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*Supporting Information*

# DABCO-catalyzed mono- and bisallylation of *β,γ*-unsaturated ketones with Morita-Baylis-Hillman carbonates

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**I. General Methods**

All reactions were carried out without strict water-free and oxygen-free conditions. All reagents were obtained from commercial suppliers unless otherwise stated. All solvents and reagents were directly used for reactions without further purification unless otherwise stated. When the reactions preformed at the condition of DABCO, 1,4-Dioxane a**nd** DCM was pre-dried with $CaH_2$. Flash chromatography was performed using silica gel (200-300 mesh). Reactions were monitored by TLC or/and colour changes of reaction solution. Visualization was achieved under a UV lamp (254 nm and 365 nm), $I_2$ and by developing the plates with anisaldehyde. $^1H$ and $^{13}C$ NMR were recorded on 400 and 600 MHz NMR spectrometers with tetramethylsilane (TMS) as the internal standard and were calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$: $^1H$ NMR= 7.26, $^{13}C$ NMR= 77.16; DMSO-$d_6$: $^1H$ NMR= 2.50, $^{13}C$ NMR= 39.52). IR spectra were acquired on an FT-IR spectrometer and are reported in wavenumbers ($cm^{-1}$). High-resolution mass spectra were obtained using electrospray ionization (ESI). The following abbreviations are used for the multiplicities: *s*: singlet, *d*: doublet, *t*: triplet, *m*: multiplet, *br s*: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

**II. Preparation of intermediates**

A mixture of ketone (4.0 mmol, 1.0 equiv.), alkyne (4.0 mmol, 1.0 equiv.) and *t*BuOK (4.0 mmol, 1.0 equiv.) in DMSO (10 mL) was heated and stirred at 100 °C for 0.5-1 h. After cooling to room temperature, the reaction mixture was diluted with $H_2O$ (10 mL), neutralized with saturated aqueous $NH_4Cl$ and extracted with ethyl acetate (3×10 mL). The organic layer was washed with $H_2O$ and dried with anhydrous $MgSO_4$. After removal of ethyl acetate, the product was purified by flash chromatography (hexane/ethyl acetate = 27/1-20/1) to afford **1** as a white or yellow solid (33-72% yield).[1] All MBH carbonates **2** were prepared by two-step reactions, including the Morta-Maylis-Hillman reaction (1 equiv. DABCO/1 equiv. aldehyde/1.5 equiv. acrylate/1:1 dioxane:$H_2O$ or THF/2-3 days)[2]and the formation of *O*-Boc derivative (0.1 equiv. DMAP/1 equiv. MBH-alcohol/1.5 equiv.$Boc_2O$/DCM/rt/overnight), with 22-64% total yields.[3]

**III. General procedure for condition optimization**

A 10 mL tube was charged with *β*,*γ*-unsaturated ketones **1a** (0.2 mmol, 1.0 equiv.), MBH carbonate **2a** (0.3-0.6 mmol, 1.5-3.0 equiv.), base (0.01-0.04 mmol, 5-20 mol%) and solvent (0.5-2 mL). The suspended solution was vigorously stirred at rt-reflux, and then base was added. The reaction mixture was stirred at room temperature and monitor by TLC plate. The solution was added by 5 mL $H_2O$ and 10 mL brine, before the resulting mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were dry with $Na_2SO_4$, filtered, and concentrated. The residue was purified by flash silica gel chromatography eluated with EtOAc:PE ( 1:25) to afford the corresponding products **3a**.

**IV. General procedure for typical procedure for monoallylation**

A tube (25 mL) was charged with *β*,*γ*-unsaturated ketones **1a** (0.5 mmol, 1.0 equiv.), MBH carbonate **2a** (0.75 mmol, 1.5 equiv.) and dioxane (1.25 mL). The suspended solution was vigorously stirred at rt, and then DABCO (0.025 mmol, 0.05 equiv., 5 mol%) was added. When the reaction mixture became clear the reaction finished (5 min-24 h). The solution was added by 10 mL $H_2O$ and 10 mL brine, before the resulting mixture was extracted with DCM (3 x 10 mL). The combined organic layers were dry with $Na_2SO_4$, filtered, and concentrated. The residue was purified by flash silica gel chromatography eluated with EtOAc:PE (1:27 to 1:20) to afford the corresponding monoallylated products **3**.

**V. General procedure for typical procedure for dialkylation**

A tube (25mL) was charged with *β*,*γ*-unsaturated ketones 1**a** (0.5 mmol, 1.0 equiv.), MBH carbonate **2a** (2.25 mmol, 4.5 equiv.) and DCM (1.25 mL). The suspended solution was vigorously stirred at rt, and then DABCO (0.1 mmol, 0.2 equiv., 20 mol%) was added. When the reaction mixture became clear the reaction finished (2-24 h). The solution was added by 10 mL $H_2O$ and 10 mL brine, before the resulting mixture was extracted with DCM (3 x 10 mL). The combined organic layers were dry with $Na_2SO_4$, filtered, and concentrated. The residue was purified by flash column chromatography eluated with EtOAc:PE (1:23 to 1:19) to afford the corresponding diallylated products **4** and **6**.

**VI. The phenomenon of the reaction and TLC.**

TLC of starting materials (**1a** and **2a**) and products (**3a**, **4a** and **6a**) showed the result (Fig. 1).

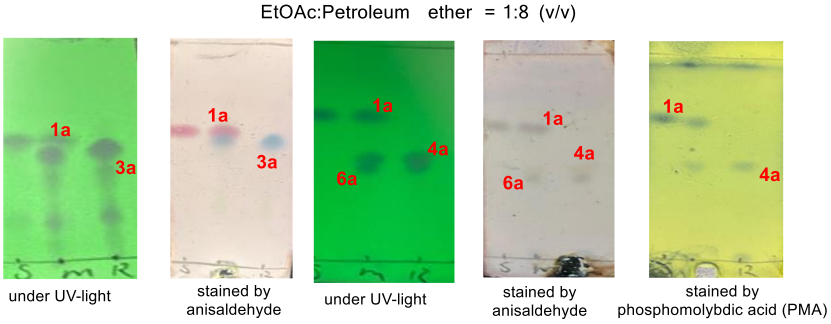
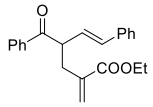


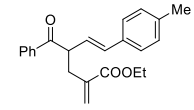

Fig. 1

**VII. Data for all new compounds**

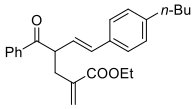


[Reaction time: 5 min]; **3a**: 158 mg, 95%, a yellow oil; IR (thin film): $\nu_{max}$ 2982, 1712, 1631, 1447, 1192, 1027, 967, 747, 692cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (m, 2H), 7.58-7.53 (m, 1H), 7.46 (ψt, *J* = 7.4 Hz, 2H), 7.33-7.25 (m, 4H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 9.2 Hz, 1H), 6.18 (d, *J* = 1.2 Hz, 1H), 5.59 (d, *J* = 0.8 Hz, 1H), 4.57 (td, *J* = 8.4, 6.8 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.02 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.67 (dd, *J* = 14.0, 8.0 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.2, 167.0, 137.4, 136.7, 133.4, 133.2, 128.7, 128.6, 128.5, 128.0, 127.7, 126.3, 60.8, 49.6, 35.5, 14.2; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}O_3Na$ [M+Na]$^+$ 357.1467, found 357 1416.

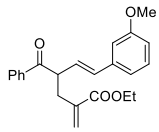
[Reaction time: 5 min]; **3b**: 139 mg, 80%, a yellow oil; IR (thin film): $\nu_{max}$ 2982, 1712, 1447, 1264, 1193, 1142, 969, 819, 709 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 7.2, 1.4 Hz, 2H), 7.58-7.52 (m, 1H), 7.49-7.43 (m, 2H), 7.21 (dt, *J* = 8.4, 2.4 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.21-6.14 (m, 2H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.55 (td, *J* = 8.4, 7.2 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.01 (ddd, *J* = 15.6, 6.4, 0.8 Hz, 1H), 2.66 (dd, *J* = 14.0, 8.0, 0.8 Hz, 1H), 2.30 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.3, 167.0, 137.5, 137.4, 136.7, 134.0, 133.3, 133.2, 129.2, 128.7, 128.0, 126.6, 126.2, 60.8, 49.6, 35.5, 21.2, 14.2; HRMS (ESI): *m/z* calcd for $C_{23}H_{24}O_3Na$ [M+Na]$^+$ 371.1623, found 371.2265.



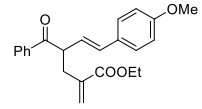
[Reaction time: 5 min]; **3c**: 160 mg, 89%, a yellow oil; IR (thin film): $\nu_{max}$ 2966, 1713, 1683, 1447, 1192, 1142, 969, 823, 707 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 6.8, 1.2 Hz, 2H), 7.57-7.52 (m, 1H), 7.50-7.42 (m, 2H), 7.24 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.21-6.14 (m, 2H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.55 (td, *J* = 8.0, 6.8 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.01 (ddd, *J* = 14.0, 6.4, 0.8 Hz, 1H), 2.66 (ddd, *J* = 14.0, 8.0, 0.8 Hz, 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.2, 167.0, 144.0, 137.5, 136.7, 134.2, 133.3, 133.2, 128.7, 128.6, 128.0, 128.0, 126.6, 126.3, 60.8, 49.6, 35.4, 28.6, 15.6, 14.2; HRMS (ESI): *m/z* calcd for $C_{24}H_{26}O_3Na$ [M+Na]$^+$ 385.1780, found 385.1842.



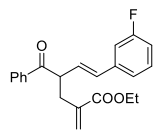
[Reaction time: 1 h]; **3d**: 148 mg, 76%, a yellow oil; IR (thin film): $\nu_{max}$ 2928, 1713, 1448, 1186,1026, 967, 820, 705 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.57-7.52 (m, 1H), 7.48-7.43 (m, 2H), 7.23 (dt, *J* = 8.0, 2.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 9.2 Hz, 1H), 6.17 (d, *J* = 1.2 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.55 (td, *J* = 8.4, 7.2 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.01 (ddd, *J* = 13.6, 6.4, 1.2 Hz, 1H), 2.66 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.1, 166.8, 142.5, 137.3, 136.5, 134.0, 133.2, 133.0, 128.5, 128.4, 1284, 127.8, 126.4, 126.1, 60.6, 49.4, 35.2, 35.2, 33.4, 22.1, 14.1, 13.8; HRMS (ESI): *m/z* calcd for $C_{26}H_{31}O_3Na$ [M+H]$^+$ 391.2273, found 391.2289.



[Reaction time: 10 h]; **3e**: 80 mg, 44%, a yellow oil; IR (thin film): $\nu_{max}$ 3932, 1712, 1599, 1449, 1192, 1045, 968, 778, 689 cm$^{-1}$;$^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 6.8, 1.2 Hz, 2H), 7.58-7.53 (m, 1H), 7.49-7.44 (m, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.85 (t, *J* = 2.0 Hz, 1H), 6.76 (ddd, *J* = 8.0, 2.4, 0.8 Hz, 1H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 16.0, 9.2 Hz, 1H), 6.18 (d, *J* = 1.6 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.57 (td, *J* = 8.4, 6.4 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.01 (ddd, *J* = 14.0, 6.8, 1.2 Hz, 1H), 2.67 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.2, 167.0, 159.8, 138.2, 137.4, 136.6, 133.3, 133.3, 129.5, 128.7, 128.1, 128.0, 119.0, 113.4, 111.5, 60.8, 55.2, 49.5, 35.5, 14.2; HRMS (ESI): *m/z* calcd for $C_{23}H_{24}O_4K$ [M+K]$^+$ 403.1312, found 403.1310.

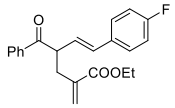


[Reaction time: 5 min]; **3f**: 148 mg, 81%, a yellow oil; IR (thin film): $\nu_{max}$ 2931, 1712, 1512, 1250, 1180, 1032, 967, 827, 708 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 6.8, 1.6 Hz, 2H), 7.58-7.53 (m, 1H), 7.48-7.44 (m, 2H), 7.25 (d, *J* = 6.8 Hz, 1H), 6.81 (dt, *J* = 8.8, 2.8 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.17 (d, *J* = 1.6 Hz, 1H), 6.08 (dd, *J* = 16.0, 9.2 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.54 (td, *J* = 8.4, 7.2 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.00 (ddd, *J* = 14.0, 6.4, 1.2 Hz, 1H), 2.66 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.3, 167.0, 159.3, 137.5, 136.7, 133.2, 132.8, 129.6, 128.7, 128.6, 127.9, 127.5, 125.4, 113.9, 60.8, 55.3, 49.6, 35.5, 29.7, 14.2; HRMS (ESI): *m/z* calcd for $C_{23}H_{24}O_4Na$ [M+Na]$^+$ 387.1572, found 387.1534.

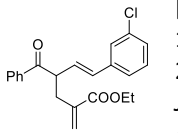


[Reaction time: 5 min]; **3g**: 132 mg, 75%, a yellow oil; IR (thin film): $\nu_{max}$ 2983, 1712, 1583, 1445, 1195, 1143, 966, 780, 687 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.59-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.23 (td, *J* = 8.0, 6.0 Hz, 1H), 7.07 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.02 (ddd, *J* = 10.0, 2.4, 1.6 Hz, 1H), 6.90 (tdd, *J* = 8.4, 2.4, 1.0 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.27 (dd, *J* = 15.9, 8.9 Hz, 1H), 6.18 (d, *J* = 1.2 Hz, 1H), 5.59 (d, *J* = 1.6 Hz, 1H), 4.58 (td, *J* = 8.0, 6.0 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.01 (ddd, *J* = 14.0, 6.4, 1.2 Hz, 1H), 2.66 (ddd, *J* = 13.6, 8.0, 1.0 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.1, 167.0, 139.2 (d, *J* = 8.0 Hz), 137.4, 136.6, 133.5, 132.1 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 8.0 Hz), 129.3, 128.9, 128.7, 128.3, 125.8, 122.2 (d, *J* = 3.0

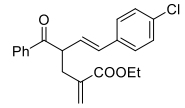
Hz), 114.5 (d, *J* = 21.0 Hz), 112.9 (d, *J* = 22.0 Hz), 61.0, 49.5, 35.6, 14.3; $^{19}$F NMR (376 MHz, $CDCl_3$): -113.5; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}FO_3Na$ $[M+Na]^+$ 375.1372, found 375.1361.



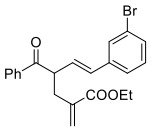
[Reaction time: 5 min]; **3h**: 141 mg, 80%, a yellow oil; IR (thin film): $\nu_{max}$ 2983, 1713, 1509, 1447, 1143, 1026, 969, 831, 711 $cm^{-1}$;$^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.58-7.54 (m, 1H), 7.50-7.45 (m, 2H), 7.30-7.26 (m, 2H), 7.00-6.93 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.18 (d, *J* = 1.6 Hz, 1H), 6.16 (dd, J = 16.0, 9.2 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.56 (td, *J* = 8.8, 7.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.00 (ddd, *J* = 14.0, 6.4, 1.2 Hz, 1H), 2.67 (ddd, *J* = 13.6, 8.0, 1.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.1, 167.0, 137.4, 136.5, 133.3, 132.9 (d, *J* = 3.0 Hz), 132.1, 128.7, 128.6, 128.0, 127.9, 127.8, 127.4 (d, *J* = 3.0 Hz), 115.5 (d, *J* = 22.0 Hz), 60.8, 49.5, 35.5, 14.2; $^{19}$F NMR (376 MHz, $CDCl_3$): -114.3; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}FO_3$ $[M+H]^+$ 353.1553, found 353.1614.



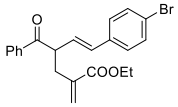
[Reaction time: 10 h]; **3i**: 88 mg, 48%, a yellow oil; IR (thin film): $\nu_{max}$ 2982, 1712, 1595, 1447, 1190, 1143, 967, 779, 687 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.60-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.23-7.15 (m, 3H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.27 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.19 (d, *J* = 1.2 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.57 (td, *J* = 8.4, 6.4 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.01 (ddd, *J* = 13.6, 6.4, 1.2 Hz, 1H), 2.66 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.9, 166.9, 138.6, 137.3, 136.4, 134.5, 133.3, 131.9, 129.7, 129.3, 128.7, 128.6, 128.1, 127.6, 126.3, 124.5, 60.8, 49.4, 35.5, 14.2; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}ClO_3$ $[M+H]^+$ 369.1257, found 369.1239.



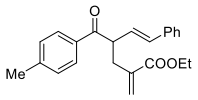
[Reaction time: 5 min]; **3j**: 125 mg, 68%, a yellow oil; IR (thin film): $\nu_{max}$ 2982, 1713, 1491, 1370, 1279, 1189, 968, 820, 693 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.79 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.55-7.50 (m, 1H), 7.40-7.35 (m, 2H), 7.30 (dt, *J* = 8.4, 2.4 Hz, 2H), 7.15 (dt, *J* = 8.4, 2.8 Hz, 2H), 6.57 (d, *J* = 11.2 Hz, 1H), 6.16 (d, *J* = 1.2 Hz, 1H), 5.72 (dd, *J* = 11.6, 10.8 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.93 (dt, *J* = 10.8, 6.8 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.99 (ddd, *J* = 13.6, 6.8, 1.2 Hz, 1H), 2.58 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.0, 166.9, 137.3, 136.5, 135.2, 133.3, 133.3, 132.0, 128.7, 128.7, 128.6, 128.4, 128.1, 127.5, 60.8, 49.5, 35.5, 14.2; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}ClO_3Na$ $[M+Na]^+$ 391.1077, found 391.1144.



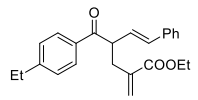
[Reaction time: 10 h]; **3k**: 92 mg, 45%, a yellow oil; IR (thin film): $\nu_{max}$ 2930, 1712, 1594, 1446, 1279, 1190, 967, 777, 688 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 6.8, 1.2 Hz, 2H), 7.59-7.55 (m, 1H), 7.49 (t, *J* = 1.6 Hz, 1H), 7.47 (dt, *J* = 5.6, 1.6 Hz, 2H), 7.33 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1H), 7.23 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.26 (dd, *J* = 15.6, 8.4 Hz, 1H), 6.19 (d, *J* = 1.2 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.57 (td, *J* = 8.4, 6.4 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.01 (ddd, *J* = 13.8, 6.4, 1.2 Hz, 1H), 2.66 (ddd, J = 13.8, 8.0, 1.0 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.6, 164.6, 136.6, 135.0, 134.1, 131.1, 129.6, 128.2, 127.7, 127.0, 126.9, 126.4, 126.3, 125.9, 122.7, 120.4, 58.6, 47.2, 33.3, 11.9; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}BrO_3$ $[M+H]^+$ 413.0752, found 413.0700.



[Reaction time: 5 min]; **3l**: 106 mg, 51%, a yellow oil; IR (thin film): $\nu_{max}$ 2755, 1881, 1257, 1167, 1024, 952, 823, 686, 641 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.59-7.54 (m, 1H), 7.50-7.45 (m, 2H), 7.39 (dt, *J* = 9.0, 2.4 Hz, 2H), 7.18 (dt, J = 8.4, 2.8 Hz, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.25 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.18 (d, *J* = 1.2 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.56 (td, J = 8.0, 6.4 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.00 (ddd, *J* = 14.0, 6.4, 1.2 Hz, 1H), 2.66 (ddd, *J* = 13.6, 8.0, 1.0 Hz, 1H), 29 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.3, 165.2, 135.6, 134.8, 134.0, 131.6, 130.4, 130.0, 127.0, 126.9, 126.8, 126.4, 126.1, 119.7, 59.1, 47.8, 33.8, 12.5; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}BrO_3Na$ $[M+Na]^+$ 435.0572, found 435.0559.

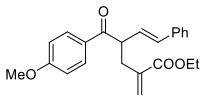


[Reaction time: 24 h]; **3m**: 126 mg, 72%, a yellow oil; IR (thin film): $\nu_{max}$ 2983, 1713, 1607, 1447, 1370, 1184, 967, 824, 744 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.95 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.33-7.28 (m, 3H), 7.27 (d, *J* = 0.8 Hz, 2H), 7.25 (d, *J* = 1.6 Hz, 1H), 7.22-7.17 (m, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.17 (d, *J* = 1.6 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.54 (td, J = 8.4, 7.2 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.00 (ddd, *J* = 14.0, 6.4, 1.2 Hz, 1H), 2.66 (ddd, *J* = 13.6, 8.0, 1.2 Hz, 1H), 2.40 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.8, 167.0, 144.1, 137.5, 136.8, 134.1, 133.2, 129.4, 128.8, 128.5, 127.9, 127.9, 127.6, 126.3, 60.8, 49.4, 35.4, 21.7, 14.2. HRMS (ESI): *m/z* calcd for $C_{23}H_{24}O_3Na$ $[M+Na]^+$ 371.1623, found 371.1579.

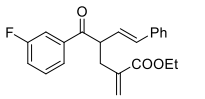


[Reaction time: 24 h]; **3n**: 117 mg, 65%, a yellow oil; IR (thin film): $\nu_{max}$ 2970, 1713, 1679, 1606, 1370, 1184, 967, 746, 694 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.98 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.31-7.28 (m, 2H), 7.28-7.26 (m, 2H), 7.25-7.17 (m, 2H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 9.2 Hz, 1H), 6.17 (d, *J* = 1.2 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.55 (dddd, *J* = 8.8, 7.5, 6.5, 0.8 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.01 (ddd, *J* = 14.0, 6.4, 1.2 Hz, 1H), 2.73-2.64 (m, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.8,

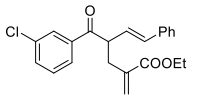
167.0, 150.2, 137.5, 136.8, 134.3, 133.2, 128.9, 128.5, 128.2, 128.0, 127.9, 127.6, 126.3, 60.8, 49.5, 35.4, 29.0, 15.2, 14.2; HRMS (ESI): *m/z* calcd for $C_{24}H_{27}O_3$ $[M+H]^+$ 363.1960, found 363.1975.



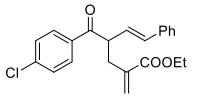

[Reaction time: 10 h]; **3o**: 112 mg, 61%, a yellow oil; IR (thin film): $\nu_{max}$ 2933, 1711, 1600, 1510, 1257, 1172, 968, 841, 746 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 8.8, 3.2 Hz, 2H), 7.33-7.30 (m, 2H), 7.29-7.26 (m, 2H), 7.22-7.18 (m, 2H), 6.94 (dt, *J* = 8.8, 2.8 Hz, 2H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.25 (dd, *J* = 15.6, 8.8 Hz, 1H), 6.17 (d, J = 1.6 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.52 (ddd, *J* = 9.2, 8.0, 6.4 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.00 (ddd, *J* = 13.6, 6.4, 1.2 Hz, 1H), 2.65 (ddd, *J* = 13.6, 8.0, 1.0 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 198.7, 167.0, 163.6, 137.5, 136.8, 133.0, 131.0, 129.6, 128.5, 128.1, 127.9, 127.6, 126.3, 113.9, 60.8, 55.5, 49.2, 35.5, 14.2; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}O_4$ $[M+H]^+$ 365.1753, found 365.1722.



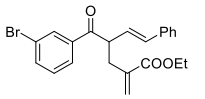

[Reaction time: 10 h]; **3p**: 129 mg, 73%, a yellow oil; IR (thin film): $\nu_{max}$ 2933, 1711, 1587, 1441, 1261, 1141, 968, 743, 693 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.84 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.71 (ddd, *J* = 9.6, 2.8, 1.6 Hz, 1H), 7.44 (td, *J* = 8.0, 5.6 Hz, 1H), 7.33-7.30 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.19 (m, 2H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.25-6.21 (m, 1H), 6.19 (d, *J* = 1.6 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.51 (ddd, *J* = 9.2, 8.4, 6.8 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.00 (ddd, *J* = 14.0, 6.4, 1.2 Hz, 1H), 2.66 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 198.9 (d, *J* = 1.0 Hz), 166.9, 138.7 (d, *J* = 6.0 Hz), 137.2, 136.6, 133.7, 130.3 (d, *J* = 8.0 Hz), 128.6, 128.3, 127.8, 127.1, 126.3, 124.3 (d, *J* = 3.0 Hz), 120.2 (d, *J* = 20.0 Hz), 115.3 (d, *J* = 23.0 Hz),, 60.9, 49.8, 35.5, 14.2; $^{19}F$ NMR (376 MHz, $CDCl_3$): -111.7; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}FO_3$ $[M+H]^+$ 353.1553 found 353.1544.



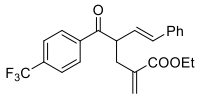

[Reaction time: 10 h]; **3q**: 117 mg, 64%, a yellow oli; IR (thin film): $\nu_{max}$ 2929, 1713, 1571, 1420, 1194, 1144, 967, 751, 694 $cm^{-1}$;$^1H$ NMR (400 MHz, $CDCl_3$): δ 7.99 (t, *J* = 1.8 Hz, 1H), 7.92 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.52 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.34-7.30 (m, 2H), 7.30-7.26 (m, 2H), 7.24-7.19 (m, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, J = 16.0, 9.2 Hz, 1H), 6.19 (d, *J* = 1.2 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.51 (ddd, *J* = 9.6, 8.4, 6.4 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.99 (ddd, *J* = 14.0, 6.8, 1.2 Hz, 1H), 2.66 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 198.9, 166.9, 138.2, 137.2, 136.6, 135.1, 133.7, 133.1, 130.0, 128.7, 128.6, 128.2, 127.8, 127.1, 126.7, 126.4, 60.9, 49.7, 35.5, 14.2; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}ClO_3$ $[M+H]^+$ 369.1257, found 369.1230.



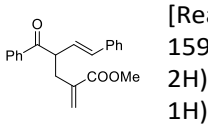

[Reaction time:24 h]; **3r**: 94 mg, 51%, a yellow oil; IR (thin film): $\nu_{max}$ 2981, 1712, 1589, 1401, 1195, 1144, 967, 747, 695 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.99 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.44 (dt, *J* = 8.4, 1.2 Hz, 2H), 7.33-7.30 (m, 2H), 7.30-7.27 (m, 2H), 7.23-7.19 (m, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 7.24-7.20 (m, 1H), 6.18 (d, *J* = 1.2 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.51 (td, *J* = 8.4, 6.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.99 (ddd, *J* = 14.0, 6.4, 1.2 Hz, 1H), 2.65 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 199.0, 167.0, 139.7, 137.2, 136.6, 134.9, 133.6, 130.1, 129.0, 128.6, 128.8, 127.8, 127.3, 126.3, 60.9, 49.6, 35.5, 14.2; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}ClO_3$ $[M+H]^+$ 369.1257, found 369.1232.




[Reaction time: 10 h]; **3s**: 108 mg, 53%, a yellow oil; IR (thin film): $\nu_{max}$ 2928, 1713, 1685, 1370, 1247, 1192, 966, 748, 704 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.15 (t, *J* = 2.0 Hz, 1H), 7.97 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.67 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.35-7.25 (m, 4H), 7.24-7.19 (m, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 16.0, 9.2 Hz, 1H), 6.18 (d, *J* = 1.6 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.50 (q, *J* = 7.8 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.99 (ddd, *J* = 14.0, 6.4, 1.2 Hz, 1H), 2.66 (ddd, *J* = 13.8, 8.0, 1.0 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 198.8, 166.9, 138.4, 137.2, 136.6, 136.1, 133.7, 131.6, 130.3, 128.6, 127.8, 127.2, 127.1, 126.4, 123.1, 60.9, 49.7, 35.5, 14.2; $^1$HRMS (ESI): *m/z* calcd for $C_{22}H_{21}BrO_3Na$ $[M+Na]^+$ 435.0572, found 435.0557.

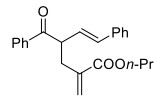



[Reaction time: 10 h]; **3t**: 120 mg, 60%, a yellow oil; IR (thin film): $\nu_{max}$ 2983, 1748, 1370, 1326, 1278, 1167, 1068, 964, 859 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.16-8.14 (m, 2H), 7.74-7.72 (m, 2H), 7.33-7.31 (m, 2H), 7.29-7.26 (m, 2H), 7.24-7.20 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 16.0, 9.2 Hz, 1H), 6.19 (d, *J* = 1.6 Hz, 1H), 5.60 (d, *J* = 1.2 Hz, 1H), 4.56 (ddd, *J* = 9.2, 8.0, 6.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.02 (ddd, *J* = 13.6, 6.4, 1.2 Hz, 1H), 2.67 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 199.3, 166.9, 139.3, 137.1, 136.5, 134.0, 129.0, 128.6, 128.3, 127.9, 126.8, 126.4, 125.8, 125.8, 125.7, 60.9, 50.0, 35.5, 14.2; $^{19}F$ NMR (376 MHz, $CDCl_3$): -63.2; HRMS (ESI): *m/z* calcd for $C_{23}H_{21}F_3O_3Na$ $[M+Na]^+$ 425.1340, found 425.1323.

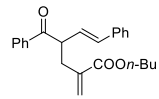



[Reaction time: 5 min]; **5a**: 154 mg, 96%, a yellow oil; IR (thin film): $\nu_{max}$ 3461, 2953, 1718, 1598, 1493, 1446, 1205, 750, 694 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.58-7.53 (m, 1H), 7.49-7.44 (m, 2H), 7.33-7.30 (m, 2H), 7.27-7.25 (m, 2H), 7.22-7.18 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.18 (d, *J* = 1.2 Hz, 1H), 5.61 (d, *J* = 1.2 Hz, 1H), 4.60-4.53 (m, 1H), 3.75 (s, 3H), 3.02 (ddd, *J* = 14.0, 6.4, 1.2 Hz, 1H), 2.68 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 200.1, 167.5, 137.1, 136.7, 136.6, 133.4,. 133.2, 128.7, 128.6, 128.5,

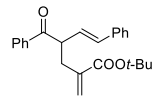
128.3, 127.7, 127.6, 126.3, 51.9, 49.6, 35.4; HRMS (ESI): *m/z* calcd for $C_{21}H_{20}O_3Na$ $[M+Na]^+$ 343.1310, found 343.1301.



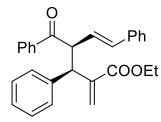

[Reaction time: 5 min]; **5b**: 161 mg, 92%, a yellow oil; IR (thin film): $\nu_{max}$ 2968, 1713, 1449, 1265, 1192, 1142, 967, 746, 692 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.59 (dt, *J* = 7.5, 3.8 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.37-7.33 (m, 2H), 7.32-7.30 (m, 2H), 7.27-7.23 (m, 1H), 6.50 (dd, *J* = 16.0, 2.4 Hz, 1H), 6.34-6.25 (m, 1H), 6.22 (s, 1H), 5.63 (s, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.16 (td, *J* = 6.6, 2.6 Hz, 2H), 3.06 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.72 (dd, *J* = 14.4, 8.0 Hz, 1H), 1.78-1.68 (m, 2H), 0.99 (td, *J* = 7.6, 2.6 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 200.2, 167.1, 137.4, 136.7, 136.6, 133.4, 133.2, 128.7, 128.6, 128.5, 128.0, 127.7, 126.3, 66.4, 49.6, 35.5, 22.0, 10.5; HRMS (ESI): *m/z* calcd for $C_{23}H_{24}O_3Na$ $[M+Na]^+$ 371.1623, found 371.1615.



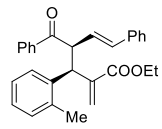

[Reaction time: 5 min]; **5c**: 170 mg, 94%, a yellow oil; IR (thin film): $\nu_{max}$ 2961, 1713, 1633, 1450, 1275, 1185, 966, 746, 692 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.34-7.34 (m, 2H), 7.32-7.30 (m, 2H), 7.27-7.23 (m, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.32-6.25 (m, 1H), 6.22 (s, 1H), 5.63 (s, 1H), 4.62 (dd, *J* = 15.8, 9.0 Hz, 1H), 4.21 (ψq, *J* = 7.6 Hz, 2H), 3.06 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.72 (dd, *J* = 14.0, 8.0 Hz, 1H), 1.69 (q, *J* = 7.5 Hz, 2H), 1.47-1.42 (m, 2H), 0.98 (dt, *J* = 9.6, 7.2 Hz, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 200.2, 167.1, 137.4, 136.7, 136.6, 133.4, 133.2, 128.7, 128.6, 128.5, 128.0, 127.7, 126.3, 64.7, 49.6, 35.5, 30.7, 19.2, 13.7; HRMS (ESI): *m/z* calcd for $C_{24}H_{26}O_3Na$ $[M+Na]^+$ 385.1780, found 385.1768.



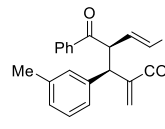

[Reaction time: 5 min]; **5d**: 167 mg, 92%, a yellow oil; IR (thin film): $\nu_{max}$ 2978, 1707, 1449, 1368, 1253, 1143, 967, 748, 692 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.05 (dt, *J* = 5.4, 1.0 Hz, 2H), 7.59-7.56 (m, 1H), 7.50-7.47 (m, 2H), 7.35-7.33 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.21 (m, 1H), 6.49 (d, *J* = 10.8 Hz, 1H), 6.26 (dd, *J* = 10.4, 6.0 Hz, 1H), 6.10 (d, *J* = 1.2 Hz, 1H), 5.54 (d, *J* = 0.8 Hz, 1H), 4.62 (td, *J* = 6.2, 5.0 Hz, 1H), 2.99 (ddd, *J* = 9.2, 4.4, 0.8 Hz, 1H), 2.68 (ddd, *J* = 9.2, 4.8, 0.6 Hz, 1H), 1.51 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 200.4, 166.2, 138.8, 136.8, 136.8, 133.2, 128.7, 128.6, 128.5, 127.9, 127.6, 127.2, 126.3, 49.7, 35.7, 28.1; HRMS (ESI): *m/z* calcd for $C_{24}H_{26}O_3Na$ $[M+Na]^+$ 385.1780, found 385.1762.



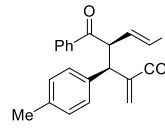

[Reaction time: 5 min]; **5e**: 157 mg, 77%, a white solid, *>20:1 dr*, m.p. 56.3-57.7°C ; IR (thin film): $\nu_{max}$ 2982, 1709, 1670, 1448, 1256, 1141, 952, 746, 703 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.05 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.59-7.54 (m, 1H), 7.49-7.45 (m, 2H), 7.30-7.24 (m, 4H), 7.22-7.12 (m, 4H), 7.11-7.08 (m, 2H), 6.27 (d, *J* = 6.0 Hz, 1H), 6.18 (s, 1H), 5.95 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.92 (dd, *J* = 11.2, 8.8 Hz, 1H), 4.69 (d, *J* = 11.2 Hz, 1H), 4.13-4.03 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 199.2, 166.3, 142.5, 140.0, 137.0, 136.7, 134.5, 133.3, 129.0, 128.8, 128.4, 128.4, 128.3, 127.6, 126.8, 126.7, 126.2, 123.8, 60.9, 54.3, 49.3, 14.0; HRMS (ESI): *m/z* calcd for $C_{28}H_{27}O_3$ $[M+H]^+$ 411.1960, found 411.1919.




[Reaction time: 24 h]; **5f**: 119 mg, 56%, a yellow solid, *>20:1 dr*, 59.3-62.1°C; IR (thin film): $\nu_{max}$ 2924, 1715, 1673, 1370, 1259, 1148, 970, 738, 689 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.59-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.26-7.21 (m, 1H), 7.21-7.18 (m, 1H), 7.17-7.11 (m, 3H), 7.08-7.03 (m, 4H), 6.21 (d, *J* = 0.8 Hz, 1H), 6.16 (d, *J* = 16.4 Hz, 1H), 5.92 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.52 (d, *J* = 1.2 Hz, 1H), 5.01 (d, *J* = 10.8 Hz, 1H), 4.80 (dd, *J* = 11.2, 8.4 Hz, 1H), 4.11-4.02 (m, 2H), 2.43 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H): δ 199.4, 166.4, 142.7, 138.3, 137.4, 137.0, 136.7, 134.3, 133.3, 130.4, 128.8, 128.4, 128.4, 127.6, 127.3, 126.6, 126.2, 125.9, 125.7, 123.7, 60.9, 55.2, 43.7, 20.1, 14.0; HRMS (ESI): *m/z* calcd for $C_{29}H_{28}O_3Na$ $[M+Na]^+$ 447.1936, found 447.1920.

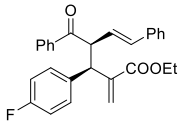



[Reaction time: 24 h]; **5g**: 142 mg, 67%, a yellow solid, *>20:1 dr*, 62.2-63.5°C; IR (thin film): $\nu_{max}$ 2925, 1711, 1667, 1277,1142, 963, 791, 714, 658 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.06 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.58-7.54 (m, 1H), 7.49-7.45 (m, 2H), 7.21-7.17 (m, 2H), 7.16-7.13 (m, 2H), 7.10-7.08 (m, 4H), 6.98-6.95 (m, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 6.17 (s, 1H), 5.95 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.91 (dd, *J* = 11.2, 8.8 Hz, 1H), 4.64 (d, *J* = 11.2 Hz, 1H), 4.13-4.03 (m, 2H), 2.28 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 199.2, 166.4, 142.6, 139.8, 137.7, 137.0, 136.8, 134.3, 133.2, 129.7, 128.8, 128.5, 128.4, 128.1, 127.6, 127.6, 126.9, 126.3, 126.1, 123.7, 60.8, 54.2, 49.2, 21.5, 14.0; HRMS (ESI): *m/z* calcd for $C_{29}H_{28}O_3Na$ $[M+Na]^+$ 447.1936, found 447.1925.

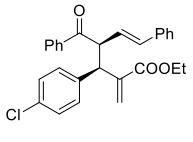



[Reaction time: 24 h]; **5h**: 112 mg, 53%, a yellow solid, *>20:1 dr*, 63.1-64.2°C; IR (thin film): $\nu_{max}$ 2945, 1715, 1678, 1448, 1262, 1146, 967, 817, 691 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.05 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.58-7.54 (m, 1H), 7.49-7.45 (m, 2H), 7.21-7.18 (m, 2H), 7.16 (t, *J* = 2.2 Hz, 2H), 7.13-7.11 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.29 (d, *J* = 16.0 Hz, 1H), 6.15 (s, 1H), 5.97 (dd, *J* = 16.0, 8.4 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.92 (dd, *J* = 11.2, 8.8 Hz, 1H), 4.64 (d, *J* = 11.2 Hz, 1H), 4.12-4.04 (m, 2H), 2.27 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 199.3, 166.4, 142.7, 137.0, 136.8, 136.8, 136.3, 134.3, 133.2, 129.0, 128.8, 128.8, 128.4, 127.6,

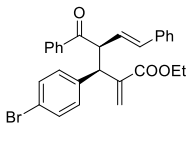
126.9, 126.3, 123.6, 60.8, 54.2, 48.9, 21.1, 14.0; HRMS (ESI): *m/z* calcd for $C_{29}H_{28}O_3Na$ [M+Na]$^+$ 447.1936, found 447.1924.



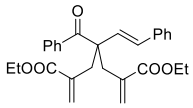
[Reaction time: 24 h]; **5i**: 113 mg, 53%, a yellow solid, *>20:1 dr*, 56.3.2-58.5°C; IR (thin film): $\nu_{max}$ 2925, 1712, 1507, 1253, 1224, 1143, 965, 829, 962 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.05 (dt, *J* = 6.8, 1.2 Hz, 2H), 7.59-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.27-7.22 (m, 2H), 7.21-7.19 (m, 2H), 7.18-7.14 (m, 1H), 7.11 (dt, *J* = 6.6, 1.8 Hz, 2H), 6.97-6.91 (m, 2H), 6.27 (d, *J* = 15.6 Hz, 1H), 6.18 (s, 1H), 5.93 (dd, *J* = 16.0, 9.2 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.88 (dd, *J* = 11.2, 8.8 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.14-4.04 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.0, 166.2, 142.3, 136.9, 136.5, 135.7 (d, *J*= 3.0 Hz), 134.8, 133.4, 130.5, 130.4, 128.8, 128.5, 128.4, 127.8, 126.4, 126.2, 123.9, 115.1 (d, *J*= 21.0 Hz), 60.9, 54.3, 48.6, 14.0; $^{19}$F NMR (376 MHz, $CDCl_3$): -116.1; HRMS (ESI): *m/z* calcd for $C_{28}H_{25}FO_3Na$ [M+Na]$^+$ 451.1685, found 451.1678.



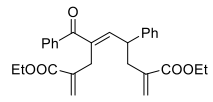
[Reaction time: 24 h]; **5j**: 150 mg, 67%, a yellow solid, *>20:1 dr*, 57.7.2-60.5°C; IR (thin film): $\nu_{max}$ 3431, 2926, 1490, 1711, 1255, 1146, 959, 751, 689 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.59-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.22 (s, 4H), 7.21-7.16 (m, 2H), 7.14-7.09 (m, 2H), 6.29 (d, *J* = 16.0 Hz, 1H), 6.18 (s, 1H), 5.93 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.89 (dd, *J* = 11.2, 8.8 Hz, 1H), 4.66 (dd, *J* = 11.2, 1.2 Hz, 1H), 4.14-4.04 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.8, 166.1, 142.1, 138.6, 136.8, 136.4, 134.9, 133.4, 132.6, 130.4, 128.8, 128.5, 128.4, 127.8, 126.3, 126.2, 124.1, 61.0, 54.0, 48.7, 29.7, 14.0; HRMS (ESI): *m/z* calcd for $C_{28}H_{25}ClO_3Na$ [M+Na]$^+$ 467.1390, found 467.1373.



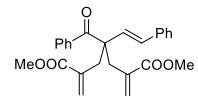
[Reaction time: 24 h]; **5k**: 125 mg, 51%, a yellow solid, *>20:1 dr*, 61.8.2-63.7°C; IR (thin film): $\nu_{max}$ 3451, 2926, 1712, 1488, 1255, 970, 751, 690 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dt, *J* = 6.8, 1.2 Hz, 2H), 7.59-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.38 (td, *J* = 4.4, 2.6 Hz, 2H), 7.24-7.20 (m, 1H), 7.20-7.14 (m, 4H), 7.22 (dt, *J* = 6.6, 1.4 Hz, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 6.18 (s, 1H), 5.93 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 4.89 (dd, *J* = 10.8, 8.8 Hz, 1H), 4.65 (d, *J* = 11.2 Hz, 1H), 4.13-4.04 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.8, 166.1, 142.0, 139.2, 136.8, 136.4, 134.9, 133.4, 131.4, 130.8, 128.8, 128.5, 128.4, 127.8, 126.3, 126.2, 124.2, 120.8, 61.0, 54.0, 48.8, 14.0; HRMS (ESI): *m/z* calcd for $C_{28}H_{25}BrO_3Na$ [M+Na]$^+$ 511.0885, found 511.0873.



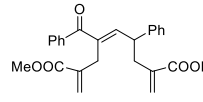
[Reaction time: 2 h]; **4a:** 145 mg, 65%, a yellow oil; IR (thin film): $\nu_{max}$ 2982, 1713, 1629, 1447, 1260, 1153, 950, 743, 695 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.91 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.47-7.43 (m, 1H), 7.37-7.32 (m, 2H), 7.28-7.26 (m, 4H), 7.24-7.19 (m, 1H), 6.42 (d, *J* = 16.8 Hz, 2H), 6.34 (d, *J* = 16.8 Hz, 2H), 6.20 (d, *J* = 1.2 Hz, 2H), 5.57 (d, *J* = 1.2 Hz, 2H), 3.95-3.84 (m, 4H), 3.24 (dd, *J* = 14.4, 0.8 Hz, 2H), 3.00 (dd, *J* = 14.4, 1.2 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.5, 167.6, 137.2, 137.1, 136.7, 132.0, 131.6, 130.6, 129.6, 128.5, 128.2, 128.1, 127.7, 126.3, 60.8, 56.5, 37.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{28}H_{30}O_5K$ [M+H]$^+$ 485.1730, found 485.1767.



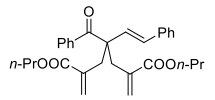
**6a**: 45 mg, 20%, a yellow oil; IR (thin film): $\nu_{max}$ 2930, 1715, 1651, 1449, 1273, 1100, 1028, 955, 700 cm$^{-1}$;$^1$H NMR (400 MHz, $CDCl_3$): δ 7.63 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.55-7.50 (m, 1H), 7.43-7.39 (m, 2H), 7.29 (td, *J* = 7.2, 1.6 Hz, 2H), 7.23-7.19 (m, 1H), 7.16 (d, *J* = 1.4 Hz, 2H), 6.50 (d, *J* = 10.0 Hz, 1H), 6.15 (dd, *J* = 17.6, 1.2 Hz, 2H), 5.42 (d, *J* = 1.2 Hz, 2H), 4.25-4.09 (m, 5H), 3.51 (s, 2H), 2.77 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.64 (dd, *J* = 14.0, 8.8 Hz, 1H), 1.27 (t, J = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.5, 166.7, 166.7, 148.6, 142.2, 138.1, 137.9, 137.8, 131.9, 129.6, 128.8, 128.2, 127.5, 127.3, 126.9, 125.5, 60.9, 60.8, 44.2, 39.6, 29.7, 28.9, 14.2, 14.2; HRMS (ESI): *m/z* calcd for $C_{28}H_{30}O_5Na$ [M+Na]$^+$ 469.1991, found 469.20862.



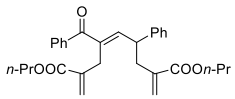
[Reaction time: 2 h]; **4b:** 143 mg, 68%, a yellow oil; IR (thin film): $\nu_{max}$ 2952, 1722, 1676, 1631, 1442, 1157, 951, 735, 695 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.91 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.47-7.43 (m, 1H), 7.37-7.33 (m, 2H), 7.30-7.28 (m, 4H), 7.24-7.20 (m, 1H), 6.36 (dd, *J* = 27.4, 16.4 Hz, 2H), 6.20 (d, *J* = 1.2 Hz, 2H), 5.58 (d, *J* = 1.2 Hz, 2H), 3.43 (s, 6H), 3.23 (dd, *J* = 14.4, 1.2 Hz, 2H), 3.01 (dd, *J* = 14.4, 1.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.4, 168.0, 137.2, 136.8, 136.6, 132.0, 131.7, 130.6, 129.6, 128.6, 128.5, 128.1, 127.8, 126.3, 56.4, 51.8, 37.3; HRMS (ESI): *m/z* calcd for $C_{26}H_{26}O_5Na$ [M+Na]$^+$ 441.1678, found 441.1667.



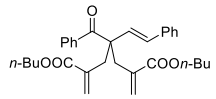
**6b**: 31 mg, 15%, a yellow oil; IR (thin film): $\nu_{max}$ 2825, 1719, 1652, 1440, 1276, 1150, 959, 759, 700 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36-7.27 (m, 3H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.54 (d, *J* = 10.0 Hz, 1H), 6.20 (d, *J* = 12.0 Hz, 2H), 5.48 (d, *J* = 6.8 Hz, 2H), 4.16 (d, *J* = 8.4 Hz, 1H), 3.80 (d, *J* = 2.0 Hz, 3H), 3.75 (d, *J* = 2.4 Hz, 3H), 3.56 (s, 2H), 2.82 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.69 (dd, *J* = 13.8, 8.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.5, 167.2, 167.1, 148.4, 142.2, 138.1, 137.8, 137.7, 137.5, 132.0, 129.6, 128.8, 128.2, 127.6, 127.5, 126.9, 125.9, 52.0, 51.9, 44.2, 39.6, 29.7; HRMS (ESI): *m/z* calcd for $C_{26}H_{26}O_5Na$ [M+Na]$^+$ 441.1678, found 441.1665.



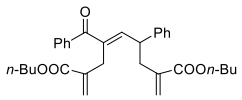
[Reaction time: 2 h]; **4c**: 131 mg, 55%, a yellow oil; IR (thin film): $\nu_{max}$ 2969, 1715, 1677, 1447, 1260, 1164, 949, 755, 694 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.91 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.47-7.43 (m, 1H), 7.36-7.32 (m, 2H), 7.29-7.27 (m, 4H), 7.24-7.19 (m, 1H), 6.38 (d, *J* = 16.7 Hz, 2H), 6.20 (d, *J* = 1.2 Hz, 2H), 5.56 (d, *J* = 1.6 Hz, 2H), 3.85-3.74 (m, 4H), 3.25 (dd, *J* = 14.4, 1.2 Hz, 2H), 3.00 (dd, *J* = 14.4, 1.2 Hz, 2H), 1.47 (td, *J* = 7.2, 7.2 Hz, 4H), 0.81 (t, *J* = 7.4 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.5, 167.7, 137.2, 137.1, 136.7, 132.0, 131.6, 130.6, 129.6, 128.5, 128.2, 128.1, 127.7, 126.3, 66.4, 56.5, 37.1, 21.7, 10.3; HRMS (ESI): *m/z* calcd for $C_{30}H_{24}O_5Na$ [M+Na]$^+$ 497.2304, found 497.2299.



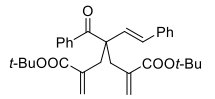
**6c**: 41 mg, 17%, a yellow oil; IR (thin film): $\nu_{max}$ 2968, 1711, 1651, 1449, 1273, 958, 758, 697, 655 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.63 (dt, *J* = 6.8, 1.2 Hz, 2H), 7.55-7.50 (m, 1H), 7.44-7.39 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 1H), 6.54 (dt, *J* = 6.8, 1.4 Hz, 2H), 6.51 (d, *J* = 10.4 Hz, 1H), 6.18 (d, *J* = 1.6 Hz, 1H), 6.12 (d, *J* = 1.2 Hz, 1H), 5.42 (dd, *J* = 10.0, 1.2 Hz, 2H), 4.15-4.05 (m, 5H), 3.51 (d, *J* = 1.6 Hz, 2H), 2.78 (ddd, *J* = 14.0, 6.8, 1.2 Hz, 1H), 2.65 (ddd, *J* = 14.0, 8.8, 1.2 Hz, 1H), 1.75-1.60 (m, 4H), 0.95 (dt, *J* = 13.6, 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.5, 166.7, 148.7, 142.3, 138.1, 138.0, 137.8, 137.8, 131.9, 129.6, 128.8, 128.2, 127.5, 127.3, 126.9, 125.4, 44.3, 39.6, 29.7, 28.9, 22.0, 22.0, 10.5, 10.5; HRMS (ESI): *m/z* calcd for $C_{30}H_{34}O_5Na$ [M+Na]$^+$ 497.2304, found 497.2298.



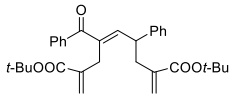
[Reaction time: 2 h]; **4d**: 144 mg, 57%, a yellow oil; IR (thin film): $\nu_{max}$ 2961, 1716, 1677, 1629, 1449, 1260, 1162, 949, 695 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.91 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.47-7.43 (m, 1H), 7.34-7.32 (m, 2H), 7.29-7.27 (m, 4H), 7.23-7.19 (m, 1H), 6.38 (q, *J* = 16.8 Hz, 2H), 6.19 (d, *J* = 1.2 Hz, 2H), 5.56 (d, *J* = 1.2 Hz, 2H), 3.90-3.78 (m, 4H), 3.24 (dd, *J* = 14.4, 0.8 Hz, 2H), 3.00 (dd, *J* = 14.0, 0.8 Hz, 2H), 1.46-1.38 (m, 4H), 1.28-1.21 (m, 4H), 0.84 (t, *J* = 7.4 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.5, 167.7, 137.2, 137.1, 136.7, 132.0, 131.6, 130.6, 129.6, 128.5, 128.2, 128.0, 127.7, 126.3, 64.7, 56.5, 37.2, 30.4, 19.1, 13.7; HRMS (ESI): *m/z* calcd for $C_{32}H_{38}O_5Na$ [M+Na]$^+$ 525.2617, found 525.2607.



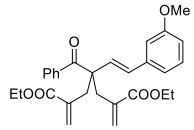
**6d**: 39 mg, 16%, a yellow oil; IR (thin film): $\nu_{max}$ 2961, 1715, 1653, 1451, 1275, 1154, 959, 699 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.65 (dt, *J* = 6.8, 1.6 Hz, 2H), 7.57-7.53 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.31 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.26-7.22 (m, 1H), 7.19-7.17 (m, 2H), 6.53 (d, *J* = 10.0 Hz, 1H), 6.19 (d, *J* = 1.6 Hz, 1H), 6.13 (d, *J* = 1.2 Hz, 1H), 5.45 (d, *J* = 1.2 Hz, 1H), 5.43 (d, *J* = 1.6 Hz, 1H), 4.21-4.11 (m, 5H), 3.53 (s, 2H), 2.80 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.66 (dd, *J* = 13.8, 8.6 Hz, 1H), 1.74-1.64 (m, 3H), 1.41 (td, *J* = 14.8, 7.6 Hz, 5H), 0.96 (dt, *J* = 14.2, 7.2 Hz, 6H; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.5, 166.7, 148.6, 142.3, 138.1, 138.0, 137.8, 137.8, 131.9, 129.6, 128.8, 128.2, 127.5, 127.2, 126.8, 125.4, 64.8, 64.7, 44.2, 39.6, 30.7, 30.6, 28.9, 19.3, 19.2, 13.7; HRMS (ESI): *m/z* calcd for $C_{32}H_{38}O_5Na$ [M+Na]$^+$ 525.2617, found 525.2602.



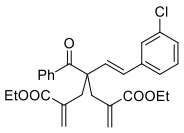
[Reaction time: 2 h]; **4e**: 152 mg, 61%, a yellow oil; IR (thin film): $\nu_{max}$ 2978, 1710, 1677, 1368, 1254, 1147, 948, 850, 694 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.90 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.46-7.42 (m, 1H), 7.36-7.32 (m, 2H), 7.30-7.26 (m, 3H), 7.24-7.17 (m, 2H), 6.43 (dd, *J* = 30.8, 16.8 Hz, 2H), 6.14 (d, *J* = 1.6 Hz, 2H), 5.50 (d, *J* = 1.6 Hz, 2H), 3.20 (d, *J* = 14.4 Hz, 2H), 2.95 (d, *J* = 14.0 Hz, 2H), 1.28 (s, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.8, 166.7, 138.3, 137.5, 137.0, 131.9, 131.7, 130.4, 129.6, 128.5, 128.0, 127.6, 126.4, 80.7, 56.6, 37.0, 27.9, 27.8; HRMS (ESI): *m/z* calcd for $C_{32}H_{38}O_5Na$ [M+Na]$^+$ 525.2617, found 525.2602.



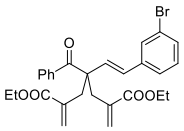
**6e**: 41 mg, 16%, a yellow oil; IR (thin film): $\nu_{max}$ 2928, 1710, 1654, 1368, 1278, 1147, 960, 850, 699 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.64 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.54-7.50 (m, 1H), 7.43-7.38 (m, 2H), 7.37-7.26 (m, 2H), 7.23-7.18 (m, 1H), 7.16 (dt, *J* = 6.8, 1.4 Hz, 2H), 6.50 (d, *J* = 10.0 Hz, 1H), 6.09 (dd, *J* = 4.6, 1.4 Hz, 1H), 6.02 (d, *J* = 1.2 Hz, 1H), 5.38 (d, *J* = 1.2 Hz, 1H), 5.33 (d, *J* = 1.6 Hz, 1H), 4.08 (td, *J* = 9.2, 6.0 Hz, 1H), 3.47 (d, *J* = 5.2 Hz, 2H), 2.74 (ddd, *J* = 13.6, 6.4, 1.2 Hz, 1H), 2.59 (dd, *J* = 13.8, 8.6 Hz, 1H), 1.48 (s, 9H), 1.45 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.6, 165.9, 165.9, 148.9, 142.5, 139.3, 139.1, 138.2, 137.8, 131.9, 129.7, 128.8, 128.1, 127.5, 126.8, 126.6, 124.4, 44.4, 39.6, 28.1, 28.0; HRMS (ESI): *m/z* calcd for $C_{32}H_{38}O_5Na$ [M+Na]$^+$ 525.2617, found 525.2605.



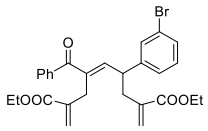
[Reaction time: 2 h]; **4f**: 77 mg, 33%, a yellow oil; IR (thin film): $\nu_{max}$ 2926, 1715, 1598, 1447, 1268, 1157, 949, 783, 691 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.93 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.50-7.45 (m, 1H), 7.40-7.35 (m, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.83-6.78 (m, 2H), 6.43 (dd, *J* = 36.2, 16.6 Hz, 2H), 6.23 (d, *J* = 1.6 Hz, 2H), 5.59 (d, *J* = 1.6 Hz, 2H), 4.00-3.86 (m, 4H), 3.81 (s, 3H), 3.25 (d, *J* = 14.4 Hz, 2H), 3.02 (d, *J* = 14.4 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.4, 167.6, 159.8, 138.2, 137.2, 137.1, 132.0, 132.0, 130.5, 129.6, 129.5, 128.2, 128.1, 118.9, 113.4, 111.6, 60.8, 56.4, 55.2, 37.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{29}H_{32}O_6Na$ [M+Na]$^+$ 499.2097, found 499.2084.



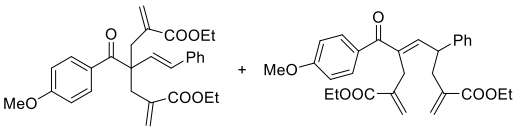
[Reaction time: 2 h]; **4h**: 137 mg, 57%, a yellow oil; IR (thin film): $\nu_{max}$ 2982, 1713, 1629, 1445, 12612, 1153, 949, 782, 691 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.89 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.48-7.44 (m, 1H), 7.38-7.34 (m, 2H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.21-7.17 (m, 2H), 7.15-7.11 (m, 1H), 6.43 (d, *J* = 16.4 Hz, 1H), 6.27 (d, *J* = 16.4 Hz, 1H), 6.22 (d, *J* = 1.6 Hz, 2H), 5.58 (d, *J* = 1.2 Hz, 2H), 3.99-3.86 (m, 4H), 3.23 (dd, *J* = 14.4, 0.8 Hz, 2H), 2.99 (dd, *J* = 14.4, 1.2 Hz, 2H), 1.09 (t, J = 7.2 Hz, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 202.1, 167.5, 138.6, 137.1, 136.9, 134.5, 133.3, 132.1, 129.8, 129.6, 129.3, 128.5, 128.1, 127.6, 126.2. 124.4, 60.9, 56.6, 37.3, 14.0; HRMS (ESI): *m/z* calcd for $C_{28}H_{29}ClO_5Na$ $[M+Na]^+$ 503.1601, found 503.1587.



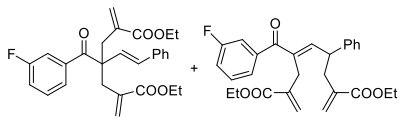
[Reaction time: 2 h]; **4i**: 145 mg, 55%, a yellow oil; IR (thin film): $\nu_{max}$ 2982, 1715, 1677, 1445, 1277, 1154, 950, 781, 695 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.89 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.49-7.44 (m, 1H), 7.40-7.33 (m, 4H), 7.19-7.12 (m, 2H), 6.42 (d, *J* = 16.4 Hz, 1H), 6.25 (d, *J* = 16.8 Hz, 1H), 6.22 (d, *J* = 1.6 Hz, 2H), 5.58 (d, *J* = 1.2 Hz, 2H), 3.99-3.86 (m, 4H), 3.23 (dd, *J* = 14.4, 1.2 Hz, 2H), 2.99 (dd, *J* = 14.4, 1.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 202.0, 167.5, 138.9, 137.0, 136.9, 133.3, 132.1, 130.5, 130.1, 129.6, 129.2, 129.1, 128.5, 128.1, 124.9, 122.8, 60.9, 56.6, 37.3, 14.0; HRMS (ESI): *m/z* calcd for $C_{28}H_{29}BrO_5Na$ $[M+Na]^+$ 547.1096, found 547.1081.



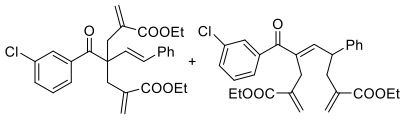
**6i**: 71 mg, 27%, a yellow oil; IR (thin film): $\nu_{max}$ 2926, 1714, 1654, 1472, 1153, 1027, 957, 816, 697 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.64 (dt, *J*= 6.8, 1.2 Hz, 2H), 7.56-7.51 (m, 1H), 7.45-7.40 (m, 2H), 7.37-7.32 (m, 2H), 7.16 (t, *J*= 7.6 Hz, 1H), 7.11-7.07 (m, 1H), 6.40 (d, *J*= 10.0 Hz, 1H), 6.19 (d, *J*= 1.2 Hz, 1H), 6.13 (d, *J*= 1.2 Hz, 1H), 5.45 (d, *J*= 1.4 Hz, 2H), 4.24-4.14 (m, 5H), 3.50 (s, 2H), 2.76 (ddd, *J*= 14.0, 6.4, 1..2 Hz, 1H), 2.61 (dd, *J*= 14.0, 9.2 Hz, 1H), 1.31 (td, *J*= 7.2, 1.6 Hz, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 197.4, 166.6, 144.7, 138.5, 138.0, 137.7, 137.6, 132.1, 130.6, 130.3, 129.7, 129.3, 128.6, 128.2, 127.5, 126.3, 125.8, 125.6, 61.0, 60.9, 43.8, 39.5, 29.7, 14.2, 14.2; HRMS (ESI): *m/z* calcd for $C_{28}H_{29}BrO_5Na$ $[M+Na]^+$ 547.1096, found 547.1078.



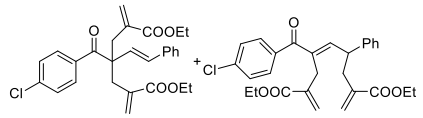
[Reaction time: 24 h]; **4k**/**6k**: 113 mg, 48%, a yellow oil mixture, 10:1 *rr*; IR (thin film): $\nu_{max}$ 2981, 1713, 1599, 1446, 1258, 1169, 948, 754, 694 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): **4k**: δ 7.97 (dt, *J* = 8.8, 3.2 Hz, 2H), 7.27 (t, *J* = 4.4 Hz, 4H), 7.24-7.19 (m, 1H), 6.83 (dt, *J* = 9.2, 2.8 Hz, 2H), 6.43 (d, *J* = 16.8 Hz, 1H), 6.33 (d, *J* = 16.8 Hz, 1H), 6.19 (d, *J* = 1.2 Hz, 2H), 5.57 (d, *J* = 1.6 Hz, 2H), 3.94-3.85 (m, 4H), 3.82 (s, 3H), 3.23 (dd, *J* = 14.4, 1.2 Hz, 2H), 2.98 (dd, *J* = 14.4, 1.2 Hz, 2H), 1.07 (t, *J* = 7.2 Hz, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): **4k**: δ 200.3, 167.7, 162.6, 137.3, 136.8, 132.2, 132.1, 130.3, 129.6, 128.5, 128.2, 127.7, 126.3, 113.2, 60.8, 56.3, 55.4, 37.2, 14.0; HRMS (ESI): *m/z* calcd for $C_{29}H_{32}O_6Na$ $[M+Na]^+$ 499.2097, found 499.2082.



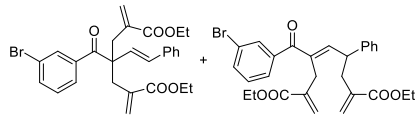
[Reaction time: 24 h]; **4l**/**6l**: 78 mg, 34%, a yellow oil mixture, 2:1 *rr*; IR (thin film): $\nu_{max}$ 2983, 1714, 1680, 1586, 1439, 1150, 964, 754, 696 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ: $^1H$ NMR (400 MHz, $CDCl_3$): δ **4l**: 7.72 (ddd, *J* = 8.0, 1.6, 1.0 Hz, 1H), 7.60 (ddd, *J* = 10.0, 2.4, 1.6 Hz, 1H), 7.35-7.31 (m, 1H), 7.31-7.27 (m, 4H), 7.25-7.19 (m, 2H), 6.35 (d, *J* = 2.4 Hz, 2H), 6.21 (d, *J* = 1.2 Hz, 2H), 5.58 (q, *J* = 1.2 Hz, 2H), 4.02-3.82 (m, 4H), 3.22 (dd, *J* = 14.2, 1.0 Hz, 2H), 3.00 (dd, *J* = 14.2, 1.0 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 6H); **6l**: 7.18-7.14 (m, 1H), 5.43 (dd, *J* = 12.0, 1.2 Hz, 1H), 4.26-4.10 (m, 2H), 3.50 (s, 1H), 1.27 (dt, *J* = 26.8, 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ **4l**/**6l**: 201.1, 196.0, 167.5, 166.6 (d, *J* = 4.0 Hz), 163.5, 161.0, 149.0, 142.1, 140.2 (d, *J* = 6.0 Hz), 139.1 (d, *J* = 6.0 Hz). 137.9, 137.7 (d, *J* = 5.0 Hz), 137.0, 136.5, 131.1, 130.0, 129.8 (d, *J* = 8.0 Hz), 129.6 (d, *J* = 8.0 Hz), 128.8, 128.6, 128.4, 127.9, 127.5, 127.4, 126.9, 126.3, 125.6, 125.4 (d, *J* = 3.0 Hz), 125.3 (d, *J* = 3.0 Hz), 119.1 (d, *J* = 21.0 Hz), 119.0 (d, *J* = 22.0 Hz), 116.5 (d, *J* = 23.0 Hz), 116.4 (d, *J* = 22.0 Hz), 60.9, 56.5, 44.2, 39.6, 37.2, 29.7, 28.9, 14.2 (d, *J* = 3.6 Hz), 13.9; $^{19}F$ NMR (376 MHz, $CDCl_3$): δ **4l**/**6l**: -111.9, -112.2; HRMS (ESI): *m/z* calcd for $C_{28}H_{29}FO_5Na$ $[M+Na]^+$ 487.1897, found 487.1882.



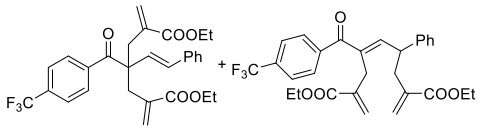
[Reaction time: 6 h]; **4m**/**6m**: 160 mg, 67%, a yellow oil mixture, 2:1 *rr*; IR (thin film): $\nu_{max}$ 2983, 1714, 1680, 1445, 1260, 955, 815, 749, 698 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ **4m**: 7.87 (t, *J* = 2.0 Hz, 1H), 7.81 (ddd, *J* = 8.0, 1.6, 1.2 Hz, 1H), 7.50 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.42 (ddd, *J* = 8.0, 2.4, 1.2 Hz, 1H), 7.33-7.26 (m, 5H), 6.34 (d, *J* = 2.4 Hz, 2H), 6.22 (d, *J* = 1.6 Hz, 2H), 5.58 (d, *J* = 1.2 Hz, 2H), 3.99-3.83 (m, 4H), 3.21 (dd, *J* = 14.2, 1.0 Hz, 2H), 2.99 (dd, *J* = 14.2, 1.0= Hz, 2H), 1.08 (t, J = 7.2 Hz, 6H); **6m**: 7.26-7.18 (m, 2H), 7.18-7.14 (m, 1H), 5.58 (dd, *J* = 24.0, 1.2 Hz, 2H), 5.49-5.38 (m, 1H), 4.27-4.13 (m, 2H), 3.49 (s, 1H), 1.27 (dt, *J* = 14.2, 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ **4m**/**6m**: 201.1, 196.6, 167.5, 166.6, 149.2, 142.1, 139.8. 138.7, 137.9, 137.7, 137.2, 137.0, 136.5, 134.4, 133.6, 131.9, 131.2, 131.1 (2C), 129.7, 129.5, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 126.9, 126.3, 125.6, 125.4, 60.9, 60.9, 56.5, 44.1, 39.7, 38.2, 37.3, 29.7, 28.9, 14.2 (d, *J* = 5.0 Hz), 13.9; HRMS (ESI): *m/z* calcd for $C_{28}H_{29}ClO_5Na$ $[M+Na]^+$ 503.1601, found 503.1589.



[Reaction time: 6 h]; **4n**/**6n**: 170 mg, 69%, a yellow oil mixture, 1.5:1 *rr*; IR (thin film): $\nu_{max}$ 2983, 1714, 1630, 1588, 1446, 1264, 949, 752, 697 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ **4n**: 7.88 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.58 (dt, *J* = 8.8, 2.2 Hz, 1H), 7.39 (dt, *J* = 8.4, 2.6 Hz, 1H), 7.30-7.26 (m, 4H), 7.25-7.20 (m, 2H), 6.34 (d, *J* = 9.2 Hz, 2H), 6.21 (d, *J* = 1.2 Hz, 2H), 5.58 (d, *J* = 1.2 Hz, 2H), 3.97-3.83 (m, 4H), 3.21 (dd, *J* = 14.4, 0.8 Hz, 2H), 2.98 (dd, *J* = 14.2, 1.2= Hz, 2H), 1.07 (t, *J* = 7.2 Hz, 6H); **6n**: 7.34-7.31 (m, 2H), 7.18-7.12 (m, 1H), 5.42 (q, *J* = 1.2 Hz, 1H), 4.23-4.12 (m, 2H), 3.50 (s, 1H), 1.27 (dt, *J* = 24.0, 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ **4n**/**6n**: 201.1, 196.2, 167.5, 166.6 (d, *J* = 4.0 Hz), 148.5, 142.1, 138.4, 138.3, 137.9, 137.7, 137.6, 137.0, 136.5, 136.4, 135.3, 132.0, 131.3, 131.2, 131.0, 130.9, 130.6, 128.8, 128.6, 128.5, 128.4, 128.3, 127.9, 127.5, 127.3, 126.9, 126.3, 125.6, 60.9, 60.8, 56.4, 44.2, 39.5, 38.2, 37.3, 29.7, 29.0, 14.2 (d, *J* = 6.0 Hz), 13.9; HRMS (ESI): *m*/*z* calcd for $C_{28}H_{29}O_5Na$ $[M+Na]^+$ 503.1601, found 503.1584.



[Reaction time: 6 h]; **4o**/**6o**: 164 mg, 62%, a yellow oil mixture, 1.5:1 *rr*; IR (thin film): $\nu_{max}$ 2983, 1714, 1679, 1445, 1260, 1153, 953, 746, 695 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ **4o**: 8.03 (t, *J* = 1.6 Hz, 1H), 7.86 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.60-7.55 (m, 1H), 7.33-7.26 (m, 4H), 7.26-7.20 (m, 2H), 6.34 (d, *J* = 1.6 Hz, 2H), 6.22 (d, *J* = 1.2 Hz, 2H), 5.58 (d, *J* = 1.2 Hz, 2H), 3.99-3.84 (m, 4H), 3.21 (dd, *J* = 14.4, 1.0 Hz, 2H), 2.99 (dd, *J* = 14.4, 1.2 Hz, 2H), 1.08 (t, J = 7.2 Hz, 6H); **6o**: 7.19-7.13 (m, 1H), 5.50-5.35 (m, 1H), 4.28-4.11 (m, 2H), 3.48 (s, 1H), 1.27 (dt, *J* = 22.8, 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 201.0, 195.9, 167.5, 162.6 (d, *J* = 2.0 Hz), 149.2, 142.1, 140.0, 138.9, 137.9, 137.7, 137.0, 136.5, 134.9, 134.8, 132.6, 132.5, 131.1, 131.0, 129.8, 129.5, 128.9, 128.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.5, 127.1, 126.9, 126.3, 125.6, 122.4, 122.3, 60.9, 56.5, 44.1, 39.7, 38.2, 37.3, 29.7, 28.9, 14.2 (d, *J* = 4.0 Hz), 13.9; HRMS (ESI): *m*/*z* calcd for $C_{28}H_{29}BrO_5Na$ $[M+Na]^+$ 547.1096, found 547.1080.



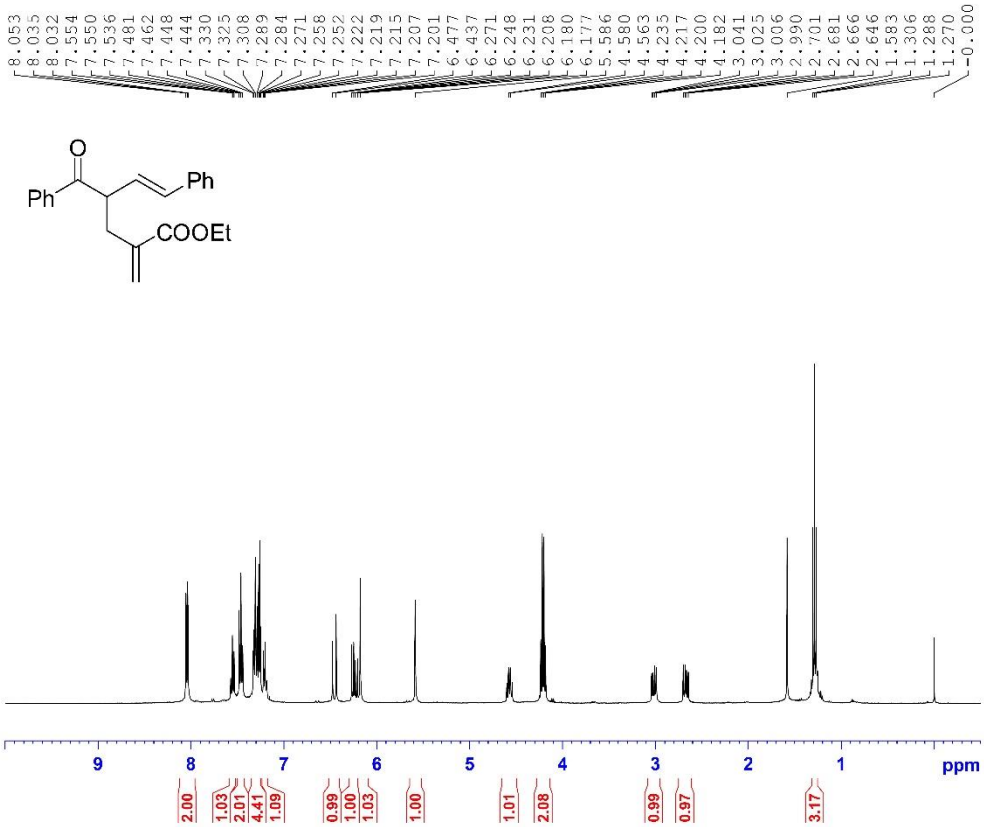
[Reaction time: 6 h]; **4p**/**6p**: 159 mg, 62%, a yellow oil mixture, 1.4:1 *rr*; IR (thin film): $\nu_{max}$ 2928, 1716, 1683, 1326, 1170, 1132, 950, 755, 697 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ **4p**: 8.04-7.99 (m, 2H), 7.61 (dd, *J* = 8.8, 0.8 Hz, 2H), 7.33-7.27 (m, 3H), 7.25-7.20 (m, 2H), 6.35 (d, *J* = 1.2 Hz, 2H), 6.23 (d, *J* = 1.2 Hz, 2H), 5.60 (d, *J* = 1.2 Hz, 2H), 3.98-3.83 (m, 4H), 3.22 (dd, *J* = 14.4, 1.2 Hz, 2H), 3.01 (dd, *J* = 14.4, 1.2 Hz, 2H), 1.07 (t, J = 7.2 Hz, 6H); **6p**: 7.68 (dd, *J* = 14.4, 8.4 Hz, 2H),7.16-7.13 (m, 1H), 6.15 (dd, *J* = 9.6, 1.3 Hz, 1H), 5.42 (dt, *J* = 4.1, 1.4 Hz, 1H), 4.24-5.13 (m, 2H), 3.52 (s, 1H), 1.27 (dt, *J* = 22.8, 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): **4p**/**6p**: δ 202.7, 196.3, 167.5, 166.6 (d, *J*= 5.0 Hz), 137.7, 137.0, 136.4, 131.2, 130.9, 129.9, 129.7, 128.9, 128.6, 128.5, 128.0, 127.5, 127.3, 127.0, 149.8, 141.9, 141.3, 140.2, 137.9, 137.7 (d, *J*= 4.0 Hz), 136.9, 136.4, 133.1, 131.2, 130.9, 129.9, 129.7, 128.9, 128.6, 128.5, 128.0, 127.5, 127.3, 127.0, 126.3, 125.6, 125.2 (d, *J*= 3.0 Hz), 125.1 (d, *J*= 4.0 Hz), 125.0, 60.9, 56.5, 44.3, 39.4, 37.3, 29.7, 32.0, 28.8, 22.8, 14.2 (d, *J*= 4.0 Hz), 13.9; $^{19}F$ NMR (376 MHz, $CDCl_3$): -63.1; HRMS (ESI): *m*/*z* calcd for $C_{29}H_{29}O_5Na$ $[M+Na]^+$ 537.1865, found 537.1845.

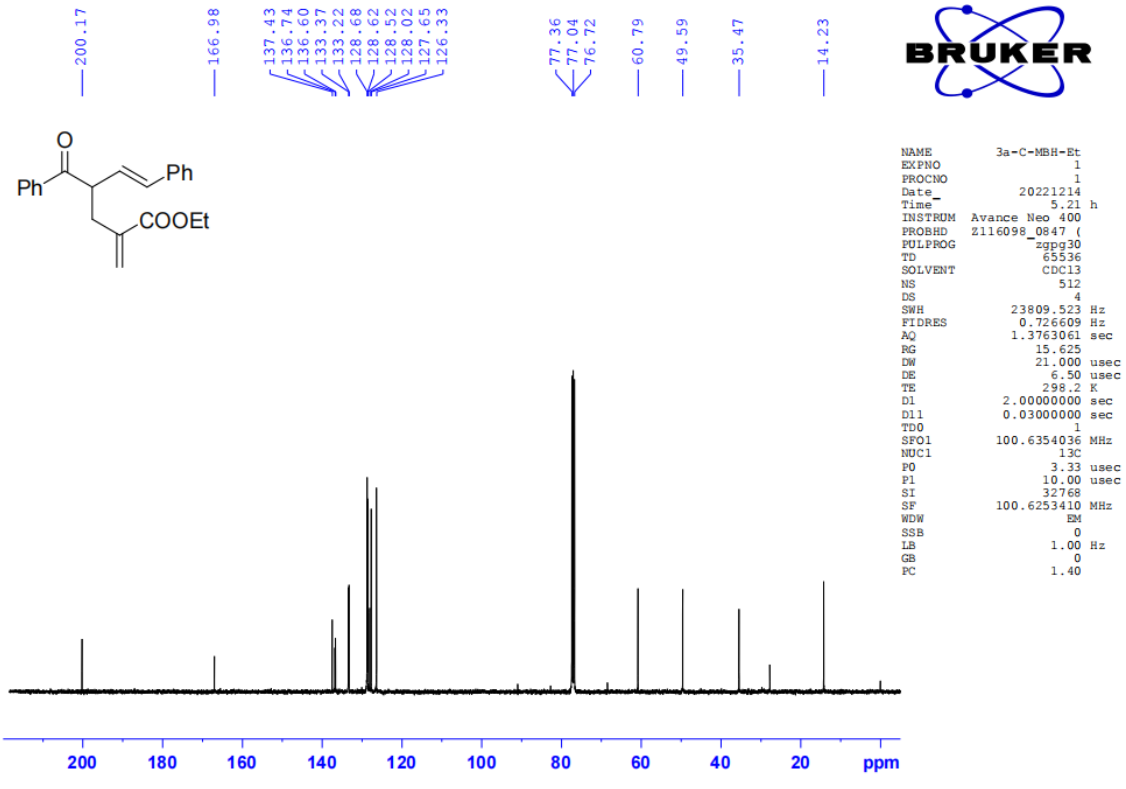
**VIII. References**


1. B. A.Trofimov, E. Y. Schmidt, N. V. Zorina, E. V. Ivanova, I. A. Ushakov, *J. Org. Chem.* 2012, **77**, 6880–6886.
2. N. S. Camilo, H. Santos, L. A. Zeoly, F. S. Fernandes, M. T. Rodrigues, T. S. Silva, S. R. Lima, J. C. Serafim, A. S. B. de Oliveira, A. G. Carpanez, et al, *Eur. J. Org. Chem.*, 2022, **2022**, e202101448.
3. B. Basel, A. Hassner, *J. Org. Chem*., 2000, **65**, 6368–6380.

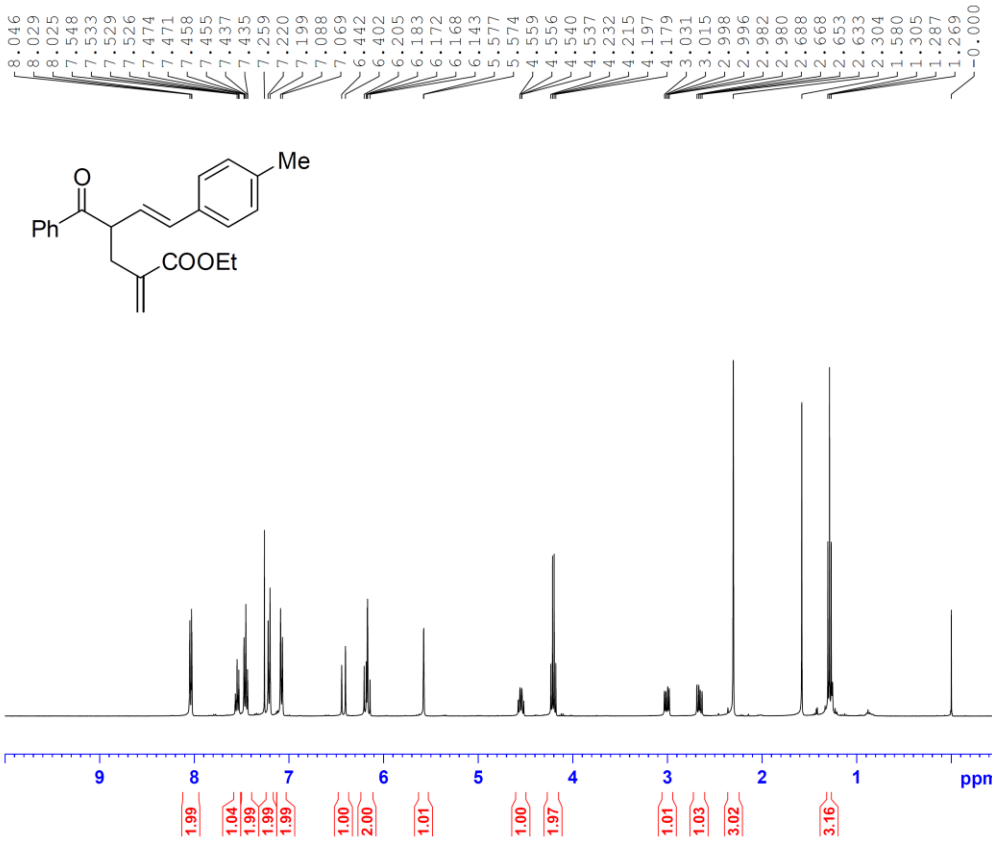
## IX. Copes of NMR for all new compounds

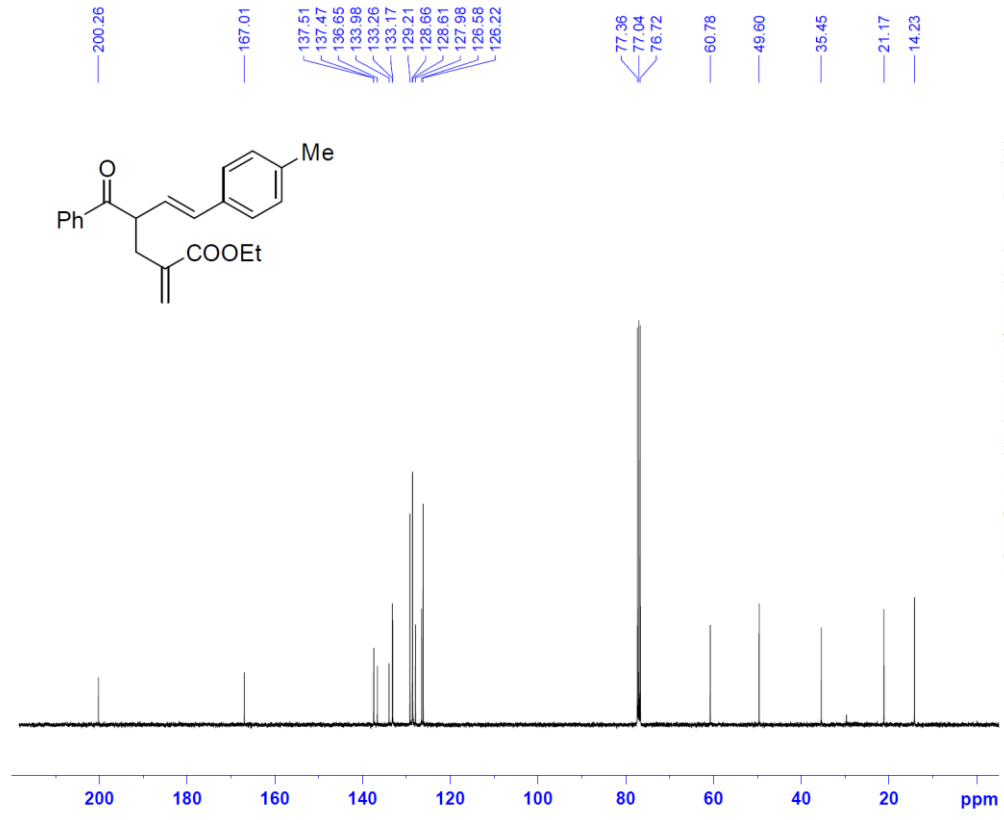
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3a**



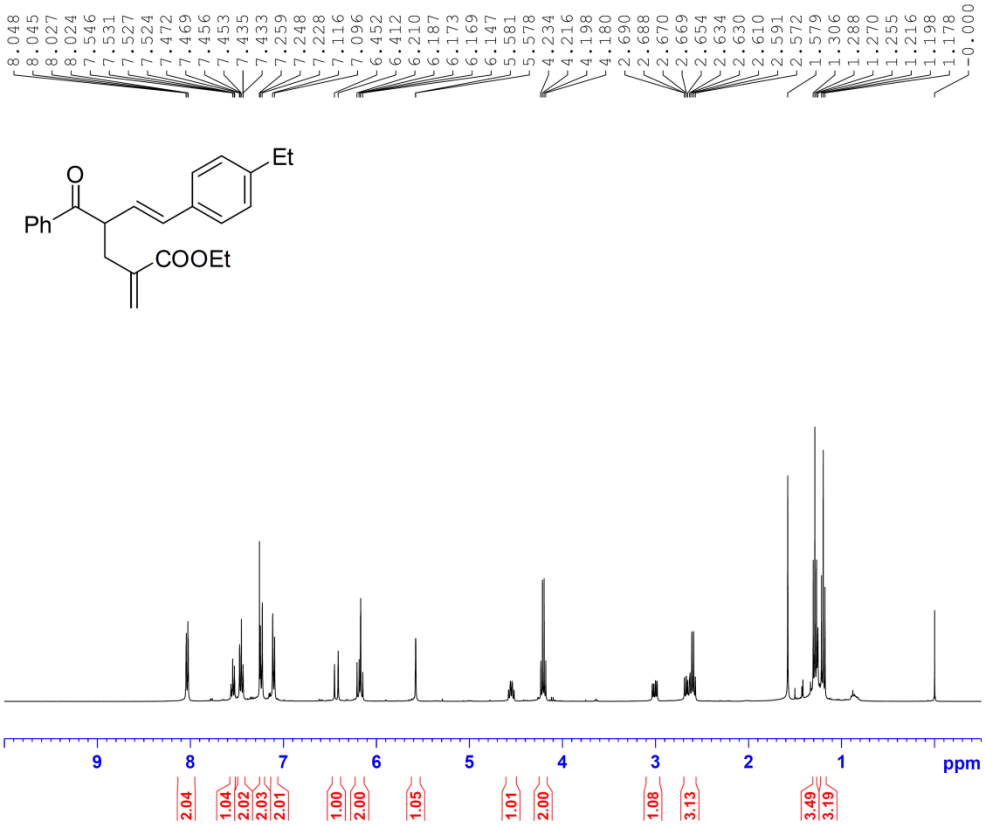



$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3b**



$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3c**

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TD                 65536
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DS                     2
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FIDRES        0.250144 Hz
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RG                   101
DW              61.000 usec
DE              13.54 usec
TE                298.1 K
D1            1.00000000 sec
TD0                    1
SFO1        400.1824711 MHz
NUC1                1H
P0               3.33 usec
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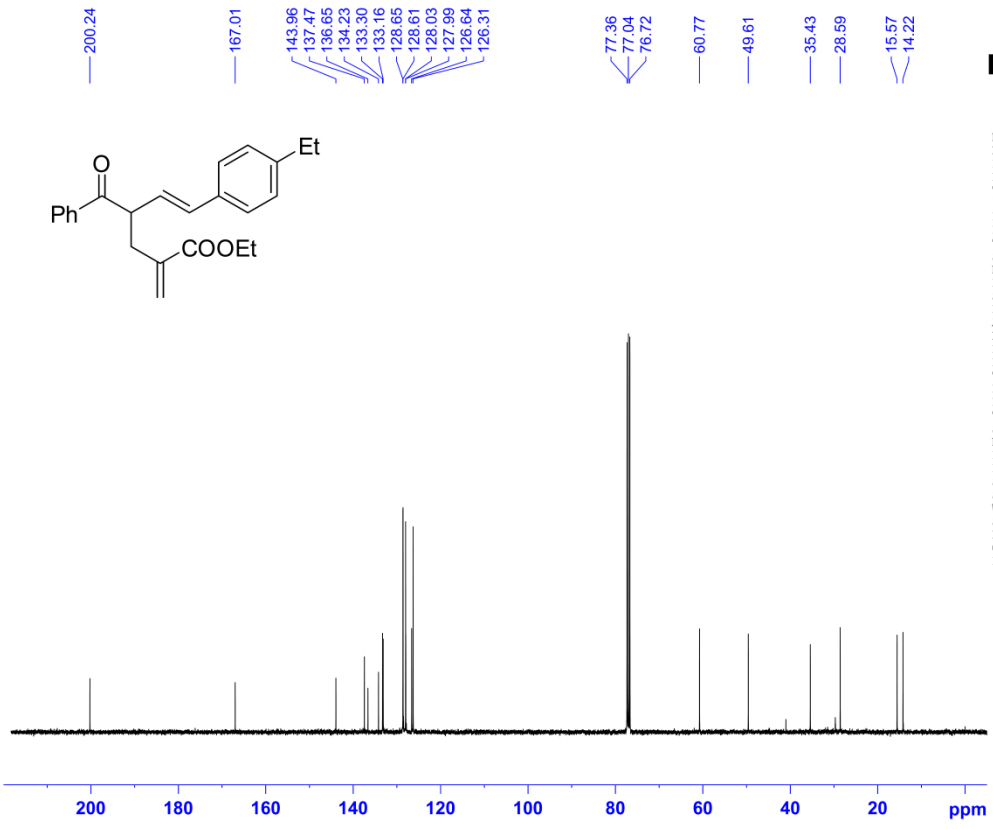


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SOLVENT            CDCl3
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DS                     4
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FIDRES        0.726609 Hz
AQ            1.3763061 sec
RG                15.625
DW              21.000 usec
DE               6.50 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
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NUC1                13C
P0               3.33 usec
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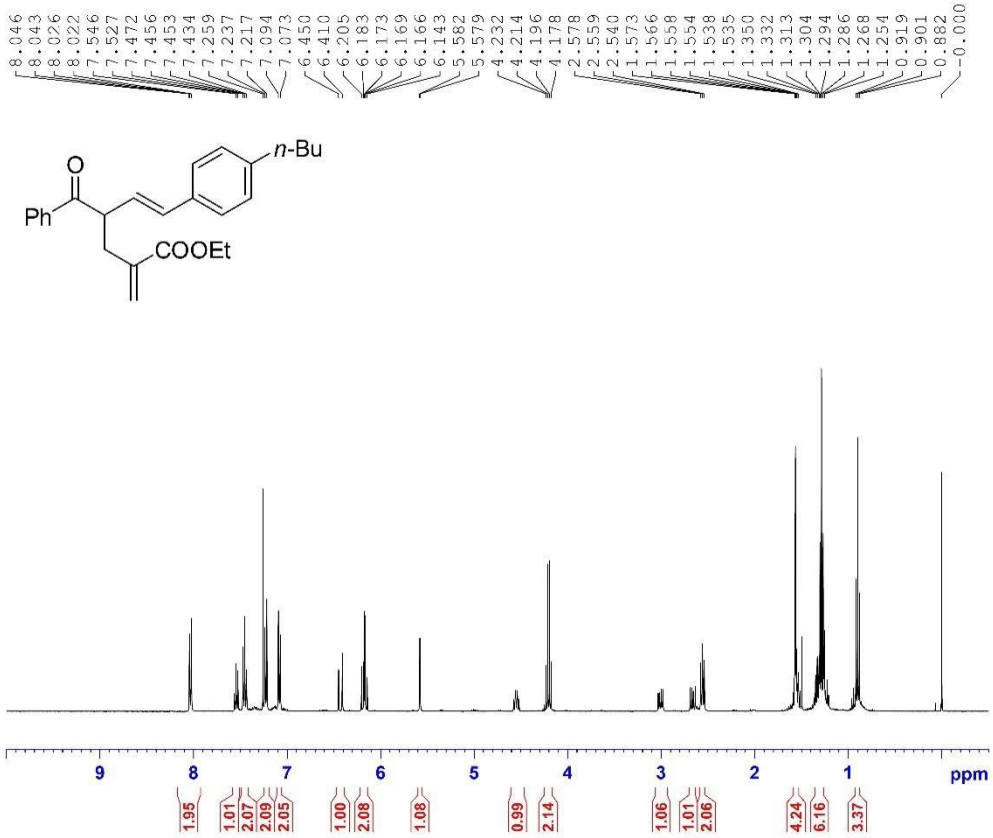
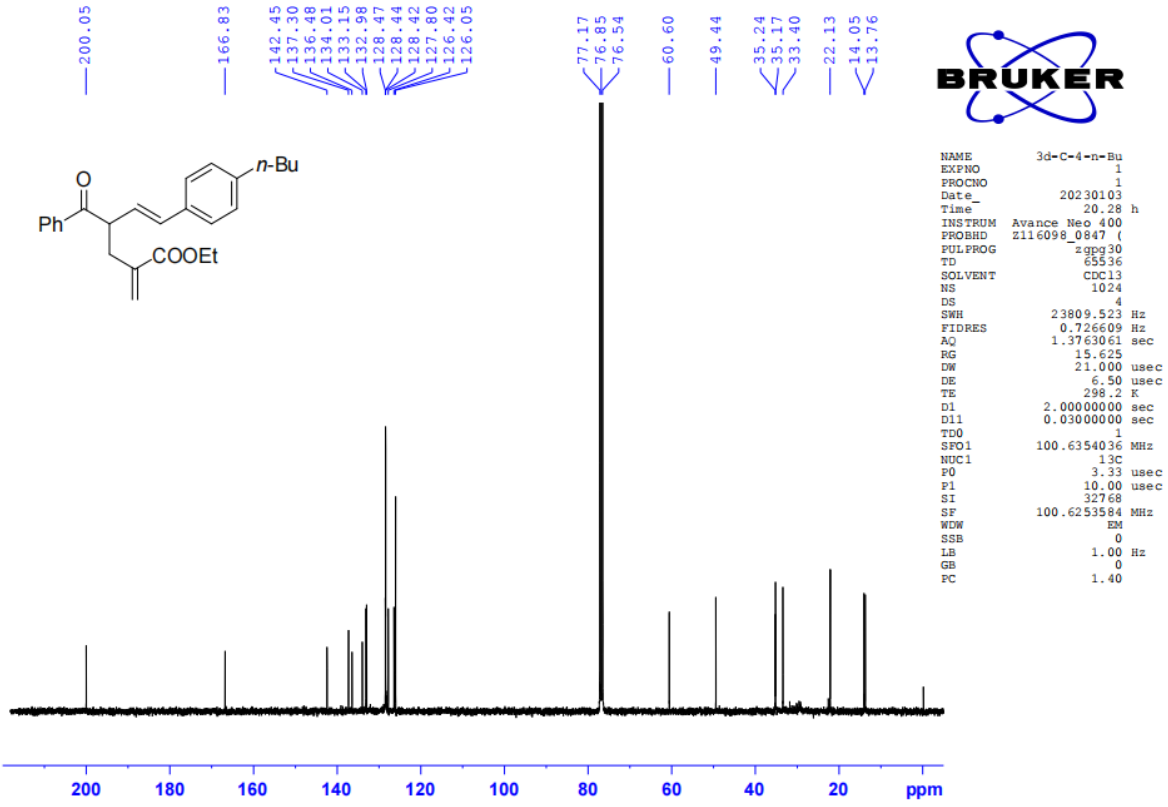
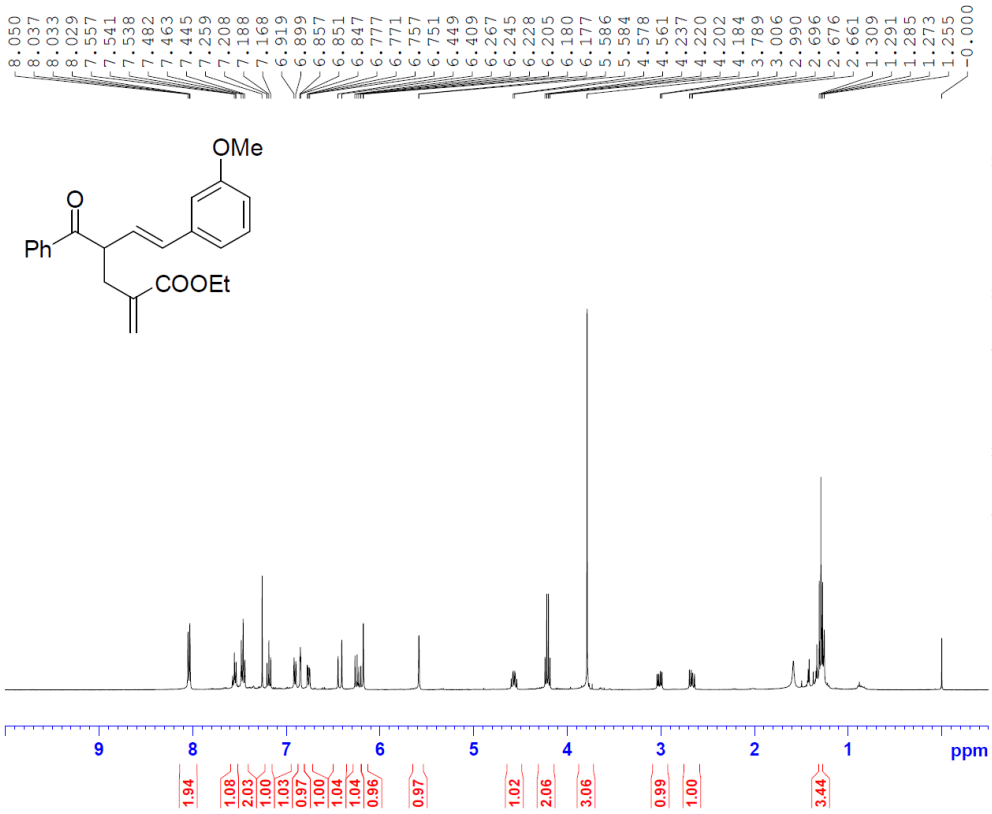
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3d**



$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3e**

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TE                298.2 K
D1            1.00000000 sec
TD0                     1
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NUC1                   1H
P0                 3.33 usec
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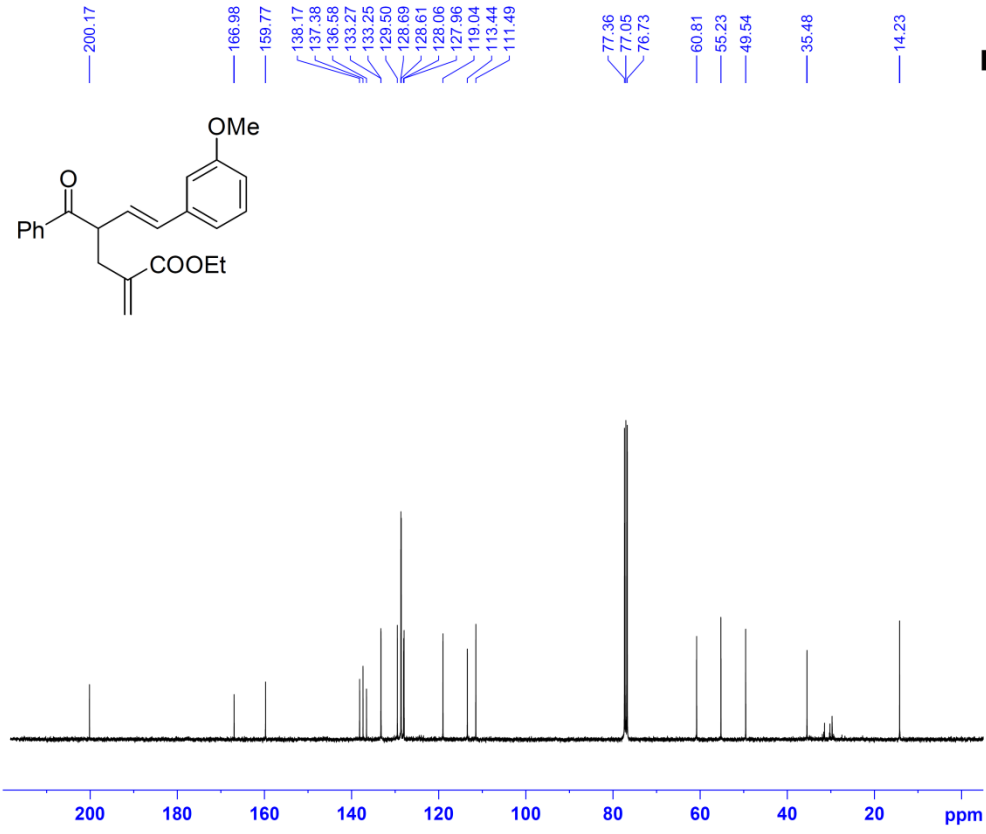


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TD                  65536
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RG                 15.625
DW               21.000 usec
DE                6.50 usec
TE                298.2 K
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D11           0.03000000 sec
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SI                 32768
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GB                      0
PC                   1.40
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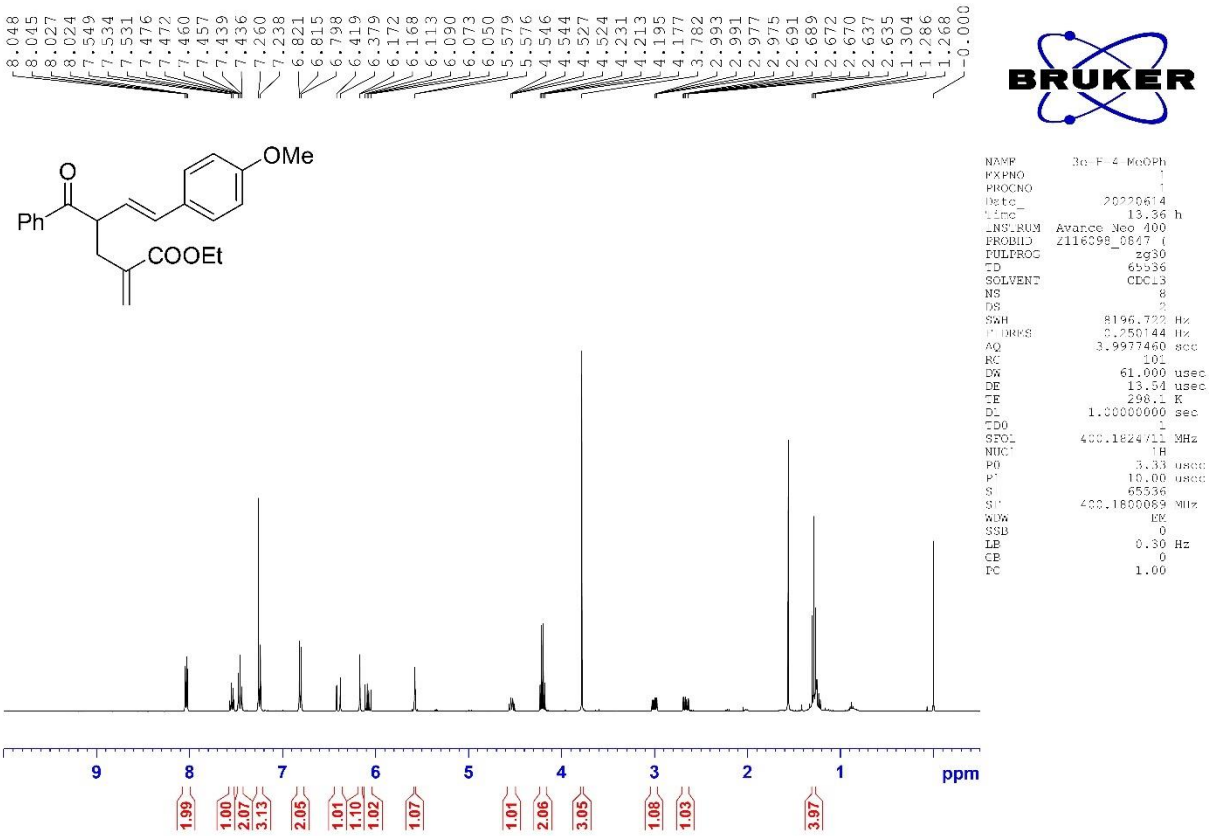
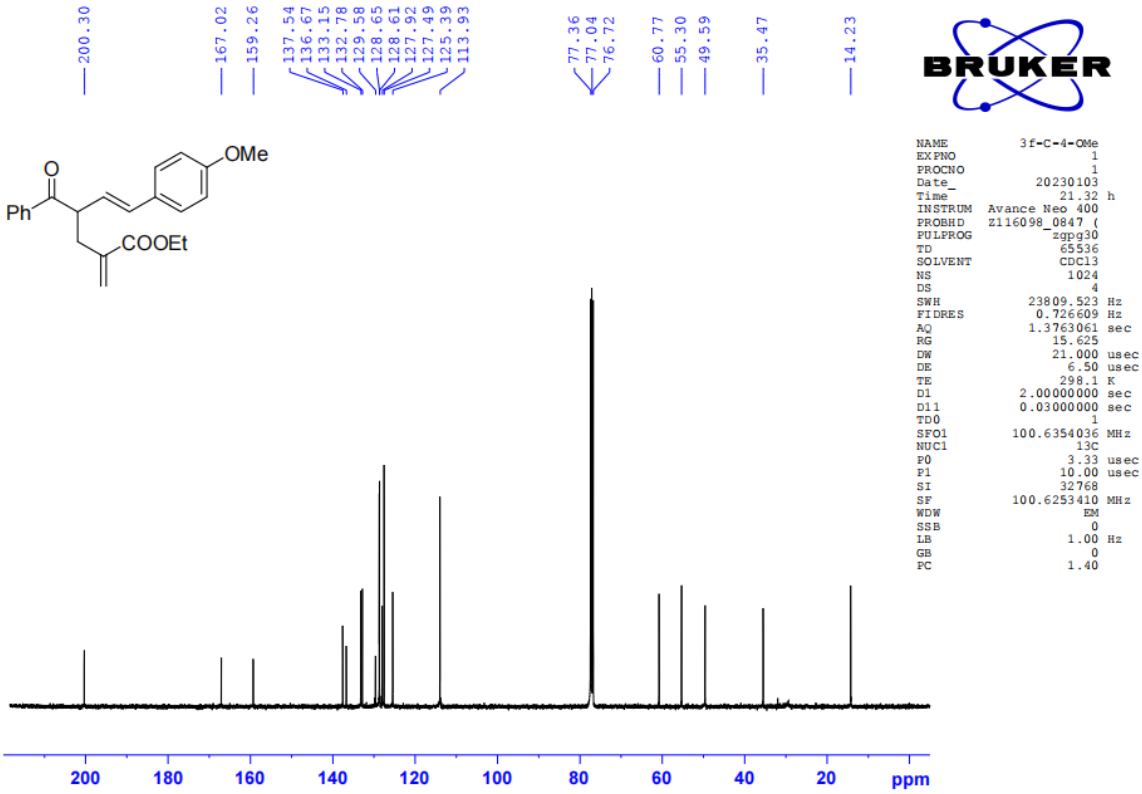
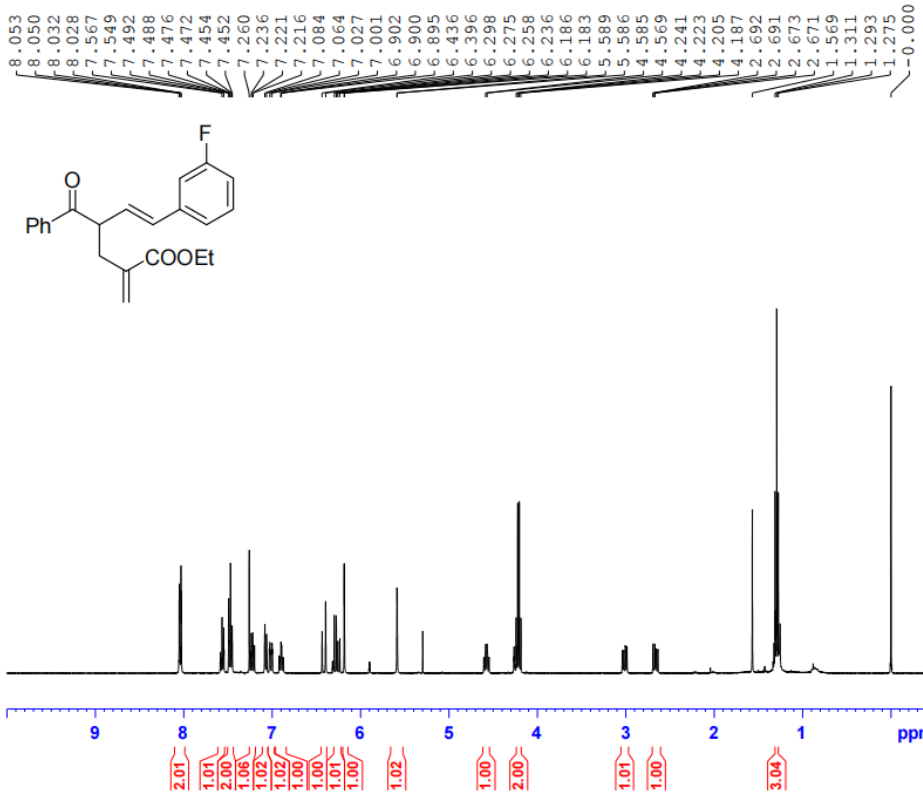
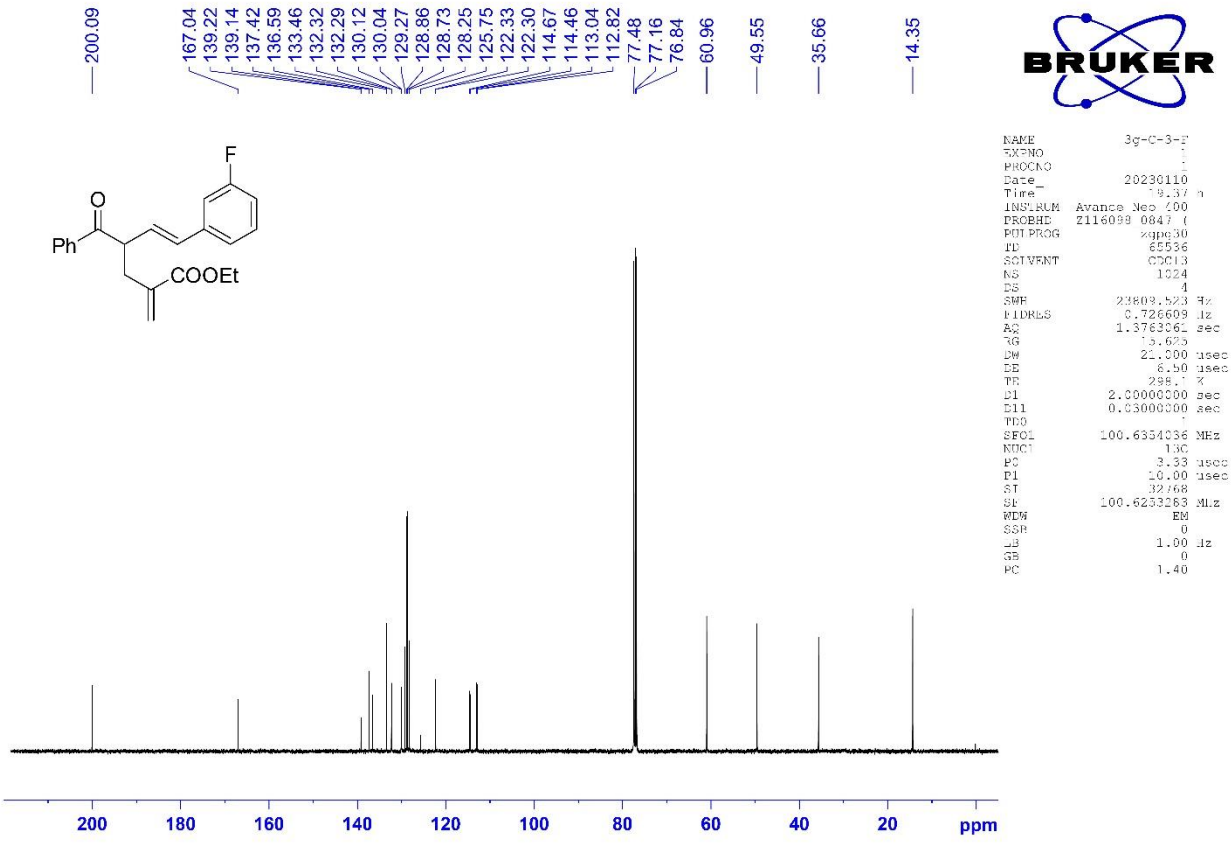
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3f**

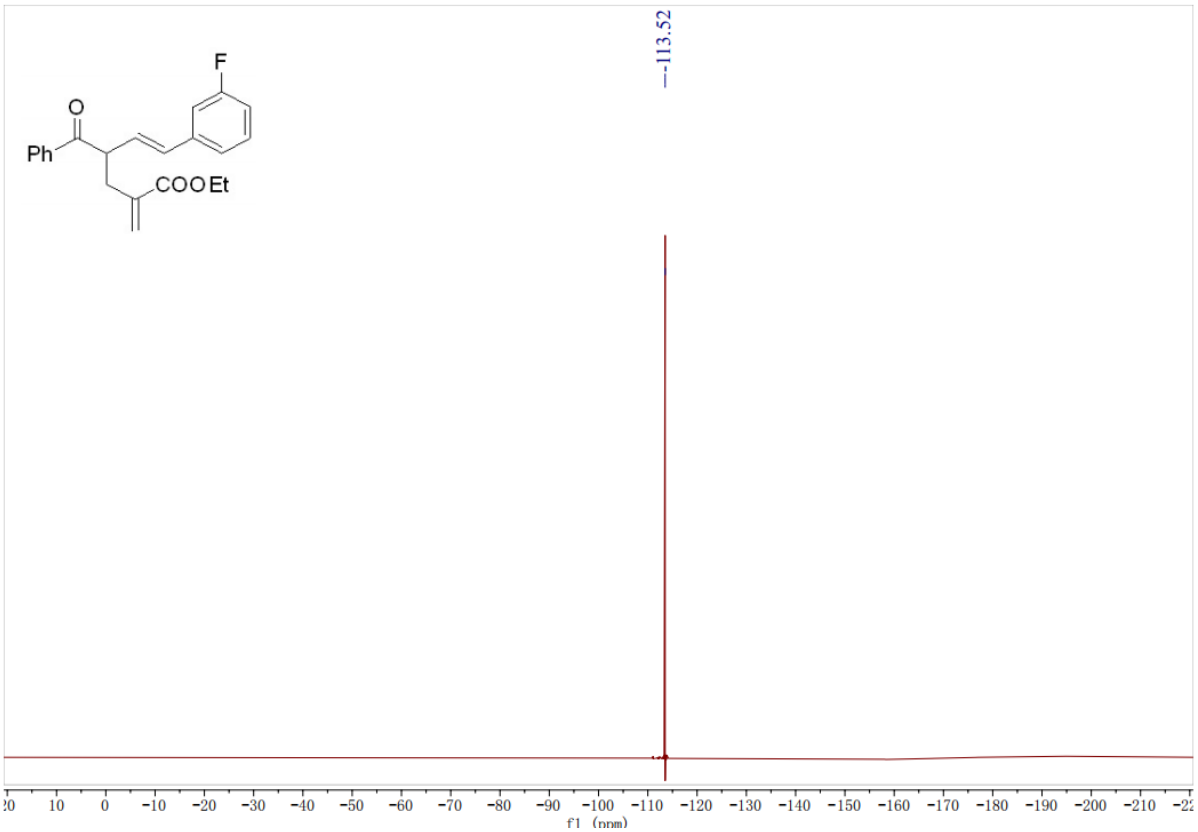


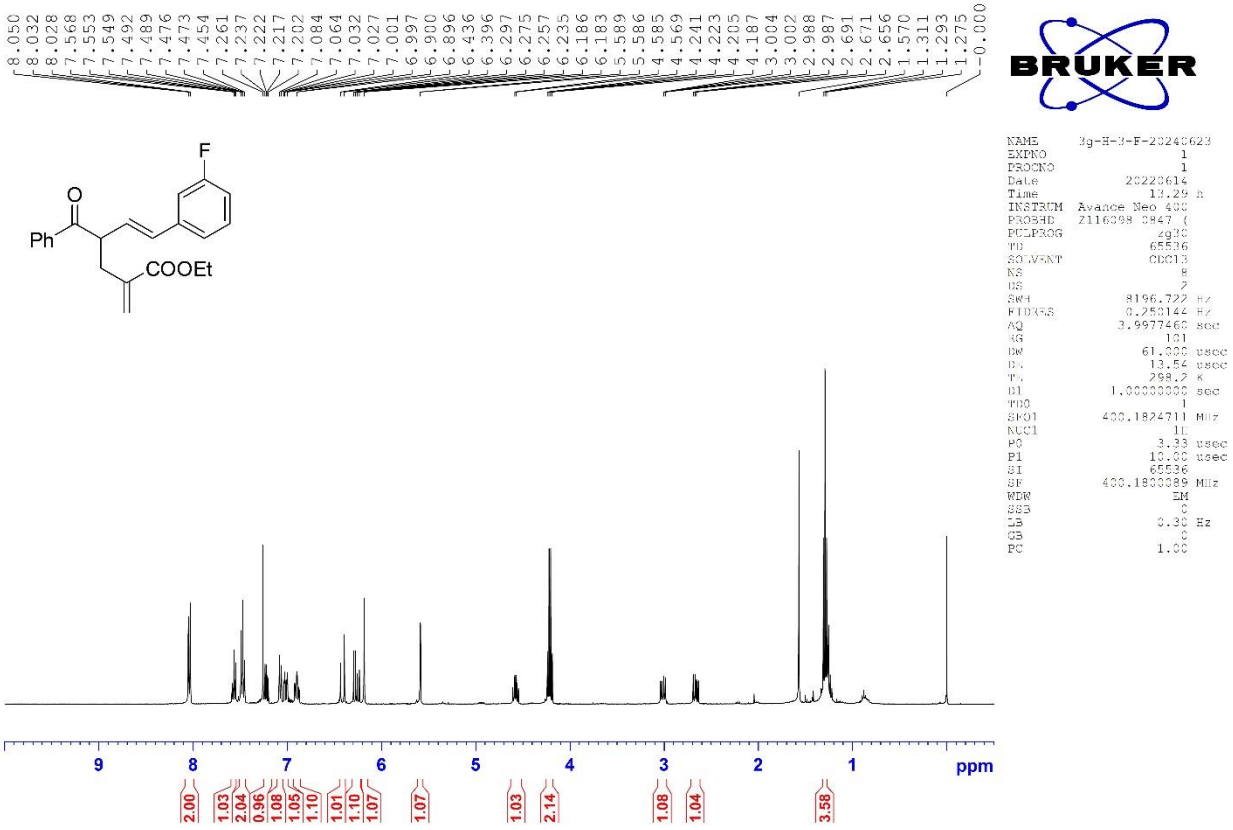
$^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra for Compound **3g**



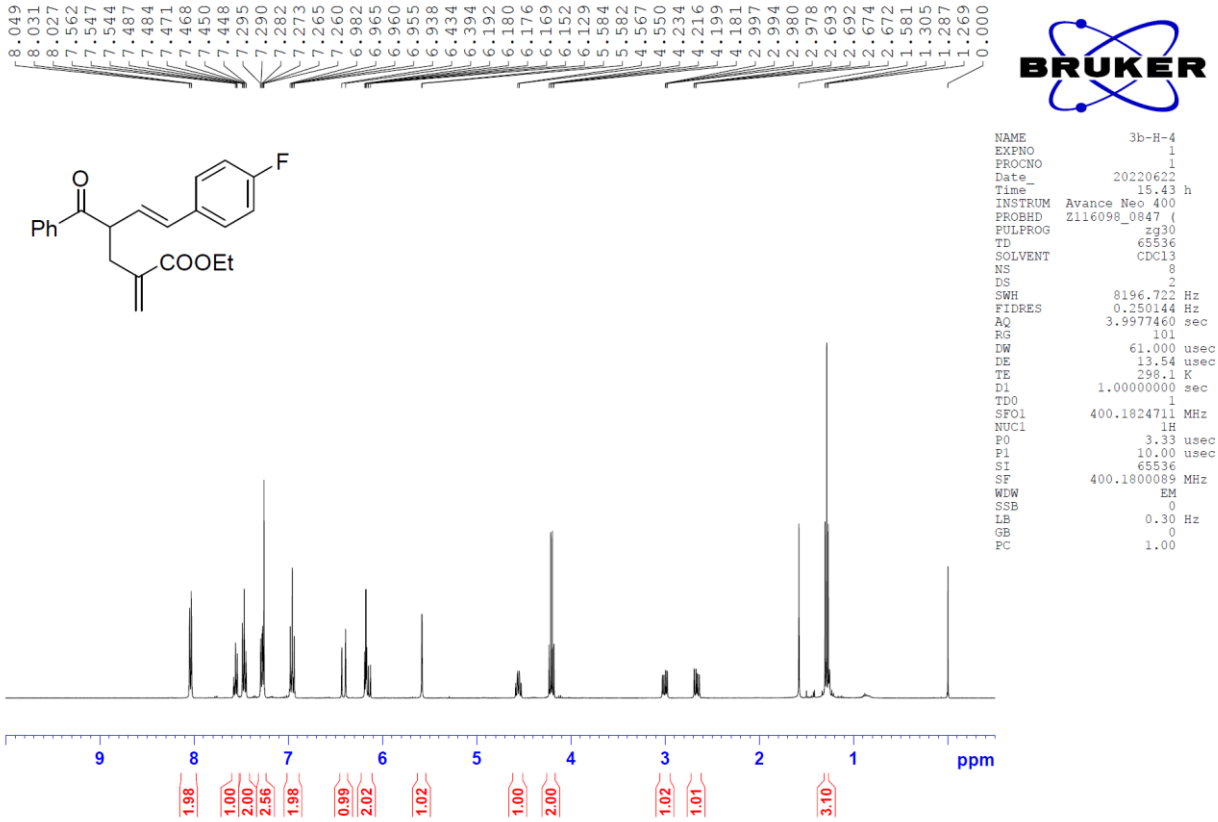



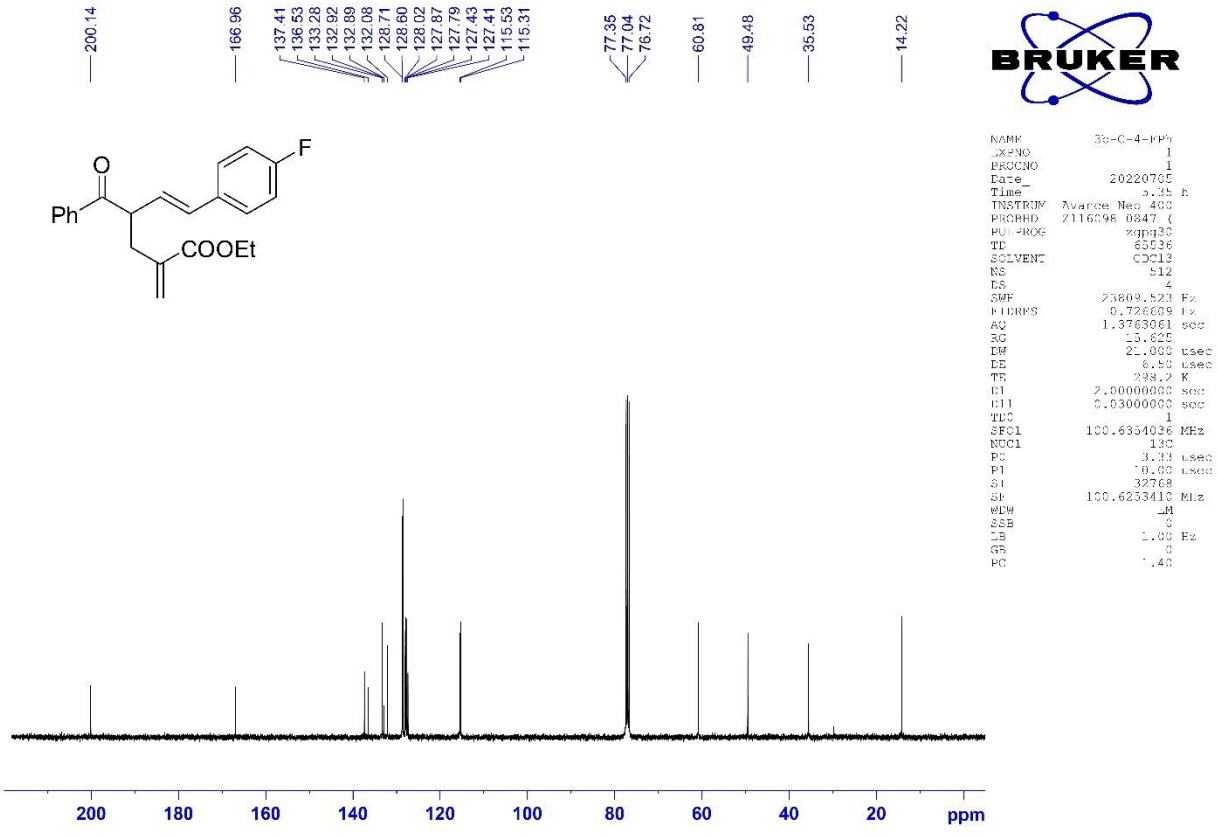


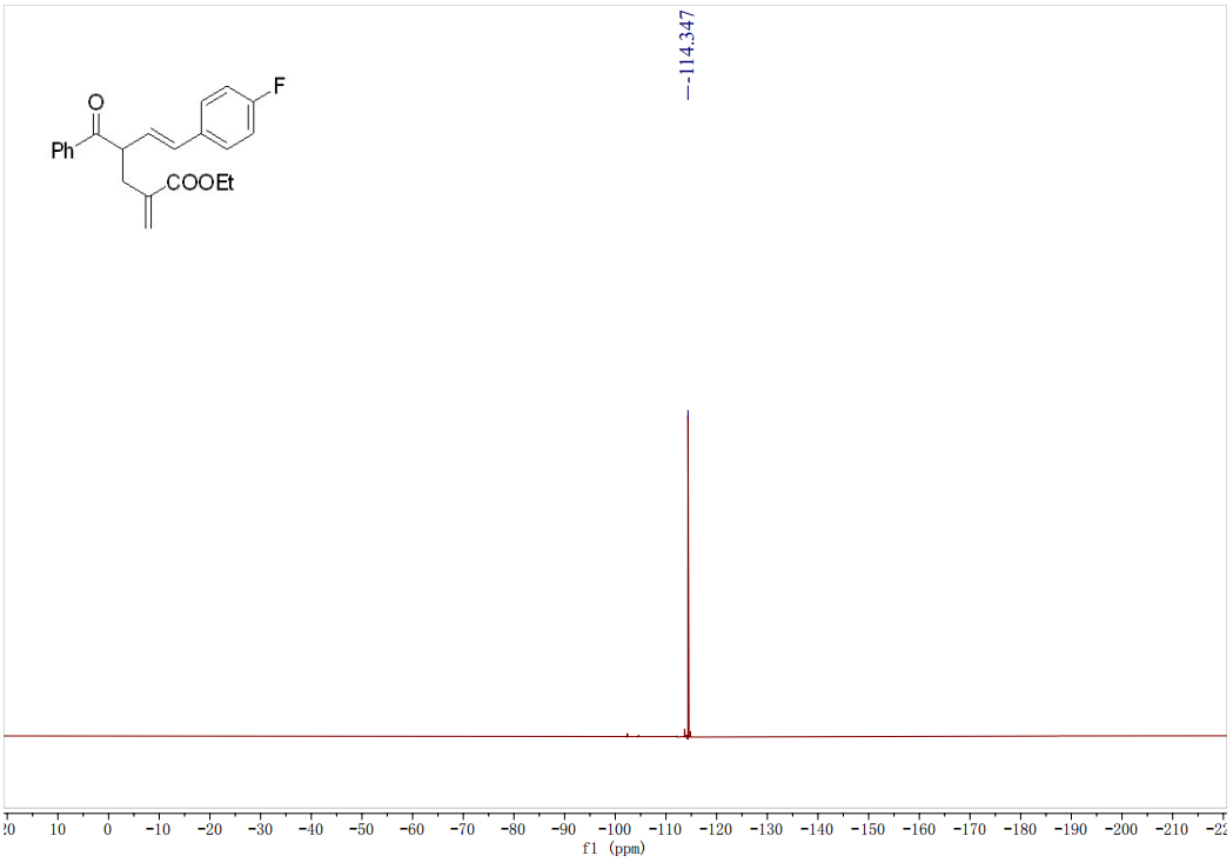

$^{1}$H NMR Spectrum for Compound **3g** (20% DABCO/DCM)



$^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra for Compound **3h**

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Ph
F
COOEt
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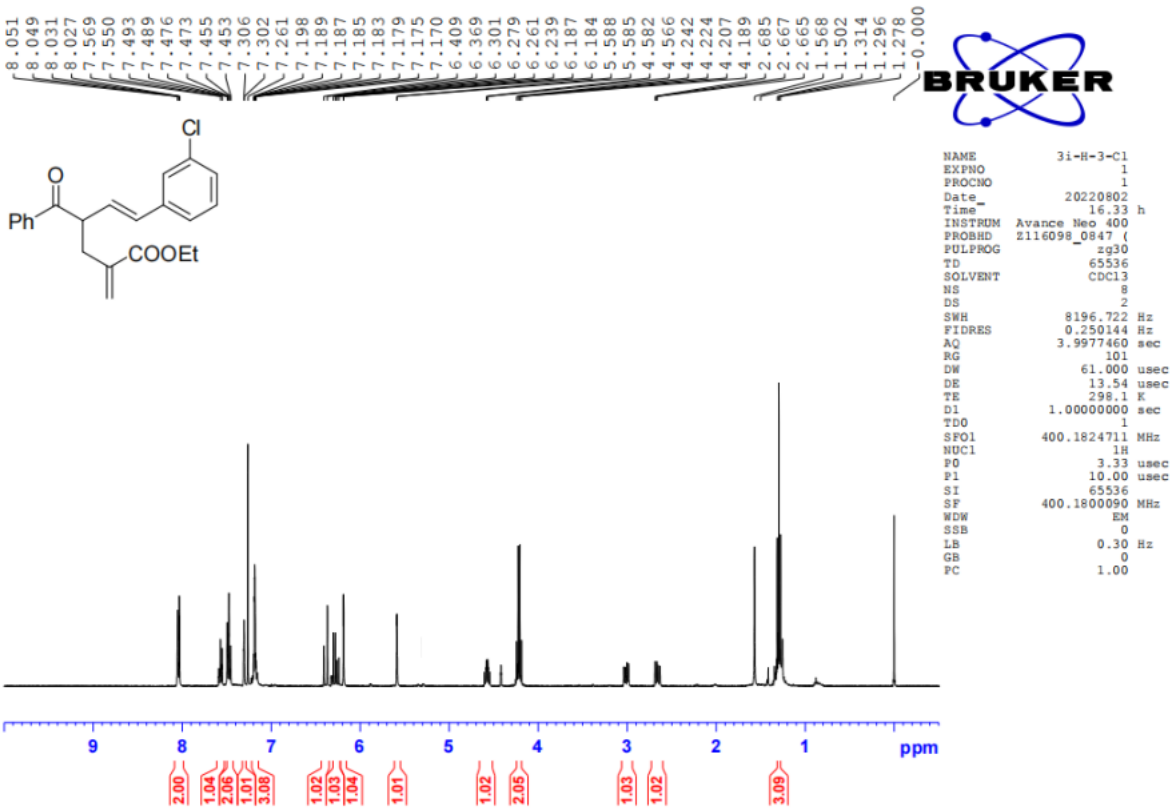
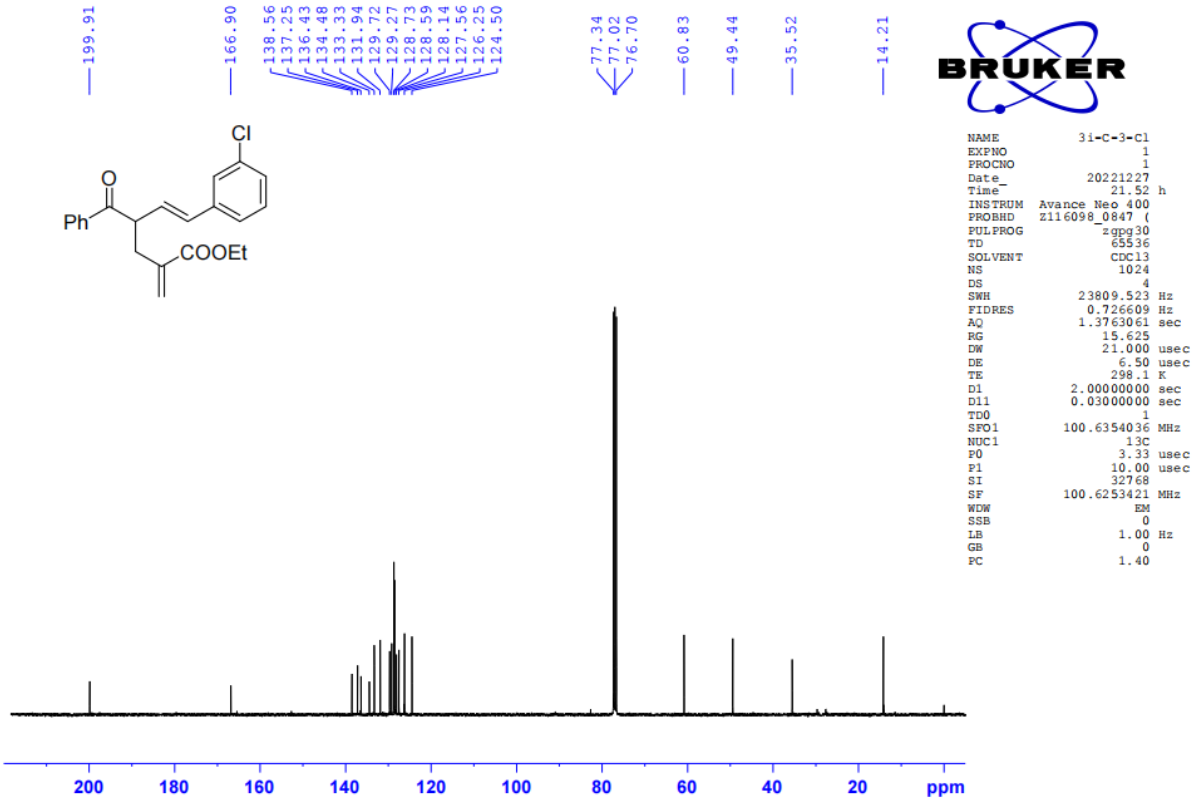
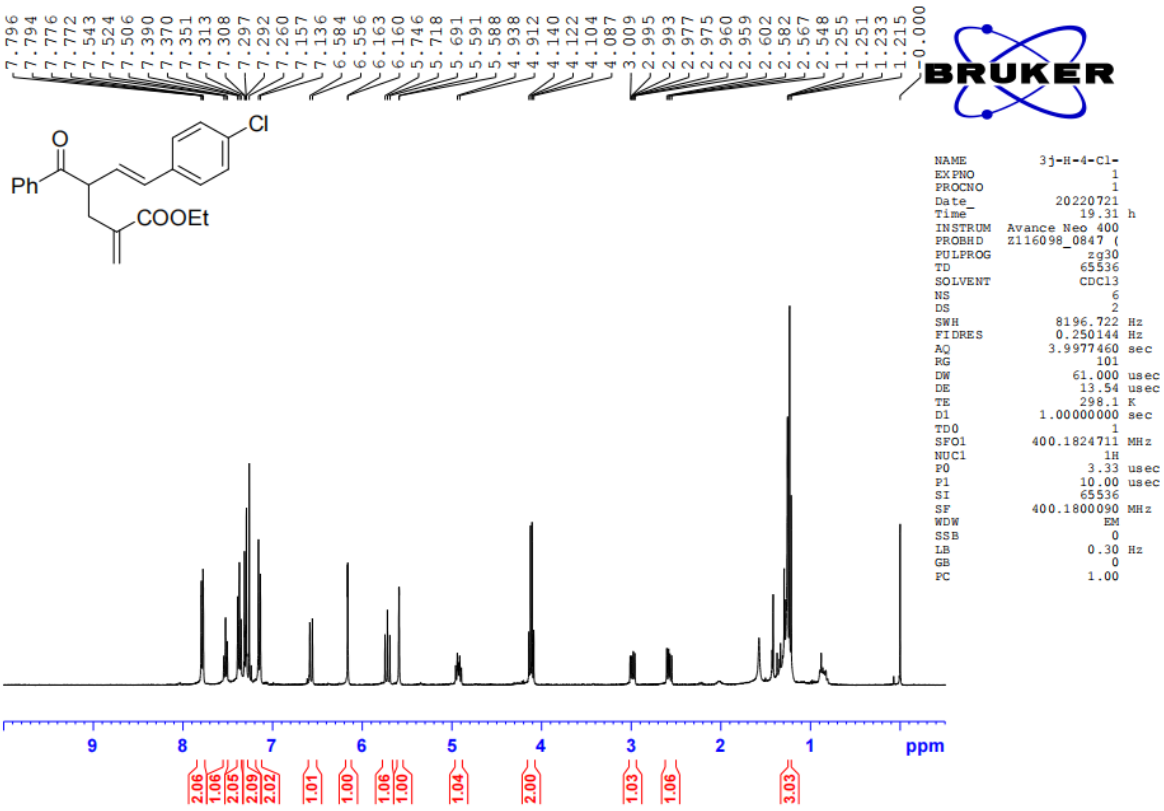
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

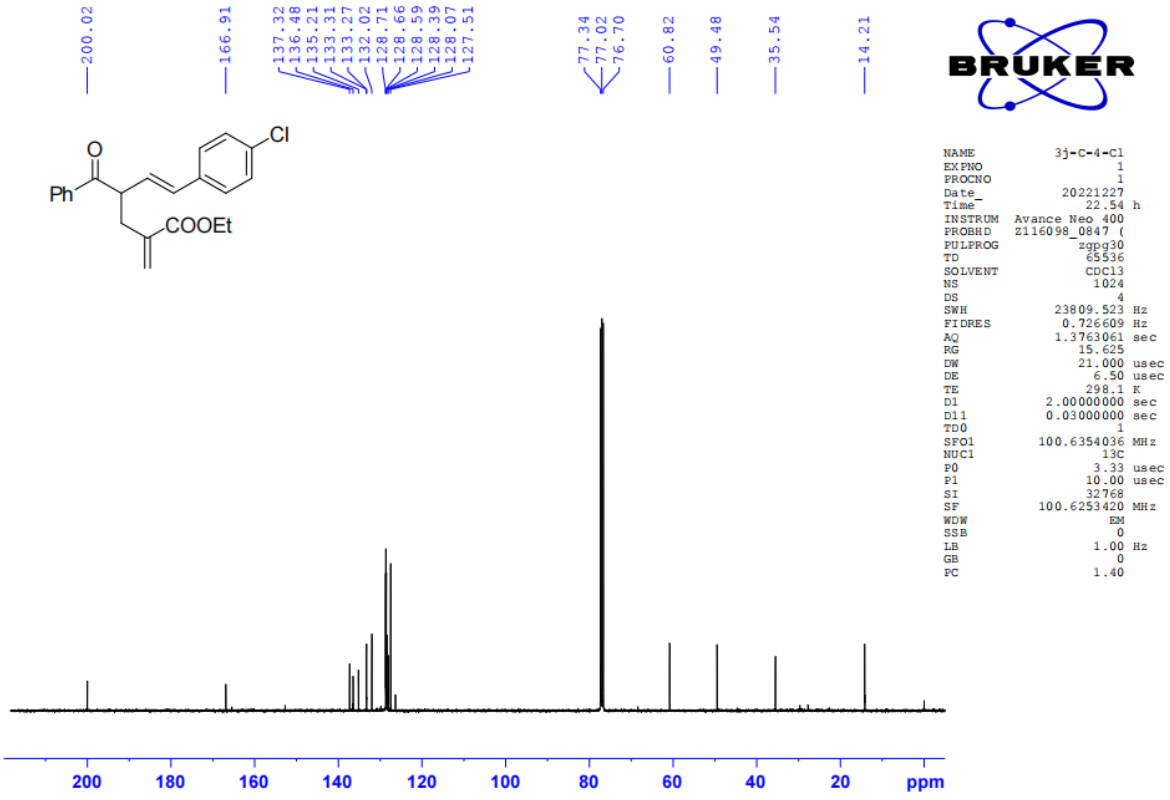
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3i**



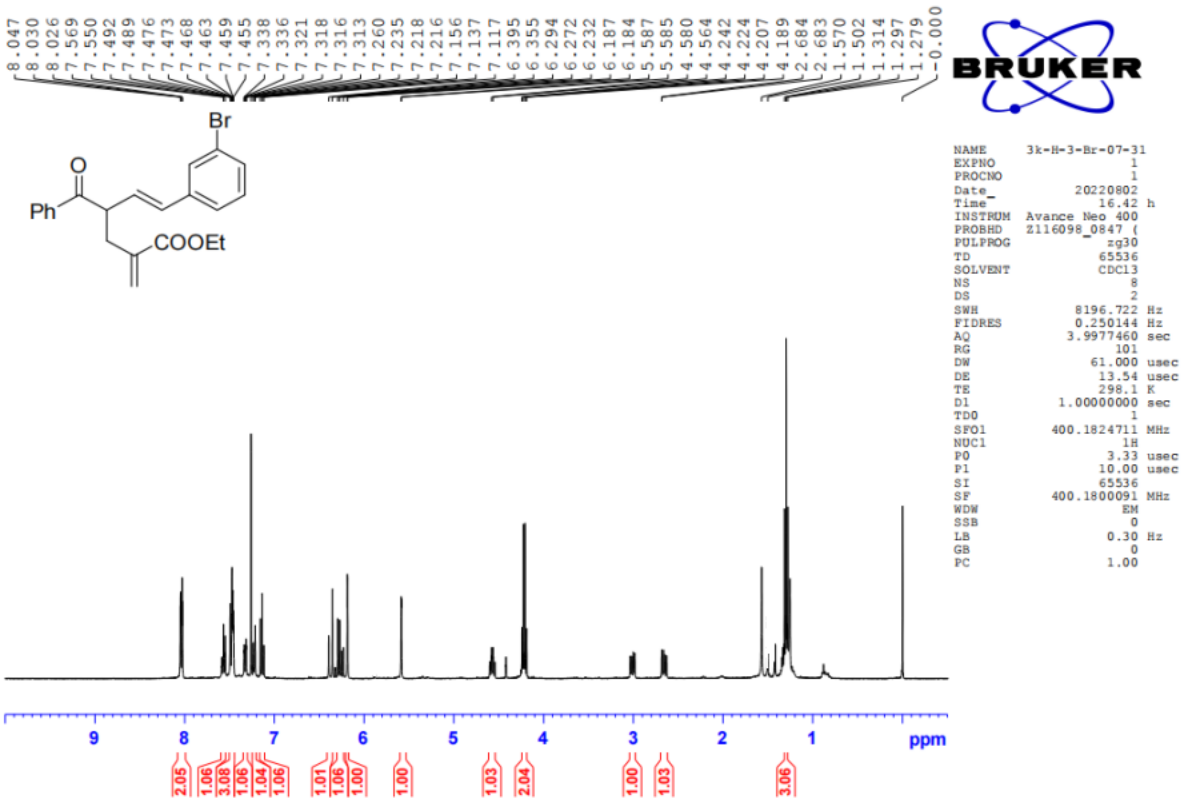



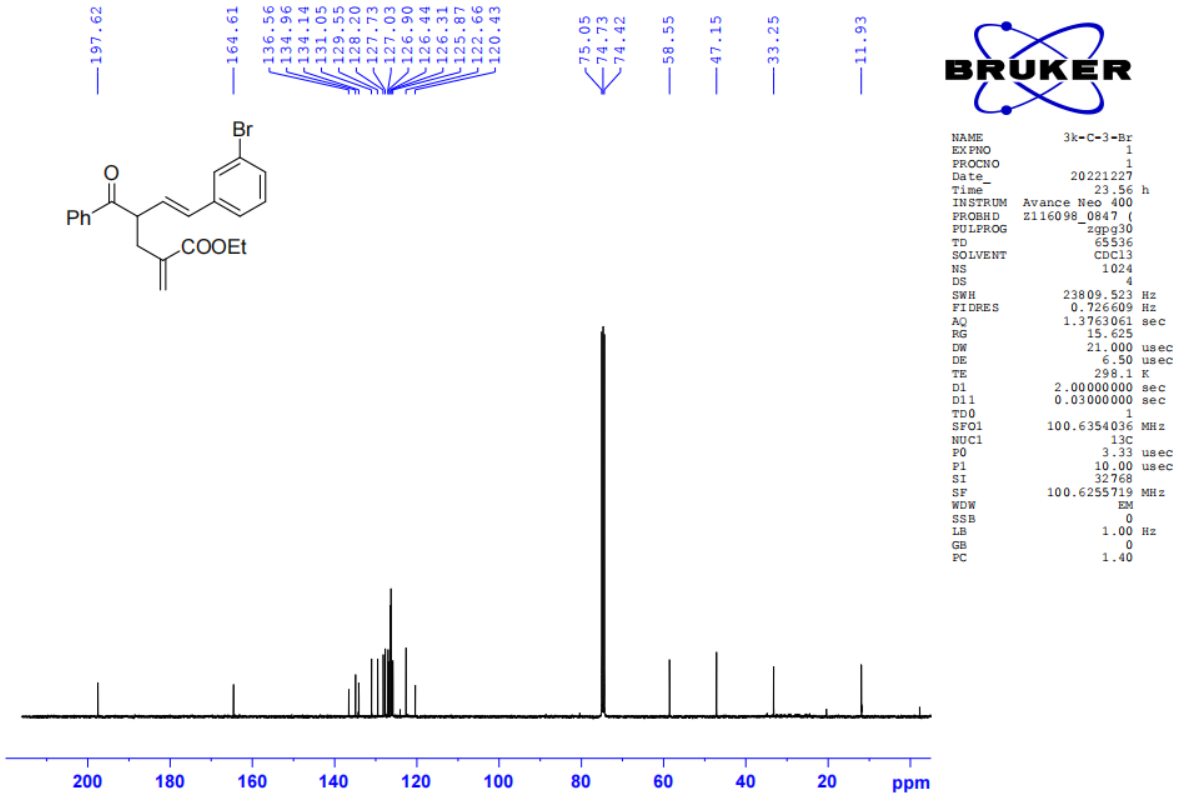
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3j**



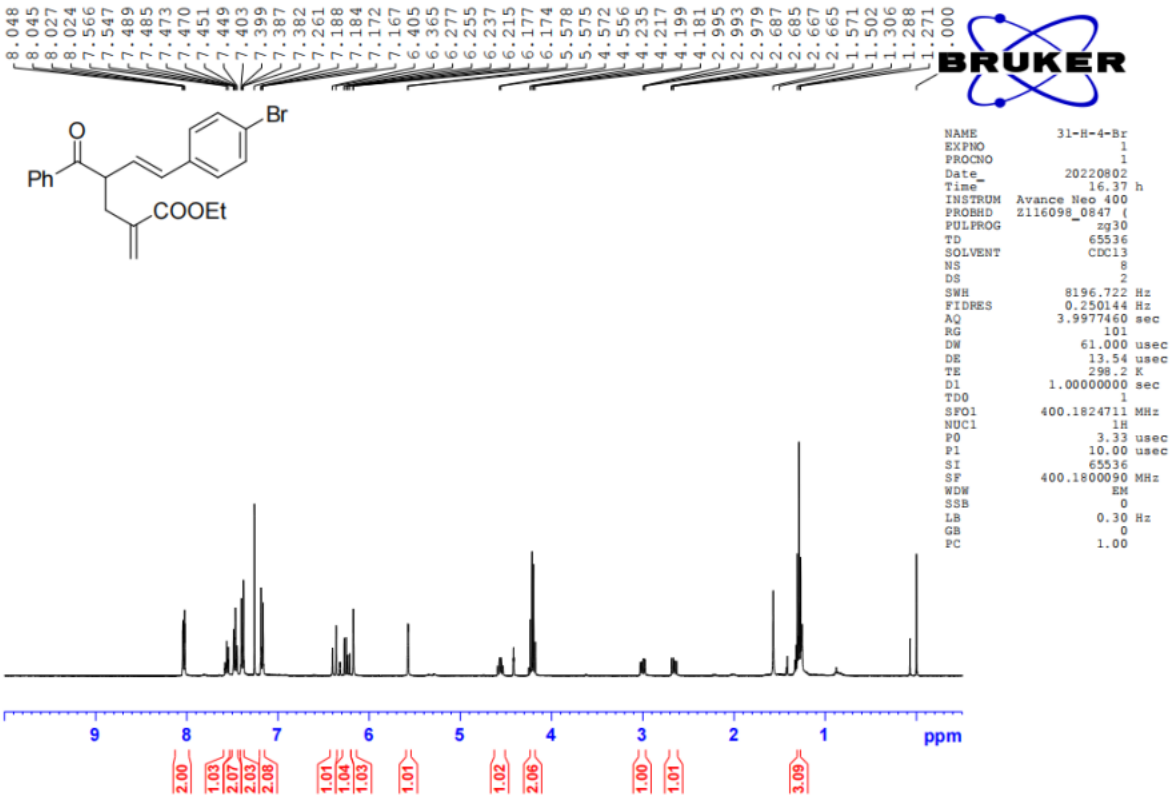



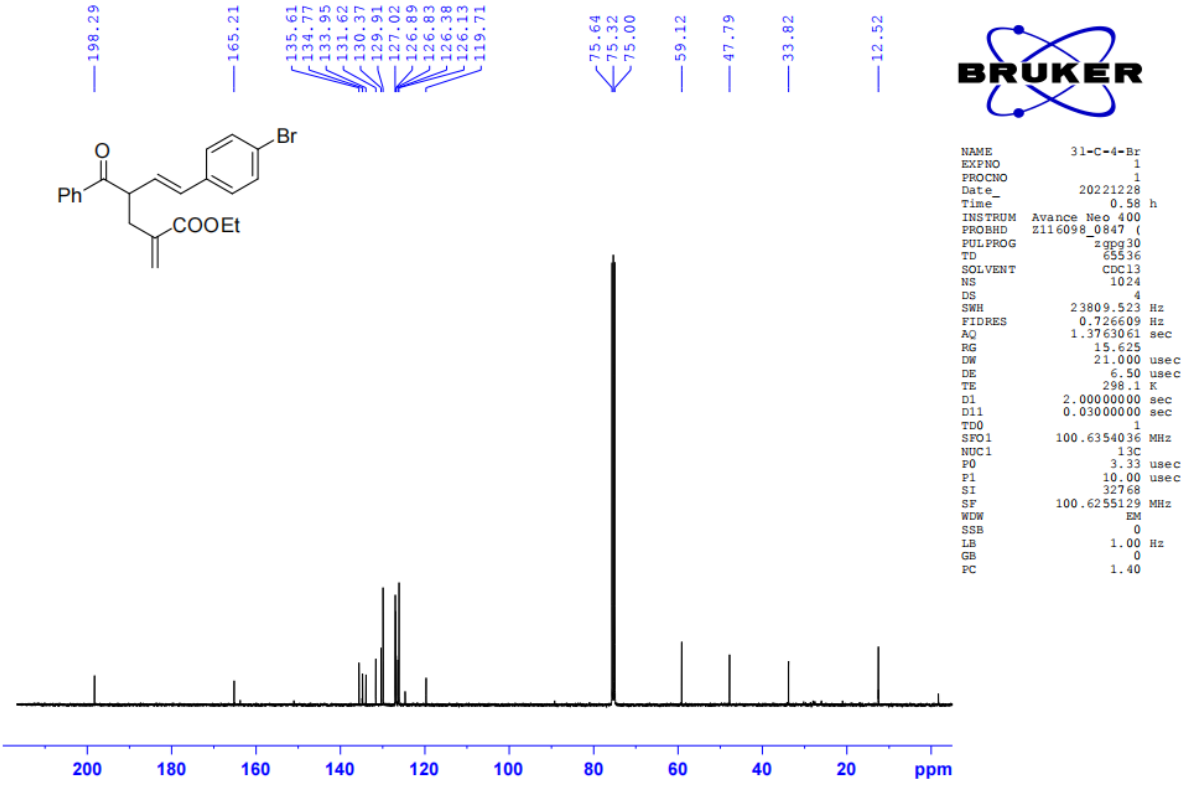
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3k**



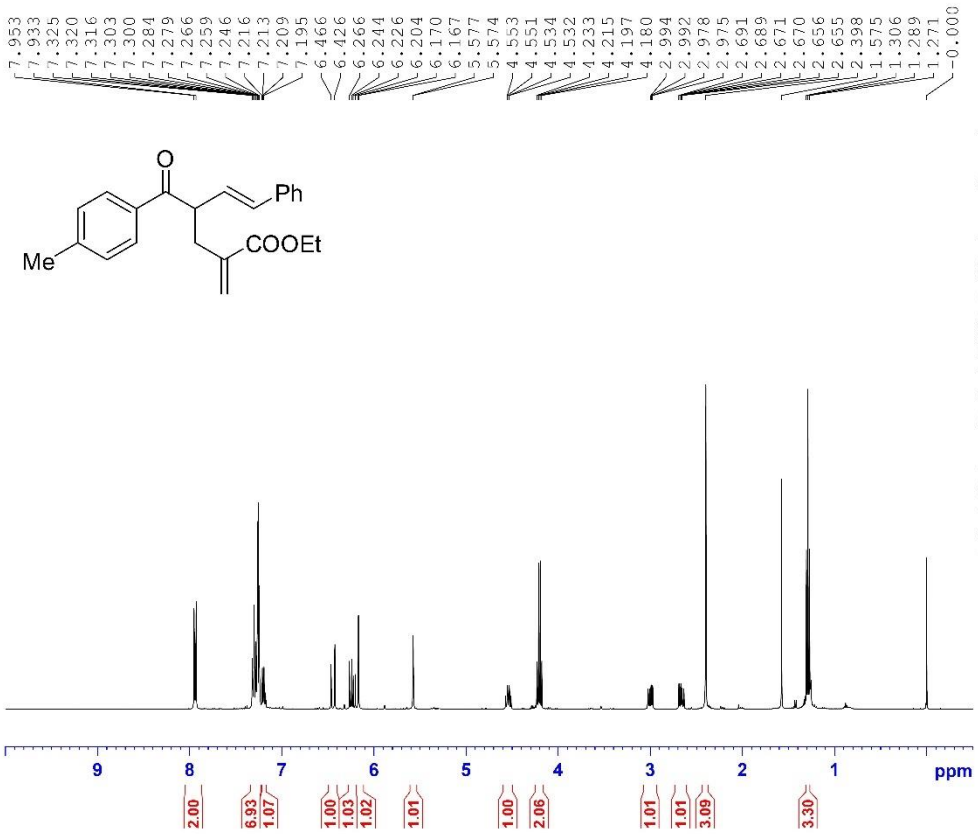



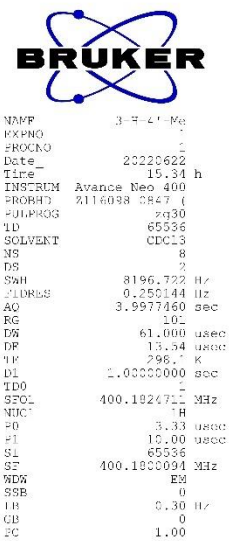
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3l**

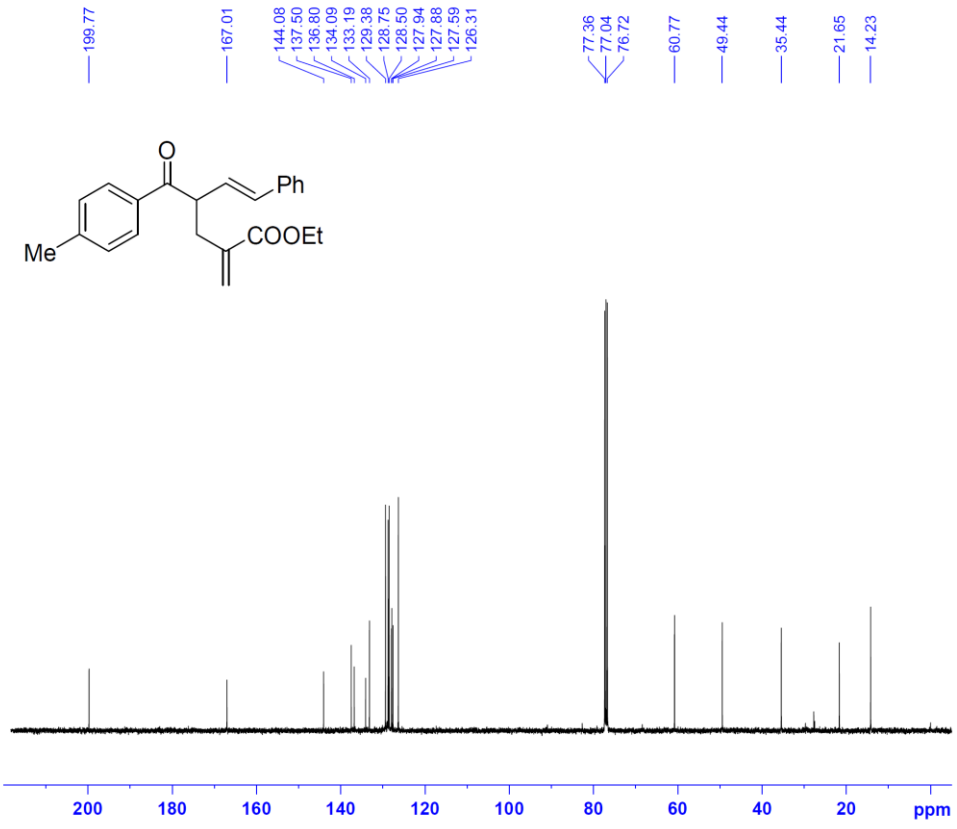


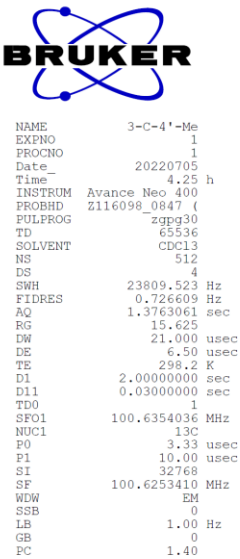



$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3m**

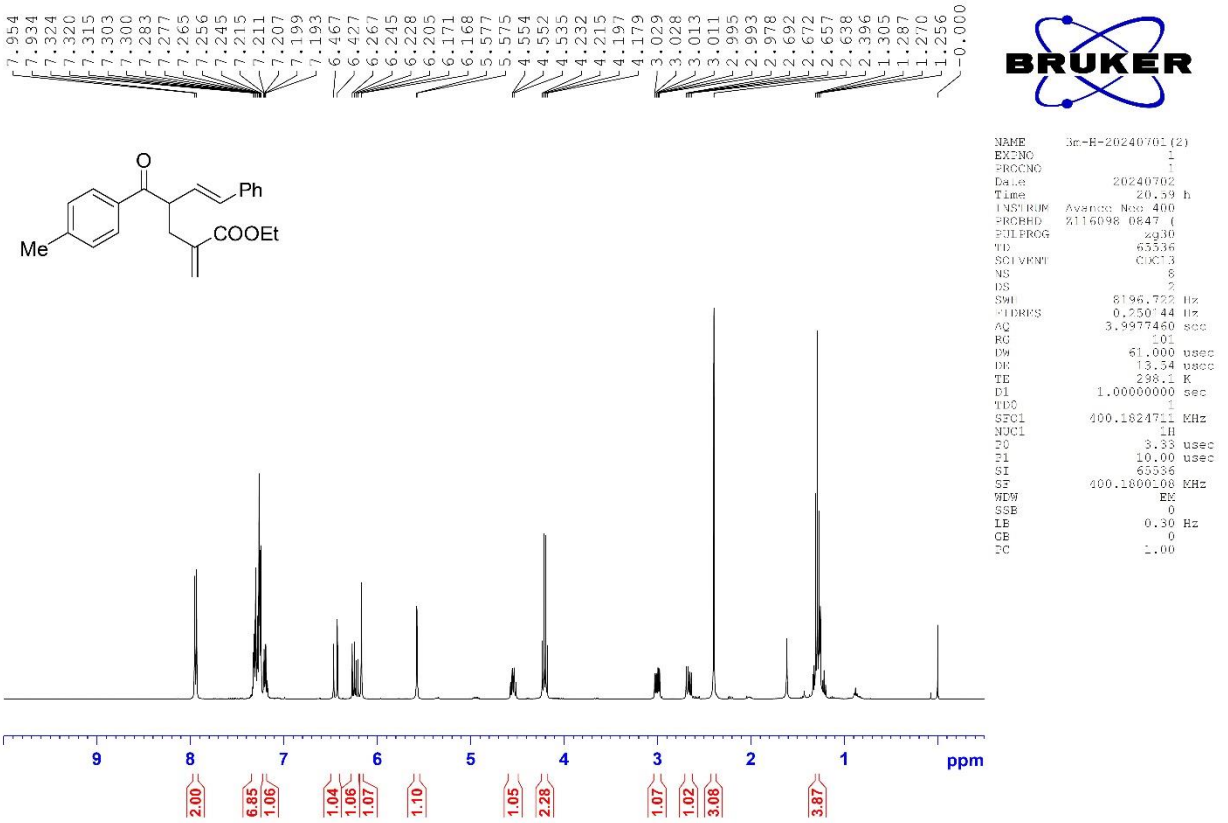


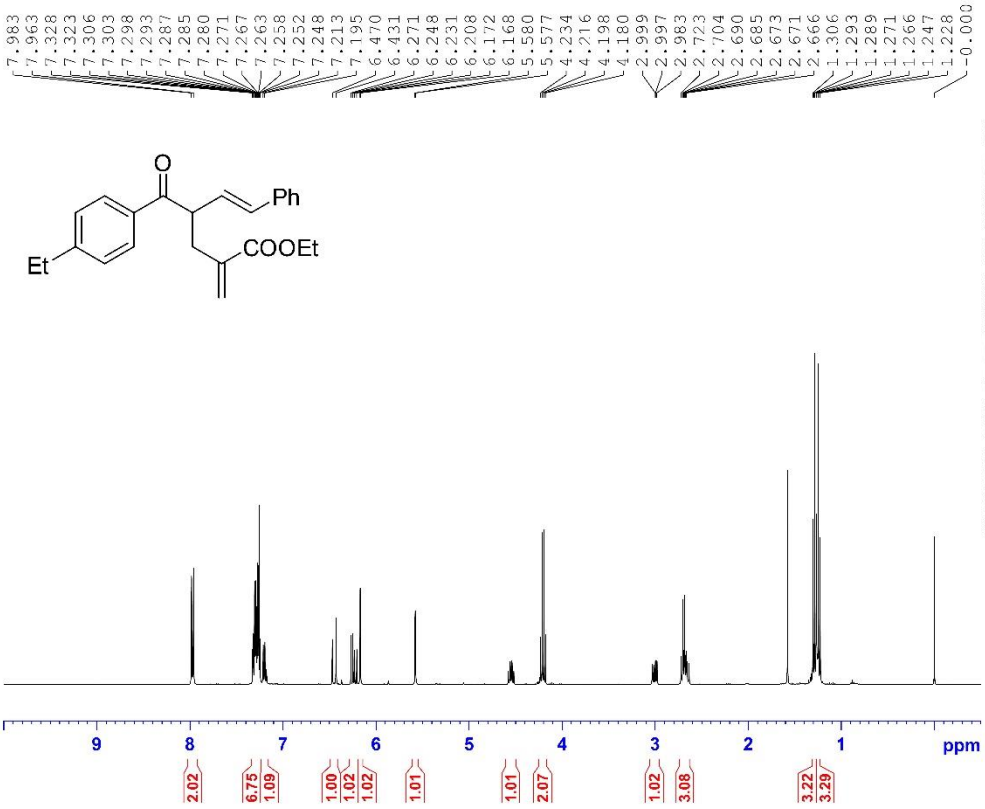



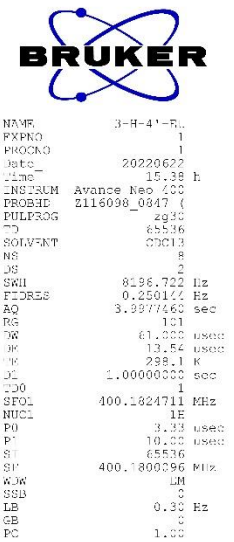



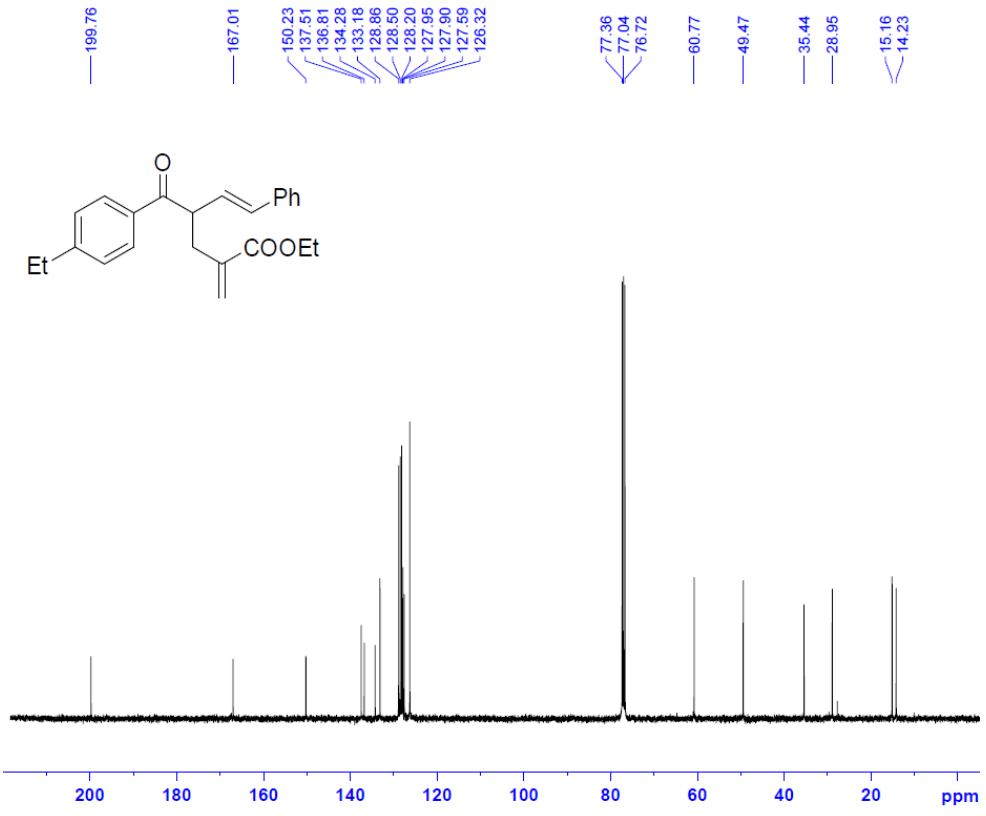
$^{1}$H NMR Spectrum for Compound **3m** (20% DABCO/DCM)

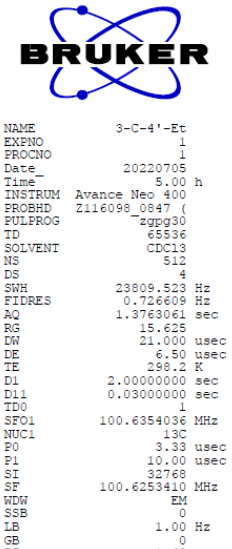


$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3n**

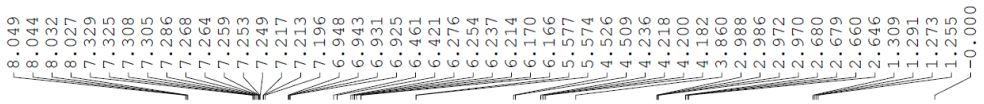


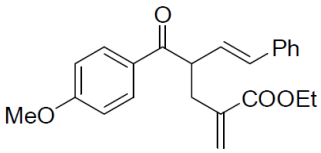



$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3o**

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PROCNO                 1
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DS                    2
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FIDRES        0.250144 Hz
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RG                  101
DW               61.000 usec
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TE               298.1 K
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TD0                   1
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NUC1                 1H
P0                 3.33 usec
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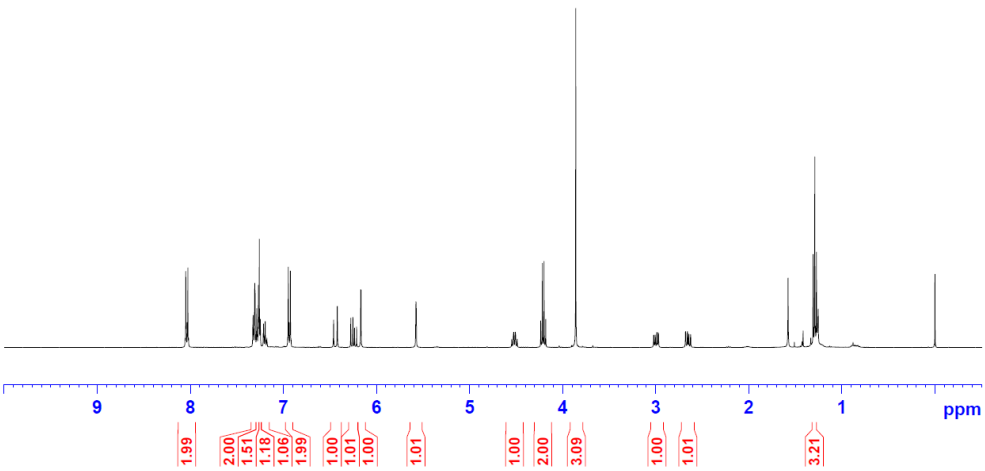



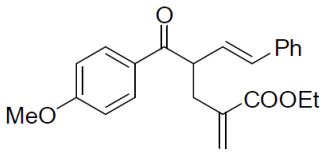


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PROCNO                 1
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TD                65536
SOLVENT           CDCl3
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DS                    4
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FIDRES        0.726609 Hz
AQ            1.3763061 sec
RG                 15.625
DW               21.000 usec
DE                6.50 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         100.6354036 MHz
NUC1                 13C
P0                 3.33 usec
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WDW                  EM
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LB                 1.00 Hz
GB                    0
PC                 1.40
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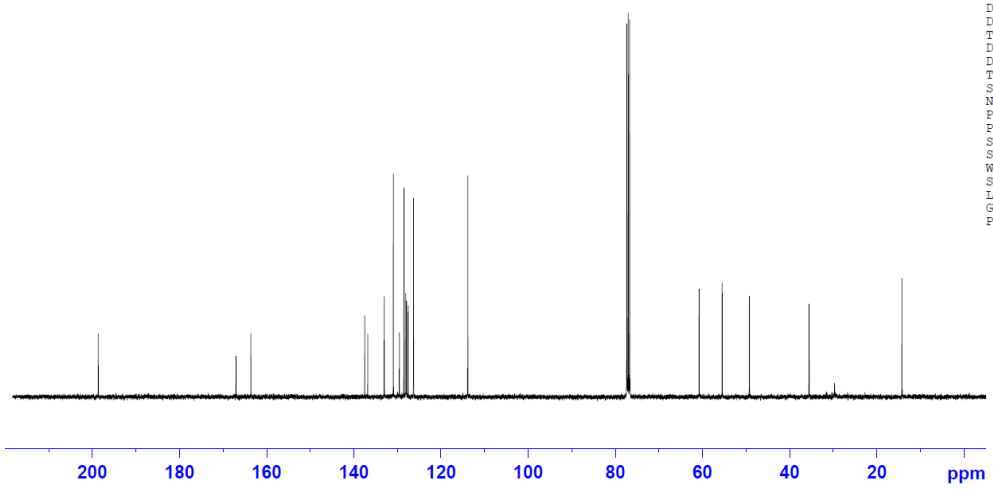
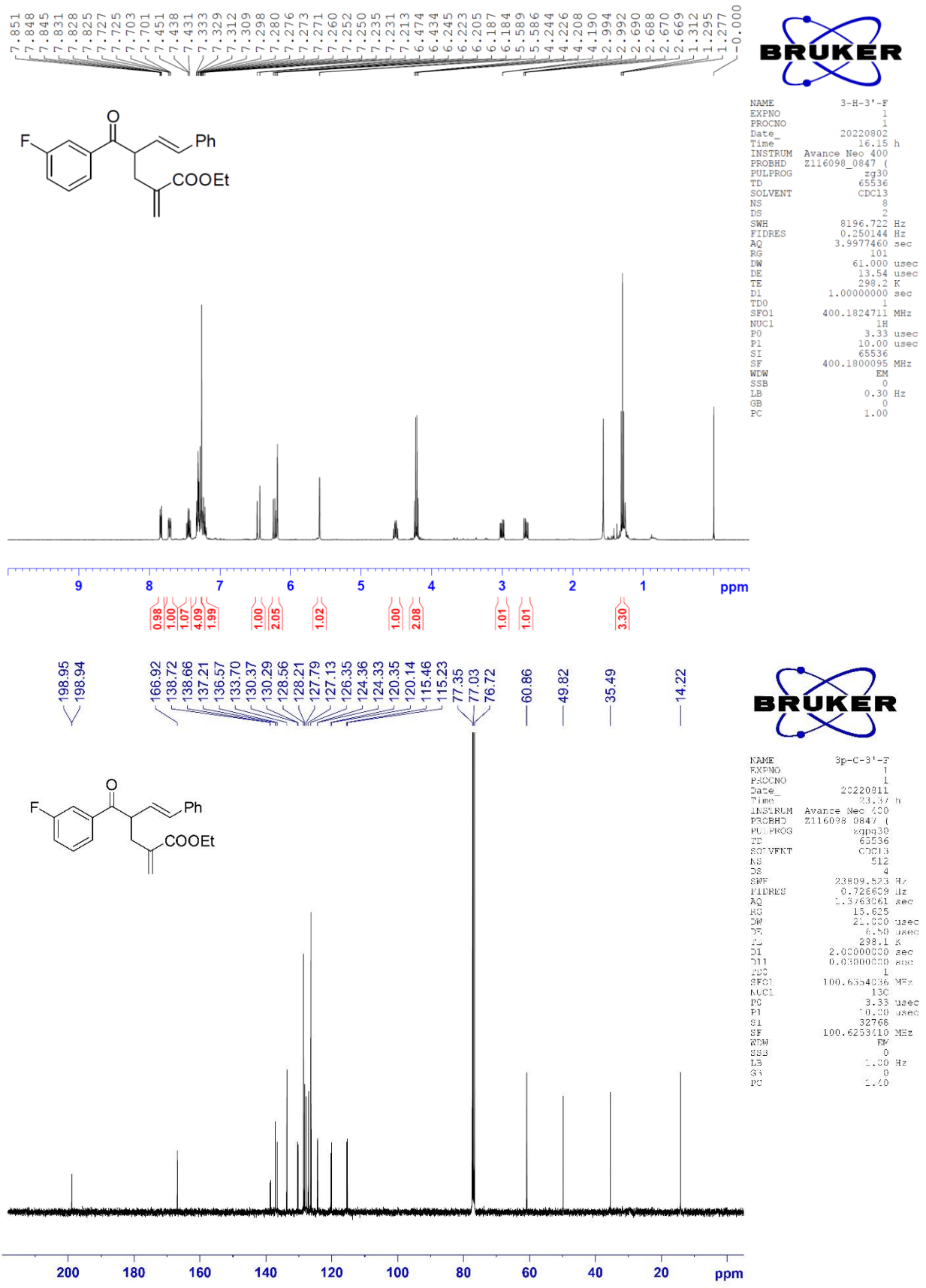
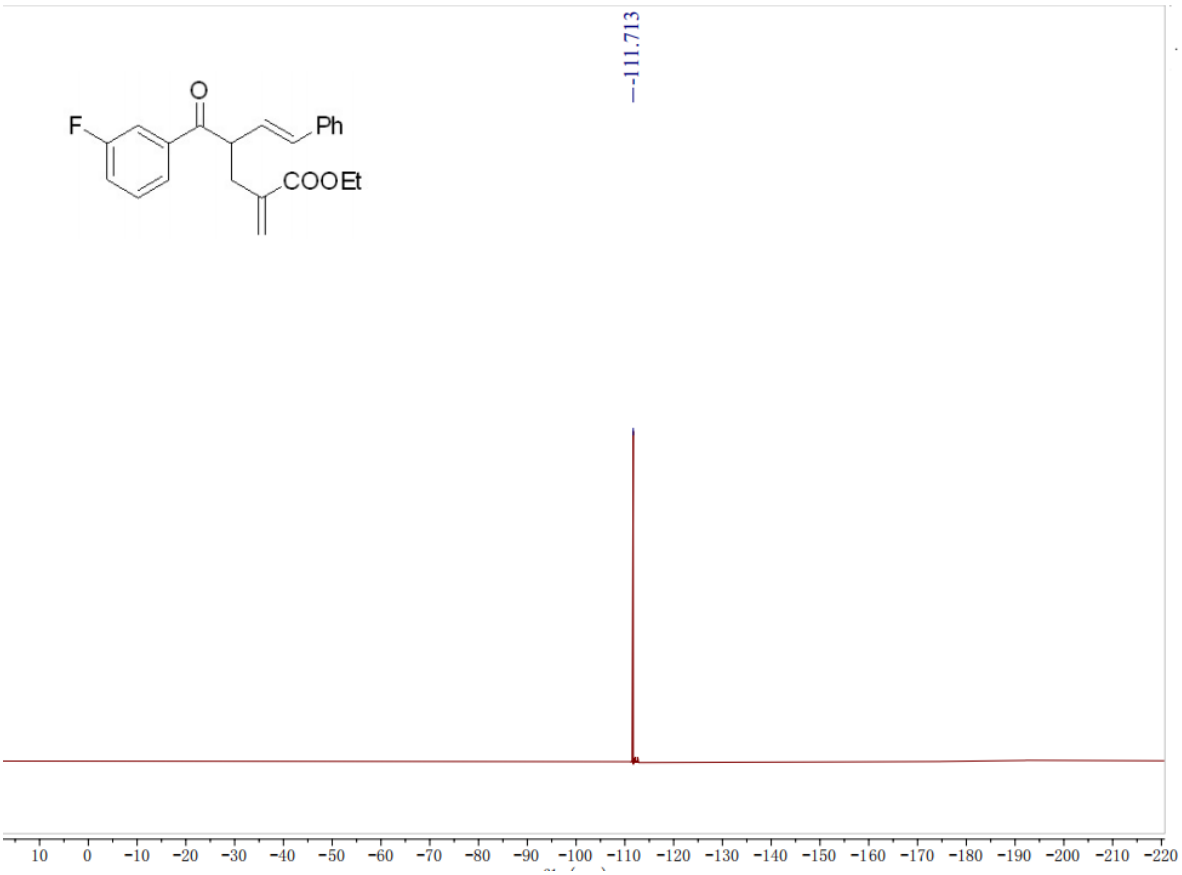
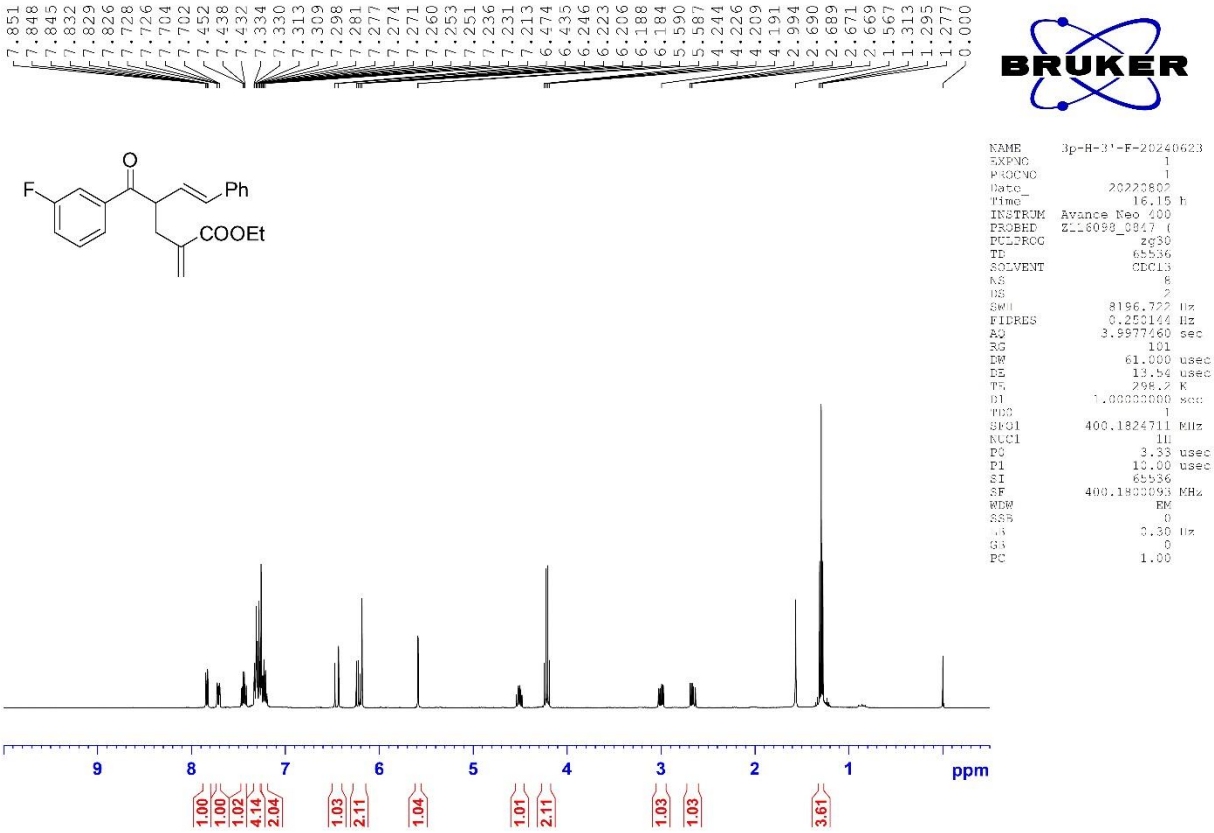


$^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra for Compound **3p**

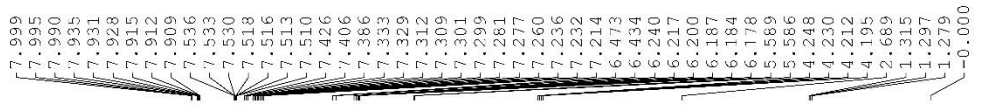


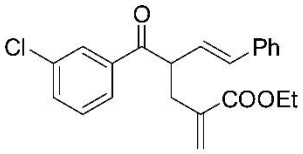


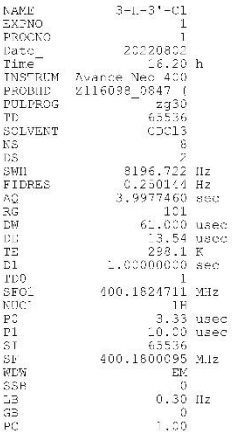

$^{1}$H NMR Spectrum for Compound **3p** (20% DABCO/DCM)

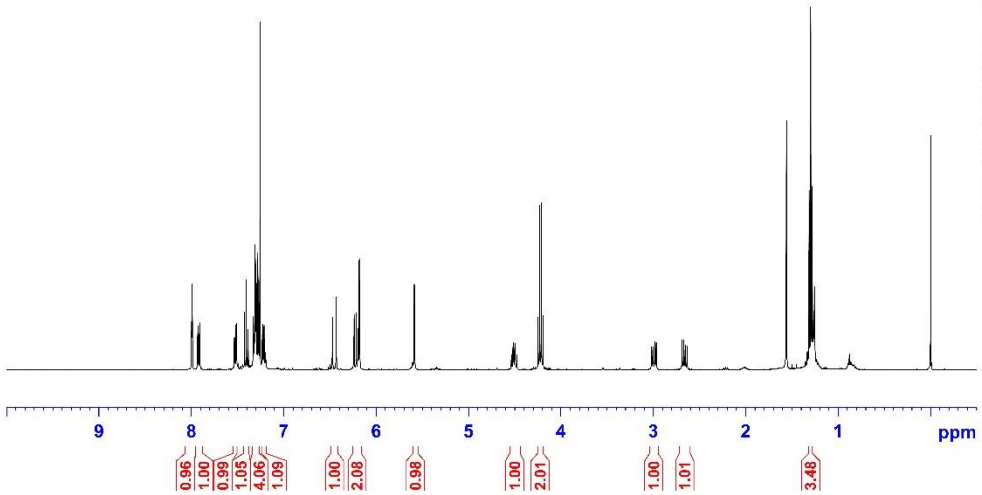


$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3q**

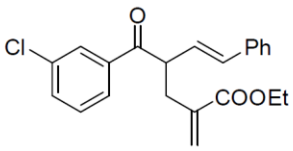


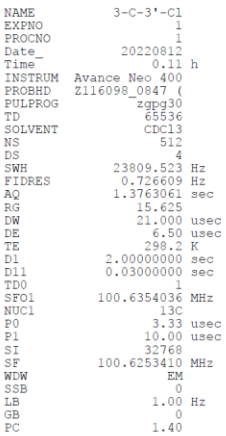



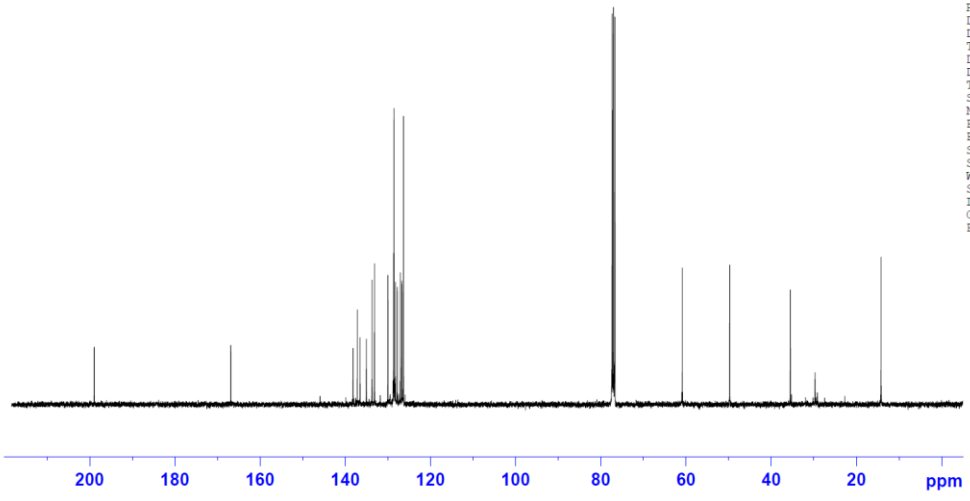



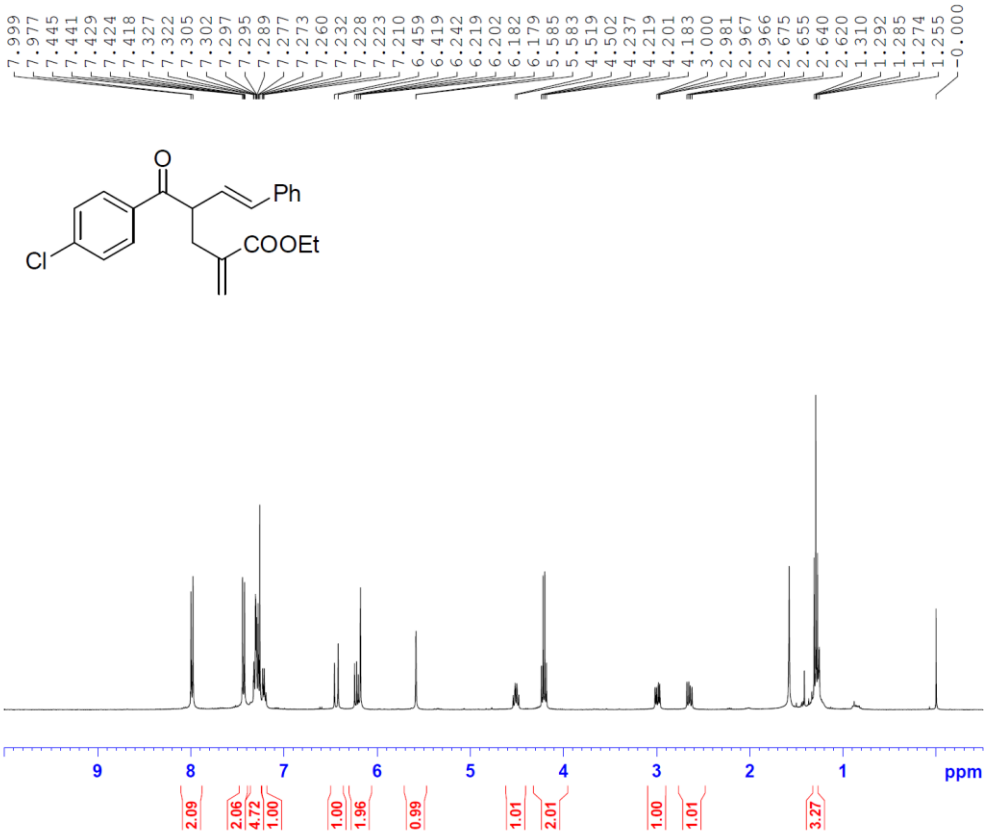




$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3r**

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DS                      2
SWH              8196.722 Hz
FIDRES           0.250144 Hz
AQ               3.9977460 sec
RG                    101
DW                 61.000 usec
DE                 13.54 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                     1
SFO1          400.1824711 MHz
NUC1                   1H
P0                  3.33 usec
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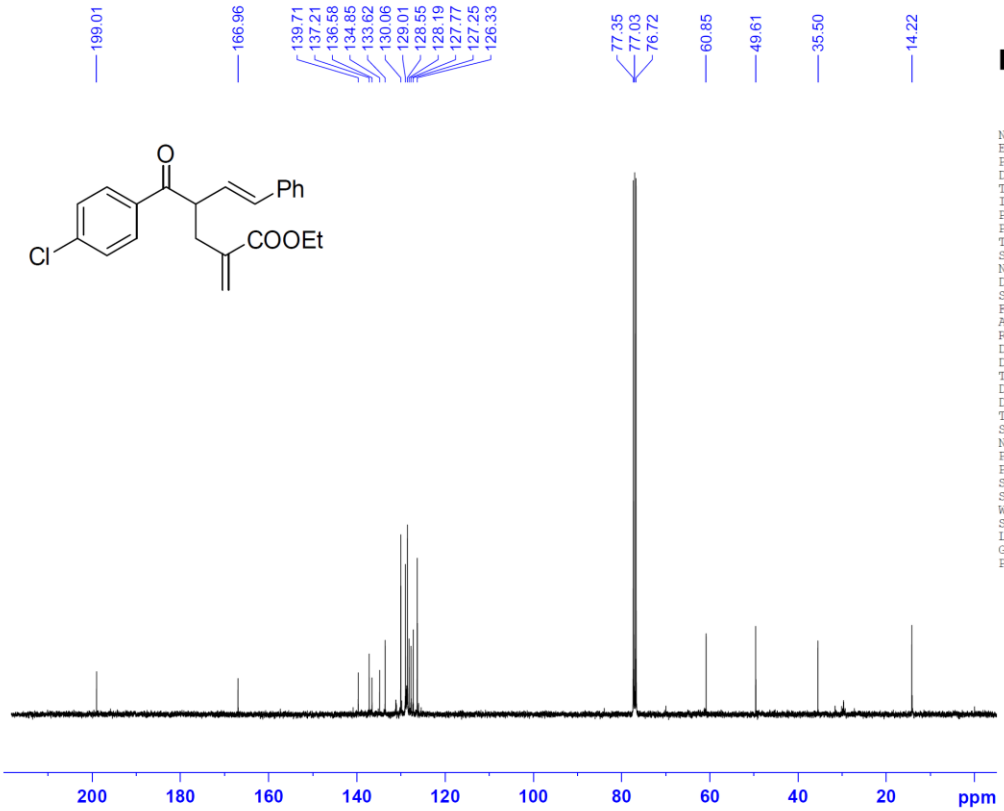


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FIDRES           0.726609 Hz
AQ               1.3763061 sec
RG                 15.625
DW                 21.000 usec
DE                  6.50 usec
TE                 298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1
SFO1          100.6354036 MHz
NUC1                   13C
P0                  3.33 usec
P1                 10.00 usec
SI                  32768
SF            100.6253410 MHz
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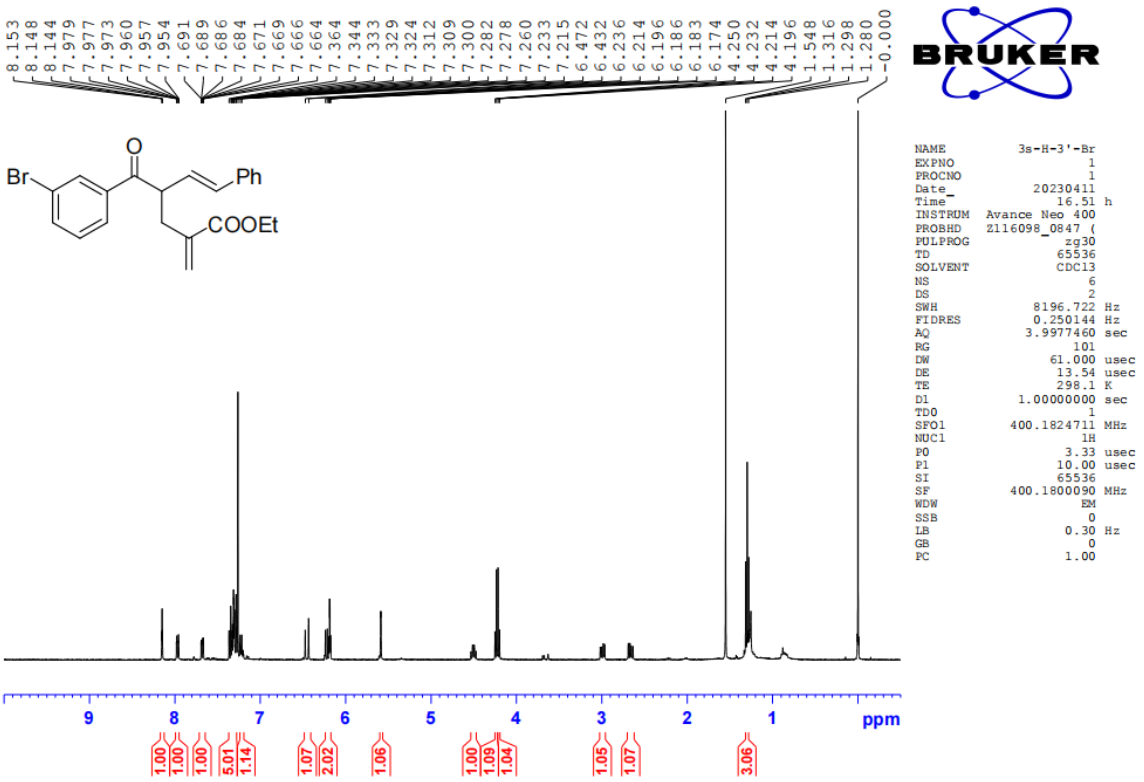
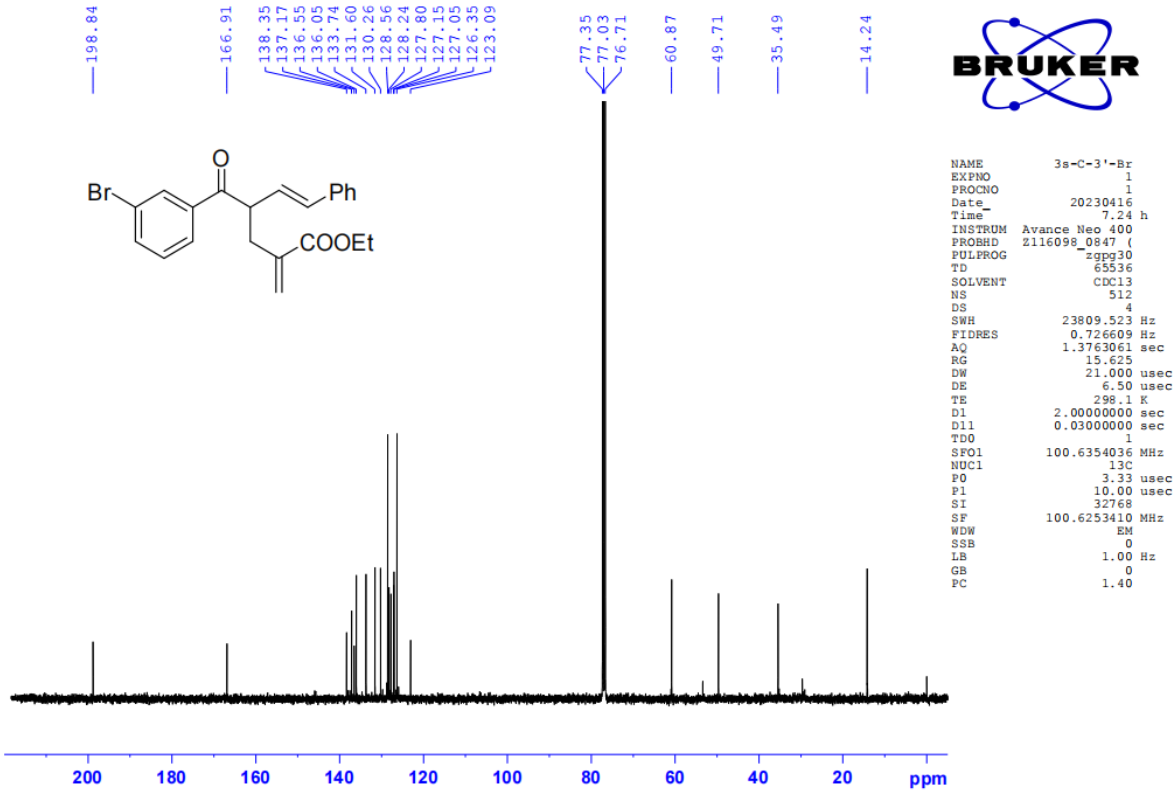
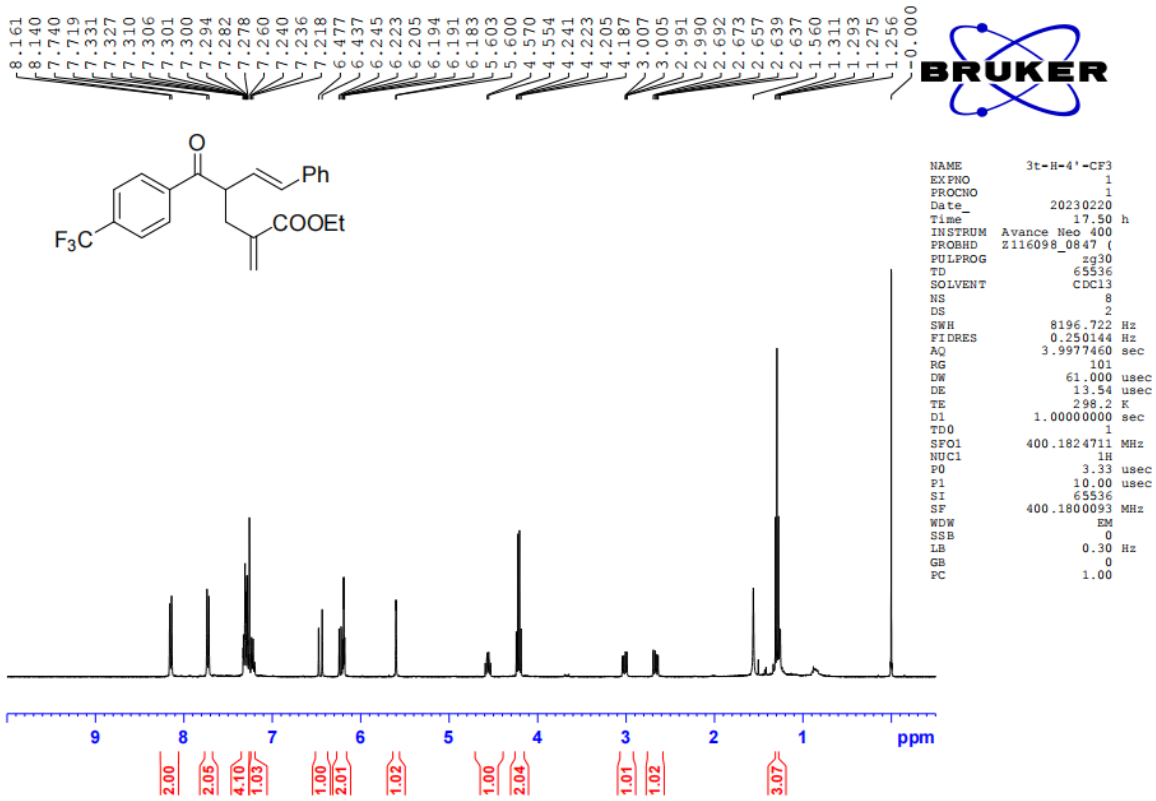
```

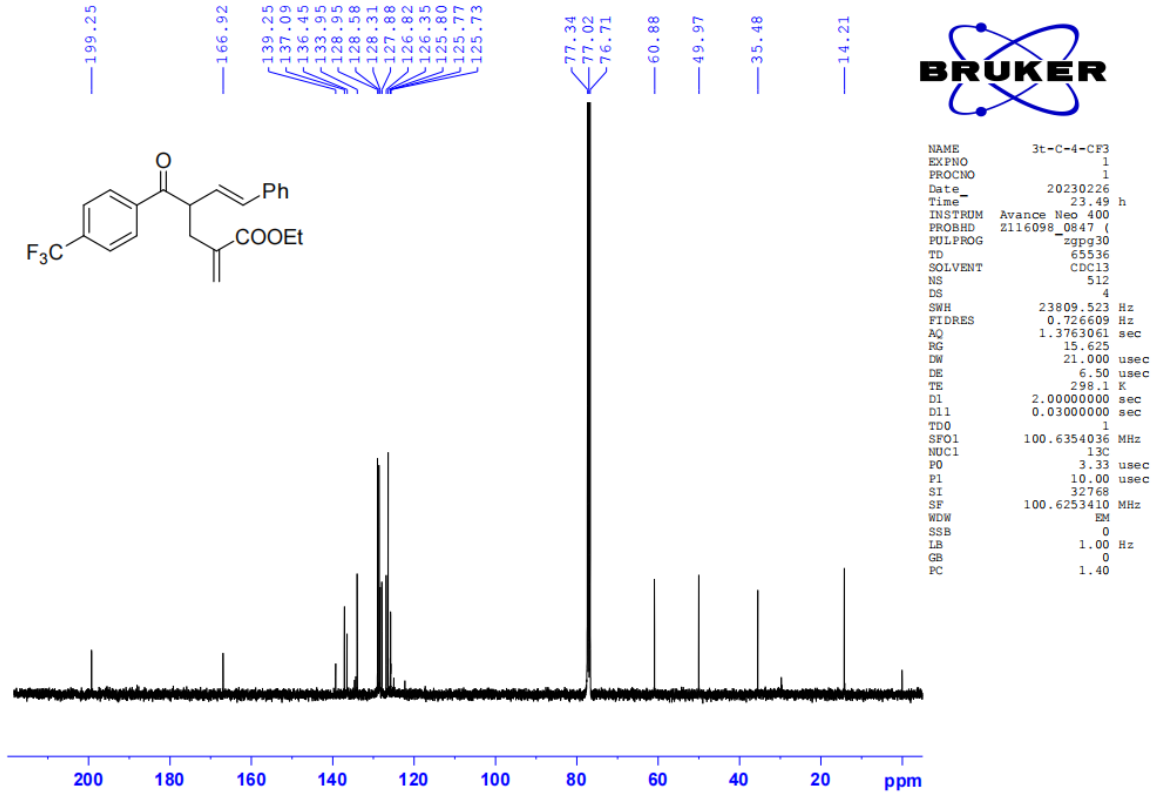
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **3s**

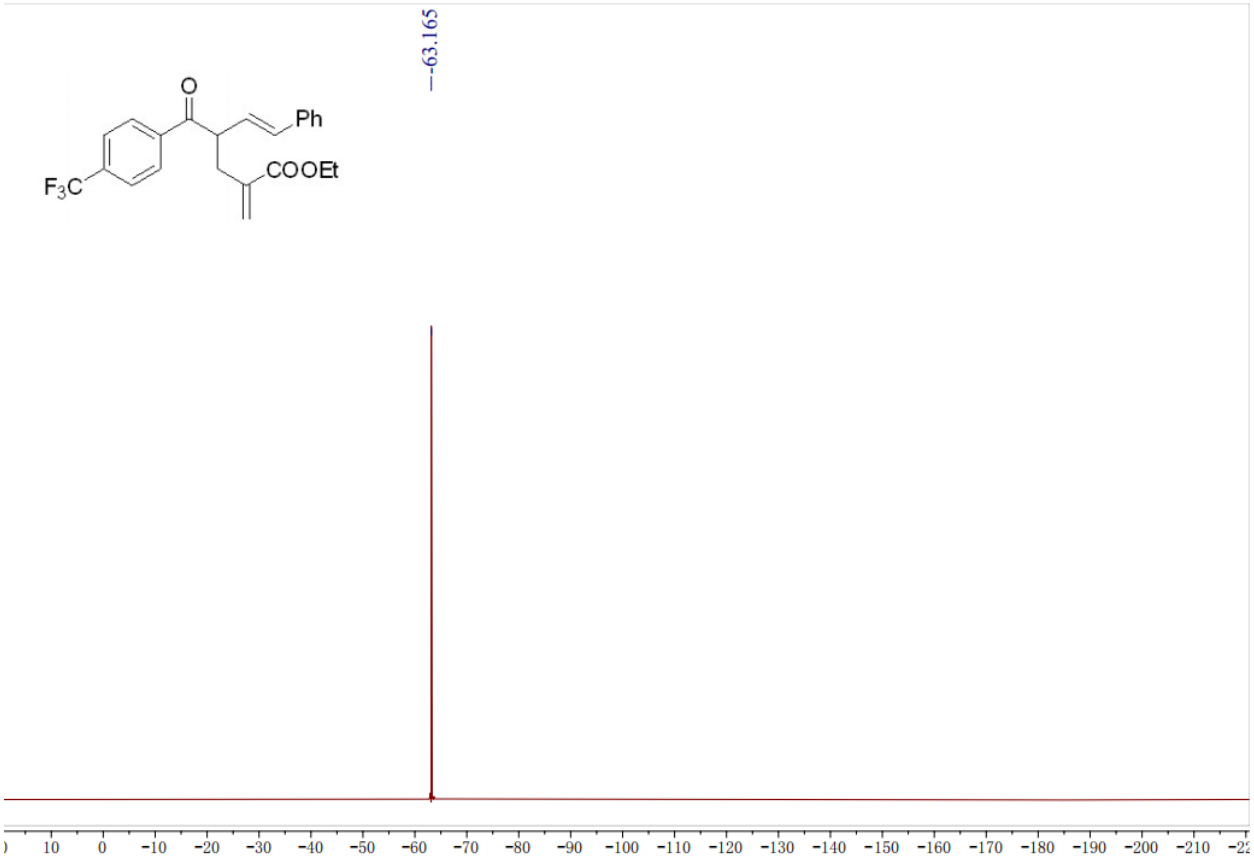


$^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra for Compound **3t**

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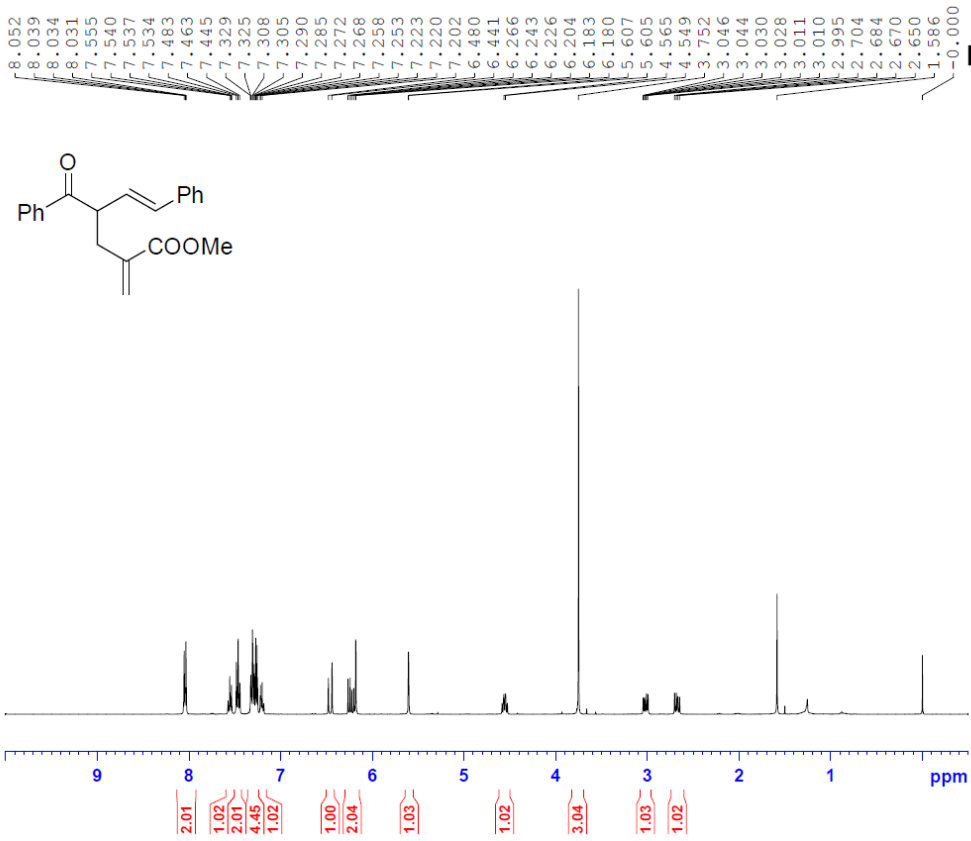
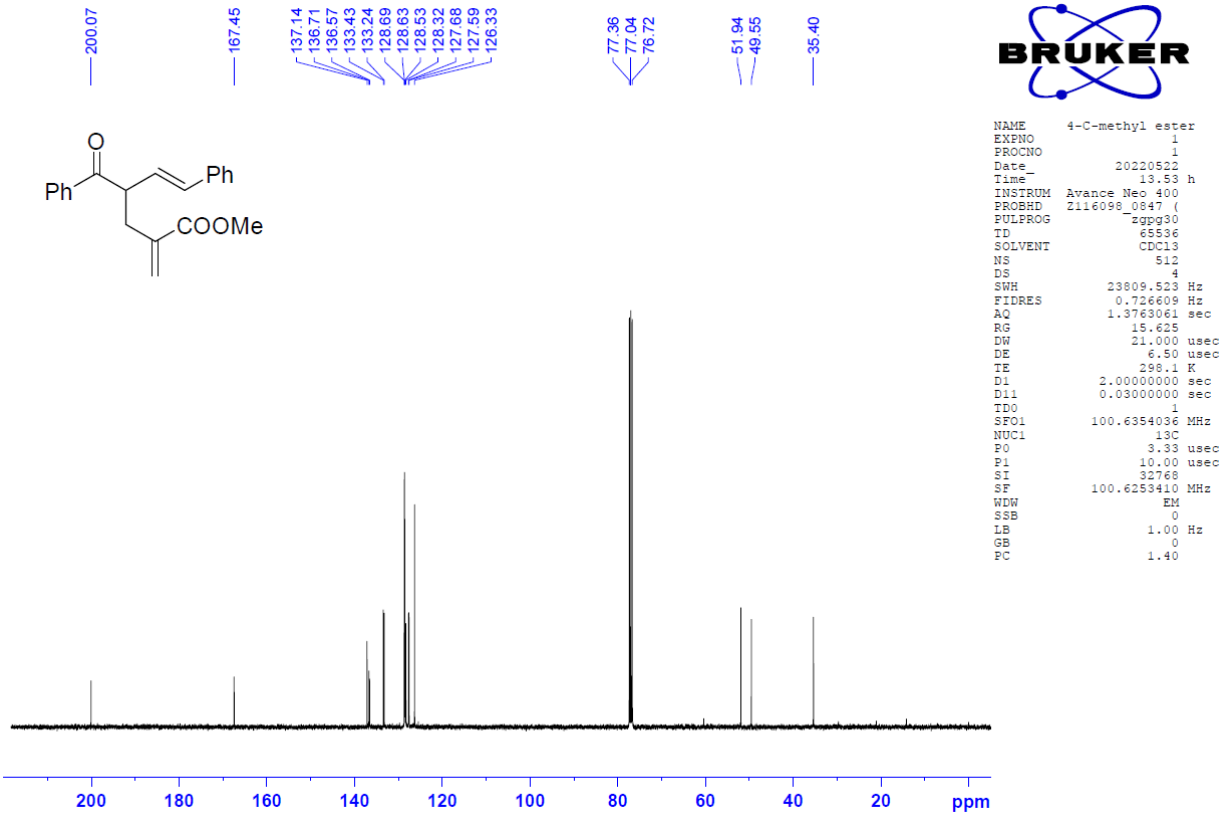
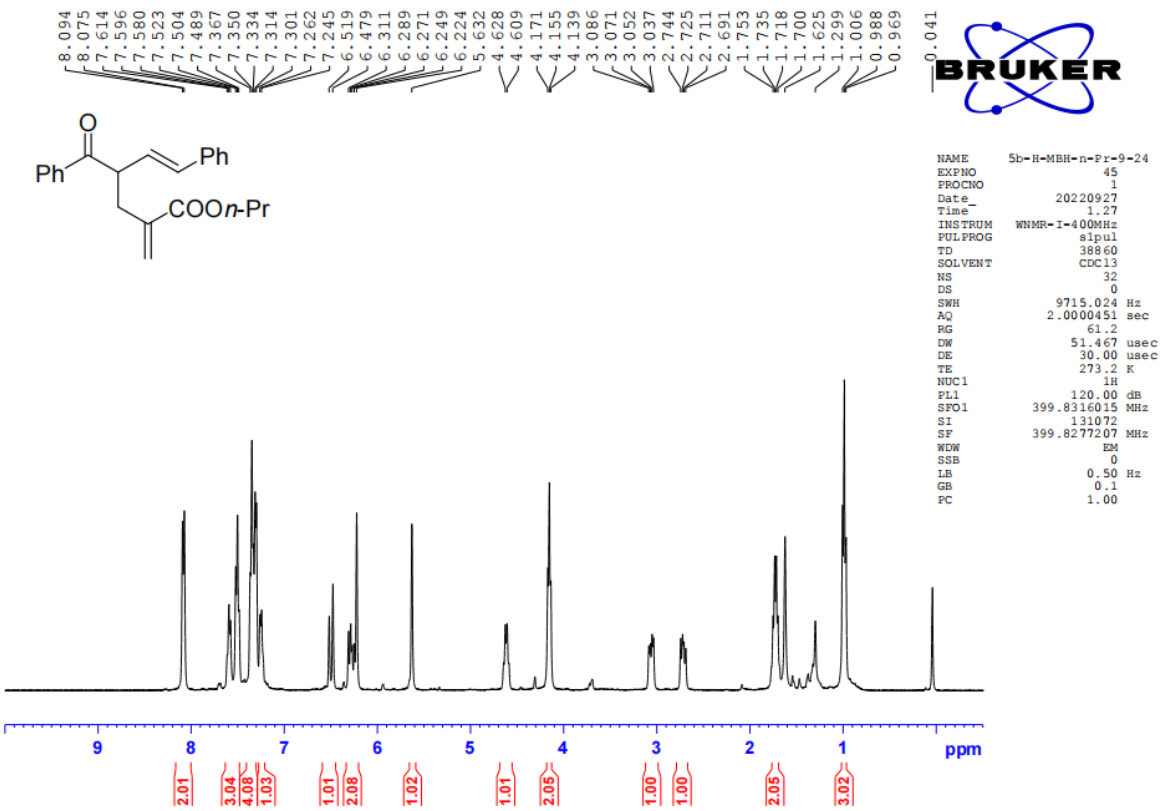
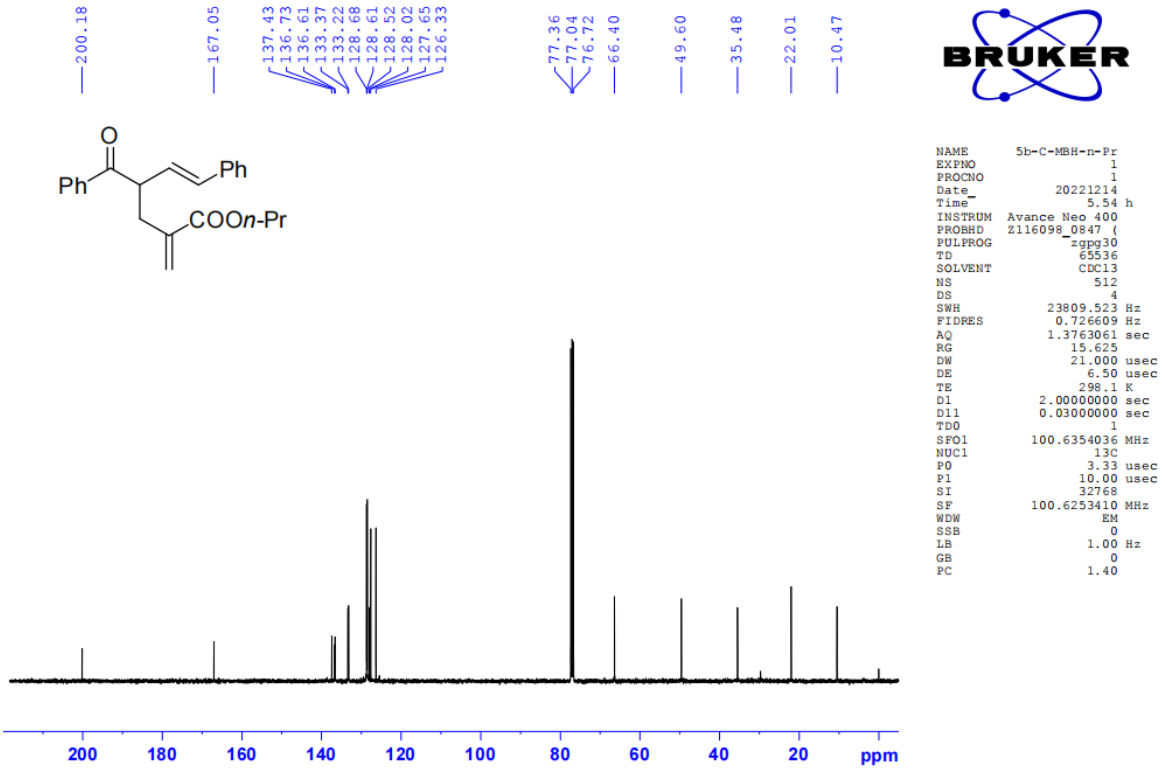
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **5a**



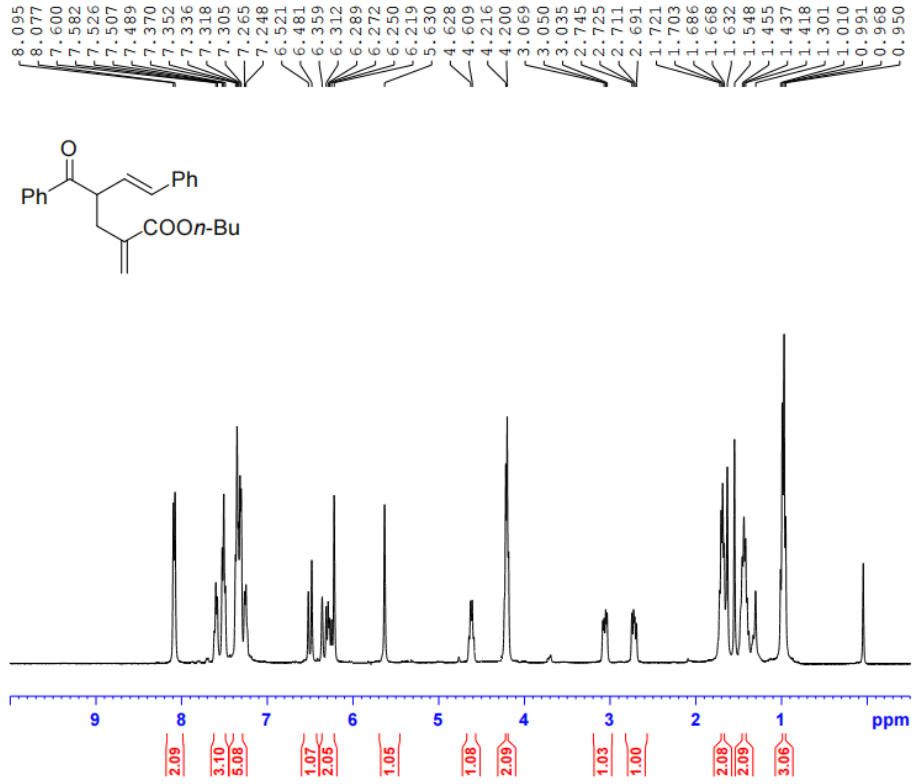



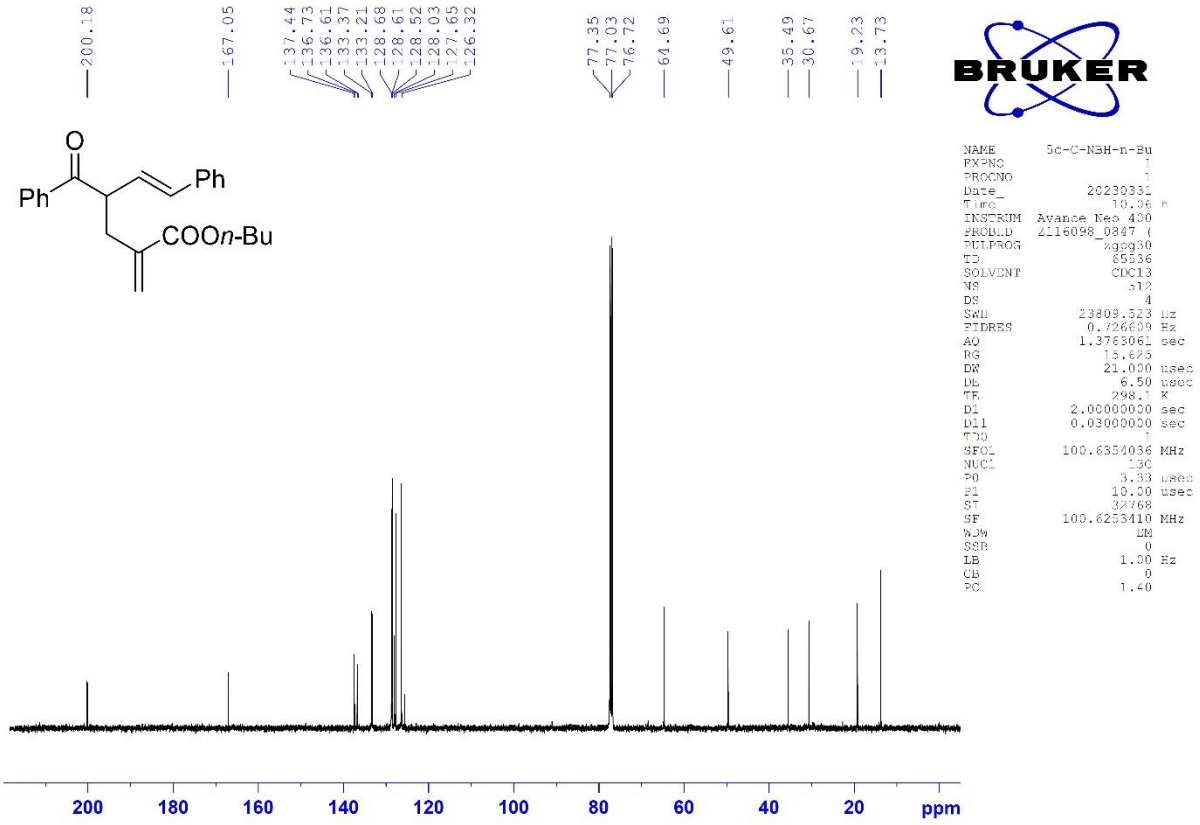
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **5b**



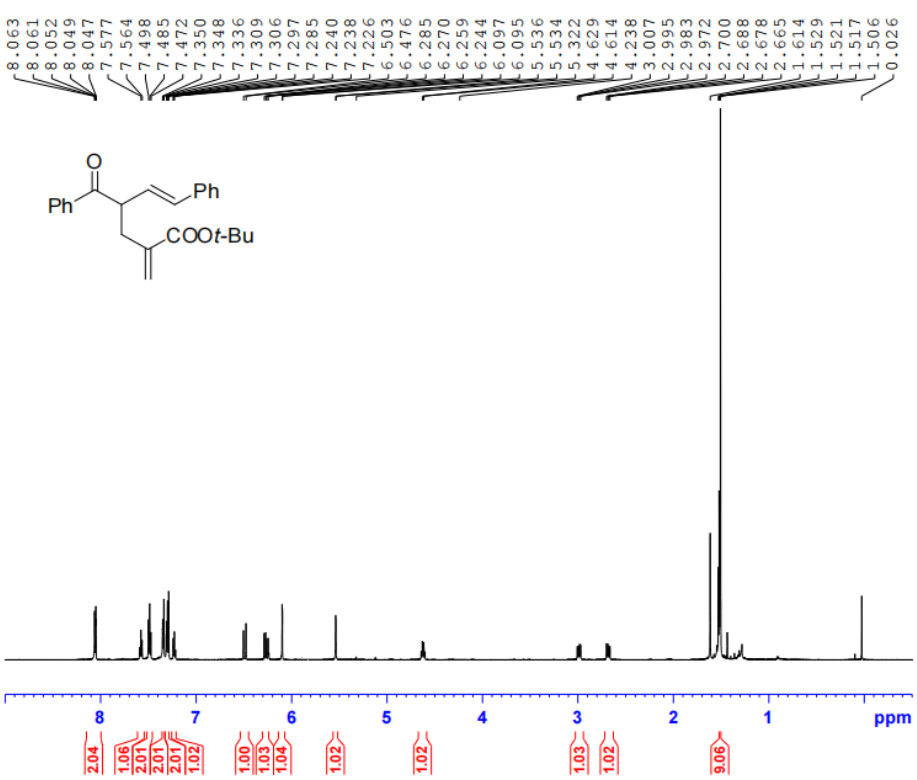



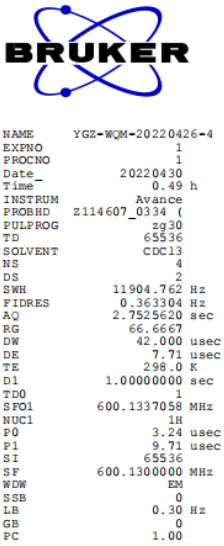
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **5c**

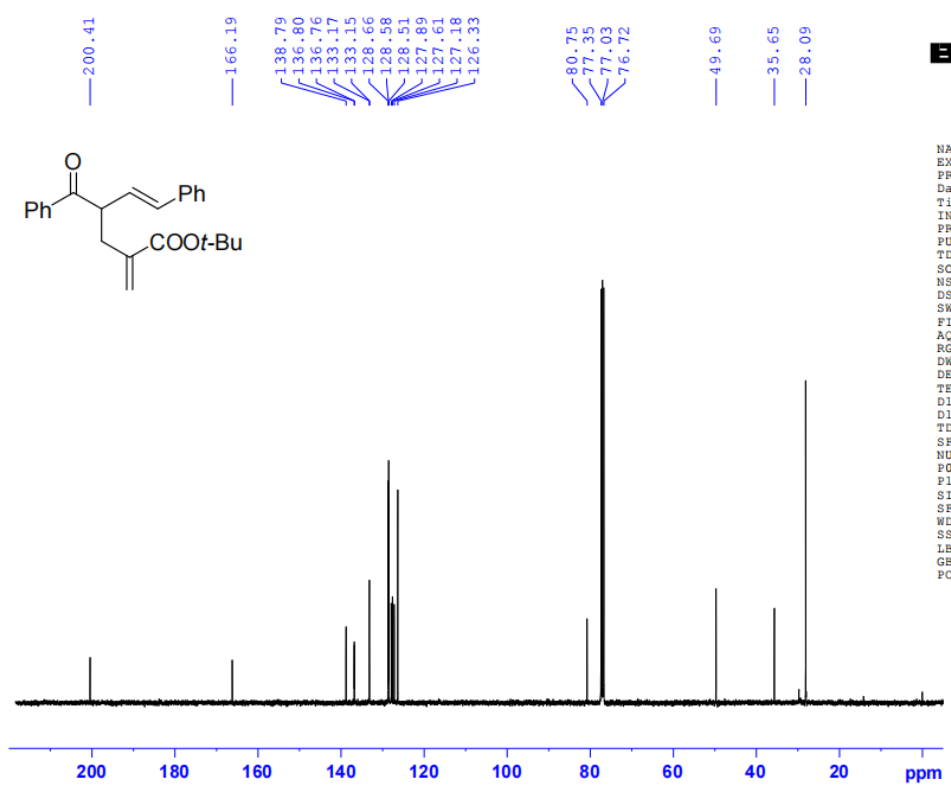


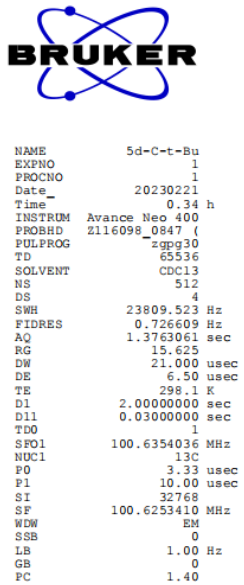



$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **5d**

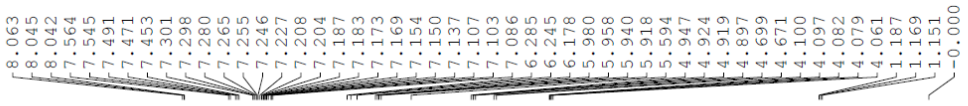


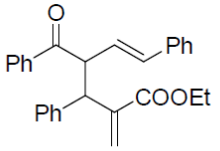



$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **5e**

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PROCNO                     1
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PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                8196.722 Hz
FIDRES             0.250144 Hz
AQ                 3.9977460 sec
RG                       101
DW                    61.000 usec
DE                    13.54 usec
TE                    298.2 K
D1                 1.00000000 sec
TD0                        1
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NUC1                      1H
P0                     3.33 usec
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WDW                       EM
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PC                      1.00
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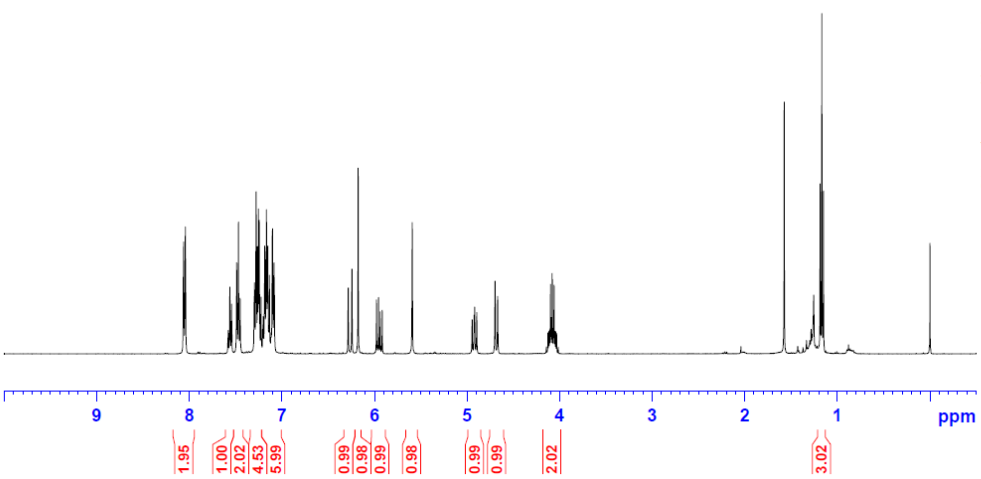


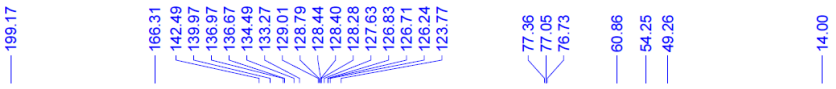


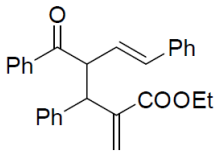


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PROCNO                     1
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TD                     65536
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FIDRES             0.726609 Hz
AQ                 1.3763061 sec
RG                    15.625
DW                    21.000 usec
DE                     6.50 usec
TE                    298.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1
SFO1             100.6354036 MHz
NUC1                      13C
P0                     3.33 usec
P1                    10.00 usec
SI                     32768
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WDW                       EM
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LB                      1.00 Hz
GB                         0
PC                      1.40
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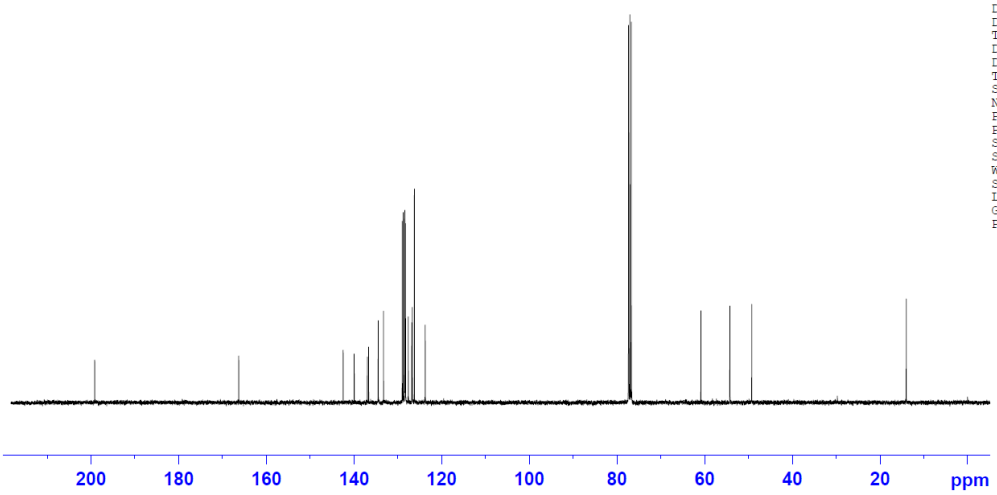
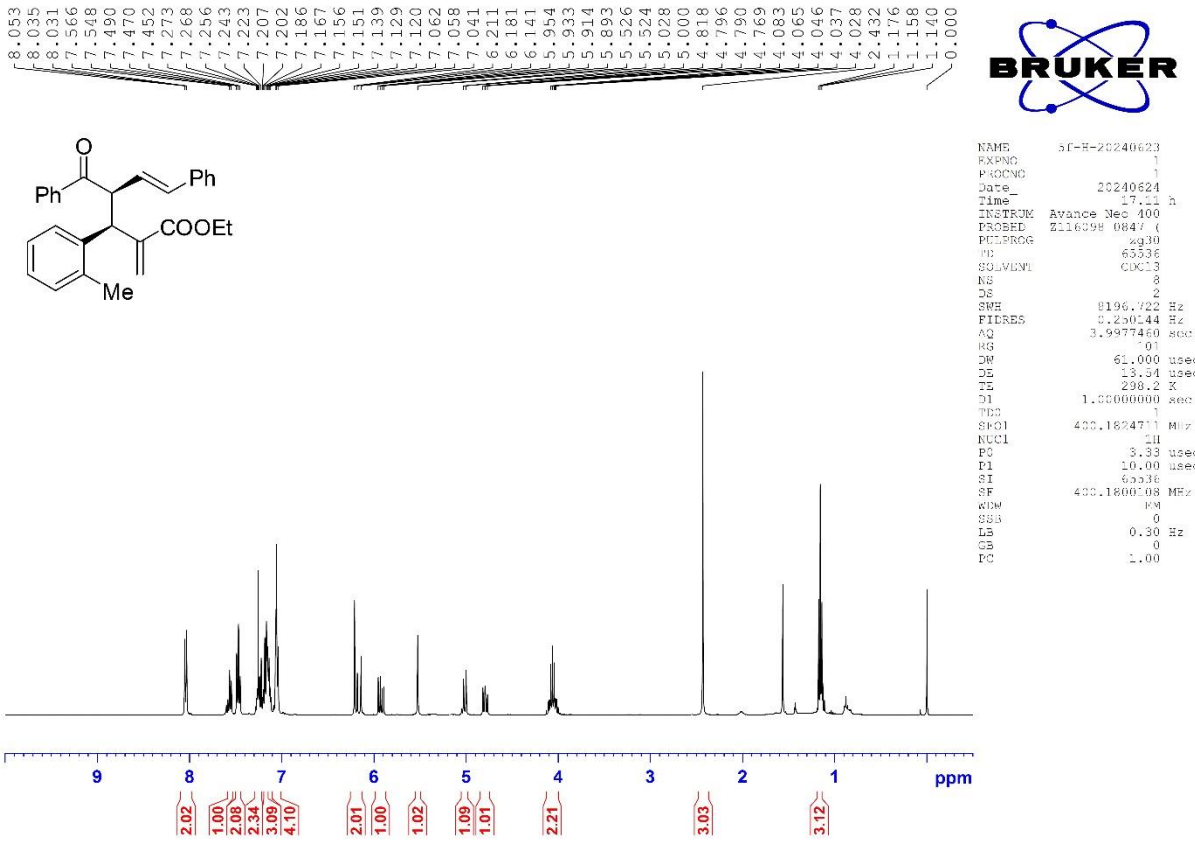
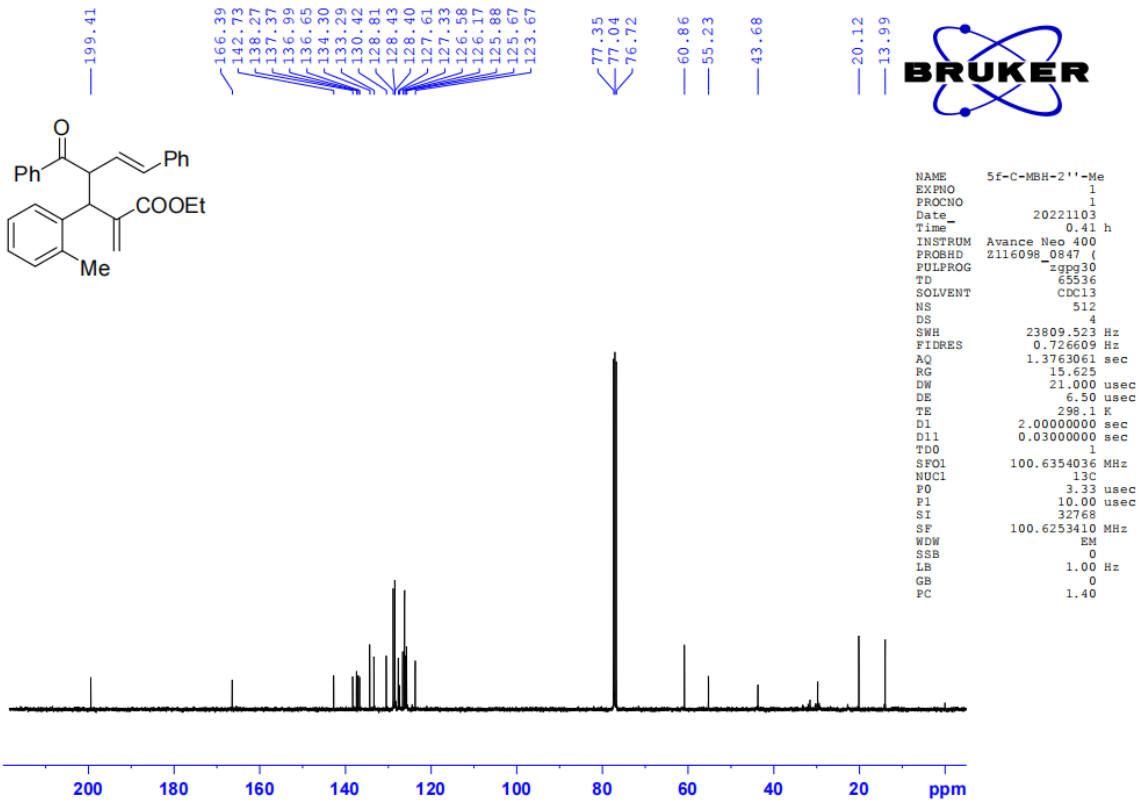
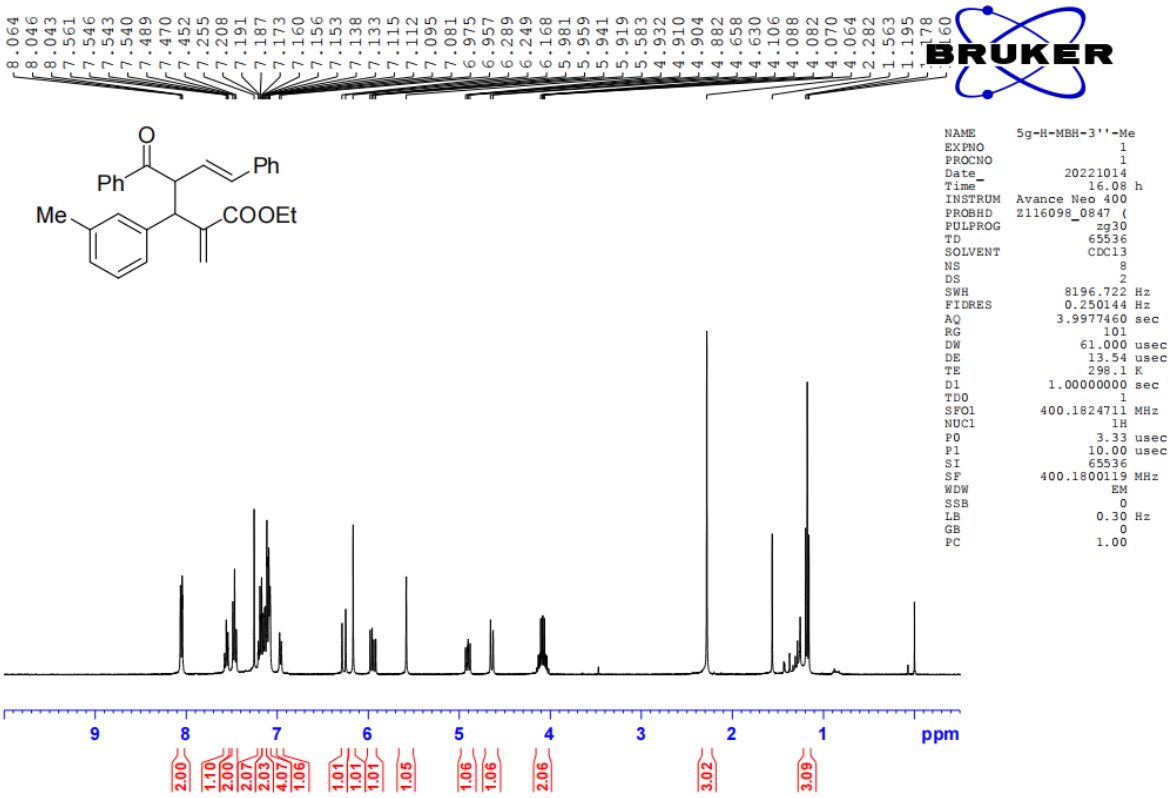


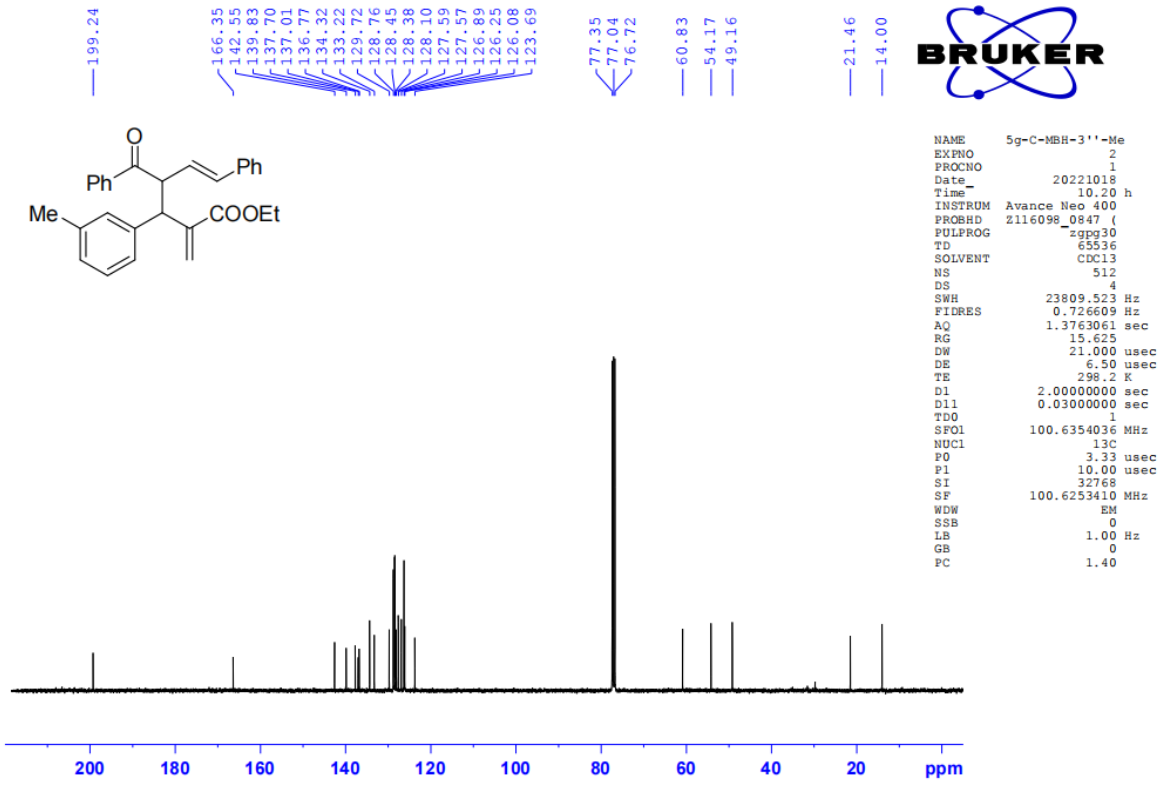
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **5f**



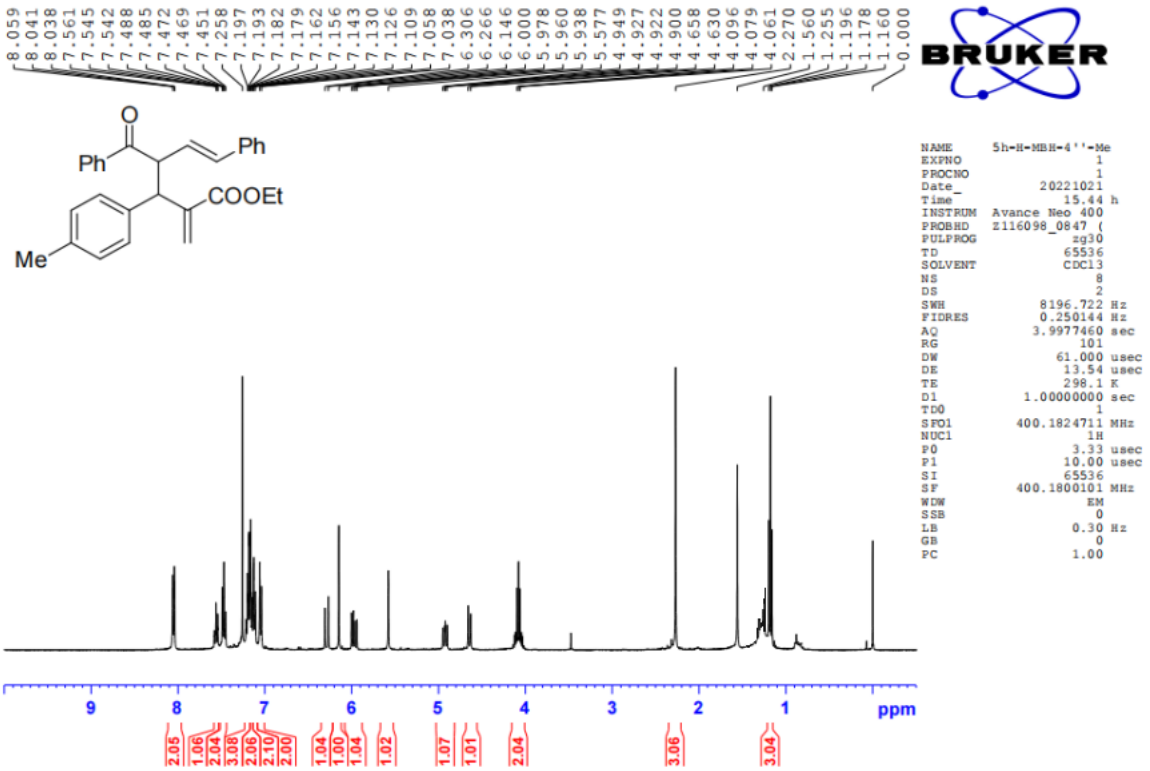



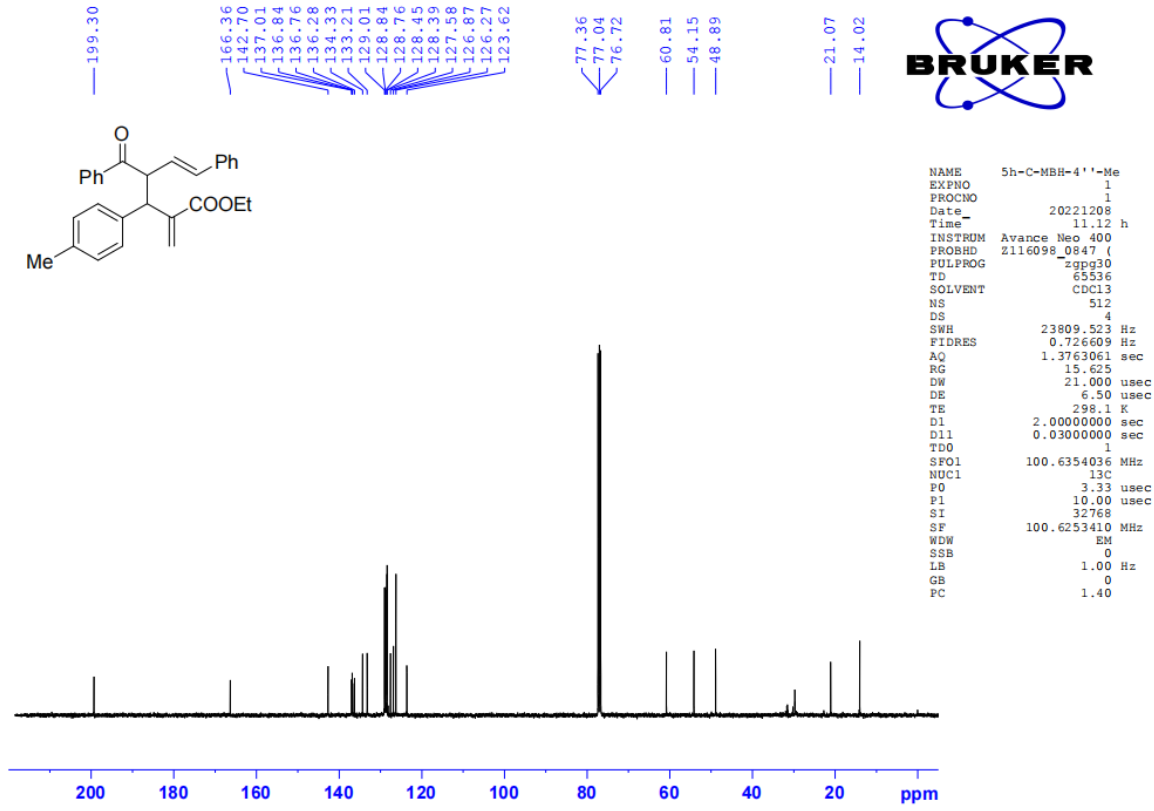
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **5g**



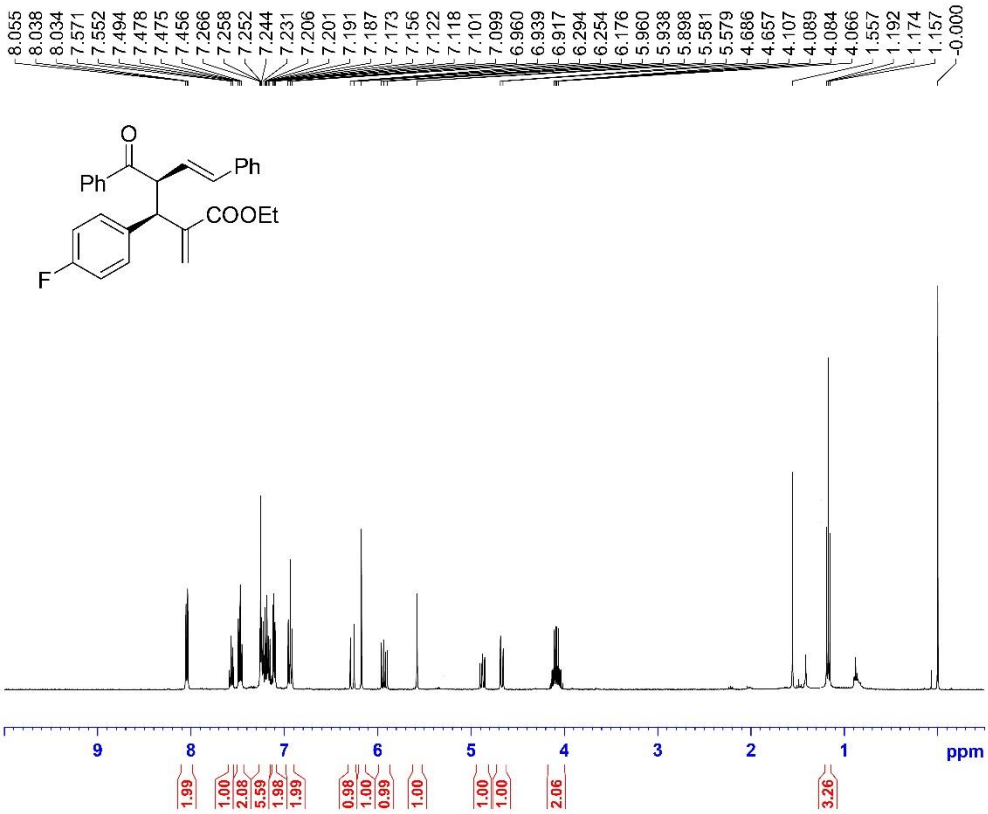



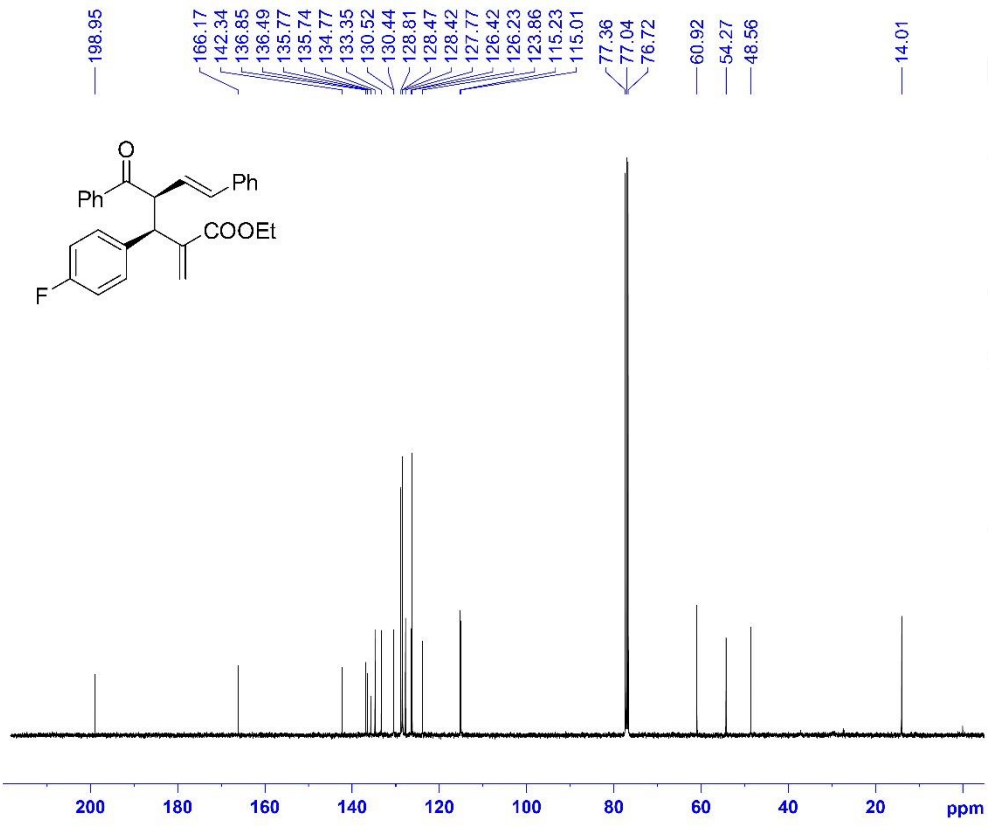
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **5h**

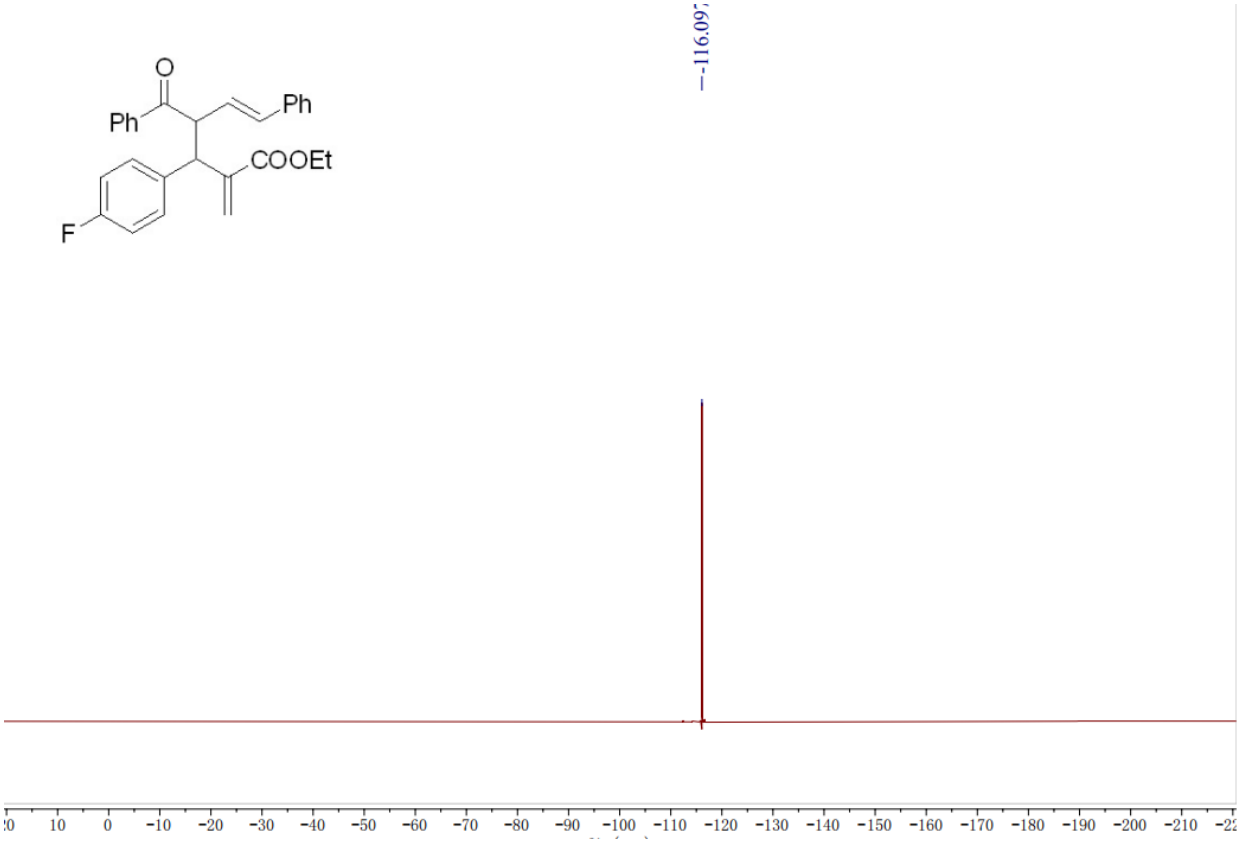


$^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra for Compound **5i**

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COOEt
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-180
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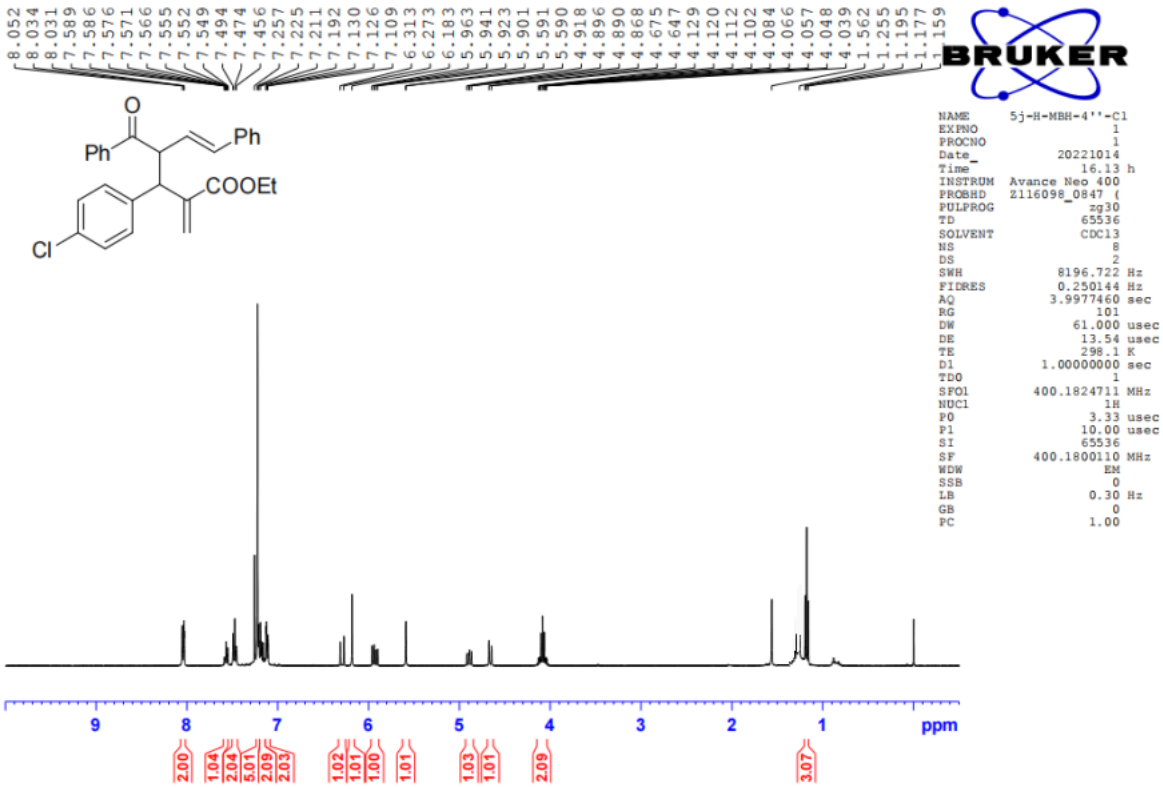
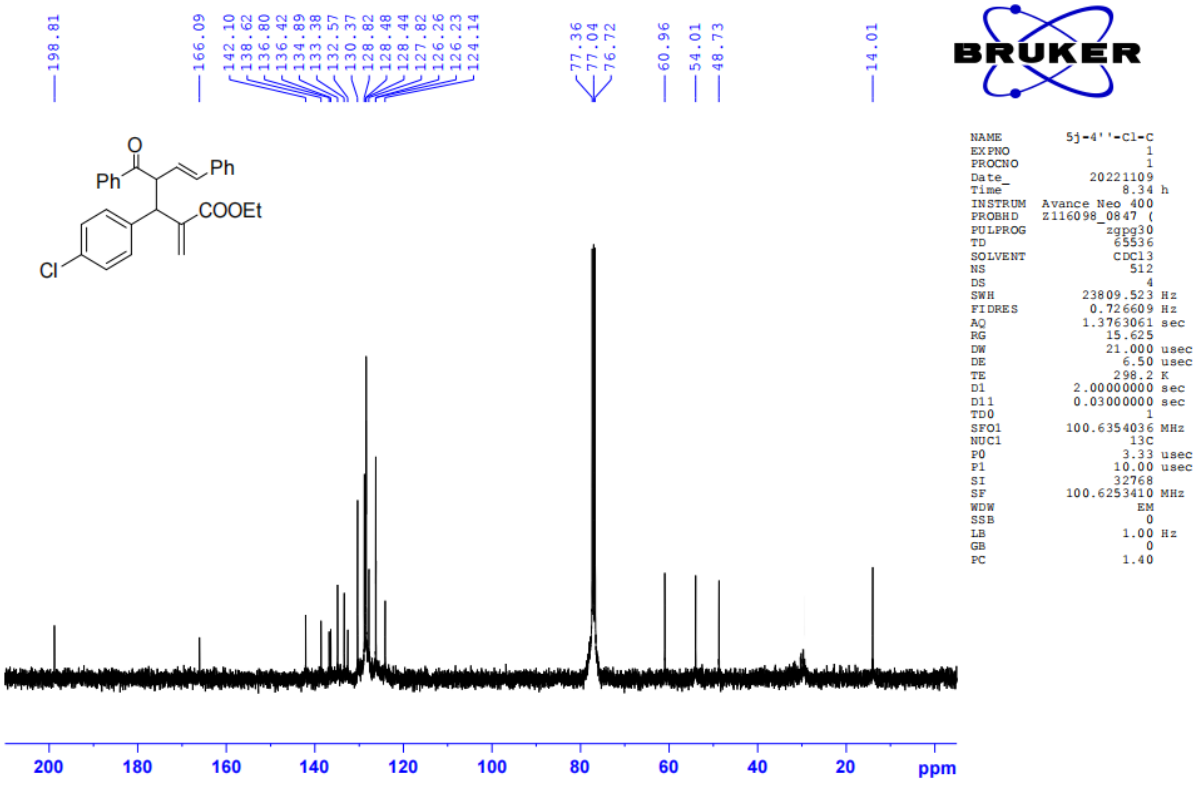
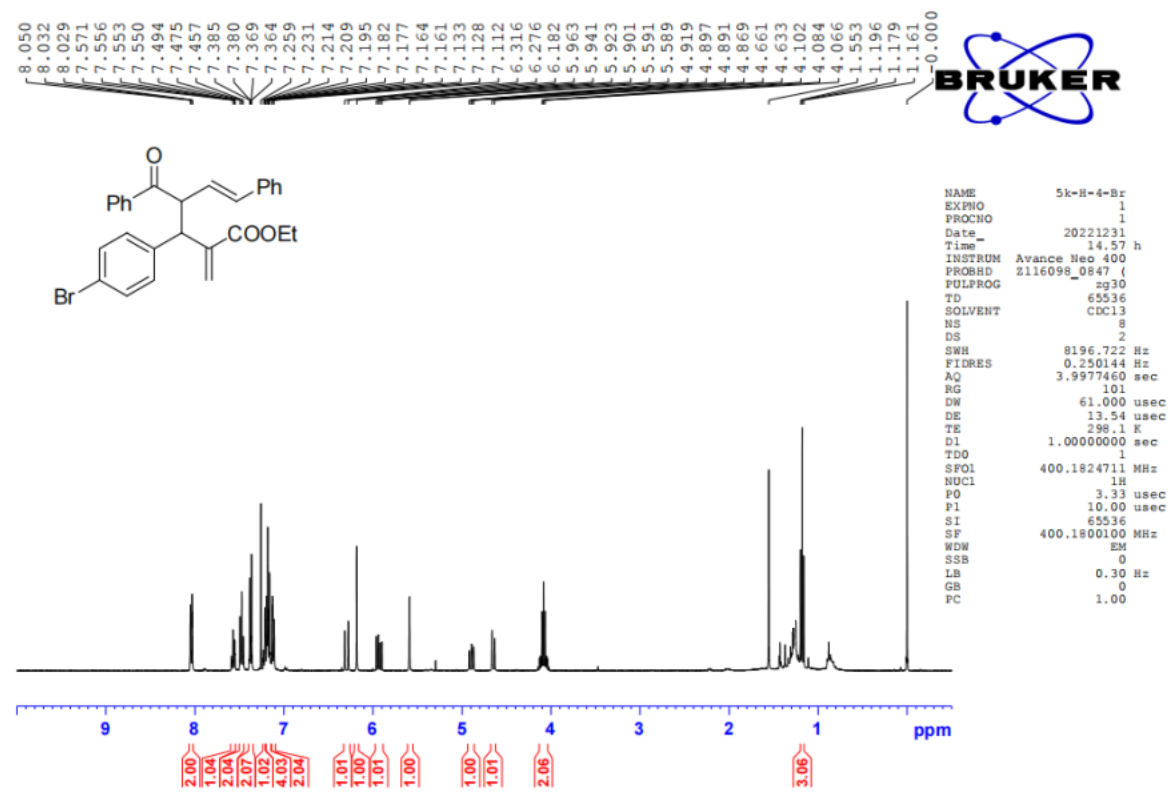
-210

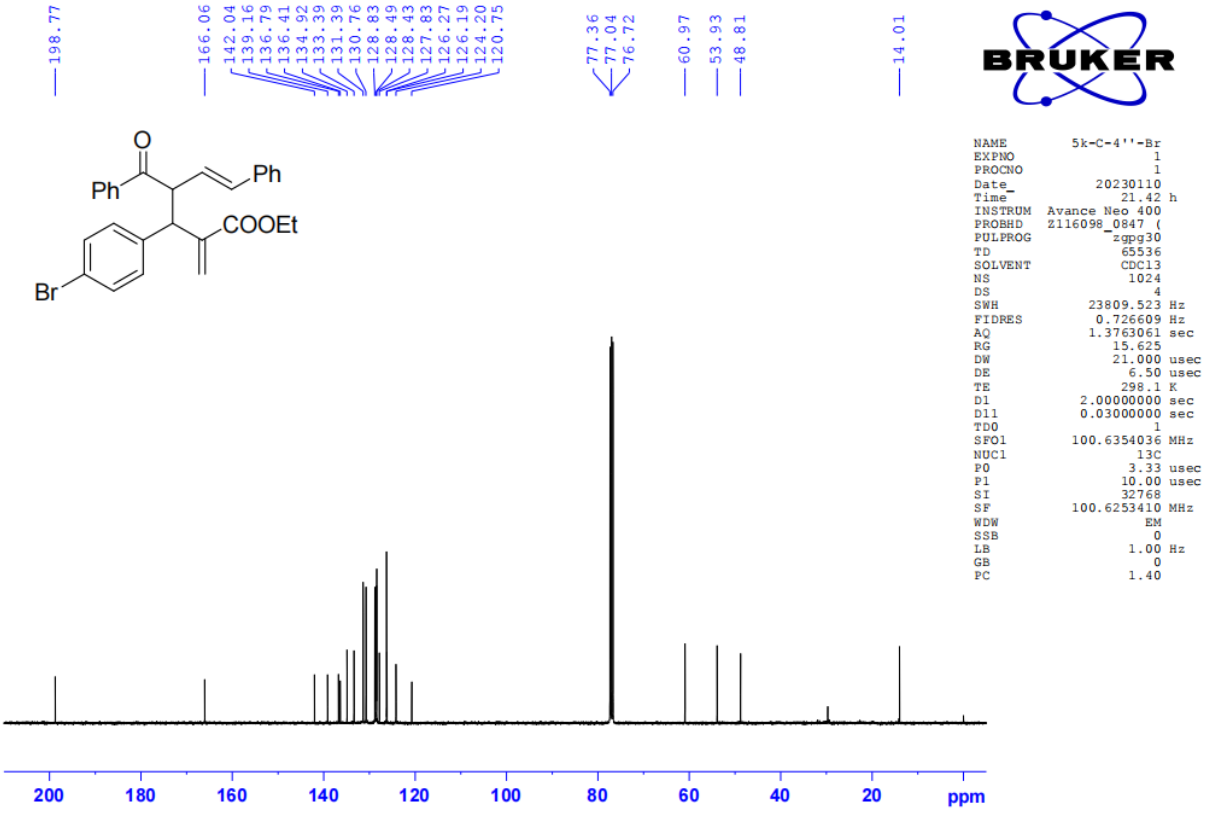
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **5j**



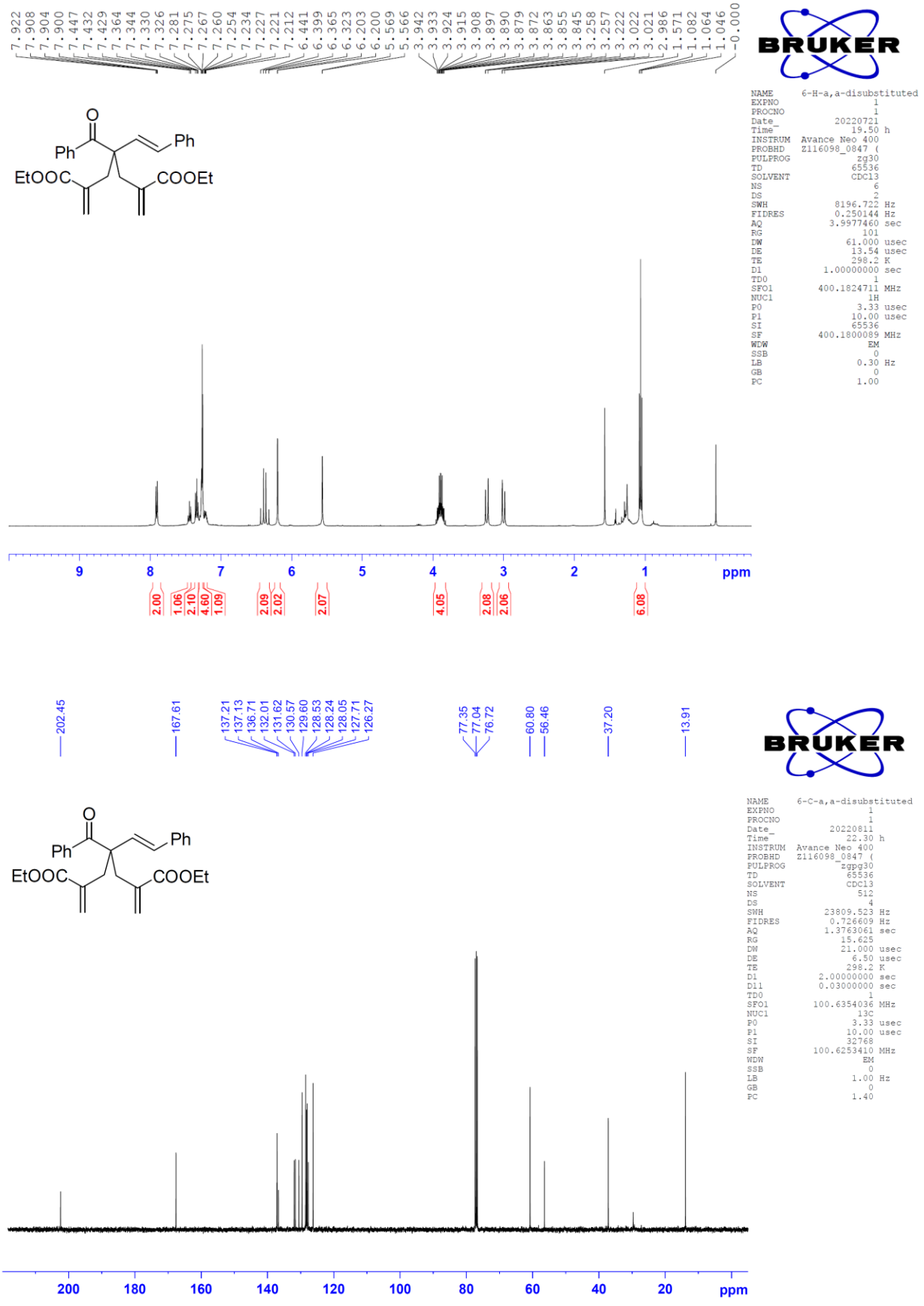



$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **5k**

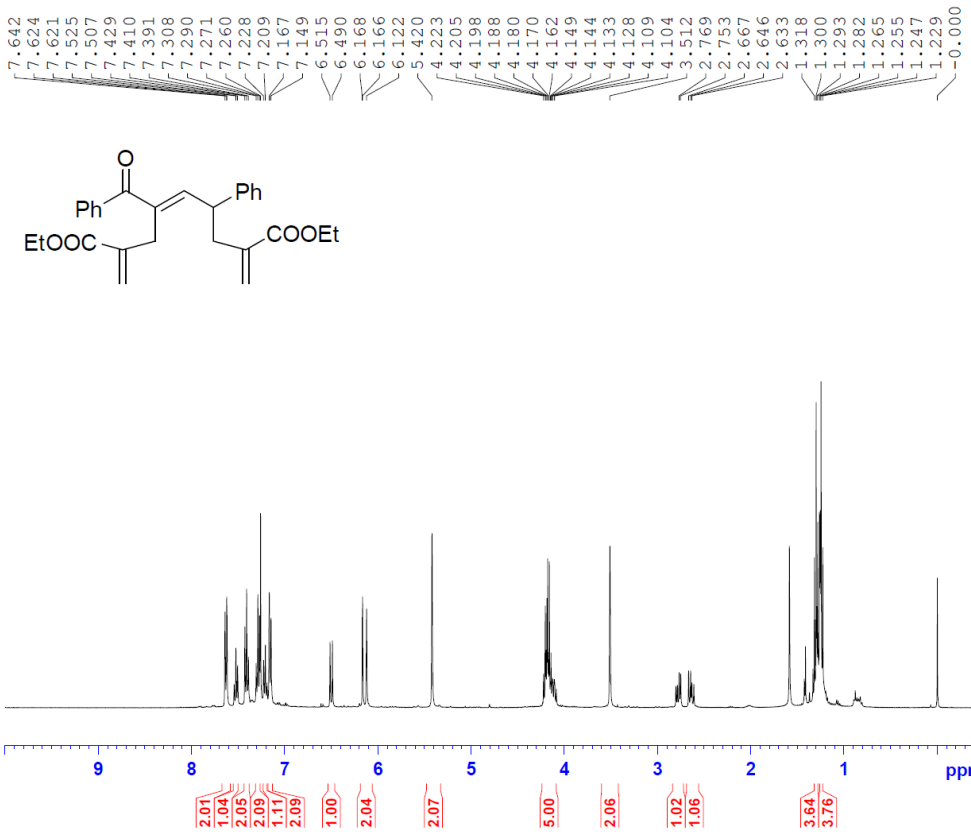


$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **4a**



$^{1}$H NMR, $^{13}$C NMR and 2D-NOESY Spectra for Compound **6a**

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PROCNO                            1
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PULPROG                        zg30
TD                            65536
SOLVENT                       CDCl3
NS                                6
DS                                2
SWH                        8196.722 Hz
FIDRES                     0.250144 Hz
AQ                         3.9977460 sec
RG                              101
DW                         61.000 usec
DE                         13.54 usec
TE                            298.1 K
D1                         1.00000000 sec
TD0                               1
SFO1                       400.1824711 MHz
NUC1                             1H
P0                          3.33 usec
P1                         10.00 usec
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SF                         400.1800091 MHz
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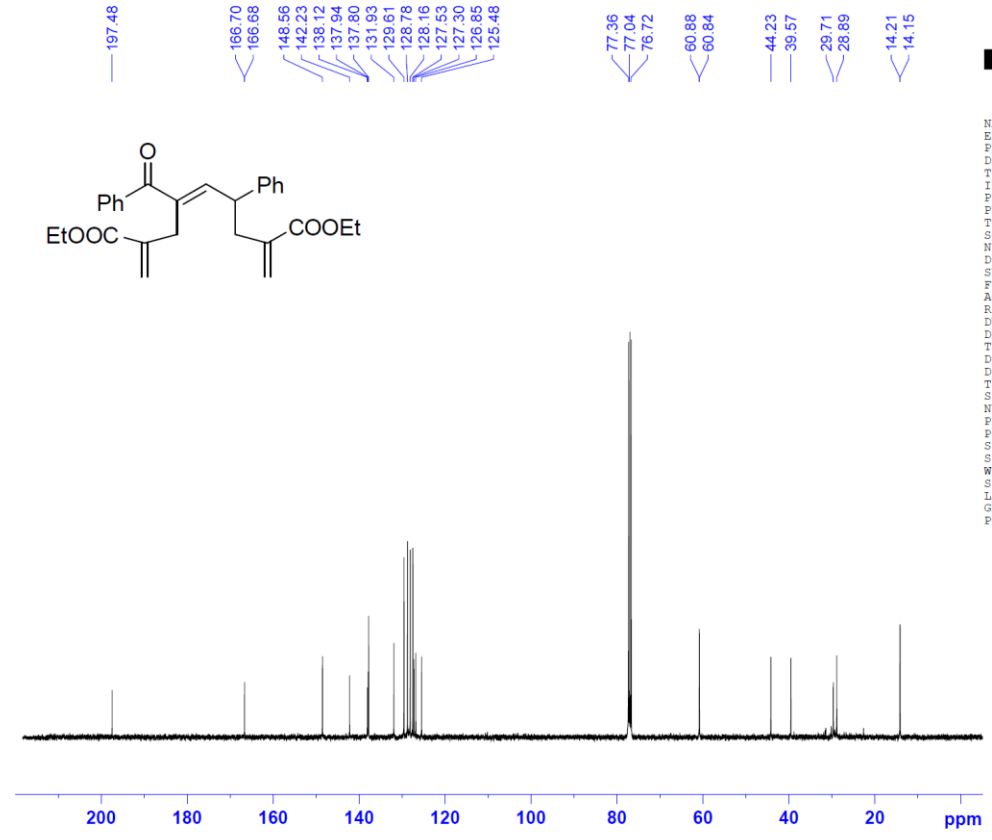


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PROCNO                            1
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PULPROG                     zgpg30
TD                            65536
SOLVENT                       CDCl3
NS                              512
DS                                4
SWH                        23809.523 Hz
FIDRES                     0.726609 Hz
AQ                         1.3763061 sec
RG                           15.625
DW                         21.000 usec
DE                          6.50 usec
TE                            298.2 K
D1                         2.00000000 sec
D11                        0.03000000 sec
TD0                               1
SFO1                       100.6354036 MHz
NUC1                             13C
P0                          3.33 usec
P1                         10.00 usec
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SSB                               0
LB                          1.00 Hz
GB                                0
PC                          1.40
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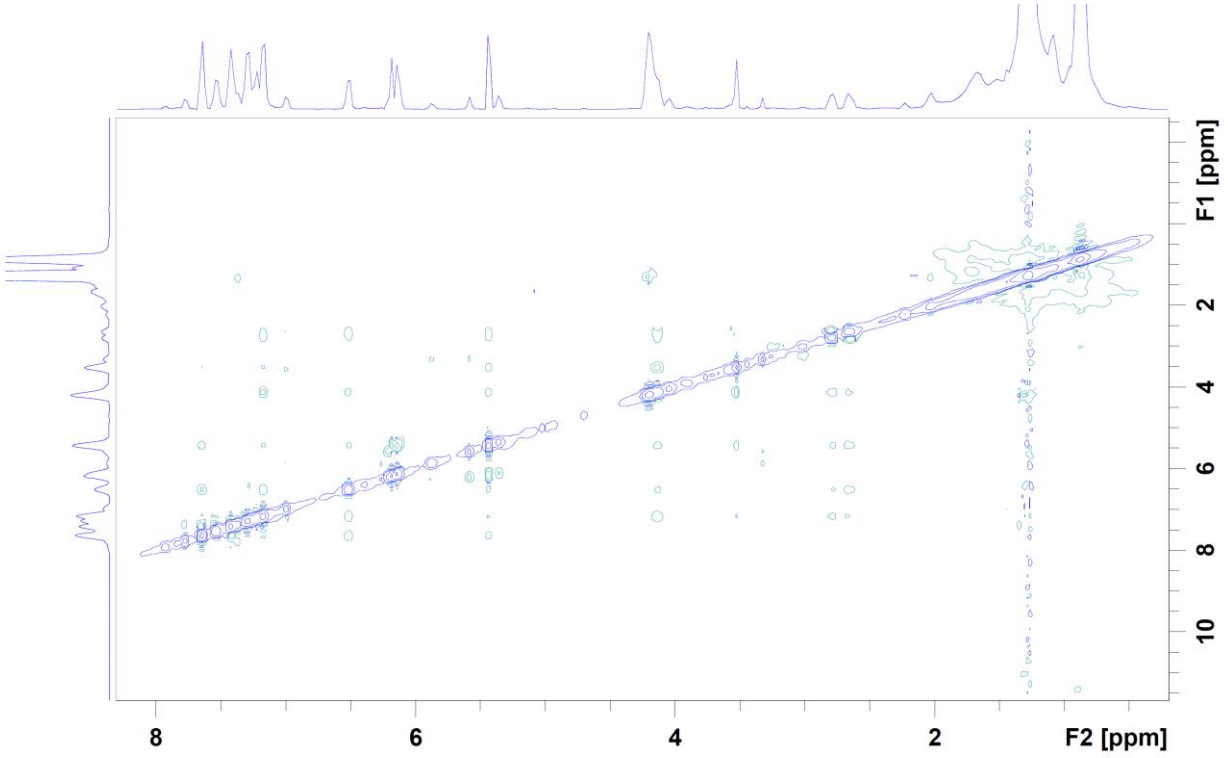
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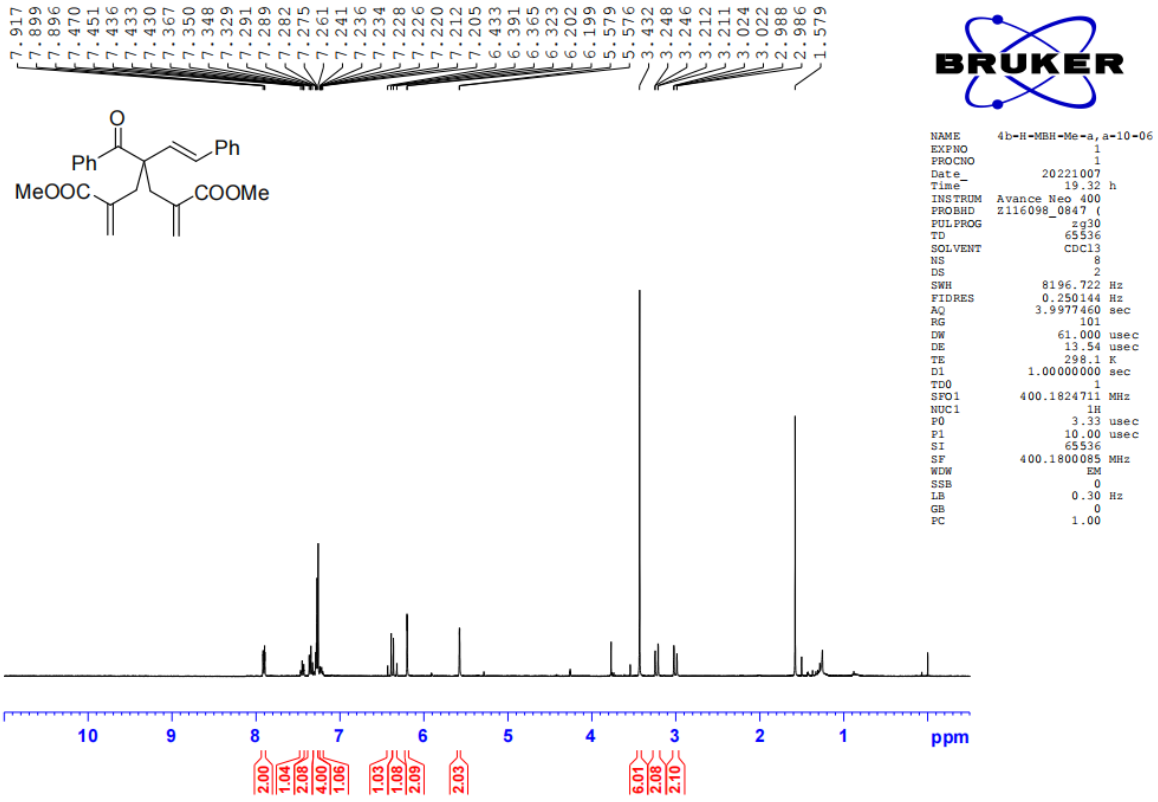
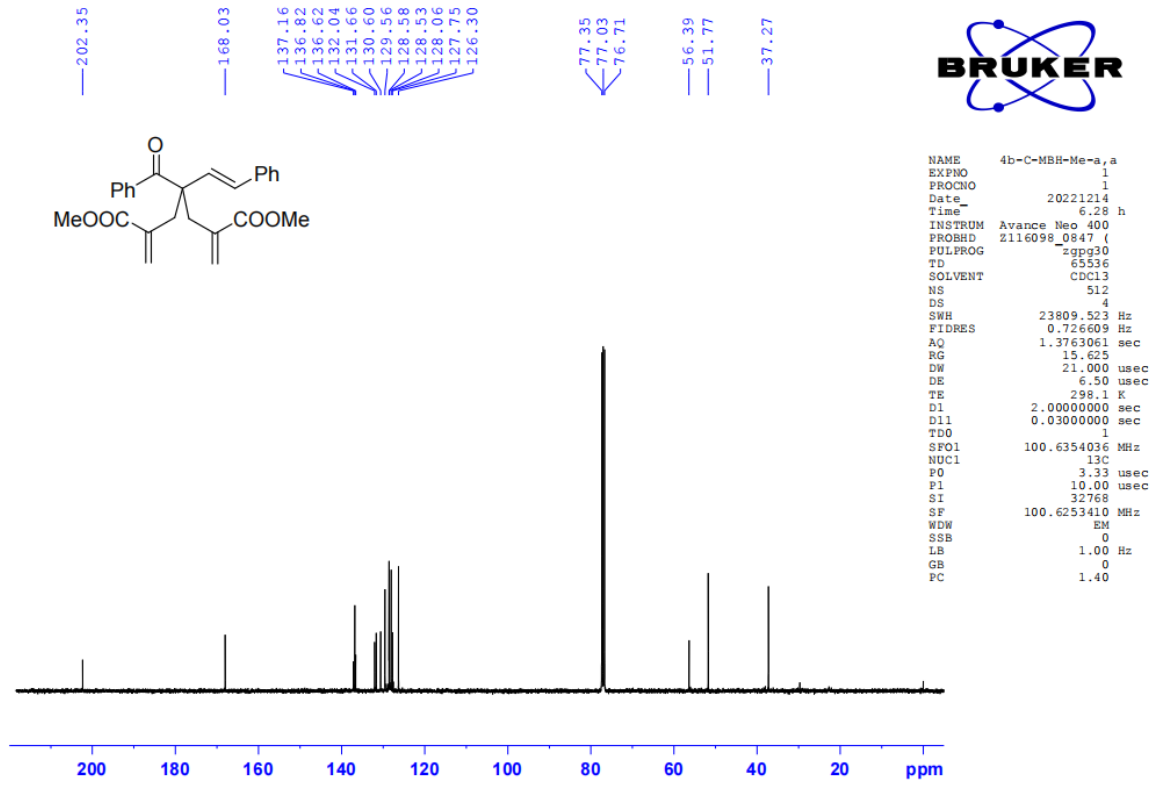
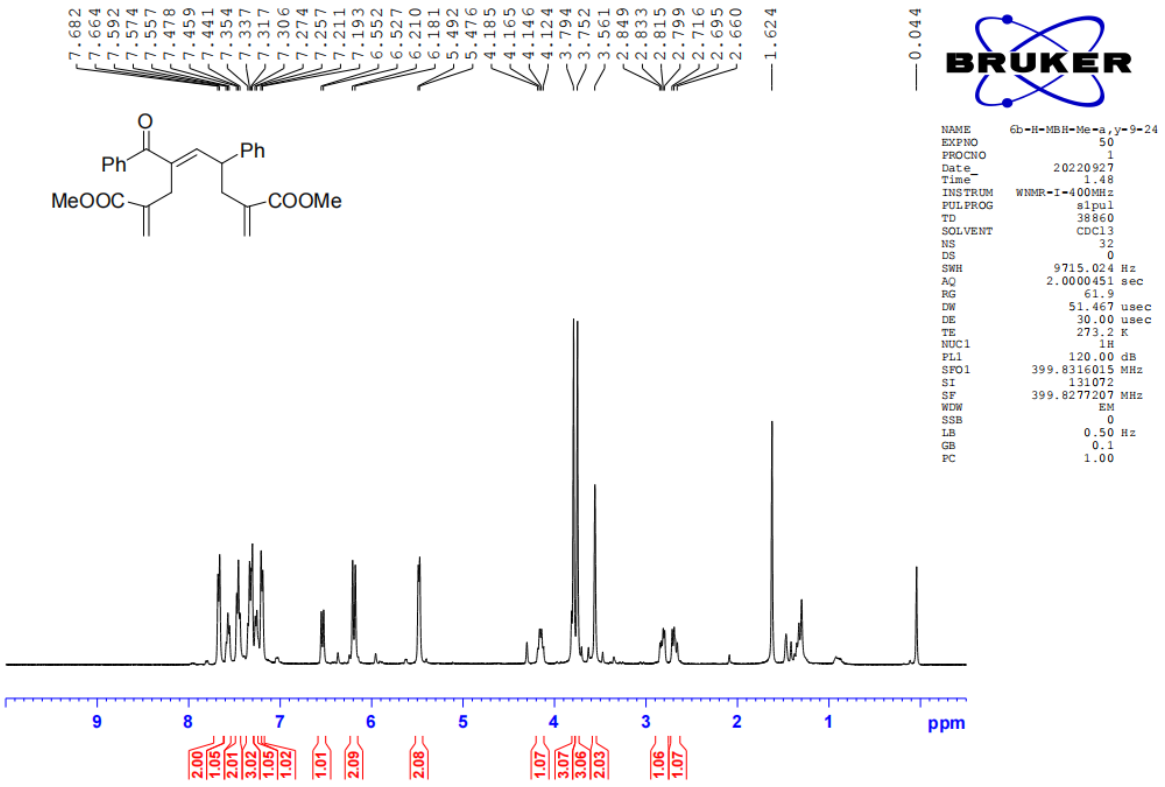
6
4
2
F2 [ppm]

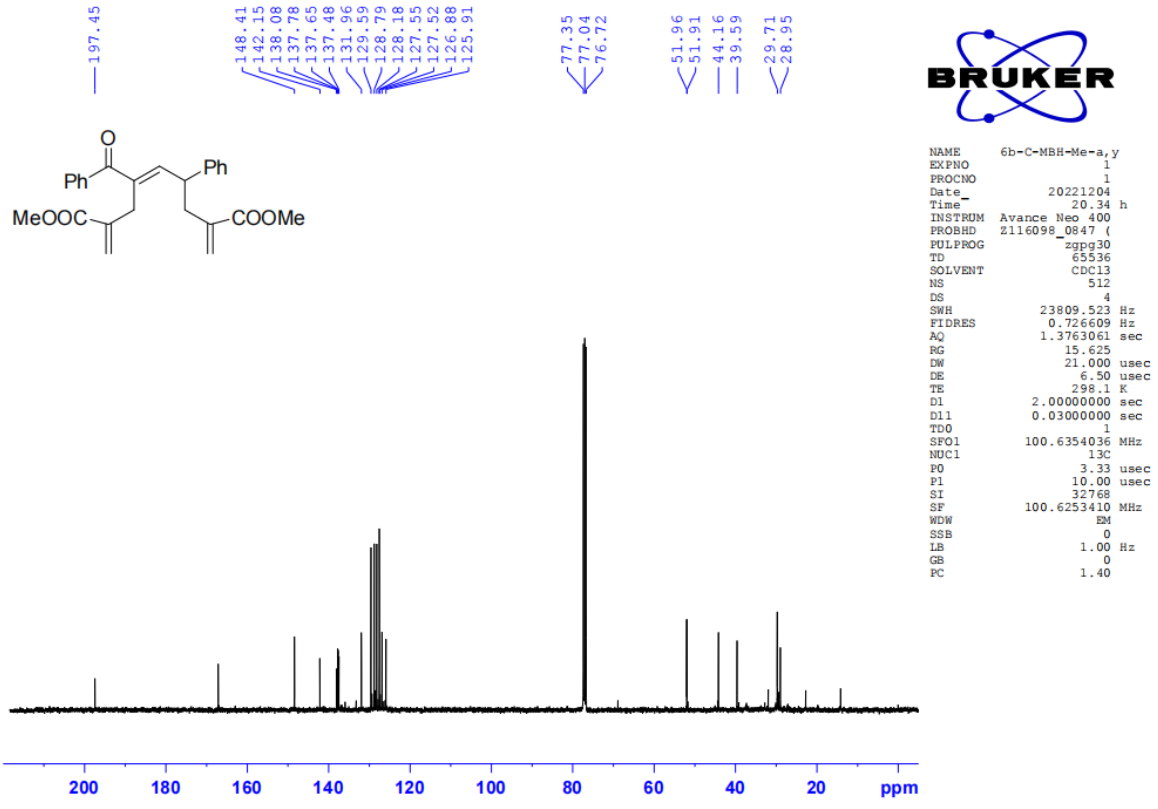
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **4b**



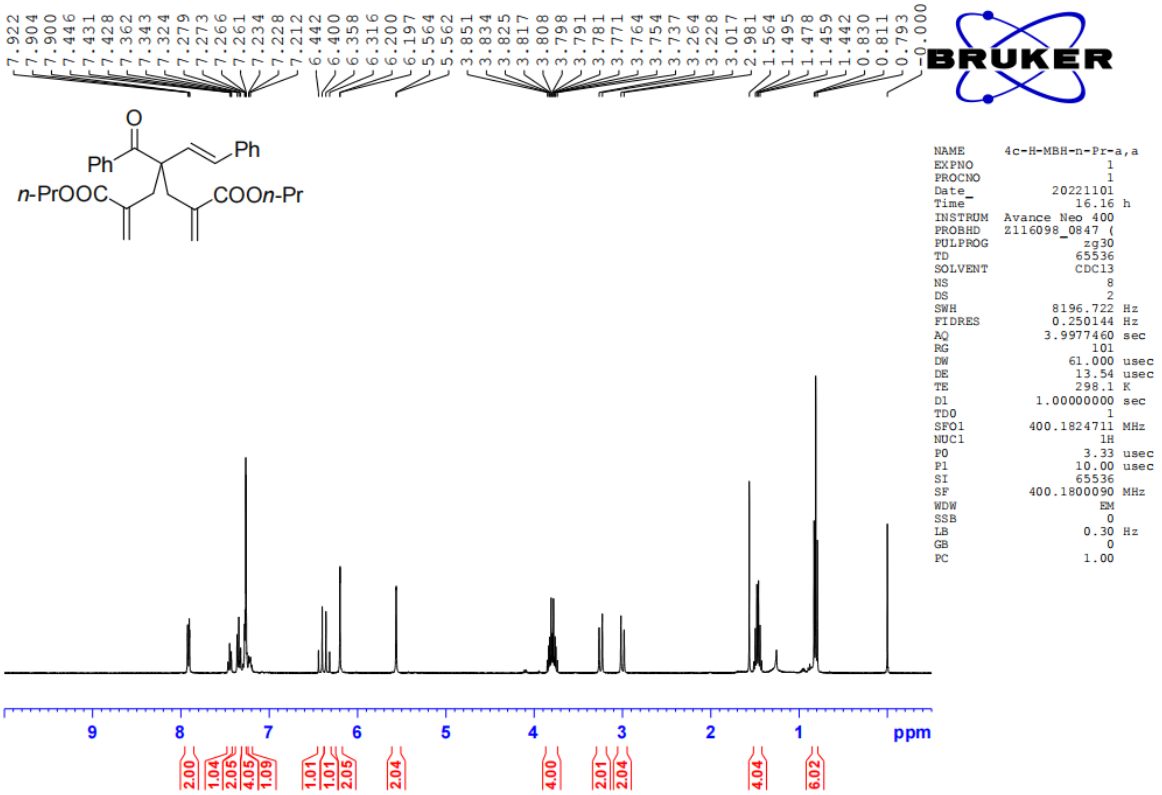



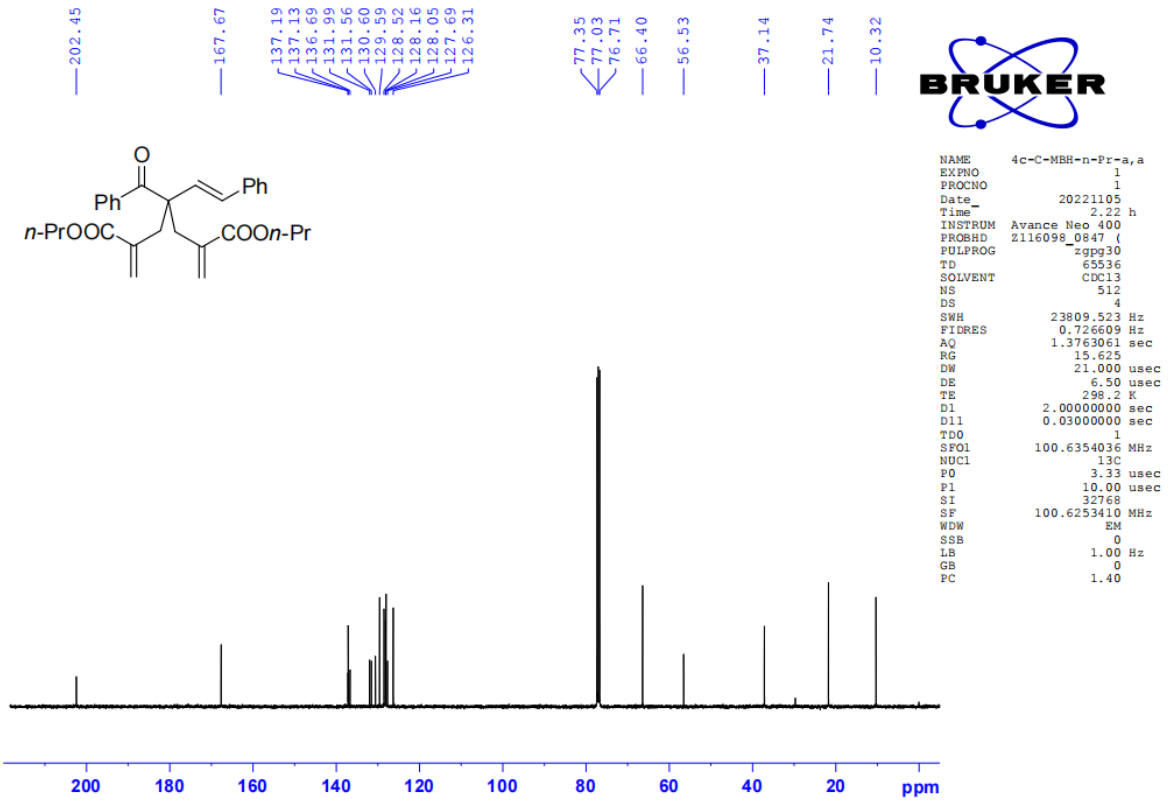
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **6b**



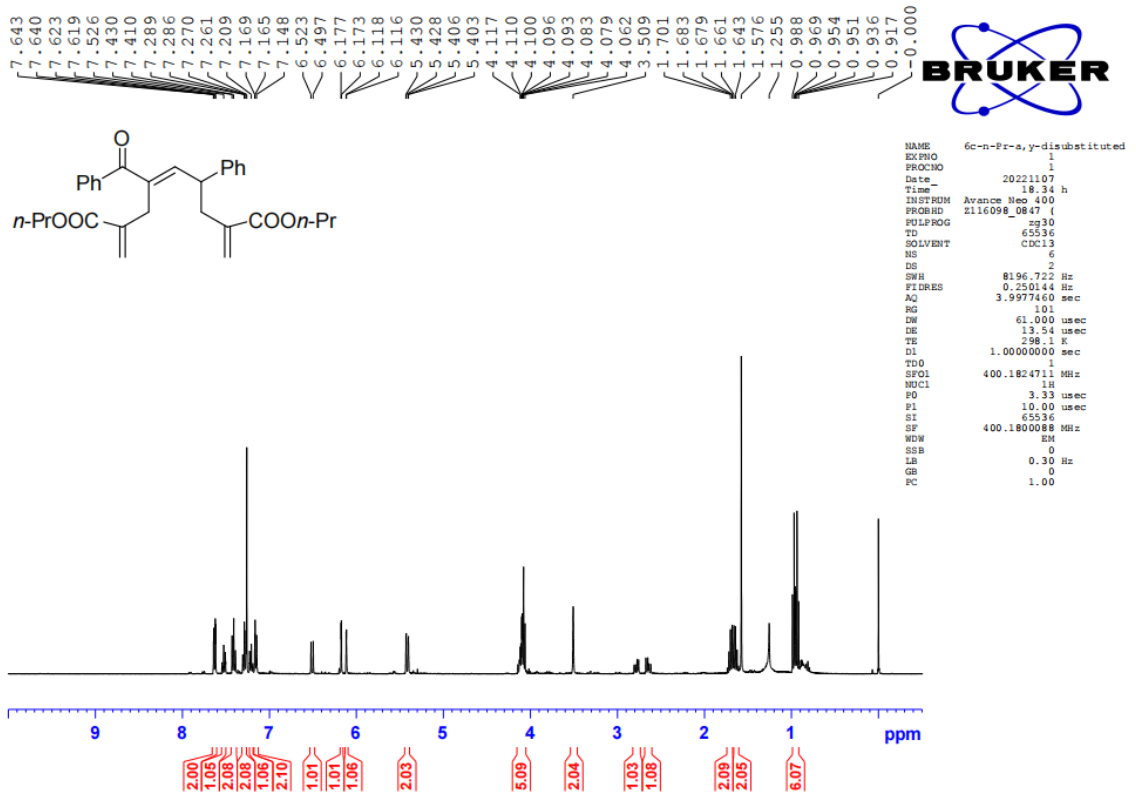



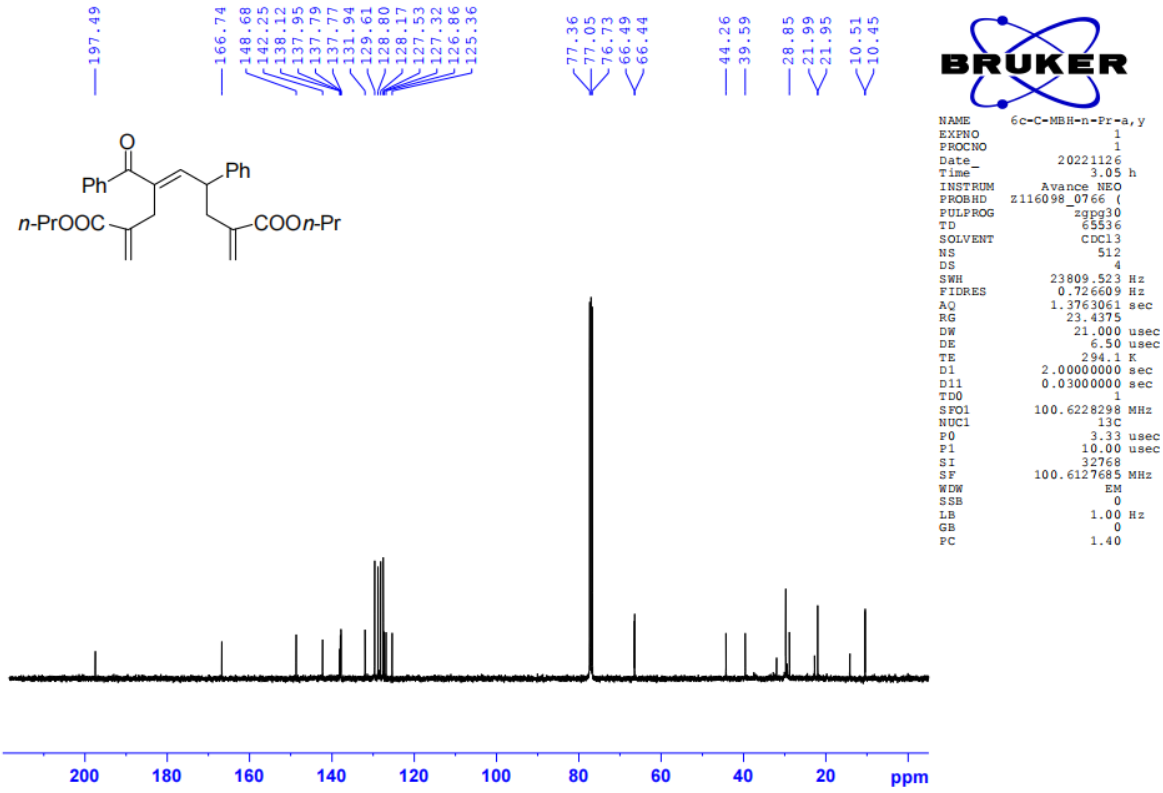
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **4c**



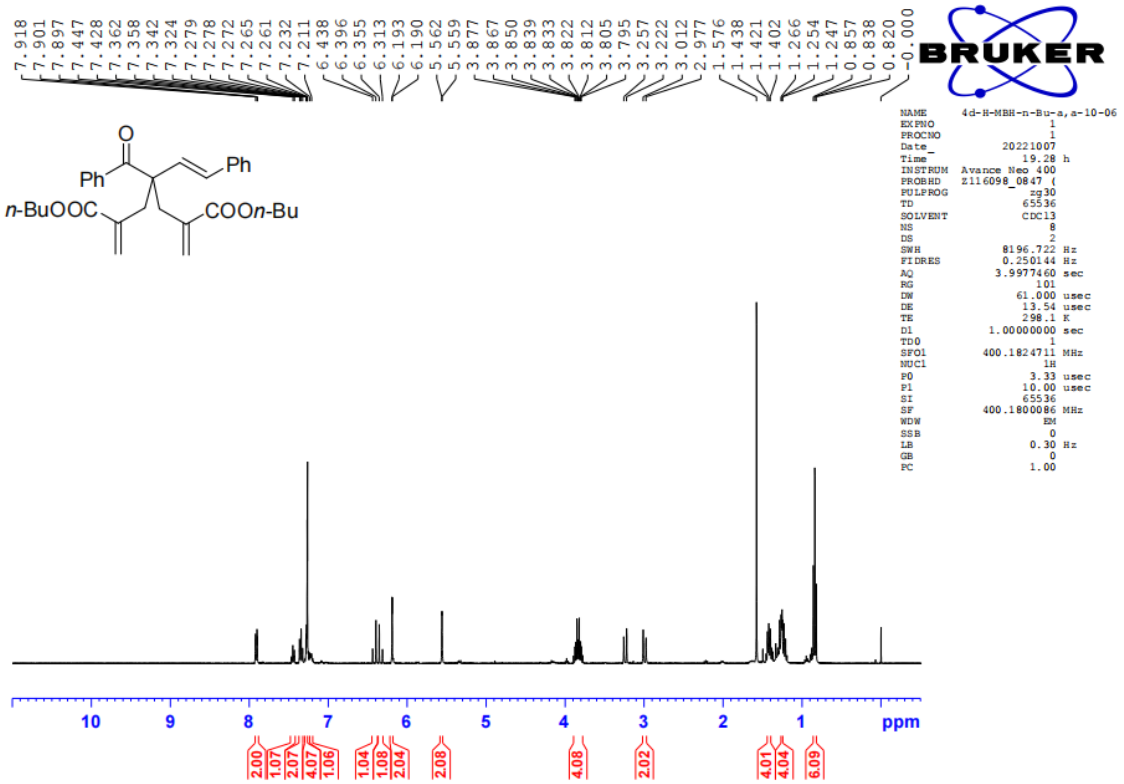



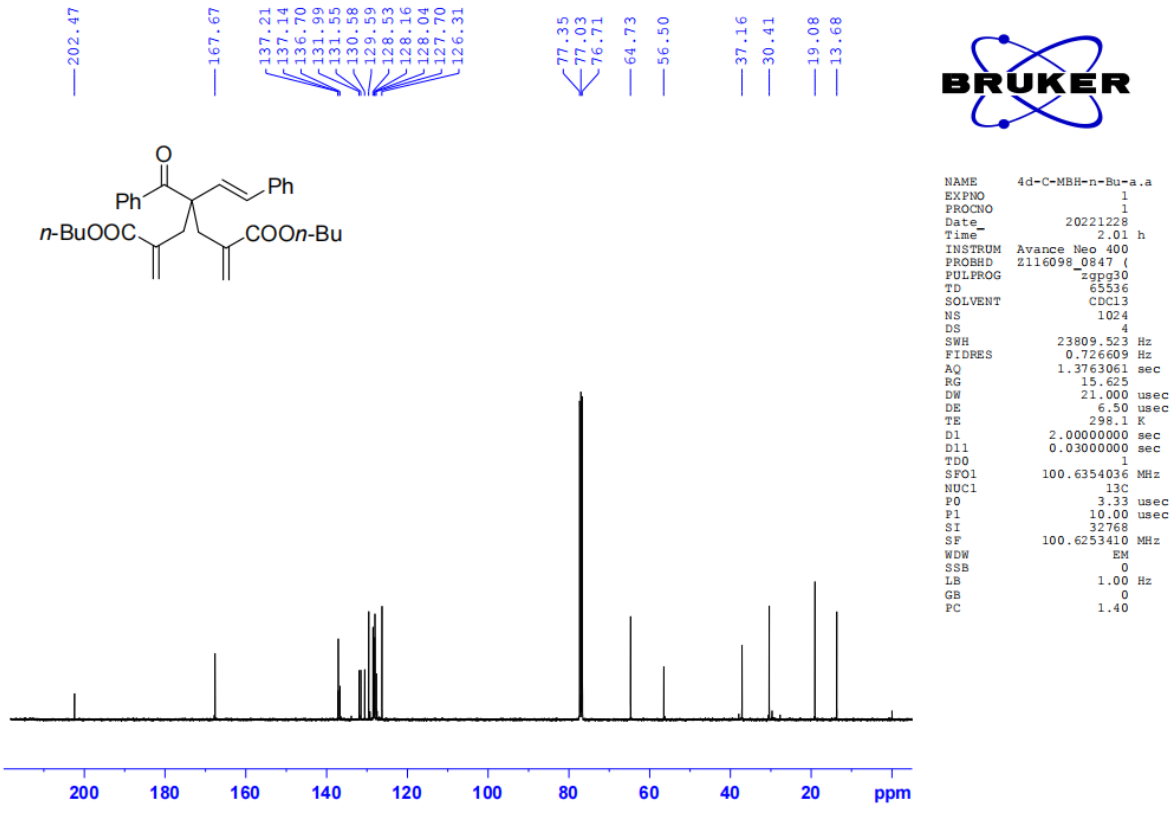
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **6c**



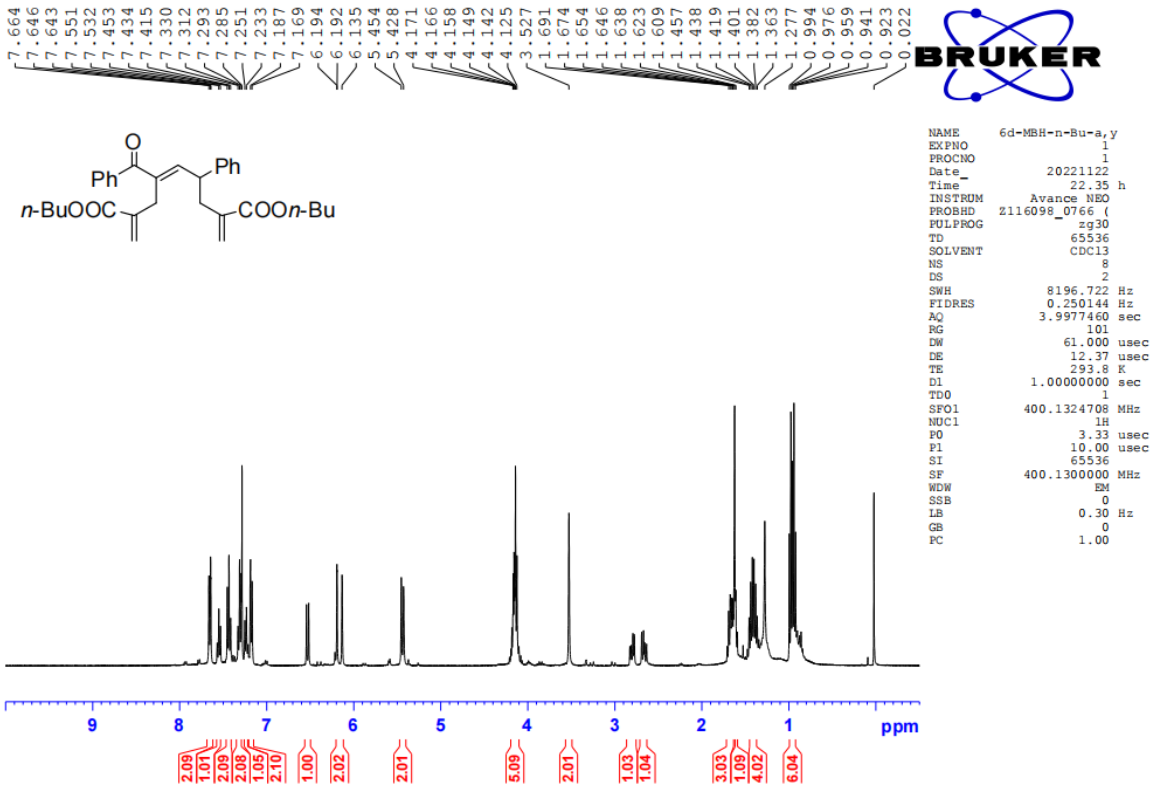



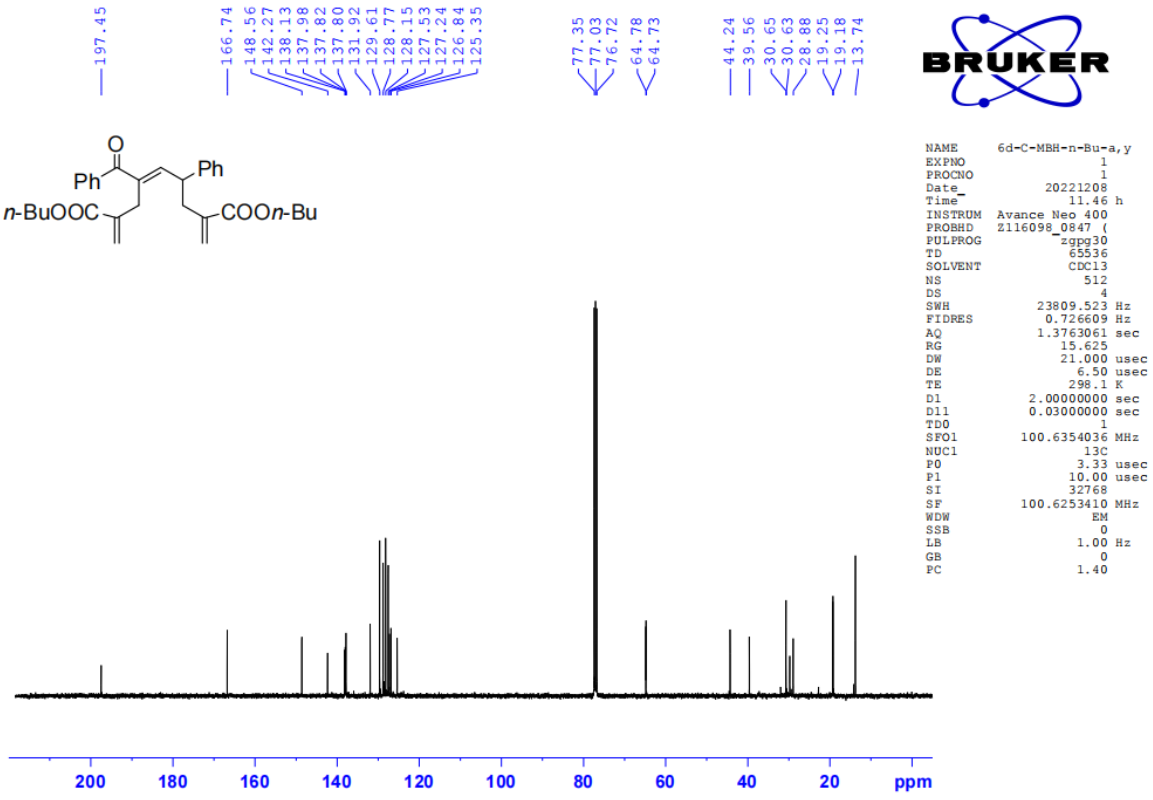
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **4d**



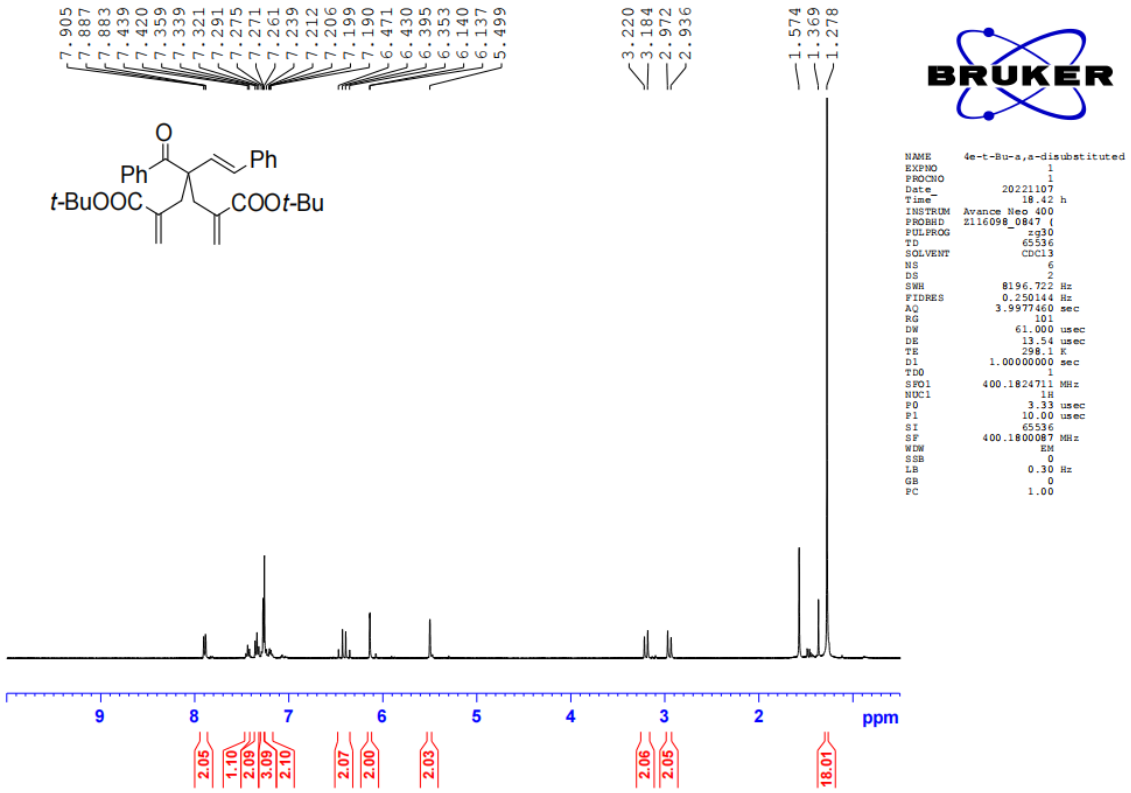



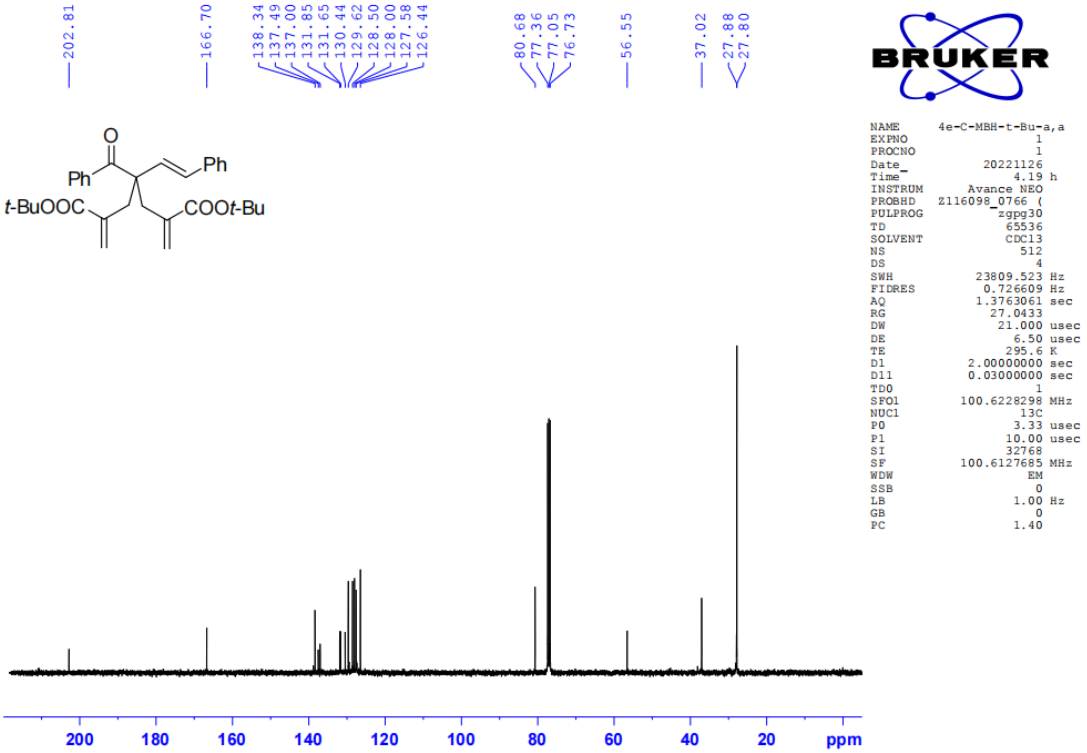
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **6d**



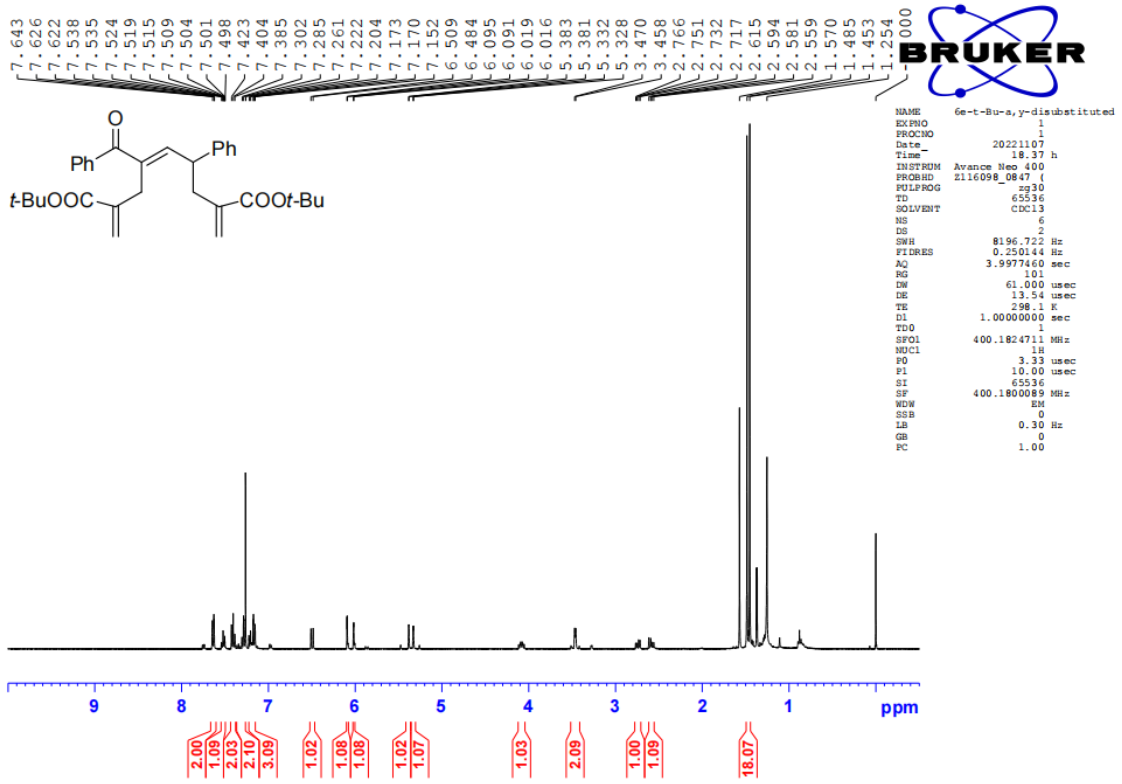



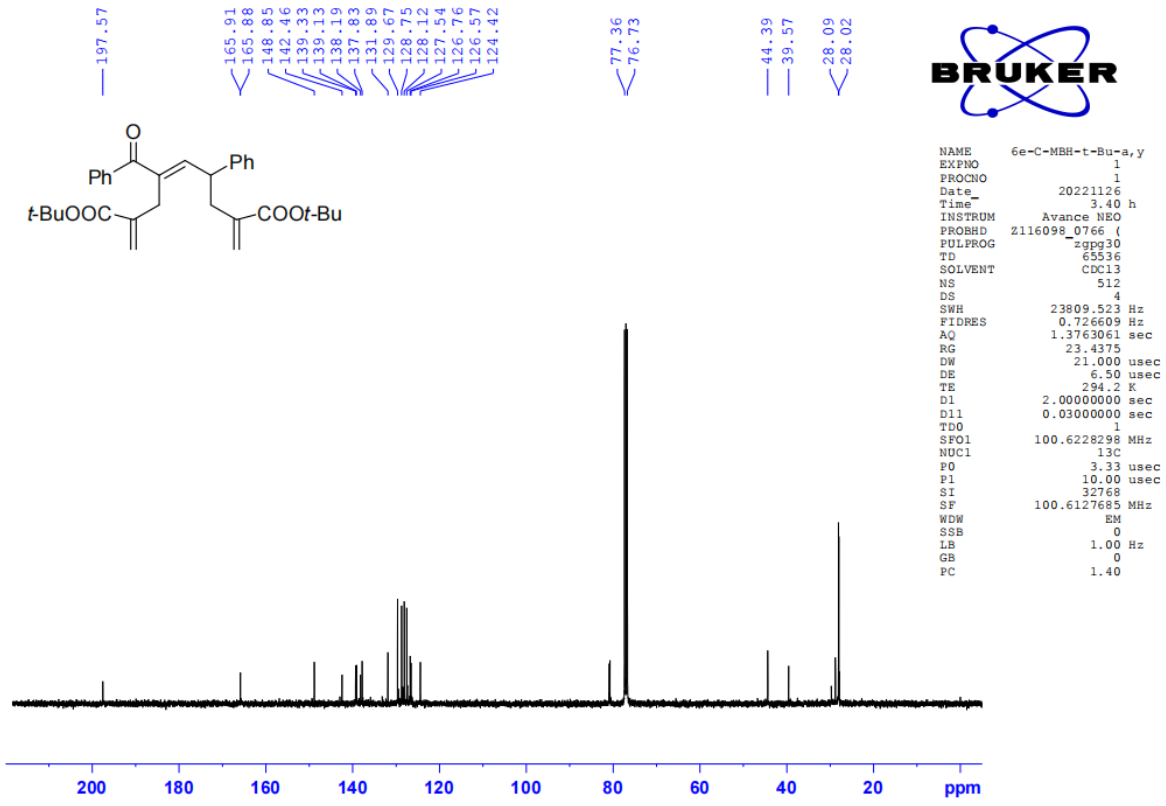
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **4e**



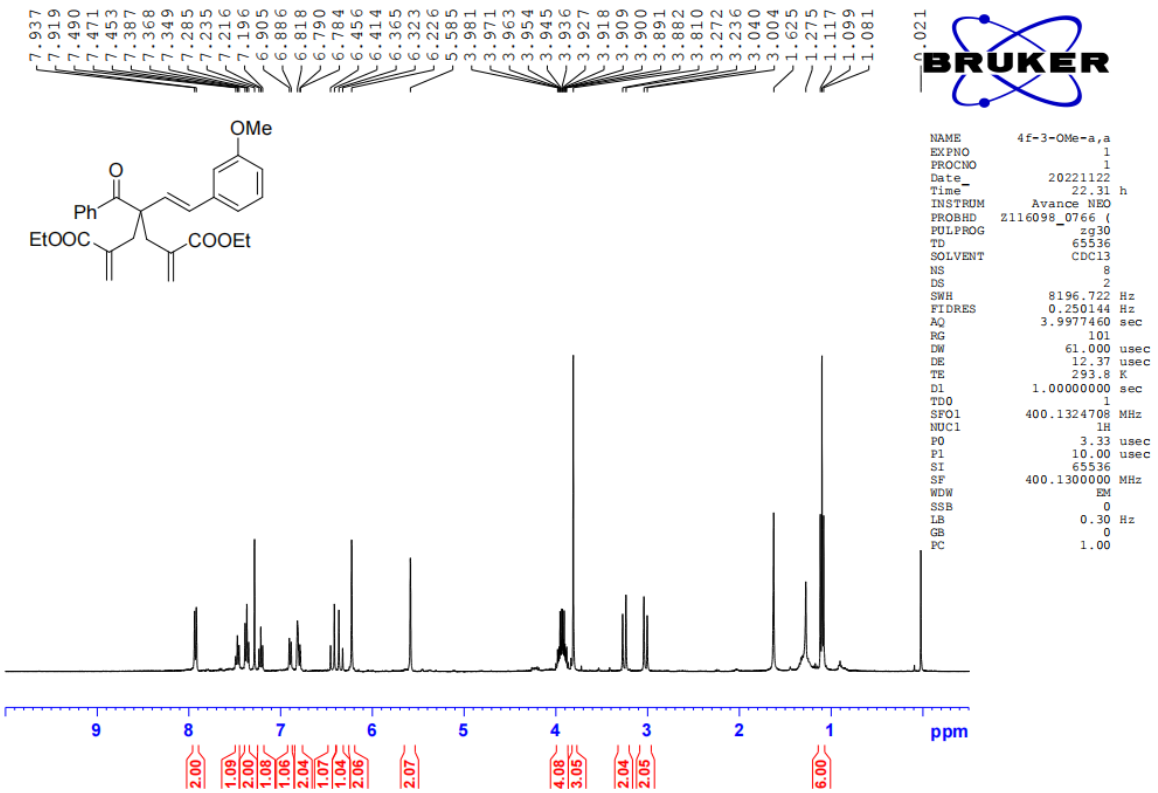



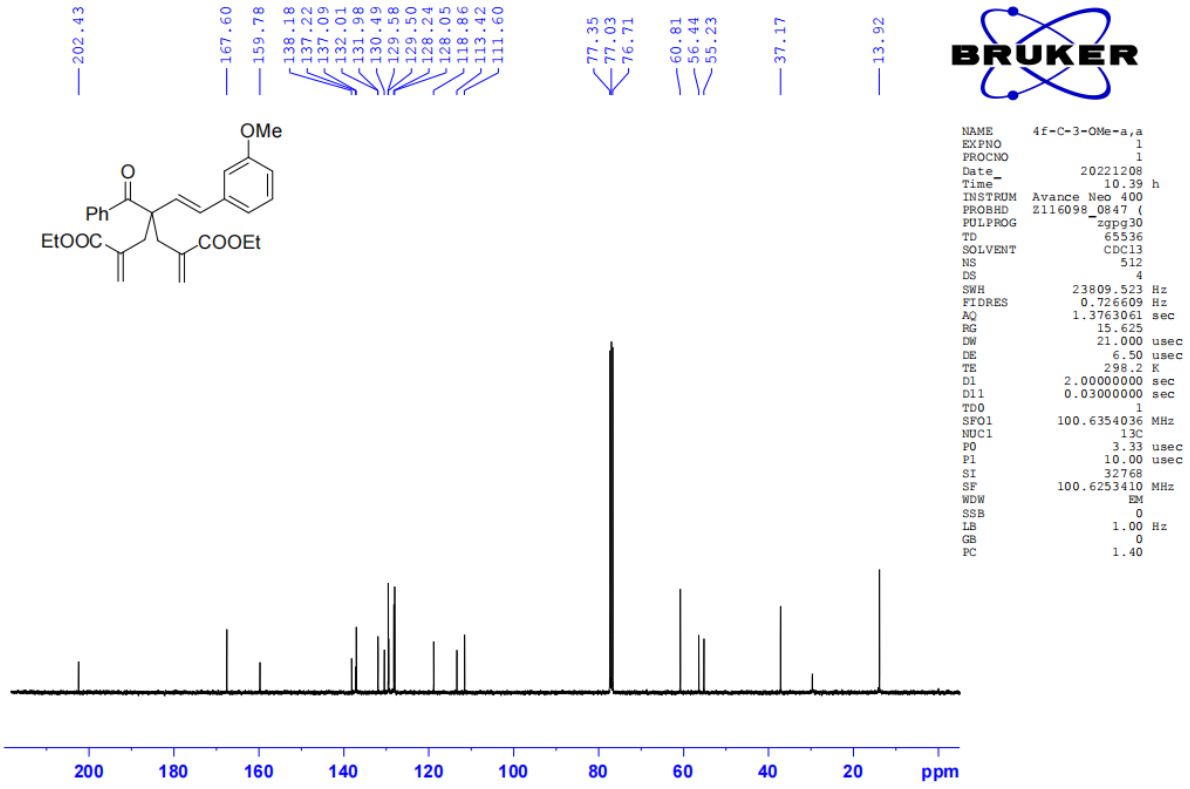
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **6e**



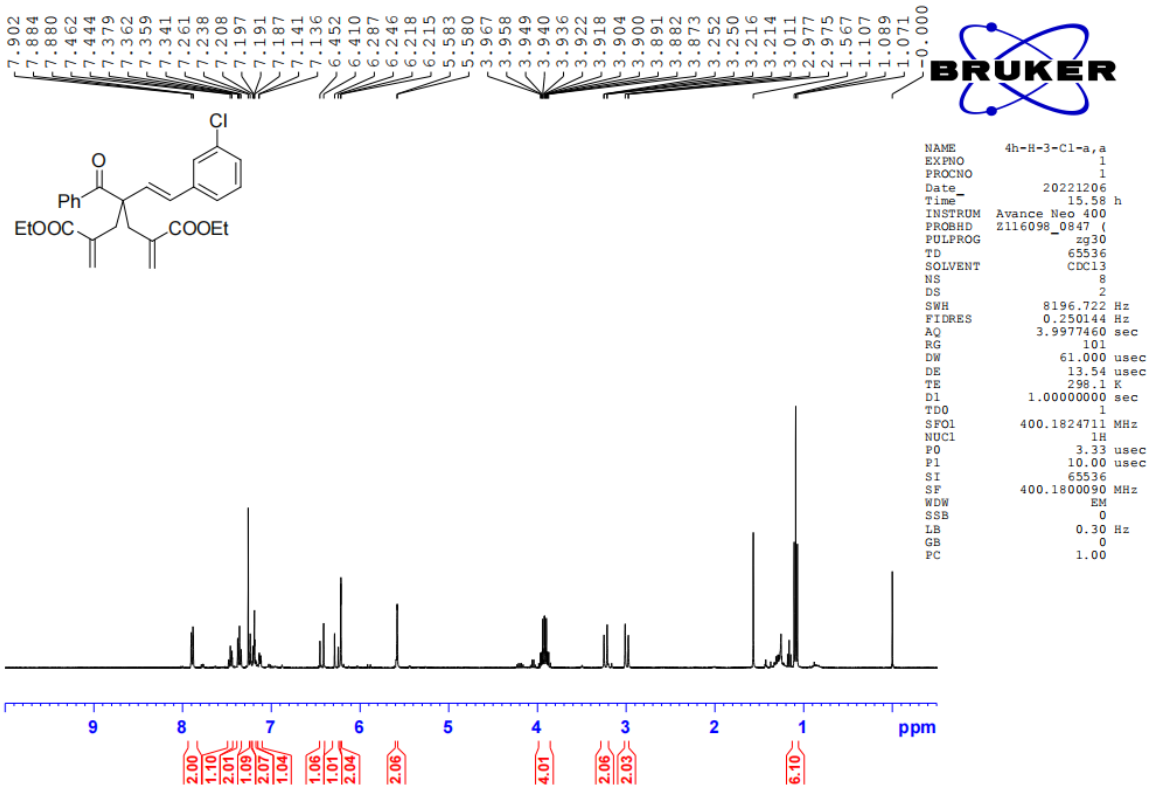



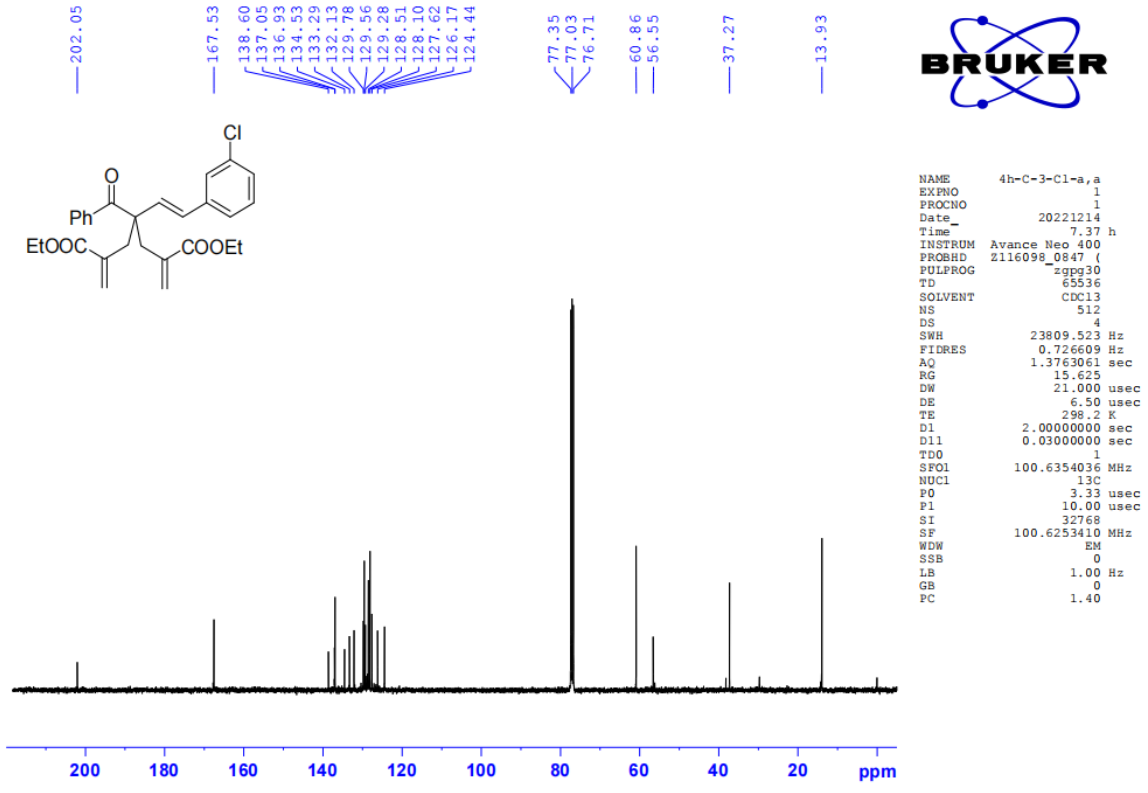
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **4f**



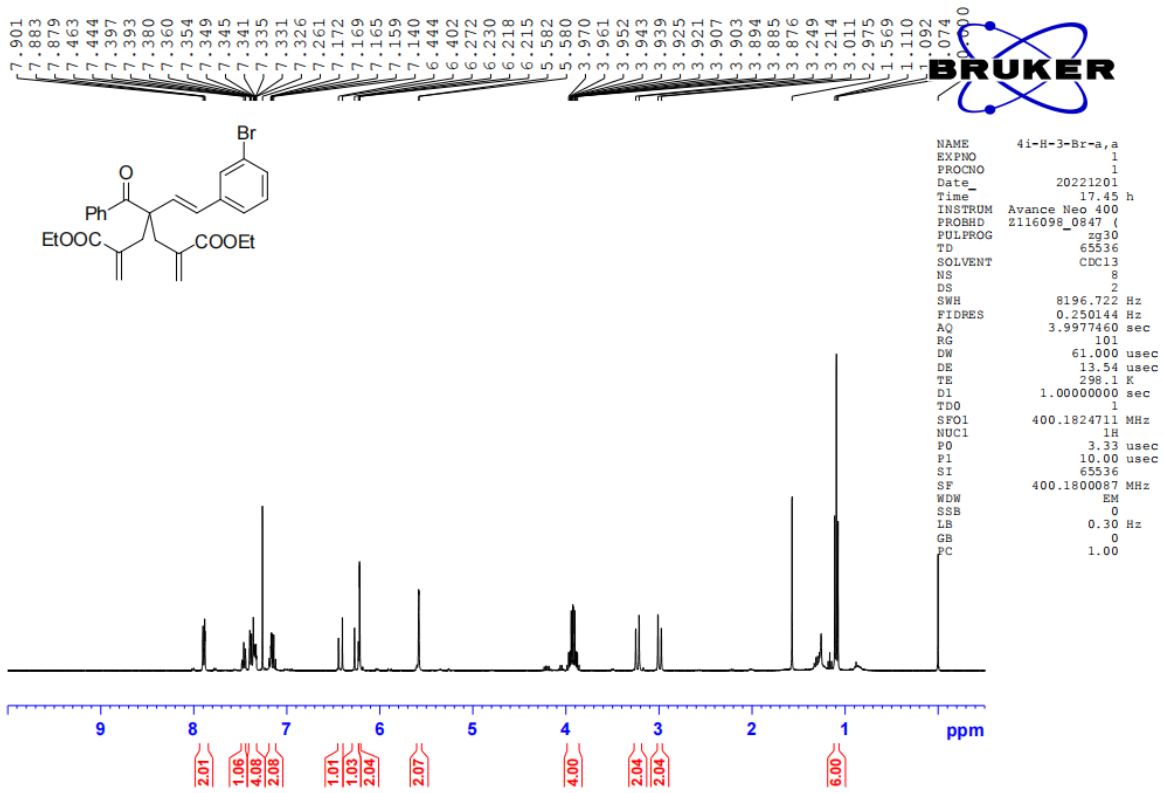



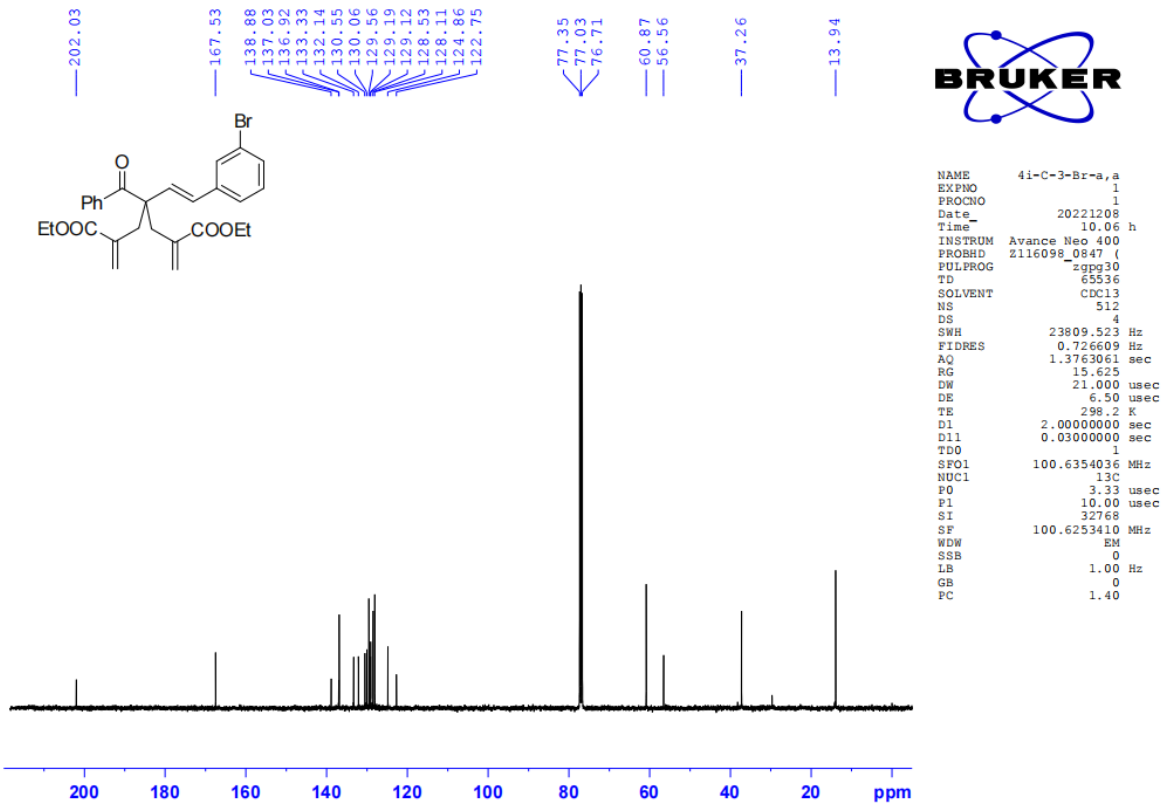
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **4h**



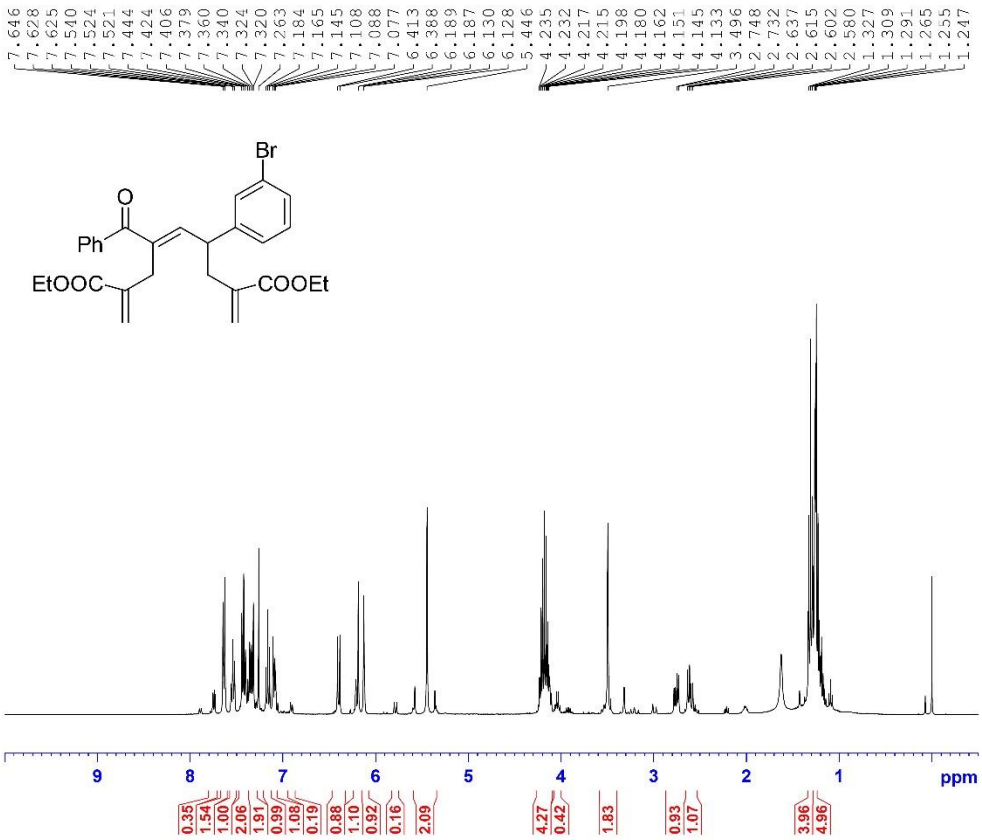



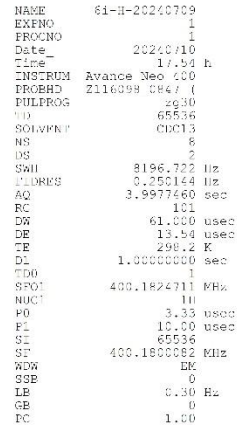
$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **4i**

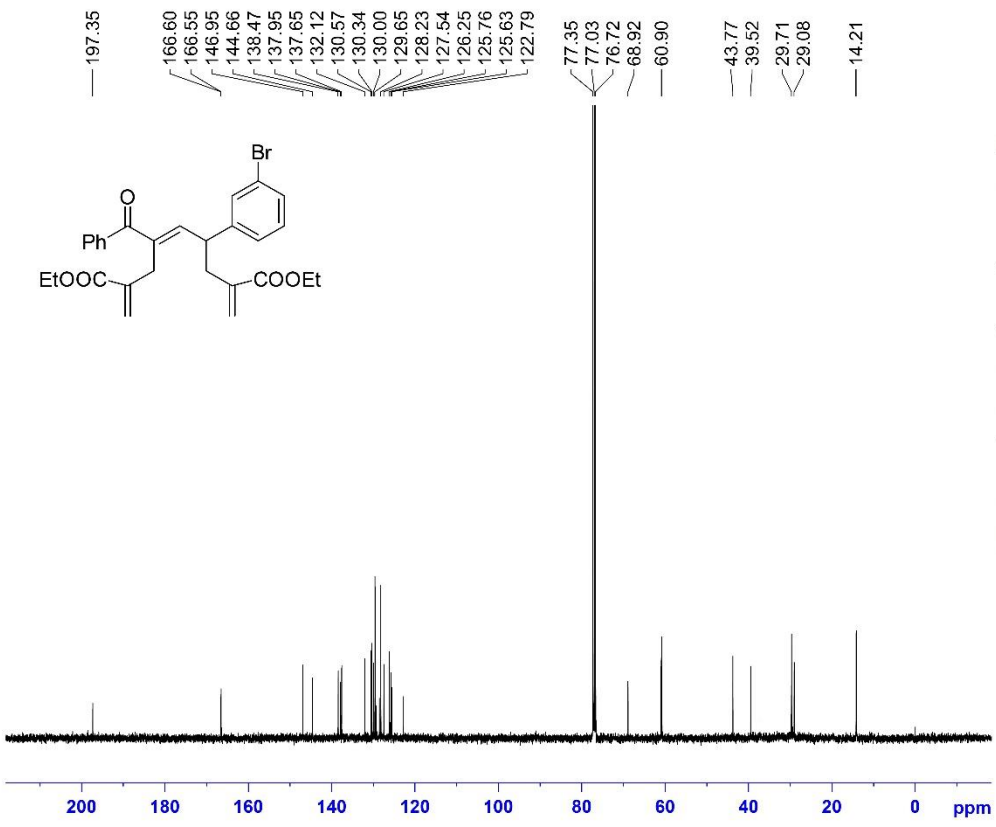


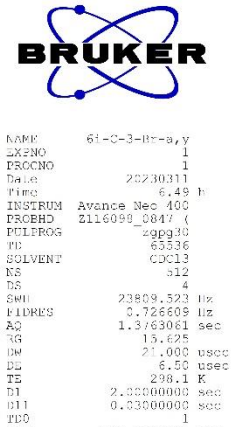



$^{1}$H NMR and $^{13}$C NMR Spectra for Compound **6i**

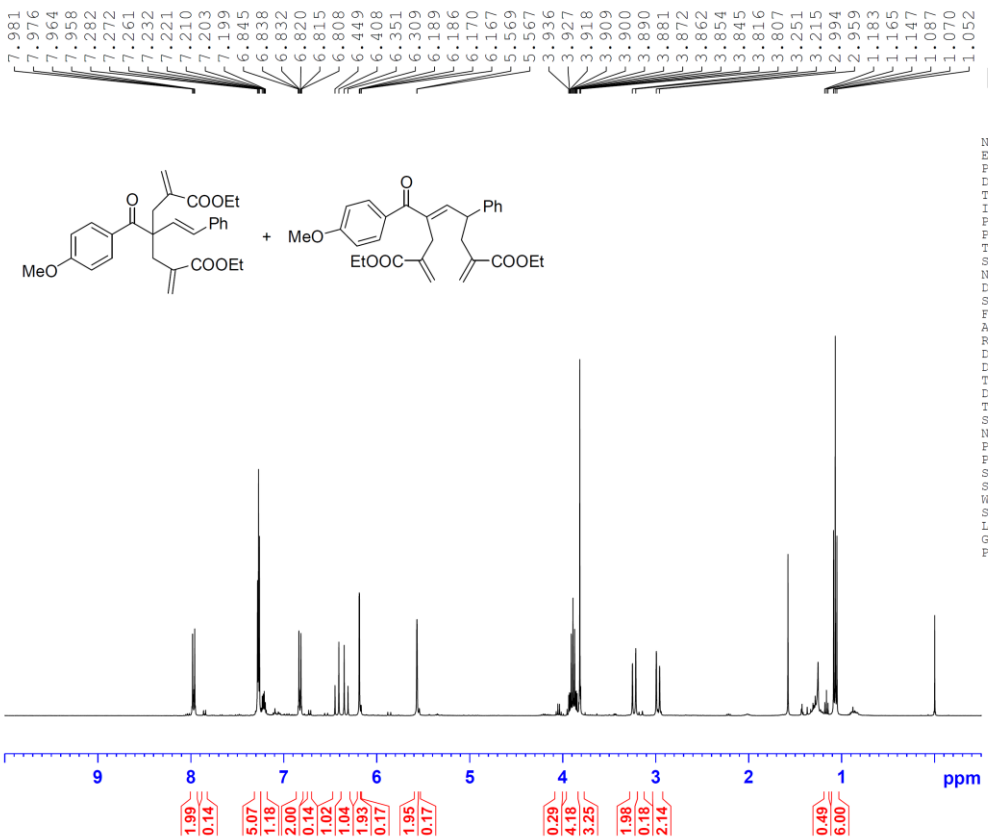


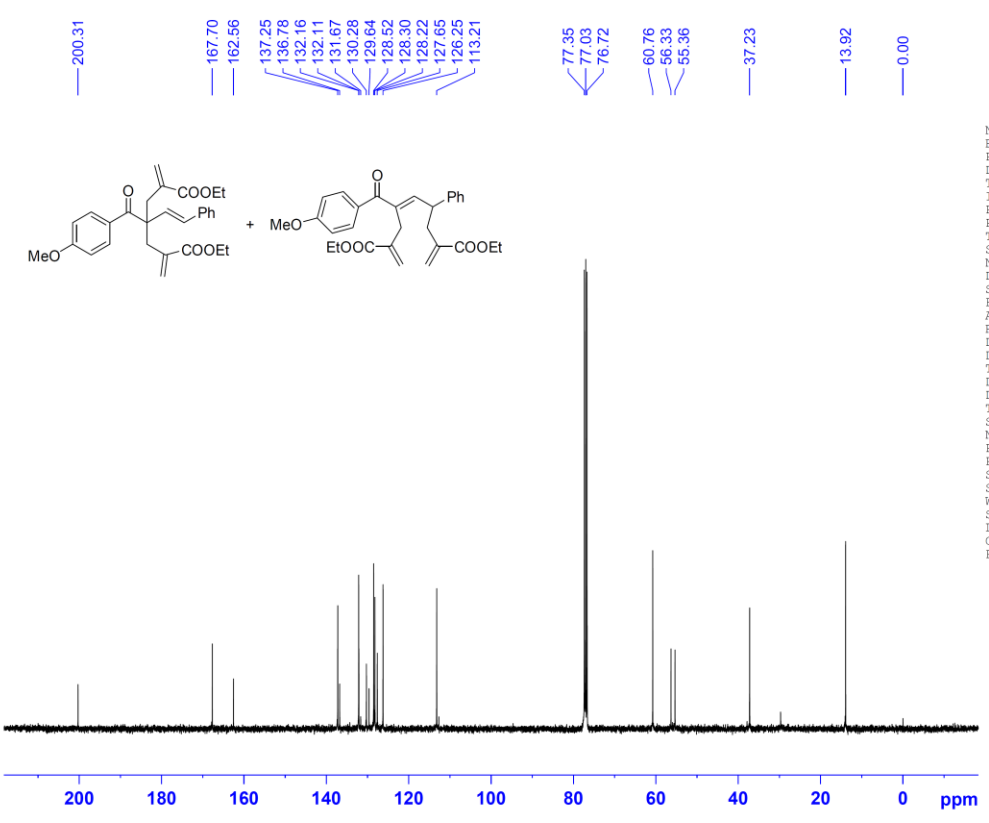



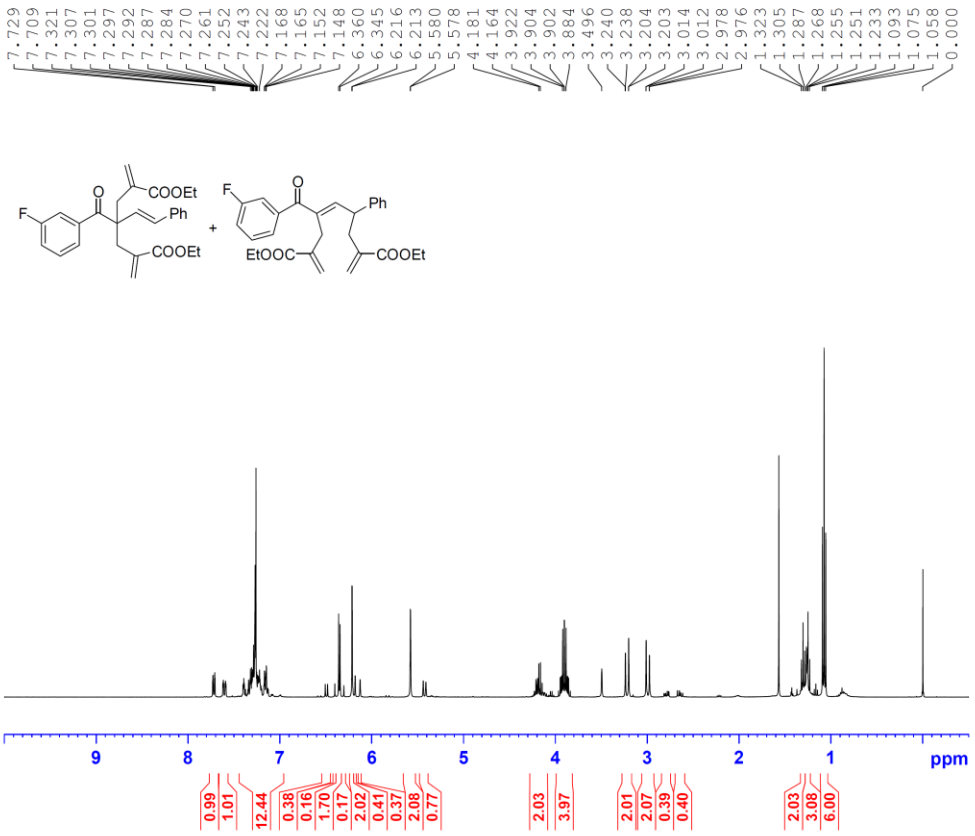



$^{1}$H NMR and $^{13}$C NMR Spectra for Compounds **4k**/**6k**



$^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra for Compounds **4l/6l**




BRUKER

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EXPNO                   1
PROCNO                  1
Date_            20221206
Time                15.44 h
INSTRUM   Avance Neo 400
PROBHD    Z116098_0847 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8196.722 Hz
FIDRES          0.250144 Hz
AQ              3.9977460 sec
RG                   101
DW                61.000 usec
DE                13.54 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1824711 MHz
NUC1                  1H
P0                  3.33 usec
P1                 10.00 usec
SI                 65536
SF            400.1800092 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

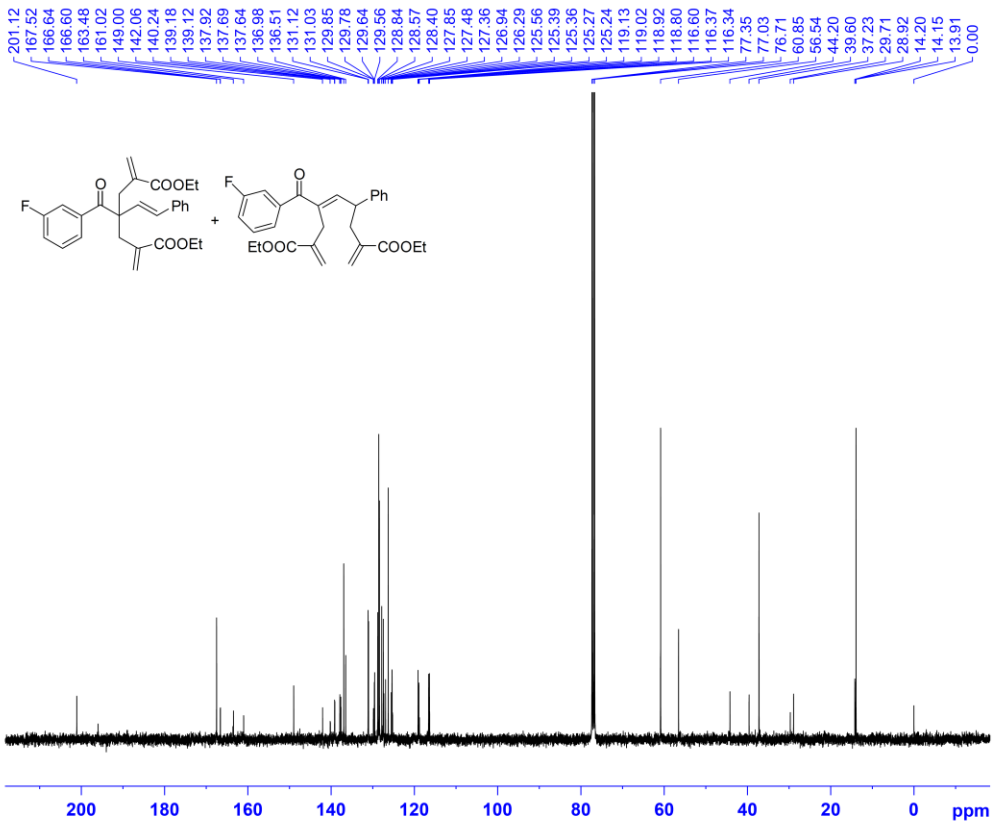


BRUKER

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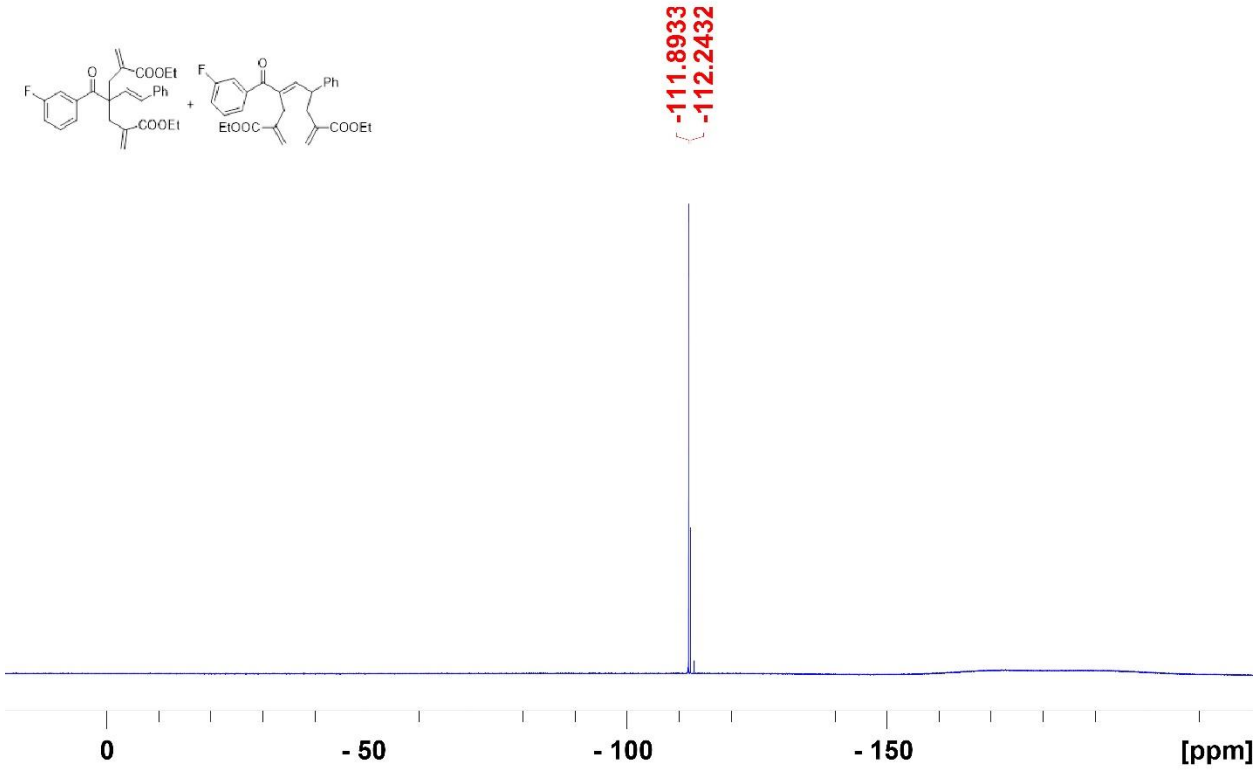
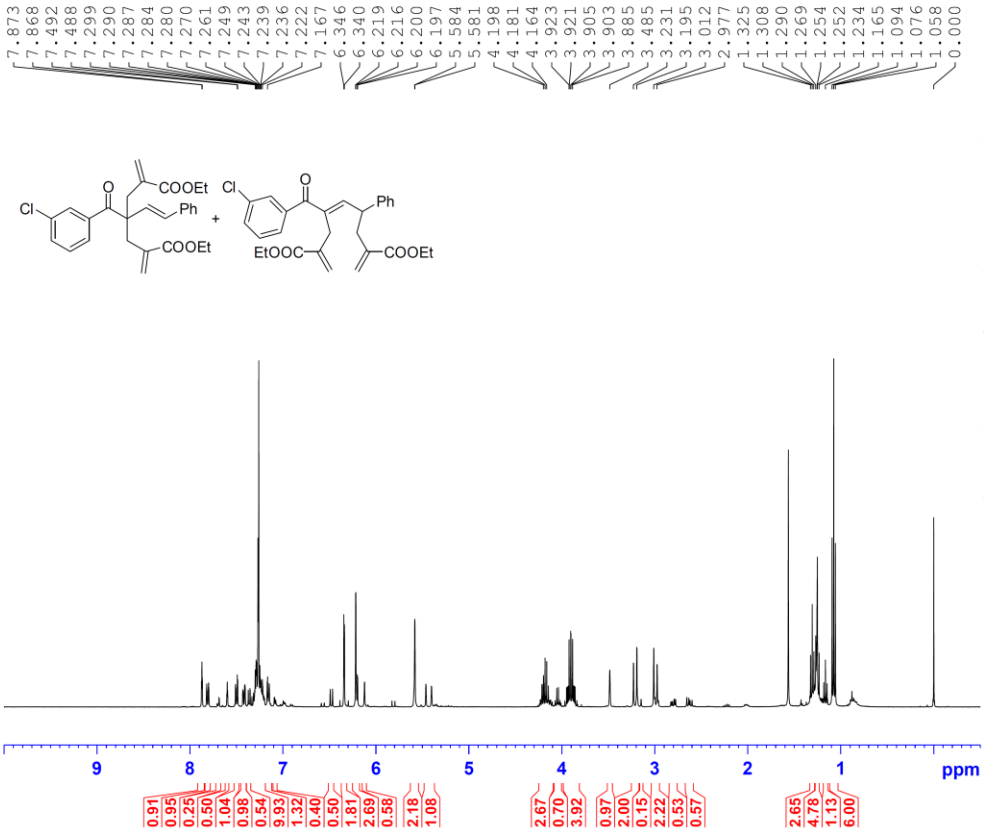
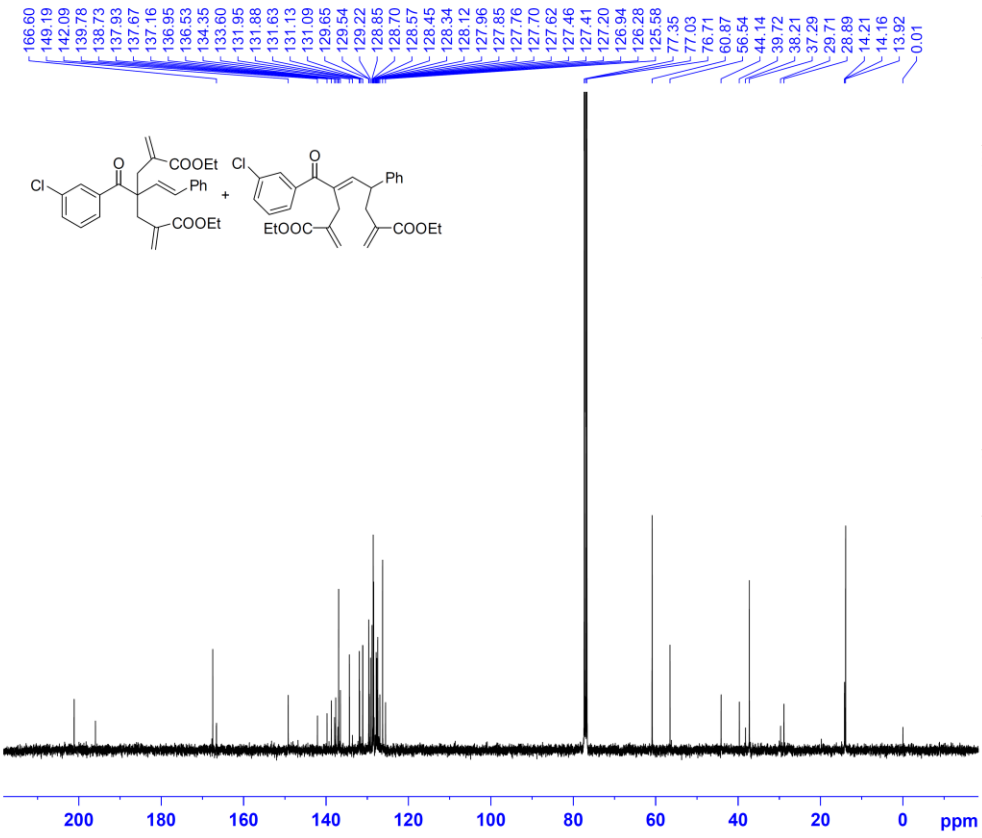
NAME          41+61-3-F-C
EXPNO                   1
PROCNO                  1
Date_            20230220
Time                22.21 h
INSTRUM   Avance Neo 400
PROBHD    Z116098_0847 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            23809.523 Hz
FIDRES          0.726609 Hz
AQ              1.3763061 sec
RG                15.625
DW                21.000 usec
DE                 6.50 usec
TE                298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          100.6354036 MHz
NUC1                  13C
P0                  3.33 usec
P1                 10.00 usec
SI                 32768
SF            100.6253410 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```


-111.8933
-112.2432
0
- 50
- 100
- 150
[ppm]

$^{1}$H NMR and $^{13}$C NMR Spectra for Compounds **4m**/**6m**

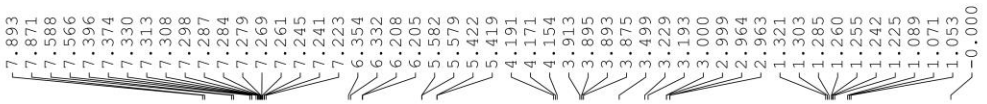


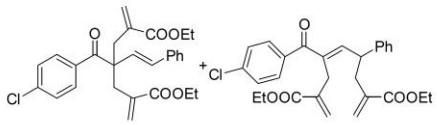

```
NAME          4m+6m-3-Cl-H
EXPNO                1
PROCNO               1
Date_         20221206
Time              15.49 h
INSTRUM   Avance Neo 400
PROBHD    Z116098_0847 (
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           8196.722 Hz
FIDRES        0.250144 Hz
AQ            3.9977460 sec
RG                 101
DW               61.000 usec
DE               13.54 usec
TE                298.1 K
D1            1.00000000 sec
TD0                  1
SFO1        400.1824711 MHz
NUC1               1H
P0                3.33 usec
P1               10.00 usec
SI               65536
SF          400.1800091 MHz
WDW                EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```



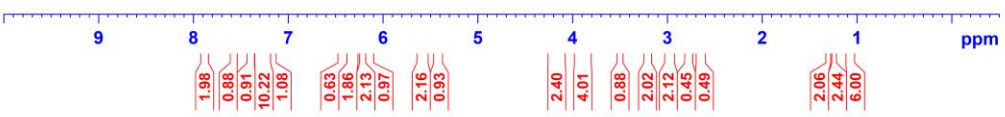

```
NAME          4m+6m-3-Cl-C
EXPNO                1
PROCNO               1
Date_         20230220
Time              22.54 h
INSTRUM   Avance Neo 400
PROBHD    Z116098_0847 (
PULPROG        zgpg30
TD               65536
SOLVENT          CDCl3
NS                 512
DS                   4
SWH          23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3763061 sec
RG                15.625
DW               21.000 usec
DE                6.50 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1
SFO1        100.6354036 MHz
NUC1               13C
P0                3.33 usec
P1               10.00 usec
SI               32768
SF          100.6253410 MHz
WDW                EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

$^{1}$H NMR and $^{13}$C NMR Spectra for Compounds **4n**/**6n**



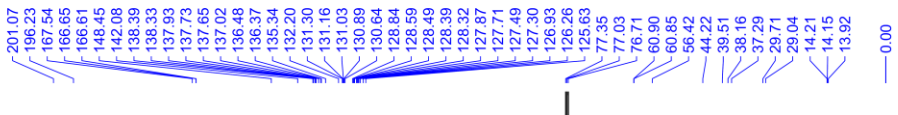



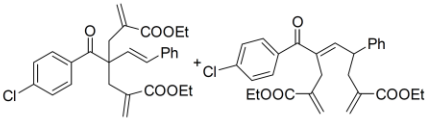

```
NAME          4n+6n-4-Cl-H
EXPNO                    1
PROCNO                   1
Date_             20221206
Time                 15.53 h
INSTRUM      Avance Neo 400
PROBHD       Z116098_0847 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH               8196.722 Hz
FIDRES            0.250144 Hz
AQ                3.9977460 sec
RG                    101
DW                 61.000 usec
DE                 13.54 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                     1
SFO1           400.1824711 MHz
NUC1                   1H
P0                 3.33 usec
P1                 10.00 usec
SI                  65536
SF             400.1800091 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```





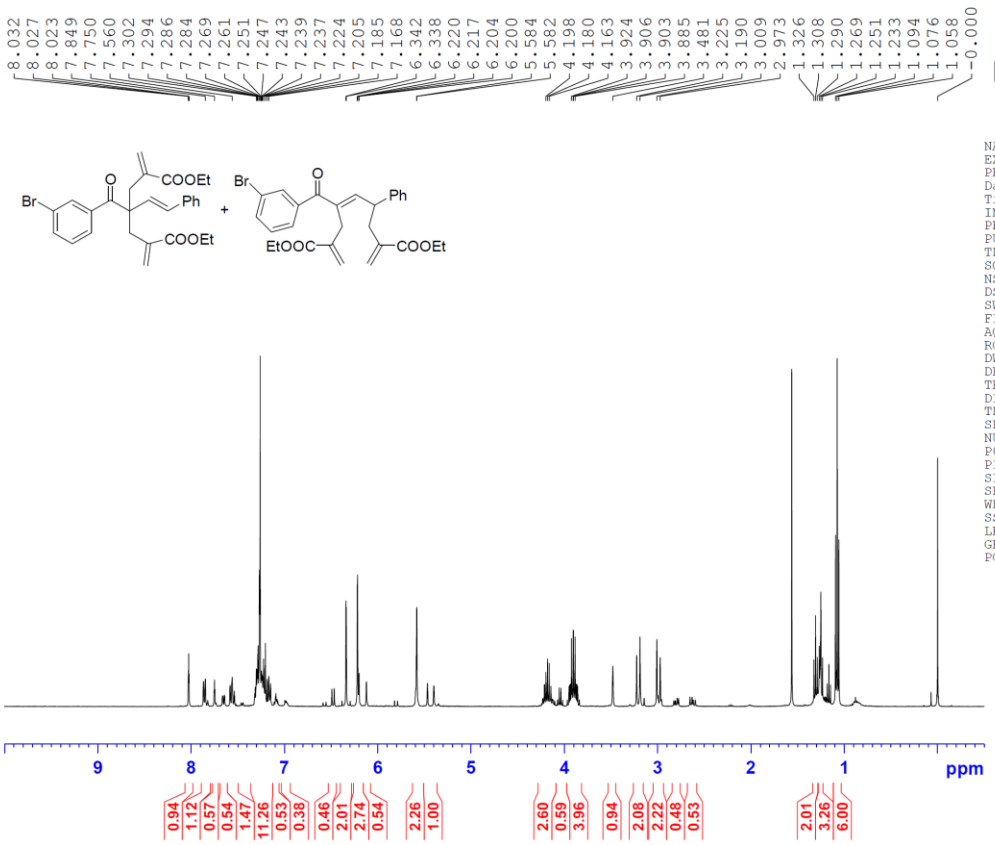


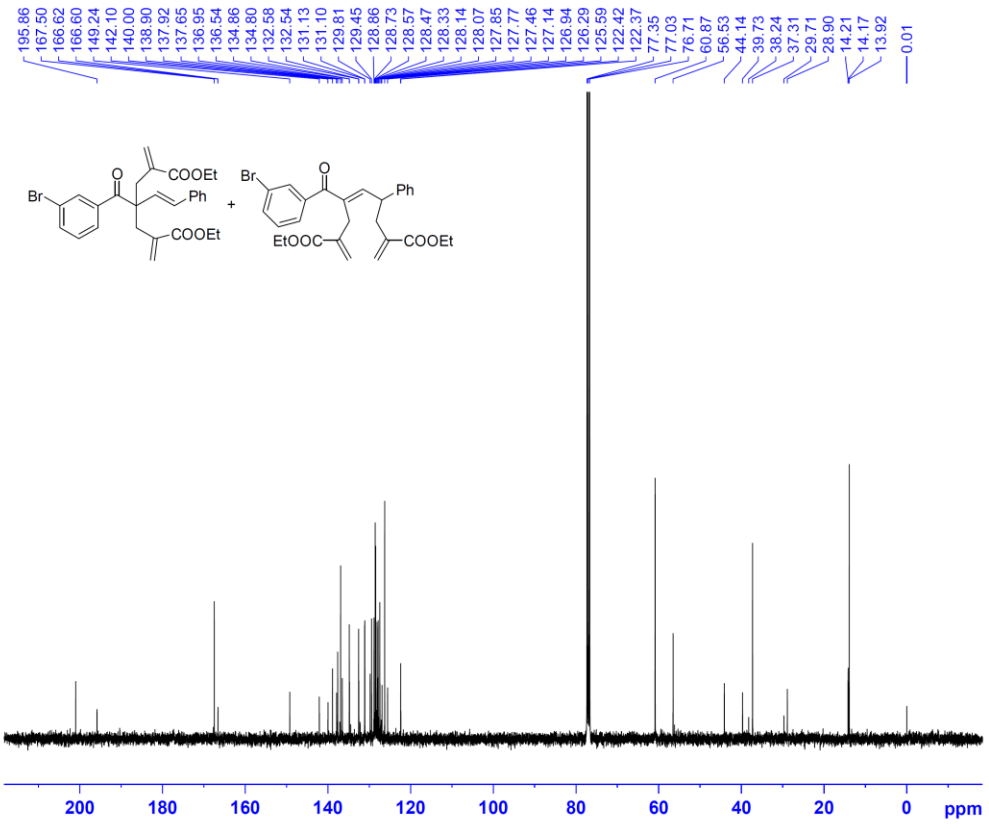


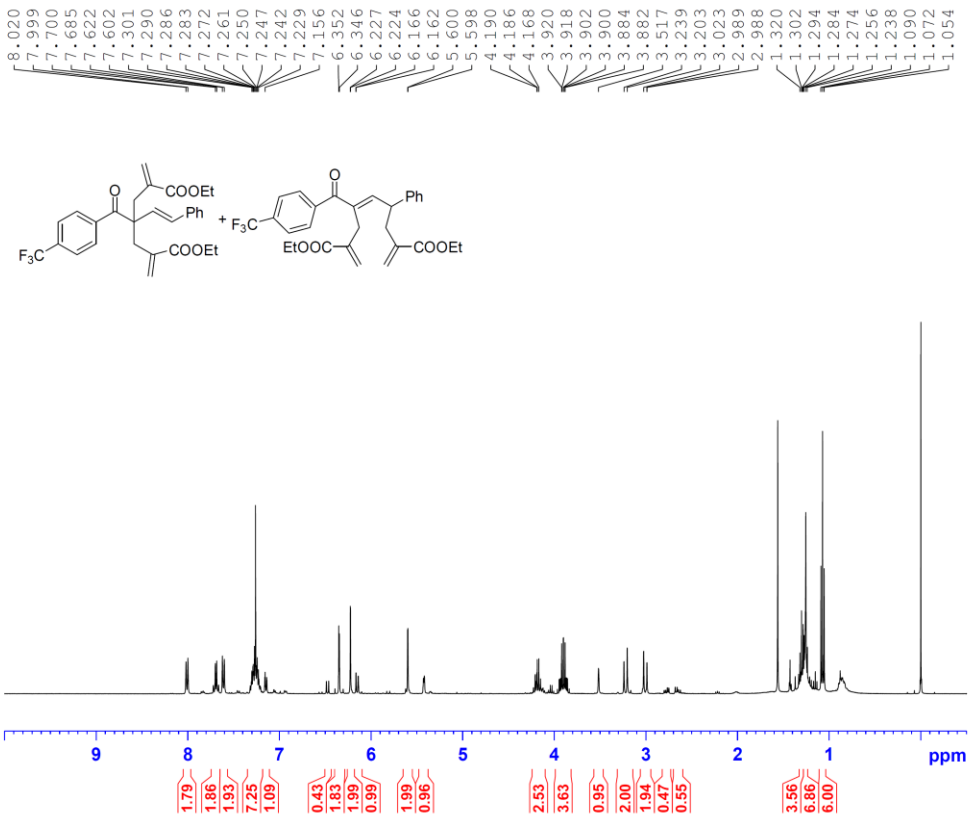

```
NAME          4n+6n-4-Cl-C
EXPNO                    1
PROCNO                   1
Date_             20230220
Time                 23.28 h
INSTRUM      Avance Neo 400
PROBHD       Z116098_0847 (
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH              23809.523 Hz
FIDRES            0.726609 Hz
AQ                1.3763061 sec
RG                   15.625
DW                 21.000 usec
DE                  6.50 usec
TE                 298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1
SFO1           100.6354036 MHz
NUC1                   13C
P0                 3.33 usec
P1                 10.00 usec
SI                  32768
SF             100.6253410 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

$^{1}$H NMR and $^{13}$C NMR Spectra for Compounds **4o**/**6o**

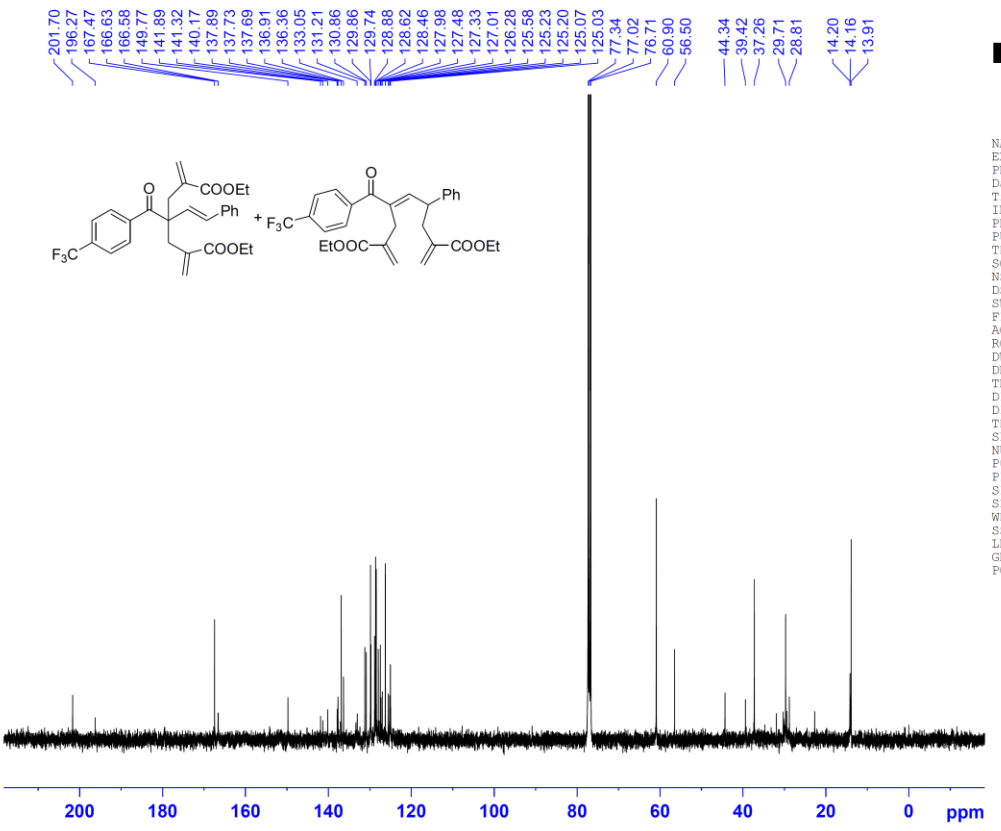


$^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra for Compounds **4p**/**6p**




```
NAME          4p+6p-CF3-H
EXPNO                   1
PROCNO                  1
Date_            20230220
Time               17.54 h
INSTRUM   Avance Neo 400
PROBHD    Z116098_0847 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8196.722 Hz
FIDRES          0.250144 Hz
AQ              3.9977460 sec
RG                   101
DW                61.000 usec
DE                13.54 usec
TE                298.2 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1824711 MHz
NUC1                  1H
P0                 3.33 usec
P1                10.00 usec
SI                 65536
SF            400.1800089 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

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EXPNO                   1
PROCNO                  1
Date_            20230309
Time               17.59 h
INSTRUM   Avance Neo 400
PROBHD    Z116098_0847 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            23809.523 Hz
FIDRES          0.726609 Hz
AQ              1.3763061 sec
RG                15.625
DW                21.000 usec
DE                 6.50 usec
TE                298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          100.6354036 MHz
NUC1                  13C
P0                 3.33 usec
P1                10.00 usec
SI                 32768
SF            100.6253410 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```
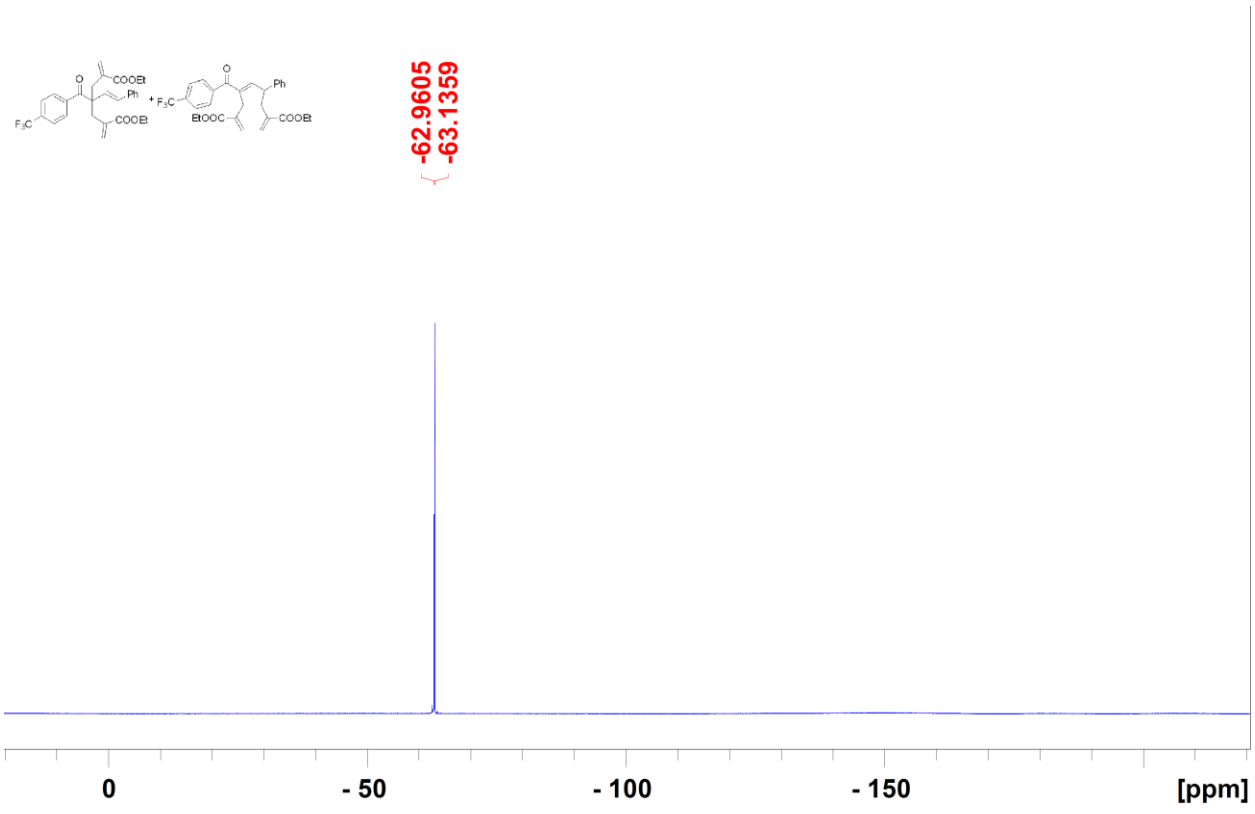
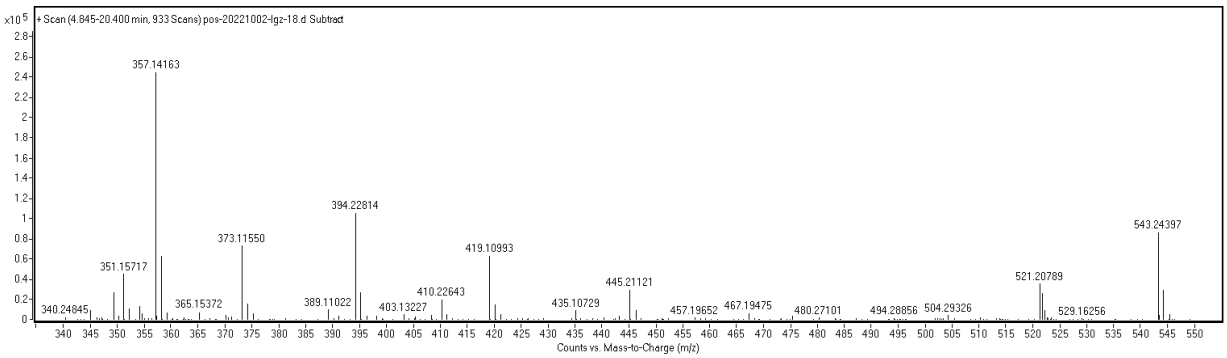
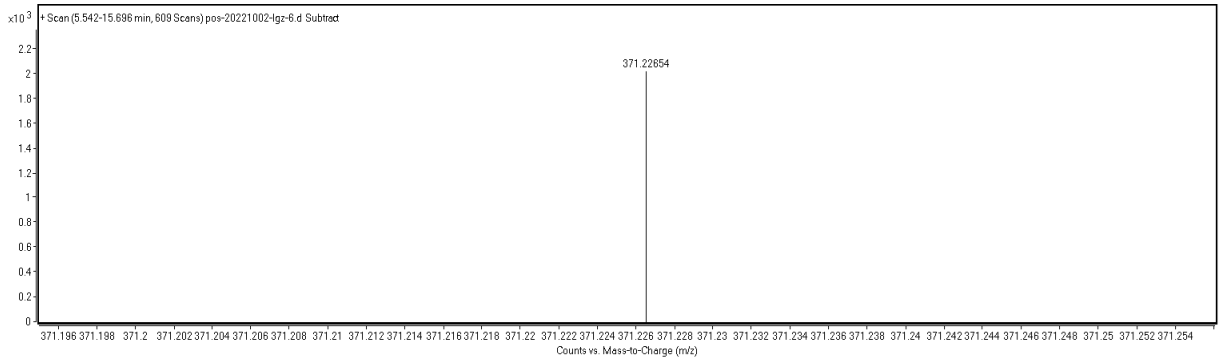


-62.9605
-63.1359
0
- 50
- 100
- 150
[ppm]

## X. Copes of HRMS for all new compounds

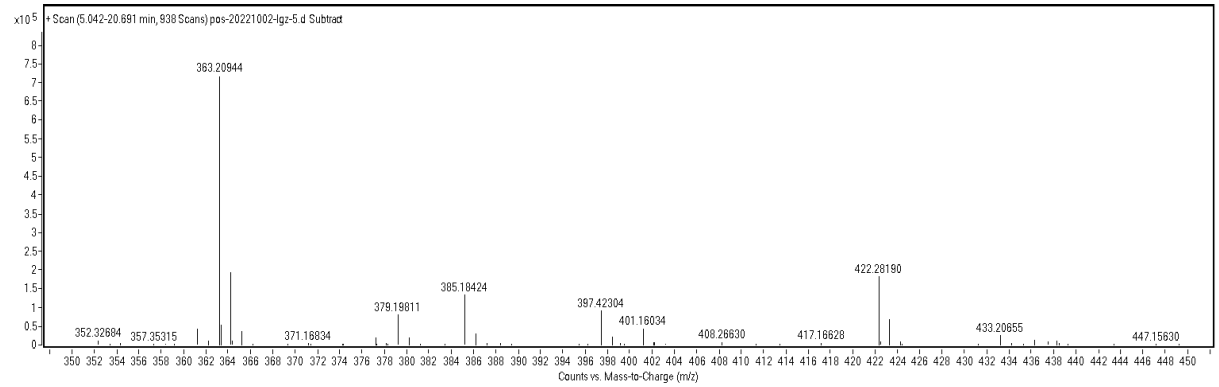
HRMS for Compound **3a**



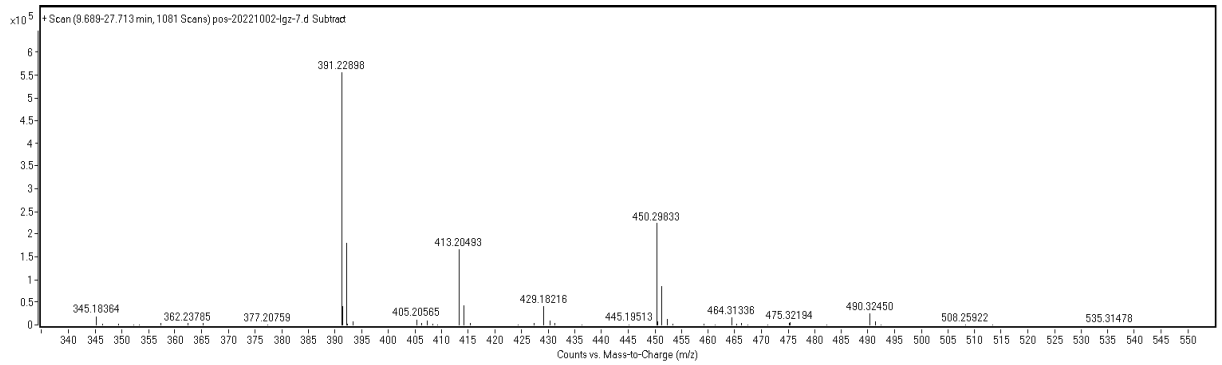

HRMS for Compound **3b**



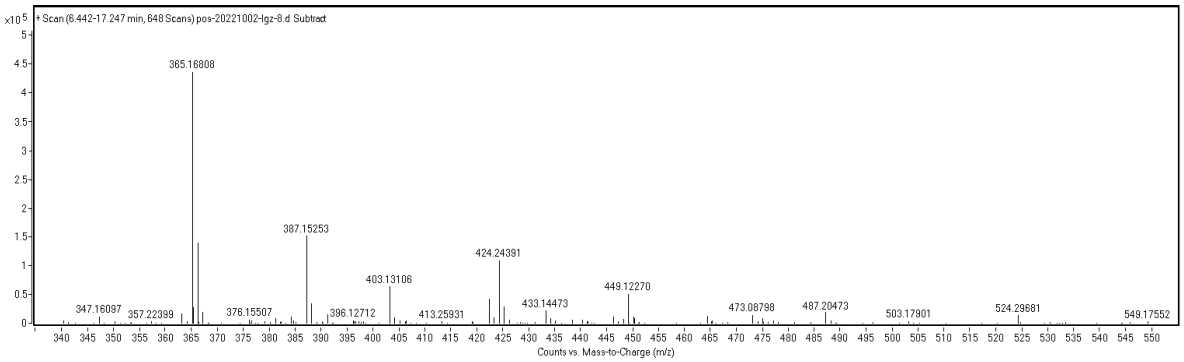

HRMS for Compound **3c**



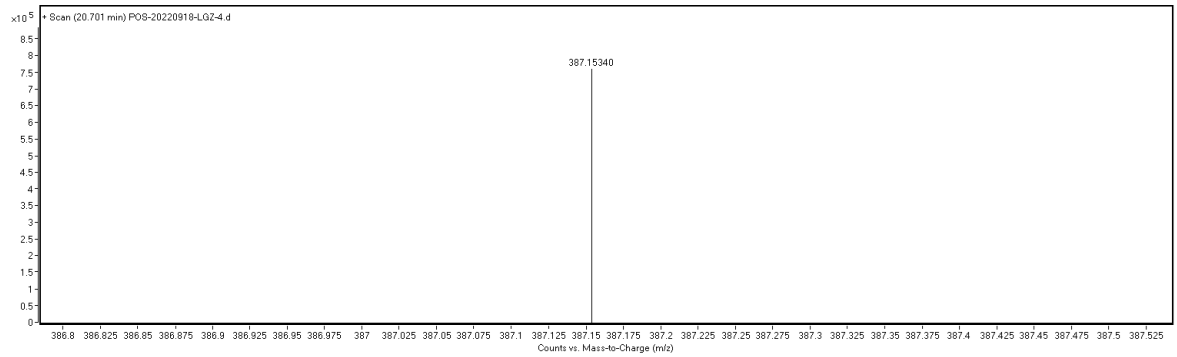

HRMS for Compound **3d**



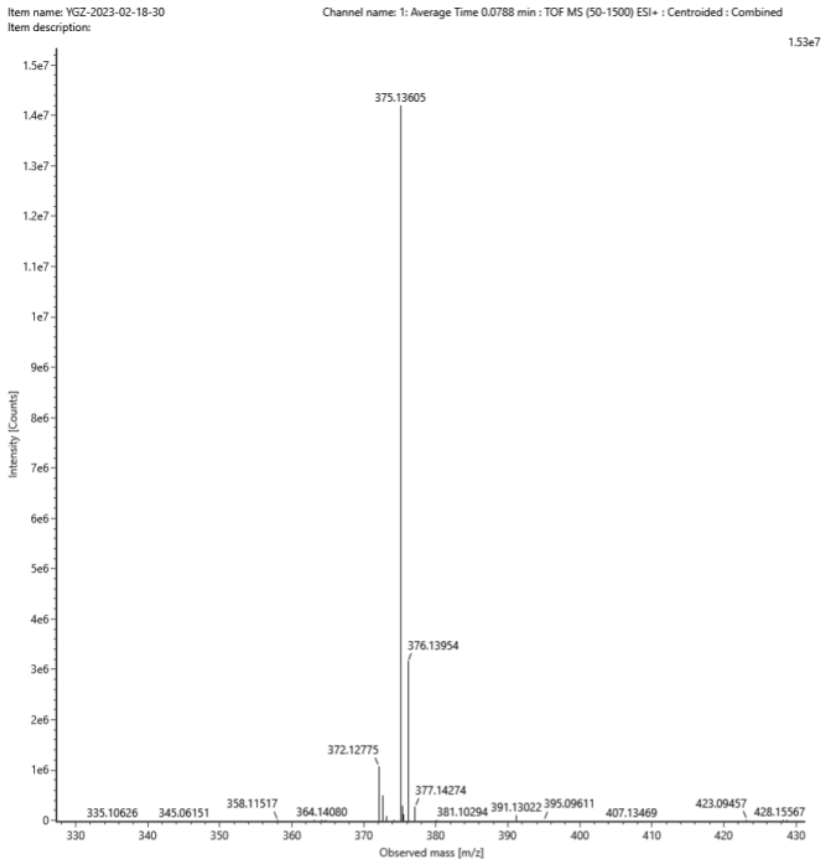
HRMS for Compound **3e**



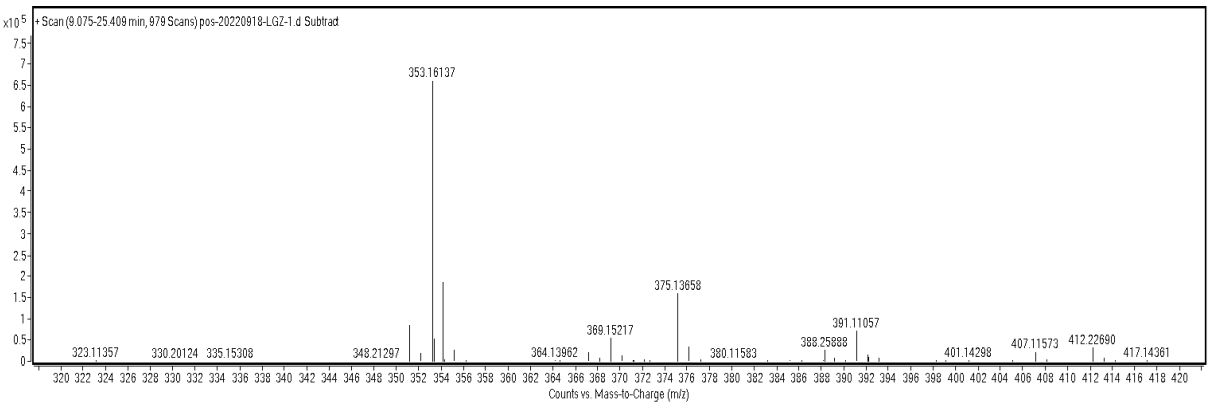

HRMS for Compound **3f**



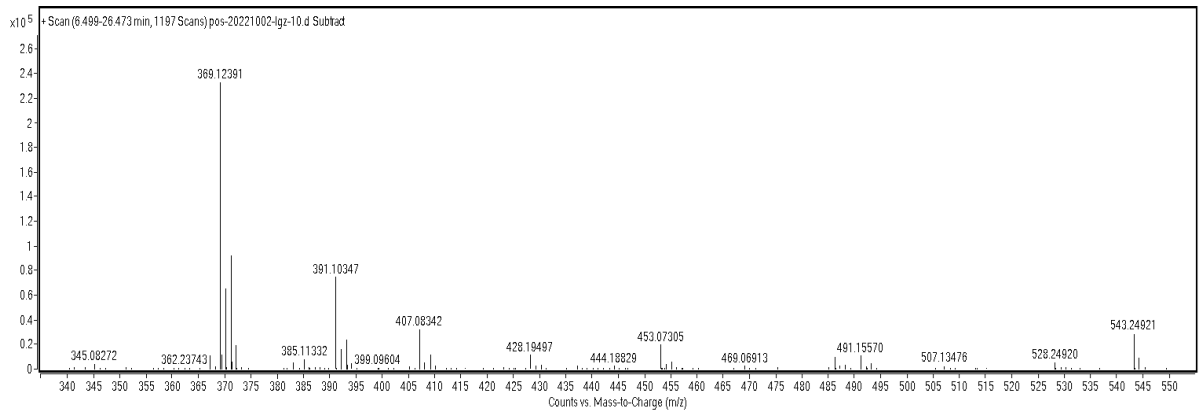

HRMS for Compound **3g**



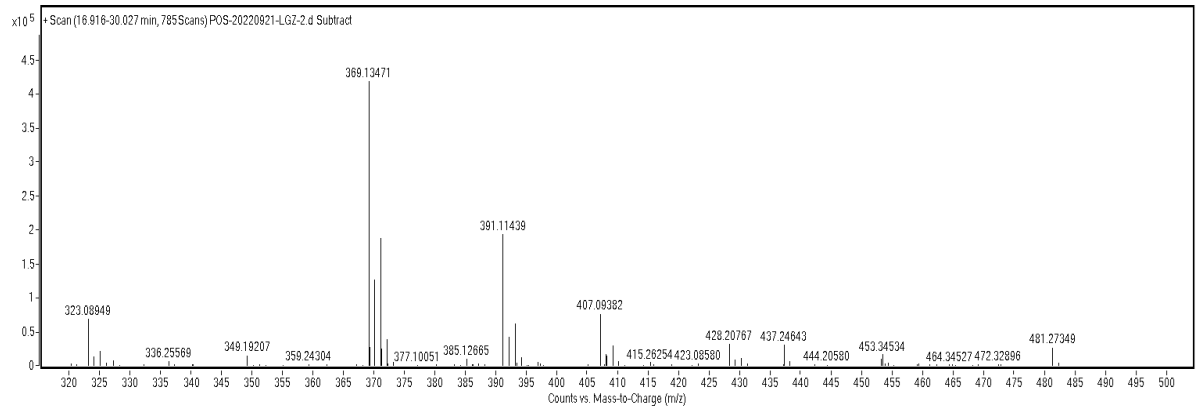
HRMS for Compound **3h**



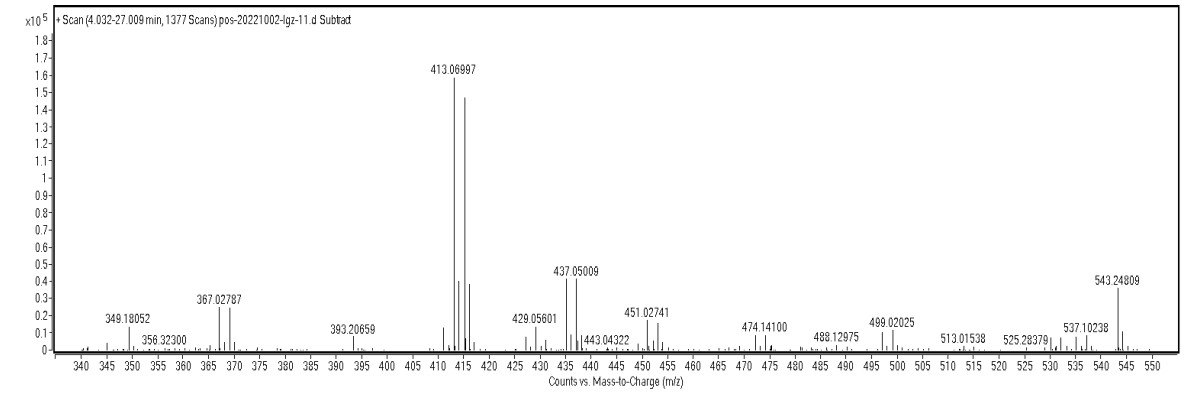

HRMS for Compound **3i**



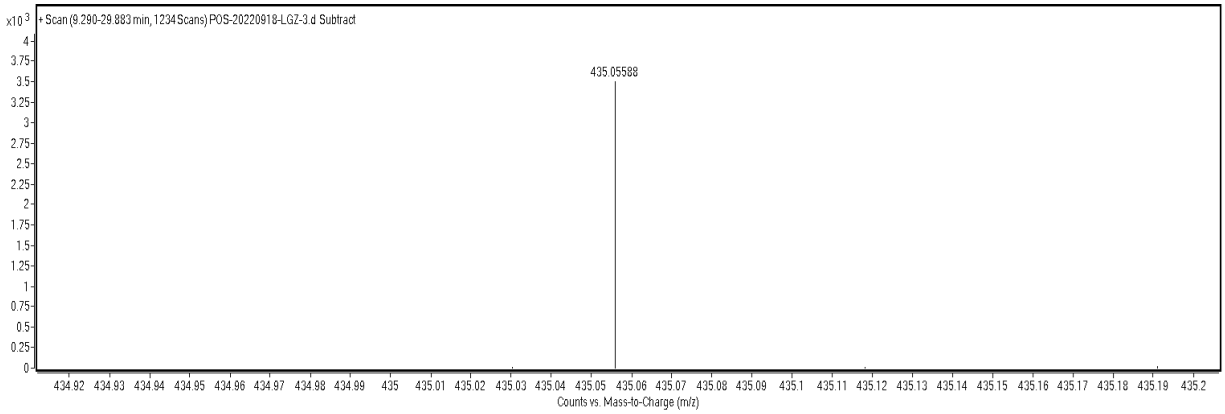

HRMS for Compound **3j**



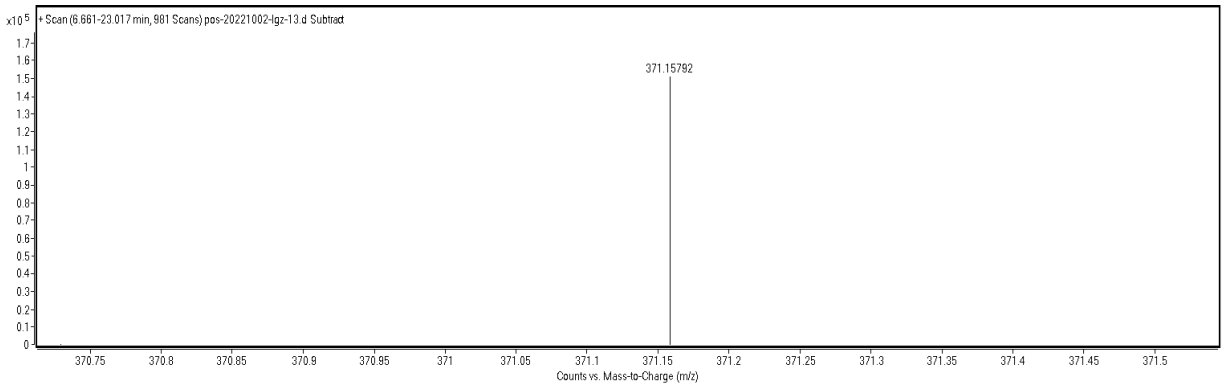

HRMS for Compound **3k**



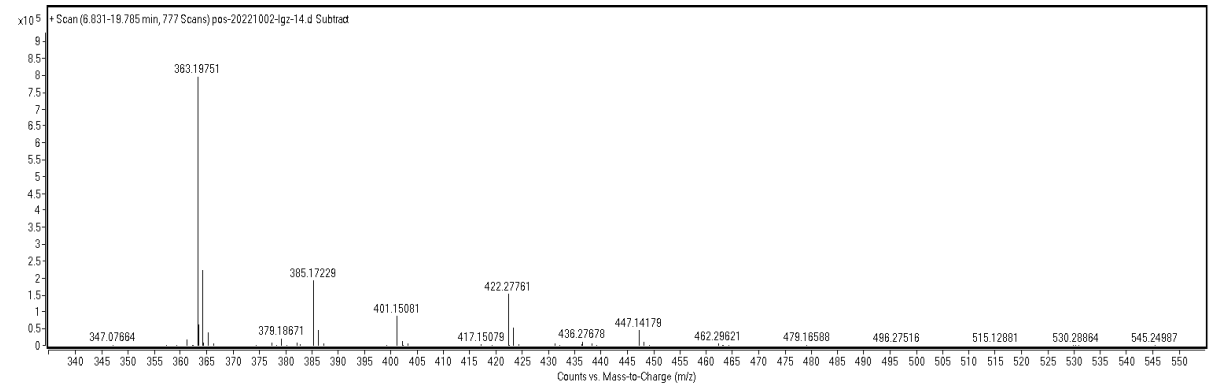
HRMS for Compound **3l**



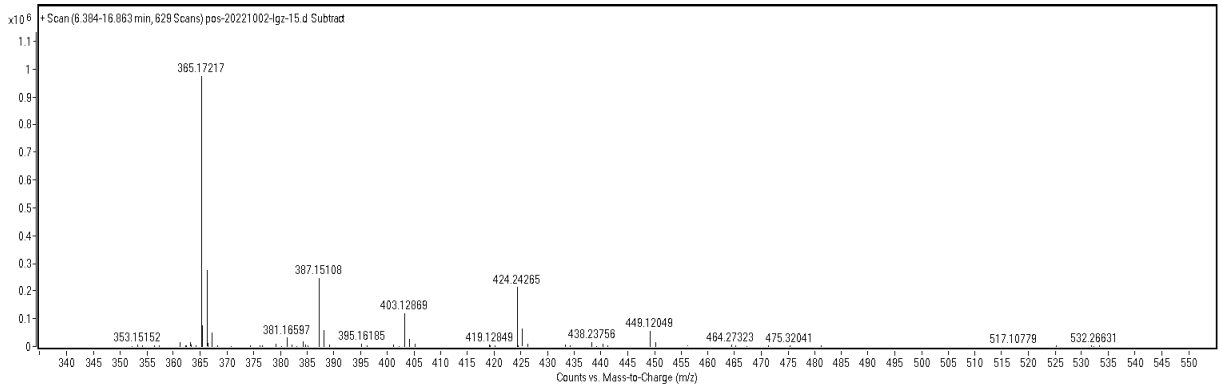

HRMS for Compound **3m**



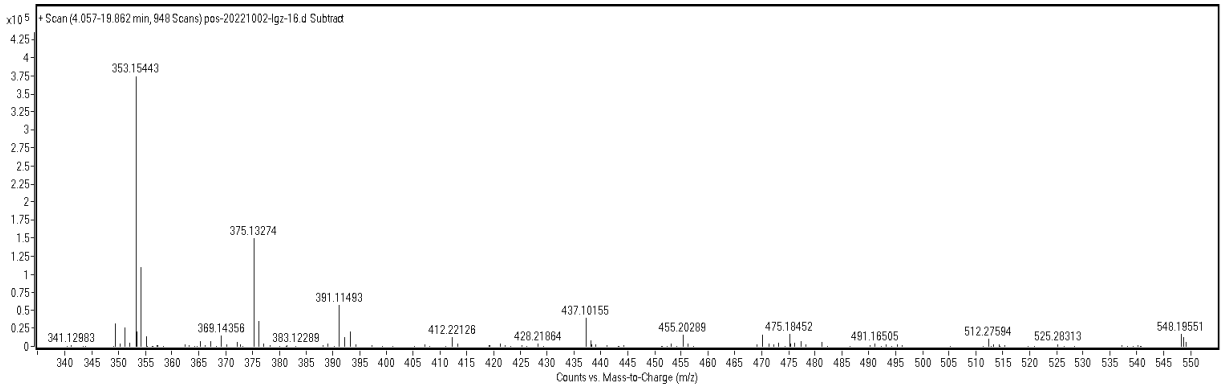

HRMS for Compound **3n**



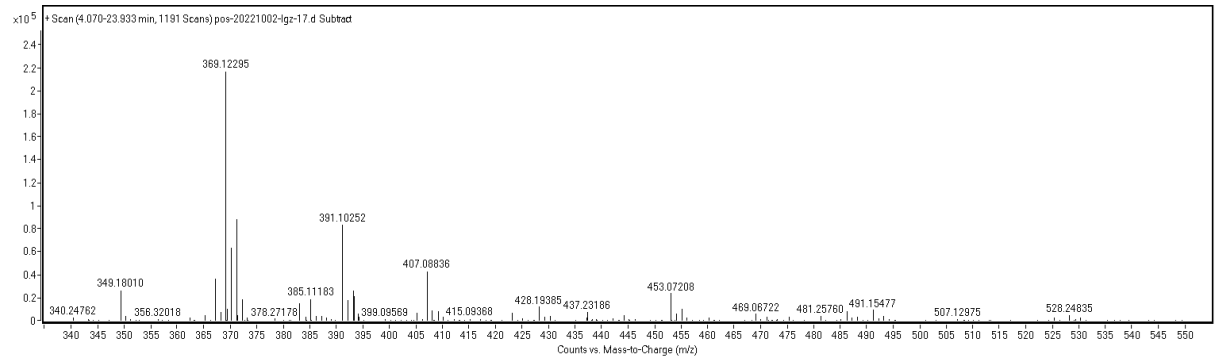

HRMS for Compound **3o**



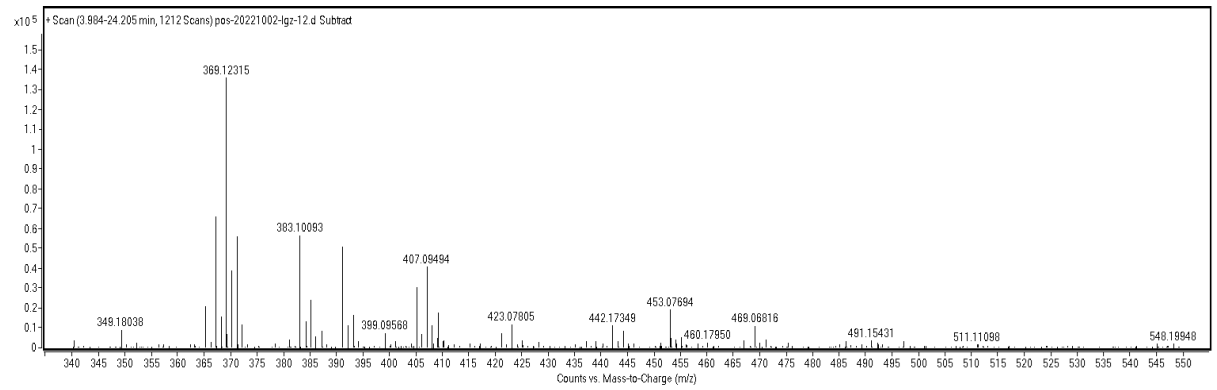
HRMS for Compound **3p**



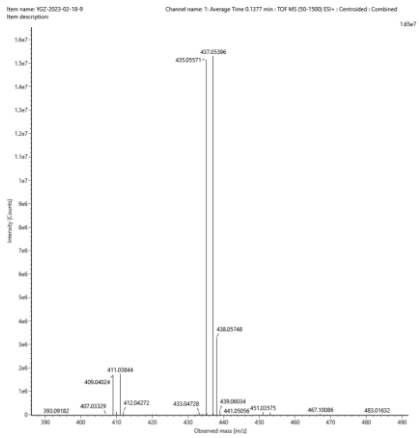

HRMS for Compound **3q**



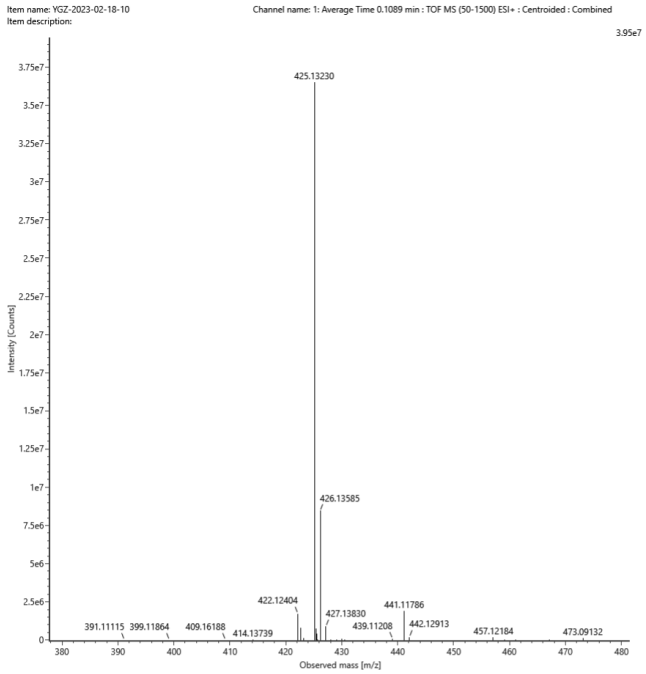

HRMS for Compound **3r**



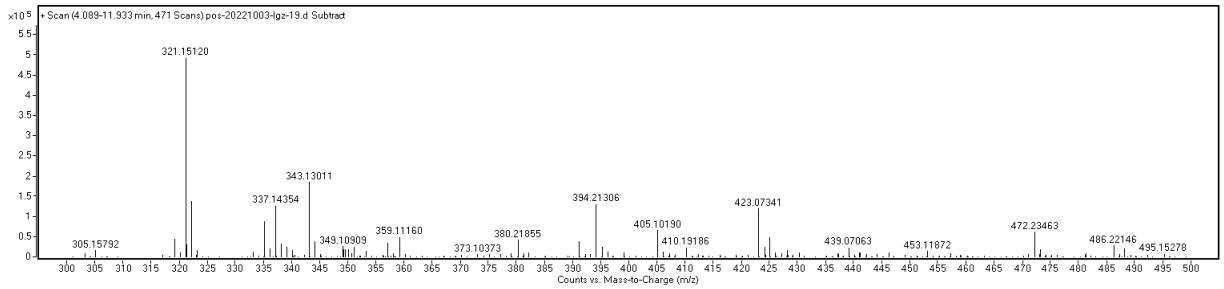

HRMS for Compound **3s**



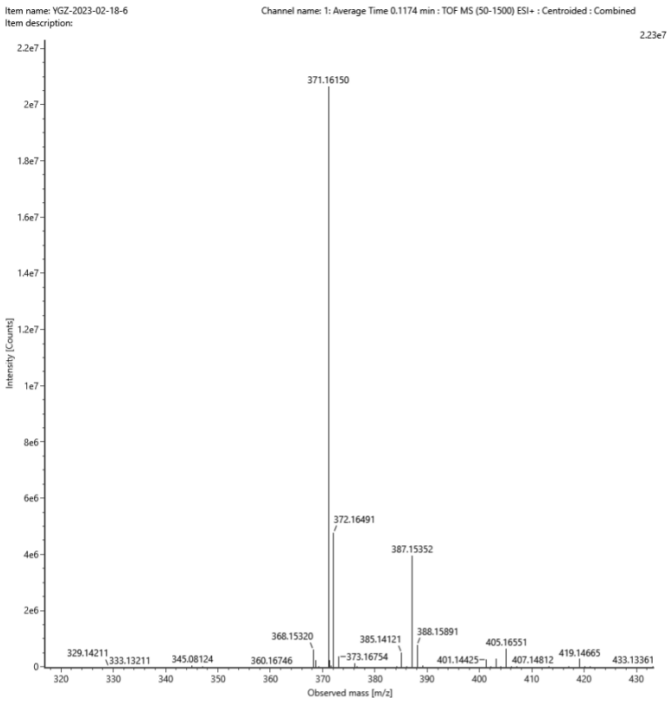
HRMS for Compound **3t**



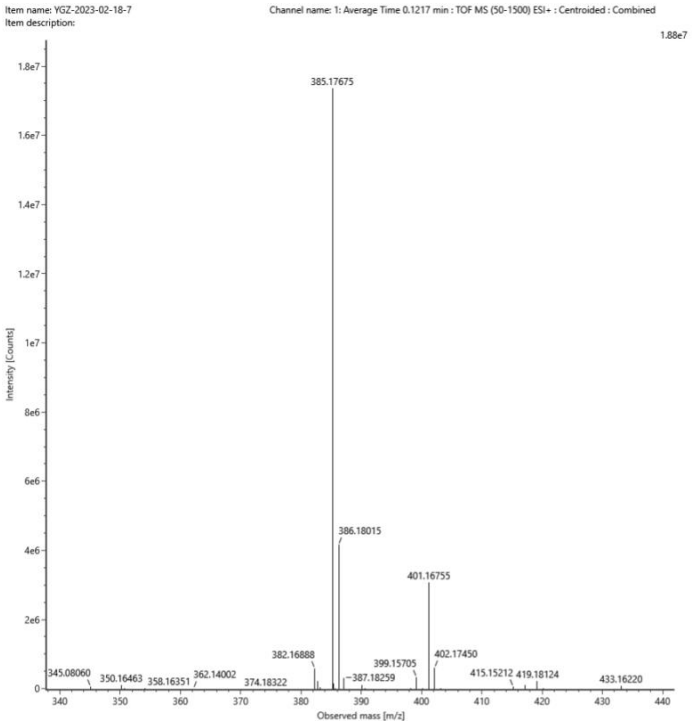

HRMS for Compound **5a**



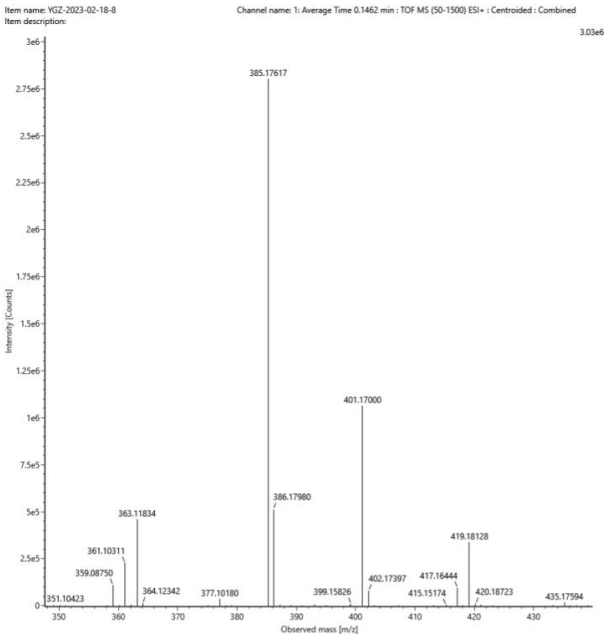

HRMS for Compound **5b**



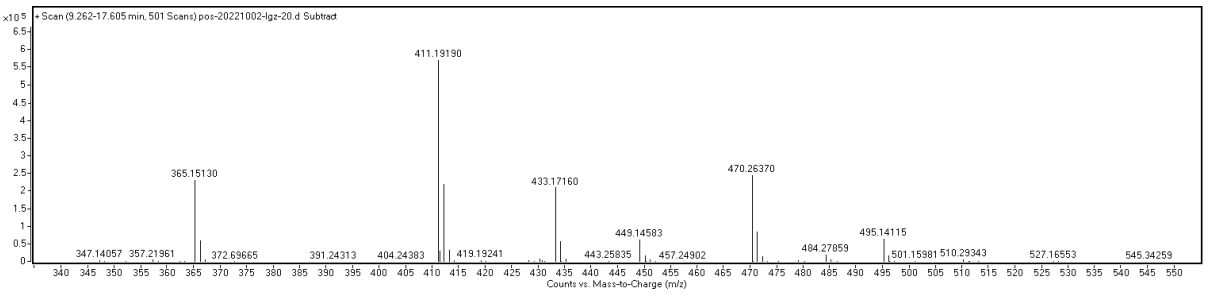
HRMS for Compound **5c**



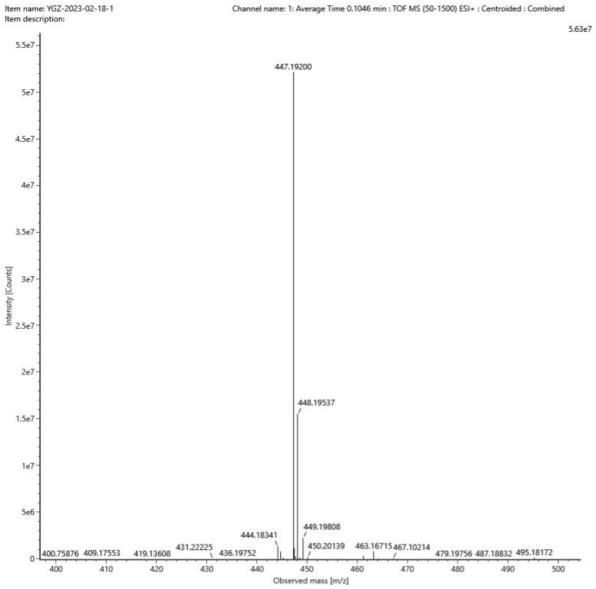

HRMS for Compound **5d**



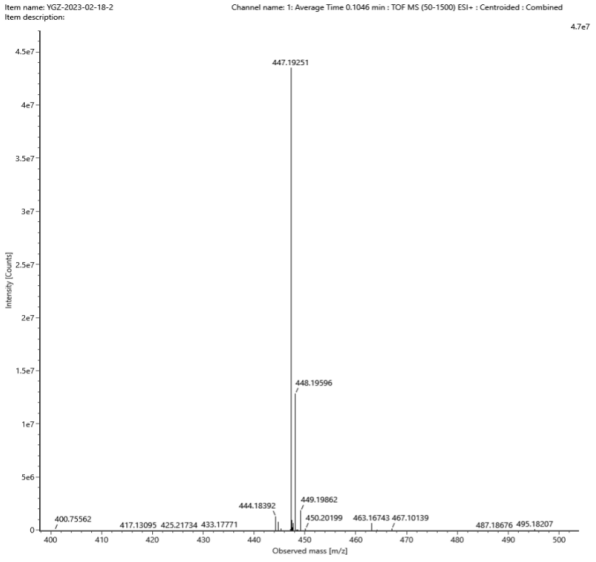

HRMS for Compound **5e**



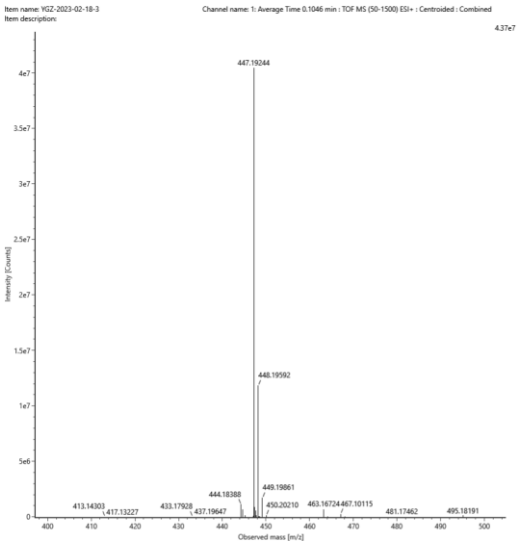
HRMS for Compound **5f**



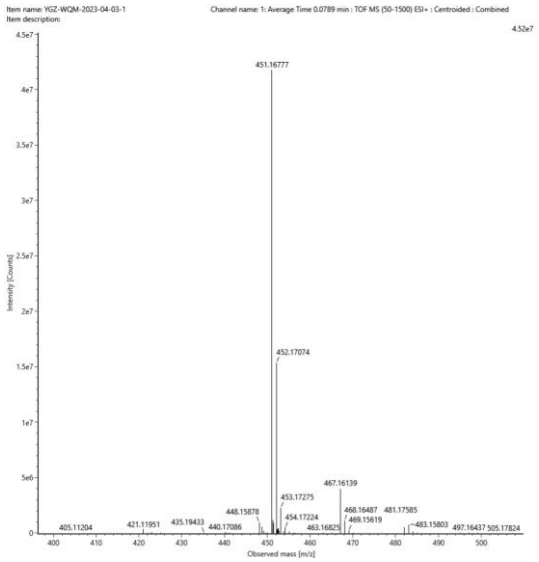

HRMS for Compound **5g**



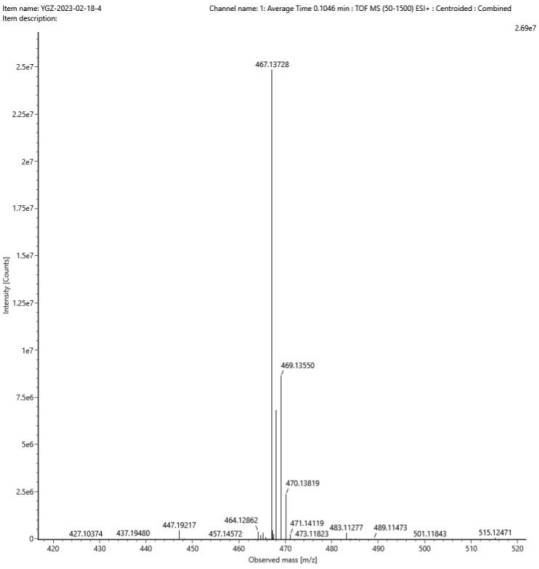

HRMS for Compound **5h**



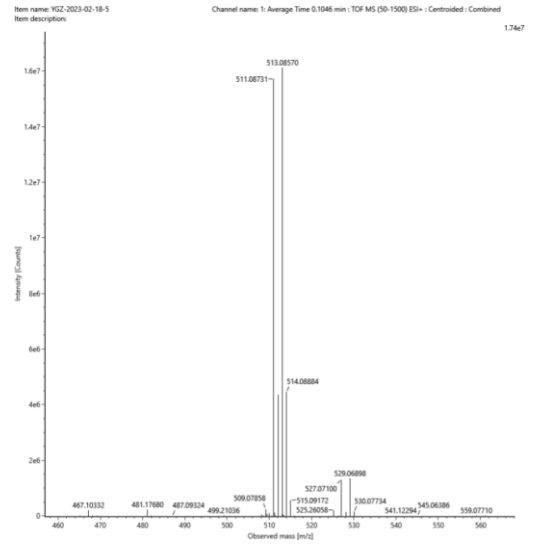
HRMS for Compound **5i**



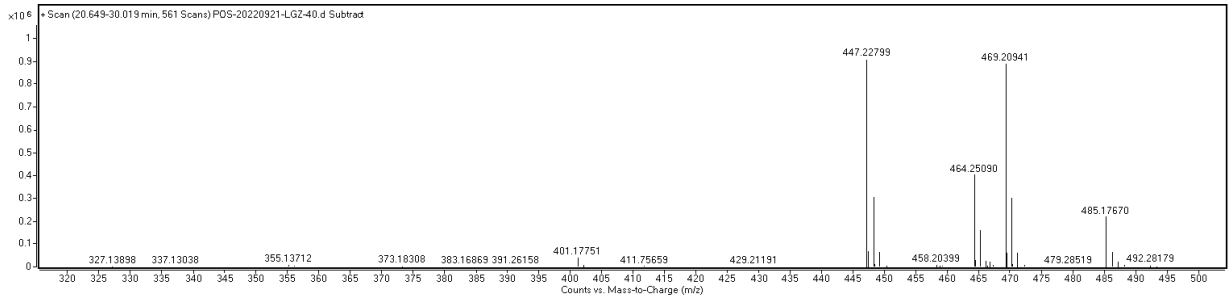

HRMS for Compound **5j**



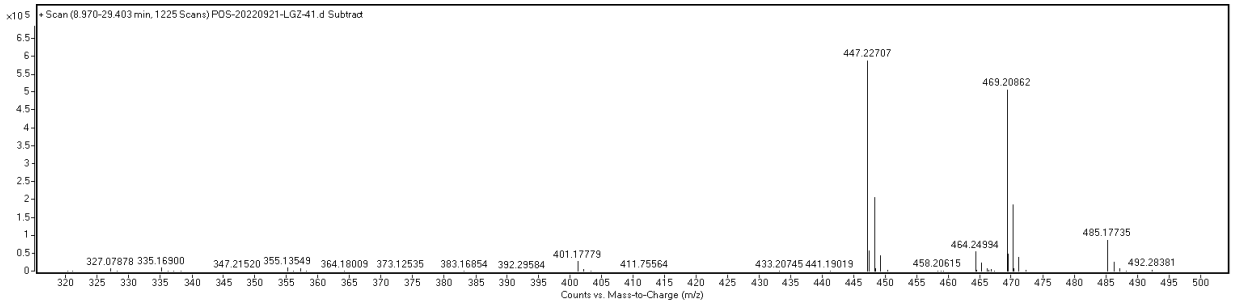

HRMS for Compound **5k**



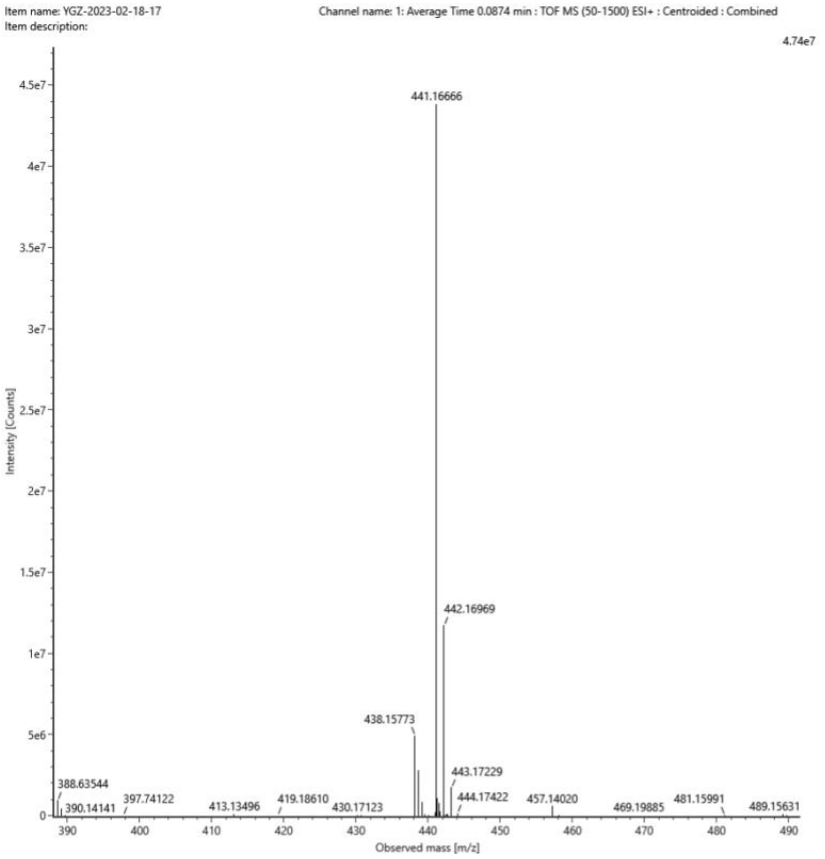
HRMS for Compound **4a**



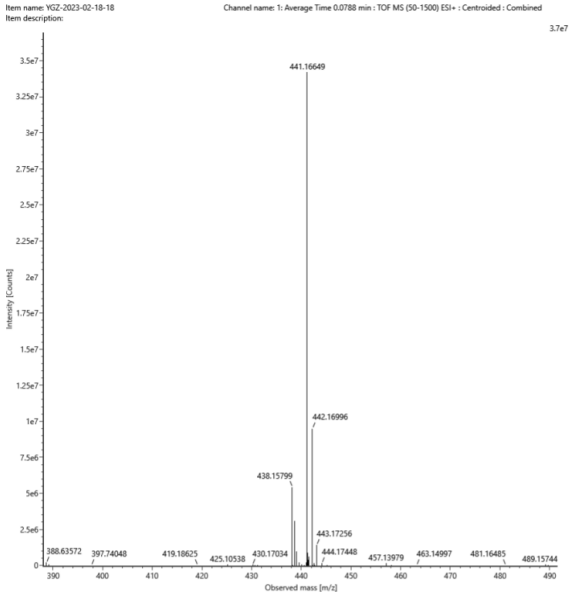

HRMS for Compound **6a**



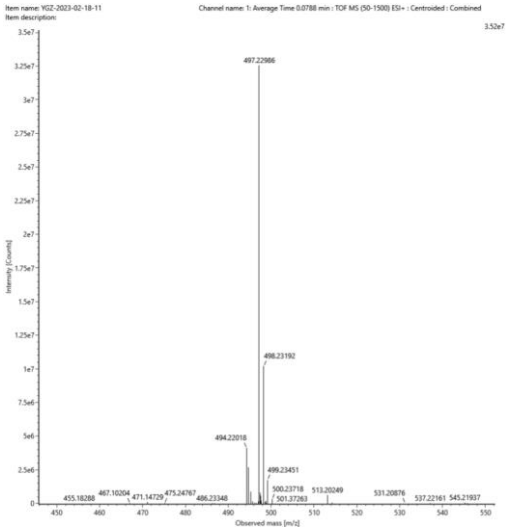

HRMS for Compound **4b**



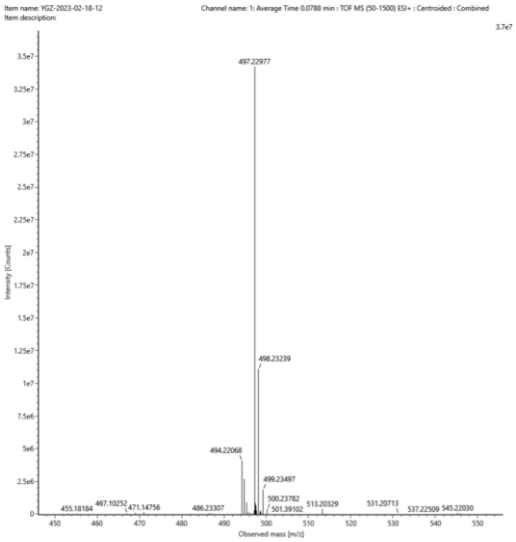
HRMS for Compound **6b**



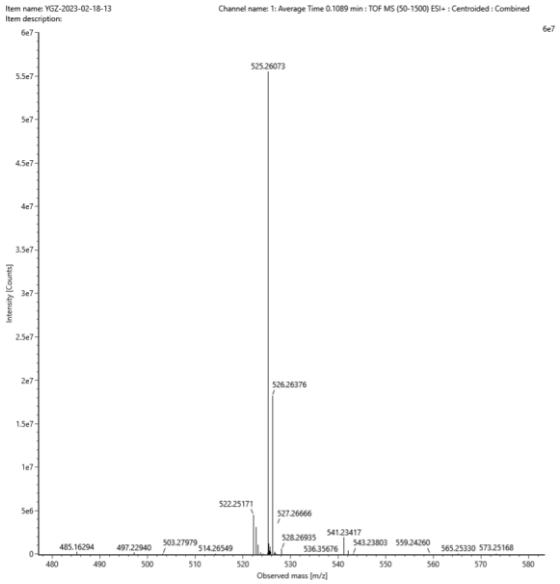

HRMS for Compound **4c**



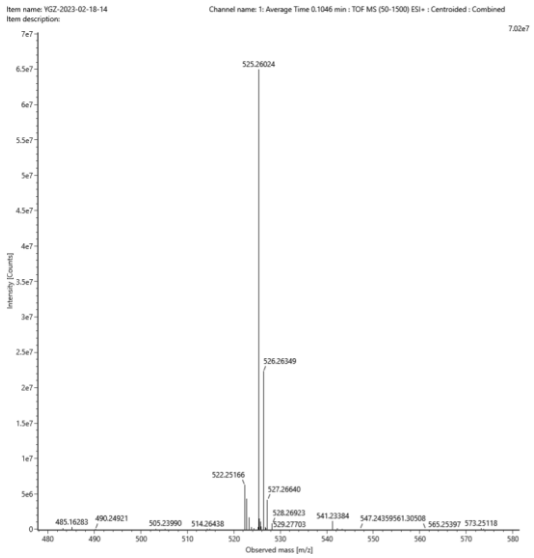

HRMS for Compound **6c**



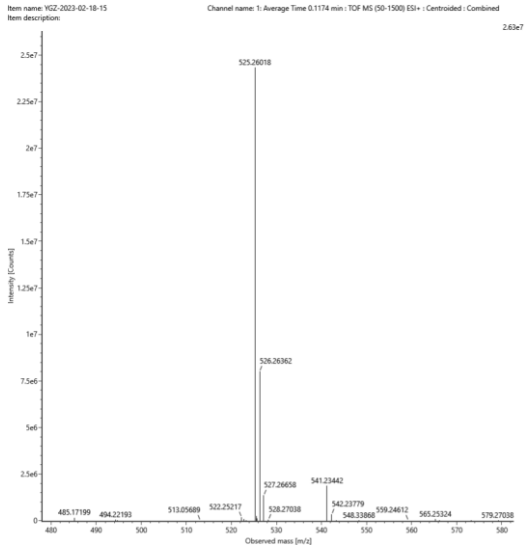
HRMS for Compound **4d**



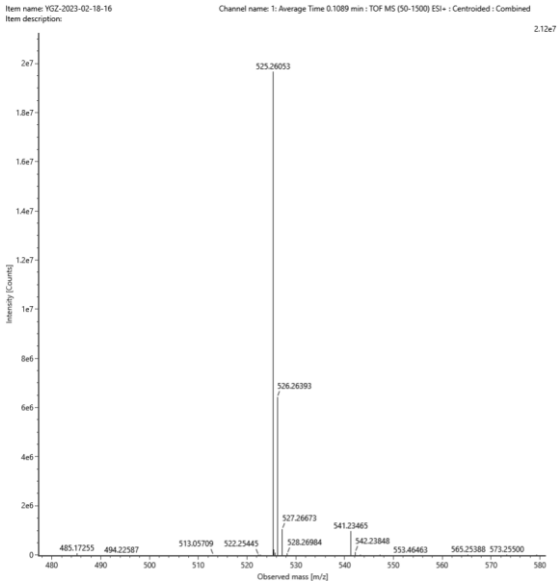

HRMS for Compound **6d**



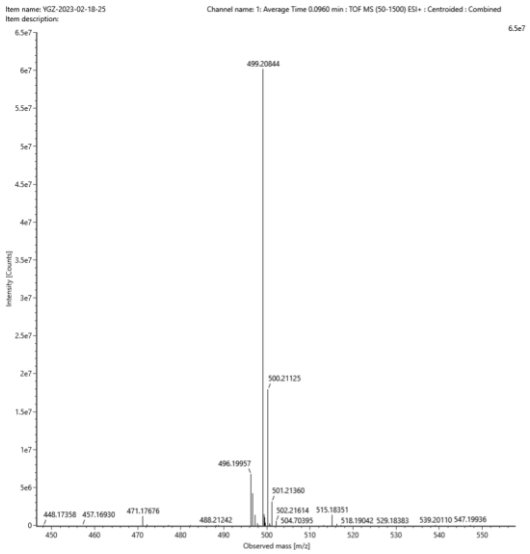

HRMS for Compound **4e**



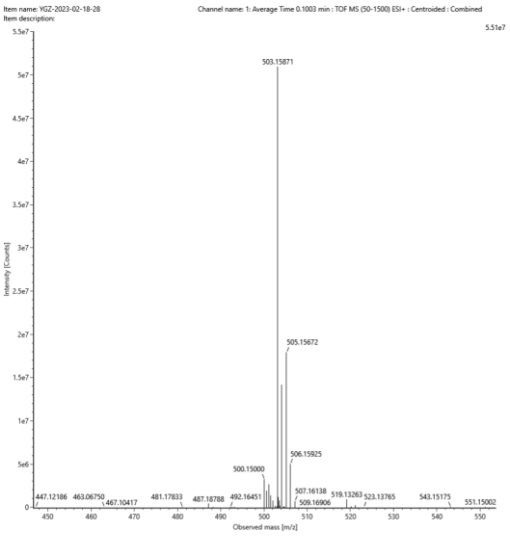
HRMS for Compound **6e**



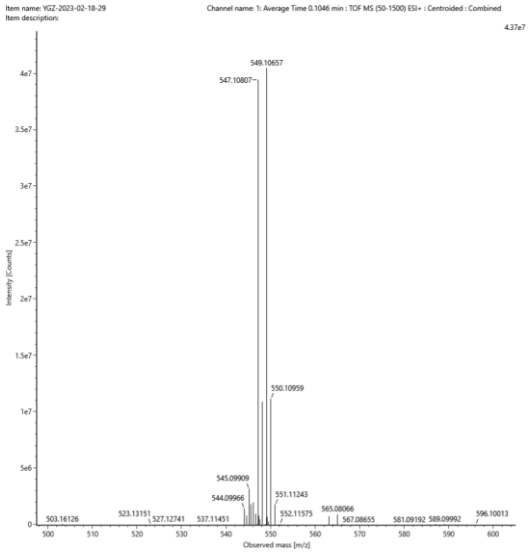

HRMS for Compound **4f**



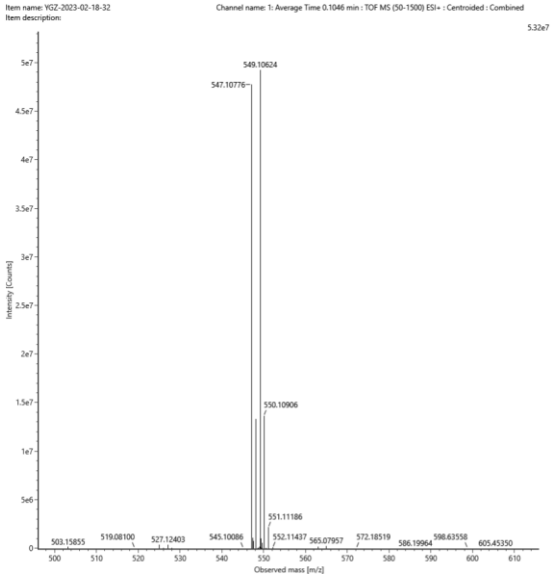

HRMS for Compound **4h**



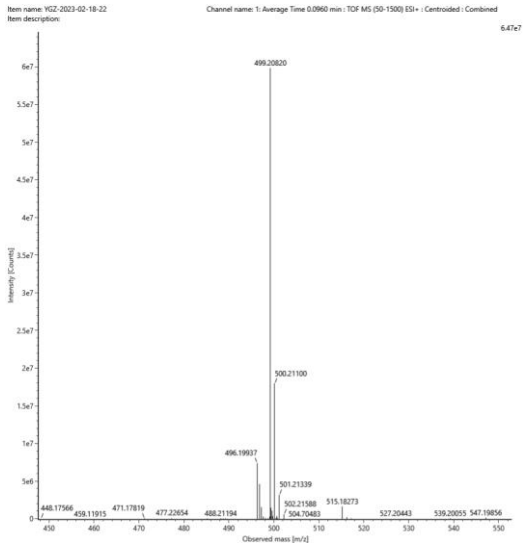
HRMS for Compound **4i**



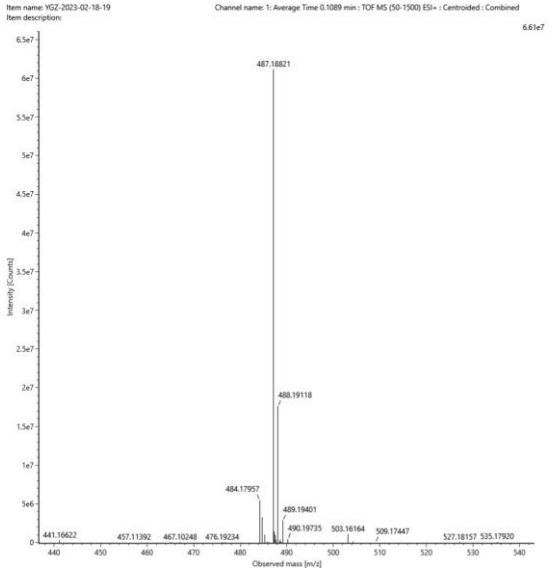

HRMS for Compound **6i**



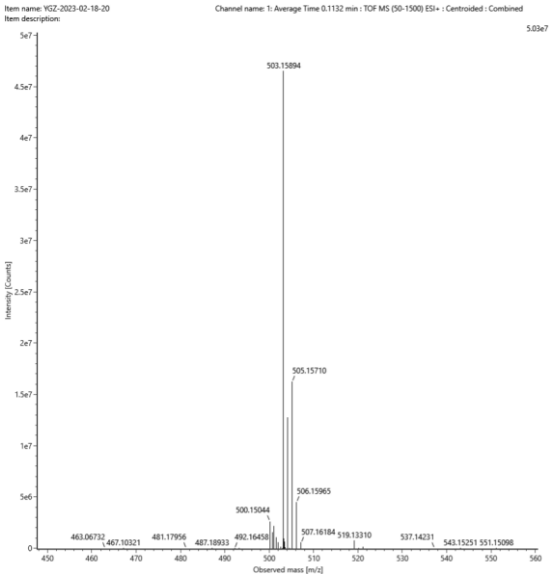

HRMS for Compounds **4k**/**6k**



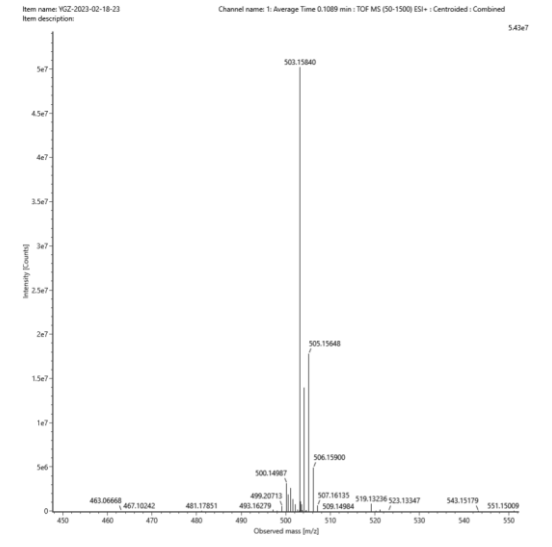
HRMS for Compounds **4l**/**6l**



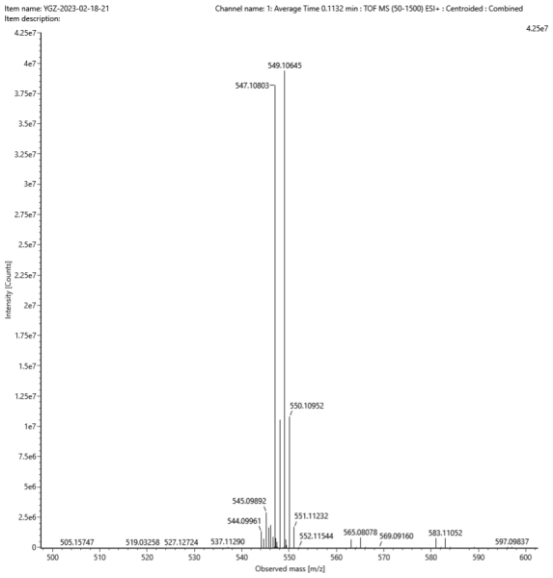

HRMS for Compounds **4m**/**6m**



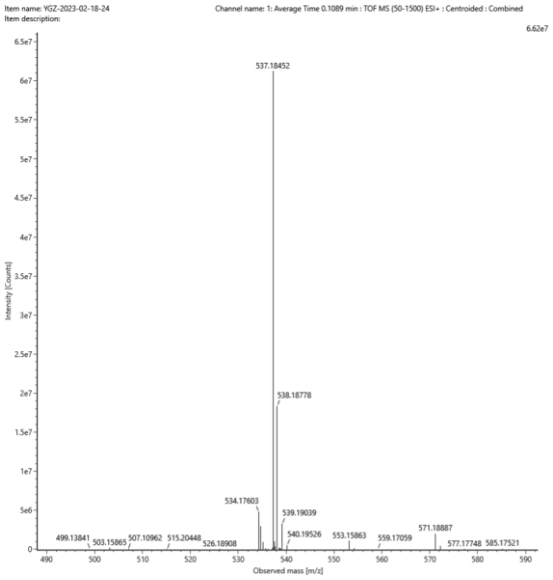

HRMS for Compounds **4n**/**6n**



HRMS for Compounds **4o**/**6o**

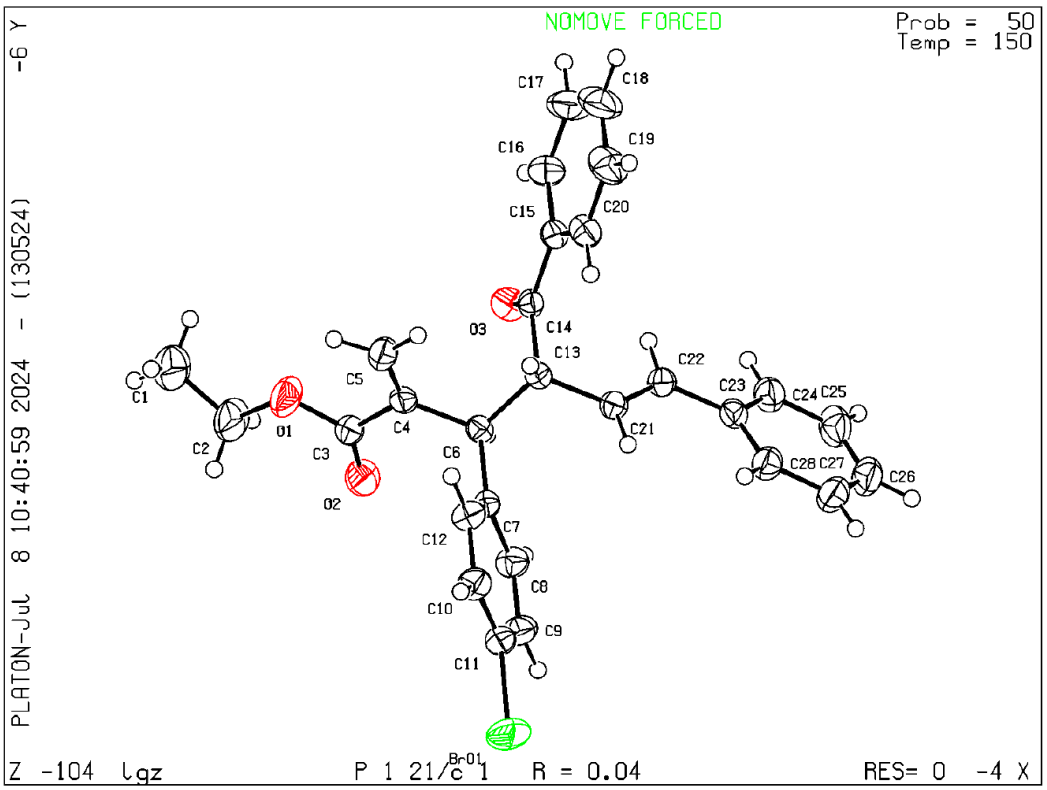



HRMS for Compounds **4p**/**6p**



## XII. Copes of Data of X-ray crystal structure for 5k (CCDC 2369042)

**Datablock lgz** - ellipsoid plot



# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) lgz

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

## Datablock: lgz

```
Bond precision:   C-C = 0.0029 A          Wavelength=1.34139

Cell:             a=10.9368(3)     b=21.6415(6)        c=10.4253(3)
                  alpha=90         beta=98.771(1)      gamma=90
Temperature:      150 K

                 Calculated                Reported
Volume           2438.70(12)               2438.69(12)
Space group      P 21/c                    P 1 21/c 1
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C28 H25 Br O3             C28 H25 Br O3
Sum formula      C28 H25 Br O3             C28 H25 Br O3
Mr               489.38                    489.39
Dx,g cm-3        1.333                     1.333
Z                4                         4
Mu (mm-1)        1.646                     1.646
F000             1008.0                    1008.0
F000'            1006.15
h,k,lmax         13,27,13                  13,27,13
Nref             5023                      4984
Tmin,Tmax        0.765,0.848               0.599,0.751
Tmin'            0.685

Correction method= # Reported T Limits: Tmin=0.599 Tmax=0.751
AbsCorr = MULTI-SCAN

Data completeness= 0.992           Theta(max)= 57.186

R(reflections)= 0.0437( 4529)                wR2(reflections)=
                                             0.1212( 4984)
S = 1.069                  Npar= 290
```

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

### Alert level C

```
PLAT601_ALERT_2_C Unit Cell Contains Solvent Accessible VOIDS of .          47 Ang**3
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          20 Report
                  2   0   0,    4   0   0,    2   4   0,    1   5   0,    0   6   0,
                  0   1   1,
                  2   1   1,   -3   2   1,    0   3   1,    1   3   1,    1   4   1,
                  3   4   1,
                 -1   0   2,    2   0   2,   -5   1   2,   -1   1   2,    0   2   2,
                  0   4   2,
                  0   6   2,   -5   0   8,
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....           9 Note
                  2   4   0,    1   5   0,    0   6   0,   -3   2   1,    3   4   1,
                 -5   1   2,
                 -1   1   2,    0   2   2,    0   6   2,
```

### Alert level G

```
ABSMU01_ALERT_1_G  Calculation of _exptl_absorpt_correction_mu
                   not performed for this radiation type.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....          1 Note
                  Br01
PLAT793_ALERT_4_G Model has Chirality at C6          (Centro SpGr)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C13         (Centro SpGr)          R Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          2 Note
                  1   0   0,    0   2   0,
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         15 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          3 Note
                  2   1   1,    0   1   1,    1   0   0,
PLAT954_ALERT_1_G Reported (CIF) and Actual (FCF) Kmax Differ by .          1 Units
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value .....       3.741 Note
                  Predicted wR2: Based on SigI**2  3.24 or SHELX Weight 11.34
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          6 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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**PLATON version of 13/05/2024; check.def file version of 04/05/2024**