

Supporting Information

Visible Light Mediated Utilization of α -Aminoalkyl Radicals: Addition to Electron Deficient Alkenes Using Photoredox Catalysts

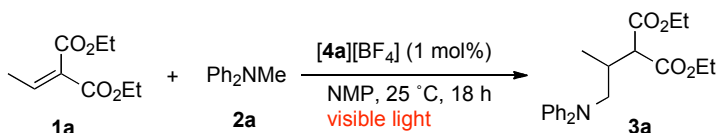
Yoshihiro Miyake, Kazunari Nakajima, and Yoshiaki Nishibayashi*

Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

General Method.

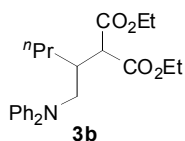
^1H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvent. ^{19}F NMR (471 MHz) spectra were recorded on a JEOL JNM-ECP 500 spectrometer. Elemental analyses were performed at Microanalytical Center of The University of Tokyo. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. Absorption spectra was recorded on Shimadzu MultiSpec-1500 spectrometer. All reactions were carried out under dry nitrogen atmosphere. Solvents were dried by the general methods, and degassed before use. Photoirradiation was carried out with 14 W white LED. Alkenes **1b**^{S1}, **1c**^{S1}, **1d**^{S2}, **1e**^{S1}, **1f**^{S1}, **1g**^{S3}, **1h**^{S1}, **1i**^{S4}, **1j**^{S5}, **1l**^{S6}, and amines **2a-d**^{S7}, **2b**^{S8}, **2c**^{S9}, **2d**^{S9}, **2e**^{S9}, **2f**^{S10}, **2g**^{S11}, **2h**^{S12}, **2i**^{S13}, **2l**^{S14} were prepared according to the literature procedures.

Photocatalytic Reactions of Electron Deficient Alkenes (1) with Amines (2).

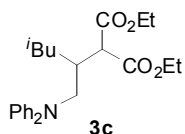


A typical experimental procedure for the reaction of diethyl ethylidenemalonate (**1a**) with methyldiphenylamine (**2a**) is described below. In a 20 mL Schlenk flask (diameter: 2.5 cm) were placed [4a][BF₄] (2.2 mg, 0.0026 mmol) and *N*-methylpyrrolidone (2.5 mL) under N₂, and then **1a** (46.3 mg, 0.249 mmol) and **2a** (55.6 mg, 0.303 mmol) were added. The reaction flask was placed in a water bath and illuminated with 14W white LED (approximately 2 cm from the light source) at 25 °C for 18 h. The resulting mixture was purified by column chromatography (SiO₂) with hexane/ethyl acetate (20/1) to give diethyl 2-(1-diphenylaminopropyl)malonate (**3a**) as a colorless oil (82.8 mg, 0.224 mmol, 90% yield). ^1H NMR (C₆D₆) δ 7.13-7.07 (m, 8H), 6.86-6.80 (m, 2H), 4.03-3.81 (m, 5H), 3.51 (dd, 1H, J = 14.6 and 8.6 Hz), 3.49 (d, 1H, J = 6.5 Hz), 2.98-2.87 (m, 1H), 1.13 (d, 3H, J = 7.0 Hz), 0.873 (t, 3H, J = 7.3 Hz), 0.868 (t, 3H, J = 7.3 Hz). ^{13}C NMR (C₆D₆) δ 168.7, 168.4, 149.3, 129.5, 122.0, 121.9, 61.1, 61.0, 56.4, 55.0, 32.5, 15.5, 14.0. HRMS (FAB) Calcd. for C₂₂H₂₈NO₄ [M+H]⁺: 370.2018. Found: 370.2024.

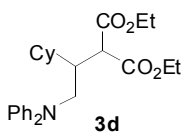
Isolated yields and spectroscopic data of other products are as follows:



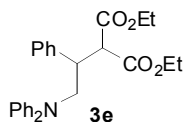
3b: 91% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.14-7.09 (m, 8H), 6.89-6.79 (m, 2H), 4.06 (dd, 1H, $J = 14.6$ and 7.3 Hz), 3.99-3.81 (m, 6H), 2.88-2.76 (m, 1H), 1.78-1.58 (m, 2H), 1.32-1.18 (m, 2H), 0.892 (t, 3H, $J = 7.3$ Hz), 0.886 (t, 3H, $J = 7.0$ Hz), 0.74 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR (C_6D_6) δ 169.0, 168.8, 149.4, 129.5, 122.1, 121.2, 61.1, 61.0, 54.3, 52.9, 37.2, 32.2, 20.5, 14.3, 13.98, 13.96. HRMS (EI) Calcd. for $\text{C}_{24}\text{H}_{31}\text{NO}_4$ [M]: 397.2253. Found: 397.2252.



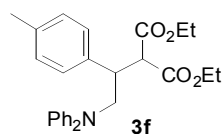
3c: 91% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.16-7.12 (m, 8H), 6.88-6.79 (m, 2H), 4.11 (dd, 1H, $J = 14.7$ and 8.2 Hz), 4.01-3.82 (m, 6H), 2.87-2.75 (m, 1H), 1.66-1.56 (m, 3H), 0.91 (t, 3H, $J = 7.0$ Hz), 0.88 (t, 3H, $J = 7.0$ Hz), 0.85 (d, 3H, $J = 6.2$ Hz), 0.76 (d, 3H, $J = 6.2$ Hz). ^{13}C NMR (C_6D_6) δ 169.0, 168.9, 149.3, 129.5, 122.2, 122.0, 61.1, 61.0, 54.5, 52.9, 39.3, 35.2, 26.0, 22.9, 22.8, 14.01, 13.98. Anal. Calcd. for $\text{C}_{25}\text{H}_{33}\text{NO}_4$: C, 72.96; H, 8.08; N, 3.40. Found: C, 72.84; H, 8.25; N, 3.28.



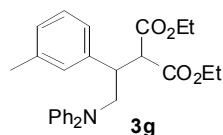
3d: 61% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.18-7.11 (m, 8H), 6.91-6.82 (m, 2H), 4.06 (dd, 1H, $J = 14.6$ and 8.4 Hz), 3.99-3.82 (m, 6H), 2.88-2.80 (m, 1H), 1.88-1.50 (brm, 6H), 1.14-0.95 (brm, 5H), 0.89 (t, 6H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 169.4, 169.2, 149.9, 129.4, 122.6, 122.2, 61.2, 61.1, 52.6, 52.3, 42.4, 38.9, 30.6, 30.5, 27.2, 27.1, 26.8, 13.9. HRMS (EI) Calcd. for $\text{C}_{27}\text{H}_{35}\text{NO}_4$ [M]: 437.2566. Found: 437.2575.



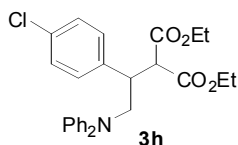
3e: 89% Yield. A white solid, m.p. 71.7-72.3 °C. ^1H NMR (C_6D_6) δ 7.12-7.04 (m, 4H), 7.00-6.94 (m, 5H), 6.91-6.87 (m, 4H), 6.83-6.77 (m, 2H), 4.36-4.26 (m, 2H), 4.00 (q, 2H, $J = 7.2$ Hz), 3.81 (d, 1H, $J = 10.3$ Hz), 3.69-3.57 (m, 3H), 0.94 (t, 3H, $J = 7.2$ Hz), 0.57 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 168.4, 167.3, 149.1, 139.9, 129.40, 129.38, 127.2, 121.9, 121.8, 61.6, 61.1, 57.4, 56.2, 43.7, 14.0, 13.6. HRMS (EI) Calcd. for $\text{C}_{27}\text{H}_{29}\text{NO}_4$ [M]: 431.2097. Found: 431.2081.



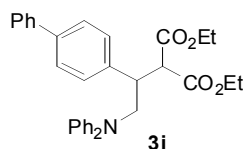
3f: 68% Yield. A white solid, m.p. 68.9-69.2 °C. ^1H NMR (C_6D_6) δ 7.12-7.05 (m, 4H), 6.95-6.90 (m, 6H), 6.83-6.77 (m, 4H), 4.34-4.24 (m, 2H), 3.99 (q, 2H, $J = 7.2$ Hz), 3.83 (d, 1H, $J = 10.3$ Hz), 3.72-3.58 (m, 3H), 2.04 (s, 3H), 0.95 (t, 3H, $J = 7.2$ Hz), 0.61 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 168.5, 167.4, 149.2, 136.9, 136.6, 129.34, 129.29, 129.0, 122.0, 121.8, 61.6, 61.1, 57.4, 56.4, 43.3, 20.9, 14.0, 13.6. HRMS (EI) Calcd. for $\text{C}_{28}\text{H}_{31}\text{NO}_4$ [M]: 445.2253. Found: 445.2246.



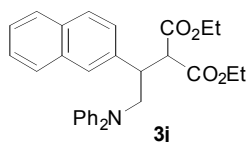
3g: 86% Yield. A white solid, m.p. 64.9-65.8 °C. ^1H NMR (C_6D_6) δ 7.12-7.04 (m, 4H), 6.96-6.77 (m, 10H), 4.36-4.26 (m, 2H), 4.00 (q, 2H, $J = 7.2$ Hz), 3.83 (d, 1H, $J = 10.0$ Hz), 3.73-3.60 (m, 3H), 1.99 (s, 3H), 0.95 (t, 3H, $J = 7.2$ Hz), 0.60 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 168.5, 167.4, 149.1, 139.7, 137.6, 130.2, 129.3, 128.3, 126.5, 121.9, 121.8, 61.6, 61.1, 57.3, 56.3, 43.7, 21.2, 14.0, 13.6. HRMS (EI) Calcd. for $\text{C}_{28}\text{H}_{31}\text{NO}_4$ [M]: 445.2253. Found: 445.2240.



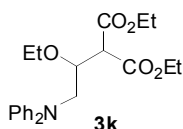
3h: 83% Yield. A white solid, m.p. 96.2-97.0 °C. ^1H NMR (C_6D_6) δ 7.11-7.03 (m, 4H), 6.94-6.77 (m, 8H), 6.69-6.66 (m, 2H), 4.25-4.16 (m, 2H), 4.01-3.93 (m, 2H), 3.68-3.47 (m, 4H), 0.93 (t, 3H, $J = 7.2$ Hz), 0.59 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 168.2, 167.1, 148.9, 138.4, 133.1, 130.8, 129.4, 121.9, 121.8, 61.7, 61.2, 57.1, 56.0, 43.2, 14.0, 13.6. HRMS (EI) Calcd. for $\text{C}_{27}\text{H}_{28}\text{NO}_4\text{Cl}$ [M]: 465.1707. Found: 465.1690.



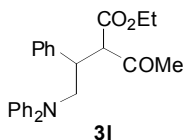
3i: 81% Yield. A white solid. m.p. 109.8-110.6 °C. ^1H NMR (C_6D_6) δ 7.41-7.37 (m, 2H), 7.26-7.19 (m, 3H), 7.14-7.01 (m, 8H), 6.94-6.91 (m, 4H), 6.82-6.78 (m, 2H), 4.43-4.31 (m, 2H), 4.05-3.97 (m, 2H), 3.86-3.63 (m, 4H), 0.96 (t, 3H, $J = 7.2$ Hz), 0.59 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 168.4, 167.3, 149.0, 141.3, 140.3, 138.9, 129.9, 129.4, 128.9, 127.4, 127.3, 127.1, 121.9, 121.8, 61.7, 61.2, 57.4, 56.2, 43.5, 14.0, 13.6. HRMS (EI) Calcd. for $\text{C}_{33}\text{H}_{33}\text{NO}_4$ [M]: 507.2410. Found: 507.2405.



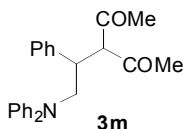
3j: 84% Yield. A white solid. m.p. 78.4-79.8 °C. ^1H NMR (C_6D_6) δ 7.56-7.43 (m, 4H), 7.22-7.10 (m, 3H), 7.03-6.97 (m, 4H), 6.90-6.87 (m, 4H), 6.77-6.71 (m, 2H), 4.52 (td, 1H, J = 10.4 and 4.7 Hz), 4.38 (dd, 1H, J = 14.2 and 4.7 Hz), 4.01 (q, 2H, J = 7.2 Hz), 3.93 (d, 1H, J = 10.4 Hz), 3.79 (dd, 1H, J = 14.2 and 10.4 Hz), 3.60-3.48 (m, 2H), 0.95 (t, 3H, J = 7.2 Hz), 0.45 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6) δ 168.4, 167.4, 149.0, 137.3, 133.7, 133.1, 129.3, 128.8, 128.1, 127.7, 127.0, 126.1, 125.9, 121.9, 121.8, 61.7, 61.1, 57.2, 56.4, 44.0, 14.0, 13.5. HRMS (EI) Calcd. for $\text{C}_{31}\text{H}_{31}\text{NO}_4$ [M]: 481.2253. Found: 481.2244.



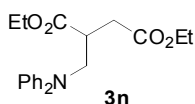
3k: 52% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.31-7.27 (m, 4H), 7.19-7.12 (m, 4H), 6.88-6.81 (m, 2H), 4.55-4.48 (m, 1H), 4.16 (dd, 1H, J = 15.2 and 2.3 Hz), 4.06-3.81 (m, 4H), 3.80 (dd, 1H, J = 15.2 and 9.3 Hz), 3.67 (d, 1H, J = 8.1 Hz), 3.60-3.40 (m, 2H), 0.96 (t, 3H, J = 7.2 Hz), 0.93 (t, 3H, J = 7.2 Hz), 0.89 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6) δ 167.5, 167.3, 148.8, 129.5, 121.7, 121.6, 75.8, 68.0, 61.4, 61.3, 56.1, 56.0, 15.7, 14.0, 13.9. HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{29}\text{NO}_5$ [M]: 399.2046. Found: 399.2050.



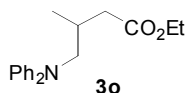
3l: 78-79% Yield (isomeric ratio 1:1). A white solid. ^1H NMR (C_6D_6) 7.12-7.06 (m each, 4H), 6.99-6.89 (m each, 4H), 6.86-6.77 (m each, 7H), 4.29-4.17 (m, 3H), 4.03 (dd, 1H, J = 14.3 and 4.9 Hz), 4.00-3.88 (m, 2H), 3.79; 3.74 (d each, 1H, J = 10.8; 10.5 Hz), 3.61-3.40 (m, 4H), 1.95; 1.66 (s each, 3H), 0.91; 0.51 (t each, 3H, J = 7.0; 7.2 Hz). ^{13}C NMR (C_6D_6) 200.6; 199.9, 168.7; 167.4, 149.2; 149.1, 140.4; 139.8, 129.41; 129.38, 129.3; 129.2, 128.6; 128.3, 127.3; 127.1, 122.0; 121.9, 121.8, 64.2; 63.8, 61.6; 61.1, 57.7; 57.4, 43.4; 43.1, 29.2; 28.9, 14.0; 13.5. HRMS (EI) Calcd. for $\text{C}_{26}\text{H}_{27}\text{NO}_3$ [M]: 401.1991. Found: 401.1987.



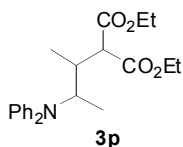
3m: 36% Yield. A white solid. m.p. 95.1-95.6 °C. ^1H NMR (C_6D_6) δ 7.13-7.07 (m, 4H), 6.98-6.96 (m, 3H), 6.87-6.78 (m, 8H), 4.20-4.10 (m, 1H), 3.86 (d, 1H, J = 11.3 Hz), 3.81 (dd, 1H, J = 14.4 and 4.6 Hz), 3.21 (dd, 1H, J = 14.4 and 10.0 Hz), 1.85 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (C_6D_6) δ 202.0, 201.1, 149.1, 140.0, 129.4, 129.1, 128.8, 127.4, 122.0, 121.9, 73.6, 58.0, 43.1, 29.9, 27.6. HRMS (EI) Calcd. for $\text{C}_{25}\text{H}_{25}\text{NO}_2$ [M]: 371.1885. Found: 371.1900.



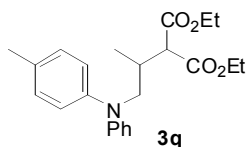
3n: 81% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.11-7.05 (m, 4H), 7.02-6.98 (m, 4H), 6.85-6.79 (m, 2H), 4.00 (dd, 1H, $J = 14.7$ and 7.7 Hz), 3.90-3.81 (m, 4H), 3.71 (dd, 1H, $J = 14.7$ and 7.2 Hz), 3.47-3.37 (m, 1H), 2.73 (dd, 1H, $J = 16.9$ and 8.8 Hz), 2.40 (dd, 1H, $J = 16.9$ and 5.1 Hz), 0.88 (t, 3H, $J = 7.0$ Hz), 0.87 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) 173.4, 171.2, 148.5, 129.6, 122.1, 121.8, 60.7, 60.5, 53.9, 40.9, 34.2, 14.1, 14.0. HRMS (FAB) Calcd. for $\text{C}_{21}\text{H}_{26}\text{NO}_4$ $[\text{M}+\text{H}]$: 356.1862. Found: 356.1869.



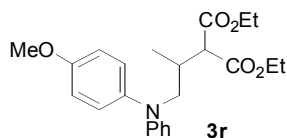
3o: 9% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.14-7.07 (m, 4H), 7.00-6.97 (m, 4H), 6.87-6.80 (m, 2H), 3.91 (q, 2H, $J = 7.2$ Hz), 3.54 (dd, 1H, $J = 14.6$ and 7.3 Hz), 3.29 (dd, 1H, $J = 14.6$ and 7.8 Hz), 2.55-2.42 (m, 1H), 2.27 (dd, 1H, $J = 15.5$ and 6.1 Hz), 1.99 (dd, 1H, $J = 15.5$ and 7.7 Hz), 0.92 (t, 3H, $J = 7.2$ Hz), 0.86 (d, 3H, $J = 6.7$ Hz). ^{13}C NMR (C_6D_6) 172.0, 149.3, 129.5, 121.80, 121.76, 60.0, 58.2, 39.2, 29.6, 17.9, 14.2. HRMS (FAB) Calcd. for $\text{C}_{19}\text{H}_{23}\text{NO}_2$ $[\text{M}]$: 297.1729. Found: 297.1724.



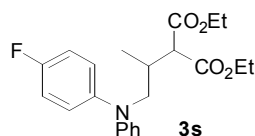
3p: 89% Yield (isomeric ratio 1:1). A colorless oil. ^1H NMR (C_6D_6) δ 7.13-7.06 (m each, 4H), 7.00-6.96 (m each, 4H), 6.88-6.81 (m each, 2H), 4.56-4.40 (m each, 1H), 4.32; 3.61 (d each, 1H, $J = 3.5$; 4.9 Hz), 4.00-3.81 (m each, 4H), 2.83-2.70; 2.70-2.58 (m each, 1H), 1.45; 1.19 (d each, 3H, $J = 7.0$; 7.0 Hz), 1.16; 1.03 (d each, 3H, $J = 7.0$; 6.8 Hz), 0.95-0.83 (m each, 6H). ^{13}C NMR (C_6D_6) δ 169.8; 169.0, 168.7; 168.5, 148.1; 148.0, 129.5; 129.4, 124.0; 123.5, 122.4; 122.1, 61.2; 61.01, 60.98; 60.8, 57.3; 56.7, 53.9; 53.0, 38.7; 38.5, 17.3; 16.5, 14.9; 14.03, 13.95; 13.94. HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{29}\text{NO}_4$ $[\text{M}]$: 383.2097. Found: 383.2096.



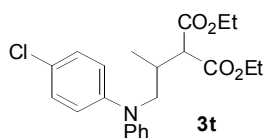
3q: 89% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.16-7.02 (m, 6H), 6.96-6.93 (m, 2H), 6.84-6.77 (m, 1H), 4.03-3.85 (m, 5H), 3.52 (q, 2H, $J = 7.3$ Hz), 3.01-2.85 (m, 1H), 2.10 (s, 3H), 1.15 (d, 3H, $J = 7.0$ Hz), 0.88 (t, 6H, $J = 7.3$ Hz). ^{13}C NMR (C_6D_6) δ 168.8, 168.4, 149.9, 146.5, 132.3, 130.3, 129.4, 124.0, 120.6, 119.9, 61.1, 61.0, 56.4, 55.0, 32.6, 20.7, 15.5, 14.0. HRMS (FAB) Calcd. for $\text{C}_{23}\text{H}_{30}\text{NO}_4$ $[\text{M}+\text{H}]$: 384.2175. Found: 384.2172.



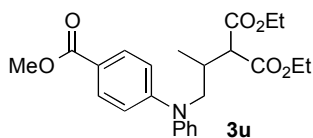
3r: 80% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.20-7.12 (m, 2H), 7.07-7.00 (m, 4H), 6.82-6.70 (m, 3H), 4.01-3.83 (m, 5H), 3.56 (d, 1H, $J = 6.2$ Hz), 3.50 (dd, 1H, $J = 14.4$ and 8.5 Hz), 3.31 (s, 3H), 3.00-2.84 (m, 1H), 1.17 (d, 3H, $J = 6.8$ Hz), 0.89 (t, 6H, $J = 7.0$ Hz). ^{13}C NMR (C_6D_6) δ 168.8, 168.5, 156.9, 150.5, 141.7, 129.3, 127.4, 119.4, 117.6, 115.2, 61.1, 61.0, 56.8, 55.0, 54.9, 32.7, 15.5, 13.9. HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{29}\text{NO}_5$ [M]: 399.2046. Found: 399.2043.



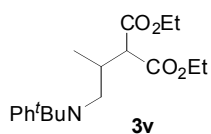
3s: 91% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.15-7.08 (m, 2H), 6.98-6.94 (m, 2H), 6.89-6.71 (m, 5H), 4.00-3.82 (m, 5H), 3.47 (d, 1H, $J = 6.2$ Hz), 3.40 (dd, 1H, $J = 14.3$ and 8.9 Hz), 2.91-2.76 (m, 1H), 1.10 (d, 3H, $J = 6.8$ Hz), 0.89 (t, 3H, $J = 7.2$ Hz), 0.88 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 168.7, 168.4, 159.1 (d, $^1J_{\text{C-F}} = 240.8$ Hz), 149.6, 145.1 (d, $^4J_{\text{C-F}} = 2.8$ Hz), 129.5, 125.3 (d, $^3J_{\text{C-F}} = 7.8$ Hz), 121.0, 120.0, 116.2 (d, $^2J_{\text{C-F}} = 22.3$ Hz), 61.2, 61.1, 56.7, 55.0, 32.4, 15.5, 14.0. HRMS (EI) Calcd. for $\text{C}_{22}\text{H}_{26}\text{NO}_4\text{F}$ [M]: 387.1846. Found: 387.1838.



3t: 79 Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.14-6.96 (m, 6H), 6.87-6.77 (m, 3H), 4.00-3.81 (m, 5H), 3.42 (d, 1H, $J = 6.5$ Hz), 3.39 (dd, 1H, $J = 14.6$ and 8.9 Hz), 2.90-2.74 (m, 1H), 1.07 (d, 3H, $J = 7.0$ Hz), 0.88 (t, 3H, $J = 7.2$ Hz), 0.87 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 168.6, 168.3, 148.7, 147.7, 129.7, 129.5, 126.4, 122.7, 122.3, 61.2, 61.1, 56.3, 55.0, 32.4, 15.4, 14.0. HRMS (EI) Calcd. for $\text{C}_{22}\text{H}_{26}\text{NO}_4\text{Cl}$ [M]: 403.1550. Found: 403.1547.

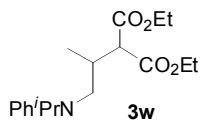


3u: 80% Yield. A pale orange oil. ^1H NMR (C_6D_6) δ 8.16-8.10 (m, 2H), 7.11-6.98 (m, 4H), 6.94-6.86 (m, 3H), 4.00-3.81 (m, 5H), 3.55 (s, 3H), 3.49 (dd, 1H, $J = 14.6$ and 9.2 Hz), 3.39 (d, 1H, $J = 6.5$ Hz), 2.89-2.74 (m, 1H), 1.04 (d, 3H, $J = 7.0$ Hz), 0.88 (t, 3H, $J = 7.2$ Hz), 0.87 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 168.5, 168.2, 166.7, 153.1, 147.2, 131.5, 130.0, 126.5, 125.2, 121.0, 115.9, 61.2, 61.1, 56.0, 55.0, 51.2, 32.5, 15.4, 14.0. HRMS (EI) Calcd. for $\text{C}_{24}\text{H}_{29}\text{NO}_6$ [M]: 427.1995. Found: 427.1989.

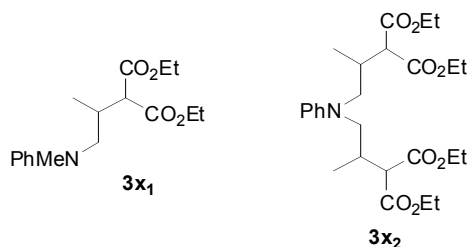


3v: 90% Yield. A colorless oil. ^1H NMR (C_6D_6) 7.14-7.08 (m, 4H), 7.04-6.95 (m, 1H), 4.03-3.86 (m, 5H), 3.32 (dd,

1H, $J = 12.7$ and 8.6 Hz), 2.99 (dd, 1H, $J = 12.7$ and 6.5 Hz), 2.27-2.12 (m, 1H), 1.20 (d, 3H, $J = 6.8$ Hz), 1.04 (s, 9H), 0.94 (t, 3H, $J = 7.2$ Hz), 0.89 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 169.6, 168.8, 148.8, 130.3, 128.5, 125.6, 60.7, 60.6, 55.2, 53.3, 52.1, 33.1, 28.3, 15.1, 14.1, 14.0. HRMS (EI) Calcd. for $\text{C}_{20}\text{H}_{31}\text{NO}_4$ [M]: 349.2253. Found. 349.2269.

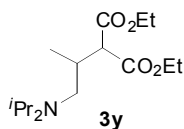


3w: 73% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.25-7.18 (m, 2H), 7.02-6.98 (m, 2H), 6.85-6.79 (m, 1H), 3.99-3.85 (m, 4H), 3.75-3.65 (m, 1H), 3.58 (d, 1H, $J = 6.2$ Hz), 3.32 (dd, 1H, $J = 13.6$ and 6.5 Hz), 2.92 (dd, 1H, $J = 13.6$ and 8.2 Hz), 2.86-2.71 (m, 1H), 1.13 (d, 3H, $J = 6.8$ Hz), 1.00-0.85 (m, 12H). ^{13}C NMR (C_6D_6) 169.0, 150.0, 129.2, 119.7, 119.3, 61.0, 60.9, 55.1, 54.0, 47.3, 31.7, 19.8, 19.7, 15.4, 14.02, 13.98. HRMS (EI) Calcd. for $\text{C}_{19}\text{H}_{29}\text{NO}_4$ [M]: 335.2097. Found. 335.2110.

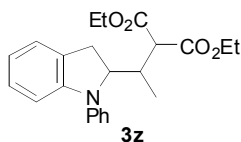


3x₁: 76% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.28-7.20 (m, 2H), 6.79-6.75 (m, 3H), 3.97-3.83 (m, 4H), 3.42 (dd, 1H, $J = 13.6$ and 6.3 Hz), 3.38 (d, 1H, $J = 6.8$ Hz), 2.97-2.80 (m, 2H), 2.62 (s, 3H), 0.99 (d, 3H, $J = 6.5$ Hz), 0.882 (t, 3H, $J = 7.2$ Hz), 0.879 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (C_6D_6) δ 168.6, 168.5, 150.1, 129.4, 117.1, 113.0, 61.09, 61.06, 57.3, 55.3, 39.2, 32.8, 15.5, 13.97, 13.95. HRMS (EI) Calcd. for $\text{C}_{17}\text{H}_{25}\text{NO}_4$ [M]: 307.1784. Found. 307.1796.

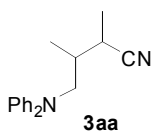
3x₂: 21% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.29-7.21 (m, 2H), 7.11-7.00 (m, 2H), 6.76-6.70 (m, 1H), 4.02-3.86 (m, 8H), 3.81 (dd, 1H, $J = 14.3$ and 5.1 Hz), 3.68 (dd, 1H, $J = 14.6$ and 6.9 Hz), 3.43 (d, 1H, $J = 6.5$ Hz), 3.36 (d, 1H, $J = 6.8$ Hz), 3.32 (dd, 1H, $J = 14.6$ and 8.1 Hz), 3.13 (dd, 1H, $J = 14.3$ and 9.2 Hz), 3.05-2.93 (m, 2H), 1.021 (d, 3H, $J = 7.0$ Hz), 1.017 (d, 3H, $J = 6.8$ Hz), 0.94-0.87 (m, 12H). ^{13}C NMR (C_6D_6) δ 168.72, 168.65, 168.5, 168.4, 148.0, 147.9, 129.7, 129.6, 117.5, 117.4, 114.41, 114.36, 61.15, 61.11, 56.5, 56.1, 55.4, 55.1, 31.7, 15.54, 15.48, 14.00, 13.98, 13.96. HRMS (EI) Calcd. for $\text{C}_{26}\text{H}_{39}\text{NO}_8$ [M]: 493.2676. Found. 493.2675.



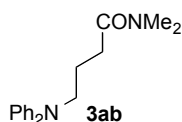
3y: 94% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 4.06-3.94 (m, 4H), 3.79 (d, 1H, $J = 5.1$ Hz), 3.00-2.86 (m, 2H), 2.67-2.50 (m, 2H), 2.37-2.26 (m, 1H), 1.23 (d, 3H, $J = 6.5$ Hz), 0.97-0.90 (m, 18H). ^{13}C NMR (C_6D_6) 169.7, 168.8, 60.9, 60.7, 54.4, 49.4, 47.7, 33.1, 21.0, 20.7, 15.4, 14.1. HRMS (EI) Calcd. for $\text{C}_{16}\text{H}_{31}\text{NO}_4$ [M]: 301.2253. Found: 301.2265.



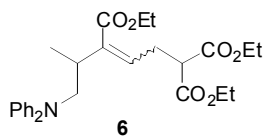
3z: 83% Yield (isomeric ratio 1:1). A colorless oil. ^1H NMR (C_6D_6) δ 7.41-7.36; 7.30-7.25 (m each, 2H), 7.22-7.12 (m, 4H), 7.01-6.86 (m, 7H), 6.79-6.71 (m, 2H), 6.61-6.58 (m, 1H), 4.56; 4.14 (td; ddd, 1H, $J = 9.0$ and 3.0 ; 12.2, 8.6 and 3.2 Hz), 4.01-3.68 (m, 8H), 3.64; 3.33 (d each, 1H, $J = 8.4$; 11.1 Hz), 3.28-3.15; 3.14-3.02 (m each, 1H), 2.99-2.82; 2.80-2.63 (m each, 2H), 0.99; 0.90 (d each, 3H, $J = 7.0$; 6.8 Hz), 0.90; 0.86 (t each, 3H, $J = 7.2$ and 7.3 Hz), 0.84; 0.70 (t each, 3H, $J = 7.2$; 7.2 Hz). ^{13}C NMR (C_6D_6) δ 168.91; 168.87, 168.3; 168.0, 151.3; 149.8, 146.0; 143.2, 129.68; 129.1, 129.65; 129.6, 127.5, 125.0, 124.8; 124.7, 123.4; 122.4, 119.5; 119.3, 109.7; 108.3, 68.6; 64.2, 61.34; 61.28, 61.2; 61.0, 55.9; 53.4, 36.2; 34.0, 31.2; 28.8, 14.8; 13.97, 13.96; 13.9, 13.6; 10.7. HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{27}\text{NO}_4$ [M]: 381.1940. Found: 381.1923.



3aa: 32% Yield (isomeric ratio 1:1). A colorless oil. ^1H NMR (C_6D_6) δ 7.13-7.06 (m each, 4H), 6.94-6.80 (m each, 6H), 3.56; 3.49 (dd each, 1H, $J = 14.6$ and 5.7 ; 15.1 and 8.5 Hz), 3.32; 3.17 (dd each, 1H, $J = 15.1$ and 6.3 ; 14.6 and 8.8 Hz), 2.50-2.41 (m, 1H), 1.97-1.78 (m, 2H), 1.63-1.53 (m, 1H), 0.73; 0.70 (d each, 3H, $J = 7.3$; 7.0 Hz), 0.62; 0.58 (d each, 3H, $J = 7.0$; 7.3 Hz). ^{13}C NMR (C_6D_6) δ 148.93; 148.86, 129.66; 129.62, 122.2; 122.1, 121.9; 121.8, 121.5; 120.9, 56.9; 55.3, 35.2; 34.6, 28.8; 28.2, 15.8; 15.2, 13.9; 12.9. HRMS (EI) Calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_2$ [M]: 264.1626. Found: 264.1623.



3ab: 45% Yield. A colorless oil. ^1H NMR (C_6D_6) δ 7.19-7.11 (m, 8H), 6.89-6.79 (m, 2H), 3.72 (t, 2H, $J = 7.4$ Hz), 2.63 (s, 3H), 2.08 (s, 3H), 2.04-1.94 (m, 2H), 1.76 (t, 2H, $J = 6.5$ Hz). ^{13}C NMR (C_6D_6) δ 171.2, 148.7, 129.5, 121.5, 121.4, 51.9, 36.0, 34.9, 29.9, 23.0. HRMS (EI) Calcd. for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}$ [M]: 282.1732. Found: 282.1731.

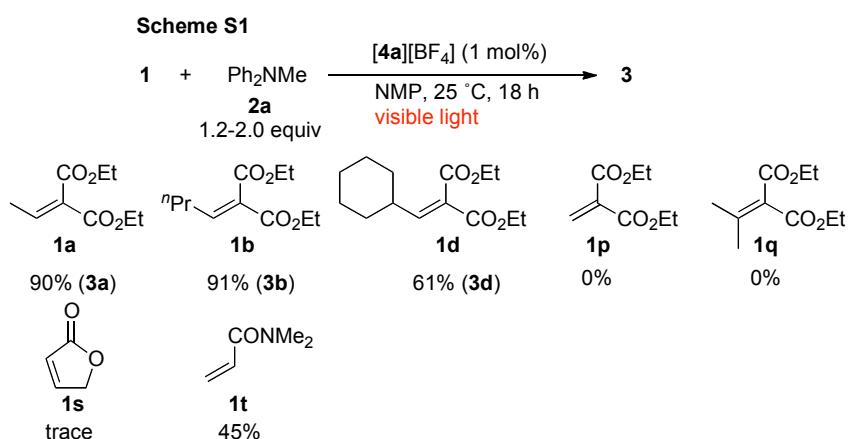


6: 64% Yield ($Z/E = 1.5:1$). A colorless oil. *Z*-isomer: ^1H NMR (acetone- d_6) δ 7.28-7.20 (m, 4H), 7.02-6.98 (m, 4H), 6.95-6.88 (m, 2H), 5.91 (t, 1H, $J = 7.4$ Hz), 4.19-4.04 (m, 6H), 3.90 (dd, 1H, $J = 14.6$ and 6.9 Hz), 3.67 (dd, 1H, $J = 14.6$ and 7.7 Hz), 3.49 (t, 1H, $J = 7.4$ Hz), 3.06-2.93 (m, 1H), 2.88 (td, 2H, $J = 7.4$ and 1.9 Hz), 1.26-1.17 (m, 9H), 1.13 (d, 3H, $J = 6.8$ Hz). ^{13}C NMR (acetone- d_6) δ 169.3, 169.0, 167.9, 149.5, 138.3, 136.1, 129.9, 122.11, 122.07, 61.9, 61.8, 60.9, 58.7, 52.2, 37.6, 29.5, 17.6, 14.4, 14.3. *E*-isomer: ^1H NMR (acetone- d_6) δ 6.64 (t, 1H, $J = 7.4$ Hz), 4.02 (dd, 1H, $J = 14.0$ and 7.0 Hz), 3.39 (dd, 1H, $J = 8.1$ and 6.3 Hz), 3.33-3.19 (m, 1H), 2.62-2.40 (m, 2H), 1.18 (d,

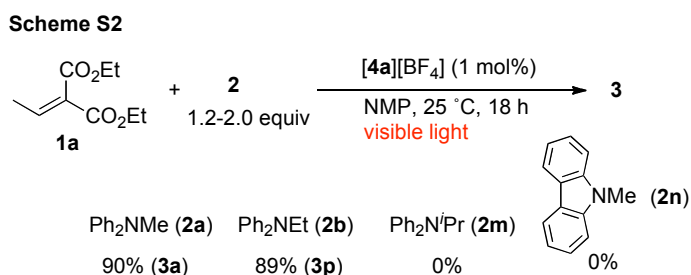
3H, $J = 5.1$ Hz). ^{13}C NMR (acetone- d_6) δ 169.1, 167.1, 149.2, 139.6, 137.0, 129.9, 122.0, 61.83, 61.76, 60.7, 56.6, 51.6, 32.6, 28.0, 16.9, 14.5. HRMS (FAB) Calcd. for $\text{C}_{28}\text{H}_{35}\text{NO}_6$ [M]: 481.2464. Found: 481.2473.

Photocatalytic Reactions of Alkenes (1) with Amines (2)

The effect of substituents at β -position of alkenes (**1**) was investigated as shown in Scheme S1. The reactions of **1a** and **1b** bearing a primary alkyl group at the β -position proceeded smoothly to give the corresponding alkylated amines **3a** and **3b** in high yields, while that of **1d** bearing a sterically hindered moiety such as cyclohexyl group afforded a slightly lower yield. Unfortunately, when diethyl methylidenemalonate (**1p**) bearing a terminal alkene moiety was used as substrates, no formation of the corresponding amine was observed probably due to the rapid polymerization of **1p** under these reaction conditions. No reaction of diethyl isopropylidenemalonate (**1q**) occurred at all because of steric hindrance at the β -position of **1q**. Additionally, in the case of furanone (**1s**), trace amount of the adduct was obtained, while reaction of acrylamide (**1t**) proceeded to give the corresponding product (**3ab**) in 45% yield.



Next, we examined the effect of substituent on the nitrogen atom of diphenylalkylamine (**2**) as shown in Scheme S2. The reactions with **2a** and **2b** bearing a primary alkyl group on the nitrogen atom proceeded smoothly to give the corresponding alkylated amines **3a** and **3p** in high yields. No reaction with **2m** occurred at all because of the steric hindrance of *iso*-propyl group. Unfortunately, the reaction with *N*-methylcarbazole (**2n**) did not proceed at all.

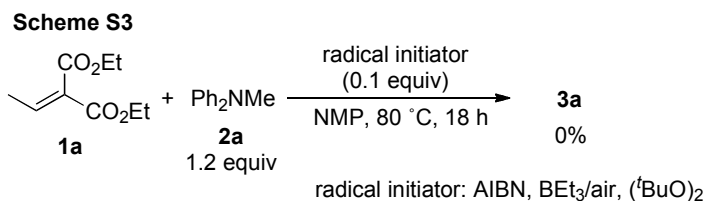


Time-Profile of Reaction of **1a** with **2a**.

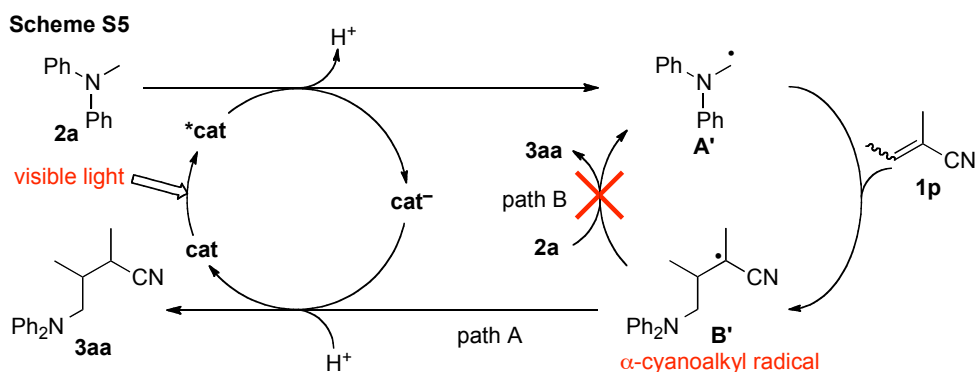
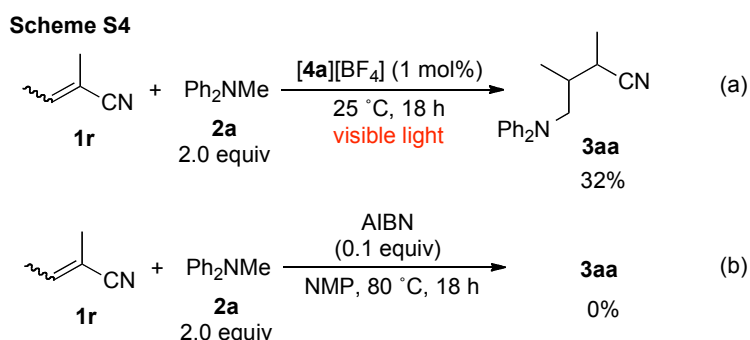
In a 20 mL Schlenk flask (diameter: 2.5 cm) were placed $[\mathbf{4a}][\text{BF}_4]$ (2.1 mg, 0.0025 mmol) and $\text{DMF-}d_7$ (2.5 mL) under N_2 . To the solution were added **1a** (46.5 mg, 0.250 mmol) and **2a** (55.7 mg, 0.304 mmol). An appropriate amount (0.7 mL) of the resulting mixture was transferred to an NMR tube and sealed under N_2 . The NMR tube was placed in a water bath and illuminated with 14W white LED (approximately 2 cm from the light source) at 25 °C during “on” periods, and placed under dark during “off” periods. At each time of measurement was quickly loaded the NMR tube to the NMR spectrometer. The ^1H NMR yield of **3a** was determined by the integral ratio of the methyl hydrogen of **1a** (δ 1.93) and **3a** (δ 1.08).

Reactions with Radical Initiators.

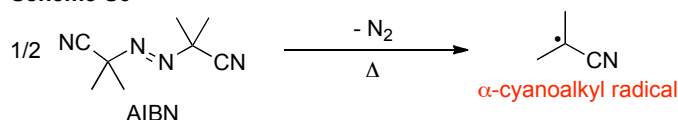
When the reactions of **1a** with **2a** in the presence of 0.1 equiv of radical initiators such as AIBN, BEt₃/air, and (^tBuO)₂ were carried out, no formation of **3a** was observed even at 80 °C (Scheme S3). These results indicate that the α-hydrogen of an amine **2** can not be abstracted by radical initiators.



To obtain further information on the reaction pathway, the reaction of cyanoalkene **1r** was carried out. The reaction of **1r** with **2a** in the presence of [4a][BF₄] under the visible light irradiation afforded the corresponding alkylated amine (**3aa**) in 32% yield (Scheme S4a). In this reaction, α-cyanoalkyl radical **B'** is considered to be formed as a reaction intermediate (Scheme S5). On the other hand, when the reaction of **1r** with **2a** in the presence of AIBN at 80 °C was carried out, **3aa** was not observed at all (Scheme S4b). In the reaction as shown in Scheme S4b, heating of AIBN results in the formation of α-cyanoalkyl radical (Scheme S6), which have the similar structure to **B** as shown in Scheme S5. These results indicate that abstraction of α-hydrogen of **2a** by intermediate **B'** (Scheme S5, path B) is not possible and the contribution of radical chain process is negligible. As a result, sequential redox pathway (Scheme S5, path A) is considered to be appropriate in our reaction system.



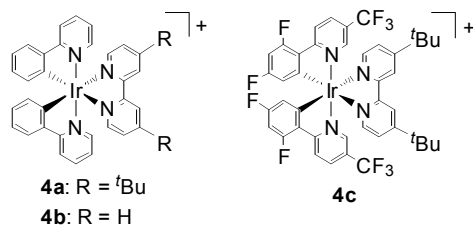
Scheme S6



Determination of Quantum Yield.

When the quantum yield of a photochemical reaction was determined, the reaction mixture was irradiated using an Ushio high pressure mercury lamp USH-250SC (250 W) with an 440 nm band-pass filter (Kenko B-440 filter). The irradiated light intensity was estimated to 1.02×10^{-7} einstein s^{-1} by using $K_3[Fe(C_2O_4)_3]$ as an actinometer.^{S15} The initial reaction rate of **1a** with 1.2 equiv of **2a** in the presence of 1 mol% of [**4a**][BF₄] in 2.5 mL of NMP (3.29×10^{-8} mol s^{-1}) was converted to quantum yield ($\Phi = 0.32$).

Preparation of Photocatalysts.



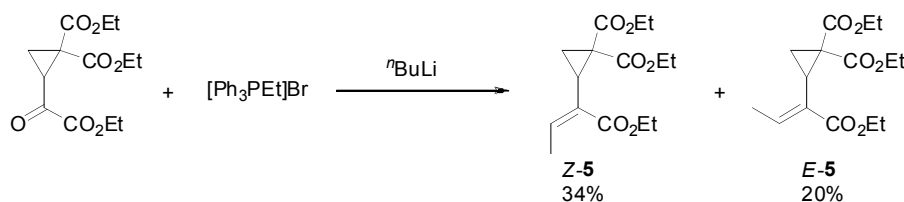
[4a][BF₄]: In a 50 mL Schlenk flask were placed [Ir(ppy)₂Cl]₂^{S16} (0.535 g, 0.499 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridyl (0.296 g, 1.10 mmol) under N₂. Ethylene glycol (25 mL) was added, and the mixture was heated at 150 °C for 12 h. After cooling to room temperature, NaBF₄ (1.09 g, 10.0 mmol) and H₂O (250 mL) was added. The resulting precipitate was collected by filtration and washed with H₂O and Et₂O. The crude product was purified by column chromatography (Al₂O₃) with MeCN to give a yellow solid. After recrystallization from MeOH afford [**4a**][BF₄] as yellow crystals (0.490 g, 0.572 mmol, 57% yield). ¹H NMR (acetone-*d*₆): 8.87 (d, 2H, *J* = 1.8 Hz), 8.23 (d, 2H, *J* = 7.8 Hz), 7.98-7.91 (m, 4H), 7.88 (dd, 2H, *J* = 7.5 and 1.4 Hz), 7.78 (ddd, 2H, *J* = 5.8, 1.4 and 0.8 Hz), 7.69 (dd, 2H, *J* = 5.9 and 1.8 Hz), 7.12 (ddd, 2H, *J* = 7.6, 5.8 and 1.6 Hz), 7.02 (td, 2H, *J* = 7.5 and 0.9 Hz), 6.89 (td, 2H, *J* = 7.5 and 1.4 Hz), 6.33 (dd, 2H, *J* = 0.9 Hz), 1.40 (s, 18H). ¹³C NMR (acetone-*d*₆): 168.8, 164.9, 156.8, 151.9, 151.0, 149.9, 144.9, 139.4, 132.4, 131.1, 126.4, 125.8, 124.4, 123.2, 122.9, 120.8, 36.4, 30.4. Anal. Calcd. for C₄₀H₄₀BF₄IrN₄: C, 56.14; H, 4.71; N, 6.55. Found: C, 55.73; H, 4.60; N, 6.54.

[4b][BF₄]: In a 50 mL Schlenk flask were placed [Ir(ppy)₂Cl]₂^{S16} (213.8 mg, 0.199 mmol) and 2,2'-bipyridyl (69.1 mg, 0.442 mmol) under N₂. Ethylene glycol (10 mL) was added, and the mixture was heated at 150 °C for 10 h. After cooling to room temperature, NaBF₄ (436.6 mg, 3.98 mmol) and H₂O (100 mL) was added. The resulting precipitate was dissolved in CH₂Cl₂ (200 mL), and the obtained organic layer was washed with H₂O (50 mL x 3) and concentrated. The crude product was purified by column chromatography (Al₂O₃) with MeCN to give a yellow solid. After recrystallization from MeCN/Et₂O afford [**4b**][BF₄] as yellow crystals (111.7 mg, 0.150 mmol, 38% yield). ¹H NMR (CD₃CN): δ 8.51 (dt, 2H, *J* = 7.9 and 0.9 Hz), 8.11 (td, 2H, *J* = 7.9 and 1.5 Hz), 8.05 (dt, 2H, *J* =

8.1 and 0.9 Hz), 7.97 (ddd, 2H, $J = 5.7, 1.5$ and 0.9 Hz), 7.86-7.78 (m, 4H), 7.59 (ddd, 2H, $J = 5.7, 1.4$ and 0.9 Hz), 7.49 (ddd, 2H, $J = 7.9, 5.7$ and 0.9 Hz), 7.06-6.99 (m, 4H), 6.90 (td, 2H, $J = 7.5$ and 1.4 Hz), 6.27 (dd, 2H, $J = 7.5$ and 0.8 Hz). ^{13}C NMR (CD_3CN): δ 168.4, 156.8, 151.6, 151.3, 150.2, 145.1, 140.3, 139.5, 132.5, 131.4, 129.4, 125.9, 125.6, 124.5, 123.5, 120.9. Anal. Calcd. for $\text{C}_{32}\text{H}_{24}\text{BF}_4\text{IrN}_4$: C, 51.69; H, 3.25; N, 7.53. Found: C, 51.70; H, 3.41; N, 7.52.

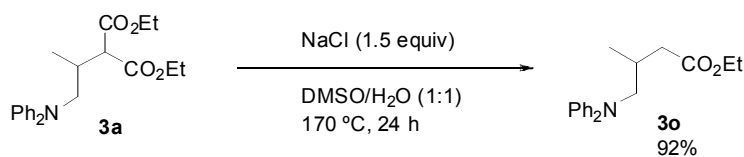
[4c][BF₄]: In a 50 mL Schlenk flask were placed $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Cl}]_2$ ^{S17} (1.29 g, 0.867 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridyl (0.511 g, 1.91 mmol) under N_2 . Ethylene glycol (43 mL) was added and the mixture was heated at 150°C for 18 h. After cooling to room temperature, NaBF_4 (1.90 g, 17.3 mmol) and H_2O (430 mL) was added. The resulting precipitate was collected by filtration and washed with H_2O and Et_2O . The crude product was purified by column chromatography (SiO_2) with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (1/0 to 1/1) to give a yellow solid. After recrystallization from acetone/(1:1 mixture of Et_2O and hexane) afford **[4c][BF₄]** as yellow crystals (1.19 g, 1.12 mmol, 65% yield). ^1H NMR (acetone- d_6): 8.93 (d, 2H, $J = 1.6$ Hz), 8.61 (dd, 2H, $J = 8.8$ and 2.6 Hz), 8.40 (dd, 2H, $J = 8.8$ and 2.2 Hz), 8.17 (d, 2H, $J = 5.9$ Hz), 7.82-7.79 (m, 4H), 6.84 (ddd, 2H, $J = 13.0, 9.5$ and 2.3 Hz), 5.96 (dd, 2H, $J = 8.4$ and 2.3 Hz), 1.42 (s, 18H). ^{19}F NMR (acetone- d_6): -65.0, -106.1, -109.3, -152.8. Anal. Calcd. for $\text{C}_{42}\text{H}_{34}\text{BF}_{14}\text{IrN}_4$: C, 47.42; H, 3.22; N, 5.27. Found: C, 47.72; H, 3.71; N, 5.11.

Preparation of 5.



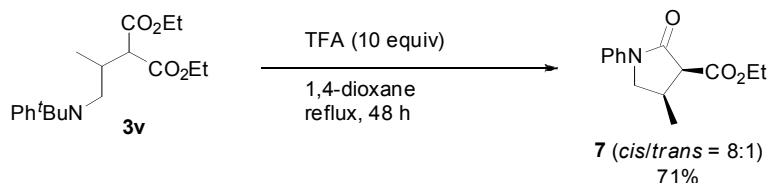
To a suspension of ethyltriphenylphosphonium bromide^{S18} (958 mg, 2.58 mmol) in THF (22 mL) was added dropwise $n\text{-BuLi}$ (1.45 mL, 2.36 mmol; 1.65 M in hexane) at 0°C , and the resulting mixture was stirred for 2 h at 0°C . To the mixture was added dropwise ethyl [1,1-bis(ethoxycarbonyl)cycloprop-2-yl]oxoacetate^{S19} (612 mg, 2.14 mmol) dissolved in THF (4.2 mL) at -78°C , and the mixture was stirred for 14 h at room temperature. H_2O (100 mL) was added and the mixture was extracted with Et_2O (50 mL x 3). The combined organic layer was washed with brine and dried over MgSO_4 . After evaporation of the solvent, the residue was purified by column chromatography (SiO_2) with hexane/ethyl acetate (10/1) to give **Z-5** (216 mg, 0.724 mmol, 34% yield) and **E-5** (131 mg, 0.438 mmol, 20% yield). **Z-5**: A colorless oil. ^1H NMR (CDCl_3) δ 6.10 (qd, 1H, $J = 7.2$ and 1.4 Hz), 4.31-4.00 (m, 6H), 2.94-2.87 (m, 1H), 2.04 (dd, 3H, $J = 7.2$ and 1.6 Hz), 1.78 (dd, 1H, $J = 8.4$ and 5.1 Hz), 1.54 (dd, 1H, $J = 8.4$ and 4.9 Hz), 1.29 (t, 3H, $J = 7.0$ Hz), 1.26 (t, 3H, $J = 7.2$ Hz), 1.18 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3): δ 169.6, 166.8, 166.3, 140.5, 126.6, 61.3, 61.2, 60.0, 35.6, 30.9, 18.0, 15.2, 14.0, 13.9. HRMS (EI) Calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_6$ [M]: 298.1416. Found: 298.1403. **E-5**: A colorless oil. ^1H NMR (CDCl_3): δ 7.01 (qd, 1H, $J = 7.2$ and 2.0 Hz), 4.33-4.01 (m, 6H), 2.67-2.59 (m, 1H), 2.04 (dd, 1H, $J = 8.9$ and 4.9 Hz), 1.90 (dd, 3H, $J = 7.2$ and 1.6 Hz), 1.75 (dd, 1H, $J = 8.9$ and 4.9 Hz), 1.30 (t, 3H, $J = 7.2$ Hz), 1.28 (t, 3H, $J = 7.0$ Hz), 1.20 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3): δ 169.6, 167.5, 166.7, 142.3, 127.8, 61.4, 61.1, 60.4, 34.6, 26.1, 21.5, 14.5, 14.01, 14.00, 13.8. HRMS (EI) Calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_6$ [M]: 298.1416. Found: 298.1410.

Synthesis of **3o** by Decarboxylation of **3a**.



In a 20 mL Schlenk flask were placed **3a** (122.5 mg, 0.332 mmol) and NaCl (29.7 mg, 0.508 mmol) under N₂. DMSO (0.33 mL) and H₂O (0.33 mL) was added and the mixture was heated at 170 °C for 24 h. After cooling to room temperature, the mixture was purified by column chromatography (SiO₂) with hexane/ethyl acetate (20/1) to give **3o** (91.1 mg, 0.306 mmol, 92% yield).

Synthesis of **7** by Dealkylation of **3v**.



In a 20 mL Schlenk flask was placed **3v** (83.3 mg, 0.238 mmol) under N₂. 1,4-dioxane (2.4 mL) and trifluoroacetic acid (182 μ L, 2.38 mmol) were added and the mixture was heated to reflux for 48 h. After cooling to room temperature, saturated aqueous NaHCO₃ (20 mL) was added, and the mixture was extracted with CH₂Cl₂ (20 mL x 3). The combined organic layer was dried over MgSO₄ and concentrated in *vacuo*. The residue was purified by column chromatography (SiO₂) with hexane/ethyl acetate (10/3) to give **7** as a colorless oil (41.5 mg, 0.168 mmol, 71% yield, *cis/trans* = 8:1). The stereoisomers of *cis*- and *trans*-**7** were confirmed by the NOE measurements. *cis*-isomer: ¹H NMR (C₆D₆) δ 7.65-7.60 (m, 2H), 7.18-7.10 (m, 2H), 6.96-6.90 (m, 1H), 4.14-3.97 (m, 2H), 3.15 (dd, 1H, *J* = 8.6 and 7.3 Hz), 2.96 (d, 1H, *J* = 9.5 Hz), 2.67-2.52 (m, 1H), 2.50 (t, 1H, *J* = 8.6 Hz), 1.01 (t, 3H, *J* = 7.2 Hz), 0.66 (d, 3H, *J* = 6.5 Hz). ¹³C NMR (C₆D₆): δ 169.5, 168.5, 139.9, 128.9, 124.4, 119.6, 61.4, 58.1, 53.1, 31.0, 17.2, 14.2. *trans*-isomer: ¹H NMR (C₆D₆) δ 7.73-7.70 (m, 2H), 3.85 (q, 2H, *J* = 7.1 Hz), 3.39 (d, 1H, *J* = 8.9 Hz), 3.28 (t, 1H, *J* = 8.9 Hz), 3.15 (dd, 1H, *J* = 8.9 and 7.3 Hz), 2.01-1.84 (m, 1H), 0.84 (t, 3H, *J* = 7.1 Hz), 0.79 (d, 3H, *J* = 7.0 Hz). ¹³C NMR (C₆D₆) δ 128.9, 124.5, 119.9, 60.9, 55.6, 54.0, 29.8, 14.1, 13.7. HRMS (EI) Calcd. for C₁₄H₁₇NO₃ [M]: 247.1208. Found: 247.1200.

X-ray Diffraction Study of 3h.

Colorless block crystals suitable for an X-ray analysis were obtained by recrystallization from ethanol. Diffraction data were collected for the 2θ range of 6 to 55° on a Rigaku Varimax Saturn 70 CCD diffractometer, using graphite monochromated Mo-K α radiation ($\lambda = 0.71075 \text{ \AA}$). Intensity data were corrected for empirical absorptions (REQAB),^{S20} and for Lorentz and polarization effects. Structure solutions and refinements were carried out by using CrystalStructure package.^{S21} The positions of non-hydrogen atoms were determined by direct methods (SIR-97)^{S22} and subsequent Fourier synthesis (DIRDIFF-99),^{S23} and were refined on F_o^2 using all the unique reflections by full-matrix least squares with anisotropic thermal parameters. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. The atomic scattering factors were taken from ref. S24, and anomalous dispersion effects were included.^{S25} The Value fo $\Delta f'$ and $\Delta f''$ were taken from ref. S26. Details of the crystal and data collection parameters are summarized in Table S1.

Table S1. Crystallographic Data for **3h**.

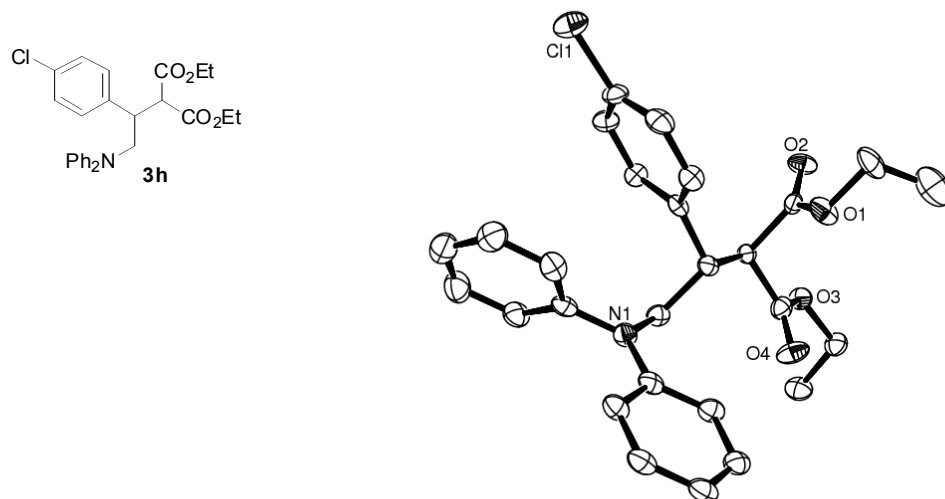
chemical formula	C ₂₇ H ₂₈ ClNO ₄
formula weight	465.97
crystal size	0.25 × 0.20 × 0.10
crystal color, habit	colorless, block
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> (Å)	21.4069(12)
<i>b</i> (Å)	10.5671(7)
<i>c</i> (Å)	21.9699(12)
α (deg)	90
β (deg)	101.1796(18)
γ (deg)	90
<i>V</i> (Å ³)	4875.5(5)
<i>Z</i>	8
<i>D</i> _{calcd} (g cm ⁻³)	1.270
<i>F</i> (000)	1968
μ _{calcd} (cm ⁻¹)	1.893
radiation	Mo-K α (λ = 0.71075 Å)
temperature (°C)	−180
transmission factors range	0.734–0.981
no. measured reflections	37211
no. unique reflections	11008 (<i>R</i> _{int} = 0.0779)
no. refined parameters	651
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0869
<i>wR</i> 2 (all data) ^b	0.1399
GOF ^c	1.000
max/min residual peaks (e ⁻ /Å ³)	+1.250/−0.914

^a $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

^b $wR2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$; $w = 4F_o^2 / 3.05F_o^2$.

^c $GOF = [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{params})]^{1/2}$.

FIGURE S1. ORTEP Drawing of **3h**.

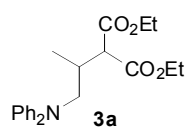


References.

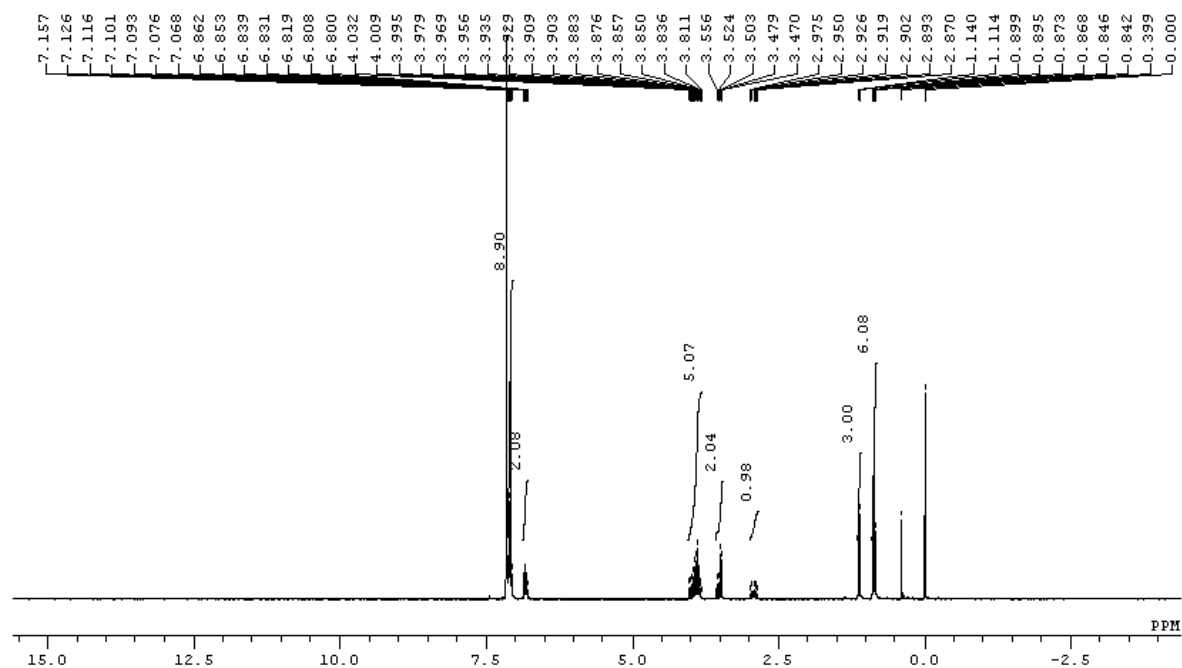
- [S1] Fraser, W.; Suckling, C. J.; Wood, H. C. S. *J. Chem. Soc., Perkin Trans. I* **1990**, 3137.
- [S2] Guanti, G.; Banfi, L.; Narisano, E. *J. Org. Chem.* **1992**, 57, 1540.
- [S3] Booher, R. N.; Smits, S. E.; Turner, W. W., Jr.; Pohland, A. *J. Med. Chem.* **1977**, 20, 885.
- [S4] Raguin, O.; Fournié-Zaluski, M.-C.; Romieu, A.; Pèlerin, A.; Chatelet, F.; Pélaprat, D.; Barbet, J.; Roques, B. P.; Gruaz-Guyon, A. *Angew. Chem. Int. Ed.* **2005**, 44, 4058.
- [S5] Miura, T.; Okazaki, K.; Ogawa, K.; Otomo, E.; Uematsu, S.; Takahashi, M.; Kawashima, Y.; Jyo, Y.; Koyata, N.; Murakami, Y.; Imai, N. *Synthesis*, **2008**, 2695.
- [S6] Ghorai, M. K.; Halder, S.; Das, R. K. *J. Org. Chem.* **2010**, 75, 7061.
- [S7] Manring, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, 107, 6452.
- [S8] Haga, K.; Oohashi, M.; Kaneko, R. *Bull. Chem. Soc. Jpn.* **1984**, 57, 1586.
- [S9] Hill, L. L.; Moore, L. R.; Huang, R.; Craciun, R.; Vincent, A. J.; Dixon, D. A.; Chou, J.; Woltermann, C. J.; Shaughnessy, K. H. *J. Org. Chem.* **2006**, 71, 5117.
- [S10] Ali, M. H.; Buchwald, S. L. *J. Org. Chem.* **2001**, 66, 2560.
- [S11] Xie, X.; Zhang, T. Y.; Zhang, Z. *J. Org. Chem.* **2006**, 71, 6522.
- [S12] Hunter, D. H.; Racok, J. S.; Rey, A. W.; Ponce, Y. Z. *J. Org. Chem.* **1988**, 53, 1278.
- [S13] Shaffer, C. L.; Morton, M. D.; Hanzlik, R. P. *J. Am. Chem. Soc.* **2001**, 123, 8502.
- [S14] Omar-Amrani, R.; Schneider, R.; Fort, Y. *Synthesis* **2004**, 2527.
- [S15] Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley and Sons: New York, 1996.
- [S16] Tian, N.; Thiessen, A.; Schiewek, R.; Schmitz, O. J.; Hertel, D.; Meerholz, K.; Holder, E. *J. Org. Chem.* **2009**, 74, 2718.
- [S17] Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A., Jr.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2005**, 17, 5712.
- [S18] Sun, J.; Wang, L.; Zhang, S.; Li, Z.; Zhang, X.; Dai, W.; Mori, R. *J. Mol. Catal. A* **2006**, 256, 295.
- [S19] Xu, H.; Zhang, W.; Shu, D.; Werness, J. B.; Tang, W. *Angew. Chem. Int. Ed.* **2008**, 47, 8933.
- [S20] Jacobson, R. A., *REQAB*, private communication to Rigaku Corp., Tokyo, Japan, 1998.
- [S21] (a) *CrystalStructure 4.0: Single Crystal Structure Analysis Software*; Rigaku Corp: Tokyo, Japan and MSC: The Woodlands, TX, 2010. (b) Carruthers, J. R.; Rollett, J. S.; Betteridge, P. W.; Kinna, D.; Pearce, L.; Larsen, A.; Gabe, E. *CRYSTALS Issue 11*; Chemical Crystallography Laboratory: Oxford, UK, 1999.
- [S22] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, 32, 115.
- [S23] Beurskens, P. T.; Beurskens, G.; de Gelder, R.; García-Granda, S.; Gould, R. O.; Israël, R.; Smits, J. M. M. *The DIRDIF-99 program system*; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1999.
- [S24] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C. Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV., Table 2.2 A.
- [S25] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, 17, 781.
- [S26] (a) Creagh, D. C.; McAuley, W. J. *International Tables for X-ray Crystallography*; Wilson, A. J. C. Ed.;

Kluwer Academic Publishers: Boston, MA, 1992; Vol. C. Table 4.2.6.8. (b) Creagh, D. C.; Hubbell, J. H. *International Tables for X-ray Crystallography*, Wilson, A. J. C. Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C. Table 4.2.4.3.

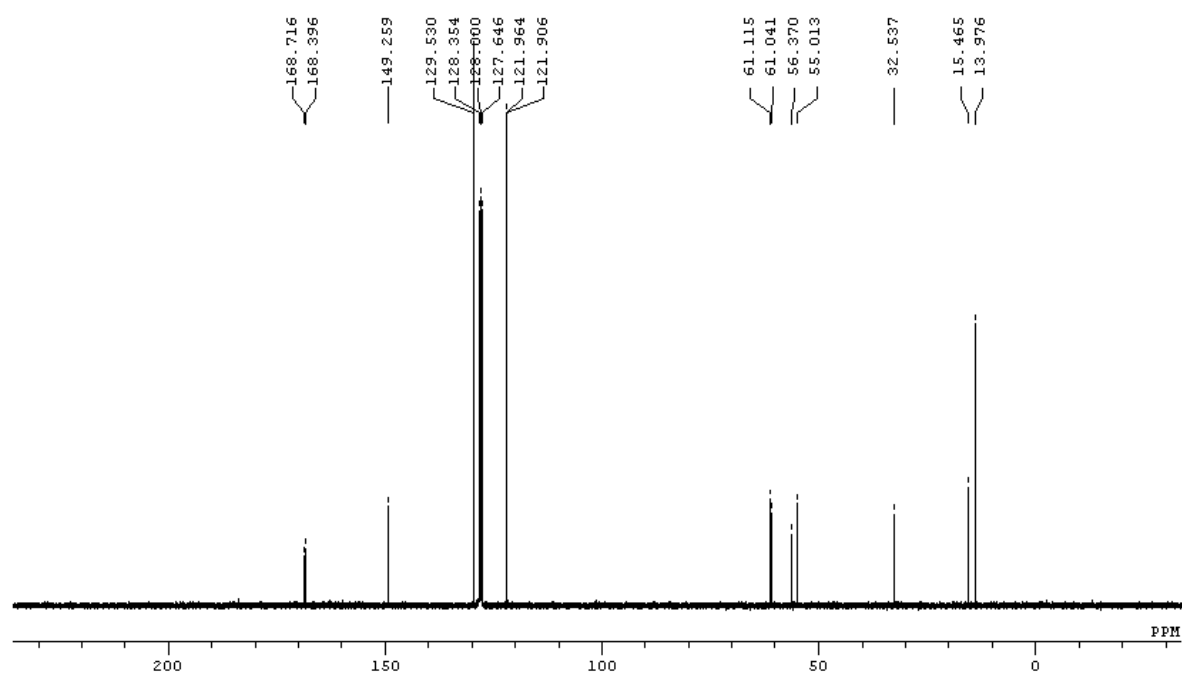
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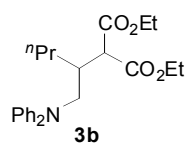


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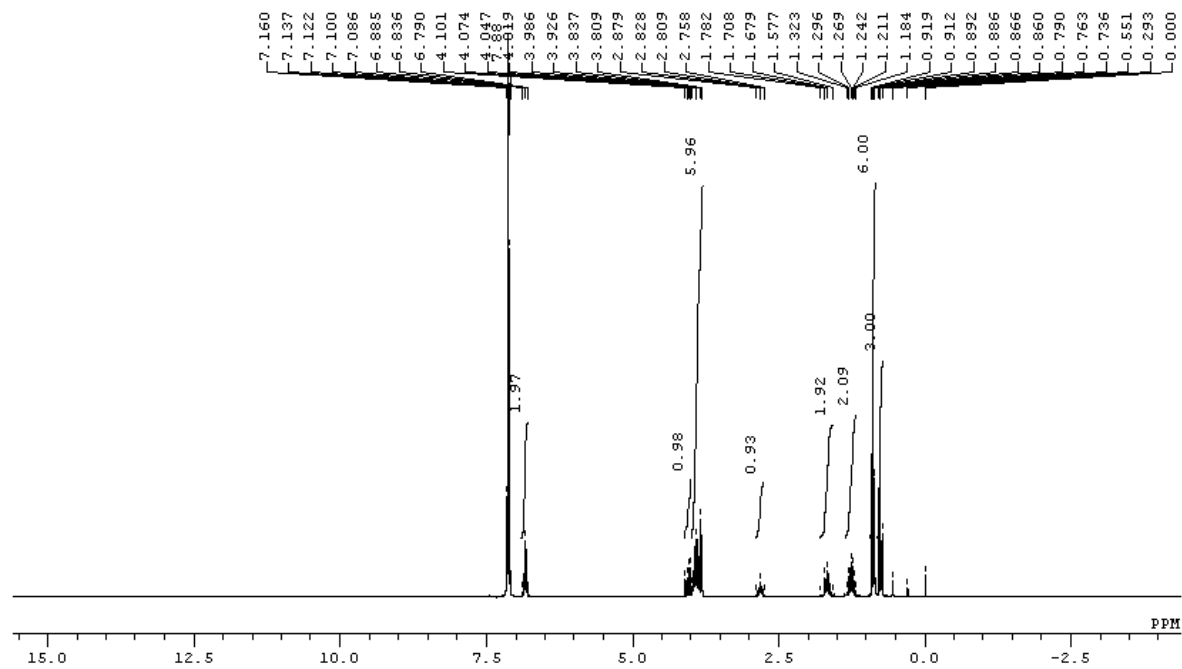


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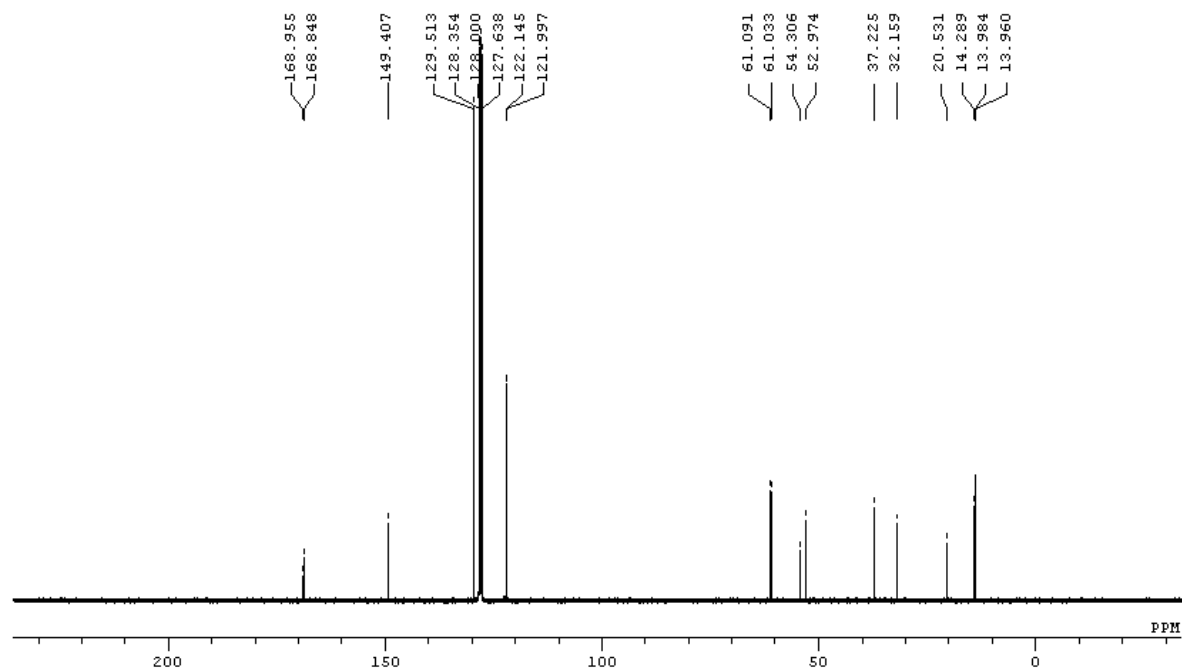


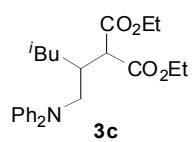


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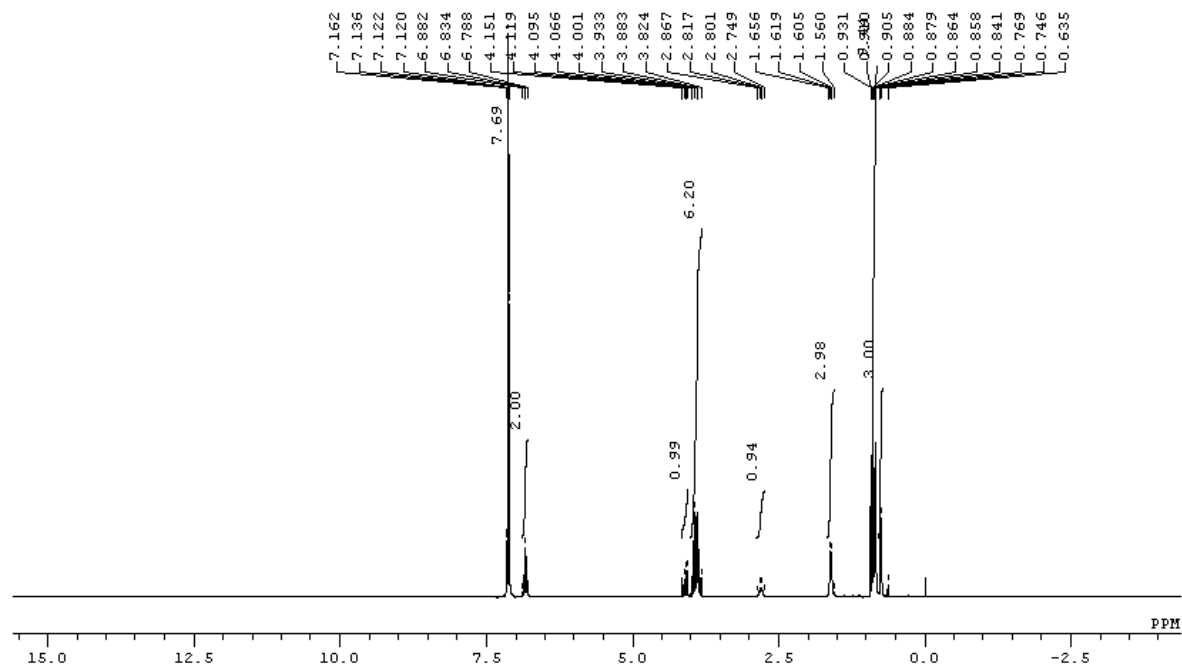


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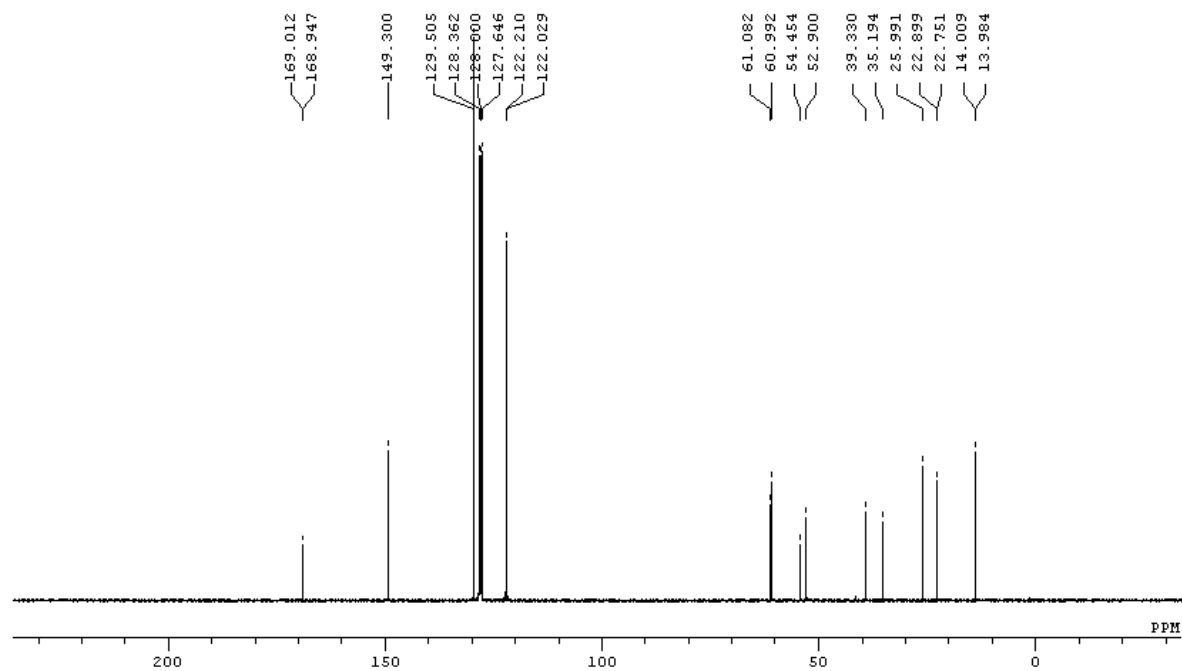


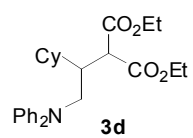


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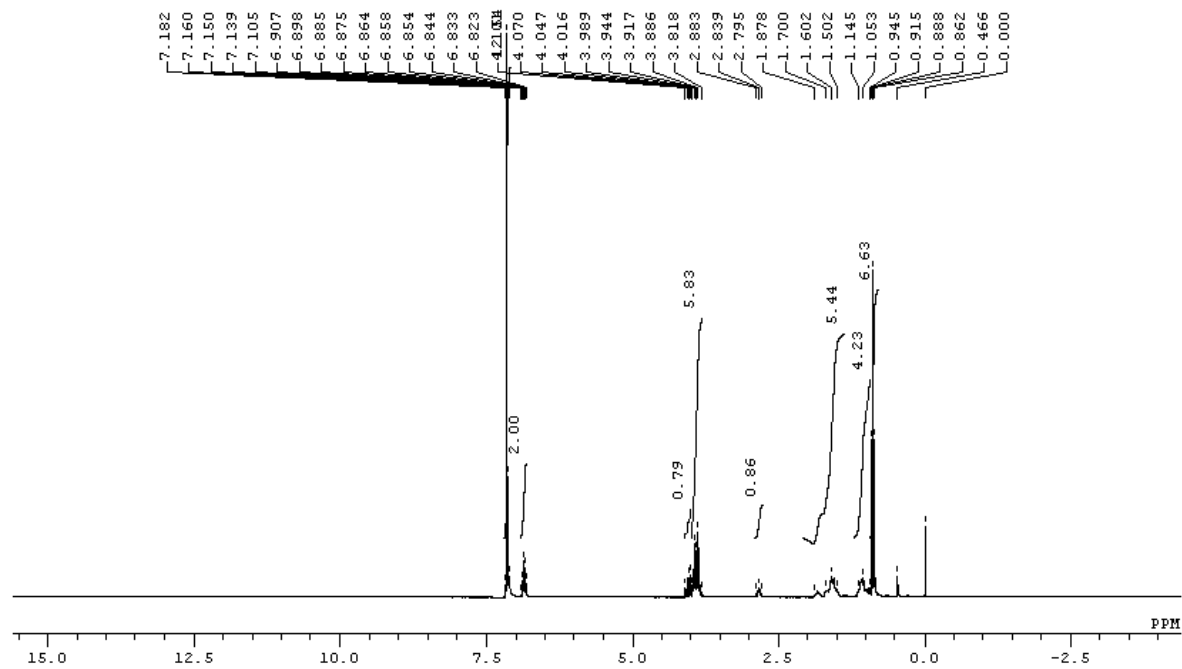


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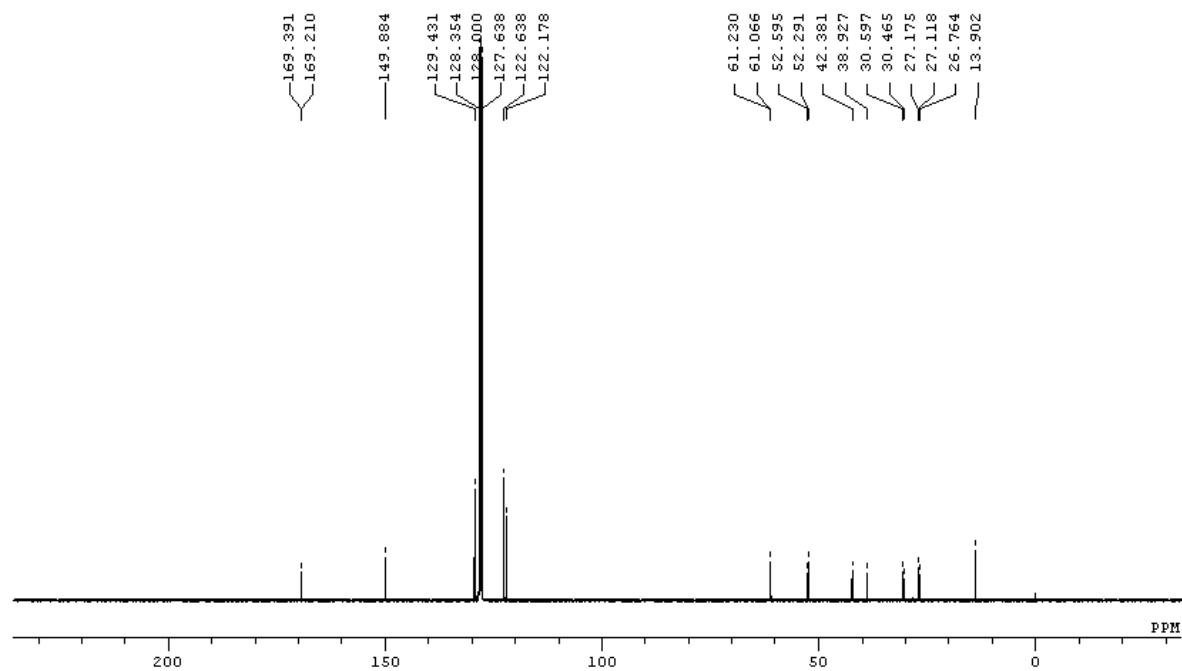


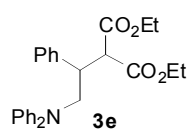


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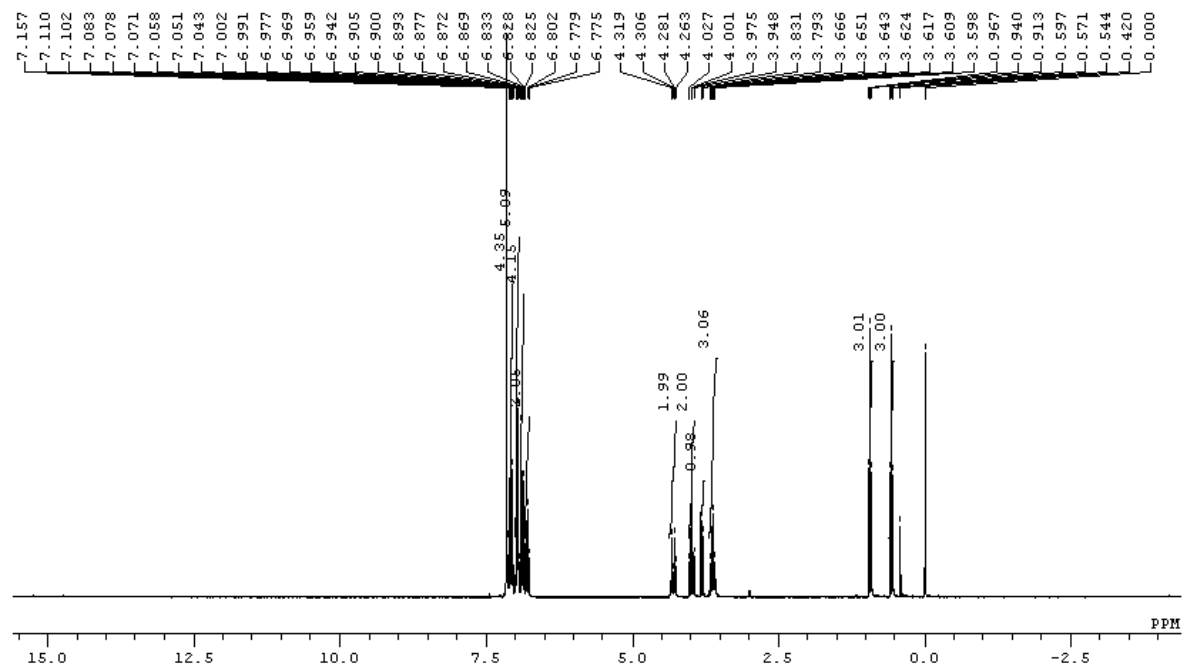


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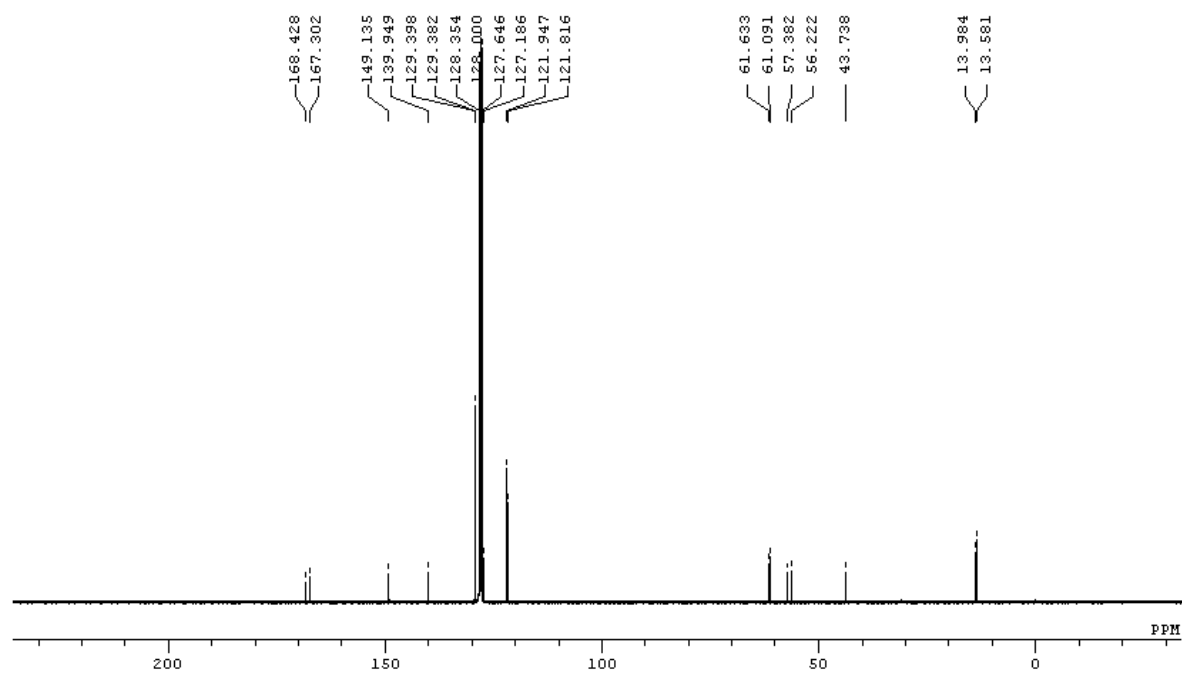


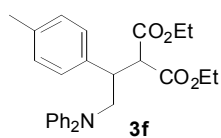


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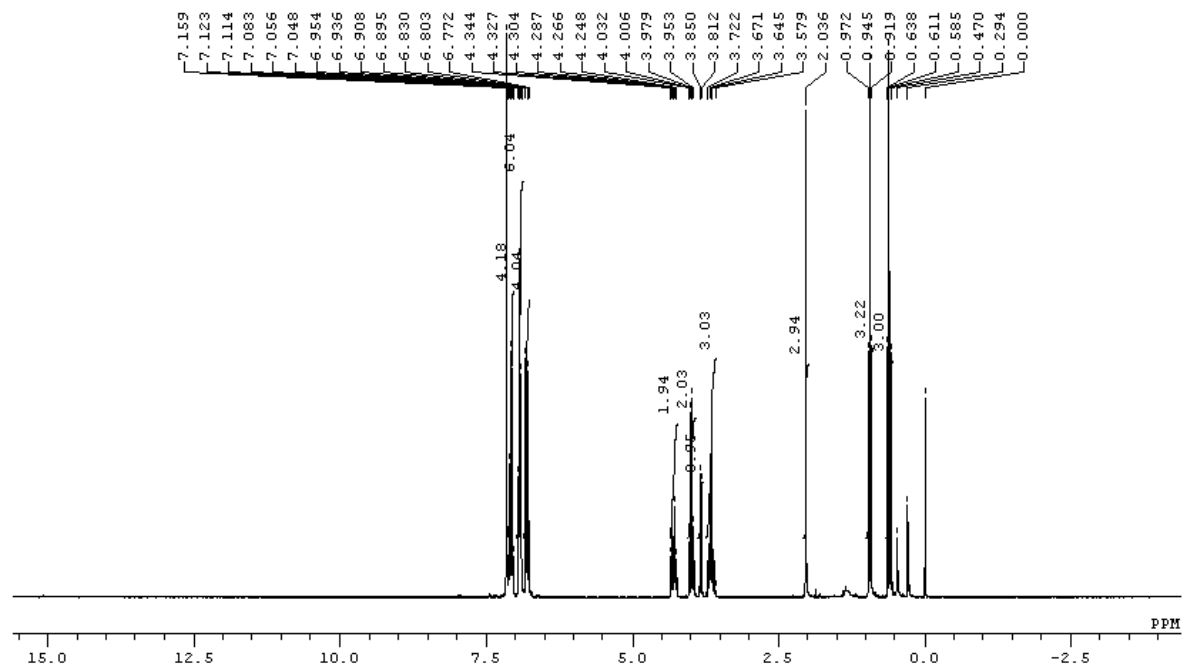


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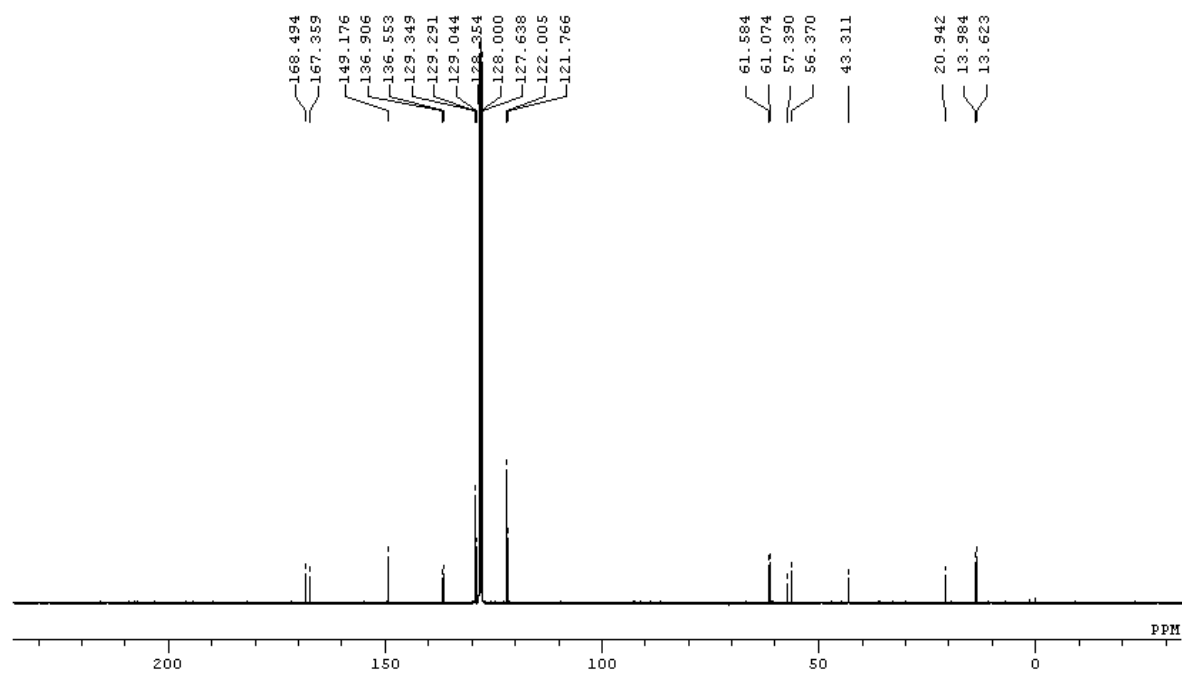


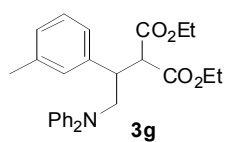


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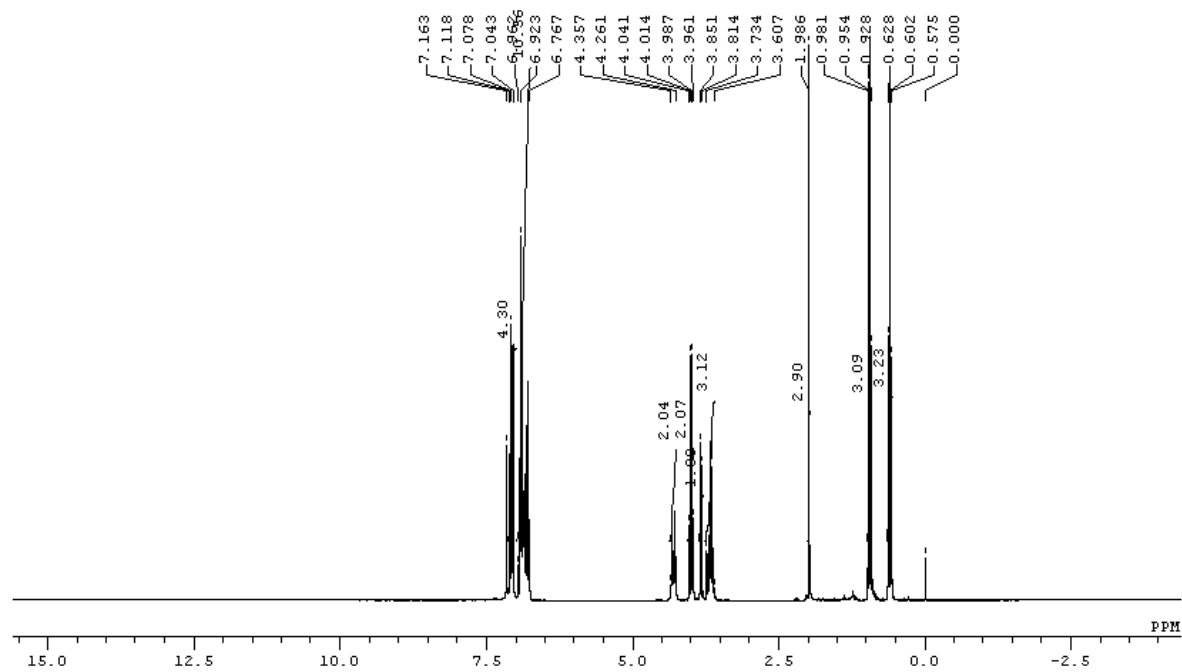


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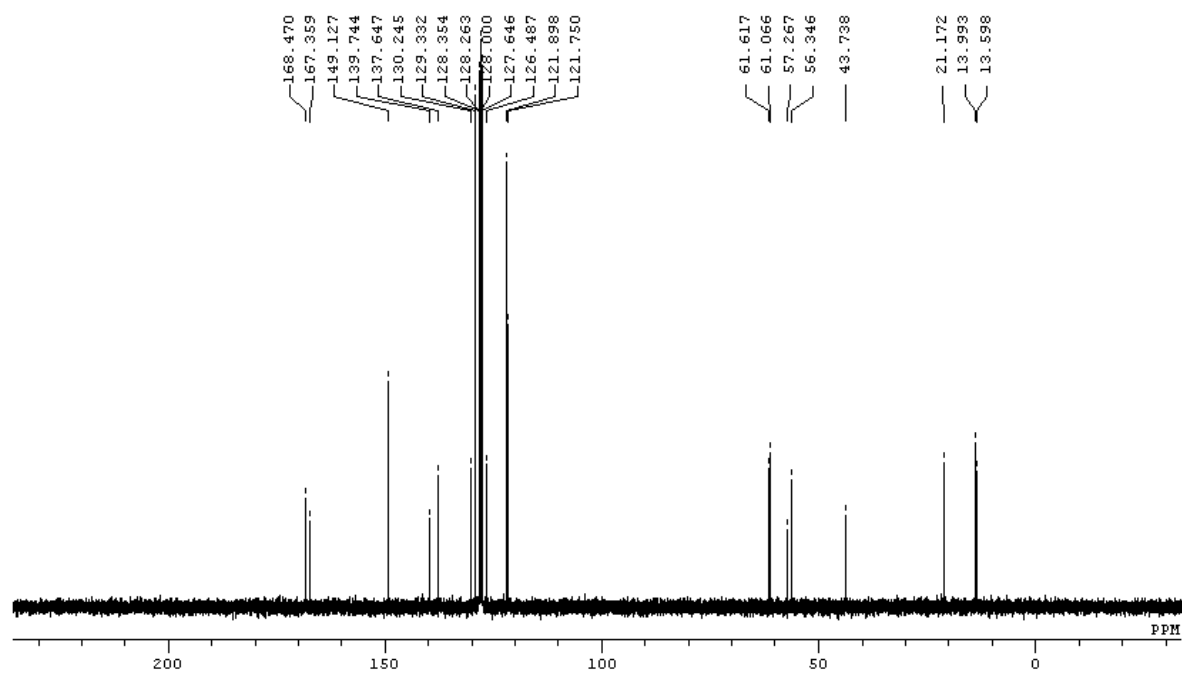


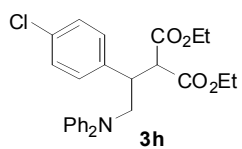


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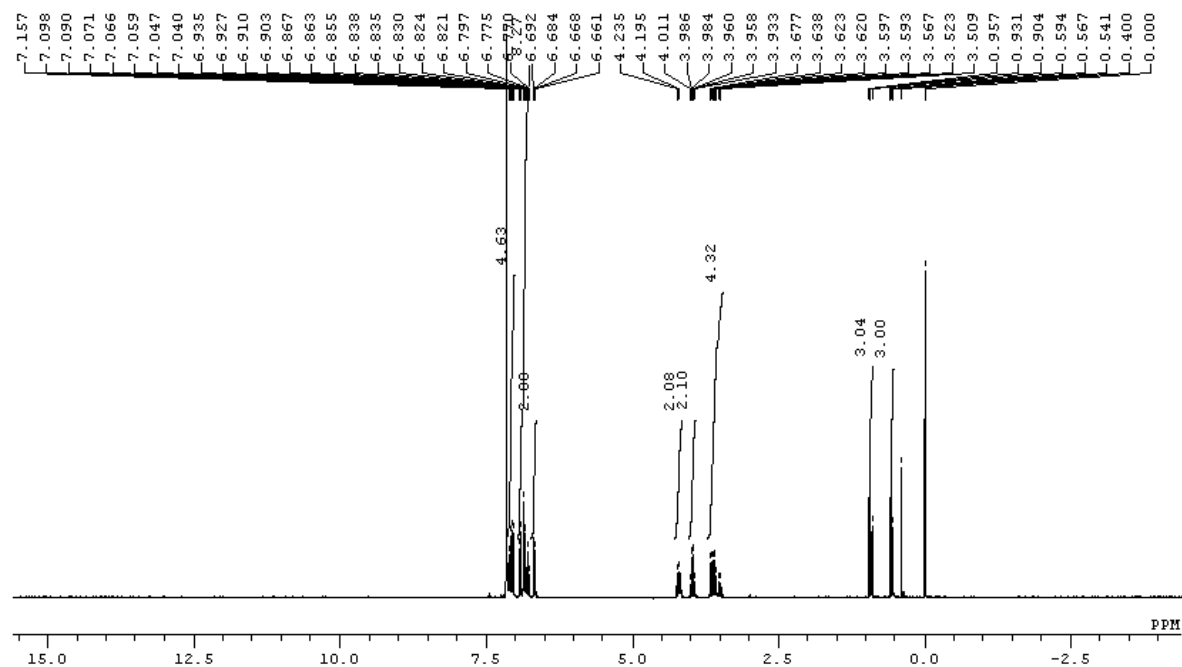


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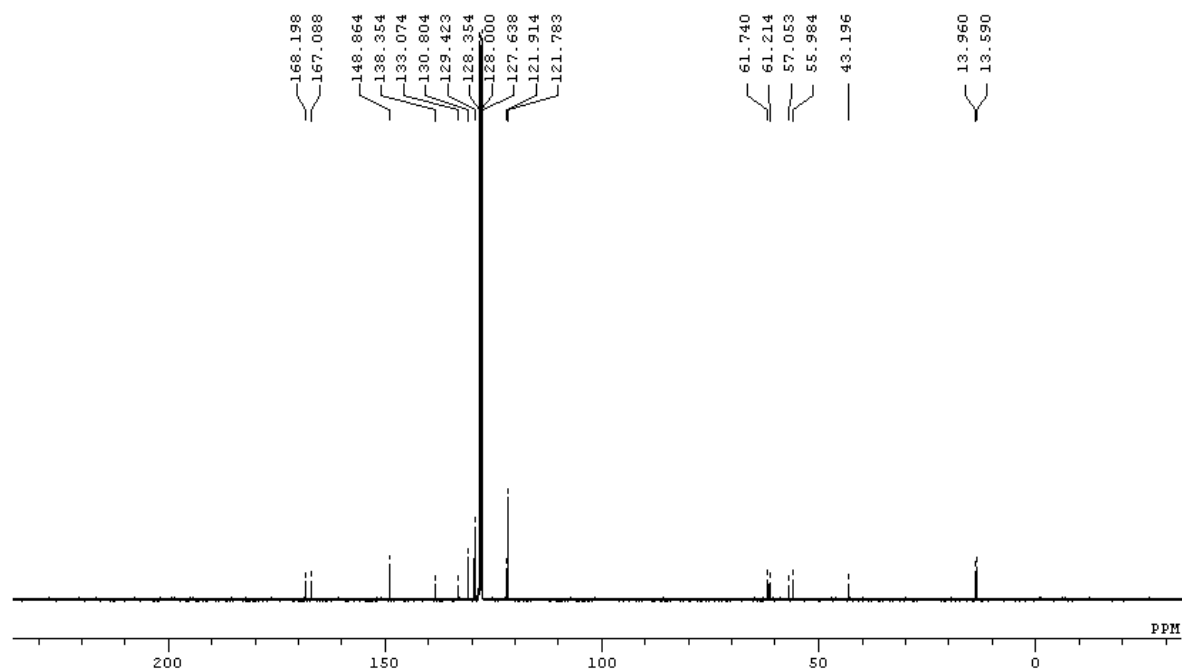


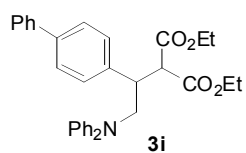


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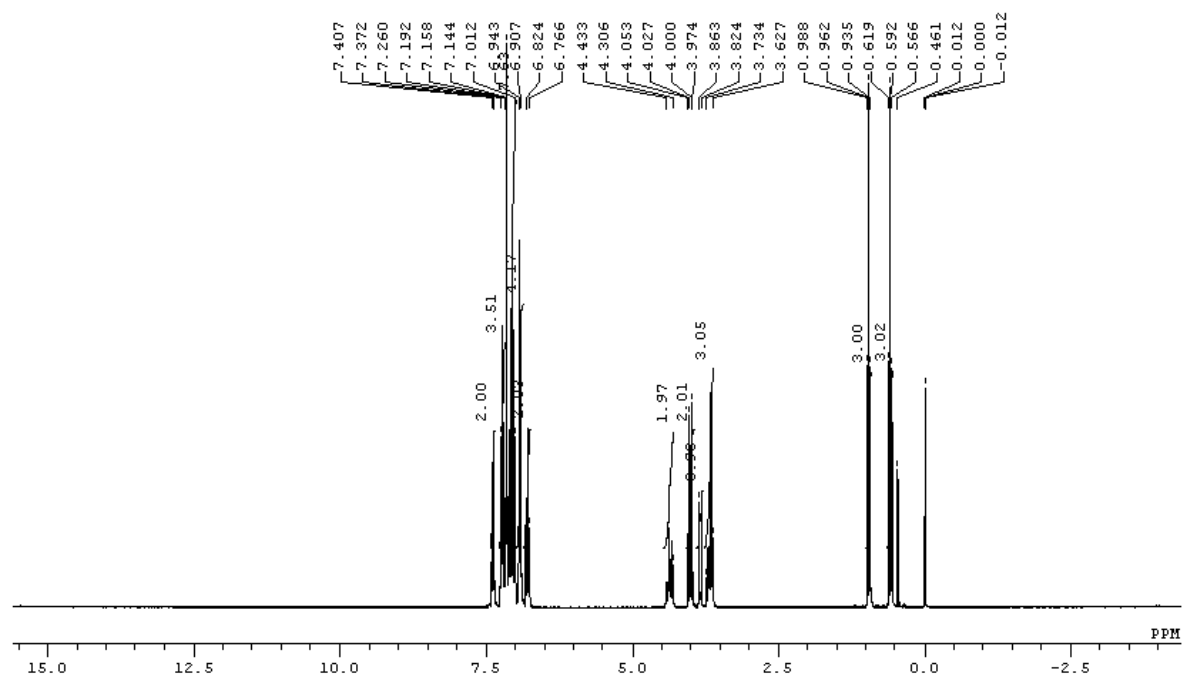


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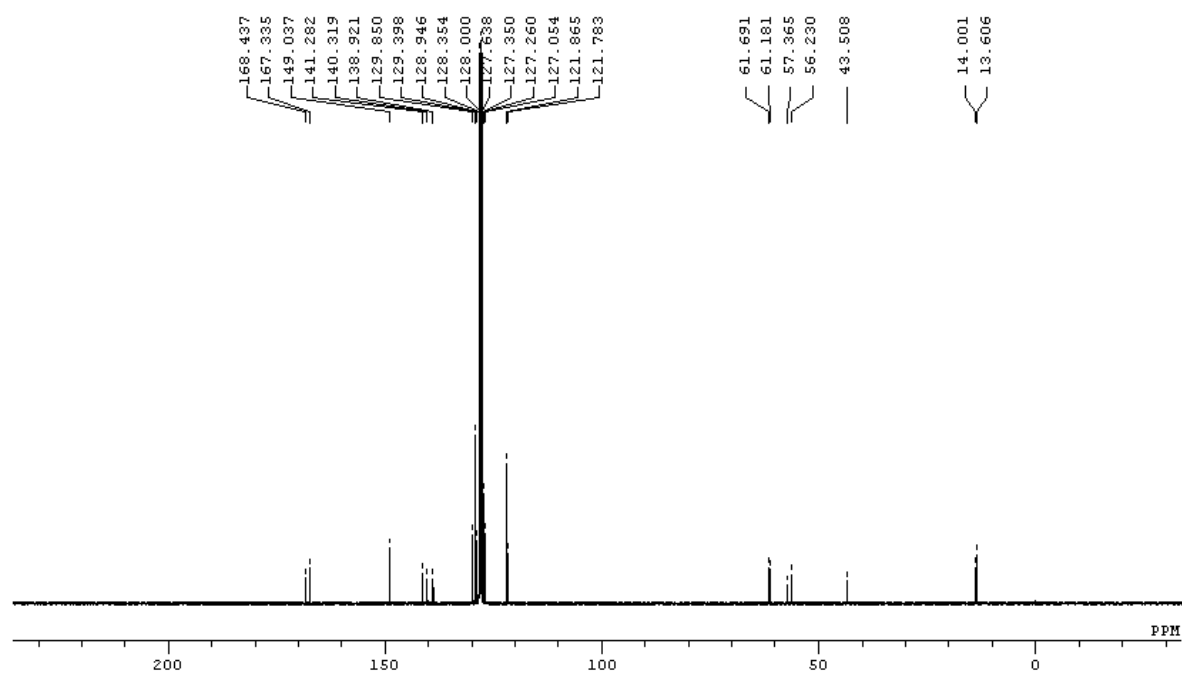


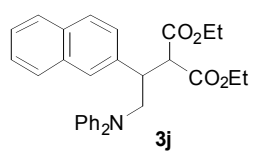


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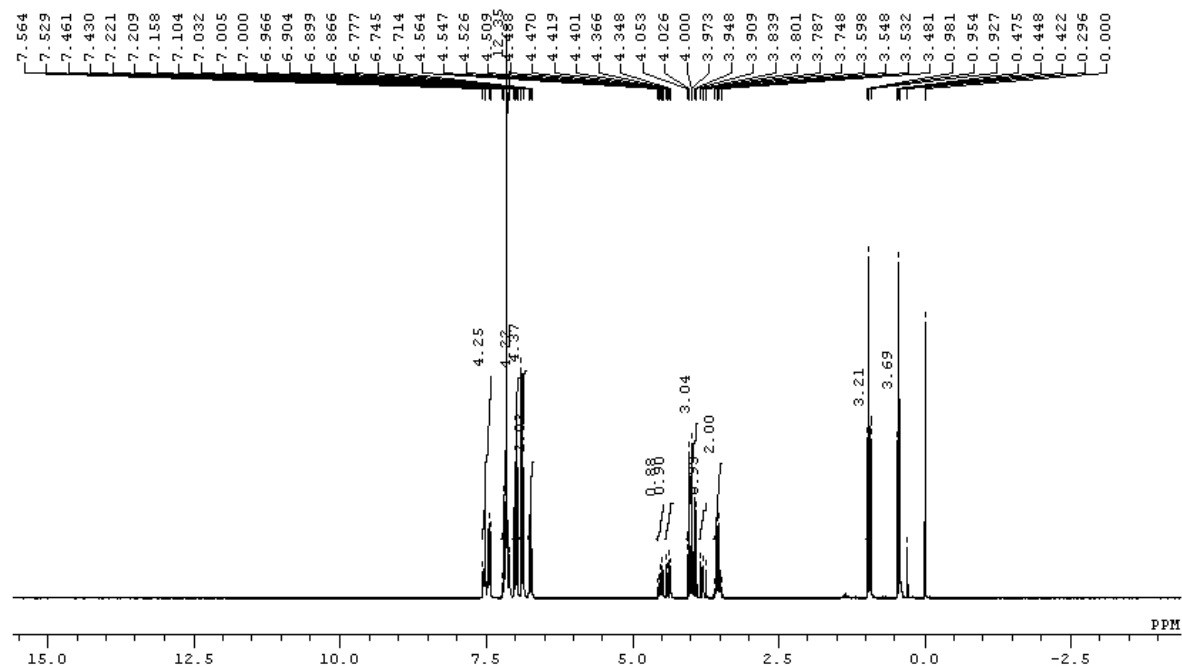


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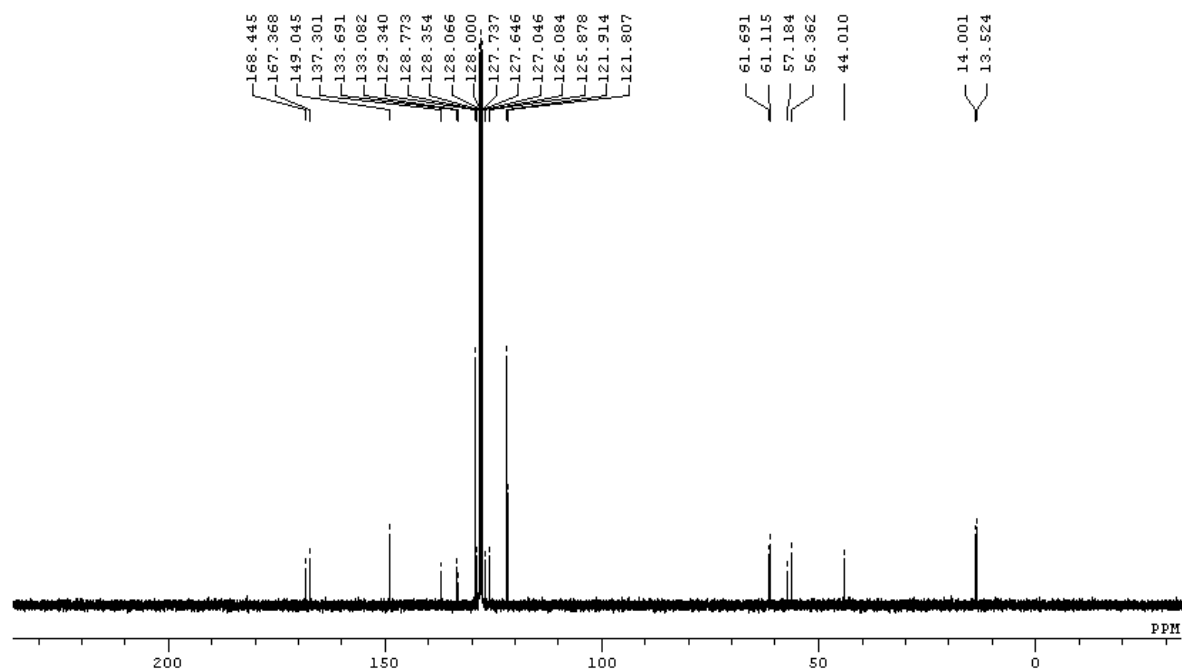


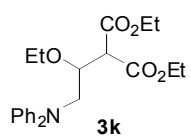


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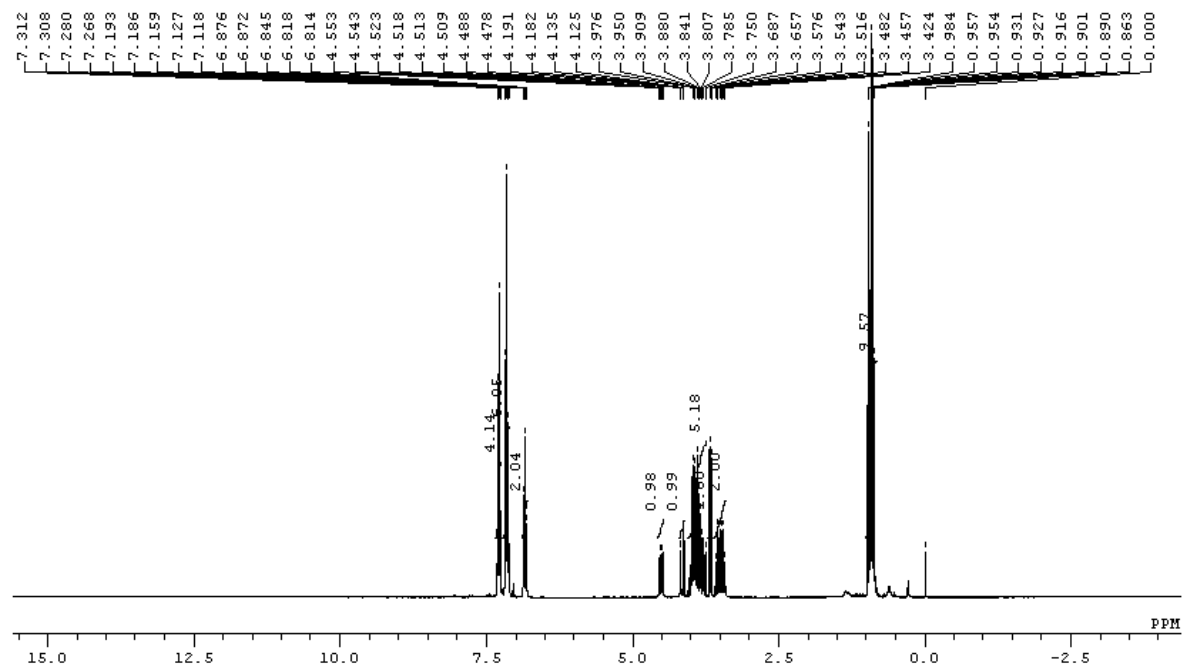


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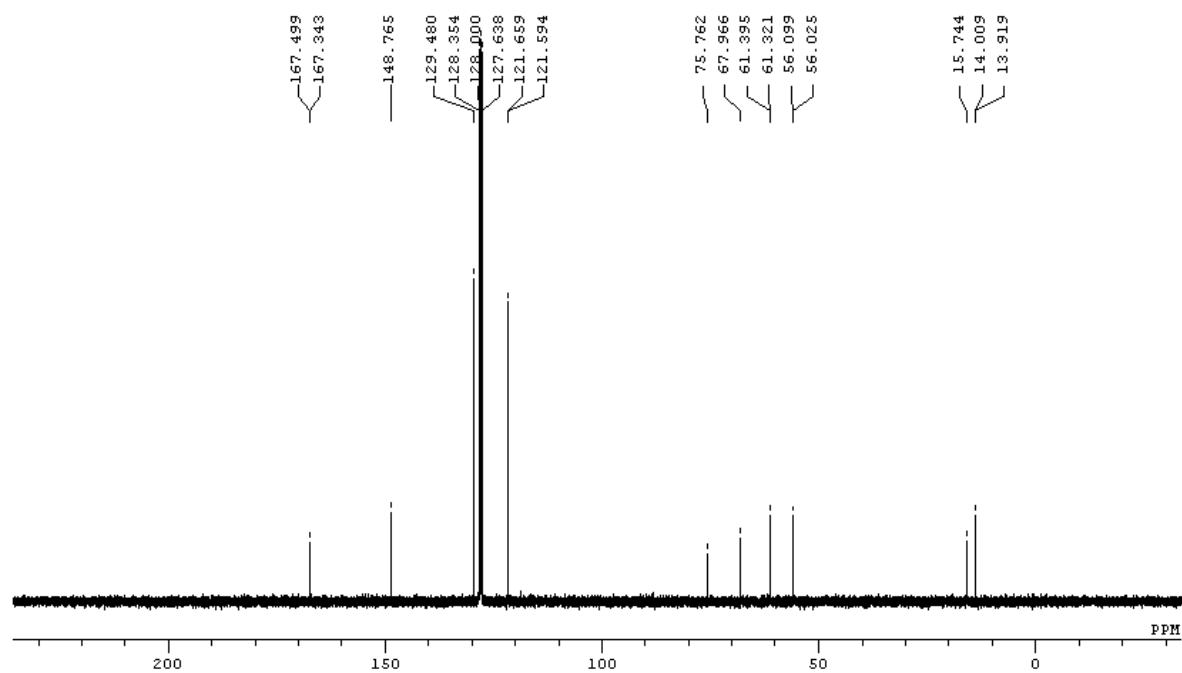


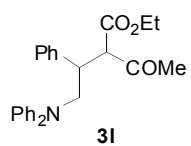


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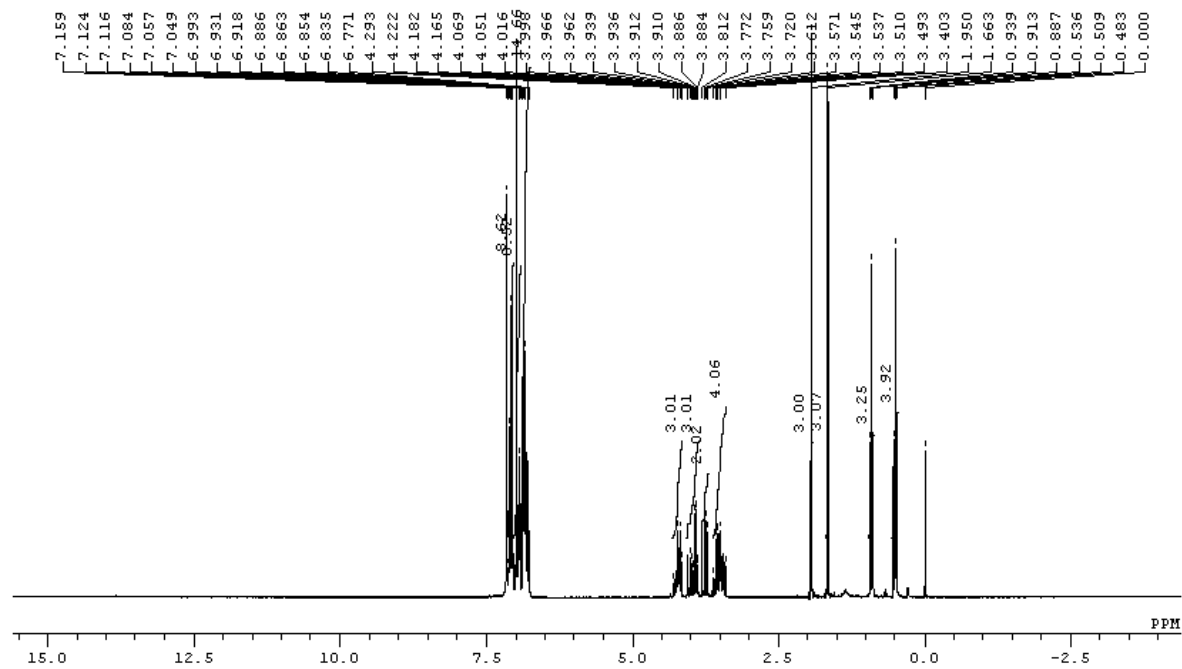


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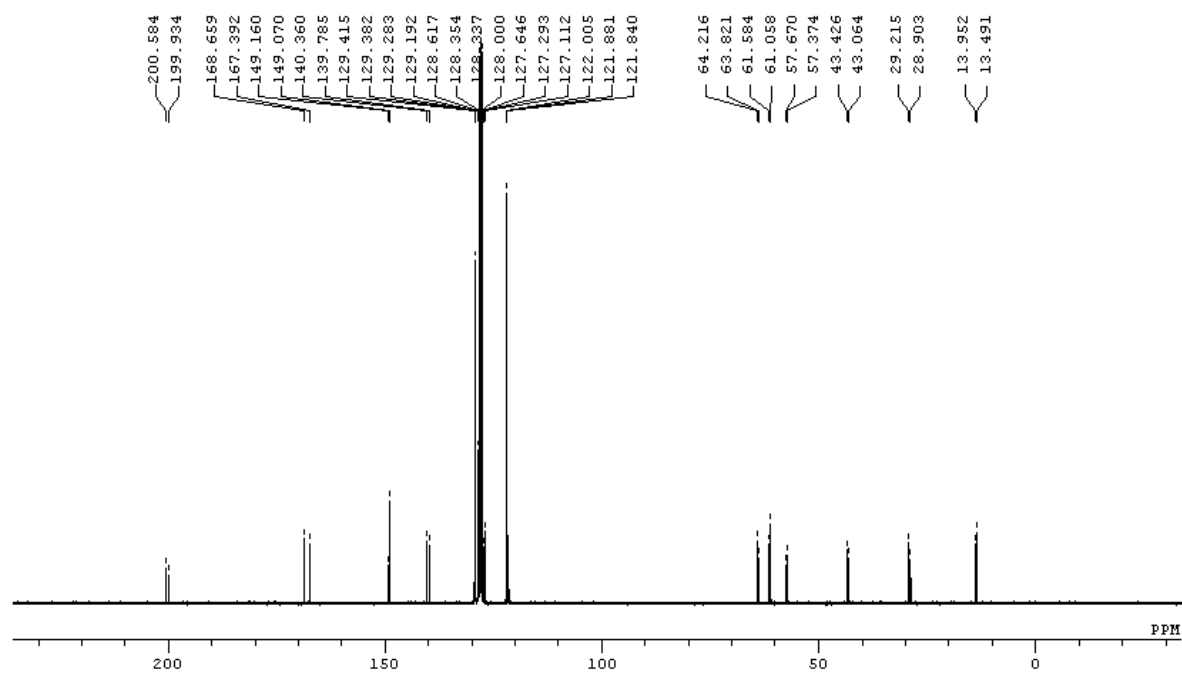


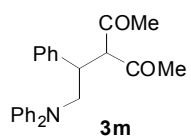


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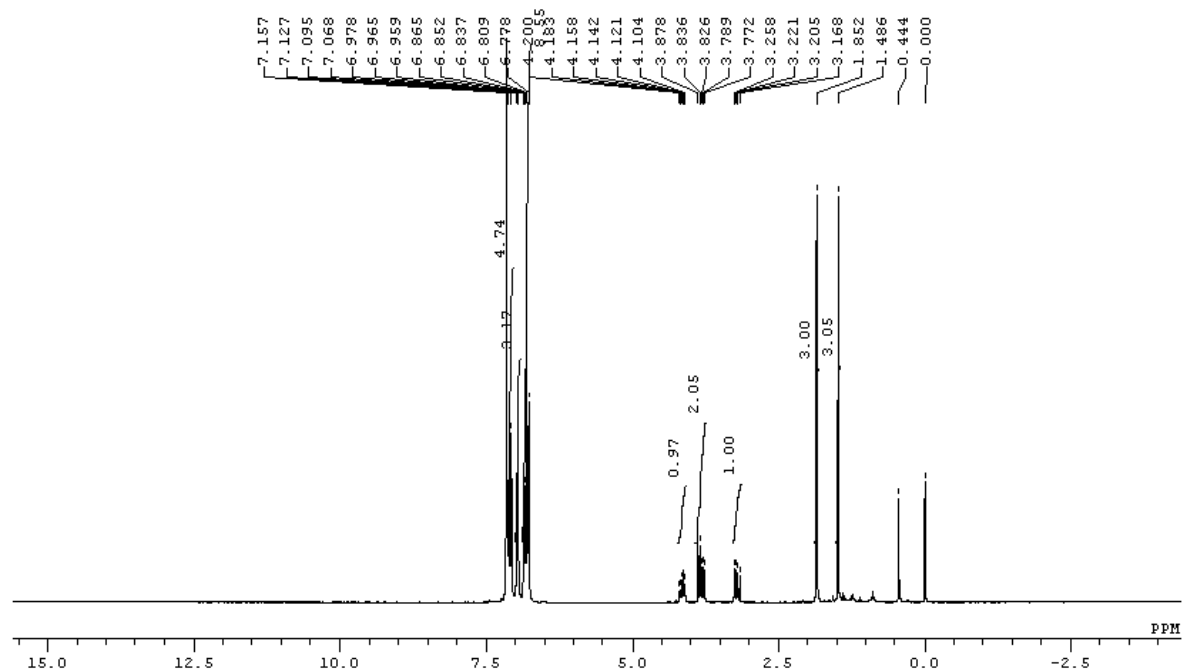


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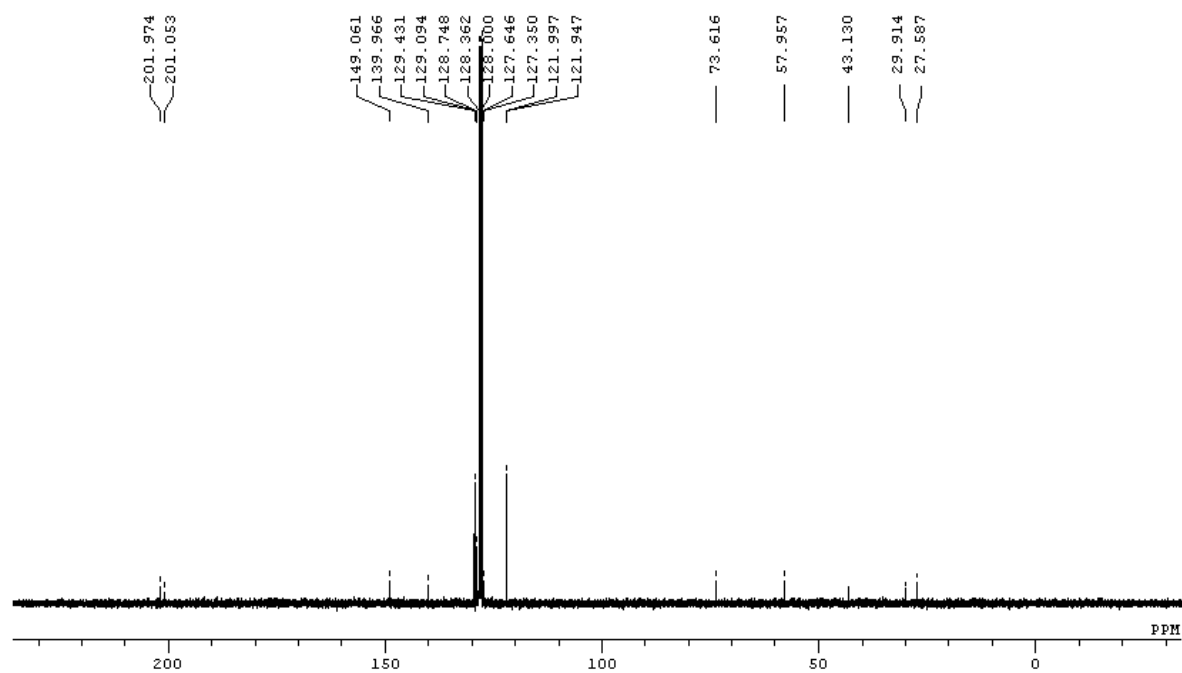


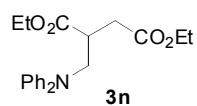


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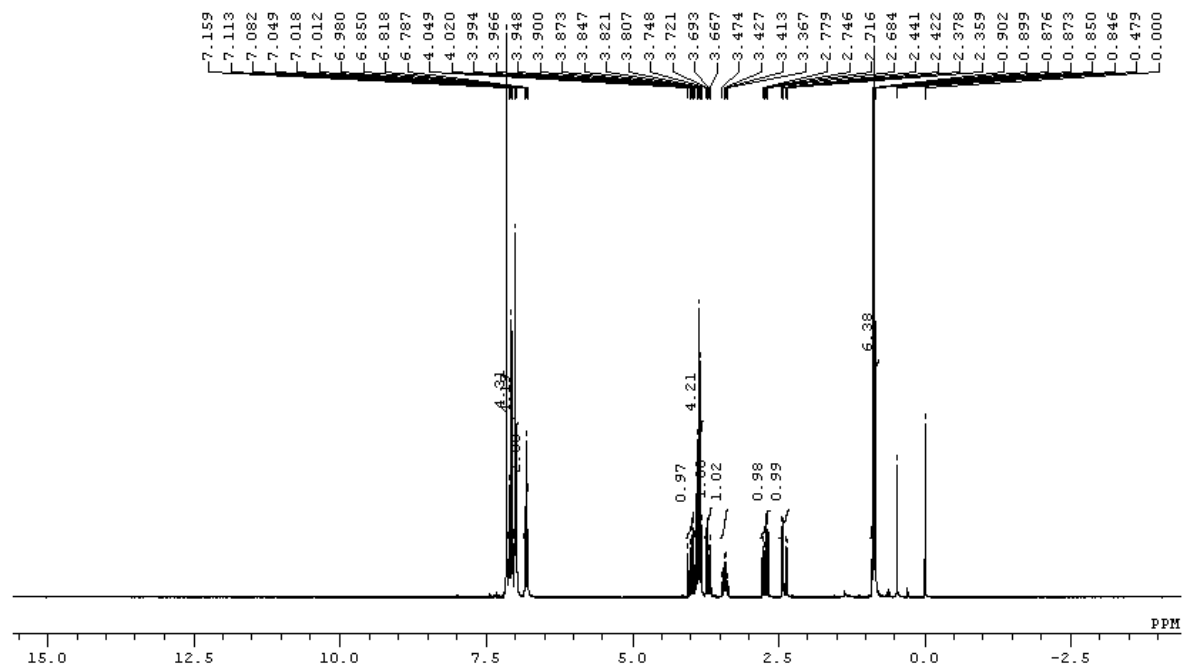


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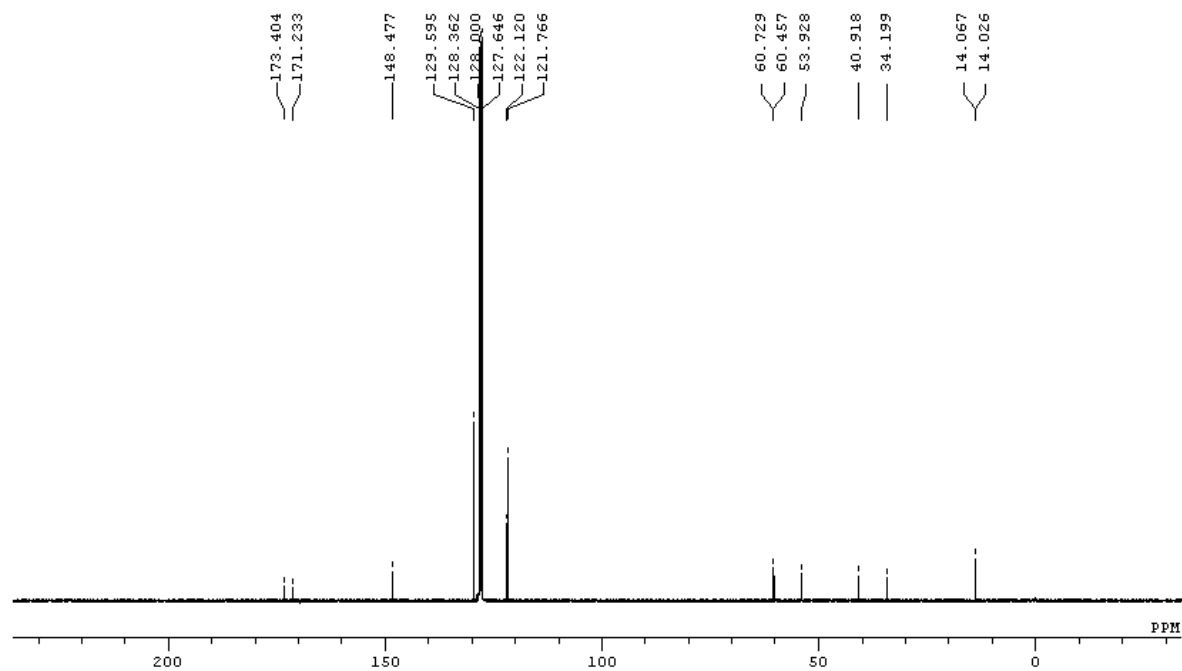


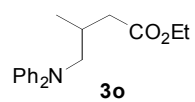


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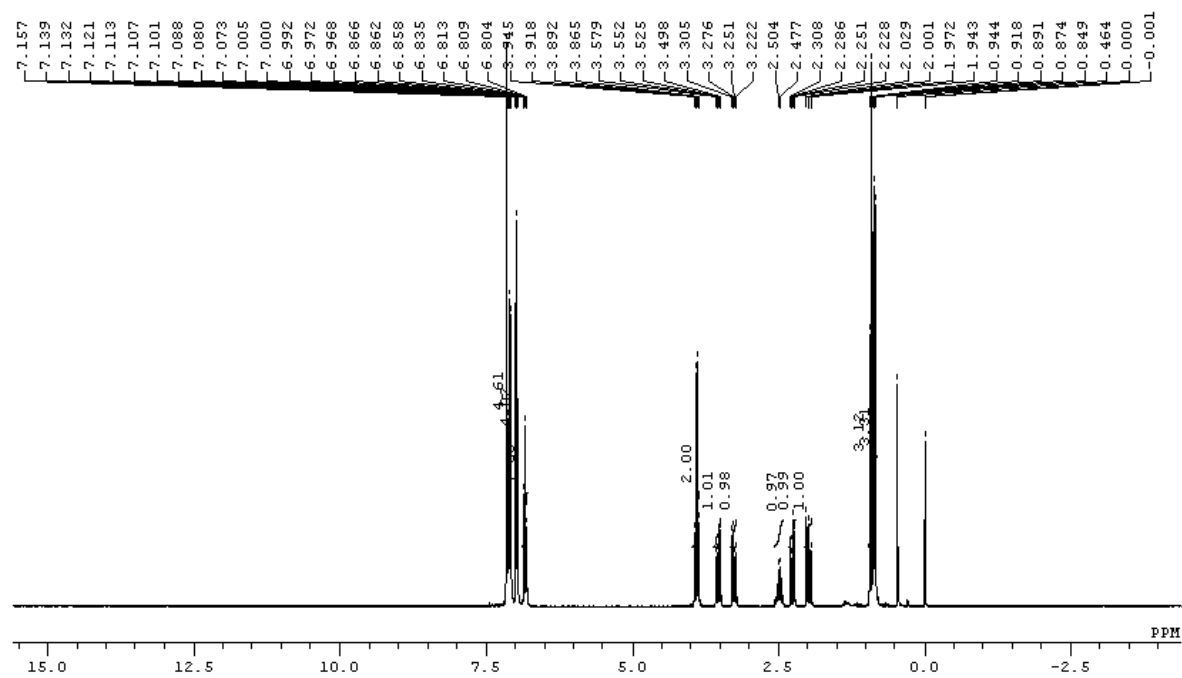


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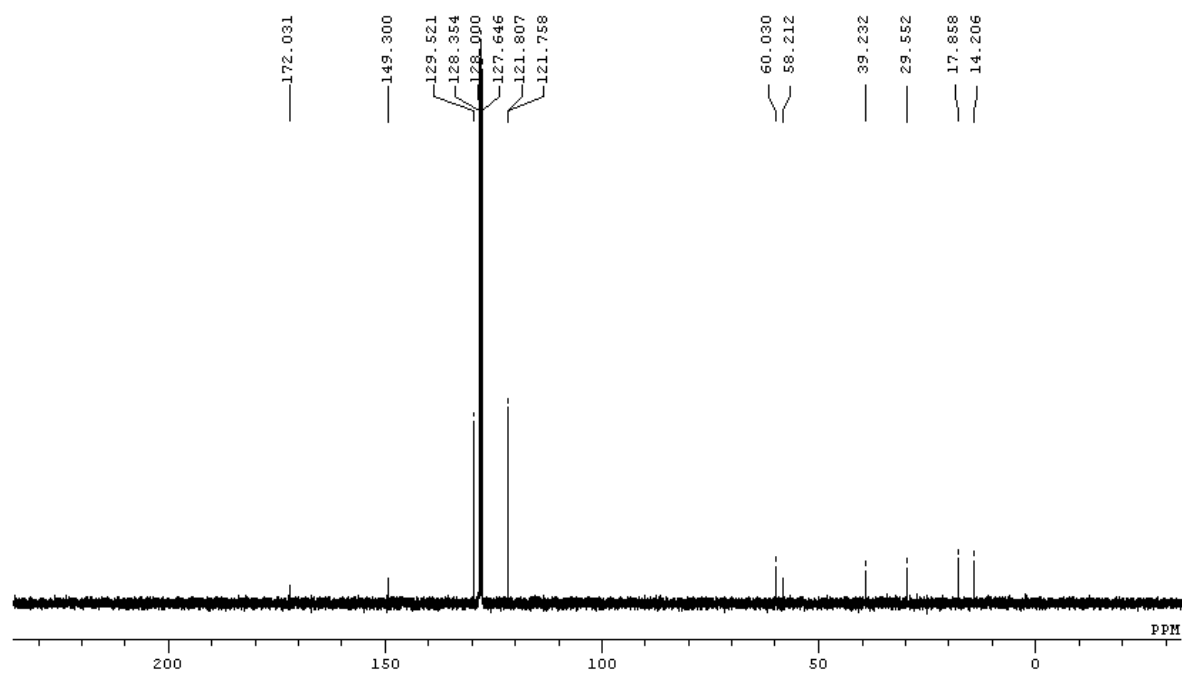


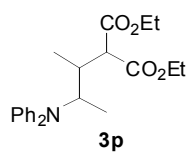


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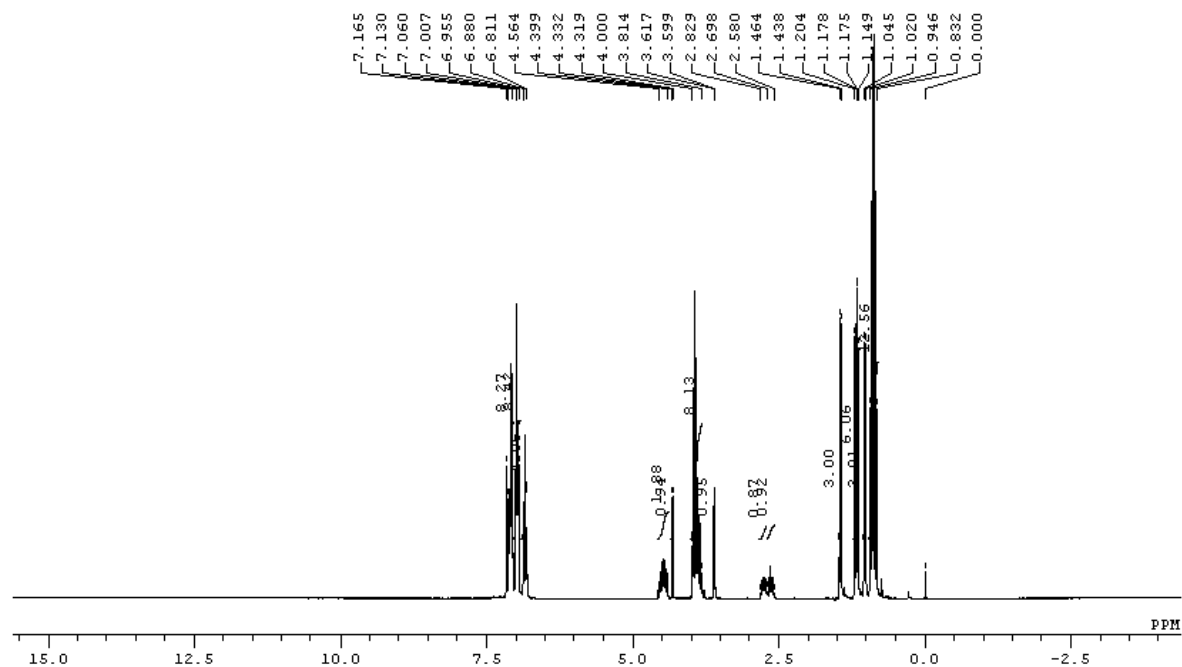


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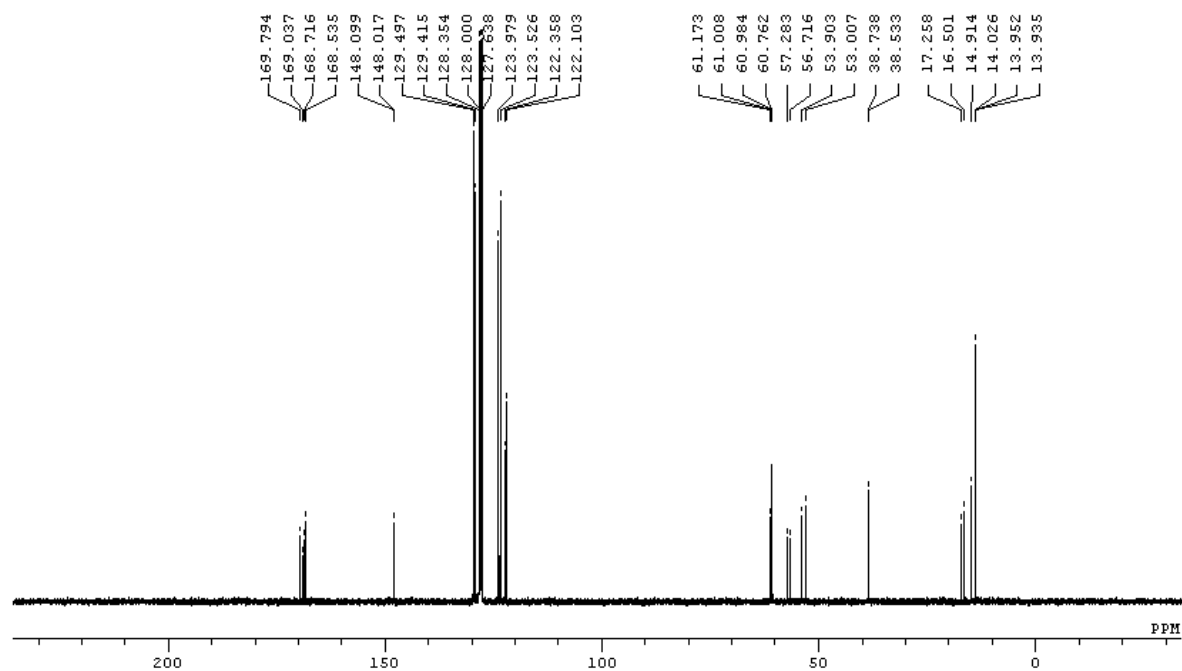


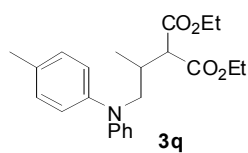


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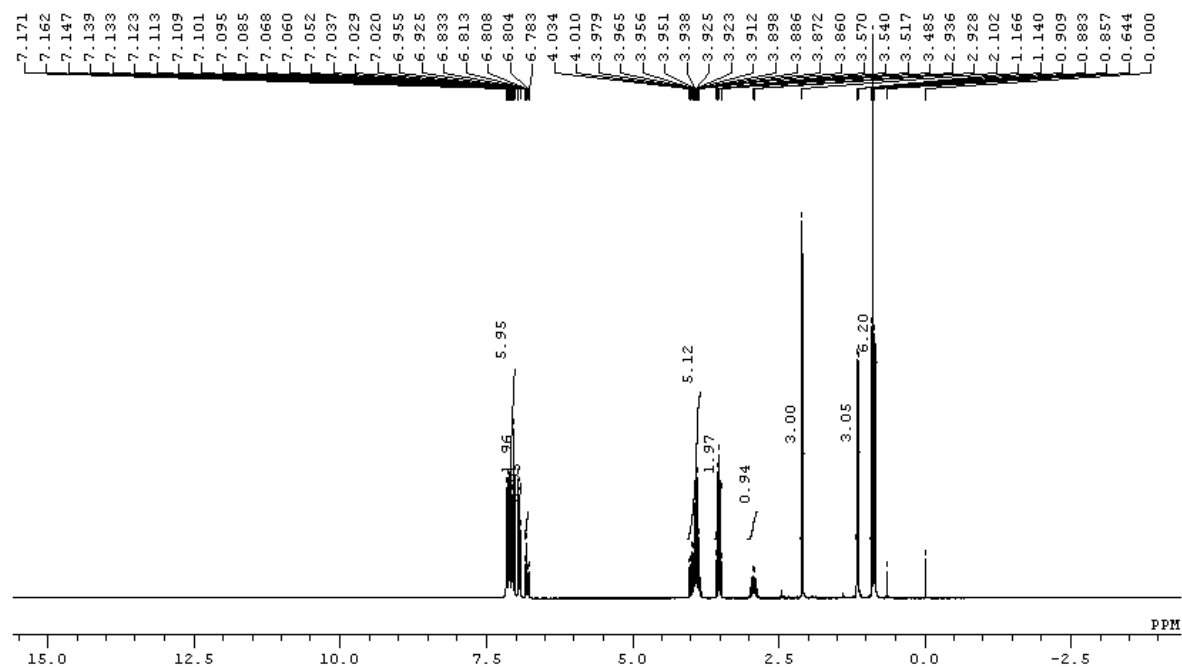


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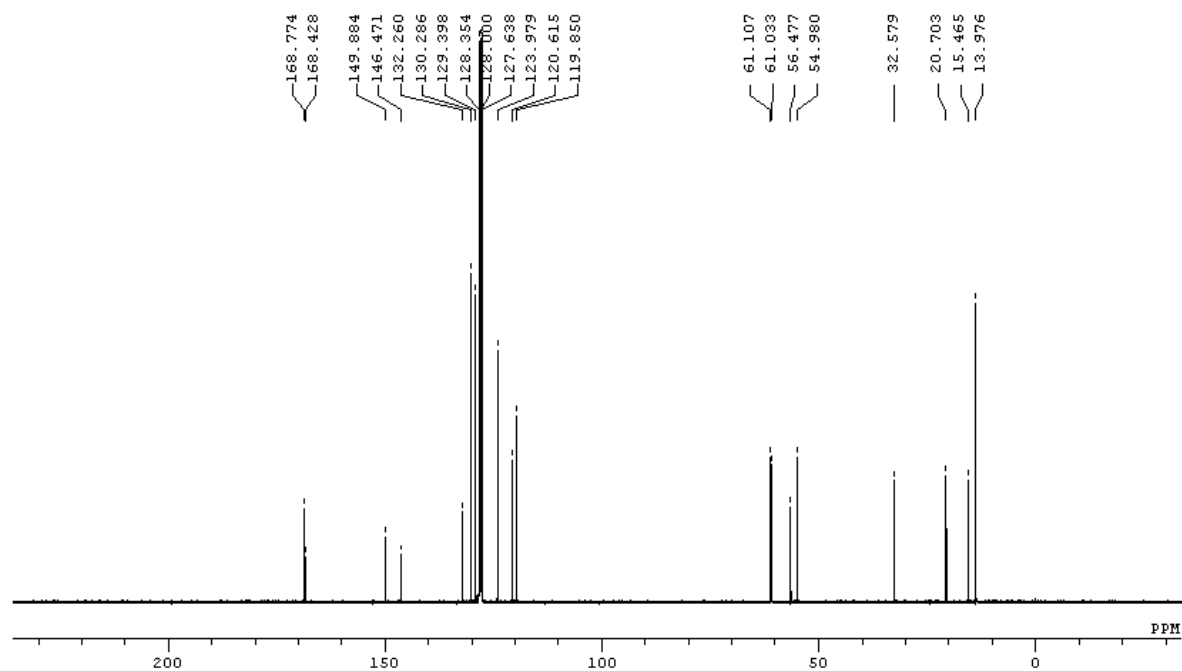


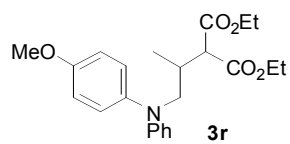


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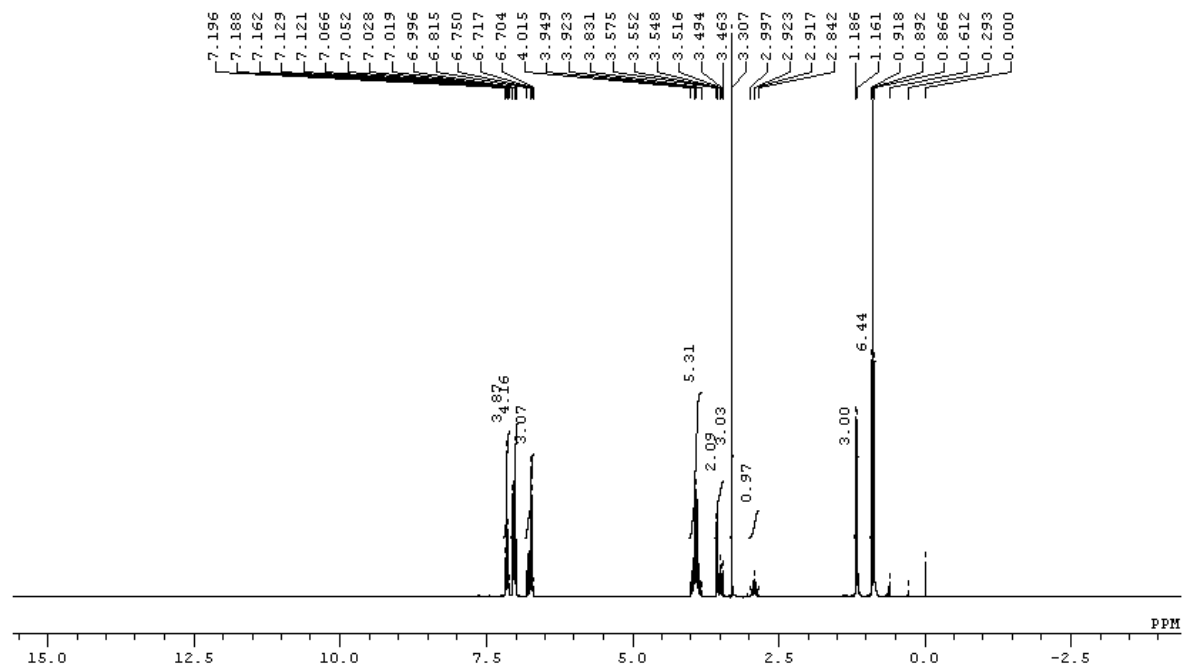


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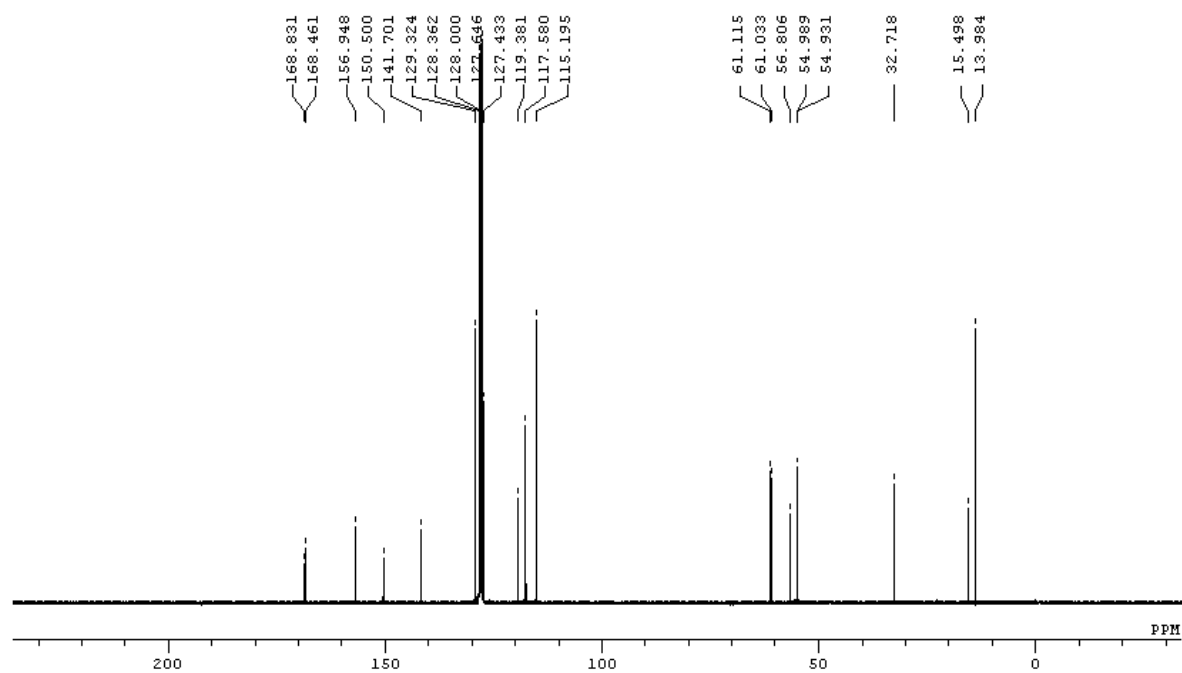


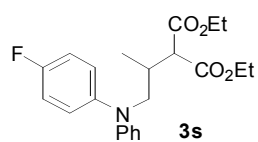


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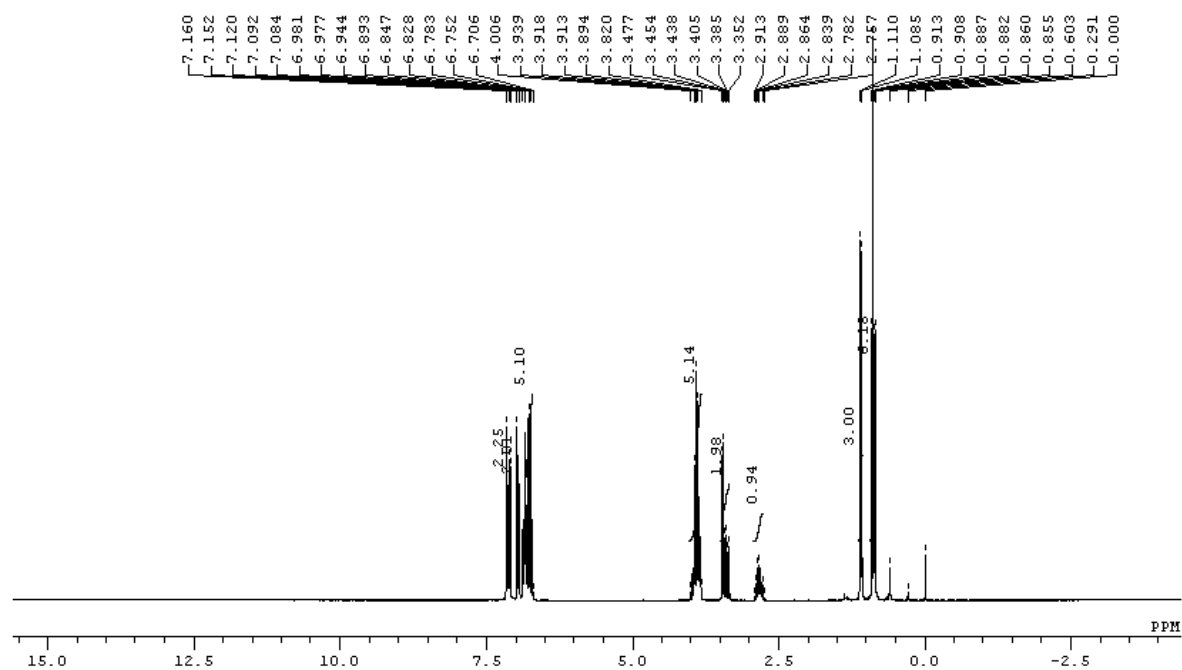


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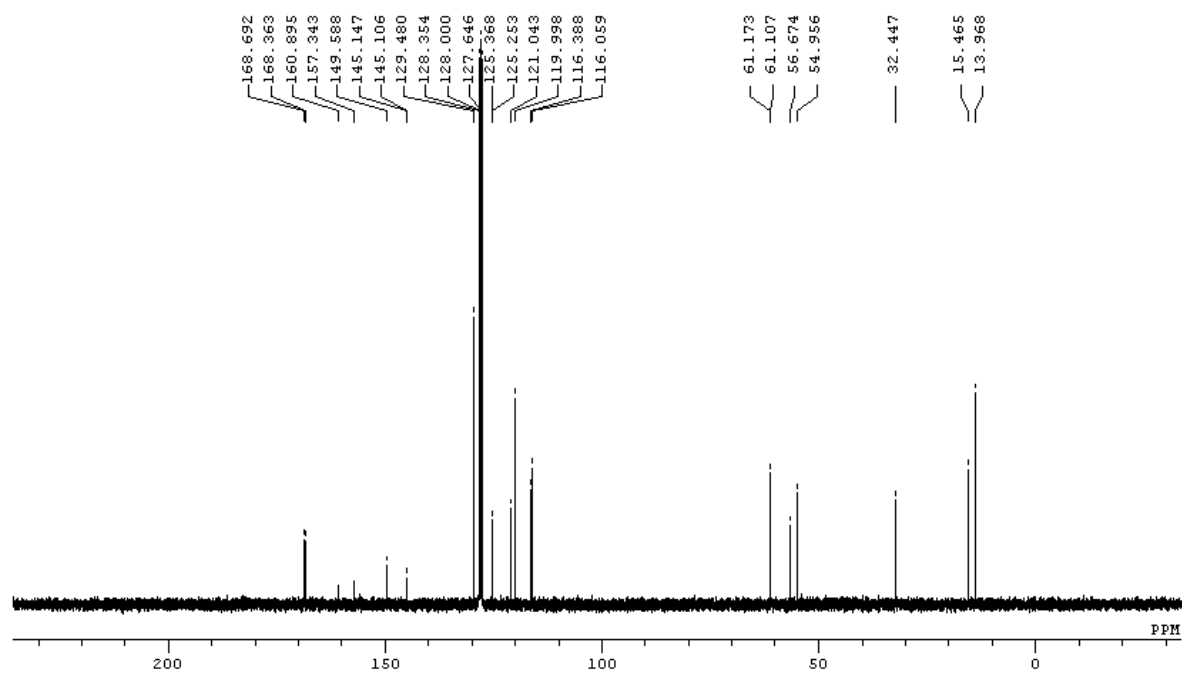


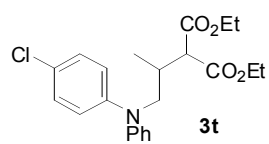


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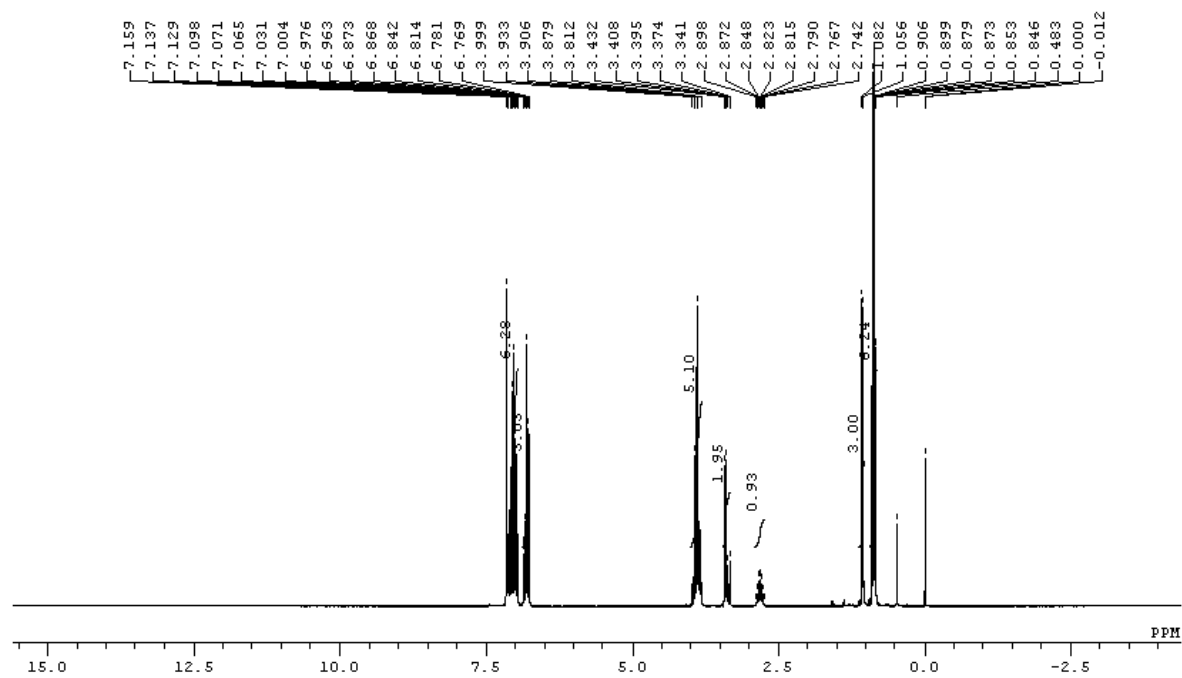


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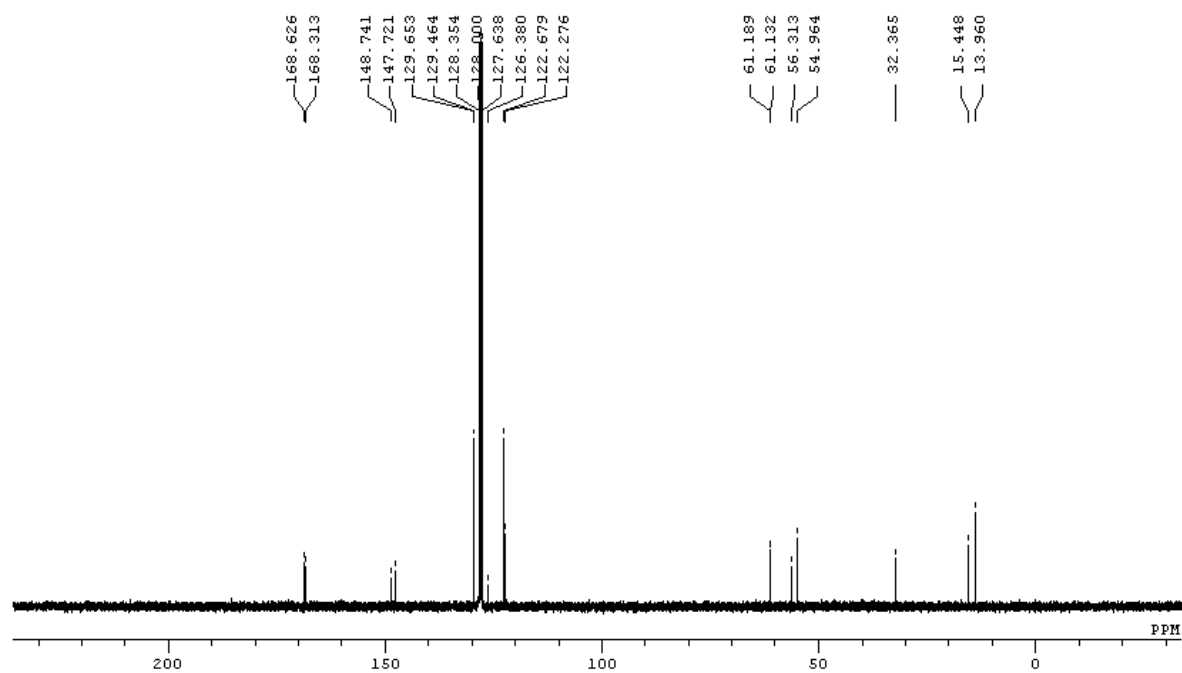


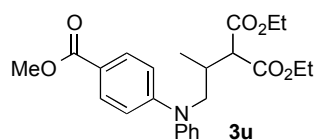


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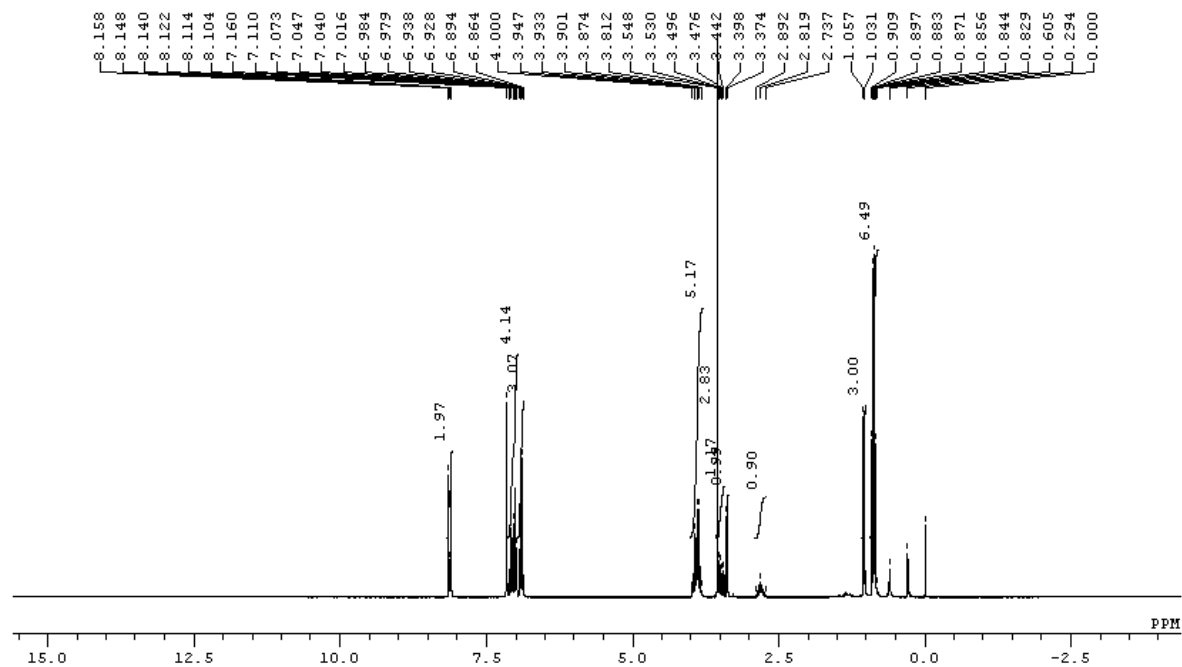


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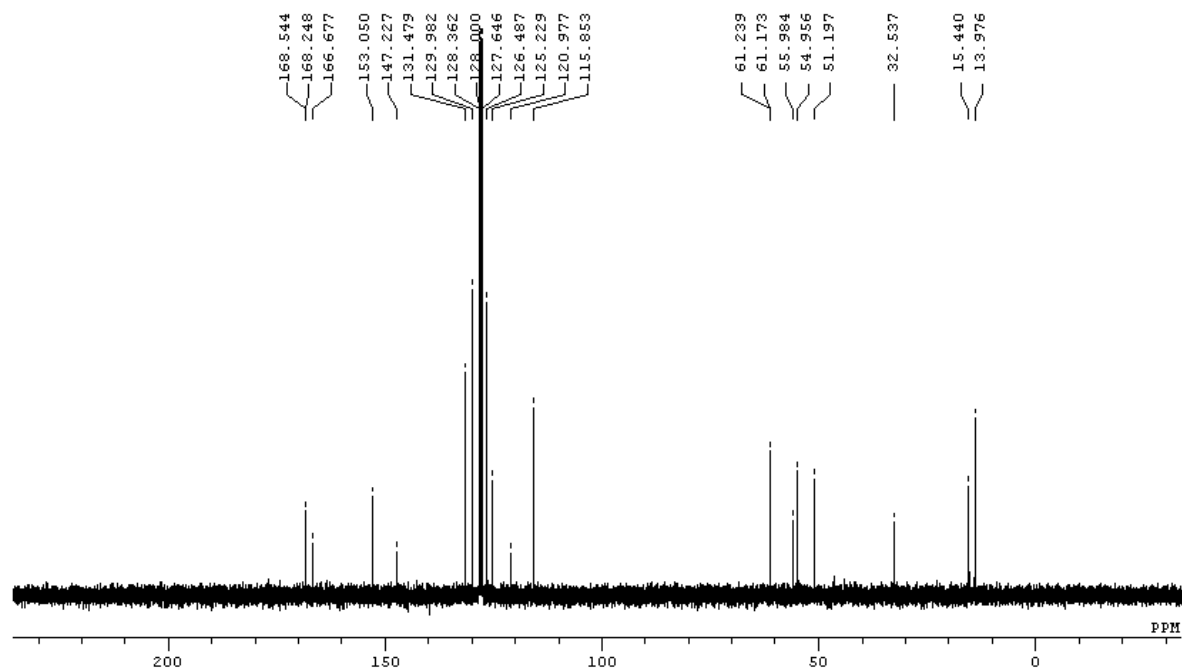


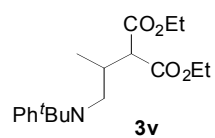


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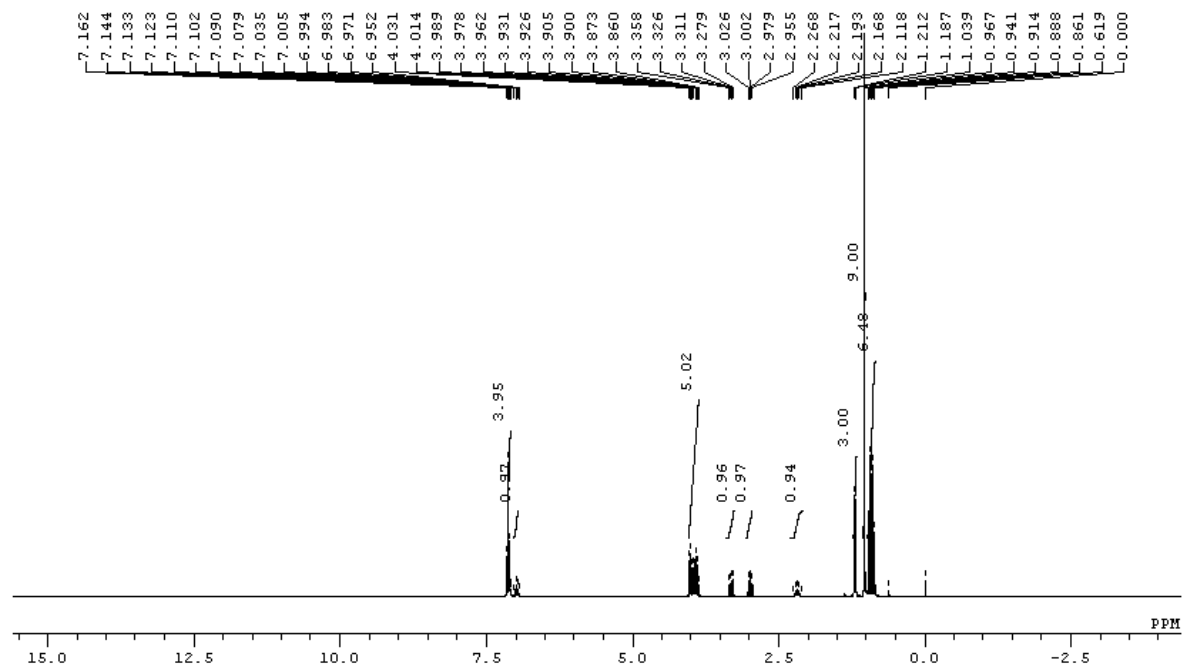


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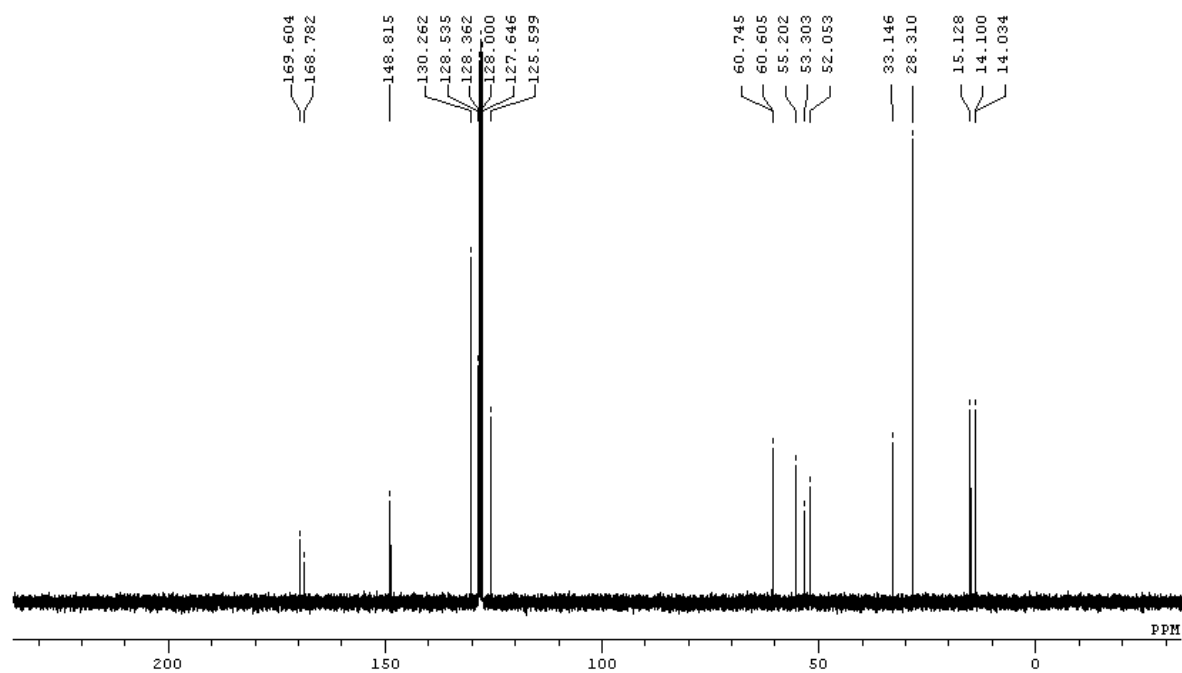


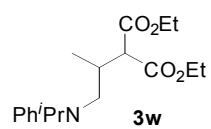


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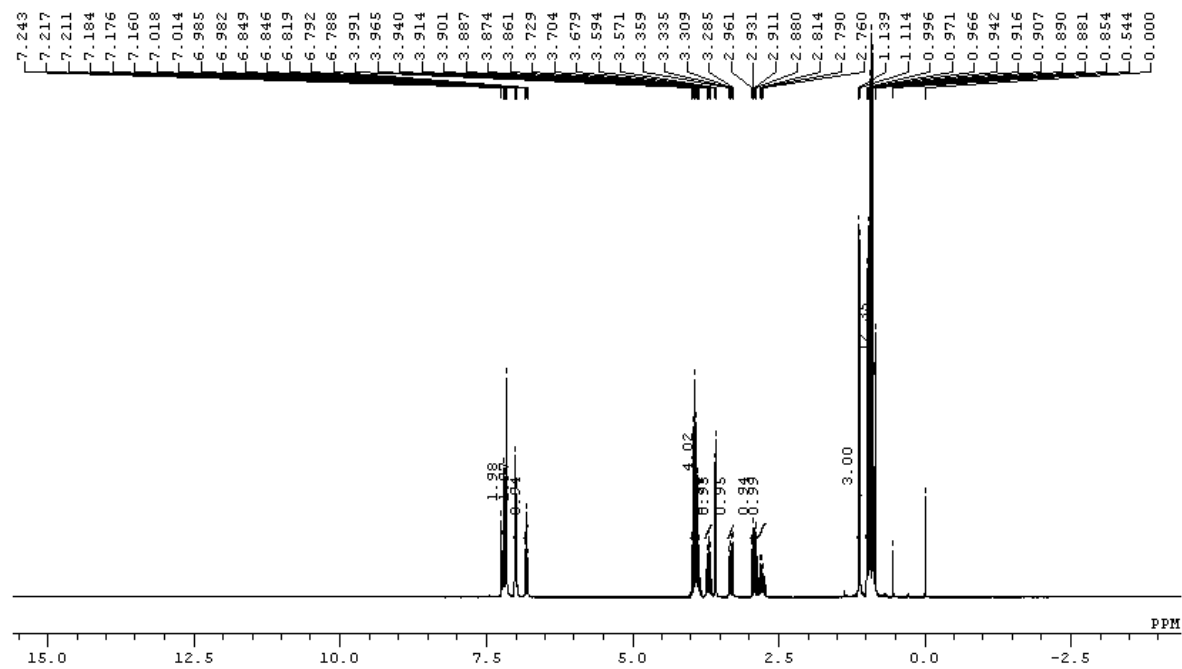


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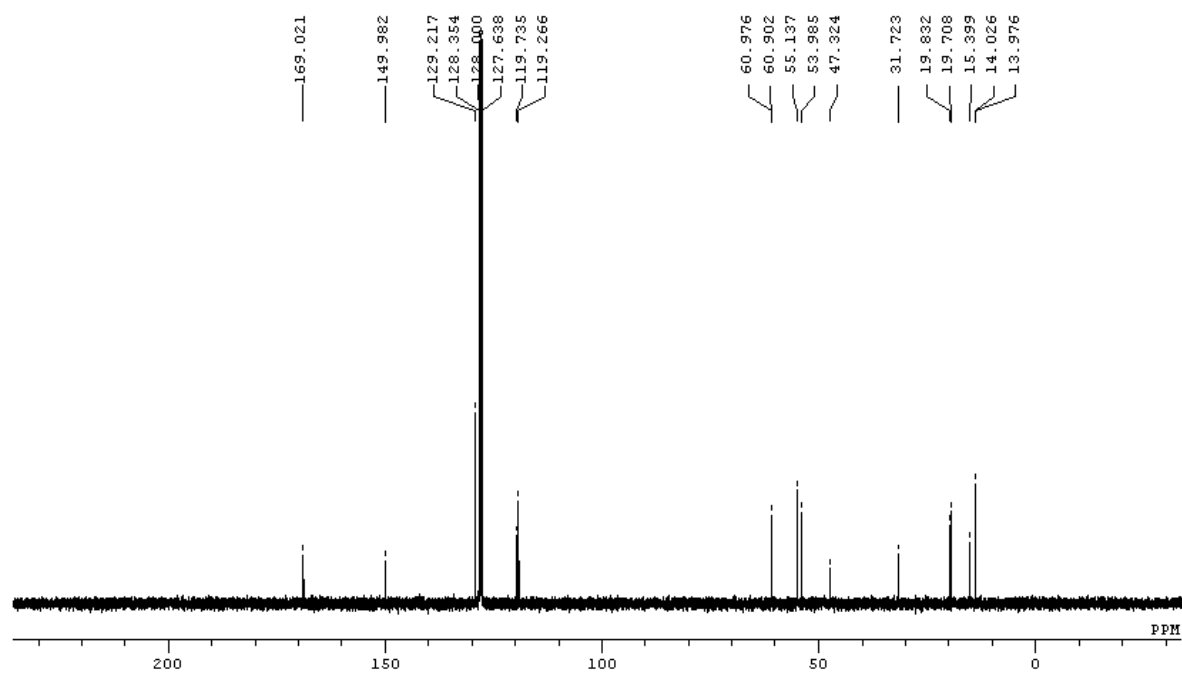


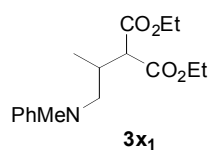


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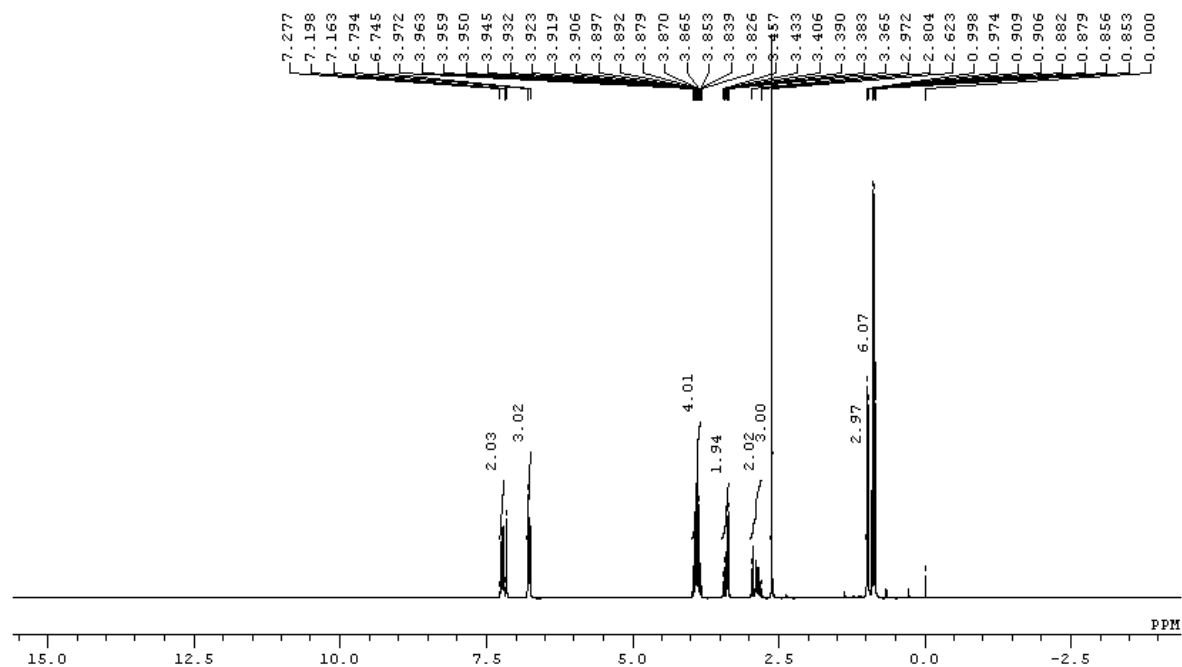


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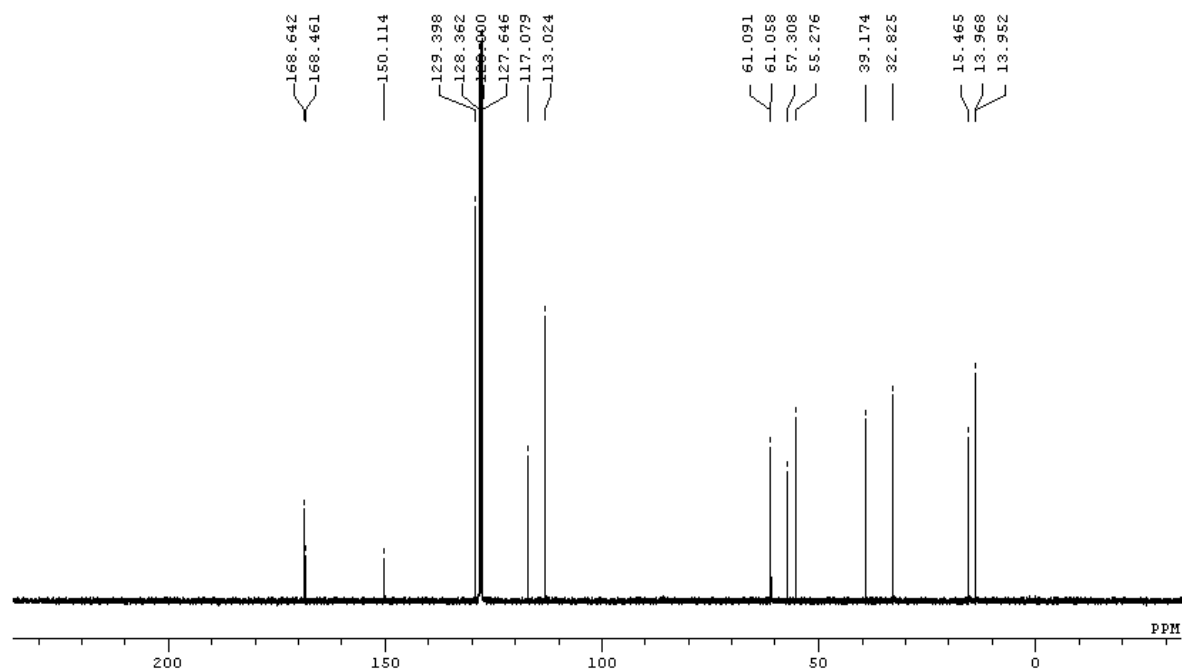


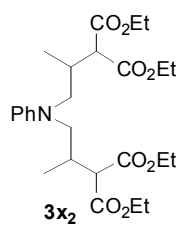


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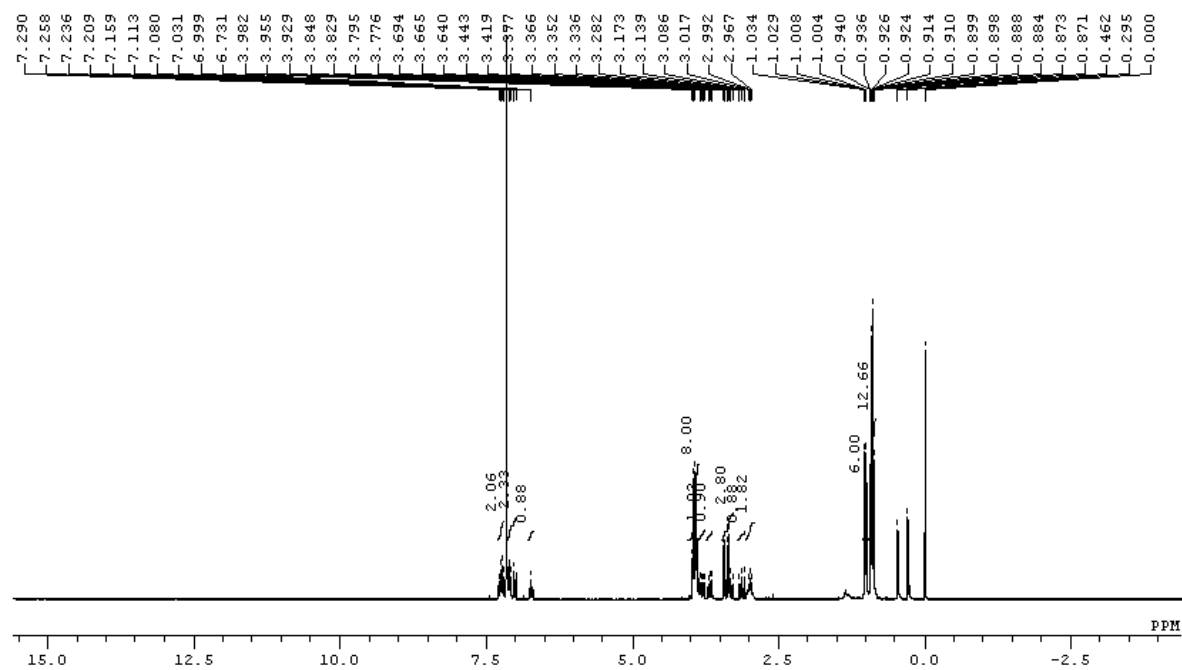


3x₁

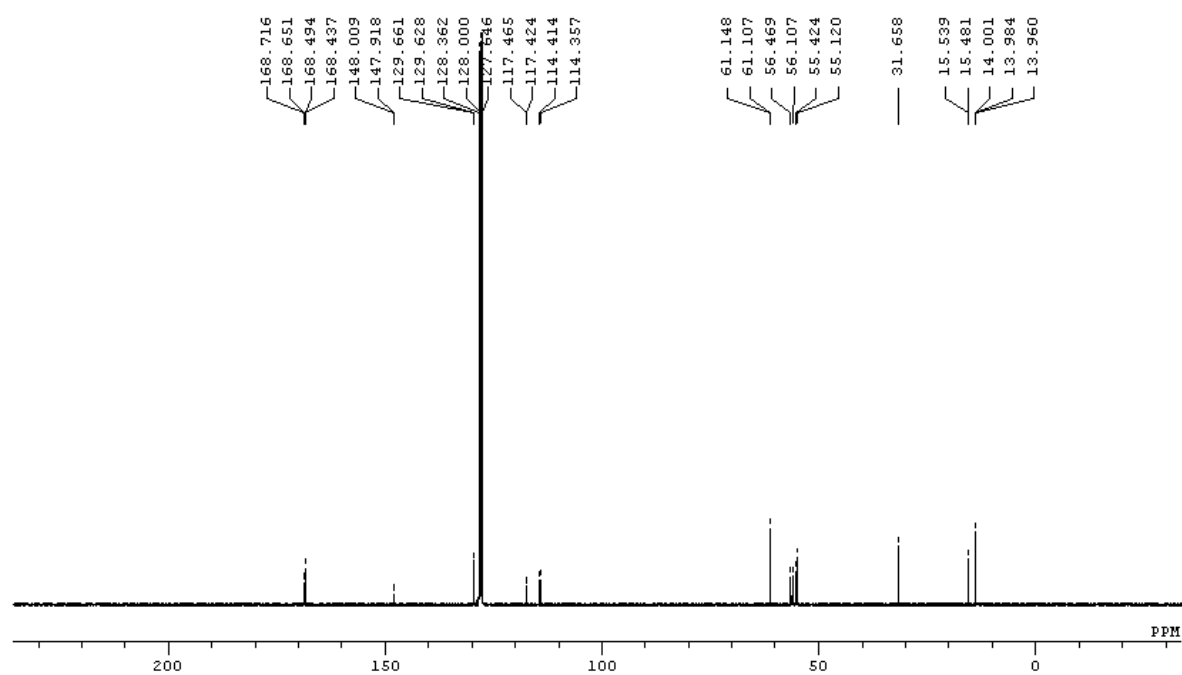




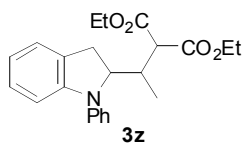
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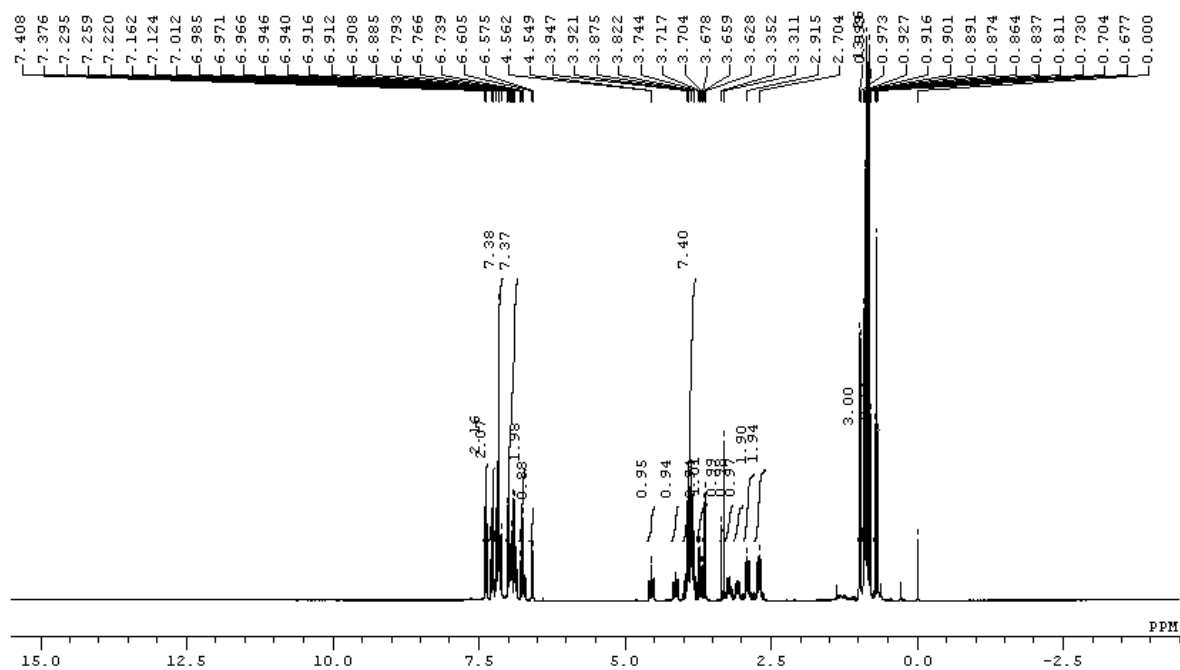
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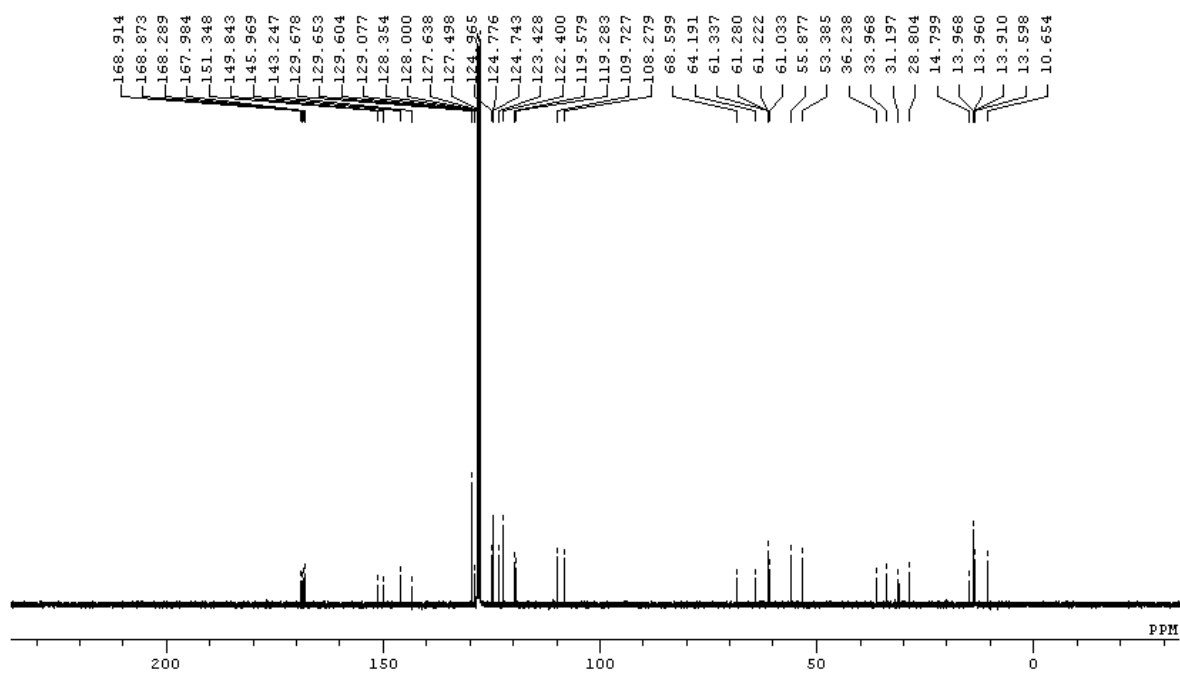


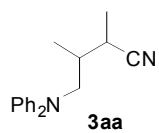


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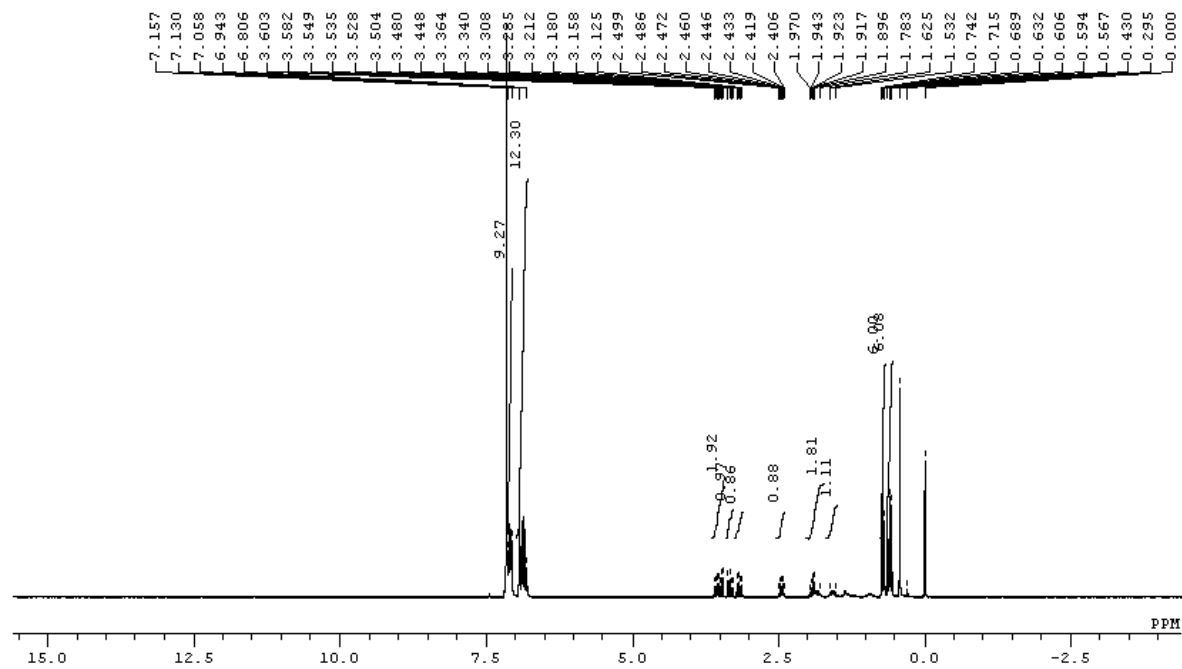


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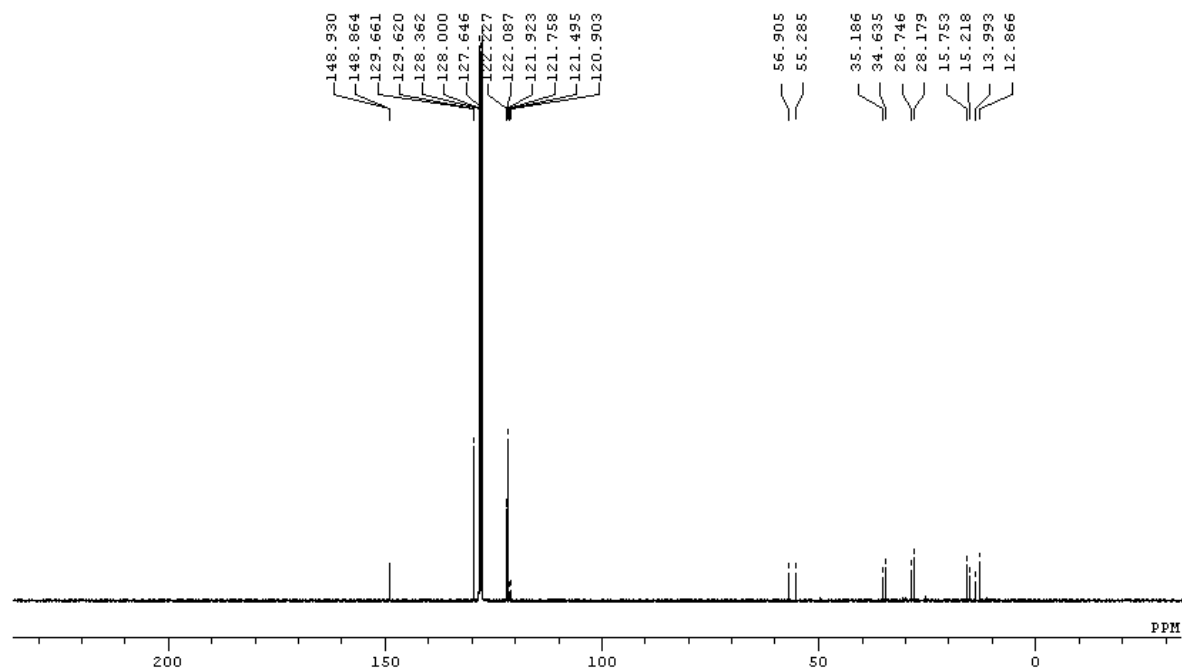


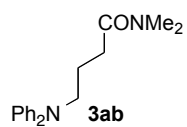


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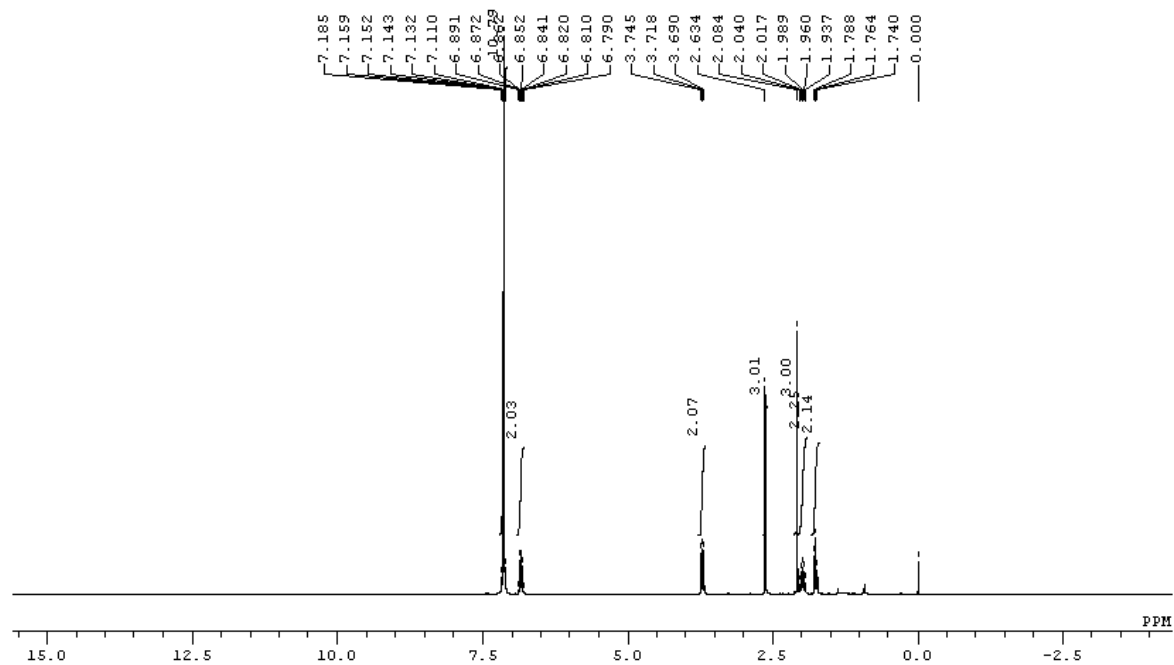


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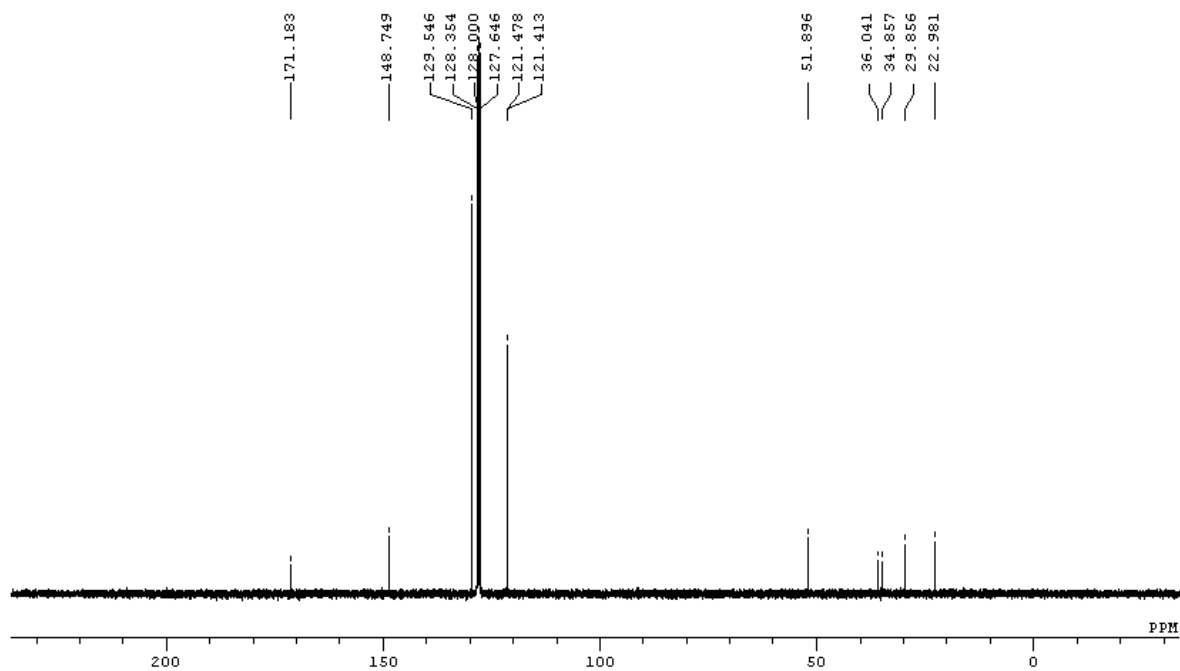


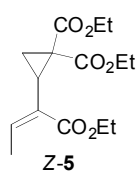


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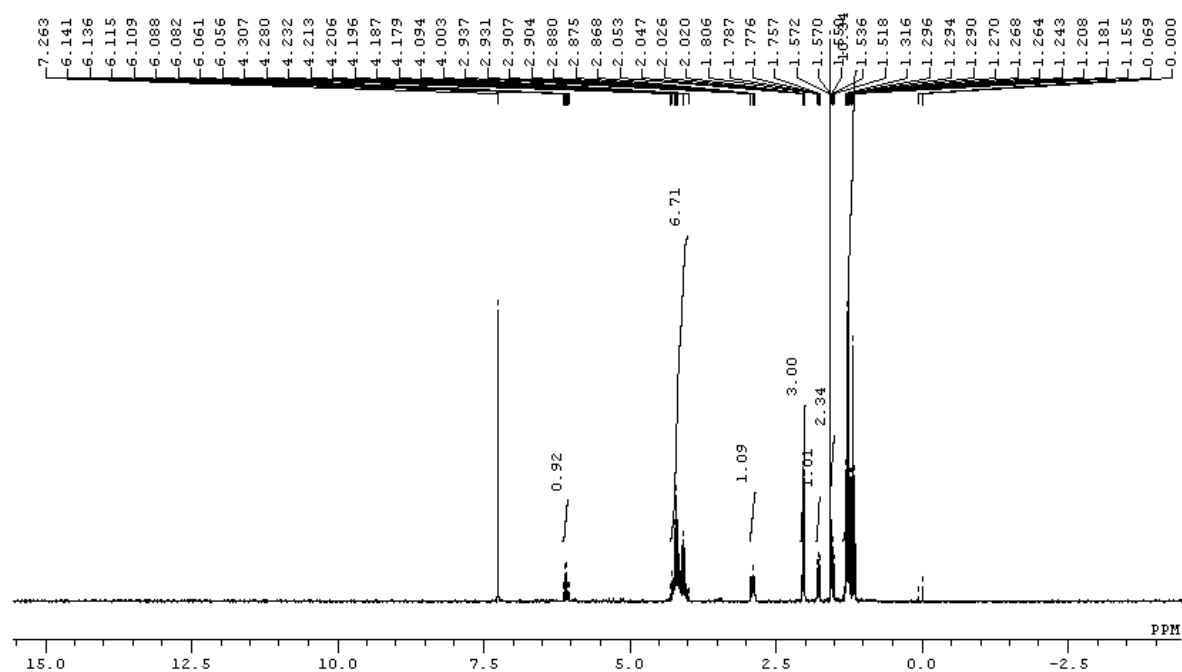


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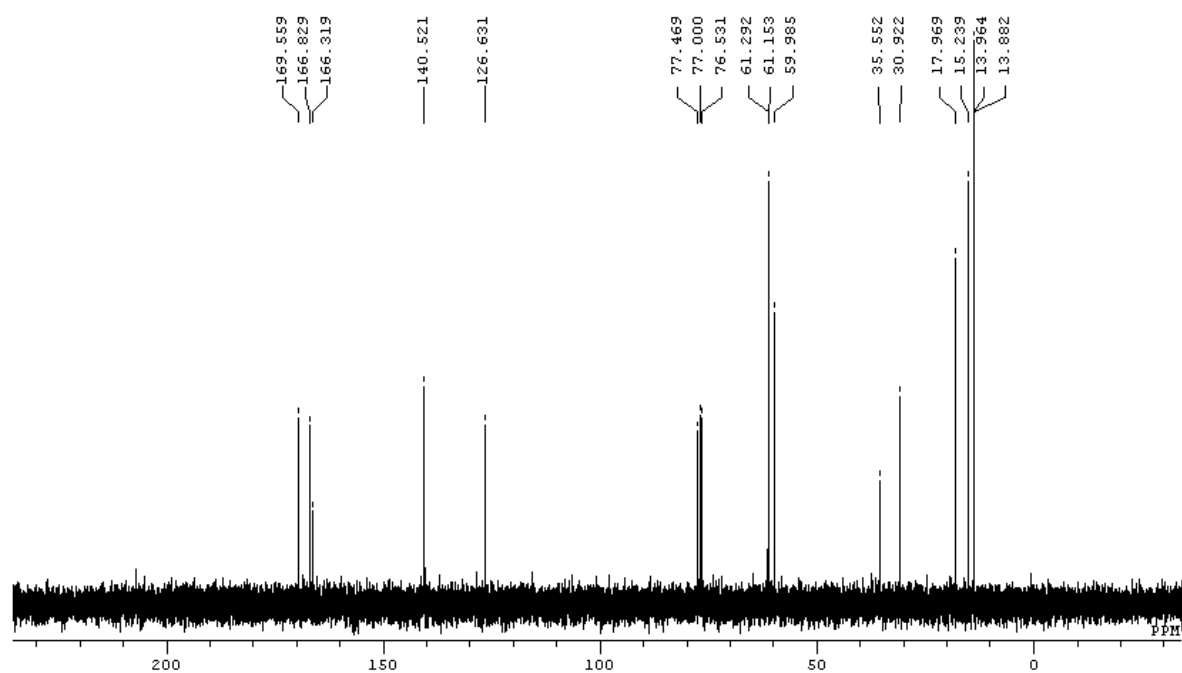


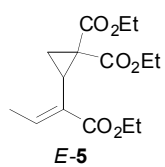


Z-5

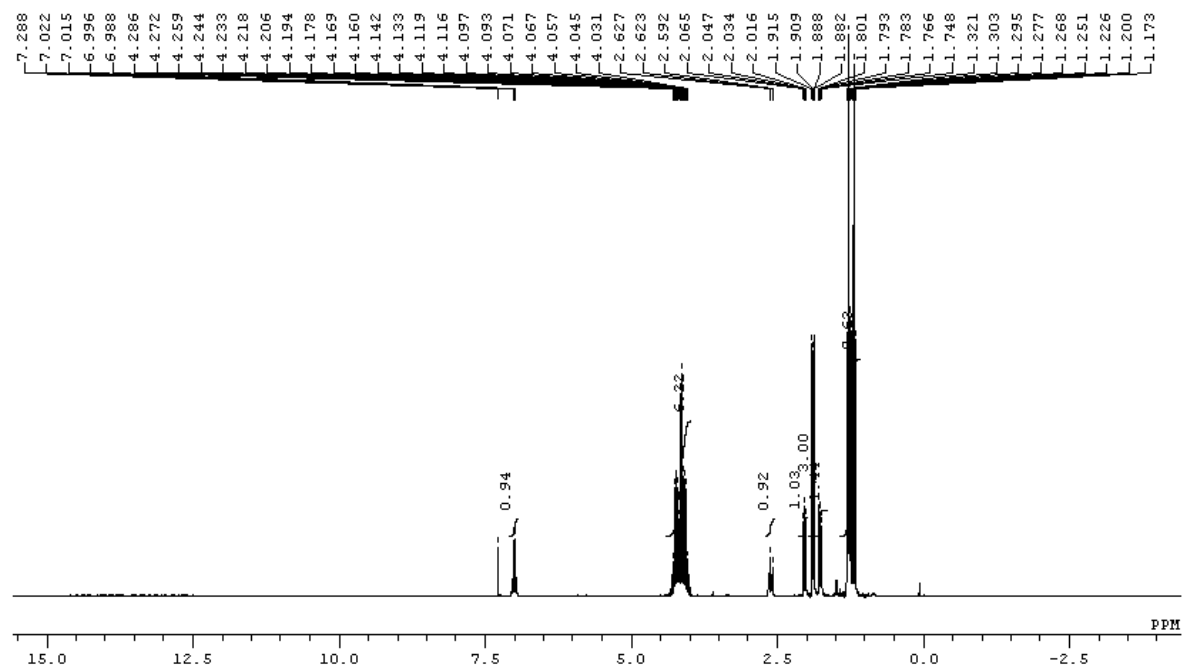


Z-5

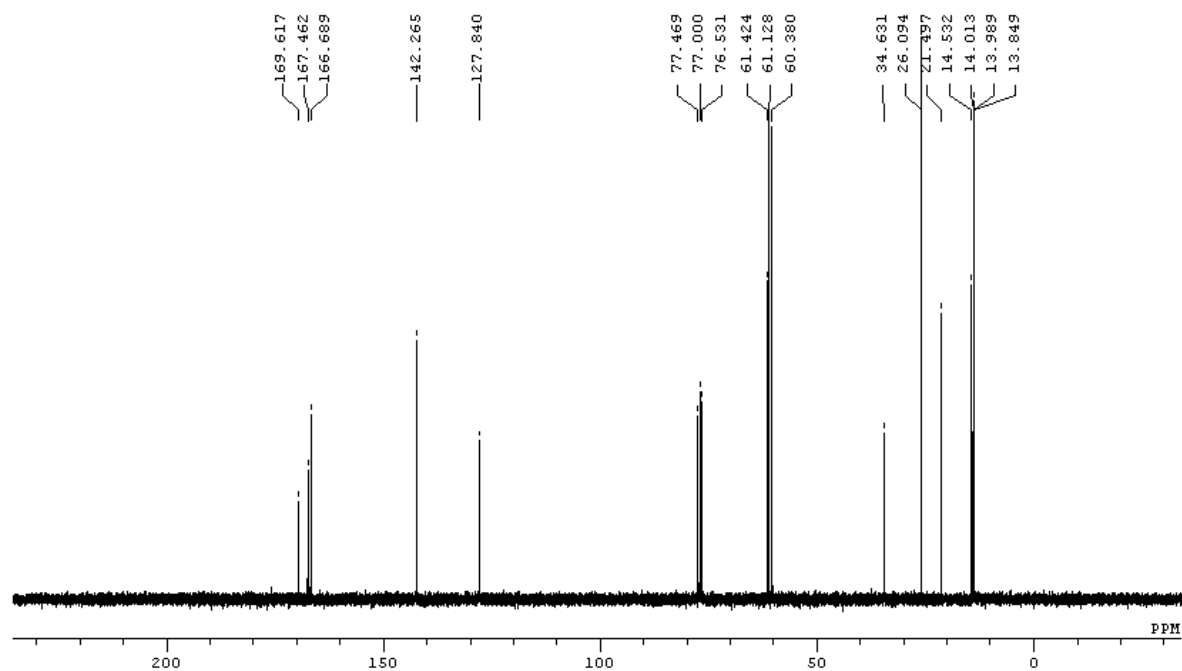


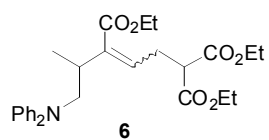


E-5

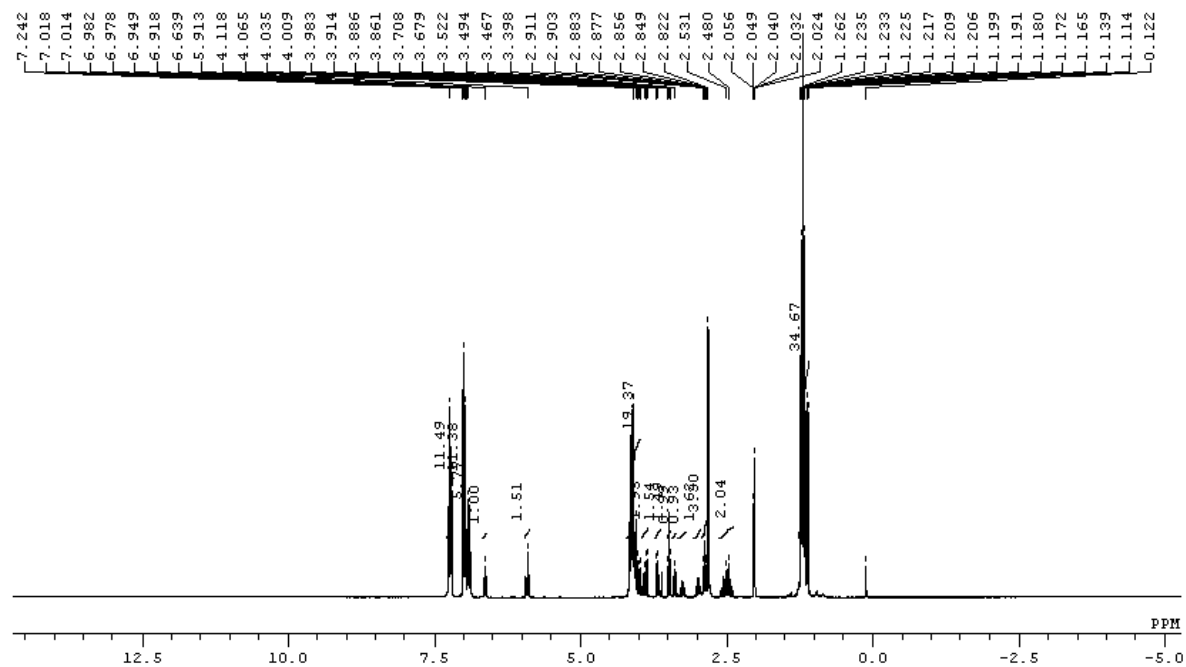


E-5





6



6

