

Supporting Information

Polymer Incarcerated Gold-palladium Nanoclusters with Boron on Carbon: A Mild and Efficient Catalyst for the Sequential Aerobic Oxidation-Michael Addition of 1,3-Dicarbonyl Compounds to Allylic Alcohols

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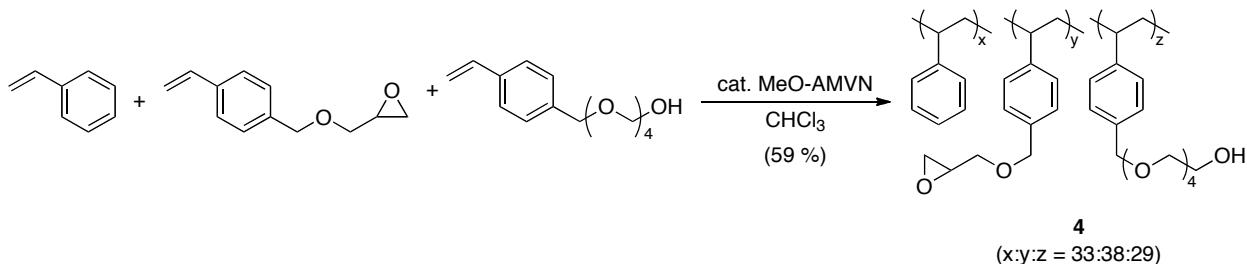
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General Information: Standard column chromatography was performed on 70-230 mesh silica gel (obtained from Merck) using flash column chromatography techniques.¹ IR spectra were measured on a JASCO FT/IR-610 spectrometer. Melting points were obtained using a Büchi Melting Point B-545 and were not corrected. ¹H and ¹³C NMR spectra were recorded on a JEOL ECX-500 in CDCl₃. Chemical shifts were reported in parts per million (ppm) from tetramethylsilane using the solvent resonance as the internal standard (chloroform: δ 7.26 ppm) for ¹H NMR and (deuterochlorofom: δ 77.0 ppm) for ¹³C NMR. ¹¹B CP-MAS NMR spectrum was recorded on a JEOL/JNM ECA-500 spectrometer with a 4mm MAS probe at spectral frequency 160.47 MHz. The boron spectrum was referenced to H₃BO₃ as a standard. High resolution mass spectrometry was carried out using a JEOL JMS-T100TD (DART). The content of all metals in the final material was determined by ICP analysis using a Shimadzu ICPS-7510 equipment: 10-20 mg of the final material was heated in a mixture of sulfuric acid and nitric acid at 200 °C for 2 hours. After cooling at room temperature, *aqua regia* (HCl:HNO₃ = 1:3 v/v) was added and the samples were diluted to 50 mL with distilled water. STEM images and EDS analyses were obtained using a JEOL JEM-2100F instrument operated at 200 kV. All TEM specimens were prepared by placing a drop of a suspension of the sample in methanol on carbon-coated copper grids and allowed to dry in air without staining. SEM images were obtained using a JEOL JSM-6700F instrument operated at 5.0 KV. Nitrogen adsorption measurements at 77 K were performed on a ASAP 2010 volumetric adsorption analyzer surface area and porosity analyzer equipped with pressure transducers covering the 1, 10, and 1000 Torr ranges (Micromeritics Instrument Corp.). The instrument was equipped with a turbo vacuum pump capable of reducing the pressure to below 10⁻⁷ Torr. The initial pressure at the start of any run was below 10⁻⁵ Torr.

Reagents: Unless stated otherwise, commercial reagents were used as received with the exception of NaBH₄, which was recrystallized from diglyme according to the literature.² The carbon black source used in this study was ketjen black EC 300J purchased from Lion Corporation. Allylic alcohols **2b**, **2d-i** were prepared according to the literature.³

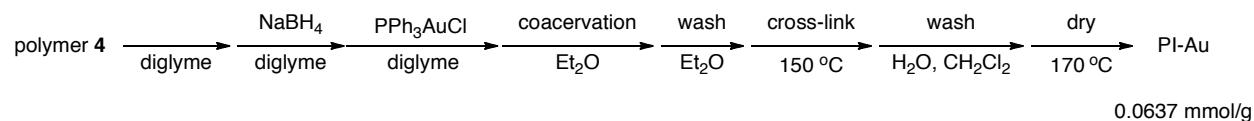
Part I: Preparation of PI-M (M = Au, Au-Sc, B) and PI/CB-B Catalysts

Preparation of Polymer 4



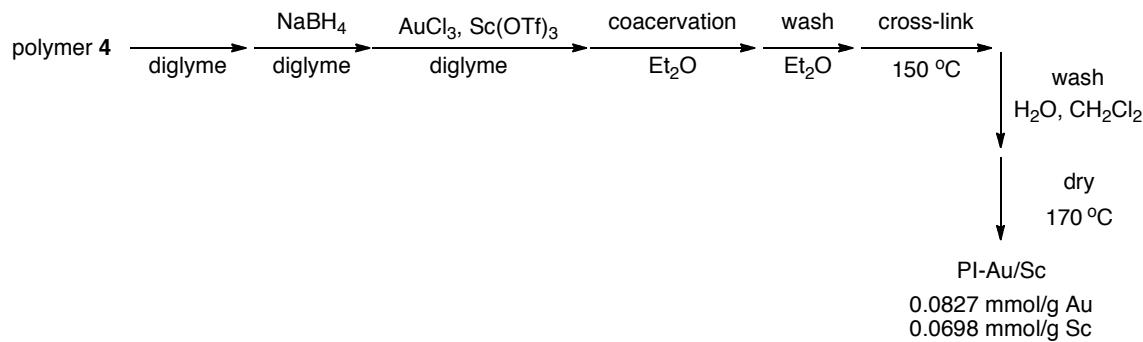
Polymer **4** was prepared according to the described procedure:⁴ styrene (3.21 g, 30.8 mmol), 4-vinylbenzyl glycidyl ether (5.88 g, 30.9 mmol), 2-(2-(2-(4-vinylbenzyl)ethoxy)ethoxy)ethanol (8.22 g, 30.9 mmol) and 2,2'-azobis(4-methoxy)-2-4-valeronitrile (0.2370 g, 0.769 mmol) were combined in chloroform (15.0 mL). The mixture was stirred for 48 h at room temperature. The resulting polymer was precipitated into diethyl ether, filtered, washed with diethyl ether and dried for 24 h *in vacuo* to afford the desired product **4** as white foam (10.25 g, 59%). The molar ratio of each functionalities was determined by ¹H NMR spectroscopy (x:y:z = 33:38:29). M_n and M_w were determined by GPC (M_n = 19,785, M_w = 23,188, M_w/M_n = 1.2).

Preparation of PI-Au



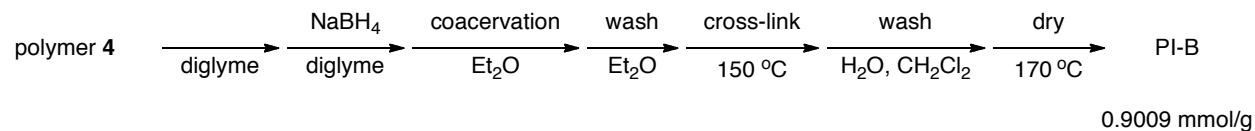
PI Au was prepared according to the described procedure:⁴ to a solution of polymer **4** (0.9028 g) in diglyme (13 mL) was added NaBH_4 (56.3 mg, 1.488 mmol). Then a solution of PPh_3AuCl (35.8 mg, 0.0722 mmol) in diglyme (4 mL) was added dropwise and the reaction was allowed to stir overnight at room temperature. Then diethyl ether (80 mL) was added dropwise. The coacervated Au polymer was washed several times with diethyl ether and was dried at room temperature. Next, the polymer was heated at 150 °C for 5 h without solvent. The cross-linked polymer was washed with DCM and H_2O , filtered, ground with a motor and pestle, and heated at 170°C for 5 h to provide a wine red solid (PI-Au, 0.9146 g, Au loading: 0.0637 mmol/g, B loading: 1.469 mmol/g).

Preparation of PI-Au/Sc



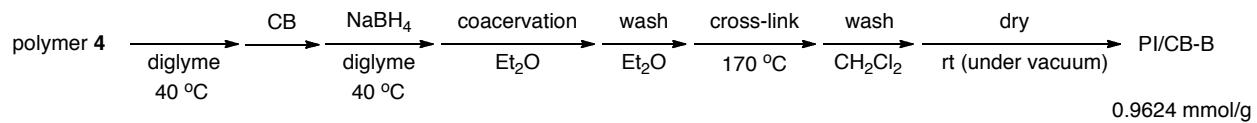
PI Au was prepared according to the described procedure: to a solution of polymer **4** (0.3768 g) in diglyme (7 mL) was added NaBH_4 (4.7 mg, 0.1242 mmol). Then a solution of AuCl_3 (9.5 mg, 0.0314 mmol) and $\text{Sc}(\text{OTf})_3$ (15.5 mg, 0.0315 mmol) in diglyme (2 mL) was added dropwise and the reaction was allowed to stir overnight at room temperature. Then diethyl ether (50 mL) was added dropwise. The coacervated Au polymer was washed several times with diethyl ether and was dried at room temperature. Next, the polymer was heated at 150 °C for 5 h without solvent. The cross-linked polymer was washed with DCM and H_2O , filtered, grounded with a motor and pestle, and heated at 170 °C for 5 h to provide a wine red solid (PI-Au/Sc, 0.2873 g, Au loading: 0.0827 mmol/g, Sc loading: 0.0698 mmol/g).

Preparation of PI-B



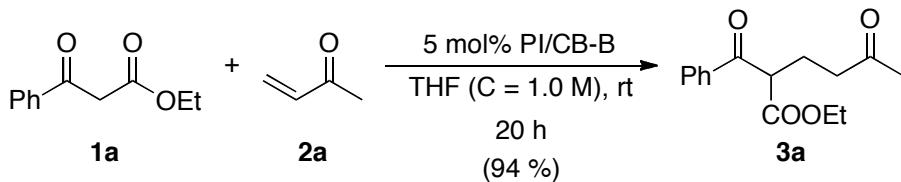
To a solution of polymer **4** (0.8695 g) in diglyme (12 mL) was added dropwise a solution of NaBH_4 (0.0570 g, 1.51 mmol) in diglyme (4 mL). After stirring for 4 h at room temperature, diethyl ether (40 mL) was added dropwise. The precipitated boron immobilized polymer was washed several times with diethyl ether and dried at room temperature. Next, the polymer was heated at 150 °C for 8 h without solvent. The cross-linked polymer was washed with DCM and H_2O , filtered, grounded with a motor and pestle and heated at 170 °C for 8 h to provide a pale yellow powder (PI-B, 0.7849 g, B loading: 0.9009 mmol/g).

Preparation of PI/CB-B



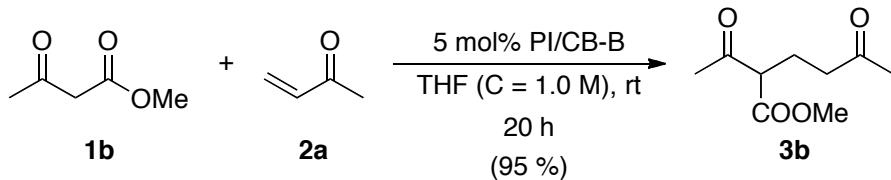
To a solution of polymer 4 (0.1563 g) in diglyme (3.9 mL) at 40 °C was added ketjen black (0.1573 g). After stirring the heterogeneous solution for 15 minutes, a solution of NaBH4 (17.7 mg, 0.469 mmol) in diglyme (1.6 mL) was added dropwise. After stirring for 4 h at 40 °C, diethyl ether (40 mL) was added dropwise. The boron containing polymer-coated carbon black was washed several times with diethyl ether and dried at room temperature. Next, the recovered solid powder was heated at 170°C for 4 h without solvent. After cooling to room temperature, the cross-linked polymer coated carbon black was washed several times with DCM, filtered, grounded with a motor and pestle and dried under vacuum to provide the desired black powder (PI/CB-B, 0.3312 g, B loading: 0.9624 mmol/g).

Part II: Scope of the Michael Addition of 1,3-Dicarbonyl Compounds to Electron-deficient Olefins



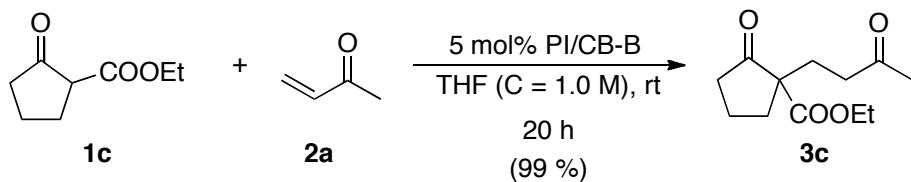
General Procedure for the PI/CB-B-catalyzed Michael Addition of 1,3-Dicarbonyl Compounds to Electron-deficient Olefins. In a screw-cap glass vial was added PI/CB-B (0.0261g, 0.0251 mmol, 5 mol %), β -ketoester **1a** (87.0 μ L, 0.502 mmol), and vinyl ketone **2a** (61.0 μ L, 0.754 mmol) and dissolved in THF (0.5 mL). The reaction mixture was allowed to stir for 20 h at room temperature. Then the reaction mixture was filtered, washed with DCM, and the resulting filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3a** (0.1239 g, 0.472 mmol, 94%) as a clear colourless oil.

Ethyl 2-benzoyl-5-oxohexanoate (3a) (Table 2, entry 1). R_f 0.22 (EtOAc:hexane = 1:4); 1 H NMR (CDCl_3 , 500 MHz) δ 8.00-7.91 (m, 2H), 7.53-7.50 (m, 1H), 7.43-7.40 (m, 2H), 4.37 (dd, J = 6.3, 6.2 Hz, 1H), 4.10-4.04 (m, 2H), 2.58-2.47 (m, 2H), 2.21-2.10 (m, 2H), 2.06 (s, 3H), 1.09 (t, J = 7.4 Hz, 3H); 13 C NMR (CDCl_3 , 125 MHz) δ 207.8, 195.2, 169.7, 135.8, 133.6, 128.7, 128.6, 61.3, 52.5, 40.4, 29.9, 22.6, 13.9. This is a known compound and the spectral data are identical to those reported in literature.⁵

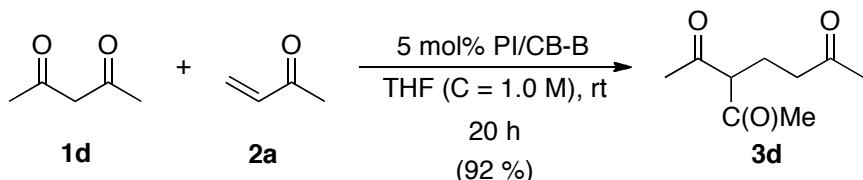


Methyl 2-acetyl-5-oxohexanoate (3b) (Table 2, entry 2). Following the above general procedure with β -ketoester **1b** (54.0 μ L, 0.500 mmol) and vinyl ketone **2a** (61.0 μ L, 0.754 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 2:3) to provide **3b** (0.0886 g, 0.476 mmol, 95%) as a clear colourless oil. R_f 0.30 (EtOAc:hexane = 2:3); 1 H NMR (CDCl_3 , 500 MHz) δ 3.67 (s, 3H), 3.46 (t, J = 7.4 Hz, 1H), 2.46-2.42 (m, 2H), 2.18 (s, 3H), 2.07 (s, 3H), 2.05-2.00 (m, 2H); 13 C NMR (CDCl_3 , 125 MHz) δ 207.4, 202.8, 169.9,

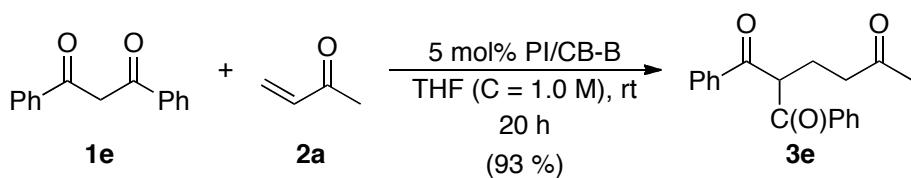
57.9, 52.4, 40.3, 29.9, 29.0, 21.6. This is a known compound and the spectral data are identical to those reported in literature.⁶



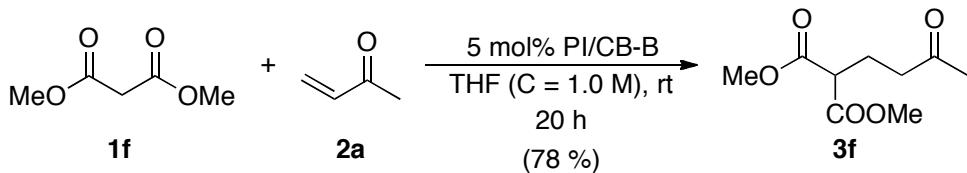
Ethyl 2-oxo-1-(3-oxobutyl)cyclopentane carboxylate (3c) (Table 2, entry 3). Following the above general procedure with β -ketoester **1c** (74.0 μ L, 0.499 mmol) and vinyl ketone **2a** (61.0 μ L, 0.754 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 2:3) to provide **3c** (0.1119 g, 0.495 mmol, 99%) as a clear colourless oil. R_f 0.43 (EtOAc:hexane = 2:3); 1 H NMR (CDCl_3 , 500 MHz) δ 4.10 (q, J = 6.8 Hz, 2H), 2.67-2.60 (m, 1H), 2.43-2.19 (m, 4H), 2.07-1.80 (m, 8H), 1.18 (t, J = 7.4 Hz, 3H); 13 C NMR (CDCl_3 , 125 MHz) δ 214.9, 207.7, 171.3, 61.3, 58.8, 38.7, 37.9, 34.2, 29.8, 26.8, 19.5, 13.9. This is a known compound and the spectral data are identical to those reported in literature.⁷



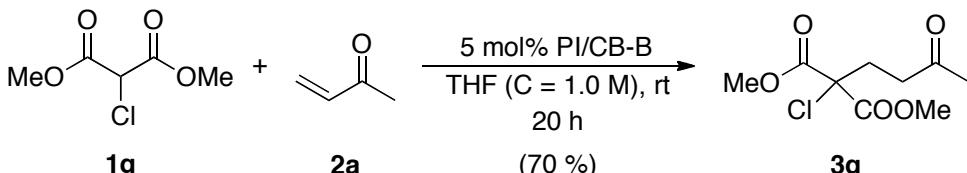
3-Acetylheptane-2,6-dione (3d) (Table 2, entry 4). Following the above general procedure with 1,3-diketone **1d** (51.0 μ L, 0.497 mmol) and vinyl ketone **2a** (60.0 μ L, 0.740 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 2:3) to provide **3d** (0.0781 g, 0.459 mmol, 92%) as a clear colourless oil. R_f 0.33 (EtOAc:hexane = 2:3); 1 H NMR (CDCl_3 , 500 MHz) δ 3.62 (t, J = 6.8 Hz, 1H), 2.38 (t, J = 6.8 Hz, 2H), 2.13 (s, 6H), 2.07 (s, 3H), 2.01 (q, J = 6.8 Hz, 2H); 13 C NMR (CDCl_3 , 125 MHz) δ 207.4, 204.1 (x2), 66.7, 40.4, 30.0, 29.9 (x2), 21.3. This is a known compound and the spectral data are identical to those reported in literature.⁷



2-Benzoyl-1-phenylhexane-1,5-dione (3e) (Table 2, entry 5). Following the above general procedure with 1,3-diketone **1e** (0.1123 g, 0.501 mmol) and vinyl ketone **2a** (61.0 μ L, 0.754 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 2:3) to provide **3e** (0.1365 g, 0.464 mmol, 93%) as a white solid. R_f 0.2 (EtOAc:hexane = 1:4); 1 H NMR (CDCl_3 , 500 MHz) δ 8.04 (d, J = 7.9 Hz, 4H), 7.57 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.9 Hz, 4H), 5.49 (t, J = 6.8 Hz, 1H), 2.70 (t, J = 6.8 Hz, 2H), 2.32 (dd, J = 13.0, 6.2 Hz, 2H), 2.12 (s, 3H); 13 C NMR (CDCl_3 , 125 MHz) δ 208.7, 196.3, 135.7, 133.6, 128.9, 128.6, 54.6, 40.7, 30.0, 23.1. This is a known compound and the spectral data are identical to those reported in literature.⁸

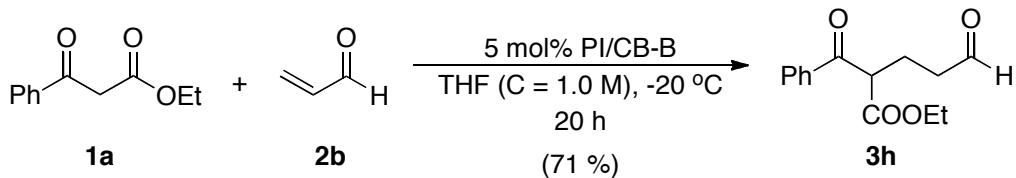


Dimethyl 2-(3-oxobutyl)malonate (3f) (Table 2, entry 6). Following the above general procedure with malonate **1f** (57.0 μ L, 0.499 mmol) and vinyl ketone **2a** (61.0 μ L, 0.754 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3f** (0.0787 g, 0.389 mmol, 78%) as a clear colourless oil. R_f 0.42 (EtOAc:hexane = 2:3); 1 H NMR (CDCl_3 , 500 MHz) δ 3.67 (s, 6H), 3.38 (t, J = 7.4 Hz, 1H), 2.48 (t, J = 7.4 Hz, 1H), 2.09 (d, J = 7.4 Hz, 2H), 2.08 (s, 3H); 13 C NMR (CDCl_3 , 125 MHz) δ 207.2, 169.5, 52.5, 50.2, 40.3, 29.9, 22.4. This is a known compound and the spectral data are identical to those reported in literature.⁹

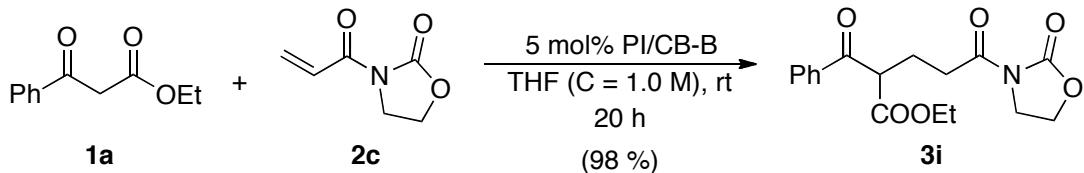


Dimethyl 2-chloro-2-(3-oxobutyl)malonate (3g) (Table 2, entry 7). Following the above general procedure with malonate **1g** (68.0 μ L, 0.501 mmol) and vinyl ketone **2a** (61.0 μ L, 0.754 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3g** (0.0829 g, 0.350 mmol, 70%) as a clear colourless oil. R_f 0.22 (EtOAc:hexane

= 1:4); IR (neat, NaCl): 3008 (m), 2958 (s), 2844 (w), 2363 (w), 1754 (s), 1719 (s), 1442 (s), 1372 (s), 1263 (s), 1169 (s), 1109 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 3.81 (s, 6H), 2.65 (t, J = 8.0 Hz, 2H), 2.53 (t, J = 7.9 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 206.1, 167.0, 69.5, 53.9, 53.9, 38.3, 31.3, 29.9; ESI-HRMS (m/z) calcd. for $\text{C}_9\text{H}_{13}\text{O}_5\text{Cl} [(\text{M}+\text{H})^+]$: 237.05298, found: 237.05352.

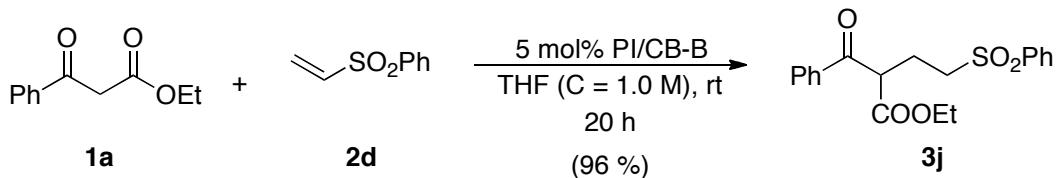


Ethyl 2-benzoyl-5-oxopentanoate (3h) (Table 2, entry 8). Following the above general procedure with β -ketoester **1a** (87.0 μL , 0.502 mmol) and vinyl aldehyde **2b** (51.0 μL , 0.763 mmol) that was distilled prior to use. The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3h** (0.0885 g, 0.356 mmol, 71%) as a clear colourless oil. R_f 0.22 (EtOAc:hexane = 1:4); ^1H NMR (CDCl_3 , 500 MHz) δ 9.77 (s, 1H), 8.01-8.00 (m, 2H), 7.60-7.57 (m, 1H), 7.48 (t, J = 7.9 Hz, 2H), 4.44-4.41 (m, 1H), 4.16-4.10 (m, 2H), 2.68-2.55 (m, 2H), 2.35-2.22 (m, 2H), 1.15 (t, J = 7.4 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 201.1, 194.8, 169.5, 135.8, 133.7, 128.8, 128.6, 61.5, 52.6, 41.1, 21.1, 13.9. This is a known compound and the spectral data are identical to those reported in literature.¹⁰



Ethyl 2-benzoyl-5-oxo-5-(2-oxooxazolidin-3-yl)pentanoate (3i) (Table 2, entry 9). Following the above general procedure with β -ketoester **1a** (87.0 μL , 0.502 mmol) and oxazolidinone **2c** (0.0780 g, 0.552 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 2:3) to provide **3i** (0.1639 g, 0.492 mmol, 98%) as a white solid. R_f 0.14 (EtOAc:hexane = 2:3); ^1H NMR (CDCl_3 , 500 MHz) δ 8.00 (d, J = 7.4 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.9 Hz, 2H), 4.49-4.46 (m, 1H), 4.39 (t, J = 7.9 Hz, 2H), 4.16-4.10 (m, 2H), 4.02-3.97 (m, 2H), 3.07-2.99 (m, 2H), 2.37-2.29 (m, 2H), 1.15 (t, J = 6.8 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 194.8, 172.3, 169.5, 153.4, 135.8, 133.5, 128.7, 128.6, 62.1, 61.5, 52.9,

42.4, 32.7, 23.2, 13.9. This is a known compound and the spectral data are identical to those reported in literature.¹⁰



Ethyl 2-benzoyl-4-(phenylsulfonyl)butanoate (3j) (Table 2, entry 10). Following the above general procedure with β -ketoester **1a** (87.0 μ L, 0.502 mmol) and vinyl sulfone **2d** (0.0930 g, 0.553 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3j** (0.1743 g, 0.484 mmol, 96%) as a clear colourless oil. R_f 0.38 (EtOAc:hexane = 2:3); IR (neat, NaCl): 3068 (m), 2988 (m), 2939 (m), 2329 (w), 1971 (w), 1739 (s), 1685 (s), 1600 (m), 1446 (s), 1248 (s), 1154 (s), 1085 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 7.98-7.96 (m, 2H), 7.90-7.88 (m, 2H), 7.66-7.54 (m, 4H), 7.47-7.46 (m, 2H), 4.66 (t, J = 6.8 Hz, 1H), 4.10 (q, J = 7.4 Hz, 2H), 3.27-3.19 (m, 2H), 2.41-2.35 (m, 2H), 1.12 (t, J = 7.4 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 194.1, 168.8, 138.6, 135.5, 133.89, 133.87, 129.3, 128.8, 128.7, 127.9, 61.8, 53.3, 51.5, 21.9, 13.8; ESI-HRMS (m/z) calcd. for $\text{C}_{19}\text{H}_{21}\text{O}_5\text{S}_2$ $[(\text{M}+\text{H})^+]$: 361.11097, found: 361.11270.

Part III: Recover and Reuse of PI/CB-B Catalyst for the Michael Reaction

General Recover and Reuse Procedure for the PI-B/C-catalyzed Michael Addition of Ethyl Benzoylacetate (1a) to Methyl Vinyl Ketone (2a). In a screw-cap glass vial was added PI/CB-B (0.0261g, 0.0251 mmol, 5 mol %), β -ketoester **1a** (87.0 μ L, 0.502 mmol), and vinyl ketone **2a** (61.0 μ L, 0.754 mmol) that was purified *via* filtration through a plug of basic alumina or by distillation and dissolved in THF (0.5 mL). The reaction mixture was allowed to stir for 20 h at room temperature. Then the reaction mixture was filtered, washed with DCM, and the resulting filtrate was concentrated under reduced pressure. The yield of Michael adduct **3a** was determined by ^1H NMR of the crude reaction mixture using mesitylene as an internal standard. The leaching of boron was checked by ICP analysis of the crude reaction mixture. The recovered PI/CB-B catalyst (approx. 1 mg was lost during filtration) was dried under vacuum for 2 h at room temperature and reused for the subsequent Michael reaction.

Part IV: Preparation of Bimetallic PI/CB Catalysts

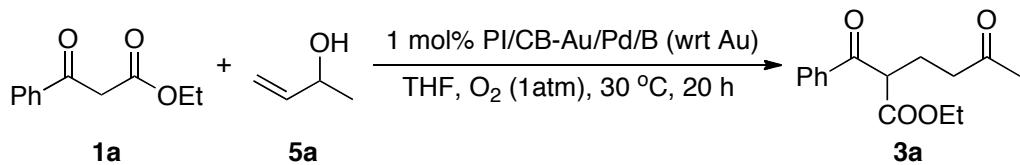
Table S-1. General Preparation Method for Bimetallic PI/CB Catalysts

Target Loading: Au = 0.28 mmol/g
 M = 0.28 mmol/g
 B = 4.2 mmol/g

entry	M	Au (mmol/g)	M (mmol/g)	B (mmol/g)
1	Na_2PtCl_6	0.1092	0.1105	2.656
2	$\text{Pd}(\text{OAc})_2$	0.2007	0.2183	2.456
3	$\text{Cu}(\text{OAc})_2$	0.2096	0.1545	2.335
4	$(\text{PPh}_3)_2\text{NiCl}_2$	0.1526	0.2241	2.306
5	CoCl_2	0.1437	0.1538	2.524
6	$[\text{RhCl}(\text{COD})]_2$	0.1605	0.1749	2.447
7	FeCl_2	0.1784	0.1687	2.564
8	$[\text{RuCl}_2(\text{p-cymene})]_2$	0.1655	0.1527	2.383

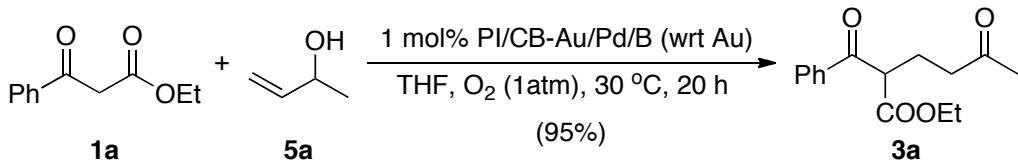
Preparation of PI/CB-Au/Pd/B: To a solution of **4** (0.1448 g) in diglyme (9.6 mL) was added ketjen black (0.1458 g). The resulting suspension was cooled to 0 °C and then a solution of NaBH_4 (46.0 mg, 1.21 mmol) in diglyme (2.2 mL) was added dropwise. The reaction mixture was allowed to stir for approximately 15 min, then a solution of PPh_3AuCl (40.2 mg, 0.0811 mmol) and $\text{Pd}(\text{OAc})_2$ (18.2 mg, 0.0811 mmol) in diglyme (5.8 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stir for 4 h. Diethyl ether (80 mL) was added dropwise and then the suspension was filtered and washed with excess diethyl ether. The isolated polymer-coated carbon black was allowed to dry, gently ground with motor and pestle, and then was heated at 170 °C for 4 h. The polymer-incarcerated catalyst was then re-suspended in DCM, filtered, washed with excess DCM, and allowed to dry to provide PI/CB-Au/Pd/B (0.4035 g, Au loading: 0.2007 mmol/g, Pd loading: 0.2183 mmol/g, B loading: 2.456 mmol/g).

Part V: Recover and Reuse of the PI/CB-Au/Pd/B Catalyst for the Sequential Aerobic Oxidation-Michael Reaction



General Recover and Reuse Procedure for the PI/CB-Au/Pd/B-catalyzed Aerobic Oxidation-Michael Addition of Ethyl Benzoylacetate (1a) to 1-Buten-3-ol (5a). In a screw-cap test tube was added PI/CB-Au/Pd/B (0.0250 g, 5.02 µmol, 1 mol % with respect to Au), β-ketoester **1a** (87.0 µL, 0.502 mmol), and allylic alcohol **5a** (65.0 µL, 0.750 mmol) and was dissolved in THF (0.5 mL). The reaction mixture was allowed to stir for 20 h at 30 °C with a balloon of oxygen gas. Then the reaction mixture was filtered, washed with DCM, and the resulting filtrate was concentrated under reduced pressure. The yield of **3a** was determined by ¹H NMR of the crude reaction mixture using mesitylene as an internal standard. The leaching of the metals was determined by ICP analysis of the crude reaction mixture. The recovered PI/CB-Au/Pd/B catalyst (approx. 1-4 mg was lost during filtration) was dried under vacuum for 2 h at room temperature and reused for the subsequent sequential reaction.

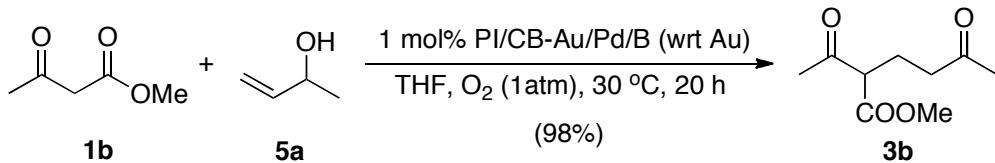
Part VI: Scope of the PI/CB-Au/Pd/B-catalyzed Sequential Reaction



General Procedure for the PI/CB-Au/Pd/B-catalyzed Sequential Aerobic Oxidation-

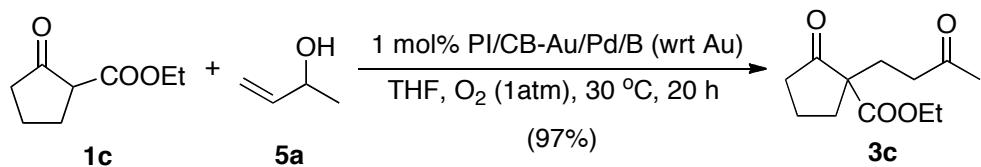
Michael Addition of 1,3-Dicarbonyl Compounds to Allylic Alcohols. In a screw-cap test tube was added PI/CB-Au/Pd/B (0.0250 g, 5.02 µmol, 1 mol % with respect to Au), β-ketoester **1a** (87.0 µL, 0.502 mmol), and allylic alcohol **5a** (65.0 µL, 0.750 mmol) and was dissolved in THF (0.5 mL). The reaction mixture was allowed to stir for 20 h at 30 °C (or 60 °C in certain cases) under a balloon of oxygen gas. Then the reaction mixture was filtered, washed with DCM, and the resulting filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3a** (0.1253 g, 0.478 mmol, 95%) as a clear colourless oil.

Ethyl 2-benzoyl-5-oxohexanoate (3a) (Table 6, entry 1). R_f 0.22 (EtOAc:hexane = 1:4); ¹H NMR (CDCl₃, 500 MHz) δ 8.00-7.91 (m, 2H), 7.53-7.50 (m, 1H), 7.43-7.40 (m, 2H), 4.37 (dd, *J* = 6.3, 6.2 Hz, 1H), 4.10-4.04 (m, 2H), 2.58-2.47 (m, 2H), 2.21-2.10 (m, 2H), 2.06 (s, 3H), 1.09 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 207.8, 195.2, 169.7, 135.8, 133.6, 128.7, 128.6, 61.3, 52.5, 40.4, 29.9, 22.6, 13.9. This is a known compound and the spectral data are identical to those reported in literature.⁵

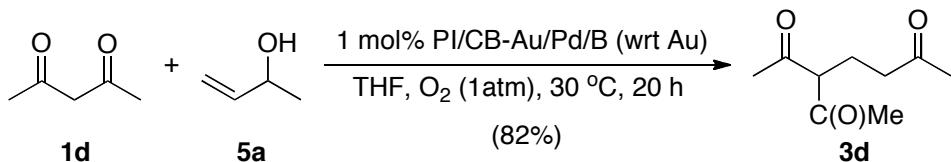


Methyl 2-acetyl-5-oxohexanoate (3b) (Table 6, entry 2). Following the above general procedure with β-ketoester **1b** (54.0 µL, 0.500 mmol) and allylic alcohol **5a** (65.0 µL, 0.750 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 2:3) to provide **3b** (0.0912 g, 0.490 mmol, 98%) as a clear colourless oil. R_f 0.30 (EtOAc:hexane = 2:3); ¹H NMR (CDCl₃, 500 MHz) δ 3.67 (s, 3H), 3.46 (t, *J* = 7.4 Hz, 1H), 2.46-2.42 (m, 2H), 2.18 (s, 3H), 2.07 (s, 3H), 2.05-2.00 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 207.4, 202.8, 169.9,

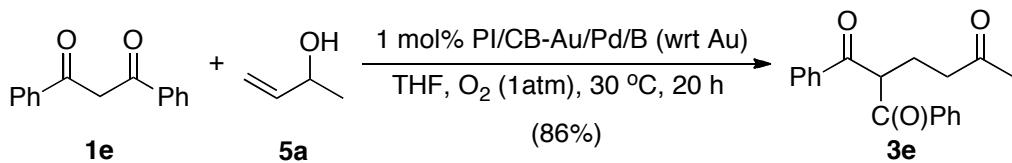
57.9, 52.4, 40.3, 29.9, 29.0, 21.6. This is a known compound and the spectral data are identical to those reported in literature.⁶



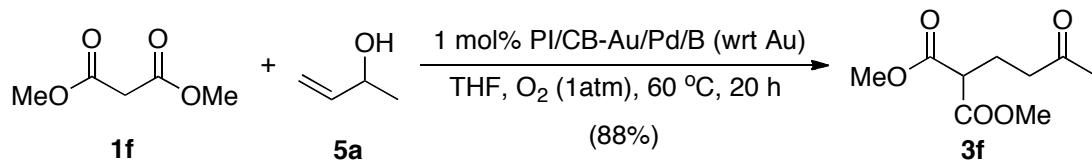
Ethyl 2-oxo-1-(3-oxobutyl)cyclopentane carboxylate (3c) (Table 6, entry 3). Following the above general procedure with β -ketoester **1c** (74.0 μ L, 0.499 mmol) and allylic alcohol **5a** (65.0 μ L, 0.750 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 2:3) to provide **3c** (0.1092 g, 0.483 mmol, 97%) as a clear colourless oil. R_f 0.43 (EtOAc:hexane = 2:3); ¹H NMR (CDCl₃, 500 MHz) δ 4.10 (q, J = 6.8 Hz, 2H), 2.67-2.60 (m, 1H), 2.43-2.19 (m, 4H), 2.07-1.80 (m, 8H), 1.18 (t, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 214.9, 207.7, 171.3, 61.3, 58.8, 38.7, 37.9, 34.2, 29.8, 26.8, 19.5, 13.9. This is a known compound and the spectral data are identical to those reported in literature.⁷



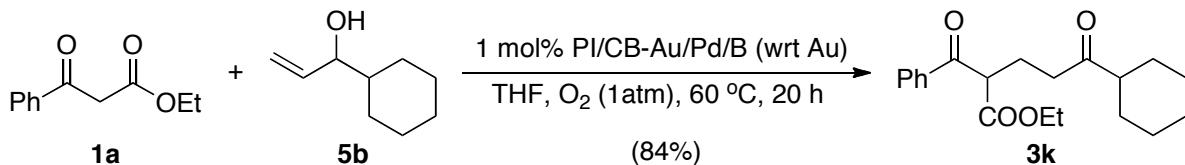
3-Acetylheptane-2,6-dione (3d) (Table 6, entry 4). Following the above general procedure with 1,3-diketone **1d** (50.0 μ L, 0.487 mmol) and allylic alcohol **5a** (65.0 μ L, 0.750 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 2:3) to provide **3d** (0.0680 g, 0.400 mmol, 82%) as a clear colourless oil. R_f 0.33 (EtOAc:hexane = 2:3); ¹H NMR (CDCl₃, 500 MHz) δ 3.62 (t, J = 6.8 Hz, 1H), 2.38 (t, J = 6.8 Hz, 2H), 2.13 (s, 6H), 2.07 (s, 3H), 2.01 (q, J = 6.8 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 207.4, 204.1 (x2), 66.7, 40.4, 30.0, 29.9, 21.3. This is a known compound and the spectral data are identical to those reported in literature.⁷



2-Benzoyl-1-phenylhexane-1,5-dione (3e) (Table 6, entry 5). Following the above general procedure with 1,3-diketone **1e** (0.1121 g, 0.500 mmol) and allylic alcohol **5a** (65.0 μ L, 0.750 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 2:3) to provide **3e** (0.1258 g, 0.427 mmol, 86%) as a white solid. R_f 0.2 (EtOAc:hexane = 1:4); 1 H NMR (CDCl_3 , 500 MHz) δ 8.04 (d, J = 7.9 Hz, 4H), 7.57 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.9 Hz, 4H), 5.49 (t, J = 6.8 Hz, 1H), 2.70 (t, J = 6.8 Hz, 2H), 2.32 (dd, J = 13.0, 6.2 Hz, 2H), 2.12 (s, 3H); 13 C NMR (CDCl_3 , 125 MHz) δ 208.7, 196.3, 135.7, 133.6, 128.9, 128.6, 54.6, 40.7, 30.0, 23.1. This is a known compound and the spectral data are identical to those reported in literature.⁸

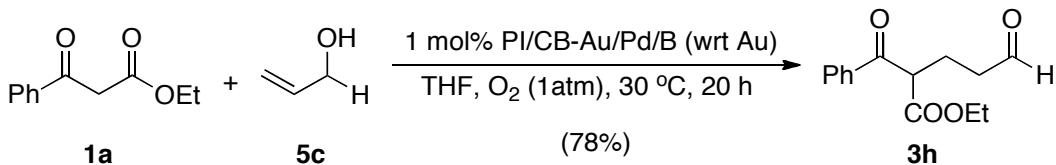


Dimethyl 2-(3-oxobutyl)malonate (3f) (Table 6, entry 6). Following the above general procedure with malonate **1f** (57.0 μ L, 0.499 mmol) and allylic alcohol **5a** (86.0 μ L, 0.992 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3f** (0.0889 g, 0.440 mmol, 88%) as a clear colourless oil. R_f 0.42 (EtOAc:hexane = 2:3); 1 H NMR (CDCl_3 , 500 MHz) δ 3.67 (s, 6H), 3.38 (t, J = 7.4 Hz, 1H), 2.48 (t, J = 7.4 Hz, 1H), 2.09 (d, J = 7.4 Hz, 2H), 2.08 (s, 3H); 13 C NMR (CDCl_3 , 125 MHz) δ 207.2, 169.5, 52.5, 50.2, 40.3, 29.9, 22.4. This is a known compound and the spectral data are identical to those reported in literature.⁹

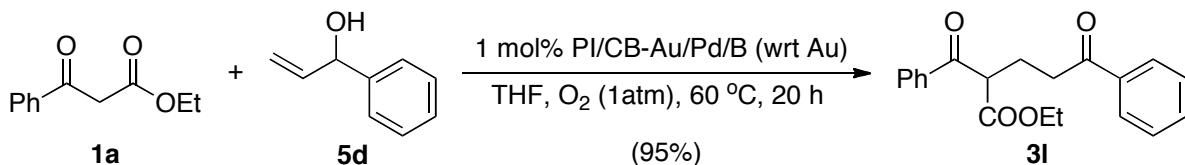


Ethyl 2-benzoyl-5-cyclohexyl-5-oxopentanoate (3k) (Table 6, entry 7). Following the above general procedure with β -ketoester **1a** (87.0 μ L, 0.502 mmol), and allylic alcohol **5b** (77.5 mg, 0.553 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3k** (0.1295 g, 0.422 mmol, 84%) as a clear colourless oil. R_f 0.43 (EtOAc:hexane = 1:4); IR (neat, NaCl): 3062 (m), 2934 (s), 2854 (s), 2666 (w), 1975 (w),

1909 (w), 1739 (s), 1693 (s), 1599 (m), 1448 (s), 1371 (m), 1247 (s), 1032 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 8.00 (d, $J = 7.3$ Hz, 2H), 7.57-7.54 (m, 1H), 7.45 (t, $J = 7.9$ Hz, 2H), 4.42 (dd, $J = 7.9, 6.2$ Hz, 1H), 4.16-4.07 (m, 2H), 2.64-2.49 (m, 2H), 2.28-2.16 (m, 3H), 1.81-1.62 (m, 4H), 1.30-1.18 (m, 6H), 1.14 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 213.1, 195.3, 169.8, 136.0, 133.5, 128.7, 128.6, 61.2, 52.7, 50.7, 37.3, 28.3, 25.7, 25.5, 22.7, 13.9; ESI-HRMS (m/z) calcd. for $\text{C}_{20}\text{H}_{36}\text{O}_4$ $[(\text{M}+\text{H})^+]$: 331.19093, found: 331.19196.

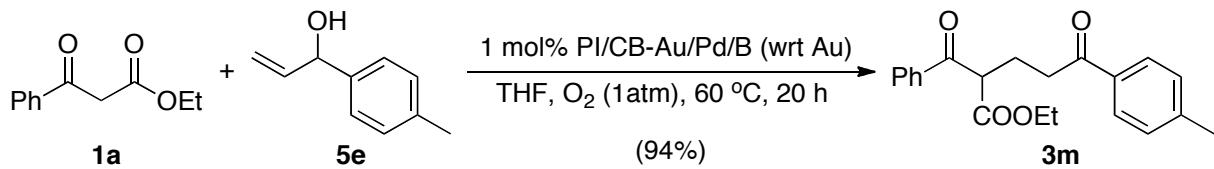


Ethyl 2-benzoyl-5-oxopentanoate (3h) (Table 6, entry 8). Following the above general procedure with β -ketoester **1a** (87.0 μL , 0.502 mmol) and allylic alcohol **5c** (32.0 μL , 0.765 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3h** (0.1029 g, 0.414 mmol, 83%) as a clear colourless oil. R_f 0.22 (EtOAc:hexane = 1:4); ^1H NMR (CDCl_3 , 500 MHz) δ 9.77 (s, 1H), 8.01-8.00 (m, 2H), 7.60-7.57 (m, 1H), 7.48 (t, $J = 7.9$ Hz, 2H), 4.44-4.41 (m, 1H), 4.16-4.10 (m, 2H), 2.68-2.55 (m, 2H), 2.35-2.22 (m, 2H), 1.15 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 201.1, 194.8, 169.5, 135.8, 133.7, 128.8, 128.6, 61.5, 52.6, 41.1, 21.1, 13.9. This is a known compound and the spectral data are identical to those reported in literature.¹⁰

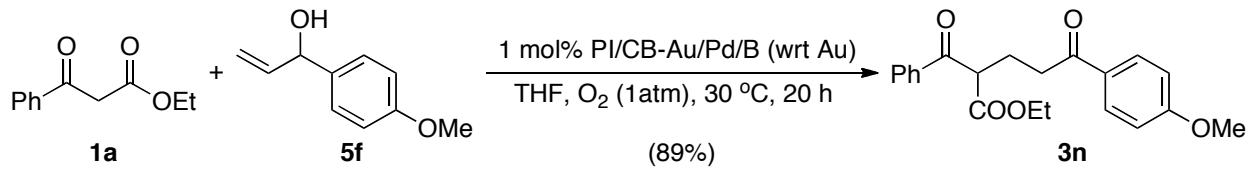


Ethyl 2-benzoyl-5-oxo-5-phenylpentanoate (3l) (Table 6, entry 9). Following the above general procedure with β -ketoester **1a** (87.0 μL , 0.502 mmol), and allylic alcohol **5d** (73.0 μL , 0.555 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3l** (0.1544 g, 0.476 mmol, 95%) as a clear colourless oil. R_f 0.36 (EtOAc:hexane = 1:4); IR (neat, NaCl): 3064 (m), 2981 (s), 2937 (s), 1974 (w), 1913 (w), 1734 (s), 1686 (s), 1596 (m), 1448 (s), 1221 (s), 974 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 8.07 (d, $J = 7.9$ Hz, 2H), 7.95 (d, $J = 7.4$ Hz, 2H), 7.59-7.53 (m, 2H), 7.50-7.43 (m, 4H), 4.57 (dd, $J =$

7.9, 6.2 Hz, 1H), 4.19-4.10 (m, 2H), 3.22-3.16 (m, 1H), 3.12-3.06 (m, 1H), 2.49-2.36 (m, 2H), 1.15 (t, J = 7.4 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 199.2, 195.3, 169.8, 136.6, 135.9, 133.6, 133.1, 128.71, 128.70, 128.6, 128.0, 61.4, 52.8, 35.6, 23.2, 13.9; ESI-HRMS (m/z) calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_4$ [(M+H) $^+$]: 325.14398, found: 325.14334.

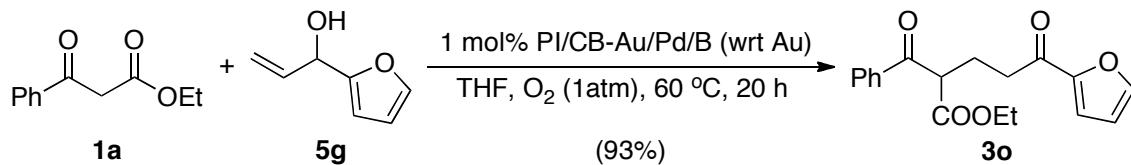


Ethyl 2-benzoyl-5-oxo-5-(*p*-tolyl)pentanoate (3m) (Table 6, entry 10). Following the above general procedure with β -ketoester **1a** (87.0 μL , 0.502 mmol), and allylic alcohol **5e** (81.9 mg, 0.553 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3m** (0.1604 g, 0.474 mmol, 94%) as a clear colourless oil. R_f 0.31 (EtOAc:hexane = 1:4); IR (neat, NaCl): 3061 (m), 3026 (m), 2981 (s), 2934 (s), 1977 (w), 1921 (w), 1737 (s), 1681 (s), 1606 (s), 1449 (m), 1369 (m), 1226 (s), 977 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 8.06 (d, J = 7.4 Hz, 2H), 7.84 (d, J = 7.9 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.9 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 4.56 (dd, J = 7.4, 6.2 Hz, 1H), 4.19-4.09 (m, 2H), 3.18-3.12 (m, 1H), 3.08-3.02 (m, 1H), 2.46-2.34 (m, 5H), 1.14 (t, J = 7.4 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 198.8, 195.3, 169.8, 143.9, 135.9, 134.1, 133.5, 129.2, 128.7, 128.0, 61.3, 52.8, 35.5, 23.3, 21.5, 13.9; ESI-HRMS (m/z) calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_4$ [(M+H) $^+$]: 339.15963, found: 339.16042.

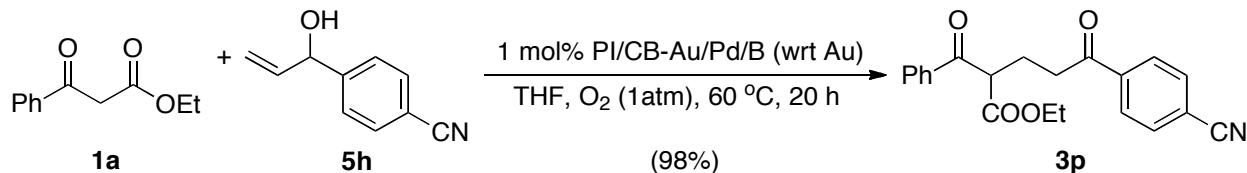


Ethyl 2-benzoyl-5-(4-Methoxyphenyl)-5-oxopentanoate (3n) (Table 6, entry 11). Following the above general procedure with β -ketoester **1a** (87.0 μL , 0.502 mmol), and allylic alcohol **5f** (90.7 mg, 0.552 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3n** (0.1597 g, 0.448 mmol, 89%) as a clear colourless oil. R_f 0.24 (EtOAc:hexane = 1:4); IR (neat, NaCl): 3061 (m), 2979 (s), 2940 (s), 2841 (m), 2057 (w), 1974 (w), 1910 (w), 1737 (s), 1681 (s), 1604 (s), 1513 (s), 1255 (s), 1030 (s), 977 (s) cm^{-1} ; ^1H

¹H NMR (CDCl₃, 500 MHz) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 9.1 Hz, 2H), 7.58-7.55 (m, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.56 (dd, *J* = 7.9, 6.8 Hz, 1H), 4.18-4.08 (m, 2H), 3.83 (s, 3H), 3.15-3.08 (m, 1H), 3.05-2.97 (m, 1H), 2.46-2.3 (m, 2H), 1.14 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 197.7, 195.4, 169.8, 163.5, 135.9, 133.5, 130.2, 129.7, 128.7, 113.6, 61.3, 55.4, 52.9, 35.2, 23.4, 13.9; ESI-HRMS (m/z) calcd. for C₂₁H₂₂O₅ [(M+H)⁺]: 355.15455, found: 355.15293.

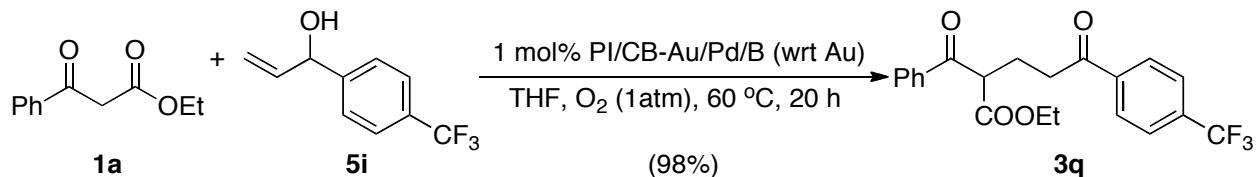


Ethyl 2-benzoyl-5-(furan-2-yl)-5-oxopentanoate (3o) (Table 6, entry 12). Following the above general procedure with β -ketoester **1a** (87.0 μ L, 0.502 mmol), and allylic alcohol **5g** (68.6 mg, 0.553 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3o** (0.1467 g, 0.467 mmol, 93%) as a clear colourless oil. R_f 0.25 (EtOAc:hexane = 1:4); IR (neat, NaCl): 3139 (s), 3067 (s), 2981 (s), 2937 (s), 2546 (w), 2393 (w), 1974 (w), 1913 (w), 1734 (s), 1678 (s), 1571 (s), 1449 (s), 1366 (s), 1239 (s), 764 (m) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.51-7.47 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 3.4 Hz, 1H), 6.44-6.43 (m, 1H), 4.46 (dd, *J* = 7.9, 6.2 Hz, 1H), 4.09-4.03 (m, 2H), 2.98-2.83 (m, 2H), 2.38-2.26 (m, 2H), 1.07 (t, *J* = 6.2 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 195.1, 188.2, 169.6, 152.3, 146.4, 135.8, 133.5, 128.64, 128.62, 117.1, 112.1, 61.3, 52.7, 35.4, 23.0, 13.8; ESI-HRMS (m/z) calcd. for C₁₈H₁₈O₅ [(M+H)⁺]: 315.12325, found: 315.12383.



Ethyl 2-benzoyl-5-(4-cyanophenyl)-5-oxopentanoate (3p) (Table 6, entry 13). Following the above general procedure with β -ketoester **1a** (87.0 μ L, 0.502 mmol), and allylic alcohol **5h** (88.0 mg, 0.553 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 2:3) to provide **3p** (0.1727 g, 0.494 mmol, 98%) as a pale yellow solid (mp. 83-84 °C). R_f 0.20 (EtOAc:hexane = 1:4); IR (KBr): 3070 (m), 2989 (m), 2931 (m), 2907 (m),

2227 (s), 1932 (w), 1744 (s), 1689 (s), 1670 (s), 1596 (m), 1449 (m), 1292 (s), 1198 (s), 1054 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 8.02-8.00 (m, 4H), 7.72 (d, J = 8.5 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.9 Hz, 2H), 4.51 (t, J = 8.4 Hz, 1H), 4.16-4.06 (m, 2H), 3.21-3.06 (m, 2H), 2.47-2.34 (m, 2H), 1.12 (t, J = 7.4 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 197.8, 194.9, 169.6, 139.4, 135.8, 133.6, 132.4, 128.7, 128.5, 128.3, 117.8, 116.3, 61.4, 52.5, 35.9, 22.9, 13.8; ESI-HRMS (m/z) calcd. for $\text{C}_{21}\text{H}_{19}\text{O}_4\text{N}$ [(M+H) $^+$]: 350.13923, found: 350.14089.



Ethyl 2-benzoyl-5-oxo-5-(4-(trifluoromethyl)phenyl)pentanoate (3q) (Table 6, entry 14). Following the above general procedure with β -ketoester **1a** (87.0 μL , 0.502 mmol), and allylic alcohol **5i** (111.7 mg, 0.553 mmol). The crude reaction mixture was purified by column chromatography (EtOAc:hexane = 1:4) to provide **3q** (0.1925 g, 0.491 mmol, 98%) as a pale yellow solid (mp. 55-56 $^{\circ}\text{C}$). R_f 0.49 (EtOAc:hexane = 1:4); IR (KBr): 3067 (w), 2984 (m), 2968 (m), 2907 (m), 1982 (w), 1921 (w), 1725 (s), 1692 (s), 1600 (m), 1452 (m), 1328 (s), 1159 (s), 991 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 8.05-8.03 (m, 4H), 7.70 (d, J = 8.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.4 Hz, 2H), 4.54 (t, J = 7.4 Hz, 1H), 4.18-4.09 (m, 2H), 3.23-3.08 (m, 2H), 2.49-2.36 (m, 2H), 1.14 (t, J = 6.8 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 198.2, 195.1, 169.7, 139.2, 135.9, 134.4 (q, $^2J_{\text{CF}}$ = 32 Hz), 133.6, 128.7, 128.6, 128.3, 125.6 (q, $^3J_{\text{CF}}$ = 4 Hz), 123.5 (q, $^1J_{\text{CF}}$ = 273 Hz), 61.4, 52.7, 36.0, 23.0, 13.8; ESI-HRMS (m/z) calcd. for $\text{C}_{21}\text{H}_{19}\text{O}_4\text{F}_3$ [(M+H) $^+$]: 393.13137, found: 393.13140.

Part VII: Control Experiments

The PI/CB catalysts used in the control experiments were prepared following the general procedure outlined in Part IV. For the direct comparison between PI/CB-Au/Pd/B (0.1791 mmol/g Au, 0.2054 mmol/g Pd, 2.898 mmol/g B) and PI/CB-Au/Pd (0.2534 mmol/g Au, 0.2860 mmol/g Pd), these catalysts was prepared by initially following the general procedure for PI/CB-Au/Pd/B, except approximately half of the composite material was removed after the cross-linking step (heated at 170 °C) and stirred overnight in a THF:H₂O (1:1, 10 mL) to completely remove any boron. The reactions were monitored by taking a small aliquot of the reaction mixture, diluting with CDCl₃, and then obtaining ¹H NMR spectra.

Part VIII: STEM, EDS, and SEM Analyses

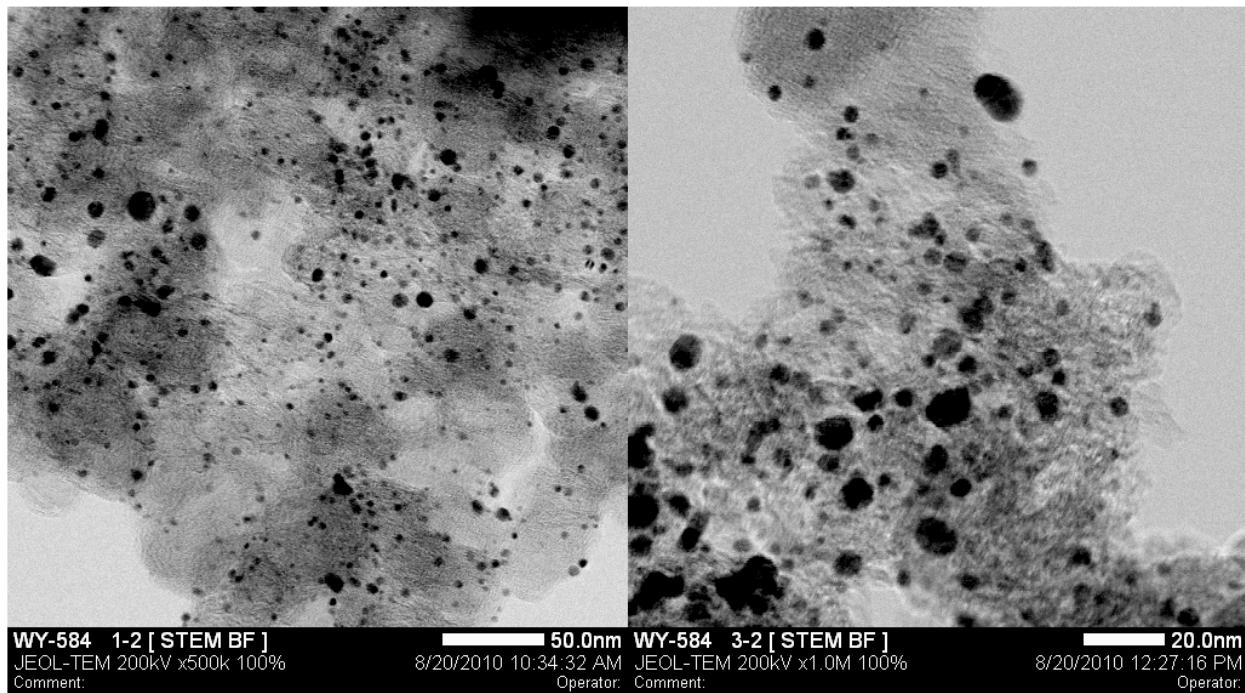


Figure S-1. Typical STEM Images of PI/CB-Au/Pd/B

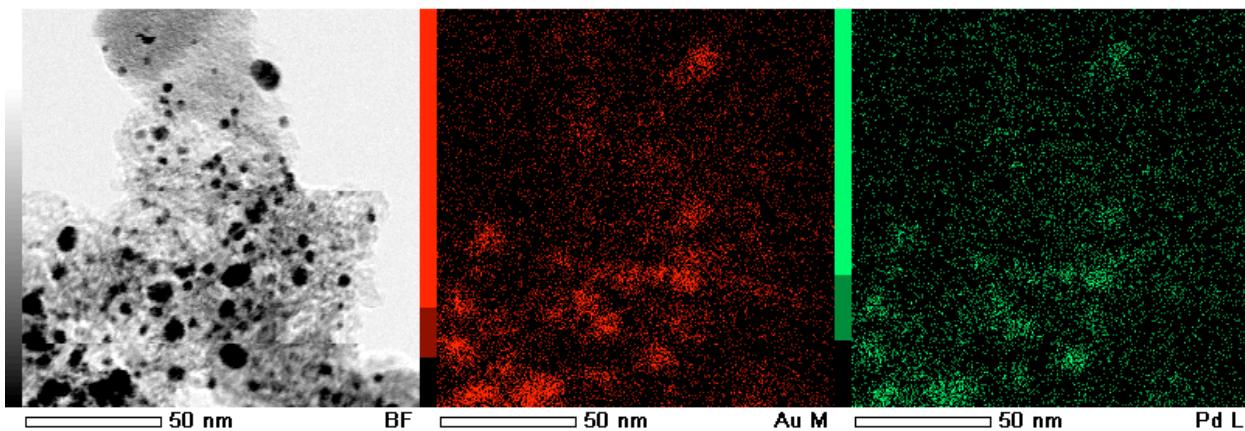


Figure S-2. EDS Mapping of PI/CB-Au/Pd/B

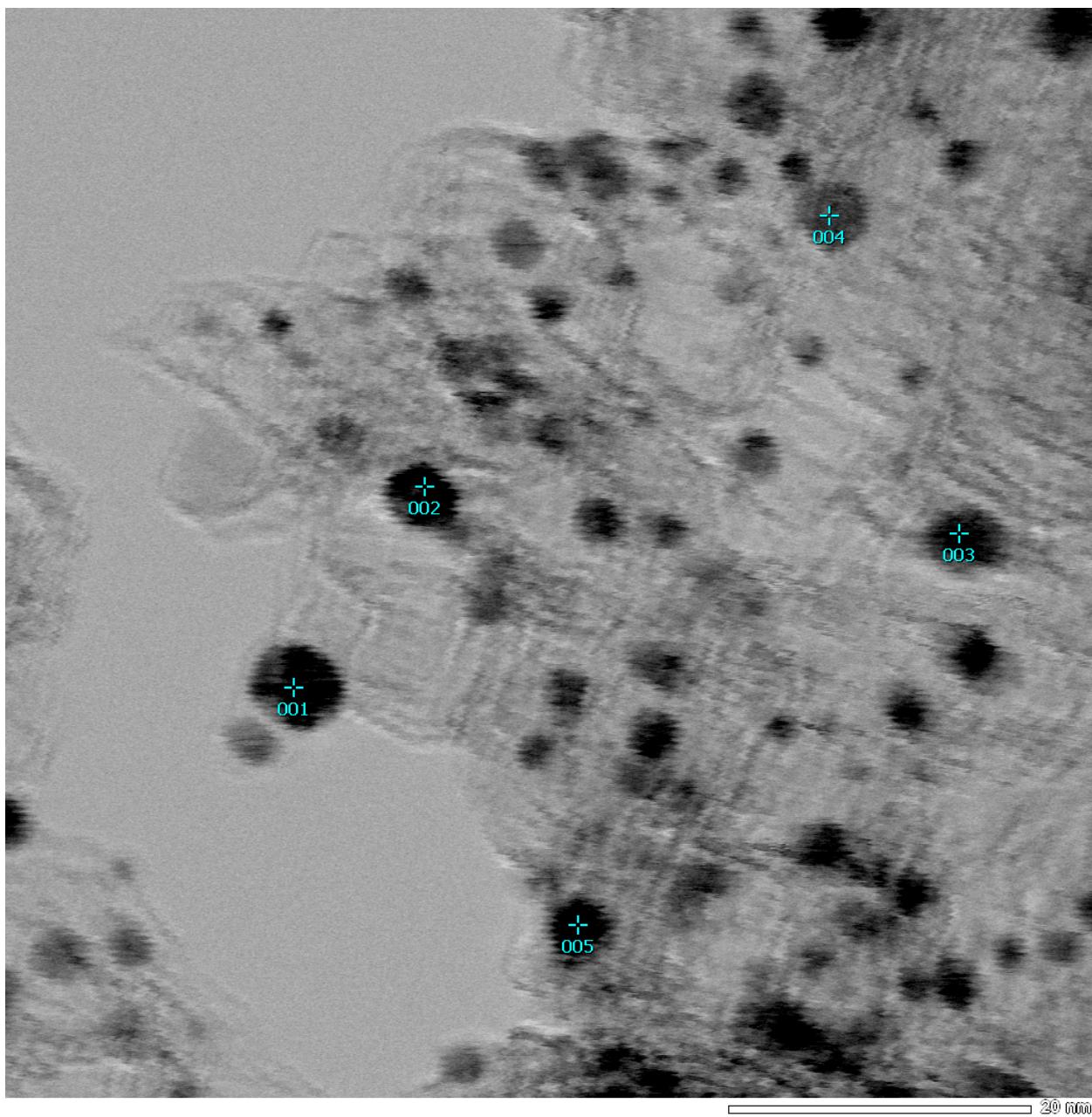


Figure S-3. EDS Spot Analysis of PI/CB-Au/Pd/B

Table S-2. Gold-Palladium Ratio Determined EDS Spot Analysis of PI/CB-Au/Pd/B

Spot	Au (%)	Pd (%)	Ratio Au:Pd
1	55.63	44.37	1.25
2	60.23	39.77	1.51
3	71.26	28.74	2.5
4	35.75	64.25	0.56
5	56.05	43.95	1.28

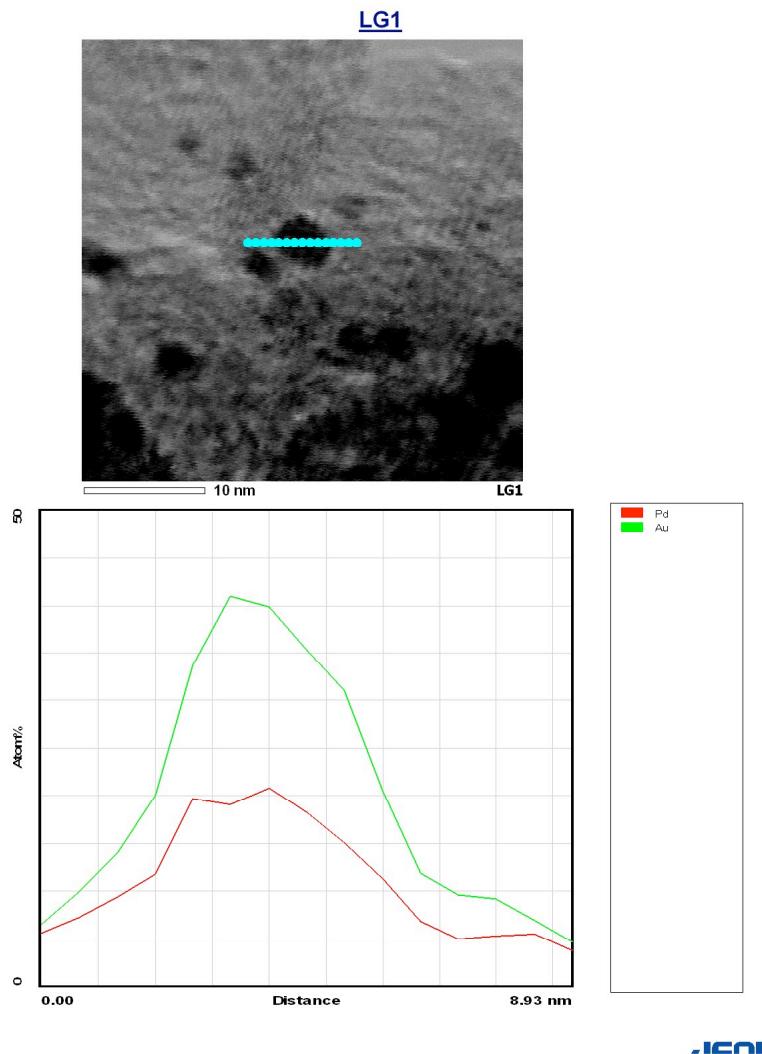


Figure S-4. EDS Line Analysis of PI/CB-Au/Pd/B

Although the gold and palladium metal loading was approximately 1:1 (determined by ICP analysis), the majority of the nanoclusters contained 1.25:1-2.5:1 ratio of gold to palladium. This suggests that palladium exists in both the nanoclusters and also along the polymer backbone. Line analysis of the nanoclusters suggests that the nanoclusters are gold/palladium alloys (green line = Au, red line = Pd).

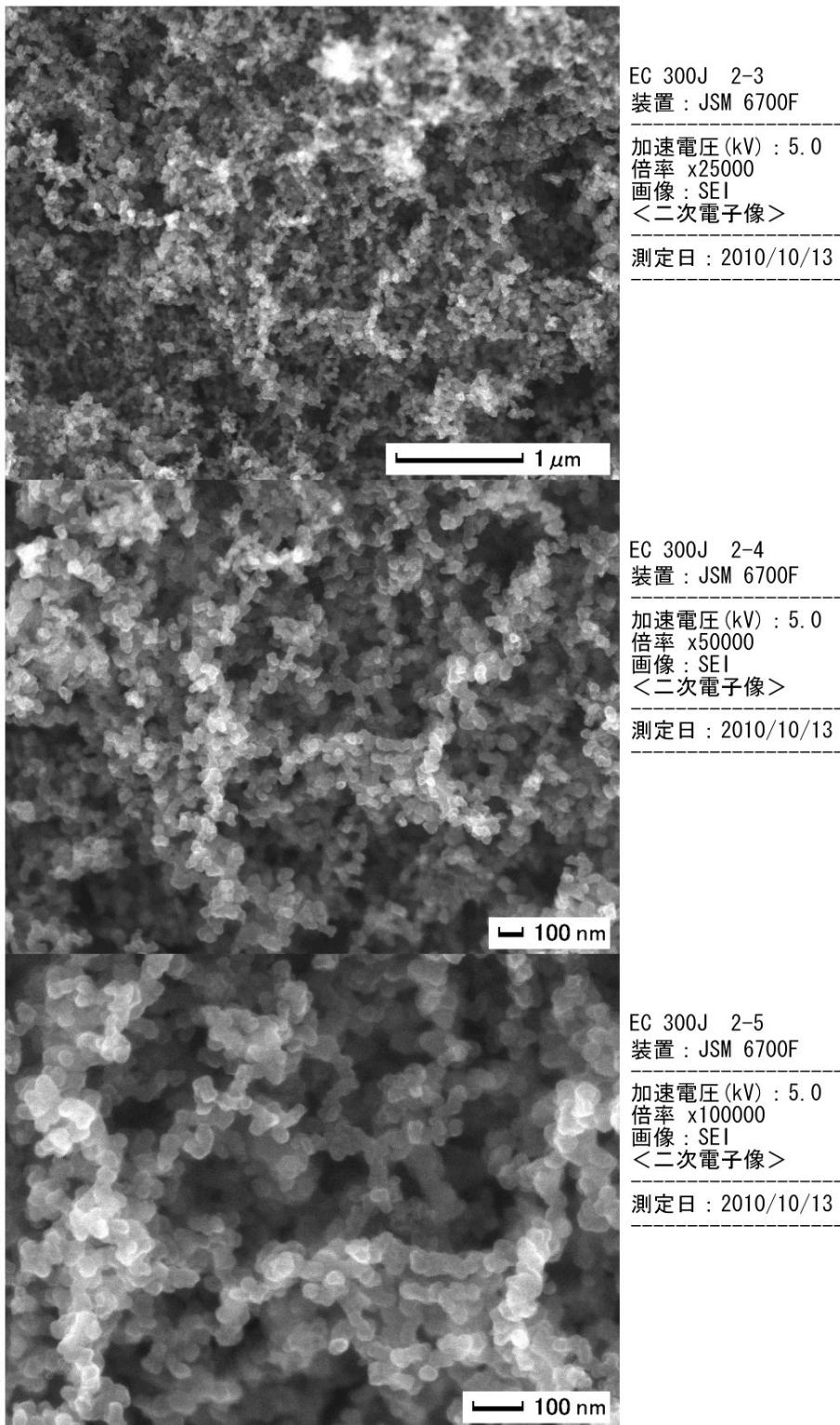


Figure S-5. Typical SEM Image of Ketjen Black EC 300J

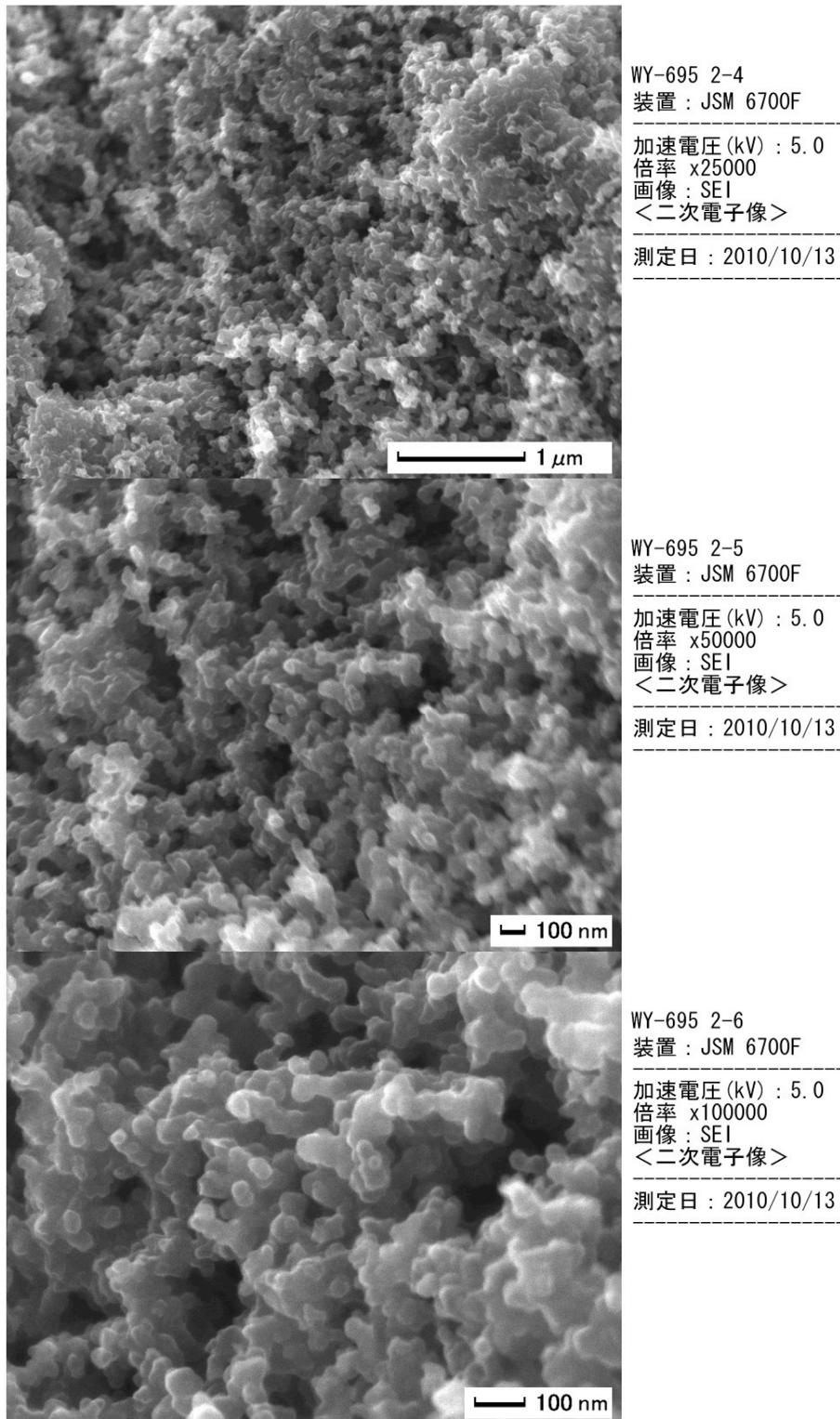
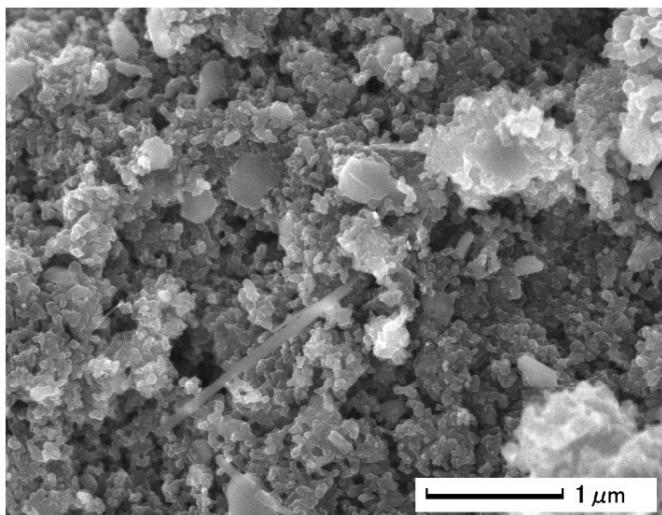


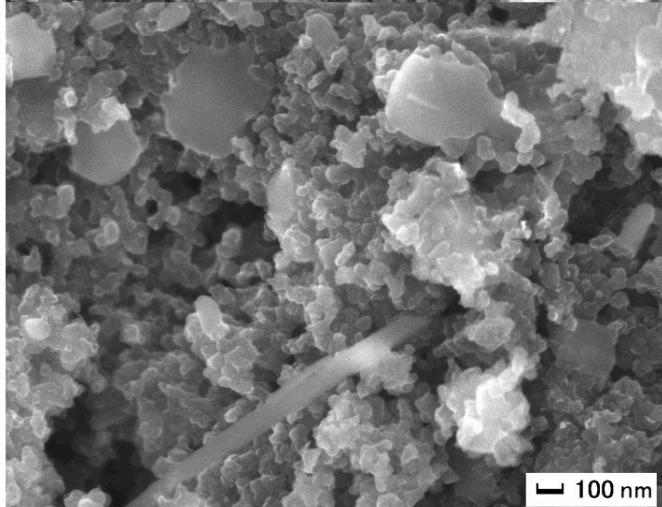
Figure S-6. Typical SEM Image of Ketjen Black EC 300J + Polymer 4



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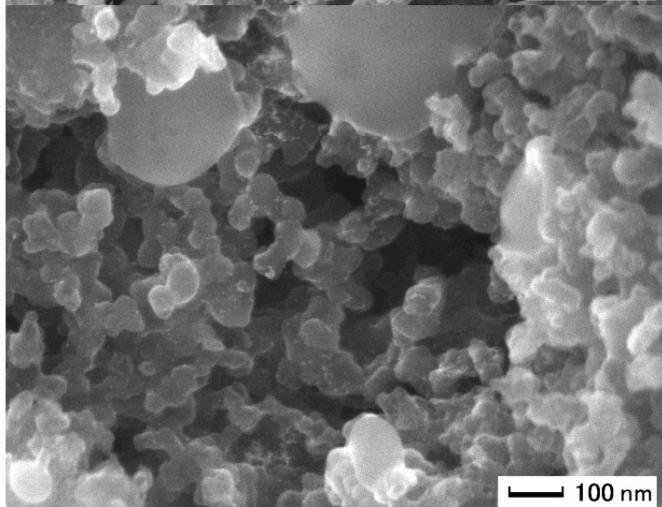
測定日 : 2010/10/06



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測定日 : 2010/10/06

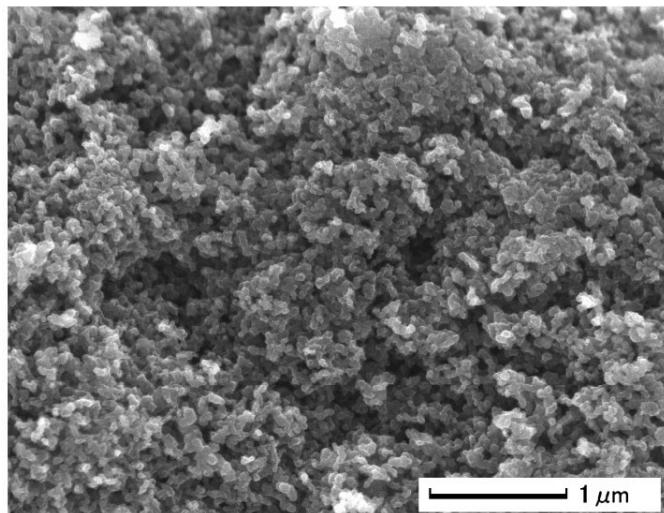


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測定日 : 2010/10/06

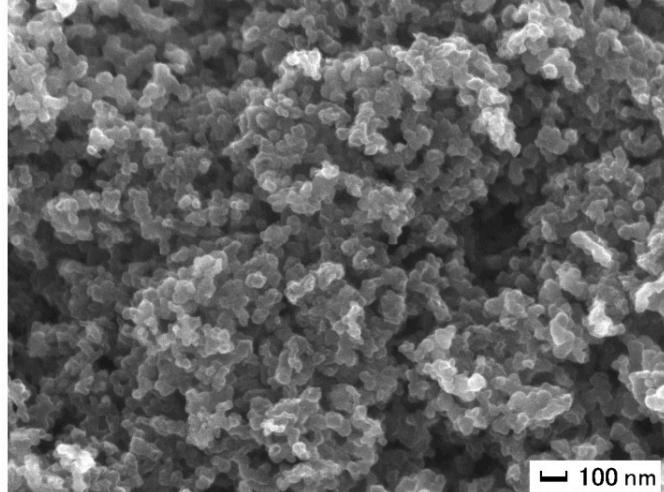
Figure S-7. Typical SEM Image of PI/CB-Au/Pd/B



WY-641 2-3
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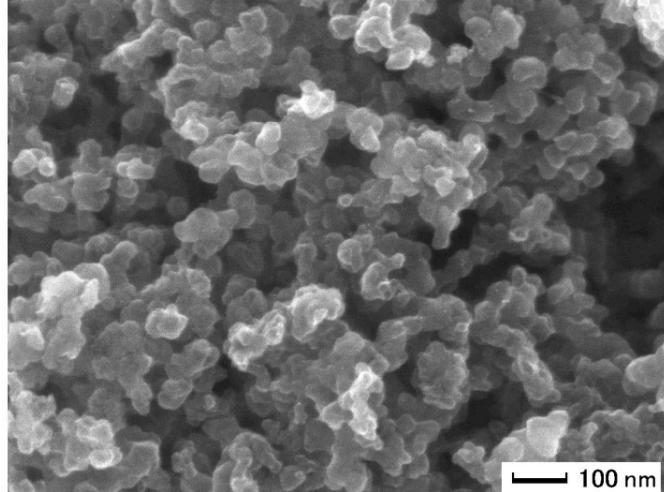
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測定日 : 2010/10/06



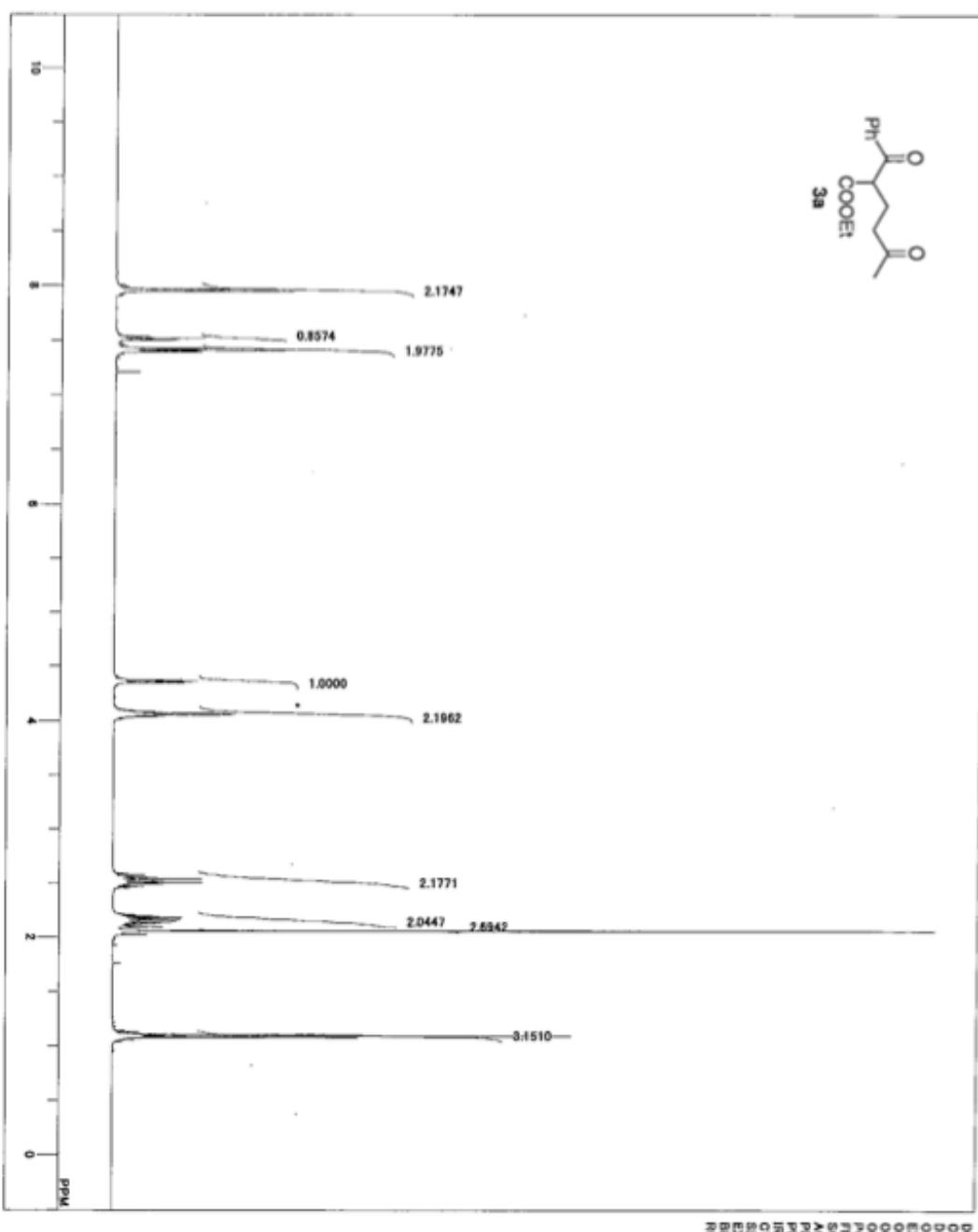
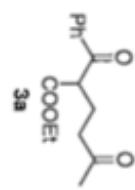
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測定日 : 2010/10/06

Figure S-8. Typical SEM Image of PI/CB-Au/Pd

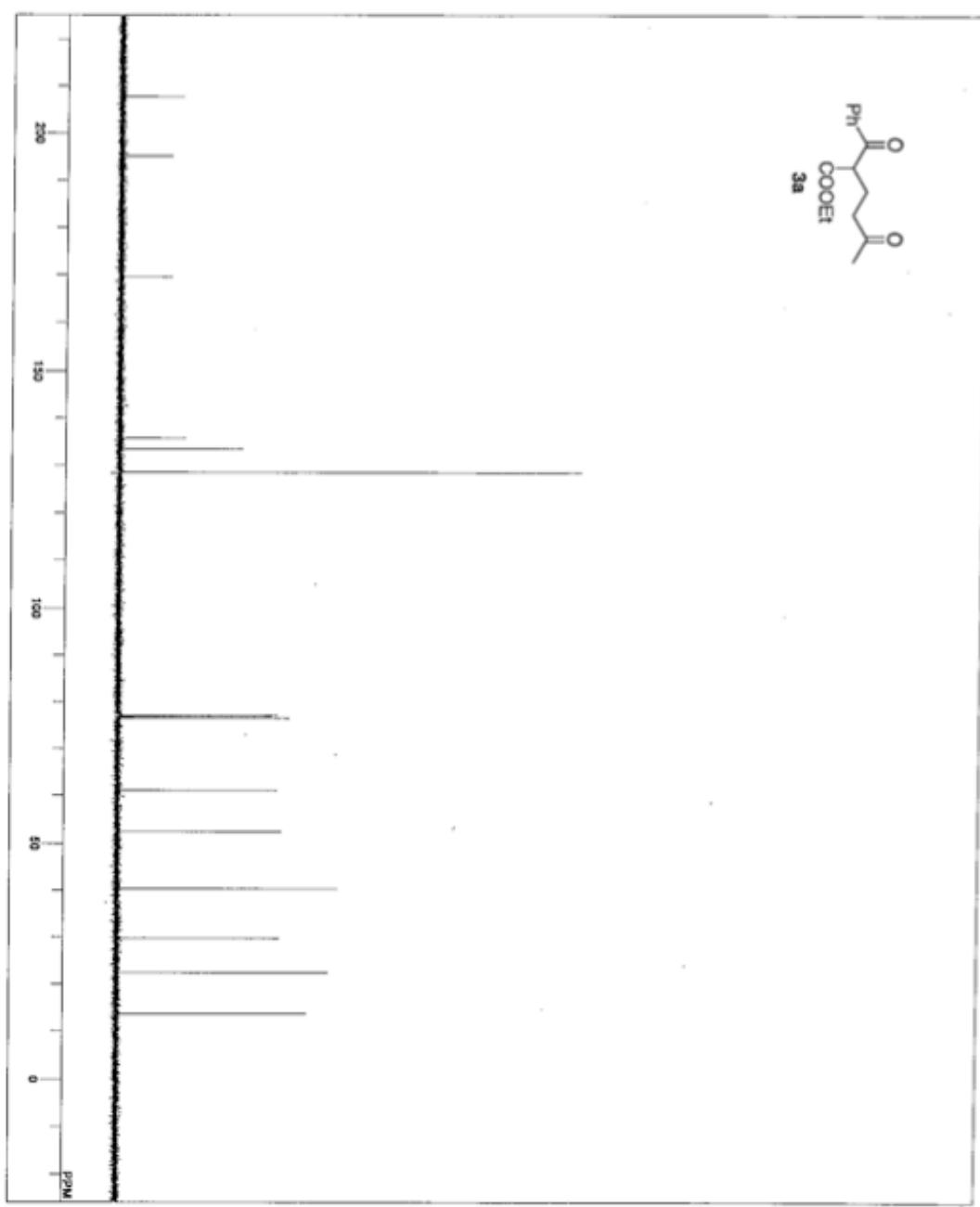
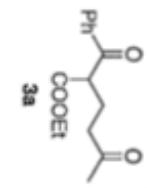
Part IX: ^1H and ^{13}C NMR Spectra of 3a-3q and ^{11}B CP-MAS of PI/CB-B



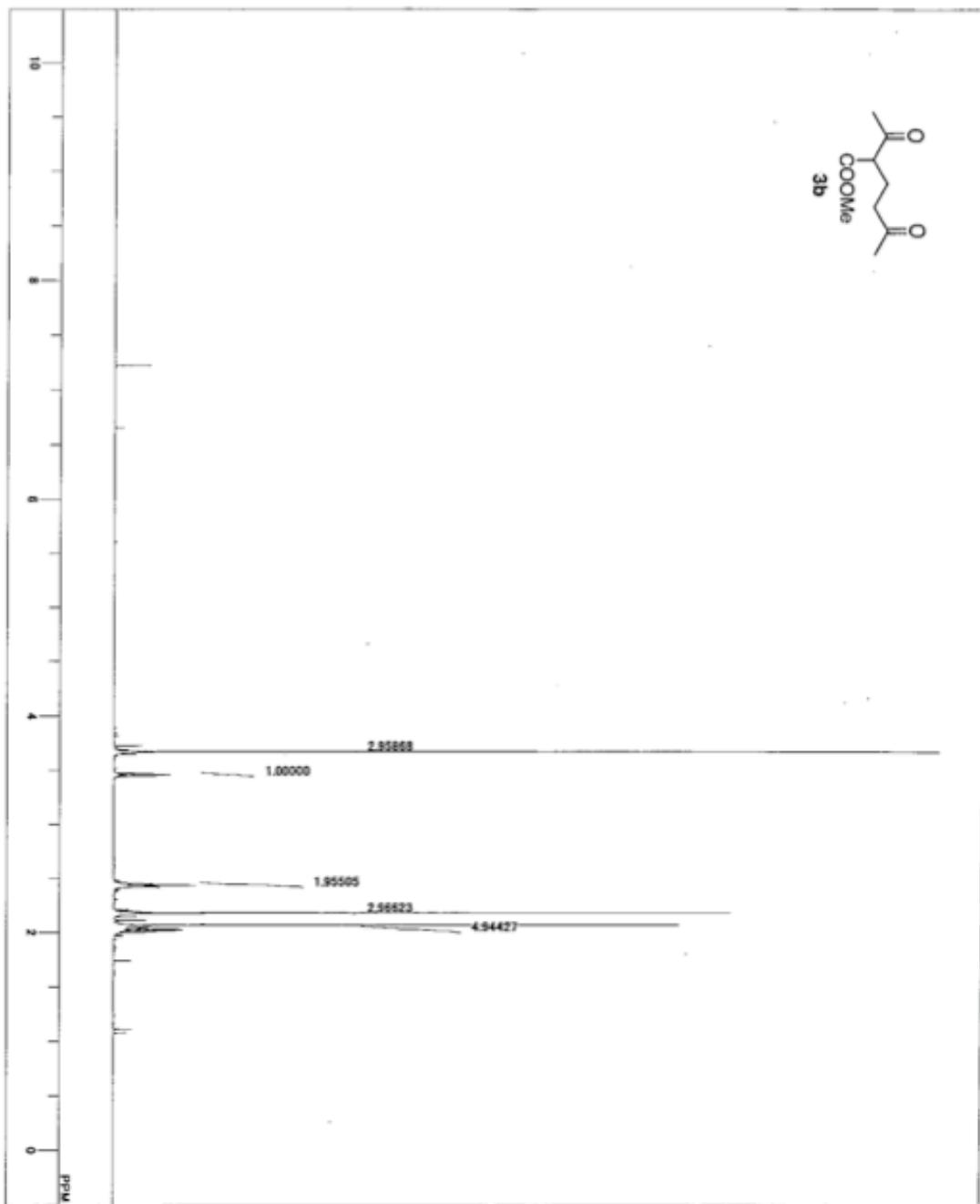
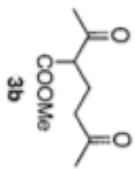
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POWD
PPI
IRINC
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SLVNT
EXREF
SP
REMAIN

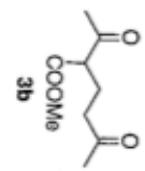
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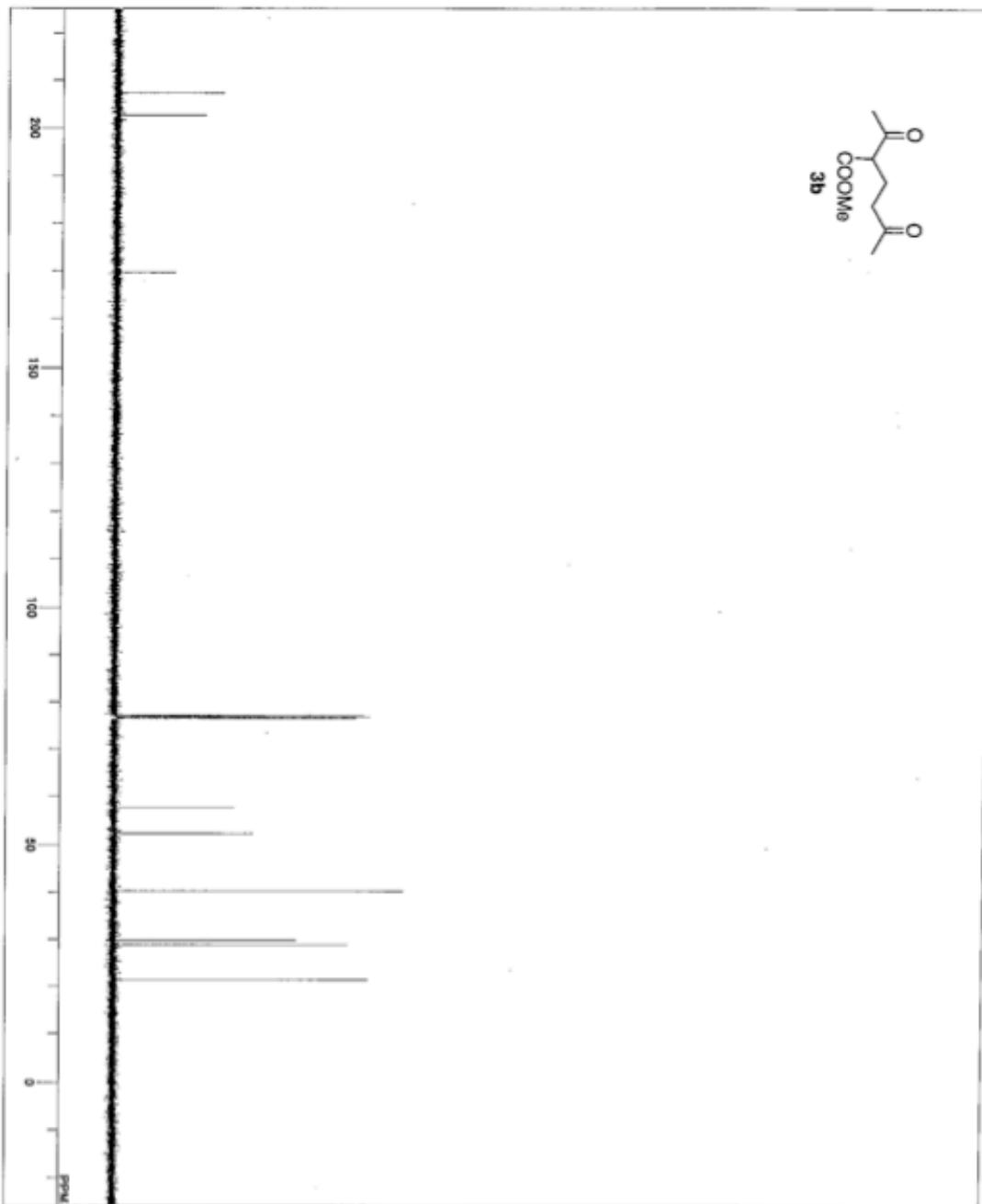
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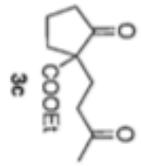


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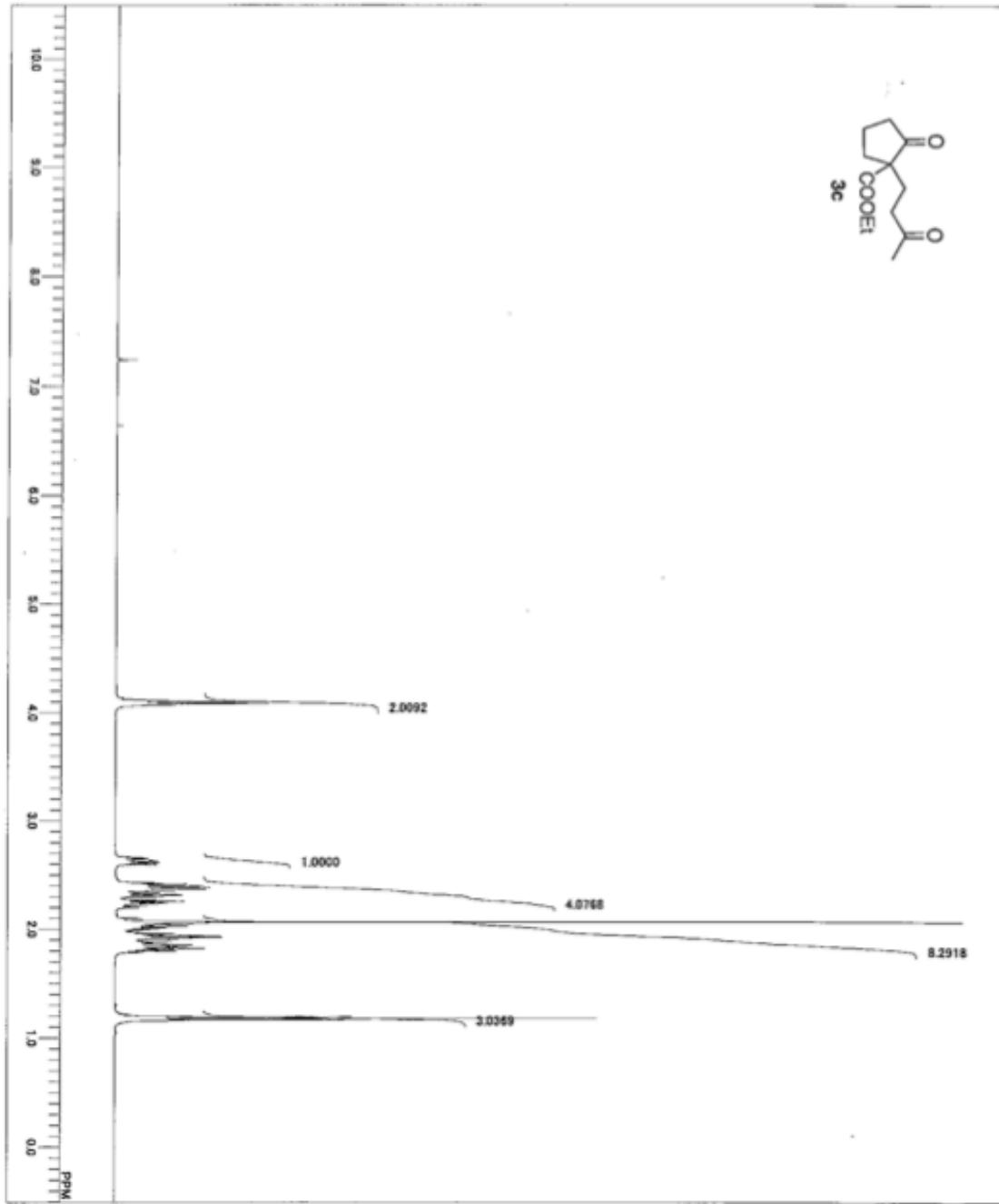
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P01788 22.7188
FREQ1 20082.50 Hz
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RGAIN 50

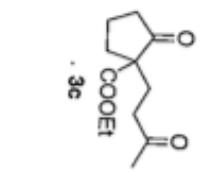




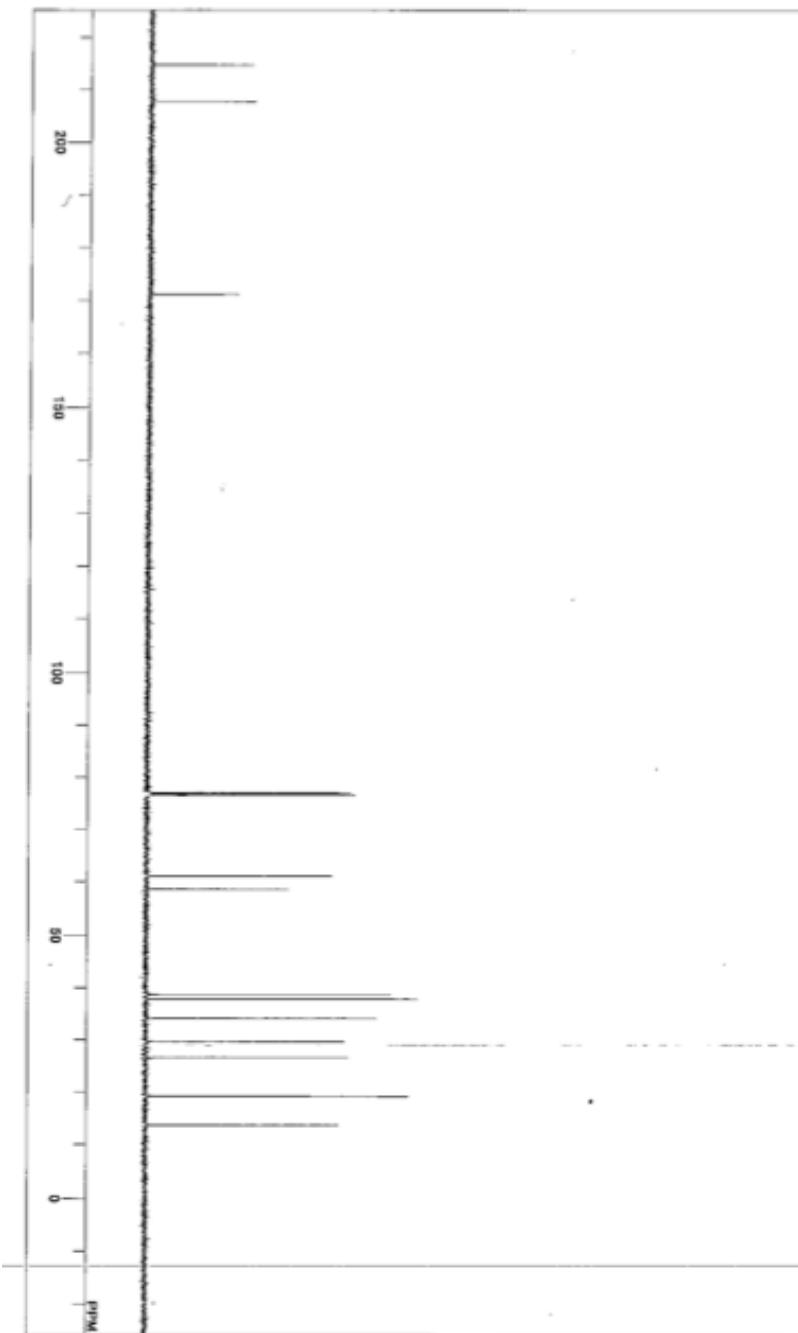
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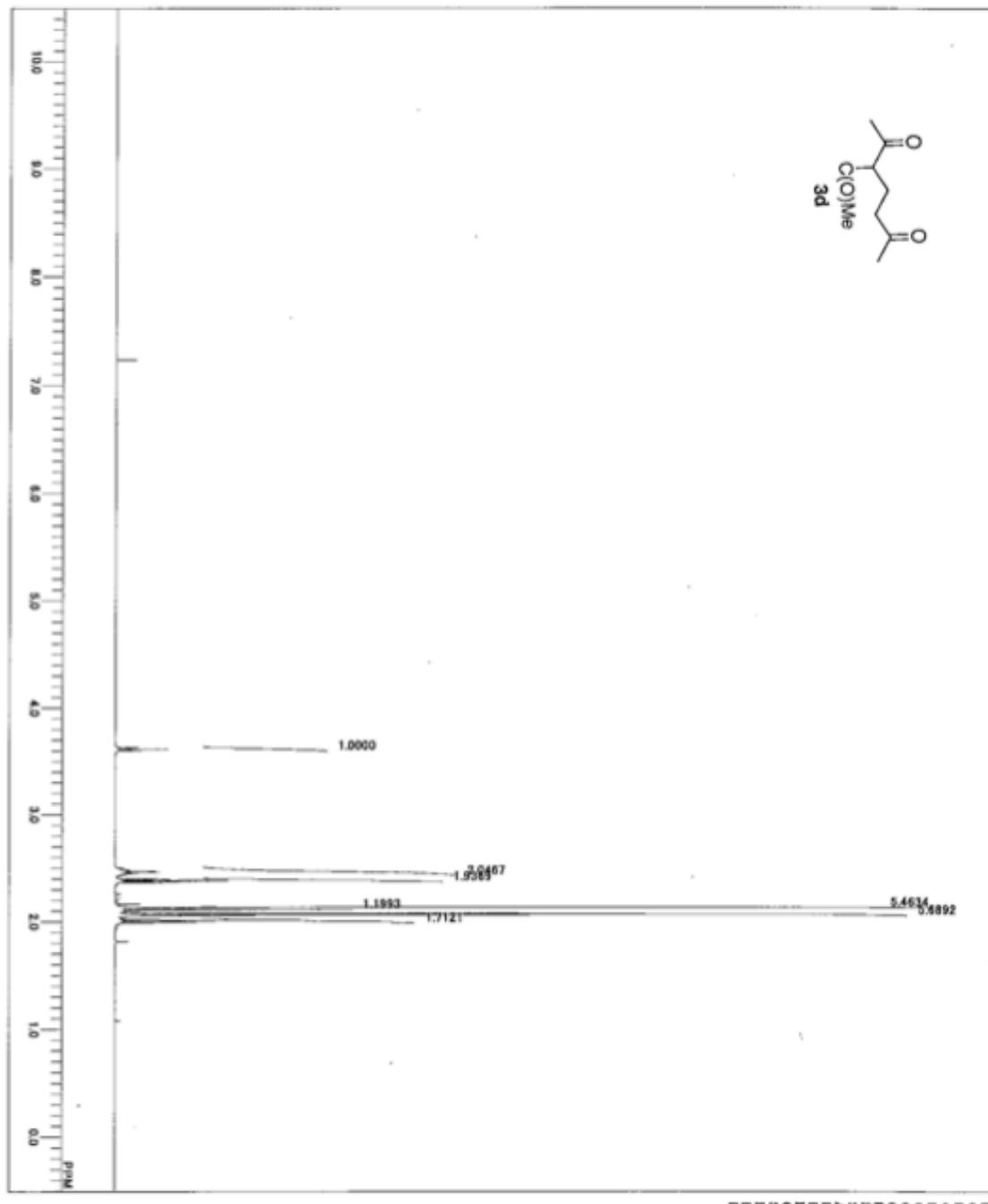
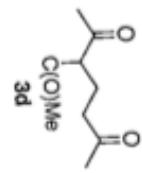
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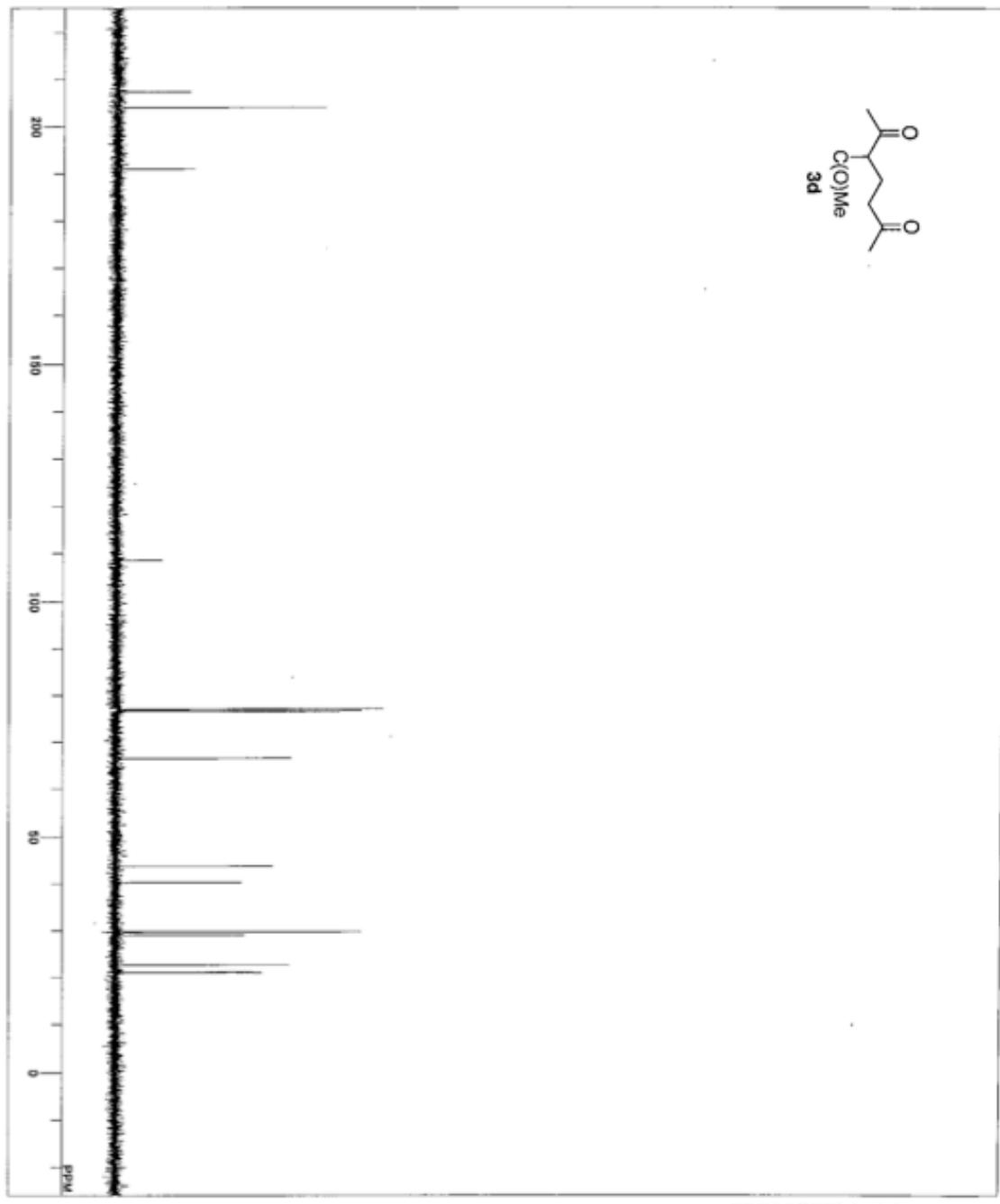
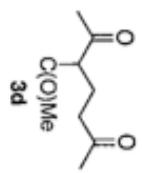


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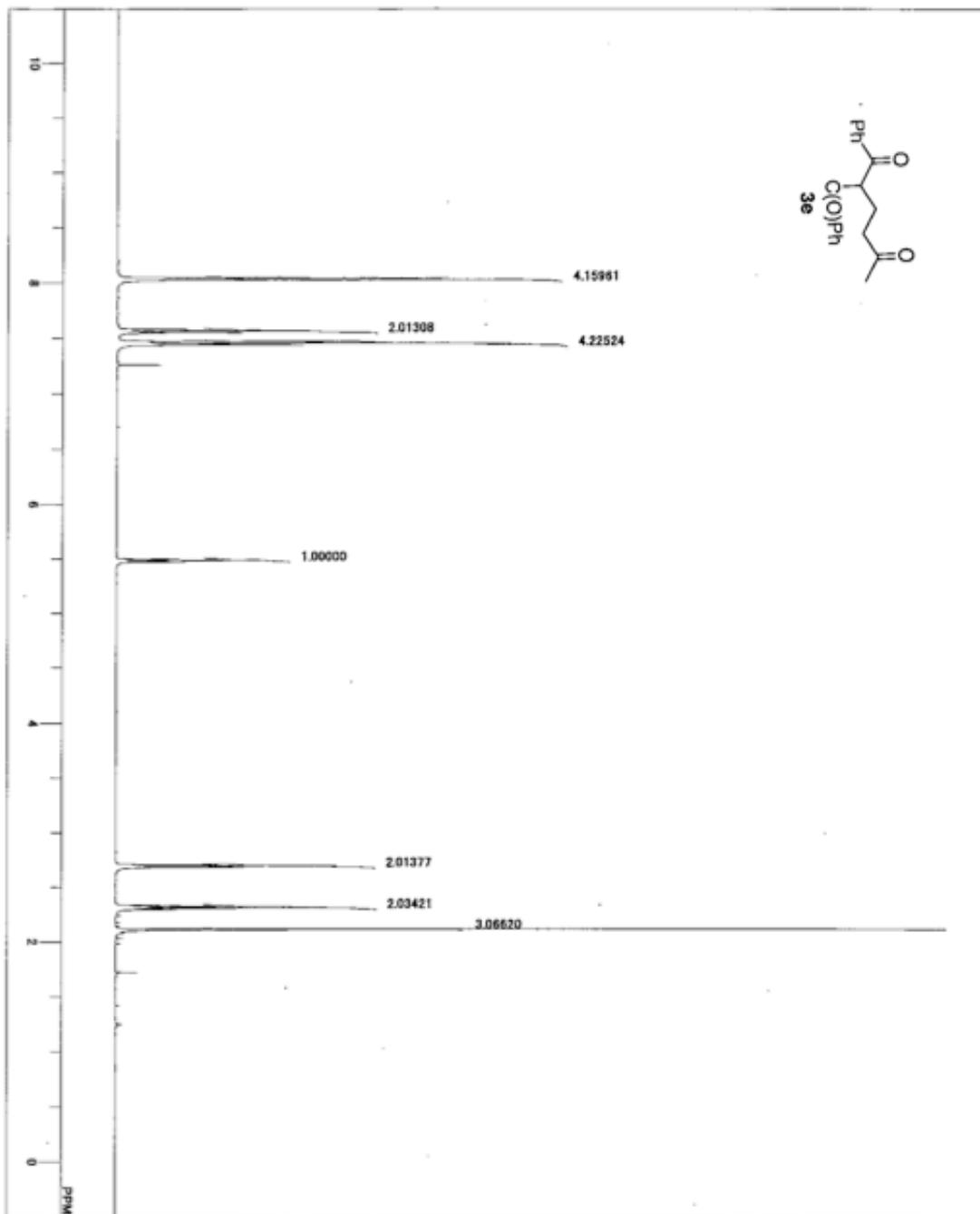
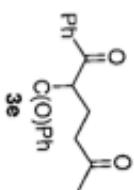




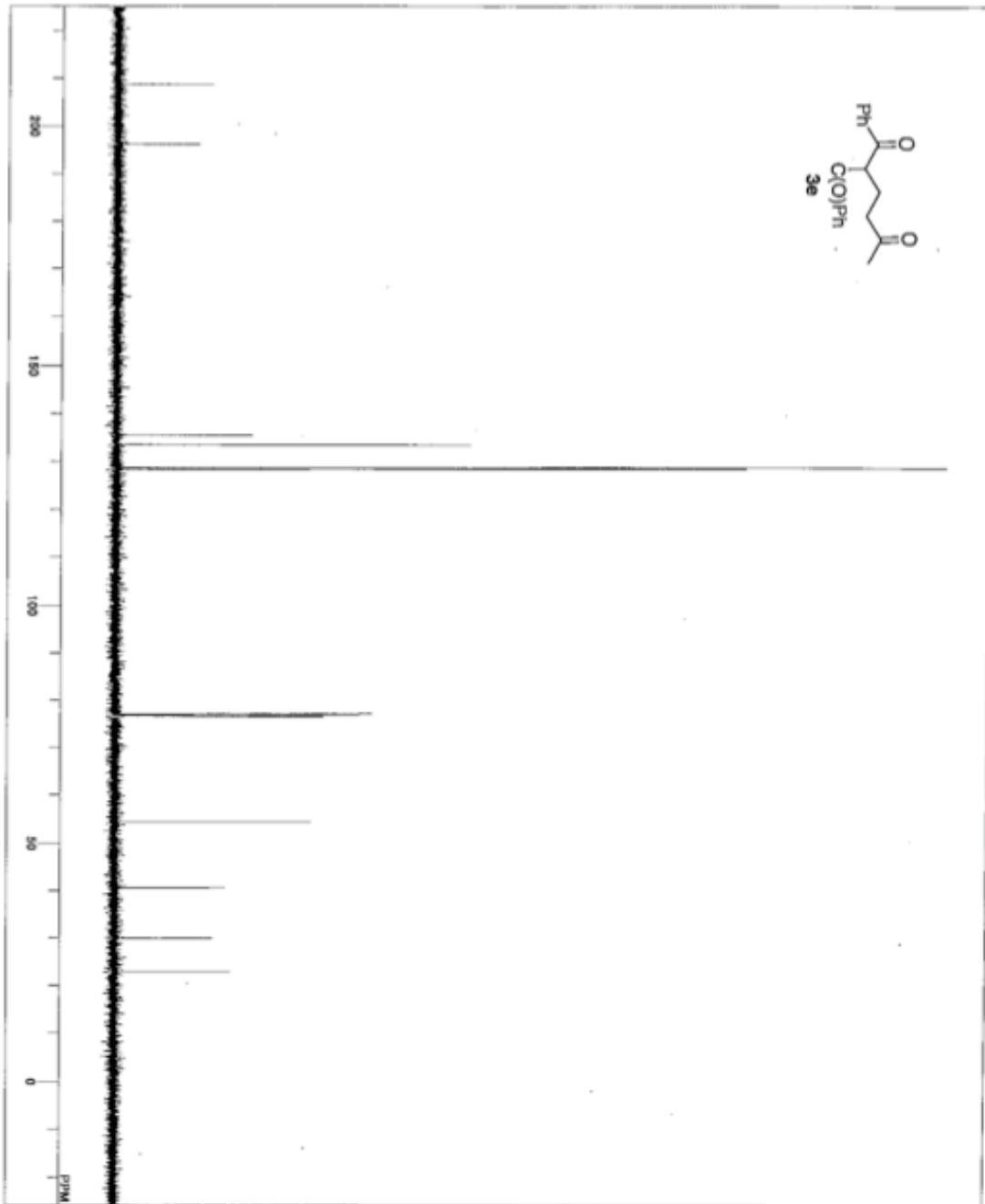
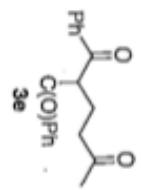
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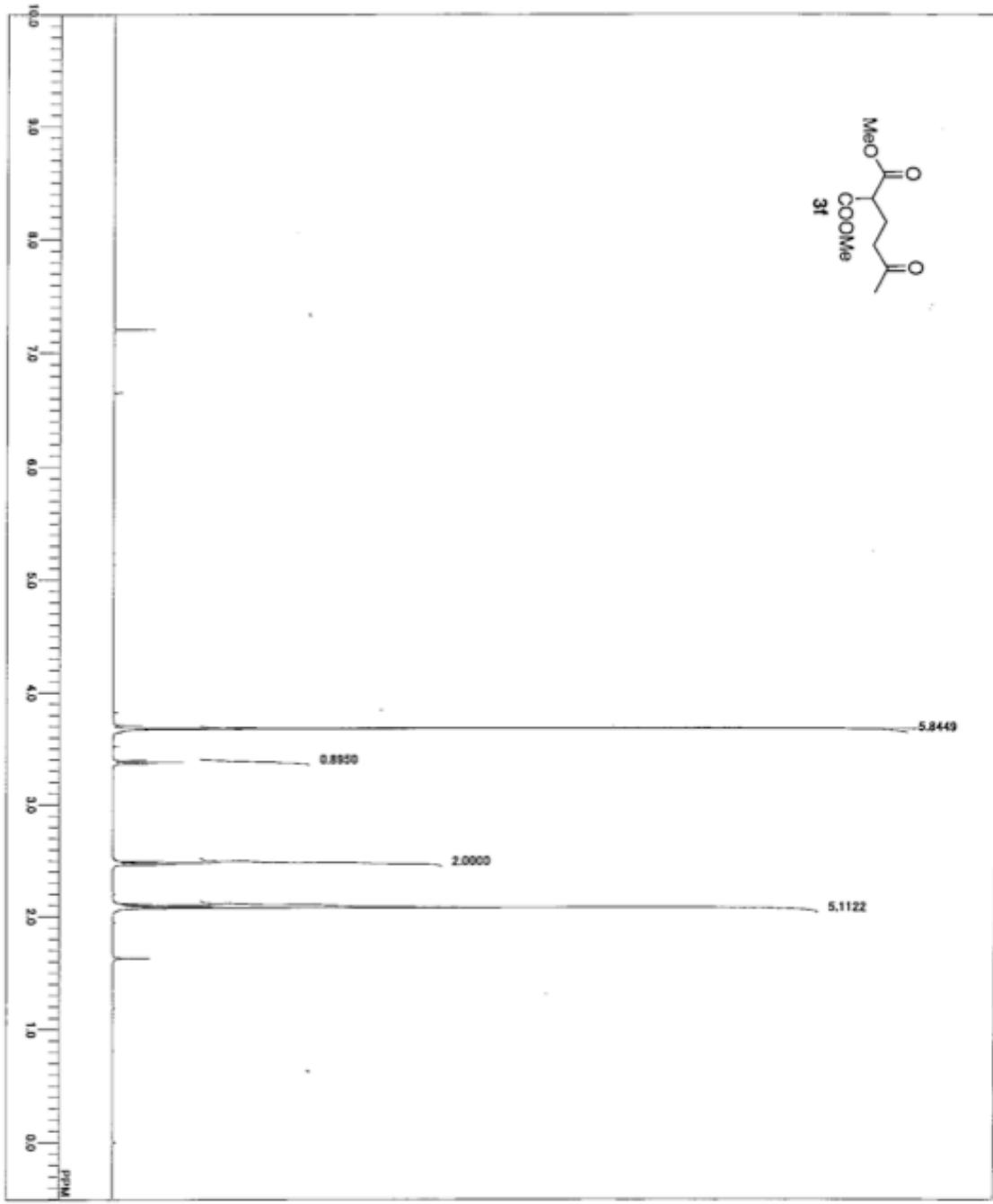
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SCANS 62
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OTAMP 20.8 °
SLNTR CDCl3
EXNCF 77.00 ppm
BF 0.12 Hz
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 OBFRQ: 485.13 MHz
 OFFSET: 4.38 kHz
 OBPN: 9.64 Hz
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 FREQU: 9288.78 Hz
 SCANS: 8
 ACQTM: 1.1542 sec
 PD: 5.0000 sec
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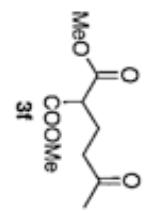
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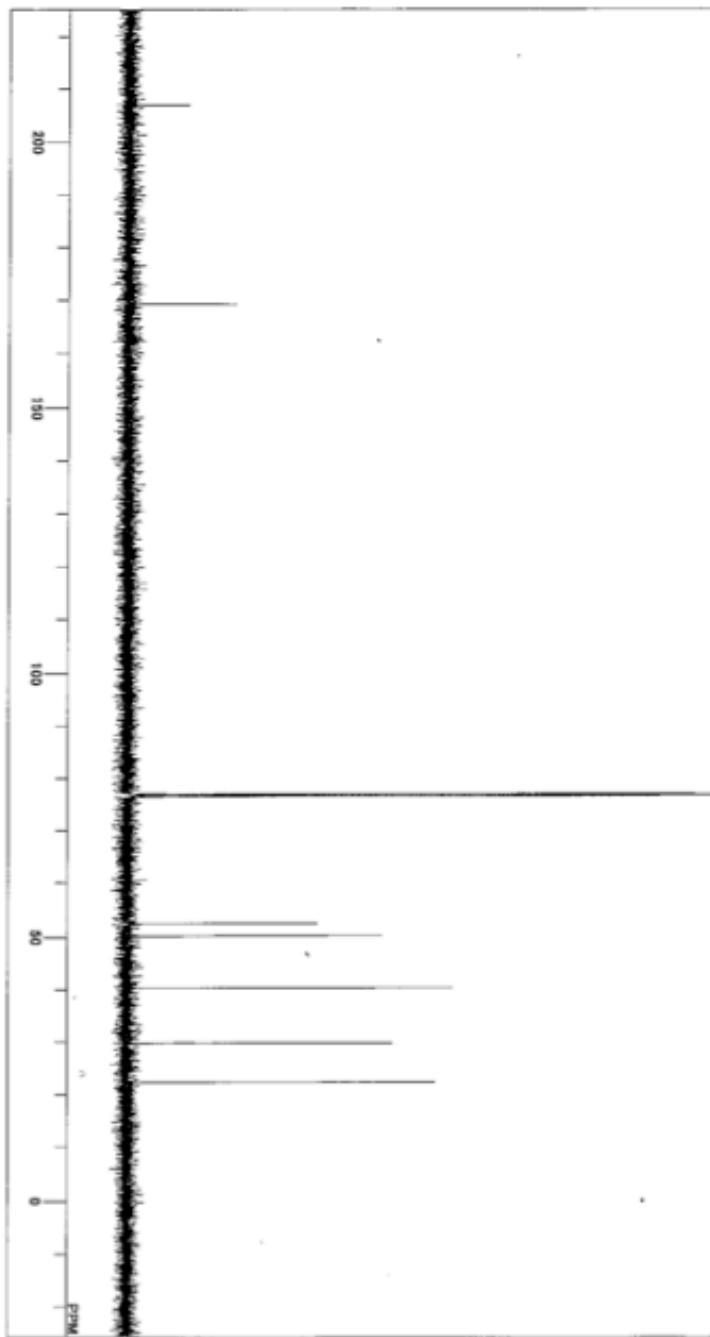
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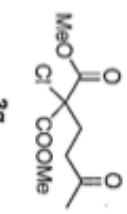
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EXAMD
ERBQ
OBSET
OBINB
POINT
FREQU
SCANS
ACQTM
PRO
PMT
TRNUC
CTMPL
EXREF
RGAU
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16.9 °
0.00 ppm
0.12 ppm
40
14-11-2006 15:14
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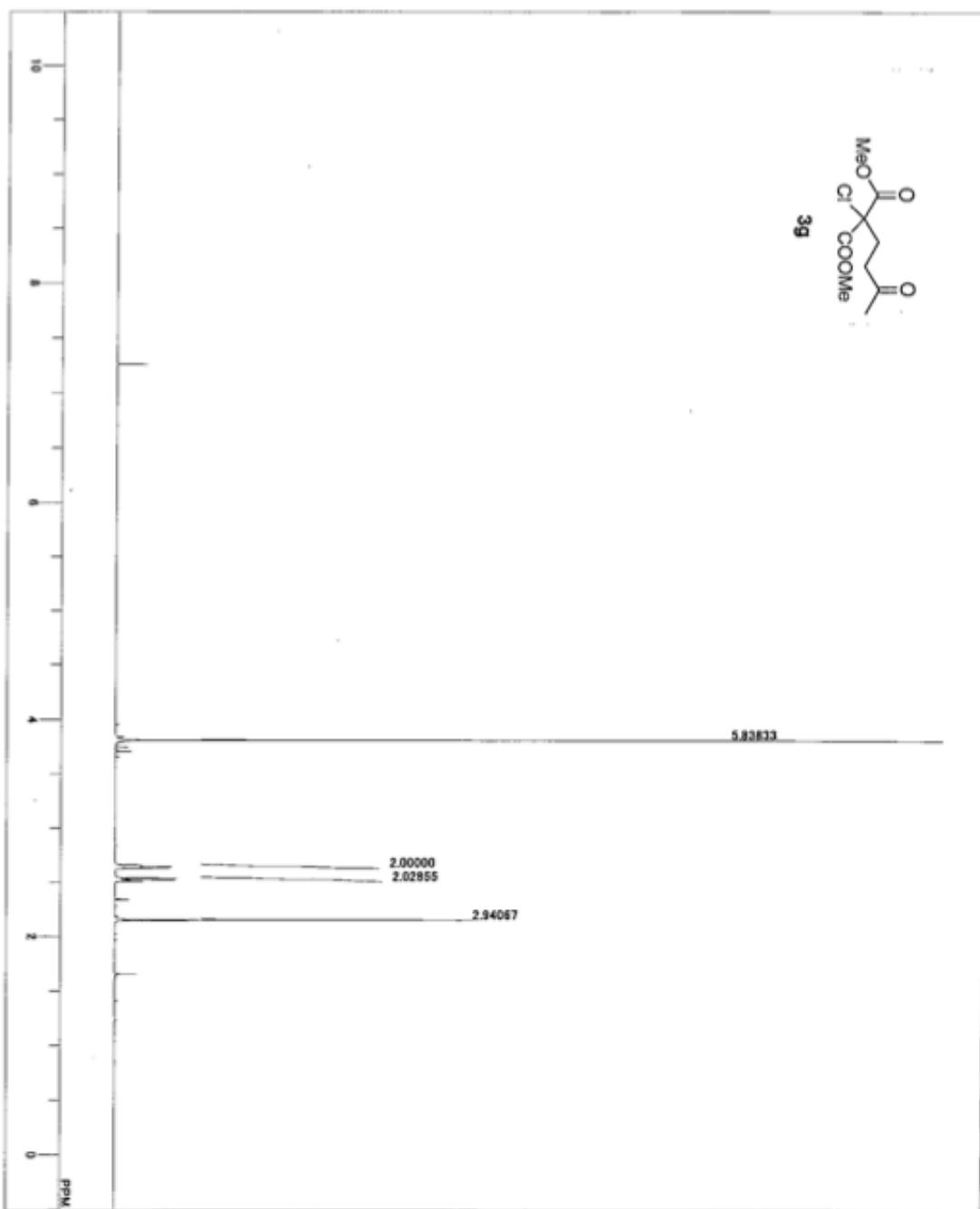


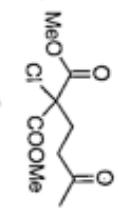
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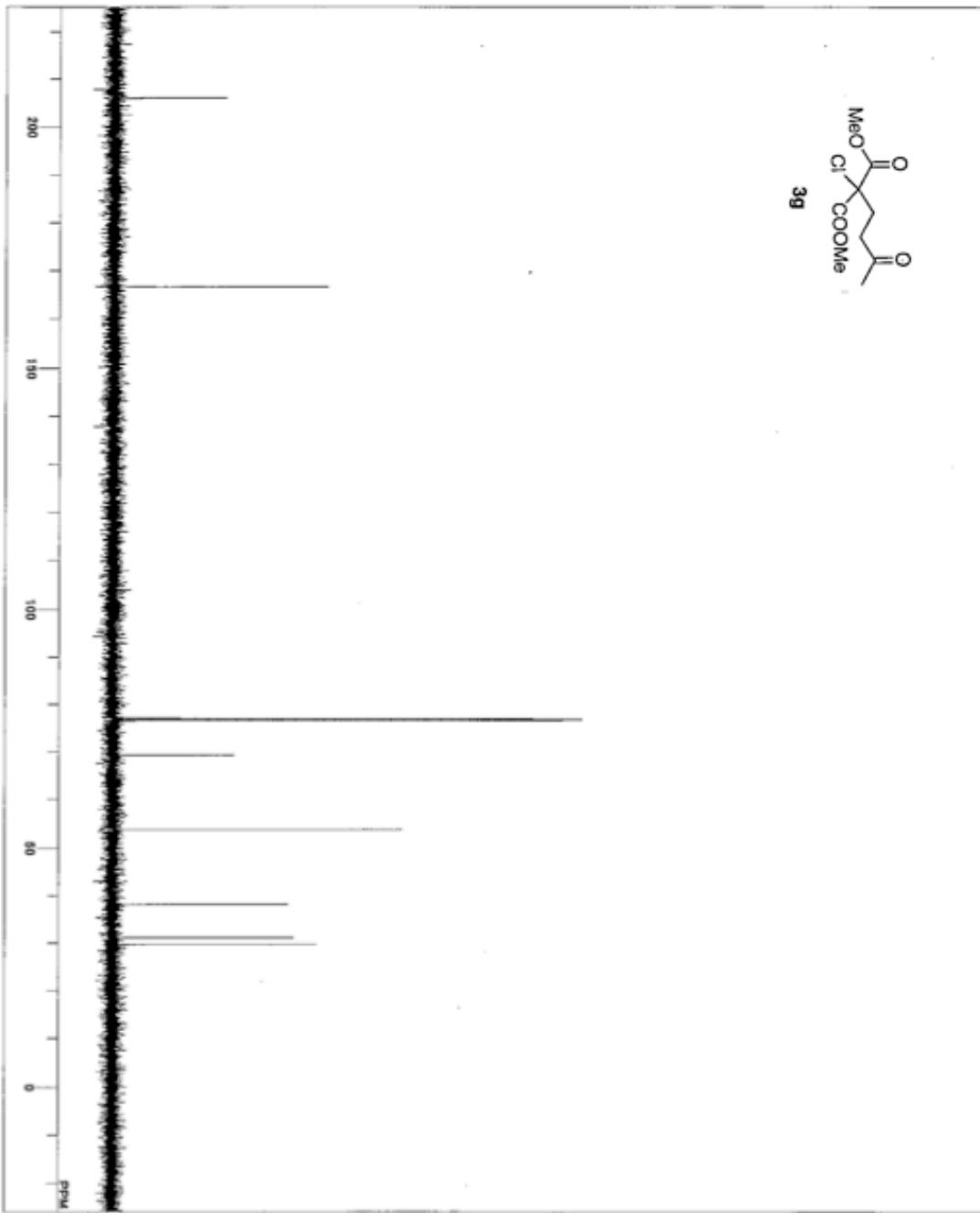


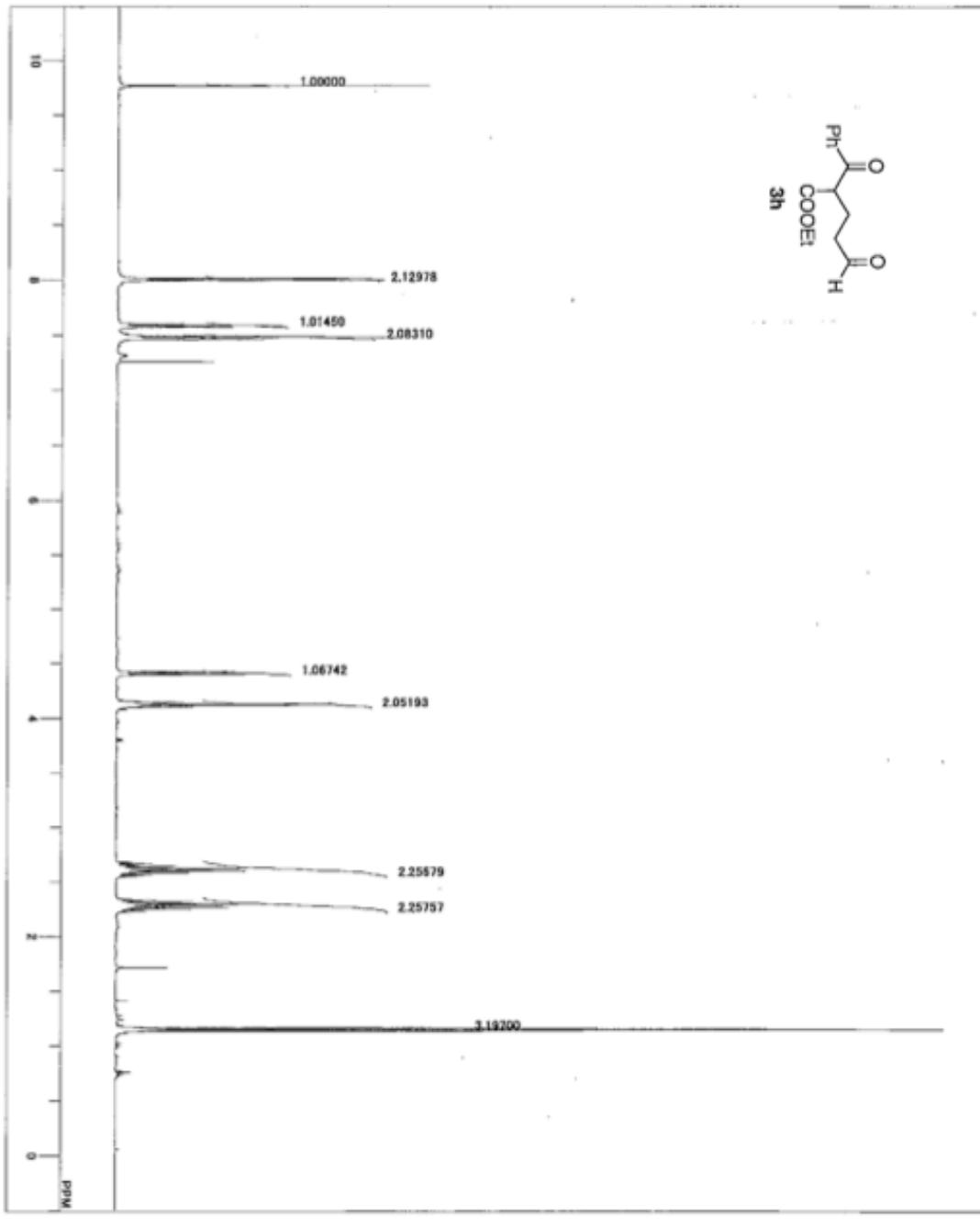
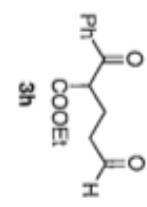
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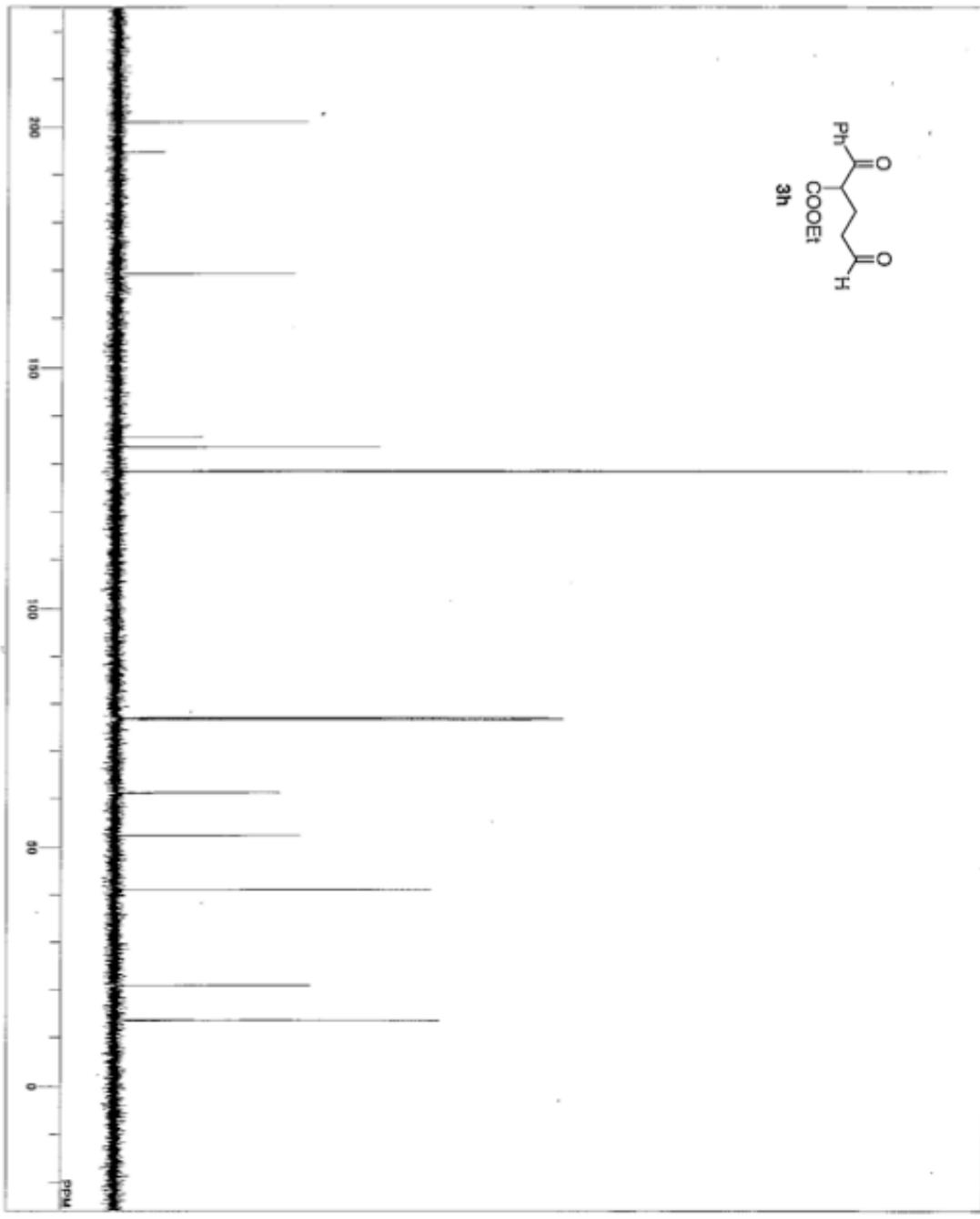
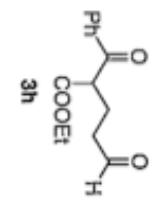
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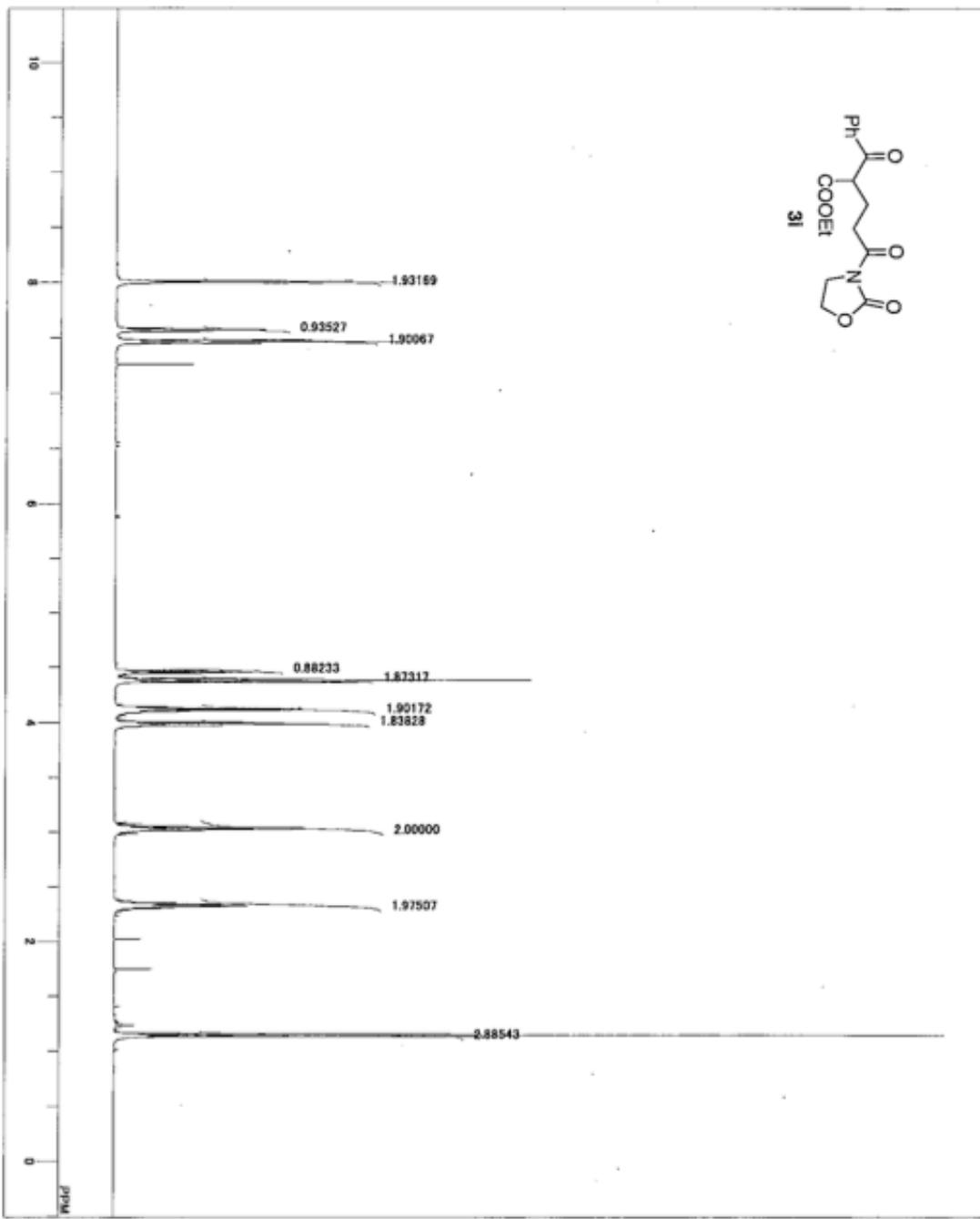
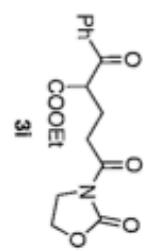


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SCANS
8
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PD
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PMT
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EXREF
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RDAN
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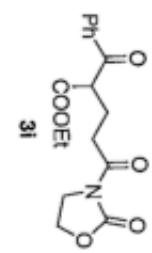
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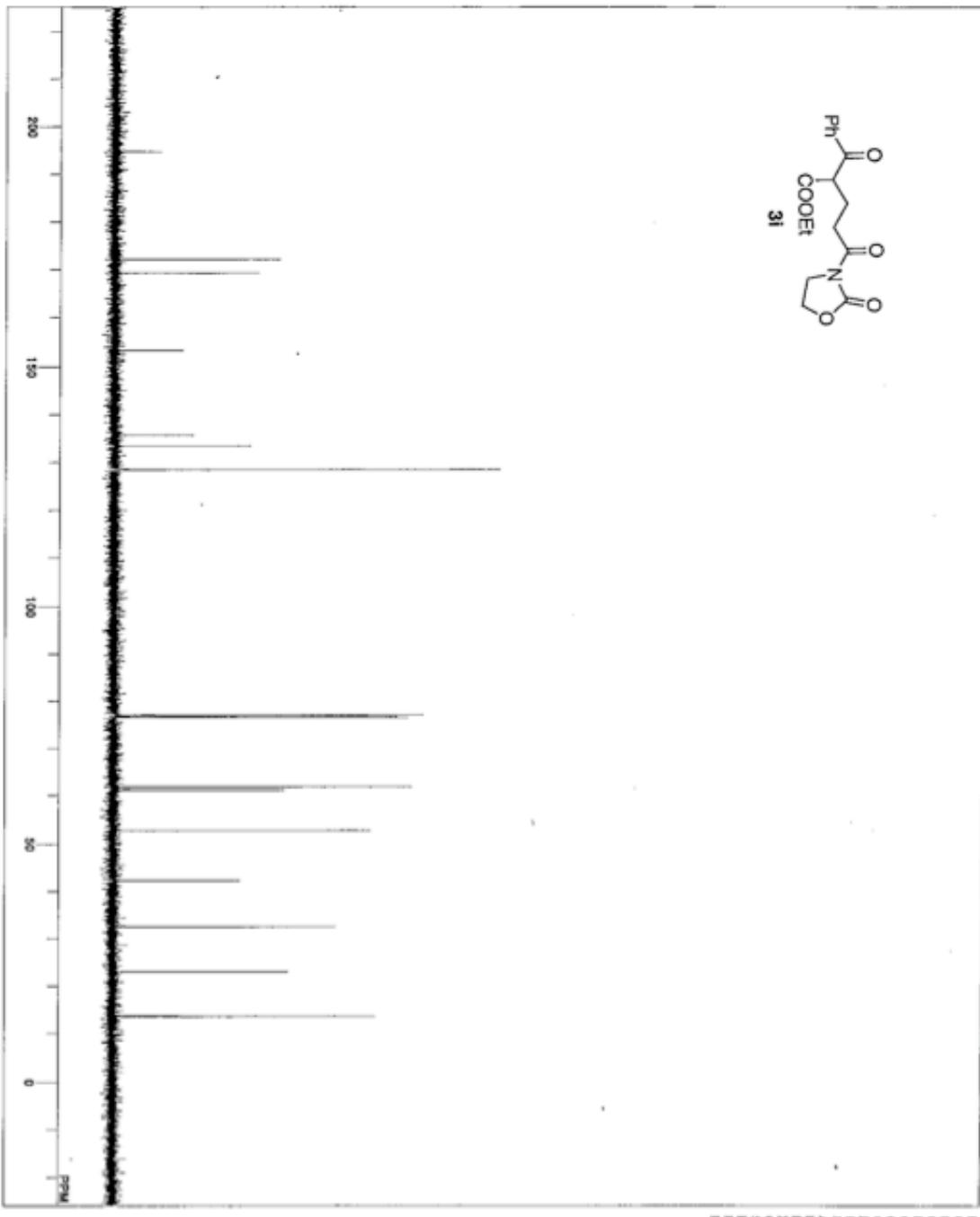
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 RGAIN 50



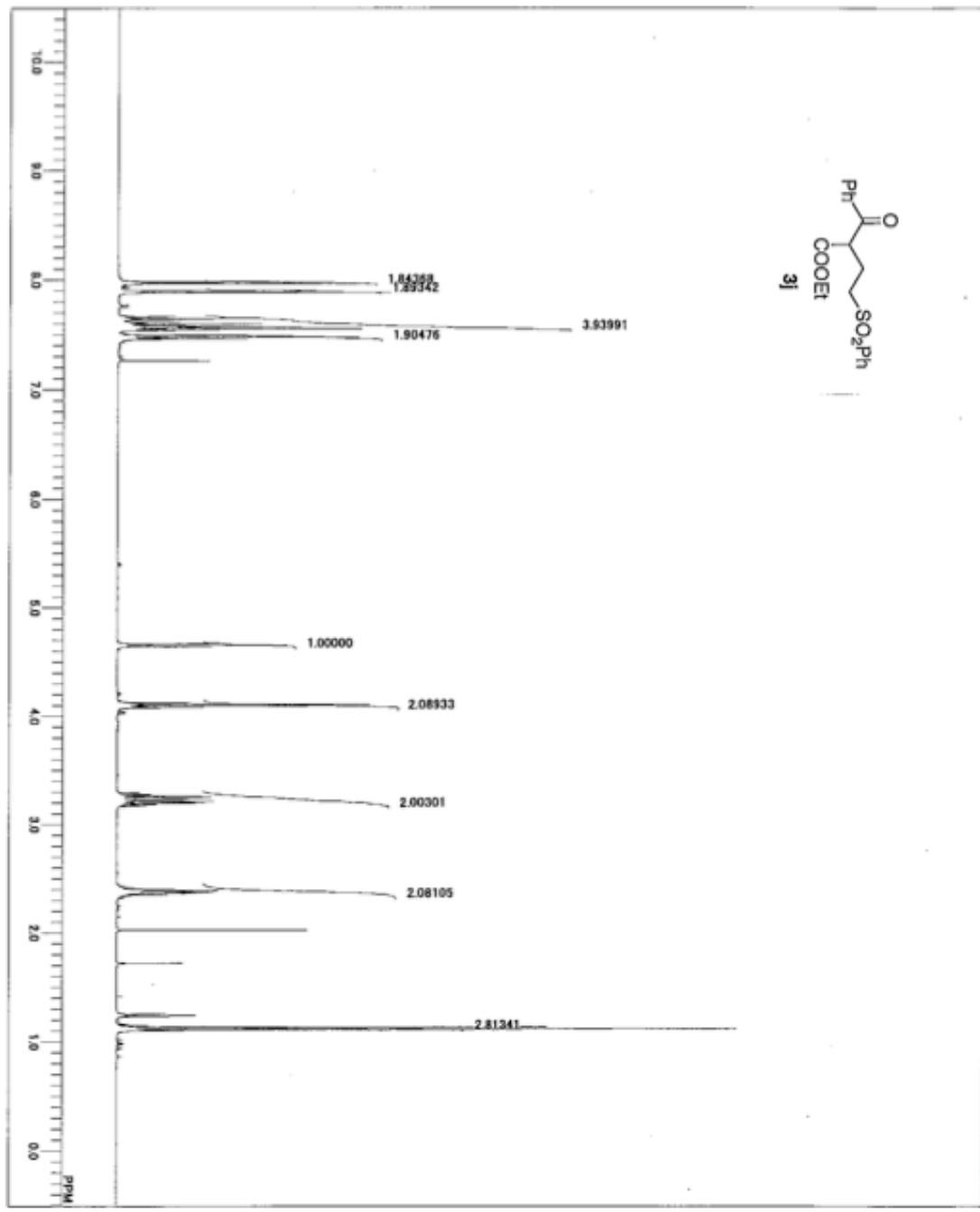
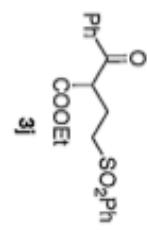
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ACQTM 1.7642 sec
PD 5.0000 sec
PR1 5.60 usec
SPNHC 1H
CTEMP 18.0 °C
SLVNT CDCl₃
EREF 7.26 ppm
SF 0.12 Hz
ROIN 34



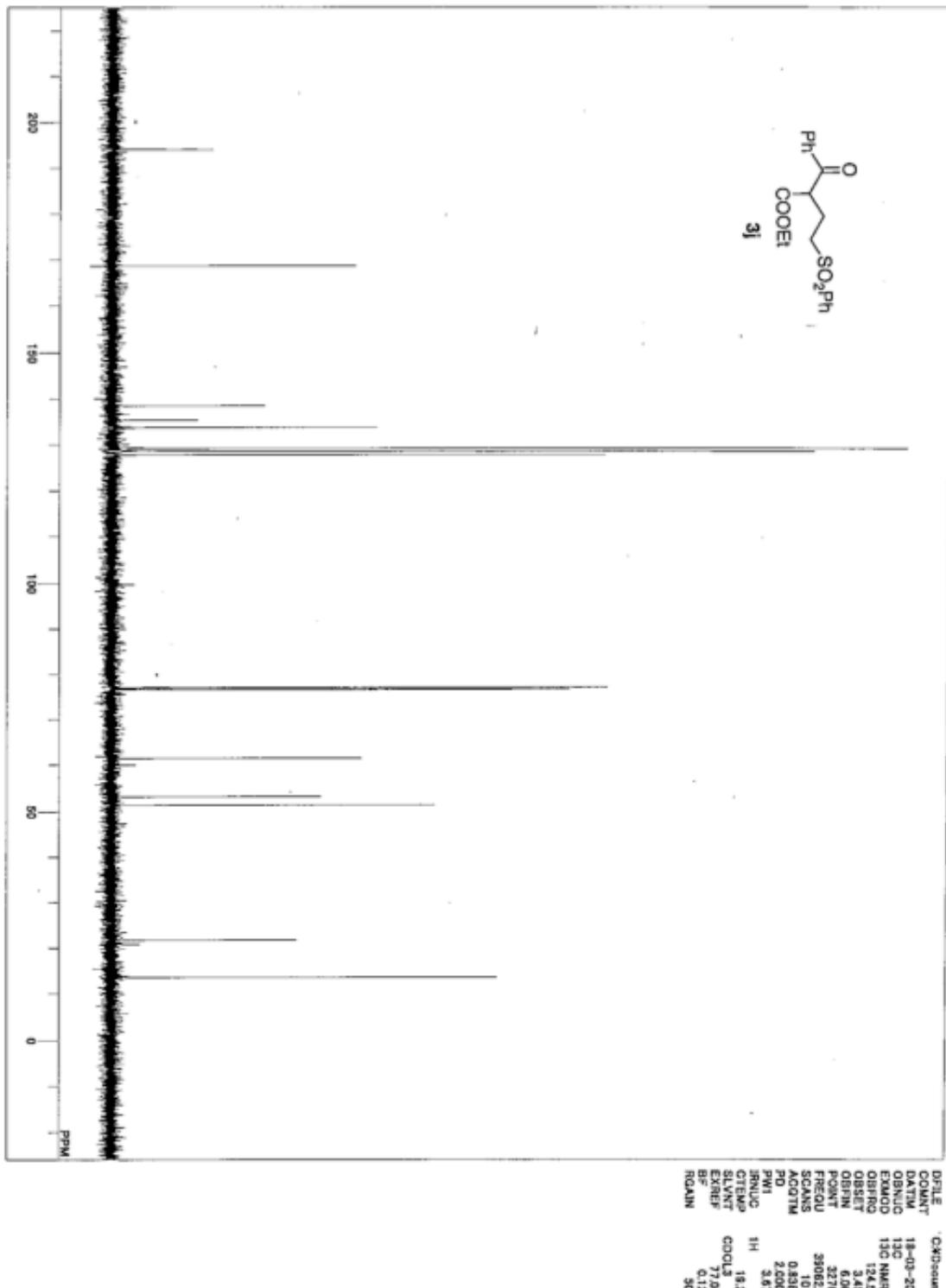
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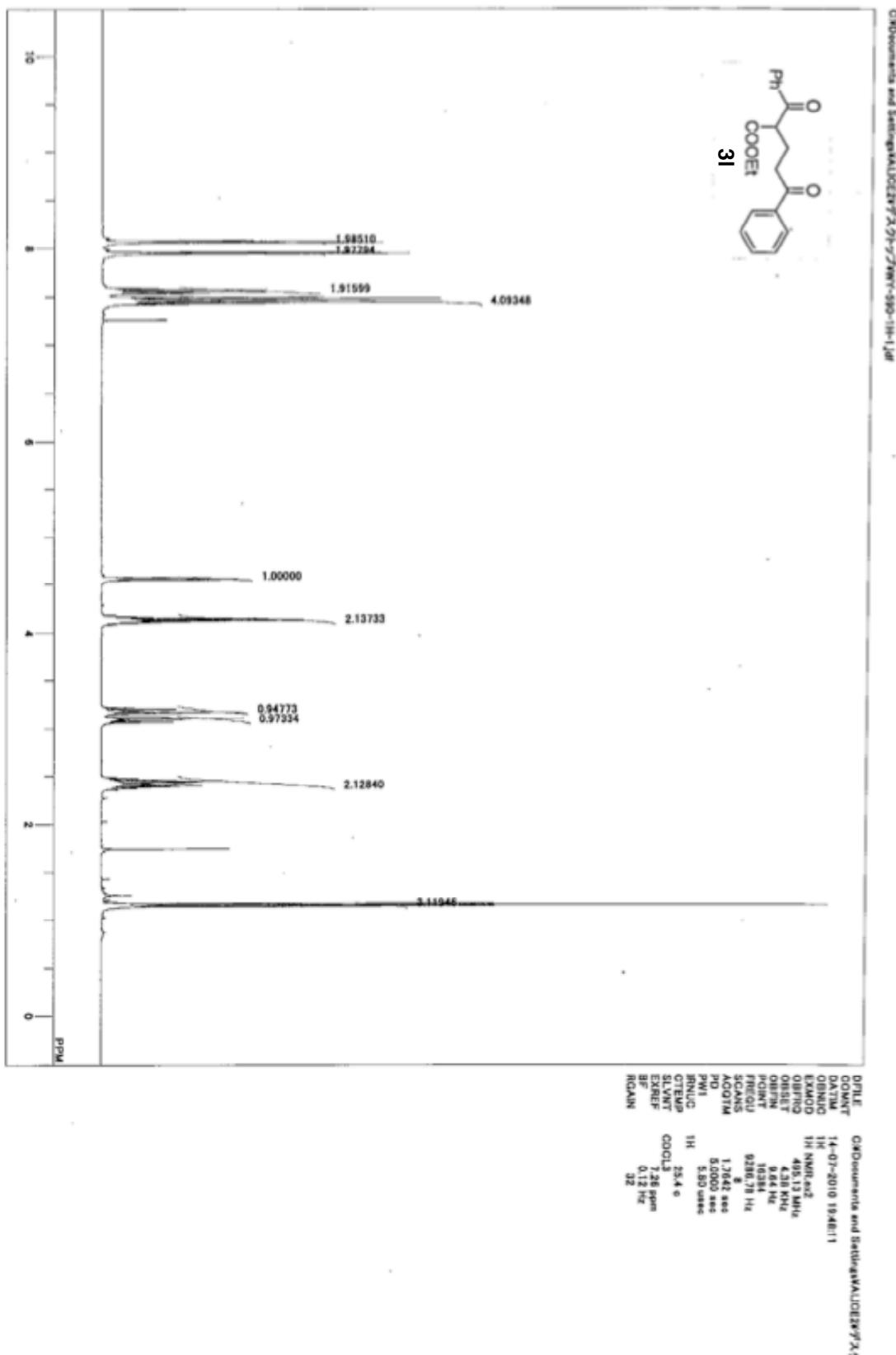


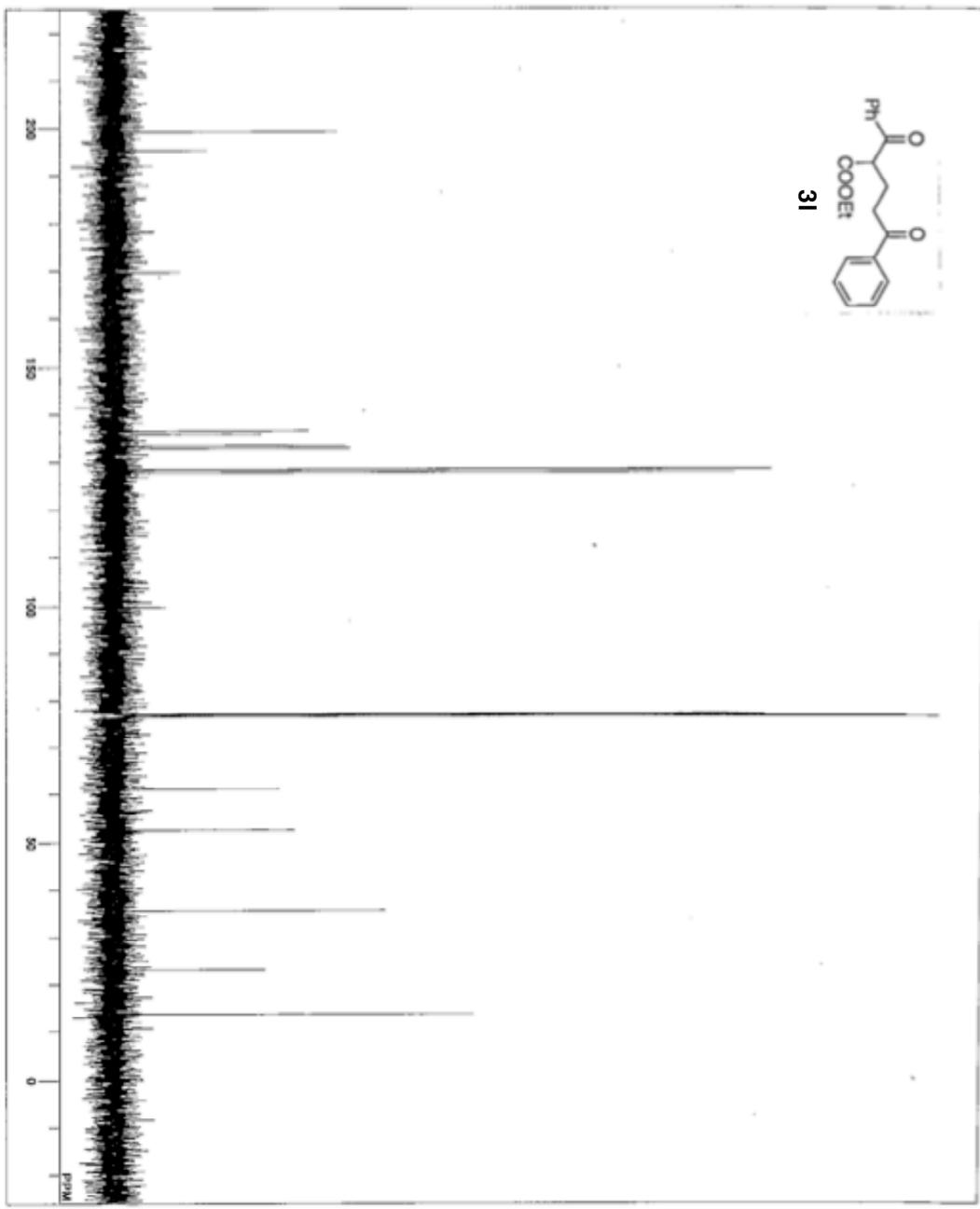
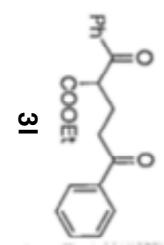
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COUNT 1840-2010 180718
DATUM 180718
OBNUC 13C
EXMOD 130 NMR sec^2
OBPROD 124.51 MHz
OBSET 3.48 sec
OBPN 6.00 Hz
POINT 32768
FREQU 39902150 Hz
SCANS 83
ACQTM 0.8389 sec
PD 2.0000 sec
PR1 3.67 uses
SW1DC 1H
CTEMP 18.4 °C
SLVNT CDCl₃
EXREF 77.00 ppm
BF 0.12 Hz
ROAM 60

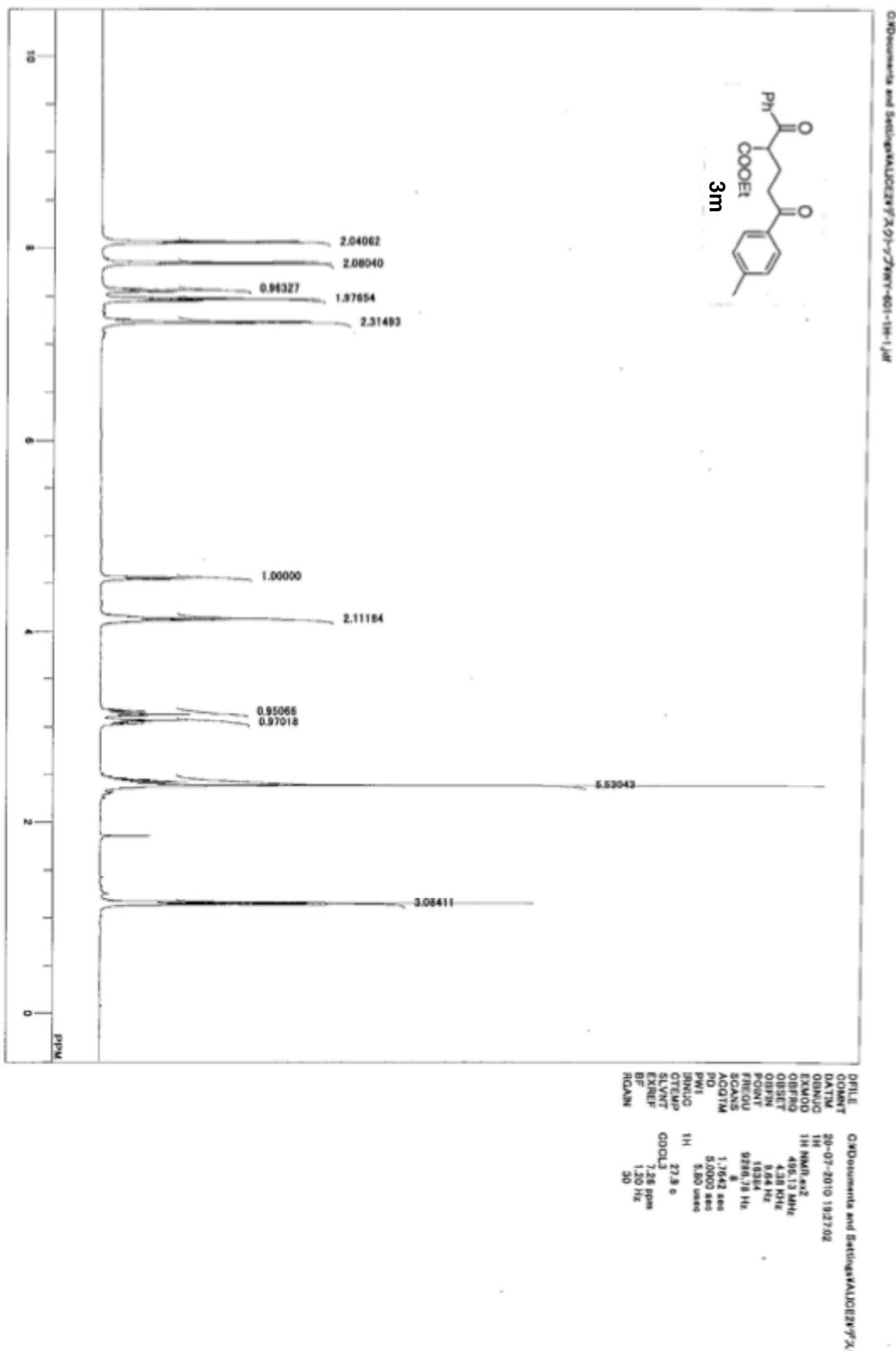


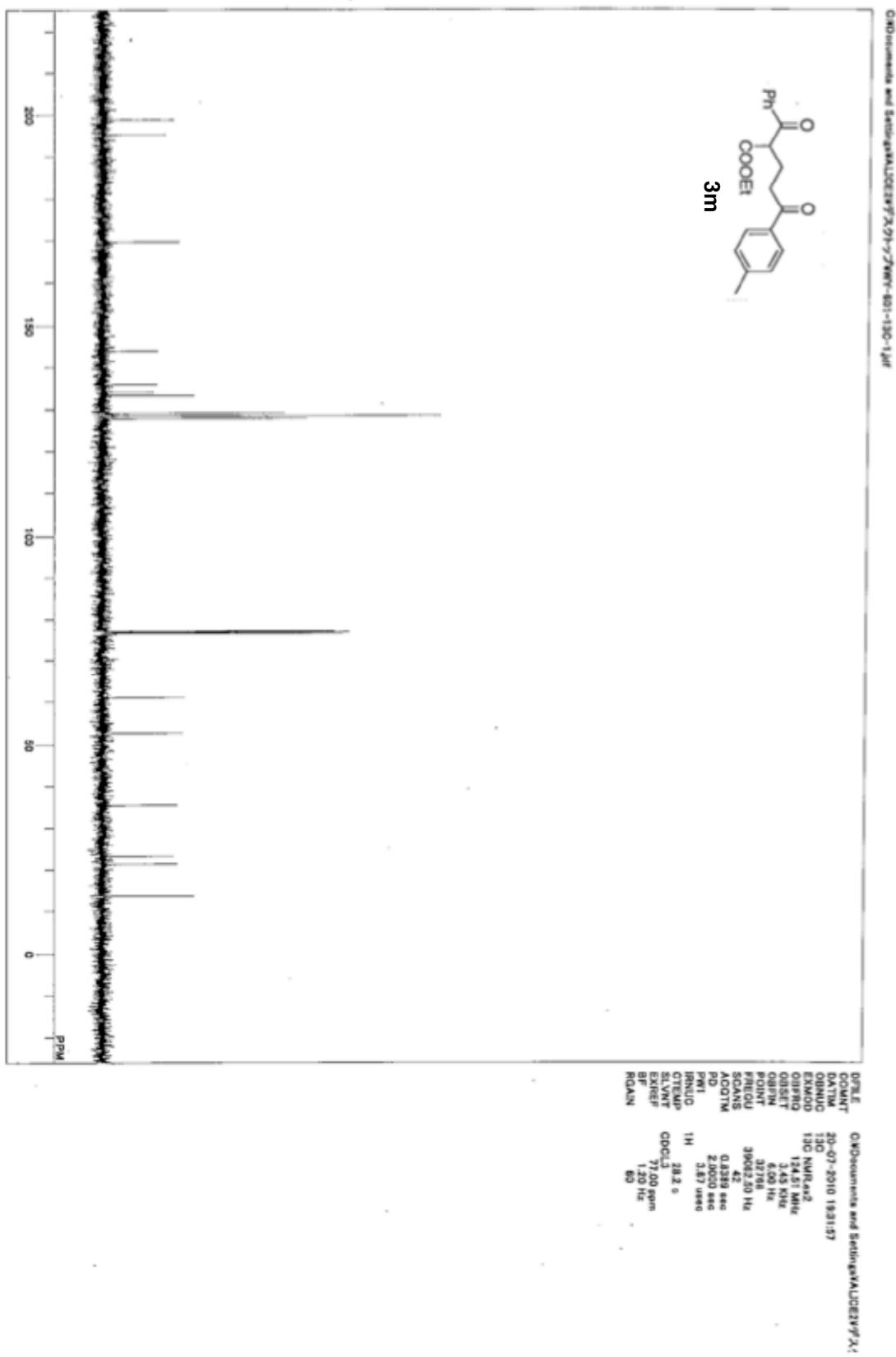
FILE
COMMENT
DATUM 18-03-2010 17:59:32
OBNUC 1H
EXMOD
OBFRQ 495.13 MHz
OBSET 4.39 kHz
CBFIN 9.64 Hz
POINT 16384
FREQU 9285.78 Hz
SCANS 8
ACQTM 1.7642 sec
PD 5.0000 sec
PPI 5.00 uses
ISNUC 1H
CTEMP 18.8 °C
SLVNT CDCl₃
EX-REF 7.26 ppm
BPP 0.12 Hz
RDAM 32

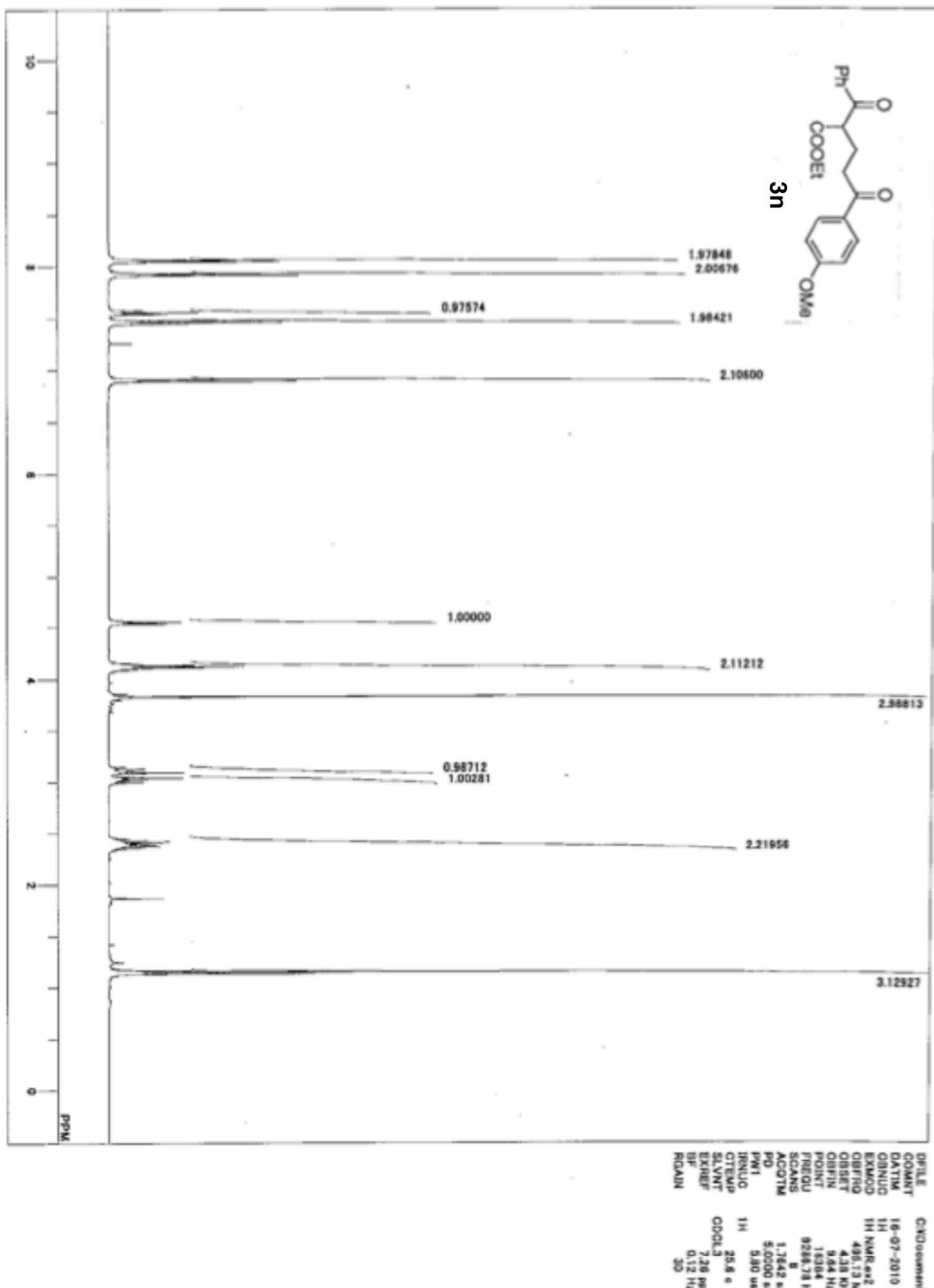


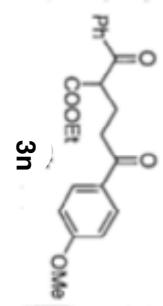






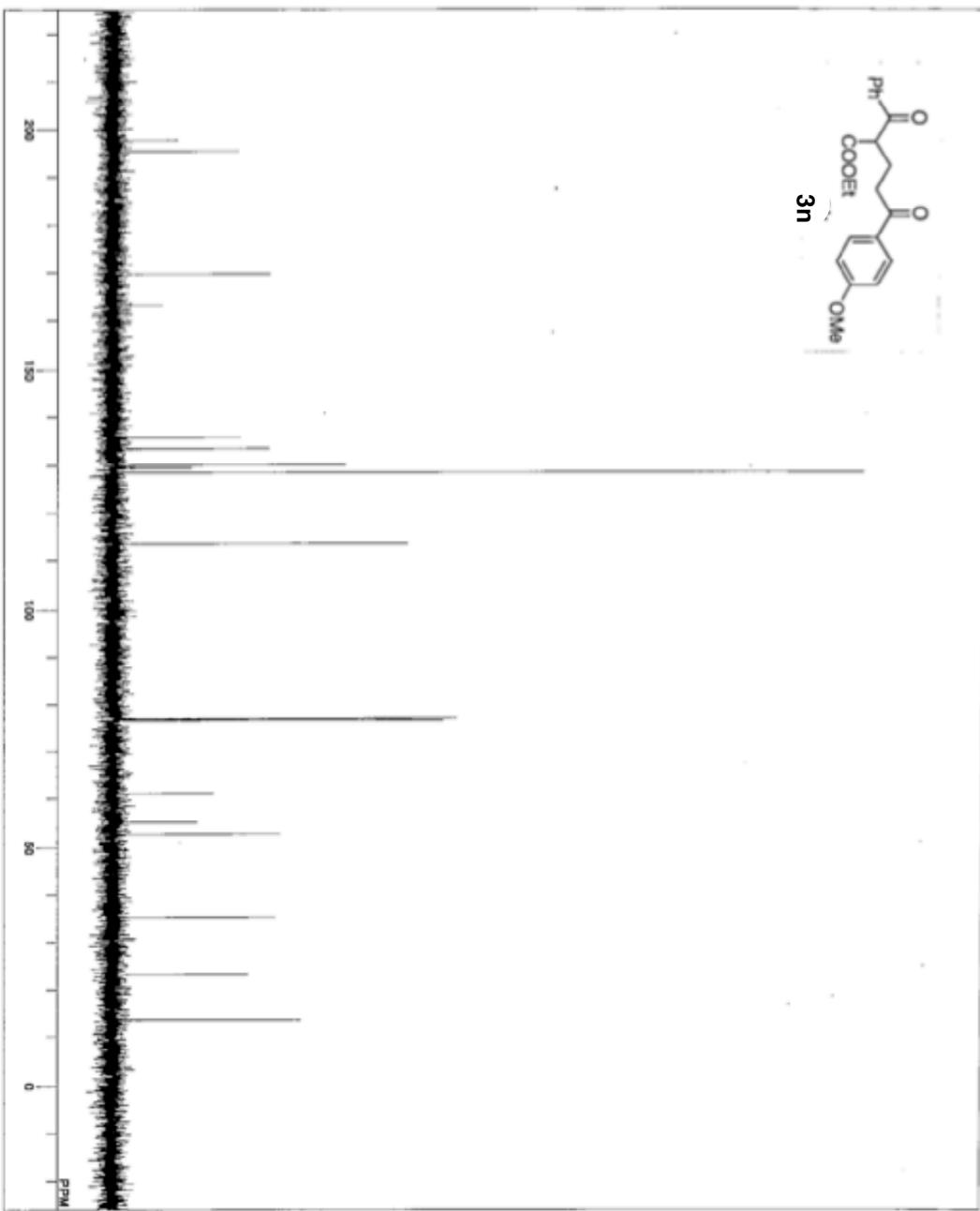


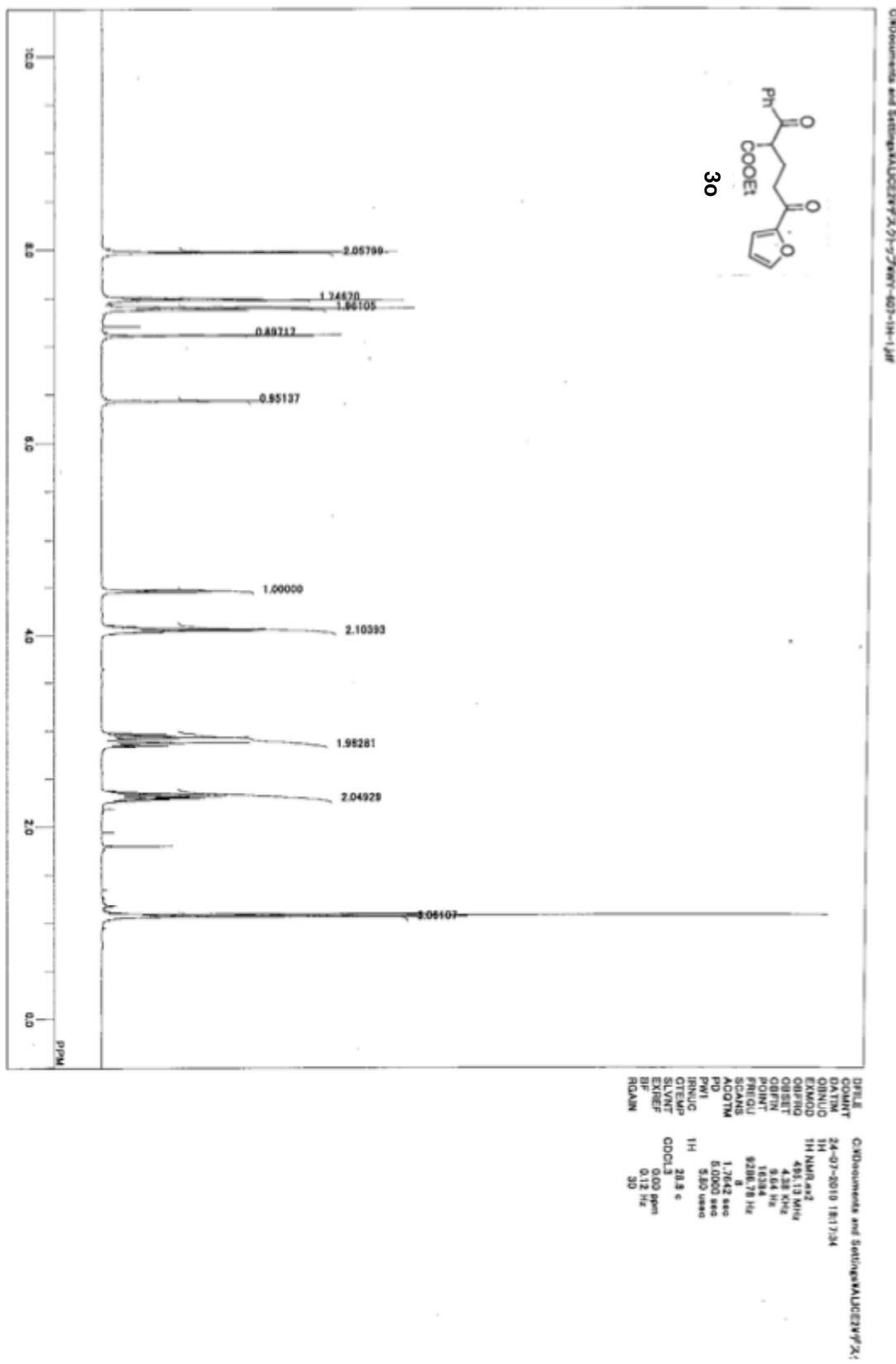


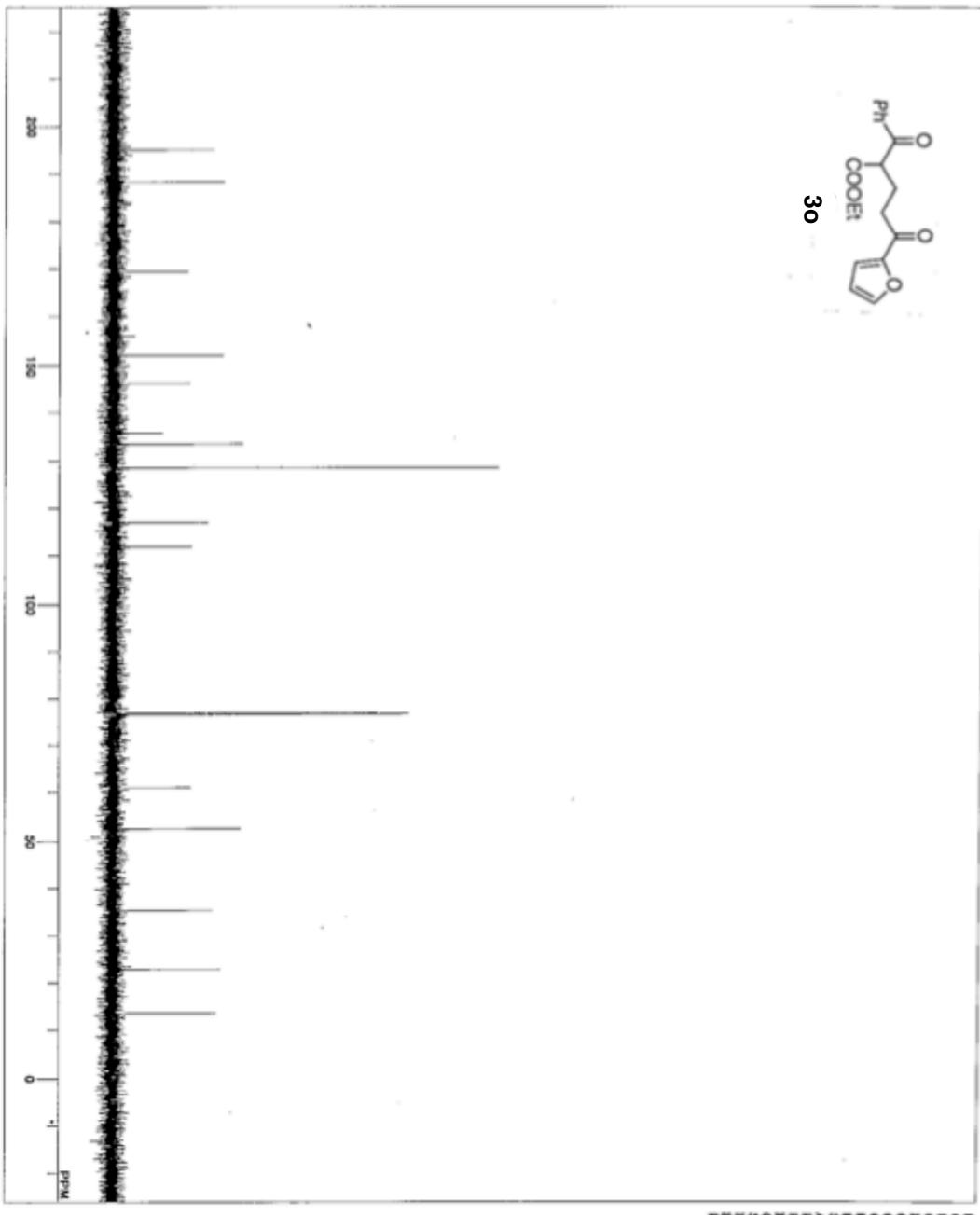
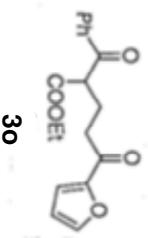


DPPG
 COUNT
 DATA
 DNUC
 ENDMOD
 GPRFQ
 GSET
 GPRIN
 POINT
 FREOU
 SCANS
 ACTIM
 PD
 PPI
 SRNG
 CTEMP
 SVNT
 EXREF
 RF
 RQAN

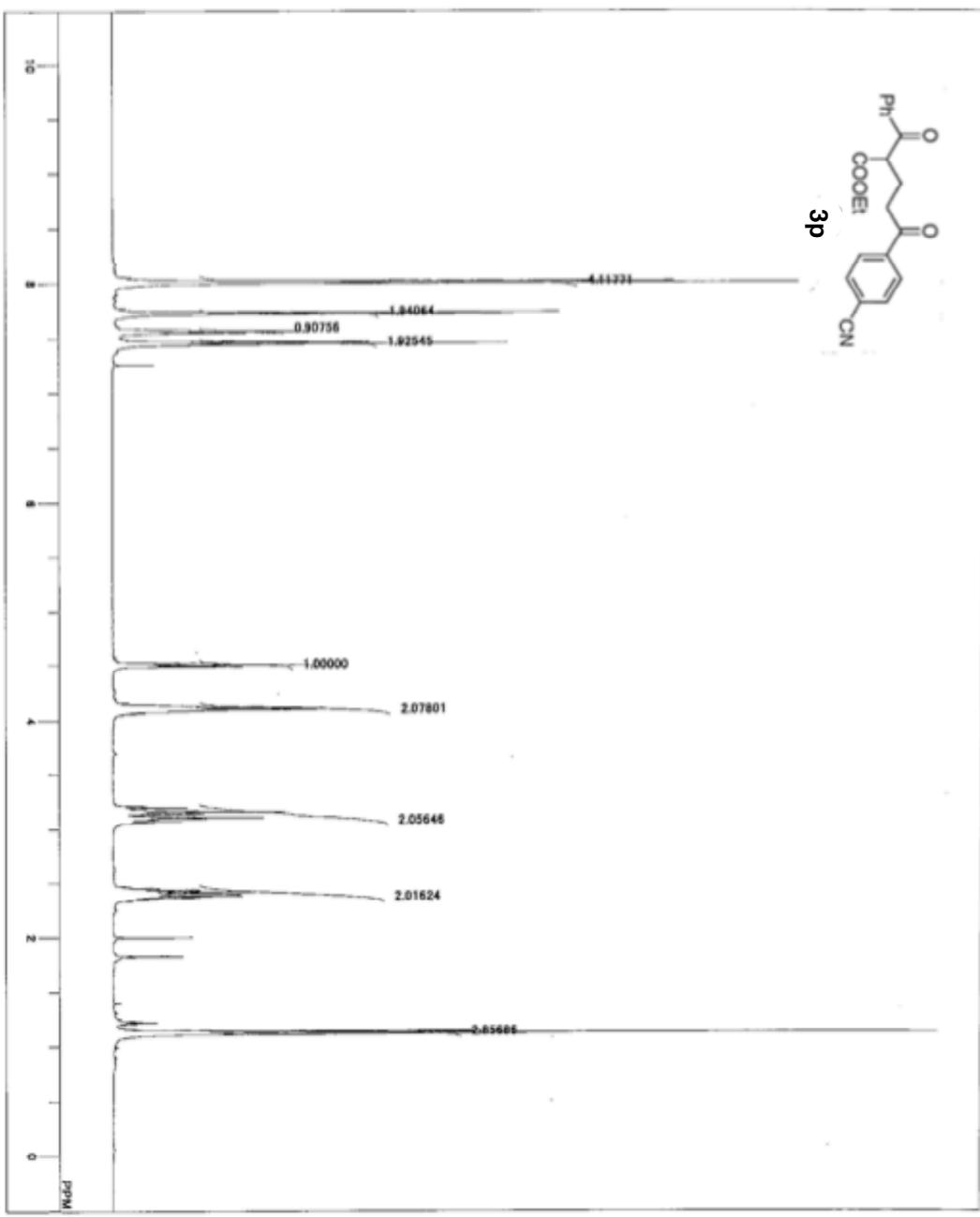
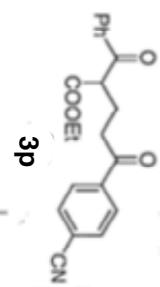
1H
 28.0 °
 CDCl₃
 77.00 ppm
 6.12 Hz
 60





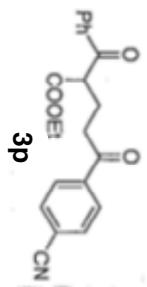


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COMNT	
DTIM	24-07-2010 18:23:55
ORNUC	13C NMR v2
EXMOD	
ODF0	134.51 MHz
DISET	3.45 kHz
DEFIN	8.00 Hz
POINT	32768.0 Hz
IREM1	38012.0 Hz
SCANS	70
ACQIN	0.0180 sec
DD	2.0000 sec
PH1	3.97 usec
IN1D	
1H	
CTEMP	28.1 °
SLVNT	
CPLIF	77.60 ppm
IF	0.12 Hz
ROAM	80



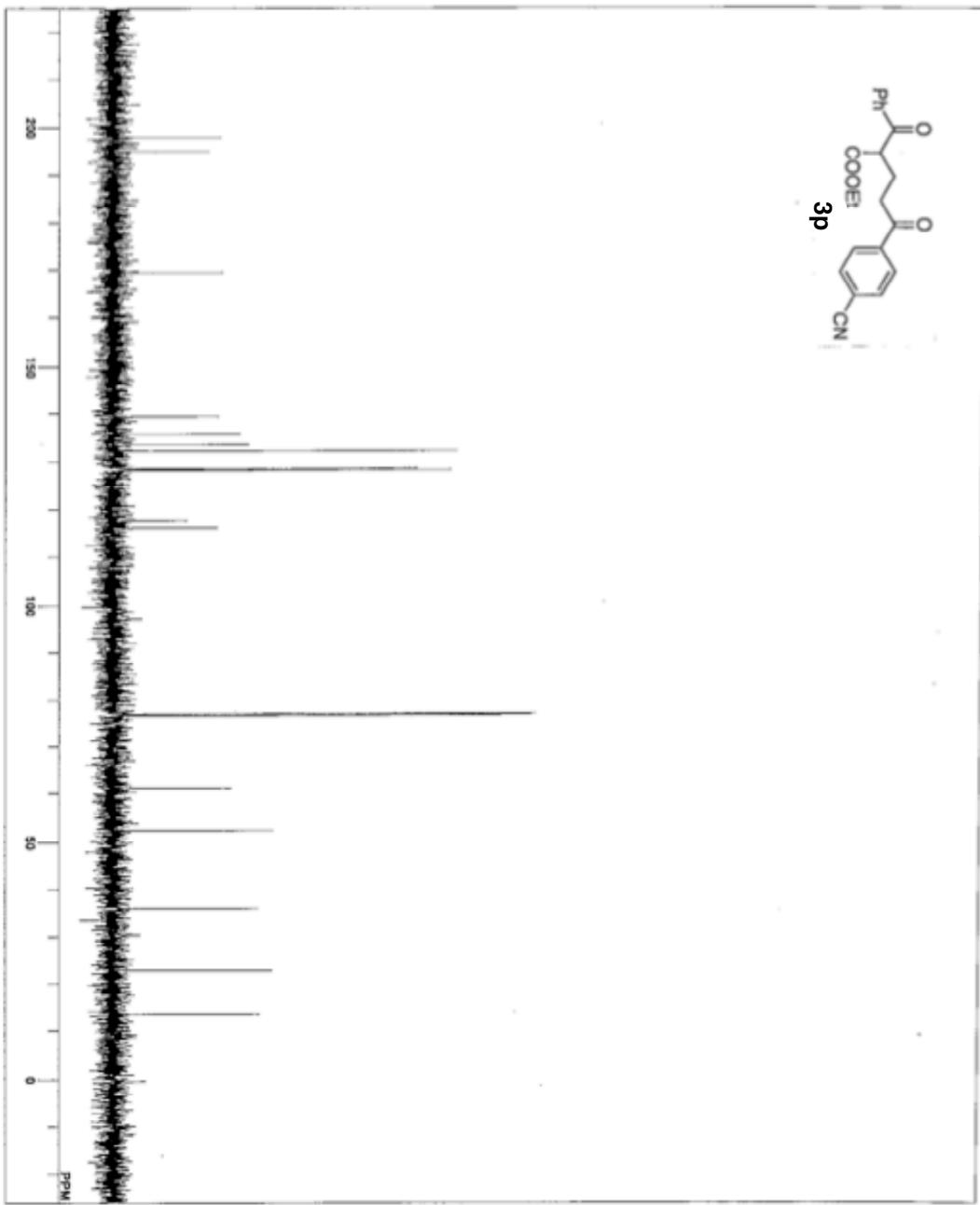
OLE
COMMENT
DATUM
COPND
EWADD
OBFFID
OBSET
OBPN
POINT
PRFLU
SCANS
ACQTRM
PD
PPM
IRNUC
OTEMP
SLVRF
EXRF
RFAN

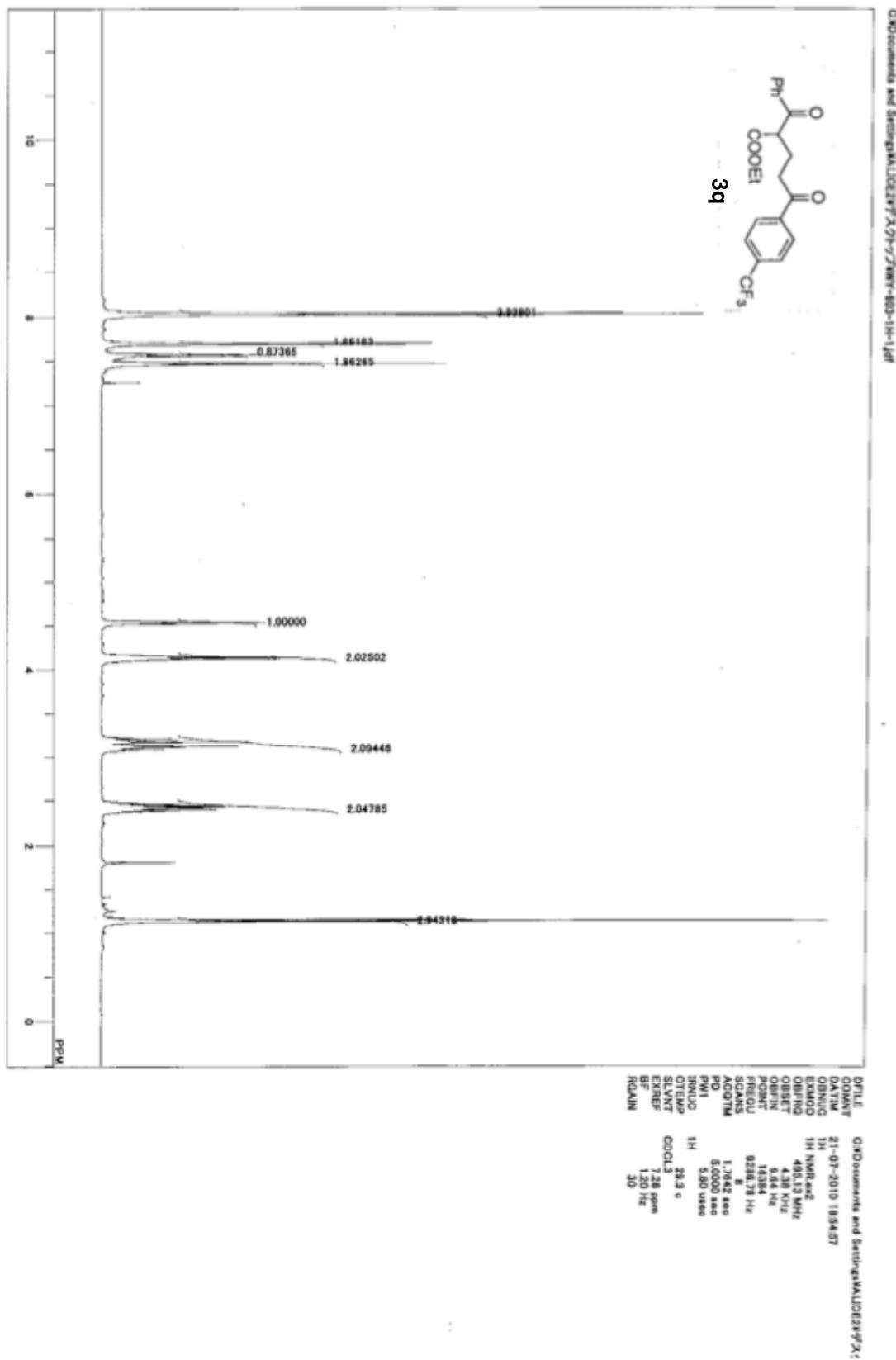
22-07-2010 18:45:52
1H NMR -¹H
489.13 MHz
4.28 kHz
9.44 kHz
11024
9286.78 Hz
8
1,7642 888
5,0000 888
5,40 8880
1H
28.3 8
CDCl₃
7.28 ppm
120 Hz
90

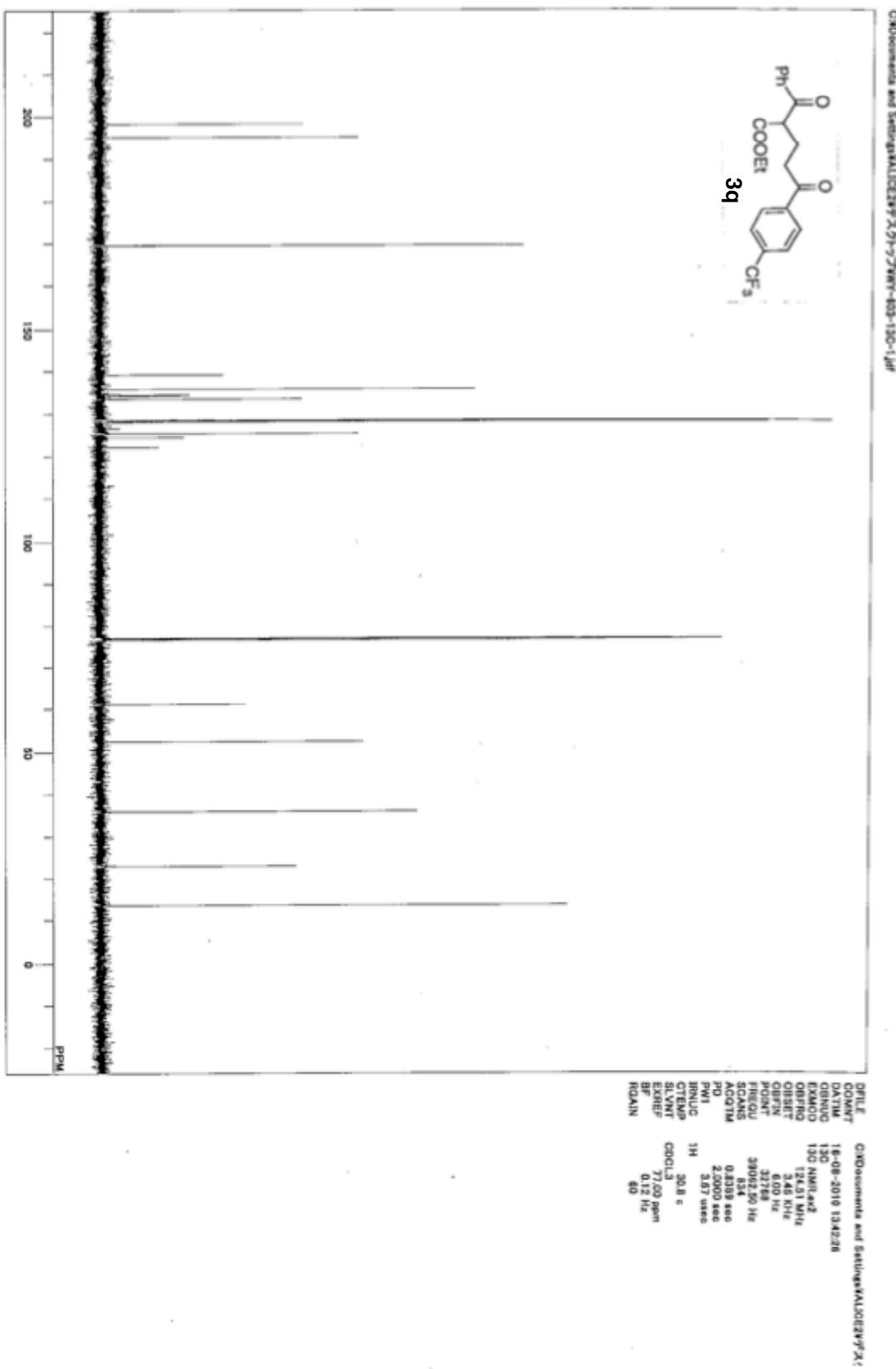


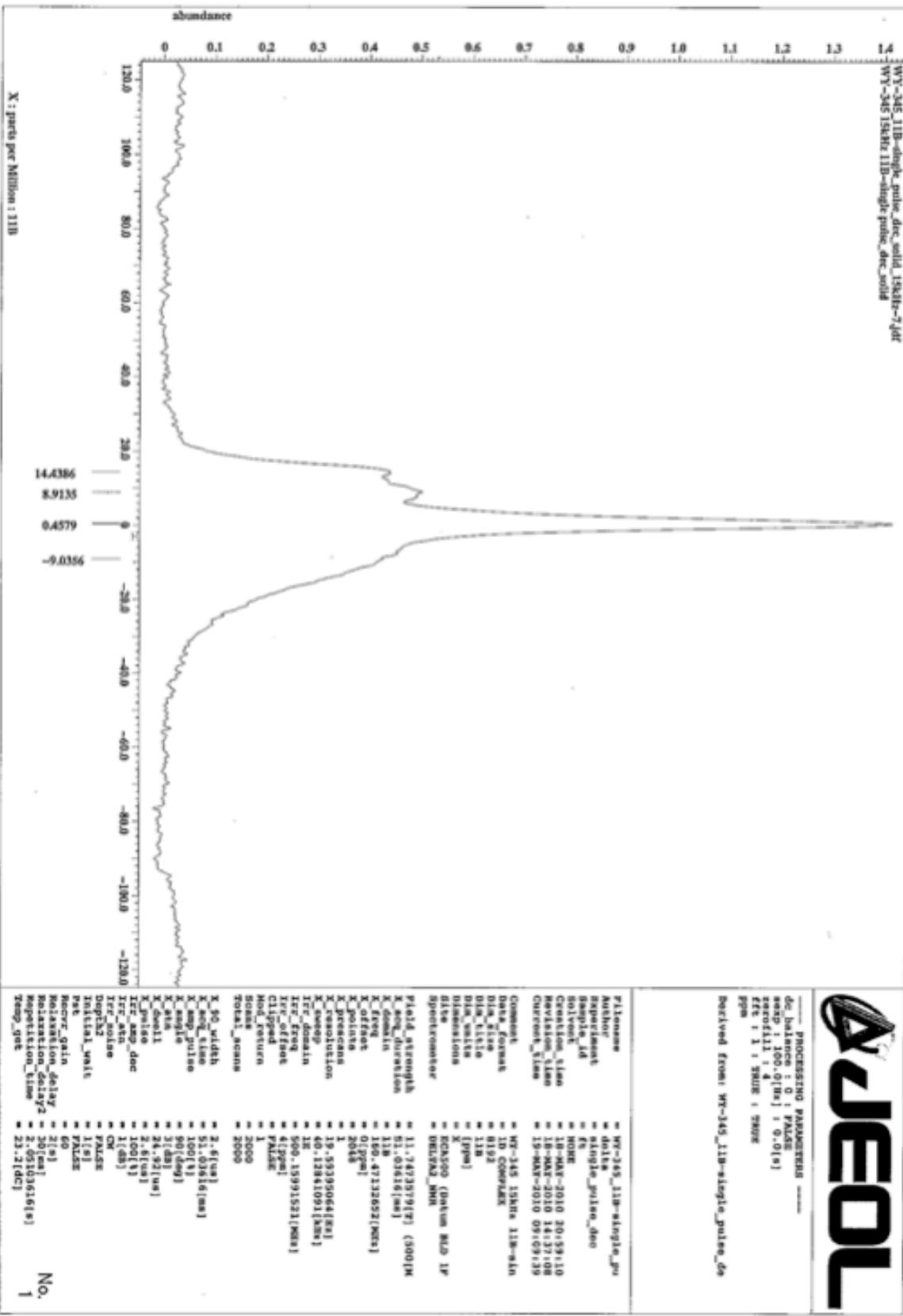
DPFLE
GOMAT
DATIM
GNDUG
EMDDO
DIFRQ
QSBET
QFIRN
JOURN
FREQU
SCANS
ACQTM
RD
PPM
SWINC
CTEMPS
SLVNT
E1REF
SIF
ROAMN

CD3DMS spectra and Structure VALUABLEY34
22-07-2016 18:48:05
130 NMR δ μ ²
134.51 MHz
3.45 MHz
6.00 Hz
27.88 Hz
39082.10 Hz
7.1 sec
0.11 sec
2,000.0 sec
2.97 usec
1H
28.3 °
COOL3
77.00 ppm
120 Hz
80









Part X: References

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