Supporting information for

A simple approach to C3-ethoxycarbonylmethylation of thiophenes/furans with diethyl bromomalonate

Mengmeng Huang, Jingzhou Tang, Na li, Jung Keun Kim, Ming Gong, Jianye Zhang, Yabo Li* and Yangjie Wu

College of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, P.R. China.

ybli@zzu.edu.cn

Experimental details and spectroscopic data

Contents

1. General information

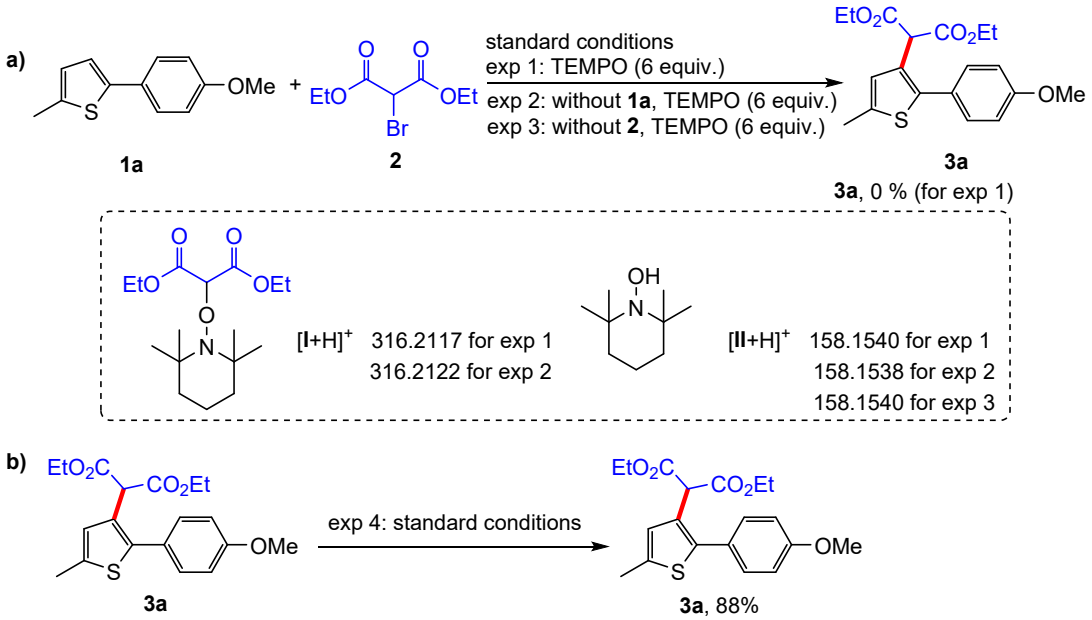
All reactions were performed using quartz tube. Commercial grade reagents and EtOH (OCEANPAK, GC ≥ 99.9%) were used without further purification except as indicated below. Solvents were dried and degassed by standard methods before they were used. Diethyl bromomalonate was purchased from commercial suppliers and Thiophenes (furans) were prepared according to reported procedures.[1] The progress of all reactions was monitored by thin-layer chromatography to ensure the reactions had reached completion. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminum plates with F-254 indicator, visualized by irradiation with UV light. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. The LCD Digital Hotplate Magnetic Stirrer MS-H-Pro$^+$ and Digital Single Channel Adjustable Automatic Electronic Pipette Micropipette dPettee$^+$ were purchased from Dragon Laboratory Instruments Limited. ^{1}H NMR spectra was recorded on a Bruker DPX-400 (400 MHz) spectrometer with deuteraterated chloroform as solution, the chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. ^{13}C NMR spectra was recorded at 100 MHz on Bruker DPX-400. The chemical shifts δ are reported relative to residual $CHCl_3$ (δ_C = 77.00 ppm). ^{19}F NMR spectra was recorded at 376.5 MHz on Bruker DPX-400, the chemical shifts δ are reported relative to $CFCl_3$ (δ = 0 ppm) as internal standard. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd = doublet of doublet, td = triplet of doublet. Coupling constants J are reported in Hertz (Hz). High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). The UV-Vis absorption spectra were recorded in DMSO on a Perkin Elmer Lambda 35 spectrometer. The cyclic voltammetry (CV) was recorded in DMSO by CHI650A. And the luminescence quenching experiment was recorded using a F-4500 FL spectrophotometer in DMSO. All reactions were carried out with photoreactor (Serial No: PEA12) which was purchased from LUOYANG JINFENG ELECTROMECHANICAL EQUIPMENT CO., LTD.

2. Experimental procedures

General procedure for the C3-ethoxycarbonylmethylation of 2-phenyl-thiophenes (furans) with diethyl bromomalonate

2-Phenyl-thiophenes (furans) **1** (0.2 mmol), diethyl bromomalonate **2** (0.6 mmol, 3 equiv.) and KH_2PO_4 (0.4 mmol, 2.0 equiv.), *fac*-Ir(ppy)$_3$ (0.001 mmol) were combined in EtOH (1.5 mL) under Ar atmosphere. The mixture was stirred at room temperature under 3 W blue LED. After 1 hour, the reaction mixture was extracted with dichloromethane and saturated salt water, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Then, the crude products were purified through silica gel column chromatography using petroleum ether/ethyl acetate (50:1, v/v) as eluent to give the corresponding product **3**.

3. Control experiments



Scheme S1. Control experiments.

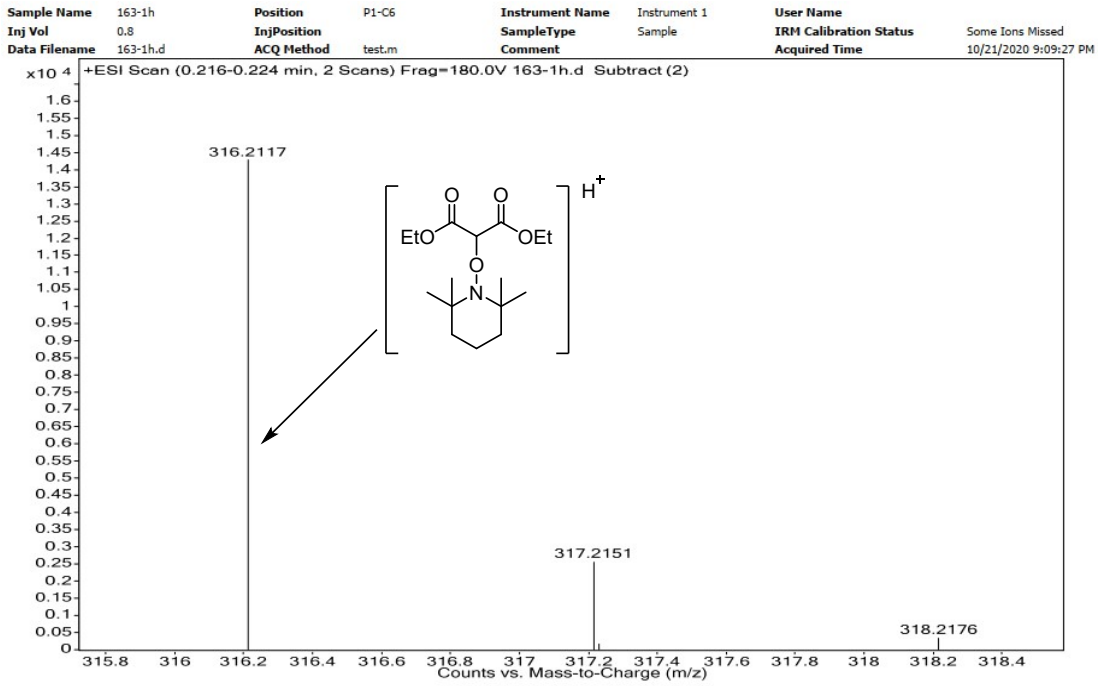


Figure S1. HRMS spectrum of compound [**I** + H]$^+$ for exp 1

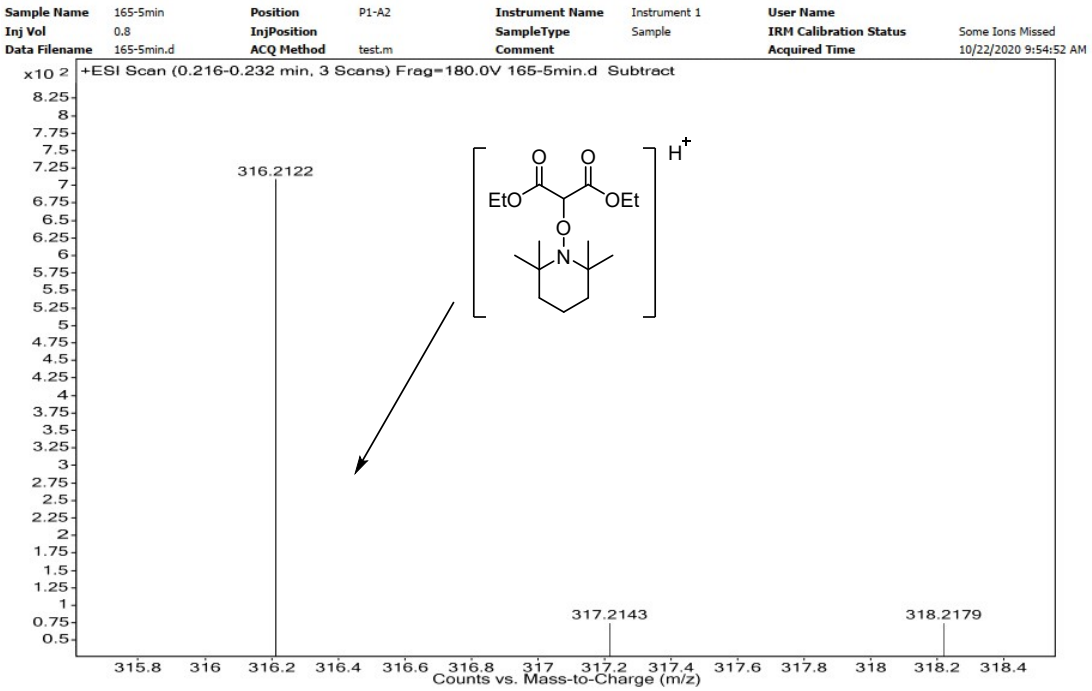


Figure S2. HRMS spectrum of compound [**I** + H]$^+$ for exp 2

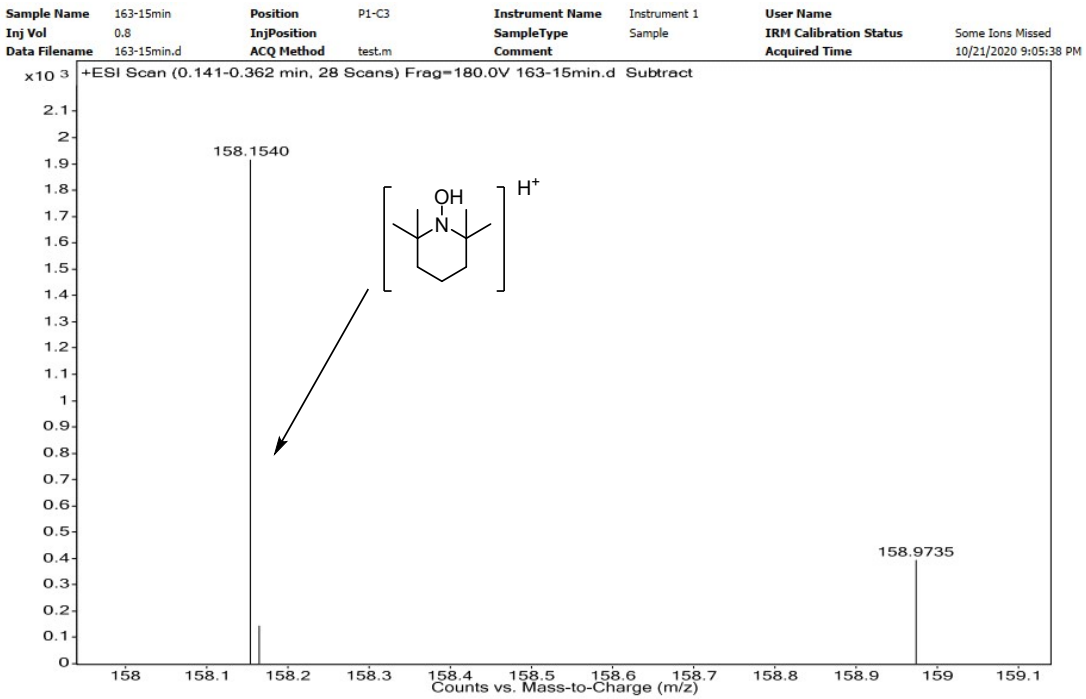


Figure S3. HRMS spectrum of compound [**II** + H]$^+$ for exp 1

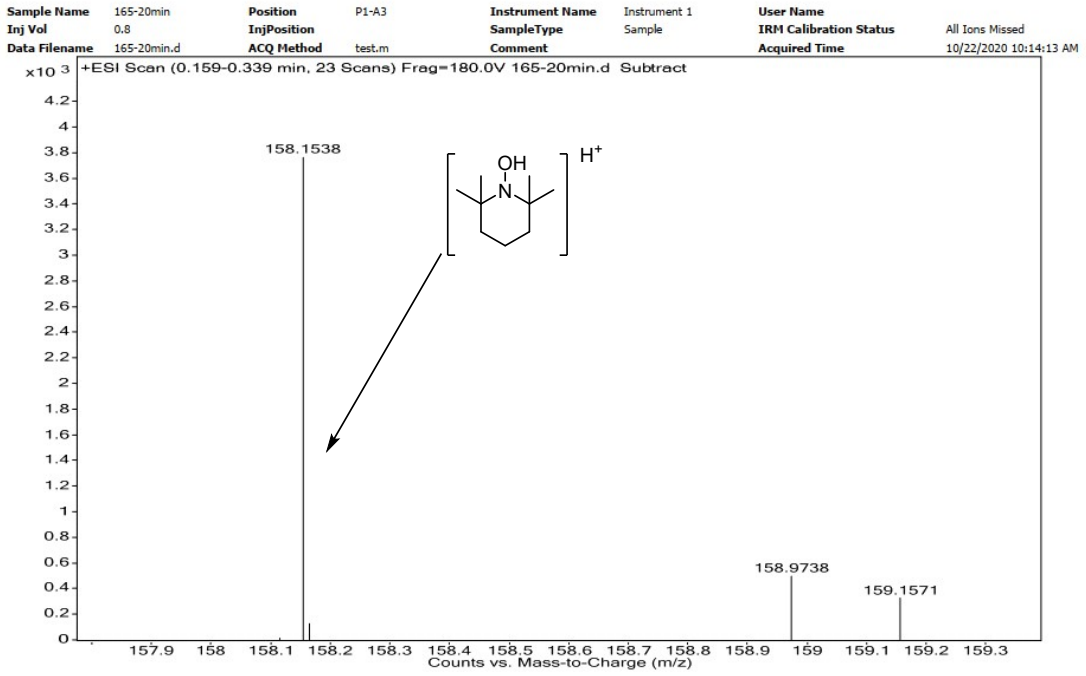


Figure S4. HRMS spectrum of compound [**II** + H]$^+$ for exp 2

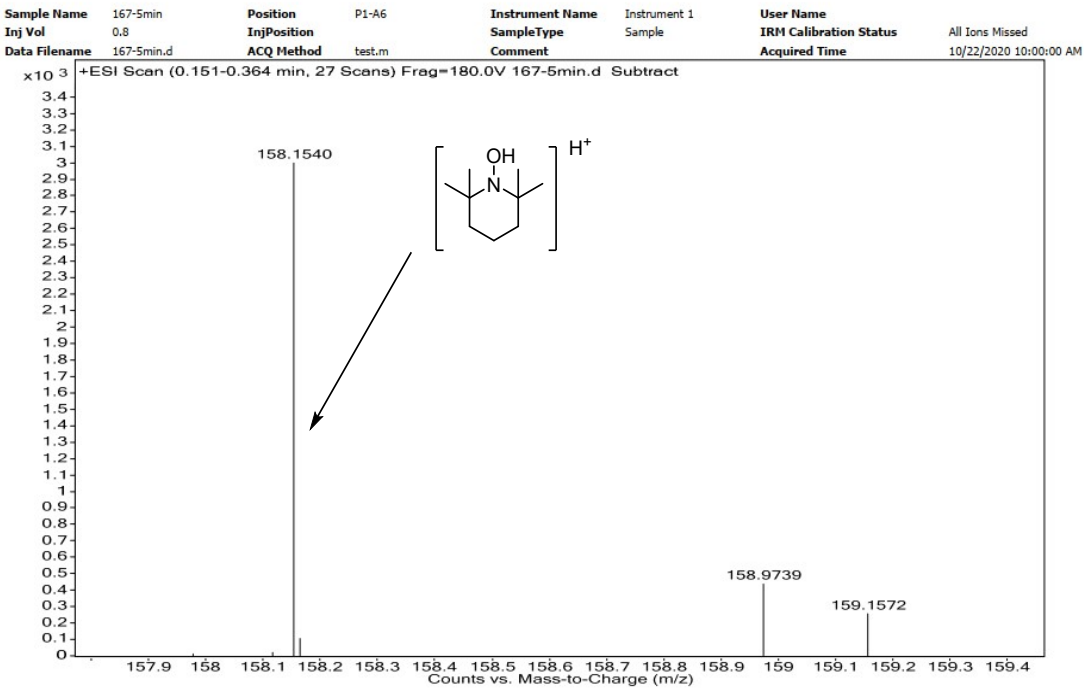


Figure S5. HRMS spectrum of compound [**II** + H]$^+$ for exp 3

4. UV-Vis absorption spectra, luminescence quenching experiments, cyclic voltammetry and data processing

4.1 The UV-Vis absorption spectra

The UV-Vis absorption spectra were recorded in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 spectrometer.

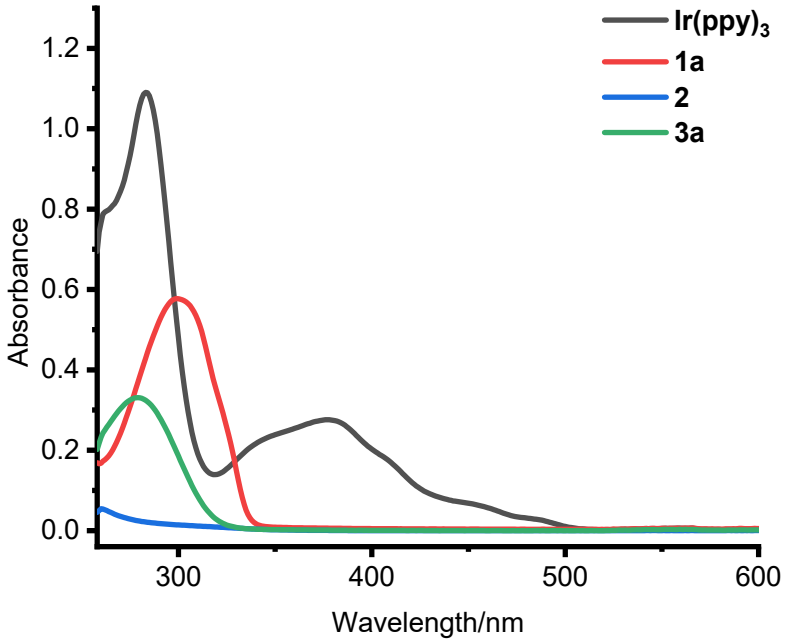


Figure S6. The UV-Vis absorption spectra of **Ir(ppy)$_3$** (λ_{max} = 505 nm), 2-(4-methoxyphenyl)-5-methylthiophene **1a** (λ_{max} = 342 nm), diethyl bromomalonate **2** (λ_{max} = 262 nm), **3a** (λ_{max} = 320 nm) in DMSO (0.05 mM).

4.2 Luminescence quenching experiments

Emission intensities were recorded using a F-4500 FL spectrophotometer. First, Ir(ppy)$_3$ solution was excited at 379 nm and the emission/intensity at 522 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of Ir(ppy)$_3$ and different concentration of 2-(4-methoxyphenyl)-5-methylthiophene **1a**, diethyl bromomalonate **2** and **3a** in DMSO in 10 mm path length quartz cuvette were collected.

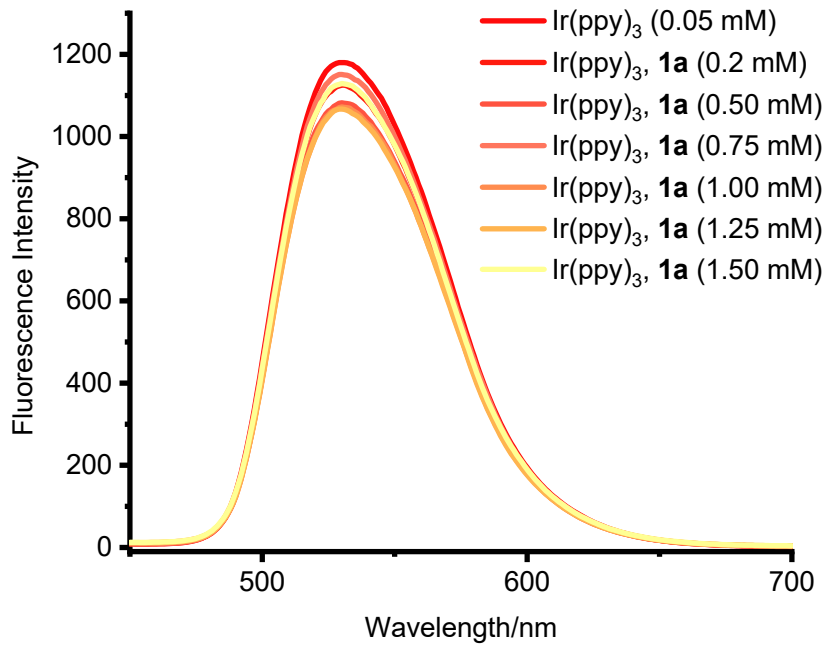


Figure S7. Luminescence quenching experiments of $Ir(ppy)_3$ with **1a**

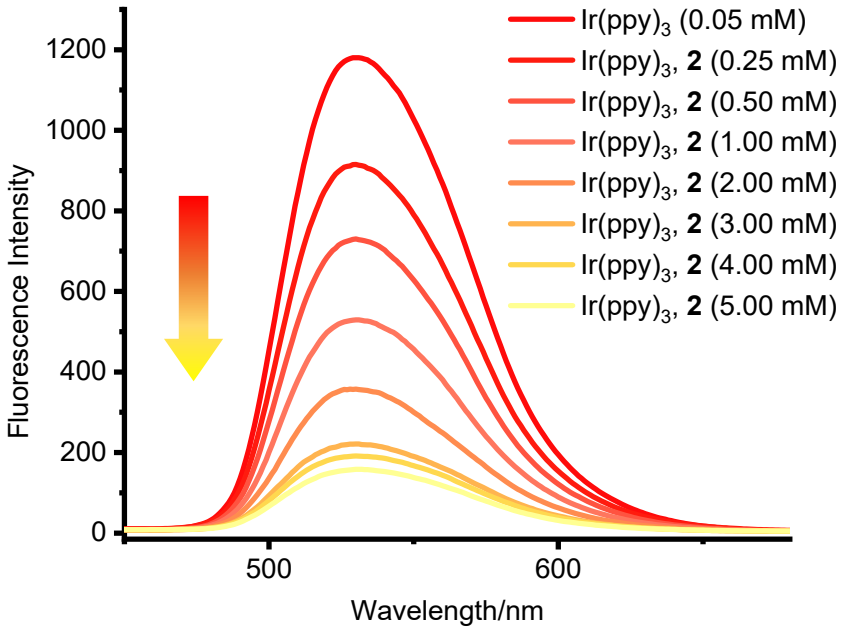


Figure S8. Luminescence quenching experiments of $Ir(ppy)_3$ with **2**

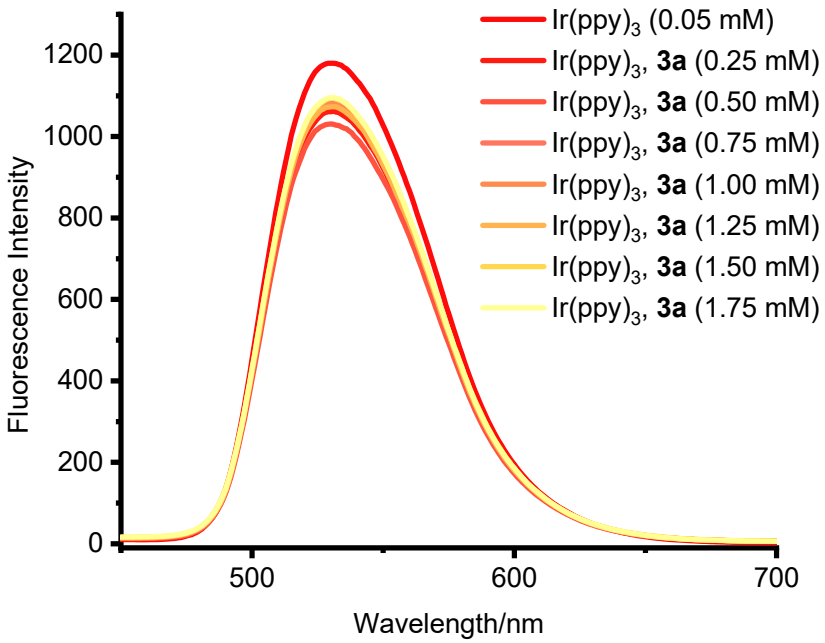


Figure S9. Luminescence quenching experiments of $Ir(ppy)_3$ with **3a**

4.3 Cyclic voltammetry

Cyclic voltammetry was measured under Ar balloon protection with conventional three-electrode system (reference electrode: Ag/AgCl, working electrode: glassy carbon, counter electrode: Pt wire, electrolyte: 0.1 M $TBAPF_6$ in DMSO) at 50 mV/sec of scan rate.

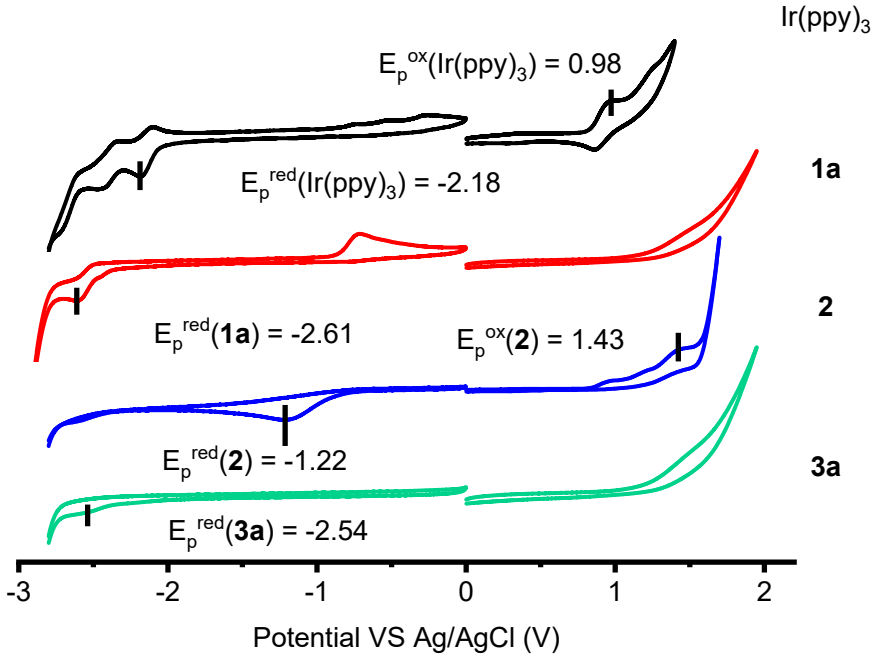


Figure S10. CV of reaction reagents (1 mM in DMSO)

4.4 Data processing

We could see the reversible reduction waves of all the reagents. With these data in hand, we calculated the excited redox potential, E_g by CV and UV absorption spectrometry theory.

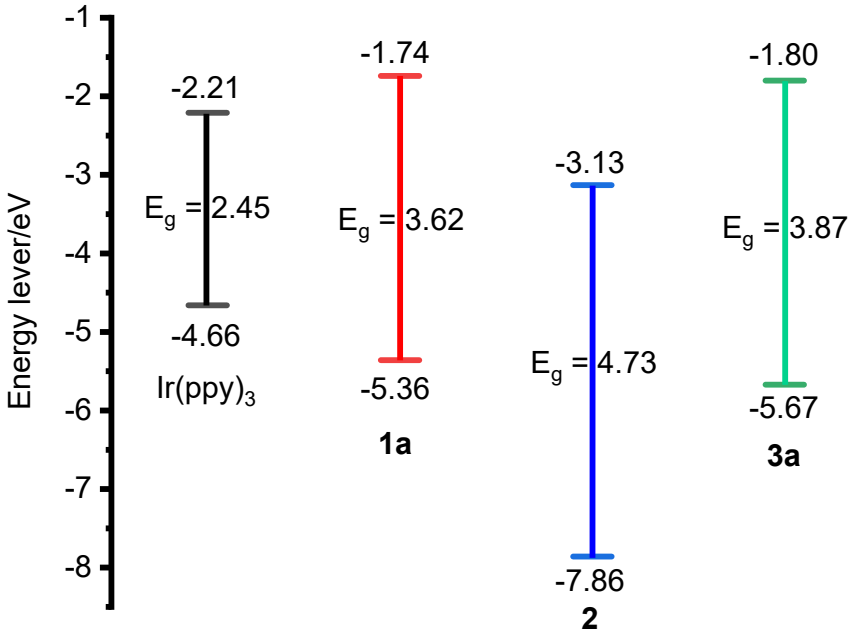
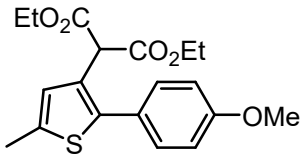


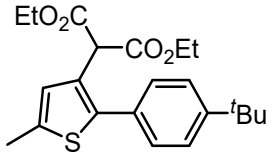
Figure S11. The E_{HOMO}, E_{LUMO} and E_g of different reagents

5. Characterization data



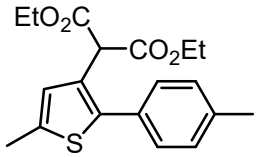
diethyl 2-(2-(4-methoxyphenyl)-5-methylthiophen-3-yl)malonate (3a)

White solid (56.5 mg, 78%), mp. 52-53 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.37 (m, 2H), 6.91-6.96 (m, 3H), 4,72 (s, 1H), 4.15-4.25 (m, 4H), 3.84 (s, 1H), 3.47 (s, 3H) 1.26 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 159.4, 140.0, 138.0, 130.9, 127.2, 126.8, 125.8, 114.1, 61.8, 55.3, 51.4, 15.4, 14.0. HRMS (ESI) calcd. for $C_{19}H_{22}O_5S$ $(M+Na)^+$: 385.1081, found: 385.1079.



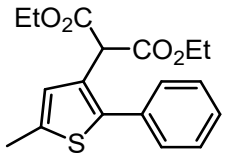
diethyl 2-(2-(4-(*tert*-butyl)phenyl)-5-methylthiophen-3-yl)malonate (3b)

Yellow oil (54.6 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.45 (m, 2H), 7.33-7.38 (m, 2H), 6.95 (d, J = 1.1 Hz, 1H), 4.78 (s, 1H), 4.15-4.26 (m, 4H), 2.48 (d, J = 1.0 Hz, 3H), 1.35 (s, 9H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 150.8, 140.2, 138.2, 130.5, 129.3, 127.2, 127.0, 125.6, 61.7, 51.5, 34.6, 31.3, 15.4, 14.0. HRMS (ESI) calcd. for $C_{22}H_{28}O_4S$ $(M+H)^+$: 389.1781, found: 389.1780



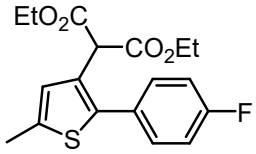
diethyl 2-(5-methyl-2-(*p*-tolyl)thiophen-3-yl)malonate (3c)

Yellow oil (51.4 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, 2H), 7.22 (d, 1H), 6.95 (d, J = 1.0 Hz, 1H), 4.75 (s, 1H), 4.15-4.25 (m, 4H), 2.48 (d, J = 1.0 Hz, 3H), 2.38 (s, 3H), 1.26 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 140.2, 138.2, 137.8, 130.5, 129.5, 129.4, 127.2, 126.9, 61.7, 51.4, 21.2, 15.4, 14.0. HRMS (ESI) calcd. for $C_{19}H_{22}O_4S$ $(M+Na)^+$: 369.1131, found: 369.1131.



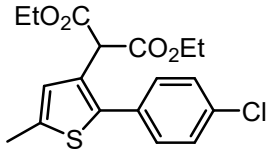
diethyl 2-(5-methyl-2-phenylthiophen-3-yl)malonate (3d)

White solid (44.4 mg, 67%), mp. 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.45 (m, 4H), 7.33-7.37 (m, 1H), 6.96 (d, J = 1.1 Hz, 1H), 4.76 (s, 1H), 4.15-4.26 (m, 4H), 2.49 (d, J = 1.0 Hz, 3H), 1.26 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 140.1, 138.6, 133.5, 129.7, 128.7, 127.9, 127.5, 127.0, 61.8, 51.4, 15.4, 14.0. HRMS (ESI) calcd. for $C_{18}H_{20}O_4S$ $(M+Na)^+$: 355.0975, found: 355.0975.



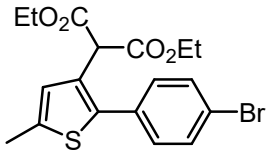
diethyl 2-(2-(4-fluorophenyl)-5-methylthiophen-3-yl)malonate (3e)

White solid (39.9 mg, 57%), mp. 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.44 (m, 2H), 7.07-7.14 (m, 2H), 6.95 (d, J = 1.1 Hz, 1H), 4.67 (s, 1H), 4.14-4.26 (m, 4H), 2.48 (d, J = 1.0 Hz, 3H), 1.26 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 162.6 (d, J = 247.9 Hz), 138.8, 138.7, 131.4 (d, J = 8.1 Hz), 129.4 (d, J = 3.7 Hz), 127.8, 126.9, 115.7 (d, J = 3.7 Hz), 61.9, 51.4, 15.4, 14.0. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -113.9. HRMS (ESI) calcd. for $C_{18}H_{19}FO_4S$ $(M+Na)^+$: 373.0881, found: 373.0880.



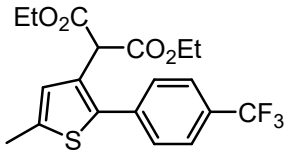
diethyl 2-(2-(4-chlorophenyl)-5-methylthiophen-3-yl)malonate (3f)

White solid (50.5 mg, 69%), mp. 79-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.43 (m, 4H), 6.96 (d, J = 1.0 Hz, 1H), 4.68 (s, 1H), 4.15-4.26 (m, 4H), 2.48 (d, J = 1.0 Hz, 3H), 1.26 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 139.0, 138.7, 134.1, 131.9, 130.9, 128.9, 128.0, 127.1, 61.9, 51.4, 15.4, 14.0. HRMS (ESI) calcd. for $C_{18}H_{19}ClO_4S$ $(M+H)^+$: 367.0766, found: 367.0764.



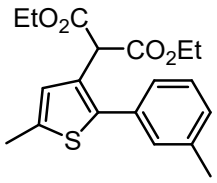
diethyl 2-(2-(4-bromophenyl)-5-methylthiophen-3-yl)malonate (3g)

White solid (54.9 mg, 67%), mp. 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.56 (m, 2H), 7.27-7.33 (m, 2H), 6.97 (d, J = 1.0 Hz, 1H), 4.68 (s, 1H), 4.15-4.26 (m, 4H), 2.48 (d, J = 1.0 Hz, 3H), 1.26 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 139.1, 138.7, 132.4, 131.9, 131.2, 128.0, 127.1, 122.2, 61.9, 51.4, 15.4, 14.0. HRMS (ESI) calcd. for $C_{18}H_{19}BrO_4S$ $(M+H)^+$: 411.0261, found: 411.0259.



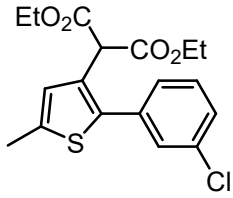
diethyl 2-(5-methyl-2-(4-(trifluoromethyl)phenyl)thiophen-3-yl)malonate (3h)

White solid (36.1 mg, 45%), mp. 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 1.0 Hz, 1H), 4.70 (s, 1H), 4.14-4.27 (m, 4H), 2.51 (d, J = 0.9 Hz, 3H), 1.27 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 139.8, 138.3, 137.2, 129.9 (d, J = 32.3 Hz), 128.5, 127.4, 125.7 (q, J = 7.3 Hz), 124.1 (d, J = 272.2 Hz), 62.0, 51.4, 15.4, 14.0. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -62.6. HRMS (ESI) calcd. for $C_{19}H_{19}FO_4S$ $(M+H)^+$: 401. 0829, found: 401. 0829.



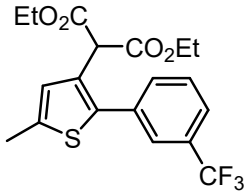
diethyl 2-(5-methyl-2-(m-tolyl)thiophen-3-yl)malonate (3i)

Yellow oil (46.4 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, J = 7.5 Hz, 1H), 7.20-7.27 (m, 2H), 7.17 (d, J = 7.5 Hz, 1H), 6.96 (d, J = 0.7 Hz, 1H), 4.77 (s, 1H), 4.14-4.27 (m, 4H), 2.48 (d, J = 0.9 Hz, 3H), 2.39 (s, 3H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 140.3, 138.4, 138.4, 133.4, 130.4, 128.7, 128.6, 127.4, 126.9, 126.7, 61.8, 51.4, 21.5, 15.4, 14.0. HRMS (ESI) calcd. for $C_{19}H_{22}O_4S$ $(M+Na)^+$: 369.1131, found: 369.1130.



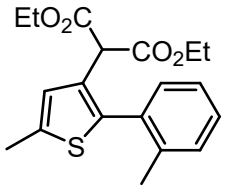
diethyl 2-(2-(3-chlorophenyl)-5-methylthiophen-3-yl)malonate (3j)

Yellow oil (49.8 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.46 (m, 1H), 7.30-7.36 (m, 3H), 6.97 (d, J = 1.0Hz, 1H), 4.71 (s, 1H), 4.15-4.27 (m, 4H), 2.49 (d, J = 1.0Hz, 3H), 1.28 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 139.3, 138.3, 135.2, 134.5, 130.0, 129.7, 128.2, 128.0, 127.8, 127.1, 61.9, 51.4, 15.4, 14.0. HRMS (ESI) calcd. for $C_{18}H_{19}ClO_4S$ $(M+H)^+$: 367.0766, found: 367.0764.



diethyl 2-(5-methyl-2-(3-(trifluoromethyl)phenyl)thiophen-3-yl)malonate (3k)

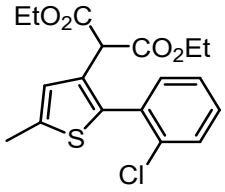
White solid (38.4 mg, 48%), mp. 58-59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.62 (d, J = 7.1 Hz, 2H), 7.00 (d, J = 1.0 Hz, 1H), 4.70 (s, 1H), 4.14-4.27 (m, 4H), 2.50 (d, J = 0.9 Hz, 3H), 1.27 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 139.6, 138.1, 134.3, 132.9, 131.1 (d, J = 32.3 Hz), 129.3, 128.5, 127.2, 126.4 (q, J = 7.3 Hz), 124.6 (q, J = 7.3 Hz), 123.9 (d, J = 272.1 Hz), 62.0, 51.4, 15.4, 14.0. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -62.7. HRMS (ESI) calcd. for $C_{19}H_{19}FO_4S$ $(M+Na)^+$: 423.0849, found: 423.0849.



diethyl 2-(5-methyl-2-(*o*-tolyl)thiophen-3-yl)malonate (3l)

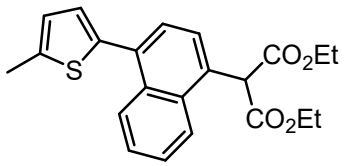
Yellow oil (17.3 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.32 (m, 1H), 7.25-7.27 (m, 1 H), 7.19-7.23 (m, 2H), 6.93 (d, J = 1.0 Hz, 1H), 4.12-4.22 (m, 4H), 2.49 (d, J = 0.9 Hz, 3H), 2.19 (s, 3H), 1.23(t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 138.7, 138.5, 132.5, 131.7, 130.1, 130.1, 129.1, 128.7, 125.6, 125.6, 61.6, 51.6, 20.1, 15.4, 14.0. HRMS

(ESI) calcd. for $C_{19}H_{22}O_4S$ $(M+H)^+$: 369.1131, found: 369.1131.



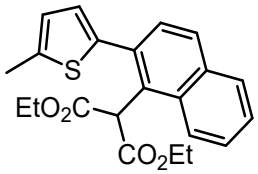
diethyl 2-(2-(2-chlorophenyl)-5-methylthiophen-3-yl)malonate (3m)

Yellow oil (17.6 mg, 24%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, J_1 = 7.4 Hz, J_2 = 1.5 Hz, 1H), 7.28-7.37 (m, 3H), 6.98 (d, J = 1.1 Hz, 1H), 4.37 (s, 1H), 4.13-4.24 (m, 4H), 2.51 (d, J = 1.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 139.6, 136.9, 135.0, 133.2, 132.0, 130.1, 129.9, 129.8, 126.6, 126.1, 61.7, 51.8, 15.5, 14.0. HRMS (ESI) calcd. for $C_{18}H_{19}ClO_4S$ $(M+Na)^+$: 389.0585, found: 389.0584.



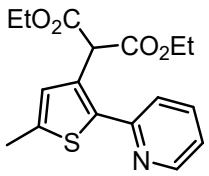
diethyl 2-(4-(5-methylthiophen-2-yl)naphthalen-2-yl)malonate (3n)

Yellow oil (45.8 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (dd, J_1 = 8.3 Hz, J_2 = 0.7 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.45-7.59 (m, 4H), 7.01 (d, J = 3.4 Hz, 1H), 6.80-6.84 (m, 1H), 5.44 (s, 1H), 4.20-4.30 (m, 4H), 2.56 (d, J = 0.7 Hz, 3H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 140.5, 139.1, 133.07, 132.4, 132.0, 129.2, 127.6, 127.6, 127.0, 126.7, 126.5, 126.2, 125.5, 123.0, 62.0, 54.5, 15.3, 14.1. HRMS (ESI) calcd. for $C_{22}H_{22}O_4S$ $(M+H)^+$: 383.1312, found: 383.1316.



diethyl 2-(2-(5-methylthiophen-2-yl)naphthalen-1-yl)malonate (3o)

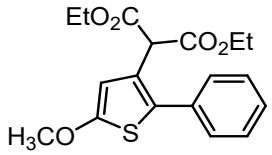
Yellow oil (47.4 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.1 Hz, 1H), 7.77-7.86 (m, 2H), 7.44-7.54 (m, 3H), 6.89 (d, J = 3.4 Hz, 1H), 6.75-6.78 (m, 1H), 5.61 (s, 1H), 4.12-4.21 (m, 4H), 2.54 (d, J = 0.7 Hz, 3H), 1.16 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 141.3, 140.1, 134.4, 133.7, 132.3, 128.9, 128.8, 128.5, 128.5, 128.0, 126.5, 126.2, 126.0, 125.4, 61.7, 54.2, 15.3, 14.0. HRMS (ESI) calcd. for $C_{22}H_{22}O_4S$ $(M+H)^+$: 383.1312, found: 383.1313.



diethyl 2-(5-methyl-2-(pyridin-2-yl)thiophen-3-yl)malonate (3p)

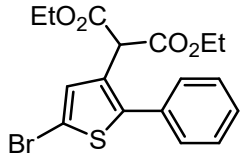
Yellow oil (12.0 mg, 18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (m, 1H), 7.66 (td, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.10-7.15 (m, 1H), 6.91 (d, J = 1.0 Hz, 1H), 5.84 (s,

1H), 4.19-4.27 (m, 4H), 2.50 (d, J = 1.0 Hz, 3H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 152.9, 149.2, 139.8, 137.7, 136.7, 130.6, 128.8, 122.0, 121.5, 61.6, 52.2, 15.5, 14.1. HRMS (ESI) calcd. for $C_{17}H_{19}NO_4S$ $(M+H)^+$: 334.1109, found: 334.1107.



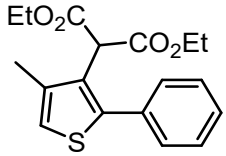
diethyl 2-(5-methoxy-2-phenylthiophen-3-yl)malonate (3q)

Yellow oil (48.7 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.44 (m, 4H), 7.31-7.36 (m, 1H), 6.41 (s, 1H), 4.76 (s, 1H), 4.16-4.27 (m, 4H), 3.91 (s, 3H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 164.7, 133.1, 129.8, 128.7, 128.6, 127.7, 125.2, 105.1, 61.8, 59.9, 51.6, 14.0. HRMS (ESI) calcd. for $C_{18}H_{20}O_5S$ $(M+Na)^+$: 371.0924, found: 371.0924.



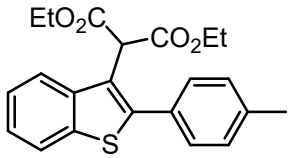
diethyl 2-(5-bromo-2-phenylthiophen-3-yl)malonate (3r)

Yellow solid (19.8 mg, 25%), mp. 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.46 (m, 5H), 7.28 (s, 1H), 4.7 (s, 1H), 4.15-4.26 (m, 4H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 143.9, 132.1, 131.6, 129.7, 128.9, 128.7, 128.5, 111.0, 62.1, 51.2, 14.0. HRMS (ESI) calcd. for $C_{17}H_{17}BrO_4S$ $(M+Na)^+$: 418.9924, found: 418.9923.



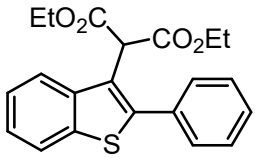
diethyl 2-(4-methyl-2-phenylthiophen-3-yl)malonate (3s)

Yellow oil (40.5 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.60 (m, 2H), 7.32-7.37 (m, 2H), 7.22-7.28 (m, 1H), 7.04 (s, 1H), 4.93 (s, 1H), 4.20-4.32 (m, 4H), 2.24 (s, 3H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 143.5, 137.5, 134.2, 128.8, 127.5, 126.8, 125.6, 125.5, 62.2, 51.7, 14.2, 14.0. HRMS (ESI) calcd. for $C_{18}H_{20}O_5S$ $(M+H)^+$: 333.1156, found: 333.1154.



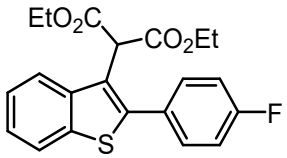
diethyl 2-(2-(*p*-tolyl)benzo[*b*]thiophen-3-yl)malonate (3t)

White solid (67.9 mg, 89%), mp. 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, J_1 = 7.7 Hz, J_2 = 0.9 Hz, 1H), 7.79 (dd, J_1 = 7.2 Hz, J_2 = 1.0 Hz, 1H), 7.45 (d, J = 8.1 Hz, 2H), 7.37 (td, J_1 = 7.1 Hz, J_2 = 1.2 Hz, 1H), 7.32 (td, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 5.08 (s, 1H), 4.12-4.23 (m, 4H), 2.42 (s, 3H), 1.21 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 143.8, 138.9, 138.8, 130.5, 130.0, 130.0, 129.5, 124.3, 124.3, 124.0, 122.8, 122.0, 61.8, 51.5, 21.4, 14.0. HRMS (ESI) calcd. for $C_{22}H_{22}O_4S$ $(M+Na)^+$: 405.1131, found: 405.1128.



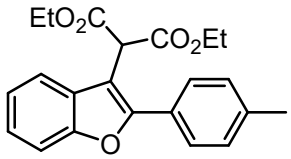
diethyl 2-(2-phenylbenzo[*b*]thiophen-3-yl)malonate (3u)

White solid (67.7 mg, 92%), mp. 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (dd, J_1 = 7.8 Hz, J_2 = 0.9 Hz, 1H), 7.81 (dd, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1H), 7.55-7.60 (m, 2H), 7.43-7.50 (m, 3H), 7.31-7.41 (m, 2H), 5.08 (s, 1H), 4.11-4.22 (m, 4H), 2.42 (s, 3H), 1.21 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 143.6, 138.9, 138.9, 133.4, 130.1, 128.8, 128.8, 124.4, 124.3, 124.1, 123.1, 122.0, 61.9, 51.4, 14.0. HRMS (ESI) calcd. for $C_{21}H_{20}O_4S$ $(M+Na)^+$: 391.0975, found: 391.0972.



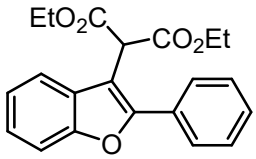
diethyl 2-(2-(4-fluorophenyl)benzo[*b*]thiophen-3-yl)malonate (3v)

White solid (61.0 mg, 79%), mp. 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, J_1 = 7.5 Hz, J_2 = 1.1 Hz, 1H), 7.81 (dd, J_1 = 7.3 Hz, J_2 = 1.5 Hz, 1H), 7.53-7.58 (m, 2H), 7.33-7.41 (m, 2H), 7.13-7.19 (m, 2H), 5.02 (s, 1H), 4.12-4.23 (m, 4H), 1.22 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 163.1 (J = 249.4 Hz), 142.3, 138.7 (J = 3.7 Hz), 132.0, 131.9, 129.4 (J = 2.9 Hz), 124.6, 124.4, 124.0, 123.4, 122.0, 115.8 (J = 22.0 Hz), 61.9, 51.4, 14.0. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -112.4. HRMS (ESI) calcd. for $C_{22}H_{22}O_5S$ $(M+H)^+$: 387.1061, found: 387.1056.



diethyl 2-(2-(*p*-tolyl)benzofuran-3-yl)malonate (3w)

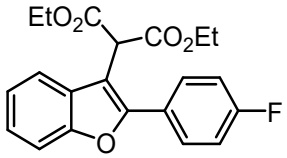
White solid (60.0 mg, 79%), mp. 79-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.67 (d J = 7.2 Hz, 2H), 7.49 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 8.3 Hz, 2H), 7.20-7.30 (m, 2H), 5.06 (s, 1H), 4.23 (q, J = 7.1 Hz, 4H), 2.42 (s, 3H), 1.24 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 154.4, 154.2, 139.4, 129.6, 128.2, 128.1, 127.1, 124.4, 122.7, 121.9, 111.1, 107.9, 62.0, 49.9, 21.4, 14.0. HRMS (ESI) calcd. for $C_{22}H_{22}O_5$ $(M+Na)^+$: 389.1360, found: 389.1360.



diethyl 2-(2-phenylbenzofuran-3-yl)malonate (3x)

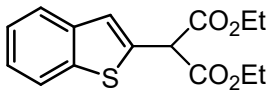
White solid (61.2 mg, 87%), mp. 79-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.81 (m, 2H), 7.71-7.75 (m, 1H), 7.49-7.54 (m, 3H), 7.43-7.48 (m, 1H), 7.31 (td, J_1 = 7.2 Hz, J_2 = 1.3 Hz, 1H), 7.23-7.28 (m, 1H), 5.08 (s, 1H), 4.23 (q, J = 7.1 Hz, 4H), 1.25 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7 154.3, 154.1, 129.8, 129.3, 128.9, 128.2, 128.1, 124.6, 122.8, 122.0, 111.2, 108.4, 62.0, 49.4, 14.0. HRMS (ESI) calcd. for $C_{21}H_{20}O_5$ (M+ Na)$^+$:

375.1203, found: 375.1198.



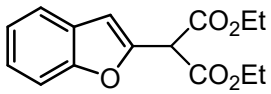
diethyl 2-(2-(4-fluorophenyl)benzofuran-3-yl)malonate (3y)

White solid (60.7 mg, 82%), mp. 86-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (td, J_1 = 5.4 Hz, J_2 = 2.2 Hz, 2H), 7.72 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.31 (td, J_1 = 7.2 Hz, J_2 = 1.3 Hz, 1H), 7.18-7.29 (m,3H), 4.99 (s, 1H), 4.23 (q, J = 7.2 Hz, 4H), 1.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 163.3 (J = 250.2 Hz), 154.2, 153.2, 132.0 (J = 8.8 Hz), 128.0, 126.1 (J = 3.7 Hz), 124.7, 122.9, 121.9, 116.2, 115.9, 111.1, 108.4, 62.1, 49.4, 14.0. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -111.1. HRMS (ESI) calcd. for $C_{21}H_{19}FO_5$ $(M+Na)^+$: 393.1109, found: 393.1109.



diethyl 2-(benzo[*b*]thiophen-2-yl)malonate (3z)

Yellow oil (23.4 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.83 (m, 1H), 7.72-7.76 (m, 1H), 7.36 (s, 1H), 7.30-7.35 (m, 2H), 4.96 (s, 1H), 4.20-4.32 (m, 4H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 140.3, 139.0, 134.4, 124.8, 124.5, 124.3, 123.7, 122.1, 62.4, 53.9, 14.0. HRMS (ESI) calcd. for $C_{15}H_{14}O_4S$ $(M+H)^+$: 293.0843, found: 293.0841.



diethyl 2-(benzofuran-2-yl)malonate (3aa)

Yellow oil (26.5 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, J_1 = 7.5 Hz, J_2 = 0.9 Hz, 1H), 7.47 (dd, J_1 = 8.0 Hz, J_2 = 0.7 Hz, 1H), 7.28 (td, J_1 = 7.2 Hz, J_2 = 1.4 Hz, 1H), 7.22 (td, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 1H), 6.85 (s, 1H), 4.90 (s, 1H), 4.24-4.32 (m, 4H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 154.9, 148.8, 128.1, 124.5, 122.9, 121.2, 111.3, 106.3, 62.4, 52.6, 14.0. HRMS (ESI) calcd. for $C_{15}H_{16}O_5$ $(M+Na)^+$: 299.0890, found: 299.0886.

6. References

(1) (a) J. Song, F. Wei, Wei Sun, X. Cao, C. Liu, L. Xie and W. Huang, *Org. Chem. Front.,* 2014, **1**, 817-820; (b) Y. Li, J. Wang, M. Huang, Z. Wang, Y. Wu and Y. Wu, *J. Org. Chem.*, 2014, **79**, 2890-2897; (c) P. Tosatti and A. Pfaltz, *Angew. Chem. Int. Ed.*, 2017, **56**, 4579-4582; (d) N. Ortega, S. Urban, B. Beiring and F. Glorius, *Angew. Chem. Int. Ed.*, 2012*,* **51**, 1710-1713.

7. ^{1}H, ^{13}C and ^{19}F NMR spectra

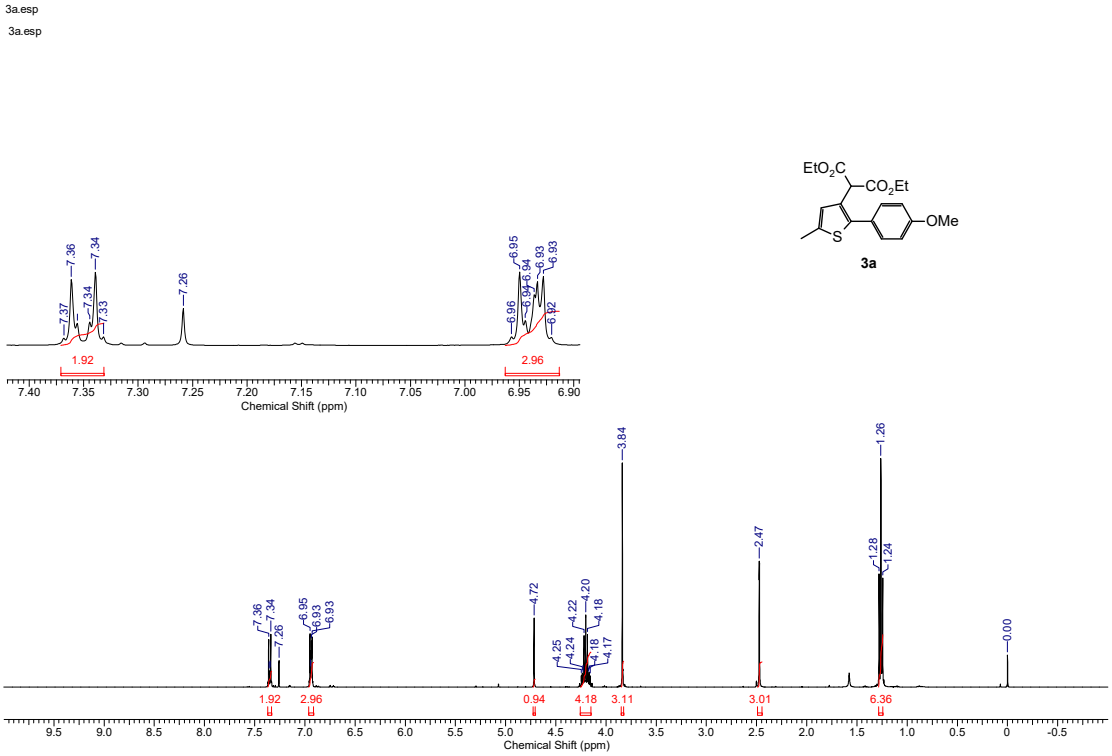


Figure S12. ^{1}H NMR spectrum of compound **3a**

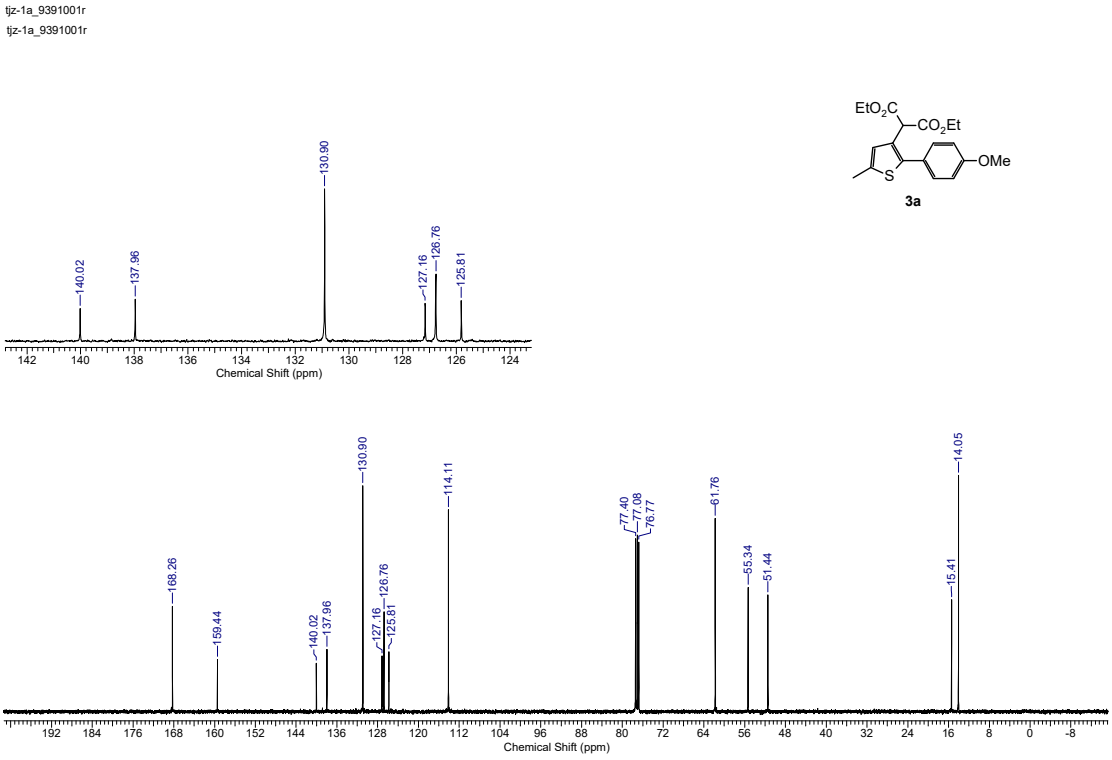


Figure S13. ^{13}C NMR spectrum of compound **3a**

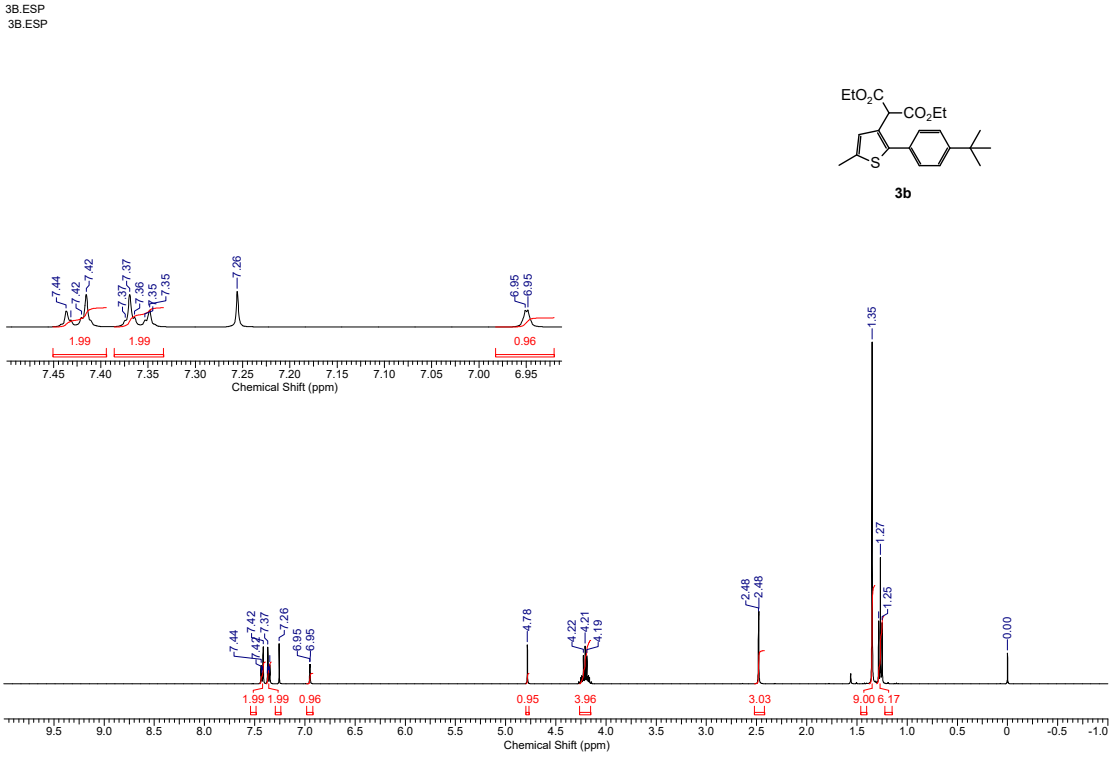


Figure S14. ^{1}H NMR spectrum of compound **3b**

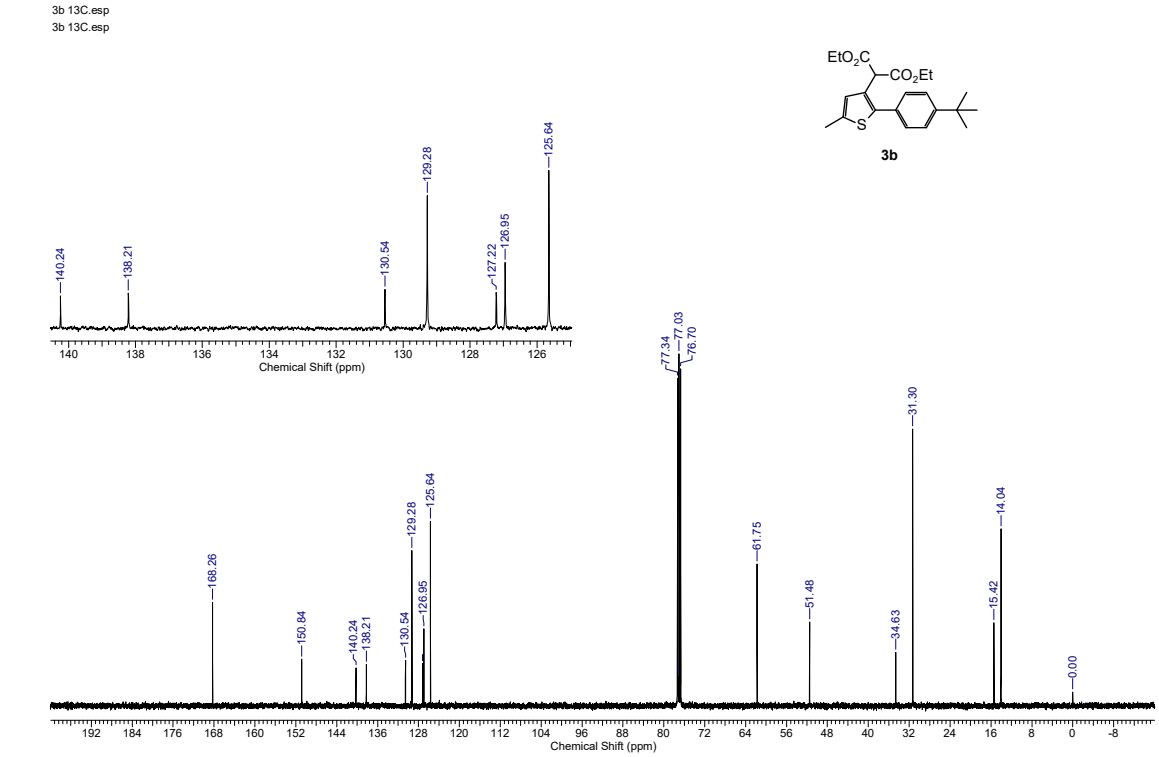


Figure S15. ^{13}C NMR spectrum of compound **3b**

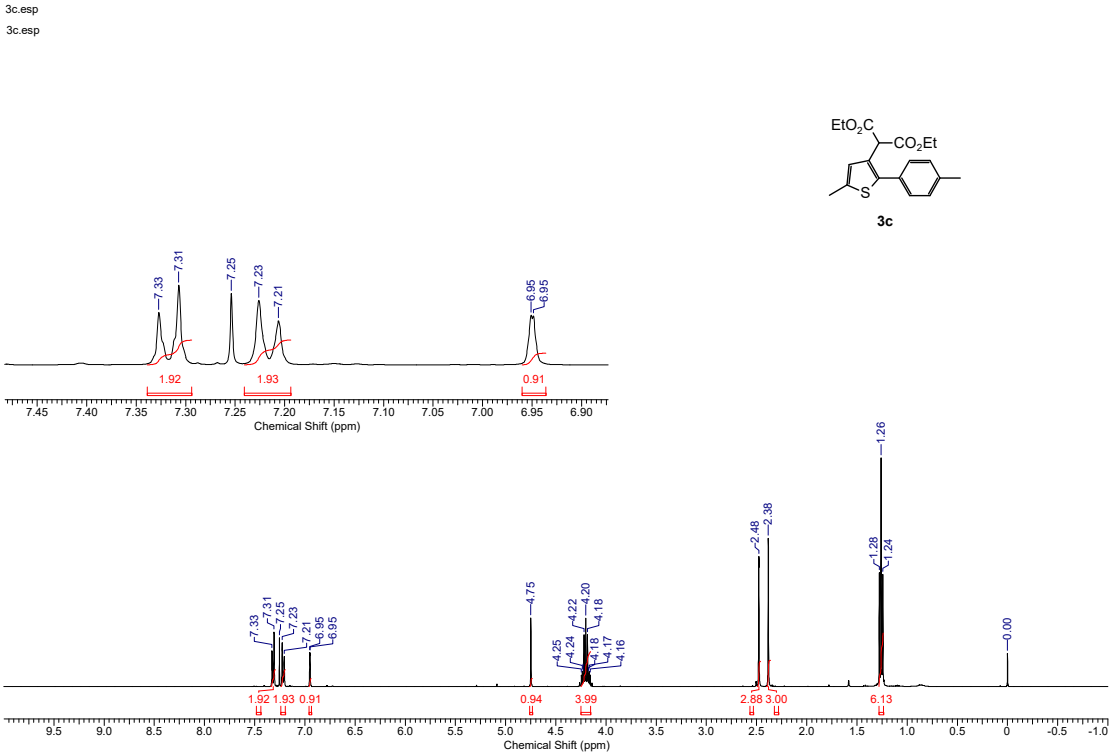


Figure 16. ^{1}H NMR spectrum of compound **3c**

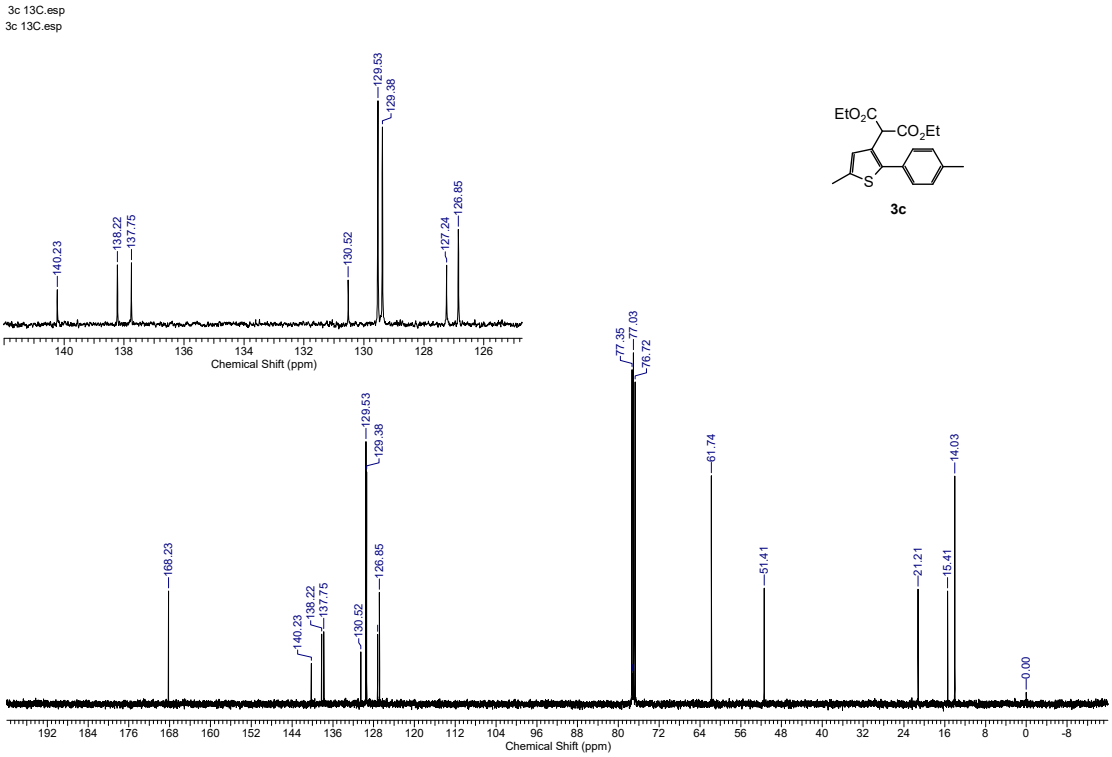


Figure S17. ^{13}C NMR spectrum of compound **3c**

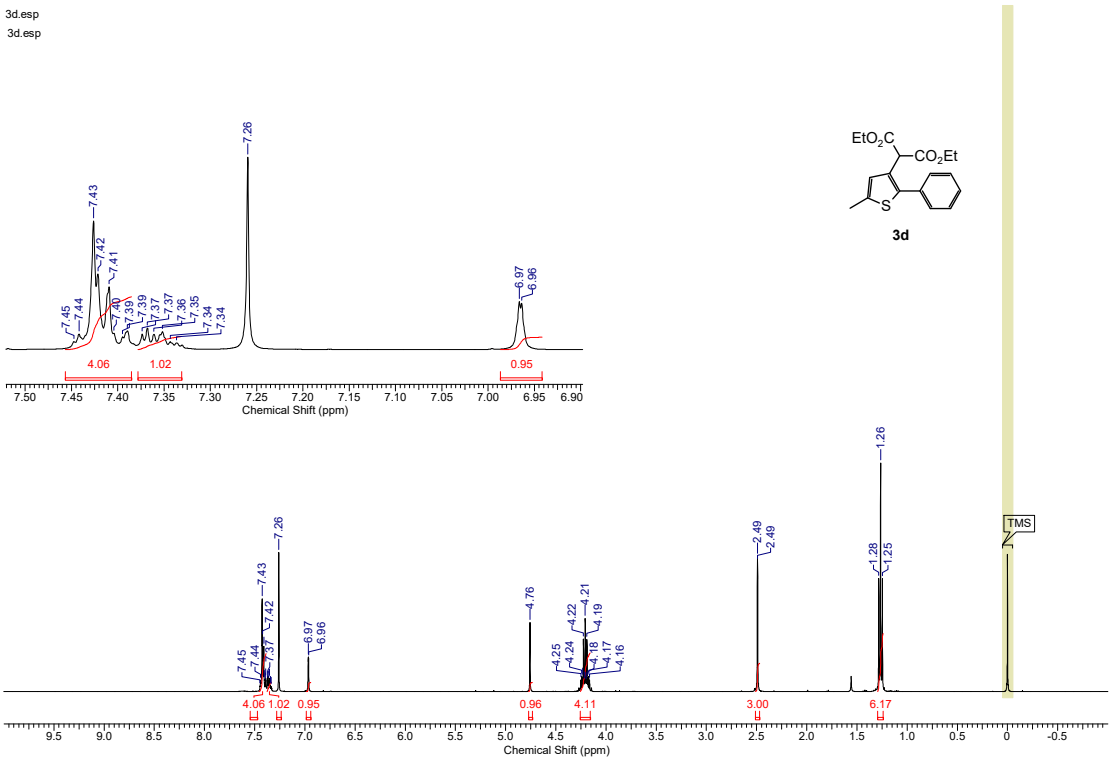


Figure S18. ^{1}H NMR spectrum of compound **3d**

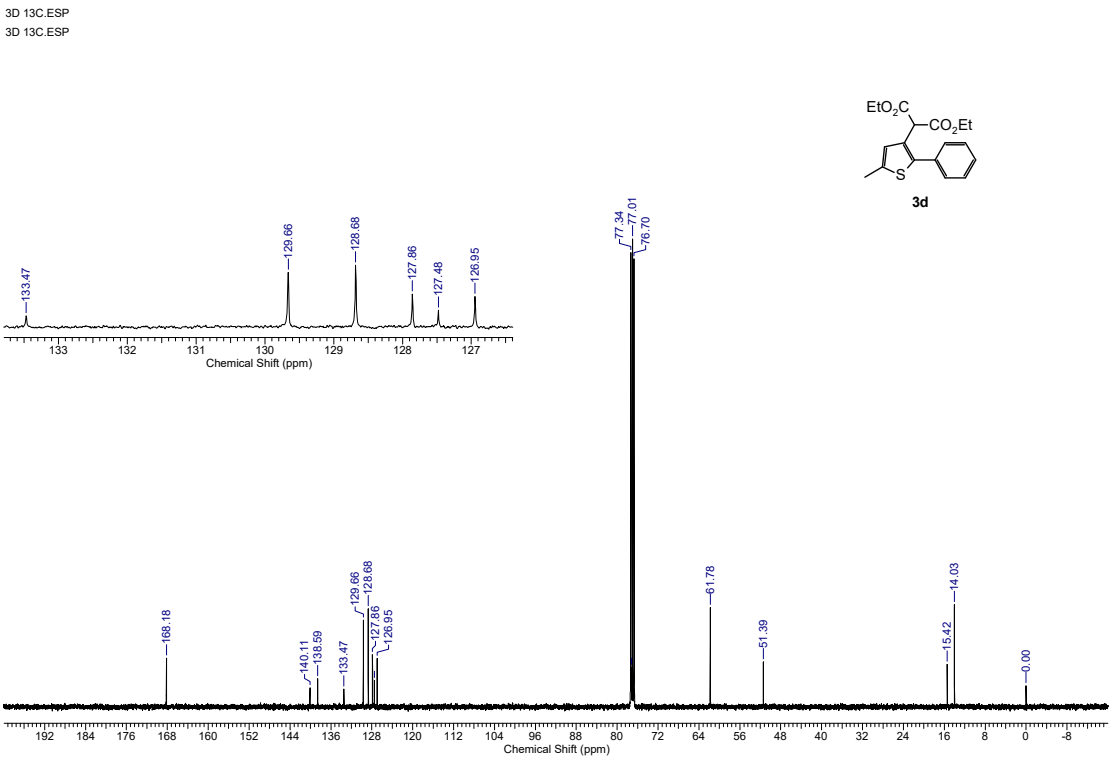


Figure S19. ^{13}C NMR spectrum of compound **3d**

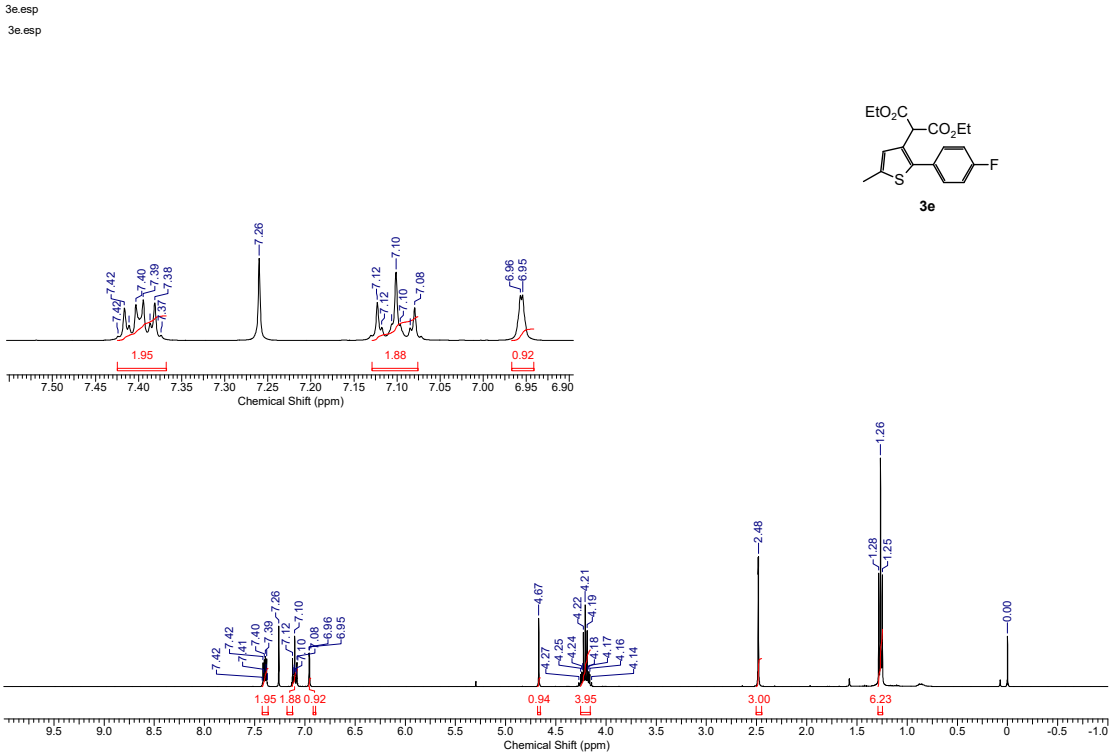


Figure S20. ^{1}H NMR spectrum of compound **3e**

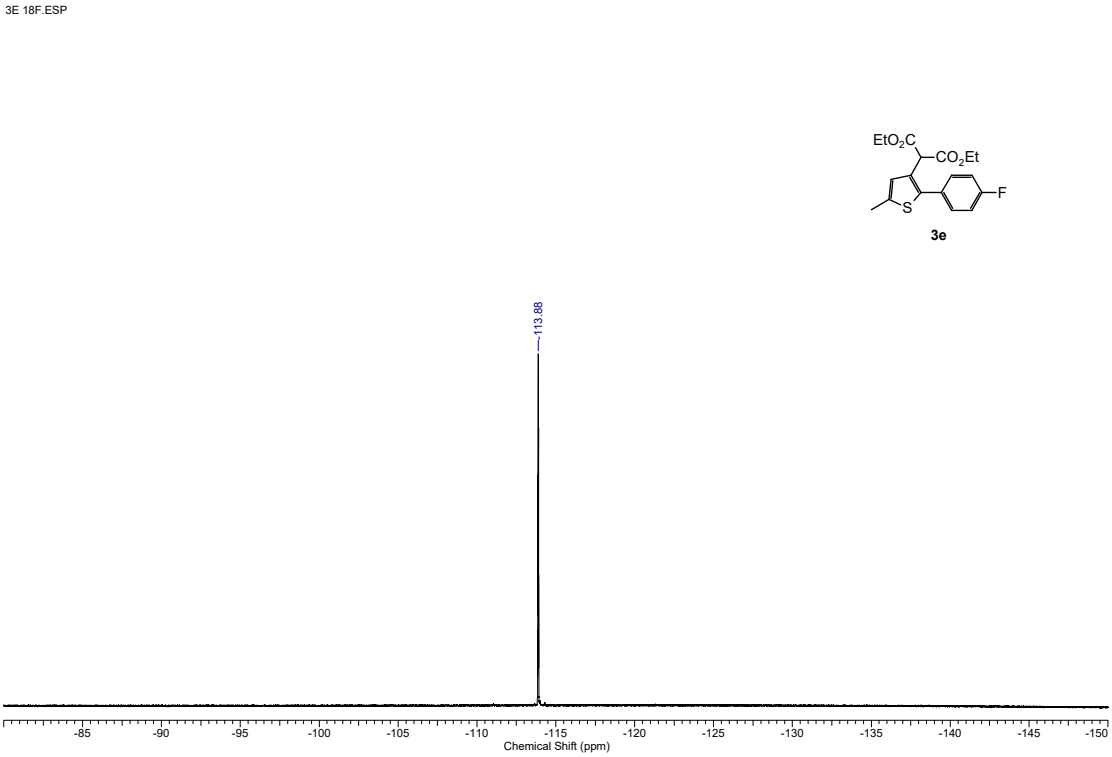


Figure S21. ^{19}F NMR spectrum of compound **3e**

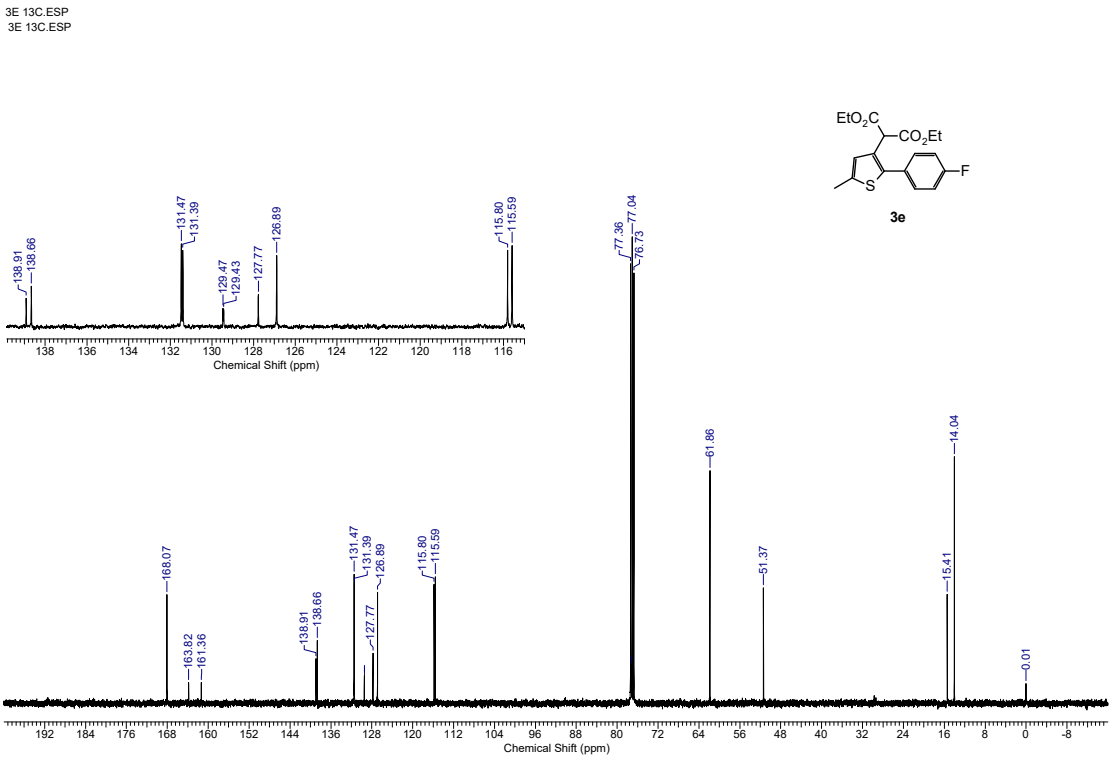


Figure S22. ^{13}C NMR spectrum of compound **3e**

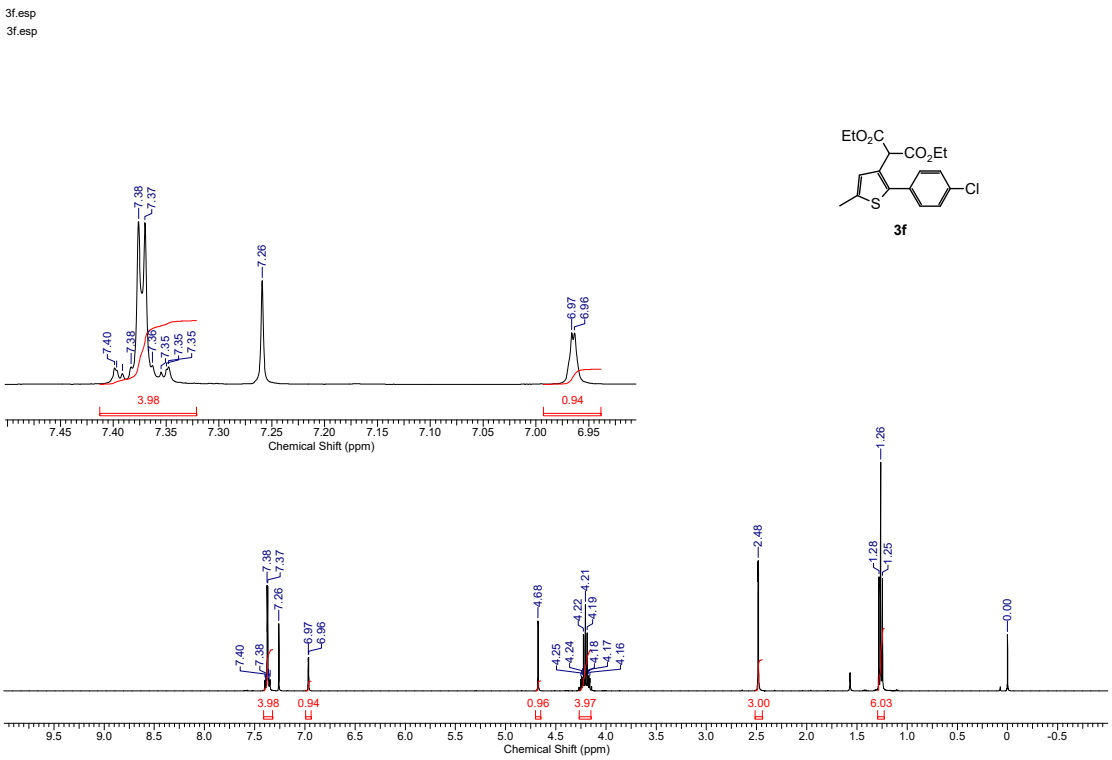


Figure S23. ^{1}H NMR spectrum of compound **3f**

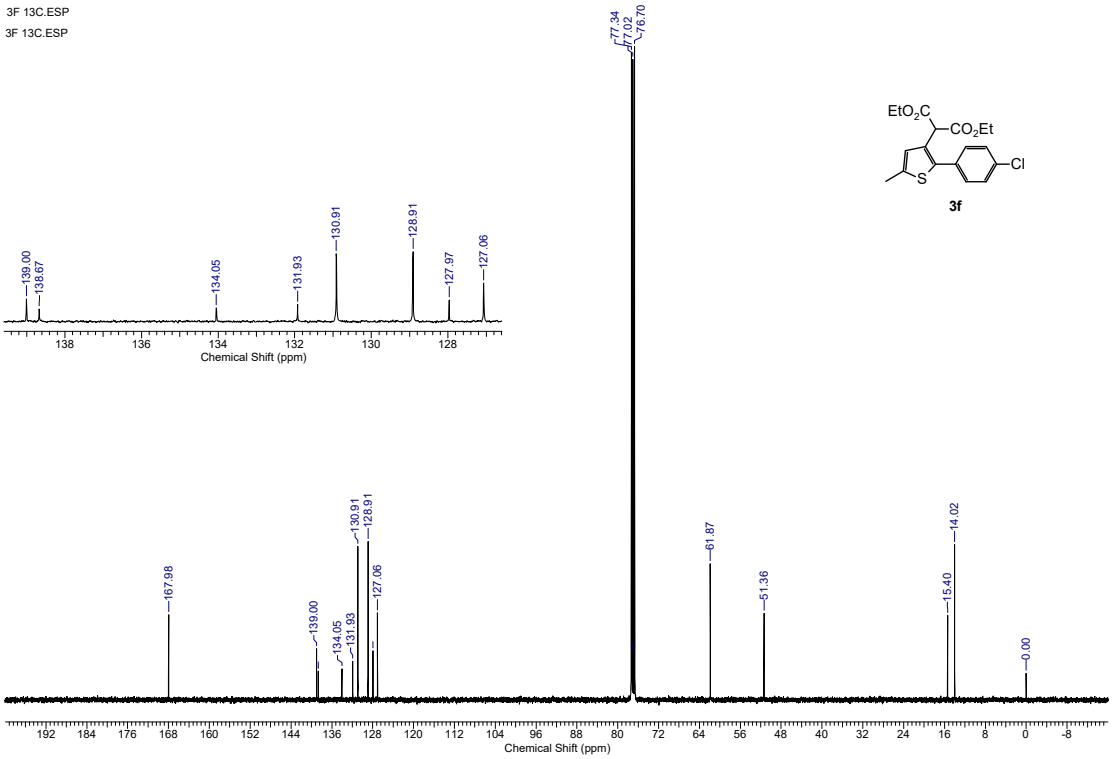


Figure S24. ^{13}C NMR spectrum of compound **3f**

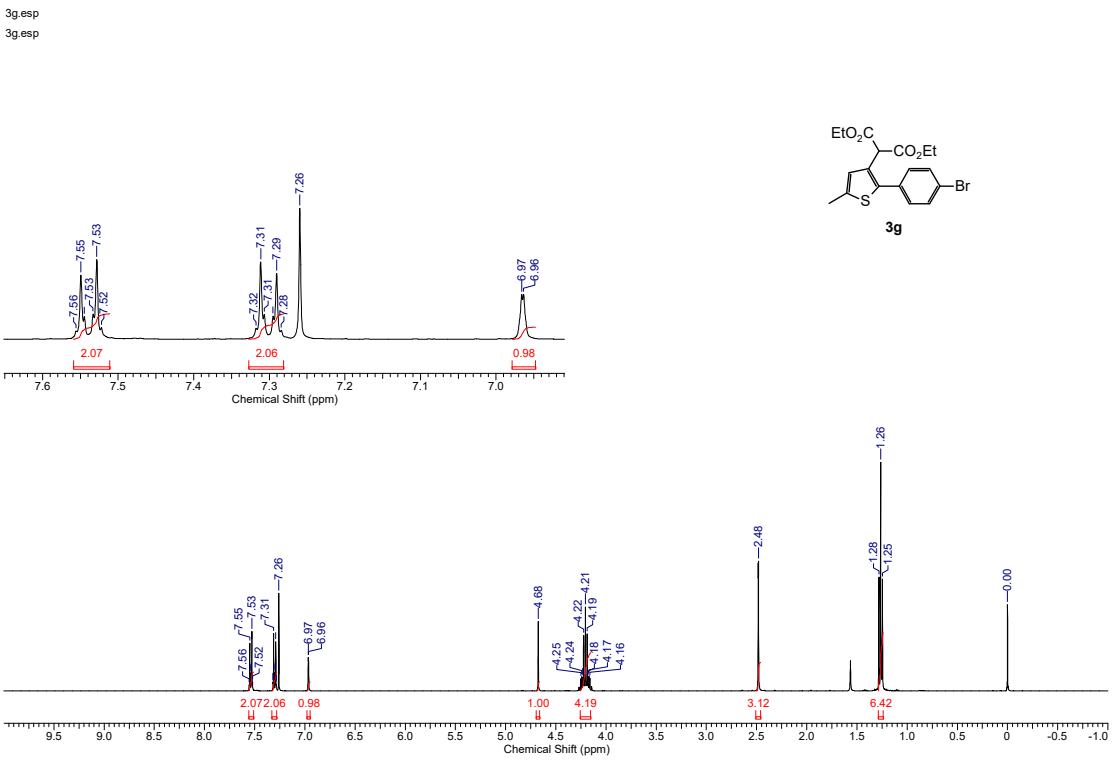


Figure S25. ^{1}H NMR spectrum of compound **3g**

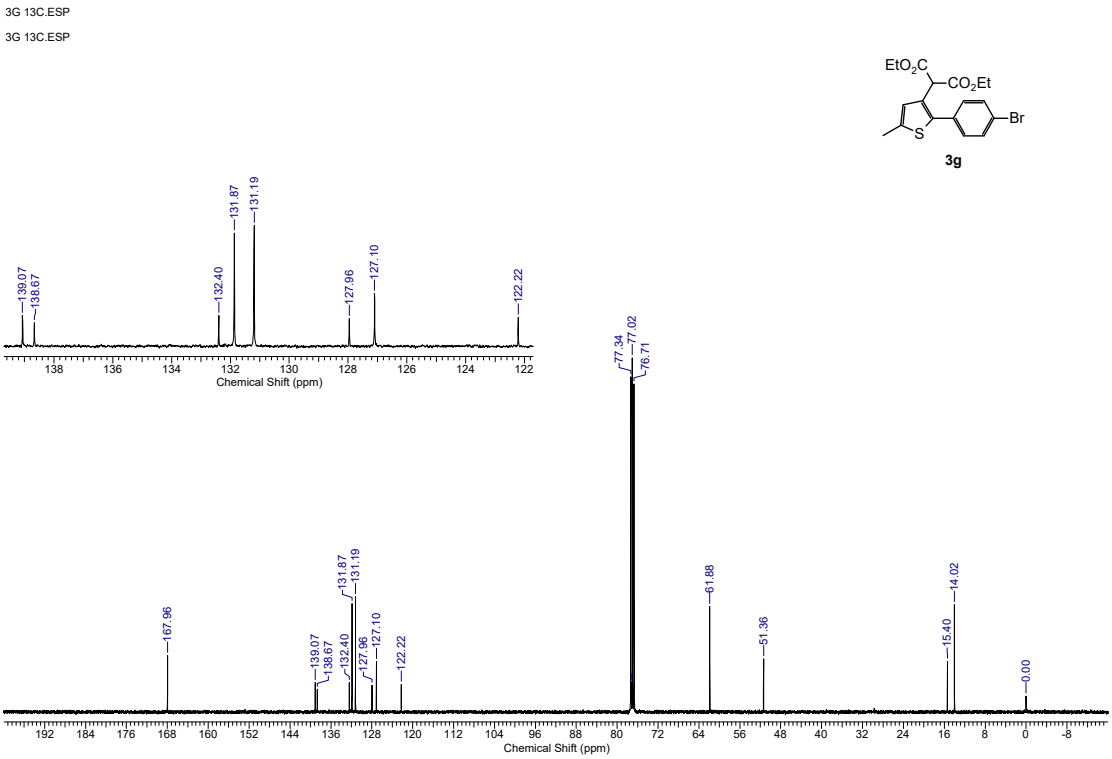


Figure S26. ^{13}C NMR spectrum of compound **3g**

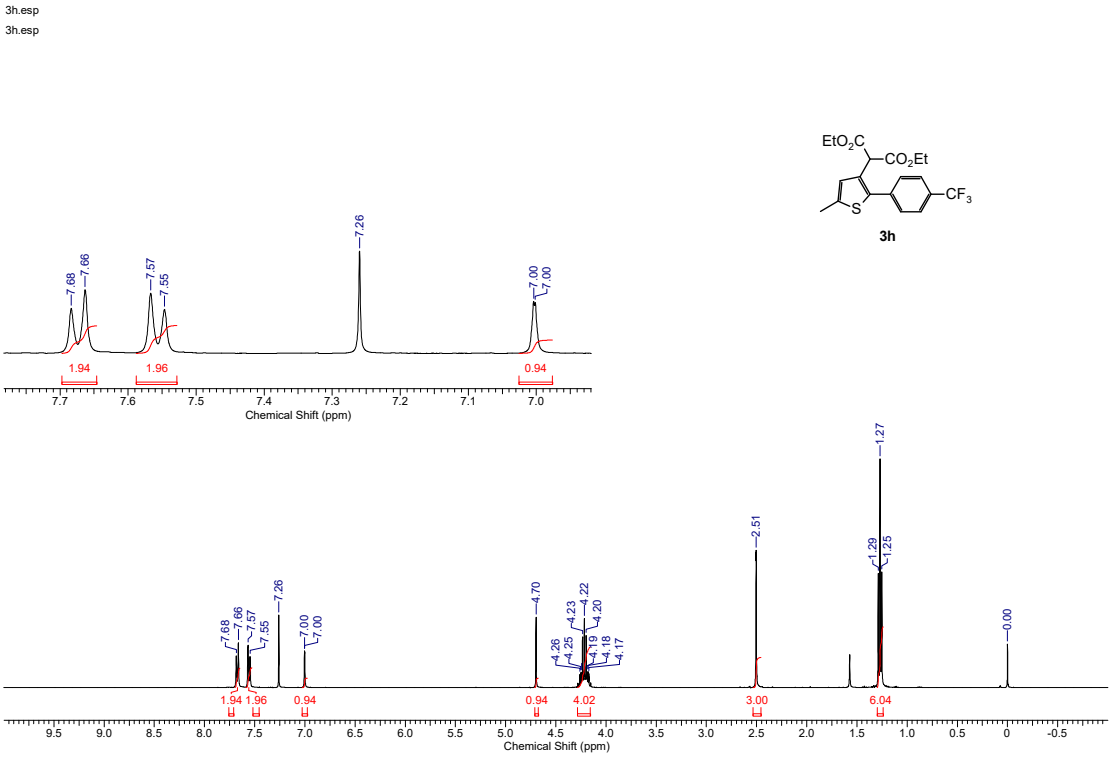


Figure S27. ^{1}H NMR spectrum of compound **3h**

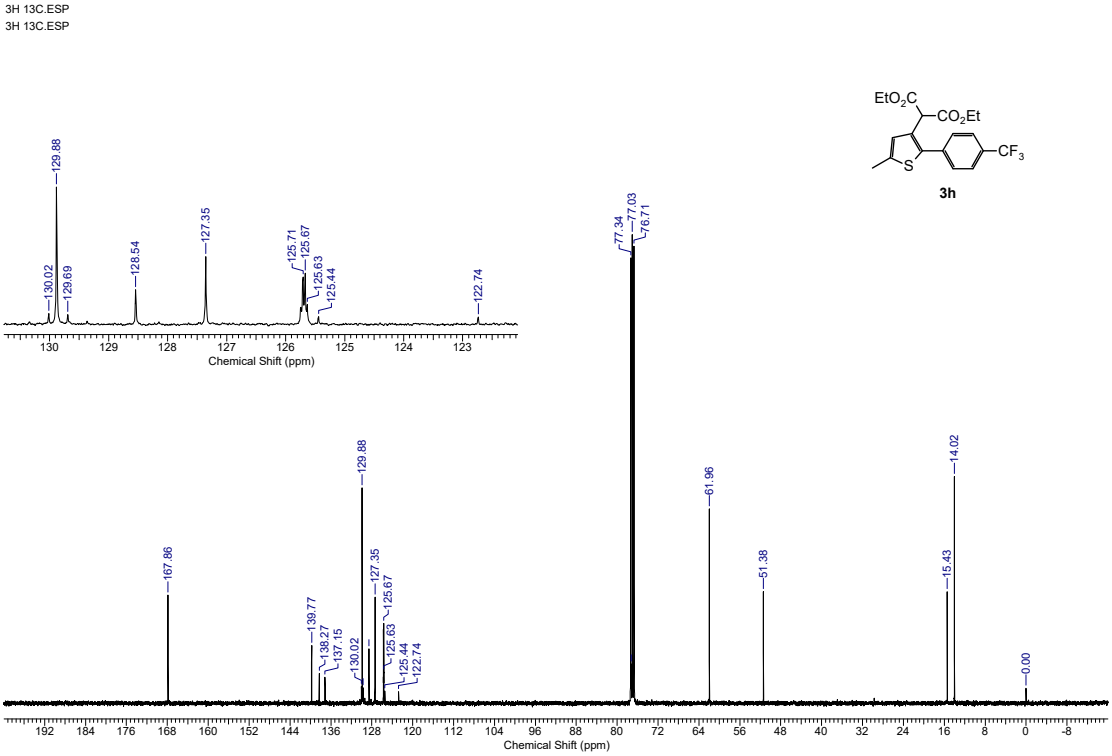


Figure S28. ^{13}C NMR spectrum of compound **3h**

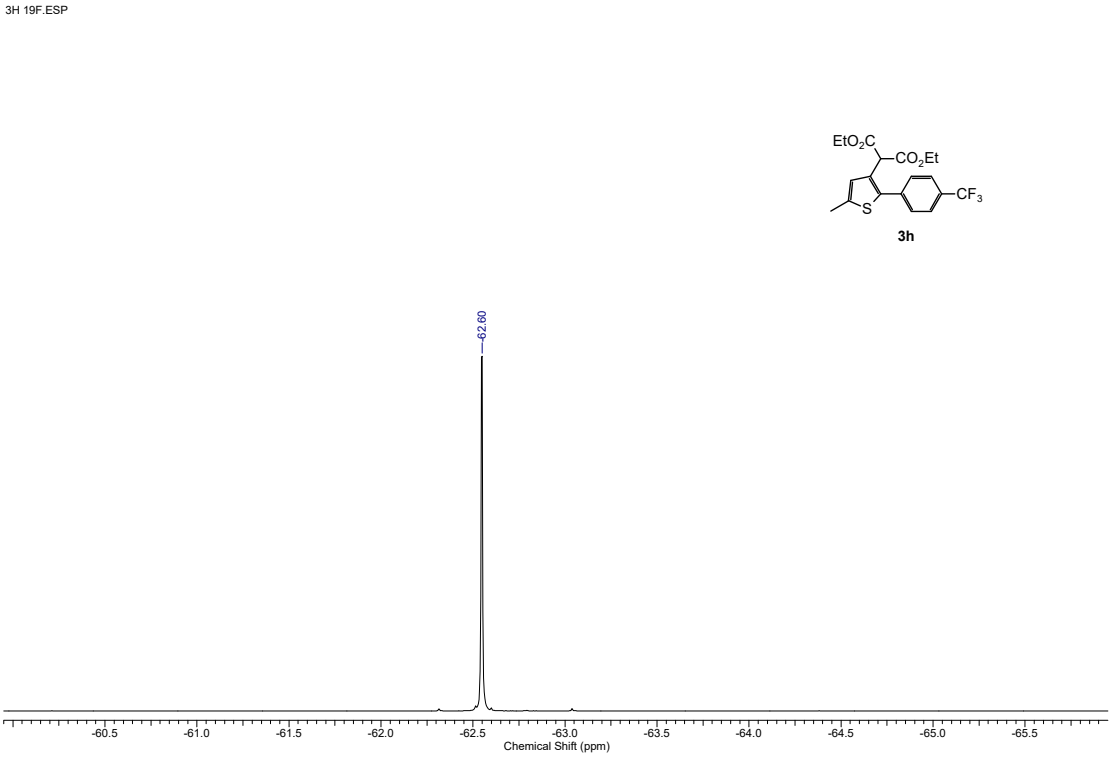


Figure S29. ^{19}F NMR spectrum of compound **3h**

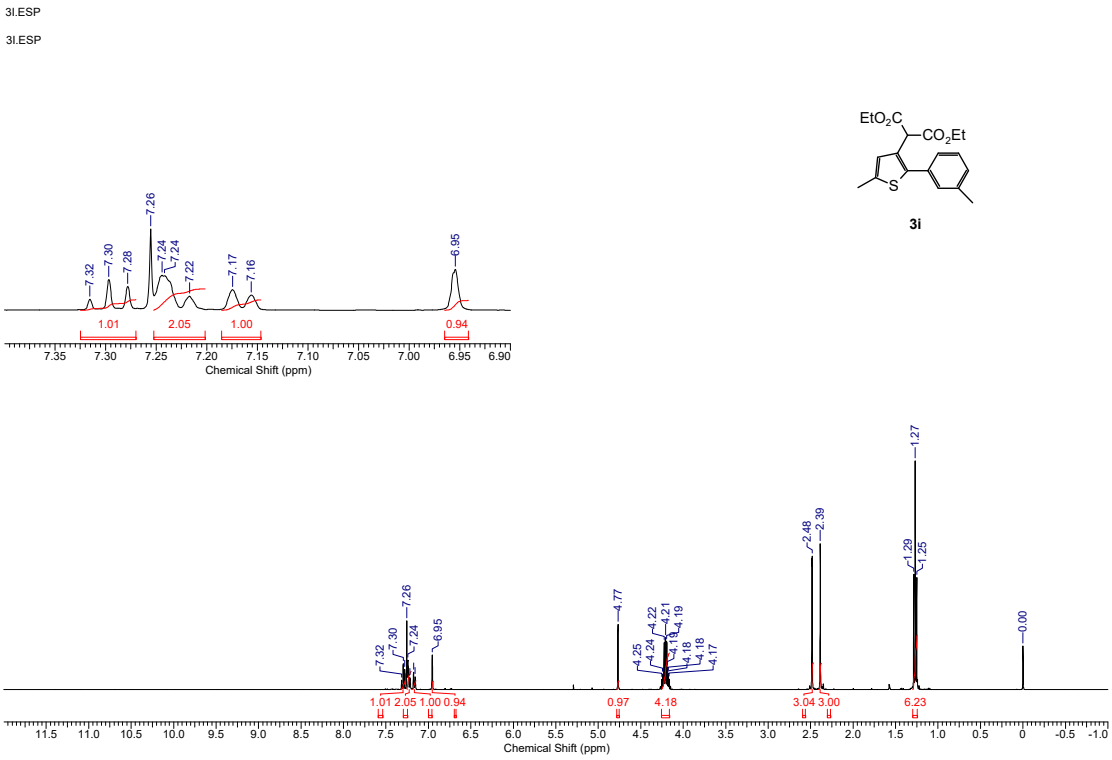


Figure S30. [1]H NMR spectrum of compound **3i**

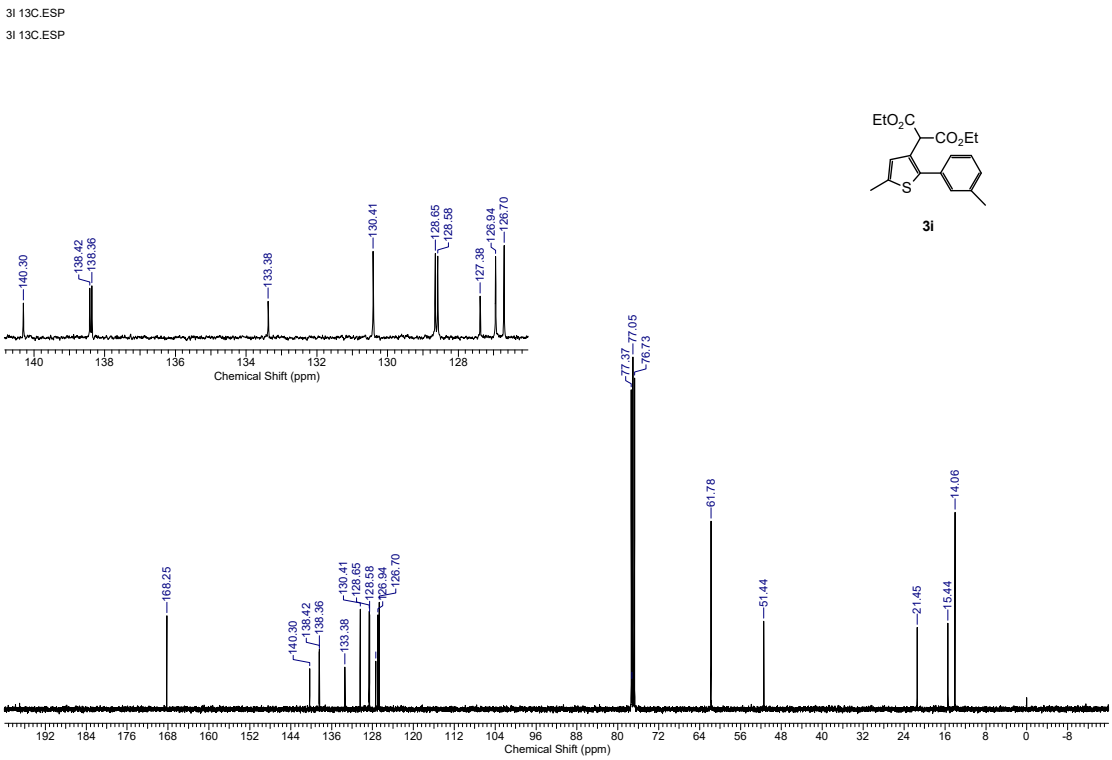


Figure S31. [13]C NMR spectrum of compound **3i**

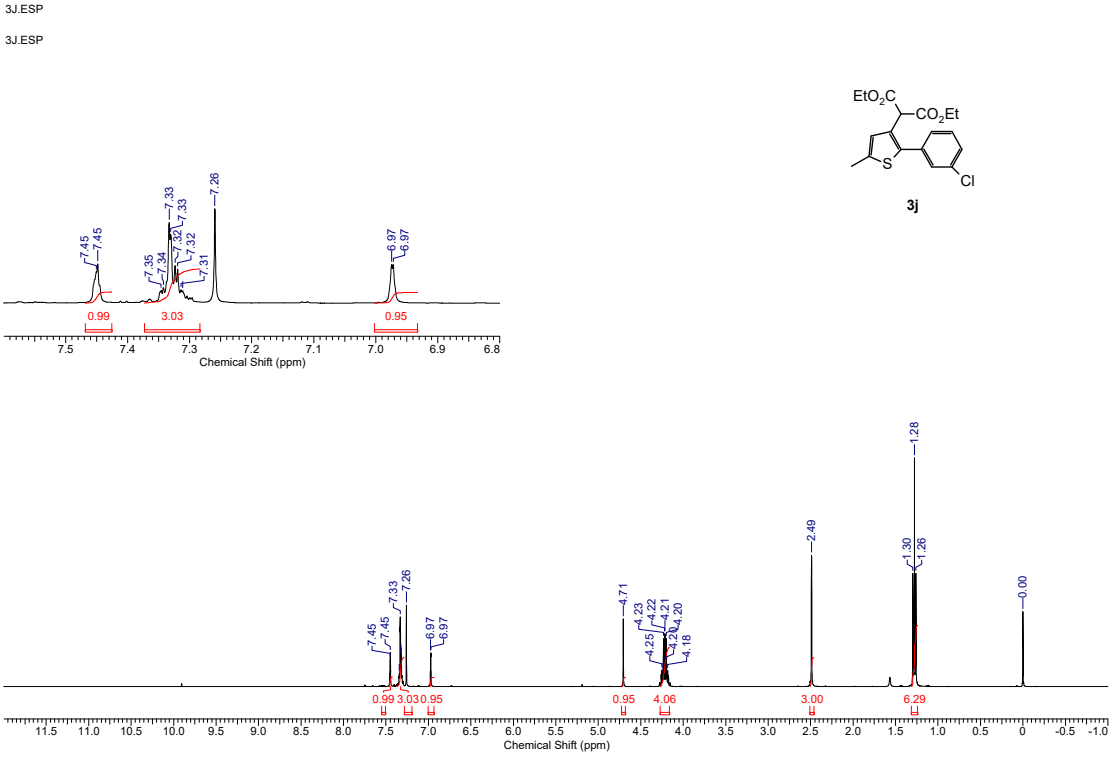


Figure S32. ^{1}H NMR spectrum of compound **3j**

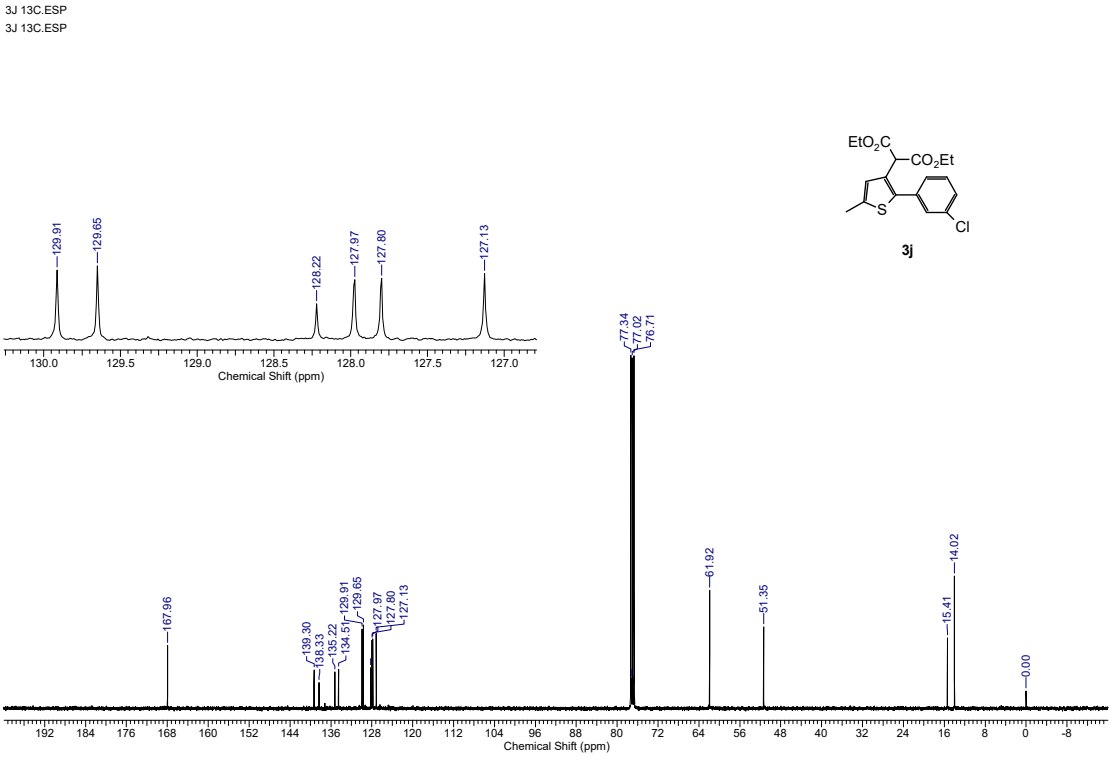


Figure S33. ^{13}C NMR spectrum of compound **3j**

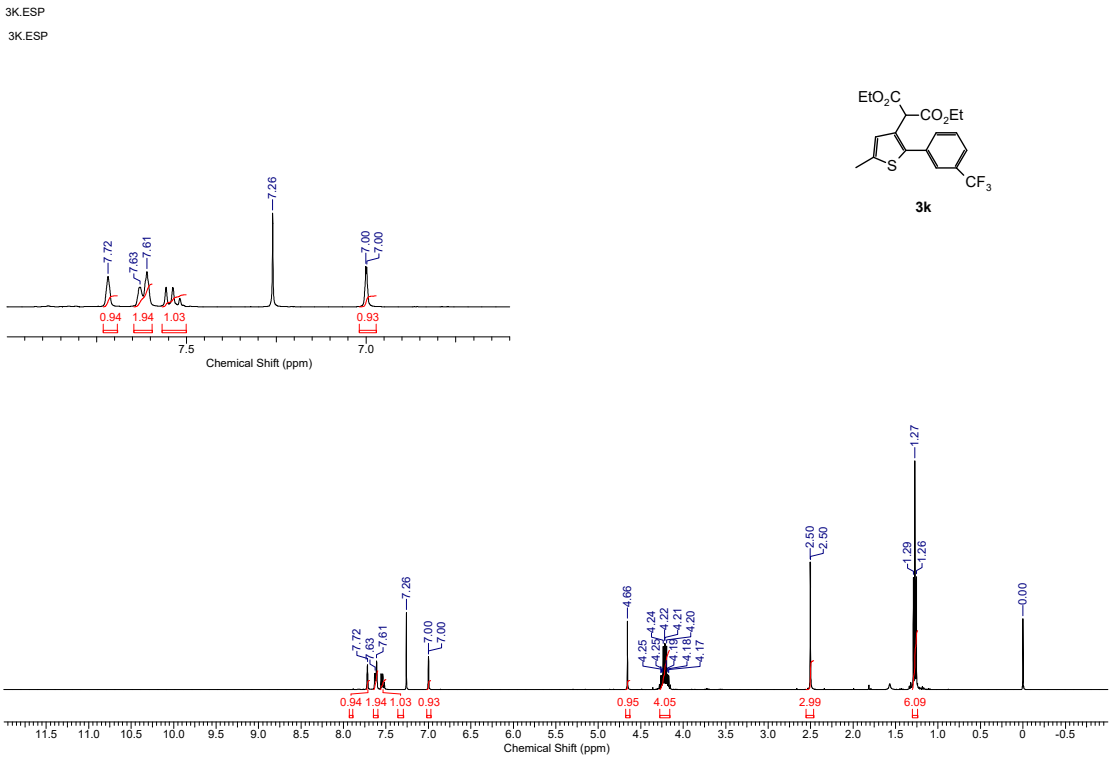


Figure S34. ^{1}H NMR spectrum of compound **3k**

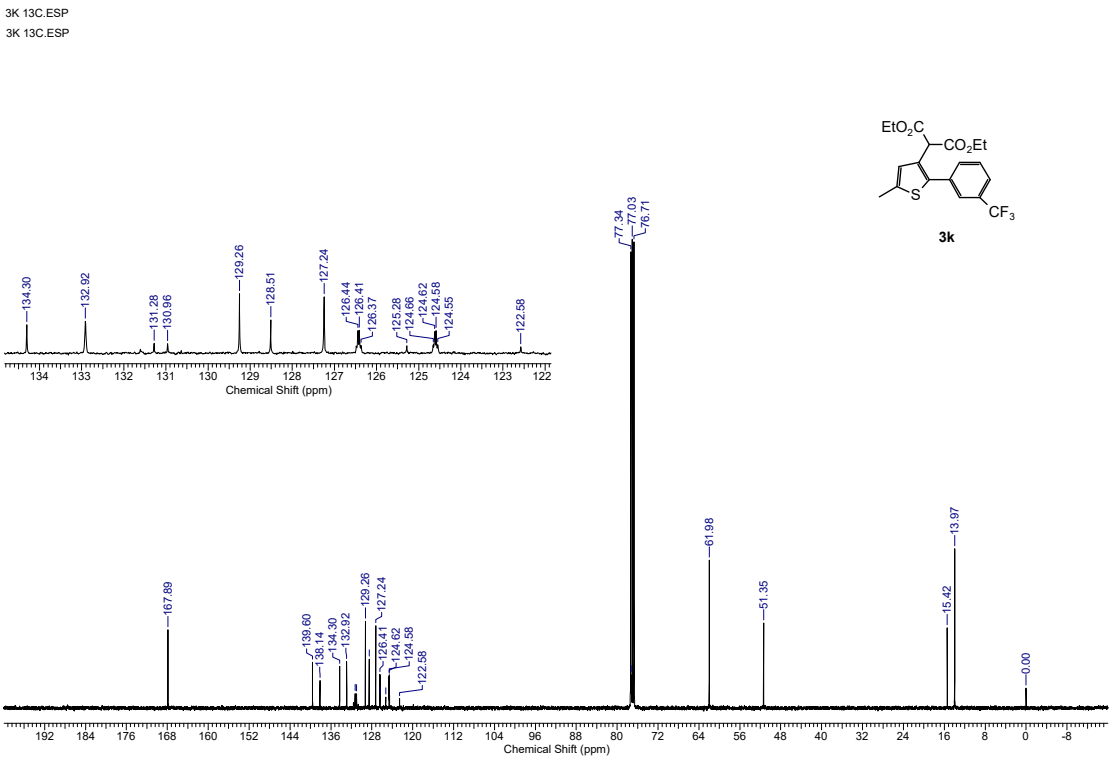


Figure S35. ^{13}C NMR spectrum of compound **3k**

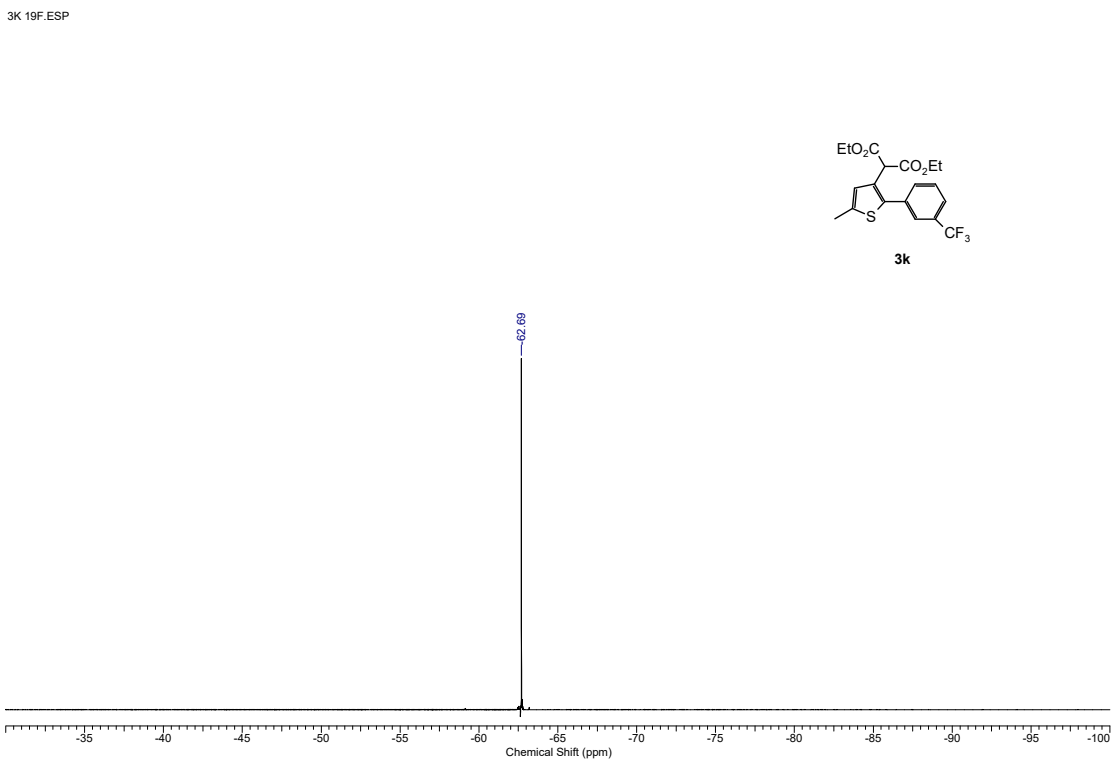


Figure S36. ^{19}F NMR spectrum of compound **3k**

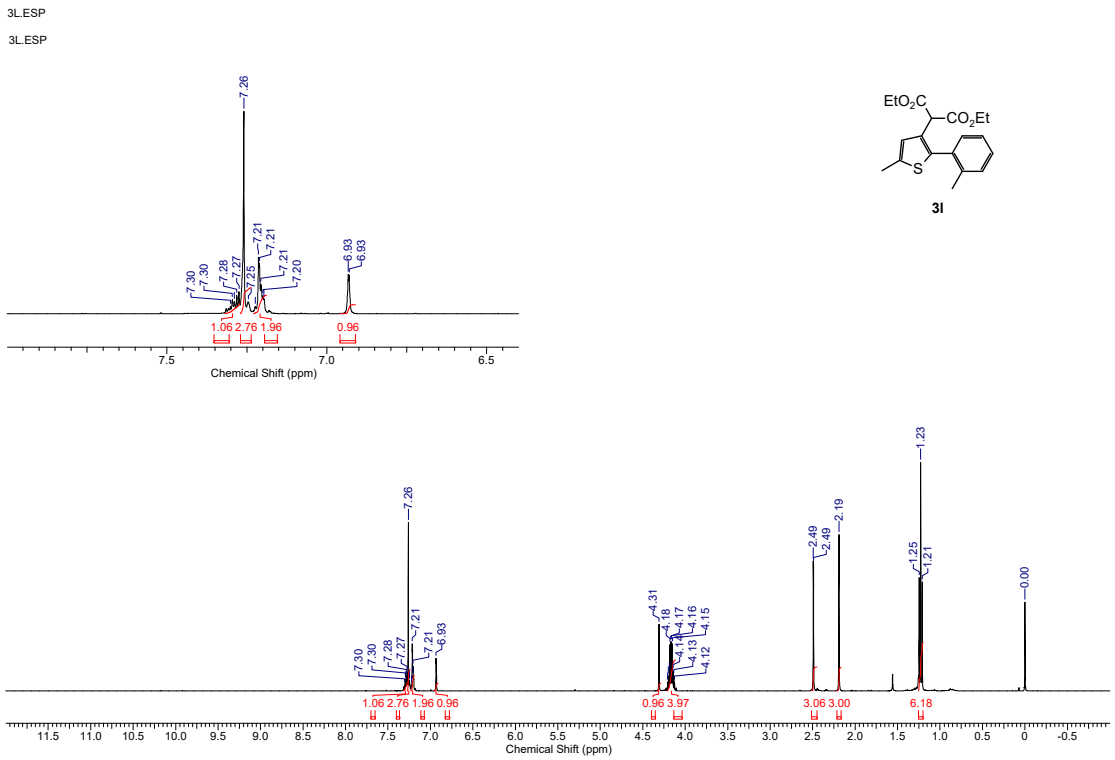


Figure S37. ^{1}H NMR spectrum of compound **3l**

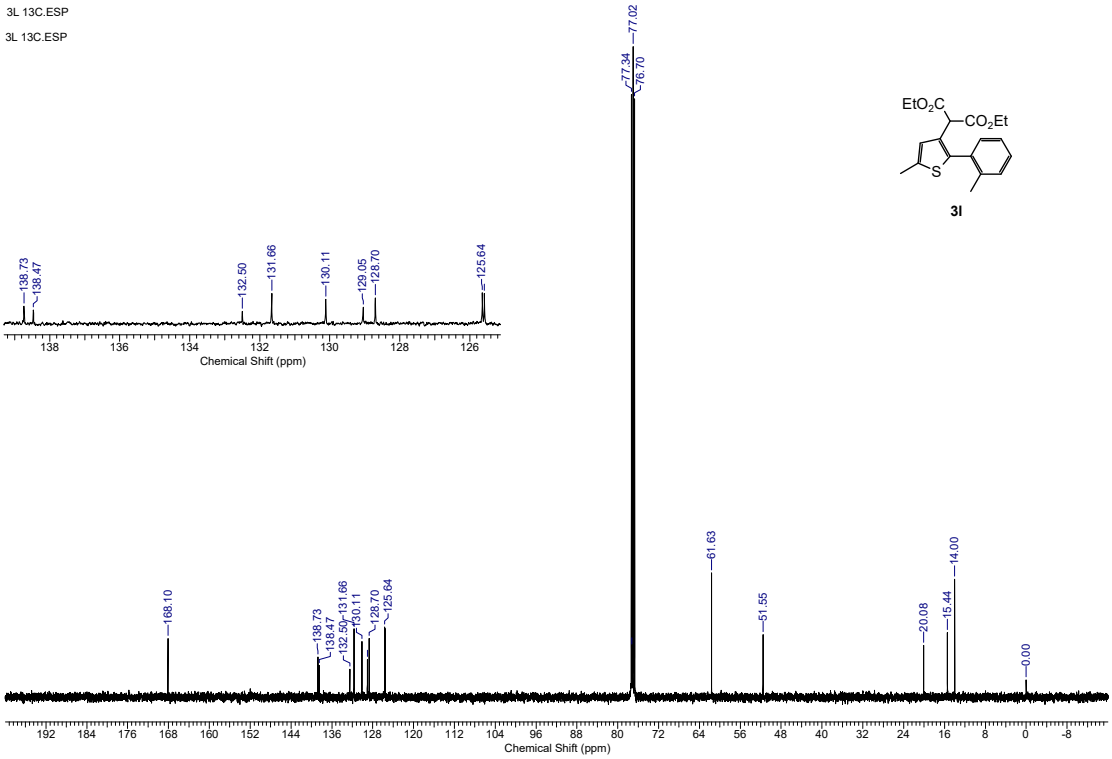


Figure S38. ^{13}C NMR spectrum of compound **3l**

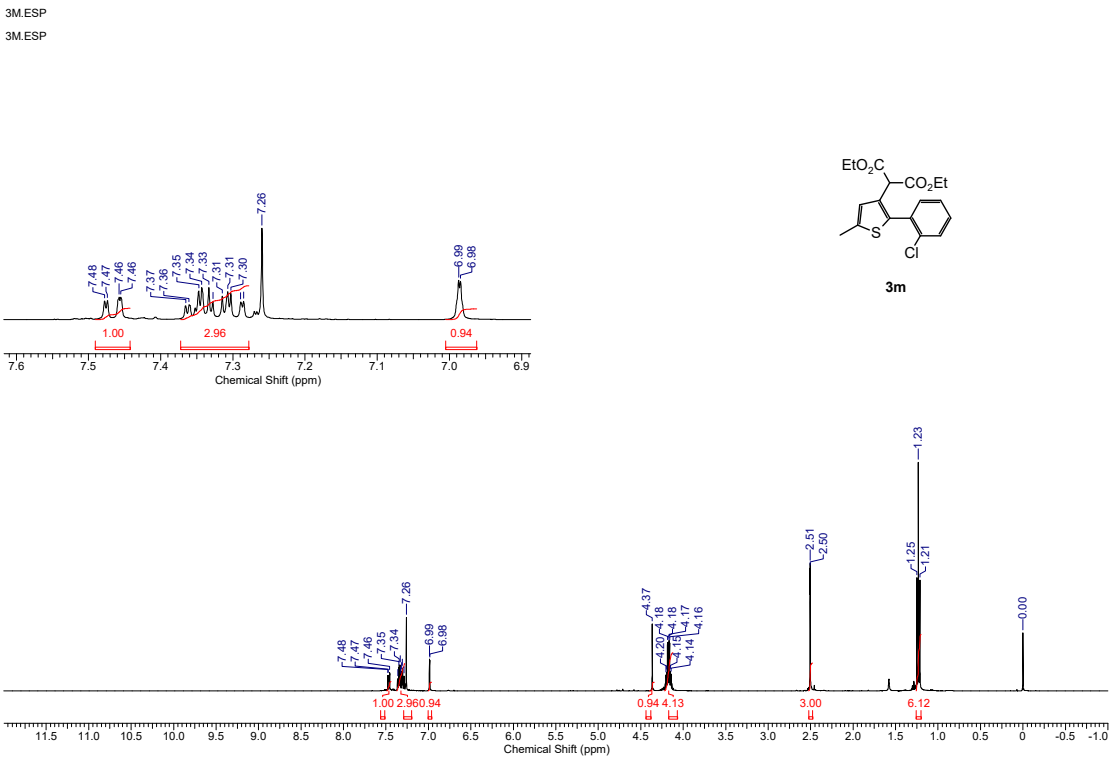


Figure S39. ^{1}H NMR spectrum of compound **3m**

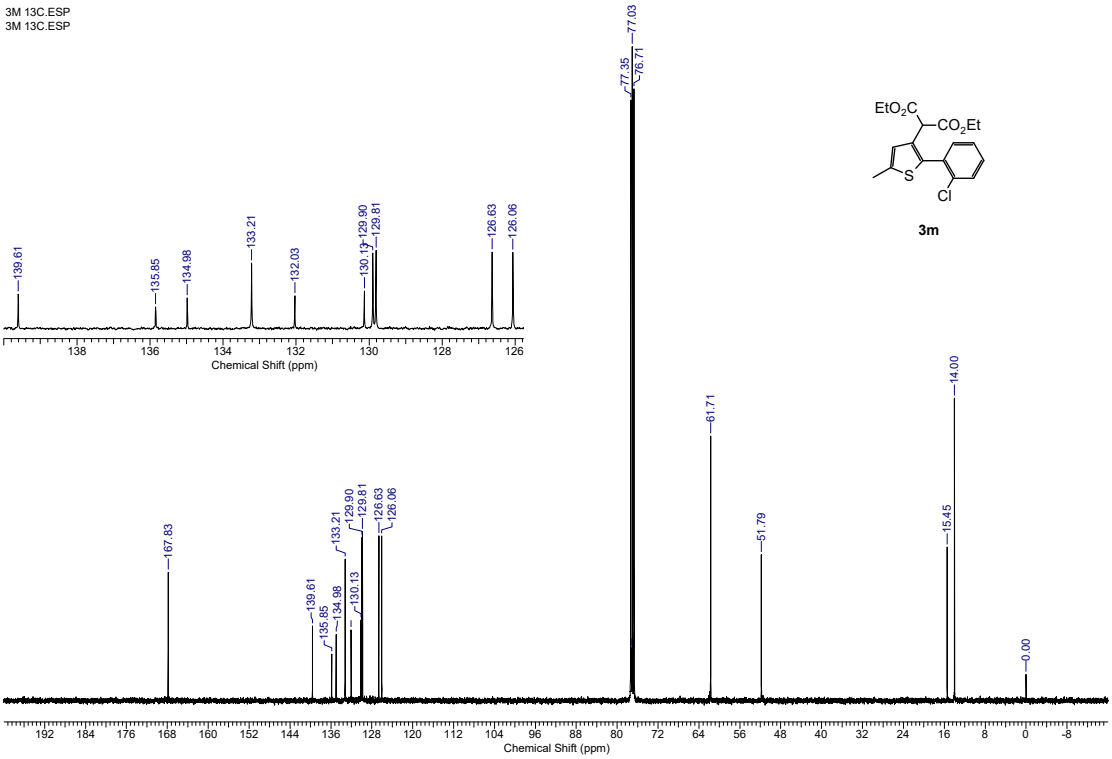


Figure S40. ^{13}C NMR spectrum of compound **3m**

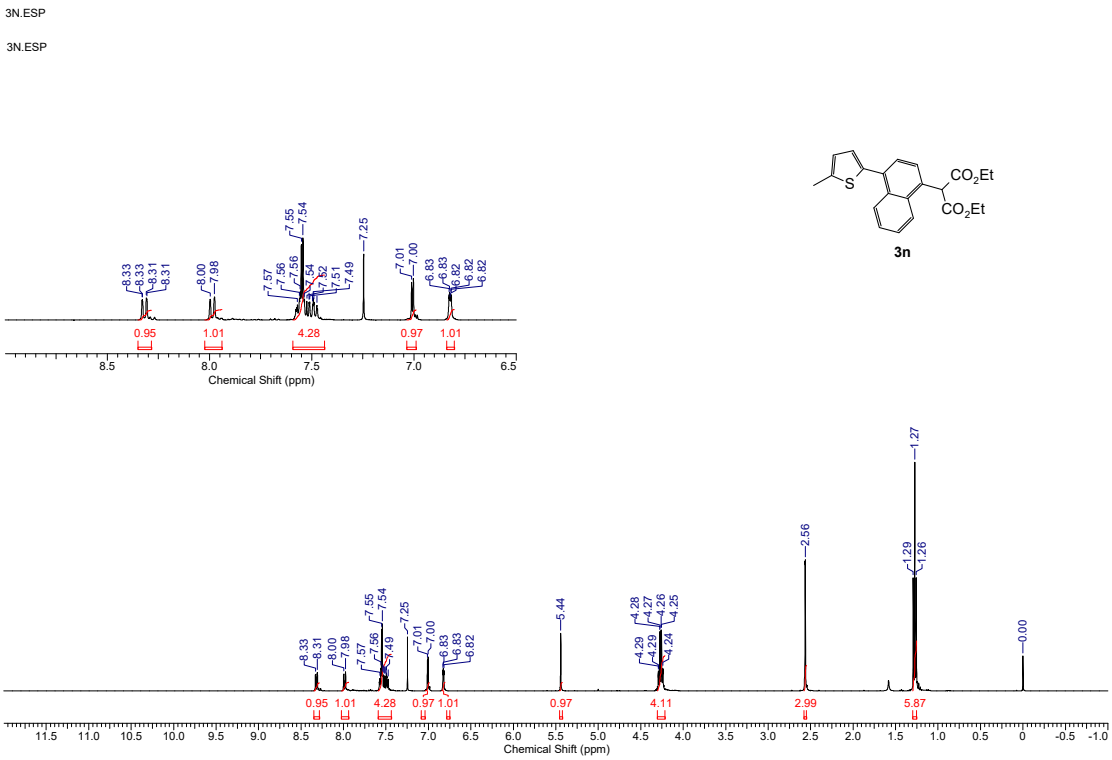


Figure S41. ^{1}H NMR spectrum of compound **3n**

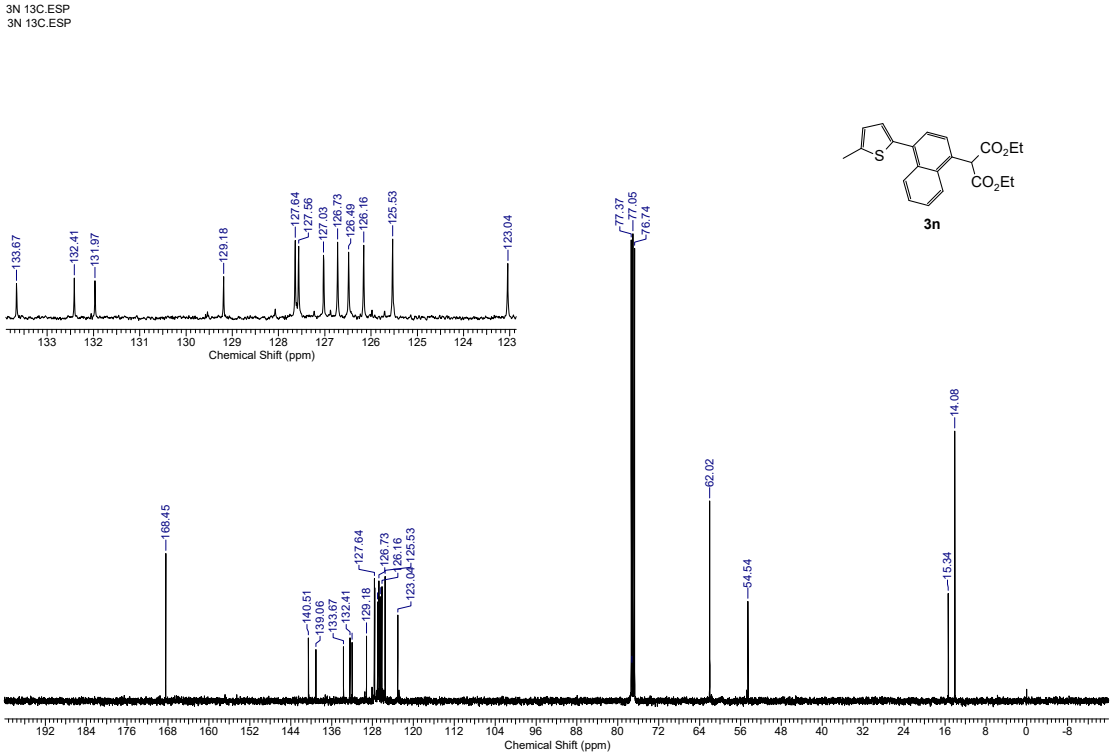


Figure S42. ^{13}C NMR spectrum of compound **3n**

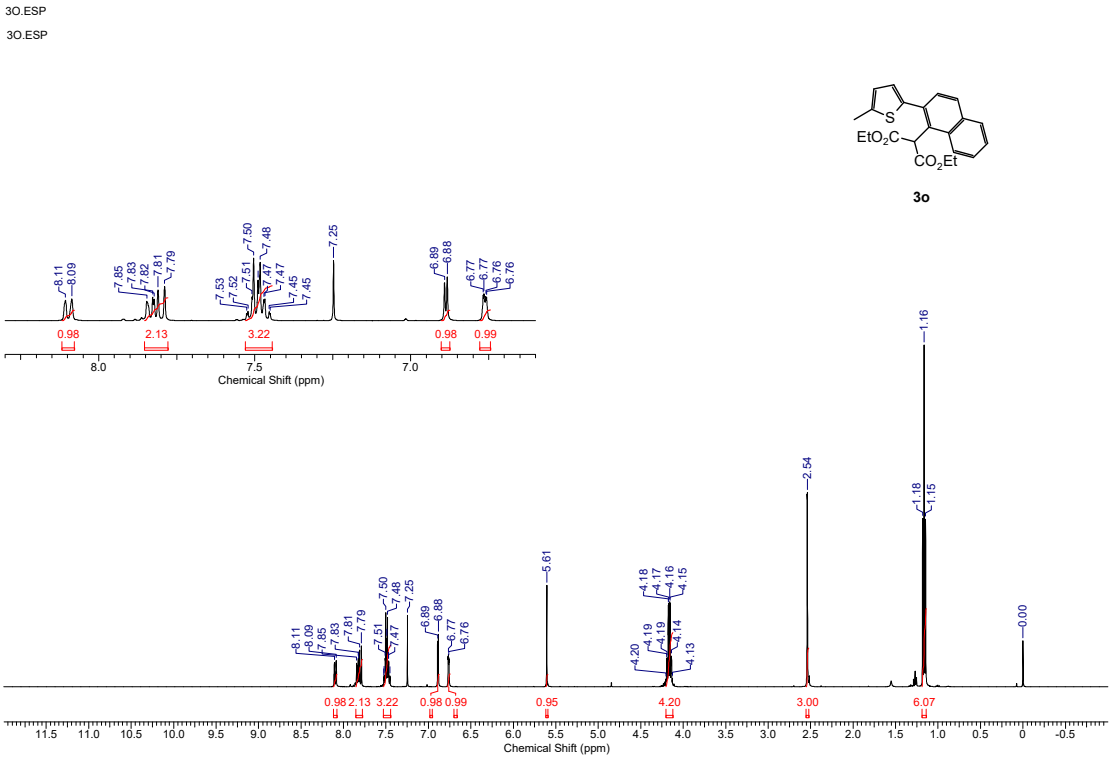


Figure S43. ^{1}H NMR spectrum of compound **3o**

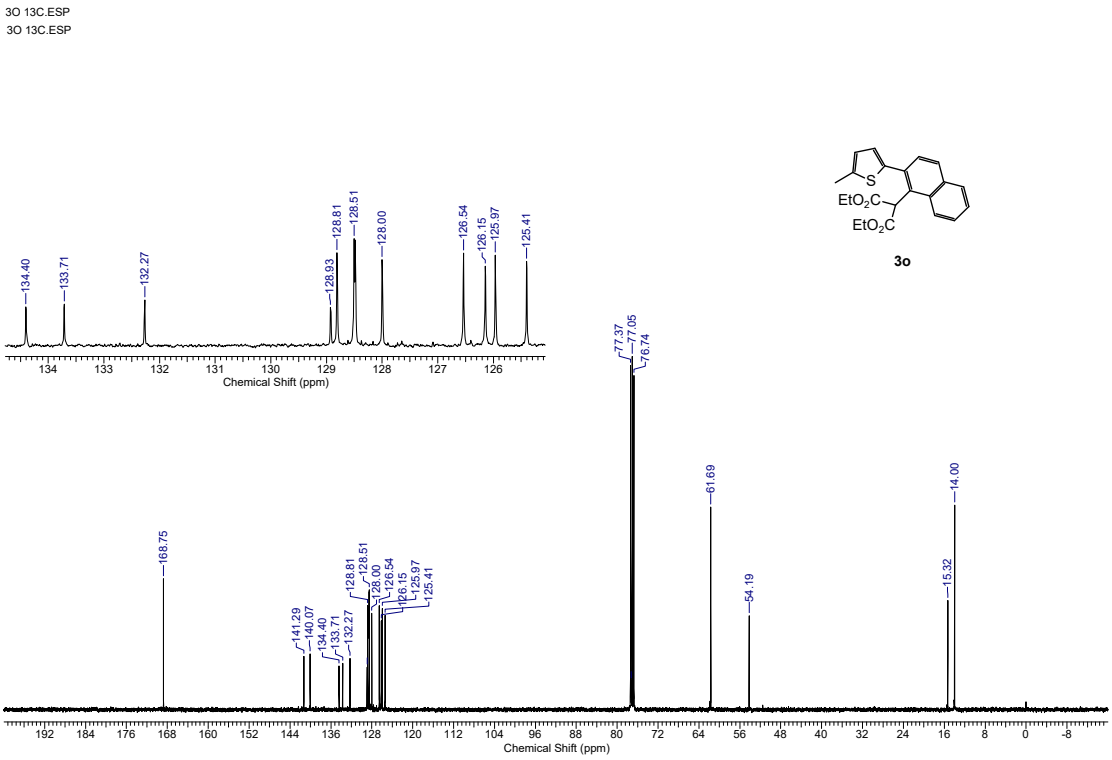


Figure S44. ^{13}C NMR spectrum of compound **3o**

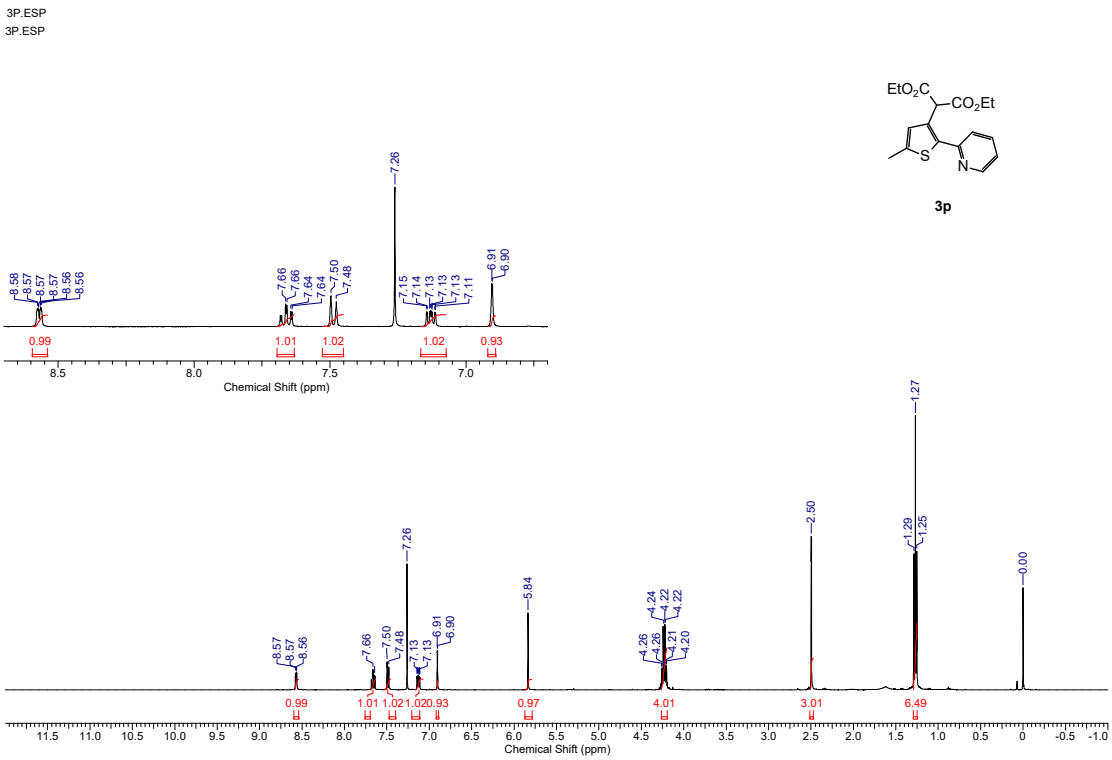


Figure S45. ^{1}H NMR spectrum of compound **3p**

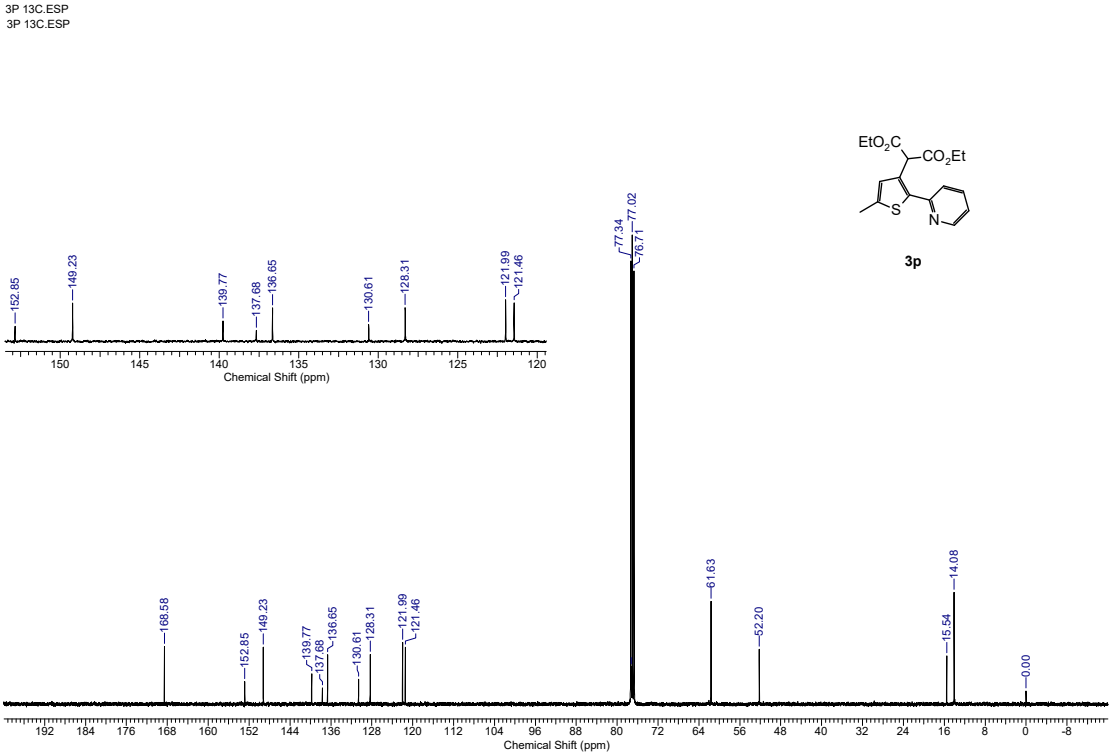


Figure S46. ^{13}C NMR spectrum of compound **3p**

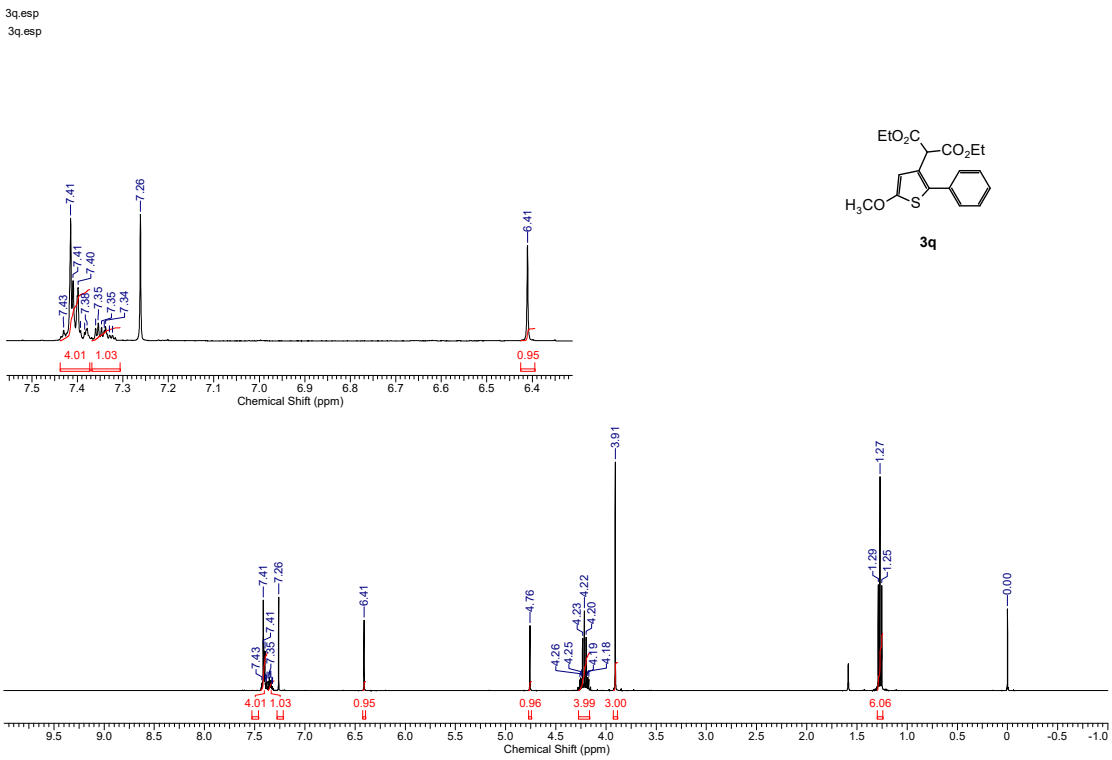


Figure S47. ^{1}H NMR spectrum of compound **3q**

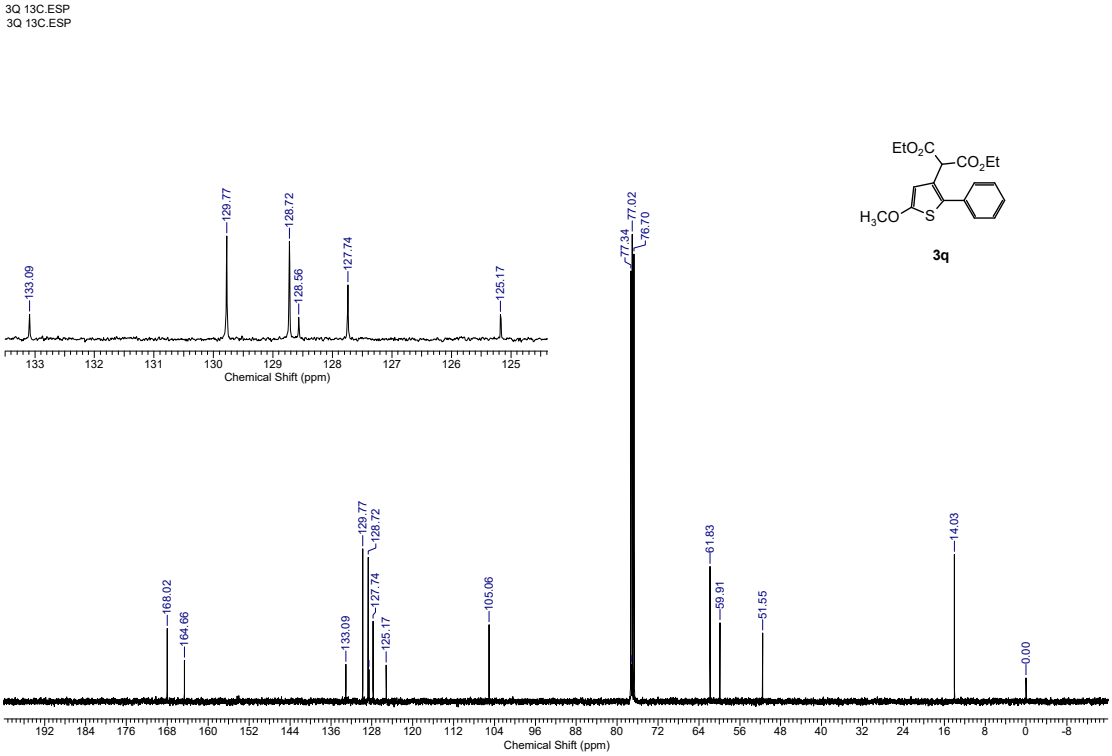


Figure S48. ^{13}C NMR spectrum of compound **3q**

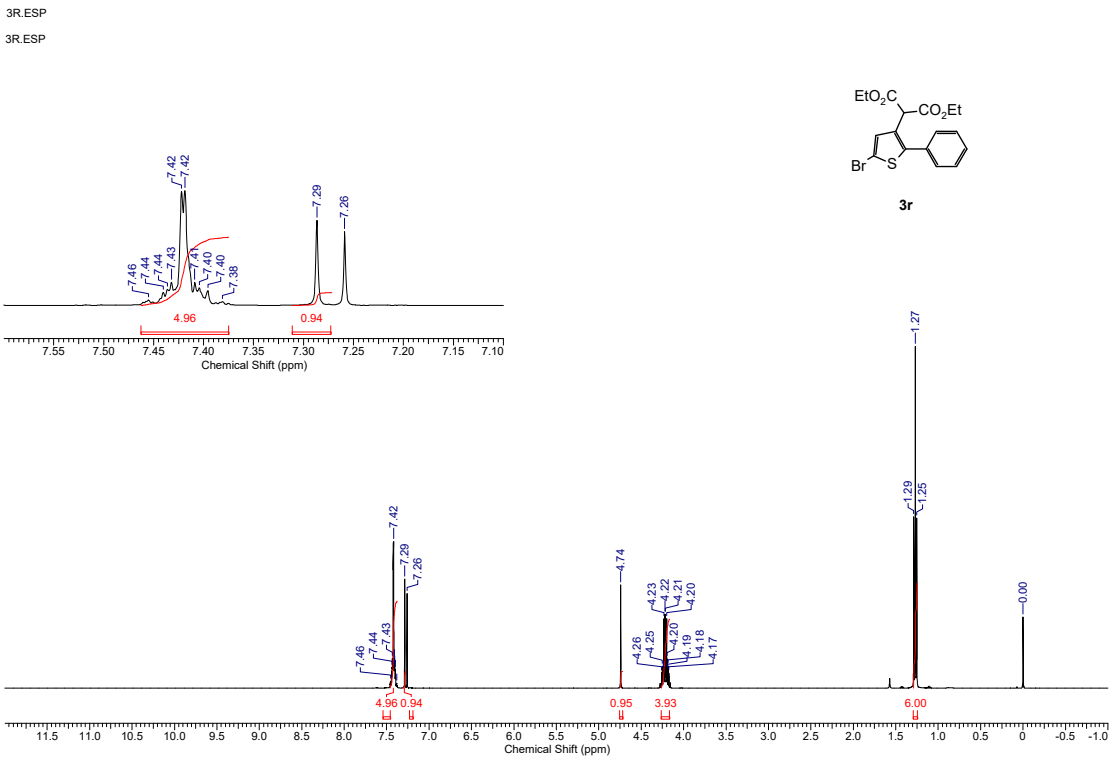


Figure S49. ^{1}H NMR spectrum of compound **3r**

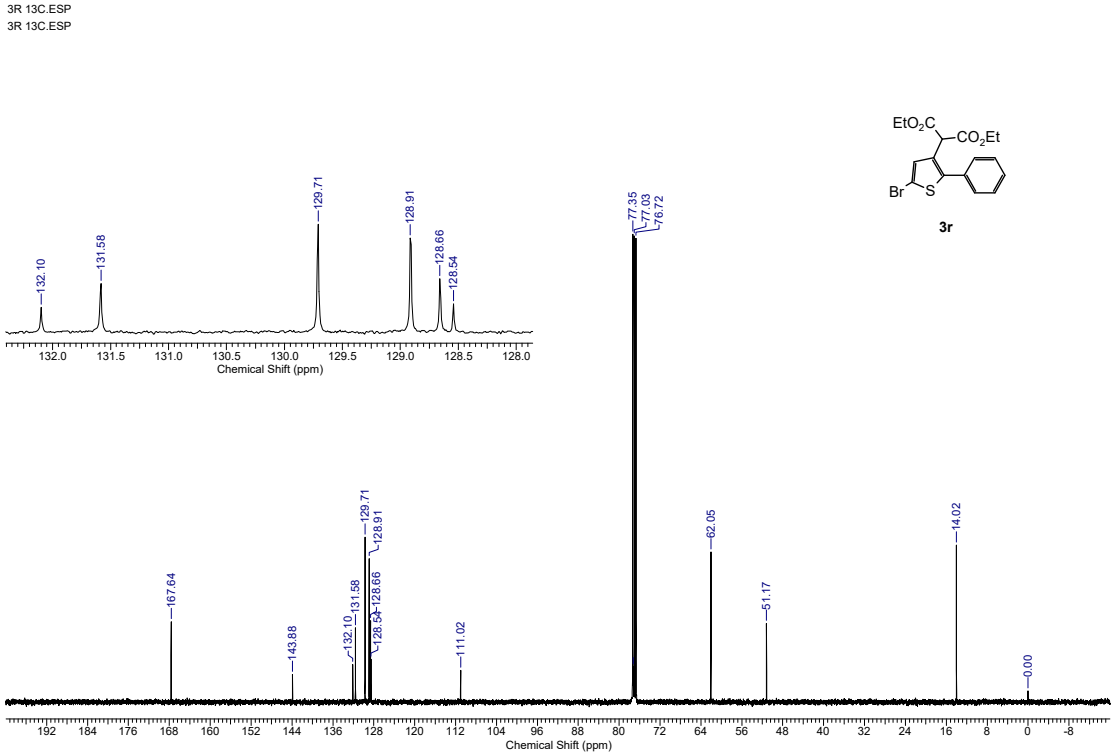


Figure S50. ^{13}C NMR spectrum of compound **3r**

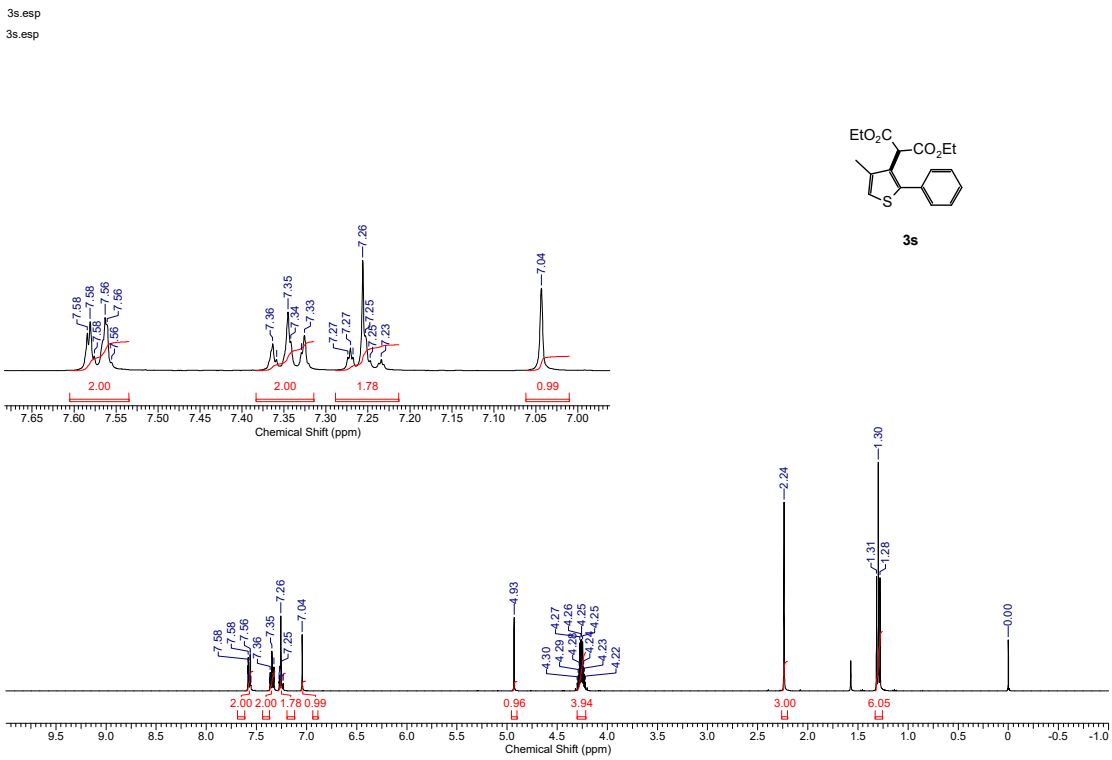


Figure S51. ^{1}H NMR spectrum of compound **3s**

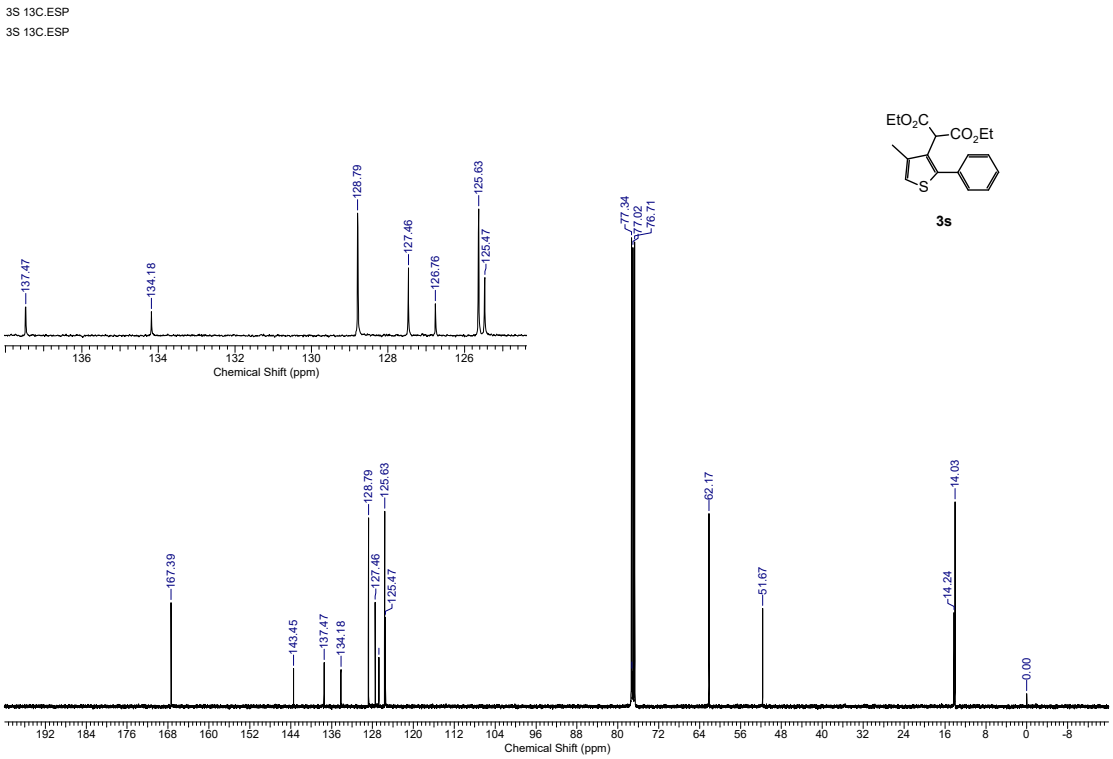


Figure S52. ^{13}C NMR spectrum of compound **3s**

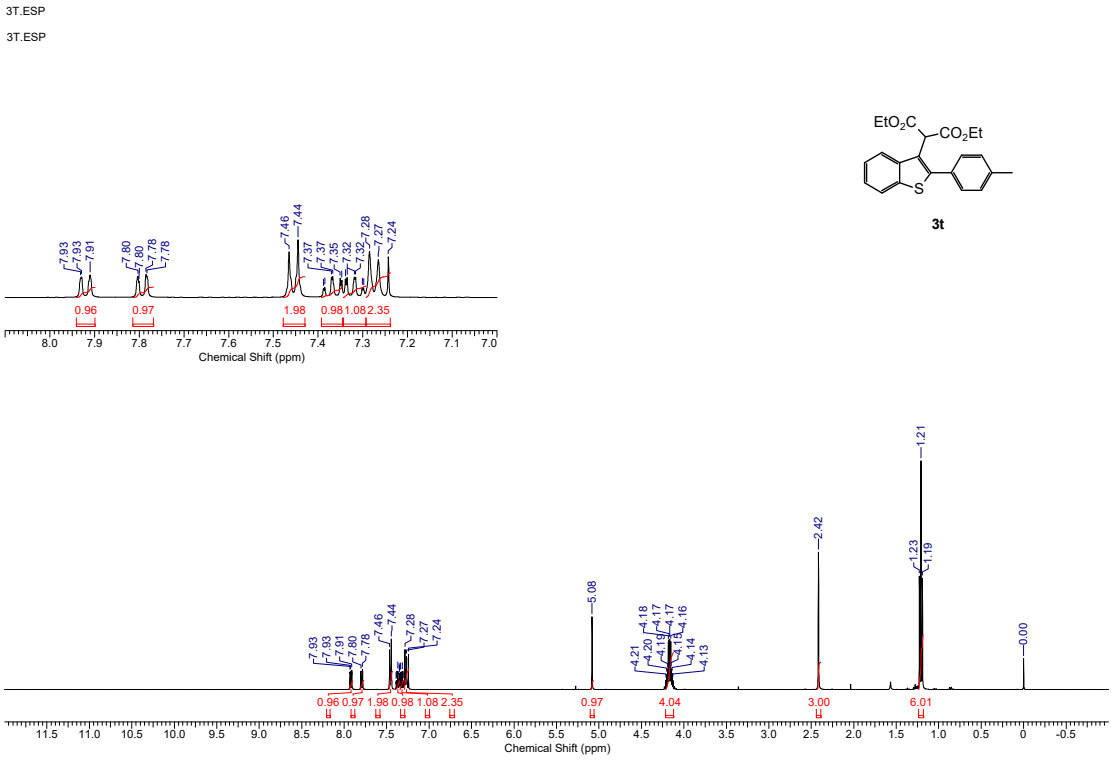


Figure S53. ^{1}H NMR spectrum of compound **3t**

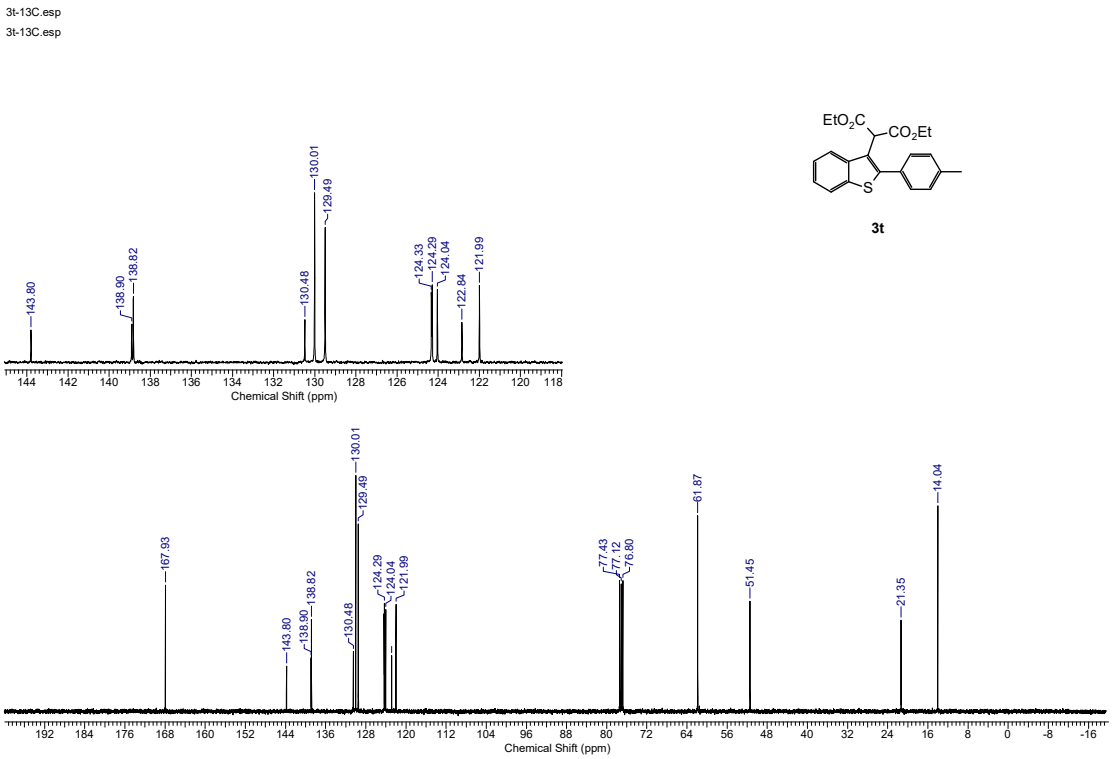


Figure S54. ^{13}C NMR spectrum of compound **3t**

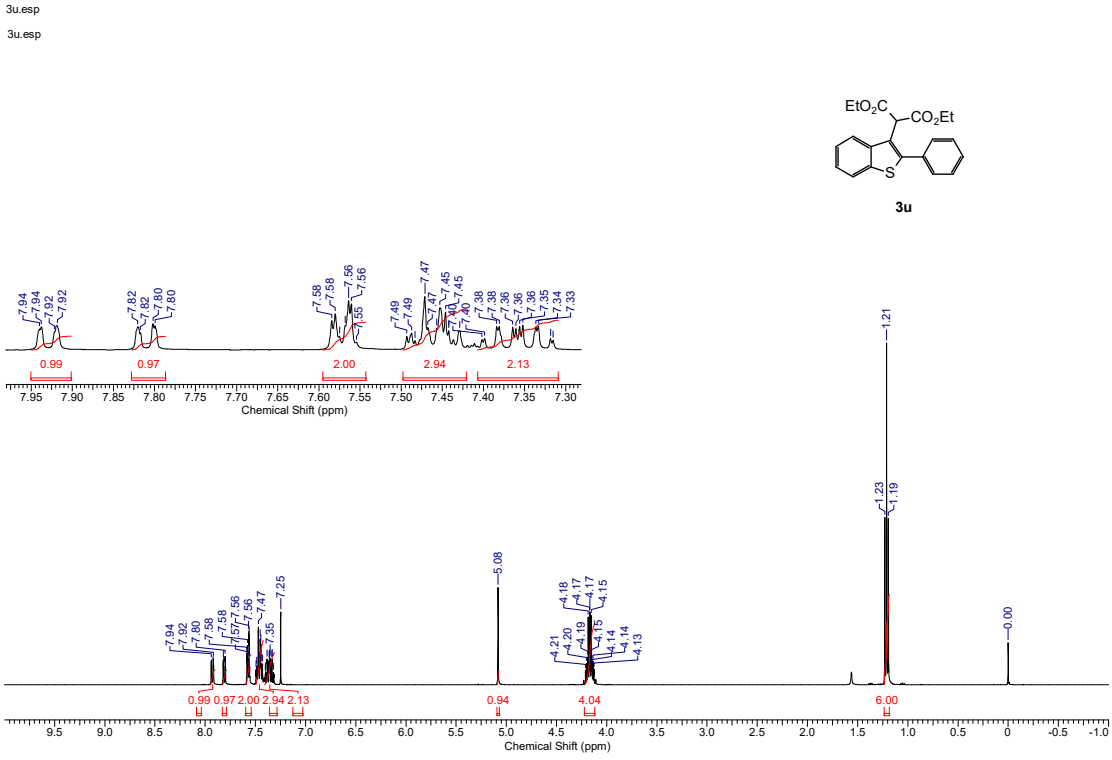


Figure S55. ^{1}H NMR spectrum of compound **3u**

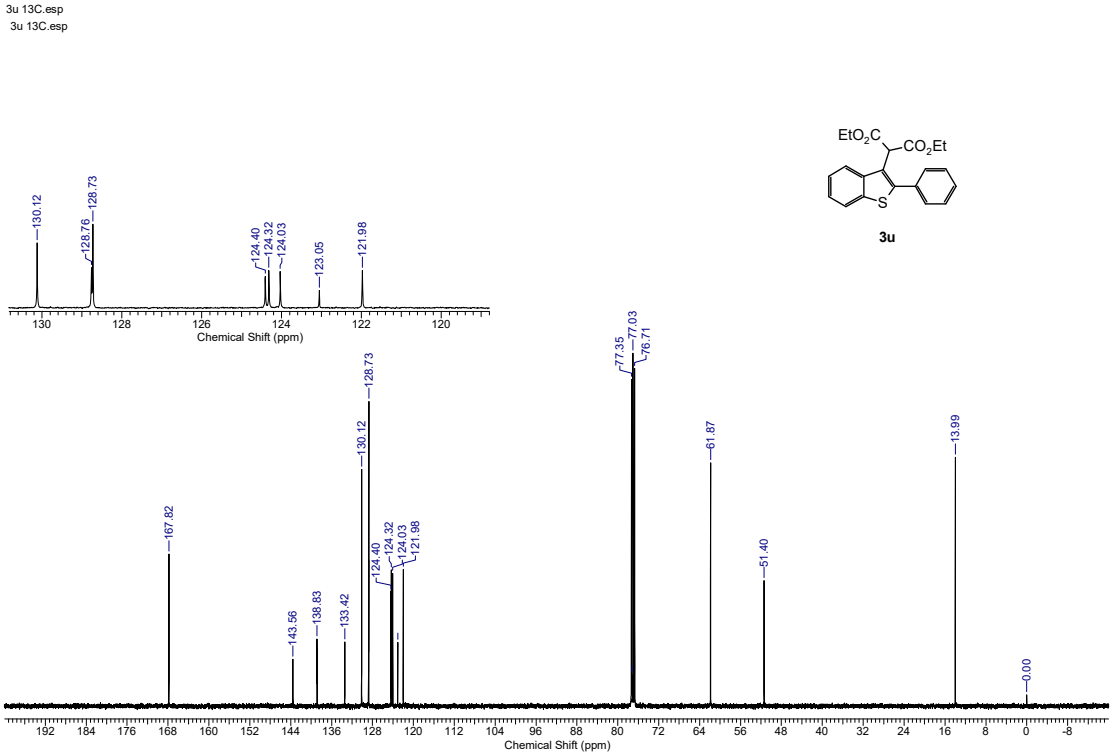


Figure S56. ^{13}C NMR spectrum of compound **3u**

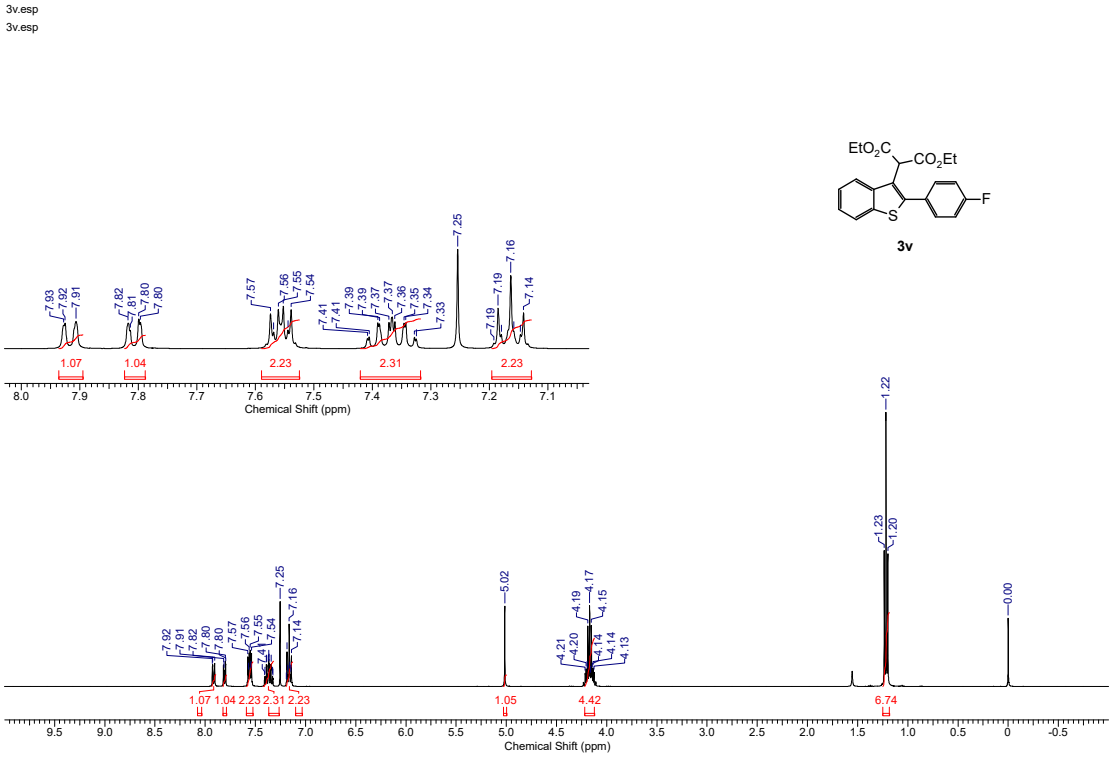


Figure S57. ^{1}H NMR spectrum of compound of **3v**

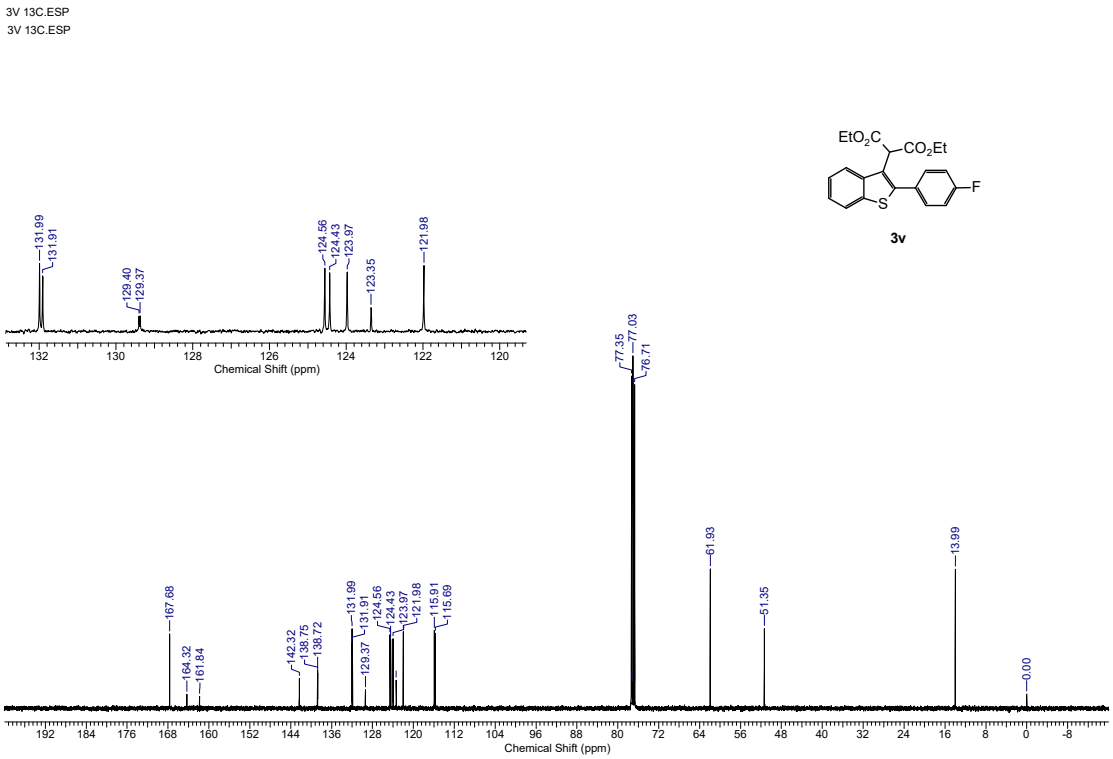


Figure S58. ^{13}C NMR spectrum of compound of **3v**

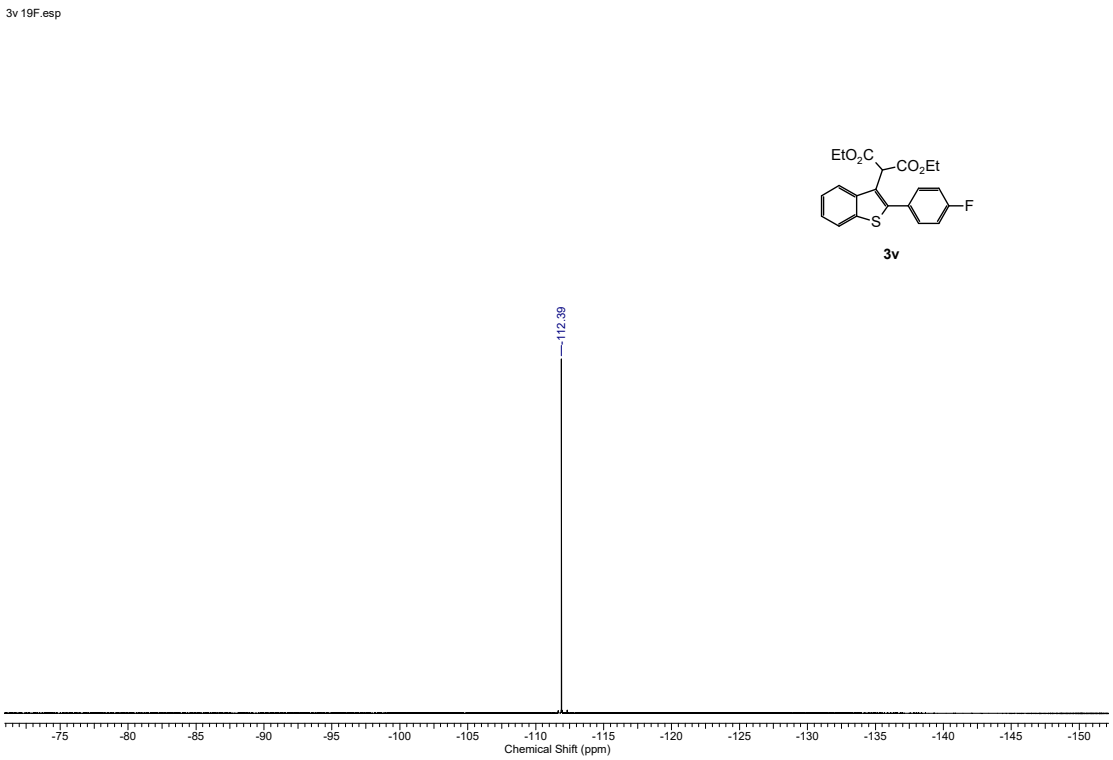


Figure S59. ^{19}F NMR spectrum of compound **3v**

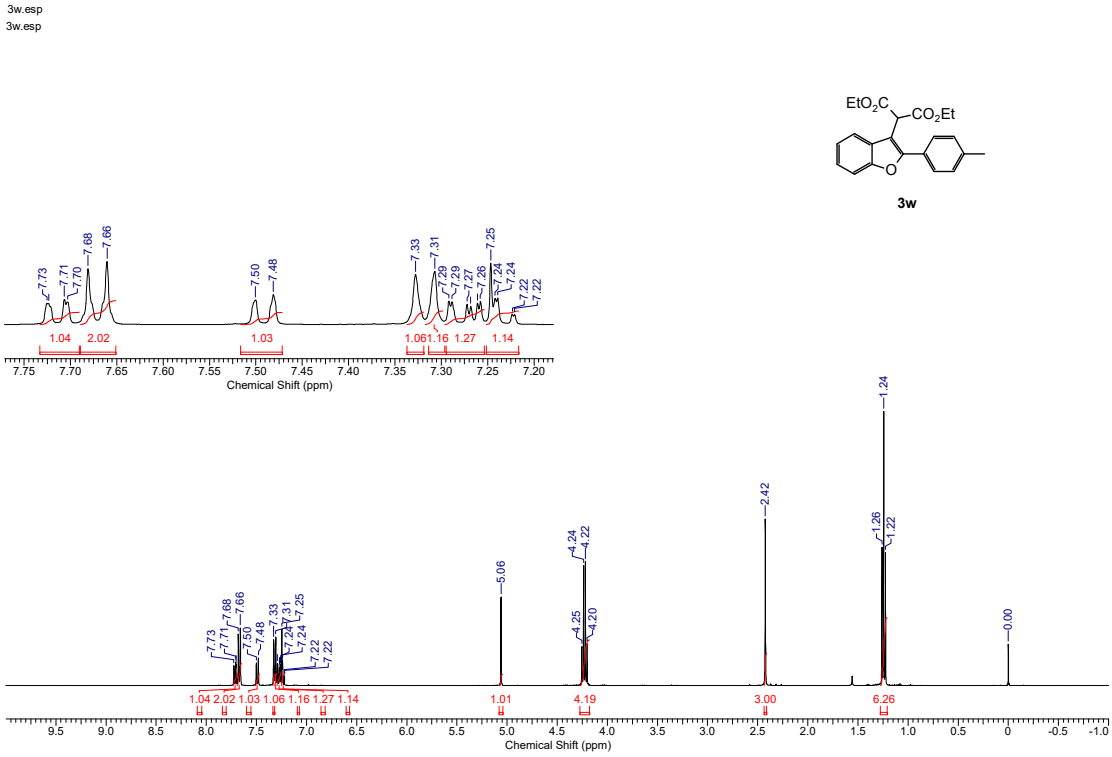


Figure S60. ^{1}H NMR spectrum of compound **3w**

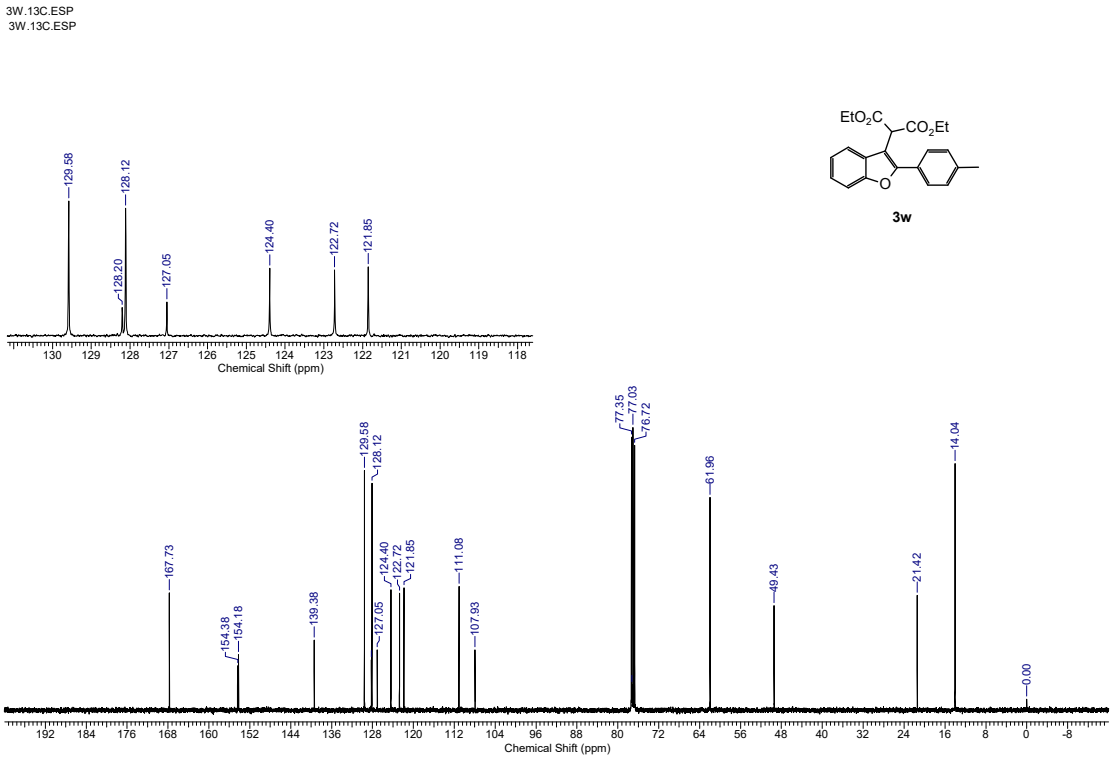


Figure S61. ^{13}C NMR spectrum of compound **3w**

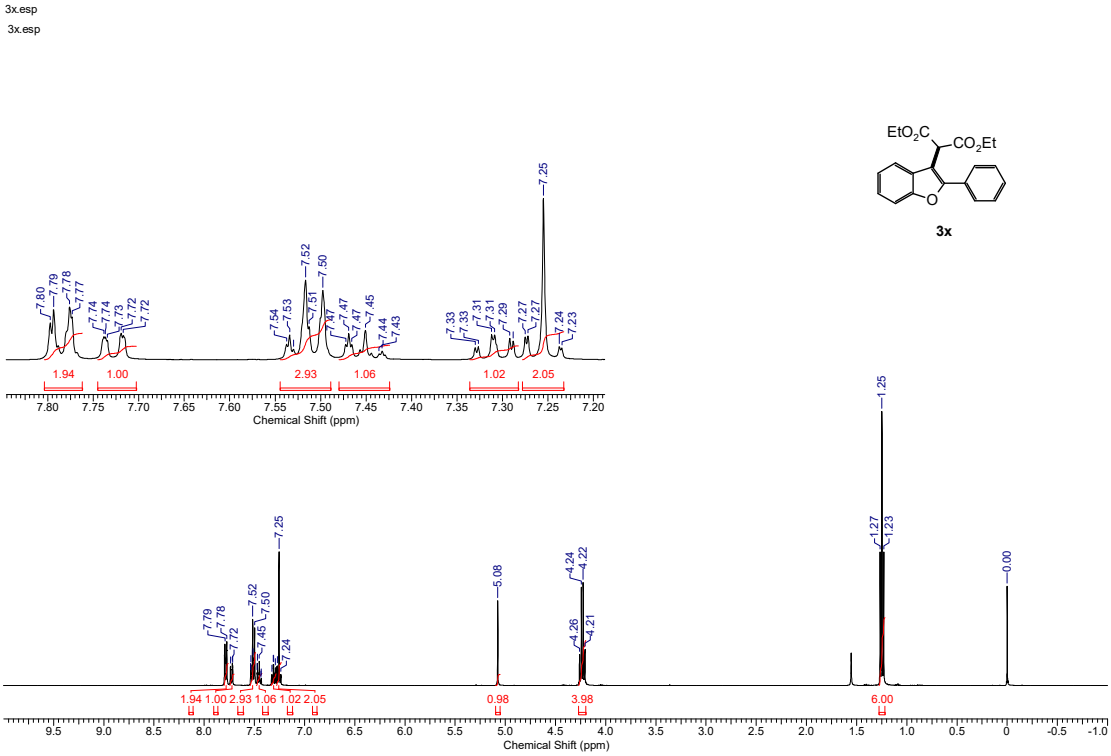


Figure S62. ^{1}H NMR spectrum of compound **3x**

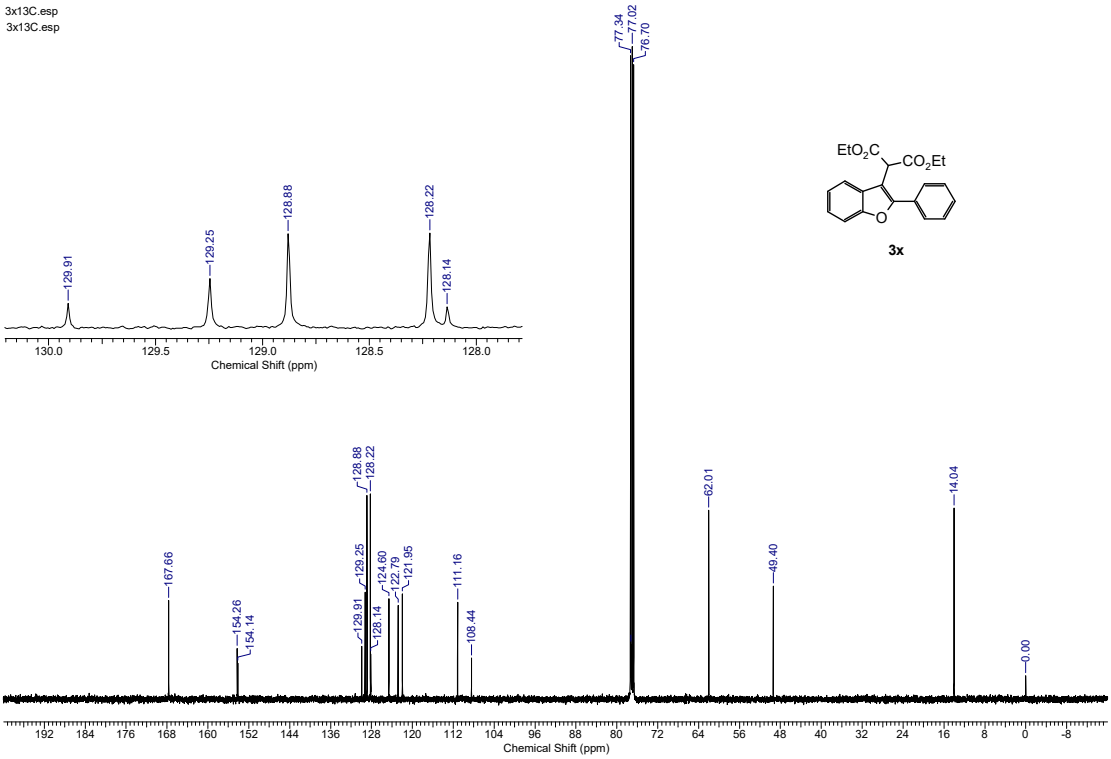


Figure S63. ^{13}C NMR spectrum of compound **3x**

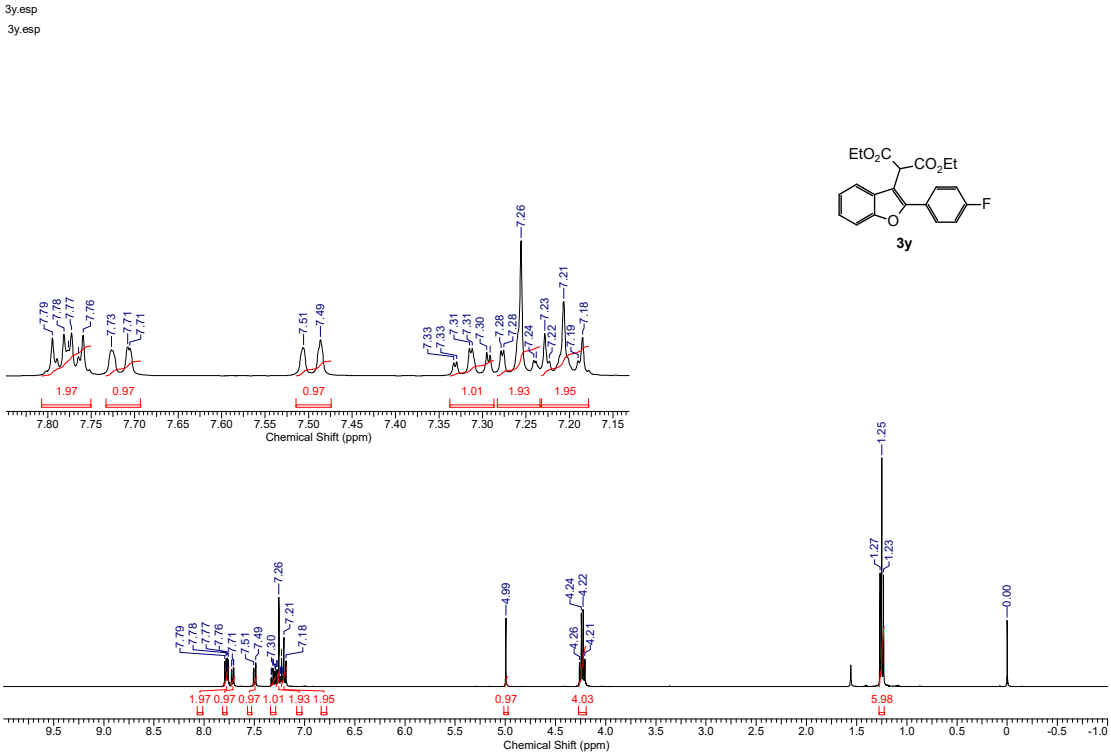


Figure S64. ^{1}H NMR spectrum of compound **3y**

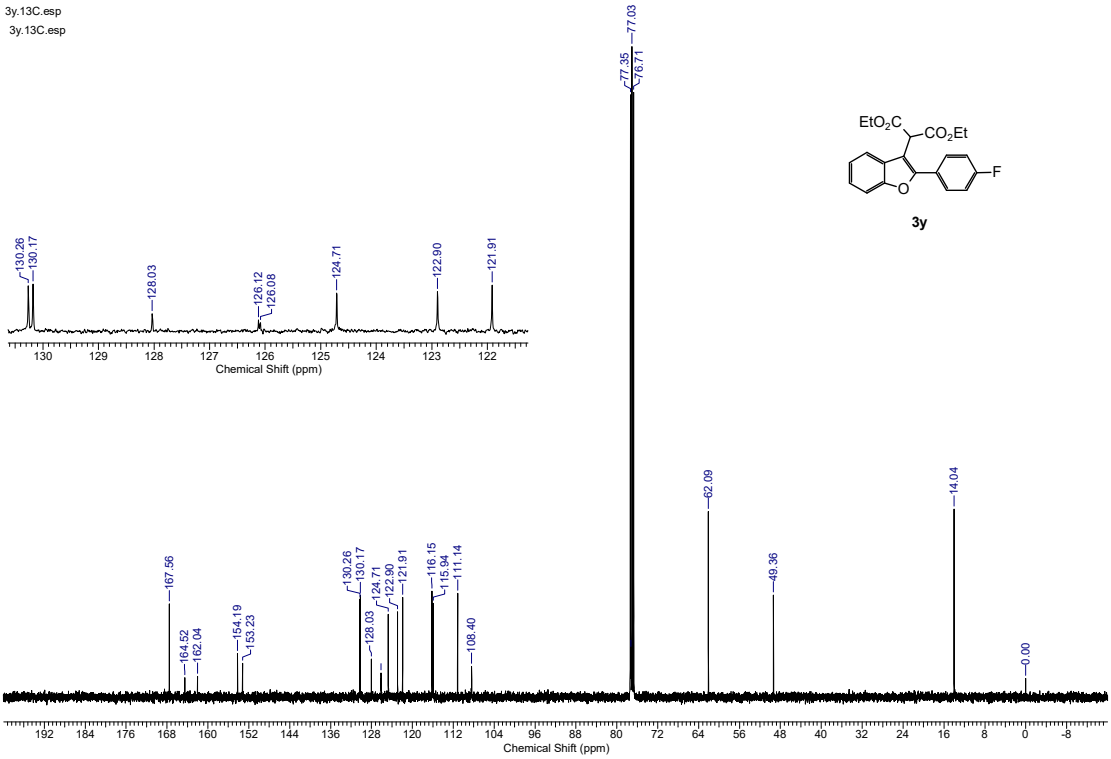


Figure S65. ^{13}C NMR spectrum of compound **3y**

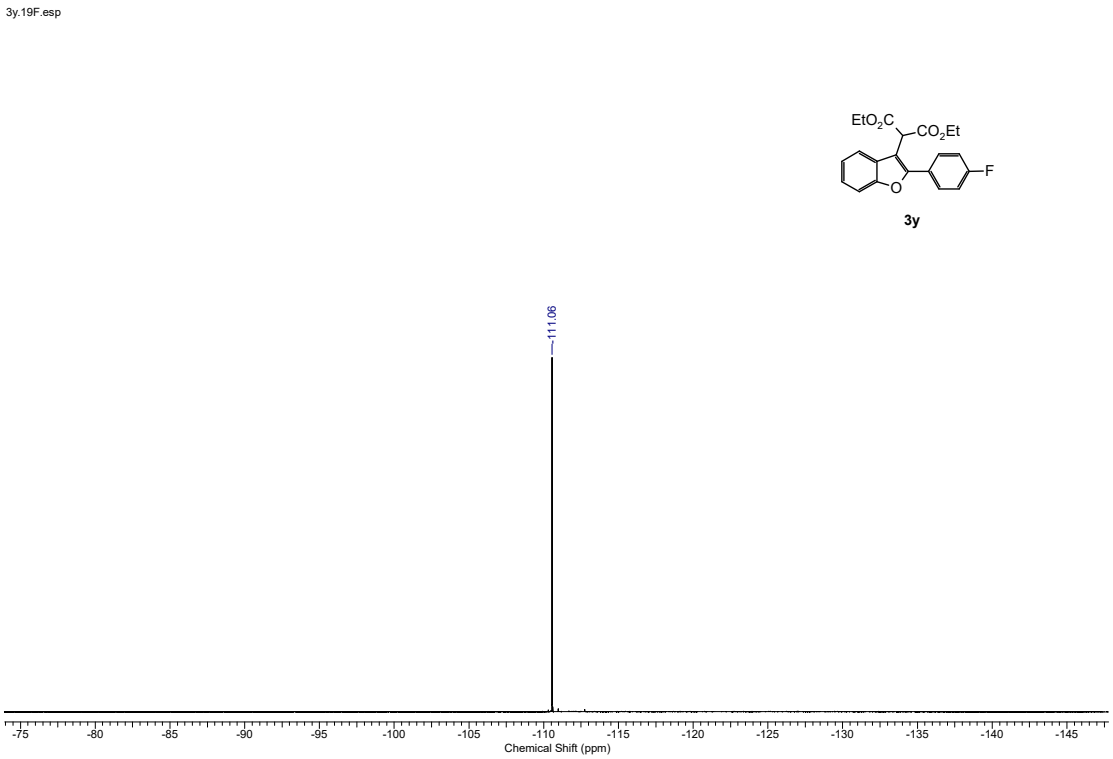


Figure S66. ^{19}F NMR spectrum of compound **3y**

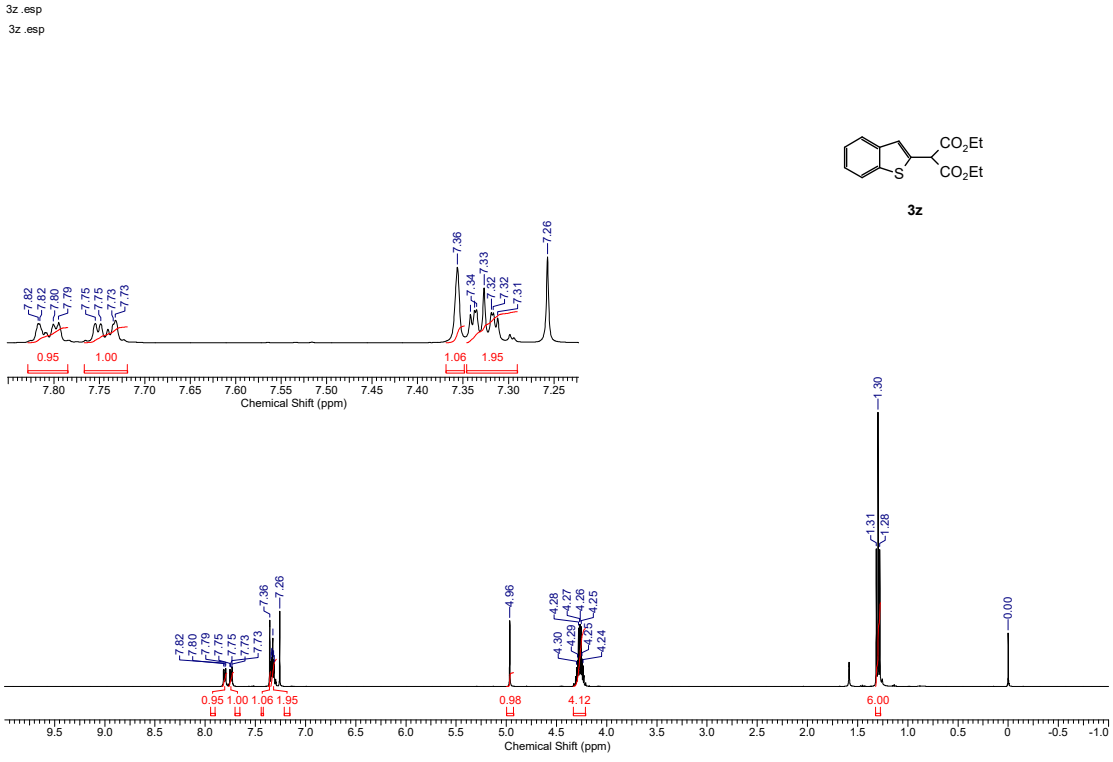


Figure S67. ^{1}H NMR spectrum of compound **3z**

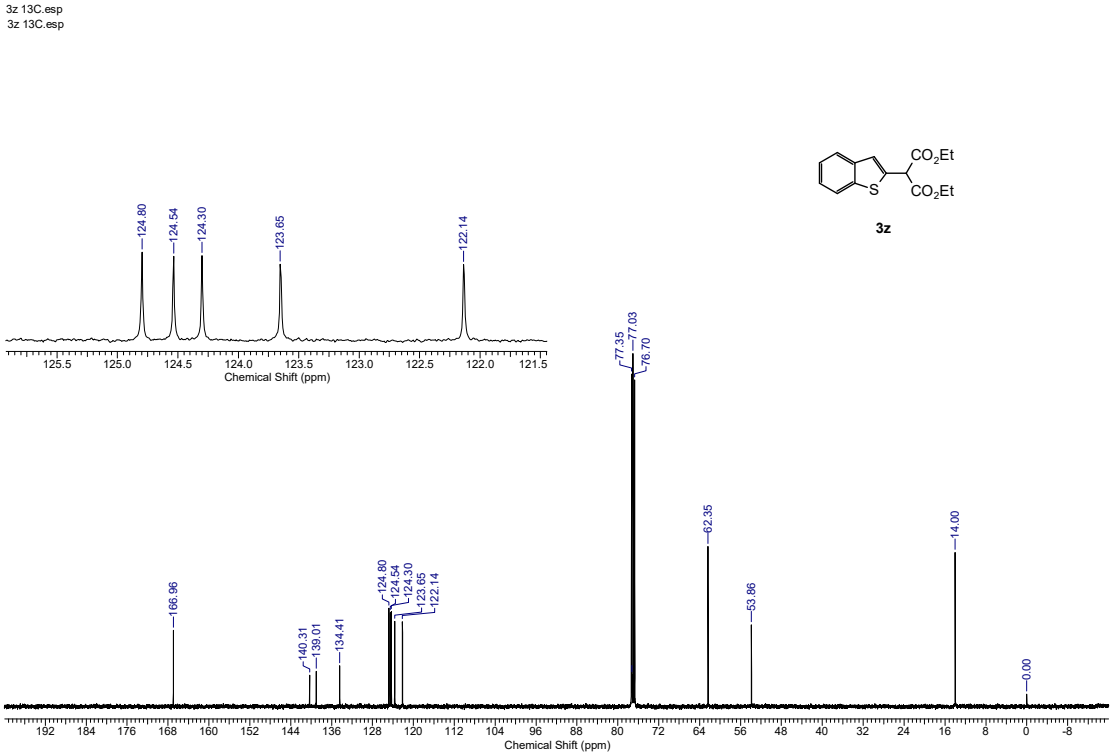


Figure S68. ^{13}C NMR spectrum of compound **3z**

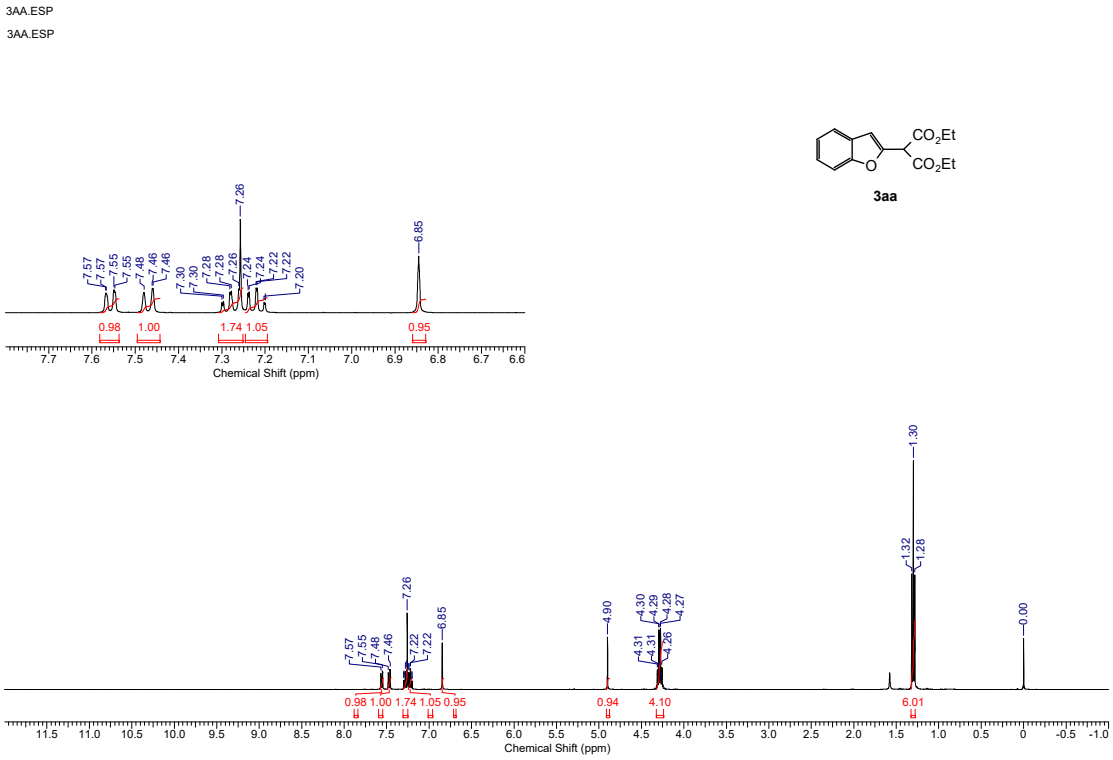


Figure S69. ^{1}H NMR spectrum of compound **3aa**

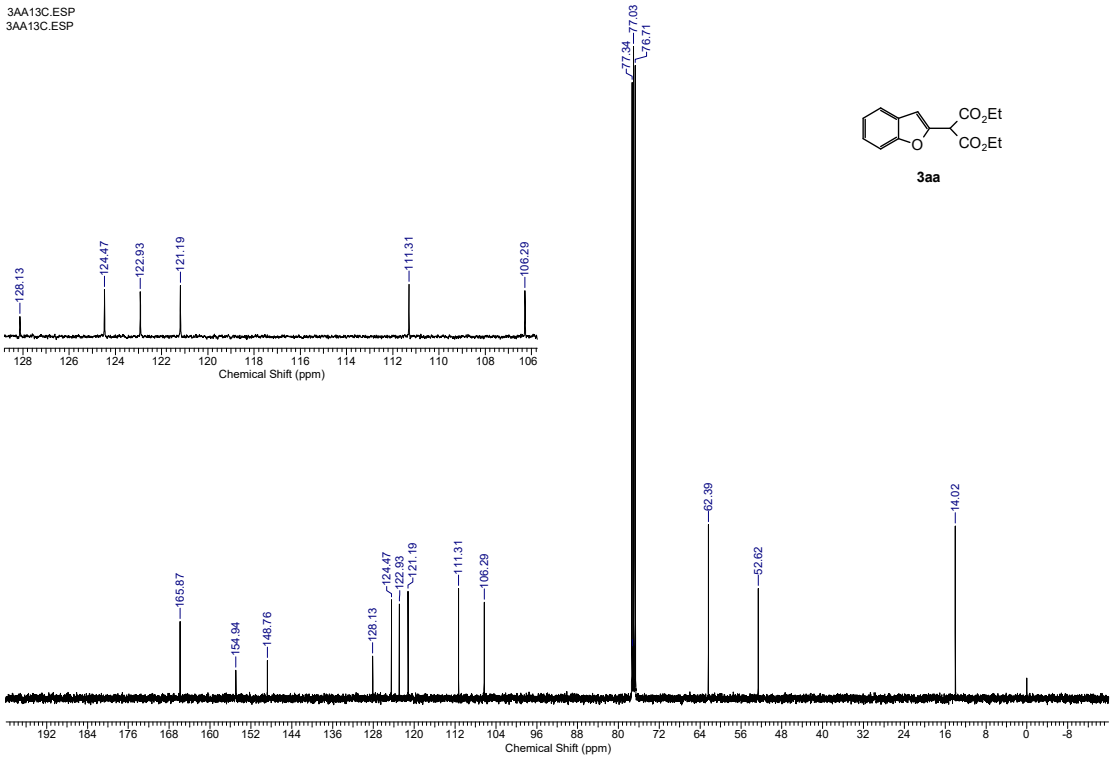


Figure S70. ^{13}C NMR spectrum of compound **3aa**