Metal-Free Cascade O-H Double Insertion Between $I^{(III)}/S^{(VI)}$-Ylides, Carboxylic Acids, and Alcohols: Modular Access to Unsymmetrical α,α-*O*,*O*-Substituted Ketones

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1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous CF_3CH_2OH, CH_3CN, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR (^1H) were recorded at 400 MHz, and Carbon NMR (^{13}C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

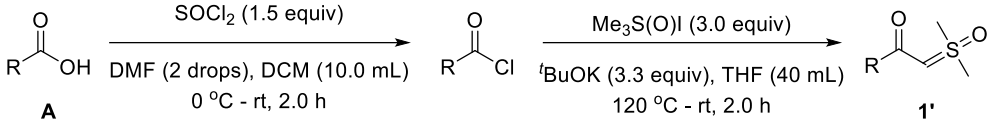
High-resolution mass spectra HRMS-ESI (TOF) was recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

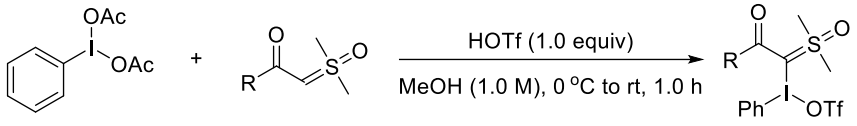
No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of substrates

2.1 General Procedure for the synthesis of sulfoxonium-iodonium hybrid ylides **1** .[1-2]



According to the literature, the slightly modified method is as follows. Under N_2, acid (5.0 mmol) in CH_2Cl_2 (10.0 mL) at 0 °C before adding $SOCl_2$ (7.5 mmol, 1.5 equiv) and two drop of DMF. After 60 minutes stirring at 50 °C, and the volatiles were carefully evaporated under high-vacuum. During that time, trimethylsulfoxonium iodide (3.3 g, 16.5 mmol, 3.0 equiv) was suspended under N_2 in dry THF (40.0 mL) in a flame-dried 100 mL round bottom flask that was protected from light with aluminium foil. Potassium tertbutoxide (1.8 g, 16.5 mmol, 3.3 equiv) was added, and the mixture was stirred at reflux for 3.0 hours. After cooling to 0 °C, a solution of acid chloride obtained above in THF (10.0 mL) was added dropwise to the mixture. The mixture was stirred at room temperature for another hour and then solvents were removed under vacuum. Then 80.0 ml water were added, extraction with CH_2Cl_2 (50.0 × 3 mL). Purification by flash chromatography (dichloromethane/MeOH = 30/1) provided the sulfoxonium ylides **1'** with high yields.

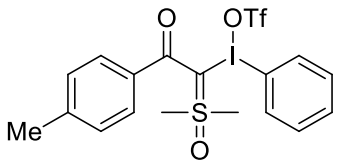


A solution of aryliodoso diacetate (5.0 mmol, 1.0 equiv.) in MeOH (5.0 mL, 1.0 M) was treated with corresponding acid HOTf (5.0 mmol, 1.0 equiv.) at room temperature. This clear solution was added dropwise to the ice bath-cooled solution of sulfoxonium ylides (5.0 mmol, 1.0 equiv.) in MeOH (5.0 mL, 1.0 M) over 10 min with stirring. The resulting reaction mixture was stirred at 0 °C for an additional 1.0 hour. During this period, a lot of white precipitate was formed. The product **1** was collected by filtration, washed successively with MeOH (5 mL × 3) and Et_2O (5 mL × 3), dried

under high vacuum and stored at -30 °C. If the hypervalent iodine reagent failed to precipitate, it was subjected to flash column chromatography, eluting with DCM/Acetone mixtures.

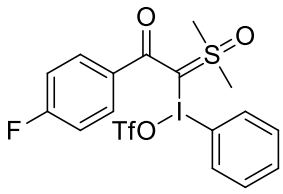
2.2 Characterization of substrates of **1**

(1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-oxo-2-(p-tolyl)ethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1b)



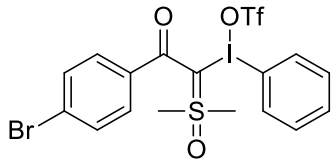
Following the general procedure 2.1. After filtration, **1b** was collected as a white solid (5.0 g, 8.89 mmol, 89% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 3.78 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ. ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 187.88, 141.18, 136.10, 132.23, 131.70, 131.51, 128.75, 127.46, 120.66 (q, J = 322.3 Hz), 119.91, 64.27, 42.02, 20.99. ^{19}F NMR (376 MHz, DMSO-d$_6$) δ -77.73. EI-MS: calculated $C_{18}H_{18}F_3IO_5S$ $[M]^+$ 561.9592; Found 561.9594.

(1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-(4-fluorophenyl)-2-oxoethyl)(phenyl)- λ^3-iodanyl trifluoromethanesulfonate (1c)



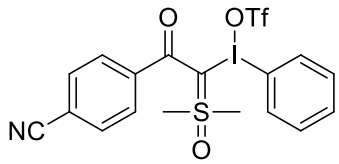
Following the general procedure 2.1. After filtration, **1c** was collected as a white solid (4.7 g, 8.29 mmol, 83% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.81 (d, J = 7.4 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.49 (dd, J = 8.7, 5.5 Hz, 2H), 7.31 (t, J = 8.9 Hz, 2H), 3.81 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 186.70, 163.45 (d, *J* = 248.7 Hz), 135.50 (d, *J* = 3.1 Hz), 132.40, 131.76, 131.59, 129.96 (d, *J* = 8.9 Hz), 120.68 (q, *J* = 322.3 Hz), 119.86, 115.39 (d, *J* = 21.9 Hz), 64.69, 41.97. ^{19}F NMR (376 MHz, DMSO-d$_6$) δ -77.72, -108.69. EI-MS: calculated $C_{17}H_{15}F_4IO_5S$ $[M]^+$ 565.9342; Found 565.9341.

(2-(4-bromophenyl)-1-(dimethyl(oxo)-λ^6 -sulfanylidene)-2-oxoethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1d)



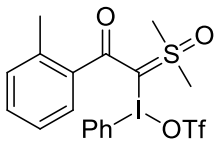
Following the general procedure 2.1. After filtration, **1d** was collected as a white solid (5.2 g, 8.29 mmol, 83% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.81 (d, J = 7.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 7.4 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 3.80 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 186.70, 138.18, 132.43, 131.77, 131.60, 131.38, 129.34, 120.67 (q, J = 322.3 Hz), 124.53, 119.89, 64.95, 41.19. ^{19}F NMR (376 MHz, DMSO-d$_6$) δ -77.72. EI-MS: calculated $C_{17}H_{15}BrF_3IO_5S$ $[M]^+$ 625.8541; Found 625.8545.

(2-(4-cyanophenyl)-1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-oxoethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1e)



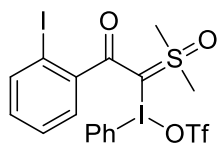
Following the general procedure 2.1. After filtration, **1e** was collected as a white solid (3.9 g, 6.80 mmol, 68% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 4H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 186.16, 143.42, 132.58, 131.80, 131.67, 127.94, 120.69 (q, J = 322.1 Hz), 119.90, 118.21, 113.29, 65.62, 41.87. ^{19}F NMR (376 MHz, DMSO-d$_6$) δ -77.70. EI-MS: calculated $C_{18}H_{15}F_3INO_5S$ $[M]^+$ 572.9388; Found 572.9384.

(1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-oxo-2-(o-tolyl)ethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1f)



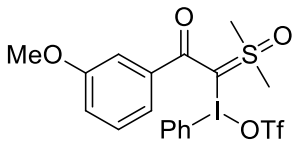
Following the general procedure 2.1. After filtration, **1f** was collected as a white solid (5.1 g, 9.07 mmol, 91% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.65 (t, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.1 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 3.85 (s, 6H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 189.30, 140.07, 134.93, 133.39, 132.03, 131.93, 131.04, 130.03, 126.66, 125.73, 121.15 (q J = 322.2 Hz), 120.25, 66.29, 42.43, 18.72. ^{19}F NMR (376 MHz, DMSO-d$_6$) δ -77.72. EI-MS: calculated $C_{18}H_{18}F_3IO_5S$ $[M]^+$ 561.9592; Found 561.9594.

(1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-(2-iodophenyl)-2-oxoethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1g)



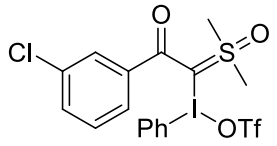
Following the general procedure 2.1. Purification by flash chromatography (dichloromethane/methanol = 20/1) provided **1g** as a yellow solid (2.1 g, 3.11mmol, 31% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.87 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.3 Hz, 1H), 7.57 (d, J = 7.7 Hz, 2H), 7.48 (t, J = 7.6 Hz, 3H), 7.21 (t, J = 7.0 Hz, 2H), 3.85 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 188.23, 144.83, 139.69, 137.59, 133.94, 132.13, 131.91, 131.64, 128.39, 127.97, 121.16 (q, J = 322.2 Hz), 94.24, 65.01, 42.23. ^{19}F NMR (376 MHz, DMSO-d$_6$) δ -77.67. EI-MS: calculated $C_{17}H_{15}F_3I_2O_5S$ $[M]^+$ 673.8402; Found 673.8404.

(1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-(3-methoxyphenyl)-2-oxoethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1h)



Following the general procedure 2.1. After filtration, **1h** was collected as a white solid (4.9 g, 8.47 mmol, 85% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.91 (s, 1H), 3.83 (s, 6H), 3.66 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 187.76, 158.84, 140.45, 132.09, 131.72, 131.48, 129.63, 120.70 (q, J = 322.3 Hz), 119.65, 119.42, 116.94, 112.34, 64.46, 55.17, 41.99. ^{19}F NMR (376 MHz, DMSO-d$_6$) δ -77.70. EI-MS: calculated $C_{18}H_{18}F_3IO_6S$ $[M]^+$ 577.9542; Found 577.9538.

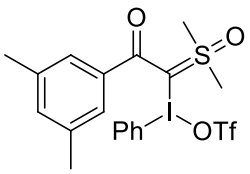
(2-(3-chlorophenyl)-1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-oxoethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1i)



Following the general procedure 2.1. After filtration, **1i** was collected as a white solid (3.6 g, 6.21 mmol, 62% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 12.3 Hz, 2H), 7.56 (s, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.34 (m, 2H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 186.73, 141.62, 133.38, 132.94, 132.23, 132.09, 131.31, 131.04, 127.56, 126.24,

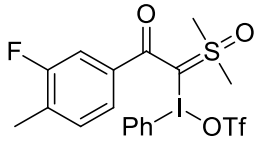
121.16 (q, J = 322.3 Hz), 120.42, 65.69, 42.36. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.70. EI-MS: calculated $C_{17}H_{15}ClF_3IO_6S$ $[M]^+$ 581.9046; Found 581.9044.

(1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-(3,5-dimethylphenyl)-2-oxoethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1j)



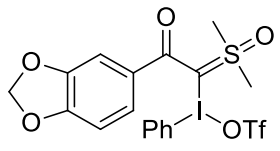
Following the general procedure 2.1. After filtration, **1j** was collected as a yellow solid (5.4 g, 9.37 mmol, 94% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.3 Hz, 1H), 7.59 (t, J = 7.6 Hz, 2H), 7.15 (s, 1H), 6.89 (s, 2H), 3.84 (s, 6H), 2.22 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.10, 139.65, 137.97, 132.91, 132.86, 132.10, 131.96, 121.18 (q, J = 644.6, 322.2 Hz), 125.37, 120.90, 65.19, 42.42, 21.17. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.70. EI-MS: calculated $C_{19}H_{20}F_3IO_5S_2$ $[M]^+$ 575.9749; Found 575.9752.

(1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-(3-fluoro-4-methylphenyl)-2-oxoethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1k)



Following the general procedure 2.1. After filtration, **1k** was collected as a white solid (4.9 g, 8.44 mmol, 84% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 (d, J = 7.3 Hz, 2H), 7.69 – 7.65 (m, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.7 Hz, 1H), 7.17 – 7.12 (m, 2H), 3.80 (s, 6H), 2.30 (s, 3H). δ -77.73, -116.48. ^{13}C NMR (101 MHz, DMSO-d_6) δ 186.76, 160.38 (d, J = 245.0 Hz), 139.07 (d, J = 6.7 Hz), 132.82, 132.23, 132.15, 132.08, 128.25 (d, J = 17.0 Hz), 123.74 (d, J = 3.3 Hz), 121.12 (q J = 322.3 Hz), 120.39, 114.45 (d, J = 23.6 Hz), 65.17, 42.42, 14.68 (d, J = 3.0 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) EI-MS: calculated $C_{18}H_{17}F_4IO_5S$ $[M]^+$ 579.9498; Found 579.9508.

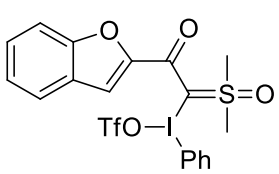
(2-(benzo[d][1,3]dioxol-5-yl)-1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-oxoethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1l)



Following the general procedure 2.1. Purification by flash chromatography (dichloromethane/methanol = 20/1) provided **1l** as a white solid (2.5 g, 4.22mmol, 42% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 (d, J = 7.7 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.56 (t, J = 7.7 Hz, 2H), 6.97 (d, J = 12.9 Hz,

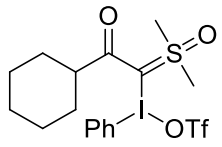
3H), 6.11 (s, 2H), 3.78 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 186.82, 149.70, 147.12, 137.10, 132.63, 132.34, 131.71, 130.66, 122.28, 120.95 (q J = 322.3 Hz), 119.07, 107.84, 101.83, 63.96, 42.06. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.73. EI-MS: calculated $C_{18}H_{16}F_3IO_7S$ $[M]^+$ 591.9334; Found 591.9340.

(2-(benzofuran-2-yl)-1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-oxoethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1m)



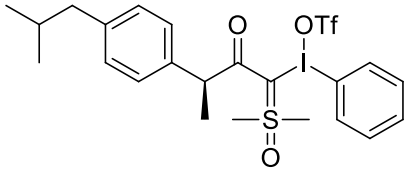
Following the general procedure 2.1. After filtration, **1m** was collected as a white solid (4.9 g, 8.33 mmol, 83% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11 (d, J = 7.4 Hz, 2H), 7.80 (d, J = 7.6 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.64 – 7.61 (m, 2H), 7.60 (s, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.39 – 7.35 (m, 1H), 3.86 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.94, 154.67, 152.33, 133.33, 132.03, 131.91, 128.16, 127.19, 121.14 (q, J = 322.3 Hz), 124.62, 123.57, 120.95, 112.36, 112.17, 63.64, 42.62. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.70. EI-MS: calculated $C_{19}H_{16}F_3IO_6S$ $[M]^+$ 587.9385; Found 587.9394.

(2-cyclohexyl-1-(dimethyl(oxo)-λ^6-sulfanylidene)-2-oxoethyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1n)



Following the general procedure 2.1. After filtration, **1n** was collected as a white solid (4.4 g, 7.93 mmol, 79% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 (d, J = 7.6 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 7.07 (t, J = 7.6 Hz, 2H), 3.20 (s, 6H), 2.89 (s, 1H), 1.13 (d, J = 13.4 Hz, 4H), 0.84 – 0.60 (m, 6H). ^{13}C NMR (101 MHz, DMSO) δ. ^{13}C NMR (101 MHz, DMSO-d_6) δ 194.17, 132.53, 131.62, 131.46, 120.71 (q, J = 322.3 Hz), 119.96, 62.10, 45.77, 42.20, 29.27, 25.37, 24.89. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.74. EI-MS: calculated $C_{17}H_{22}F_3IO_5S$ $[M]^+$ 553.9905; Found 553.9902.

***(R)*-(1-(dimethyl(oxo)-λ^6-sulfanylidene)-3-(4-isobutylphenyl)-2-oxobutyl)(phenyl)-λ^3-iodanyl trifluoromethanesulfonate (1o)**



Following the general procedure 2.1. After filtration, **1o** was collected as a white solid (4.4 g, 6.96 mmol, 70% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (d, *J* = 81.8 Hz, 5H), 7.04 (d, *J* = 46.1 Hz, 4H), 4.41 (s, 1H), 3.72 (s, 3H), 3.62 (s, 3H), 2.35 (s, 2H), 1.76 (s, 1H), 1.25 (s, 3H), 0.83 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 192.01, 140.13, 139.26, 137.01, 136.22, 132.41, 131.46, 129.74, 127.73, 121.17 (q, J = 322.3 Hz), 63.03, 47.18, 42.13, 29.99, 22.73, 22.66, 20.61. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.72. $[\alpha]^{20}_D$=·+1.33·(c·=0.15, MeOH). EI-MS: calculated $C_{23}H_{28}F_3IO_5S$ $[M]^+$ 632.0375; Found 632.0381.

3 General procedure and characterization of products

General procedure A

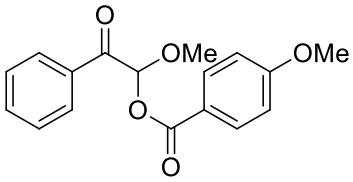
In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (0.2 mmol, 1.0 equiv), carb oxylic acid **2** (0.24 mmol, 1.2 equiv), Et_3N (2.0 equiv) and methanol (2.0 mL, 0.1 M) was st irred at 35 °C in the oil bath for 0.5 h. The pure product was purified by flash column chro matography on silica with an appropriate solvent to afford the pure product **3** and **4**.

General procedure B

In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (0.2 mmol, 1.0 equiv), carboxylic acid **2** (0.5 mmol, 2.5 equiv), CuI (0.02 mmol, 10.0 mol%), Et_3N (2.0 equiv) and DCM (2.0 mL, 0.1 M) was stirred at 35 °C in the oil bath for 0.5 h. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **5**.

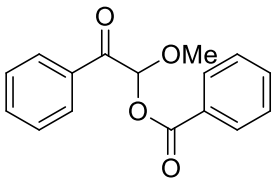
Characterization of products

1-methoxy-2-oxo-2-phenylethyl 4-methoxybenzoate（3a）



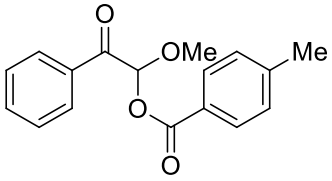
Following the above procedure A, the product **3a** was obtained in 97% yield (58.4 mg, 0.194 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.21. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 7.4 Hz, 2H), 7.46 – 7.34 (m, 3H), 6.93 (d, J = 8.6 Hz, 2H), 6.15 (s, 1H), 3.86 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.59, 165.68, 163.92, 134.27, 132.19, 129.33, 128.94, 127.75, 127.73, 121.68, 113.84, 74.74, 55.56, 52.74. ESI-MS: calculated $C_{17}H_{16}O_5Na$ $[M+Na]^+$ 323.0895; Found 323.0898.

1-methoxy-2-oxo-2-phenylethyl benzoate (3b)



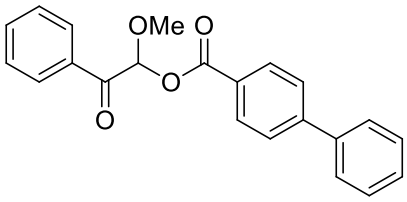
Following the above procedure A, the product **3b** was obtained in 94% yield (51.0 mg, 0.188 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). R_f (Petroleum ether/EtOAc 32:1): 0.19. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.8 Hz, 3H), 7.48 – 7.42 (m, 5H), 6.19 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.40, 165.97, 134.06, 133.60, 130.08, 129.41, 129.32, 128.97, 128.56, 127.75, 74.97, 52.78. ESI-MS: calculated $C_{16}H_{14}O_4Na$ $[M+Na]^+$ 293.0790; Found 293.0793.

1-methoxy-2-oxo-2-phenylethyl 4-methylbenzoate(3c)



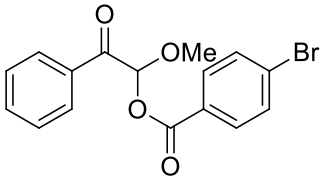
Following the above procedure A, the product **3c** was obtained in 61% yield (34.9 mg, 0.134 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). R_f (Petroleum ether/EtOAc 8:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 2H), 7.58 (dd, J = 7.6, 1.9 Hz, 2H), 7.41 (d, J = 0.6 Hz, 3H), 7.25 (d, J = 8.0 Hz, 2H), 6.15 (s, 1H), 3.74 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.45, 165.98, 144.34, 134.08, 130.05, 129.29, 129.20, 128.88, 127.67, 126.46, 74.76, 52.70, 21.77. ESI-MS: calculated $C_{17}H_{16}O_4Na$ $[M+Na]^+$ 307.0946; Found 307.0953.

1-methoxy-2-oxo-2-phenylethyl [1,1'-biphenyl]-4-carboxylate (3d)



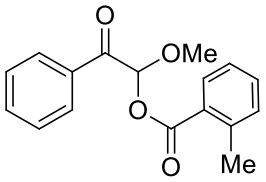
Following the above procedure A, the product **3d** was obtained in 82% yield (57.1mg, 0.164 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 7.65 – 7.61 (m, 4H), 7.49 – 7.41 (m, 6H), 6.21 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.45, 165.88, 146.34, 140.00, 134.08, 130.63, 129.44, 129.06, 129.00, 128.36, 127.78, 127.41, 127.33, 127.25, 74.99, 52.82. ESI-MS: calculated $C_{22}H_{18}O_4Na$ $[M+Na]^+$ 369.1103; Found 369.1100.

1-methoxy-2-oxo-2-phenylethyl 4-bromobenzoate (3e)



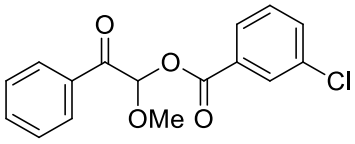
Following the above procedure A, the product **3e** was obtained in 52% yield (36.2 mg, 0.104 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). R_f (Petroleum ether/EtOAc 32:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.0 Hz, 2H), 7.61 – 7.55 (m, 4H), 7.43 (d, *J* = 5.5 Hz, 3H), 6.15 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.24, 165.28, 133.80, 131.95, 131.58, 129.55, 129.04, 128.85, 128.21, 127.79, 75.14, 52.87. ESI-MS: calculated $C_{16}H_{13}BrO_4Na$ $[M+Na]^+$ 370.9895; Found 370.9891, 372.9871.

1-methoxy-2-oxo-2-phenylethyl 2-methylbenzoate (3f)



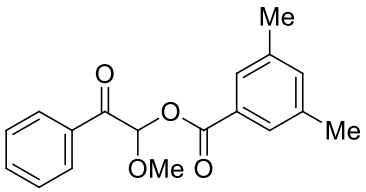
Following the above procedure A, the product **3f** was obtained in 60% yield (34.0 mg, 0.120 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). R_f (Petroleum ether/EtOAc 32:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.04 (m, 1H), 7.57 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.42 (dd, *J* = 9.1, 3.4 Hz, 5H), 7.24 (d, *J* = 2.8 Hz, 1H), 6.15 (s, 1H), 3.75 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.58, 166.88, 140.86, 134.04, 132.62, 131.83, 131.14, 129.37, 128.96, 128.65, 127.82, 125.92, 74.94, 52.80, 21.86. ESI-MS: calculated $C_{17}H_{16}O_4Na$ $[M+Na]^+$ 307.0946; Found 307.0952.;372.9871

1-methoxy-2-oxo-2-phenylethyl 3-chlorobenzoate (3g)



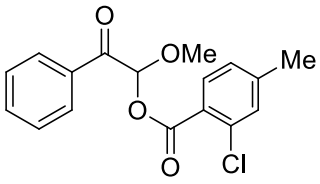
Following the above procedure A, the product **3g** was obtained in 79% yield (48.3 mg, 0.158 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). R_f (Petroleum ether/EtOAc 32:1): 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (t, *J* = 1.8 Hz, 1H), 8.03 – 7.99 (m, 1H), 7.58 – 7.55 (m, 3H), 7.46 – 7.39 (m, 4H), 6.16 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.18, 164.83, 134.75, 133.72, 133.68, 131.04, 130.08, 129.93, 129.59, 129.07, 128.25, 127.83, 75.27, 52.91. ESI-MS: calculated $C_{16}H_{13}ClO_4Na$. $[M+Na]^+$ 327.0400; Found 327.0403; 329.0376.

1-methoxy-2-oxo-2-phenylethyl 3,5-dimethylbenzoate (3h)



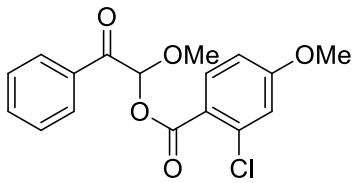
Following the above procedure A, the product **3h** was obtained in 73% yield (43.3 mg, 0.146 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). R_f (Petroleum ether/EtOAc 32:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.59 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.45 – 7.42 (m, 3H), 7.22 (s, 1H), 6.16 (s, 1H), 3.76 (s, 3H), 2.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.52, 166.38, 138.24, 135.32, 134.14, 129.38, 129.12, 128.98, 127.81, 127.77, 74.90, 52.78, 21.27. ESI-MS: calculated ESI-MS: calculated $C_{18}H_{18}O_4Na$ $[M+Na]^+$ 321.1103; Found 321.1099.

1-methoxy-2-oxo-2-phenylethyl 2-chloro-4-methylbenzoate (3i)



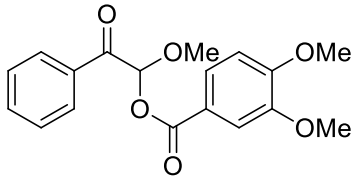
Following the above procedure A, the product **3i** was obtained in 86% yield (55.1 mg, 0.172 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). R_f (Petroleum ether/EtOAc 32:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 2H), 7.43 – 7.40 (m, 3H), 7.29 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.17 (s, 1H), 3.75 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.25, 164.63, 144.51, 134.50, 133.72, 132.25, 131.91, 129.39, 128.92, 127.80, 127.56, 125.62, 75.19, 52.80, 21.31. ESI-MS: calculated $C_{17}H_{15}ClO_4Na$ $[M+Na]^+$ 341.0557; Found 341.0557; 343.0522.

1-methoxy-2-oxo-2-phenylethyl 2-chloro-4-methoxybenzoate (3j)



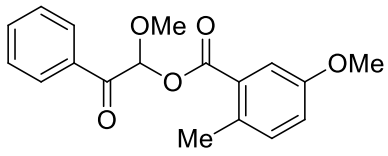
Following the above procedure A, the product **3j** was obtained in 75% yield (50.3 mg, 0.150 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). R_f (Petroleum ether/EtOAc 16:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.56 (d, *J* = 1.7 Hz, 1H), 7.45 – 7.36 (m, 3H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.15 (s, 1H), 3.83 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.33, 164.09, 163.06, 136.63, 134.05, 133.80, 129.32, 128.87, 127.75, 120.27, 116.60, 112.71, 75.02, 55.77, 52.74. ESI-MS: calculated $C_{17}H_{15}ClO_4Na$ $[M+Na]^+$ 357.0506; Found 357.0510; 359.0482.

1-methoxy-2-oxo-2-phenylethyl 3,4-dimethoxybenzoate (3k)



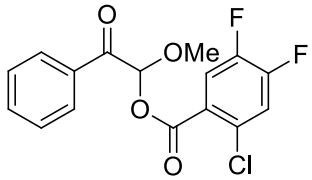
Following the above procedure A, the product **3k** was obtained in 45% yield (29.5 mg, 0.090 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). R_f (Petroleum ether/EtOAc 8:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.59 – 7.56 (m, 3H), 7.42 (d, *J* = 6.6 Hz, 3H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.14 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.58, 165.80, 153.59, 148.79, 134.17, 129.37, 128.97, 127.75, 124.32, 121.69, 112.32, 110.37, 74.89, 56.16, 56.12, 52.78. ESI-MS: calculated $C_{18}H_{18}O_6Na$ $[M+Na]^+$ 353.1001; Found 353.0999.

1-methoxy-2-oxo-2-phenylethyl 5-methoxy-2-methylbenzoate (3l)



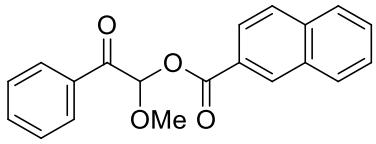
Following the above procedure A, the product **3l** was obtained in 77% yield (48.3 mg, 0.154 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 7.2, 2.2 Hz, 3H), 7.43 – 7.40 (m, 3H), 7.17 (d, J = 8.4 Hz, 1H), 6.99 (dd, J = 8.4, 2.8 Hz, 1H), 6.15 (s, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.51, 166.80, 157.49, 133.96, 132.81, 132.73, 129.38, 129.31, 128.96, 127.81, 118.65, 115.92, 75.05, 55.56, 52.79, 20.97. ESI-MS: calculated $C_{18}H_{18}O_5Na$ $[M+Na]^+$ 337.1052; Found 337.1057.

1-methoxy-2-oxo-2-phenylethyl 2-chloro-4,5-difluorobenzoate (3m)



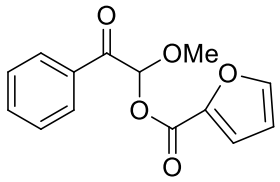
Following the above procedure A, the product **3m** was obtained in 87% yield (59.4 mg, 0.174 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.20: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 10.3, 8.3 Hz, 1H), 7.54 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.43 (d, *J* = 2.1 Hz, 2H), 7.33 (dd, *J* = 9.7, 6.9 Hz, 1H), 6.16 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.93, 162.81, 152.53 (dd, *J* = 259.8, 13.5 Hz), 148.70 (dd, *J* = 251.2, 12.6 Hz), 133.29, 130.86 (dd, *J* = 8.5, 3.7 Hz), 129.72, 129.11, 127.91, 125.29 – 125.15 (m), 121.22 (dd, *J* = 20.2, 1.9 Hz), 120.68 (d, *J* = 20.4 Hz), 75.70, 53.01. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.74, -137.47. ESI-MS: calculated $C_{16}H_{11}ClF_2O_4Na$. $[M+Na]^+$ 363.0212; Found 363.0208; 365.0173.

1-methoxy-2-oxo-2-phenylethyl 2-naphthoate (3n)



Following the above procedure A, the product **3n** was obtained in 40% yield (25.5 mg, 0.080 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.58 (dd, *J* = 15.1, 8.0 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 3H), 6.25 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.50, 166.19, 135.89, 134.09, 132.53, 131.82, 129.58, 129.48, 129.04, 128.64, 128.40, 127.91, 127.86, 126.86, 126.50, 125.42, 75.12, 52.85. ESI-MS: calculated $C_{20}H_{16}O_4Na$. $[M+Na]^+$ 343.0946; Found 343.0950.

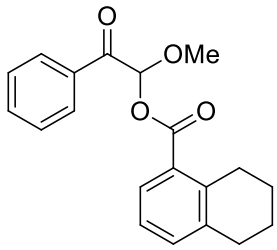
1-methoxy-2-oxo-2-phenylethyl furan-2-carboxylate (3o)



Following the above procedure A, the product **3o** was obtained in 93% yield (48.6 mg, 0.186 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.19: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.43 – 7.39 (m, 3H), 7.31 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.53

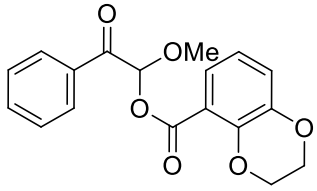
(dd, *J* = 3.5, 1.7 Hz, 1H), 6.15 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.14, 157.86, 147.13, 143.82, 133.65, 129.49, 128.98, 127.79, 119.39, 112.13, 74.65, 52.87. ESI-MS: calculated $C_{14}H_{12}O_5Na$ $[M+Na]^+$ 283.0582; Found 283.0584.

1-methoxy-2-oxo-2-phenylethyl 5,6,7,8-tetrahydronaphthalene-1-carboxylate (3p)



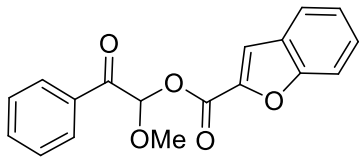
Following the above procedure A, the product **3p** was obtained in 33% yield (21.2 mg, 0.066 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.21: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.2 Hz, 1H), 7.56 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.41 (dd, *J* = 4.8, 2.5 Hz, 3H), 7.24 (s, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.13 (s, 1H), 3.76 (s, 3H), 3.11 (s, 2H), 2.82 (s, 2H), 1.81 – 1.77 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.55, 167.26, 139.26, 138.46, 133.97, 133.71, 129.24, 129.07, 128.85, 128.45, 127.71, 125.07, 74.80, 52.70, 30.21, 27.77, 23.09, 22.41. ESI-MS: calculated $C_{20}H_{20}O_4Na$ $[M+Na]^+$ 347.1259; Found 347.1259.

1-methoxy-2-oxo-2-phenylethyl 2,3-dihydrobenzo[b][1,4]dioxine-5-carboxylate (3q)



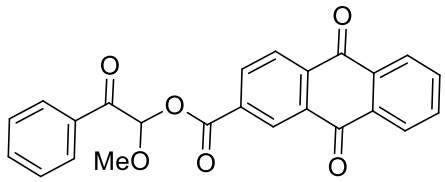
Following the above procedure A, the product **3q** was obtained in 60% yield (39.3 mg, 0.120 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.21: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 3H), 7.40 (d, *J* = 6.9 Hz, 3H), 7.05 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.86 (t, *J* = 8.0 Hz, 1H), 6.14 (s, 1H), 4.37 (d, *J* = 3.3 Hz, 2H), 4.29 (d, *J* = 4.1 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.49, 164.38, 145.00, 144.19, 134.05, 129.26, 128.87, 127.70, 124.37, 122.12, 120.44, 118.56, 74.74, 64.72, 63.89, 52.76. ESI-MS: calculated $C_{18}H_{16}O_6Na$ $[M+Na]^+$ 351.0845; Found 351.0844.

1-methoxy-2-oxo-2-phenylethyl benzofuran-2-carboxylate (3r)



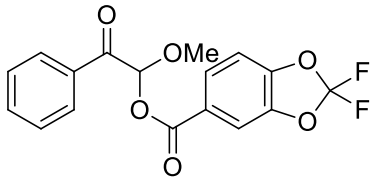
Following the above procedure A, the product **3r** was obtained in 49% yield (30.6 mg, 0.098 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.23: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.2 Hz, 2H), 7.62 – 7.58 (m, 3H), 7.49 – 7.43 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.23 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.99, 158.83, 156.11, 144.61, 133.52, 129.61, 129.04, 128.11, 127.86, 126.93, 124.02, 123.08, 115.35, 112.58, 75.06, 52.95. ESI-MS: calculated $C_{18}H_{14}O_5Na$ $[M+Na]^+$ 333.0739; Found 333.0744.

1-methoxy-2-oxo-2-phenylethyl 9,10-dioxo-9,10-dihydroanthracene-2-carboxylate (3s)



Following the above procedure A, the product **3s** was obtained in 22% yield (17.8 mg, 0.044 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.20: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 1.2 Hz, 1H), 8.50 (dd, *J* = 8.1, 1.6 Hz, 1H), 8.40 (d, *J* = 8.1 Hz, 1H), 8.35 – 8.31 (m, 2H), 7.83 (dd, *J* = 5.3, 3.8 Hz, 2H), 7.61 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.48 – 7.45 (m, 3H), 6.23 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.63, 182.28, 169.04, 164.54, 136.55, 134.99, 134.70, 134.60, 134.34, 133.71, 133.52, 133.46, 129.74, 129.18, 127.93, 127.78, 127.61, 127.57, 75.67, 53.02. ESI-MS: calculated $C_{24}H_{16}O_6Na$ $[M+Na]^+$ 423.0845; Found 423.0850.

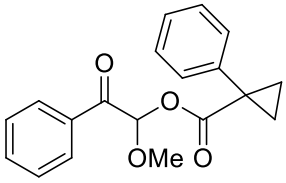
1-methoxy-2-oxo-2-phenylethyl 2,2-difluorobenzo[d][1,3]dioxole-5-carboxylate (3t)



Following the above procedure A, the product **3t** was obtained in 50% yield (35.0 mg, 0.100 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.18: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 1H), 7.82 (s, 1H), 7.56 (dd, J = 6.4, 2.0 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.13 (d, J = 8.4 Hz, 1H), 6.16 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.18, 164.49, 145.70 (d, *J* = 370.8 Hz), 134.36, 133.71, 131.80, 129.62, 129.08, 127.80, 127.22, 125.52, 111.23,

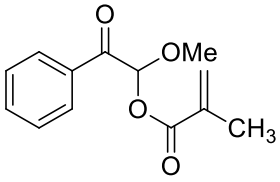
109.42, 75.30, 52.90. ESI-MS: calculated $C_{17}H_{12}F_2O_6Na$. ^{19}F NMR (377 MHz, $CDCl_3$) δ -49.73, -49.74. $[M+Na]^+$ 373.0500; Found 373.0502; 374.0533.

1-methoxy-2-oxo-2-phenylethyl 1-phenylcyclopropanecarboxylate (3x)



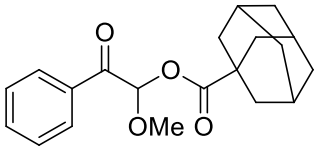
Following the above procedure A, the product **3x** was obtained in 77% yield (43.2 mg, 0.154 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.18: ^1H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.28 (m, 8H), 5.91 (s, 1H), 3.70 (s, 3H), 1.77 (dtd, *J* = 9.7, 6.7, 3.1 Hz, 2H), 1.36 (td, *J* = 6.3, 3.3 Hz, 1H), 1.29 (dd, *J* = 7.7, 4.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.98, 169.37, 138.93, 133.83, 130.64, 129.03, 128.71, 128.24, 127.40, 127.17, 74.59, 52.67, 29.18, 17.21, 16.71. ESI-MS: calculated $C_{19}H_{18}O_4Na$ $[M+Na]^+$ 333.1103; Found 333.1104.

1-methoxy-2-oxo-2-phenylethyl methacrylate (3y)



Following the above procedure A, the product **3y** was obtained in 64% yield (29.5 mg, 0.128 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1) :0.21: ^1H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.3, 1.3 Hz, 2H), 7.39 (d, J = 7.1 Hz, 3H), 6.28 (s, 1H), 5.99 (d, 1H), 5.67 (d, 1H), 3.72 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.41, 166.69, 135.52, 134.04, 129.30, 128.90, 127.62, 127.09, 74.69, 52.69, 18.27. ESI-MS: calculated $C_{13}H_{14}O_4Na$ $[M+Na]^+$ 257.0790; Found 257.0790.

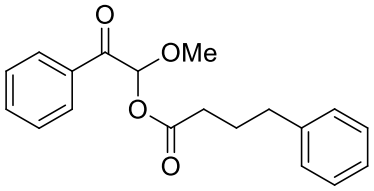
1-methoxy-2-oxo-2-phenylethyl adamantane-1-carboxylate (3z)



Following the above procedure A, the product **3z** was obtained in 71% yield (46.8 mg, 0.142 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.21: ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.41 – 7.37 (m, 3H), 5.89 (s, 1H), 3.71 (s, 3H), 2.04 (s, 3H), 2.00 – 1.98 (m, 6H), 1.75 – 1.72 (m, 6H).

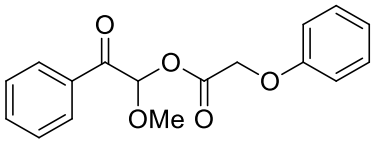
^{13}C NMR (151 MHz, $CDCl_3$) δ 177.06, 169.62, 134.28, 129.17, 128.86, 127.55, 74.07, 52.66, 40.87, 38.80, 36.59, 28.02. ESI-MS: calculated $C_{20}H_{24}O_4Na$ $[M+Na]^+$ 351.1572; Found 351.1573 .

1-methoxy-2-oxo-2-phenylethyl 4-phenylbutanoate (3aa)



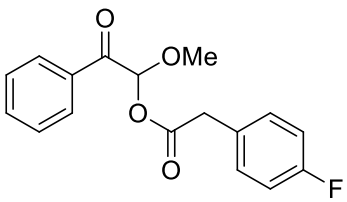
Following the above procedure A, the product **3aa** was obtained in 59% yield (36.8 mg, 0.118 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.42 (d, *J* = 7.1 Hz, 3H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.20 (m, 3H), 5.98 (s, 1H), 3.74 (s, 3H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.51 (dd, *J* = 23.4, 16.0, 8.3 Hz, 2H), 2.05 (dt, *J* = 7.6, 5.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.89, 169.43, 141.37, 133.91, 129.33, 128.89, 128.62, 128.48, 127.72, 126.08, 74.43, 52.67, 35.03, 33.33, 26.52. ESI-MS: calculated $C_{19}H_{20}O_4Na$ $[M+Na]^+$ 335.1259; Found 335.1265.

1-methoxy-2-oxo-2-phenylethyl 2-phenoxyacetate (3ab)



Following the above procedure A, the product **3ab** was obtained in 60% yield (36.2mg, 0.120 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.19: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H), 7.41 – 7.38 (m, 3H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.06 (s, 1H), 4.80 (s, *J* = 43.0, 16.5 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.99, 168.67, 157.92, 133.41, 129.81, 129.74, 129.13, 127.93, 122.10, 114.97, 75.09, 65.26, 53.04. ESI-MS: calculated $C_{17}H_{16}O_5Na$ $[M+Na]^+$ 323.0895; Found 323.0899.

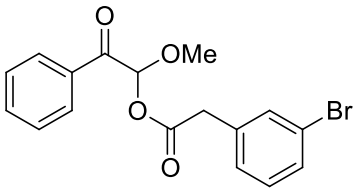
1-methoxy-2-oxo-2-phenylethyl 2-(4-fluorophenyl)acetate (3ac)



Following the above procedure A, the product **3ac** was obtained in 71% yield (43.2 mg, 0.142 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 1.7 Hz, 2H), 7.41 – 7.37 (m, 3H), 7.30 – 7.26 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.95

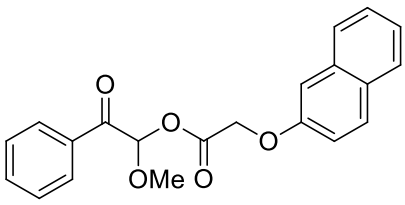
(s, 1H), 3.79 (d, *J* = 15.8 Hz, 1H), 3.73 (d, *J* = 15.8 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.93, 169.22, 162.23(d, J = 245.5 Hz), 133.68, 131.11(d, J = 8.1 Hz), 129.46, 129.17(d, J = 3.2 Hz), 128.96, 127.71, 115.58(d, J = 21.5 Hz), 74.92, 52.80, 40.10. ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.51. ESI-MS: calculated $C_{17}H_{15}FO_4Na$ $[M+Na]^+$ 325.0852; Found 325.0857; 326.0888.

1-methoxy-2-oxo-2-phenylethyl 2-(3-bromophenyl)acetate (3ad)



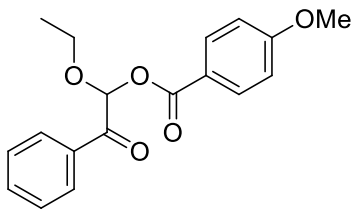
Following the above procedure A, the product **3ad** was obtained in 68% yield (49.6 mg, 0.136 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.22: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.48 – 7.41 (m, 6H), 7.28 (d, *J* = 6.5 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 5.99 (s, 1H), 3.83 – 3.76 (m, 2H), 3.73 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.40, 169.14, 135.55, 133.59, 132.60, 130.54, 130.20, 129.48, 128.97, 128.22, 127.71, 122.62, 75.00, 52.81, 40.41. ESI-MS: calculated $C_{17}H_{15}BrO_4Na$ $[M+Na]^+$ 385.0051; Found 385.0057; 387.0038.

1-methoxy-2-oxo-2-phenylethyl 2-(naphthalen-2-yloxy)acetate (3ae)



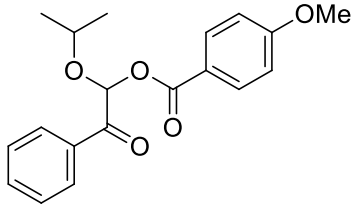
Following the above procedure A, the product **3ae** was obtained in 87% yield (68.9 mg, 0.174 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.22: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.5, 3.8 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.37 (m, 8H), 7.29 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.19 (d, *J* = 2.3 Hz, 1H), 6.14 (s, 1H), 4.99 (d, *J* = 16.4 Hz, 1H), 4.91 (d, *J* = 16.3 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.78, 168.33, 155.63, 134.31, 133.22, 129.76, 129.57, 129.51, 128.95, 127.76, 127.68, 127.04, 126.54, 124.17, 118.59, 107.44, 74.95, 65.16, 52.86. ESI-MS: calculated $C_{21}H_{18}O_5Na$ $[M+Na]^+$ 373.1052; Found 373.1049.

1-ethoxy-2-oxo-2-phenylethyl 4-methoxybenzoate (3ah)



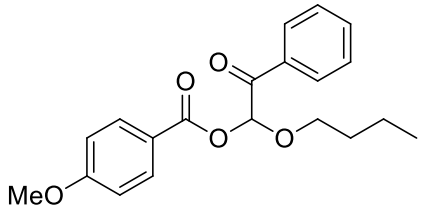
Following the above procedure A, the product **3ah** was obtained in 58% yield (36.3 mg, 0.116 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.20: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 7.1 Hz, 2H), 7.44 – 7.40 (m, 3H), 6.93 (d, J = 8.8 Hz, 2H), 6.12 (s, 1H), 4.27 – 4.16 (m, 2H), 3.86 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.10, 165.72, 163.90, 134.42, 132.20, 129.25, 128.91, 127.73, 127.72, 121.80, 113.84, 74.89, 61.81, 55.59, 14.15. ESI-MS: calculated $C_{18}H_{18}O_5Na$ $[M+Na]^+$ 337.1052; Found 337.1058.

1-isopropoxy-2-oxo-2-phenylethyl 4-methoxybenzoate (3ai)



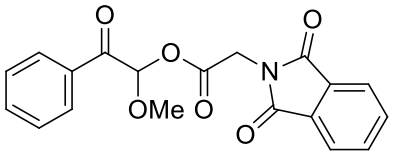
Following the above procedure A, the product **3ai** was obtained in 45% yield (29.8 mg, 0.009 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.20: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.39 (m, 3H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.08 (s, 1H), 3.86 (s, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.12 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.59, 165.72, 163.85, 134.51, 132.16, 129.14, 128.84, 127.66, 121.88, 113.81, 75.04, 69.51, 55.57, 21.81, 21.54. ESI-MS: calculated $C_{19}H_{20}O_5Na$ $[M+Na]^+$ 351.1208; Found 351.1214.

1-butoxy-2-oxo-2-phenylethyl 4-methoxybenzoate (3aj)



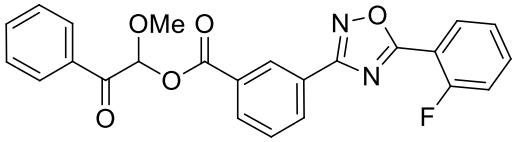
Following the above procedure A, the product **3aj** was obtained in 26% yield (17.5 mg, 0.052 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.22: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.44 – 7.39 (m, 3H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.13 (s, 1H), 4.18 – 4.13 (m, 2H), 3.85 (s, 3H), 1.60 – 1.55 (m, 2H), 1.27 (d, *J* = 8.0 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.15, 165.68, 163.87, 134.46, 132.15, 129.20, 128.86, 127.66, 121.79, 113.80, 74.87, 65.55, 55.55, 30.53, 18.99, 13.67. ESI-MS: calculated $C_{20}H_{22}O_5Na$ $[M+Na]^+$ 365.1365; Found 365.1372.

1-methoxy-2-oxo-2-phenylethyl 2-(1,3-dioxoisoindolin-2-yl) acetate (3an)



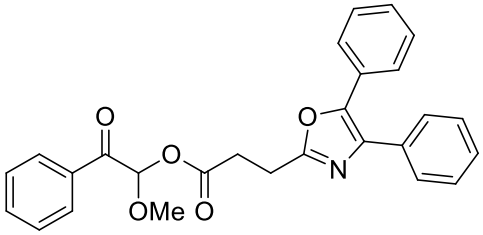
Following the above procedure A, the product **3an** was obtained in 18% yield (12.7 mg, 0.036 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). Rf (Petroleum ether/EtOAc 4:1): 0.22: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.76 – 7.73 (m, 2H), 7.44 (d, *J* = 2.1 Hz, 2H), 7.40 – 7.38 (m, 3H), 6.01 (s, 1H), 4.68 (d, *J* = 17.6 Hz, 1H), 4.54 (d, *J* = 17.6 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.60, 167.42, 166.95, 134.42, 133.26, 132.11, 129.65, 129.02, 127.78, 123.81, 75.54, 52.93, 38.90. ESI-MS: calculated $C_{19}H_{15}NO_6Na$ $[M+Na]^+$ 376.0797; Found 376.0802.

1-methoxy-2-oxo-2-phenylethyl 3-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl) benzoate (3ao)



Following the above procedure A, the product **3ao** was obtained in 65% yield (56.1 mg, 0.130 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). Rf (Petroleum ether/EtOAc 4:1): 0.19: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.43 (d, *J* = 7.7 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 8.24 (t, *J* = 7.4 Hz, 1H), 7.66 – 7.61 (m, 4H), 7.49 – 7.45 (m, 3H), 7.36 (t, J = 7.6 Hz, 1H), 7.30 (t, 1H), 6.25 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.13, 169.25, 168.01, 165.28, 160.87 (d, *J* = 260.8 Hz) 134.84 (d, *J* = 8.6 Hz), 133.82, 132.52 (d, *J* = 29.3 Hz), 130.27 (d, *J* = 232.0 Hz), 130.20, 129.21 (d, *J* = 13.1 Hz), 129.03, 127.82, 127.48, 124.83 (d, *J* = 3.7 Hz), 117.26 (d, *J* = 20.8 Hz), 112.73 (d, *J* = 11.3 Hz), 75.27, 52.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.11. ESI-MS: calculated $C_{24}H_{17}FN_2O_5Na$ $[M+Na]^+$ 455.1019; Found 455.1017; 456.1046.

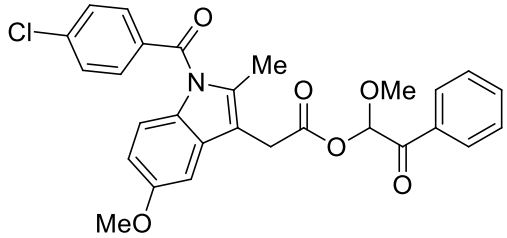
1-methoxy-2-oxo-2-phenylethyl 3-(4,5-diphenyloxazol-2-yl)propanoate (3ap)



Following the above procedure A, the product **3ap** was obtained in 35% yield (30.8 mg, 0.070 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.22: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.8 Hz,

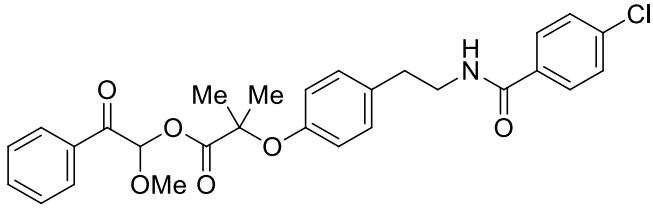
2H), 7.46 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.37 – 7.31 (m, 9H), 6.00 (s, 1H), 3.71 (s, 3H), 3.26 – 3.23 (m, 2H), 3.13 – 3.06 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.47, 169.25, 161.53, 145.58, 135.24, 133.71, 132.53, 129.40, 129.06, 128.91, 128.74, 128.64, 128.56, 128.16, 128.00, 127.71, 126.61, 74.81, 52.78, 31.04, 23.52. ESI-MS: calculated $C_{27}H_{23}NO_5Na$ $[M+Na]^+$ 464.1474; Found 464.1481.

1-methoxy-2-oxo-2-phenylethyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (3aq)



Following the above procedure A, the product **3aq** was obtained in 59% yield (59.4 mg, 0.118 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.22: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.44 (dd, *J* = 9.0, 6.0 Hz, 4H), 7.39 – 7.37 (m, 3H), 6.99 (s, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.68 (dd, *J* = 9.0, 1.8 Hz, 1H), 5.95 (s, 1H), 3.84 (s, 2H), 3.79 (s, 3H), 3.69 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.27, 169.16, 168.39, 156.15, 139.32, 136.12, 133.95, 133.63, 131.30, 130.85, 130.58, 129.43, 129.19, 128.91, 127.67, 115.04, 112.13, 112.10, 101.14, 74.96, 55.71, 52.76, 30.06, 13.53. ESI-MS: calculated $C_{28}H_{24}ClNO_6Na$ $[M+Na]^+$ 528.1190; Found 528.1193; 530.1168.

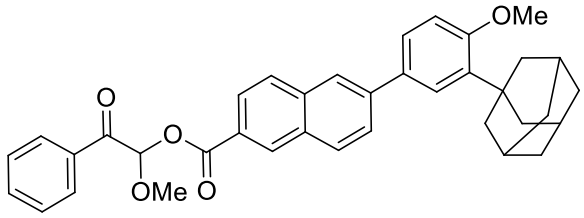
1-methoxy-2-oxo-2-phenylethyl 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate (3ar)



Following the above procedure A, the product **3ar** was obtained in 52% yield (53.3 mg, 0.104 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.20: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.36 – 7.31 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 4.9 Hz, 1H), 5.97 (s, 1H), 3.69 (s, 3H), 3.60 (q, *J* = 6.7 Hz, 2H), 2.82 (t, *J* = 7.0 Hz, 2H), 1.66 (d, *J* = 8.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.60, 168.95, 166.50, 153.95, 137.57, 133.34, 133.05, 132.73, 129.49, 129.40, 128.87, 128.78, 128.40,

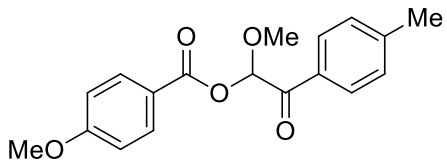
127.51, 120.10, 79.21, 75.04, 52.75, 41.34, 34.77, 25.86, 25.24. ESI-MS: calculated $C_{28}H_{28}ClNO_6Na$ $[M+Na]^+$ 532.1503; Found 532.1505; 534.1485.

1-methoxy-2-oxo-2-phenylethyl 6-(3-(adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (3as)



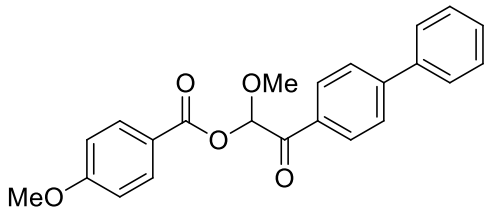
Following the above procedure A, the product **3as** was obtained in 27% yield (30.8 mg, 0.054 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.17 (s, 1H), 8.05 (d, 2H), 7.96 (s, 1H), 7.84 (s, 1H), 7.67 (d, *J* = 22.5 Hz, 3H), 7.58 (s, 1H), 7.53 – 7.46 (m, 3H), 7.03 (s, 1H), 6.29 (s, 1H), 3.94 (s, 3H), 3.83 (s, 3H), 2.25 – 2.22 (m, 6H), 2.17 – 2.13 (m, 3H), 1.87 – 1.83 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.55, 166.24, 159.10, 141.78, 139.14, 136.38, 134.21, 132.59, 131.61, 131.31, 129.95, 129.47, 129.05, 128.47, 127.89, 126.69, 126.10, 126.03, 125.88, 125.80, 124.86, 112.24, 75.11, 55.28, 52.84, 40.74, 37.26, 29.24. ESI-MS: calculated $C_{37}H_{36}O_5Na$ $[M+Na]^+$ 583.2460; Found 583.2456.

1-methoxy-2-oxo-2-(p-tolyl)ethyl 4-methoxybenzoate (4a)



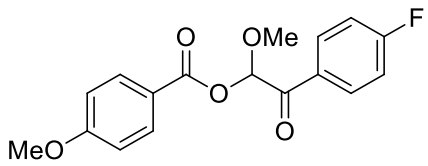
Following the above procedure A, the product **4a** was obtained in 61% yield (38.5 mg, 0.122mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.19: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.13 (s, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.73, 165.73, 163.88, 139.33, 132.18, 131.31, 129.63, 127.73, 121.74, 113.80, 74.64, 55.55, 52.68, 21.37. ESI-MS: calculated $C_{18}H_{18}O_5Na$ $[M+Na]^+$ 337.1052; Found 337.1051.

2-([1,1'-biphenyl]-4-yl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4b)



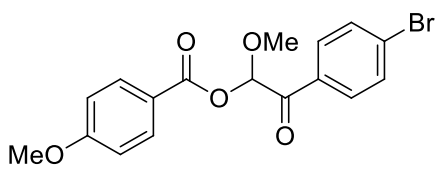
Following the above procedure A, the product **4b** was obtained in 58% yield (44.0 mg, 0.116 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.23: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.66 (s, 4H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.21 (s, 1H), 3.87 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.52, 165.69, 163.95, 159.97, 135.64, 132.24, 130.02, 121.68, 120.08, 114.85, 113.97, 113.86, 113.47, 113.35, 74.67, 55.61, 55.49, 52.80. ESI-MS: calculated $C_{23}H_{20}O_5Na$ $[M+Na]^+$ 399.1208; Found 399.1215.

2-(4-fluorophenyl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4c)



Following the above procedure A, the product **4c** was obtained in 58% yield (36.9 mg, 0.116 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.23: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.1, 5.5 Hz, 2H), 7.11 (d, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.12 (s, 1H), 3.86 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.47, 165.59, 164.01, 163.32 (d, *J* = 248.4 Hz), 132.20, 130.21 (d, *J* = 3.1 Hz), 129.65 (d, *J* = 8.4 Hz), 121.54, 115.99 (d, *J* = 21.8 Hz), 113.89, 74.03, 55.60, 52.83. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.04. ESI-MS: calculated $C_{17}H_{15}FO_5Na$ $[M+Na]^+$ 341.0801; Found 341.0807; 342.0836.

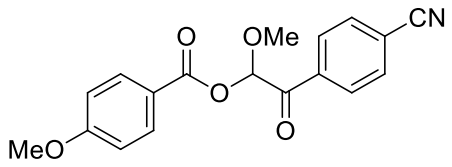
2-(4-bromophenyl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4d)



Following the above procedure A, the product **4d** was obtained in 69% yield (52.0 mg, 0.138 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.22: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.10 (s, 1H), 3.86 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.17, 165.50, 164.03, 132.20,

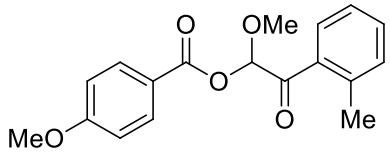
132.15, 129.36, 123.57, 121.44, 114.00, 113.90, 74.04, 55.61, 52.90. ESI-MS: calculated $C_{17}H_{15}BrO_5Na$ $[M+Na]^+$ 401.0001; Found 401.0003; 402.9984.

2-(4-cyanophenyl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4e)



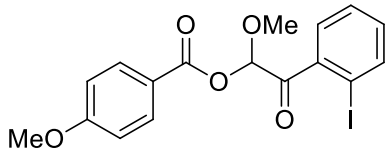
Following the above procedure A, the product **4e** was obtained in 55% yield (38.5 mg, 0.110 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.20: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.74 (s, 4H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.22 (s, 1H), 3.89 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.55, 165.24, 164.18, 139.27, 132.71, 132.22, 128.25, 121.10, 118.37, 113.98, 73.80, 55.62, 53.11. ESI-MS: calculated $C_{18}H_{15}NO_5Na$ $[M+Na]^+$ 348.0848; Found 348.0853.

1-methoxy-2-oxo-2-(o-tolyl)ethyl 4-methoxybenzoate (4f)



Following the above procedure A, the product **4f** was obtained in 59% yield (37.0 mg, 0.118 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.26 (m, 3H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.46 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.84, 165.73, 163.89, 137.05, 132.90, 132.17, 130.99, 129.27, 128.18, 126.51, 121.73, 113.82, 71.91, 55.56, 52.68, 19.55. ESI-MS: calculated $C_{18}H_{18}O_5Na$ $[M+Na]^+$ 337.1052; Found 337.1047.

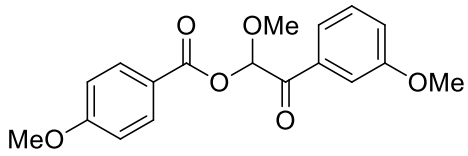
2-(2-iodophenyl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4g)



Following the above procedure A, the product **4g** was obtained in 41% yield (35.0 mg, 0.082 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.41 (t, 1H), 7.09 (t, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.53 (s, 1H), 3.86 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.27, 165.39,

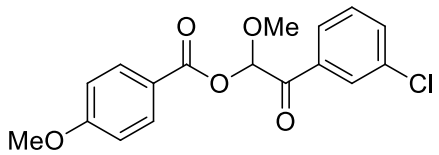
163.97, 140.22, 137.64, 132.31, 130.95, 129.28, 128.83, 121.50, 113.86, 99.76, 78.02, 55.61, 52.89. ESI-MS: calculated $C_{17}H_{15}IO_5Na$ $[M+Na]^+$ 448.9862; Found 448.9865; 449.9893.

1-methoxy-2-(3-methoxyphenyl)-2-oxoethyl 4-methoxybenzoate (4h)



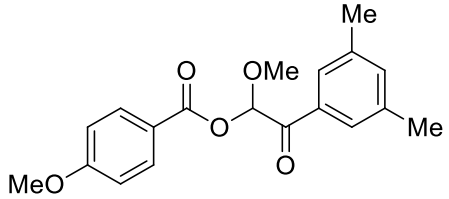
Following the above procedure A, the product **4h** was obtained in 35% yield (23.1 mg, 0.070 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1):0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 6.93 (d, *J* = 8.3 Hz, 3H), 6.11 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.09, 165.49, 164.07, 136.17, 134.88, 132.26, 130.24, 129.55, 127.79, 125.91, 121.41, 113.94, 73.99, 55.63, 52.96. ESI-MS: calculated $C_{18}H_{18}O_6Na$ $[M+Na]^+$ 353.1001; Found 353.1000.

2-(3-chlorophenyl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4i)



Following the above procedure A, the product **4i** was obtained in 49% yield (32.9 mg, 0.098mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.58 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.36 (dd, *J* = 13.2, 5.9 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.11 (s, 1H), 3.87 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.09, 165.49, 164.07, 136.17, 134.88, 132.26, 130.24, 129.55, 127.79, 125.91, 121.41, 113.94, 73.99, 55.63, 52.96. ESI-MS: calculated $C_{17}H_{15}ClO_5Na$ $[M+Na]^+$ 357.0506; Found 357.0505; 359.0471.

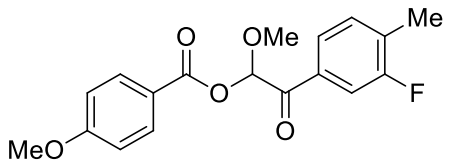
2-(3,5-dimethylphenyl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4j)



Following the above procedure A, the product **4j** was obtained in 57% yield (37.2 mg, 0.114 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.19: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 2H), 7.18 (s, 2H), 7.04 (s, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.07 (s, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 2.36 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

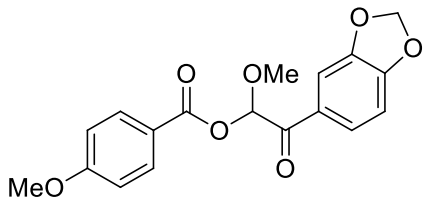
169.77, 165.76, 163.88, 138.62, 134.01, 132.20, 131.08, 125.59, 121.77, 113.79, 74.88, 55.55, 52.71, 21.41. ESI-MS: calculated $C_{19}H_{20}O_5Na$ $[M+Na]^+$ 351.1208; Found 351.1214.

2-(3-fluoro-4-methylphenyl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4k)



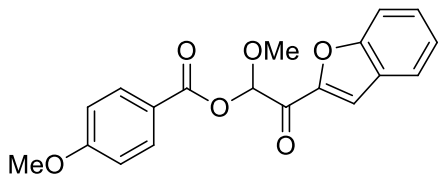
Following the above procedure A, the product **4k** was obtained in 61% yield (40.3 mg, 0.122 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.19: ^{1}H NMR (600 MHz, CDCl3) δ 8.10 (d, J = 8.7 Hz, 2H), 7.27 (d, 2H), 7.25 (s, 1H), 6.96 (d, J = 8.7 Hz, 2H), 6.12 (s, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 2.31 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.30, 165.56, 164.00, 161.37 (d, J = 245.9 Hz), 133.69 (d, J = 7.6 Hz), 132.21, 131.92 (d, J = 5.3 Hz), 126.21 (d, J = 17.2 Hz), 123.16 (d, J = 3.4 Hz), 121.53, 114.33 (d, J = 23.8 Hz), 113.88, 74.00, 73.99, 55.59, 52.84, 14.54 (d, J = 3.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.13. ESI-MS: calculated $C_{18}H_{17}FO_5Na$ $[M+Na]^+$ 355.0958; Found 355.0959; 356.0987.

2-(benzo[d][1,3]dioxol-5-yl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4l)



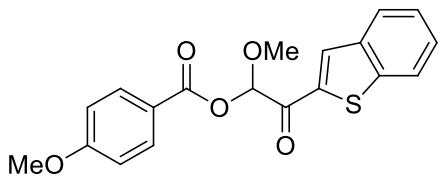
Following the above procedure A, the product **4l** was obtained in 46% yield (31.8 mg, 0.092 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.19: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.05 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.03 (s, 1H), 5.99 (d, *J* = 1.8 Hz, 2H), 3.86 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.65, 165.68, 163.95, 148.57, 148.17, 132.21, 127.92, 121.97, 121.68, 113.85, 108.61, 108.11, 101.54, 74.56, 55.60, 52.78. ESI-MS: calculated $C_{18}H_{16}O_7Na$ $[M+Na]^+$ 367.0794; Found 367.0800.

2-(benzofuran-2-yl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4m)



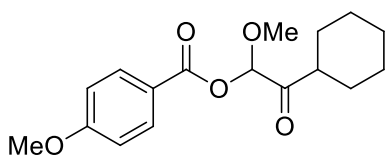
Following the above procedure A, the product **4m** was obtained in 37% yield (25.0 mg, 0.050 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). Rf (Petroleum ether/EtOAc 16:1): 0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.36 (s, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 3H), 6.47 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.25, 165.35, 164.10, 155.43, 149.59, 132.40, 127.69, 125.46, 123.36, 121.71, 121.24, 113.89, 111.84, 107.84, 68.36, 55.61, 53.23. ESI-MS: calculated $C_{19}H_{16}O_6Na$ $[M+Na]^+$ 363.0845; Found 363.0850.

2-(benzo[b]thiophen-2-yl)-1-methoxy-2-oxoethyl 4-methoxybenzoate (4n)



Following the above procedure A, the product **4n** was obtained in 66% yield (47.1 mg, 0.132 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.50 (s, 1H), 7.38 – 7.36 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.51 (s, 1H), 3.87 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.42, 165.31, 164.10, 140.20, 139.09, 136.62, 132.38, 132.35, 125.19, 124.75, 124.40, 122.49, 121.24, 113.93, 71.07, 55.59, 53.13. ESI-MS: calculated $C_{19}H_{16}O_5SNa$ $[M+Na]^+$ 379.0616; Found 379.0620.

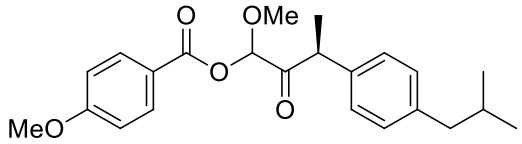
2-cyclohexyl-1-methoxy-2-oxoethyl 4-methoxybenzoate (4o)



Following the above procedure A, the product **4o** was obtained in 70% yield (42.7 mg, 0.140 mmol) as a yellow oil after column chromatography (eluent = Petroleumether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.19: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 5.02 (d, *J* = 4.6 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 2.01 (d, *J* = 10.2 Hz, 1H), 1.79 – 1.70 (m, 4H), 1.28 (m, *J* = 52.9, 32.8, 21.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$)

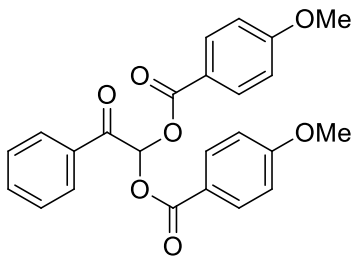
δ 170.52, 165.99, 163.75, 131.99, 122.08, 113.78, 76.78, 55.55, 52.14, 39.88, 29.30, 28.03, 26.12, 26.03. ESI-MS: calculated $C_{17}H_{22}O_5Na$ $[M+Na]^+$ 329.1365; Found 329.1368.

(3*S*)-3-(4-isobutylphenyl)-1-methoxy-2-oxobutyl 4-methoxybenzoate (4p)



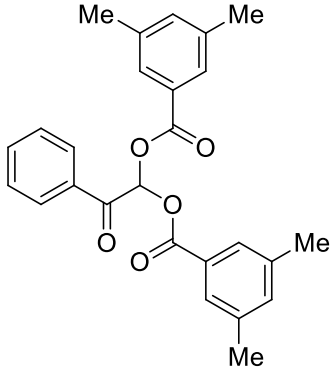
Following the above procedure A, the product **4p** was obtained in 86% yield (66.2 mg, 0.172 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). Rf (Petroleum ether/EtOAc 32:1): 0.20: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.11 – 7.06 (m, 2H), 6.94 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 5.28 (dd, *J* = 24.6, 5.7 Hz, 1H), 3.85 (d, *J* = 10.1 Hz, 3H), 3.65 (d, *J* = 19.7 Hz, 3H), 3.51 – 3.44 (m, 1H), 2.44 (dd, *J* = 10.2, 7.3 Hz, 2H), 1.84 (dd, *J* = 14.0, 7.0 Hz, 1H), 1.46 (dd, *J* = 32.6, 7.2 Hz, 3H), 0.89 – 0.87 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.36, 165.87, 163.89, 140.70, 138.85, 132.10, 129.38, 127.80, 122.07, 113.92, 77.05, 55.65, 52.25, 45.24, 41.28, 30.38, 22.54, 17.83, 16.16. $[\alpha]^{20}_D$=·+1.04·(c·=0.28, MeOH). ESI-MS: calculated $C_{23}H_{28}O_5Na$ $[M+Na]^+$ 407.1834; Found 407.1842.

2-oxo-2-phenylethane-1,1-diyl bis(4-methoxybenzoate) (5a)



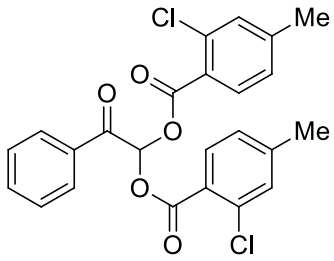
Following the above procedure B, the product **5a** was obtained in 86% yield (72.4 mg, 0.172 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.19: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 8.06 – 8.04 (m, 5H), 7.61 (s, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 4H), 3.86 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.44, 164.35, 164.22, 134.31, 133.55, 132.63, 129.19, 129.05, 120.77, 114.00, 87.16, 55.67. ESI-MS: calculated $C_{24}H_{20}O_7Na$ $[M+Na]^+$ 443.1107; Found 443.1113.

2-oxo-2-phenylethane-1,1-diyl bis(3,5-dimethylbenzoate) (5b)



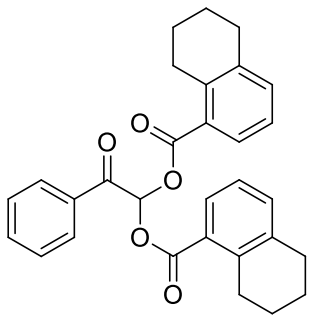
Following the above procedure B, the product **5b** was obtained in 19% yield (15.7 mg, 0.038 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.20: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.09 – 8.07 (m, 2H), 7.72 (s, 4H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.23 (s, 2H), 2.34 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.19, 164.85, 138.44, 135.83, 134.35, 133.55, 129.16, 129.06, 128.28, 128.10, 87.14, 21.24. ESI-MS: calculated $C_{26}H_{24}O_5Na$ $[M+Na]^+$ 439.1521; Found 439.1529.

2-oxo-2-phenylethane-1,1-diyl bis(2-chloro-4-methylbenzoate) (5c)



Following the above procedure B, the product **5c** was obtained in 11% yield (10.5 mg, 0.022 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.20: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 5.7 Hz, 3H), 7.88 (s, 1H), 7.87 (s, 1H), 7.63 – 7.61 (m, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.29 (s, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.75, 162.93, 145.23, 135.11, 134.44, 133.41, 132.52, 132.15, 129.21, 129.06, 127.69, 124.66, 87.52, 21.45. ESI-MS: calculated $C_{24}H_{18}Cl_2O_5Na$ $[M+Na]^+$ 479.0429; Found 479.0435; 481.0409.

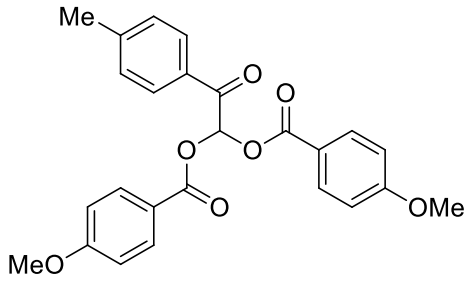
2-oxo-2-phenylethane-1,1-diyl bis(5,6,7,8-tetrahydronaphthalene-1-carboxylate) (5d)



Following the above procedure B, the product **5d** was obtained in 42% yield (39.6 mg, 0.084 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.20: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.08 (m, 2H), 8.06 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 2H), 7.64 (M, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.15 (t, *J* = 7.7 Hz, 2H), 3.12 (s, 4H), 2.83 (d, *J* = 4.8 Hz, 4H), 1.82 – 1.79 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

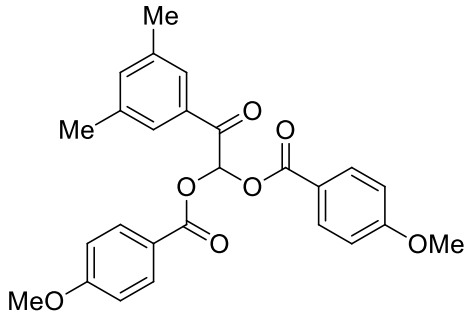
189.45, 165.44, 140.10, 138.78, 134.40, 134.26, 133.63, 129.13, 129.01, 128.91, 128.06, 125.22, 87.30, 30.34, 27.94, 23.14, 22.44. ESI-MS: calculated $C_{30}H_{28}O_5Na$ $[M+Na]^+$ 491.1834; Found 491.1837.

2-oxo-2-(p-tolyl)ethane-1,1-diyl bis(4-methoxybenzoate) (5i)



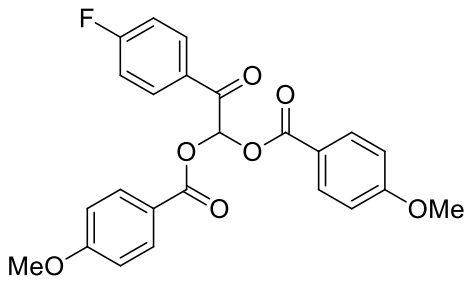
Following the above procedure B, the product **5i** w as obtained in 70% yield (61.0 mg, 0.140 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum et her/EtOAc 8:1): 0.21: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.04 (m, 4H), 8.04 (s, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.9 1 (d, *J* = 9.0 Hz, H), 3.85 (s, 6H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.95, 164. 30, 164.22, 145.42, 132.59, 131.01, 129.75, 129.30, 120.82, 113.97, 87.14, 55.64, 21.95. ESI-MS: calculated $C_{25}H_{22}O_7Na$ $[M+Na]^+$ 457.1263; Found 457.1268.

2-(3,5-dimethylphenyl)-2-oxoethane-1,1-diyl bis(4-methoxybenzoate) (5j)



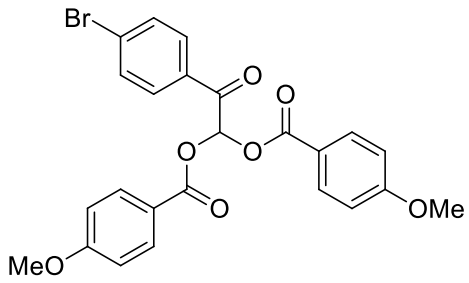
Following the above procedure B, the product **5j** was obtained in 58% yield (52.4 mg, 0.116 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1):0.20: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 5H), 7.67 (s, 2H), 7.23 (s, 1H), 6.91 (d, *J* = 8.7 Hz, 4H), 3.85 (s, 6H), 2.35 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.28, 164.24, 138.69, 136.04, 133.69, 132.94, 132.56, 126.86, 120.85, 114.25, 113.95, 87.01, 55.62, 21.36.ESI-MS: calculated $C_{26}H_{24}O_7Na$ $[M+Na]^+$ 471.1420; Found 471.1420.

2-(4-fluorophenyl)-2-oxoethane-1,1-diyl bis(4-methoxybenzoate) (5k)



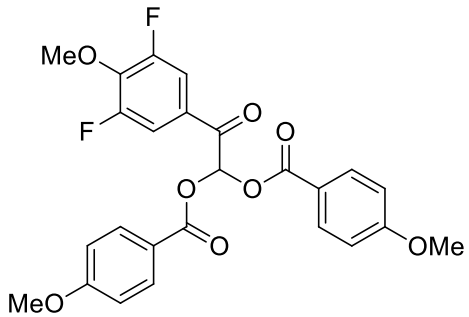
Following the above procedure B, the product **5k** was obtained in 65% yield (57.1 mg, 0.130 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.20: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 2H), 8.06 – 8.02 (m, 5H), 7.18 – 7.14 (m, 2H), 6.92 (d, J = 8.9 Hz, 4H), 3.85 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 187.95, 166.38 (d, *J* = 256.9 Hz), 164.39, 164.13, 132.57, 131.96 (d, *J* = 9.5 Hz), 129.96 (d, *J* = 2.8 Hz), 120.61, 116.31 (d, *J* = 22.0 Hz), 114.01, 87.17, 55.63. ^{19}F NMR (377 MHz, CDCl3) δ -102.65. ESI-MS: calculated $C_{24}H_{19}FO_7Na$ $[M+Na]^+$ 461.1013; Found 461.1017; 476.1204.

2-(4-bromophenyl)-2-oxoethane-1,1-diyl bis(4-methoxybenzoate) (5l)



Following the above procedure B, the product **5l** was obtained in 56% yield (56.3 mg, 0.112 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 8.9 Hz, 4H), 8.00 (s, 1H), 7.94 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.9 Hz, 4H), 3.85 (s, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 188.66, 164.41, 164.10, 132.59, 132.40, 132.29, 130.59, 129.67, 120.57, 114.04, 87.20, 55.65. ESI-MS: calculated $C_{24}H_{19}Br\ O_7Na$ $[M+Na]^+$ 521.0212; Found 521.0219; 523.0204.

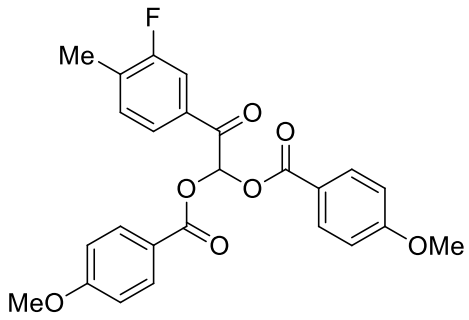
2-(3,5-difluoro-4-methoxyphenyl)-2-oxoethane-1,1-diyl bis(4-methoxybenzoate) (5m)



Following the above procedure B, the product **5m** was obtained in 41% yield (40.1 mg, 0.082 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.19: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.0 Hz, 1H), 8.05 – 8.01 (m, 3H), 7.90 (s,

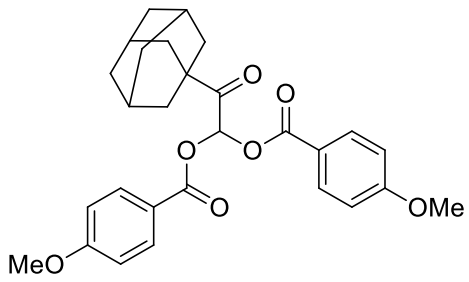
1H), 7.66 (d, *J* = 9.3 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 1H), 6.93 – 6.87 (m, 4H), 4.10 (t, *J* = 1.7 Hz, 3H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.59, 164.39, 163.48 (d, *J* = 230.9 Hz),162.33, 154.73 (dd, *J* = 250.3, 5.9 Hz), 141.69 (t, *J* = 13.1 Hz), 132.83, 132.49, 126.85 (t, *J* = 7.3 Hz), 121.22, 120.31, 114.17, 113.54 (d, *J* = 24.3 Hz), 113.54 (d, *J* = 9.6 Hz), 87.10, 61.64, 55.59 (d, *J* = 6.0 Hz). ^{19}F NMR (376 MHz, CDCl3) δ -126.51, -126.51, -126.53 ESI-MS: calculated $C_{25}H_{20}F_2O_8Na$ $[M+Na]^+$ 509.1024; Found 509.1019; 528.2074.

2-(3-fluoro-4-methoxyphenyl)-2-oxoethane-1,1-diyl bis(4-methoxybenzoate) (5n)



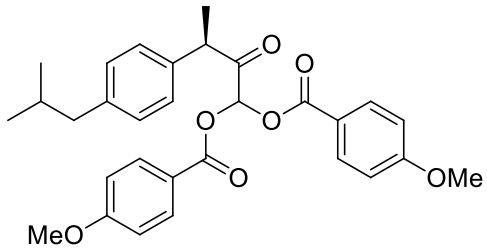
Following the above procedure B, the product **5n** was obtained in 48% yield (43.8 mg, 0.096 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.22: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05, 8.04, 7.99, 7.76, 7.74, 7.74, 7.72, 7.31, 7.29, 7.28, 6.92, 6.91, 3.87, 3.85, 2.33. ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.20, 164.38, 164.14, 161.41 (d, *J* = 247.2 Hz), 133.14 (d, *J* = 6.7 Hz), 132.88 (d, *J* = 27.7 Hz), 132.61, 132.06 (d, *J* = 4.8 Hz), 124.79 (d, *J* = 3.2 Hz), 120.68, 115.52 (d, *J* = 23.8 Hz), 114.02, 87.21, 55.65, 15.14 (d, *J* = 3.3 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.32.ESI-MS: calculated $C_{25}H_{21}FO_7Na$ $[M+Na]^+$ 475.1169; Found 475.1173; 476.1204.

2-(adamantan-1-yl)-2-oxoethane-1,1-diyl bis(4-methoxybenzoate) (5o)



Following the above procedure B, the product **5o** was obtained in 64% yield (61.6 mg, 0.128 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.22: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 9.0 Hz, 4H), 7.61 (s, 1H), 6.93 (d, J = 9.0 Hz, 4H), 3.86 (s, 6H), 2.05 (s, 3H), 2.01 – 1.96 (m, 6H), 1.77 – 1.69 (m, 5H), 1.61 (s, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 203.71, 164.30, 164.27, 132.51, 120.84, 114.01, 85.19, 55.66, 45.88, 37.90, 36.45, 27.80. ESI-MS: calculated $C_{28}H_{30}O_7Na$ $[M+Na]^+$ 501.1889; Found 501.1895.

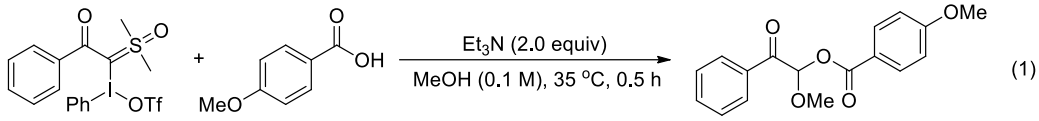
(R)-3-(4-isobutylphenyl)-2-oxobutane-1,1-diyl bis(4-methoxybenzoate) (5p)



Following the above procedure B, the product **5p** was obtained in 66% yield (66.9 mg, 0.132 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). Rf (Petroleum ether/EtOAc 8:1): 0.21: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.9 Hz, 2H), 7.14 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.23 (d, *J* = 6.9 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 2.39 (d, *J* = 7.2 Hz, 2H), 1.78 (s, *J* = 13.5, 6.7 Hz, 1H), 1.49 (d, *J* = 6.9 Hz, 3H), 0.85 (dd, *J* = 6.6, 3.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.38, 164.18, 163.94, 141.01, 136.03, 132.50, 129.85, 127.92, 120.80, 113.95, 87.91, 55.64, 55.60, 48.61, 45.10, 30.25, 22.48, 18.11. ESI-MS: calculated $C_{30}H_{32}O_7Na$ $[M+Na]^+$ 527.2046; Found 527.2053.

4. Synthetic application of the product

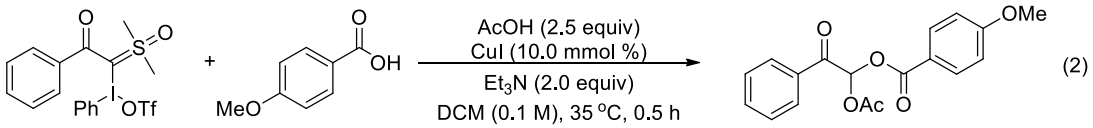
(a) Gram-scale-experiment:



1a, 2.74 g, 5 mmol **2a** **3a**, 1.01 g, 67%

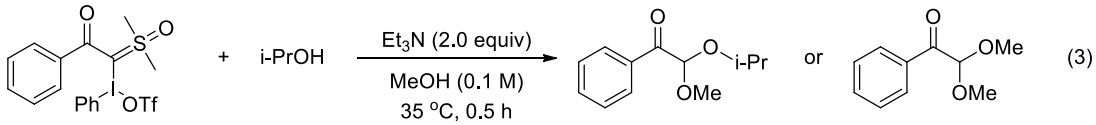
In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (5.0 mmol, 1.0 equiv), 4-methoxybenzoic acid **2a** (6.0 mmol, 1.2 equiv), Et_3N (2.0 equiv) and methanol (50.0 mL, 0.1 M) was stirred at 35 °C in the oil bath for 0.5 h. The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 32:1) to give **3a** (1.01 g, 67 %) as a yellow oil.

(b) control experiment:



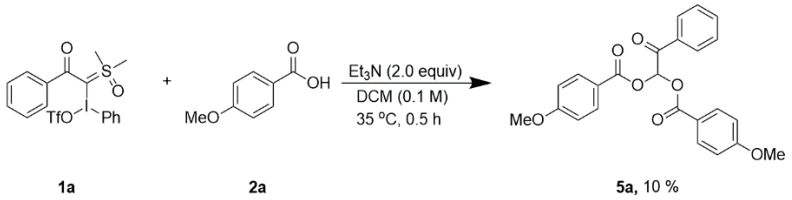
1a **2a** **5a'**, not detected

In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (0.2 mmol, 1.0 equiv), 4-m ethoxybenzoic acid **2a** (0.5 mmol, 2.5 equiv), AcOH (0.5 mmol, 2.5 equiv), Et_3N (2.0 equiv), CuI (0.02 mmol, 10.0 mol%) and DCM (2.0 mL, 0.1 M) was stirred at 35 °C in the oil bat h for 0.5 h. The product **5a'** was not detected.

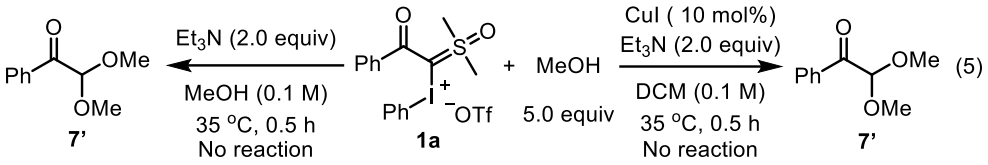


1a **6** **7** **7'**

In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (0.20 mmol, 1.0 equiv), *i*-P rOH **6** (0.24 mmol, 1.2 equiv), Et_3N (2.0 equiv) and methanol (2.0 mL, 0.1 M) was stirred a t 35 °C in the oil bath for 0.5 h. The product **7** and **7'** were not detected.

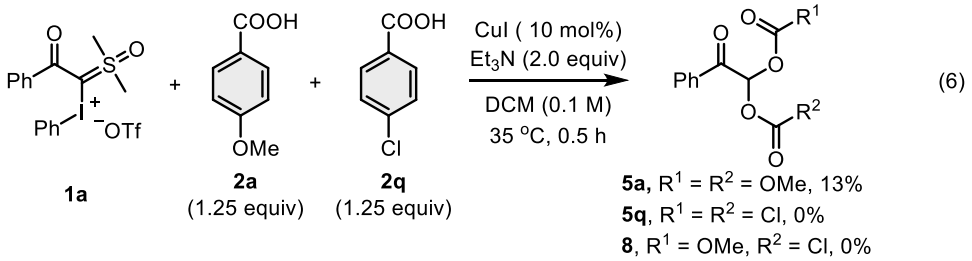


In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (0.2 mmol, 1.0 equiv), 4-methoxybenzoic acid **2a** (0.5 mmol, 2.5 equiv), Et_3N (2.0 equiv) and DCM (2.0 mL, 0.1 M) was stirred at 35 °C in the oil bath for 0.5 h. The product was purified by flash column chromatography (petroleum ether: ethyl acetate = 8:1) to give **5a** (8.3 mg, 10%) as a white solid.



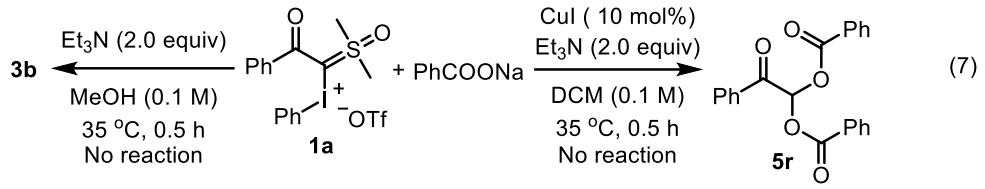
In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (0.2 mmol, 1.0 equiv), Et_3N (2.0 equiv) and MeOH (2.0 mL, 0.1 M) was stirred at 35 °C in the oil bath for 0.5 h. The product **7'** were not detected.

In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (0.2 mmol, 1.0 equiv), MeOH (1.0 mmol, 5.0 equiv), CuI (0.02 mmol, 10.0 mol%), Et_3N (2.0 equiv) and DCM (2.0 mL, 0.1 M) was stirred at 35 °C in the oil bath for 0.5 h. The product **7'** were not detected.



In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (0.2 mmol, 1.0 equiv), 4-methoxybenzoic acid **2a** (0.25 mmol, 1.25 equiv), 4-chlorophenyl carboxylic acid **2q** (0.25 mmol, 1.25 equiv), CuI (0.02 mmol, 10.0 mol%), Et_3N (2.0 equiv) and DCM (2.0 mL, 0.1 M) was stirred at 35 °C in the oil bath for 0.5 h. The product **5a** was purified by flash column chromatography

(petroleum ether: ethyl acetate = 8:1) (11.0 mg, 13 %) as a white solid. The product **5q** and **8** were not detected.



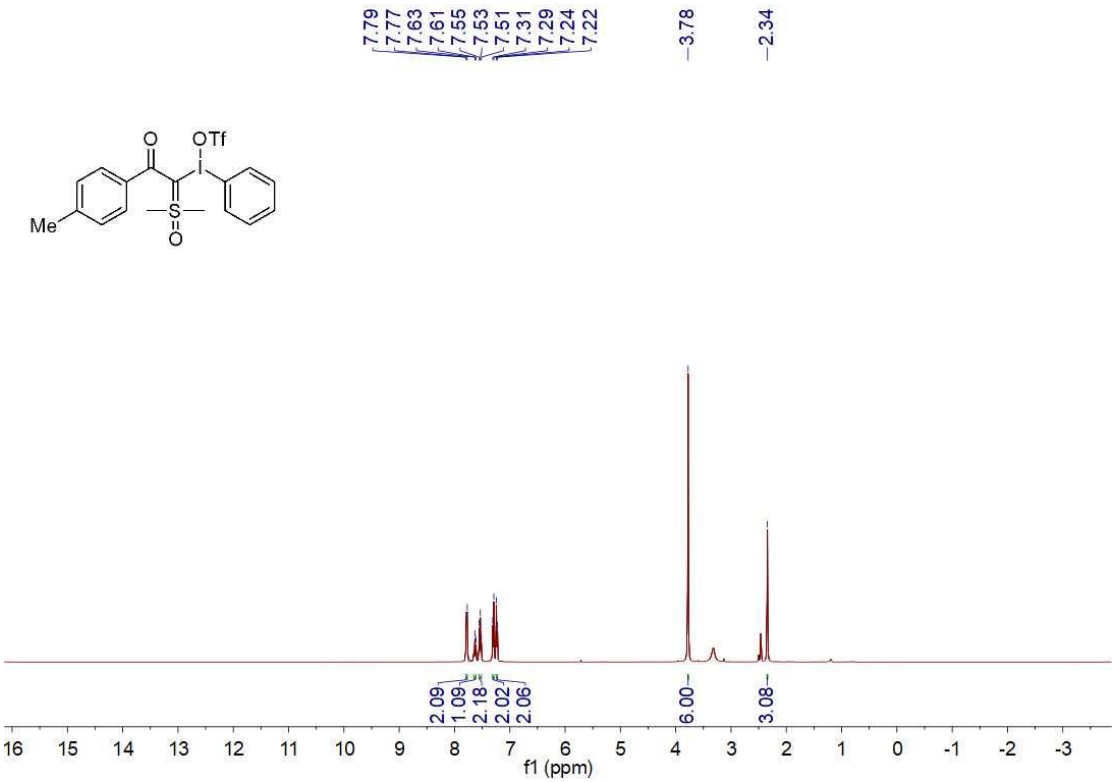
(7)

In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (0.2 mmol, 1.0 equiv), PhCOONa (0.24 mmol, 1.2 equiv), Et_3N (2.0 equiv) and MeOH (2.0 mL, 0.1 M) was stirred at 35 °C in the oil bath for 0.5 h. The product **3b** were not detected.

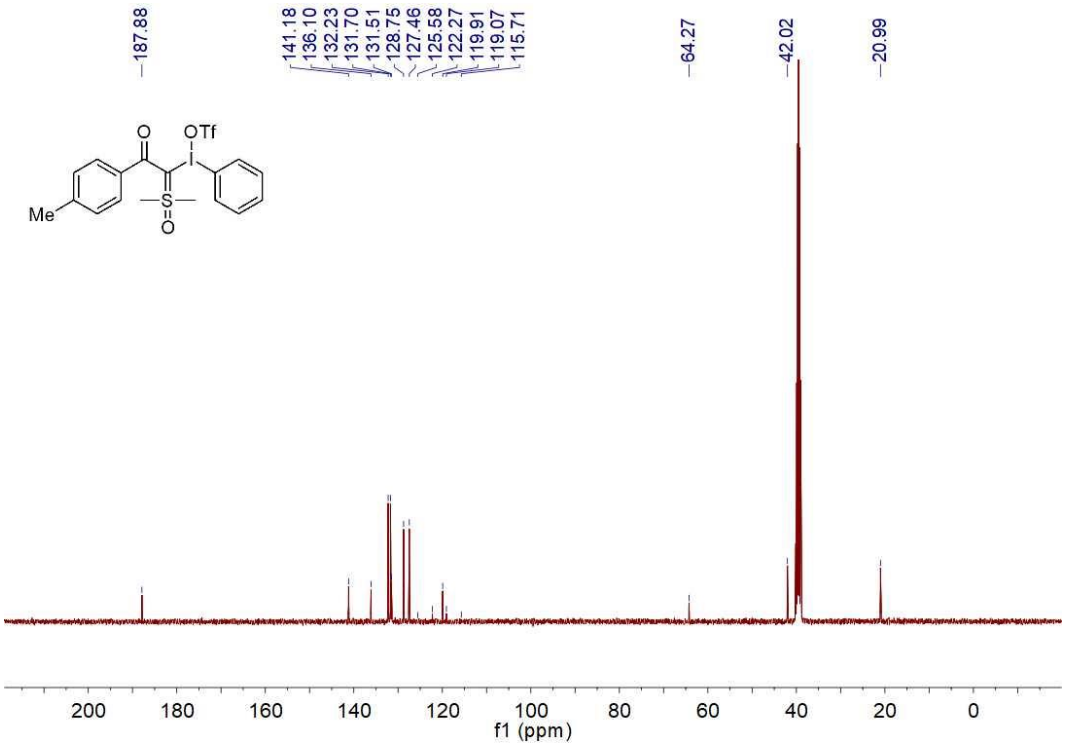
In an oven-dried Schlenk tube, a mixture of the I,S-ylide **1a** (0.2 mmol, 1.0 equiv), PhCOONa (0.5 mmol, 2.5 equiv), CuI (0.02 mmol, 10.0 mol%), Et_3N (2.0 equiv) and DCM (2.0 mL, 0.1 M) was stirred at 35 °C in the oil bath for 0.5 h. The product **5r** were not detected.

5. NMR Spectra for New Compounds

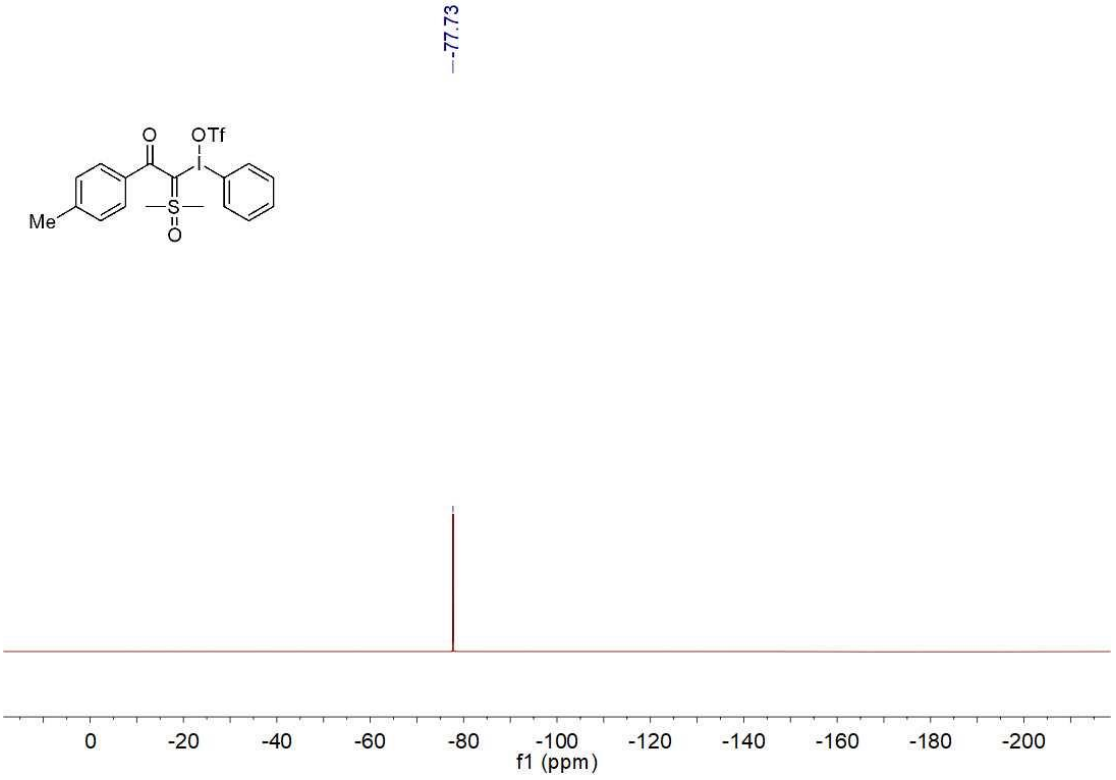
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1b**



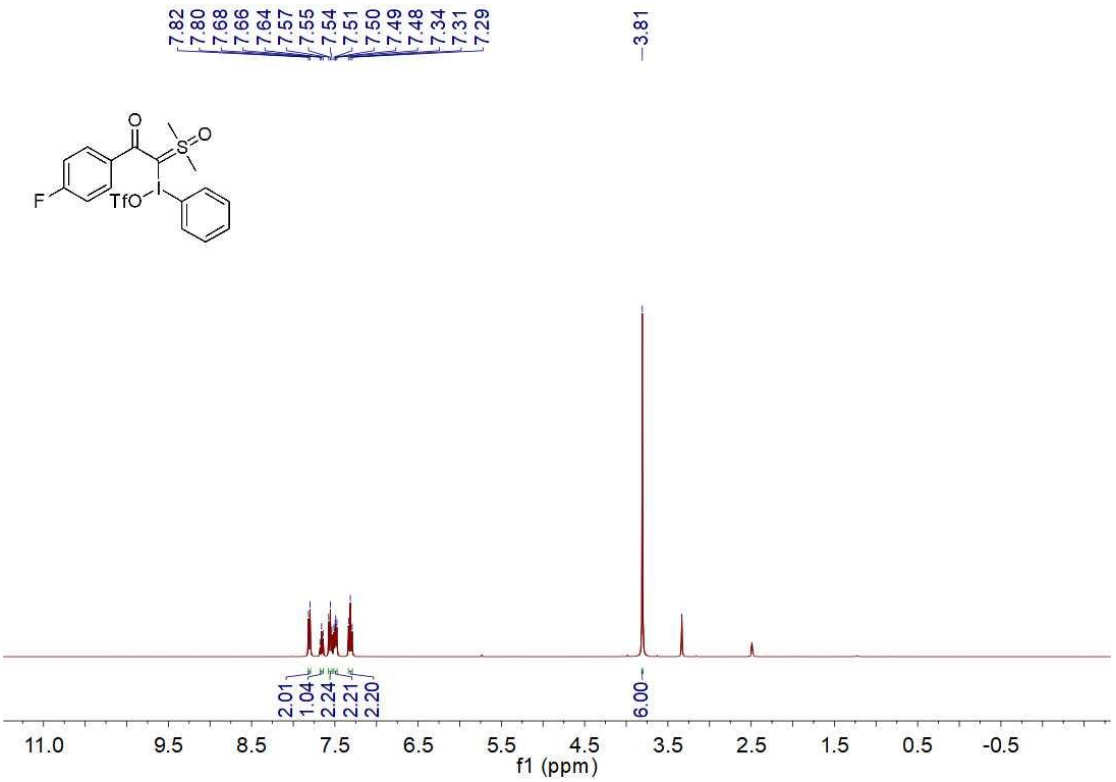
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1b**



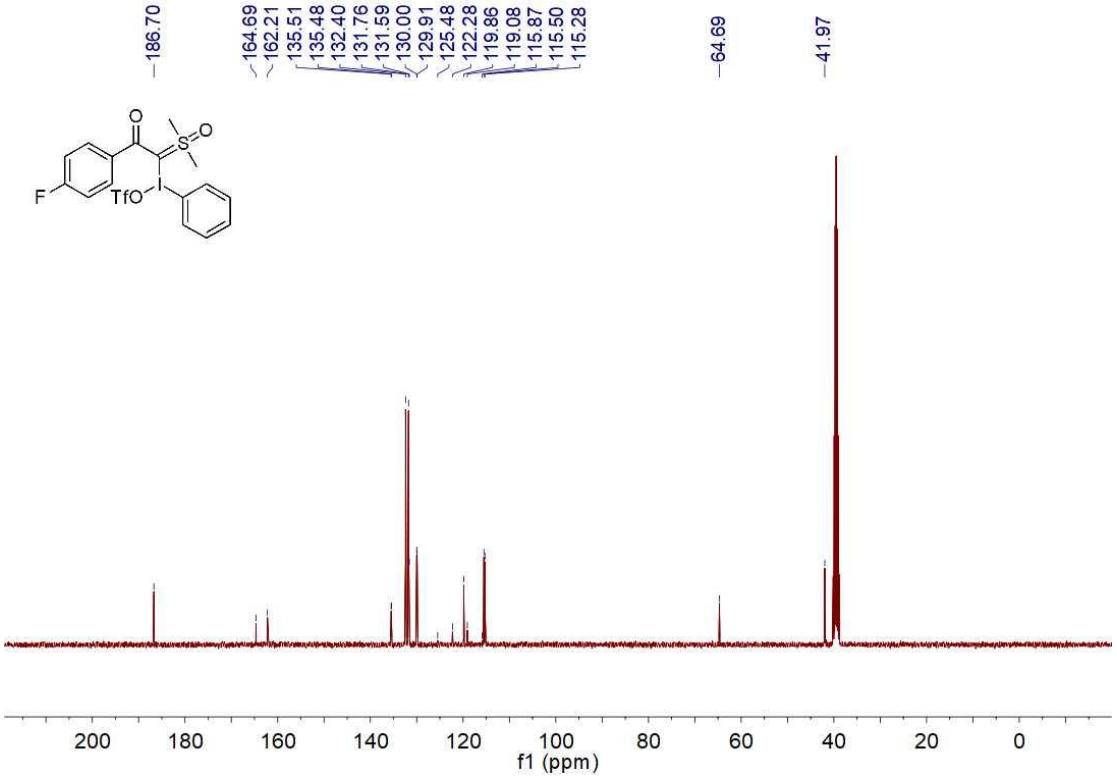
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1b**



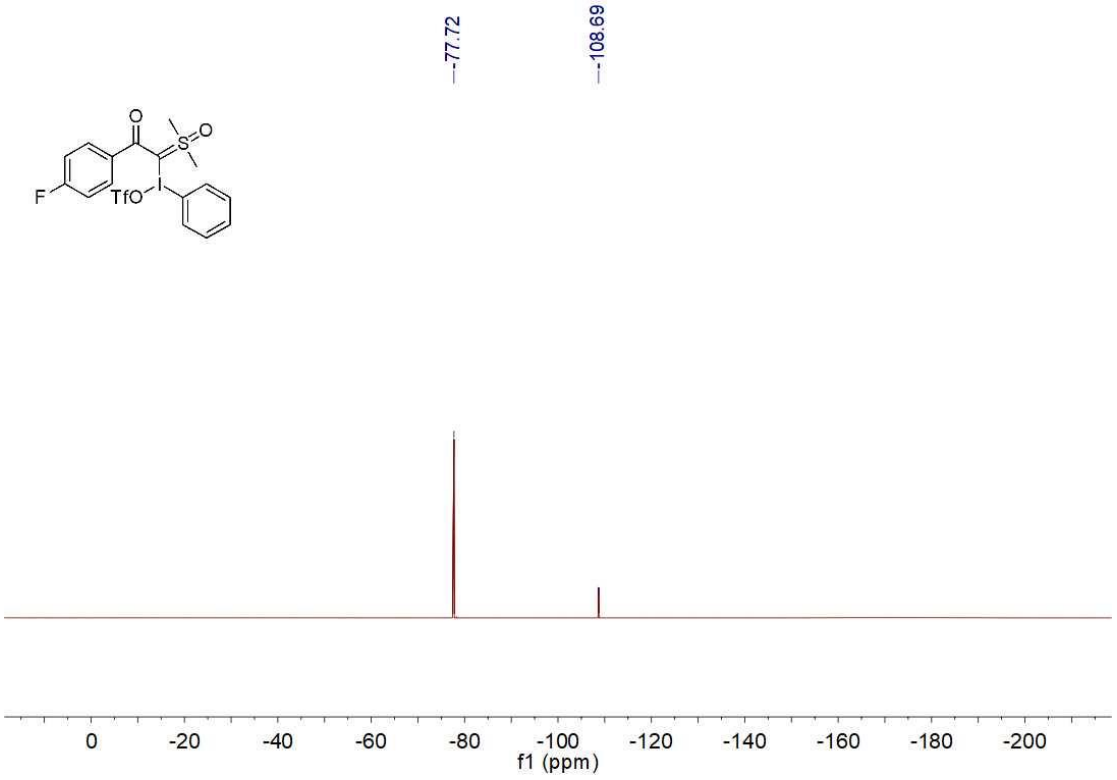
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1c**



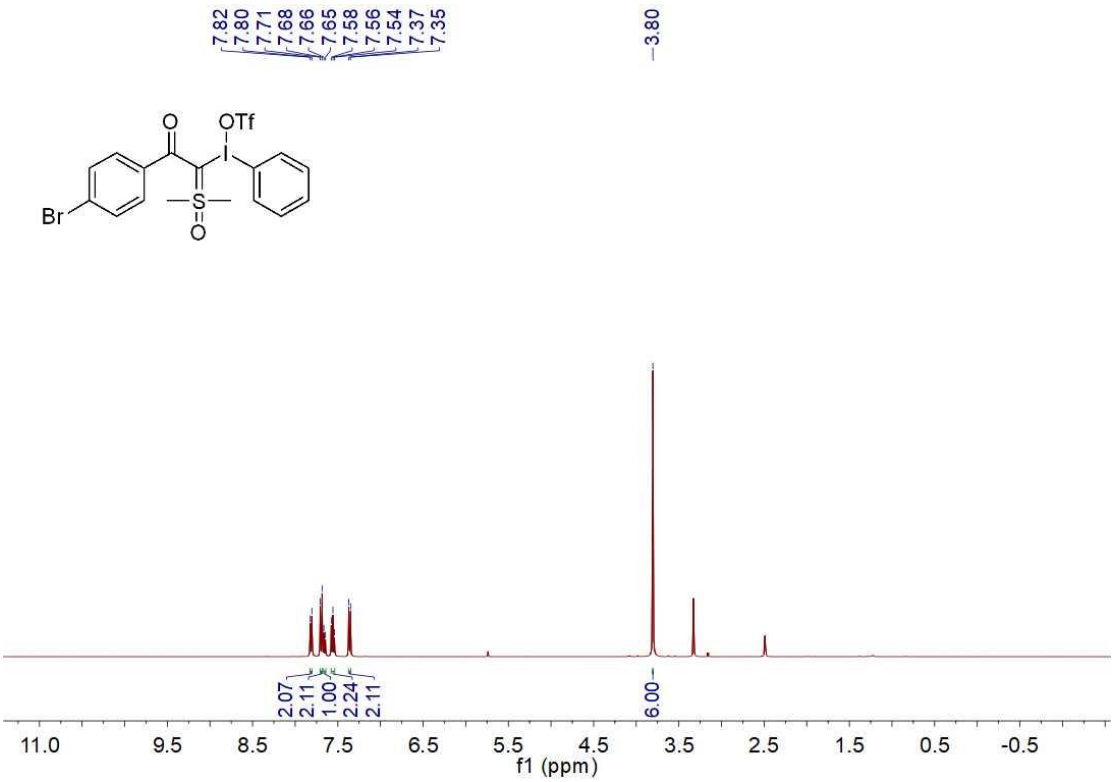
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1c**



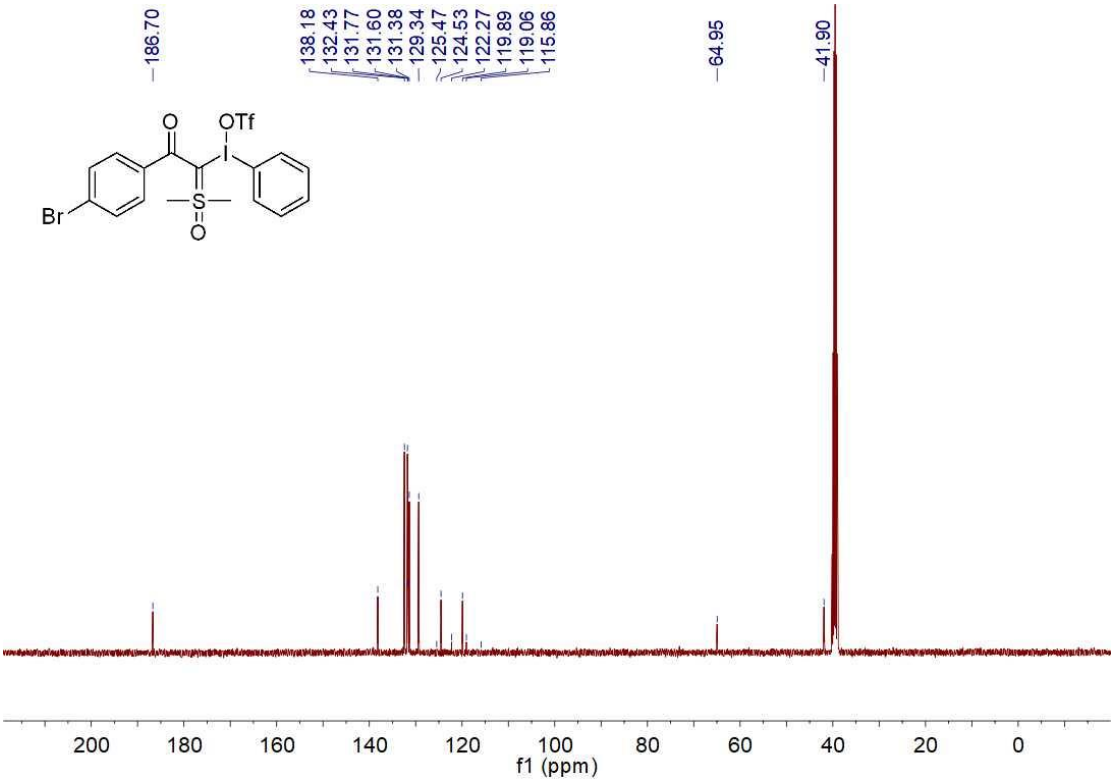
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1c**



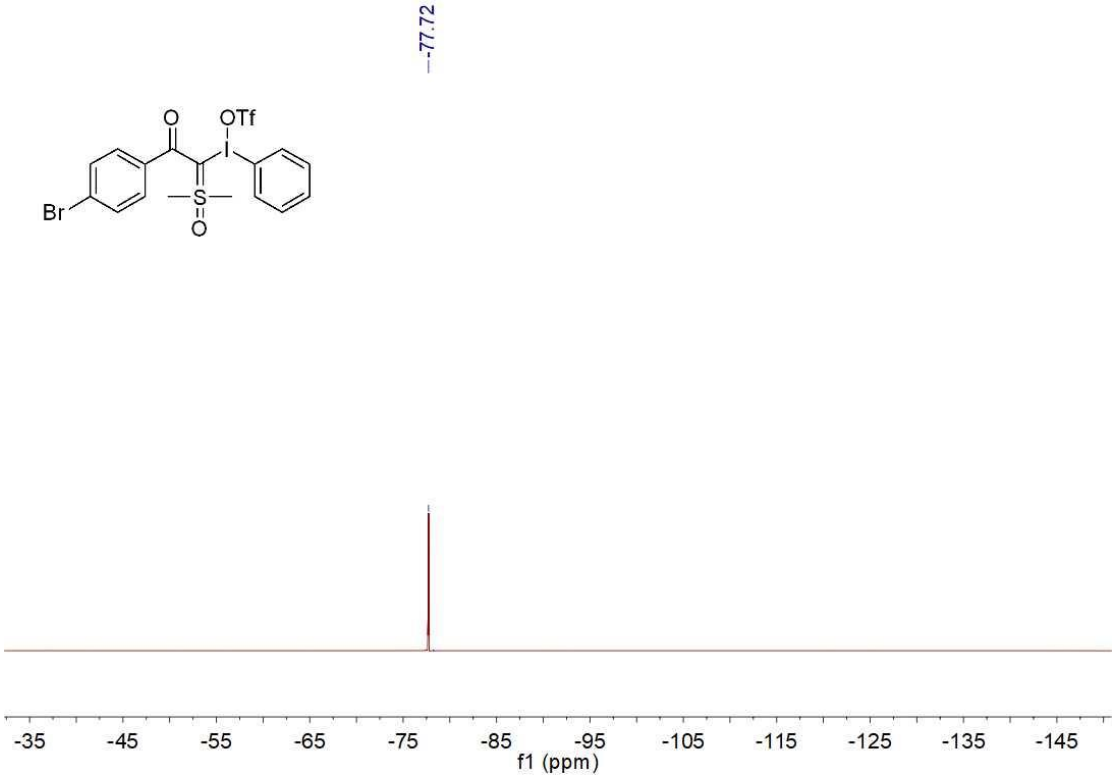
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1d**



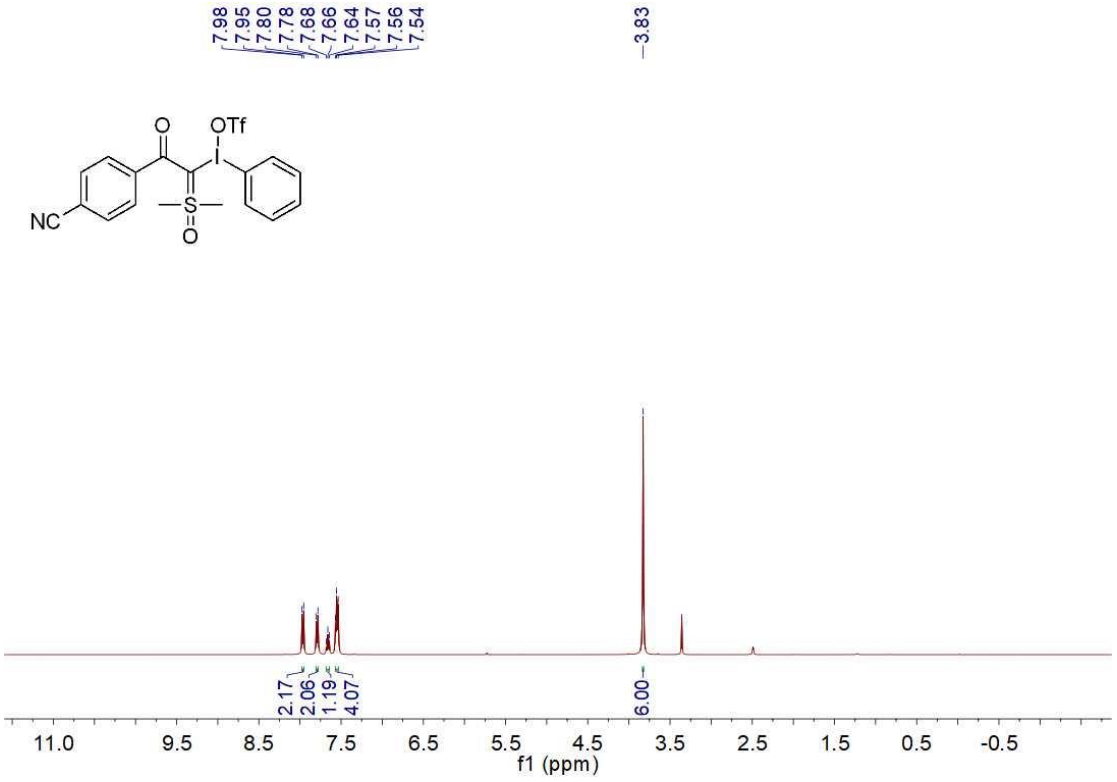
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1d**



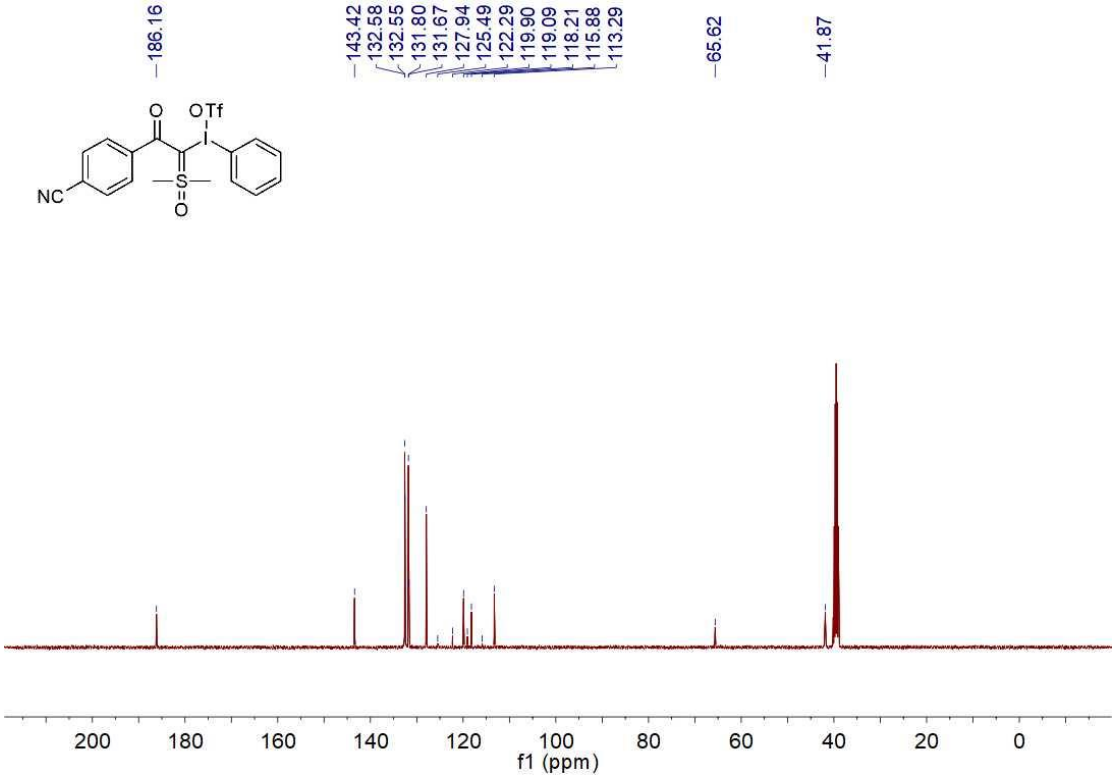
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1d**



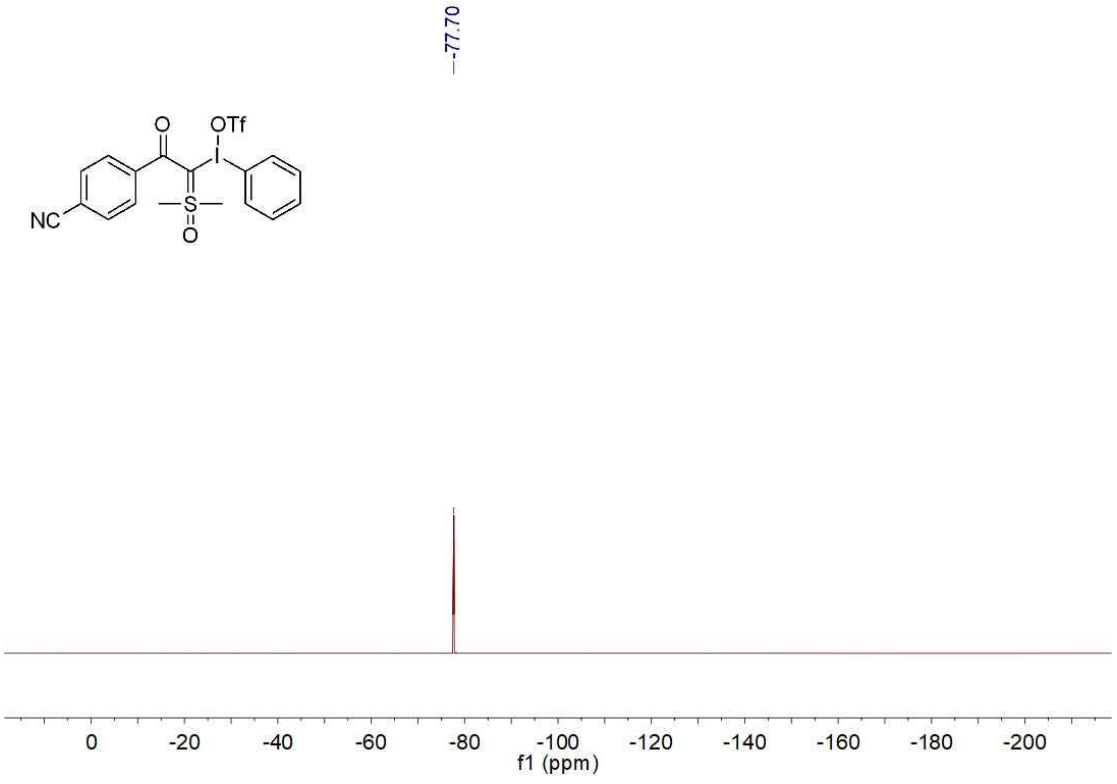
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1e**



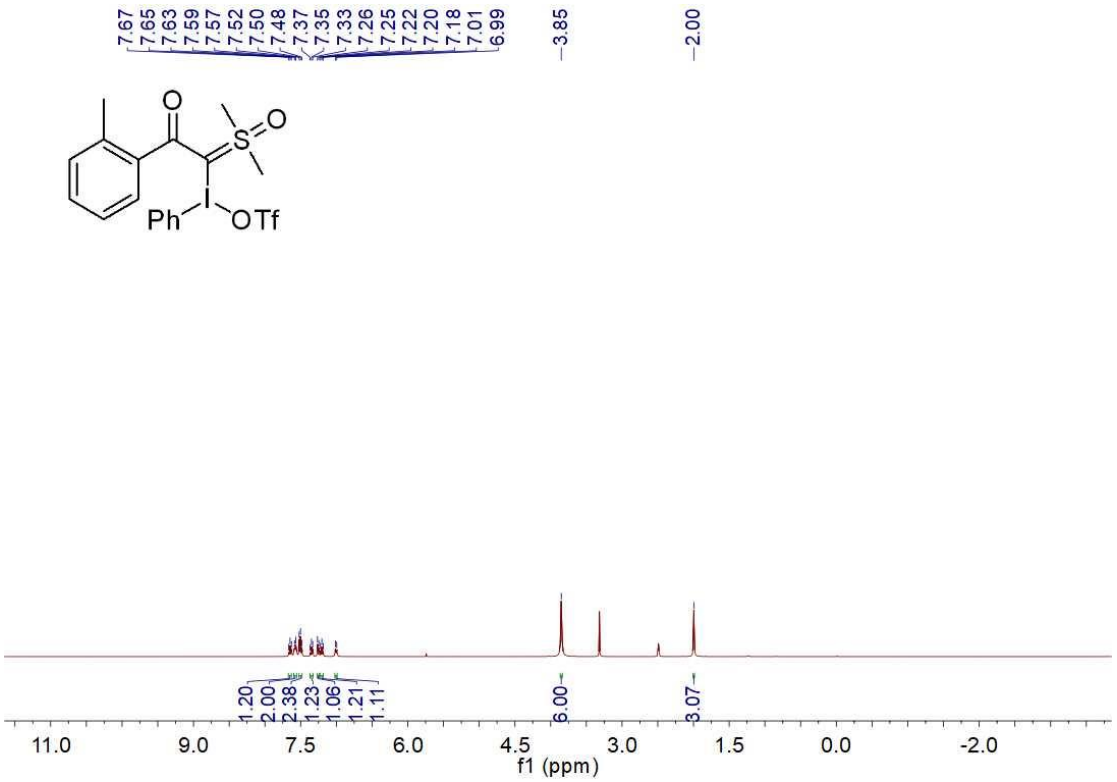
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1e**



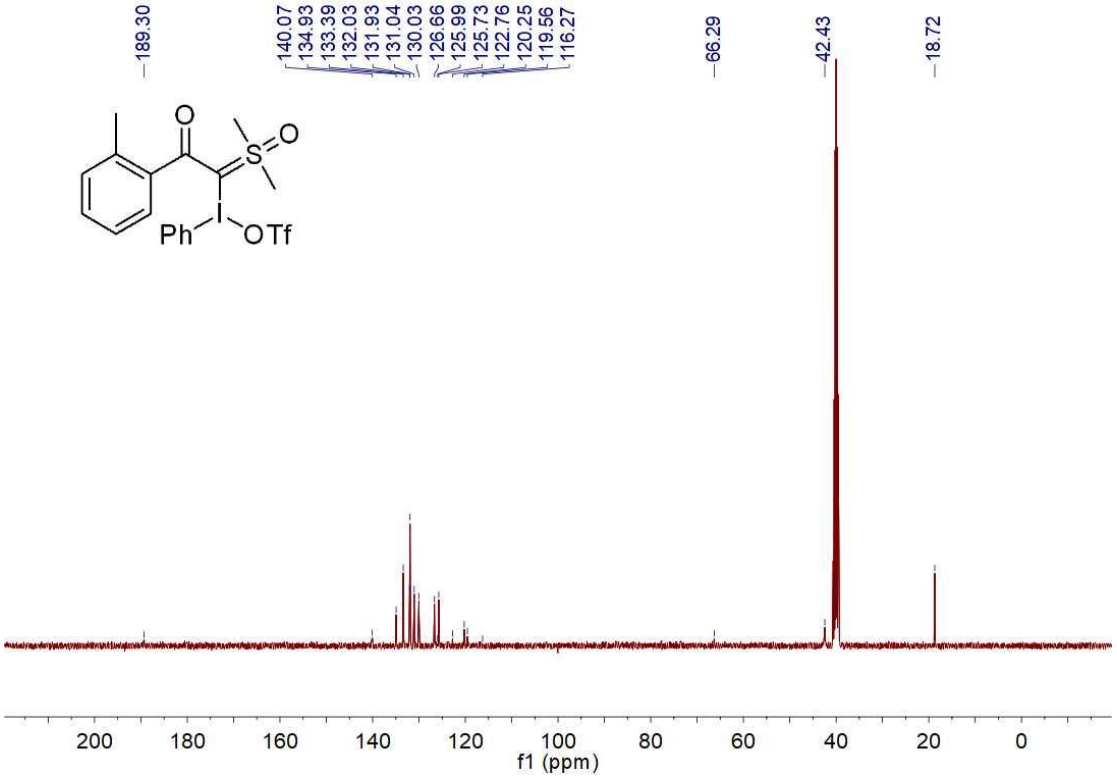
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1e**



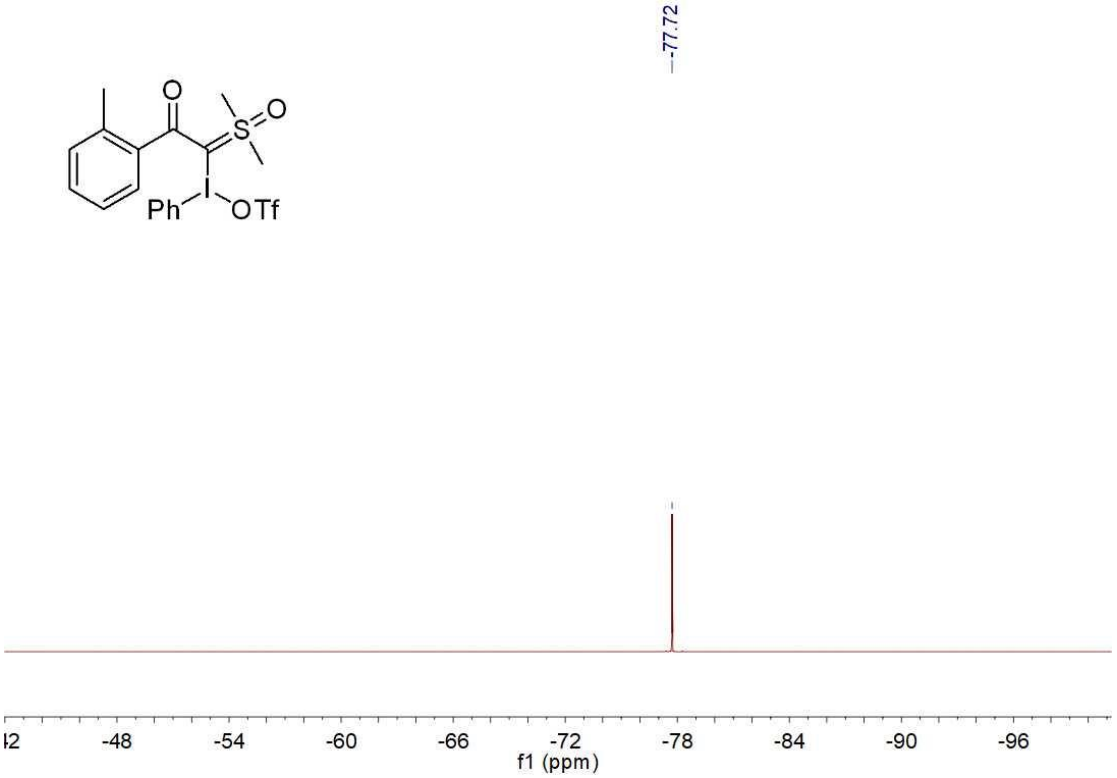
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1f**



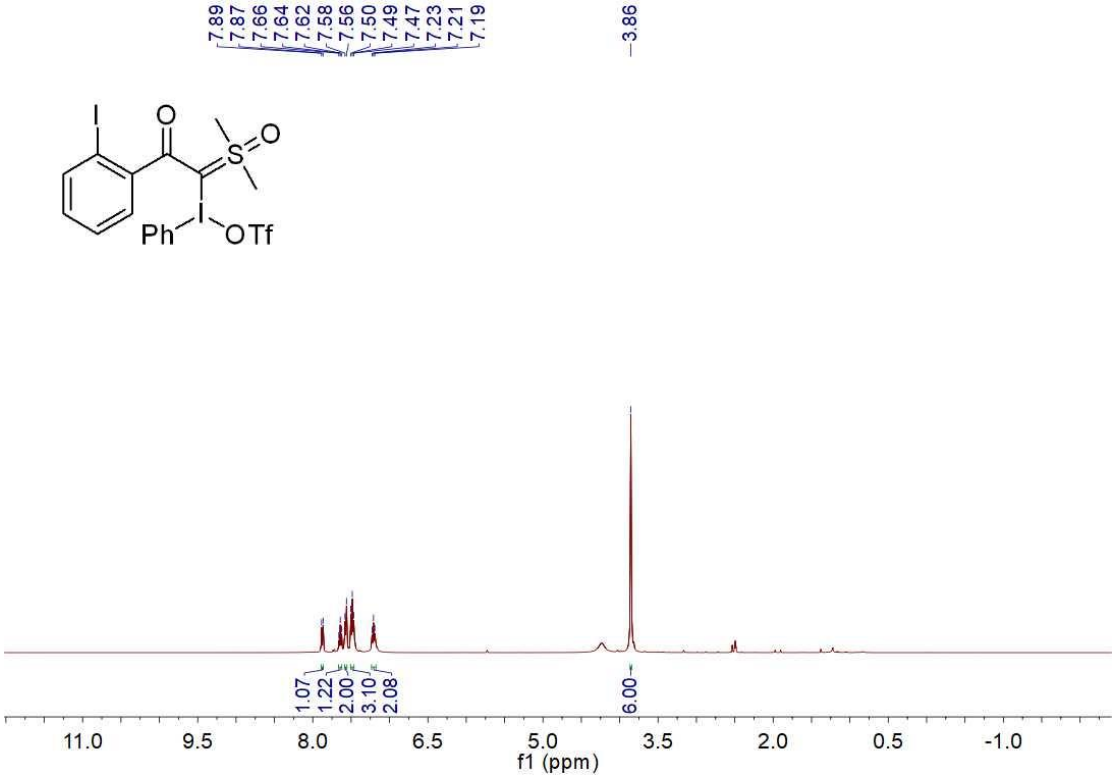
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1f**



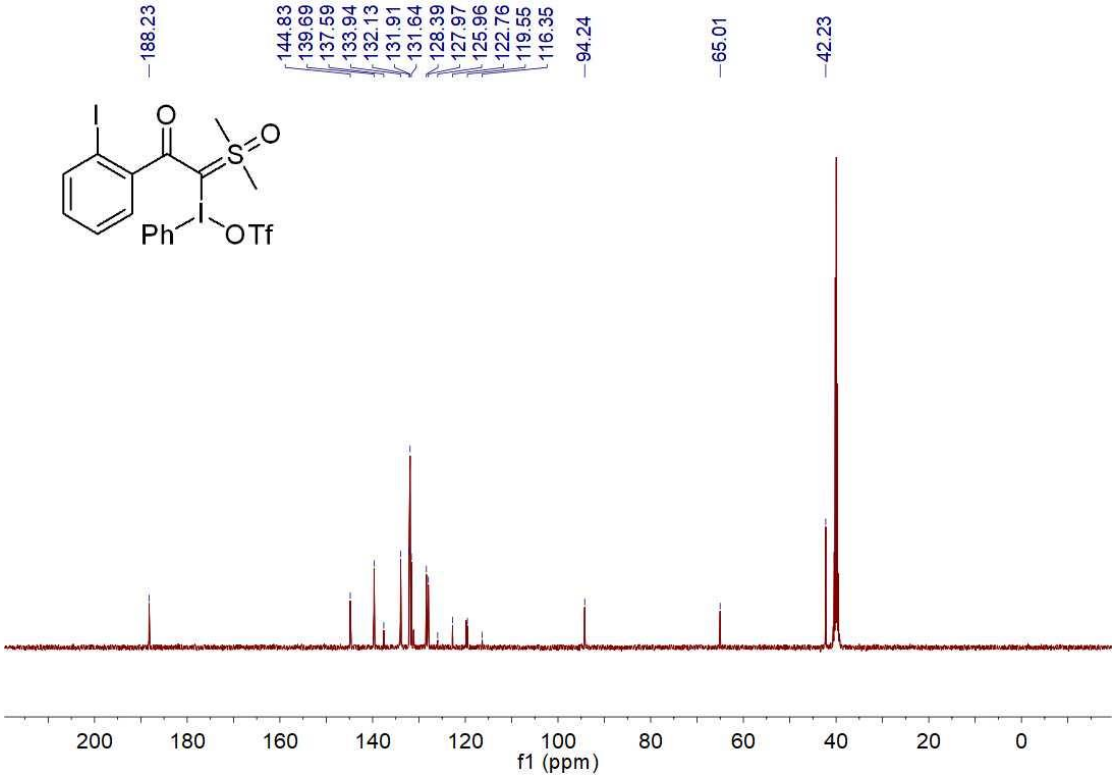
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1f**



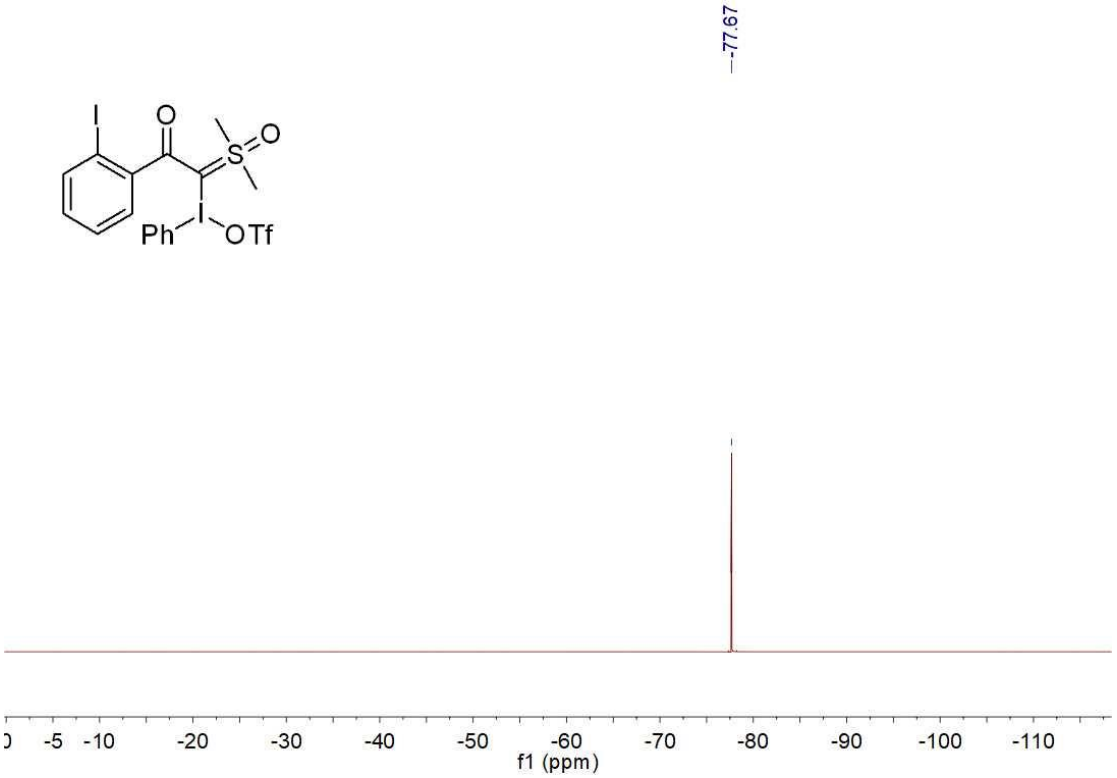
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1g**



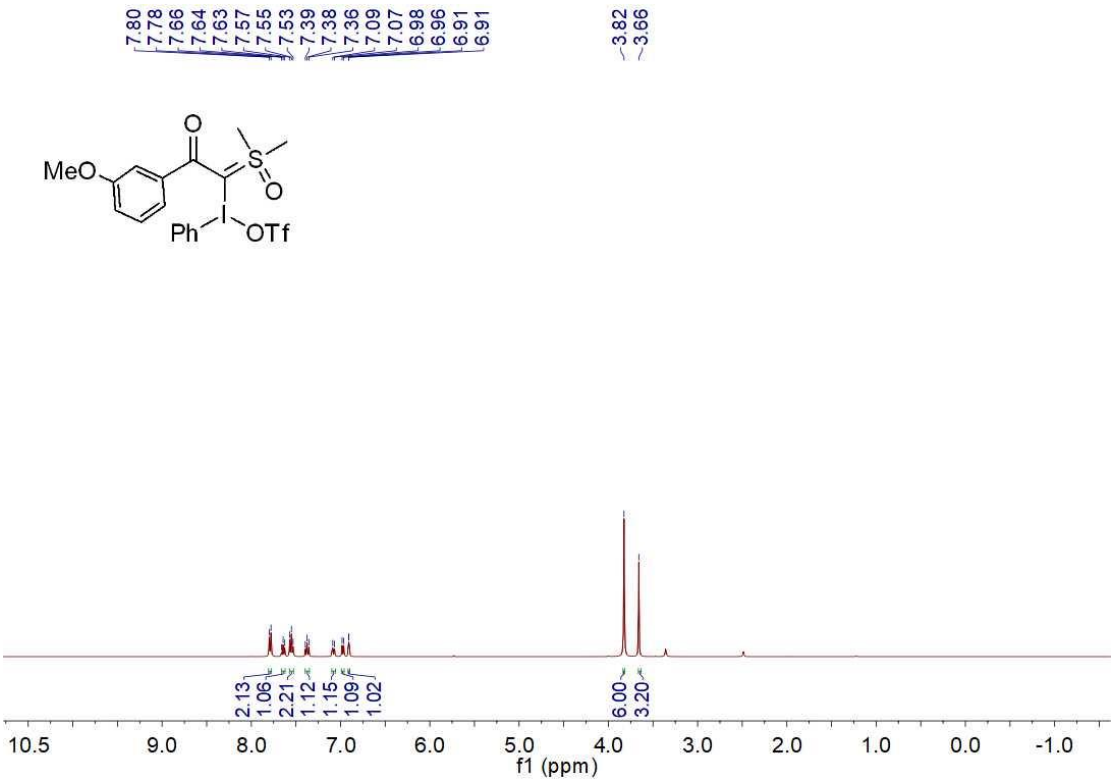
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1g**



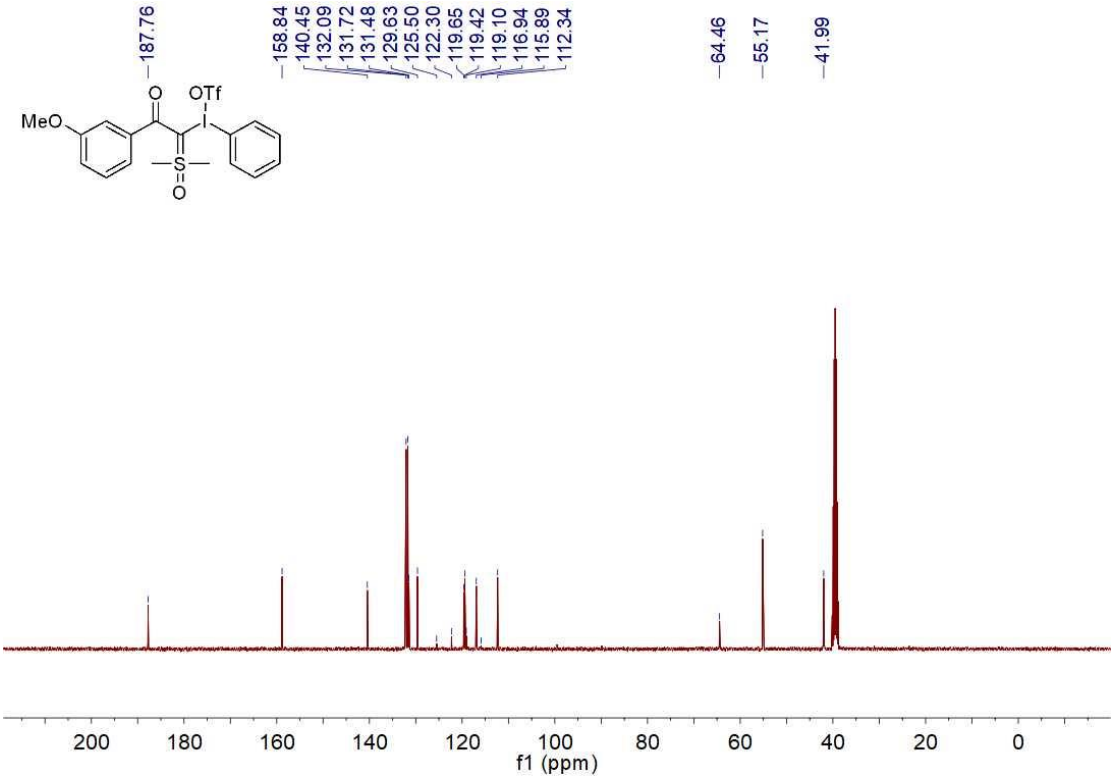
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1g**



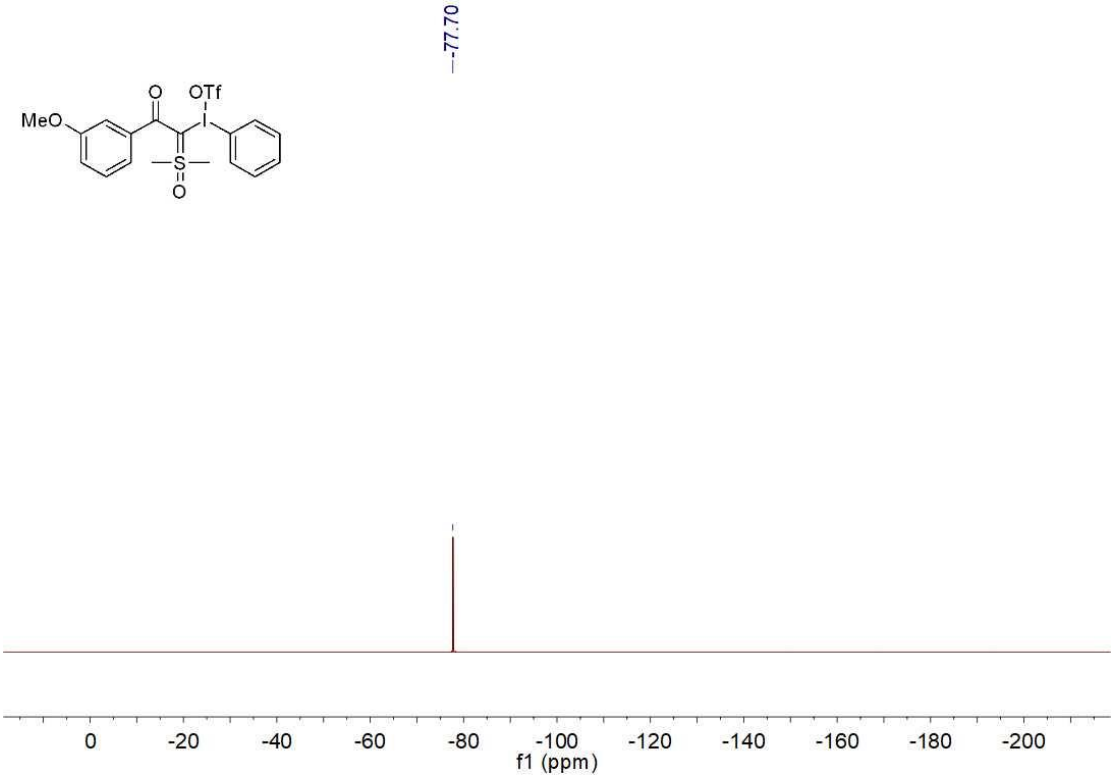
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1h**



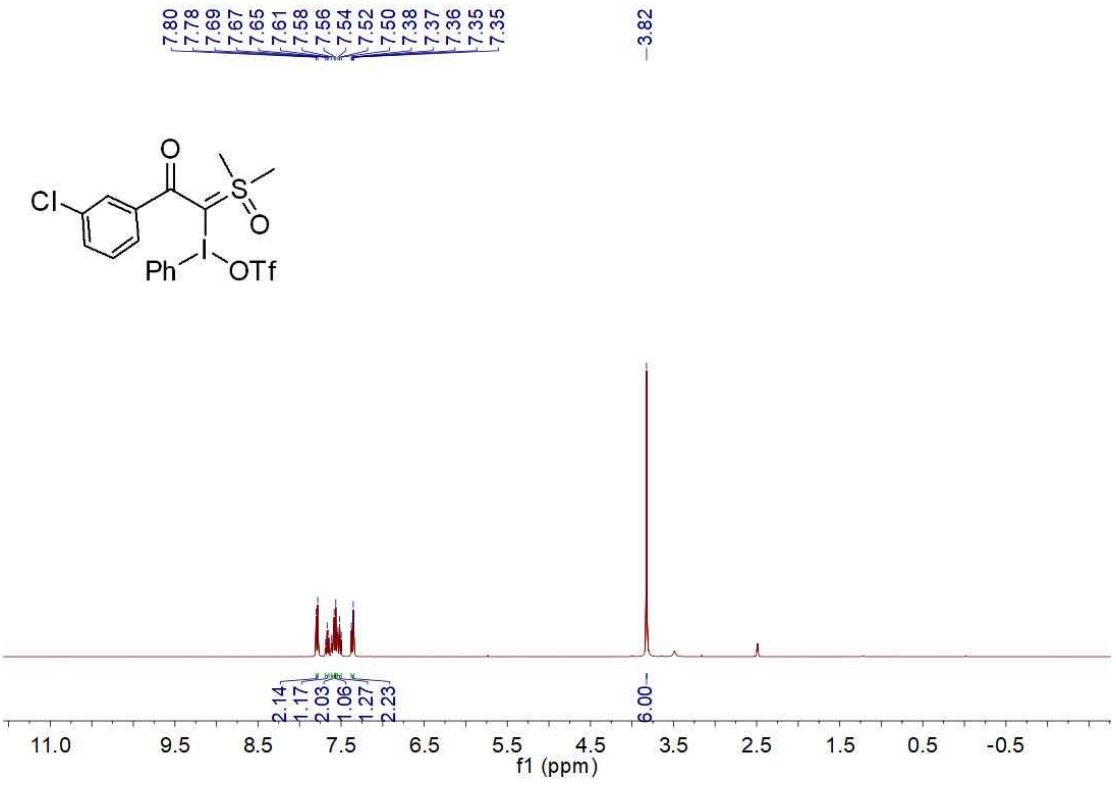
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1h**



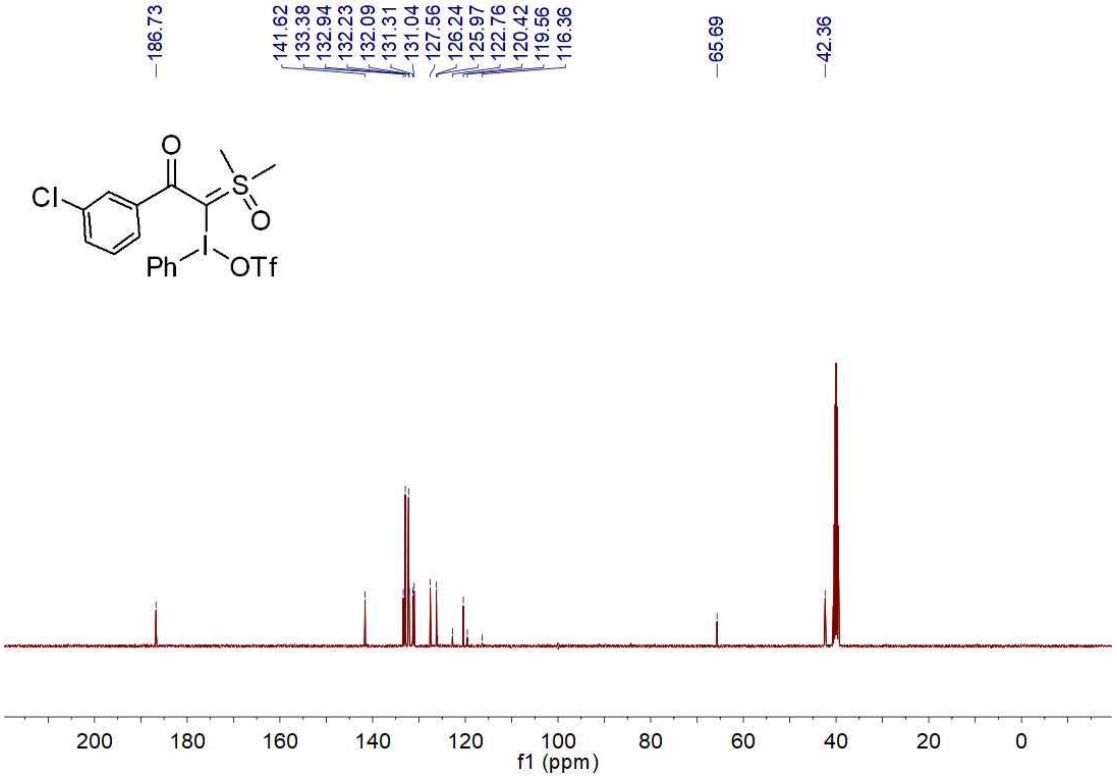
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1h**



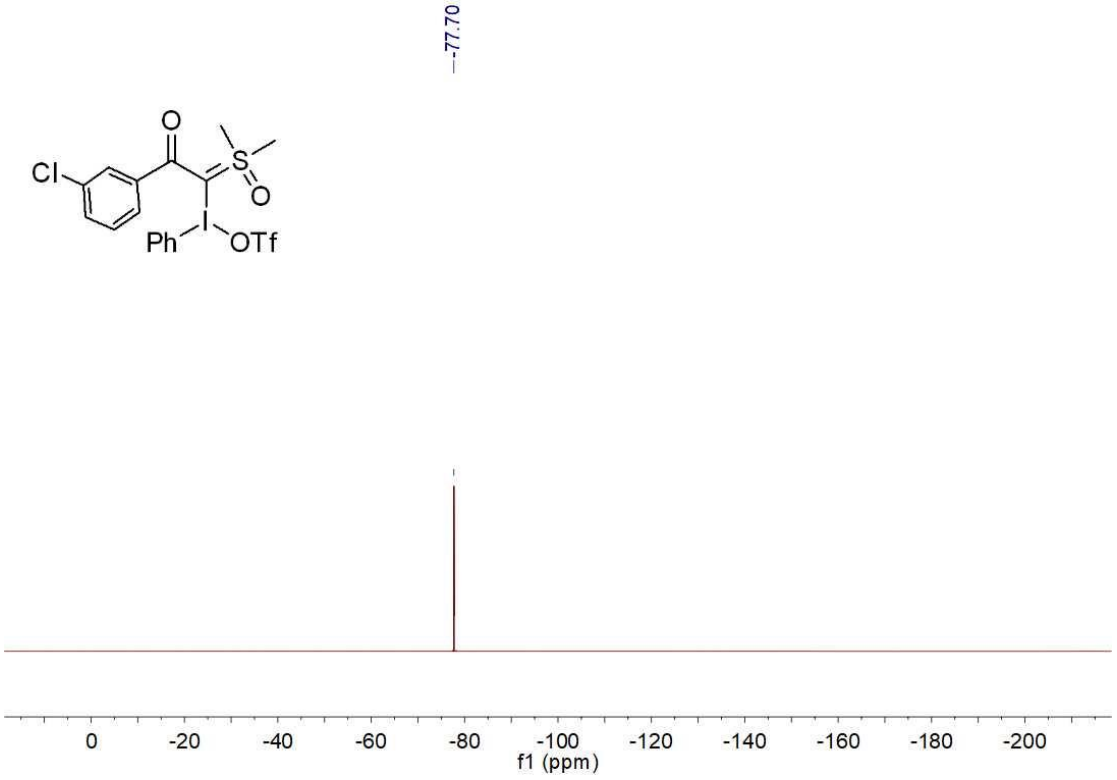
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1i**



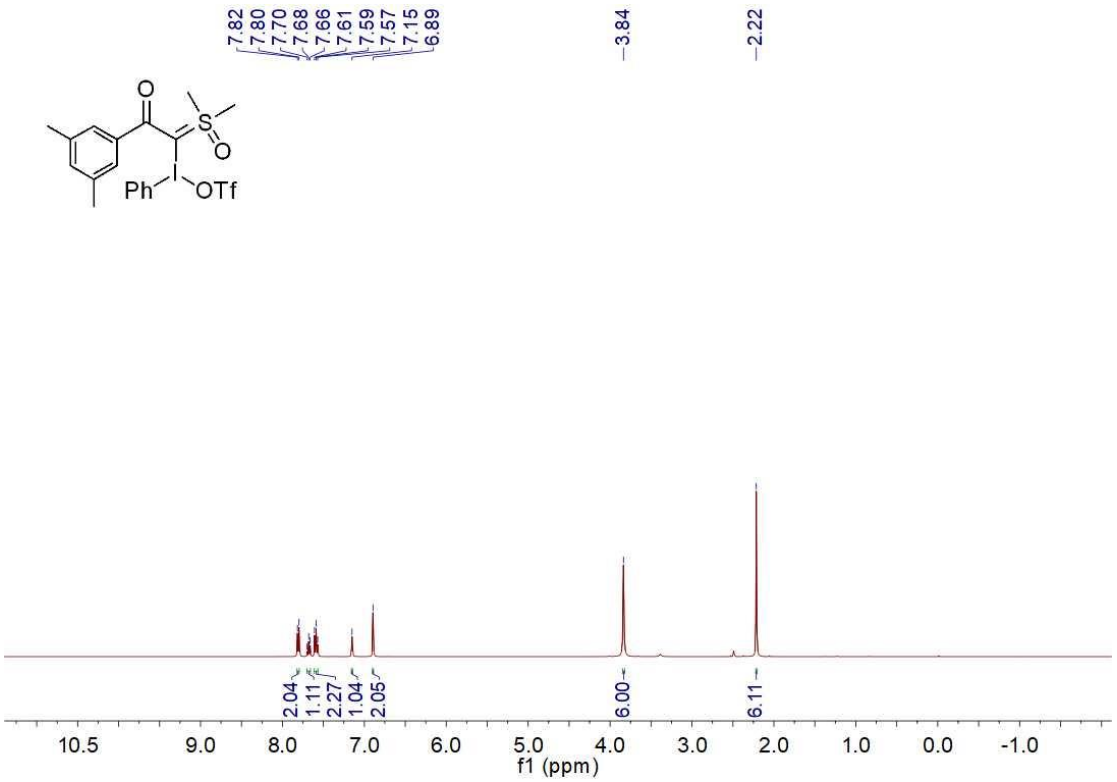
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1i**



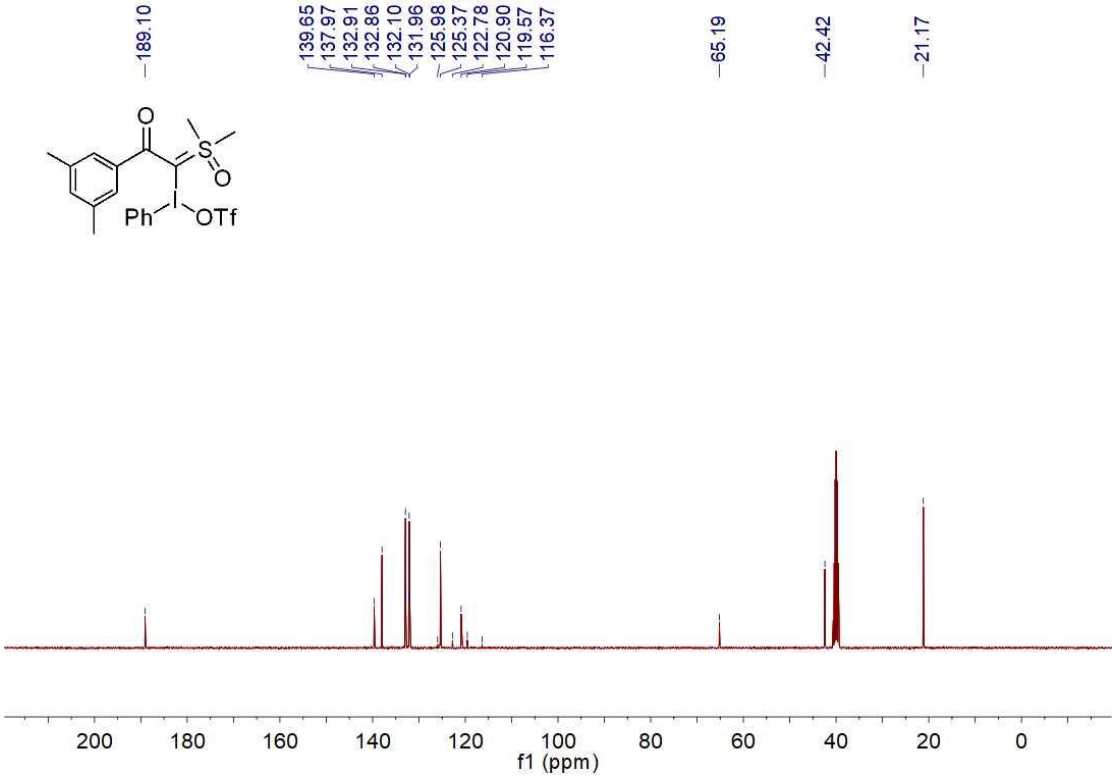
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1i**



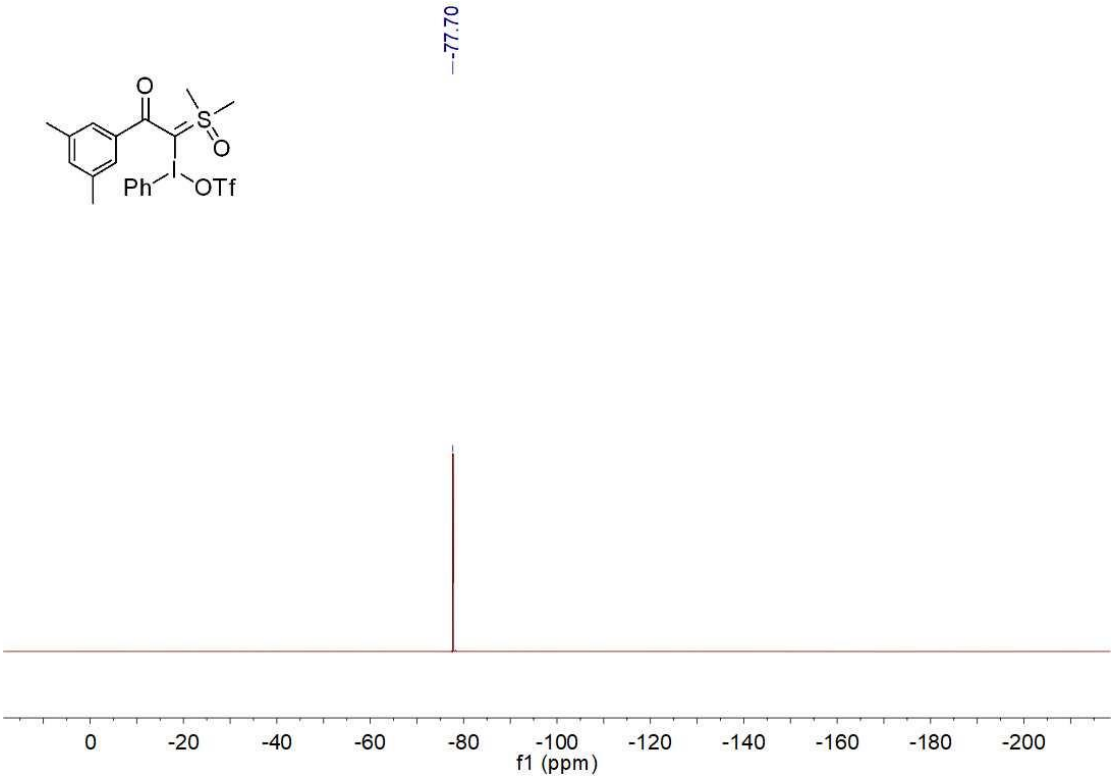
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1j**



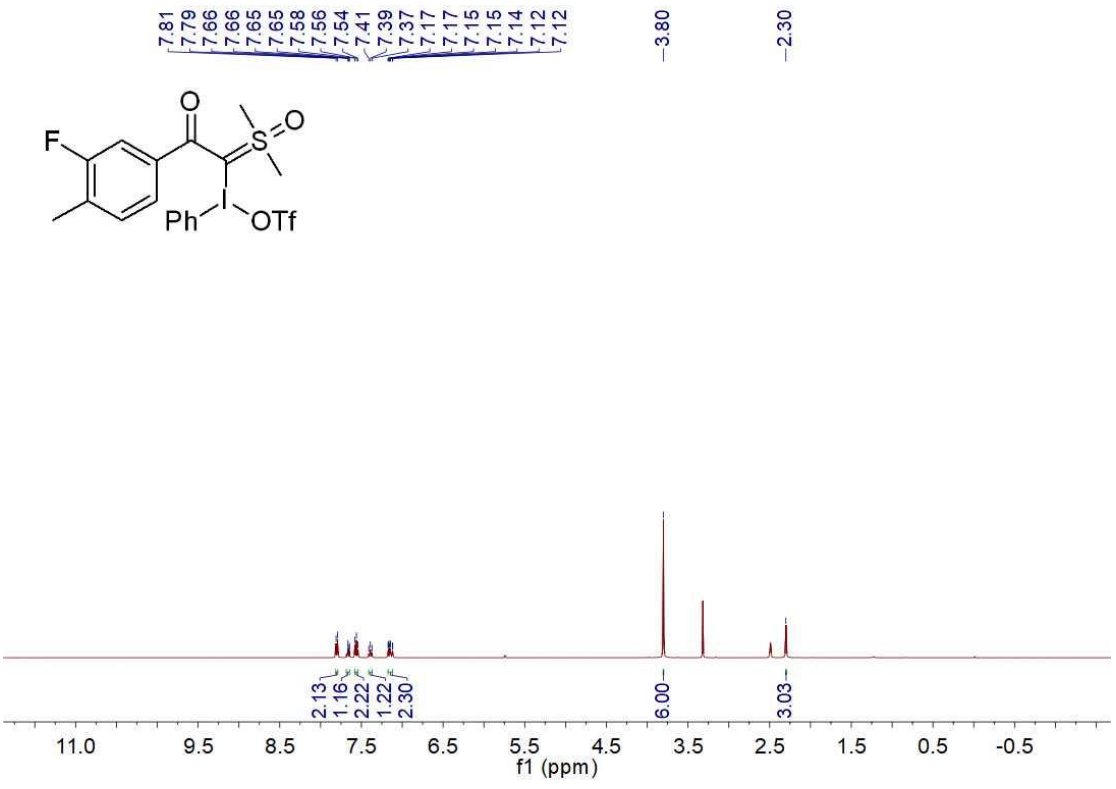
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1j**



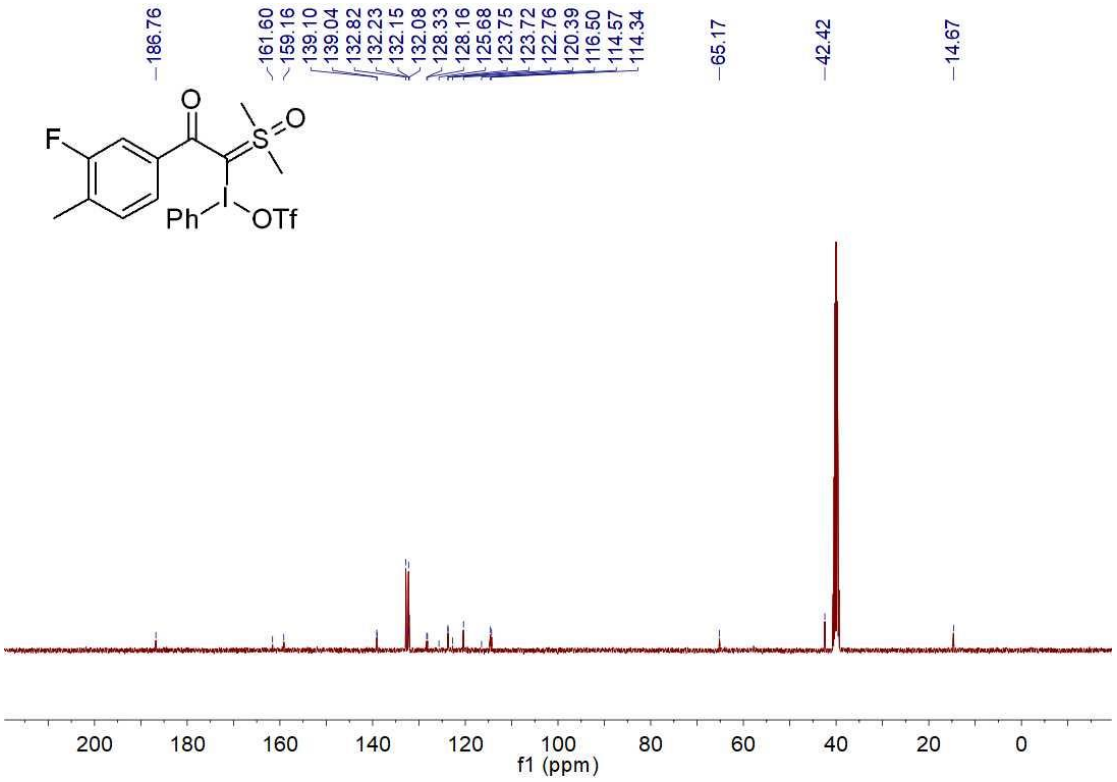
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1j**



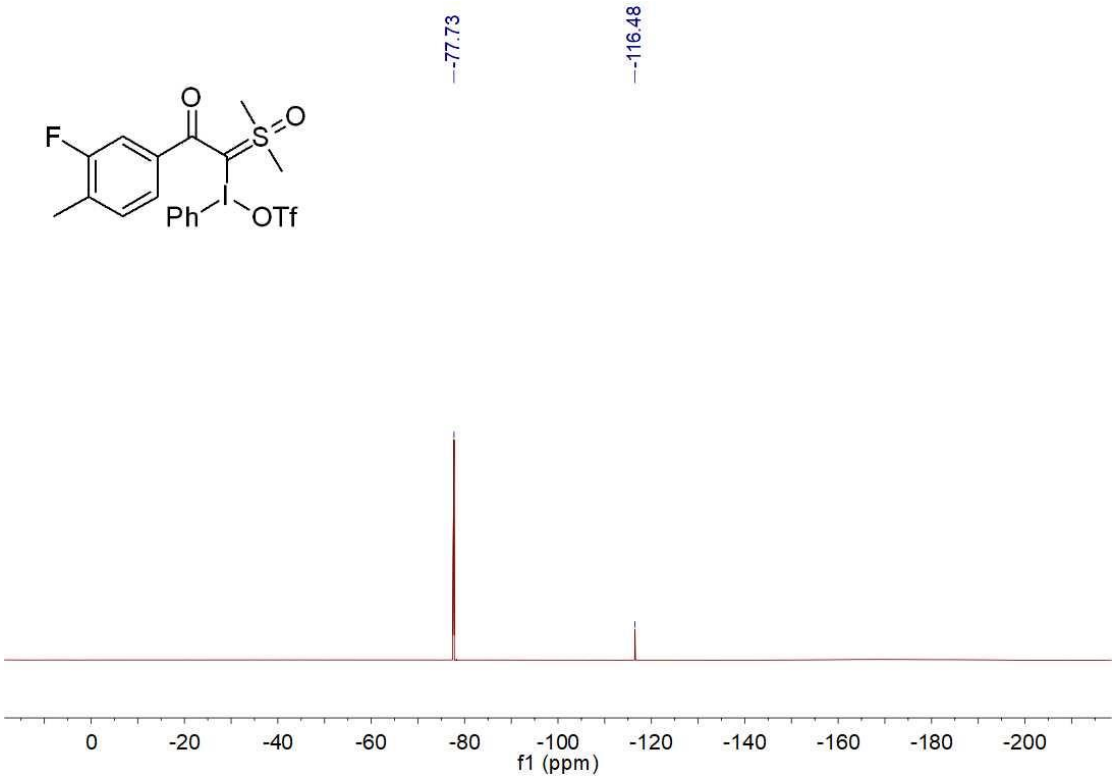
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1k**



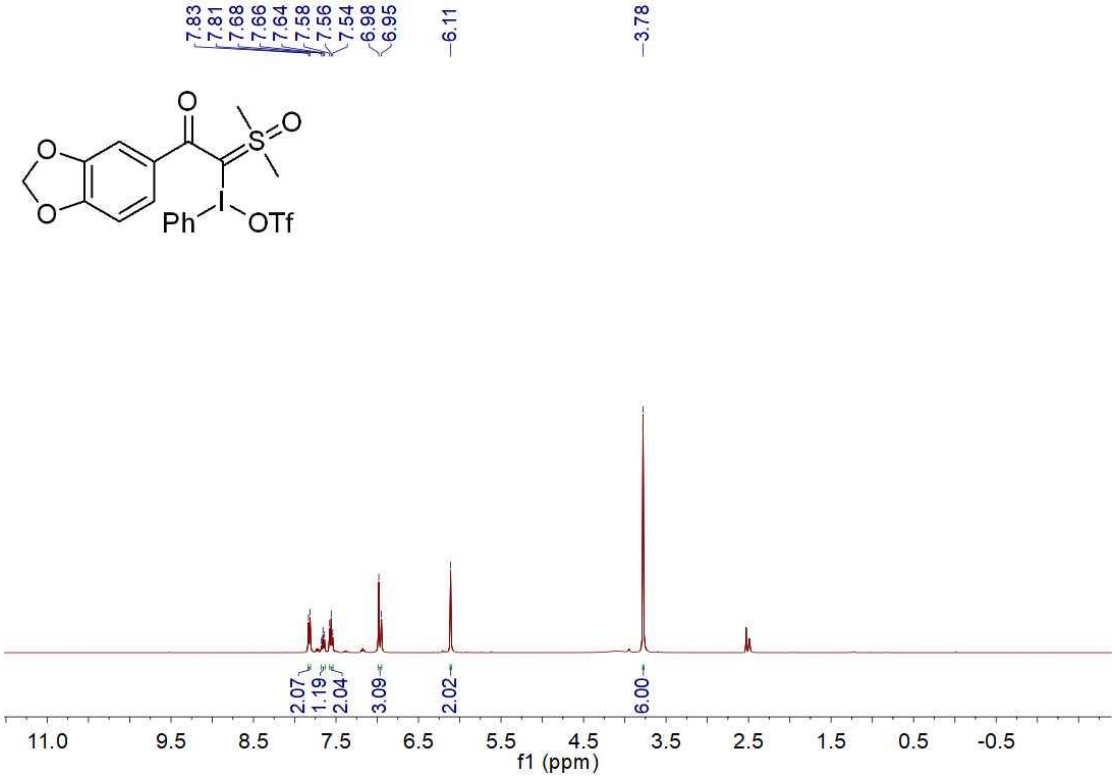
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1k**



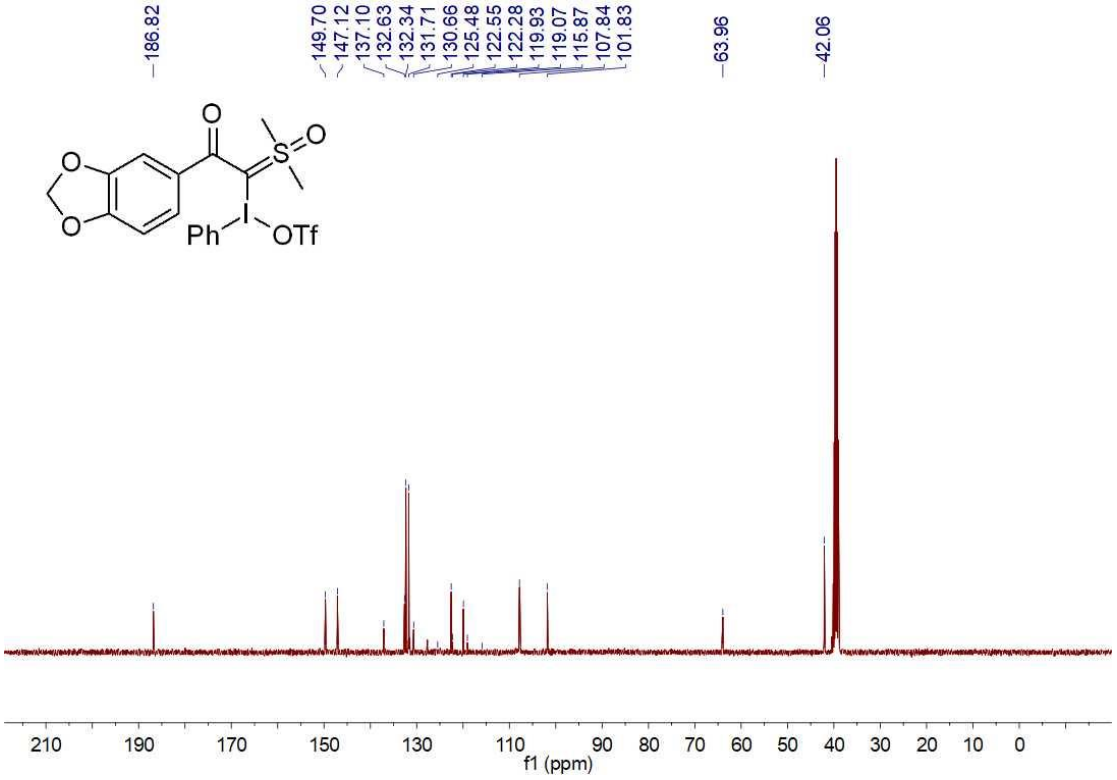
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1k**



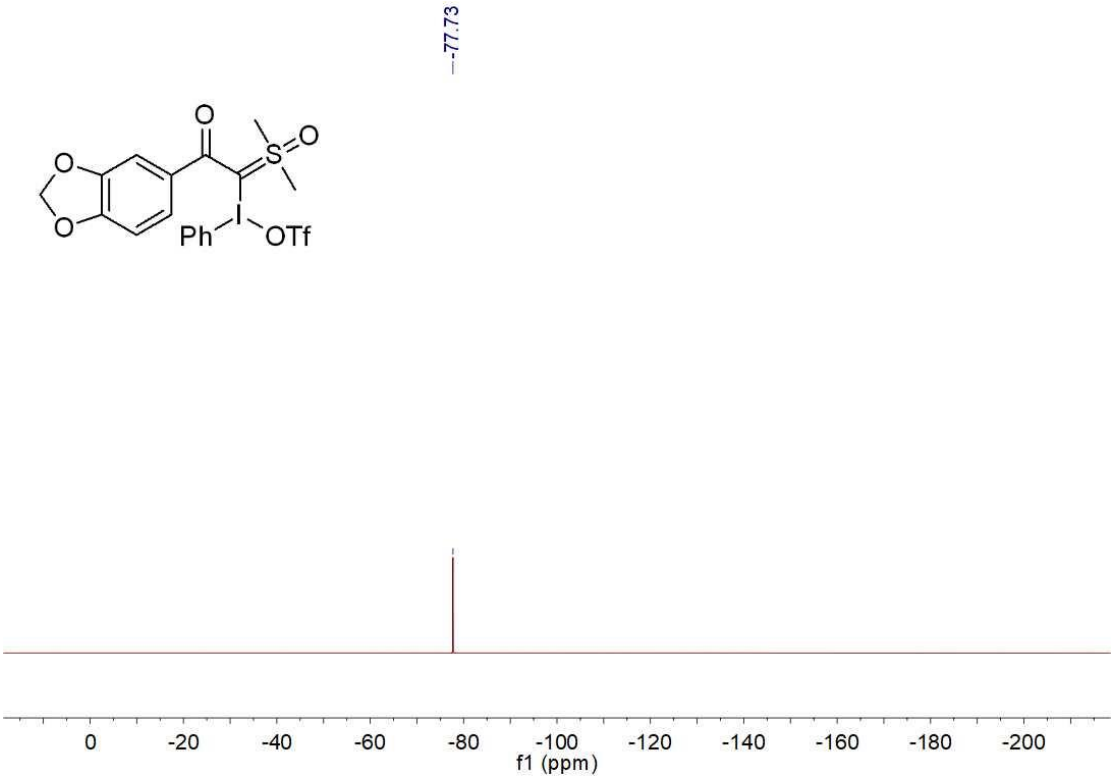
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **4l**



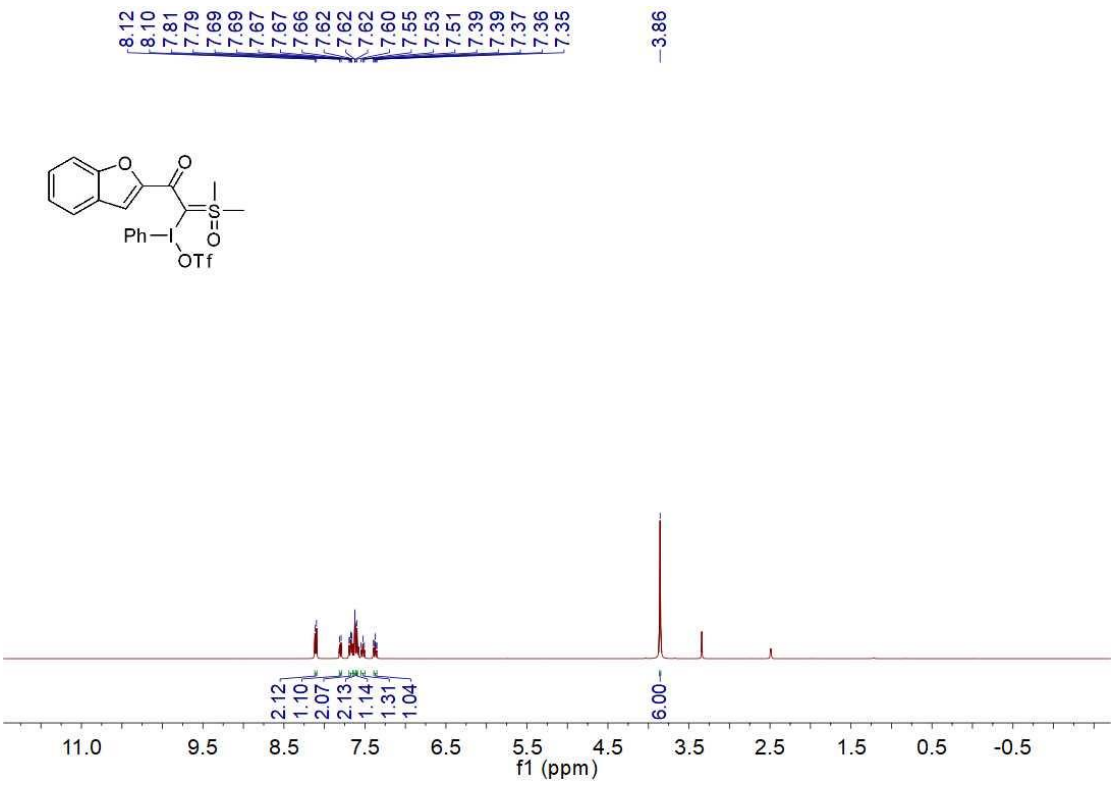
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **4l**



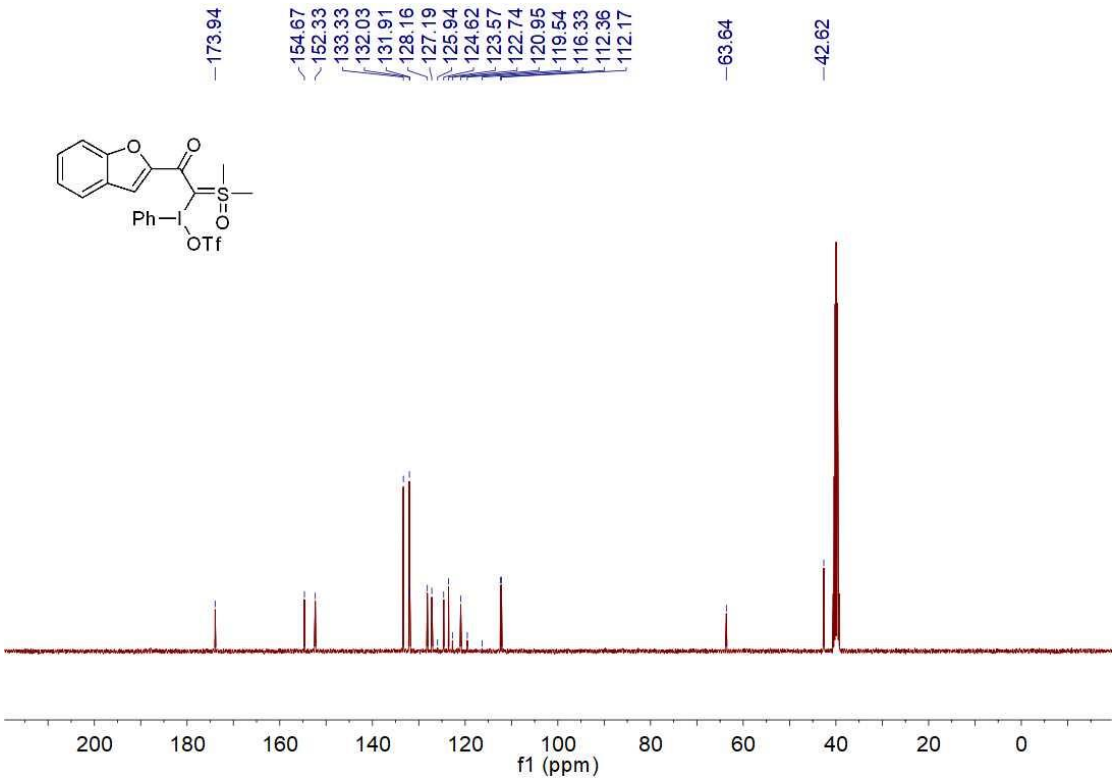
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **4l**



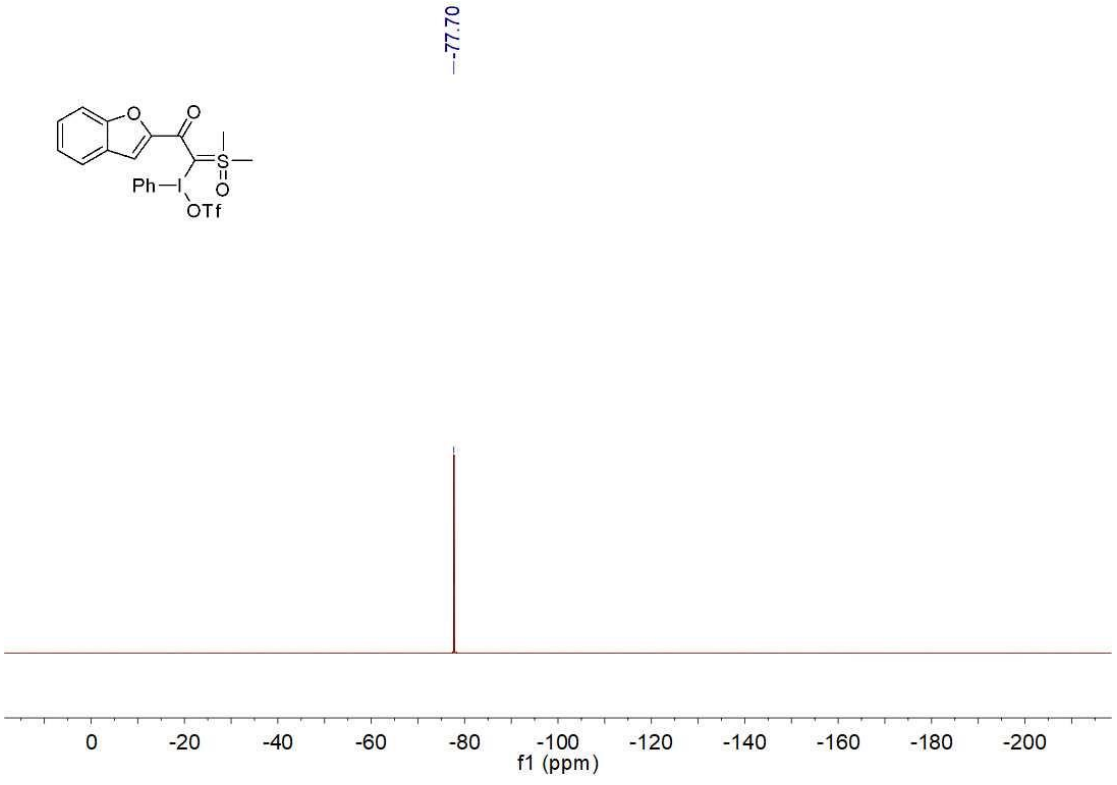
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1m**



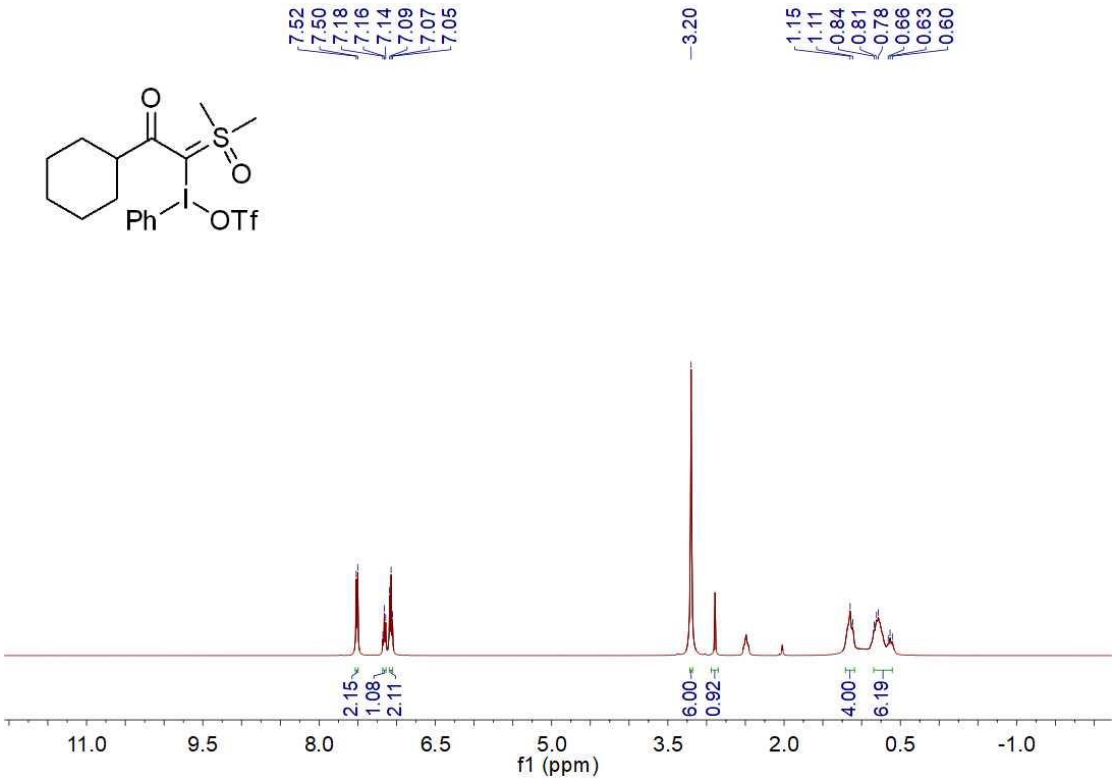
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1m**



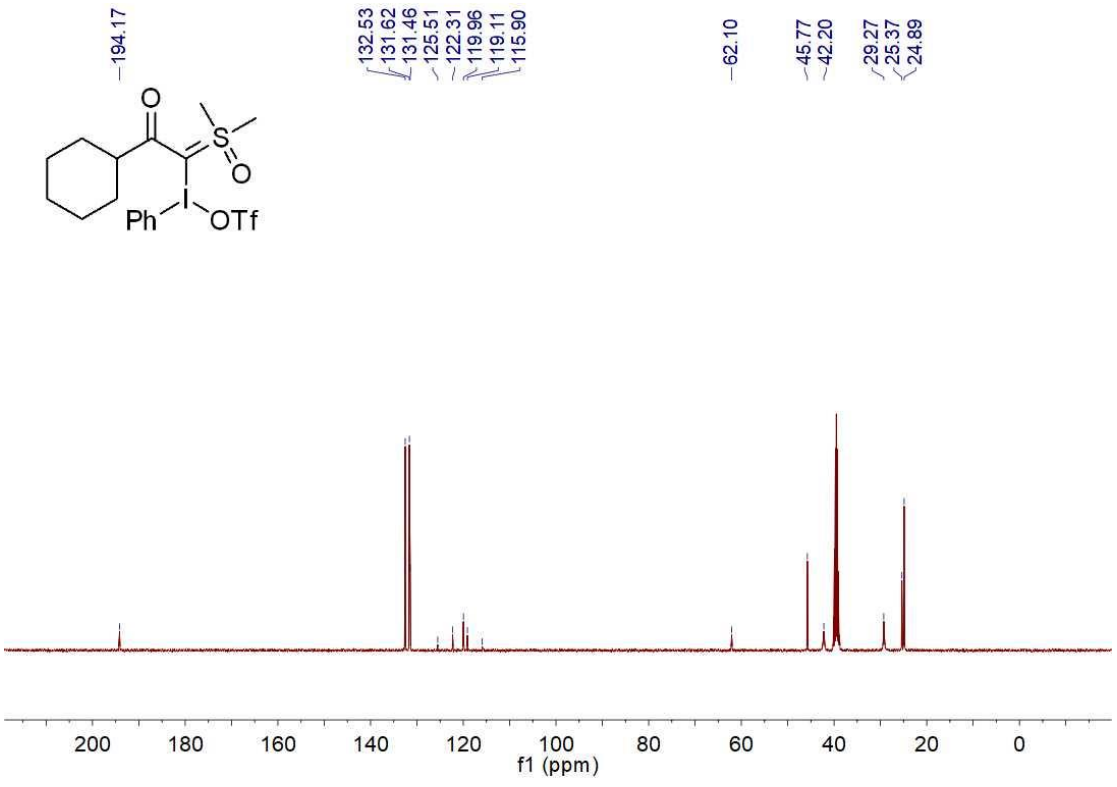
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1m**



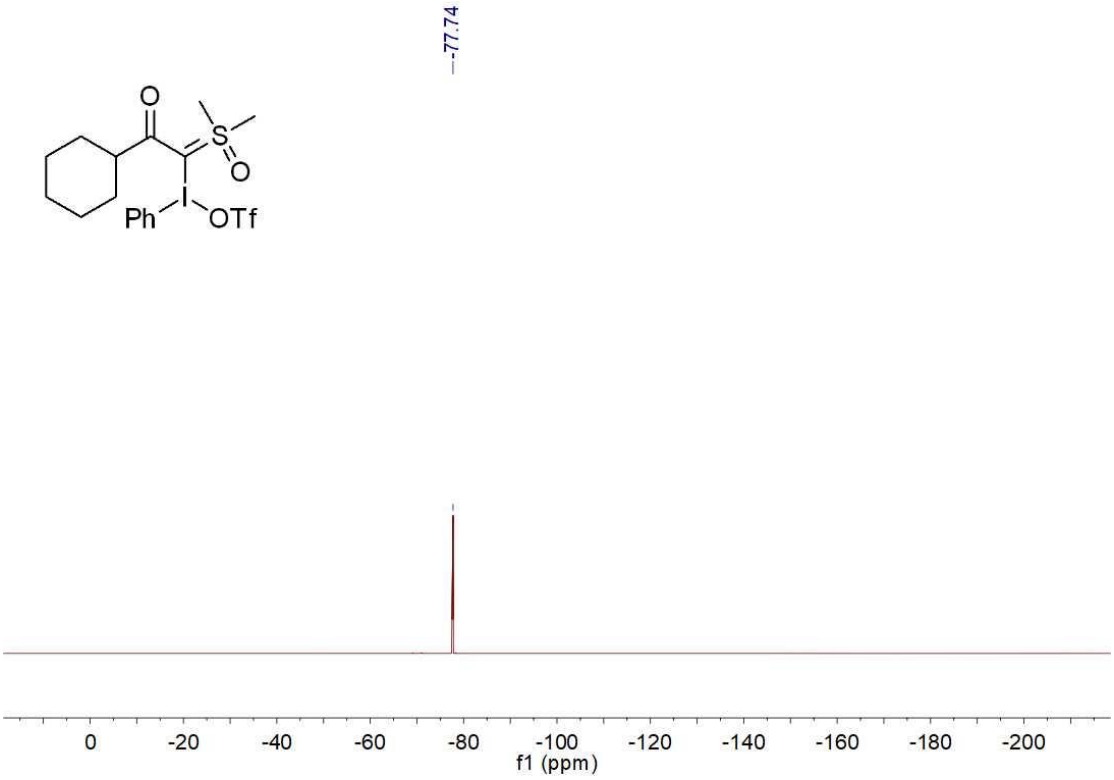
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1n**



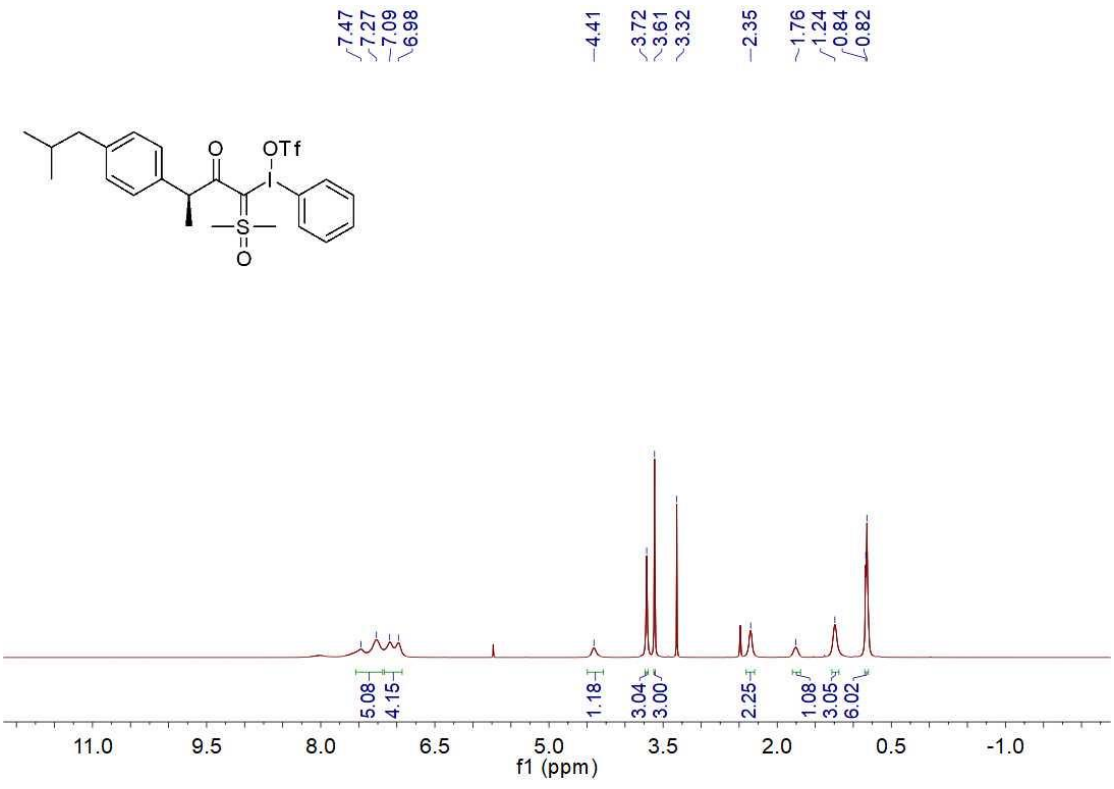
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1n**



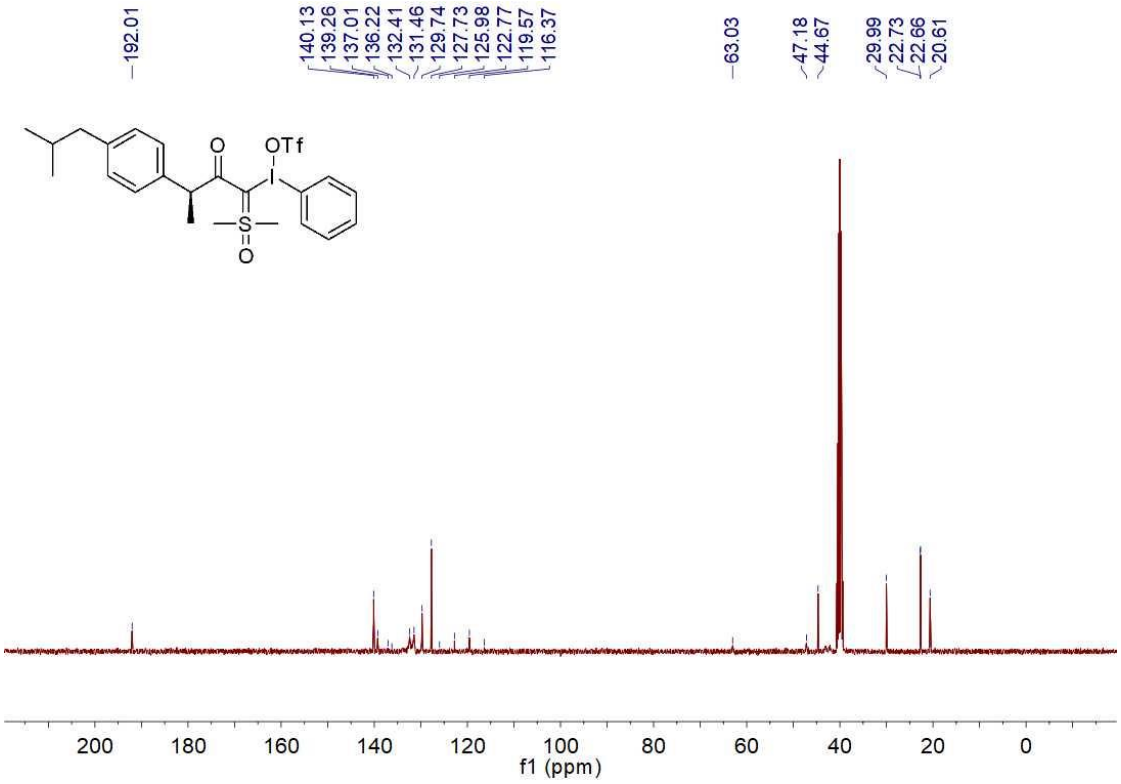
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1n**



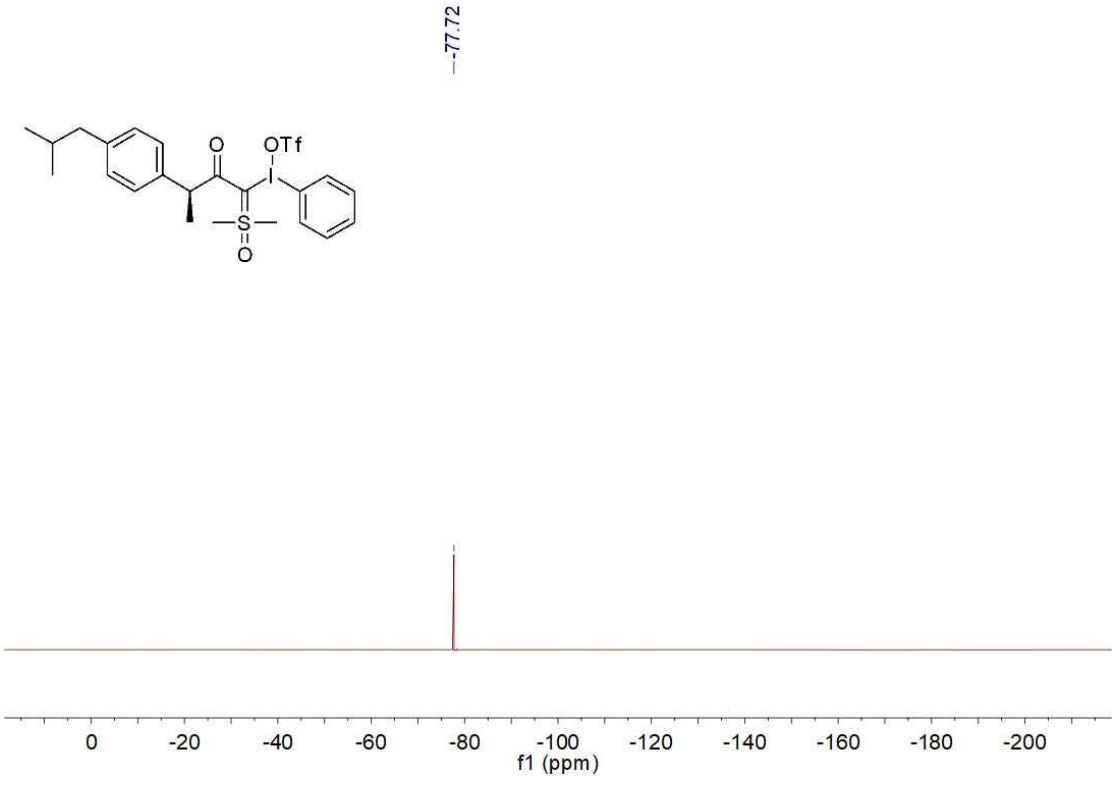
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **1o**



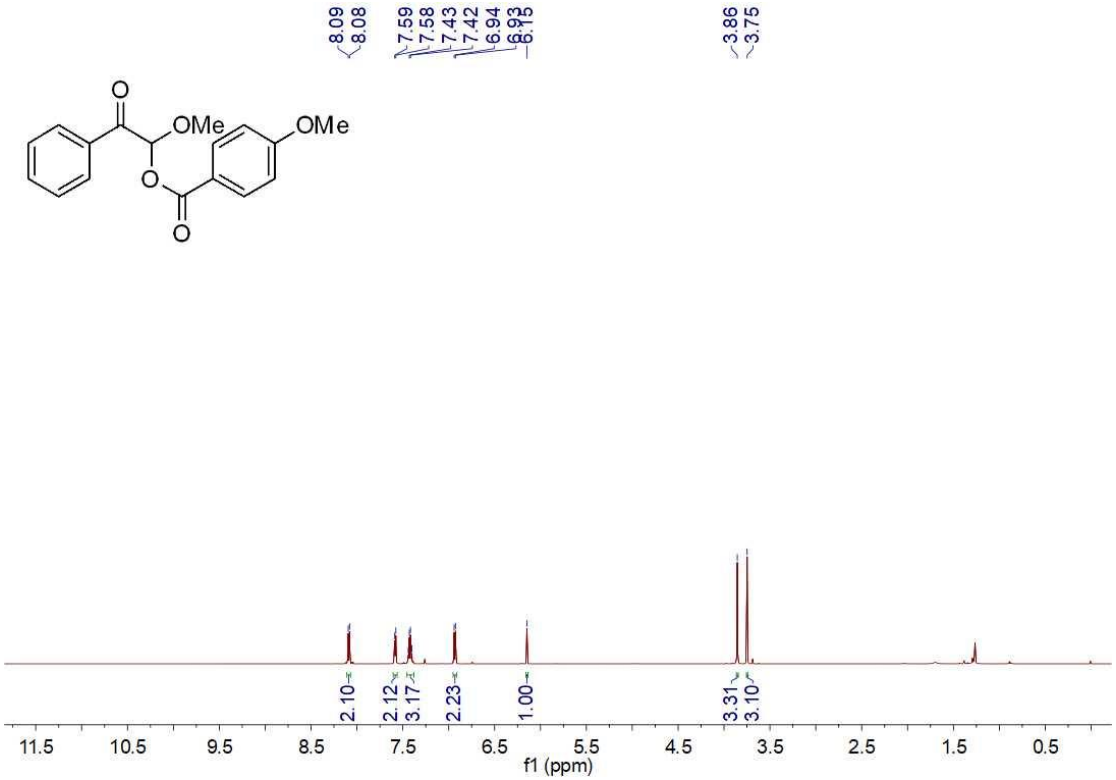
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of **1o**



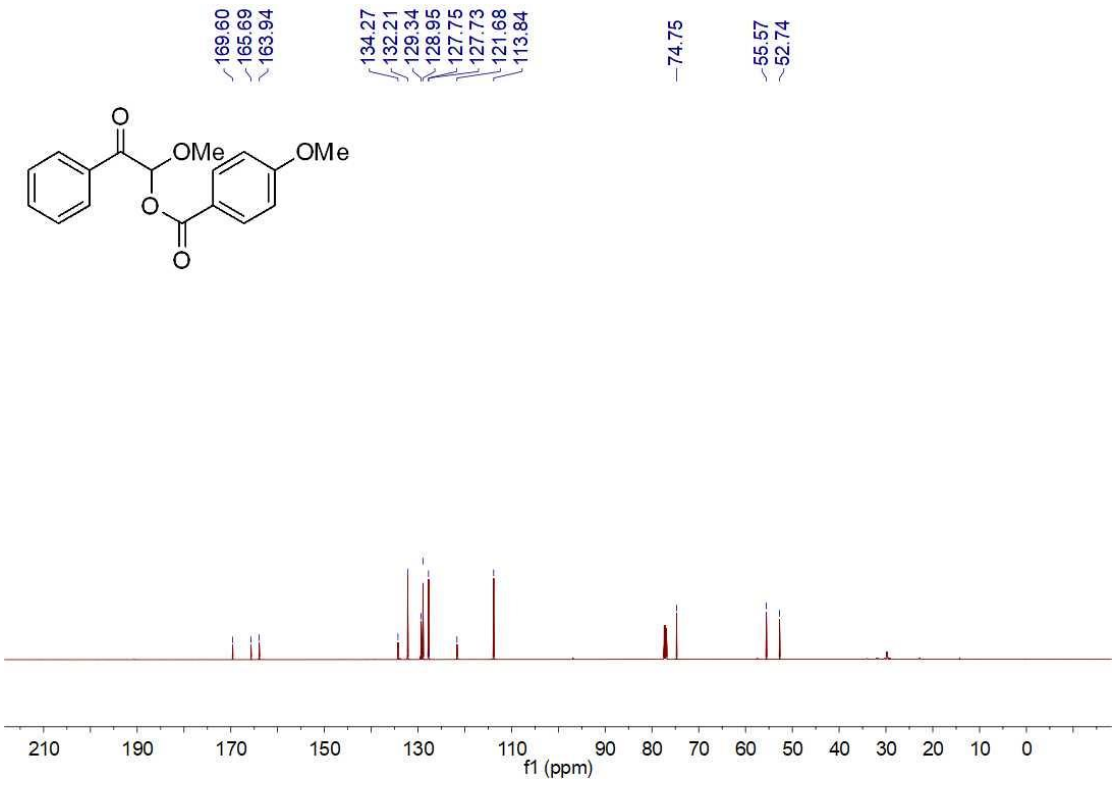
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of **1o**



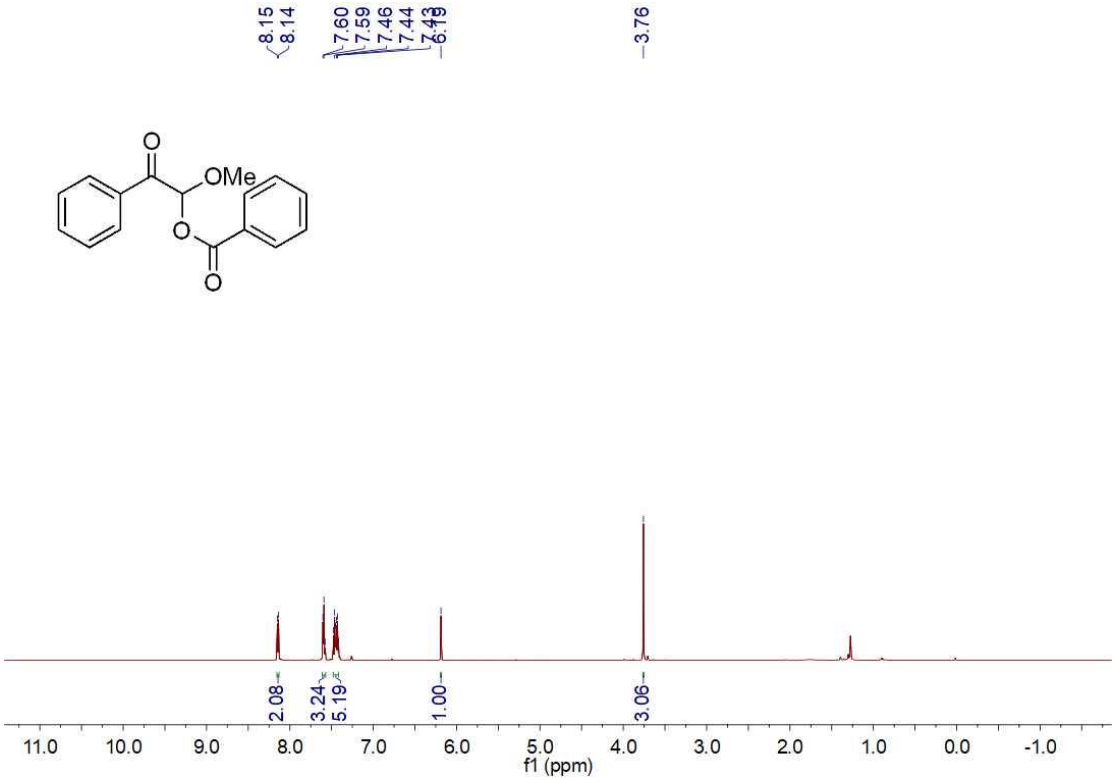
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3a**



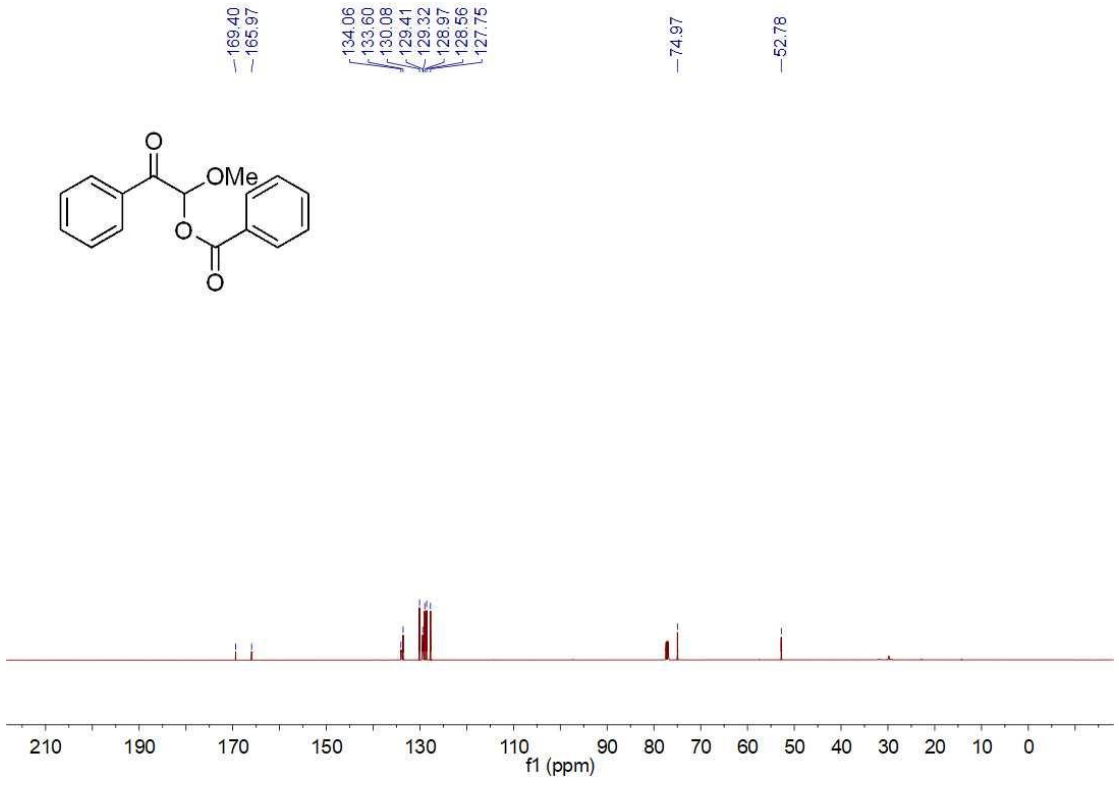
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3a**



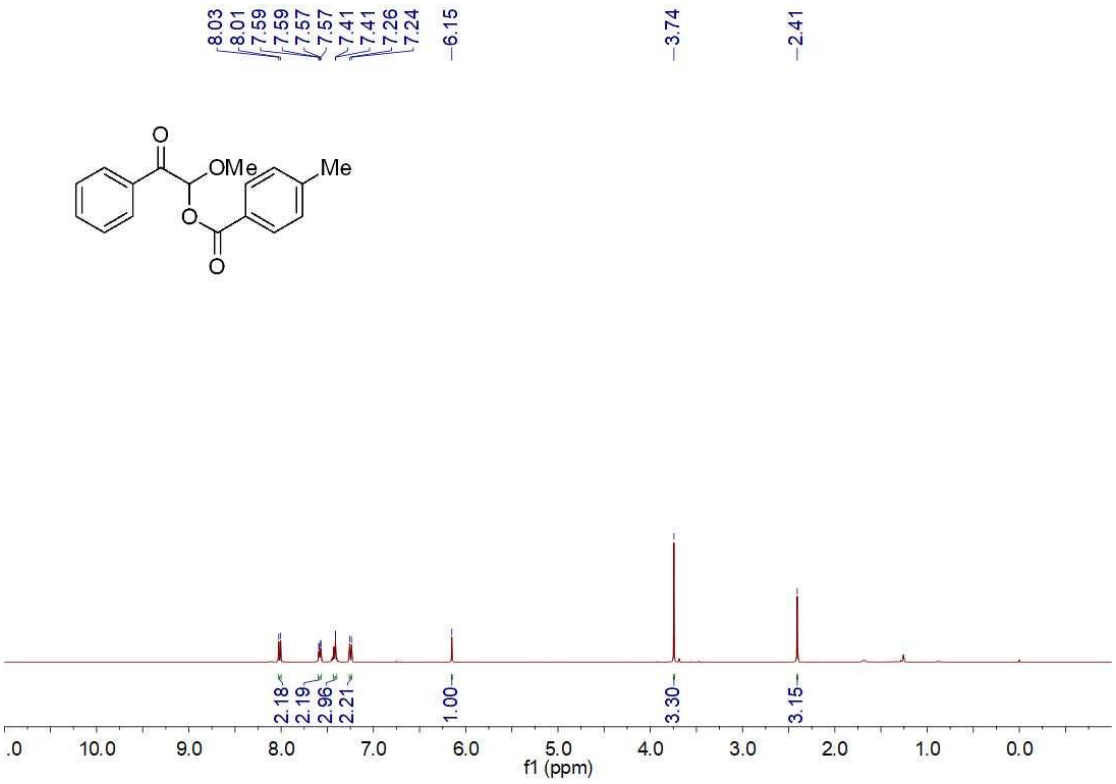
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3b**



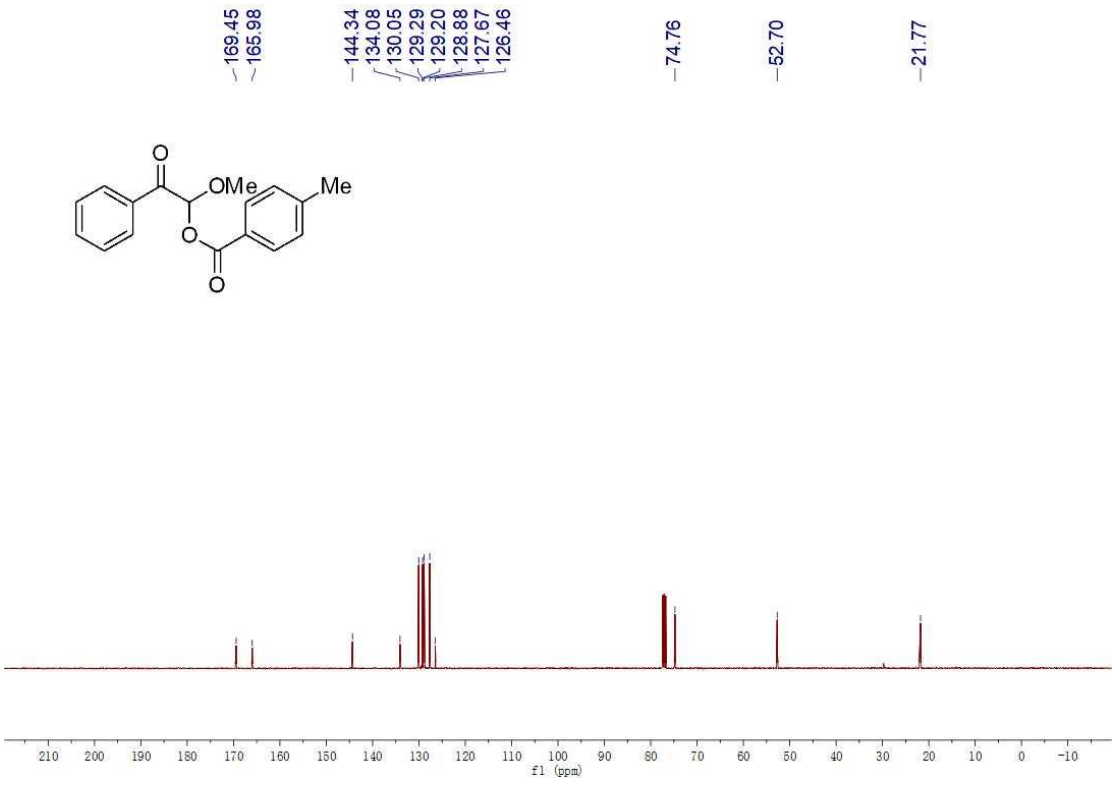
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3b**



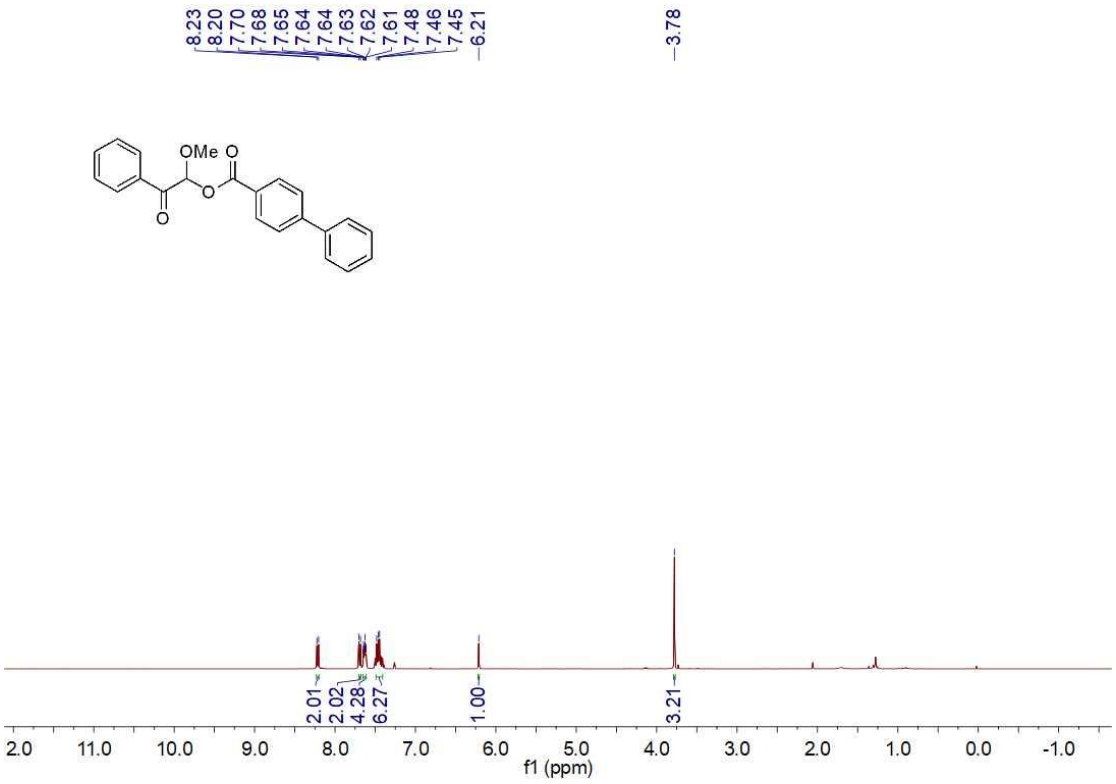
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3c**



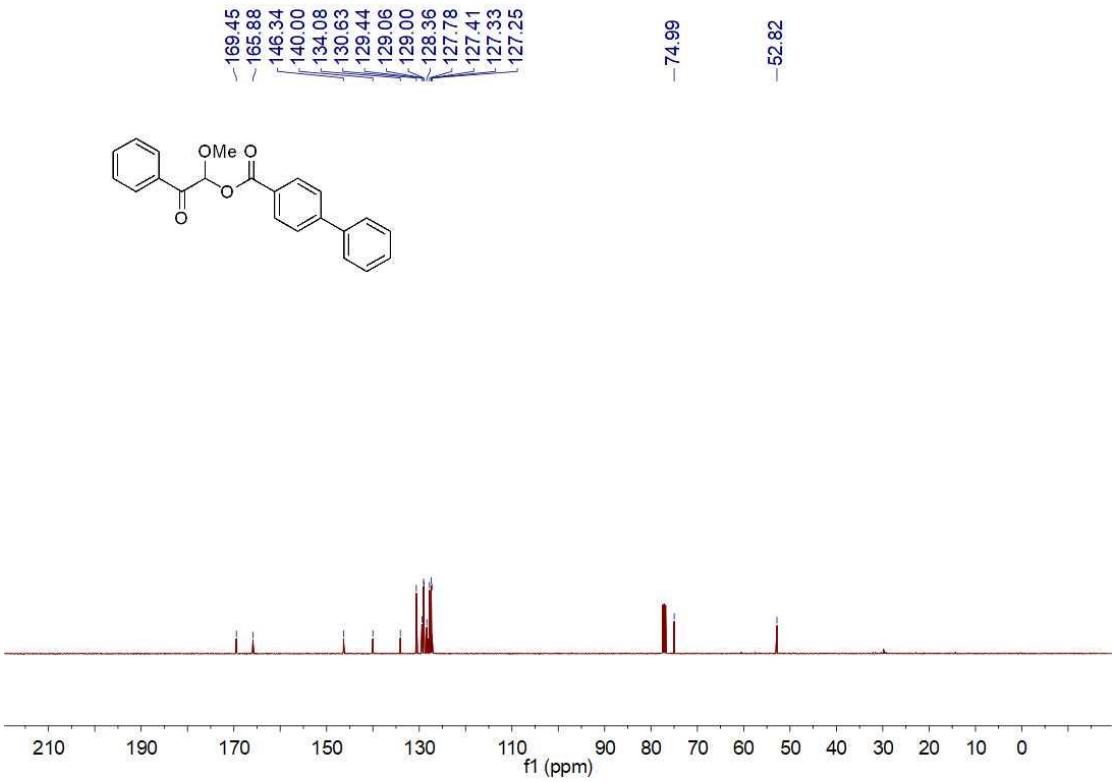
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3c**



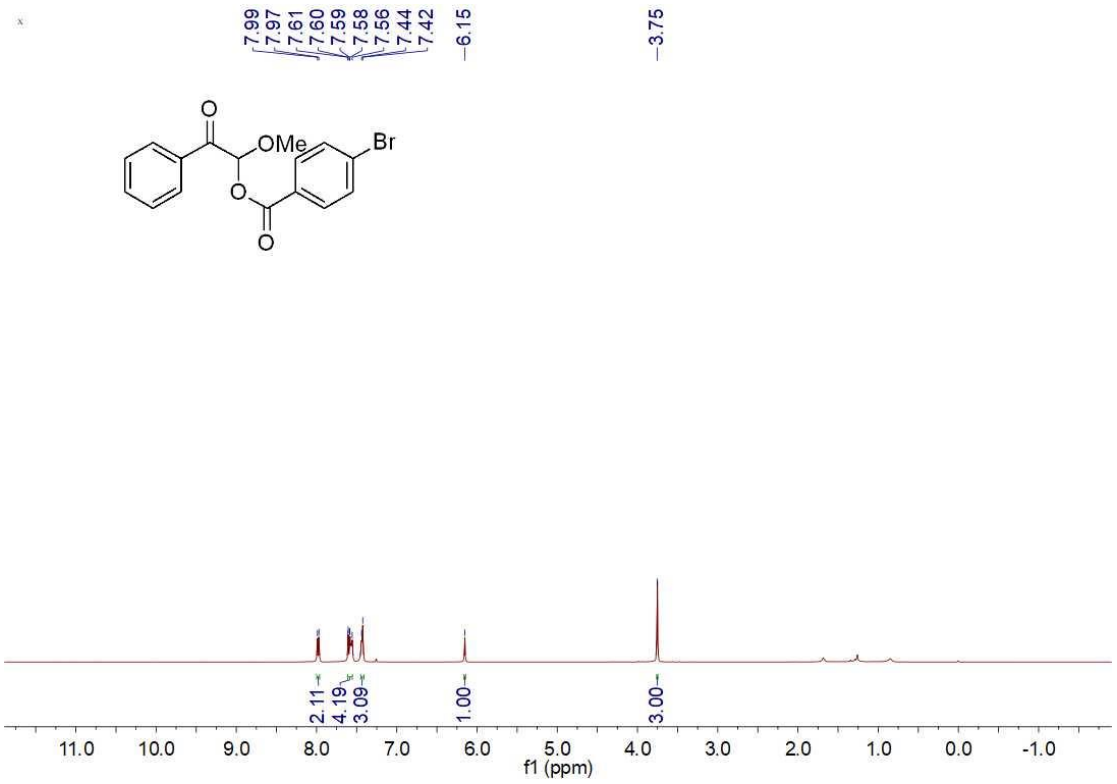
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3d**



^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3d**



^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3e**



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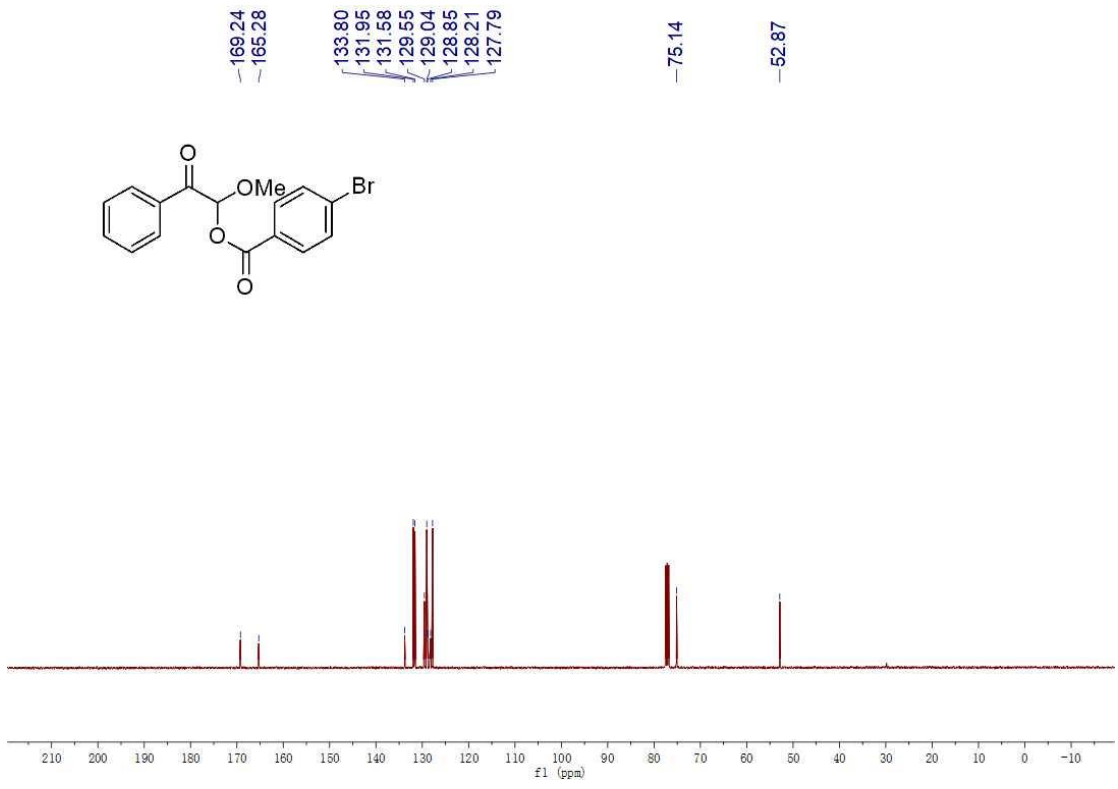
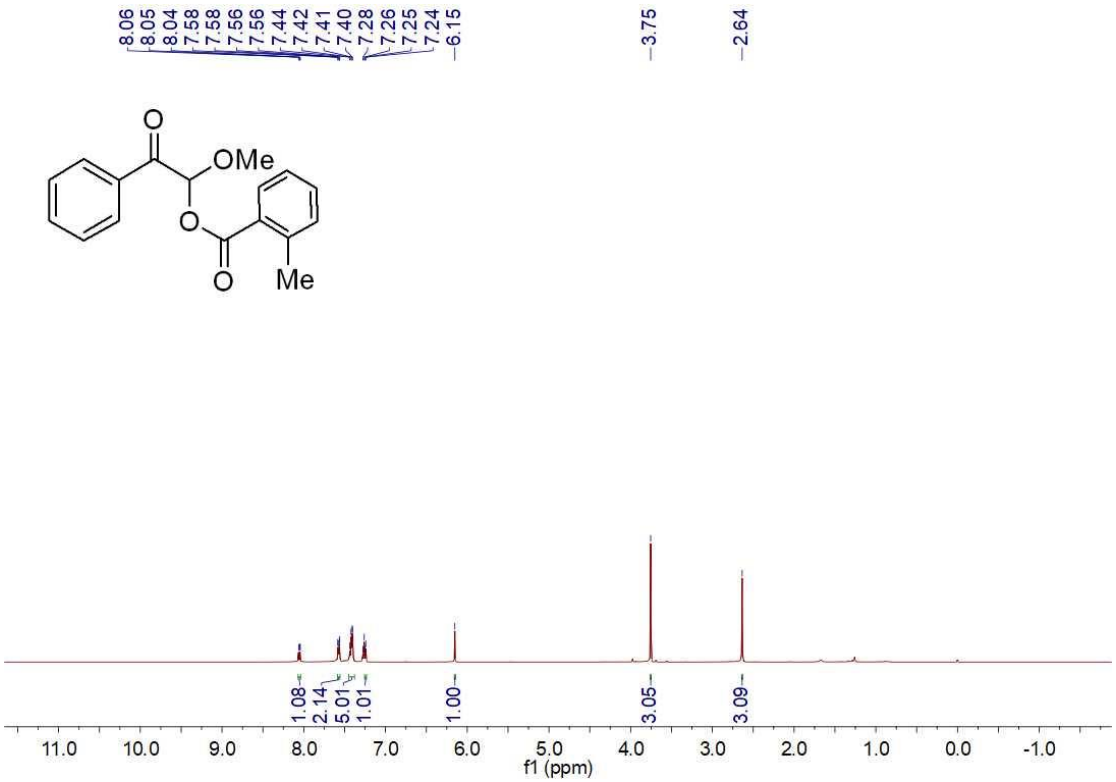
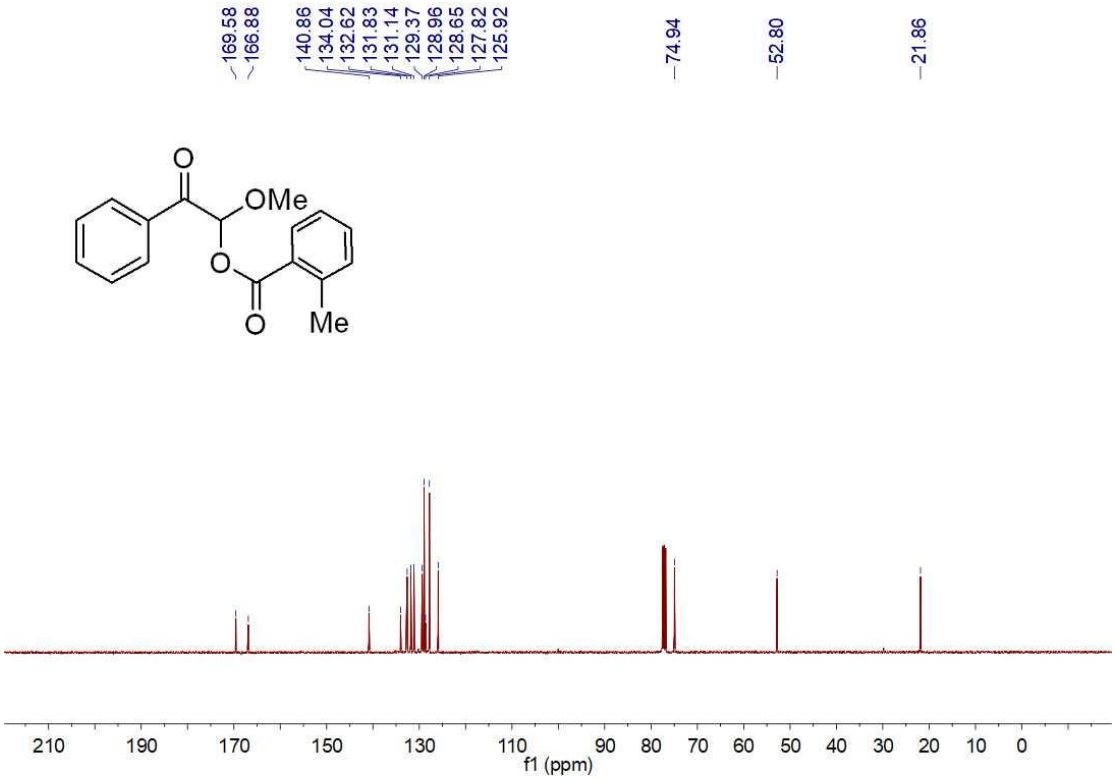


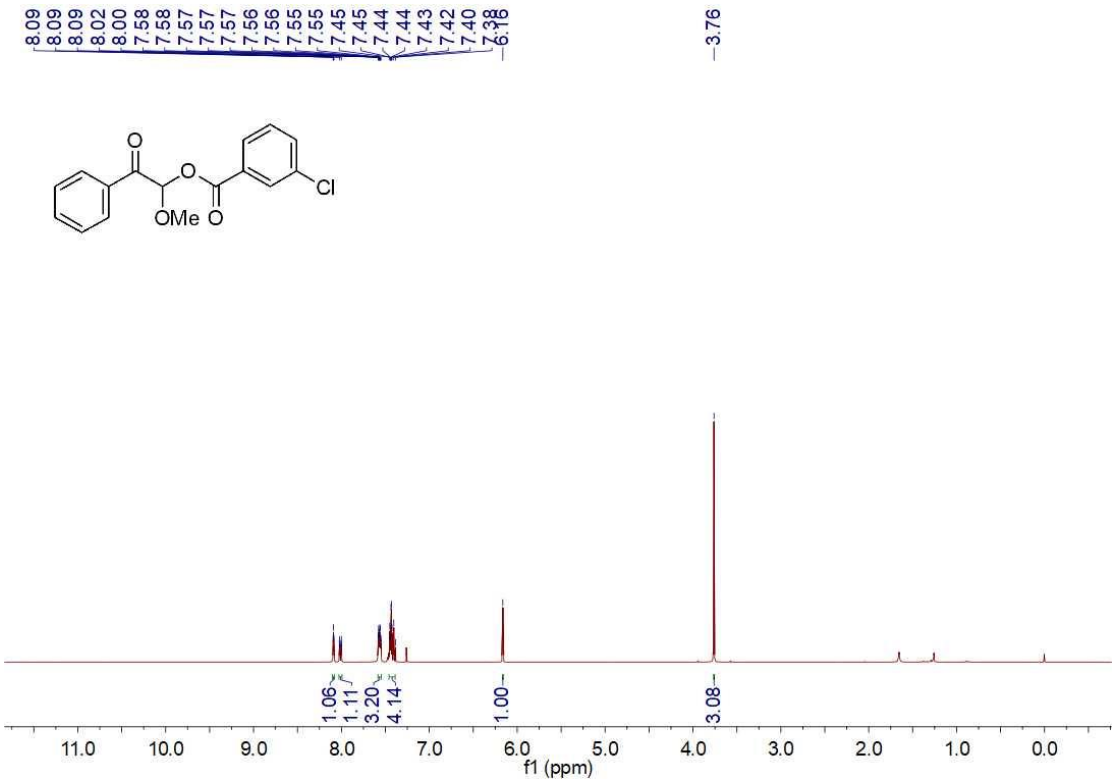
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3f**



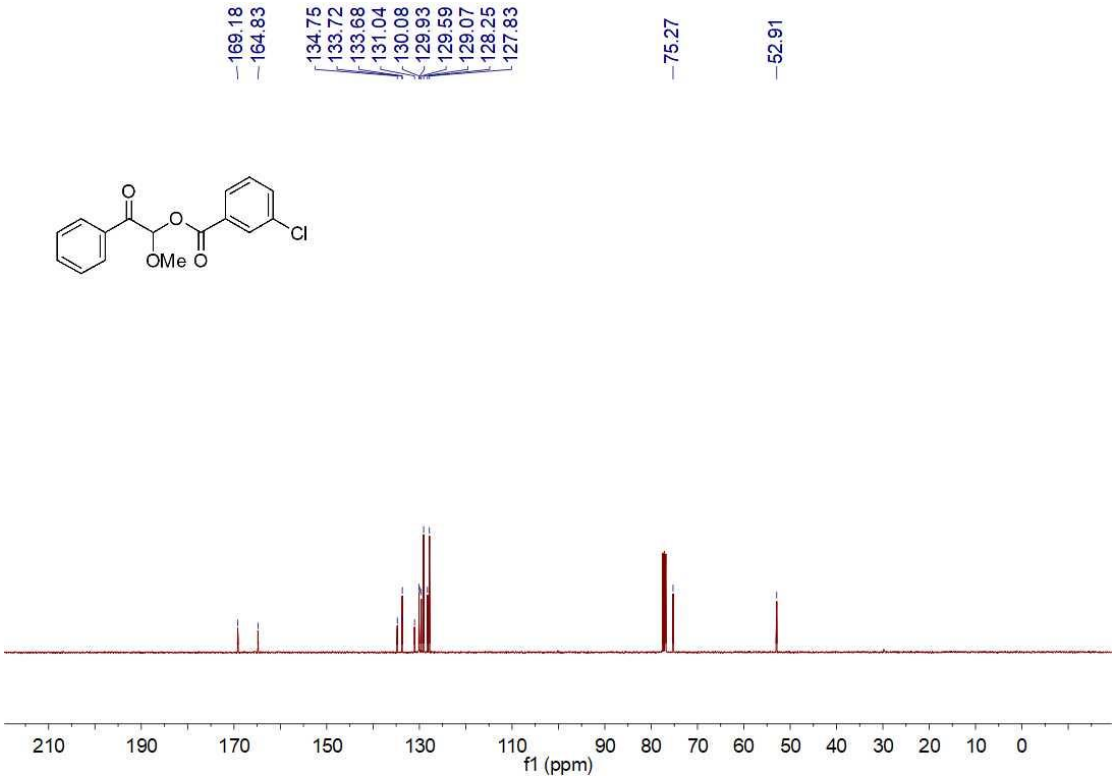
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3f**



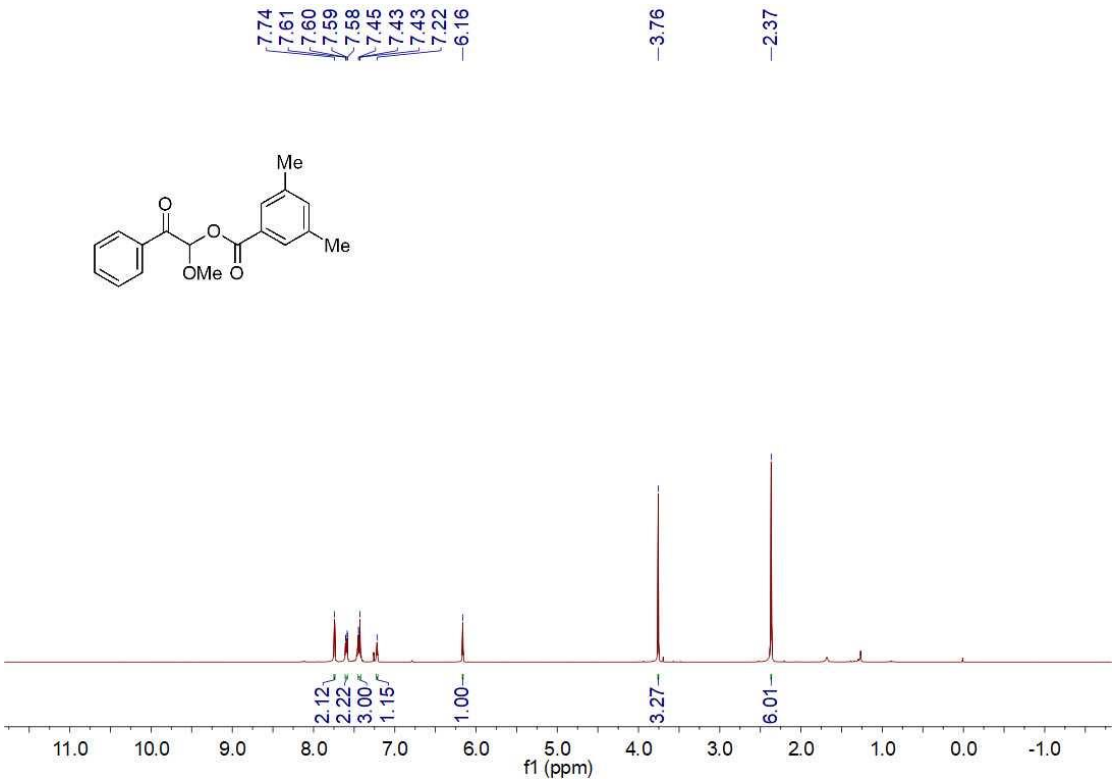
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3g**



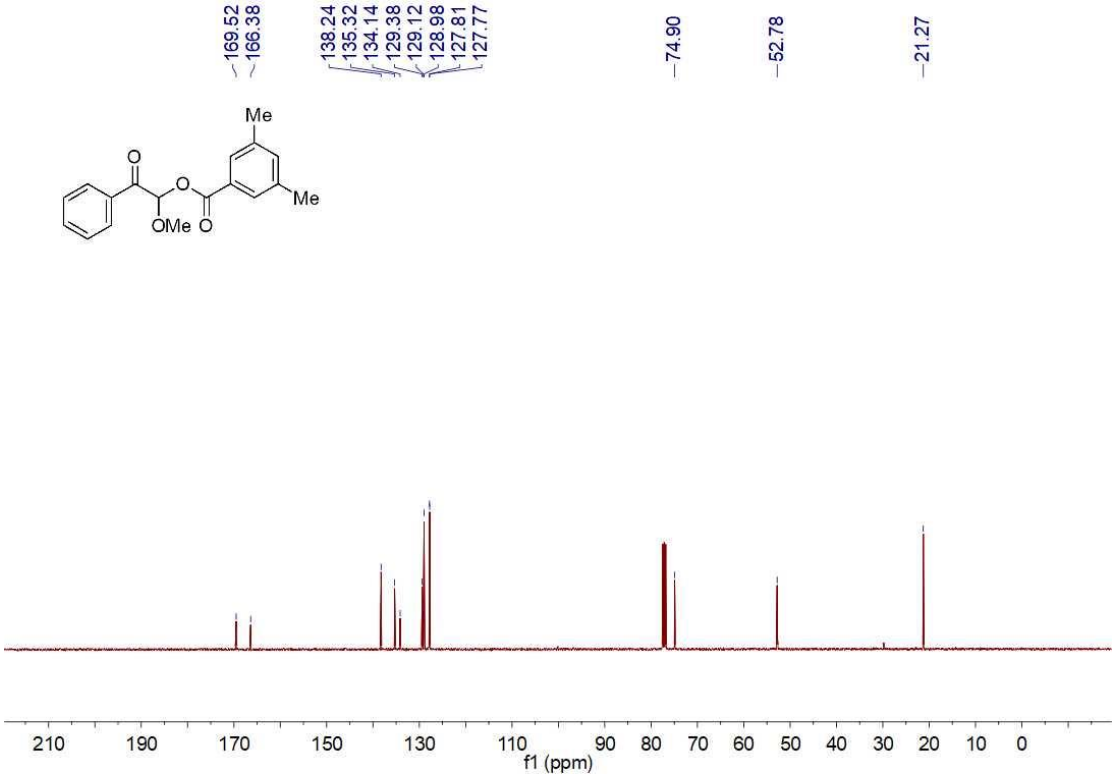
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3g**



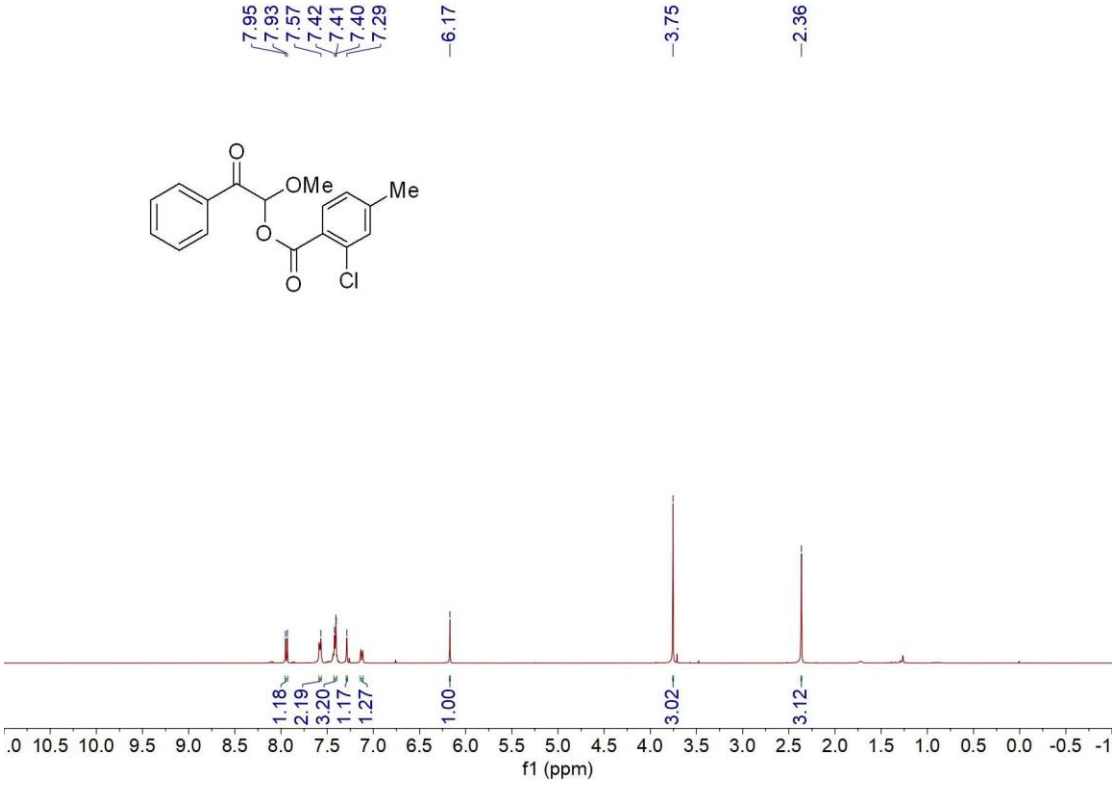
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3h**



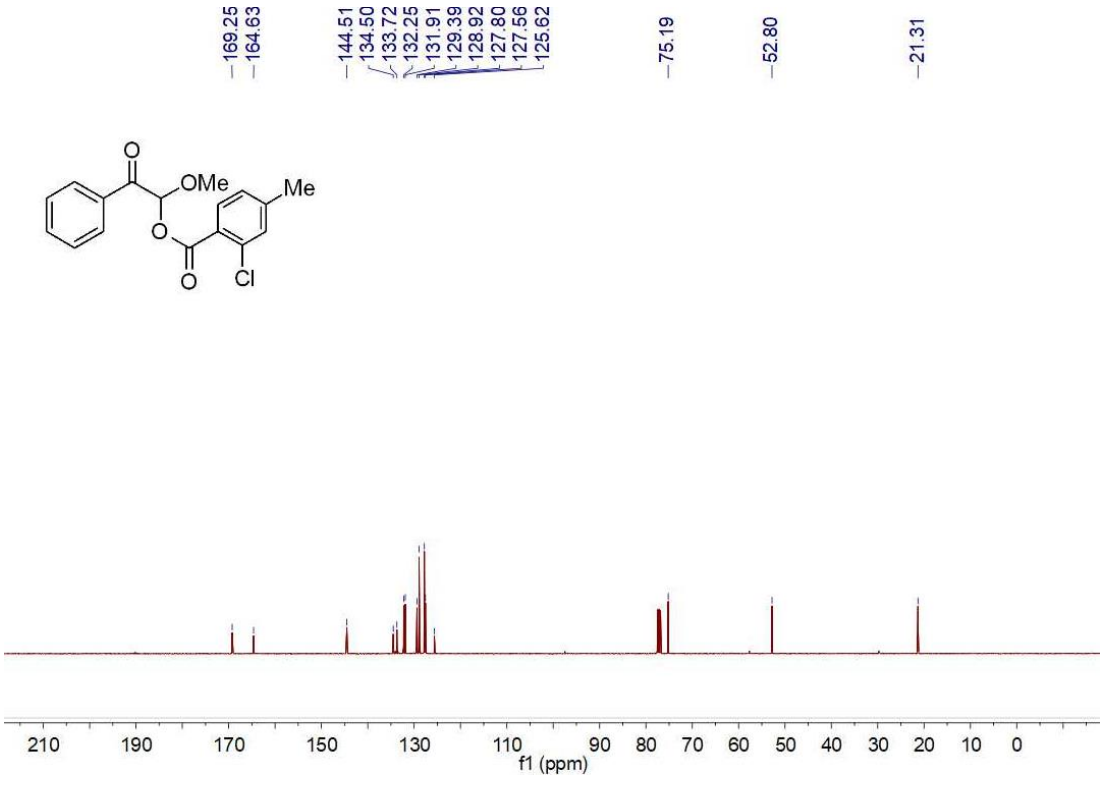
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3h**



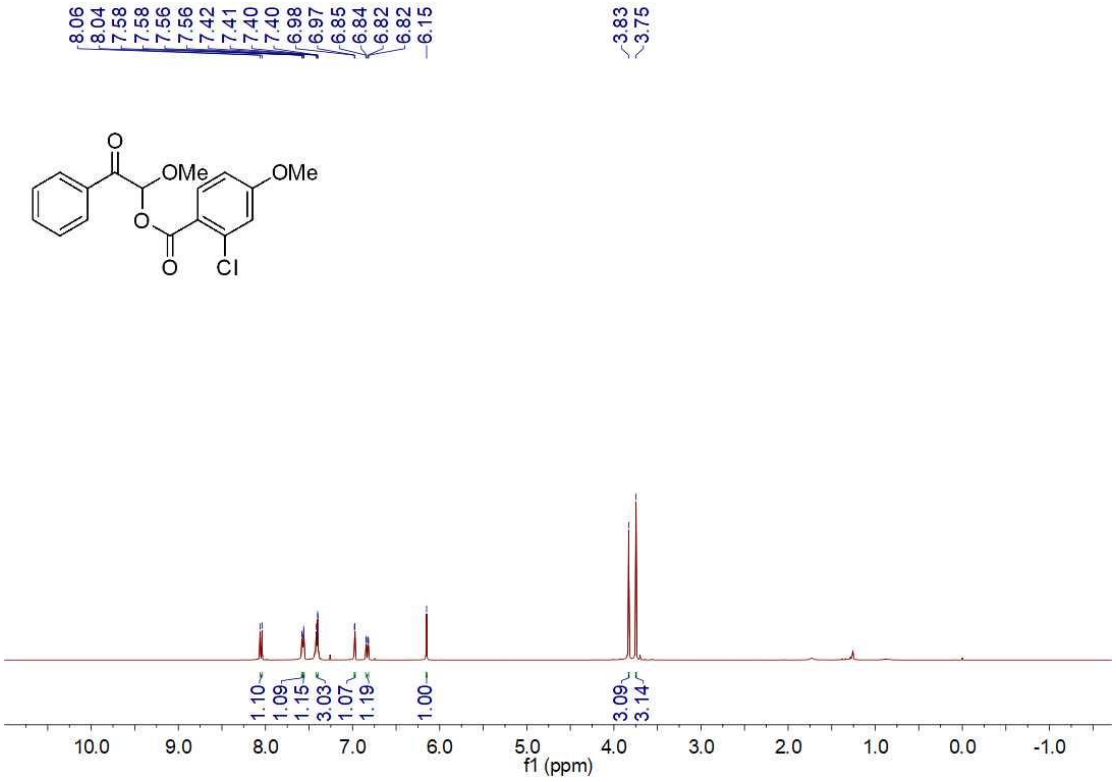
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3i**



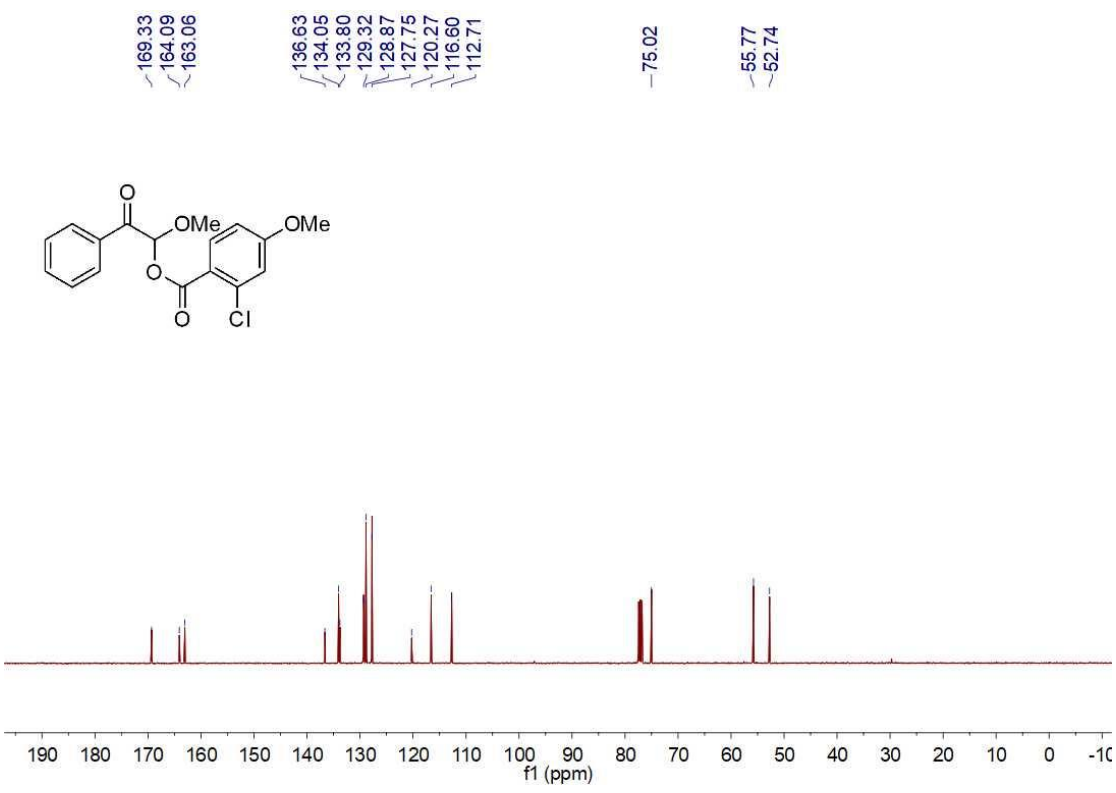
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3i**



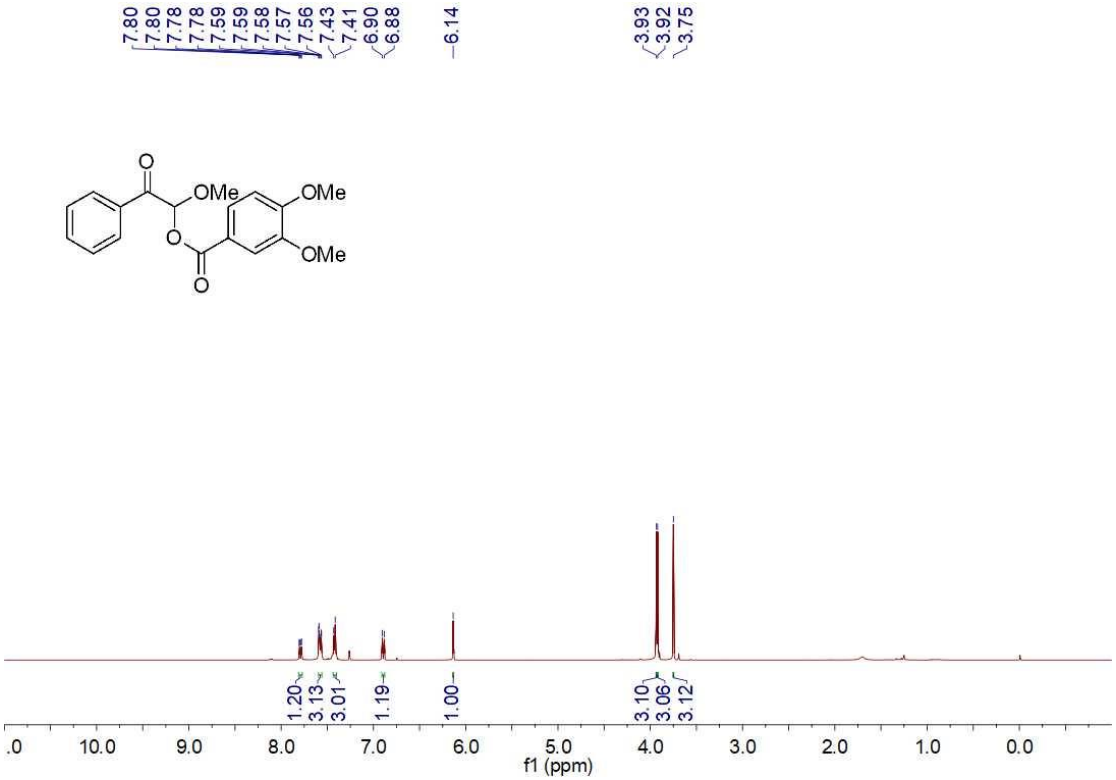
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3j**



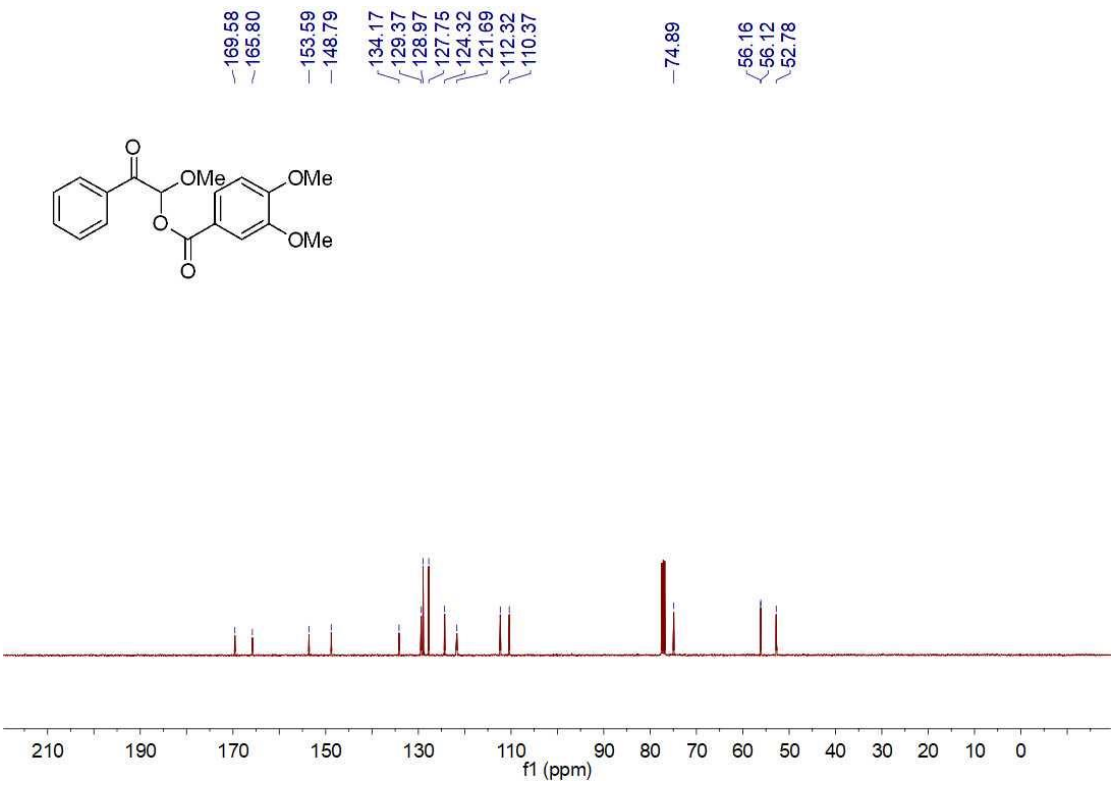
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3j**



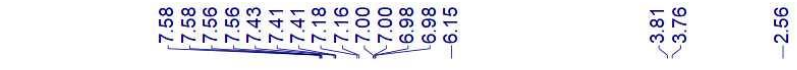
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3k**

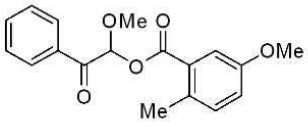


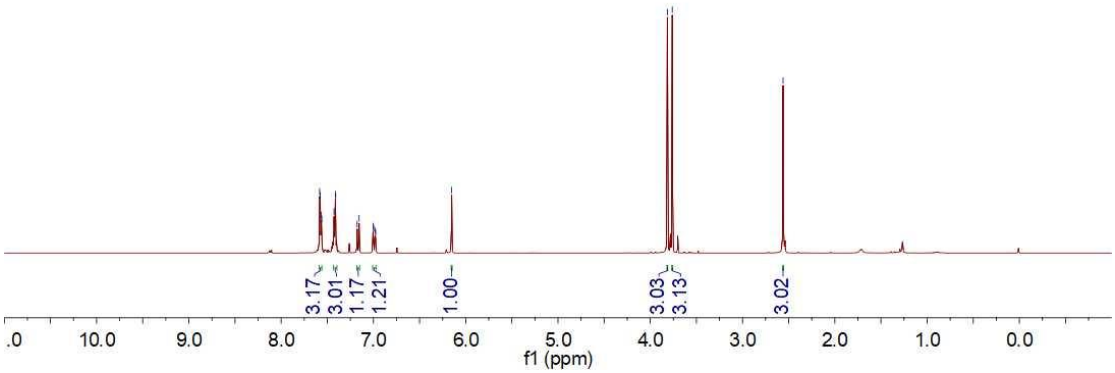
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3k**



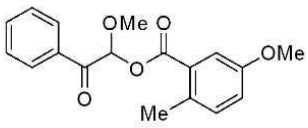
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3l**

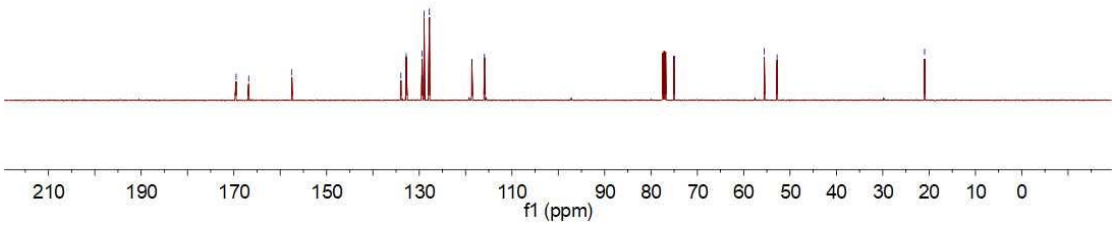




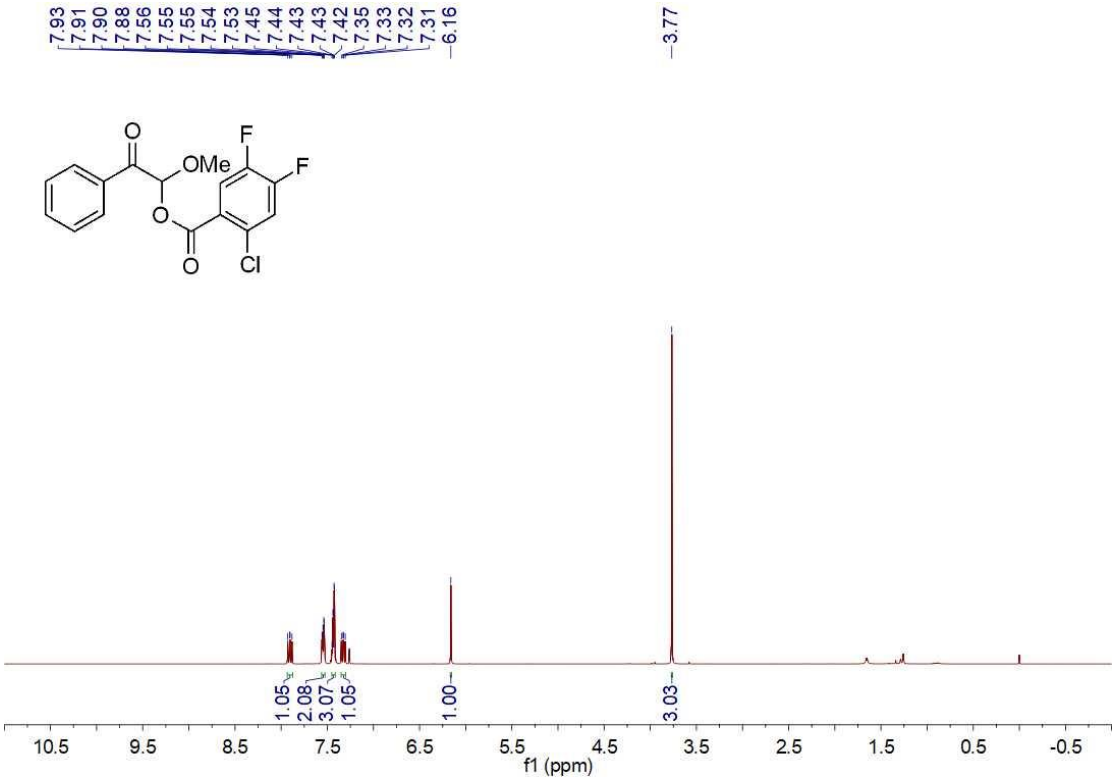


^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3l**

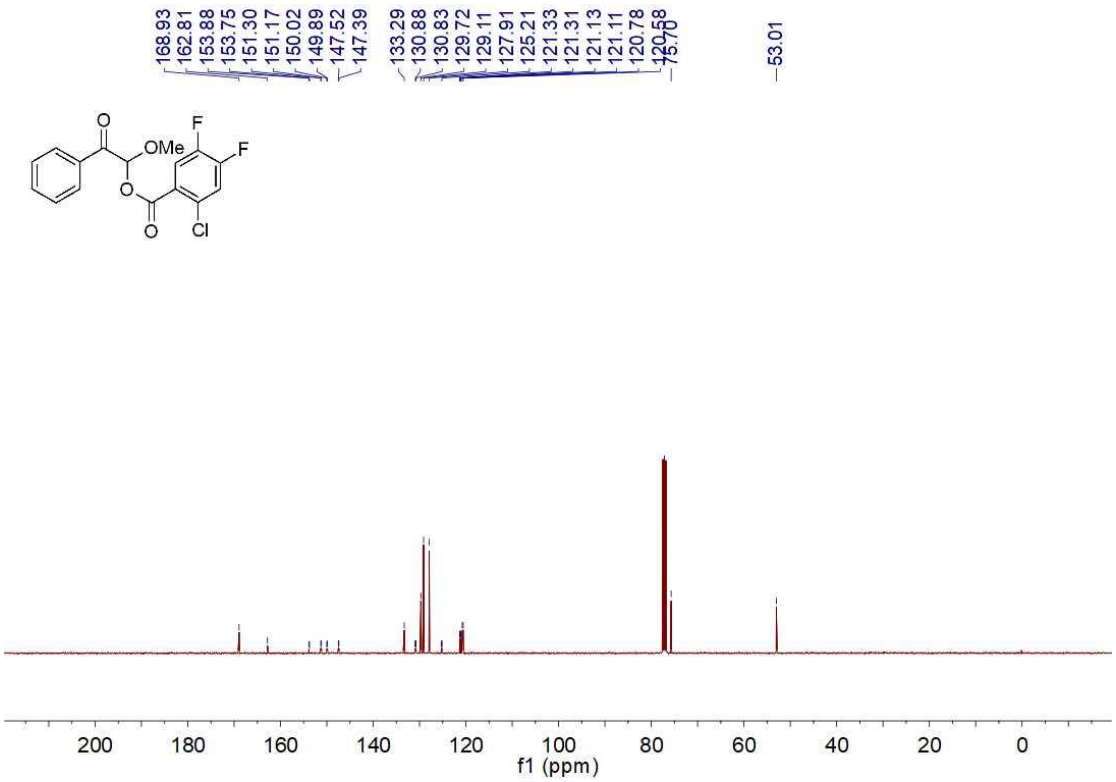




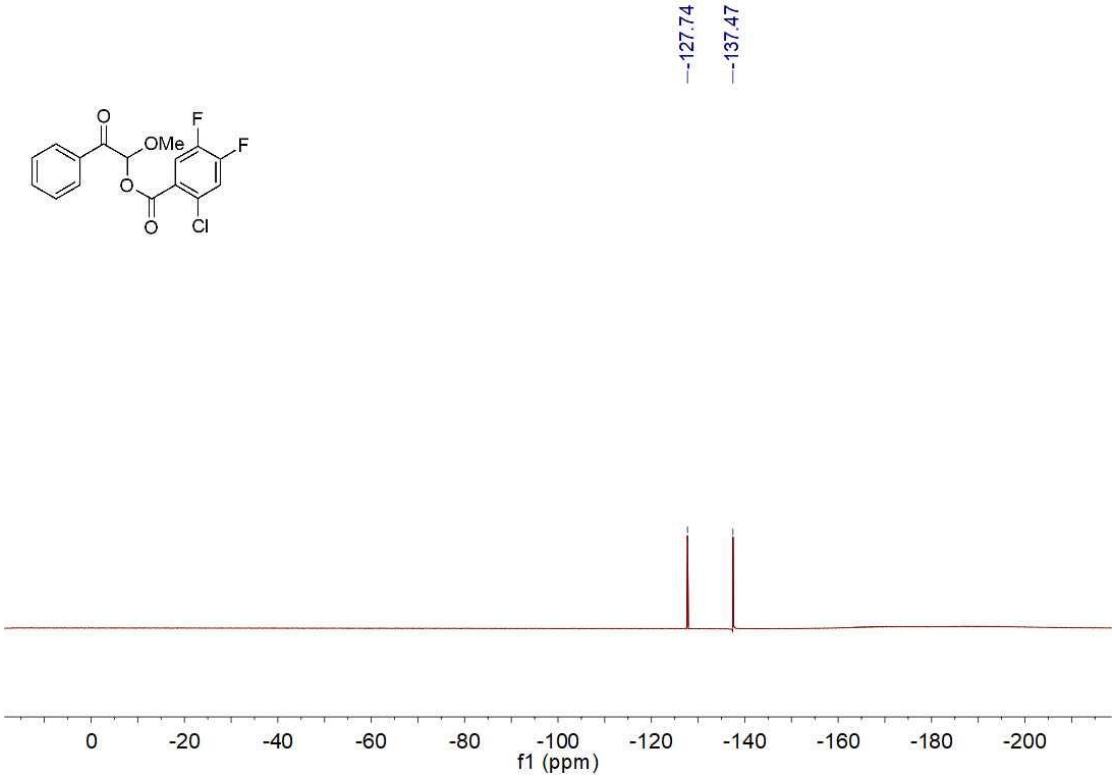
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3m**



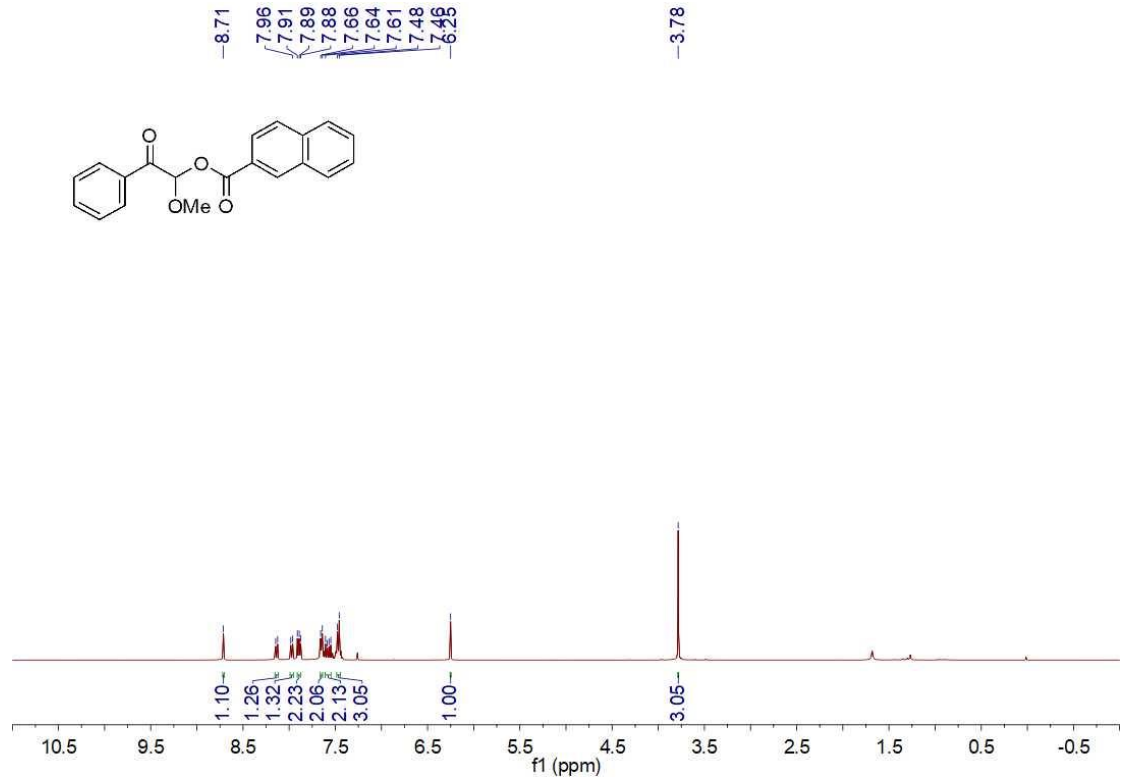
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3m**



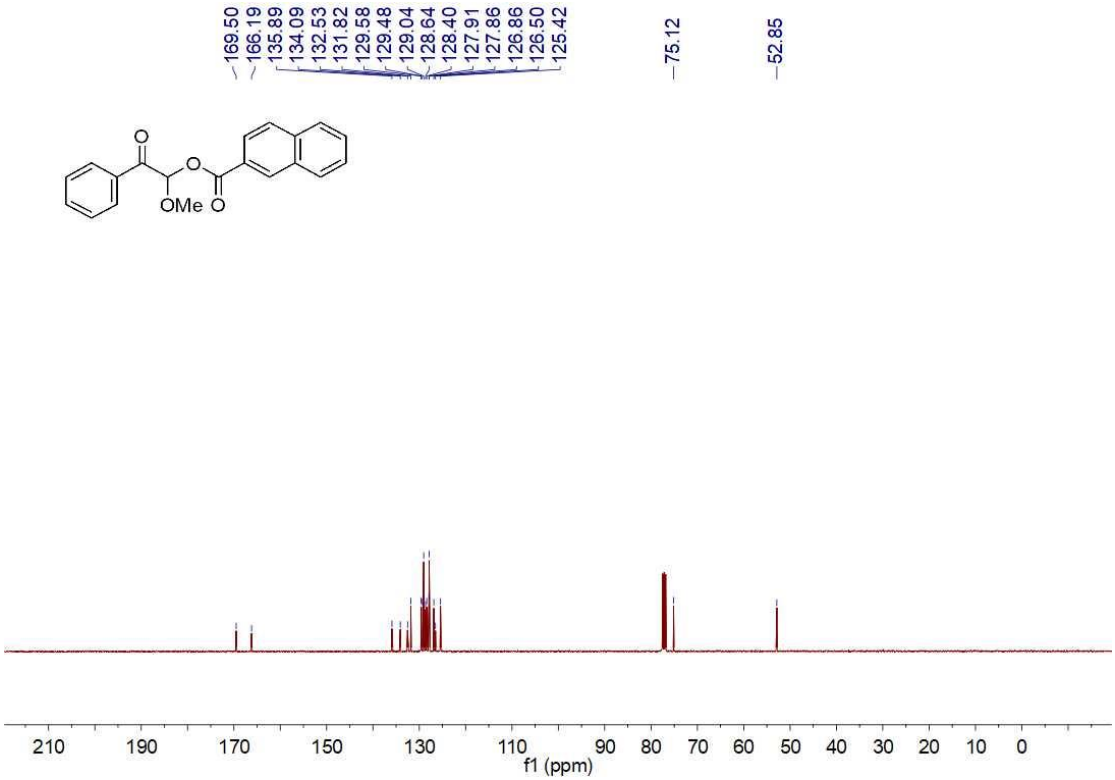
^{19}F NMR (376 MHz, $CDCl_3$) Spectra of **3m**



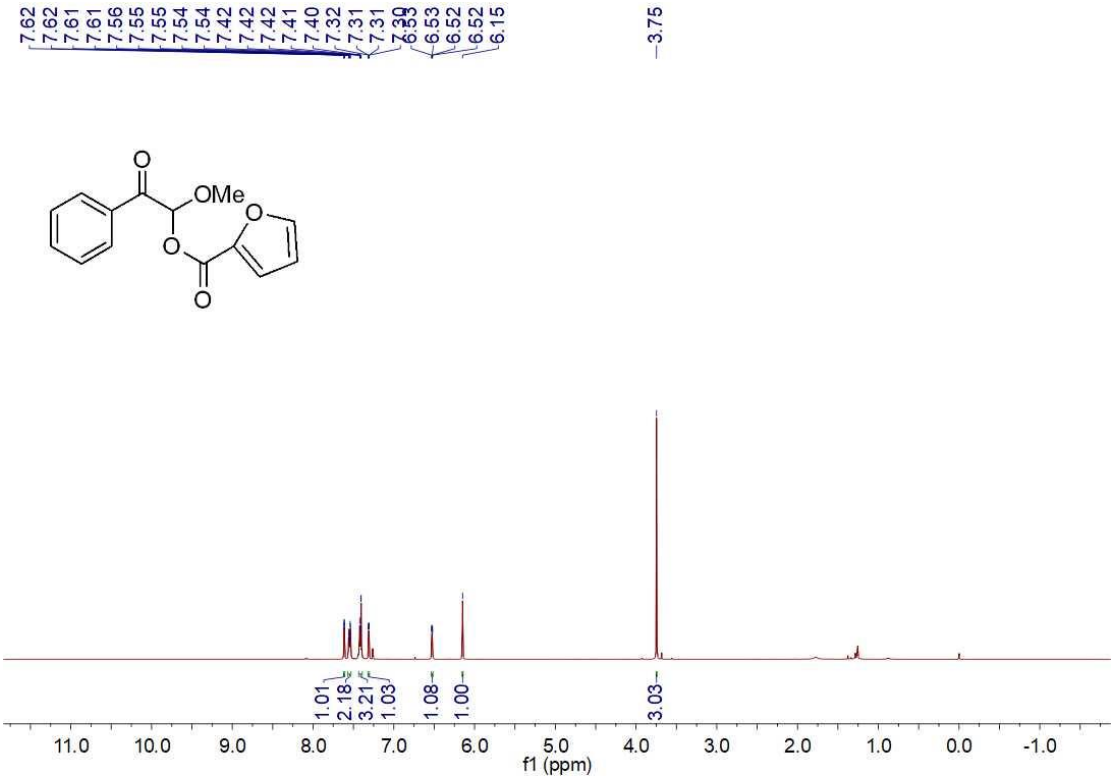
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3n**



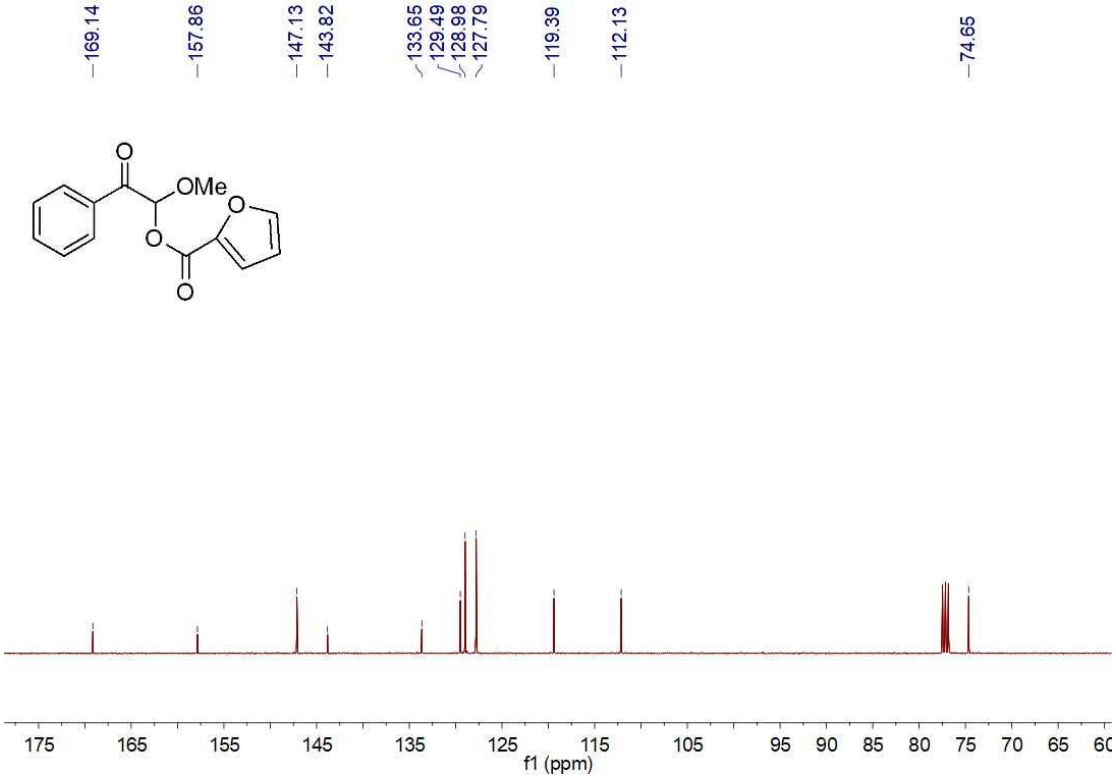
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3n**



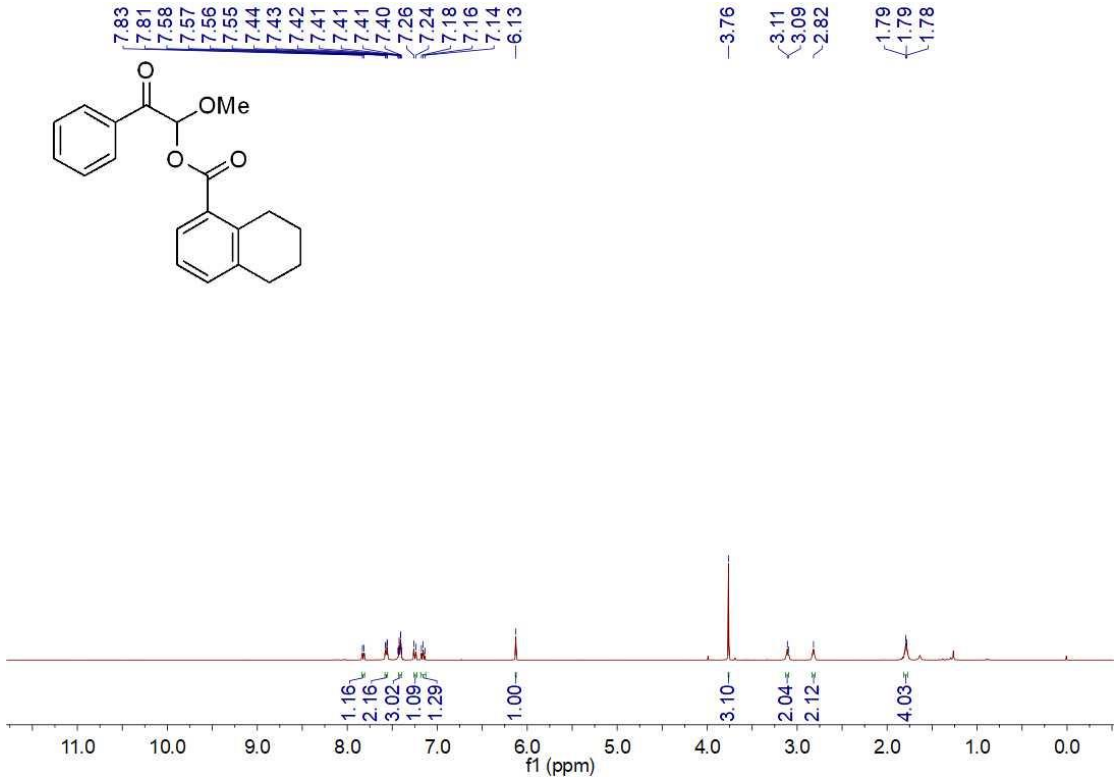
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3o**



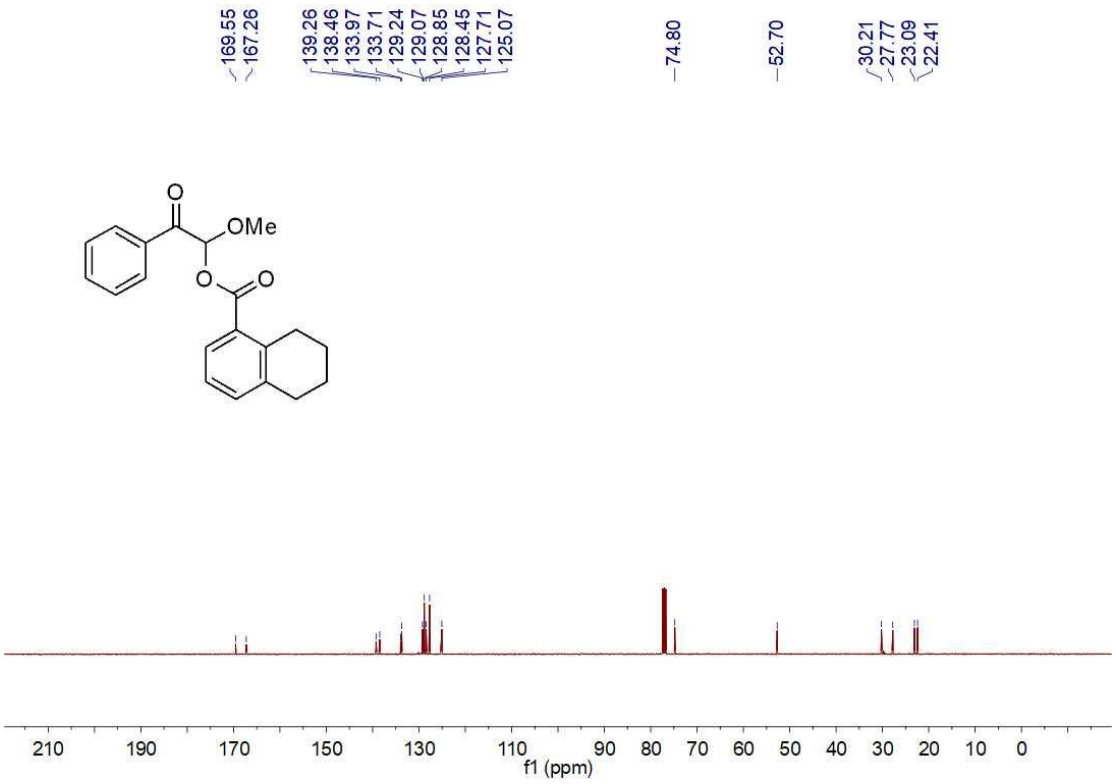
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3o**



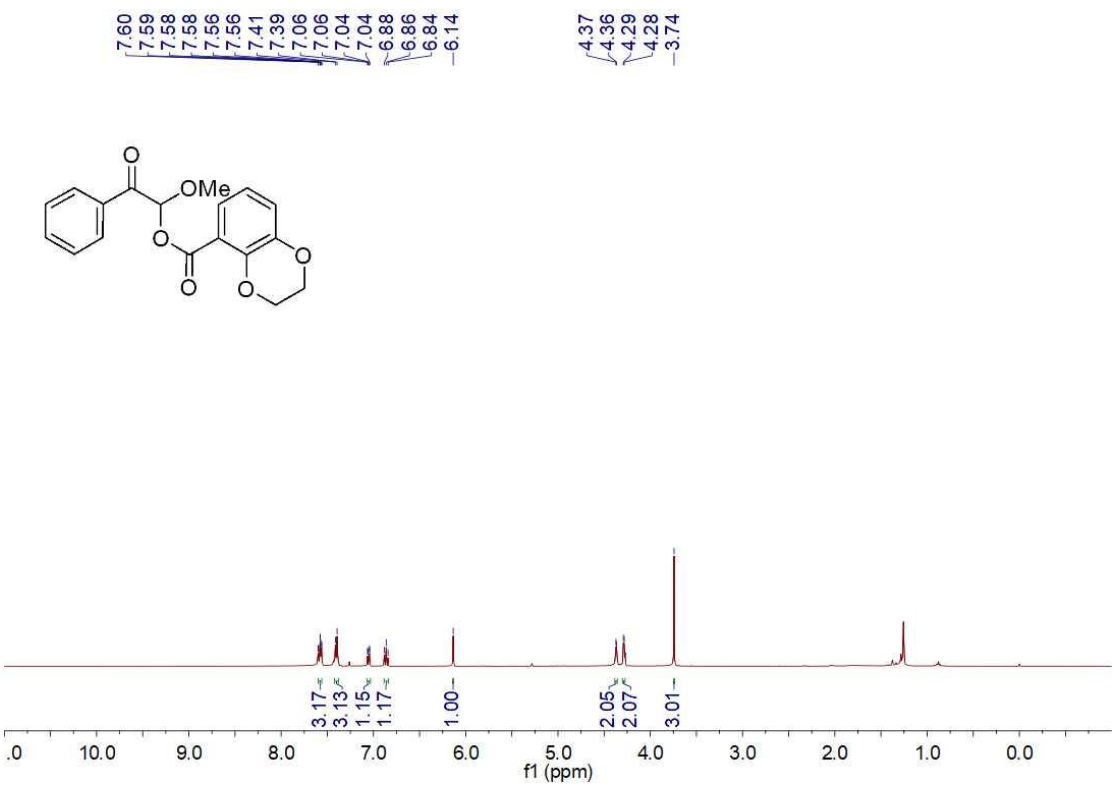
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3p**



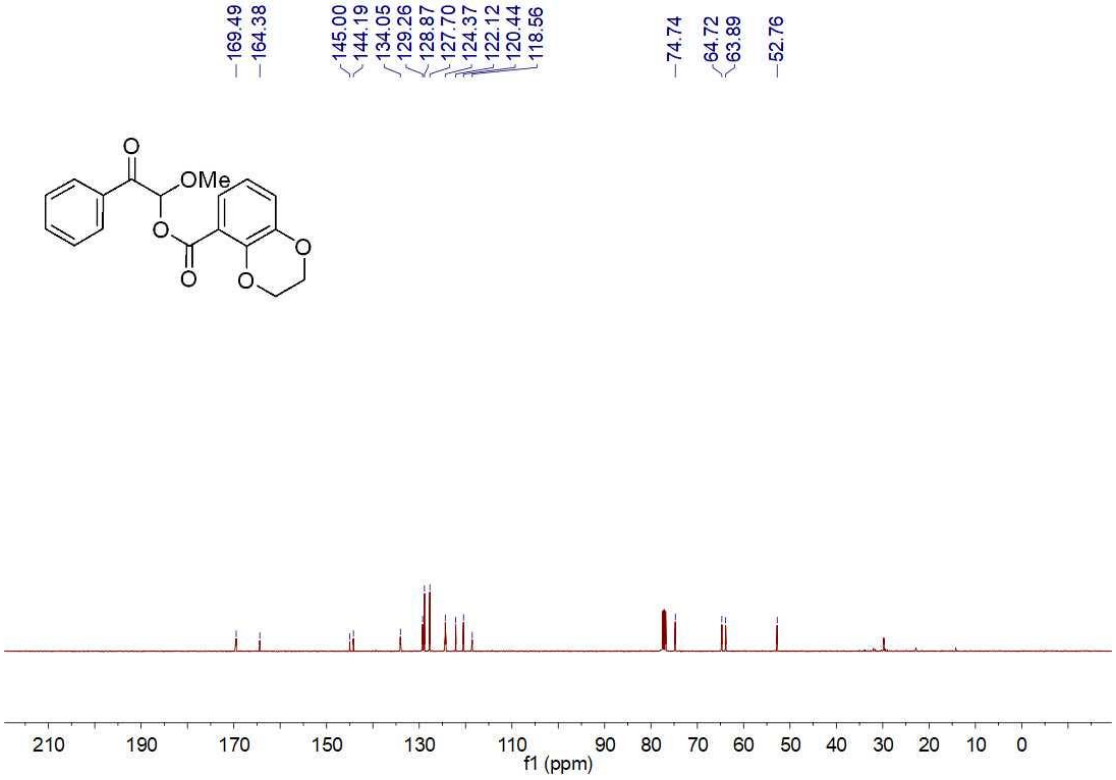
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3p**



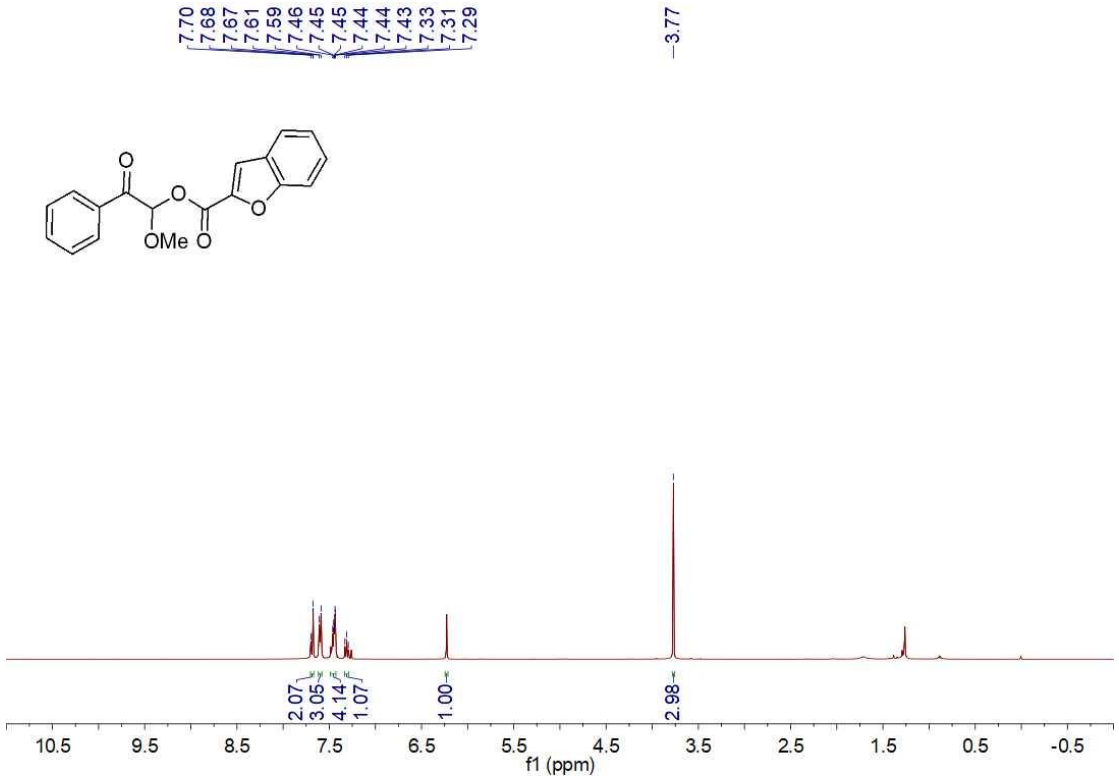
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3q**



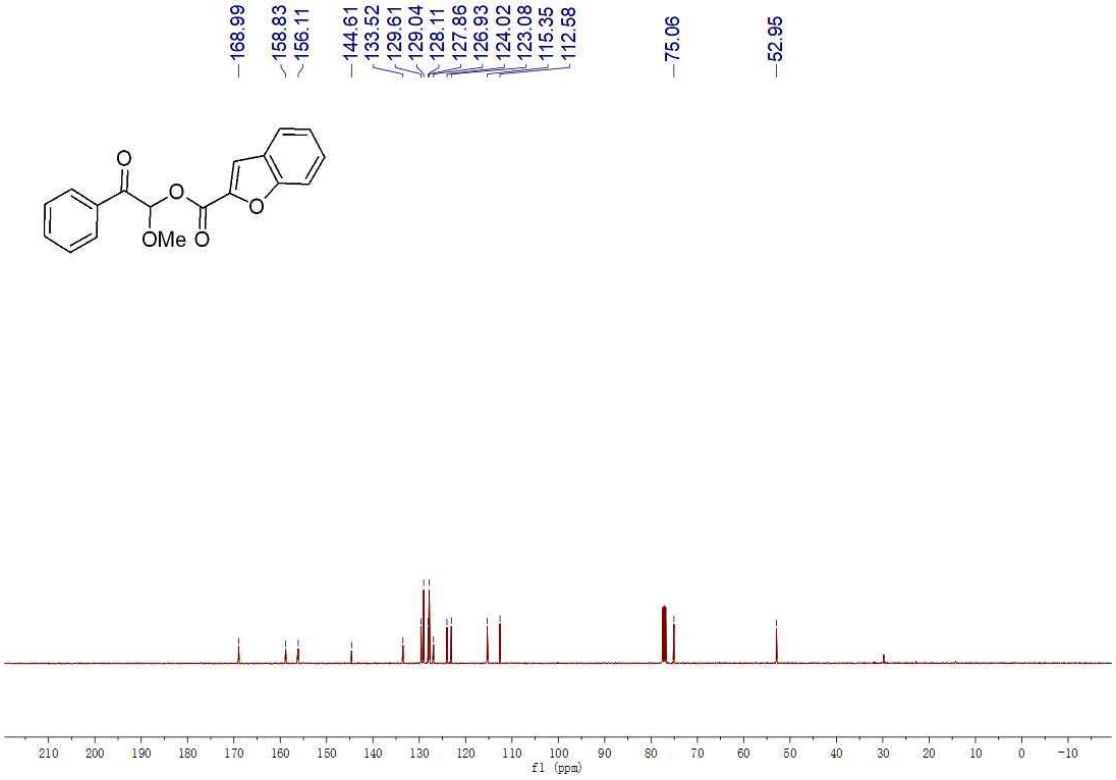
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3q**



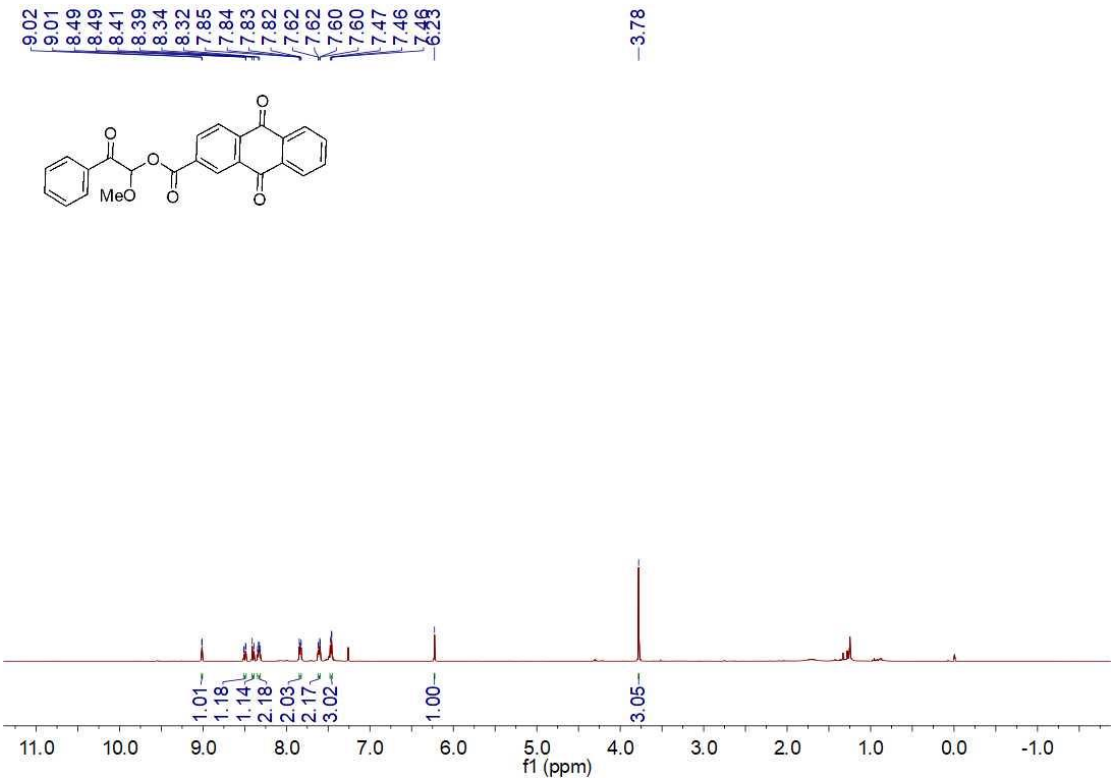
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3r**



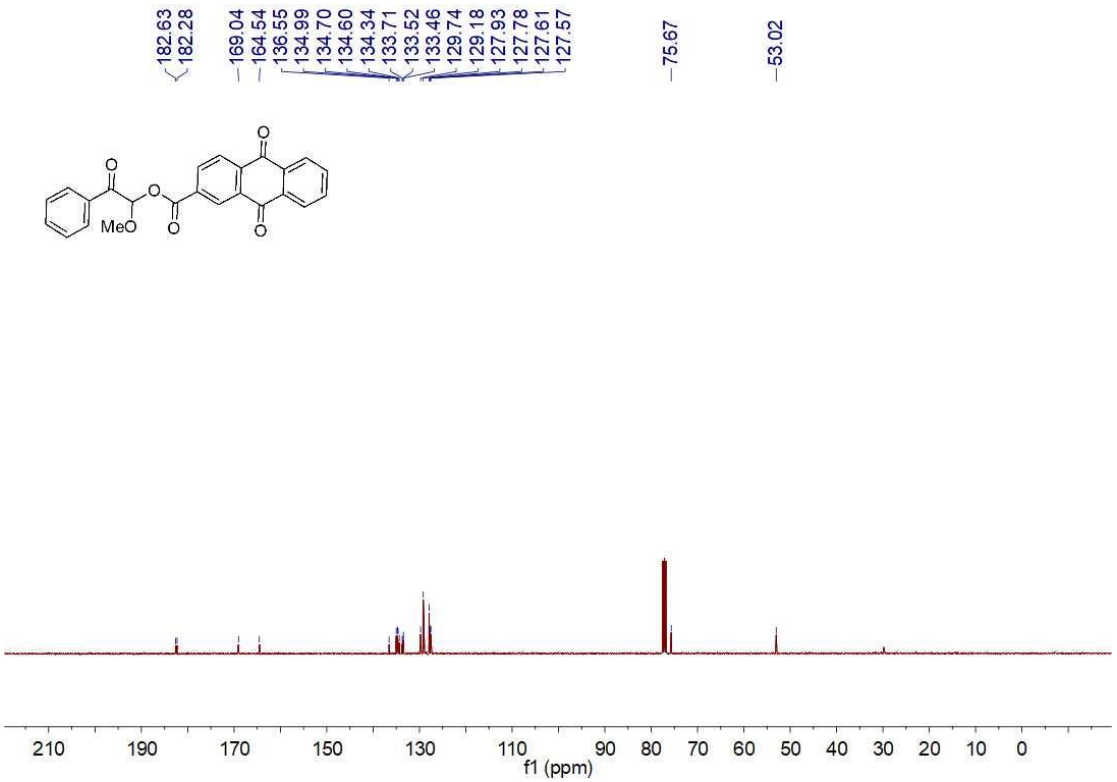
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3r**



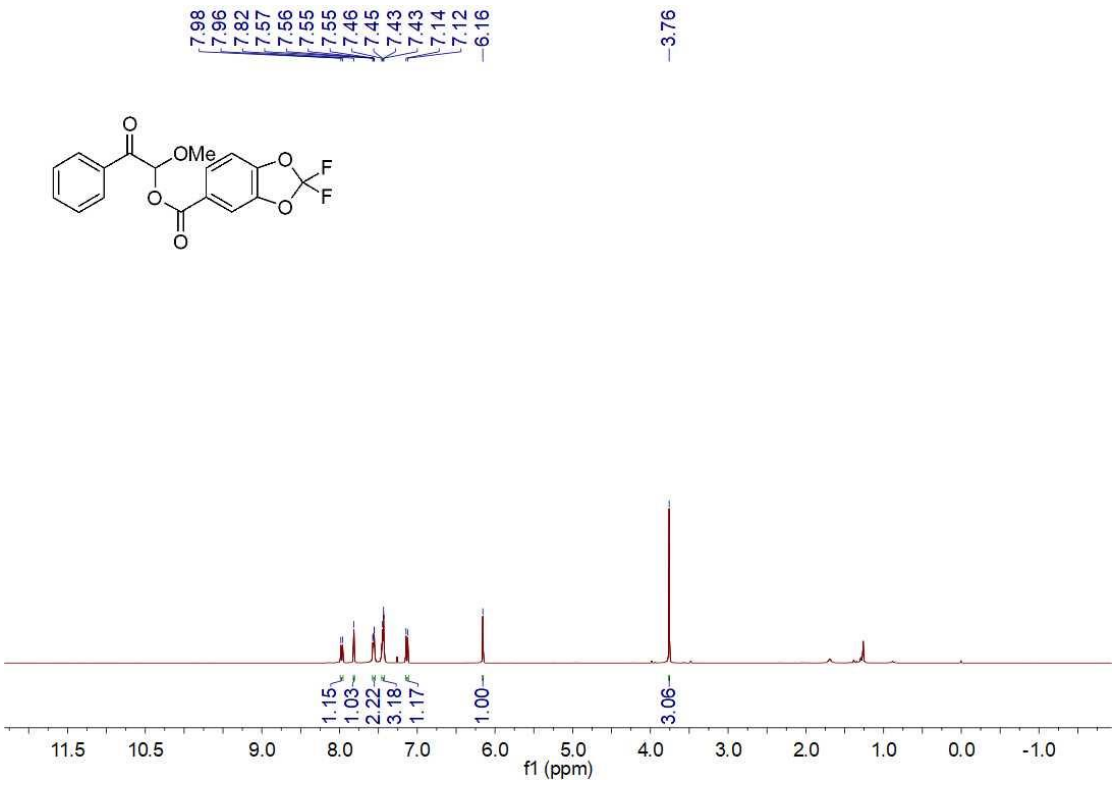
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3s**



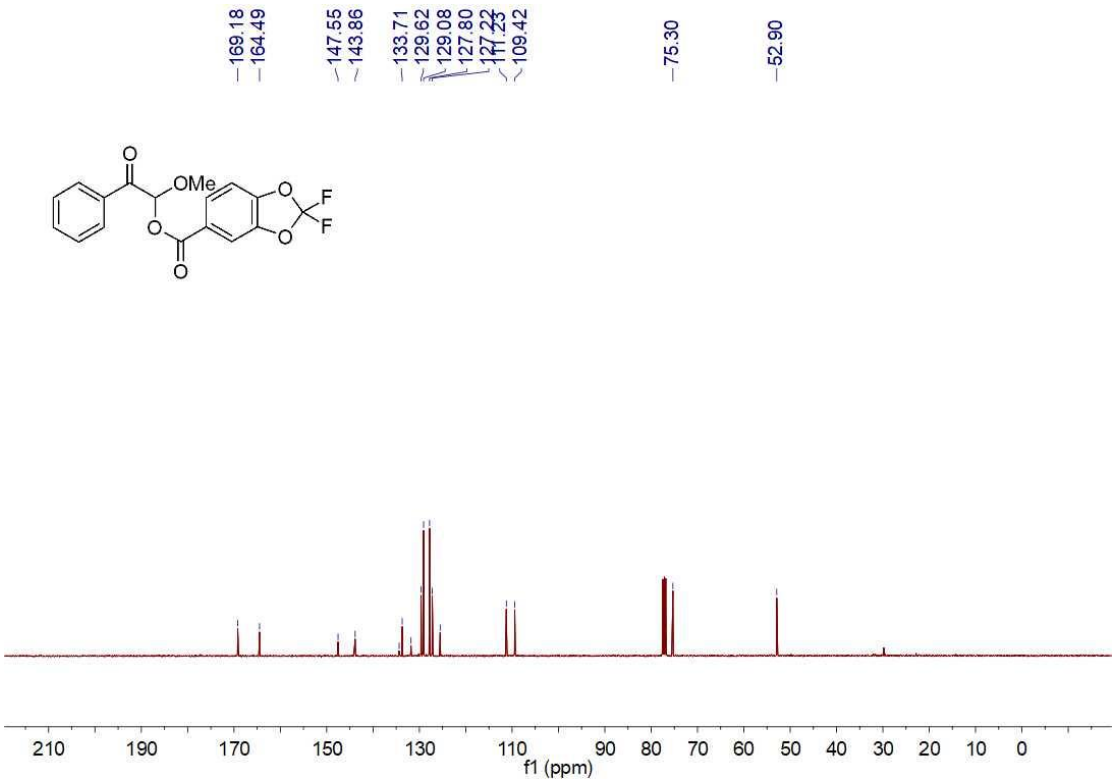
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3s**



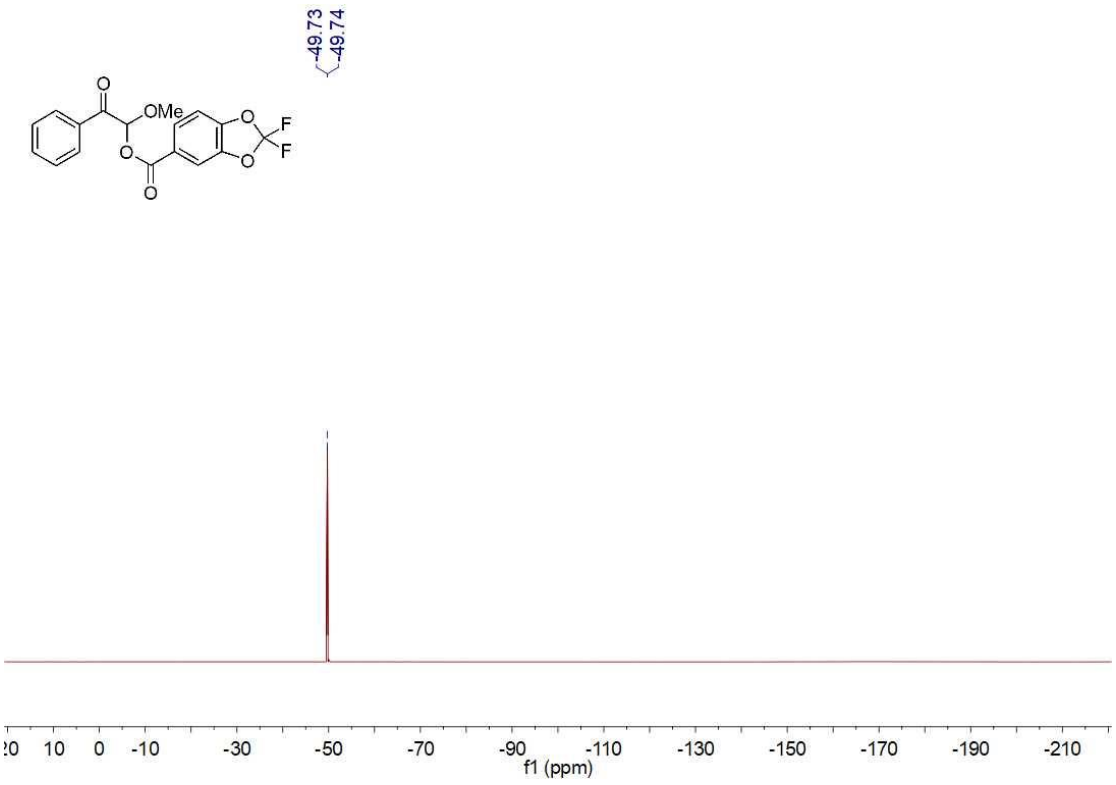
^{1}H NMR (400 MHz, CDCl3) Spectra of **3t**



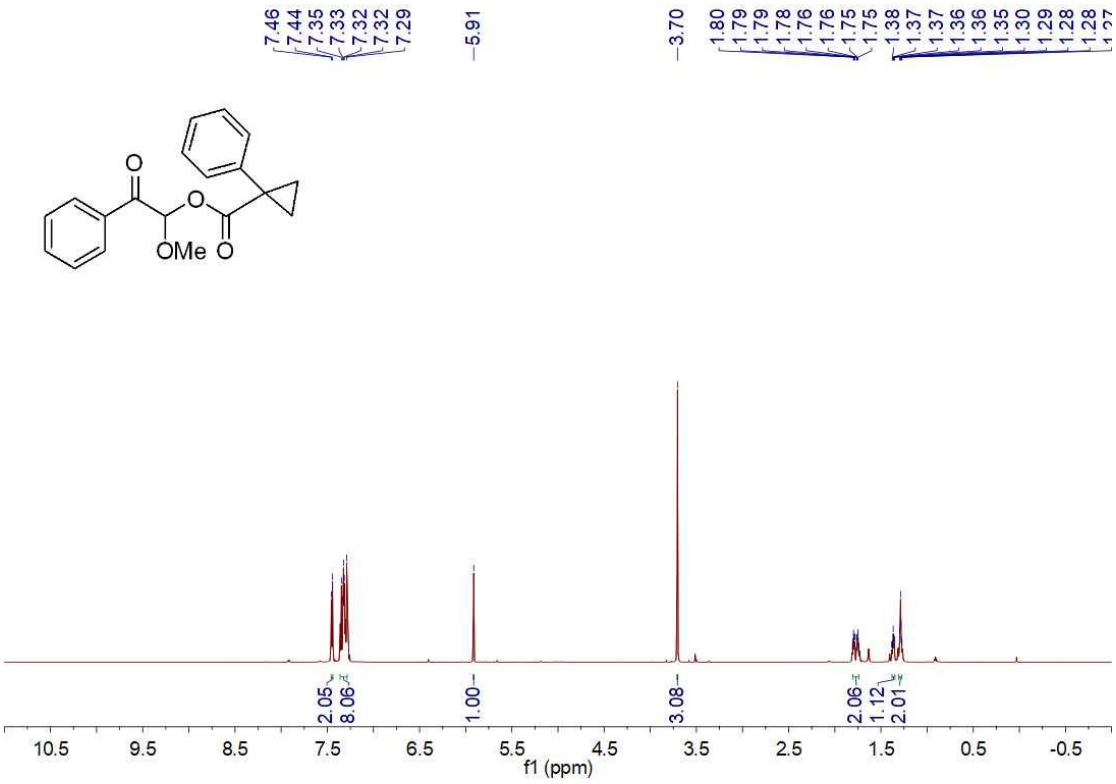
^{13}C NMR (101 MHz, CDCl3) Spectra of **3t**



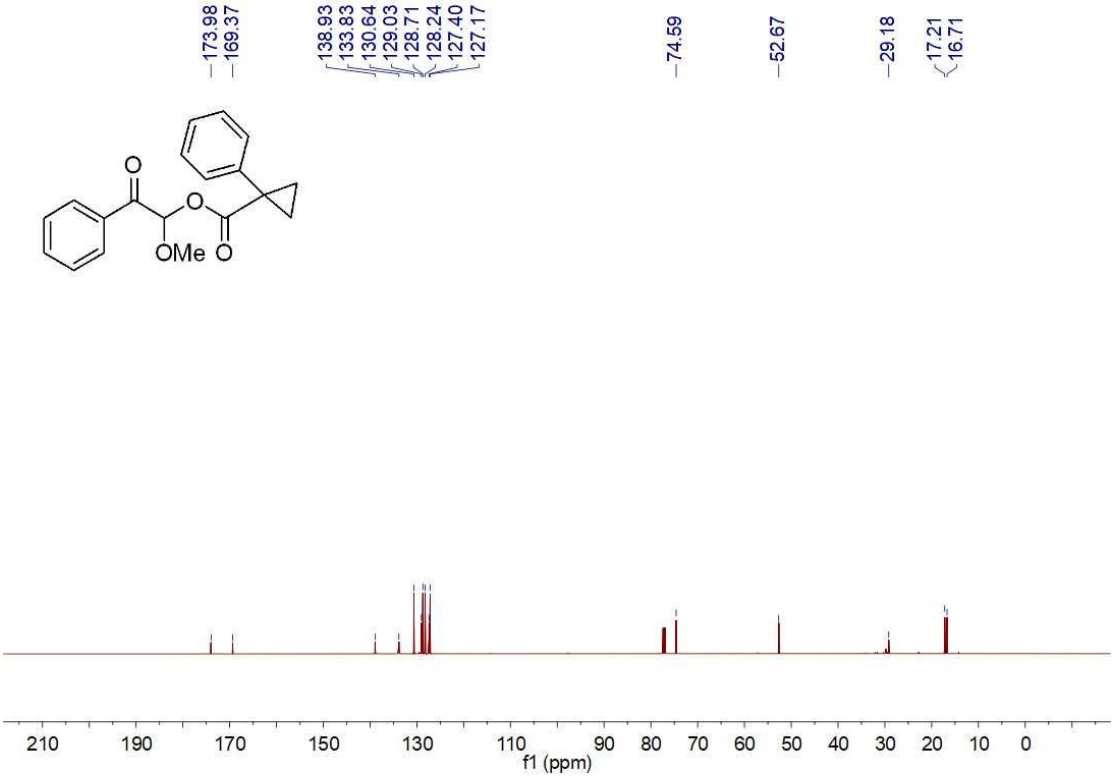
^{9}F NMR (377 MHz, $CDCl_3$) Spectra of **3t**



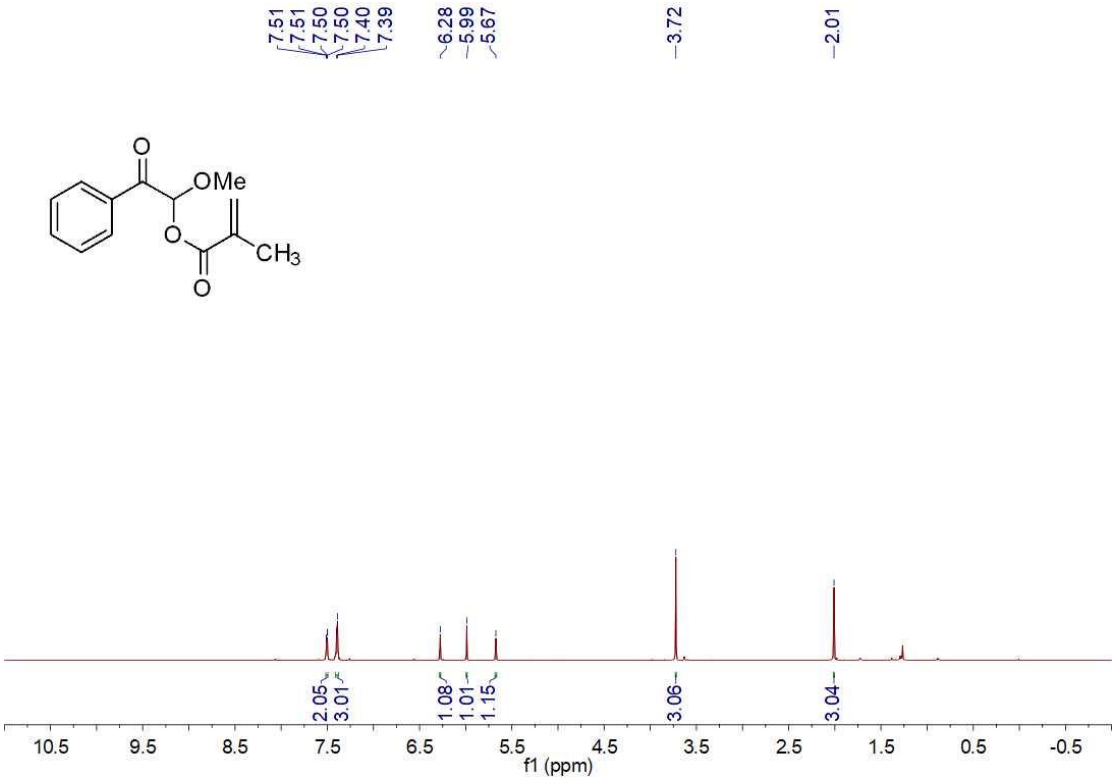
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3x**



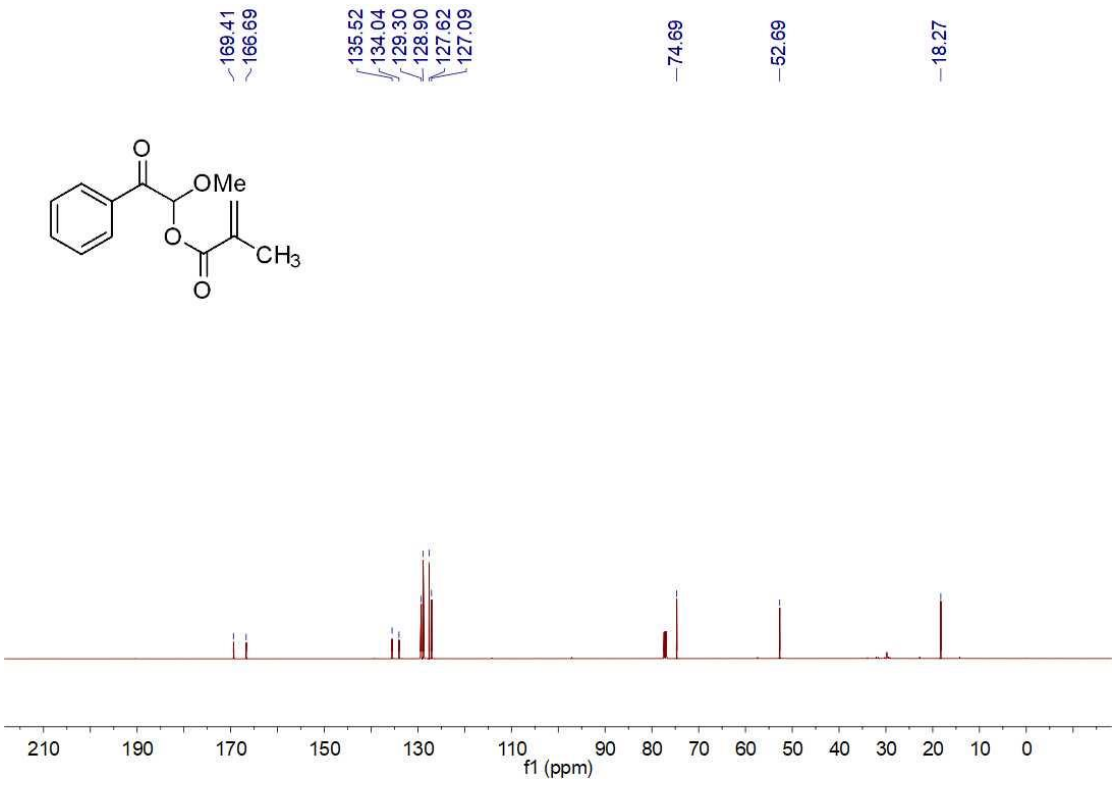
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3x**



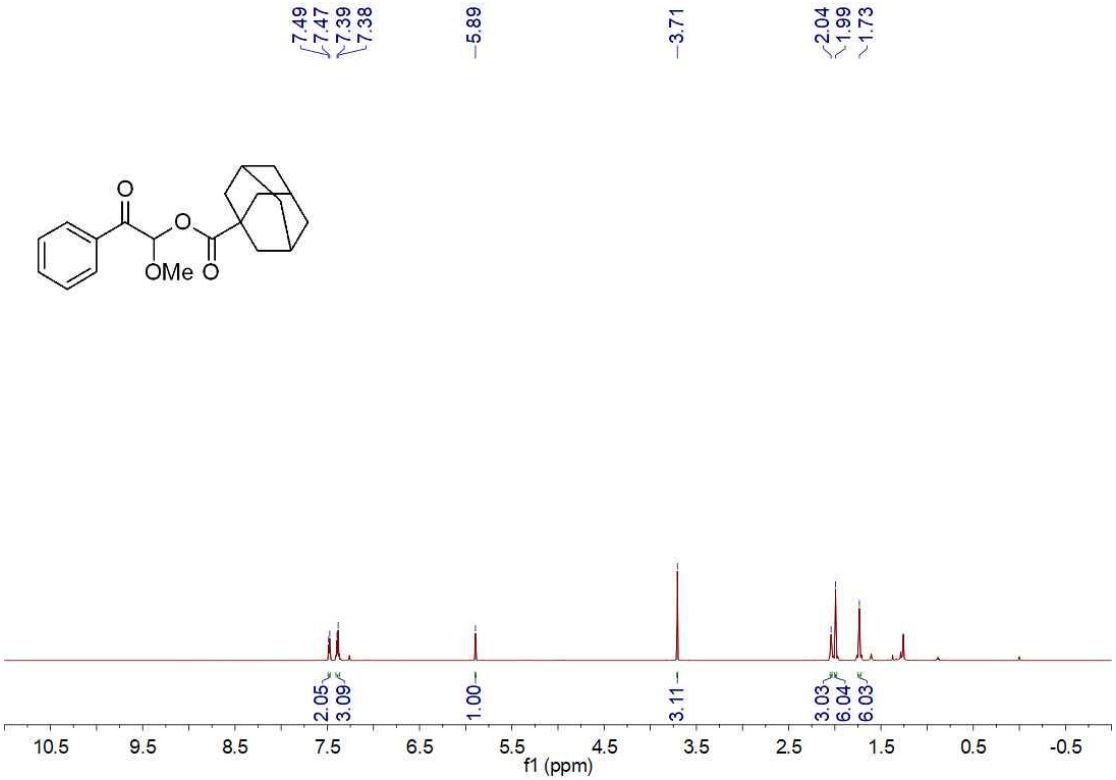
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3y**



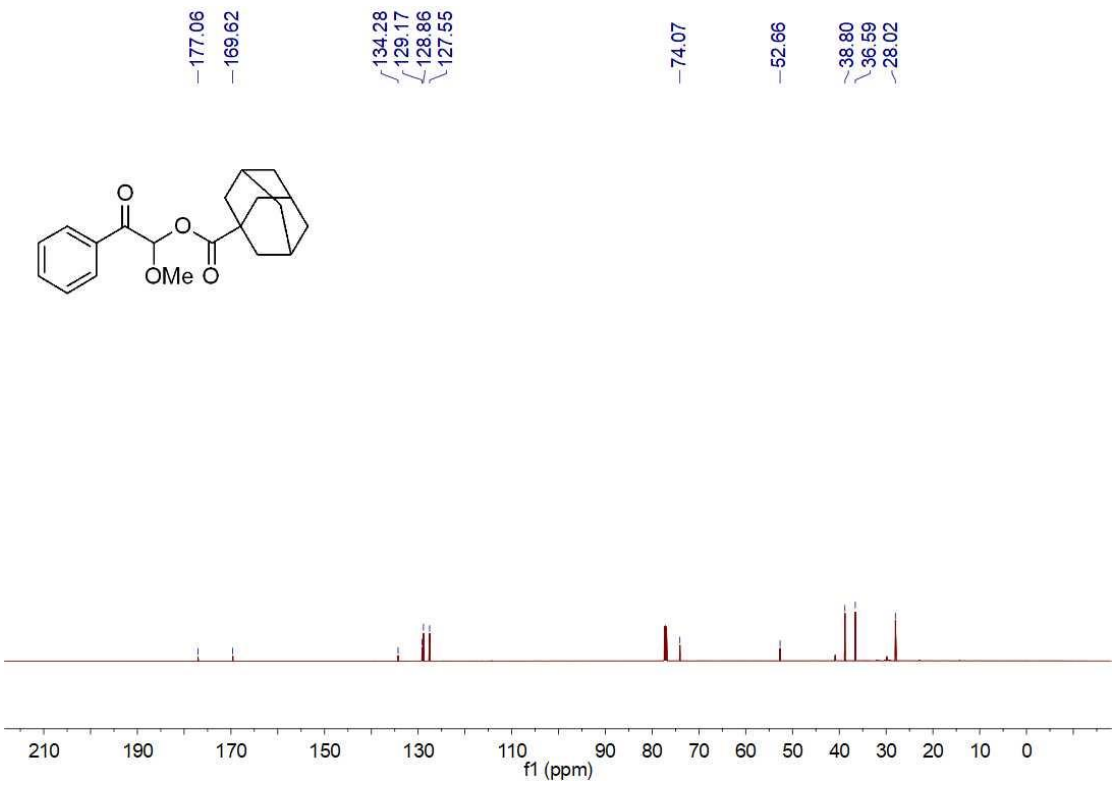
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3y**



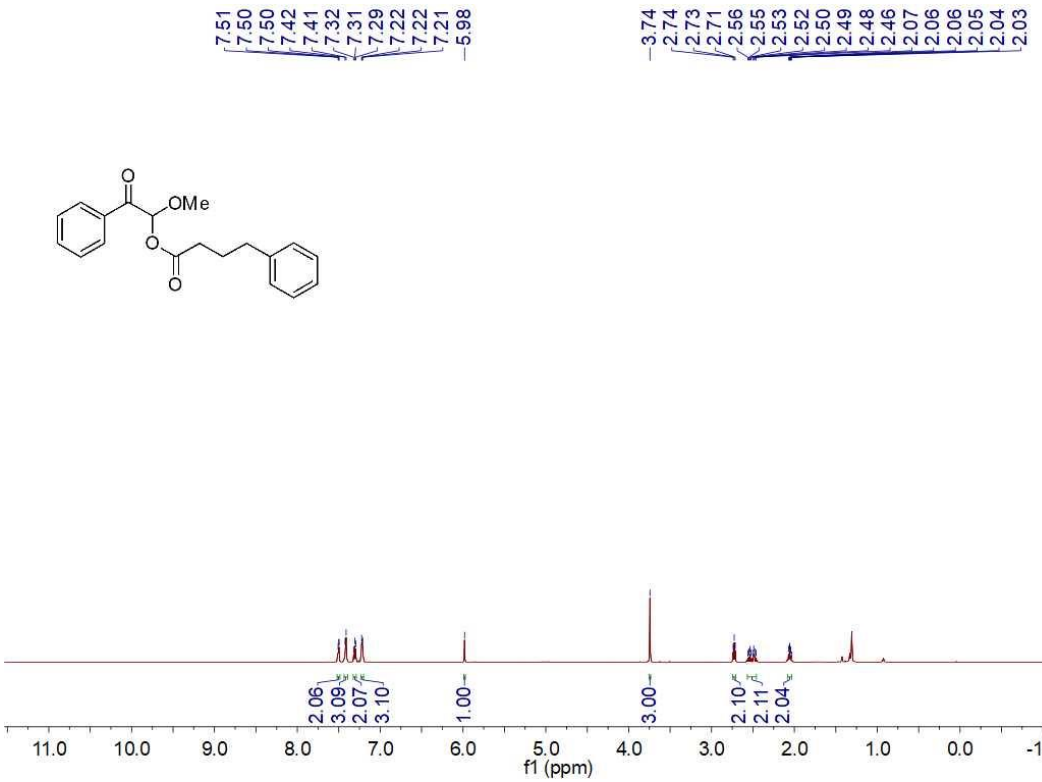
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3z**



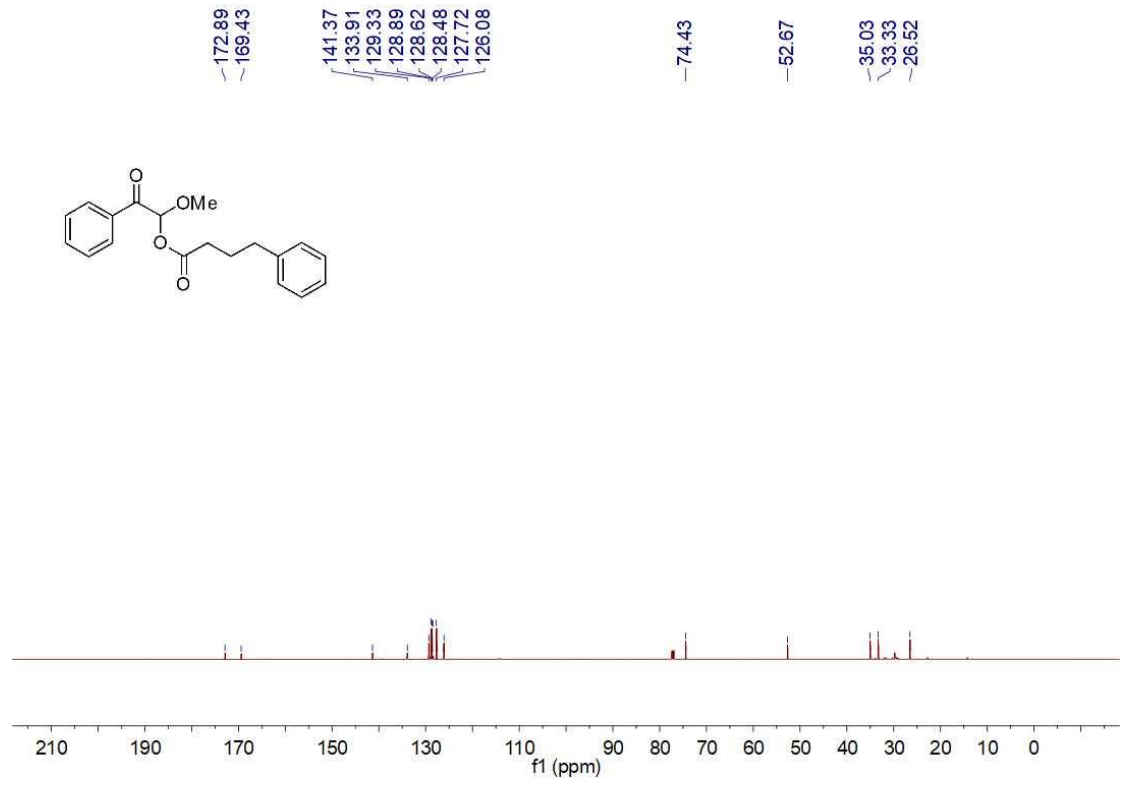
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3z**



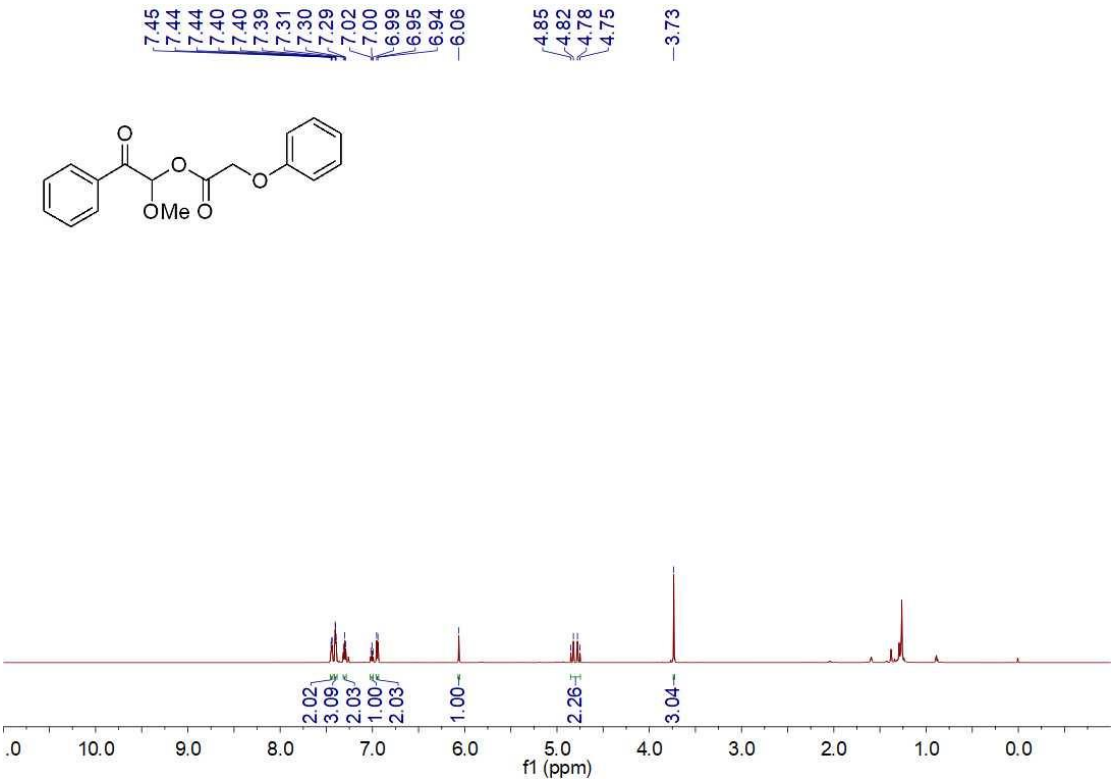
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3aa**



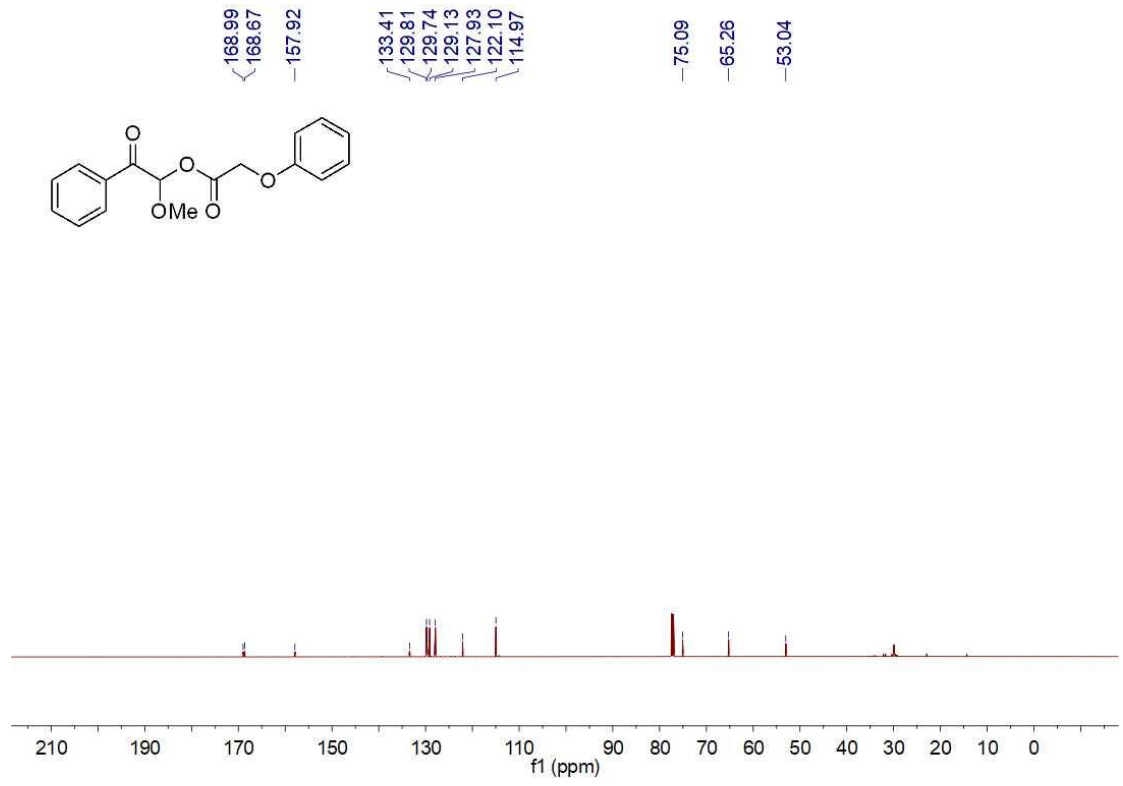
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3aa**



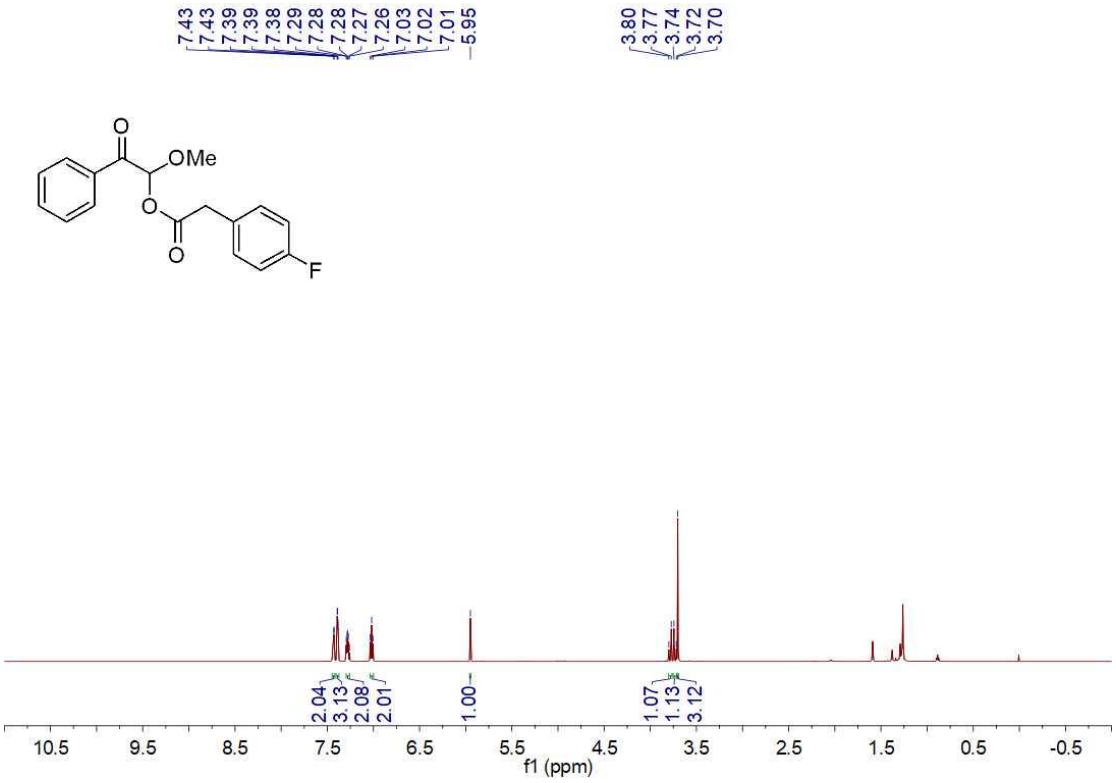
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3ab**



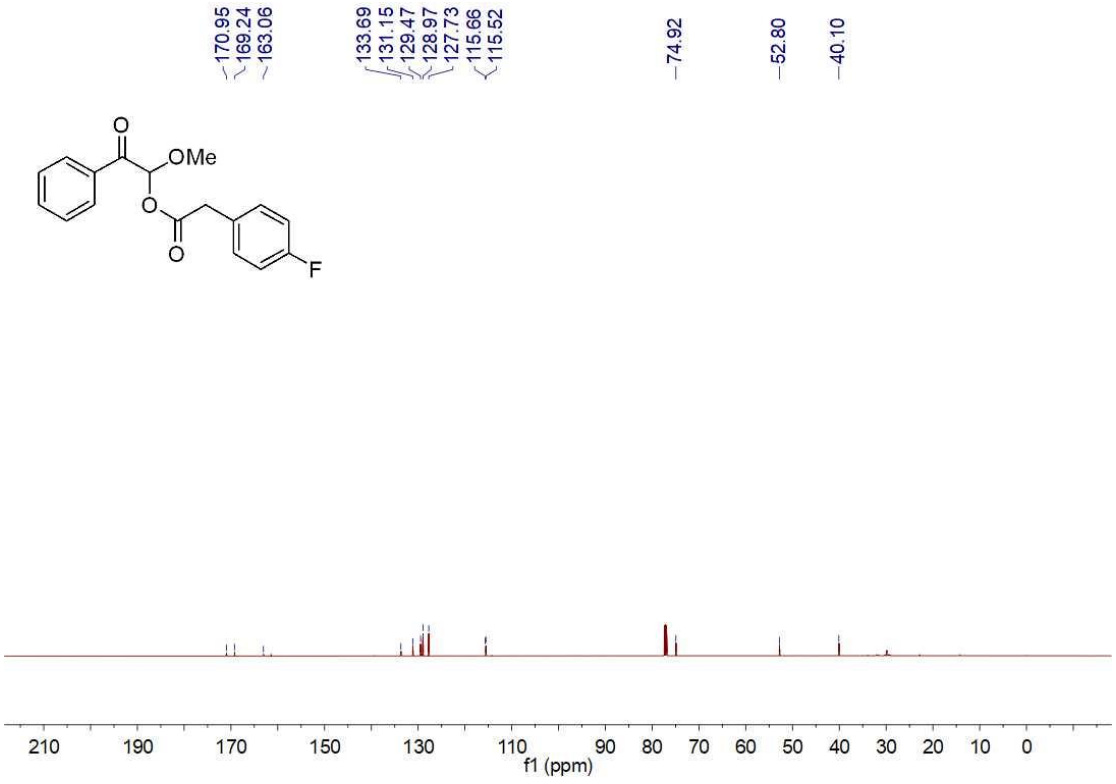
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3ab**



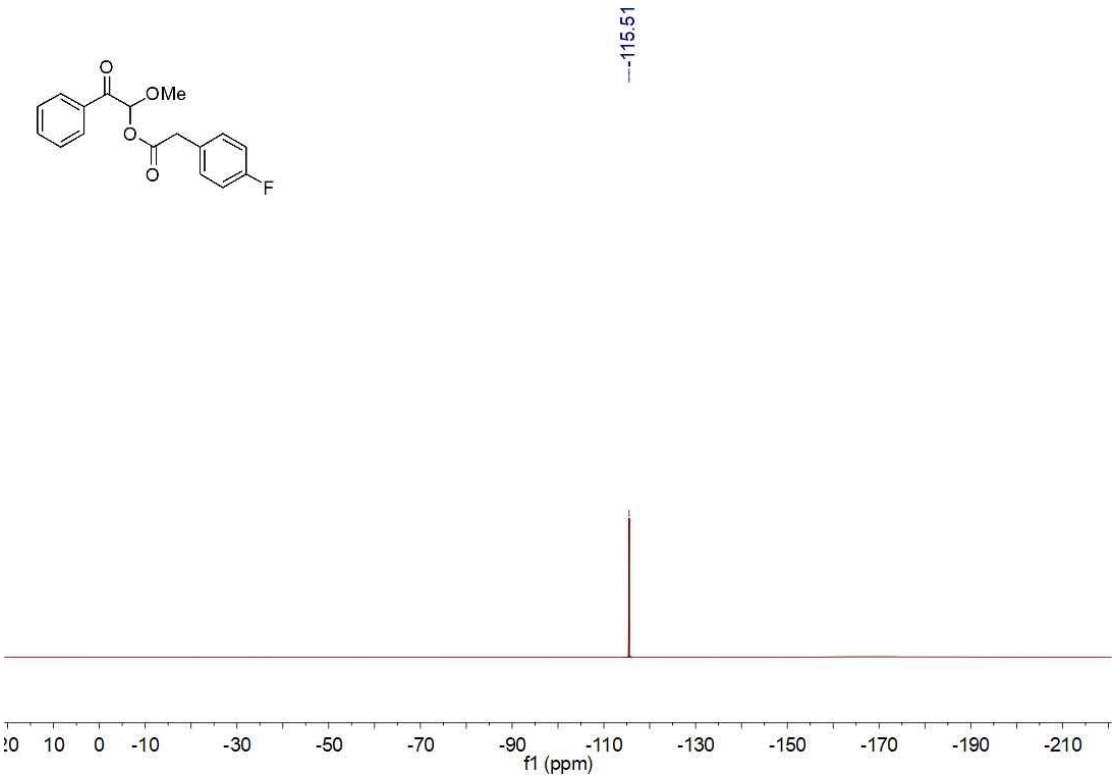
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3ac**



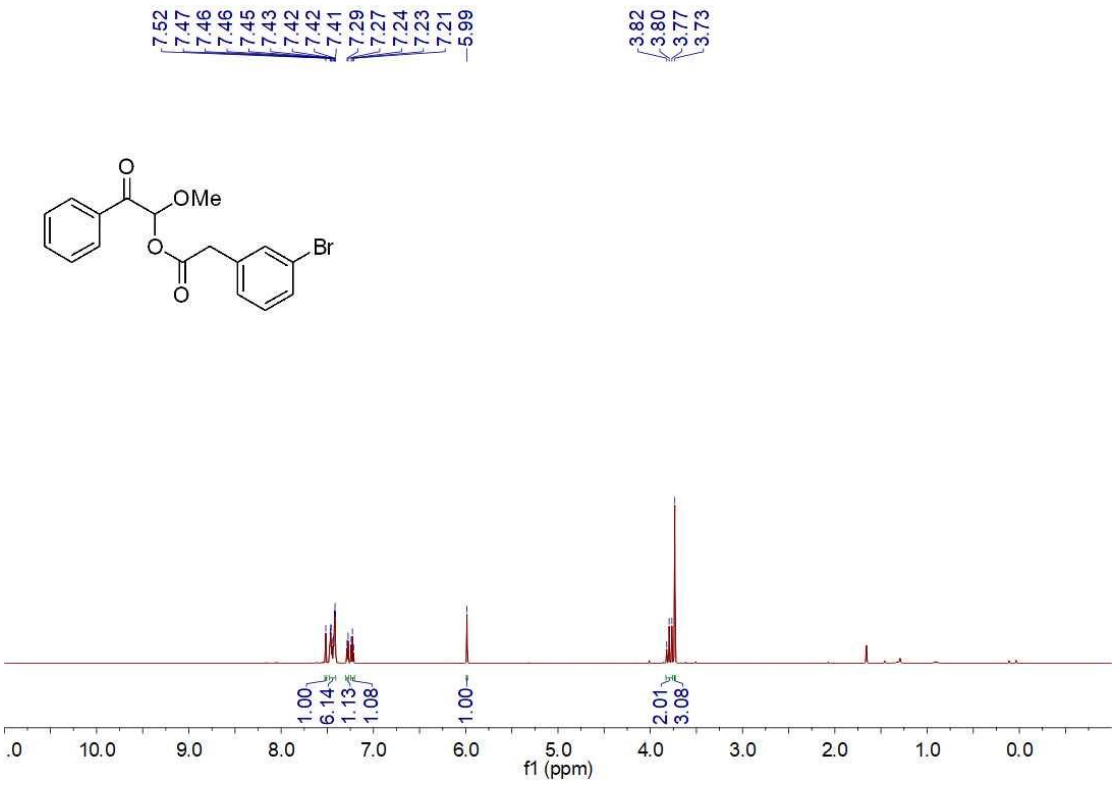
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3ac**



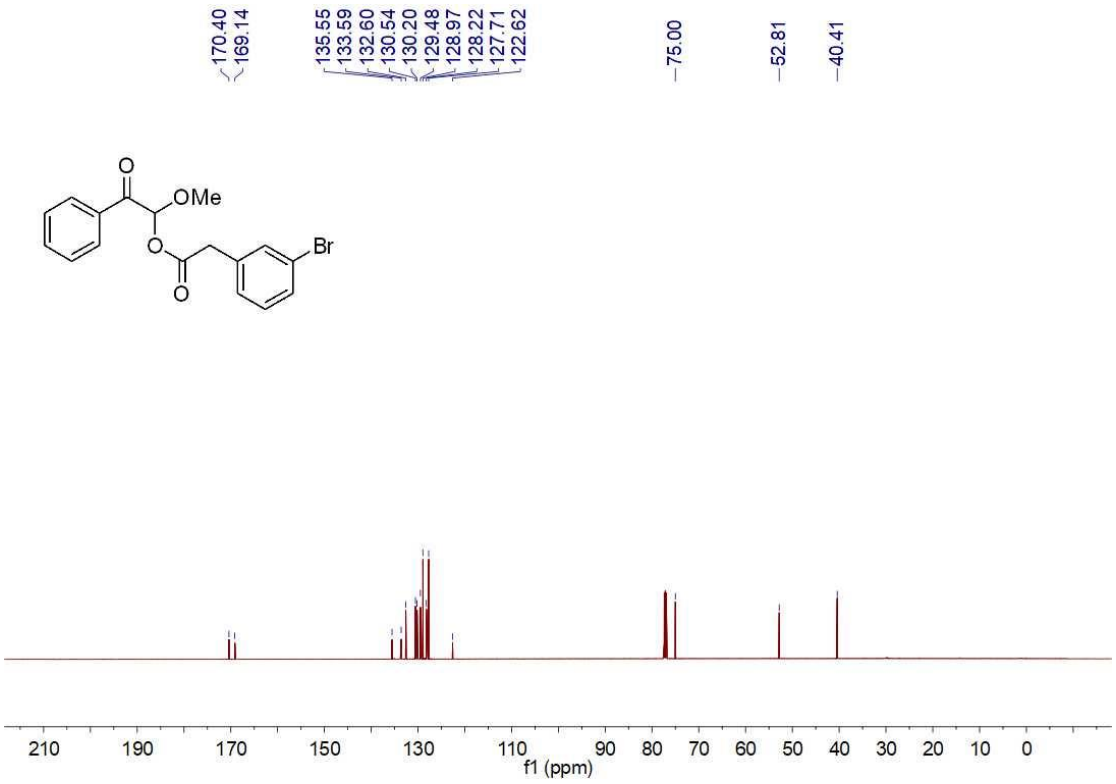
^{19}F NMR (377 MHz, $CDCl_3$) Spectra of **3ac**



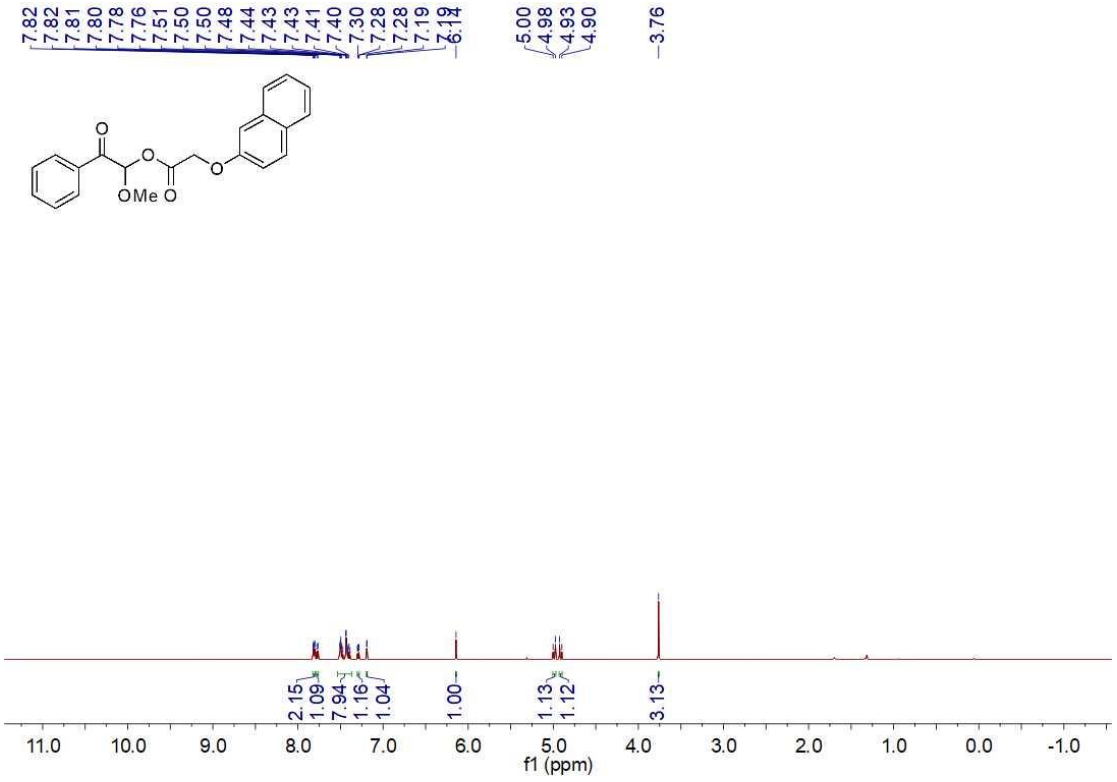
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3ad**



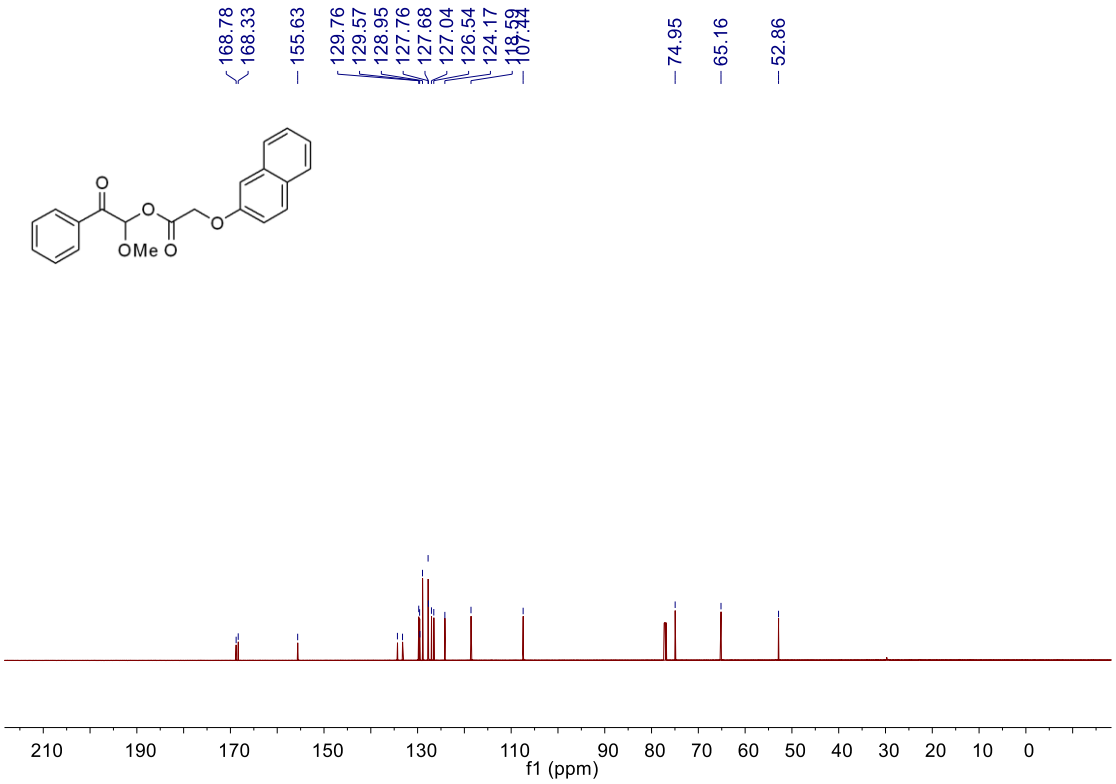
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3ad**



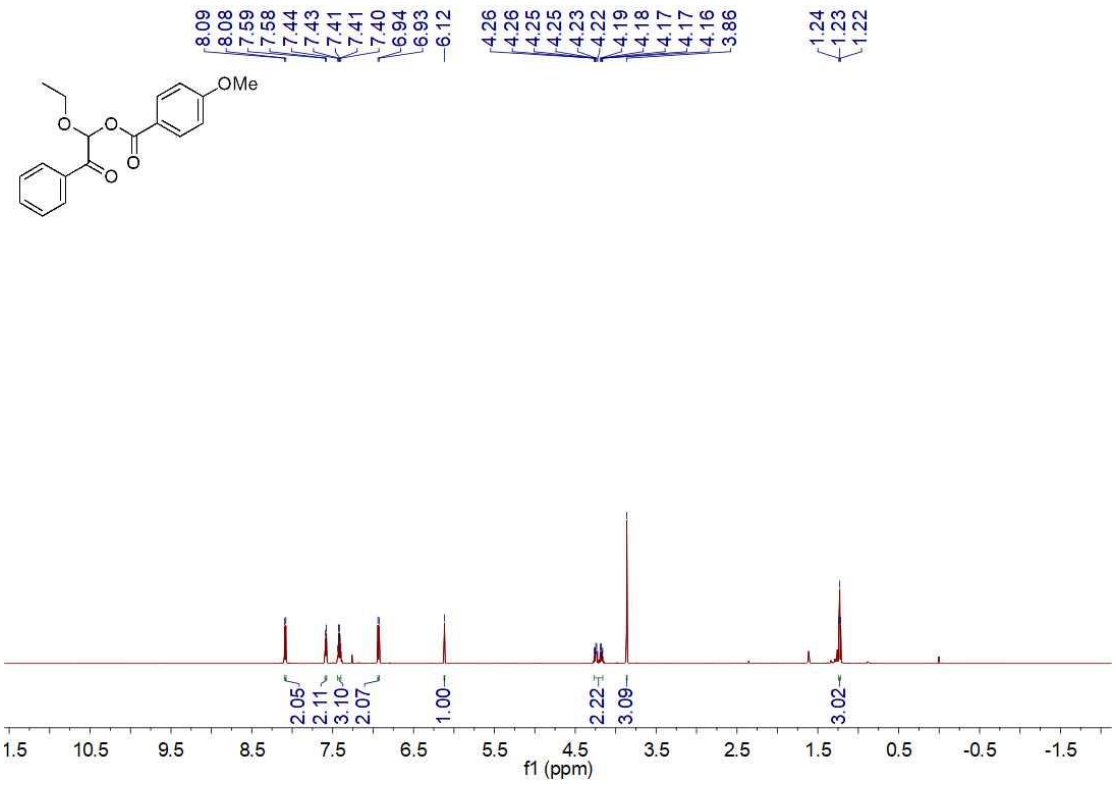
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3ae**



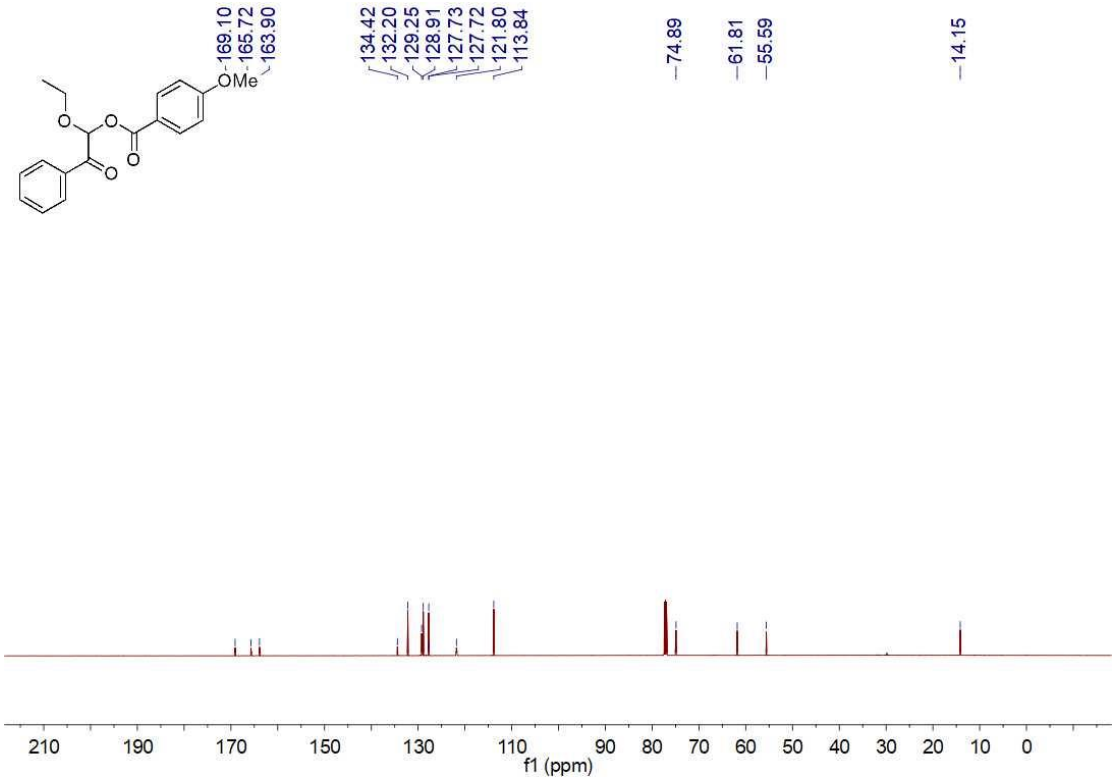
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3ae**



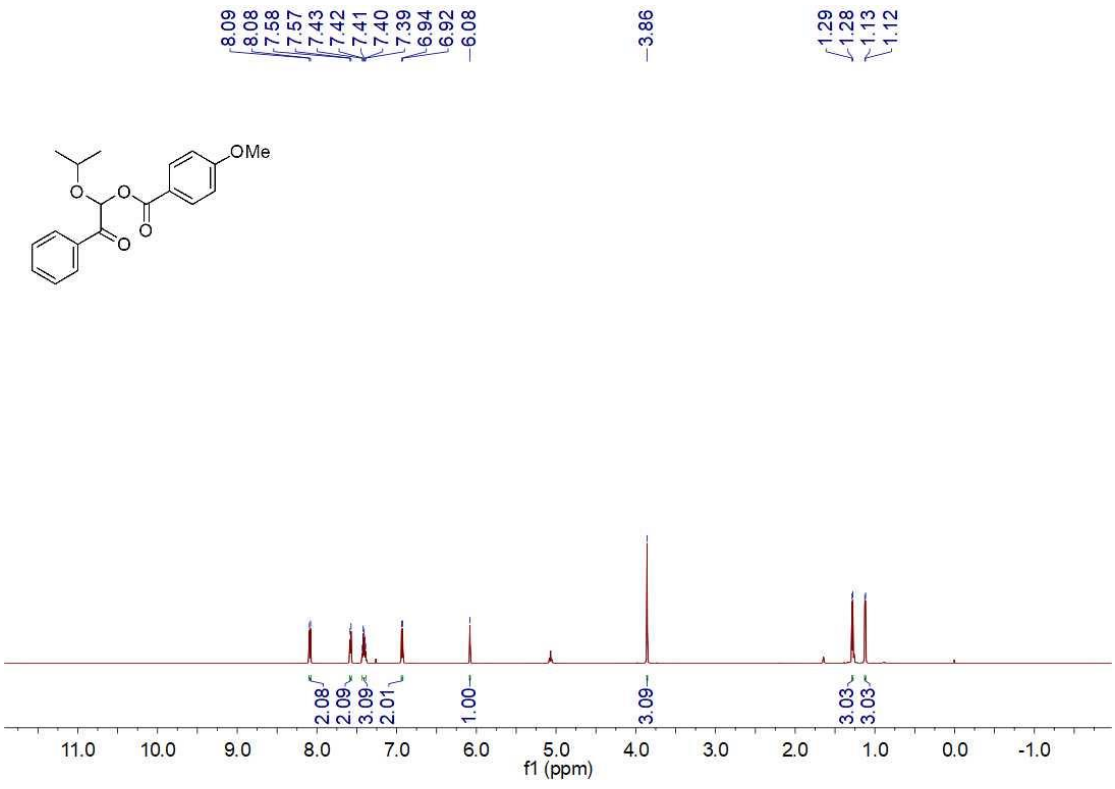
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3ah**



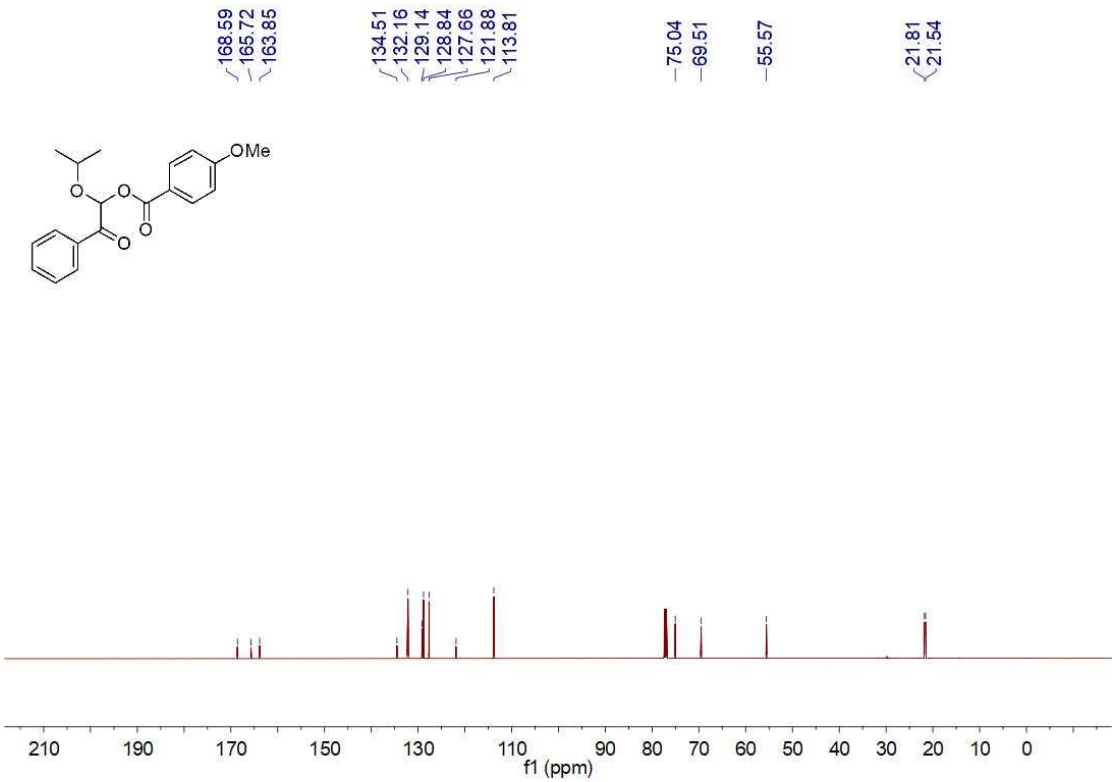
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3ah**



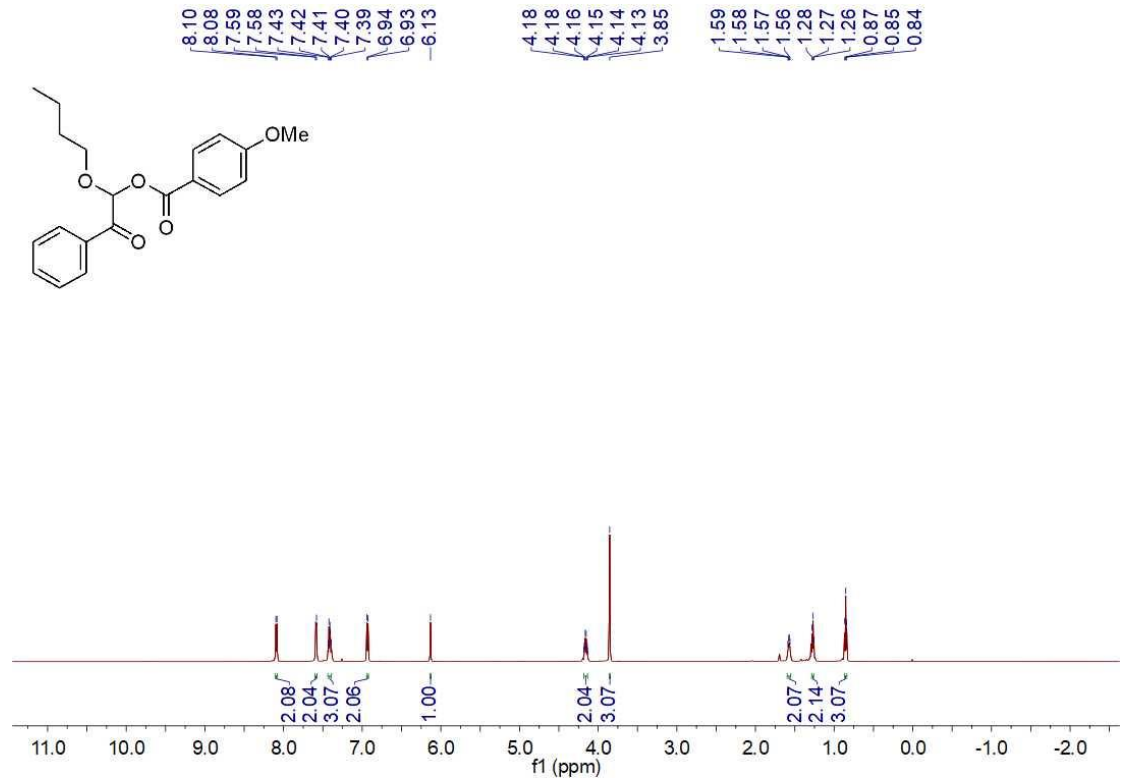
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3ai**



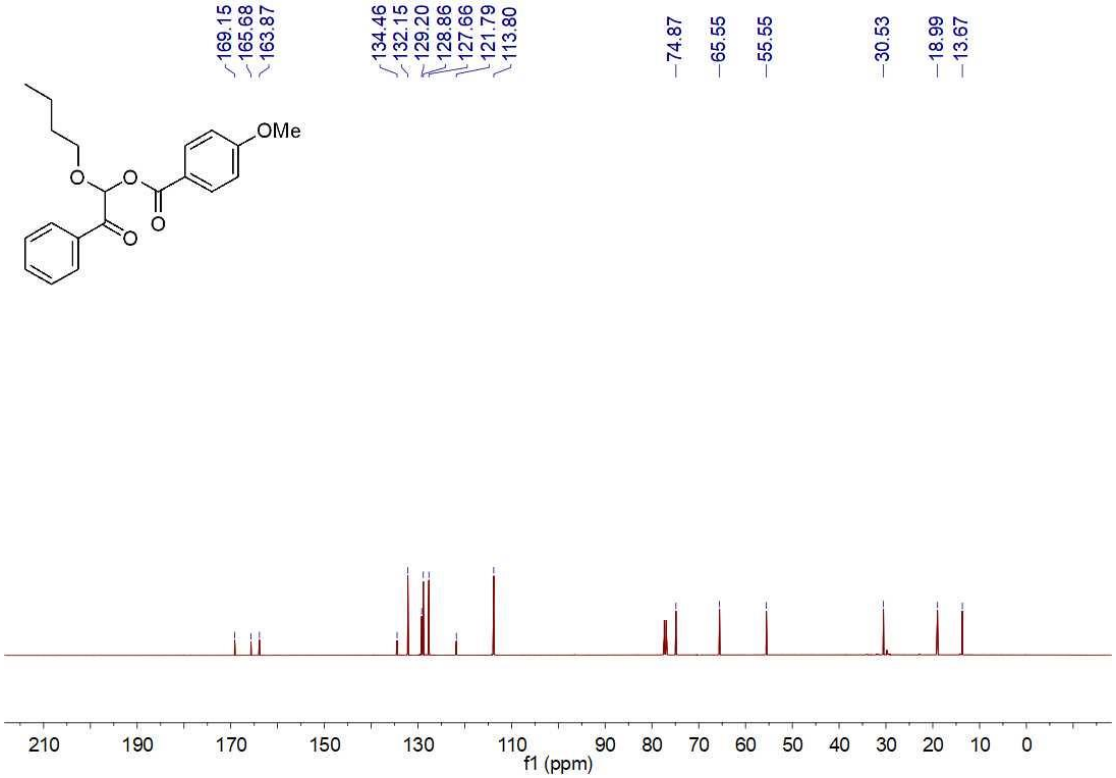
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3ai**



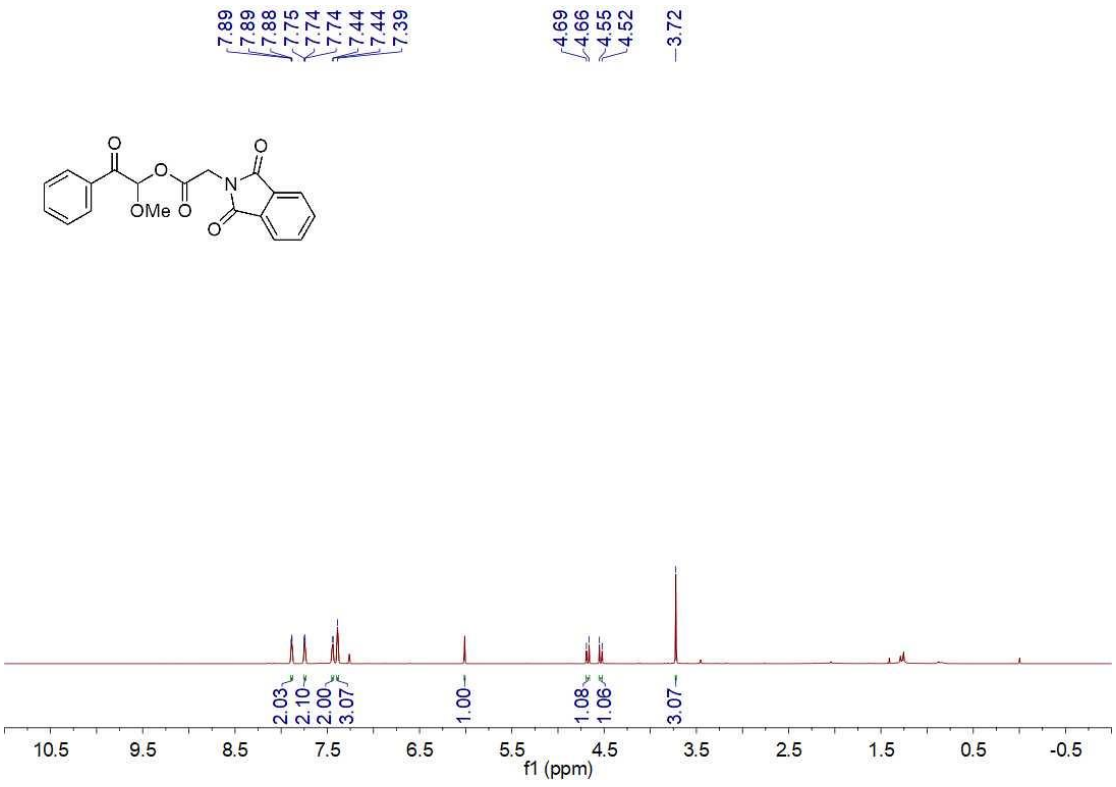
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3aj**



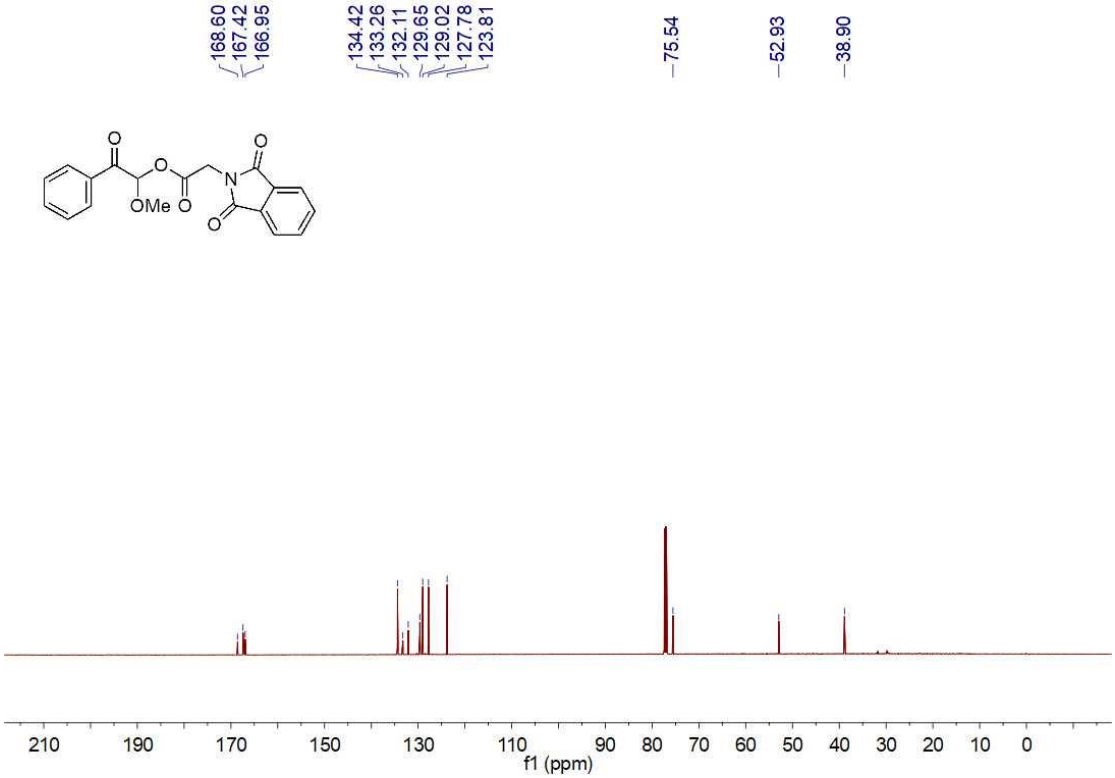
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3aj**



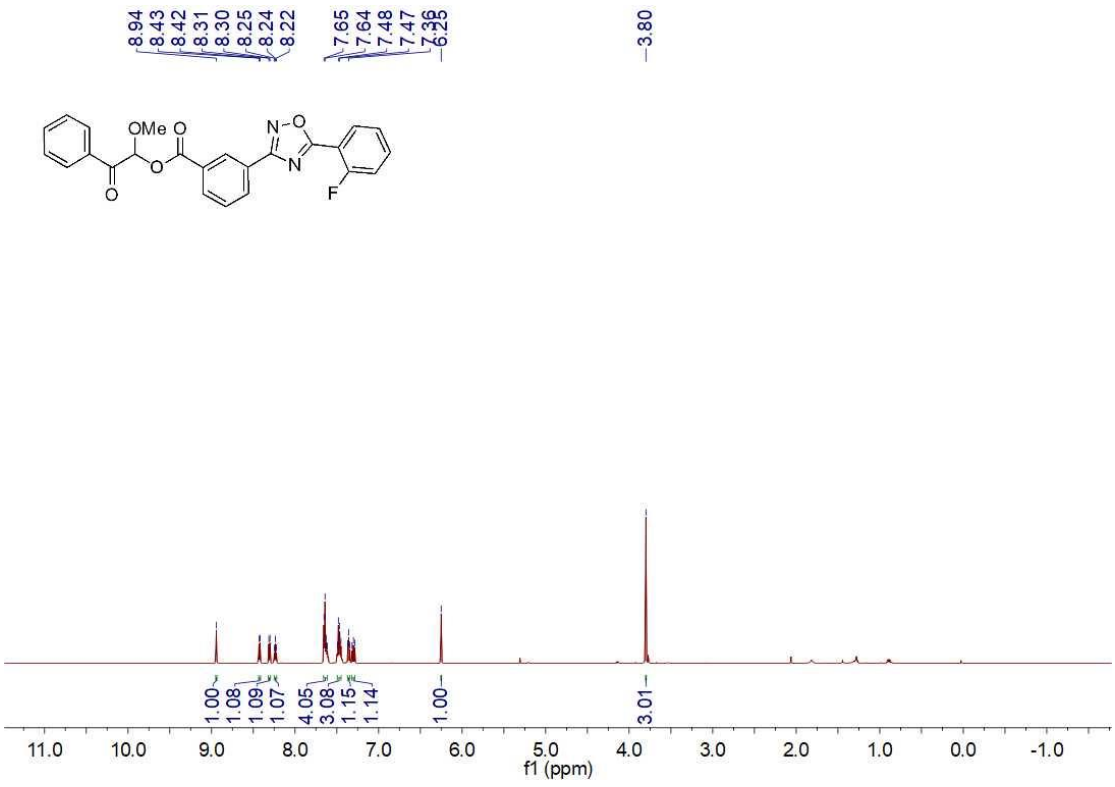
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3an**



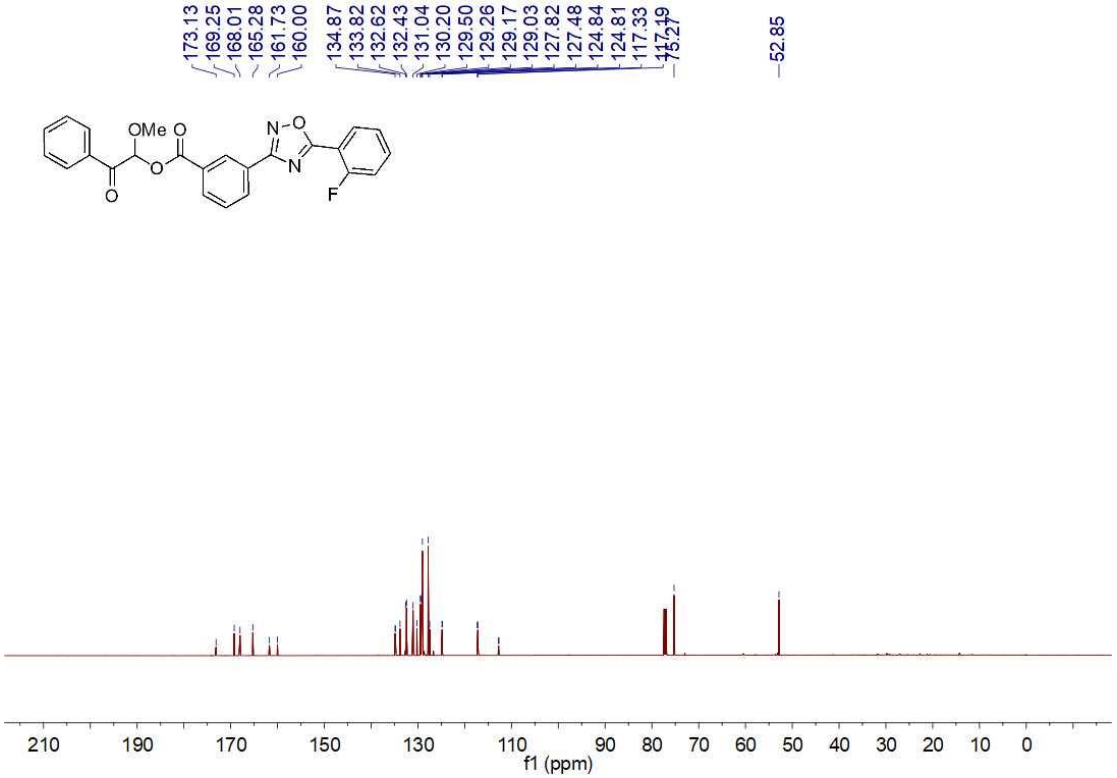
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3an**



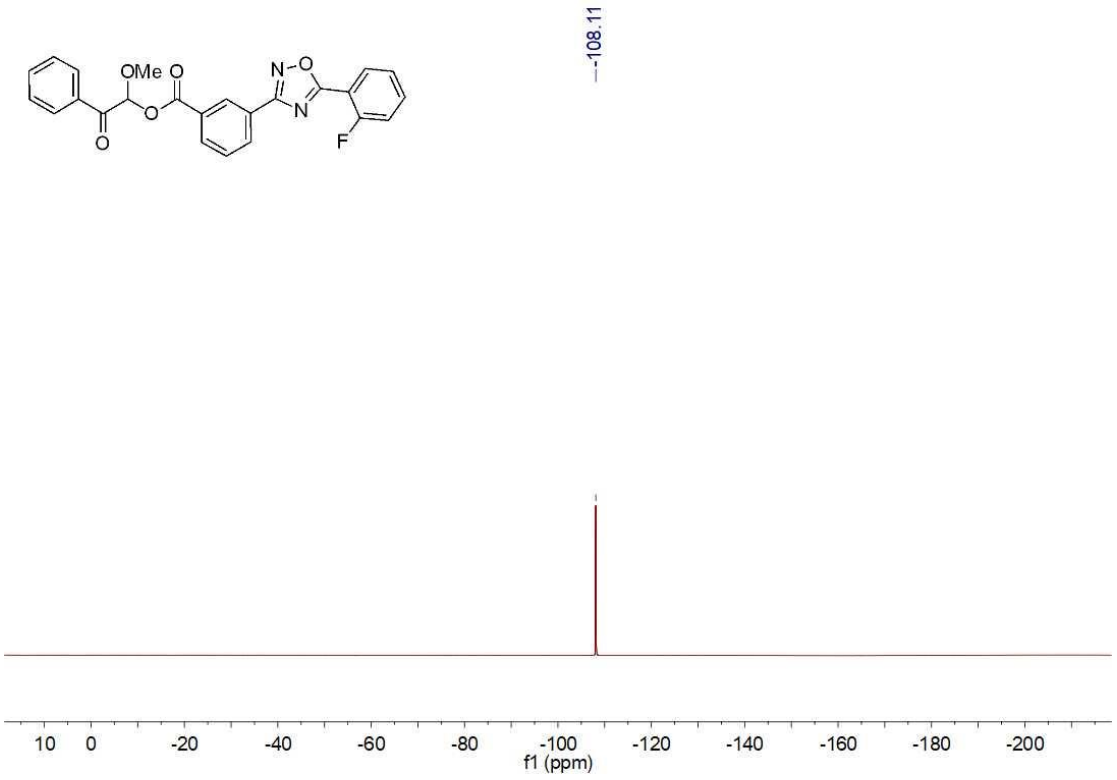
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3ao**



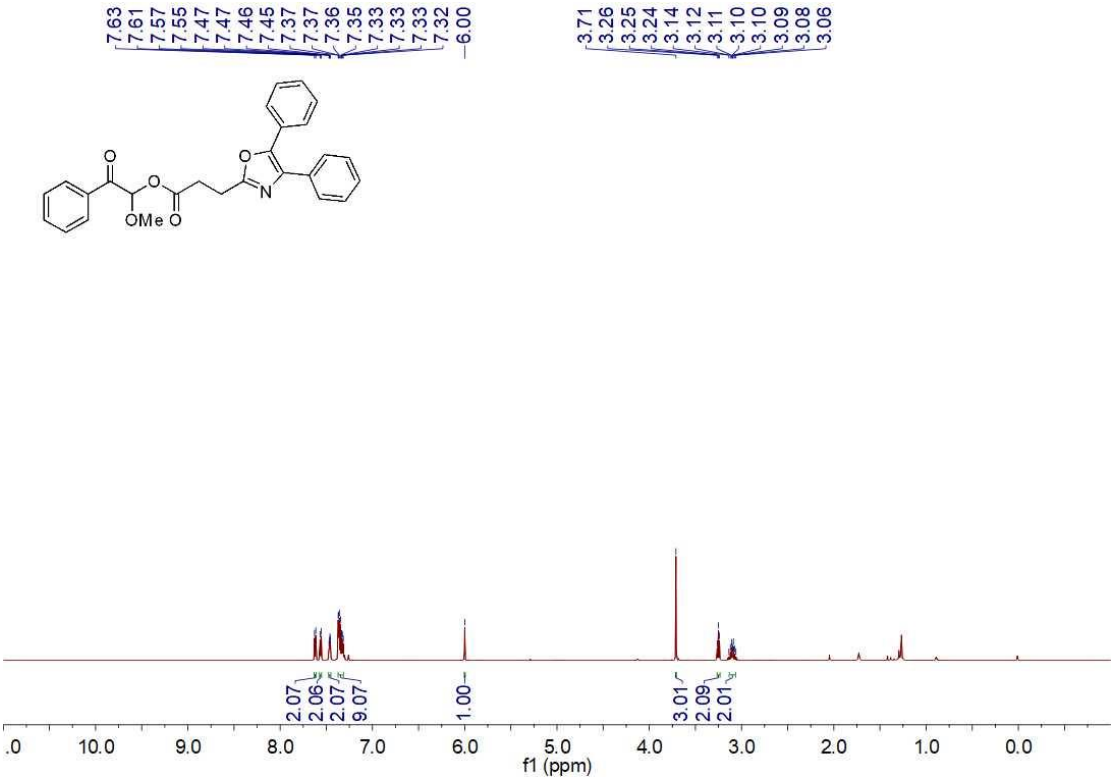
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3ao**



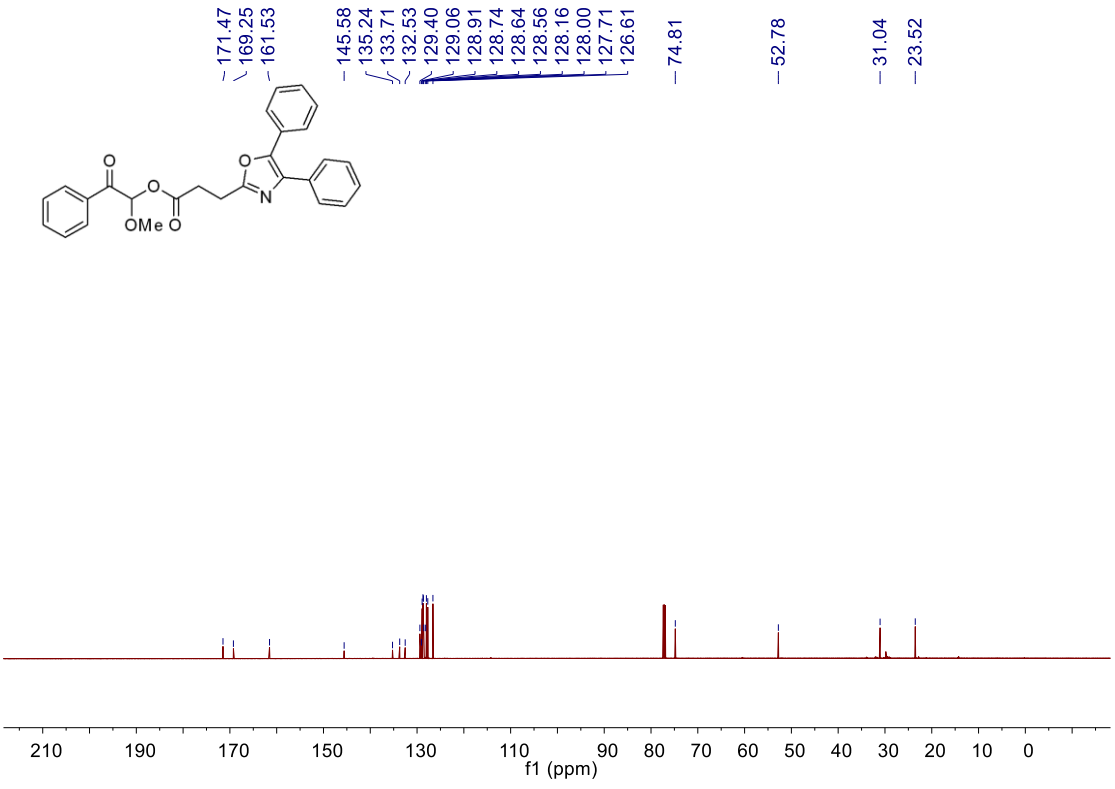
^{19}F NMR (376 MHz, $CDCl_3$) Spectra of **3ao**



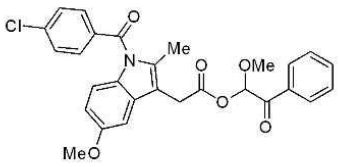
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3ap**

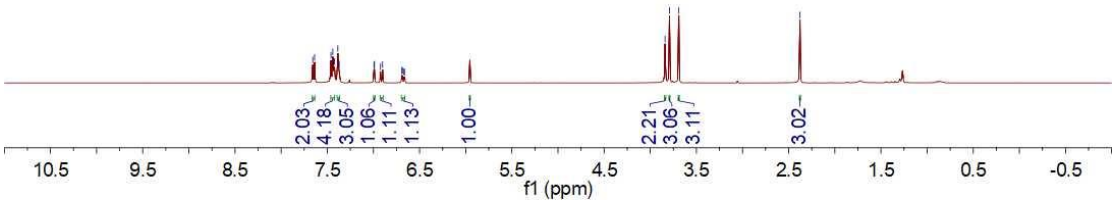


^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3ap**

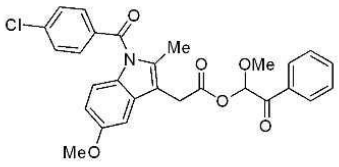


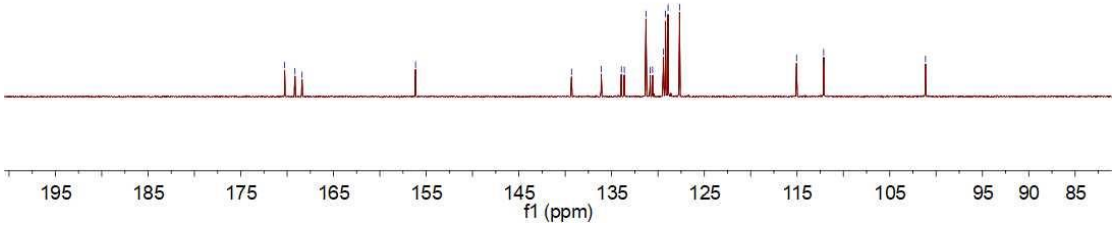
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **3aq**



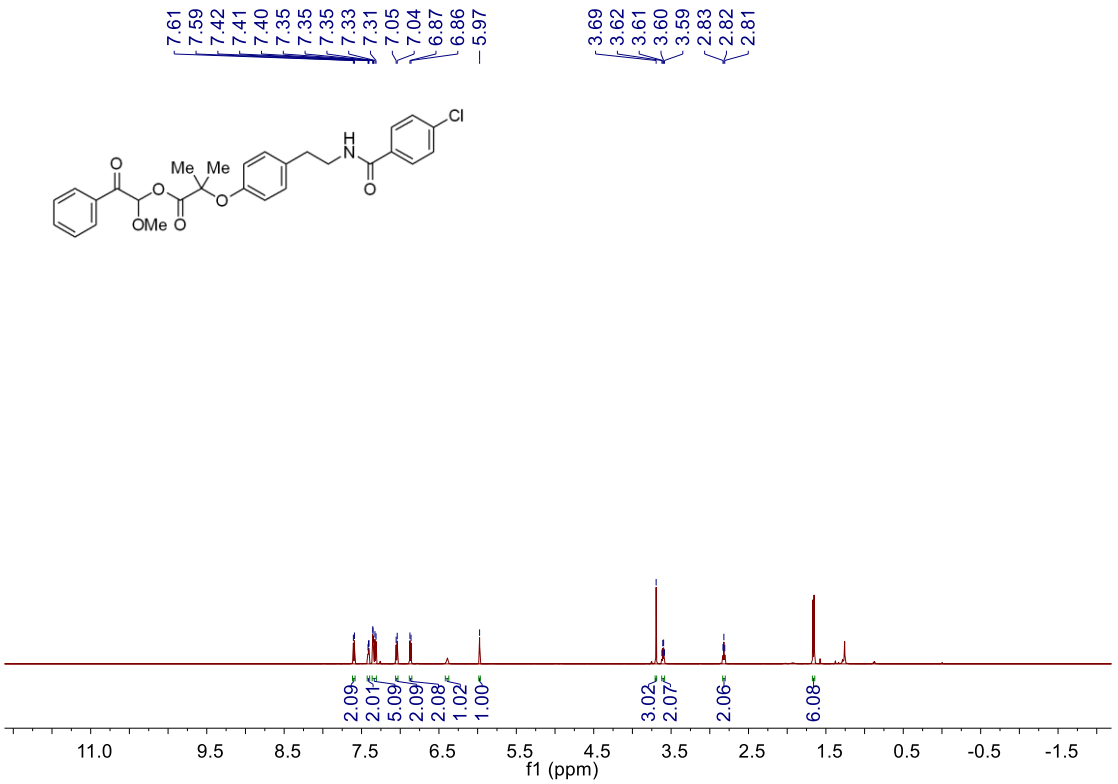


^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **3aq**

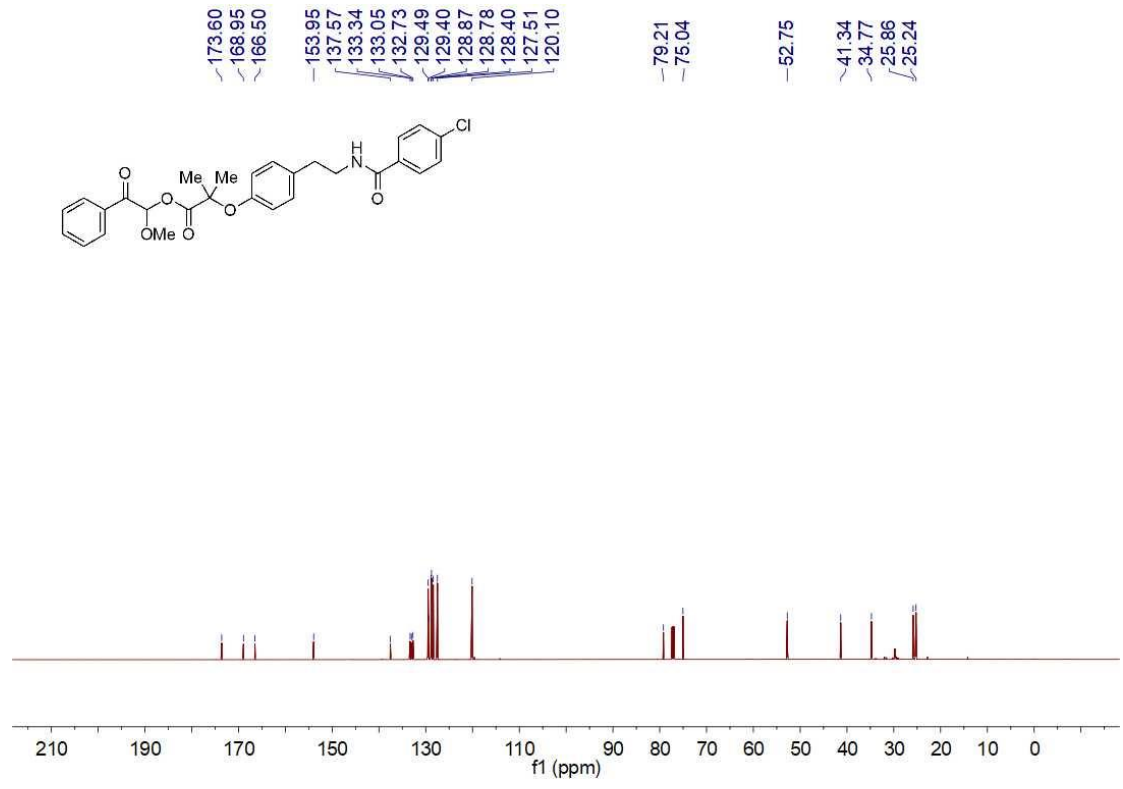




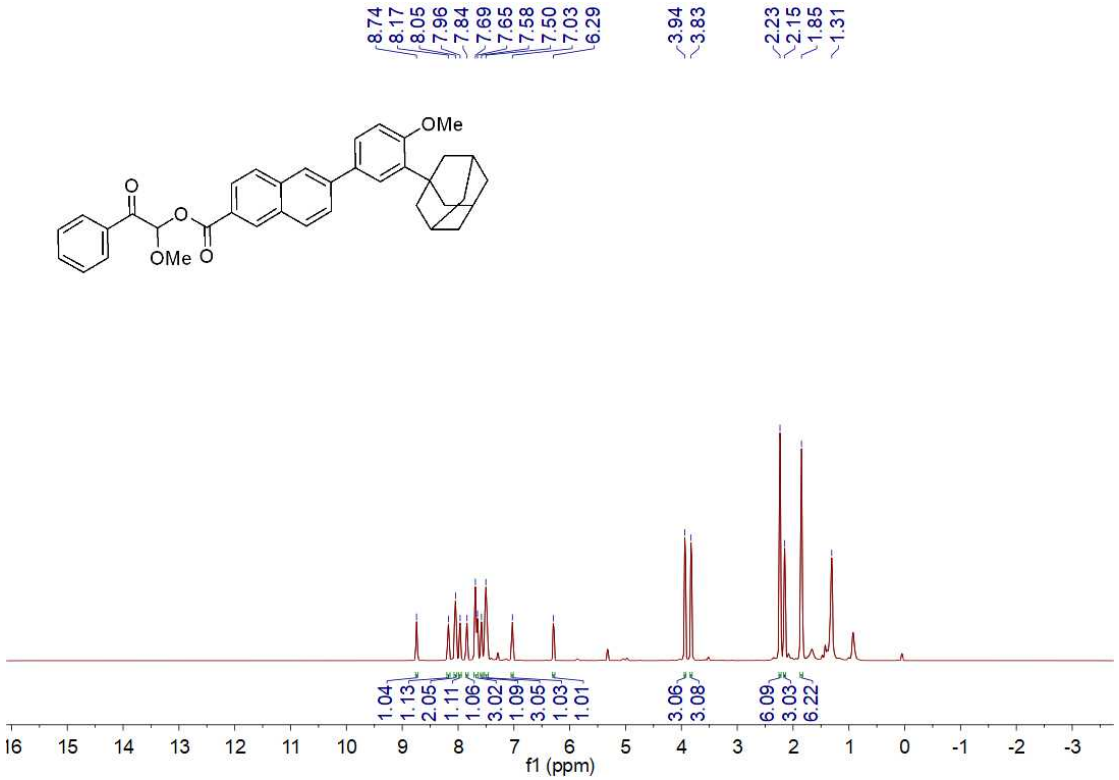
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3ar**



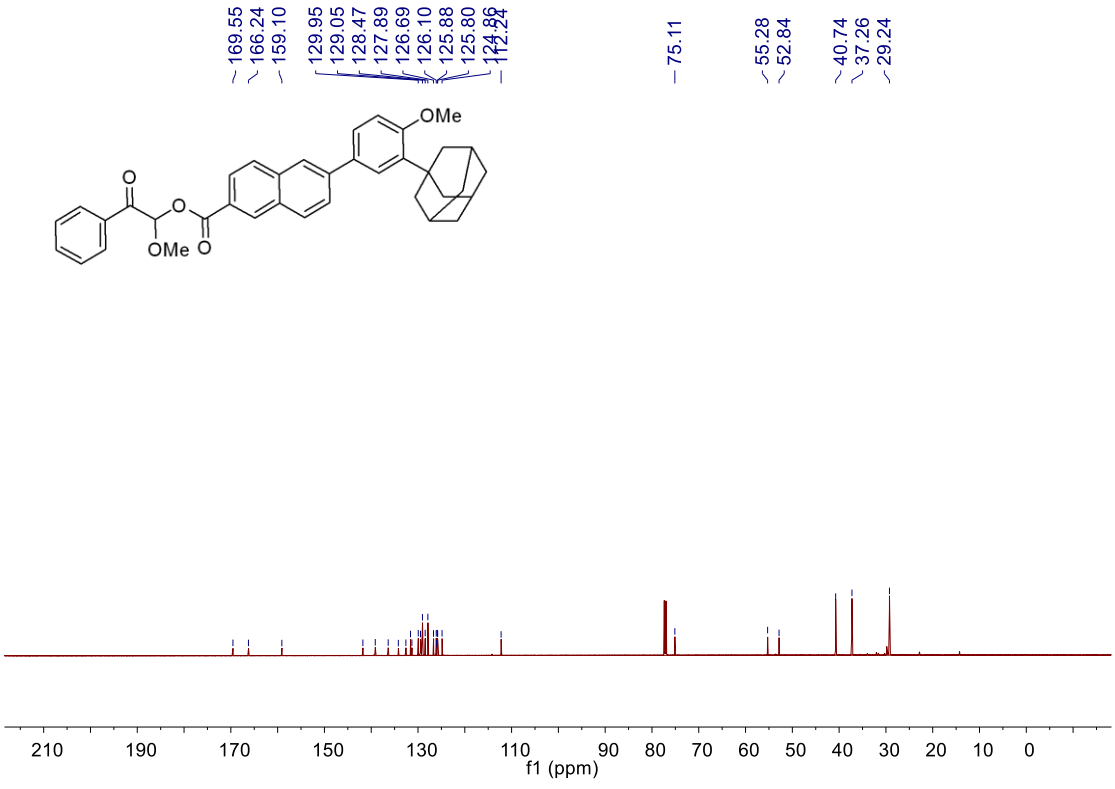
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3ar**



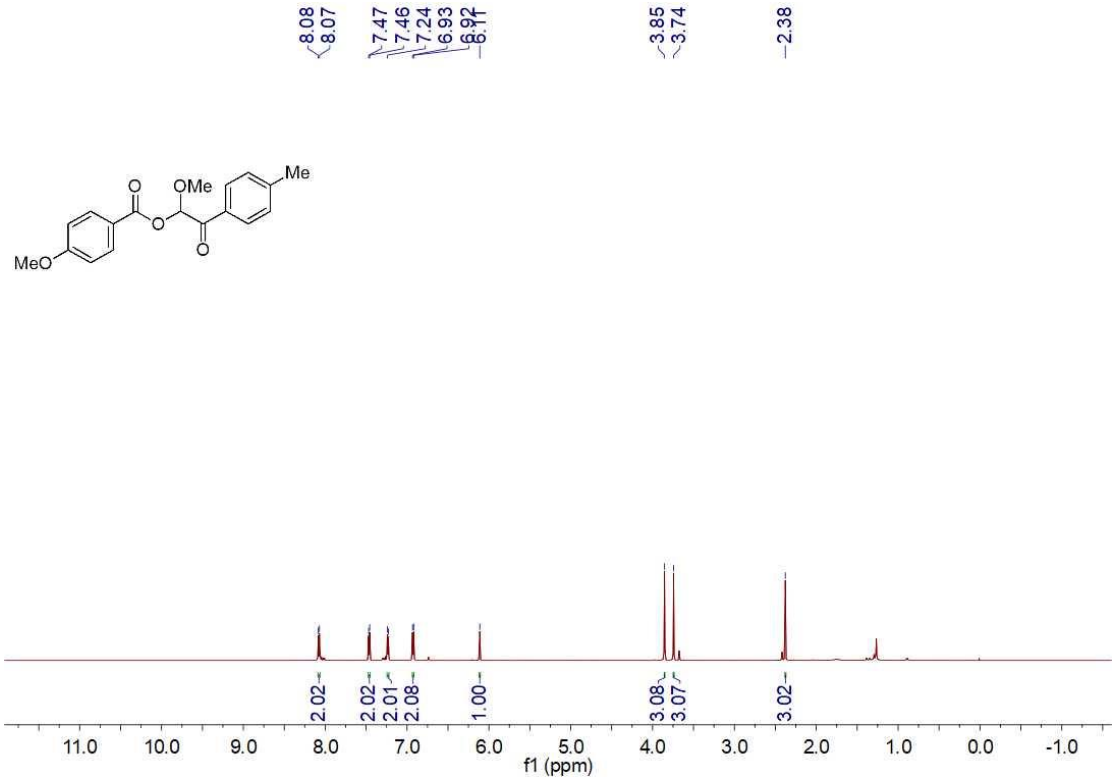
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **3as**



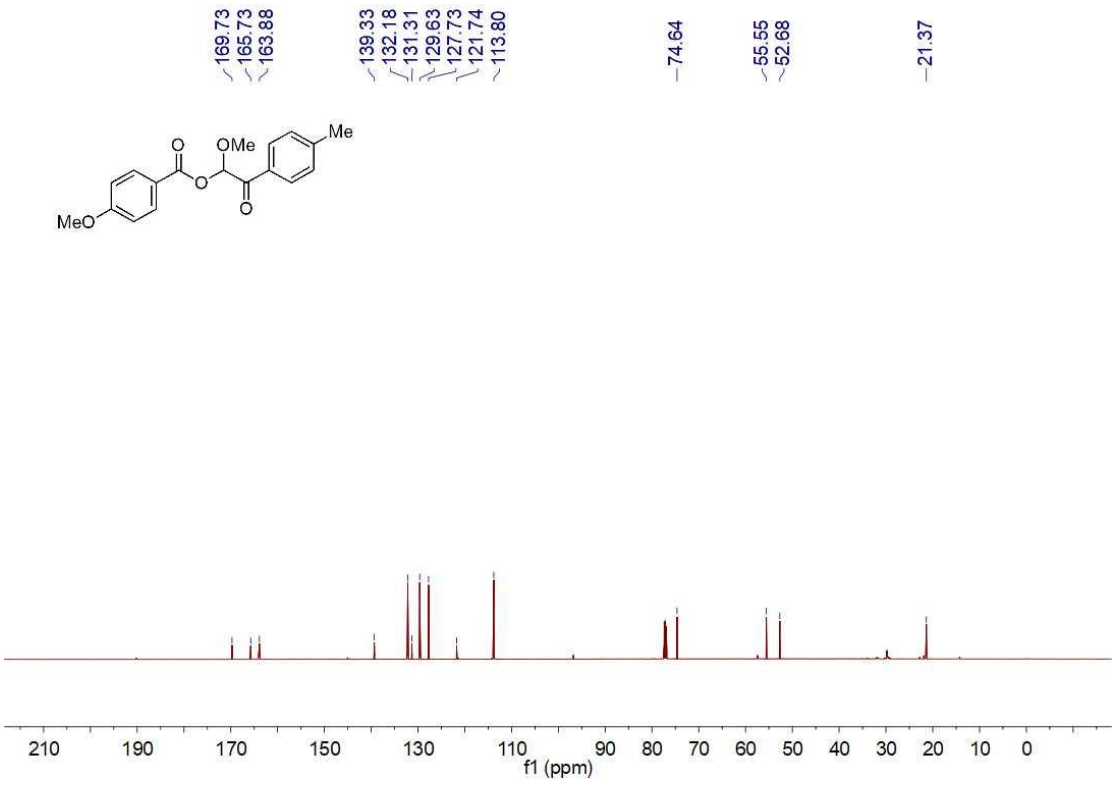
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **3as**



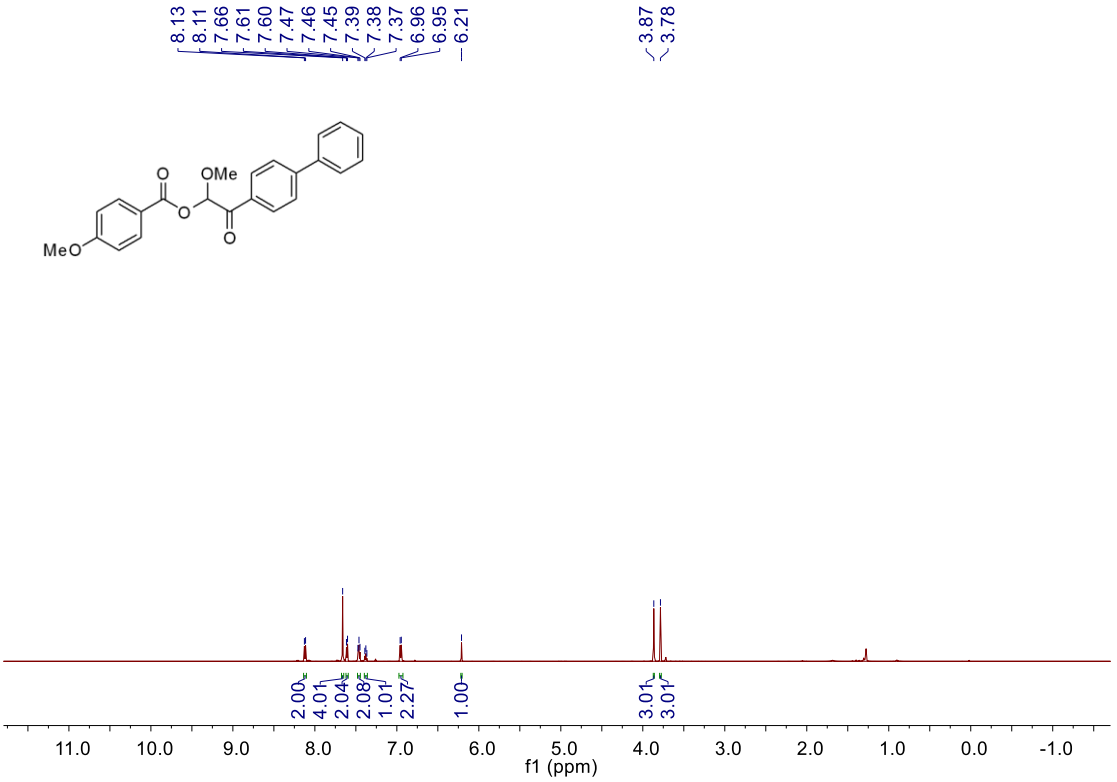
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4a**



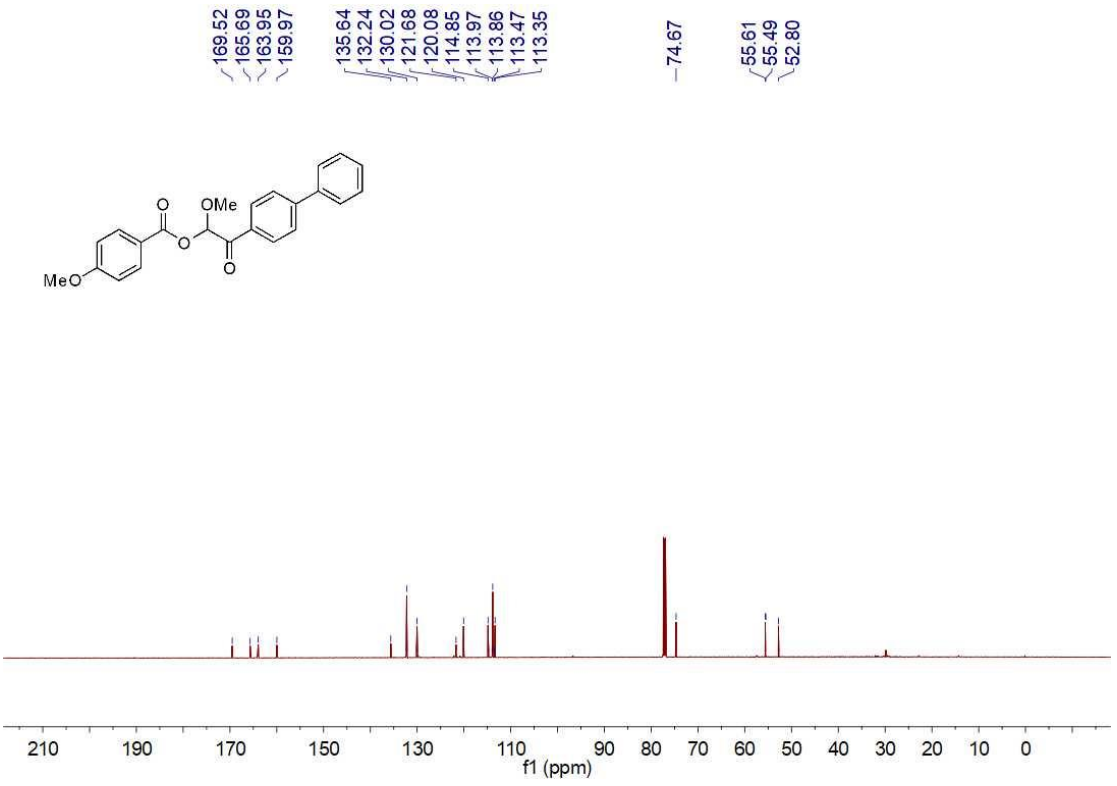
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4a**



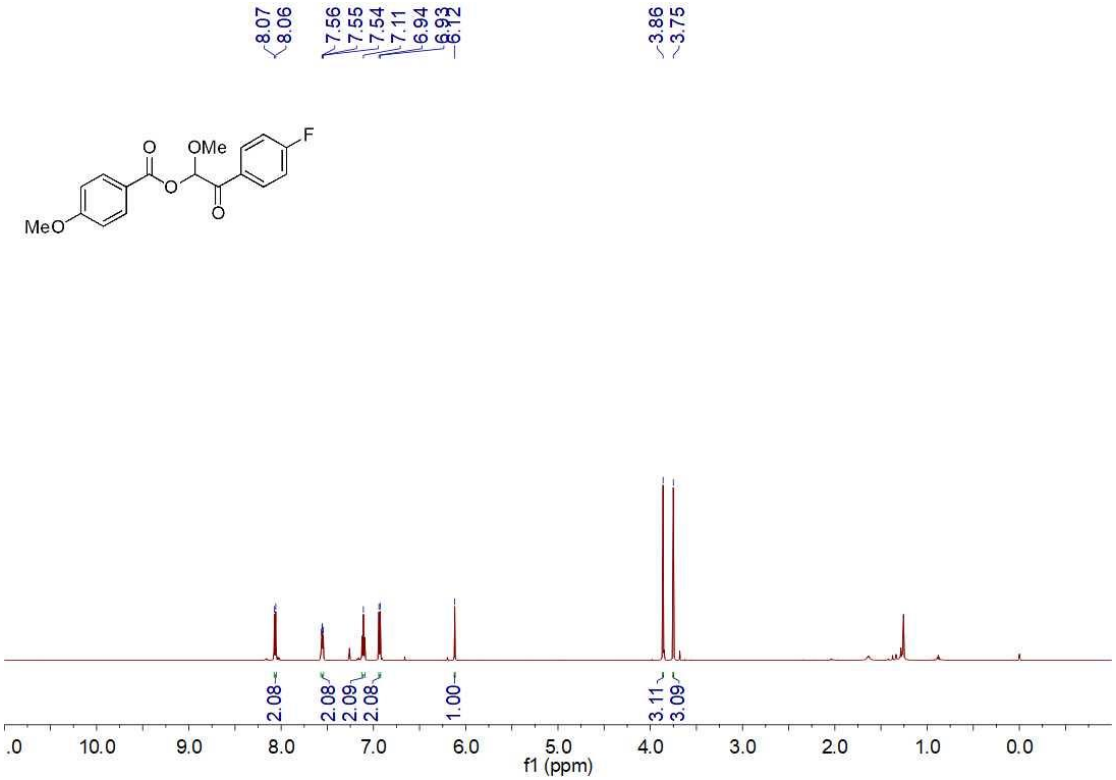
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4b**



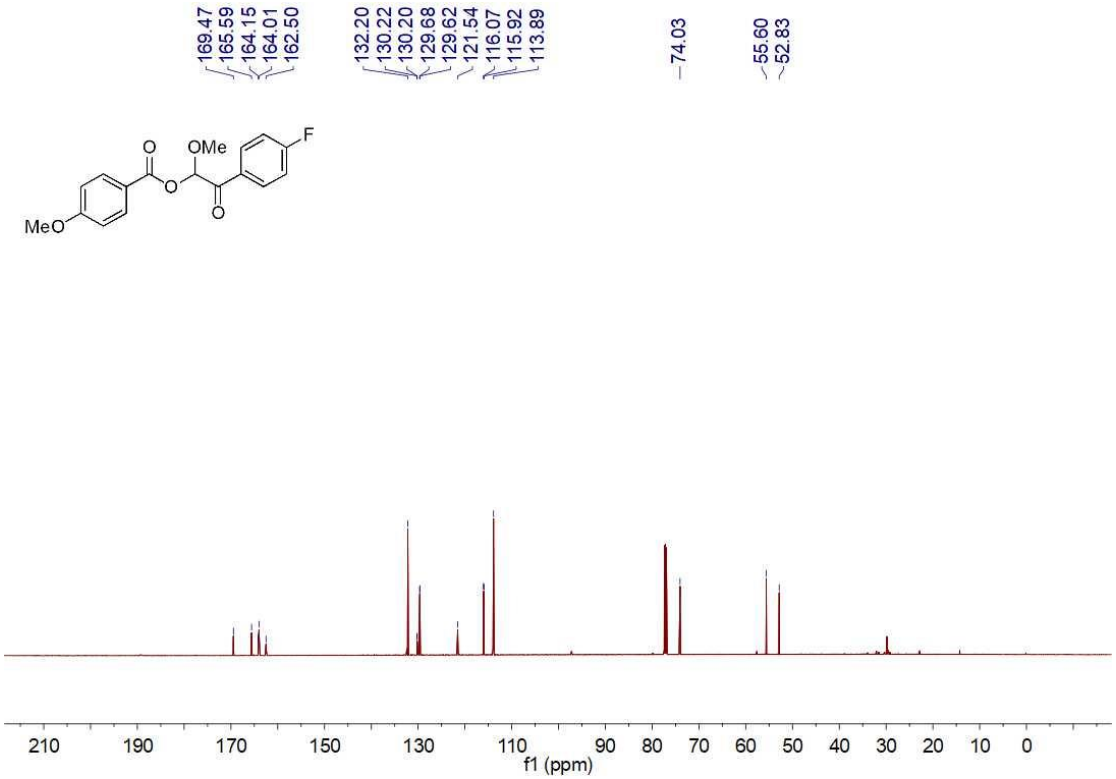
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4b**



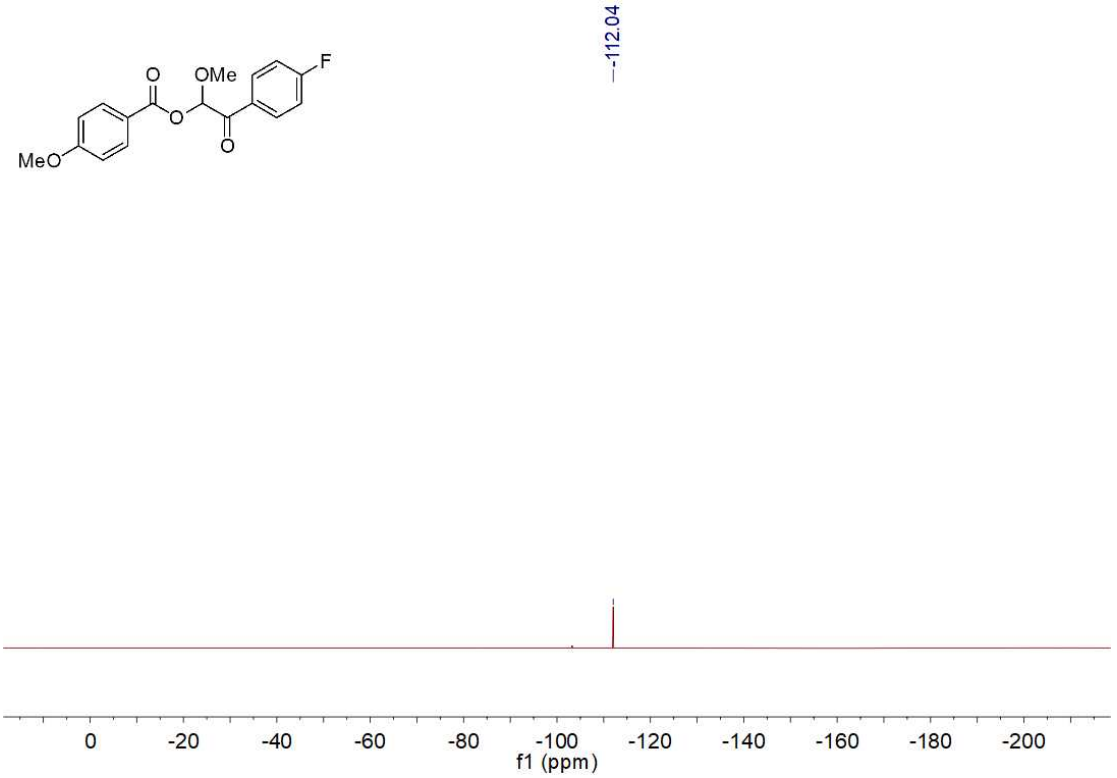
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4c**



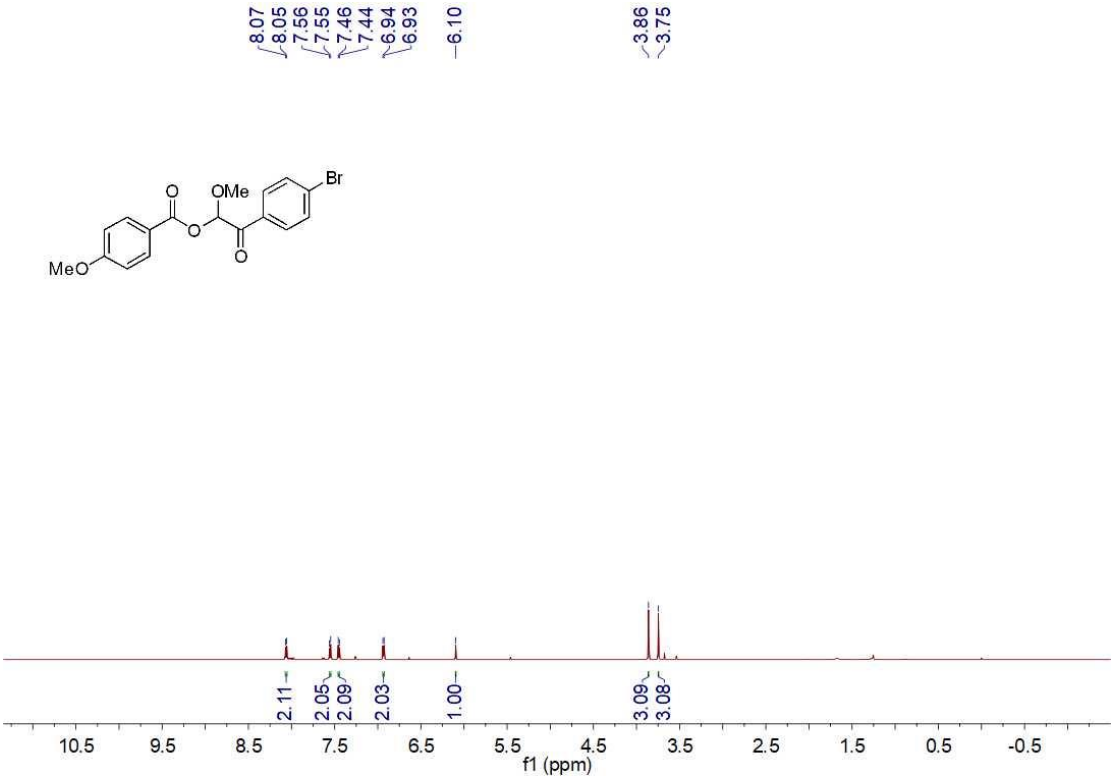
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4c**



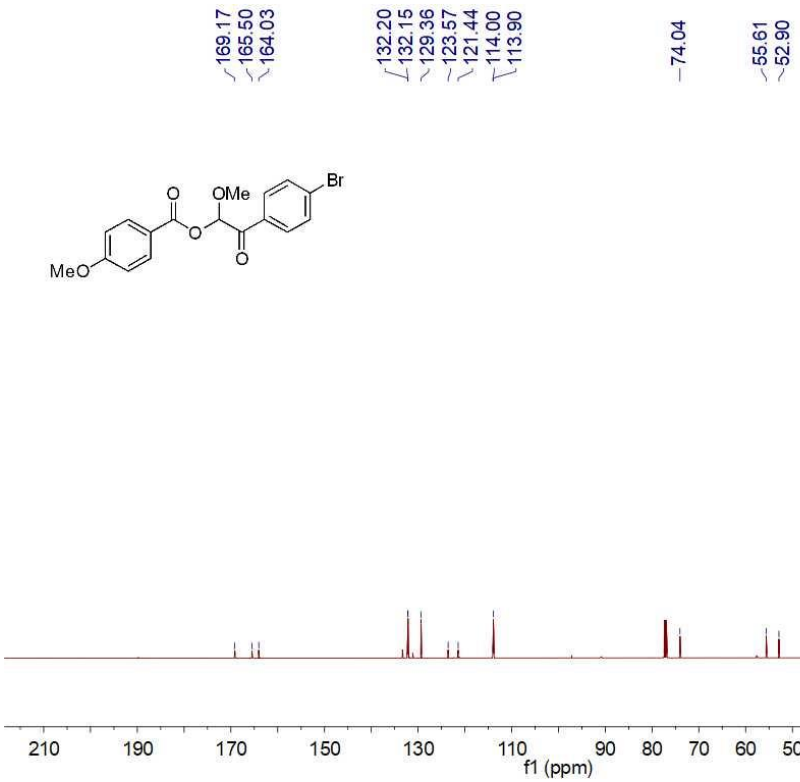
^{19}F NMR (376 MHz, $CDCl_3$) Spectra of **4c**



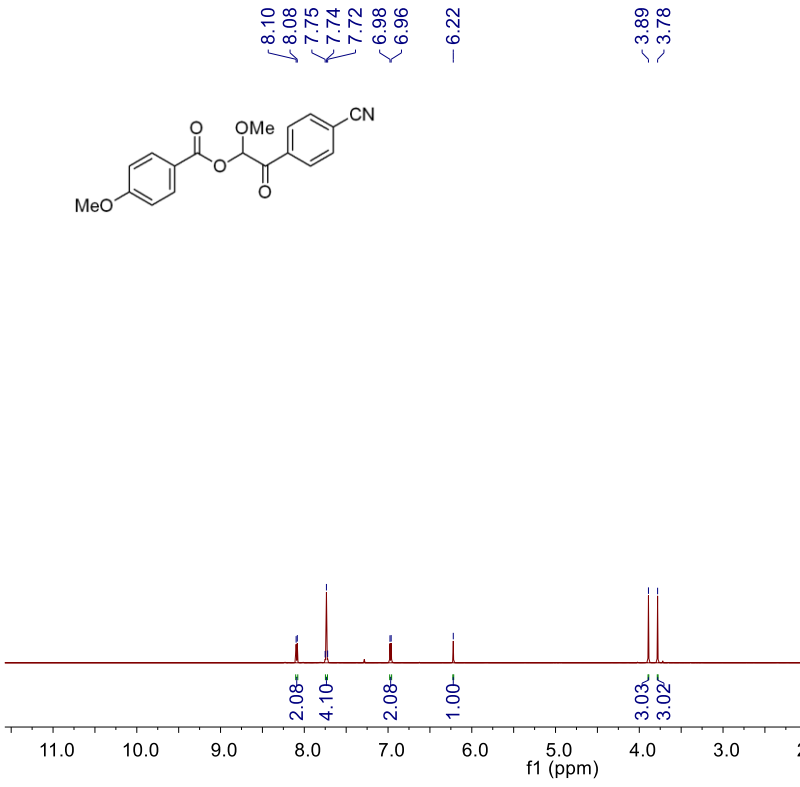
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4d**



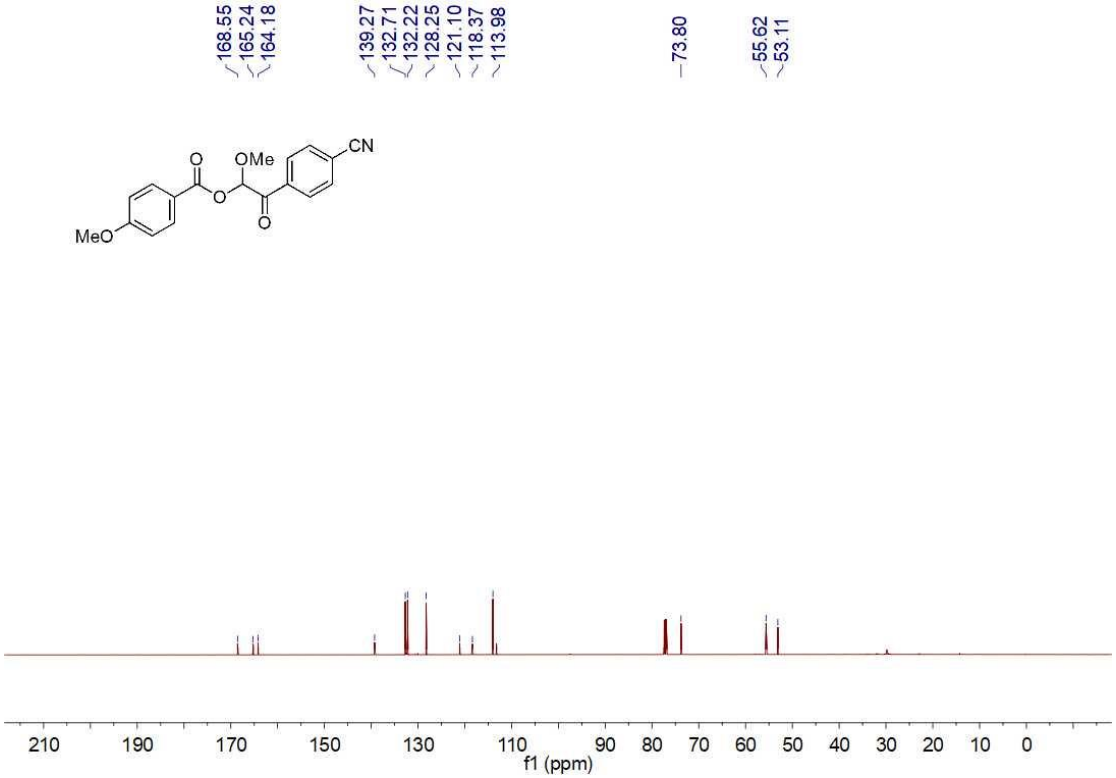
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4d**



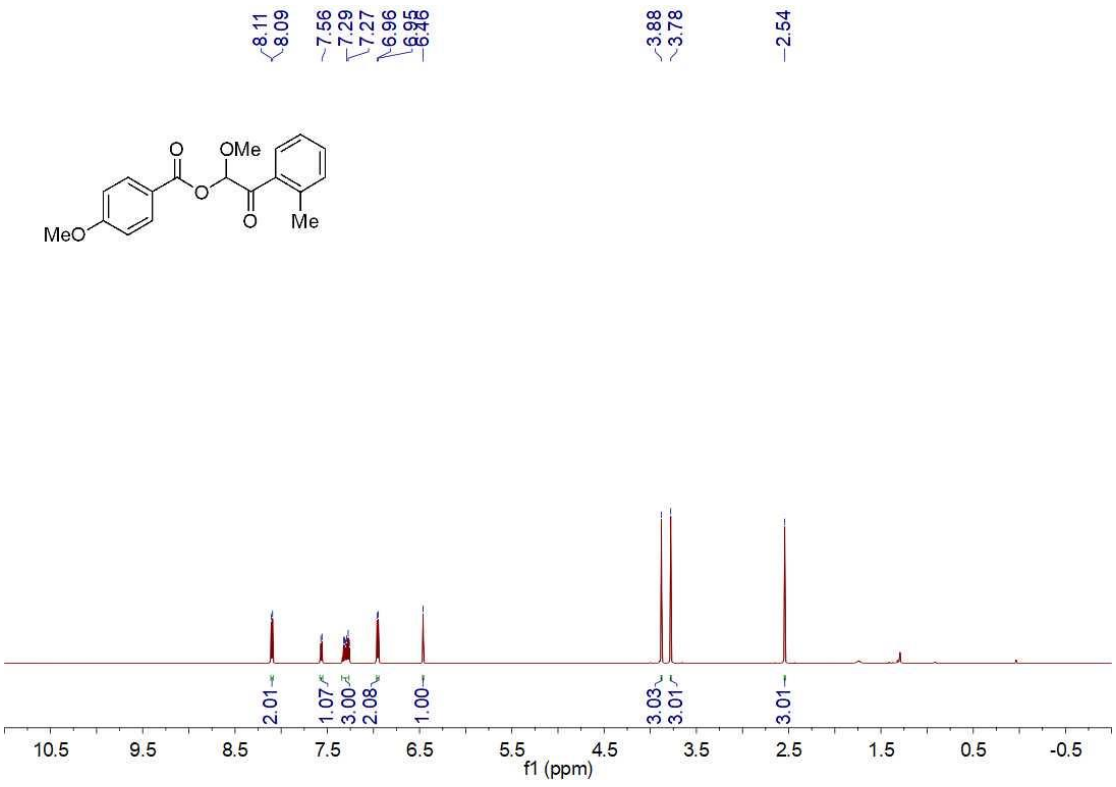
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4e**



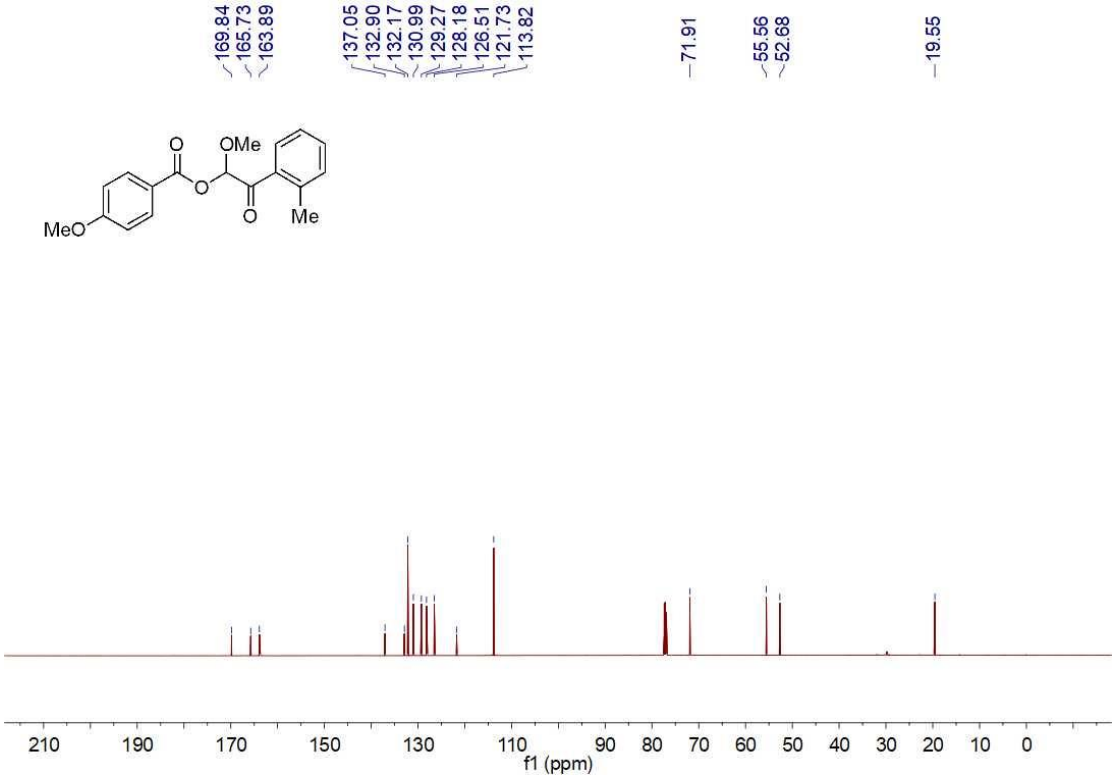
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4e**



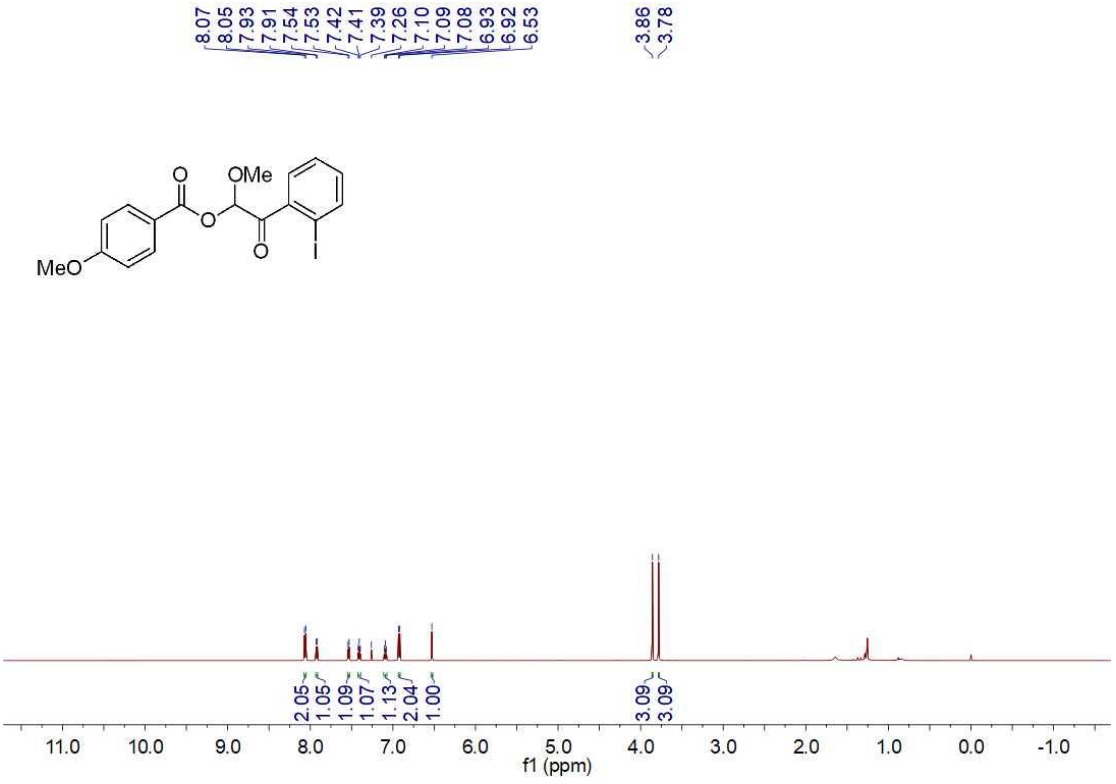
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4f**



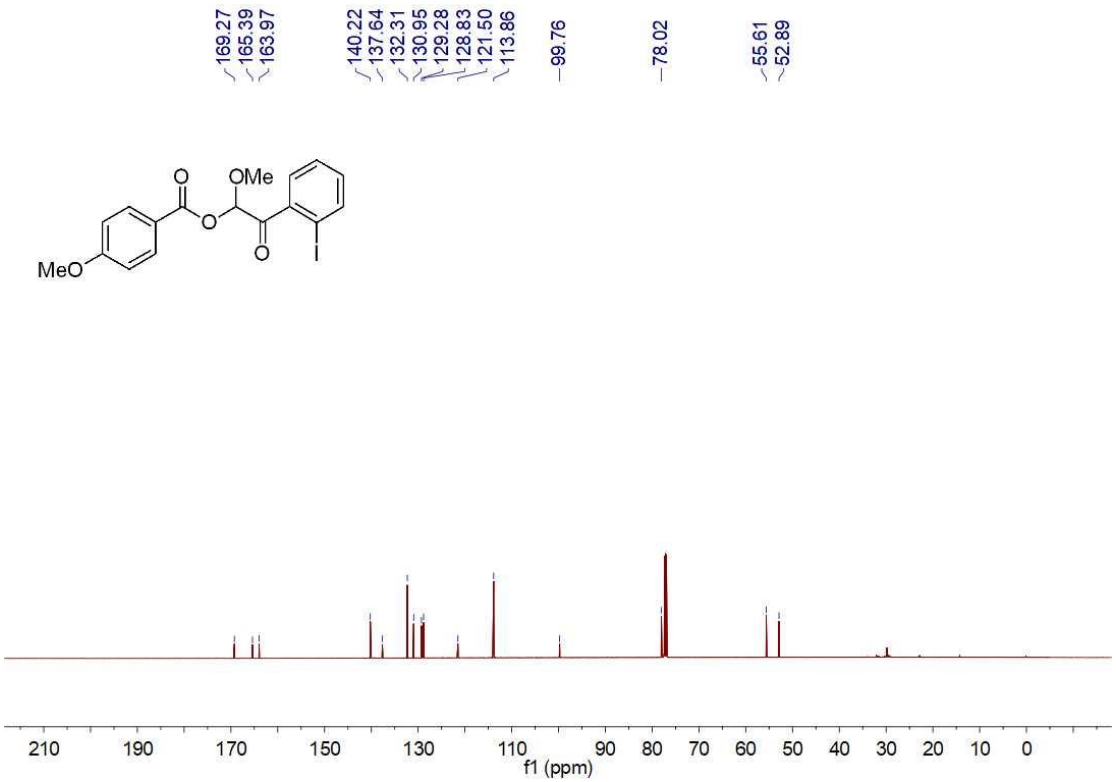
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4f**



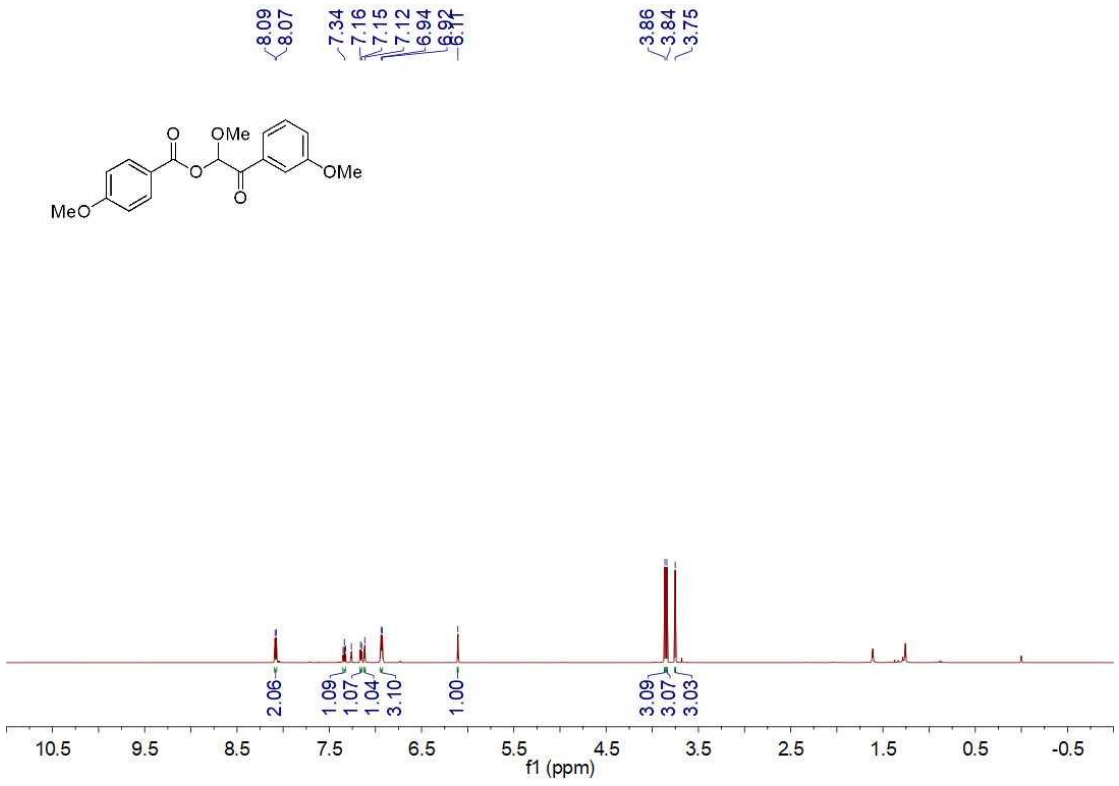
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4g**



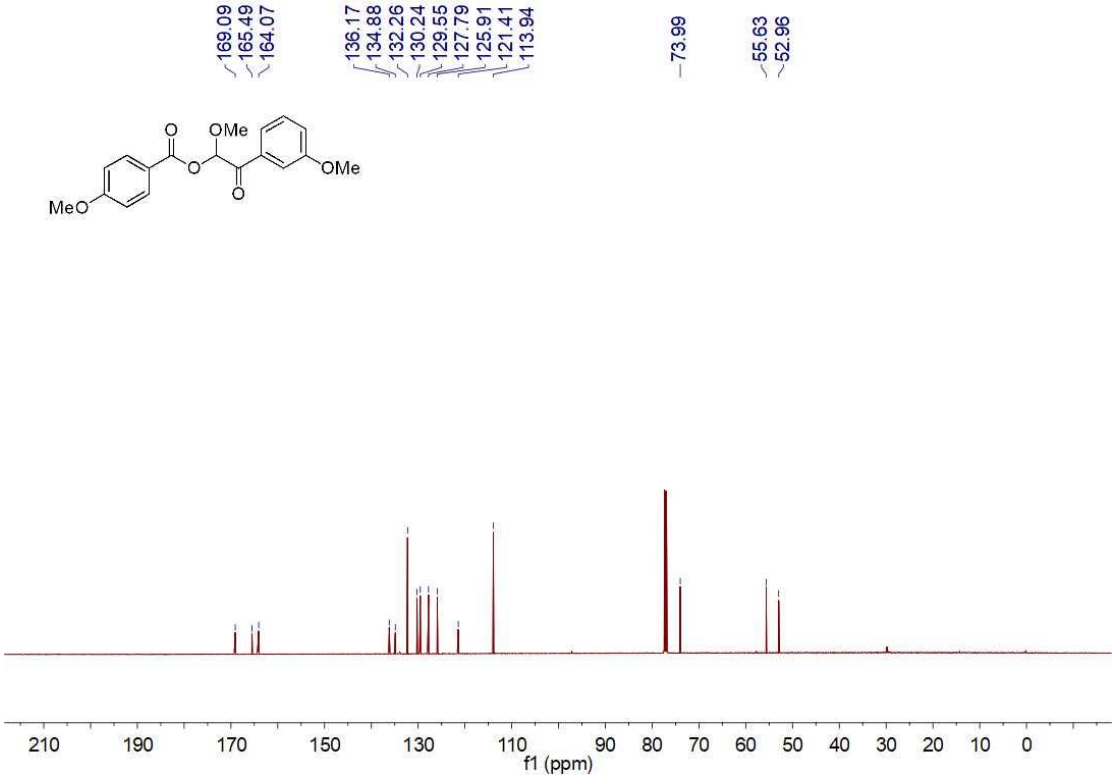
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4g**



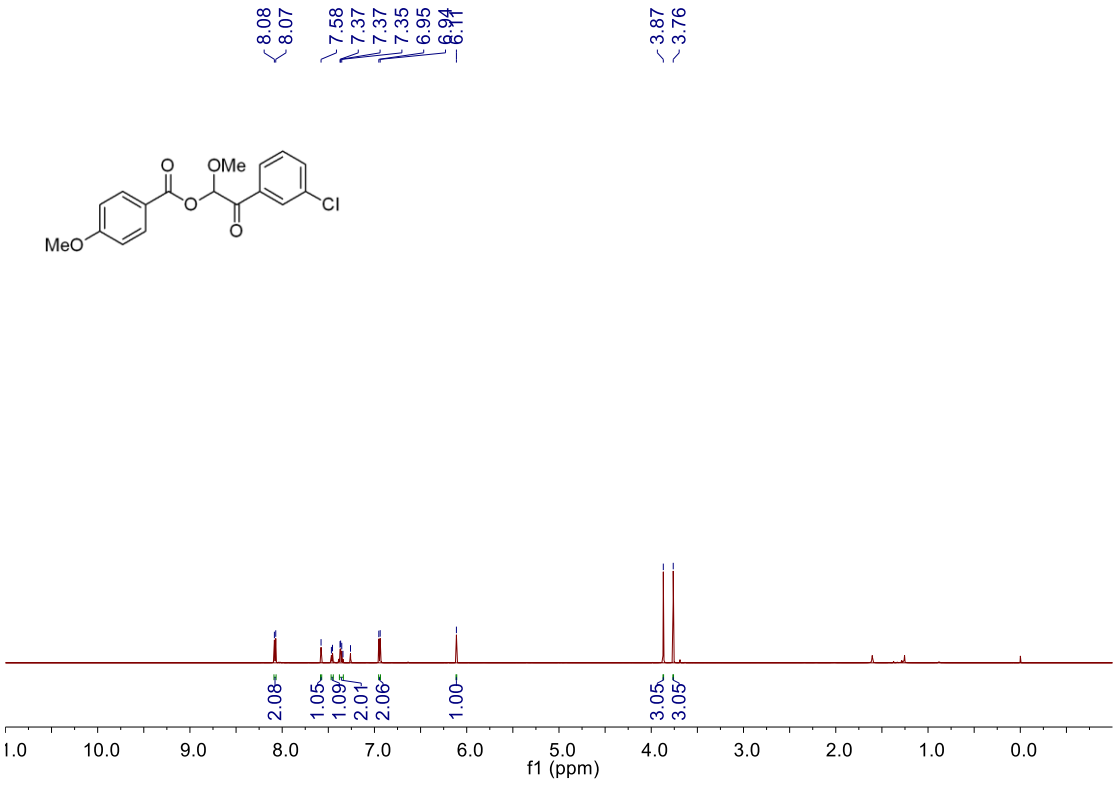
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4h**



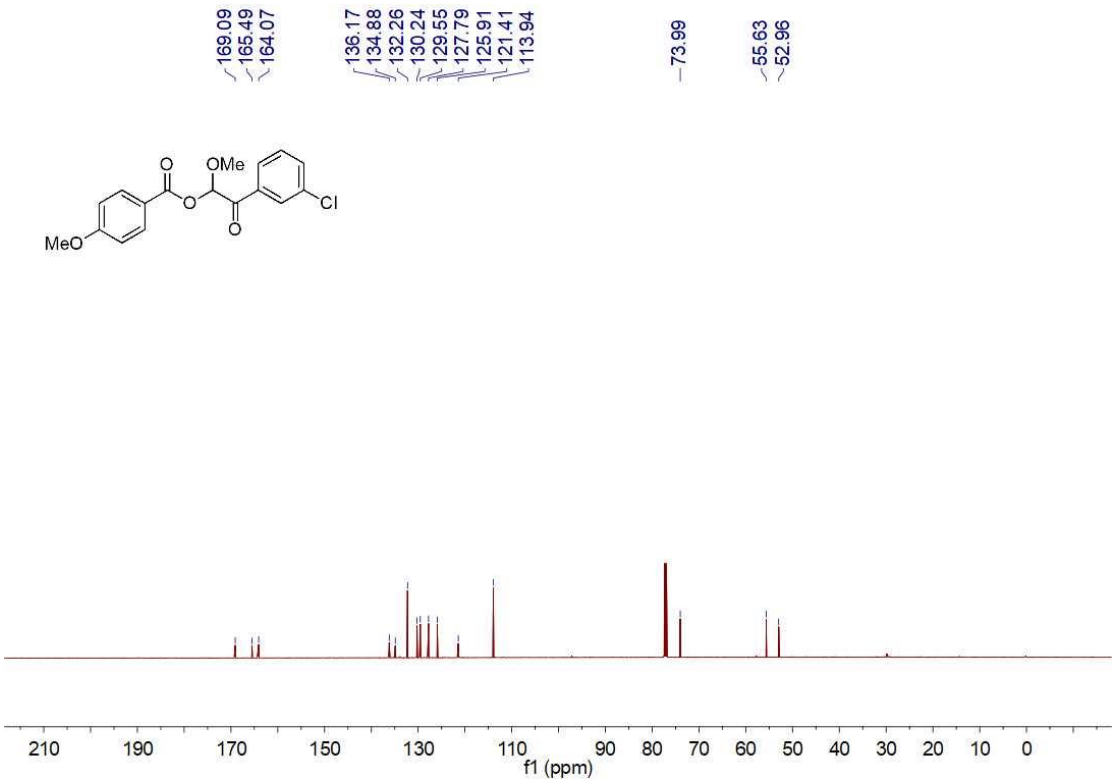
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4h**



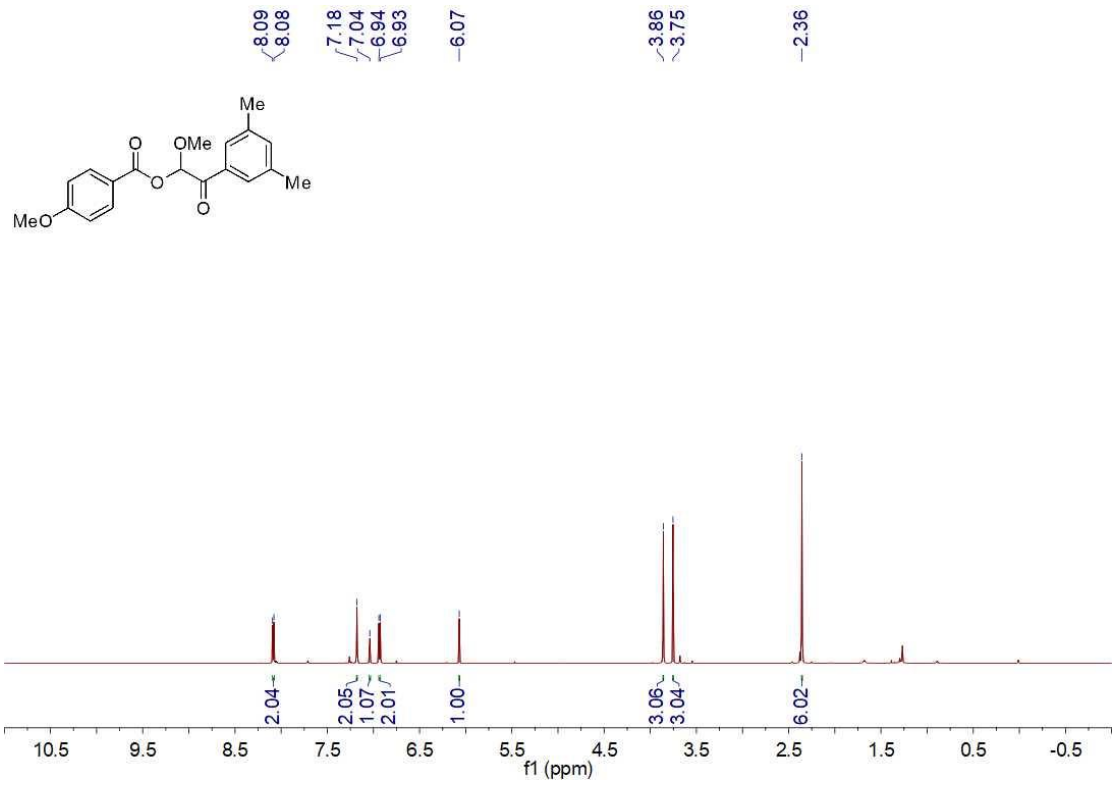
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4i**



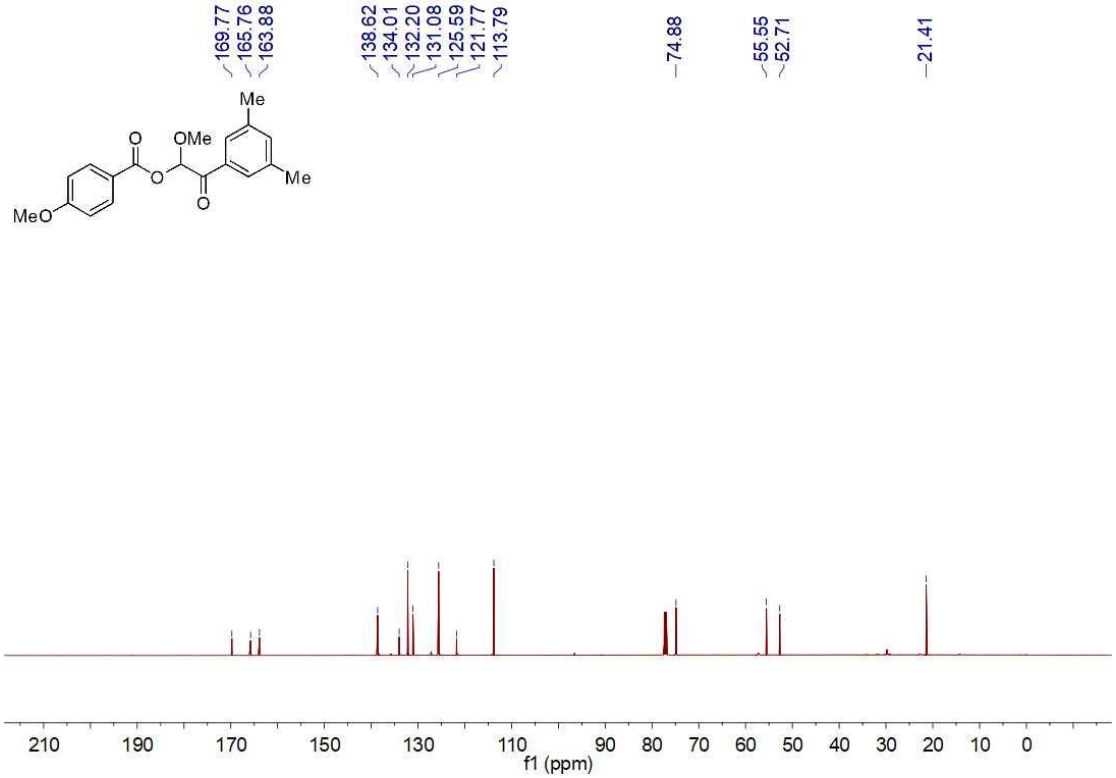
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4i**



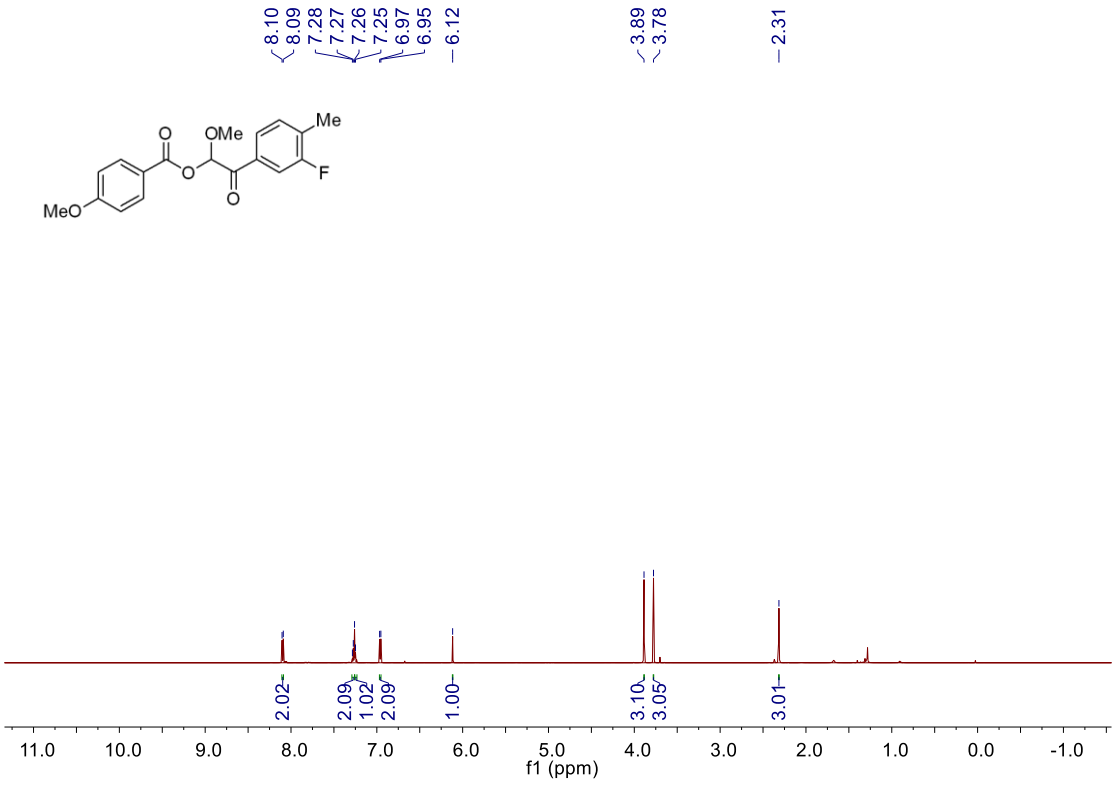
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4j**



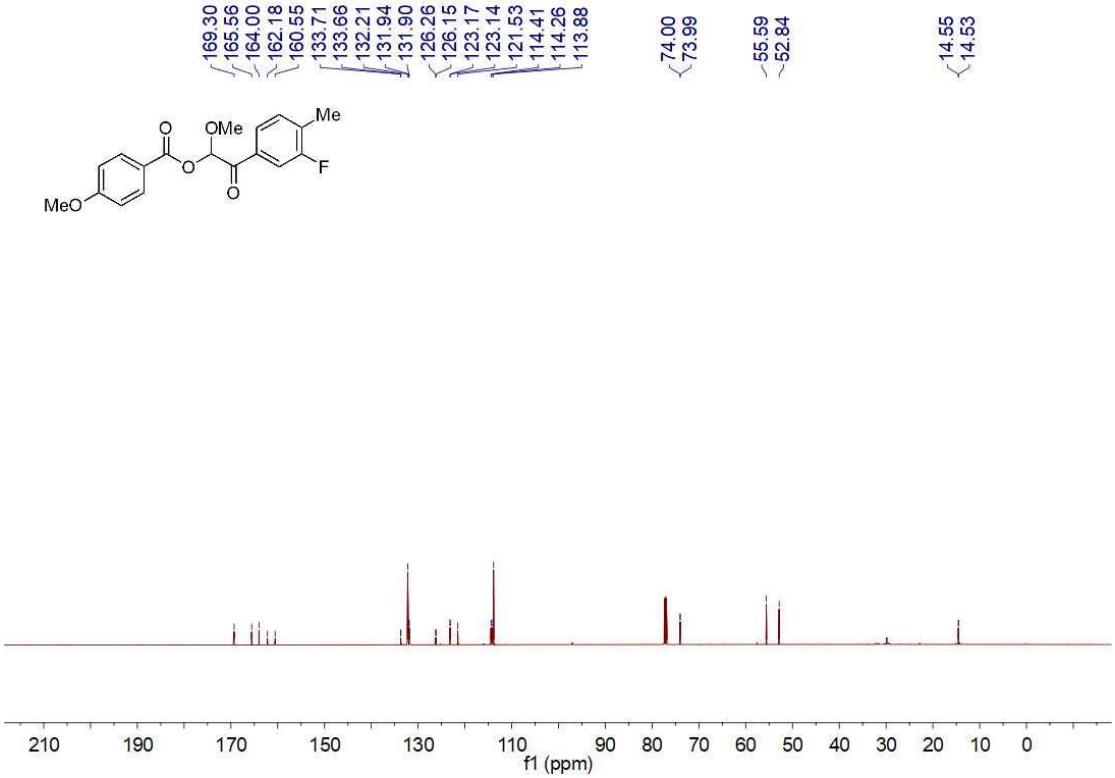
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4j**



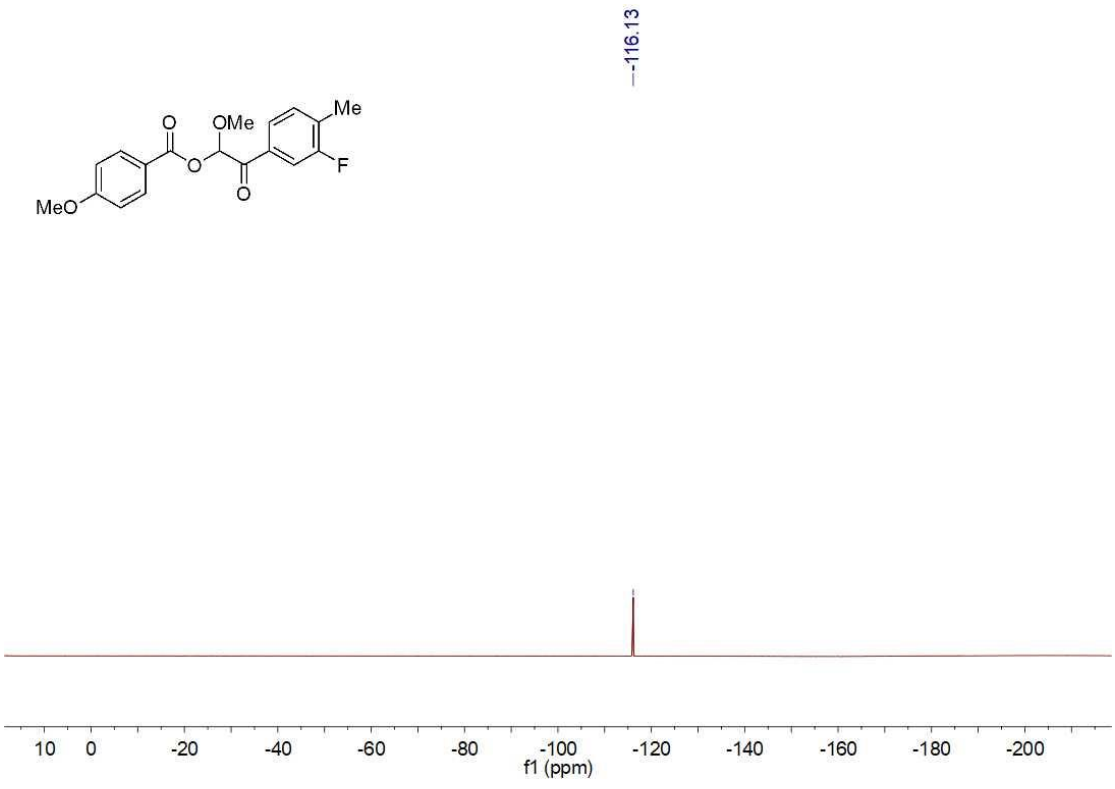
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4k**



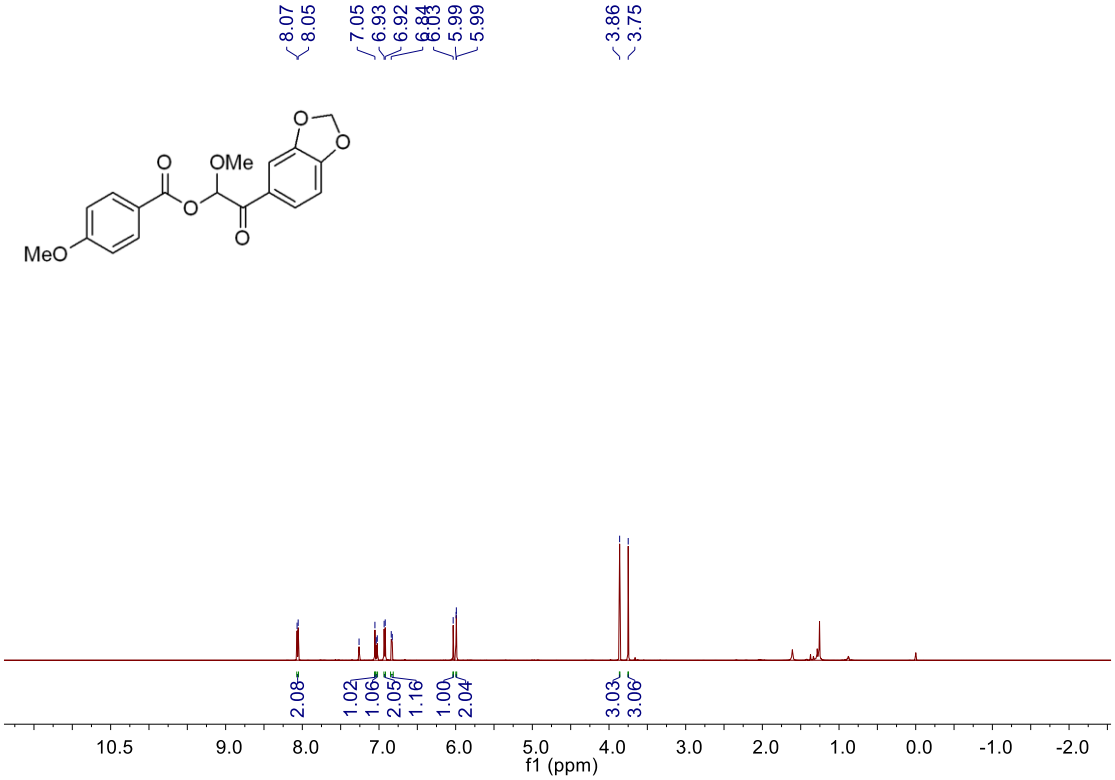
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4k**



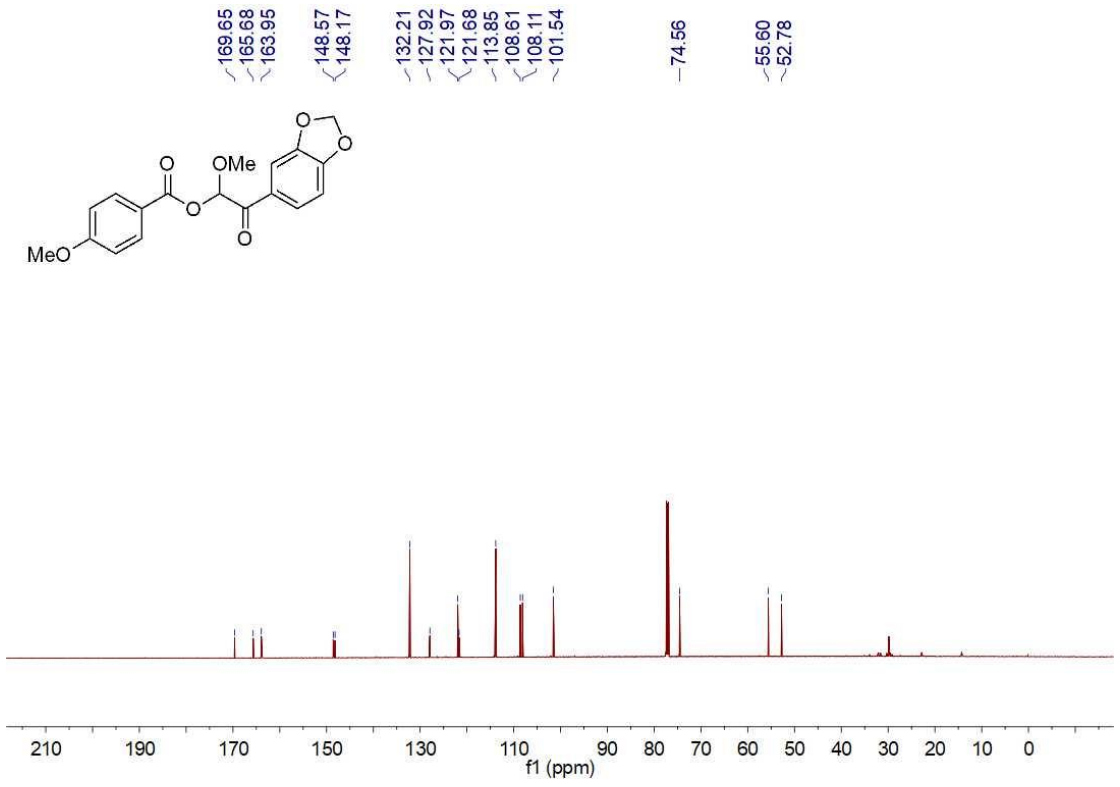
^{19}F NMR (376 MHz, $CDCl_3$) Spectra of **4k**



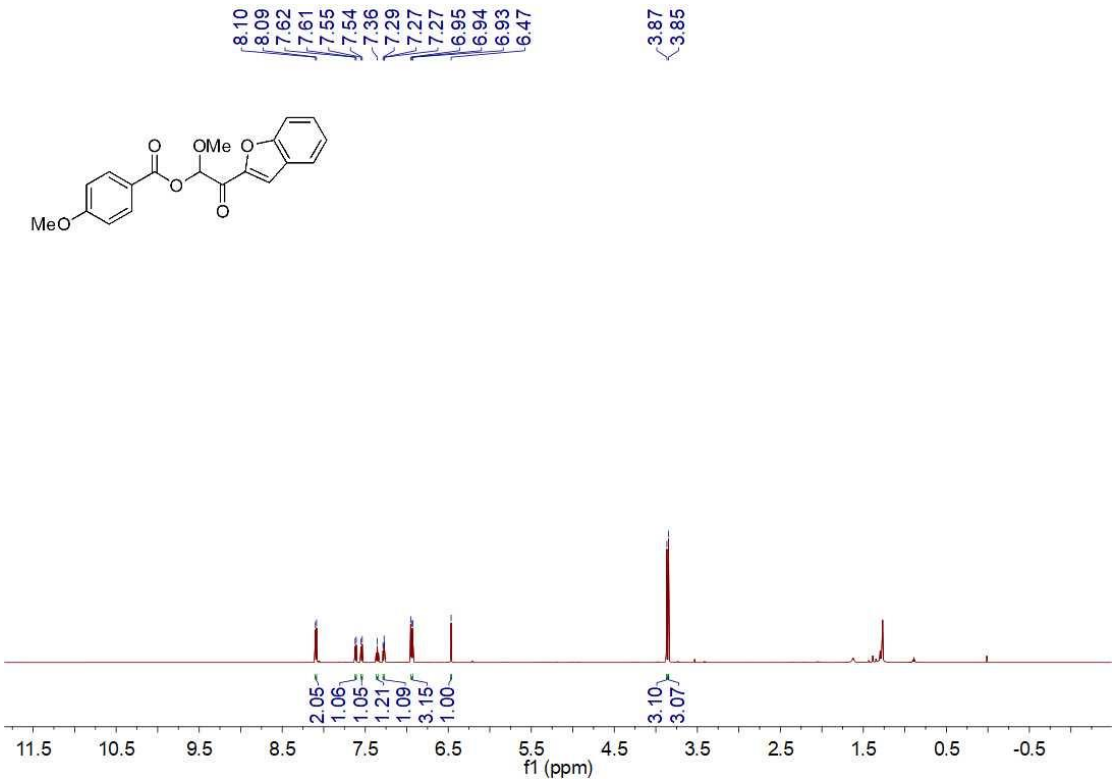
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4l**



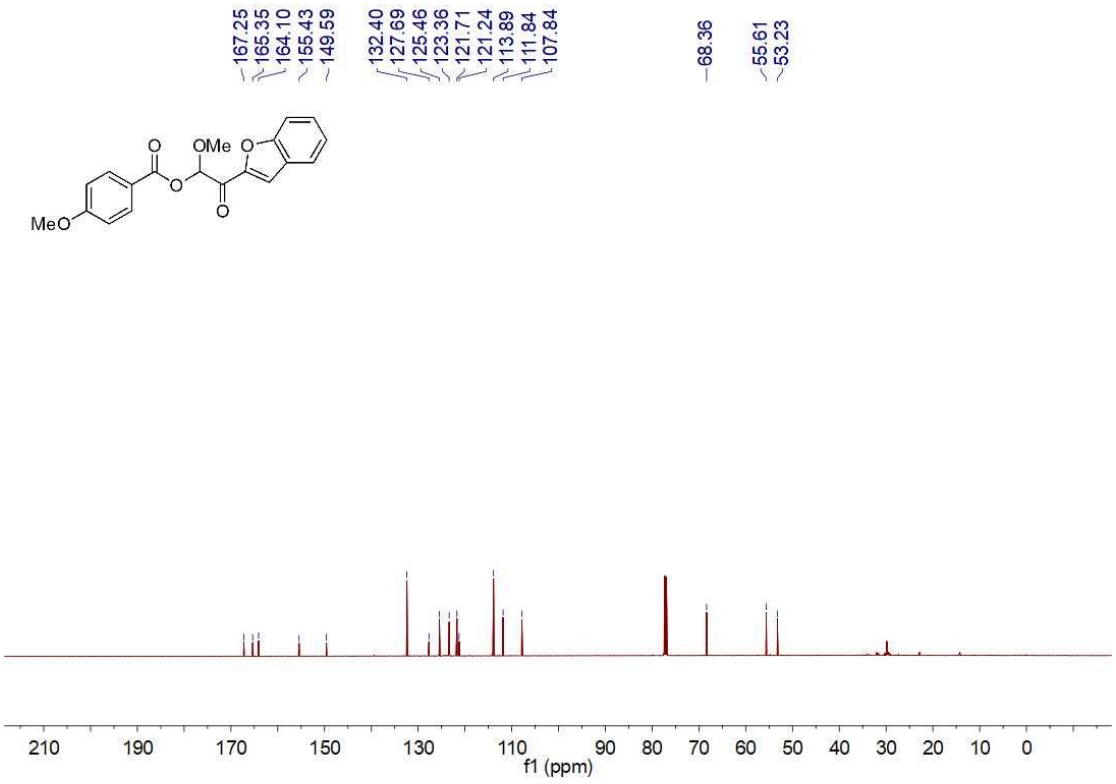
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4l**



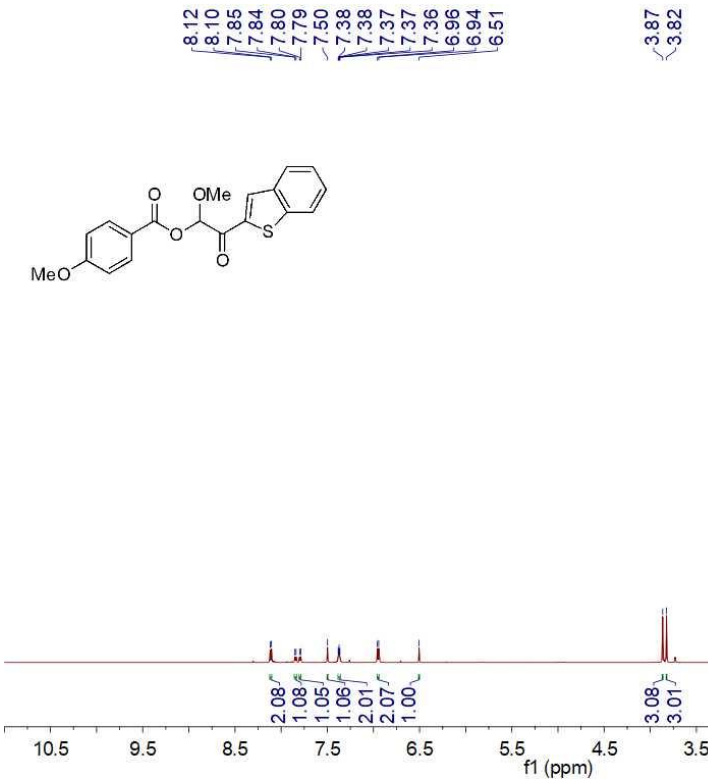
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4m**



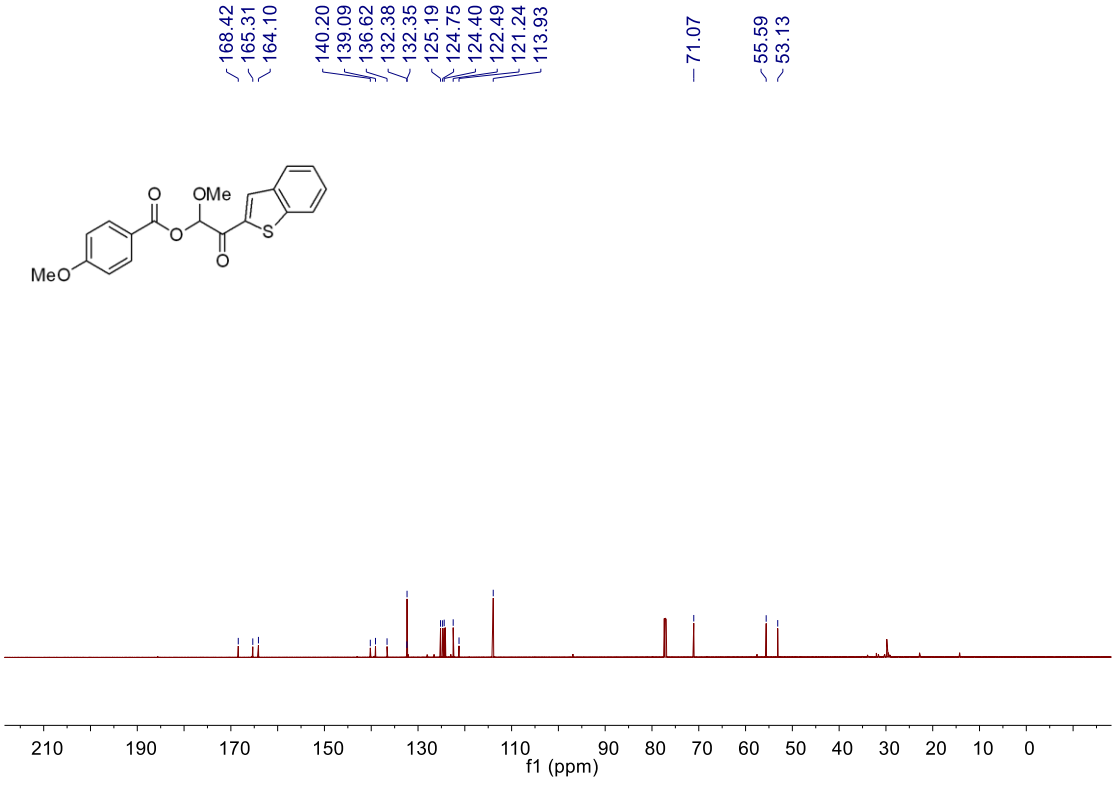
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4m**



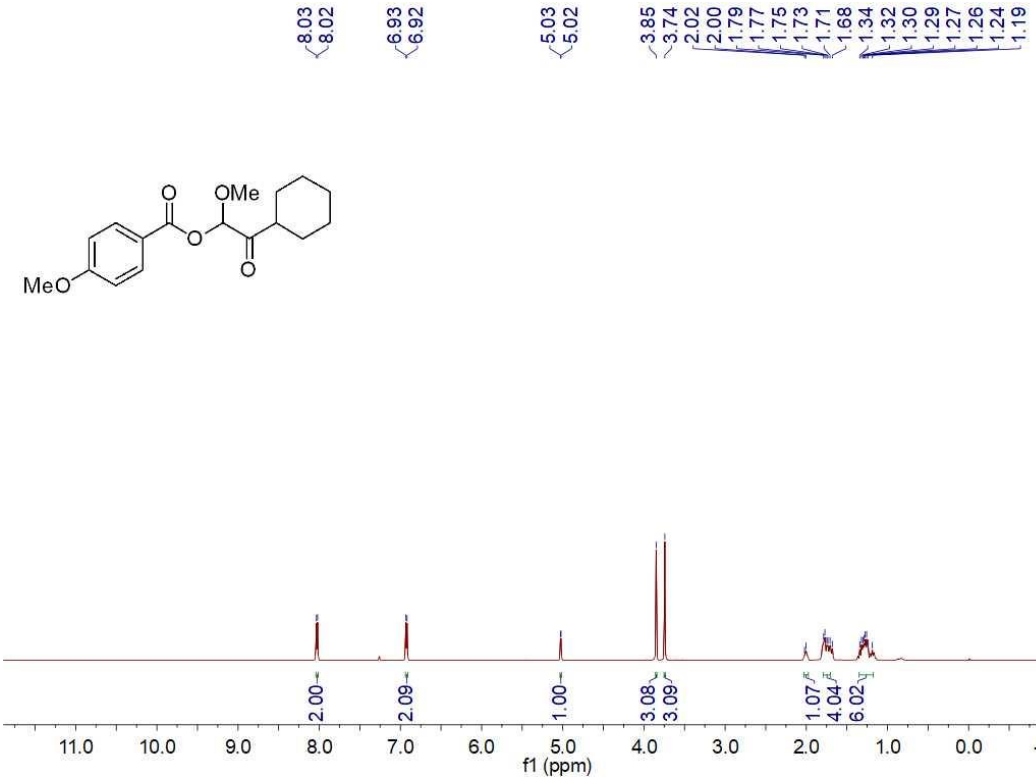
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4n**



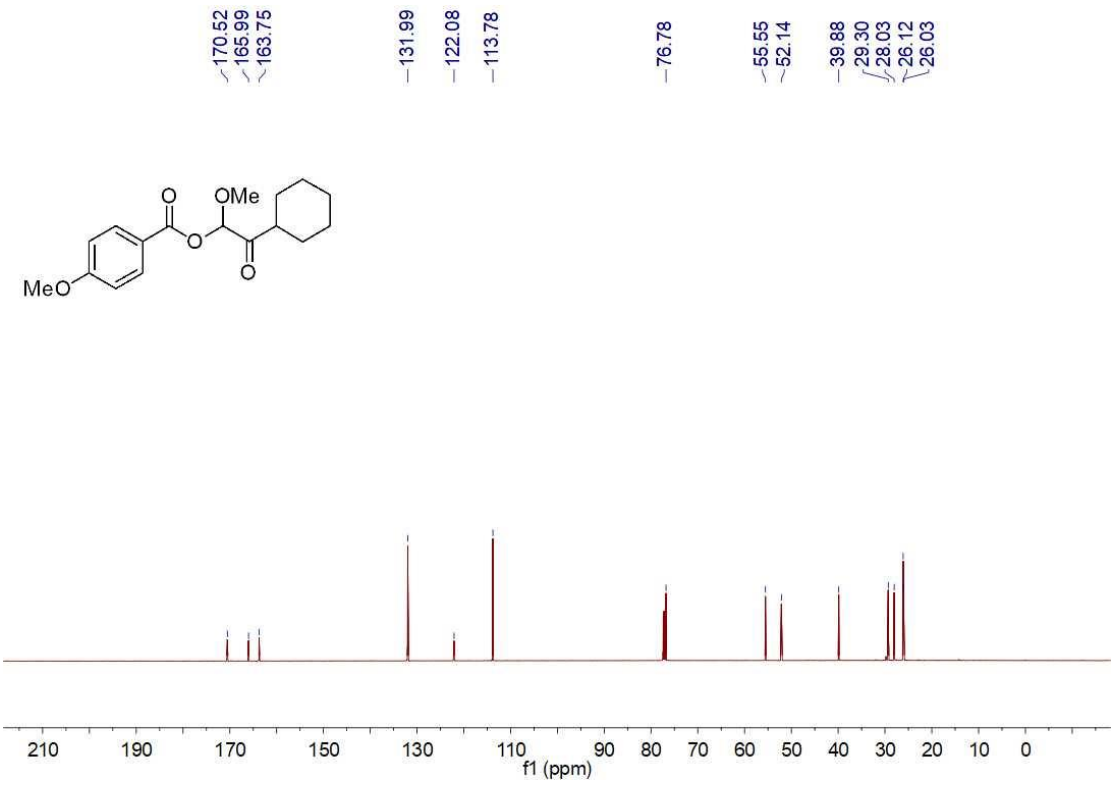
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4n**



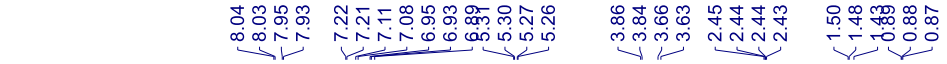
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4o**

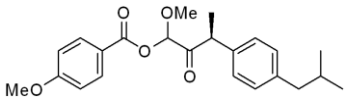


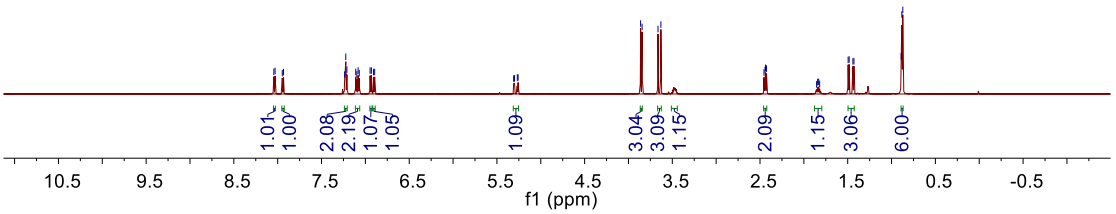
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4o**



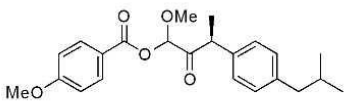
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **4p**

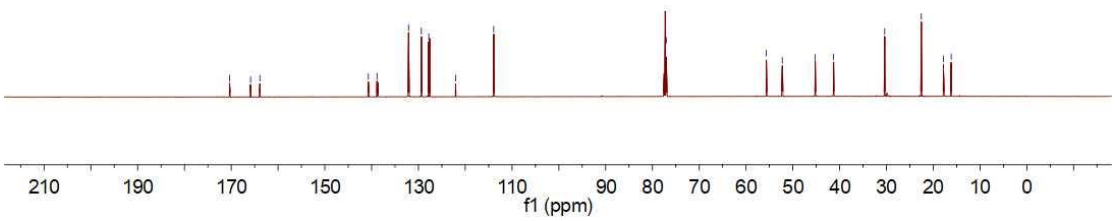




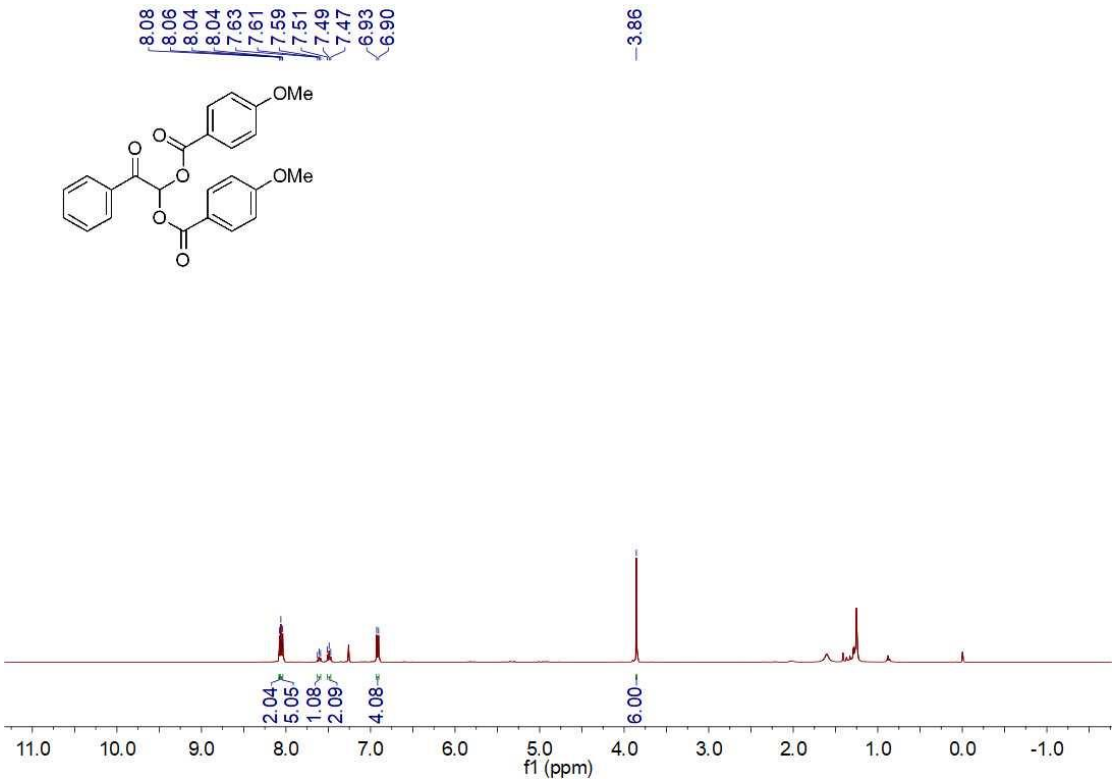


^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **4p**

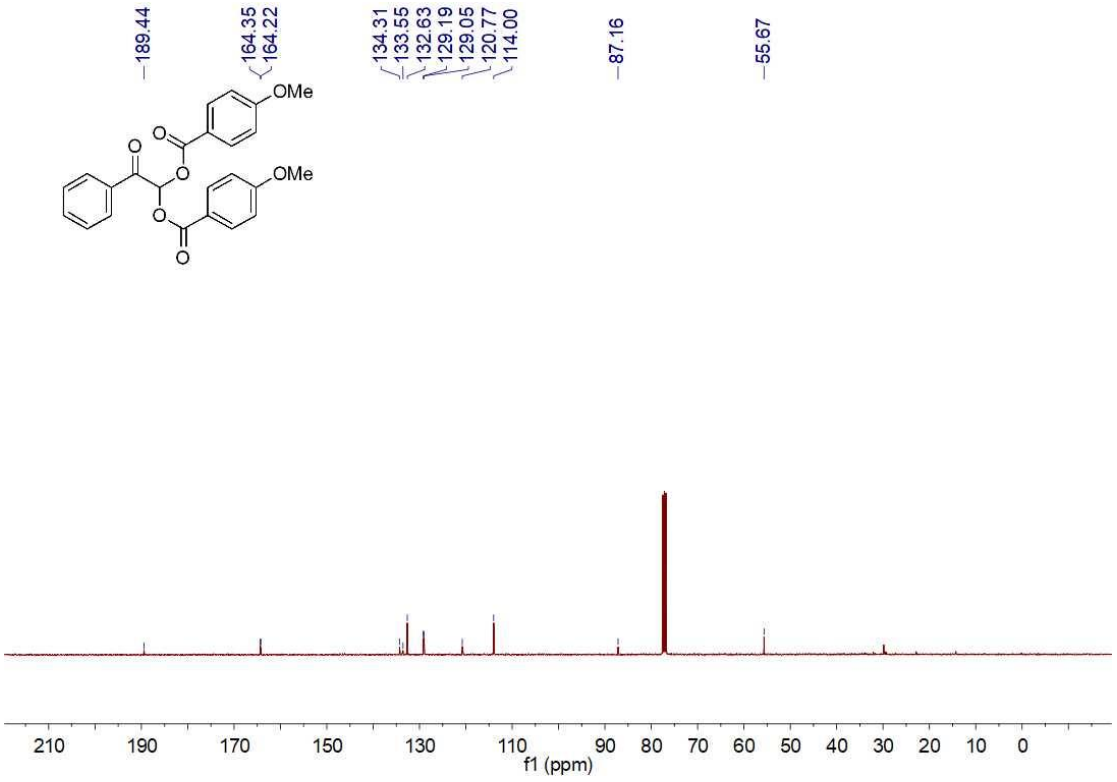




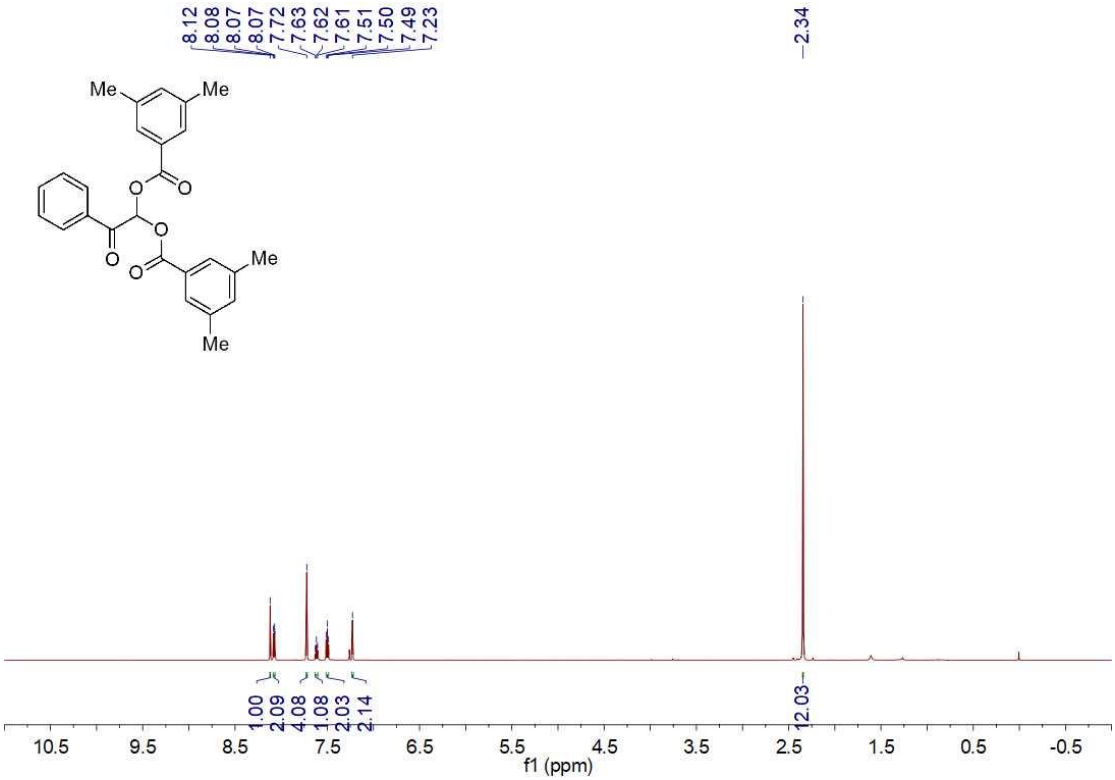
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **5a**



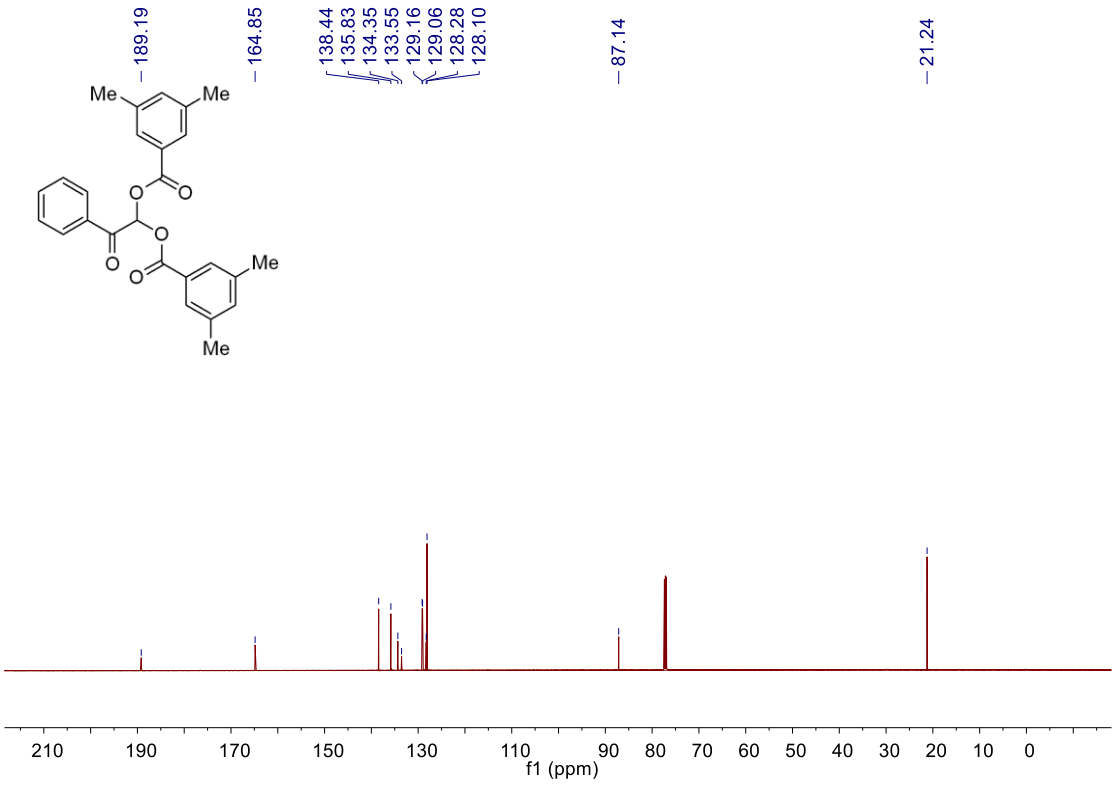
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **5a**



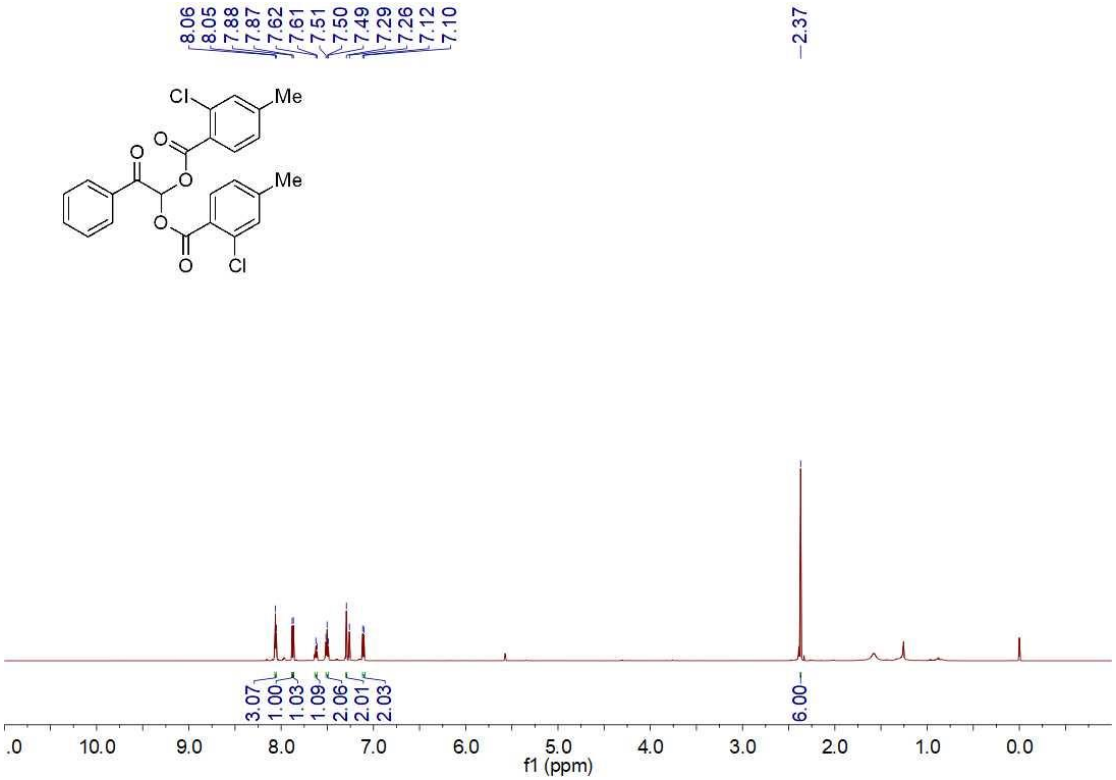
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **5b**



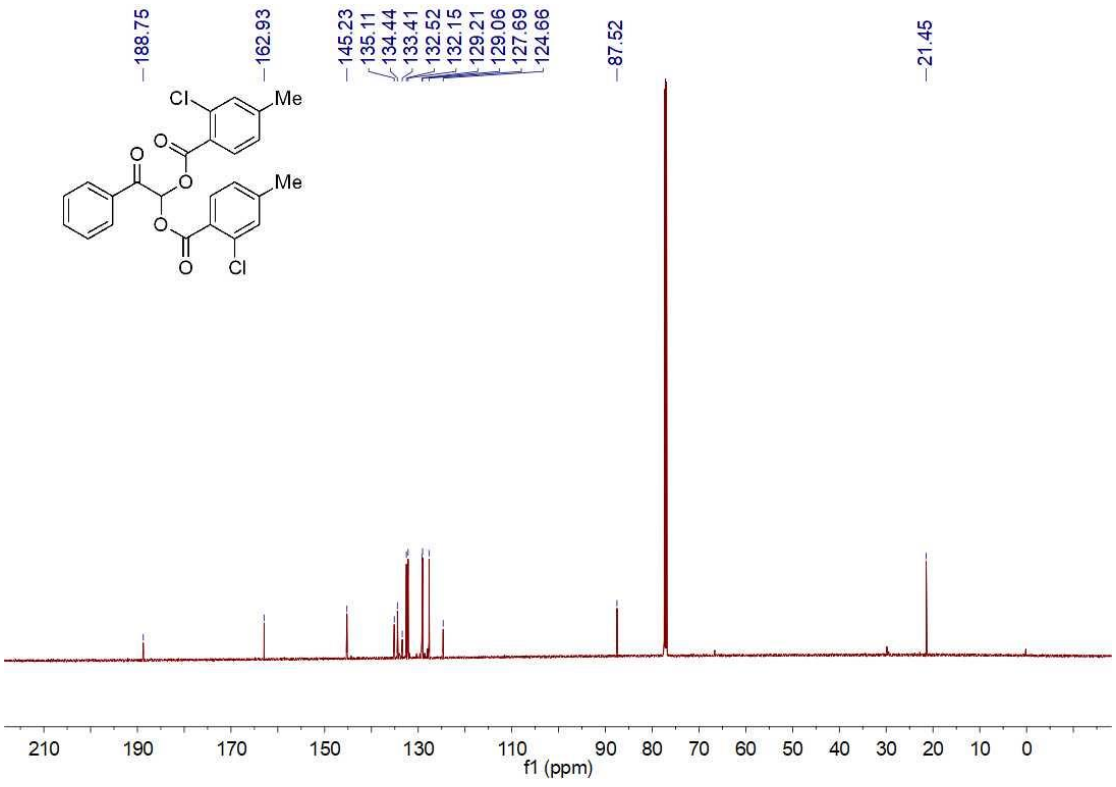
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **5b**



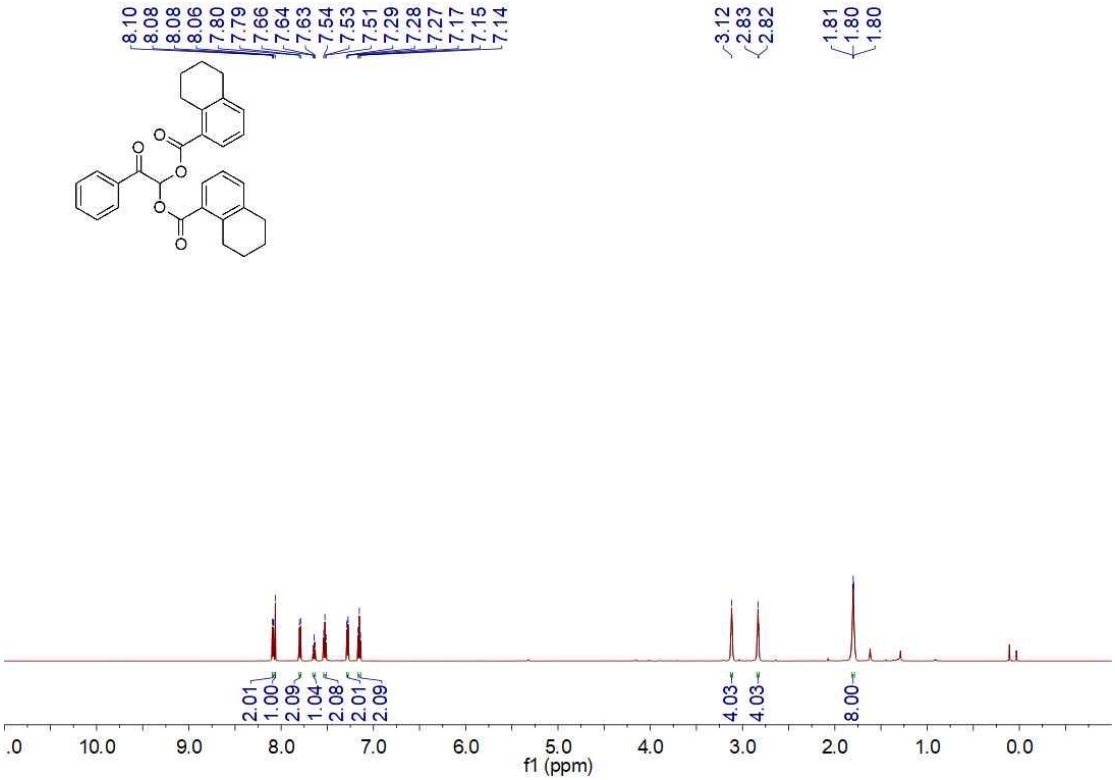
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **5c**



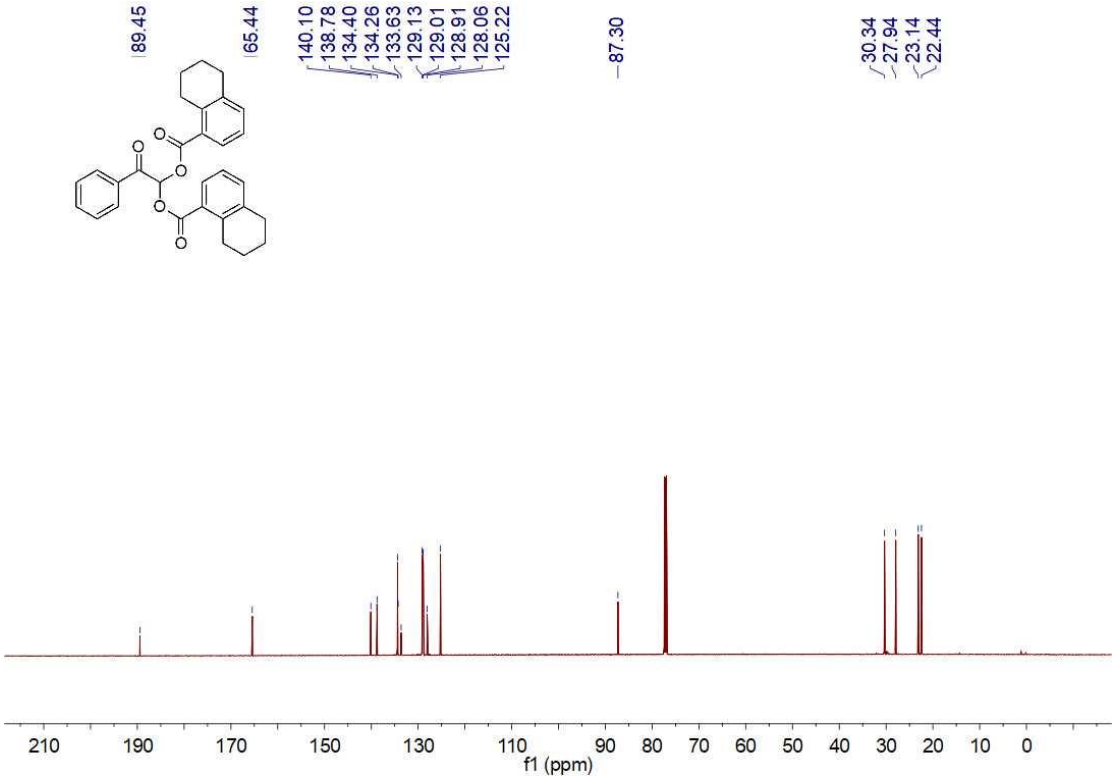
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **5c**



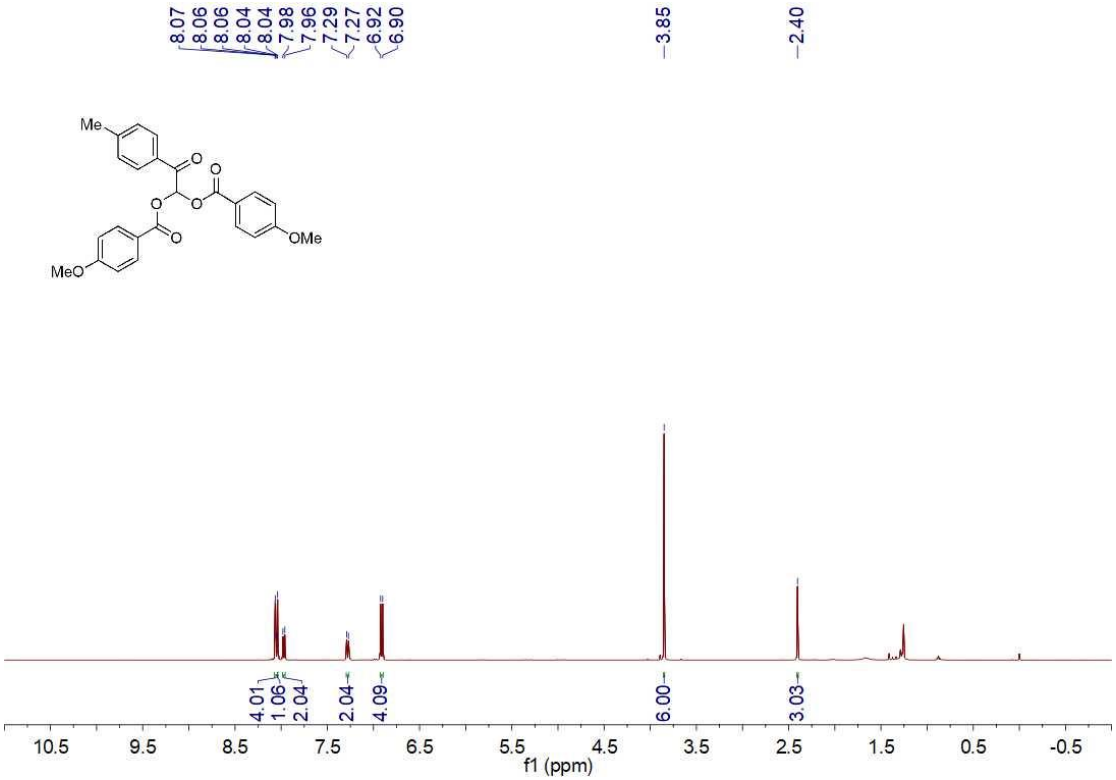
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **5d**



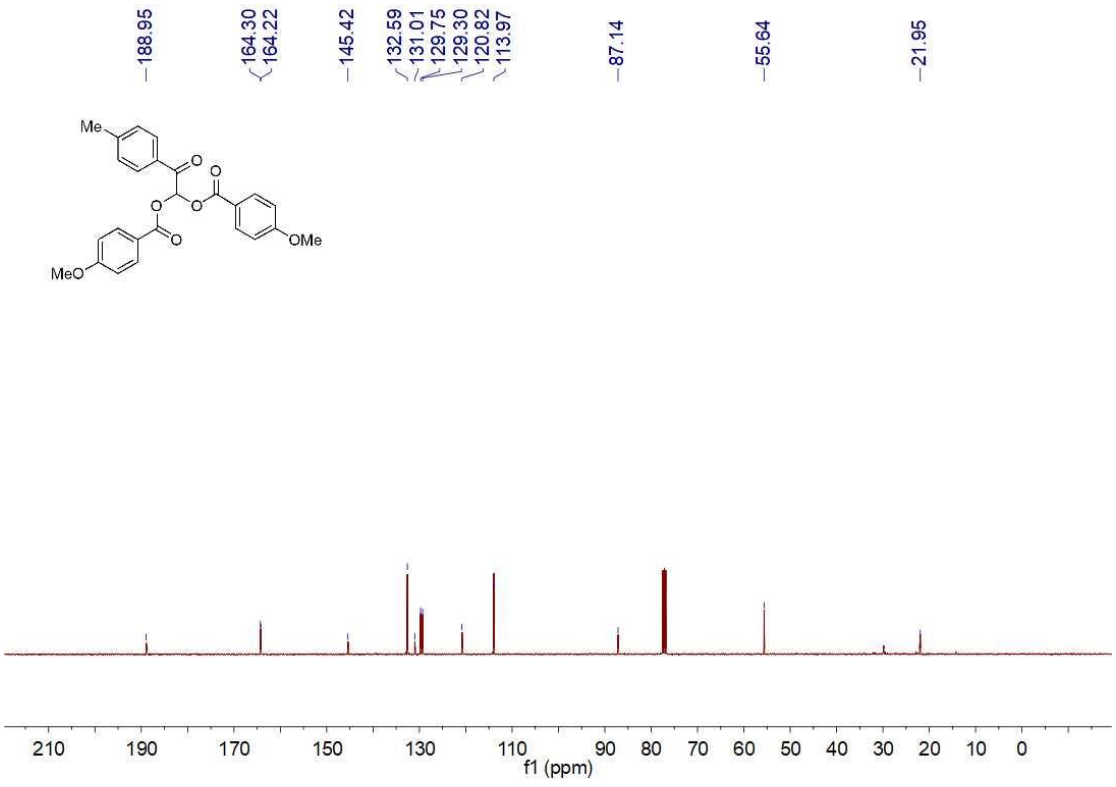
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **5d**



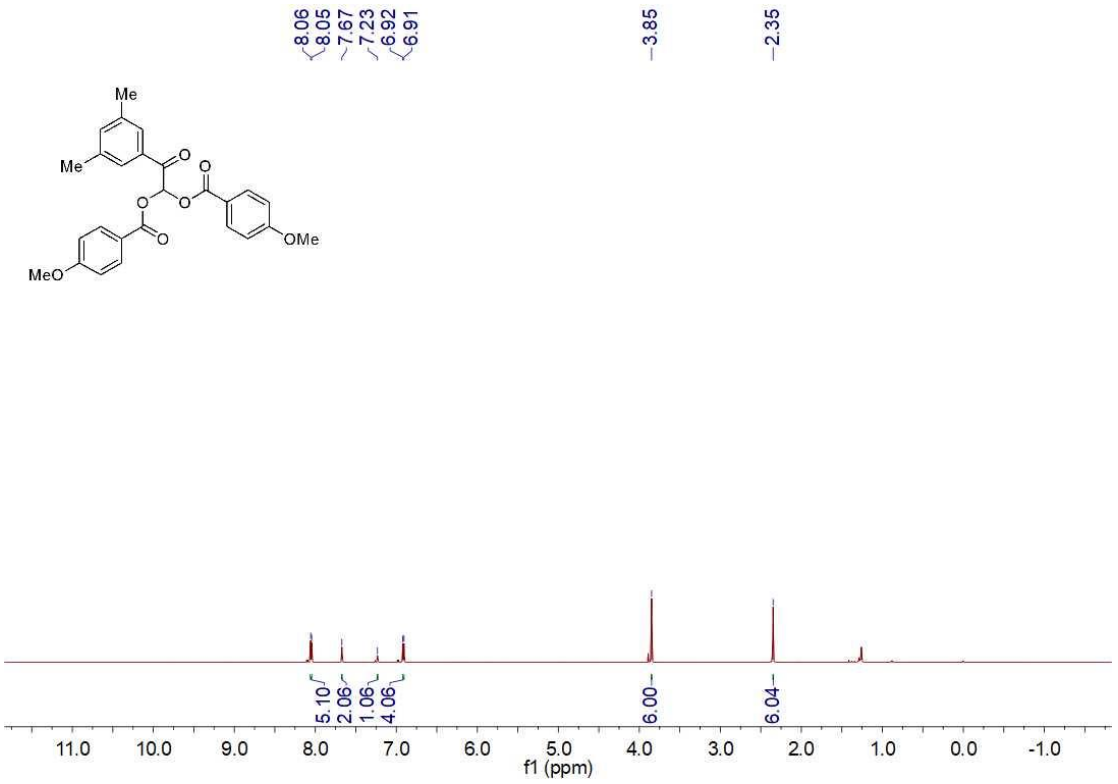
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **5i**



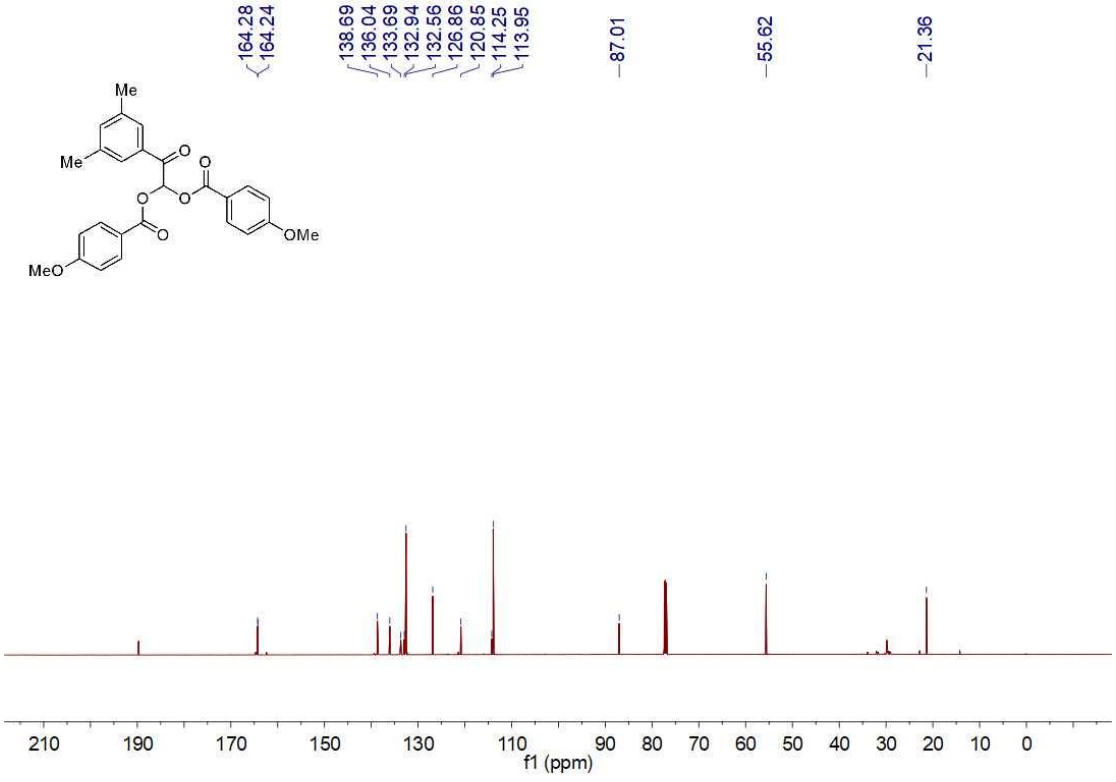
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **5i**



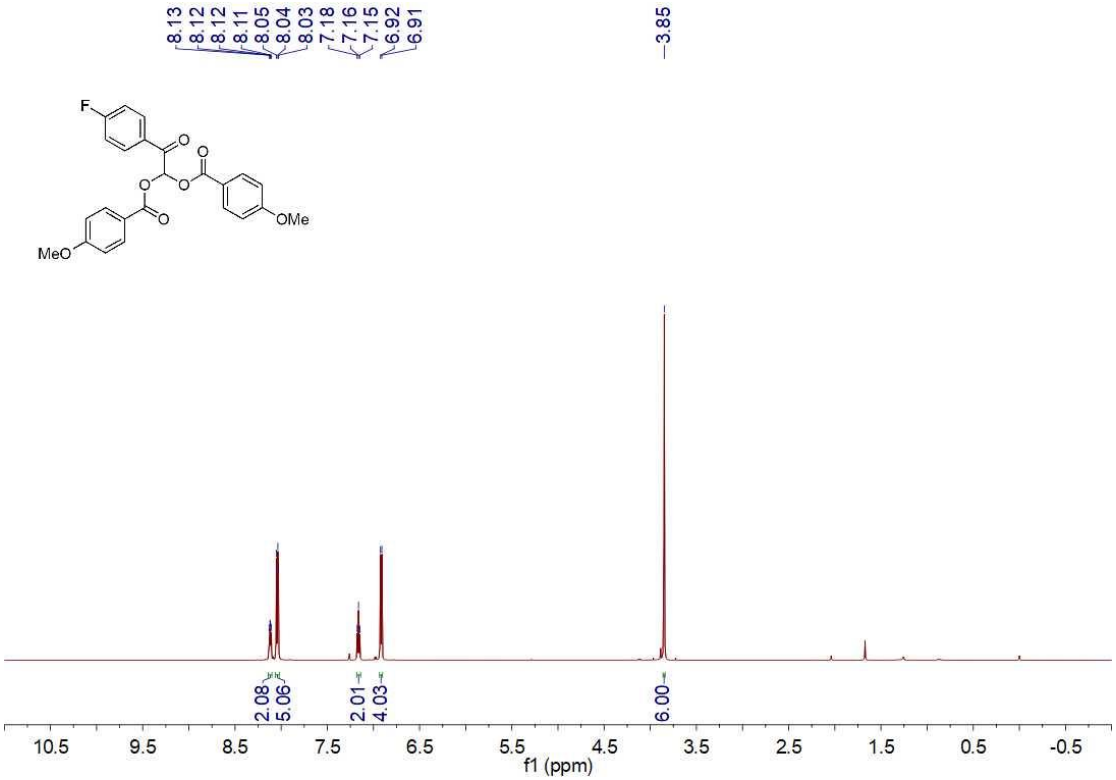
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **5j**



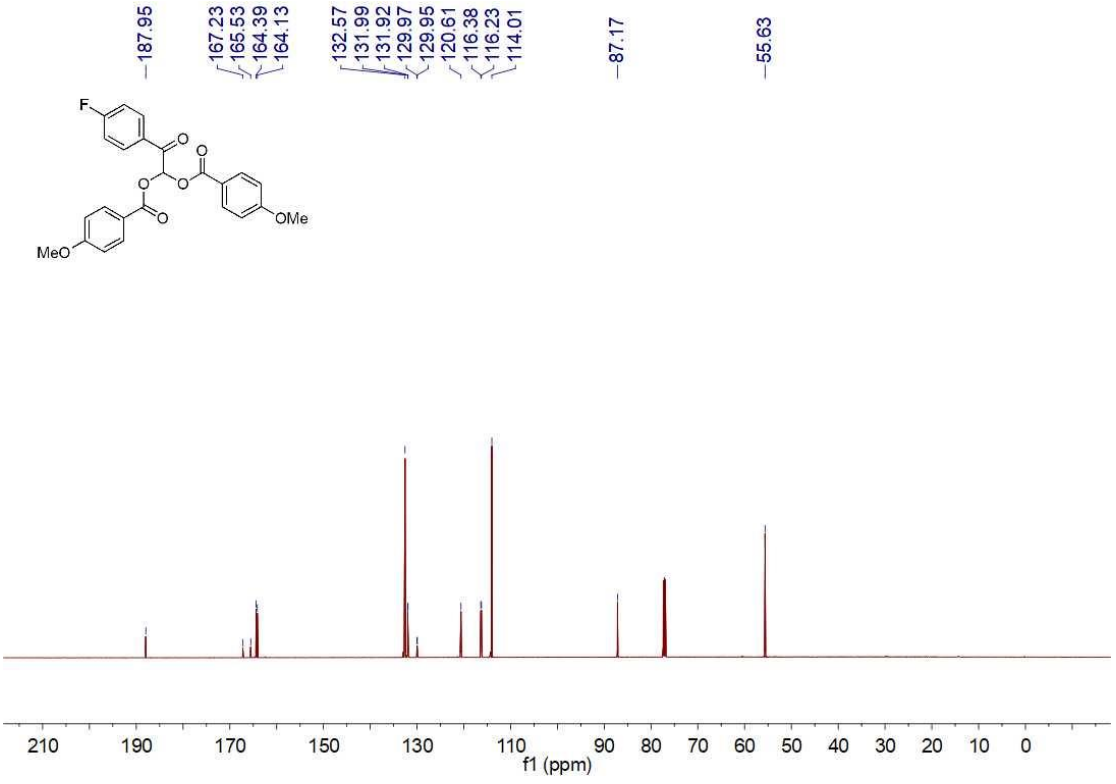
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **5j**



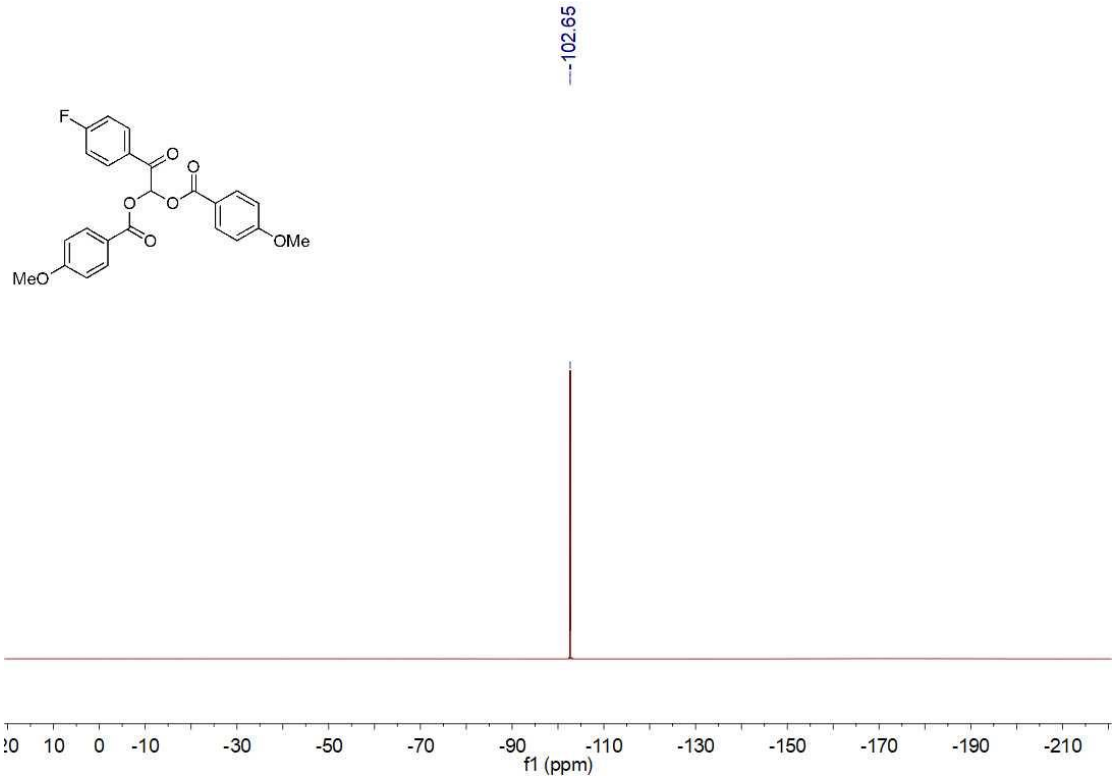
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **5k**



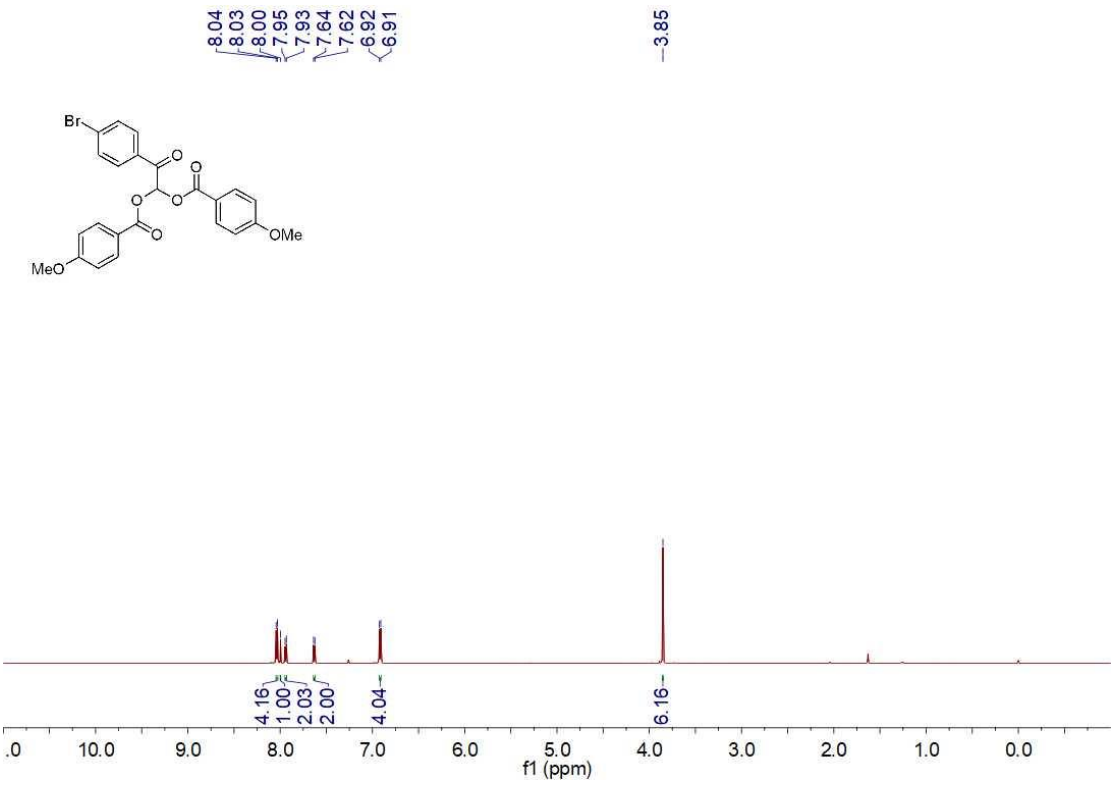
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **5k**



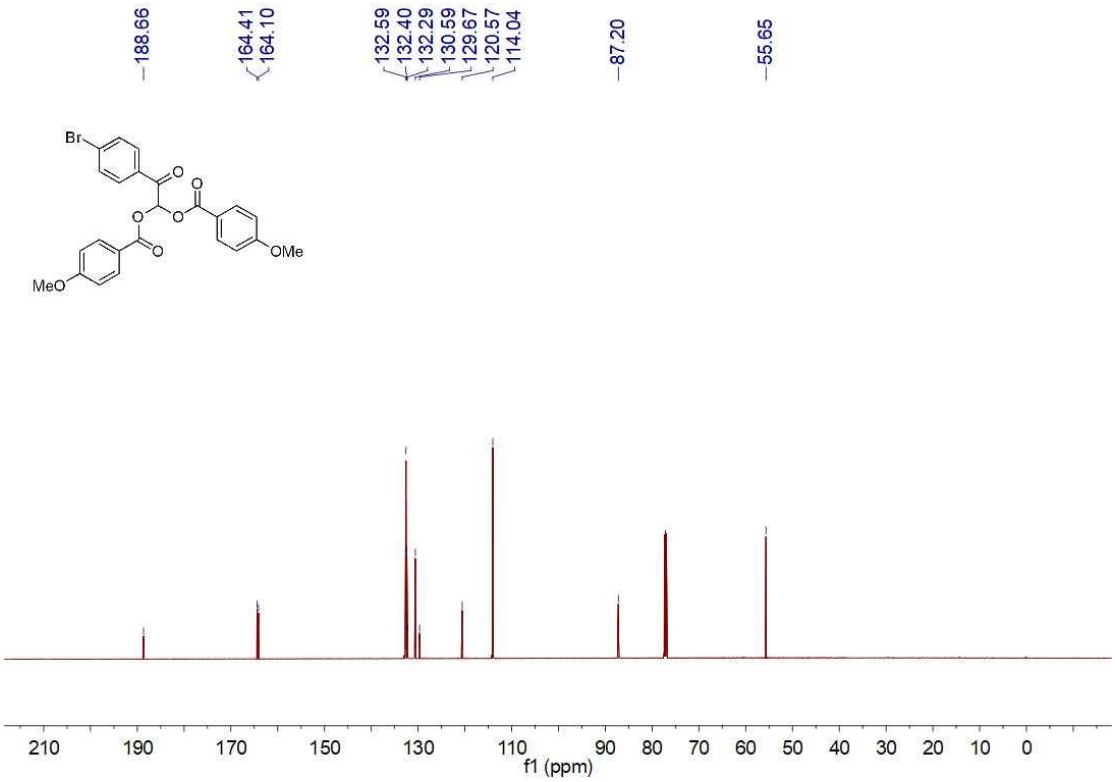
^{19}F NMR (377 MHz, $CDCl_3$) Spectra of **5k**



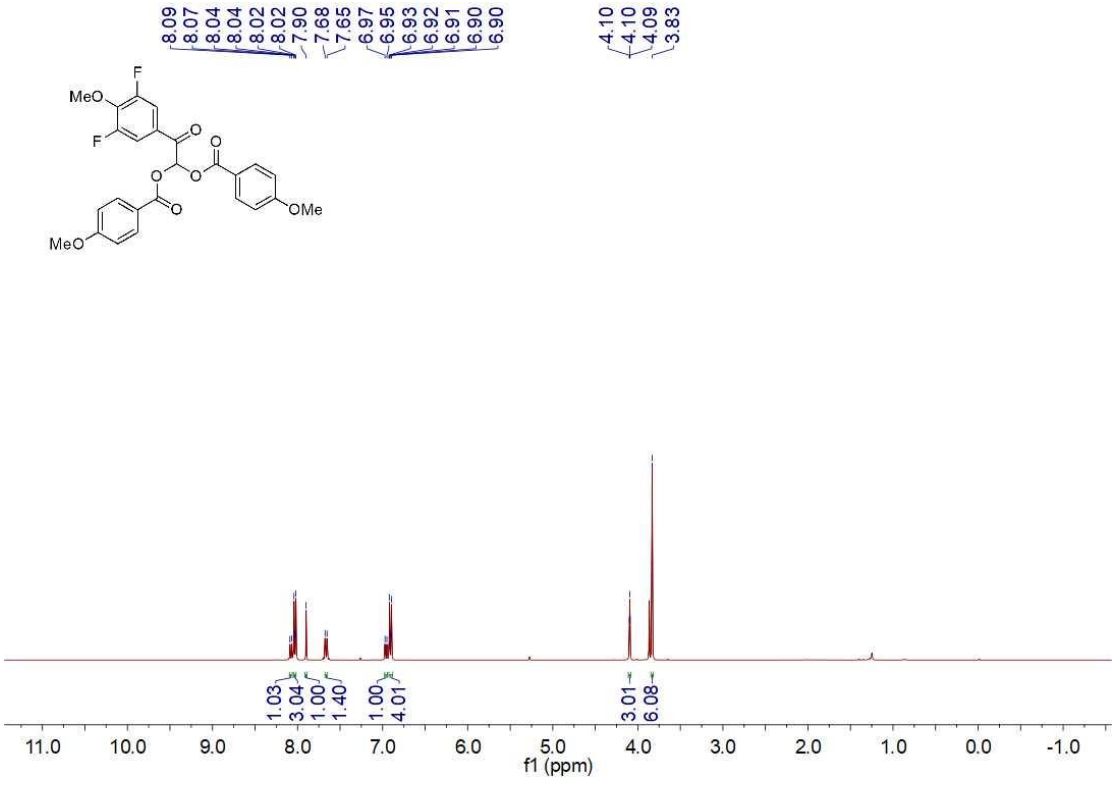
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **5l**



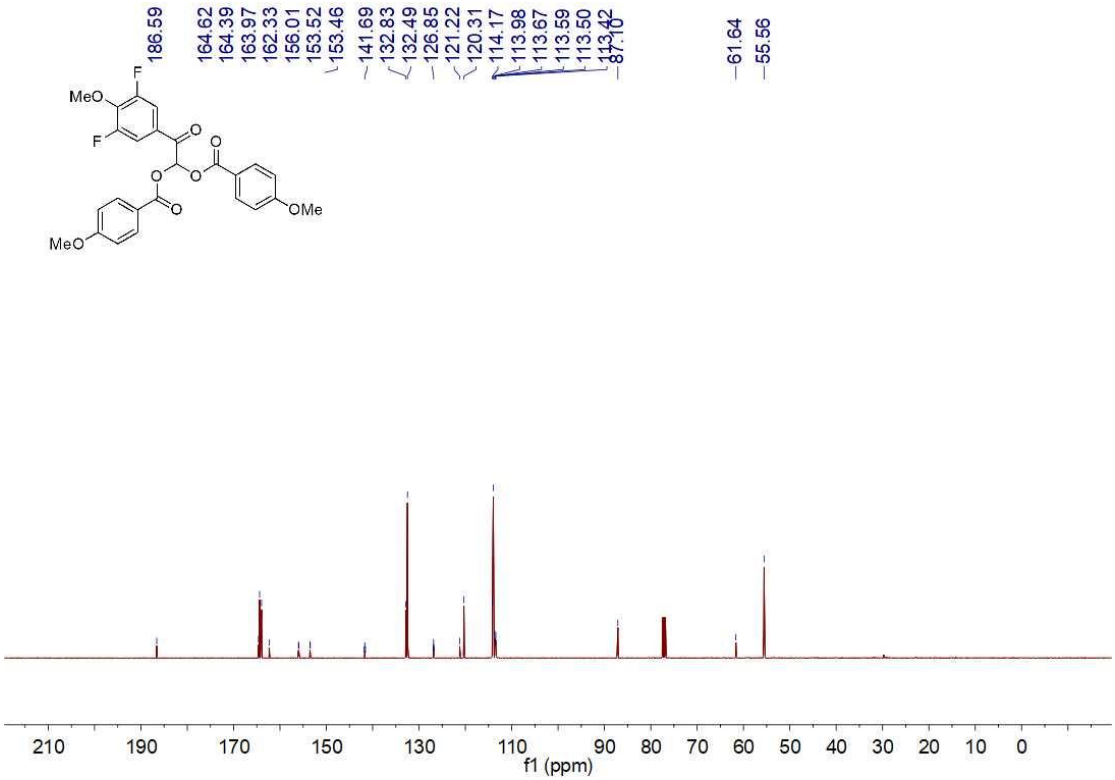
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **5l**



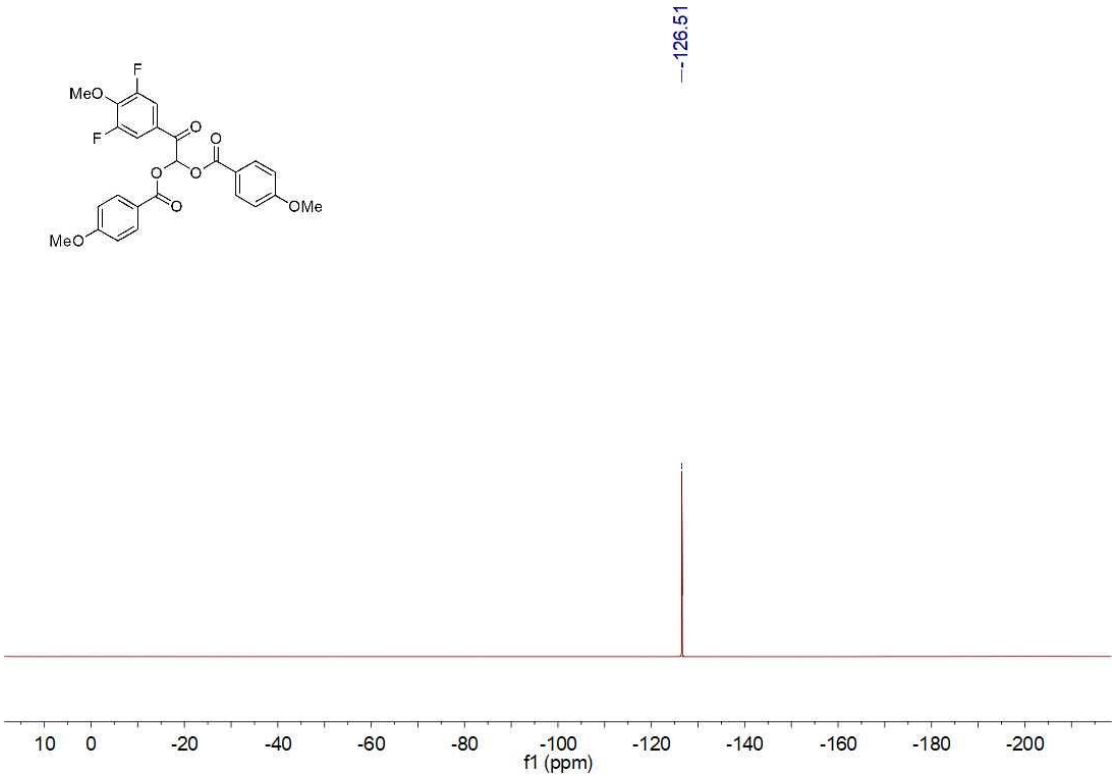
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of **5m**



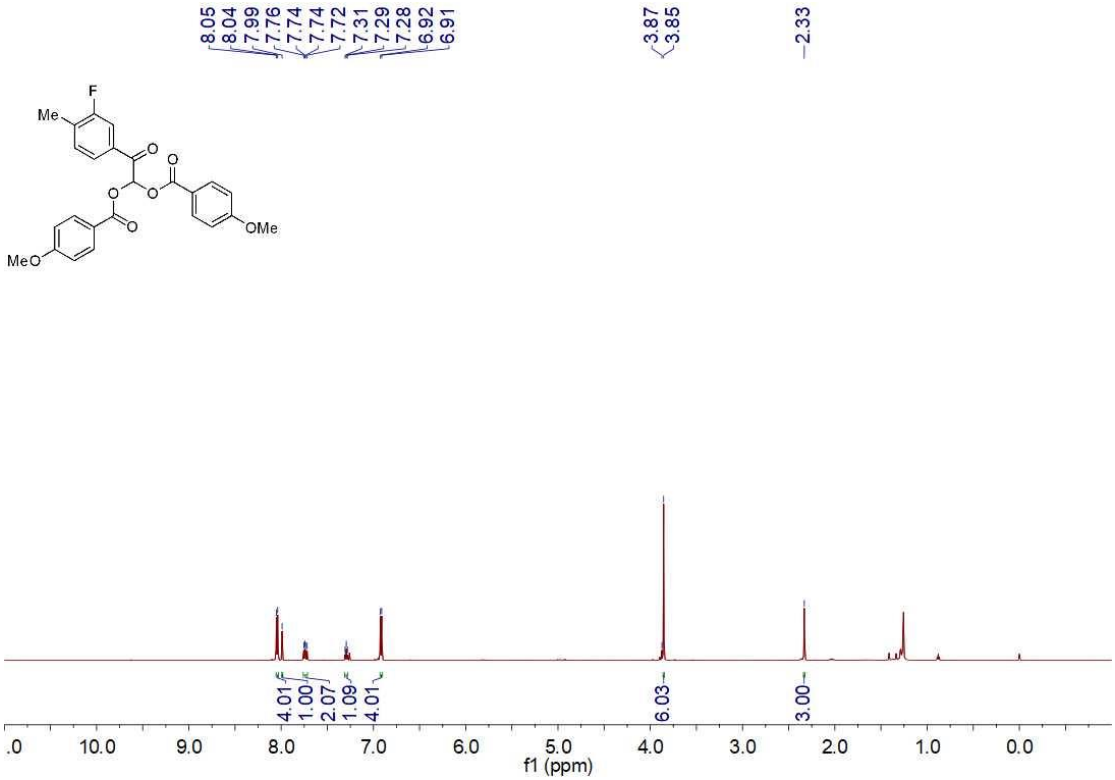
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of **5m**



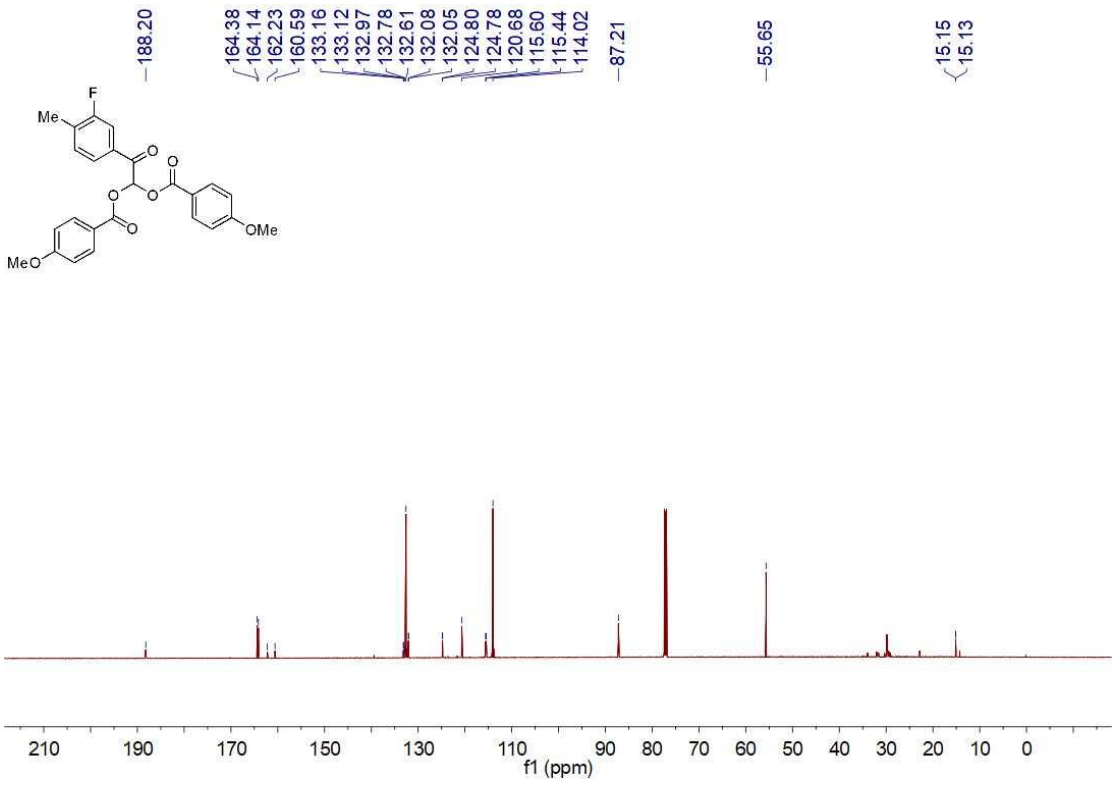
^{19}F NMR (376 MHz, $CDCl_3$) Spectra of **5m**



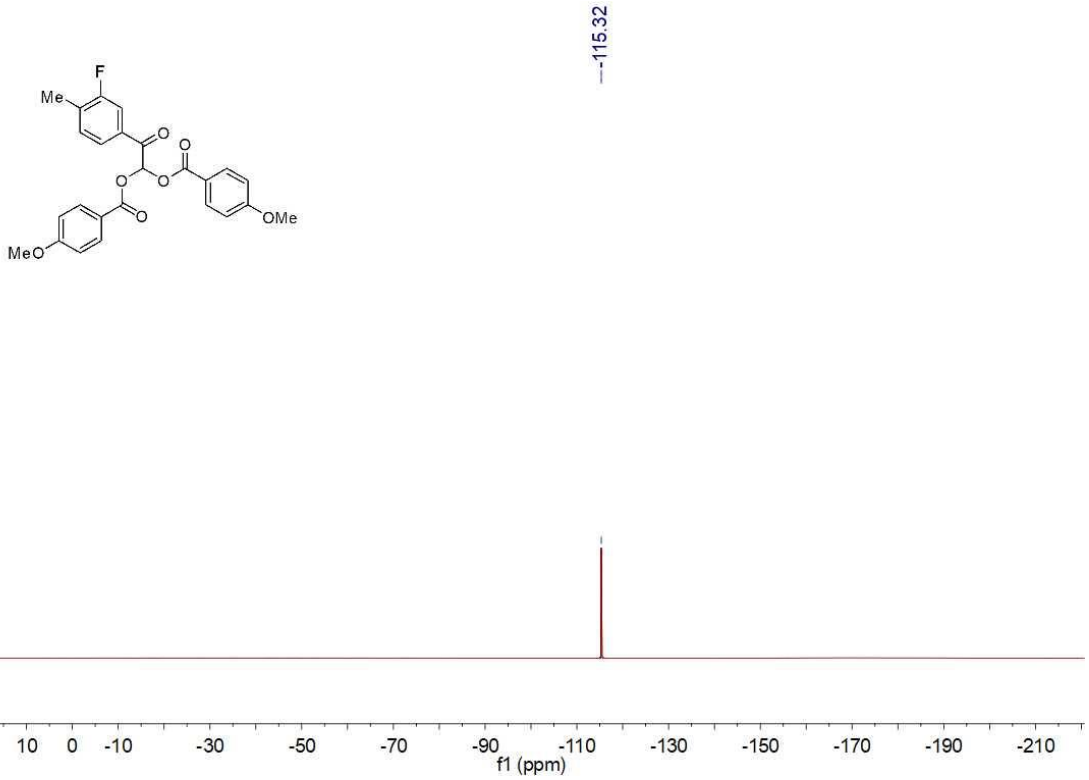
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **5n**



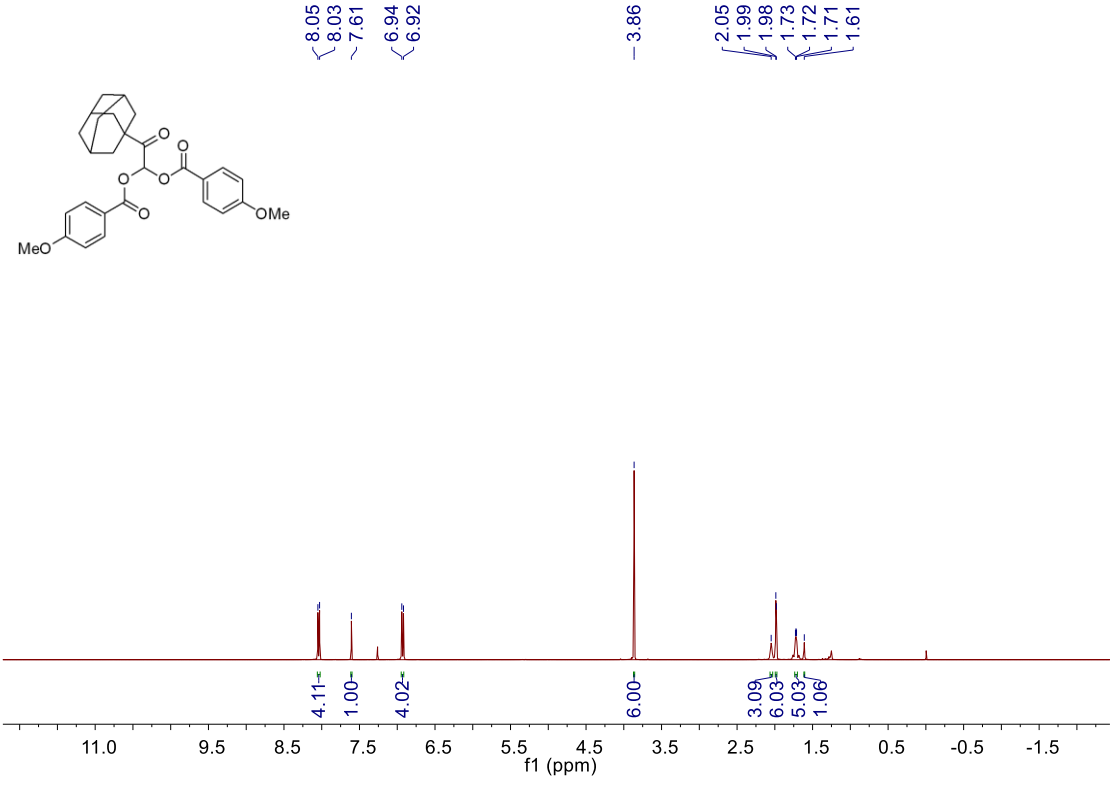
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **5n**



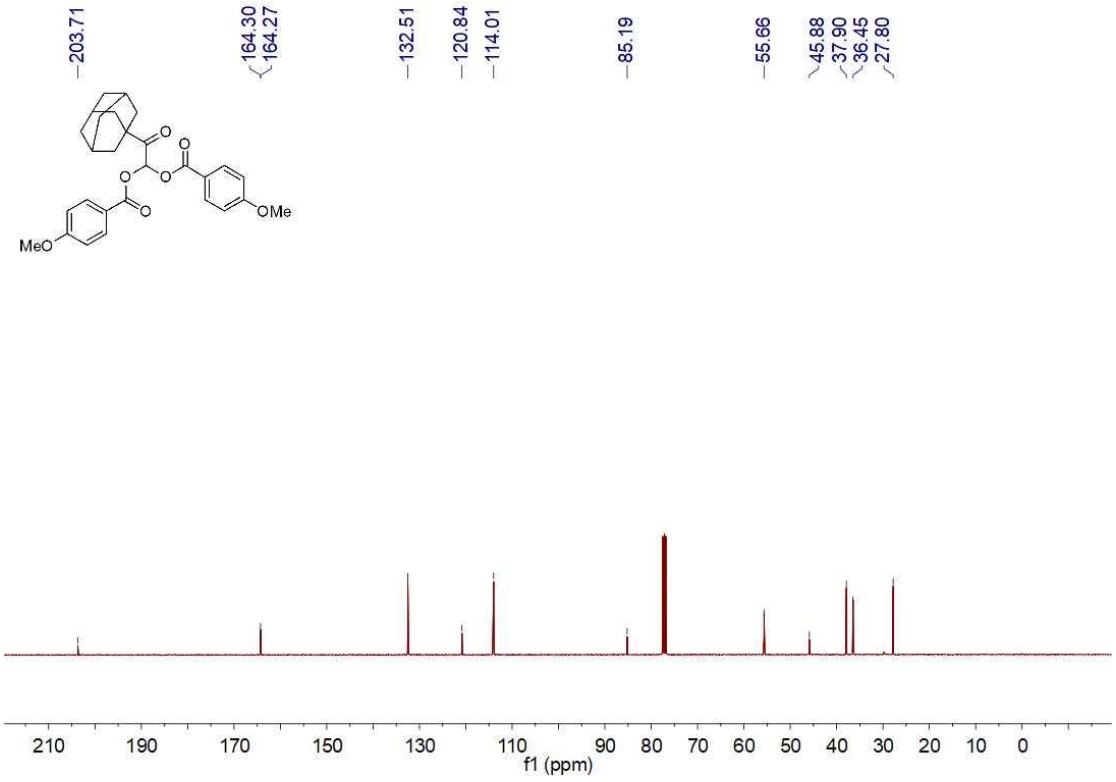
^{19}F NMR (377 MHz, $CDCl_3$) Spectra of **5n**



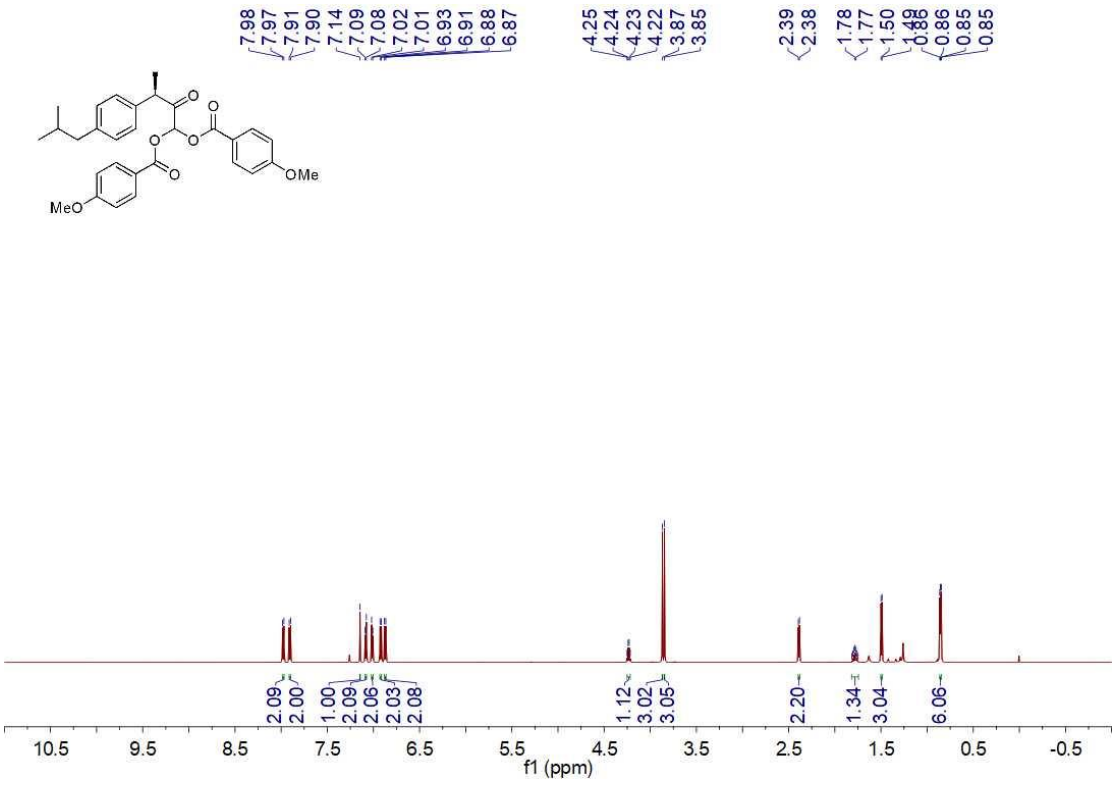
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **5o**



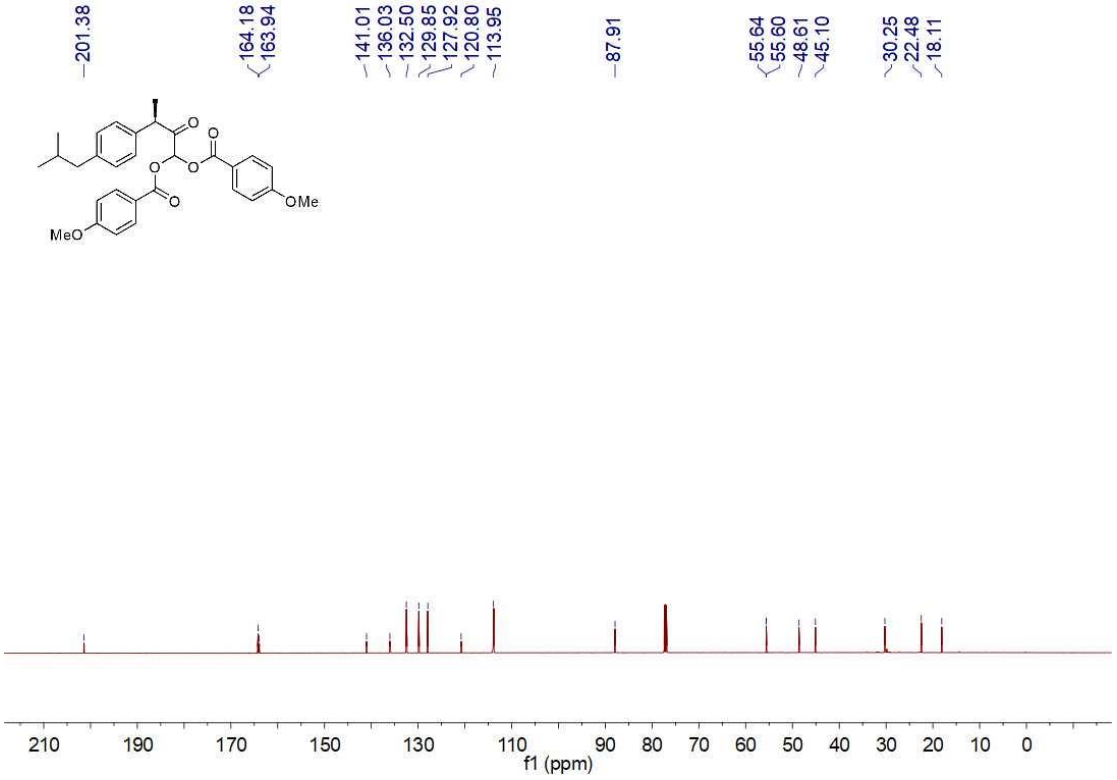
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **5o**



^{1}H NMR (600 MHz, $CDCl_3$) Spectra of **5p**



^{13}C NMR (151 MHz, $CDCl_3$) Spectra of **5p**



6. Reference

[1] Y-C, Zheng. B, Shu. et al. A cascade indazolone-directed Ir(III)- and Rh(III)-catalyzed C(sp^2)–H functionalization/[4+2] annulation of 1-arylindazolones with sulfoxonium ylides to access chemically divergent 8*H*-indazolo [1,2-*a*] cinnolines. *Org. Chem. Front.* **2022**, *9*, 5185-5190.

[2] L, Li. C-G, Mi. G-W, Huang. et al. A Carbene Relay Strategy for Cascade Insertion Reactions. *Angew. Chem. Int. Ed*. **2023**, e202312793.