

Supporting Information

Cyclization Reaction of Cyano-Substituted Unsaturated Esters Prompted by Conjugate Addition of Organoborons

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General. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300 MHz and ^{13}C at 75 MHz), a Varian Mercury VX400 (^1H at 400 MHz and ^{13}C at 100 MHz), or a JEOL JNM-ECA (^1H at 600 MHz and ^{13}C at 150 MHz) spectrometer using CHCl_3 (^1H , $\delta = 7.26$) and CDCl_3 (^{13}C , $\delta = 77.0$) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. All reactions were carried out under a nitrogen atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF₂₅₄ (Merck).

(1a)¹

IR (nujol): 2222, 1710 cm^{-1} ; ^1H NMR (300 MHz): $\delta = 3.84$ (s, 3H), 6.61 (d, $J = 15.9$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.62 (t, $J = 7.8$ Hz, 1H), 7.72 (t, $J = 7.2$ Hz, 2H), 7.98 (d, $J = 15.9$ Hz, 1H); ^{13}C NMR (75 MHz): $\delta = 52.1, 112.7, 117.1, 122.6, 126.9, 130.0, 132.9, 133.5, 137.3, 139.5, 166.2$; HRMS (EI^+): Calcd for $\text{C}_{11}\text{H}_9\text{NO}_2$, M^+ 187.0633. Found m/z 187.0634.

(1b)

IR (nujol): 2217, 1721, 1636 cm^{-1} ; ^1H NMR (300 MHz): $\delta = 3.87$ (s, 3H), 6.74 (d, $J = 15.9$ Hz, 1H), 7.60–7.80 (m, 3H), 7.91 (d, $J = 8.1$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 8.22 (d, $J = 15.9$ Hz, 1H), 8.28 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (75 Hz): $\delta = 52.1, 111.0, 115.8, 122.2, 123.2, 126.0, 128.4, 128.5, 129.2, 132.6, 133.09, 133.15, 137.2, 139.9, 166.2$; HRMS (EI^+): Calcd for $\text{C}_{15}\text{H}_{11}\text{NO}_2$, M^+ 237.0790. Found m/z 237.0786.

¹ Busacca, C. A.; Johnson, R. E. *Tetrahedron Lett.* **1992**, 33, 165.

(1c)

IR (KBr): 2203, 1713, 1642 cm^{-1} ; ^1H NMR (300 MHz): δ = 3.86 (s, 3H), 3.88 (s, 3H), 7.10 (d, J = 16.2 Hz, 1H), 7.27–7.34 (m, 1H), 7.37–7.41 (m, 2H), 7.73–7.78 (m, 1H), 7.79 (d, J = 16.2 Hz, 1H); ^{13}C NMR (75 MHz): δ = 65.4, 70.7, 79.3, 85.4, 86.8, 87.8, 88.6, 88.8, 89.1, 89.8, 90.0, 92.1, 92.7, 99.5; HRMS (EI^+): Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$, M^+ 240.0899. Found m/z 240.0900.

(1d)

IR (KBr): 2230, 1725, 1632, 1312, 1175 cm^{-1} ; ^1H NMR (300 MHz): δ = 3.82 (s, 3H), 6.47 (d, J = 15.9 Hz, 1H), 7.25 (d, J = 5.1 Hz, 1H), 7.41 (d, J = 5.7 Hz, 1H), 7.89 (d, J = 15.9 Hz, 1H); ^{13}C NMR (75 MHz): δ = 52.1, 112.0, 113.9, 121.6, 128.2, 129.8, 132.8, 147.7, 165.8; HRMS (EI^+): Calcd for $\text{C}_9\text{H}_7\text{O}_2\text{NS}$, M^+ 193.0197. Found m/z 193.0201.

(1e)²

IR (KBr): 2247, 1713, 1634, 1320, 1169 cm^{-1} ; ^1H NMR (300 MHz): δ = 3.82 (s, 3H), 3.86 (s, 2H), 6.40 (d, J = 15.9 Hz, 1H), 7.34–7.52 (m, 3H), 7.57–7.62 (m, 1H), 7.82 (d, J = 15.6 Hz, 1H); ^{13}C NMR (75 MHz): δ = 21.6, 51.8, 117.0, 121.4, 127.2, 128.7, 128.9, 129.1, 130.5, 133.1, 139.7, 166.5; HRMS (EI^+): Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2$, M^+ 201.0790. Found m/z 201.0791.

(1f)

IR (nujol): 2224, 1653, 1611 cm^{-1} ; ^1H NMR (300 MHz): δ = 1.81 (s, 6H), 3.83 (s, 3H), 6.30 (d, J = 15.6 Hz, 1H), 7.32–7.47 (m, 3H), 7.52–7.56 (m, 1H), 8.50 (d, J = 15.6 Hz, 1H); ^{13}C NMR (75 MHz): δ = 28.8, 35.4, 51.9, 121.4, 124.0, 125.4, 128.5, 129.2, 130.1, 133.9, 138.5, 142.7, 166.6; HRMS (EI^+): Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$, M^+ 229.1103. Found m/z 229.1106.

(1g)³

IR (neat): 2249, 1717, 1659, 1269, 1210, 1161 cm^{-1} ; ^1H NMR (300 MHz): δ = 1.29 (t, J = 7.2 Hz, 3H), 2.45–2.60 (m, 4H), 4.20 (q, J = 7.2 Hz, 2H), 5.95 (d, J = 15.9 Hz, 1H), 6.90 (dt, J = 15.6, 6.2 Hz, 1H); ^{13}C NMR (75 MHz): δ = 13.6, 15.4, 27.1, 59.8, 118.2, 123.1, 143.1, 165.0; HRMS (CI^+): Calcd for $\text{C}_8\text{H}_{12}\text{NO}_2$, $\text{M}+\text{H}^+$ 154.0868. Found m/z 154.0869.

² Kolsaker, P.; Ellingsen, P. O. *Acta Chem. Scand., Series B: Organic Chemistry and Biochemistry* **1979**, B33, 138.

³ Bhandal, H.; Howell, A. R.; Patel, V. F.; Pattenden, G. J. *Chem. Soc. Perkin Trans. 1: Organic and Bio-Organic Chemistry* **1990**, 2709.

(1h)⁴

IR (neat): 2247, 1719, 1655, 1271, 1198, 1156 cm⁻¹; ¹H NMR (300 MHz): δ = 1.28 (t, *J* = 7.1 Hz, 3H), 1.83 (quint, *J* = 7.2 Hz, 2H), 2.31–2.43 (m, 4H), 4.18 (q, *J* = 7.2 Hz, 2H), 5.88 (d, *J* = 15.9 Hz, 1H), 6.87 (dt, *J* = 15.6, 6.9 Hz, 1H); ¹³C NMR (75 MHz): δ = 14.2, 16.6, 23.8, 30.6, 60.4, 118.9, 123.2, 145.6, 166.1; HRMS (FAB⁺): Calcd for C₉H₁₄NO₂, M+H⁺ 168.1025. Found m/z 168.1025.

General procedure: To an oven-dried, N₂-purged flask was added substrate **1** (0.3 mmol, 1.0 equiv), [Rh(OMe)(cod)]₂ (15 μmol, 10 mol% of Rh), and a solution of *B*-Ar-9BBN (**2**, 0.6 mmol, 2.0 equiv) in toluene (3.0 mL). The resulting reaction mixture was stirred for 8~17 h at 110 °C. After the reaction mixture was cooled, water (5~10 mL) was added, and the aqueous layer was extracted with ethyl acetate (15 mL x 5). The combined extracts were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (dichloromethane) to give the product **3**. The second chromatography (hexane:ethyl acetate) was carried out in some cases to remove small amounts of impurities.

(3aa)

IR (nujol): 3499, 3349, 1659, 1628, 1536 cm⁻¹; ¹H NMR (400 MHz): δ = 3.62 (s, 3H), 4.81 (s, 1H), 6.11 (br s, 2H), 7.10–7.14 (m, 2H), 7.14–7.25 (m, 4H), 7.30–7.38 (m, 2H), 7.39–7.44 (m, 1H); ¹³C NMR (75 MHz): δ = 50.4, 52.1, 102.6, 118.8, 124.8, 126.2, 126.6, 127.5, 128.1, 129.4, 136.7, 141.4, 149.4, 156.9, 167.9; elemental analysis: Calcd for C₁₇H₁₅NO₂: C 76.96, H 5.70; found: C 76.86, H 5.64.

(3ab)

IR (nujol): 3438, 3337, 1659, 1638, 1545, 1509 cm⁻¹; ¹H NMR (300 MHz): δ = 3.63 (s, 3H), 3.76 (s, 3H), 4.77 (s, 1H), 6.15 (br s, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 7.16–7.21 (m, 1H), 7.29–7.35 (m, 2H), 7.38–7.44 (m, 1H); ¹³C NMR (75 MHz): δ = 50.4, 51.4, 55.1, 102.9, 113.6, 118.7, 124.8, 126.6, 128.5, 129.4, 133.4, 136.6, 149.7, 156.7, 158.0, 167.9; HRMS (EI⁺): Calcd for C₁₈H₁₇NO₃, M⁺ 295.1208. Found m/z 295.1207.

⁴ Rozema, M. J.; Sidduri, A.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 1956.

(3ac)

IR (KBr): 3449, 3364, 1673, 1653, 1626 cm^{-1} ; ^1H NMR (300 MHz): δ = 3.62 (s, 3H), 4.76 (s, 1H), 6.11 (br s, 2H), 7.04 (d, J = 8.1 Hz, 2H), 7.13–7.22 (m, 3H), 7.30–7.45 (m, 3H); ^{13}C NMR (75 MHz): δ = 50.5, 51.5, 102.6, 118.9, 124.9, 127.0, 128.3, 129.0, 129.7, 131.9, 136.7, 140.1, 149.0, 156.9, 167.7; HRMS (EI^+): Calcd for $\text{C}_{17}\text{H}_{14}\text{ClNO}_2$, M^+ 299.0713. Found m/z 299.0712.

(3ba)

IR (KBr): 3403, 3305, 1653, 1628, 1522, 1262, 1100 cm^{-1} ; ^1H NMR (300 MHz): δ = 3.63 (s, 3H), 4.83 (s, 1H), 6.68 (br s, 2H), 7.09–7.27 (m, 5H), 7.30 (d, J = 8.7 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 8.33 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz): δ = 50.4, 52.5, 104.7, 121.9, 122.9, 125.4, 126.4, 127.2, 127.8, 128.2, 128.5, 129.6, 130.6, 130.7, 133.3, 140.5, 150.1, 160.8, 168.0; HRMS (CI^+): Calcd for $\text{C}_{21}\text{H}_{18}\text{NO}_2$, $\text{M}+\text{H}^+$ 316.1338. Found m/z 316.1335.

(3ca)

IR (KBr): 3391, 3301, 3214, 1624, 1489 cm^{-1} ; ^1H NMR (400 MHz): δ = 3.42 (s, 3H), 3.57 (br s, 3H), 4.77 (s, 1H), 7.10–7.15 (m, 2H), 7.15–7.33 (m, 6H), 7.66–7.71 (m, 1H) ($-\text{NH}_2$ missing); ^{13}C NMR (150 MHz): δ = 30.7, 46.4, 49.8, 98.5, 110.4, 114.8, 118.5, 120.9, 121.0, 121.6, 126.6, 128.1, 128.3, 138.8, 141.3, 156.7, 159.1, 167.7; HRMS (CI^+): Calcd for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_2$, $\text{M}+\text{H}^+$ 319.1447. Found m/z 319.1445.

(3da)

IR (KBr): 3472, 3345, 1655, 1607, 1534 cm^{-1} ; ^1H NMR (300 MHz): δ = 3.59 (s, 3H), 4.87 (s, 1H), 6.14 (br s, 2H), 7.03 (d, J = 4.8 Hz, 1H), 7.08–7.16 (m, 2H), 7.16–7.29 (m, 3H), 7.34 (d, J = 5.7 Hz, 1H); ^{13}C NMR (150 MHz): δ = 50.1, 50.2, 104.5, 116.9, 126.6, 127.4, 128.3, 129.7, 141.2, 141.8, 155.5, 156.0, 167.1; HRMS (FAB^+): Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_2\text{S}$, M^+ 271.0667. Found m/z 271.0666.

(3ea)

IR (nujol): 3463, 3322, 1668, 1609 cm^{-1} ; ^1H NMR (400 MHz): δ = 3.31 (d, J = 18.8 Hz, 1H), 3.70 (s, 3H), 3.83 (d, J = 18.8 Hz, 1H), 5.22 (s, 1H), 7.07–7.21 (m, 8H), 7.30–7.34 (m, 1H) ($-\text{NH}_2$ missing); ^{13}C NMR (75 MHz): δ = 36.3, 45.4, 50.6, 95.0, 125.7, 126.0, 126.7, 127.2, 127.3, 128.1, 128.3, 131.8, 140.1, 145.9, 156.9, 169.5; HRMS (EI^+): Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2$, M^+ 279.1259. Found m/z 279.1260.

(3fa) To an oven-dried, N₂-purged flask was added a solution of **1f** (44.0 mg, 0.19 mmol) in 1,4-dioxane (2.0 mL), 2-phenyl[1,3,2]dioxaborolane **2a'** (59.0 mg, 0.40 mmol, 2.0 equiv), [Rh(OMe)(cod)]₂ (4.7 mg, 9.7 μmol, 10 mol% of Rh), and H₂O (0.7 μL, 39 μmol, 0.2 equiv). The resulting reaction mixture was stirred for 13 h at 100 °C. After the reaction mixture was cooled, the reaction was quenched with water (5~10 mL). The aqueous layer was extracted with ethyl acetate (15 mL x 5). The combined extracts were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (dichloromethane) to give the product **3fa** (46.9 mg, 0.15 mmol, 80%): IR (nujol): 3426, 3312, 1653, 1624, 1522 cm⁻¹; ¹H NMR (300 MHz): δ = 1.63 (s, 3H), 1.65 (s, 3H), 3.59 (s, 3H), 5.16 (s, 1H), 6.76 (br s, 2H), 7.04–7.14 (m, 2H), 7.15–7.23 (m, 6H), 7.33–7.39 (m, 1H); ¹³C NMR (75 MHz): δ = 29.4, 31.9, 39.2, 44.5, 50.5, 93.1, 125.4, 125.8, 126.1, 126.2, 127.9, 128.0, 129.5, 136.9, 140.0, 147.9, 162.0, 170.3; HRMS (EI⁺): Calcd for C₂₀H₂₁NO₂, M⁺ 307.1572. Found m/z 307.1570.

(3ga)

[α]_D²⁶ – 9.51 (c 1.365, CHCl₃) for the sample of 95% ee.

IR (KBr): 3478, 3335, 1651, 1620, 1566 cm⁻¹; ¹H NMR (300 MHz): δ = 1.01 (t, *J* = 7.2 Hz, 3H), 1.70–1.82 (m, 1H), 2.30–2.50 (m, 2H), 2.62–2.77 (m, 1H), 3.91–4.05 (m, 2H), 4.06–4.13 (m, 1H), 5.83 (br s, 2H), 7.12–7.29 (m, 5H); ¹³C NMR (75 MHz): δ = 14.2, 31.4, 33.6, 48.3, 58.4, 99.0, 125.4, 126.8, 127.8, 147.6, 162.6, 167.8; HRMS (EI⁺): Calcd for C₁₄H₁₇NO₂, M⁺ 231.1259. Found m/z 231.1257.

(3gb)

[α]_D²³ – 1.05 (c 1.045, CHCl₃) for the sample of 89% ee.

IR (neat): 3446, 3320, 1651, 1634, 1557 cm⁻¹; ¹H NMR (300 MHz): δ = 1.04 (t, *J* = 7.1 Hz, 3H), 1.65–1.78 (m, 1H), 2.26–2.48 (m, 2H), 2.58–2.77 (m, 1H), 3.77 (s, 3H), 3.93–4.08 (m, 3H), 5.71 (br s, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz): δ = 14.4, 31.6, 33.6, 47.5, 55.2, 58.5, 99.4, 113.3, 127.8, 139.7, 157.5, 162.3, 167.9; HRMS (EI⁺): Calcd for C₁₅H₁₉NO₃, M⁺ 261.1365. Found m/z 261.1362.

(3gc)

[α]_D²³ – 5.36 (c 0.765, CHCl₃) for the sample of 95% ee.

IR (KBr): 3422, 3314, 1659, 1624, 1547 cm⁻¹; ¹H NMR (300 MHz): δ = 1.02 (t, *J* = 7.2 Hz, 3H),

1.63–1.75 (m, 1H), 2.28–2.52 (m, 2H), 2.61–2.76 (m, 1H), 3.91–4.09 (m, 3H), 5.76 (br s, 2H), 7.10 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75 MHz): $\delta = 14.3, 31.3, 33.6, 47.8, 58.6, 98.7, 128.0, 128.2, 131.0, 146.2, 162.6, 167.7$; HRMS (EI⁺): Calcd for $\text{C}_{14}\text{H}_{16}\text{ClNO}_2$, M^+ 265.0870. Found m/z 265.0877.

(4ha)⁵

keto:enol=45:55; IR (neat): 2940, 1744, 1715, 1647, 1617 cm^{-1} ; ^1H NMR (300 MHz): $\delta = 0.94$ (t, $J = 7.2$ Hz, 1.65H), 1.04 (t, $J = 7.2$ Hz, 1.35H), 1.50–2.00 (m, 3H), 2.04–2.62 (m, 3H), 3.38 (dt, $J = 11.7, 3.7$ Hz, 0.45H), 3.67 (d, $J = 12.6$ Hz, 0.45H), 3.86–3.93 (m, 0.55H), 3.93–4.08 (m, 2H), 7.12–7.34 (m, 5H), 12.57 (s, 0.55H); ^{13}C NMR (150 MHz): $\delta = 13.8, 13.9, 17.2, 25.4, 29.1, 31.6, 33.0, 38.6, 41.1, 47.6, 60.0, 60.7, 63.7, 100.0, 125.6, 126.98, 127.01, 127.5, 127.9, 128.6, 142.2, 146.4, 168.7, 172.4, 173.6, 205.3$; HRMS (EI⁺): Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$, M^+ 246.1256. Found m/z 246.1253.

⁵ Bunce, R. A.; Harris, C. R. *J. Org. Chem.* **1992**, *57*, 6981.

Asymmetric procedure: To an oven-dried, N₂-purged flask was added [RhCl(C₂H₄)₂]₂ (3.9 mg, 10 μmol, 10 mol% of Rh), (*R*)-H₈-BINAP (12.6 mg, 20 μmol, 10 mol%), KOH (5.48 mg, 98 μmol, 0.5 equiv), and a solution of *B*-Ph-9BBN (**2a**, 77.8 mg, 0.39 mmol, 2.0 equiv) in toluene (1.0 mL). The resulting reaction mixture was stirred for 30 min at 70 °C, and then a solution of **1g** (30.5 mg, 0.2 mmol) in toluene (1.0 mL) was added. After stirring for 12 h at 70 °C, the reaction was quenched with water (5~10 mL). The aqueous layer was extracted with ethyl acetate (15 mL x 5). The combined extracts were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (dichloromethane). The second chromatography (hexane:ethyl acetate=3:1) was carried out to remove small amounts of impurities, leading to the product **3ga** (30.2 mg, 0.13 mmol, 66%, 95% ee).

3ga: The ee was determined on a Daicel Chiralcel OD-H column with hexane:isopropanol = 9:1, flow rate = 0.6 mL/min, λ = 220 nm. Retention times: 13.0 min, 14.6 min.

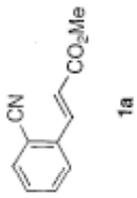
3gb: The ee was determined on a Daicel Chiralcel AS-H column with hexane:isopropanol = 9:1, flow rate = 0.6 mL/min, λ = 220 nm. Retention times: 15.8 min, 18.6 min.

3gc: The ee was determined on a Daicel Chiralcel OD-H column with hexane:isopropanol = 9:1, flow rate = 0.6 mL/min, λ = 220 nm. Retention times: 14.2 min, 15.5 min.

(6) To an oven-dried, N₂-purged flask was added a solution of **3ga** (49.7 mg, 0.22 mmol) in DMF (2 mL) and NaH (9.3 mg, 0.39 mmol, 1.8 equiv) at 0 °C. The resulting reaction mixture was stirred for 50 min at 0 °C, and then phenyl isocyanate (36.0 mg, 0.3 mmol, 1.4 equiv) was added at 0 °C. After stirring for 1 h at room temperature, the reaction was quenched with water (5~10 mL). The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (dichloromethane) to give the product **6** (52.2 mg, 0.17 mmol, 80%): IR (KBr): 3200, 1721, 1650, 1418 cm⁻¹; ¹H NMR (600 MHz): δ = 1.92–2.00 (m, 1H), 2.38–2.44 (m, 1H), 2.46–2.55 (m, 1H), 2.58–2.66 (m, 1H), 4.24–4.29 (m, 1H), 7.14–7.21 (m, 5H), 7.25–7.29 (m, 2H), 7.35–7.39 (m, 1H), 7.42–7.46 (m, 2H), 10.13 (br s, 1H); ¹³C NMR (150 MHz): δ = 30.5, 32.0, 46.6, 114.3, 126.5, 126.9, 128.4, 128.5, 128.6, 129.1, 134.9, 143.8, 153.3, 154.9, 160.8; HRMS (EI⁺): Calcd for C₁₉H₁₆N₂O₂, M⁺ 304.1212. Found m/z 304.1212.

(7) To an oven-dried, N₂-purged flask was added a solution of **3ea** (49.0 mg, 0.175 mmol) in benzene and DDQ (60.2 mg, 0.265 mmol, 1.5 equiv). The resulting reaction mixture was stirred

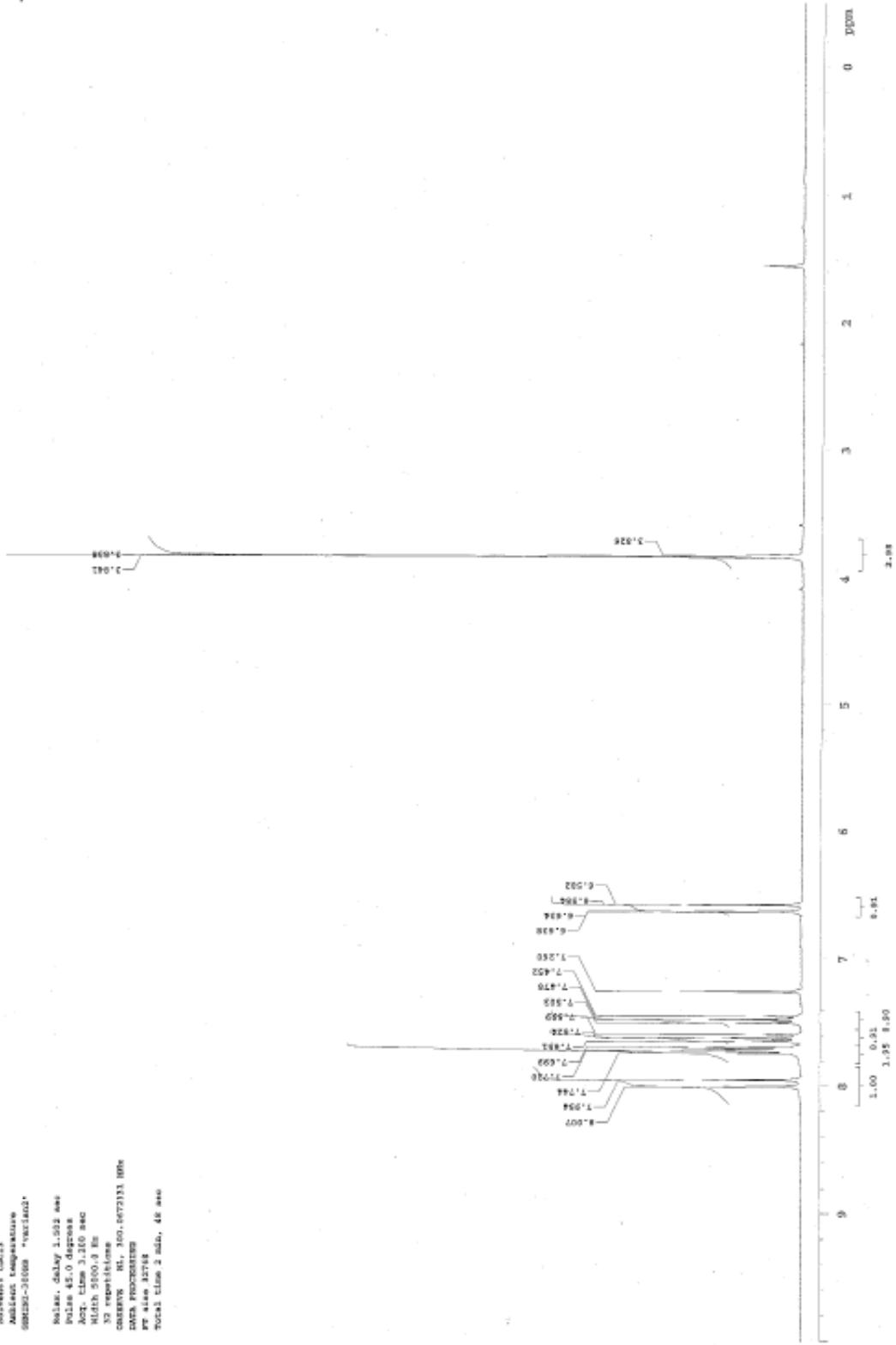
for 2 h at 80 °C. After the reaction mixture was cooled, the solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (dichloromethane) to give the product **7** (29.6 mg, 0.11 mmol, 61%): IR (KBr): 3457, 3370, 1715, 1622 cm^{-1} ; ^1H NMR (400 MHz): δ = 3.40 (s, 3H), 4.57 (br s, 2H), 7.08 (s, 1H), 7.10–7.17 (m, 1H), 7.29–7.49 (m, 7H), 7.61 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz): δ = 51.7, 109.9, 120.8, 123.0, 125.7, 126.4, 127.3, 127.4, 127.6, 127.8, 129.7, 135.6, 139.2, 141.4, 142.2, 169.6; HRMS (EI^+): Calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_2$, M^+ 277.1103. Found m/z 277.1104.

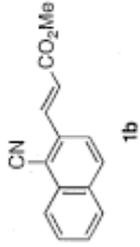


STANDARD IN ORBITER

Pulse sequence: adyul
 Solvent: CDCl3
 Analysis temperature
 QM120-21008 "variable"

Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.200 sec
 Width 5000.0 Hz
 32 repetitions
 CHANNEL F1, 300.007313 MHz
 LOCK PROCEDURE
 PR also 32718
 Total time 2 min, 48 sec

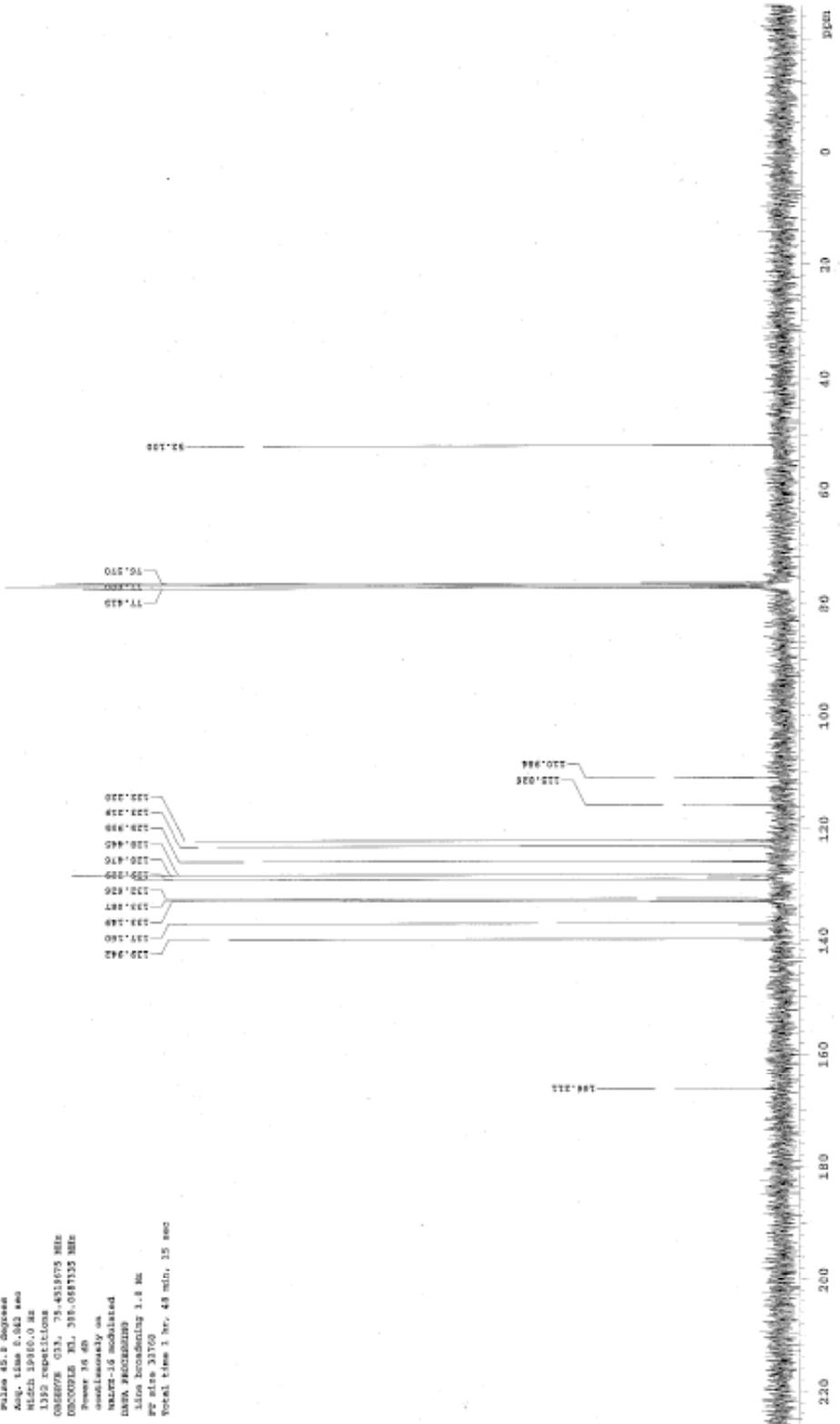


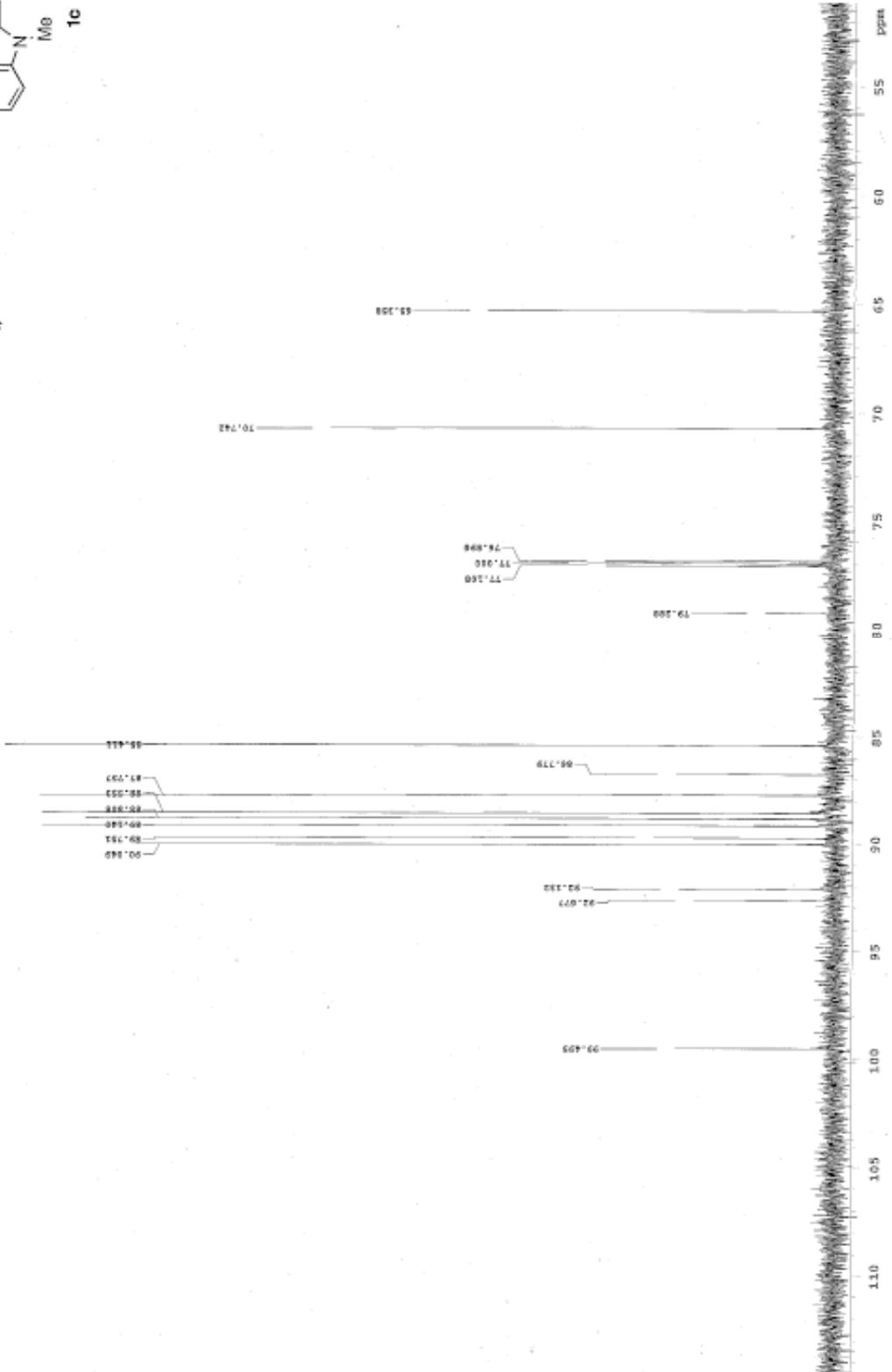
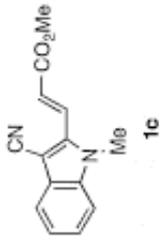


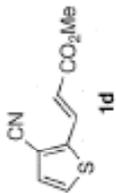
11C 0088978

Pulse sequence: zgpg30
 Solvent: CDCl3
 Ambient temperature
 ORBITAL-300MR "Varian"

Pulse delay: 1.100 sec
 Relax: 45.0 seconds
 Acq. time: 0.042 sec
 MHz: 101.620 MHz
 1382 repetitions
 ORBITAL 033, 75-4518675 MHz
 DECOUPLE CH, 310.0481325 MHz
 Power: 35 dB
 continuously on
 WATER-35 solvated
 DATA ACQUISITION
 Date_Recording: 1.1.14
 File: 11C0088978
 Total time: 1 hr. 43 min. 35 sec



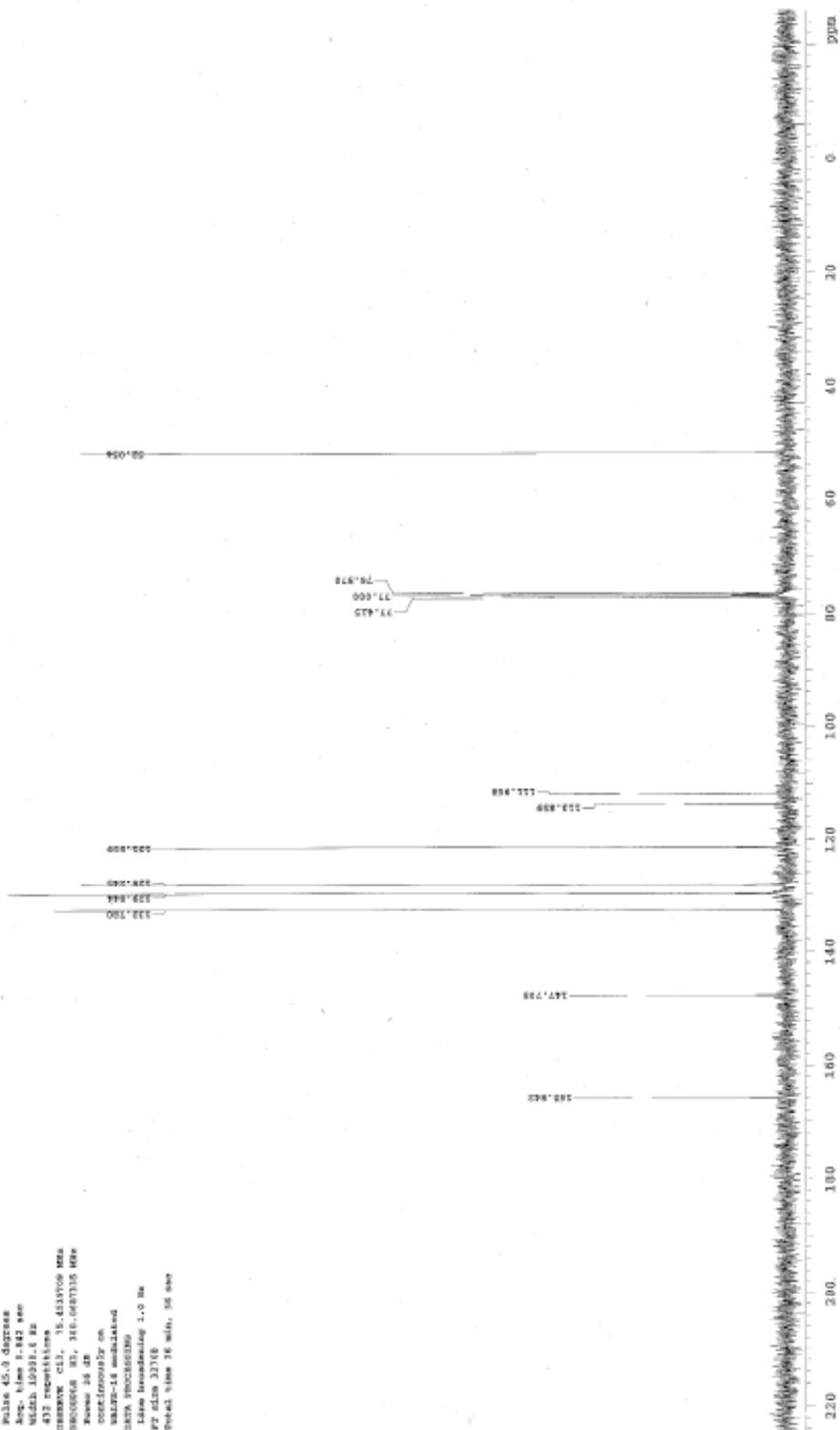


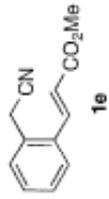


13C NMR

Pulse Program: zgpg30
 Solvent: CDCl3
 Acq. Temp: 300.2 K
 NS: 1024
 DS: 4
 SWH: 15000.0 Hz
 F2: 125.761 MHz
 AQ: 1.00000000 sec
 RG: 327.680 Hz

NUC1: 13C
 P1: 12.00 nsec
 PL1: 0.00 dB
 PC: 1.00 nsec
 PL: 0.00 dB
 PD: 1.00 nsec
 PL: 0.00 dB
 PE: 1.00 nsec
 PL: 0.00 dB
 PF: 1.00 nsec
 PL: 0.00 dB
 PG: 1.00 nsec
 PL: 0.00 dB
 PH: 1.00 nsec
 PL: 0.00 dB
 PI: 1.00 nsec
 PL: 0.00 dB
 PJ: 1.00 nsec
 PL: 0.00 dB
 PK: 1.00 nsec
 PL: 0.00 dB
 Total time 36.000 sec

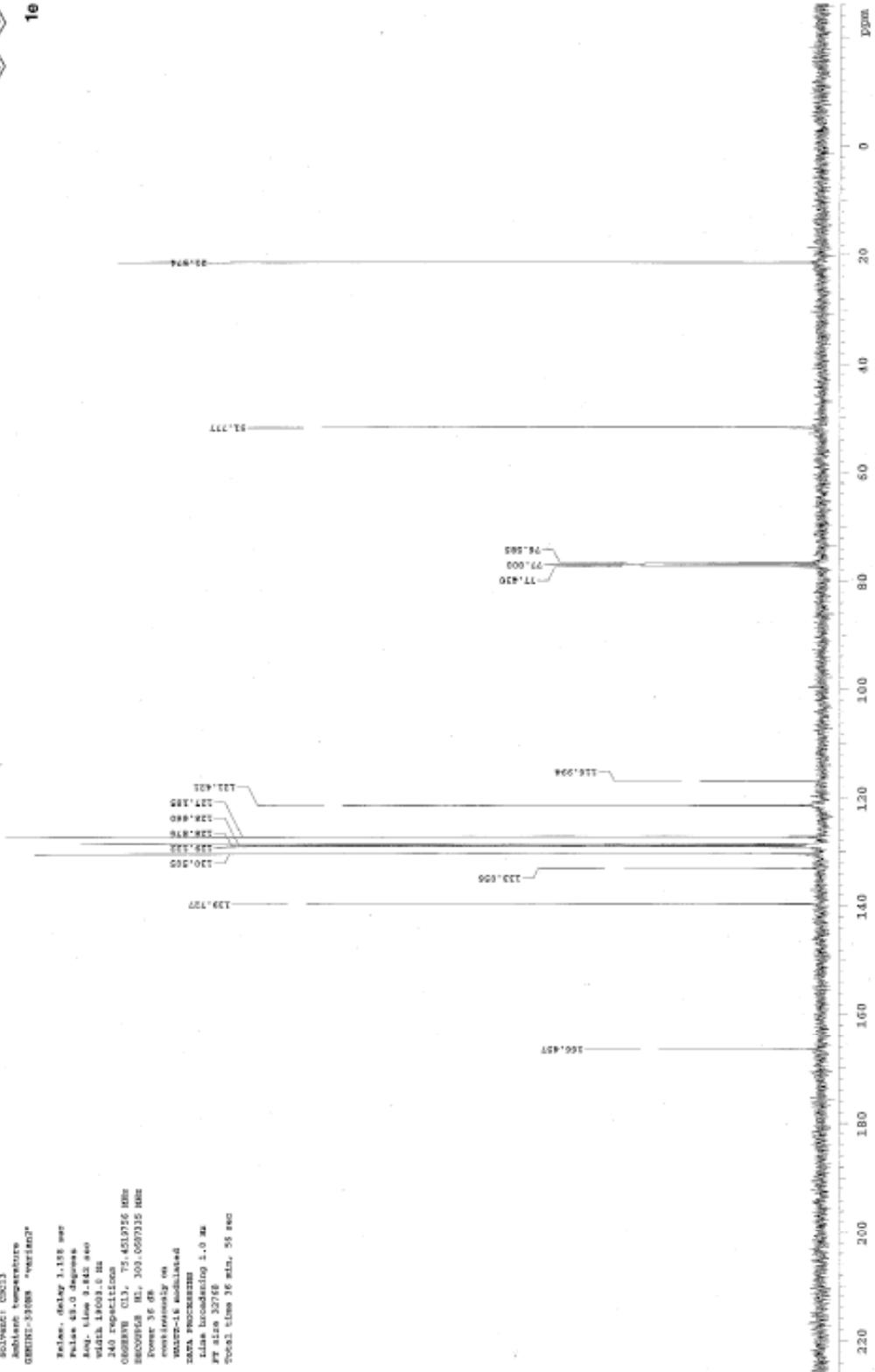


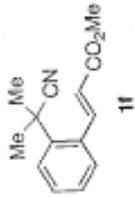


13C NMR

Pulse Sequence: zgpg30
 Solvent: CDCl3
 Lock: none
 GBLOCKS: 30000 "variance"

Relax. delay: 1.100 sec
 Pulse: 6.0000000000000000
 Pulse width: 12.0000000000000000
 Width: 14.0000000000000000
 340 repetitions
 0.0000000000000000000000000000000000
 0.0000000000000000000000000000000000
 Power: 35.0000000000000000000000000000000000
 continuously on
 WALTZ-16 modulation
 DATA PROCESSING
 time broadening: 1.0 Hz
 FT size: 32768
 total time: 36 min, 55 sec

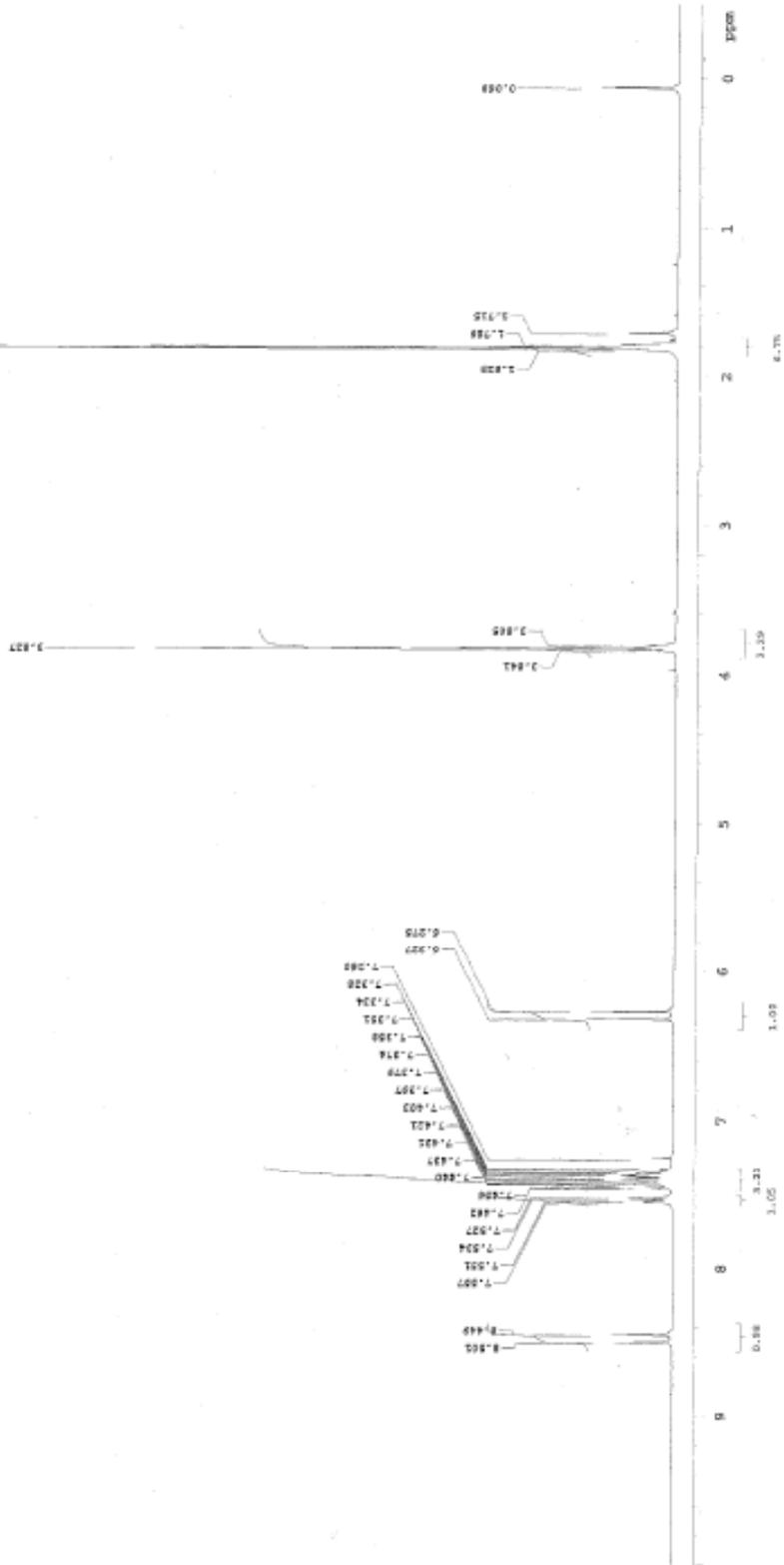


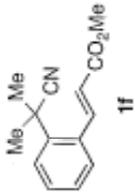


STANDARD IN OBSERVE

Nucleus acquisition: 42jw4
 SOLVENT: CDCl3
 nucleus temperature: 300.2
 CDCl3-300MHz "standard"

Relax. delay: 1.000 sec
 Pulse: 45.0 degrees
 Acq. time: 3.280 sec
 MHz: 500.130 MHz
 DA experiment: zgpg30
 CDCl3-300MHz-99.643320 MHz
 JAWA: 2000000000
 FT: NMR 327000
 Total time: 5 min, 37 sec

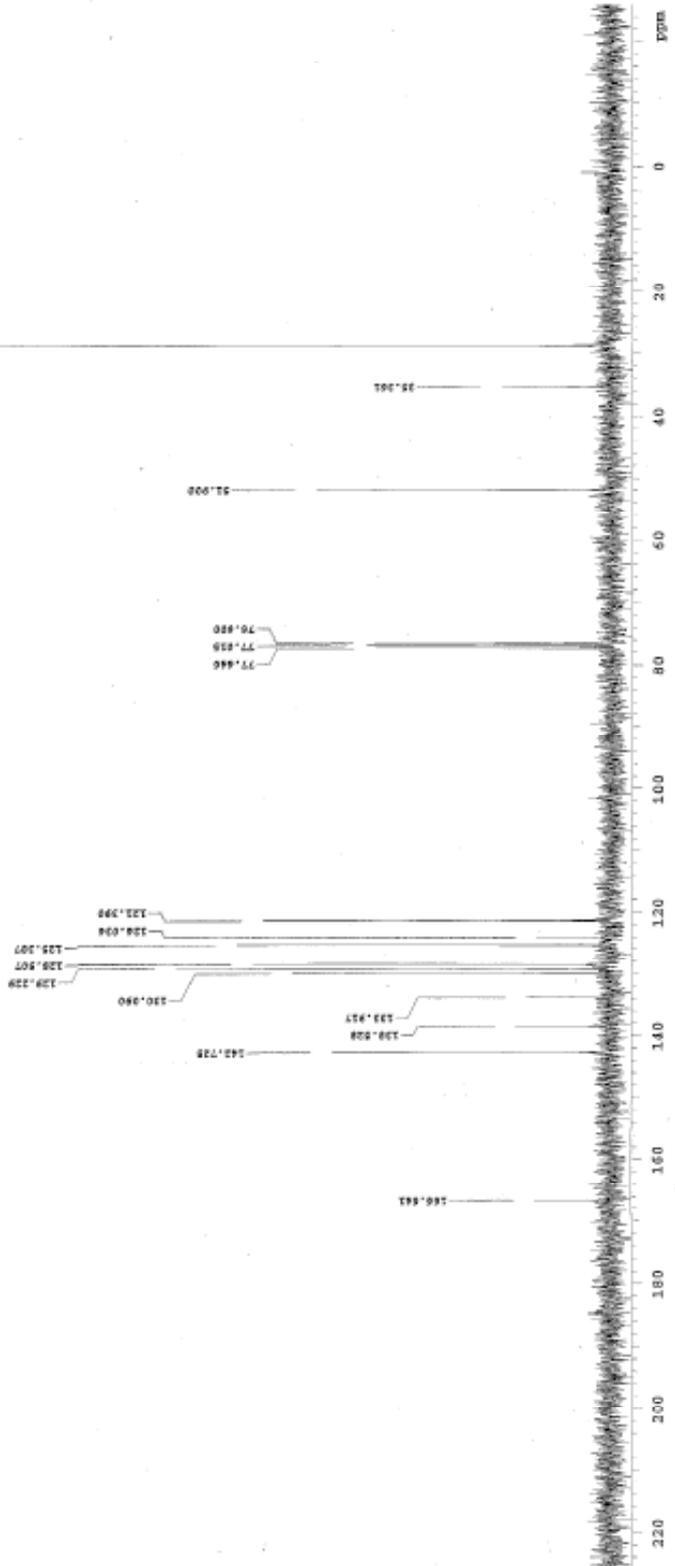


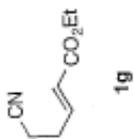


13C- OBSERVE

Pulse Sequence: zgpg30
 Solvent: CDCl3
 Ambient Temperature
 CMTHT-101M "variable"

Relax. delay 1.100 sec
 Pulse 45.0 degrees
 Acq. time 0.342 sec
 SFO25 125460.9 MHz
 160 repetitions
 OMS9098 C13, 75-4519475 MHz
 RECORDS EL 310.0487335 MHz
 Power 35 dB
 continuously on
 WATER-16 multichannel
 DATA PROCESSING
 FILE PROCESSING 1.0 Hz
 PR size 32768
 Total time 36 min, 55 sec





STANDARD 3H C080706

Pulse Sequence: zgpg30

Solvent: CDCl3

Acquisition Temperature:

QNP1H1-300MHz "gprsdm3"

Pulse: Delay 2.000 sec

Pulse: 45.0 degrees

Acq. time: 3.200 min

File: 300M10101

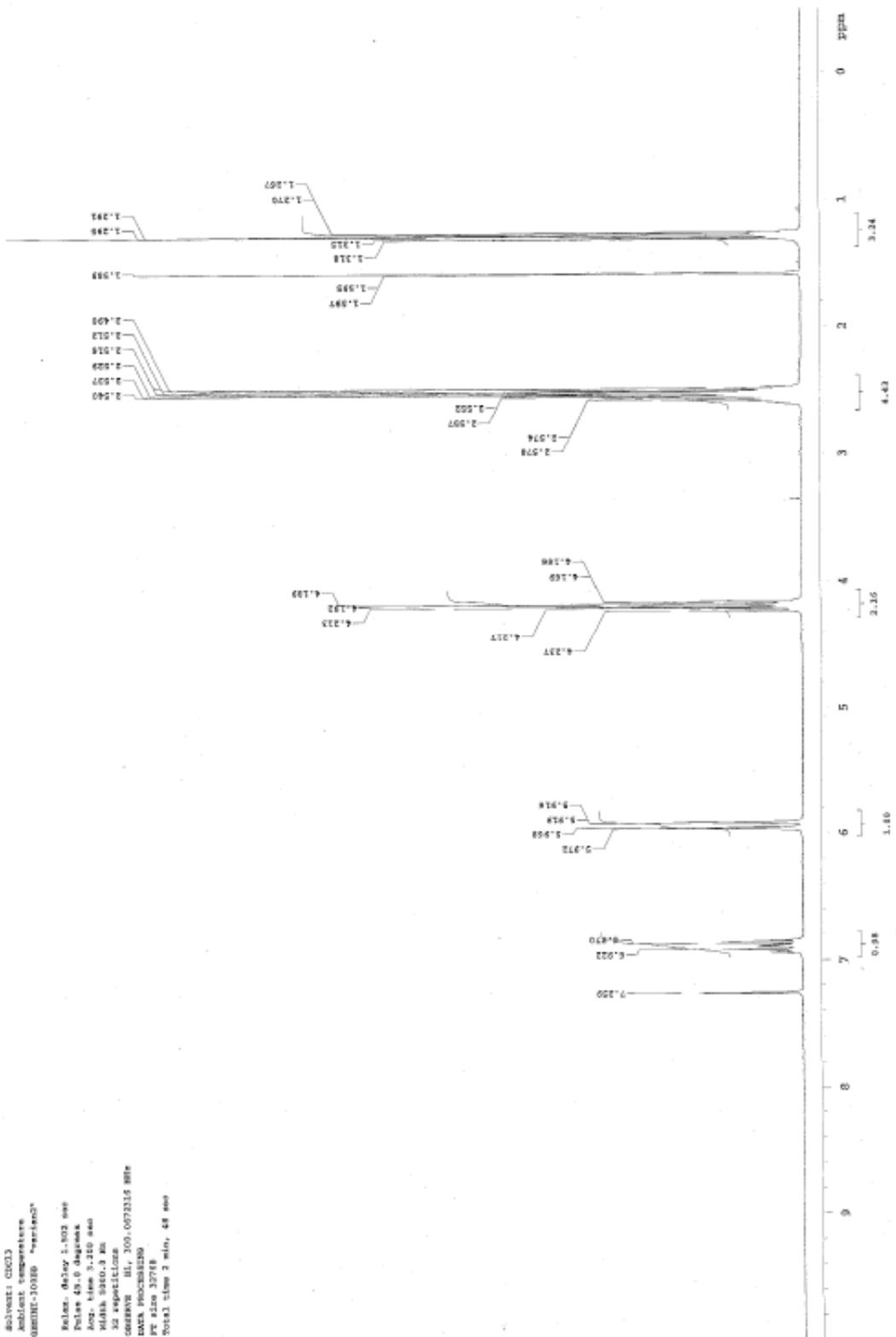
300M1010101

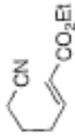
CONV: 101.0073315 MHz

DATA PROCESSING:

PC size: 32768

Total time: 3 min, 48 sec



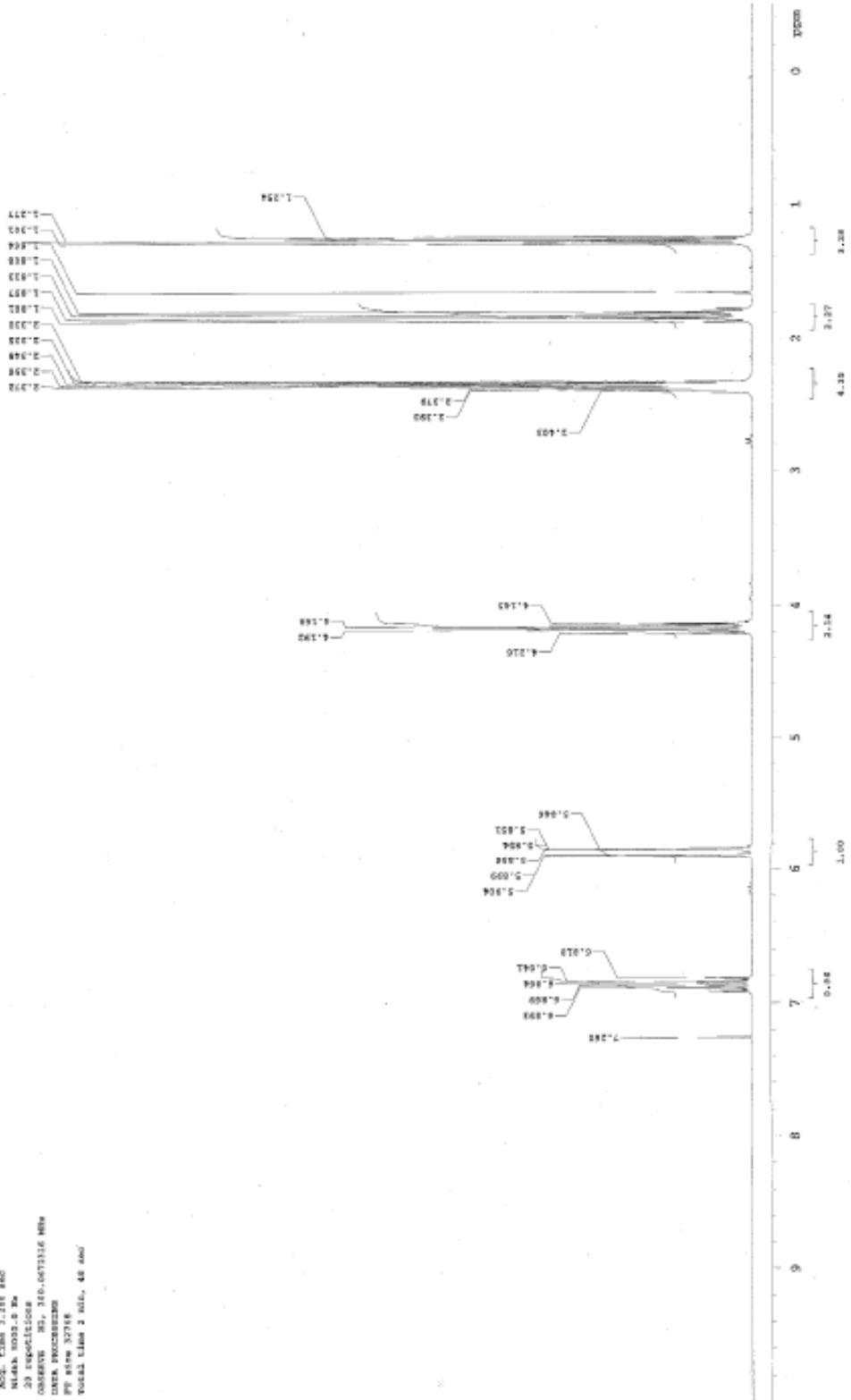


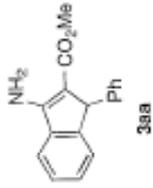
1h

STANDARD 3H UNRESOLVED

Pulse Sequence: zgpg30
 Solvent: CDCl3
 Ambient Temperature
 ORIGIN: 30000 "acifad3"

Acq. On: 04/09 11:52:00
 Pulse: 40.0 degrees
 Acq. Time: 3.316 sec
 Nuclei: 13C
 20 REPETITIONS
 OBSERVE: 90, 160.007316 MHz
 DATA PROCESSING:
 PP: 85W 32716
 Total time: 3 min, 48 sec

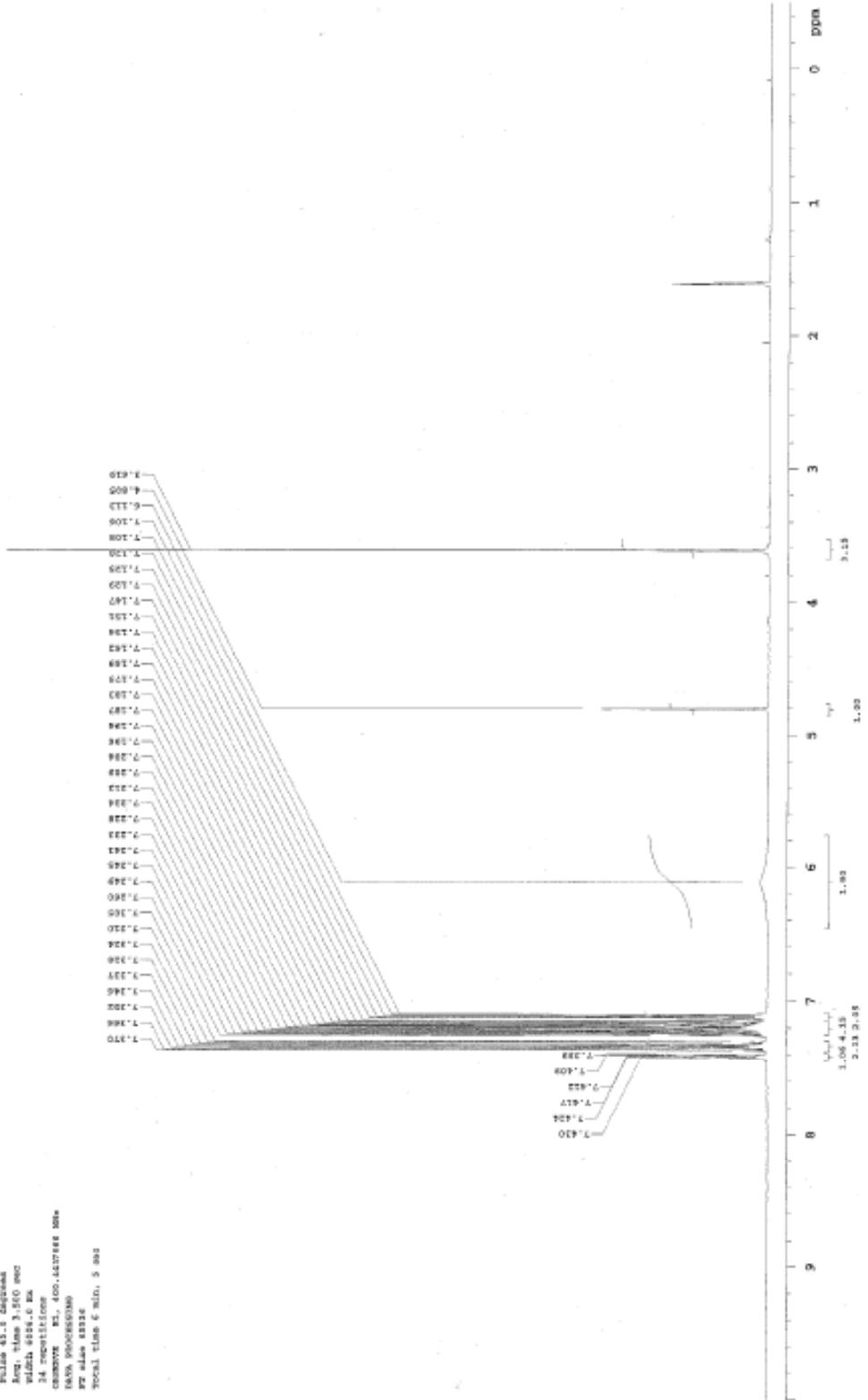


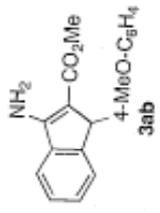


STANDARD IS OBSERVE

Pulse Program: eZsol
 nucleus: C13C1
 ABLDCT TEMPERATURE
 INVERTY=52288 "vvar1an"

Relax. delay 1.500 sec
 pulse 45.5 degrees
 Acq. time 3.500 sec
 width 4524.6 Hz
 34 repetitions
 OBSERVE W1, 400.645788 MHz
 INVX 9000850190
 PR ALIA 43324
 TOTAL time 6 min, 5 sec

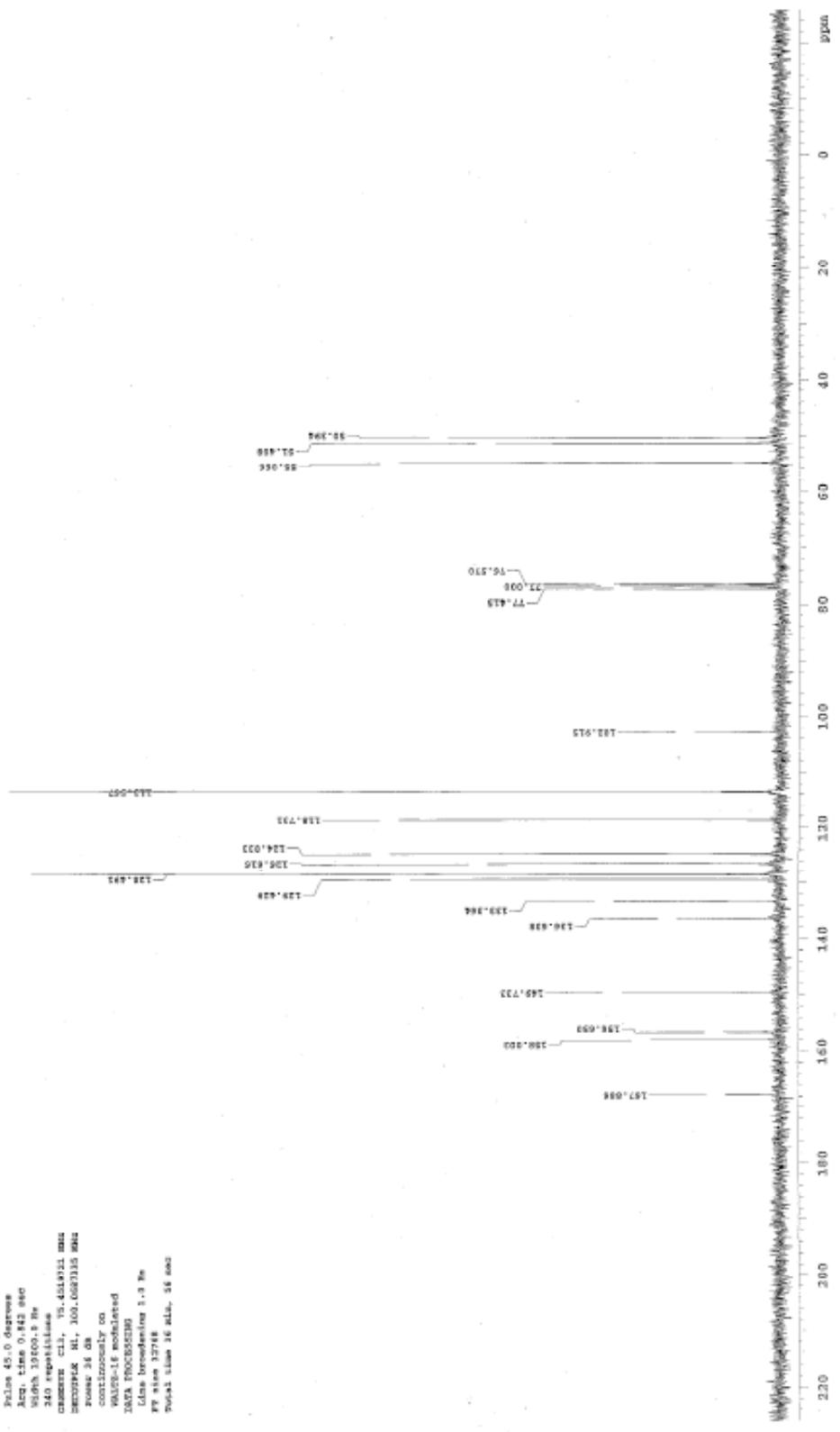


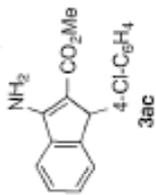


330 CHANNELS

Pulse sequence: zgpg30
 Solvent: CDCl₃
 Ambient temperature
 QMPCX-30100 "rec1and"

Relax. delay 1.120 sec
 Pulse 45.0 degrees
 Acq. time 0.842 sec
 95.0MHz 32000.0 Hz
 340 repetitions
 Channel: c13, 75.4614912 MHz
 Reference: H₂O, 100.6271125 MHz
 F2: none 31.00
 Acquisition on
 13C-13C J-coupling
 120.00000000 Hz
 Line broadening 1.3 Hz
 RF noise 12748
 Total time 30.414, 35 sec





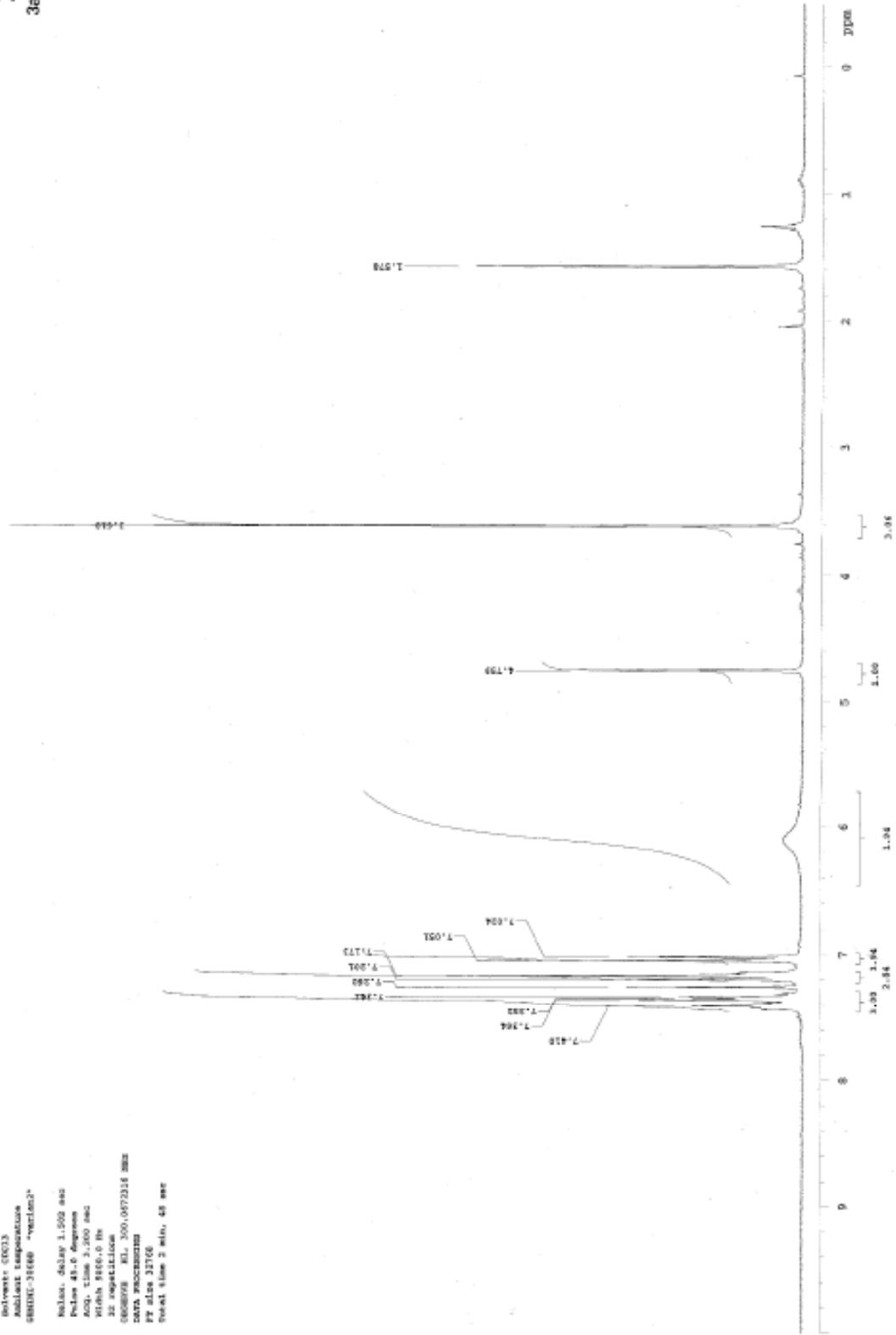
STRONGER IN CONCENTR

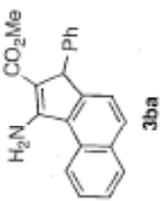
Pulse Sequence: sfgpul

Solvent: DMSO

Acquisition Temperature

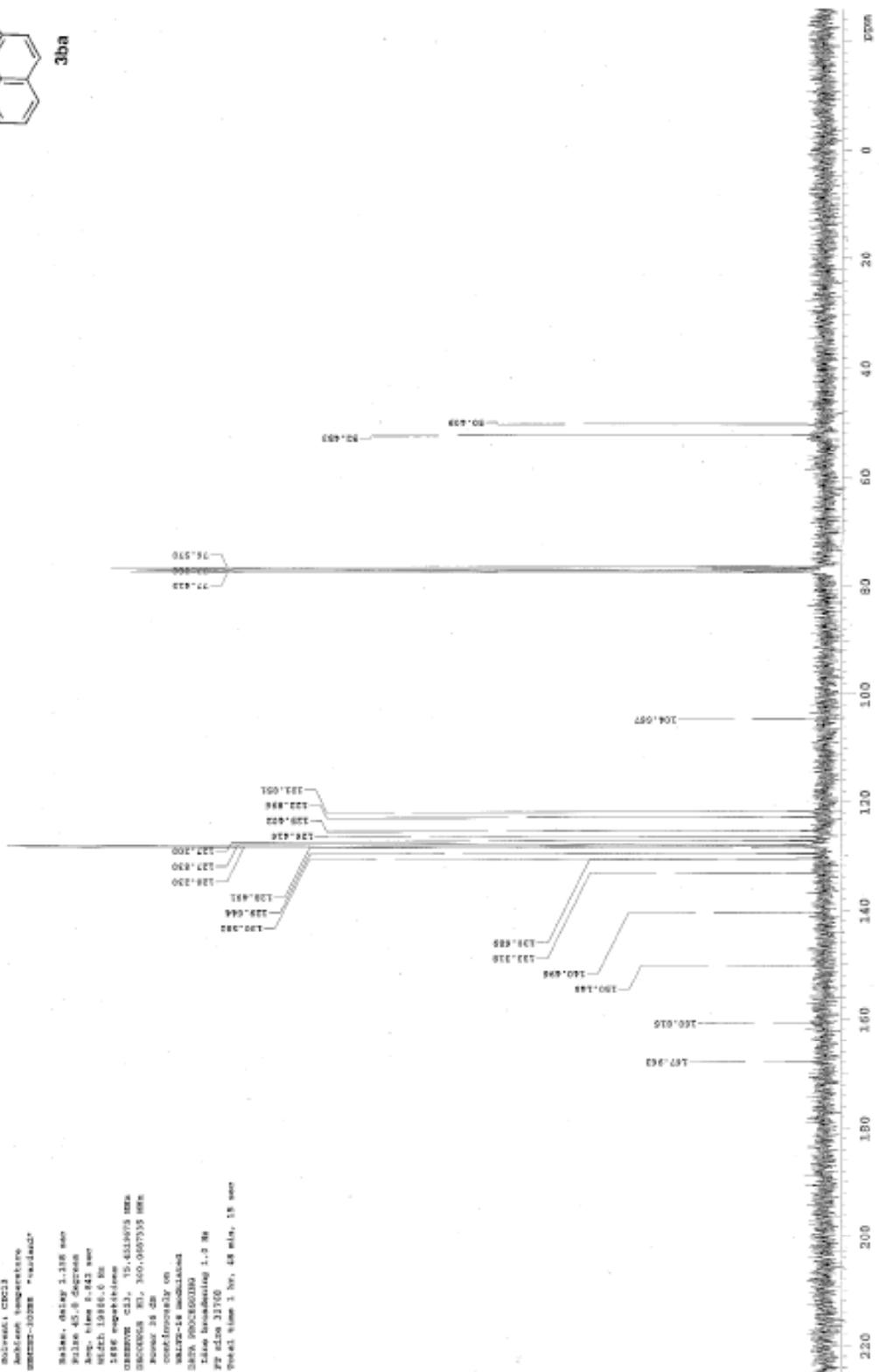
300K (27°C)

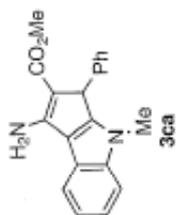




13C QM08090

Pulse Program: zgpg30
 Solvent: CDCl3
 Ambient temperature
 90MHz-302MR "zgpg30"
 Name: 04104 1.118 sec
 File: 45.8 Acquire
 Acq. time: 0.842 sec
 90.425 19986.0 Hz
 1486 exp44-11000
 08090904 03. 15.4318075 hrs
 08090904 03. 300.0007355 MHz
 F2: 90.425
 Processed on
 contiguously on
 WALTZ-16 modules
 DATA ACQUISITION
 Line broadening 1.0 Hz
 FT size 13100
 Total time 1.00, 48 min, 15 sec





STANDARD 14 CONTINUED

Pulse Program: e2pr1

Solvent: CDCl3

Acquire Temperature:

Method: zgpg30 "gpg30"

Relax. delay: 1.500 sec

Pulse: 65.0 degrees

Acq. time: 3.350 sec

Stack: 626.0 sc

20 repetitions

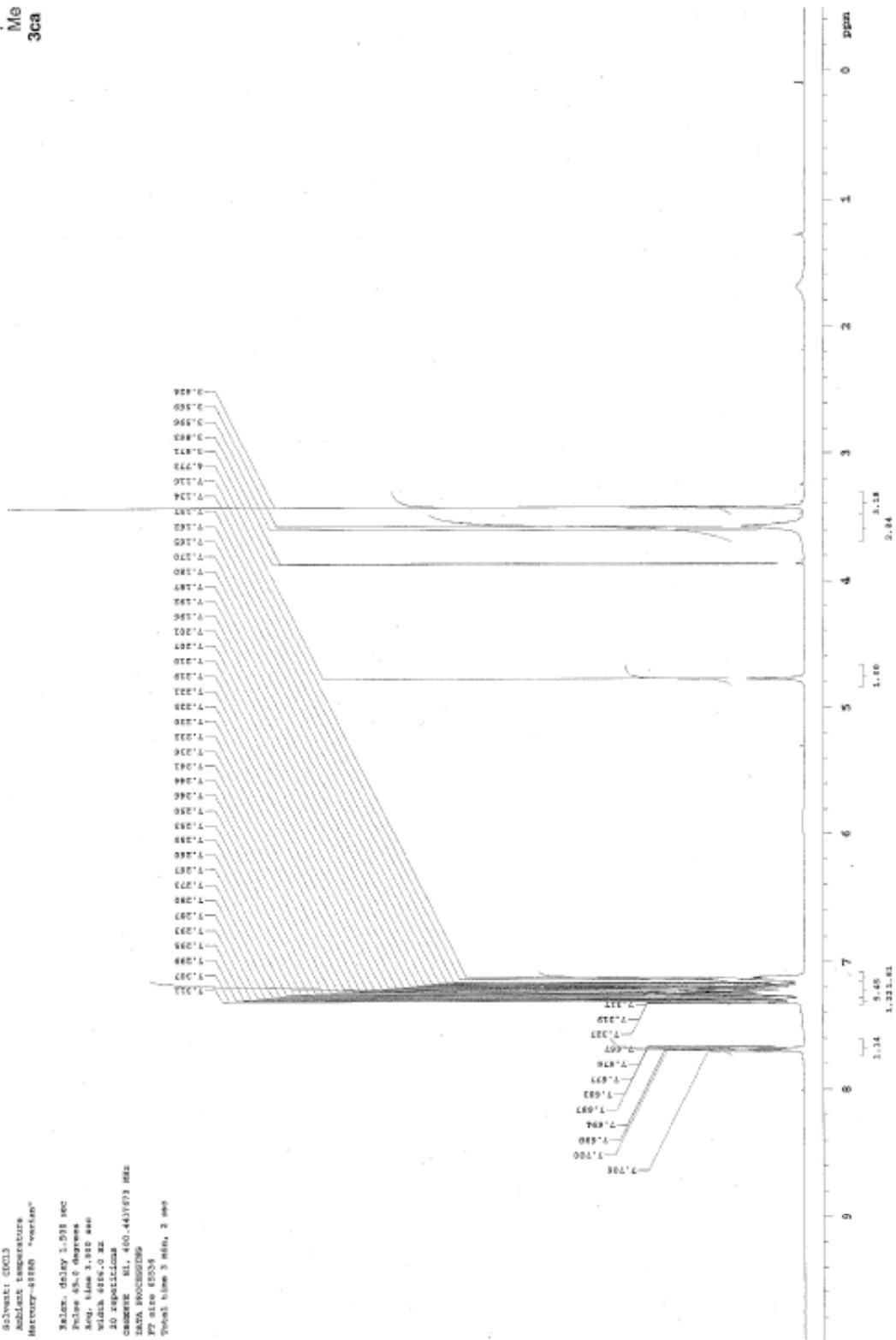
DATE_: 00-443783.MK

TIME: 11:11:00

EXP: 60000000

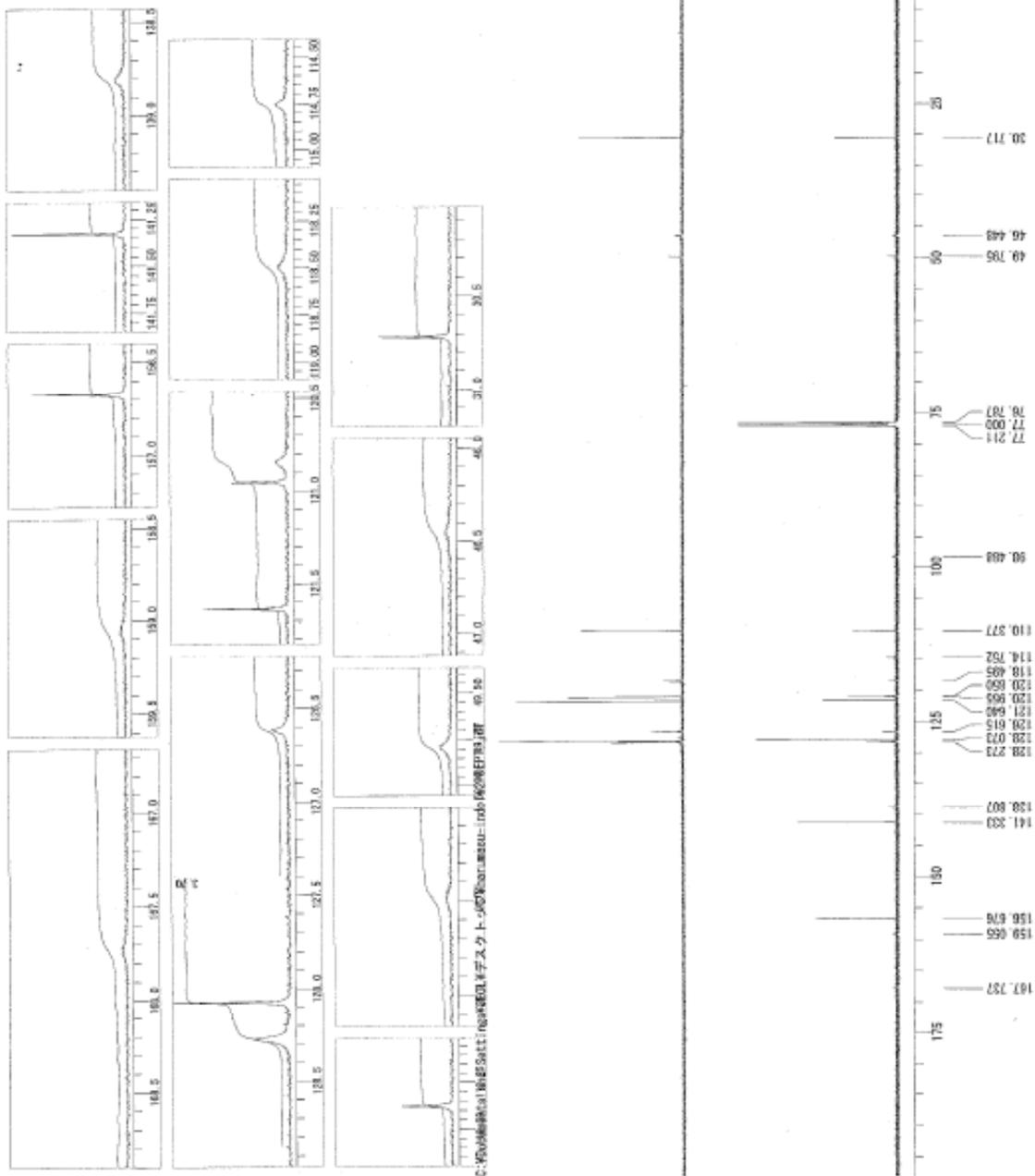
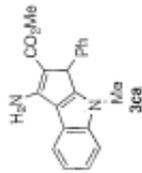
RF: 500.13

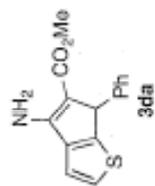
Total time: 3 min, 2 sec



C:\NMR\PMW\FUJ\to\tharumazu-indolico-NMR11_816

QMWT 13-12-2008 09:03:49
 DATIM single_pulse_obs
 EXPNO 130
 PROCNO 130
 F2 150.92 MHz
 CBF IN 1.74 Hz
 POINT 104859
 FREQZ 38332.82 Hz
 AQTIM 1.5729 sec
 PD 7.0000 sec
 SCANS 6000
 SFO 150.916000
 PULPROG zgpg30
 PC 3.75 usppp
 PRG2 0.00 usppp
 PWS 0.00 usppp
 P1 0.00000 msec
 P13 0.00000 msec
 IRMWD 1H
 IRNUC 1H
 RFNUC 1H
 RSET 0
 INVM 0
 GAMMA 22.0 C
 SFO2 150.916000
 SFO3 77.00 ppm
 RBAIN 0.32 Hz
 RUSIL 22.0 C
 PROBE measurement no
 by FUJITA

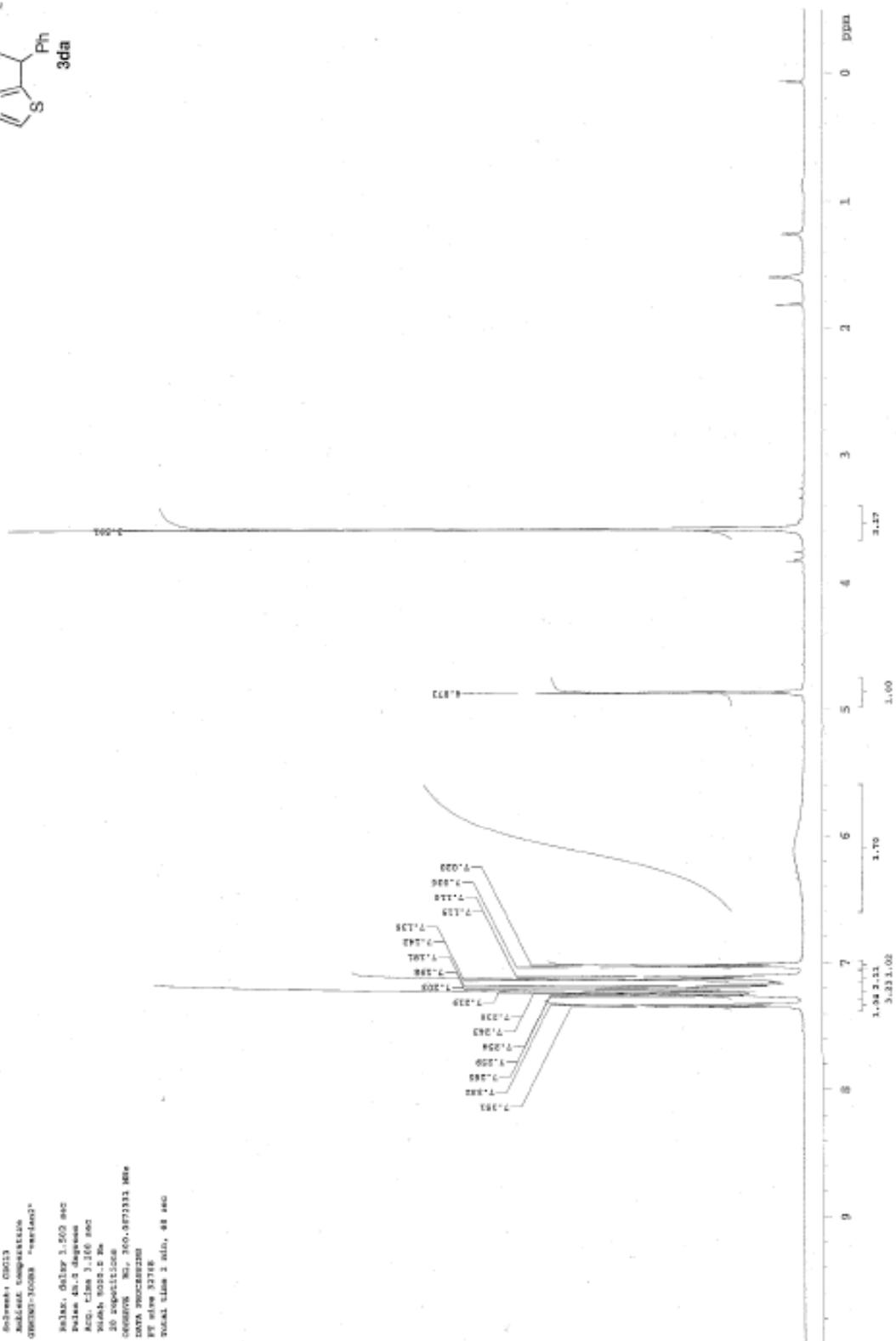


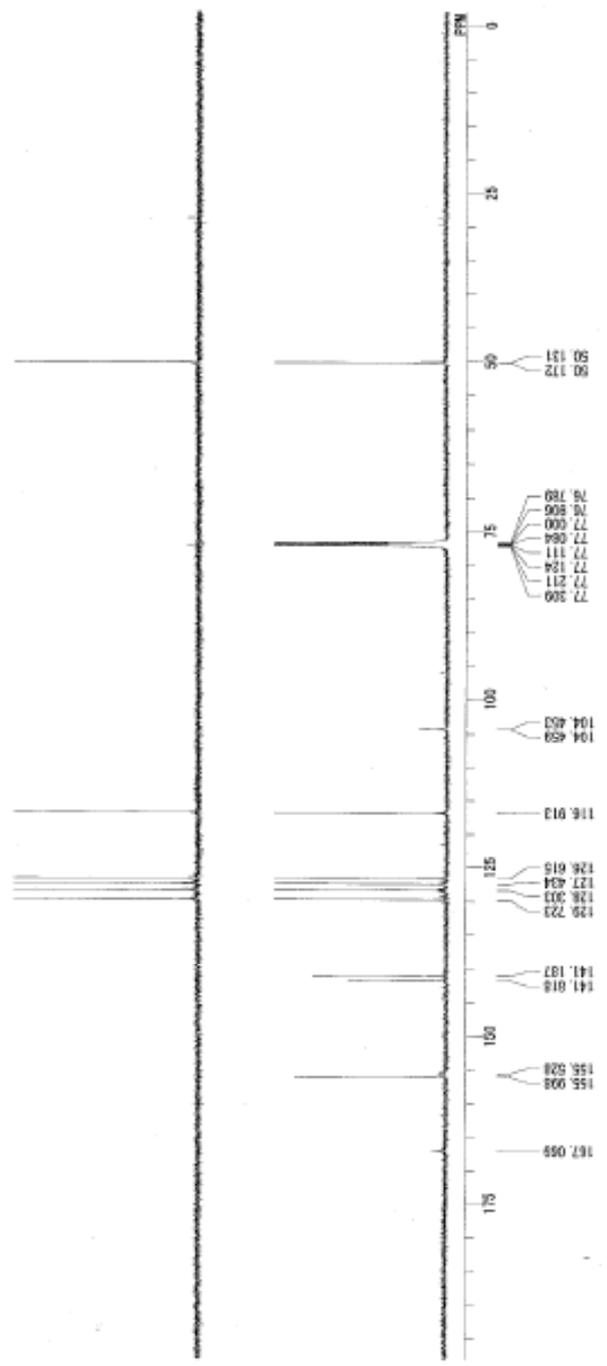
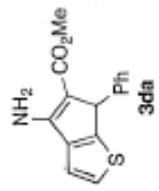
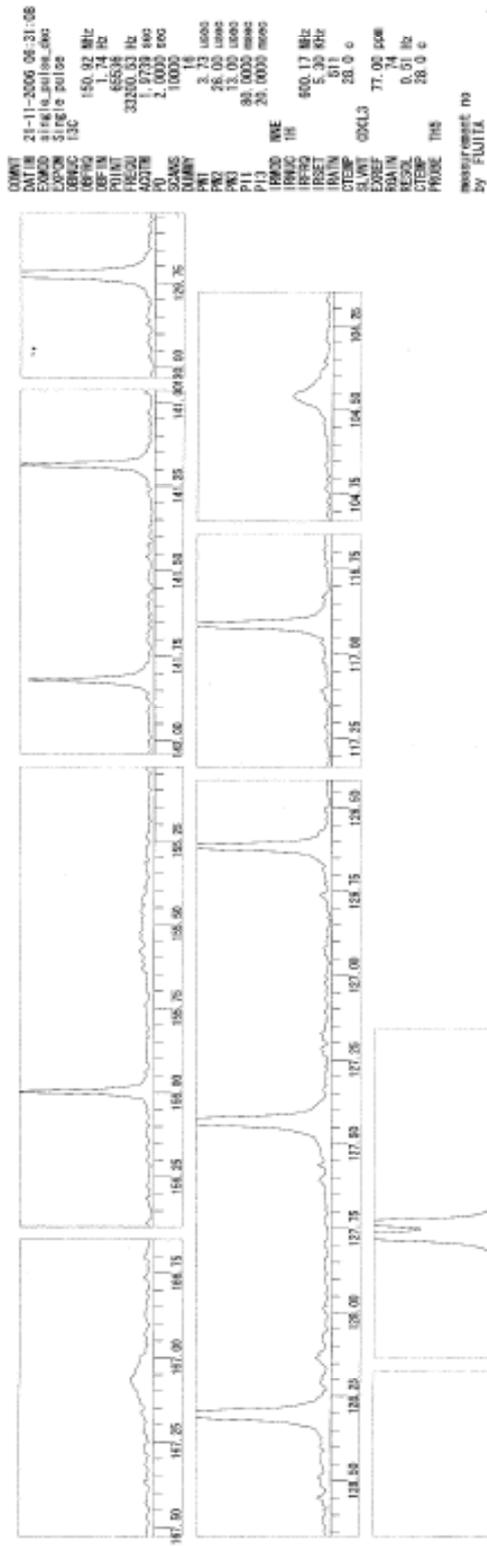


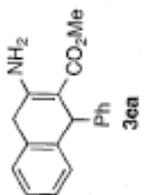
STANDARD IN ORBITER

Pulse Sequence: e1p1
 Solvent: CDCl3
 Address: COMPASS100
 QM0001-30000 "acq1ac2"

Pulse: 9d1p1 1.500 sec
 Relax: 4h.2 depress
 Accq. time: 3.160 sec
 Trans: 9025.2 Hz
 20 repetitions
 CHANNEL: M1, 300.017333 MHz
 DATA PROCESSING:
 FT size 32768
 Total time 3 min, 48 sec



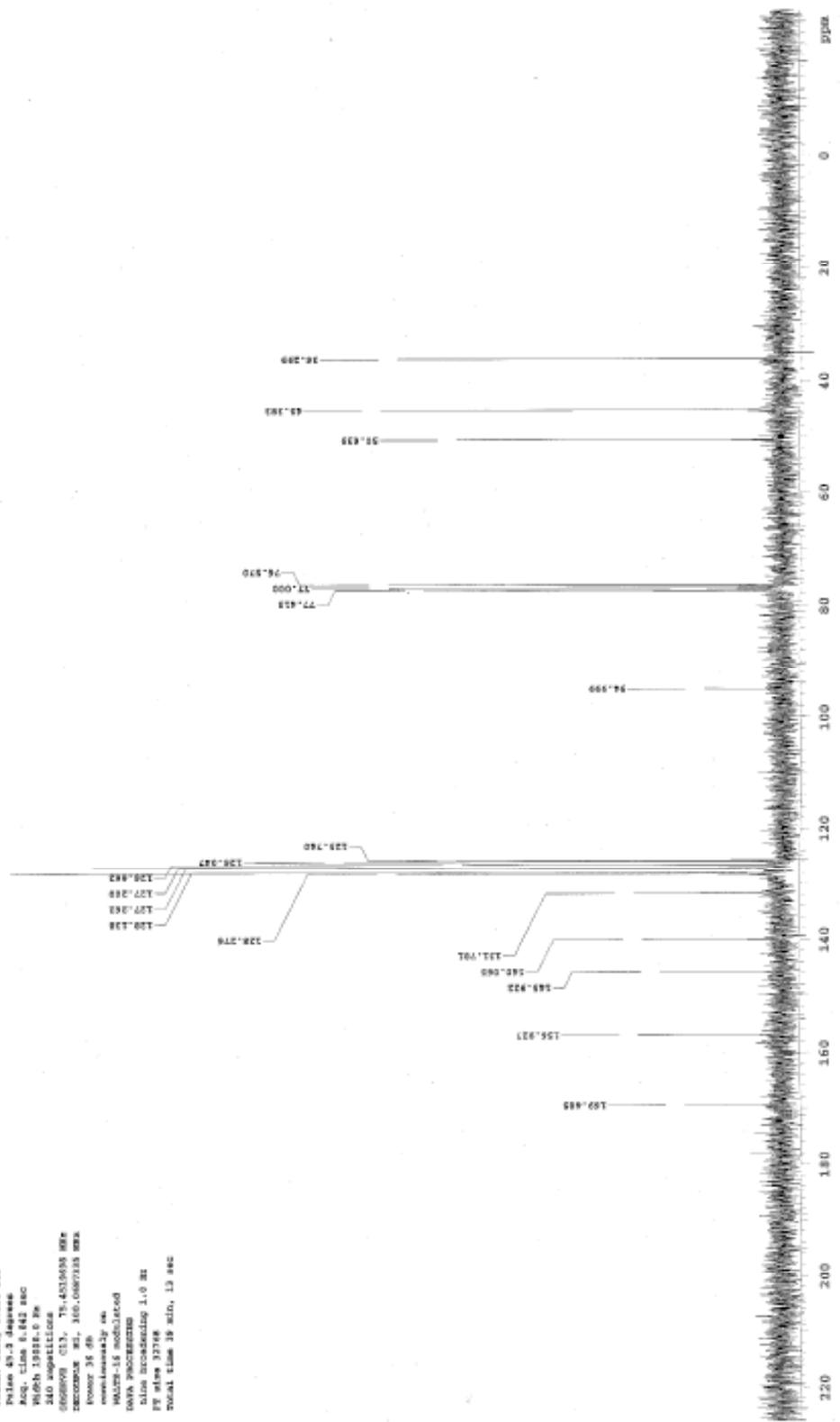


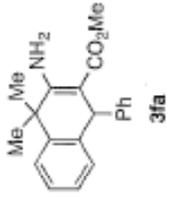


LIC: 000000

Print Sequence: 0000
 Solvent: CHCl3
 Injected Temperature:
 GCINLET-TEMP: "ambient"

INJECT: 04507 1.120 sec
 Pulse: 40.3 degree
 Acq. time: 6.842 sec
 Wavelength: 193.0 nm
 240 repetitions
 G050000 013, 75-451600 MP
 RECORD: 01, 100-0007100.MMA
 Rows: 35 @
 resolution: 24.0
 P0200-15: 000116000
 Data: 0000000000
 File: 0000000000
 FT: 0100 127168
 Total time: 10 min, 13 sec





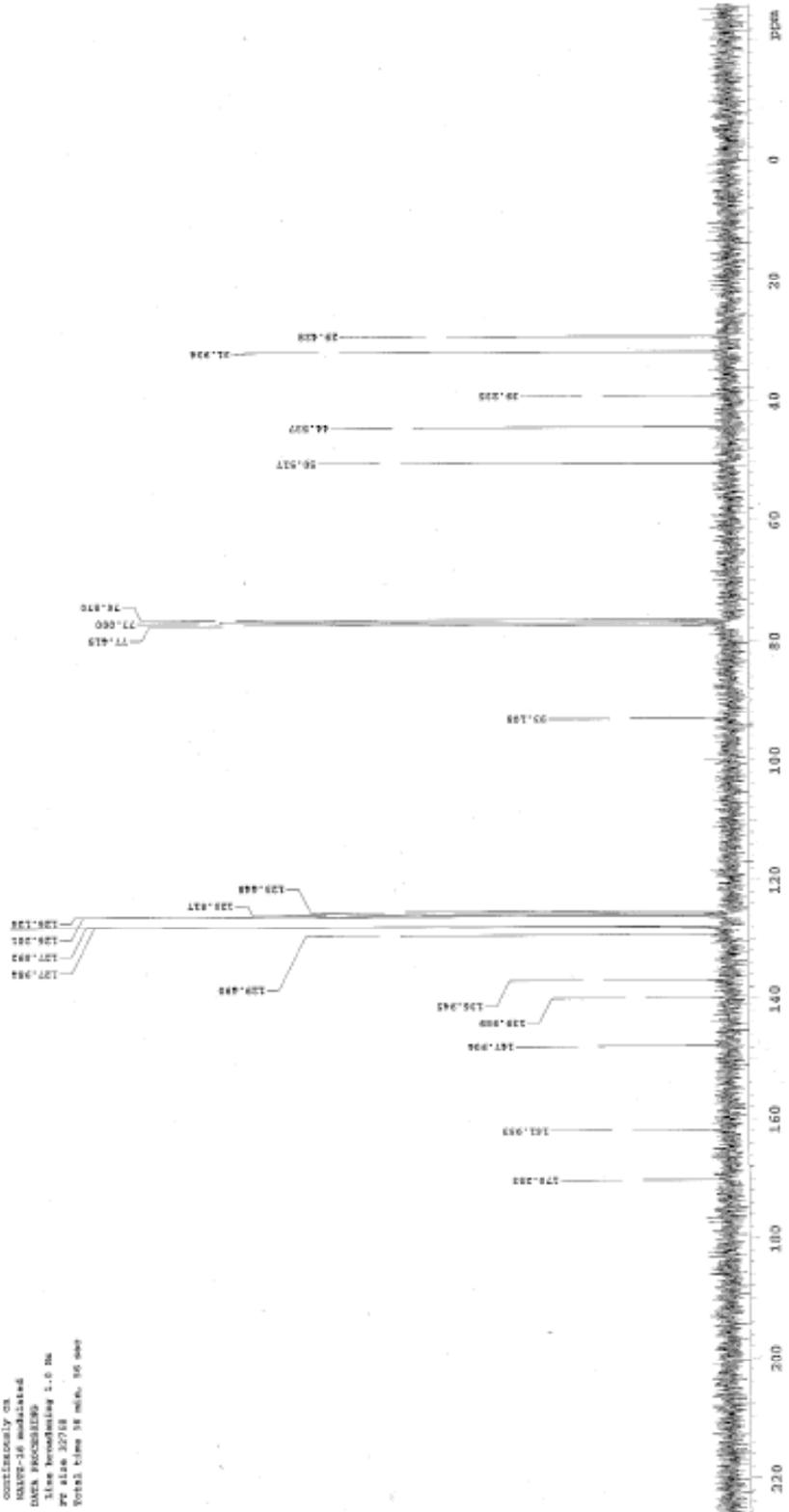
L3C 088809

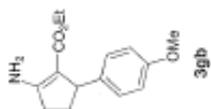
Pulse Program: efgel
 solvent: CDCl3
 solvent temperature: 30.000000
 channel: 3328 "vax1a02"

F1acq: delay 1.100 sec
 Pulse 41.000000
 Pulse 41.000000
 Relax 0.300000 sec
 Relax 0.300000 sec
 High 18100.0 Hz
 574 repetitions

channel: C13, 75.4318075 MHz
 DECOUPLER H1, 399.8487335 MHz
 Power 16 dB

continuously on
 NMR-26 mediated
 DATA PROCESSING
 line broadening 1.0 Hz
 FT size 32710
 Total time 18 min, 16 sec

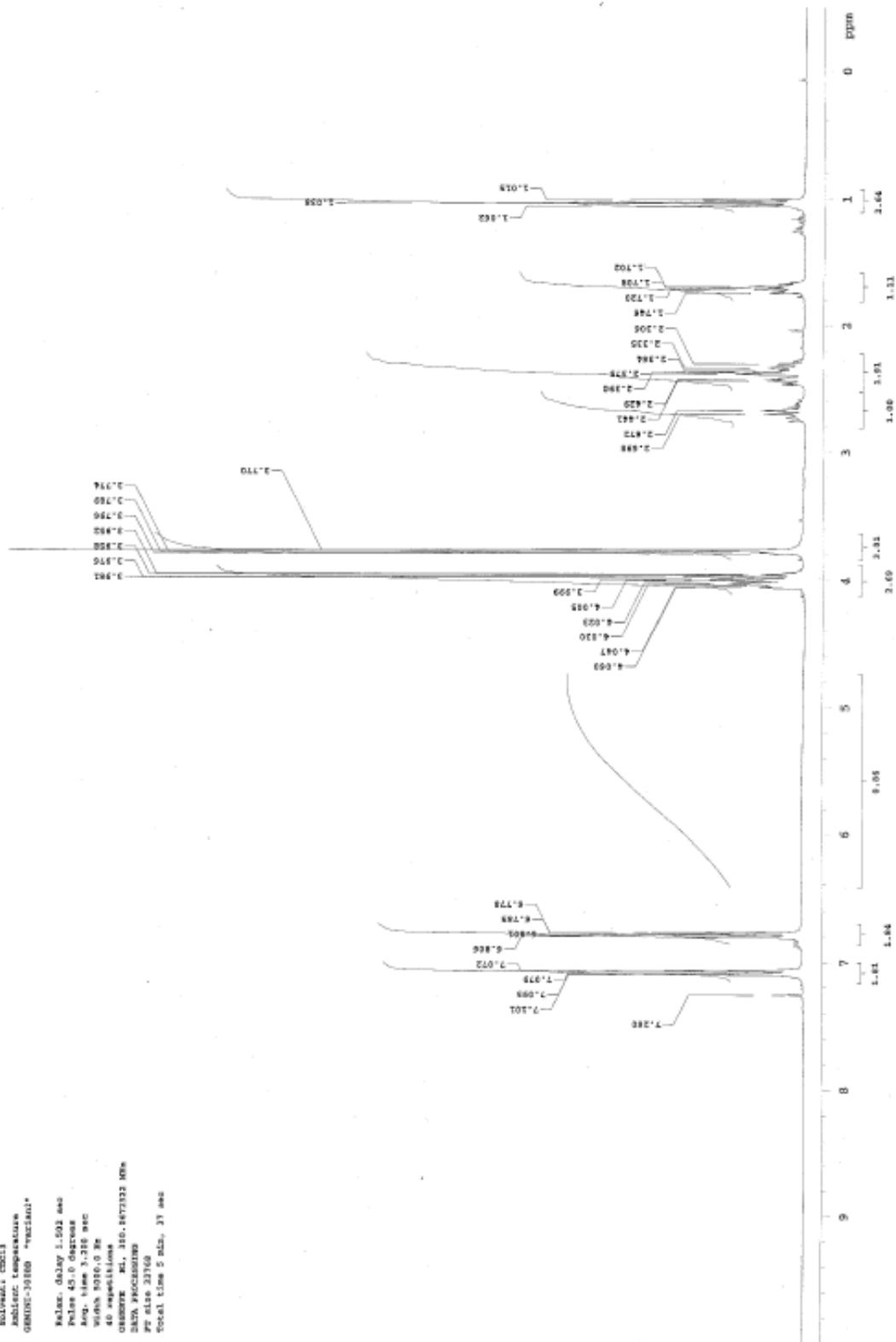


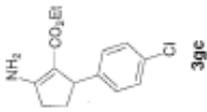


STANDARD IN CHROM/70

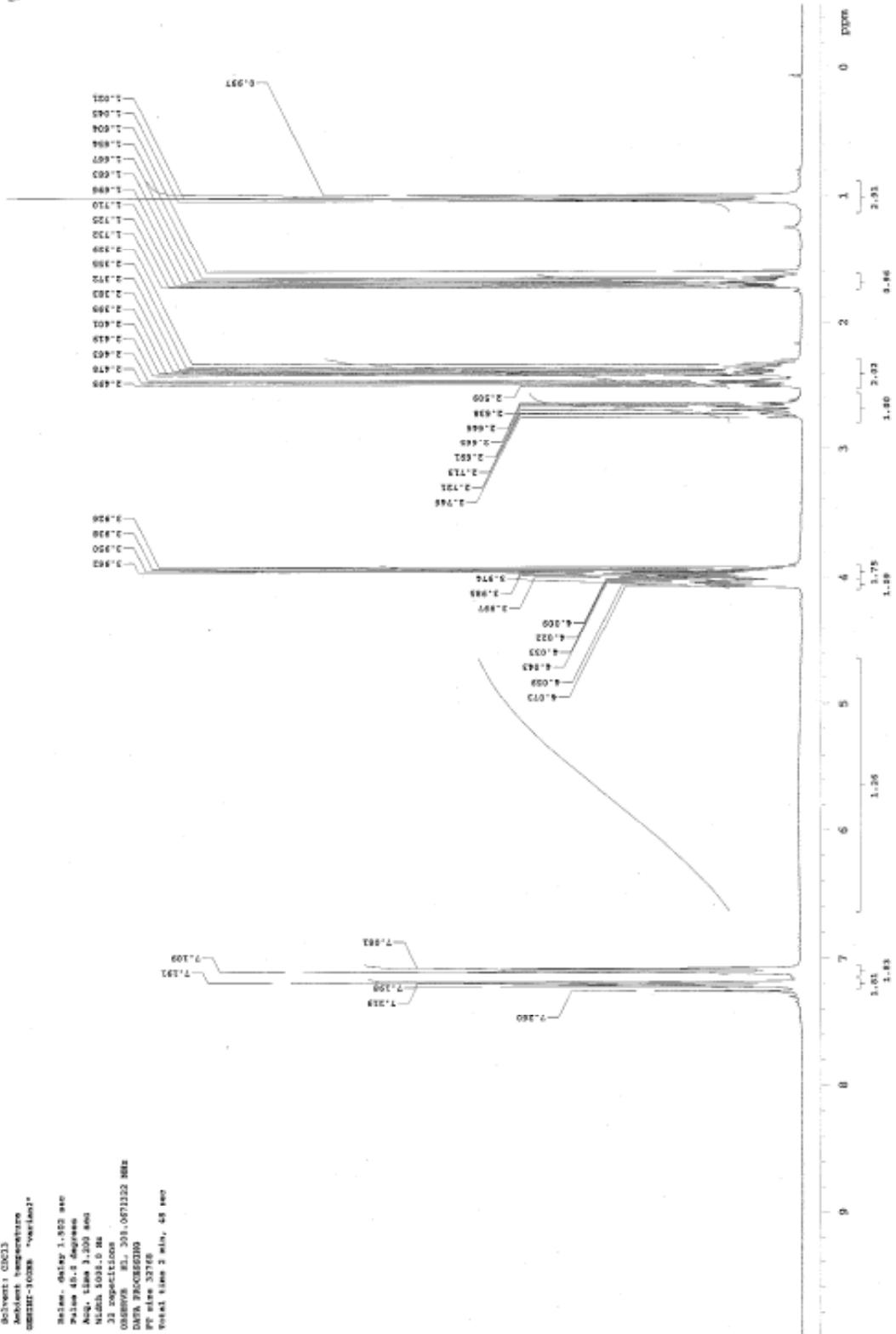
Pulse sequence: zgpg30
solvent: accl
injection: 1000
injection temperature: 200
CHROM/301000 *p0000001*

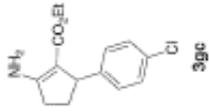
Relax. delay 1.000 sec
Pulse 45.0 degrees
Pulse width 10.000 sec
Width 10.000 sec
40 repetitions
CHROM/301000 *p0000001*
DATA PROCESSING
PR file 33760
Total time 5 min, 37 sec





STANDARD 111 CHLORURE
 Pulse Program: 42101
 SCHWAB: CMC13
 Ambient temperature
 CHSHE-10000 "variable"
 Reten. delay 1.000 sec
 Pulse 40.0 degrees
 Acq. time 3.200 sec
 NMRH 500.0 MHz
 31 repetitions
 CHANNEL F1: 301.0071322 MHz
 DATA FREQ: 301.0071322 MHz
 Total time 3 min, 48 sec



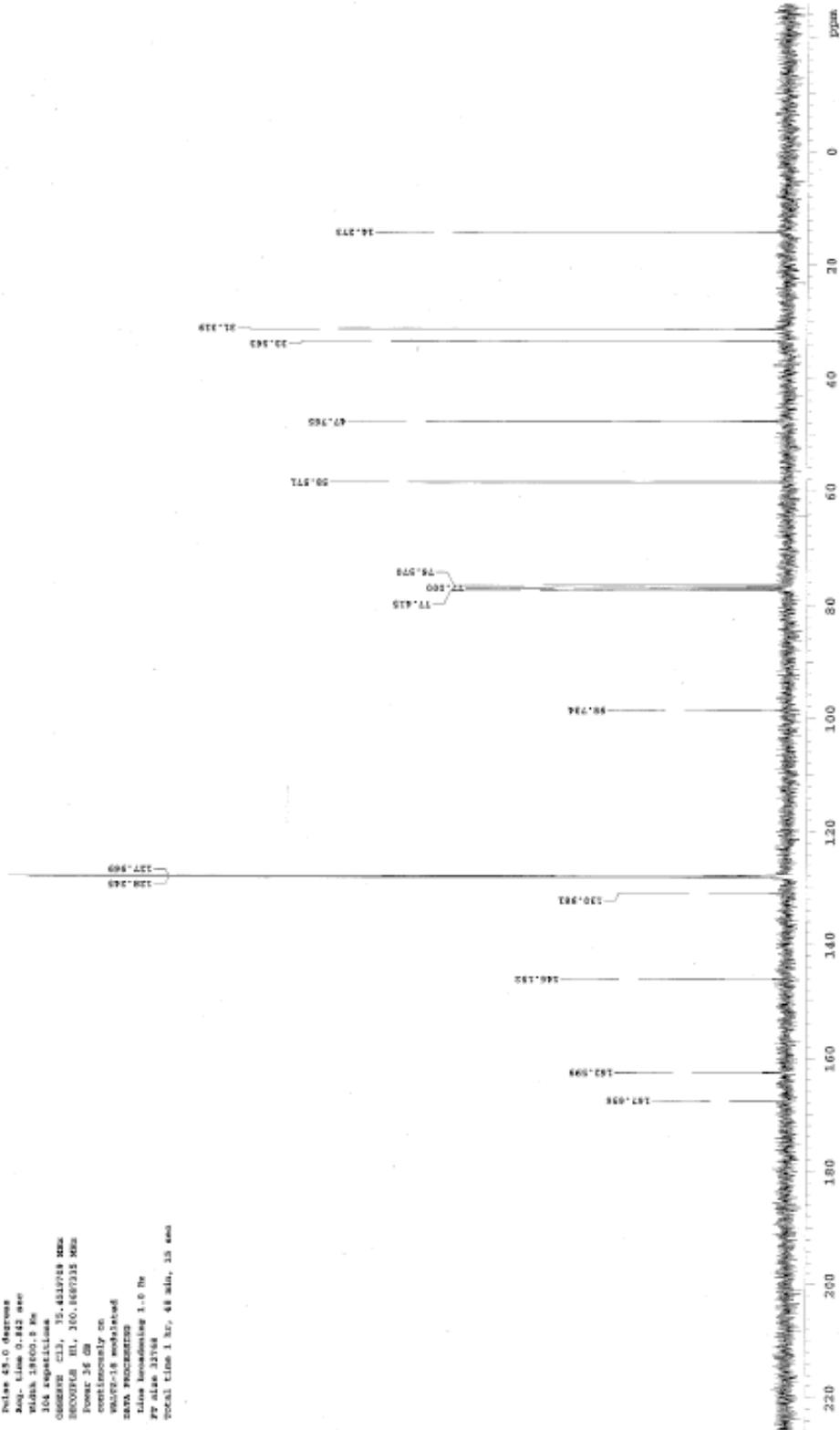


13C NMR

Pulse sequence: zgpg30
 solvent: CDCl3
 nucleus: 13C
 channel: zgpg30

Relax. delay: 3.158 sec
 Pulse: 15.0 degrees
 Acq. time: 0.142 sec
 No. of scans: 64
 104 Experiments

NAME: 39c
 PROCNO: 11
 F2: 100.626135 MHz
 Power: 25.00
 continuously on
 VNUC2-18 modulated
 DATA ACQUISITION
 Line broadening: 1.0 Hz
 F2 alias: 31748
 Total time: 1 hr, 48 min, 15 sec





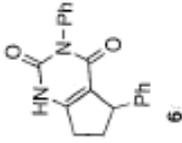
RECORDED IN CHROMYON

Pulse sequence: sfgpl

Solvent: CDCl3

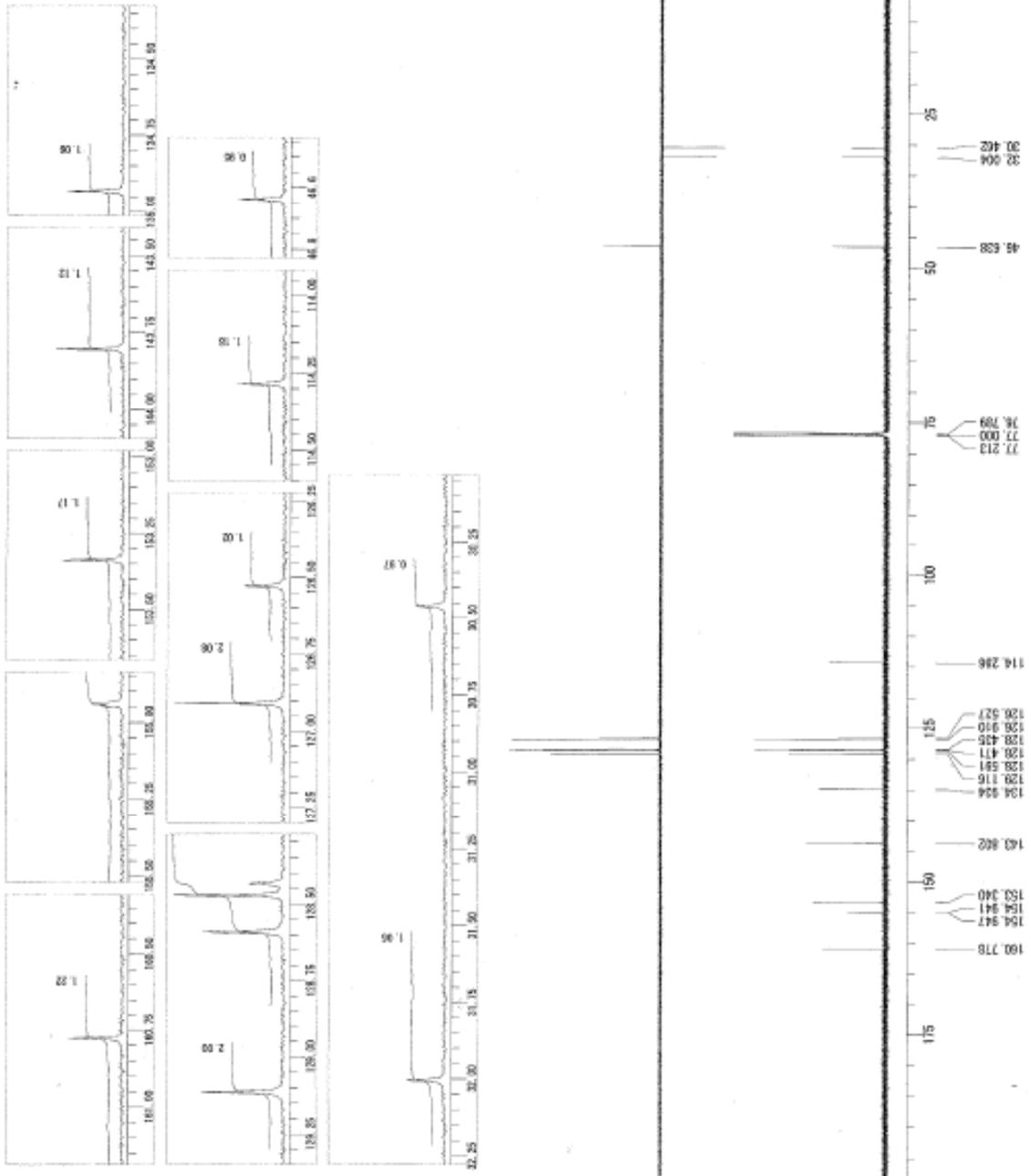
Acquisition temperature: 300 K

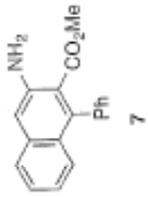
NAME: 4ha



C:\WINLPRM\FUJITA\Pharmaceuticals\1-NHEt3.ms

20-11-2004 16:07:11
 single_pulse_dec
 130
 100.32 MHz
 104.874 Hz
 33332.82 Hz
 1.5719 sec
 6.0000 sec
 800
 4
 3.75 usec
 0.00 usec
 0.00 usec
 0.0000 usec
 0.0000 usec
 111
 1H
 600.17 MHz
 5.30 MHz
 0
 36.0 g
 77.00 ppm
 60
 0.32 Hz
 36.0 g
 measurement no
 by FUJITA



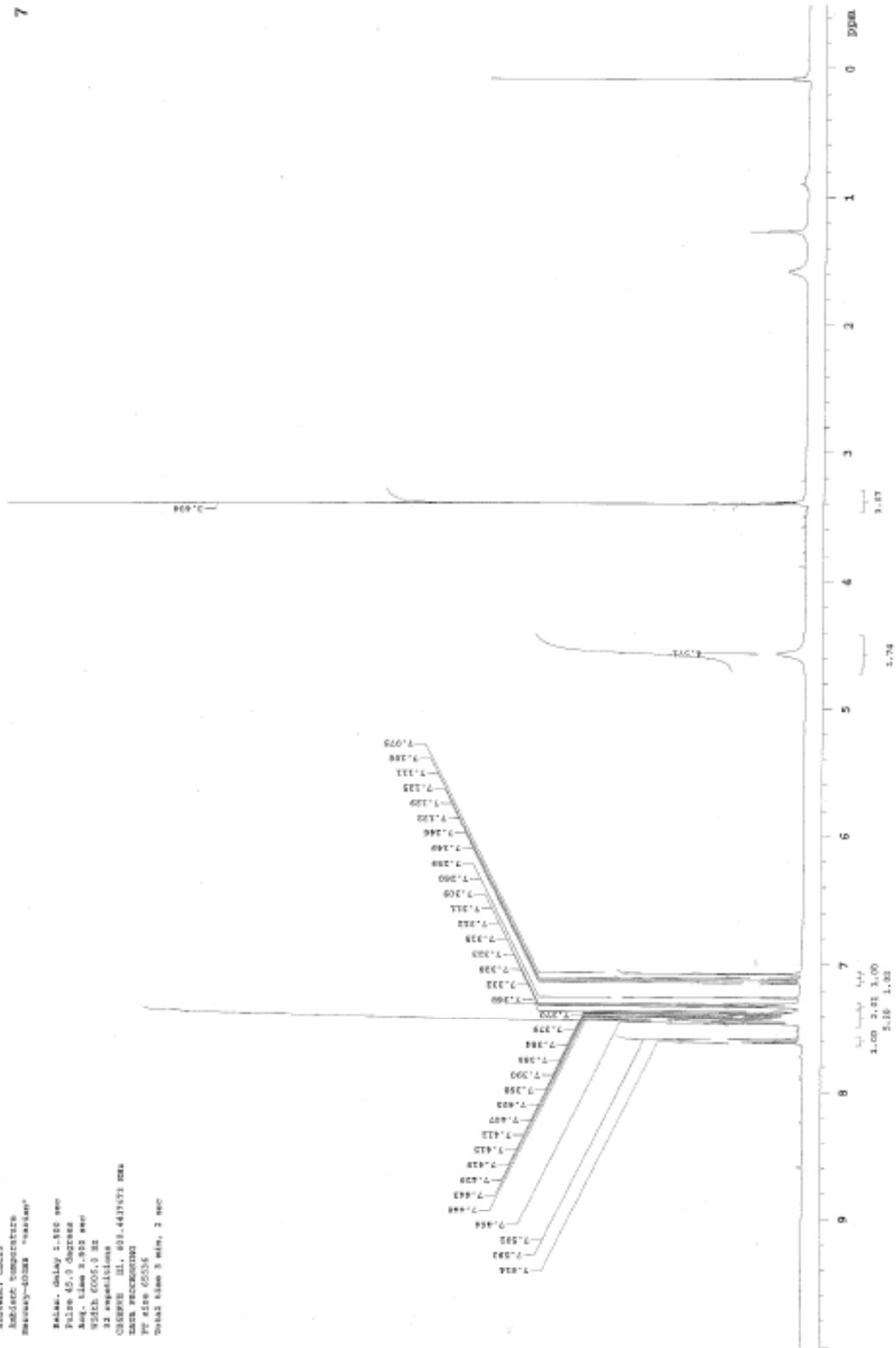


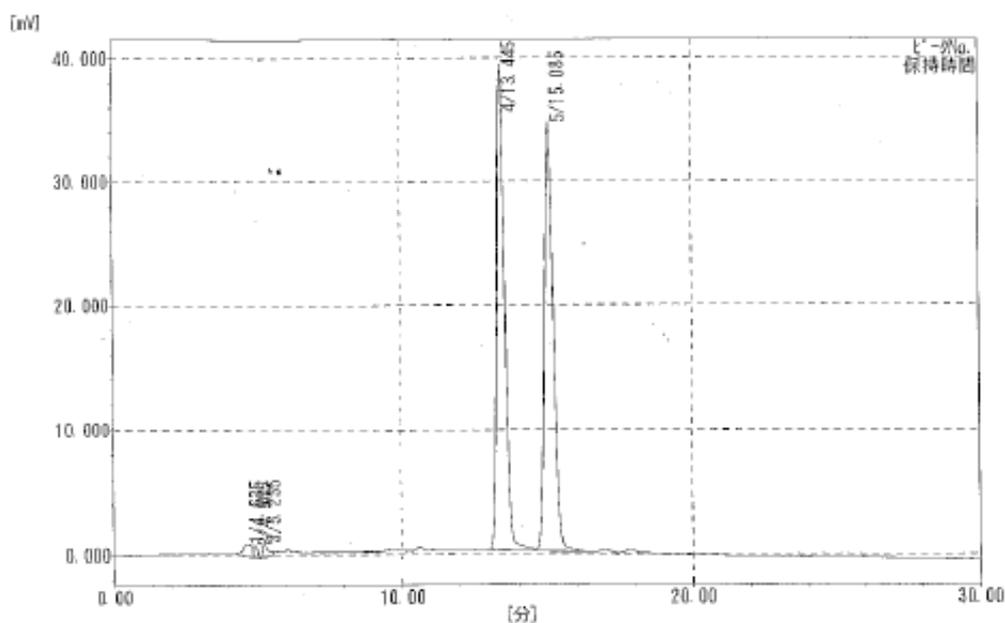
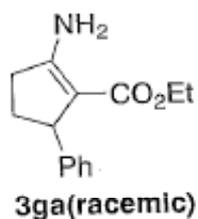
STANDARD IN CURRENT

Pulse Program: w/gm3
 solvent: CDCl3
 solvent temperature:
 Shutter-Open "onset"

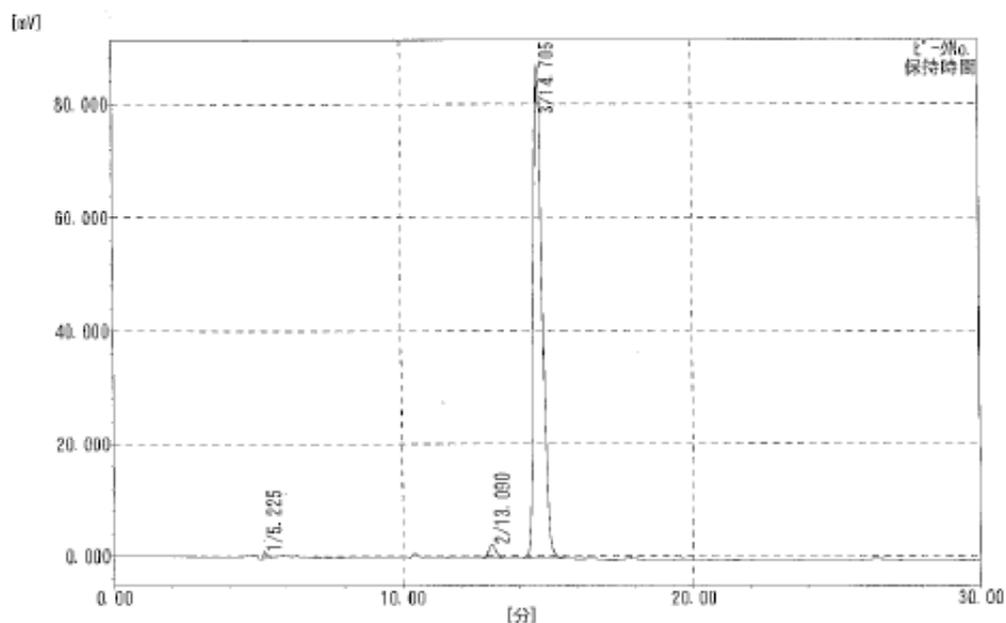
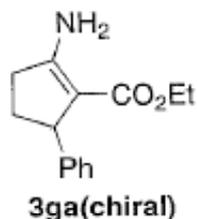
Relax. delay 1.000 sec
 Pulse 45.0 degree
 Acq. time 3.300 sec
 92515 0005.0 32
 33 repetitions

CHERKE IL 031-4437473 004
 NMR RECORDING
 FT 416 0035
 Total time 3 min, 3 sec

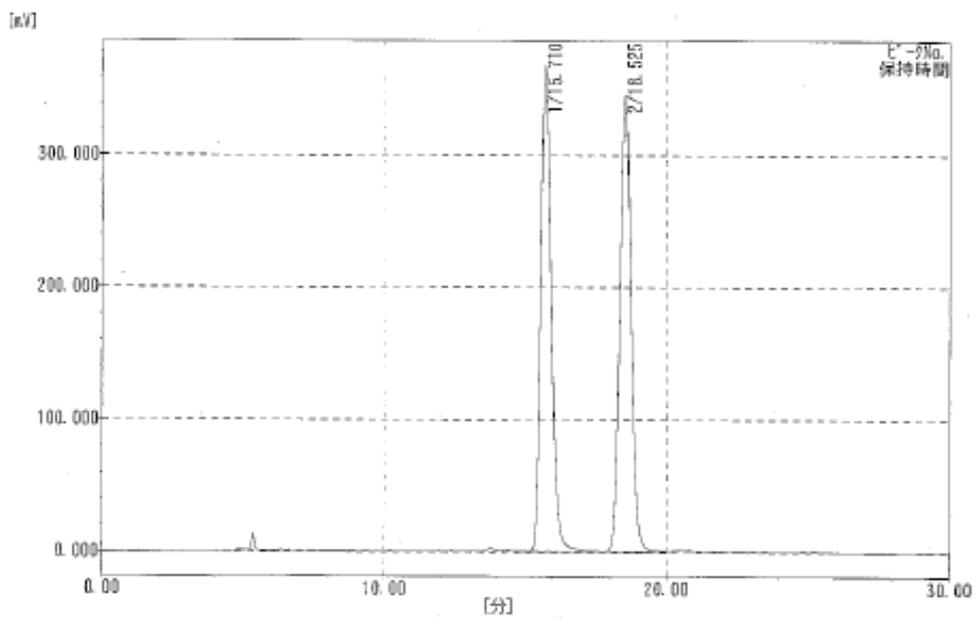
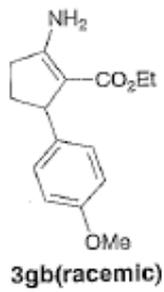




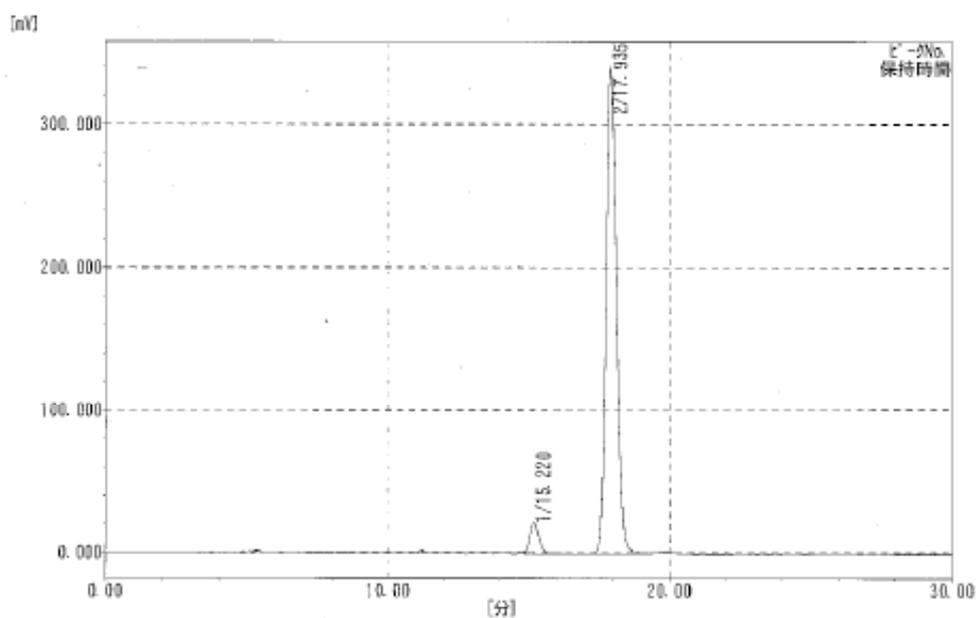
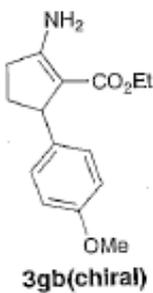
No.	Ch	時間 [分]	高さ [mV]	半値幅 [秒]	面積 [mV×秒]	面積%	理論段数	分離能	非対称係数
1	1	4.635	1.00	0.00	20.89	1.39	0	0.00	0.00
2	1	4.905	1.02	0.00	10.66	0.71	0	0.00	0.00
3	1	5.235	1.21	11.10	16.17	1.08	4435	0.00	0.00
4	1	13.445	39.23	16.85	728.33	48.59	12696	20.76	1.17
5	1	15.085	34.51	19.27	722.99	48.23	12222	3.21	1.15
			76.98		1499.04	100.00			



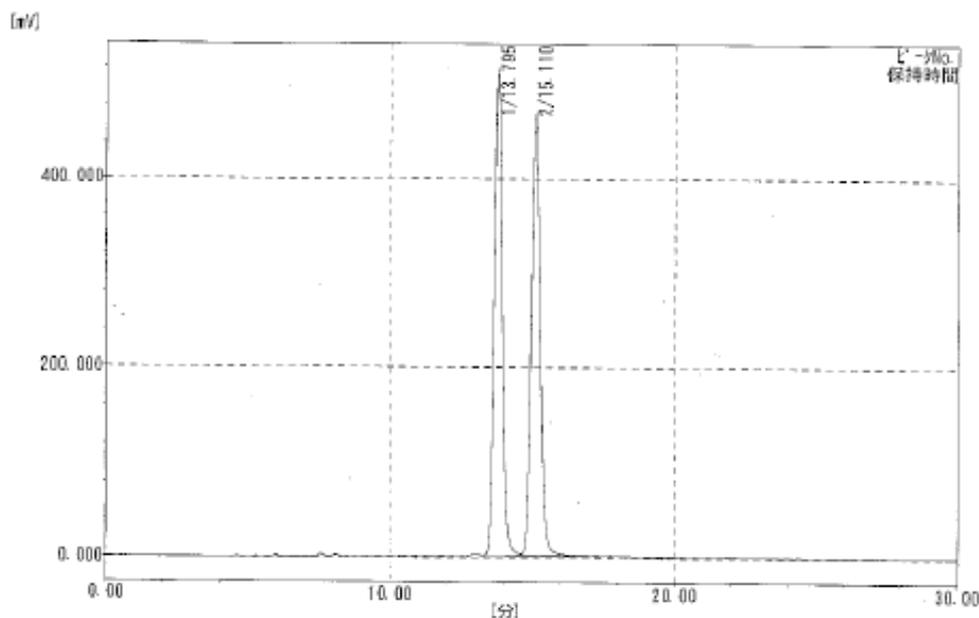
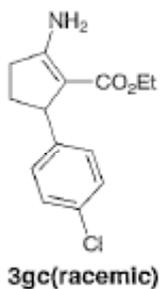
No.	Ch	時間 [分]	高さ [mV]	半値幅 [秒]	面積 [mV×秒]	面積%	理論段数	分離能	非対称係数
1	1	5.225	1.28	9.28	14.91	0.81	6319	0.00	2.27
2	1	13.090	2.57	16.20	44.98	2.46	13014	21.81	1.07
3	1	14.705	87.26	18.78	1771.72	96.73	12226	3.26	1.15
			91.12		1831.62	100.00			



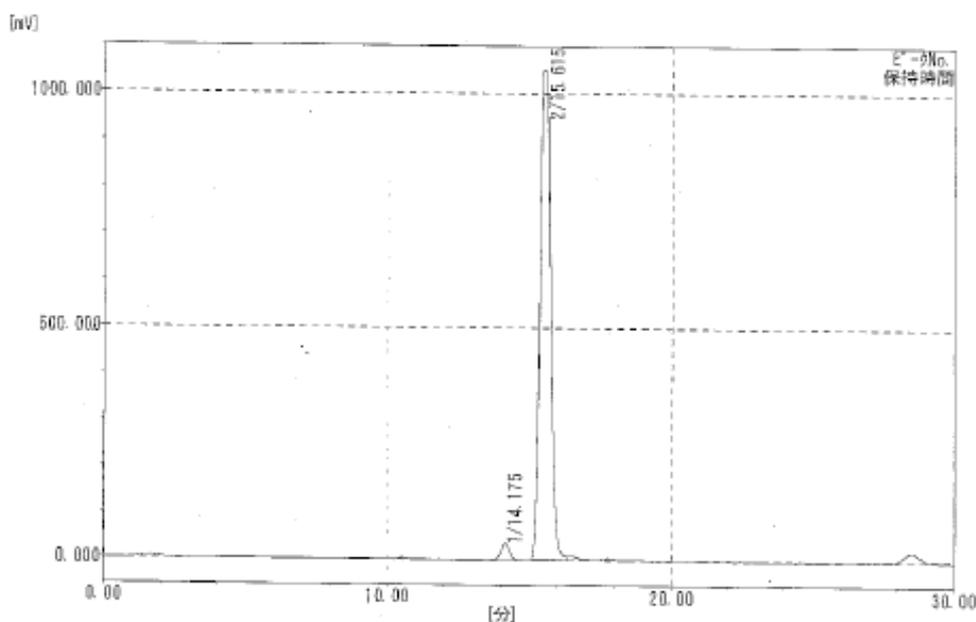
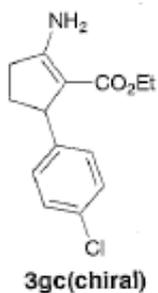
No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mV×秒]	面積%	理論段数	分離能	非対称係数
1	1	15.710	368.73	23.46	9530.38	50.02	8943	0.00	1.56
2	1	18.525	346.01	25.40	9521.54	49.98	10612	4.07	1.24
			714.74		19051.91	100.00			



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mV×秒]	面積%	理論段数	分離能	非対称係数
1	1	15.220	21.80	20.93	499.46	5.43	10544	0.00	1.23
2	1	17.935	341.11	23.53	8690.33	94.57	11582	4.32	1.20
			362.91		9189.79	100.00			



No.	Ch	時間 [分]	高さ [mV]	半値幅 [秒]	面積 [mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	13.795	518.28	17.63	9992.03	49.73	12214	0.00	1.22
2	1	15.110	468.90	19.60	10099.12	50.27	11855	2.50	1.23
			987.18		20091.15	100.00			



No.	Ch	時間 [分]	高さ [mV]	半値幅 [秒]	面積 [mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	14.175	34.39	18.69	727.03	2.58	11477	0.00	1.04
2	1	15.615	1048.45	23.96	27406.12	97.42	6470	2.39	0.84
			1082.84		28133.15	100.00			