Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information

Visible Light-Mediated Oxidative Decarboxylation of Arylacetic Acids into Benzyl Radicals: Addition to Electron-Deficient Alkenes by Using Photoredox Catalysts

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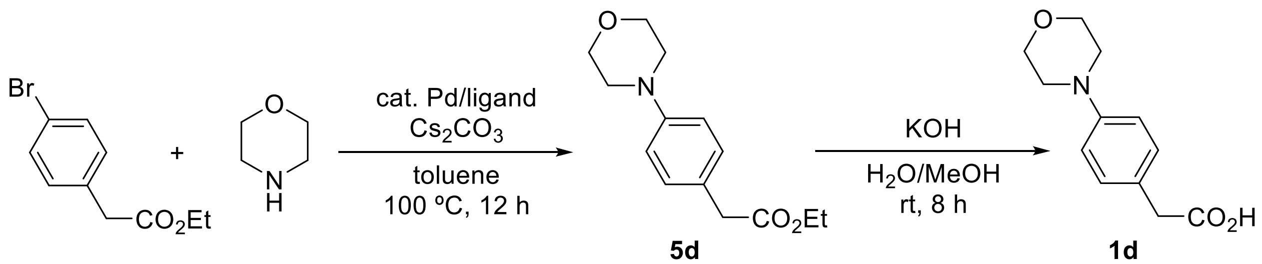
General Method. ^{1}H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvent. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. Absorption and emission spectra were recorded on Shimadzu MultiSpec-1500 and Shimadzu RF-5300PC spectrometers, respectively. 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 white LED (14 W). Arylacetic acids **1a**, **1g**, **1i**, and **5a** are commercially available. Alkenes (**2**) were prepared by Knövenagel condensastion.[S1] Synthesis of photocatalysts (**4a-c**) were reported previously.[S2c]

Preparation of Arylacetic Acids (1b-f, 1h). Arylacetic acids (**1b-f, 1h**) were prepared from the corresponding bromophenylacetates and amines (Scheme S1). A typical procedure for the preparation of **1d** is described below.

Scheme S1.

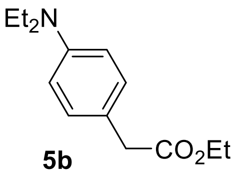


In a 50 mL Schlenk flask were placed $Pd(OAc)_2$ (45.6 mg, 0.203 mmol), 2-dicyclohexylphosphino-2',4',6'-tri-*iso*-propylbiphenyl (191.7 mg, 0.402 mmol), Cs_2CO_3 (2.458 g, 7.54 mmol) and toluene (25 mL) under N_2. Then, to the mixture were added ethyl

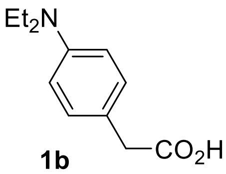
4-bromophenylacetate (1.245 g, 5.12 mmol) and morpholine (0.87 mL, 10 mmol). The reaction flask was stirred at 100 °C for 12 h. After celite filtration with hexane as eluent and concentration under reduced pressure, the residue was purified by column chromatography (SiO_2) with hexane/ethyl acetate (10/1 to 5/1) to give ethyl 4-(morpholine-4-yl)phenylacetate (**5d**) (1.18 g, 4.73 mmol).

In a 200 mL round bottom flask were placed **5d** (1.18 g, 4.73 mmol), methanol (19 mL), water (1.6 mL), and KOH (0.307 g, 4.65 mmol). The mixture was stirred at room temperature for 8 h, then, aqueous HCl (2N, 2.36 mL) and water (*ca.* 50 mL) were added. The mixture was extracted with dichloromethane (*ca.* 50 mL x 3), and the combined organic layer was dried over $MgSO_4$. After concentration under reduced pressure, the residue was purified by column chromatography (SiO_2) with hexane/ethyl acetate (2/1 to 0/1) to give 4-(morpholine-4-yl)phenylaceticacid (**1d**) (0.829 g, 3.75 mmol).

Isolated yields and spectroscopic data for **6** and **1** are as follows:



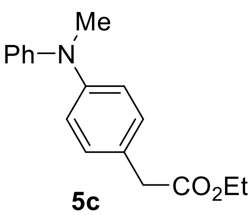
5b



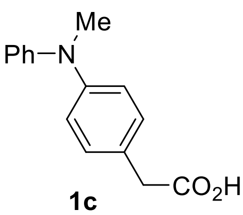
1b

5b: 37% Yield. A colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.14-7.09 (m, 2H), 6.66-6.60 (m, 2H), 4.13 (q, 2H, J = 7.1 Hz), 3.48 (s, 2H), 3.33 (q, 4H, J = 7.1 Hz), 1.24 (t, 3H, J = 7.1 Hz), 1.14 (t, 6H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 172.4, 146.8, 130.0, 120.6, 111.9, 60.6, 44.3, 40.4, 14.2, 12.5. HRMS (EI) Calcd. for $C_{14}H_{21}NO_2$ [M]: 235.1572. Found: 235.1562.

1b: 66% Yield. A colorless oil. ^{1}H NMR ($CDCl_3$): δ 10.55 (s, 1H), 7.14-7.09 (m, 2H), 6.68-6.63 (m, 2H), 3.51 (s, 2H), 3.31 (q, 4H, J = 7.0 Hz), 1.12 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ 178.5, 146.5, 130.2, 120.7, 112.5, 44.7, 40.2, 12.4. HRMS (EI) Calcd. for $C_{12}H_{17}NO_2$ [M]: 207.1259. Found: 207.1268.



5c

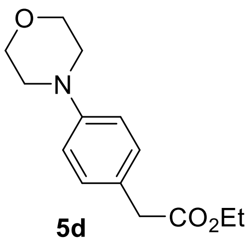


1c

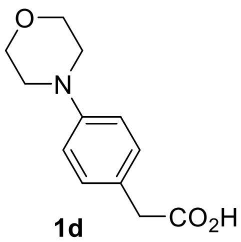
5c: 66% Yield. A colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.30-7.16 (m, 4H), 7.03-6.92 (m, 5H), 4.16

(q, 2H, J = 7.1 Hz), 4.12 (s, 2H), 3.30 (s, 3H), 1.26 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 171.9, 148.9, 147.9, 129.9, 129.1, 126.7, 121.2, 120.4, 60.7, 40.6, 40.2, 14.2. HRMS (EI) Calcd. for $C_{17}H_{19}NO_2$ [M]: 269.1416. Found: 269.1407.

1c: 57% Yield. A white solid (m.p. 98.2-99.5 °C). ^{1}H NMR ($CDCl_3$): δ 7.31-7.24 (m, 2H), 7.20-7.15 (m, 2H), 7.06-6.93 (m, 5H), 3.59 (s, 2H), 3.30 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 178.5, 148.8, 148.2, 130.1, 129.2, 125.4, 121.6, 121.0, 119.9, 40.3, 40.2. HRMS (EI) Calcd. for $C_{15}H_{15}NO_2$ [M]: 241.1103. Found: 241.1109.



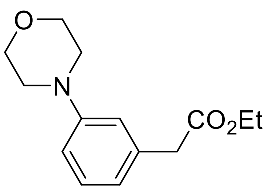
5d



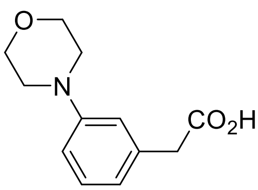
1d

5d: 92% Yield. A colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.22-7.16 (m, 2H), 6.90-6.84 (m, 2H), 4.13 (q, 2H, J = 7.1 Hz), 3.87-3.83 (m, 4H), 3.53 (s, 2H), 3.15-3.12 (m, 4H), 1.24 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 171.9, 150.2, 129.9, 125.5, 115.8, 66.8, 60.7, 49.3, 40.4, 14.1. HRMS (EI) Calcd. for $C_{14}H_{19}NO_3$ [M]: 249.1365. Found: 249.1372.

1d: 79% Yield. A white solid (m.p. 115.1-116.8 °C). ^{1}H NMR ($CDCl_3$): δ 7.21-7.17 (m, 2H), 6.90-6.85 (m, 2H), 3.87-3.84 (m, 4H), 3.57 (s, 2H), 3.16-3.12 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 177.6, 150.3, 130.1, 124.8, 115.9, 66.8, 49.3, 40.1. HRMS (EI) Calcd. for $C_{12}H_{15}NO_3$ [M]: 221.1052. Found: 221.1045.



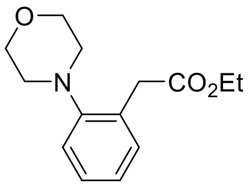
5d'



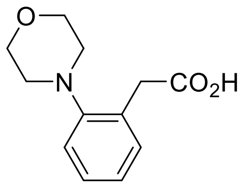
1d'

5d': 54% Yield. A colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.24-7.19 (m, 1H), 6.84-6.79 (m, 3H), 4.14 (q, 2H, J = 7.1 Hz), 3.87-3.83 (m, 4H), 3.57 (s, 2H), 3.17-3.14 (m, 4H), 1.25 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 171.6, 151.4, 135.0, 129.2, 120.8, 116.4, 114.3, 66.9, 60.8, 49.2, 41.7, 14.1. HRMS (EI) Calcd. for $C_{14}H_{19}NO_3$ [M]: 249.1365. Found: 249.1372.

1d': 32% Yield. A colorless oil. ^{1}H NMR ($CDCl_3$): δ 10.40 (br, 1H), 7.25-7.20 (m, 1H), 6.84-6.79 (m, 3H), 3.87-3.83 (m, 4H), 3.59 (s, 2H), 3.17-3.13 (m, 4H). ^{13}C NMR (CDCl$_3$): δ 177.2, 151.4, 134.3, 129.4, 121.1, 116.8, 114.6, 66.8, 49.2, 41.3. HRMS (EI) Calcd. for $C_{12}H_{15}NO_3$ [M]: 221.1052. Found: 221.1042.



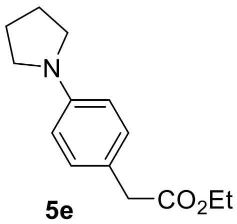
5d''



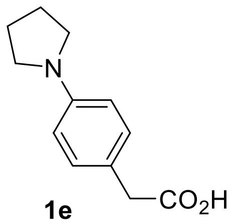
1d''

5d'': 28% Yield. A colorless oil. ^{1}H NMR (CDCl$_3$): δ 7.32-7.25 (m, 2H), 7.19-7.08 (m, 2H), 4.17 (q, 2H, J = 7.2 Hz), 3.83-3.79 (m, 4H), 3.72 (s, 2H), 2.89-2.85 (m, 4H), 1.26 (t, 3H, J = 7.2 Hz). ^{13}C NMR (CDCl$_3$): δ 172.3, 151.5, 131.1, 131.0, 128.3, 124.7, 121.1, 67.4, 60.6, 52.9, 37.3, 14.2. HRMS (EI) Calcd. for $C_{14}H_{19}NO_3$ [M]: 249.1365. Found: 249.1353.

1d'': 55% Yield. A white solid (m.p. 120.1-121.9 °C). ^{1}H NMR (CDCl$_3$): δ 7.37-7.14 (m, 4H), 3.89-3.86 (m, 4H), 3.75 (s, 2H), 3.00-2.97 (m, 4H). ^{13}C NMR (CDCl$_3$): δ 175.0, 149.5, 131.6, 130.1, 129.0, 126.1, 121.3, 66.8, 52.8, 39.4. HRMS (EI) Calcd. for $C_{12}H_{15}NO_3$ [M]: 221.1052. Found: 221.1043.



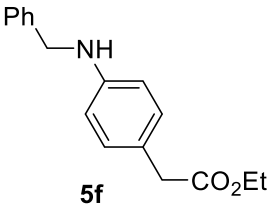
5e



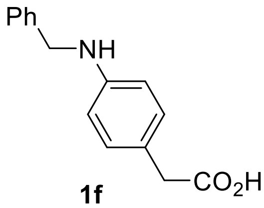
1e

5e: 76% Yield. A colorless oil. ^{1}H NMR (CDCl$_3$): δ 7.16-7.10 (m, 2H), 6.54-6.49 (m, 2H), 4.12 (q, 2H, J = 7.1 Hz), 3.49 (s, 2H), 3.28-3.24 (m, 4H), 2.03-1.93 (m, 4H), 1.23 (t, 3H, J = 7.1 Hz). ^{13}C NMR (CDCl$_3$): δ 172.4, 147.0, 129.9, 120.7, 111.7, 60.5, 47.6, 40.5, 25.4, 14.2. HRMS (EI) Calcd. for $C_{14}H_{19}NO_2$ [M]: 233.1416. Found: 233.1404.

1e: 64% Yield. A white solid (decomposition at 135.3 °C). ^{1}H NMR (CDCl$_3$): δ 7.14-7.08 (m, 2H), 6.54-6.49 (m, 2H), 3.52 (s, 2H), 3.27-3.23 (m, 4H), 2.02-1.93 (m, 4H). ^{13}C NMR (CDCl$_3$): δ 178.8, 147.2, 130.0, 119.7, 111.8, 47.6, 40.1, 25.4. HRMS (EI) Calcd. for $C_{12}H_{15}NO_2$ [M]: 205.1103. Found: 205.1095.



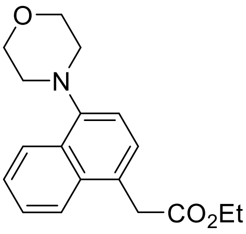
5f



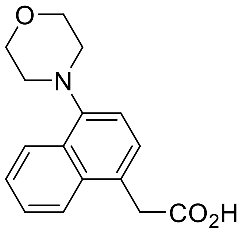
1f

5f: 79% Yield. A white solid (m.p. 66.2-66.8 °C). ^{1}H NMR ($CDCl_3$): δ 7.38-7.23 (m, 5H), 7.10-7.05 (m, 2H), 6.60-6.55 (m, 2H), 4.29 (s, 2H), 4.11 (q, 2H, J = 7.1 Hz), 4.04 (br, 1H), 3.47 (s, 2H), 1.23 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 172.2, 147.1, 139.4, 130.0, 128.6, 127.4, 127.2, 122.9, 112.9, 60.6, 48.3, 40.5, 14.2. HRMS (EI) Calcd. for $C_{17}H_{19}NO_2$ [M]: 269.1416. Found: 269.1421.

1f: 52% Yield. A white solid (m.p. 118.1-119.6 °C). ^{1}H NMR ($CDCl_3$): δ 7.34-7.24 (m, 5H), 7.10-7.05 (m, 2H), 6.63-6.57 (m, 2H), 4.31 (s, 2H), 3.52 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 178.0, 147.3, 139.3, 130.1, 128.6, 127.5, 127.3, 122.1, 113.0, 48.4, 40.1. HRMS (EI) Calcd. for $C_{15}H_{15}NO_2$ [M]: 241.1103. Found: 241.1106.



5h



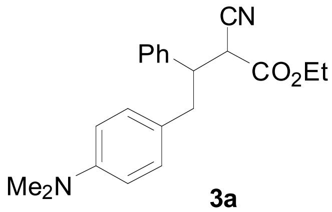
1h

5h: 52% Yield. An orange oil. ^{1}H NMR ($CDCl_3$): δ 8.30-8.22 (m, 1H), 7.99-7.93 (m, 1H), 7.55-7.45 (m, 2H), 7.32 (d, 1H, J = 7.6 Hz), 7.03 (d, 1H, J = 7.6 Hz), 4.14 (q, 2H, J = 7.1 Hz), 3.98 (s, 2H), 3.97-3.94 (m, 4H), 3.09-3.06 (m, 4H), 1.22 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 171.7, 149.2, 133.2, 129.1, 127.9, 126.20, 126.19, 125.2, 124.4, 124.0, 114.3, 67.4, 60.8, 53.5, 38.9, 14.1. HRMS (EI) Calcd. for $C_{18}H_{21}NO_3$ [M]: 299.1521. Found: 299.1529.

1h: 72% Yield. A white solid (decomposition at 164.0 °C). ^{1}H NMR ($CDCl_3$): δ 8.29-8.24 (m, 1H), 7.96-7.90 (m, 1H), 7.55-7.46 (m, 2H), 7.33 (d, 1H, J = 7.6 Hz), 7.04 (d, 1H, J = 7.6 Hz), 4.01 (s, 2H), 3.99-3.96 (m, 4H), 3.10-3.07 (m, 4H) ^{13}C NMR ($CDCl_3$): δ 177.6, 149.4, 133.1, 129.1, 128.2, 126.5, 125.40, 125.37, 124.3, 124.1, 114.4, 67.3, 53.4, 38.5. HRMS (EI) Calcd. for $C_{16}H_{17}NO_3$ [M]: 271.1208. Found: 271.1195.

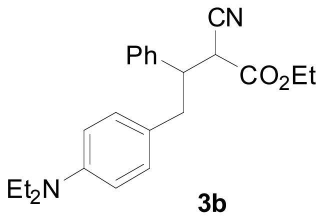
Photocatalytic Reactions of Arylacetic Acids (1) with Alkenes (2). A typical experimental procedure for the reaction of 4-dimethylaminophenylacetic acid (**1a**) with (*E*)-ethyl 2-cyano-3-phenylpropenoate (**2a**) is described below. In a 20 mL Schlenk flask (diameter: 2.5 cm) were placed [Ir(ppy)$_2$(bpy)][BF$_4$] (1.9 mg, 0.0026 mmol), **2a** (55.1 mg, 0.274 mmol), and acetonitrile (2.5 mL) under N_2, and then **1a** (44.8 mg, 0.250 mmol) was added. The reaction flask was placed in a water bath (25 °C) and illuminated with white LED (14 W, approximately 2 cm from the light source) for 18 h. After concentration *in vacuo*, the resulting mixture was purified by column chromatography (SiO_2) with hexane/ethyl acetate (10/1 to 2/1) to give ethyl 2-cyano-4-(4-dimethylaminophenyl)-3-phenylbutanoate (**3a**) (71.2 mg, 0.212 mmol).

Isolated yields and spectroscopic data of products (**3**) are as follows:



3a

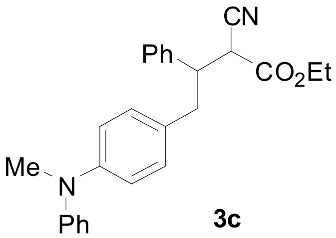
3a: 85% Yield (isomeric ratio 2:1). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 7.46-7.41 (m, 2H), 7.14-6.97 (m, 5H), 6.56-6.50 (m, 2H), 3.66-3.50 (m, 4H), 3.11 (dd, 1H, J = 14.0 and 10.0 Hz), 3.02-2.93 (m, 1H), 2.51 (s, 6H), 0.60 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.7, 149.9, 139.5, 129.9, 128.8, 128.7, 126.0, 115.7, 113.3, 62.1, 48.1, 42.9, 40.22, 39.2, 13.6. Minor-isomer: ^{1}H NMR (C_6D_6): δ 6.95-6.90 (m, 2H), 6.45-6.40 (m, 2H), 3.34 (d, 1H, J = 6.2 Hz), 3.28 (dd, 1H, J = 13.8 and 5.7 Hz), 0.68 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.3, 149.6, 139.9, 130.3, 128.7, 128.5, 125.8, 116.4, 112.9, 62.2, 48.5, 43.8, 40.18, 38.4. HRMS (EI) Calcd. for $C_{21}H_{24}N_2O_2$ [M]: 336.1838. Found: 336.1833.



3b

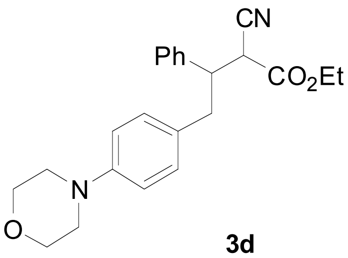
3b: 84% Yield (isomeric ratio 2:1). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 7.47-7.42 (m, 2H), 7.14-6.98 (m, 5H), 6.54-6.49 (m, 2H), 3.67-3.53 (m, 4H), 3.12 (dd, 1H, J = 14.2 and 10.1 Hz), 3.02-2.88 (m, 5H), 0.90 (t, 6H, J = 7.2 Hz), 0.61 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.7, 147.2, 139.7, 130.2, 128.84, 128.77, 128.67, 124.9, 115.7, 112.6, 62.0, 48.1, 44.4, 42.8, 39.2, 13.57, 12.7. Minor-isomer: ^{1}H NMR (C_6D_6): δ 6.96-6.90 (m, 2H), 6.43-6.38 (m, 2H), 3.36 (d, 1H, J = 6.2

Hz), 3.28 (dd, 1H, J = 13.8 and 5.9 Hz), 0.84 (t, 6H, J = 7.2 Hz), 0.70 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.3, 146.8, 140.1, 130.6, 129.3, 128.68, 128.5, 124.8, 116.4, 112.3, 62.2, 48.5, 44.3, 43.8, 38.4, 13.61, 12.6. HRMS (EI) Calcd. for $C_{23}H_{28}N_2O_2$ [M]: 364.2151. Found: 364.2135.



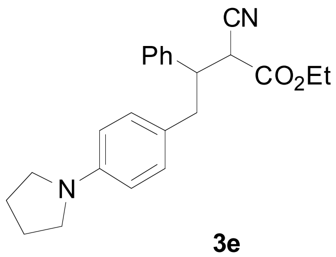
3c

3c: 89% Yield (isomeric ratio 2:1). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 7.41-7.36 (m, 2H), 7.15-6.79 (m, 12H), 3.73-3.47 (m, 3H), 3.48 (d, 1H, J = 5.4 Hz), 3.06 (dd, 1H, J = 14.0 and 9.7 Hz), 2.97-2.87 (m, 1H), 2.91 (s, 3H), 0.61 (t, 3H, J = 7.3 Hz). ^{13}C NMR (C_6D_6): δ 165.5, 149.3, 148.3, 139.2, 130.5, 130.0, 129.5, 128.8, 128.6, 128.1, 122.1, 121.5, 120.3, 115.6, 62.1, 47.8, 43.0, 39.9, 39.3, 13.6. Minor-isomer: ^{1}H NMR (C_6D_6): δ 6.76-6.71 (m, 2H), 3.30 (d, 1H, J = 6.5 Hz), 3.24 (dd, 1H, J = 13.8 and 5.7 Hz), 2.84 (s, 3H), 0.70 (t, 3H, J = 7.0 Hz). ^{13}C NMR (C_6D_6): δ 165.2, 149.4, 147.9, 139.6, 130.9, 130.4, 129.4, 128.7, 127.8, 121.5, 120.7, 120.6, 116.2, 62.3, 48.1, 44.0, 40.0, 38.5, 13.6. HRMS (EI) Calcd. for $C_{26}H_{26}N_2O_2$ [M]: 398.1994. Found: 398.1979.



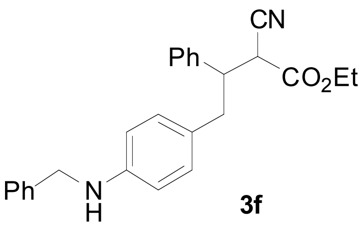
3d

3d: 96% Yield (isomeric ratio 2:1). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 7.44-7.41 (m, 2H), 7.14-6.97 (m, 5H), 6.63-6.57 (m, 2H), 3.67-3.47 (m, 8H), 3.10 (dd, 1H, J = 14.0 and 9.7 Hz), 3.01-2.92 (m, 1H), 2.74-2.71 (m, 4H), 0.61 (t, 3H, J = 7.6 Hz). ^{13}C NMR (C_6D_6): δ 165.5, 150.7, 139.3, 129.9, 129.2, 128.8, 128.6, 128.1, 116.2, 115.8, 66.83, 62.1, 49.33, 47.9, 42.9, 39.2, 13.60. Minor-isomer: ^{1}H NMR (C_6D_6): δ 6.92-6.89 (m, 2H), 6.52-6.47 (m, 2H), 3.33-3.25 (m, 2H), 2.66-2.62 (m, 4H), 0.69 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.2, 150.3, 139.7, 130.2, 129.1, 128.7, 128.4, 127.8, 116.3, 115.6, 66.81, 62.3, 49.31, 48.3, 43.9, 38.4, 13.57. HRMS (EI) Calcd. for $C_{23}H_{26}N_2O_3$ [M]: 378.1943. Found: 378.1939.



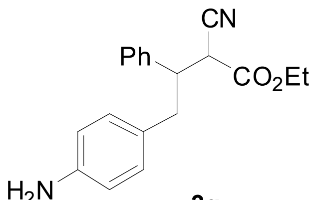
3e

3e: 74% Yield (isomeric ratio 2:1). A colorless oil. Major isomer: ^1H NMR (C_6D_6): δ 7.47-7.42 (m, 2H), 7.14-6.94 (m, 5H), 6.45-6.40 (m, 2H), 3.74-3.54 (m, 4H), 3.14 (dd, 1H, J = 13.9 and 9.6 Hz), 3.05-2.95 (m, 1H), 2.94-2.89 (m, 4H), 1.53-1.49 (m, 4H), 0.61 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.7, 147.3, 139.6, 130.0, 128.83, 128.68, 128.5, 124.8, 115.7, 112.4, 62.1, 48.3, 47.5, 42.9, 39.4, 25.44, 13.58. Minor-isomer: ^1H NMR (C_6D_6): δ 6.34-6.29 (m, 2H), 3.38 (d, 1H, J = 6.8 Hz), 3.32 (dd, 1H, J = 13.8 and 5.7 Hz), 2.86-2.81 (m, 4H), 1.47-1.44 (m, 4H), 0.69 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.3, 147.0, 139.9, 130.3, 129.3, 128.76, 128.65, 124.6, 116.4, 111.9, 62.2, 48.7, 47.4, 43.8, 38.6, 25.38, 13.59. HRMS (EI) Calcd. for $C_{23}H_{26}N_2O_2$ [M]: 362.1994. Found: 362.1985.



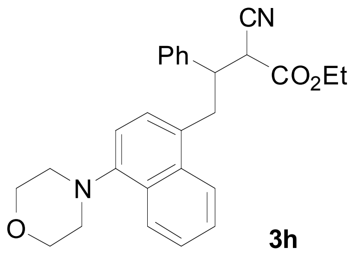
3f

3f: 81% Yield (isomeric ratio 2:1). A colorless oil. Major isomer: ^1H NMR (C_6D_6): δ 7.42-7.38 (m, 2H), 7.14-6.93 (m, 10H), 6.37-6.32 (m, 2H), 3.92 (s, 2H), 3.66-3.52 (m, 3H), 3.48 (d, 1H, J = 5.1 Hz), 3.44 (br, 1H), 3.05 (dd, 1H, J = 14.0 and 10.0 Hz), 2.95-2.89 (m, 1H), 0.60 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.6, 147.5, 139.93, 139.5, 130.0, 128.8, 128.7, 127.63, 127.3, 126.8, 115.7, 113.4, 62.1, 48.29, 48.0, 42.8, 39.3, 13.6. Minor-isomer: ^1H NMR (C_6D_6): δ 6.83-6.78 (m, 2H), 6.26-6.21 (m, 2H), 3.84 (s, 2H), 3.31 (d, 1H, J = 5.1 Hz), 3.23 (dd, 1H, J = 13.6 and 5.8 Hz), 0.68 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.2, 147.2, 140.0, 139.85, 130.4, 128.6, 128.4, 127.59, 127.2, 126.7, 116.4, 113.0, 62.2, 48.4, 48.25, 43.8, 38.5. HRMS (EI) Calcd. for $C_{26}H_{26}N_2O_2$ [M]: 398.1994. Found: 398.1996.



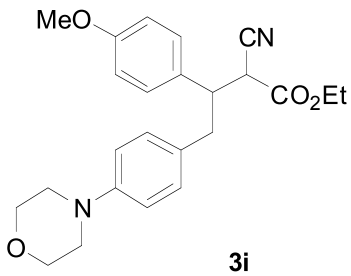
3g

3g: 87% Yield (isomeric ratio 2:1). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 7.42-7.37 (m, 2H), 7.12-6.96 (m, 3H), 6.94-6.89 (m, 2H), 6.31-6.26 (m, 2H), 3.66-3.52 (m, 3H), 3.47 (d, 1H, *J* = 5.1 Hz), 3.03 (dd, 1H, *J* = 13.9 and 9.9 Hz), 2.93-2.84 (brm, 3H), 0.61 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.6, 146.1, 139.5, 130.0, 128.8, 128.6, 127.4, 115.7, 115.3, 62.1, 48.0, 42.8, 39.3, 13.6. Minor-isomer: ^{1}H NMR (C_6D_6): δ 6.79-6.73 (m, 2H), 6.20-6.16 (m, 2H), 3.31 (d, 1H, *J* = 6.2 Hz), 3.21 (dd, 1H, *J* = 13.8 and 5.7 Hz), 0.69 (t, 3H, *J* = 7.0 Hz) ^{13}C NMR (C_6D_6): δ 165.2, 145.7, 139.8, 130.4, 128.7, 128.4, 127.3, 116.4, 114.9, 62.3, 48.4, 43.8, 38.5. HRMS (EI) Calcd. for $C_{19}H_{20}N_2O_2$ [M]: 308.1525. Found: 308.1513.



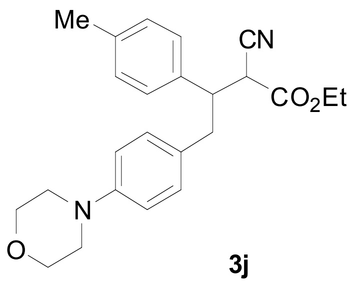
3h

3h: 61% Yield (isomeric ratio 3:2). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 8.39-8.31 (m, 1H), 8.04-8.00 (m, 1H), 7.45-7.32 (m, 3H), 7.29 (d, 1H, *J* = 7.6 Hz), 7.14-6.98 (m, 4H), 6.71 (d, 1H, *J* = 7.6 Hz), 3.96-3.82 (m, 1H), 3.70-3.64 (m, 3H), 3.60-3.38 (m, 5H), 3.32 (dd, 1H, *J* = 9.9 and 5.0 Hz), 2.77-2.73 (m, 4H), 0.57 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR (C_6D_6): δ 165.3, 149.7, 139.5, 133.4, 130.0, 129.6, 128.9, 128.5, 128.3, 128.1, 126.7, 125.5, 125.0, 124.3, 115.9, 114.7, 67.28, 62.2, 53.8, 46.47, 43.3, 37.3, 13.50. Minor-isomer: ^{1}H NMR (C_6D_6): δ 8.22-8.19 (m, 1H), 6.57 (d, 1H, *J* = 7.8 Hz), 2.70-2.60 (m, 4H), 0.63 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.1, 149.3, 140.0, 133.6, 129.7, 129.5, 128.8, 128.6, 128.2, 127.8, 126.5, 125.3, 124.8, 124.4, 116.3, 114.5, 67.27, 62.3, 53.7, 46.45, 44.4, 36.3, 13.51. HRMS (EI) Calcd. for $C_{27}H_{28}N_2O_3$ [M]: 428.2100. Found: 428.2098.



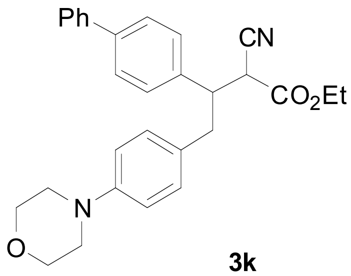
3i

3i: 74% Yield (isomeric ratio 2:1). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 7.39-7.34 (m, 2H), 7.11-7.06 (m, 2H), 6.76-6.59 (m, 4H), 3.72-3.49 (m, 8H), 3.26 (s, 3H), 3.16-2.95 (m, 2H), 2.75-2.72 (m, 4H), 0.67 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.7, 159.8, 150.7, 131.1, 129.9, 129.7, 129.46, 116.2, 114.3, 66.83, 62.1, 54.7, 49.34, 47.2, 43.3, 39.4, 13.6. Minor-isomer: ^{1}H NMR (C_6D_6): δ 7.04-6.98 (m, 2H), 6.97-6.92 (m, 2H), 6.55-6.50 (m, 2H), 3.35 (dd, 1H, J = 13.2 and 5.9 Hz), 3.28-3.24 (m, 4H), 2.68-2.64 (m, 4H), 0.74 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.3, 159.5, 150.3, 131.4, 130.3, 129.5, 129.41, 115.8, 114.2, 66.81, 62.3, 54.6, 49.32, 47.7, 44.3, 38.5. HRMS (EI) Calcd. for $C_{24}H_{28}N_2O_4$ [M]: 408.2049. Found: 408.2061.



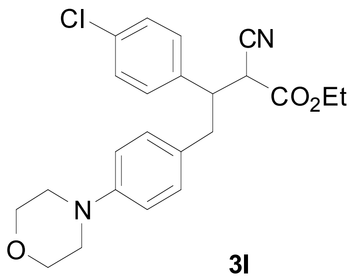
3j

3j: 93% Yield (isomeric ratio 2:1). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 7.37-7.34 (m, 2H), 7.10-7.04 (m, 2H), 6.96-6.92 (m, 2H), 6.63-6.58 (m, 2H), 3.70-3.59 (m, 3H), 3.56-3.48 (m, 5H), 3.12 (dd, 1H, J = 13.9 and 9.6 Hz), 3.05-2.96 (m, 1H), 2.74-2.71 (m, 4H), 2.05 (s, 3H), 0.65 (t, 3H, J = 7.3 Hz). ^{13}C NMR (C_6D_6): δ 165.6, 150.7, 137.7, 137.3, 129.9, 129.6, 129.5, 128.6, 116.2, 115.8, 66.83, 62.1, 49.35, 47.6, 43.2, 39.3, 21.0, 13.61. Minor-isomer: ^{1}H NMR (C_6D_6): δ 7.02-6.99 (m, 2H), 6.89-6.86 (m, 2H), 6.53-6.48 (m, 2H), 3.37 (d, 1H, J = 6.2 Hz), 3.30 (dd, 1H, J = 13.8 and 5.4 Hz), 2.66-2.63 (m, 4H), 2.02 (s, 3H), 0.72 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.3, 150.3, 136.6, 136.3, 130.3, 129.4, 129.3, 116.3, 115.7, 66.81, 62.3, 49.33, 47.9, 44.2, 38.3, 20.9, 13.62. HRMS (EI) Calcd. for $C_{24}H_{28}N_2O_3$ [M]: 392.2100. Found: 392.2102.



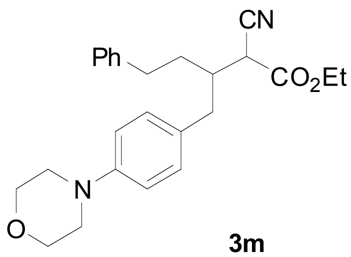
3k

3k: 66% Yield (isomeric ratio 2:1). A white solid. Major isomer: ^{1}H NMR (C_6D_6): δ 7.54-7.49 (m, 2H), 7.45-7.34 (m, 4H), 7.24-7.10 (m, 5H), 6.66-6.61 (m, 2H), 3.75-3.59 (m, 4H), 3.57-3.54 (m, 4H), 3.20-3.01 (m, 2H), 2.76-2.72 (m, 4H), 0.64 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.6, 150.7, 141.1, 140.83, 138.3, 129.9, 129.1, 129.0, 128.5, 127.6, 127.5, 127.3, 116.2, 115.8, 66.82, 62.2, 49.31, 47.6, 43.0, 39.2, 13.64. Minor-isomer: ^{1}H NMR (C_6D_6): δ 7.01-6.96 (m, 2H), 6.55-6.50 (m, 2H), 3.52-3.48 (m, 4H), 3.40 (d, 1H, J = 5.9 Hz), 3.33 (dd, 1H, J = 13.9 and 5.5 Hz), 2.68-2.64 (m, 4H), 0.64 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.3, 150.4, 140.81, 140.76, 138.7, 130.3, 129.2, 128.9, 127.6, 127.5, 127.2, 116.3, 115.7, 66.81, 62.4, 49.30, 47.9, 44.0, 38.3, 13.61. HRMS (EI) Calcd. for $C_{29}H_{30}N_2O_3$ [M]: 454.2256. Found: 454.2264.



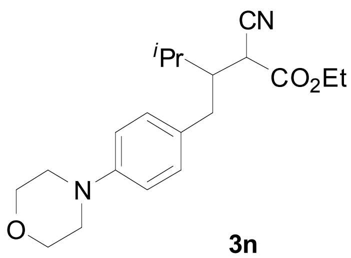
3l

3l: 52% Yield (isomeric ratio 2:1). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 7.16-7.14 (m, 2H), 7.08-6.96 (m, 4H), 6.62-6.57 (m, 2H), 3.67-3.46 (m, 7H), 3.40 (d, 1H, J = 5.1 Hz), 2.96 (dd, 1H, J = 14.0 and 9.7 Hz), 2.88-2.79 (m, 1H), 2.74-2.71 (m, 4H), 0.61 (t, 3H, J = 7.0 Hz). ^{13}C NMR (C_6D_6): δ 165.3, 150.8, 138.1, 134.1, 130.1, 129.8, 129.0, 128.9, 116.2, 115.7, 66.81, 62.3, 49.28, 47.2, 42.8, 39.0, 13.60. Minor-isomer: ^{1}H NMR (C_6D_6): δ 6.87-6.82 (m, 2H), 6.80-6.74 (m, 2H), 6.53-6.47 (m, 2H), 3.22-3.15 (m, 2H), 2.67-2.63 (m, 4H), 0.70 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.0, 150.5, 137.6, 133.7, 130.2, 128.8, 128.7, 116.0, 115.3, 66.79, 62.4, 49.27, 47.5, 43.7, 38.2, 13.57. HRMS (EI) Calcd. for $C_{23}H_{25}N_2O_3Cl$ [M]: 412.1554. Found: 412.1544.



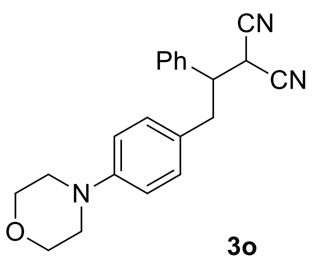
3m

3m: 80% Yield (isomeric ratio 3:2). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 7.19-6.94 (m, 7H), 6.64-6.59 (m, 2H), 3.79-3.65 (m, 2H), 3.58-3.53 (m, 4H), 3.31 (d, 1H, *J* = 3.5 Hz), 2.88-2.24 (m, 9H), 1.97-1.80 (m, 2H), 0.75 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR (C_6D_6): δ 166.3, 150.7, 141.4, 129.8, 129.6, 128.8, 128.7, 126.3, 116.3, 116.0, 66.8, 62.2, 49.4, 41.5, 41.1, 37.4, 33.4, 33.16, 13.7. Minor-isomer: ^{1}H NMR (C_6D_6): δ 3.29 (d, 1H, *J* = 3.9 Hz), 1.77-1.67 (m, 2H), 0.86 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.9, 150.5, 141.2, 130.3, 129.5, 128.6, 115.7, 115.4, 62.3, 49.5, 41.2, 33.7, 33.23, 13.8. HRMS (EI) Calcd. for $C_{25}H_{30}N_2O_3$ [M]: 406.2256. Found: 406.2246.



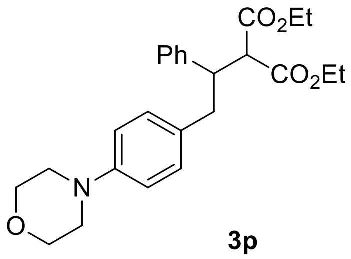
3n

3n: 51% Yield (isomeric ratio 1:1). A colorless oil. ^{1}H NMR (C_6D_6): δ 7.17-7.12; 7.11-7.05 (m each, 2H), 6.67-6.59 (m each, 2H), 3.75-3.60 (m each, 2H), 3.57-3.54 (m each, 4H), 3.41; 3.20 (d each, 1H, *J* = 3.8; 2.4 Hz), 2.90-2.71 (m, 11H), 2.49-2.33 (m, 3H), 1.98-1.86; 1.73-1.61 (m each, 1H), 1.04; 0.95 (d each, 3H, *J* = 6.8; 6.8 Hz), 0.829; 0.73 (d each, 3H, *J* = 7.0; 6.8 Hz), 0.834; 0.78 (t each, 3H, *J* = 7.0; 7.2 Hz). ^{13}C NMR (C_6D_6): δ 166.8; 166.5, 150.7; 150.4, 130.5; 130.1, 129.8, 116.4, 115.9; 115.8, 66.87; 66.86, 62.3; 62.2, 49.6; 49.4, 47.6; 47.5, 40.2; 39.2, 35.5; 34.6, 30.7; 30.6, 21.6; 20.5, 19.2; 19.1, 13.8; 13.6. HRMS (EI) Calcd. for $C_{20}H_{28}N_2O_3$ [M]: 344.2100. Found: 344.2105.



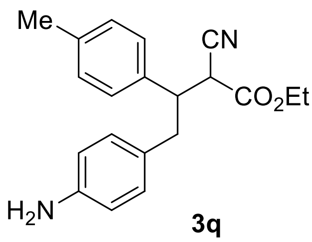
3o

3o: 70% Yield. A colorless oil. ^{1}H NMR (C_6D_6): δ 7.10-6.97 (m, 5H), 6.80-6.75 (m, 2H), 6.55-6.50 (m, 2H), 3.55-3.51 (m, 4H), 3.02 (d, 1H, *J* = 5.4 Hz), 2.97-2.89 (m, 2H), 2.76 (dd, 1H, *J* = 16.9 and 11.2 Hz), 2.72-2.68 (m, 4H). ^{13}C NMR (C_6D_6): δ 150.8, 137.2, 129.8, 129.1, 128.8, 128.3, 116.0, 112.7, 112.3, 66.8, 49.2, 48.3, 37.9, 28.4. HRMS (EI) Calcd. for $C_{21}H_{21}N_3O$ [M]: 331.1685. Found: 331.1687.



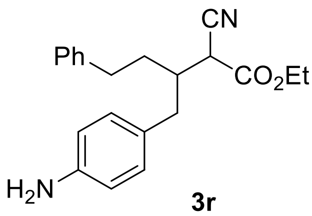
3p

3p: 16% Yield. A white solid (m.p. 91.4-93.0 °C). ^{1}H NMR (C_6D_6): δ 7.10-6.94 (m, 7H), 6.54-6.48 (m, 2H), 4.07-3.96 (m, 4H), 3.68 (q, 2H, *J* = 7.1 Hz), 3.51-3.47 (m, 4H), 3.30-3.24 (m, 1H), 2.84-2.76 (m, 1H), 2.65-2.61 (m, 4H), 0.98 (t, 3H, 7.0 Hz), 0.64 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (C_6D_6): δ 168.6, 167.7, 150.1, 141.1, 130.6, 130.2, 129.2, 128.3, 126.9, 115.7, 66.9, 61.4, 61.0, 58.4, 49.4, 48.4, 40.4, 14.1, 13.7. HRMS (EI) Calcd. for $C_{25}H_{31}NO_5$ [M]: 425.2202. Found: 425.2211.



3q

3q: 90% Yield (isomeric ratio 2:1). A colorless oil. ^{1}H NMR (C_6D_6): δ 7.35-7.31 (m, 2H), 7.01-6.92 (m, 4H), 6.34-6.29 (m, 2H), 3.69-3.54 (m, 3H), 3.50 (d, 1H, *J* = 5.1 Hz), 3.05 (dd, 1H, *J* = 13.8 and 9.7 Hz), 2.97-2.88 (brm, 3H), 2.04 (s, 3H), 0.65 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.7, 146.1, 137.5, 136.4, 130.0, 129.5, 128.5, 127.5, 115.3, 114.9, 62.1, 47.7, 43.0, 39.3, 20.94, 13.6. Minor-isomer: ^{1}H NMR (C_6D_6): δ 6.88-6.85 (m, 2H), 6.82-6.77 (m, 2H), 6.23-6.18 (m, 2H), 3.37 (d, 1H, *J* = 6.2 Hz), 3.23 (dd, 1H, *J* = 13.8 and 5.9 Hz), 2.02 (s, 3H), 0.72 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 165.3, 145.7, 137.2, 136.7, 130.4, 129.4, 128.3, 127.4, 116.5, 115.8, 62.3, 48.1, 44.0, 38.4, 20.92. HRMS (EI) Calcd. for $C_{20}H_{22}N_2O_2$ [M]: 322.1681. Found: 322.1696.



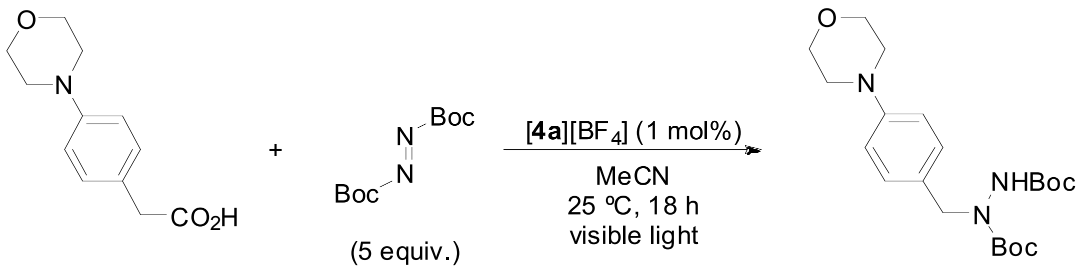
3r

3r: 51% Yield (isomeric ratio 3:2). A colorless oil. Major isomer: ^{1}H NMR (C_6D_6): δ 7.15-6.86 (m, 7H), 6.32-6.24 (m, 2H), 3.77-3.64 (m, 2H), 3.31 (d, 1H, J = 3.2 Hz), 2.84-2.71 (brm, 3H), 2.63-2.22 (m, 4H), 1.94-1.78 (m, 2H), 0.73 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6): δ 166.4, 146.0, 141.5, 129.9, 128.7, 128.6, 126.3, 115.4, 115.0, 62.17, 41.5, 41.1, 37.43, 33.4, 33.2, 13.7. Minor-isomer: ^{1}H NMR (C_6D_6): δ 3.24 (d, 1H, J = 3.8 Hz), 1.74-1.66 (m, 2H), 0.84 (t, 3H, J = 7.0 Hz). ^{13}C NMR (C_6D_6): δ 165.9, 145.8, 141.3, 130.4, 128.6, 115.8, 62.24, 41.4, 37.41, 33.6, 33.3, 13.8. HRMS (EI) Calcd. for $C_{21}H_{24}N_2O_2$ [M]: 336.1838. Found: 336.1837.

Determination of Quantum Yield. When the quantum yield of a photochemical reaction was determined, the reaction mixture was irradiated with an Ushio high pressure mercury lamp USH-250SC (250 W) equipped with an 440 nm band-pass filter (Kenko B-440 filter). The irradiated light intensity was estimated to be 1.13 x 10^{-7} einstein s^{-1} by using $K_3[Fe(C_2O_4)_3]$ as an actinometer.[S3] The initial reaction rate of **1a** with 1.1 equiv of **2a** in the presence of 1 mol% of [**4a**][BF_4] in 2.5 mL of acetonitrile (2.17 x 10^{-8} mol s^{-1}) was converted to quantum yield (Φ = 0.21).

Photochemical addition of benzyl radical to azodicarboxylate ester. Recently our group has reported addition reaction of α-aminoalkyl radicals to azodicarboxylate ester under photochemical conditions.[S2a] We also investigated the reaction of **1d** with di-*tert*-butyl azodicarboxylate to give the corresponding aminated product **7** (Scheme S2).

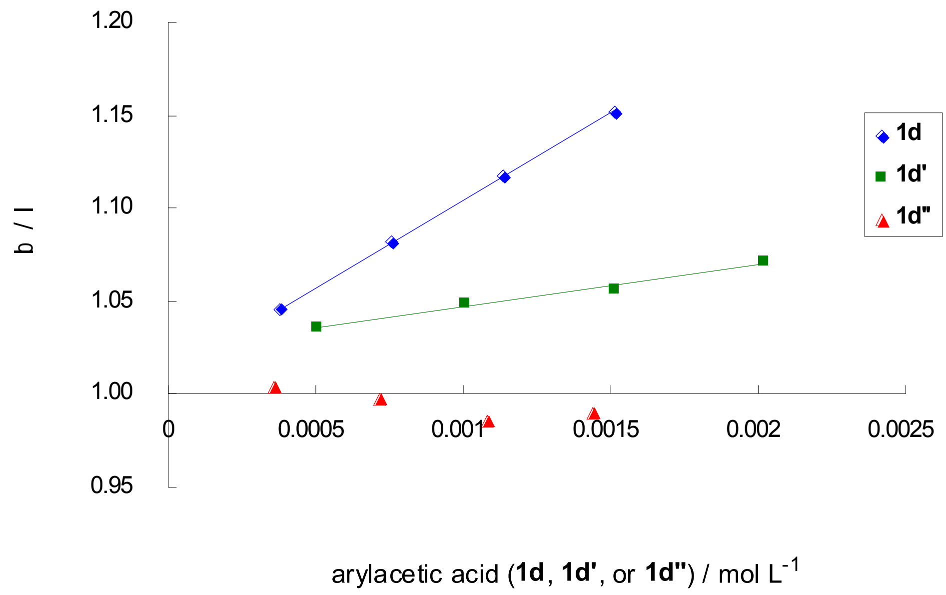
Scheme S2.



In a 20 mL Schlenk flask (diameter: 2.5 cm) were placed [Ir(ppy)$_2$(bpy)][BF$_4$] (1.9 mg, 0.0026 mmol), di-*tert*-butyl azodicarboxylate (288.9 mg, 1.25 mmol), and acetonitrile (2.5 mL) under N_2, and then **1d** (55.1 mg, 0.249 mmol) was added. The reaction flask was placed in a water bath (25 °C) and illuminated with white LED (14 W, approximately 2 cm from the light source) for 18 h. After concentration *in vacuo*, the residue was purified by column chromatography (SiO_2) with hexane/ethyl acetate (10/1 to 10/2) to give **7** (71.2 mg, 0.212 mmol) in 82% yield as a viscous oil. ^{1}H NMR (C_6D_6, 50 °C): δ 7.19 (d, 2H, J = 8.8 Hz), 6.64 (d, 2H, J = 8.8 Hz), 6.14 (br, 1H), 4.70 (br, 2H), 3.57-3.54 (m, 4H), 2.78-2.75 (m, 4H), 1.46 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (C_6D_6, 50 °C): δ 151.3, 129.9, 129.1, 116.0, 80.6, 80.3, 66.9, 49.6, 28.33, 28.26. HRMS (FAB) Calcd. for $C_{21}H_{33}N_3O_5$ [M]: 420.2420. Found: 407.2401.

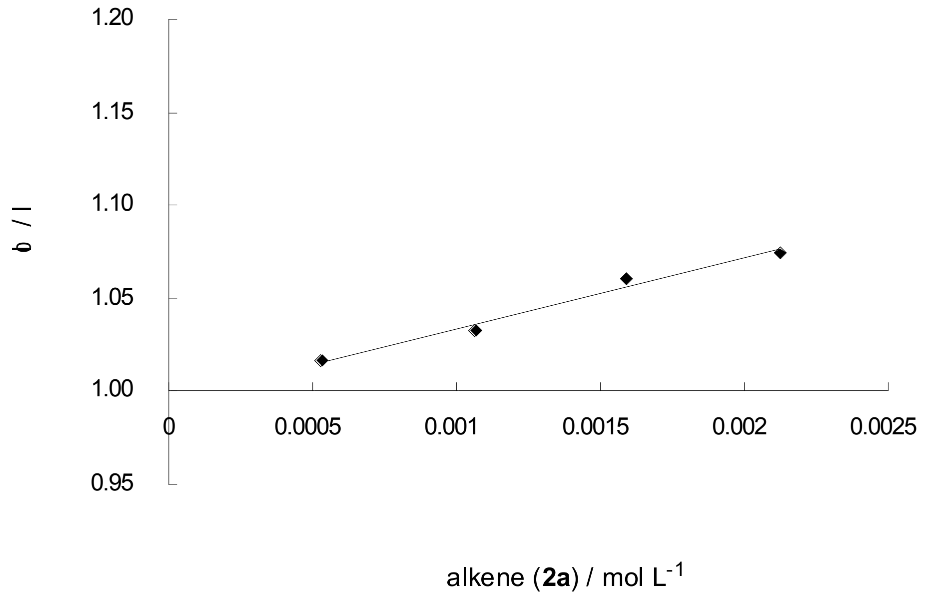
Stern-Volmer plot for 1d, 1d', and 1d''. Stern-Volmer plot for emission quenching of [**4a**][BF$_4$] by **1d**, **1d'**, and **1d''** in MeCN solution was shown in Figure S1. The slope (94.0 for **1d** and 22.3 for **1d'**) and excited-state lifetime of **4a** (329 ns)[S4] was converted to kinetic constant (2.86 × 10^8 M^{-1} s^{-1} for **1d** and 6.78 × 10^7 M^{-1} s^{-1} for **1d'**). On the other hand, no fluorescence quenching of **4a** was observed at all in the presence of **1d''**. These results indicate that single-electron oxidation of **1d** and **1d'** certainly proceeds, but oxidation of **1d''** scarcely occur.

Figure S1.



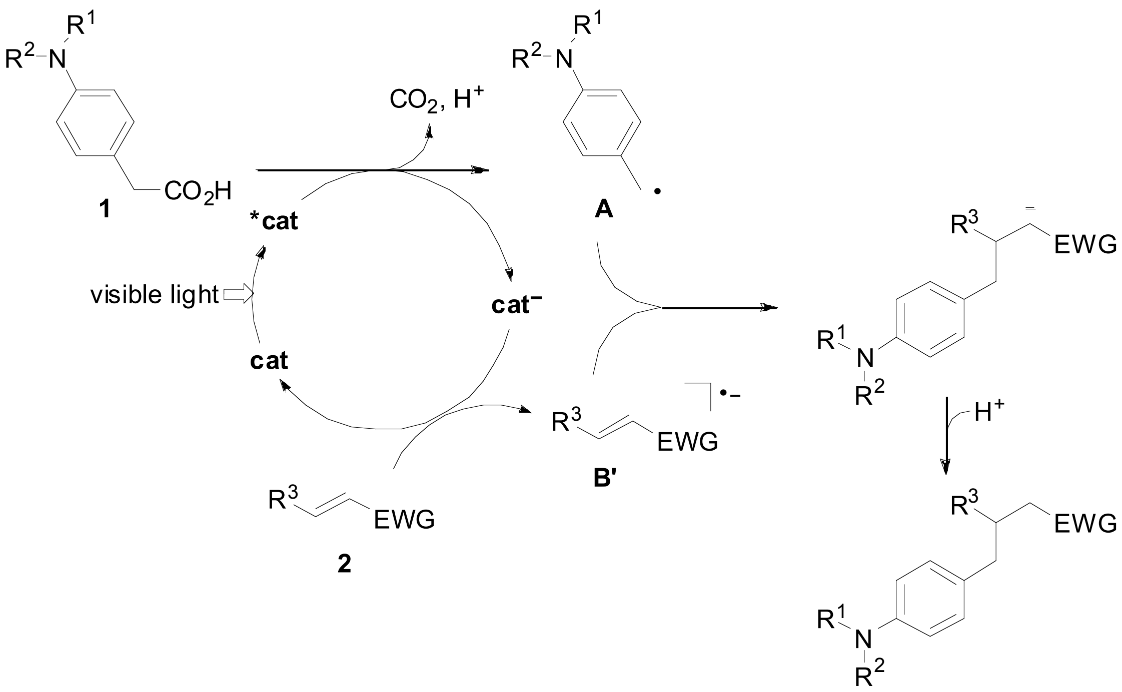
Stern-Volmer plot for 2a. Stern-Volmer plot for emission quenching of [**4a**][BF_4] by **2a** in MeCN solution was shown in Figure S2. The slope (38.4) and excited-state lifetime of **4a** (329 ns)[S4] was converted to kinetic constant (1.17×10^8 M^{-1} s^{-1}).

Figure S2.



Recently our group has reported addition reactions of α-aminoalkyl radicals to electron-deficient alkenes.[S2b, S2c] As discussed in main text, a plausible reaction pathway shown in Scheme 4 in main text is similar to that of these reactions. On the other hand, the result of the Stern-Volmer plot indicates that single electron reduction of alkenes to give the corresponding radical anions is also possible. By considering the contribution of radical anion, another reaction pathway based on radical-radical coupling of benzyl radicals and radical anions is also possible (Scheme S3).[S2a] Detailed mechanistic studies to clarify whether addition of benzyl radicals occurs toward neutral alkenes or radical anions are now under way.

Scheme S3.



Photoirradiation Source

We have confirmed that the range of wavelength of the white LED used in this paper is 400 nm to 750 nm according to the irradiation spectrum of the white LED (Figure S3). Separately, we confirmed that no reaction occurred at all when the reaction flask was placed under a household ceiling light.

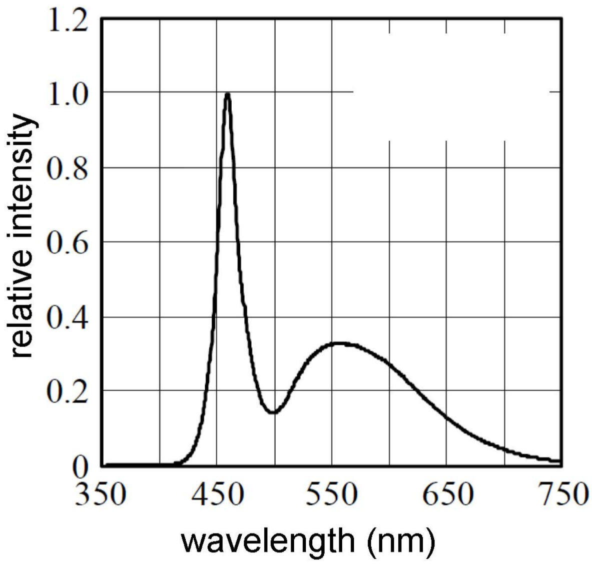


Figure S3. Irradiation Spectrum of the White LED

References and Notes

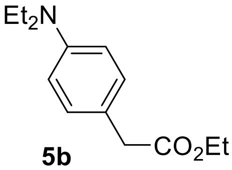
(S1) (a) Dong, Z.; Liu, X.; Feng, J.; Wang, M.; Lin, L.; Feng, X. *Eur. J. Org. Chem.* **2011**, 137. (b) Jenner, G. *Tetrahedron Lett.* **2001**, *42*, 243.

(S2) (a) Miyake, Y; Nakajima K. Nishibayashi, Y. *Chem. Eur. J.* **2012**, *18*, 16473. (b) Miyake, Y; Ashida, Y.; Nakajima K. Nishibayashi, Y. *Chem. Commun.* **2012**, *48*, 6966. (c) Miyake, Y; Nakajima K. Nishibayashi, Y. *J. Am. Chem. Soc.* **2012**, *134*, 3338.

(S3) (a) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl. Chem.* **2004**, *76*, 2105. (b) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley and Sons: New York, 1996.

(S4) Lowry, M. S.; Hudson, W. R.; Pascal, R. A. Jr.; Bernhard, S. *J. Am. Chem. Soc.* **2004**, *126*, 14129.

[1]H and [13]C NMR spectra.



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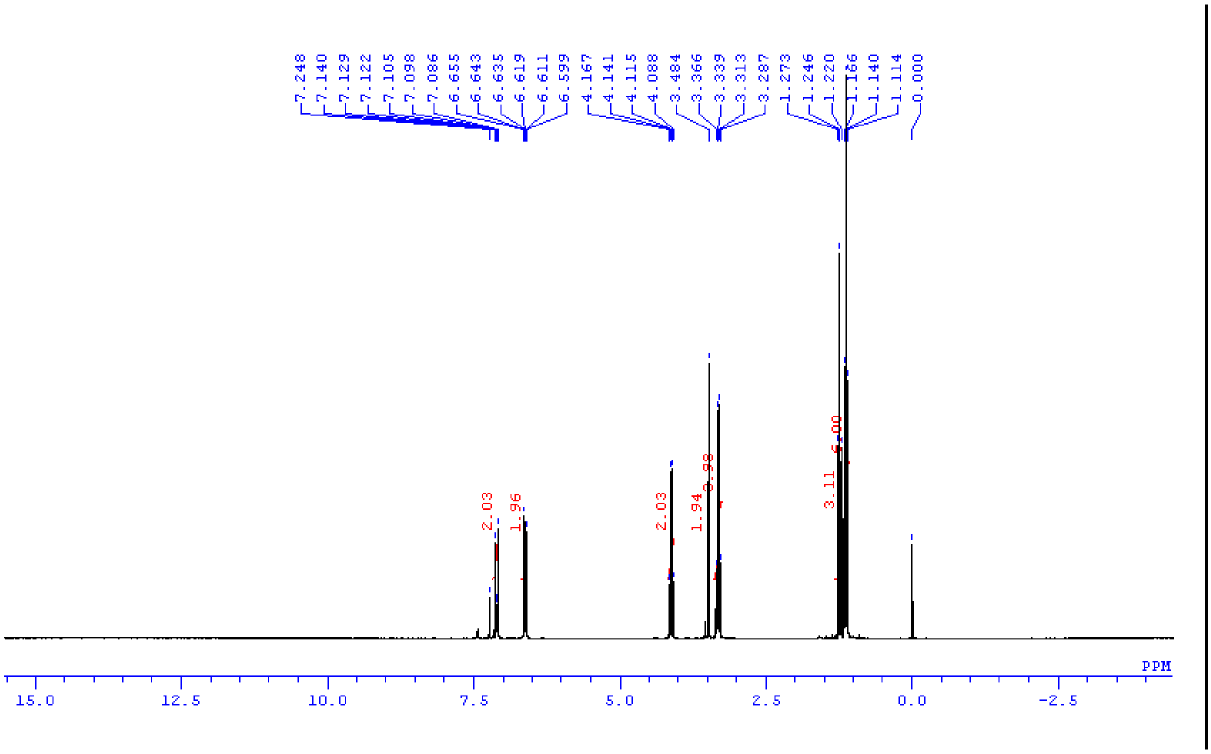

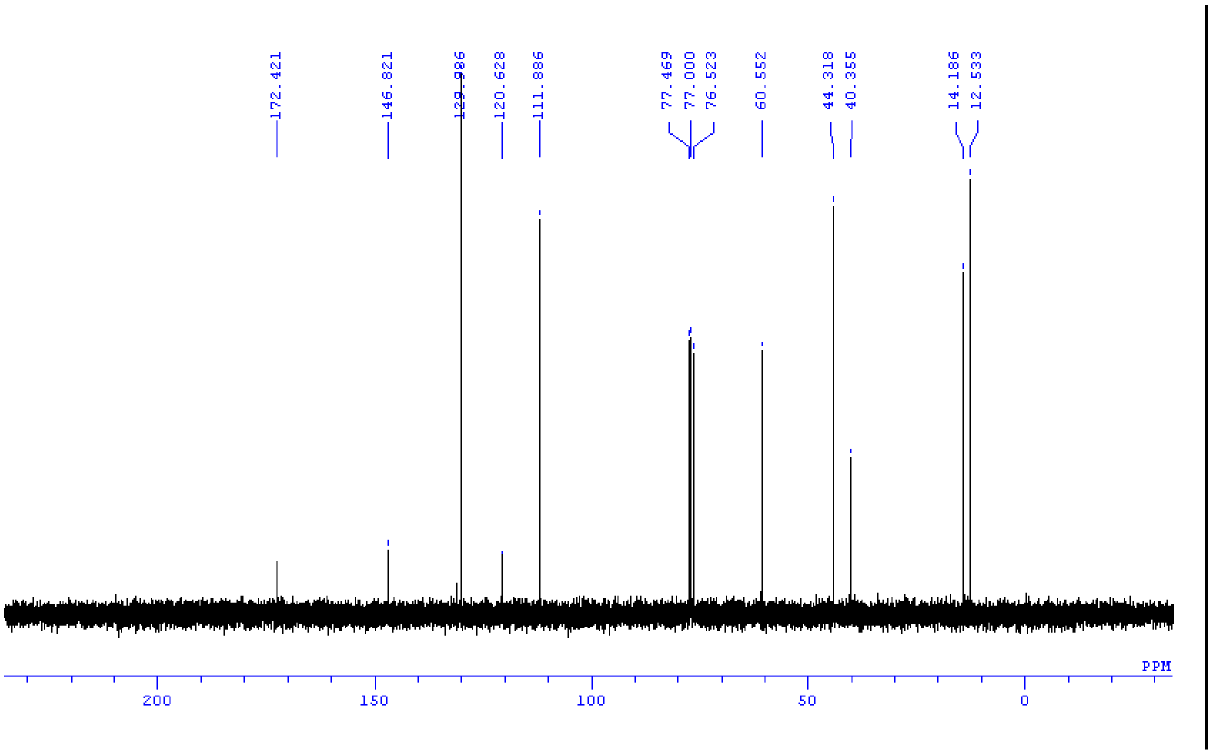

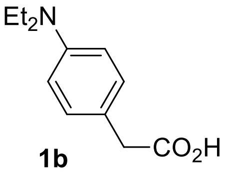
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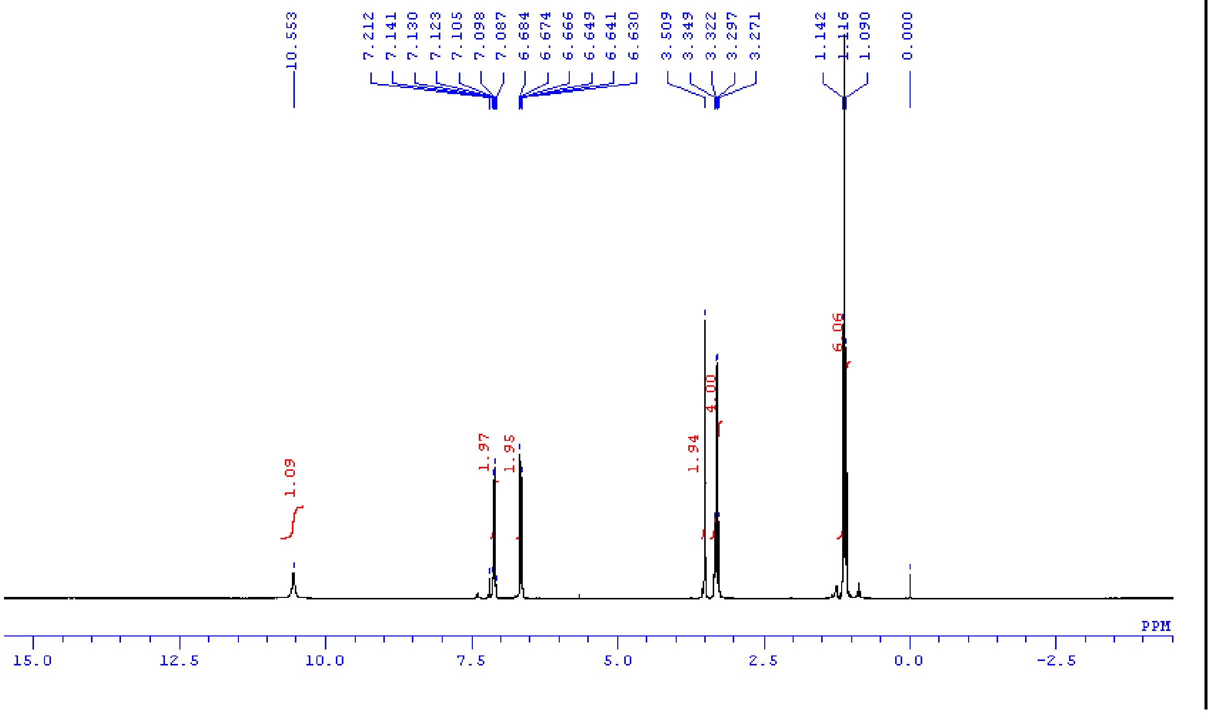
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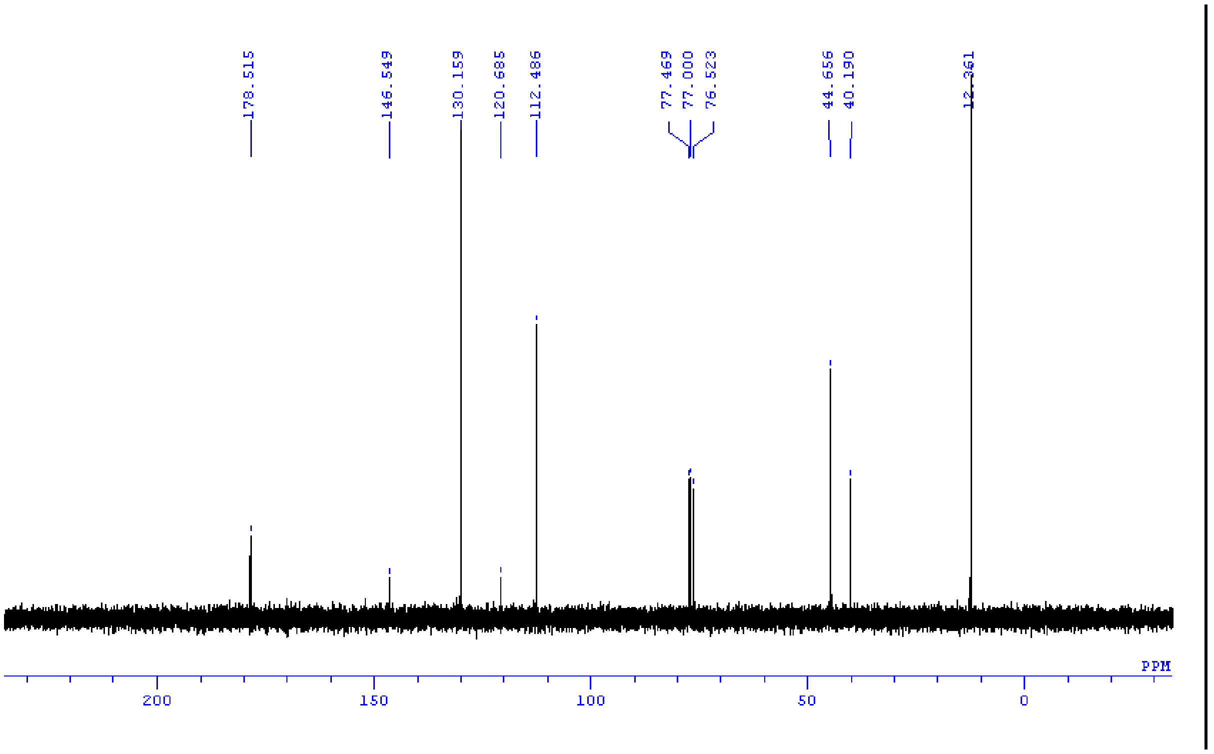
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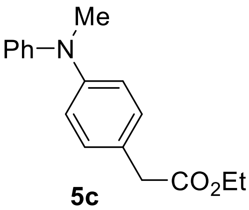
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Ph—N
CO2Et

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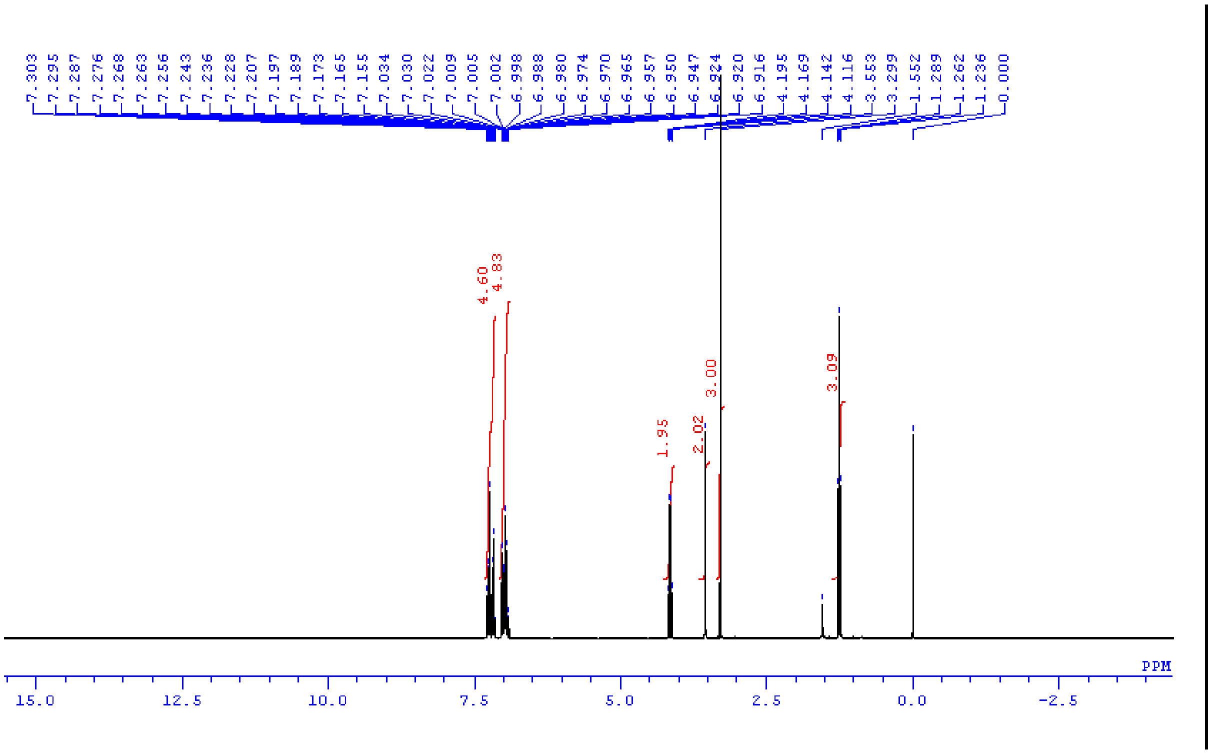
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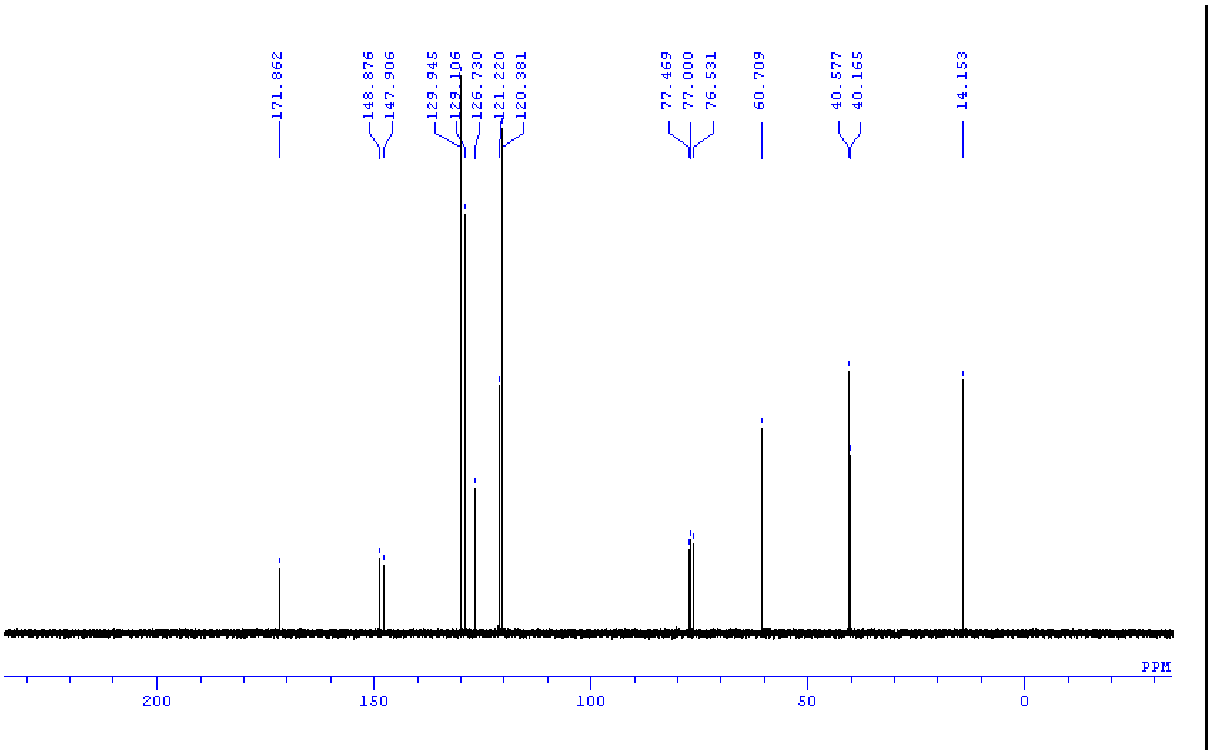
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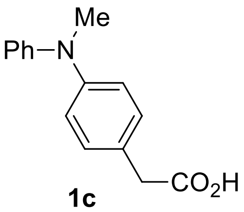

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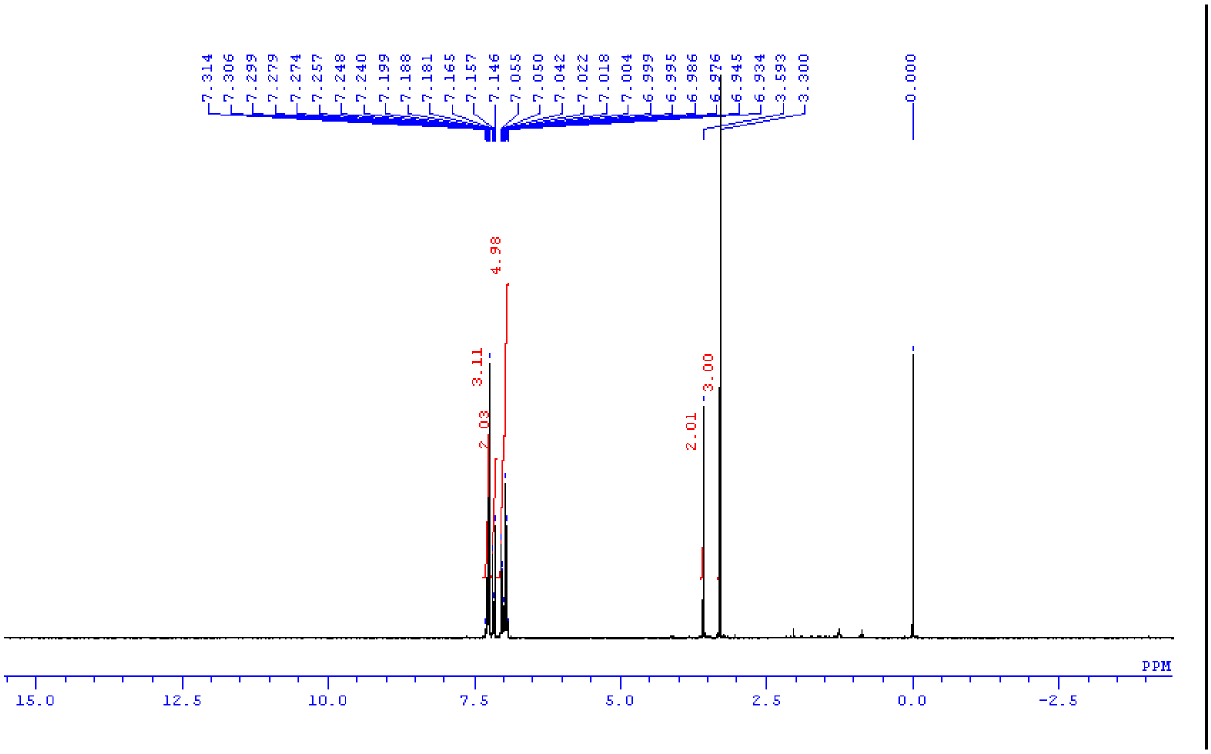

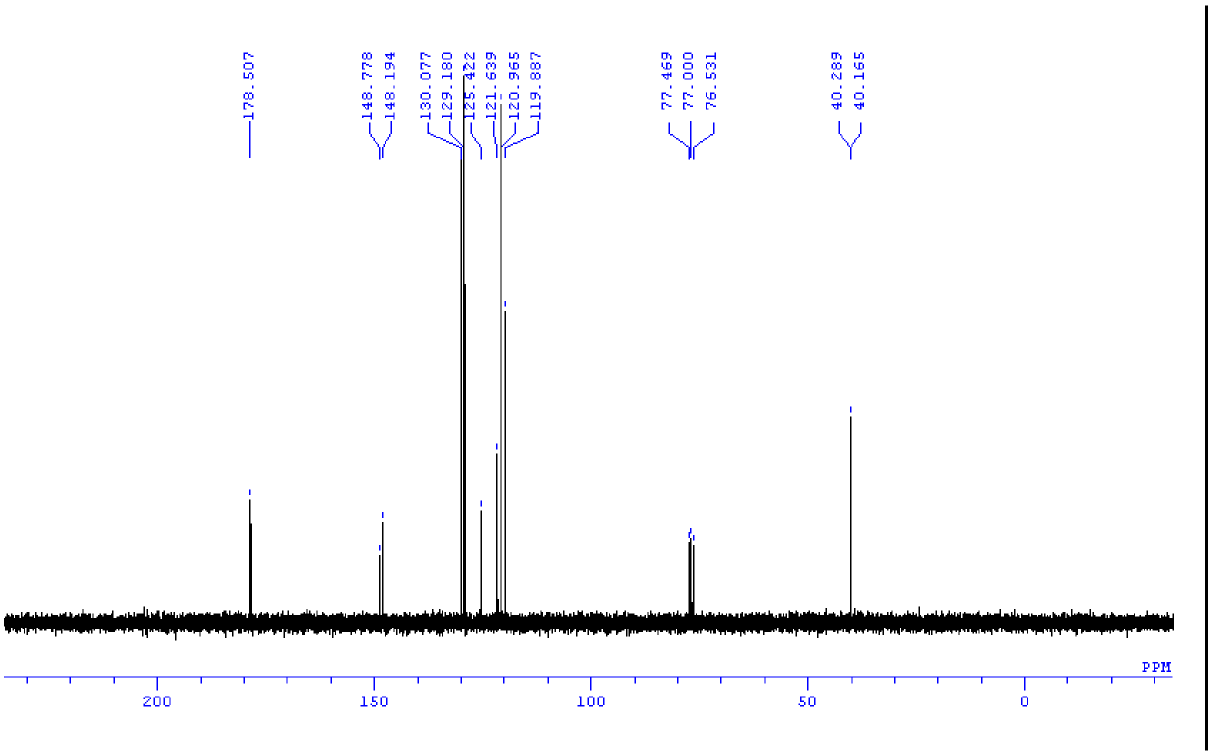

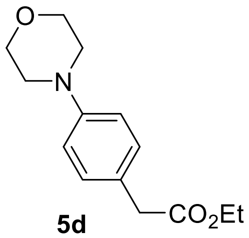

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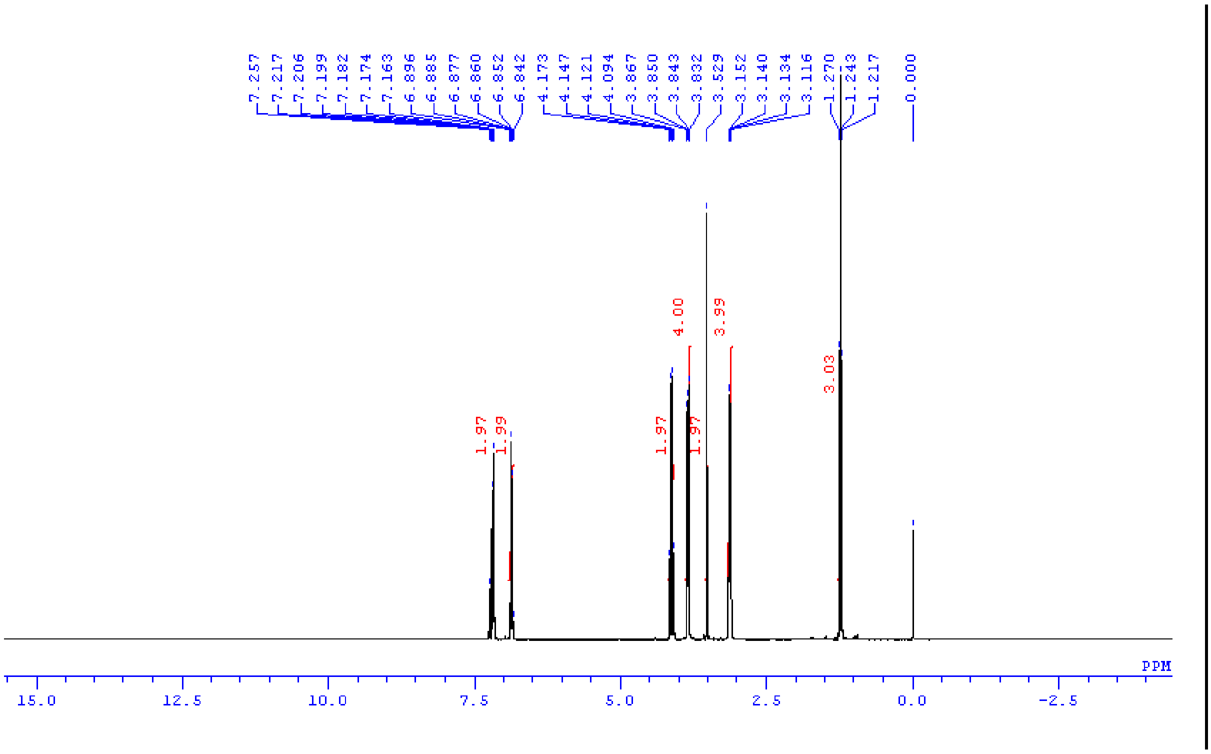

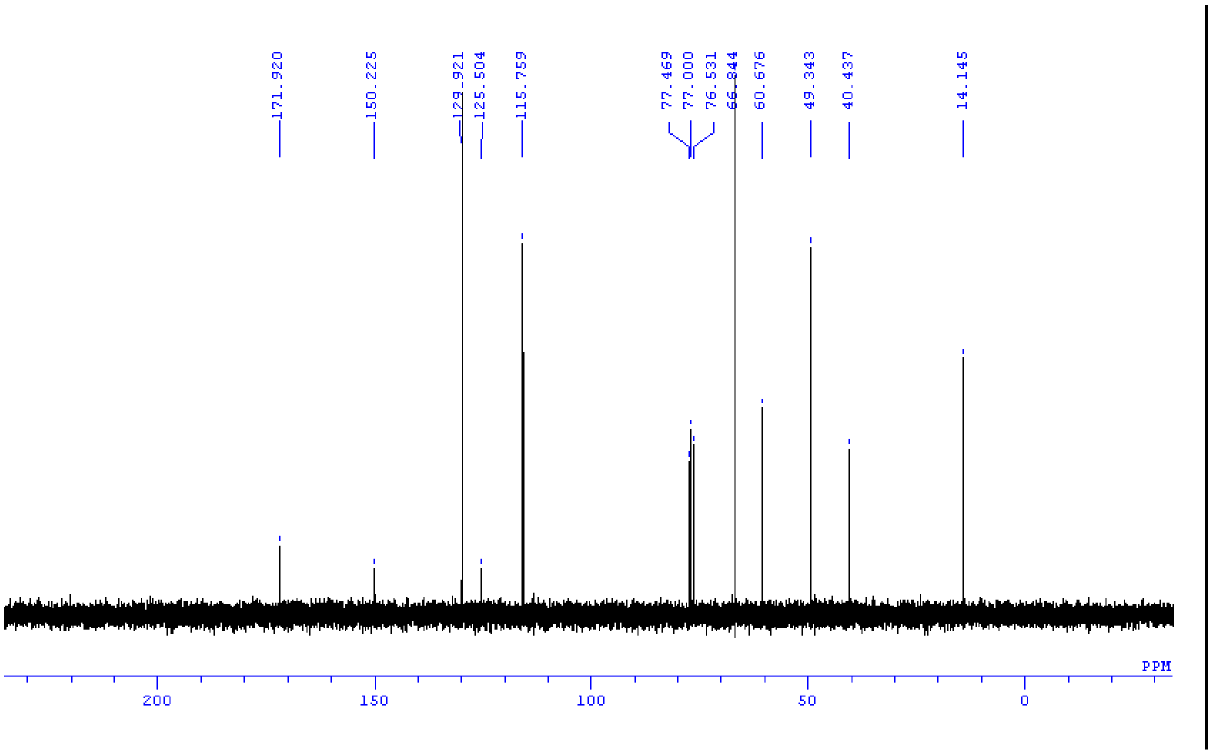

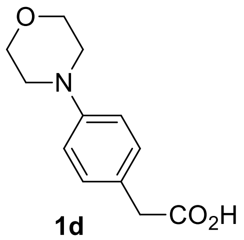

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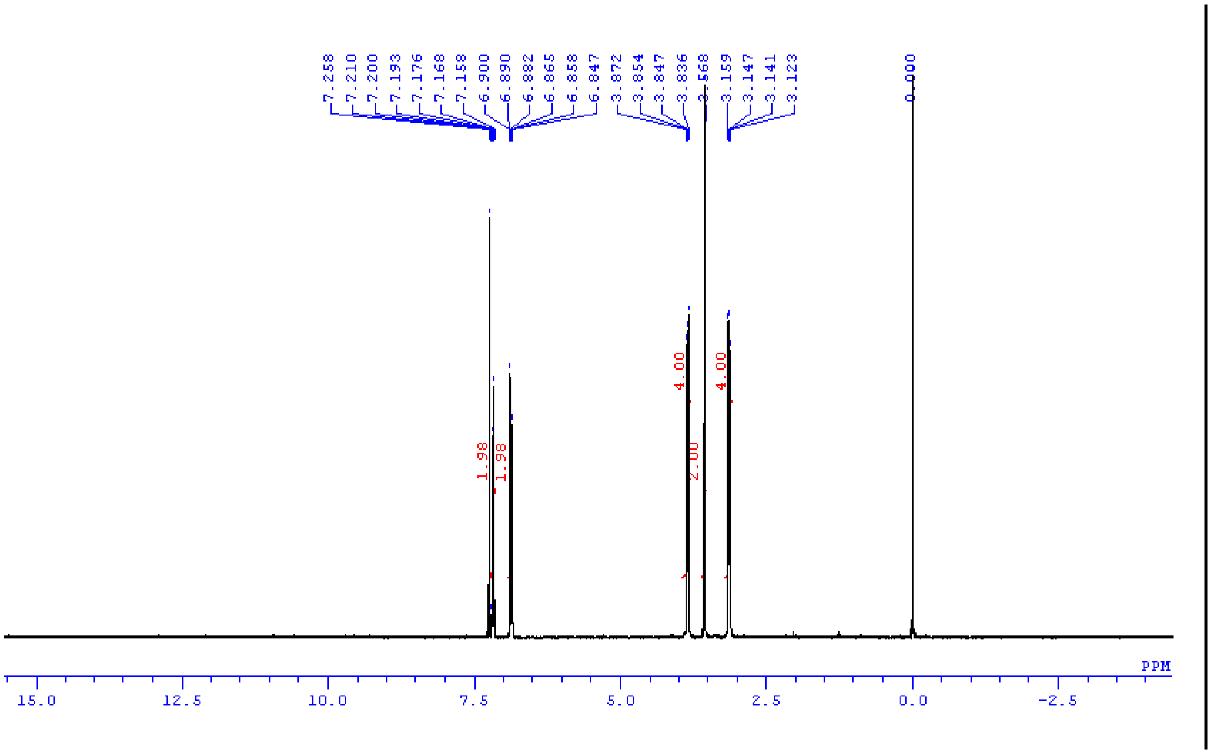
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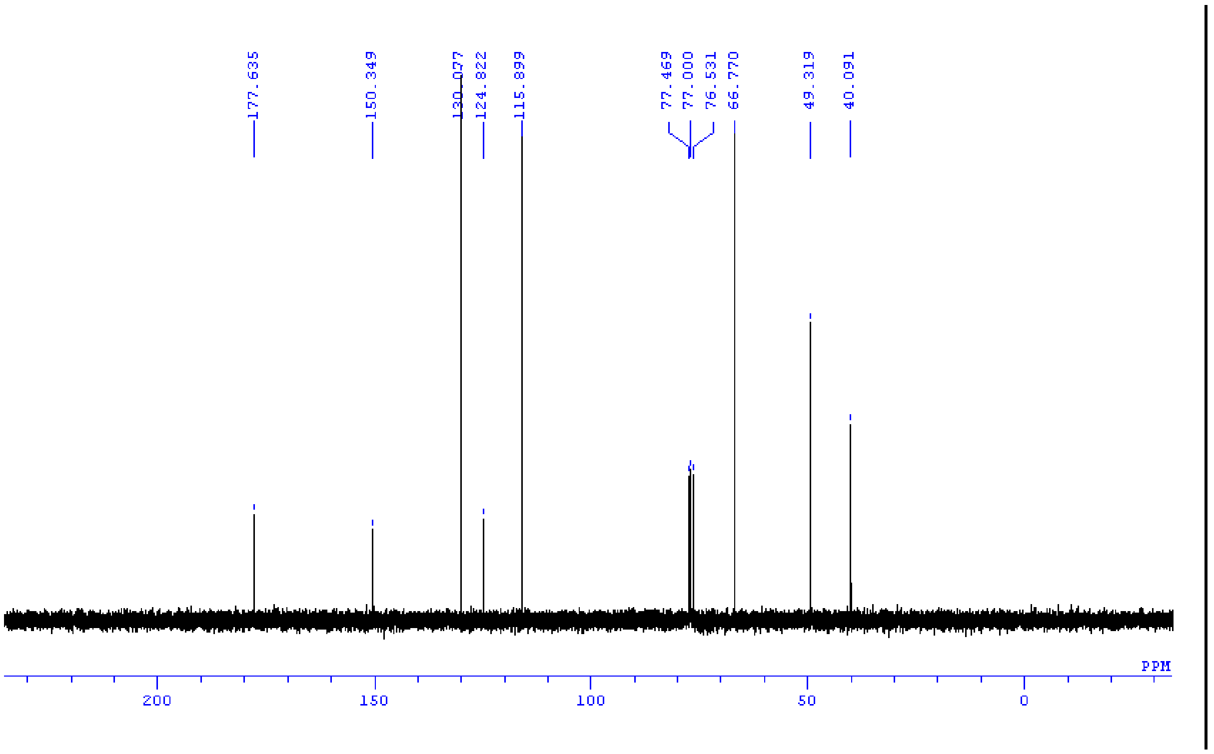
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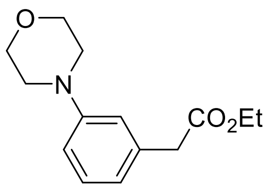

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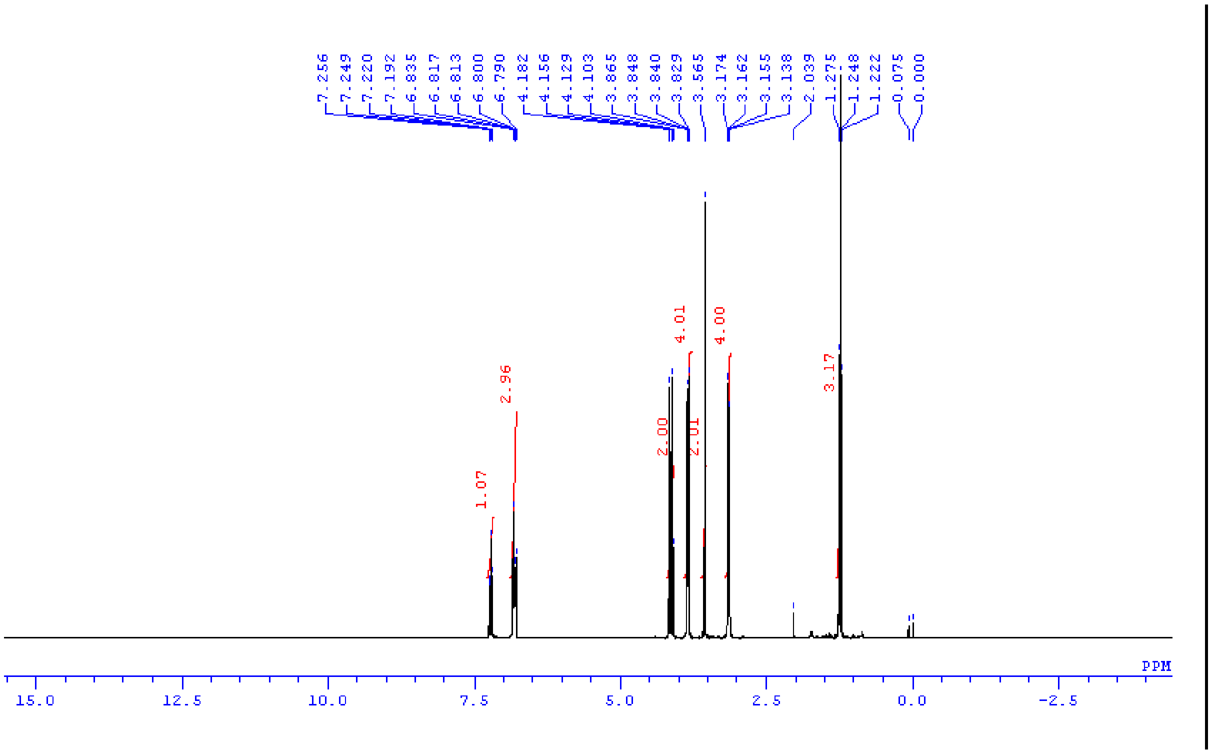

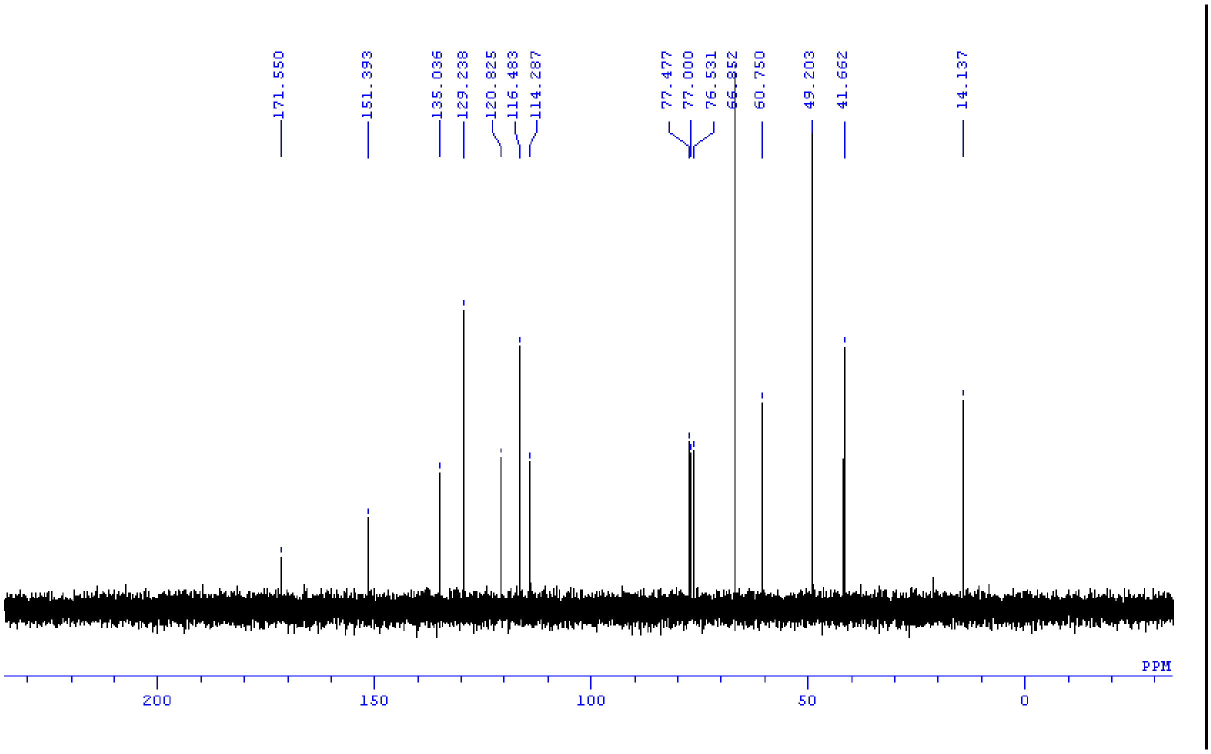

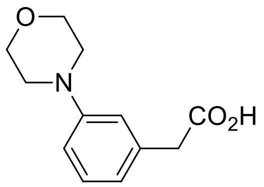

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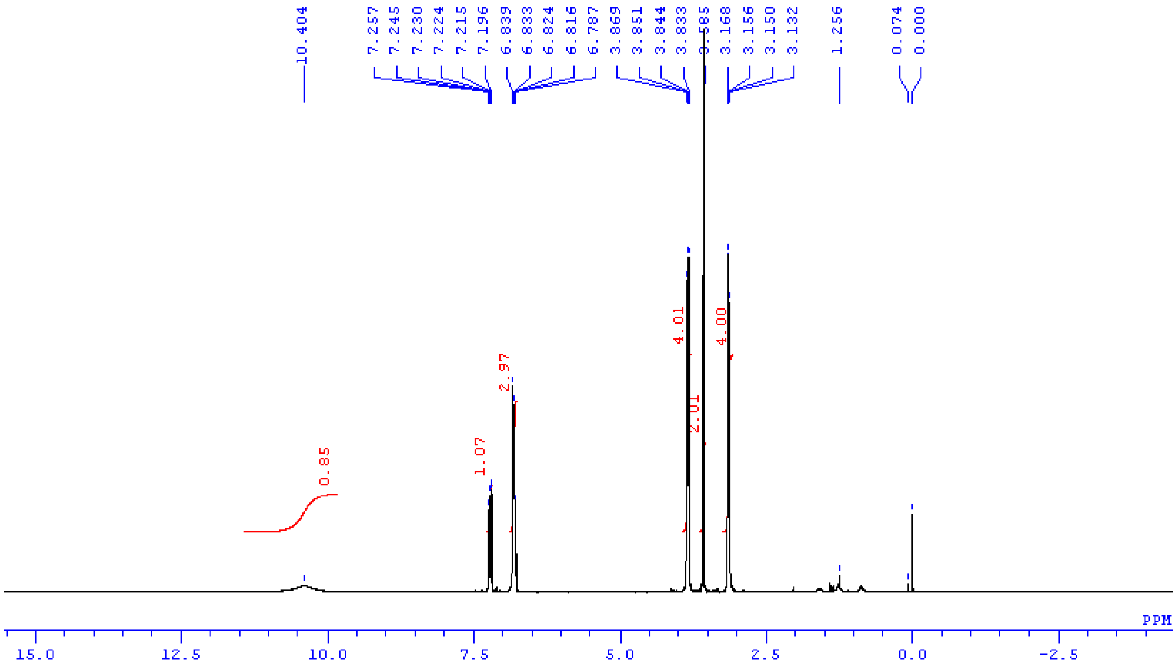
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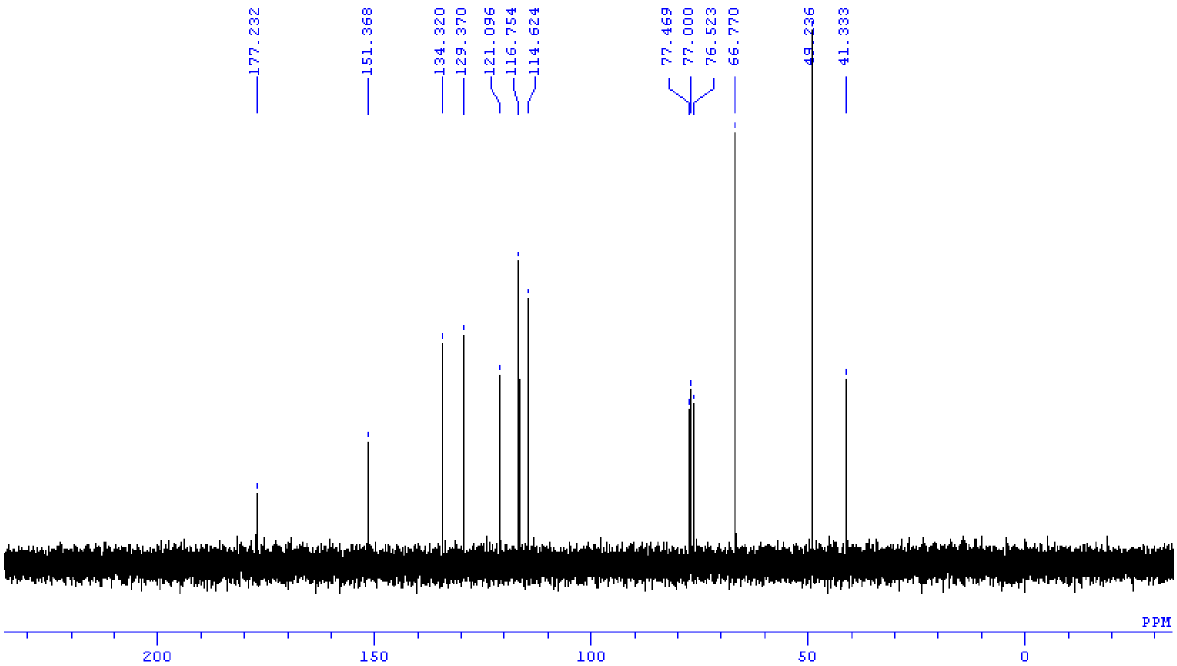
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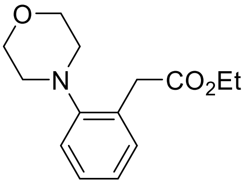
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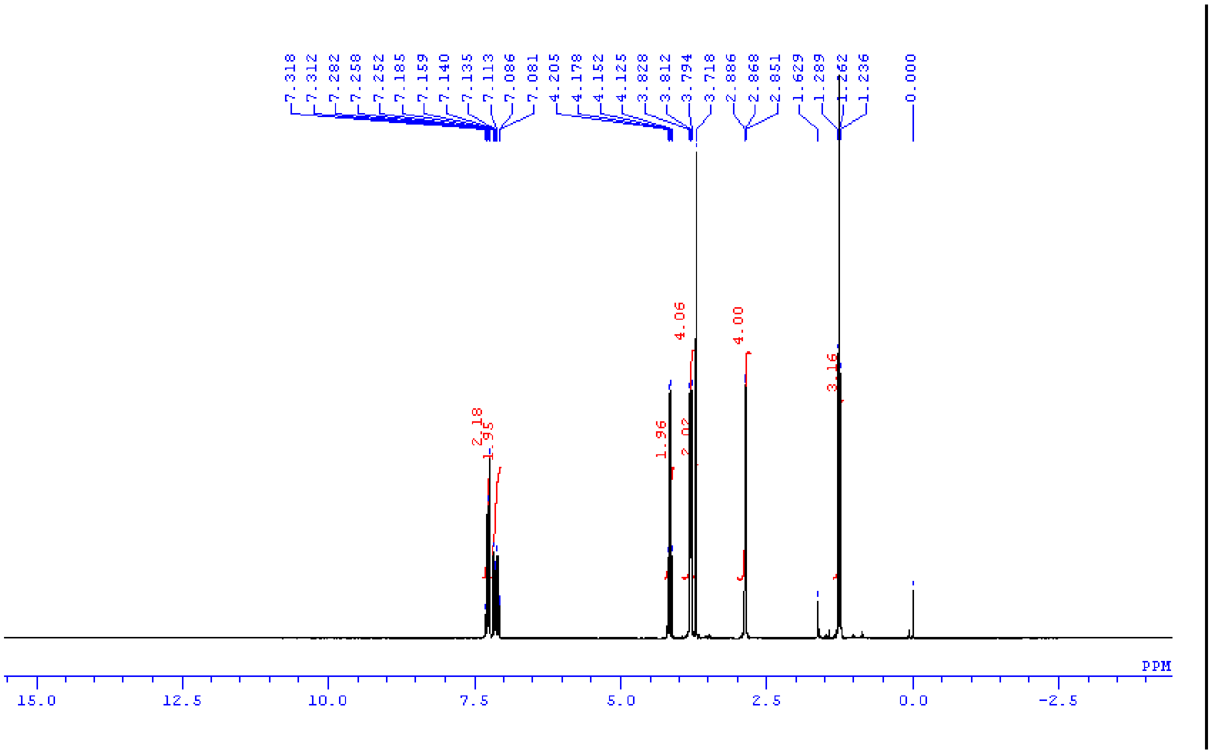
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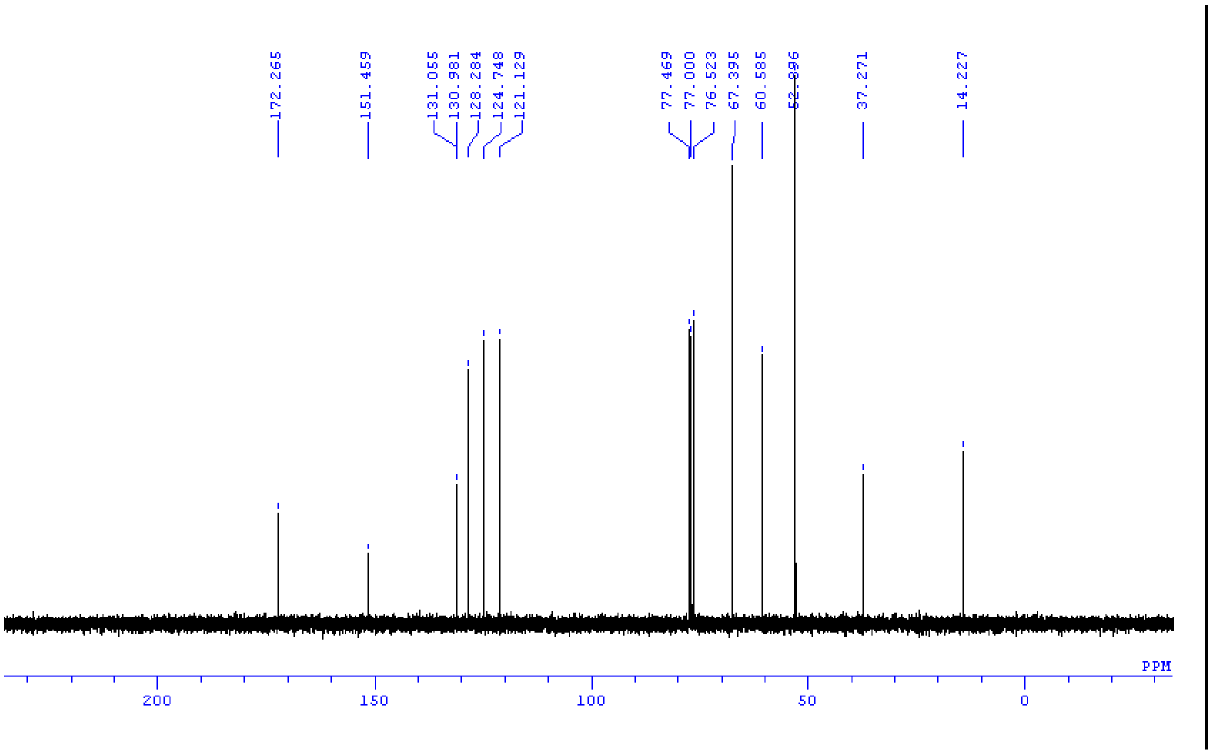
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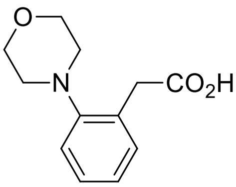
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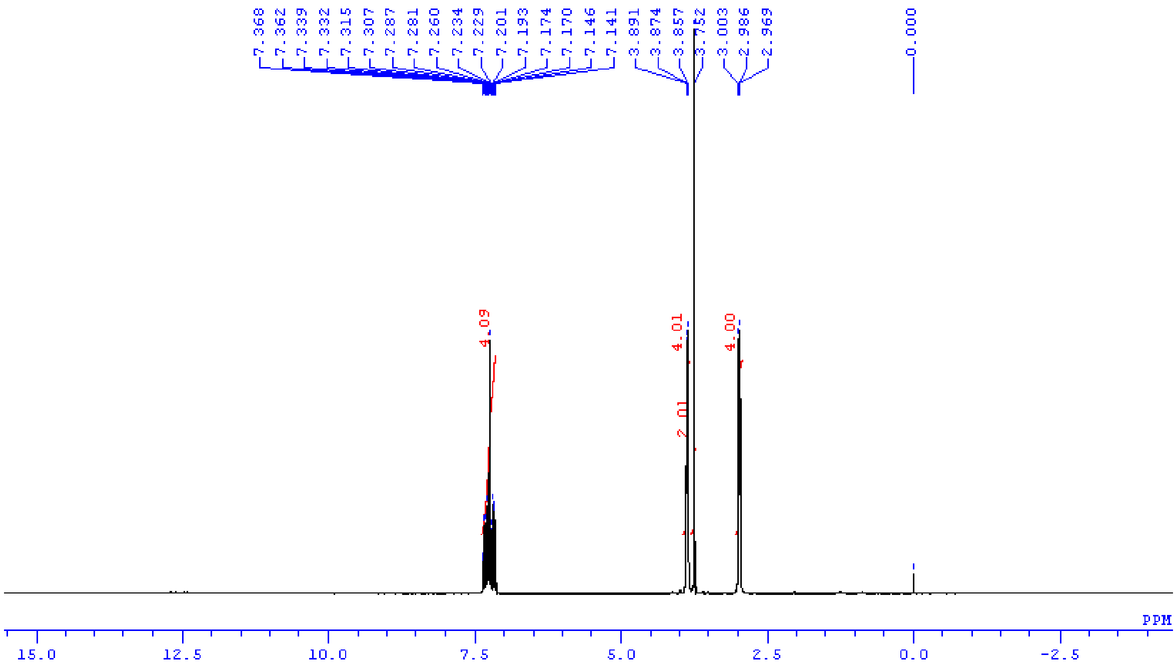
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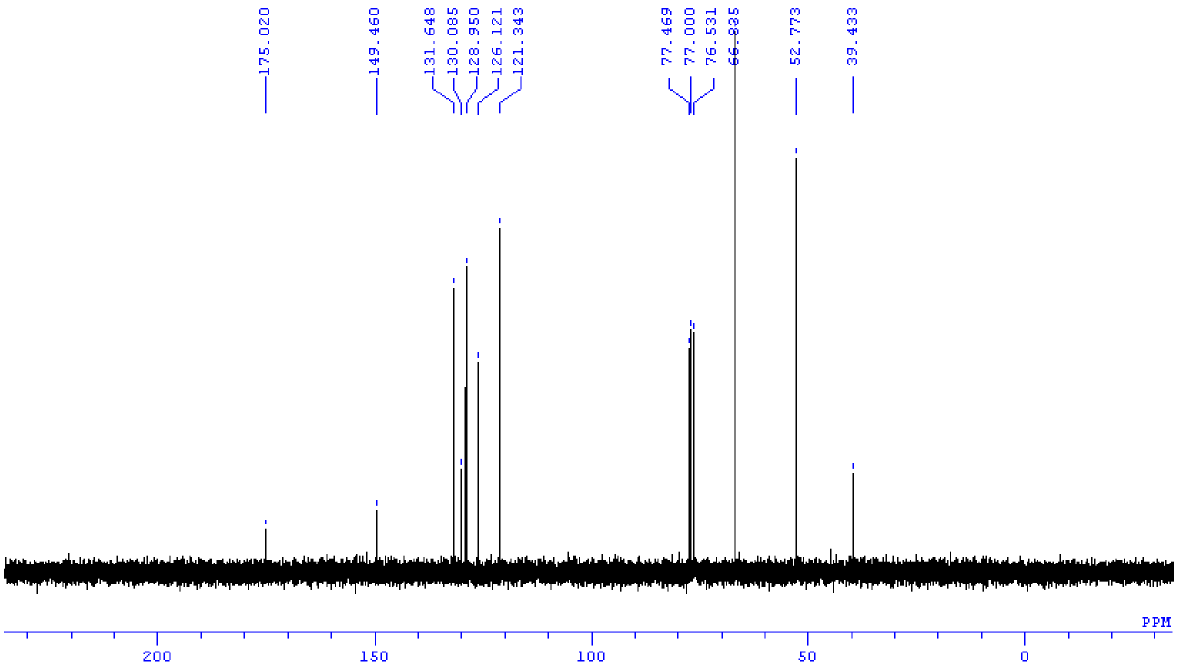
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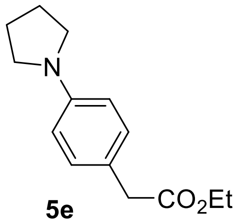
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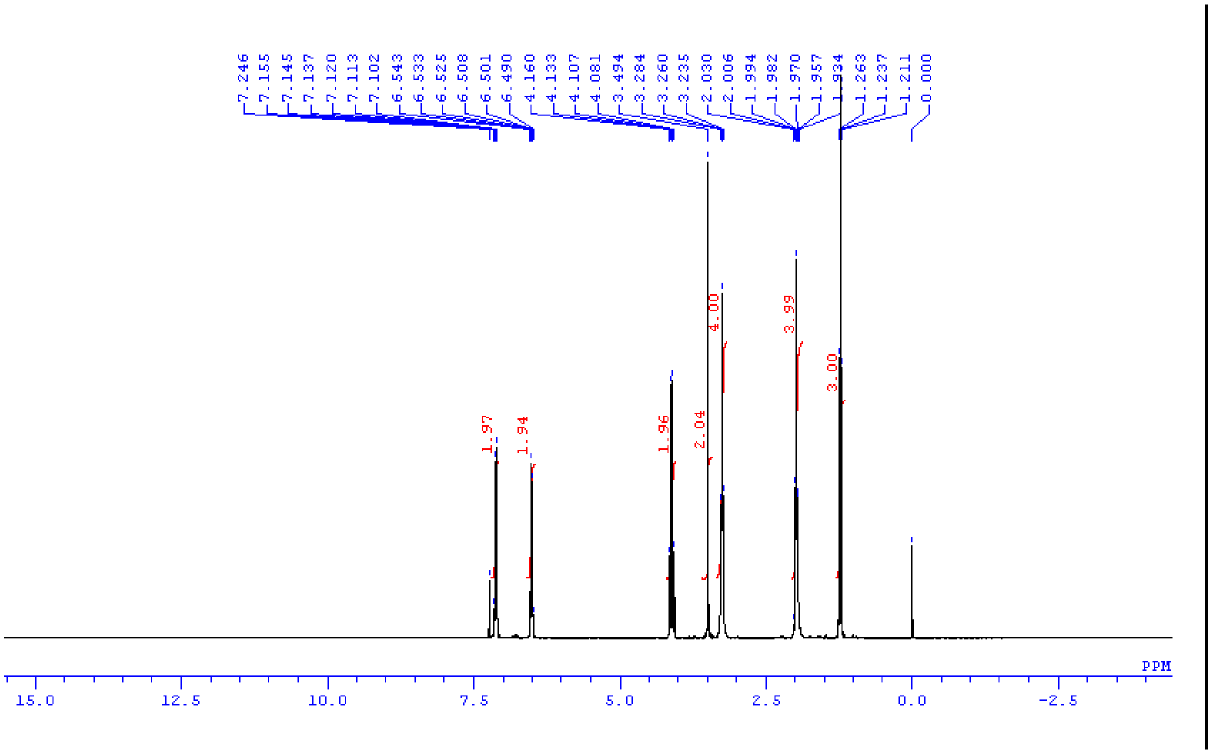
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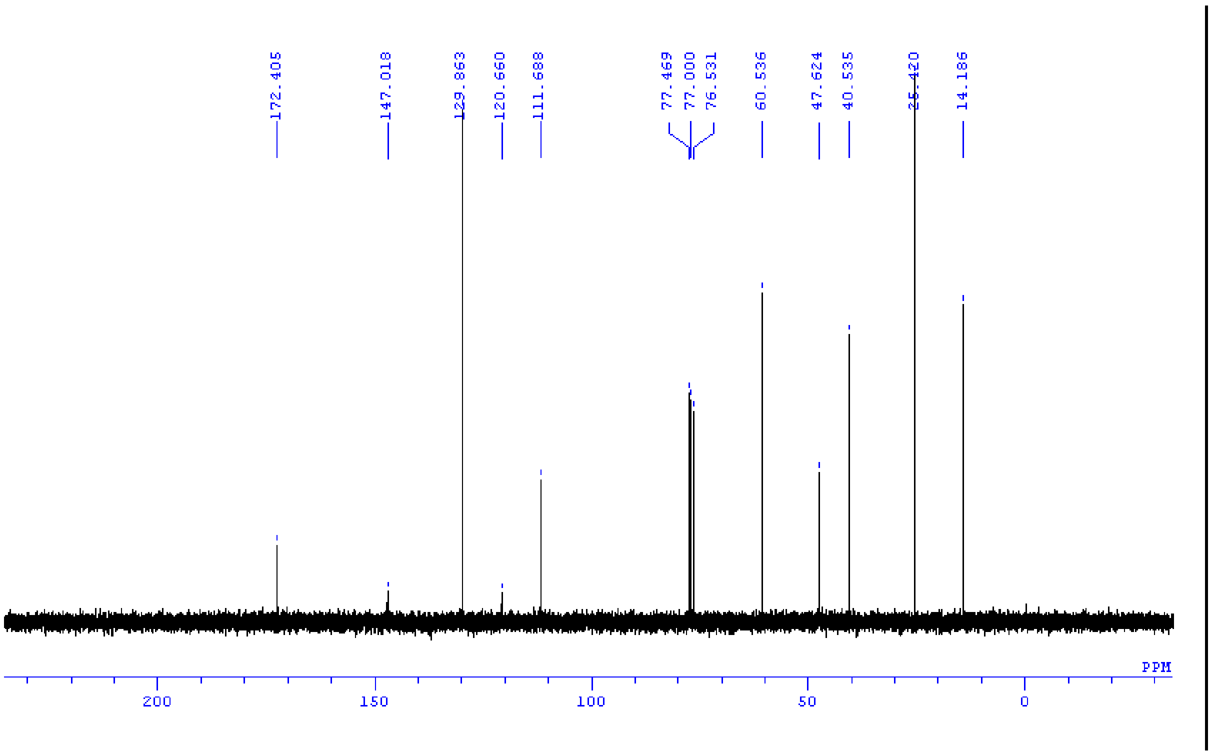
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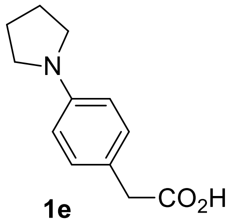

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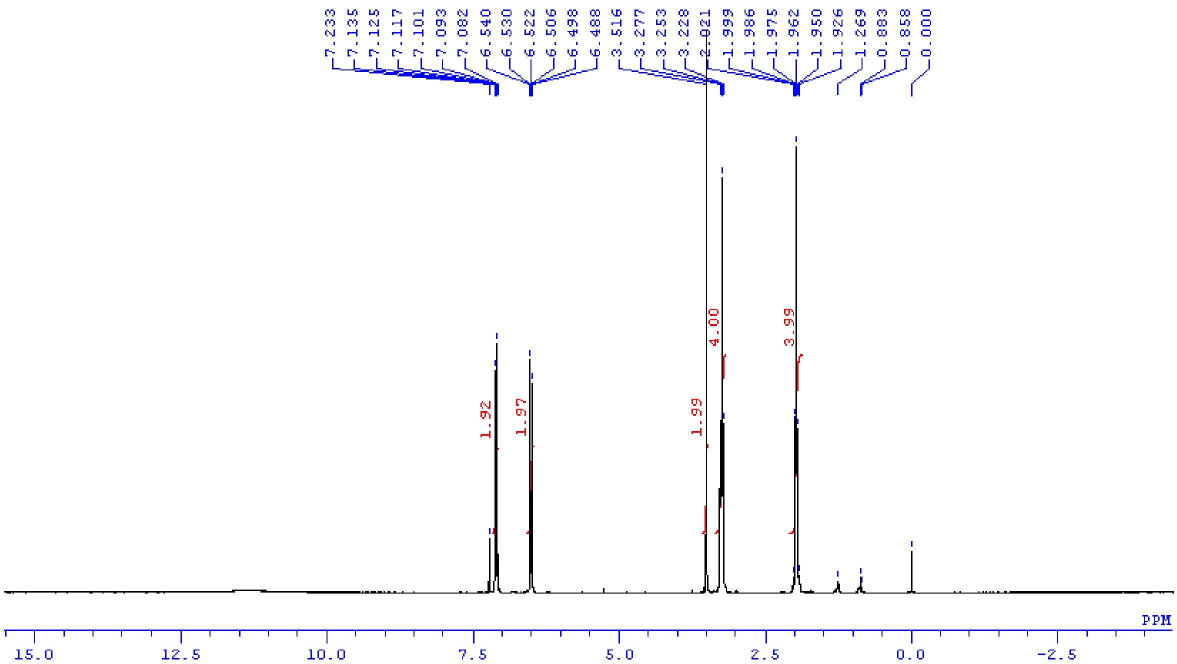
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3.516
3.277
3.253
3.228
2.921
1.999
1.986
1.975
1.962
1.950
1.926
1.269
0.883
0.858
0.000
1.92
1.97
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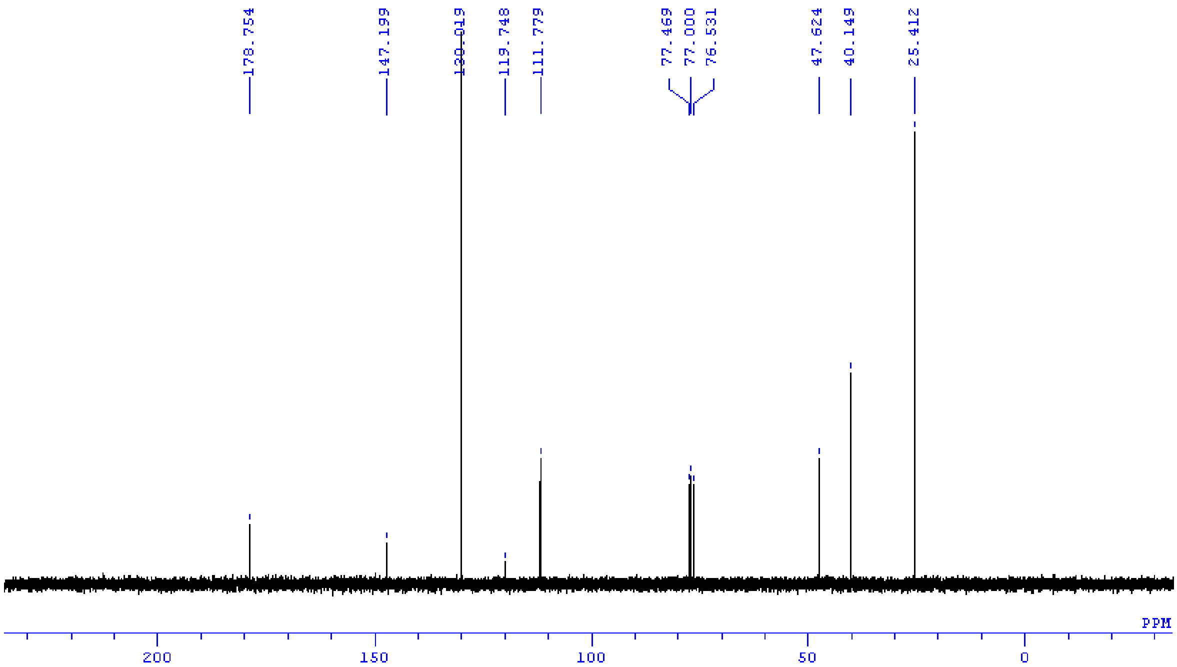
-2.5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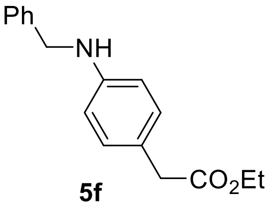

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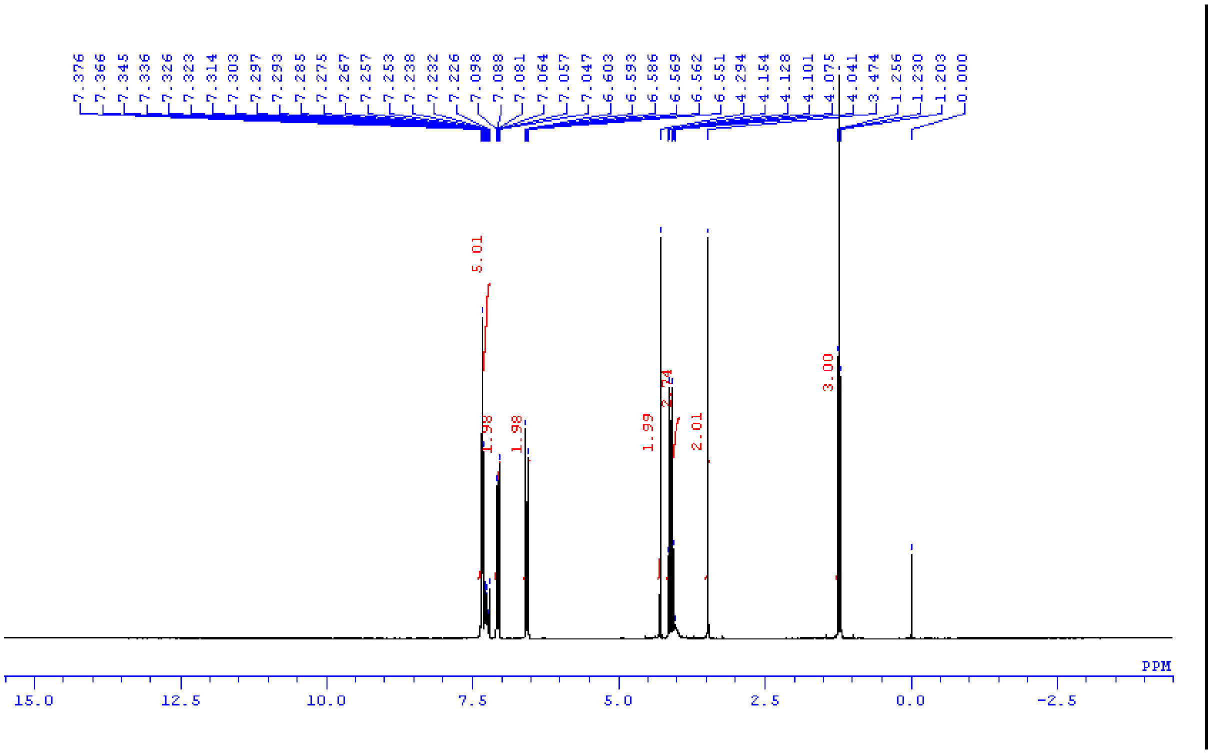

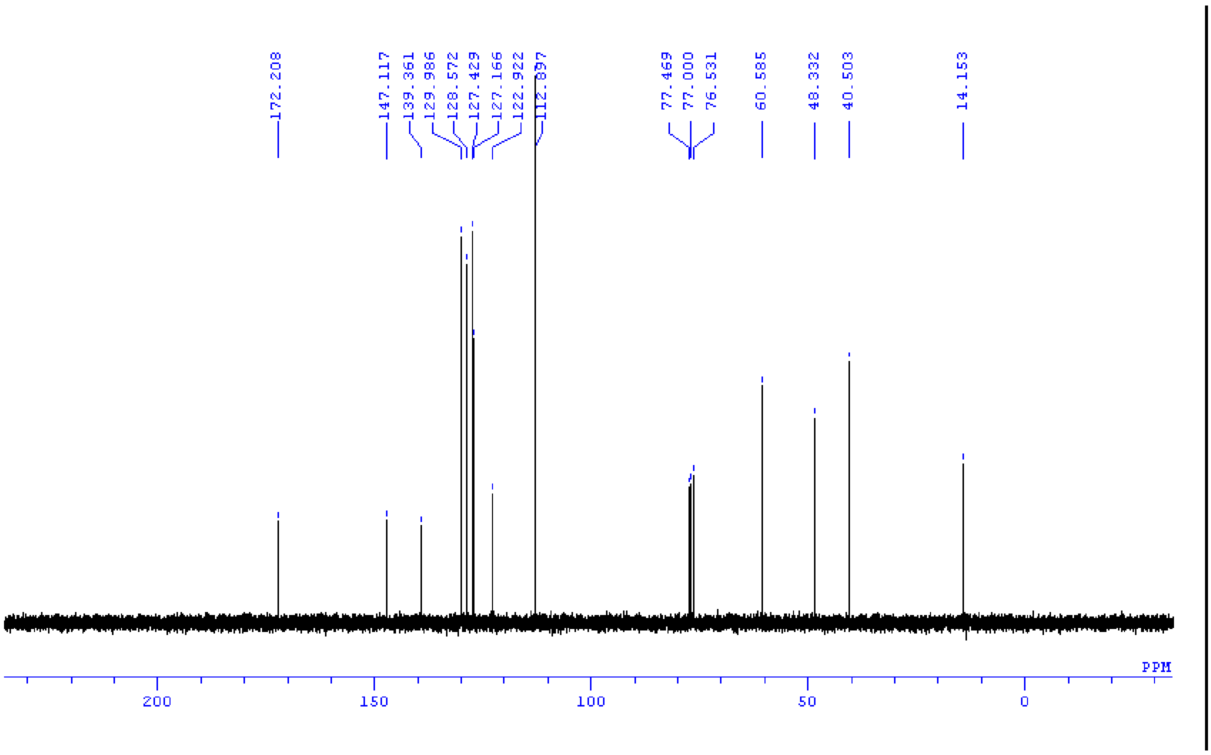

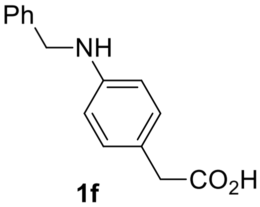

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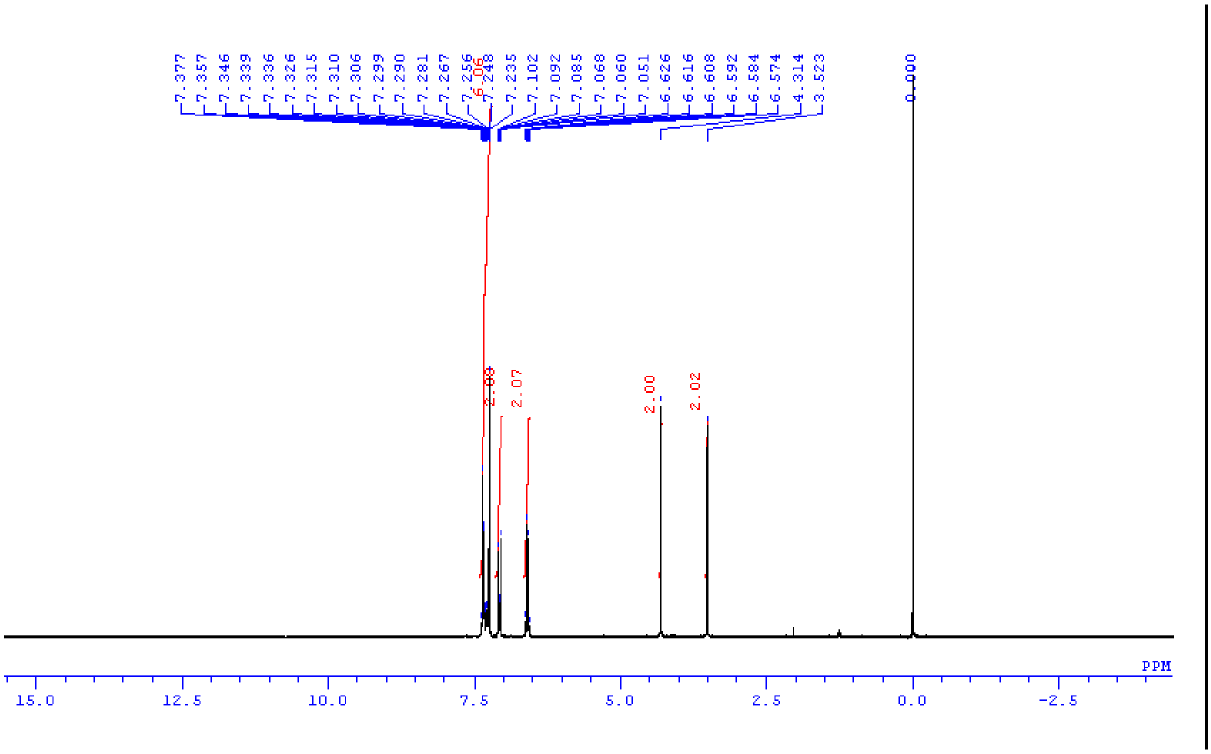
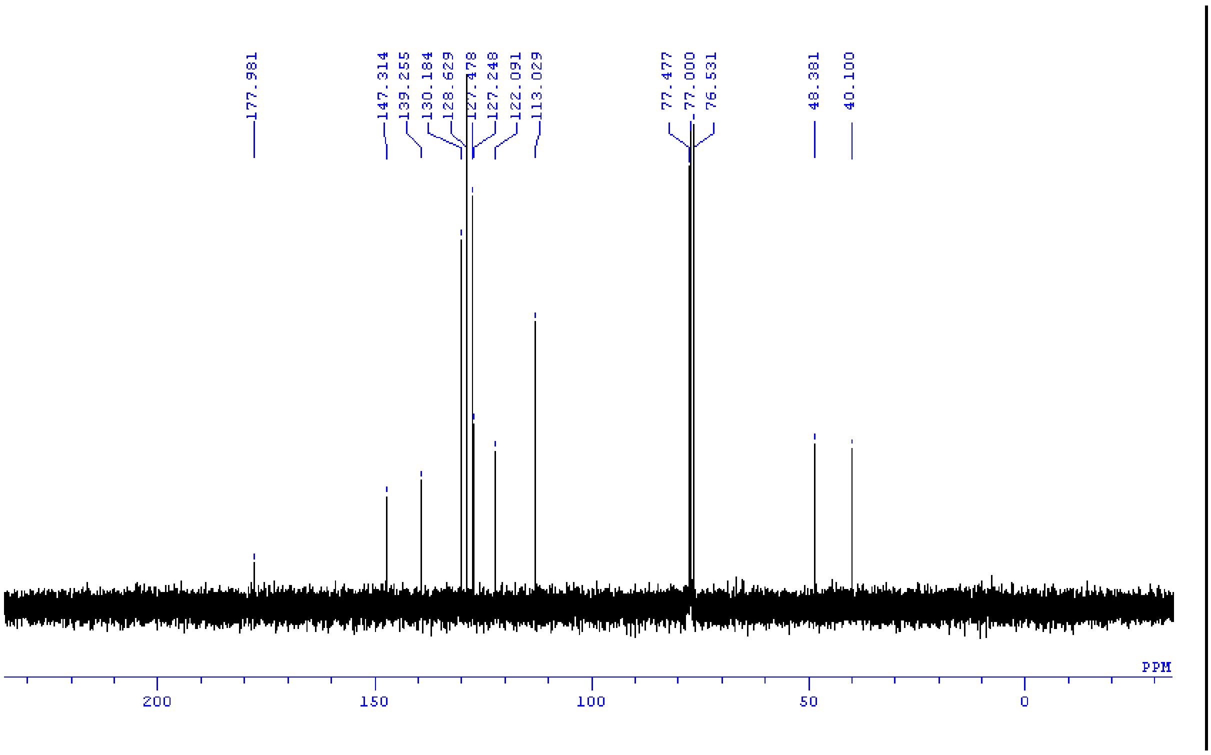
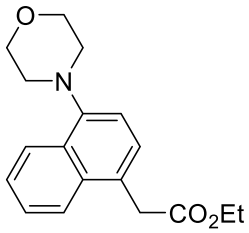
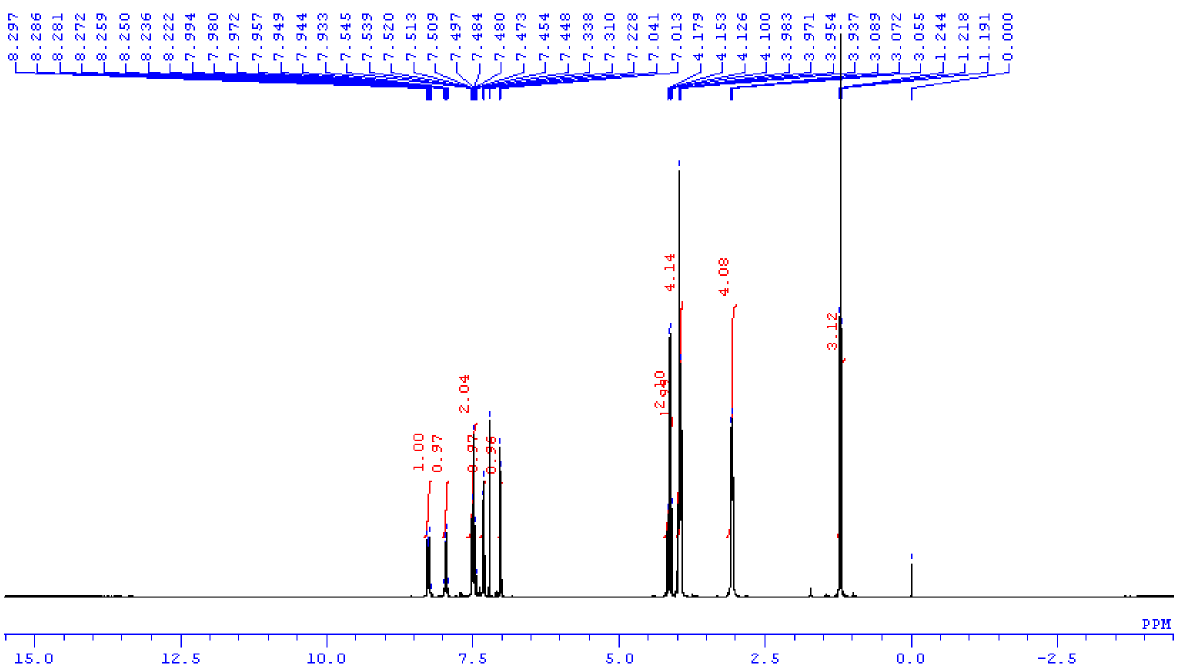





O
N
CO_2Et

5h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7.480
7.473
7.454
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7.338
7.310
7.228
7.041
7.013
4.179
4.153
4.126
4.100
3.983
3.971
3.954
3.937
3.089
3.072
3.055
1.244
1.218
1.191
0.000
1.00
0.97
2.04
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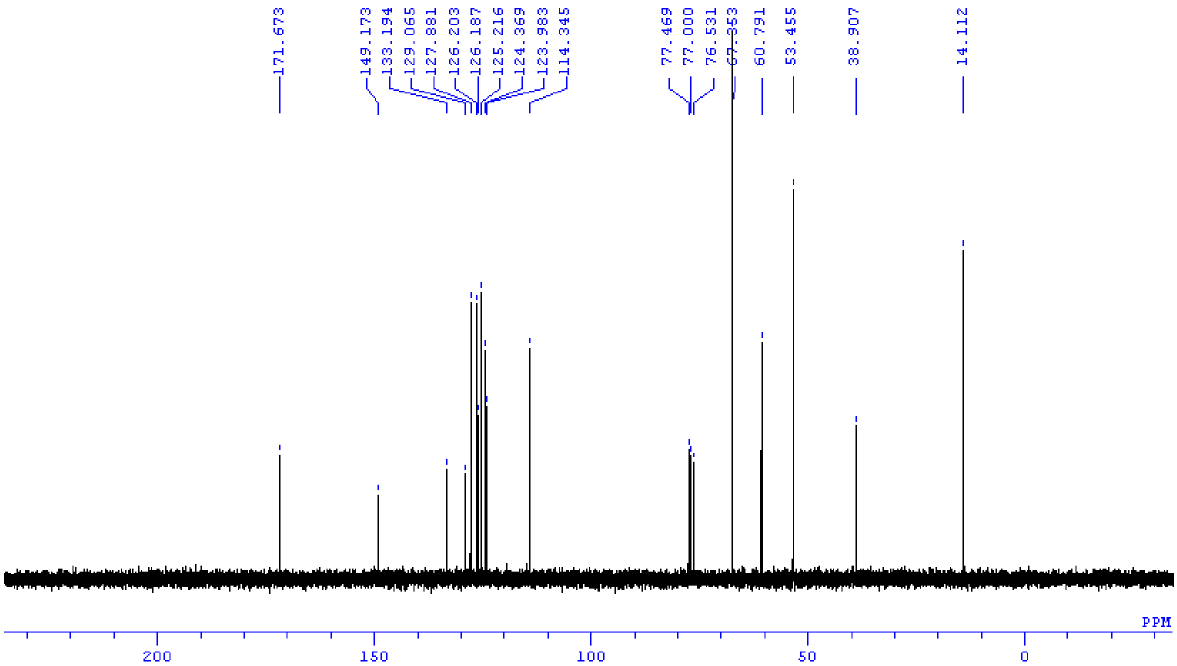
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125.216
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123.983
114.345
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67.353
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53.455
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14.112
PPM
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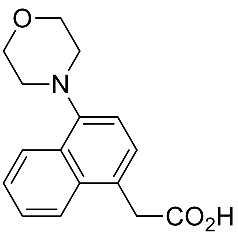
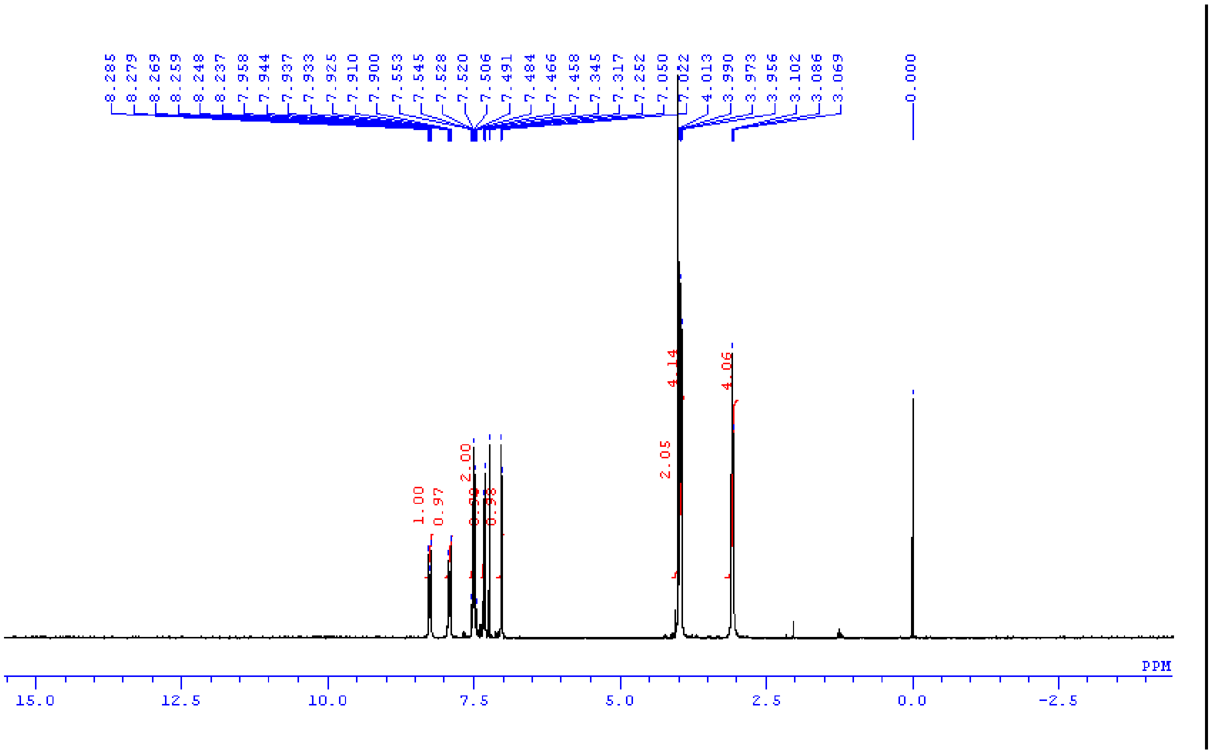
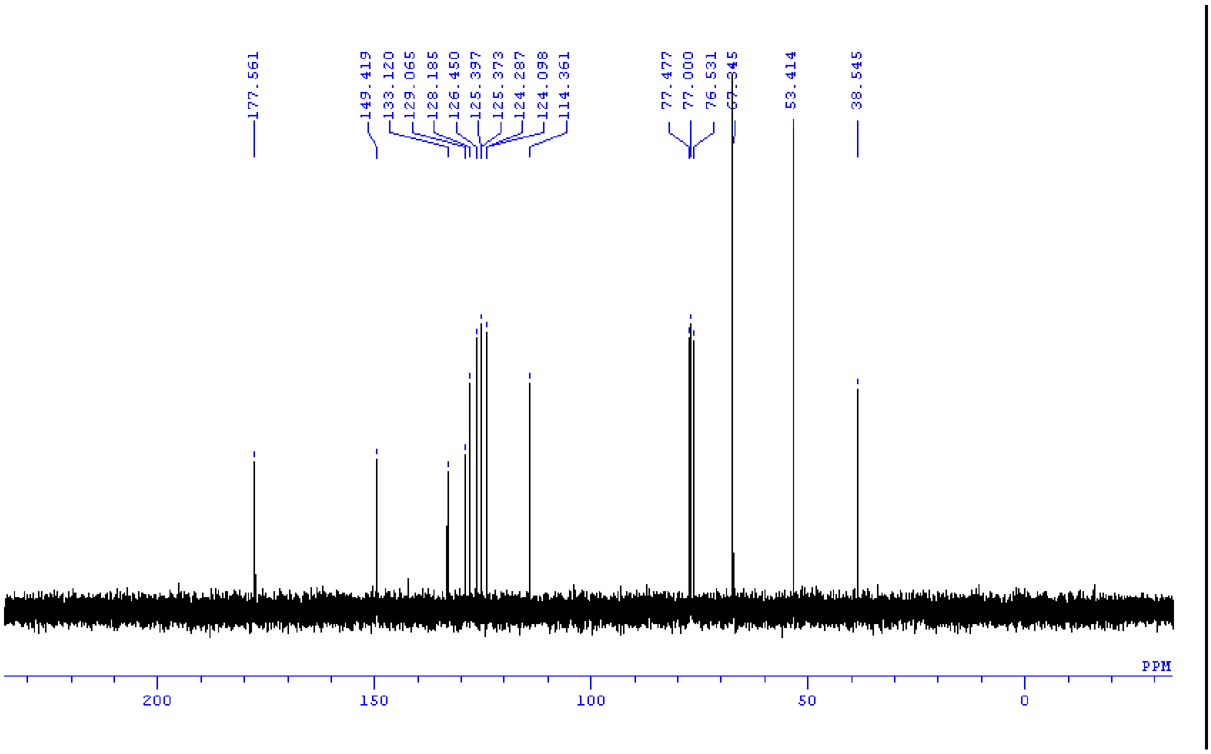
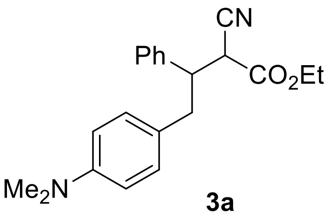
150
100
50
0



1h







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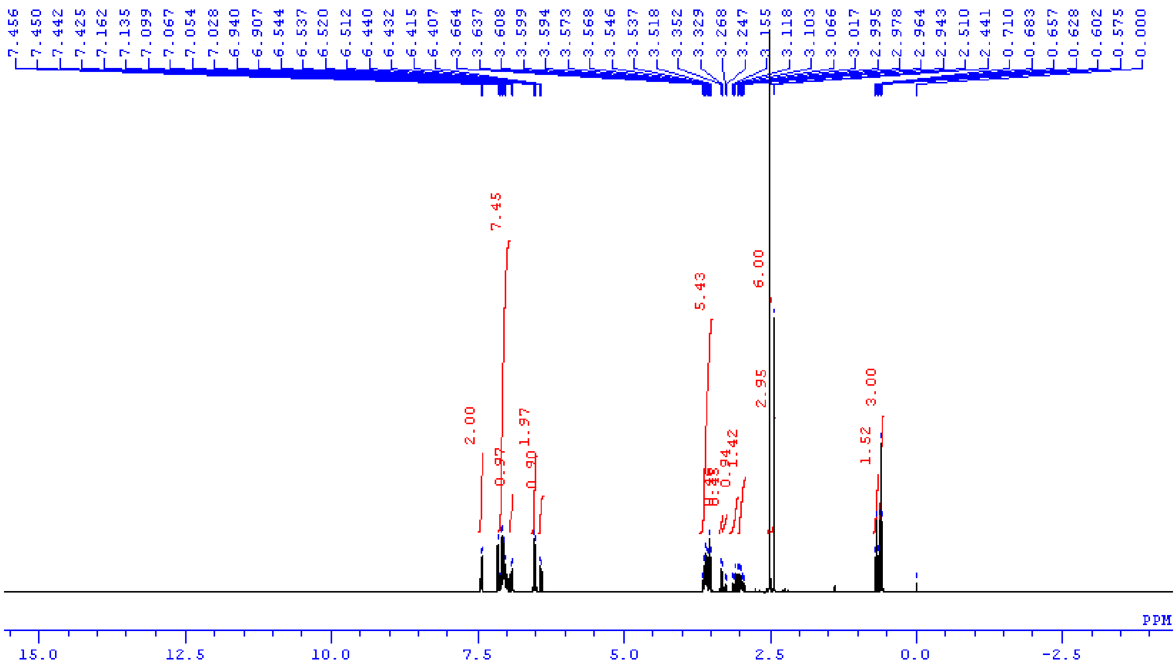

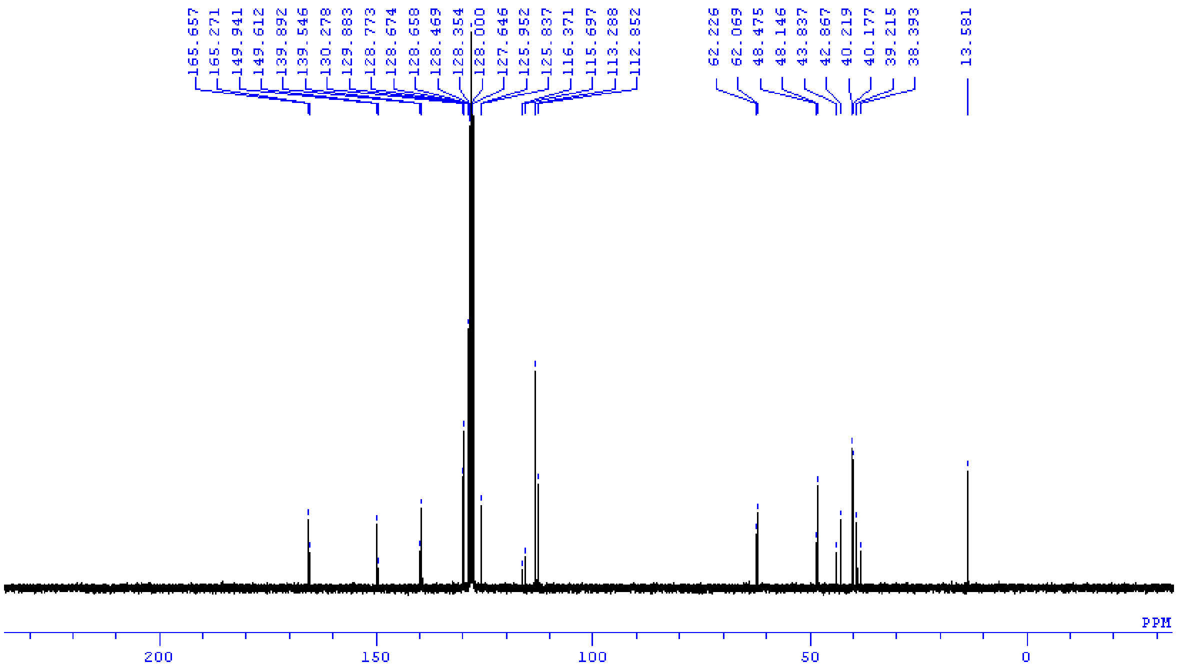

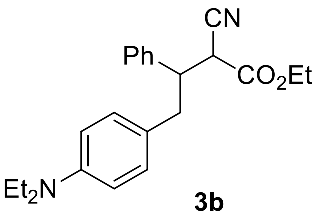

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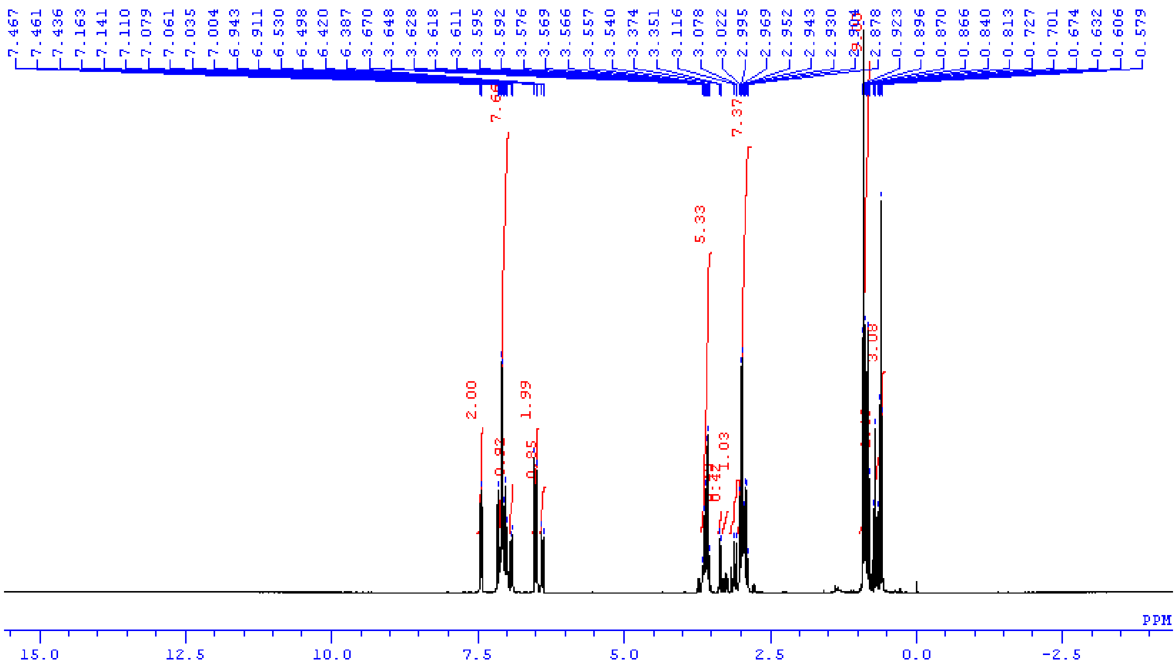
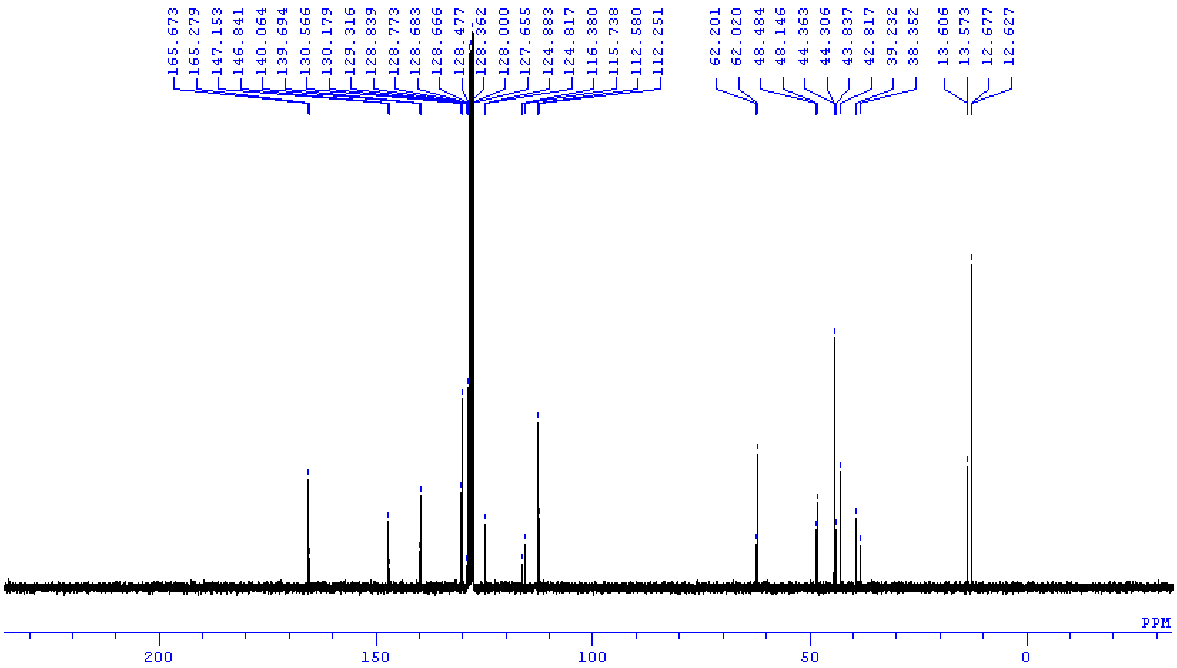
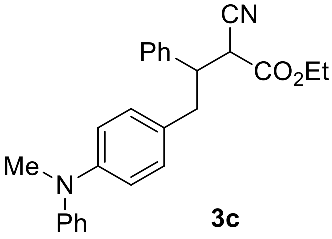
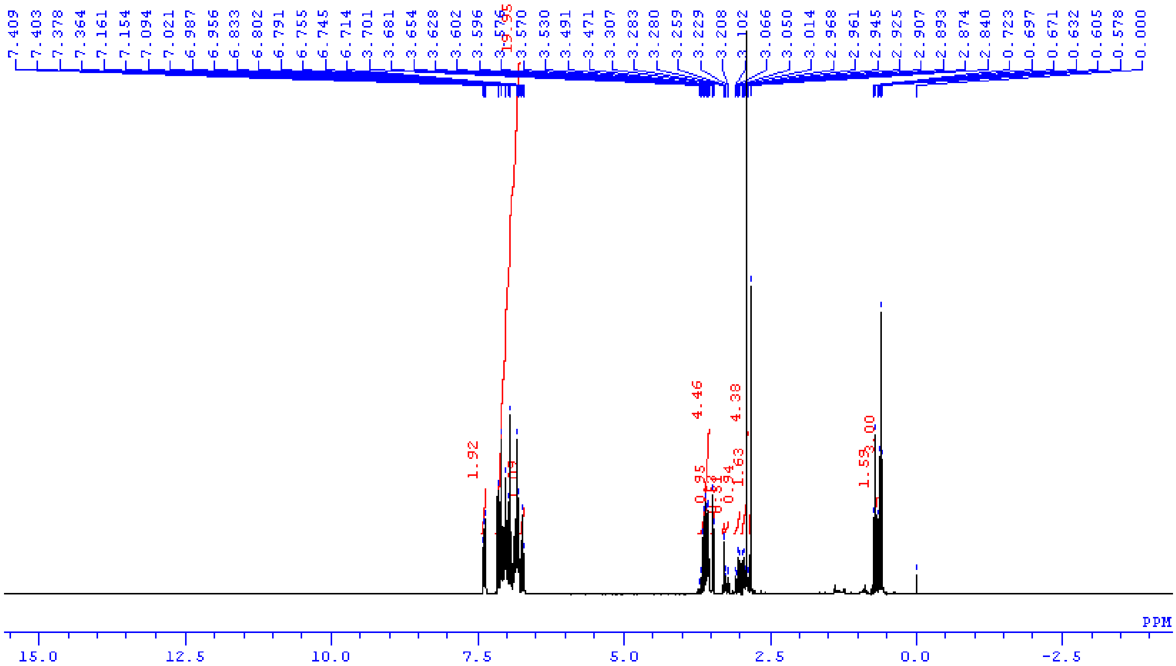





CN
Ph
CO_2Et
Me
N
Ph

3c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1.92
19.95
4.46
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3.00
PPM
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10.0
7.5
5.0
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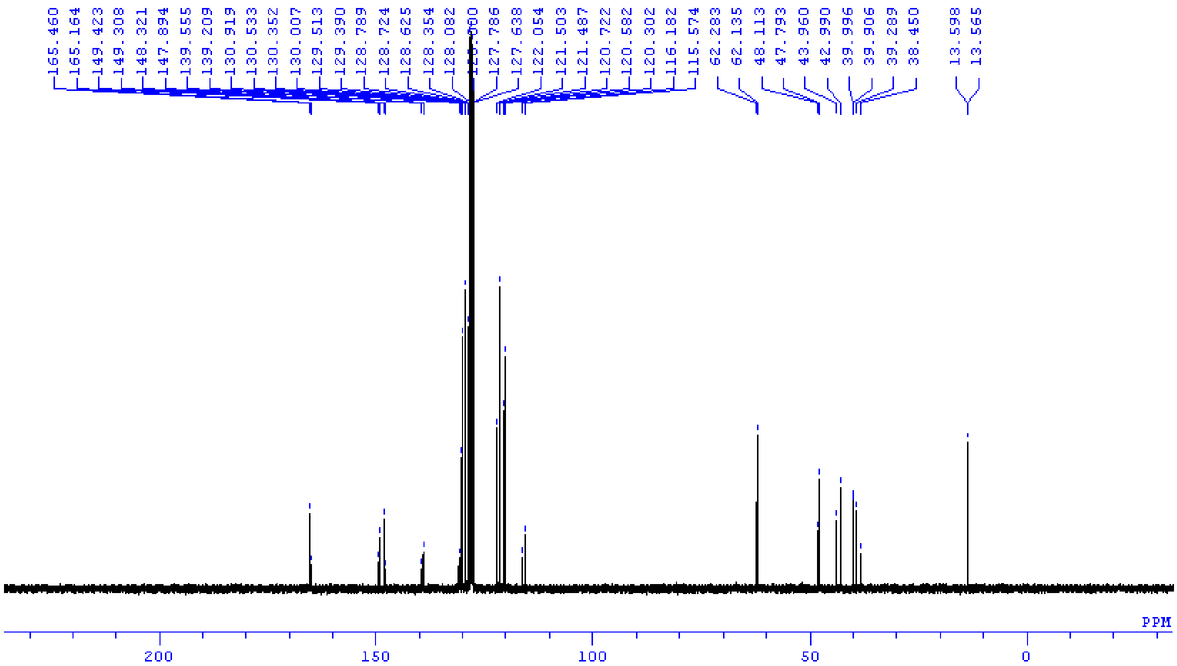
0.0
-2.5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PPM
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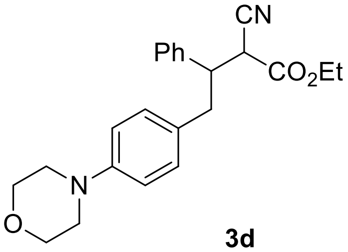
150
100
50
0



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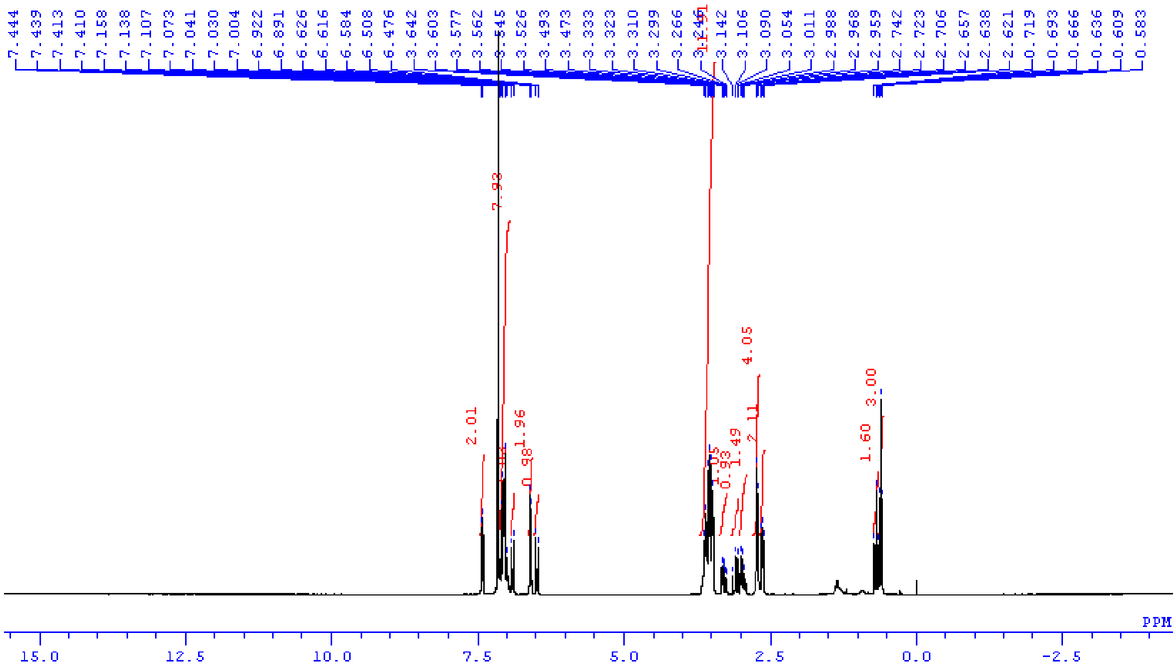
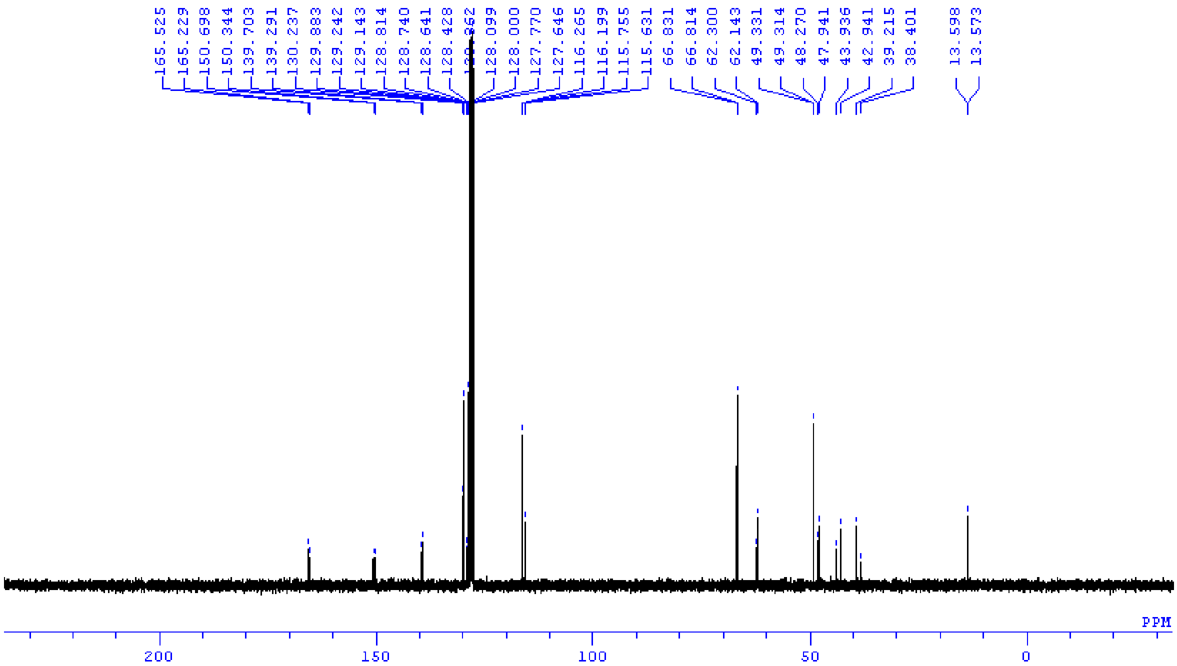
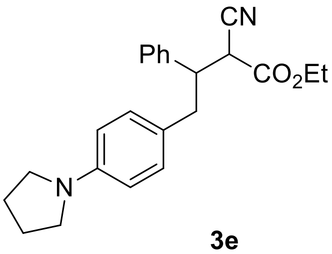
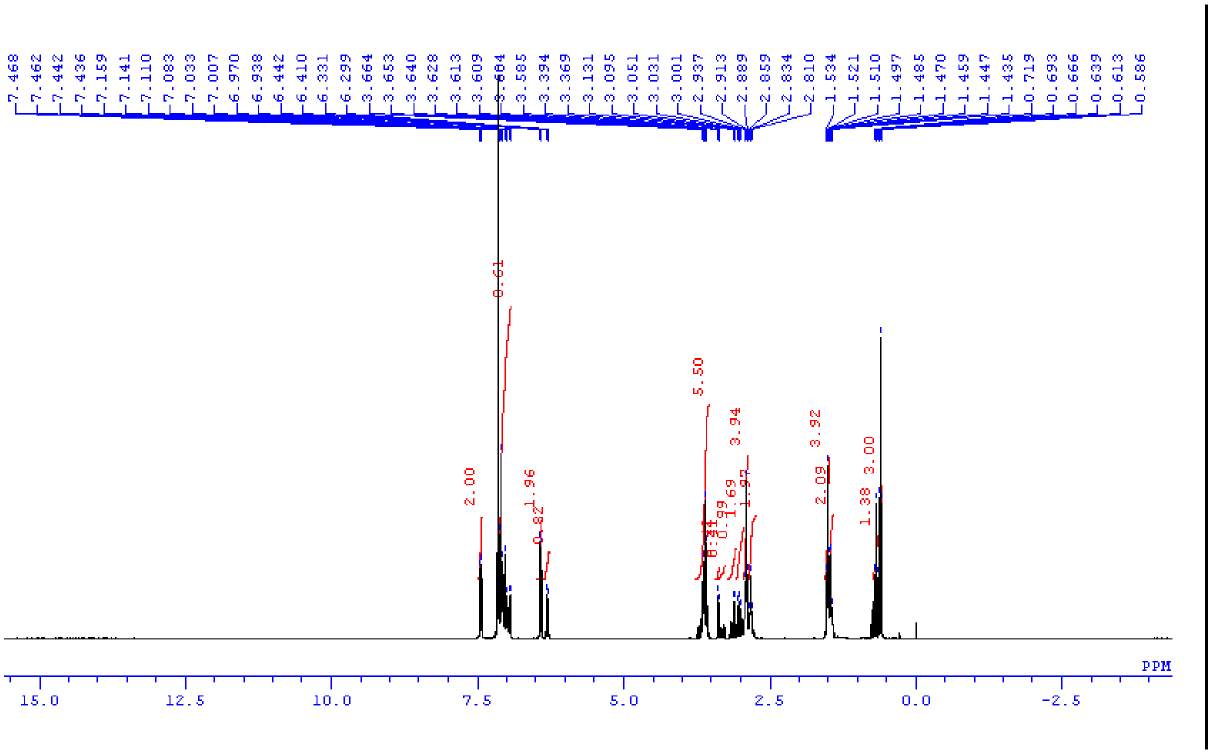





CN
Ph
CO_2Et
N

3e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PPM
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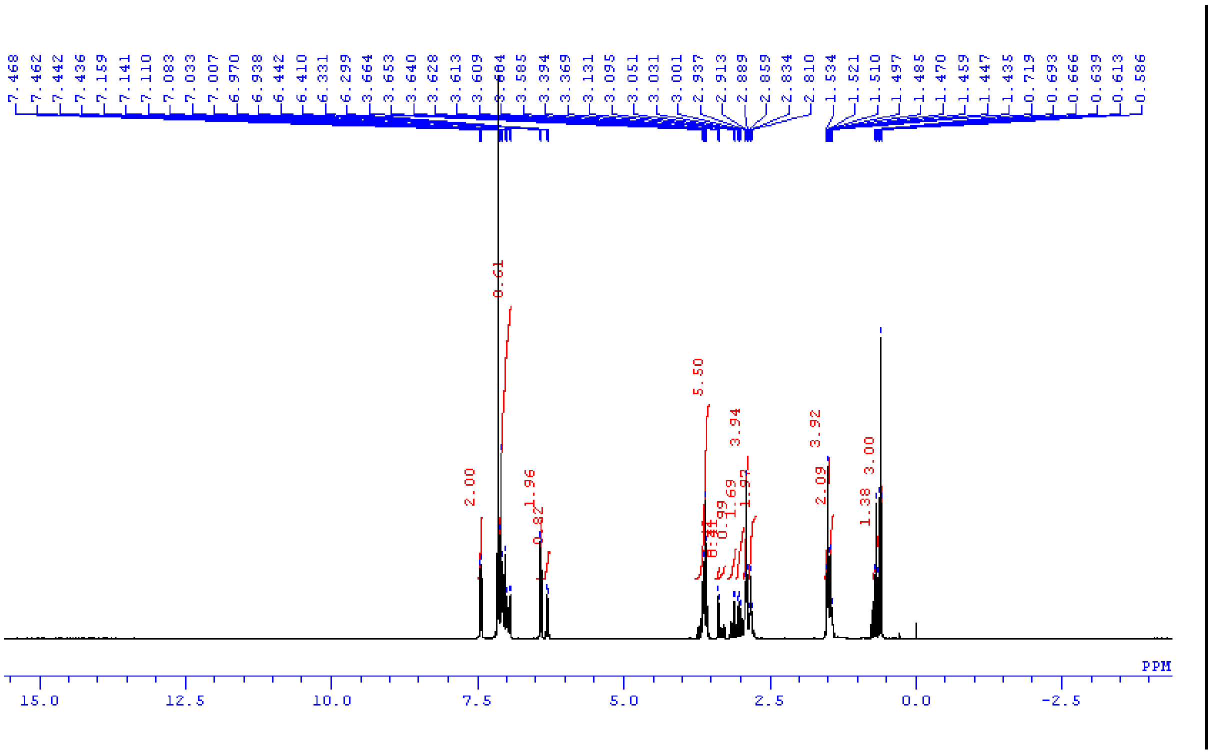
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PPM
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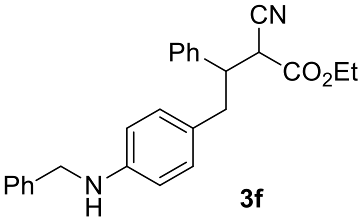
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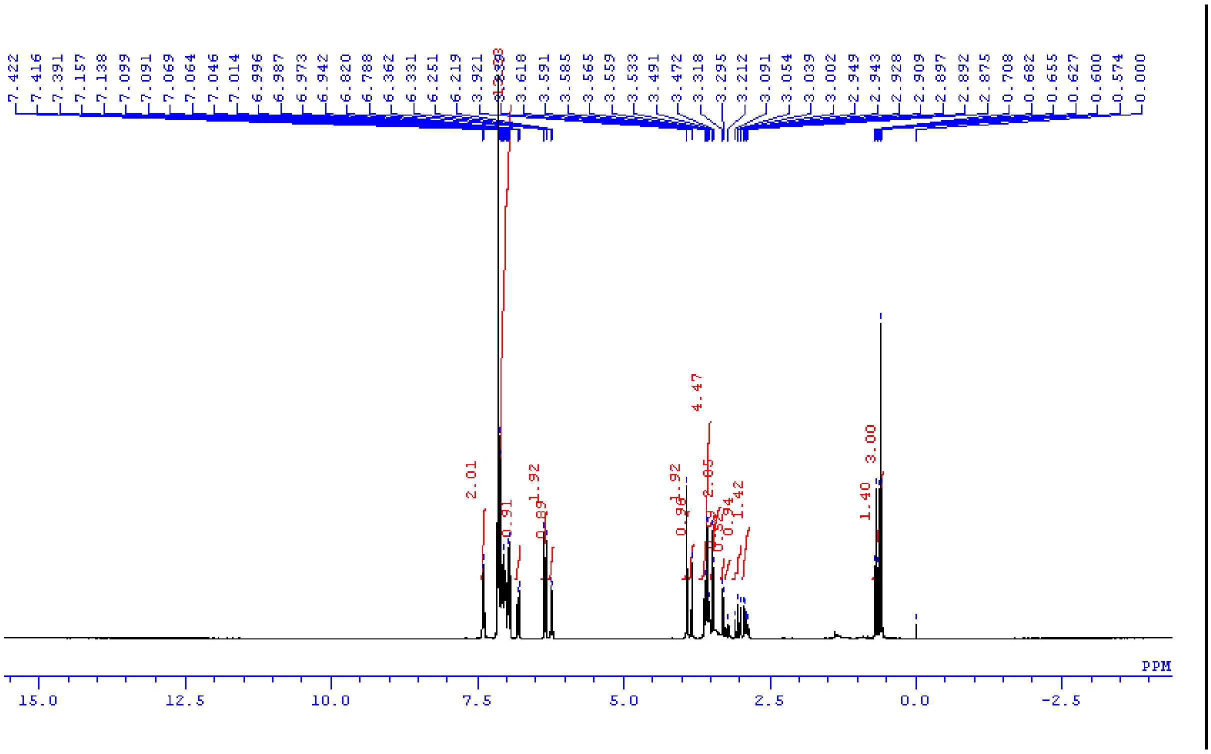
CO2Et
Ph
N
H

3f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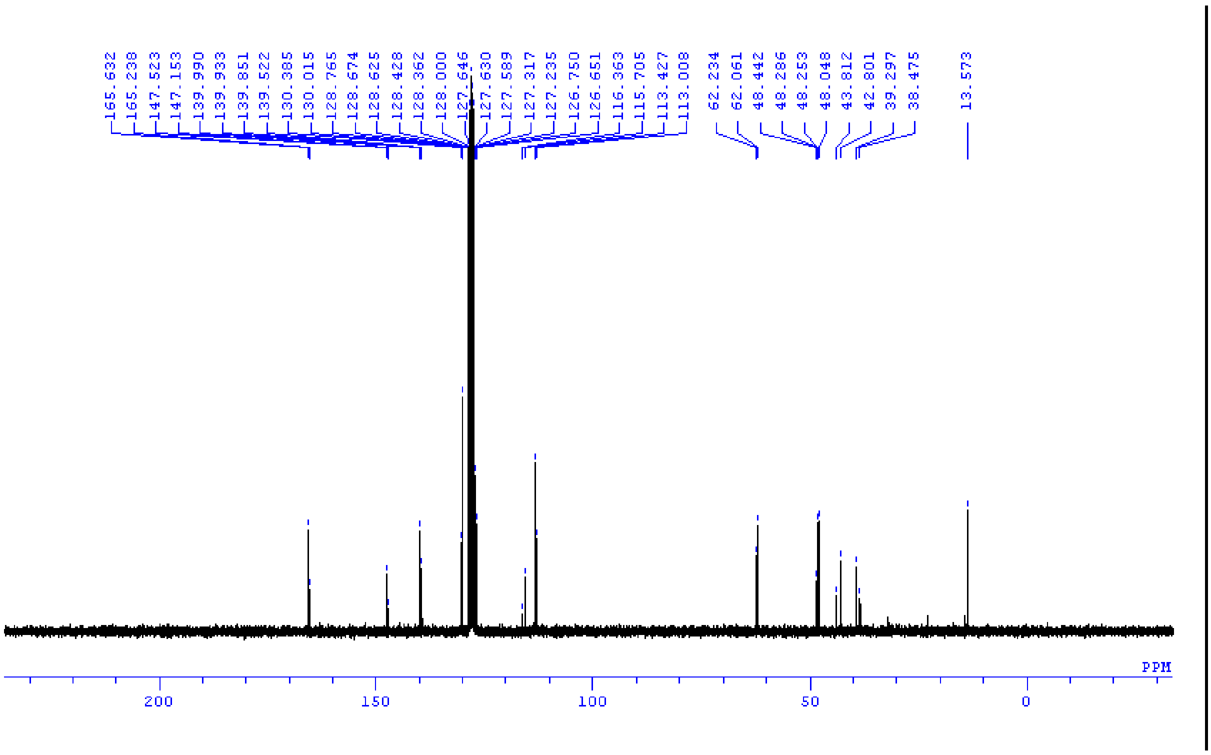
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13.573
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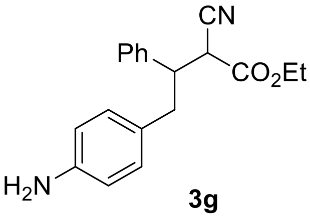
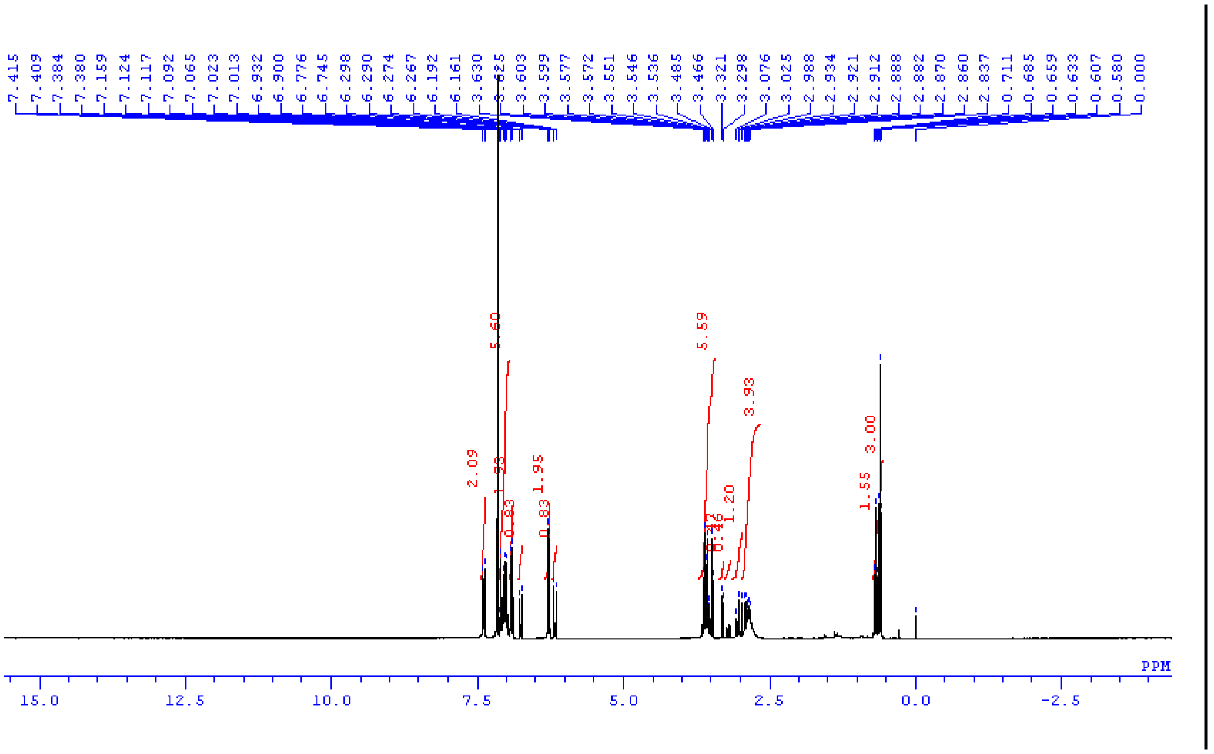
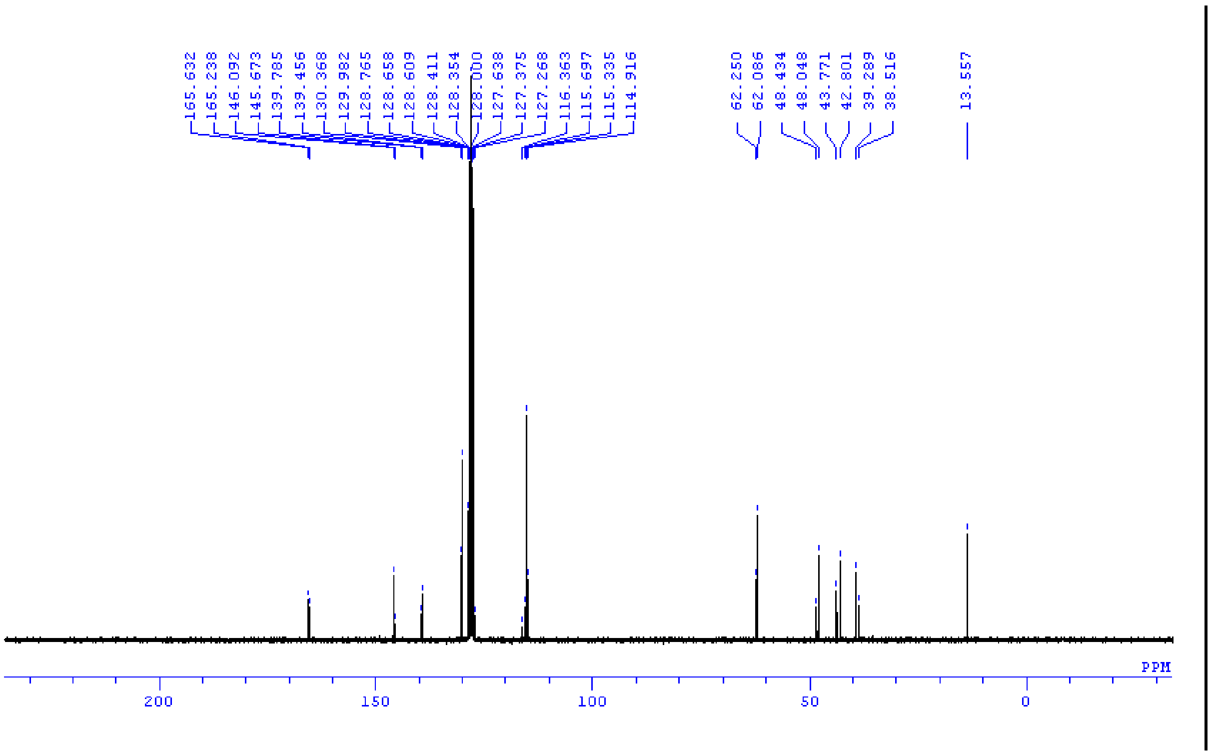
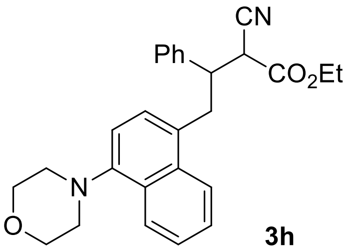


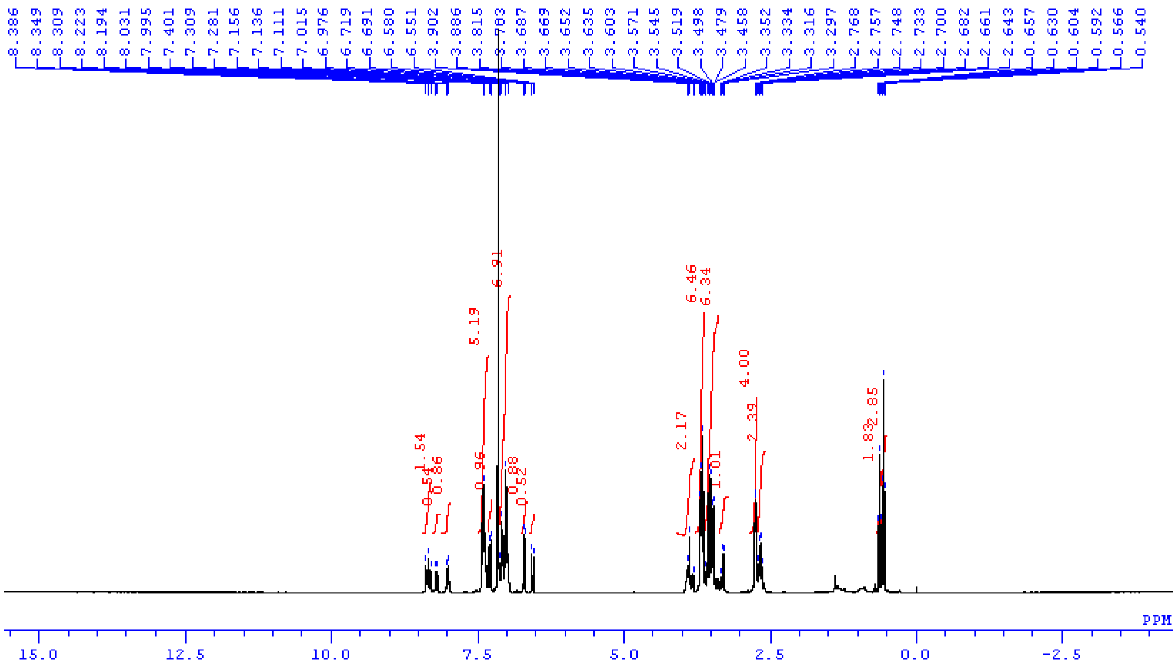
3g






CN
Ph
CO_2Et
N
O

3h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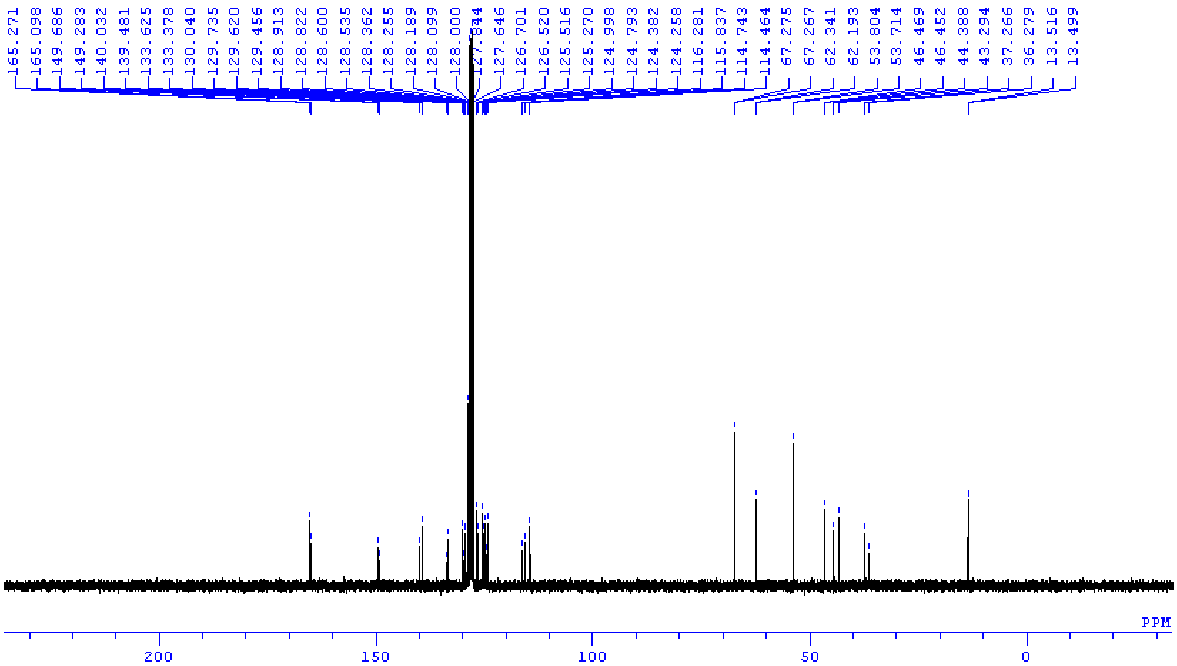
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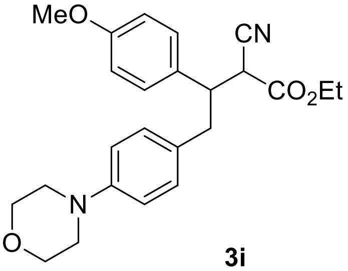
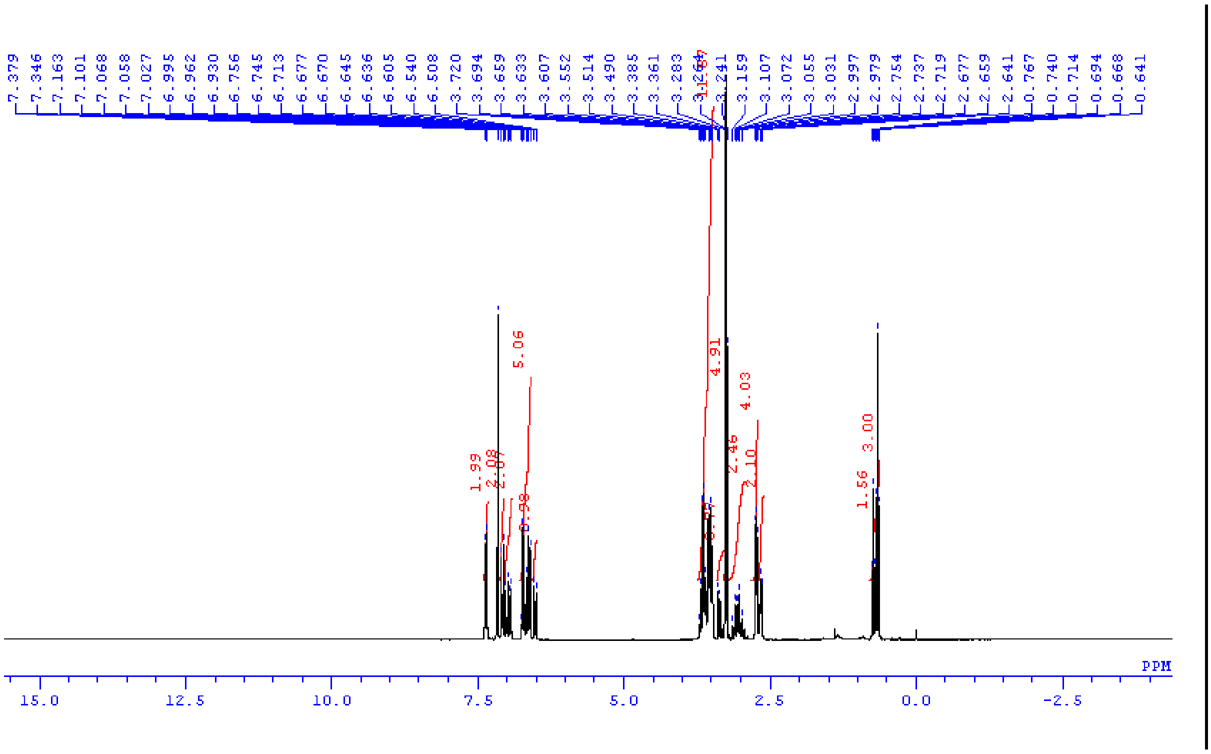

MeO
CN
CO2Et
N
O

3i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1.99 2.08 2.07 5.06 4.91 2.46 4.03 2.10 1.56 3.00
PPM
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12.5
10.0
7.5
5.0
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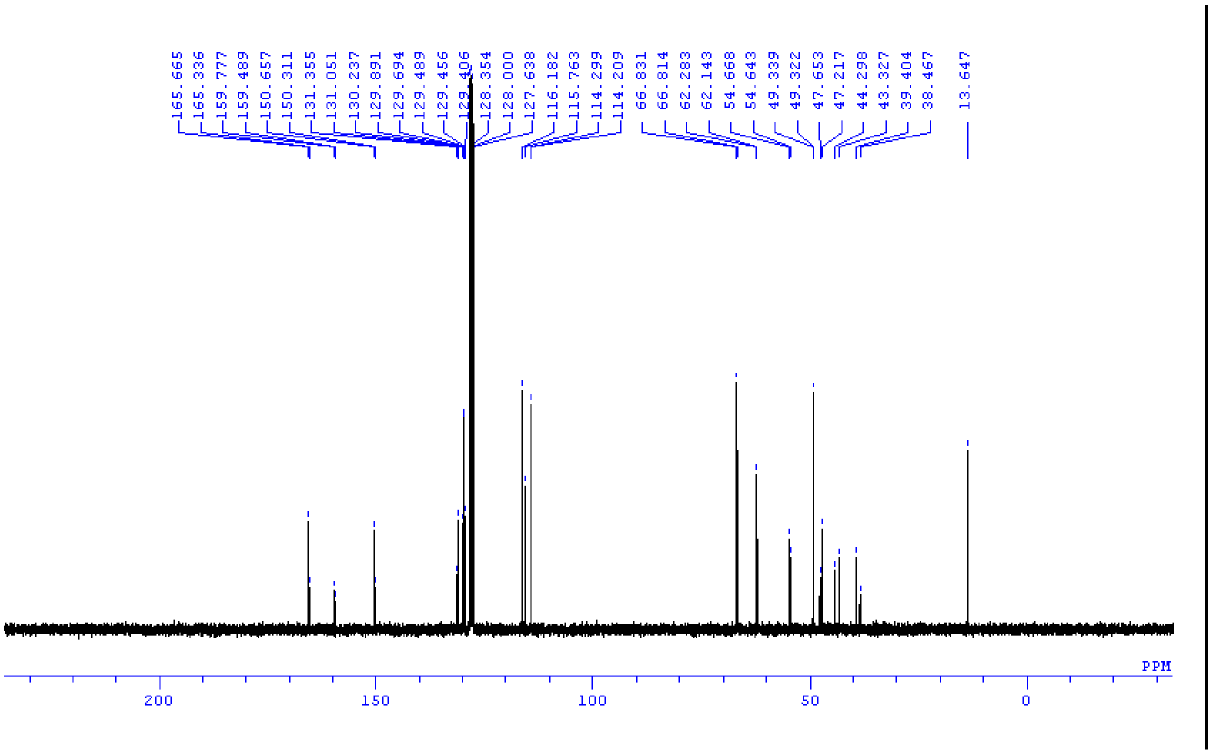
-2.5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PPM
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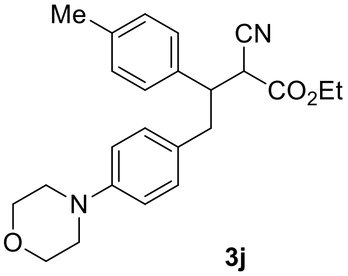
150
100
50
0



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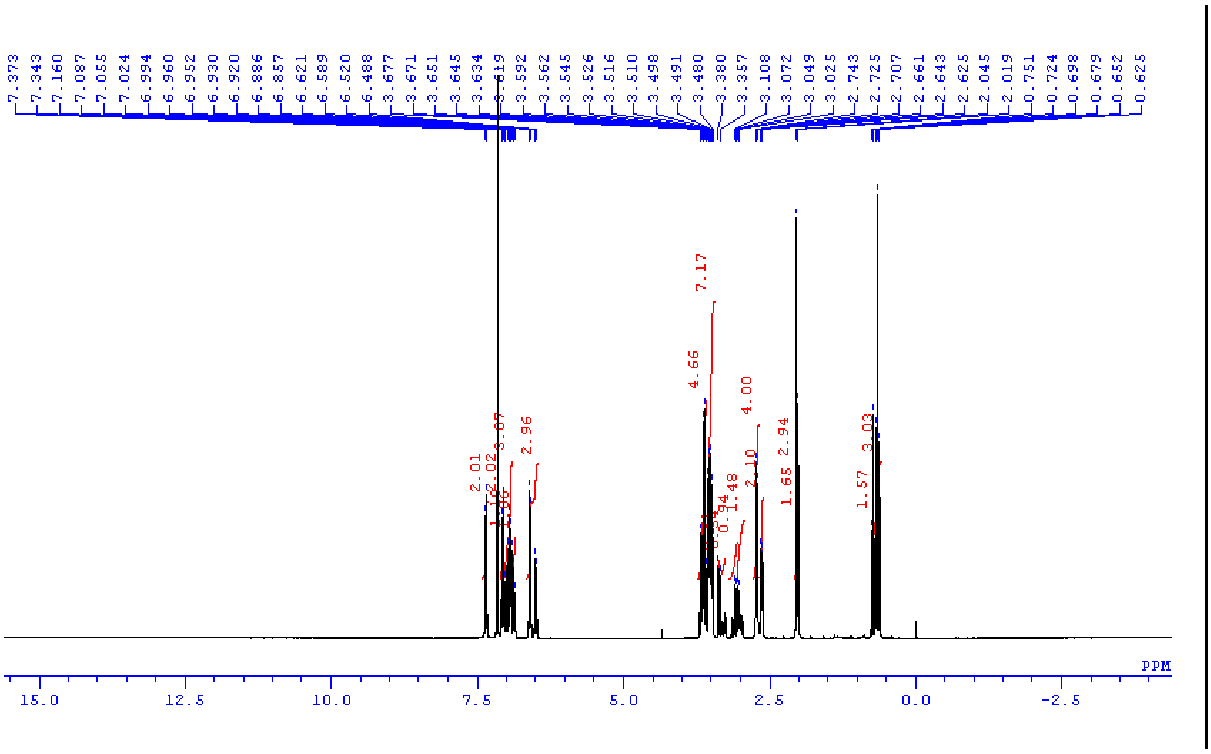

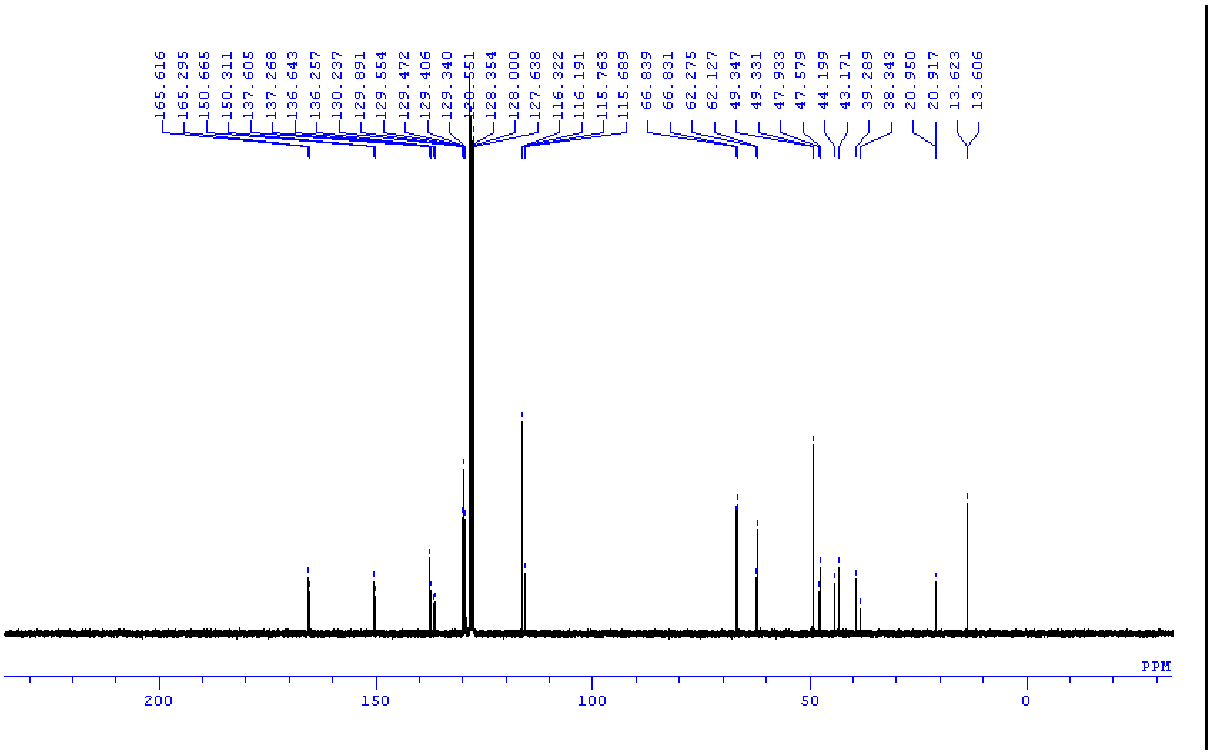

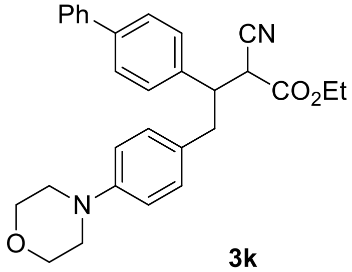

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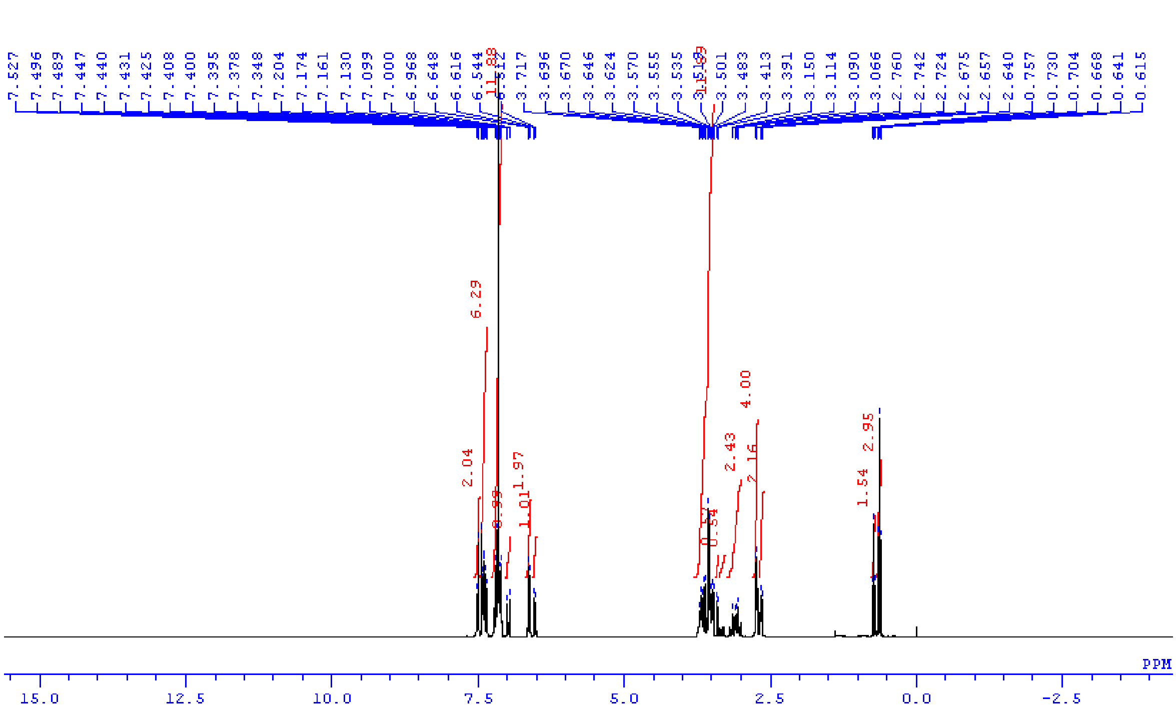

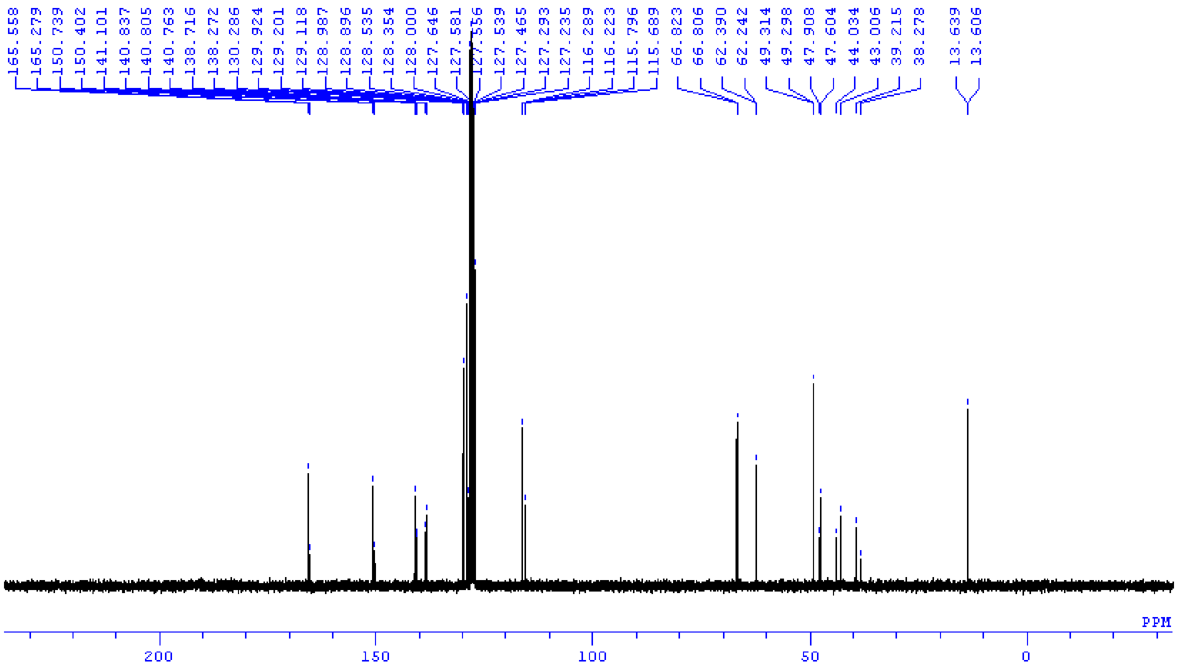

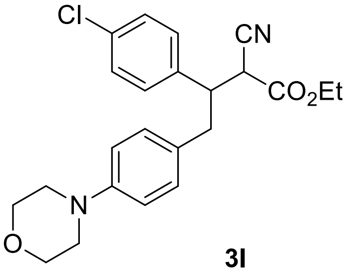
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CN
CO2Et
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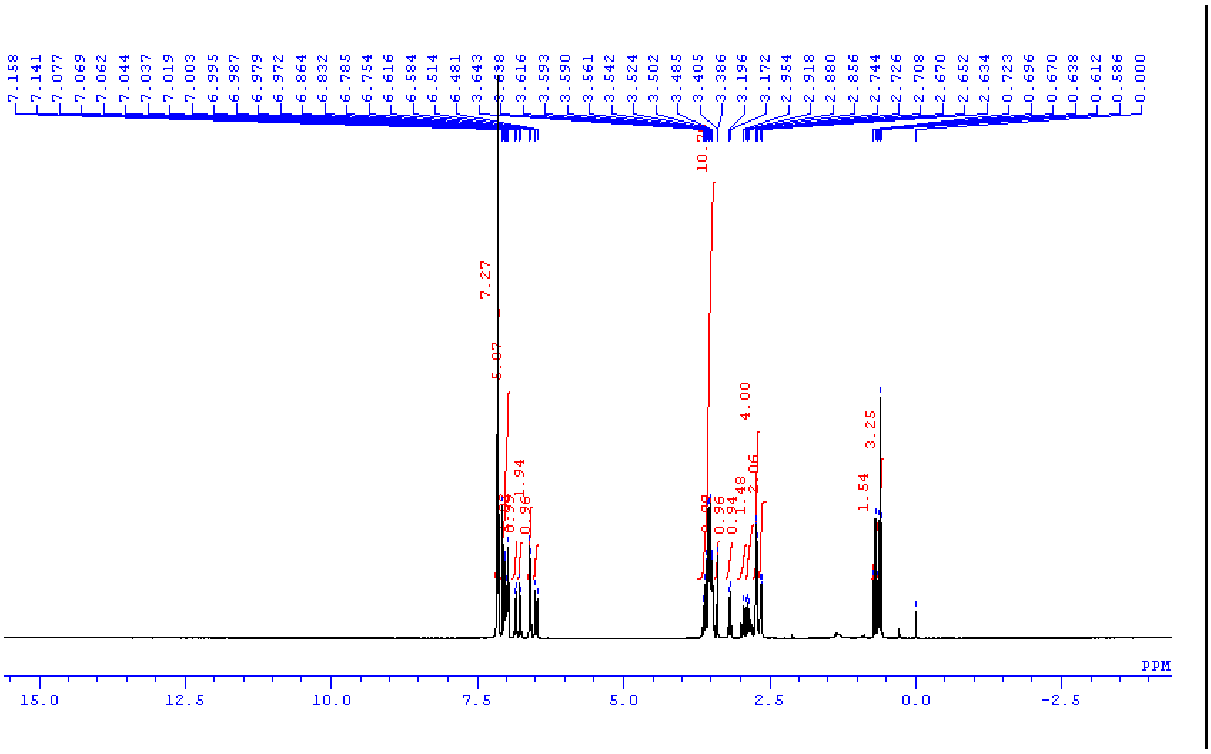
O

3l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6.972
6.864
6.832
6.785
6.754
6.616
6.584
6.514
6.481
3.643
3.638
3.616
3.593
3.590
3.561
3.542
3.524
3.502
3.485
3.405
3.386
3.196
3.172
2.954
2.918
2.880
2.856
2.744
2.726
2.708
2.670
2.652
2.634
0.723
0.696
0.670
0.638
0.612
0.586
0.000
7.27
5.07
1.94
4.00
3.25
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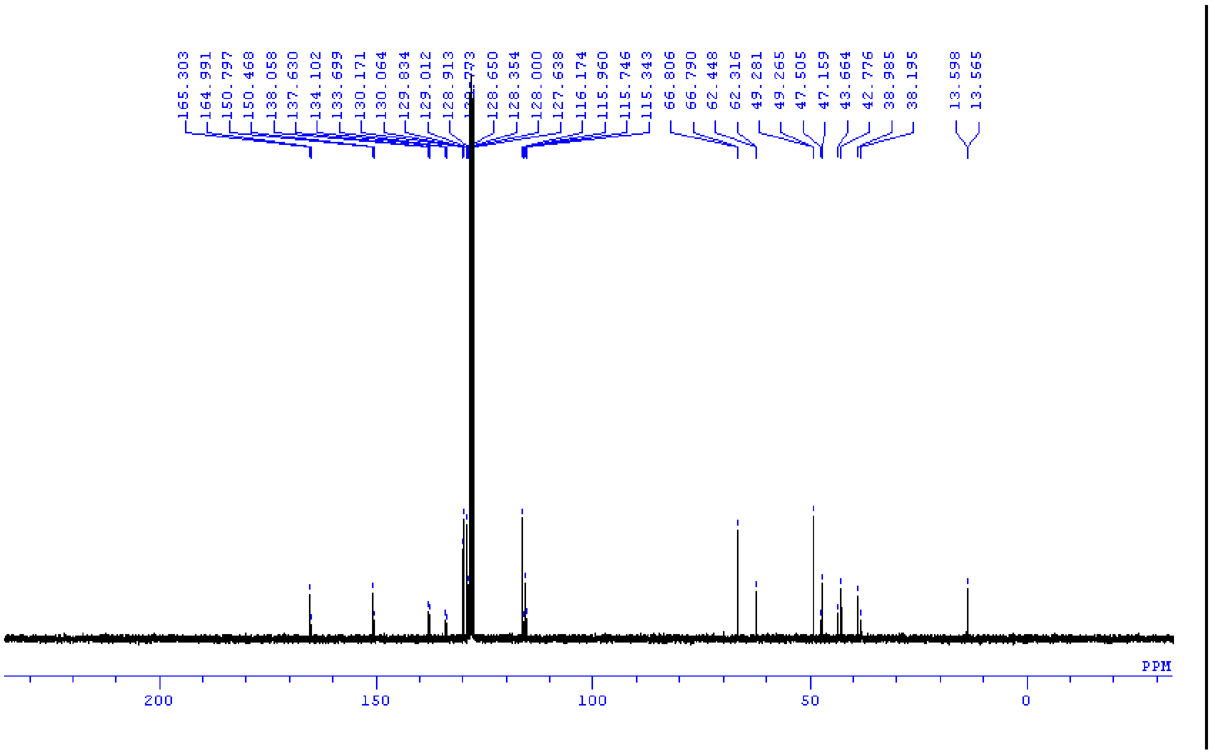
PPM
15.0
12.5
10.0
7.5
5.0
2.5
0.0
-2.5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128.650
128.354
128.000
127.638
116.174
115.960
115.746
115.343
66.806
66.790
62.448
62.316
49.281
49.265
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42.776
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13.565
PPM
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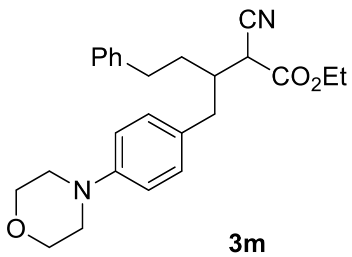
150
100
50
0



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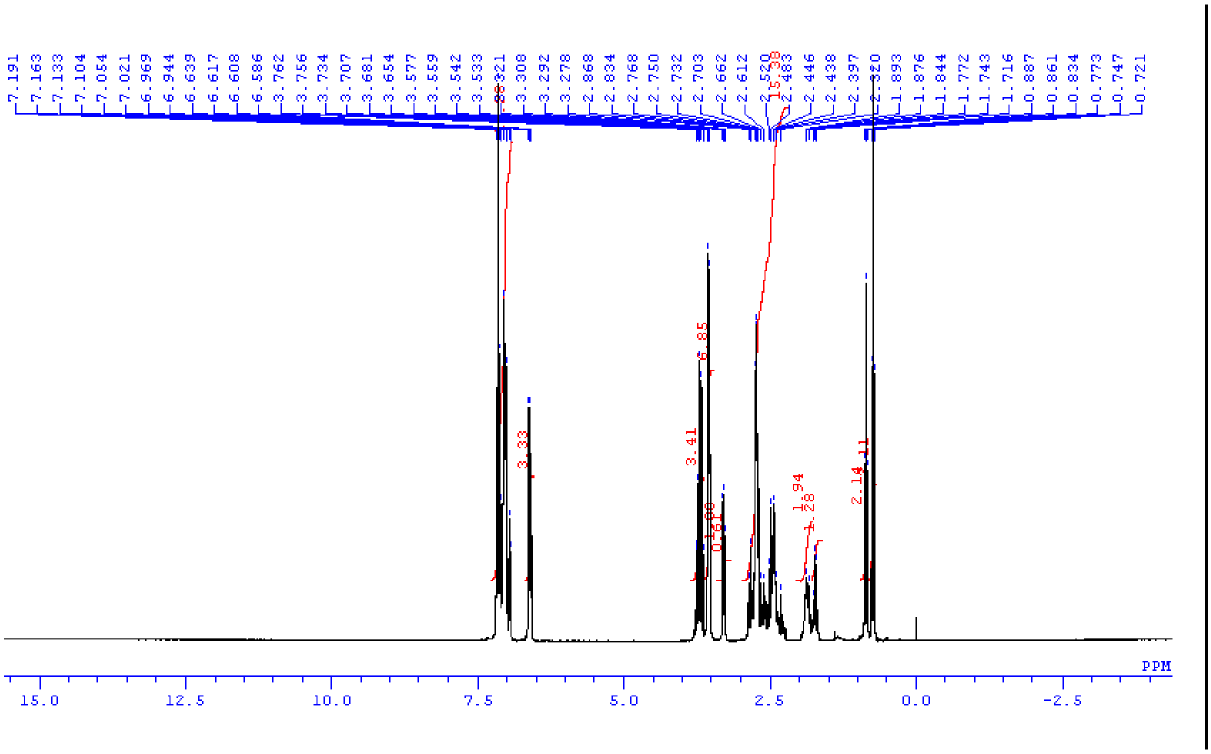
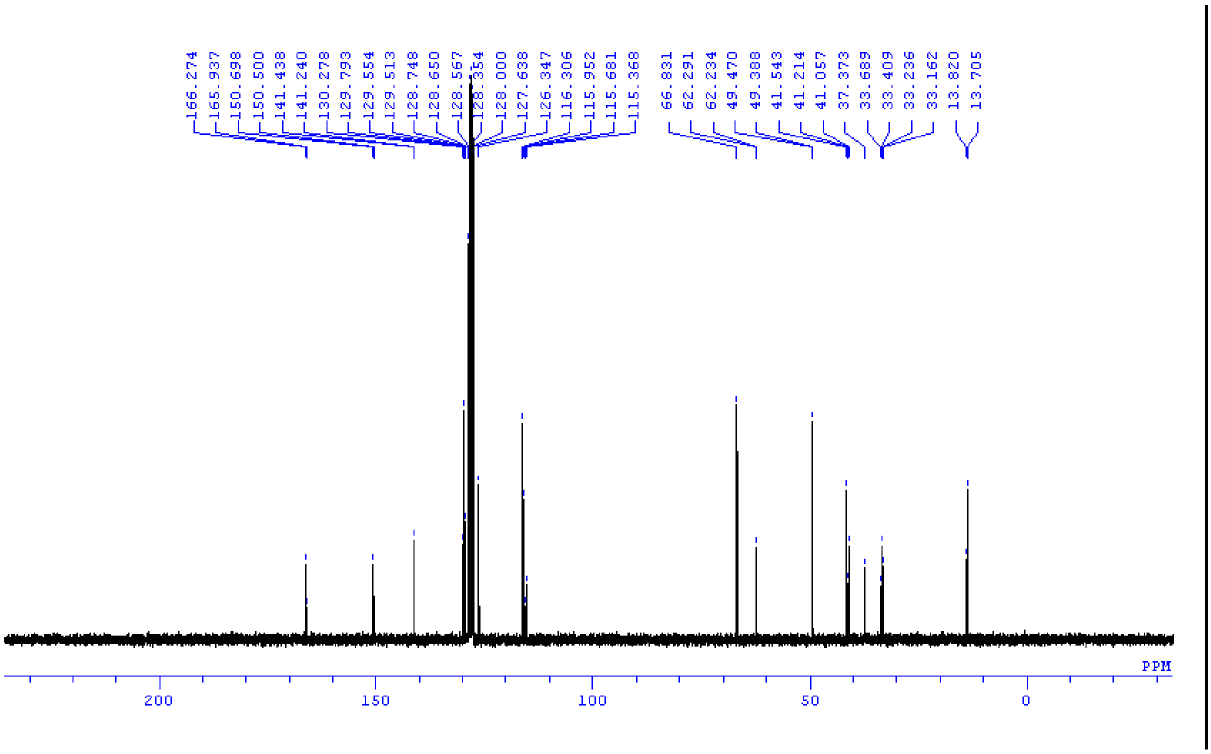
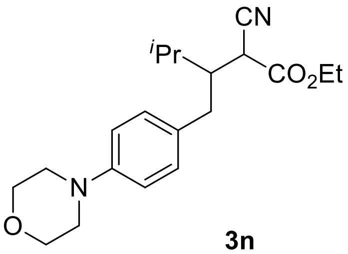
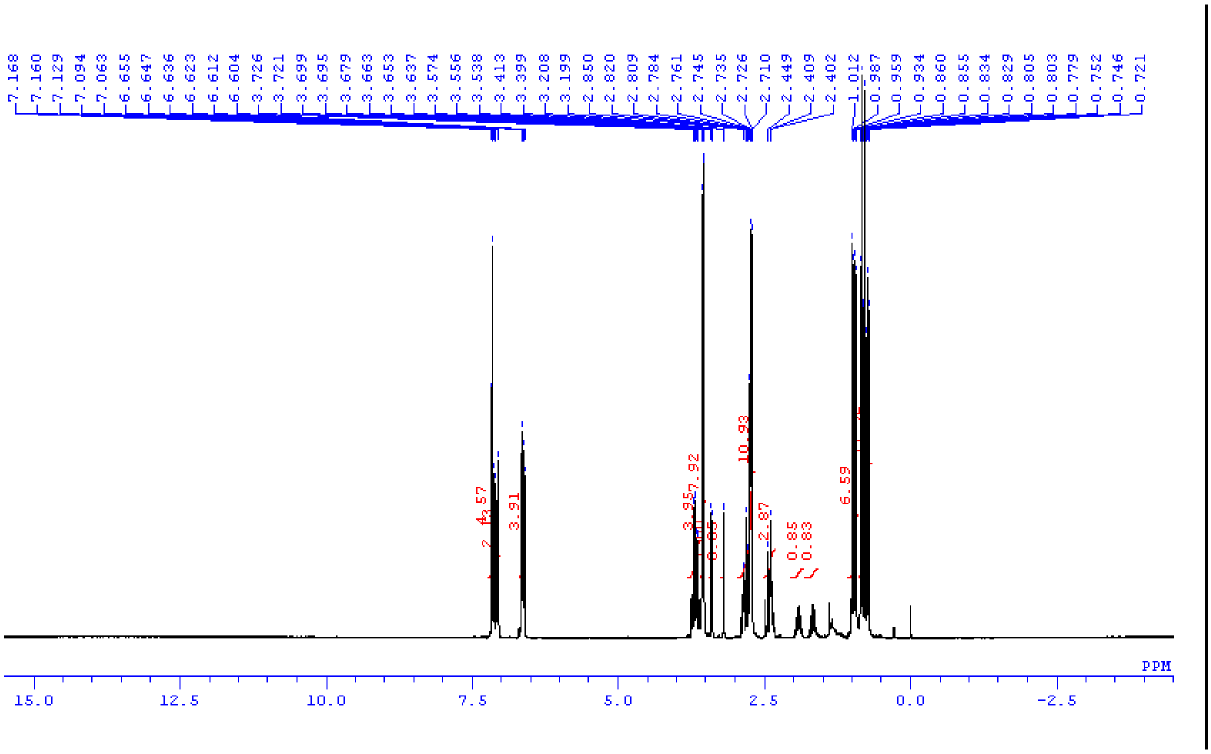





CN
iPr
CO2Et
N
O

3n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4.57
3.91
3.95
7.92
10.93
2.87
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PPM
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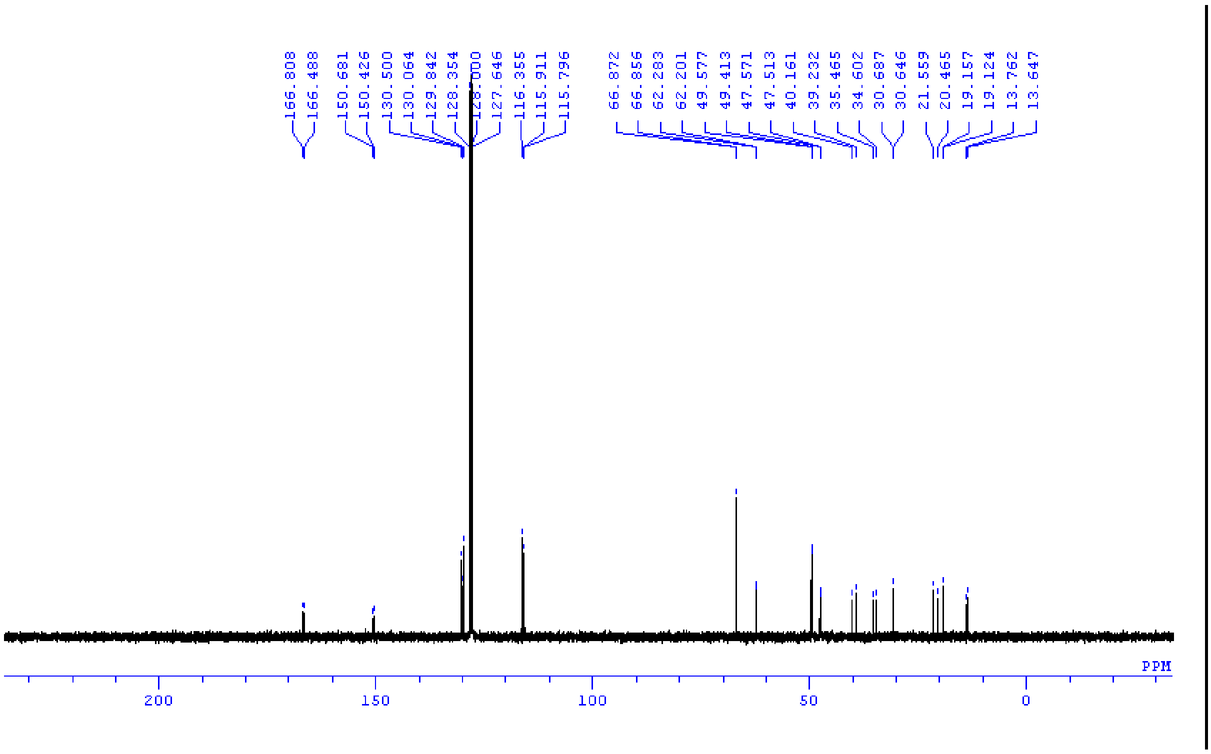
-2.5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50
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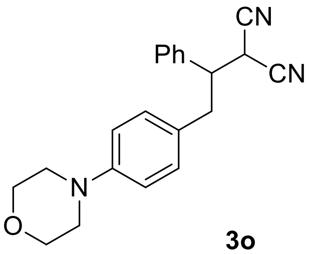

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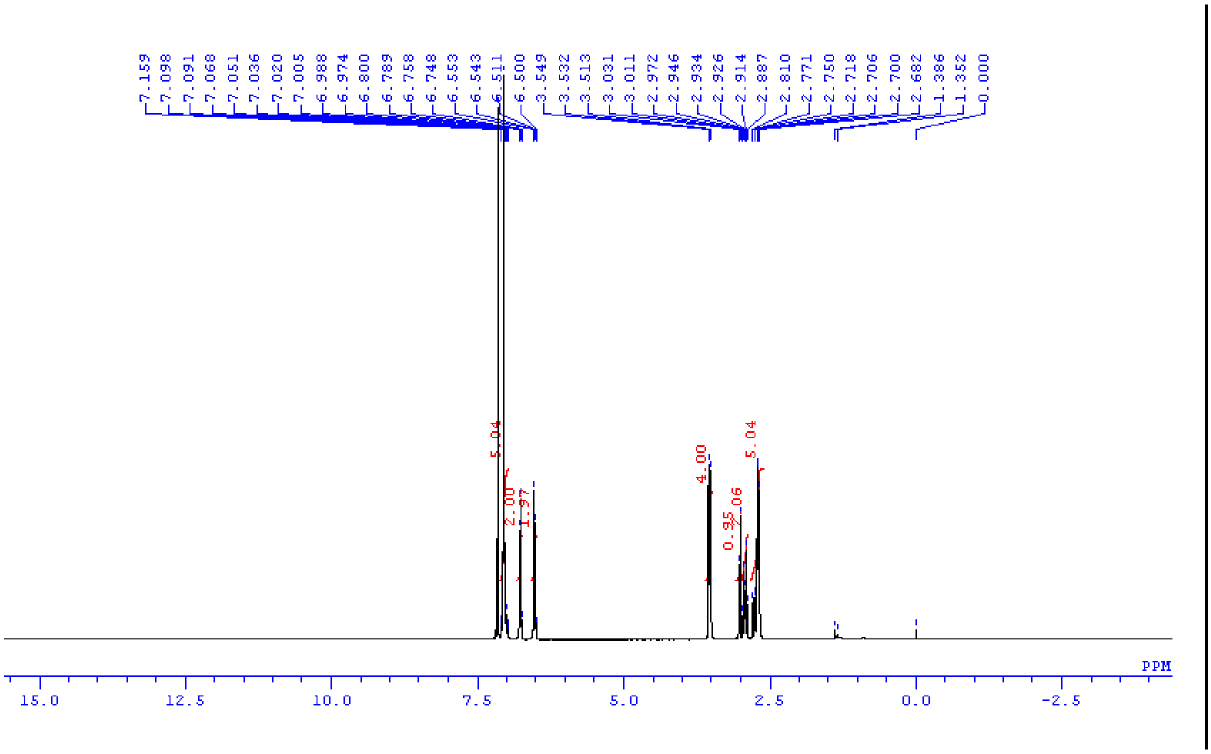

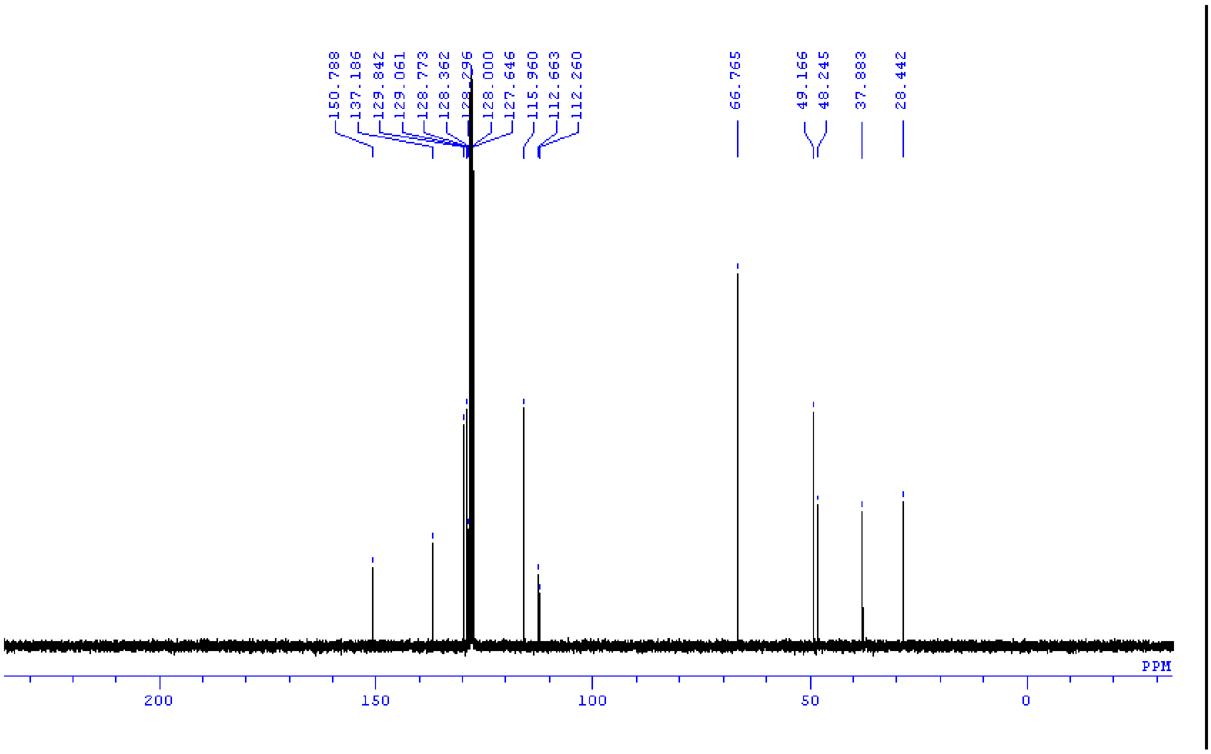

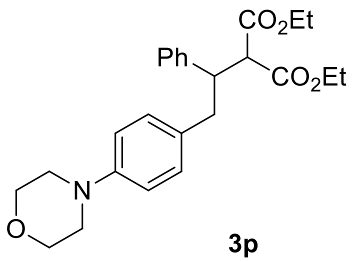

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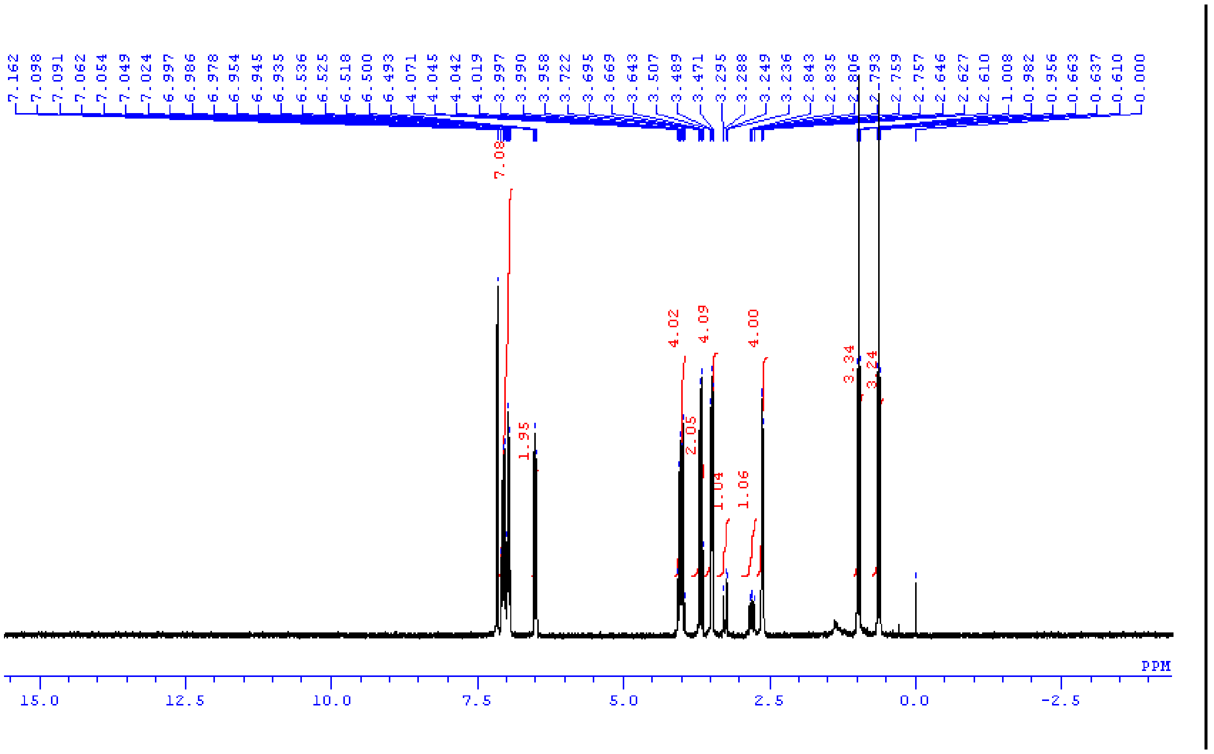

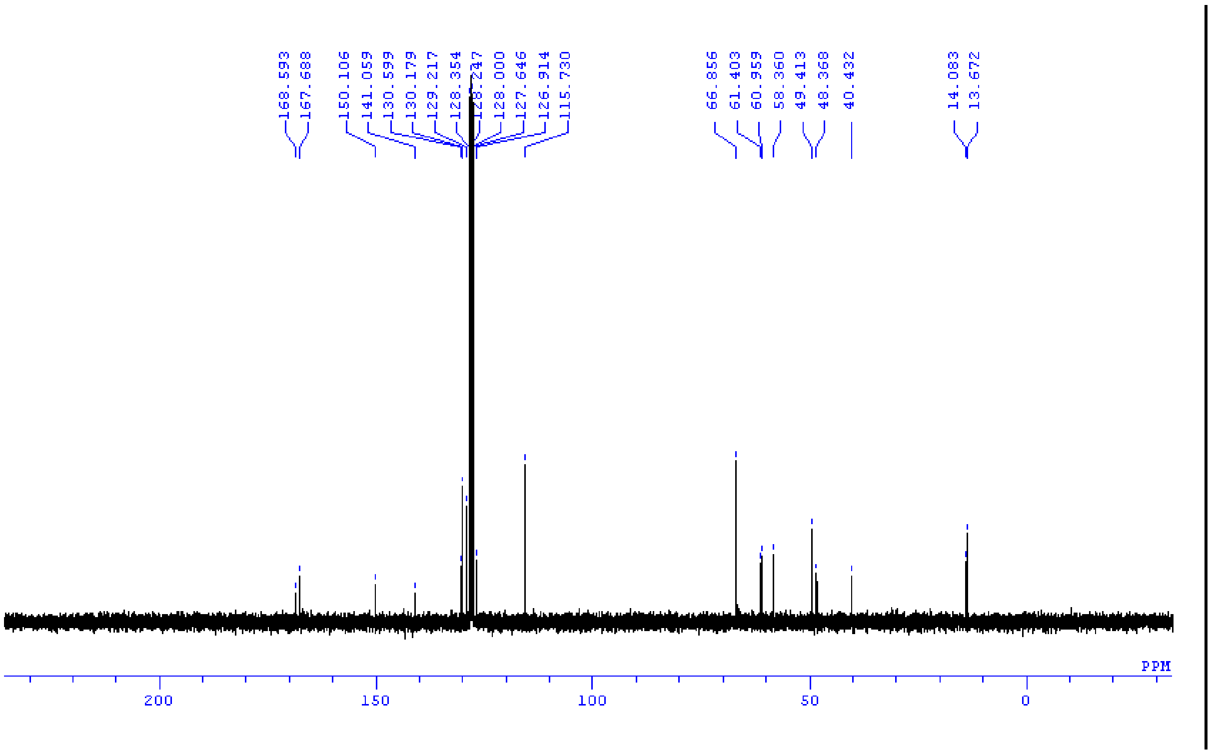

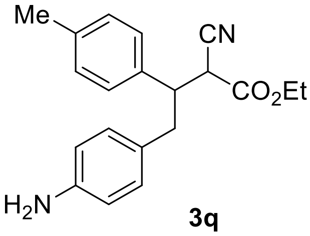

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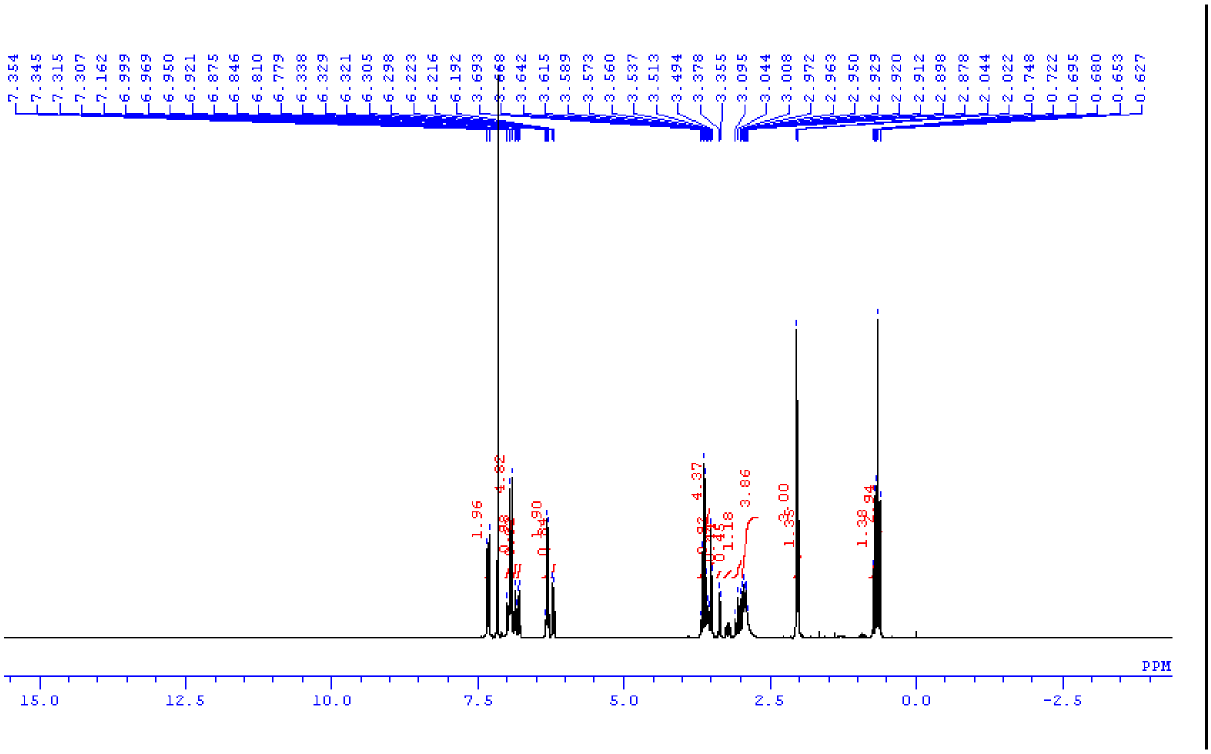

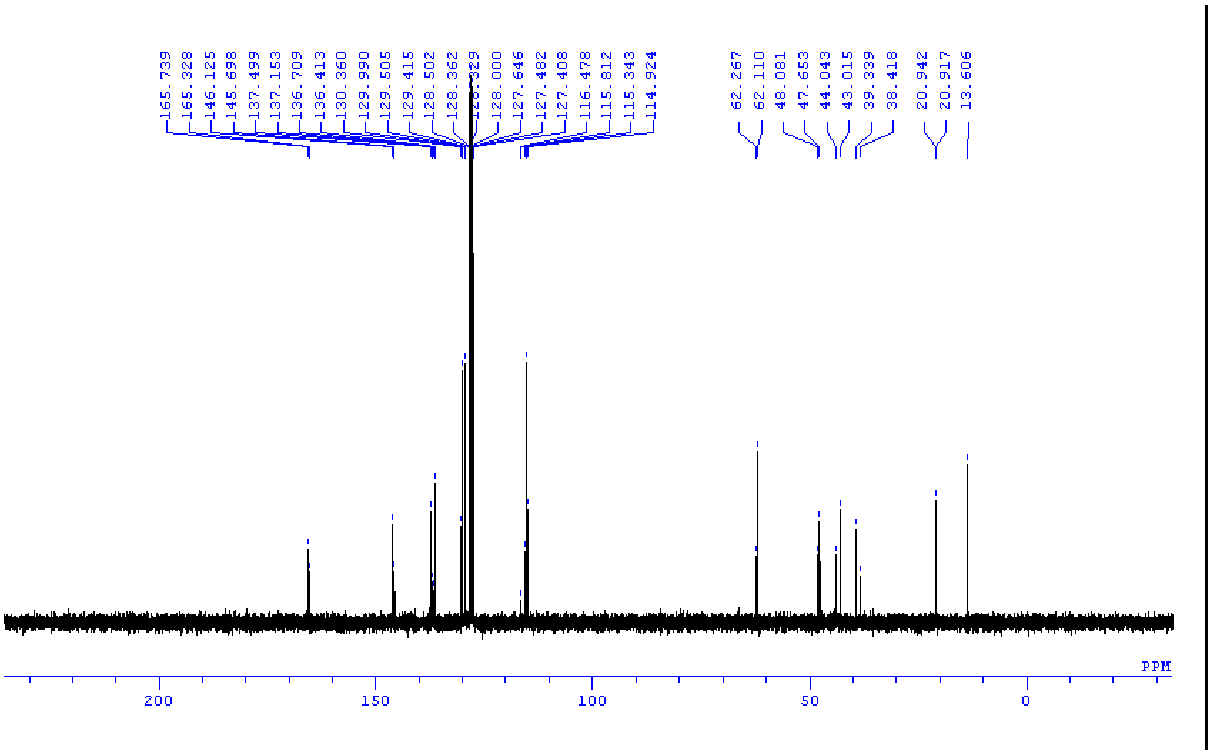

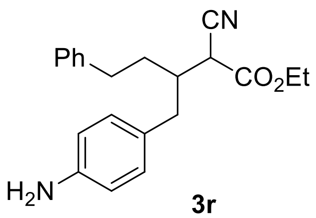

3r