m, 3H), 3.90 (s, 3H*), 3.89 (s, 3H), 3.84 (s, 3H*), 3.82 (s, 3H), 3.55 (d, *J* = 15.6 Hz, 1H), 3.36 (d, *J* = 16.0 Hz, 1H*), 3.20-2.78 (m, 3H), 2.62 (d, *J* = 15.6 Hz, 1H), 2.43 (t, *J* = 13.6 Hz, 1H*), 1.46-1.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 176.9, 173.1, 172.6, 171.8, 171.3, 153.4, 152.8, 144.3, 142.6, 134.2, 132.13, 132.05, 130.7, 129.8, 129.7, 128.9, 128.7, 127.4, 126.6, 126.2 (q, *J* = 275.0 Hz), 125.9 (q, *J* = 275.0 Hz), 125.8, 125.5, 122.5, 121.6, 121.0, 67.0, 66.4, 60.3, 59.3, 53.6, 53.4, 53.3, 43.4, 41.7, 40.5, 40.3, 39.9, 39.7, 33.3 (q, *J* = 29.0 Hz), 33.0 (q, *J* = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 (t, *J* = 11.3 Hz), -65.2* (t, *J* = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3008, 2955, 1730, 1586, 1491, 1461, 1254, 1200, 1173, 1128, 1073, 1043, 1008, 994, 937, 881, 856, 750, 703. HRMS (ESI) calcd for $C_{24}H_{22}BrF_3NO_4$ $[M+H]^+$: 524.0679. Found: 524.0667.

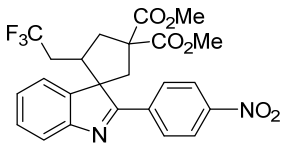


3h, yellow oil, 78.0 mg, 77% yield, 1.2/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.14 (m, 3H), 8.01-7.72 (m, 1H), 7.68-7.28 (m, 4H), 3.96 (br, 6H), 3.90 (br, 6H*), 3.85 (s, 3H*), 3.83 (s, 3H) 3.59 (d, *J* = 15.6 Hz, 1H), 3.43 (d, *J* = 16.0 Hz, 1H*), 3.24-2.36 (m, 4H), 1.76-1.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 177.0, 173.0, 172.6, 171.8, 171.2, 166.4, 166.3, 153.3, 152.8, 144.2, 142.7, 139.6, 135.8, 131.8, 130.0, 129.9, 128.9, 128.8, 128.3, 128.1, 127.7, 126.9, 126.2 (q, *J* = 275.0 Hz), 125.9* (q, *J*

= 275.0 Hz), 122.6, 121.9, 121.6, 121.2, 67.1, 66.7, 60.2, 59.4, 53.6, 53.4, 53.3, 52.3, 43.3, 41.5, 40.3, 40.2, 39.8, 39.7, 33.1 (q, *J* = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.7 (t, *J* = 11.3 Hz), -65.2* (t, *J* = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3003, 2954, 1725, 1610, 1519, 1435, 1401, 1273, 1253, 1174, 1107, 1043, 1017, 994, 964, 865, 839, 752, 707. HRMS (ESI) calcd for $C_{26}H_{25}F_3NO_6$ $[M+H]^+$: 504.1628. Found: 504.1619.

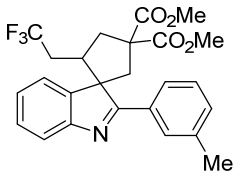


3i, yellow oil, 68.0 mg, 72% yield, 1.4/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H*), 7.83-7.78 (m, 2H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H*), 7.47-7.30 (m, 3H), 3.91 (s, 3H*), 3.90 (s, 3H), 3.85 (s, 3H*), 3.83 (s, 3H), 3.58 (d, *J* = 15.6 Hz, 1H), 3.36 (d, *J* = 16.0 Hz, 1H*), 3.19-2.35 (m, 4H), 1.71-1.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 175.9, 173.2, 172.4, 171.6, 171.3, 153.1, 152.5, 144.3, 142.7, 139.4, 135.7, 132.6, 132.4, 129.0, 128.89, 128.85, 128.7, 128.0, 127.3, 126.1 (q, *J* = 276.0 Hz), 125.8 (q, *J* = 276.0 Hz), 122.6, 122.1, 121.6, 121.4, 118.3, 118.0, 114.2, 114.1, 67.0, 66.6, 60.2, 59.2, 53.7, 53.5, 53.4, 43.4, 41.3, 40.2, 40.0, 39.7, 33.2 (q, *J* = 29.0 Hz), 33.1 (q, *J* = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.0 (t, *J* = 11.3 Hz), -65.5* (t, *J* = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3020, 2956, 2230, 1729, 1435, 1395, 1256, 1173, 1129, 994, 963, 844, 750, 665, 627. HRMS (ESI) calcd for $C_{25}H_{22}F_3N_2O_4$ $[M+H]^+$: 471.1526. Found: 471.1518.

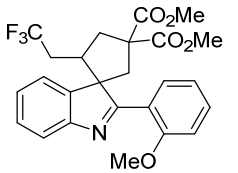


3j, yellow oil, 66.0 mg, 67% yield, 1.4/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.4 Hz, 1H), 8.35 (t, *J* = 9.6 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H*), 7.48-7.32 (m, 3H), 3.92 (br, 6H*), 3.86 (s, 3H), 3.84 (s, 3H), 3.60 (d, *J* = 15.6 Hz, 1H), 3.39 (d, *J* = 16.4 Hz, 1H*), 3.21-2.36 (m, 4H), 1.76-1.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 175.6, 173.2, 172.4, 171.6, 171.3, 153.1, 152.5, 148.8, 144.3, 142.7, 141.1, 137.5, 129.3, 129.14, 129.06, 128.9, 128.2, 127.5, 126.0 (q, *J* = 276.0 Hz), 125.9* (q, *J* = 276.0 Hz), 124.0, 123.9, 122.6, 122.3,

121.6, 121.5, 67.1, 66.7, 60.2, 59.2, 53.7, 53.5, 53.5, 53.4, 41.3, 40.2, 40.1, 39.7, 33.2 (q, J = 29.0 Hz), 33.1* (q, J = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8 (t, J = 11.3 Hz), -65.2* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 2956, 2924, 1729, 1598, 1528, 1435, 1395, 1345, 1254, 1128, 994, 851, 753, 703, 652. HRMS (ESI) calcd for $C_{24}H_{22}F_3N_2O_6$ $[M+H]^+$: 491.1424. Found: 491.1420.

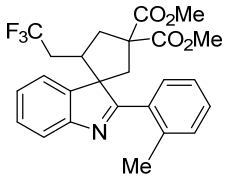


3k, yellow oil, 70.0 mg, 76% yield, 1.3/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.97 (m, 1H), 7.71-7.63 (m, 2H), 7.47-7.24 (m, 5H), 3.89 (s, 3H*), 3.87 (s, 3H), 3.84 (s, 3H*), 3.82 (s, 3H), 3.58 (d, J = 15.6 Hz, 1H), 3.44 (d, J = 16.0 Hz, 1H*), 3.29-2.67 (m, 4H), 2.46 (s, 3H), 2.43 (s, 3H*), 1.81-1.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 178.4, 172.9, 172.8, 171.9, 171.2, 153.5, 153.0, 144.2, 142.6, 138.7, 138.6, 135.6, 131.8, 131.6, 128.8, 128.7, 128.6, 128.6, 127.1, 126.3 (q, J = 276.0 Hz), 126.3, 126.1* (q, J = 275.0 Hz), 125.3, 125.1, 122.5, 121.6, 121.4, 120.7, 67.2, 66.5, 60.2, 59.5, 53.5, 53.4, 53.3, 53.2, 43.3, 41.7, 40.5, 40.2, 39.6, 33.3 (q, J = 29.0 Hz), 32.9* (q, J = 28.0 Hz), 21.4, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.5 (t, J = 11.3 Hz), -65.1* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3027, 2955, 1731, 1524, 1458, 1435, 1394, 1255, 1200, 1172, 1128, 1042, 1001, 879, 751, 666. HRMS (ESI) calcd for $C_{25}H_{25}F_3NO_4$ $[M+H]^+$: 460.1730. Found: 460.1720.

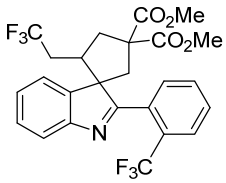


3l, yellow oil, 70.5 mg, 74% yield, 1.4/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.64 (m, 1H), 7.48-7.36 (m, 3H), 7.30-7.27 (m, 1H), 7.21-7.15 (m, 1H), 7.08-6.97 (m, 2H), 3.80 (s, 3H*), 3.79 (s, 3H*), 3.78 (s, 3H), 3.75 (s, 3H), 3.55 (s, 3H), 3.27 (d, J = 14.8 Hz, 1H), 3.06 (d, J = 15.6 Hz, 1H*), 2.92-2.11 (m, 4H), 1.83-1.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 181.0, 173.4, 171.9, 170.8, 157.1, 156.5, 154.2, 153.7, 141.3, 140.8, 130.9, 130.8, 129.9, 128.6, 128.5, 126.97, 126.70 (q, J = 275.0 Hz), 126.5* (q, J = 275.0 Hz), 126.3, 122.8, 122.5, 121.5, 121.4, 120.9, 120.5, 120.3, 111.5, 110.9, 69.2, 68.7, 59.3, 58.9, 55.2, 55.1, 53.4, 53.2, 53.0, 52.7, 43.9, 39.4, 39.1, 38.8,

38.6, 33.7 (q, J = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0 (t, J = 11.3 Hz), -65.1* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3006, 2954, 2842, 1732, 1601, 1582, 1563, 1491, 1459, 1435, 1255, 1174, 1145, 1124, 1023, 993, 750, 731, 645. HRMS (ESI) calcd for $C_{25}H_{25}F_3NO_5$ $[M+H]^+$: 476.1679. Found: 476.1670.

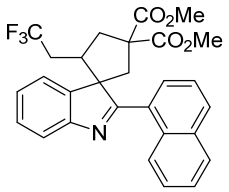


3m, yellow oil, 61.5 mg, 67% yield, 5/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H*), 7.45-7.27 (m, 6H), 7.14 (d, J = 7.2 Hz, 1H), 3.82 (s, 3H*), 3.78 (s, 3H), 3.61 (s, 3H*), 3.58 (s, 3H), 3.20-2.57 (m, 5H), 2.37 (s, 3H*), 2.26 (s, 3H), 1.58-1.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 181.2, 173.2, 171.8, 171.7, 170.8, 154.0, 153.3, 141.6, 140.0, 137.4, 136.8, 135.1, 132.7, 131.8, 130.8, 129.4, 129.2, 128.7, 127.8, 127.3, 127.1, 126.5, 126.5 (q, J = 276.0 Hz), 126.1 (q, J = 275.0 Hz), 125.5, 125.3, 125.1, 122.8, 121.5, 121.4, 120.9, 68.9, 59.1, 53.2, 39.9, 39.5, 39.4, 38.7, 38.2, 33.7 (q, J = 29.0 Hz), 20.5, 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.2 (t, J = 11.3 Hz), -65.2* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3013, 2954, 1732, 1563, 1489, 1435, 1394, 1257, 1198, 1175, 1145, 1128, 1043, 994, 753, 730, 648. HRMS (ESI) calcd for $C_{25}H_{25}F_3NO_4$ $[M+H]^+$: 460.1730. Found: 460.1720.

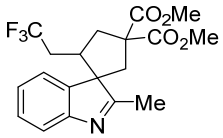


3n, yellow oil, 65.8 mg, 64% yield, 6/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.3 Hz, 1H), 7.71-7.64 (m, 3H), 7.45-7.27 (m, 4H), 3.79 (s, 3H), 3.59 (s, 3H), 3.05-2.98 (m, 1H), 2.91 (d, J = 15.2 Hz, 1H), 2.81-2.68 (m, 2H), 2.53 (d, J = 15.1 Hz, 1H), 1.61-1.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 172.2, 171.7, 153.7, 139.9, 131.7, 131.7, 131.6, 129.7, 128.9, 128.8, 127.60, 127.56, 127.51, 127.46, 126.9, 126.5 (q, J = 275.0 Hz), 123.71 (q, J = 272.0 Hz), 122.8, 121.9, 69.1, 58.7, 53.19, 53.16, 39.2, 38.88, 38.86, 38.31, 38.29, 33.4 (q, J = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.0 (s, 1F), -64.2 (t, J = 11.3 Hz, 3F). IR (thin film): ν_{max} (cm^{-1}) = 3004, 2956, 1733,

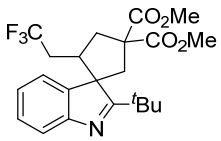
1565, 1437, 1394, 1354, 1313, 1257, 1171, 1126, 1047, 1035, 995, 753, 685, 646. HRMS (ESI) calcd for $C_{25}H_{22}F_6NO_4$ $[M+H]^+$: 514.1448. Found: 514.1439.



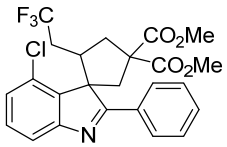
3o, yellow oil, 42.7 mg, 43% yield, 6/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.60-7.33 (m, 7H), 3.80 (s, 3H*), 3.75 (s, 3H), 3.39 (s, 3H*), 3.33 (s, 3H), 3.17-2.58 (m, 5H), 1.67-1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 171.7, 171.6, 154.0, 140.5, 133.6, 132.2, 130.8, 129.8, 129.2 (q, *J* = 275.0 Hz), 128.9, 128.5, 127.0, 126.8, 126.3, 125.5, 125.1, 124.7, 122.9, 121.8, 69.3, 59.2, 53.2, 52.9, 39.7, 39.1, 38.6, 33.9 (q, *J* = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.3 (t, *J* = 11.3 Hz), -65.3* (t, *J* = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3053, 3007, 1732, 1586, 1457, 1435, 1394, 1252, 1197, 1174, 1144, 1128, 1046, 1021, 803, 777, 752, 646. HRMS (ESI) calcd for $C_{28}H_{25}F_3NO_4$ $[M+H]^+$: 496.1730. Found: 496.1721.



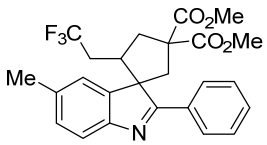
3p, yellow oil, 44.5 mg, 58% yield, 2/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H*), 7.50 (d, *J* = 7.6 Hz, 1H), 7.38-7.18 (m, 3H), 3.87 (s, 3H), 3.86 (s, 3H*), 3.81 (s, 3H), 3.80 (s, 3H*), 3.12-2.49 (m, 5H), 2.35 (s, 3H*), 2.34 (s, 3H), 1.88-1.74 (m, 1H), 1.49-1.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 182.6, 172.63, 172.56, 171.7, 171.6, 154.2, 153.8, 141.7, 140.9, 128.6, 126.4, 126.3* (q, *J* = 275.0 Hz), 126.1 (q, *J* = 275.0 Hz), 125.7, 122.6, 121.6, 120.5, 119.9, 66.9, 66.2, 59.5, 59.1, 53.4, 53.4, 53.3, 53.2, 42.7, 40.0, 39.7, 39.5, 39.4, 33.2* (q, *J* = 28.0 Hz), 32.7 (q, *J* = 29.0 Hz), 29.7, 19.4, 15.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (t, *J* = 11.3 Hz), -65.1* (t, *J* = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3002, 2956, 1731, 1574, 1458, 1435, 1257, 1201, 1152, 1128, 1050, 1015, 866, 840, 819, 752, 663. HRMS (ESI) calcd for $C_{19}H_{21}F_3NO_4$ $[M+H]^+$: 384.1417. Found: 384.1410.



3q, yellow oil, 47.0 mg, 55% yield, 7/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H*), 7.35-7.16 (m, 3H), 3.89 (s, 3H*), 3.84 (s, 3H), 3.81 (s, 3H), 3.57-2.54 (m, 5H), 1.47 (s, 9H), 1.35-1.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 172.8, 171.9, 152.9, 141.7, 129.4, 128.4, 128.1, 126.6 (q, *J* = 275.0 Hz), 125.9, 122.2, 120.6, 68.7, 59.3, 53.4, 53.3, 39.1, 38.5, 38.5, 33.3 (q, *J* = 28.0 Hz), 31.6, 30.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.5 (t, *J* = 11.3 Hz), -65.2* (t, *J* = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3069, 2957, 2925, 1732, 1542, 1458, 1435, 1253, 1199, 1174, 1145, 1127, 1000, 840, 754, 650. HRMS (ESI) calcd for $C_{22}H_{27}F_3NO_4$ $[M+H]^+$: 426.1887. Found: 426.1879.

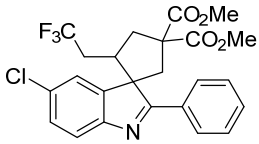


3r, yellow oil, 72.0 mg, 75% yield, 1.2/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 1H), 7.59-7.56 (m, 2H), 7.50-7.43 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 8.4 Hz, 1H), 3.82-3.26 (m, 9H), 3.05-2.80 (m, 2H), 1.89-1.76 (m, 1H), 1.47-1.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.4, 182.4, 171.6, 171.5, 170.8, 170.6, 156.2, 155.4, 138.5, 136.7, 136.4, 133.2, 130.6, 130.2, 130.1, 130.1, 129.5, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.0, 127.9, 126.2 (q, *J* = 276.0 Hz), 126.1* (q, *J* = 275.0 Hz), 120.4, 119.9, 68.8, 68.7, 61.2, 59.8, 53.4, 53.3, 53.2, 53.0, 40.6, 39.7, 38.2, 37.8, 36.3, 34.3, 34.3 (q, *J* = 29.0 Hz), 32.66* (q, *J* = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8 (t, *J* = 11.3 Hz), -65.2* (t, *J* = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3007, 2954, 1766, 1731, 1601, 1574, 1494, 1434, 1249, 1195, 1176, 1147, 1123, 1107, 1061, 990, 840, 800, 774, 752, 727, 649. HRMS (ESI) calcd for $C_{24}H_{22}ClF_3NO_4$ $[M+H]^+$: 480.1184. Found: 480.1179.

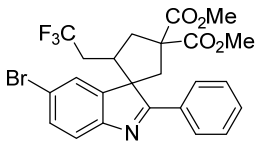


3s, yellow oil, 54.0 mg, 58% yield, 1.3/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 6.7, 2.8 Hz, 1H), 7.85-7.83 (m, 1H), 7.57-7.47 (m, 4H), 7.22-7.18 (m, 2H), 3.89-

3.82 (m, 6H), 3.55 (d, J = 15.2 Hz, 1H), 3.42 (d, J = 16.4 Hz, 1H*), 3.26-2.35 (m, 7H), 1.86-1.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 177.2, 173.0, 172.8, 171.8, 171.3, 151.4, 150.9, 144.2, 142.8, 137.2, 136.3, 135.8, 132.1, 130.7, 130.5, 129.3, 129.2, 128.8, 128.7, 128.1, 128.0, 126.4 (q, J = 275.0 Hz), 126.11* (q, J = 275.0 Hz), 123.3, 122.2, 121.0, 120.4, 67.0, 66.5, 60.2, 59.5, 53.4, 53.41, 53.35, 53.3, 53.23, 53.20, 53.15, 53.1, 43.4, 41.5, 40.5, 40.3, 39.7, 39.6, 33.3 (q, J = 28.0 Hz), 32.9* (q, J = 29.0 Hz), 21.8, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (t, J = 11.3 Hz), -65.4* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3005, 2955, 1730, 1521, 1436, 1393, 1255, 1198, 1163, 1128, 1040, 994, 964, 939, 860, 822, 754, 695, 670, 648. HRMS (ESI) calcd for $C_{25}H_{25}F_3NO_4$ $[M+H]^+$: 460.1730. Found: 460.1720.

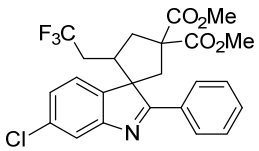


3t, yellow oil, 81.0 mg, 84% yield, 1.1/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.16 (m, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.62-7.35 (m, 6H), 3.91 (s, 3H*), 3.88 (s, 3H), 3.85 (s, 3H*), 3.83 (s, 3H), 3.57 (d, J = 15.6 Hz, 1H), 3.40 (d, J = 16.0 Hz, 1H*), 3.24-2.42 (m, 4H), 1.84-1.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 178.6, 172.8, 172.6, 171.7, 171.1, 152.1, 151.6, 146.1, 144.2, 135.1, 132.8, 132.0, 131.6, 131.2, 131.0, 129.0, 128.94, 128.87, 128.85, 128.2, 128.1, 126.1 (q, J = 276.0 Hz), 125.9* (q, J = 275.0 Hz), 123.1, 122.24, 122.23, 121.7, 67.6, 66.8, 60.2, 59.4, 53.5, 53.4, 53.2, 43.2, 41.8, 40.5, 40.3, 39.7, 33.3* (q, J = 27.0 Hz), 33.2 (q, J = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 (t, J = 11.3 Hz), -65.1* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3026, 2955, 1726, 1520, 1492, 1437, 1262, 1198, 1175, 1147, 1126, 1039, 1024, 858, 822, 791, 756, 694, 668. HRMS (ESI) calcd for $C_{24}H_{22}ClF_3NO_4$ $[M+H]^+$: 480.1184. Found: 480.1175.

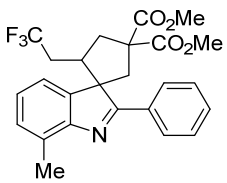


3u, yellow oil, 84.0 mg, 80% yield, 1.1/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.16 (m, 1H), 7.88-7.86 (m, 1H), 7.59-7.45 (m, 6H), 3.91 (s, 3H*), 3.88 (s, 3H), 3.85 (s, 3H*), 3.83 (s, 3H), 3.57 (d, J = 15.6 Hz, 1H), 3.41 (d, J = 16.4 Hz, 1H*), 3.25-2.42 (m, 4H), 1.86-1.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 178.5, 172.8, 172.6,

171.6, 171.1, 152.5, 152.0, 146.4, 144.6, 135.0, 131.9, 131.8, 131.5, 131.2, 131.0, 129.0, 128.9, 128.2, 128.1, 126.1 (q, J = 275.0 Hz), 125.93, 125.88* (q, J = 276.0 Hz), 125.1, 122.7, 122.2, 120.7, 120.0, 67.6, 66.8, 60.2, 59.4, 53.5, 53.4, 53.2, 43.2, 41.8, 40.5, 40.3, 39.7, 33.3 (q, J = 29.0 Hz), 33.0* (q, J = 27.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 (t, J = 11.3 Hz), -65.0* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3005, 2955, 1729, 1576, 1521, 1493, 1437, 1259, 1200, 1173, 1145, 1128, 884, 857, 822, 756, 695, 666, 628. HRMS (ESI) calcd for $C_{24}H_{22}BrF_3NO_4$ $[M+H]^+$: 524.0679. Found: 524.0667.



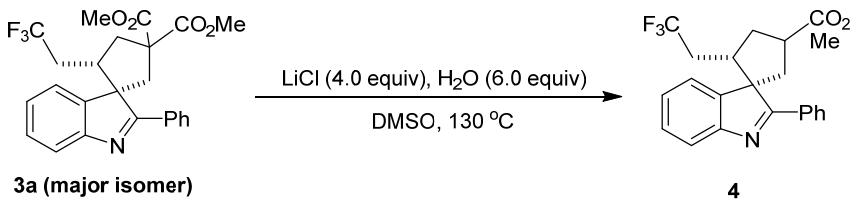
3v, yellow oil, 86.5 mg, 90% yield, 1.2/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.19 (m, 1H), 7.88-7.86 (m, 1H), 7.68-7.62 (m, 1H), 7.53-7.22 (m, 5H), 3.89 (s, 3H*), 3.88 (s, 3H), 3.83 (s, 3H*), 3.82 (s, 3H), 3.59 (d, J = 15.6 Hz, 1H), 3.38 (d, J = 16.0 Hz, 1H*), 3.25-2.43 (m, 4H), 1.80-1.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.1, 179.8, 172.81, 172.76, 171.8, 171.1, 154.9, 154.2, 142.6, 140.9, 135.2, 134.4, 134.1, 131.6, 131.4, 131.1, 129.0, 128.9, 128.3, 128.2, 127.1, 126.17, 126.16 (q, J = 276.0 Hz), 125.9* (q, J = 275.0 Hz), 123.3, 122.5, 121.8, 121.2, 67.0, 66.4, 60.2, 59.3, 53.54, 53.47, 53.4, 53.2, 43.2, 41.8, 40.6, 40.2, 39.7, 39.7, 33.3 (q, J = 29.0 Hz), 32.95* (q, J = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 (t, J = 11.3 Hz), -65.2* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3009, 2957, 1752, 1727, 1517, 1493, 1438, 1401, 1261, 1150, 1130, 1103, 1063, 1042, 775, 752, 695, 671, 639. HRMS (ESI) calcd for $C_{24}H_{22}ClF_3NO_4$ $[M+H]^+$: 480.1184. Found: 480.1177.



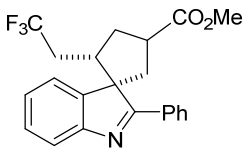
3w, yellow oil, 65.0 mg, 70% yield, 1.3/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.18 (m, 1H), 7.88-7.86 (m, 1H), 7.53-7.44 (m, 3H), 7.24-7.12 (m, 3H), 3.88 (s, 3H*), 3.85 (s, 3H), 3.813 (s, 3H*), 3.808 (s, 3H), 3.53 (d, J = 15.2 Hz, 1H), 3.41 (d, J = 16.0 Hz, 1H*), 3.24-2.35 (m, 7H), 1.85-1.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 176.9, 173.0, 172.8, 171.9, 171.3, 152.2, 151.7, 144.0, 142.4, 136.0, 132.4, 131.4,

130.8, 130.6, 130.4, 129.94, 129.86, 128.8, 128.7, 128.3, 128.1, 127.0, 126.4 (q, J = 276.0 Hz), 126.2, 126.1* (q, J = 276.0 Hz), 119.9, 118.8, 67.3, 66.8, 60.2, 59.5, 53.4, 53.4, 53.34, 53.33, 53.23, 53.22, 53.14, 53.12, 43.4, 41.4, 40.4, 40.3, 39.7, 39.6, 33.4 (q, J = 29.0 Hz), 32.94 (q, J = 29.0 Hz), 16.8, 16.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 (t, J = 11.3 Hz), -65.1* (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3022, 2954, 1731, 1522, 1435, 1393, 1253, 1196, 1171, 1151, 1126, 1039, 989, 939, 756, 695, 652. HRMS (ESI) calcd for $C_{25}H_{25}F_3NO_4$ $[M+H]^+$: 460.1730. Found: 460.1720.

4. Transformations of 3a

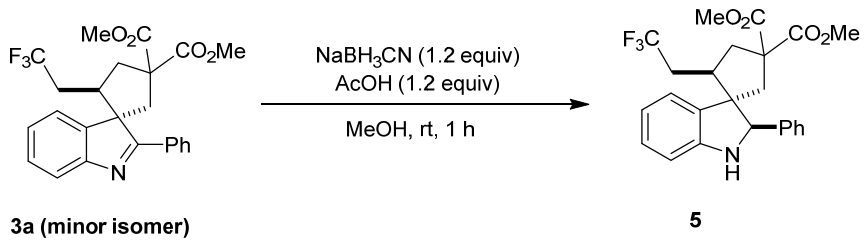


3a (major isomer) (445.0 mg, 1.0 mmol), LiCl (210.0 mg, 5.0 mmol), H_2O (0.2 mL) were added into a flask containing DMSO (10 mL). The reaction mixture was heated to 130 ˚C and gradually turned dark. After heating at 130 ˚C for 3 h, the solution was cooled to rt, diluted with ether and repeatedly washed with brine (6 mL x 5). The organic extracts were dried with Na_2SO_4, filtered, and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 15/1) to afford the desired product **4**.

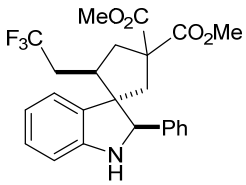


4, yellow oil, 290.0 mg, 76% yield, 1.6/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.05 (m, 2H), 7.73 (d, J = 8.0 Hz, 1H*), 7.70 (d, J = 8.0 Hz, 1H), 7.52-7.24 (m, 6H), 3.76 (s, 3H*), 3.75 (s, 3H), 3.59-3.45 (m, 1H), 3.33-2.95 (m, 2H), 2.71-2.15 (m, 3H), 1.53-1.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 178.8, 176.2, 174.8, 153.7, 153.5, 144.0, 142.0, 132.3, 131.8, 130.8, 130.7, 128.8, 128.7, 128.6, 128.4, 127.9, 127.8, 126.3 (q, J = 276.0 Hz), 126.2, 126.0, 122.7, 122.0, 121.5, 121.2, 68.4, 65.7, 52.2,

52.0, 43.1, 42.8, 41.7, 40.5, 37.2, 36.9, 36.2, 34.7, 33.8* (q, J = 28.0 Hz), 33.4 (q, J = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.6 - -64.7 (m, 3F). IR (thin film): ν_{max} (cm^{-1}) = 3062, 2953, 1730, 1521, 1493, 1464, 1437, 1345, 1254, 1204, 1173, 1138, 1107, 1079, 1022, 753, 694, 649. HRMS (ESI) calcd for $C_{22}H_{21}F_3NO_2$ $[M+H]^+$: 388.1519. Found: 388.1511.



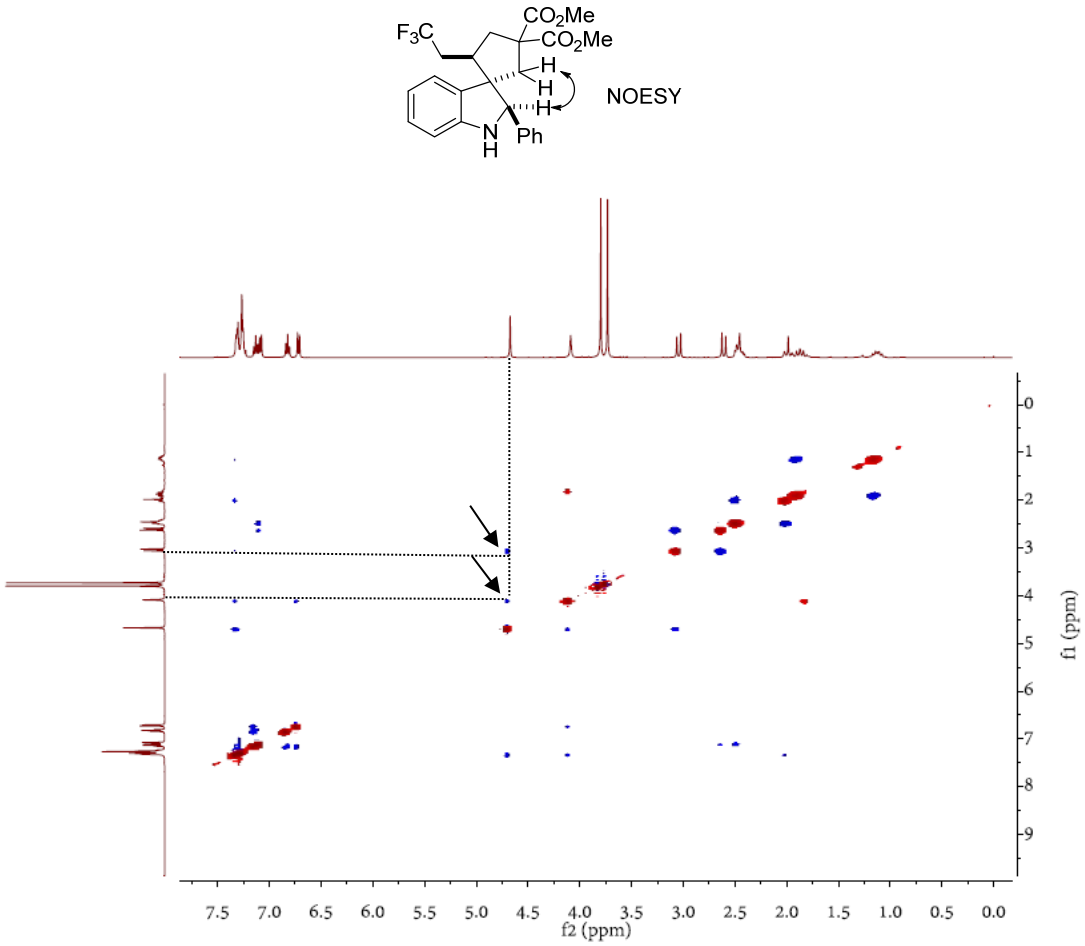
To a mixture of **3a** (minor isomer) (300.0 mg, 0.67 mmol) and $NaBH_3CN$ (52 mg, 0.81 mmol) was added a solution of AcOH (49.0 mg, 0.81 mmol) in MeOH (12 mL) under argon at room temperature. The reaction was stirred for 1 h at room temperature. After the reaction was complete (monitored by TLC), it was quenched with water. The mixture was extracted with EtOAc (30 mL x 3). The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 12/1) to afford the desired product **5**.



5, white solid, m.p. = 140.5-142.2 ºC, 200.0 mg, 70% yield, >20/1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 5H), 7.13 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 4.67 (s, 1H), 4.09 (s, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 3.04 (d, J = 14.8 Hz, 1H), 2.61 (d, J = 14.8 Hz, 1H), 2.50-2.41 (m, 2H), 2.02-1.78 (m, 2H), 1.20-1.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 172.6, 150.7, 139.9, 131.2, 128.5, 128.4, 127.6, 126.7 (q, J = 276.0 Hz), 122.5, 119.5, 108.8, 72.02, 71.99, 60.0, 57.4, 53.00, 52.96, 52.91, 52.87, 47.6, 41.3, 38.5, 31.7 (q, J = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.8 (t, J = 11.3 Hz). IR (thin film): ν_{max} (cm^{-1}) = 3364, 2953, 1742, 1721, 1607, 1485, 1469, 1433, 1354, 1325, 1254, 1148,

1118, 1029, 1012, 785, 758, 712, 665. HRMS (ESI) calcd for $C_{24}H_{25}F_3NO_4$ $[M+H]^+$: 448.1730. Found: 448.1724.

The relative configuration of **5** is assigned via NOESY spectra.



5. Experimental details for mechanistic studies

5.1 UV/Vis absorption spectra

UV/vis absorption spectra based on indole derivative **1a** (0.1 M in DCE), Umemoto's reagent **2a** (0.1 M in DCE) and the mixture of **1a** and **2a** (**1a**:**2a** = 1:1.5, 0.1 M in DCE) were recorded respectively in 1 cm path quartz cuvettes using a Thermo Nanodrop 2000c UV/Vis spectrometer.

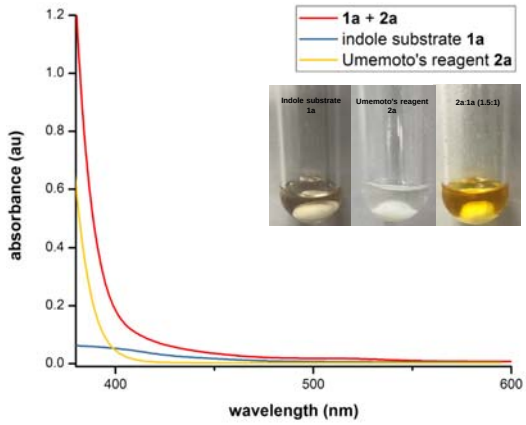


Figure S1. UV/vis absorption spectra

5.2 Stoichiometry of the EDA complex in solution (Job's plot)

The Job's plot was constructed to evaluate the stoichiometry of the EDA complex [2] between the Umemoto's reagent **2a** and indole derivative **1a**. We measured the absorption of DCE solutions at 425 nm with different donor/acceptor ratios with constant concentration (0.01 M) of the two components. All the absorption spectra were recorded in 1 cm path quartz cuvettes using a Thermo Nanodrop 2000c UV/Vis spectrometer. The absorbance values were plotted against the molar fraction (%) of indole derivative **1a**. The maximal absorbance at 50% molar fraction of **1a** indicated the 1:1 stoichiometry of the EDA complex in solution.

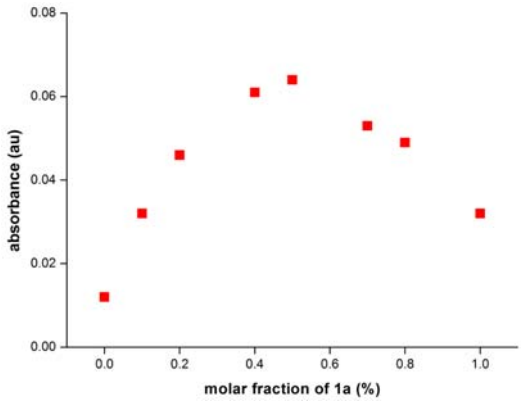


Figure S2. Job's plots of the EDA complexes between indole derivative 1a and Umemoto's reagent 2a.

5.3 Determination of the Association Constant (K_{EDA})

The association constant of the EDA complex formed between the Umemoto's reagent **2a** and indole derivative **1a** was determined spectrophotometrically in DCE, employing the non-linear curve-fitting methodology.[3] We measured the absorption of solutions with constant concentration of Umemoto's reagent **2a** (0.01 M) at 425 nm, and added an excess of indole derivative **1a** to increase the donor/acceptor ratios. All the absorption spectra were recorded in 1 cm path quartz cuvettes using a Thermo Nanodrop 2000c UV/Vis spectrometer. According to the methodology, a curved line was obtained when the absorbance (A) was plotted against the concentration of **1a**. Data obtained were displayed in Table S1. The association constants (K_{EDA}) were calculated to be 4.5 M^{-1}.

Table S1: Data obtained by UV/vis absorption spectra for EDA in DCE, with [2a] = 0.01 M

[**1a**] (M)	Abs_{EDA}
0.01	0.134
0.02	0.206
0.03	0.243
0.04	0.338
0.05	0.419
0.06	0.508
0.07	0.589
0.08	0.616

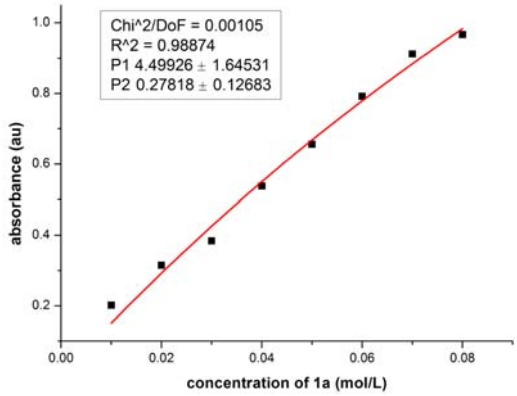


Figure S3. Non-linear plots for the EDA complexes generated in DCE upon association of the indole derivative 1a and Umemoto's reagent 2a.

5.4 Light/Dark Cycle Experiments for the Model Reaction

To study the necessity of continuous irradiation with visible light for the progress of the reaction. The reaction was monitored by ^{19}F NMR spectroscopy using CF_3Ph as internal standard before and after light irradiation and dark periods.

The experiments with successive intervals of irradiation and dark periods resulted in total interruption of the reaction progress in the absence of light, and recuperation of reactivity upon further illumination. These results demonstrated that light is a necessary component for the reaction.

Table S2: The Data for "dark and light" experiment.

Time / min	Yield / % (by ^{19}F NMR)	Remarks
0	0	/
5	33	Light (5 min)
30	33	Dark (25 min)
35	38	Light (5 min)
60	38	Dark (25 min)
80	51	Light (20 min)
150	51	Dark (70 min)
170	68	Light (20 min)

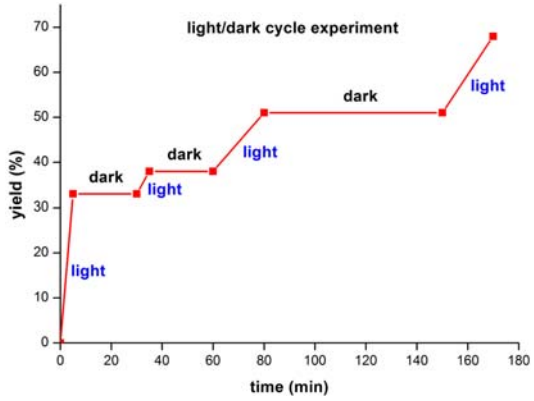


Figure S4. Discontinuous light experiment, each point of the graphic represents the NMR yield.

5.5 EPR Experiments

EPR spectra were recorded at room temperature using DMPO as free radical spin trapping agent. According to general procedure, a 10 mL nap vial was equipped magnetic stir bar and was charged with **1a** (19 mg, 0.05 mmol, 1.0 equiv), Umemoto's reagent **2a** (26.0 mg, 0.075 mmol, 1.5 equiv), DMPO (0.022 mL, 0.2 mmol, 4.0 equiv) and DCE (0.5 mL). The reaction mixture was stirred under standard conditions for 10 min and measured by Bruker EMX-10/12 EPR spectrometer immediately.[4]

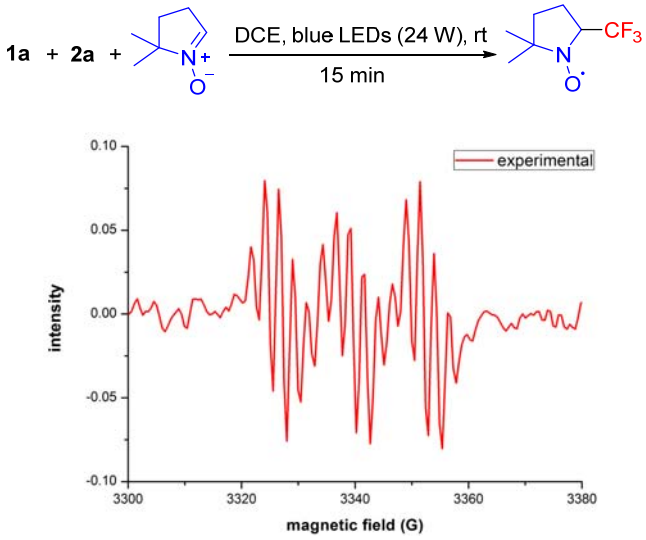
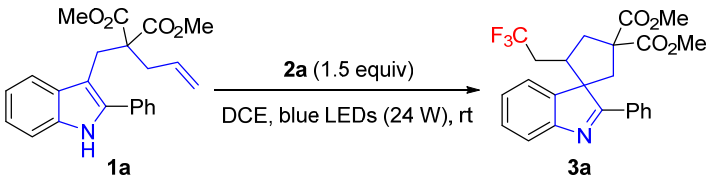


Figure S5. EPR spectrum.

5.6 Determination of Quantum Yield



The reaction mixture of indole derivative **1a** (75.5 mg, 0.2 mmol) and Umemoto's reagent **2a** (102 mg, 0.3 mmol) in DCE (2.0 mL) was filled into a fluorescence cuvette with a stirring bar and septum and degassed by bubbling with argon (5 min). Then, the cuvette was put into the setup (irradiation area: 2.5 cm x 3.7 cm), illuminated under 425 nm at a distance of 15 cm from 24 W blue LEDs. The transmitted radiant power was measured by ILT1400 Radiometer Photometer (International Light Technologies) during the irradiation. After illumination for 120 s (ΔP = 1 umol•S^{-1} •mol^{-2}), the yield for the reaction was 3% determined by ^{19}F NMR spectroscopy using CF_3Ph as internal standard. Accordingly, the quantum yield is calculated to be 0.69.

$$\Phi = \frac{N_{prod}}{N_{abs'}\ \text{photon}} = 0.69$$

References:

[1] Bandini, M.; Eichholzer, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 9533.

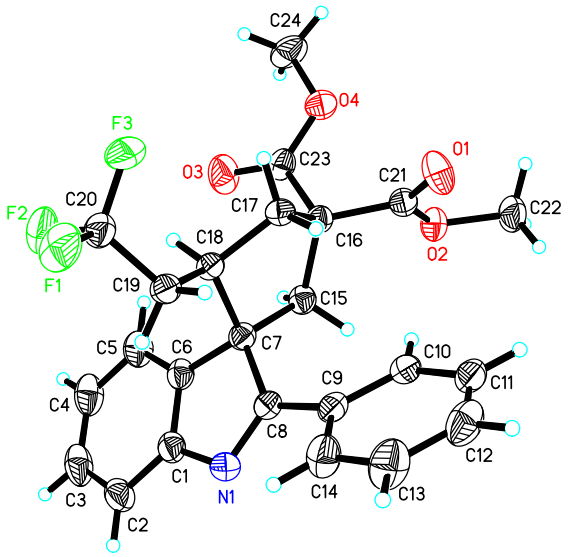
[2] Job, P. *Ann. Chim.* **1928**, *9*, 113.

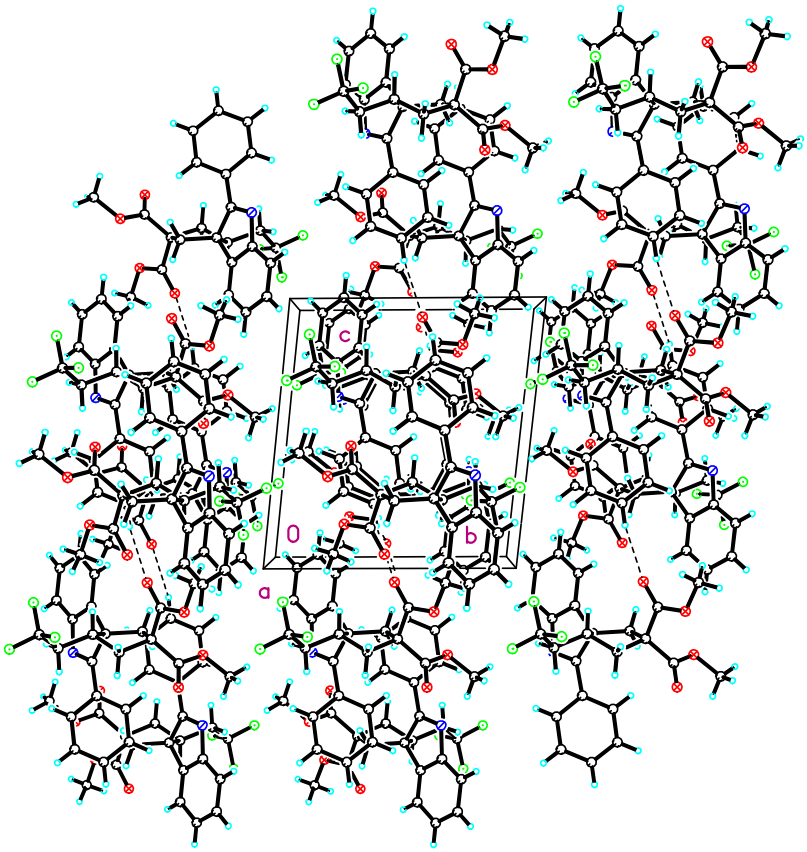
[3] Connors, K. A. *Binding Constants: The Measurement of Molecular Complex Stability*; Wiley: New York, **1987**.

[4] Janzen, E. G.; Zhang, Y-K.; Arimura, M. *J. Org. Chem.* **1995**, *60*, 5434.

6. X-Ray crystal data of 3a (minor isomer)

Figure S7: X-Ray crystal structure of **3a** (minor isomer), (The crystal was obtained by slow evaporation of the solution of DCM and PE) (CCDC 1844566):





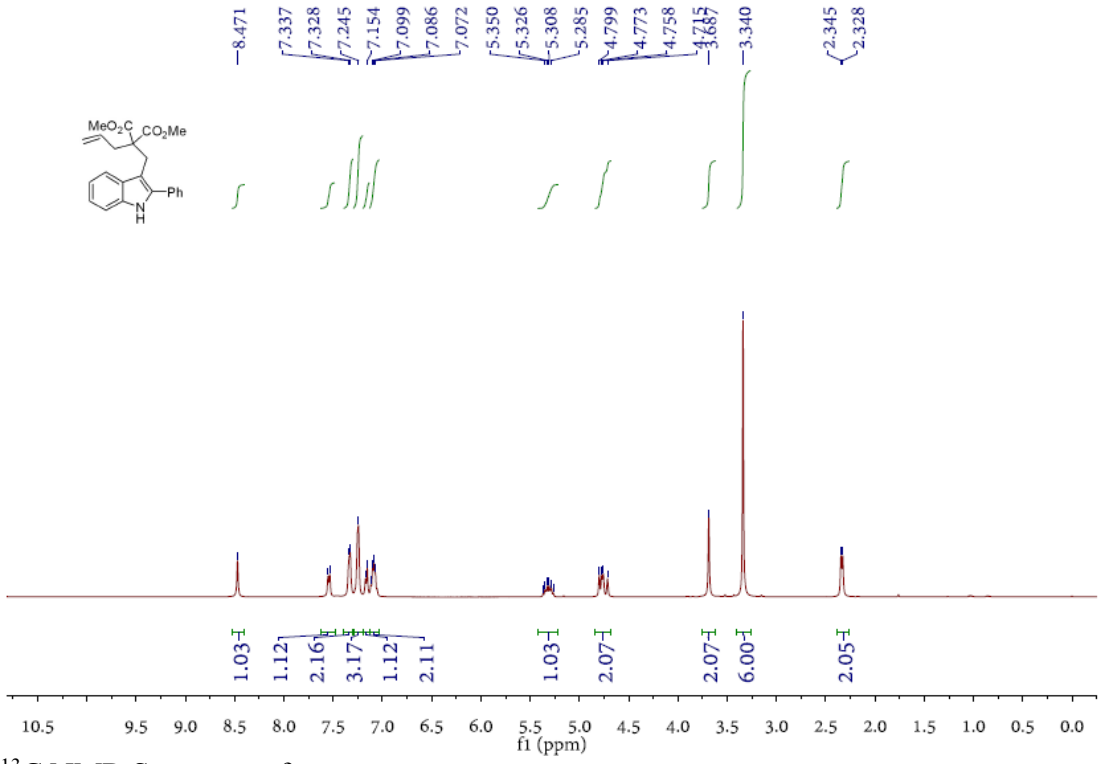
Crystal data and structure refinement for mo_d8v17591_0m.

Identification code	mo_d8v17591_0m	
Empirical formula	C24 H22 F3 N O4	
Formula weight	445.42	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.7265(7) Å	a= 83.532(2)°.
	b = 10.2044(7) Å	b= 82.442(2)°.
	c = 11.0062(9) Å	g = 87.866(2)°.
Volume	1075.74(14) $Å^3$	
Z	2	
Density (calculated)	1.375 Mg/m^3	
Absorption coefficient	0.110 mm^{-1}	
F(000)	464	

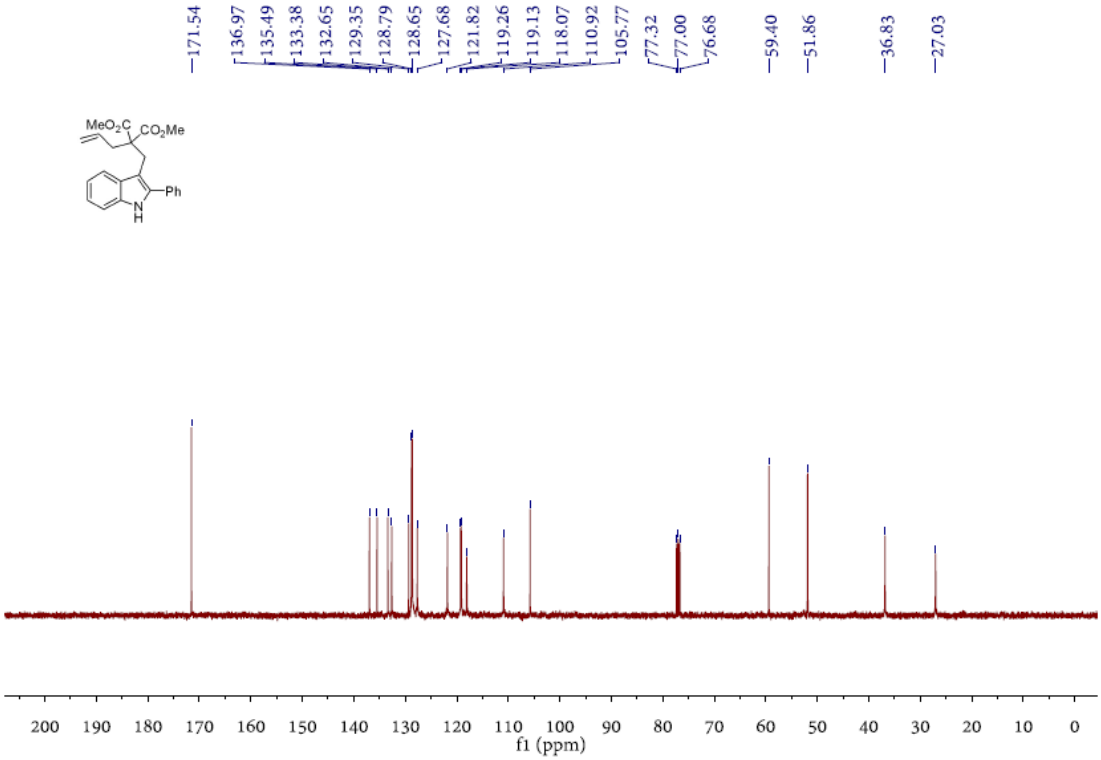
Crystal size	0.220 x 0.200 x 0.150 mm^3
Theta range for data collection	2.113 to 25.996°.
Index ranges	-11<=h<=11, -12<=k<=12, -13<=l<=13
Reflections collected	16344
Independent reflections	4178 [R(int) = 0.0302]
Completeness to theta = 25.242°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6943
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4178 / 0 / 291
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.1020
R indices (all data)	R1 = 0.0564, wR2 = 0.1136
Extinction coefficient	n/a
Largest diff. peak and hole	0.210 and -0.190 e.$Å^{-3}$

7. Copies of NMR spectra

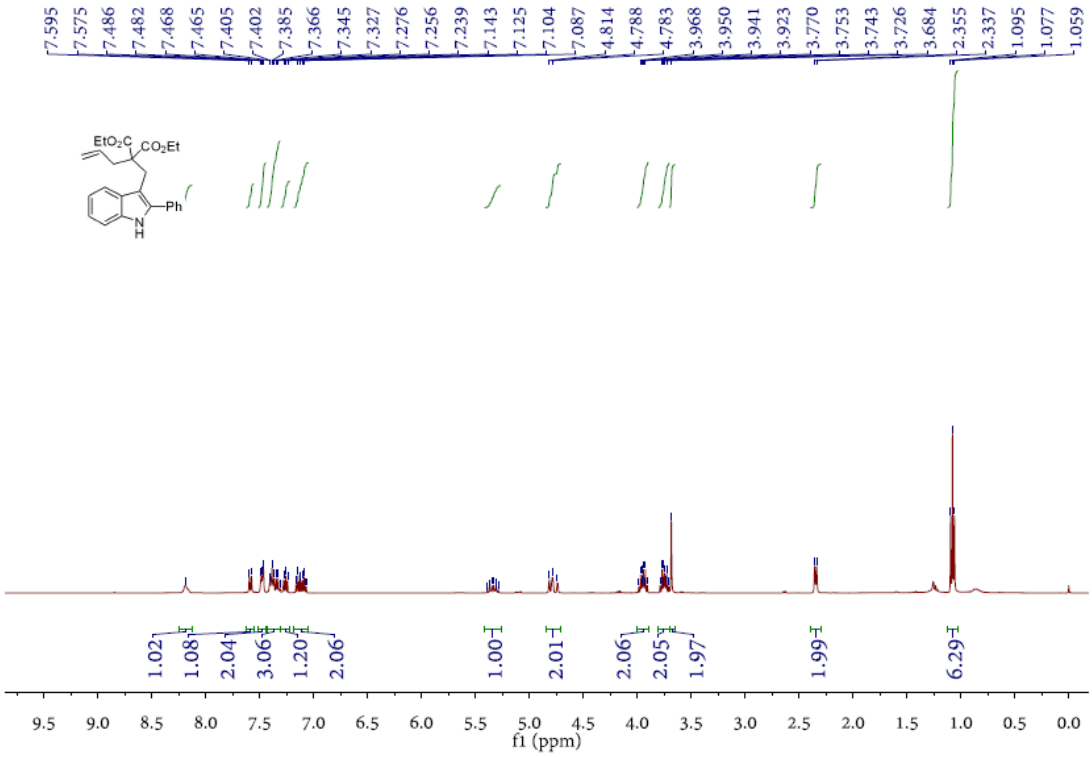
^{1}H NMR Spectrum of **1a**



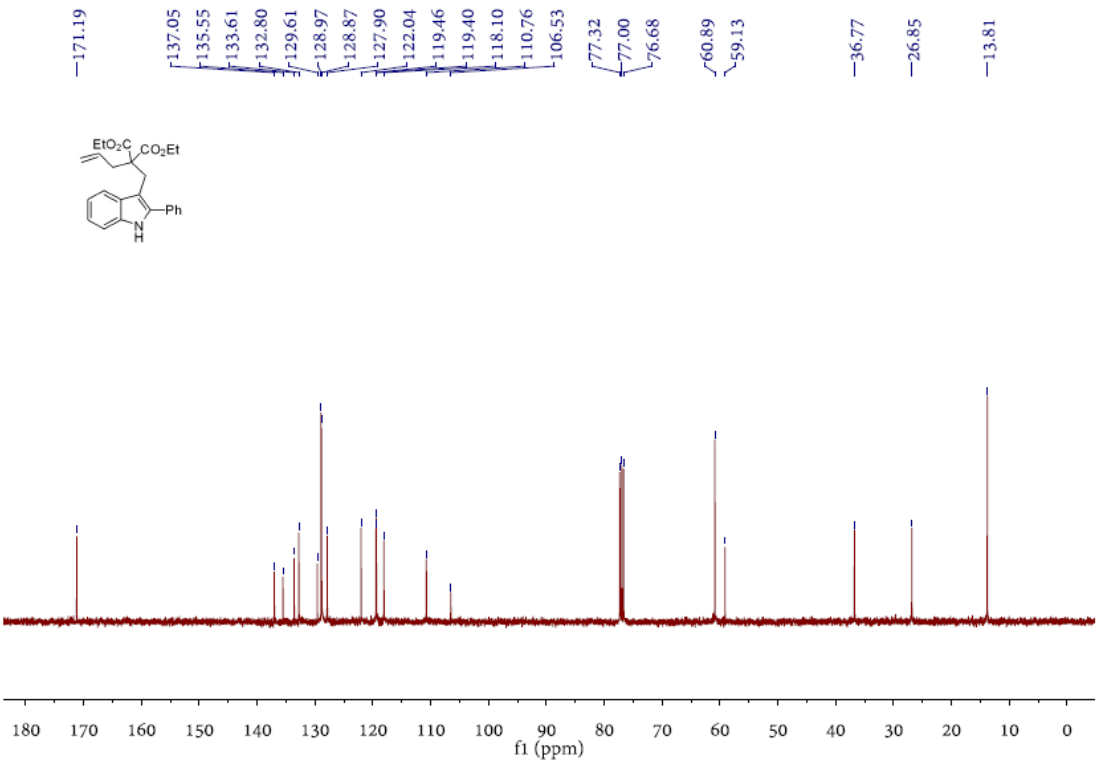
^{13}C NMR Spectrum of **1a**



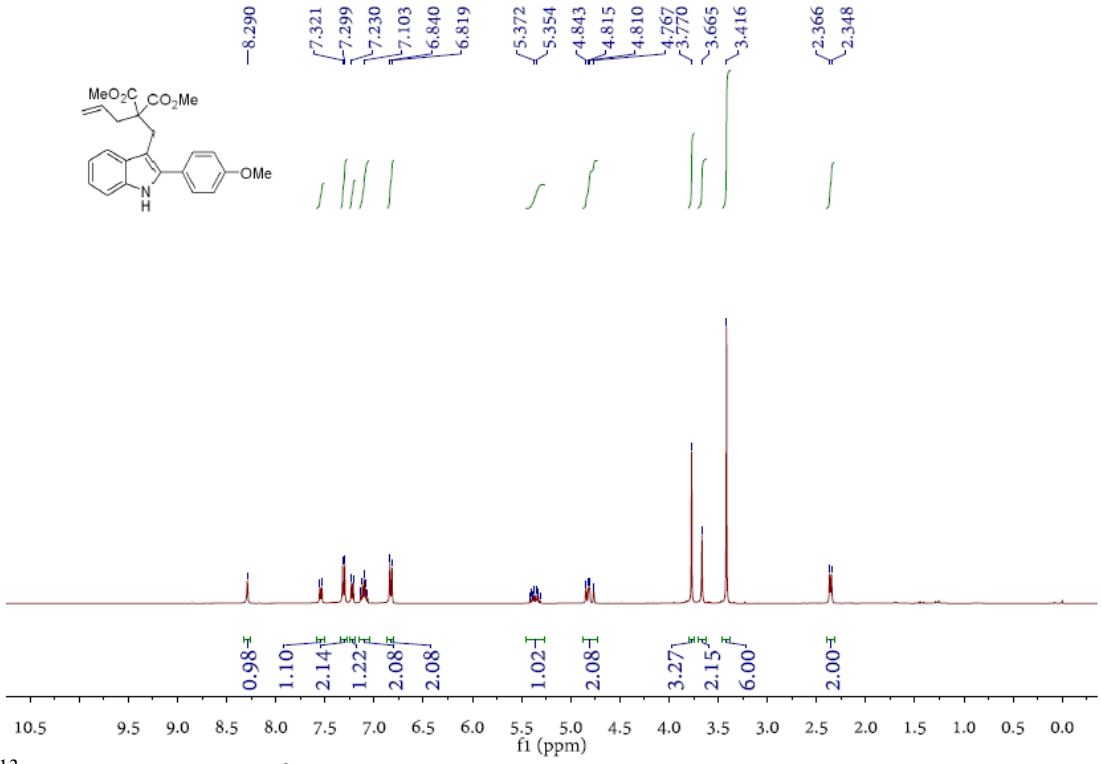
^{1}H NMR Spectrum of **1b**



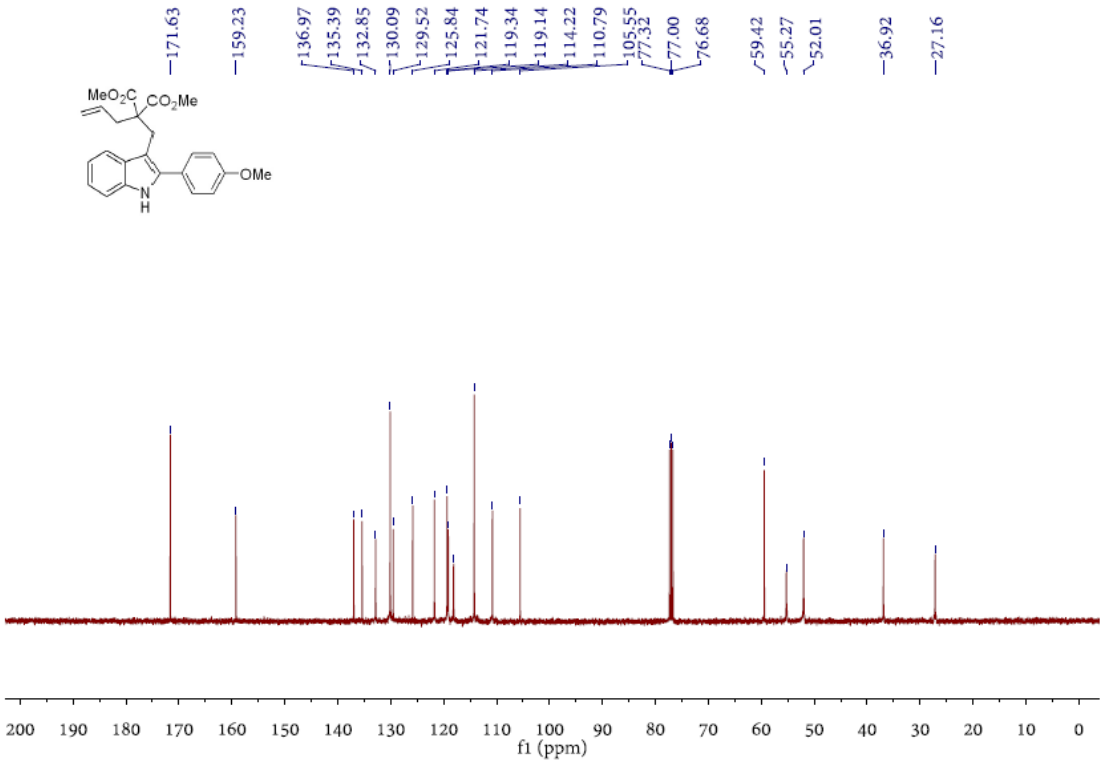
^{13}C NMR Spectrum of **1b**



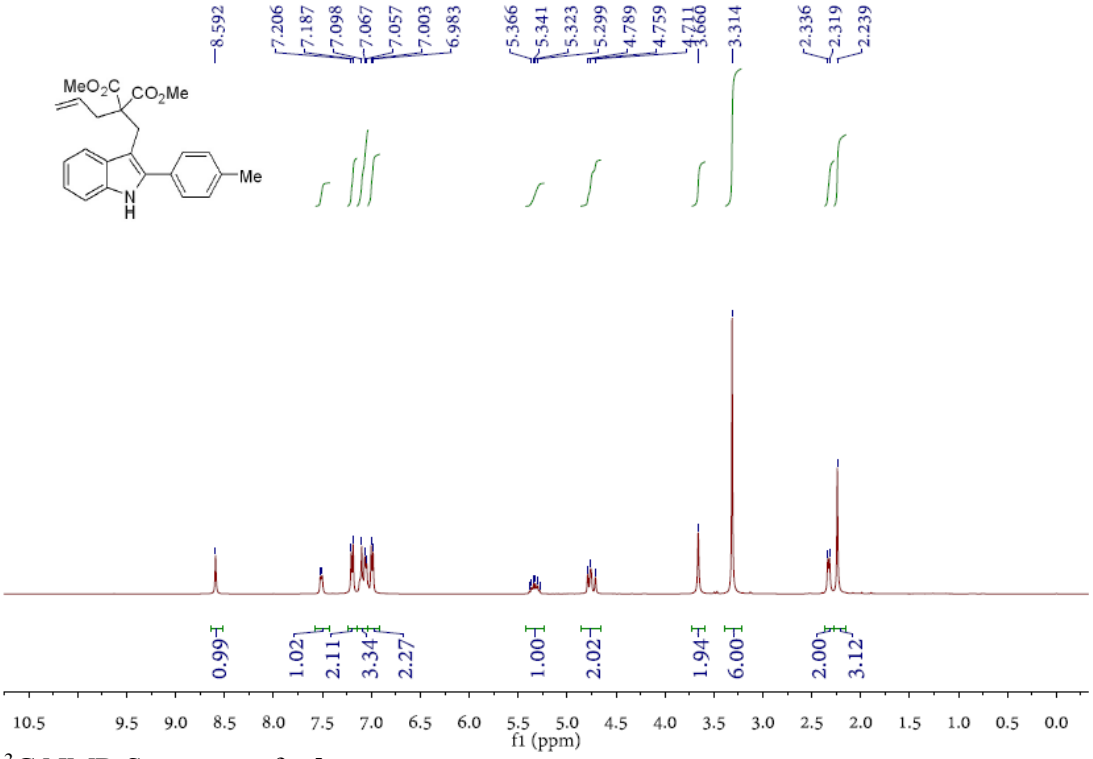
^{1}H NMR Spectrum of **1c**



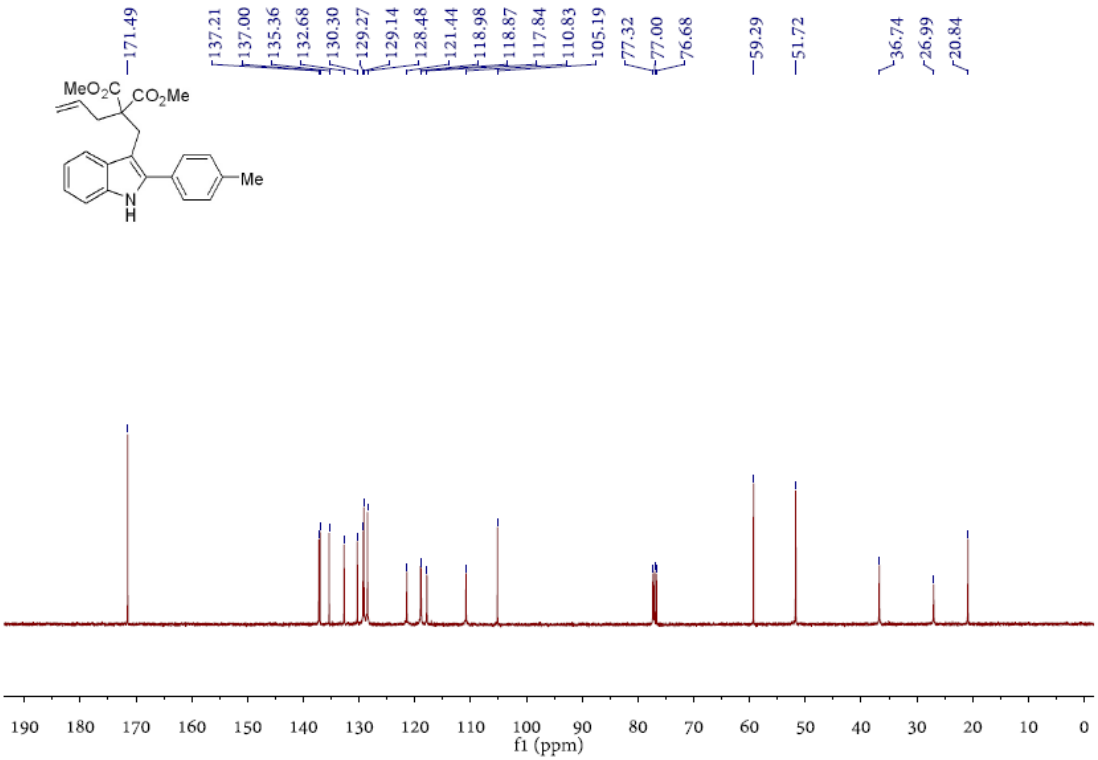
^{13}C NMR Spectrum of **1c**



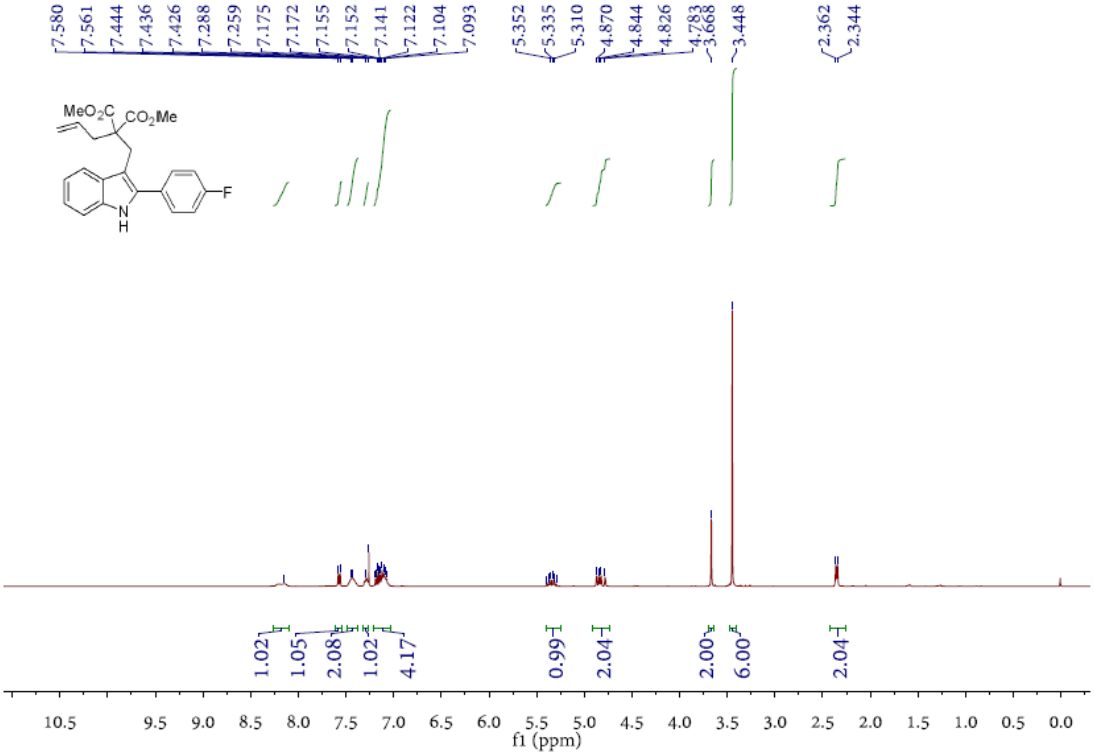
^{1}H NMR Spectrum of **1d**



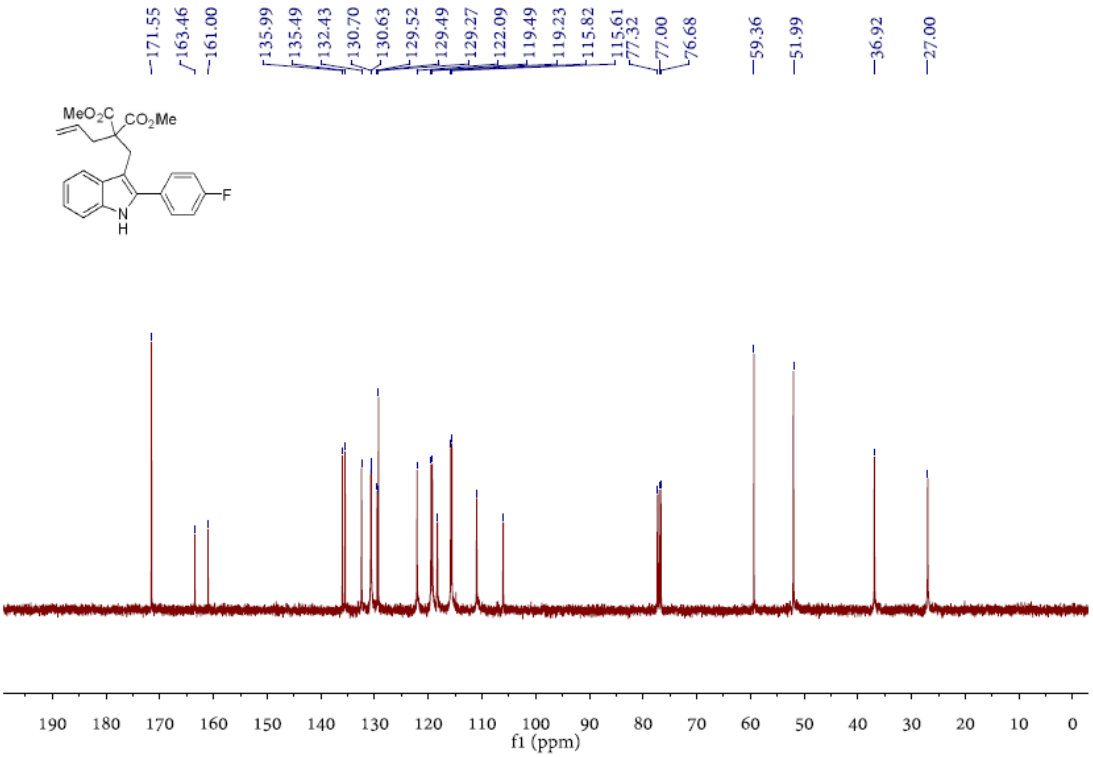
^{13}C NMR Spectrum of **1d**



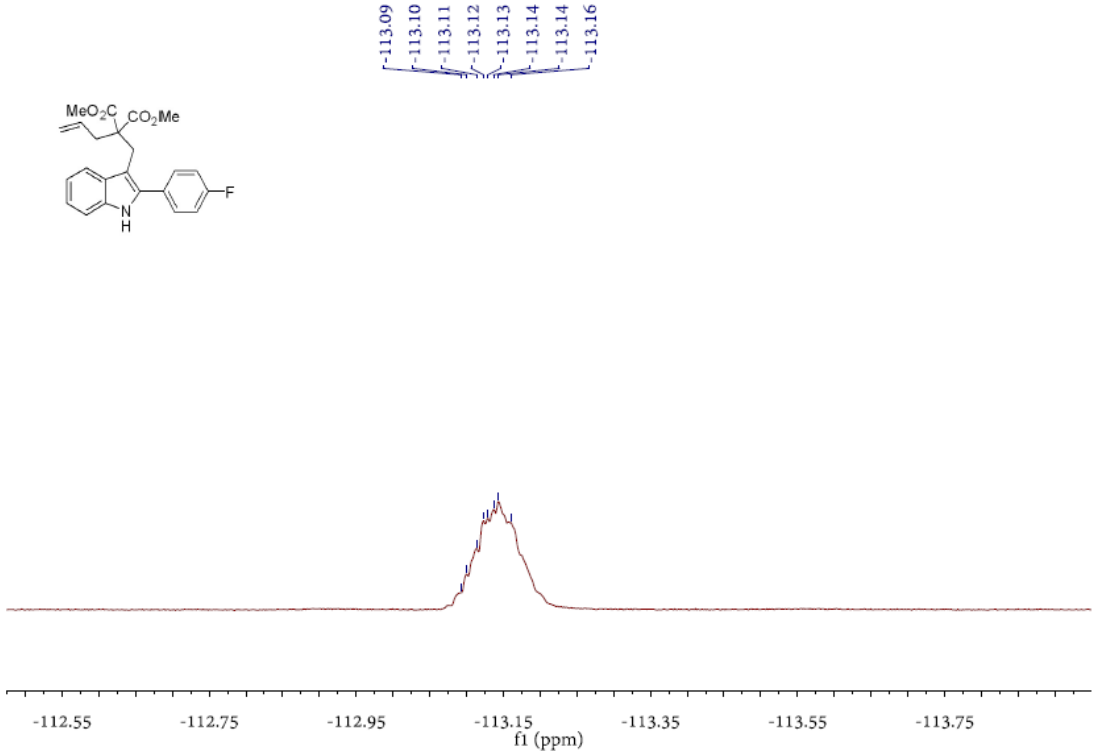
^{1}H NMR Spectrum of **1e**



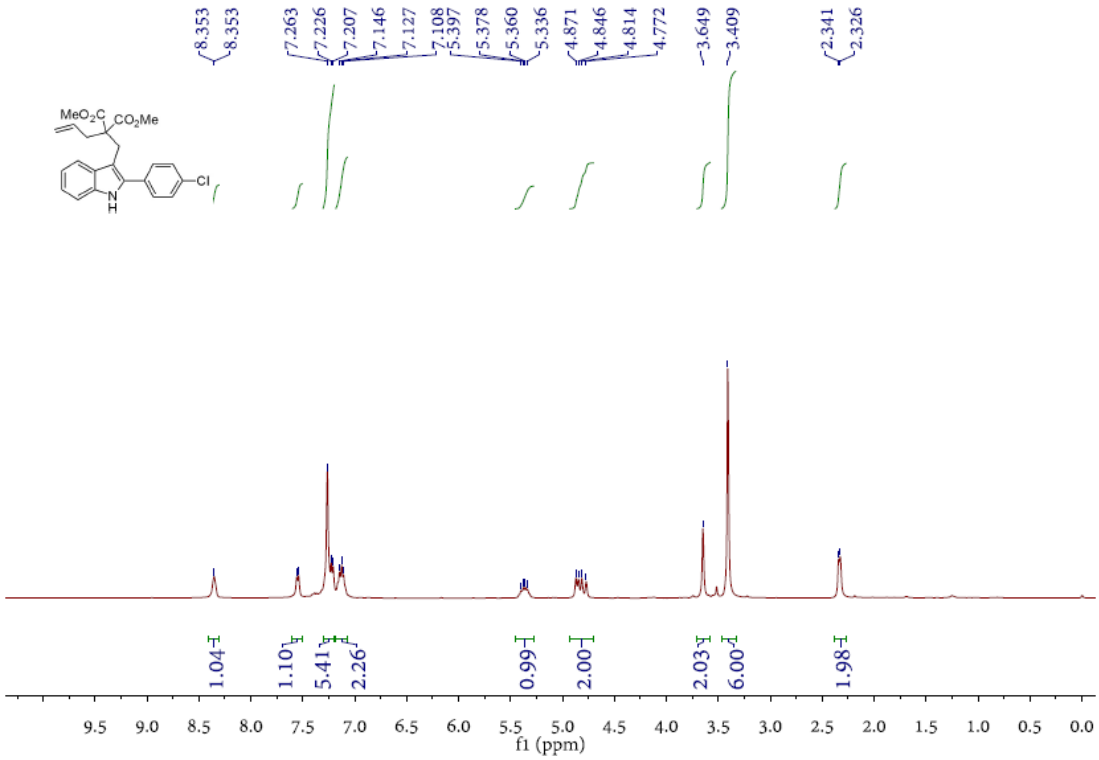
^{13}C NMR Spectrum of **1e**



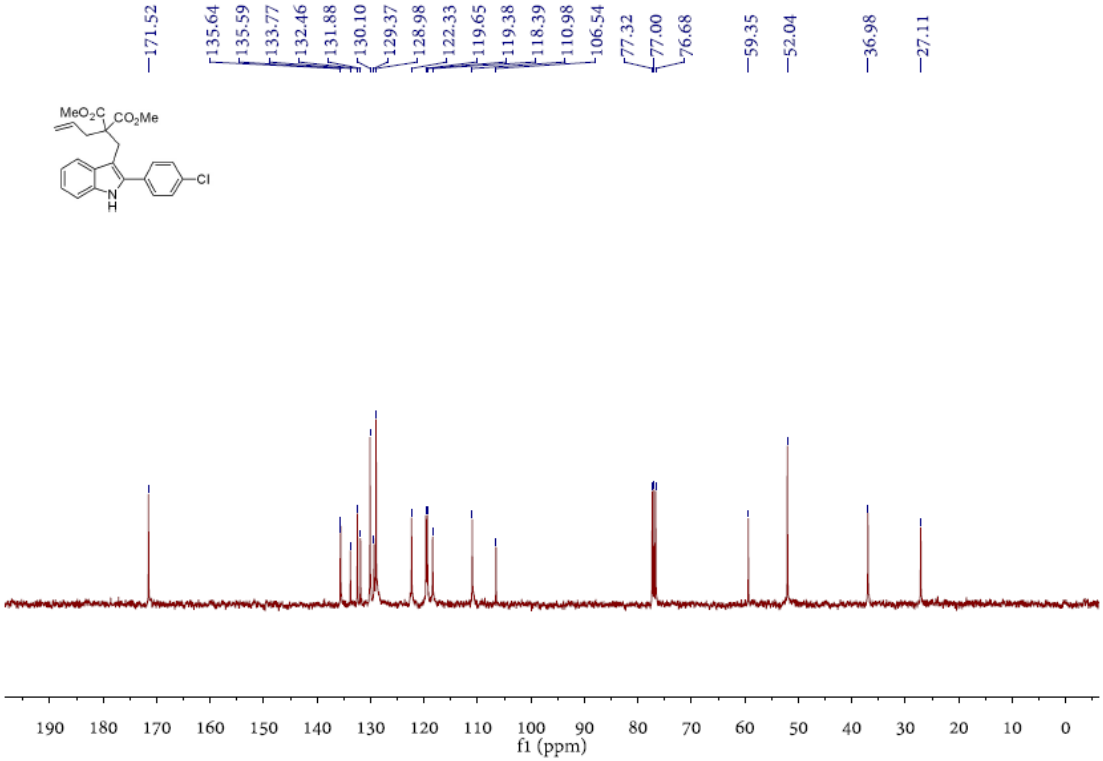
^{19}F NMR Spectrum of **1e**



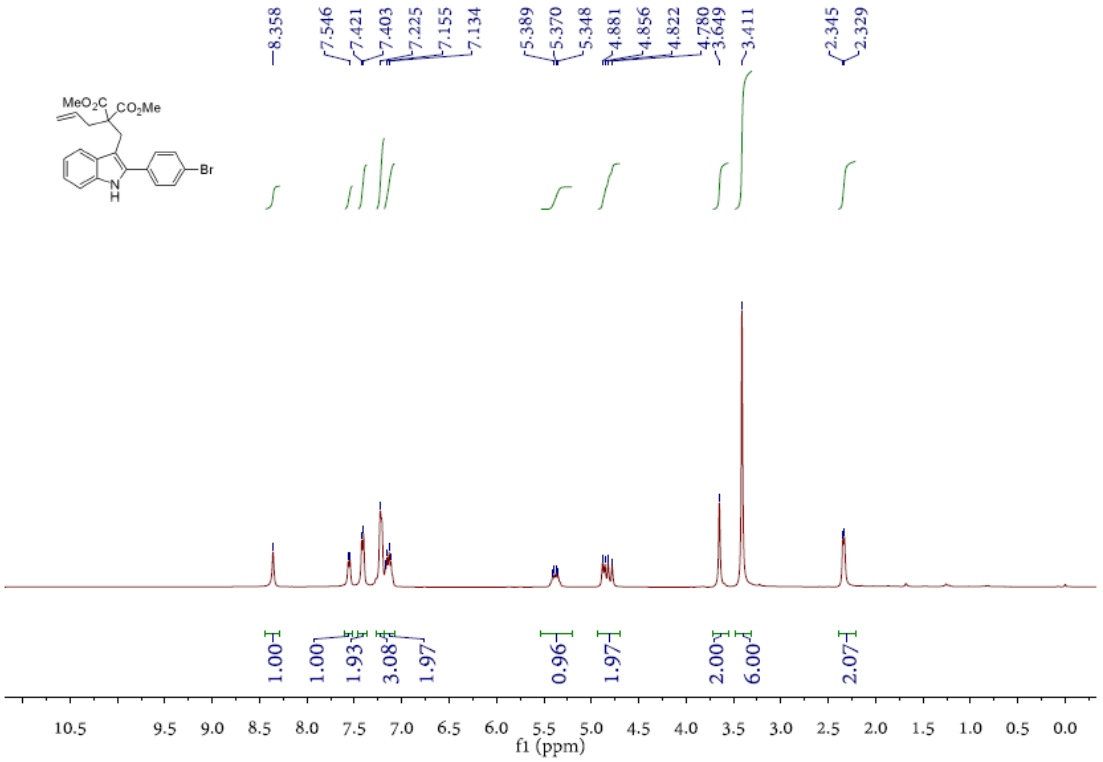
^{1}H NMR Spectrum of **1f**



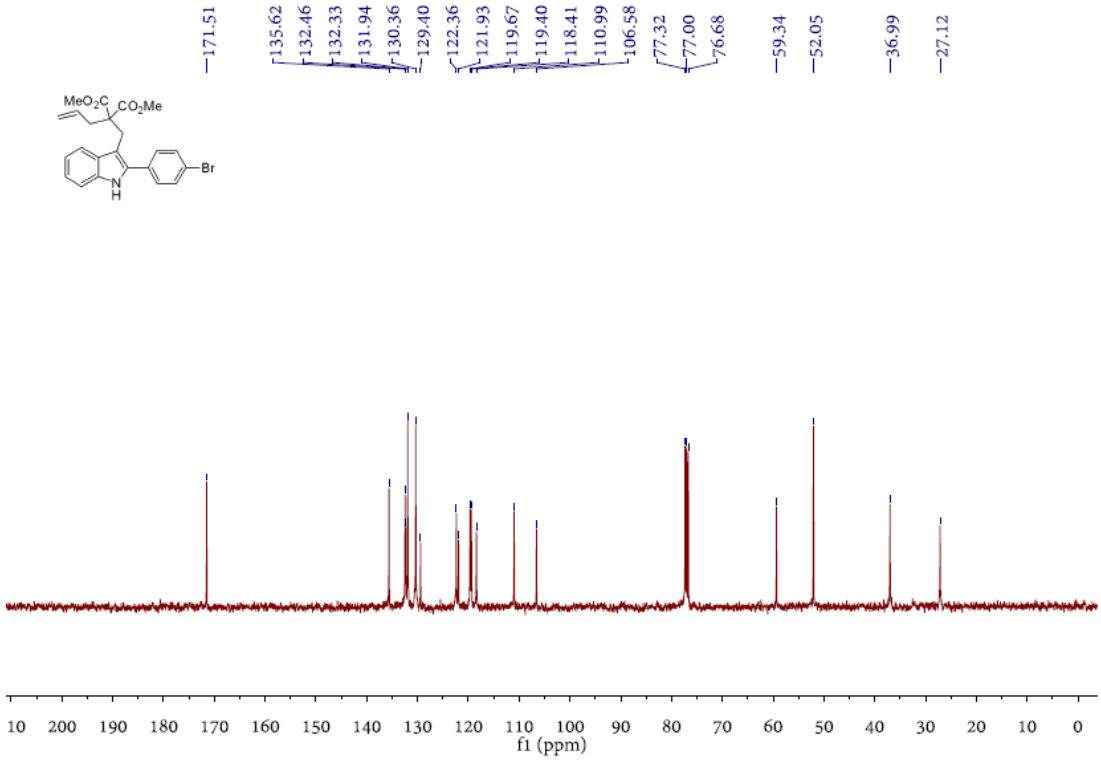
^{13}C NMR Spectrum of **1f**



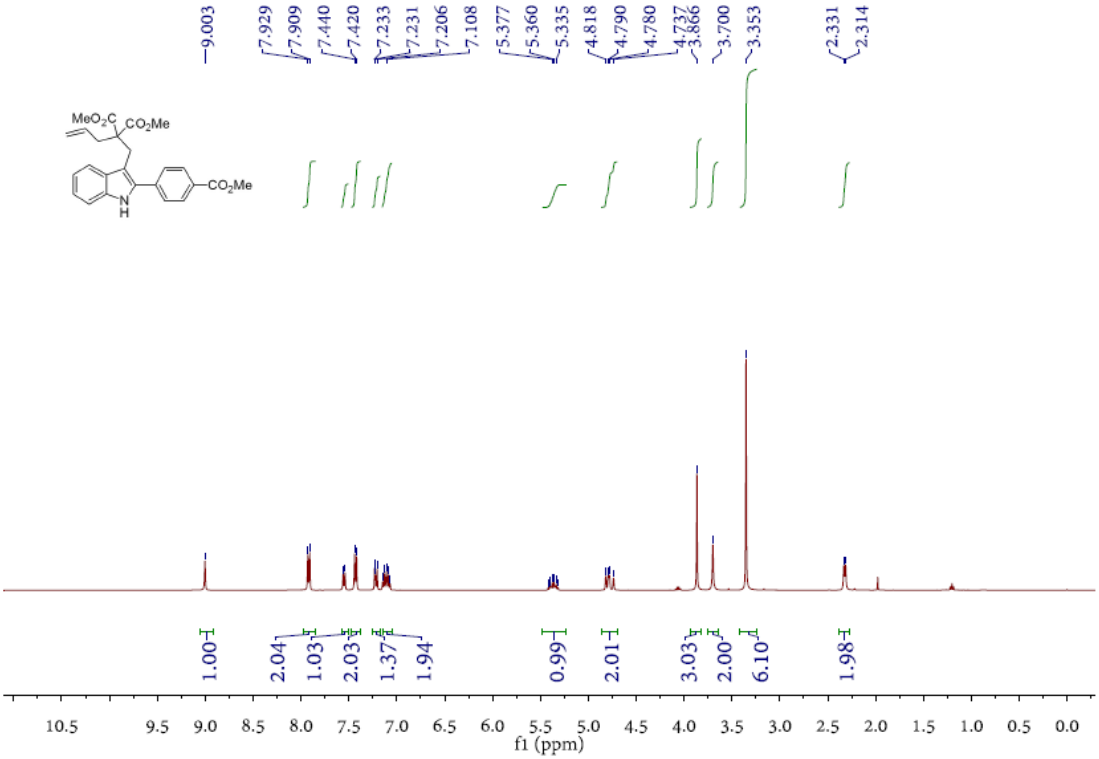
^{1}H NMR Spectrum of **1g**



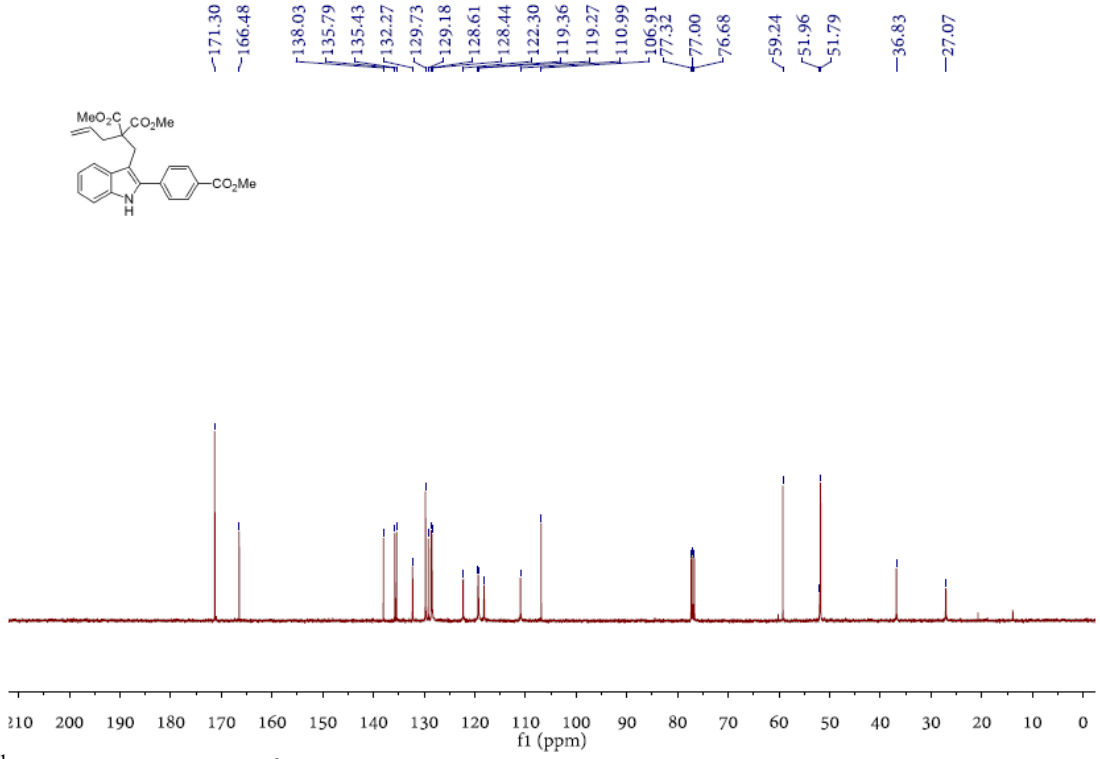
^{13}C NMR Spectrum of **1g**



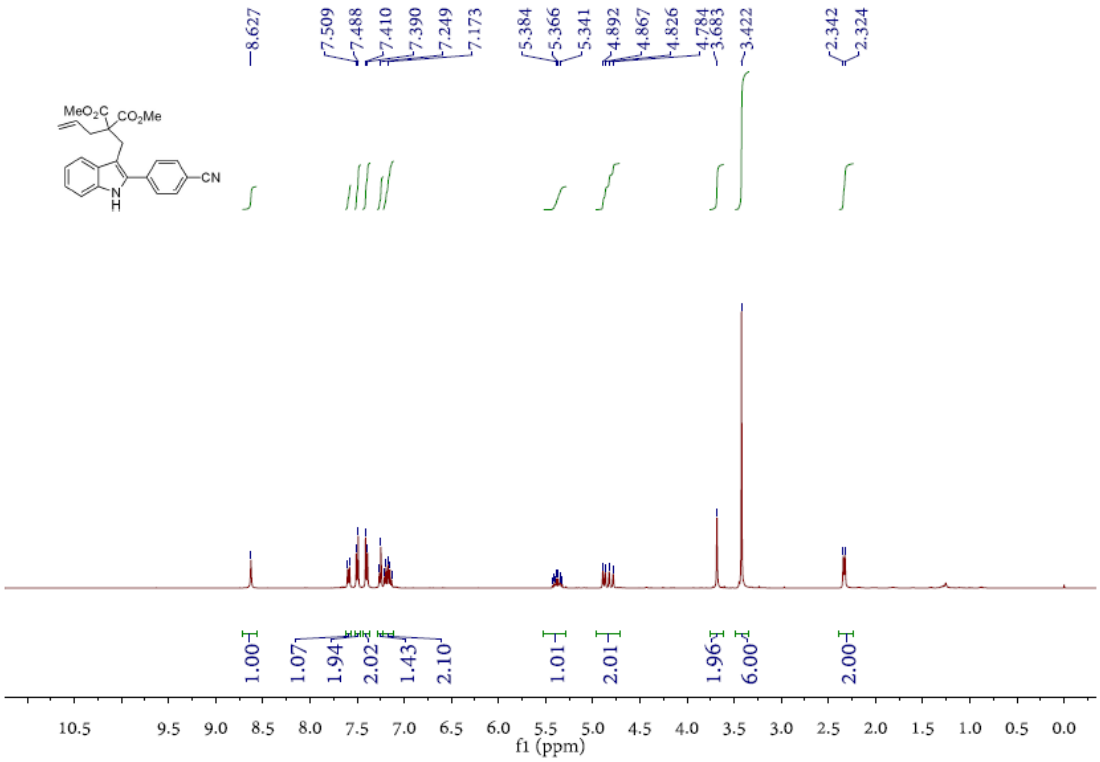
^{1}H NMR Spectrum of **1h**



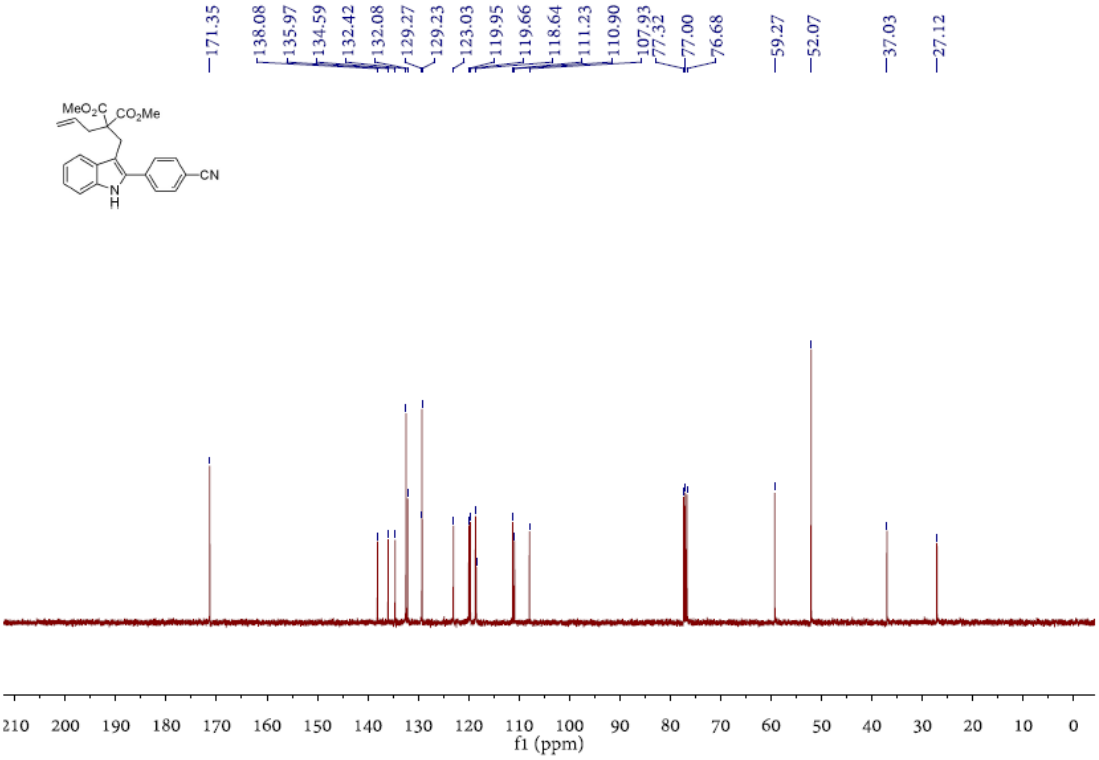
^{13}C NMR Spectrum of **1h**



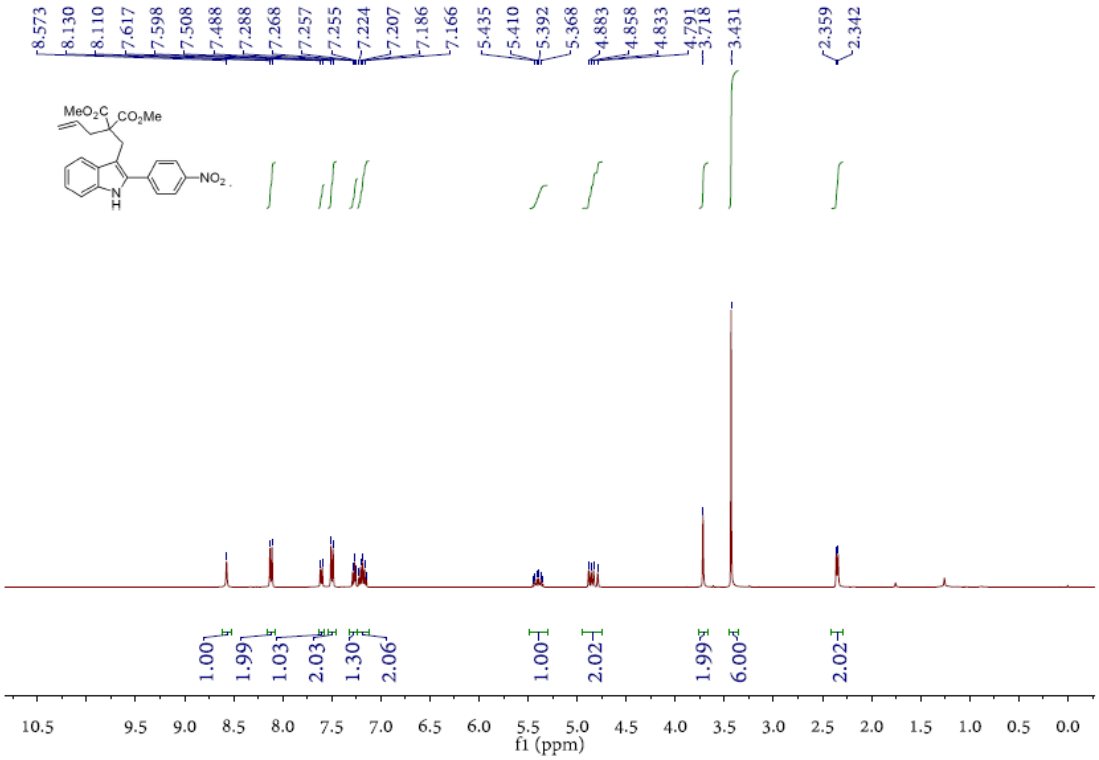
^{1}H NMR Spectrum of **1i**



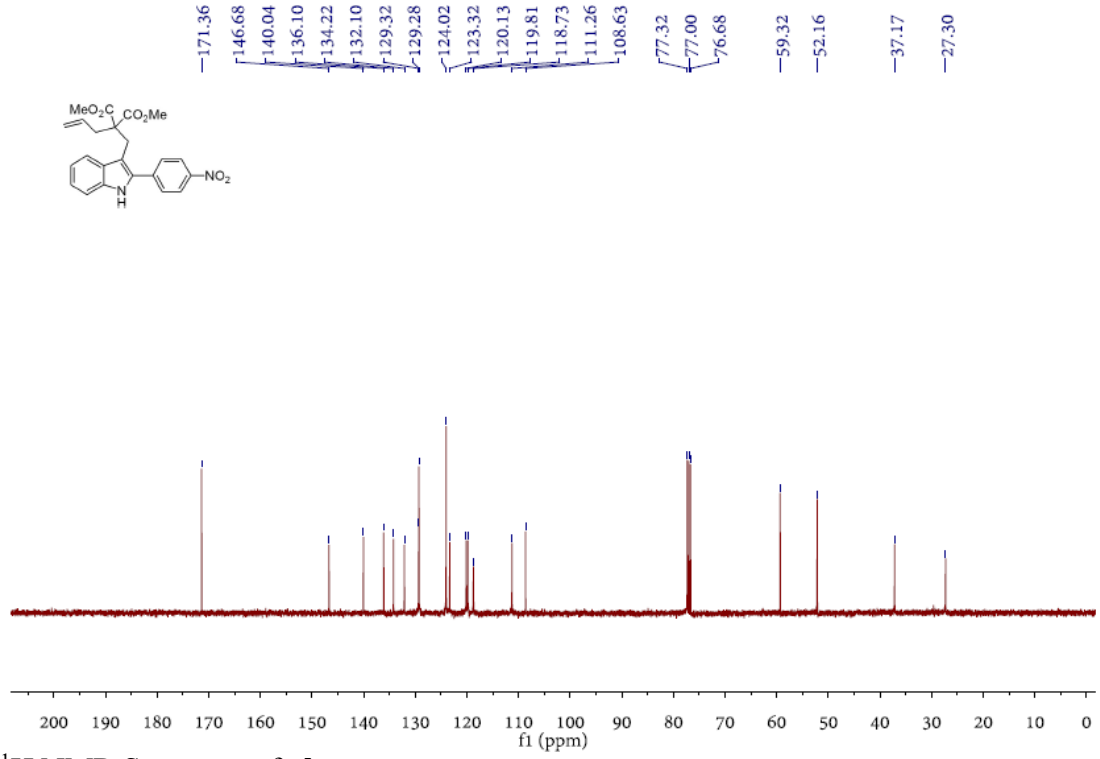
^{13}C NMR Spectrum of **1i**



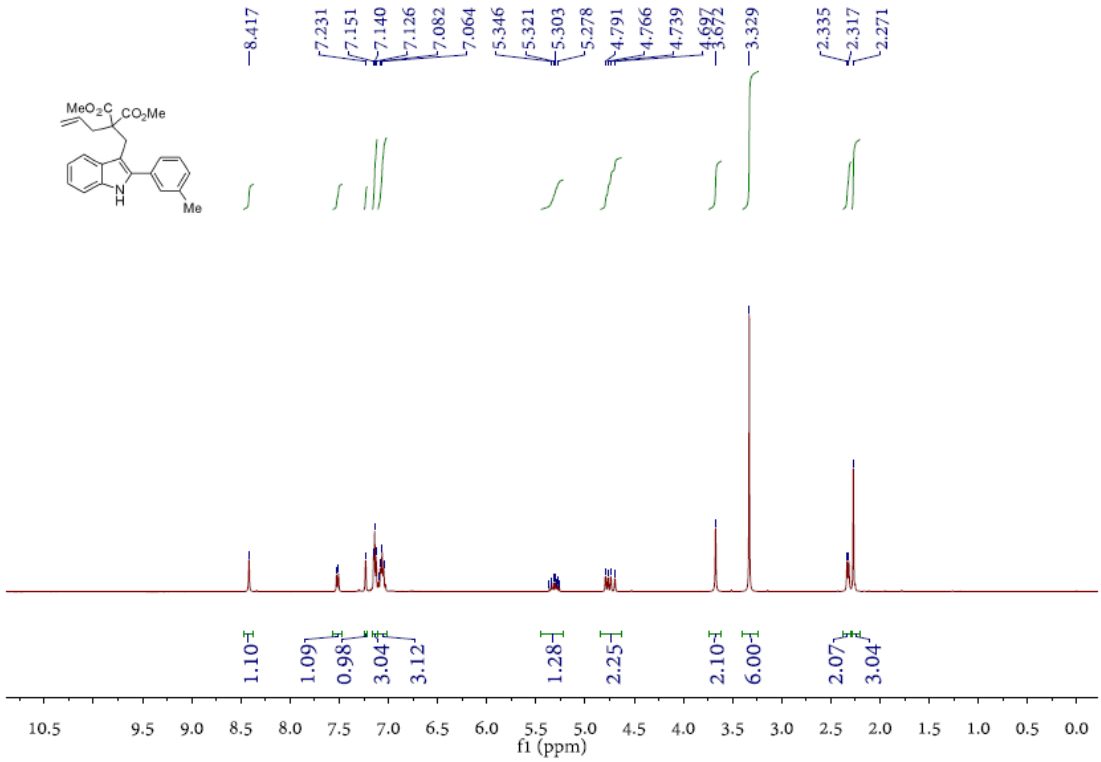
^{1}H NMR Spectrum of **1j**



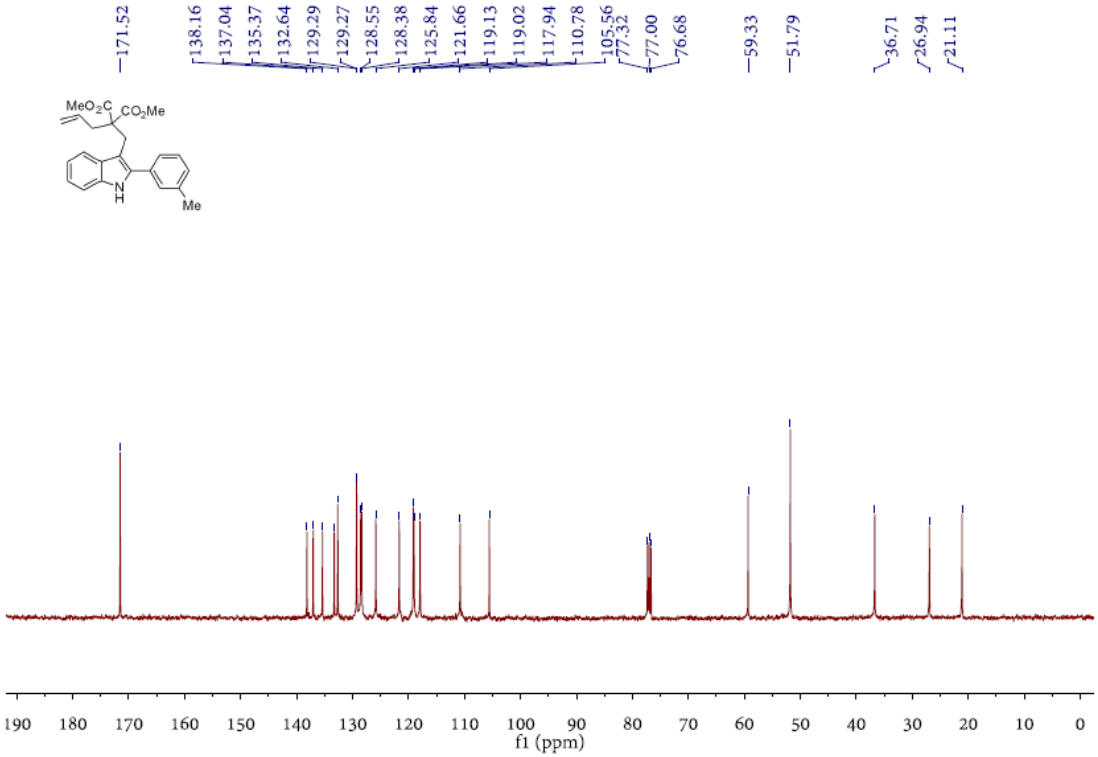
^{13}C NMR Spectrum of **1j**



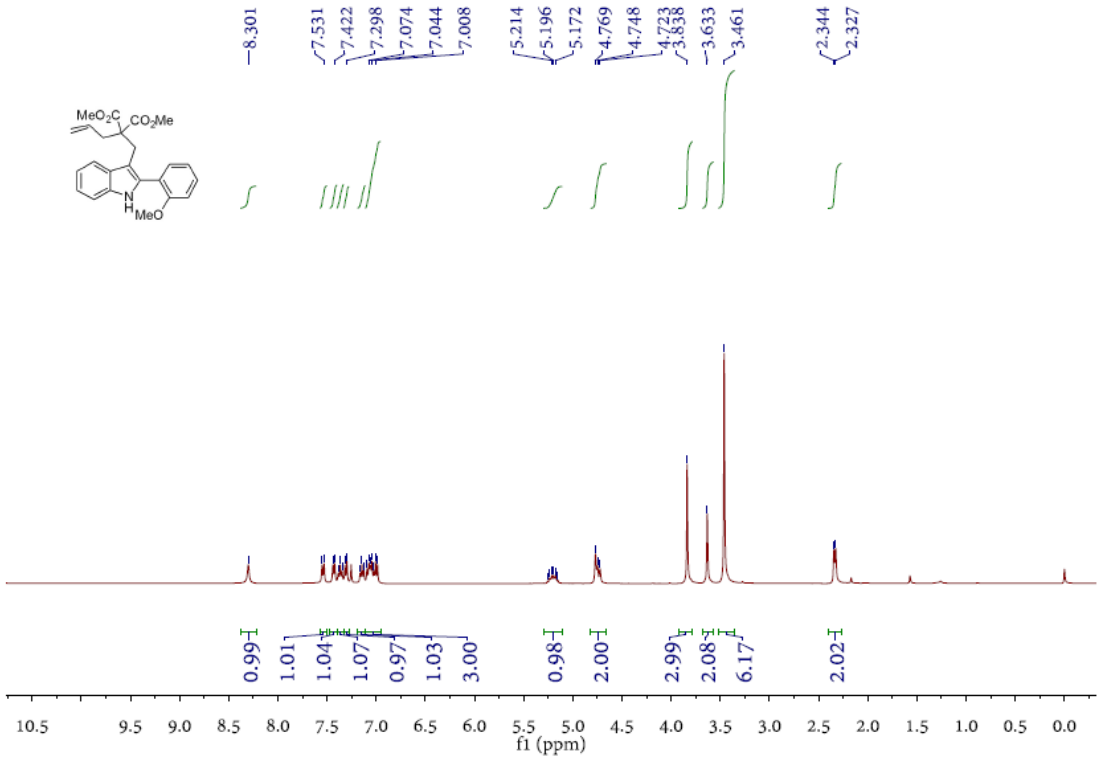
^{1}H NMR Spectrum of **1k**



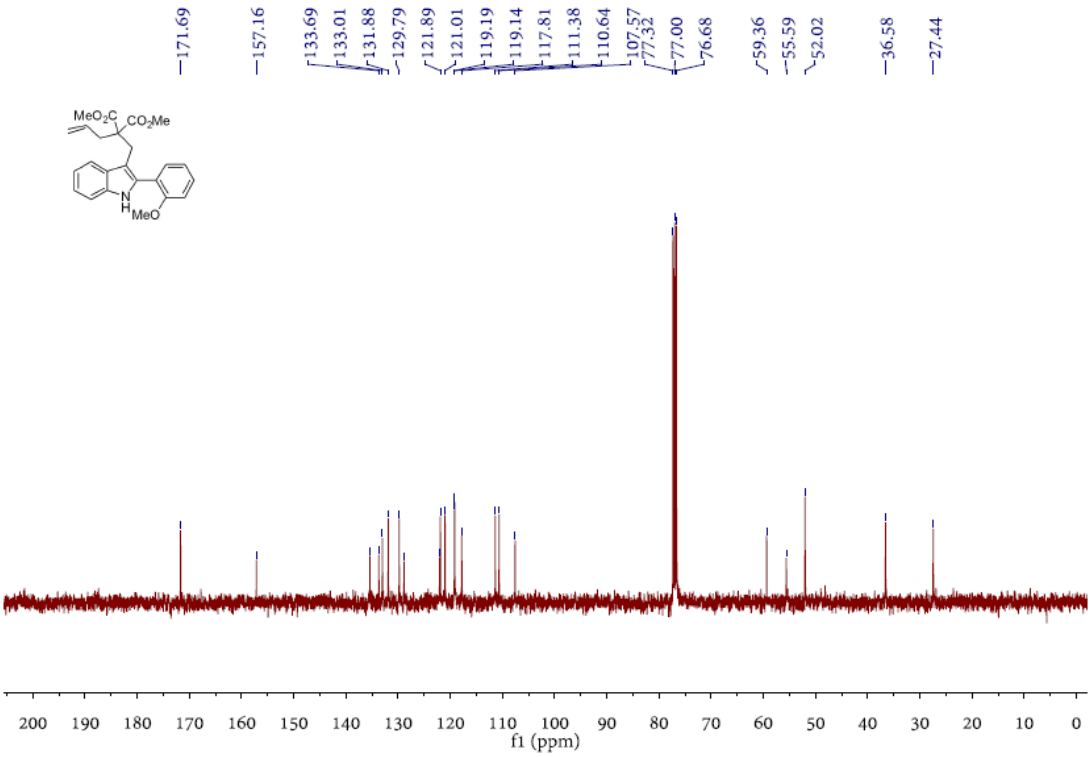
^{13}C NMR Spectrum of **1k**



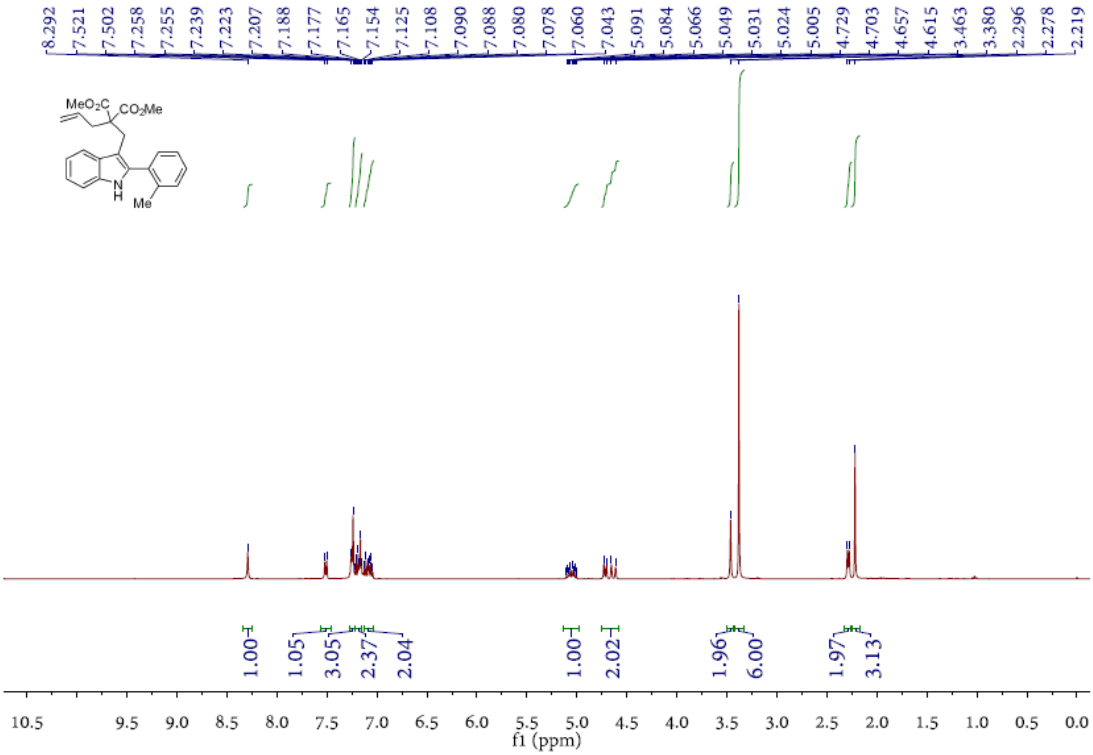
^{1}H NMR Spectrum of **1l**



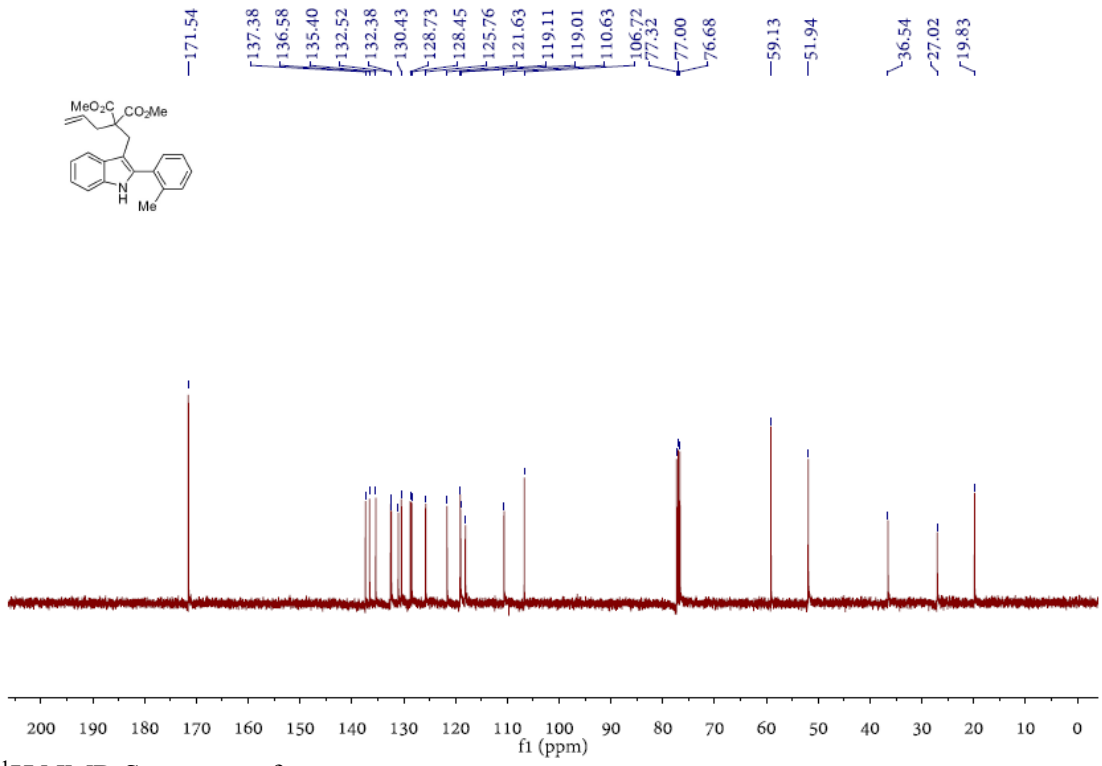
^{13}C NMR Spectrum of **1l**



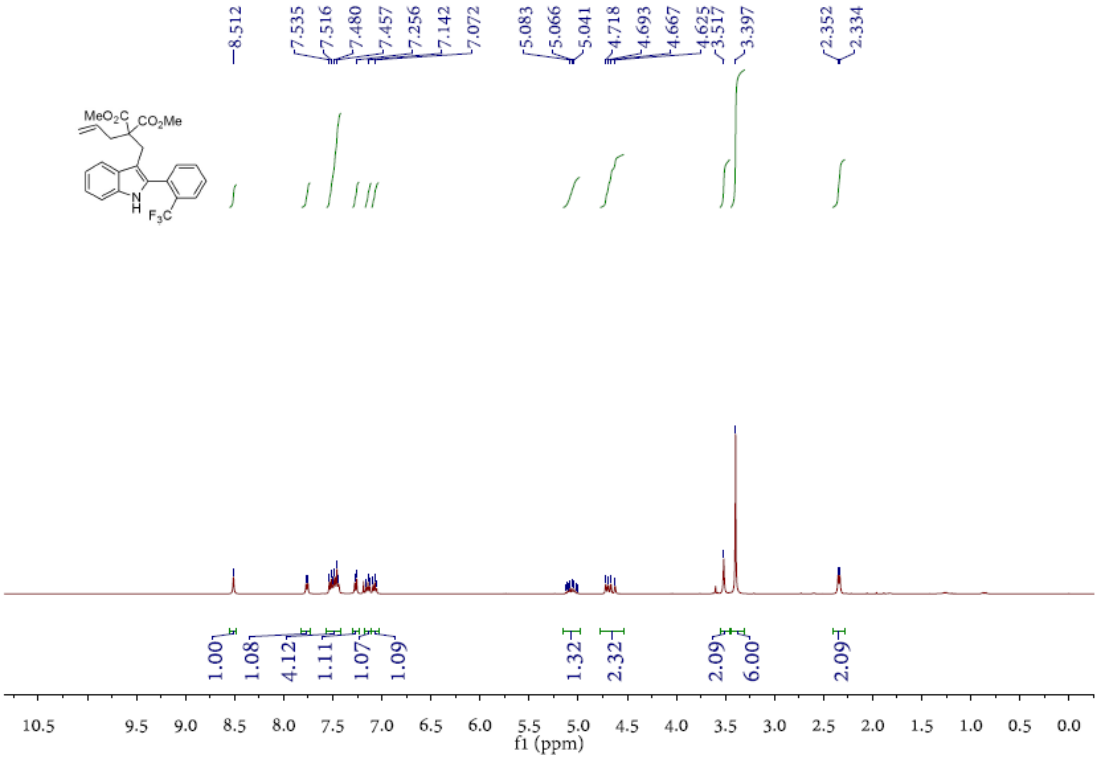
^{1}H NMR Spectrum of **1m**



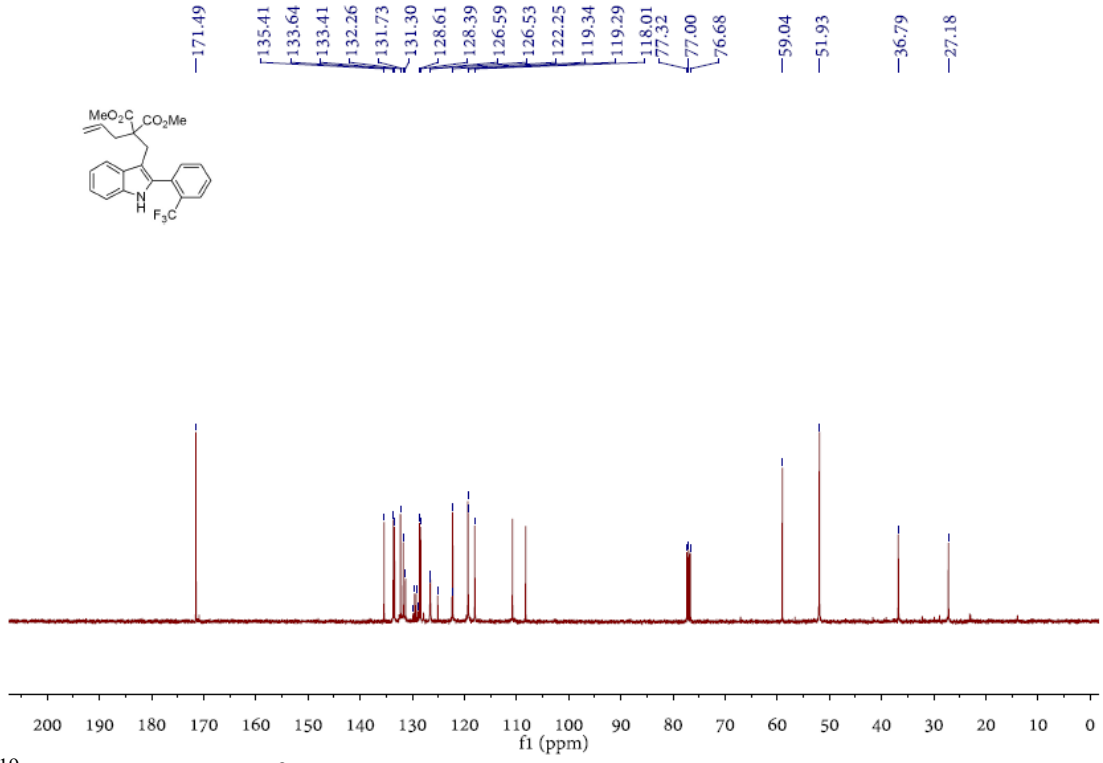
^{13}C NMR Spectrum of **1m**



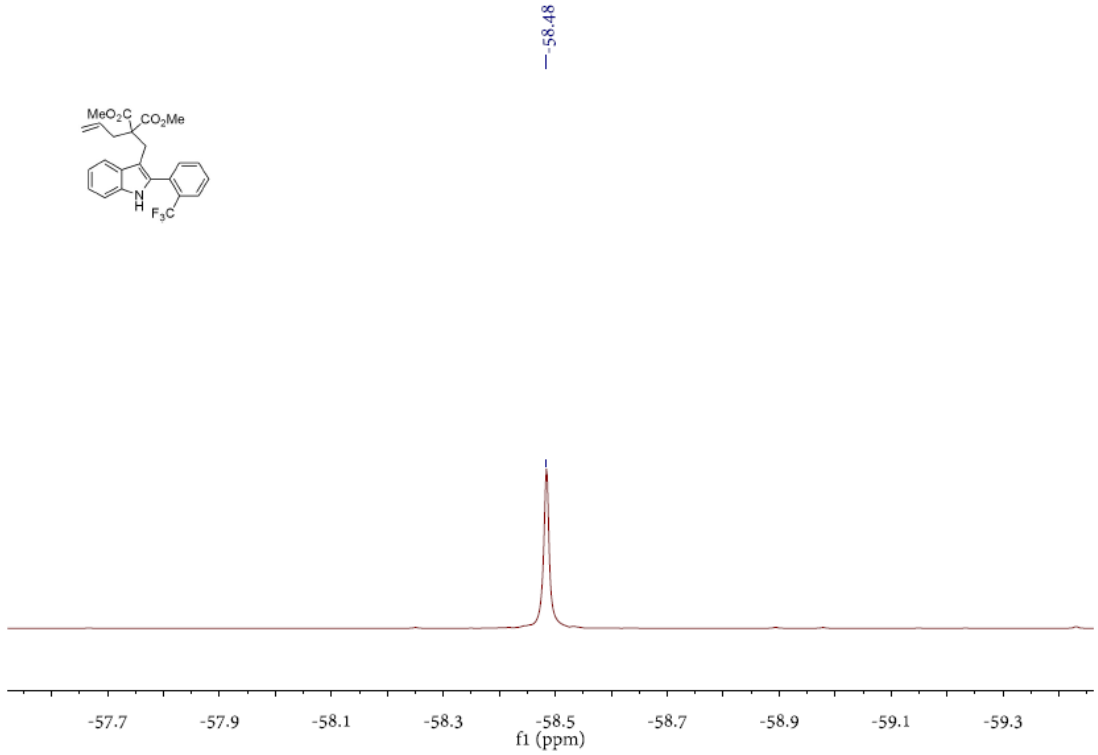
^{1}H NMR Spectrum of **1n**



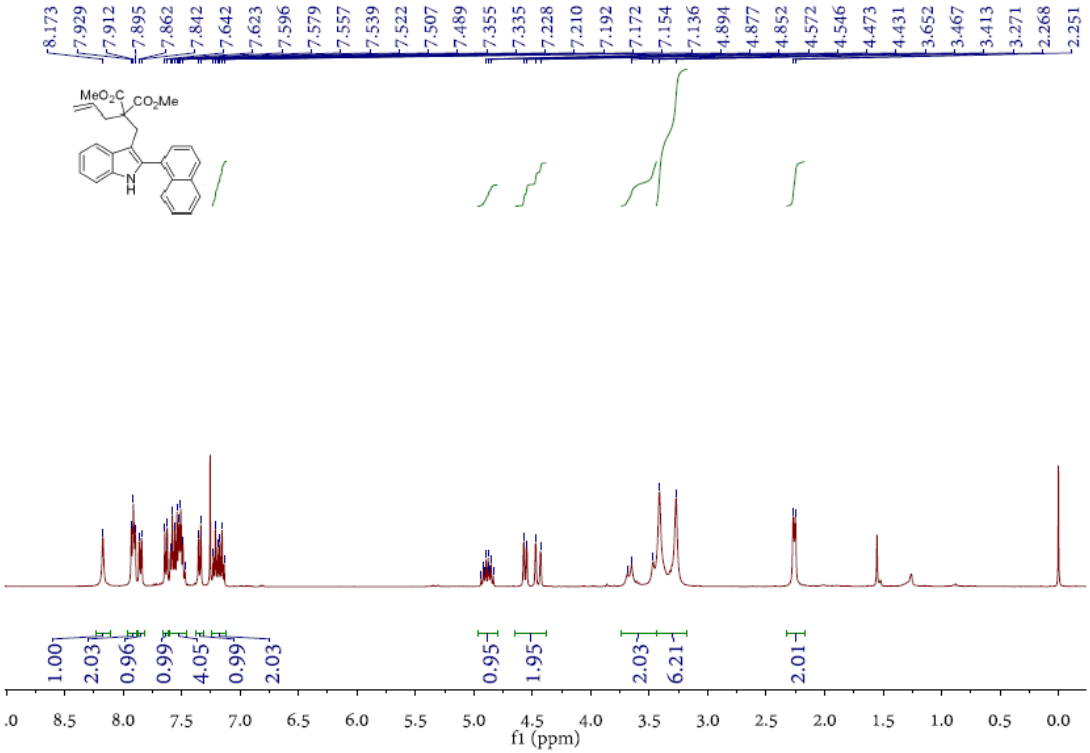
^{13}C NMR Spectrum of **1n**



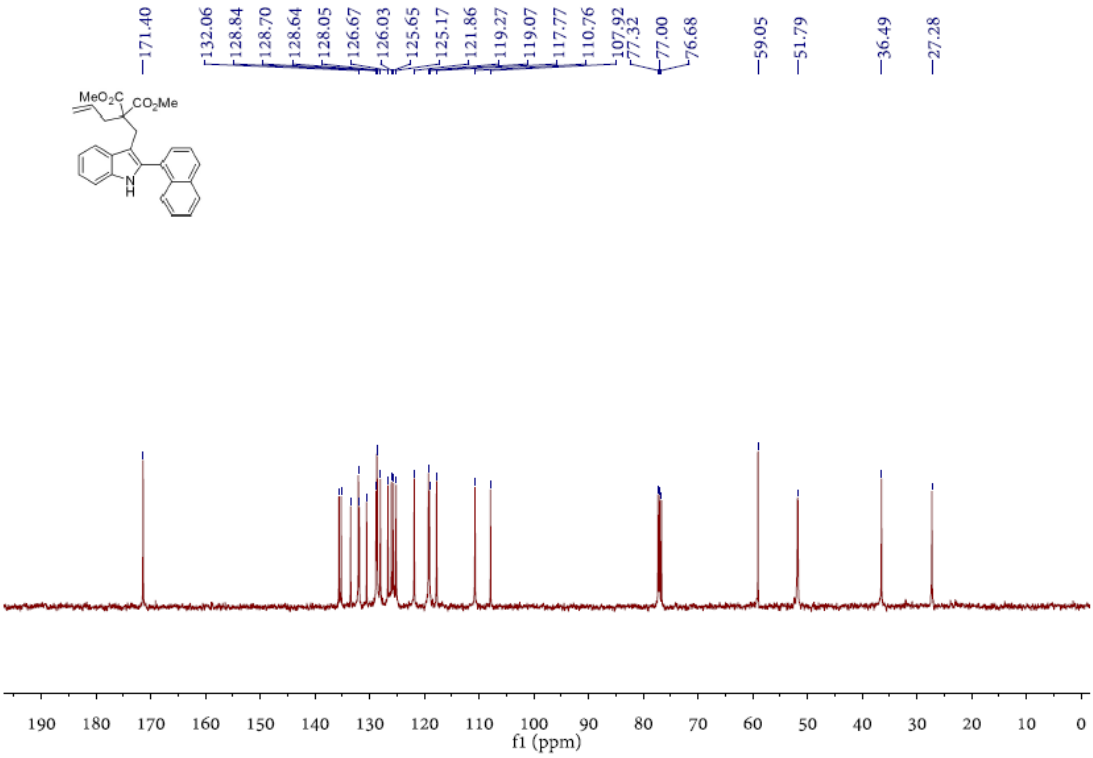
^{19}F NMR Spectrum of **1n**



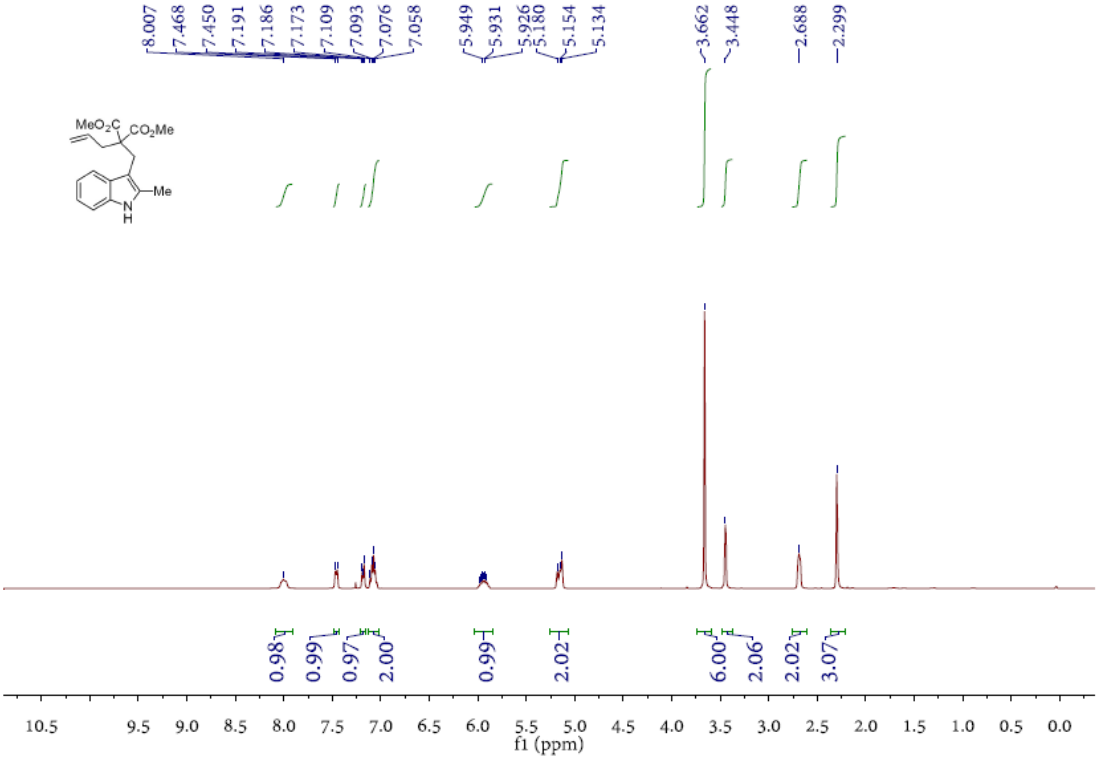
^{1}H NMR Spectrum of **1o**



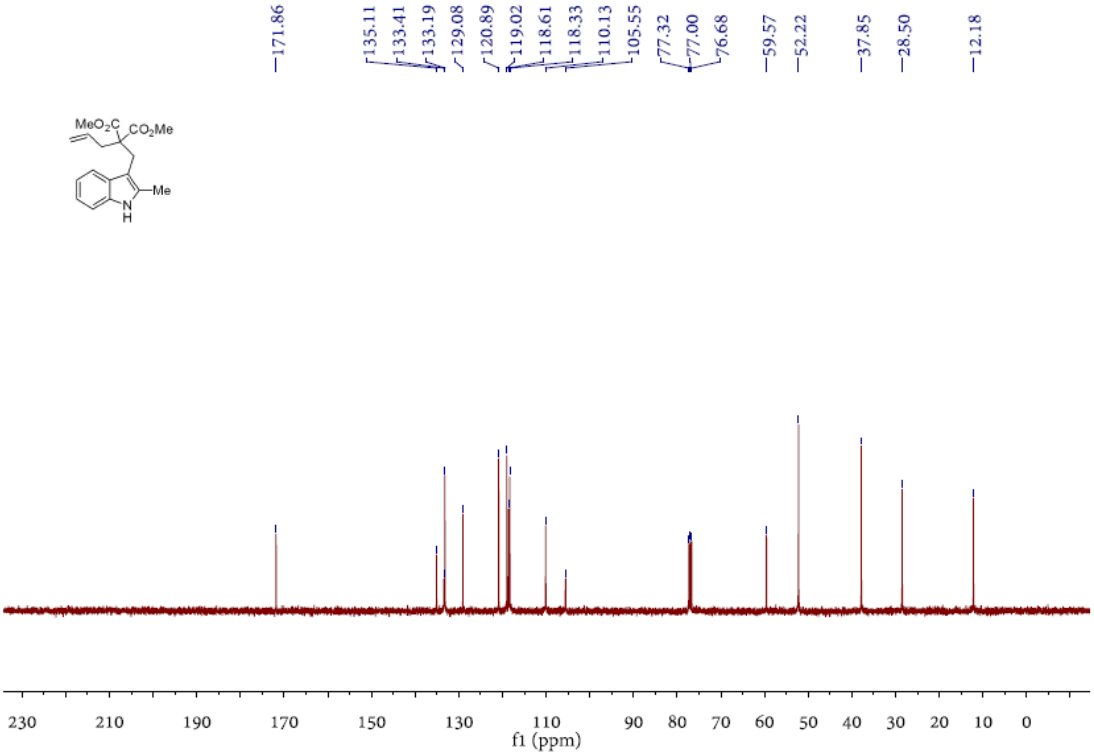
^{13}C NMR Spectrum of **1o**



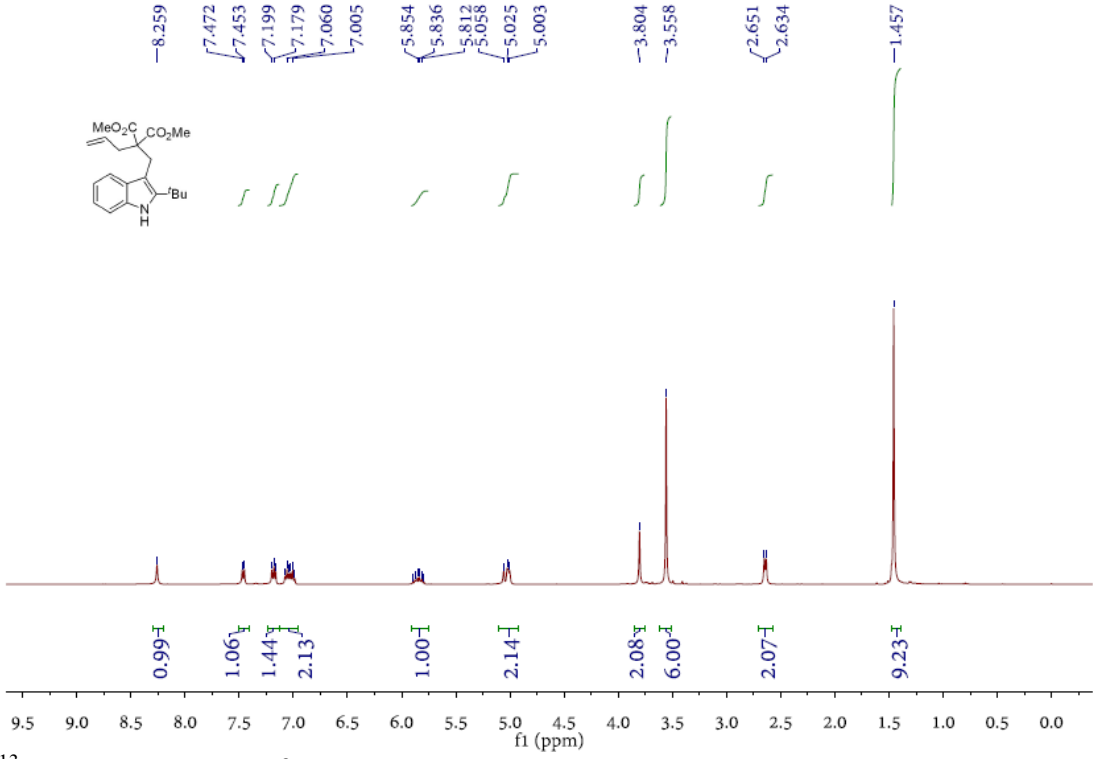
^{1}H NMR Spectrum of **1p**



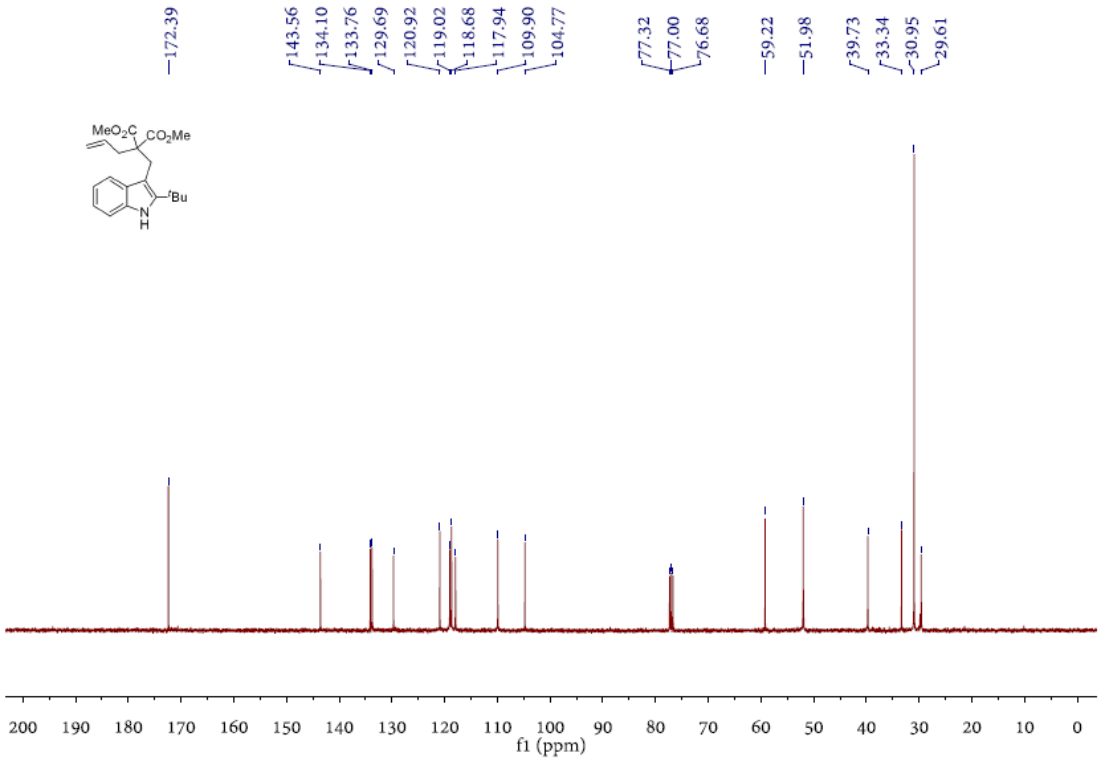
^{13}C NMR Spectrum of **1p**



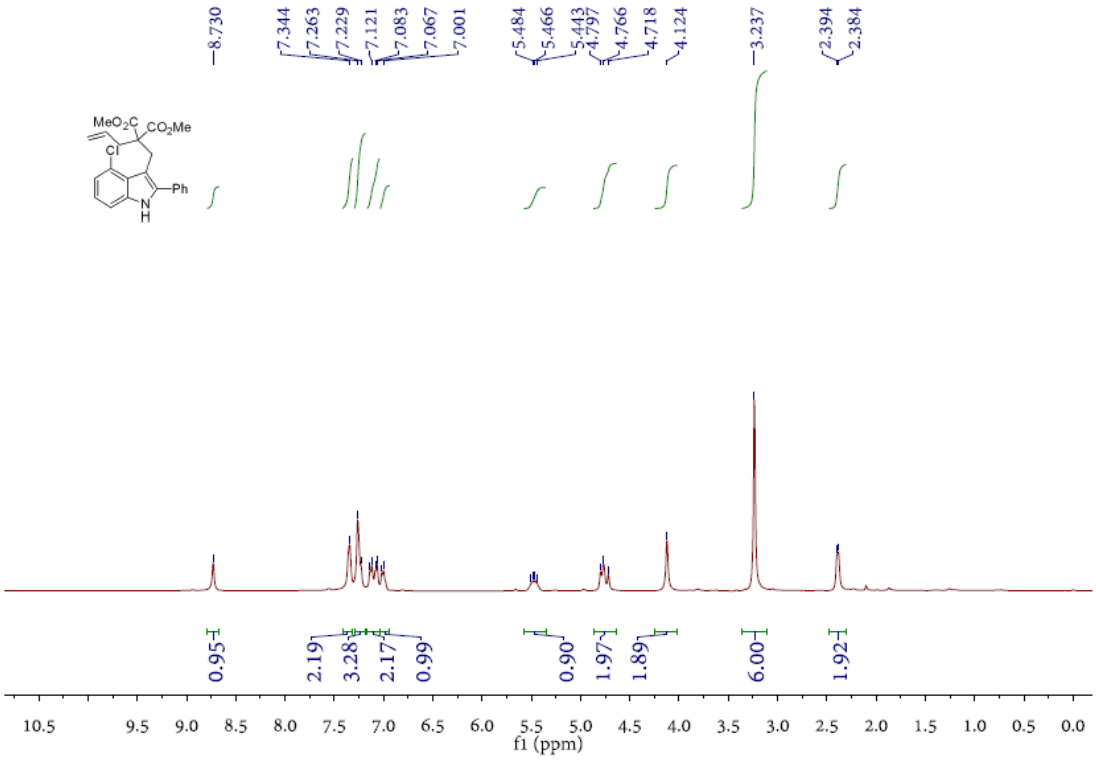
^{1}H NMR Spectrum of **1q**



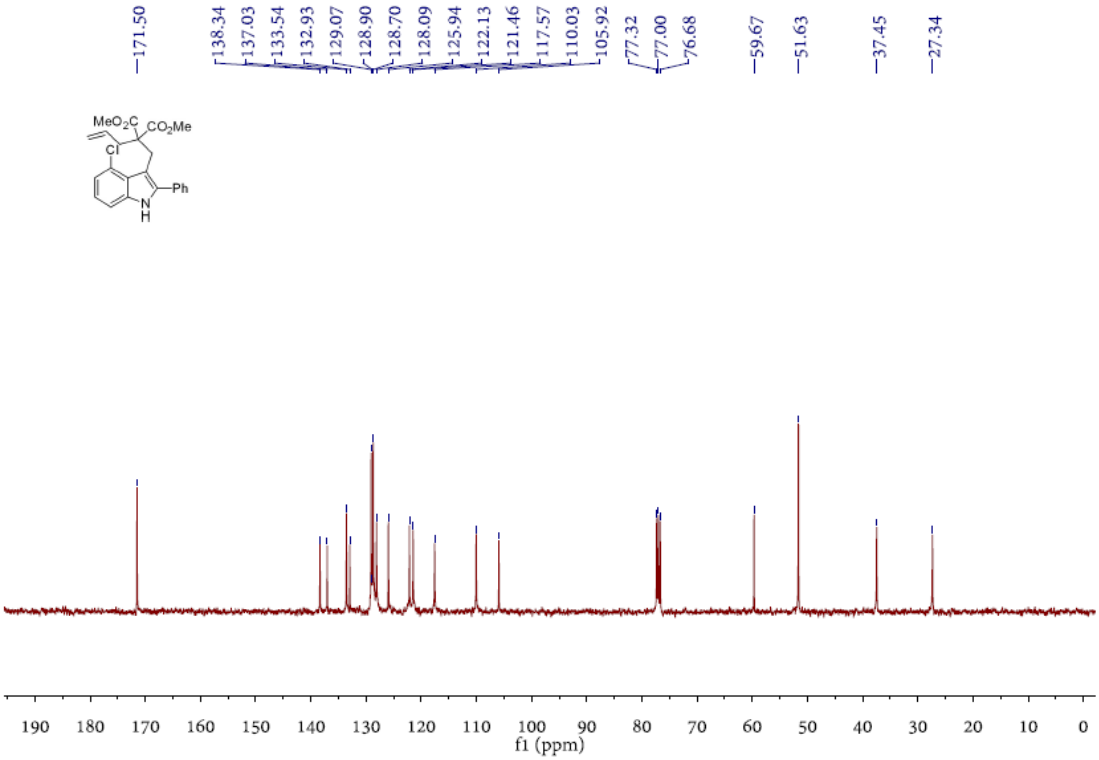
^{13}C NMR Spectrum of **1q**



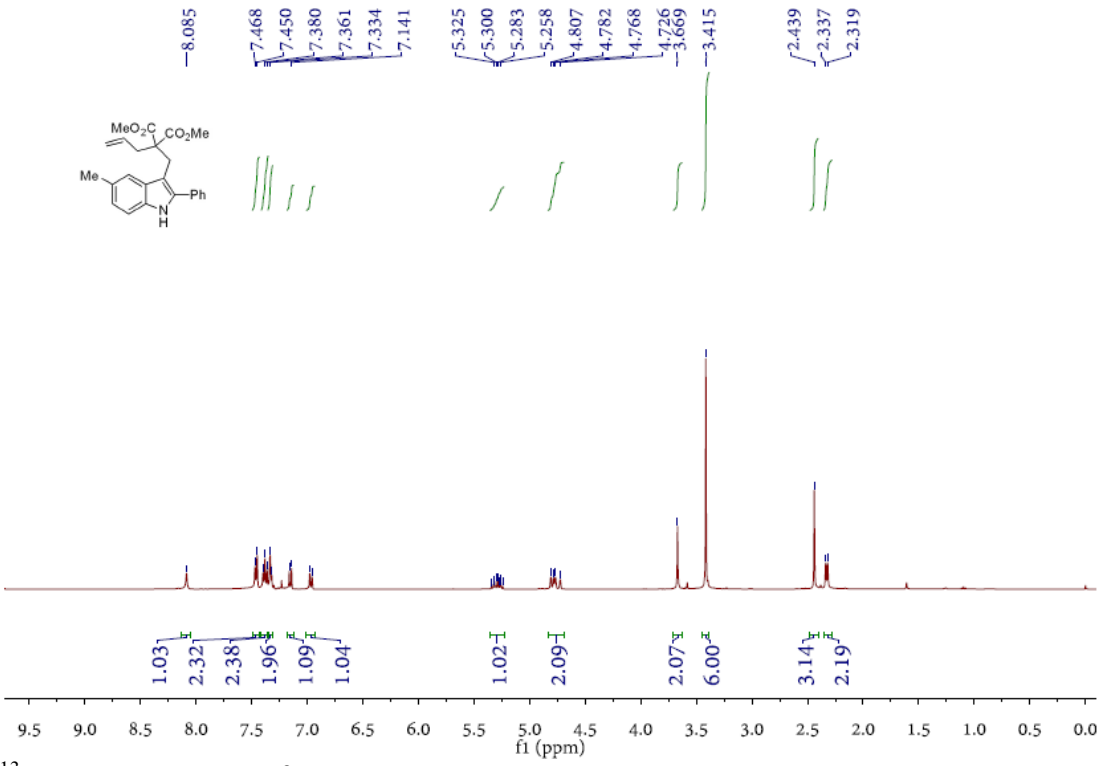
^{1}H NMR Spectrum of **1r**



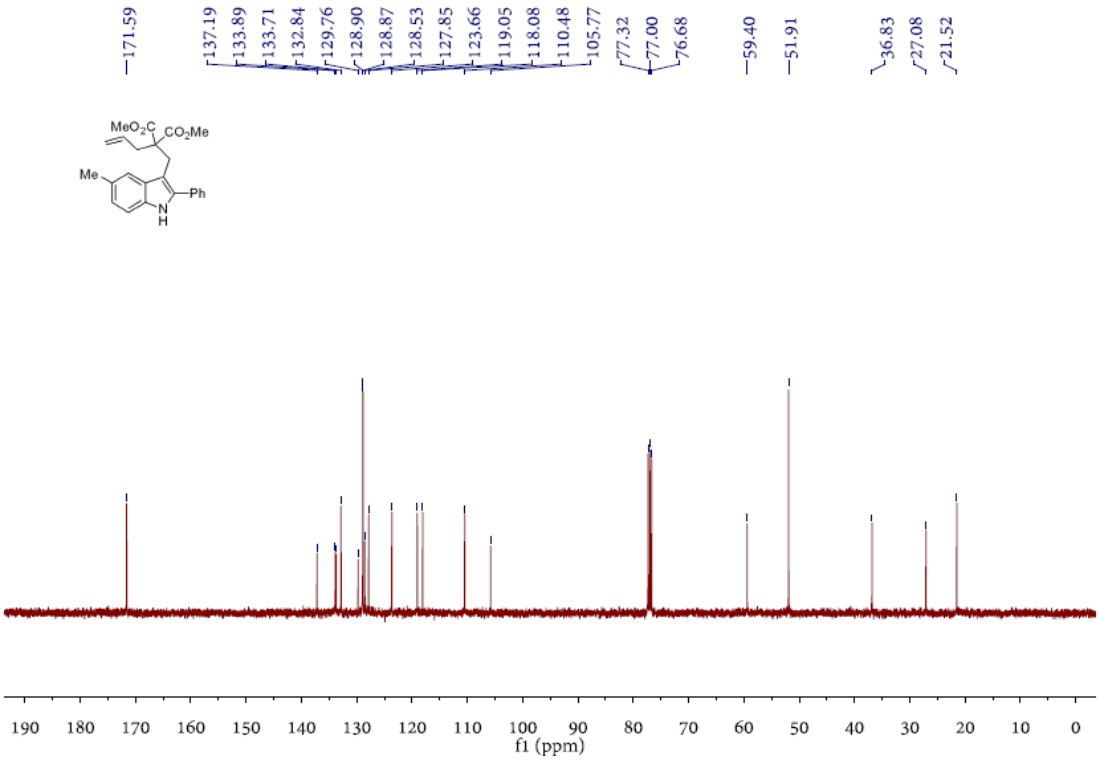
^{13}C NMR Spectrum of **1r**



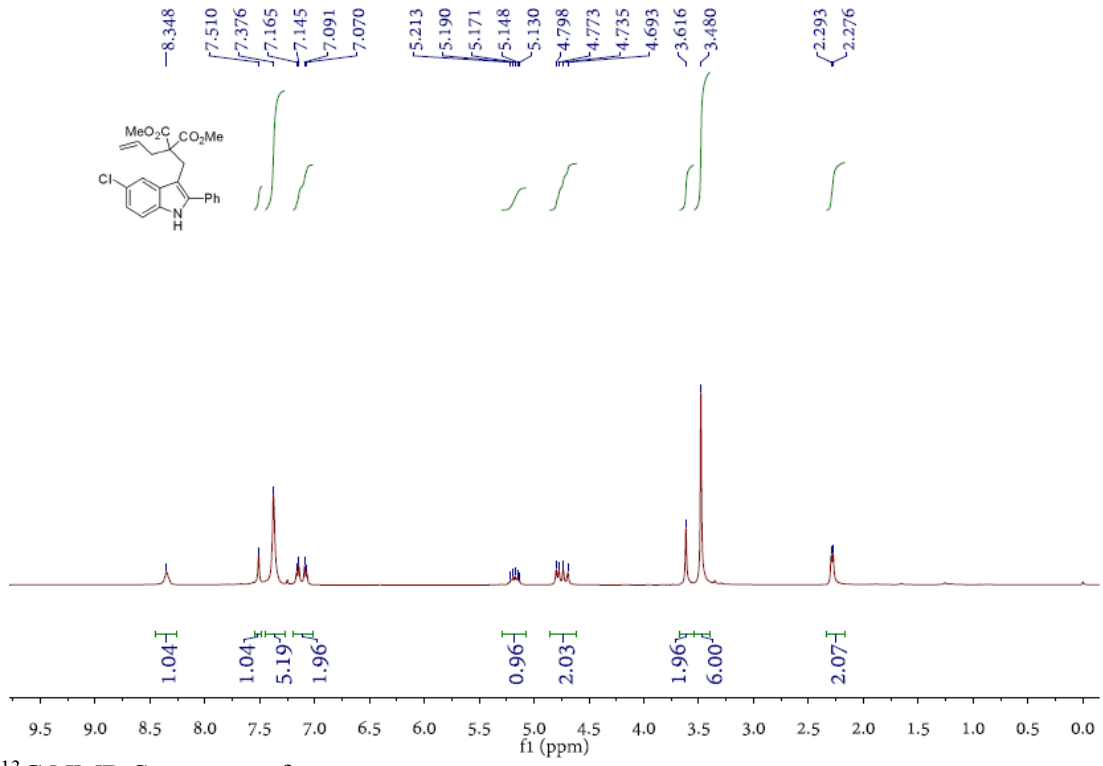
^{1}H NMR Spectrum of **1s**



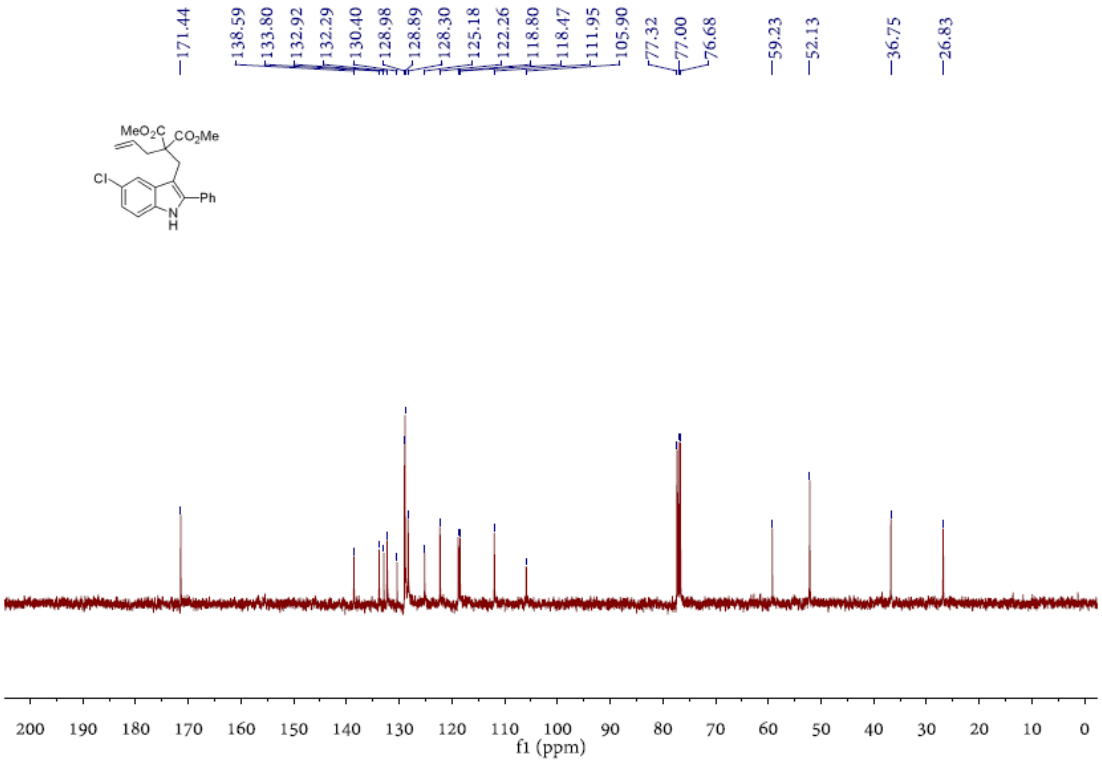
^{13}C NMR Spectrum of **1s**



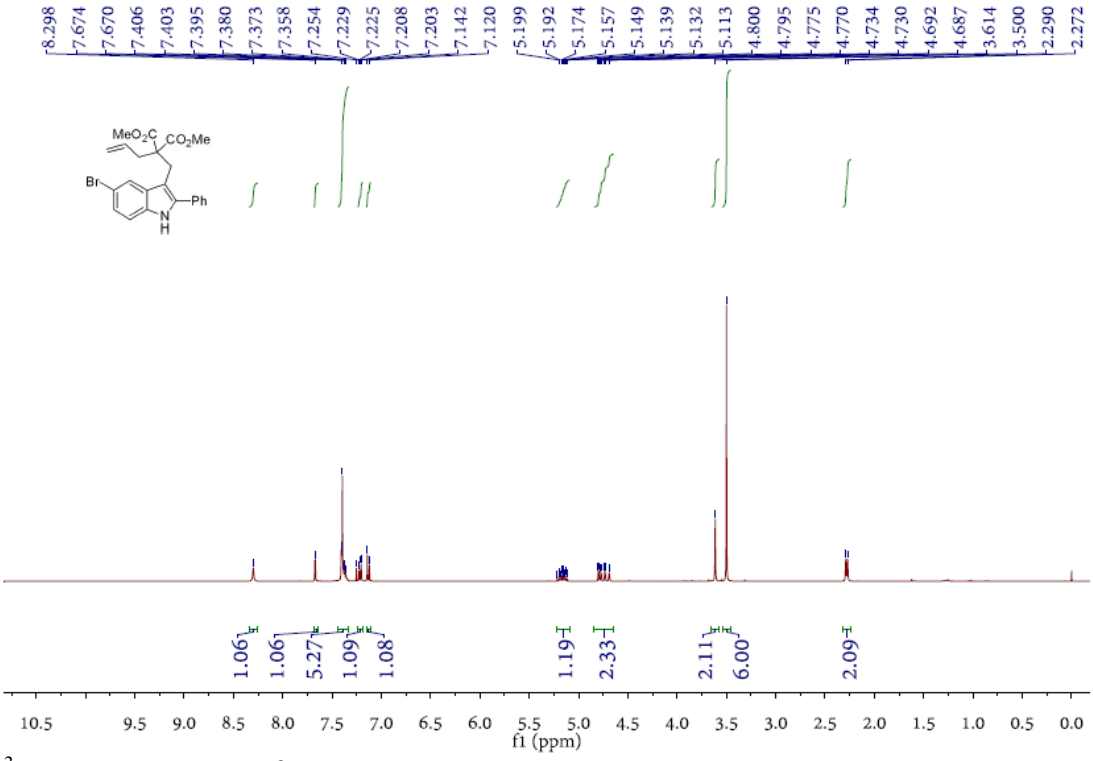
^{1}H NMR Spectrum of **1t**



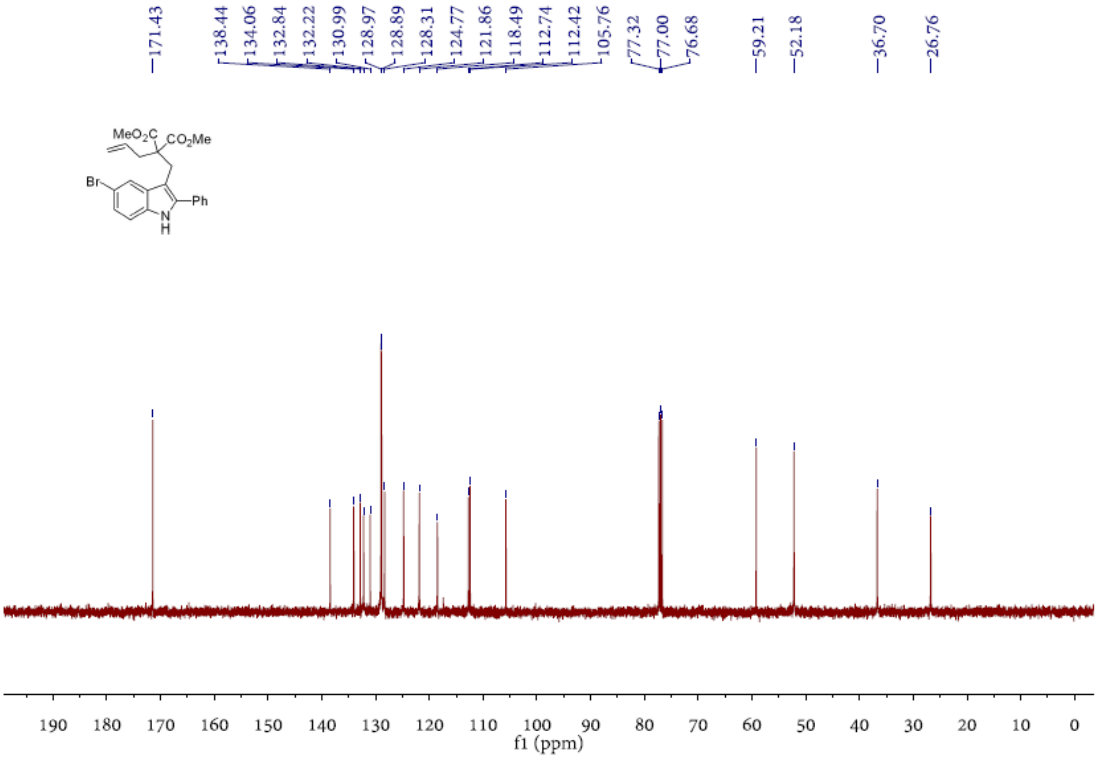
^{13}C NMR Spectrum of **1t**



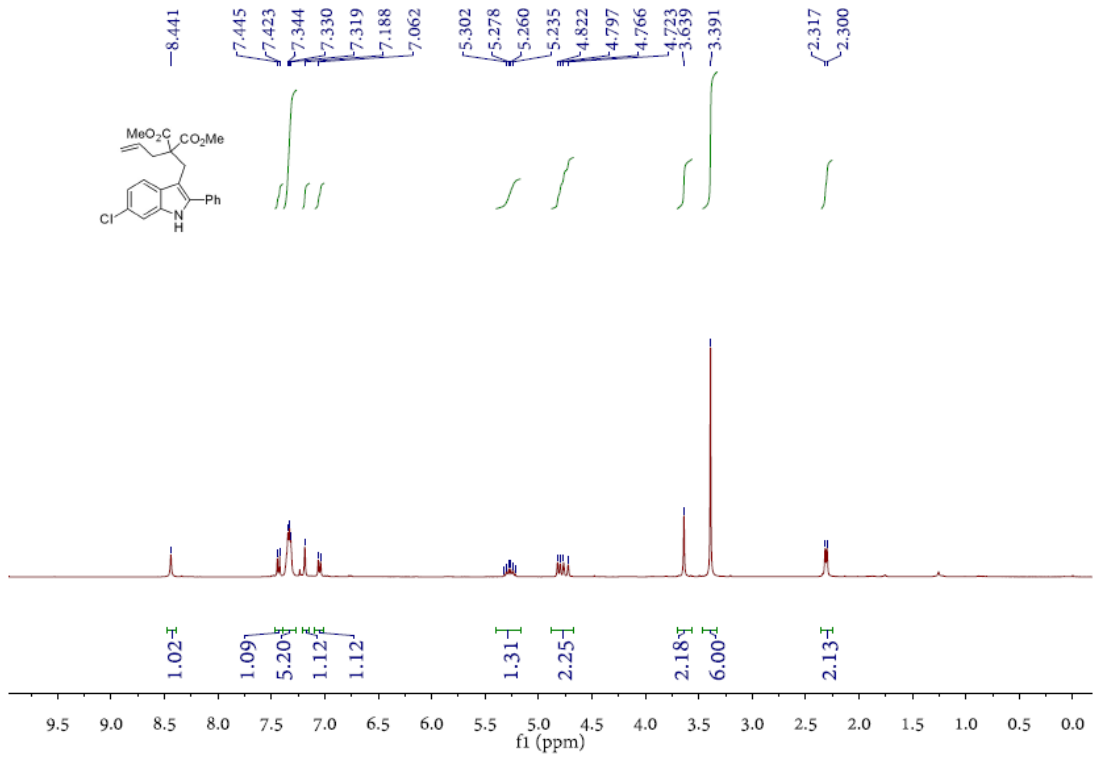
^{1}H NMR Spectrum of **1u**



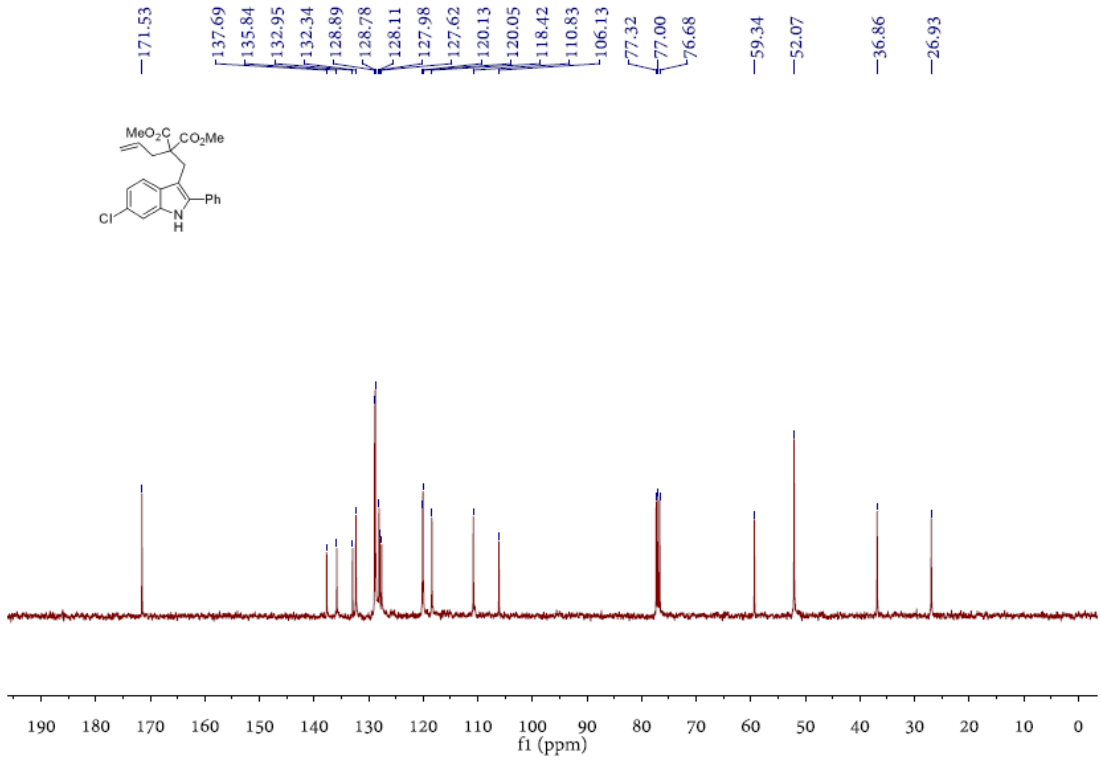
^{13}C NMR Spectrum of **1u**



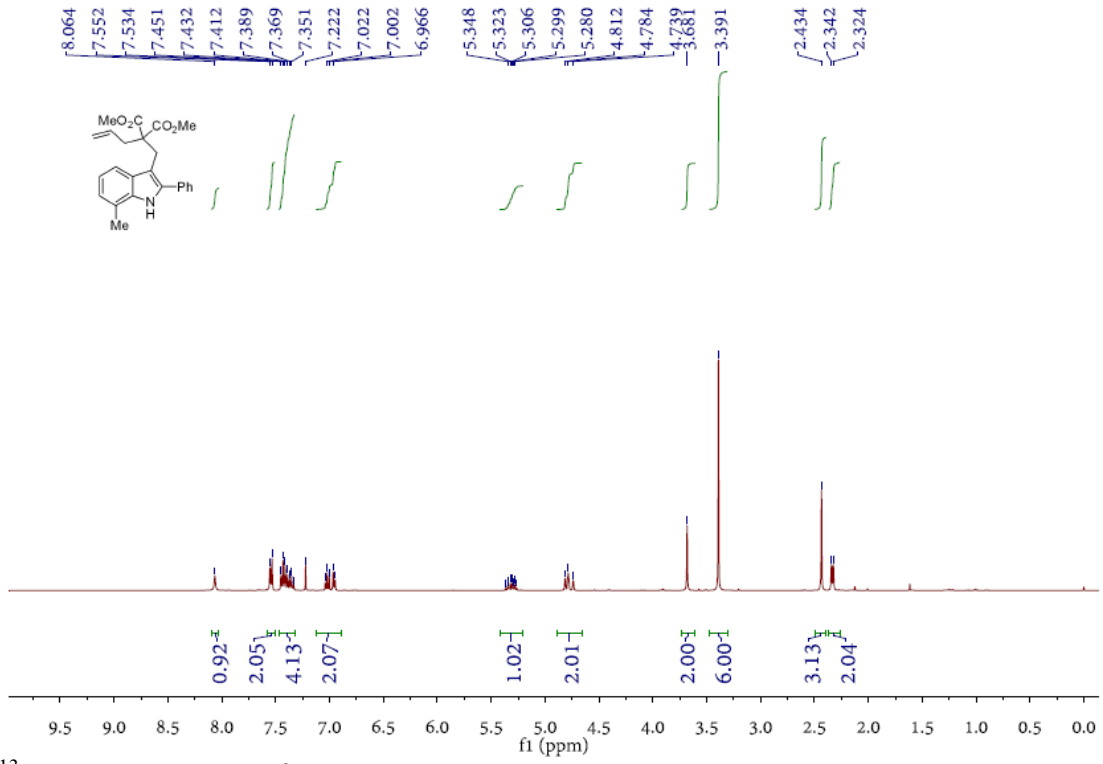
^{1}H NMR Spectrum of **1v**



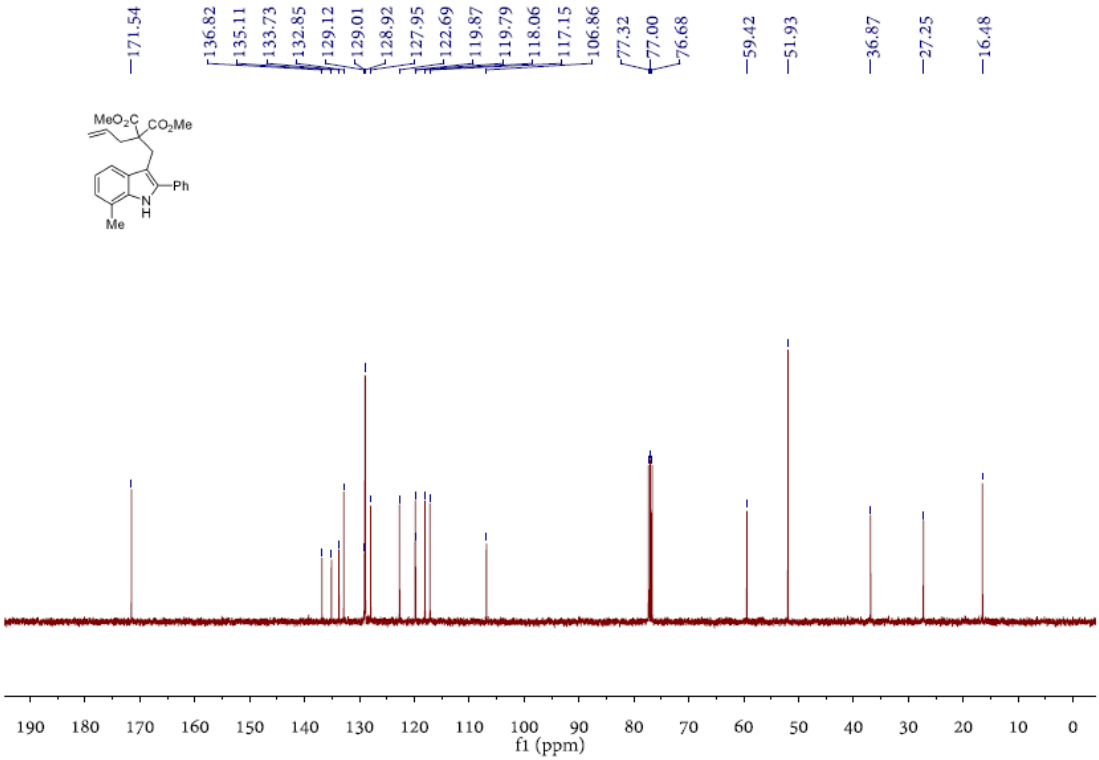
^{13}C NMR Spectrum of **1v**



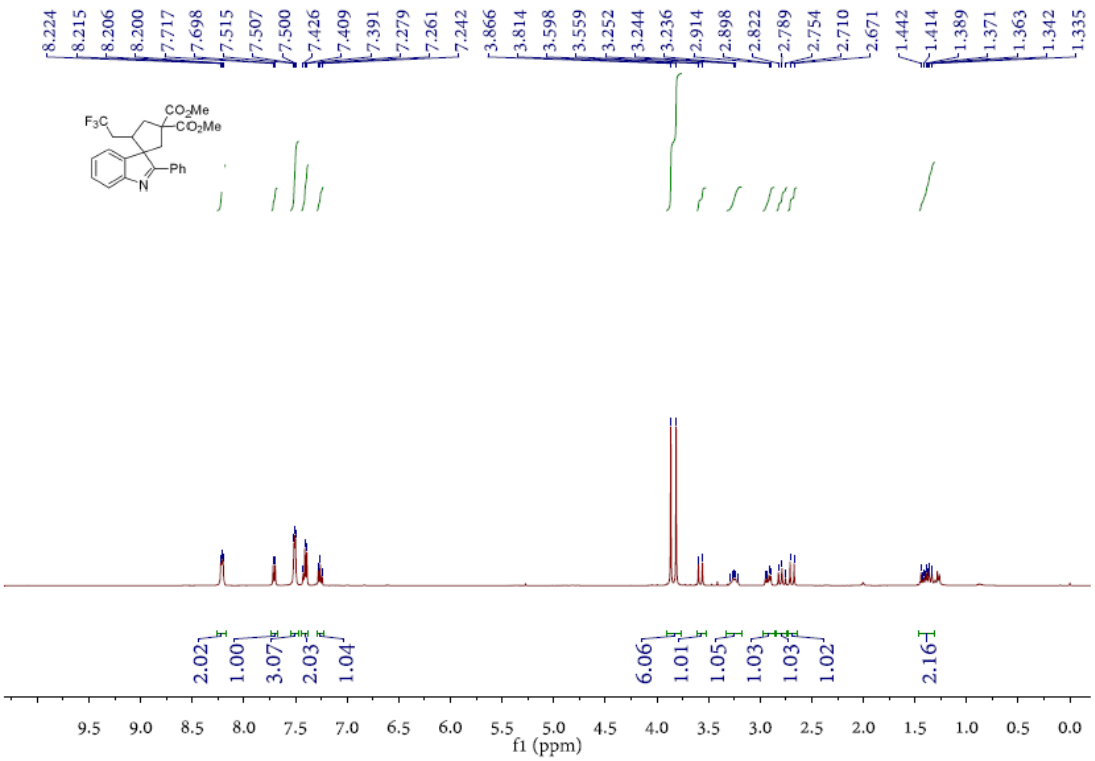
^{1}H NMR Spectrum of **1w**



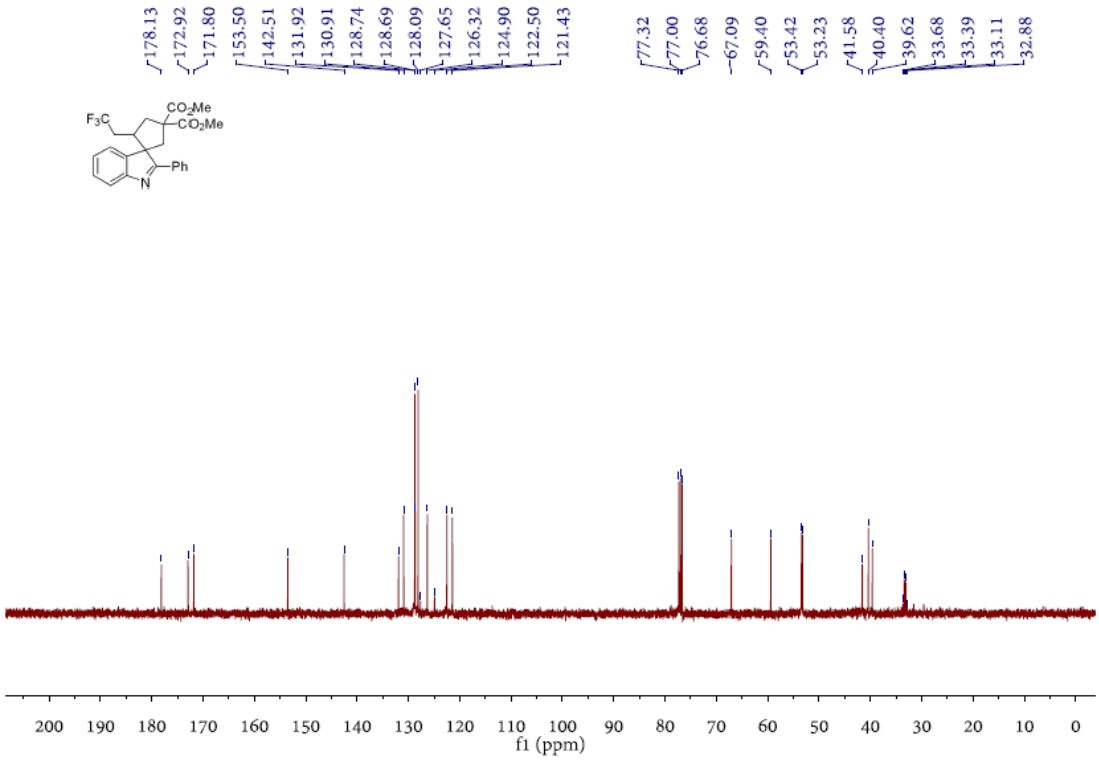
^{13}C NMR Spectrum of **1w**



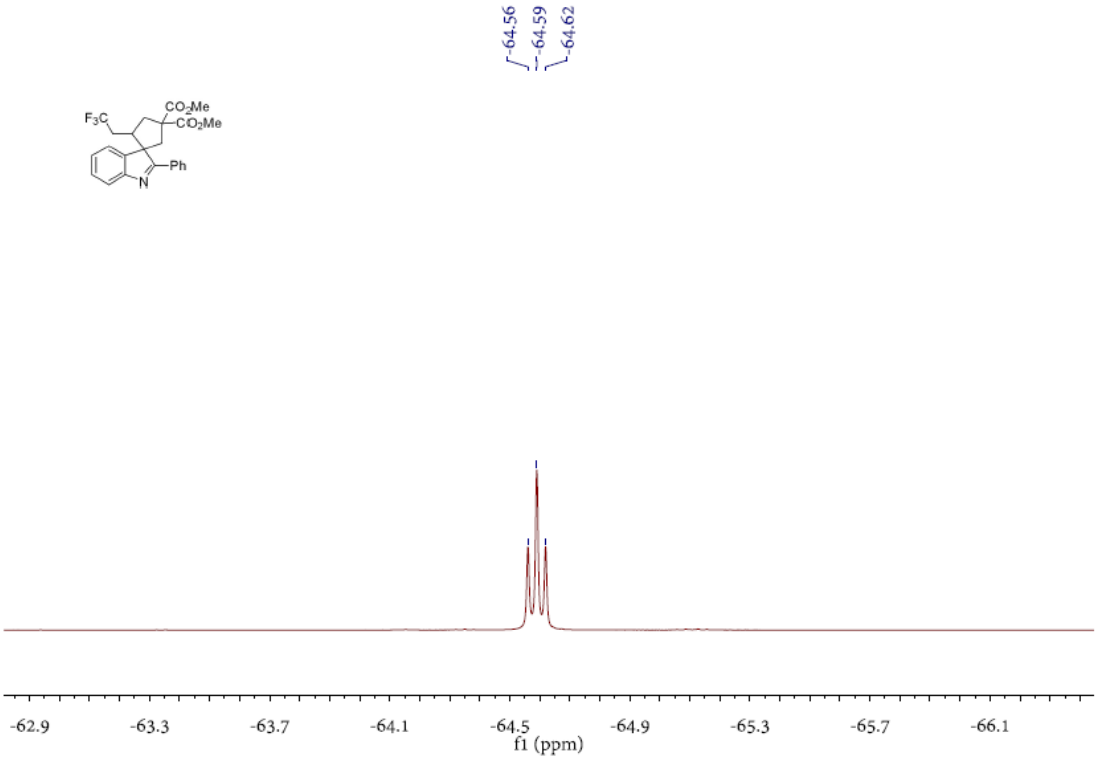
^{1}H NMR Spectrum of **3a (major isomer)**



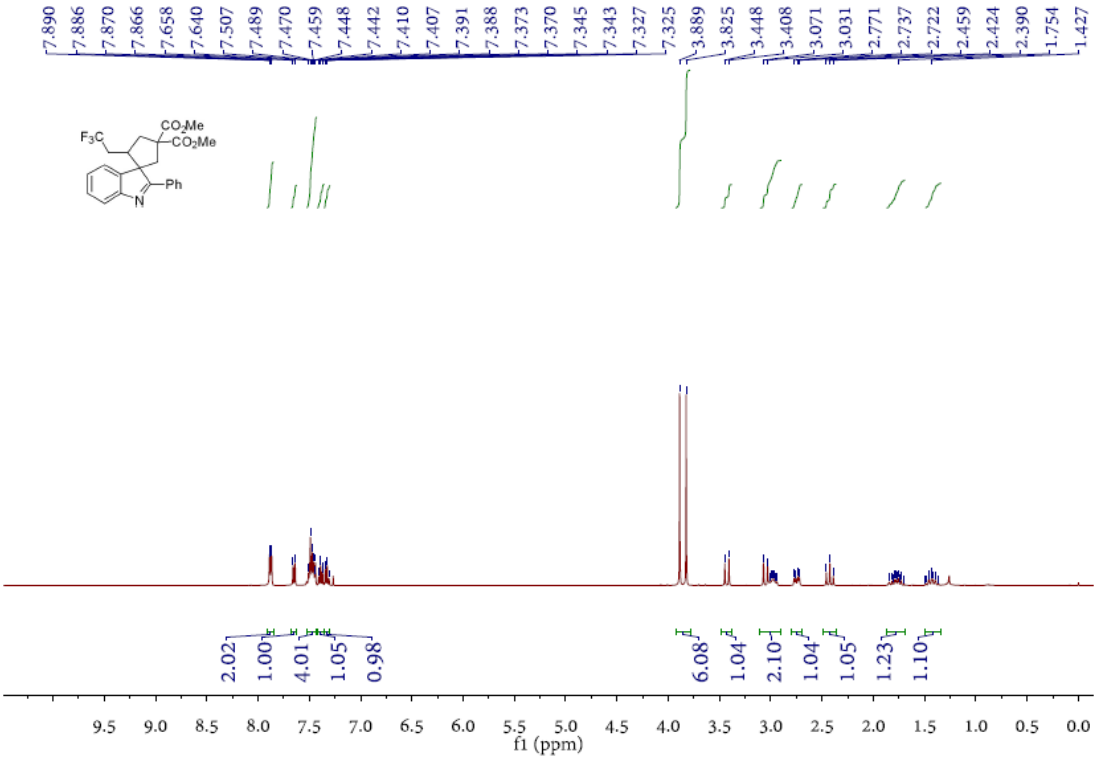
^{13}C NMR Spectrum of **3a (major isomer)**



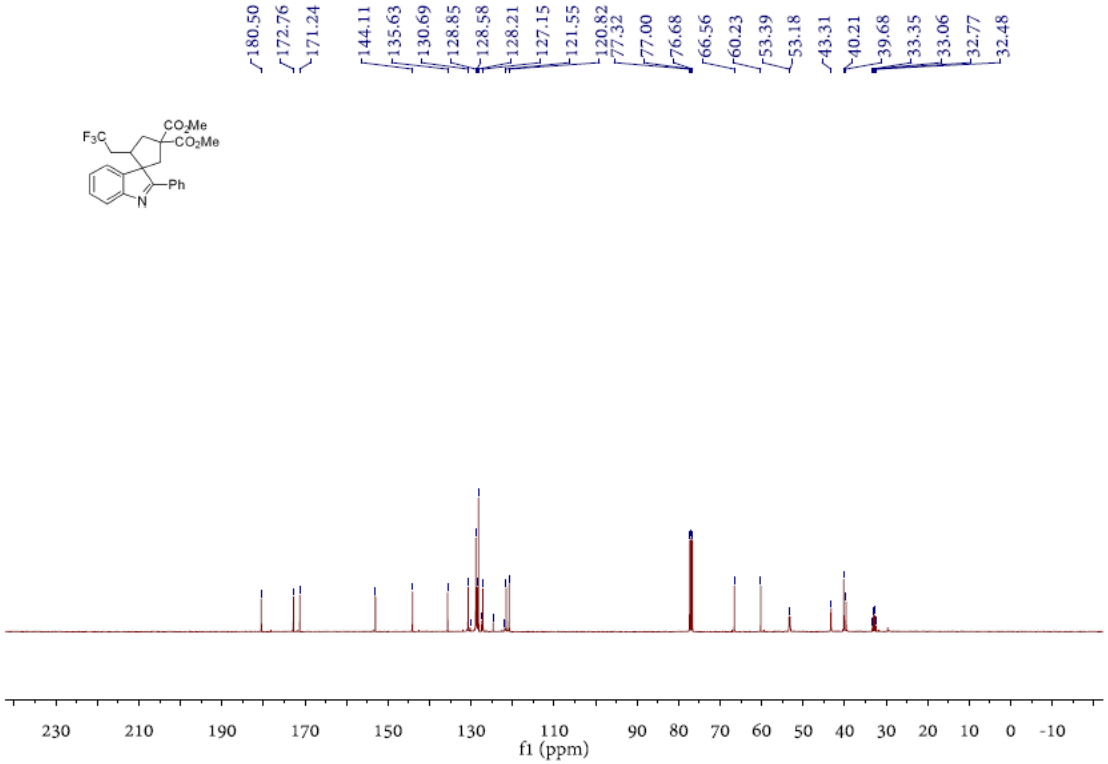
^{19}F NMR Spectrum of **3a (major isomer)**



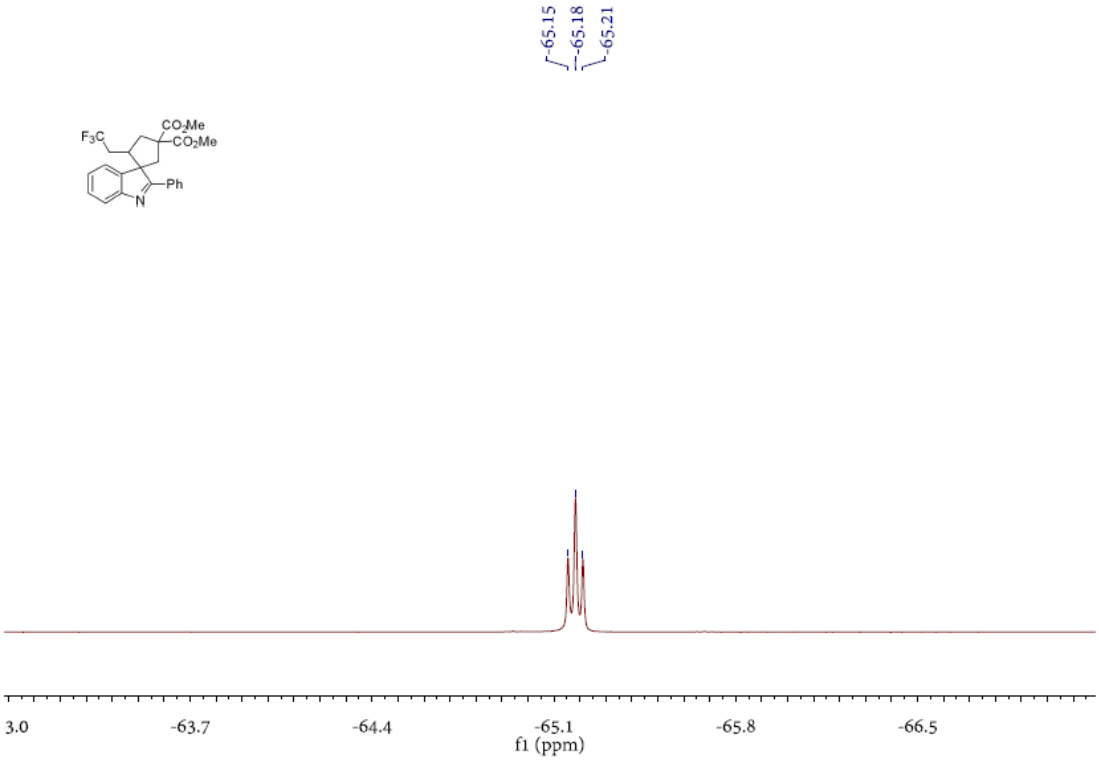
^{1}H NMR Spectrum of **3a (minor isomer)**



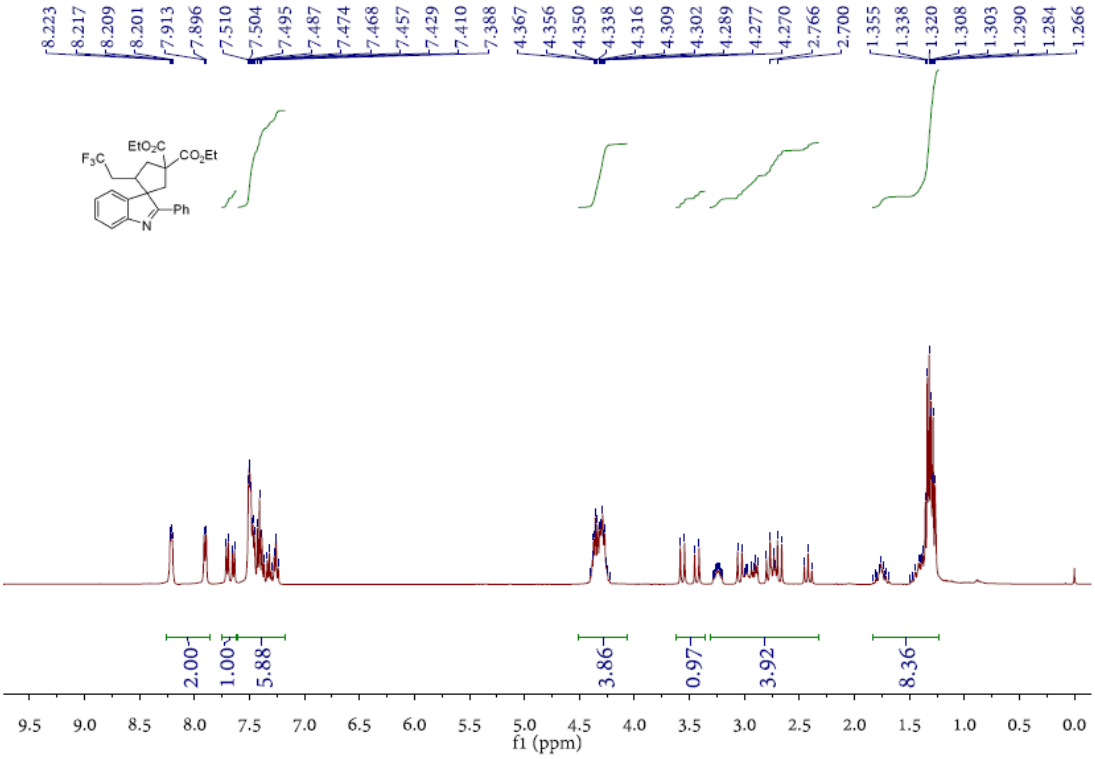
^{13}C NMR Spectrum of **3a (minor isomer)**



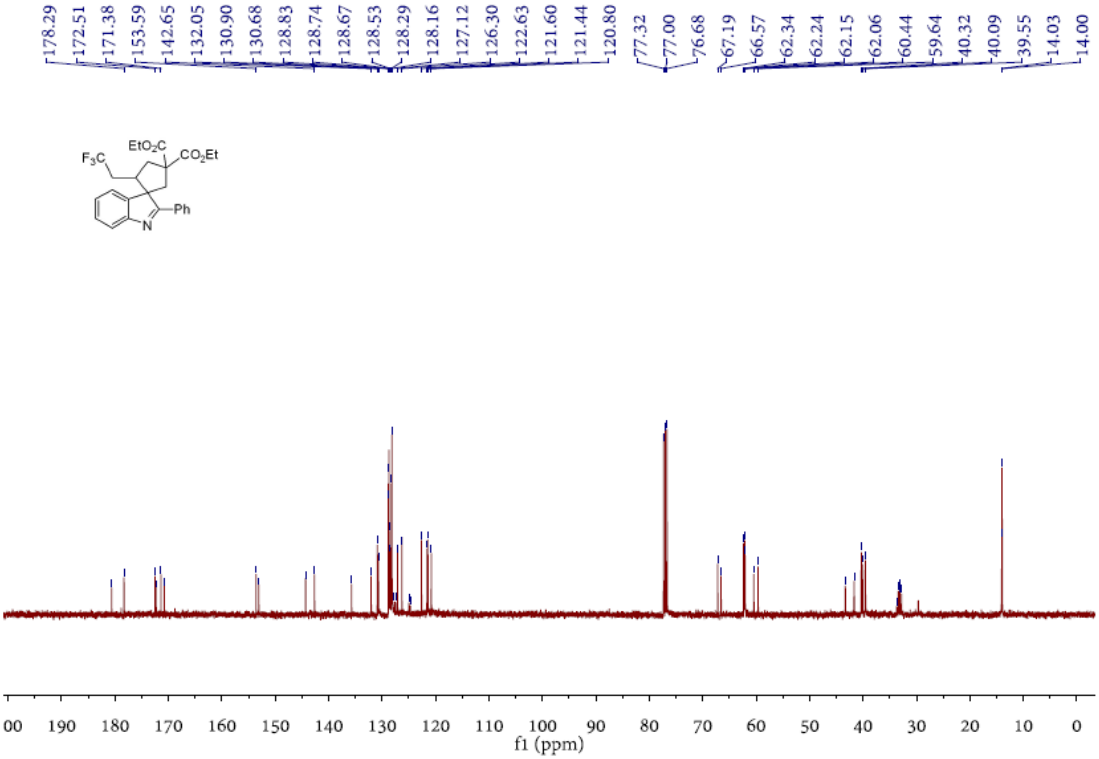
^{19}F NMR Spectrum of **3a (minor isomer)**



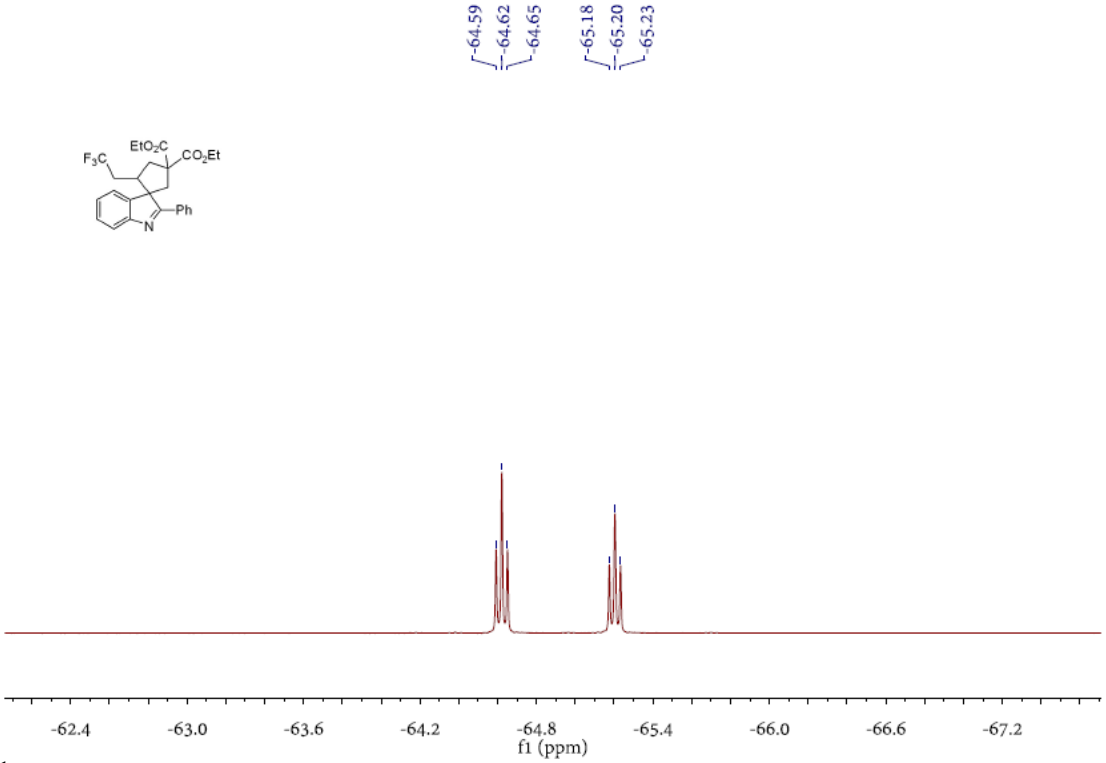
^{1}H NMR Spectrum of **3b**



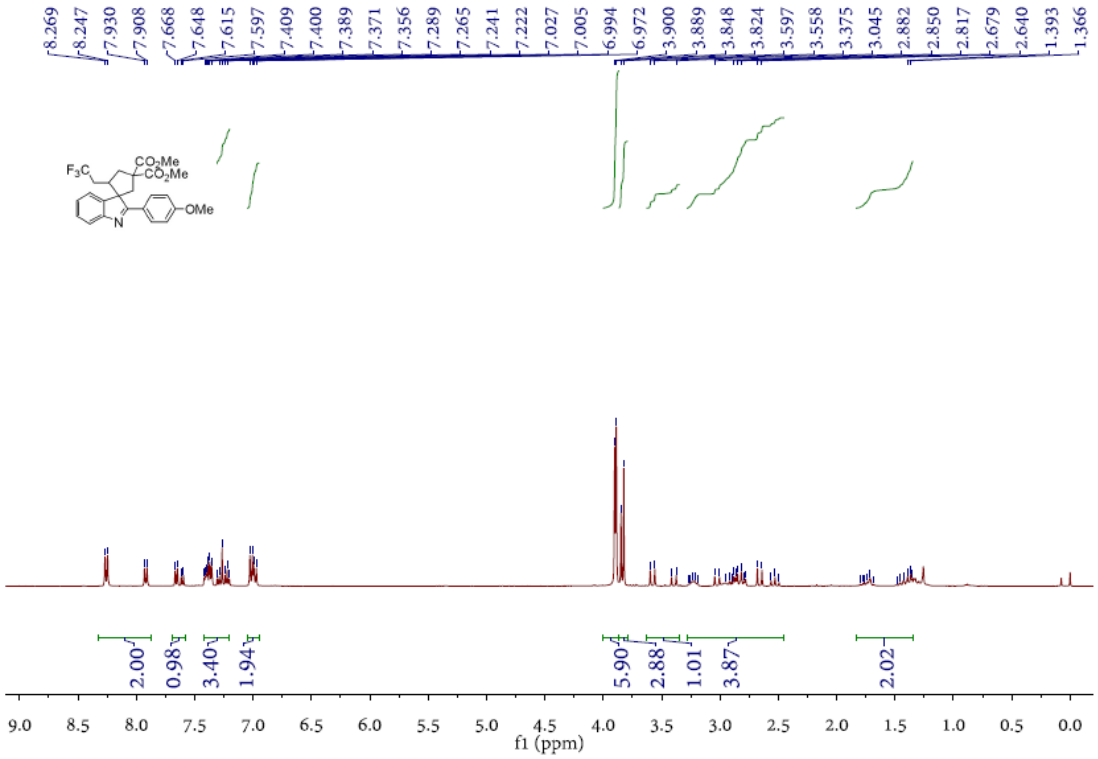
^{13}C NMR Spectrum of **3b**



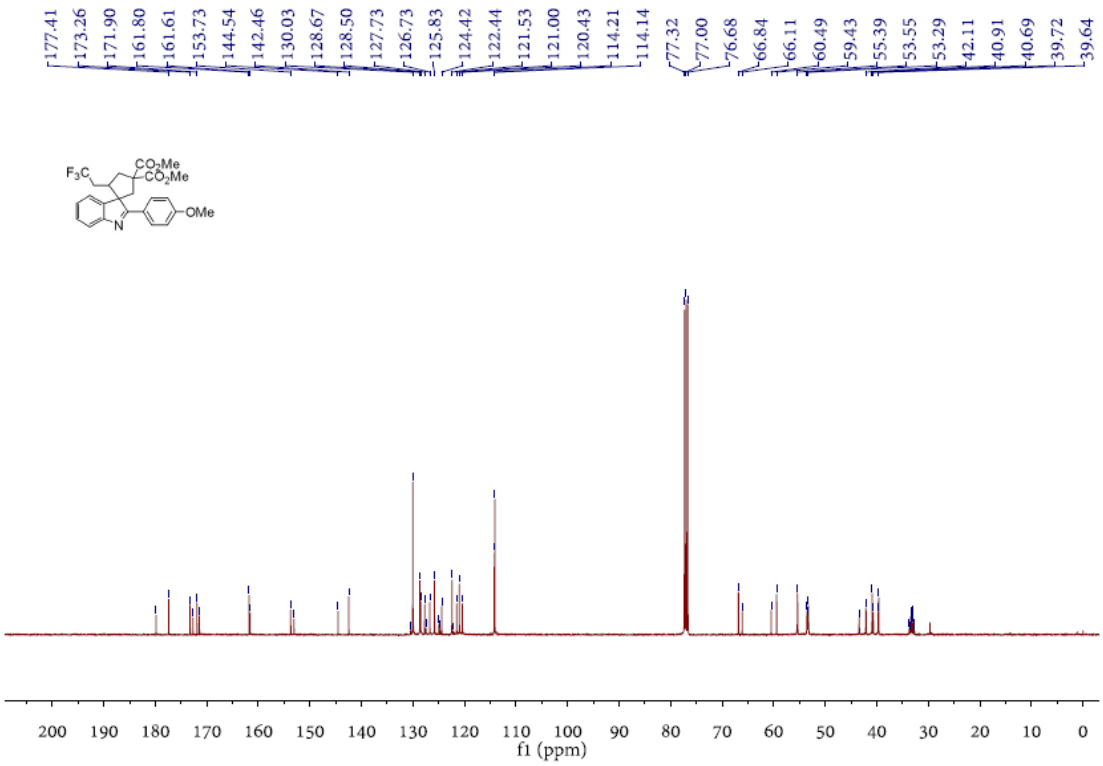
^{19}F NMR Spectrum of **3b**



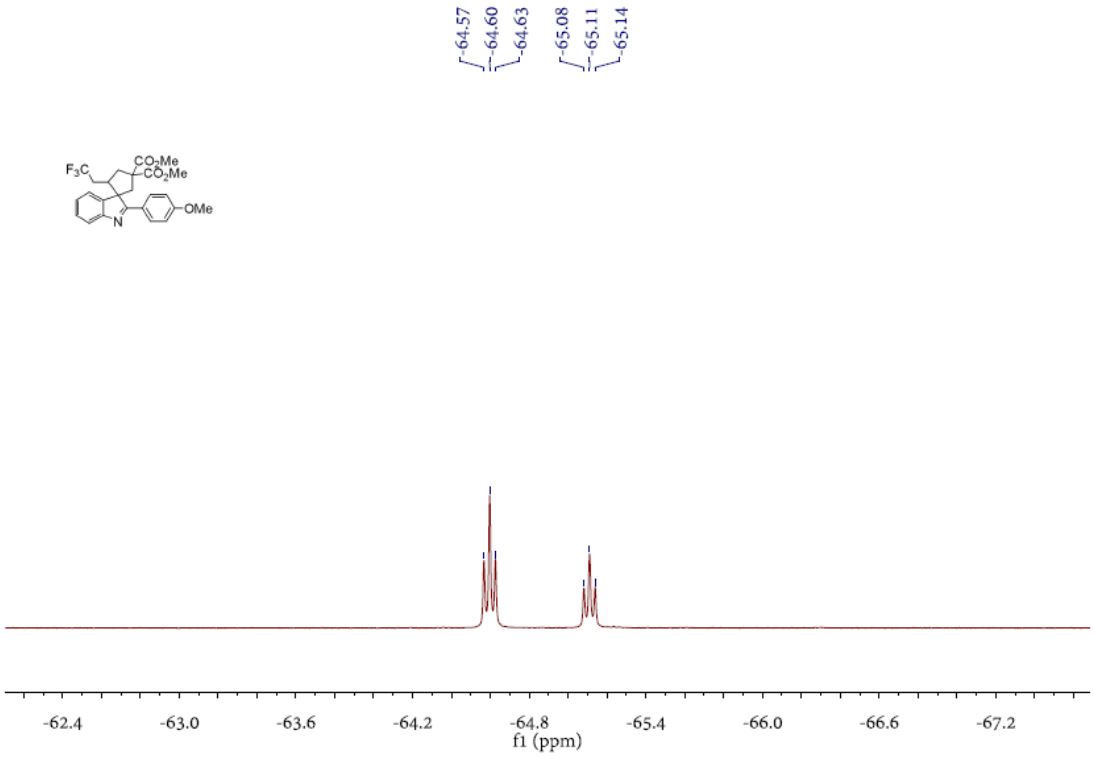
^{1}H NMR Spectrum of **3c**



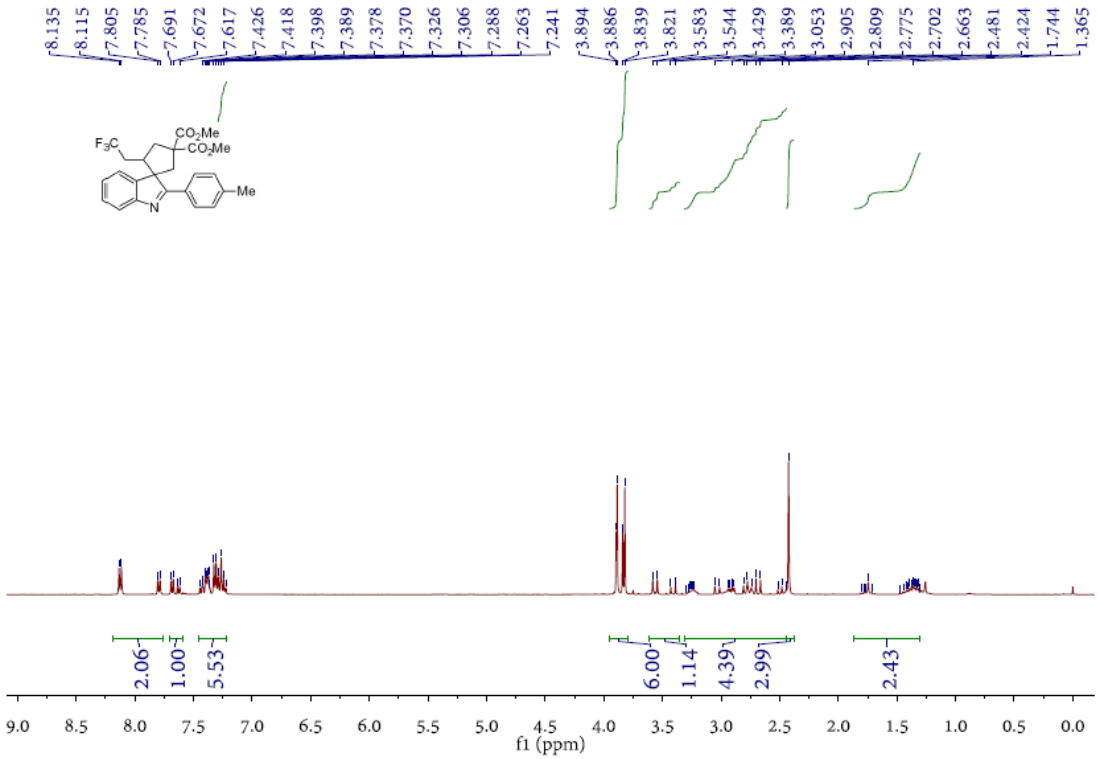
^{13}C NMR Spectrum of **3c**



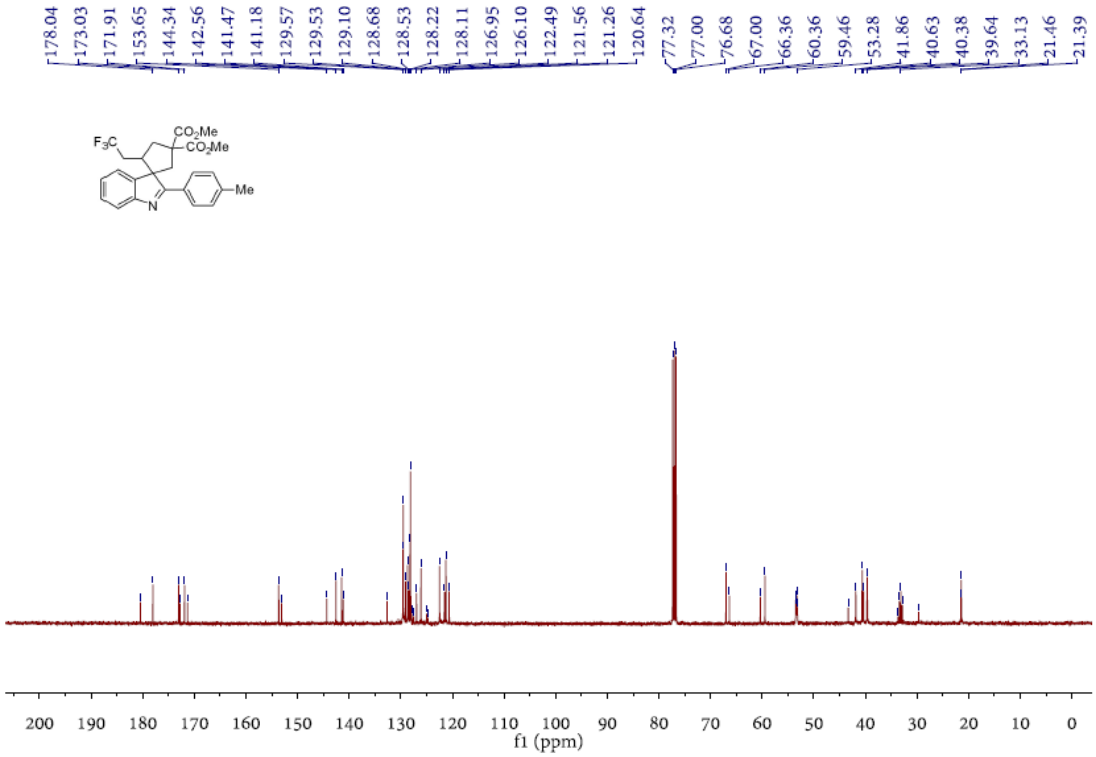
^{19}F NMR Spectrum of **3c**



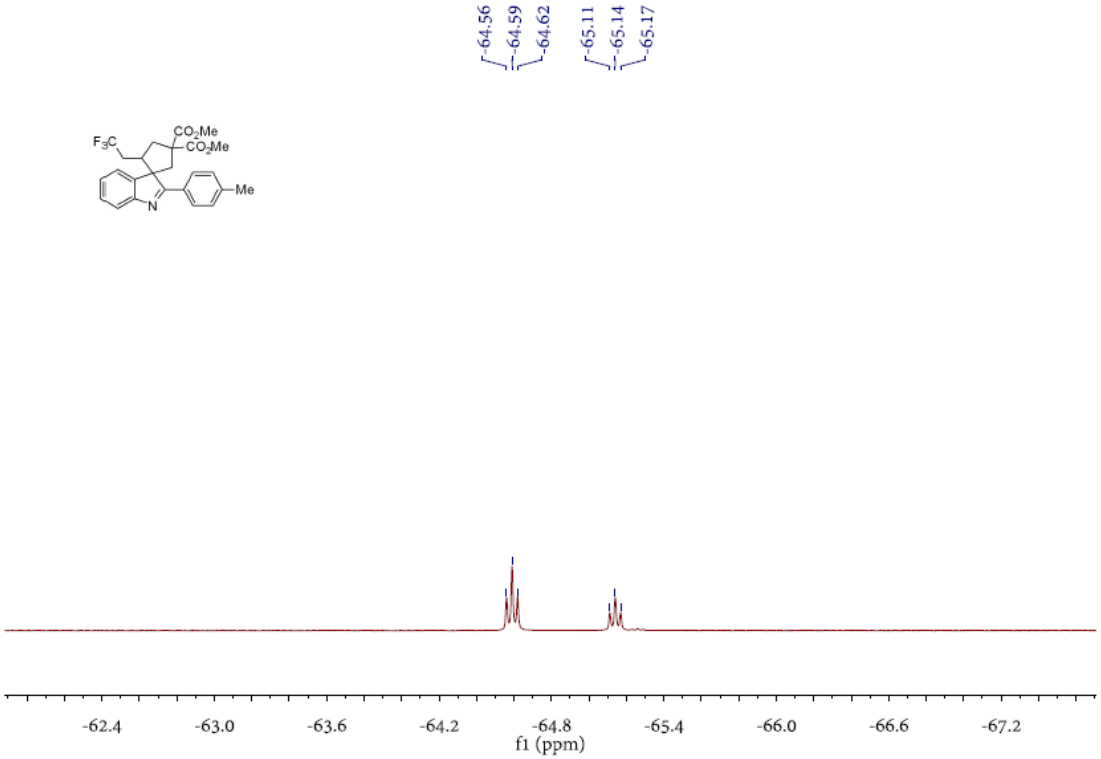
^{1}H NMR Spectrum of **3d**



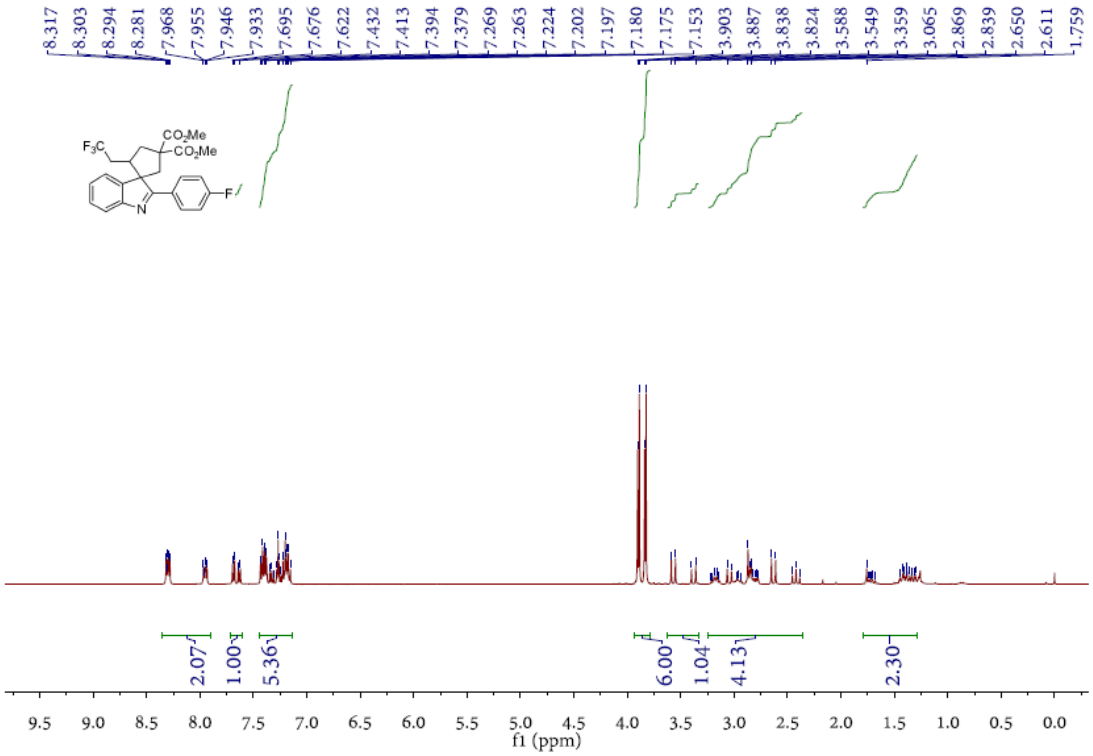
^{13}C NMR Spectrum of **3d**



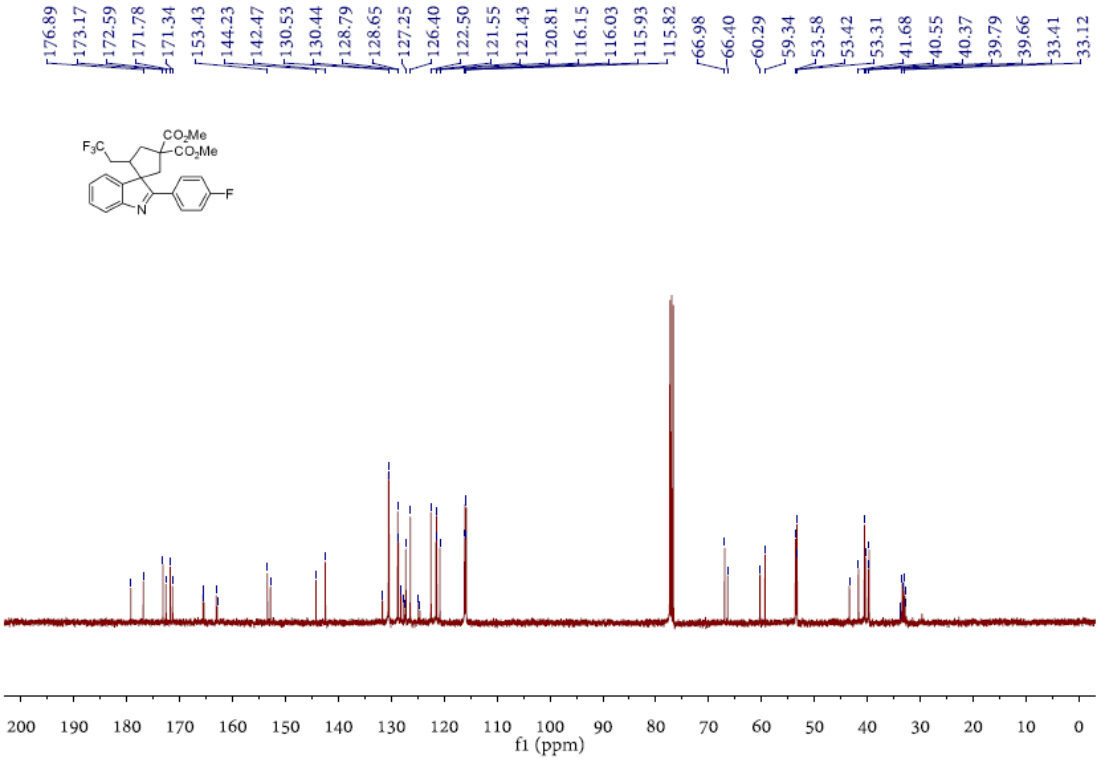
^{19}F NMR Spectrum of **3d**



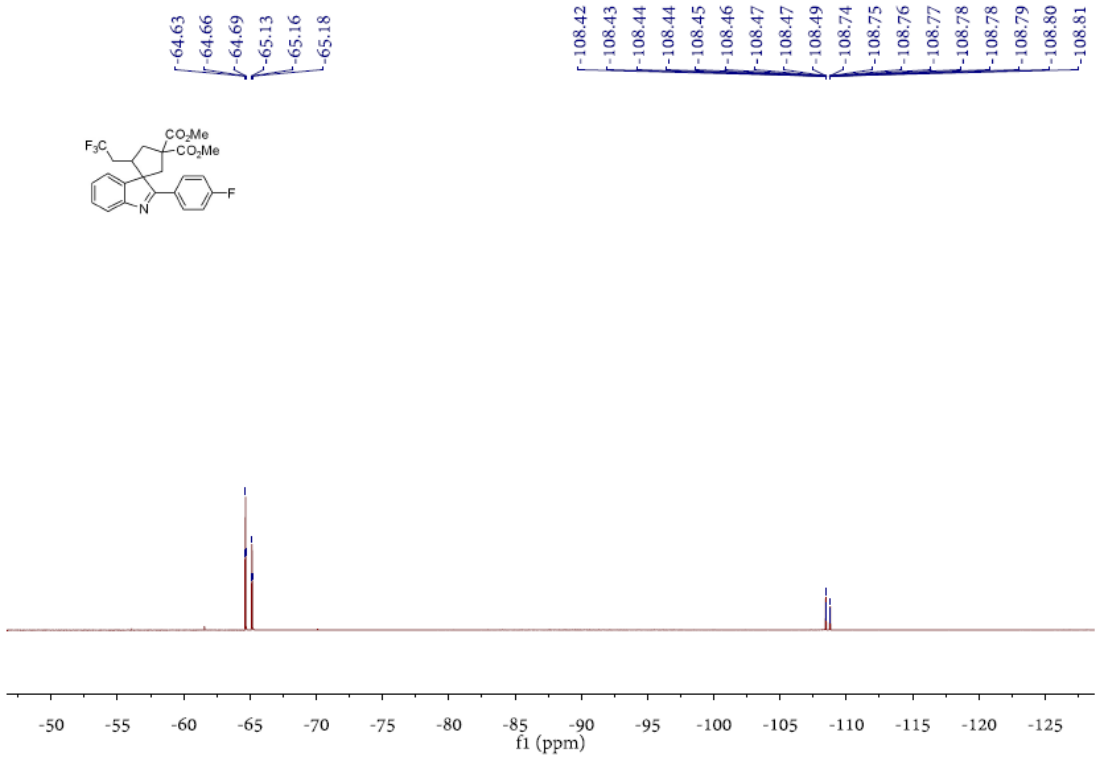
^{1}H NMR Spectrum of **3e**



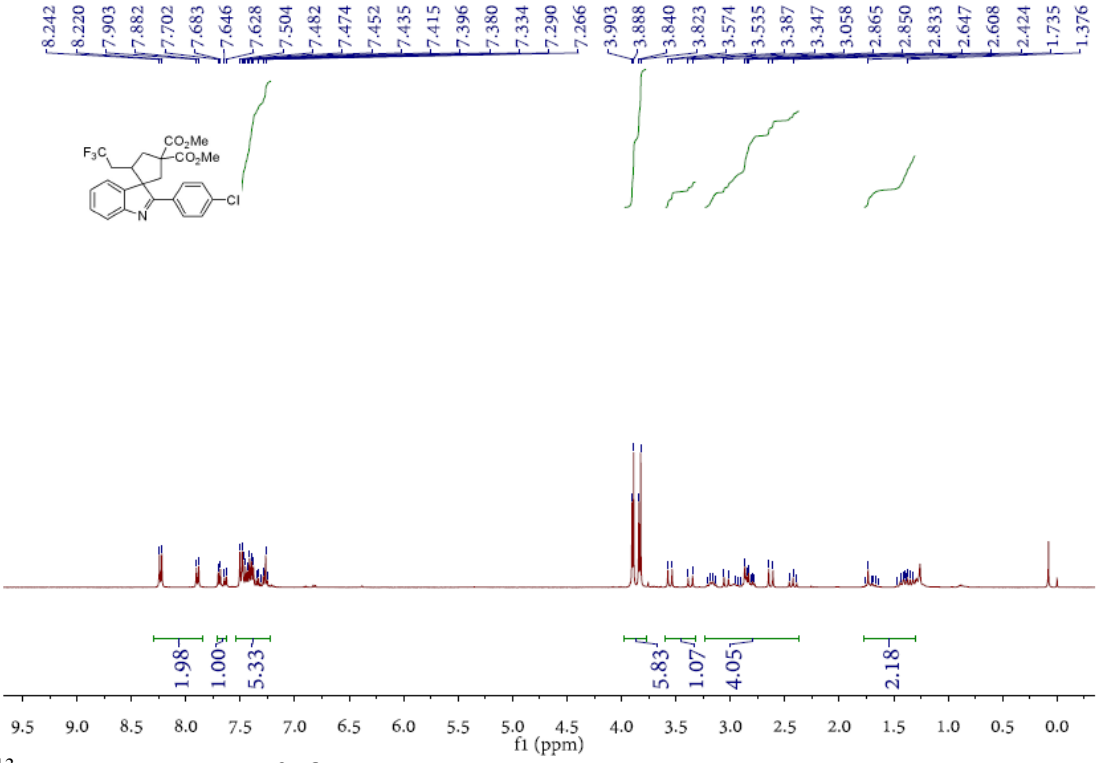
^{13}C NMR Spectrum of **3e**



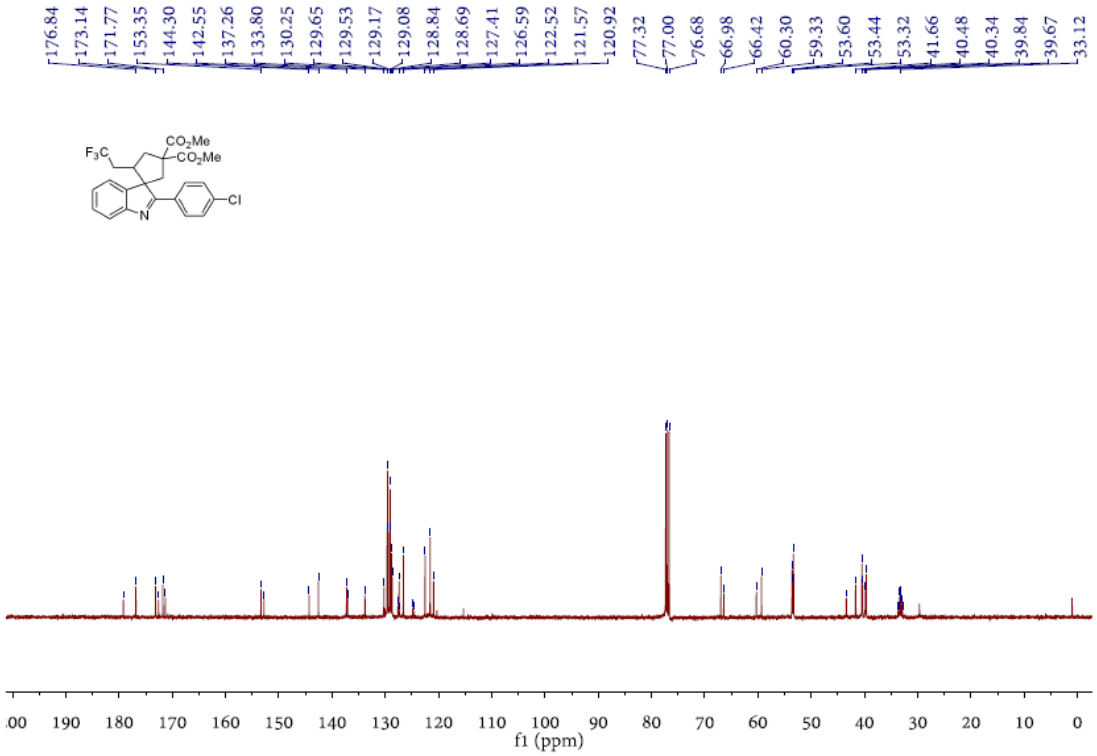
^{19}F NMR Spectrum of **3e**



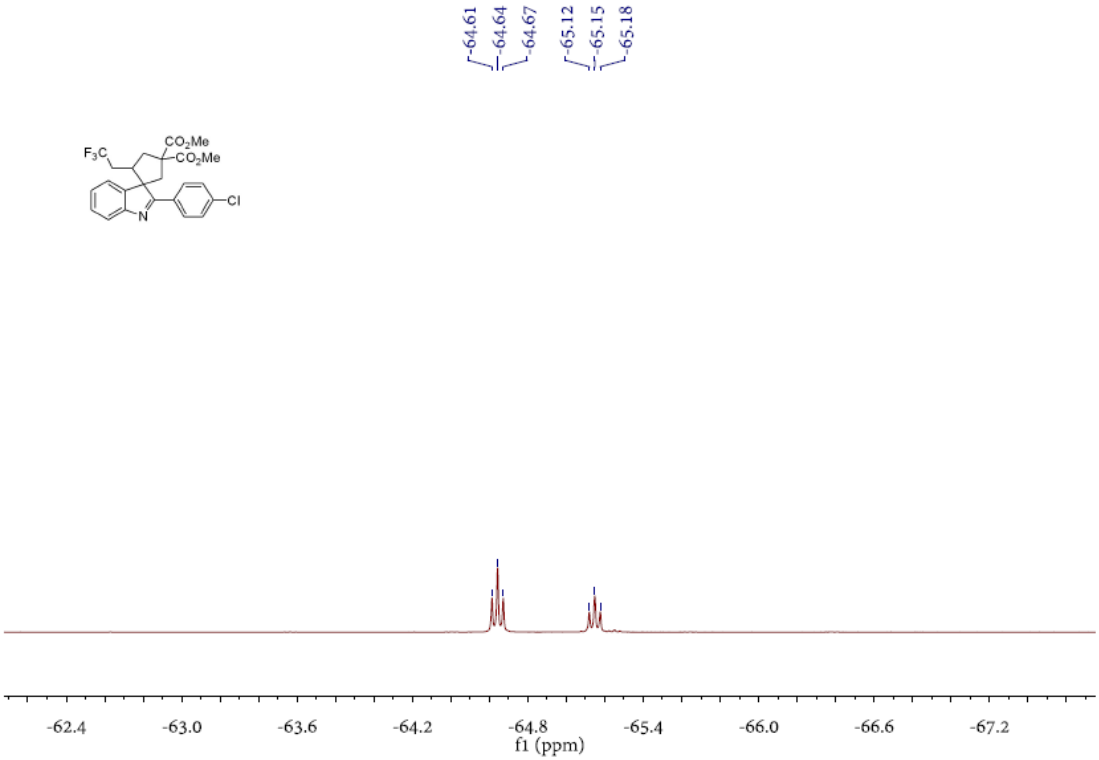
^{1}H NMR Spectrum of **3f**



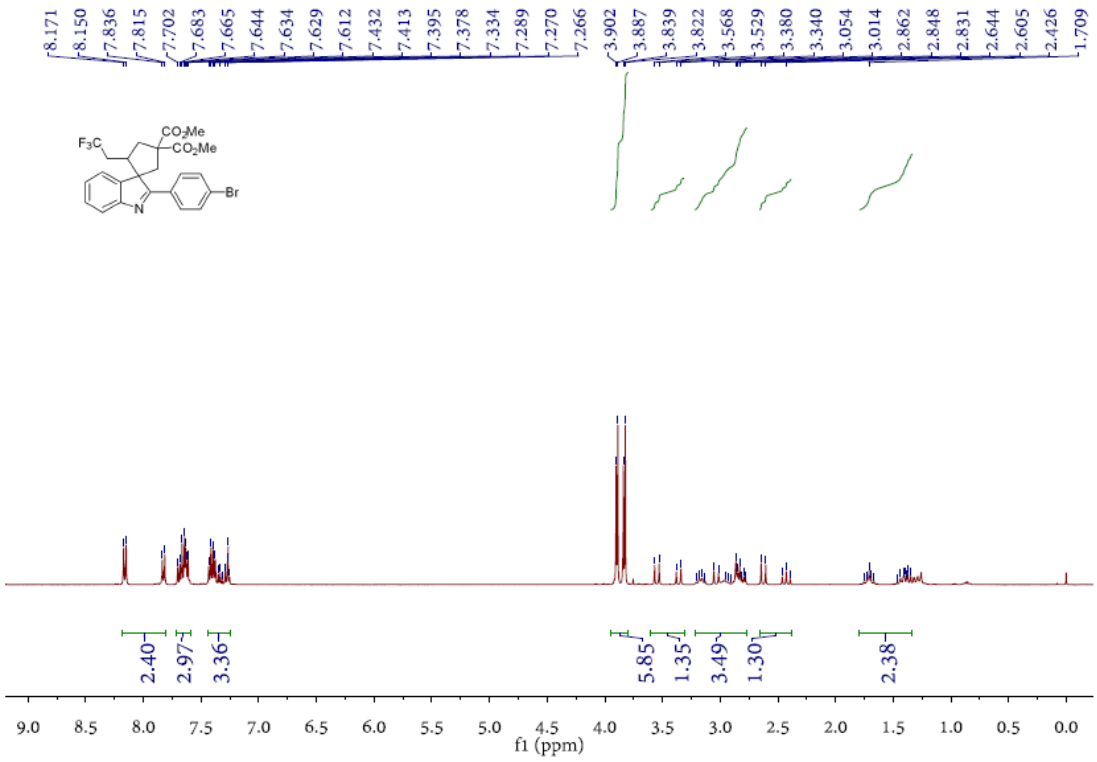
^{13}C NMR Spectrum of **3f**



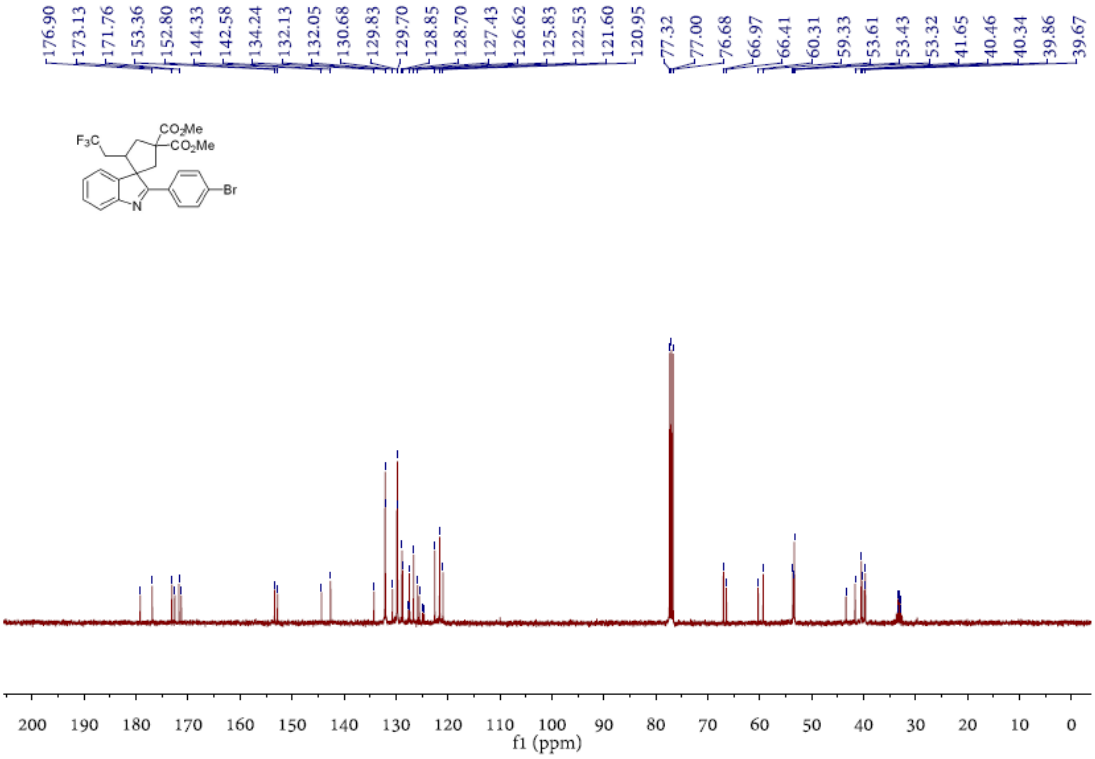
^{19}F NMR Spectrum of **3f**



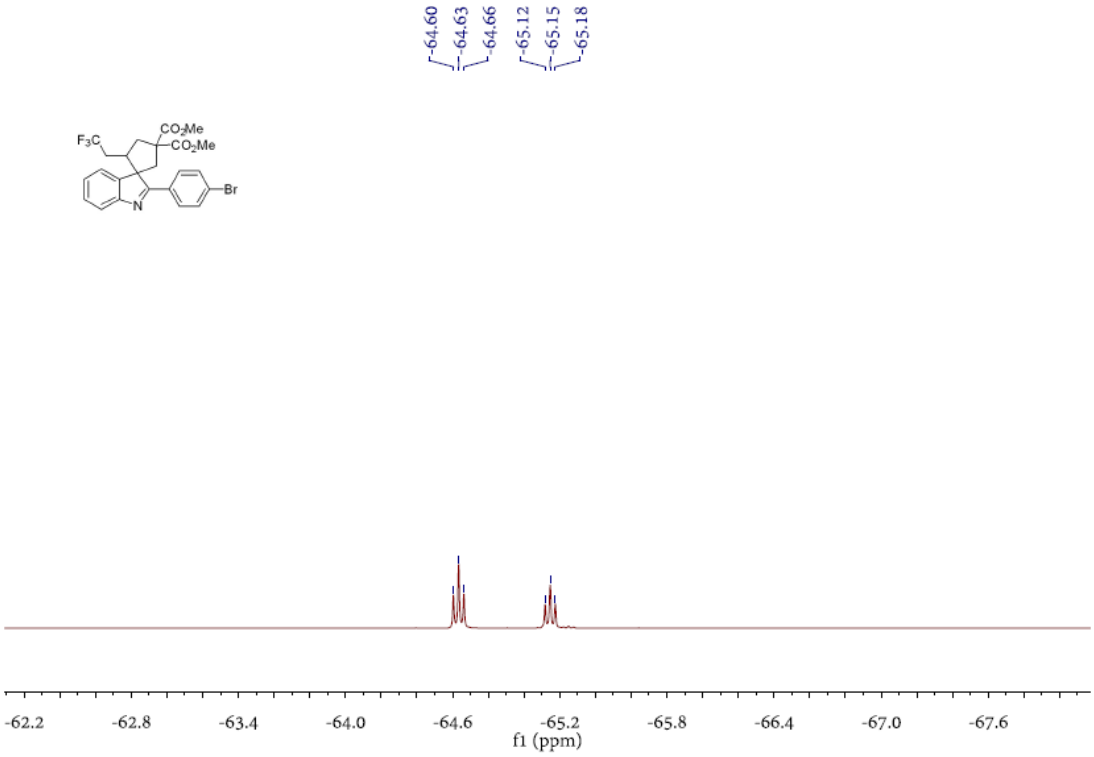
^{1}H NMR Spectrum of **3g**



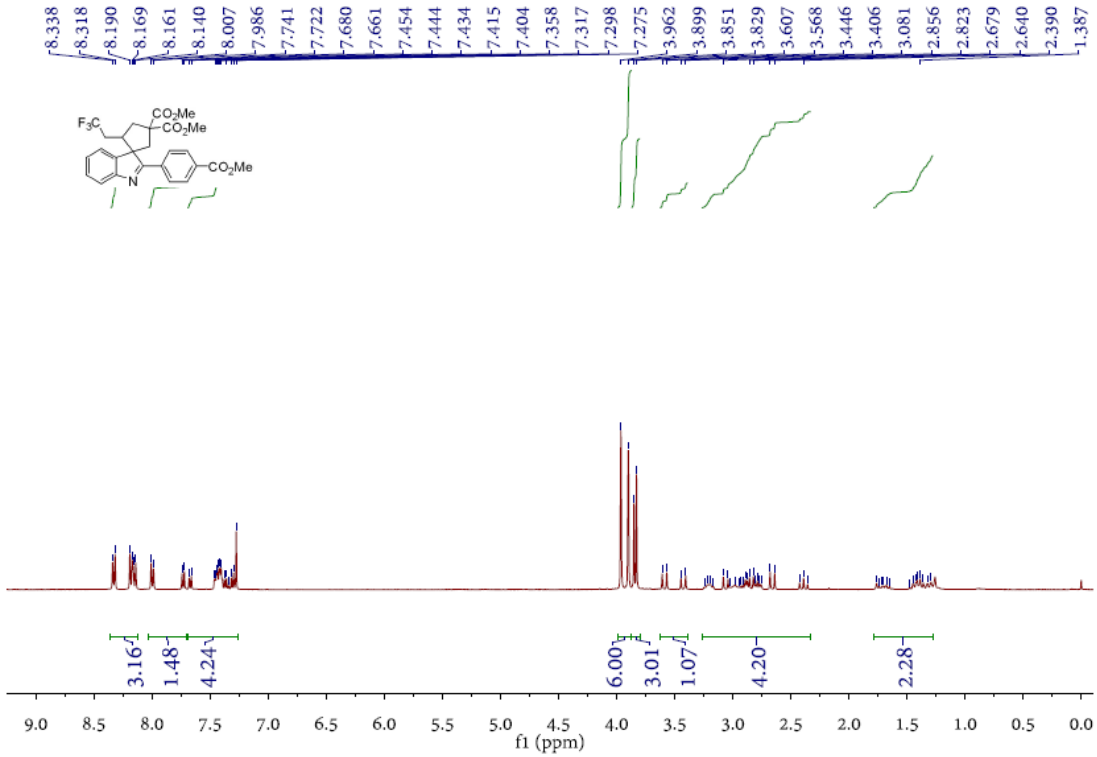
^{13}C NMR Spectrum of **3g**



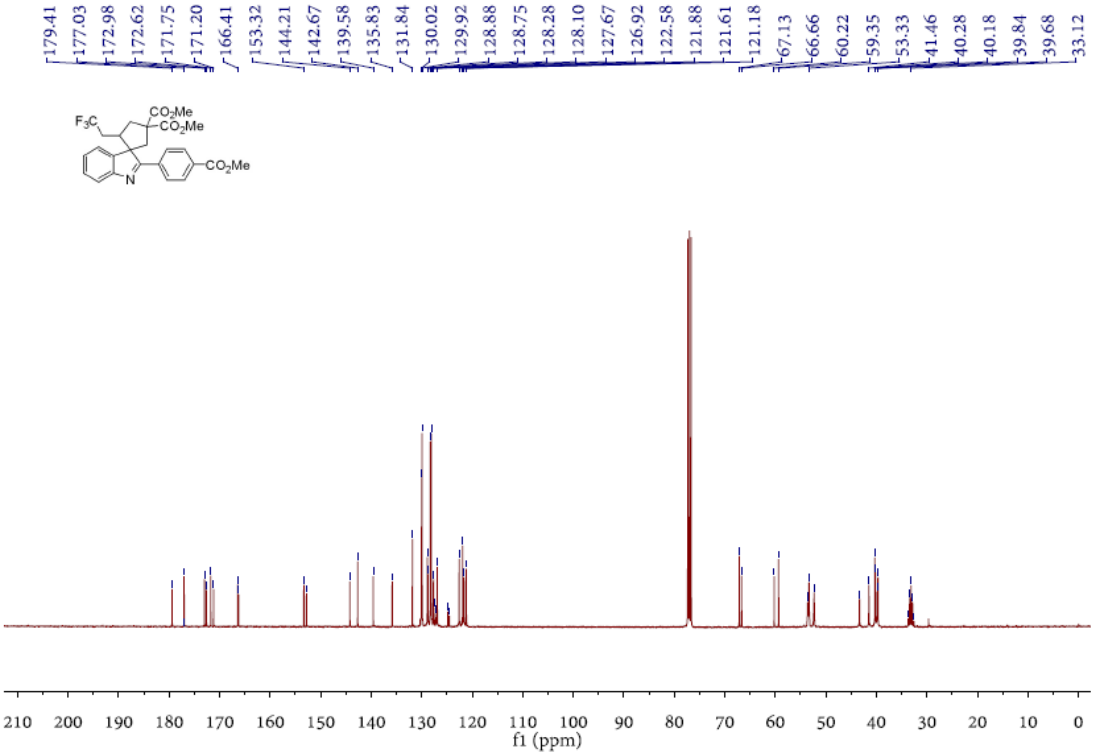
^{19}F NMR Spectrum of **3g**



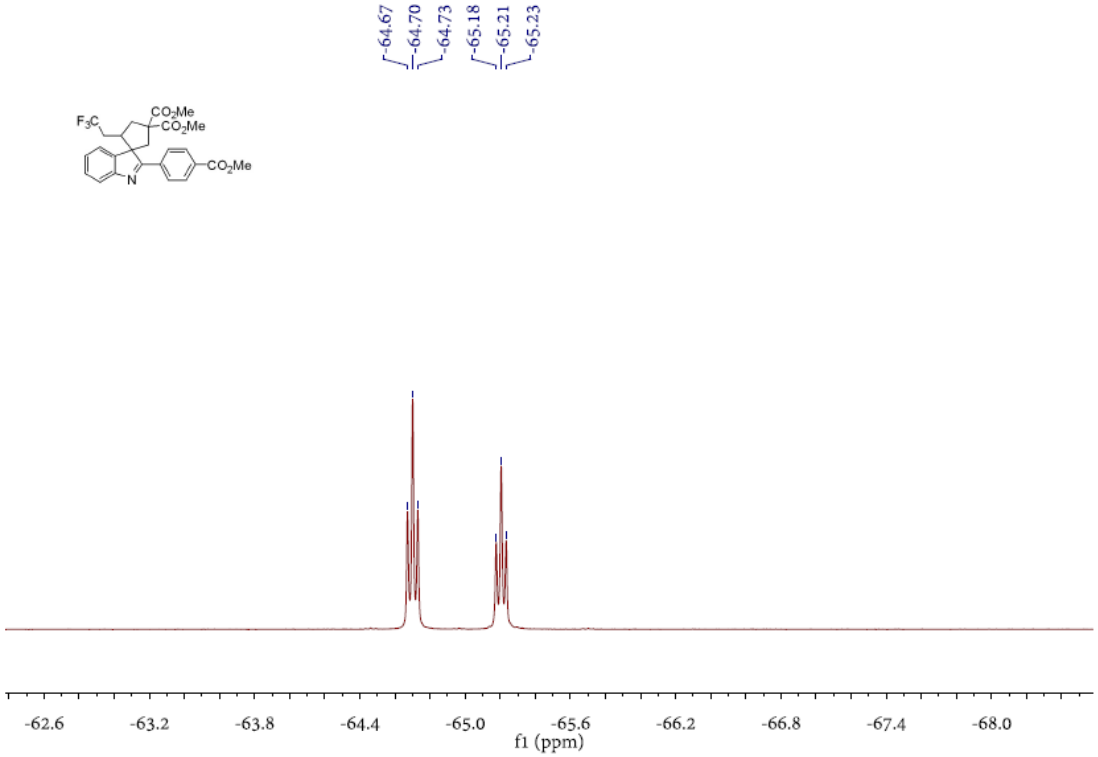
^{1}H NMR Spectrum of **3h**



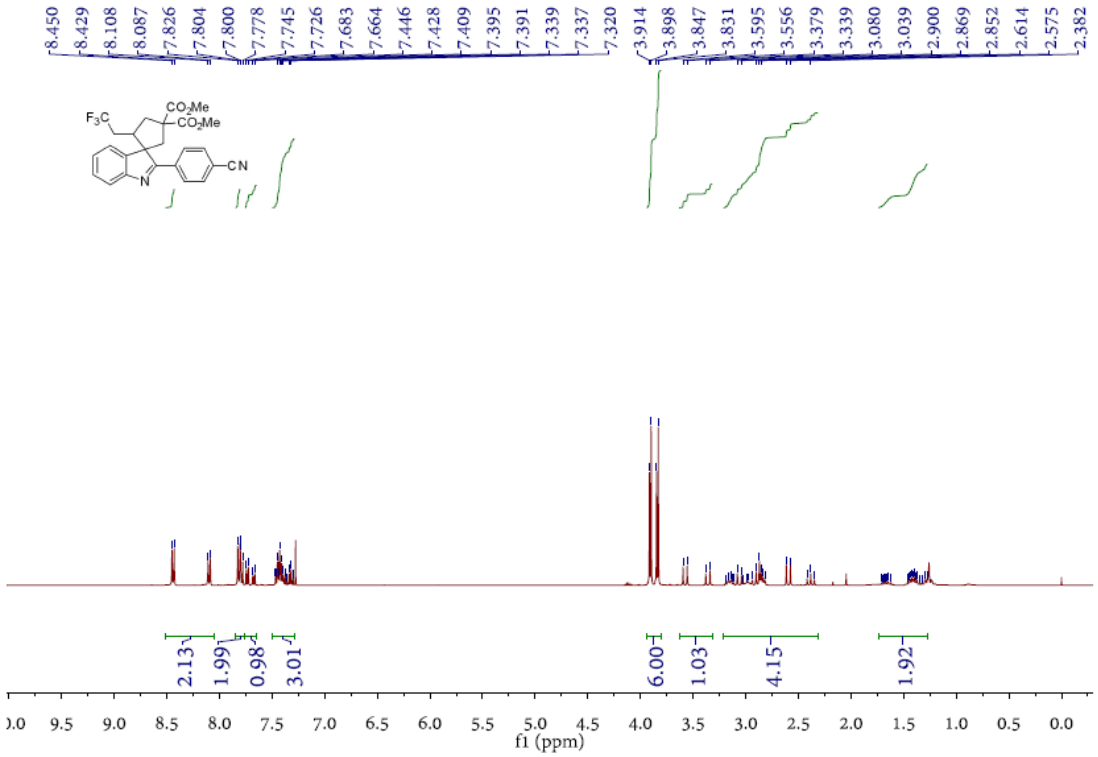
^{13}C NMR Spectrum of **3h**



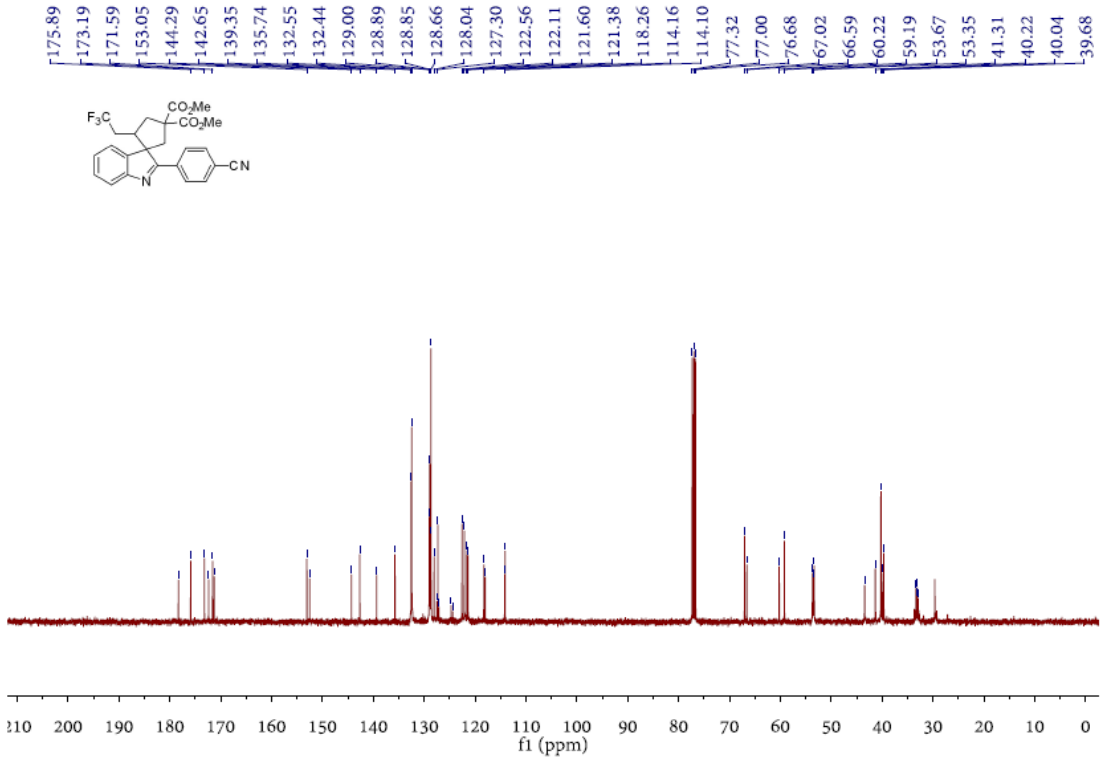
^{19}F NMR Spectrum of **3h**



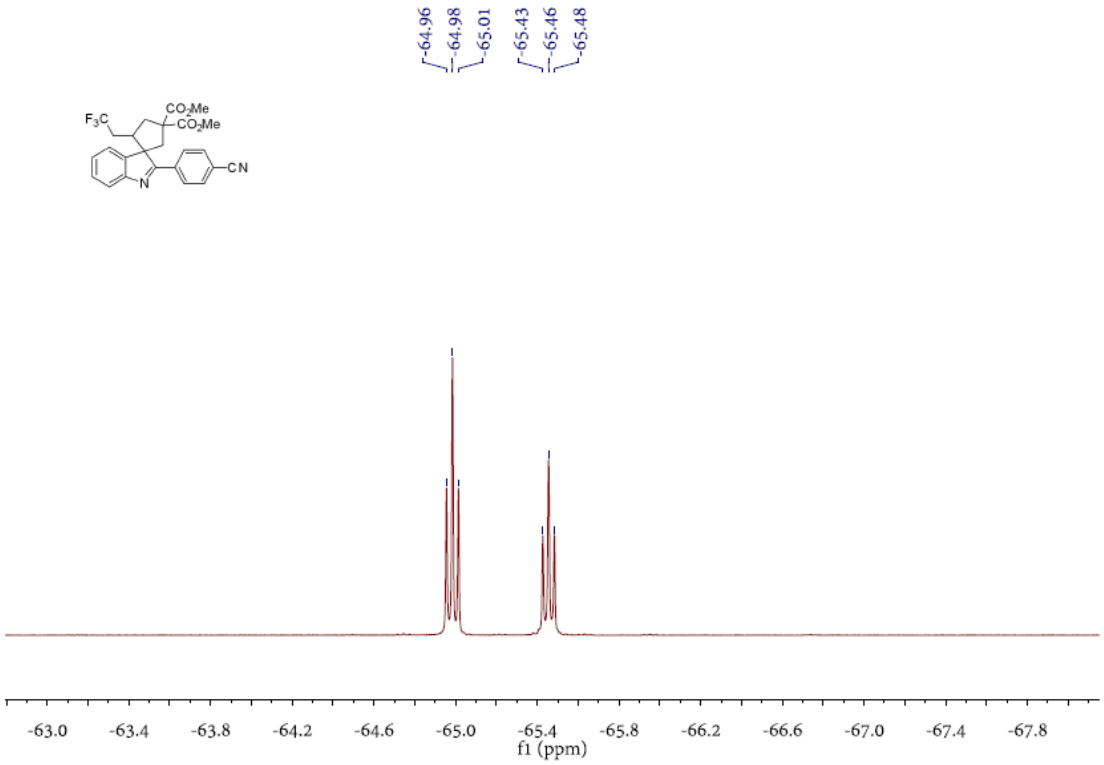
^{1}H NMR Spectrum of **3i**



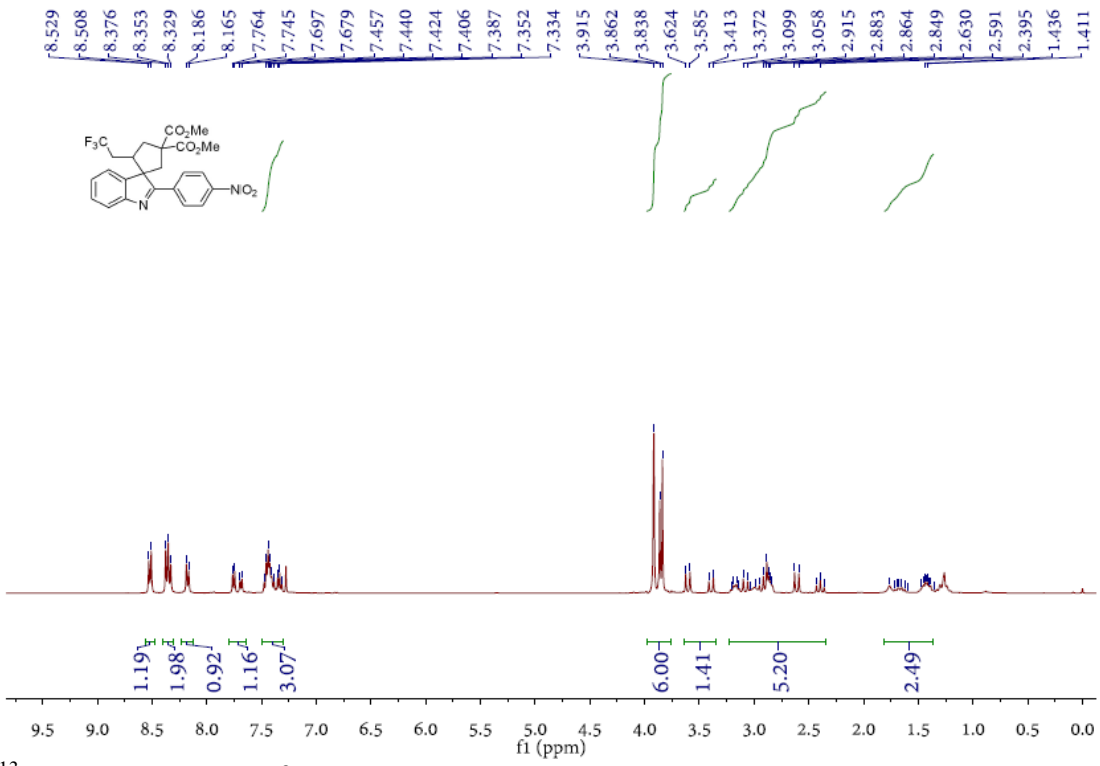
^{13}C NMR Spectrum of **3i**



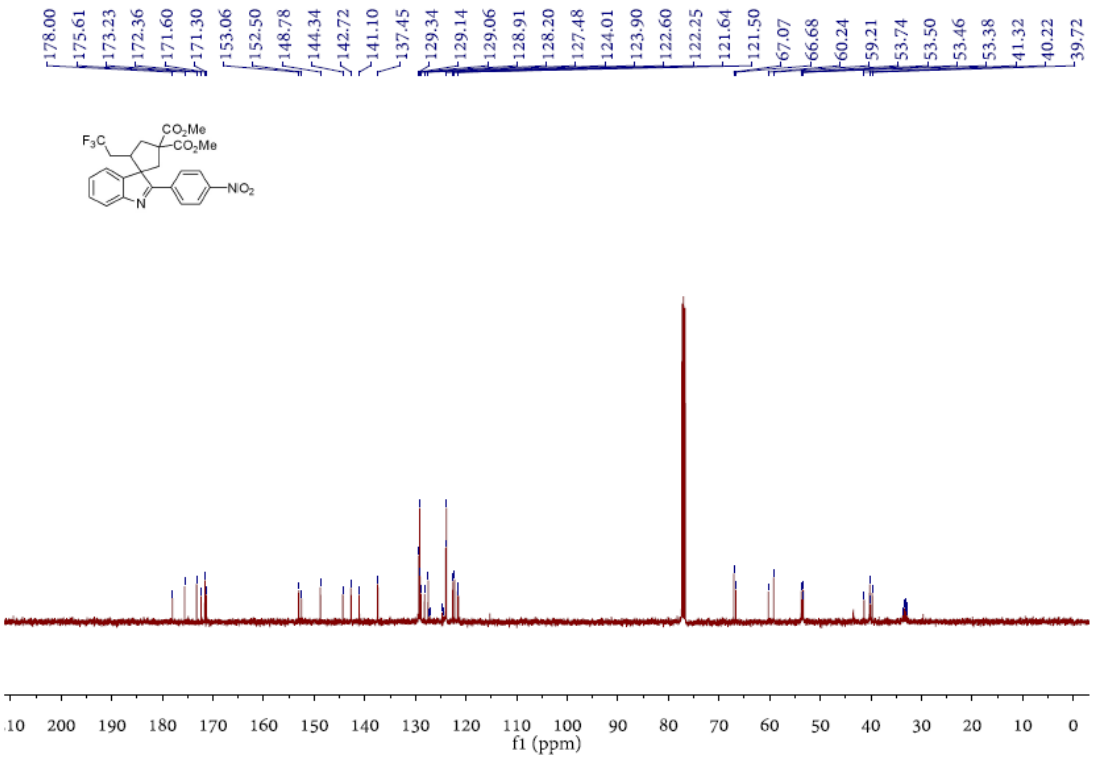
^{19}F NMR Spectrum of **3i**



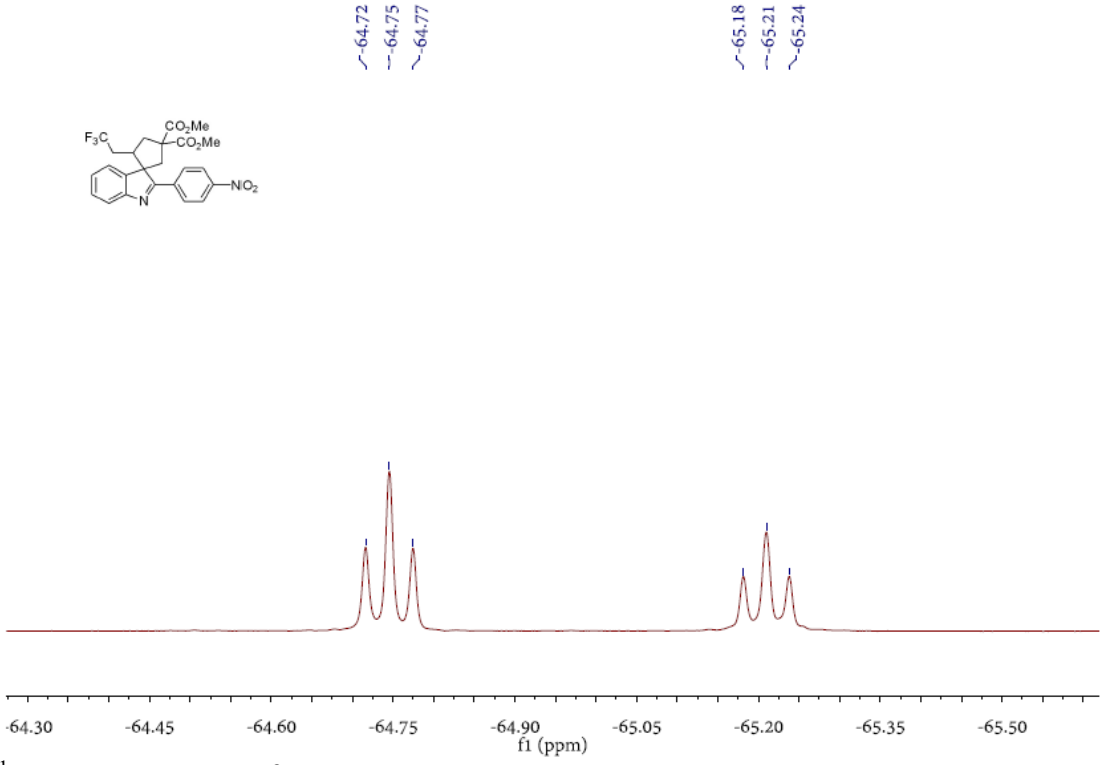
^{1}H NMR Spectrum of **3j**



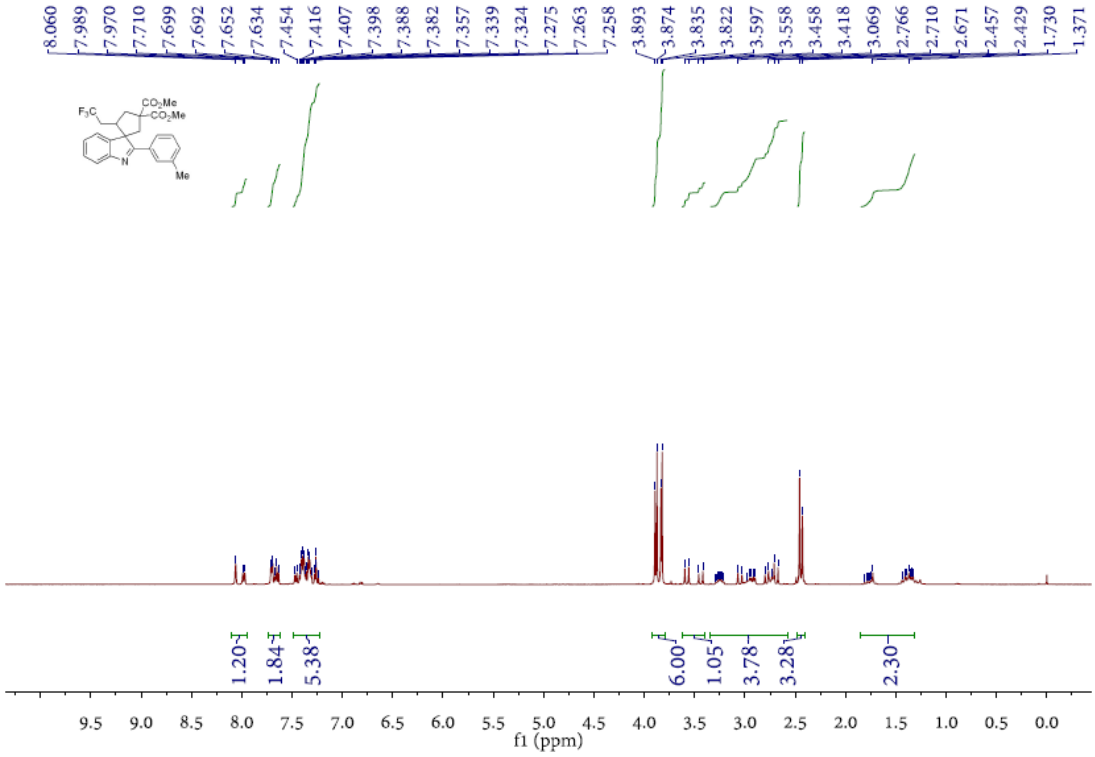
^{13}C NMR Spectrum of **3j**



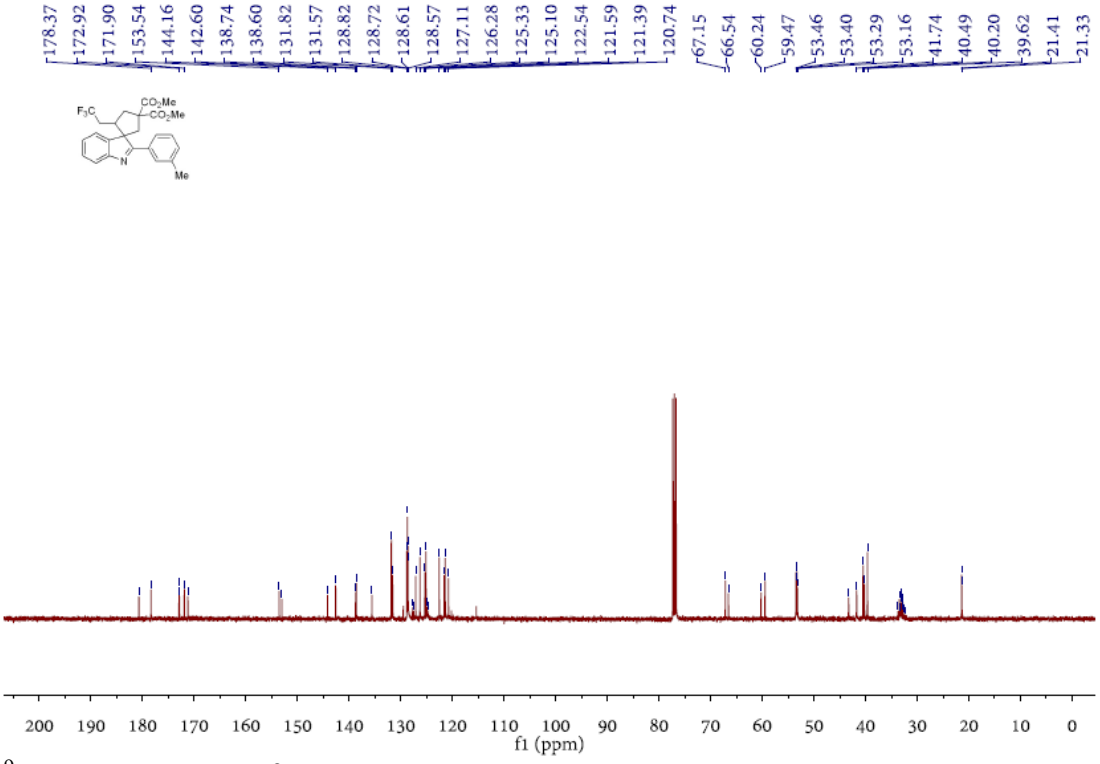
^{19}F NMR Spectrum of **3j**



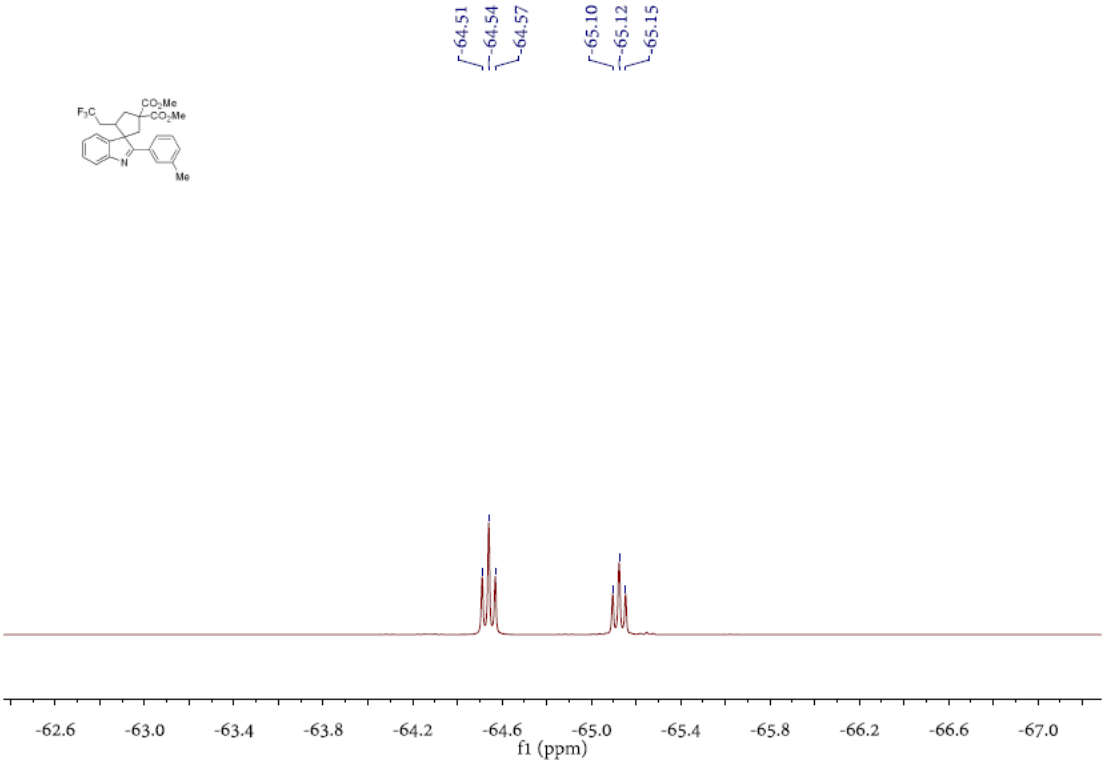
^{1}H NMR Spectrum of **3k**



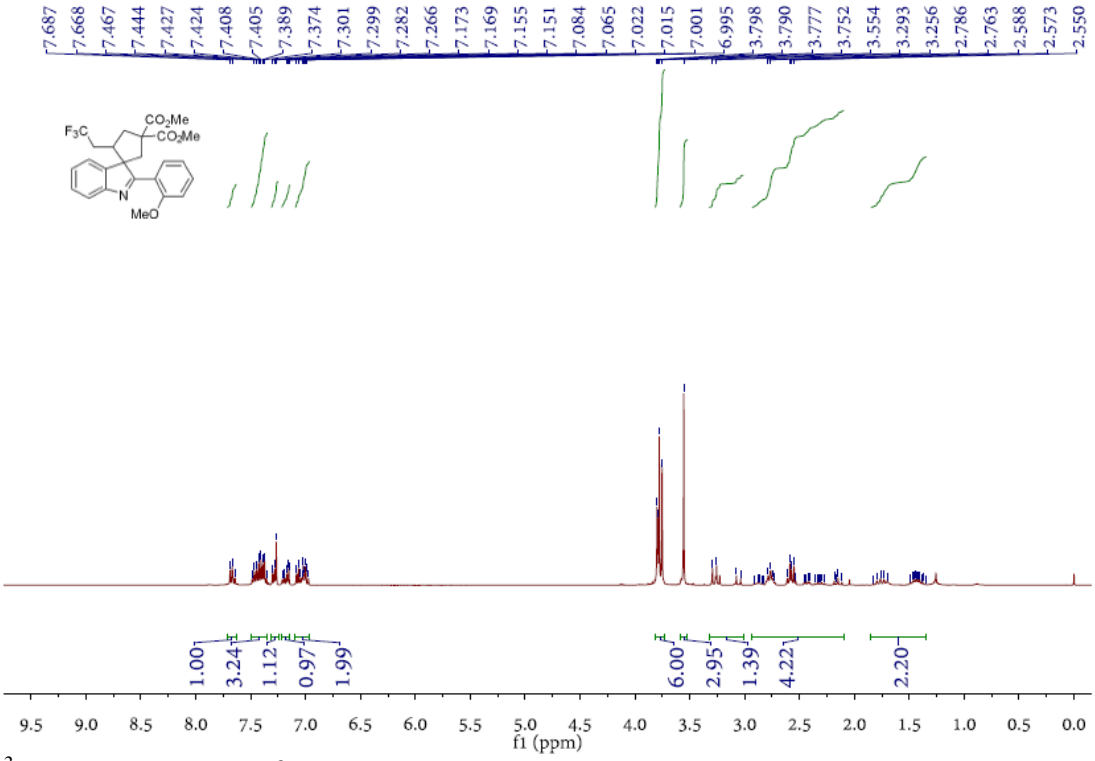
^{13}C NMR Spectrum of **3k**



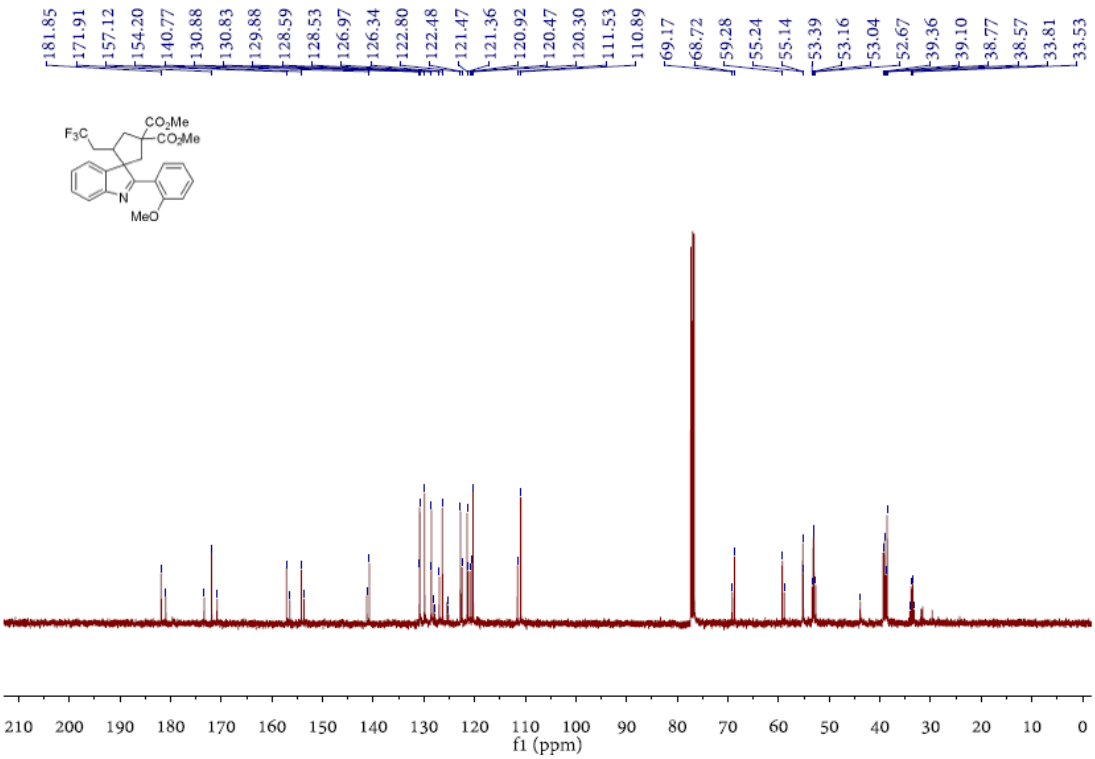
^{19}F NMR Spectrum of **3k**



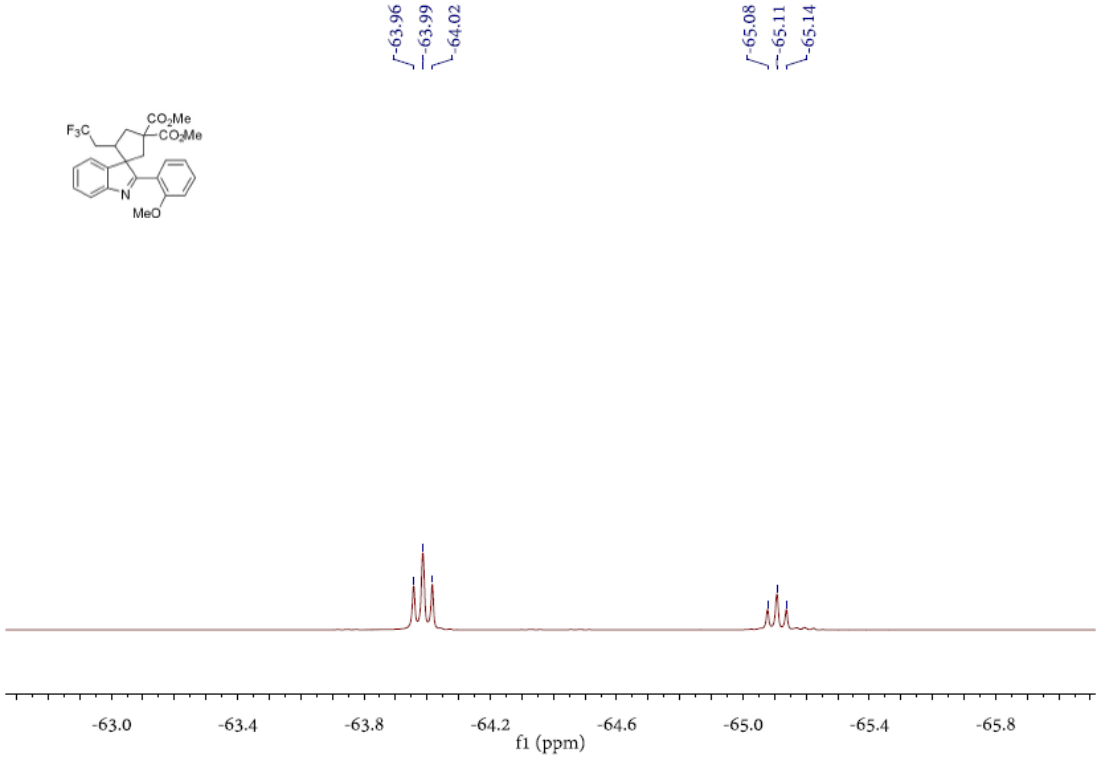
^{1}H NMR Spectrum of **3l**



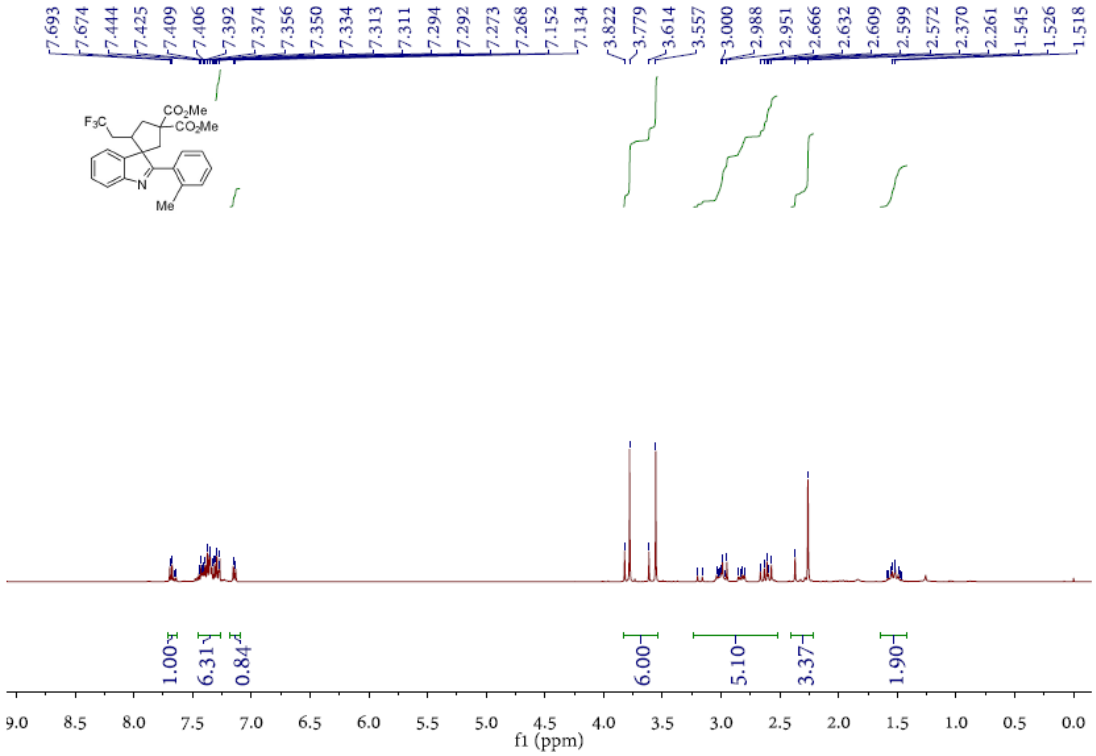
^{13}C NMR Spectrum of **3l**



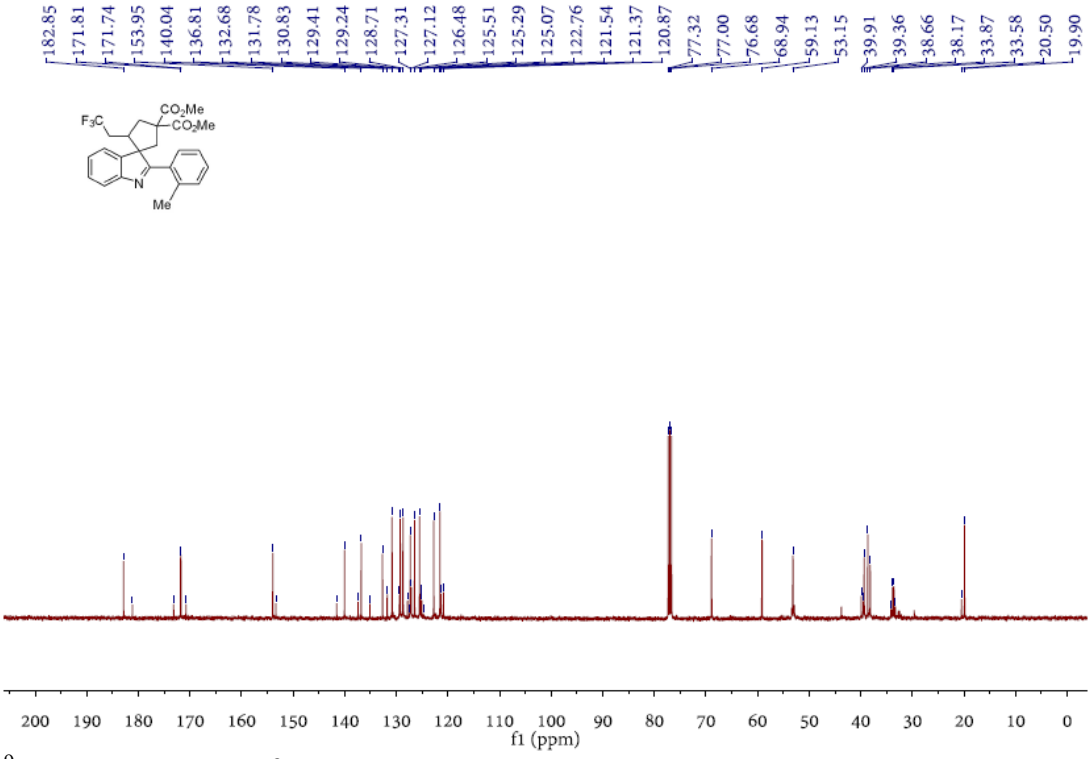
^{19}F NMR Spectrum of **3l**



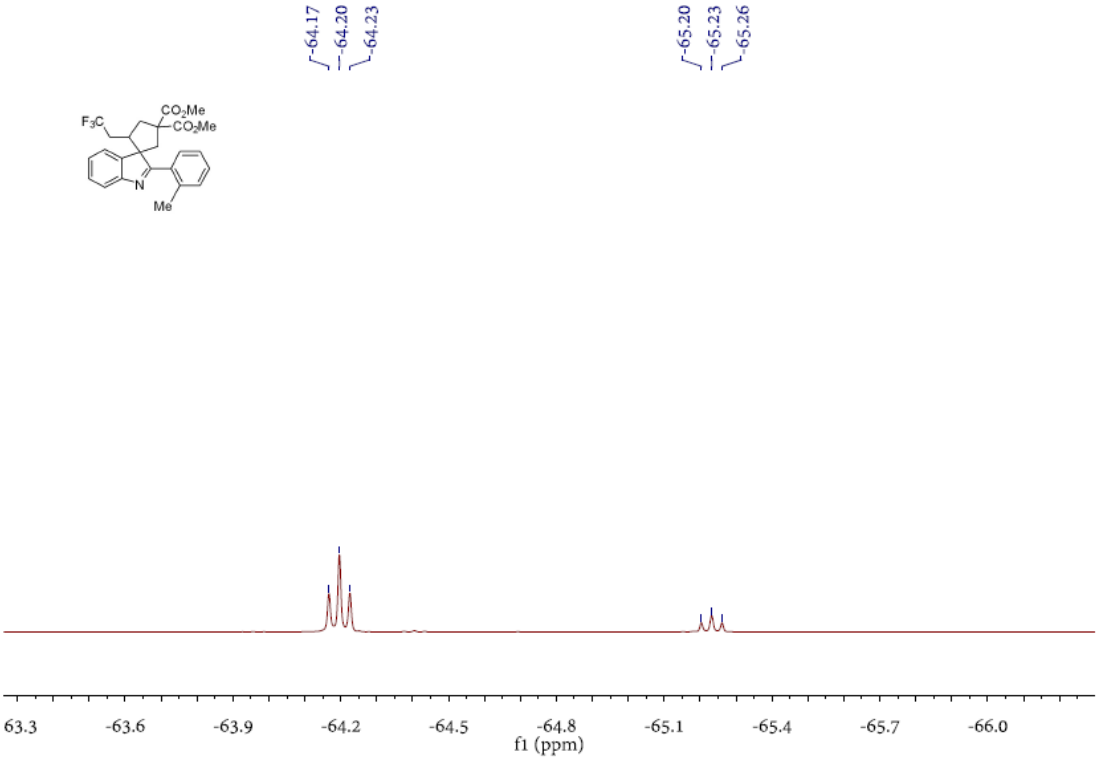
^{1}H NMR Spectrum of **3m**



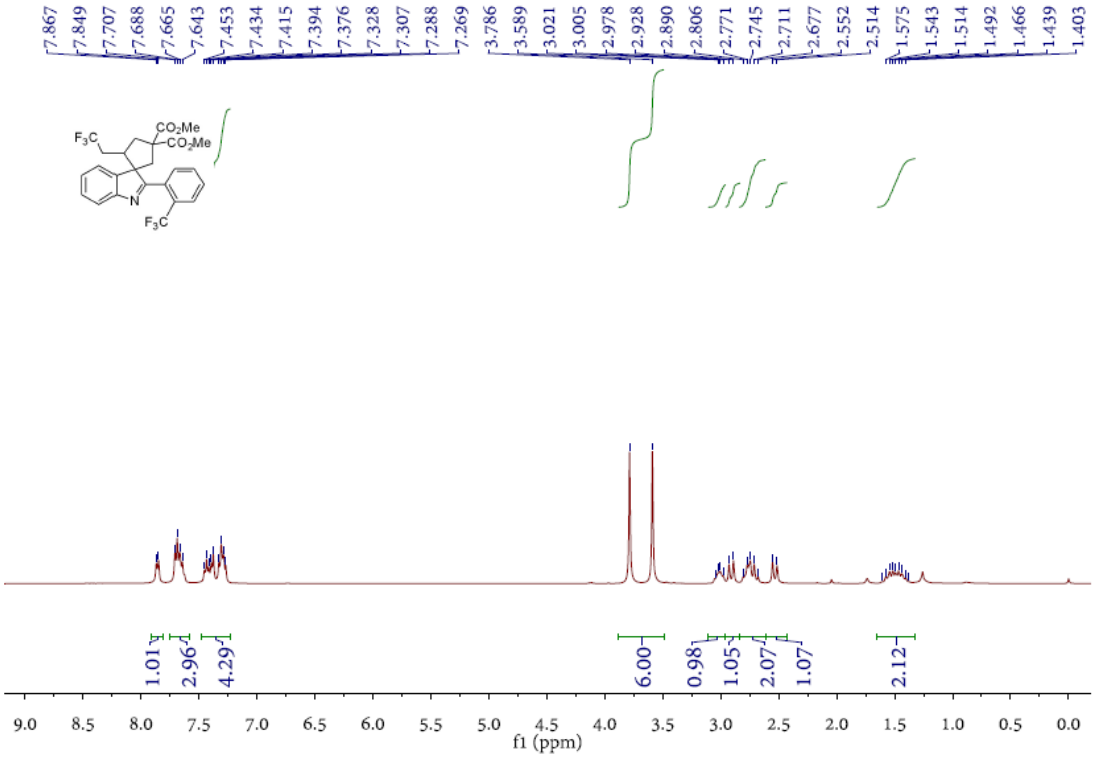
^{13}C NMR Spectrum of **3m**



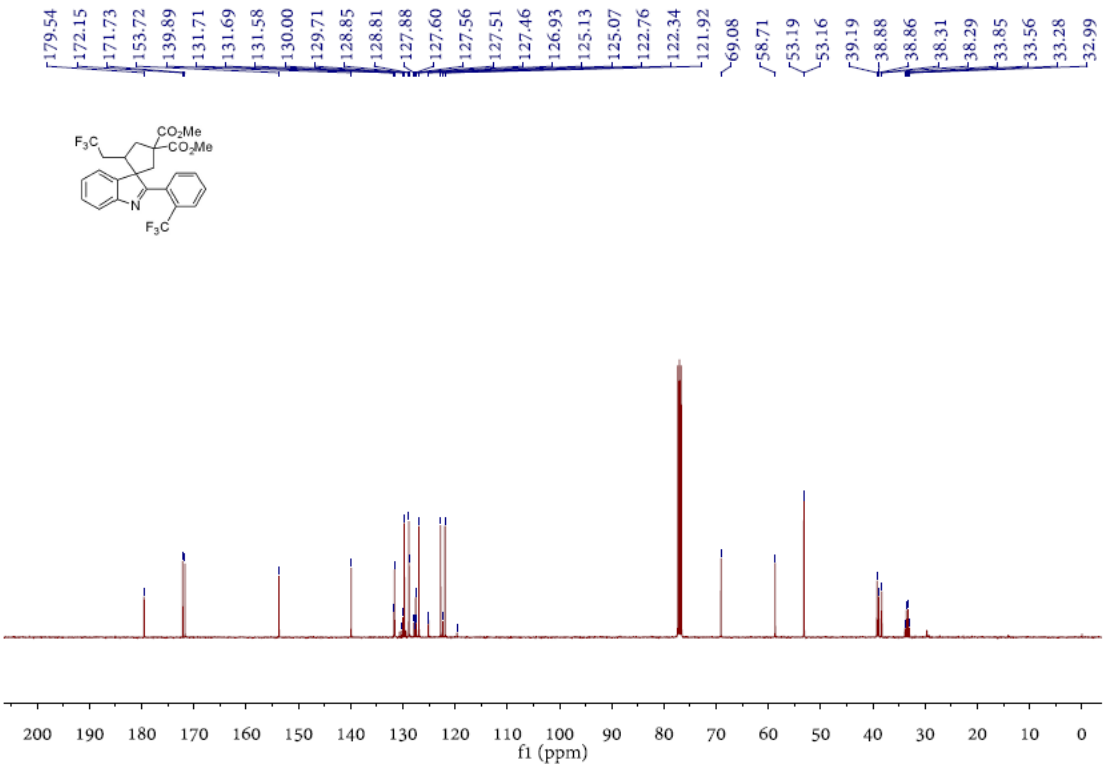
^{19}F NMR Spectrum of **3m**



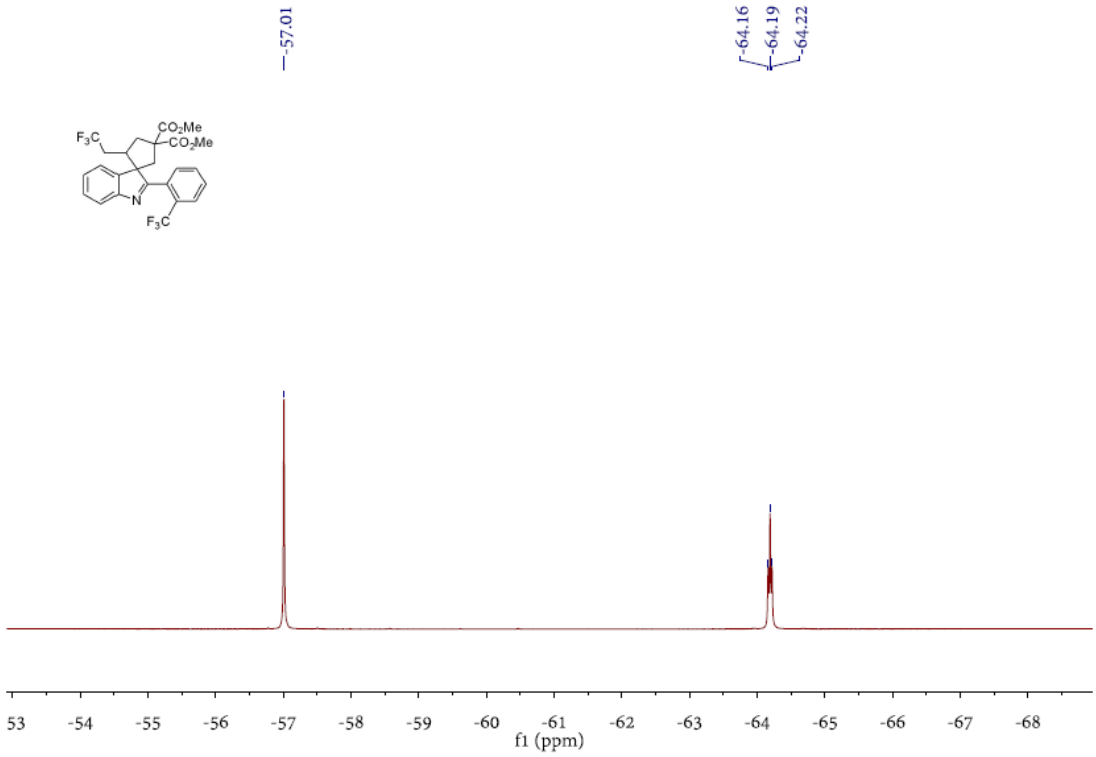
^{1}H NMR Spectrum of **3n**



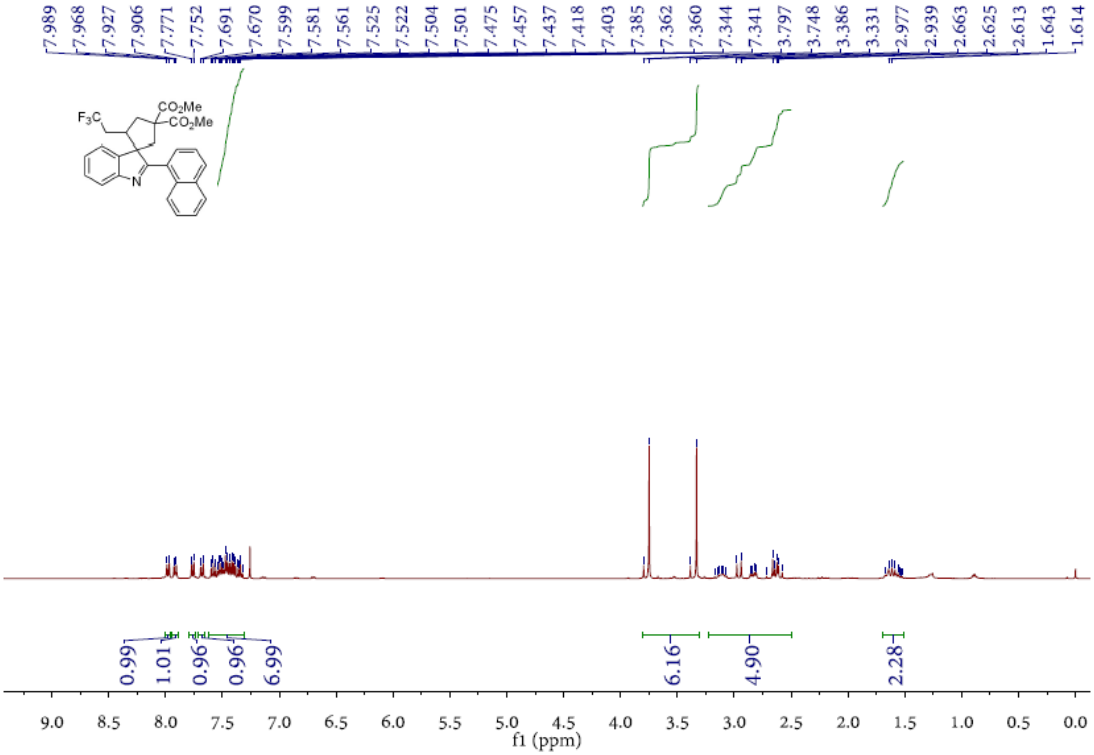
^{13}C NMR Spectrum of **3n**



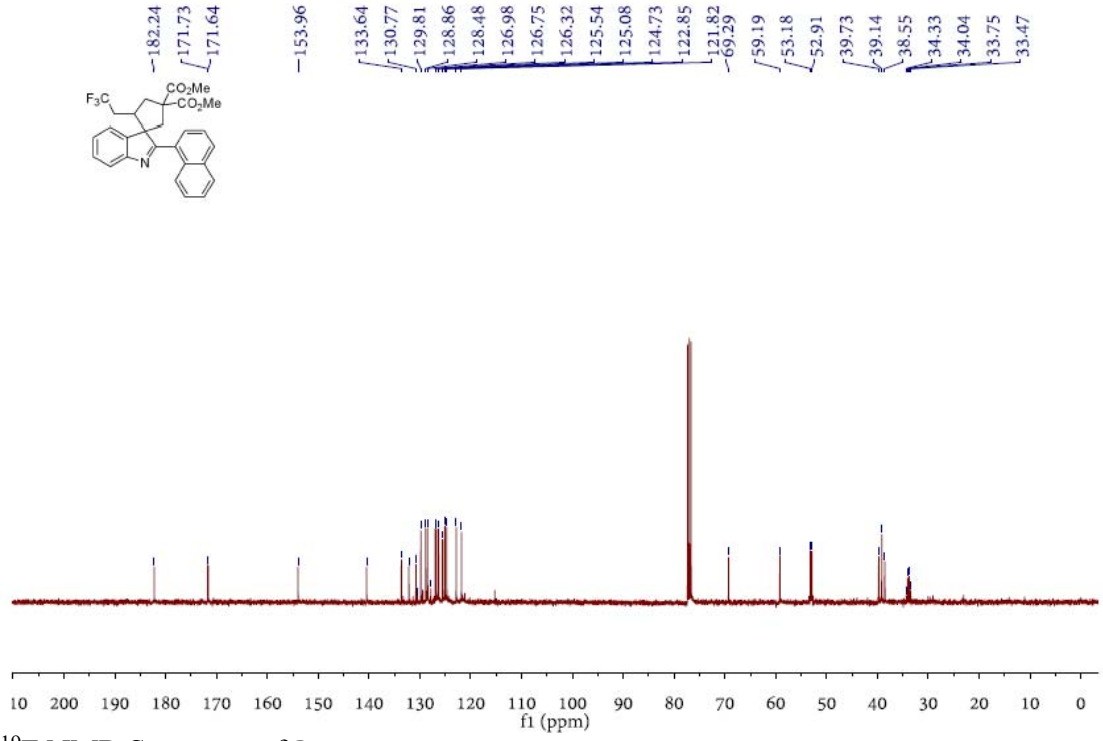
^{19}F NMR Spectrum of **3n**



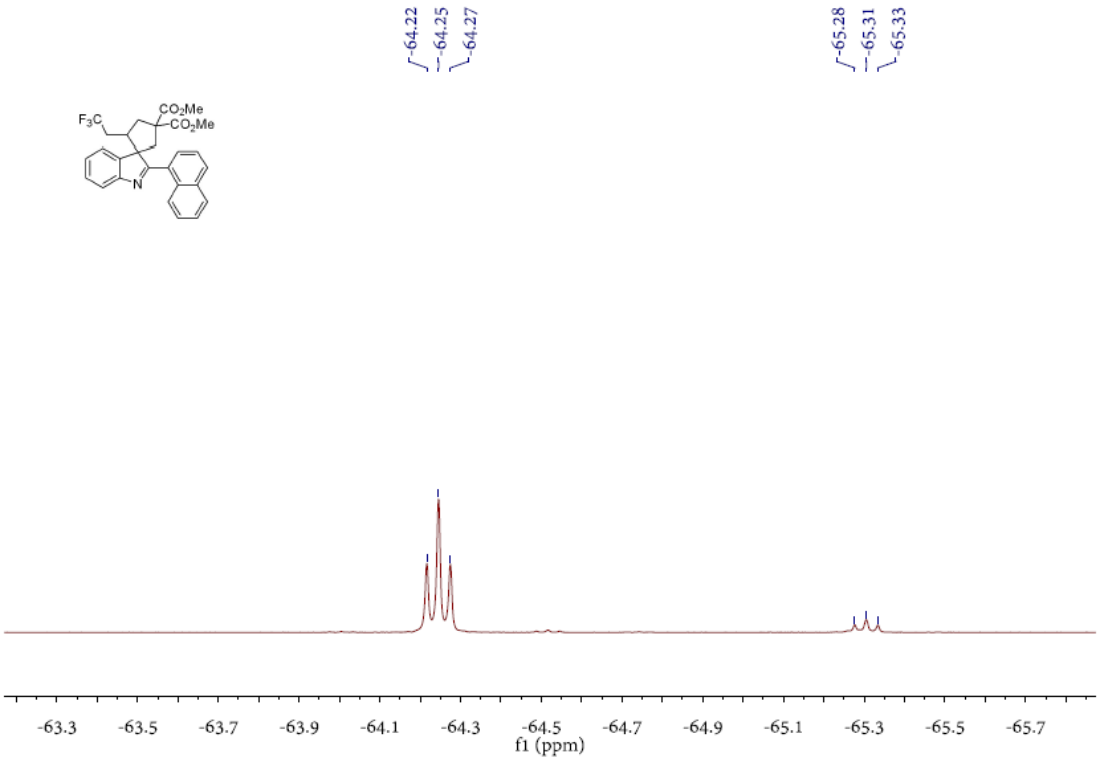
^{1}H NMR Spectrum of **3o**



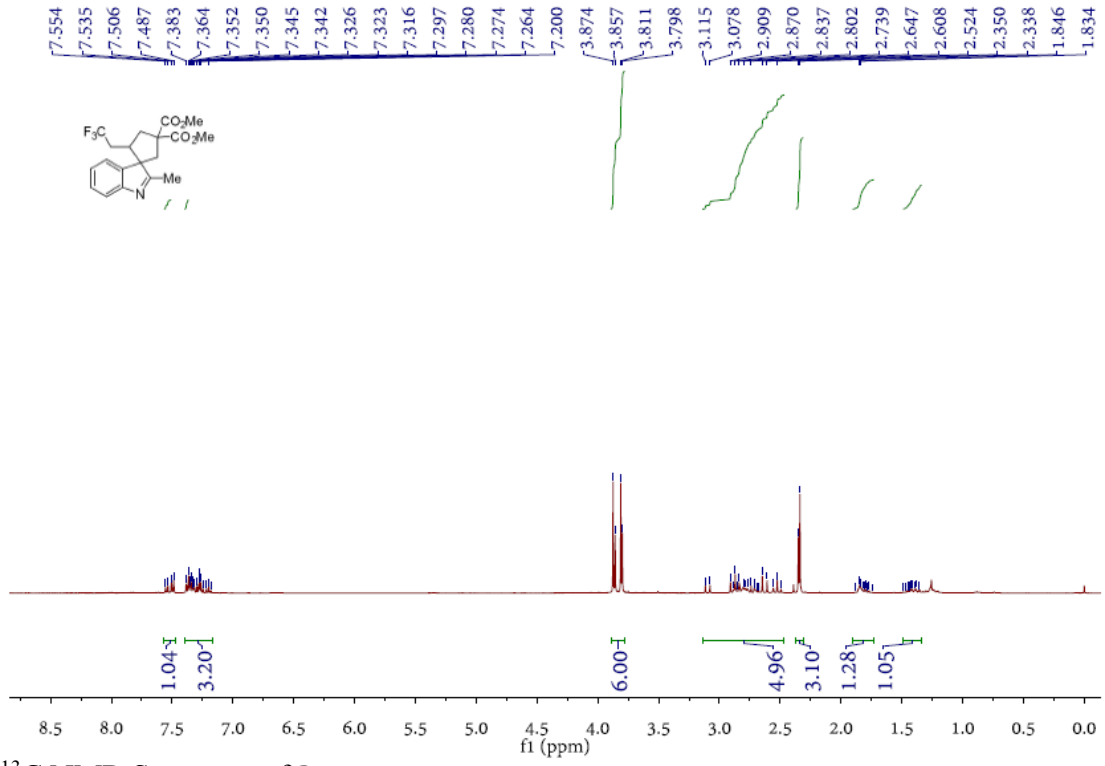
^{13}C NMR Spectrum of **3o**



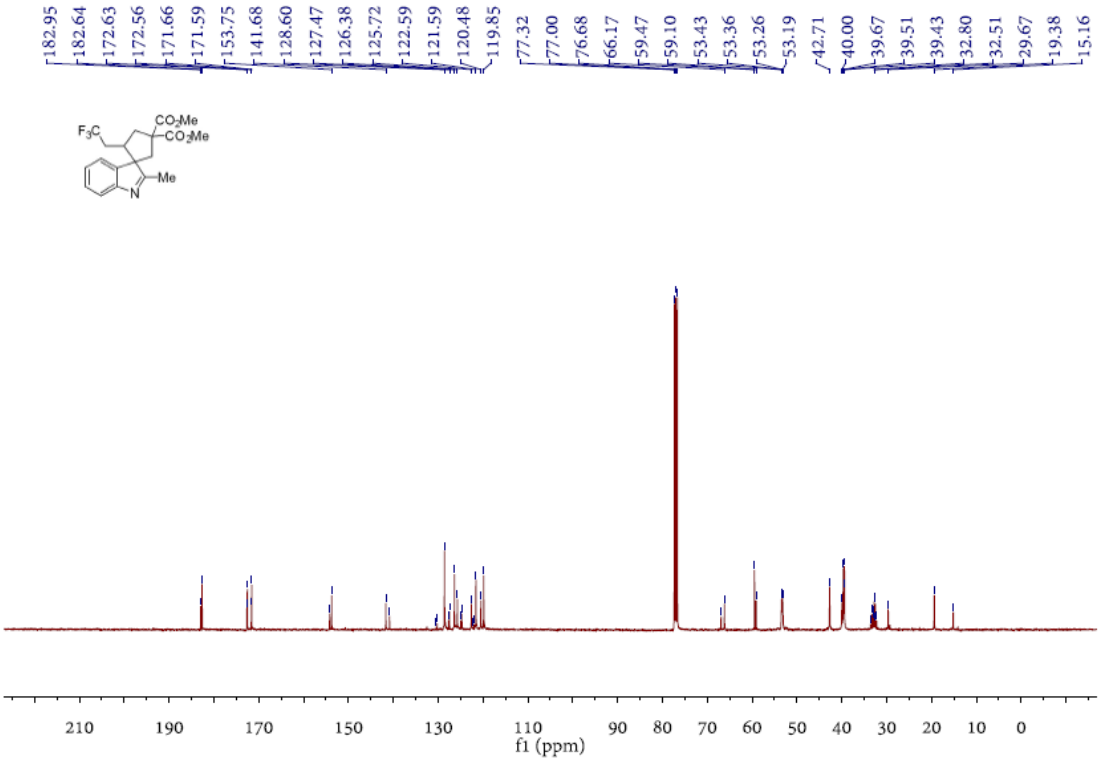
^{19}F NMR Spectrum of **3o**



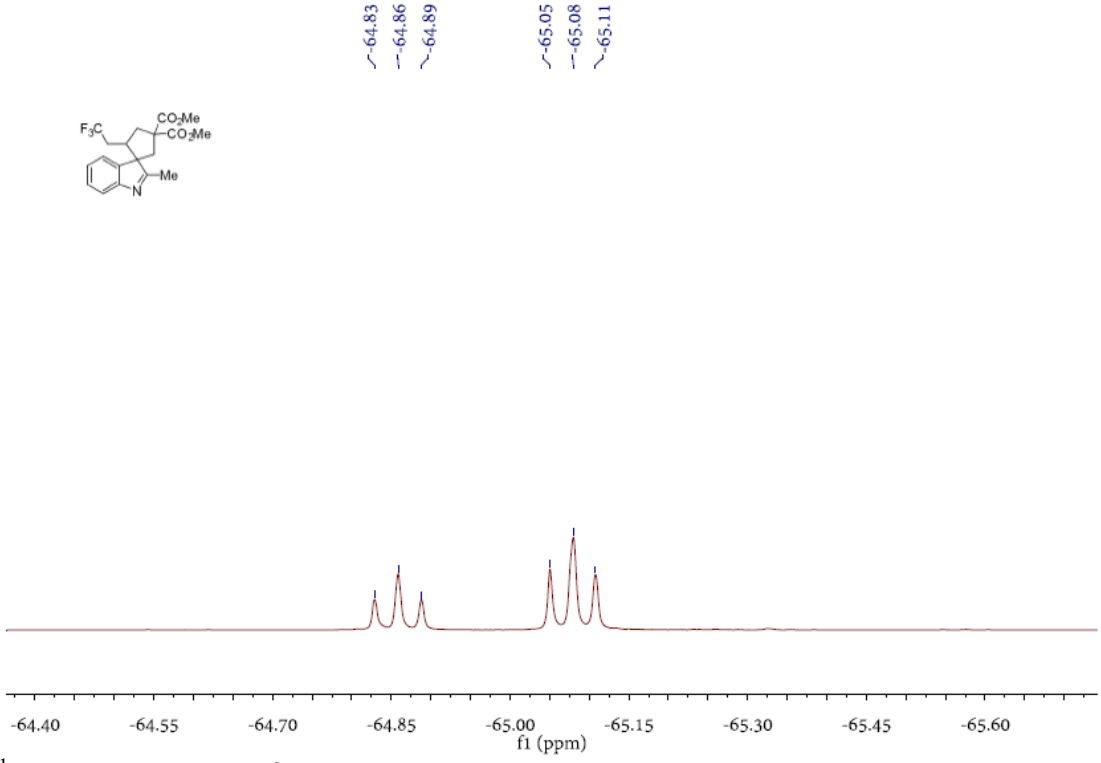
^{1}H NMR Spectrum of **3p**



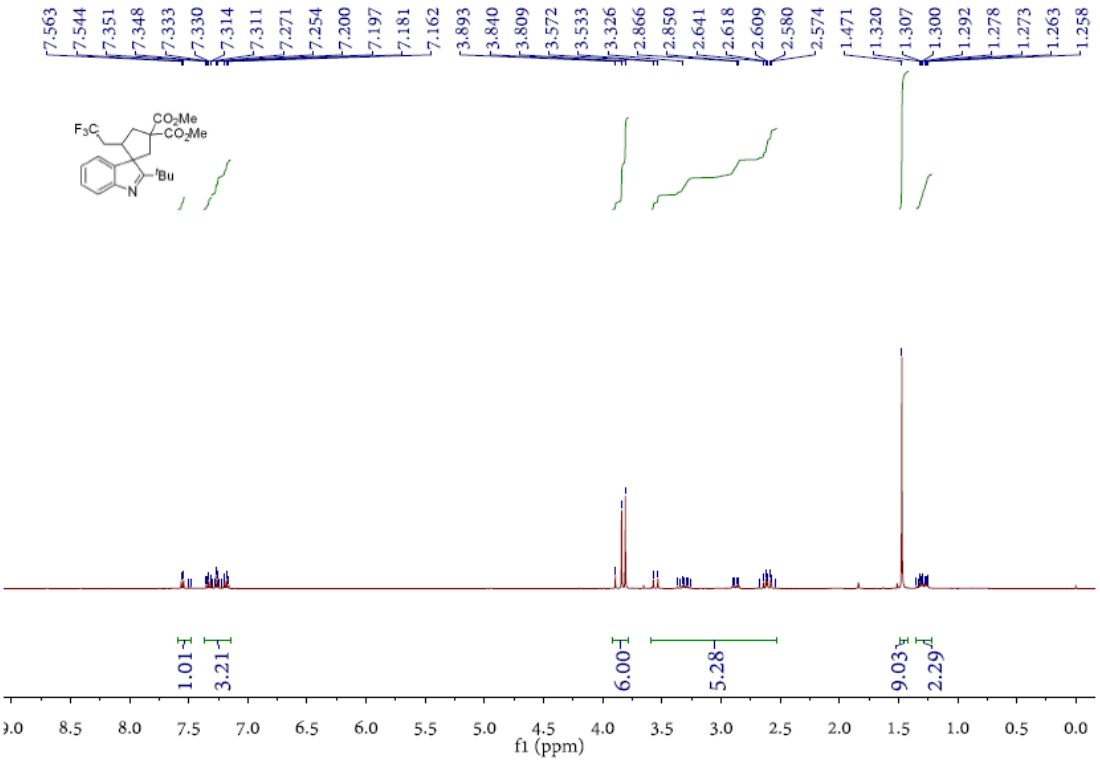
^{13}C NMR Spectrum of **3p**



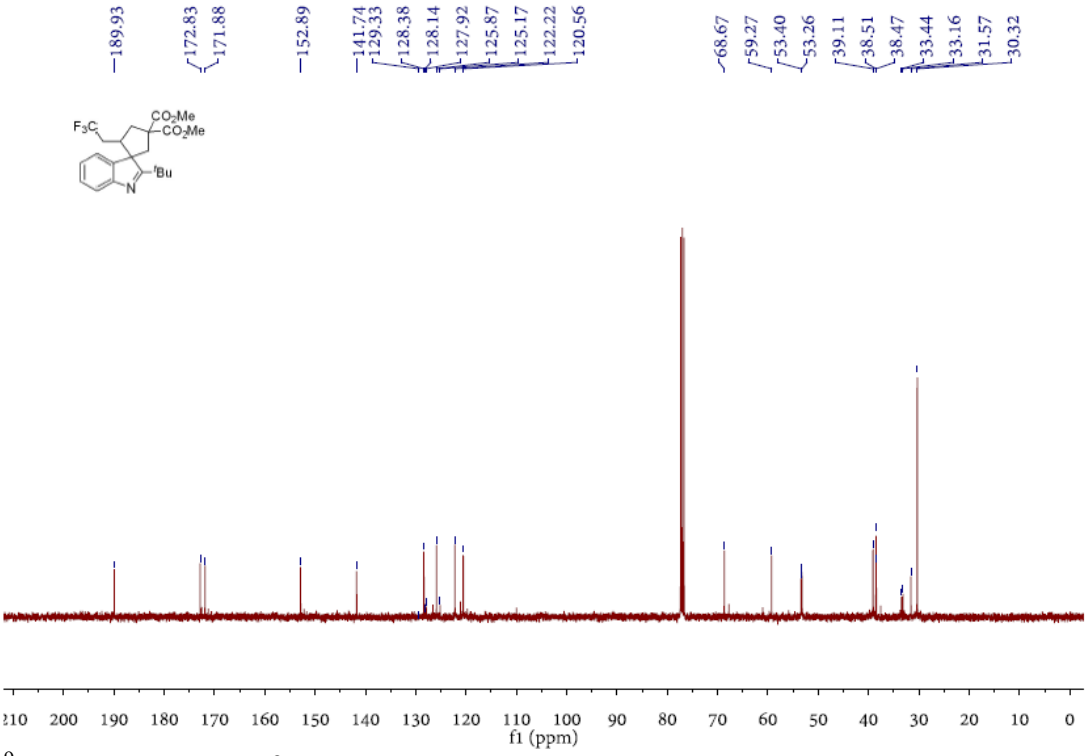
^{19}F NMR Spectrum of **3p**



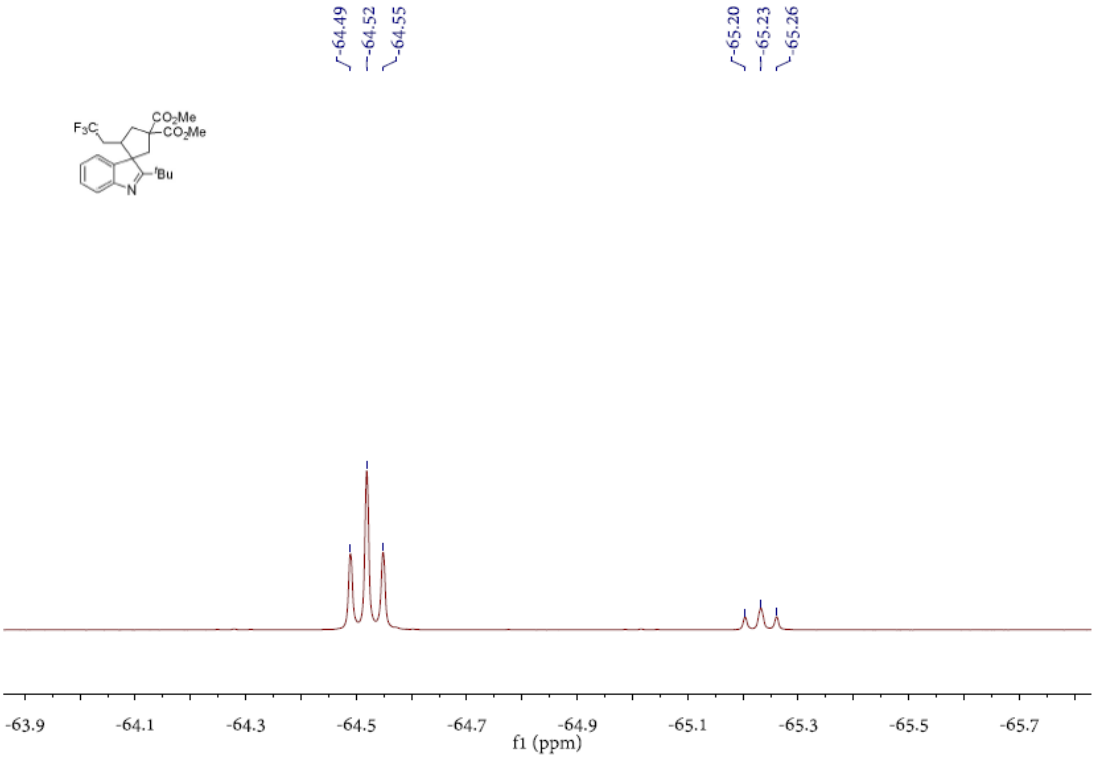
^{1}H NMR Spectrum of **3q**



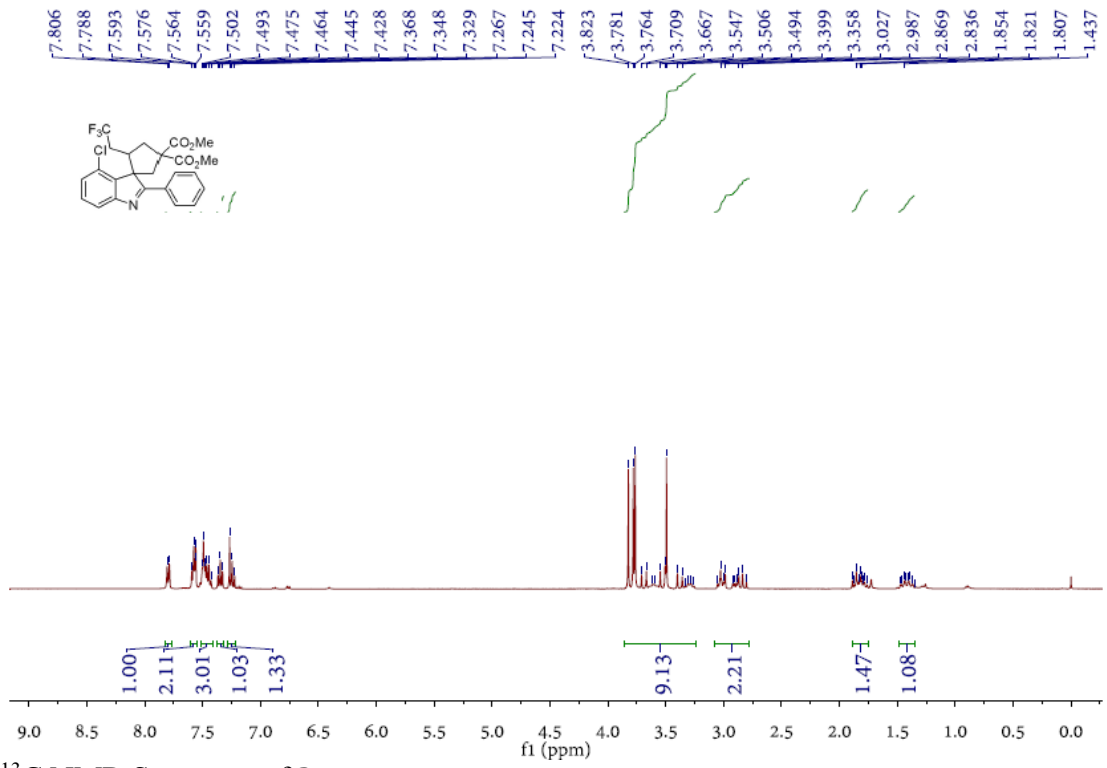
^{13}C NMR Spectrum of **3q**



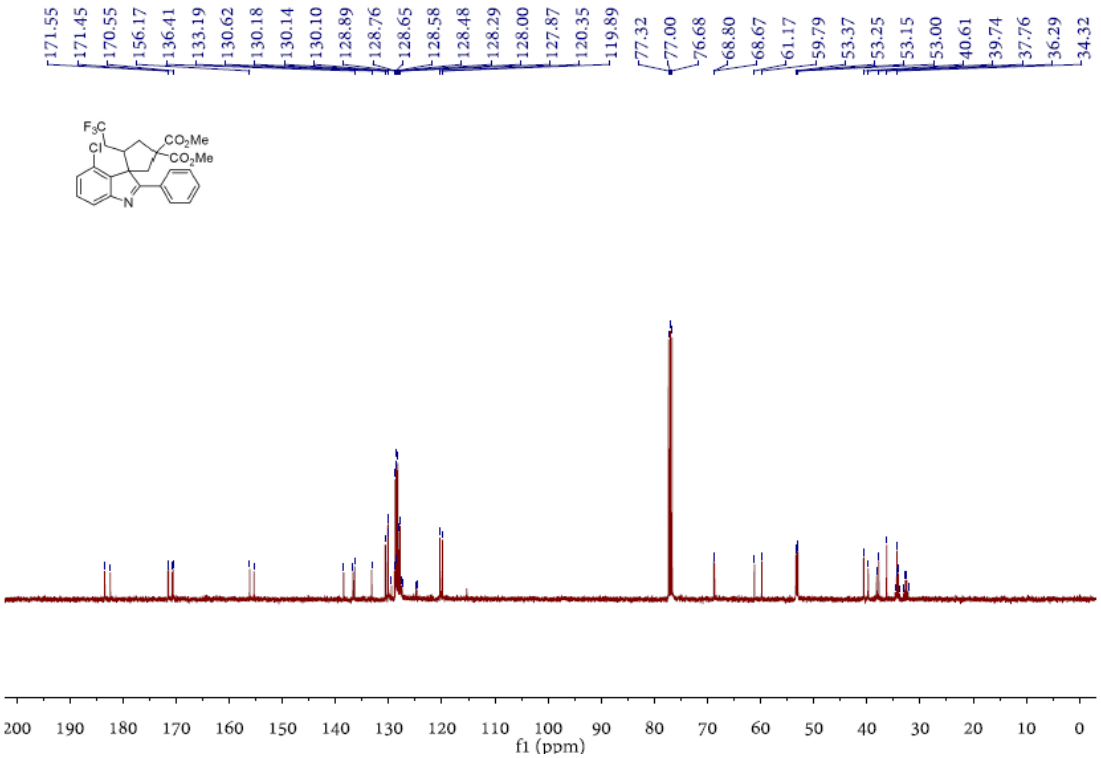
^{19}F NMR Spectrum of **3q**



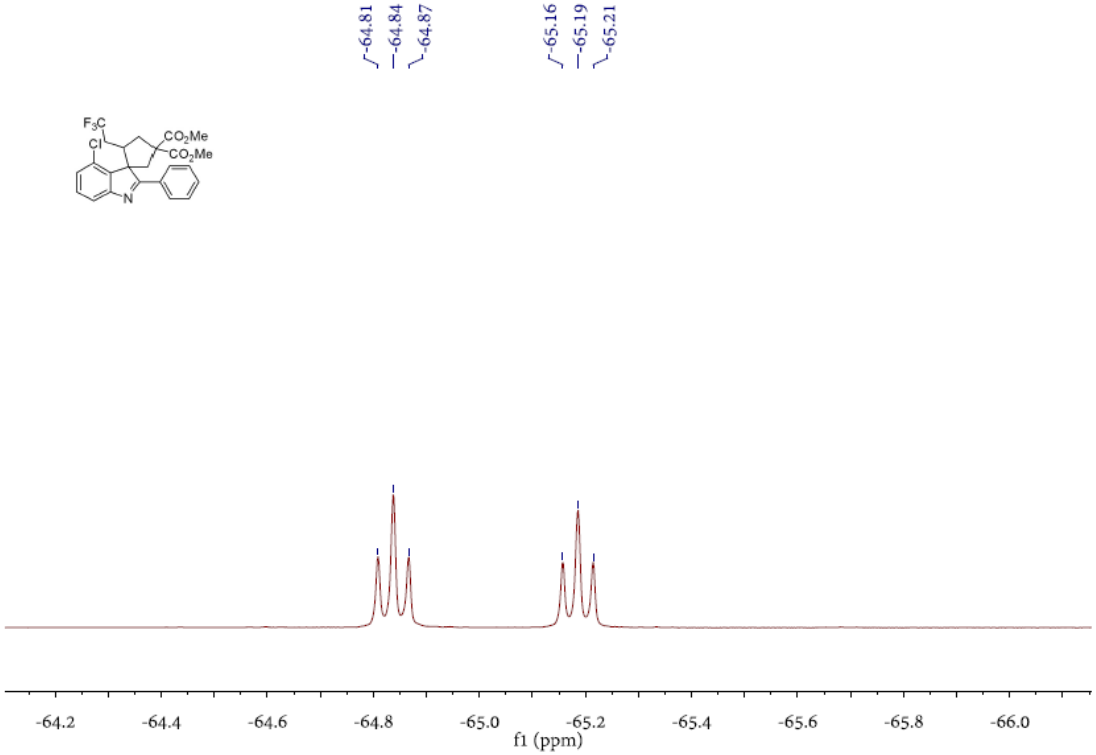
^{1}H NMR Spectrum of **3r**



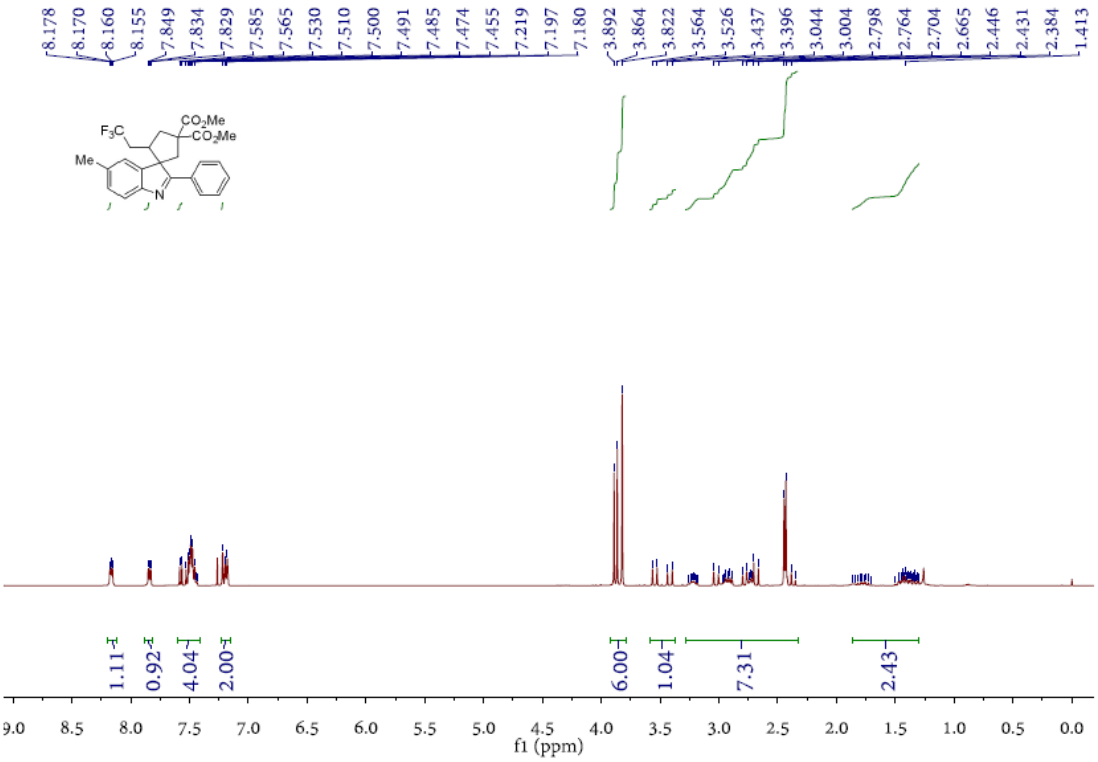
^{13}C NMR Spectrum of **3r**



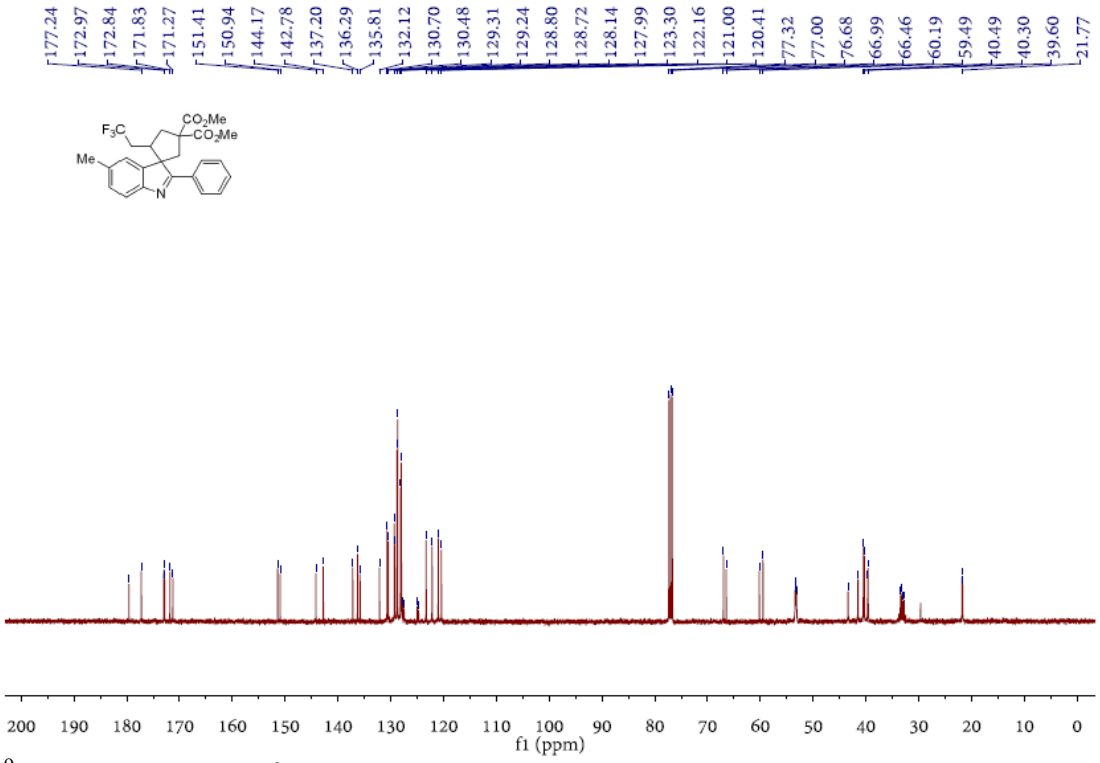
^{19}F NMR Spectrum of **3r**



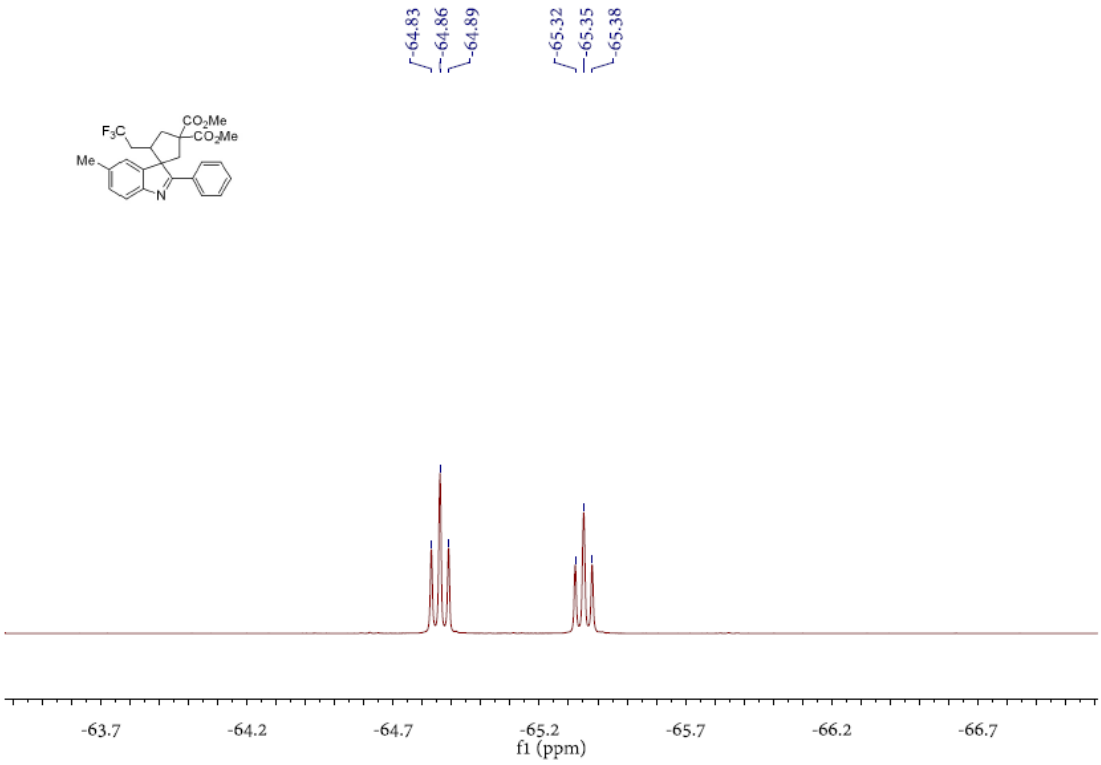
^{1}H NMR Spectrum of **3s**



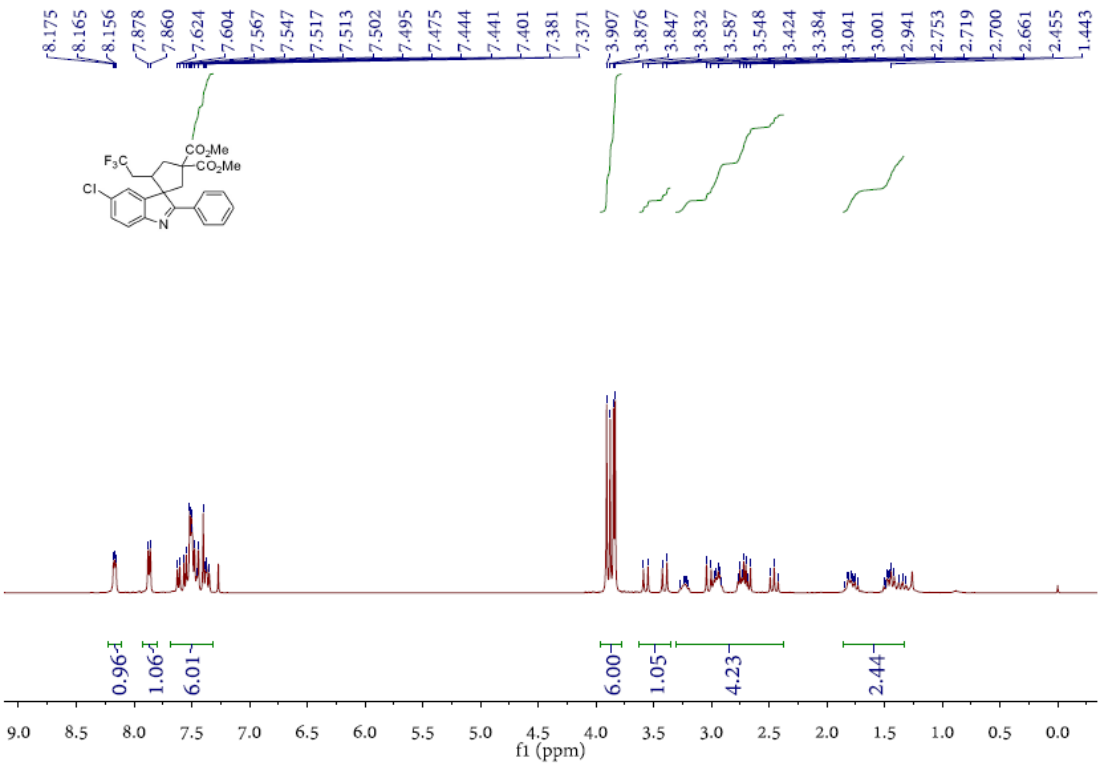
^{13}C NMR Spectrum of **3s**



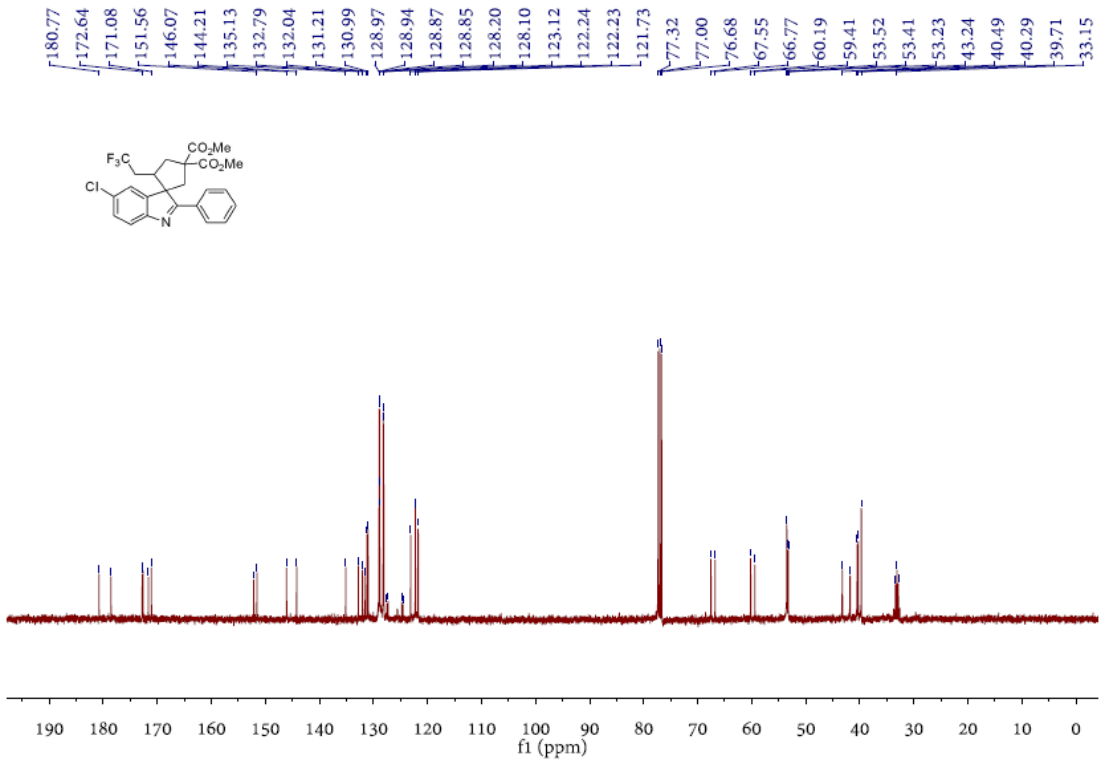
^{19}F NMR Spectrum of **3s**



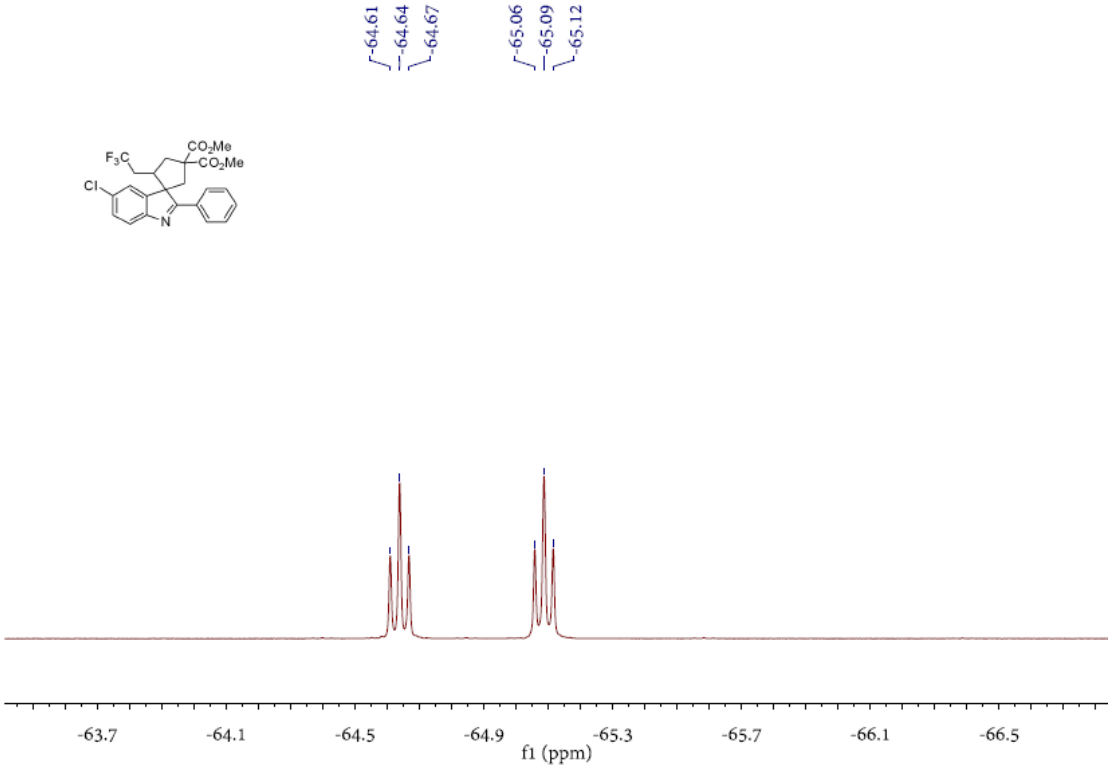
^{1}H NMR Spectrum of **3t**



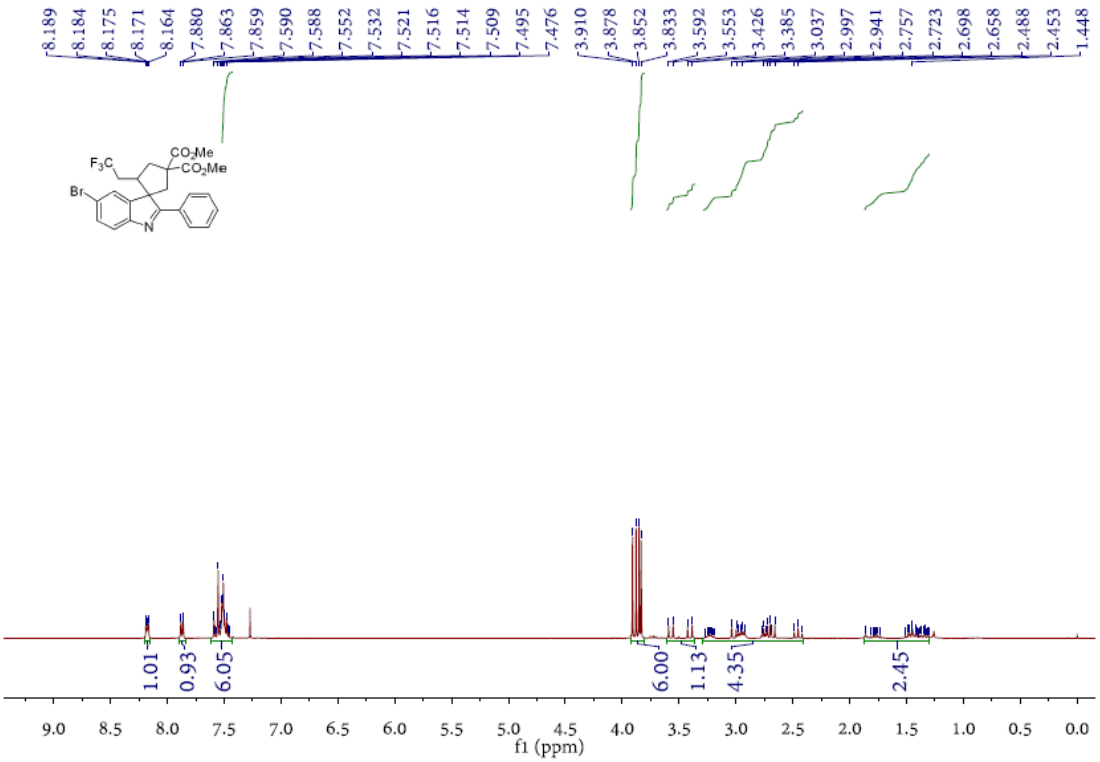
^{13}C NMR Spectrum of **3t**



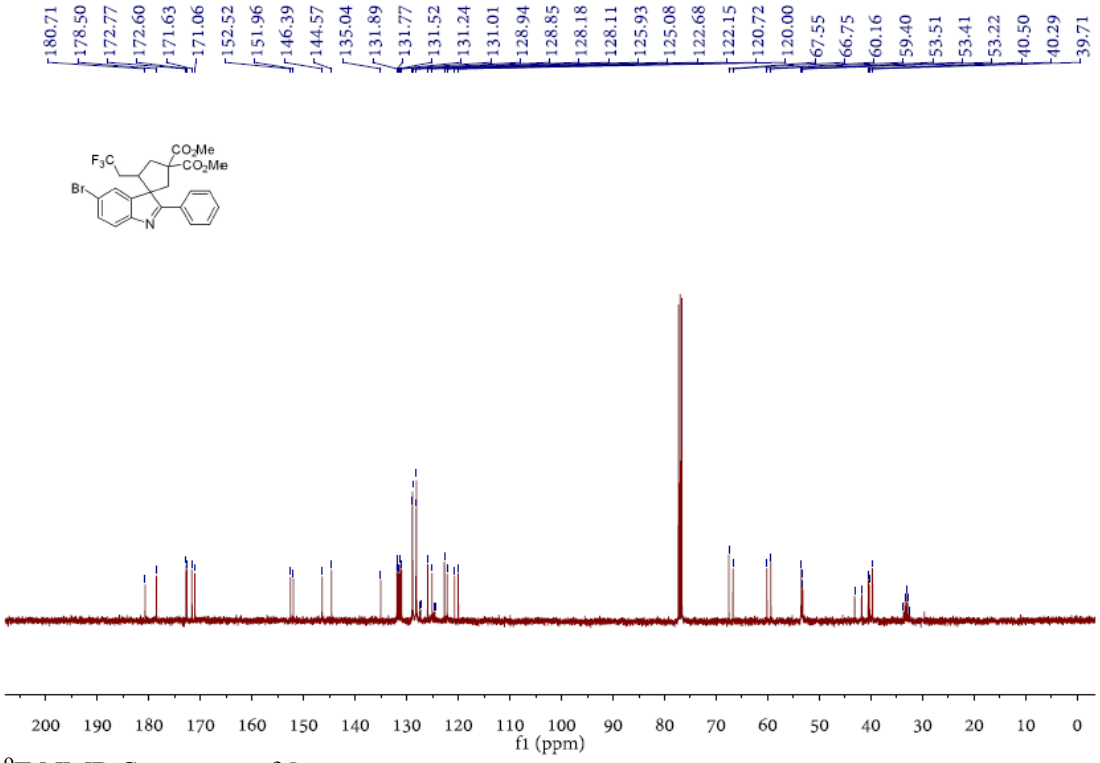
^{19}F NMR Spectrum of **3t**



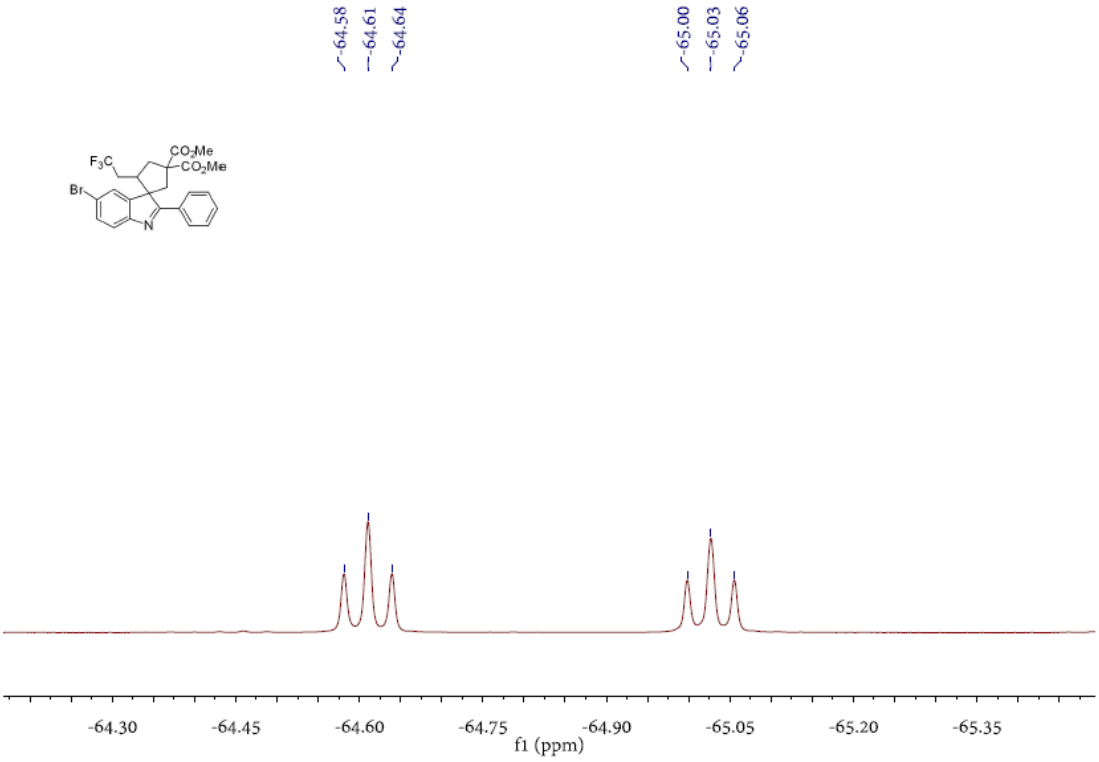
^{1}H NMR Spectrum of **3u**



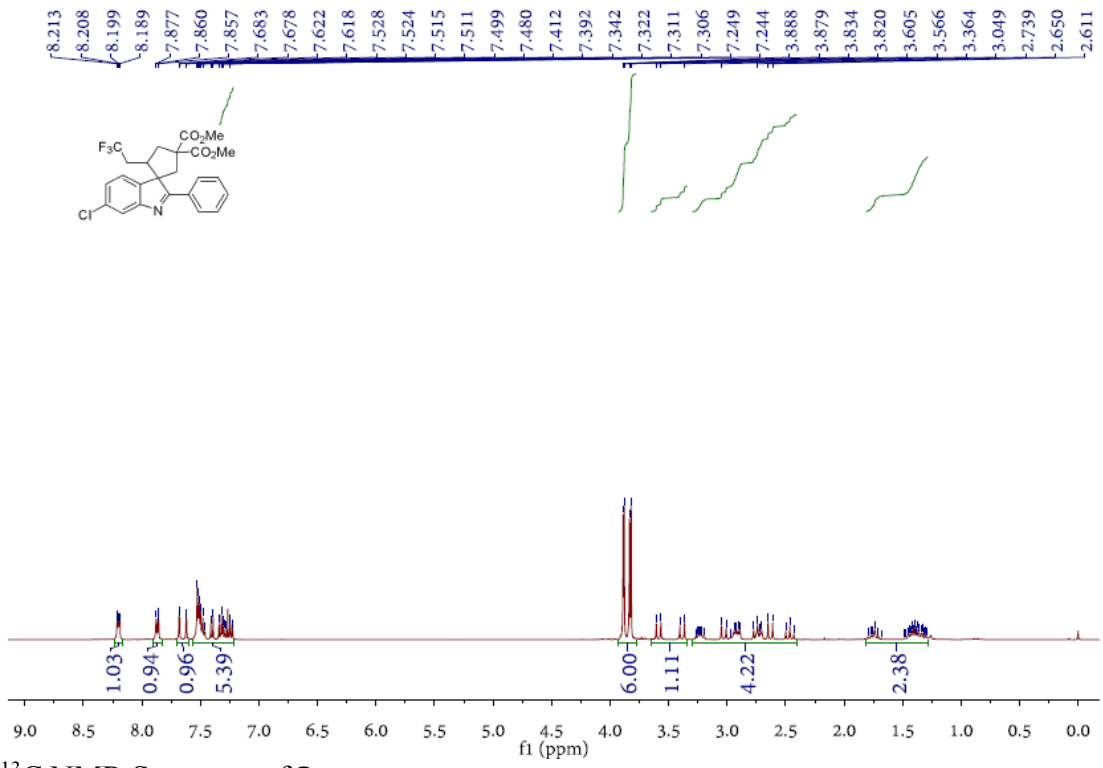
^{13}C NMR Spectrum of **3u**



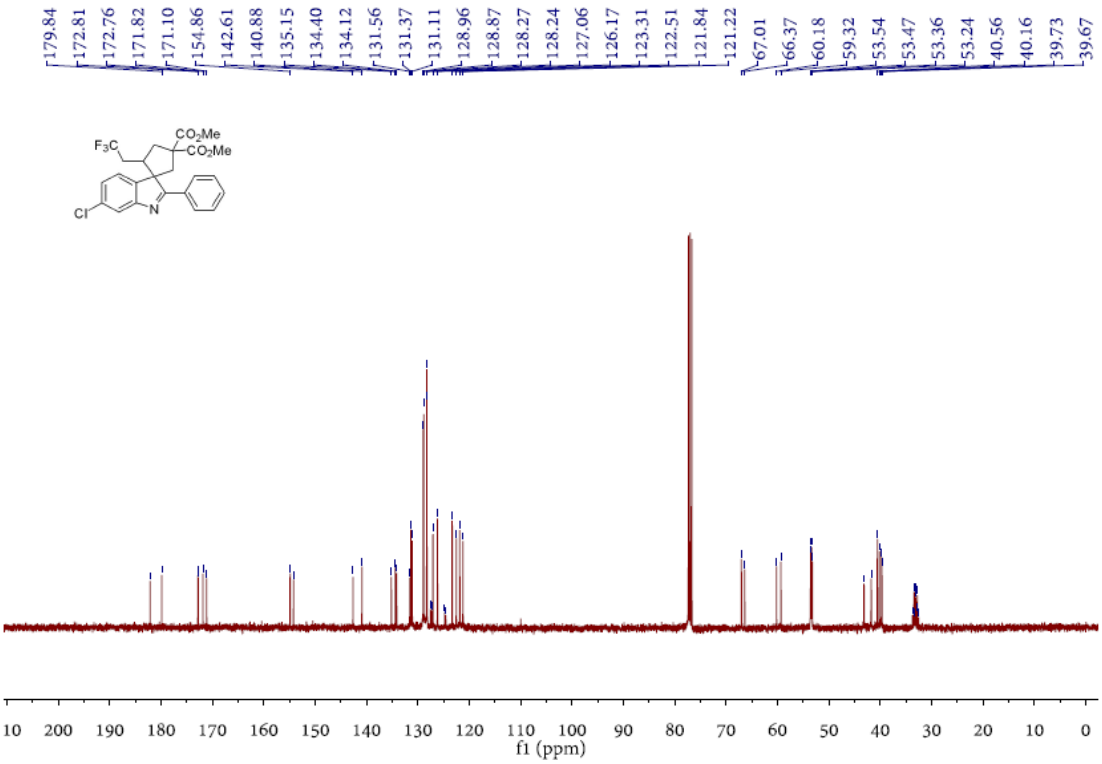
^{19}F NMR Spectrum of **3u**



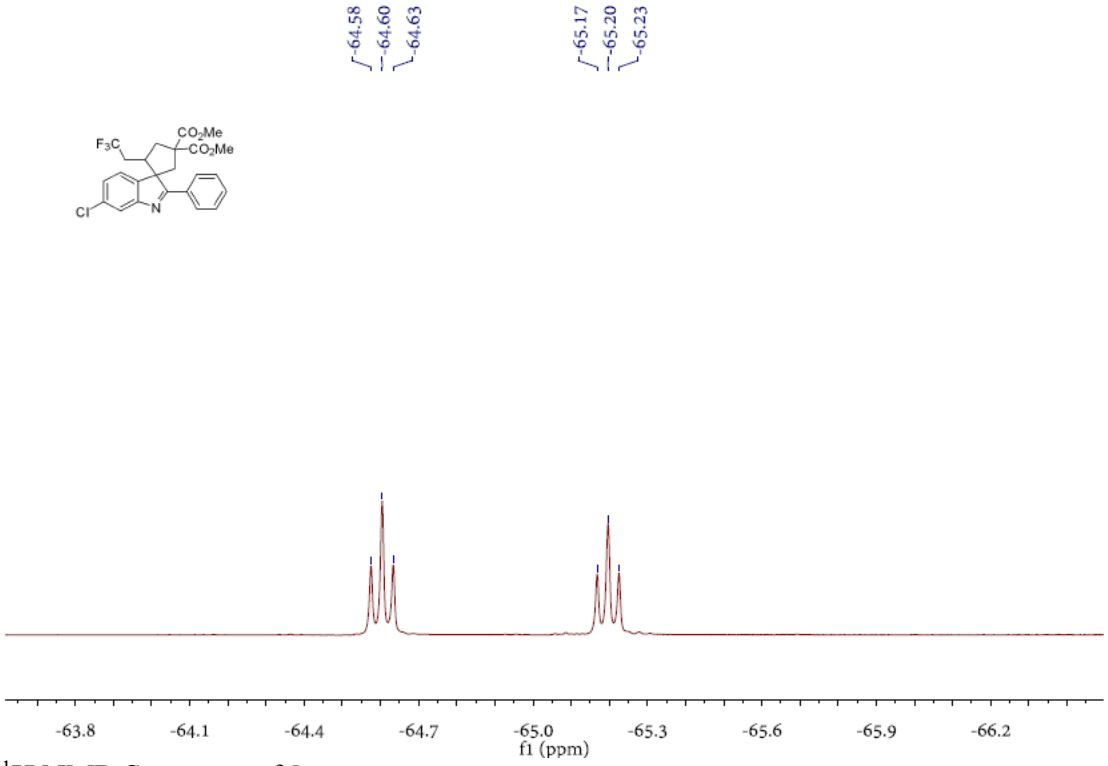
^{1}H NMR Spectrum of **3v**



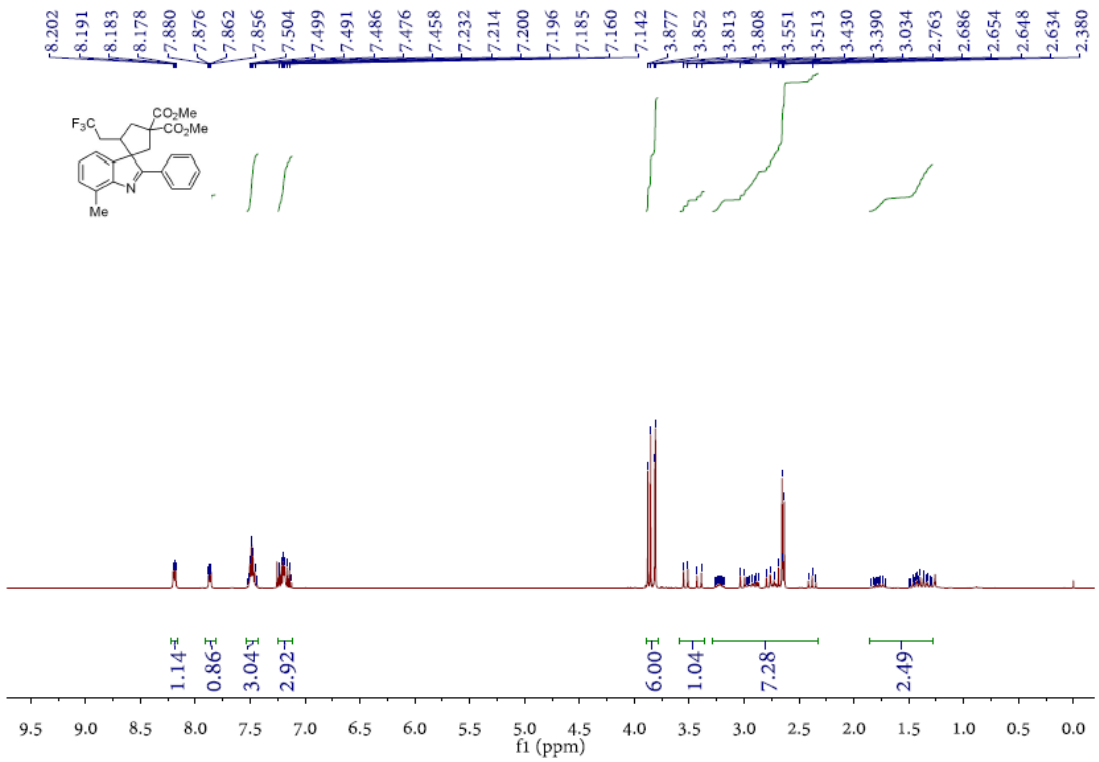
^{13}C NMR Spectrum of **3v**



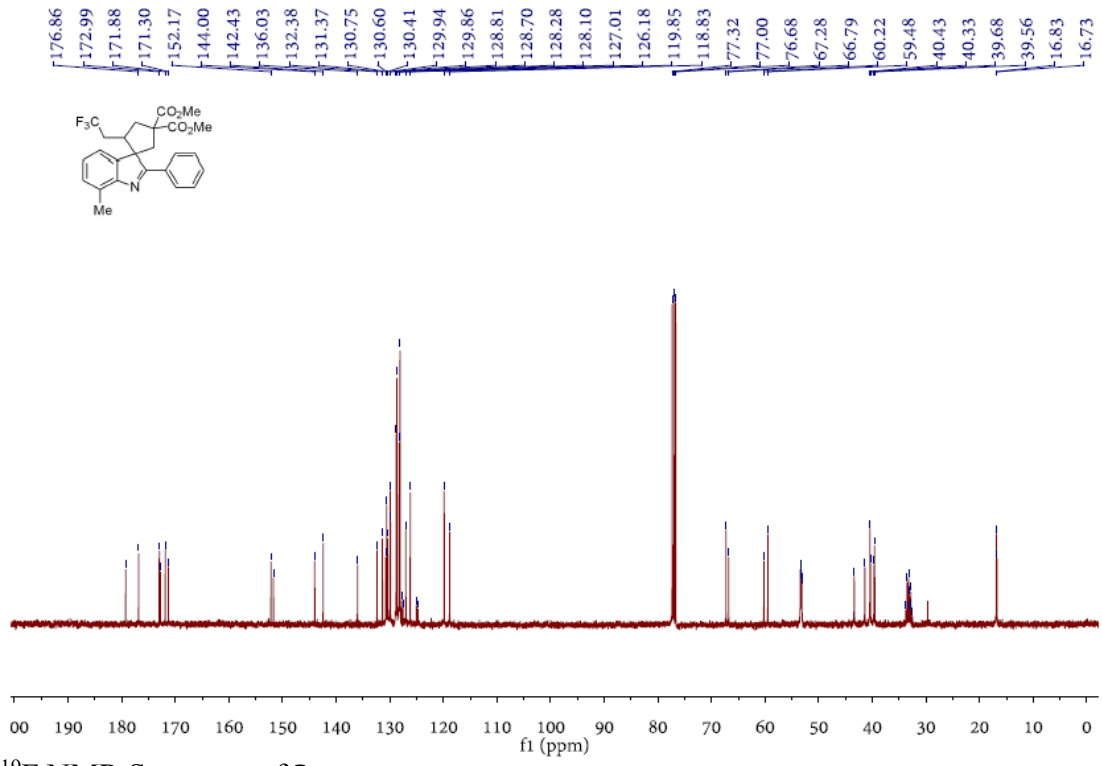
^{19}F NMR Spectrum of **3v**



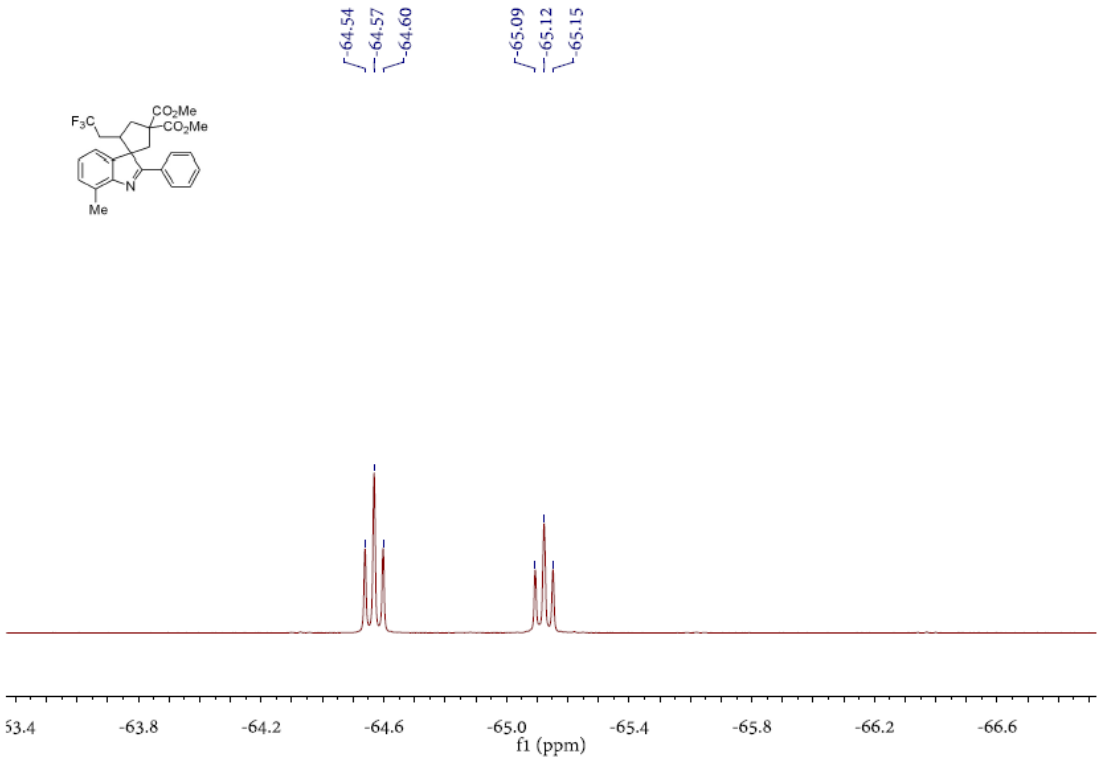
^{1}H NMR Spectrum of **3w**



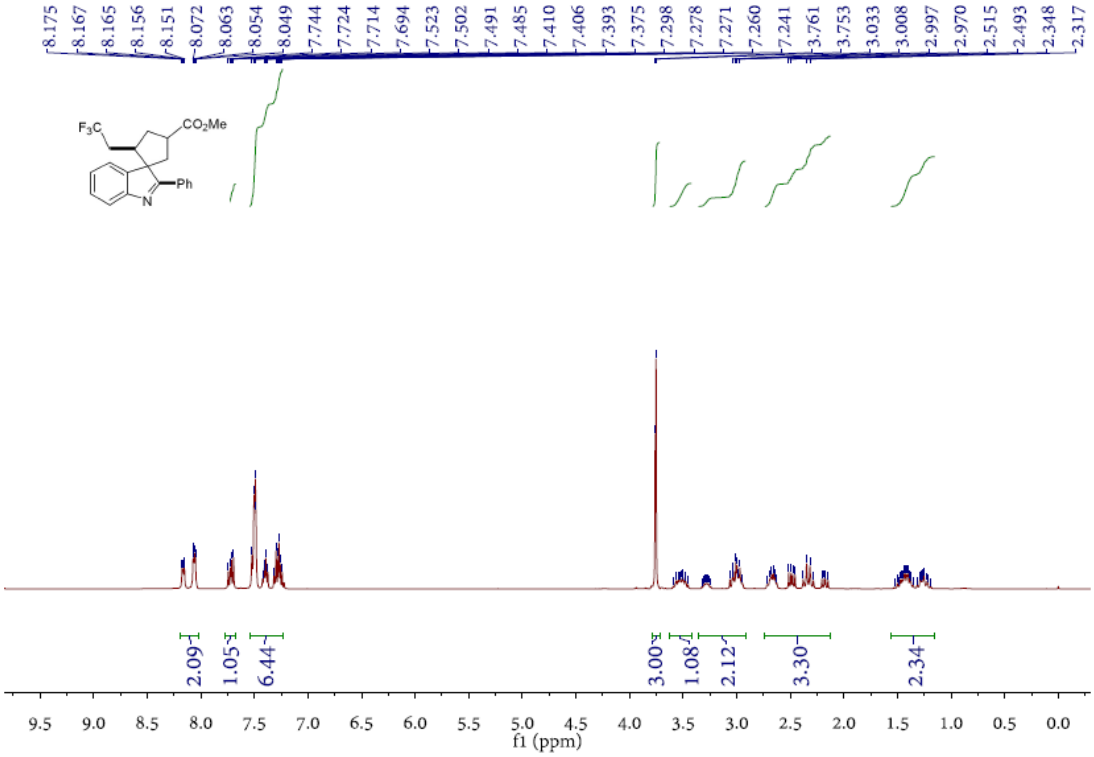
^{13}C NMR Spectrum of **3w**



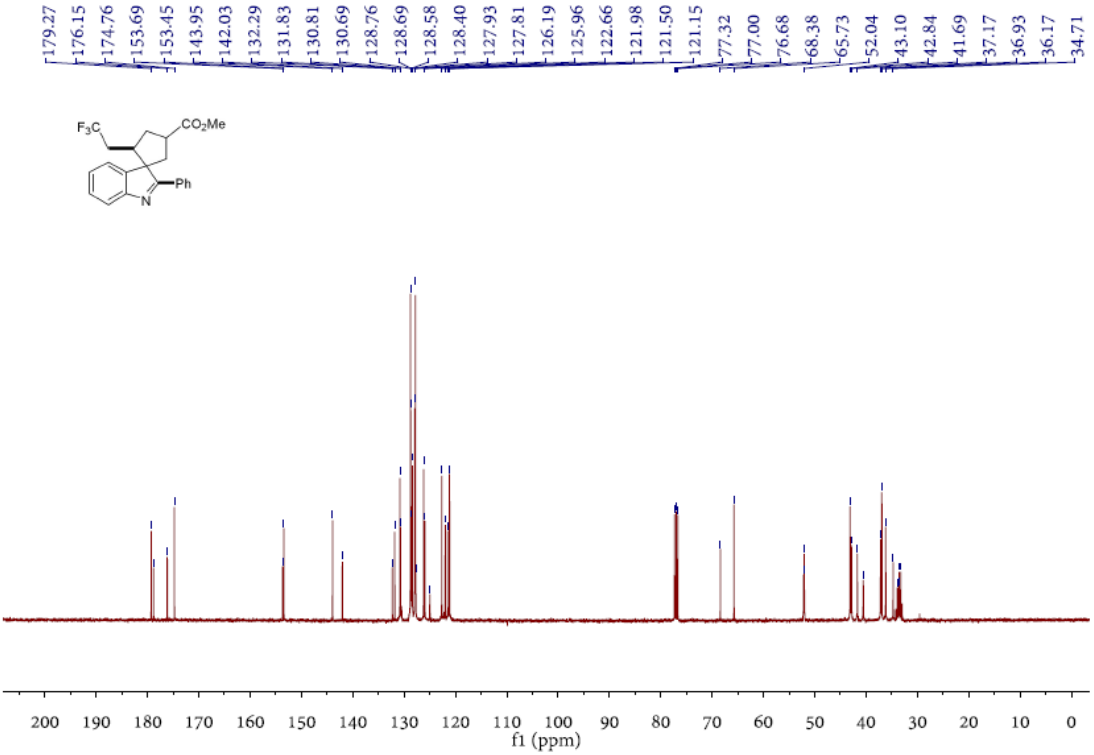
^{19}F NMR Spectrum of **3w**



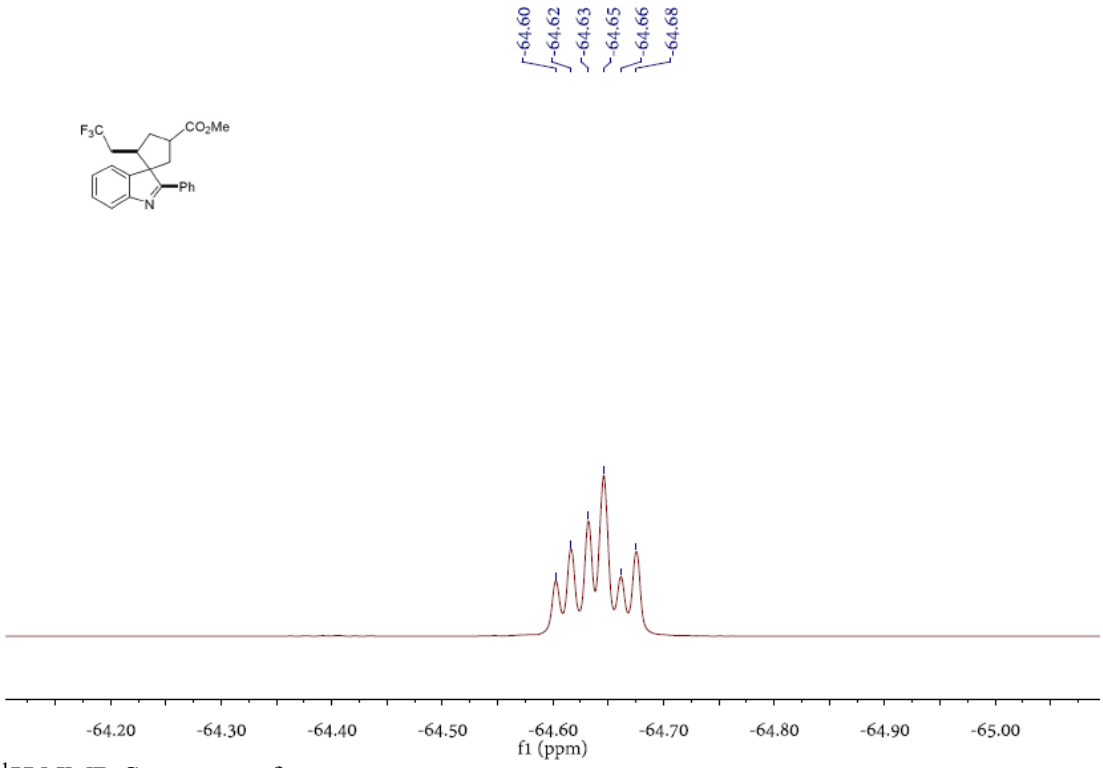
^{1}H NMR Spectrum of **4**



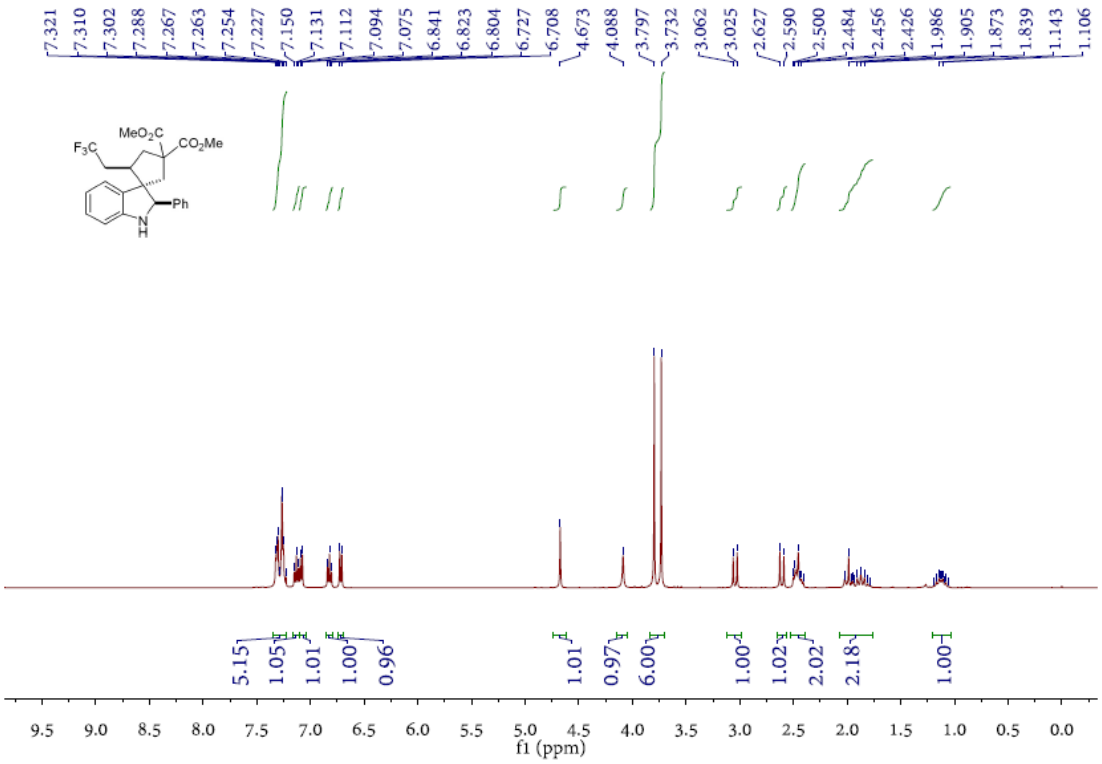
^{13}C NMR Spectrum of **4**



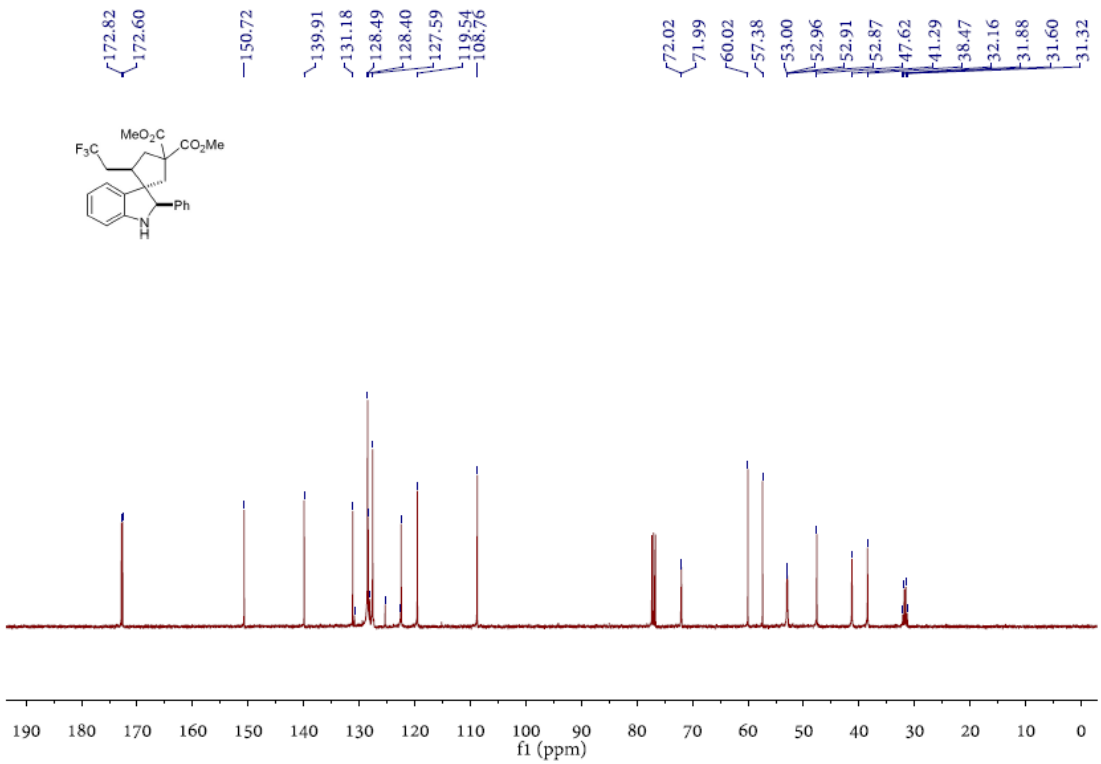
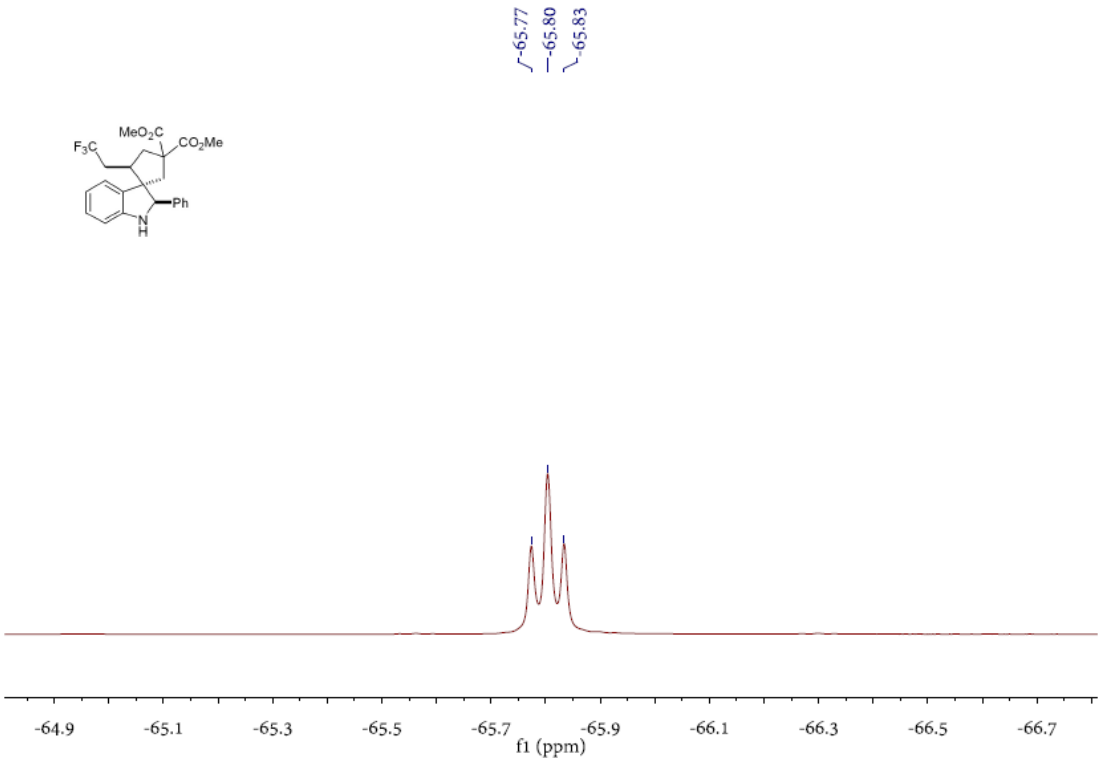
^{19}F NMR Spectrum of **4**



^{1}H NMR Spectrum of **5**



^{13}C NMR Spectrum of **5**



^{19}F NMR Spectrum of **5**