

Supplementary Information

Cobalt-catalyzed asymmetric addition of silylacetylenes to oxa- and azabenzonorbornadienes

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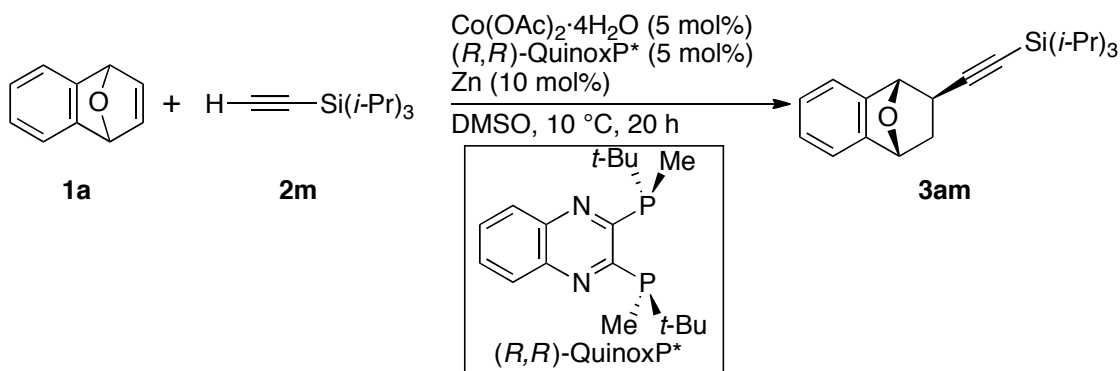
1. General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H , 125 MHz for ^{13}C). Chemical shifts are reported in δ (ppm) referenced to the residual peaks of CDCl_3 (δ 7.26) or $\text{DMSO}-d_6$ (δ 2.49) for ^1H NMR and CDCl_3 (δ 77.00) or $\text{DMSO}-d_6$ (δ 39.52) for ^{13}C NMR. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. Optical rotations were measured on a JASCO P-2200 polarimeter. High-resolution mass spectra were obtained with a Bruker micrOTOF spectrometer.

2. Materials

DMSO was distilled over CaH_2 under N_2 . $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (99.0%, Kanto Chemicals) and zinc powder (99.9%, 75~150 μm , Wako Chemicals) were used as received. $\text{Co}(\text{OAc})_2$ (KISHIDA chemicals) was dried under reduced pressure before use. Alumina (activated 200) for column chromatography was purchased from Nacalai Tesque. Oxabenzonorbornadiene **1a** [573-57-9], **1b** [19061-36-0], **1c** [173276-99-8], **1d** [106750-88-3], **1e** [115695-65-3], **1f** [26002-73-3], **1g** [648921-68-0], and **1h** [885691-68-9] were prepared according to the reported procedures.¹ All other chemicals were purchased from commercial suppliers and used as received.

3. A typical procedure for cobalt-catalyzed asymmetric addition of terminal alkynes to oxabenzonorbornadienes (Table 2)



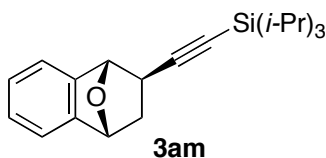
A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2.5 mg, 0.010 mmol), (R,R) -QuinoxP* (3.3 mg, 0.010 mmol), and Zn powder (1.3 mg, 0.020 mmol) in DMSO (0.3 mL) was stirred at room temperature for 15 min. The mixture was cooled to 10 °C, and oxabenzonorbornadiene **1a** (28.8 mg, 0.200 mmol) and (triisopropylsilyl)acetylene **2m** (90 μL , 0.40 mmol) were added. The mixture was stirred at 10 °C for 20 h, and then it was passed through a short column of alumina with diethyl ether as eluent.

1 a) M. Davoust, J. A. Kitching, M. J. Fleming and M. Lautens, *Chem. Eur. J.*, 2010, **16**, 50. b) M. Lautens, K. Fagnou and D. Yang, *J. Am. Chem. Soc.*, 2003, **125**, 14884. c) Y.-H. Cho, V. Zunic, H. Senboku, M. Olsen and M. Lautens, *J. Am. Chem. Soc.*, 2006, **128**, 6837.

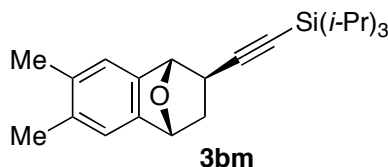
After removal of the solvent on a rotary evaporator, the residue was subjected to preparative TLC (silica gel, hexane/ethyl acetate = 10/1) to give compound **3am** (59.5 mg, 0.182 mmol, 91%).

The absolute configuration of **3em** produced by (*R,R*)-QuinoxP* was determined to be (1*S*,2*R*,4*R*) by X-ray analysis of **4**, which was derived from **3em** (vide infra). For others, they were assigned by analogy with (1*S*,2*R*,4*R*)-**3em**.

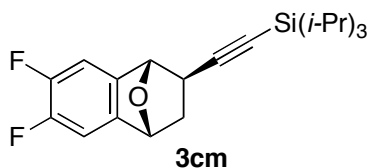
4. Characterization of the products



Compound 3am (91% yield, 99% ee (1*S*,2*R*,4*R*)). The ee was measured by HPLC (Chiralcel OD-H column, flow 0.5 mL/min, hexane/2-propanol = 500/1, 254 nm, t_1 = 13.3 min (minor), t_2 = 22.0 min (major)); $[\alpha]_D^{20}$ +72 (c 0.63, CHCl₃) for 99% ee. ¹H NMR (CDCl₃) δ 1.03–1.13 (m, 21H), 1.88 (dd, J = 11.4, 8.4 Hz, 1H), 2.15 (dt, J = 11.4, 4.6 Hz, 1H), 2.55 (dd, J = 8.4, 4.6 Hz, 1H), 5.36 (s, 1H), 5.47 (d, J = 4.6 Hz, 1H), 7.13–7.19 (m, 2H), 7.20–7.24 (m, 1H), 7.25–7.30 (m, 1H); ¹³C NMR (CDCl₃) δ 11.3, 18.7, 32.7, 37.1, 79.1, 81.1, 84.7, 111.0, 119.0, 119.1, 126.7, 127.0, 144.6, 145.3. HRMS (ESI) calcd for C₂₁H₃₀NaOSi (M+Na)⁺ 349.1958, found 349.1953.

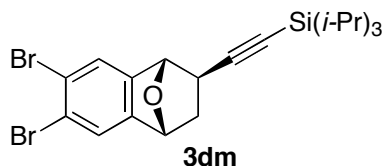


Compound 3bm (82% yield, 99% ee (1*S*,2*R*,4*R*)). The ee was measured by HPLC (Chiralcel OD-H column, flow 0.5 mL/min, hexane/2-propanol = 500/1, 254 nm, t_1 = 18.3 min (major), t_2 = 26.1 min (minor)); $[\alpha]_D^{20}$ +78 (c 0.62, CHCl₃) for 99% ee. ¹H NMR (CDCl₃) δ 1.04–1.12 (m, 21H), 1.84 (dd, J = 11.4, 8.4 Hz, 1H), 2.12 (dt, J = 11.4, 4.5 Hz, 1H), 2.24 (s, 6H), 2.55 (dd, J = 8.4, 4.5 Hz, 1H), 5.30 (s, 1H), 5.41 (d, J = 4.5 Hz, 1H), 7.01 (s, 1H), 7.05 (s, 1H); ¹³C NMR (CDCl₃) δ 11.3, 18.7, 19.89, 19.90, 33.0, 37.5, 79.0, 80.8, 84.6, 111.4, 120.4, 120.5, 134.7, 135.0, 142.5, 143.2. HRMS (ESI) calcd for C₂₃H₃₄NaOSi (M+Na)⁺ 377.2271, found 377.2265.

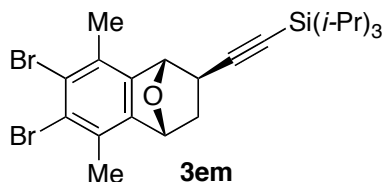


Compound 3cm (86% yield, 90% ee (1*S*,2*R*,4*R*)). The ee was measured by HPLC (Chiralcel OD-H column×2, flow 0.5 mL/min, hexane/2-propanol = 100/1, 254 nm, t_1 = 17.7 min (major), t_2 =

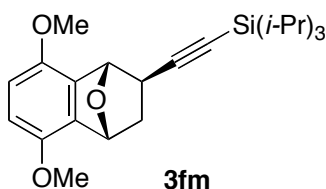
19.6 min (minor)); $[\alpha]_D^{20} +62$ (*c* 0.77, CHCl₃) for 90% ee. ¹H NMR (CDCl₃) δ 1.02–1.12 (m, 21H), 1.85 (dd, *J* = 11.6, 8.5 Hz, 1H), 2.14 (dt, *J* = 11.6, 4.5 Hz, 1H), 2.52 (dd, *J* = 8.5, 4.5 Hz, 1H), 5.32 (s, 1H), 5.44 (d, *J* = 4.5 Hz, 1H), 7.05 (dd, *J*_{F-H} = 8.9, 6.7 Hz, 1H), 7.10 (dd, *J*_{F-H} = 9.0, 6.9 Hz, 1H); ¹³C NMR (CDCl₃) δ 11.2, 18.6, 32.6, 36.9, 78.9 (d, *J*_{F-C} = 2 Hz), 81.8, 84.4 (d, *J*_{F-C} = 2 Hz), 109.1 (d, *J*_{F-C} = 15 Hz), 109.3 (d, *J*_{F-C} = 14 Hz), 110.0, 140.5 (dd, *J*_{F-C} = 6, 4 Hz), 141.2 (dd, *J*_{F-C} = 6, 3 Hz), 149.2 (dd, *J*_{F-C} = 247, 13 Hz), 149.4 (dd, *J*_{F-C} = 246, 12 Hz). HRMS (ESI) calcd for C₂₁H₂₈F₂NaOSi (M+Na)⁺ 385.1770, found 385.1763.



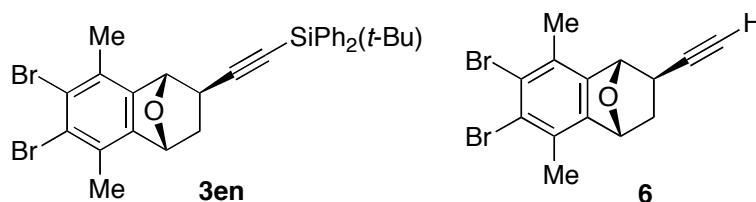
Compound 3dm (81% yield, 94% ee (1*S*,2*R*,4*R*)). The ee was measured by HPLC (Chiralcel OD-H column×2, flow 0.5 mL/min, hexane/2-propanol = 100/1, 254 nm, *t*₁ = 19.2 min (major), *t*₂ = 25.8 min (minor)); $[\alpha]_D^{20} +69$ (*c* 0.72, CHCl₃) for 94% ee. ¹H NMR (CDCl₃) δ 1.02–1.11 (m, 21H), 1.87 (dd, *J* = 11.8, 8.4 Hz, 1H), 2.15 (dt, *J* = 11.8, 4.7 Hz, 1H), 2.55 (dd, *J* = 8.4, 4.7 Hz, 1H), 5.31 (s, 1H), 5.42 (d, *J* = 4.7 Hz, 1H), 7.49 (s, 1H), 7.54 (s, 1H); ¹³C NMR (CDCl₃) δ 11.2, 18.6, 32.5, 36.7, 78.6, 82.0, 84.1, 109.8, 122.7, 123.0, 124.6, 124.7, 145.6, 146.3. HRMS (ESI) calcd for C₂₁H₂₈Br₂NaOSi (M+Na)⁺ 505.0168, found 505.0165.



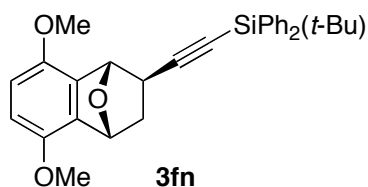
Compound 3em (70% yield, 95% ee (1*S*,2*R*,4*R*)). The ee was measured by HPLC (Chiralcel OD-H column×2, flow 0.5 mL/min, hexane/2-propanol = 100/1, 254 nm, *t*₁ = 15.2 min (major), *t*₂ = 17.6 min (minor)); $[\alpha]_D^{20} +76$ (*c* 0.72, CHCl₃) for 95% ee. ¹H NMR (CDCl₃) δ 1.05–1.12 (m, 21H), 1.84 (dd, *J* = 11.6, 8.5 Hz, 1H), 2.15 (dt, *J* = 11.6, 4.6 Hz, 1H), 2.40 (s, 3H), 2.45 (s, 3H), 2.50 (dd, *J* = 8.5, 4.6 Hz, 1H), 5.38 (s, 1H), 5.51 (d, *J* = 4.6 Hz, 1H); ¹³C NMR (CDCl₃) δ 11.3, 18.63, 18.64, 20.9, 21.1, 32.0, 36.4, 78.8, 81.8, 84.4, 110.3, 126.3, 126.7, 129.1, 129.3, 143.0, 143.7. HRMS (ESI) calcd for C₂₃H₃₂Br₂NaOSi (M+Na)⁺ 533.0481, found 533.0483.



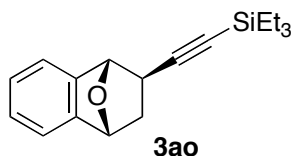
Compound 3fm (91% yield, 97% ee (1*S*,2*R*,4*R*)). The ee was measured by HPLC (Chiralcel OD-H column, flow 0.5 mL/min, hexane/2-propanol = 100/1, 254 nm, t_1 = 11.7 min (major), t_2 = 19.4 min (minor)); $[\alpha]_D^{20}$ +69 (c 0.65, CHCl₃) for 97% ee. ¹H NMR (CDCl₃) δ 1.03–1.12 (m, 21H), 1.89 (dd, J = 11.4, 8.5 Hz, 1H), 2.12 (dt, J = 11.4, 4.5 Hz, 1H), 2.55 (dd, J = 8.5, 4.5 Hz, 1H), 3.79 (s, 3H), 3.80 (s, 3H), 5.50 (s, 1H), 5.62 (d, J = 4.5 Hz, 1H), 6.64 (d, J = 8.8 Hz, 1H), 6.65 (d, J = 8.8 Hz, 1H); ¹³C NMR (CDCl₃) δ 11.3, 18.7, 32.2, 36.6, 56.01, 56.03, 77.0, 80.9, 82.6, 111.1, 111.5, 133.7, 134.6, 146.5, 146.6. HRMS (ESI) calcd for C₂₃H₃₄NaO₃Si (M+Na)⁺ 409.2169, found 409.2167.



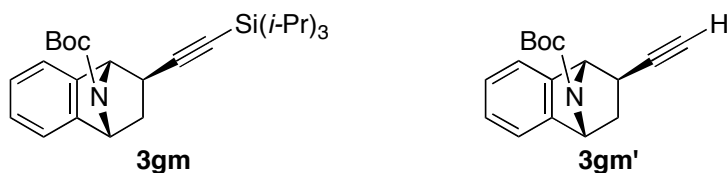
Compound 3en (60% yield, 90% ee (1*S*,2*R*,4*R*)). The ee of **3en** was determined by HPLC analysis of compound **6**, which was obtained by removal of a silyl group with tetrabutylammonium fluoride. **Compound 3en**: $[\alpha]_D^{20}$ +67 (c 1.02, CHCl₃) for 90% ee. ¹H NMR (CDCl₃) δ 1.11 (s, 9H), 1.93 (dd, J = 14.0, 10.1 Hz, 1H), 2.29 (dt, J = 14.0, 5.4 Hz, 1H), 2.43 (s, 3H), 2.48 (s, 3H), 2.64 (dd, J = 10.1, 5.4 Hz, 1H), 5.52 (s, 1H), 5.58 (d, J = 5.4 Hz, 1H), 7.34–7.44 (m, 6H), 7.78–7.84 (m, 4H); ¹³C NMR (CDCl₃) δ 18.6, 20.9, 21.2, 27.1, 32.2, 36.3, 78.8, 81.2, 84.2, 112.6, 126.4, 126.8, 127.7, 129.1, 129.37, 129.44, 133.47, 133.49, 135.6, 142.8, 143.7. HRMS (ESI) calcd for C₃₀H₃₀Br₂NaOSi (M+Na)⁺ 615.0325, found 615.0325. **Compound 6** (83% yield from **3en**): The ee was measured by HPLC (Chiralcel OD-H column, flow 0.5 mL/min, hexane/2-propanol = 100/1, 254 nm, t_1 = 17.1 min (major), t_2 = 22.3 min (minor)); $[\alpha]_D^{20}$ +67 (c 0.91, CHCl₃) for 90% ee. ¹H NMR (CDCl₃) δ 1.85 (dd, J = 11.8, 8.5 Hz, 1H), 2.19 (ddd, J = 11.8, 5.0, 4.1 Hz, 1H), 2.22 (d, J = 2.5 Hz, 1H), 2.40 (s, 3H), 2.45 (s, 3H), 2.49 (ddd, J = 8.5, 4.1, 2.5 Hz, 1H), 5.44 (s, 1H), 5.54 (d, J = 5.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 20.9, 21.1, 30.8, 35.9, 69.6, 78.8, 84.0, 86.1, 126.5, 126.9, 129.2, 129.4, 142.5, 143.7. HRMS (ESI) calcd for C₁₄H₁₂Br₂NaO (M+Na)⁺ 376.9147, found 376.9151.



Compound 3fn (90% yield, 96% ee (1*S*,2*R*,4*R*)). The ee was measured by HPLC (Chiralcel OD-H column, flow 0.5 mL/min, hexane/2-propanol = 100/1, 254 nm, t_1 = 18.0 min (major), t_2 = 29.0 min (minor)); $[\alpha]_D^{20}$ +62 (c 0.62, CHCl₃) for 96% ee. ¹H NMR (CDCl₃) δ 1.11 (s, 9H), 1.97 (dd, J = 11.5, 8.5 Hz, 1H), 2.26 (dt, J = 11.5, 4.5 Hz, 1H), 2.69 (dd, J = 8.5, 4.5 Hz, 1H), 3.81 (s, 3H), 3.82 (s, 3H), 5.65 (s, 1H), 5.69 (d, J = 4.5 Hz, 1H), 6.66 (d, J = 8.8 Hz, 1H), 6.67 (d, J = 8.8 Hz, 1H), 7.32–7.42 (m, 6H), 7.78–7.84 (m, 4H); ¹³C NMR (CDCl₃) δ 18.6, 27.1, 32.5, 36.6, 56.0, 56.1, 77.1, 80.3, 82.4, 111.2, 111.6, 113.5, 127.6, 129.3, 133.55, 133.69, 133.71, 134.5, 135.6, 146.6, 146.7. HRMS (ESI) calcd for C₃₀H₃₂NaO₃Si (M+Na)⁺ 491.2013, found 491.2017.

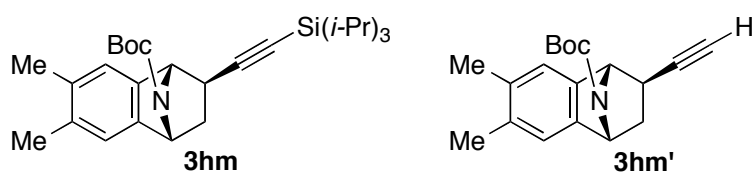


Compound 3ao (7% yield, 80% ee (1*S*,2*R*,4*R*)). The ee was measured by HPLC (Chiralpak AD-H column \times 2, flow 0.5 mL/min, hexane/2-propanol = 200/1, 254 nm, t_1 = 24.7 min (major), t_2 = 27.3 min (minor)); $[\alpha]_D^{20}$ +58 (c 0.21, CHCl₃) for 80% ee. ¹H NMR (CDCl₃) δ 0.61 (q, J = 8.0 Hz, 6H), 1.01 (t, J = 8.0 Hz, 9H), 1.87 (dd, J = 11.5, 8.5 Hz, 1H), 2.16 (dt, J = 11.5, 4.6 Hz, 1H), 2.55 (dd, J = 8.5, 4.6 Hz, 1H), 5.37 (s, 1H), 5.48 (d, J = 4.6 Hz, 1H), 7.13–7.19 (m, 2H), 7.20–7.24 (m, 1H), 7.24–7.29 (m, 1H); ¹³C NMR (CDCl₃) δ 4.5, 7.5, 32.7, 37.0, 79.1, 82.4, 84.6, 110.2, 119.1, 119.2, 126.8, 127.1, 144.5, 145.2. HRMS (ESI) calcd for C₁₈H₂₄NaOSi (M+Na)⁺ 307.1489, found 307.1486.

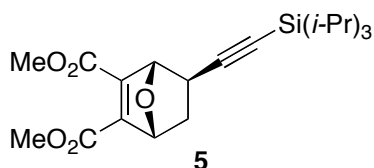


Compound 3gm (73% yield, 96% ee (1*S*,2*R*,4*R*)). The ee of **3gm** was determined by HPLC analysis of compound **3gm'**, which was obtained by removal of a silyl group with tetrabutylammonium fluoride. **Compound 3gm**: $[\alpha]_D^{20}$ +96 (c 0.42, CHCl₃) for 96% ee. ¹H NMR (DMSO-*d*₆, 60 °C) δ 0.99–1.10 (m, 21H), 1.30 (s, 9H), 1.75 (dd, J = 11.6, 8.5 Hz, 1H), 2.04 (dt, J = 11.6, 4.3 Hz, 1H), 2.44 (dd, J = 8.5, 4.3 Hz, 1H), 5.06 (s, 1H), 5.14 (d, J = 4.3 Hz, 1H), 7.09–7.17 (m, 2H), 7.25–7.31 (m, 1H), 7.34–7.40 (m, 1H); ¹³C NMR (DMSO-*d*₆, 60 °C) δ 10.5, 18.05, 18.06, 27.5, 32.1, 36.7, 59.8, 66.3, 78.8, 80.6, 111.2, 119.4, 119.7, 126.0, 126.4, 143.7, 144.8,

153.3. HRMS (ESI) calcd for $C_{26}H_{39}NNaO_2Si$ ($M+Na$)⁺ 448.2642, found 448.2632. **Compound 3gm'** (62% yield from **3gm**): The ee was measured by HPLC (Chiralpak AD-H column, flow 0.5 mL/min, hexane/2-propanol = 98/2, 230 nm, t_1 = 18.4 min (minor), t_2 = 20.0 min (major)); $[\alpha]_D^{20} +70$ (c 0.91, $CHCl_3$) for 96% ee. 1H NMR ($DMSO-d_6$, 60 °C) δ 1.34 (s, 9H), 1.74 (dd, J = 11.7, 8.4 Hz, 1H), 2.05 (dt, J = 11.6, 4.4 Hz, 1H), 2.41 (ddd, J = 8.4, 4.4, 2.3 Hz, 1H), 2.86 (d, J = 2.3 Hz, 1H), 5.09 (s, 1H), 5.14 (d, J = 4.4 Hz, 1H), 7.10–7.17 (m, 2H), 7.25–7.31 (m, 1H), 7.32–7.37 (m, 1H); ^{13}C NMR ($DMSO-d_6$, 60 °C) δ 27.5, 31.1, 35.8, 60.1, 65.7, 71.6, 79.0, 85.9, 119.2, 119.5, 126.0, 126.4, 143.6, 144.3, 153.6. HRMS (ESI) calcd for $C_{17}H_{19}NNaO_2$ ($M+Na$)⁺ 292.1308, found 292.1306.



Compound 3hm (70% yield, 95% ee (1*S*,2*R*,4*R*)). The ee of **3hm** was determined by HPLC analysis of compound **3hm'**, which was obtained by removal of a silyl group with tetrabutylammonium fluoride. **Compound 3hm**: $[\alpha]_D^{20} +96$ (c 0.61, $CHCl_3$) for 95% ee. 1H NMR ($DMSO-d_6$, 60 °C) δ 0.99–1.08 (m, 21H), 1.30 (s, 9H), 1.70 (dd, J = 11.4, 8.4 Hz, 1H), 2.00 (dt, J = 11.4, 4.3 Hz, 1H), 2.18 (s, 6H), 2.39 (dd, J = 8.4, 4.3 Hz, 1H), 4.97 (s, 1H), 5.06 (d, J = 4.3 Hz, 1H), 7.05 (s, 1H), 7.13 (s, 1H); ^{13}C NMR ($DMSO-d_6$, 60 °C) δ 10.5, 18.065, 18.074, 18.9, 27.5, 32.5, 37.1, 59.6, 66.1, 78.6, 80.4, 111.4, 120.6, 120.9, 133.6, 134.0, 141.4, 142.5, 153.2. HRMS (ESI) calcd for $C_{28}H_{43}NNaO_2Si$ ($M+Na$)⁺ 476.2955, found 476.2954. **Compound 3hm'** (76% yield from **3hm**): The ee was measured by HPLC (Chiralpak AD-H column \times 2, flow 0.5 mL/min, hexane/2-propanol = 98/2, 230 nm, t_1 = 38.9 min (major), t_2 = 46.3 min (minor)); $[\alpha]_D^{20} +81$ (c 0.56, $CHCl_3$) for 95% ee. 1H NMR ($DMSO-d_6$, 60 °C) δ 1.33 (s, 9H), 1.68 (dd, J = 11.6, 8.4 Hz, 1H), 2.01 (dt, J = 11.6, 4.4 Hz, 1H), 2.17 (s, 6H), 2.34 (ddd, J = 8.4, 4.4, 2.6 Hz, 1H), 2.81 (d, J = 2.6 Hz, 1H), 5.01 (s, 1H), 5.05 (d, J = 4.4 Hz, 1H), 7.03 (s, 1H), 7.09 (s, 1H); ^{13}C NMR ($DMSO-d_6$, 60 °C) δ 18.91, 18.94, 27.6, 31.5, 36.3, 59.9, 65.7, 71.4, 78.9, 86.1, 120.5, 120.7, 133.6, 134.1, 141.4, 142.0, 153.6. HRMS (ESI) calcd for $C_{19}H_{23}NNaO_2$ ($M+Na$)⁺ 320.1621, found 320.1615.

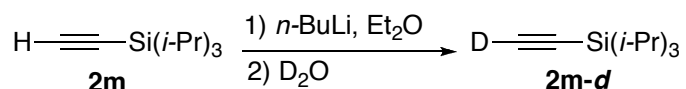


Compound 5 (60% yield, 95% ee (1*S*,2*R*,4*R*)). The ee was measured by HPLC (Chiralcel OD-H column, flow 0.5 mL/min, hexane/2-propanol = 500/1, 254 nm, t_1 = 49.5 min (major), t_2 =

58.1 min (minor)); $[\alpha]_D^{20} +16$ (c 0.98, CHCl_3) for 95% ee. ^1H NMR (CDCl_3) δ 1.00–1.10 (m, 21H), 1.97 (dd, $J = 11.7, 8.3$ Hz, 1H), 2.05 (dt, $J = 11.7, 4.4$ Hz, 1H), 2.66 (dd, $J = 8.3, 4.4$ Hz, 1H), 3.81 (s, 3H), 3.83 (s, 3H), 5.19 (d, $J = 1.0$ Hz, 1H), 5.30 (dd, $J = 4.4, 0.9$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 11.2, 18.6, 30.6, 34.5, 52.32, 52.36, 80.6, 81.9, 86.1, 109.1, 143.0, 144.1, 162.56, 162.58. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{32}\text{NaO}_5\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 415.1911, found 415.1906.

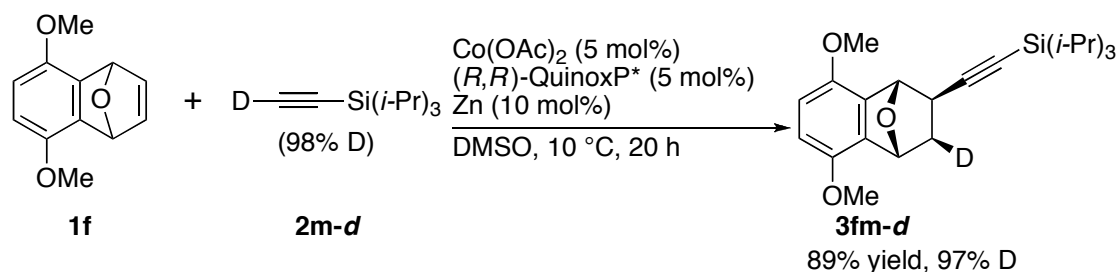
5. Deuterium labeling experiments

5.1. A procedure for preparation of deuterated alkyne **2m-d** [CAS: 112440-16-1]



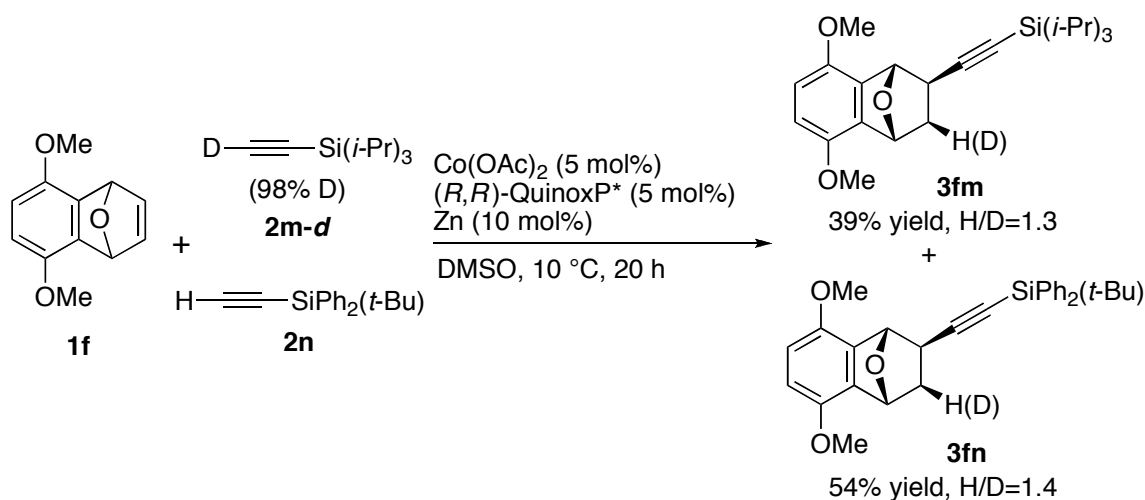
To a solution of (triisopropylsilyl)acetylene **2m** (4.49 mL, 20.0 mmol) in Et_2O (20 mL) was slowly added $n\text{-BuLi}$ (14.7 mL, 24.0 mmol, 1.63 M solution in hexane) at -78 °C, and it was stirred at the same temperature for 30 min and at room temperature for 1 h. D_2O (1.1 mL, 60 mmol) was added at 0 °C and the mixture was passed through a short column of silica gel. Evaporation of the solvent followed by bulb-to-bulb distillation gave deuterated acetylene **2m-d** (3.02 g, 16.5 mmol, 82% yield, 98% D determined by ^1H NMR).

5.2 A procedure for cobalt-catalyzed addition of deuterated alkyne **2m-d** to oxabenzonorbornadiene **1f**



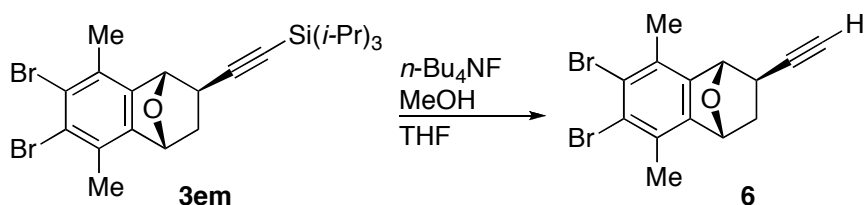
A mixture of Co(OAc)_2 (1.8 mg, 0.010 mmol), (R,R) -QuinoxP* (3.3 mg, 0.010 mmol), and Zn powder (1.3 mg, 0.020 mmol) in DMSO (0.3 mL) was stirred at room temperature for 15 min. The mixture was cooled to 10 °C, and oxabenzonorbornadiene **1f** (28.8 mg, 0.200 mmol) and deuterated alkyne **2m-d** (73.4 mg, 0.400 mmol) were added. The mixture was stirred at 10 °C for 20 h, and then it was passed through a short column of alumina with diethyl ether as eluent. After removal of the solvent on a rotary evaporator, the residue was subjected to preparative TLC (silica gel, hexane/ethyl acetate = 10/1) to give compound **3fm-d** (69.2 mg, 0.18 mmol, 89%, 97% D determined by ^1H -NMR). Compound **3fm-d**. ^1H NMR (CDCl_3) δ 1.02–1.11 (m, 21H), 1.87 (d, $J = 8.4$ Hz, 1H), 2.54 (d, $J = 8.4$ Hz, 1H), 3.79 (s, 3H), 3.80 (s, 3H), 5.50 (s, 1H), 5.62 (s, 1H), 6.64 (d, $J = 8.8$ Hz, 1H), 6.65 (d, $J = 8.8$ Hz, 1H).

5.3 A procedure for deuterium labeling experiment of alkyne **2m-d** and **2n** with oxabenzonorbornadiene **1f** in the presence of $\text{Co}(\text{OAc})_2/(\text{R,R})\text{-QuinoxP}^*$



A mixture of $\text{Co}(\text{OAc})_2$ (1.8 mg, 0.010 mmol), $(\text{R,R})\text{-QuinoxP}^*$ (3.3 mg, 0.010 mmol), and Zn powder (1.3 mg, 0.020 mmol) in DMSO (0.3 mL) was stirred at room temperature for 15 min. The mixture was cooled to 10 °C, and oxabenzonorbornadiene **1f** (40.8 mg, 0.20 mmol), deuterated alkyne **2m-d** (36.7 mg, 0.200 mmol), and (*tert*-butyldiphenylsilyl)acetylene **2n** (52.9 mg, 0.200 mmol) were added. The mixture was stirred at 10 °C for 20 h, and then it was passed through a short column of alumina with diethyl ether as eluent. After removal of the solvent on a rotary evaporator, the residue was subjected to preparative TLC (silica gel, hexane/ethyl acetate = 10/1) to give **3fm** (30.0 mg, 0.0775 mmol, 39%, H/D = 1.3 determined by ¹H-NMR) and **3fn** (50.2 mg, 0.107 mmol, 54%, H/D = 1.4 determined by ¹H-NMR). Compound **3fn-d**. ¹H NMR (CDCl_3) δ 1.12 (s, 9H), 1.97 (d, $J = 8.4$ Hz, 1H), 2.71 (d, $J = 8.4$ Hz, 1H), 3.81 (s, 3H), 3.83 (s, 3H), 5.66 (s, 1H), 5.71 (s, 1H), 6.67 (d, $J = 8.9$ Hz, 1H), 6.68 (d, $J = 8.9$ Hz, 1H), 7.35–7.44 (m, 6H), 7.81–7.88 (m, 4H).

6. Transformation of **3em** into **6** and the data for X-ray crystal structure of compound **6**



To a mixture of **3em** (60.2 mg, 0.117 mmol), MeOH (9.5 μL , 0.23 mmol), and THF (0.6 mL) was added tetrabutylammonium fluoride (0.23 mL, 0.23 mmol, 1.0 M solution in THF) at room temperature, and it was stirred for 2 h. The resulting mixture was passed through a short column of alumina with diethyl ether as eluent. After evaporation of the solvent, the residue was subjected to preparative TLC (silica gel, hexane/ethyl acetate = 20/1) and GPC purification to give compound

6 (34.8 mg, 0.0977 mmol, 84%). The ee was measured by HPLC (Chiralcel OD-H column, flow 0.5 mL/min, hexane/2-propanol = 100/1, 254 nm, $t_1 = 16.4$ min (major), $t_2 = 21.1$ min (minor)); $[\alpha]_D^{20} +74$ (c 0.70, CHCl_3) for 95% ee. Colorless crystals of **6** suitable for X-ray crystallographic analysis were obtained by recrystallization from hexane. The ORTEP drawing of **6** is shown in Figure S1. The crystal structure has been deposited at the Cambridge Crystallographic Centre (deposition number: CCDC 865189). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

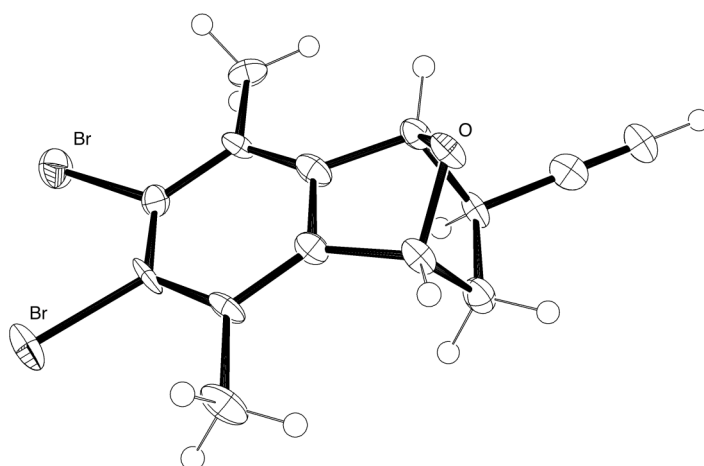


Figure S1. ORTEP illustration of **6** with thermal ellipsoids drawn at the 50% probability level.

X-Ray data were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer using a graphite monochromator with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54187 \text{ \AA}$) at 93 K. The structure was solved by direct method (SHELXS-97) and refined with full-matrix least-square technique (SHELXL-97).² The absolute structure was deduced based on Flack parameter³ 0.03(4), refining using 977 Friedel pairs. The data for **6** was shown in Table S1.

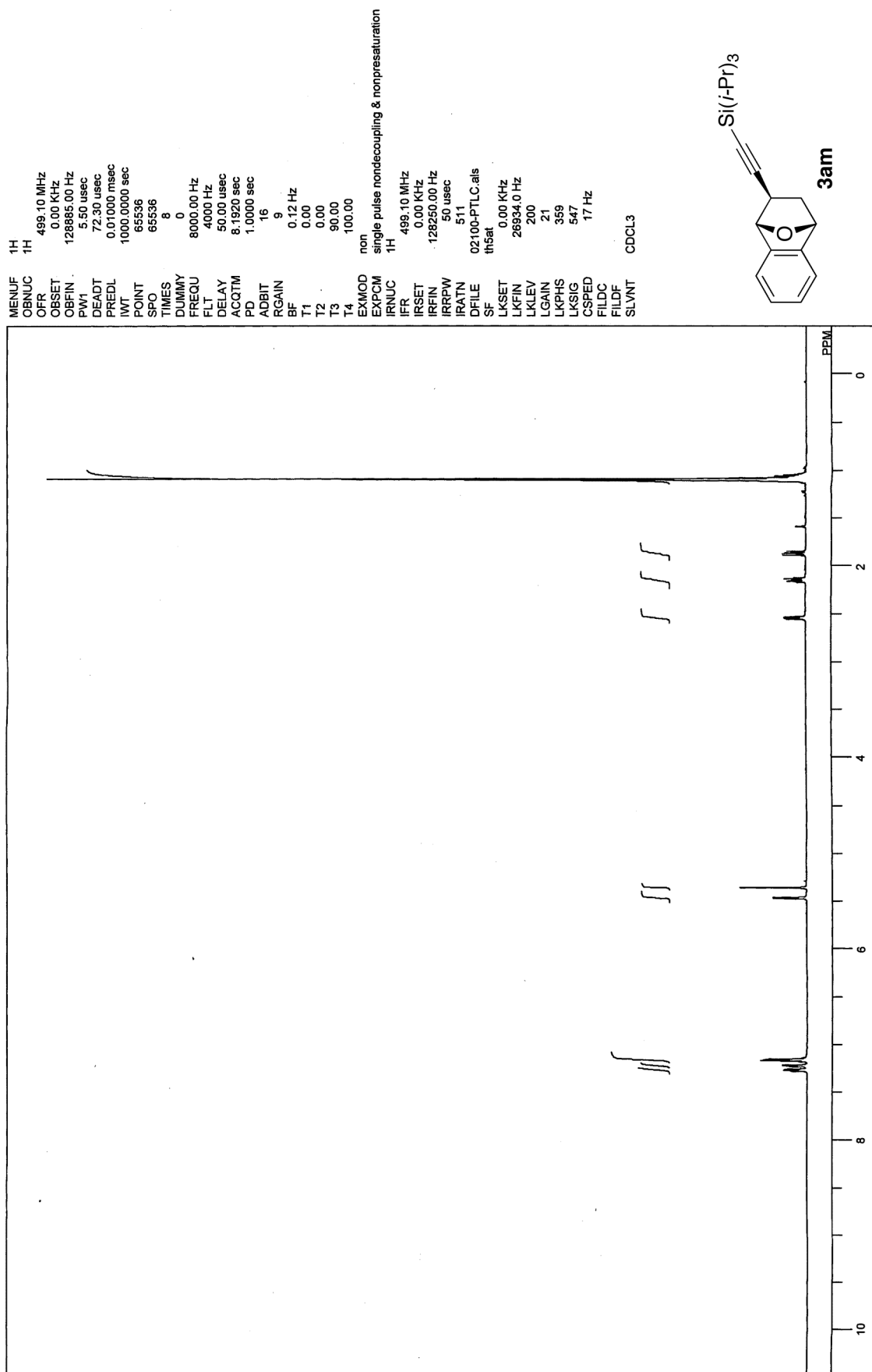
2 Sheldrick, G. M. Program for the solution and refinement of crystal structures, University of Göttingen, Göttingen, Germany, 1997.

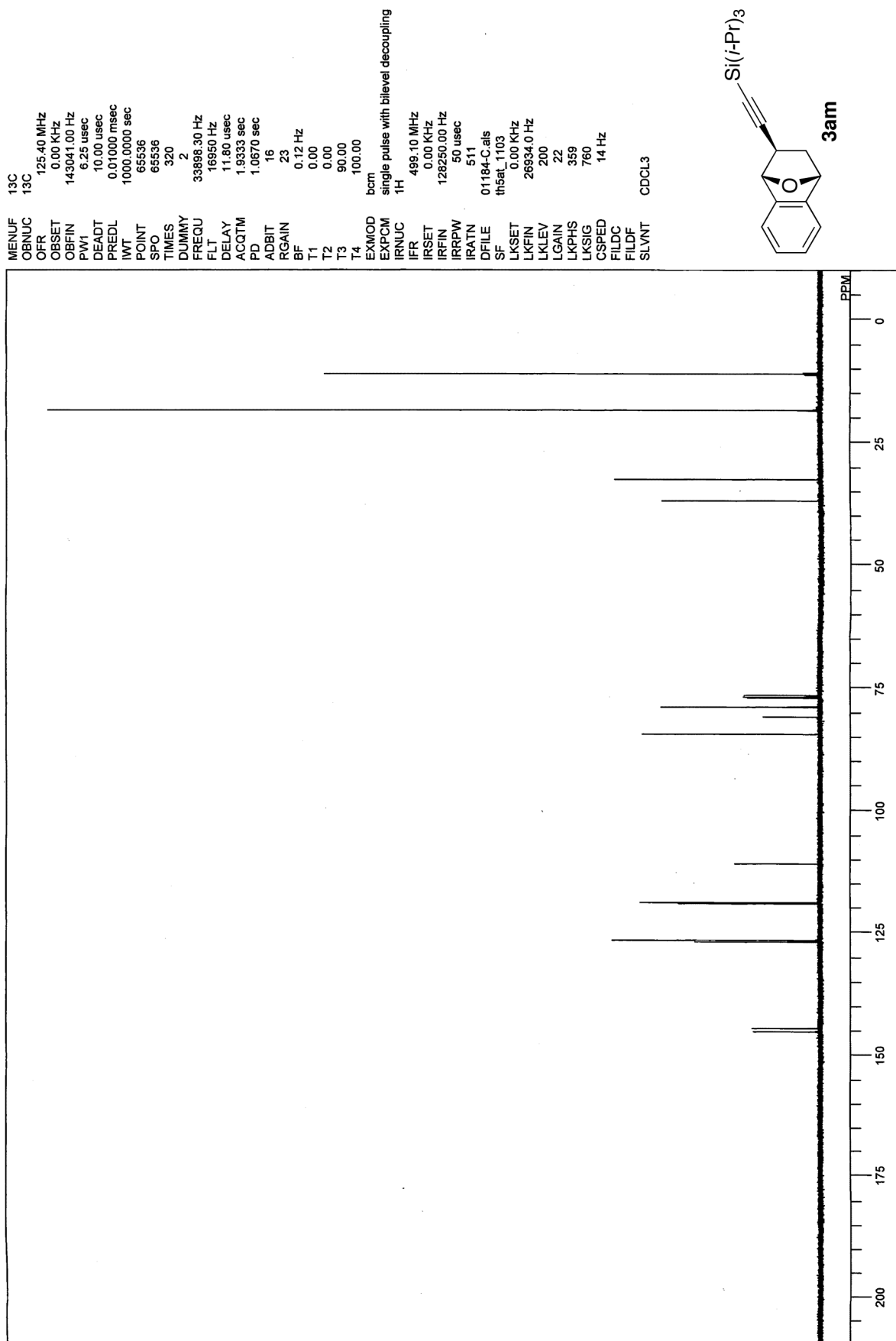
3 Flack, H. D. *Acta Cryst.* 1983, **A39**, 876.

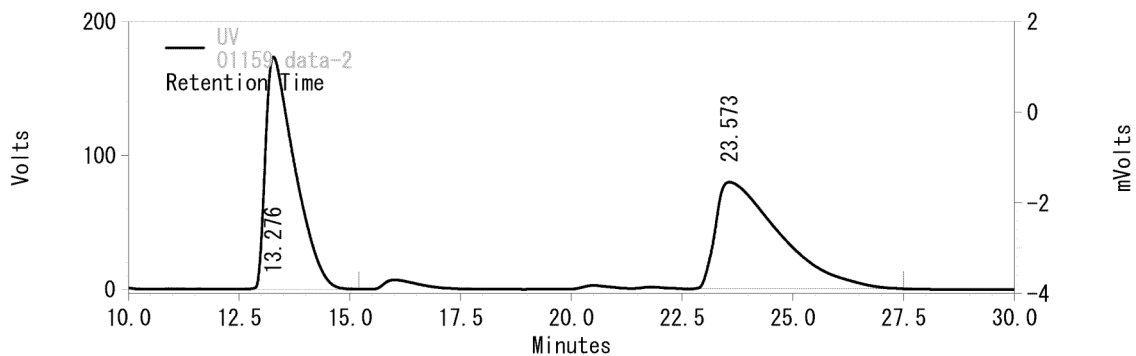
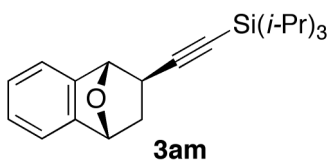
Table S1. Crystal data and structure refinement for **6**

Empirical formula	C ₁₄ H ₁₂ Br ₂ O
Formula weight	356.06
Temperature	93(2) K
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁ (#19)
Unit cell dimensions	a = 6.96810(10) Å b = 9.1696(2) Å c = 20.5119(4) Å
Volume	1310.60(4) Å ³
Z	4
Density (calculated) [Mg/m ³]	1.804
μ (mm ⁻¹)	2.340
F(000)	696.00
No. of reflections	12088
Independent reflections	2391 [R(int) = 0.089]
No. of parameters	156
Completeness to θ (%)	99.9
GOF	0.838
R_1 [$I > 2\sigma(I)$]	0.0392
wR_2 (all data)	0.0465
Flack Parameter	0.03(4) (Friedel pairs: 977)
Largest diff. peak and hole [e ⁻ /Å ⁻³]	0.73 and -0.81

7. ^1H , ^{13}C NMR spectra, and chiral HPLC charts

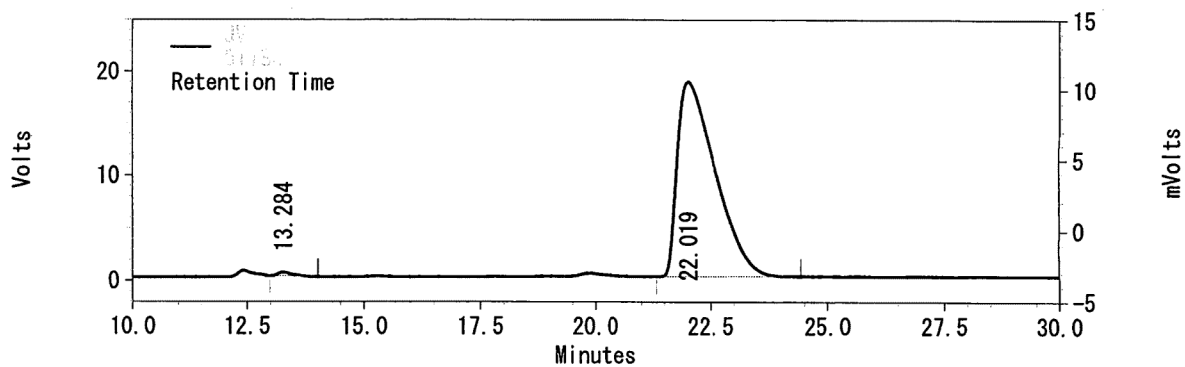






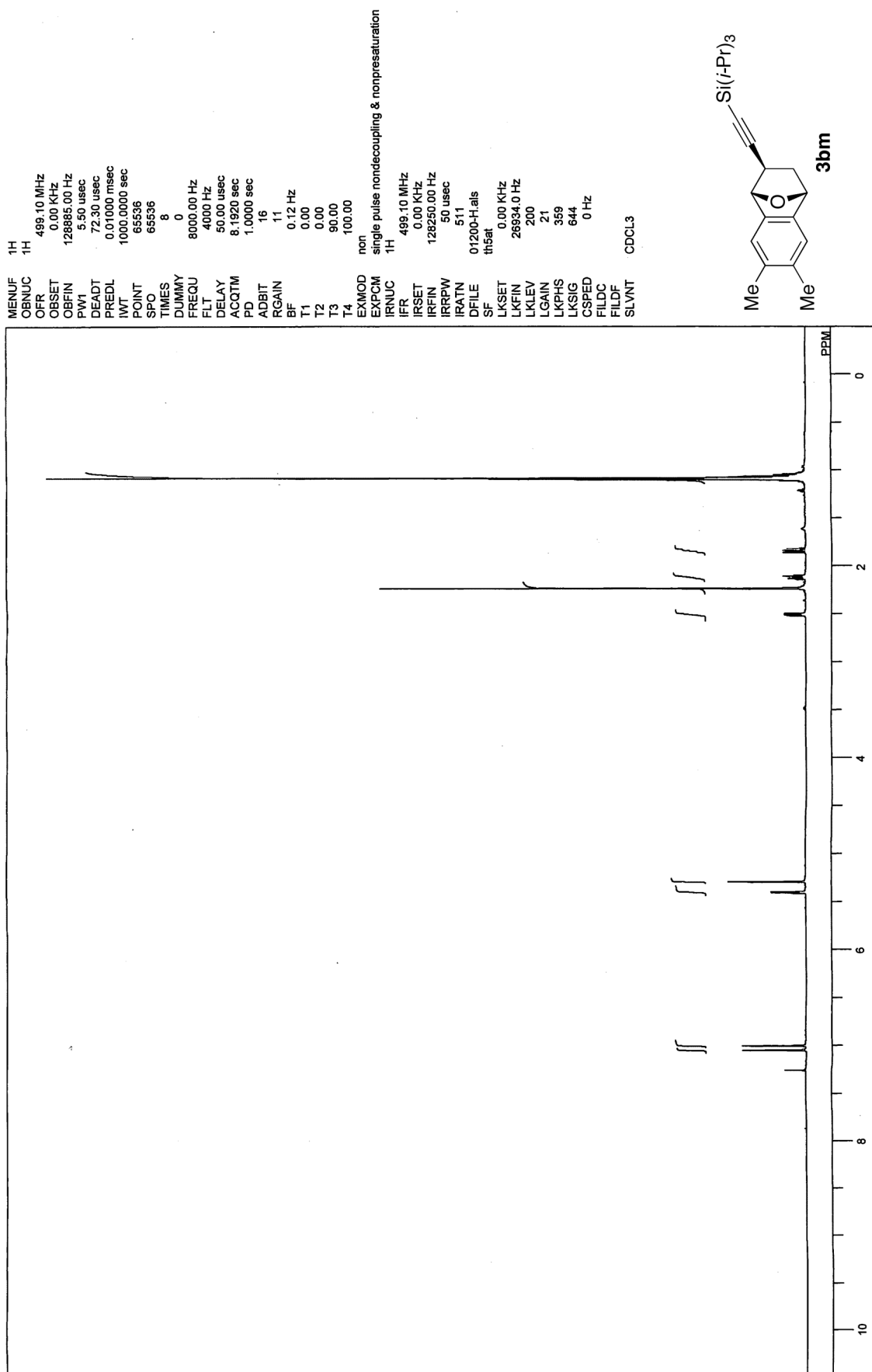
UV Results

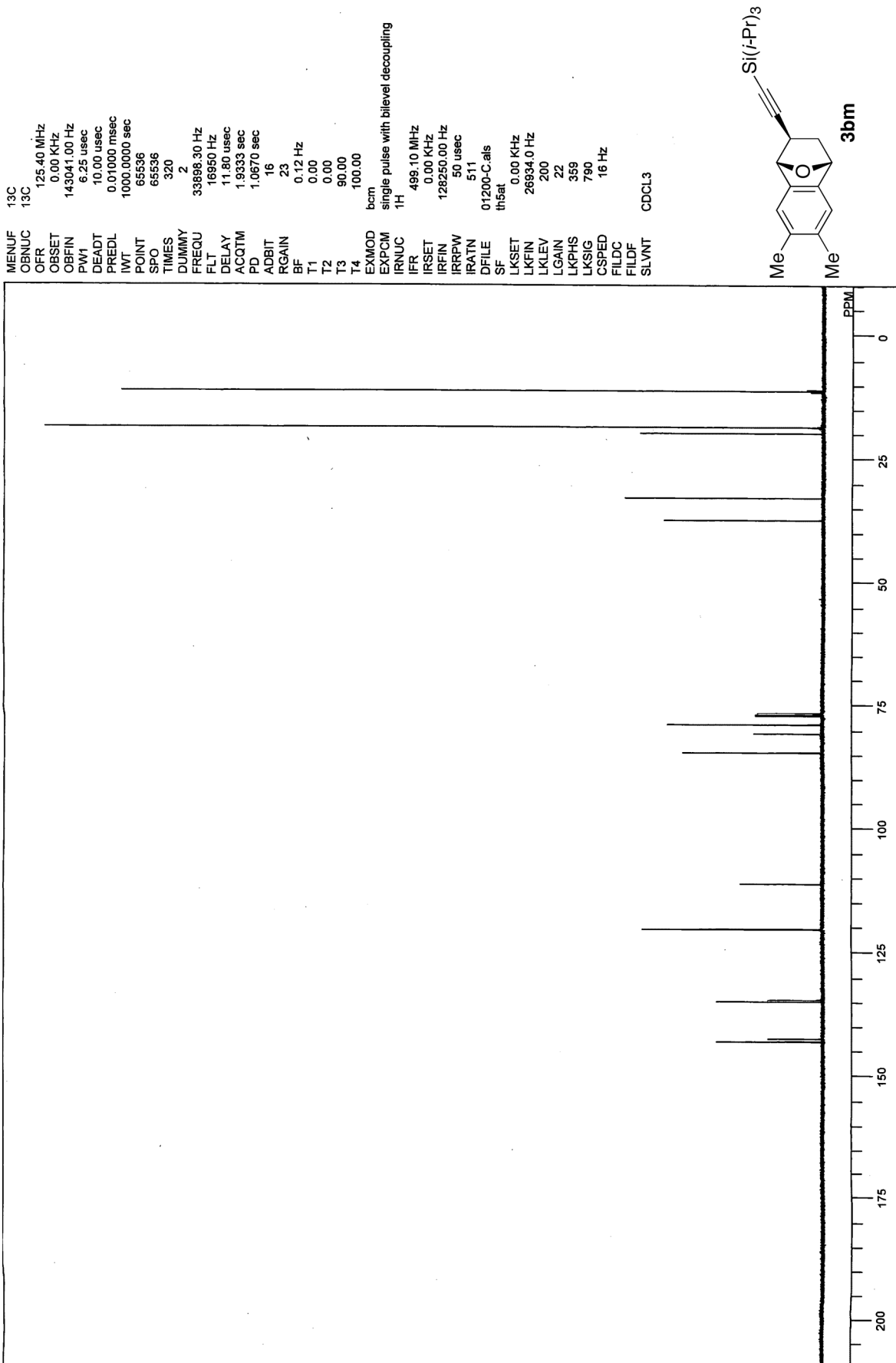
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2	23.573	8013965	50.248	79596
Totals		15948843	100.000	252925

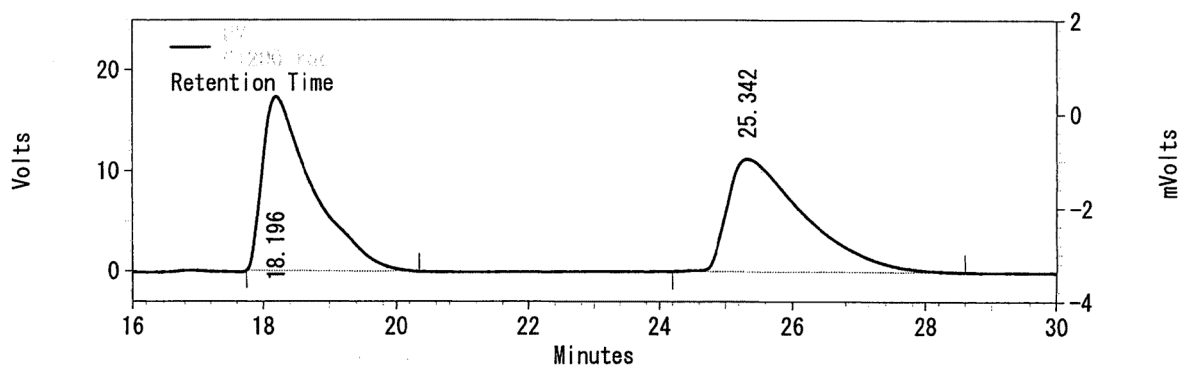
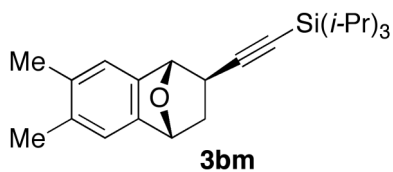


UV Results

Pk #	Retention Time	Area	Area Percent	Height
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Totals		1075064	100.000	18982

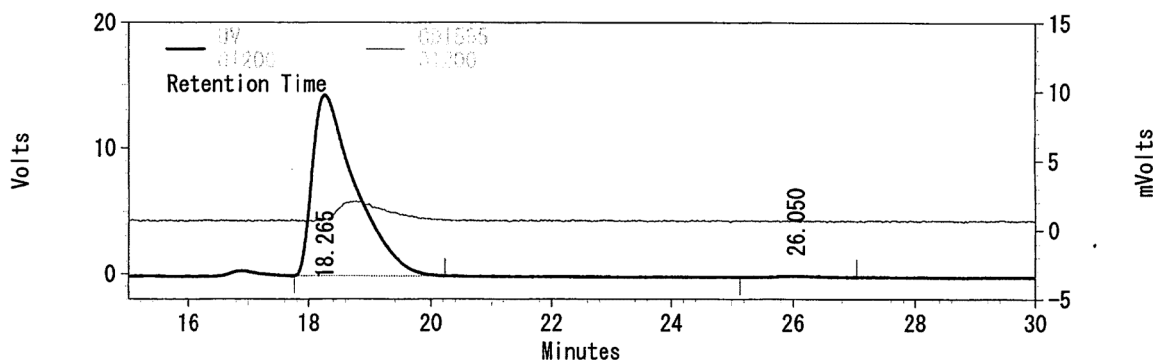






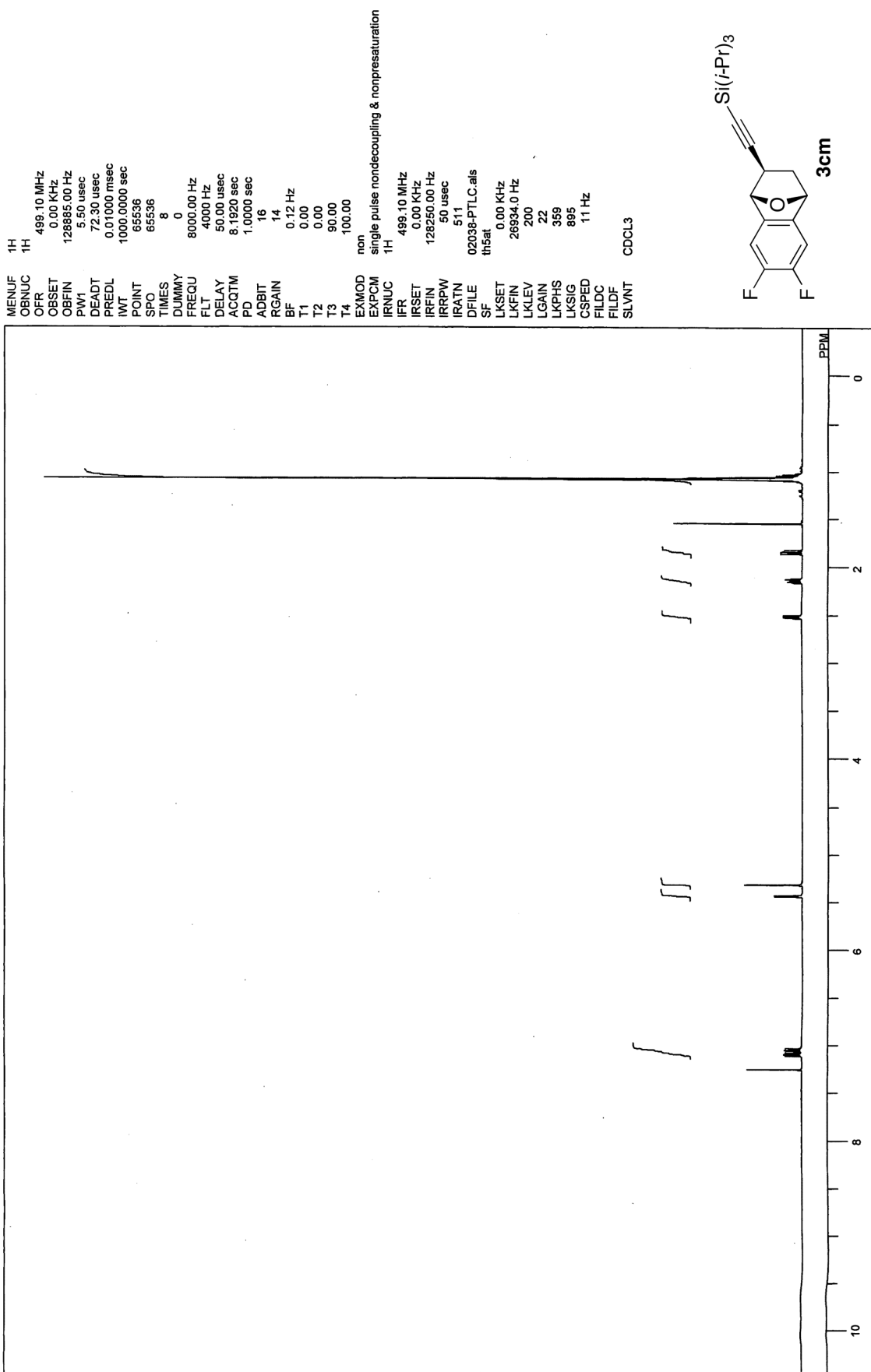
UV Results

Pk #	Retention Time	Area	Area Percent	Height
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Totals		1804811	100.000	28579

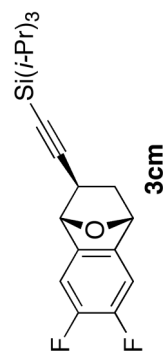
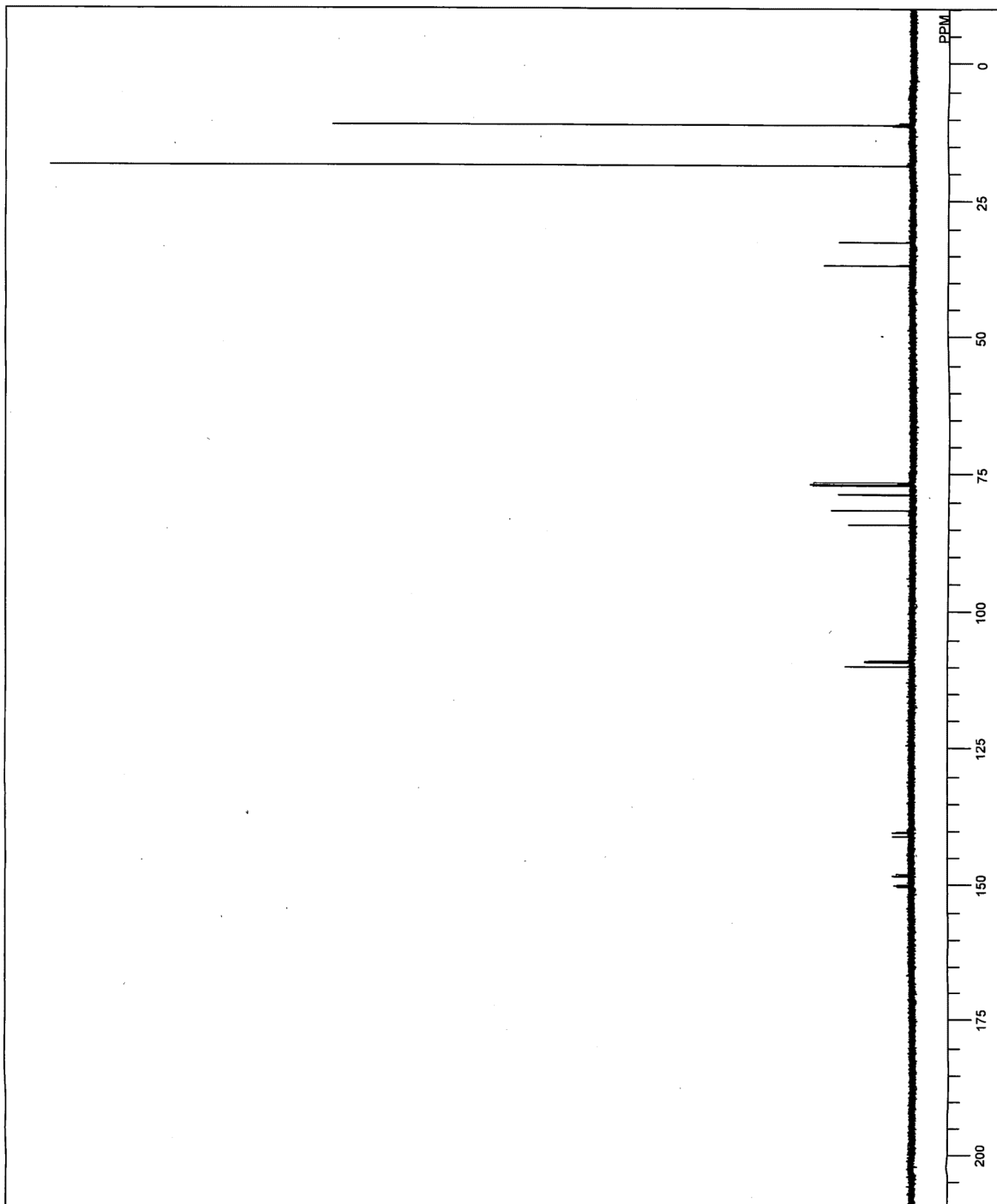


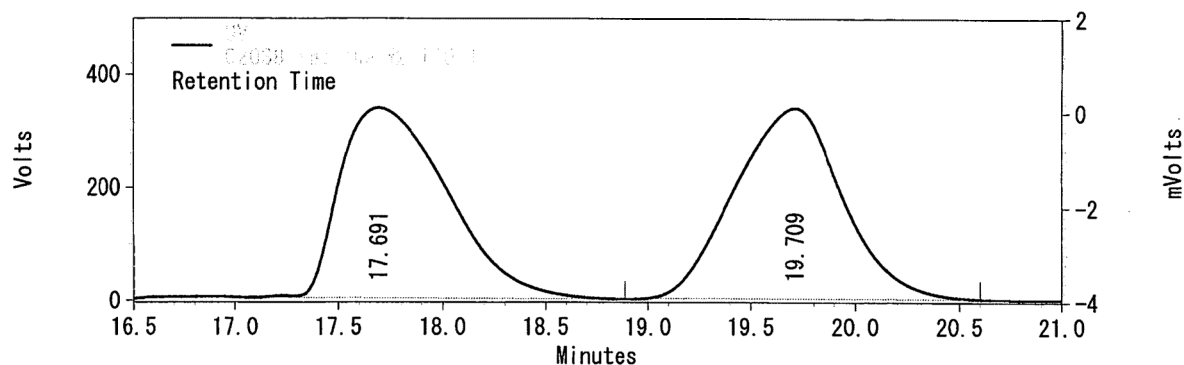
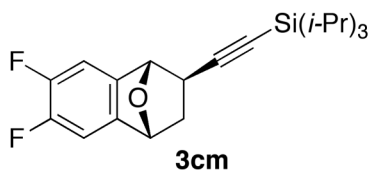
UV Results

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Totals		706014	100.000	14420



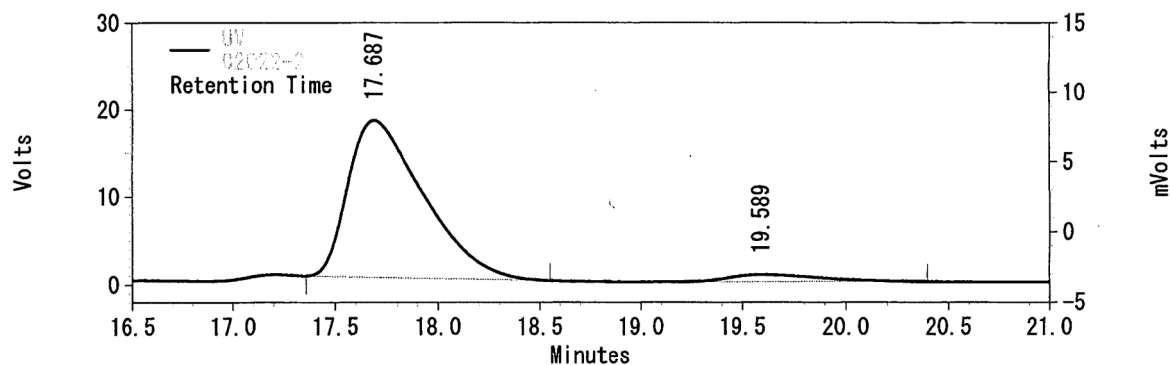
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 OFR 0.00 KHz
 OBSSET 143041.00 Hz
 OBFIN 6.25 usec
 PW1 10.00 usec
 DEADT 0.01000 msec
 PREDL 1000.0000 sec
 IWT 65536
 POINT SPO 65536
 SPO 320
 TIMES 2
 DUMMY 33868.30 Hz
 FREQU 16960 Hz
 FLT 11.80 usec
 DELAY 1.9333 sec
 ACQTM 1.0670 sec
 PD 16
 ADBIT 24
 RGAIN 0.12 Hz
 BF 0.00
 T1 0.00
 T2 90.00
 T3 100.00
 T4
 EXMOD bcm
 EXPCM single pulse with bilevel decoupling
 IRNUC 1H
 IFR 499.10 MHz
 IRSET 0.00 KHz
 IRFIN 128250.00 Hz
 IRRPW 50 usec
 IRATN 511
 DFILE 02022-C.als
 SF th5at
 LKSET 0.00 KHz
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 LGAIN 21
 LKPHS 359
 LKSIG 612
 CSPED 16 Hz
 FILDC
 FILDF
 SLVNT CDCL3





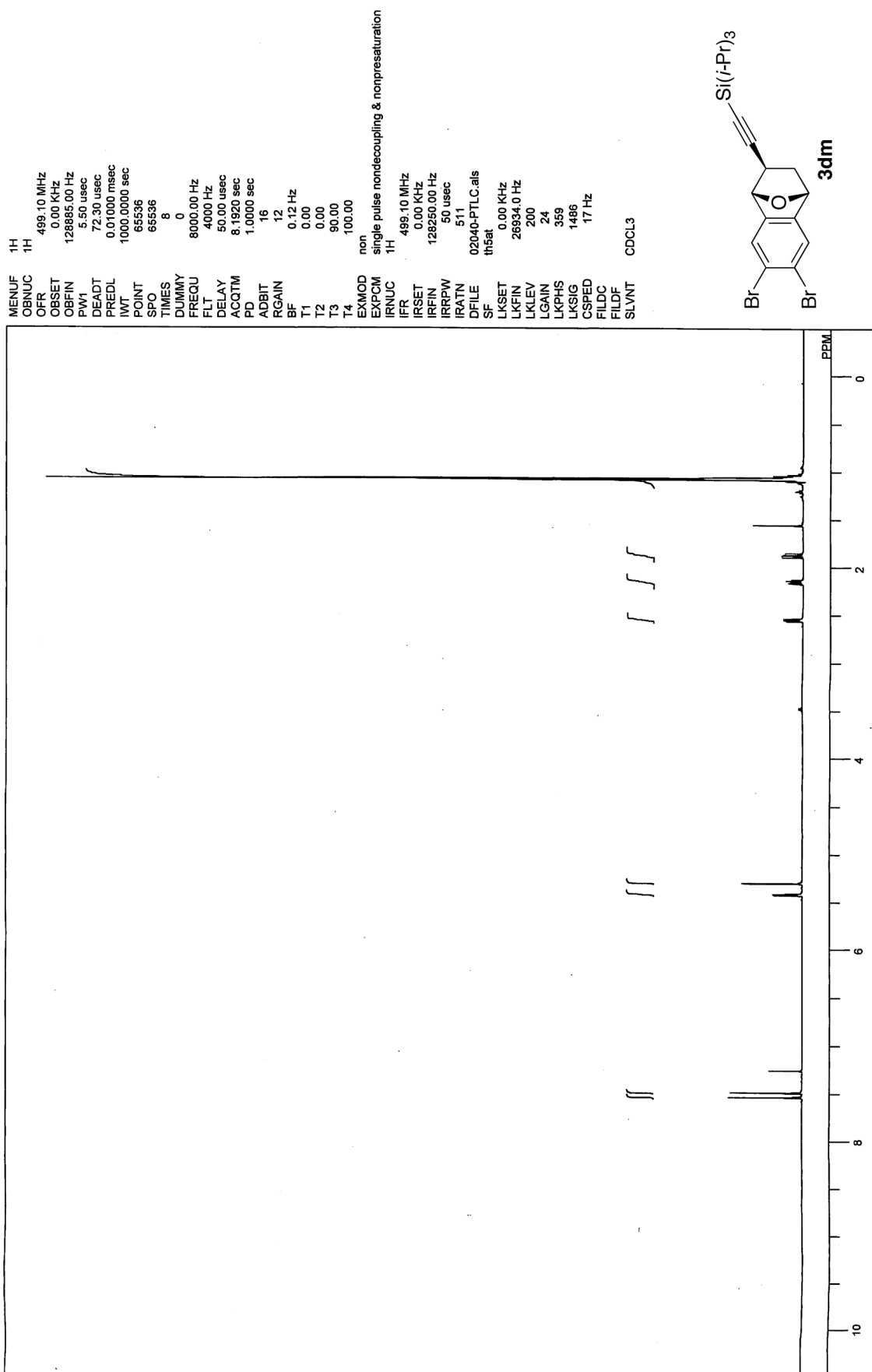
UV Results

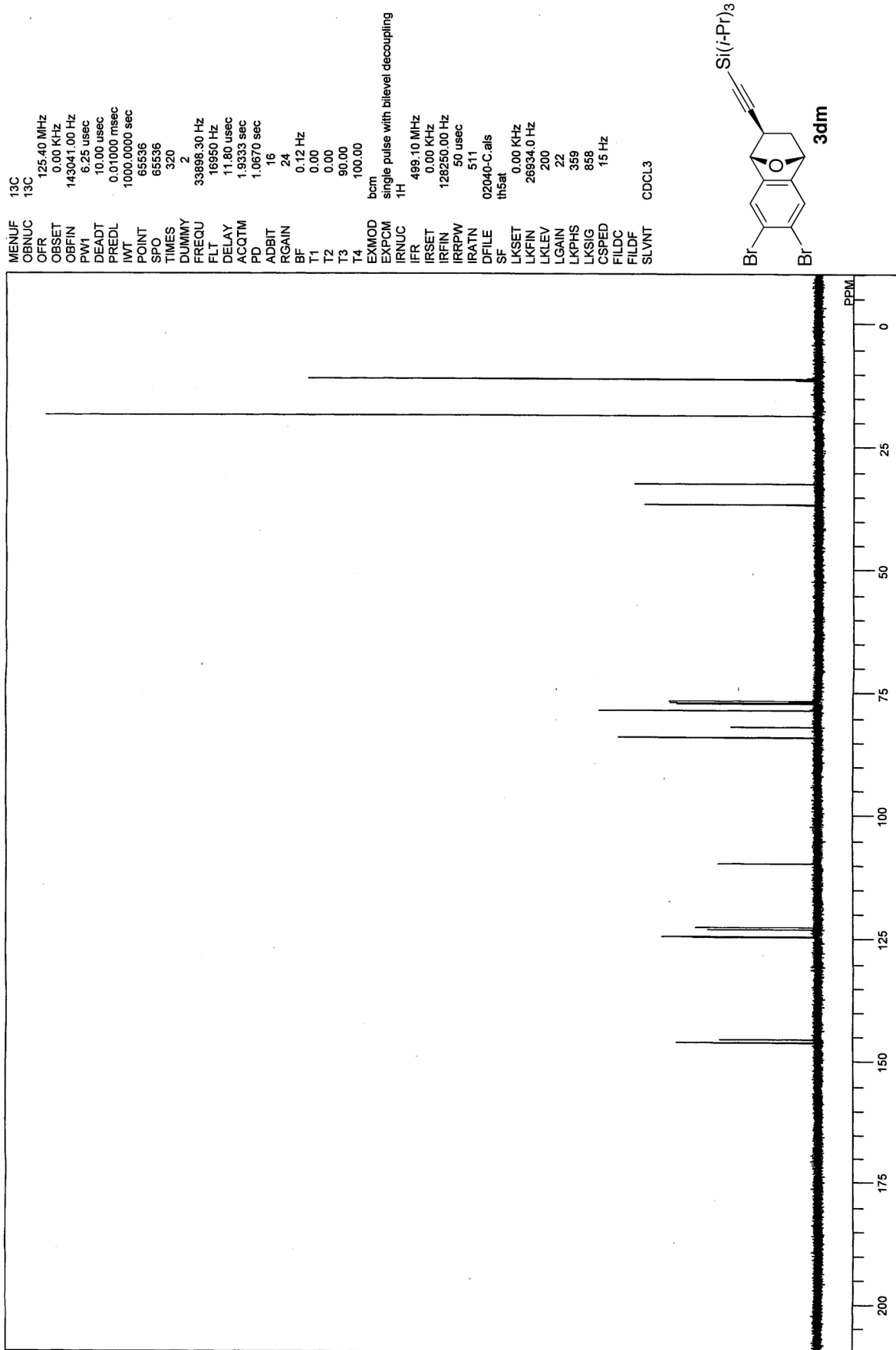
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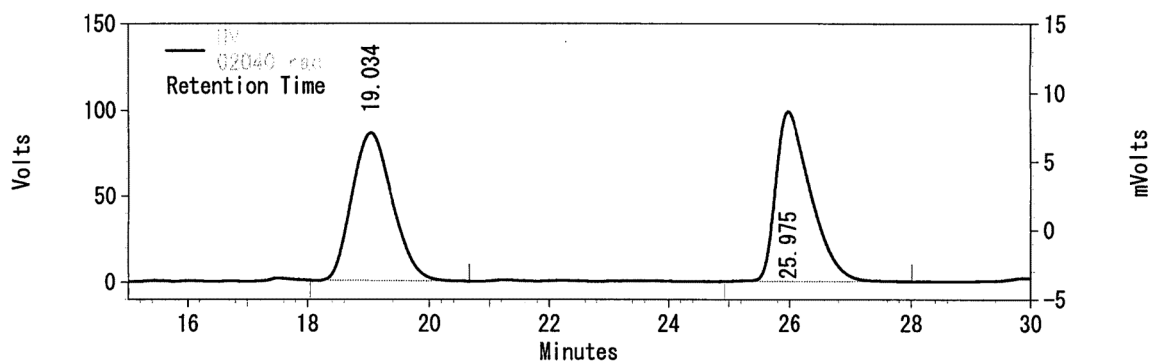
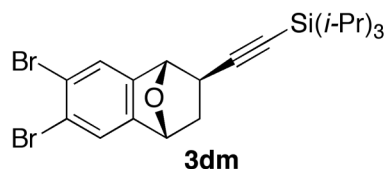


UV Results

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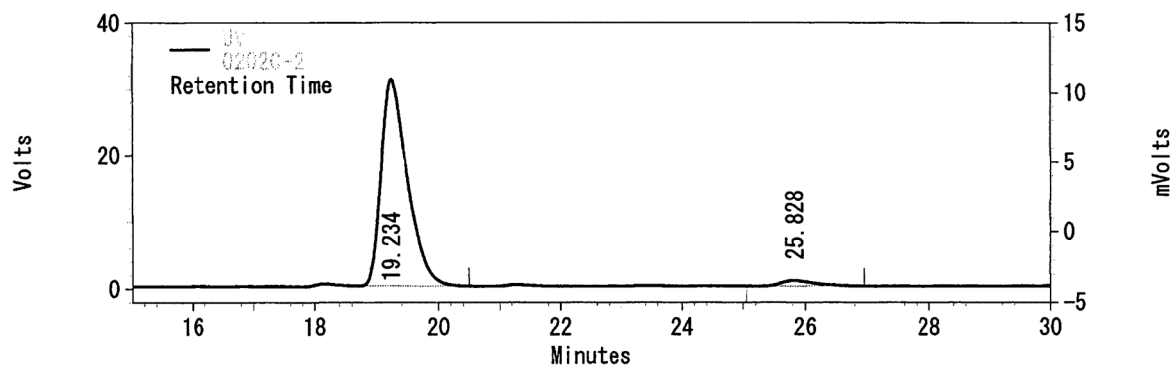






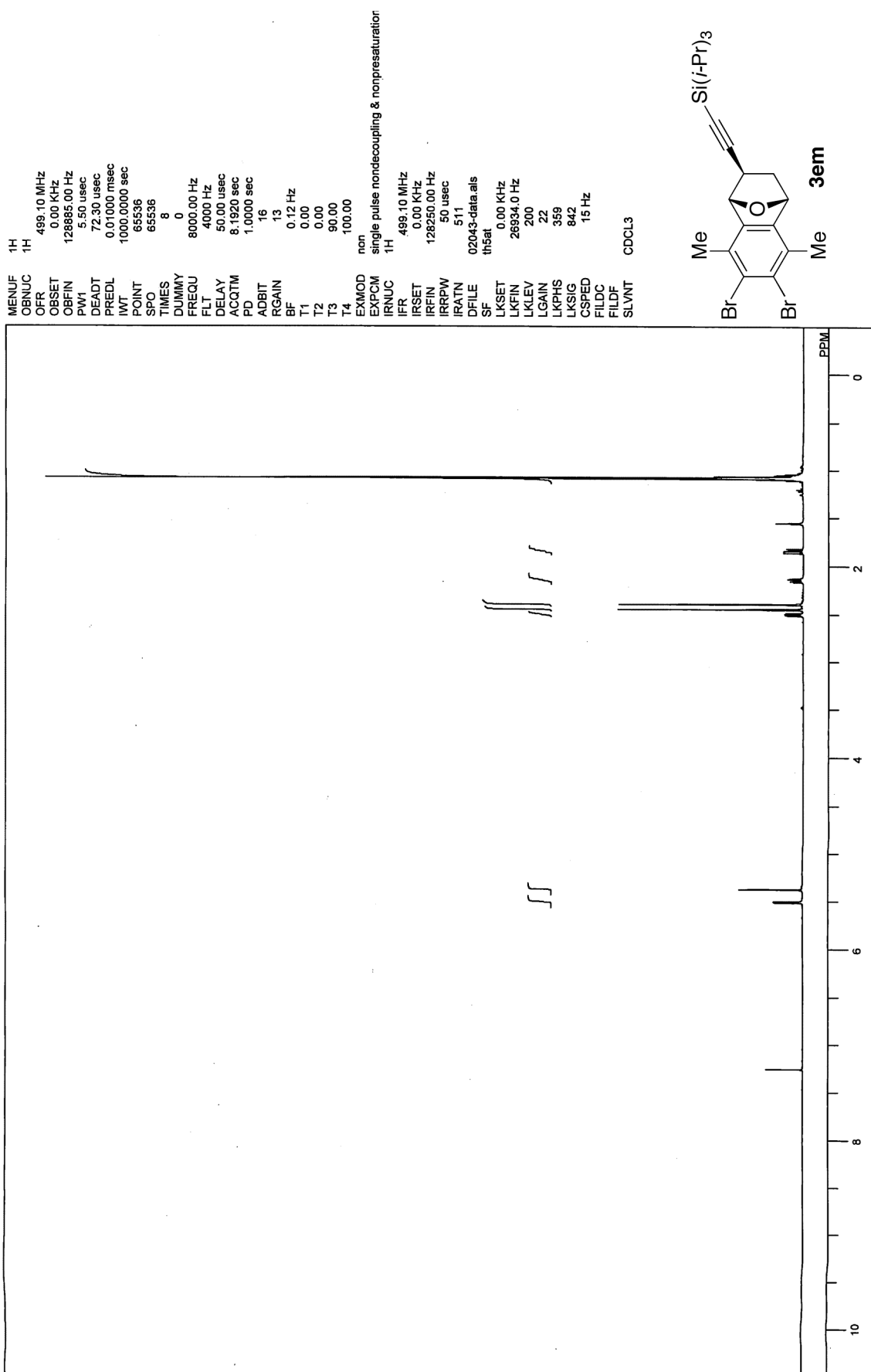
UV Results

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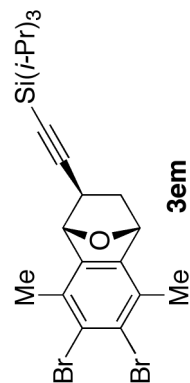
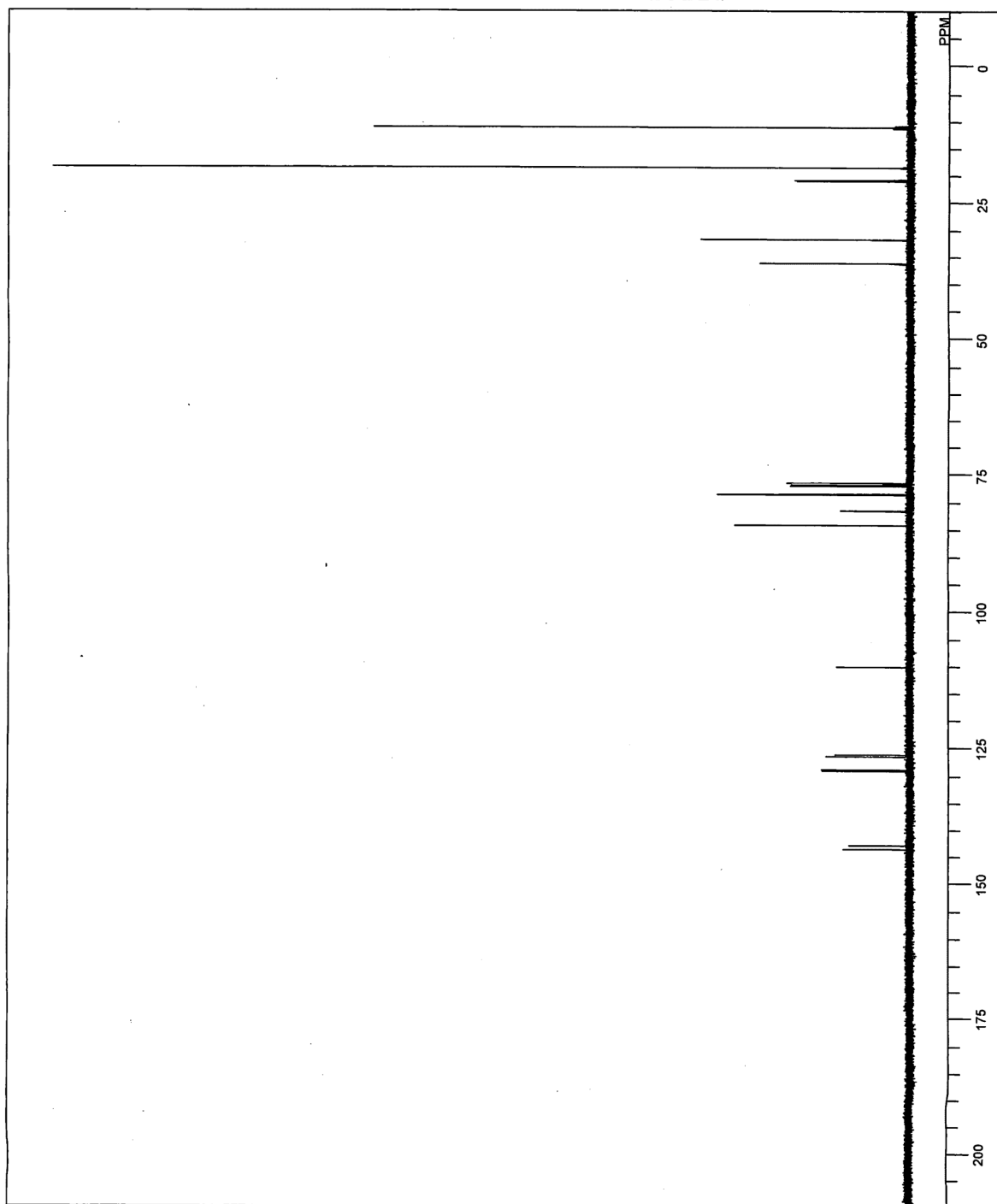


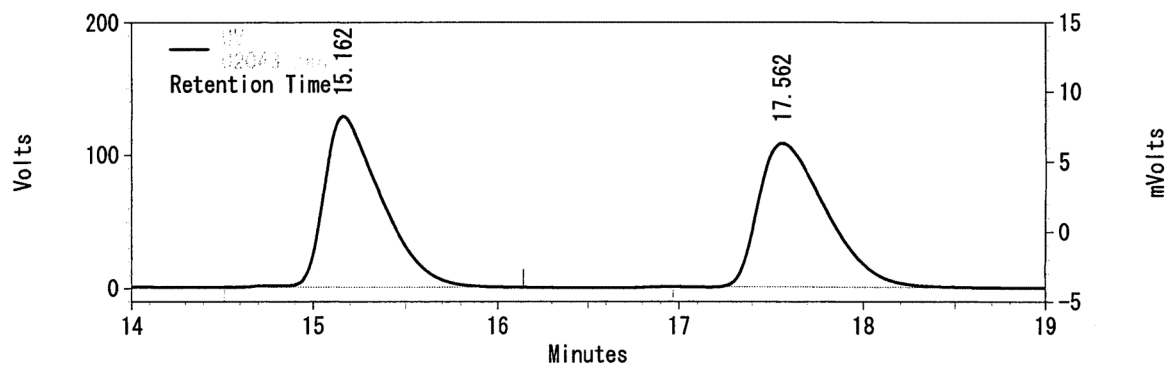
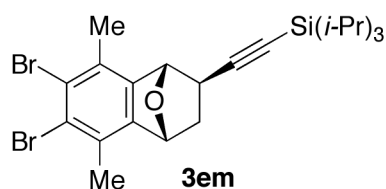
UV Results

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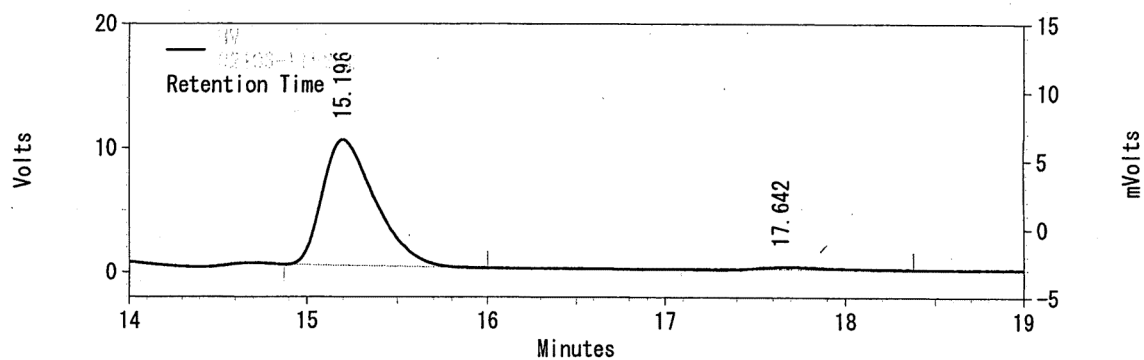
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 320
 2
 33898.30 Hz
 16950 Hz
 11.80 usec
 1.9333 sec
 1.0670 sec
 16
 24
 0.12 Hz
 0.00
 0.00
 90.00
 100.00
 bcm
 single pulse with bilevel decoupling
 1H
 499.10 MHz
 0.00 KHz
 128250.00 Hz
 50 usec
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 th5at
 SF
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 21
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 640
 13 Hz
 CDCL3
 CDCL3





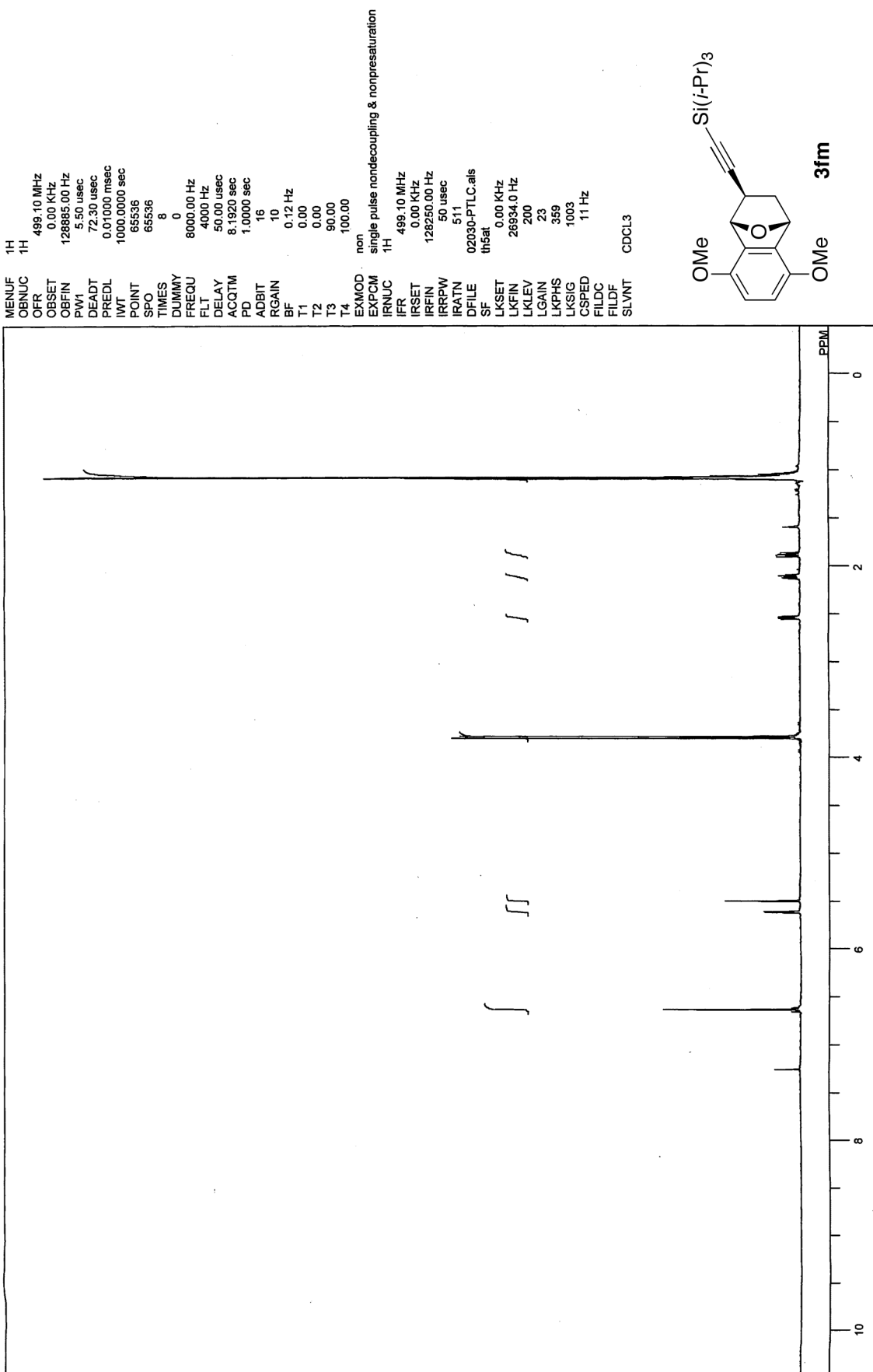
UV Results

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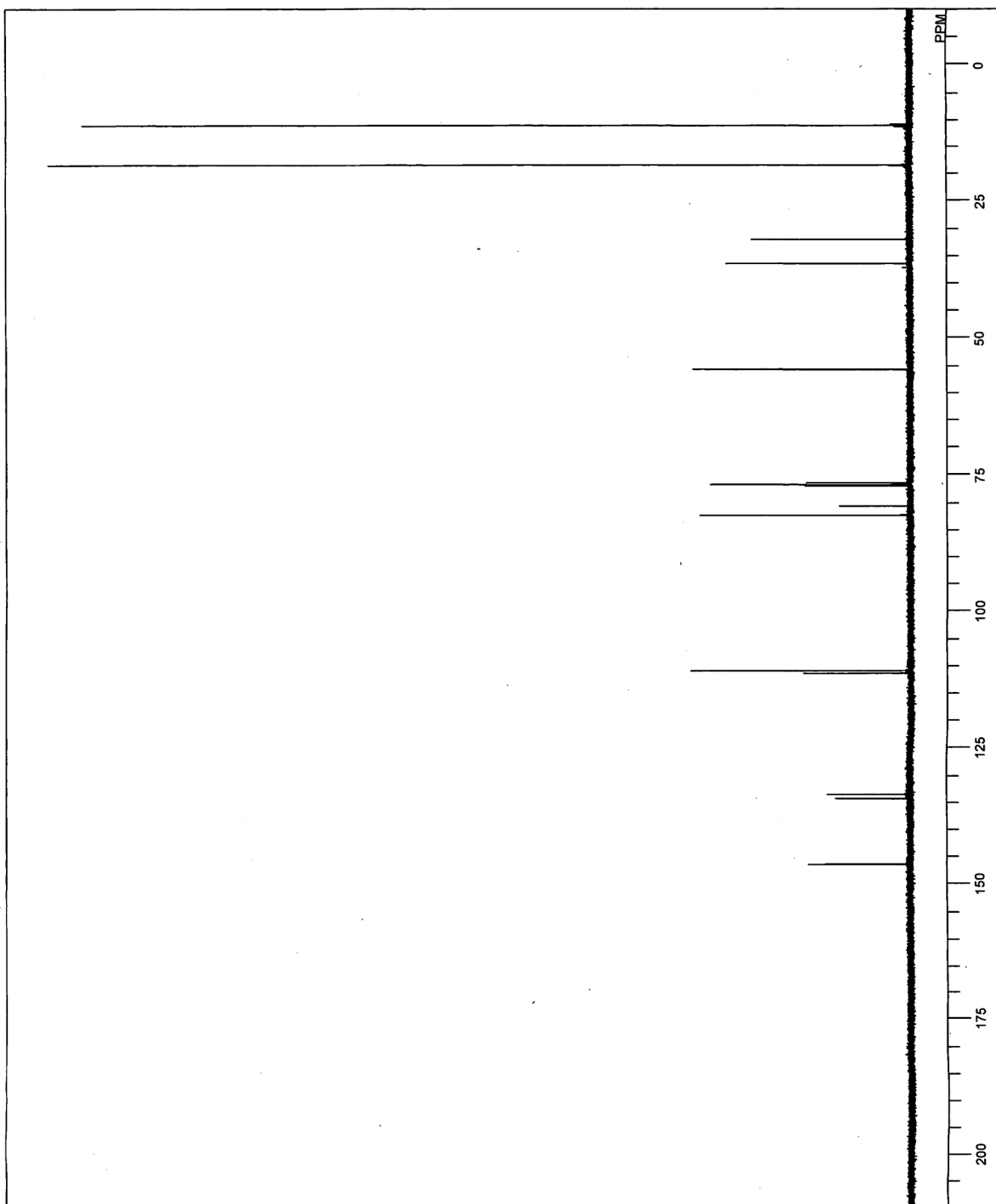


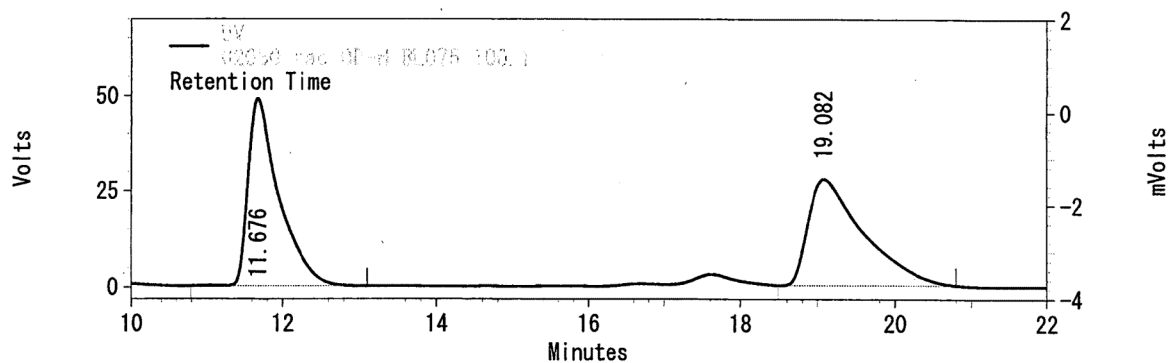
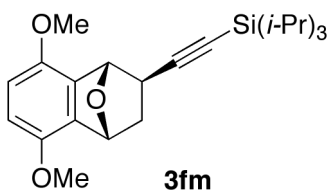
UV Results

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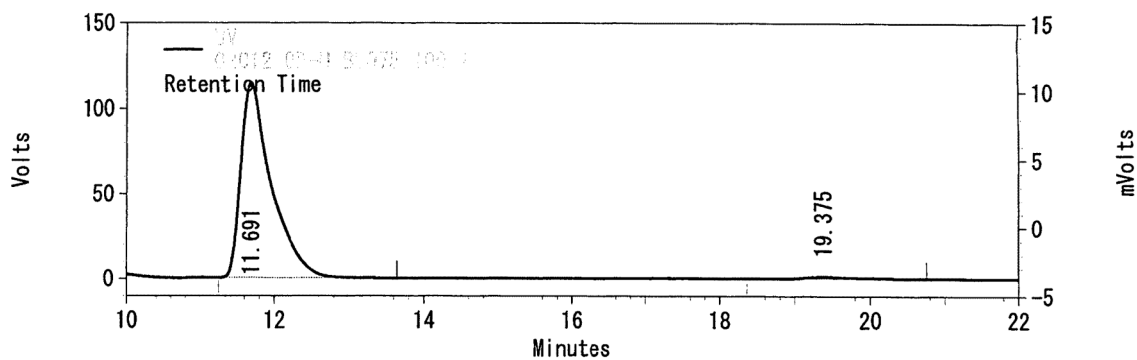
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PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 320
DUMMY 2
FREQ 33898.30 Hz
FLT 16950 Hz
DELAY 11.80 usec
ACQTM 1.9333 sec
PD 1.0670 sec
ADBIT 16
RGAIN 23
BF 0.12 Hz
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T2 0.00
T3 90.00
T4 100.00
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EXPCM single pulse with bilevel decoupling
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IFR 499.10 MHz
IRSET 0.00 KHz
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DFILE 02012-C.als
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LKSET 0.00 KHz
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LKSIG 773
CSPED 16 Hz
FILDC
FILDF
SLVNT CDCL3





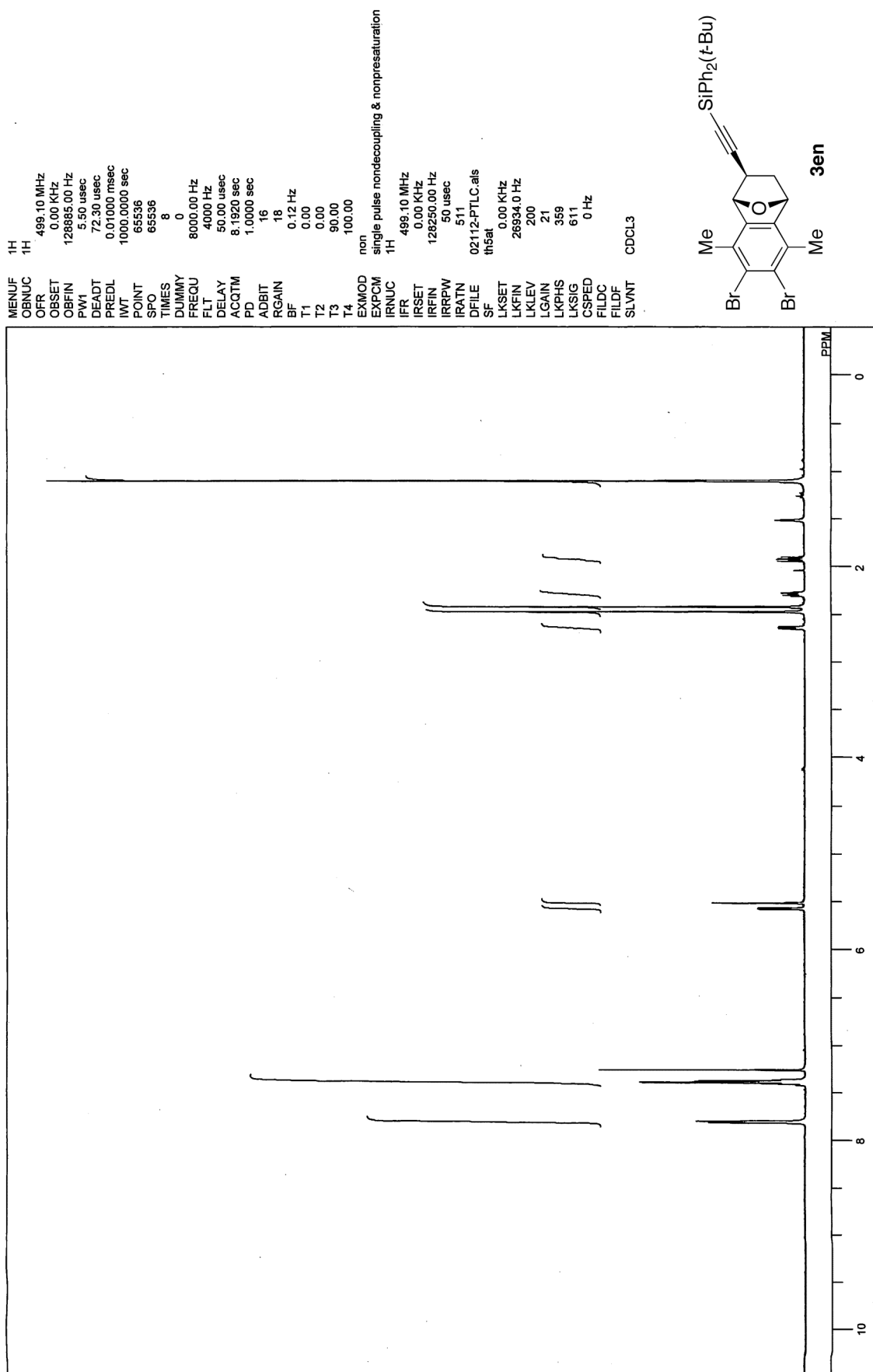
UV Results

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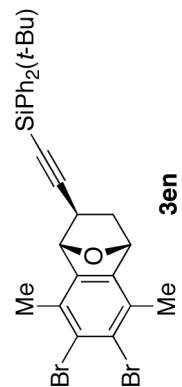
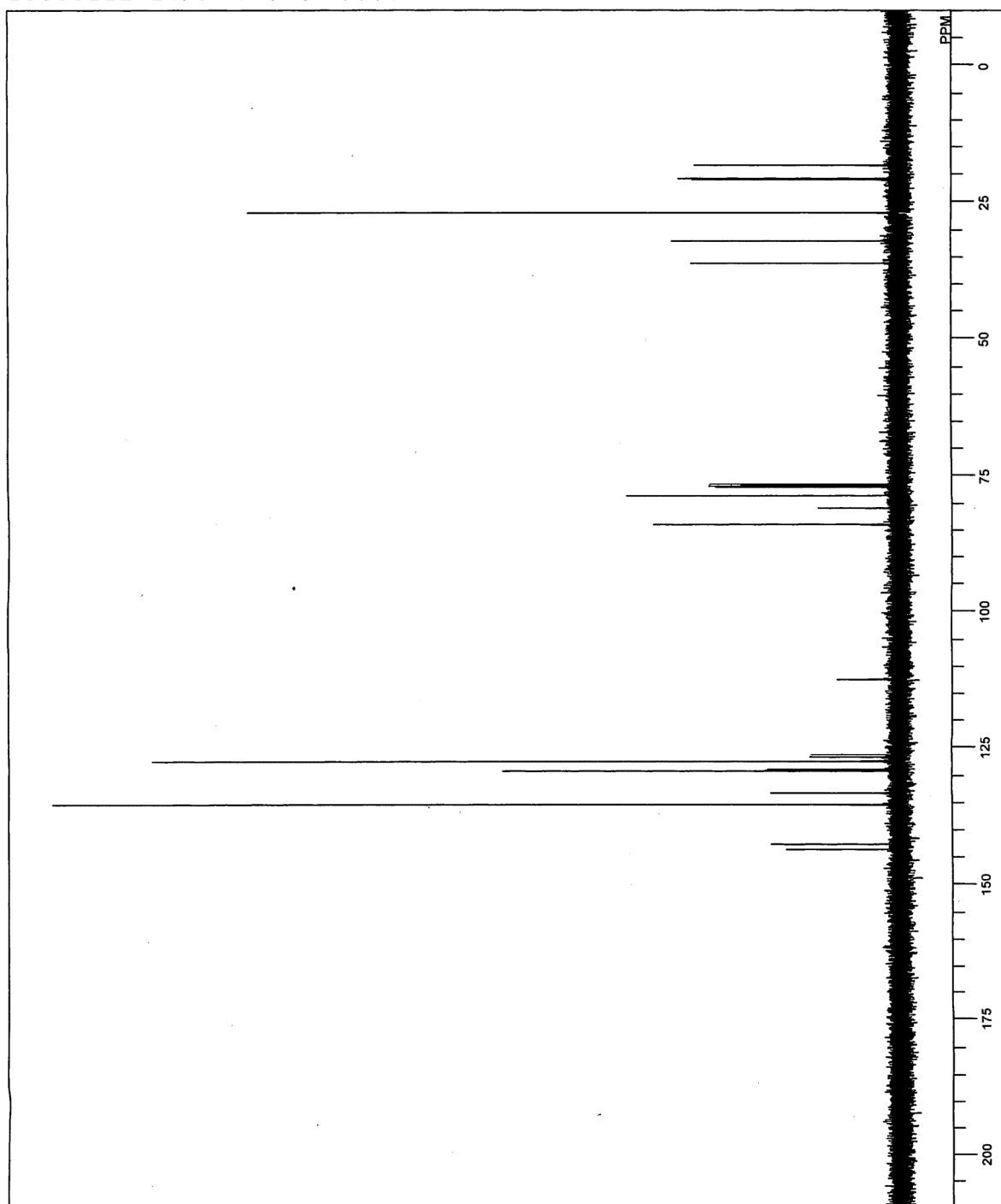


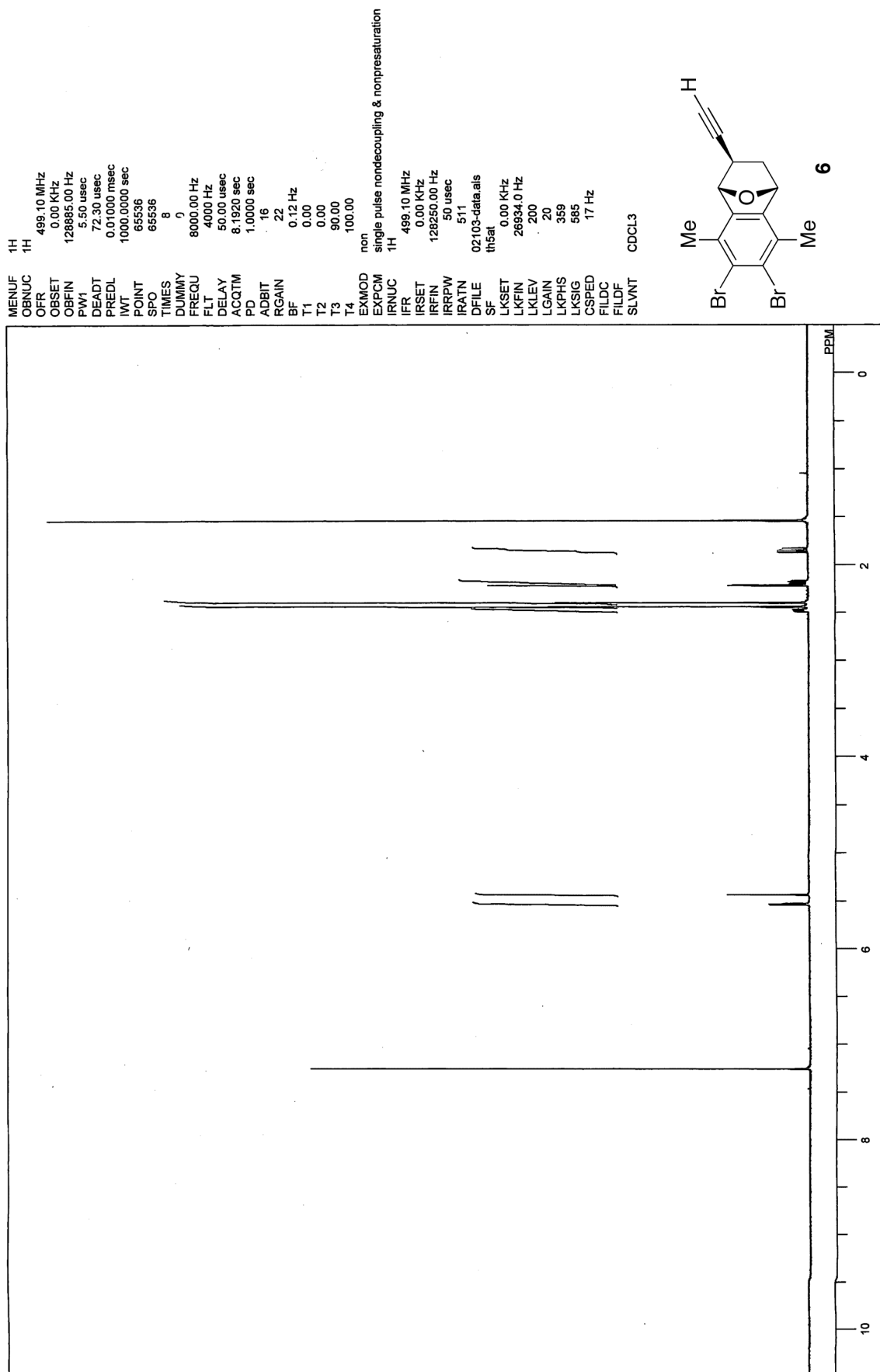
UV Results

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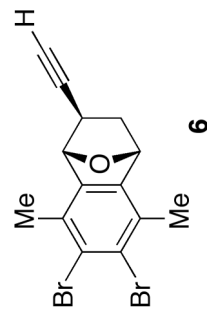
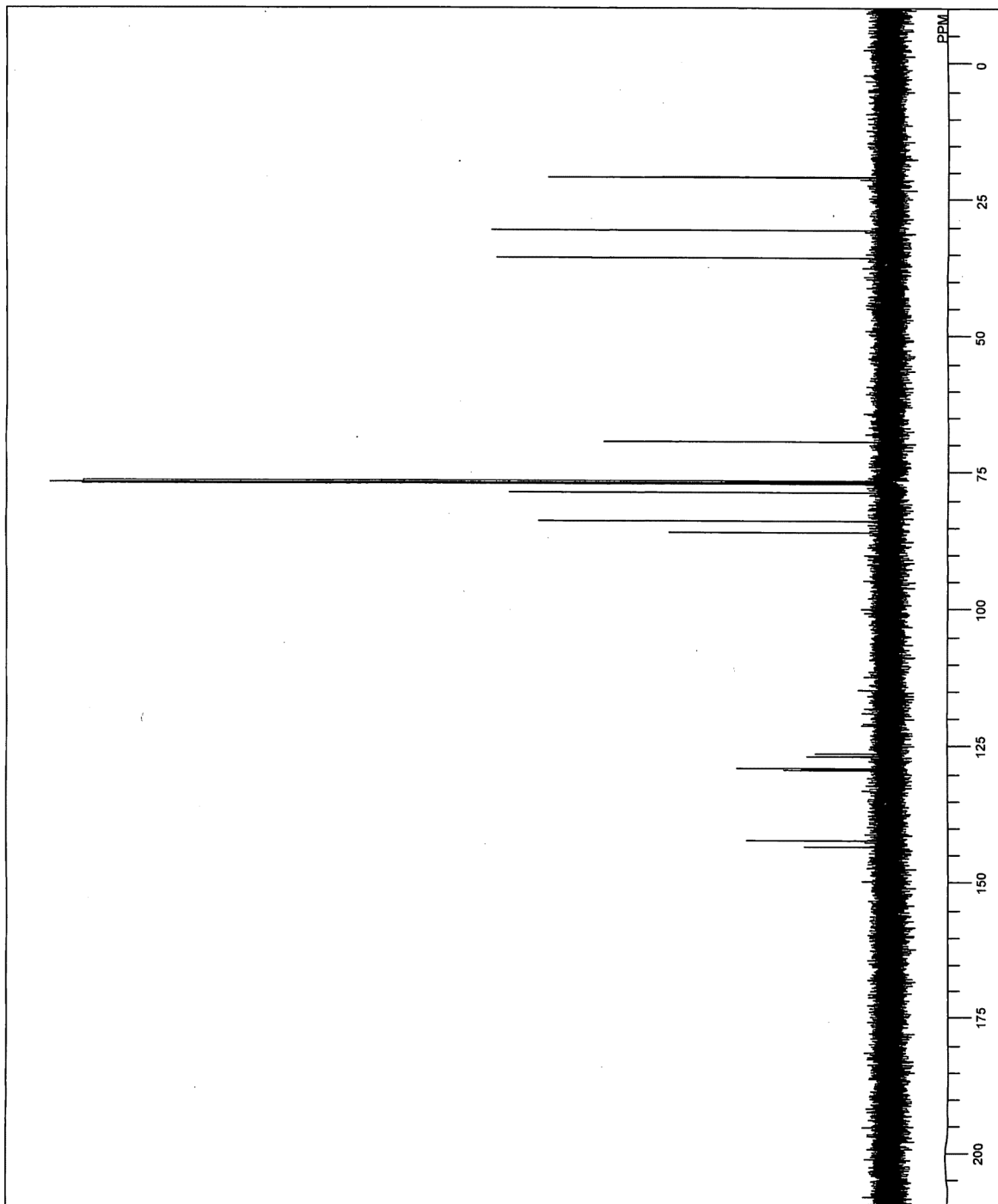


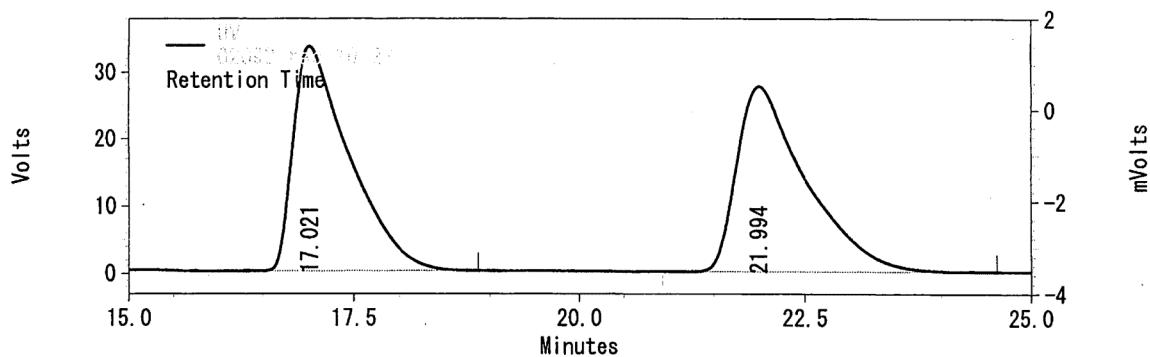
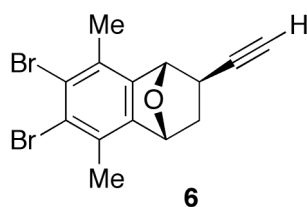
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OBNUC 13C
OFR 125.40 MHz
OBSET 0.00 KHz
OBFIN 143041.00 Hz
PW1 6.25 usec
DEADT 10.00 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 320
DUMMY 2
FREQU 33898.30 Hz
FLT 16950 Hz
DELAY 11.80 usec
ACQTM 1.9333 sec
PD 1.0670 sec
ADBIT 16
RGAIN 24
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD bcm
EXPCM single pulse with bilevel decoupling
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE 02112-C(4).ais
SF th5at
LKSET 0.00 KHz
LKFIN 26834.0 Hz
LKLEV 200
LGAIN 26
LKPHS 359
LKSIG 1347
CSPED 15 Hz
FILDC
FILDF
SLVNT CDCL3





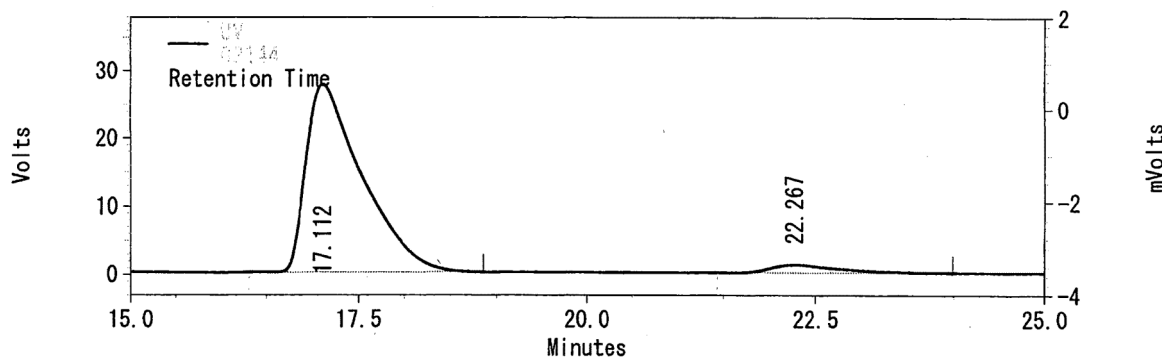
MENUF 13C
OBRUC 13C
OFR 125.40 MHz
OBSET 0.00 KHz
OBFIN 143041.00 Hz
PW1 6.25 usec
DEADT 10.00 usec
PREDL 0.01000 msec
IWT 1000.0000 sec
POINT 65536
SPO 65536
TIMES 320
DUMMY 2
FREQU 33698.30 Hz
FLT 16950 Hz
DELAY 11.80 usec
ACQTM 1.8333 sec
PD 1.0670 sec
ADBIT 16
RGAIN 25
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD bcm
EXPCM single pulse with bilevel decoupling
IRNUC 1H
IFR 499.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE 02067-C(5).als
SF th5at
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 22
LKPHS 359
LKSIG 694
CSPED 15 Hz
FILDC
FILDF
SLVNT CDCL3





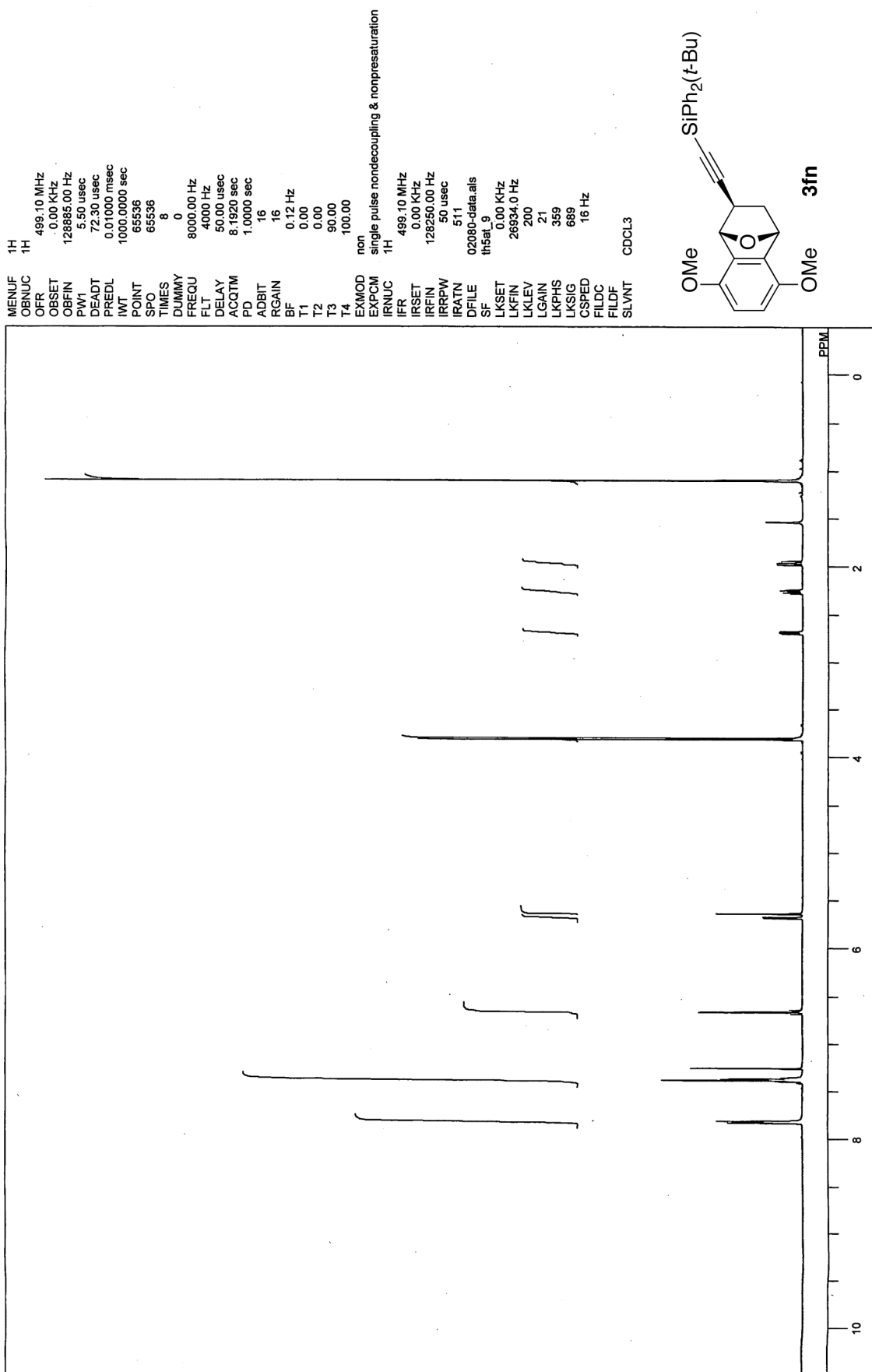
UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	17.021	1433486	49.883	33469
2	21.994	1440231	50.117	27586
Totals		2873717	100.000	61055

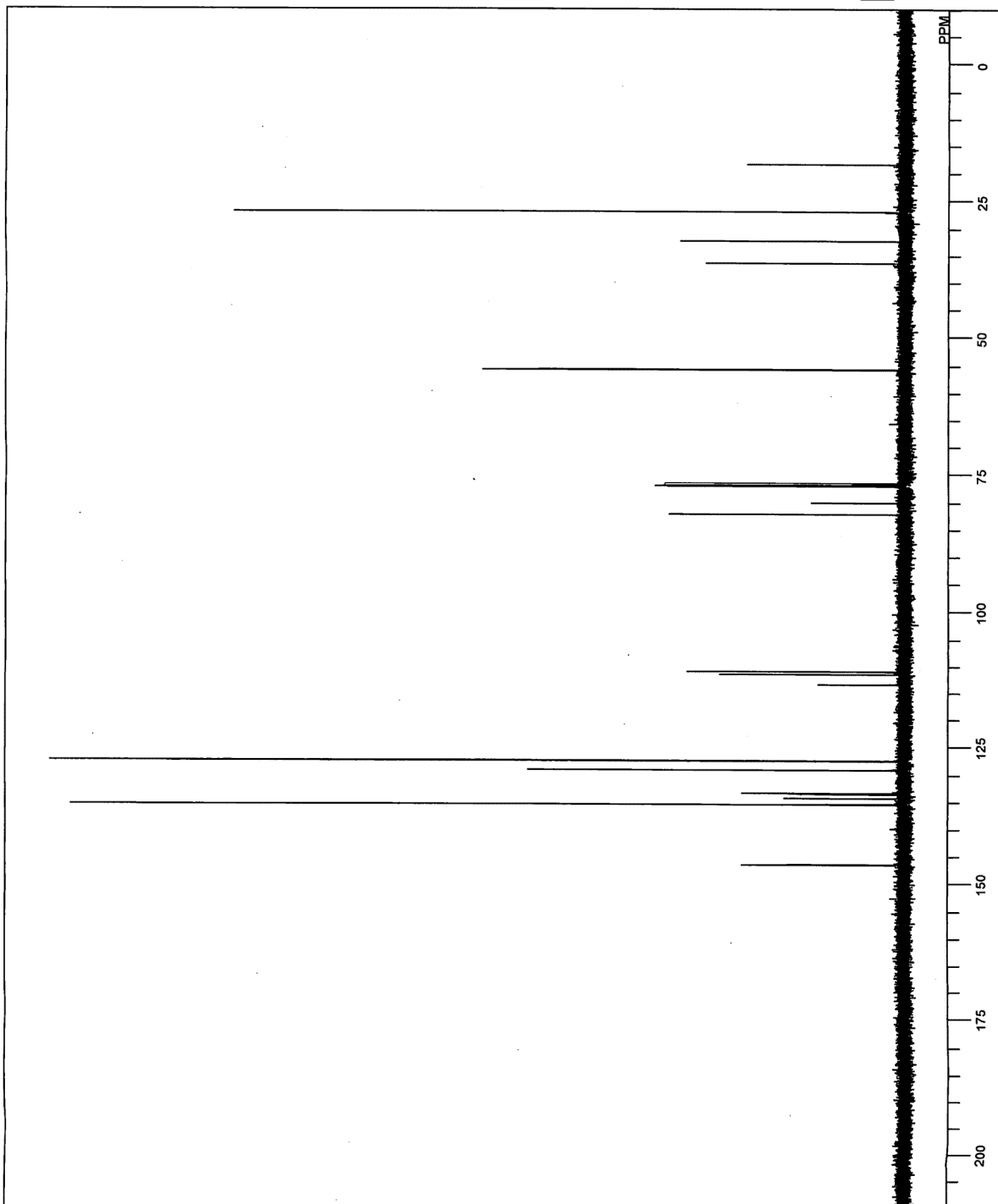


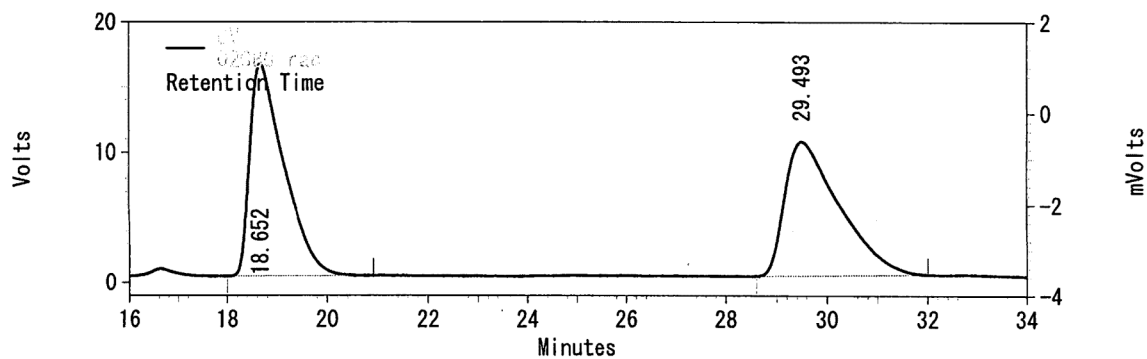
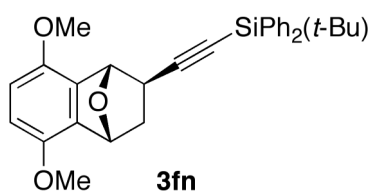
UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	17.112	1165100	95.085	27662
2	22.267	60226	4.915	1194
Totals		1225326	100.000	28856



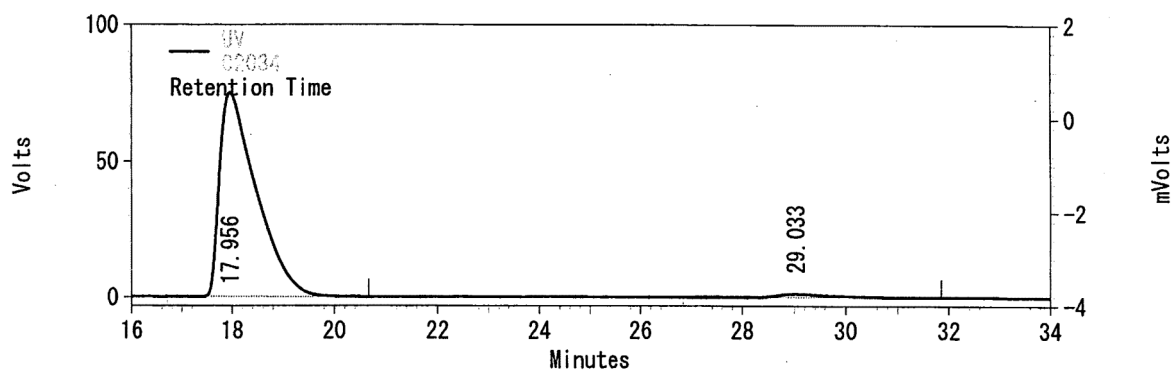
13C
MENUMF 13C
OBNUC 125.40 MHz
OFR 0.00 KHz
OBSET 143041.00 Hz
ORFIN 6.25 usec
PW1 10.00 usec
DEADT 0.01000 msec
PREDL 1000.0000 sec
IWT 65536
POINT 320
SPO 2
TIMES 33898.30 Hz
DUMMY 16950 Hz
FREQU 11.80 usec
FLT 1.9333 sec
DELAY 1.0670 sec
ACCTM 16
PD 25
ADBIT 0.12 Hz
RGAIN 0.00
BF 0.00
T1 90.00
T2 100.00
T3
T4
EXMOD bcm
EXPCM single pulse with bilevel decoupling
IRNUC 1H
IFR 489.10 MHz
IRSET 0.00 KHz
IRFIN 128250.00 Hz
IRRPW 50 usec
IRATN 511
DFILE th5at_8
SF 02080-C.als
LKSET 0.00 KHz
LKFIN 26934.0 Hz
LKLEV 200
LGAIN 23
LKPHS 359
LKSIG 980
CSPED 16 Hz
FILDC
FILDF
SLVNT CDCL3





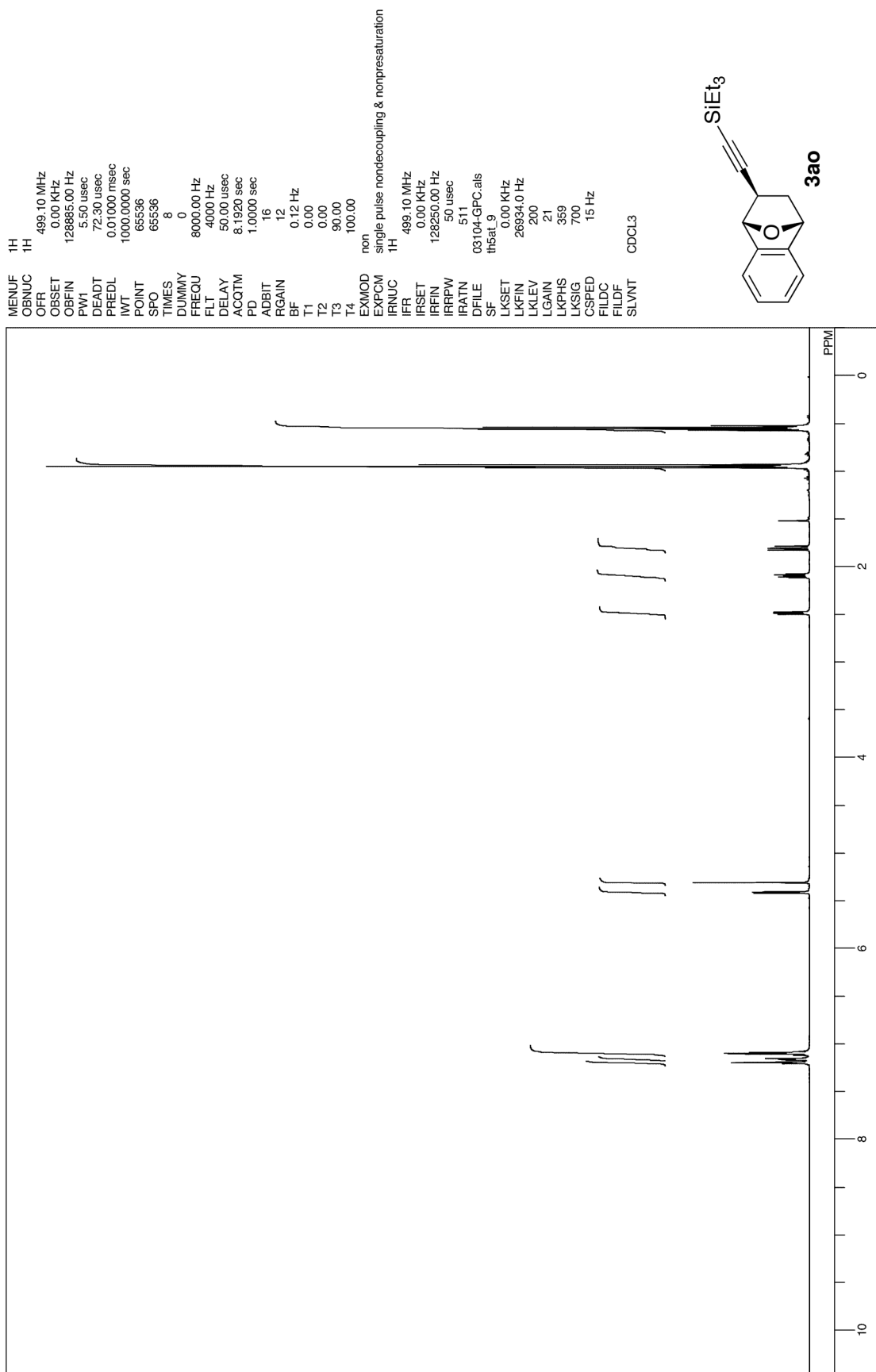
UV Results

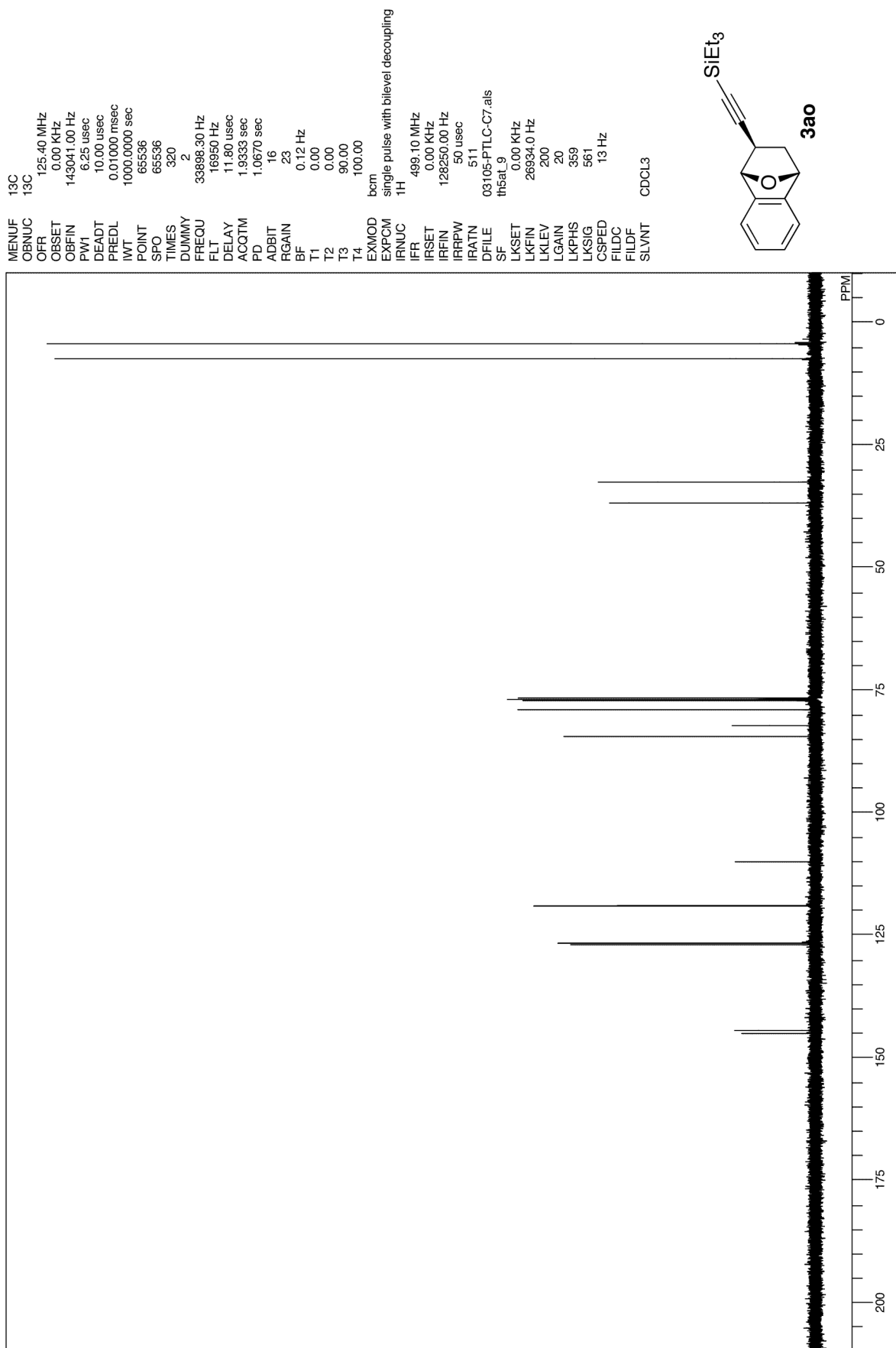
Pk #	Retention Time	Area	Area Percent	Height
1	18.652	773406	49.769	16242
2	29.493	780594	50.231	10298
Totals		1554000	100.000	26540

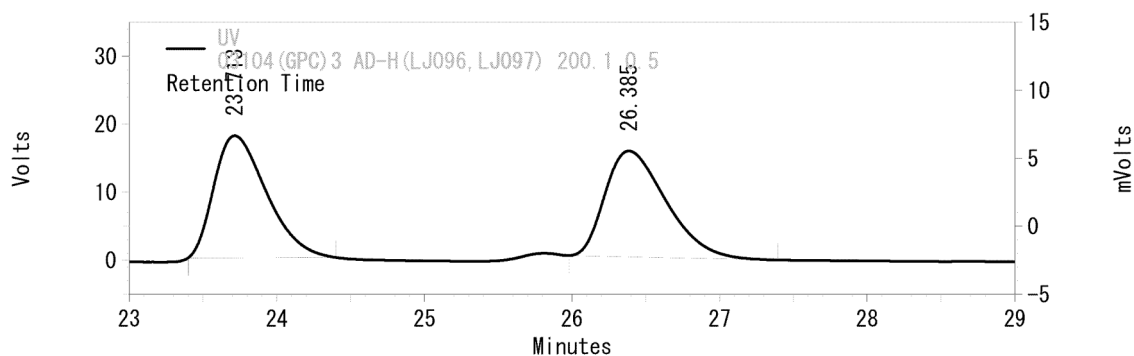
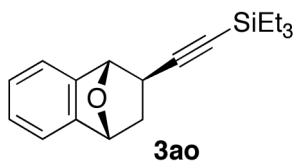


UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	17.956	3759936	97.942	74914
2	29.033	79018	2.058	1228
Totals		3838954	100.000	76142

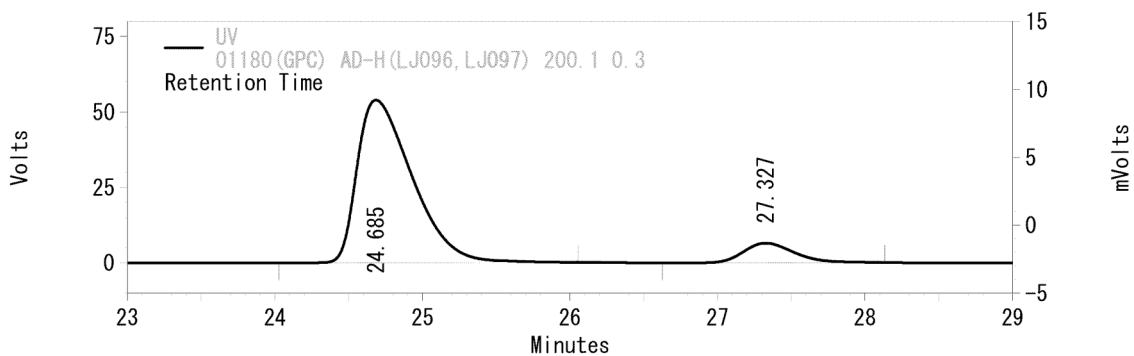






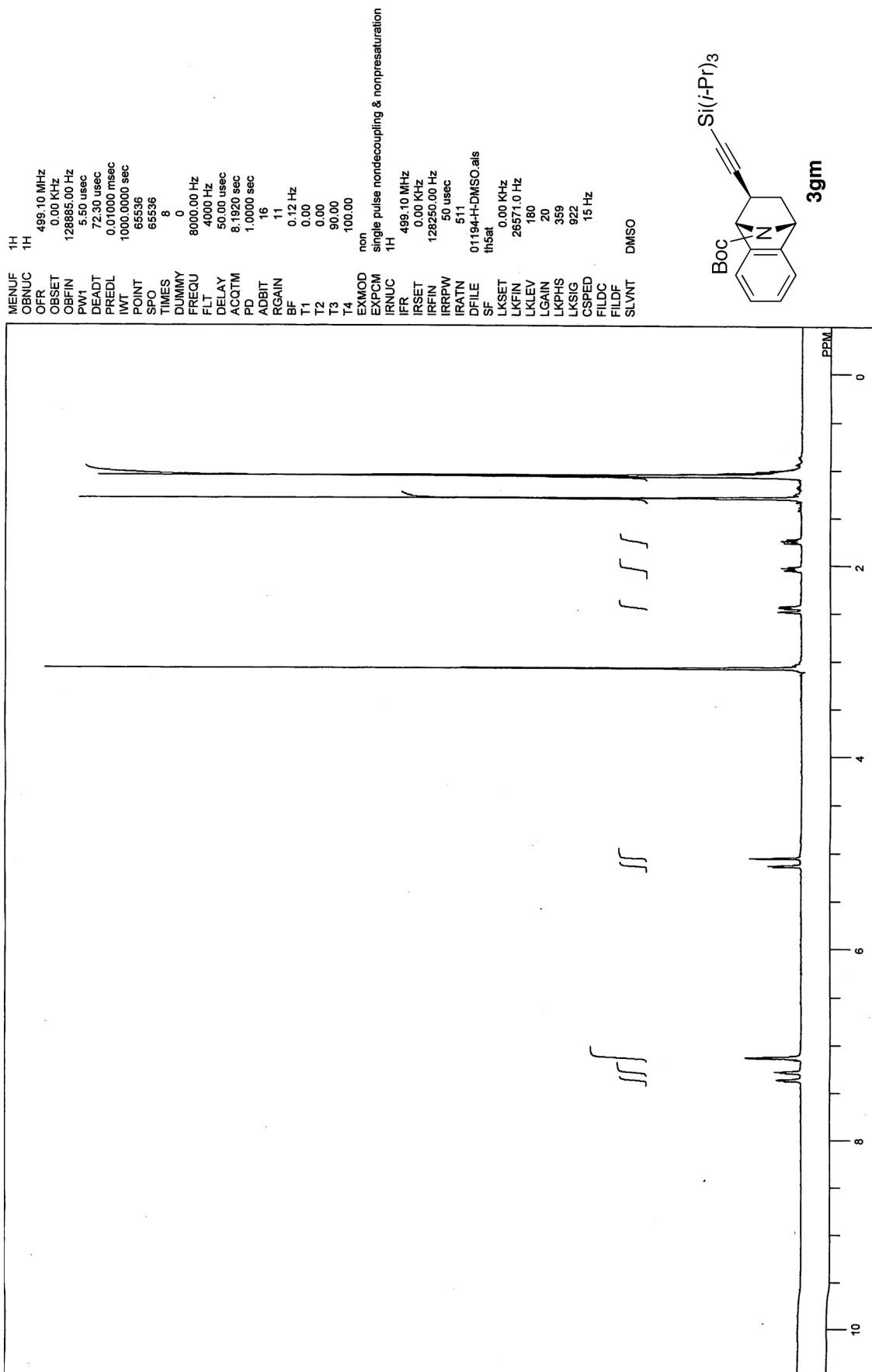
UV Results

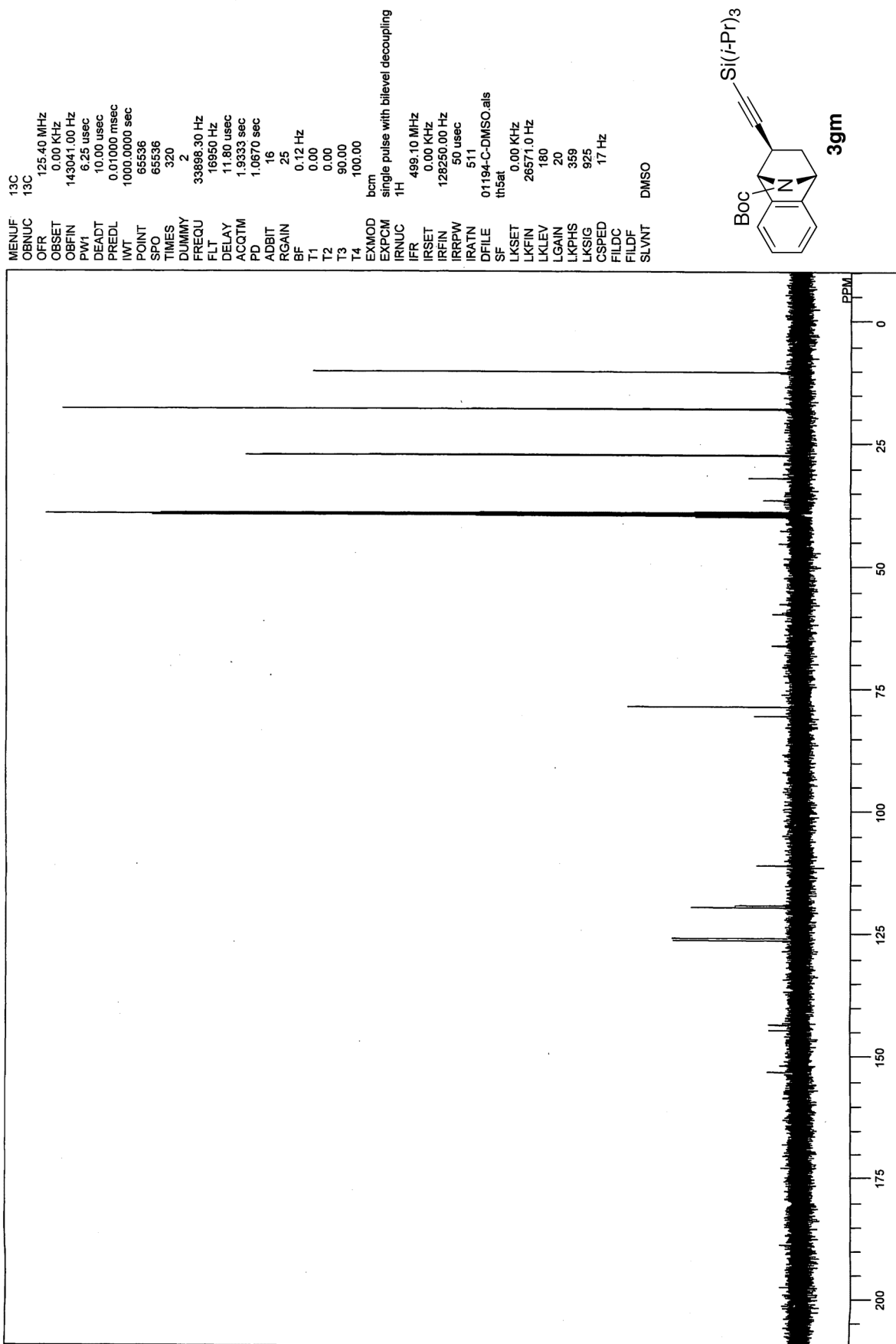
Pk #	Retention Time	Area	Area Percent	Height
1	23.713	441989	49.796	17927
2	26.385	445606	50.204	15555
Totals		887595	100.000	33482

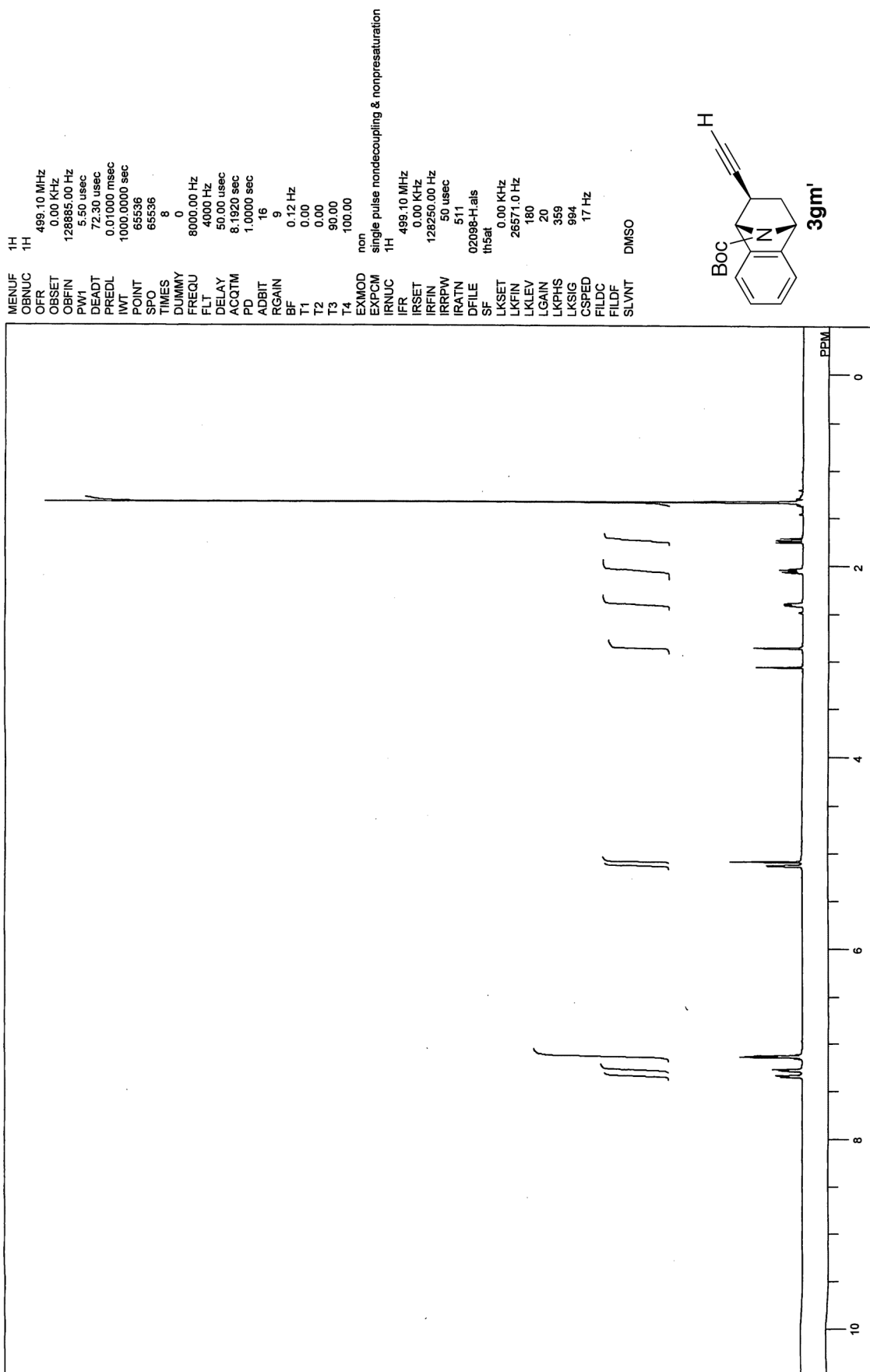


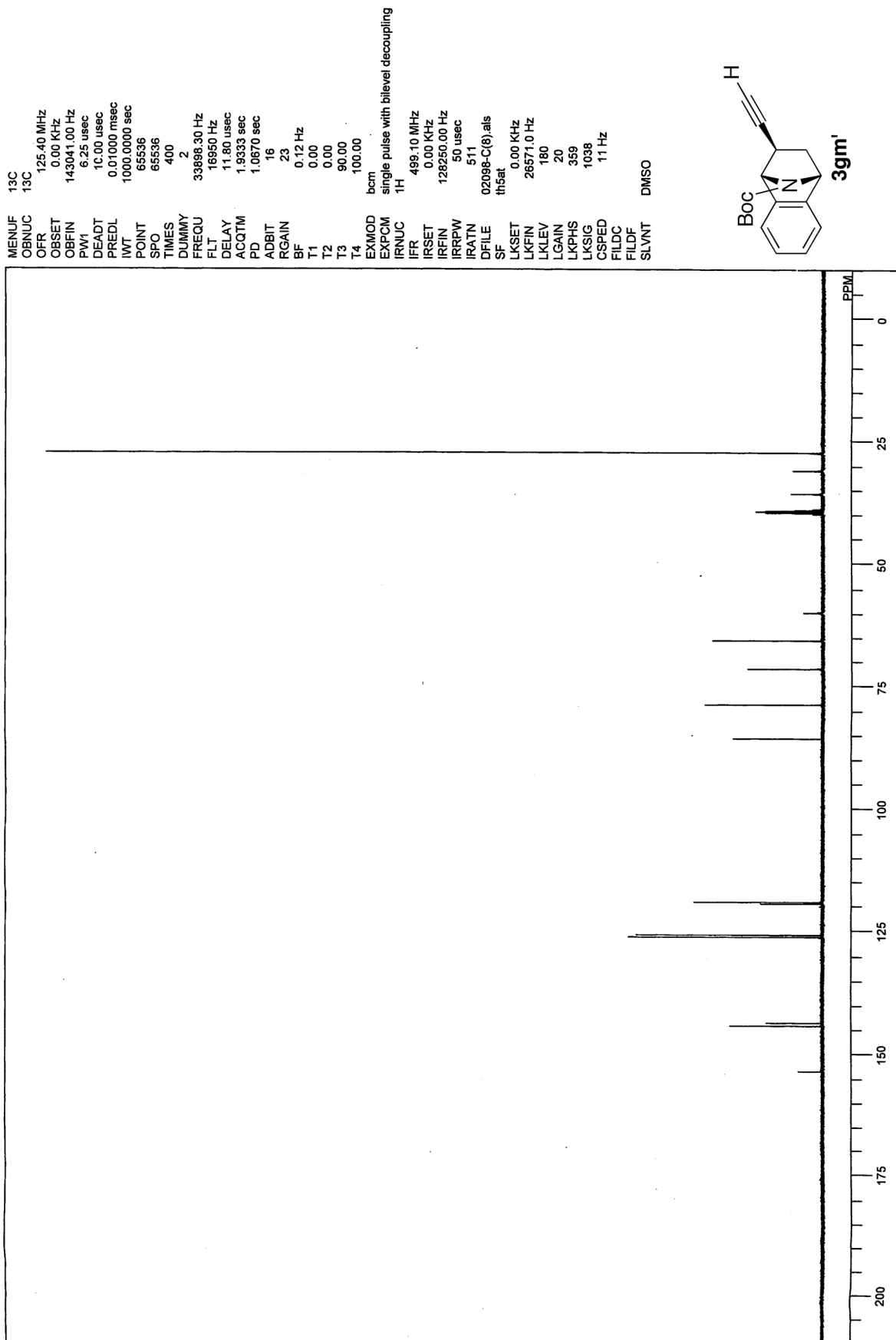
UV Results

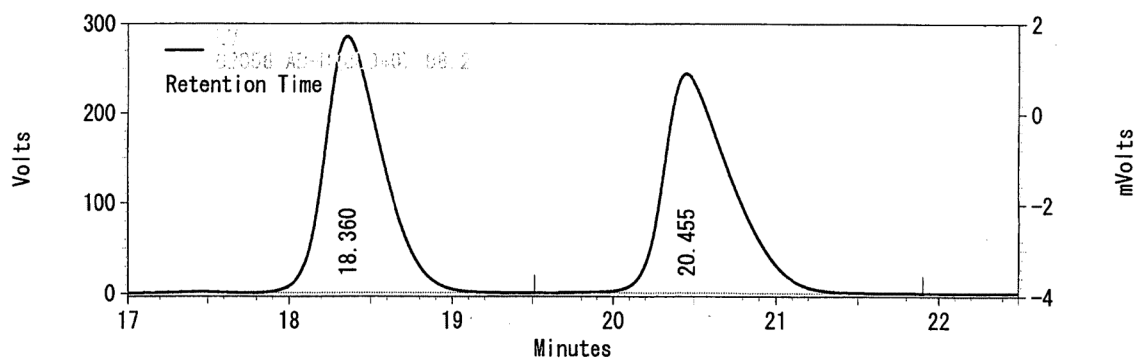
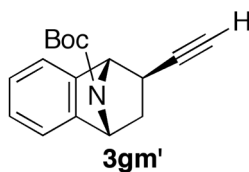
Pk #	Retention Time	Area	Area Percent	Height
1	24.685	1387479	90.024	53802
2	27.327	153745	9.976	6485
Totals		1541224	100.000	60287





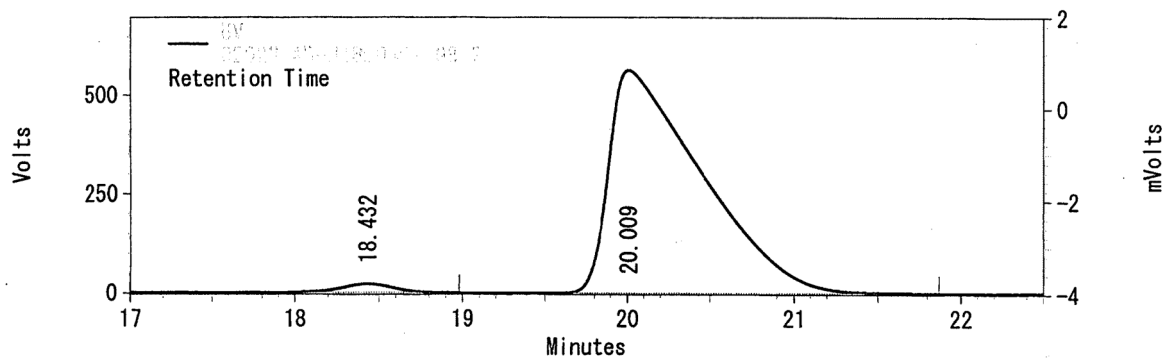






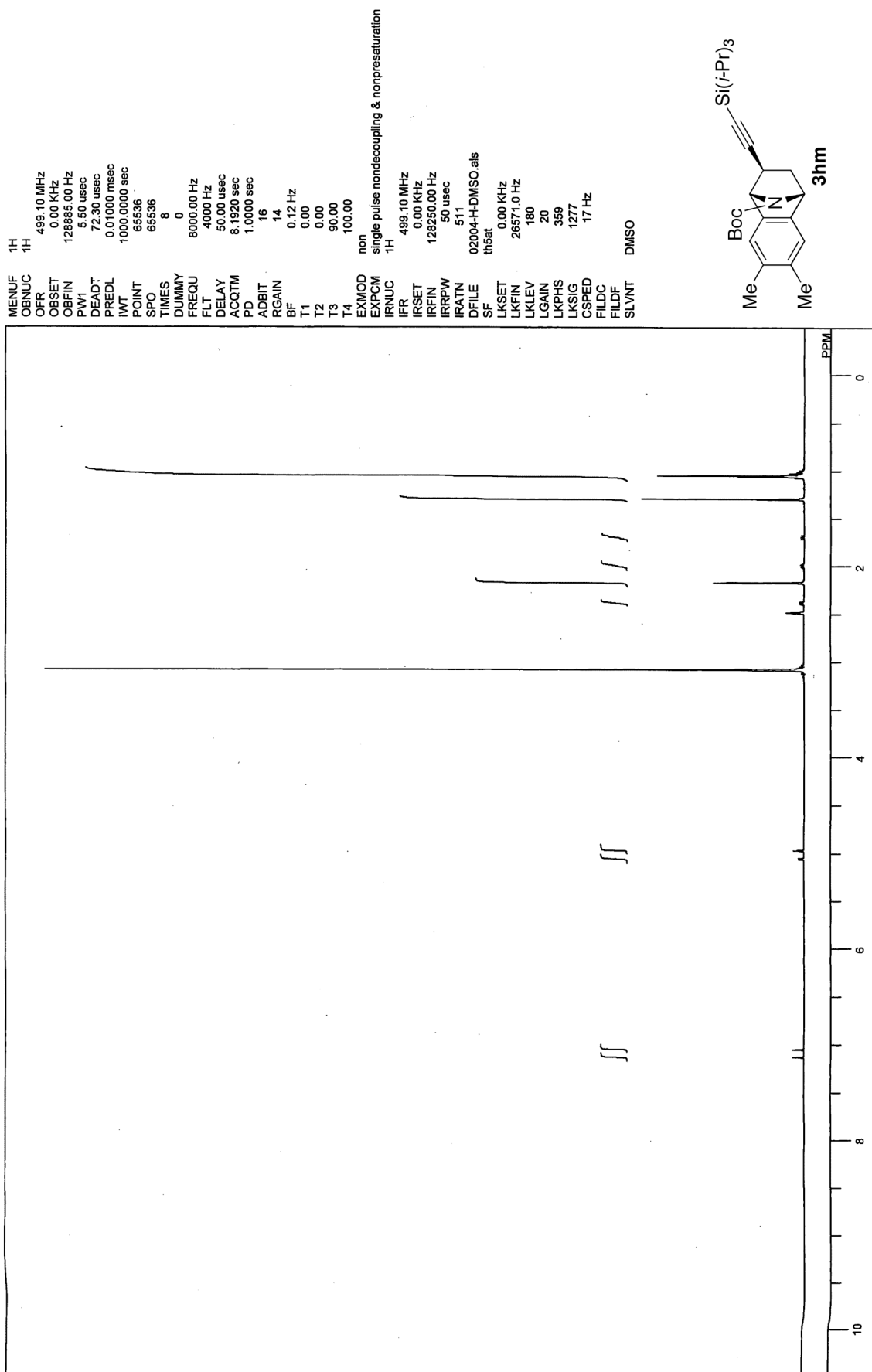
UV Results

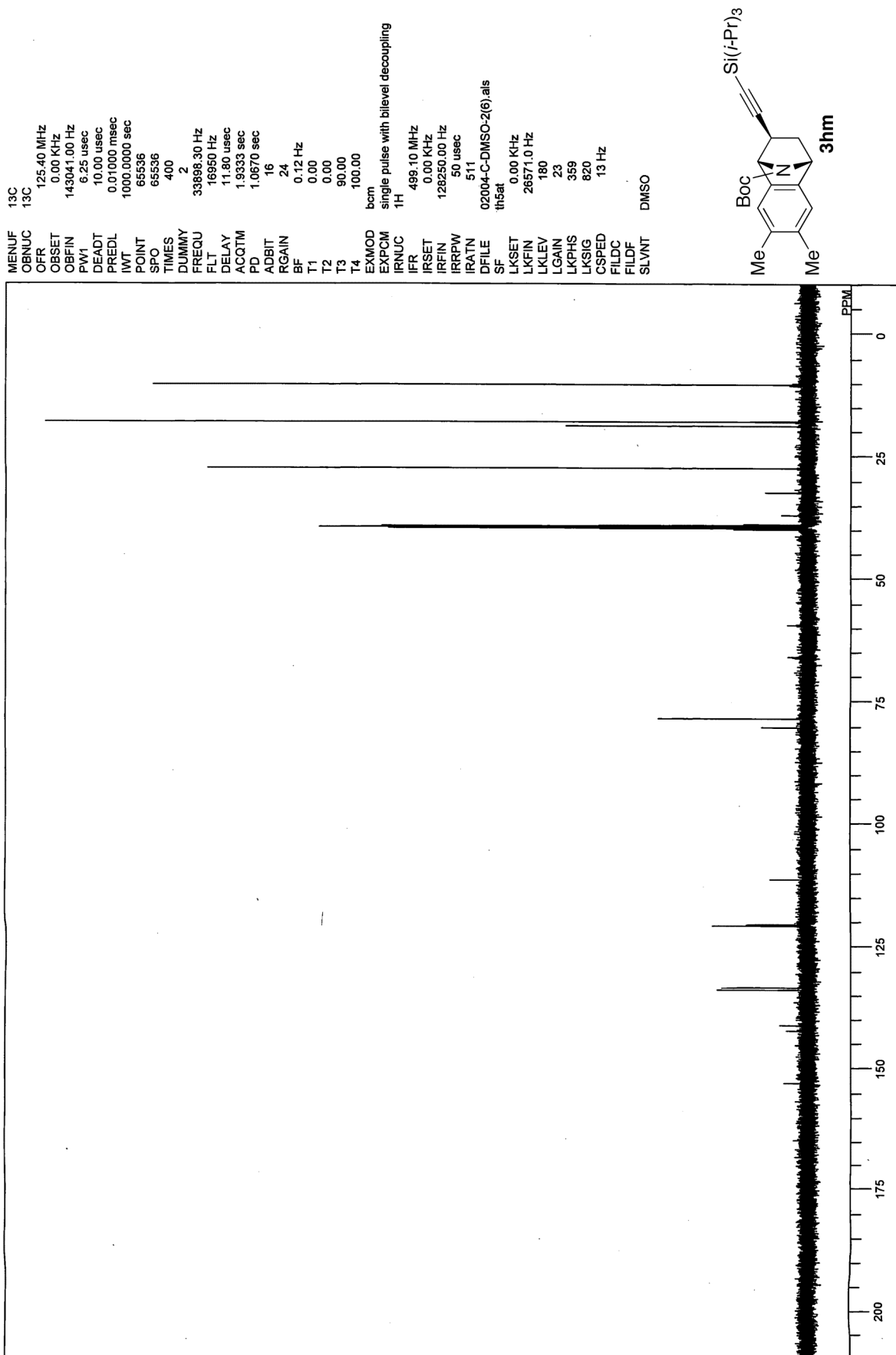
Pk #	Retention Time	Area	Area Percent	Height
1	18.360	6901503	49.748	284622
2	20.455	6971408	50.252	243389
Totals		13872911	100.000	528011

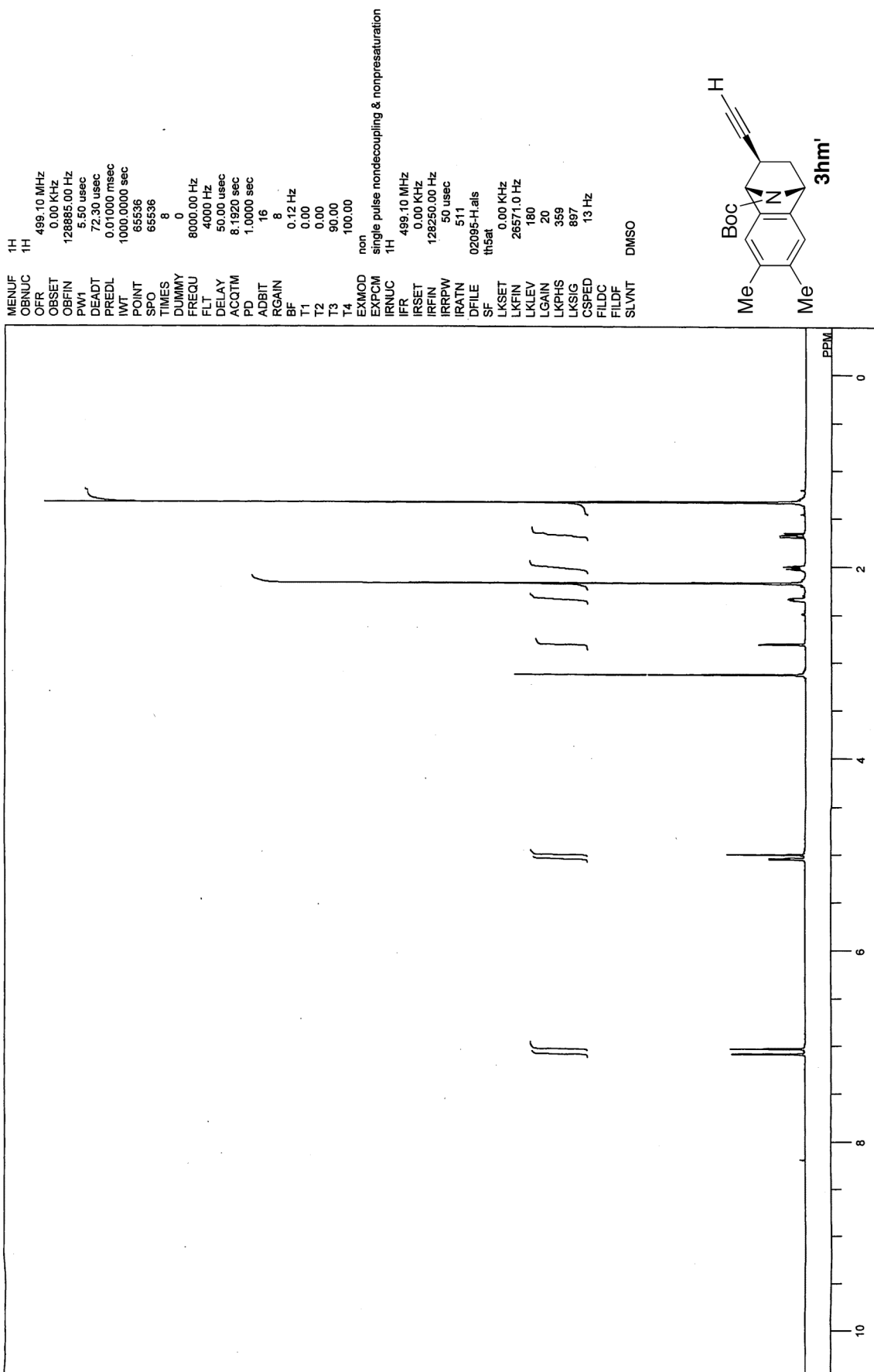


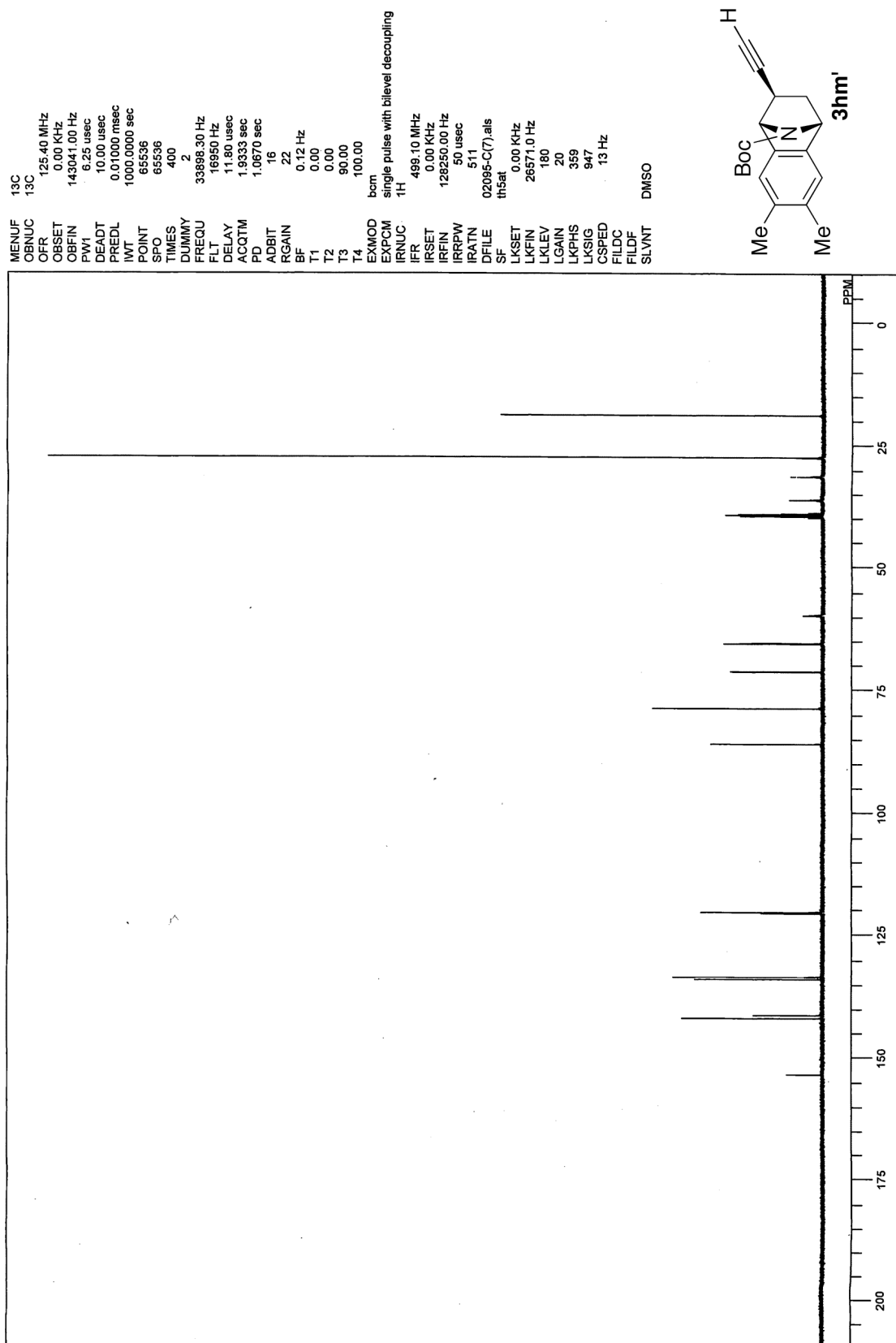
UV Results

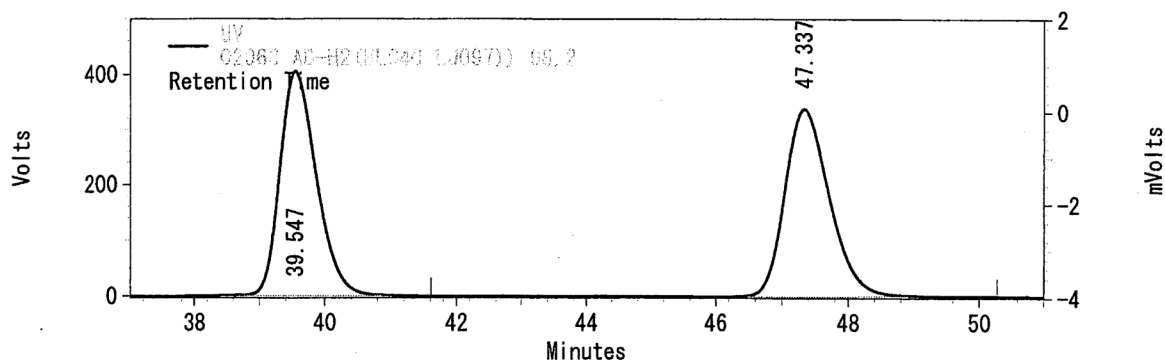
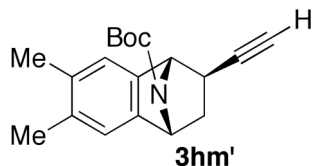
Pk #	Retention Time	Area	Area Percent	Height
1	18.432	458939	2.058	21557
2	20.009	21841478	97.942	563329
Totals		22300417	100.000	584886





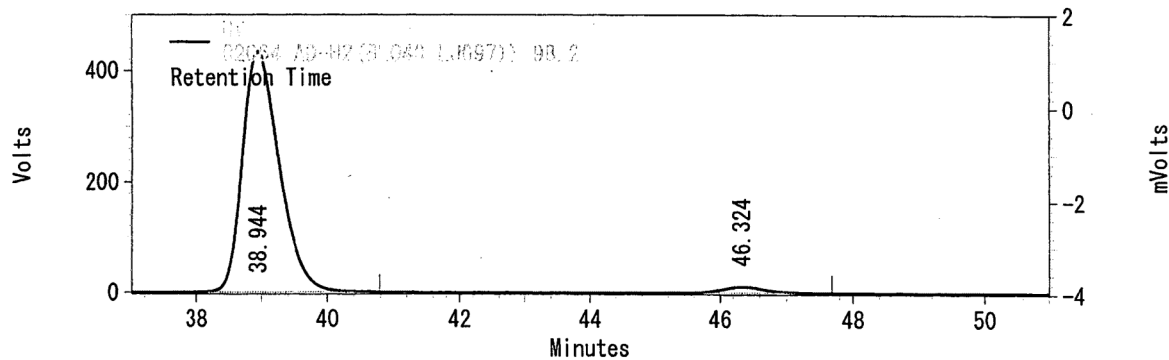






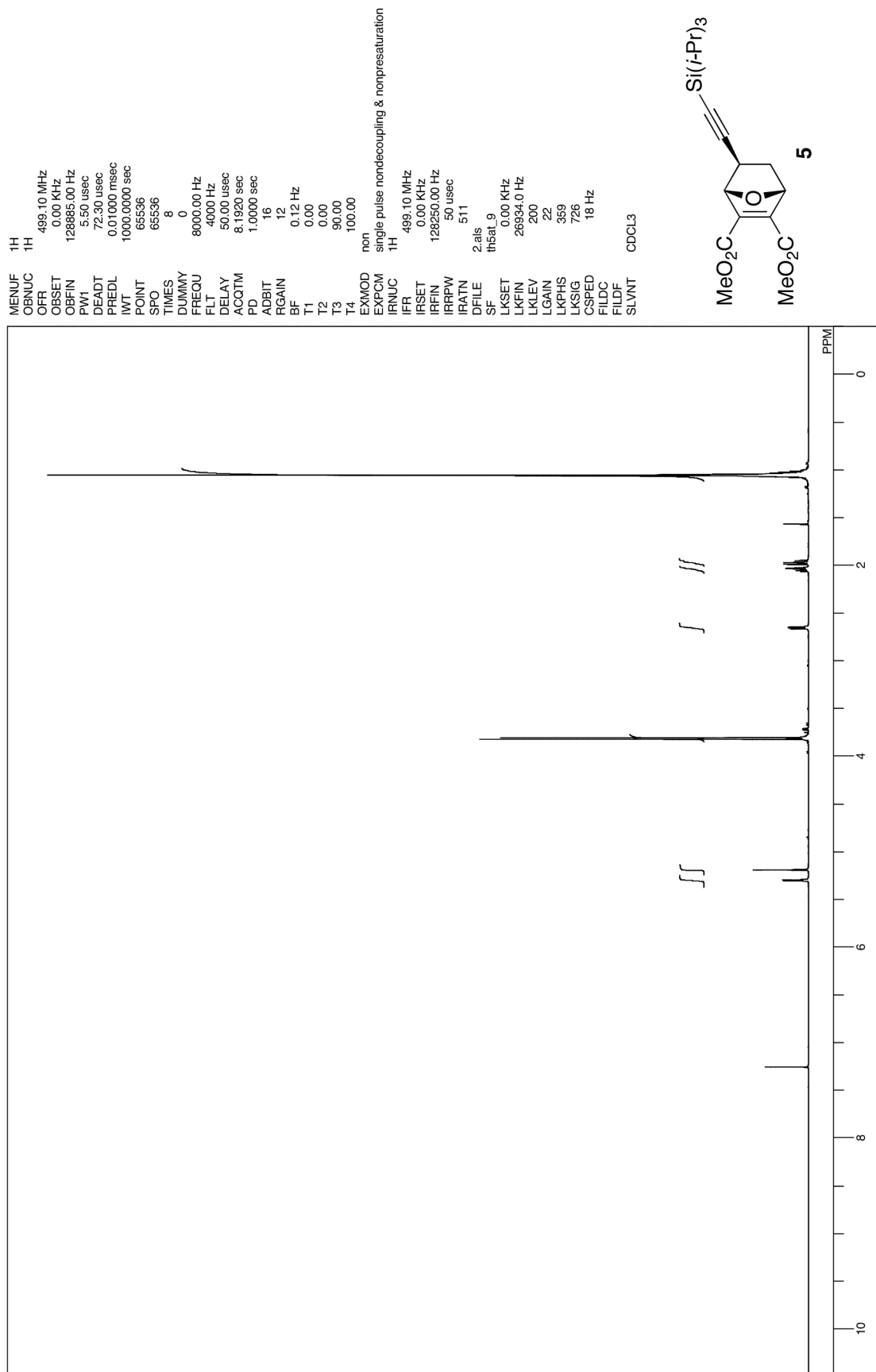
UV Results

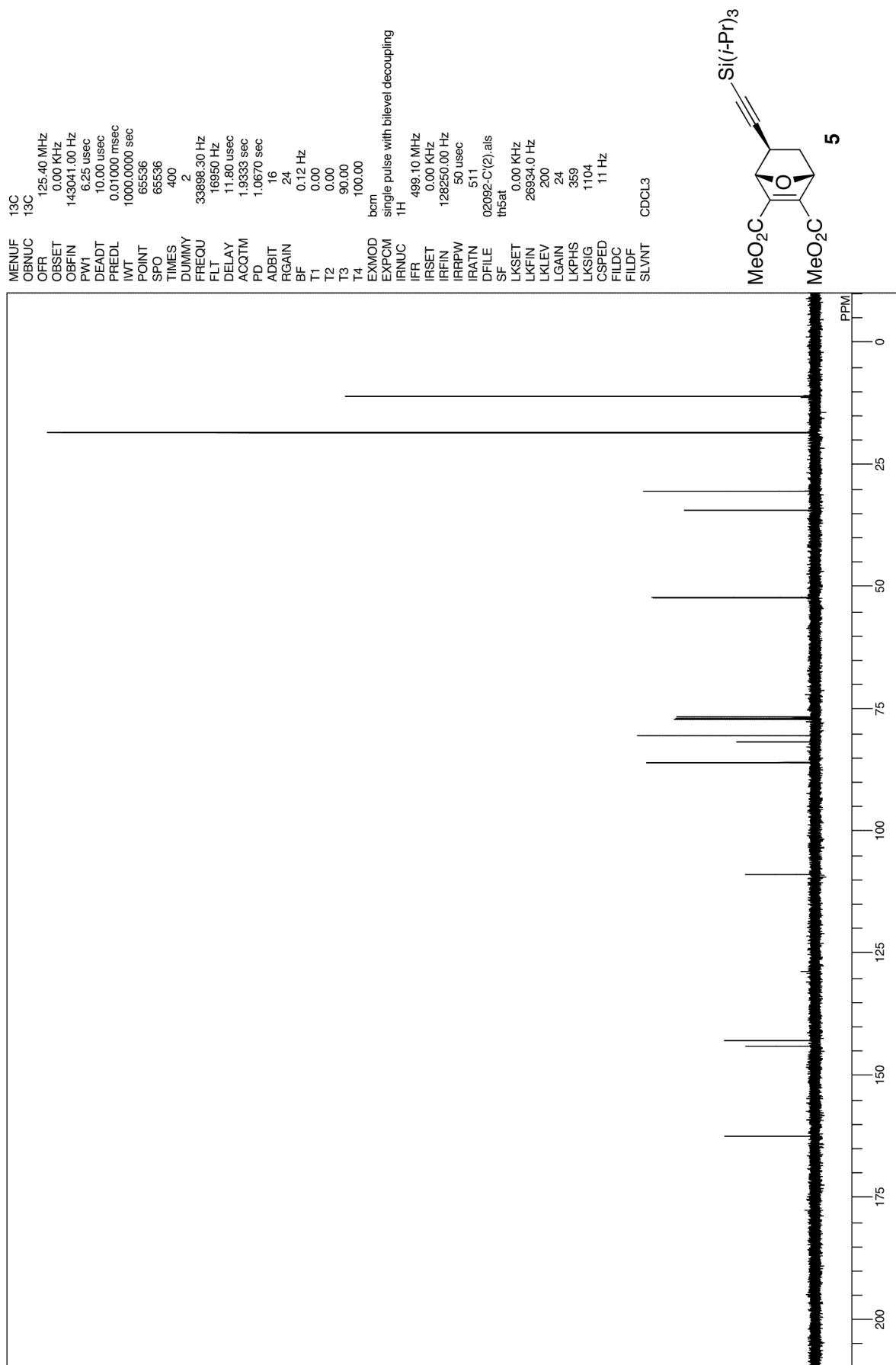
Pk #	Retention Time	Area	Area Percent	Height
1	39.547	15758023	49.803	405459
2	47.337	15882642	50.197	338417
Totals		31640665	100.000	743876

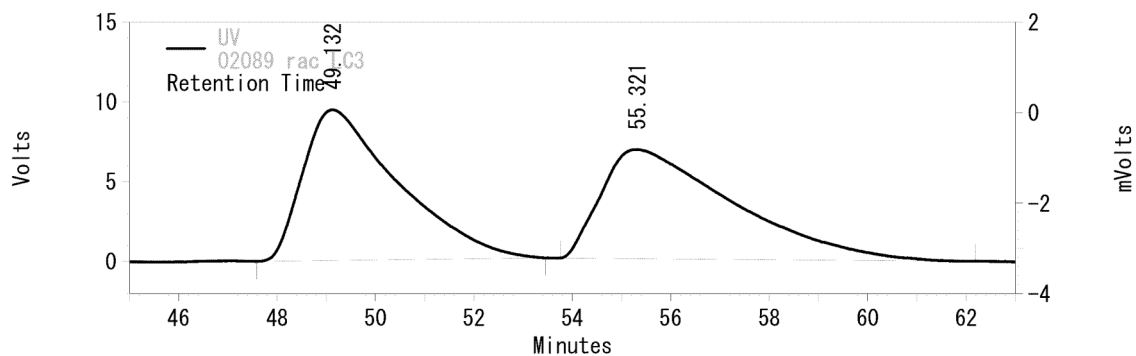
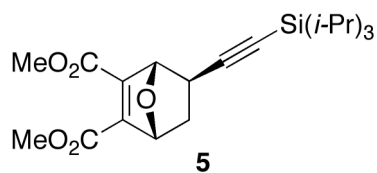


UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	38.944	16916376	97.297	432575
2	46.324	469938	2.703	10644
Totals		17386314	100.000	443219

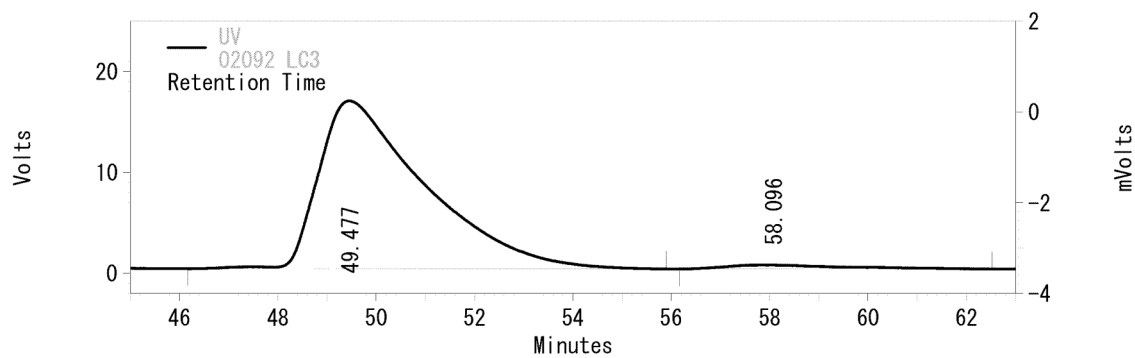






UV Results

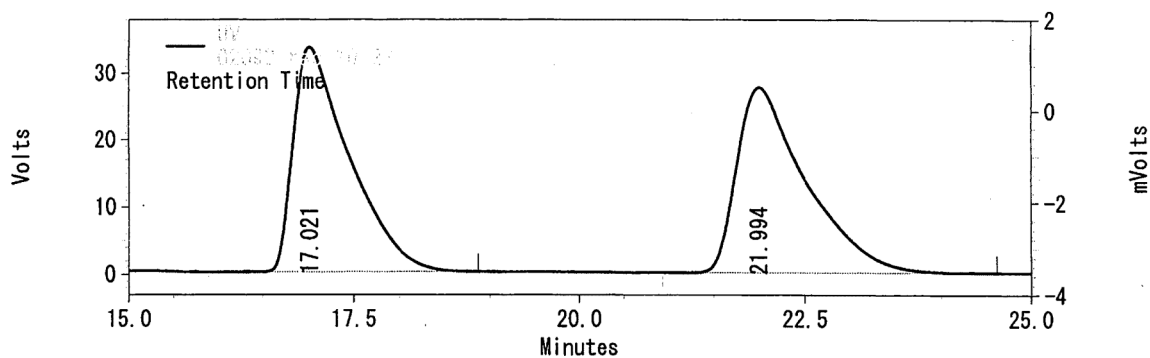
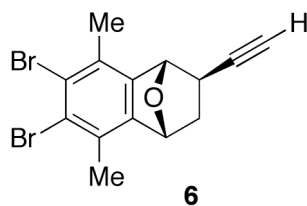
Pk #	Retention Time	Area	Area Percent	Height
1	49.132	1264739	49.875	9429
2	55.321	1271068	50.125	6832
Totals		2535807	100.000	16261



UV Results

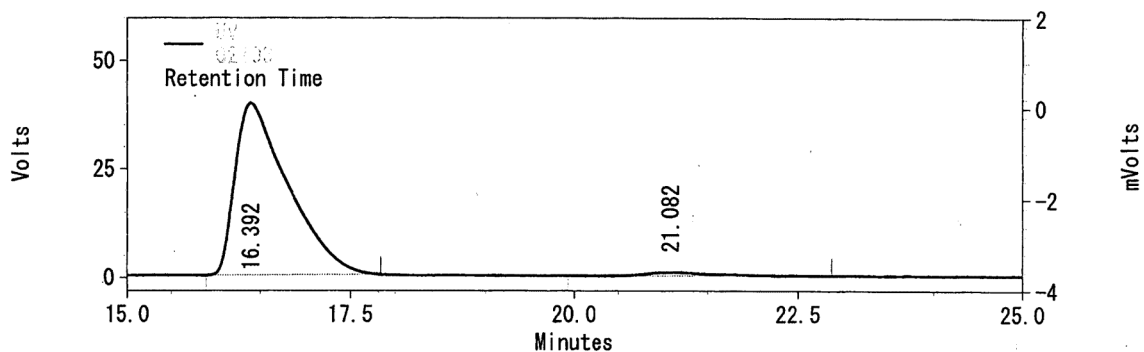
Pk #	Retention Time	Area	Area Percent	Height
1	49.477	2493568	97.399	16651
2	58.096	66584	2.601	398
Totals		2560152	100.000	17049

Chiral HPLC charts for eqn 2



UV Results

PK #	Retention Time	Area	Area Percent	Height
1	17.021	1433486	49.883	33469
2	21.994	1440231	50.117	27586
Totals		2873717	100.000	61055



UV Results

PK #	Retention Time	Area	Area Percent	Height
1	16.392	1625589	97.731	39526
2	21.082	37735	2.269	781
Totals		1663324	100.000	40307