Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Oxidative Coupling of Michael Acceptors with Aryl Nucleophiles produced through Rhodium-Catalyzed C-C Bond Activation

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Supporting Information

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General Methods. All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring. Solvents, including toluene, tetrahydrofuran (THF), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), were purged with argon and passed through two columns of neutral alumina or molecular sieves. Quinolinyl ketones were prepared according to literature precedent.[1,2,3,4] Starting materials were obtained from Alfa Aesar or Aldrich Chemical and used with further purification. Catalysts, specifically $[Rh(C_2H_4)_2Cl]_2$ and $Rh(PPh_3)_3Cl$, were obtained from Strem Chemical, Inc. or Pressure Chemical Co. and utilized without further purification. ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance III 400 MHz spectrometer using standard acquisition parameters.

Method for Synthesis of Quinolinyl Ketones will be illustrated with a specific example. A oven-dried 250 mL round bottomed flask was charged with 8-bromoquinoline (2.81 g, 13.5 mmol) and dissolved in THF under an Ar atmosphere. The reaction was cooled to -78 °C and *n*BuLi (2.5 M in hexanes, 6 mL, 15.0 mmol) was added over approximately 15 minutes. 2-Fluorobenzaldehdye (1.58 mL, 15 mmol) was added via syringe over approximately 10 minutes. Following addition, the reaction was allowed to warm to room temperature and stirred for 2 hours. The reaction mixture was quenched with sat. NH_4Cl (50 mL) and the layers separated. The organic layer was washed with water (20 mL), and the combined aqueous layers were extracted with ether (2 × 50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was dissolved in DMSO (40 mL) and IBX (4.38 g, 15.0 mmol) was added. The solution was allowed to stir at room temperature for 2 hours. A solution of 1:1 EtOAc:H_2O (50 mL) was added and the reaction mixture was filtered through a pad of Celite. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The orange oil was purified by column chromatography (9:1 hexane:EtOAc) to provide the product as an orange oil.

Method A. Oxidative Coupling of Aryl Nucleophiles with Low Boiling Michael Acceptors will be illustrated with a specific example. An oven dried 5 mL pressure tube was charged with

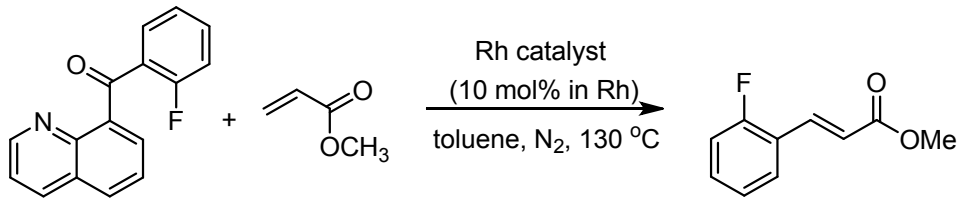
100mg (0.4 mmol) of 2-fluorophenyl quinolinyl ketone **1**. This tube was transferred into an inert atmosphere glovebox, and 7.8 mg $[Rh(C_2H_4)_2Cl]_2$ (0.02 mmol, 5 mol%), 0.36 mL methyl acrylate (4 mmol, 10 equiv) and toluene (1 mL) was added. The pressure tube was sealed, removed from the glove box, and placed in a 130 °C oil bath. After 16 h, the tube was removed from the oil bath and cooled to room temperature. The reaction mixture was filtered through a silica gel-filled pipette using 2 mL of EtOAc for transferring. The solution was concentrated under reduced pressure to yield a yellowish oil that was purified via column chromatography (9:1 hex:EtOAc) to provide the product as a pale yellow oil.

Method B. Oxidative Coupling of Aryl Nucleophiles with Higher Boiling Michael Acceptors will be illustrated with a specific example. An oven dried 5 mL pressure tube was charged with 100mg (0.4 mmol) of 2-fluorophenyl quinolinyl ketone **1**. This tube was transferred into an inert atmosphere glovebox, and 7.8 mg $[Rh(C_2H_4)_2Cl]_2$ (0.02 mmol, 5 mol%), 0.20 mL *N*,*N*-dimethylacrylamide (2 mmol, 5 equiv) and toluene (1 mL) was added. The pressure tube was sealed, removed from the glove box, and placed in a 130 °C oil bath. After 16 h, the tube was removed from the oil bath and cooled to room temperature. The reaction mixture was filtered through a silica gel-filled pipette using 2 mL of EtOAc for transferring. Following filtration, 1 mL of DMF was added, and the mixture was concentrated under reduced pressure. The residue was dissolved in 10 mL Et_2O, washed with 10 mL of H_2O and 10 mL brine, and dried over Na_2SO_4. The solution was concentrated under reduced pressure to yield a dark oil that was purified via column chromatography (9:1 hex:EtOAc) to provide the product as a yellow oil.

Direct Competition Reaction to Assess Reactivity of Michael Acceptors will be illustrated with a specific example. In an inert atmosphere glovebox, 2.6 mg $[Rh(C_2H_4)_2Cl]_2$ (0.0067 mmol, 5 mol%) was added to a resealable NMR tube. A solution of 2-fluorophenl quinolinyl ketone **1** (33 mg, 0.13 mmol) in toluene-d_8 (0.5 mL) was added to the NMR tube, followed by 0.1 mL of methyl acrylate (1 mmol, 2.5 equiv) and 0.10 mL of *N*,*N*-dimethylacrylamide (1 mmol, 2.5 equiv). The NMR tube was sealed and an initial ^{1}H NMR spectrum was acquired. The sample was then placed in a 130 °C oil and periodically removed and analyzed by ^{1}H NMR spectroscopy. This process was repeated until the reaction was complete or no further reaction was observed.

Optimization Data

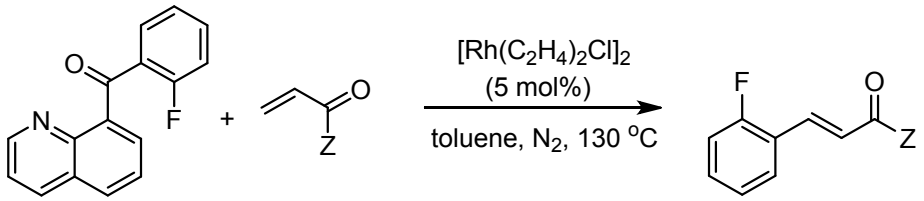
Table S1. Examination of catalysts



Entry[a]	Catalyst	Ligand	Yield (%)[b]
1	$[Rh(C_2H_4)_2Cl]_2$	-	99
2	$Rh(PPh_3)_3Cl$	-	63
3	$Rh(COD)_2BF_4$	-	15
4	$Rh(COD)_2BF_4$	PPh_3 (1:1 w/ Rh)	12
5	$Rh(COD)_2OTf$	-	<5
6	$[Rh(C_2H_4)_2Cl]_2$	PPh_3 (1:1 w/ Rh)	43
7	$[Rh(C_2H_4)_2Cl]_2$	PPh_3 (2:1 w/ Rh)	27

a) Standard reaction conditions: Quinolinyl ketone (0.4 mmol), methyl acrylate (4 mmol, 10 equiv), 5 mol% [Rh], in toluene (1 mL) heated in a sealed tube at 130 °C for 16 hours. *b*) Yield determined by GC/MS.

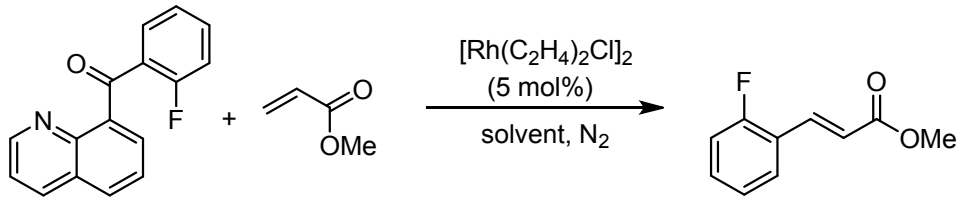
Table S2. Variation of concentration of Michael acceptors



Entry[a]	Z	Equiv of Michael Acceptor	Yield (%)[b]
1	OMe	2	56
2	OMe	5	87
3	OMe	10	99 (79)[c]
4	OMe	20	96
5	NMe_2	1	44
6	NMe_2	2	78
7	NMe_2	5	99 (76)[c]
8	NMe_2	10	94

a) Standard reaction conditions: Quinolinyl ketone (0.4 mmol), Michael Acceptor, 5 mol% $[Rh(C_2H_4)_2Cl]_2$, in toluene (1 mL) heated in a sealed tube at 130 °C for 16 hours. *b*) Yield determined by GC/MS. *c*) Isolated yield.

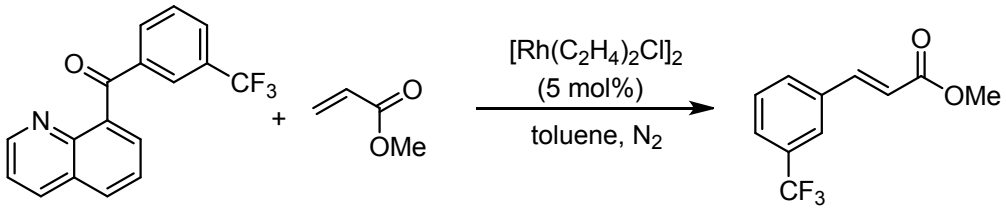
Table S3. Variation of solvent



Entry[a]	Solvent	Temperature (°C)	Yield (%)[b]
1	Toluene	130	99 (79)[c]
2	Xylene	140	87
3	THF	80	57
4	DCE	85	<5
5	DME	85	32
6	CH_2Cl_2	45	<5

a) Standard reaction conditions: Quinolinyl ketone (0.4 mmol), methyl acrylate (4 mmol, 10 equiv), 5 mol% $[Rh(C_2H_4)_2Cl]_2$, in the indicated solvent (1 mL) heated in a sealed tube at the indicated temperature for 16 hours. *b*) Yield determined by GC/MS. *c*) Isolated yield.

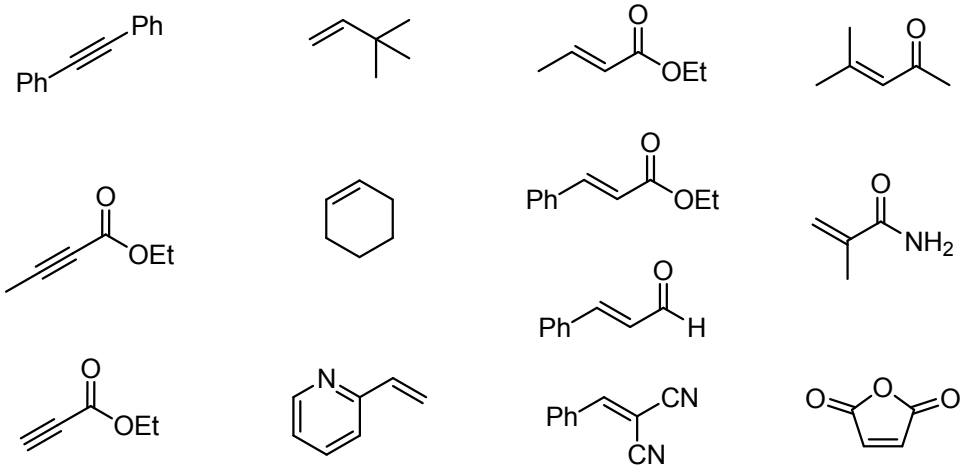
Table S4. Variation of temperature.



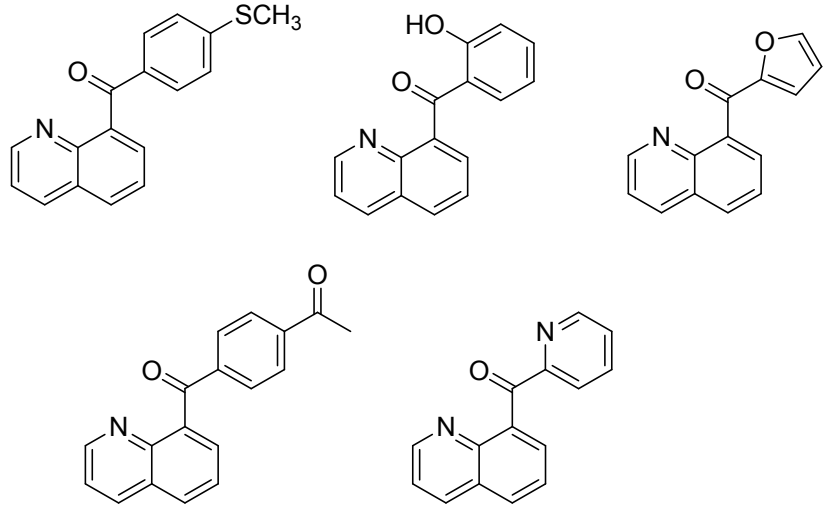
Entry[a]	Temperature (°C)	Yield (%)[b]
1	90	23
2	110	54
3	130	96 (76)[c]
4	140	89
5	150	76

a) Standard reaction conditions: Quinolinyl ketone (0.4 mmol), methyl acrylate (4 mmol, 10 equiv), 5 mol% $[Rh(C_2H_4)_2Cl]_2$, in toluene (1 mL) heated in a sealed tube at the indicated temperature for 16 hours. *b*) Yield determined by GC/MS. *c*) Isolated yield.

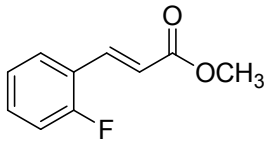
Scheme S1. Substrates attempted under optimized conditions with little or no observed formation of an addition product:



Scheme S2. Quinolinyl ketones attempted under optimized conditions with little or no formation of an addition product:

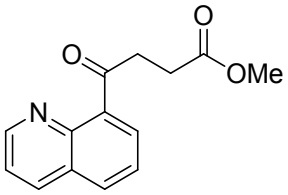


Product Characterization Data

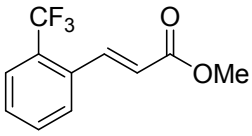


***trans*-methyl 3-(2-fluorophenyl)acrylate (2)** Using general method A, the product was isolated as a pale yellow oil (79% yield) by column chromatography, $R_f = 0.21$ (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, $J = 16.2$ Hz, 1H), 7.54 (td, $J = 7.5$, 1.4 Hz, 1H), 7.40-7.32

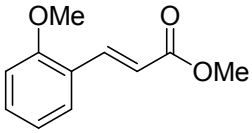
(mult, 1H), 7.16 (t, J =7 .4 Hz, 1H), 7.10 (dd, J = 9.8, 8.6 Hz, 1H), 6.54 (d, J = 16.21, 1H), 3.82 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 167.3, 161.4 (d, J = 255.3 Hz), 137.5 (d, J = 2.9 Hz), 131.7 (d, J = 8.7 Hz), 129.1 (d, J = 2.8 Hz), 124.4 (d, J = 3.7 Hz), 122.5 (d, J = 11.64 Hz), 120.4 (d, J = 6.8 Hz), 116.2 (d, J = 21.9), 51.80. IR (diamond ATR) 2951, 1716, 1637, 1487, 1321, 1277, 1170, 983, 756 cm^{-1}. HRMS for $C_{10}H_{10}FO_2^+$, calcd 181.0659. Found 181.0664.



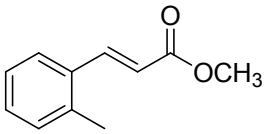
methyl 4-oxo-4-(quinolin-8-yl)butanoate (3) Using general method A, the product was isolated from the reaction of 3-fluoroquinolinyl ketone with methyl acrylate (method A) as a white solid (22% from quinolinyl starting material) via column chromatography, R_f = 0.08 (4:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, J = 3 Hz, 1H), 8.20 (d, J = 7.9 Hz, 1H), 7.96 (t, J = 7.1 Hz, 2H), 7.60 (t, J = 7.9 Hz, 1H), 7.46 (q, J = 4.2 Hz, 1H), 3.73 (t, J = 6.7 Hz, 2H), 3.71 (s, 3H), 2.86 (t, J = 6.7 Hz, 2H). ^{13}C (100 MHz, $CDCl_3$) δ 204.0, 173.7, 150.5, 145.6, 139.1, 136.3, 131.3, 129.6, 128.3, 126.1, 121.4, 51.8, 29.7, 28.7. IR (diamond ATR) 1678, 1632, 1428, 1179, 1036 cm^{-1}. HRMS for $C_{14}H_{14}NO_3^+$, calcd 244.0974. Found 244.0991.



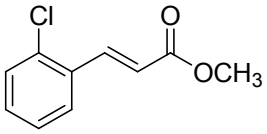
***trans*-methyl 3-(2-(trifluoromethyl)phenyl)acrylate (4)** Using general method A, the product was isolated as a clear yellow oil (34% yield) via column chromatography, R_f = 0.41 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 15.8, 2.1 Hz, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 6.42 (d, J = 15.8 Hz, 1H), 3.83 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 165.5, 139.3 (d, J = 1.8 Hz), 132.2 (d, J = 1.4 Hz), 131.1, 128.6, 127.8 (qrt, J = 30.1 Hz), 126.9, 125.1 (qrt, J = 5.6 Hz), 122.9 (qrt, J = 274.0 Hz), 121.2, 50.9. IR (diamond ATR) 2954, 1719, 1312, 1159, 1106, 1035, 977, 763, 652 cm^{-1}. HRMS for $C_{11}H_9F_3NaO_2^+$, calcd 253.0447. Found 253.0444.



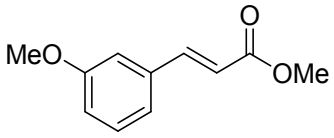
***trans*-methyl 3-(2-methoxyphenyl)acrylate (5)** Using general method A, the product was isolated as a clear yellow oil (38% yield) via column chromatography, R_f = 0.37 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 16.2 Hz, 1H), 7.50 (dd, J = 7.7, 1.6 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.53 (d, J = 16.2 Hz, 1H), 3.89 (s, 3H), 3.80 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 167.9, 158.4, 140.3, 131.5, 128.9, 123.4, 120.7, 118.3, 111.1, 55.5, 51.6. IR (diamond ATR) 2949, 1709, 1630, 1319, 1245, 1160, 1023, 986, 749 cm^{-1}. HRMS for $C_{11}H_{13}O_3^+$, calcd 193.0859. Found 193.0860.



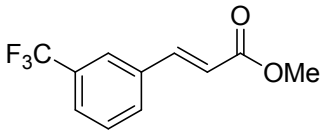
***trans*-methyl 3-(o-tolyl)acrylate (6)** Using general method A, the product was isolated as a yellow oil (12% yield) via column chromatography, R_f = 0.65 (1:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.98 (d, *J* = 15.9 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.32 -7.17 (multi, 3H), 6.36 (d, *J* = 15.9 1H), 3.82 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 142.6, 137.7, 133.4, 130.8, 130.0, 126.4, 126.35, 118.9, 51.7, 19.8. IR (diamond ATR) 2950, 1712, 1632, 1434, 1314, 1269, 978, 783 cm^{-1}. HRMS for $C_{11}H_{13}O_2^+$, calcd 177.0910. Found 177.0919.



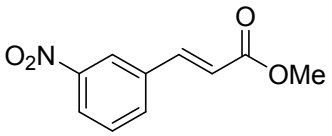
***trans*-methyl 3-(2-chlorophenyl)acrylate (7)** Using general method A, the product was isolated as a yellow oil (77% yield) by column chromatography, R_f = 0.59 (1:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 16.1 Hz, 1H), 7.62 (dd, *J* = 9.1, 1.6, Hz, 1H), 7.42 (d, *J* = 7.5, 1H), 7.30 (mult, 1H), 6.44 (d, *J* = 16.0, Hz, 2H), 3.83 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 166.9, 140.7, 135.0, 132.7, 131.1, 130.2, 127.6, 127.1, 120.5, 51.9. IR (diamond ATR) 2949, 1712, 1635, 1434, 1317, 1286, 1170, 934, 758 cm^{-1}. HRMS for $C_{10}H_9ClNaO_2^+$, calcd 219.0183. Found 219.0182.



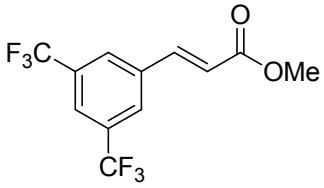
***trans*-methyl 3-(3-methoxyphenyl)acrylate (8)**. Using general method A, the product was isolated as a yellow oil (73% yield) via column chromatograph, R_f = 0.27 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16.4 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 1.8 Hz, 1H), 6.93 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.43 (d, *J* = 16.4 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 167.4, 159.9, 144.8, 135.8, 129.9, 120.8, 118.1, 116.1, 113.0, 55.0, 51.7. IR (diamond ATR) 2975, 2954, 1698, 1523, 1487, 1423, 1225 cm^{-1}. HRMS for $C_{11}H_{13}O_3^+$, calcd 193.0859. Found 193.0854.



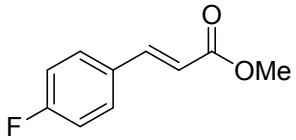
***trans*-methyl 3-(3-(trifluoromethyl)phenyl)acrylate (9)** Using general method A, the product was isolated as a clear yellow oil (76% yield) via column chromatography, R_f = 0.45 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.71 (d, *J* = 16.2 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 166.9, 143.0, 135.2, 131.5 (qrt, *J* = 32.8 Hz), 131.0, 129.5, 126.7 (qrt, *J* = 3.3 Hz), 124.6 (qrt, *J* = 3.9 Hz), 123.7 (qrt, *J* = 274.0 Hz), 119.8, 51.9. IR (diamond ATR) 2954, 1716, 1333, 1162, 1120, 1075, 977, 801, 692, 658 cm^{-1}. HRMS for $C_{10}H_9F_3NaO_2^+$, calcd 253.0447. Found 253.0422.



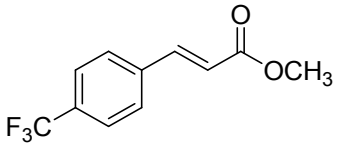
***trans*-methyl 3-(3-nitro)phenyl)acrylate (10)** Using general method A, the product was isolated as a dark oil (68% yield) via column chromatography, R_f = 0.42 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (t, *J* = 1.8 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 16 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 16 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 148.7, 142.0, 136.1, 133.6, 130.0, 124.5, 122.4, 121.0, 52.0. IR (diamond ATR) 3090, 2963, 1740, 1708, 1649, 1539, 1353, 1201, 973 cm^{-1}. HRMS for $C_{10}H_{10}NO_4^+$, calcd 208.0604. Found 208.0613.



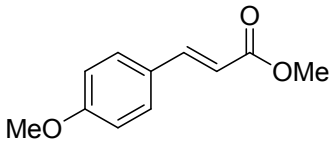
***trans*-methyl 3-(3,5-bis(trifluoromethyl)phenyl)acrylate (11)** Using general method A, the product was isolated as a yellow solid (75% yield), via column chromatography, R_f = 0.58 (2:1 hex:EtOAc). mp = 88 - 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.80 (s, 1H), 7.66 (d, *J* = 16.1 Hz, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 3.77 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 166.3, 141.2, 136.5, 132.5 (qrt, *J* = 33.7 Hz), 127.6 (d, *J* = 3.2 Hz), 123.4 (heptet, *J* = 3.7 Hz), 123.1 (quartet, *J* = 272.8 Hz), 121.8, 52.0. IR (diamond ATR) 3089, 2962, 1716, 1648, 1278, 1116, 906, 667 cm^{-1}. HRMS for $C_{12}H_8F_6NaO_2^+$, calcd 321.0320. Found 321.0301.



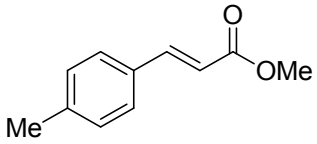
***trans*- methyl 3-(4-fluorophenyl)acrylate (12)** Using general method A, the product was isolated as a white solid (40% yield) via column chromatography, R_f = 0.42 (2:1 hex:EtOAc). mp = 42 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1 H), 7.51 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 166.3, 163.1 (d, *J* = 250.2 Hz) 142.5, 129.6 (d, *J* = 3.3 Hz), 128.9 (d, *J* = 9.8 Hz), 116.5 (d, *J* = 2.8 Hz), 115.0 (d, *J* = 20.2 Hz), 50.7. IR (diamond ATR) 2956, 1705, 1509, 1318, 1160, 1005, 831, 511 cm^{-1}. HRMS for $C_{10}H_9FNaO_2^+$, calcd 203.0479. Found 203.0491.



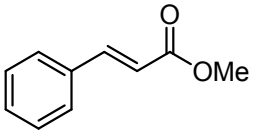
***trans*-methyl 3-(4-(trifluoromethyl)phenyl)acrylate (13)** Using general method A, the product was isolated as a yellow oil (72% yield) by column chromatography, R_f = 0.70 (1:1 hex: EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.9 Hz, 1H), 7.66-7.58 (mult, 4H), 6.51 (d, *J* = 16.9 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 143.0, 137.8, 131.9 (qrt, *J* = 32.8 Hz), 128.2, 125.9 (qrt, *J* = 4.2 Hz), 123.9 (qrt, *J* = 272.1 Hz), 120.4, 52.0. IR (diamond ATR) 3086, 2956, 1709, 1648, 1509, 1274, 1116, 831, 660 cm^{-1}. HRMS for $C_{11}H_9F_3NaO_2^+$, calcd 253.0447. Found 253.0441.



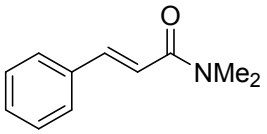
3-(4-methoxyphenyl)-2-propenoic acid methyl ester (14) Using general method A, the product was isolated as a clear solid (21% yield) by column chromatography, $R_f = 0.37$ (2:1 hex:EtOAc). mp = 83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 16.0 Hz, 1H), 7.47 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.31 (d, J = 16.0 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 167.8, 161.4, 144.5, 129.7, 127.1, 115.3, 114.3, 55.4, 51.6. IR (diamond ATR) 2947, 1711, 1599, 1510, 1249, 1168, 981, 819, 525 cm^{-1}. HRMS for $C_{11}H_{12}NaO_3^+$, calcd 215.0679. Found 215.0667.



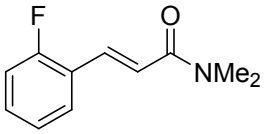
***trans*-3-(4-methylphenyl)-2-propenoic acid methyl ester (15)** Using general method A, the product was isolated as a white solid (46% yield) by column chromatography, $R_f = 0.51$ (2:1 hex:EtOAc). mp = 55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 16.0 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 3.80 (s, 3H), 2.37 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ167.6, 144.9, 140.7, 131.7, 129.6, 128.1, 116.7, 51.6, 21.5. IR (diamond ATR) 2920, 1703, 1631, 1434, 1316, 1166, 998, 814, 509, 491 cm^{-1}. HRMS for $C_{11}H_{13}O_2^+$, calcd 177.0910. Found 177.0922.



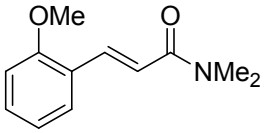
methyl cinnamate (16) Using general method A, the product was isolated as a white solid (38% yield) by column chromatography, $R_f = 0.42$ (1:1 hex:EtOAc). mp = 32 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 15.9 Hz, 1H), 7.56-7.48 (mult, 2H), 7.42-7.36 (mult, 3H), 6.44 (d, J = 15.9 Hz, 1H), 3.81 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 167.4, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7. IR (diamond ATR) 2938, 1710, 1617, 1467, 1134, 817, 538 cm^{-1}. HRMS for $C_{10}H_{11}O_2^+$, calcd 163.0754. Found 163.0749.



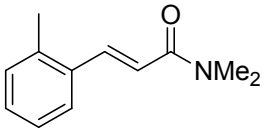
***trans*-*N*,*N*-dimethylcinnamamide (19)** Using general method B, the product was isolated as a white solid (59% yield) by column chromatography, $R_f = 0.12$ (2:1 hex:EtOAc). mp = 91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 15.5 Hz, 1H), 7.53 (dd, J = 9.1, 1.7 Hz, 2H), 7.36 (mult, 3H), 6.89 (d, J =15.4 Hz, 1H), 3.18 (s, 3H), 3.08 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 166.7, 142.3, 135.4, 129.5, 128.8, 127.8, 117.5, 37.4, 35.9. IR (diamond ATR) 2924, 1649, 1598, 1497, 1395, 1138, 995, 766, 708, 682 cm^{-1}. HRMS for $C_{11}H_{14}NO^+$, calcd 176.0170. Found 176.1082.



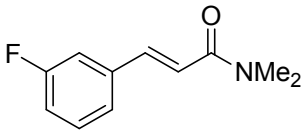
***trans*-3-(2-fluorophenyl)-*N,N*-dimethylacrylamide (20)** Using general method B, the product was isolated as a yellow oil (76% yield) via column chromatography, $R_f = 0.13$ (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 15.6 Hz, 1H), 7.50 (t, *J* = 15.1, 7.6 Hz, 1H), 7.31 (mult, 1H), 7.14 (t, *J* = 15.1, 7.4 Hz, 1H), 7.09 (mult, 1H), 7.03 (d, *J* = 15.7 Hz, 1H), 3.17 (s, 3H), 3.08 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 160.0, 155.1 (d, *J* = 273 Hz), 133.3, 130.7 (d, J=8.7 Hz), 129.9, 124.3 (d, J= 3.7), 122.5, 120.6 (d, J= 8.0 Hz), 116.1 (d, J= 22 Hz), 30.9, 30.6. IR (diamond ATR) 2968, 2942, 1643, 1602, 1476, 1386, 1106, 943. HRMS for $C_{11}H_{13}FNO^+$, calcd 194.0976. Found 194.0987.



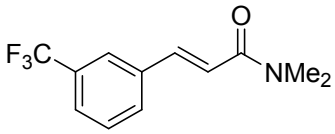
***trans*-3-(2-methoxyphenyl)-*N,N*-dimethylacrylamide (21)** Using general method B, the product was isolated as a viscous yellow oil (43% yield) via column chromatography, $R_f = 0.15$ (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 15.4, 1H), 7.49 (d, *J* = 7.6, 1H), 7.30 (t, *J* = 17.0, 8.4, 1H), 7.00 (d, *J* = 15.6, 1H), 6.94 (t, *J* = 15.1, 7.5, 1H), 6.90 (d, *J* = 8.3, 1H), 3.87 (s, 3H), 3.16 (s, 3H), 3.06 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 167.3, 158.2, 137.9, 130.5, 129.6 128.9, 120.6, 118.5, 111.1, 55.5, 37.5, 35.9. IR (diamond ATR) 2929, 1644, 1596, 1392, 1244, 1137, 1023, 750. HRMS for $C_{12}H_{16}NO_2^+$, calcd 206.1176. Found 206.1183.



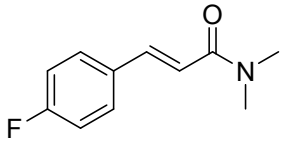
***trans*-*N,N*-dimethyl-3-(o-tolyl)acrylamide (22)** Using general method B, the product was isolated as a yellow oil (72% yield) via column chromatography, $R_f = 0.22$ (1:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 15.3 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 7.22 (m, 3 H), 6.79 (d, *J* = 15.3 Hz, 1 H), 3.17 (s, 3 H), 3.08 (s, 3 H), 2.43 (s, 3 H). ^{13}C (100 MHz, $CDCl_3$) δ 165.7, 139.2, 136.4, 133.5, 129.7, 128.3, 125.1, 125.1, 117.8, 36.4, 34.9, 18.8. IR (diamond ATR) 2929, 1645, 1598, 1487, 1393, 1137, 975, 761, 592, 445 cm^{-1}. HRMS for $C_{12}H_{15}NNaO^+$, calcd 212.1046. Found 212.1026.



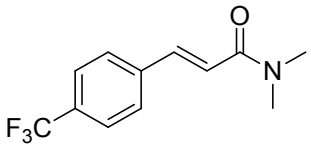
***trans*-3-(3-fluorophenyl)-*N,N*-dimethylacrylamide (23)** Using general method B, the product was isolated as a yellow solid (71% yield) via column chromatography, $R_f = 0.19$ (2:1 hex: EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16, 1H), 7.37-7.27 (mult, 2H), 7.22 (d, *J* = 9.9 Hz, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 16 Hz, 1H), 3.18 (s, 3H), 3.08 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 166.3, 163.1 (d, *J* = 248 Hz), 141.0 (d, *J* = 2 Hz), 137.7 (d, *J* = 8 Hz), 130.3 (d, *J* = 8 Hz), 123.9 (d, *J* = 2 Hz), 118.8, 116.4 (d, *J* = 21 Hz), 113.9 (d, *J* = 22 Hz), 37.4, 36.0. IR (diamond ATR) 2976, 1647, 1615, 1230, 1172, 982, 801. HRMS for $C_{11}H_{13}FNO^+$, calcd 194.0976. Found 194.0968.



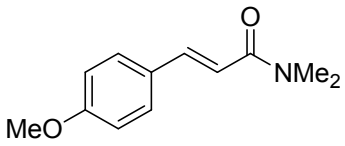
***trans*-3-(3-tifluoromethylphenyl)-*N,N*- dimethylacrylamide (24)** Using general method B, the product was isolated as a yellow solid (68% yield) via column chromatography, R_f = 0.17 (1:1 hex: EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.68 (d, *J* = 16, 1H), 7.67 (d, *J* = 8 Hz, 1H), 7.60 (d, *J* = 8 Hz, 1H), 7.50 (t, *J* = 7 Hz, 1H), 6.95 (d, *J* = 16 Hz, 1H), 3.20 (s, 3H), 3.09 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 166.3, 140.7, 136.2, 131.4 (q, J=33 Hz), 131.2, 129.34, 126.0 (qrt, *J* = 4 Hz), 124.0 (qrt, *J* = 270 Hz), 123.9 (qrt, *J* = 4 Hz), 119.3, 35.9. IR (diamond ATR) 2925, 1649, 1612, 1330, 1160, 1121, 1098, 982, 802, 695. HRMS for $C_{12}H_{13}F_3NO^+$, calcd 244.0944. Found 244.0929.



***trans*-3-(4-fluorophenyl)-*N,N*-dimethylacrylamide (25)** Using general method B, the product was isolated as a yellow solid (20% yield) via column chromatography, R_f = 0.13 (2:1 hex:EtOAc). mp = 95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 15.4 Hz, 1H), 7.55-7.48 (mult, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 15.5 Hz, 1H), 3.18 (s, 3H), 3.07 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 166.5, 163.5 (d, *J* = 249 Hz), 141.1, 131.6 (d, *J* = 3.4 Hz), 129.6 (d, *J* = 8.3 Hz), 117.2 (d, *J* = 2.3 Hz), 115.9 (d, *J* = 21.9 Hz), 37.4, 36.0. IR (diamond ATR) 2923, 1649, 1598, 1508, 1135, 987, 833, 510 cm^{-1}. HRMS for $C_{11}H_{13}FNO^+$, calcd 194.0976. Found 194.0979.

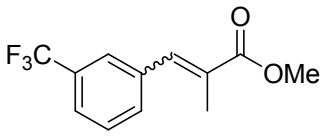


***trans*-*N,N*-dimethyl-3-(4-(trifluoromethyl)phenyl)acrylamide (26)** Using general method B, the product was isolated as a white solid (71% yield) via column chromatography, R_f = 0.10 (1:1 Hex:EtOAc). mp = 81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 15.1 Hz, 1H), 7.63 (s, 4H), 6.97 (d, *J* = 15.7 Hz, 1H), 3.19 (s, 3H), 3.09 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 171.2, 166.1, 140.6, 131.1 (qrt, *J* = 32.0 Hz), 128.7 (qrt, *J* = 271 Hz), 128.0, 125.8 (qrt, *J* = 3.8 Hz), 120.0, 37.5, 36.0. IF (diamond ATR) 3010, 2987, 2978, 1711, 1628, 1428, 1328 cm^{-1}. HRMS for $C_{12}H_{13}F_3NO^+$, calcd 244.0944. Found 244.0951.

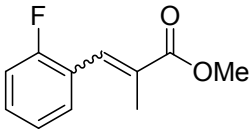


3-(4-methoxyphenyl)-*N,N*-dimethyl-2-propenamide (27) Using general method B, the product was isolated as a white solid (79% yield) by column chromatography, R_f = 0.09 (1:1 hex:EtOAc). mp = 77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 15.4 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J*= 8.7 Hz, 2H), 6.76 (d, *J* = 15.4 Hz, 1H), 3.83 (s, 3H), 3.16 (s, 3H), 3.06 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 167.0, 160.8, 142.0, 129.3, 128.1, 115.0, 114.2, 55.3,

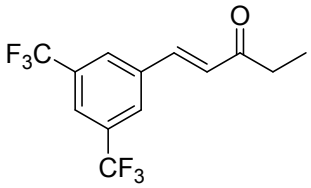
37.4, 35.9. IR (diamond ATR) 2931, 1597, 1509, 1249, 1135, 981, 814, 511 cm^{-1}. HRMS for $C_{12}H_{16}NO_2^+$, calcd 206.1176. Found 06.1182.



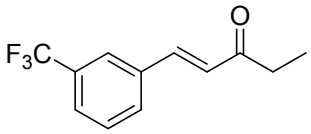
methyl 2-methyl-3-(3-(trifluoromethyl)phenyl)acrylate (30) Using general method A, the product was isolated (as an E/Z mixture) as a pale yellow oil (31% yield) via column chromatography, $R_f = 0.51$ (2:1 hex: EtOAc). ^1H NMR (400 MHz, $CDCl_3$) *E* isomer: δ 7.69 (s, 1H), 7.49 (m, 3H), 6.28 (s, 1H), 3.74 (s, 3H), 2.11 (d, $J = 1.4$ Hz, 3H). *Z* isomer: 7.62 (s, 1H), 7.49 (m, 3H), 5.52 (t, $J = 1.2$ Hz, 1H), 3.84 (s, 3H), 3.69 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 168.7, 167.0, 139.7, 139.3, 137.2, 136.6, 132.6, 132.4, 130.2, 128.9, 128.8, 126.9, 126.2, 126.1, 125.7, 124.9, 124.8, 123.4, 123.3, 52.2, 52.0, 37.9, 29.7, 14.0. IR (diamond ATR) 2955, 1716, 1327, 1116, 1073, 833, 699, 657. HRMS for $C_{12}H_{11}F_3NaO_2^+$, calcd 267.0603. Found 267.0596.



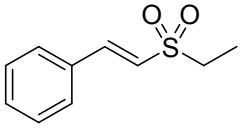
methyl 3-(2-fluorophenyl)-2-methylacrylate (31) Using general method A, the product was isolated as a yellow oil (25% yield) via column chromatography, $R_f = 0.48$ (2:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ *E* isomer: δ 7.71 (s, 1H); 7.40-7.00 (m, 4H), 3.83 (s, 3H), 2.05 (t, $J = 1.3$ Hz, 3H). *Z*: δ 7.00-7.70 (m, 4H), 5.44 (s, 1H), 3.76 (s, 3H), 3.65 (br s, 3H). *Z* isomer: δ 7.40-7.00 (m, 4H), 6.26 (s, 1H). ^{13}C (100 MHz, $CDCl_3$) δ 168.6, 167.2, 161.0 (d, $J = 248$ Hz), 160.3 (d, $J = 248$ Hz), 138.5, 131.7 (d, $J = 3$ Hz), 131.3 (d, $J = 3$ Hz), 130.7, 130.5 (d, $J = 2$ Hz), 130.1 (d, $J = 8$ Hz), 128.3 (d, $J = 8$ Hz), 126.4, 124.0 (d, $J = 4$ Hz), 123.8 (d, $J = 4$ Hz), 115.7 (d, $J = 22$ Hz), 115.4 (d, $J = 22$ Hz), 52.1, 52.0, 31.1, 31.0, 14.3. IR (diamond ATR) 2952, 1716, 1485, 1455, 1257, 1192, 948, 801. HRMS for $C_{11}H_{11}FNaO_2^+$, calcd 217.0635. Found 217.0650.



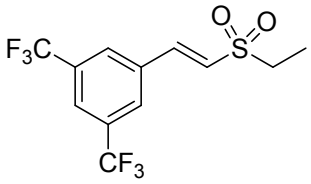
***trans*-1-(3,5-bis(trifluoromethyl)phenyl)pent-1-en-3-one (32)** Using general method A, the product was isolated as a white solid (56% yield) via column chromatography, $R_f = 0.45$ (4:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.88 (s, 1H), 7.59 (d, $J = 16$, 1H), 6.87 (d, $J = 16$ Hz, 1H), 2.73 (qrt, $J = 7$ Hz, 2H), 1.14 (t, $J = 7$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 138.3, 136.8, 132.5 (qrt, $J = 34$ Hz), 128.9, 127.8, 123.4 (m), 123.1 (qrt, $J = 270$ Hz), 34.9, 7.9. IR (diamond ATR) 1702, 1626, 1376, 1275, 1122, 1107, 1037, 994, 903, 844, 683. HRMS for $C_{13}H_{10}F_6NaO^+$, calcd 319.0528. Found 319.0516.



***trans*-1-(3-(trifluoromethyl)phenyl)pent-1-en-3-one (33)** Using general method A, the product was isolated as a white solid (75% yield) via column chromatography, $R_f = 0.36$ (4:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.72 (d, J = 8 Hz, 1H), 7.63 (d, J = 8 Hz, 1H), 7.57 (d, J = 16 Hz, 1H), 7.53 (t, J = 7Hz, 1H), 6.80 (d, J = 16 Hz, 1H), 2.72 (qrt, J = 7 Hz, 2H), 1.18 (t, J = 7Hz, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 200.4, 140.3, 135.5, 131.5 (qrt, J = 33 Hz), 131.3, 129.5, 127.5, 126.7 (qrt, J = 4 Hz), 124.7 (qrt, J = 4 Hz), 123.9 (q, J=270 Hz), 34.5, 8.1. IR (diamond ATR) 1670, 1617, 1330, 1164, 1117, 1069, 974, 803, 694 cm^{-1}. HRMS for $C_{12}H_{11}F_3NaO^+$, calcd 251.0654. Found 251.0637.

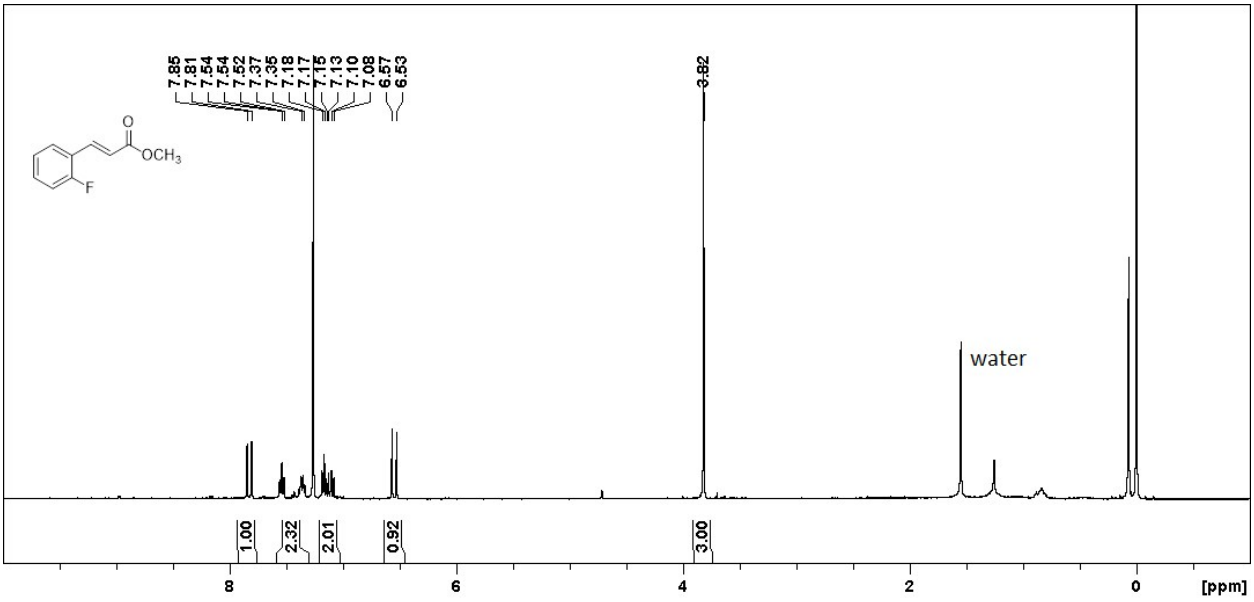


***trans*-(2-(ethylsulfonyl)vinyl)benzene (34)** Using general method B, the product was isolated as a yellow solid (49% yield) via column chromatography, $R_f = 0.29$ (1:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 15.5 Hz, 1H), 7.52 (d, J = 7.6 Hz, 2H), 7.23 (t, J = 8.1 Hz, 2H), 6.81 (d, J = 15.4 Hz, 1H), 3.09 (qrt, J = 7.5 Hz, 2H), 1.39 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 132.3, 131.4, 129.2, 128.6, 124.0, 49.5, 7.3. IR (diamond ATR) 3051, 2944, 1593, 1449, 1273, 1119, 750. HRMS for $C_{10}H_{12}NaO_2S^+$, calcd 219.0450. Found 219.0437.

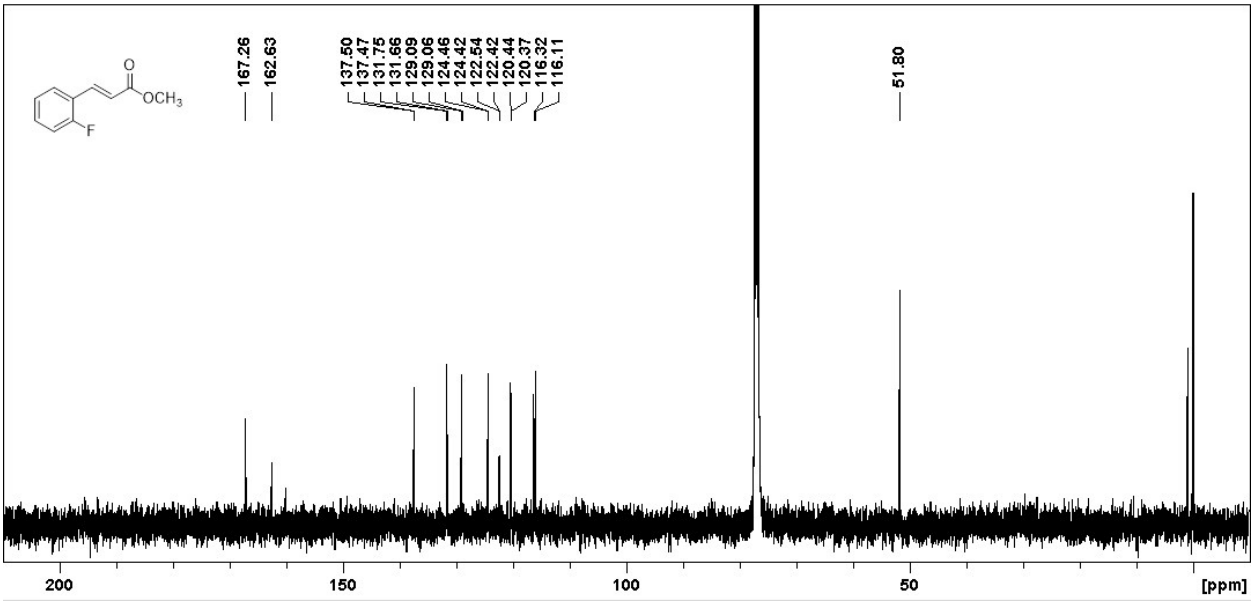


***trans*-1-(2-(ethylsulfonyl)vinyl)-3,5-bis(trifluoromethyl)benzene (35)** Using general method B, the product was isolated as a white solid (67%) via column chromatography, $R_f = 0.16$ (4:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (m, 3H), 7.68 (d, J = 16 Hz, 1H), 7.02 (d, J = 16 Hz, 1H), 3.14 (qrt, J = 7 Hz, 2H), 1.41 (t, J = 7 Hz, 3H). ^{13}C (100 MHz, $CDCl_3$) δ 141.4, 134.3, 132.8 (qrt, J = 44 Hz), 128.4, 128.1 (d, J = 2.6 Hz), 124.4 (m), 122.8 (qrt, J = 275 Hz), 49.2, 7.1. IR (diamond ATR) 1634, 1417, 1279, 1116, 761, 681, 543 cm^{-1}. HRMS for $C_{12}H_{10}F_6NaO_2S^+$, calcd 355.0198. Found 355.0190.

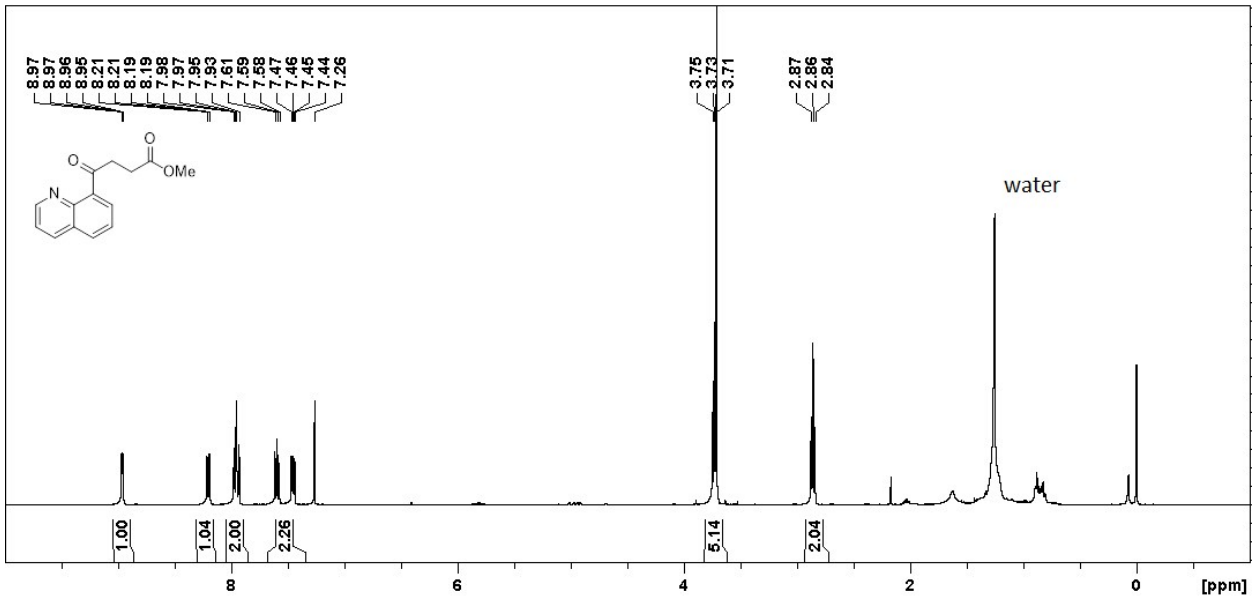
^{1}H NMR Spectrum for **2**



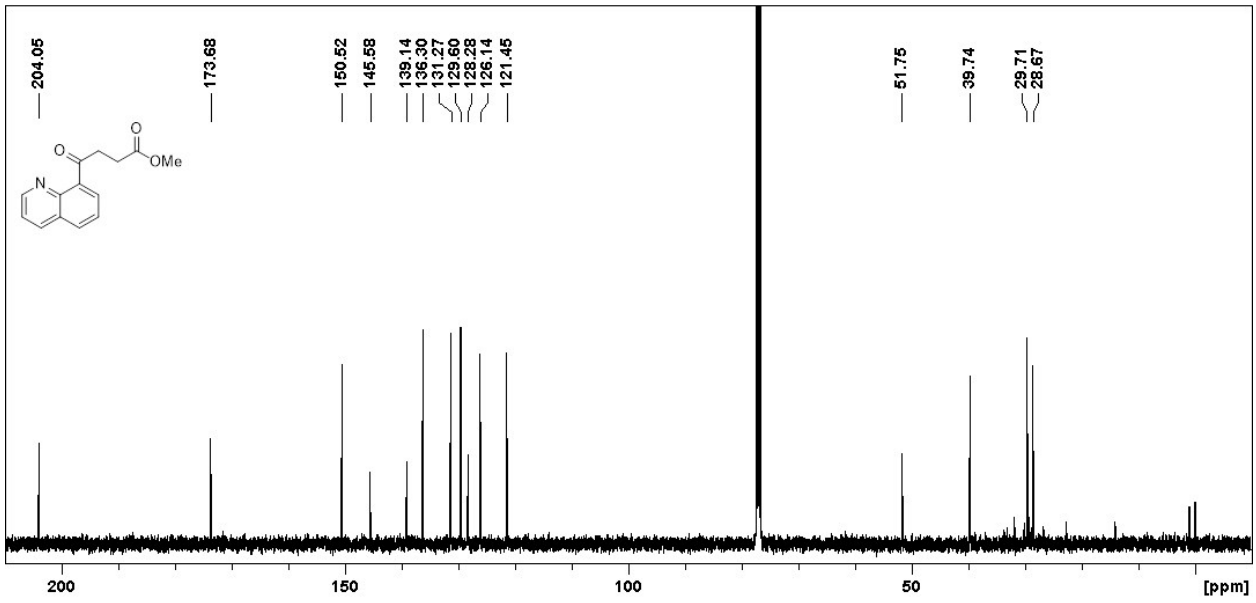
^{13}C NMR Spectrum for **2**



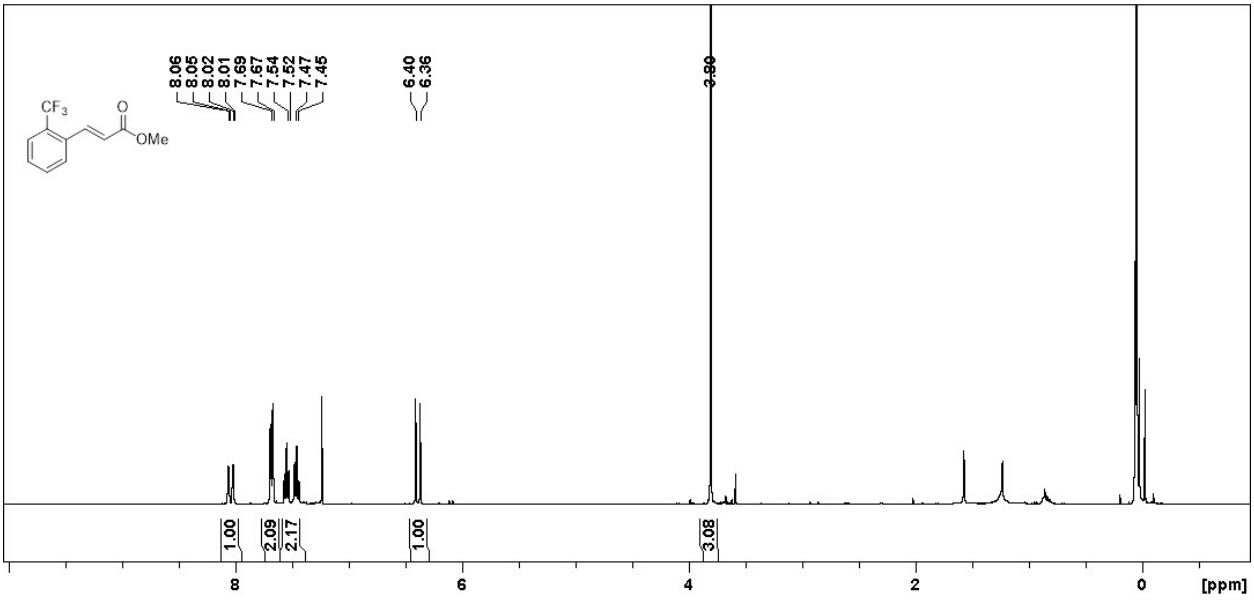
^{1}H NMR Spectrum for **3**



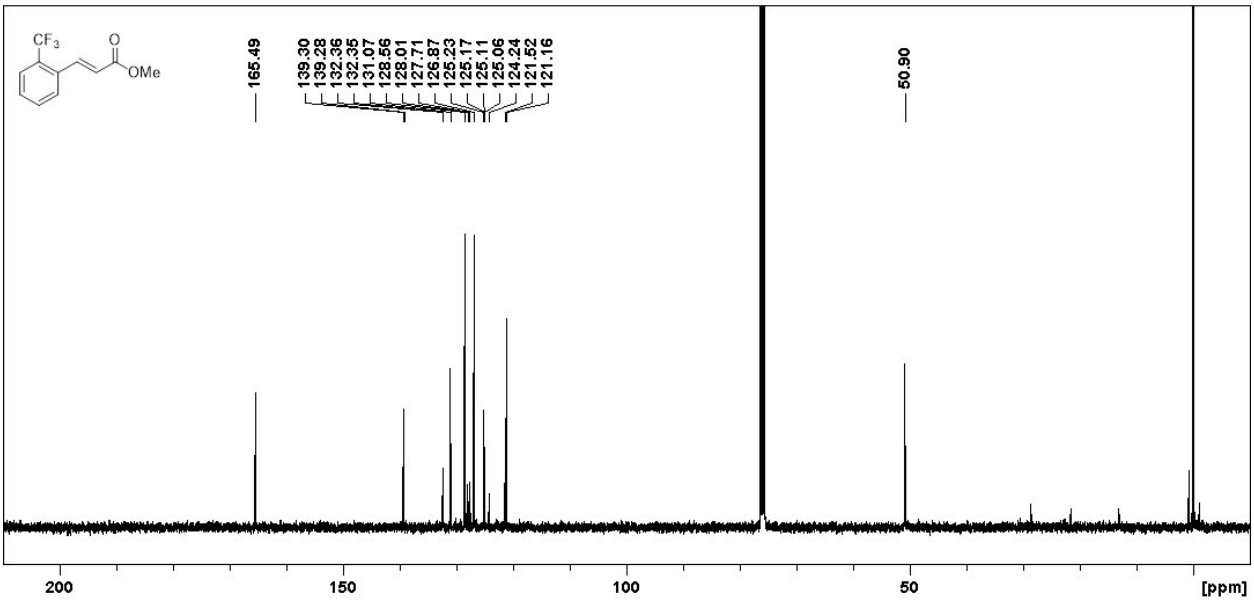
^{13}C NMR Spectrum for **3**



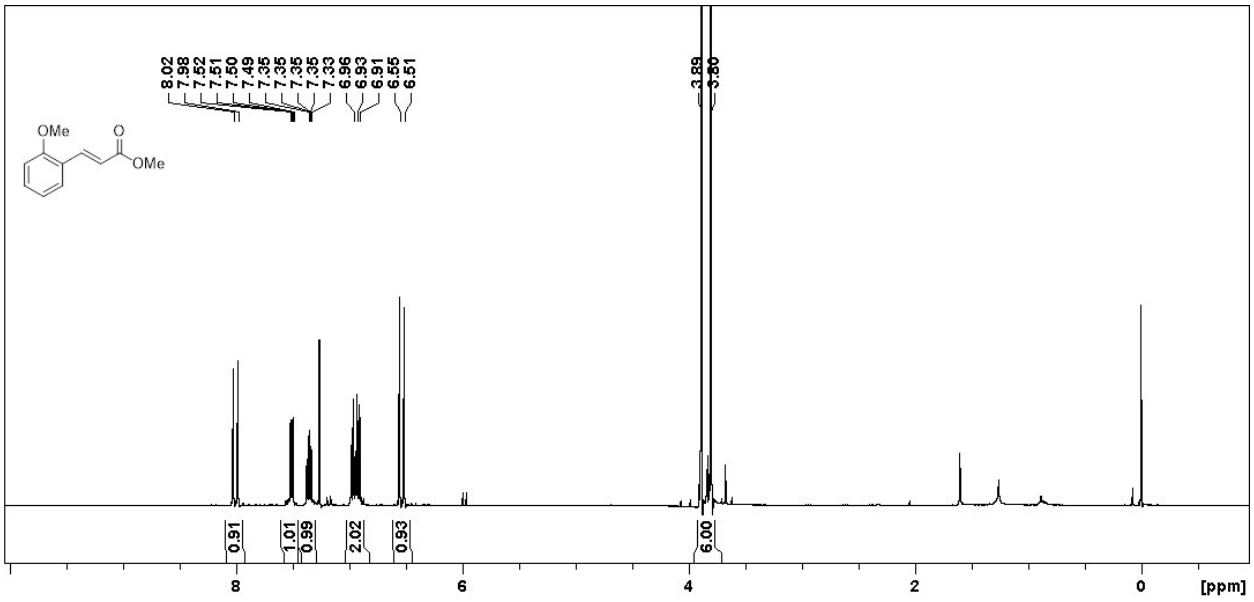
^{1}H NMR Spectrum for **4**



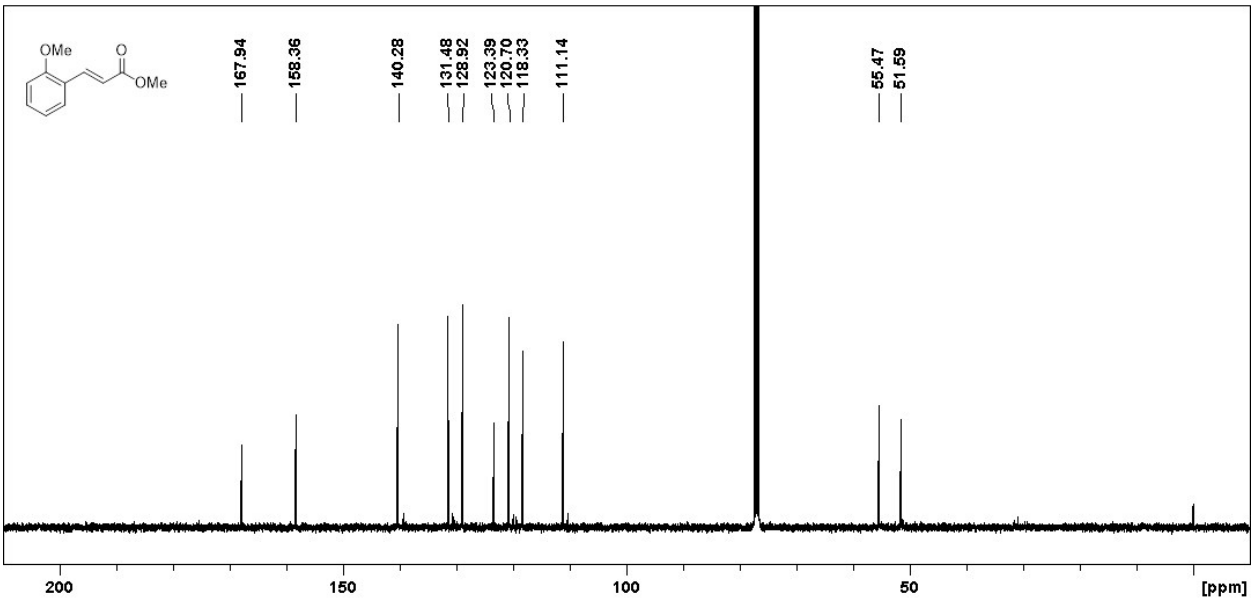
^{13}C NMR Spectrum for **4**



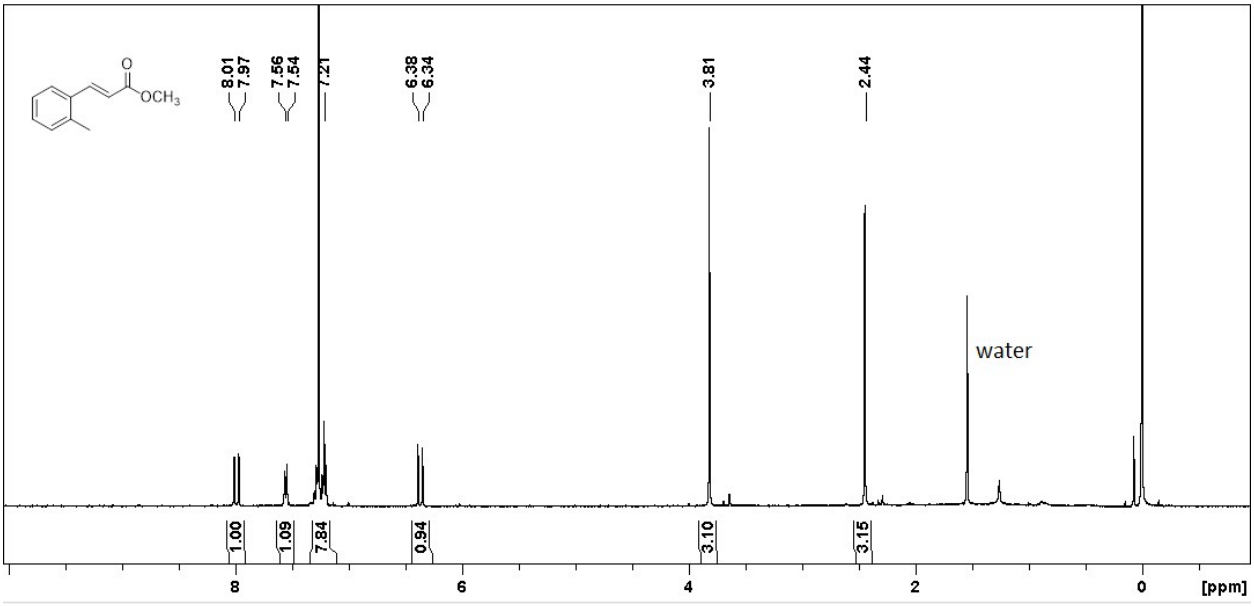
^{1}H NMR Spectrum for **5**



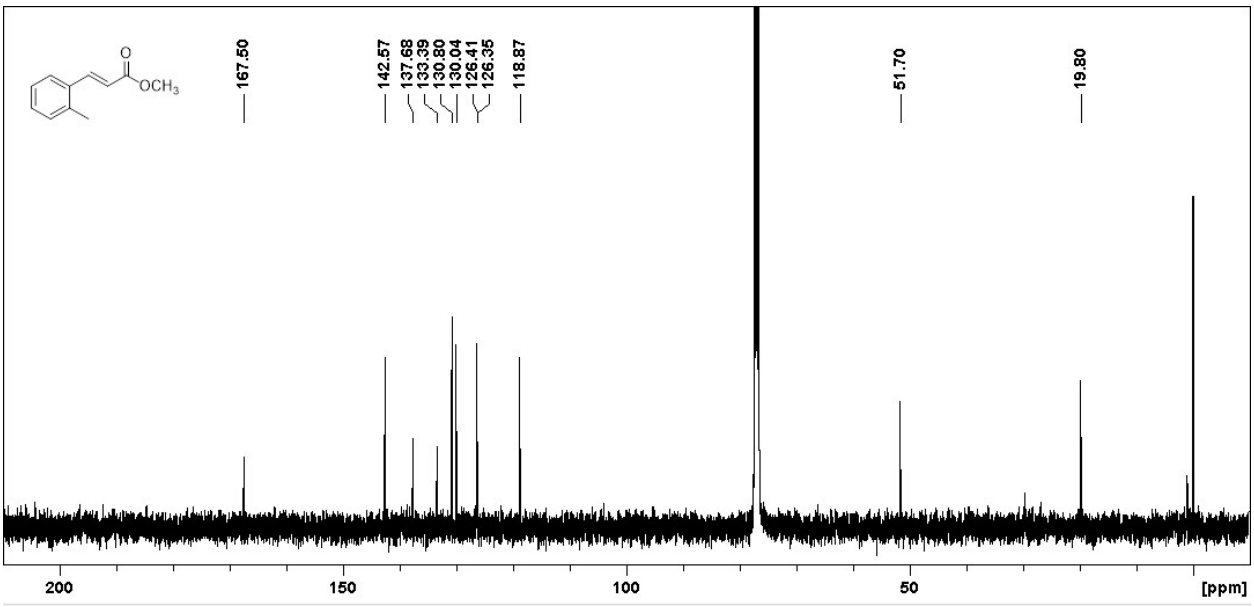
^{13}C NMR Spectrum for **5**



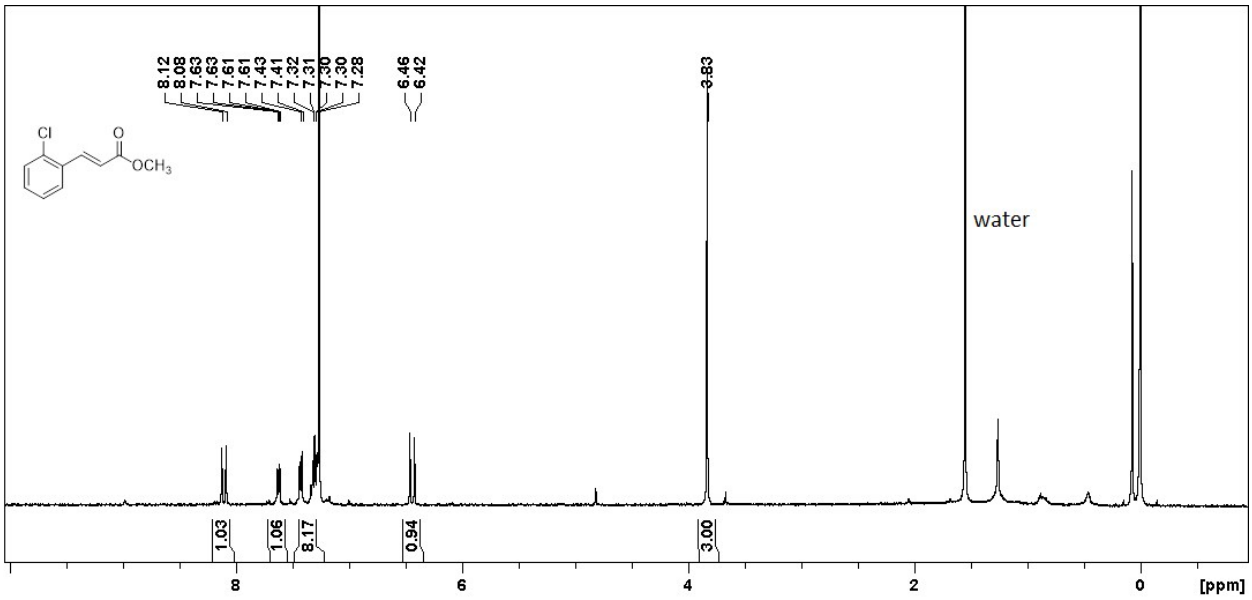
^{1}H NMR Spectrum for **6**



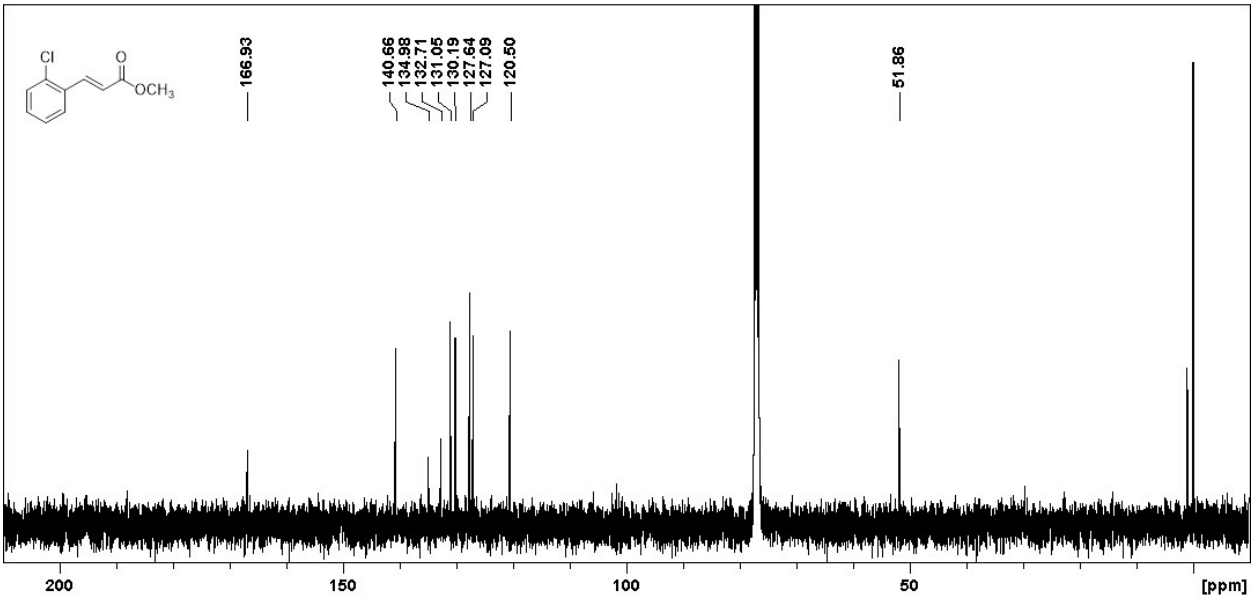
^{13}C NMR Spectrum for **6**



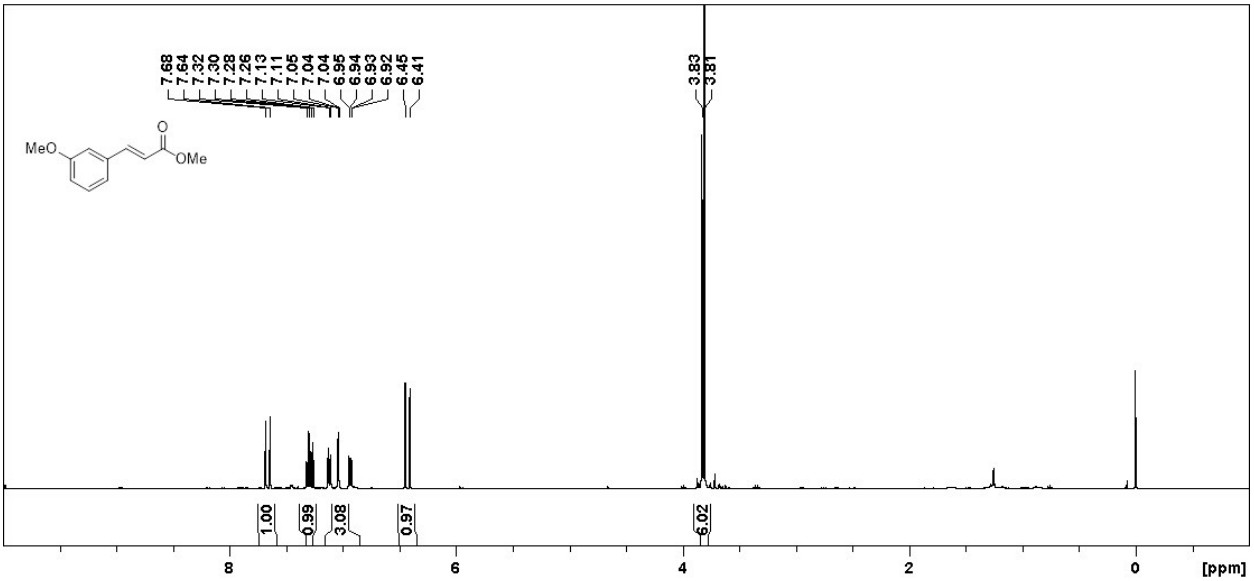
^{1}H NMR Spectrum for **7**



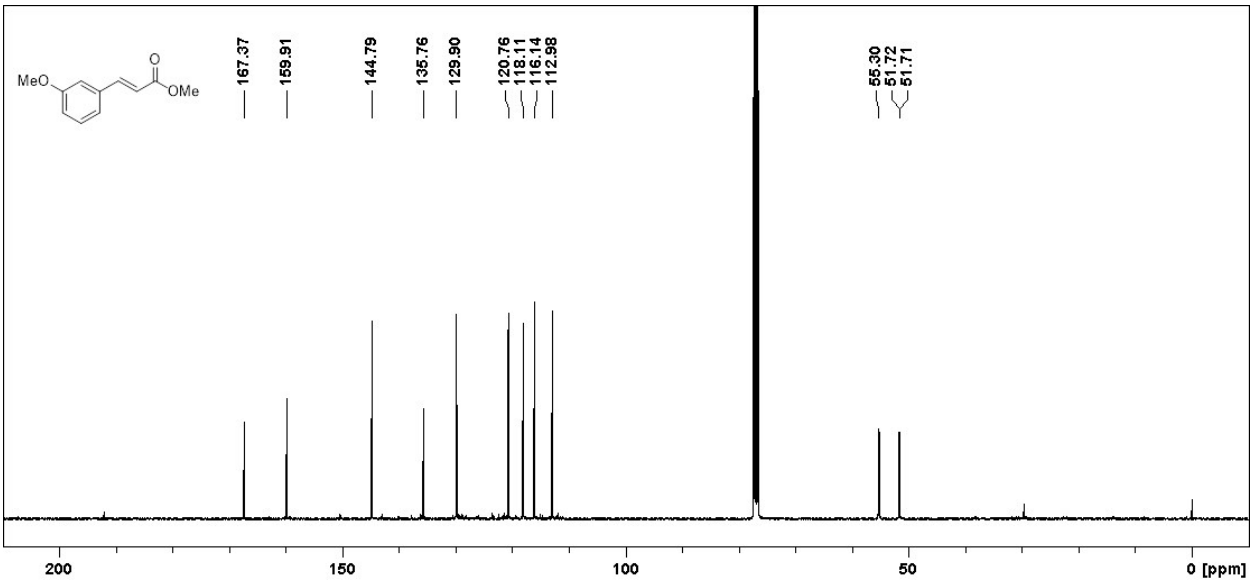
^{13}C NMR Spectrum for **7**



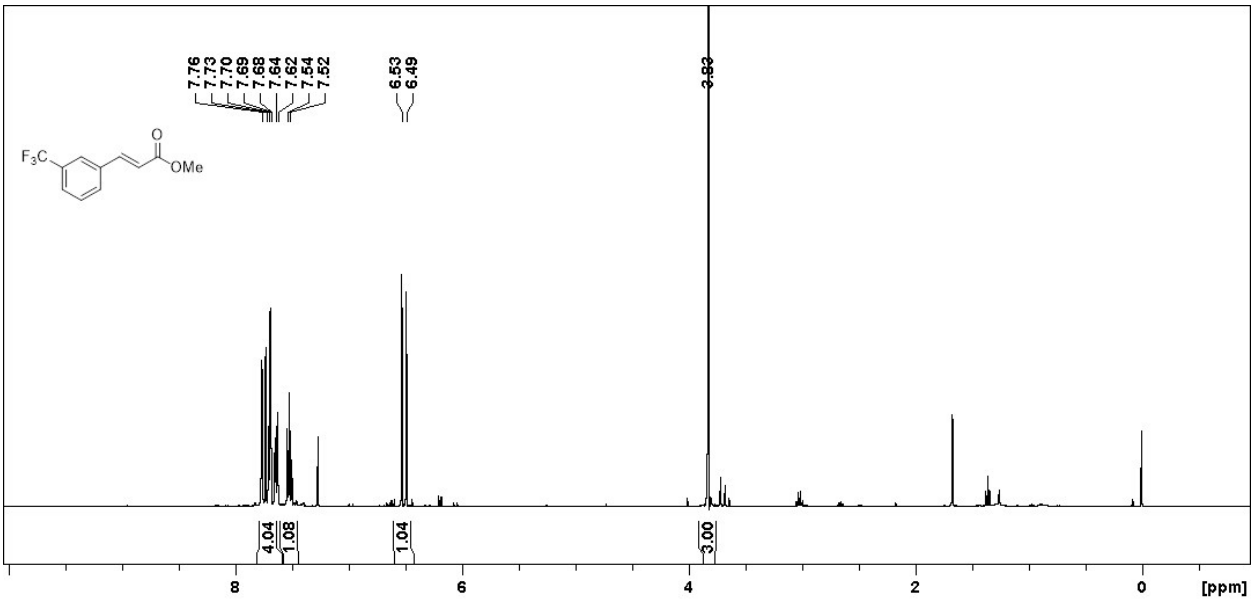
^{1}H NMR Spectrum for **8**



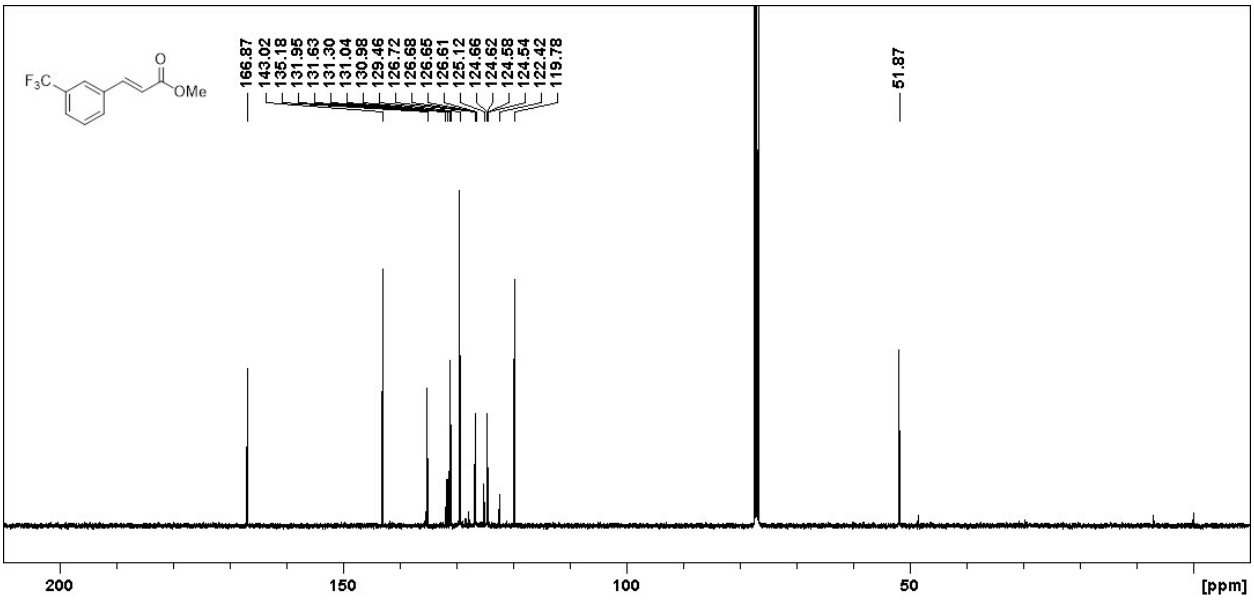
^{13}C NMR Spectrum for **8**



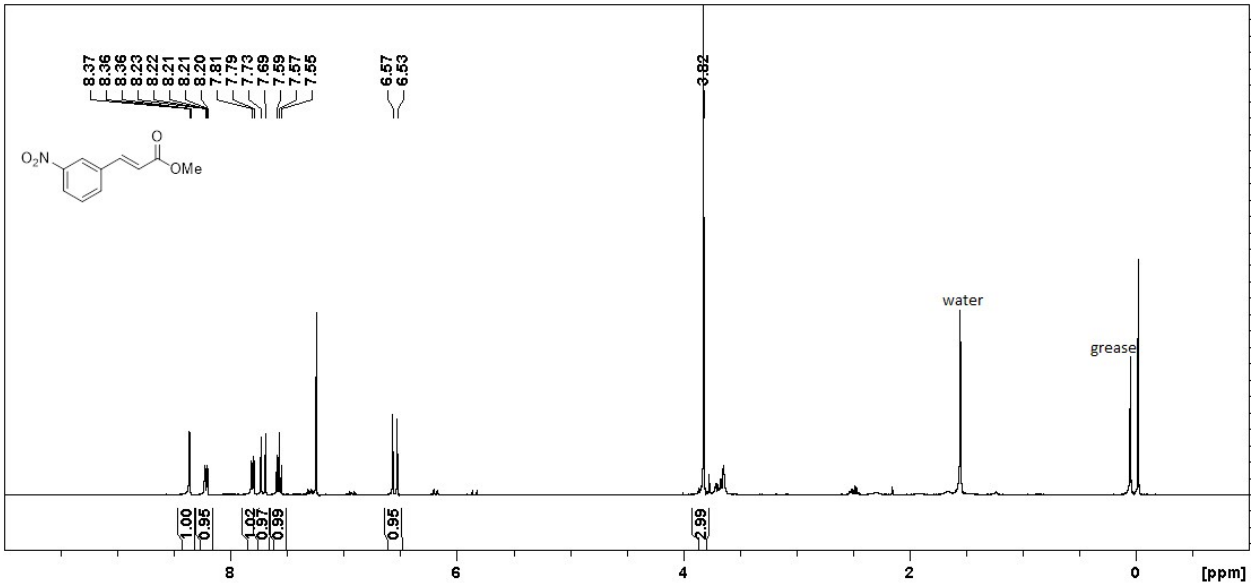
^{1}H NMR Spectrum for **9**



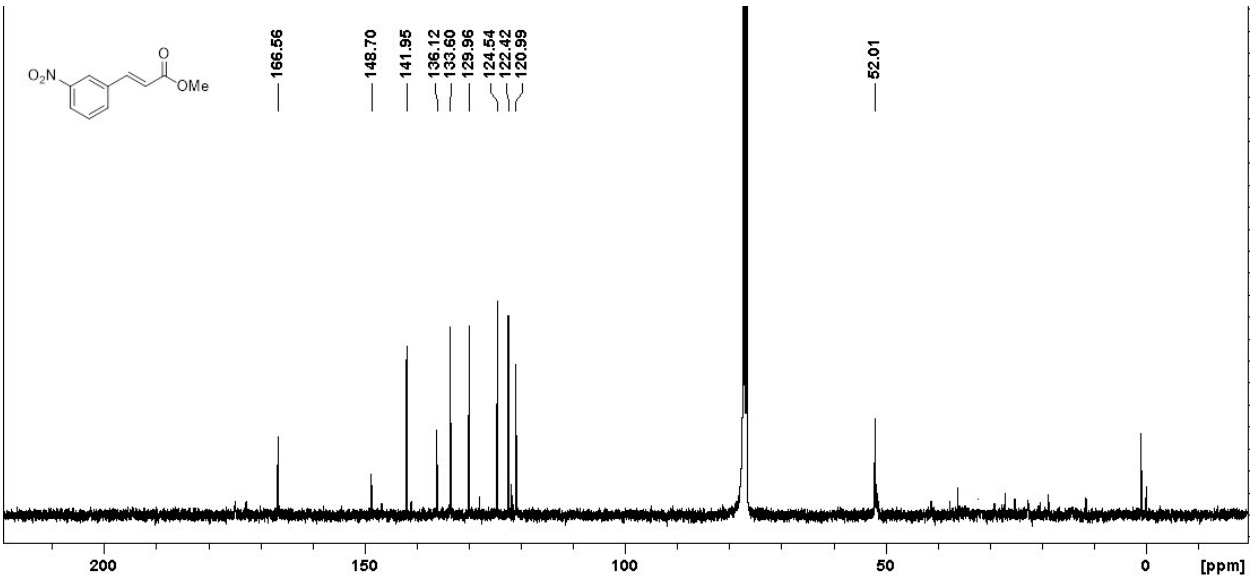
^{13}C NMR Spectrum for **9**



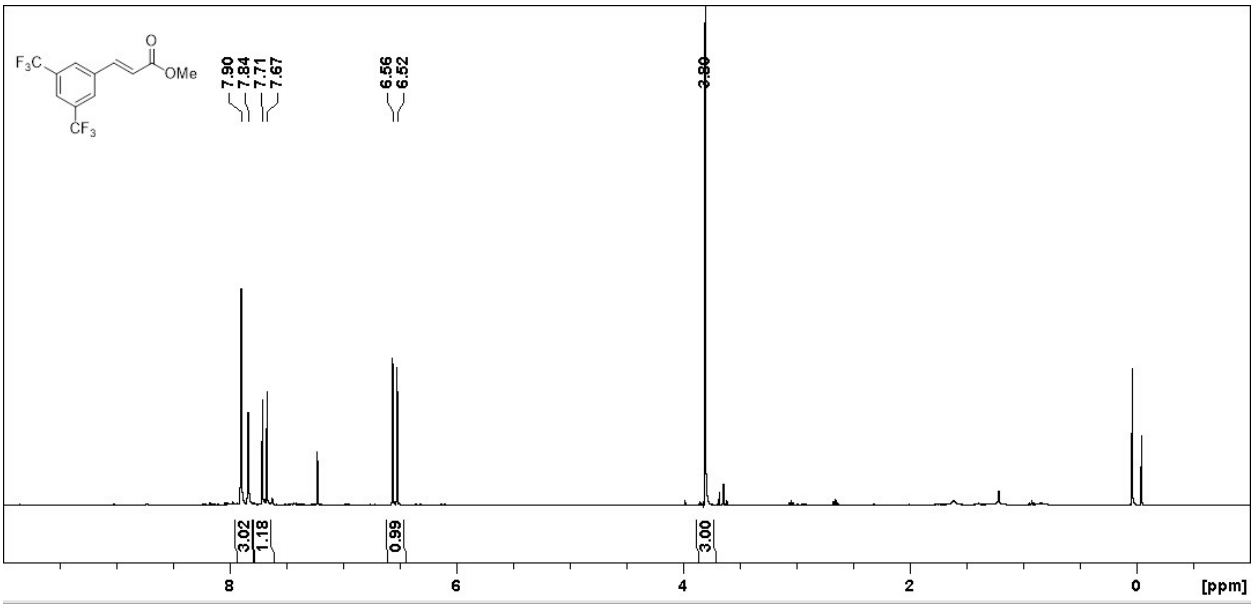
^{1}H NMR Spectrum for **10**



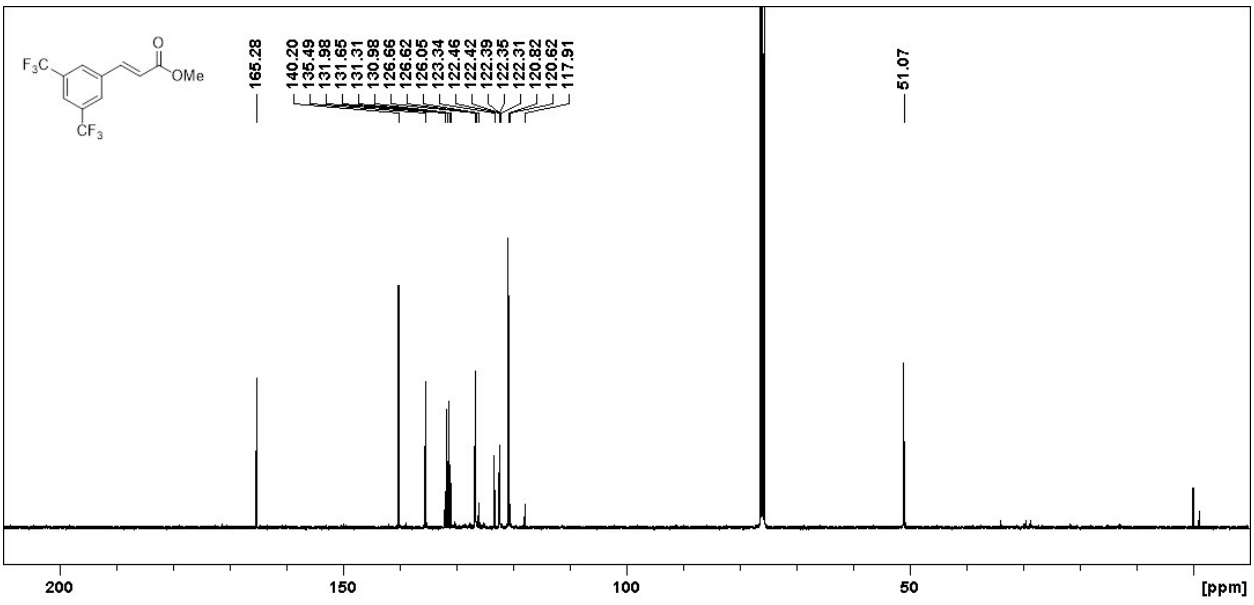
^{13}C NMR Spectrum for **10**



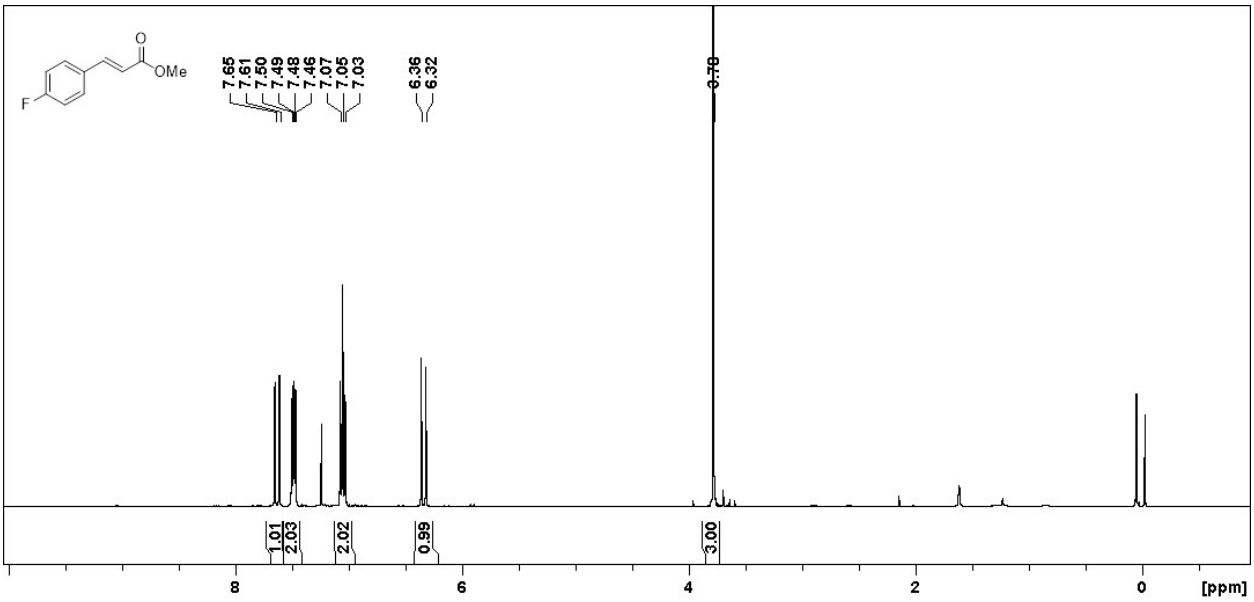
^{1}H NMR Spectrum for **11**



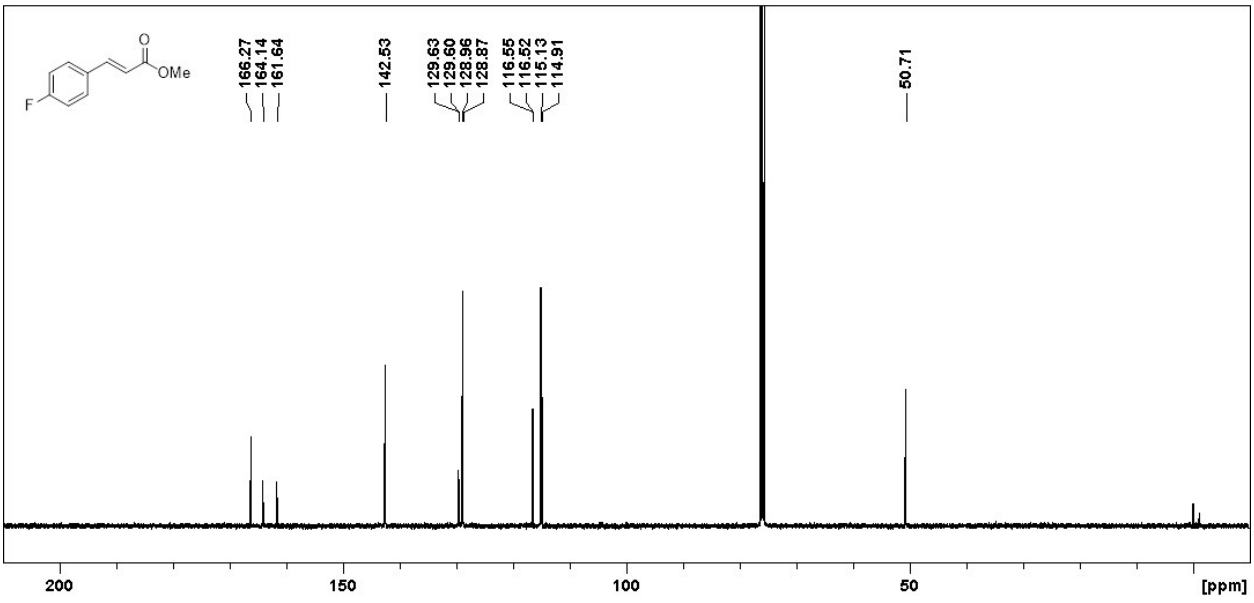
^{13}C NMR Spectrum for **11**



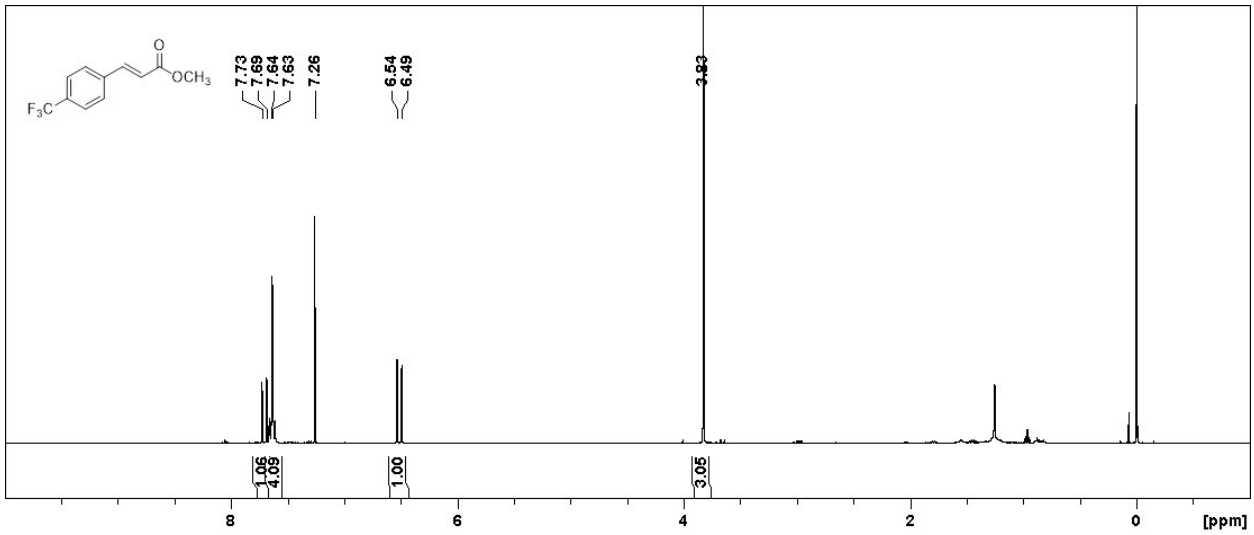
^{1}H NMR Spectrum for **12**



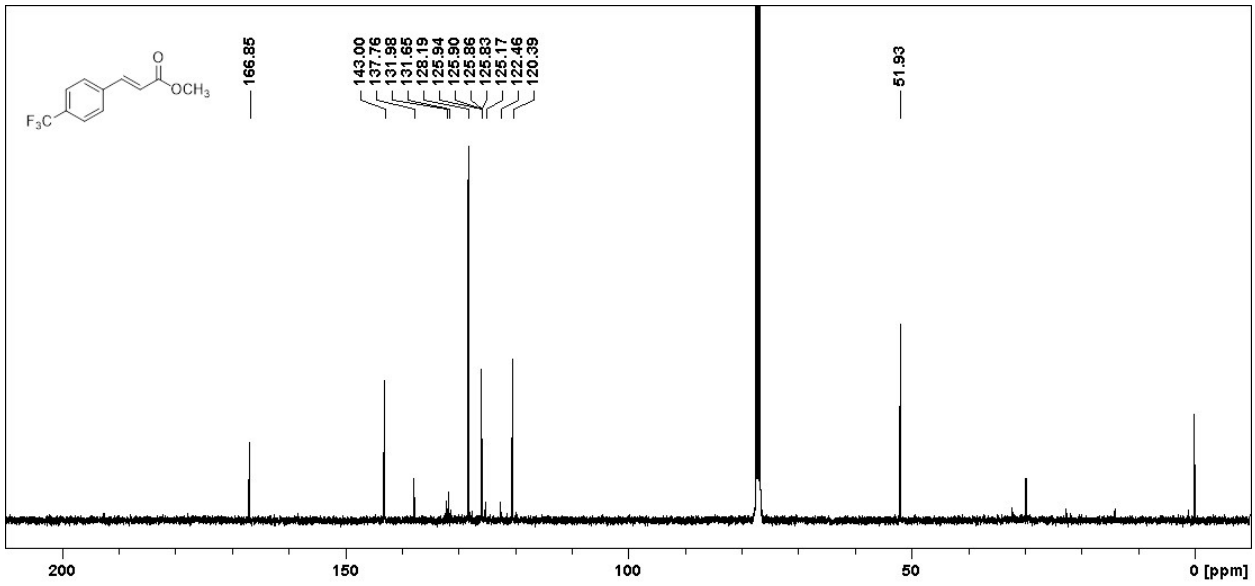
^{13}C NMR Spectrum for **12**



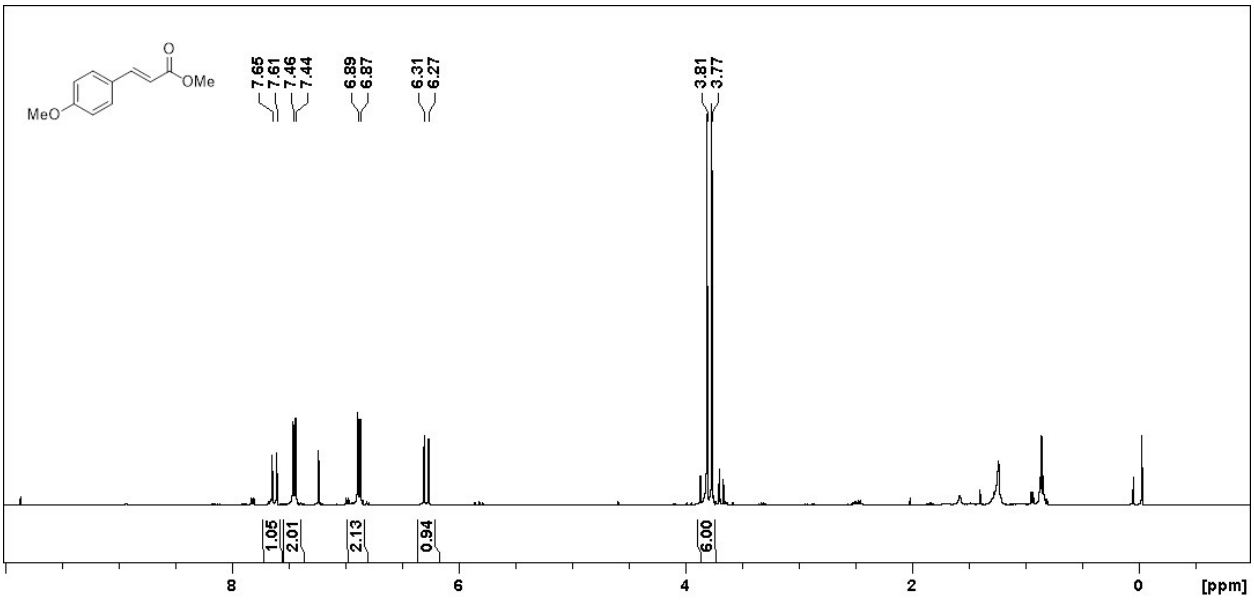
^{1}H NMR Spectrum for **13**



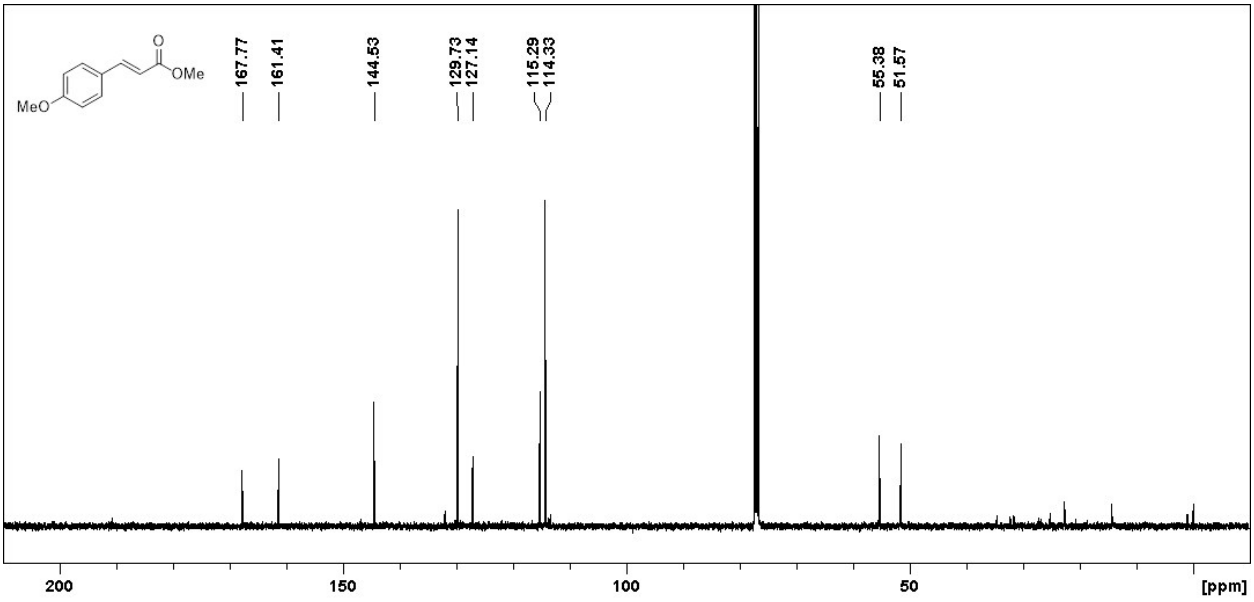
^{13}C NMR Spectrum for **13**



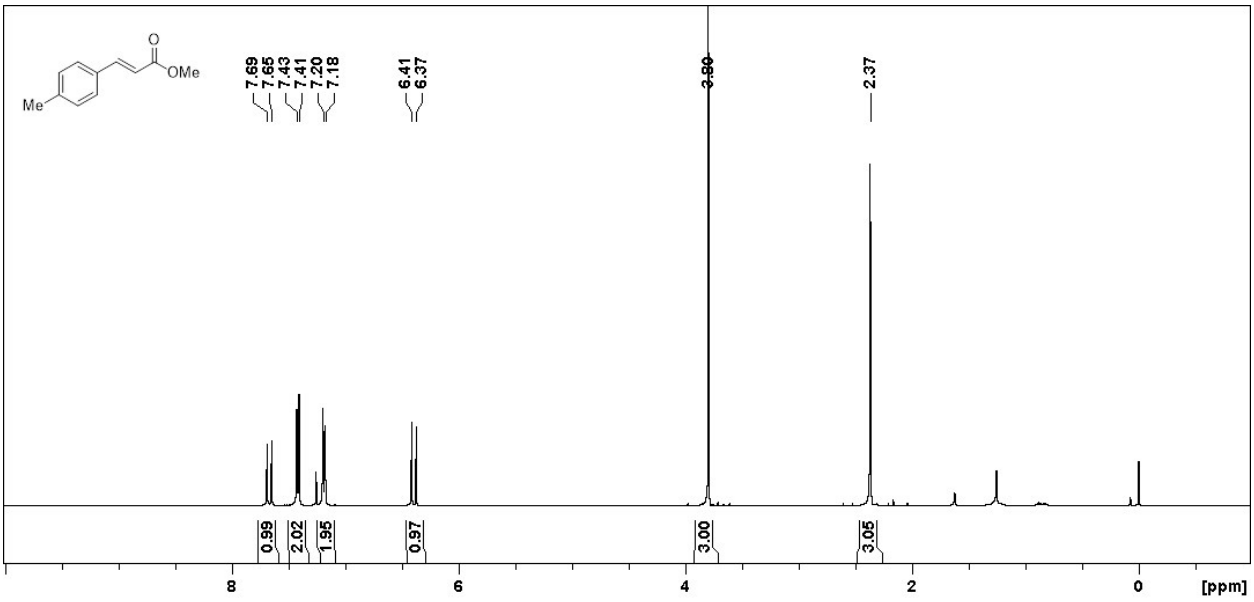
^{1}H NMR Spectrum for **14**



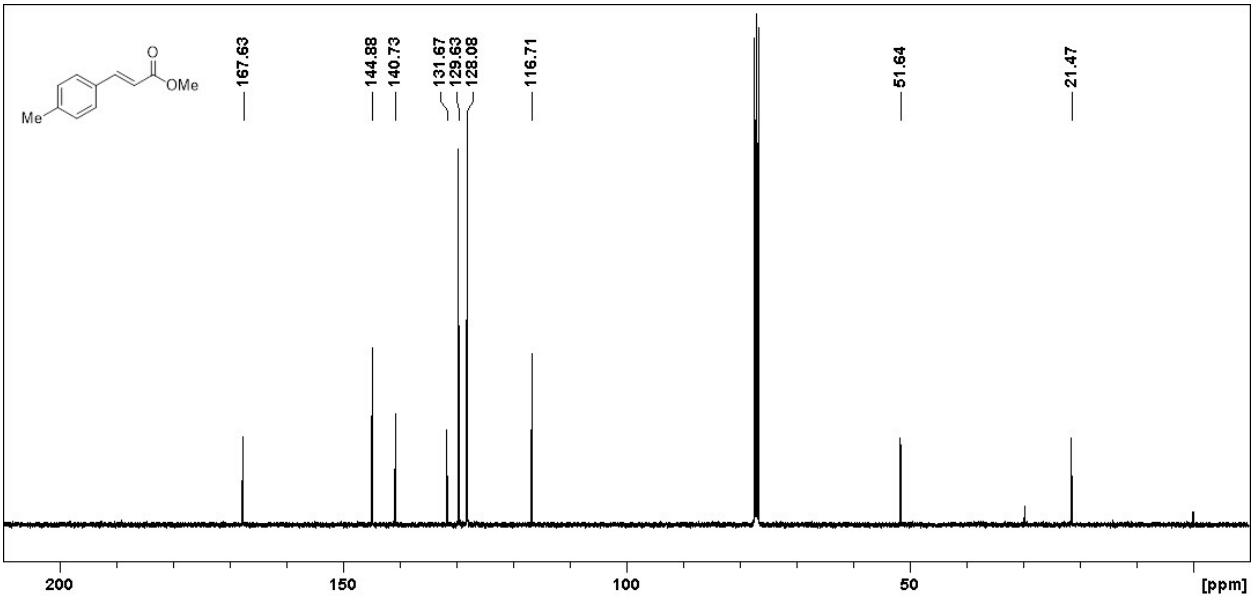
^{13}C NMR Spectrum for **14**



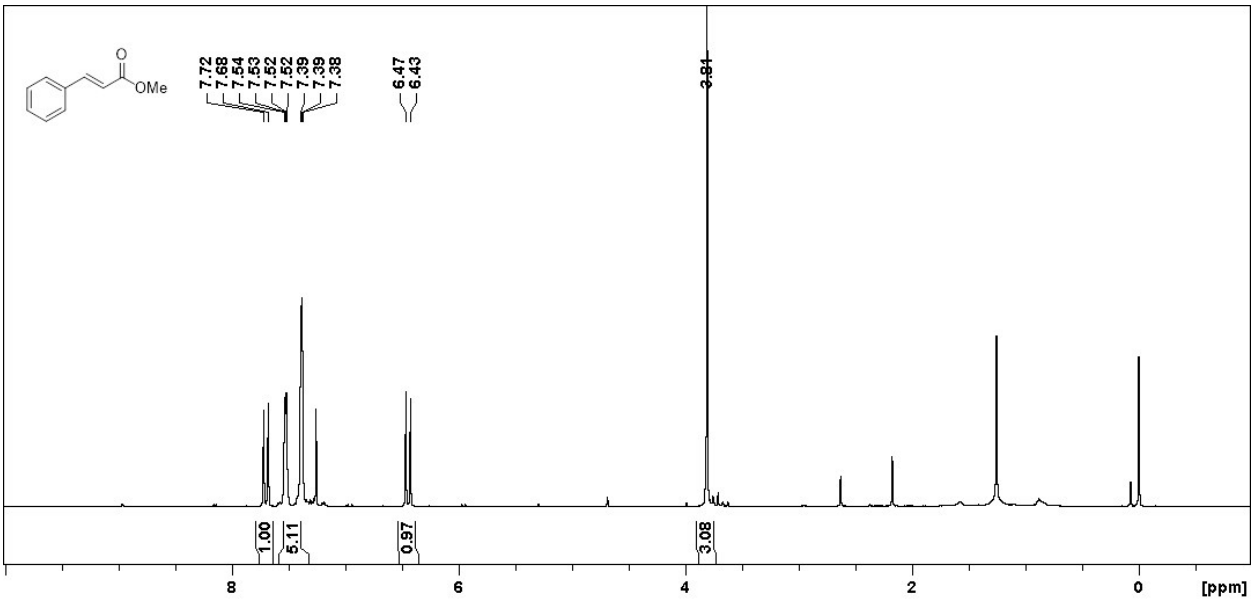
^{1}H NMR Spectrum for **15**



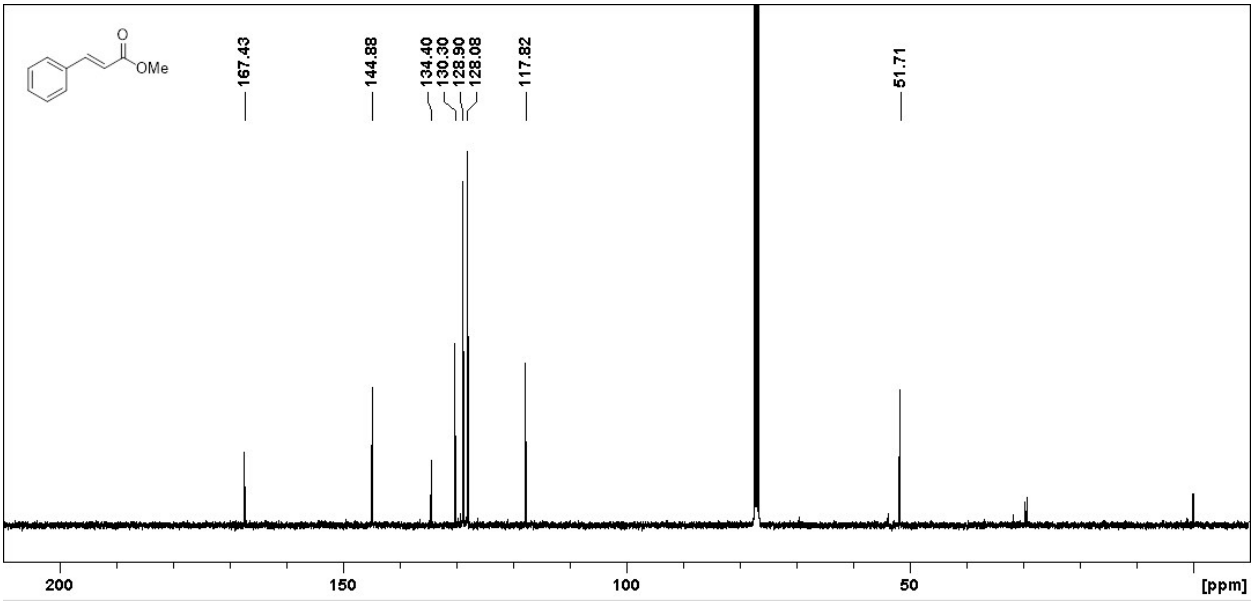
^{13}C NMR Spectrum for **15**



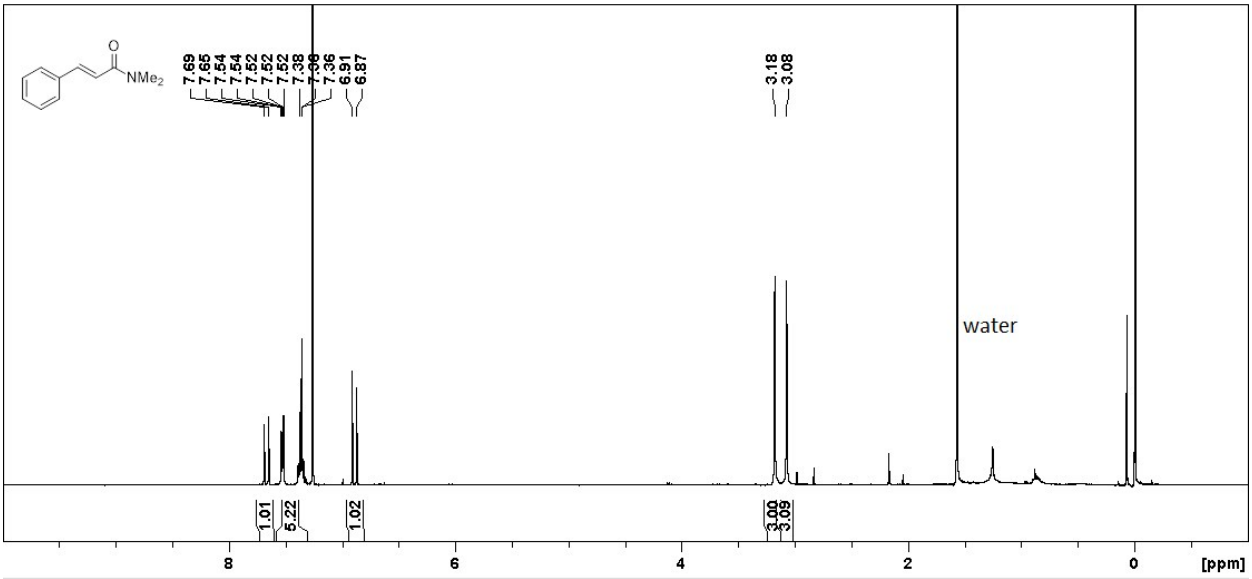
^{1}H NMR Spectrum for **16**



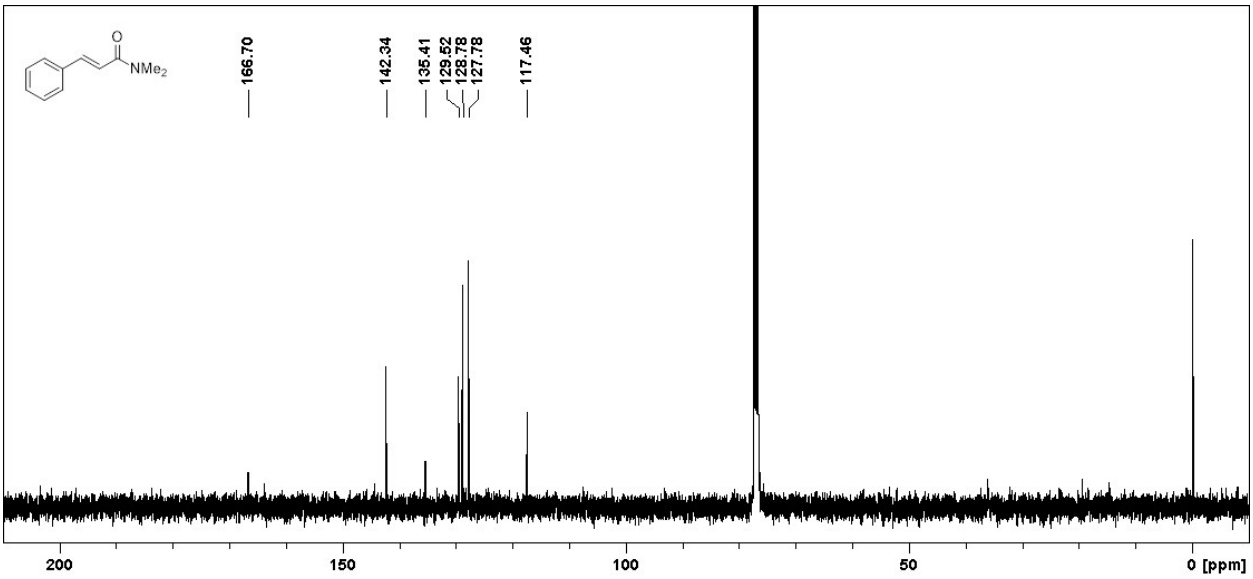
^{13}C NMR Spectrum for **16**



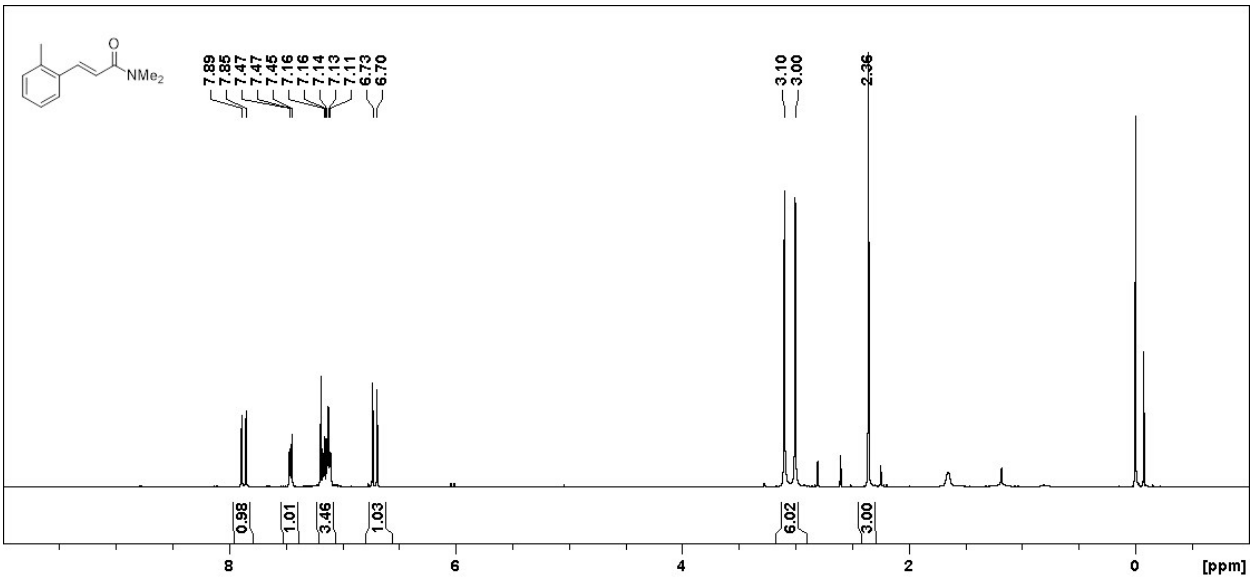
^{1}H NMR Spectrum for **19**



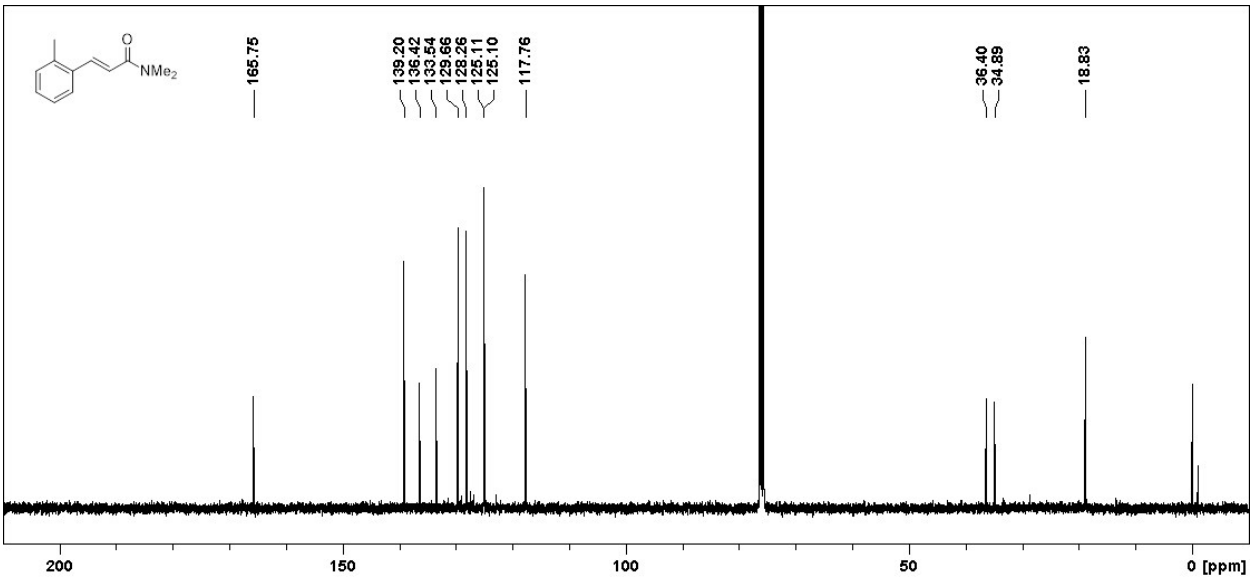
^{13}C NMR Spectrum for **19**



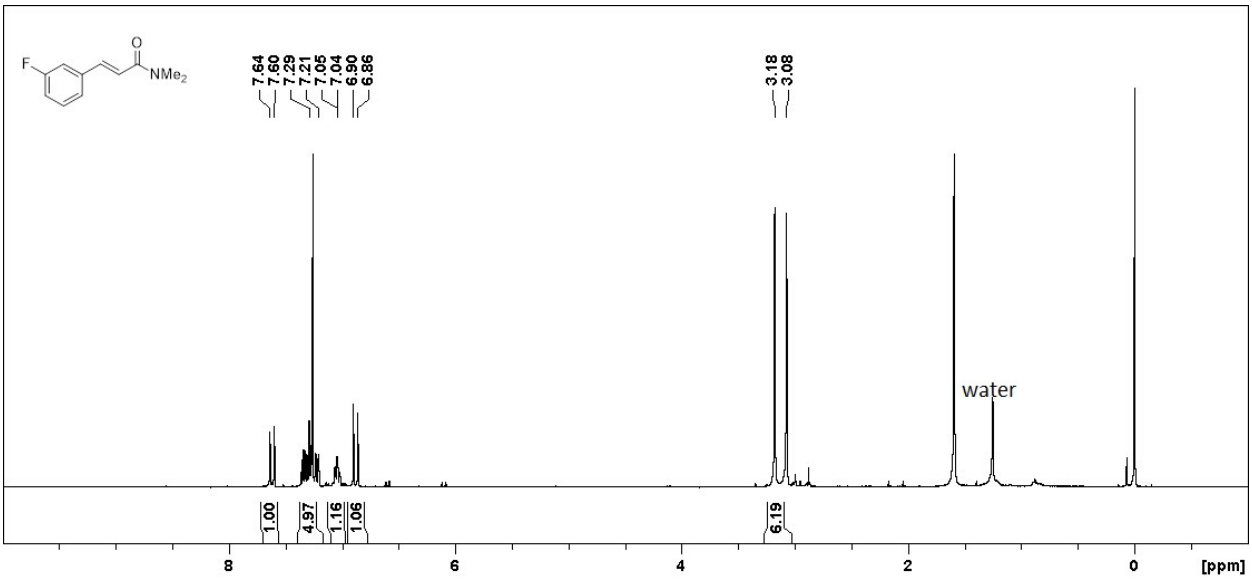
^{1}H NMR Spectrum for **22**



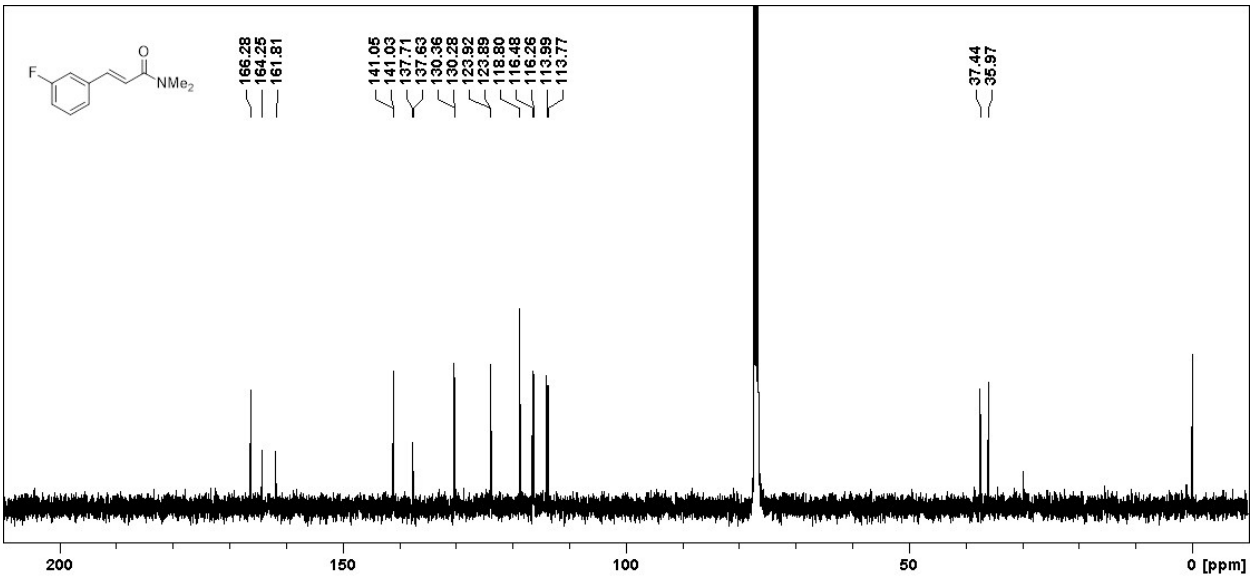
^{13}C NMR Spectrum for **22**



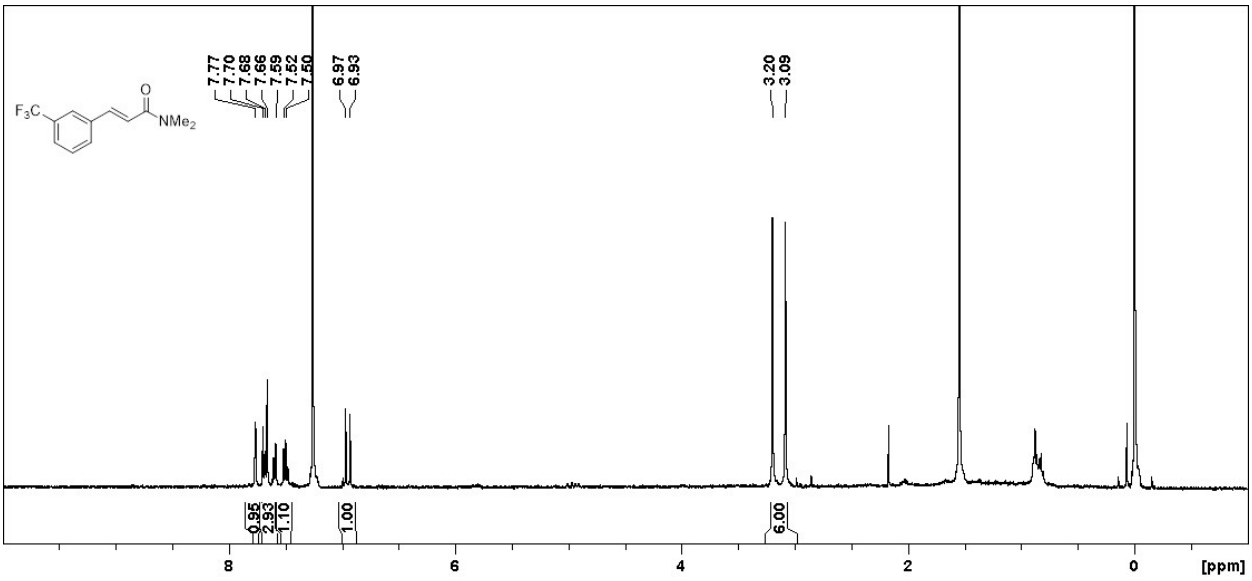
^{1}H NMR Spectrum for **23**



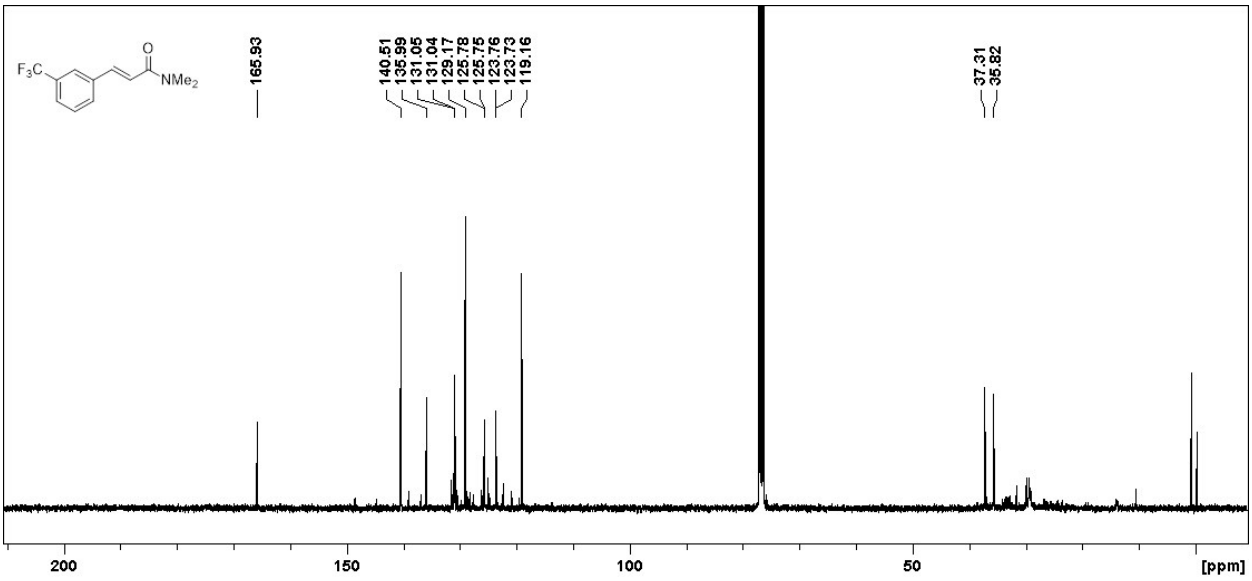
^{13}C NMR Spectrum for **23**



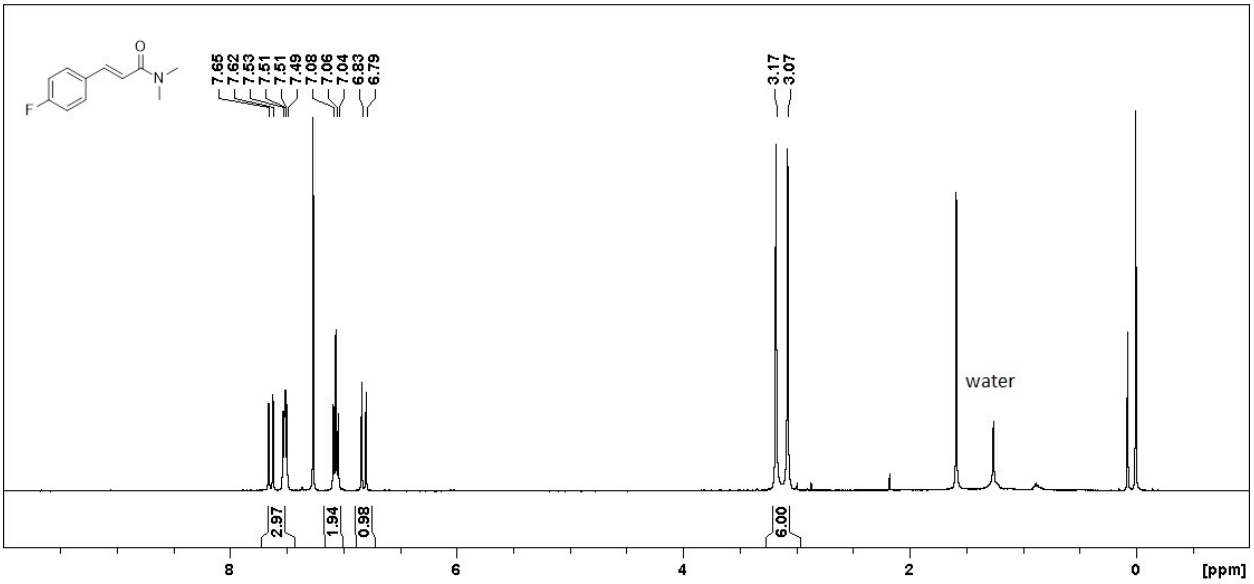
^{1}H NMR Spectrum for **24**



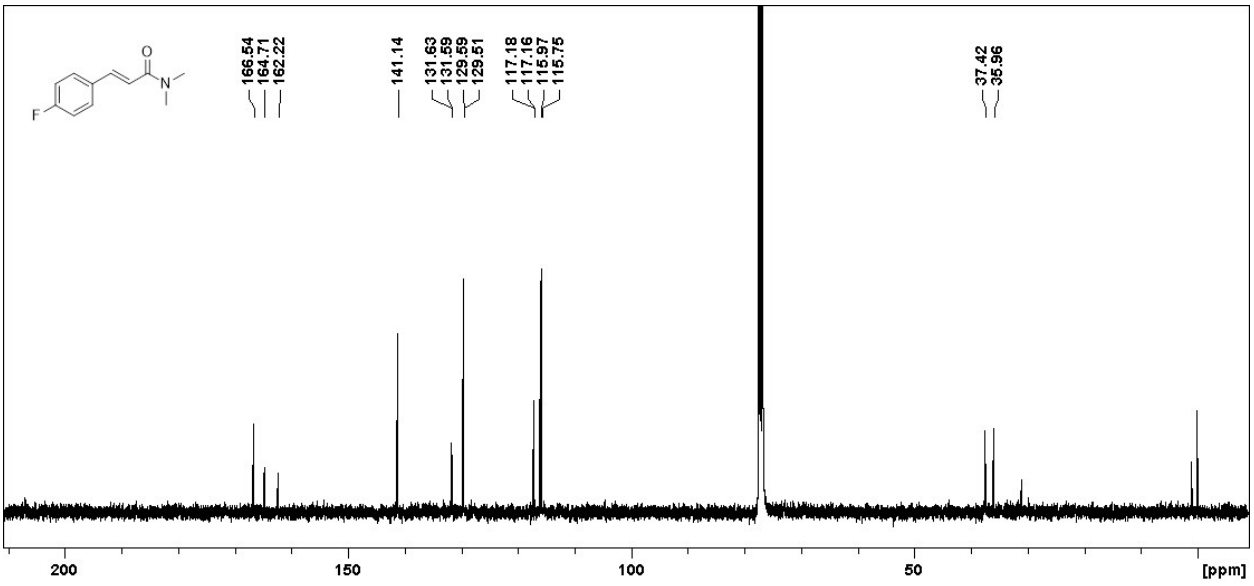
^{13}C NMR Spectrum for **24**



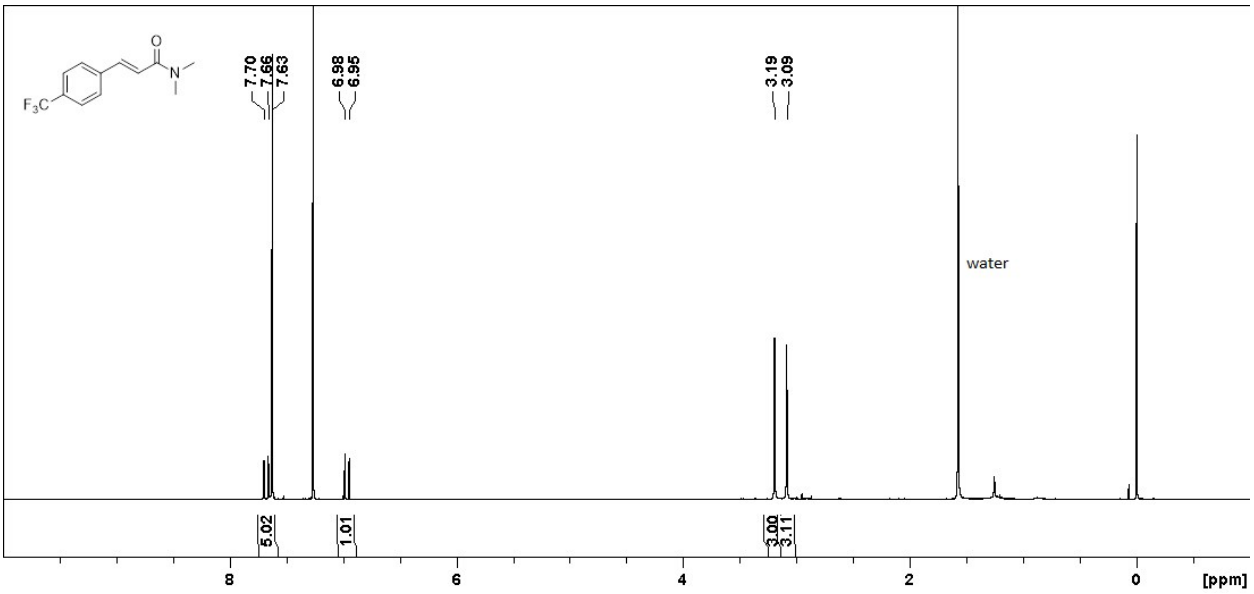
^{1}H NMR Spectrum for **25**



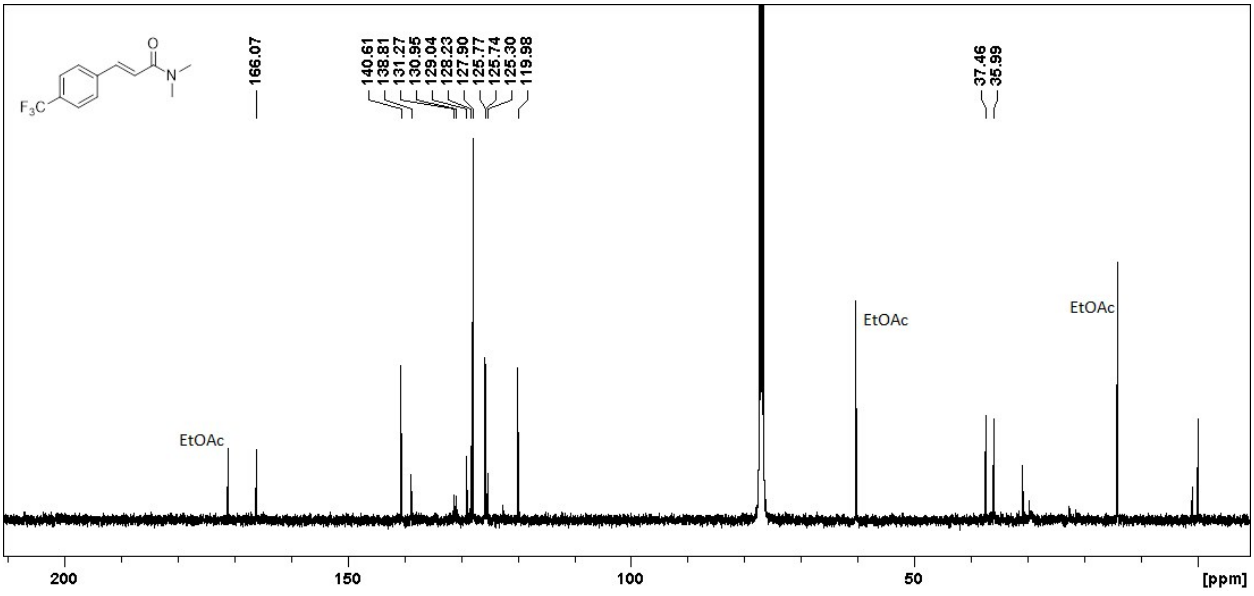
^{13}C NMR Spectrum for **25**



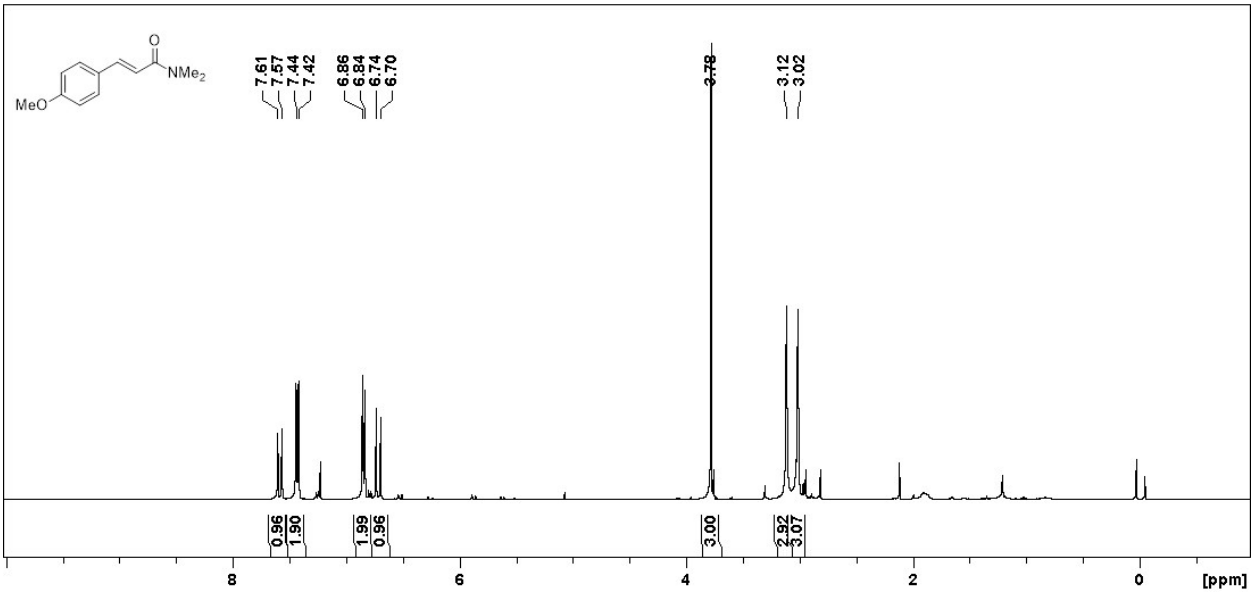
^{1}H NMR Spectrum for **26**



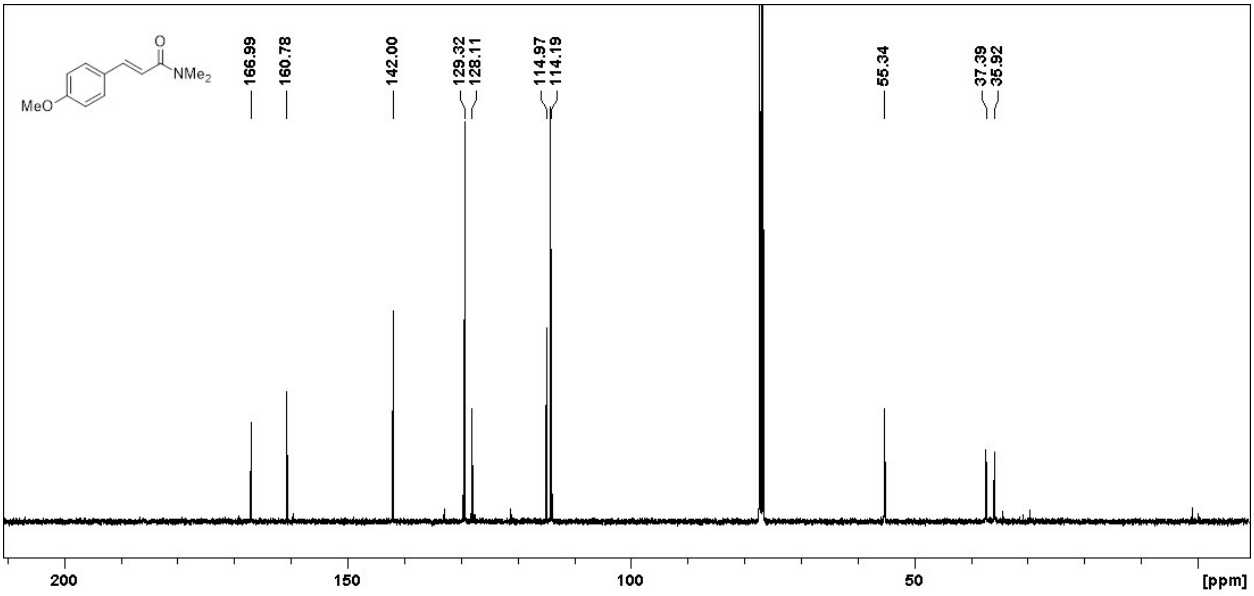
^{13}C NMR Spectrum for **26**



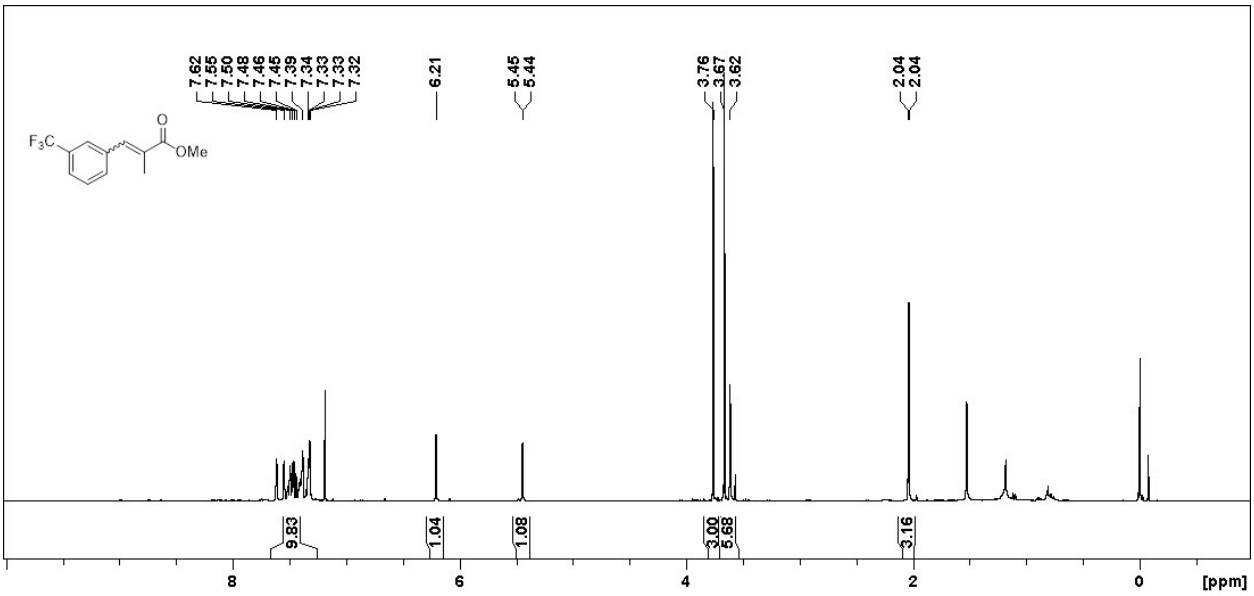
^{1}H NMR Spectrum for **27**



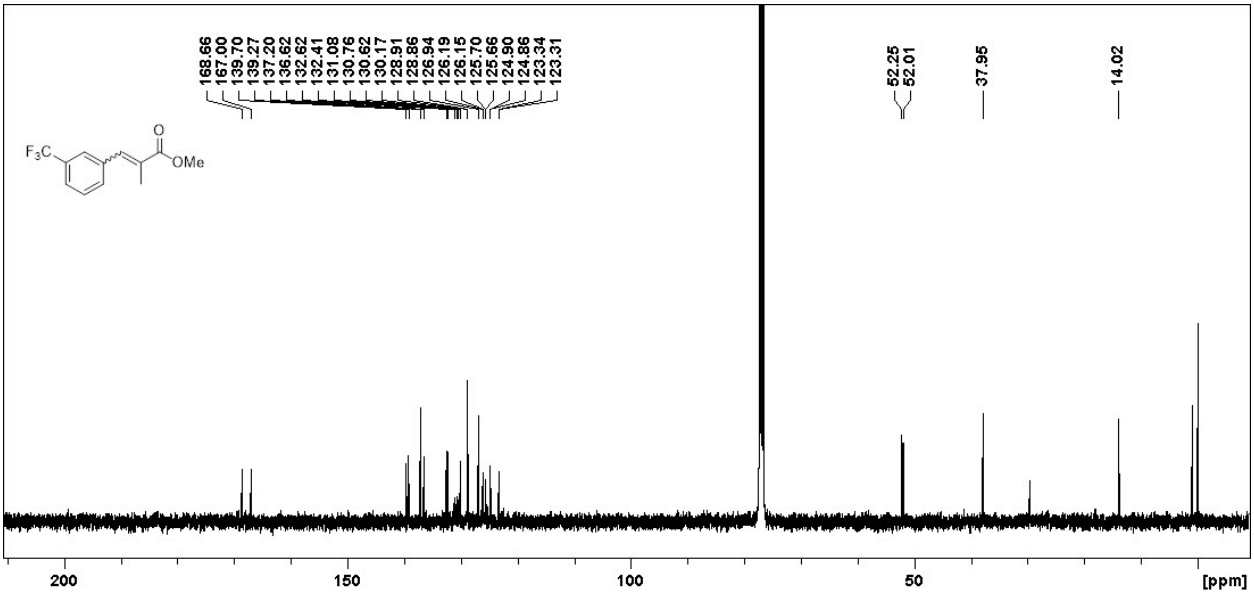
^{13}C NMR Spectrum for **27**



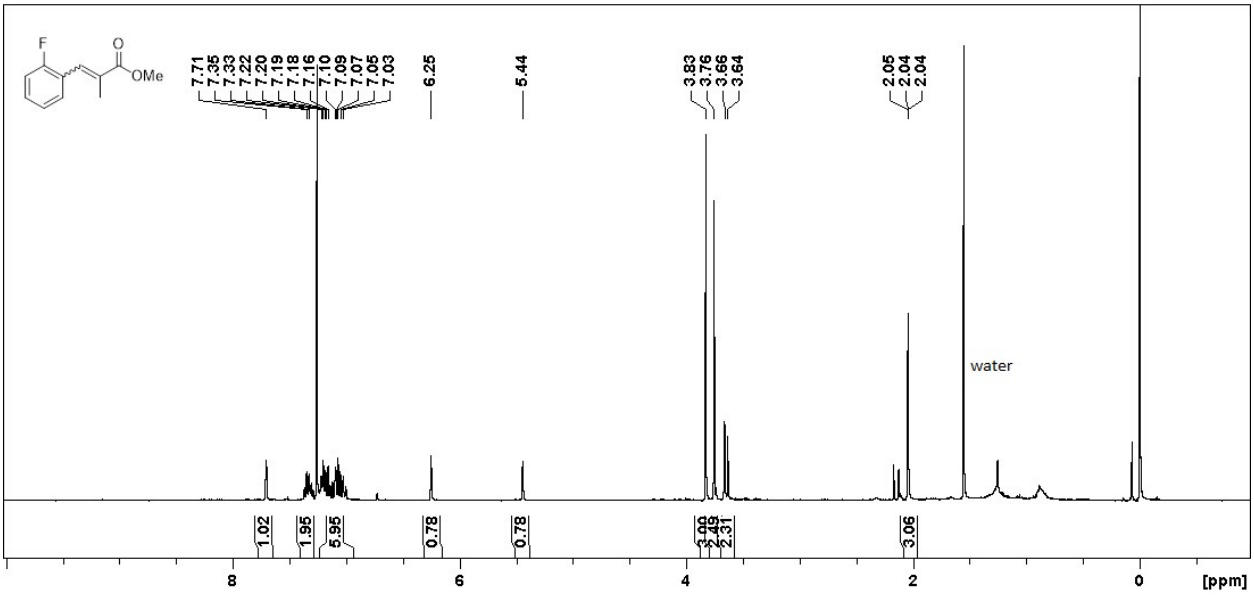
^{1}H NMR Spectrum for **30**



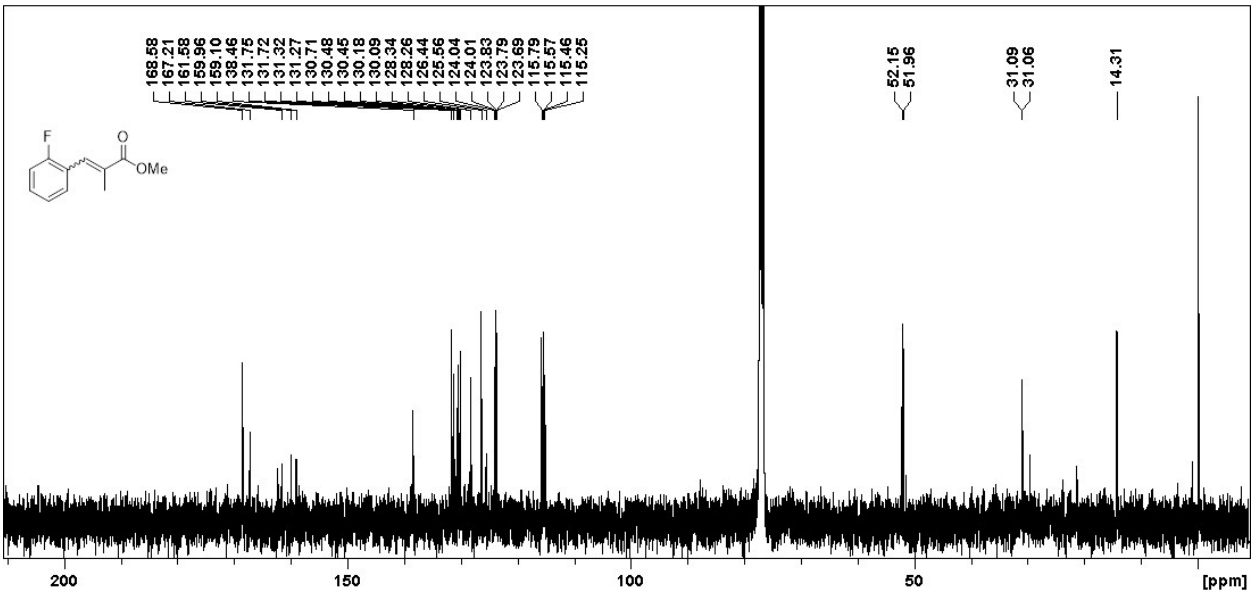
^{13}C NMR Spectrum for **30**



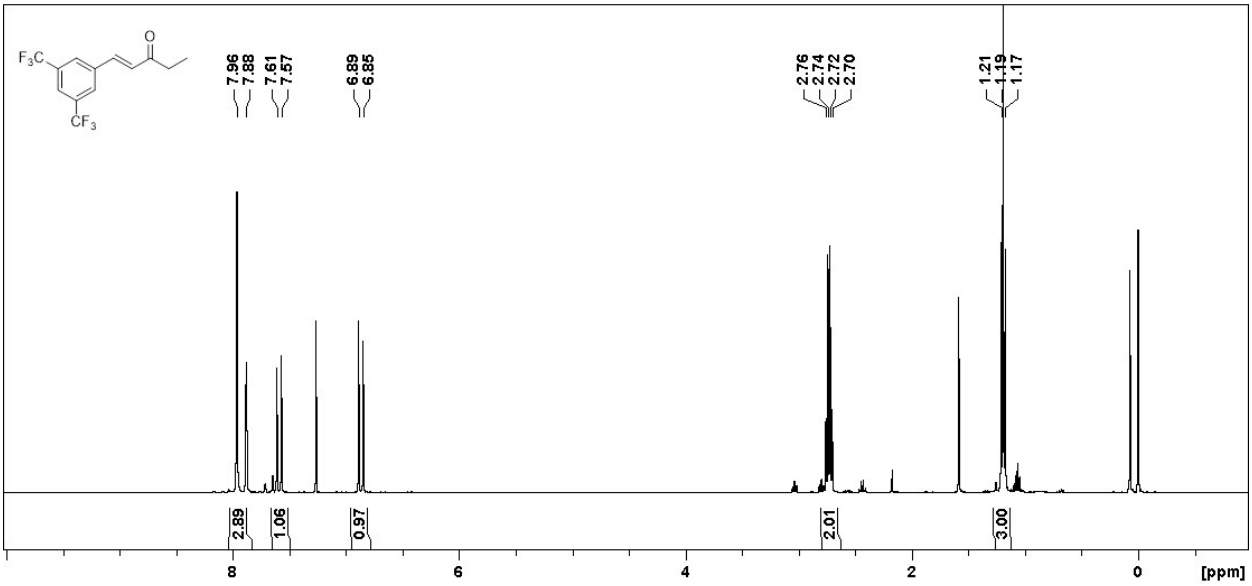
^{1}H NMR Spectrum for **31**



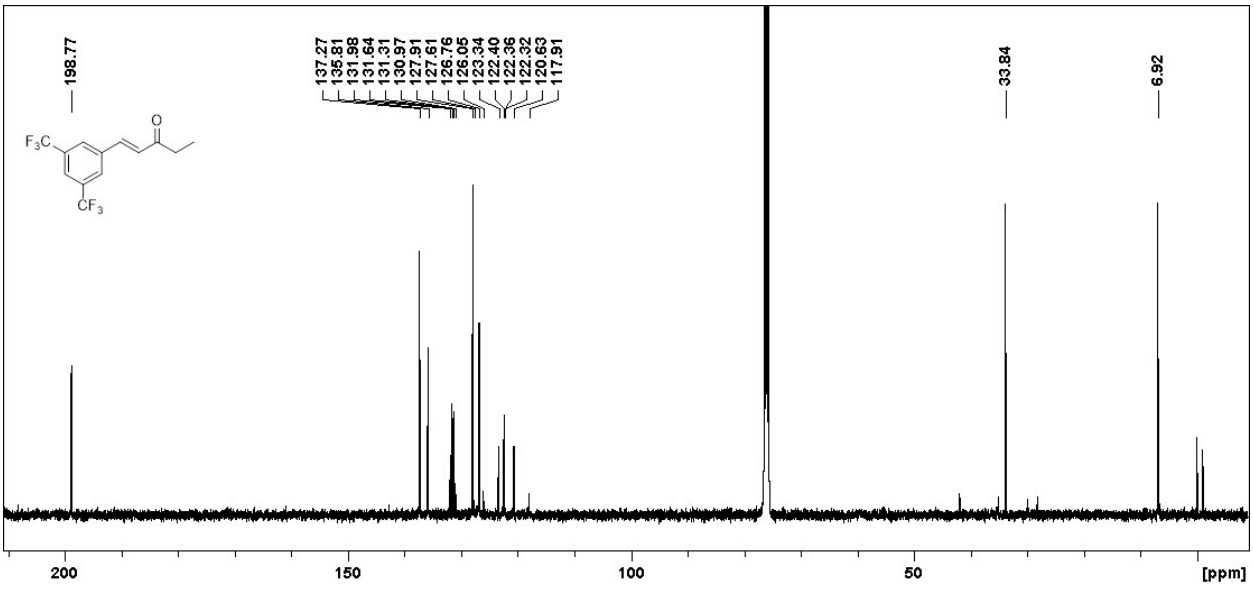
^{13}C NMR Spectrum for **31**



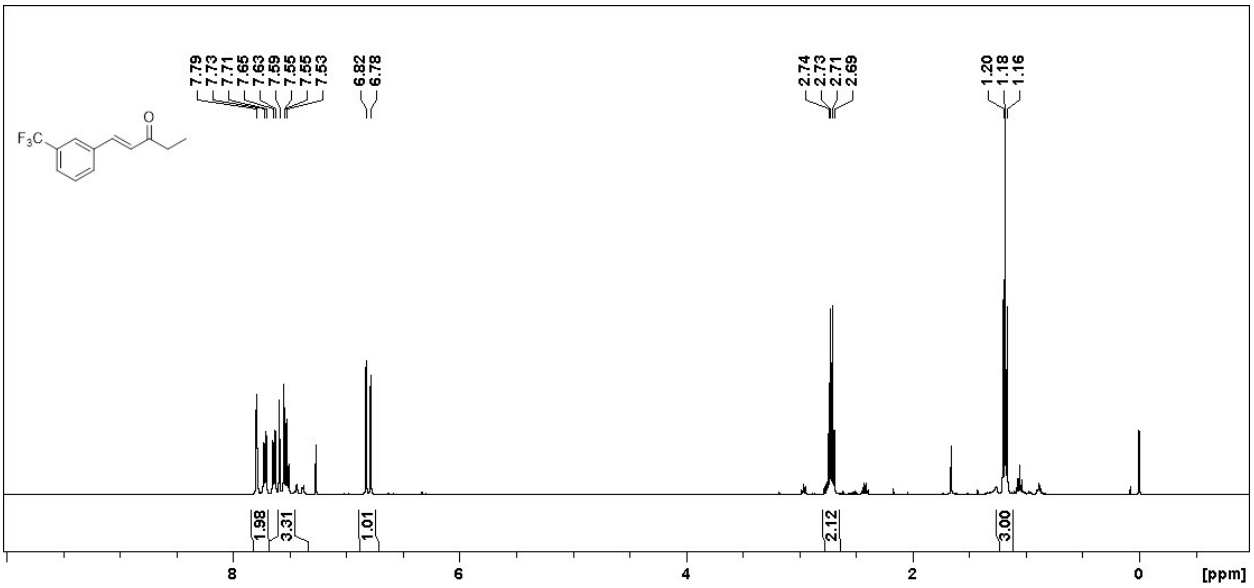
^{1}H NMR Spectrum for **32**



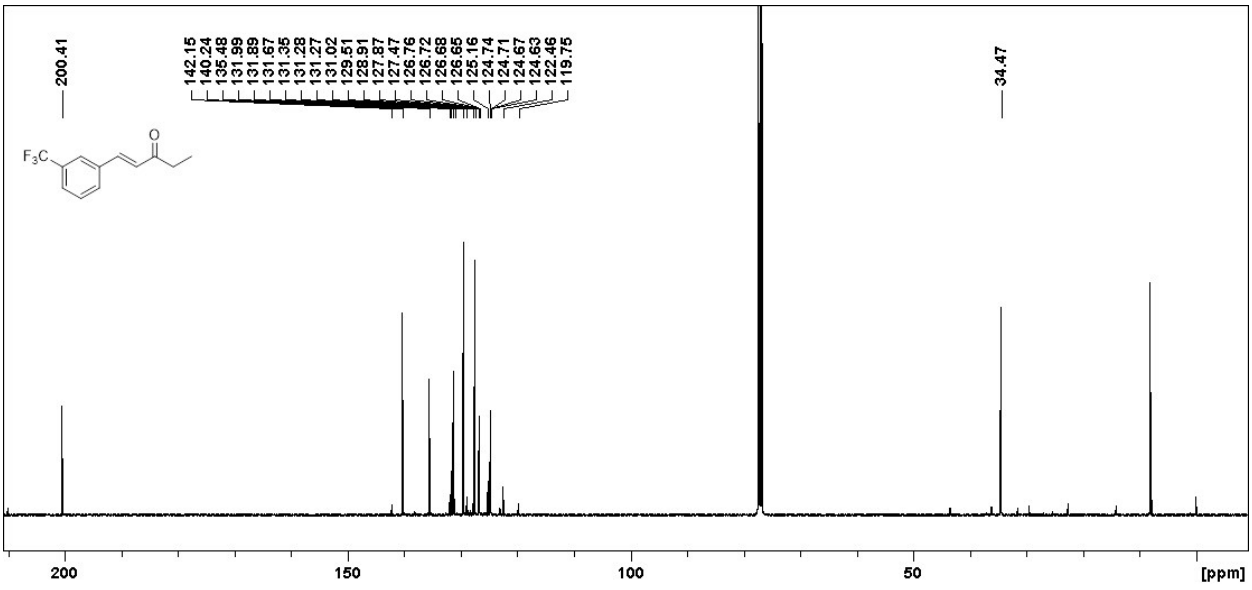
^{13}C NMR Spectrum for **32**



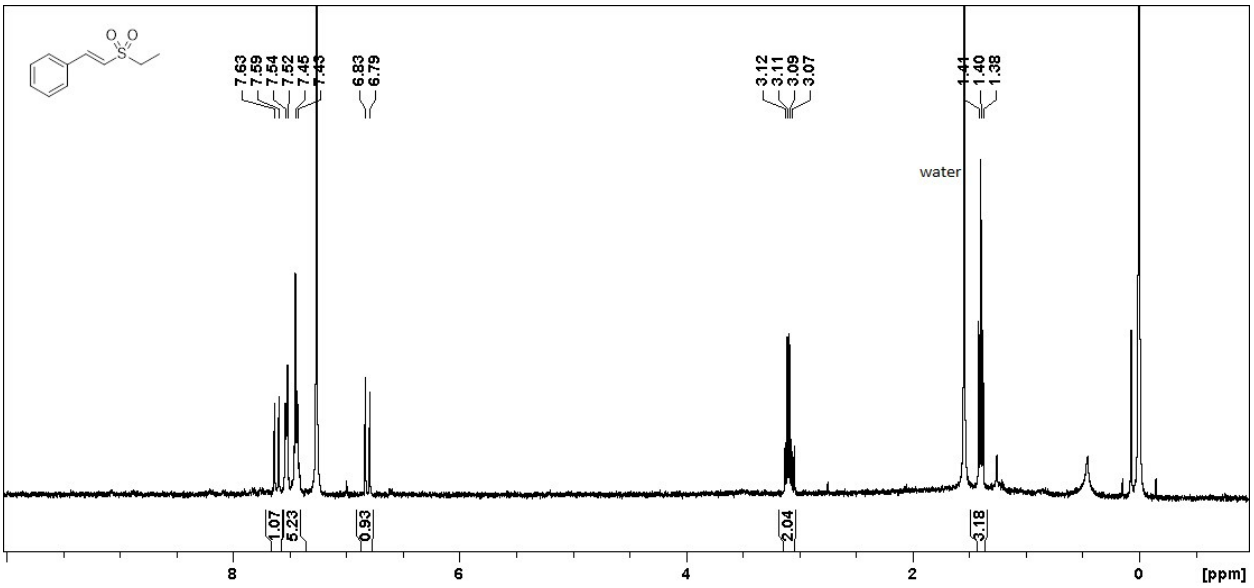
^{1}H NMR Spectrum for **33**



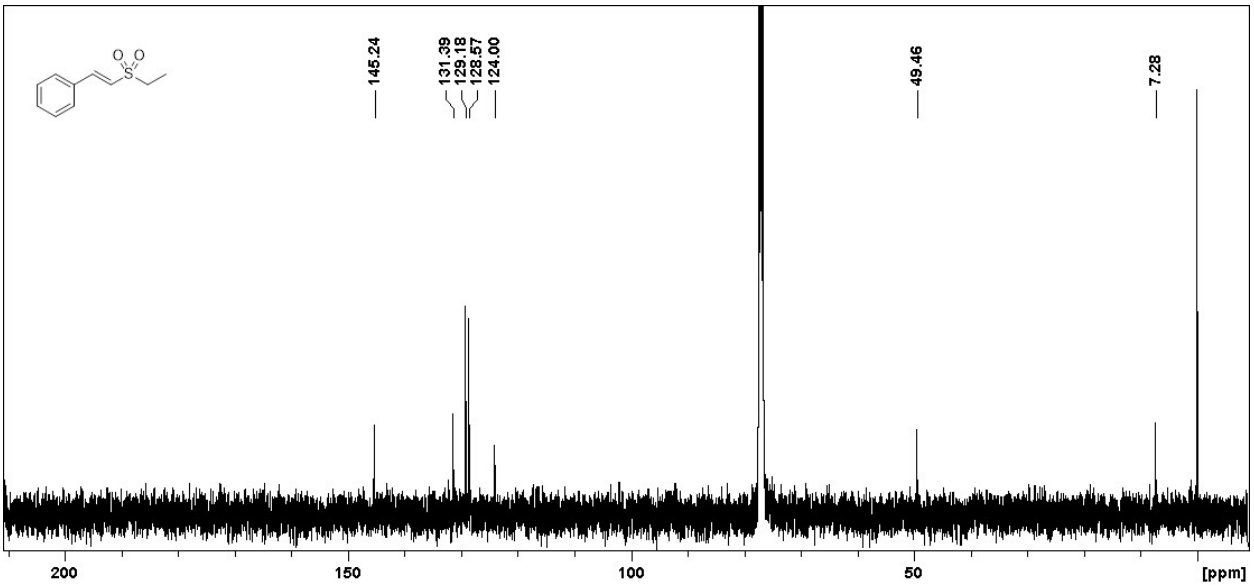
^{13}C NMR Spectrum for **33**



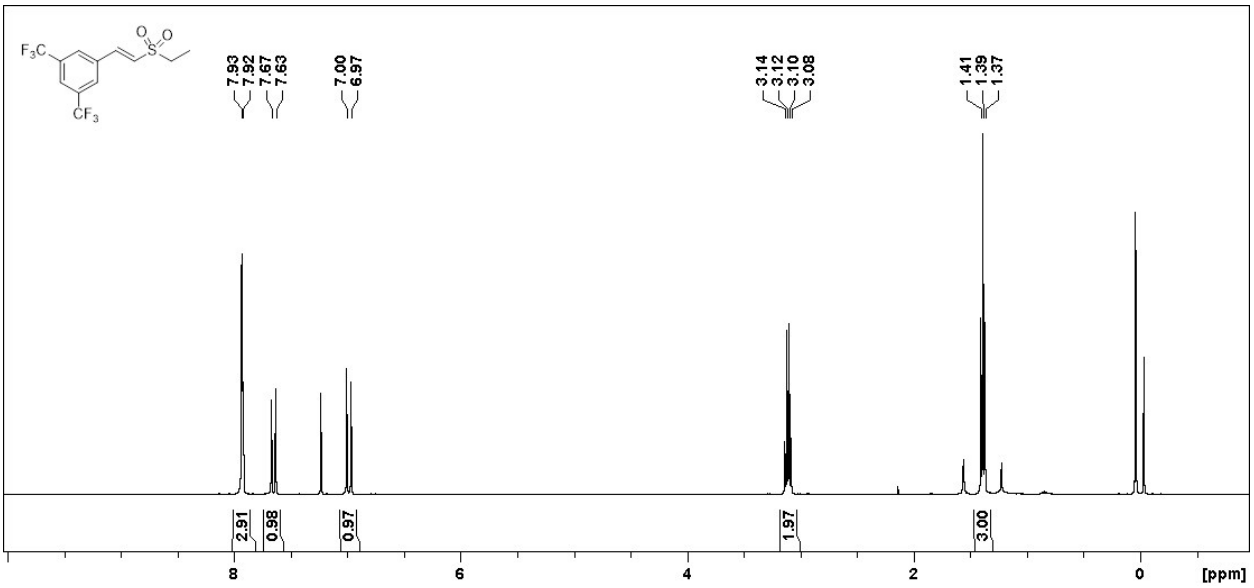
^{1}H NMR Spectrum for **34**



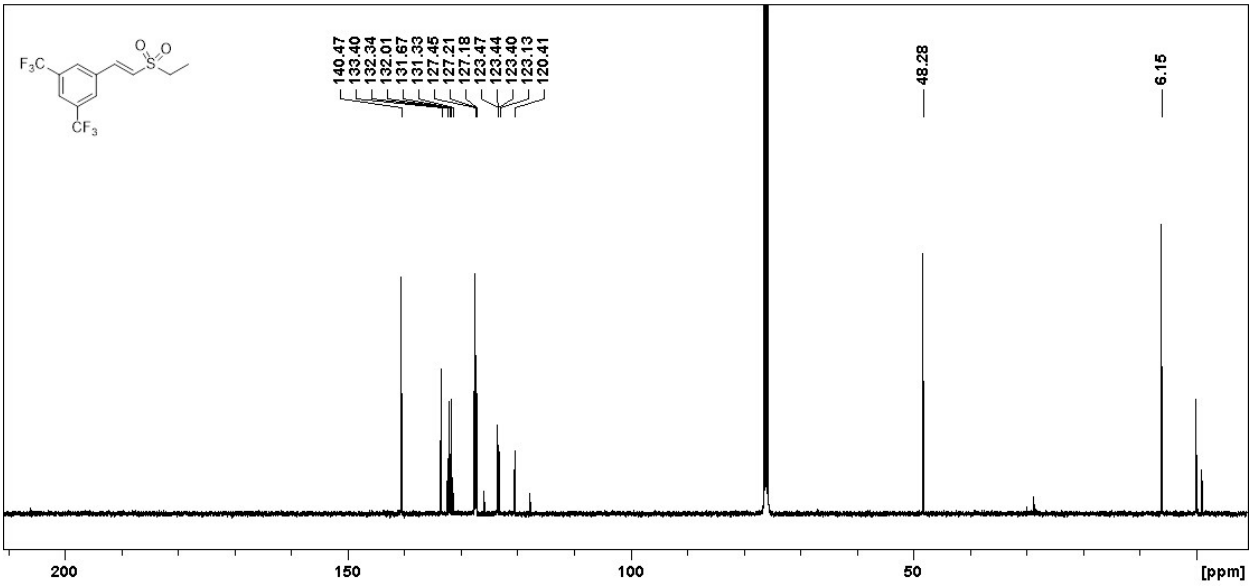
^{13}C NMR Spectrum for **34**



^{1}H NMR Spectrum for **35**



^{13}C NMR Spectrum for **35**



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