Electronic Supplementary Material (ESI) for ChemComm.

Synthesis of nitrogen heterocycles via α-aminoalkyl radicals generated from α-silyl secondary-amines under visible light irradiation

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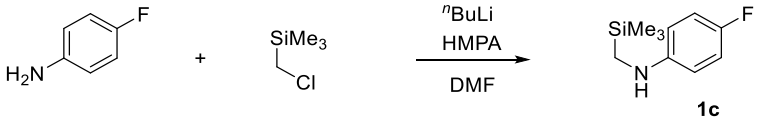
General method.

^{1}H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvents. 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 spectrometers. 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.

Nitrogen heterocycles **3f**,[S1a] **3h**,[S1b] **3r**,[S1c] **3s**,[S1d] **7a**,[S2a] and **7b**[S2b] are known compounds. Preparation of α-silylamines **1a**,[S3a] **1b**,[S3b] **1d**,[S3b] **1f**,[S3a] and **1h**[S3c] were reported elsewhere. α,β-Unsaturated carbonyl compounds **2** and **5** were prepared by Knövenagel condensation.[S4] Photocatalysts were synthesized according to the literature procedure.[S5]

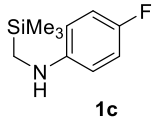
Preparation of α-silylamines 1c, 1e, and 1g.



1c

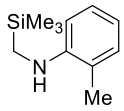
A typical experimental procedure for the synthesis of *N*-(trimethylsilyl)methyl-4-fluoroaniline **1c** is described below. To a flame-dried 100 mL flask were placed THF (40 mL) and 4-fluoroaniline (1.20 mL, 12.7 mmol). ^{n}BuLi (1.65 M in hexane, 6.20 mL, 10.2 mmol) was added dropwise at -78 °C, and the resulting mixture was stirred at room temperature for 1 h. Hexamethylphosphoramide (HMPA, 1.70 mL, 9.77 mmol) and (chloromethyl)trimethylsilane (1.40 mL, 10.0 mmol) were added at -78 °C, then the resulting mixture was stirred at room temperature for 16 h. Water (*ca.* 50 mL) was added, and the resulting mixture was extracted with Et_2O (*ca.* 30 mL x 3). The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography (eluent: hexane) to give *N*-(trimethylsilyl)methyl-4-fluoroaniline **1c** (1.45 g, 7.34 mmol).

Isolated yields and spectroscopic data of α-silylamines **1c**, **1e**, and **1g** are as follows:



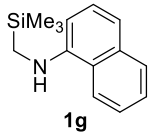
1c

1c: 73% Yield. An orange oil. ^{1}H NMR ($CDCl_3$) δ 6.98-6.89 (m, 2H), 6.66-6.58 (m, 2H), 3.39 (br, 1H), 2.49 (s, 2H), 0.2 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 155.6 (d, $^{1}J_{C\text{-}F}$ = 233.6 Hz), 146.9 (d, $^{4}J_{C\text{-}F}$ = 1.7 Hz), 115.4 (d, $^{2}J_{C\text{-}F}$ = 22.3 Hz), 113.0 (d, $^{3}J_{C\text{-}F}$ = 7.3 Hz), 34.2, -2.8. ^{19}F NMR ($CDCl_3$) δ -128.8. HRMS (EI) Calcd. for $C_{10}H_{16}FNSi$ [M]: 197.1036. Found: 197.1034.



1e

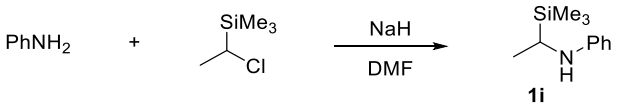
1e: 67% Yield. An orange oil. ^{1}H NMR ($CDCl_3$) δ 7.10 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 3.27 (br, 1H), 2.47 (s, 2H), 2.07 (s, 3H), 0.10 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 148.2, 129.7, 127.1, 121.5, 116.5, 109.3, 33.2, 17.1, -2.7. HRMS (EI) Calcd. for $C_{11}H_{19}NSi$ [M]: 193.1287. Found: 193.1289.



1g

1g: 23% Yield. A pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.93-7.86 (m, 2H), 7.58-7.46 (m, 3H), 7.33 (d, *J* = 8.1 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 4.33 (br, 1H), 2.74 (s, 2H), 0.33 (s, 9H).^{13}C NMR ($CDCl_3$) δ 145.5, 134.2, 128.7, 126.7, 125.6, 124.5, 123.4, 119.4, 116.9, 104.0, 33.4, -2.5. HRMS (EI) Calcd. for $C_{14}H_{19}NSi$ [M]: 229.1287. Found: 229.1293.

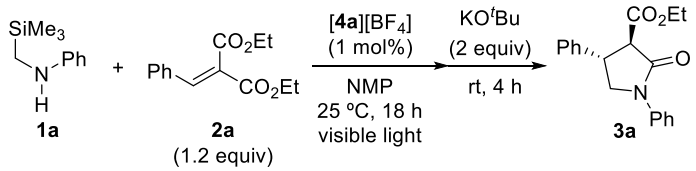
Preparation of α-silylamine 1i.



1i

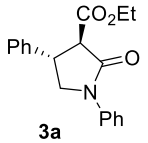
To a flame-dried 50 mL Schlenk flask were placed DMF (10 mL), aniline (0.910 mL, 9.97 mmol), and NaH (60% dispersion in paraffin liquid, 302.3 mg, 7.56 mmol), and the mixture was stirred at room temperature for 1 h. Then, (1-chloroethyl)trimethylsilane (1.60 mL, 10.3 mmol) was added, and the resulting mixture was stirred at room temperature for 14 h. Water (*ca.* 50 mL) was added, and the resulting mixture was extracted with Et_2O (*ca.* 30 mL x 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After concentration *in vacuo*, the residue was purified by column chromatography (eluent: hexane) to give *N*-(1-(trimethylsilyl)ethyl)aniline **1i** (497 mg, 2.43 mmol, 24% yield) as a colorless oil. ^{1}H NMR (C_6D_6) δ 7.19-7.12 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 2H), 3.11 (br, 1H), 2.77 (q, *J* = 7.0 Hz, 1H), 0.98 (d, *J* = 7.0 Hz, 3H), -0.9 (s, 9H). ^{13}C NMR (C_6D_6) δ 149.0, 129.5, 117.3, 113.5, 37.5, 15.6, -3.9. HRMS (EI) Calcd. for $C_{11}H_{19}NSi$ [M]: 193.1287. Found: 193.1290.

Photocatalytic reactions for synthesis of γ-lactams (3).

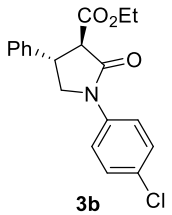


A typical experimental procedure for the reaction of *N*-(trimethylsilylmethyl)aniline (**1a**) with diethyl benzylidenemalonate (**2a**) is described below. To a flame-dried Schlenk flask (diameter: 2.5 cm) were placed [**4a**][BF_4] (2.2 mg, 0.0026 mmol) and NMP (2.5 mL). Then, **1a** (43.8 mg, 0.244 mmol) and **2a** (75.4 mg, 0.303 mmol) were added. The reaction flask was placed in a water bath (25 °C) and illuminated with a 14 W white LED (approximately 2 cm from the light source) for 18 h. The resulting mixture was treated with KO*t*Bu (56.5 mg, 0.503 mmol) at room temperature for 4 h. Then, saturated aqueous $NaHCO_3$ (*ca.* 50 mL) was added and the mixture was extracted with Et_2O (*ca.* 30 mL x 4). The combined organic layer was washed with brine (*ca.* 50 mL) and dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography (eluent: hexane/ethyl acetate = 10/1) to give *N*-phenyl-3-ethoxycarbonyl-4-phenyl-2-pyrrolidone (**3a**, 67.2 mg, 0.217 mmol).

Isolated yields and spectroscopic data of the γ-lactams (**3**) are as follows:

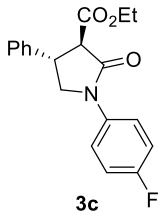


3a: 89% yield (*trans*/*cis* ratio 14/1). A colorless solid. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.57-7.52 (m, 2H), 7.32-7.16 (m, 7H), 7.14-7.05 (m, 1H), 4.26-4.11 (m, 3H), 4.01 (dd, *J* = 17.1 and 8.0 Hz, 1H), 3.84-3.78 (m, 1H), 3.72 (d, *J* = 9.2 Hz, 1H), 1.21 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.0, 167.9, 139.4, 138.6, 129.0, 128.86, 127.7, 126.9, 125.0, 120.0, 61.8, 57.1, 53.6, 41.1, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 128.89, 128.6, 127.5 120.5. HRMS (EI) Calcd. for $C_{19}H_{19}NO_3$ [M]: 309.1365. Found: 309.1363. The relative configuration of major isomer is determined to be *trans*-**3a** (m.p. 64.1-65.8 °C) by X-ray analysis (see below for details).



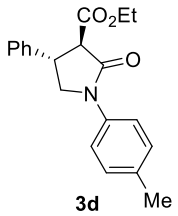
3b: 95% yield (*trans*/*cis* ratio >20/1). A yellow solid. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.50 (d, *J* = 8.9 Hz, 2H), 7.32-7.17 (m, 7H), 4.26-3.97 (m, 4H), 3.81-3.70 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 168.8, 168.0, 139.1, 137.1, 130.2, 129.1, 128.9, 127.8, 126.9, 121.1, 61.9,

57.0, 53.5, 41.1, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.82 (t, *J* = 7.0 Hz, 3H). HRMS (EI) Calcd. for $C_{19}H_{18}ClNO_3$ [M]: 343.0975. Found: 343.0964.



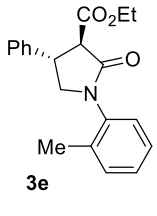
3c

3c: 85% yield (*trans*/*cis* ratio 19/1). A yellow oil. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.58-7.48 (m, 2H), 7.32-7.17 (m, 5H), 7.01-6.94 (m, 2H), 4.26-4.09 (m, 3H), 4.02 (dd, *J* = 16.3 and 8.2 Hz, 1H), 3.82-3.70 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 168.9, 167.9, 159.8 (d, $^{1}J_{C\text{-}F}$ = 244.8 Hz), 139.3, 134.7 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 129.1, 127.7, 126.9, 121.8 (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 115.6 (d, $^{2}J_{C\text{-}F}$ = 22.3 Hz), 61.9, 56.9, 53.9, 41.1, 14.1. ^{19}F NMR ($CDCl_3$) δ -116.6. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.83 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 40.7, 13.6. HRMS (EI) Calcd. for $C_{19}H_{18}FNO_3$ [M]: 327.1271. Found: 327.1283.



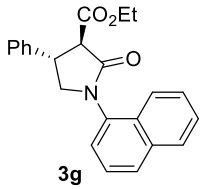
3d

3d: 90% yield (*trans*/*cis* ratio 20/1). A pale yellow oil. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.43-7.40 (m, 2H), 7.27-7.21 (m, 5H), 7.10-7.07 (m, 2H), 4.22-4.08 (m, 3H), 4.00 (dd, *J* = 16.5 and 8.4 Hz, 1H), 3.82-3.68 (m, 2H), 2.24 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.1, 167.7, 139.5, 136.1, 134.8, 129.3, 129.0, 127.6, 126.9, 120.1, 61.8, 57.1, 53.8, 41.2, 20.8, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.82 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 128.6, 120.6, 56.1, 52.1. HRMS (EI) Calcd. for $C_{20}H_{21}NO_3$ [M]: 323.1521. Found: 323.1519.



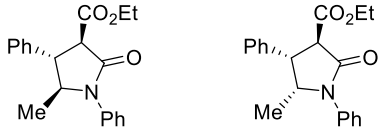
3e

3e: 66% yield (*trans*/*cis* ratio 15/1). A yellow oil. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.33-7.07 (m, 9H), 4.25-4.12 (m, 2H), 4.09-3.99 (m, 2H), 3.74-3.66 (m, 2H), 2.20 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.4, 168.1, 140.3, 136.5, 135.6, 131.2, 129.0, 128.5, 128.1, 127.6, 126.8, 126.4, 61.8, 56.0, 55.8, 42.1, 17.9, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 3.81 (dd, *J* = 15.7 and 8.4 Hz), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 61.1, 13.7 HRMS (EI) Calcd. for $C_{20}H_{21}NO_3$ [M]: 323.1521. Found: 323.1525.



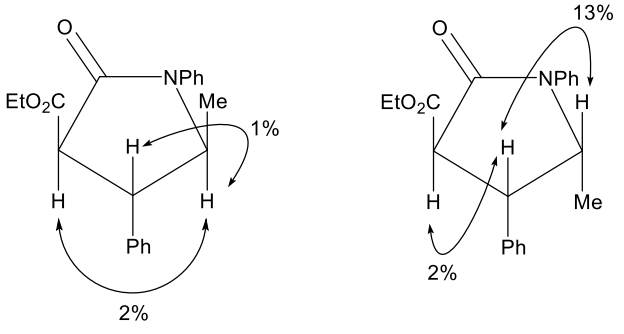
3g

3g: 75% yield (*trans*/*cis* ratio 9/1). A pale yellow oil. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.83-7.75 (m, 3H), 7.49-7.20 (m, 9H), 4.30-4.14 (m, 4H), 3.91-3.79 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.5, 169.1, 140.2, 134.6, 134.5, 129.5, 129.1, 128.7, 128.51, 127.7, 126.97, 126.9, 126.4, 125.5, 124.6, 122.5, 61.9, 56.8, 56.2, 42.3, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 128.8, 128.6, 128.46, 127.01, 125.6, 61.2, 13.7. HRMS (EI) Calcd. for $C_{23}H_{21}NO_3$ [M]: 359.1521. Found: 359.1508.

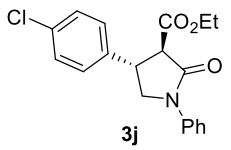


major-**3i** minor-**3i**

3i: 62% yield (isomeric ratio 6/1). A pale yellow solid. Major isomer: ^{1}H NMR ($CDCl_3$) δ 7.36-7.21 (m, 9H), 7.20-7.15 (m, 1H), 4.27-4.05 (m, 3H), 3.72 (d, *J* = 10.4 Hz, 1H), 3.50 (dd, *J* = 10.4 and 7.7 Hz, 1H), 1.20 (t, *J* = 7.3 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.2, 167.9, 138.9, 136.7, 129.0, 128.9, 127.8, 127.7, 126.4, 124.7, 61.7, 60.6, 56.7, 50.6, 18.5, 14.1. Minor isomer: ^{1}H NMR ($CDCl_3$) δ 7.54-7.46 (m, 2H), 4.69-4.58 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H). HRMS (EI) Calcd. for $C_{20}H_{21}NO_3$ [M]: 323.1521. Found: 323.1511. The stereochemistry of major- and minor-**3i** was confirmed by the NOE measurements:



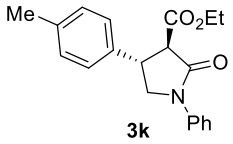
major-**3i** minor-**3i**



3j

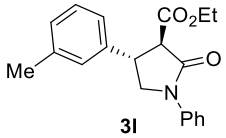
3j: 79% yield (*trans*/*cis* ratio >20/1). A pale yellow solid. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.56-7.51 (m, 2H), 7.33-7.26 (m, 4H), 7.18-7.08 (m, 3H), 4.28-3.96 (m, 3H), 4.00 (dd, *J* = 17.1 and 8.2 Hz, 1H), 3.82-3.75 (m, 1H), 3.67 (d, *J* = 9.2 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$)

δ 168.7, 167.6, 138.5, 137.8, 133.6, 129.2, 128.9, 128.4, 125.2, 120.0, 61.9, 57.1, 53.4, 40.6, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.76 (t, *J* = 7.0 Hz, 3H). HRMS (EI) Calcd. for $C_{19}H_{18}ClNO_3$ [M]: 343.0975. Found: 343.0964.



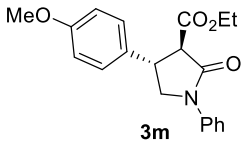
3k

3k: 79% yield (*trans*/*cis* ratio 20/1). A yellow oil. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.56-7.52 (m, 2H), 7.32-7.26 (m, 2H), 7.16-7.06 (m, 5H), 4.24-4.07 (m, 3H), 3.98 (dd, *J* = 17.4 and 8.2 Hz, 1H), 3.82-3.75 (m, 1H), 3.70 (d, *J* = 9.5 Hz, 1H), 2.26 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.0, 168.0, 138.7, 137.4, 136.3, 129.7, 128.9, 126.8, 125.0, 120.0, 61.8, 57.3, 53.7, 40.8, 21.0, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 137.3, 129.2, 127.4, 120.5. HRMS (EI) Calcd. for $C_{20}H_{21}NO_3$ [M]: 323.1521. Found: 323.1506.



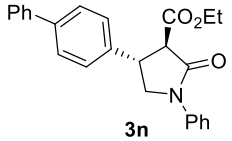
3l

3l: 62% yield (*trans*/*cis* ratio >20/1). A pale yellow oil. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.57-7.52 (m, 2H), 7.33-7.26 (m, 2H), 7.21-7.01 (m, 5H), 4.24-4.09 (m, 3H), 3.99 (dd, *J* = 17.0 and 8.1 Hz, 1H), 3.84-3.78 (m, 1H), 3.72 (d, *J* = 9.2 Hz, 1H), 2.28 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.0, 168.0, 139.4, 138.8, 138.7, 129.0, 128.9, 128.4, 127.7, 125.0, 123.9, 120.1, 62.0, 57.2, 53.7, 41.1, 21.4, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 7.5 Hz, 3H). HRMS (EI) Calcd. for $C_{20}H_{21}NO_3$ [M]: 323.1521. Found: 323.1535.



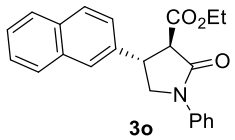
3m

3m: 81% yield (*trans*/*cis* ratio 20/1). A yellow oil. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.64-7.59 (m, 2H), 7.40-7.33 (m, 2H), 7.25-7.14 (m, 3H), 6.92-6.87 (m, 2H), 4.32-4.15 (m, 3H), 4.04 (dd, *J* = 17.3 and 8.4 Hz, 1H), 3.88-3.74 (m, 5H), 1.29 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.0, 168.0, 159.0, 138.6, 131.2, 128.9, 128.0, 125.0, 120.0, 114.4, 61.7, 57.4, 55.2, 53.8, 40.6, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 128.7, 125.1, 120.5, 114.0. HRMS (EI) Calcd. for $C_{20}H_{21}NO_4$ [M]: 339.1471. Found: 339.1480.



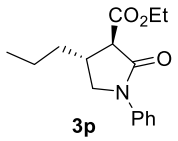
3n

3n: 61% yield (*trans*/*cis* ratio 14/1). A colorless solid. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.59-7.49 (m, 6H), 7.40-7.25 (m, 7H), 7.15-7.08 (m, 1H), 4.27-4.03 (m, 4H), 3.90-3.84 (m, 1H), 3.77 (d, *J* = 9.2 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.0, 167.9, 140.7, 140.4, 138.6, 138.4, 128.9, 128.8, 127.8, 127.5, 127.4, 126.99, 125.1, 120.1, 61.9, 57.2, 53.7, 40.9, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 128.0, 126.95, 126.9. HRMS (EI) Calcd. for $C_{25}H_{23}NO_3$ [M]: 385.1678. Found: 385.1672.



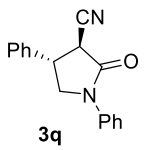
3o

3o: 61% yield (*trans*/*cis* ratio 19/1). A pale yellow oil. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.88-7.80 (m, 3H), 7.76 (br, 1H), 7.67-7.63 (m, 2H), 7.54-7.45 (m, 2H), 7.42-7.35 (m, 3H), 7.22-7.15 (m, 1H), 4.33-4.17 (m, 4H), 4.05-3.90 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.0, 167.9, 138.7, 136.7, 133.4, 132.7, 129.1, 128.9, 127.73, 127.66, 126.6, 126.2, 126.0, 125.1, 124.6, 120.1, 61.9, 57.2, 53.6, 41.4, 14.1. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 0.79 (t, *J* = 7.0 Hz, 3H).
HRMS (EI) Calcd. for $C_{23}H_{21}NO_3$ [M]: 359.1521. Found: 323.1507.



3p

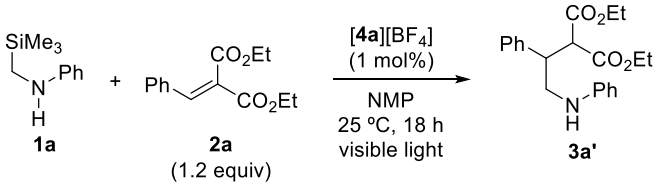
3p: 79% yield (*trans*/*cis* ratio 11/1). A yellow oil. *trans*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.15 (t, *J* = 7.7 Hz, 1H), 4.27 (q, *J* = 7.0 Hz, 2H), 3.99 (dd, *J* = 9.2 and 8.1 Hz, 1H), 3.48 (dd, *J* = 9.2 and 7.7 Hz, 1H), 3.32 (d, *J* = 8.6 Hz, 1H), 2.93-2.78 (m, 1H), 1.62-1.50 (m, 2H), 1.47-1.30 (m, 5H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.7, 168.7, 138.9, 128.8, 124.8, 120.0, 61.6, 56.6, 52.7, 35.8, 35.7, 20.2, 14.1, 13.89. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 3.81 (dd, *J* = 8.8 and 5.5 Hz, 1H), 3.58 (d, *J* = 8.6 Hz, 1H), 2.76-2.66 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 124.9, 120.4, 61.2, 54.6, 53.4, 31.2, 20.7, 14.2, 13.94. HRMS (EI) Calcd. for $C_{16}H_{21}NO_3$ [M]: 275.1521. Found: 275.1526.



3q

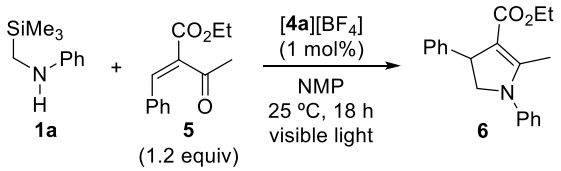
3q: 81% yield (*trans*/*cis* ratio 8/1). A pale yellow oil. *trans*-Isomer: ^{1}H NMR (CD_2Cl_2) δ 7.67-7.60 (m, 2H), 7.50-7.37 (m, 7H), 7.27-7.22 (m, 1H), 4.24-4.08 (m, 1H), 4.05-3.89 (m, 3H). ^{13}C NMR (CD_2Cl_2) δ 164.5, 138.6, 136.8, 129.8, 129.46, 129.0, 127.4, 126.1, 120.67, 116.6, 53.6, 43.5, 43.2. *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ 7.35-7.29 (m, 2H), 4.31 (dd, *J* = 10.4 and 6.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 138.1, 129.6, 129.49, 128.9, 127.7, 126.2, 120.71, 53.6, 43.0, 40.1. HRMS (EI) Calcd. for $C_{17}H_{14}N_2O$ [M]: 262.1106. Found: 262.1106.

Synthesis of 3a'.



To a flame-dried Schlenk flask (diameter: 2.5 cm) were placed [**4a**][BF_4] (2.2 mg, 0.0026 mmol) and NMP (2.5 mL). Then, **1a** (43.9 mg, 0.245 mmol) and **2a** (74.1 mg, 0.298 mmol) were added. The reaction flask was placed in a water bath (25 °C) and illuminated with a 14 W white LED (approximately 2 cm from the light source) for 18 h. The resulting mixture was purified by column chromatography (eluent: hexane/ethyl acetate = 10/1) to give **3a'** (51.0 mg, 0.143 mmol, 58% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.42-7.15 (m, 7H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.98-3.86 (m, 2H), 3.84-3.76 (m, 2H), 3.70-3.63 (brm, 2H), 3.42-3.31 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 168.3, 167.6, 147.5, 139.2, 129.2, 128.6, 128.4, 127.4, 117.6, 113.0, 61.7, 61.3, 56.2, 47.5, 44.5, 14.0, 13.6. HRMS (EI) Calcd. for $C_{21}H_{25}NO_4$ [M]: 355.1784. Found: 355.1777.

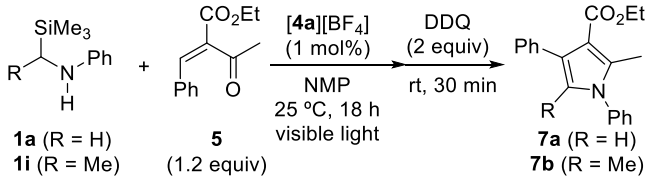
Photocatalytic reactions for synthesis of dihydropyrrole 6.



To a flame-dried Schlenk flask (diameter: 2.5 cm) were placed [**4a**][BF_4] (2.1 mg, 0.0025 mmol) and NMP (2.5 mL). Then, **1a** (44.8 mg, 0.250 mmol) and **5** (65.4 mg, 0.300 mmol) were added. The reaction flask was placed in a water bath (25 °C) and illuminated with a 14 W white LED (approximately 2 cm from the light source) for 18 h. Then, saturated aqueous $NaHCO_3$ (*ca.* 50 mL) was added and the mixture was extracted with Et_2O (*ca.* 30 mL x 3). The combined organic layer was washed with brine (*ca.* 50 mL) and dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography (eluent: hexane/ethyl acetate = 10/1) to give dihydropyrrole **6** (49.3 mg, 0.160 mmol, 64% yield) as a pale yellow oil. ^{1}H NMR ($CDCl_3$)

δ 7.31-7.17 (m, 6H), 7.14-7.07 (m, 2H), 7.04-6.98 (m, 2H), 4.31 (dd, *J* = 11.1 and 9.9 Hz, 1H), 4.17 (ddd, *J* = 11.1, 3.9 and 0.9 Hz, 1H), 4.02-3.84 (m, 2H), 3.70 (dd, *J* = 9.9 and 3.9 Hz, 1H), 2.30 (s, 3H), 0.98 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 166.9, 158.2, 146.0, 141.7, 129.2, 128.2, 127.0, 126.4, 124.7, 123.6, 106.1, 62.2, 58.5, 45.1, 14.3, 14.1. HRMS (EI) Calcd. for $C_{20}H_{21}NO_2$ [M]: 307.1572. Found: 307.1583.

Photocatalytic reactions for synthesis of pyrroles 7a and 7b.



A typical experimental procedure for the reaction of **1a** with **5** is described below. To a flame-dried Schlenk flask (diameter: 2.5 cm) were placed [**4a**][BF_4] (2.1 mg, 0.0025 mmol) and NMP (2.5 mL). Then, **1a** (44.8 mg, 0.250 mmol) and **5** (66.4 mg, 0.304 mmol) were added. The reaction flask was placed in a water bath (25 °C) and illuminated with a 14 W white LED (approximately 2 cm from the light source) for 18 h. The resulting mixture was treated with DDQ (114.3 mg, 0.503 mmol) at room temperature for 30 min. Then, water (*ca.* 50 mL) was added and the mixture was extracted with Et_2O (*ca.* 30 mL x 4). The combined organic layer was washed with brine (*ca.* 50 mL) and dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography (eluent: hexane/ethyl acetate = 10/1) to give **7a** (55.1 mg, 0.180 mmol, 72% yield). Spectroscopic characterization of **7a**[S2a] and **7b**[S2b] were reported elsewhere.

Determination of the quantum yield.

When the quantum yield of the photochemical reaction of **1a** with **2a** was determined, the reaction mixture was irradiated with an Ushio high pressure mercury lamp USH-250SC (250 W) with a 440 nm band-pass filter Kenko B-440 filter. The irradiated light intensity was estimated to be 1.41 x 10^{-7} einstein s^{-1} by using $K_3[Fe(C_2O_4)_3]$ as an actinometer.[S6] The quantum yield of the reaction of **1a** with 1.2 equiv. of **2a** in the presence of 1 mol% of [**4a**][BF_4] in 2.5 mL of NMP was determined to be Φ = 0.13 by the initial reaction rate (1.83 x 10^{-8} mol s^{-1}).

Effect of visible light irradiation on the initial stage of the reaction.

To obtain information on the reaction pathway, we investigated the effect of visible light irradiation at the initial stage of the reaction. When the reaction of **1a** with **2a** was carried out under

visible light illumination for 1 h, the addition product **3a'** was observed in 27% yield along with a trace amount of **3a**. Then, the reaction mixture was stirred under dark for 17 h, and the same amount of the addition products were obtained. This result indicates that no further increase of the product yield was observed under dark. Considering this result, the contribution of *radical chain mechanism initiated by visible light* is negligible.

X-ray diffraction study of *trans*-3a.

After repeated recrystallization of **3a** from ethanol, the pure major isomer *trans*-**3a** was obtained as colorless crystals. Colorless block crystals suitable for an X-ray analysis were obtained by recrystallization of *trans*-**3a** from ethanol. Diffraction data were collected on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71075 Å) with Varimax optics. Reflections were collected for the 2θ range of 6° to 55°. Intensity data were corrected for empirical absorptions and Lorentz and polarization effects. Structure solutions and refinements were carried out by using CrystalStructure package.[S7] The positions of non-hydrogen atoms were determined by direct methods (SIR-97)[S8] and subsequent Fourier synthesis, and were refined on F_o^2 using all the unique reflections by full-matrix least squares with anisotropic thermal paramteters. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Anomalous dispersion effects were included in F_c, and atom scattering factors and the value for $\Delta f'$ and $\Delta f''$ were taken from ref. S9. Details of the crystal and data collection parameters are summarized in Table S1. An ORTEP drawing of *trains*-**3a** is shown in Fig. S1.

CCDC 992086 (*trans*-**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystallographic data for *trans*-**3a**

chemical formula	$C_{19}H_{19}NO_3$
formula weight	309.36
crystal size	0.20 x 0.10 x 0.10
crystal color, habit	colorless, block
crystal system	triclinic
space group	*P*-1(no. 2)
a (Å)	7.949(2)
b (Å)	9.913(3)
c (Å)	11.241(3)
α (deg)	96.837(5)
β (deg)	105.663(5)
γ (deg)	109.836(5)
V (Å^3)	780.3(3)
Z	2
D_{calcd} (g cm^{-3})	1.317
F(000)	328
μ_{calcd} (cm^{-1})	0.889
radiation	Mo-Kα (λ = 0.71075 Å)
temperature (°C)	-180
transmission factors rage	0.561-0.991
no. measured reflections	7619
no. unique reflections	3541 (R_{int} = 0.0501)
no. refined parameters	227
*R*1 ($I > 2\sigma(I)$)[a]	0.0579
*wR*2 (all data)[b]	0.1583
GOF[c]	0.914
max/min residual peaks (e$^-$/Å^3)	+0.39/-0.29

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

[b] $wR2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$; $w = 4F_o^2/(0.0023F_o^2+2\sigma(F_o^2))$.

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

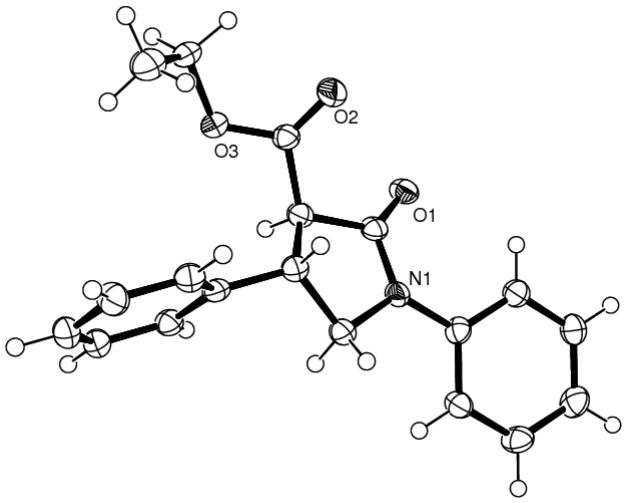


Fig. S1 ORTEP drawing of *trans*-**3a**.

References.

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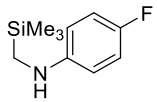
^{1}H, ^{13}C, and ^{19}F NMR spectra.



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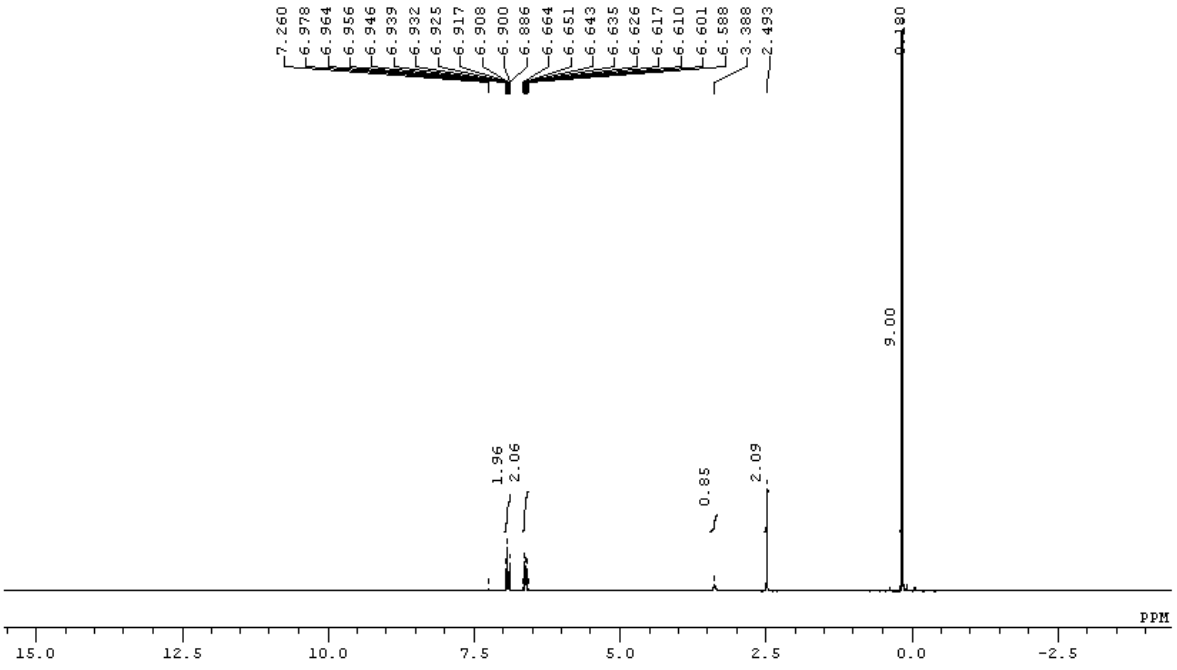

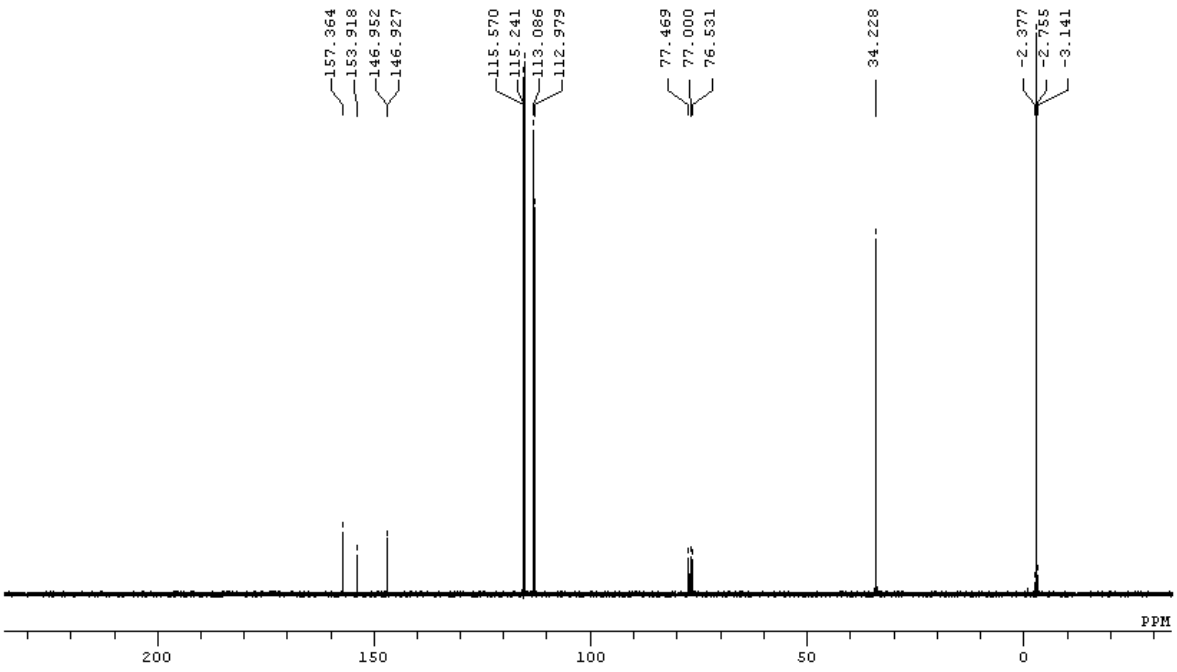

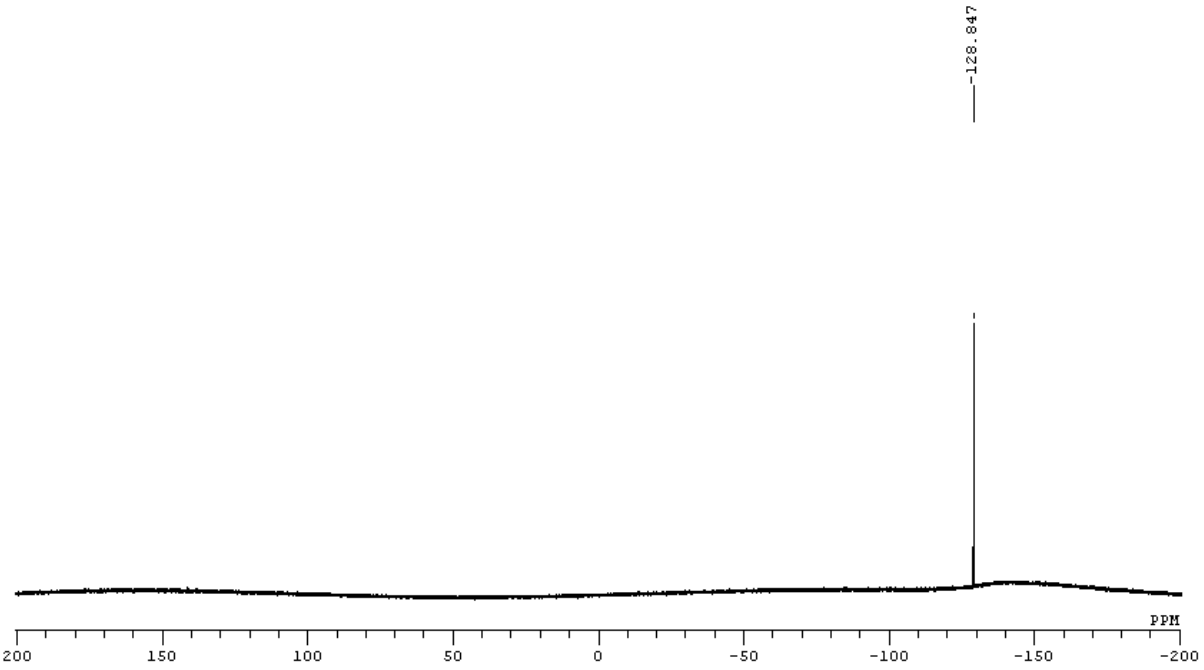
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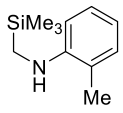
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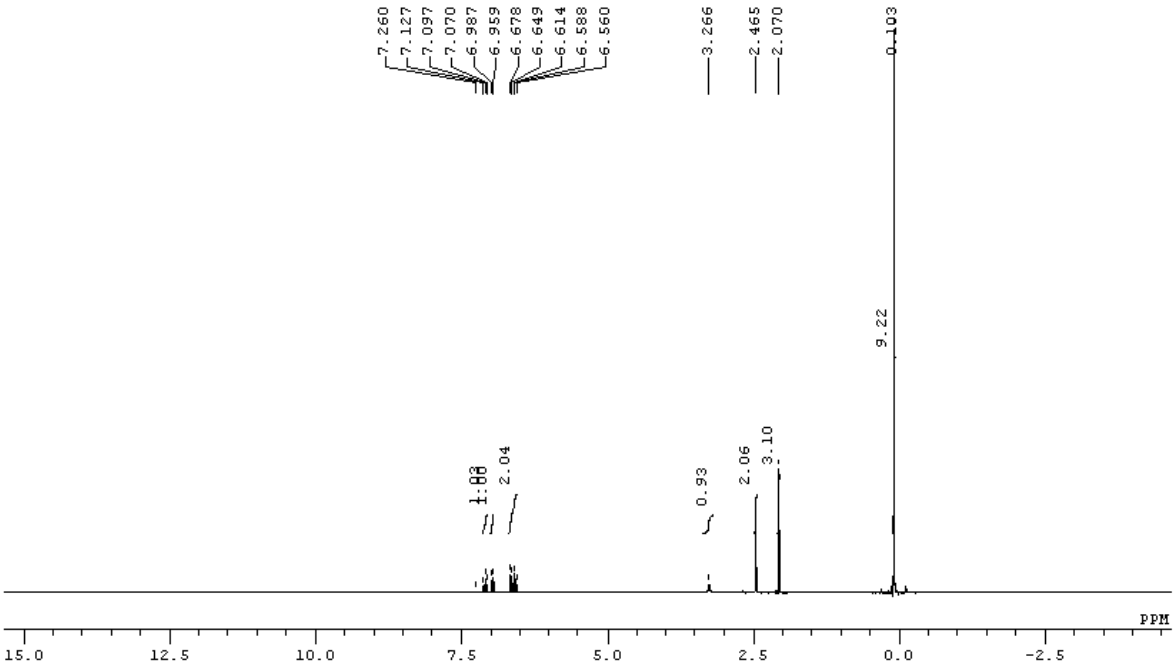
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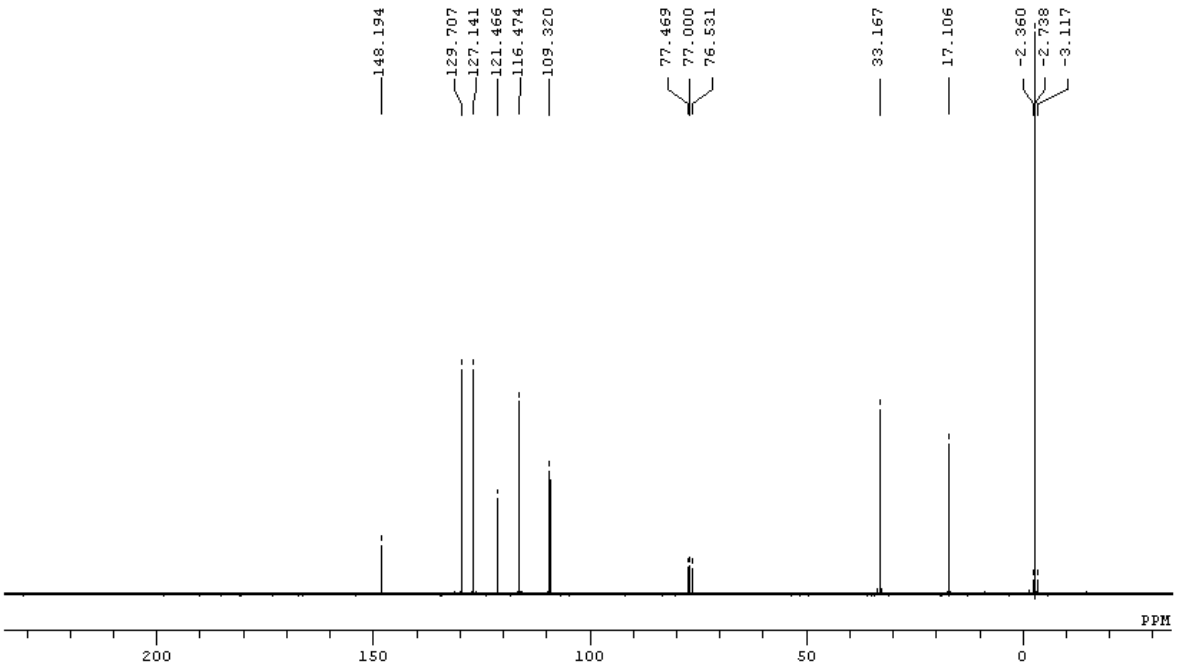
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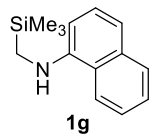
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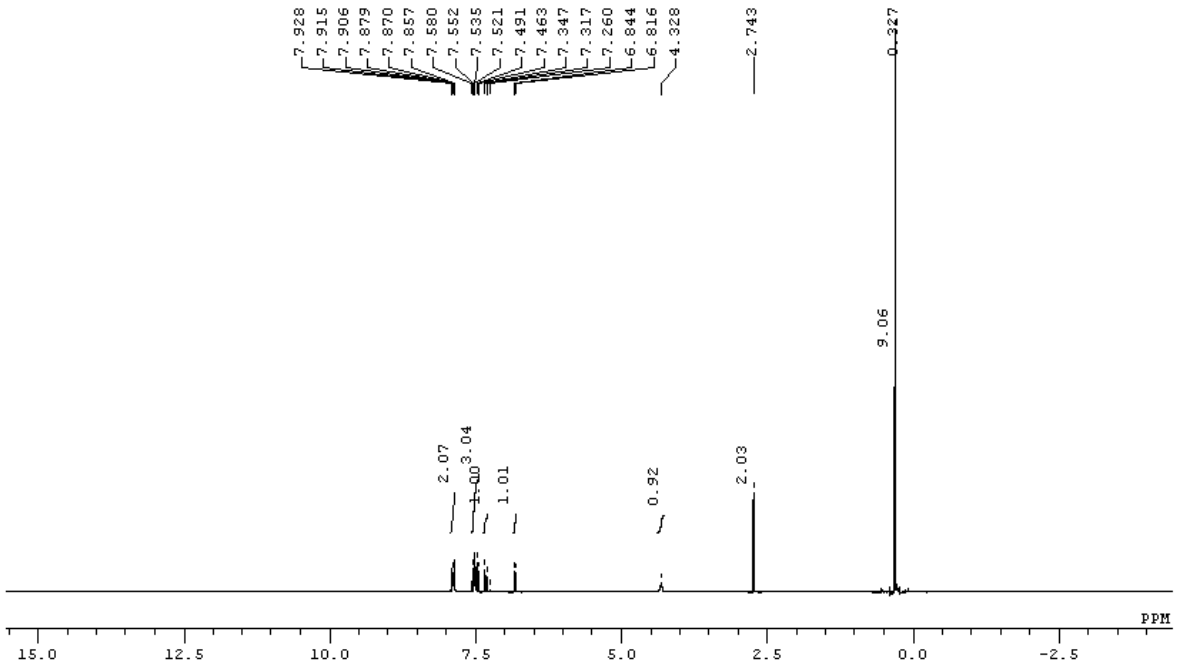
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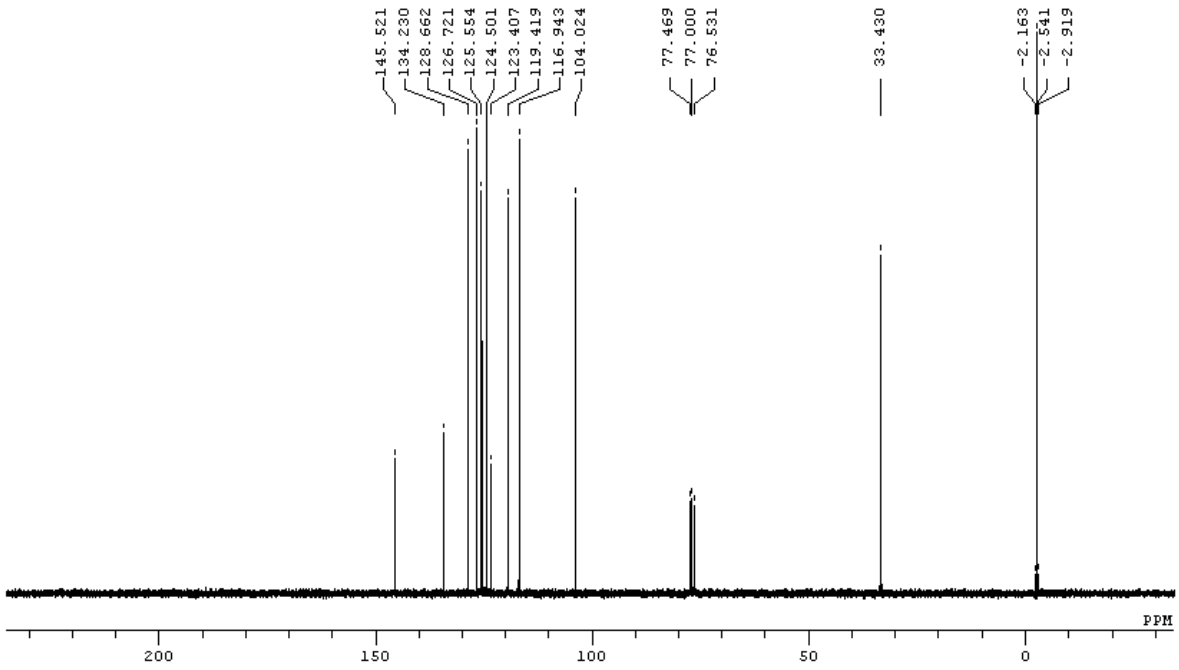
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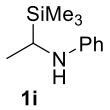
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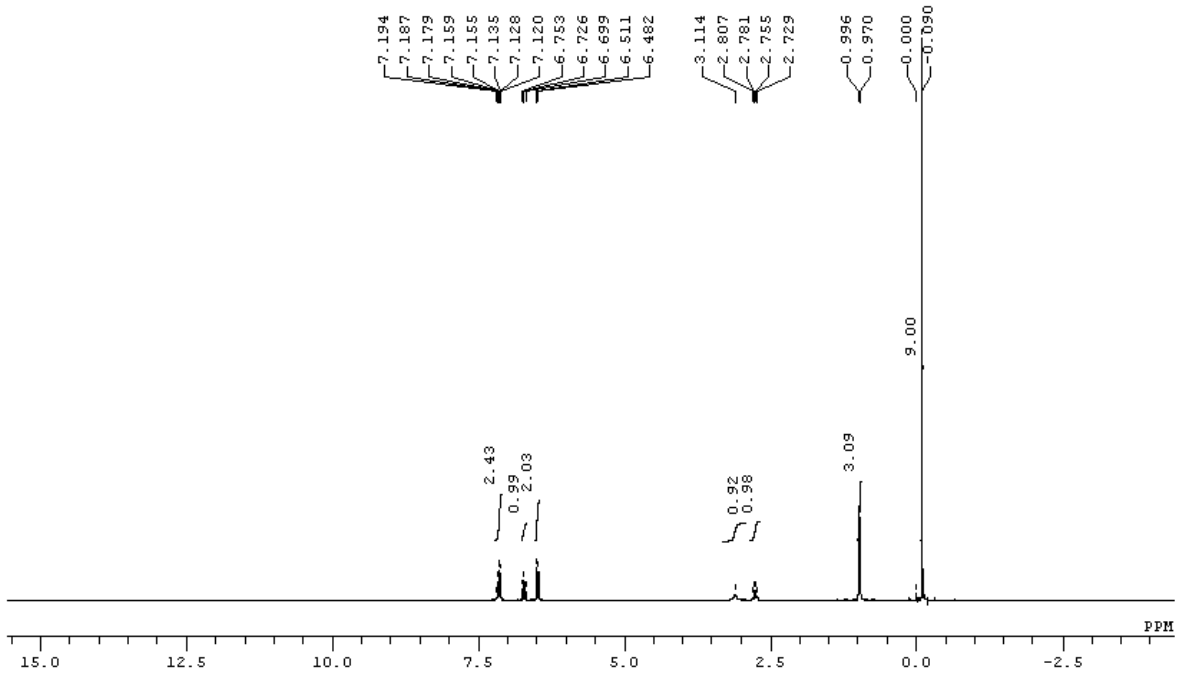
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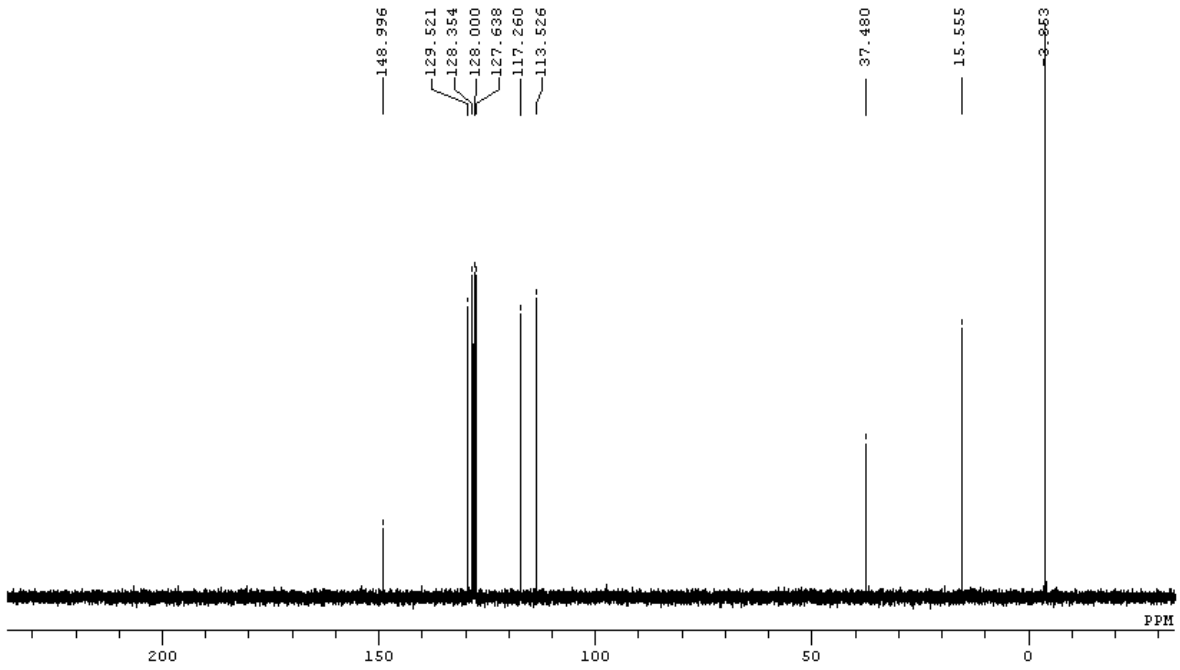
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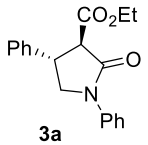
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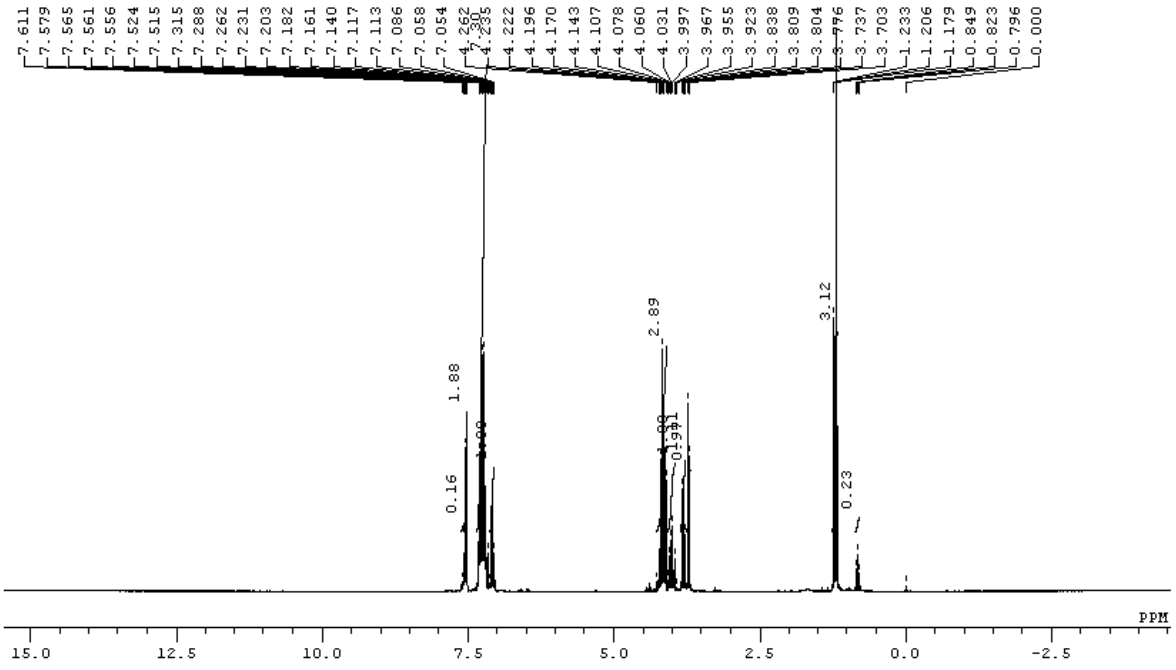
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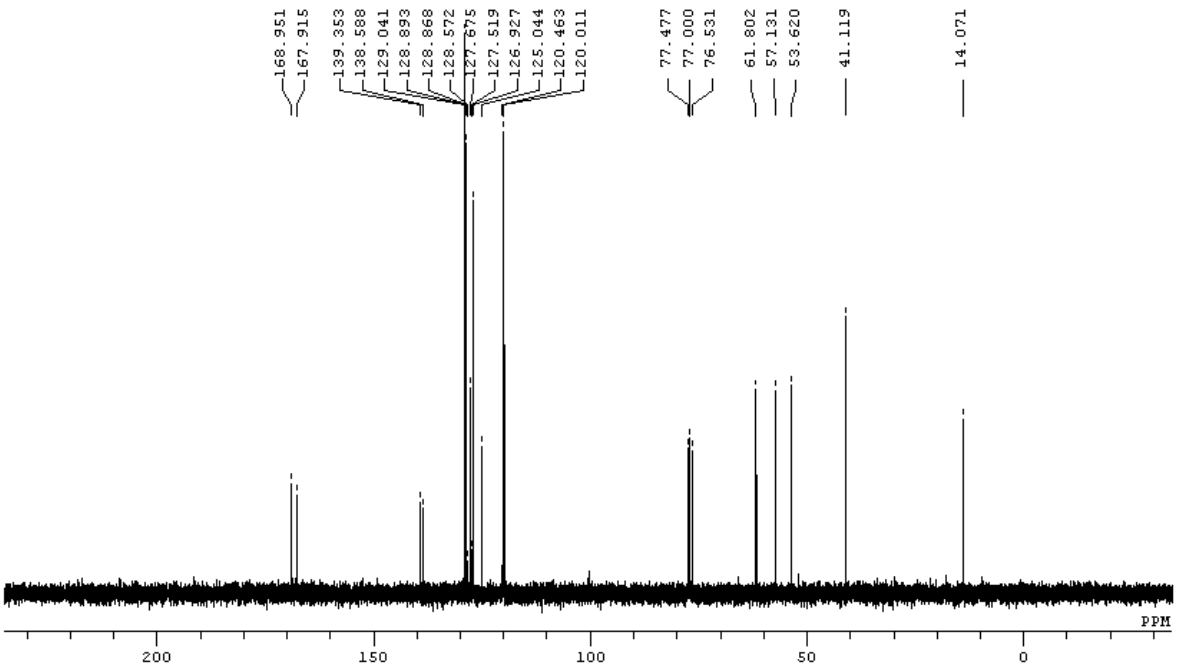
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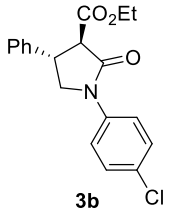
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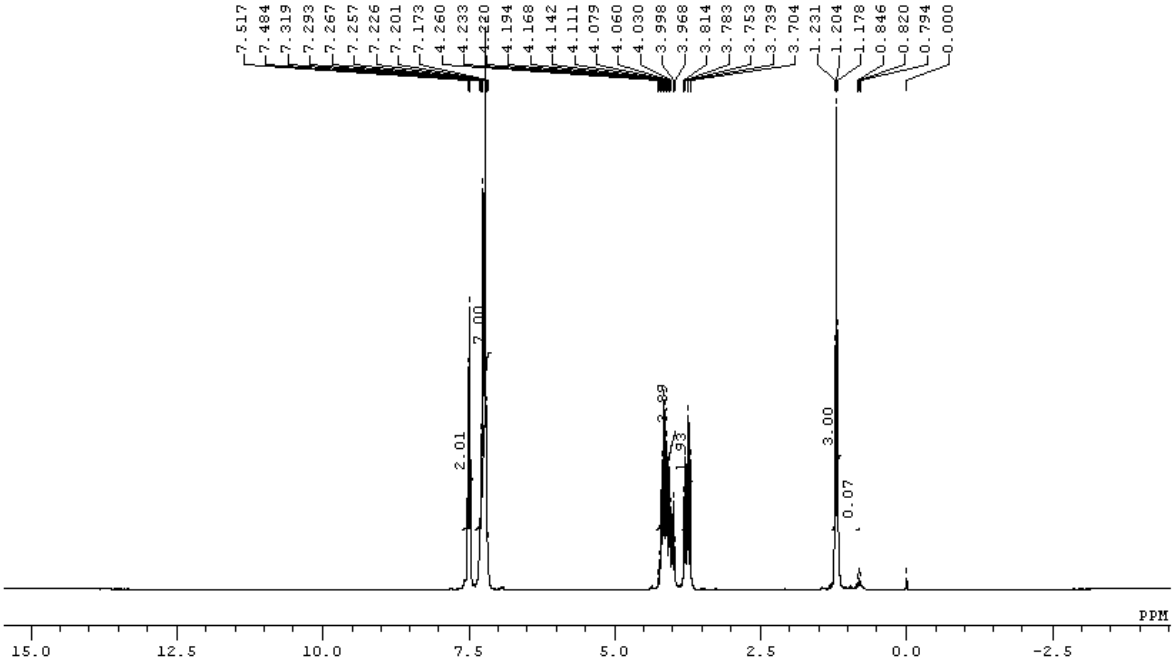
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3.814
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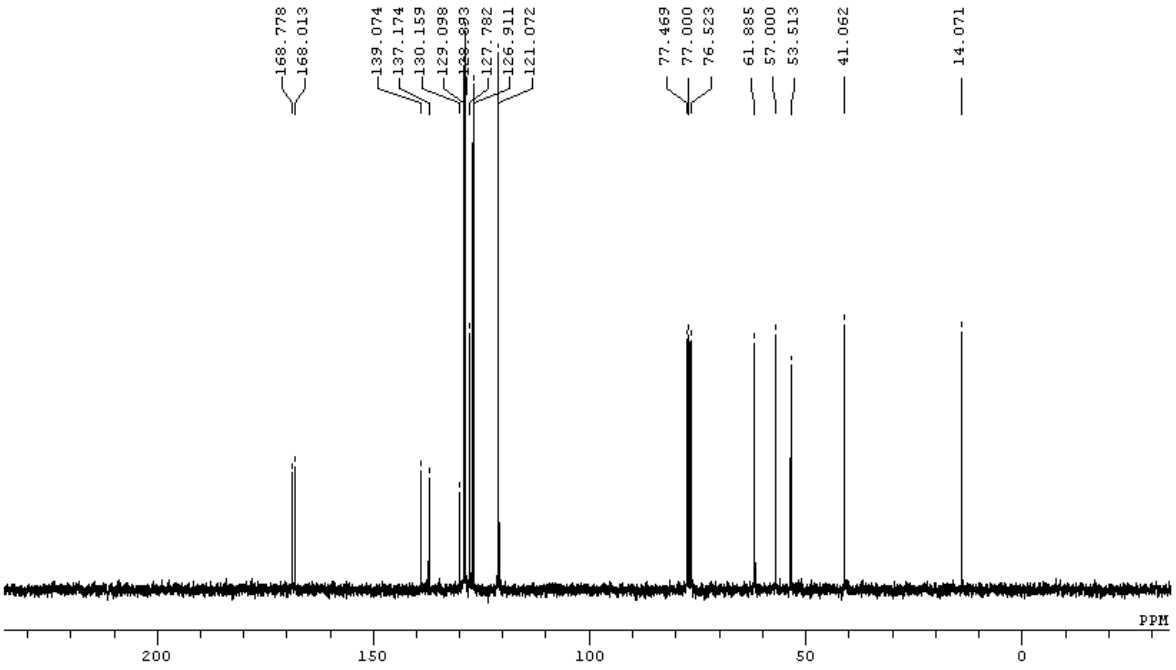
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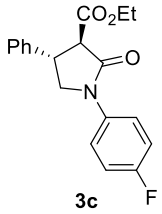
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F

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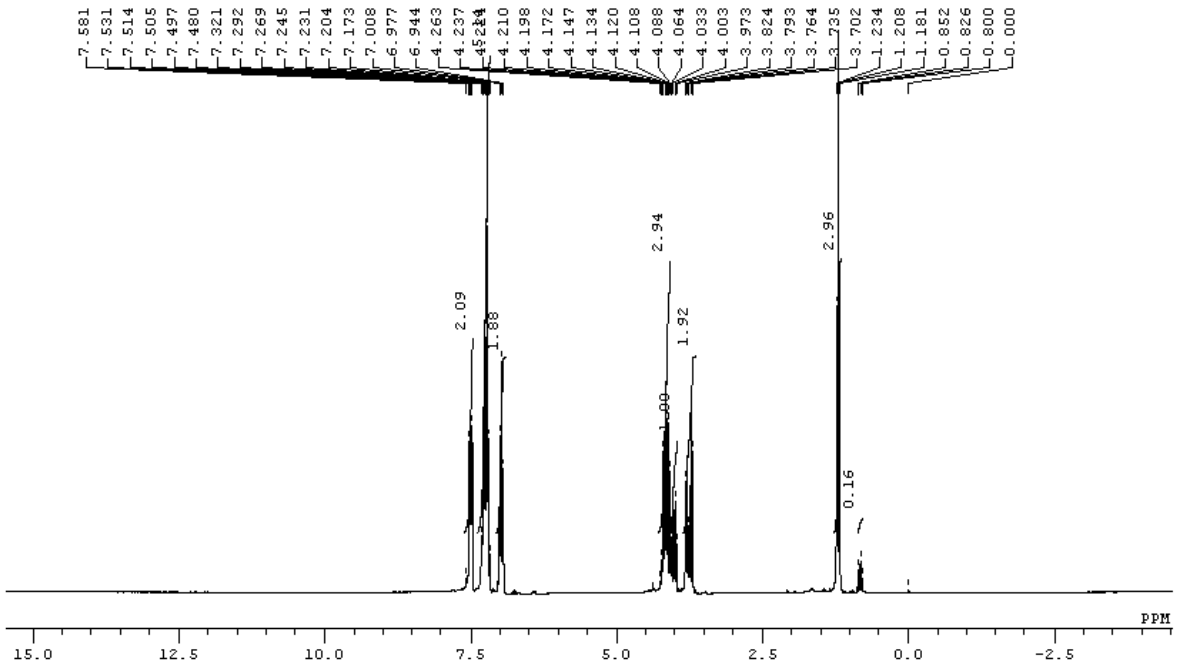
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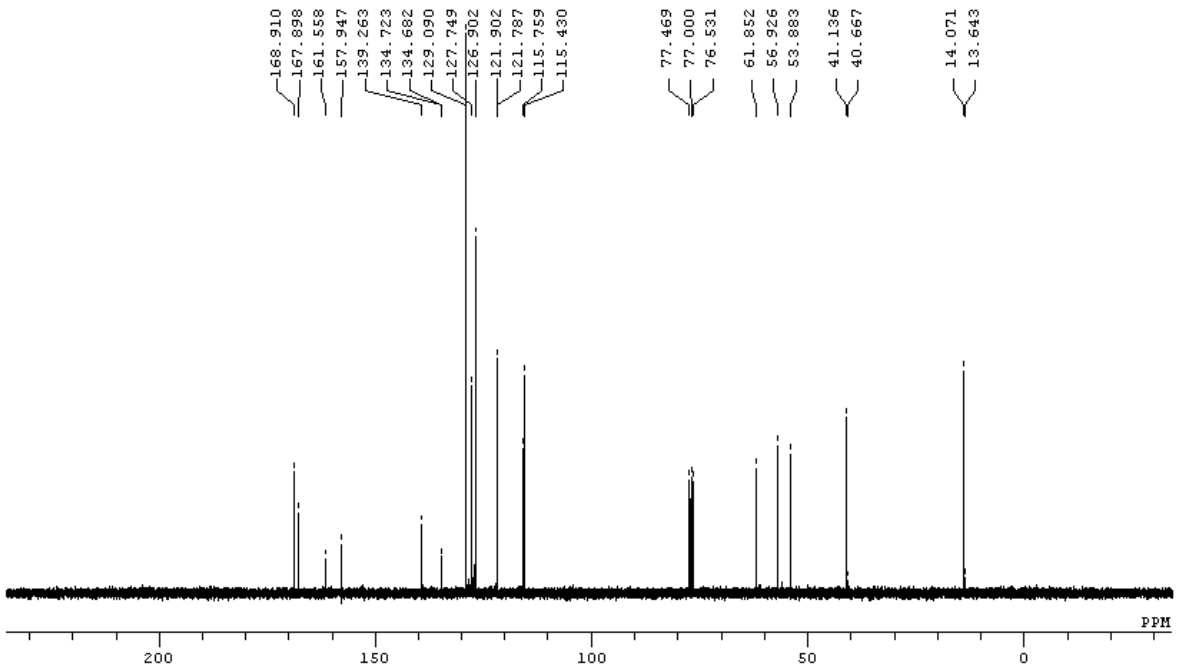
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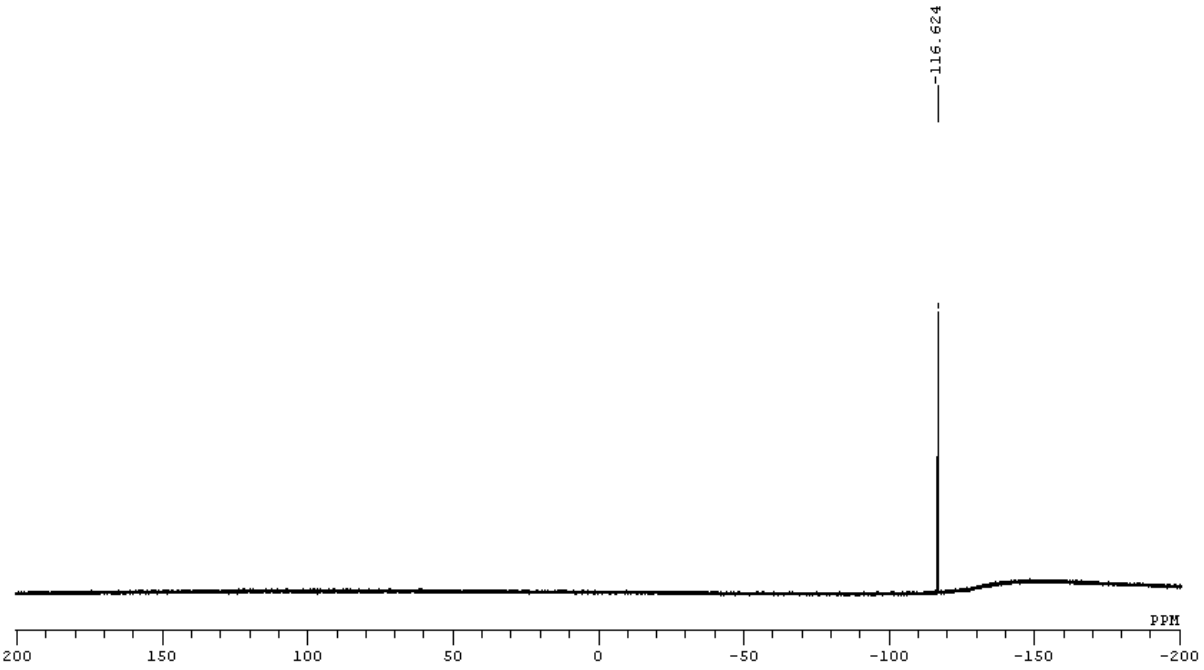
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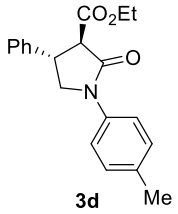
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Ph
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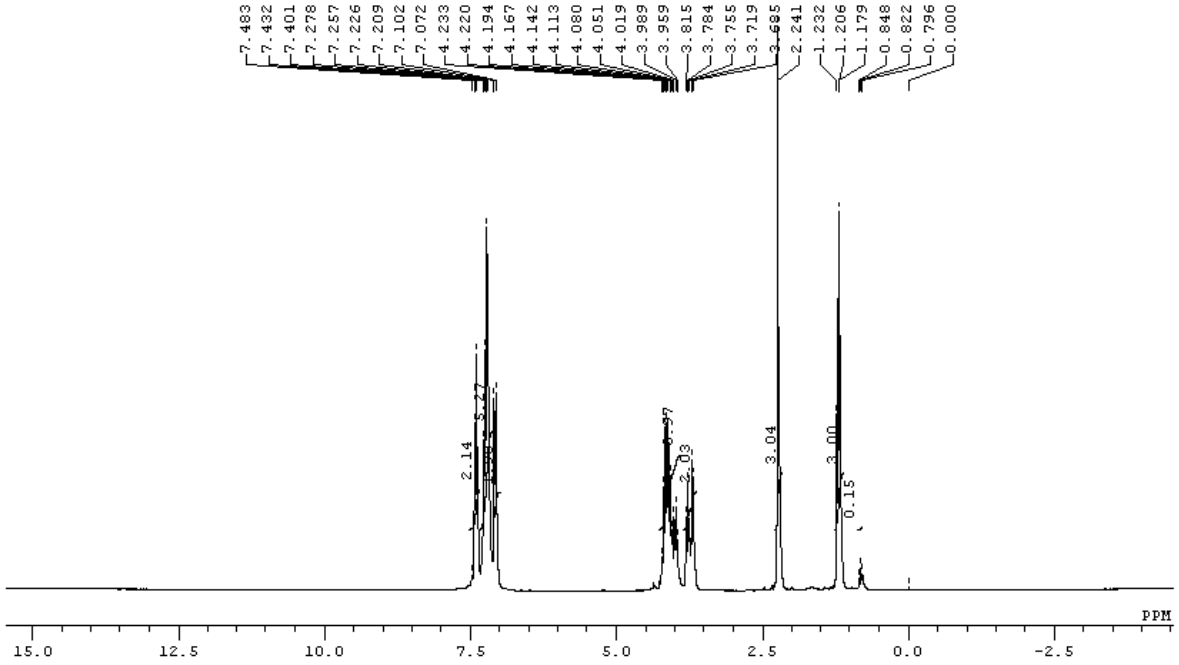
3d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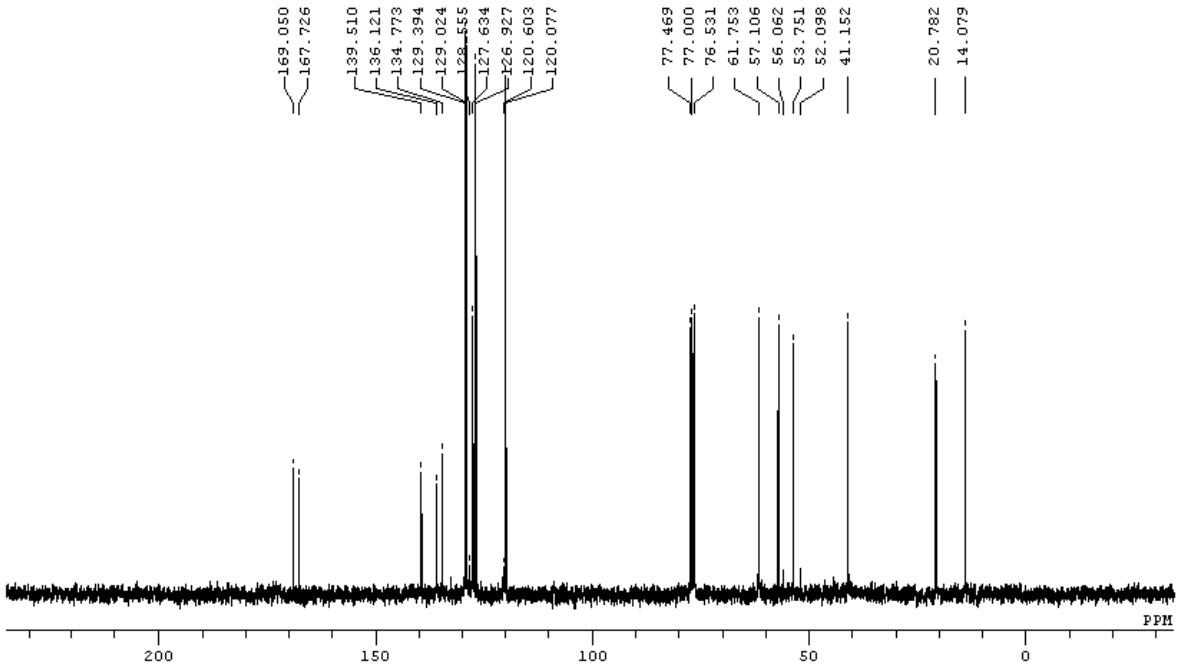
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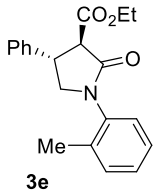
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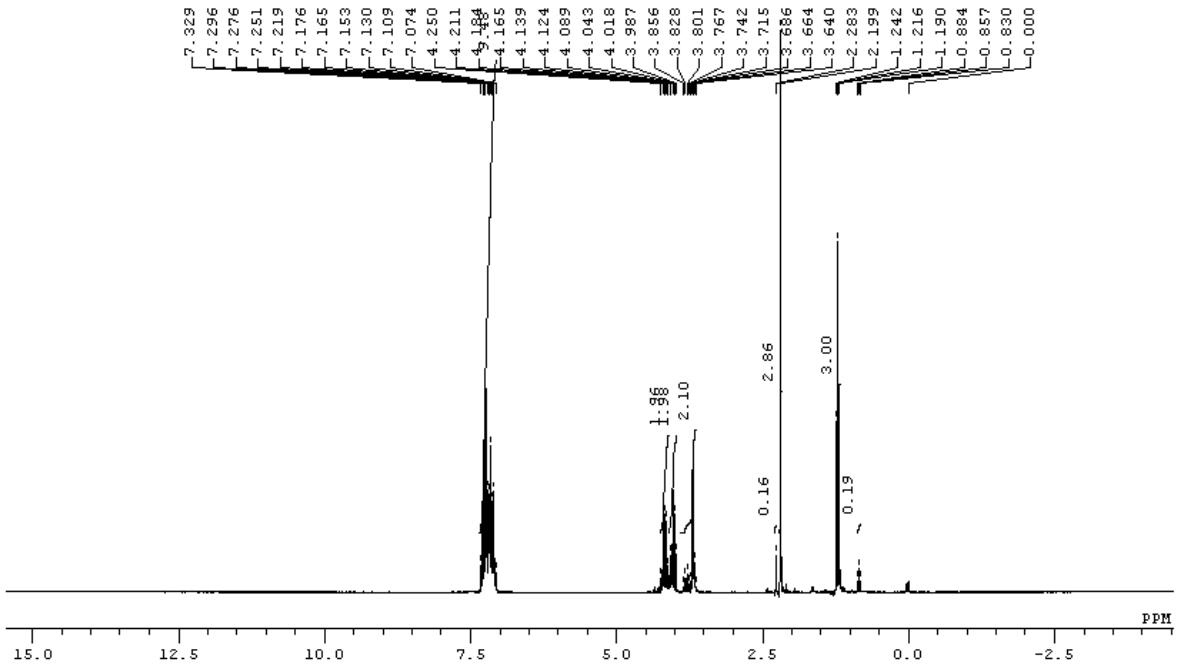
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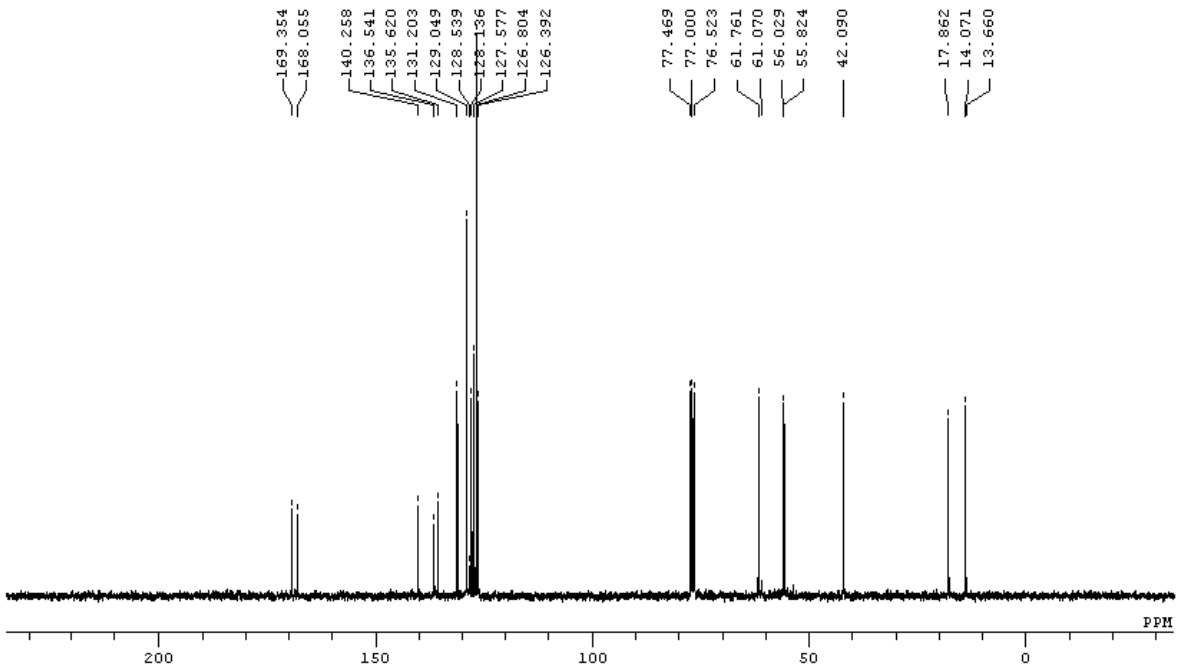
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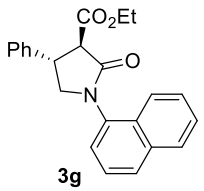
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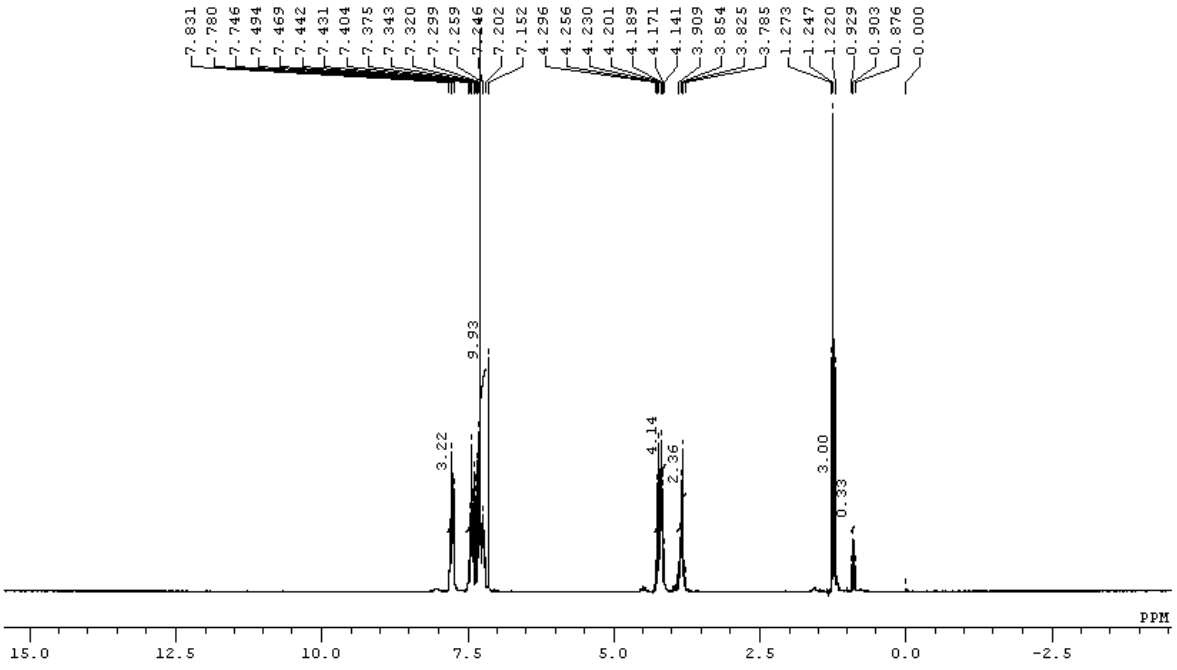
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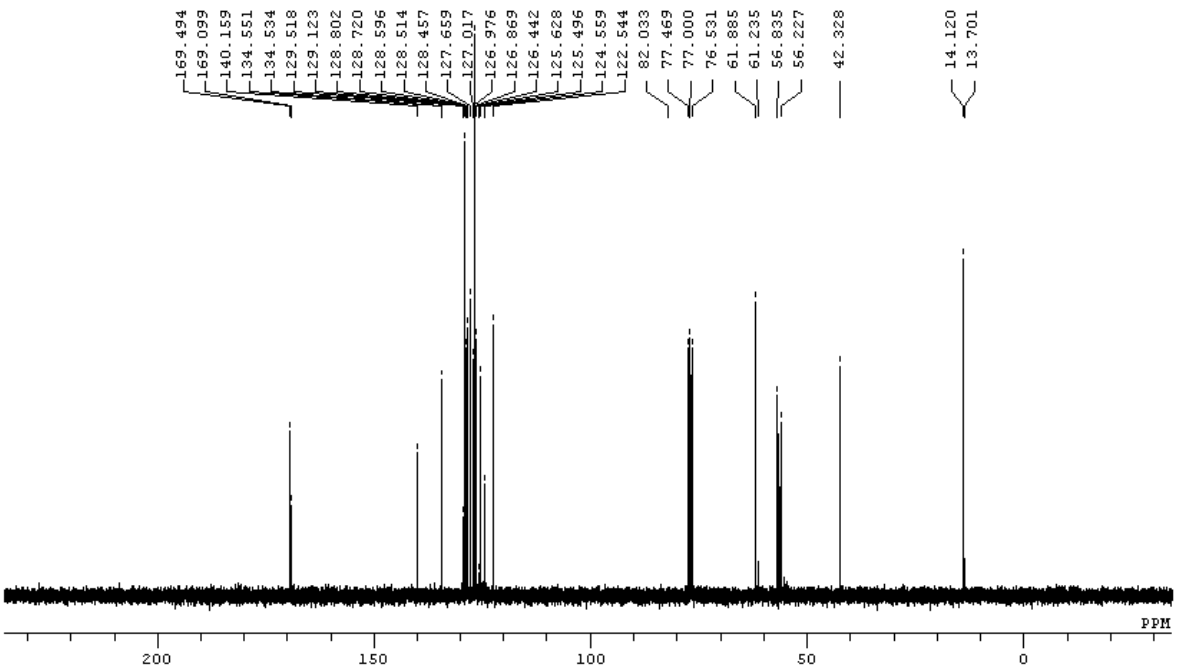
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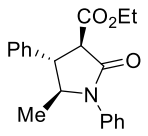
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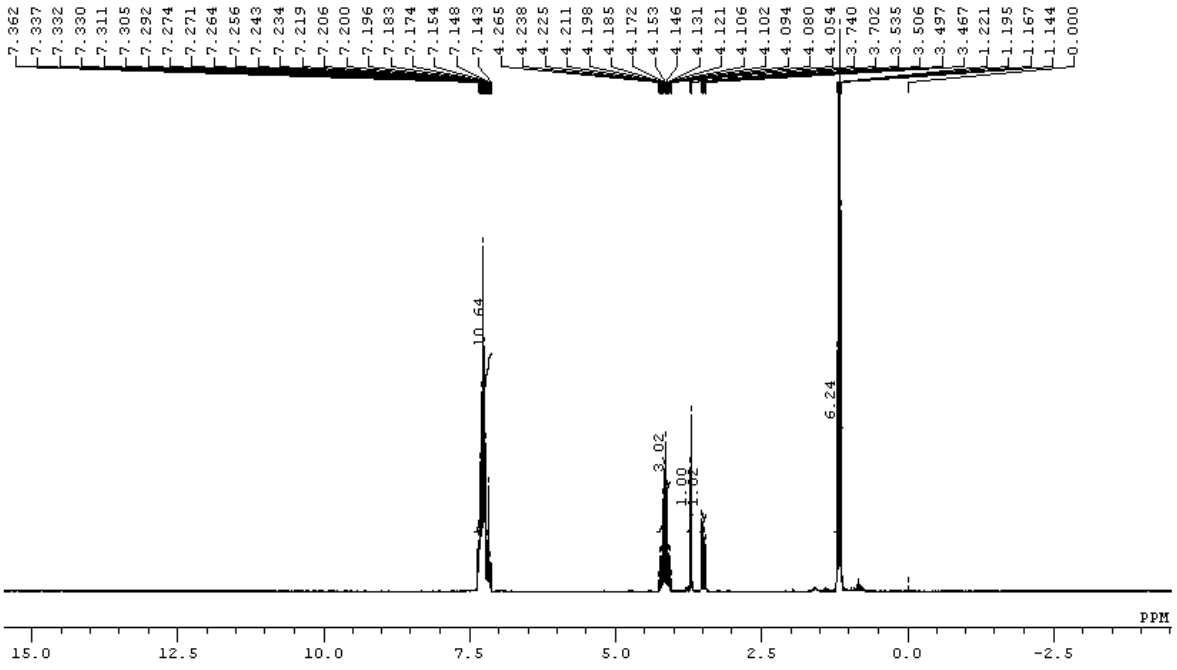
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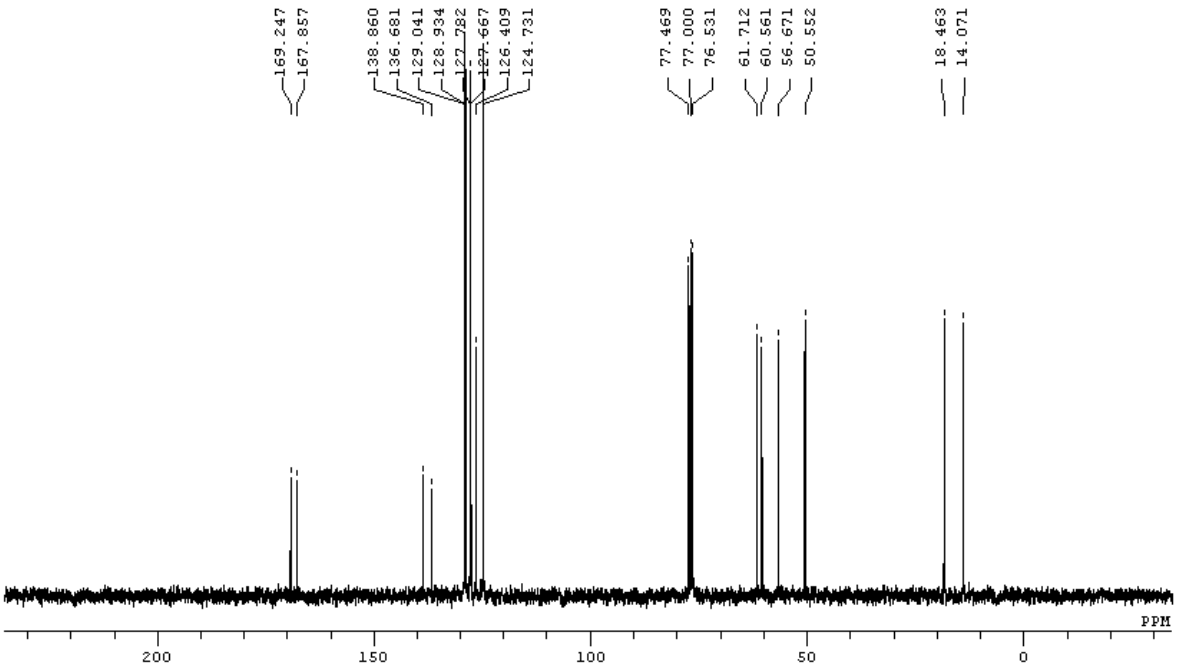
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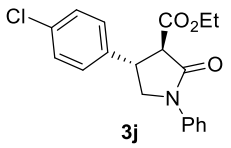
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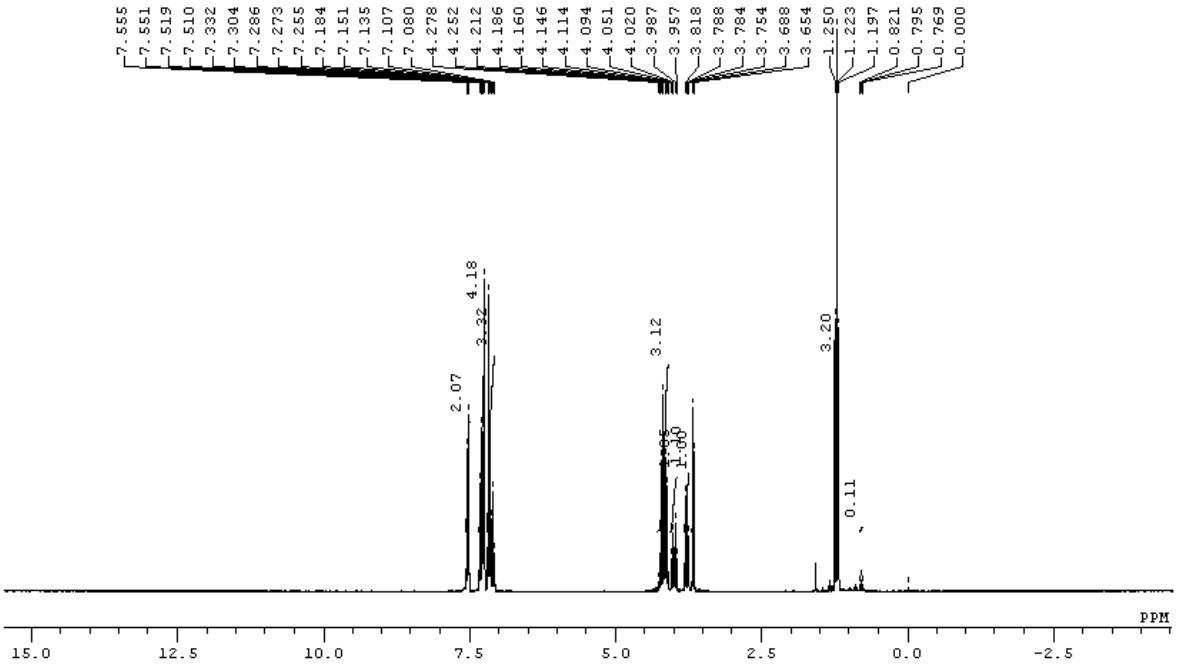
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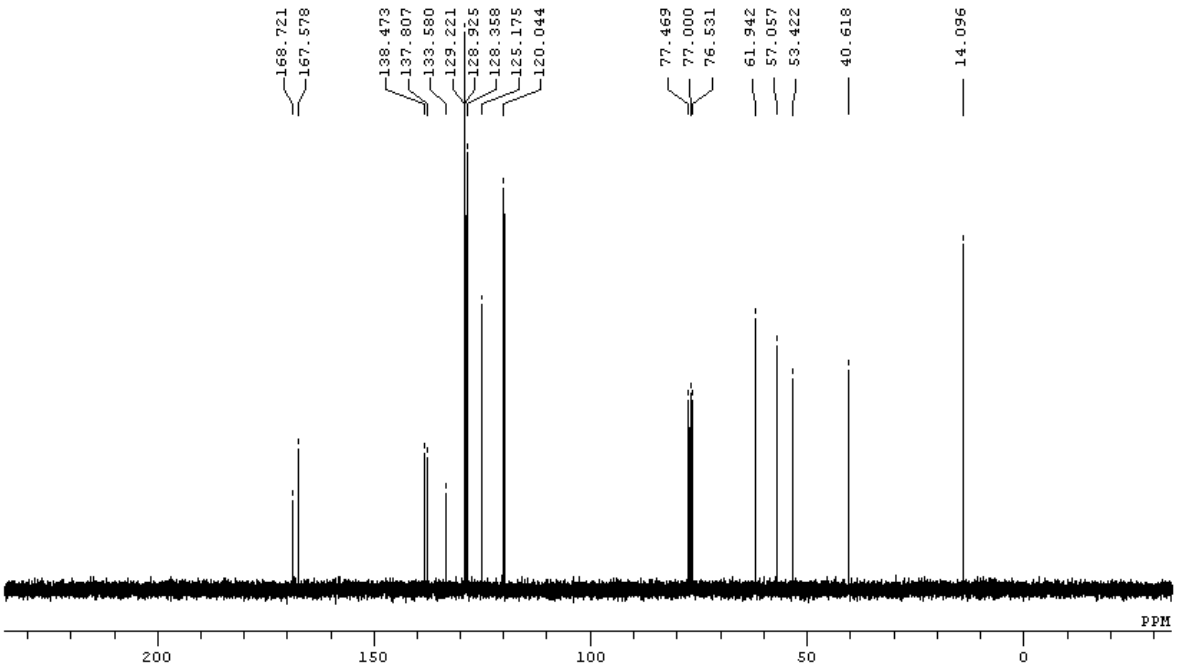
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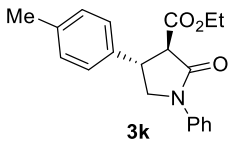
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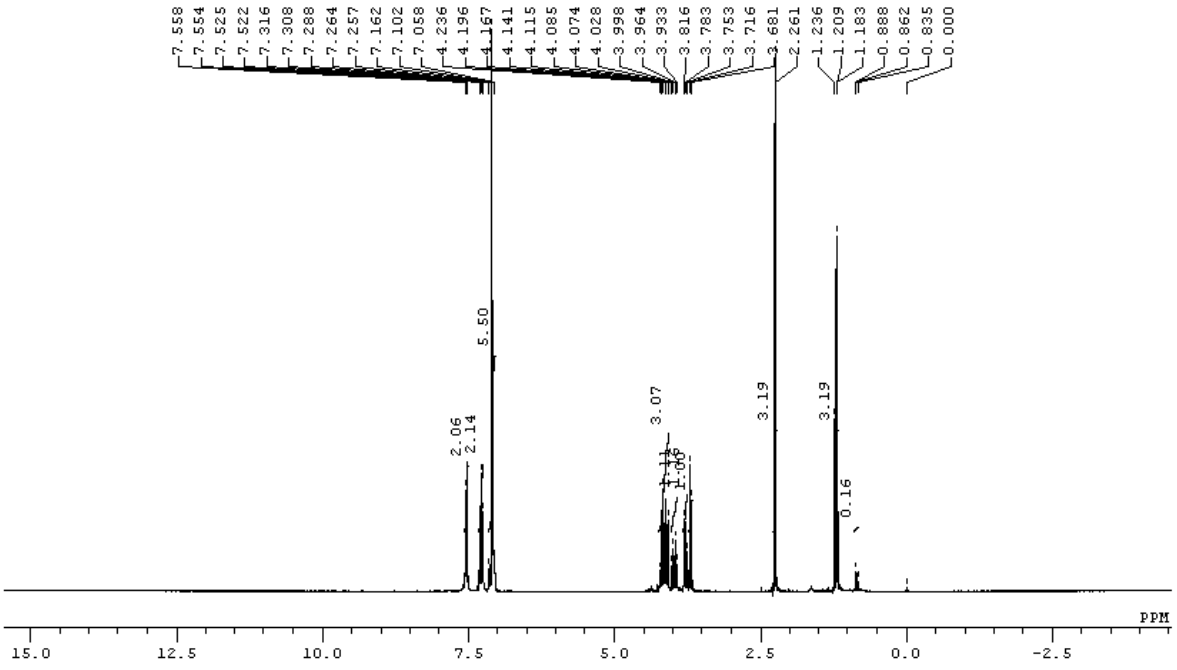
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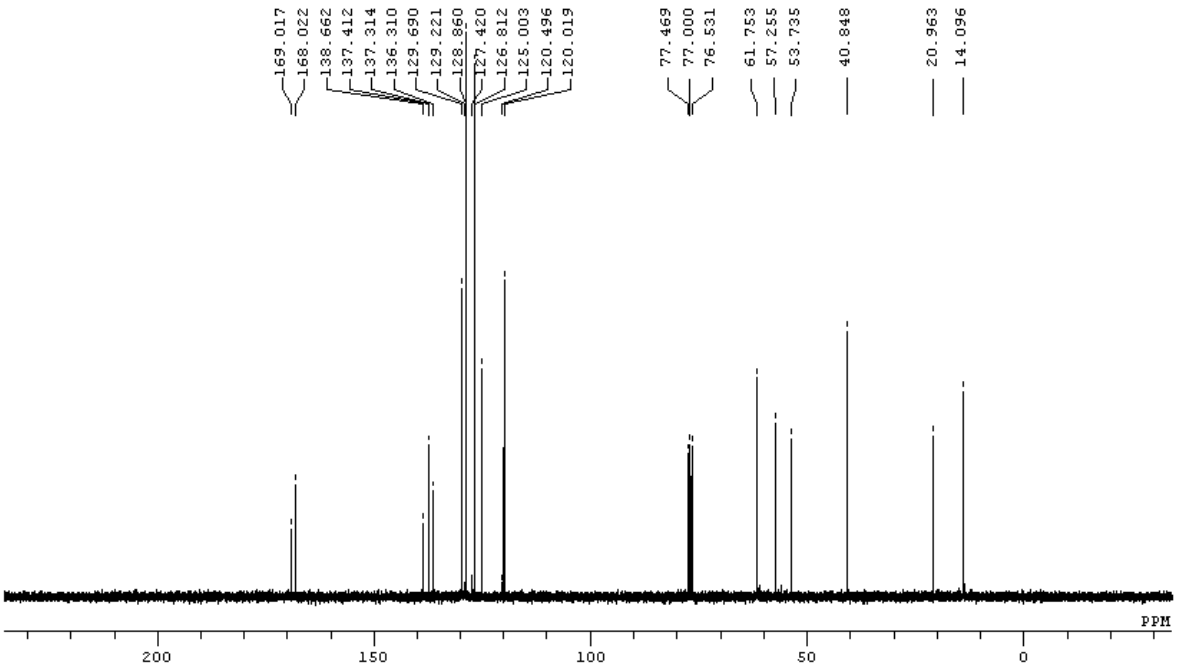
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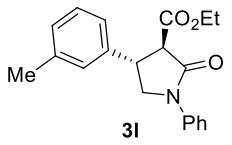
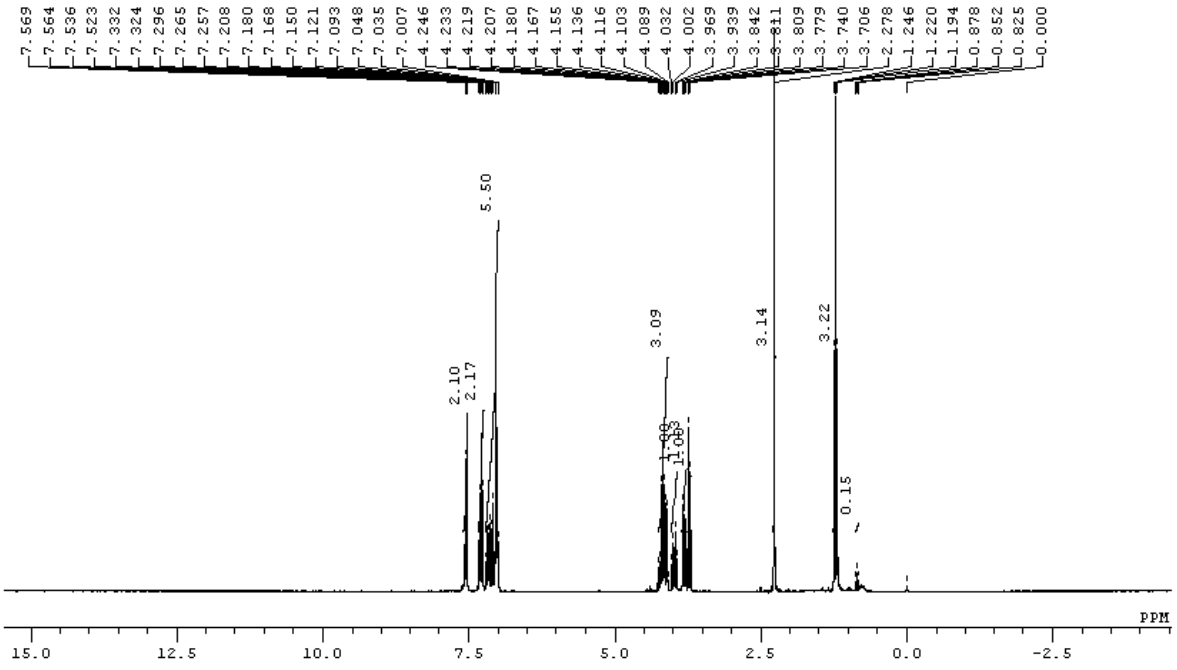

CO2Et
Me
O
N
Ph

3l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7.121
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7.048
7.035
7.007
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4.233
4.219
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4.155
4.136
4.116
4.103
4.089
4.032
4.002
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3.809
3.779
3.740
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2.278
1.246
1.220
1.194
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0.852
0.825
0.000
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3.09
3.14
3.22
2.10
2.17
1.00
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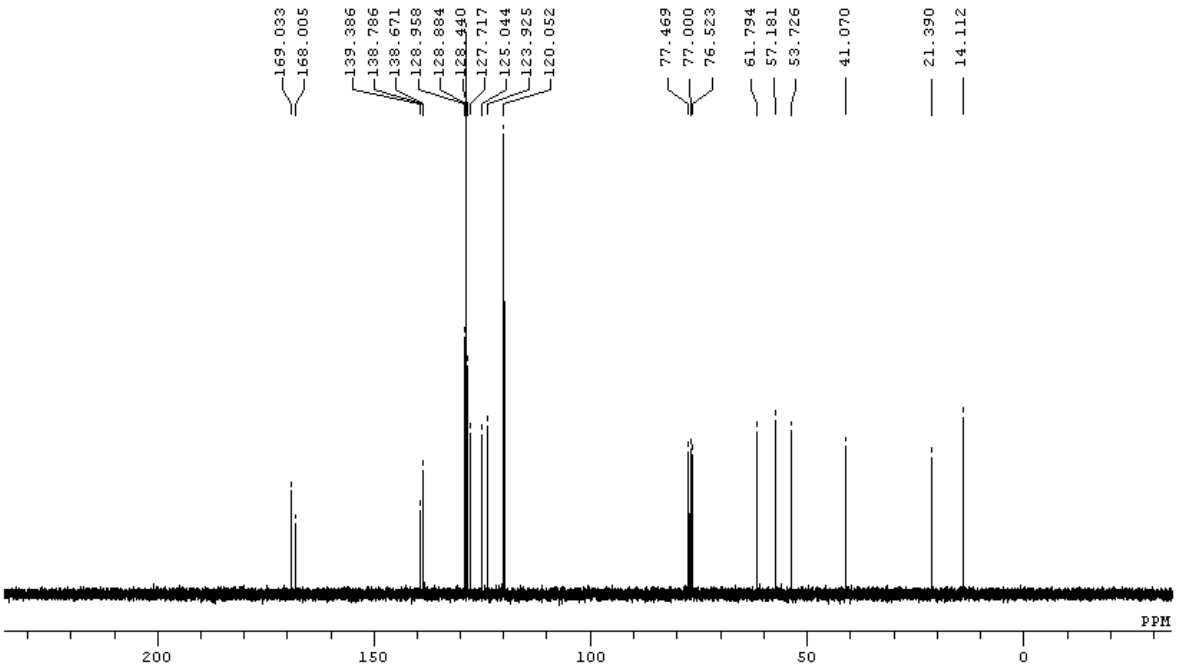
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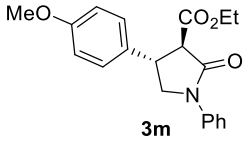
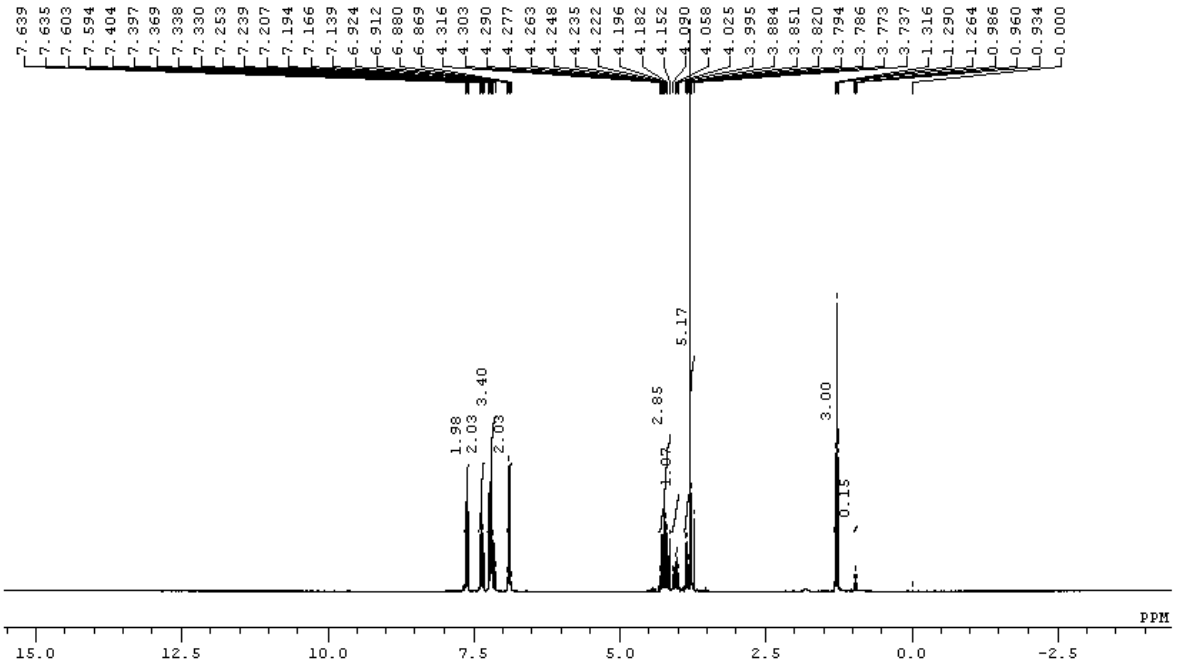

MeO
CO2Et
O
N
Ph

3m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7.166
7.139
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6.912
6.880
6.869
4.316
4.303
4.290
4.277
4.263
4.248
4.235
4.222
4.196
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4.152
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4.025
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3.820
3.794
3.786
3.773
3.737
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1.290
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0.960
0.934
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2.85
1.07
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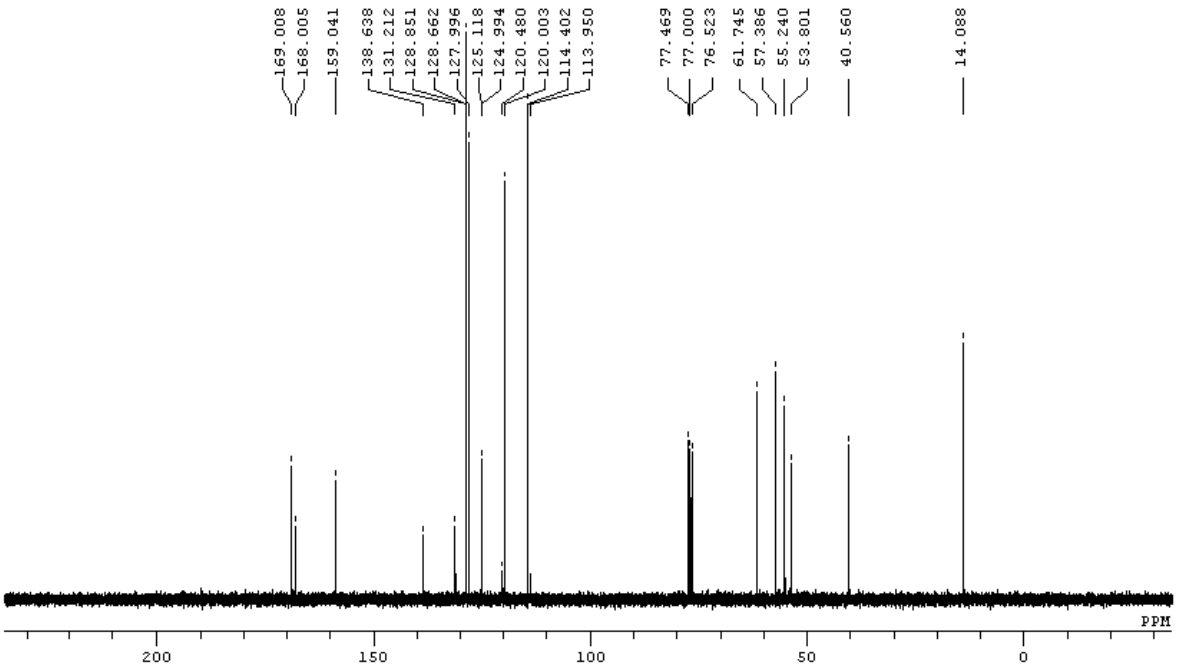
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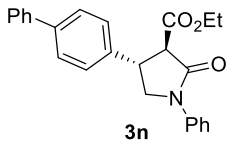
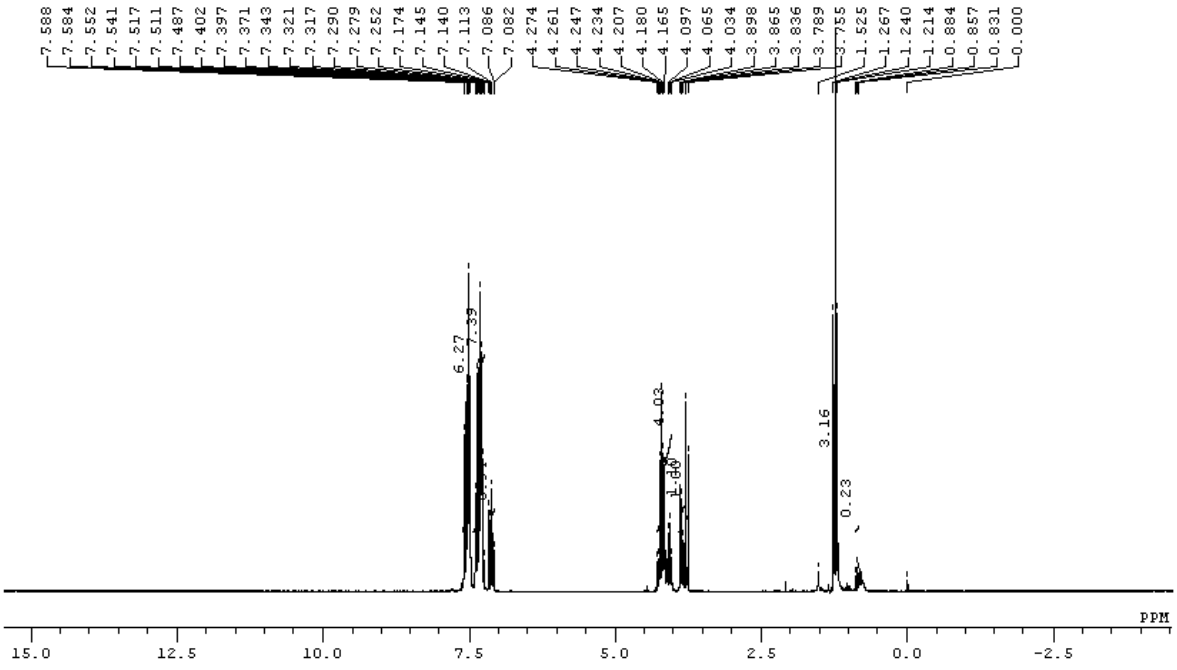

Ph
CO2Et
O
N
Ph

3n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7.290
7.279
7.252
7.174
7.145
7.140
7.113
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7.082
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4.261
4.247
4.234
4.207
4.180
4.165
4.097
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4.034
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0.857
0.831
0.000
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7.39
4.03
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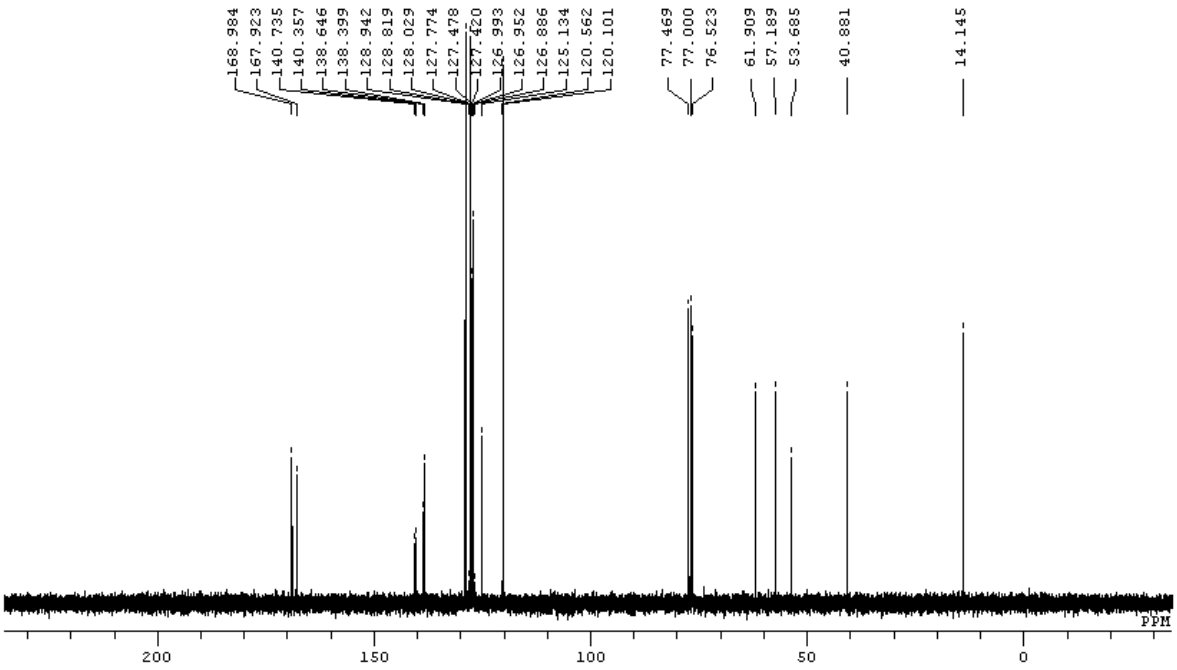
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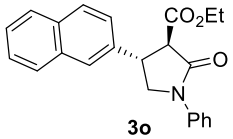
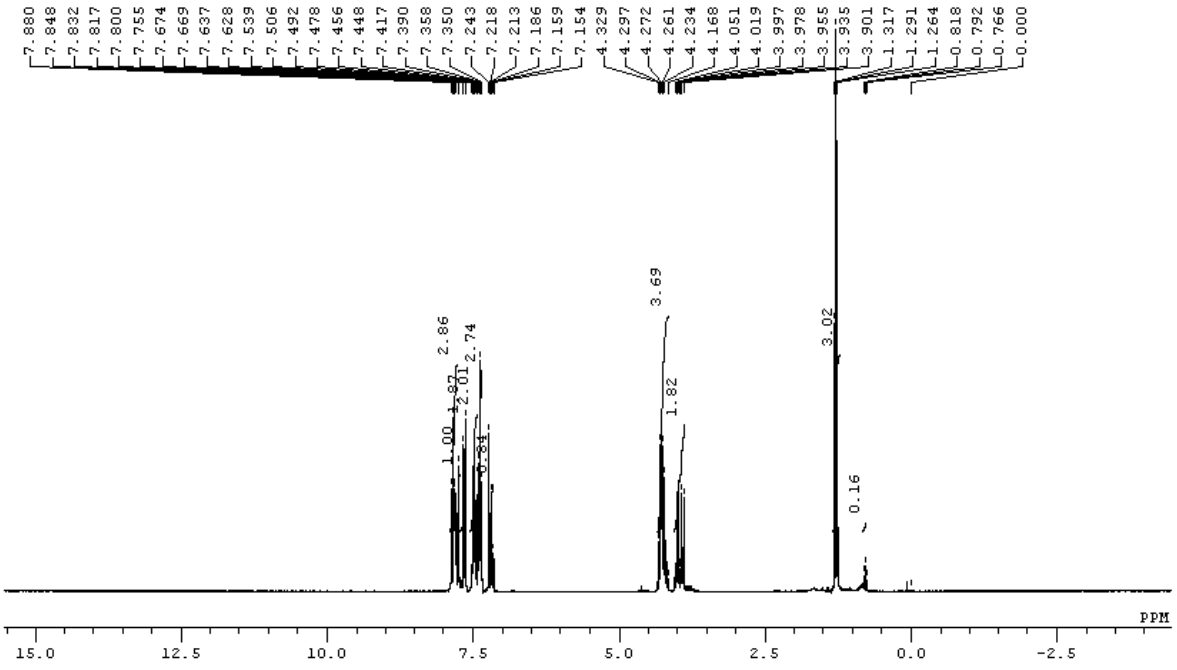

CO2Et
O
N
Ph

3o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7.478
7.456
7.448
7.417
7.390
7.358
7.350
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7.218
7.213
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7.159
7.154
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4.261
4.234
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3.935
3.901
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1.291
1.264
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0.792
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0.000
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1.87
2.01
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0.84
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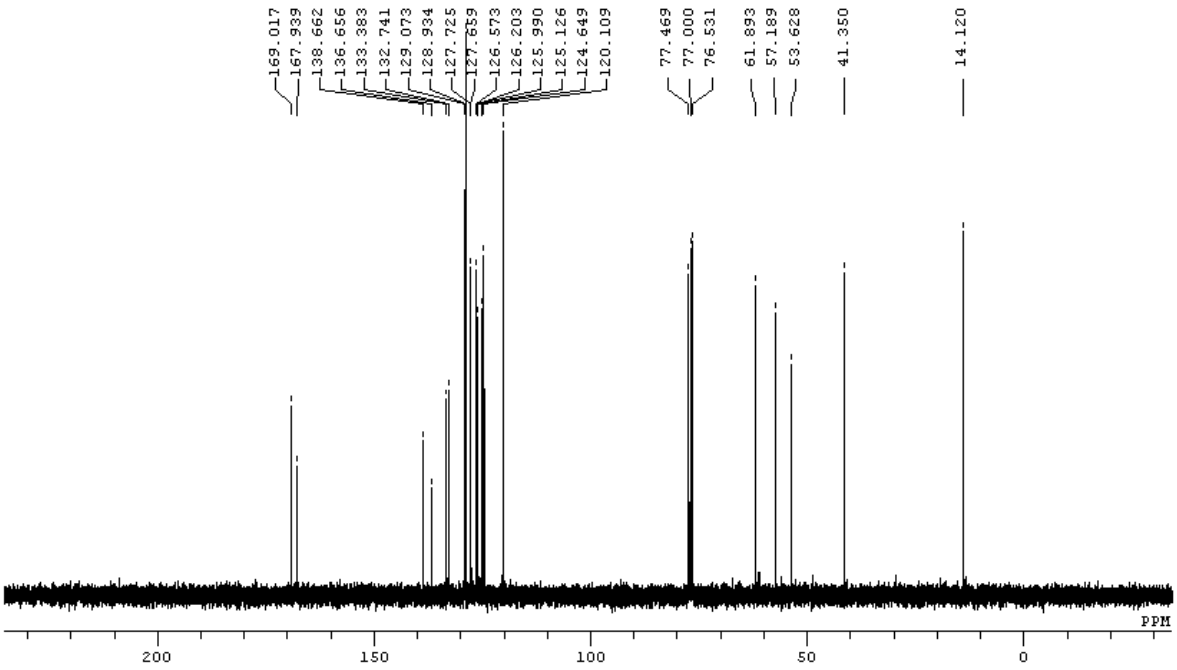
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127.659
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125.990
125.126
124.649
120.109
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77.000
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14.120
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150
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50
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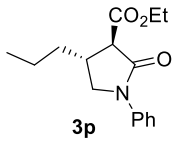
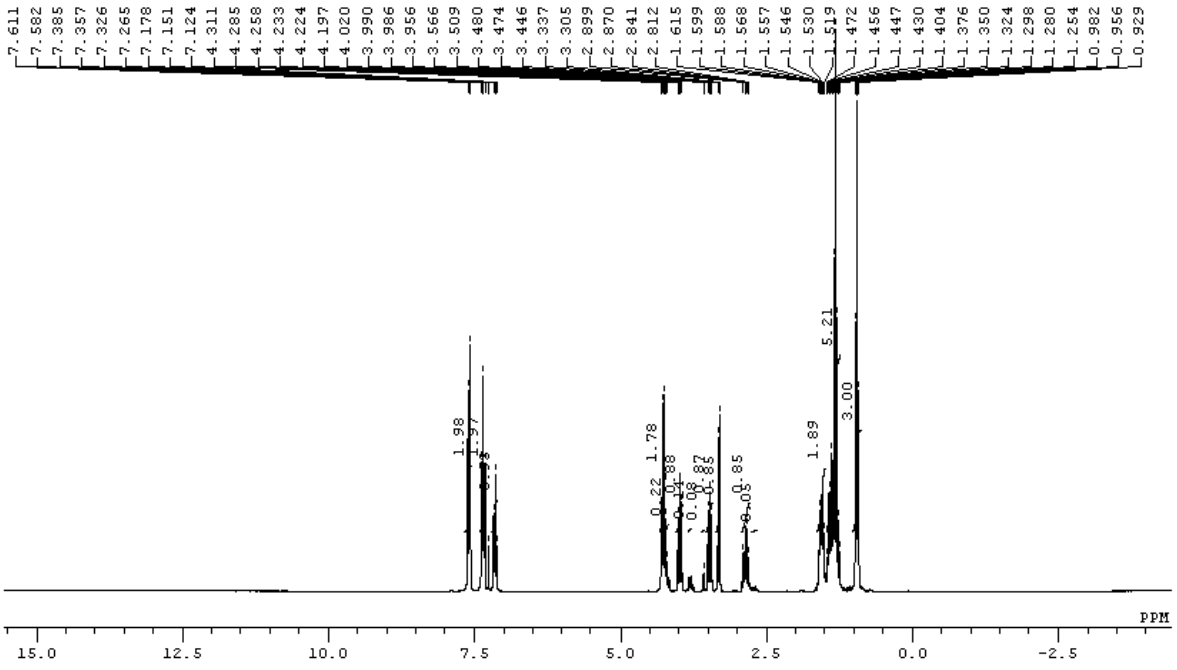

CO2Et
O
N
Ph

3p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4.233
4.224
4.197
4.020
3.990
3.986
3.956
3.566
3.509
3.480
3.474
3.446
3.337
3.305
2.899
2.870
2.841
2.812
1.615
1.599
1.588
1.568
1.557
1.546
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1.456
1.447
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1.324
1.298
1.280
1.254
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0.956
0.929
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1.97
1.78
0.88
0.87
0.85
0.85
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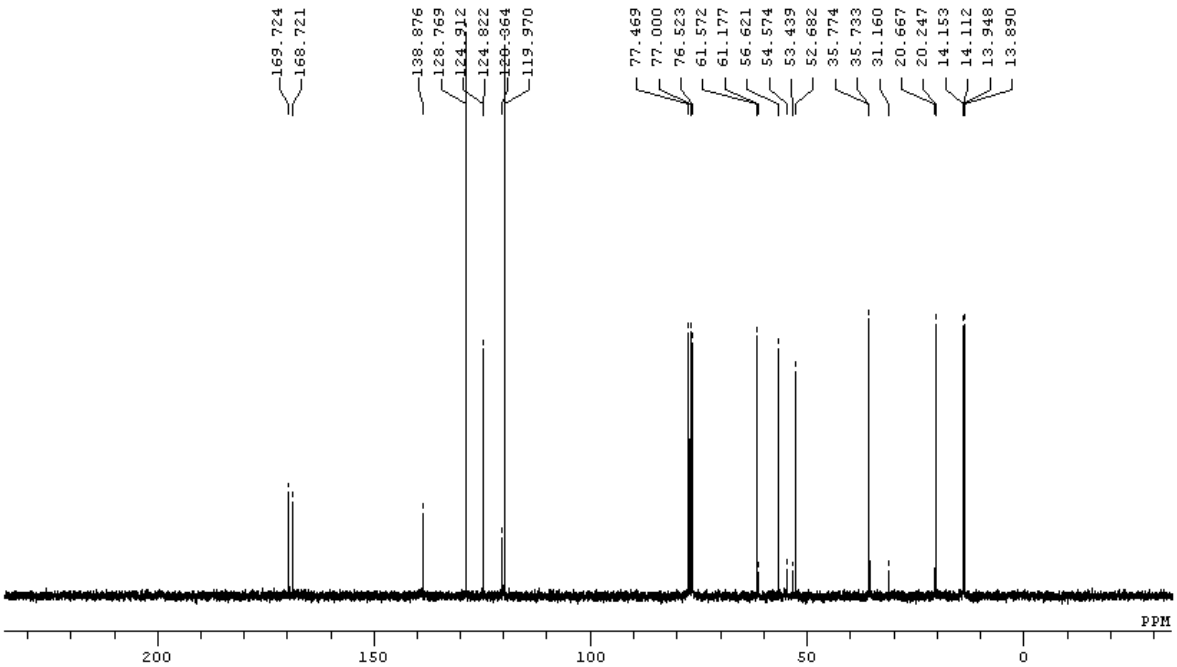
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54.574
53.439
52.682
35.774
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13.948
13.890
PPM
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150
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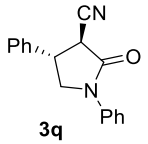
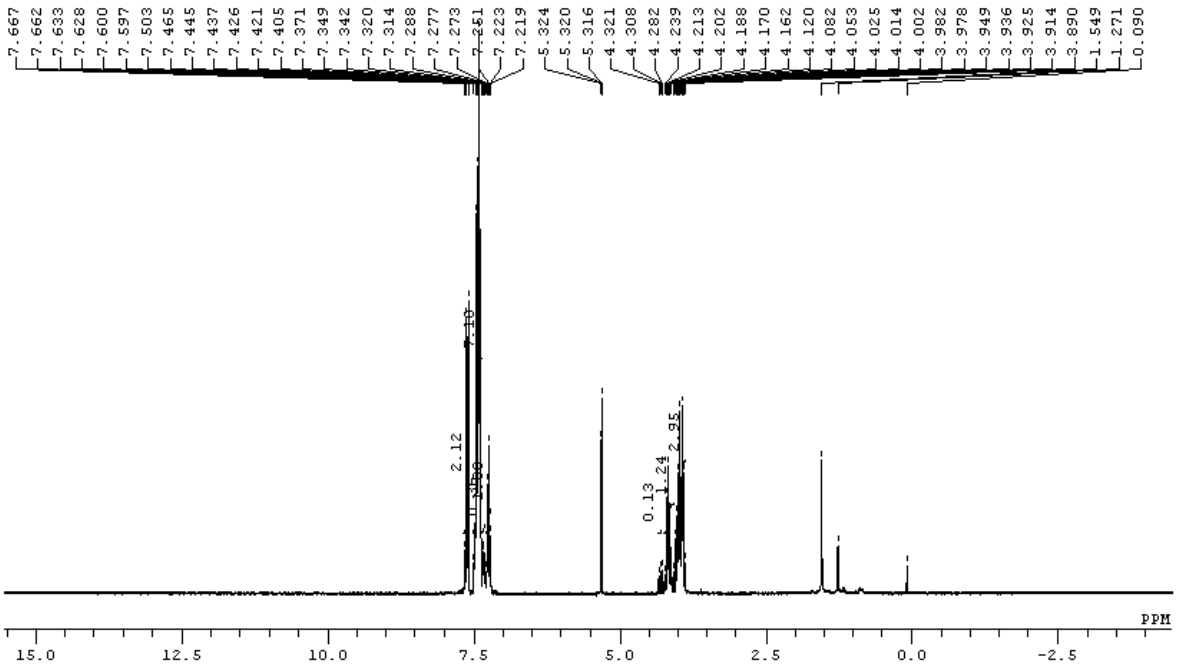
50
0


CN
Ph
O
N
Ph

3q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5.316
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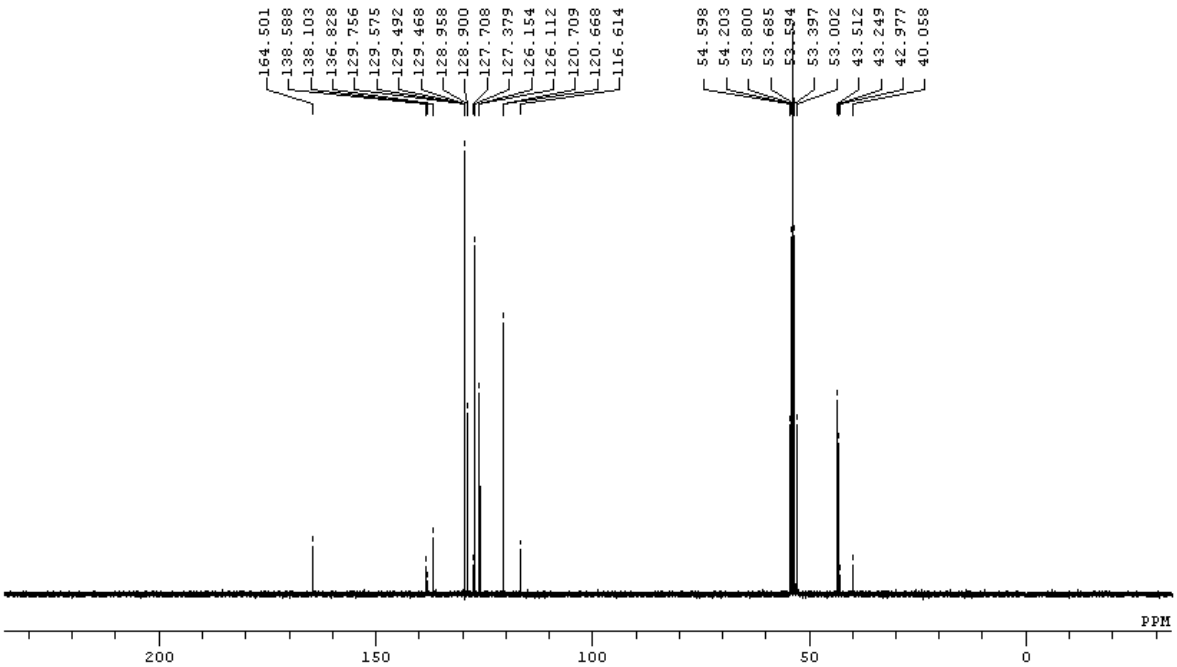
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126.112
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54.203
53.800
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150
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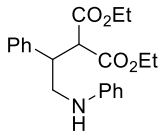
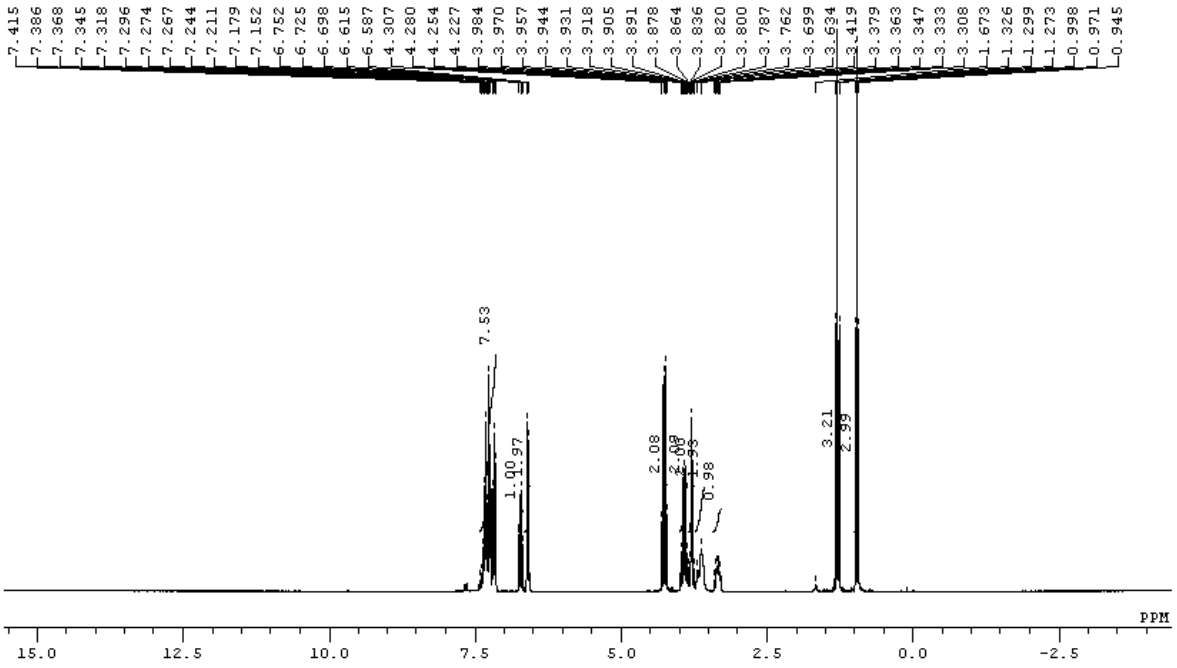

CO2Et
Ph
CO2Et
N
Ph
H

3a'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3.419
3.379
3.363
3.347
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0.0
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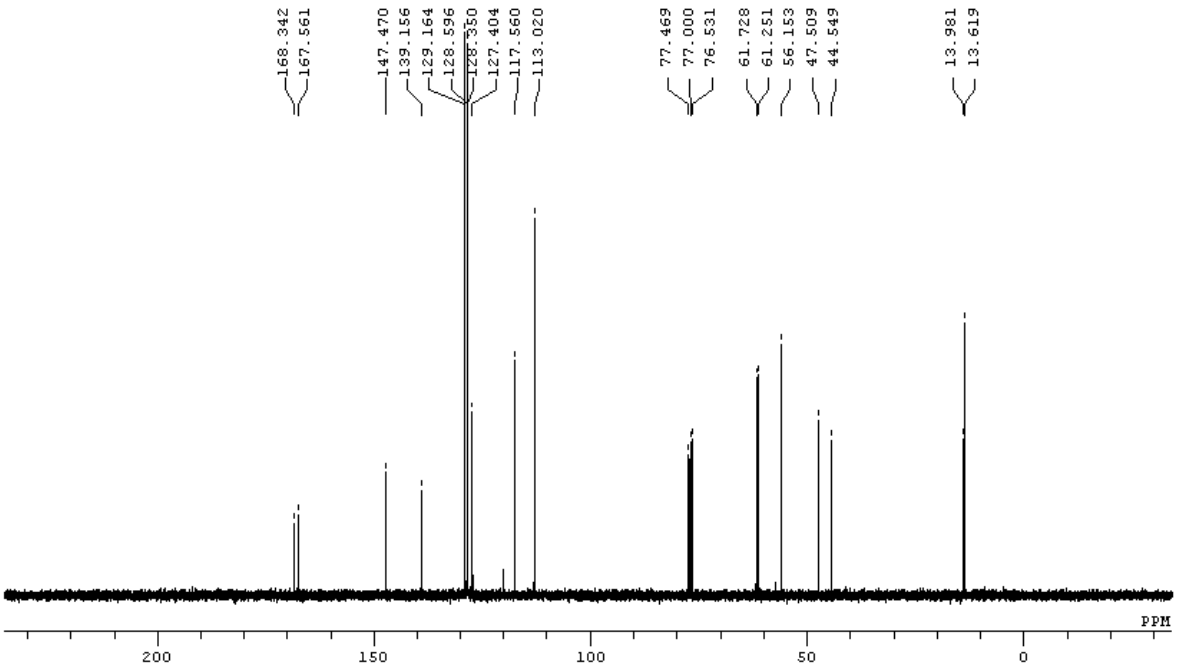
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128.596
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113.020
77.469
77.000
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44.549
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13.619
PPM
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150
100
50
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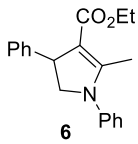
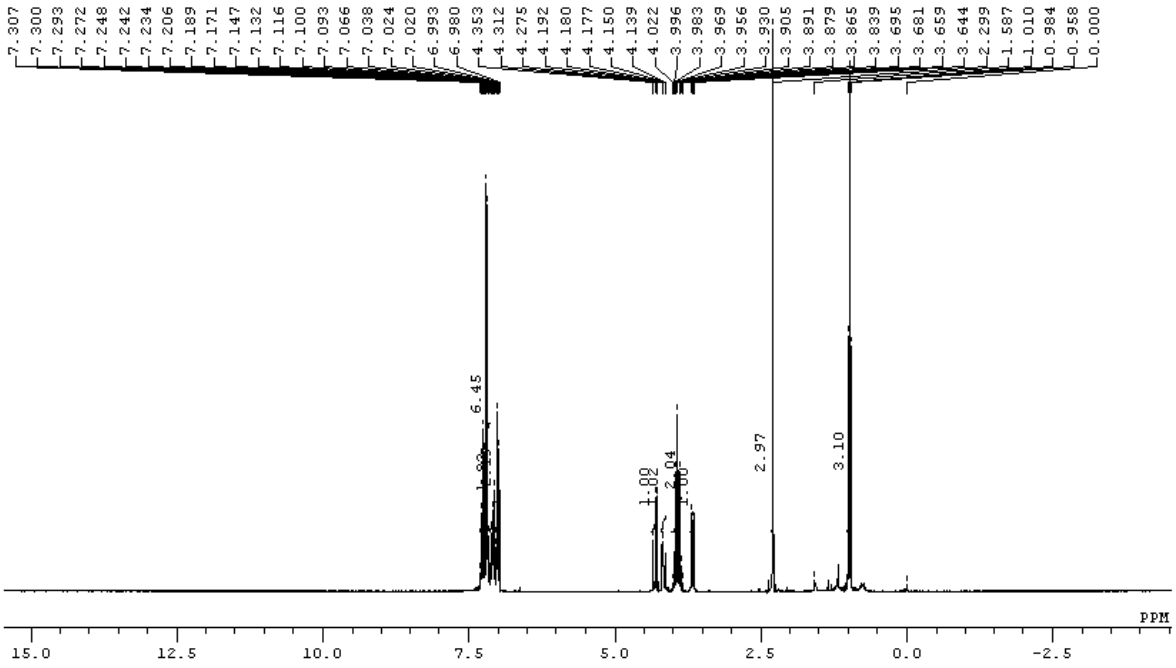

CO2Et
Ph
N
Ph

6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7.171
7.147
7.132
7.116
7.100
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7.066
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6.980
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4.139
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3.983
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3.891
3.879
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3.839
3.695
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0.000
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1.00
1.02
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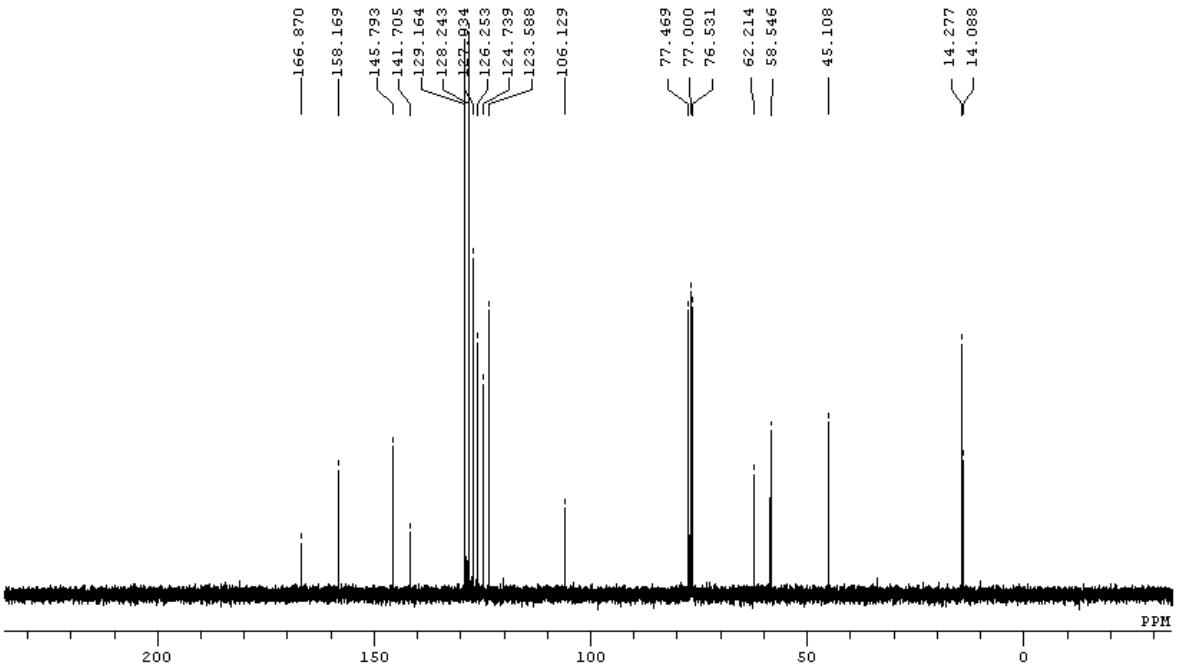
-2.5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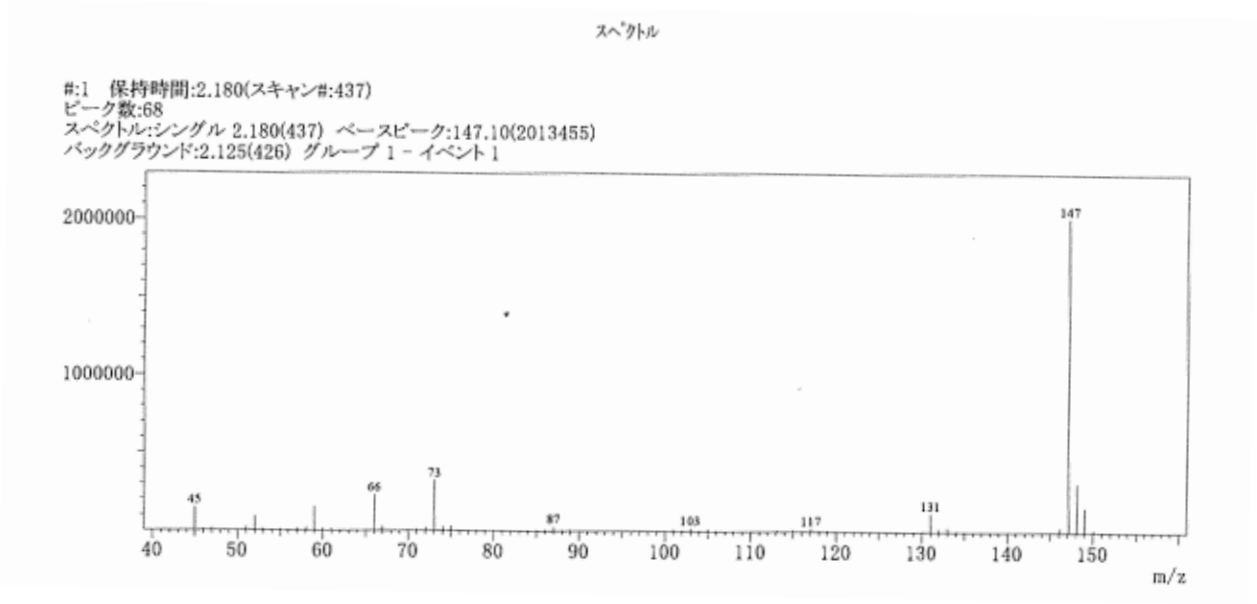
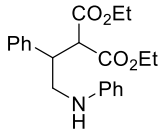
106.129
77.469
77.000
76.531
62.214
58.546
45.108
14.277
14.088
PPM
200
150
100
50
0

GCMS spectra.

Hexamethyldisiloxane ($C_5H_{15}OSi_2$ [M-CH_3]: *m/z* = 147):





3a' ($C_{21}H_{25}NO_4$ [M]: *m/z* = 355)