

Supporting Information

The Phosphine-Catalyzed Ring-Opening Reaction of Cyclopropenones with Dicarboxyl Compounds

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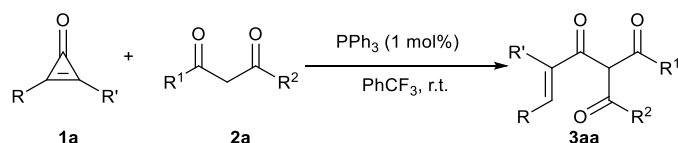
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1. General Information

All reagents and solvents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros and Meryer. All reactions were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300 – 400 mesh). ^1H NMR and ^{13}C NMR spectra were measured on a 400 MHz Bruker AVANCE spectrometer, using DMSO- d_6 or CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts were reported in ppm. ^1H NMR spectra were referenced to CDCl_3 (7.26 ppm) or DMSO- d_6 (2.50 ppm), and ^{13}C NMR spectra were referenced to CDCl_3 (77.0 ppm) or DMSO- d_6 (39.5 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. Analysis of crude reaction mixture was done on the Varian 4000 GC/MS and Agilent 7890A/5975C. High-resolution mass spectra were recorded on a micrOTOF-Q II 10410 mass spectrometer. A 15 W UV light and a 500 W super high-pressure mercury lamp were used for photoirradiation. Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. The cyclopropenones¹ were prepared according to corresponding literature procedures.

2. General Experimental Procedures

General procedure (method A, 3aa-3ia, 3ab-3aj)

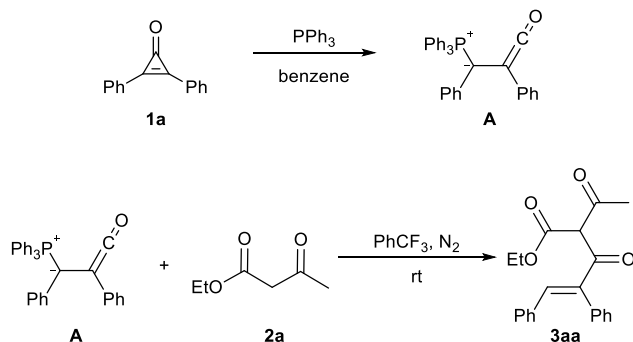


Scheme S1

A 10 mL pressure tube equipped with a stir bar was charged with cyclopropenones (0.2 mmol, 1.0 equiv.), dicarbonyl compounds (0.4 mmol, 2.0 equiv), PPh₃ (0.002 mmol, 0.01 equiv.) and PhCF₃ (2 mL). The reaction mixture was stirred at room temperature under N₂ atmosphere for 12 h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, then 2.0 ml of water was added, and the reaction solution was extracted with ethyl acetate (3 x 2 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

3. Mechanism study

3.1 The reaction of zwitterionic phosphine/cyclopropenone adduct A with ethyl acetoacetate

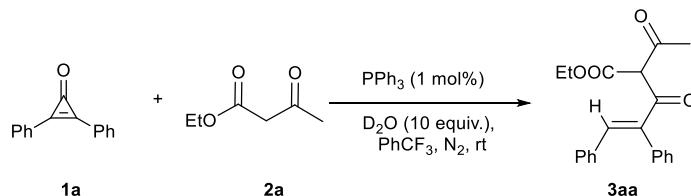


A solution of 1,2-diphenylcyclopropenone (1.03 g, 5 mmol) and PPh₃ (1.31 g, 5 mmol) in dry benzene solution was stirred at room temperature under nitrogen

atmosphere for 3 h to give the zwitterionic phosphine/cyclopropenone adduct **A**.² (orange crystal, 2.1 g, 91%). ¹H NMR (400 MHz, CDCl₃) δ 7.75 (m, 2H), 7.37 – 7.34 (m, 6H), 7.30 (m, 3H), 7.21 (m, 2H), 7.15 (m, 8H), 6.99 (m, 4H).; ¹³C NMR (101 MHz, CDCl₃) δ 163.63, 144.03, 134.91, 134.06, 133.92, 133.72, 131.48, 131.09, 130.02, 129.80, 128.99, 128.80, 128.54, 128.42, 128.31.

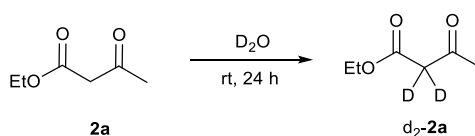
Then a 10 mL pressure tube equipped with a stir bar was charged with **A** (0.2 mmol, 1.0 equiv.), ethyl acetoacetate (0.4 mmol, 2.0 equiv.) and dry PhCF₃ (2 mL). The reaction mixture was stirred at room temperature under N₂ atmosphere for 12 h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product **3aa** (55.1 mg, 82%).

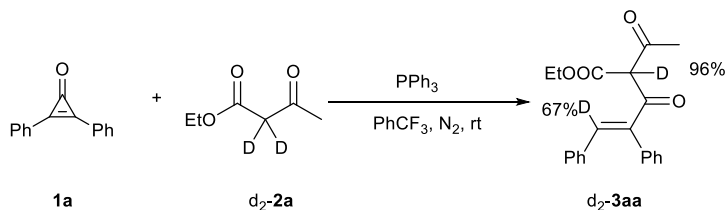
3.2 The reaction of cyclopropenone adduct **A** with ethyl acetoacetate in the presence of D₂O



A 10 mL pressure tube equipped with a stir bar was charged with 1,2-diphenylcyclopropenone (0.2 mmol, 1.0 equiv.), ethyl acetoacetate (0.4 mmol, 2.0 equiv.), PPh₃ (0.002 mmol, 0.01 equiv.), D₂O (10 equiv.) and PhCF₃ (2 mL). The reaction mixture was stirred at room temperature under N₂ atmosphere for 12 h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product **3aa** (58.5 mg, 87%).

3.3 The reaction of cyclopropenone adduct **A** with d₂-ethyl acetoacetate



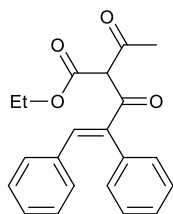


Ethyl acetoacetate **2a** (4.0 g, 4.1 ml) was stirred with D₂O (12 mL) for 24 h, then extracted with ethyl ether and concentrated under reduced pressure to get the deuterated ethyl acetoacetate d₂-**2a** (> 99% D).³ ¹H NMR (400 MHz, CDCl₃) δ 4.13 (q, *J* = 7.0 Hz, 2H), 2.21 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 200.78, 167.12, 61.27, 50.12, 30.04, 14.01.

Then a 10 mL pressure tube equipped with a stir bar was charged with 1,2-diphenylcyclopropenone (0.2 mmol, 1.0 equiv.), deuterated ethyl acetoacetate (0.4 mmol, 2.0 equiv.), PPh₃ (0.002 mmol, 0.01equiv.) and PhCF₃ (2 mL). The reaction mixture was stirred at room temperature under N₂ atmosphere for 12 h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product d₂-**3aa** in 92% yield (67% D in vinyl). ¹H NMR (400 MHz, CDCl₃) δ 7.23 (m, 3H), 7.11 – 7.09 (m, 3H), 7.05 – 7.01 (m, 2H), 6.93 (d, *J* = 7.4 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 166.06, 165.21, 164.44, 142.54, 135.18, 134.23, 134.16, 131.53, 131.42, 130.90, 129.79, 129.70, 128.88, 128.39, 128.24, 110.15, 60.20, 18.23, 14.30.

4. Characterization of Products in Details

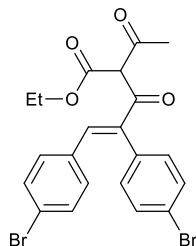
ethyl (*E*)-2-acetyl-3-oxo-4,5-diphenylpent-4-enoate (**3aa**)



Following the general procedure (Method A), using 20/1 petroleum ether/EtOAc as the eluant afford a colorless oil (54.4 mg, 81%), ¹H NMR (400 MHz, CDCl₃) δ 7.93

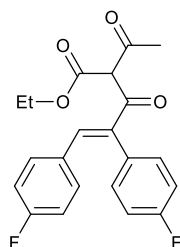
(s, 1H), 7.42-7.40 (m, 3H), 7.29-7.25 (m, 3H), 7.22-7.19 (m, 2H), 7.10-7.08 (m, 2H), 5.76 (s, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 2.43 (s, 3H), 1.30 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.03, 165.17, 164.43, 142.47, 135.12, 134.18, 131.47, 130.83, 129.73, 129.62, 128.81, 128.33, 128.17, 110.10, 60.17, 18.22, 14.24. HRMS: (ESI) calculated for $\text{C}_{21}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$ 337.1434, found 337.1437.

ethyl (*E*)-2-acetyl-4,5-bis(4-bromophenyl)-3-oxopent-4-enoate (3ba)



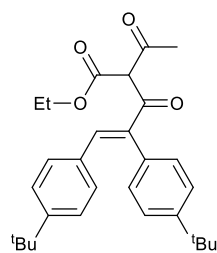
Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a yellow oil (61.8 mg, 63%), ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.5$ Hz, 2H), 7.14 (d, $J = 8.2$ Hz, 2H), 6.97 (d, $J = 8.5$ Hz, 2H), 5.75 (s, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 2.43 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.85, 164.42, 164.10, 141.55, 133.57, 132.74, 132.20, 132.07, 131.80, 131.44, 130.97, 124.31, 122.71, 110.32, 60.27, 18.16, 14.25. HRMS: (ESI) calculated for $\text{C}_{21}\text{H}_{19}\text{Br}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 492.9645, found 492.9647.

ethyl (*E*)-2-acetyl-4,5-bis(4-fluorophenyl)-3-oxopent-4-enoate (3ca)



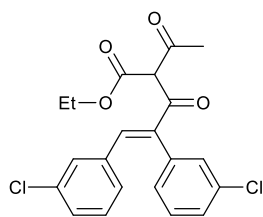
Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a colorless oil (51.3 mg, 69%), ^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1H), 7.25-7.22 (m, 2H), 7.14-7.06 (m, 4H), 6.94-6.89 (m, 2H), 5.76 (s, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 2.43 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.93, 164.86, 164.25, 164.22, 163.62, 162.22, 161.65, 141.58, 132.80, 132.73, 131.63, 131.56, 130.71, 130.68, 130.20, 130.17, 130.09, 130.07, 116.18, 116.01, 115.73, 115.56, 110.21, 60.23, 18.17, 14.22. HRMS: (ESI) calculated for $\text{C}_{21}\text{H}_{18}\text{F}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 395.1065, found 395.1055.

ethyl (*E*)-2-acetyl-4,5-bis(4-(*tert*-butyl)phenyl)-3-oxopent-4-enoate (3da)



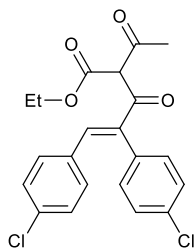
Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a white solid (53.8 mg, 60%), Melting Point: 117.2-118.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.21-7.17 (m, 4H), 7.02 (d, *J* = 8.2 Hz, 2H), 5.74 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.37 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 166.16, 165.63, 164.78, 153.21, 151.09, 142.26, 132.36, 131.51, 130.94, 130.35, 129.32, 125.82, 125.40, 110.05, 60.17, 34.85, 34.74, 31.47, 31.15, 18.35, 14.33. HRMS: (ESI) calculated for C₂₉H₃₆O₄Na [M+Na]⁺ 471.2506, found 471.2506.

ethyl (*E*)-2-acetyl-4,5-bis(3-chlorophenyl)-3-oxopent-4-enoate (3ea)



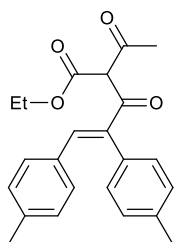
Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a yellow oil (37.2 mg, 46%), ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.42-7.34 (m, 2H), 7.29-7.27 (m, 2H), 7.18-7.11 (m, 3H), 6.94 (d, *J* = 7.9 Hz, 1H), 5.77 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.90, 164.30, 164.12, 141.55, 136.32, 135.51, 134.79, 134.47, 131.48, 130.73, 130.27, 129.89, 129.75, 129.72, 128.76, 128.64, 127.99, 110.44, 60.34, 18.20, 14.29. HRMS: (ESI) calculated for C₂₁H₁₈Cl₂O₄Na [M+Na]⁺ 427.0474, found 427.0475.

ethyl (*E*)-2-acetyl-4,5-bis(4-chlorophenyl)-3-oxopent-4-enoate (3fa)



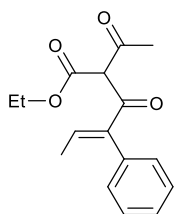
Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a yellow oil (42.8 mg, 53%), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 4H), 7.04 (dd, $J = 8.6, 1.8$ Hz, 2H), 5.75 (s, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 2.43 (s, 3H), 1.31 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 165.87, 164.52, 164.12, 141.52, 135.85, 134.48, 133.11, 132.32, 131.89, 131.17, 130.81, 129.25, 128.81, 110.30, 60.26, 18.15, 14.24. HRMS: (ESI) calculated for $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 427.0474, found 427.0475.

ethyl (*E*)-2-acetyl-3-oxo-4,5-di-*p*-tolylpent-4-enoate (3ga)



Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a colorless oil (64.1 mg, 88%), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 (s, 1H), 7.25-7.23 (m, 2H), 7.19-7.17 (m, 2H), 7.04-7.03 (m, 4H), 5.77 (s, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 2.46 (s, 3H), 2.44 (s, 3H), 2.33 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.08, 165.48, 164.64, 142.35, 140.01, 137.84, 132.34, 131.56, 130.91, 130.41, 129.61, 129.59, 129.11, 110.02, 60.13, 21.40, 18.26, 14.27. HRMS: (ESI) calculated for $\text{C}_{23}\text{H}_{25}\text{O}_4$ $[\text{M}+\text{H}]^+$ 365.1747, found 365.1749.

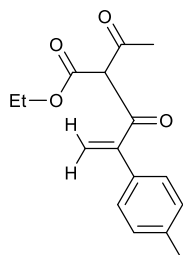
ethyl (*E*)-2-acetyl-3-oxo-4-phenylhex-4-enoate (3ha)



Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a colorless oil (26.3 mg, 48%), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46-7.39 (m, 3H), 7.37-7.31 (m, 1H), 7.26-7.24 (m, 2H), 5.74 (s, 1H), 4.22 (q, $J =$

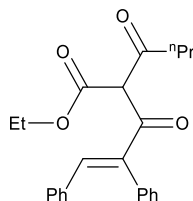
7.1 Hz, 2H), 2.42 (s, 3H), 1.86 (d, $J = 7.1$ Hz, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.10, 164.41, 142.83, 134.21, 133.98, 129.78, 128.20, 127.79, 110.04, 60.17, 29.74, 18.22, 15.85, 14.26. HRMS: (ESI) calculated for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 297.1097, found 297.1087.

ethyl 2-acetyl-3-oxo-4-(*p*-tolyl)pent-4-enoate (3ia)



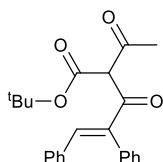
Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a yellow oil (29.6 mg, 54%), ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 7.8$ Hz, 2H), 6.57 (s, 1H), 6.08 (s, 1H), 5.69 (s, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 2.41 (s, 3H), 2.12 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.77, 163.68, 159.84, 140.20, 138.30, 133.40, 128.92, 128.42, 128.24, 108.88, 60.18, 29.76, 21.65, 21.27, 14.26. HRMS: (ESI) calculated for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 297.1097, found 297.1098.

ethyl (*E*)-2-(2,3-diphenylacryloyl)-3-oxoheptanoate (3ab)



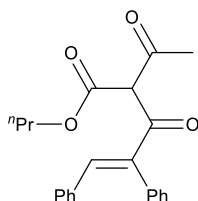
Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a colorless oil (67.0 mg, 92%), ^1H NMR (400 MHz, CDCl_3) δ 7.93 (s, 1H), 7.42-7.40 (m, 3H), 7.28-7.25 (m, 3H), 7.22-7.18 (m, 2H), 7.10-7.09 (m, 2H), 5.79 (s, 1H), 4.20 (q, $J = 7.4$, 2H), 2.88 (t, $J = 7.6$ Hz, 2H), 1.54 (q, $J = 7.5$ Hz, 2H), 1.30 (t, $J = 6.9$ Hz, 3H), 0.96-0.92 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.40, 165.94, 165.16, 142.35, 135.22, 134.19, 131.57, 130.87, 129.65, 129.62, 128.79, 128.33, 128.12, 110.02, 60.14, 32.70, 20.08, 14.23, 13.64. HRMS: (ESI) calculated for $\text{C}_{23}\text{H}_{25}\text{O}_4$ $[\text{M}+\text{H}]^+$ 365.1747, found 365.1746.

***tert*-butyl (*E*)-2-acetyl-3-oxo-4,5-diphenylpent-4-enoate (3ac)**



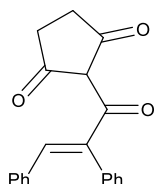
Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a colorless oil (54.6 mg, 75%), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.41-7.39 (m, 3H), 7.28-7.26 (m, 3H), 7.25-7.18 (m, 2H), 7.10-7.08 (m, 2H), 5.67 (s, 1H), 2.40 (s, 3H), 1.50 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.37, 165.36, 142.38, 135.19, 134.23, 131.55, 130.88, 129.76, 129.64, 128.85, 128.37, 128.18, 111.87, 80.58, 28.25, 18.08. HRMS: (ESI) calculated for $\text{C}_{23}\text{H}_{25}\text{O}_4$ $[\text{M}+\text{H}]^+$ 365.1747, found 365.1747.

propyl (*E*)-2-acetyl-3-oxo-4,5-diphenylpent-4-enoate (3ad)



Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a colorless oil (53.9 mg, 77%), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.40-7.38 (m, 3H), 7.26-7.23 (m, 2H), 7.22-7.16 (m, 2H), 7.08-7.06 (m, 2H), 5.75 (s, 1H), 4.09 (t, $J = 6.6$ Hz, 2H), 2.42 (s, 3H), 1.68 (dd, $J = 14.1, 7.1$ Hz, 3H), 0.96(t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.13, 165.19, 164.41, 142.49, 135.11, 134.17, 131.46, 130.85, 129.73, 129.63, 128.83, 128.34, 128.18, 110.12, 77.31, 77.06, 76.80, 65.86, 22.00, 18.24, 10.46. HRMS: (ESI) calculated for $\text{C}_{22}\text{H}_{23}\text{O}_4$ $[\text{M}+\text{H}]^+$ 351.1591, found 351.1593.

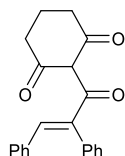
(*E*)-2-(2,3-diphenylacryloyl)cyclopentane-1,3-dione (3ae)



Following the general procedure (Method A), using 3 / 1 petroleum ether / EtOAc as the eluant afford a white solid (37.1 mg, 61%), Melting Point: 101.2-102.1 $^{\circ}\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (s, 1H), 7.44-7.43 (m, 3H), 7.29-7.27 (m, 3H), 7.24-7.22 (m, 2H), 7.12-7.11 (m, 2H), 6.33 (s, 1H), 2.83-2.77 (m, 2H), 2.49-2.47 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 195.69, 164.66, 158.43, 142.91, 135.28, 134.28,

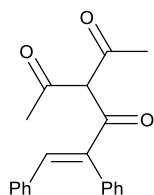
131.43, 131.00, 129.97, 129.68, 128.89, 128.36, 128.21, 117.04, 31.10, 21.63. HRMS: (ESI) calculated for $C_{20}H_{17}O_3$ $[M+H]^+$ 305.1172, found 305.1171.

(E)-2-(2,3-diphenylacryloyl)cyclohexane-1,3-dione (3af)



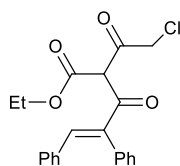
Following the general procedure (Method A), using 3 / 1 petroleum ether / EtOAc as the eluant afford a colorless oil (52.1 mg, 82%), 1H NMR (400 MHz, DMSO) δ 7.98 (s, 1H), 7.33-7.31 (m, 3H), 7.19-7.17 (m, 3H), 7.14-7.10 (m, 2H), 7.02-7.00 (m, 2H), 5.80 (s, 1H), 2.46 (t, $J = 5.9$ Hz, 2H), 2.33 (t, $J = 6.6$ Hz, 2H), 1.87 (dd, $J = 6.4, 6.0$ Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.60, 170.55, 164.50, 143.25, 134.96, 134.06, 131.11, 130.98, 129.92, 129.78, 128.96, 128.45, 128.38, 117.69, 36.83, 28.44, 21.37. HRMS: (ESI) calculated for $C_{21}H_{18}O_3Na$ $[M+Na]^+$ 341.1148, found 341.1144.

(E)-3-acetyl-5,6-diphenylhex-5-ene-2,4-dione (3ag)



Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a yellow oil (50.8 mg, 83%), 1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.44-7.42 (m, 3H), 7.37-7.34 (m, 2H), 7.30-7.26 (m, 1H), 7.23-7.19 (m, 2H), 7.13-7.11 (m, 2H), 5.87 (s, 1H), 2.20 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.67, 164.64, 158.42, 142.88, 135.28, 134.26, 131.43, 130.98, 129.96, 129.67, 128.88, 128.35, 128.20, 117.00, 31.06, 21.59. HRMS: (ESI) calculated for $C_{20}H_{18}O_3Na$ $[M+Na]^+$ 329.1148, found 329.1150.

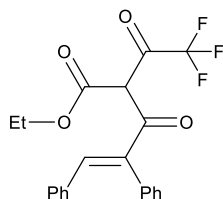
ethyl (E)-2-(2-chloroacetyl)-3-oxo-4,5-diphenylpent-4-enoate (3ah)



Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as

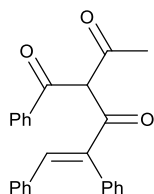
the eluant afford a colorless oil (51.8 mg, 70%), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.02 (s, 1H), 7.44-7.42 (m, 3H), 7.34-7.32 (m, 2H), 7.31-7.27 (m, 1H), 7.24-7.20 (m, 2H), 7.14-7.12 (m, 2H), 5.97 (s, 1H), 4.91 (s, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.94, 159.58, 143.46, 134.92, 134.15, 131.08, 130.89, 129.94, 129.88, 128.96, 128.47, 128.40, 112.70, 61.00, 38.85, 14.24. HRMS: (ESI) calculated for $\text{C}_{21}\text{H}_{19}\text{ClO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 393.0864, found 393.0865.

ethyl (*E*)-3-oxo-4,5-diphenyl-2-(2,2,2-trifluoroacetyl)pent-4-enoate (3ai)



Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a colorless oil (40.5 mg, 52%), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.05 (s, 1H), 7.45-7.42 (m, 2H), 7.37-7.35 (m, 2H), 7.29-7.27 (m, 1H), 7.24-7.20 (m, 2H), 7.15-7.13 (m, 2H), 6.41 (s, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.28, 162.11, 144.10, 134.76, 134.08, 131.16, 131.12, 130.18, 129.98, 128.90, 128.41, 113.46, 113.43, 61.48, 14.12. $J_{\text{C-F}}$: 3.03 HRMS: (ESI) calculated for $\text{C}_{21}\text{H}_{18}\text{F}_3\text{O}_4$ $[\text{M}+\text{H}]^+$ 391.1152, found 391.1153.

(*E*)-3-benzoyl-5,6-diphenylhex-5-ene-2,4-dione (3aj)

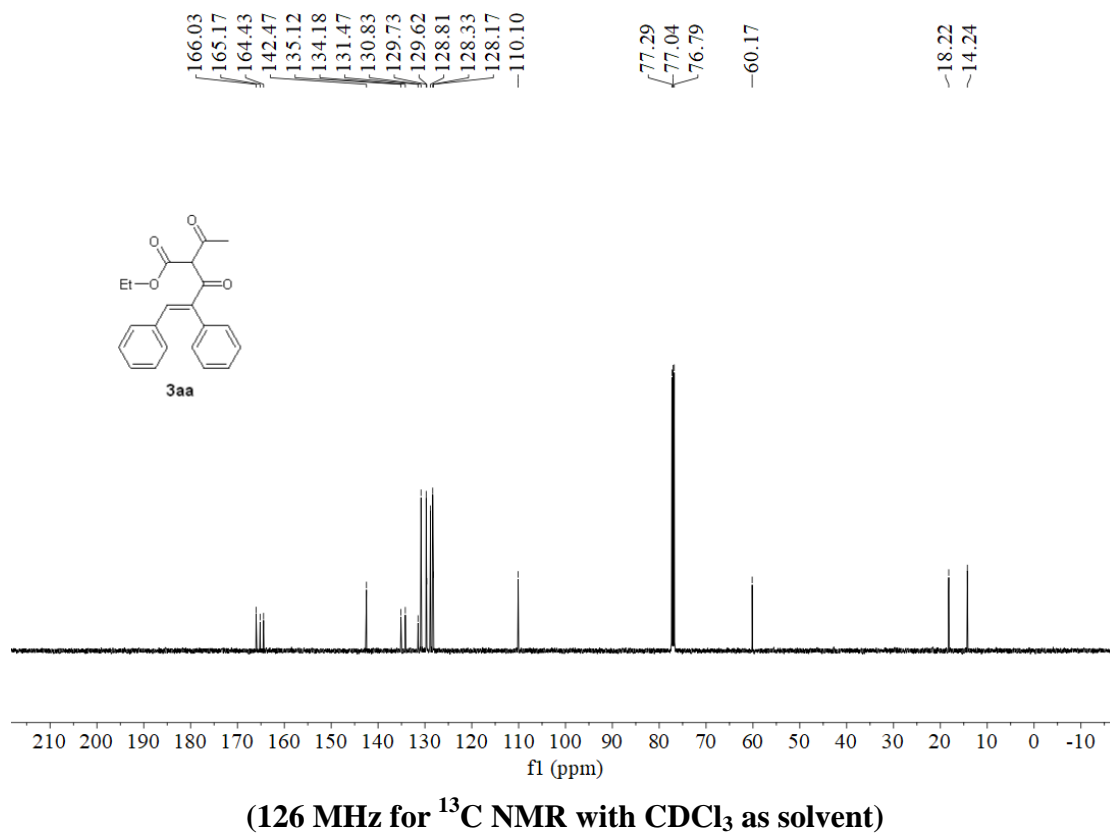
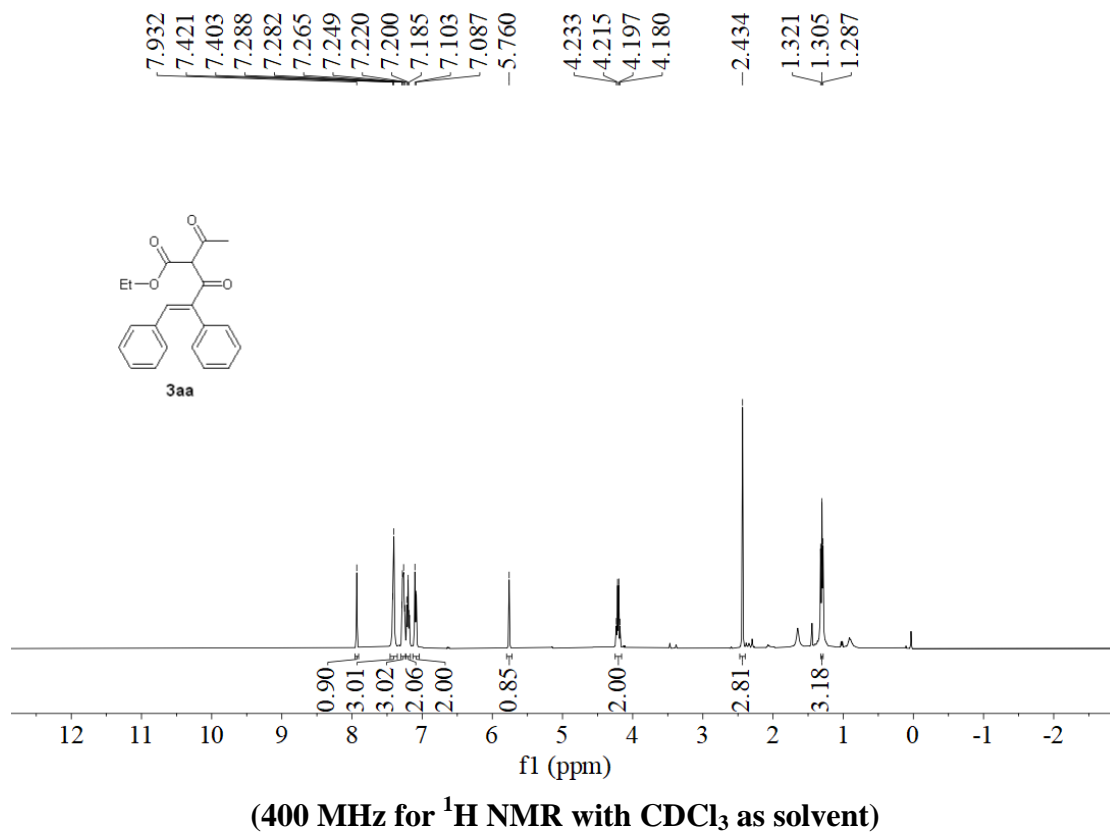


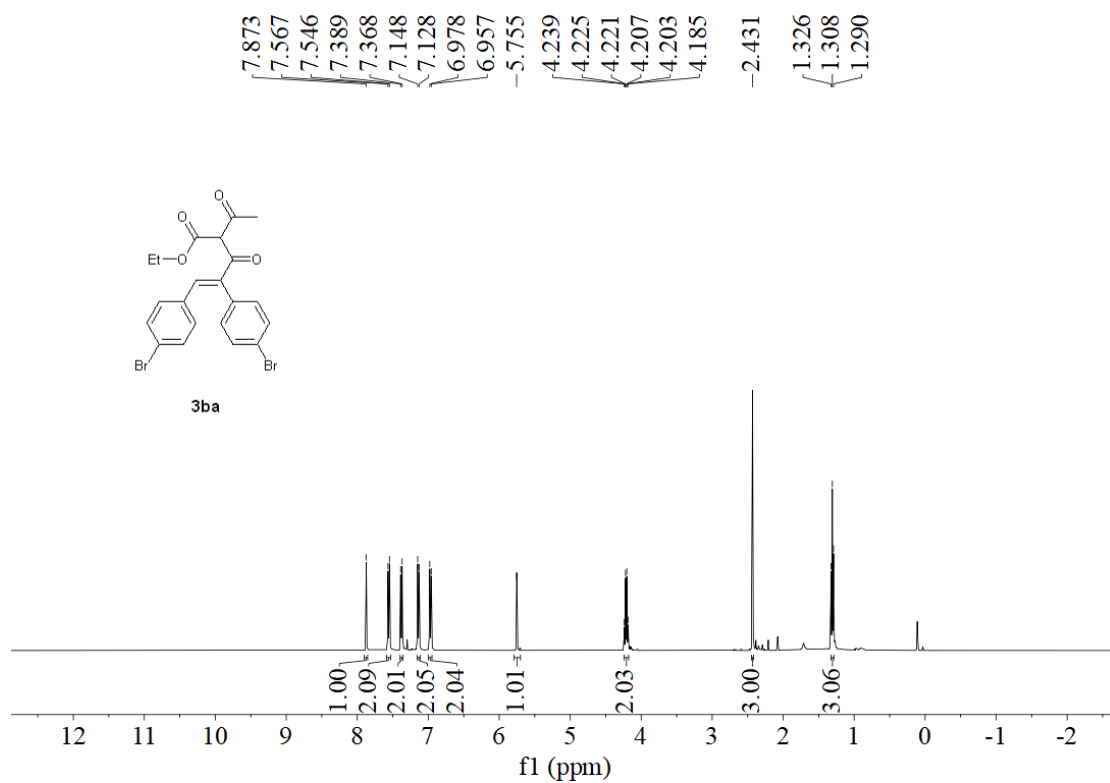
Following the general procedure (Method A), using 20 / 1 petroleum ether / EtOAc as the eluant afford a colorless oil (57.4 mg, 78%), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.02 (s, 1H), 7.99-7.96 (m, 2H), 7.60-7.56 (m, 1H), 7.49-7.44 (m, 5H), 7.35-7.32 (m, 2H), 7.29-7.27 (m, 1H), 7.25-7.21 (m, 2H), 7.14-7.12 (m, 2H), 6.92 (s, 1H), 2.51 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 190.47, 165.37, 164.46, 142.73, 138.76, 135.19, 134.22, 132.93, 131.56, 130.96, 129.84, 128.97, 128.66, 128.45, 128.27, 113.66, 19.22. HRMS: (ESI) calculated for $\text{C}_{25}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$ 369.1485, found 369.1487.

Reference

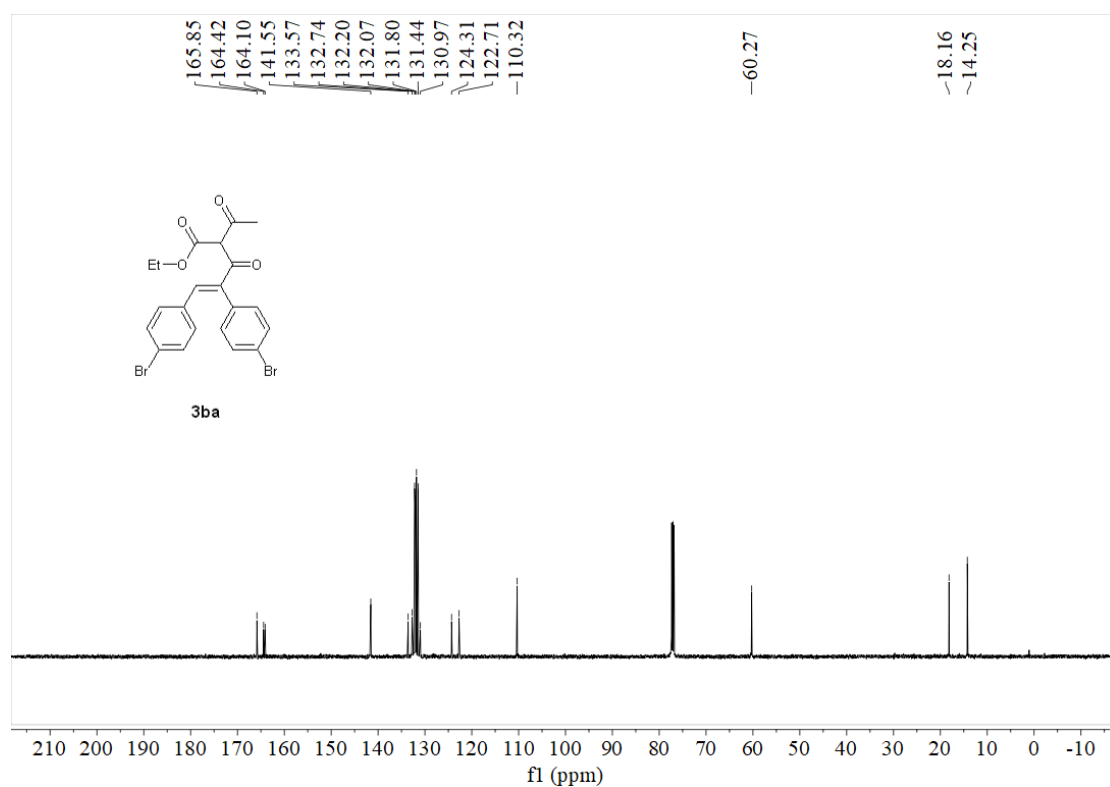
1. (a) J. Zhou, X. Shi, H. Zheng, G. Chen, C. Zhang, X. Liu, and H. Cao, *Org. Lett.*, 2022, **24**, 3238–3243; (b) T. Nanda, P. Biswal, B. V. Pati, S. K. Banjare and P. C. Ravikumar, *J. Org. Chem.*, 2021, **86**, 2682-2695; (c) J. Chen, B. Tang, X. Liu, G. Lv, Y. Shi, T. Huang, H. Xing, X. Guo, L. Hai and Y. Wu, *Org. Chem. Front.*, 2020, **7**, 2944-2949; (d) R. Ando, Y. Morinaka, H. Tokuyama, M. Isaka and E. Nakamura, *J. Am. Chem. Soc.*, 1993, **115**, 1174-1175; (e) L. Yao, Q. Hu, L. Bao, W. Zhu and Y. Hu, *Org. Lett.*, 2021, **23**, 4971-4975; (f) W. Miao, W. Gao, X. Huang, M. Liu, Y. Zhou, and H. Wu, *Org. Lett.*, 2021, **23**, 9425–9430; (g) R. David, H. Shih, A. Alexander, R. Mehl and J. Prescher, *J. Am. Chem. Soc.*, 2017, **139**, 7370–7375; (h) B. Muriel, A. Gagnebin, and J. Waser, *Org. Chem. Front.*, 2020, **7**, 2944; (i) R. D. M. a. A. JOSE, *Asian J. Org. Chem.*, 2018, **30**, 1075-1077; (j) F. Wang, W. Zhang, J. Zhu, H. Li, K. Huang and J. Hu, *Chem. Commun.*, 2011, **47**, 2411–2413.
2. A. Hamada and T. Takizawa, *Chem. Pharm. Bull.*, 1975, **23**, 2933.
3. H. V. Thulasiram, R. M. Phan, S. B. Rivera and C. Dale Poulter, *J. Org. Chem.*, 2006, **71**, 1739-1741.

5. NMR Spectra

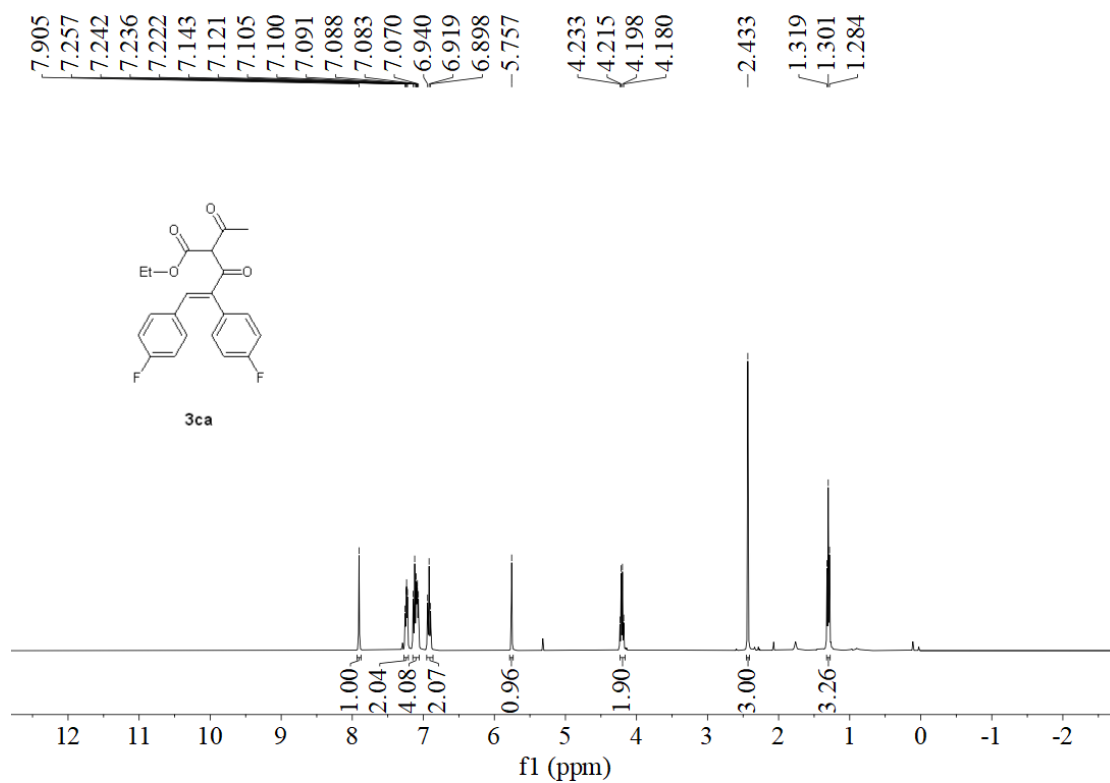




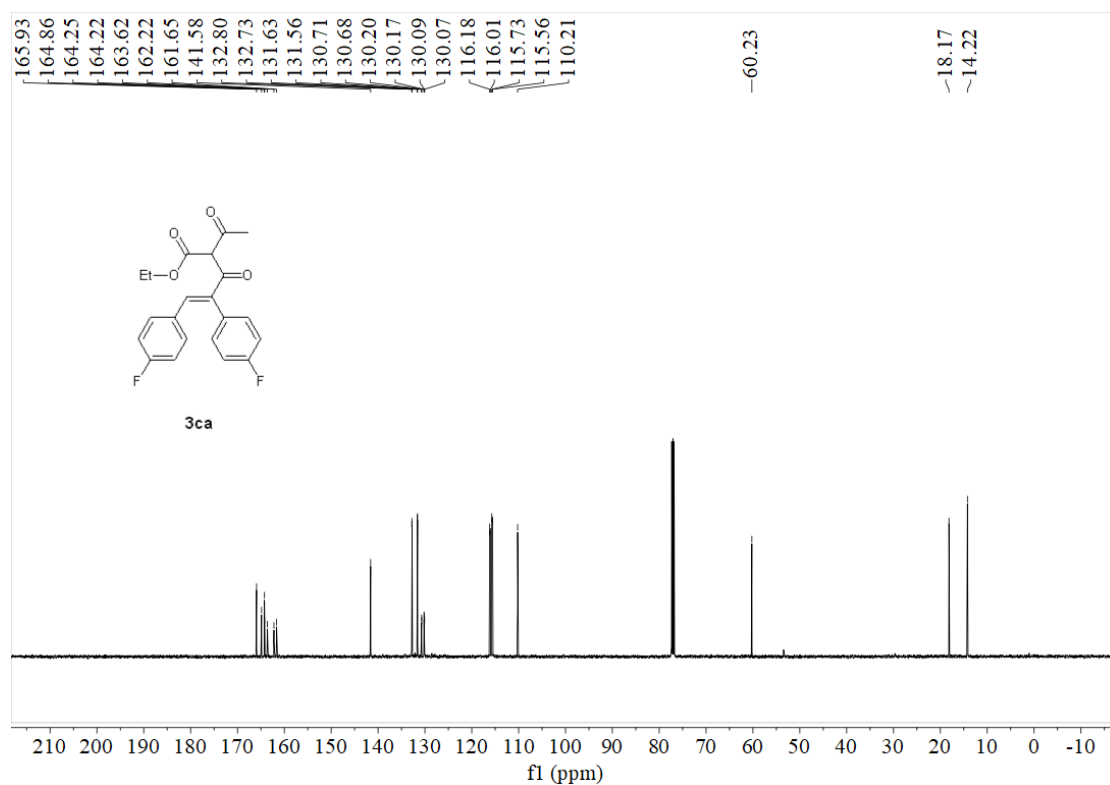
(400 MHz for ¹H NMR with CDCl₃ as solvent)



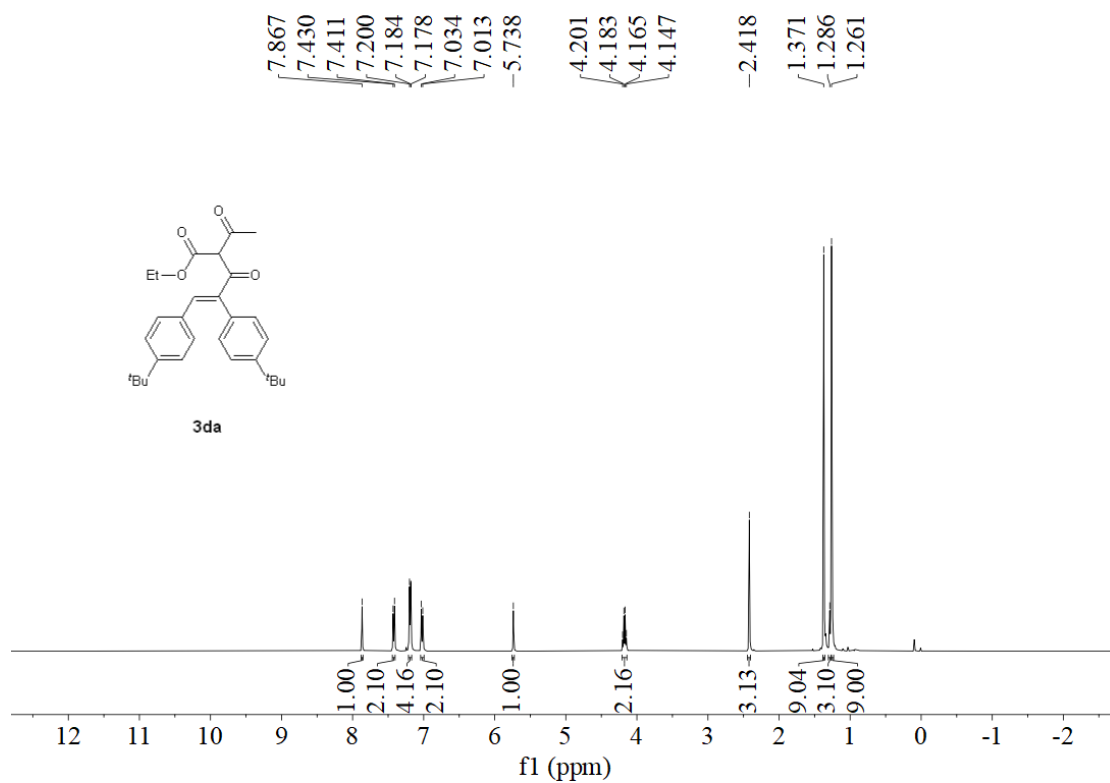
(126 MHz for ¹³C NMR with CDCl₃ as solvent)



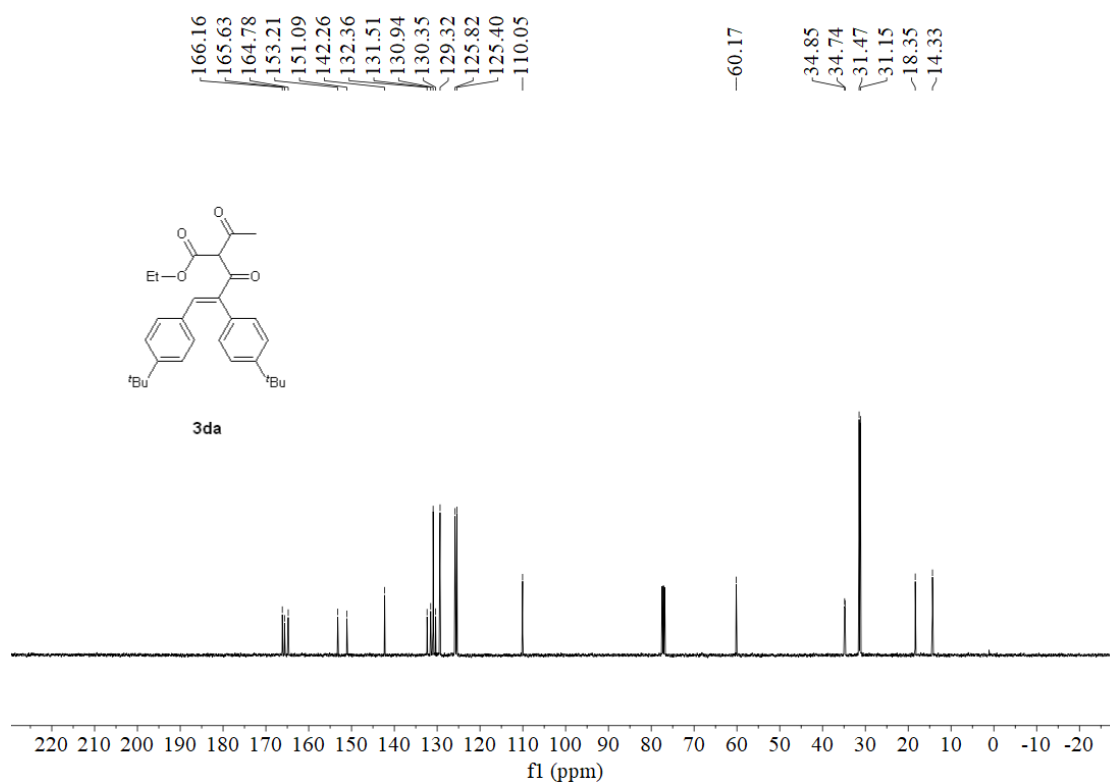
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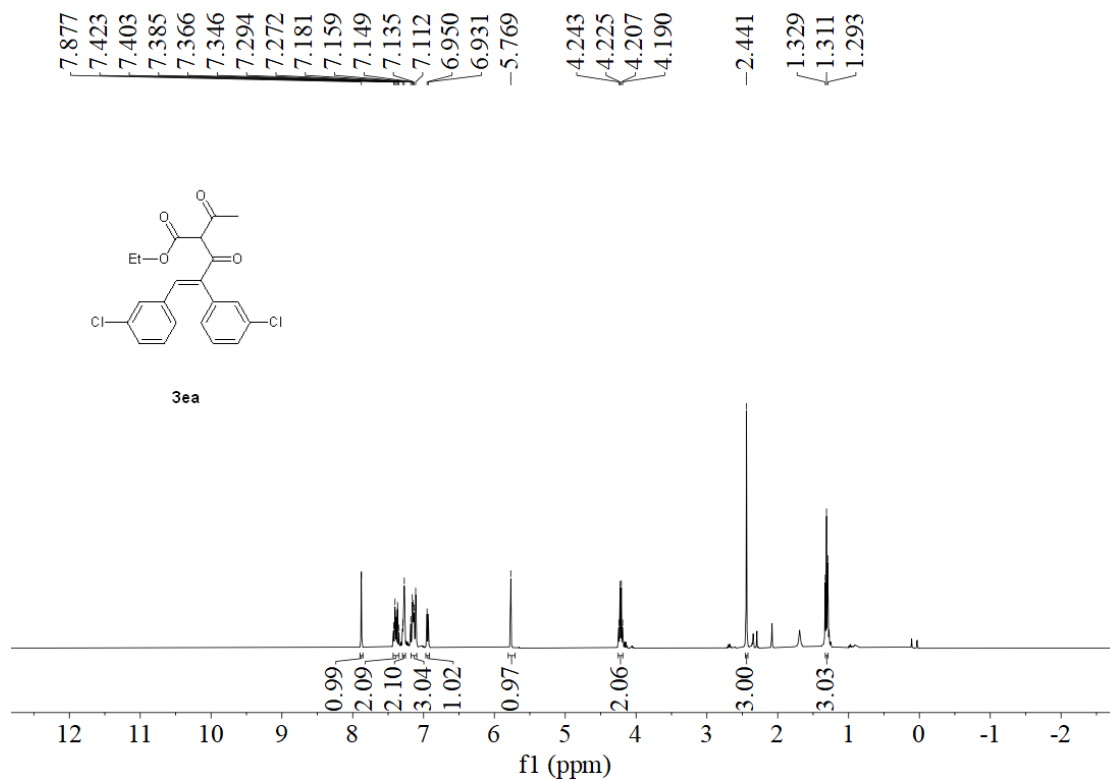
(126 MHz for ¹³C NMR with CDCl₃ as solvent)



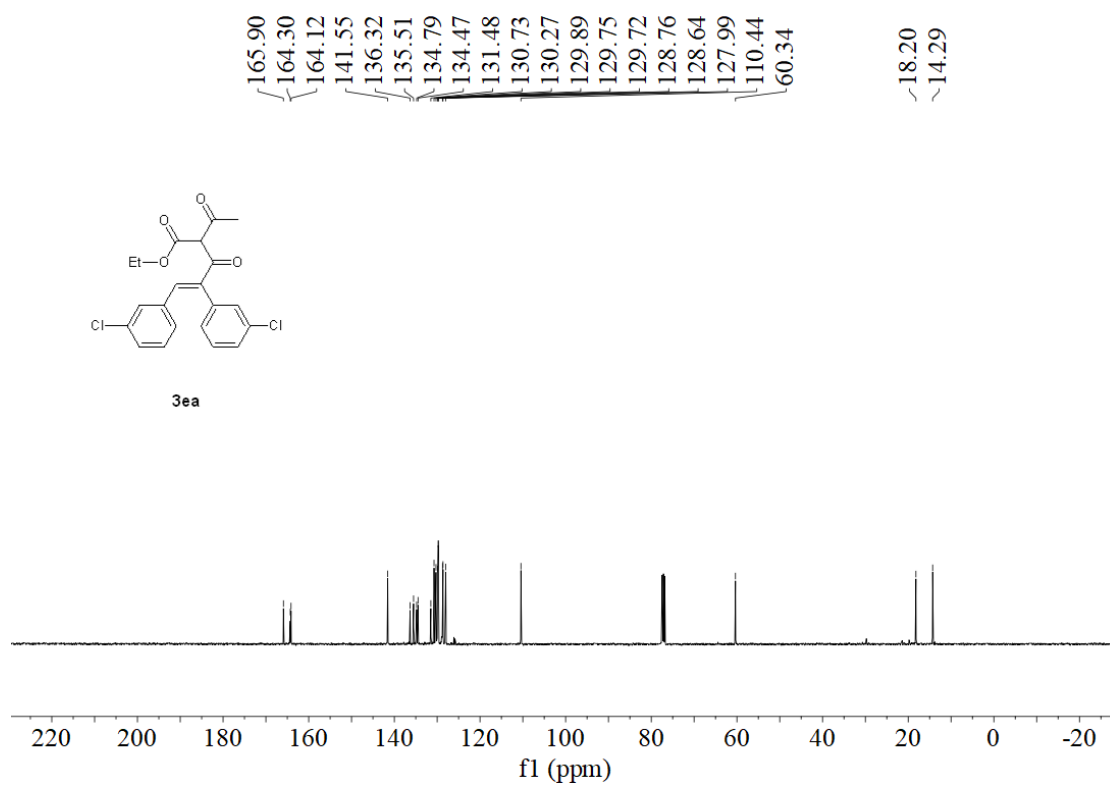
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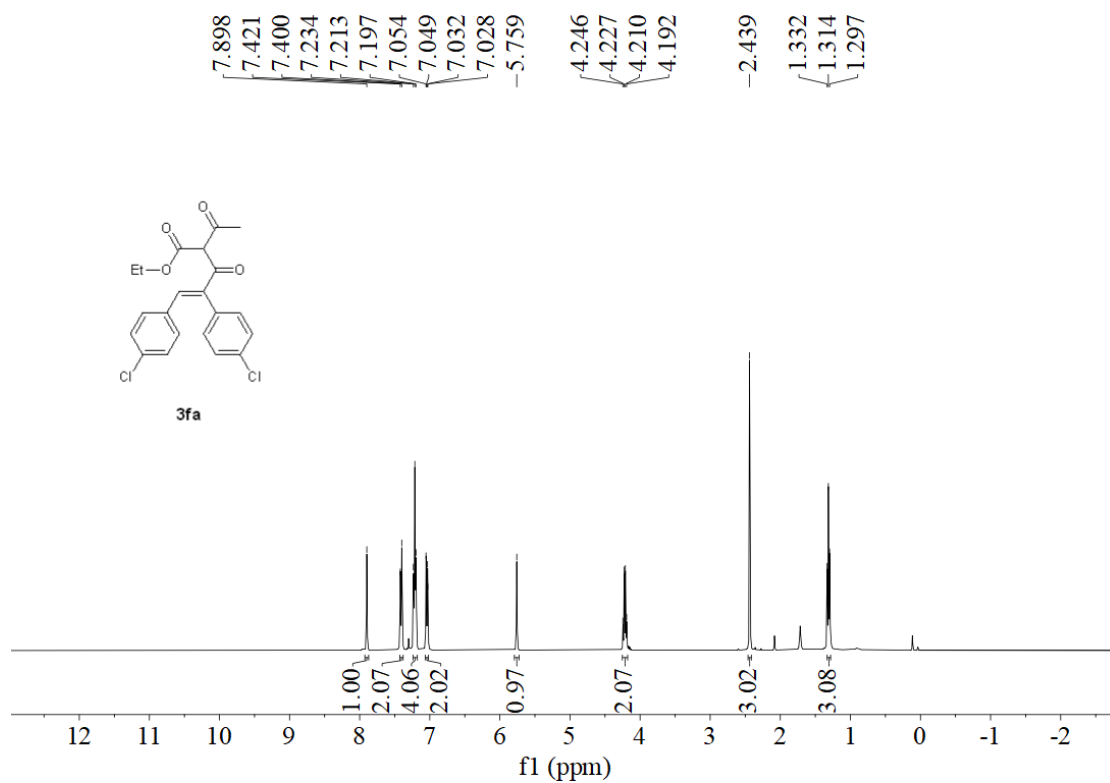
(101 MHz for ^{13}C NMR with CDCl_3 as solvent)



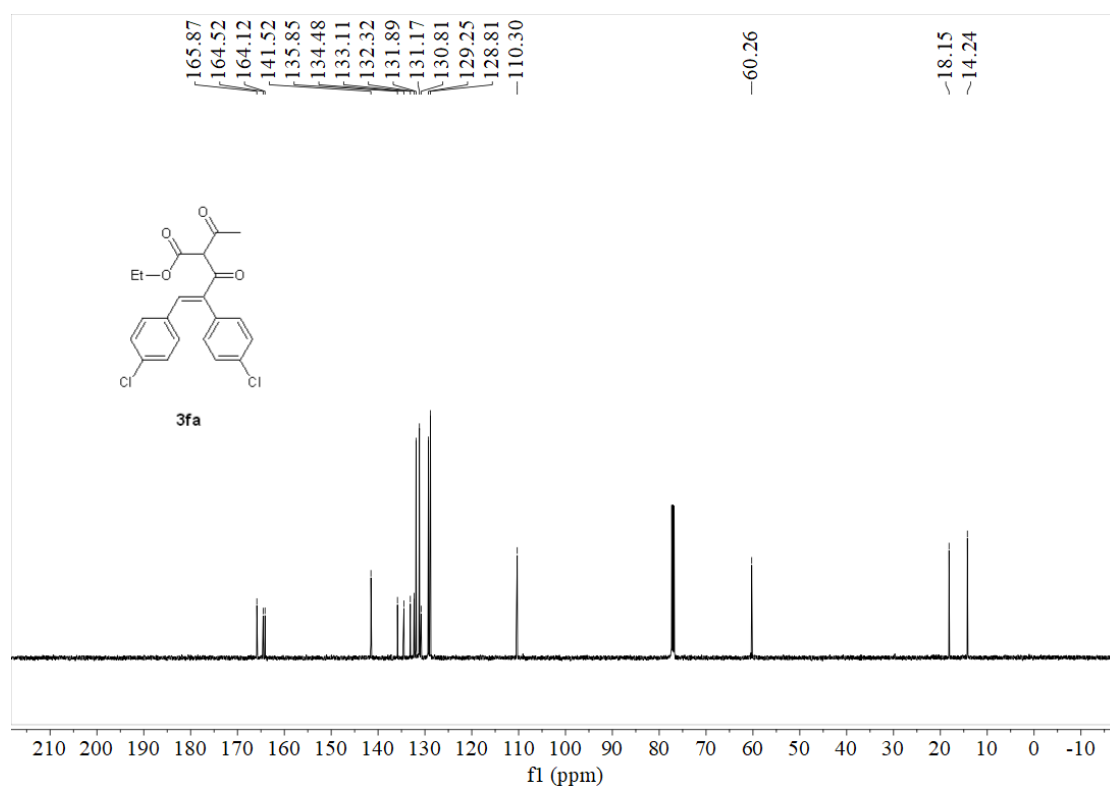
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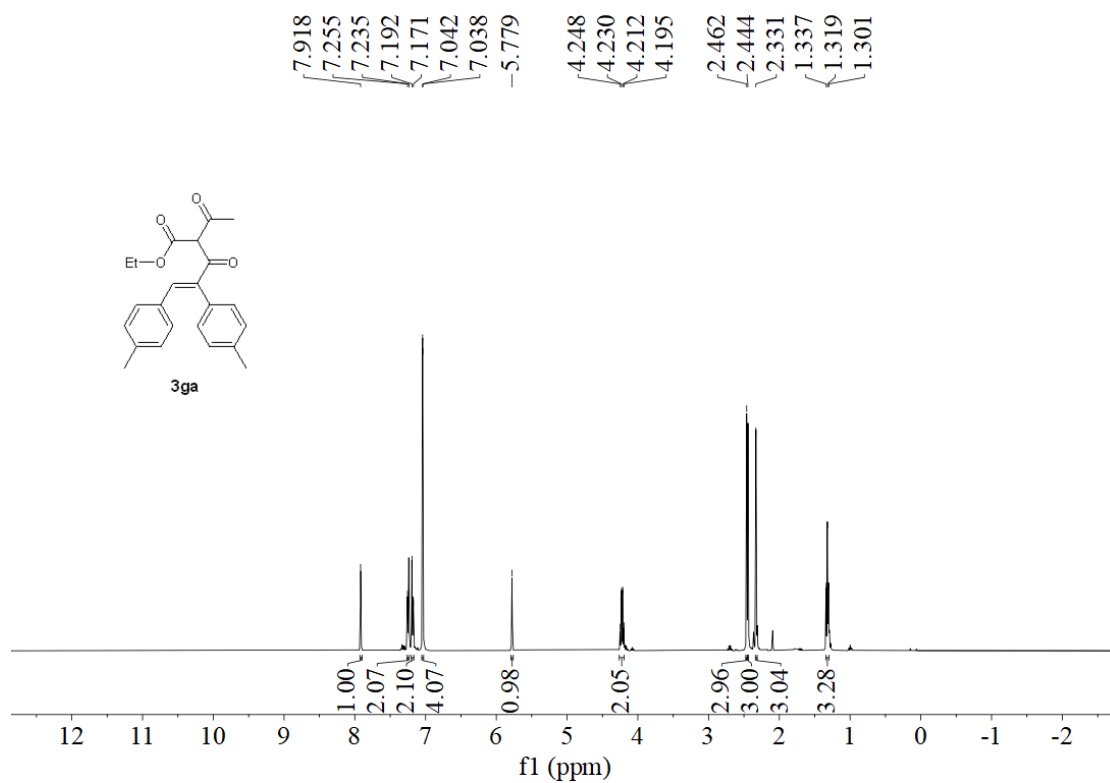
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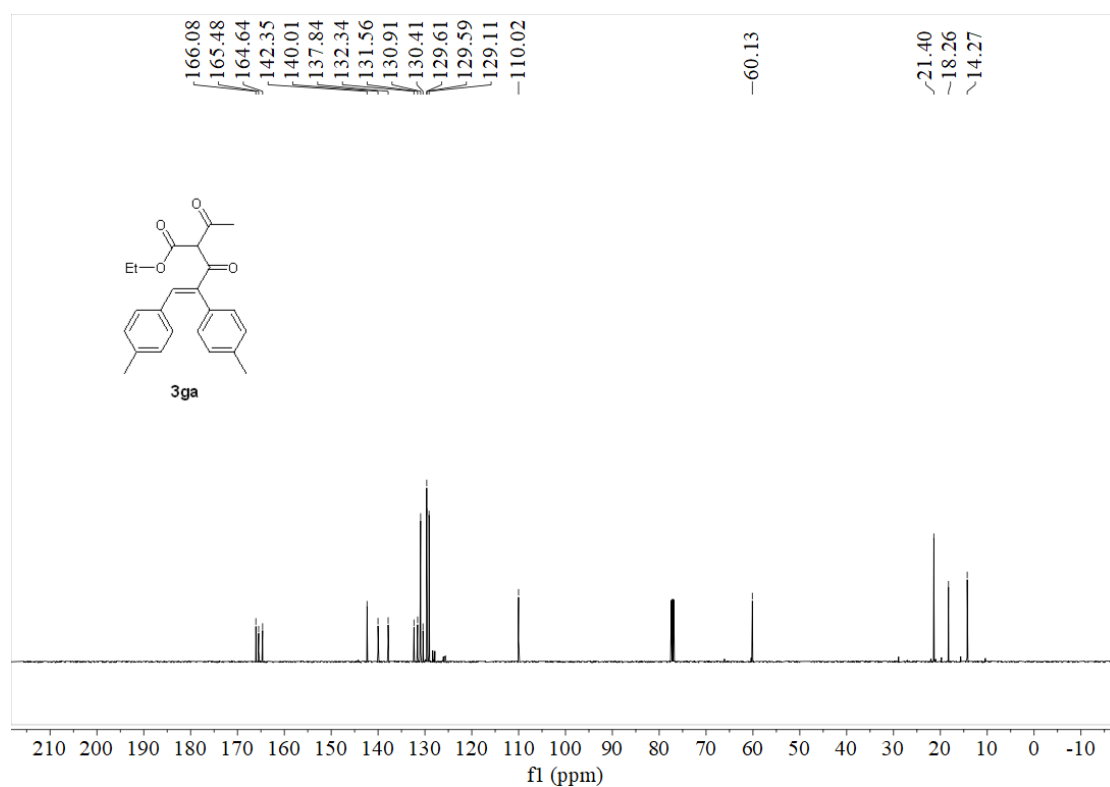
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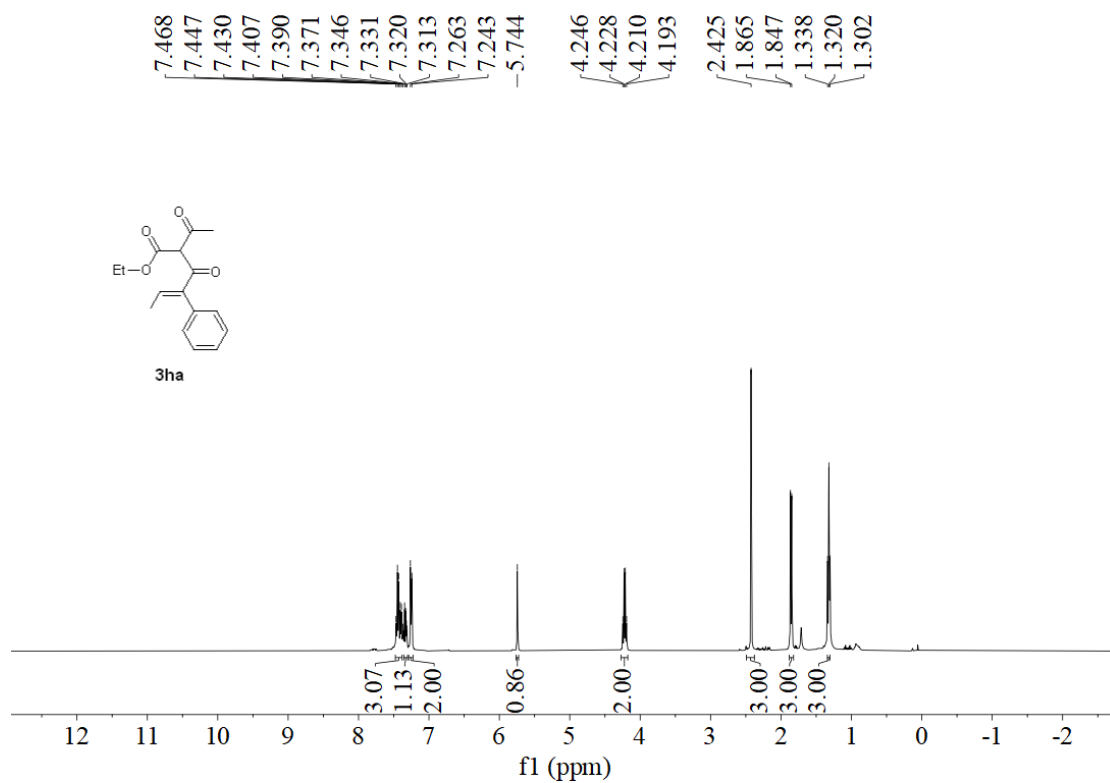
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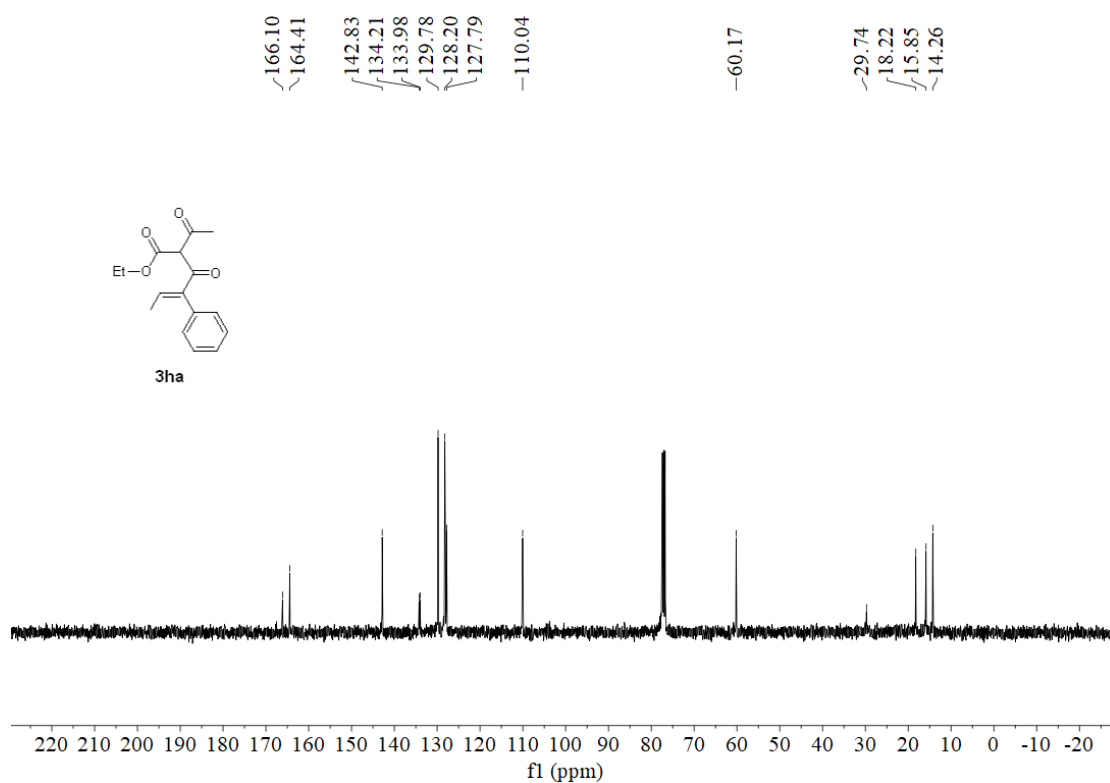
(400 MHz for ^1H NMR with CDCl_3 as solvent)



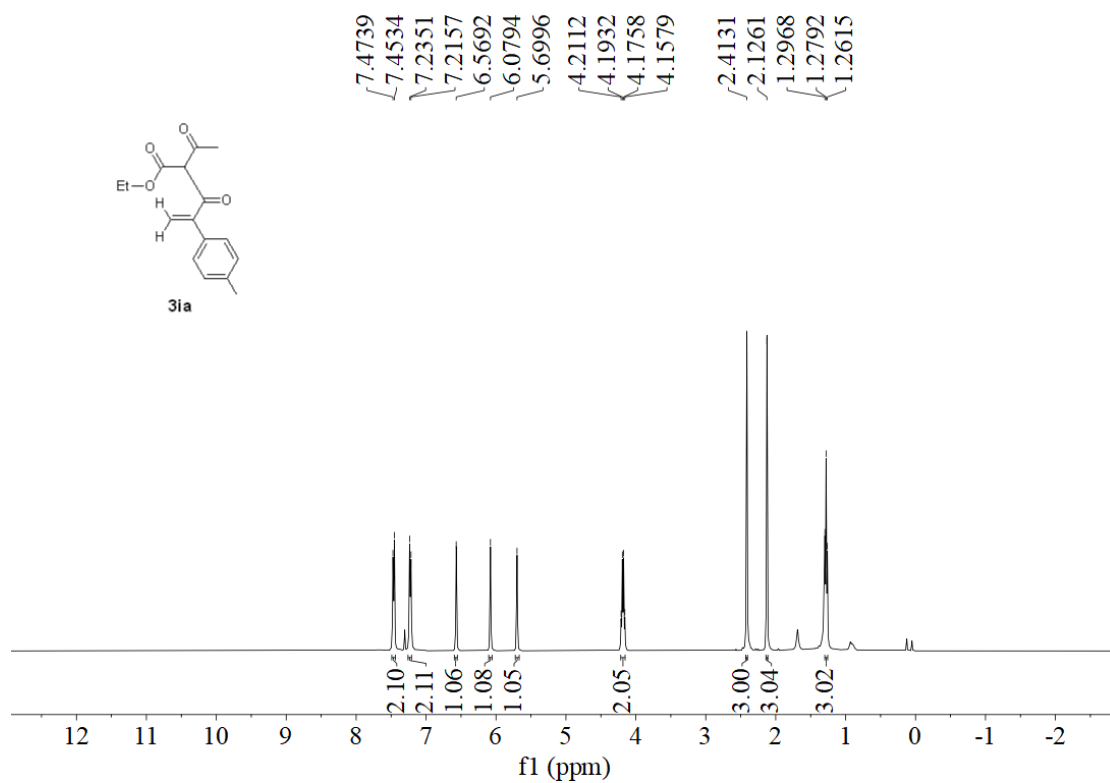
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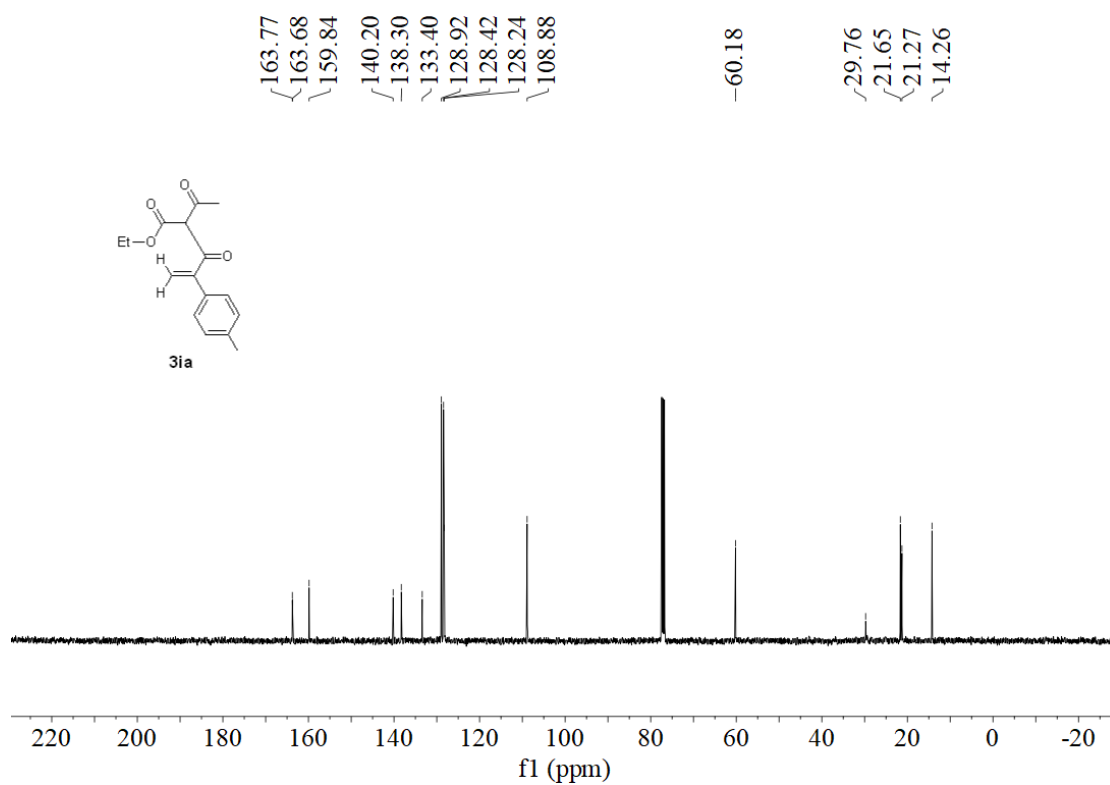
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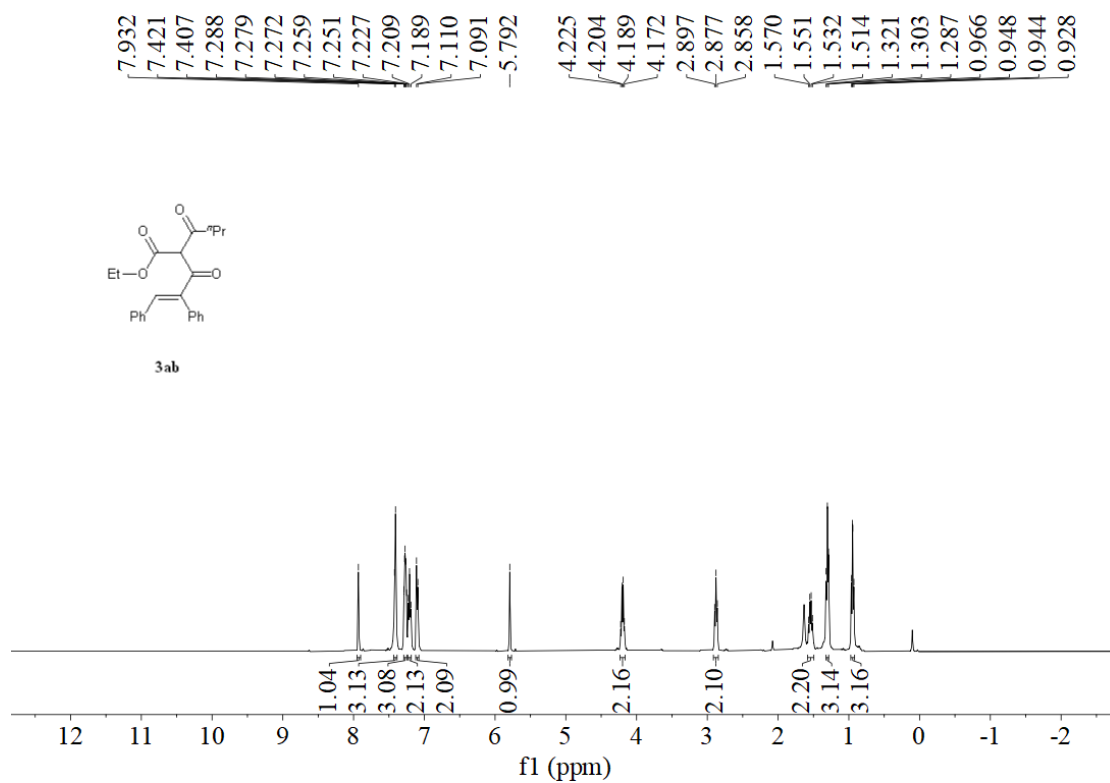
(101 MHz for ^{13}C NMR with CDCl_3 as solvent)



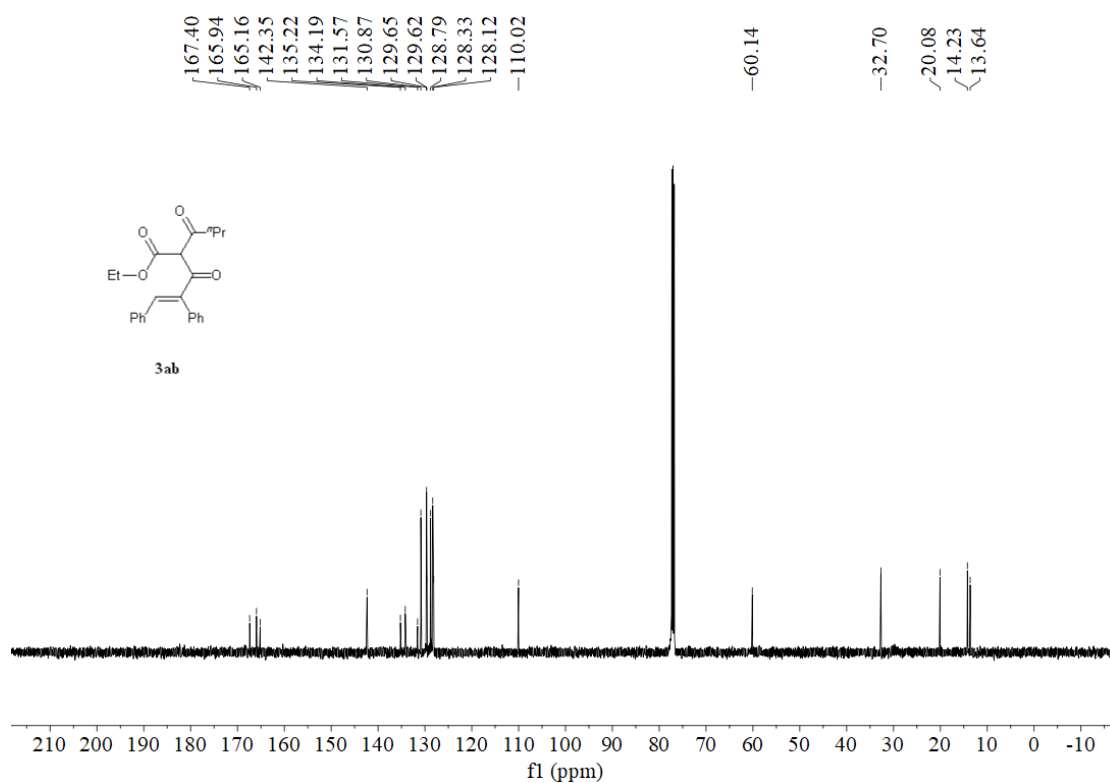
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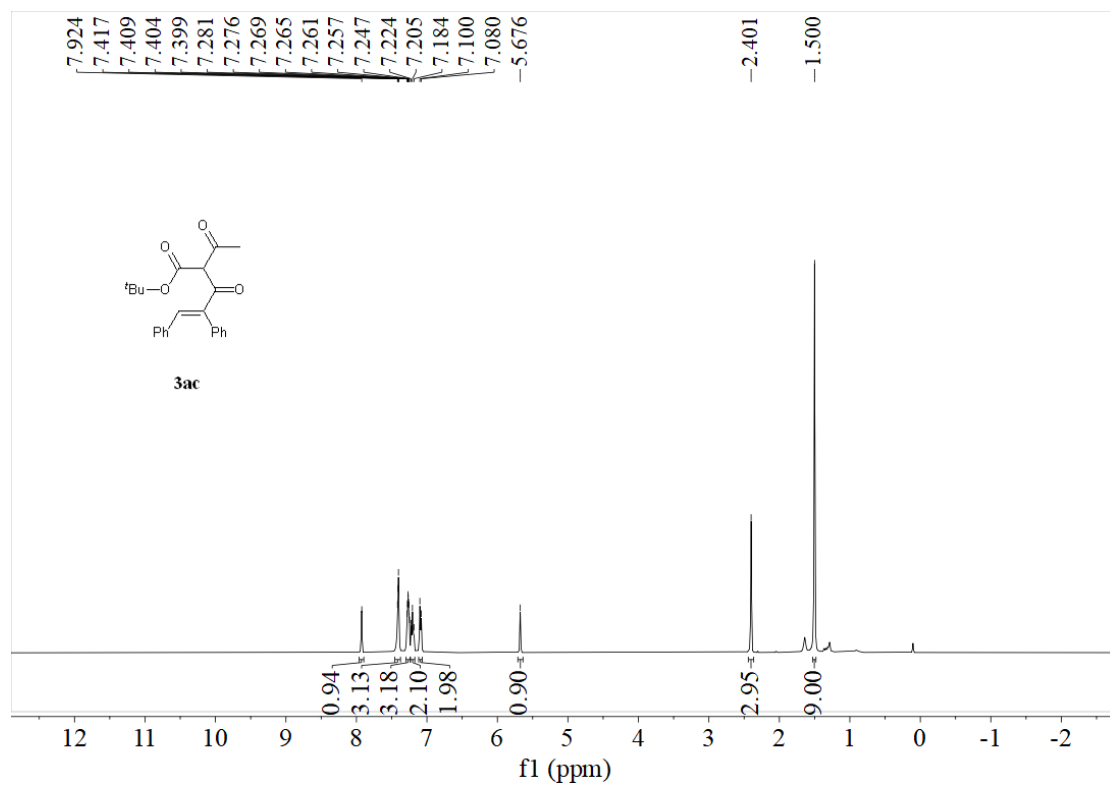
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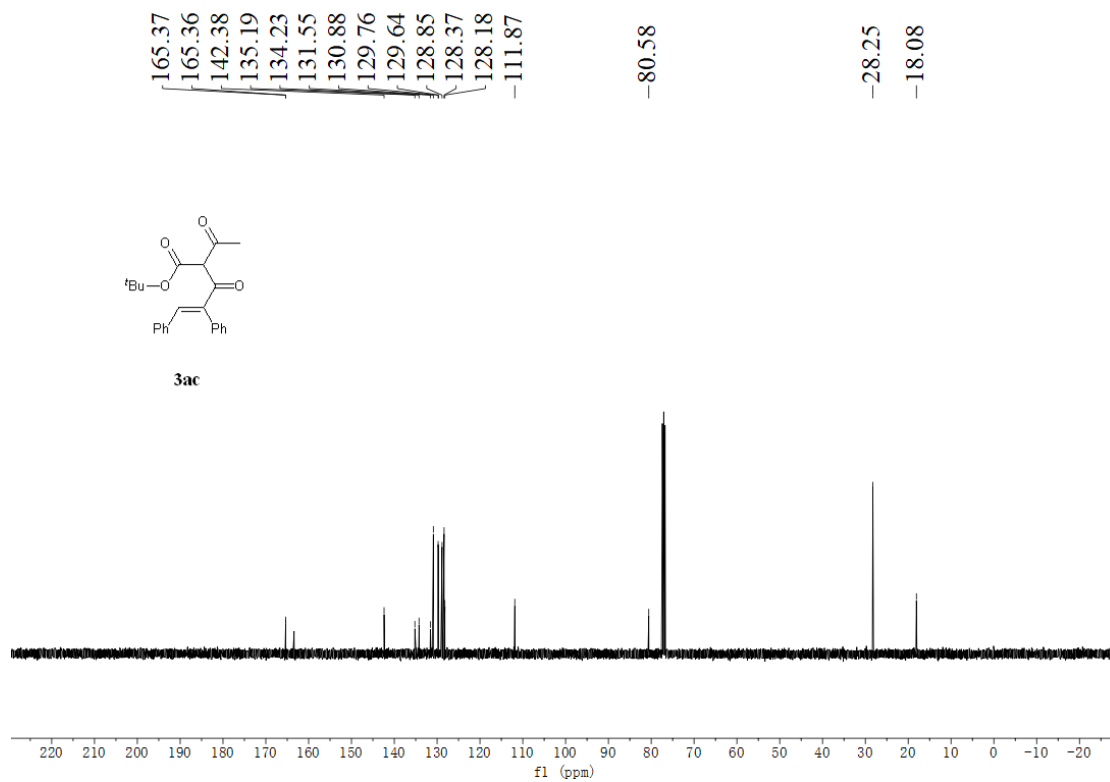
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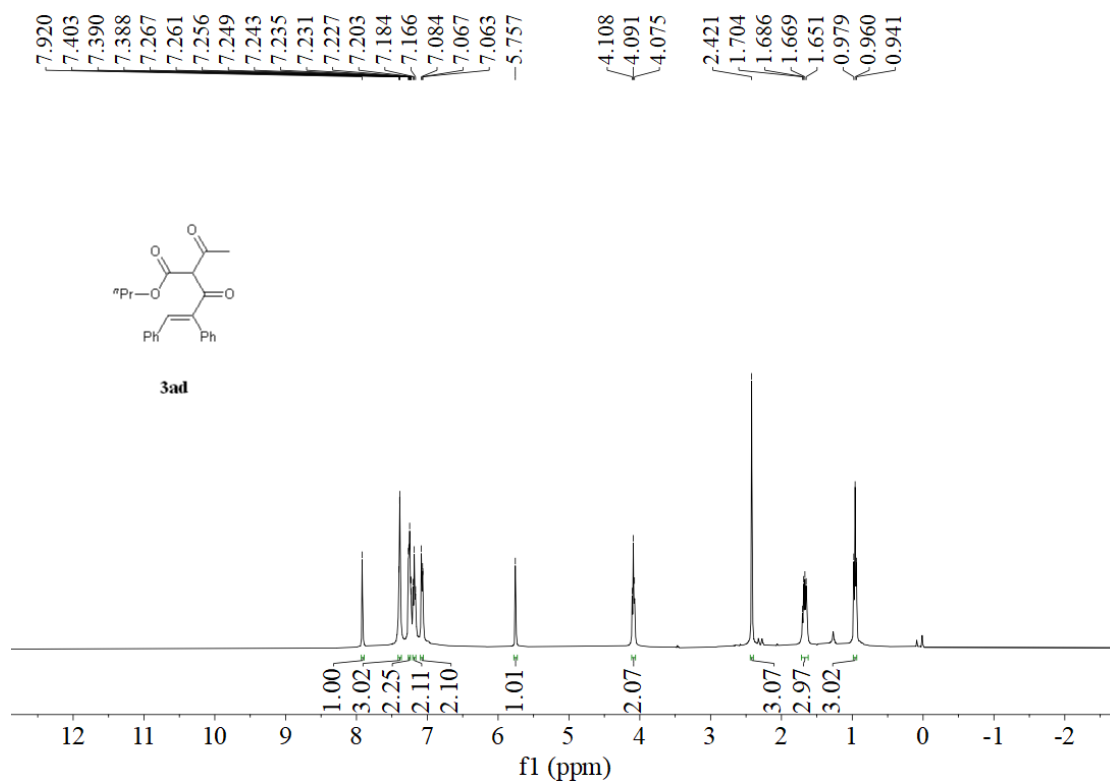
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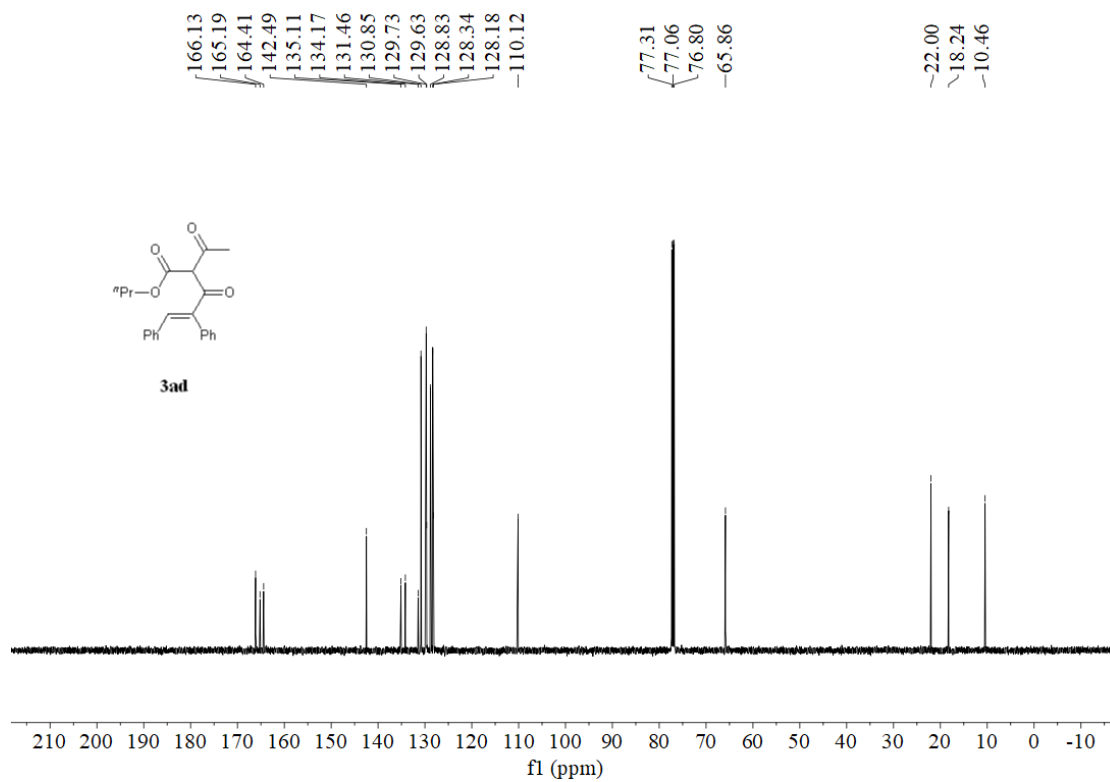
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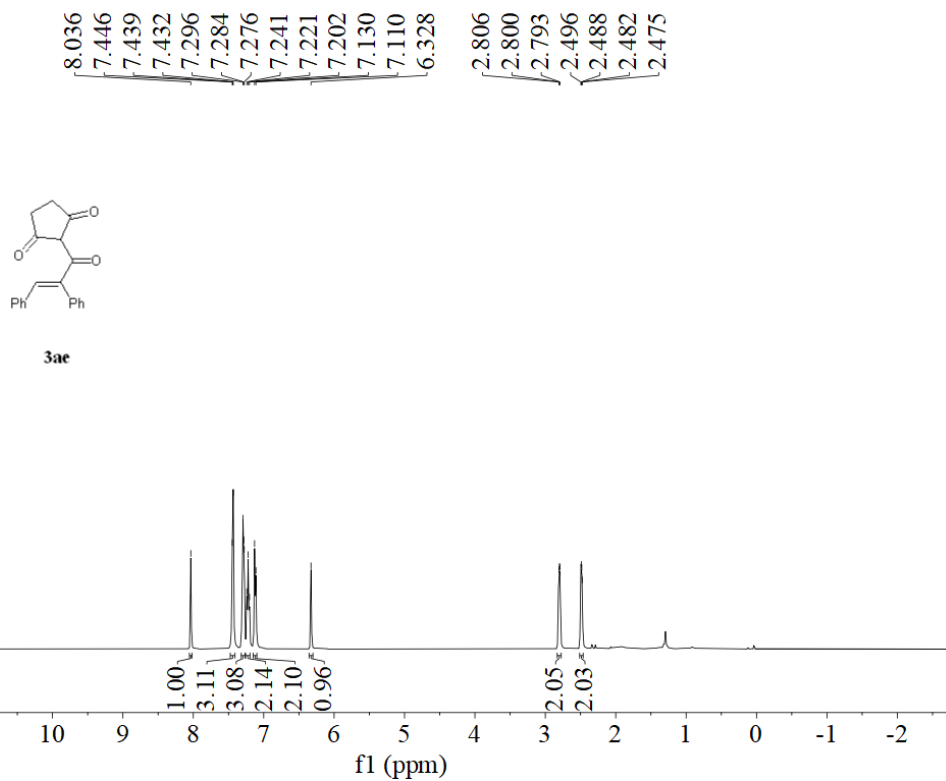
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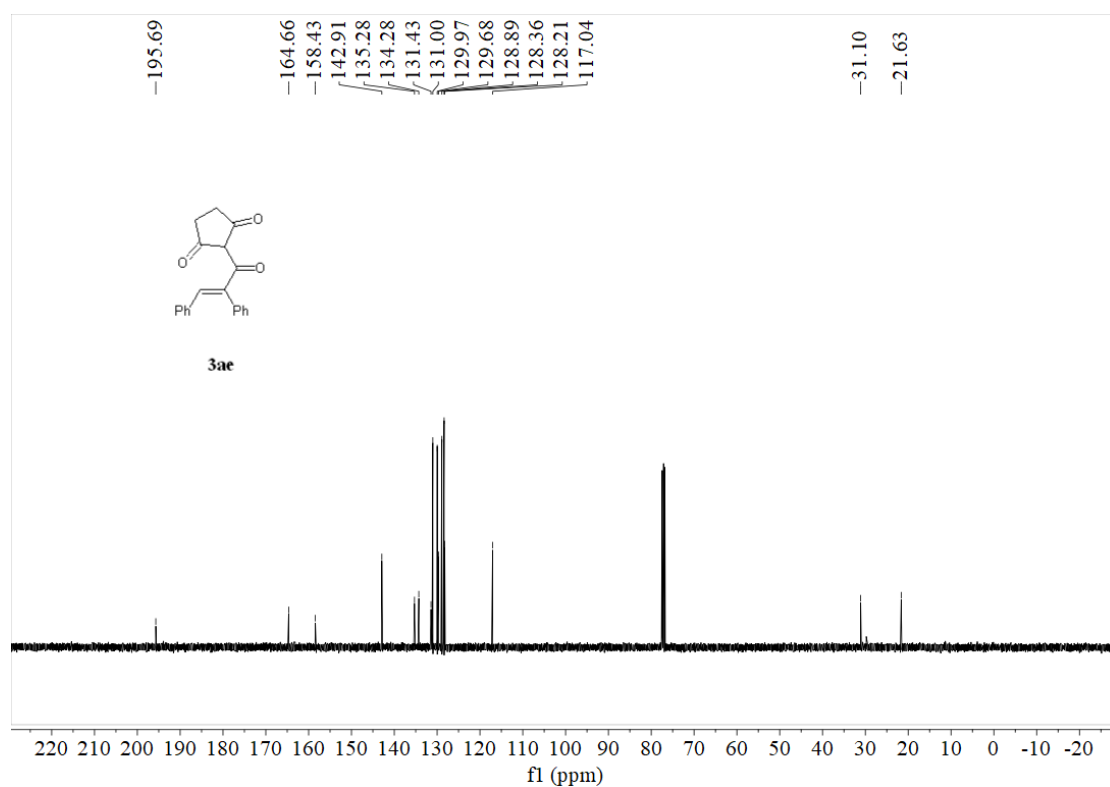
(400 MHz for ^1H NMR with CDCl_3 as solvent)



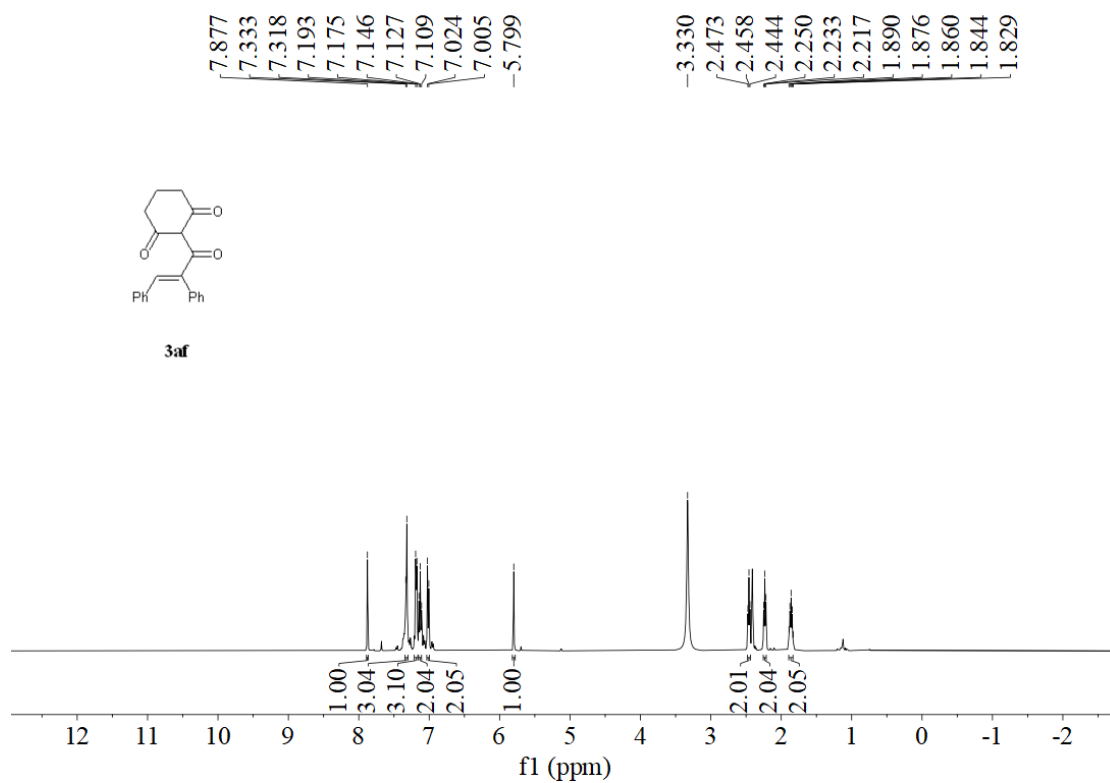
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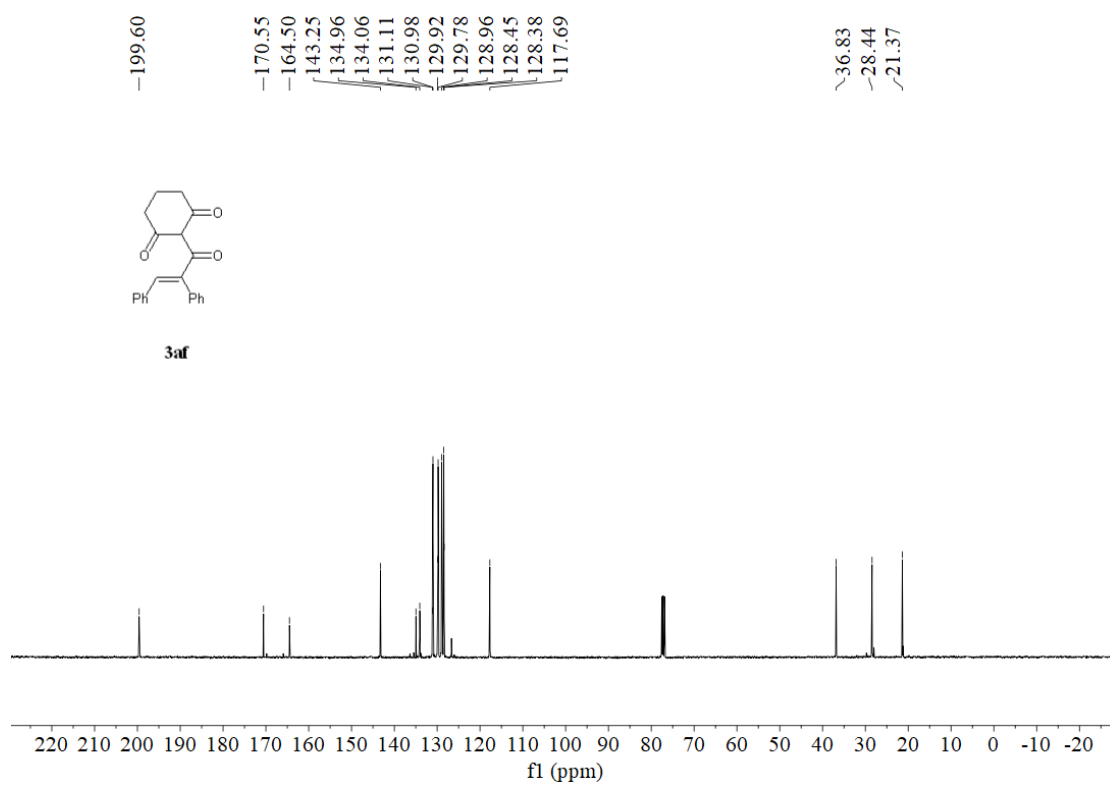
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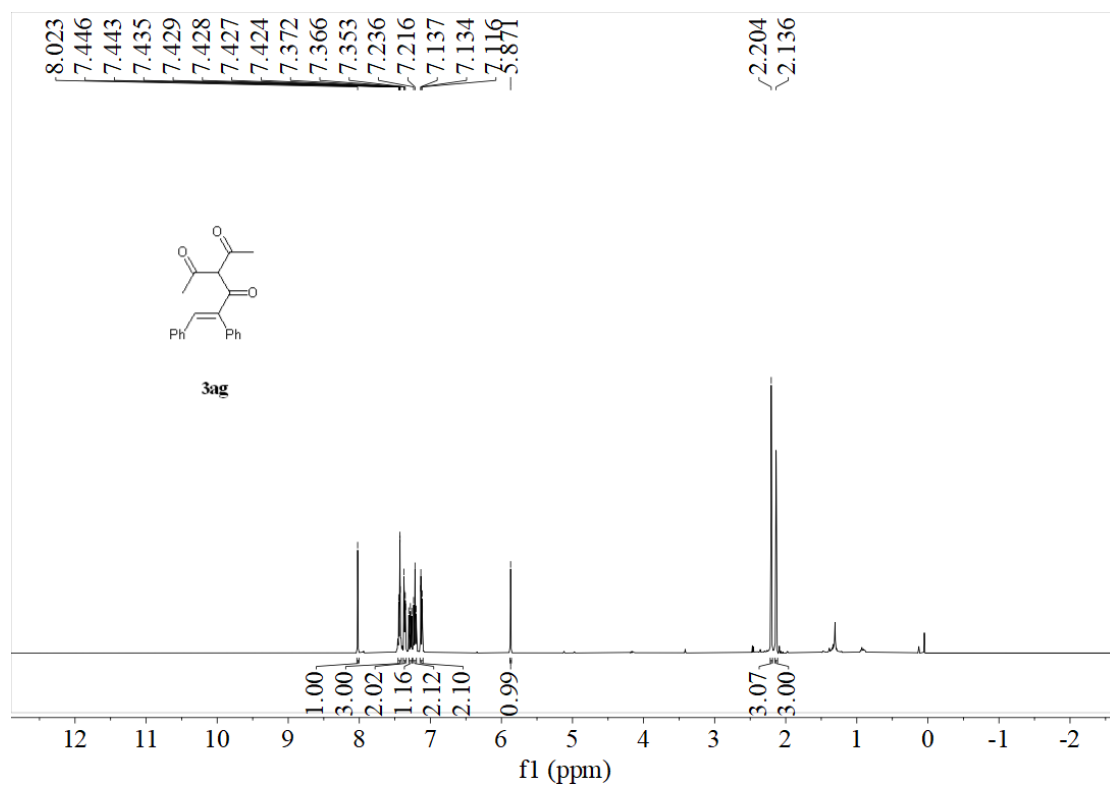
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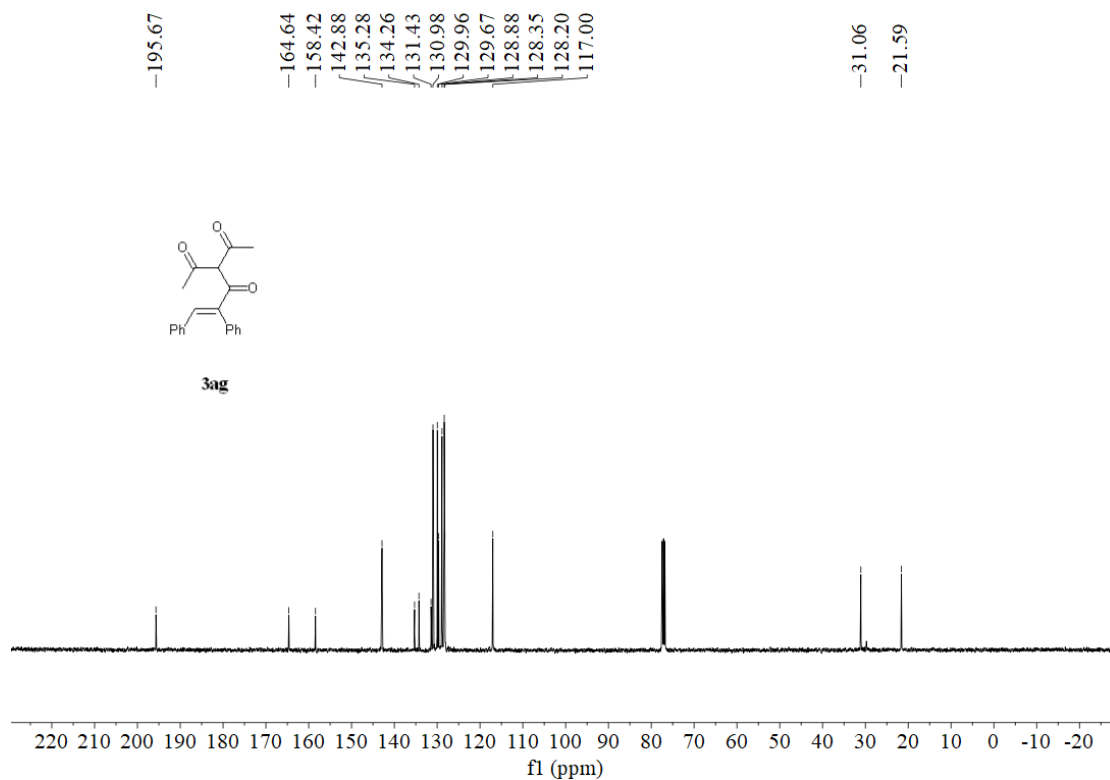
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(101 MHz for ^{13}C NMR with CDCl_3 as solvent)

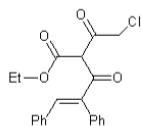


(400 MHz for ¹H NMR with CDCl₃ as solvent)

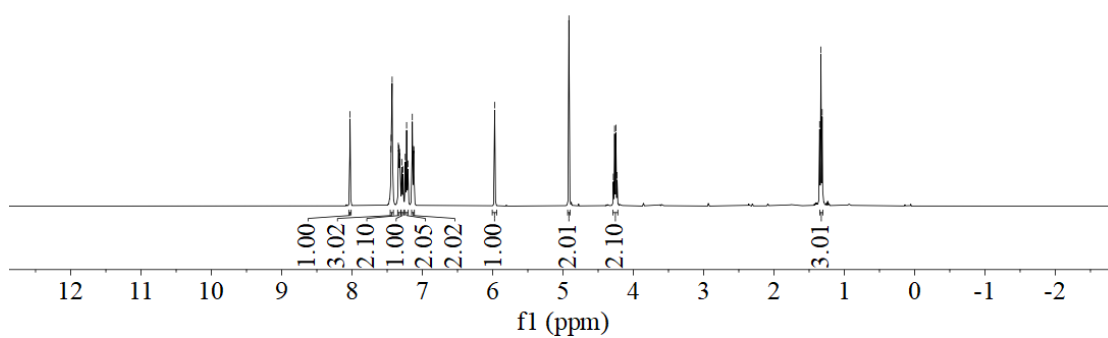


(126 MHz for ¹³C NMR with CDCl₃ as solvent)

8.028
7.447
7.443
7.434
7.429
7.342
7.336
7.331
7.323
7.318
7.292
7.243
7.224
7.142
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4.266
4.248
4.230
1.351
1.333
1.315

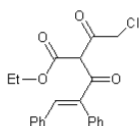


3ah

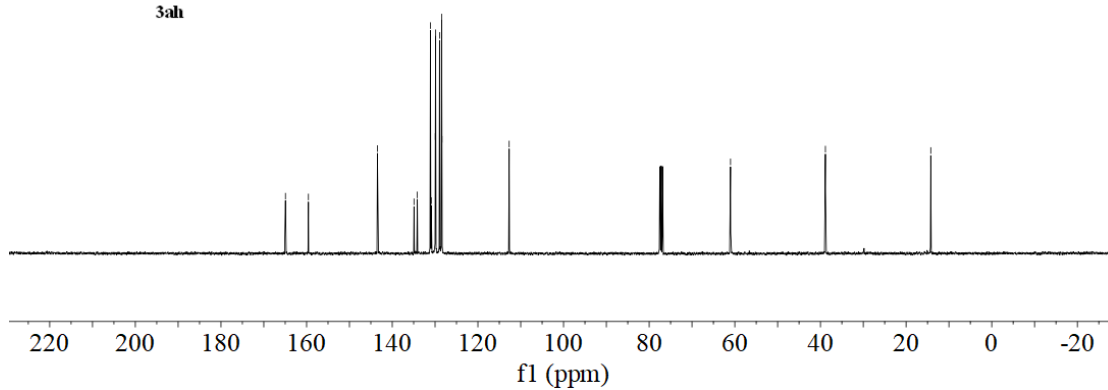


(400 MHz for ^1H NMR with CDCl_3 as solvent)

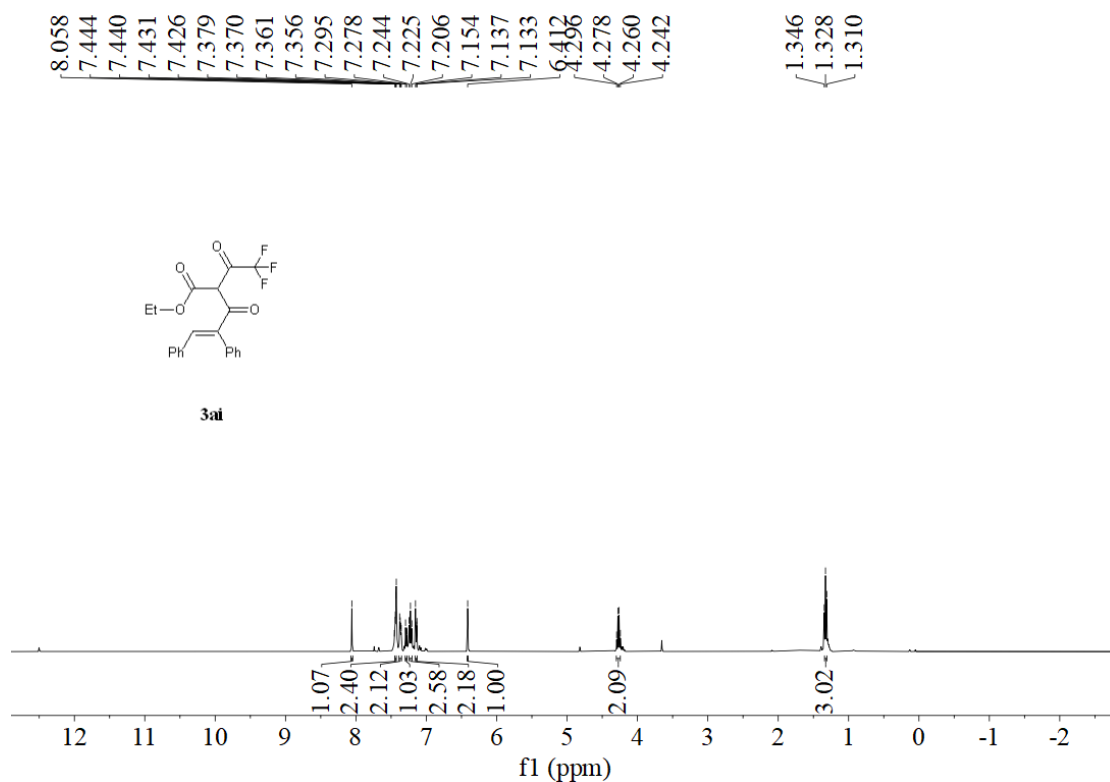
164.94
159.58
143.46
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131.08
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112.70
-61.00
-38.85
-14.24



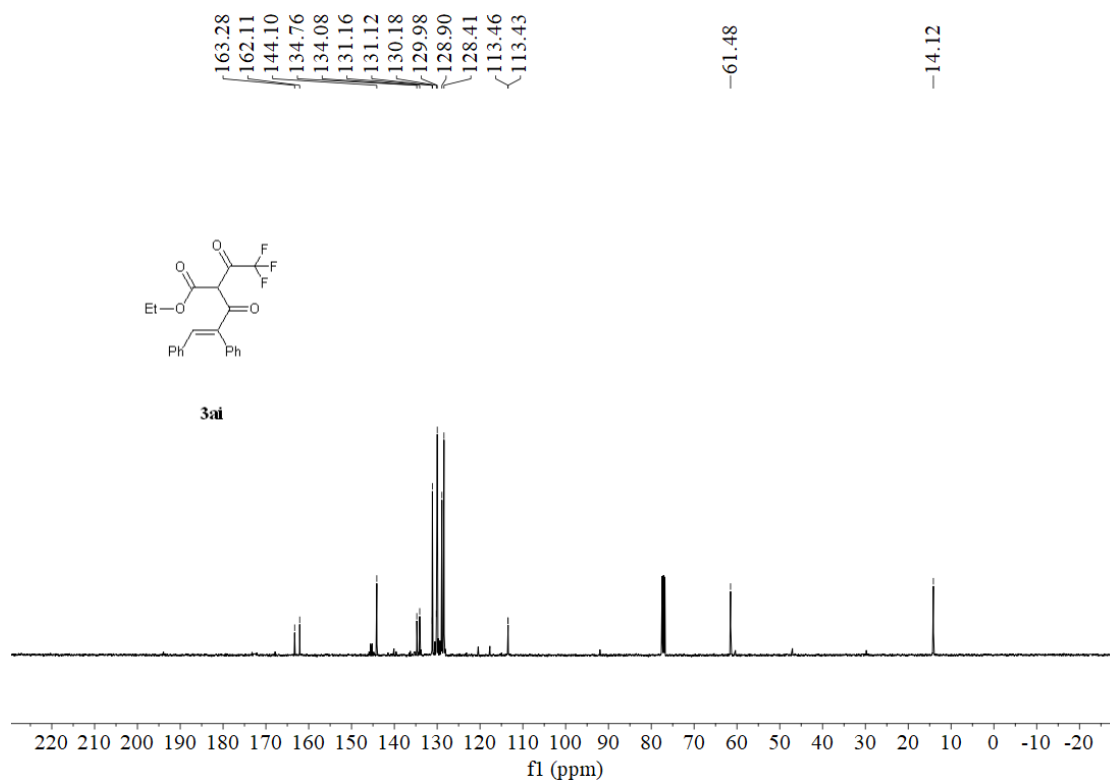
3ah



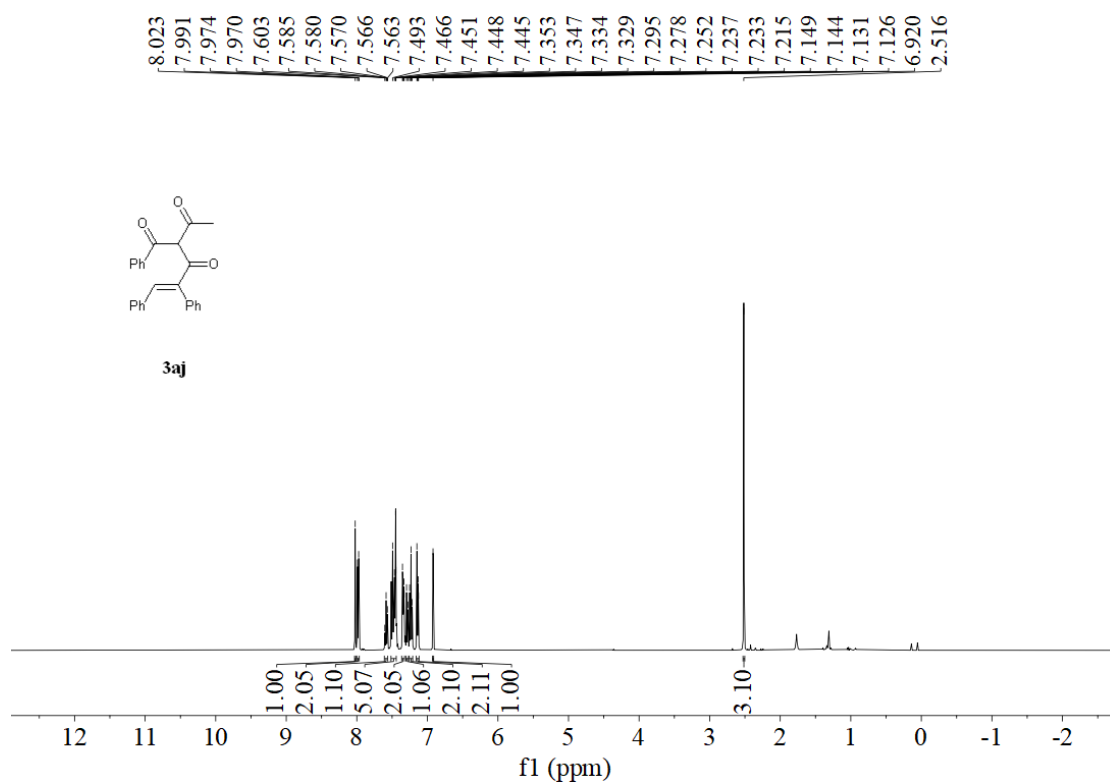
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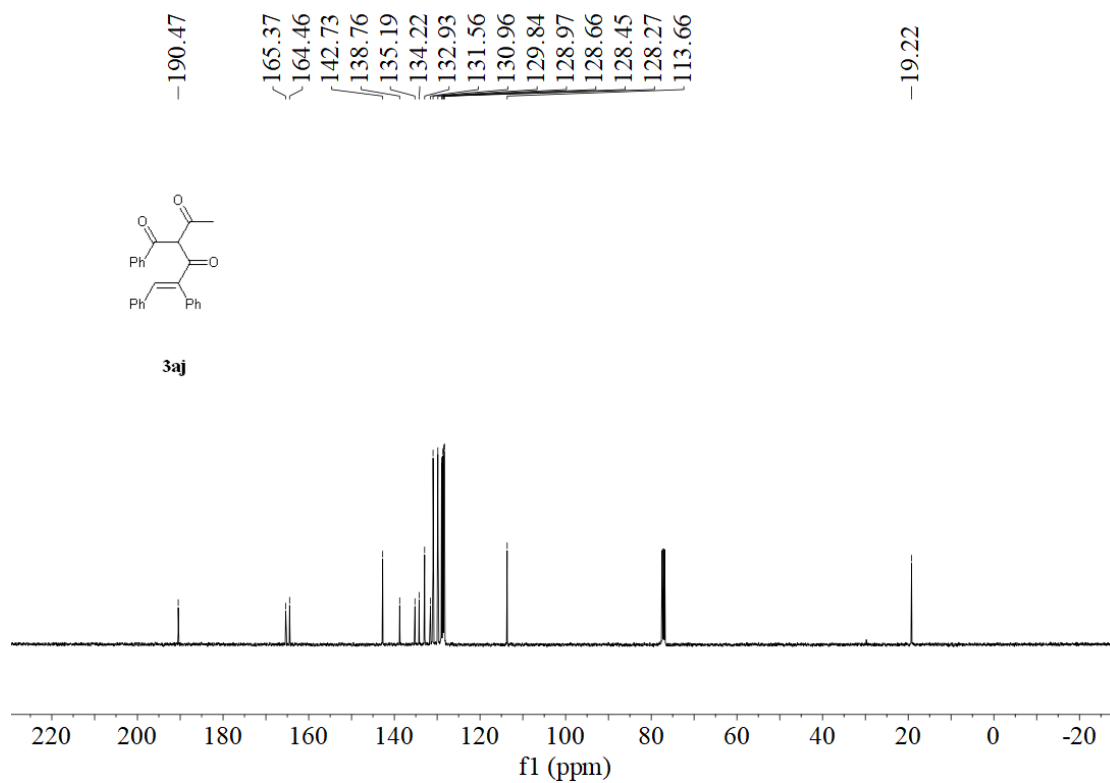
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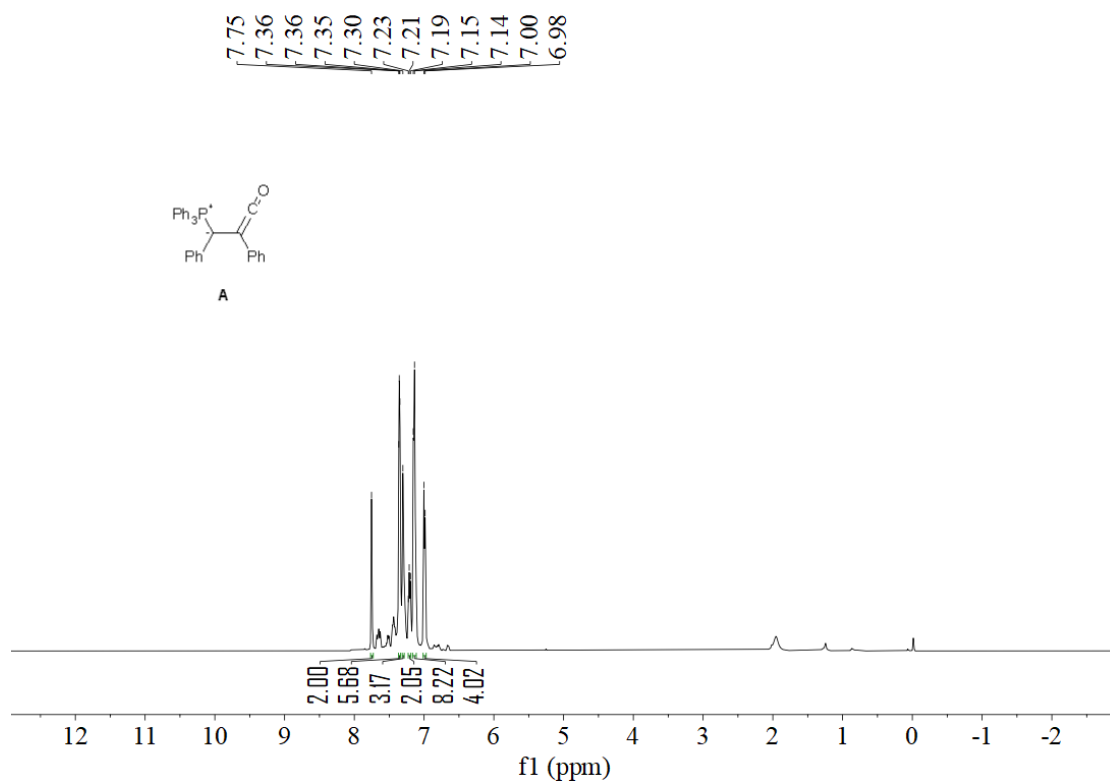
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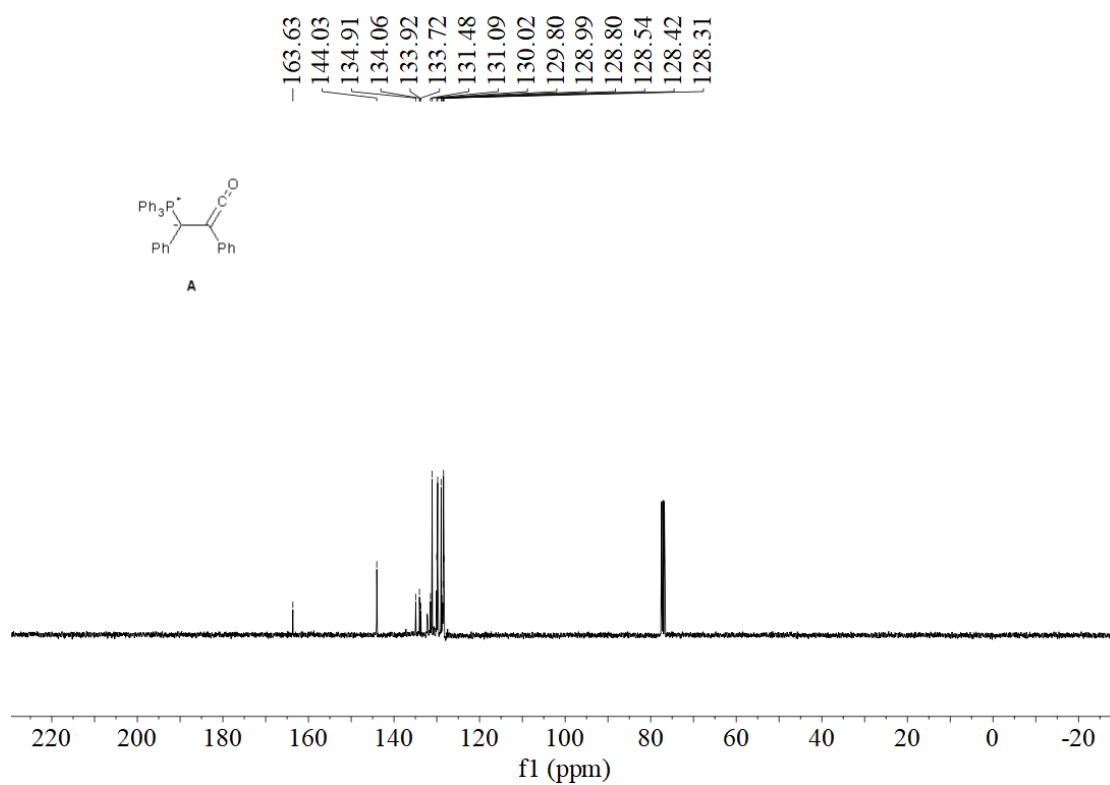
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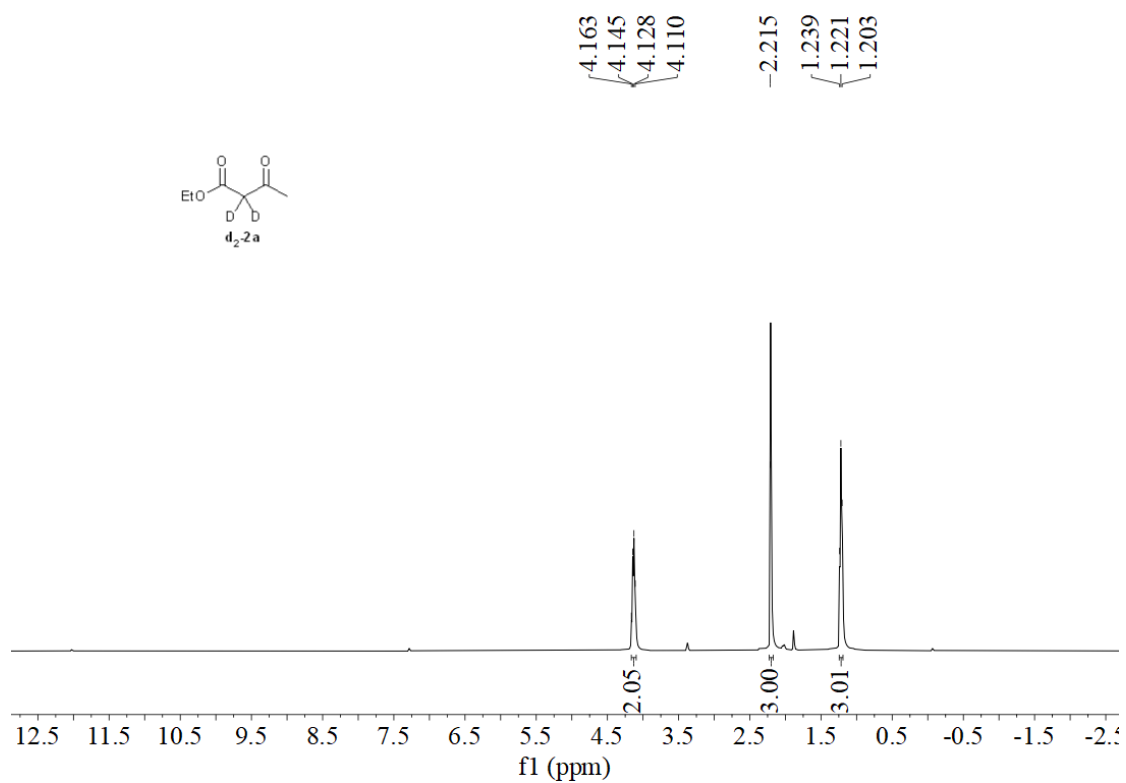
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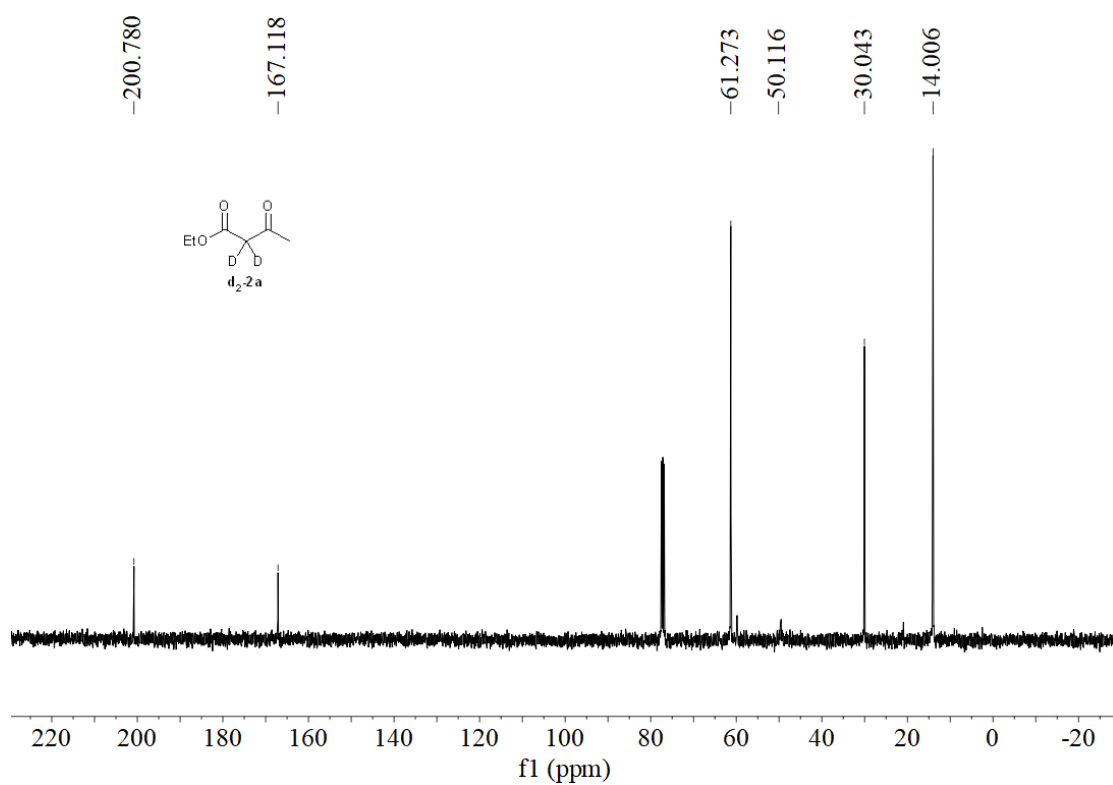
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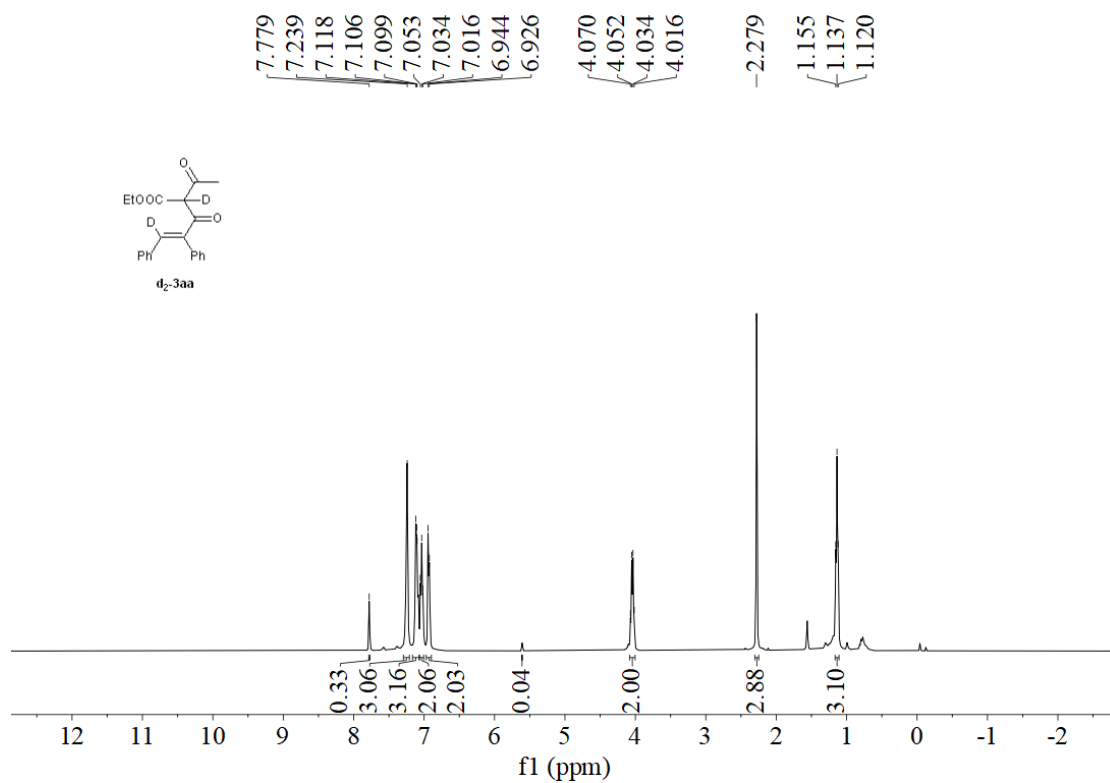
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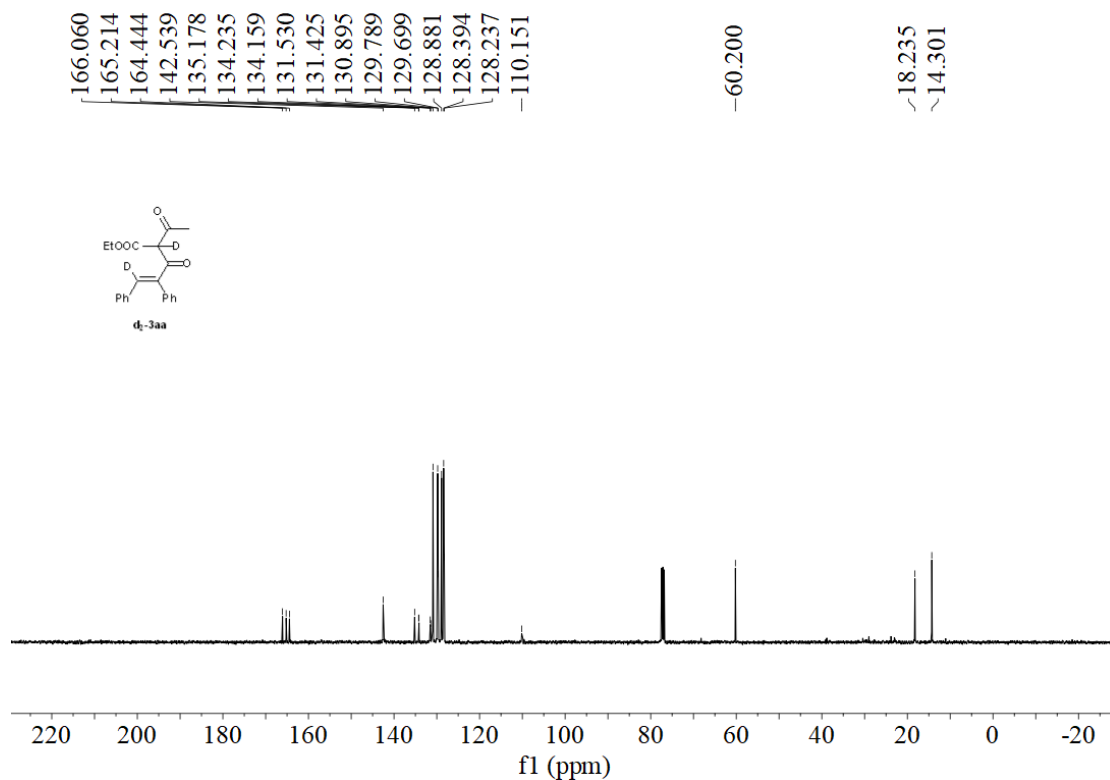
(400 MHz for ¹H NMR with CDCl₃ as solvent)



(101 MHz for ¹³C NMR with CDCl₃ as solvent)



(400 MHz for ^1H NMR with CDCl_3 as solvent)



(101 MHz for ^{13}C NMR with CDCl_3 as solvent)