

Supporting Information

Selective synthesis of 3-formylbenzofurans and 3-acylbenzofurans using a chalcone rearrangement strategy

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Table of Content

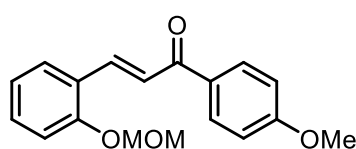
Experimental Procedures and Data	S2
References	S13
¹ H NMR and ¹³ C NMR Spectra	S14
High Resolution Mass Spectra and Data	S55

Experimental Section

All chemicals were obtained from Sigma Aldrich, TCI, Nakalai Chemical or Fujifilm Wako chemical as reagent grade and were used as received. TLC were performed on Merck Silica gel F254 plates (0.25 mm). ^1H and ^{13}C NMR spectra were recorded on the JEOL JMN-400 or Bruker AVANCE III 600 spectrometers in CDCl_3 , $\text{DMSO-}d_6$ or MeOD. Chemical shifts are expressed in ppm (δ) and coupling constants (J) are in hertz (Hz). Standard abbreviations were used for defining signal multiplicities. High-resolution mass spectra were measured by SHIMAZU IRAffinity-1 instrument (FABMS) or Exactive Plus mass spectrometer (Thermo Fisher Scientific Inc.) (ESIMS).

General procedure for synthesis of chalcone

To the solution of aldehyde (1 equiv.) and acetophenone (1-2 equiv.) in MeOH (0.2-0.5 M) was added NaOH (3 equiv.) and then stirred at room temperature. The organic layer was extracted with AcOEt, washed with brine, dried over with Na_2SO_4 and concentrated under the reduced pressure. The residue was purified by SiO_2 column chromatography (eluent: Hexane/AcOEt) to give the desired chalcone.

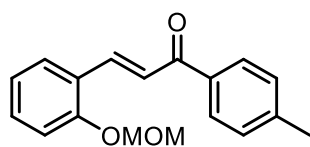


(*E*)-3-(2-(Methoxymethoxy)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one

(**1a**)

According to the general procedure, the reaction of aldehyde (720 mg, 4.3 mmol) and 4'-methoxyacetophenone (646 mg, 4.3 mmol) with NaOH (516 mg, 12.9 mmol) in MeOH (7.2 mL) gave **1a** (1.22 g, 95%) as yellow solid. Reaction time: 22 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

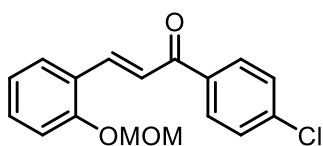
$^1\text{H-NMR}$ (CDCl_3) δ : 8.18 (d, $J = 15.6$ Hz, 1H), 8.05 (d, $J = 8.8$ Hz, 2H), 7.68 (dd, $J = 7.6, 2.0$ Hz, 1H), 7.61 (d, $J = 15.6$ Hz, 1H), 7.35 (td, $J = 7.6, 1.6$ Hz, 1H), 7.18 (d, $J = 7.6$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 1H), 6.99 (d, $J = 8.8$ Hz, 2H), 5.29 (s, 2H), 3.89 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.8, 163.3, 156.3, 138.8, 131.4, 131.2, 130.7, 128.2, 124.7, 122.3, 121.8, 114.8, 113.7, 94.4, 56.1, 55.2; HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4$ [M] $^+$: 298.1205, found 298.1212.



(*E*)-3-(2-(Methoxymethoxy)phenyl)-1-(*p*-tolyl)prop-2-en-1-one (**1b**)

According to the general procedure, the reaction of aldehyde (400 mg, 2.4 mmol) and 4'-metylacetophenone (720 mg, 4.3 mmol) with NaOH (288 mg, 7.2 mmol) in MeOH (4.5 mL) gave **1b** (580 mg, 93%) as yellow oil. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

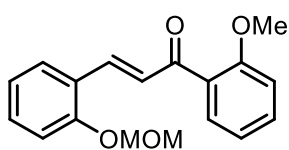
^1H NMR (400 MHz, CDCl_3) δ : 8.18 (d, $J = 16.0$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 16.0$ Hz, 1H), 7.36 (t, $J = 7.2, 1.2$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 1H), 5.28 (s, 2H), 3.51 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.6, 156.6, 143.7, 139.7, 136.0, 131.8, 129.5, 128.8, 128.6, 124.9, 122.9, 122.1, 115.0, 94.7, 21.7; HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3$ [M] $^+$: 282.1256, found 282.1255.



(E)-1-(4-Chlorophenyl)-3-(2-(methoxymethoxy)phenyl)prop-2-en-1-one (1c)

According to the general procedure, the reaction of aldehyde (331 mg, 2.0 mmol) and 4'-chloroacetophenone (338 mg, 2.2 mmol) with NaOH (394 mg, 6.0 mmol) in MeOH (4.0 mL) gave **1c** (425 mg, 72%) as yellow oil. Reaction time: 23 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 4/1.

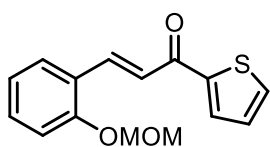
¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 15.6 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.67 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.55 (d, *J* = 15.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.37 (td, *J* = 7.2, 1.2 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 5.29 (s, 2H), 3.51 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.5, 156.6, 140.5, 139.0, 136.8, 132.0, 130.0, 128.9, 128.5, 124.4, 122.1, 122.0, 114.9, 94.6, 56.3; HRMS (ESI) calcd for C₁₇H₁₅O₃Cl [M+H]⁺ : 302.0710, found 302.0735.



(E)-3-(2-(Methoxymethoxy)phenyl)-1-(2-methoxyphenyl)prop-2-en-1-one (1d)

According to the general procedure, the reaction of aldehyde (778 mg, 4.7 mmol) and 2'-methoxyacetophenone (773 mg, 5.2 mmol) with NaOH (561 mg, 14 mmol) in MeOH (16 mL) gave **1d** (1.18 g, 85%) as yellow oil. Reaction time: 2 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 8/1.

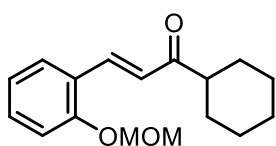
¹H NMR (400MHz, CDCl₃) δ 8.02 (d, *J* = 16.0 Hz, 1H), 7.61-7.64 (m, 2H), 7.40-7.49 (m, 2H), 7.33 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 6.99-7.06 (s, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 5.25 (2H, s), 3.90 (s, 3H), 3.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 193.2, 158.1, 156.3, 138.2, 132.8, 131.5, 130.3, 129.5, 128.3, 127.6, 124.8, 121.9, 120.7, 114.9, 111.6, 94.5, 56.12, 56.11, 55.6; HRMS (ESI) calcd for C₁₈H₁₈O₄ [M+Na]⁺ 321.1097, found 321.1085.



(E)-3-(2-(Methoxymethoxy)phenyl)-1-(thiophen-2-yl)prop-2-en-1-one (1e)

According to the general procedure, the reaction of aldehyde (1.50 g, 9.0 mmol) and 1-(thiophen-2-yl)ethan-1-one (1.14 g, 9.0 mmol) with NaOH (1.10 g, 27 mmol) in MeOH (18 mL) gave **1e** (2.20 g, 91%) as yellow oil. Reaction time: 1 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 4/1.

¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 16.0 Hz, 1H), 7.86 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.68-7.67 (m, 2H), 7.51 (d, *J* = 16.0 Hz, 1H), 7.37 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.20-7.17 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 5.30 (2H, s), 3.52 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 182.2, 156.3, 145.6, 138.9, 133.6, 131.7, 131.7, 128.4, 128.2, 124.2, 122.1, 121.8, 114.7, 94.3, 56.0; HRMS (ESI) calcd for C₁₅H₁₄O₃SNa [M+Na]⁺ : 297.0556, found 297.0545.

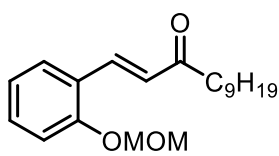


(E)-1-Cyclohexyl-3-(2-(methoxymethoxy)phenyl)prop-2-en-1-one (1f)

According to the general procedure, the reaction of aldehyde (405 mg, 2.4 mmol) and 1-cyclohexylethan-1-one (280 mg, 2.2 mmol) with NaOH (292 mg, 7.3 mmol) in MeOH (4.9 mL) gave **1f** (455 mg, 68%) as yellow oil. Reaction time: 15 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 9/1.

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 16.0 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.33 (td, *J* = 7.2, 1.6 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 16.0 Hz, 1H), 5.26 (s, 2H), 3.50 (s, 3H), 2.70-2.63 (m, 1H), 1.92-1.69 (m, 5H), 1.49-1.23 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 203.6, 156.3, 137.3, 131.6, 128.1, 125.3, 124.6, 122.0, 114.9, 94.7, 56.2, 49.3, 28.7, 25.9, 25.7; HRMS (ESI) calcd for C₁₇H₂₂O₃ [M+Na]⁺ 297.1461, found

297.1459.



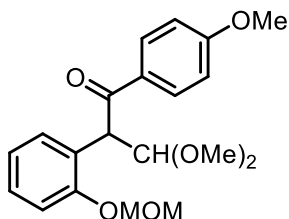
(E)-1-(2-(Methoxymethoxy)phenyl)dodec-1-en-3-one (1g)

According to the general procedure, the reaction of aldehyde (997 mg, 6.0 mmol) and 2-undecanone (1.23 g, 7.20 mmol) with NaOH (720 mg, 18 mmol) in MeOH (30 mL) gave **1g** (1.20 g, 63%) as colorless oil. Reaction time: 3.5 h at 70 °C. Eluent of SiO₂ column

chromatography: Hexane/AcOEt = 10/1.

¹H NMR (600 MHz, CDCl₃) δ 7.94 (d, *J* = 16.2 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 5.26 (s, 2H), 3.51 (s, 3H), 2.67 (t, *J* = 7.2 Hz, 2H), 1.70-1.66 (m, 2H), 1.36-1.27 (m, 12H), 0.88 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ ¹³C NMR (151 MHz, CDCl₃) δ 201.8, 147.7, 147.4, 137.2, 131.7, 125.4, 120.2, 117.3, 116.1, 110.3, 40.3, 32.0, 29.6, 29.5, 29.4, 26.2, 24.7, 22.8, 14.3; HRMS (ESI) calcd for C₂₀H₃₀O₃Na [M+Na]⁺: 341.2087, found : 341.2077.

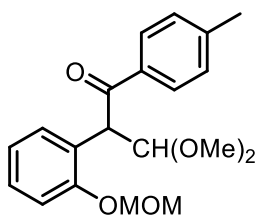
Genral procedure for oxidative rearrangement of chalcones: To the solution of **1** in MeOH (0.1 M) was added PhI(OH)OTs (2 equiv.) and then stirred at room temperature. The reaction was quenched with saturated aq. NaHCO₃ and the mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under the reduced pressure. The residue was purified by SiO₂ column chromatography (eluent: Hexane/AcOEt) to give the desired **2**.



3,3-Dimethoxy-2-(2-(methoxymethoxy)phenyl)-1-(4-methoxyphenyl)propan-1-one (2a)

According to the general procedure, the reaction of chalcone **1a** (1.48 g, 5.0 mmol) with PhI(OH)OTs (3.90 g, 10.0 mmol) in MeOH (50 mL) gave **2a** (1.15 g, 64%) as yellow oil. Reaction time: 1 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 4/1.

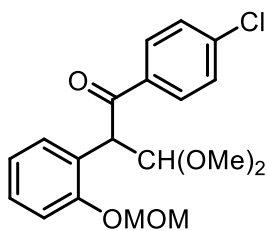
¹H NMR (100 MHz, CDCl₃) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 5.48 (d, *J* = 8.8 Hz, 1H), 5.29 (s, 2H), 5.18 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H), 3.51 (s, 3H), 3.45 (s, 3H), 3.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.0, 163.8, 154.7, 131.2, 130.1, 129.1, 128.7, 124.6, 122.2, 114.7, 113.7, 107.0, 95.0, 56.24, 56.18, 55.5, 54.0, 47.8; HRMS (ESI) calcd for C₂₀H₂₄O₆ [M+Na]⁺ 383.1465, found 383.1450.



3,3-Dimethoxy-2-(2-(methoxymethoxy)phenyl)-1-(p-tolyl)propan-1-one (2b)

According to the general procedure, the reaction of chalcone **1b** (80.2 mg, 0.28 mmol) with PhI(OH)OTs (220 mg, 0.56 mmol) in MeOH (2.8 mL) gave **2b** (67.7 mg, 70%) as yellow oil. Reaction time: 2 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 10/1.

¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.19-7.10 (m, 4H), 6.95 (t, *J* = 7.4 Hz, 1H), 5.51 (d, *J* = 8.4 Hz, 1H), 5.29 (s, 2H), 5.19 (d, *J* = 8.4 Hz, 1H), 3.51 (s, 3H), 3.45 (s, 3H), 3.21 (s, 3H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.1, 154.8, 144.0, 134.6, 129.3, 129.1, 129.0, 128.7, 124.4, 122.2, 114.7, 107.0, 94.9, 56.24, 56.20, 54.0, 48.1, 21.6; HRMS (ESI) calcd for C₂₀H₂₄O₅ [M+H]⁺ 367.1516, found 367.1514.

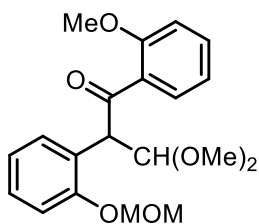


1-(4-Chlorophenyl)-3,3-dimethoxy-2-(2-(methoxymethoxy)phenyl)propan-1-one (2c)

According to the general procedure, the reaction of chalcone **1c** (50.0 mg, 0.17 mmol) with $\text{PhI}(\text{OH})\text{OTs}$ (130 mg, 0.33 mmol) in MeOH (1.7 mL) gave **2c** (35.5 mg, 65%) as yellow oil. Reaction time: 2 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 10/1.

^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 7.6$ Hz, 2H), 7.39-7.35 (m, 3H), 7.19 (td, $J = 7.2$, 1.6 Hz, 1H), 7.12 (d, $J = 7.2$ Hz, 1H), 6.96 (t, $J = 7.2$ Hz, 1H), 5.45 (d, $J = 8.8$ Hz, 1H),

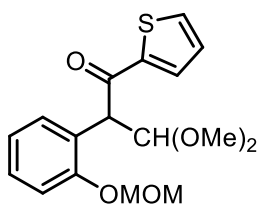
5.28 (s, 2H), 5.16 (d, $J = 8.8$ Hz, 1H), 3.50 (s, 3H), 3.45 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 154.7, 139.7, 135.4, 130.3, 129.1, 129.0, 128.9, 123.9, 122.3, 114.8, 106.8, 94.9, 56.3, 54.0, 48.4; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{O}_5\text{Cl}$ $[\text{M}+\text{Na}]^+$ 387.0970, found 387.0967.



3,3-Dimethoxy-2-(2-(methoxymethoxy)phenyl)-1-(2-methoxyphenyl)propan-1-one (2d)

According to the general procedure, the reaction of chalcone **1d** (1.04 g, 3.5 mmol) with $\text{PhI}(\text{OH})\text{OTs}$ (2.74 g, 7.0 mmol) in MeOH (35 mL) gave **2d** (970 mg, 78%) as yellow oil. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

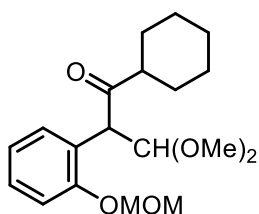
^1H NMR (400 MHz, CDCl_3) δ : 7.53 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.39 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.33 (td, $J = 7.6$, 1.2 Hz, 1H), 7.14 (td, $J = 7.2$, 1.6 Hz, 1H), 7.03 (d, $J = 7.6$ Hz, 1H), 6.96-6.83 (m, 3H), 5.49 (d, $J = 8.4$ Hz, 1H), 5.14 (d, $J = 8.0$ Hz, 1H), 5.09 (s, 2H), 3.80 (s, 3H), 3.49 (s, 3H), 3.39 (s, 3H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.5, 158.2, 155.6, 133.0, 130.5, 129.8, 129.1, 128.5, 124.7, 121.9, 120.4, 114.6, 111.6, 106.6, 94.9, 55.92, 55.88, 55.5, 54.3, 53.2; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{24}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 383.1465, found 383.1450.



3,3-Dimethoxy-2-(2-(methoxymethoxy)phenyl)-1-(thiophen-2-yl)propan-1-one (2e)

According to the general procedure, the reaction of chalcone **1e** (81.4 mg, 0.30 mmol) with $\text{PhI}(\text{OH})\text{OTs}$ (233 mg, 0.60 mmol) in MeOH (3.0 mL) gave **2e** (25.2 mg, 23%) as yellow oil. Reaction time: 2.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

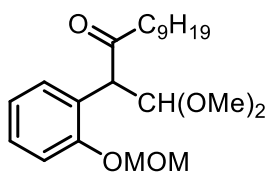
^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 4.0$ Hz, 1H), 7.59 (dd, $J = 4.8$, 1.2 Hz, 1H), 7.47 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.20 (td, $J = 8.8$, 1.6 Hz, 1H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.06 (1H, dd, $J = 4.8$, 4.0 Hz), 6.98 (t, $J = 7.2$ Hz, 1H), 5.37 (d, $J = 8.8$ Hz, 1H), 5.29 (s, 2H), 5.17 (d, $J = 8.8$ Hz, 1H), 3.50 (s, 3H), 3.47 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 154.8, 144.8, 134.4, 132.9, 129.1, 128.9, 128.1, 124.3, 122.3, 114.7, 106.4, 94.9, 56.32, 56.28, 53.8, 49.6; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{O}_5\text{SNa}$ $[\text{M}+\text{Na}]^+$ 359.0924, found 359.0910.



1-Cyclohexyl-3,3-dimethoxy-2-(2-(methoxymethoxy)phenyl)propan-1-one (2f)

According to the general procedure, the reaction of chalcone **1f** (116 mg, 0.42 mmol) with $\text{PhI}(\text{OH})\text{OTs}$ (332 mg, 0.85 mmol) in MeOH (4.0 mL) gave **2f** (89.2 mg, 63%) as yellow oil. Reaction time: 2 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 8.4$ Hz, 1H), 7.11 (d, $J = 8.4$ Hz, 1H), 6.96 (t, $J = 7.6$ Hz, 1H), 5.24 (s, 2H), 4.99 (d, $J = 8.8$ Hz, 1H), 4.80 (d, $J = 8.8$ Hz, 1H), 3.51 (s, 3H), 3.42 (s, 3H), 3.13 (s, 3H), 2.39-2.33 (m, 1H), 1.91-1.61 (m, 4H), 1.32-1.13 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 211.3, 155.1, 129.4, 128.6, 123.8, 122.1, 114.4, 106.2, 94.8, 56.3, 56.2, 53.2, 51.2, 51.1, 28.4, 27.8, 25.9, 25.8, 25.5; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{28}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 359.1829, found 359.1826.

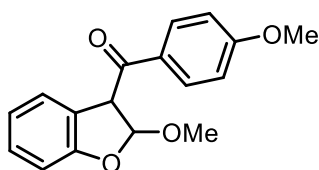


1,1-Dimethoxy-2-(2-(methoxymethoxy)phenyl)dodecan-3-one (**2g**)

According to the general procedure, the reaction of chalcone **1g** (50.2 mg, 0.16 mmol) with PhI(OH)OTs (124 mg, 0.32 mmol) in MeOH (1.6 mL) gave **2g** (35.1 mg, 58%) as yellow oil. Reaction time: 1.5 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 8/1.

¹H NMR (400 MHz, CDCl₃) δ 7.30 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 (td, *J* = 7.2, 2.0 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 5.23 (s, 2H), 5.04 (d, *J* = 8.8 Hz, 1H), 4.62 (d, *J* = 8.8 Hz, 1H), 3.50 (s, 3H), 3.45 (s, 3H), 3.15 (s, 3H), 2.45-2.39 (m, 2H), 1.52-1.44 (m, 2H), 1.28-1.18 (m, 12H), 0.86 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 208.5, 155.0, 129.4, 128.6, 123.9, 122.2, 114.4, 105.4, 94.8, 56.3, 53.3, 53.0, 43.5, 32.0, 29.6, 29.5, 29.4, 29.1, 23.4, 22.8, 14.2; HRMS (ESI) calcd for C₂₂H₃₆O₅Na [M+Na]⁺: 403.2455, found: 403.2438.

General procedure for the synthesis of dihydrobenzofuran: To the solution of **2** in MeCN (0.1 M) was added *p*-TsOH·H₂O (0.1-0.2 equiv.) and then stirred at room temperature. The reaction was quenched with saturated aq. NaHCO₃ and the mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under the reduced pressure. The residue was purified by SiO₂ column chromatography (eluent: Hexane/AcOEt) to give the desired **3**.

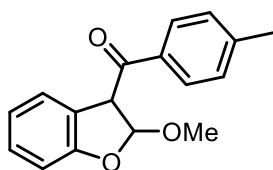


(2-Methoxy-2,3-dihydrobenzofuran-3-yl)(4-methoxyphenyl)methanone (**3a**)

According to the general procedure, the reaction of acetal **2a** (43.6 mg, 0.13 mmol) with *p*-TsOH·H₂O (2.2 mg, 0.013 mmol) in MeCN (1.3 mL) gave **3a** (30.7 mg, 83%) as white solid. Reaction time: 1 h. Eluent of SiO₂ column chromatography:

Hexane/AcOEt = 4/1.

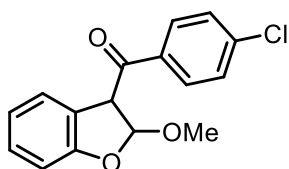
¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.04-7.01 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.02 (d, *J* = 2.0 Hz, 1H), 5.01 (d, *J* = 2.0 Hz, 1H), 3.92 (s, 3H), 3.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.0, 164.4, 158.5, 131.7, 129.6, 128.9, 125.2, 124.3, 121.1, 114.3, 110.6, 109.4, 56.6, 56.5, 55.7; HRMS (FAB) calcd for C₁₇H₁₆O₄ [M]⁺ calcd for 284.1049, found 284.1042.



(2-Methoxy-2,3-dihydrobenzofuran-3-yl)(*p*-tolyl)methanone (**3b**)

According to the general procedure, the reaction of acetal **2b** (67.7 mg, 0.20 mmol) with *p*-TsOH·H₂O (3.4 mg, 0.020 mmol) in MeCN (2.0 mL) gave **3b** (31.2 mg, 58%) as white solid. Reaction time: 1 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 10/1.

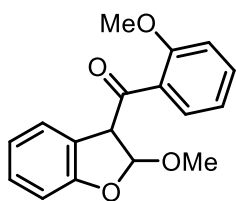
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.03 (d, *J* = 2.4 Hz, 1H), 5.03 (d, *J* = 1.2 Hz, 1H), 3.61 (s, 3H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 195.1, 158.5, 145.1, 133.4, 129.9, 129.6, 129.5, 125.3, 124.1, 121.1, 110.6, 109.3, 56.8, 56.5, 21.8; HRMS (FAB) calcd for C₁₇H₁₆O₃ [M]⁺ 268.1099, found 268.1094.



(4-Chlorophenyl)(2-methoxy-2,3-dihydrobenzofuran-3-yl)methanone (**3c**)

According to the general procedure, the reaction of acetal **2c** (45.4 mg, 0.12 mmol) with *p*-TsOH·H₂O (2.0 mg, 0.012 mmol) in MeCN (1.2 mL) gave **3c** (24.3 mg, 70%) as white solid. Reaction time: 1 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 10/1.

^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 1H), 7.21 (t, $J = 8.0$ Hz, 1H), 6.98 (d, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 6.83 (t, $J = 7.2$ Hz), 6.00 (d, $J = 2.0$ Hz, 1H), 4.99 (d, $J = 1.2$ Hz, 1H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.3, 158.5, 140.7, 134.3, 130.7, 129.8, 129.5, 125.3, 123.5, 121.3, 110.8, 109.0, 57.0, 56.5; HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{13}\text{O}_3\text{Cl}$ $[\text{M}]^+$ 288.0553, found 288.0567.

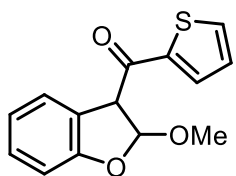


(2-Methoxy-2,3-dihydrobenzofuran-3-yl)(2-methoxyphenyl)methanone (3d)

According to the general procedure, the reaction of acetal **2d** (516 mg, 1.4 mmol) with *p*-TsOH \cdot H $_2$ O (54.4 mg, 0.28 mmol) in MeCN (14 mL) gave **3d** (307 mg, 75%) as white solid.

Reaction time: 1 h. Eluent of SiO $_2$ column chromatography: Hexane/AcOEt = 9/1.

^1H NMR (400 MHz, CDCl_3) δ 7.59 (dd, $J = 7.6, 2.0$ Hz, 1H), 7.53 (td, $J = 7.6, 2.0$ Hz, 1H), 7.16 (t, $J = 8.0$ Hz, 1H), 7.06-7.00 (m, 2H), 6.92-6.87 (m, 2H), 6.77 (t, $J = 7.6$ Hz, 1H), 6.03 (d, $J = 2.0$ Hz, 1H), 5.24 (s, 1H), 3.97 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.8, 158.6, 158.4, 134.4, 131.4, 129.3, 126.8, 125.2, 124.6, 121.2, 121.1, 111.7, 110.5, 108.9, 61.0, 56.2, 55.6; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 307.0941, found 307.0939.

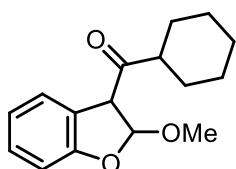


(2-Methoxy-2,3-dihydrobenzofuran-3-yl)(thiophen-2-yl)methanone (3e)

According to the general procedure, the reaction of acetal **2e** (23.2 mg, 0.069 mmol) with *p*-TsOH \cdot H $_2$ O (1.3 mg, 0.007 mmol) in MeCN (0.7 mL) gave **3e** (9.2 mg, 51%) as white solid.

Reaction time: 1 h. Eluent of SiO $_2$ column chromatography: Hexane/AcOEt = 4/1.

^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 3.2$ Hz, 1H), 7.77 (d, $J = 4.8$ Hz, 1H), 7.25-7.20 (m, 2H), 7.11 (d, $J = 7.2$ Hz, 1H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.86 (t, $J = 7.6$ Hz, 1H), 6.00 (d, $J = 2.0$ Hz, 1H), 4.86 (s, 1H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.5, 158.6, 143.4, 135.5, 133.6, 129.9, 128.7, 125.2, 121.3, 110.7, 109.2, 58.3, 56.5; HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{12}\text{O}_3\text{S}$ $[\text{M}]^+$ 260.0507, found 260.0481.

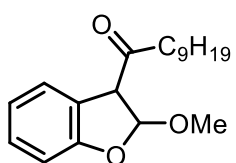


Cyclohexyl(2-methoxy-2,3-dihydrobenzofuran-3-yl)methanone (3f)

According to the general procedure, the reaction of acetal **2f** (89.2 mg, 0.27 mmol) with *p*-TsOH \cdot H $_2$ O (5.0 mg, 0.027 mmol) in MeCN (3.0 mL) gave **3f** (43.1 mg, 63%) as white solid.

Reaction time: 1 h. Eluent of SiO $_2$ column chromatography: Hexane/AcOEt = 10/1.

^1H NMR (400 MHz, CDCl_3) δ 7.27-7.20 (m, 2H), 6.94-6.88 (m, 2H), 5.82 (d, $J = 2.0$ Hz, 1H), 4.27 (s, 1H), 3.54 (s, 3H), 2.74-2.66 (m, 1H), 1.98-1.95 (m, 1H), 1.84-1.68 (m, 4H), 1.46-1.23 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.5, 158.5, 129.7, 124.7, 123.7, 121.4, 110.8, 108.5, 59.9, 56.3, 49.1, 29.0, 27.9, 25.9, 25.8, 25.3; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ $[\text{M}+\text{Na}]^+$ 283.1305, found 283.1302.



1-(2-Methoxy-2,3-dihydrobenzofuran-3-yl)decan-1-one (3g)

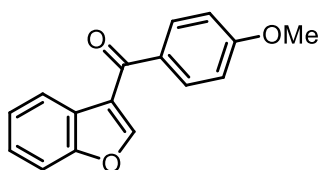
According to the general procedure, the reaction of acetal **2g** (41.3 mg, 0.11 mmol) with *p*-TsOH \cdot H $_2$ O (4.1 mg, 0.022 mmol) in MeCN (1.0 mL) gave **3g** (19.7 mg, 59%) as colorless oil.

Reaction time: 1 h. Eluent of SiO $_2$ column chromatography: Hexane/AcOEt = 6/1.

^1H NMR (600 MHz, CDCl_3) δ 7.29 (d, $J = 7.8$ Hz, 1H), 7.23 (t, $J = 7.8$ Hz, 1H), 6.94 (t, $J = 7.8$ Hz, 1H), 6.89 (d, $J = 7.8$ Hz, 1H), 5.84 (d, $J = 1.8$ Hz, 1H), 4.11 (d, $J = 1.8$ Hz, 1H), 3.55 (s, 3H), 2.64-2.53 (m, 2H), 1.60-1.56 (m, 2H), 1.30-1.25 (12H, m), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 205.5, 158.3, 129.7, 124.9, 123.5, 121.4,

110.8, 108.3, 61.8, 56.3 41.0, 32.0, 29.52, 29.49, 29.37, 29.2, 23.5, 22.8, 14.2; HRMS (ESI) calcd for C₁₉H₂₈O₃Na [M+Na]⁺ : 327.1931, found : 327.1927.

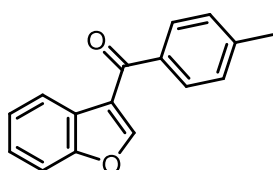
General procedure for the synthesis of 3-acylbenzofuran: To the solution of **3** in THF (0.1 M) was added K₂CO₃ (2 equiv.) and then stirred at room temperature. The reaction was quenched with saturated aq. NH₄Cl and the mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under the reduced pressure. The residue was purified by SiO₂ column chromatography (eluent: Hexane/AcOEt) to give the desired **4**.



Benzofuran-3-yl(4-methoxyphenyl)methanone (4a)

According to the general procedure, the reaction of **3a** (30.0 mg, 0.11 mmol) with K₂CO₃ (30.4 mg, 0.22 mmol) in THF (1.1 mL) gave **4a** (25.7 mg, 97%) as white solid. Reaction time: 4 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 10/1.

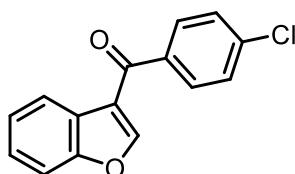
¹H NMR (400 MHz, CDCl₃) δ 8.19-8.17 (m, 1H), 8.08 (s, 1H), 7.93 (d, *J* = 9.2 Hz, 2H), 7.58-7.56 (m, 1H), 7.43-7.37 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.0, 163.6, 155.8, 151.3, 132.1, 131.4, 125.9, 125.7, 124.6, 123.0, 121.5, 114.1, 111.7, 55.6; HRMS (FAB) calcd for C₁₆H₁₂O₃ [M]⁺ 252.0786, found 252.0815.



Benzofuran-3-yl(p-tolyl)methanone (4b)

According to the general procedure, the reaction of **3b** (24.1 mg, 0.09 mmol) with K₂CO₃ (24.9 mg, 0.18 mmol) in THF (0.9 mL) gave **4b** (20.0 mg, 94%) as white solid. Reaction time: 6 h.

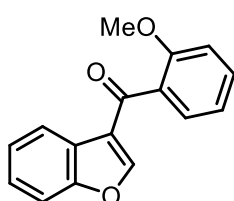
¹H NMR (400 MHz, CDCl₃) δ 8.24-8.22 (m, 1H), 8.09 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.58-7.56 (m, 1H), 7.43-7.38 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 190.2, 155.8, 152.0, 143.5, 136.8, 129.5, 129.2, 125.9, 125.6, 124.6, 123.1, 121.5, 111.6, 21.7; HRMS (FAB) calcd for C₁₆H₁₂O₂ [M]⁺ : 236.0837, found : 236.0834.



Benzofuran-3-yl(4-chlorophenyl)methanone (4c)

According to the general procedure, the reaction of **3c** (10.1 mg, 0.035 mmol) with K₂CO₃ (9.7 mg, 0.070 mmol) in THF (0.35 mL) gave **4c** (8.8 mg, 98%) as other solid. Reaction time: 2.5 h.

¹H NMR (400 MHz, CDCl₃) δ 8.22-8.20 (m, 1H), 8.08 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.59-7.57 (m, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.45-7.40 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 189.1, 155.9, 152.2, 139.2, 137.7, 130.4, 129.2, 126.2, 125.2, 124.9, 123.0, 121.3, 111.8; HRMS (FAB) calcd for C₁₅H₉O₂Cl [M]⁺ 256.0291, found 256.0276.

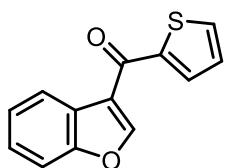


Benzofuran-3-yl(2-methoxyphenyl)methanone (4d)

According to the general procedure, the reaction of **3d** (62.5 mg, 0.22 mmol) with K₂CO₃ (60.8 mg, 0.44 mmol) in THF (2.2 mL) gave **4d** (55.2 mg, 99%) as white solid. Reaction time: 23 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 4/1.

¹H NMR (400 MHz, CDCl₃) δ 8.26-8.23 (m, 1H), 7.92 (s, 1H), 7.55-7.43 (m, 3H), 7.41-7.37

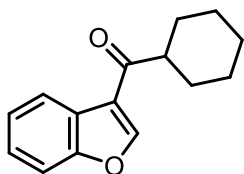
(m, 2H), 7.07-7.02 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.4, 157.2, 156.0, 153.9, 132.2, 130.0, 129.3, 125.8, 124.9, 124.7, 123.1, 120.6, 120.6, 111.9, 111.6, 55.8; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{12}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 275.0679, found 275.0667.



Benzofuran-3-yl(thiophen-2-yl)methanone (**4e**)

According to the general procedure, the reaction of **3e** (9.1 mg, 0.035 mmol) with K_2CO_3 (9.7 mg, 0.070 mmol) in THF (0.4 mL) gave **4e** (7.7 mg, 96%) as white solid. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 10/1.

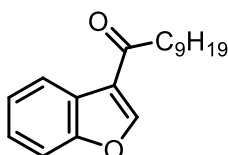
^1H NMR (400 MHz, CDCl_3) δ 8.32 (s, 1H), 8.22-8.20 (m, 1H), 7.84 (dd, $J = 3.6, 0.8$ Hz, 1H), 7.72 (dd, $J = 4.4, 1.2$ Hz, 1H), 7.59-7.57 (m, 1H), 7.44-7.38 (m, 2H), 7.21 (dd, $J = 4.8, 4.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 181.1, 155.7, 150.4, 144.5, 133.5, 132.5, 128.2, 126.1, 125.3, 124.6, 122.9, 121.5, 111.7; HRMS (FAB): calcd for $\text{C}_{13}\text{H}_8\text{O}_2\text{S}$ $[\text{M}]^+$: 228.0245, found : 228.0244.



Benzofuran-3-yl(cyclohexyl)methanone (**4f**)

According to the general procedure, the reaction of **3f** (50.0 mg, 0.19 mmol) with K_2CO_3 (52.5 mg, 0.38 mmol) in THF (1.9 mL) gave **4f** (38.9 mg, 90%) as white solid. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 10/1.

^1H NMR (400 MHz, CDCl_3) δ : 8.73-8.24 (m, 2H), 7.54-7.51 (m, 1H), 7.38-7.36 (m, 2H), 3.00-2.94 (m, 1H), 1.95-1.86 (m, 4H), 1.76-1.55 (m, 4H), 1.43-1.26 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.9, 156.0, 150.7, 125.7, 124.9, 124.7, 123.2, 121.4, 111.6, 48.9, 29.6, 25.90, 25.88; HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$: 228.1150, found 228.1166.

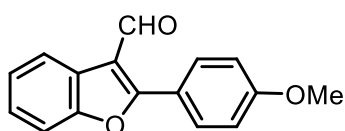


1-(Benzofuran-3-yl)decan-1-one (**4g**)

According to the general procedure, the reaction of **3g** (13.6 mg, 0.045 mmol) with K_2CO_3 (12.3 mg, 0.089 mmol) in THF (0.5 mL) gave **4g** (11.3 mg, 92%) as white solid. Reaction time: 2.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 10/1.

^1H NMR (600 MHz, CDCl_3) δ 8.26-8.24 (m, 2H), 7.53-7.52 (m, 1H), 7.38-7.36 (m, 2H), 7.55-7.59 (m, 1H), 2.86 (t, $J = 7.2$ Hz, 3H), 1.79-1.76 (m, 2H), 1.39-1.24 (12H, m), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 196.3, 155.8, 150.8, 125.7, 124.6, 124.5, 123.1, 122.5, 111.6, 40.8, 32.0, 29.63, 29.60, 29.5, 29.4, 24.7, 22.8, 14.2; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$: 273.1849, found : 273.1836.

General procedure for the synthesis of 3-formylbenzofuran: To the solution of **3** in $(\text{CF}_3)_2\text{CHOH}$ (0.1 M) was added *p*-TsOH \cdot H $_2\text{O}$ (2 equiv.) and then stirred at room temperature. The reaction was quenched with saturated aq. NaHCO_3 and the mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under the reduced pressure. The residue was purified by SiO_2 column chromatography (eluent: Hexane/AcOEt) to give the desired **5**.

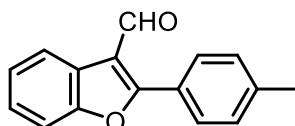


2-(4-Methoxyphenyl)benzofuran-3-carbaldehyde (**5a**)¹⁾

According to the general procedure, the reaction of **3a** (19.9 mg, 0.07 mmol) and *p*-TsOH•H₂O (26.6 mg, 0.14 mmol) in (CF₃)₂CHOH (0.7 mL) gave **5a** (17.3 mg, 98%) as white solid. Reaction time: 20 min. Eluent of SiO₂ column chromatography:

Hexane/AcOEt = 2/1.

¹H NMR (400 MHz, CDCl₃) δ 10.33 (s, 1H), 8.27-8.25 (m, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.55-7.53 (m, 1H), 7.39-7.37 (m, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 186.8, 165.8, 162.2, 153.9, 130.9, 125.8, 125.8, 124.9, 122.6, 121.2, 116.7, 114.8, 111.1, 55.7.

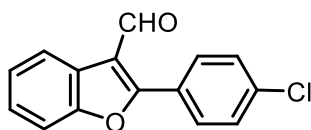


2-(*p*-Tolyl)benzofuran-3-carbaldehyde (**5b**)

According to the general procedure, the reaction of **3b** (20.0 mg, 0.075 mmol) and *p*-TsOH•H₂O (28.5 mg, 0.15 mmol) in (CF₃)₂CHOH (0.8 mL) gave **5b** (17.3 mg, 98%) as yellow solid. Reaction time: 20 min. Eluent of SiO₂ column chromatography:

Hexane/AcOEt = 2/1.

¹H NMR (400 MHz, CDCl₃) δ 10.34 (s, 1H), 8.29-8.26 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.57-7.55 (m, 1H), 7.42-7.37 (m, 4H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 187.0, 154.2, 142.0, 130.1, 129.3, 126.1, 126.0, 125.7, 125.0, 122.8, 111.3, 21.6; HRMS (ESI) calcd for C₁₆H₁₂O₂Na [M+Na]⁺ 259.0730, found 259.0727.

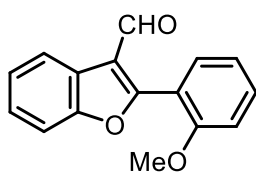


2-(4-Chlorophenyl)benzofuran-3-carbaldehyde (**5c**)

According to the general procedure, the reaction of **3c** (20.2 mg, 0.07 mmol) and *p*-TsOH•H₂O (26.3 mg, 0.14 mmol) in (CF₃)₂CHOH (0.7 mL) gave **5c** (17.5 mg, 97%) as white solid. Reaction time: 25 min. Eluent of SiO₂ column chromatography:

Hexane/AcOEt = 2/1.

¹H NMR (400 MHz, CDCl₃) δ 10.35 (s, 1H), 8.28-8.26 (m, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.58-7.55 (m, 3H), 7.45-7.38 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 186.3, 154.3, 137.8, 130.4, 129.7, 127.3, 126.5, 125.6, 125.2, 122.9, 117.9, 111.4; HRMS (ESI) calcd for C₁₅H₁₀O₂Cl [M+H]⁺ 257.0364, found 257.0360.

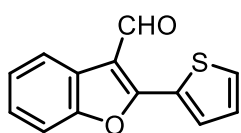


2-(2-Methoxyphenyl)benzofuran-3-carbaldehyde (**5d**)

According to the general procedure, the reaction of **3d** (60.0 mg, 0.21 mmol) and *p*-TsOH•H₂O (81.2 mg, 0.42 mmol) in (CF₃)₂CHOH (2.1 mL) gave **5d** (48.6 mg, 91%) as white solid. Reaction time: 25 min. Eluent of SiO₂ column chromatography: Hexane/AcOEt

= 2/1.

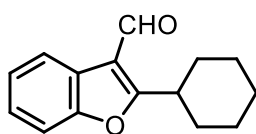
¹H NMR (400 MHz, CDCl₃) δ 10.11 (s, 1H), 8.28-8.26 (m, 1H), 7.64 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.57-7.52 (m, 2H), 7.39-7.37 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 188.0, 162.9, 157.6, 154.8, 132.8, 132.0, 125.8, 125.4, 124.8, 122.8, 121.1, 118.4, 117.9, 111.9, 111.3, 55.9; HRMS (ESI) calcd for C₁₆H₁₃O₃ [M+H]⁺ 253.0859, found 253.0852.



2-(Thiophen-2-yl)benzofuran-3-carbaldehyde (**5e**)

According to the general procedure, the reaction of **3e** (28.8 mg, 0.11 mmol) and *p*-TsOH·H₂O (41.8 mg, 0.22 mmol) in (CF₃)₂CHOH (1.1 mL) gave **5e** (22.5 mg, 90%) as yellow solid. Reaction time: 40 min. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 4/1.

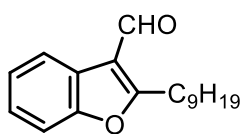
¹H NMR (400 MHz, CDCl₃) δ 10.56 (s, 1H), 8.23-8.21 (m, 1H), 7.85 (d, *J* = 4.0 Hz, 1H), 7.64 (d, *J* = 5.2 Hz, 1H), 7.54-7.52 (m, 1H), 7.42-7.35 (m, 2H), 7.25-7.23 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 185.6, 154.0, 130.7, 130.5, 130.5, 128.6, 126.3, 125.8, 125.1, 122.5, 116.5, 111.2; HRMS (ESI) calcd for C₁₃H₉O₂S [M+H]⁺ 229.0318, found : 229.0315.



2-Cyclohexylbenzofuran-3-carbaldehyde (**5f**)

According to the general procedure, the reaction of **3f** (20.1 mg, 0.077 mmol) and *p*-TsOH·H₂O (28.5 mg, 0.15 mmol) in (CF₃)₂CHOH (0.8 mL) gave **5f** (17.1 mg, 98%) as white solid. Reaction time: 25 min. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 3/1.

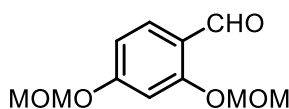
¹H NMR (400 MHz, CDCl₃) δ 10.28 (s, 1H), 8.15-8.13 (m, 1H), 7.47-7.45 (m, 1H), 7.35-7.30 (m, 2H), 3.35-3.28 (m, 1H), 1.98-1.91 (m, 4H), 1.87-1.80 (m, 3H), 1.50-1.34 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 185.0, 174.5, 154.0, 125.2, 124.9, 124.6, 122.1, 116.2, 111.1, 37.1, 31.5, 26.1, 25.6; HRMS (ESI) calcd for C₁₅H₁₇O₂ [M+H]⁺ 229.1223, found 229.1222.



2-Nonylbenzofuran-3-carbaldehyde (**5g**)

According to the general procedure, the reaction of **3g** (13.1 mg, 0.043 mmol) and *p*-TsOH·H₂O (16.4 mg, 0.086 mmol) in (CF₃)₂CHOH (0.5 mL) gave **5g** (9.1 mg, 78%) as yellow oil. Reaction time: 30 min. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 10/1.

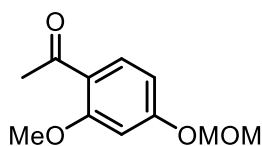
¹H NMR (600 MHz, CDCl₃) δ 10.23 (s, 1H), 8.14-8.13 (m, 1H), 7.47-7.46 (m, 1H), 7.34-7.32 (m, 2H), 3.10 (t, *J* = 7.8 Hz, 2H), 1.87-1.82 (m, 2H), 1.42-1.26 (m, 12H), 0.88 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 185.0, 170.9, 154.1, 125.3, 124.8, 124.6, 121.9, 117.7, 111.0, 32.0, 29.5, 29.4, 29.37, 29.35, 28.4, 27.3, 22.8, 14.2; HRMS (ESI) calcd for C₁₈H₂₅O₂ [M+H]⁺ : 273.1849, found : 273.1849.



2,4-Bis(methoxymethoxy)benzaldehyde (**6**)²

To the solution of 2,4-dihydroxybenzaldehyde (2.00 g, 14.5 mmol) in DCM (30 mL) was added MOMCl (3.3 mL, 43.5 mmol) and *i*-Pr₂NEt (10.1 mL, 72.4 mmol) at room temperature. After stirring at same temperature for 2.5 h, the reaction was quenched with MeOH, and the resulting solution was extracted with CHCl₃. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by SiO₂ column chromatography (Hexane/AcOEt = 10/1) to give **6** (3.18 g, 97%) as white solid.

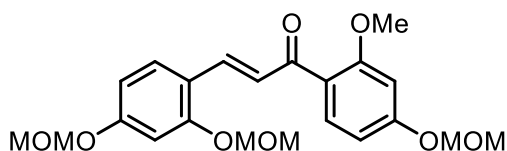
¹H NMR (400 MHz, CDCl₃) δ 10.35 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 6.75 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.28 (s, 2H), 5.22 (s, 2H), 3.53 (s, 3H), 3.49 (s, 3H).



1-(2-Methoxy-4-(methoxymethoxy)phenyl)ethan-1-one (7)

To the solution of 2,4-dihydroxyacetophenone (1.27 g, 9.2 mmol) in acetone (9.2 mL) was added K_2CO_3 (3.17 g, 23 mmol) and MOMCl (1.4 mL, 18.4 mmol). After stirring at room temperature for 17 h, the reaction was quenched with MeOH, and the resulting solution was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under the reduced pressure. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt = 6/1) to give 1-(2-hydroxy-4-(methoxymethoxy)phenyl)-ethan-1-one (1.41 g, 80%) as colorless oil. To the solution of 1-(2-hydroxy-4-(methoxymethoxy)phenyl)-ethan-1-one (1.40 g, 7.1 mmol) in dry DMF (3.6 mL) was added K_2CO_3 (2.78 g, 21.3 mmol) and MeI (0.53 mL, 8.5 mmol) under Ar. After stirring at 80 °C for 0.5 h, the reaction was quenched with H_2O , and the resulting solution was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under the reduced pressure. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt = 4/1) to give **7** (1.34 g, 88%) as yellow oil.

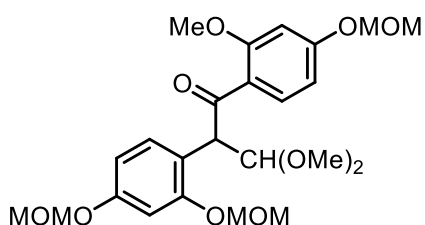
1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.8 Hz, 1H), 6.65 (dd, J = 8.8, 2.0 Hz, 1H), 6.61 (d, J = 2.0 Hz, 1H), 5.21 (s, 2H), 3.89 (s, 3H), 3.49 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 162.0, 160.8, 132.1, 121.5, 107.3, 99.5, 93.8, 55.8, 55.1, 31.4; HRMS (ESI) calcd for $C_{11}H_{14}O_4Na$ $[M+Na]^+$: 233.0784, found : 233.0777.



(E)-3-(2,4-Bis(methoxymethoxy)phenyl)-1-(2-methoxy-4-(methoxymethoxy)phenyl)prop-2-en-1-one (8)

To the solution of **6** (1.27 g, 5.6 mmol) and **7** (1.30 g, 6.2 mmol) in EtOH (10 mL) was added KOH (1.11 g, 16.8 mmol) at room temperature, then stirred for 22 h. The reaction was quenched with H_2O , and the resulting solution was extracted with CH_2Cl_2 , washed with brine, dried over Na_2SO_4 and concentrated under the reduced pressure. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt = 2/1) to give **8** (2.09 g, 89%) as yellow oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 16.0 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 16.0 Hz, 1H), 6.84 (d, J = 2.4 Hz, 1H), 6.73-6.68 (m, 2H), 6.64 (d, J = 2.0 Hz, 1H), 5.23 (s, 2H), 5.22 (s, 2H), 5.19 (s, 2H), 3.89 (s, 3H), 3.50 (s, 3H), 3.49 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 161.5, 160.2, 160.1, 157.6, 137.3, 132.5, 129.5, 125.8, 123.5, 119.1, 109.3, 107.7, 103.4, 100.1, 94.6, 94.3, 94.2, 56.3, 56.2, 56.1, 55.7; HRMS (ESI): calcd for $C_{22}H_{26}O_8Na$ $[M+Na]^+$: 441.1520, found 441.1501.

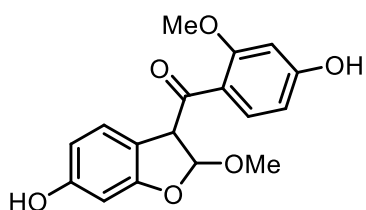


2-(2,4-Bis(methoxymethoxy)phenyl)-3,3-dimethoxy-1-(2-methoxy-4-(methoxymethoxy)phenyl)propan-1-one (9)

To the solution of **8** (53.9 mg, 0.13 mmol) in MeOH (1.3 mL) was added $PhI(OCOCF_3)_2$ (83.1 mg, 0.19 mmol) at room temperature, then stirred at same temperature for 3 h. The reaction was extracted with $CHCl_3$, washed with brine, dried over Na_2SO_4 and concentrated under the reduced pressure. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt = 2/1) to give **9** (42.3 mg, 69%) as yellow oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 6.63 (dd, J = 8.4, 2.4 Hz, 1H), 6.56 (dd, J = 8.4, 2.4 Hz, 1H), 6.50 (d, J = 2.0 Hz, 1H), 5.44 (d, J = 8.4 Hz, 1H), 5.16 (s, 2H), 5.13 (s, 2H), 5.11 (s, 2H), 5.06 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H), 3.46 (s, 3H), 3.449 (s, 3H), 3.446 (s, 3H), 3.44 (s, 3H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 161.8, 160.6, 157.5, 156.4, 133.0, 130.1, 122.3, 118.6, 109.0,

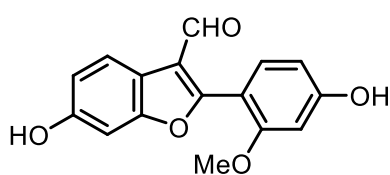
107.3, 107.1, 103.8, 100.1, 95.1, 94.7, 94.2, 56.3, 56.2, 56.1, 56.0, 55.6, 54.4, 51.9; HRMS (ESI): calcd for $C_{24}H_{32}O_{10}Na$ $[M+Na]^+$: 503.1893, found 503.1866.



(6-Hydroxy-2-methoxy-2,3-dihydrobenzofuran-3-yl)(4-hydroxy-2-methoxyphenyl)methanone (10)

To the solution of **9** (49.8 mg, 0.10 mmol) in MeCN (1.0 mL) was added *p*-TsOH·H₂O (3.9 mg, 0.02 mmol) and then stirred at 0 °C. After stirring for 1 h, *p*-TsOH·H₂O (74.8 mg, 0.38 mmol) and EtOH (36 μL, 0.6 mmol) was added, and then stirred at 10 °C for 2.5 h. The reaction was quenched with saturated aq. NaHCO₃ and the mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under the reduced pressure. The residue was purified by SiO₂ column chromatography (Hexane/AcOEt = 2:1) to give **10** (17.8, 54%) as yellow foam.

¹H NMR (600 MHz, MeOD) δ 7.37 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 6.35 (d, *J* = 1.2 Hz, 1H), 6.24 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.06 (s, 1H), 6.01 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.67 (d, *J* = 1.8 Hz, 1H), 4.90 (s, 1H), 3.72 (s, 3H); ¹³C NMR (151 MHz, MeOD) δ 197.7, 165.7, 162.9, 160.9, 159.9, 134.5, 126.1, 118.9, 117.5, 111.1, 109.4, 108.9, 100.0, 98.7, 61.0, 56.3, 56.0; HRMS (ESI): calcd for $C_{17}H_{16}O_6Na$ $[M+Na]^+$ 339.0839, found 339.0840.



Puerariafuran³⁾

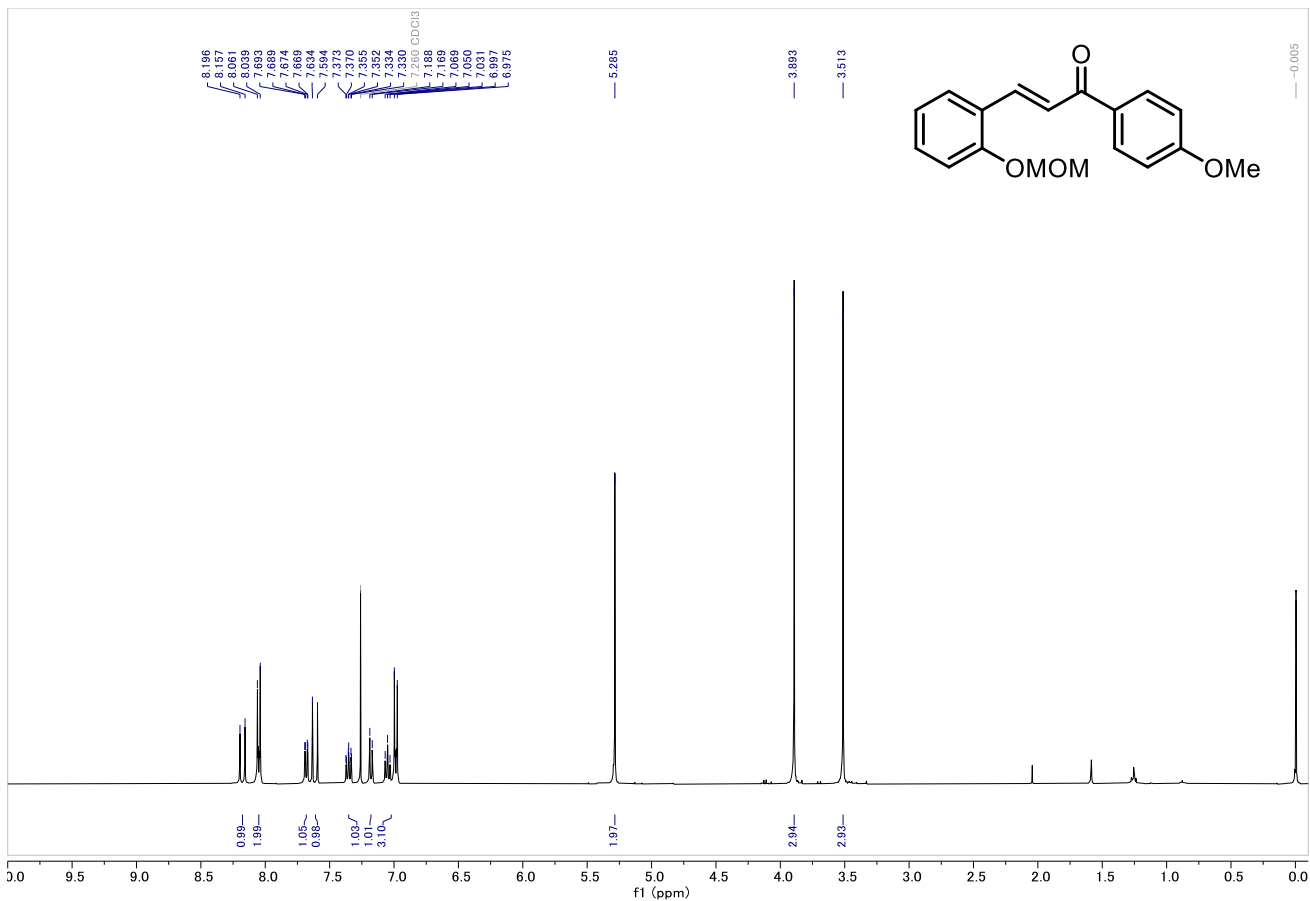
According to the general procedure, the reaction of **10** (16.2 mg, 0.051 mmol) and *p*-TsOH·H₂O (19.5 mg, 0.10 mmol) in (CF₃)₂CHOH (0.5 mL) gave puerariafuran (11.7 mg, 81%) as a yellow solid. Reaction time: 1 h. Eluent of SiO₂ column chromatography: Hexane/AcOEt = 2/1.

¹H NMR (600 MHz, DMSO-*d*₆) δ 10.24 (brs, 1H), 9.89 (s, 1H), 9.77 (brs, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 6.99 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.61 (s, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 3.77 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 187.1, 162.3, 161.6, 158.6, 156.3, 154.8, 132.7, 121.6, 116.5, 113.5, 108.0, 107.8, 99.7, 97.6, 55.6; HRMS (ESI): calcd for $C_{16}H_{12}O_5Na$ $[M+Na]^+$ 307.0577, found 307.0556.

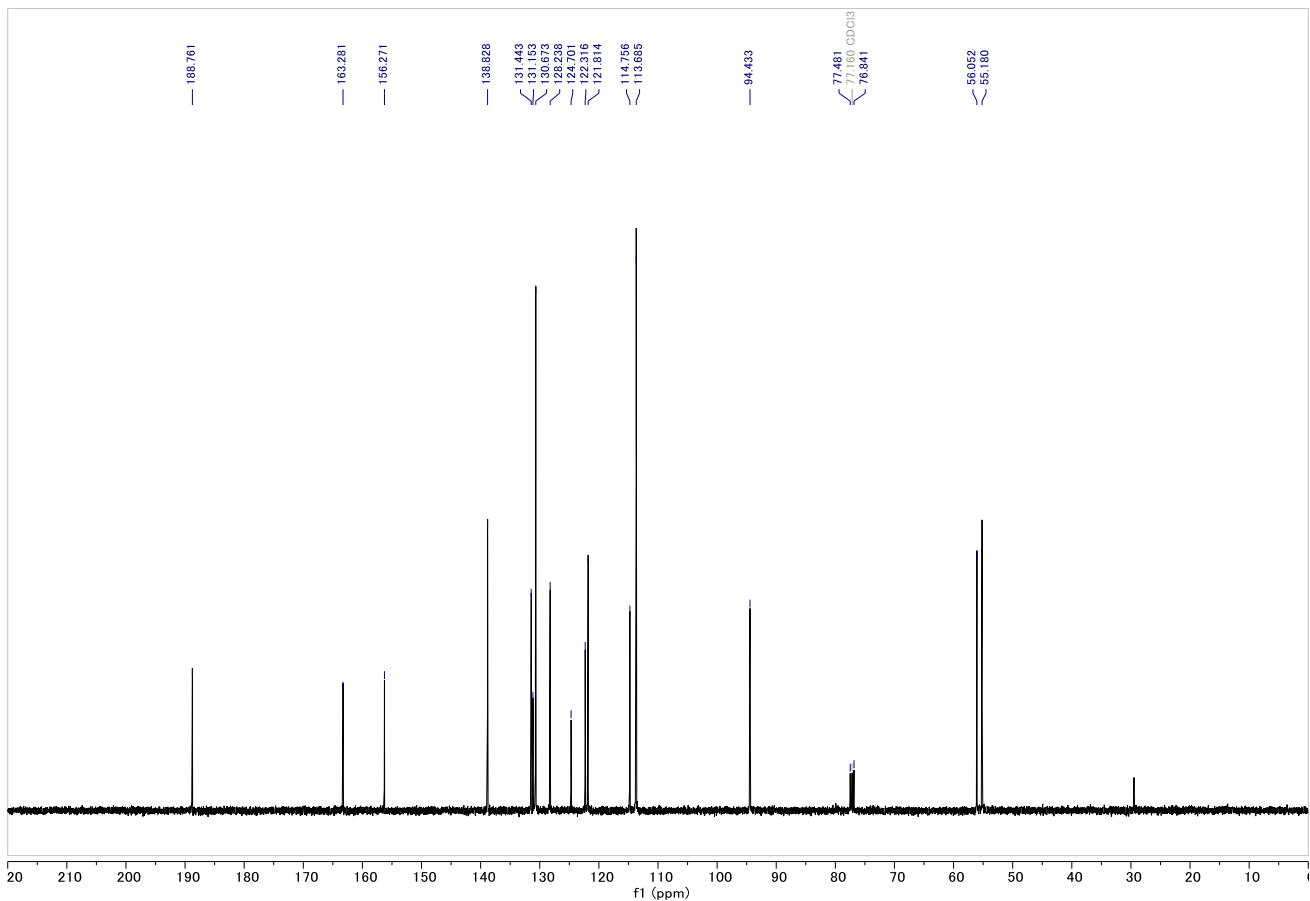
References

- 1) Bresser, T.; Mosrin, M.; Monzon, G.; Knochel, P. *J. Org. Chem.* **2010**, *75*, 4686.
- 2) Jogireddy, R.; Maier, M. E. *J. Org. Chem.* **2006**, *71*, 6999.
- 3) Jang, D. S.; Kim, J. M.; Lee, Y. M.; Kim, Y. S.; Kim, J.-H.; Kim, J. S. *Chem. Pharm. Bull.* **2006**, *54*, 1315.

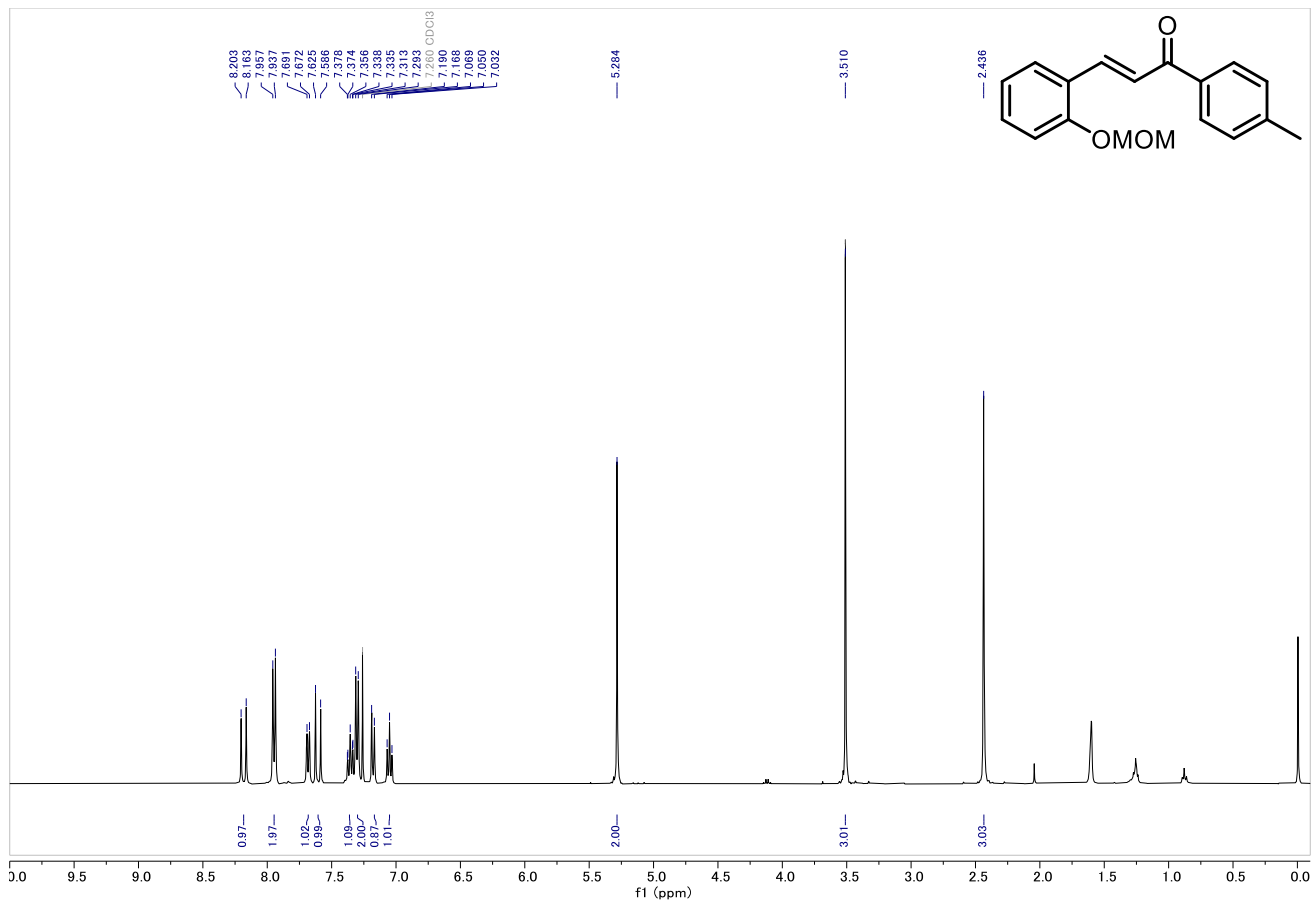
¹H NMR 1a



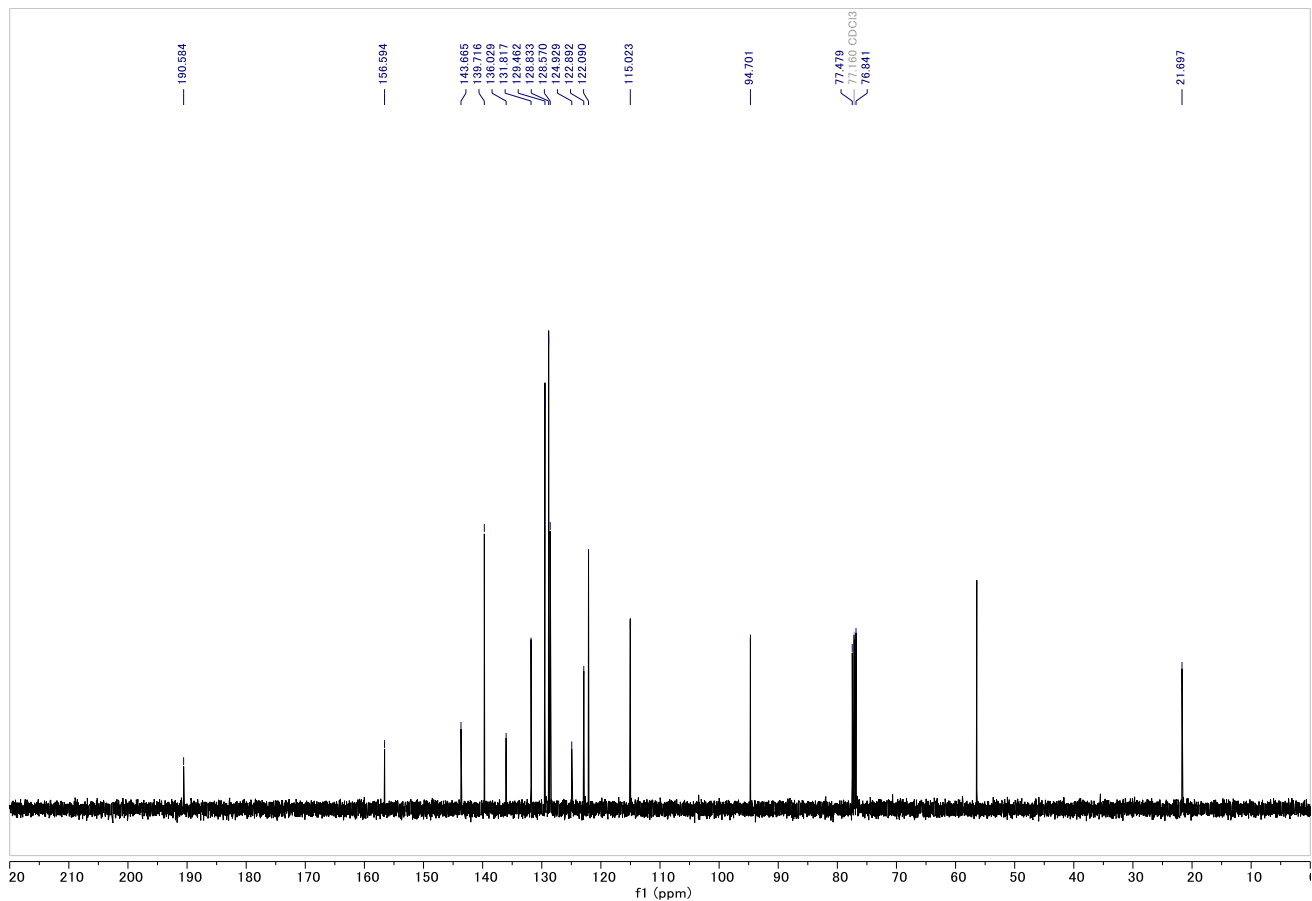
¹³C NMR 1a



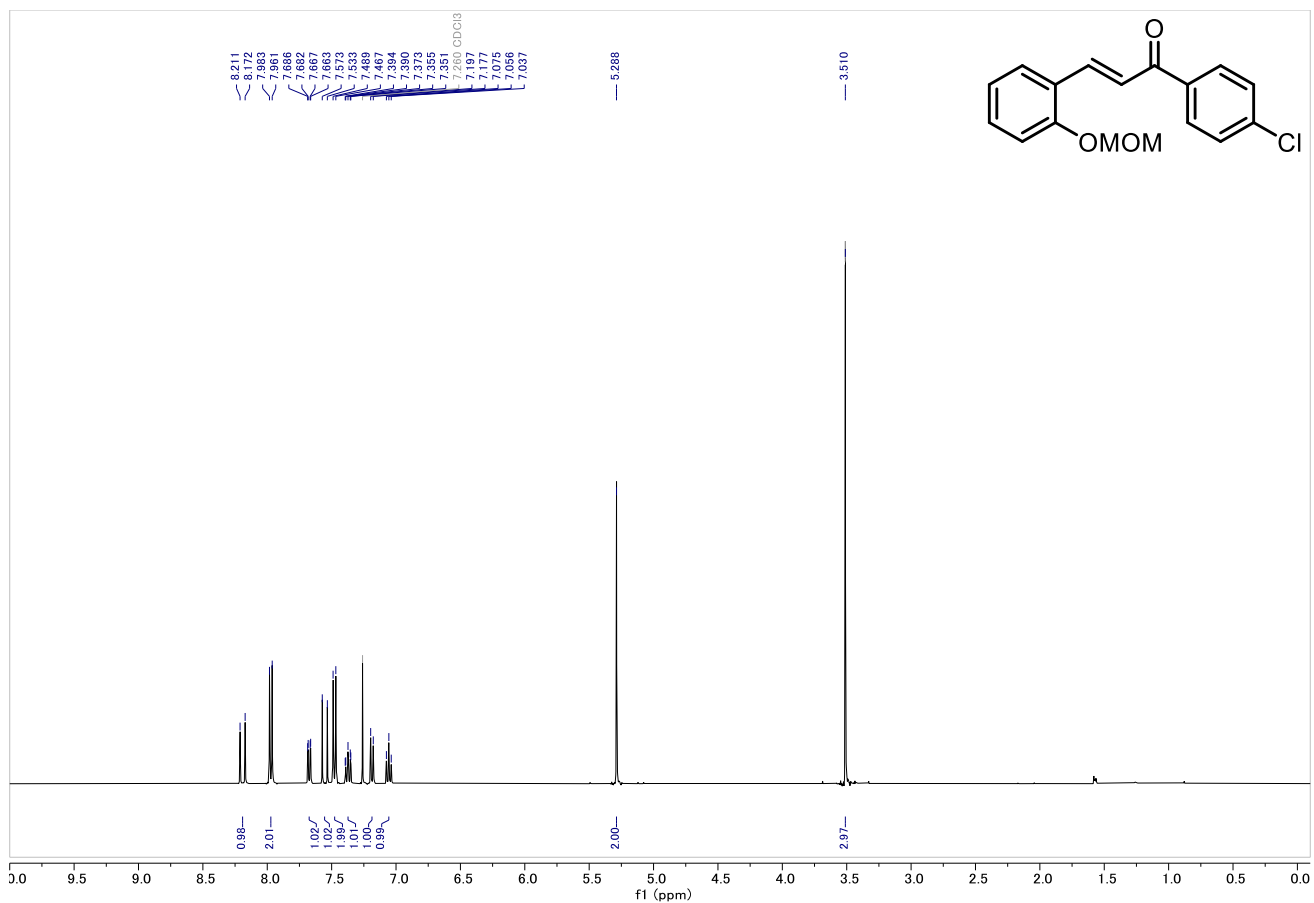
¹H NMR **1b**



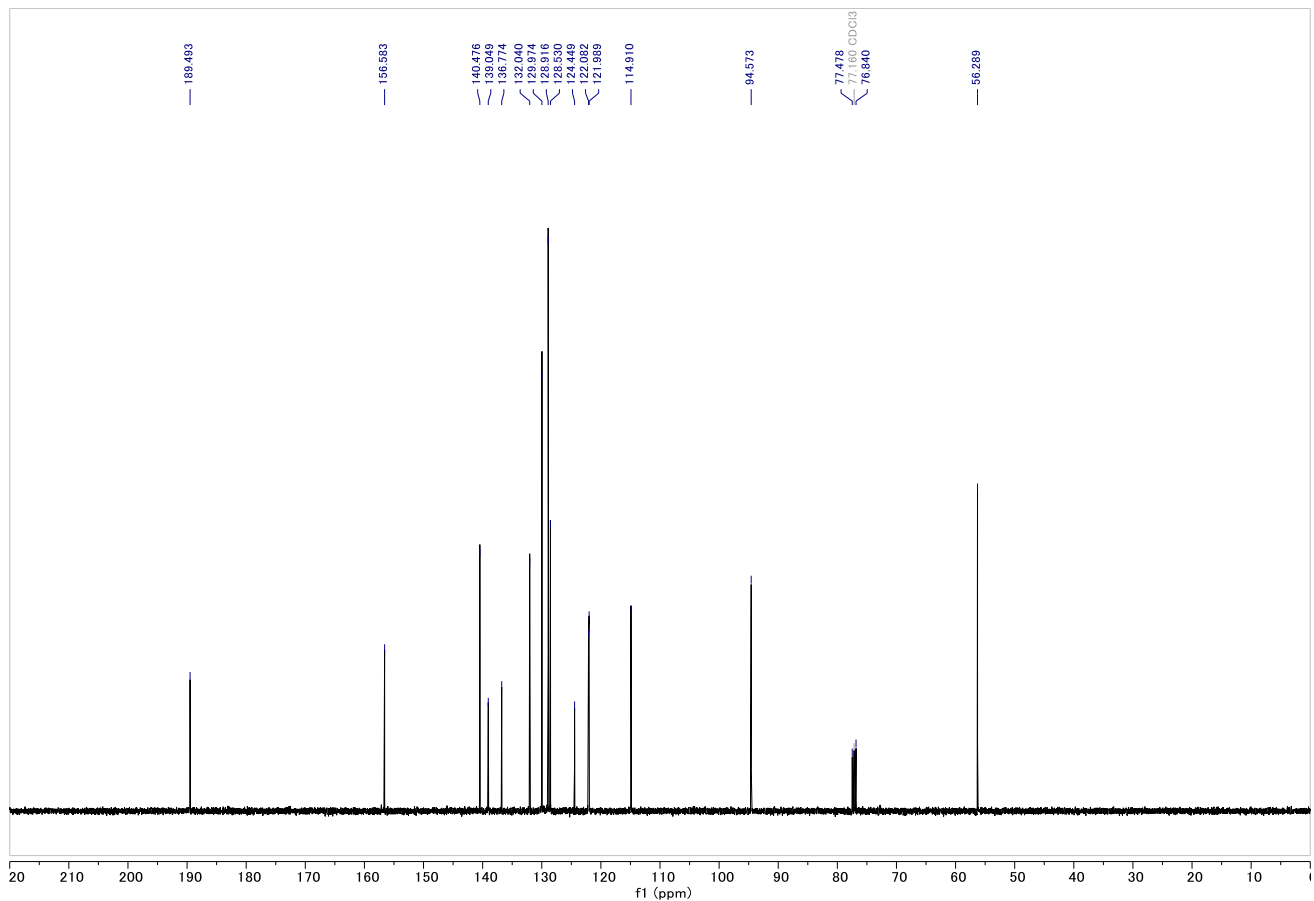
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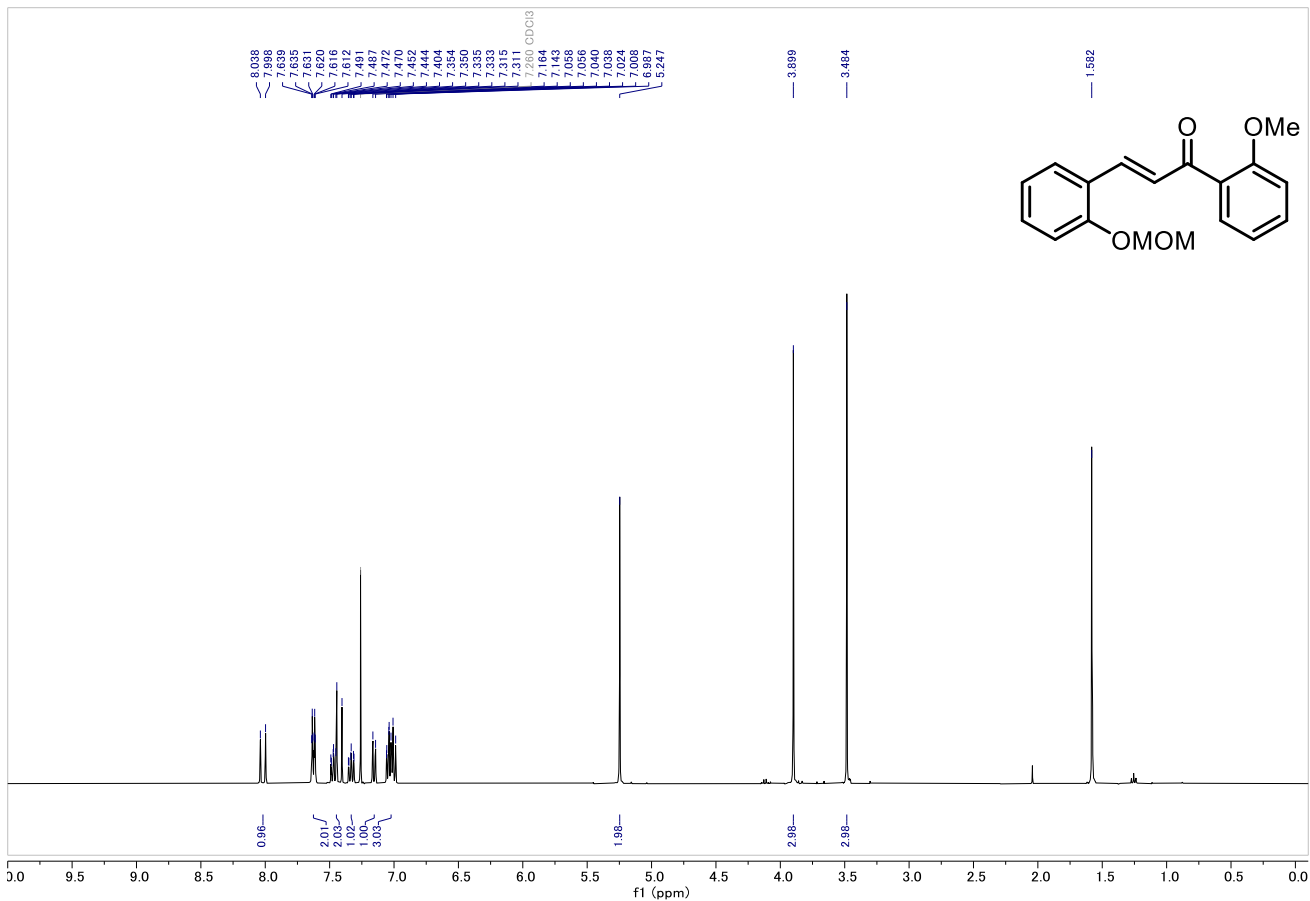
¹H NMR 1c



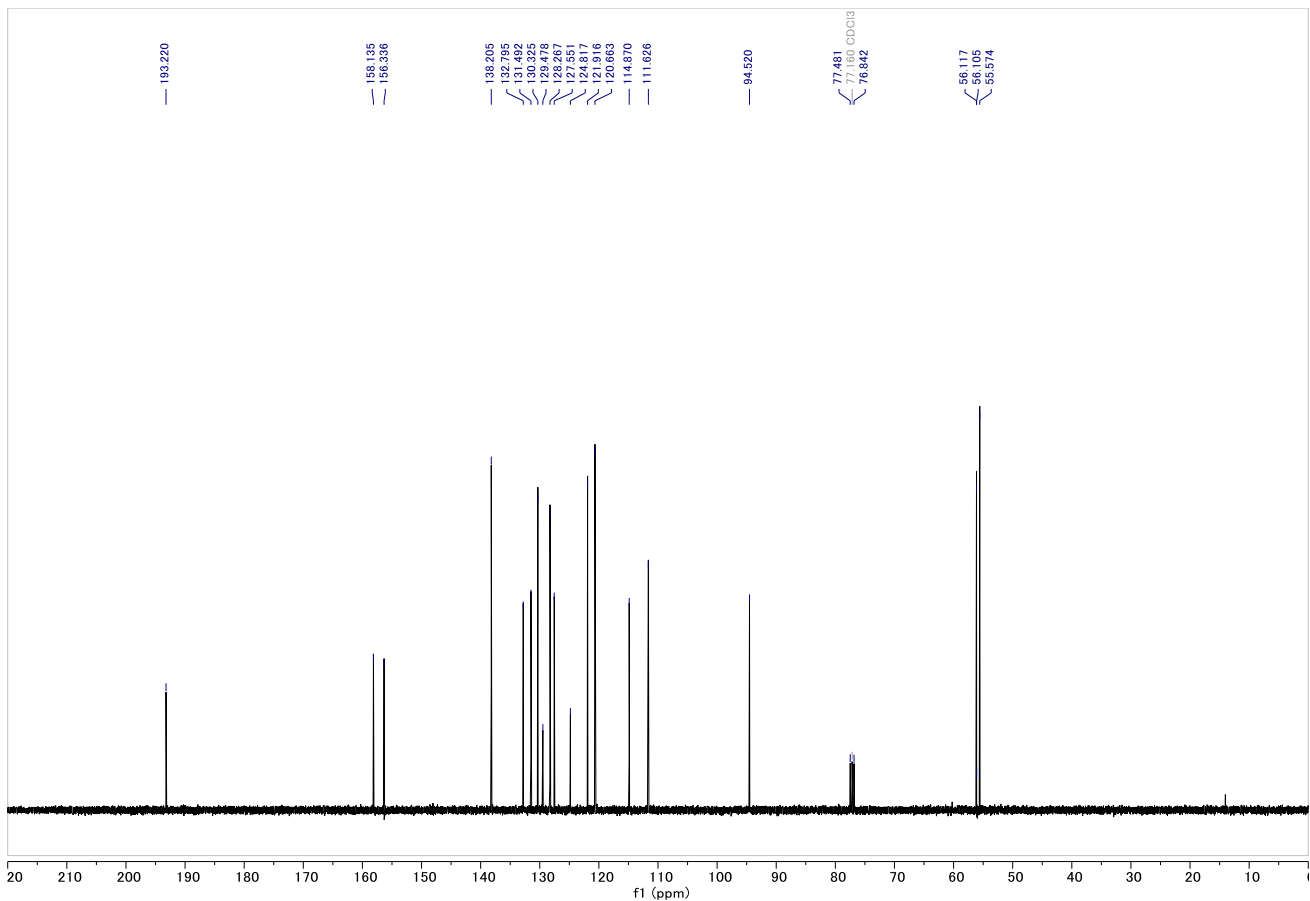
¹³C NMR 1c



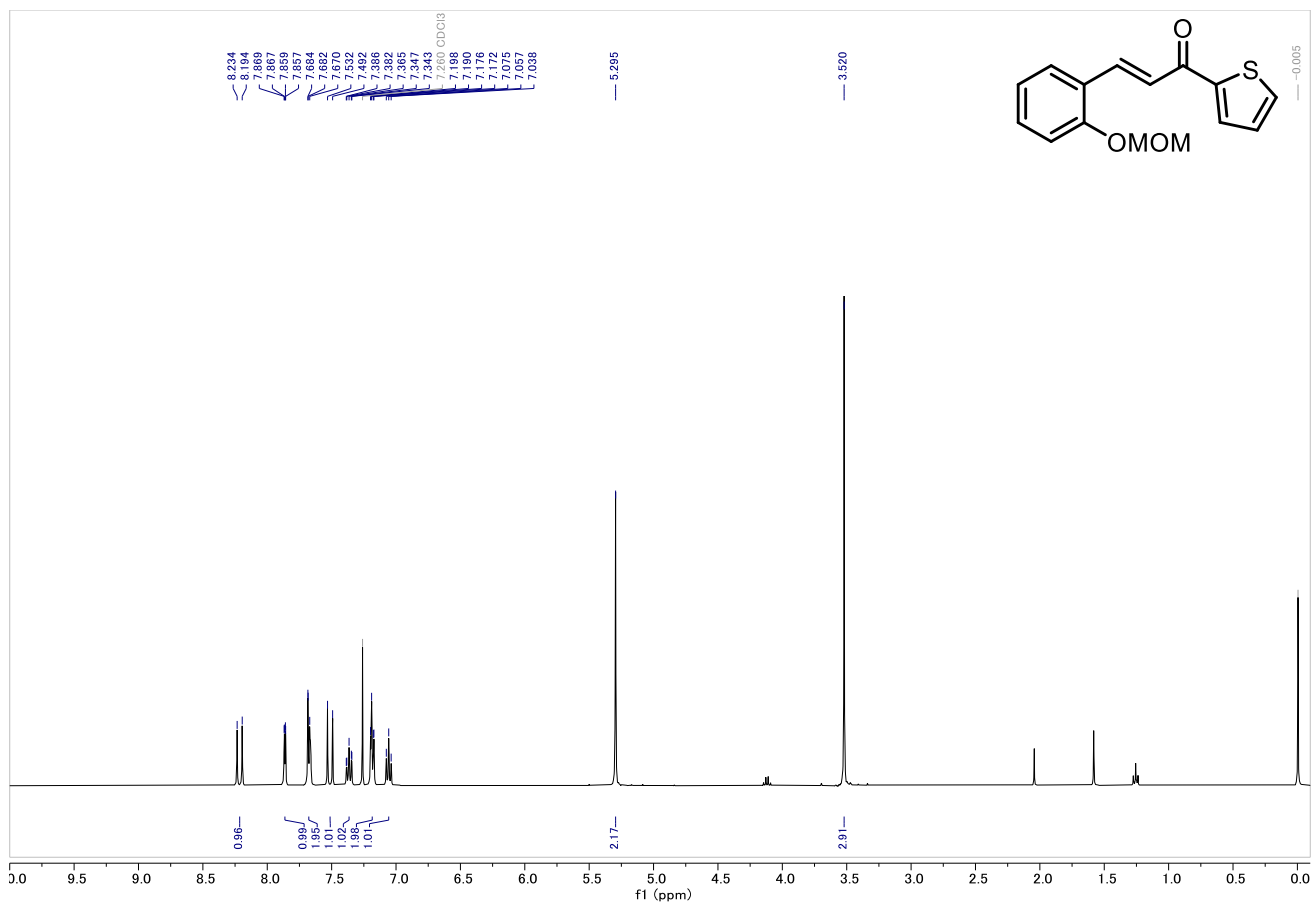
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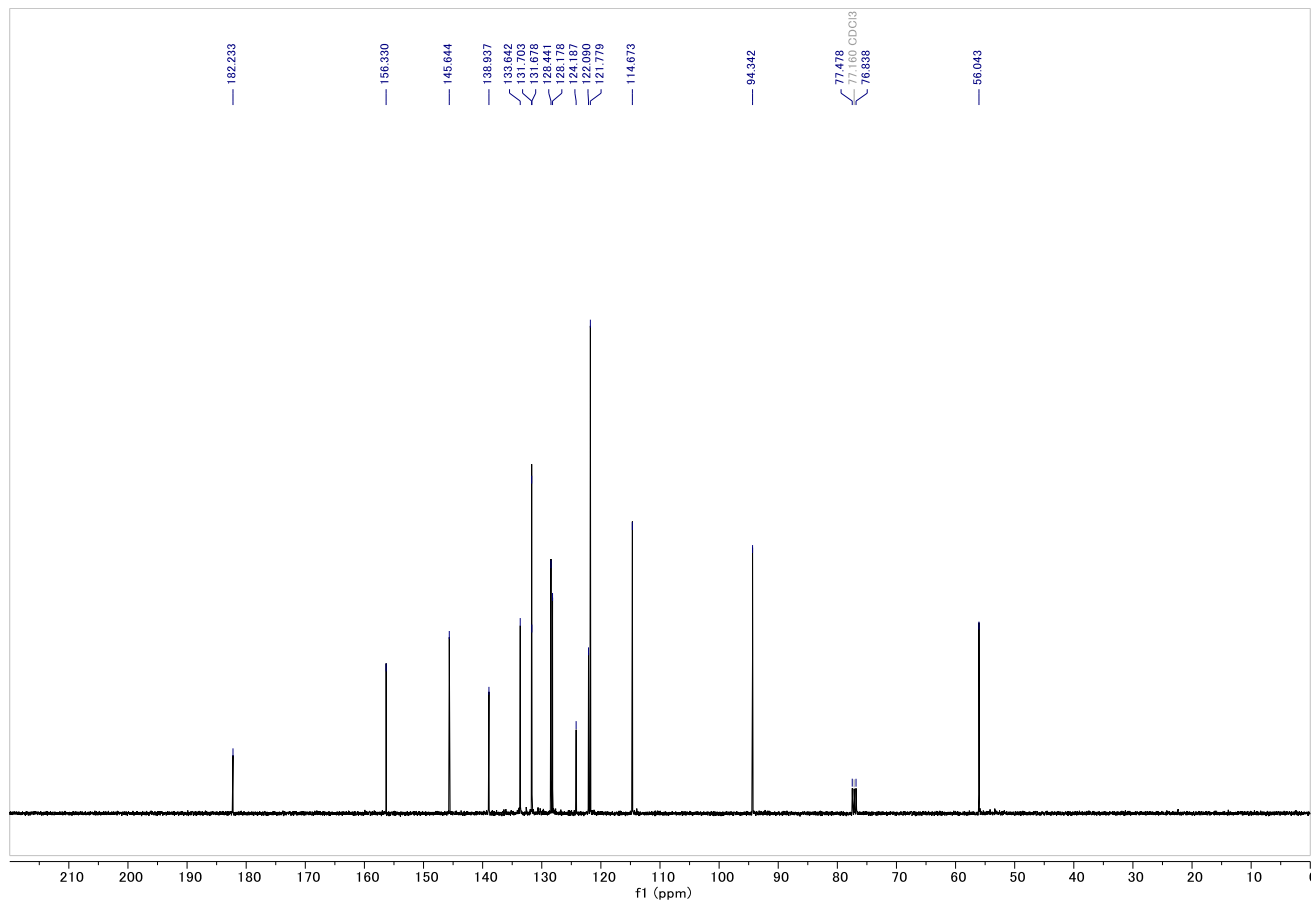
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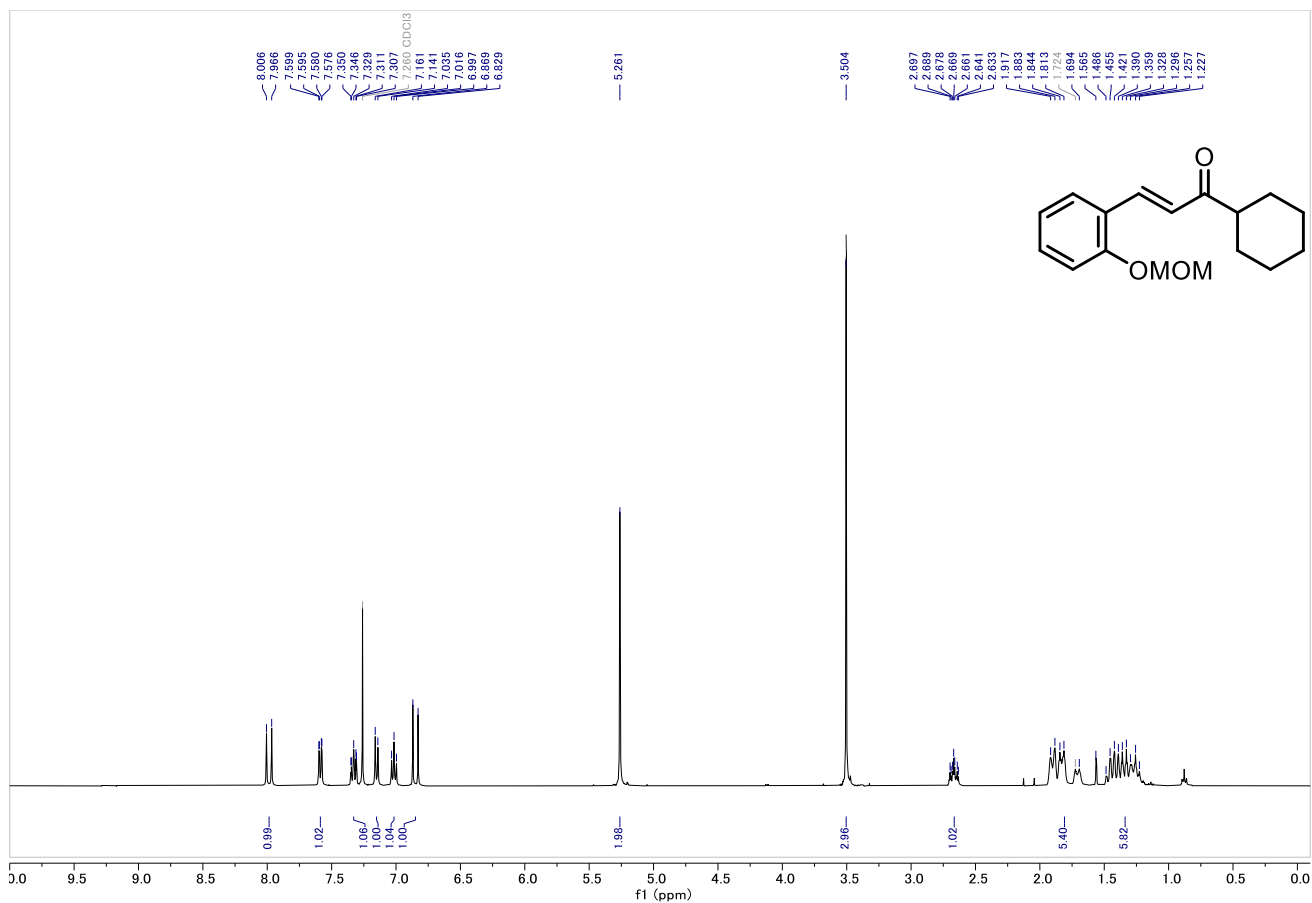
¹H NMR 1e



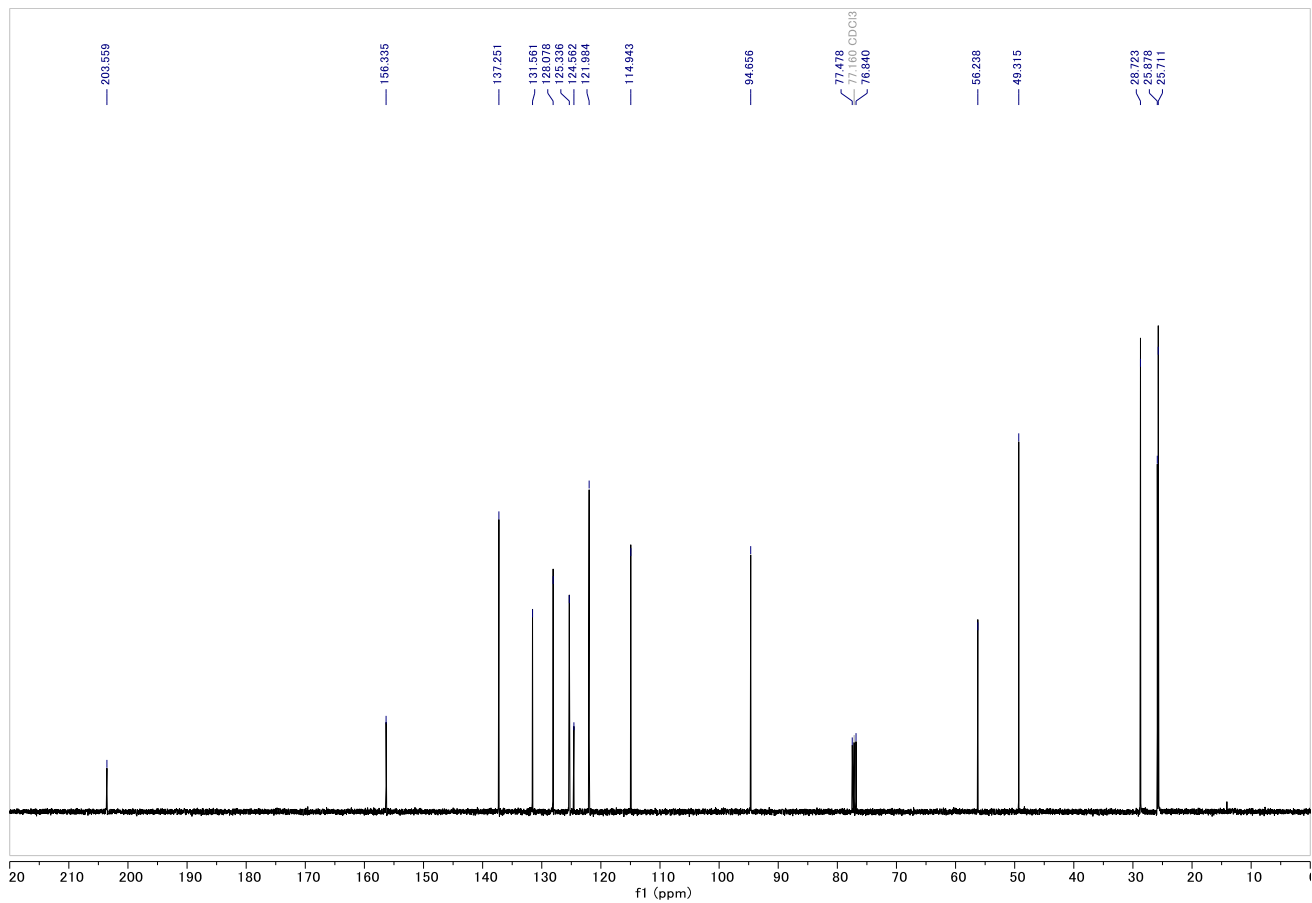
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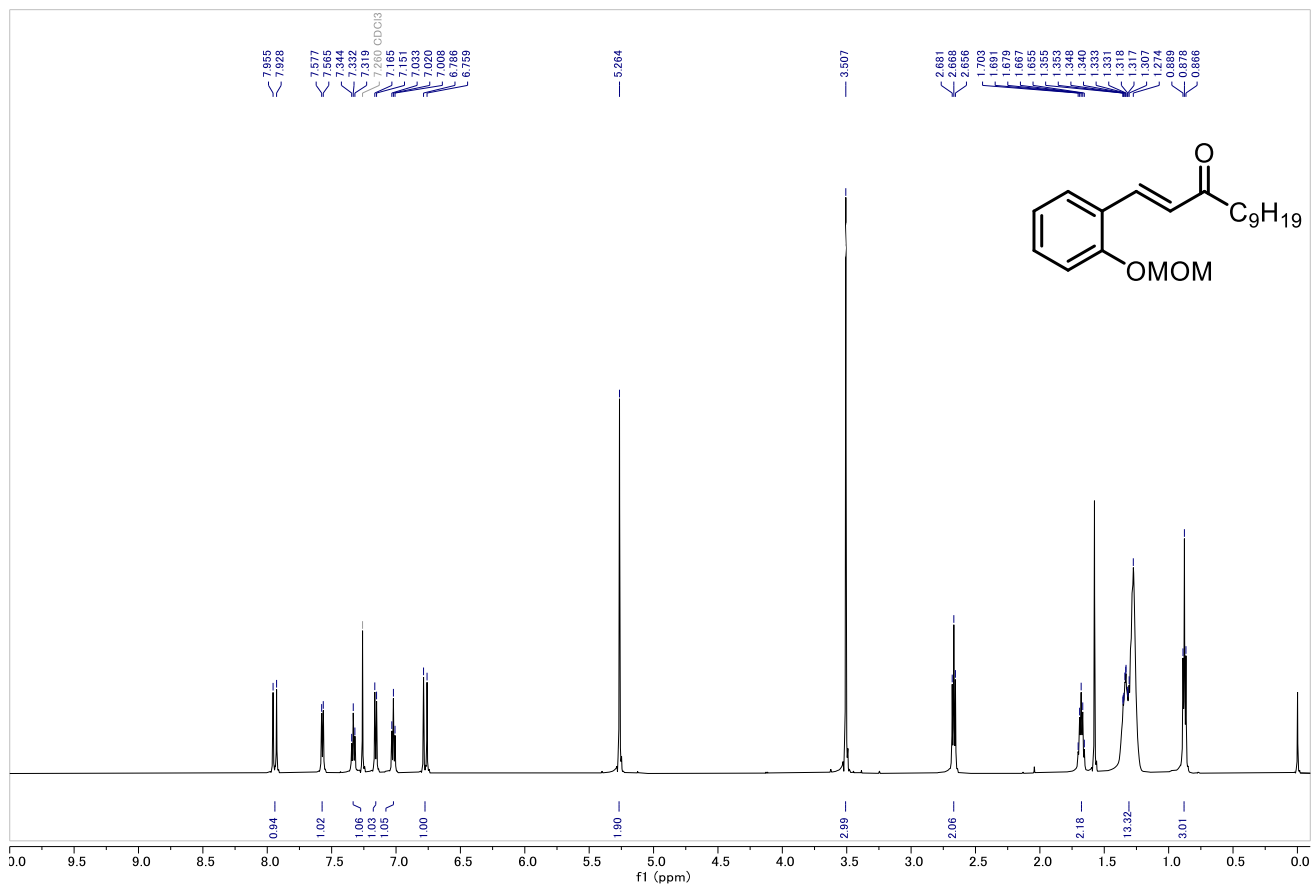
¹H NMR **1f**



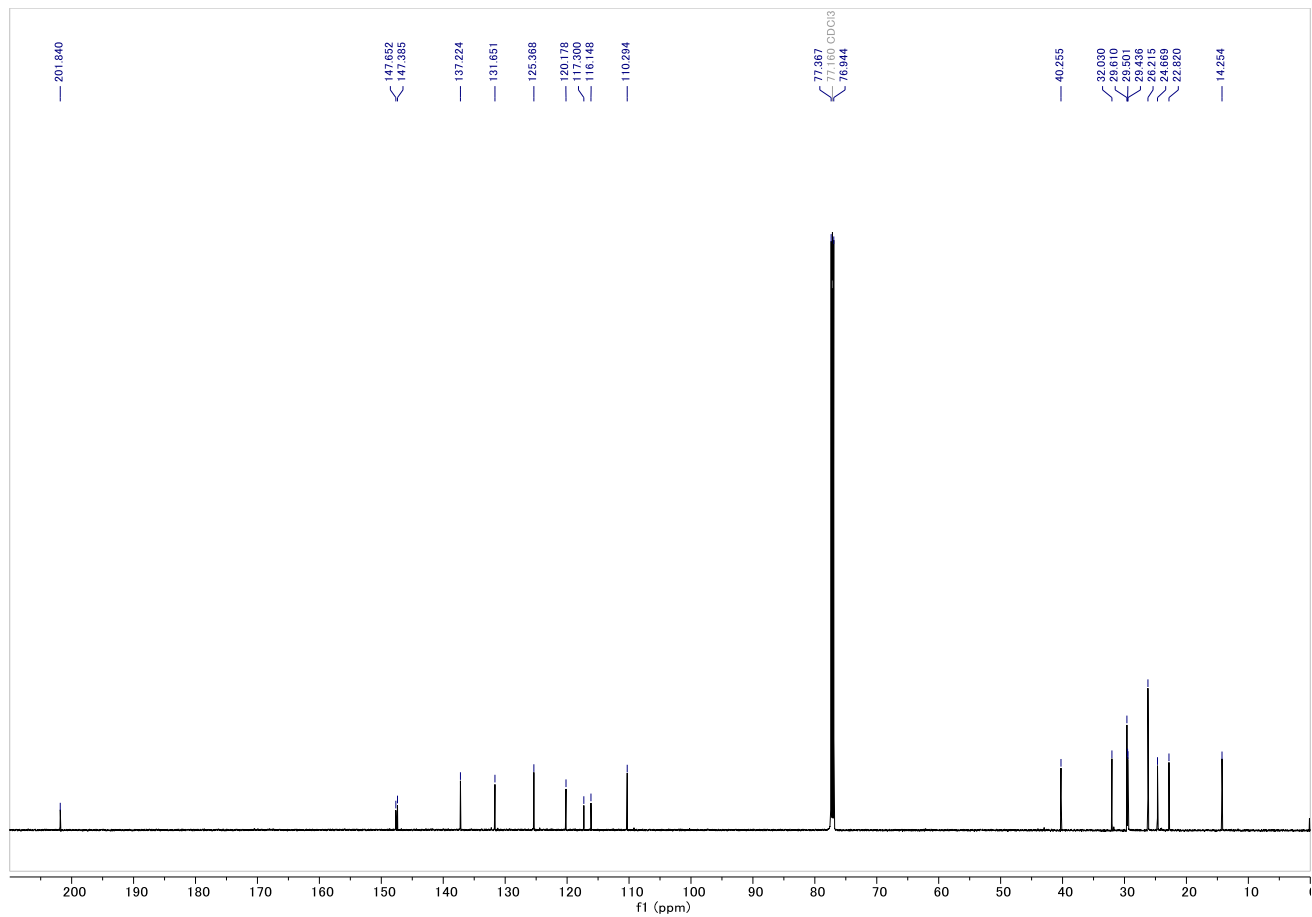
¹³C NMR **1f**



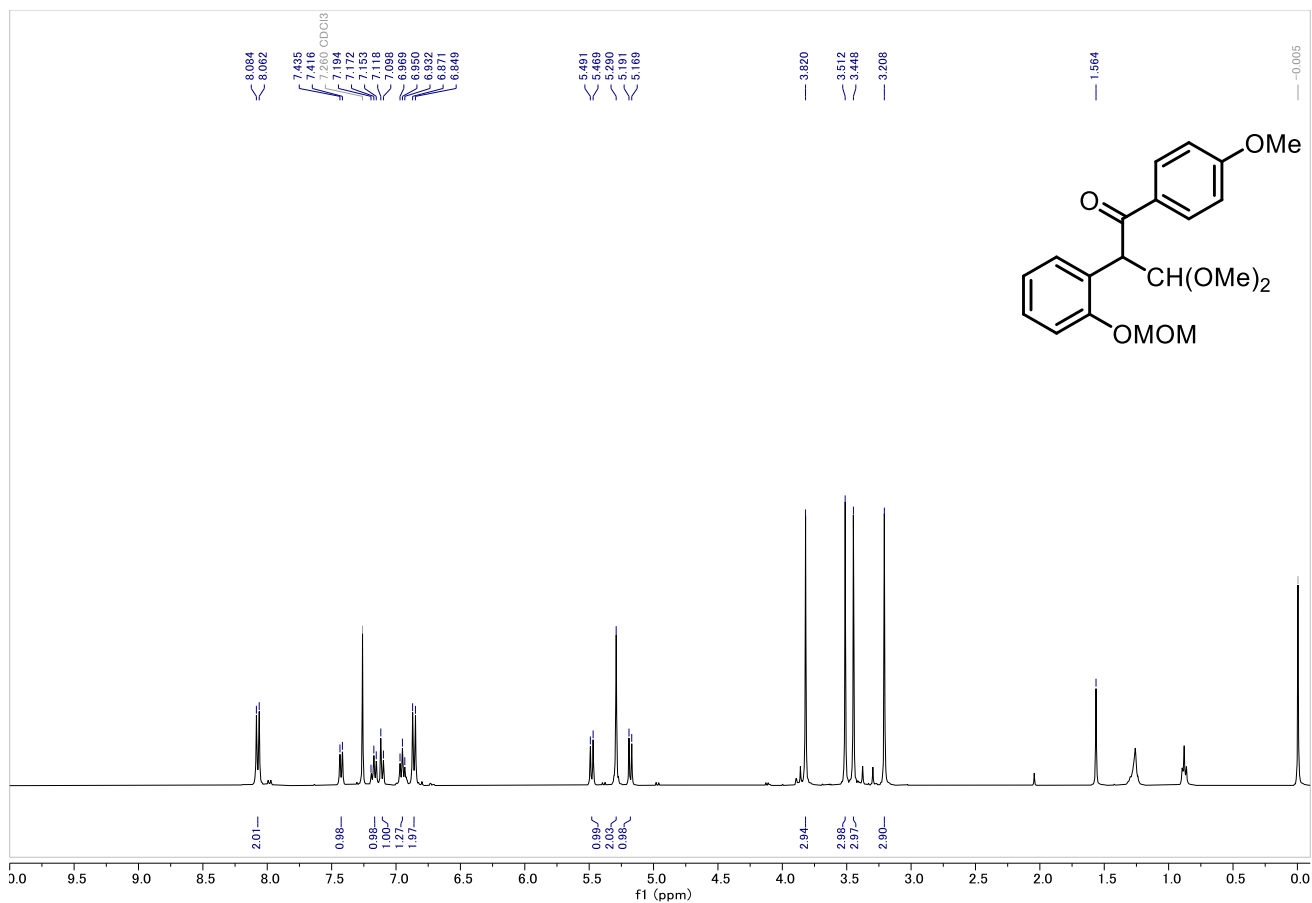
¹H NMR **1g**



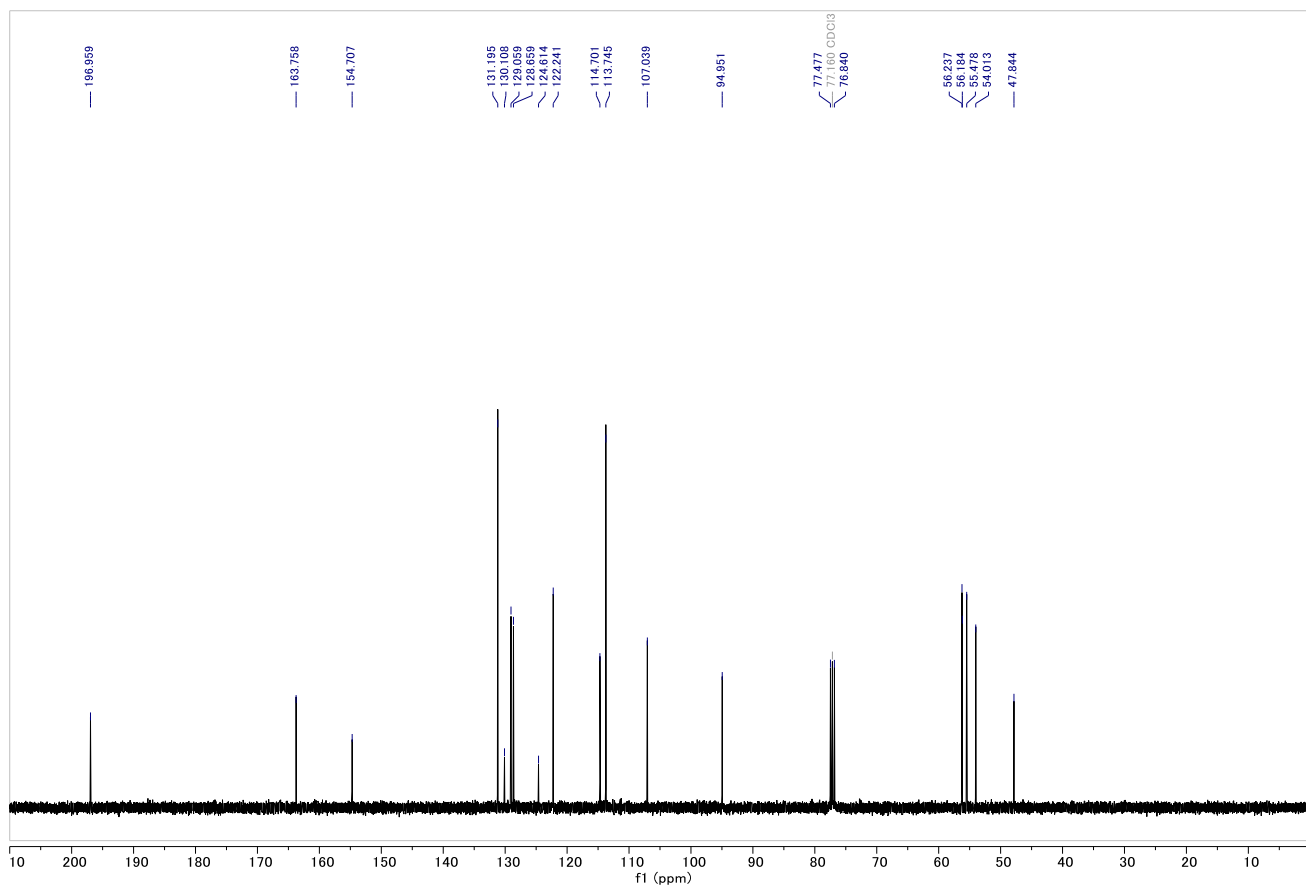
¹³C NMR **1g**



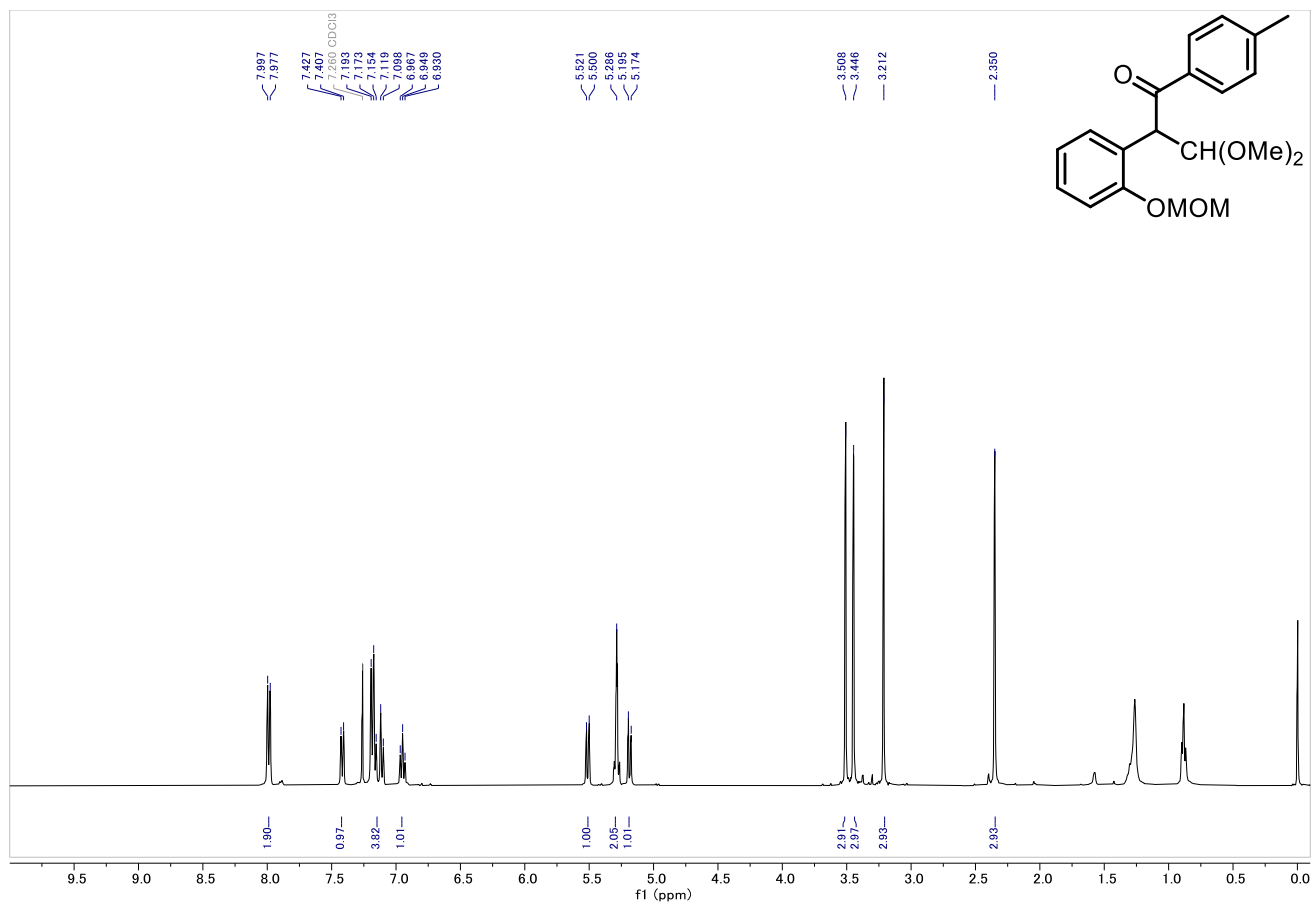
¹H NMR 2a



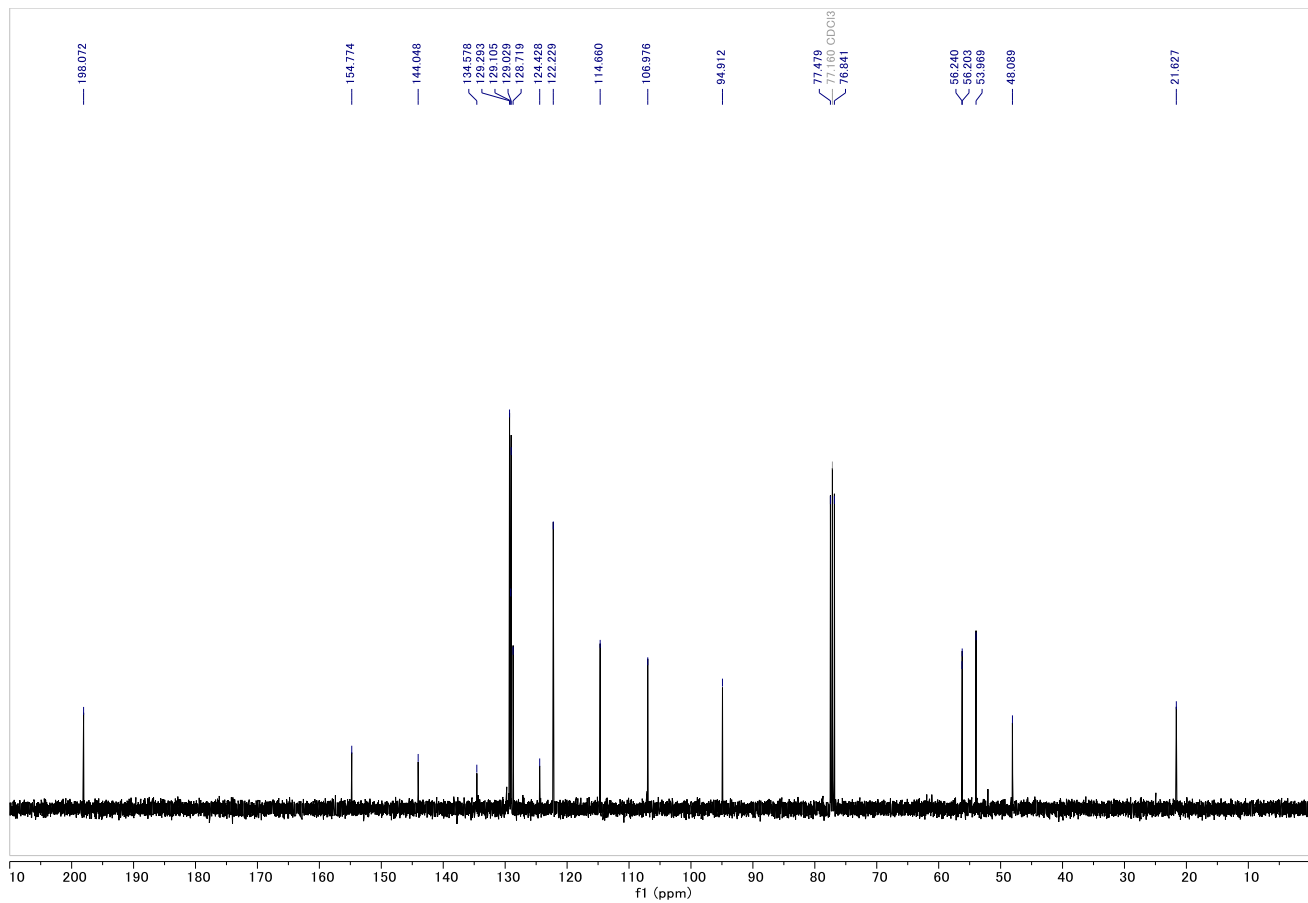
¹³C NMR 2a



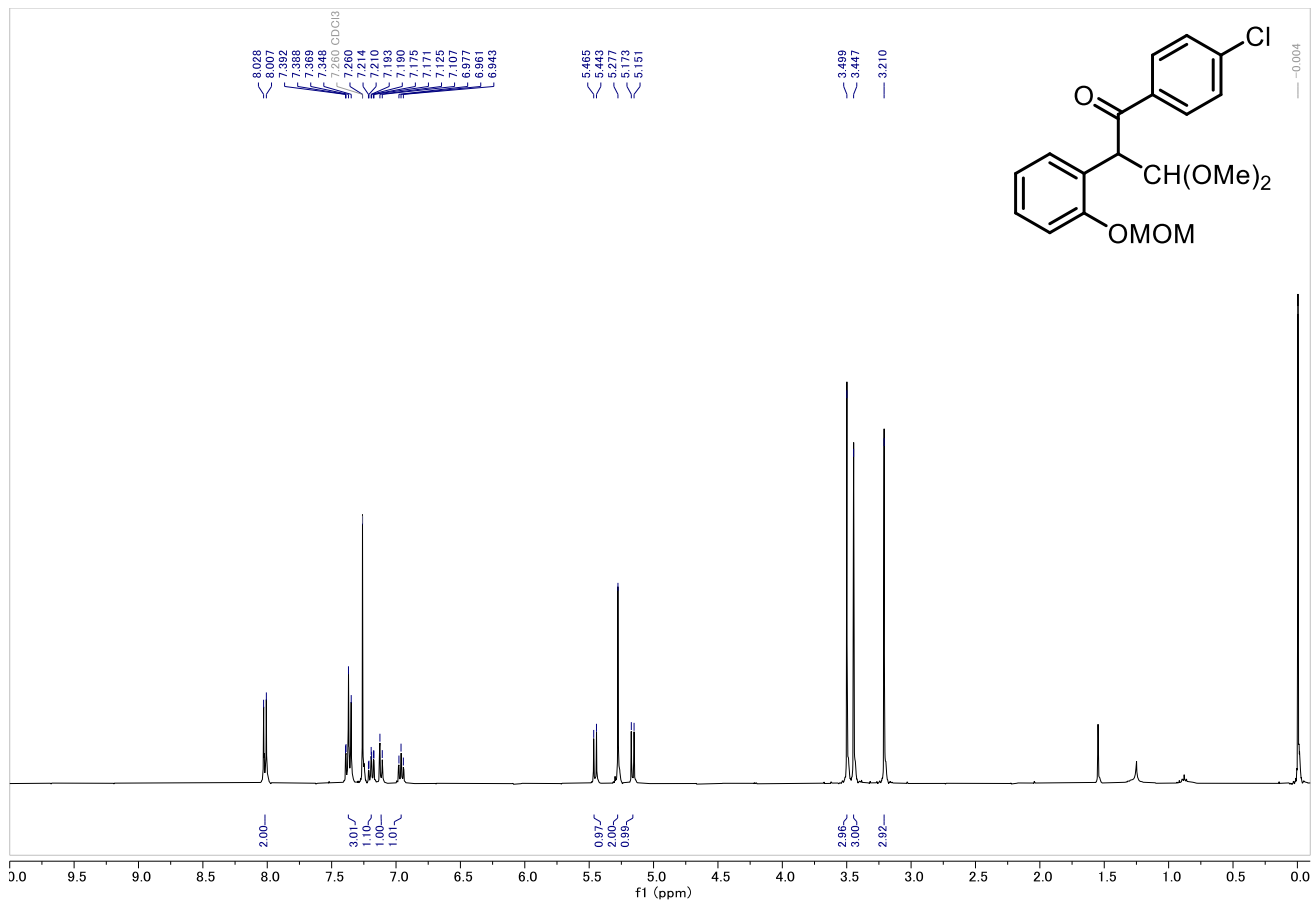
¹H NMR 2b



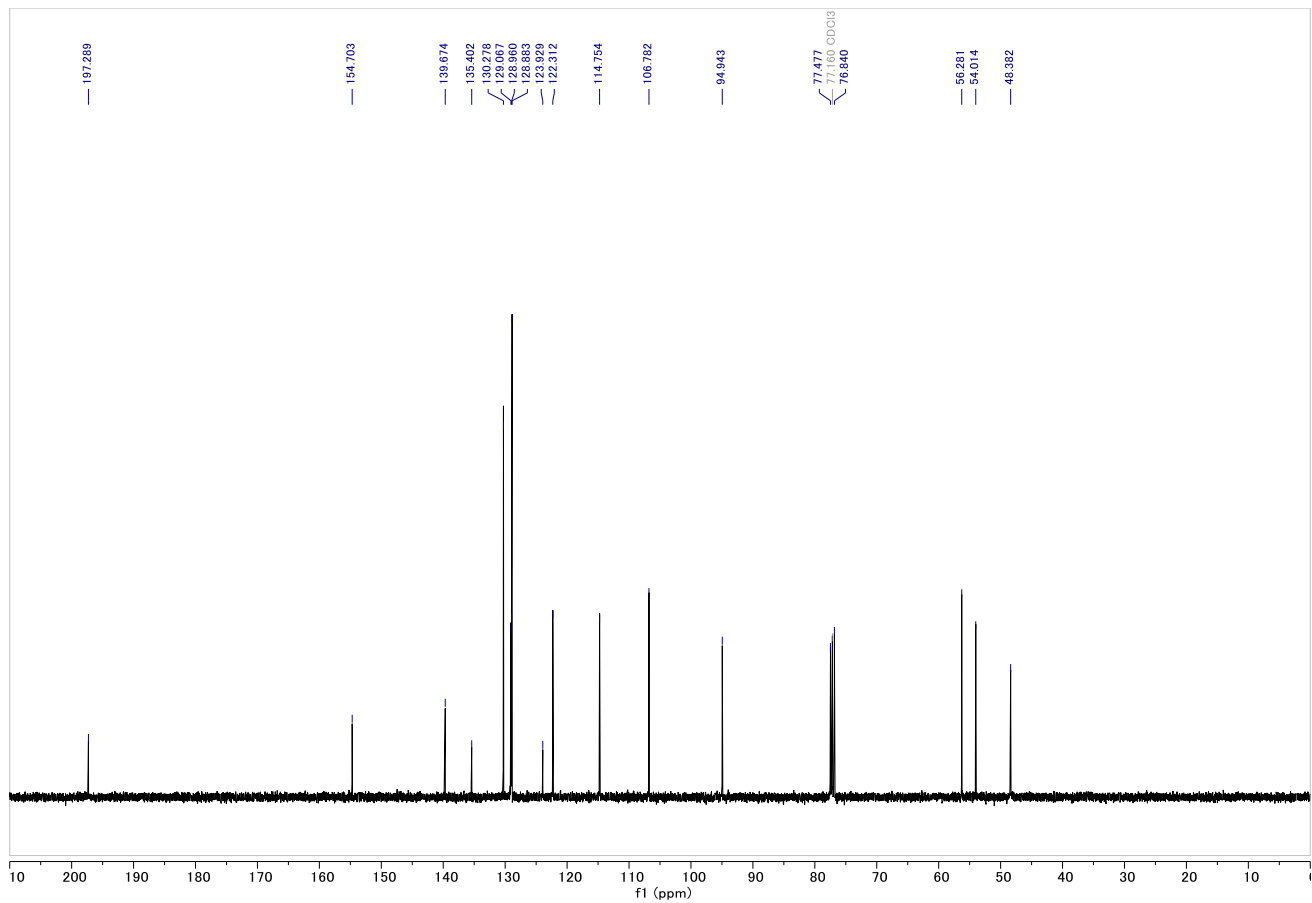
¹³C NMR 2b



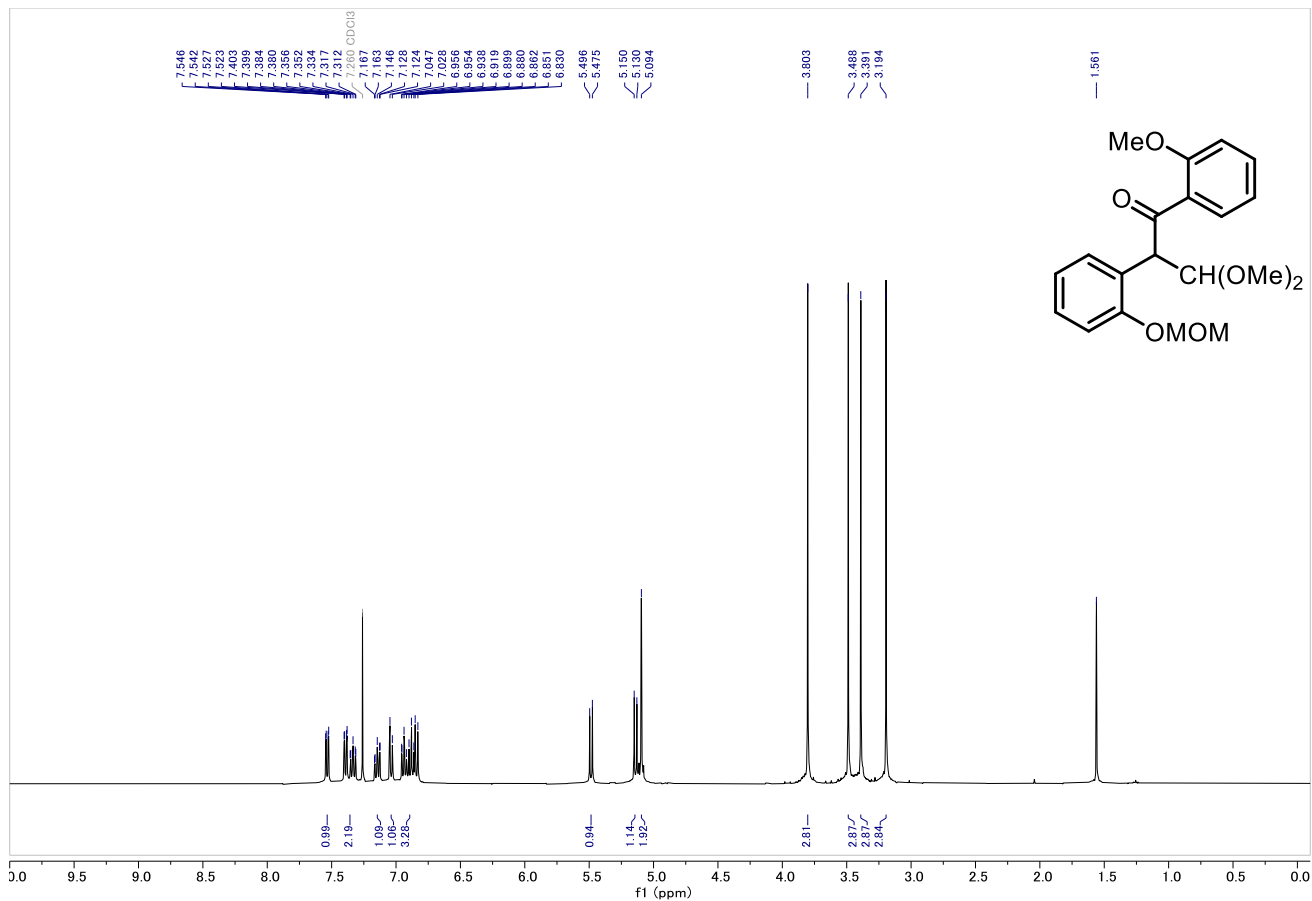
¹H NMR 2c



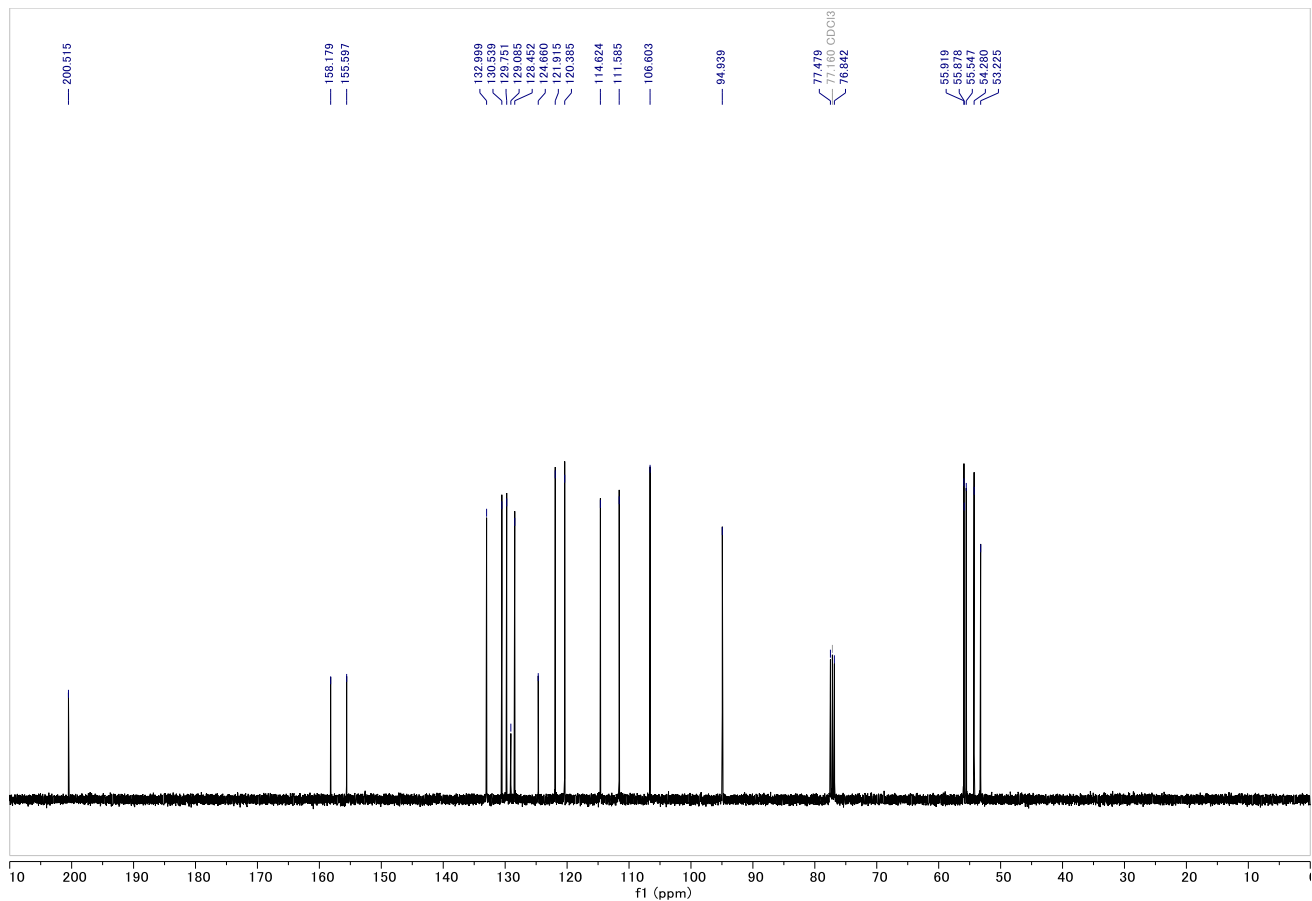
¹³C NMR 2c



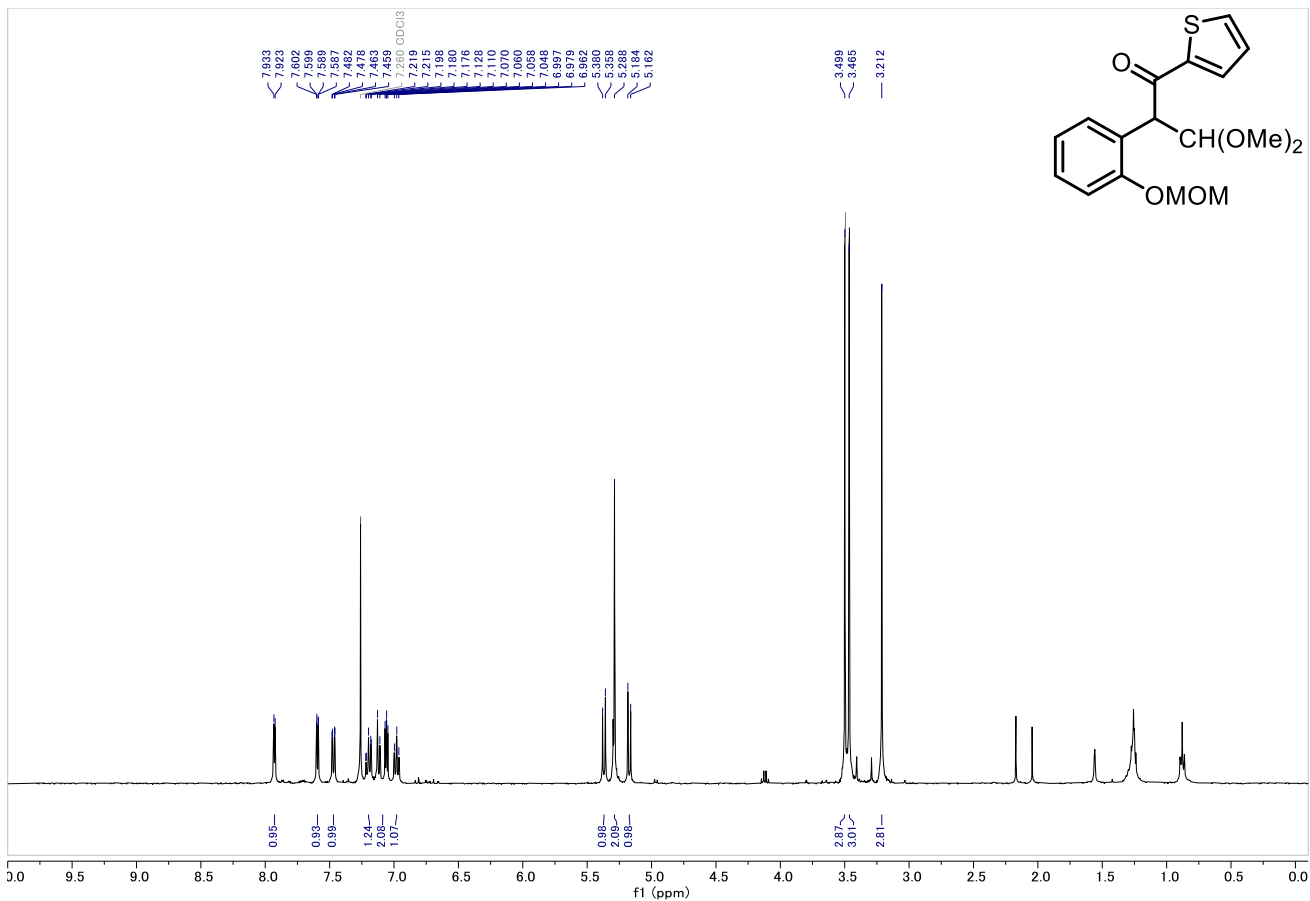
¹H NMR 2d



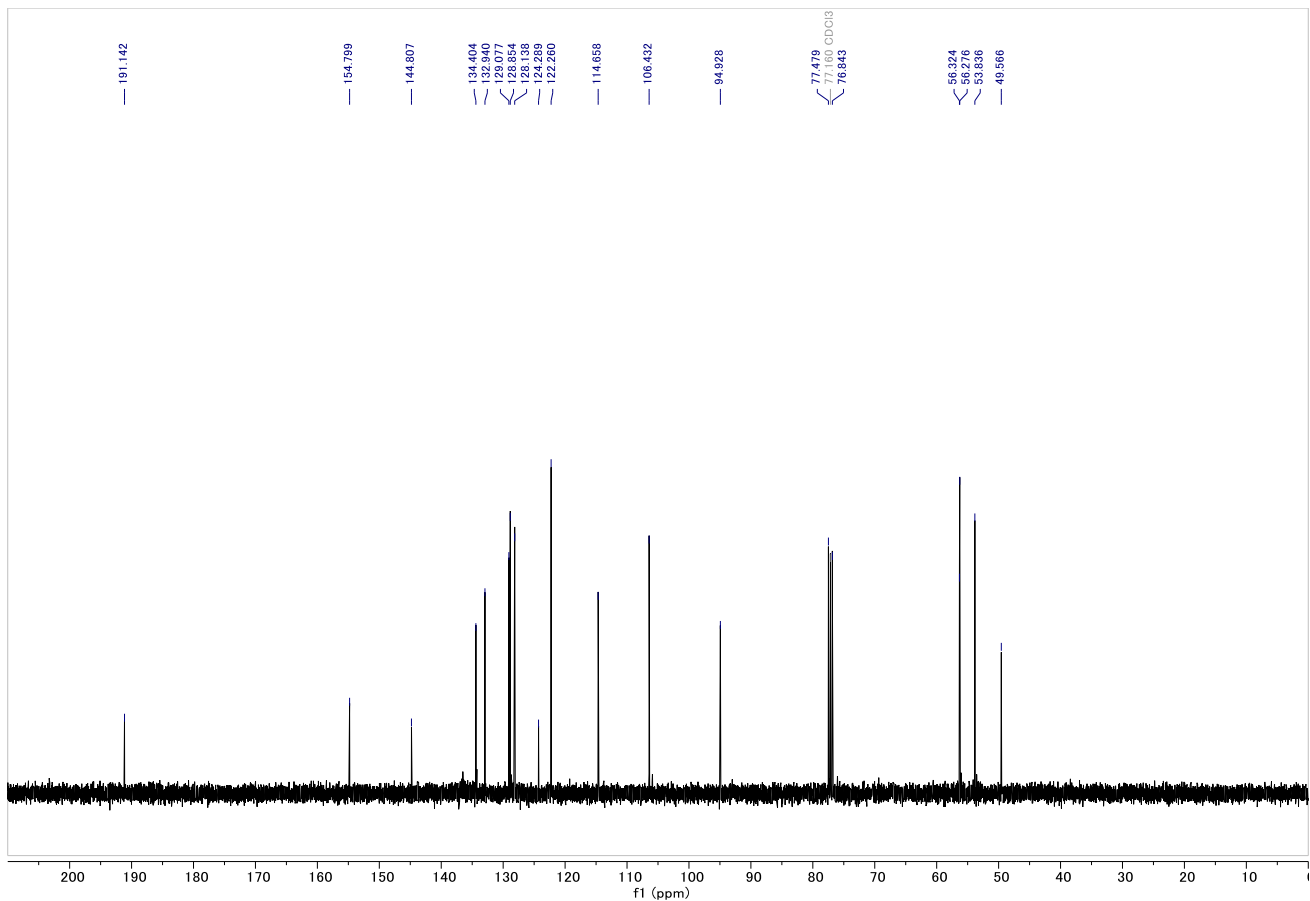
¹³C NMR 2d



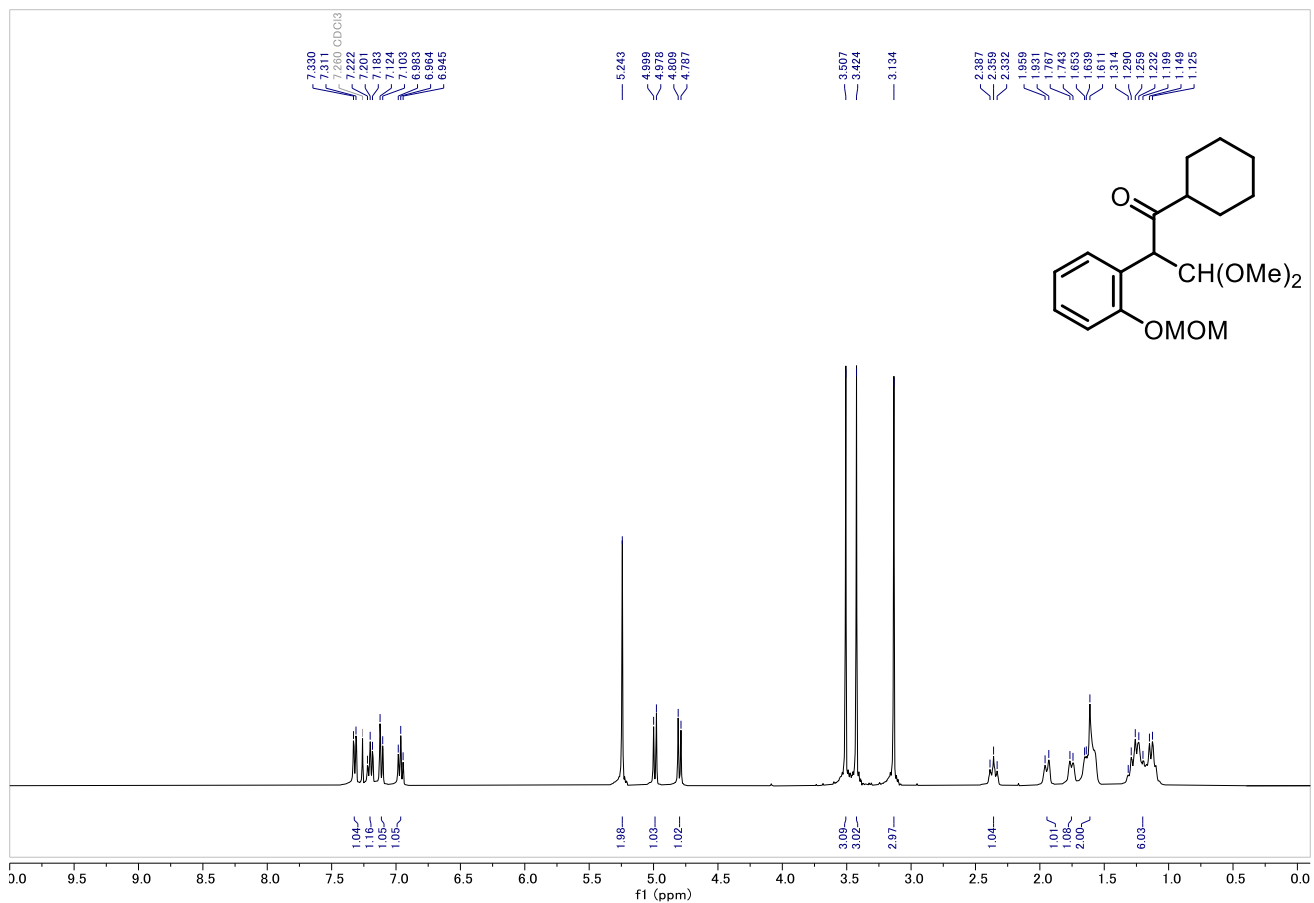
¹H NMR 2e



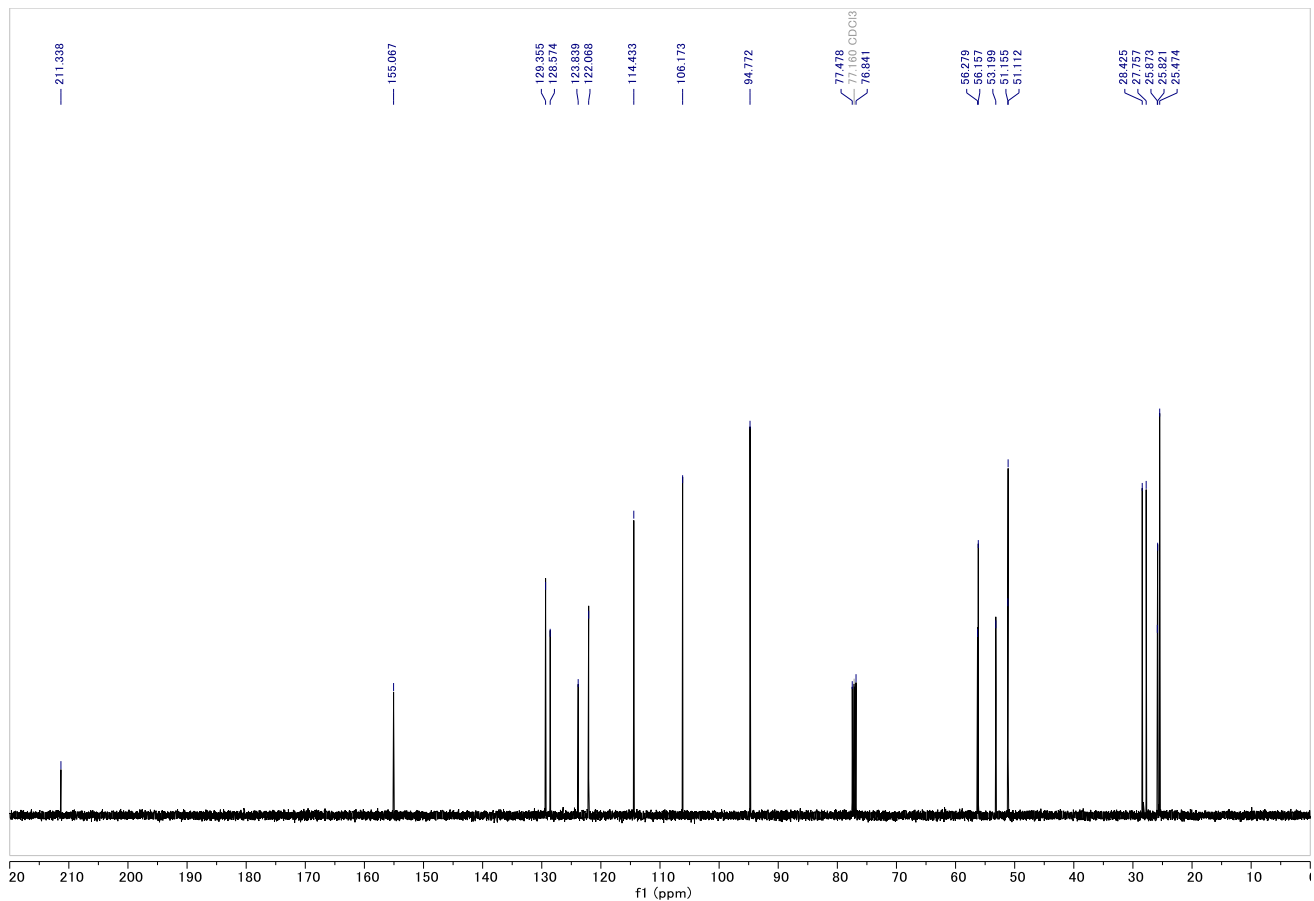
¹³C NMR 2e



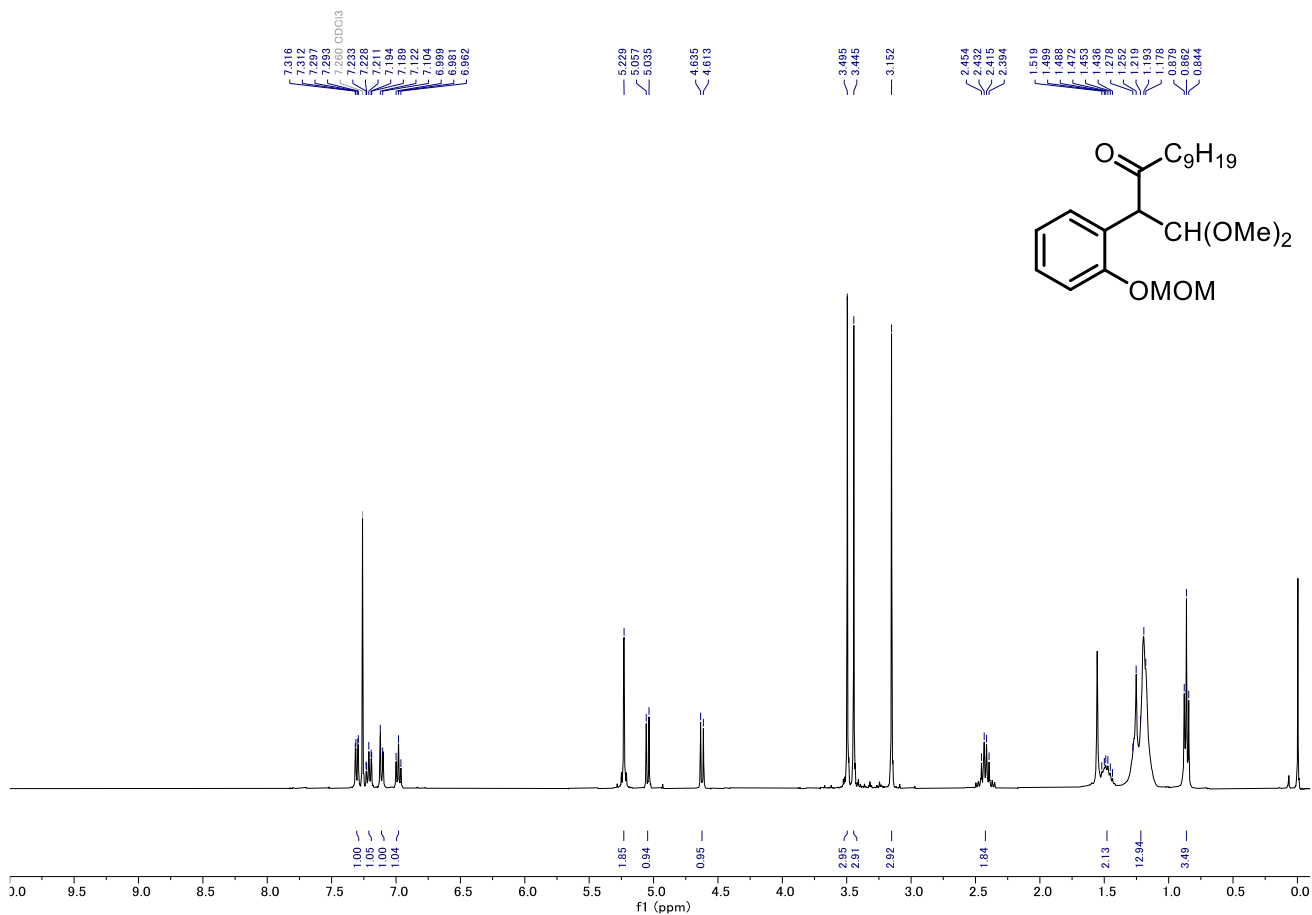
¹H NMR 2f



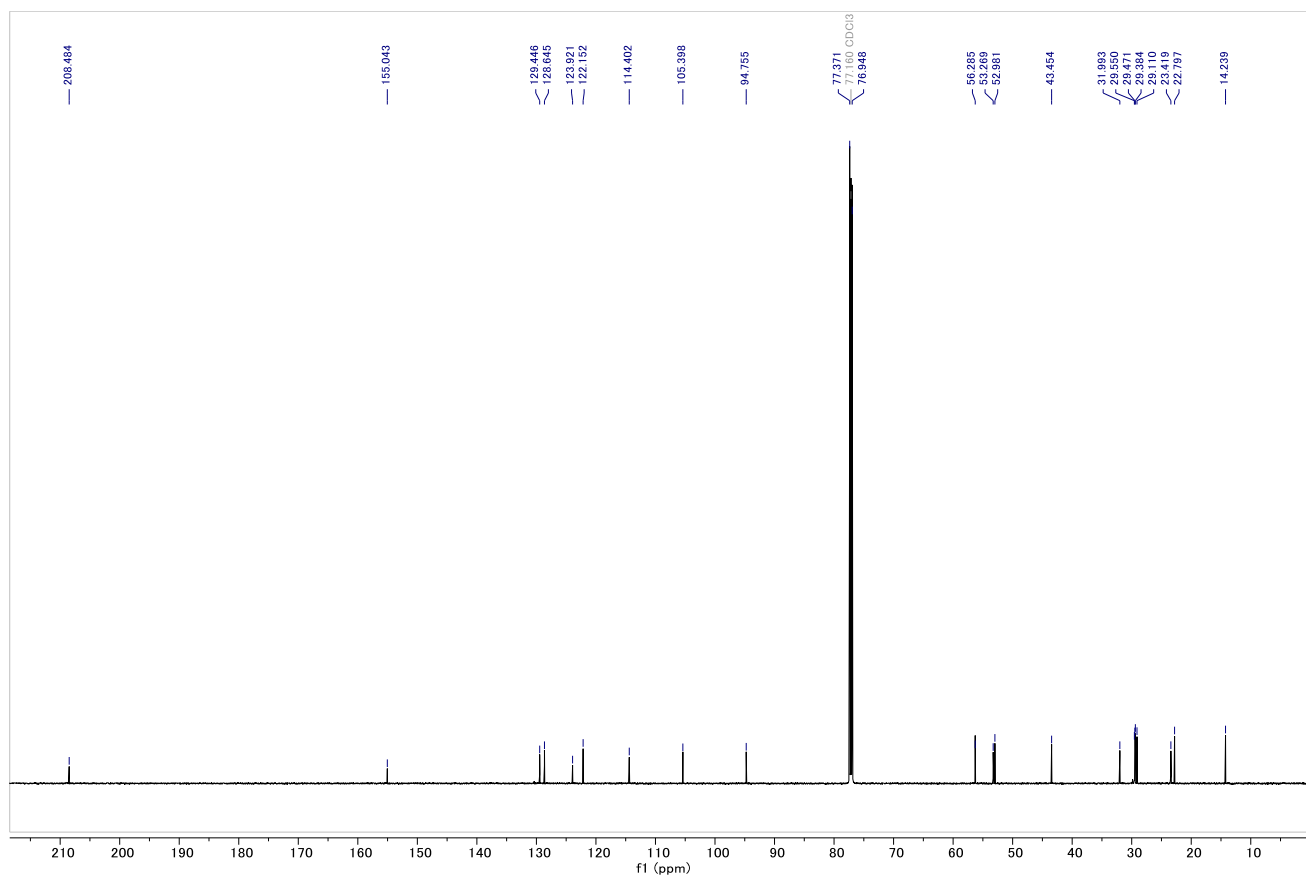
¹³C NMR 2f



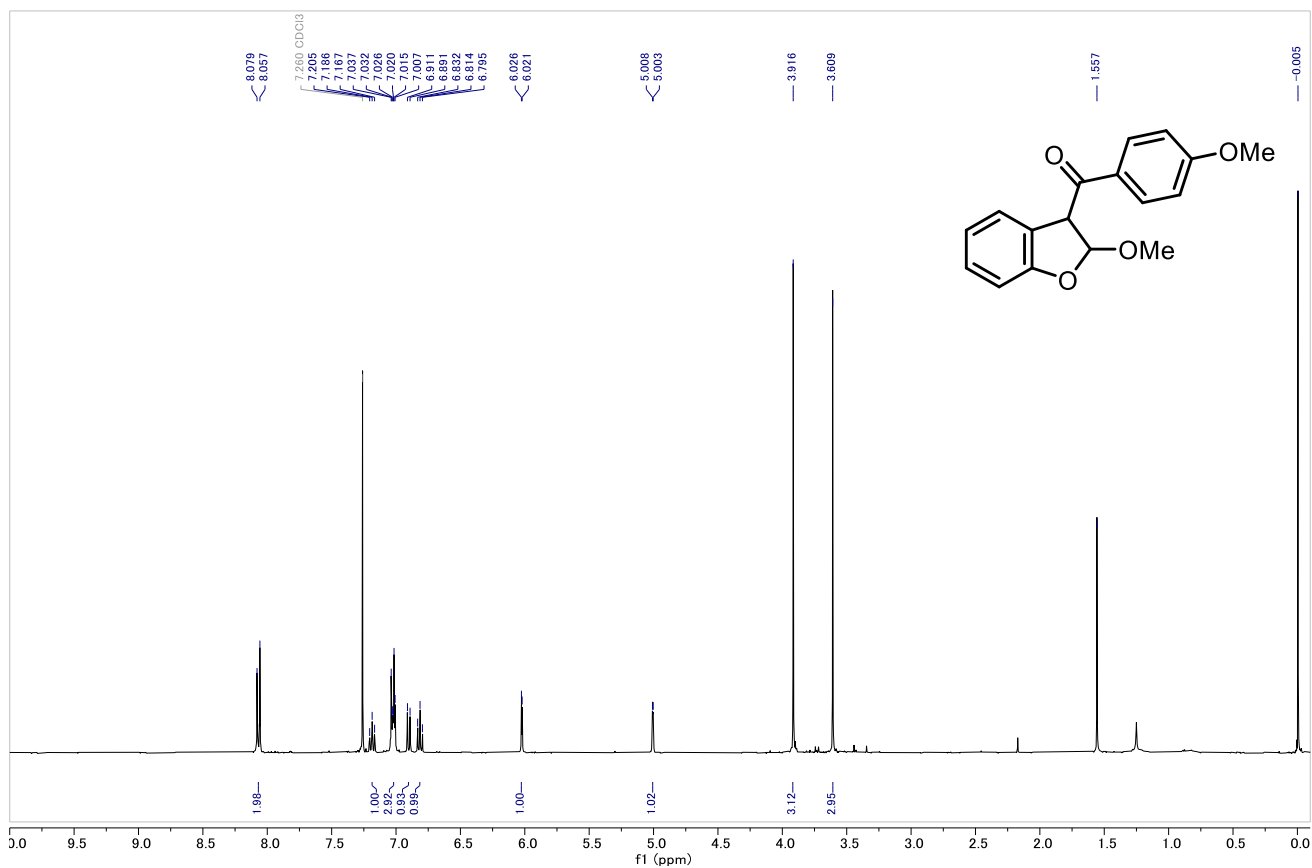
¹H NMR 2g



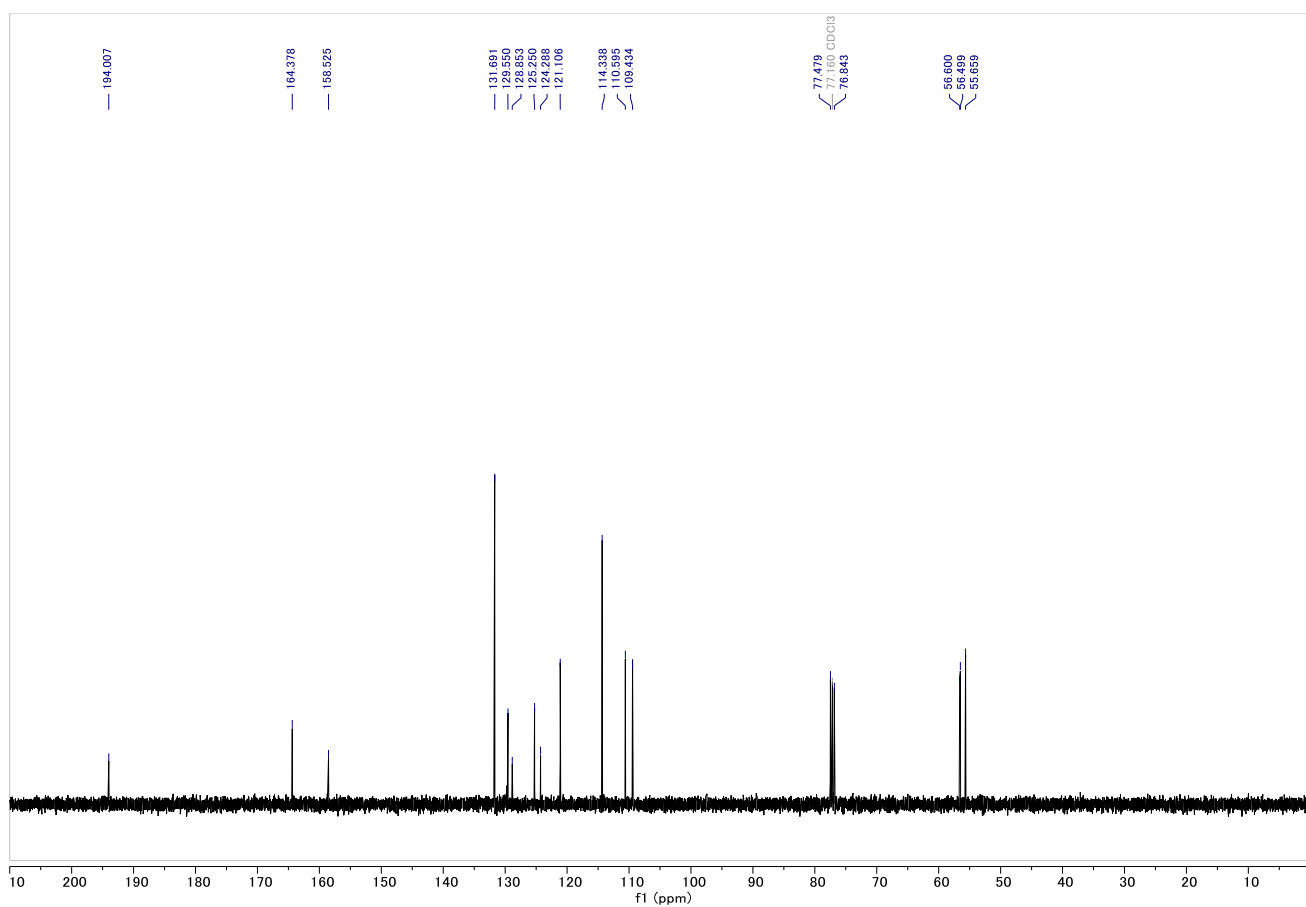
¹³C NMR 2g



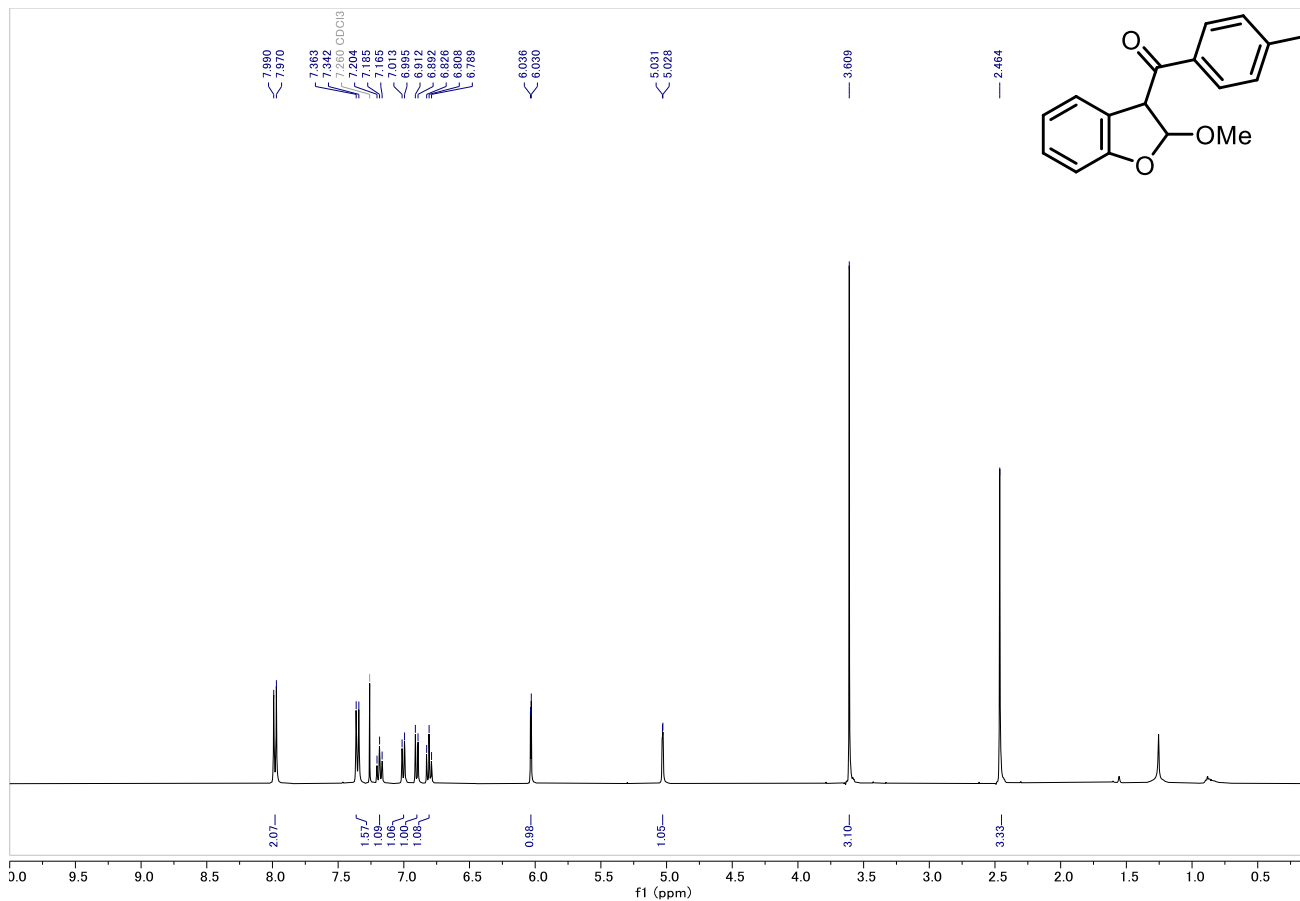
¹H NMR 3a



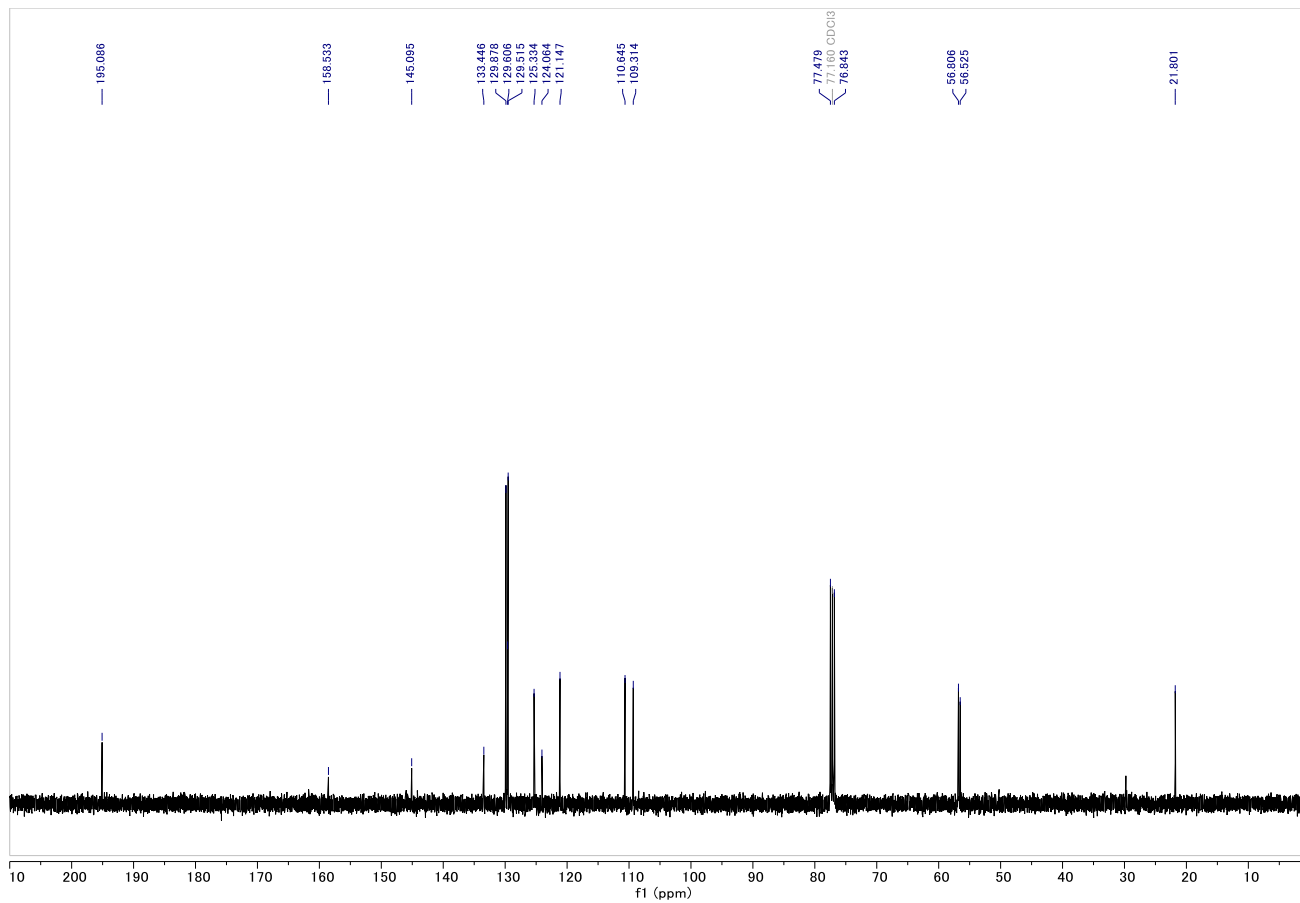
¹³C NMR 3a



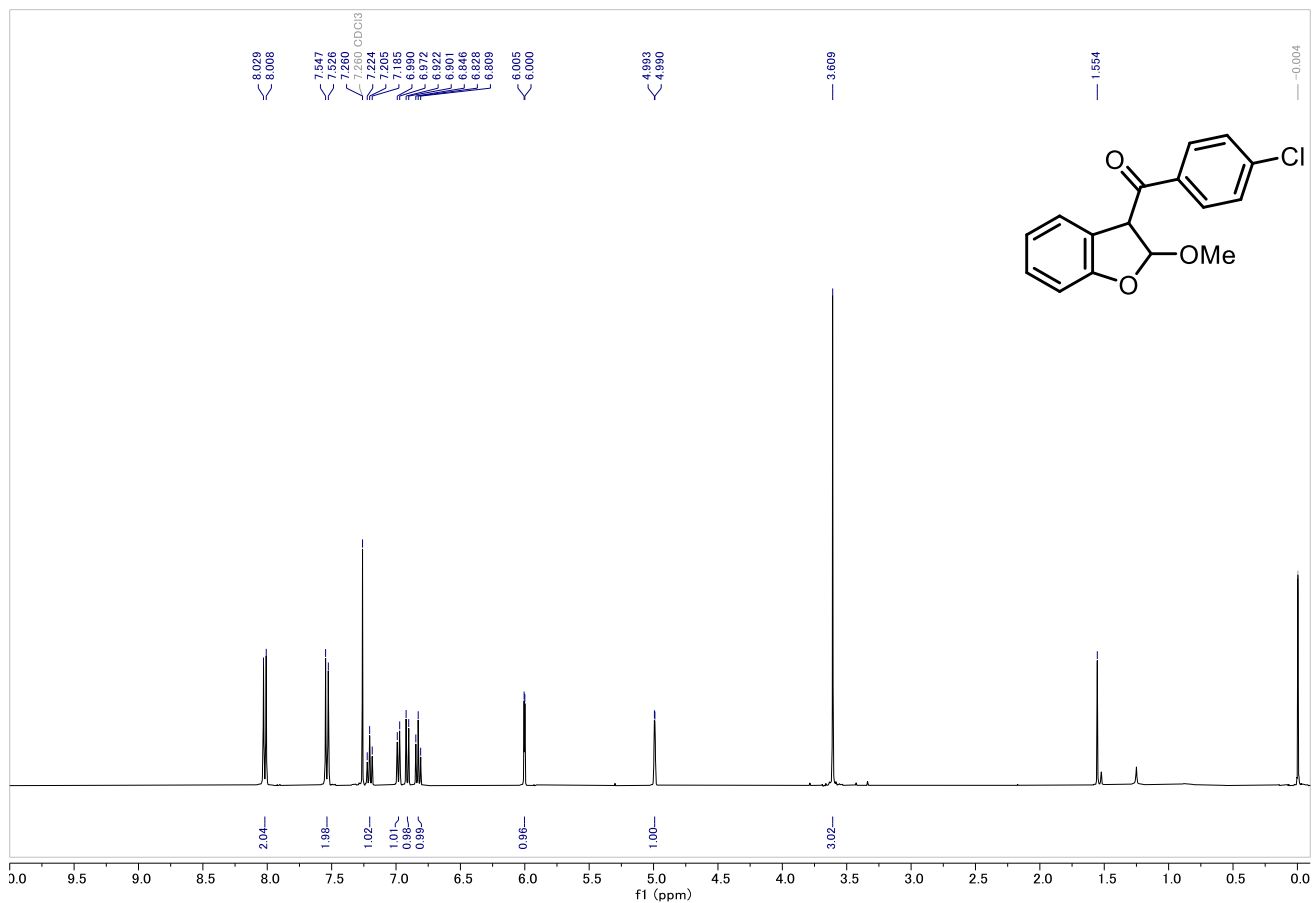
¹H NMR 3b



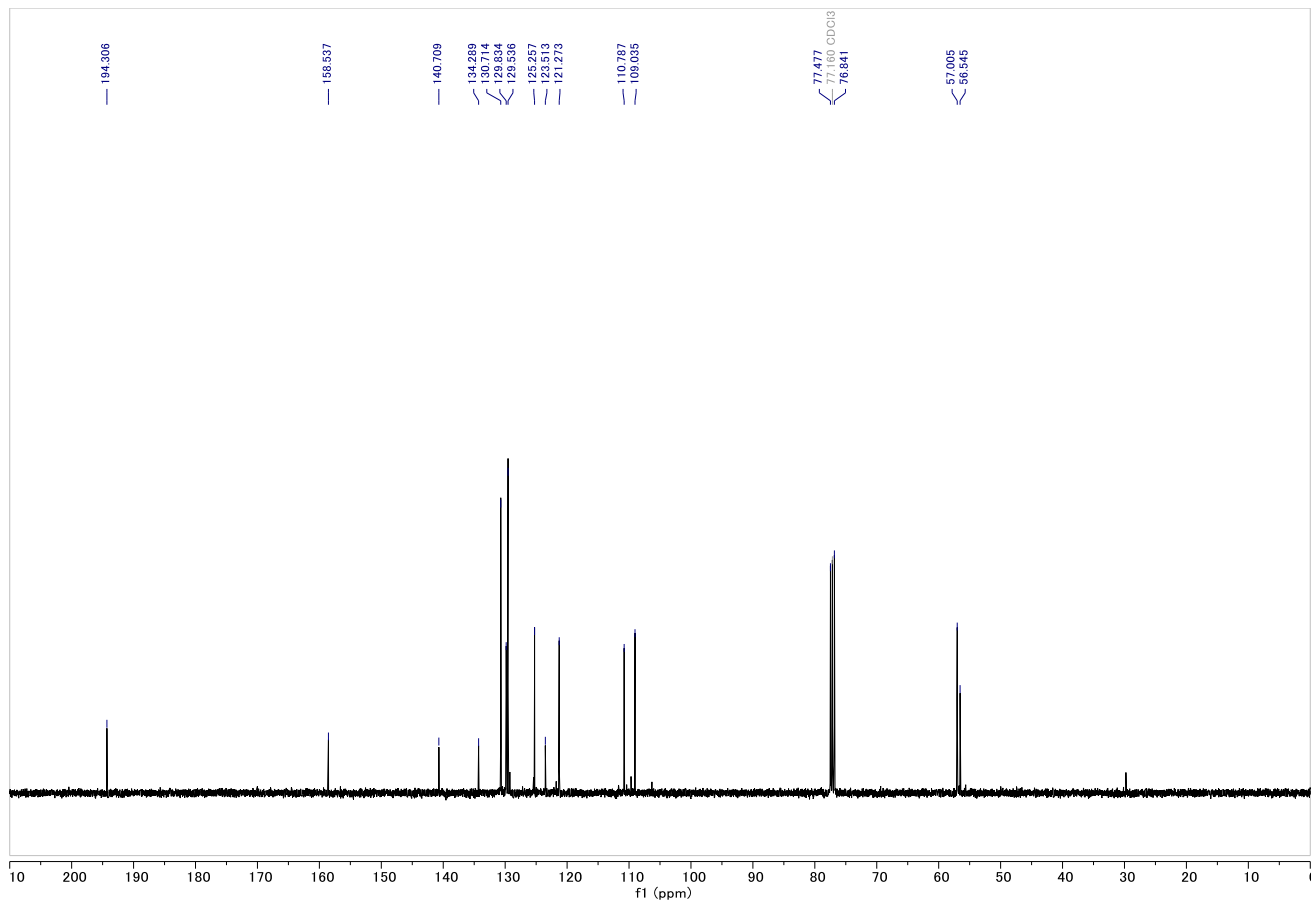
¹³C NMR 3b



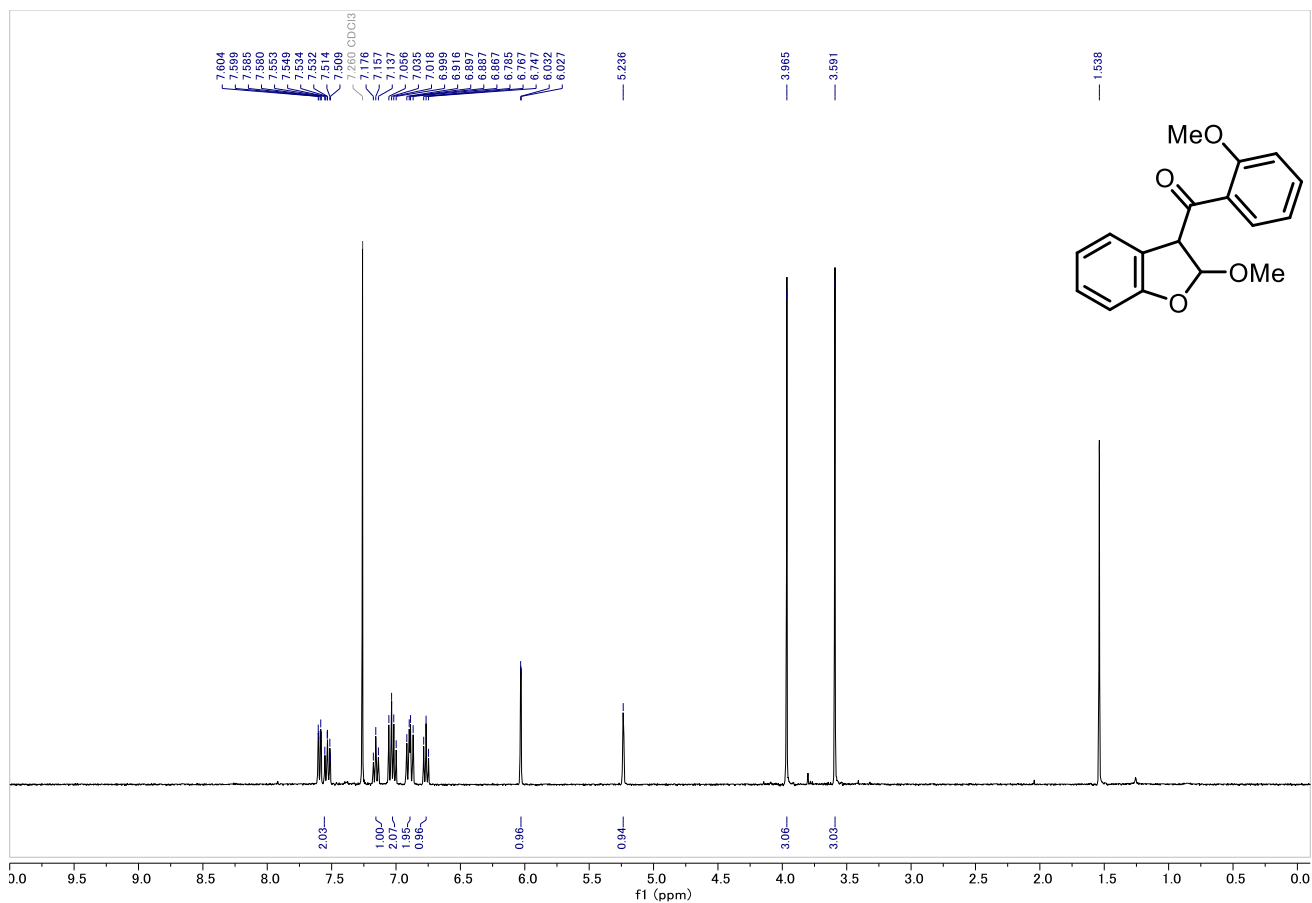
¹H NMR 3c



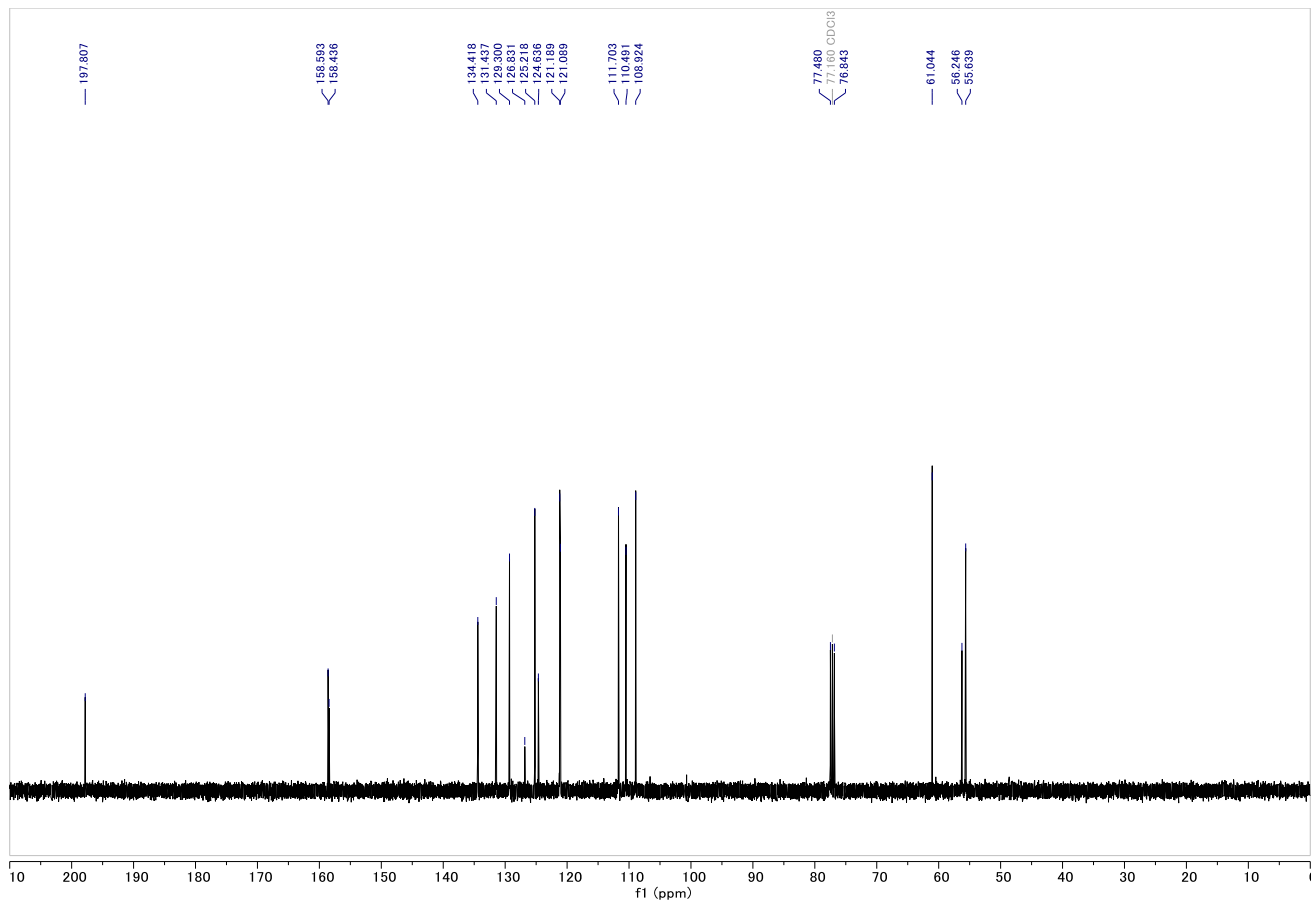
¹³C NMR 3c



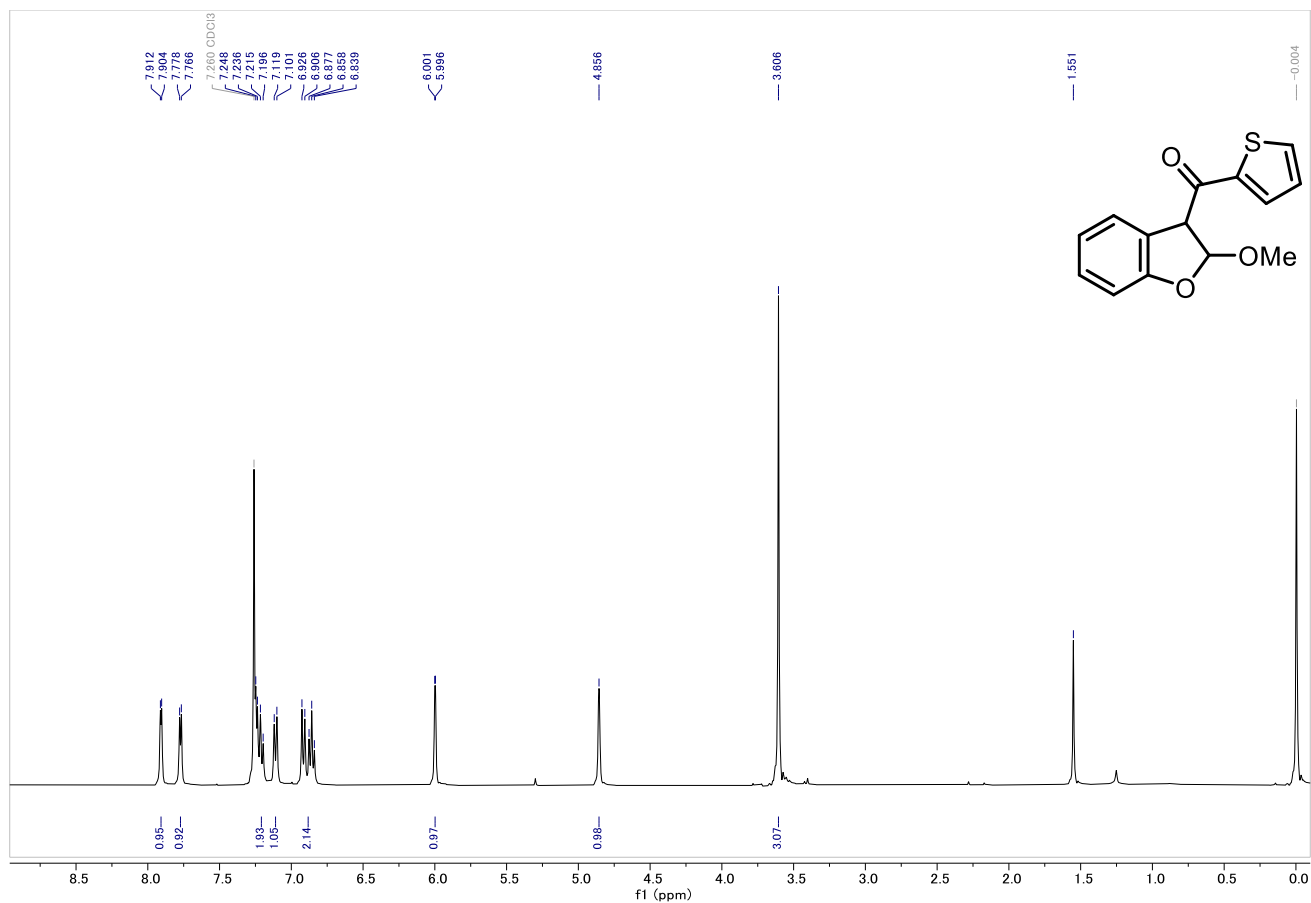
¹H NMR 3d



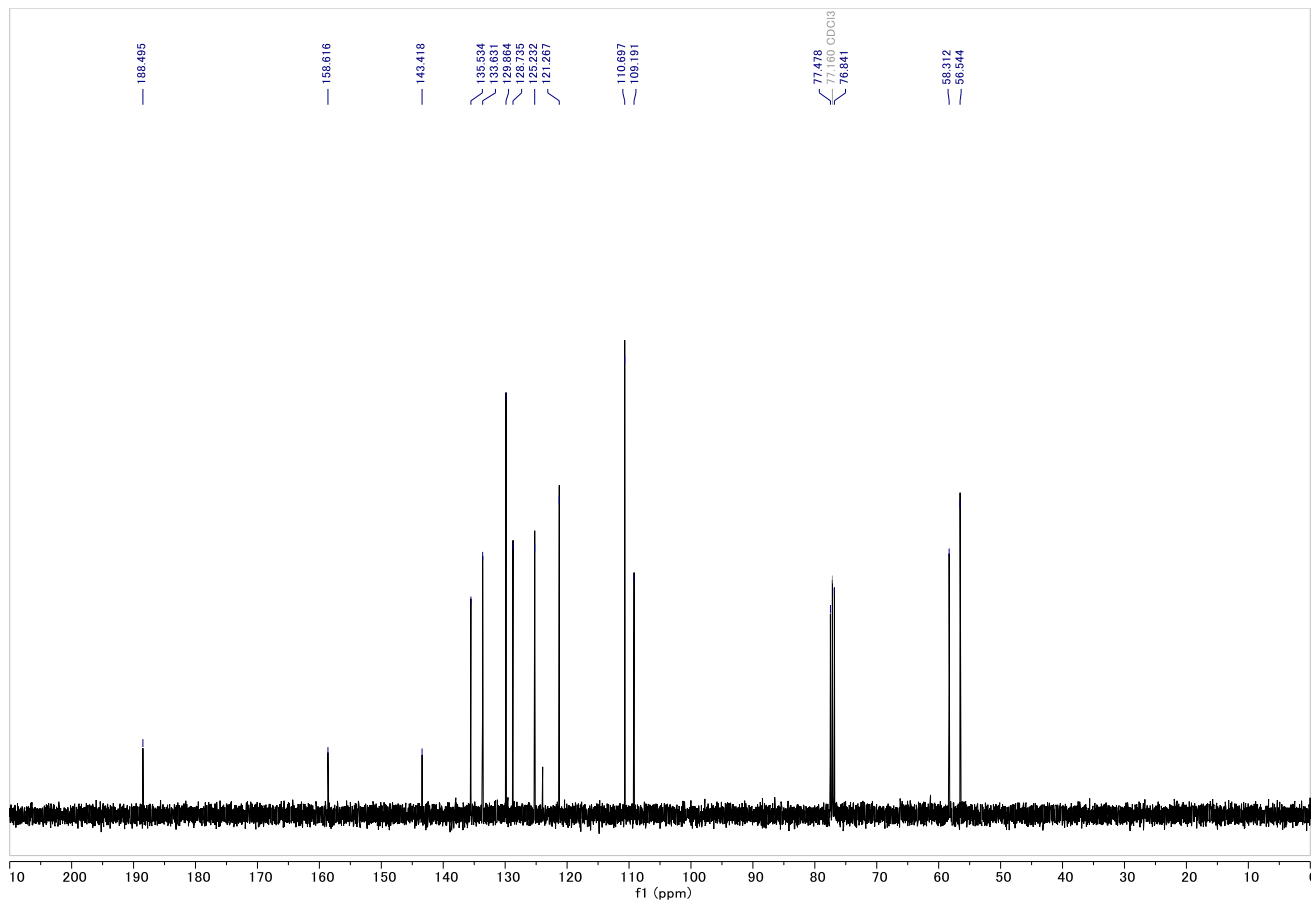
¹³C NMR 3d



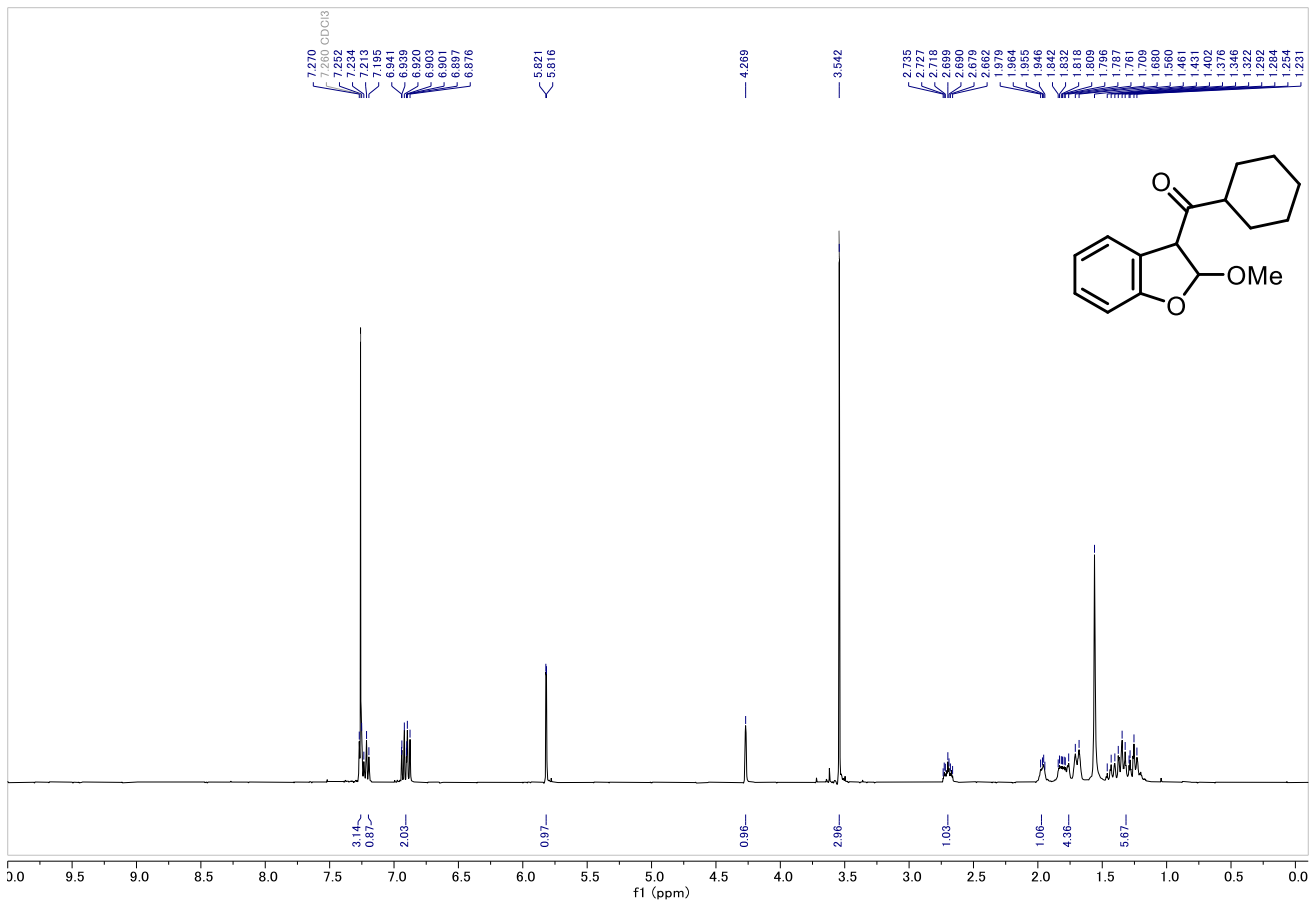
¹H NMR 3e



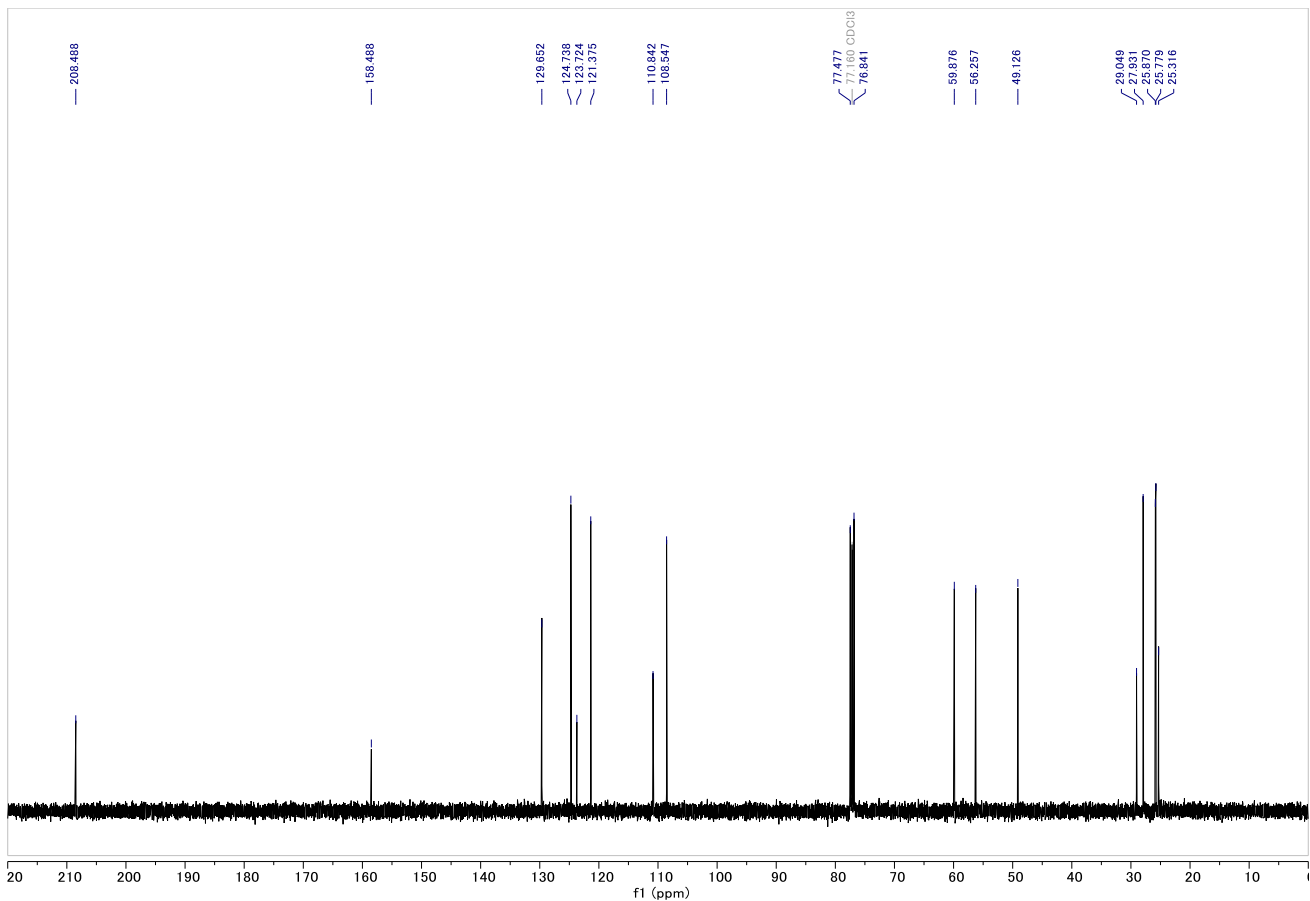
¹³C NMR 3e



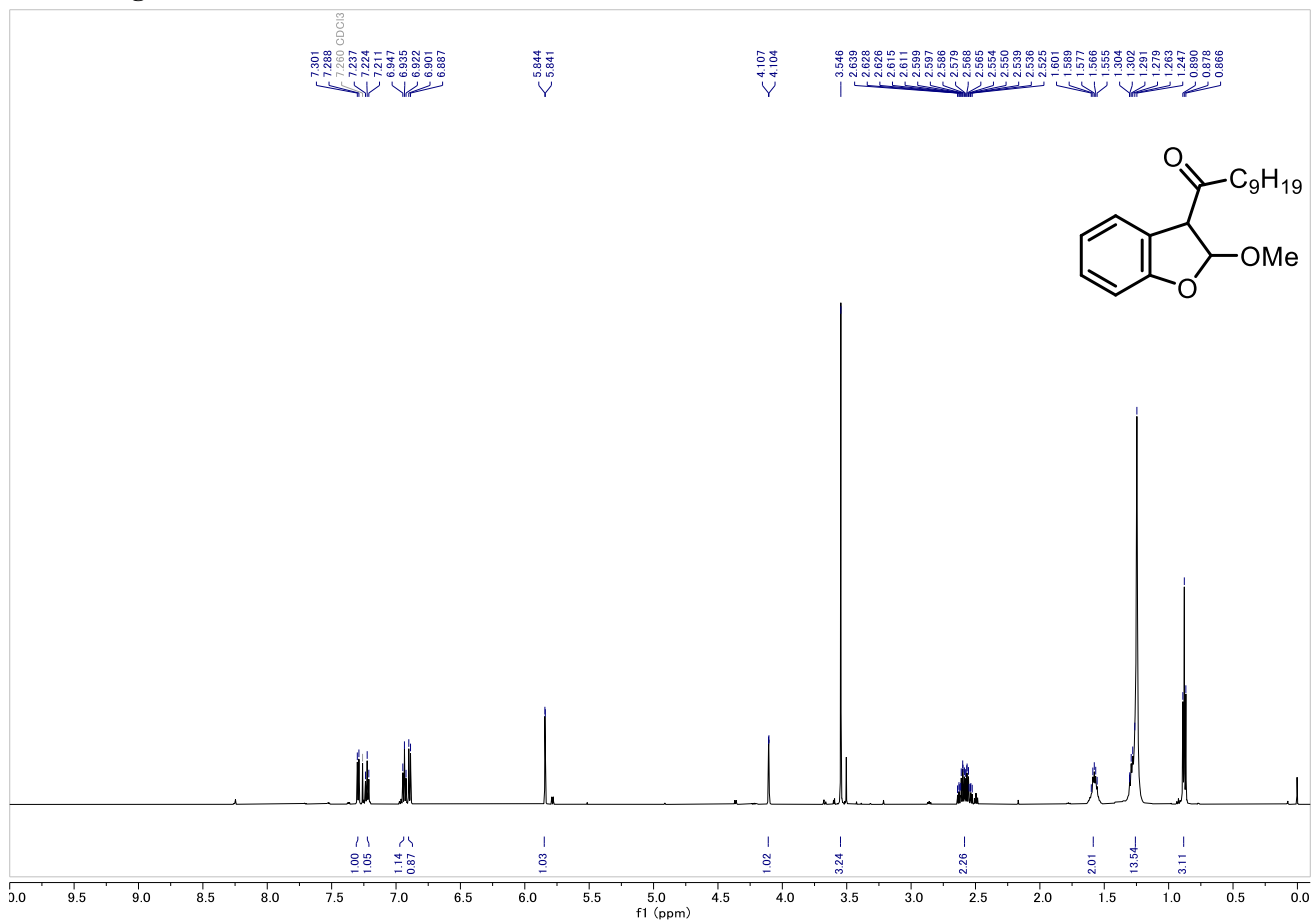
¹H NMR 3f



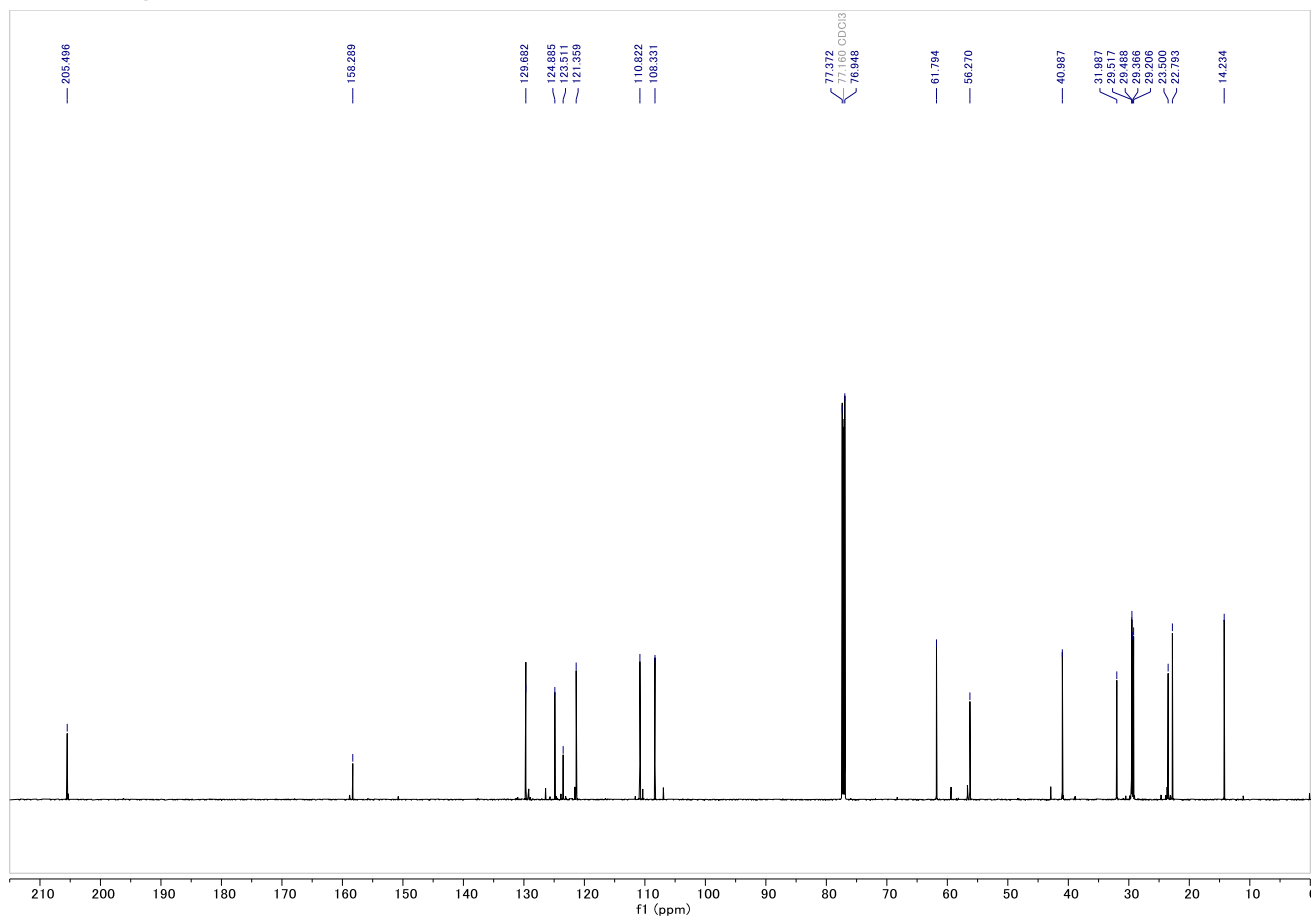
¹³C NMR 3f



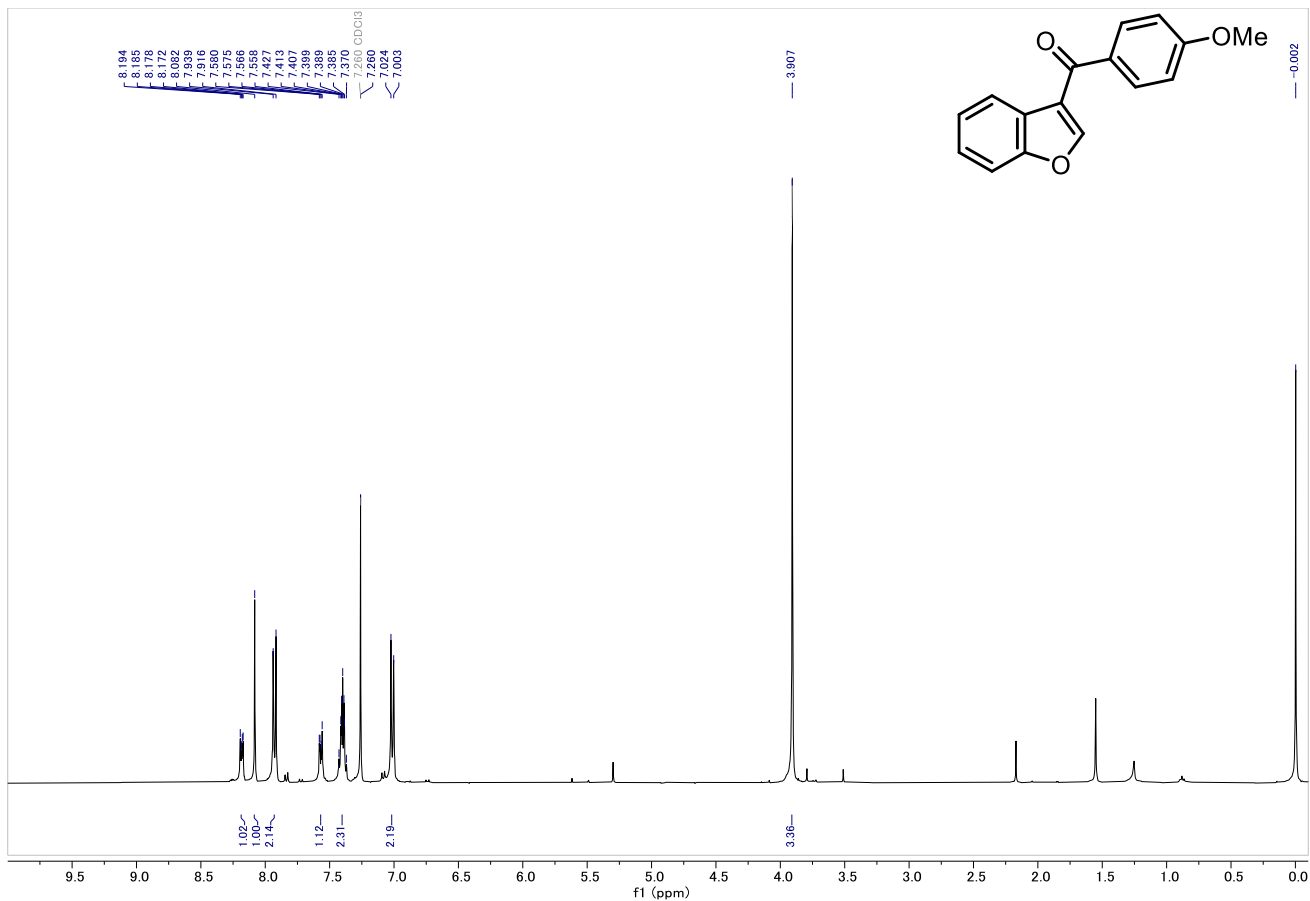
¹H NMR 3g



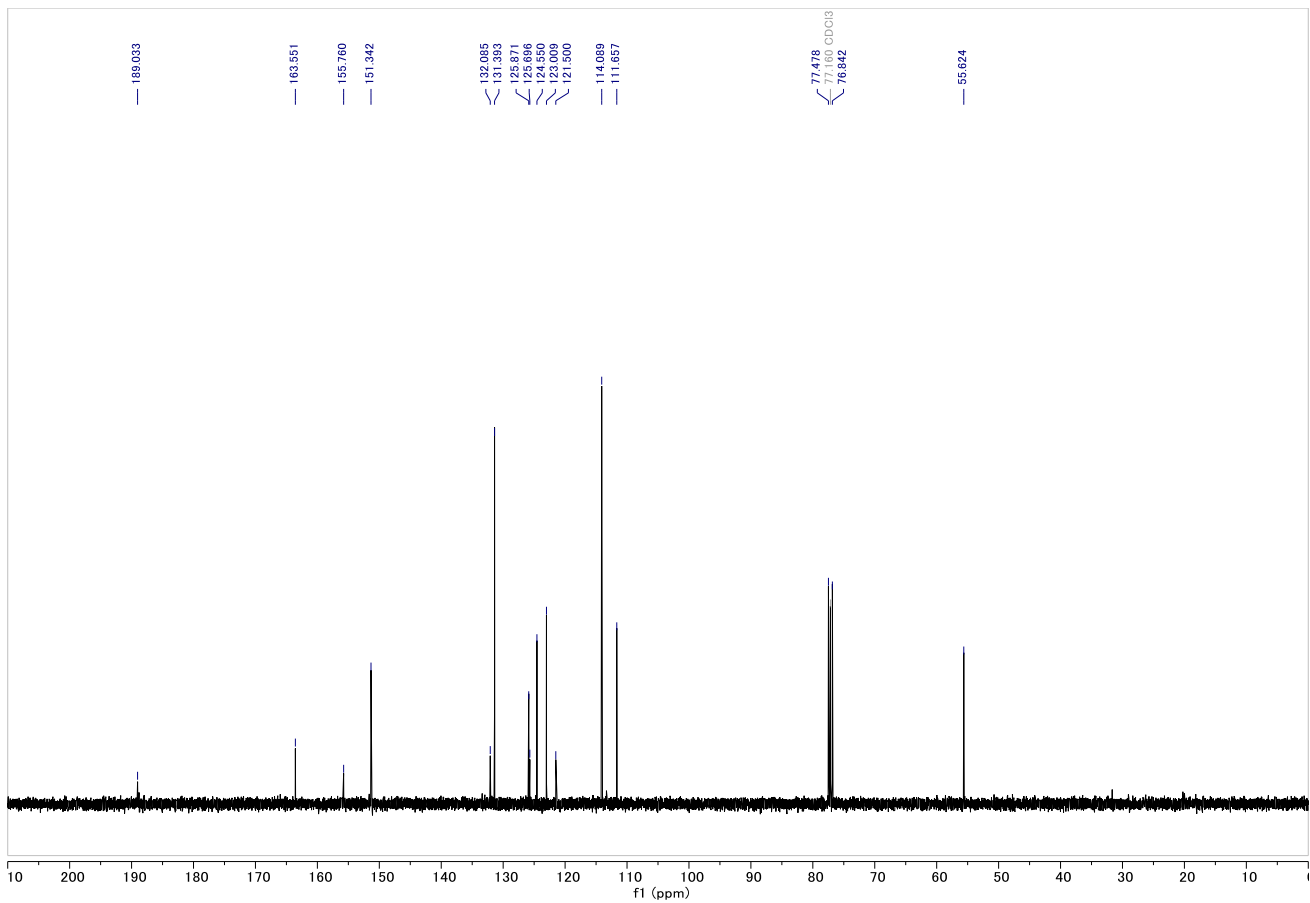
¹³C NMR 3g



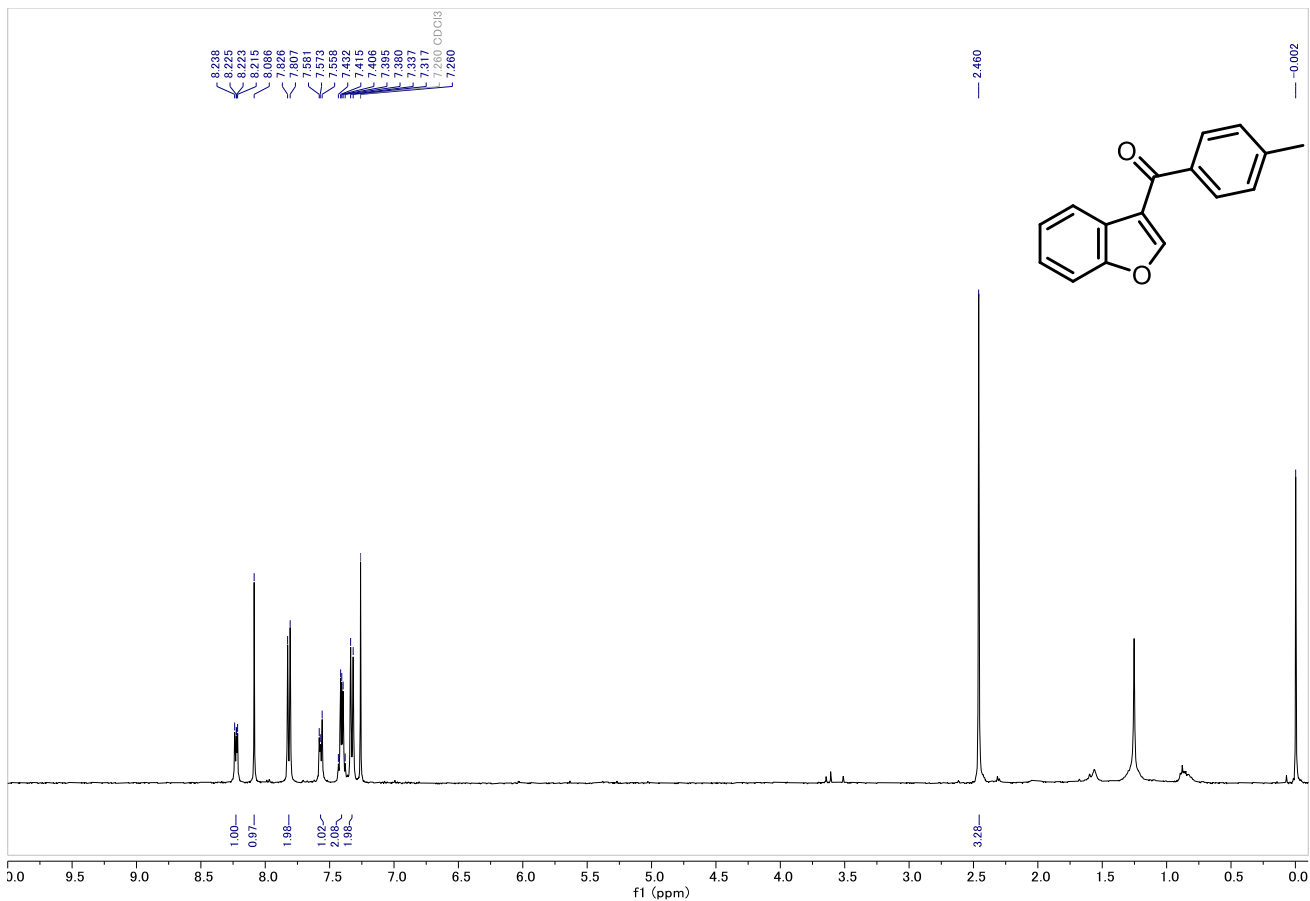
¹H NMR 4a



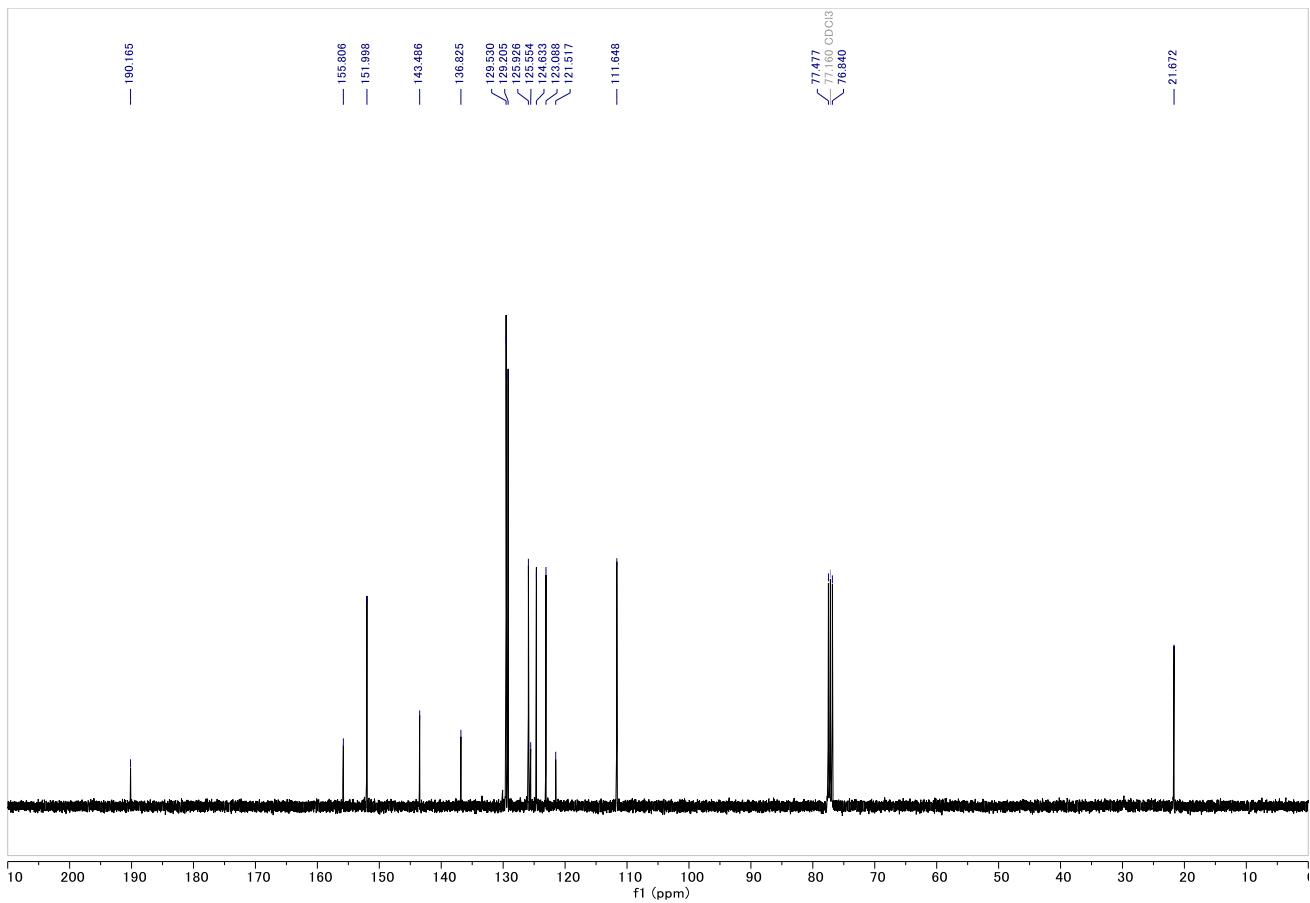
¹³C NMR 4a



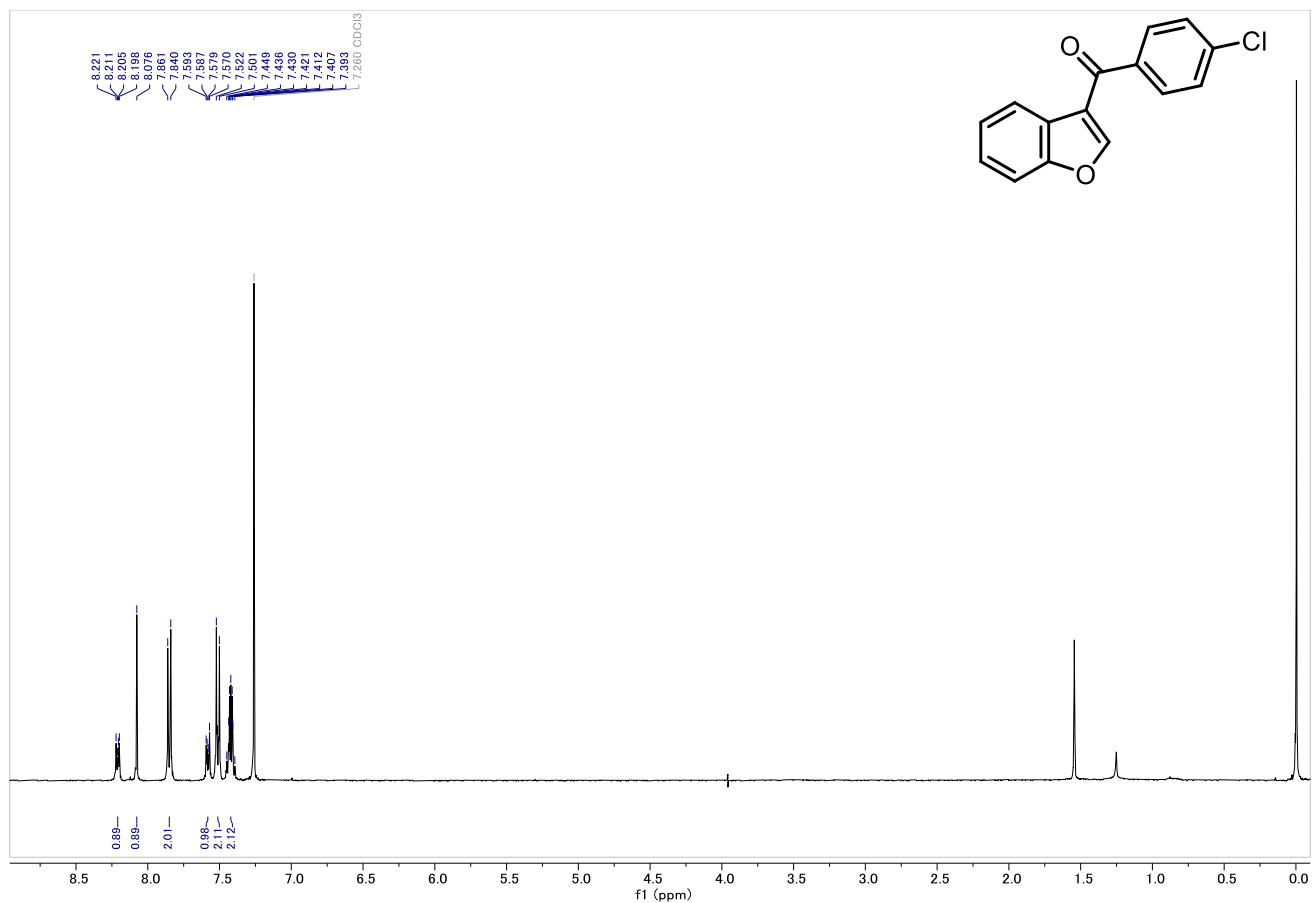
¹H NMR 4b



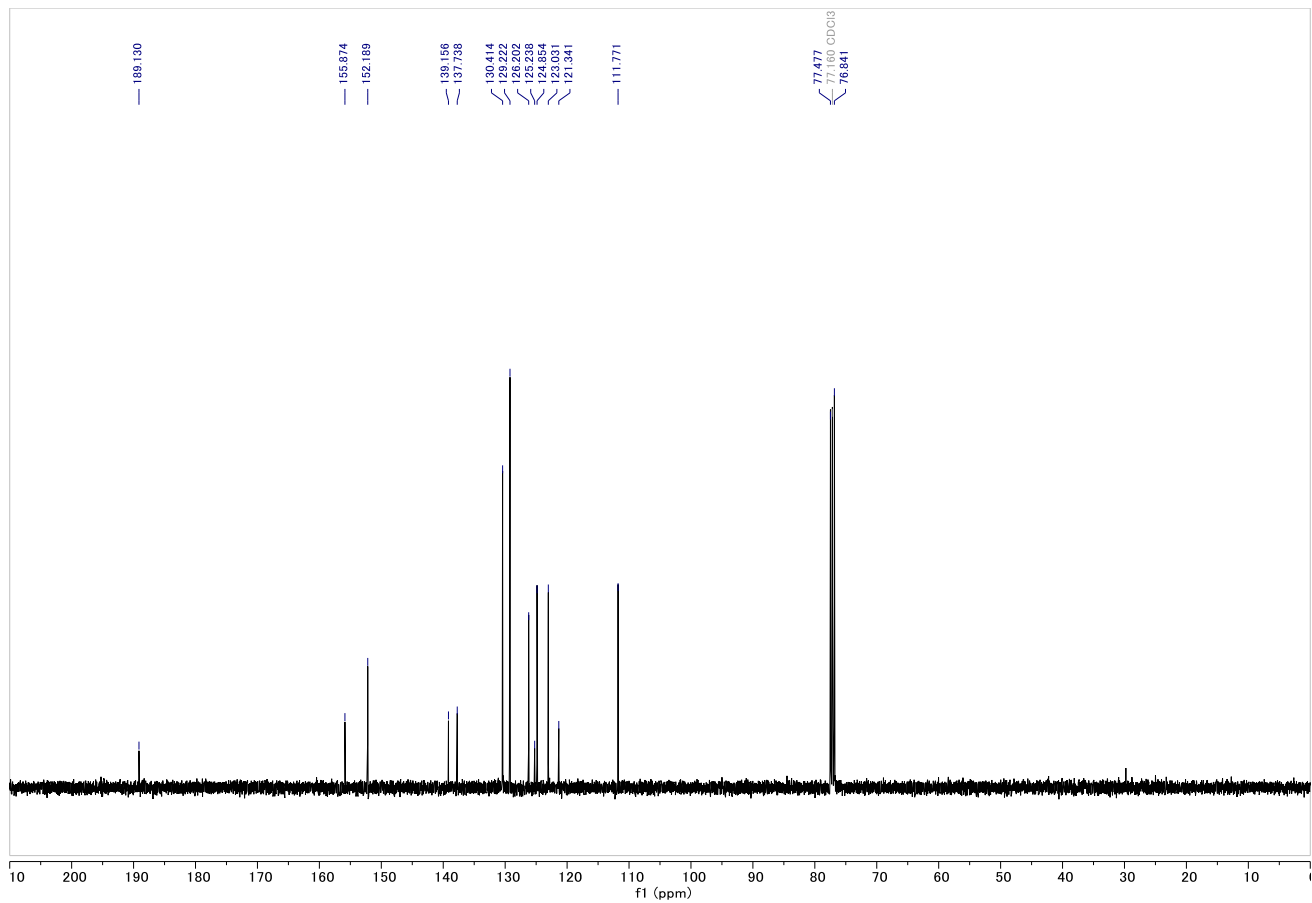
¹³C NMR 4b



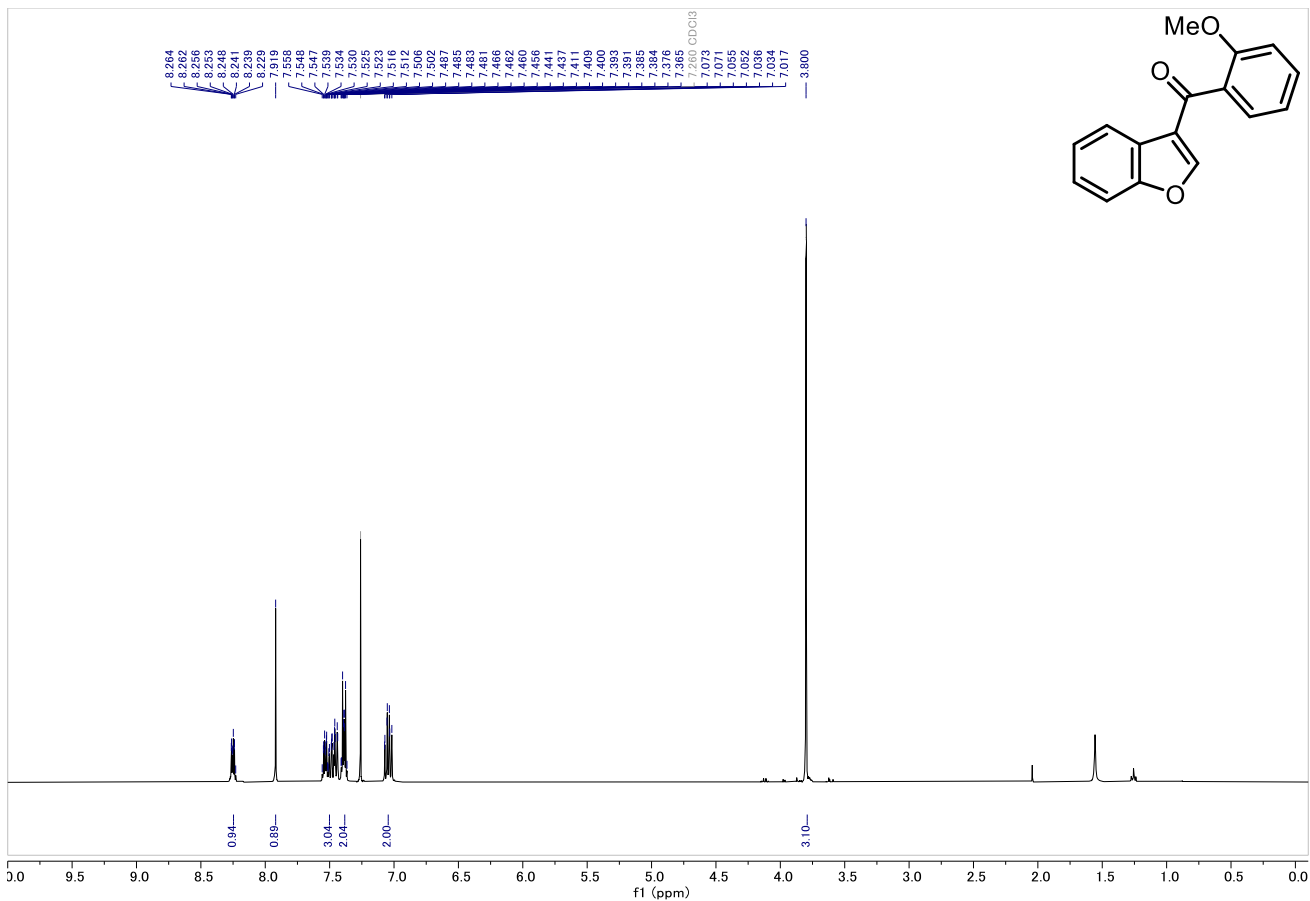
¹H NMR 4c



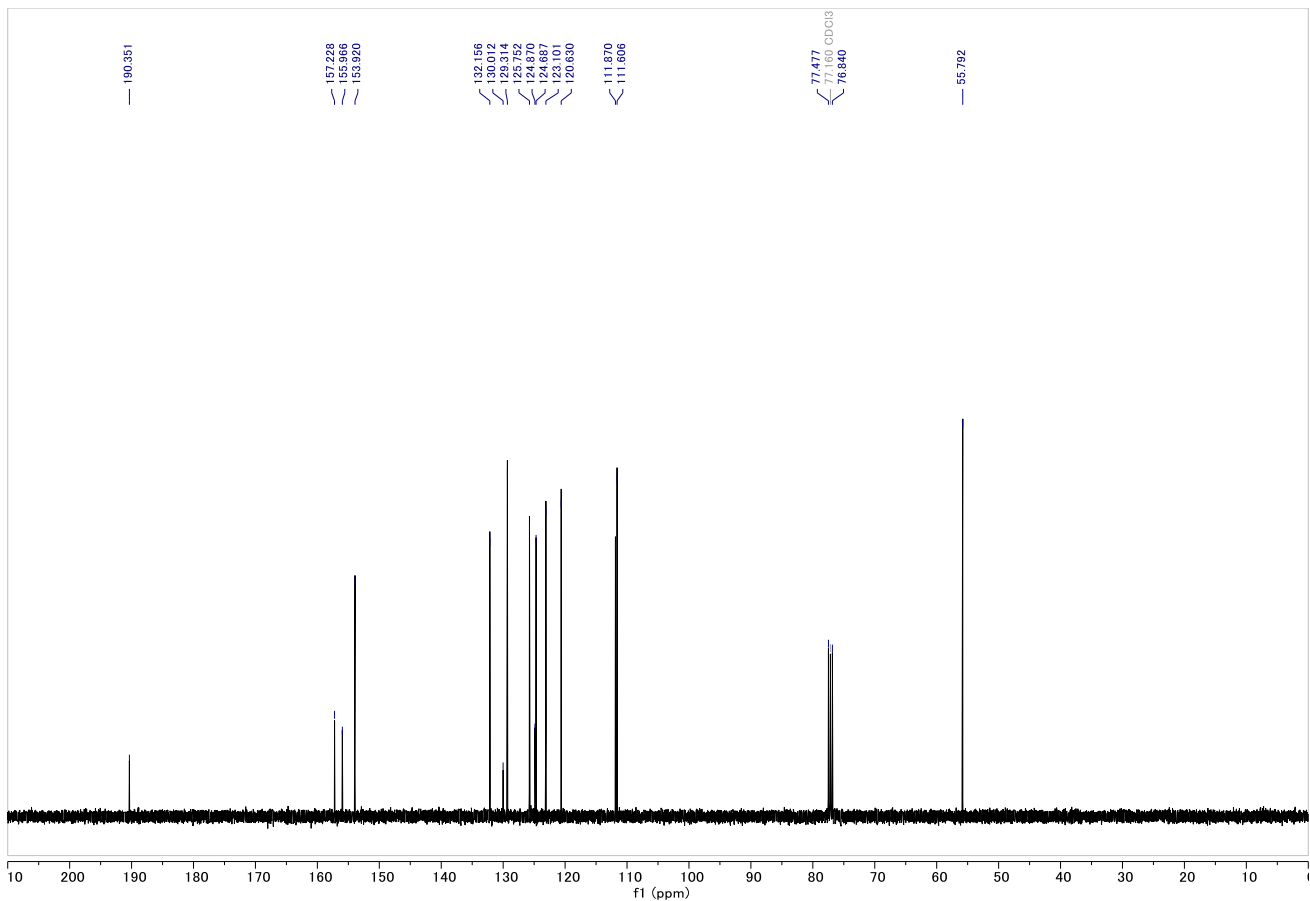
¹³C NMR 4c



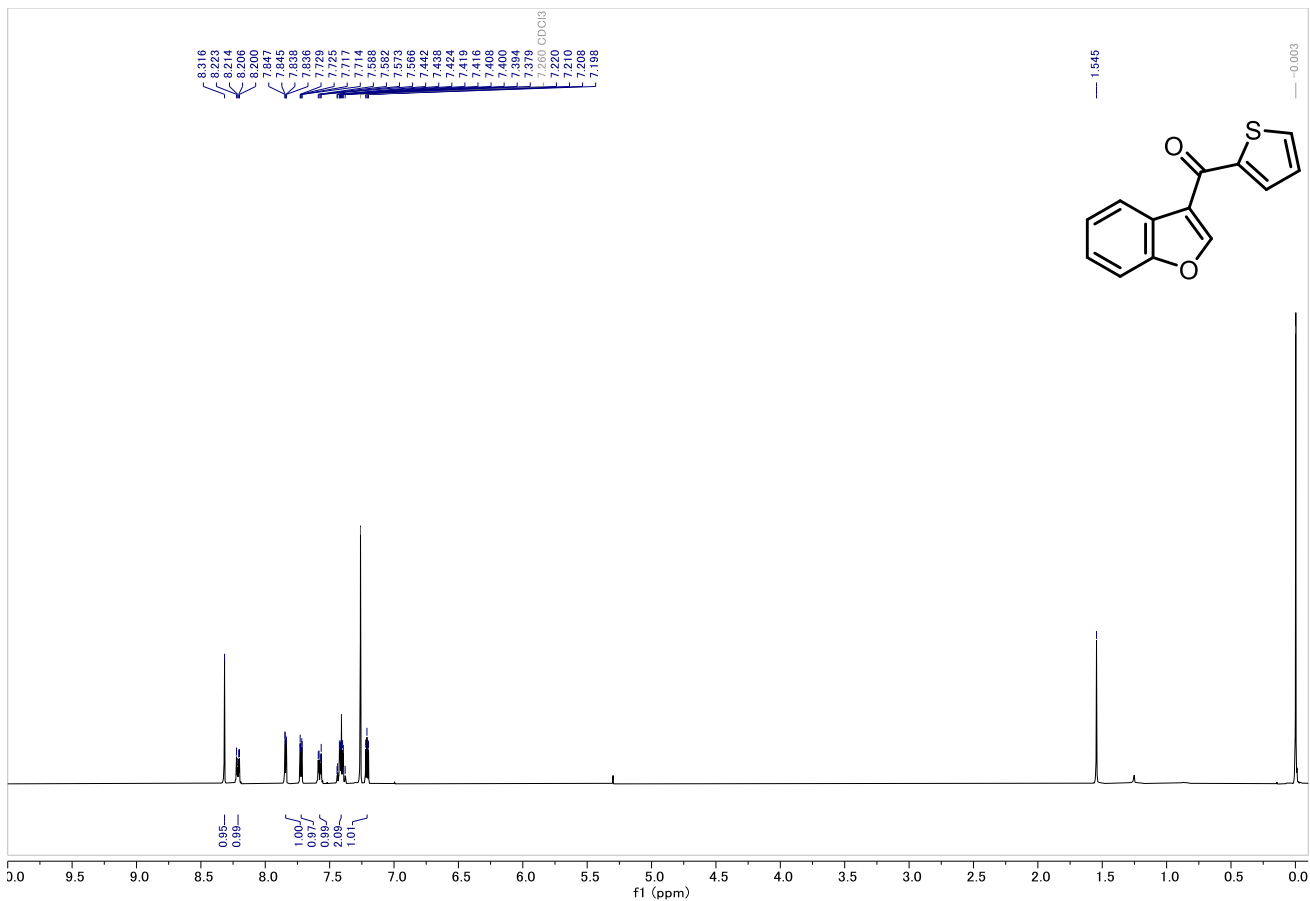
¹H NMR 4d



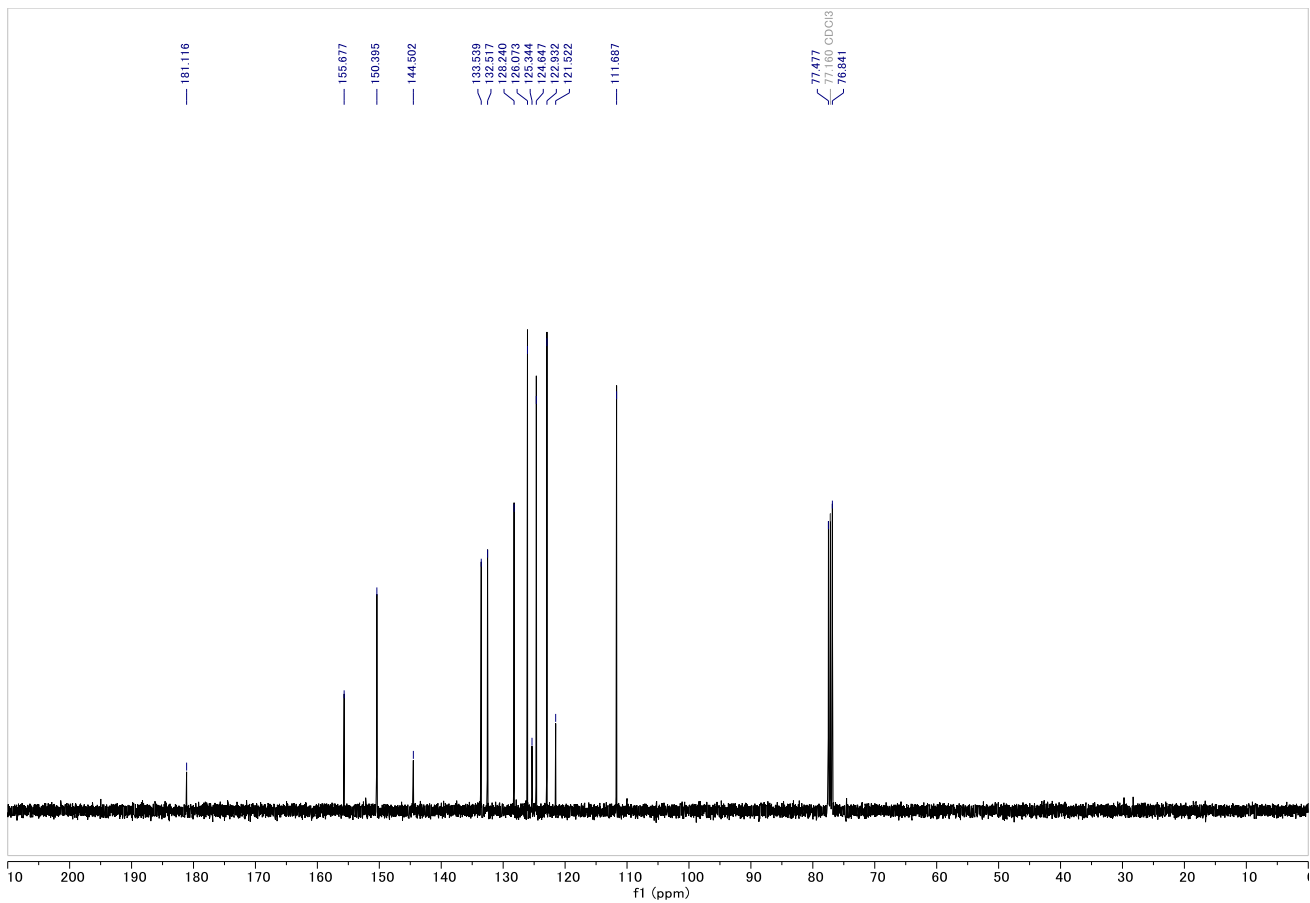
¹³C NMR 4d



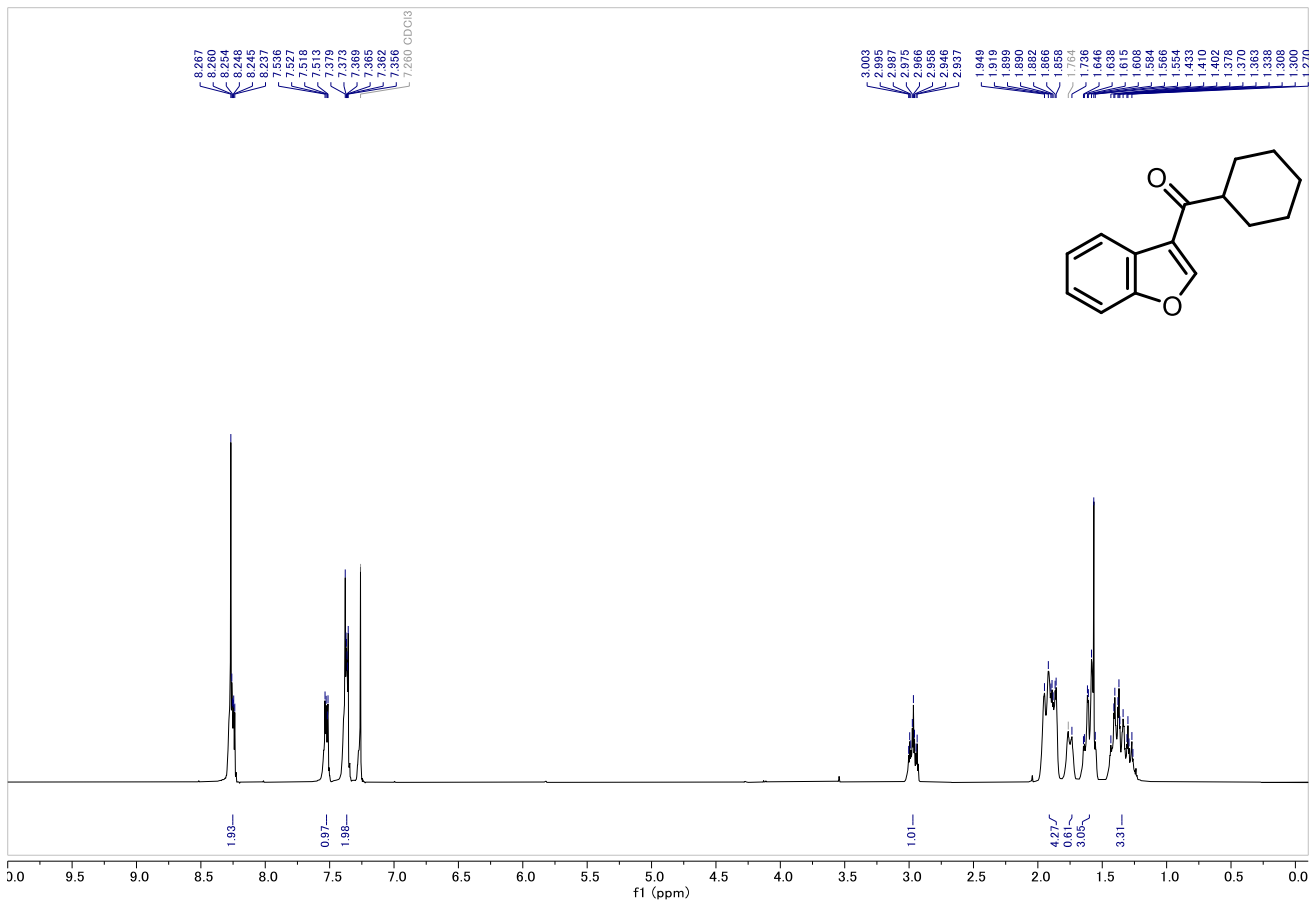
¹H NMR 4e



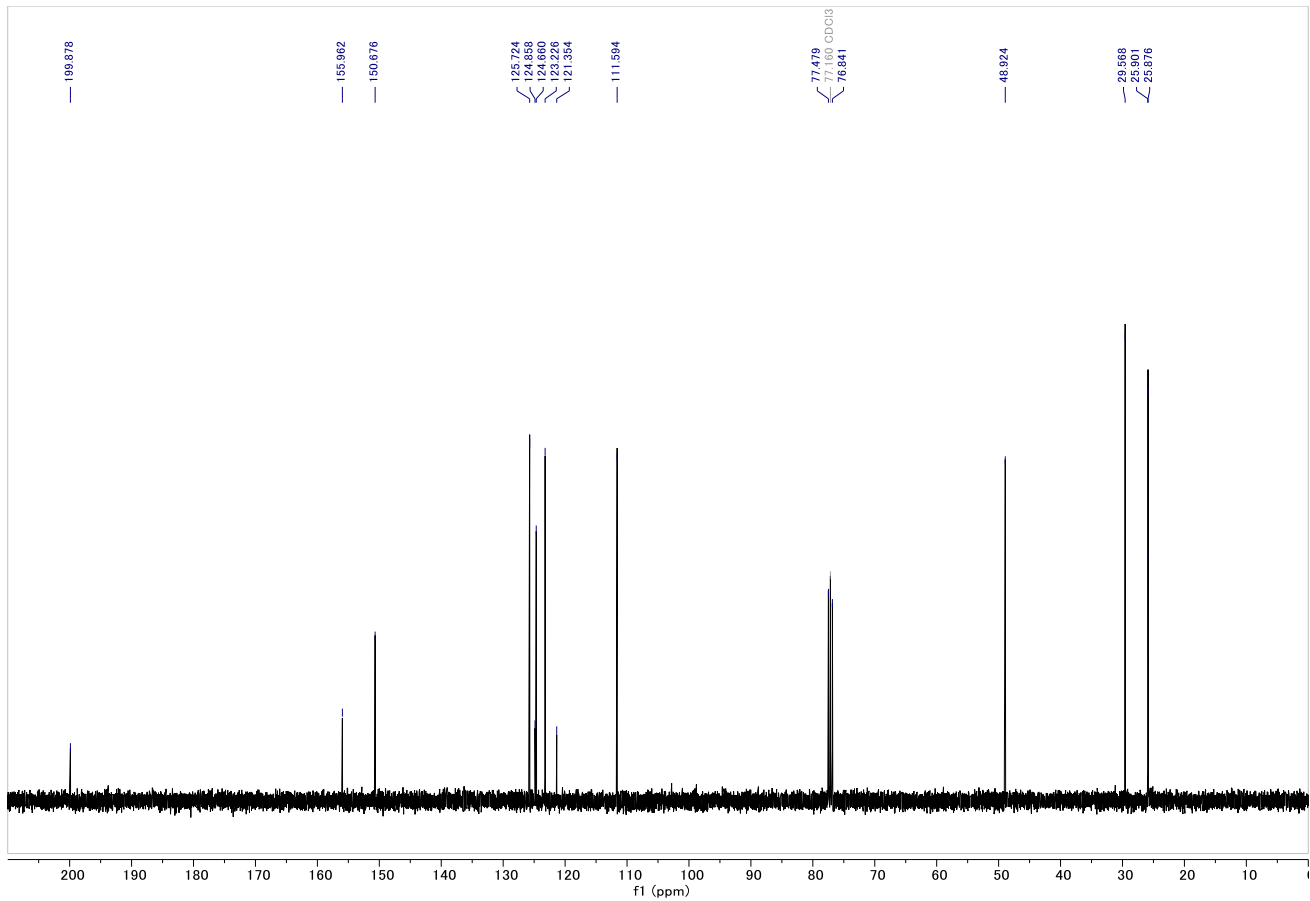
¹³C NMR 4e



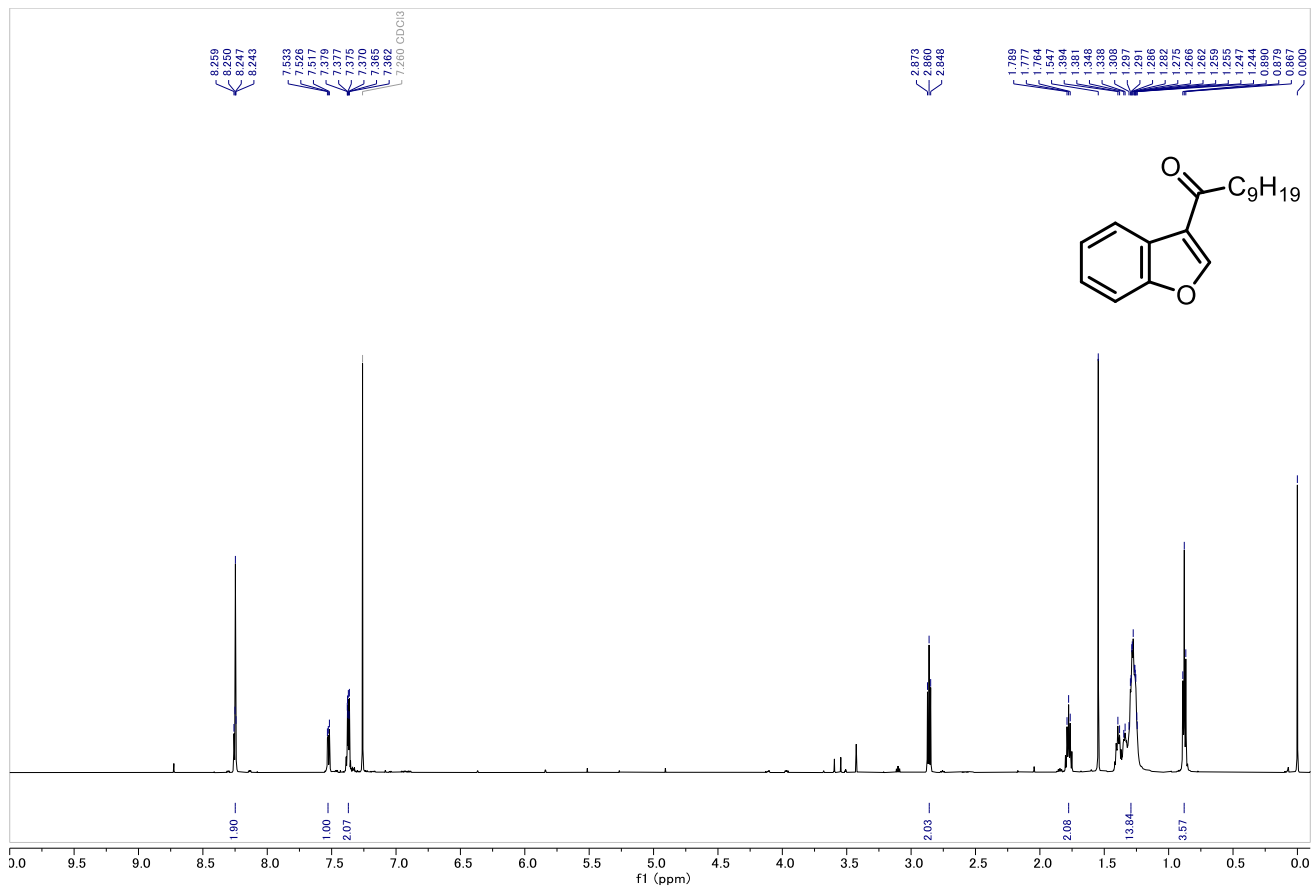
¹H NMR 4f



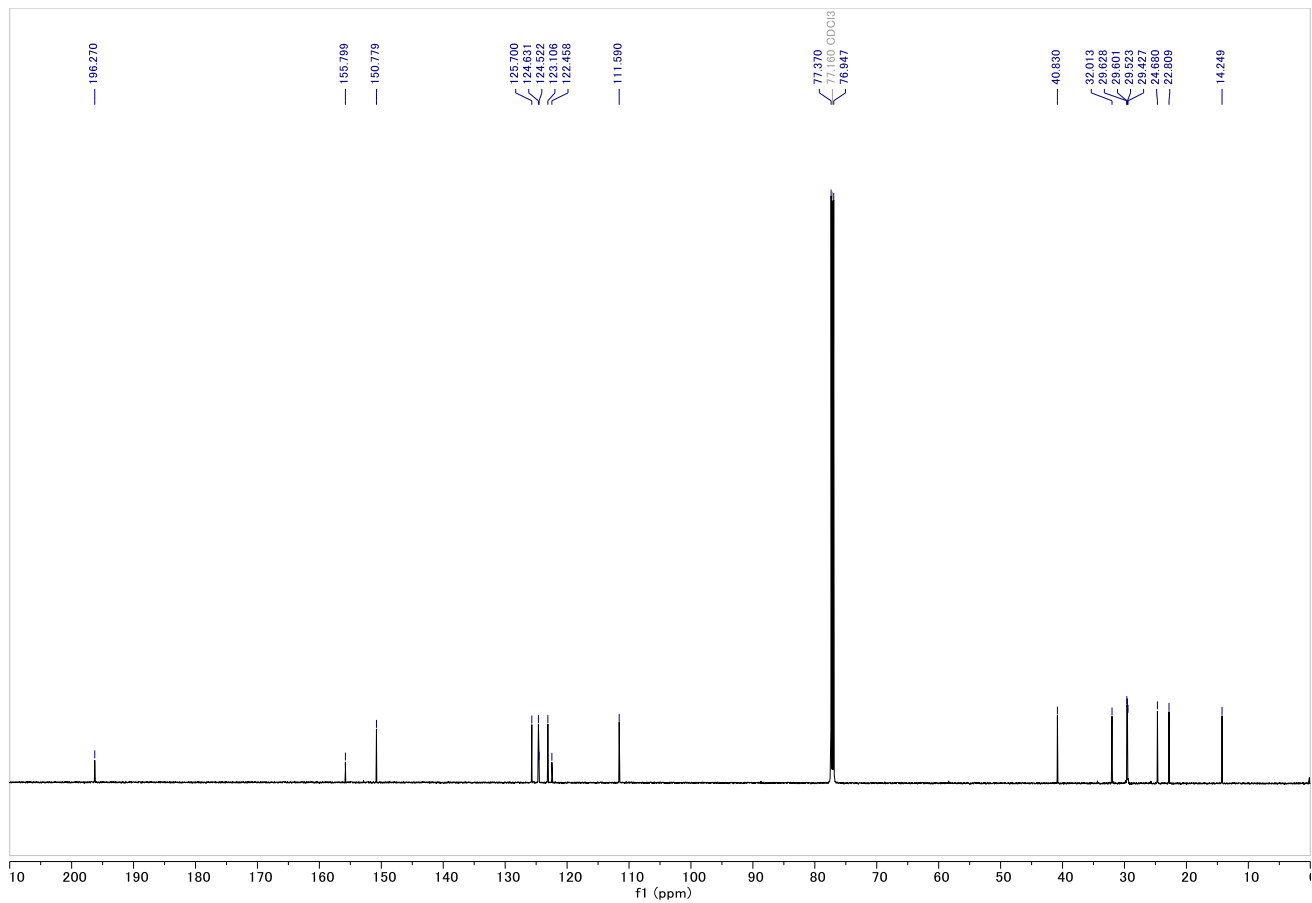
¹³C NMR 4f



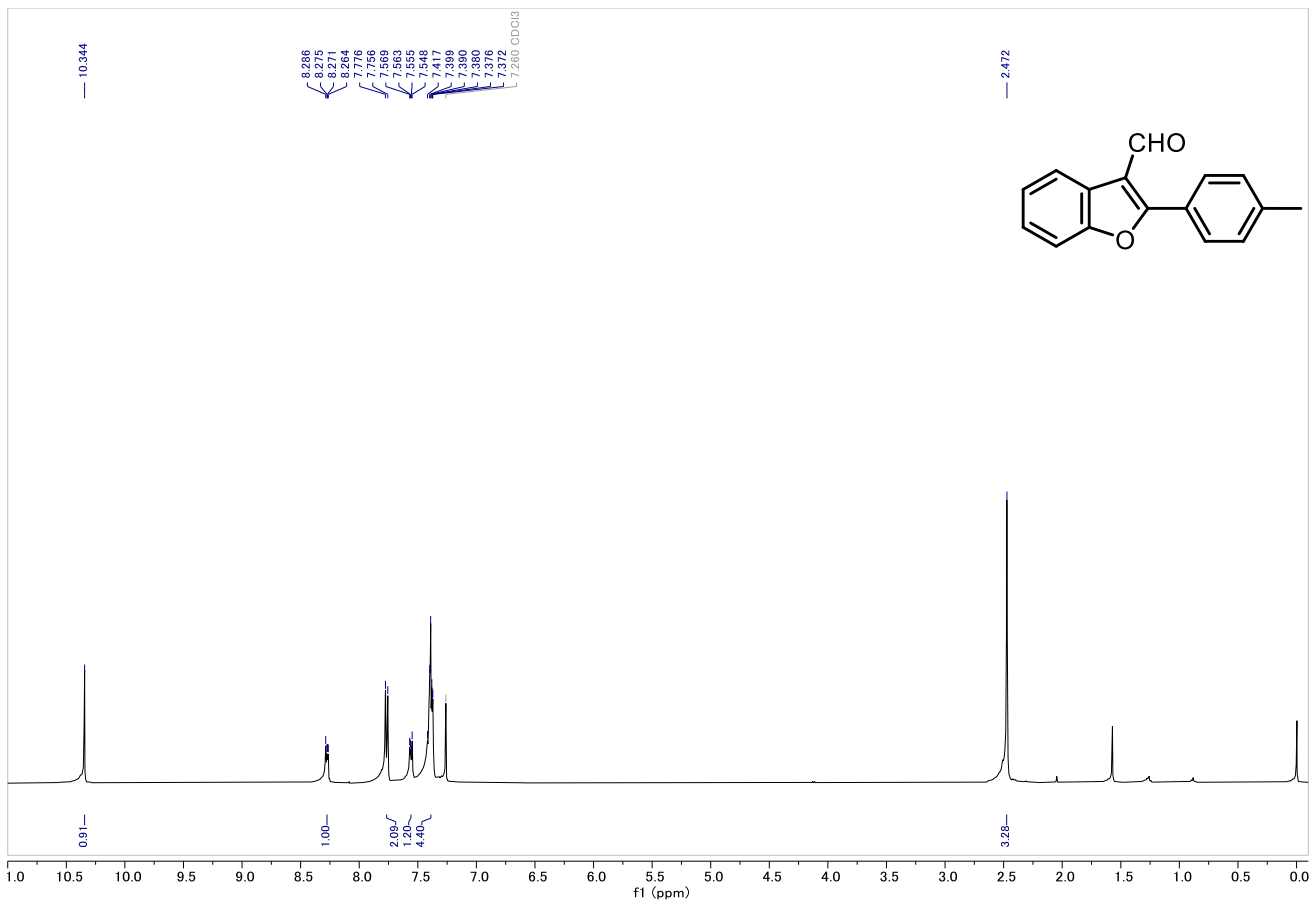
¹H NMR 4g



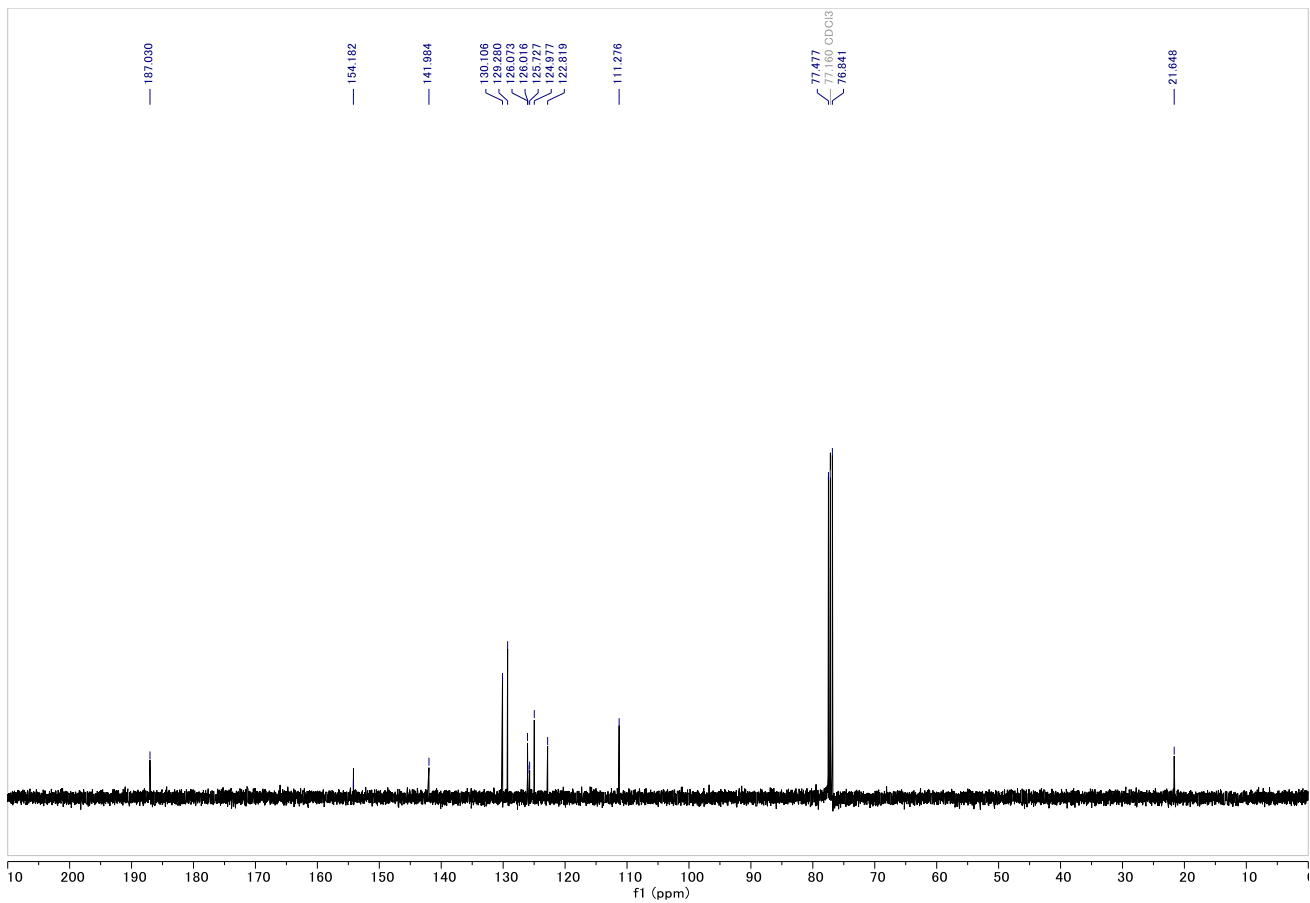
¹³C NMR 4g



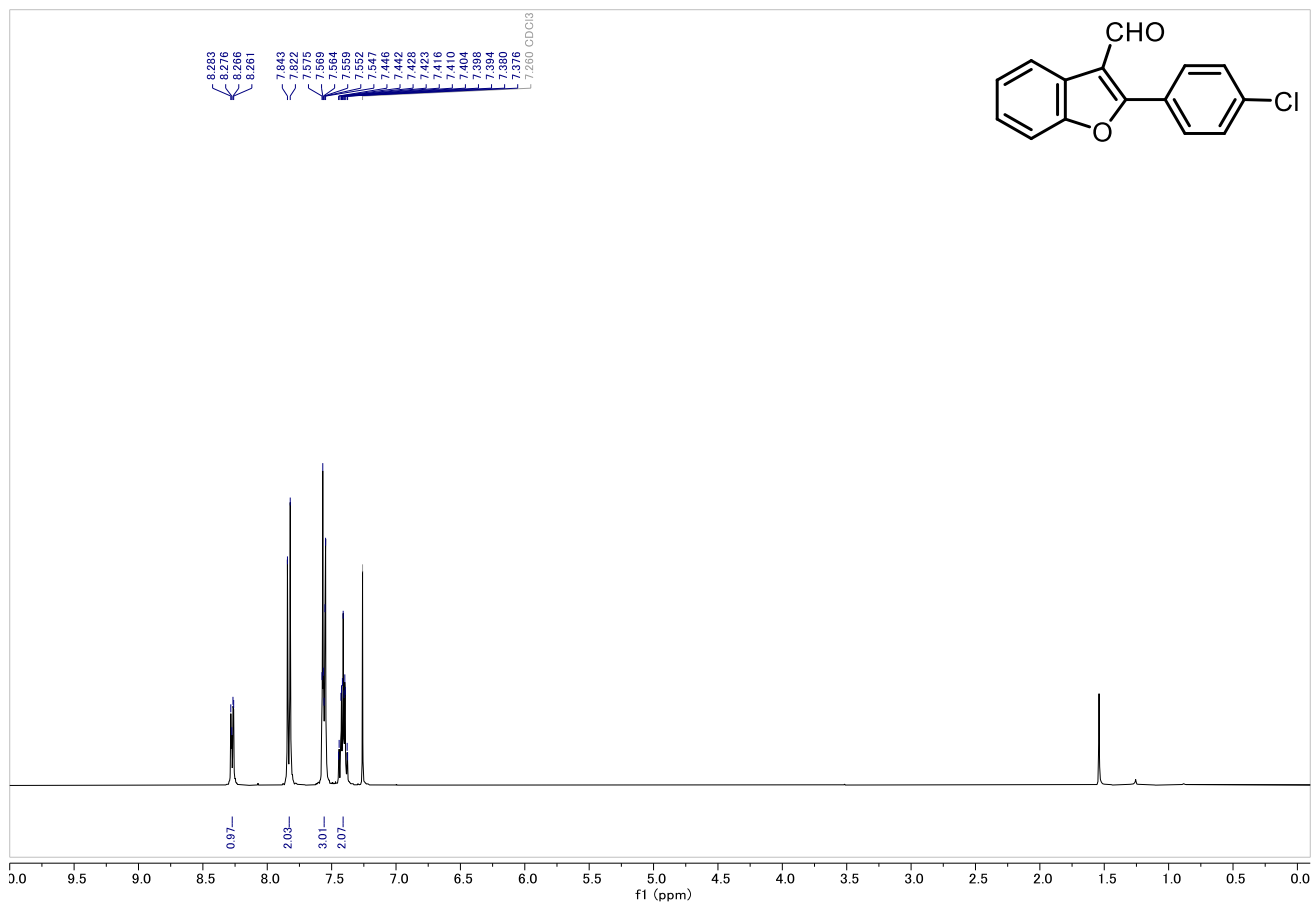
¹H NMR 5b



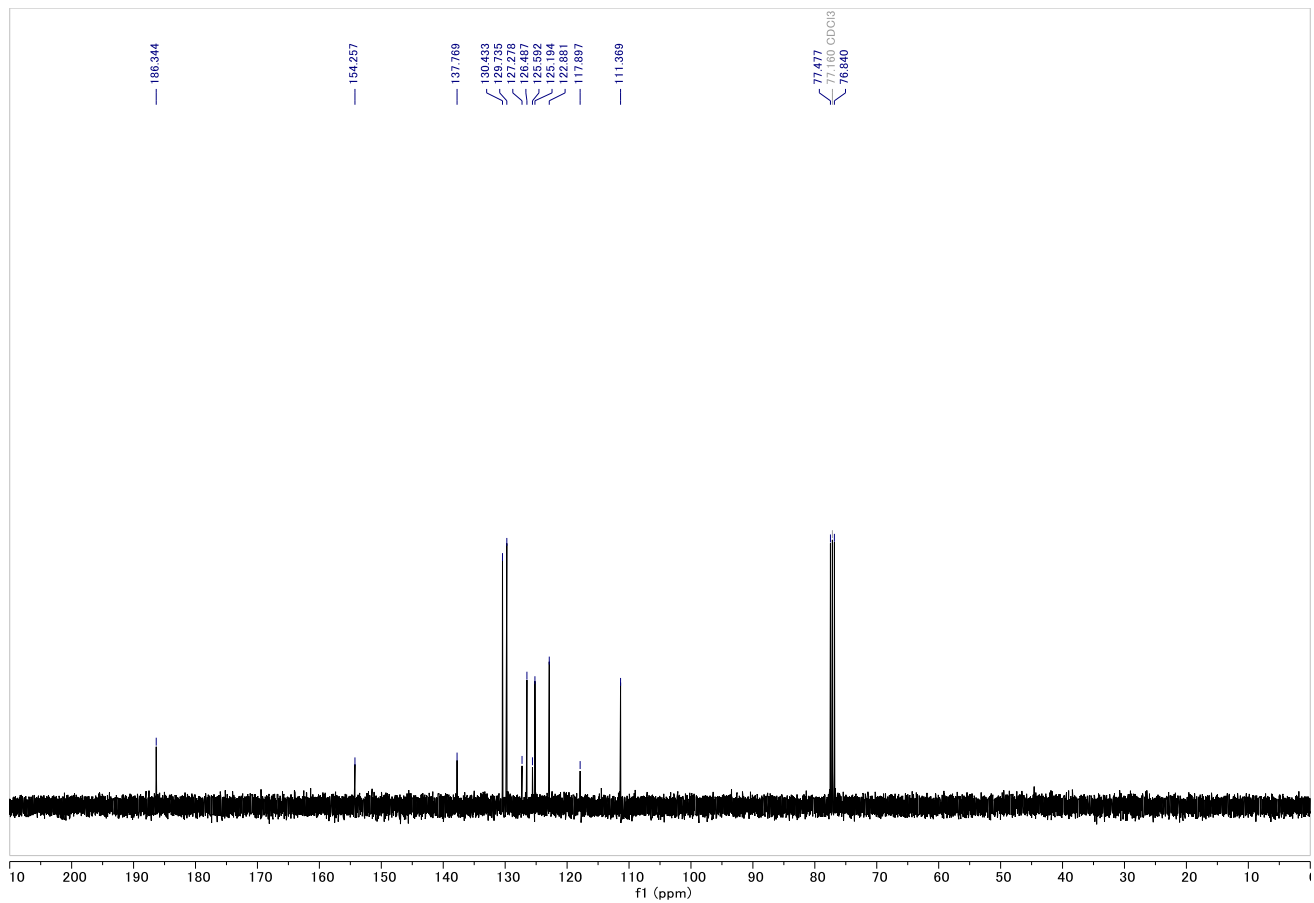
¹³C NMR 5b



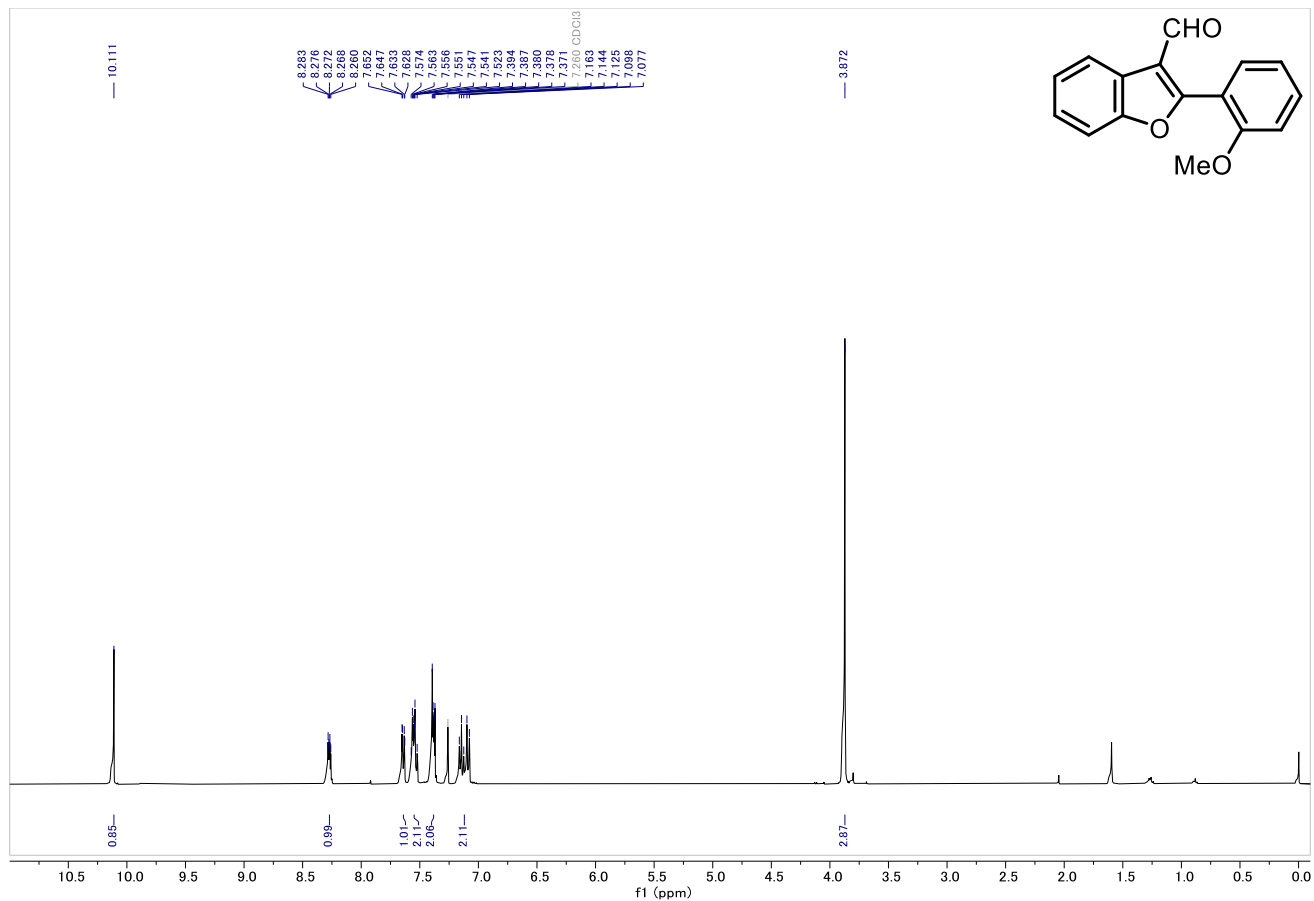
¹H NMR 5c



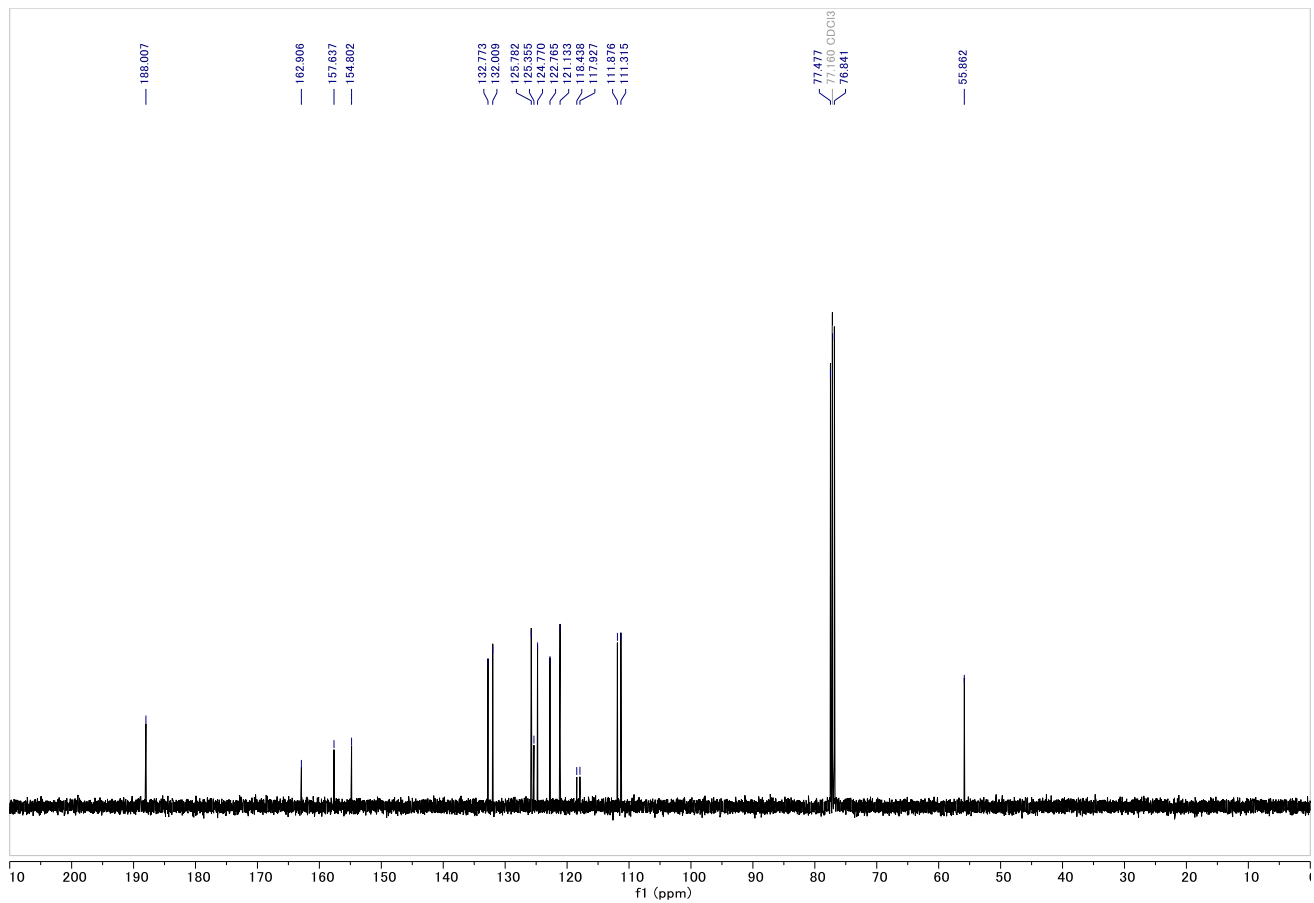
¹³C NMR 5c



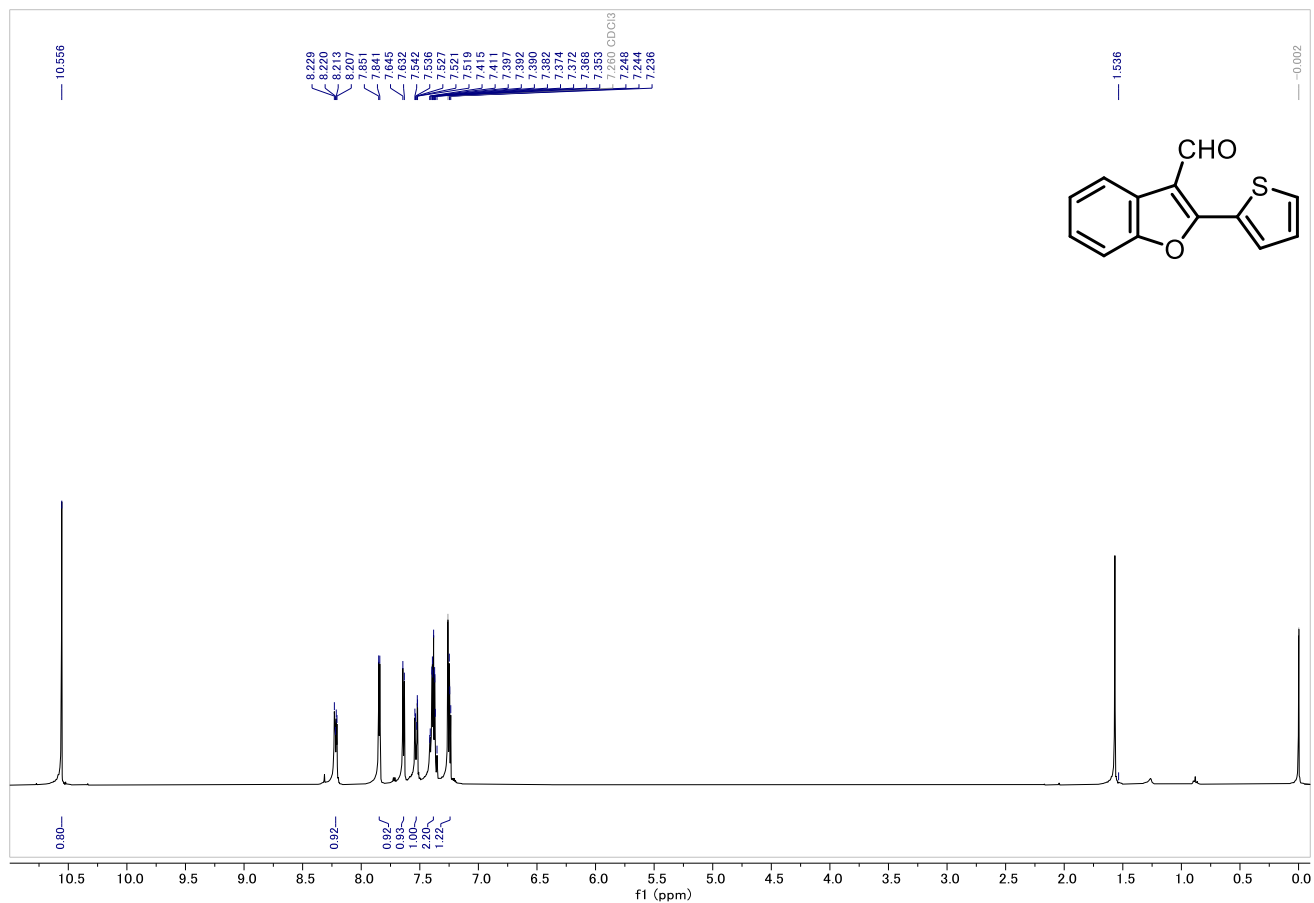
¹H NMR 5d



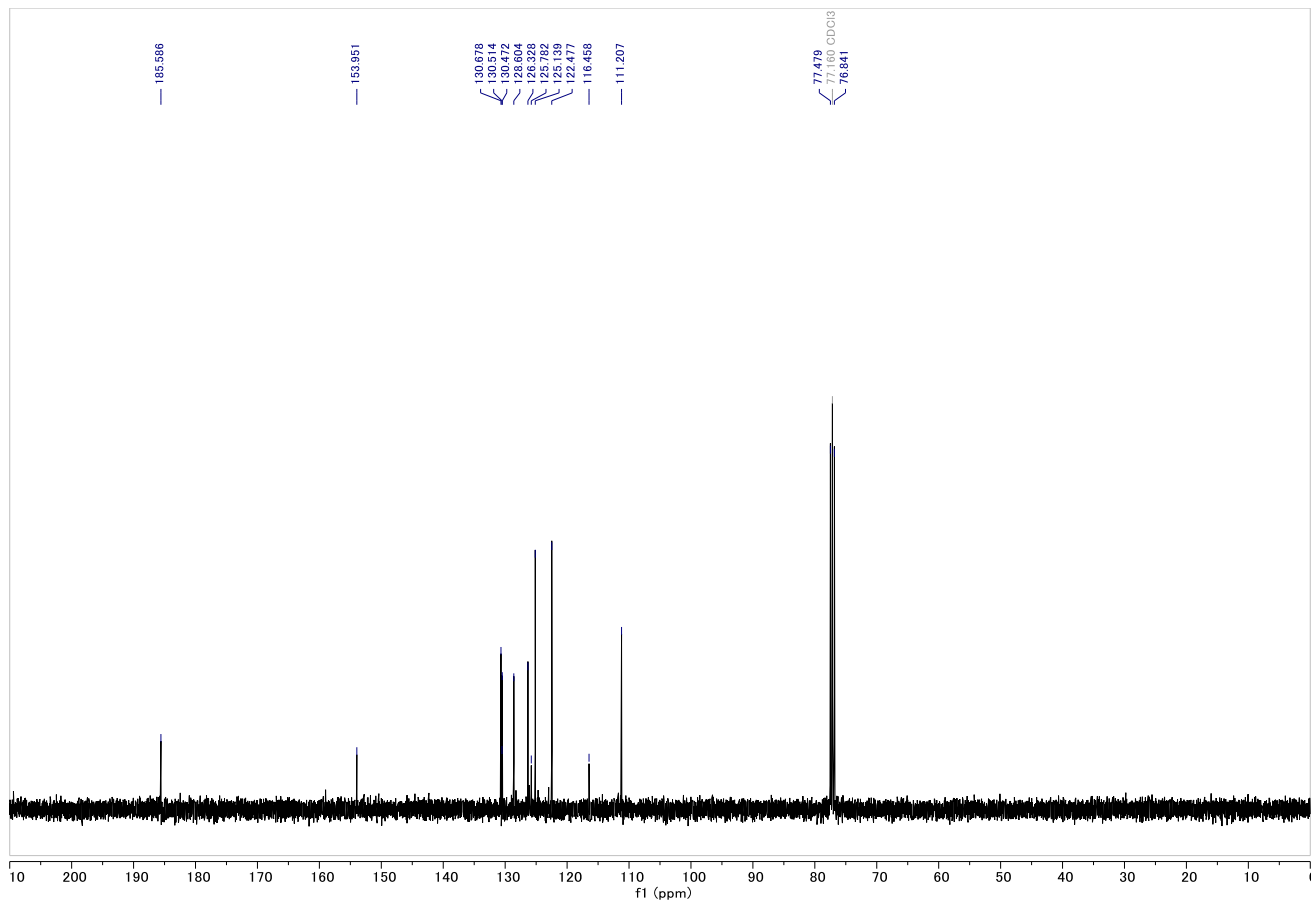
¹³C NMR 5d



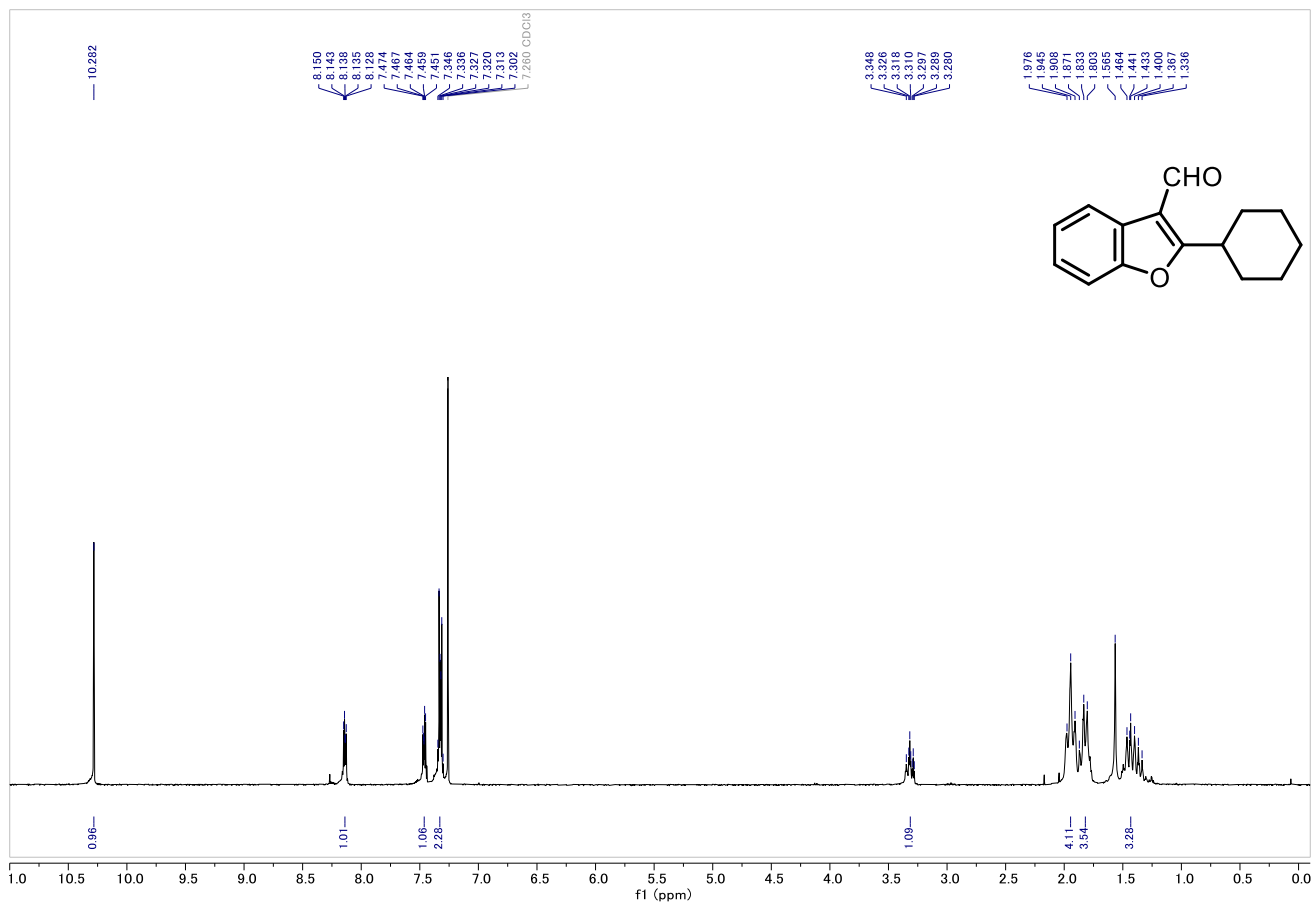
¹H NMR 5e



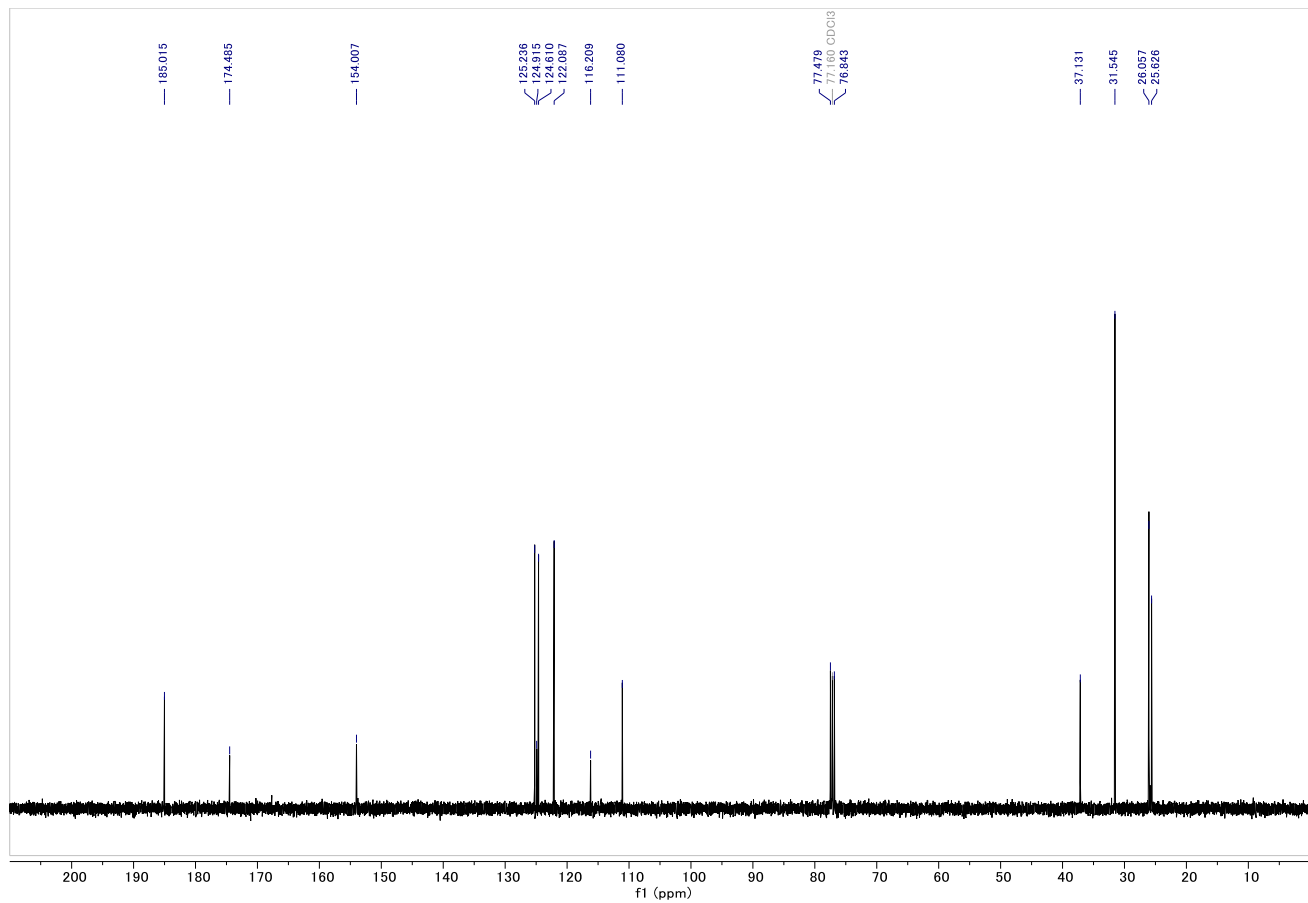
¹³C NMR 5e



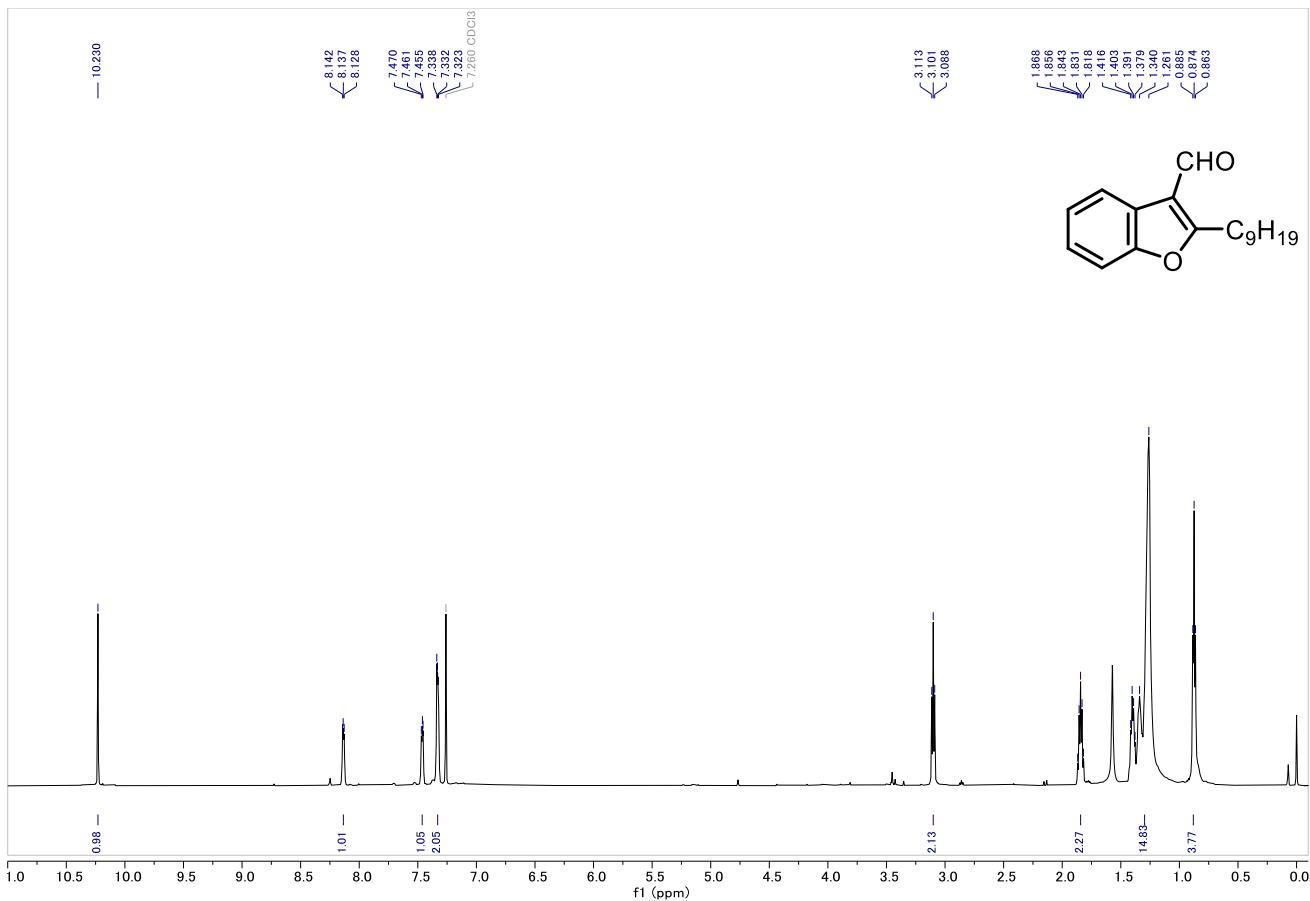
¹H NMR 5f



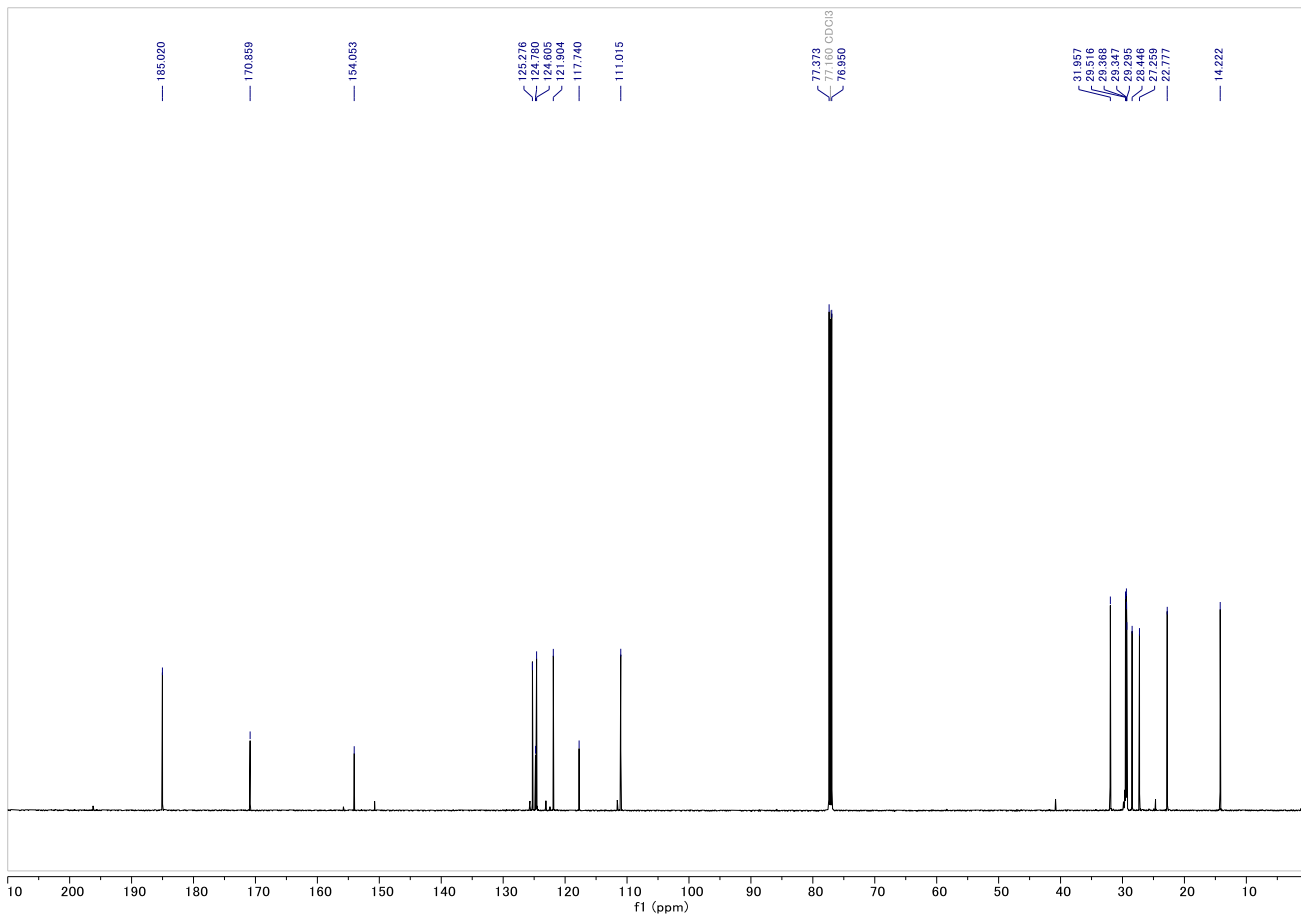
¹³C NMR 5f



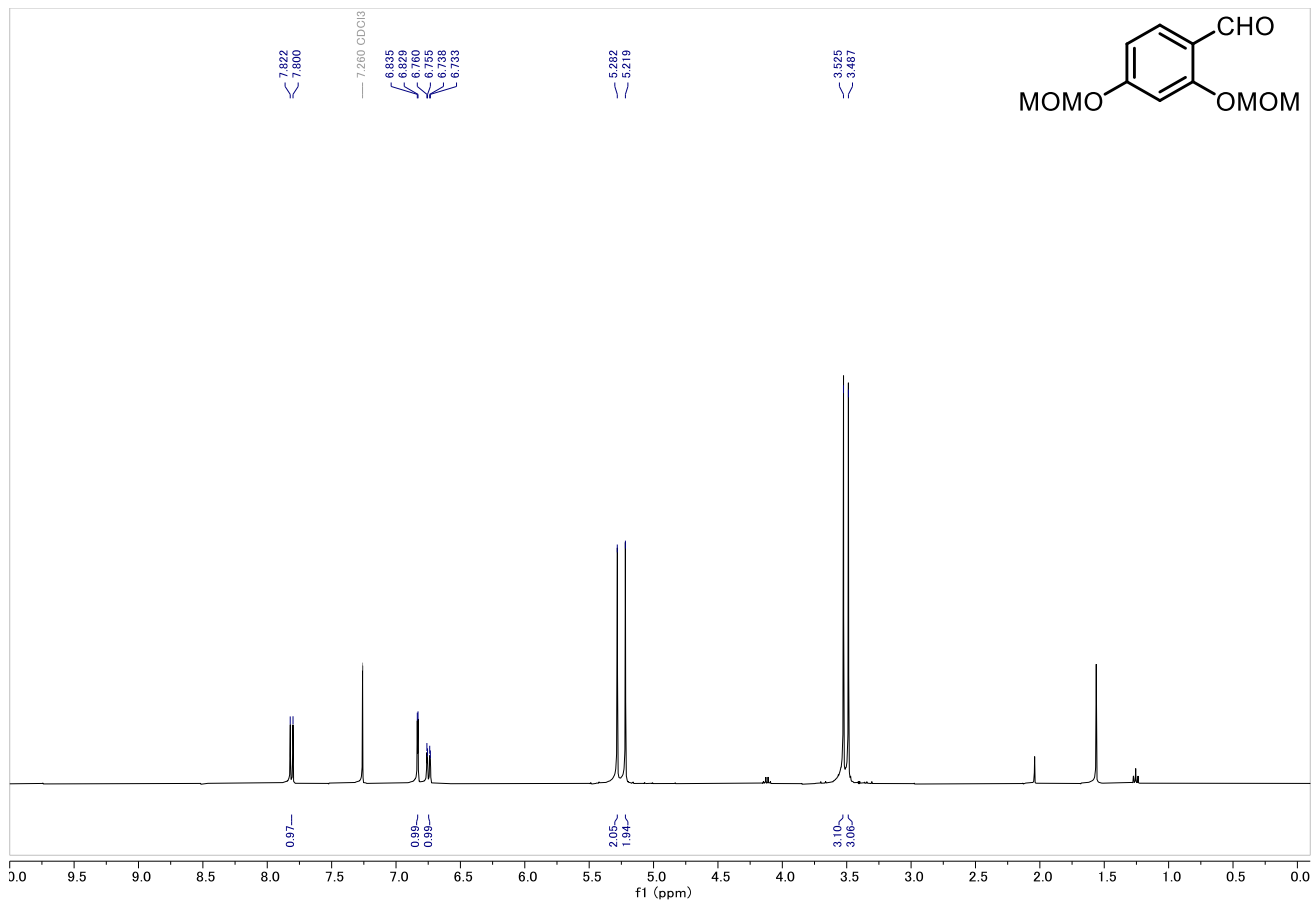
¹H NMR 5g



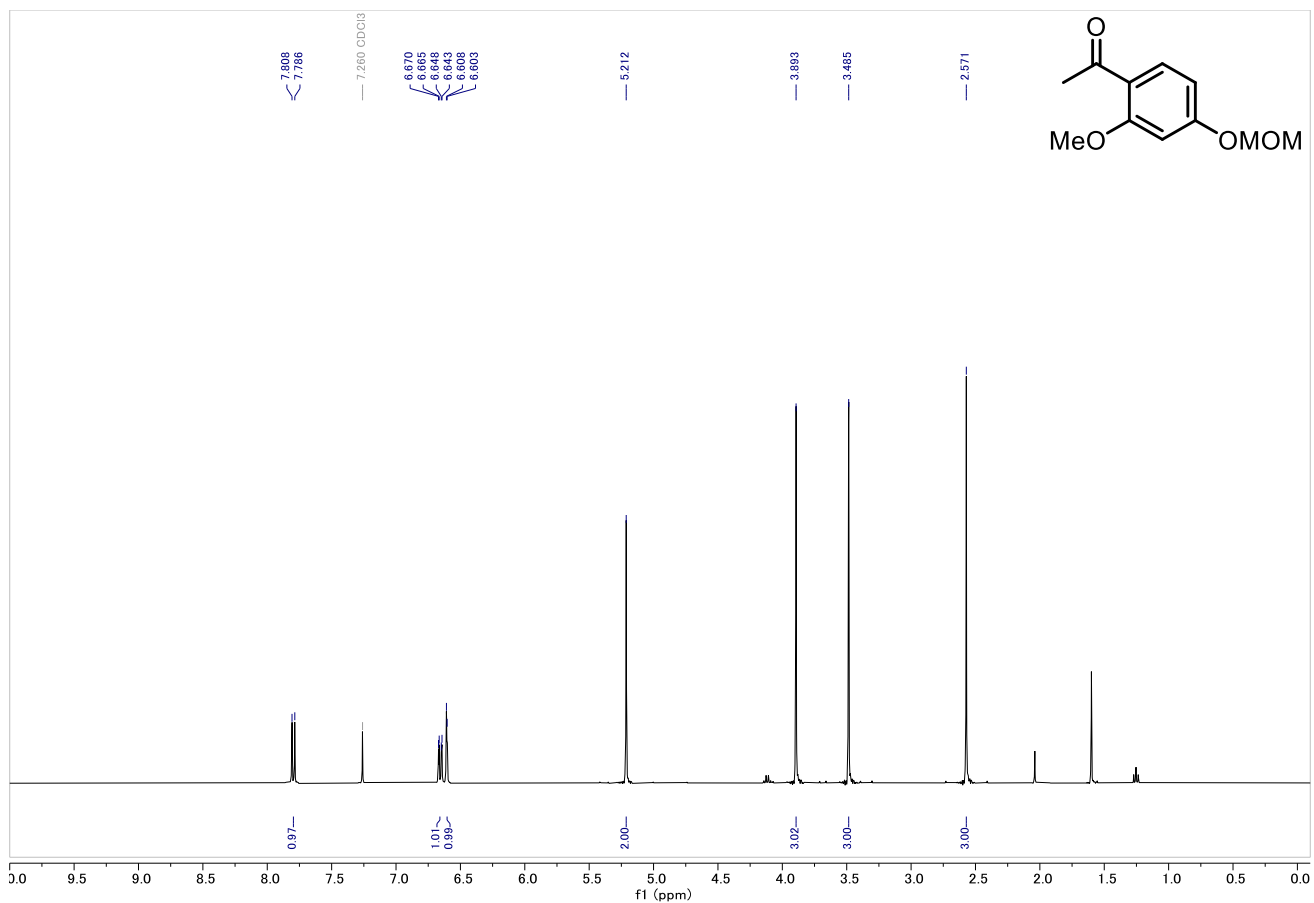
¹³C NMR 5g



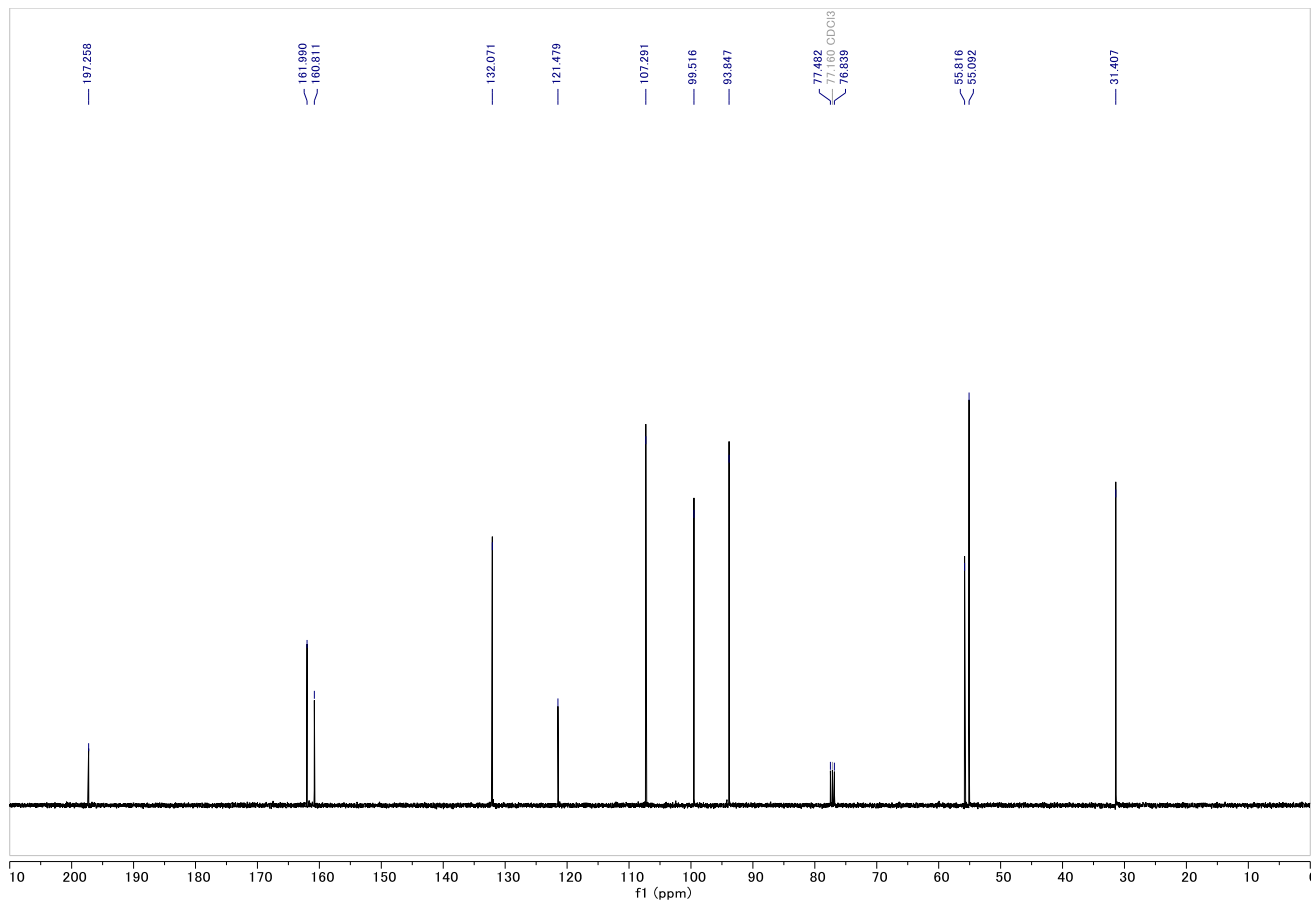
¹H NMR 6



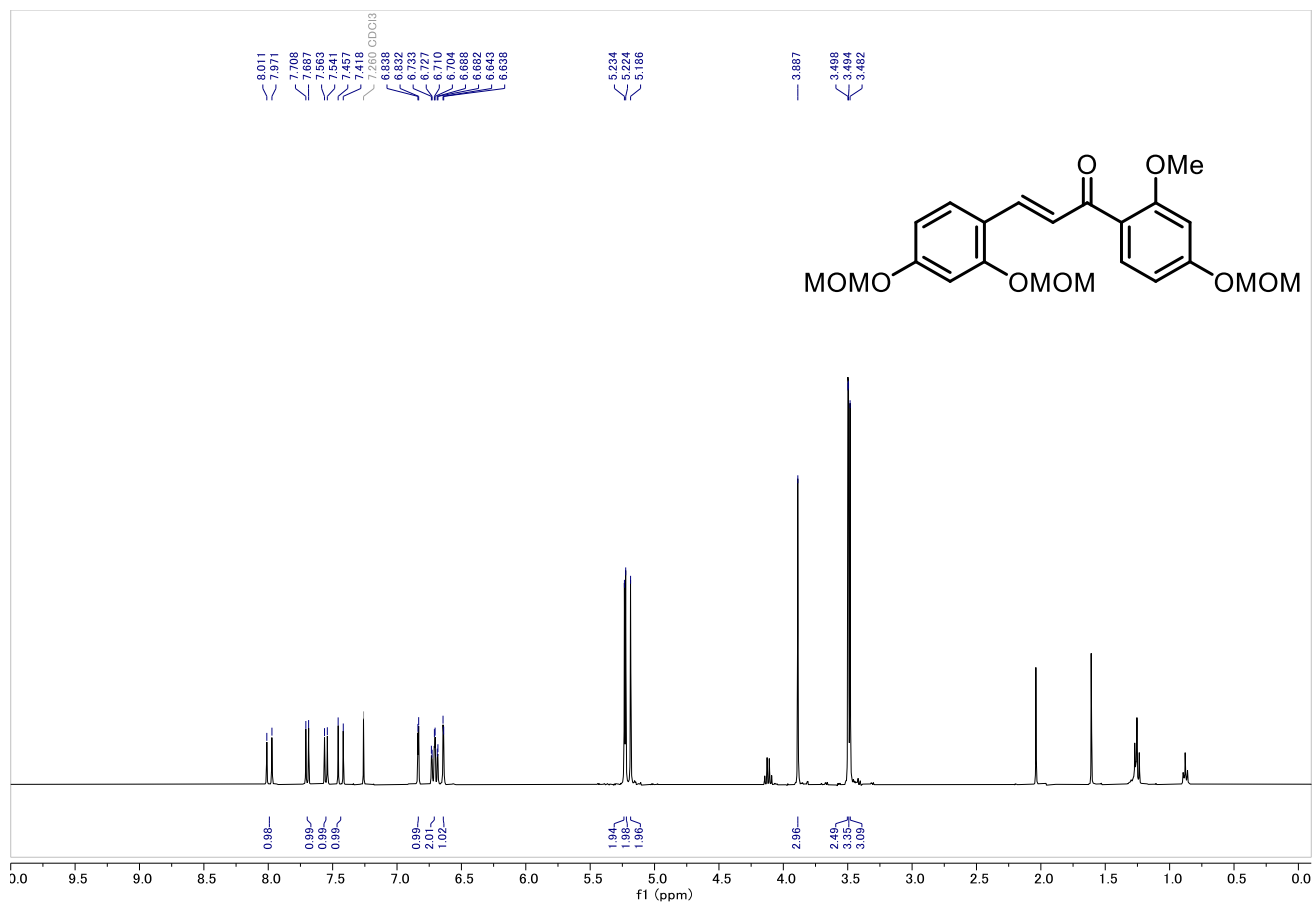
¹H NMR 7



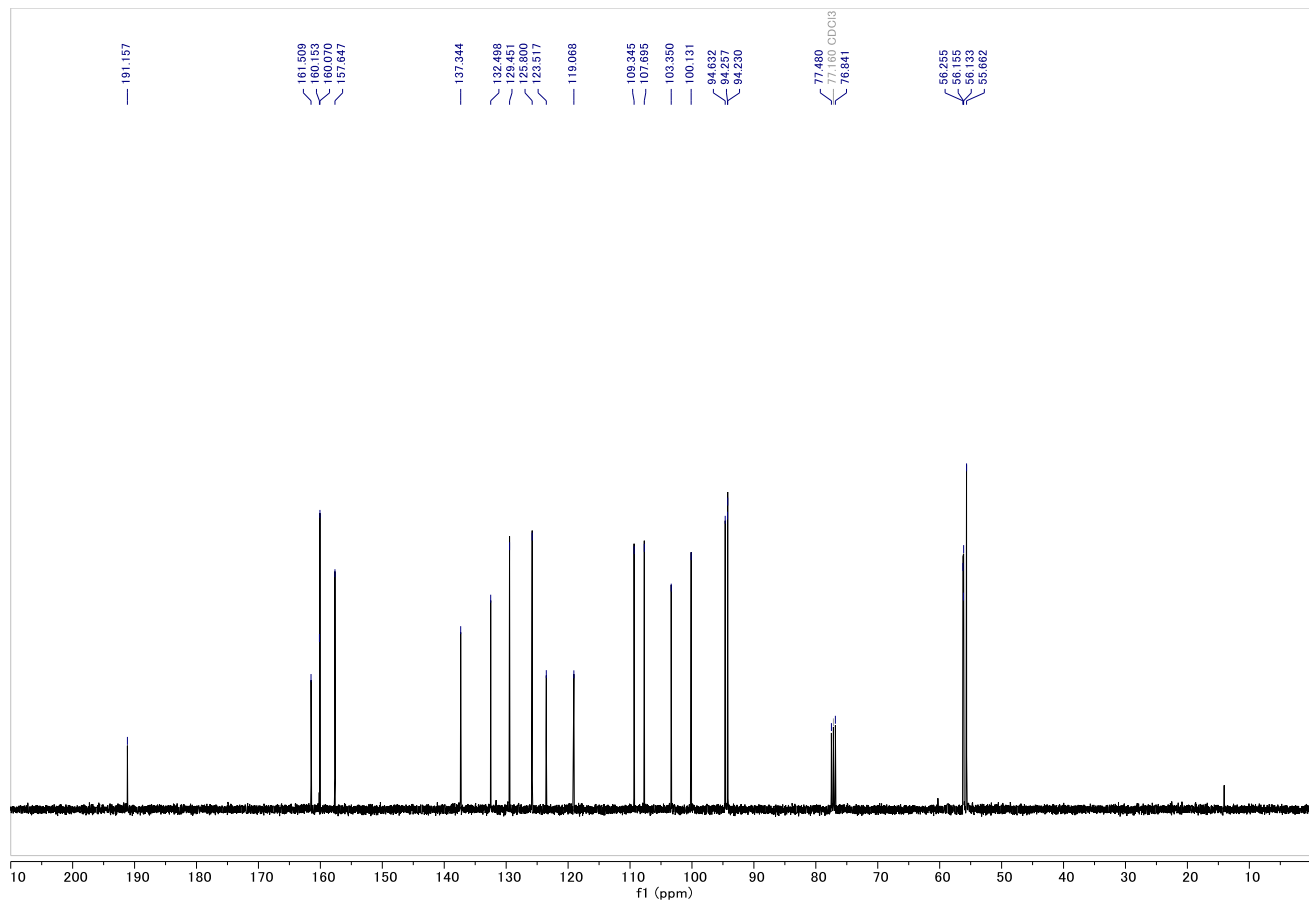
¹³C NMR 7



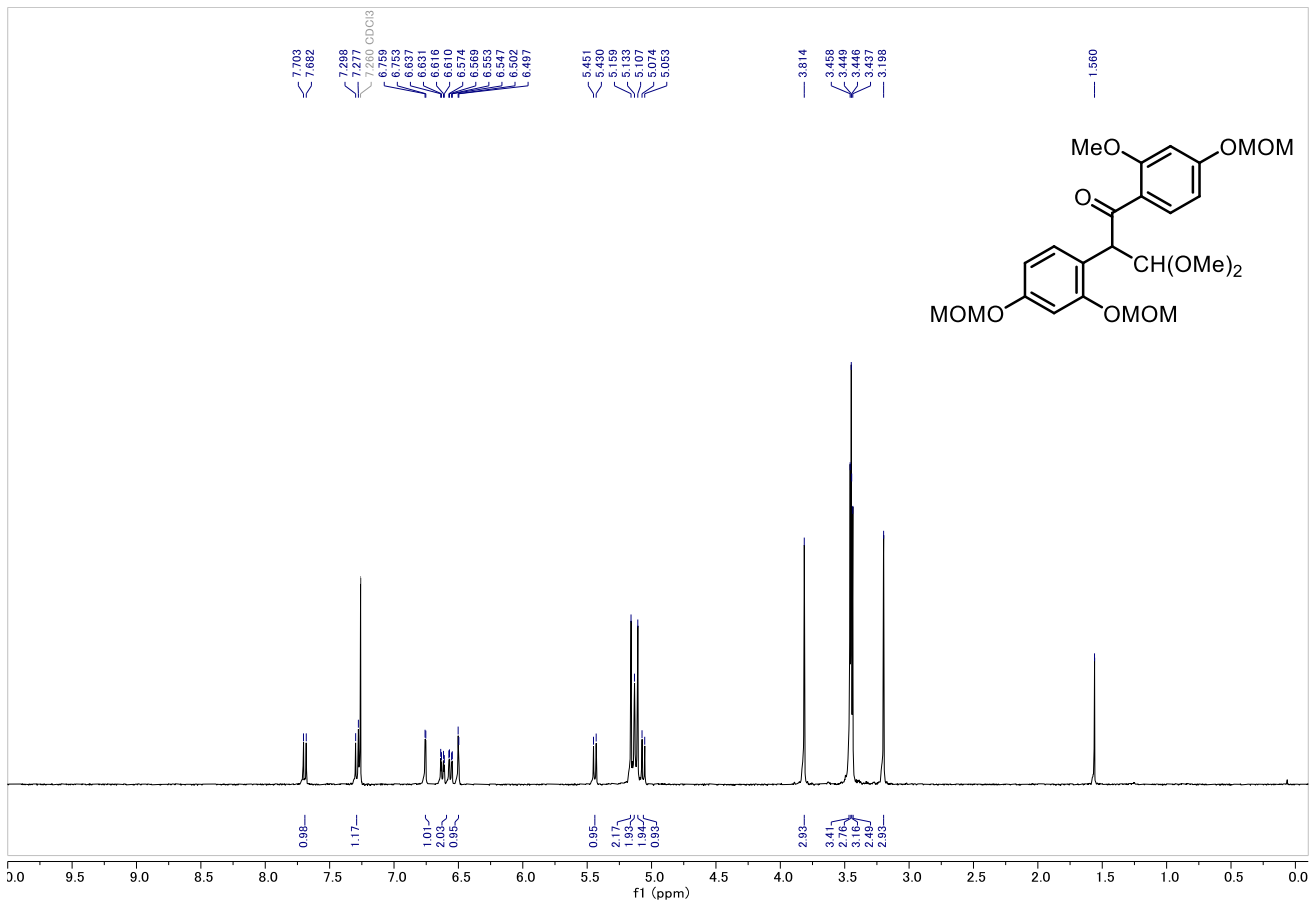
¹H NMR 8



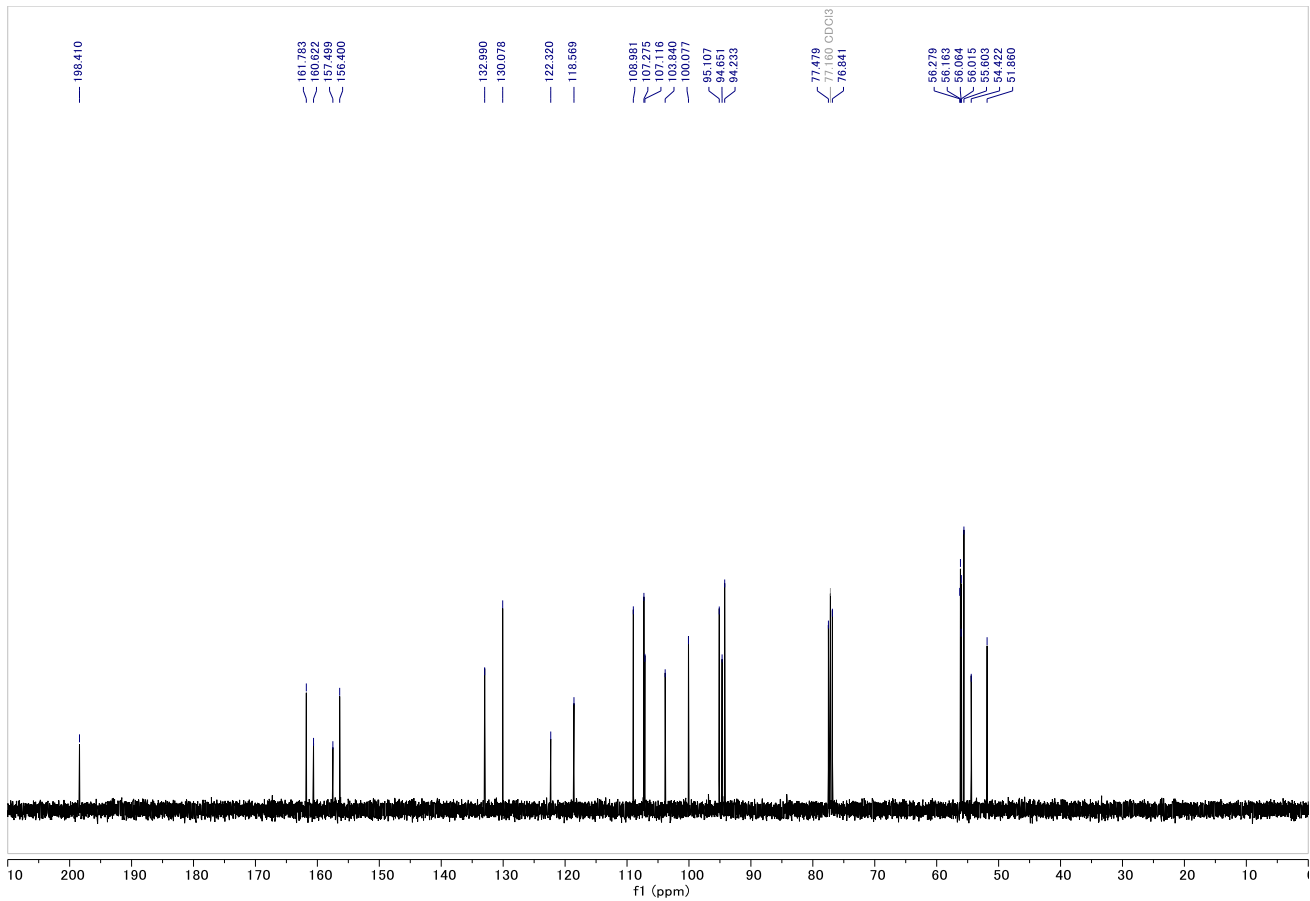
¹³C NMR 8



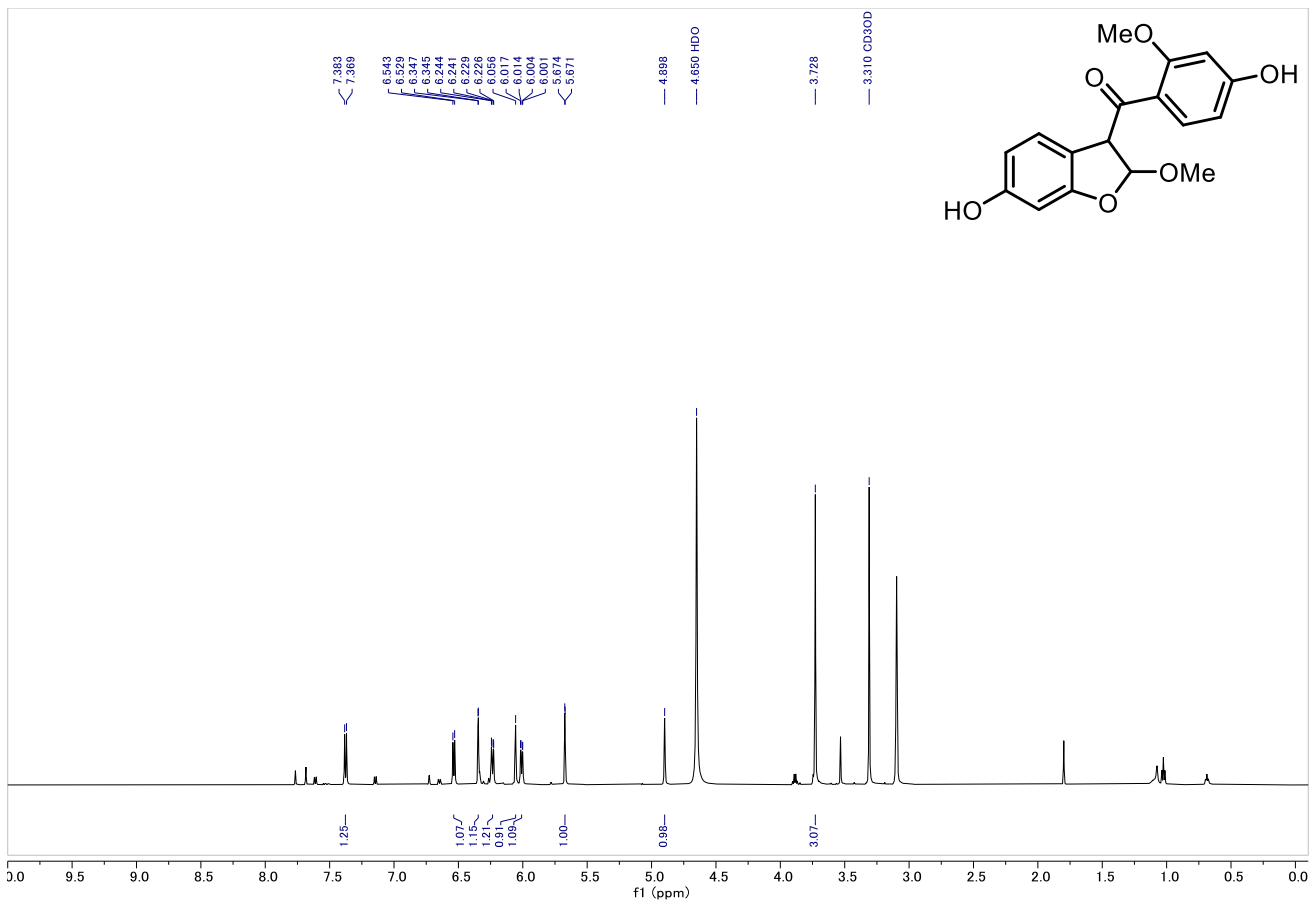
¹H NMR 9



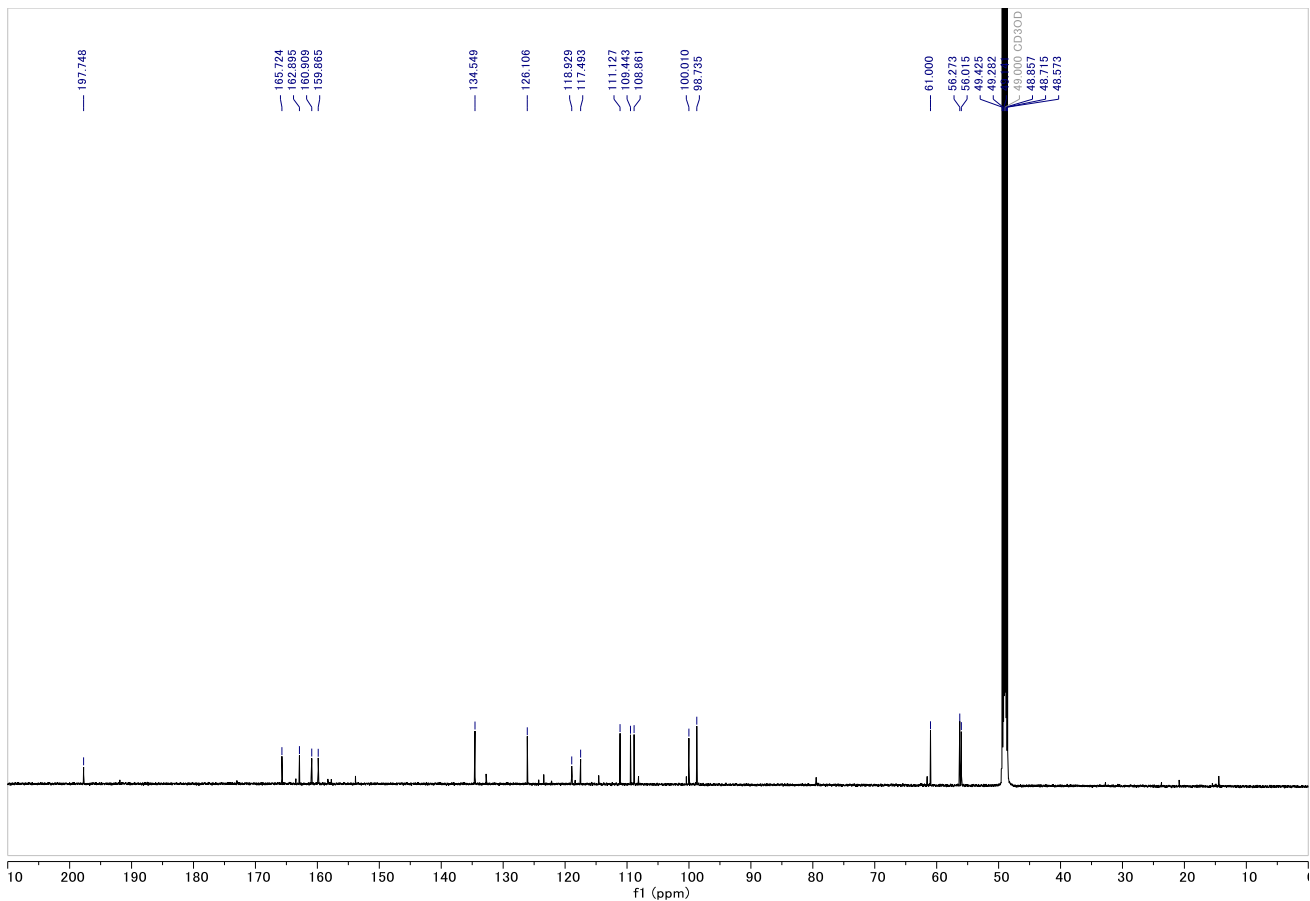
¹³C NMR 9



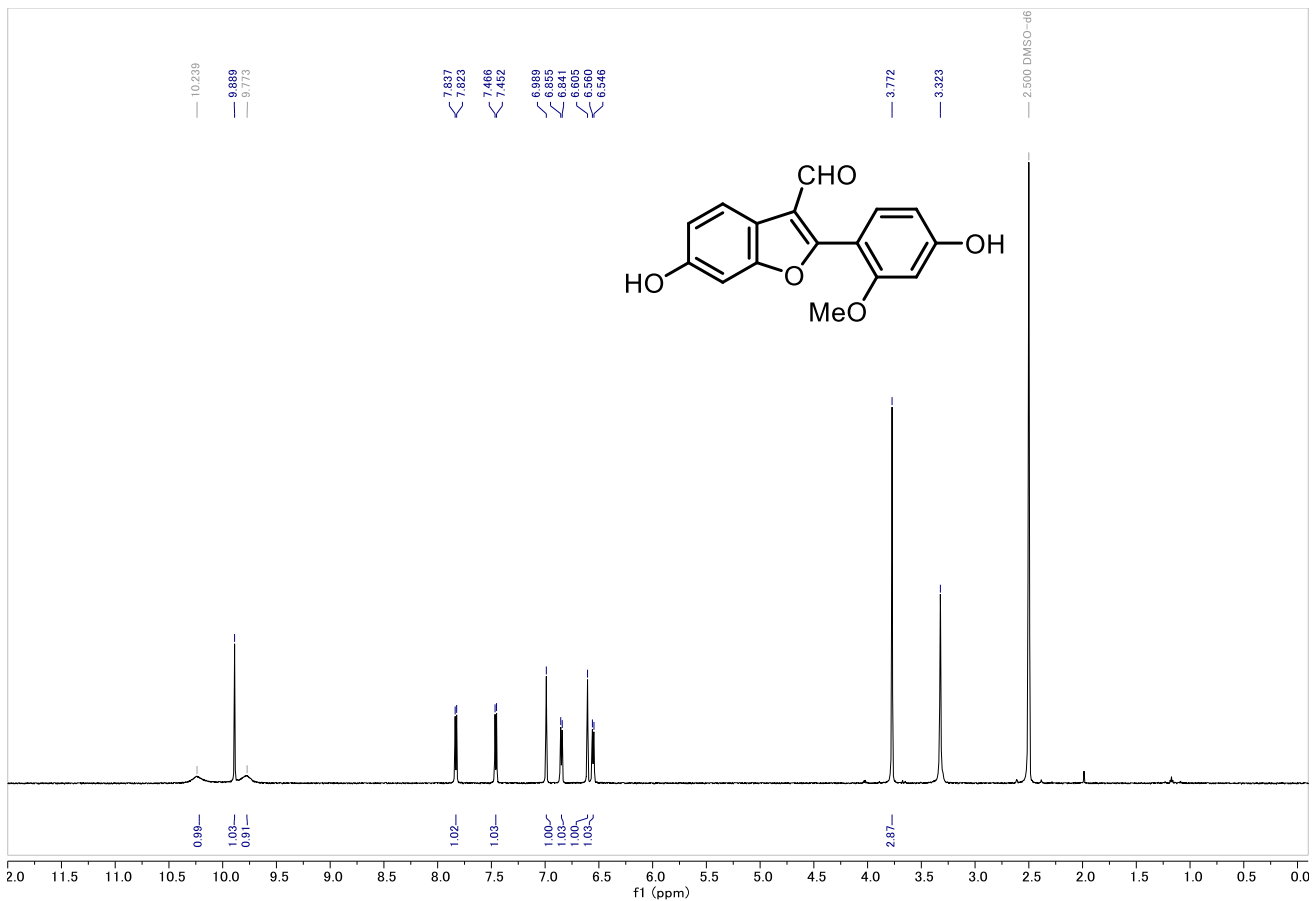
¹H NMR 10



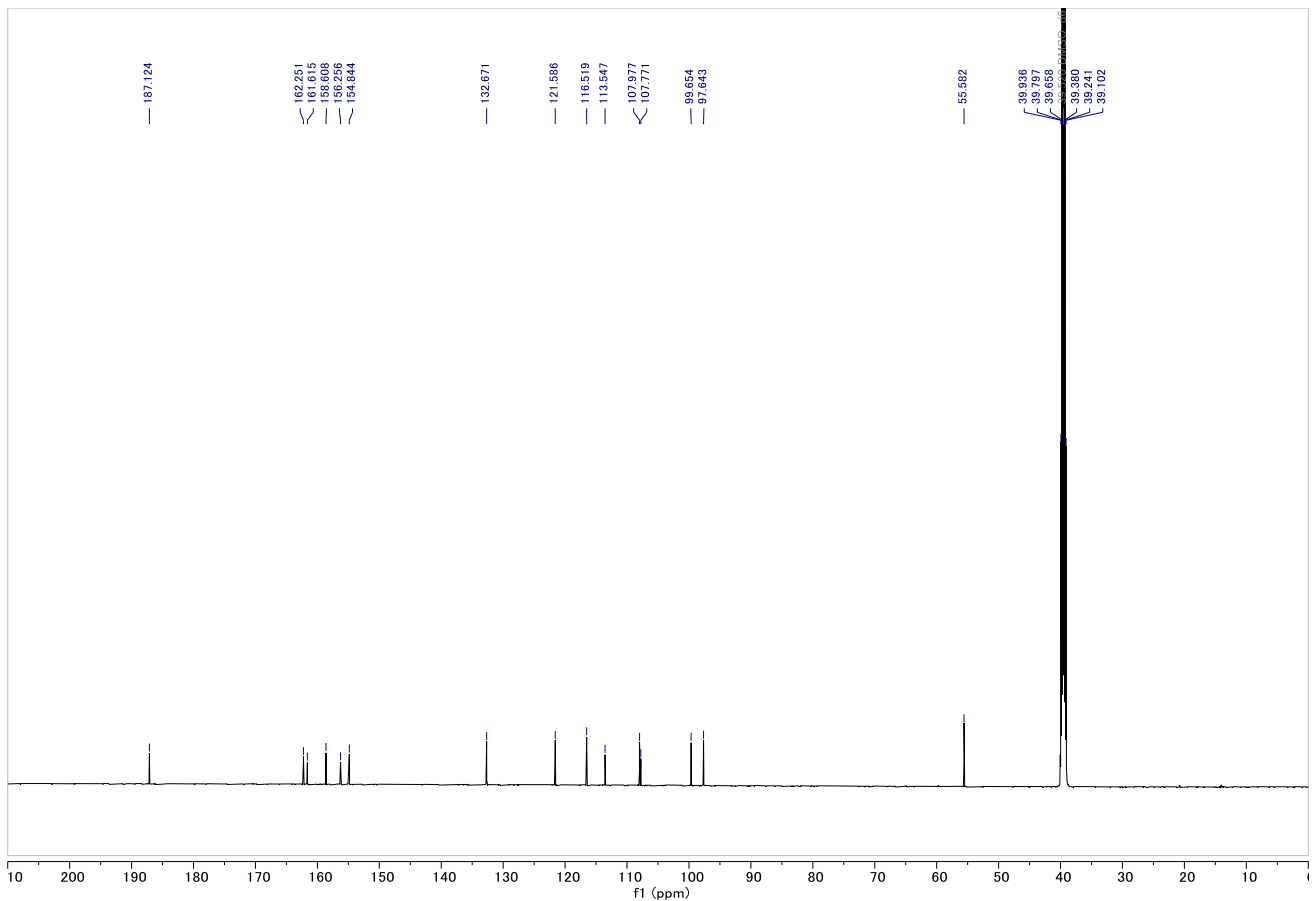
¹³C NMR 10



¹H NMR Puerariafuran



¹³C NMR Puerariafuran



HRMS (FAB) 1a

OMe Chalcone

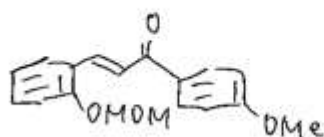
Page: 1

[Elemental Composition]
 Data : K.Sakaida-12-1-001
 Sample: -
 Note : -
 Inlet : Direct
 RT : 0.60 min
 Elements : C 20/0, H 20/0, O 5/0
 Mass Tolerance : 5mmu
 Unsaturation (U.S.) : -0.5 - 15.0

Date : 02-May-2017 16:42

Ion Mode : FAB+
 Scan#: (3,5)

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
298.1212	8.1	+2.3 / +0.7	10.0	C 18 H 18 O 4
237.0928	28.5	+5.2 / +1.2	10.5	C 16 H 13 O 2



HRMS (FAB) 1b

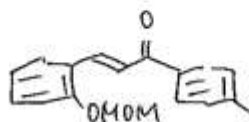
Page: 1

[Elemental Composition]
 Data : K.Sakaida-9-2-001
 Sample: -
 Note : -
 Inlet : Direct
 RT : 0.40 min
 Elements : C 20/0, H 20/0, O 5/0
 Mass Tolerance : 5mmu
 Unsaturation (U.S.) : -0.5 - 10.0

Date : 02-May-2017 15:42

Ion Mode : FAB+
 Scan#: (2,4)

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
282.1255	12.1	-0.4 / -0.1	10.0	C 18 H 18 O 3
283.1357	100.0	+7.9 / +2.2	9.5	C 18 H 19 O 3
284.1396	20.7	-5.6 / -1.6	9.0	C 18 H 20 O 3



HRMS (FAB) 1c

[Elemental Composition]

Data : Cl-chalcone006

Date : 11-Apr-2017 18:14

Sample: sakaida

Note : -

Inlet : Direct

Ion Mode : FAB+

RT : 0.59 min

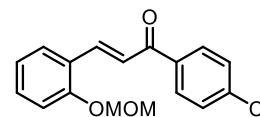
Scan#: (3,6)

Elements : C 20/10, H 20/10, O 5/0, Cl 1/0(35Cl 1/0, 37Cl 1/0)

Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 50mmu if m/z > 50

Unsaturation (U.S.) : -0.5 - 15.0

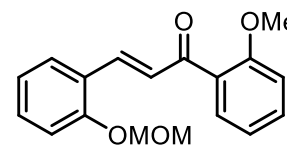
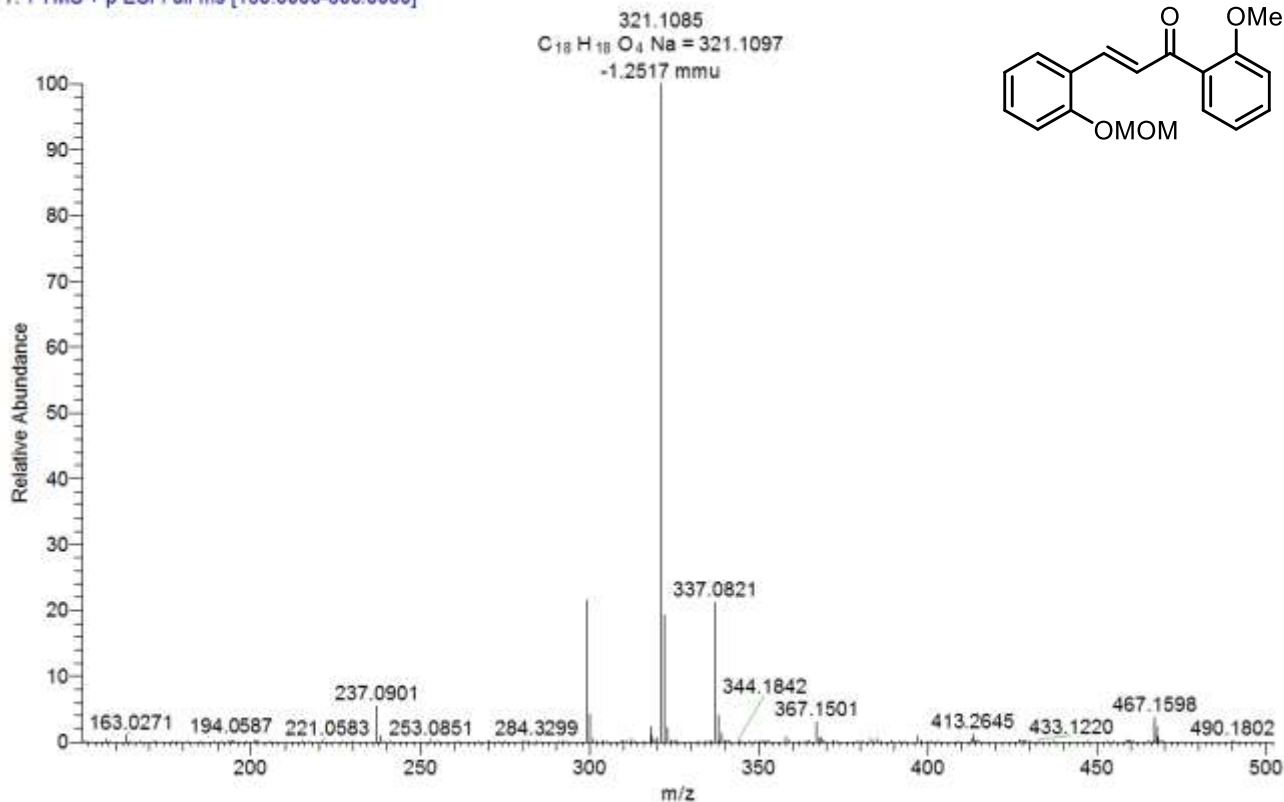
Page: 1



Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition		
303.0813	100.0	-68.7 / -20.8	13.5	C 20 H 15 O 3		
		+51.4 / +15.6	14.5	C 19 H 11 O 4		
		-138.4 / -42.0	8.5	C 17 H 19 O 5		
		+78.0 / +23.6	14.5	C 20 H 12 O 35Cl		
		-111.8 / -33.9	8.5	C 18 H 20 O 2 35Cl		
		+8.3 / +2.5	9.5	C 17 H 16 O 3 35Cl		
		+128.3 / +38.9	10.5	C 16 H 12 O 4 35Cl		
		-61.5 / -18.6	4.5	C 14 H 20 O 5 35Cl		
		-50.4 / -15.3	9.5	C 18 H 18 O 2 37Cl		
		+69.6 / +21.1	10.5	C 17 H 14 O 3 37Cl		
		-0.1 / +0.0	5.5	C 14 H 18 O 5 37Cl		
		302.0735	8.8	-68.9 / -20.8	14.0	C 20 H 14 O 3
				+51.6 / +15.6	15.0	C 19 H 10 O 4
				-138.8 / -41.9	9.0	C 17 H 18 O 5
+78.3 / +23.6	15.0			C 20 H 11 O 35Cl		
-112.1 / -33.9	9.0			C 18 H 19 O 2 35Cl		
+8.3 / +2.5	10.0			C 17 H 15 O 3 35Cl		
+128.8 / +38.9	11.0			C 16 H 11 O 4 35Cl		
-61.6 / -18.6	5.0			C 14 H 19 O 5 35Cl		
-50.6 / -15.3	10.0			C 18 H 17 O 2 37Cl		
+69.9 / +21.1	11.0			C 17 H 13 O 3 37Cl		
-0.1 / +0.0	6.0			C 14 H 17 O 5 37Cl		

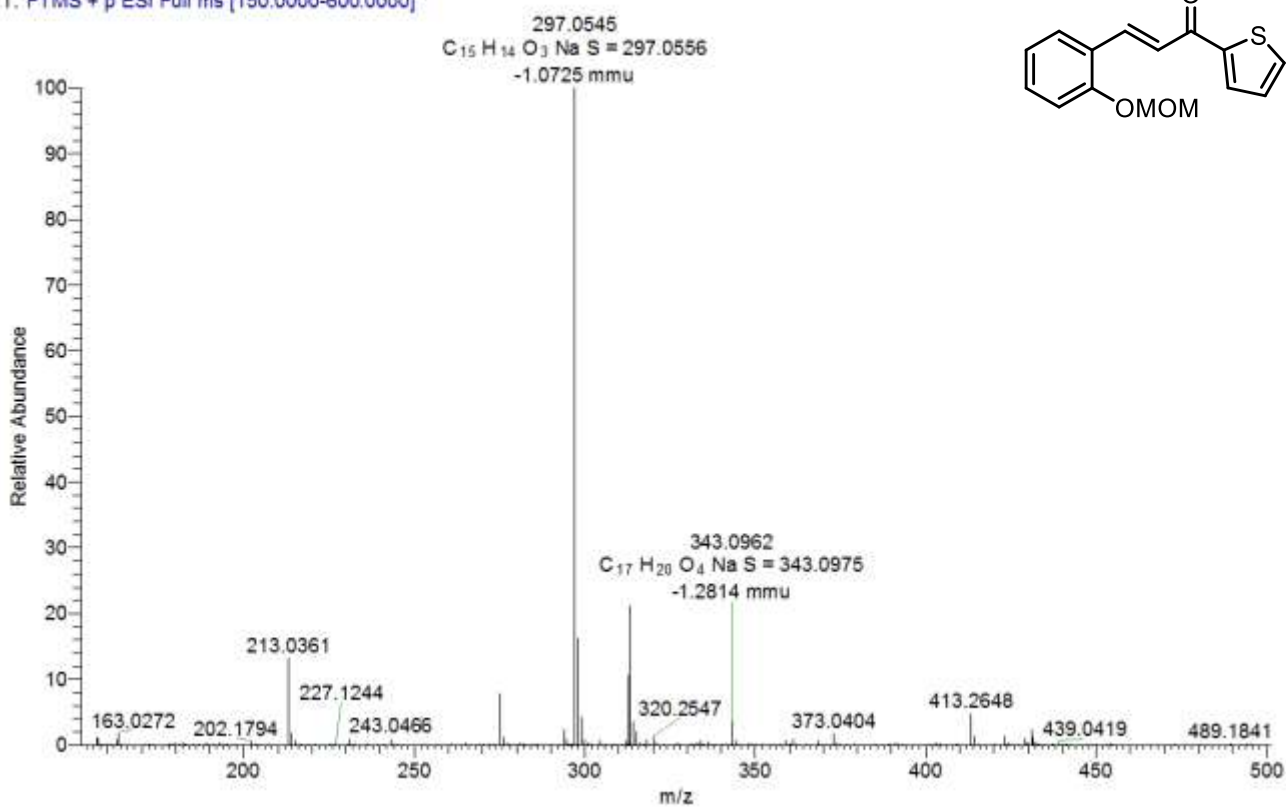
HRMS (ESI) 1d

IKGM240 191001105609 #19-32 RT: 0.10-0.16 AV: 14 NL: 1.63E9
T: FTMS + p ESI Full ms [150.0000-600.0000]



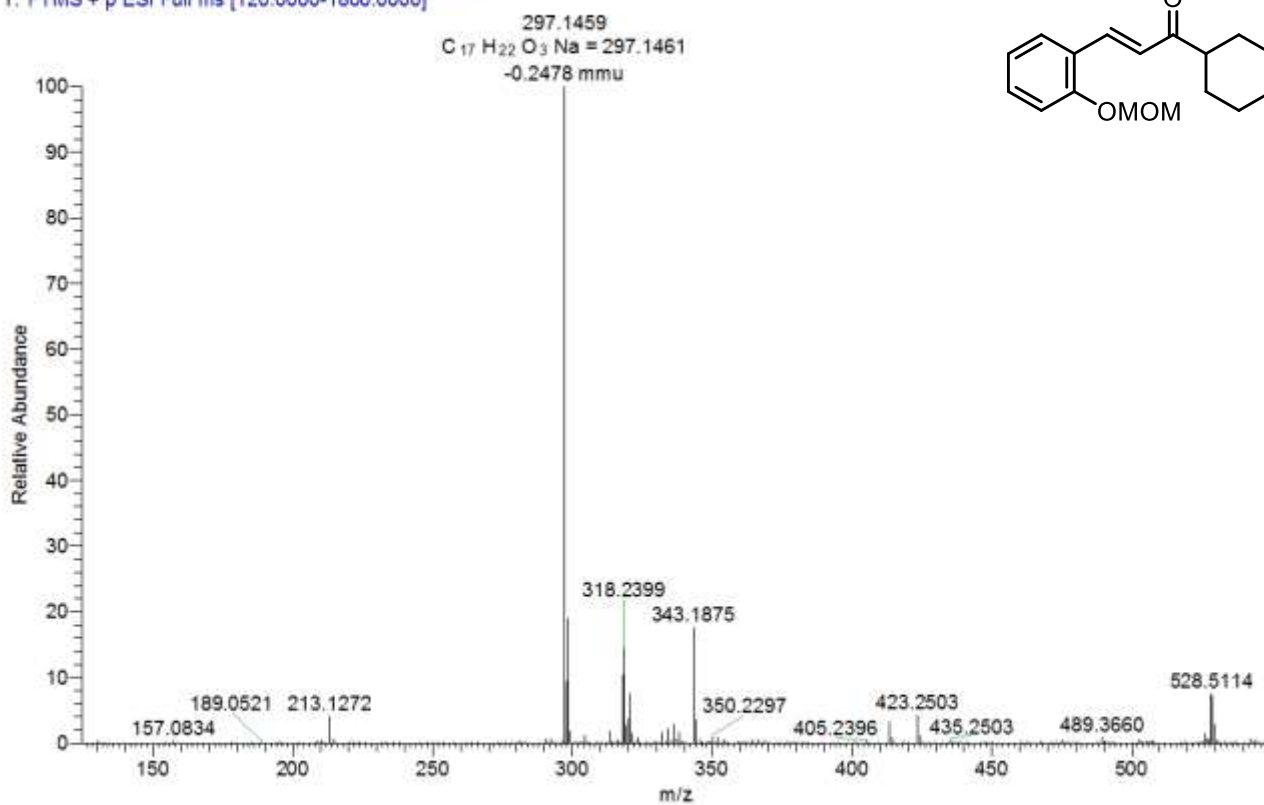
HRMS (ESI) 1e

IKGM249#16-30 RT: 0.08-0.15 AV: 15 NL: 1.22E9
T: FTMS + p ESI Full ms [150.0000-600.0000]



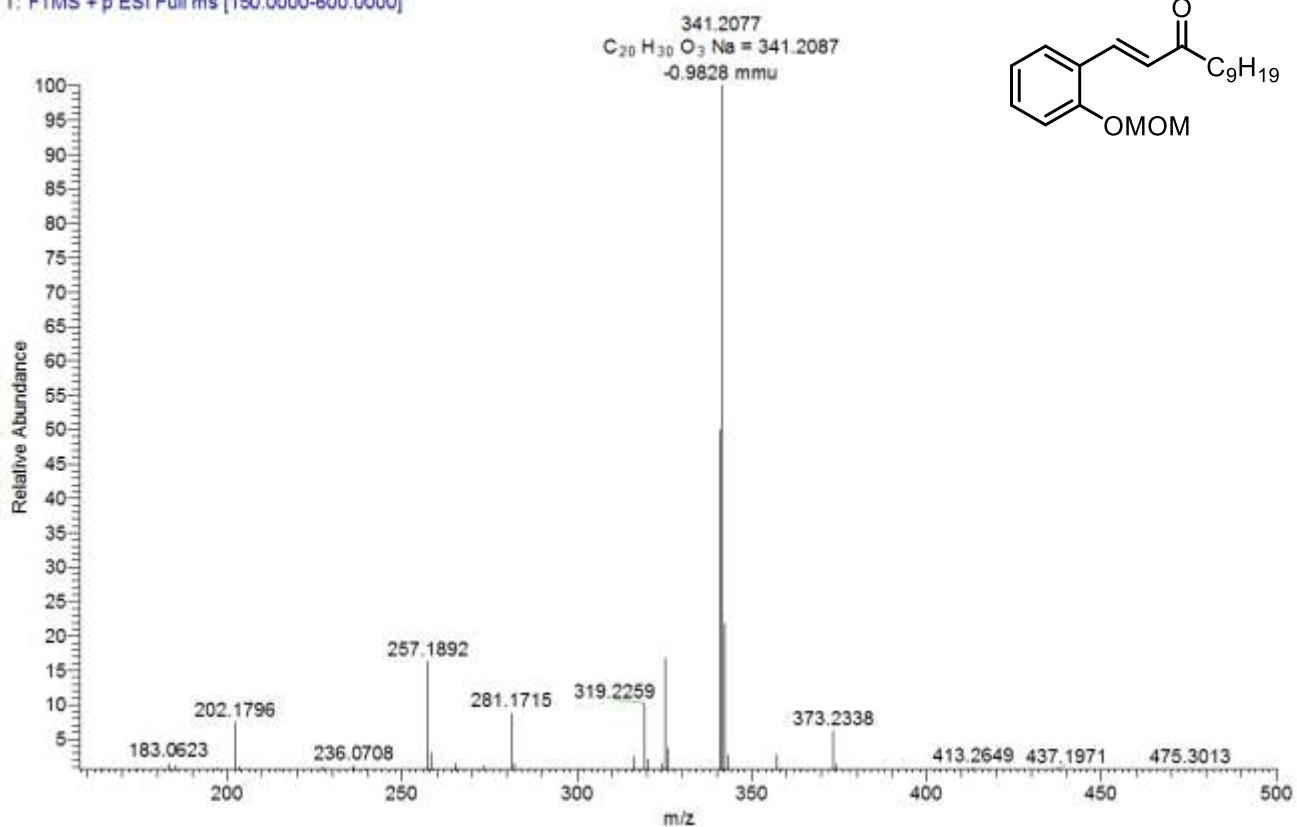
HRMS (ESI) 1f

IKGM229#15-17 RT: 0.08-0.09 AV: 3 NL: 3.52E9
T: FTMS + p ESI Full ms [120.0000-1800.0000]



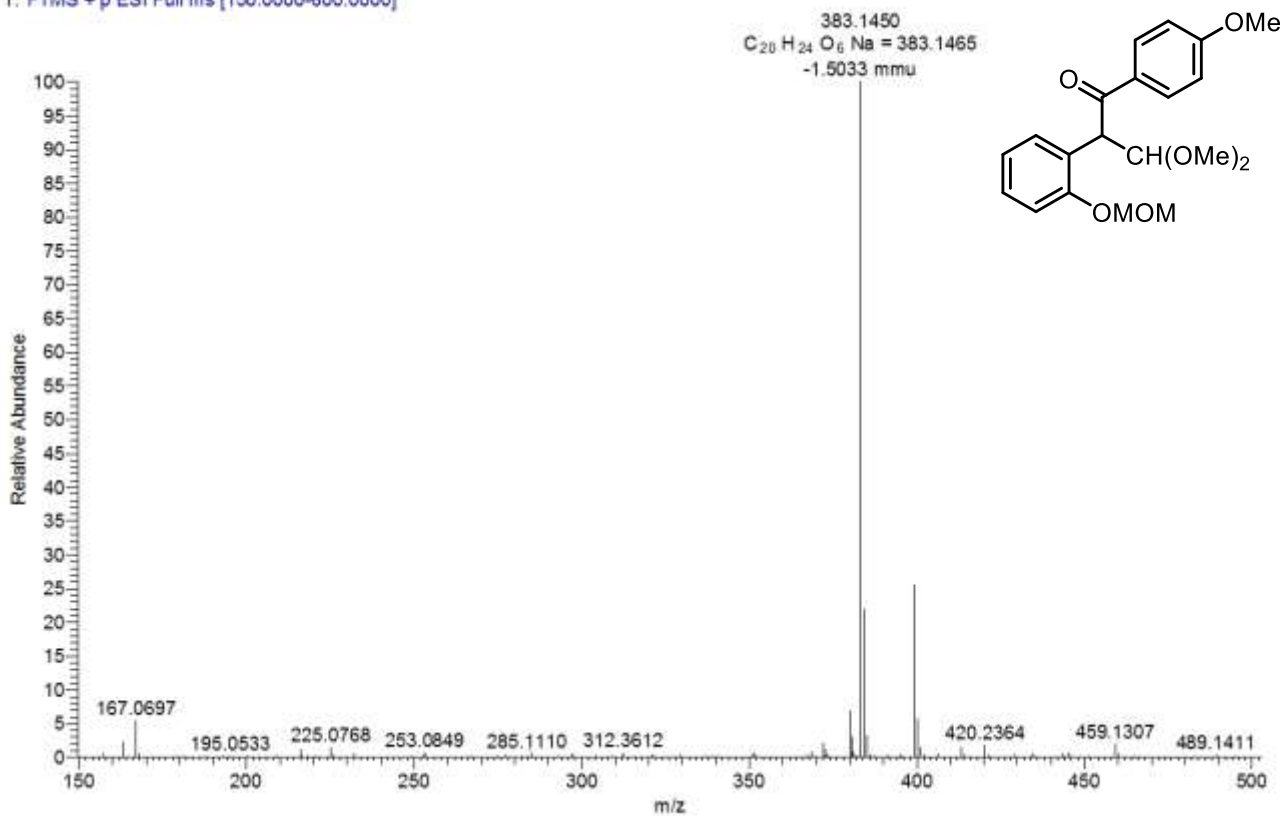
HRMS (ESI) 1g

YGT_66 #18 RT: 0.10 AV: 1 NL: 1.15E8
T: FTMS + p ESI Full ms [150.0000-600.0000]



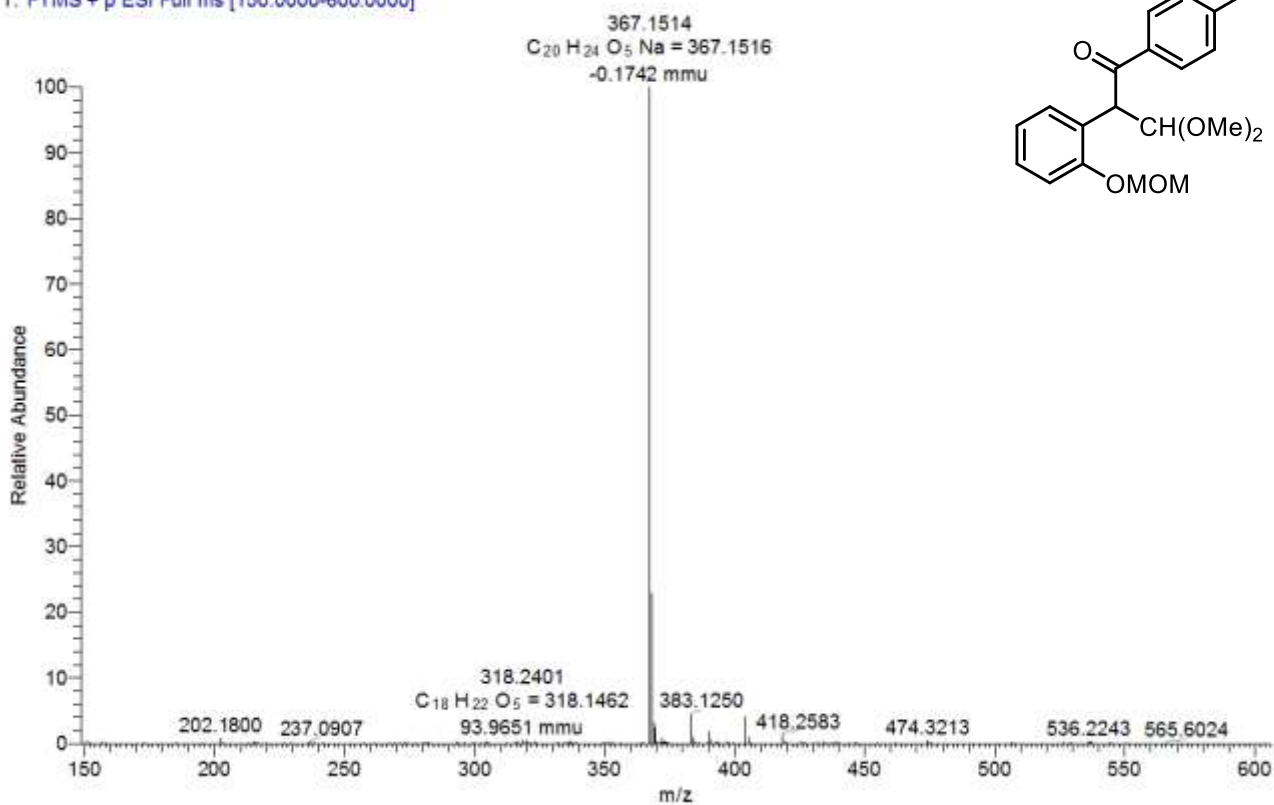
HRMS (ESI) 2a

IKGM-4OMe-ten1 #29-33 RT: 0.15-0.17 AV: 5 NL: 1.06E9
T: FTMS + p ESI Full ms [150.0000-600.0000]



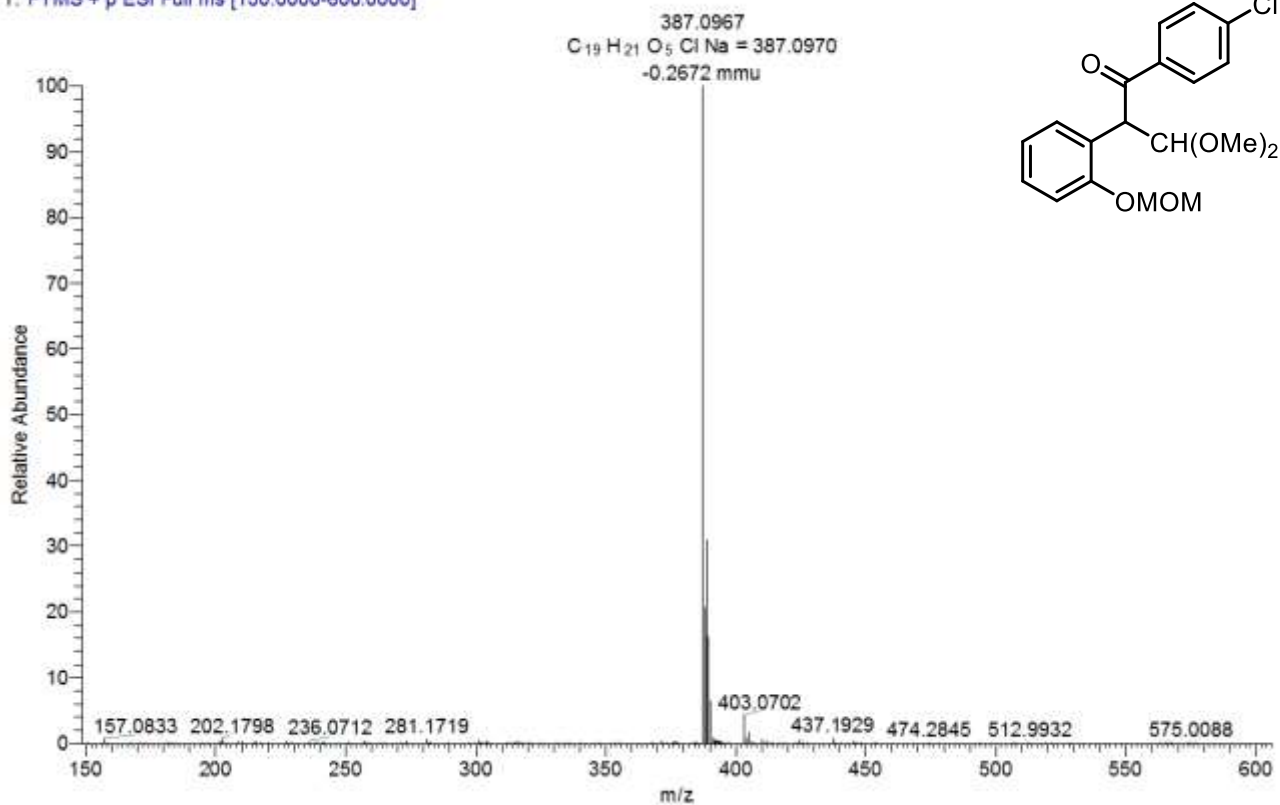
HRMS (ESI) 2b

[KGM-Me-teni #11-15 RT: 0.08-0.10 AV: 5 NL: 2.68E8
T: FTMS + p ESI Full ms [150.0000-600.0000]



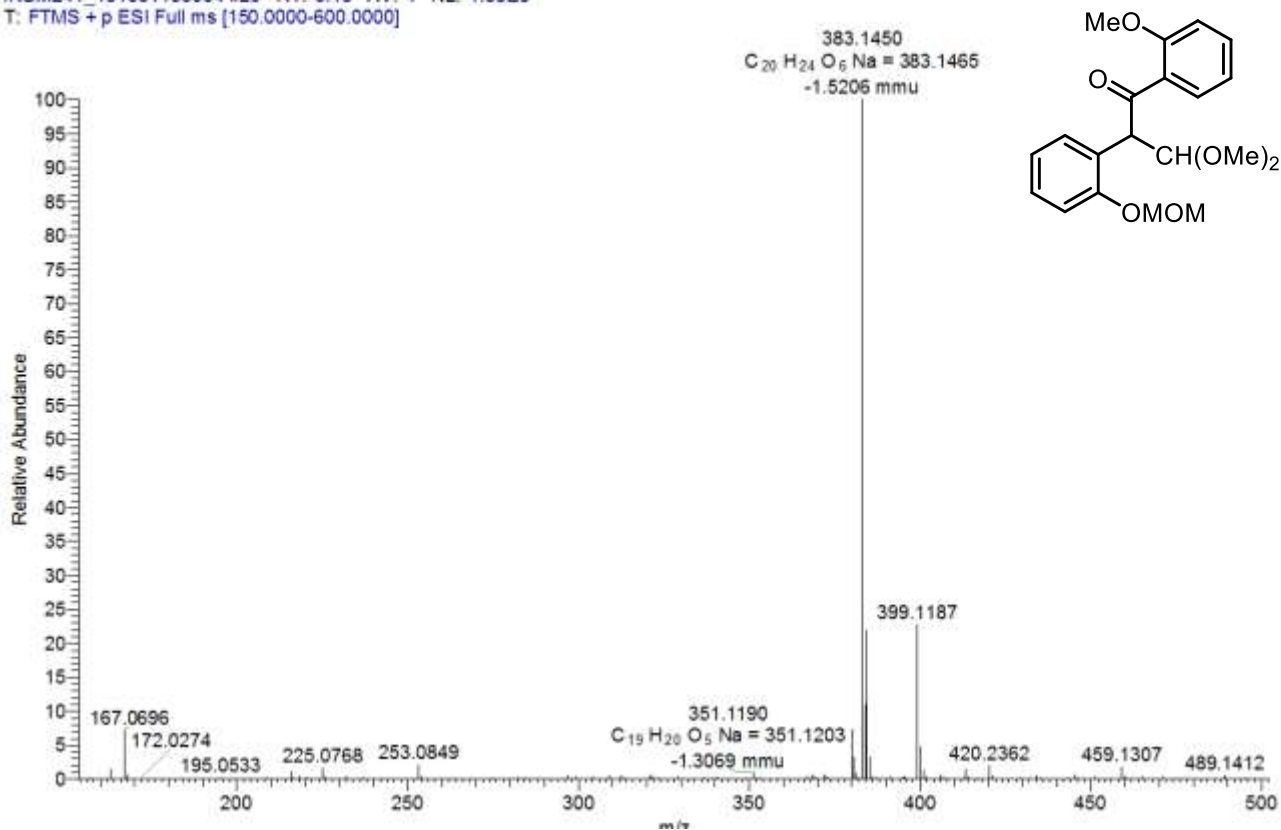
HRMS (ESI) 2c

[KGM-Cl-teni #15-17 RT: 0.09-0.10 AV: 3 NL: 1.39E9
T: FTMS + p ESI Full ms [150.0000-600.0000]



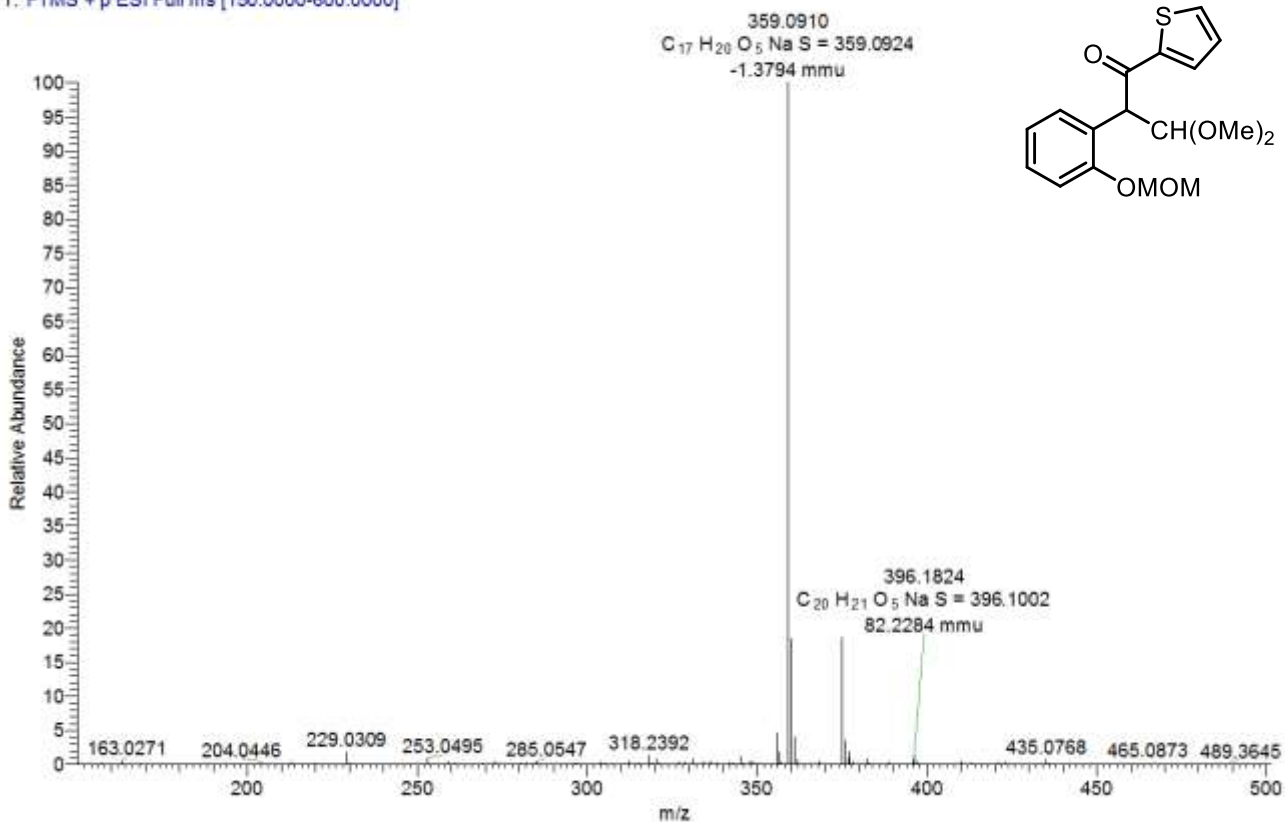
HRMS (ESI) 2d

IKGM241_191001105904 #29 RT: 0.15 AV: 1 NL: 1.39E9
T: FTMS + p ESI Full ms [150.0000-600.0000]



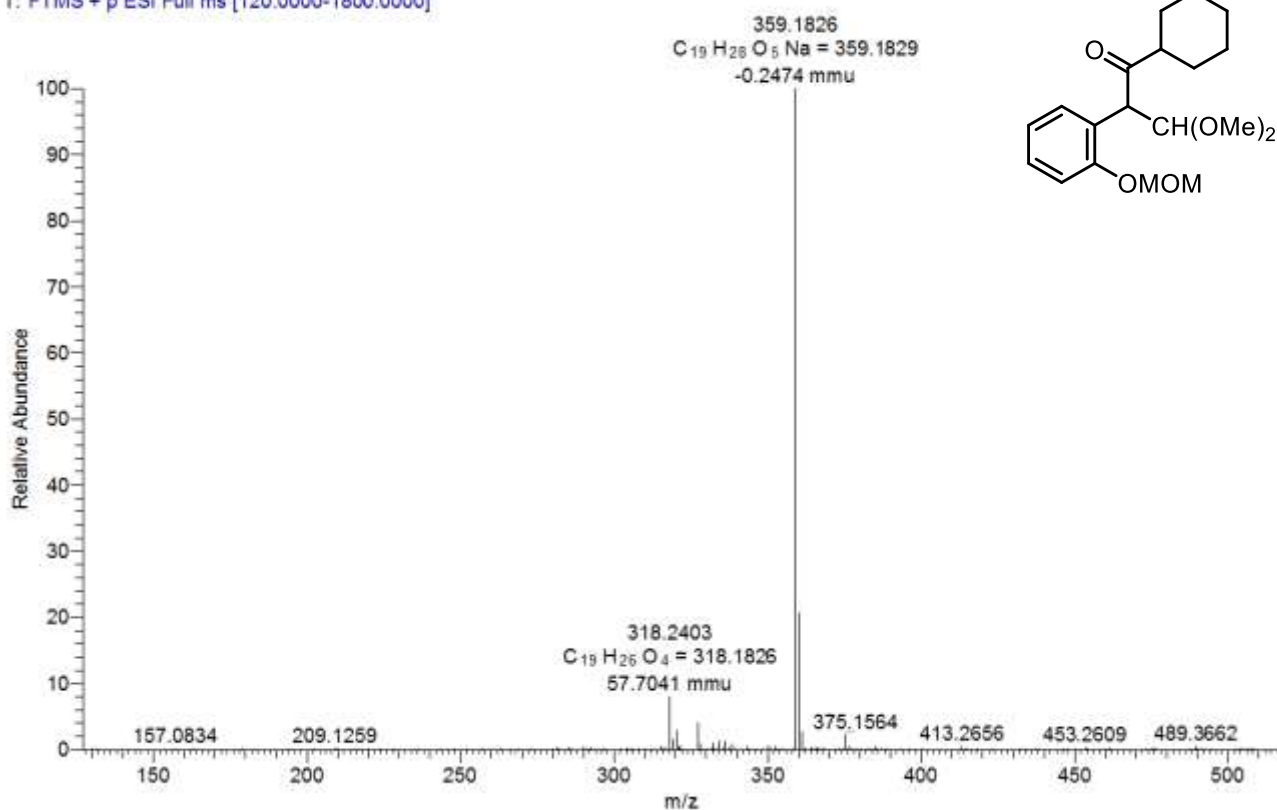
HRMS (ESI) 2e

IKGM251 #20-26 RT: 0.10-0.13 AV: 7 NL: 1.35E9
T: FTMS + p ESI Full ms [150.0000-600.0000]



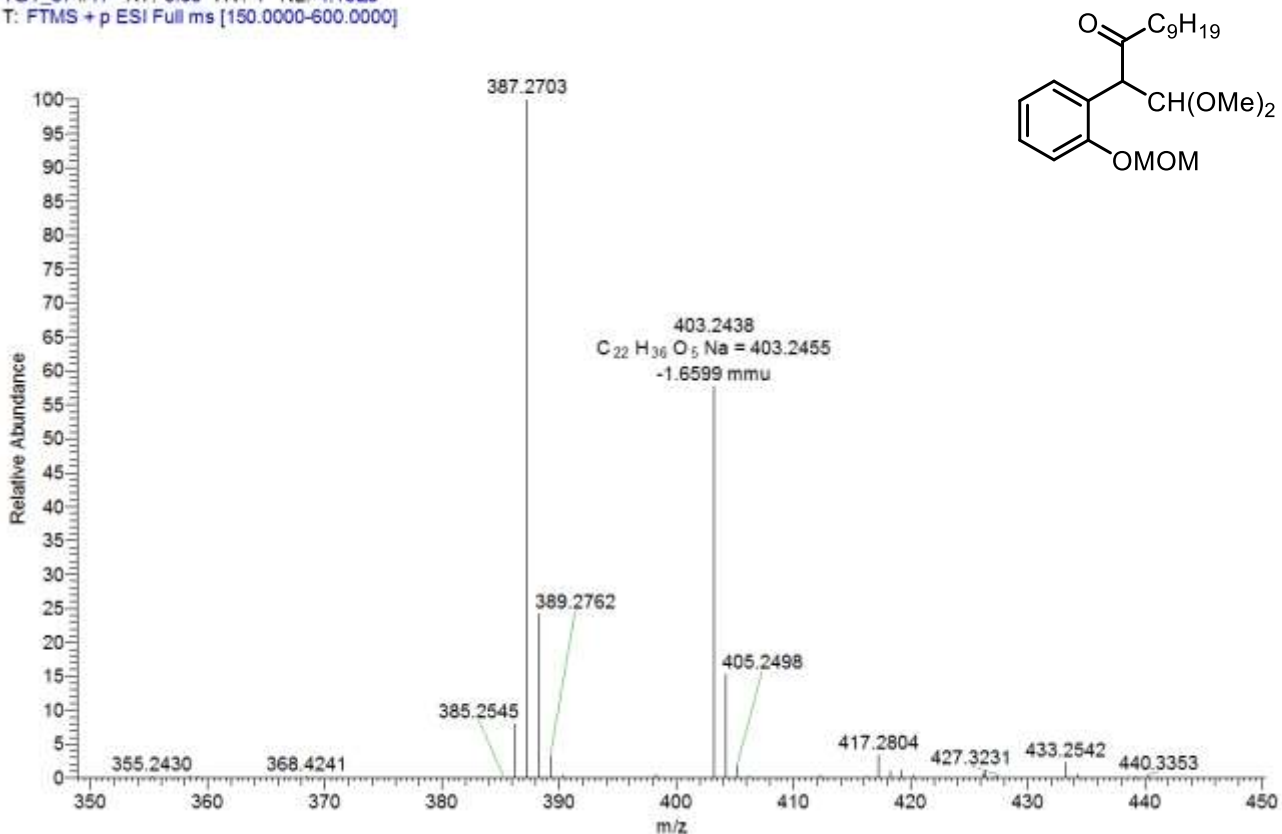
HRMS (ESI) 2f

IKGM238 190621135456 #18 RT: 0.09 AV: 1 NL: 5.58E9
T: FTMS + p ESI Full ms [120.0000-1800.0000]



HRMS (ESI) 2g

YGT_67 #17 RT: 0.09 AV: 1 NL: 4.13E8
T: FTMS + p ESI Full ms [150.0000-600.0000]



HRMS (FAB) 3a

Page: 1

[Elemental Composition]

Data : K.Sakaida-1-2-001

Date : 02-May-2017 14:39

Sample: -

Note : -

Inlet : Direct

Ion Mode : FAB+

RT : 0.50 min

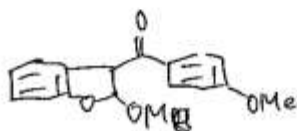
Scan#: (3,4)

Elements : C 20/0, H 20/0, O 5/0

Mass Tolerance : 5mmu

Unsaturation (U.S.) : -0.5 - 10.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
290.0854	26.8			
289.0813	100.0			
285.1091	14.6	-12.6 / -3.6	9.5	C 17 H 17 O 4
284.1042	8.3	-2.4 / -0.7	10.0	C 17 H 16 O 4



HRMS (FAB) 3b

Page: 1

[Elemental Composition]

Data : K.Sakaida-10-2-001

Date : 02-May-2017 15:52

Sample: -

Note : -

Inlet : Direct

Ion Mode : FAB+

RT : 0.40 min

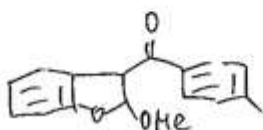
Scan#: (2,4)

Elements : C 20/0, H 20/0, O 5/0

Mass Tolerance : 5mmu

Unsaturation (U.S.) : -0.5 - 10.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
267.1037	11.9			
268.1094	100.0	-2.0 / -0.5	10.0	C 17 H 16 O 3
269.1155	81.3	-8.4 / -2.3	9.5	C 17 H 17 O 3
270.1195	16.7			



HRMS (FAB) 3c

[Elemental Composition]

Data : K.Sakaida-02-001

Date : 28-Apr-2017 14:20

Page: 1

Sample: -

Note: -

Inlet : Direct

Ion Mode : FAB+

RT : 0.09 min

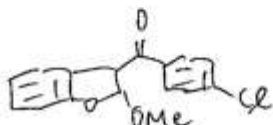
Scan#: (1,2)

Elements : C 20/0, H 20/0, O 5/0, Cl 1/0 (35Cl 1/0, 37Cl 1/0)

Mass Tolerance : 5mmu

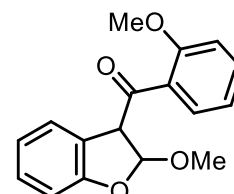
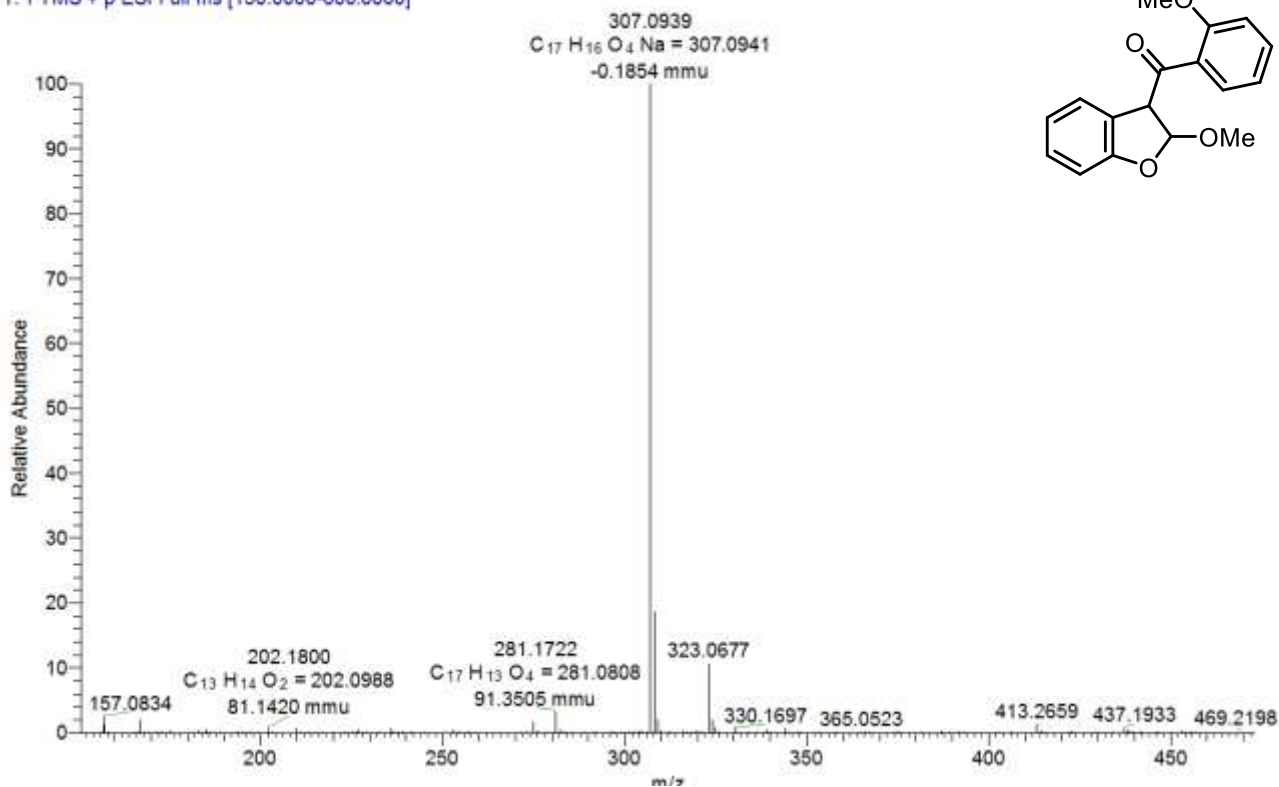
Unsaturation (U.S.) : -0.5 - 10.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
291.0621	25.5	+6.4 / +1.9	9.5	C 16 H 14 O 3 37Cl
290.0553	40.6	+10.1 / +2.9	10.0	C 16 H 13 O 3 37Cl
289.0703	94.5	+15.8 / +4.6	5.5	C 13 H 16 O 5 37Cl
288.0567	100.0	+4.7 / +1.3	10.0	C 16 H 13 O 3 35Cl
		-4.1 / -1.2	6.0	C 13 H 15 O 5 37Cl
287.0501	8.3	+0.4 / +0.1	6.5	C 13 H 14 O 5 37Cl



HRMS (ESI) 3d

IKGM-o-OMe-dihydro #15-18 RT: 0.09-0.10 AV: 4 NL: 1.64E9
T: FTMS + p ESI Full ms [150.0000-600.0000]



HRMS (FAB) 3e

[Elemental Composition]

Data : K.Sakaida-04-001

Date : 28-Apr-2017 15:09

Sample: -

Note : -

Inlet : Direct

Ion Mode : FAB+

RT : 0.09 min

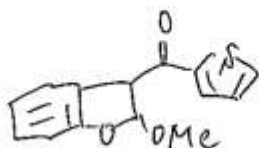
Scan#: (1,2)

Elements : C 20/0, H 20/0, O 5/0, S 1/0

Mass Tolerance : 5mmu

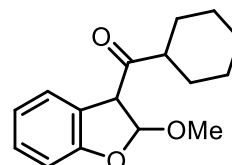
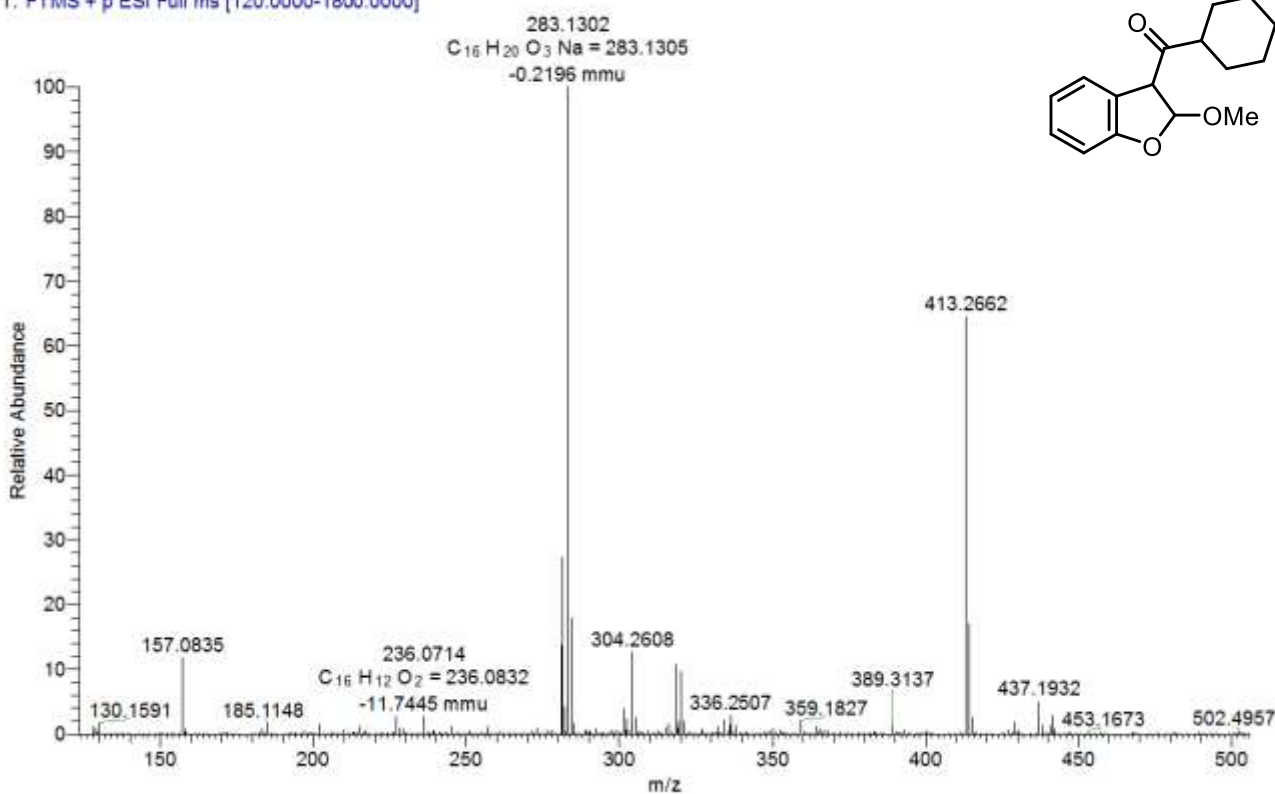
Unsaturation (U.S.) : -0.5 - 10.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
260.0481	100.0	-10.2 / -2.7	10.0	C 14 H 12 O 3 S
261.0546	91.0	-15.0 / -3.9	9.5	C 14 H 13 O 3 S



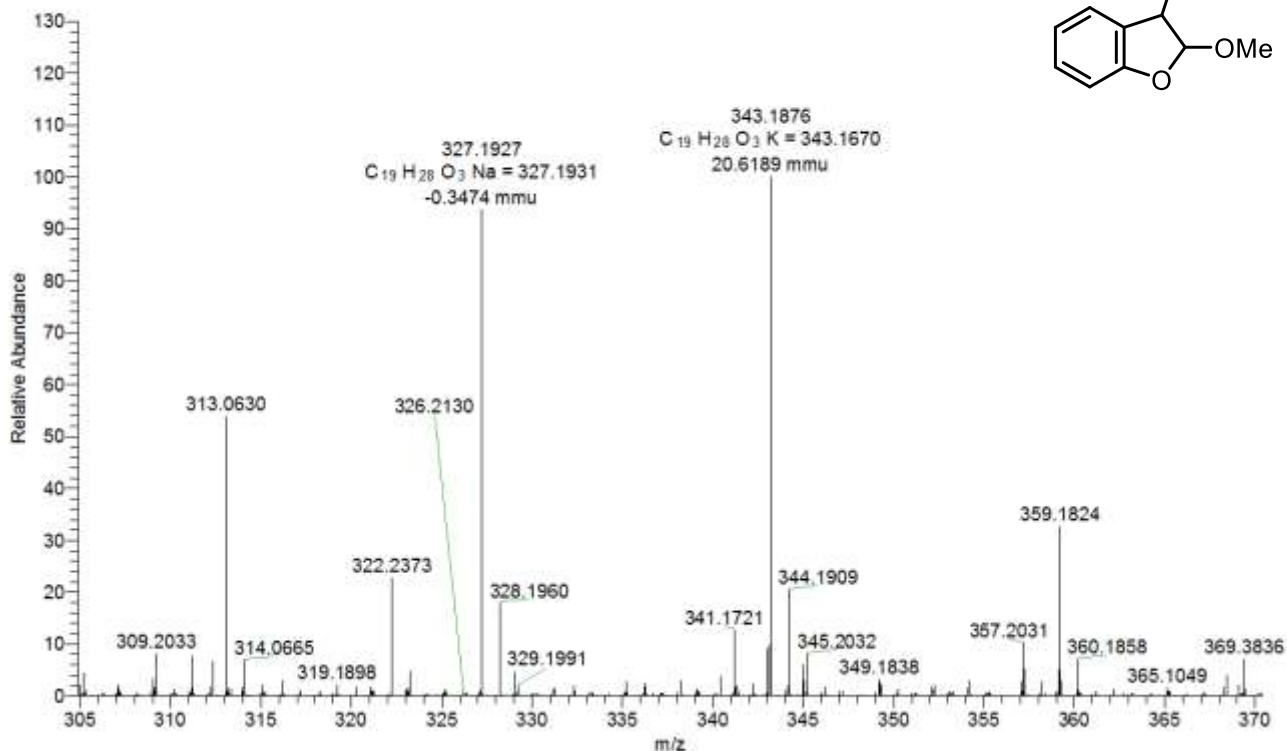
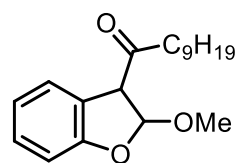
HRMS (ESI) 3f

IKGM239#17-20 RT: 0.09-0.11 AV: 4 NL: 7.54E8
T: FTMS + p ESI Full ms [120.0000-1800.0000]



HRMS (ESI) 3g

YGT_68 #23 RT: 0.13 AV: 1 NL: 6.02E6
T: FTMS + p ESI Full ms [150.0000-600.0000]



HRMS (FAB) 4a

[Elemental Composition]

Data : AI-benzofuran-isomer-001

Date : 25-Jan-2017 11:14

Page: 1

Sample: AI-145-F2-HRMS

Note : -

Inlet : Direct

Ion Mode : FAB+

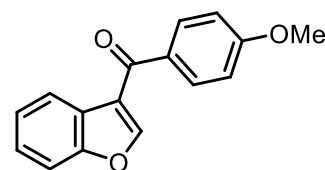
RT : 0.17 min

Scan#: (1,3)

Elements : C 20/0, H 15/0, O 5/0

Mass Tolerance : 1000ppm, 5mmu if m/z > 5

Unsaturation (U.S.) : -0.5 - 20.0



Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
252.0815	36.6	+11.4 / +2.9	11.0	C 16 H 12 O 3
253.0862	100.0	-1.1 / -0.3	10.5	C 16 H 13 O 3

HRMS (FAB) 4b

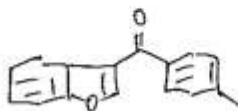
Page: 1

[Elemental Composition]
 Data : K.Sakaida-11-3-001
 Sample: -
 Note : -
 Inlet : Direct
 RT : 0.10 min
 Elements : C 20/0, H 15/0, O 5/0
 Mass Tolerance : 5mmu
 Unsaturation (U.S.) : -0.5 - 15.0

Date : 02-May-2017 16:29

Ion Mode : FAB+
 Scan#: (1,2)

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
238.0941	7.3			
237.0910	38.5	-2.2 / -0.5	10.5	C 16 H 13 O 2
236.0834	13.4	-1.4 / -0.3	11.0	C 16 H 12 O 2



HRMS (FAB) 4c

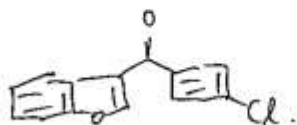
Page: 1

[Elemental Composition]
 Data : K.Sakaida-3-4-001
 Sample: -
 Note : -
 Inlet : Direct
 RT : 0.60 min
 Elements : C 20/0, H 10/0, O 5/0, Cl 5/0 (35Cl 5/0, 37Cl 5/0)
 Mass Tolerance : 5mmu
 Unsaturation (U.S.) : -0.5 - 15.0

Date : 02-May-2017 16:16

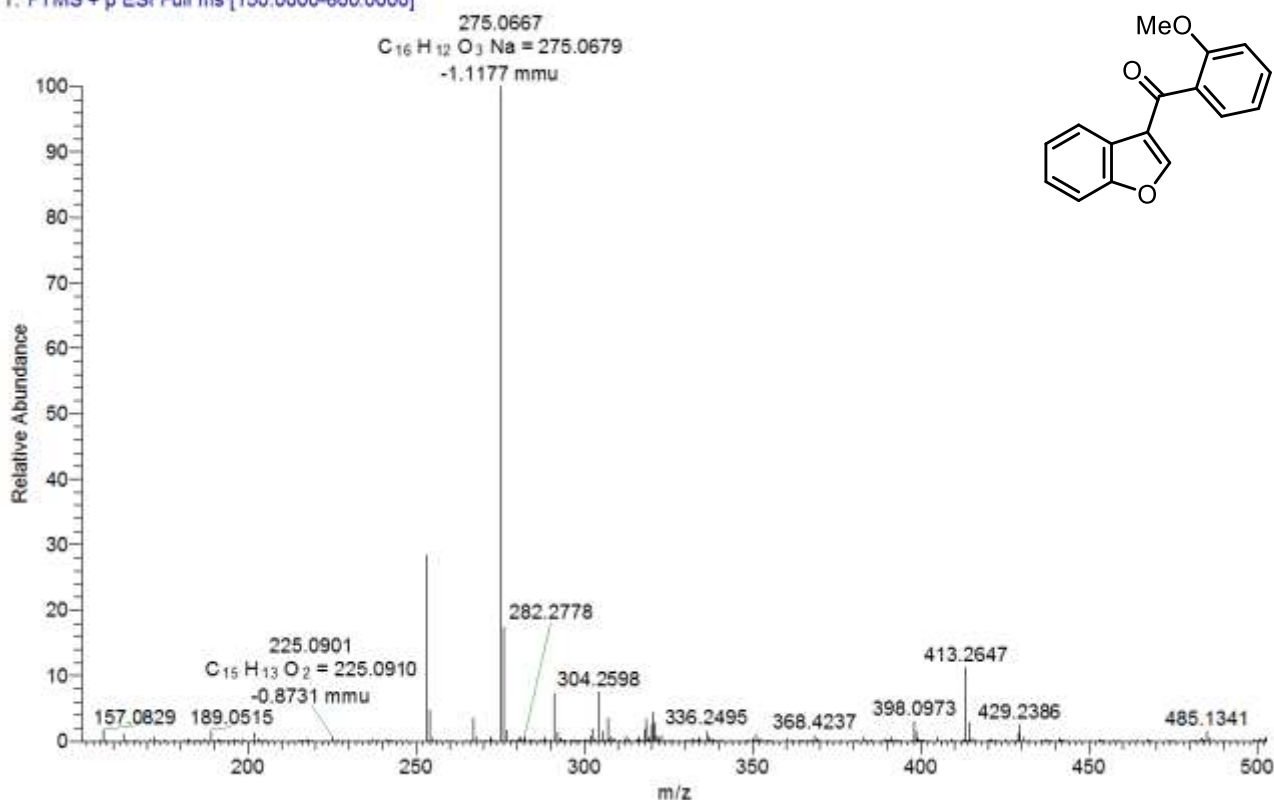
Ion Mode : FAB+
 Scan#: (3,5)

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
256.0276	30.1	-5.9 / -1.5	11.0	C 15 H 9 O 2 35Cl
257.0349	80.4	-7.9 / -2.0	10.5	C 15 H 10 O 2 35Cl
258.0369	19.4			
259.0333	26.9	+7.1 / +1.8	14.5	C 18 H 8 35Cl
		-2.7 / -0.7	10.5	C 15 H 10 O 2 37Cl



HRMS (ESI) 4d

IKGM243#16-25 RT: 0.08-0.13 AV: 10 NL: 7.46E8
 T: FTMS + p ESI Full ms [150.0000-600.0000]



HRMS (FAB) 4e

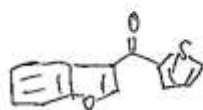
[Elemental Composition]
 Data : K.Sakaida-3-6-001
 Sample: -
 Note : -
 Inlet : Direct
 RT : 0.50 min
 Elements : C 15/0, H 10/0, O 5/0, S 5/0
 Mass Tolerance : 5mmu
 Unsaturation (U.S.) : -0.5 - 15.0

Date : 06-May-2017 10:25

Page: 1

Ion Mode : FAB+
 Scan#: (3,4)

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
230.0341	9.2			
229.0319	47.8	-2.0 / -0.5	10.5	C 13 H 9 O 2 S
228.0244	20.1	-0.2 / -0.1	11.0	C 13 H 8 O 2 S



HRMS (FAB) 4f

[Elemental Composition]

Data : K.Sakaida-8-2-001

Sample: -

Note : -

Inlet : Direct

RT : 0.50 min

Elements : C 20/0, H 20/0, O 5/0

Mass Tolerance : 5mmu

Unsaturation (U.S.) : -0.5 - 10.0

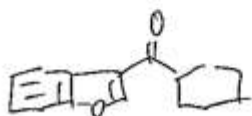
Date : 02-May-2017 15:34

Ion Mode : FAB+

Scan#: (3,4)

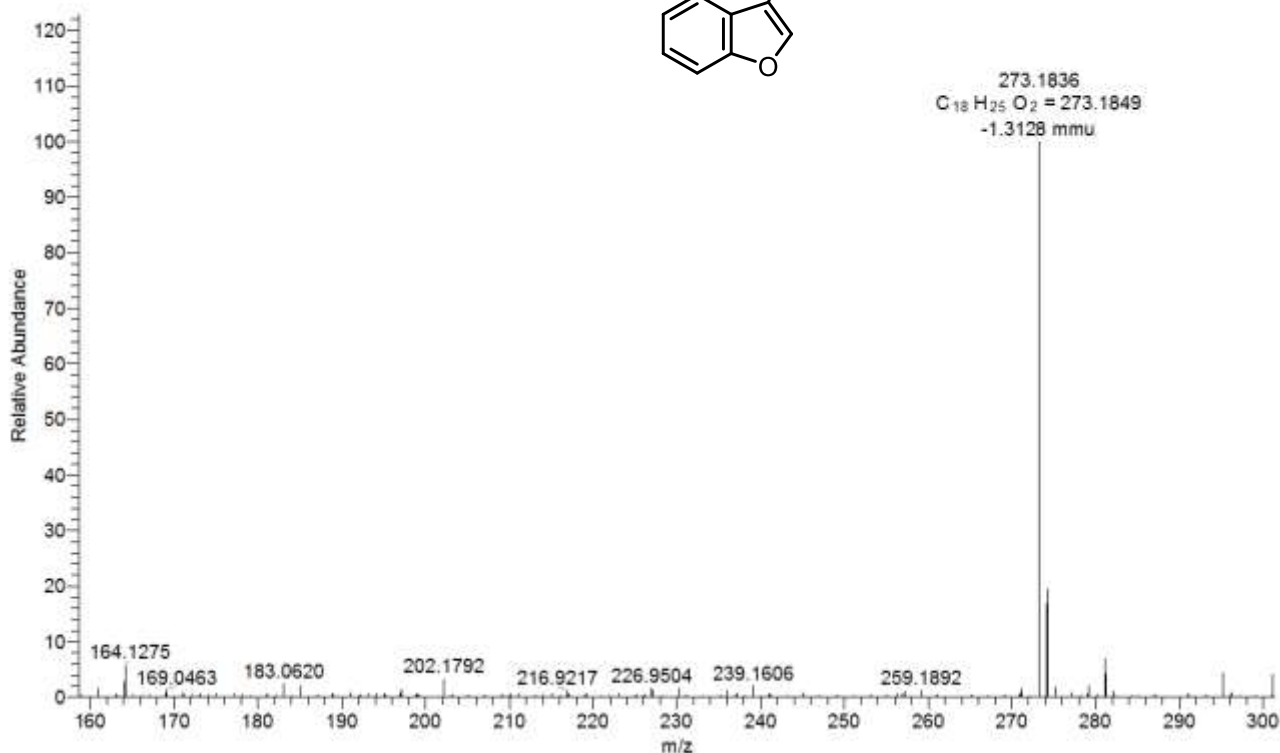
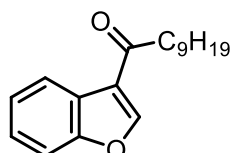
Page: 1

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
230.1257	17.0			
229.1237	100.0	+3.8 / +0.9	7.5	C 15 H 17 O 2
228.1166	34.7	+6.9 / +1.6	8.0	C 15 H 16 O 2
227.1080	5.8	+3.5 / +0.8	8.5	C 15 H 15 O 2



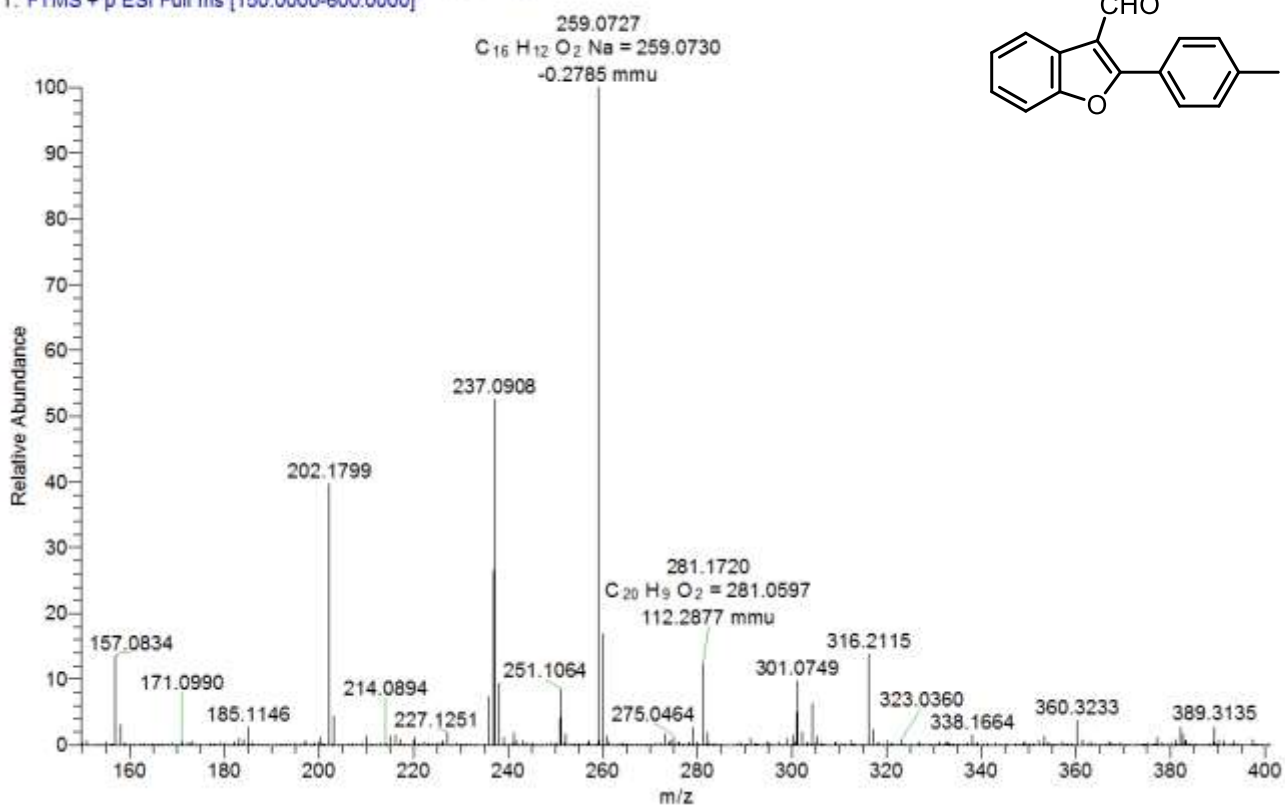
HRMS (ESI) 4g

YGT_61acyl #27 RT: 0.15 AV: 1 NL: 3.19E7
T: FTMS + p ESI Full ms [150.0000-600.0000]



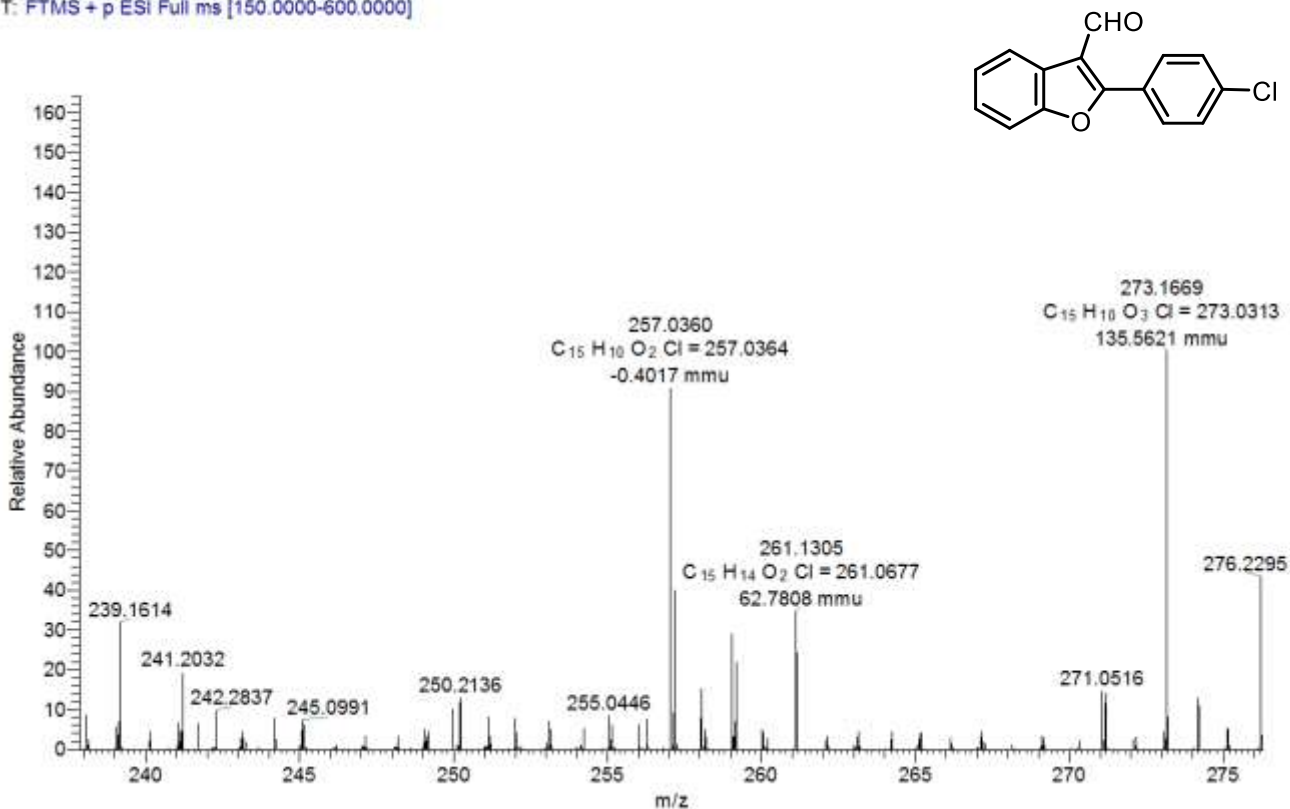
HRMS (ESI) 5b

IKGM-Me-nitikan #14-17 RT: 0.09-0.10 AV: 4 NL: 5.20E7
T: FTMS + p ESI Full ms [150.0000-600.0000]



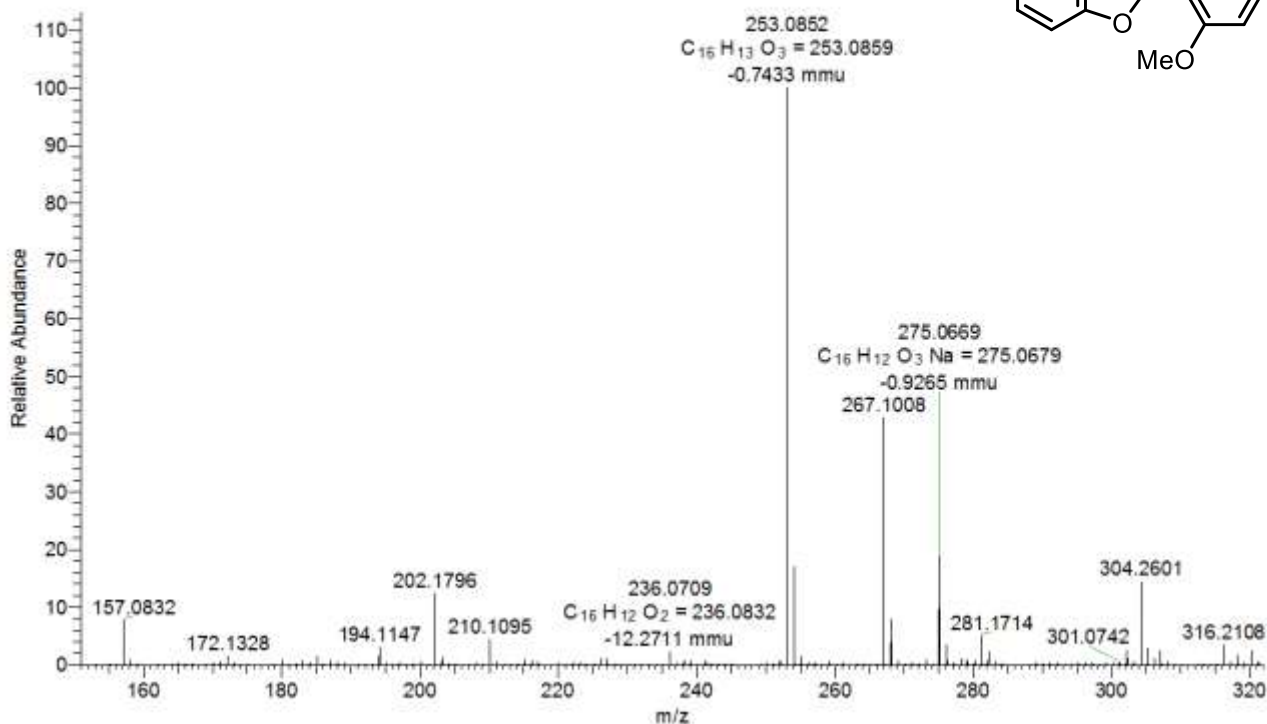
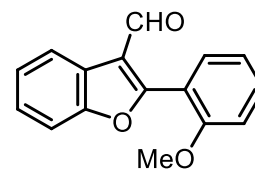
HRMS (ESI) 5c

IKGM-Cl-nitikan #14-21 RT: 0.08-0.12 AV: 8 NL: 1.97E6
T: FTMS + p ESI Full ms [150.0000-600.0000]



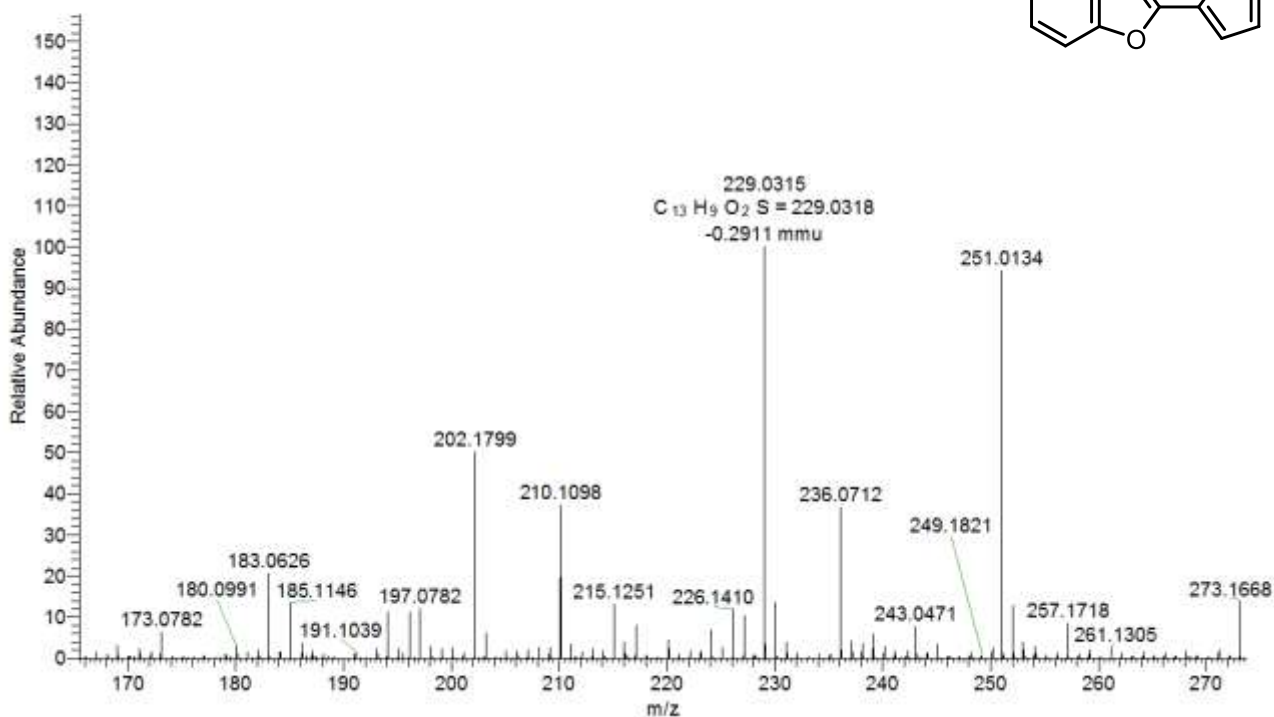
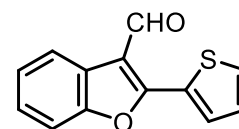
HRMS (ESI) 5d

IKGM-OMe-nitikan #12-15 RT: 0.09-0.11 AV: 4 NL: 5.24E7
T: FTMS + p ESI Full ms [150.0000-600.0000]



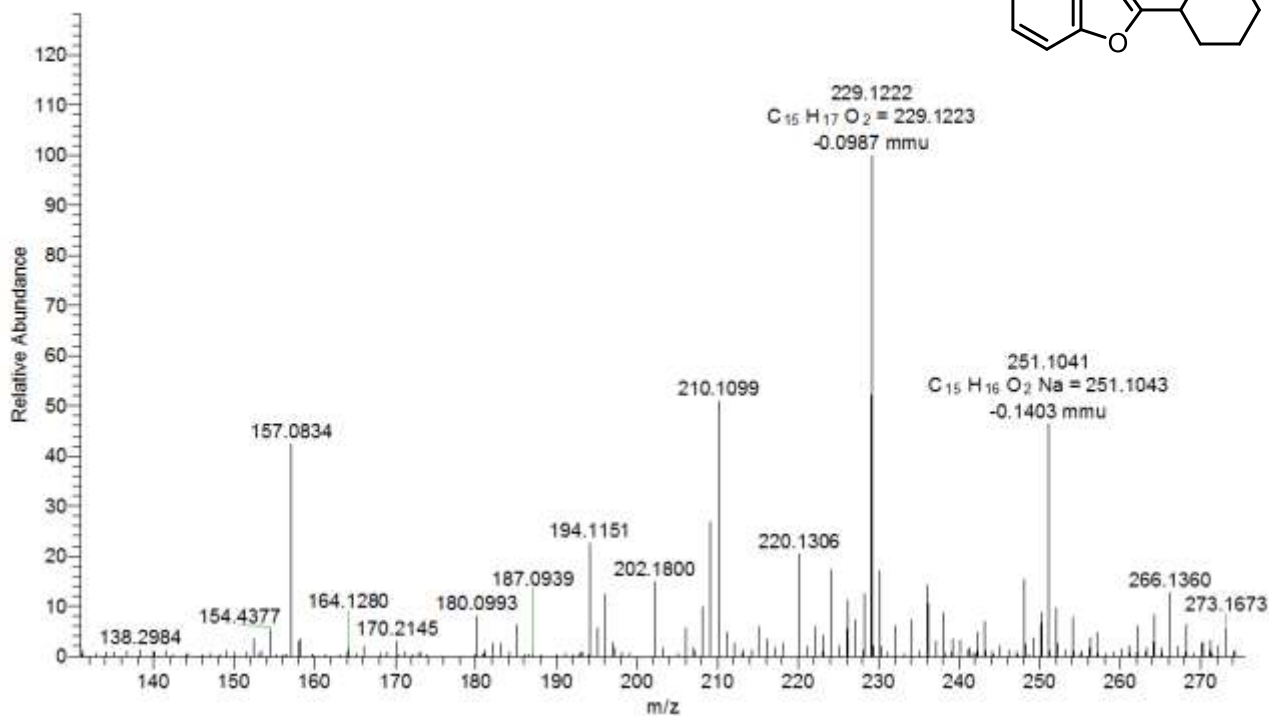
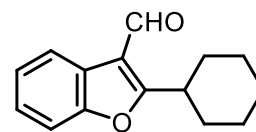
HRMS (ESI) 5e

IKGM-tio-nitikan #10-12 RT: 0.08-0.10 AV: 3 NL: 2.03E5
T: FTMS + p ESI Full ms [150.0000-600.0000]



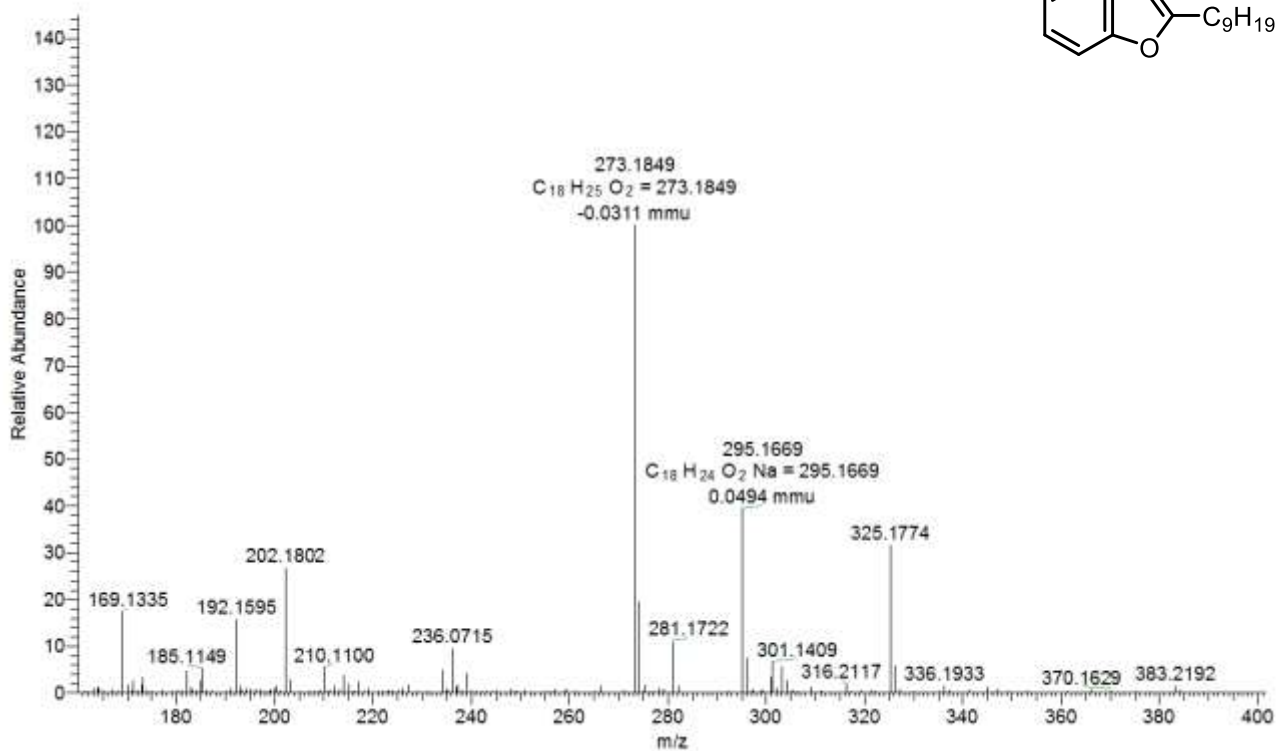
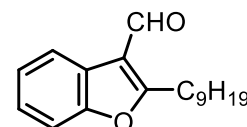
HRMS (ESI) 5f

IKGM235 #22 RT: 0.12 AV: 1 NL: 4.30E7
T: FTMS + p ESI Full ms [120.0000-1800.0000]



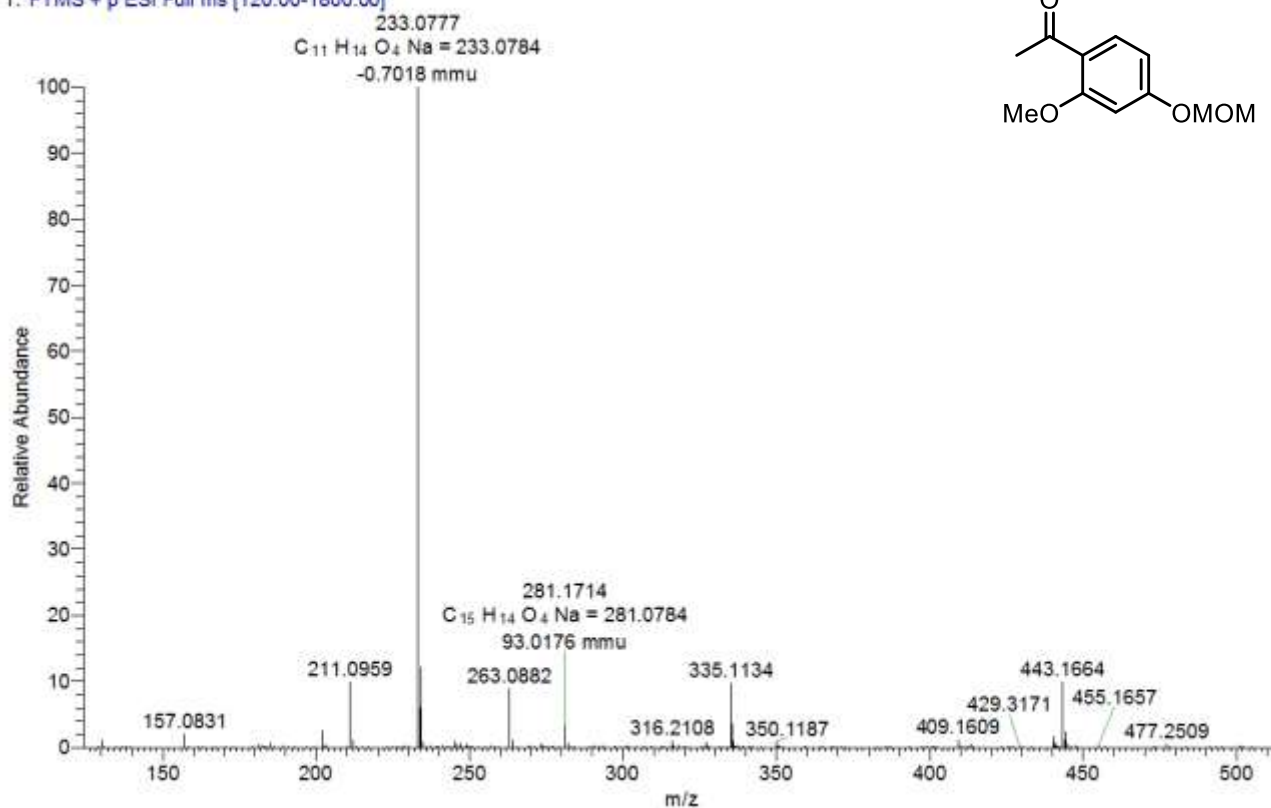
HRMS (ESI) 5g

AN-B4g #12 RT: 0.10 AV: 1 NL: 2.85E5
T: FTMS + p ESI Full ms [150.0000-600.0000]



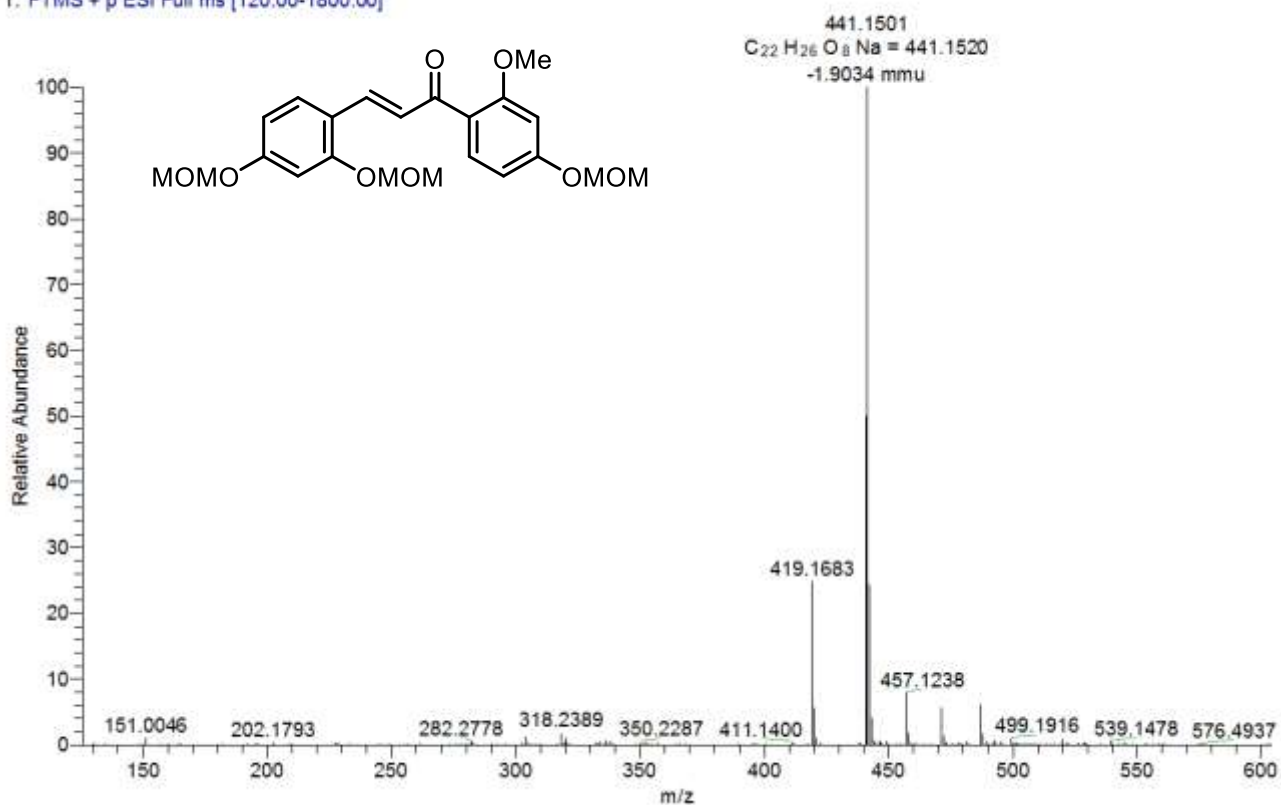
HRMS (ESI) 7

IKGM-134 #20 RT: 0.11 AV: 1 NL: 1.44E9
T: FTMS + p ESI Full ms [120.00-1800.00]



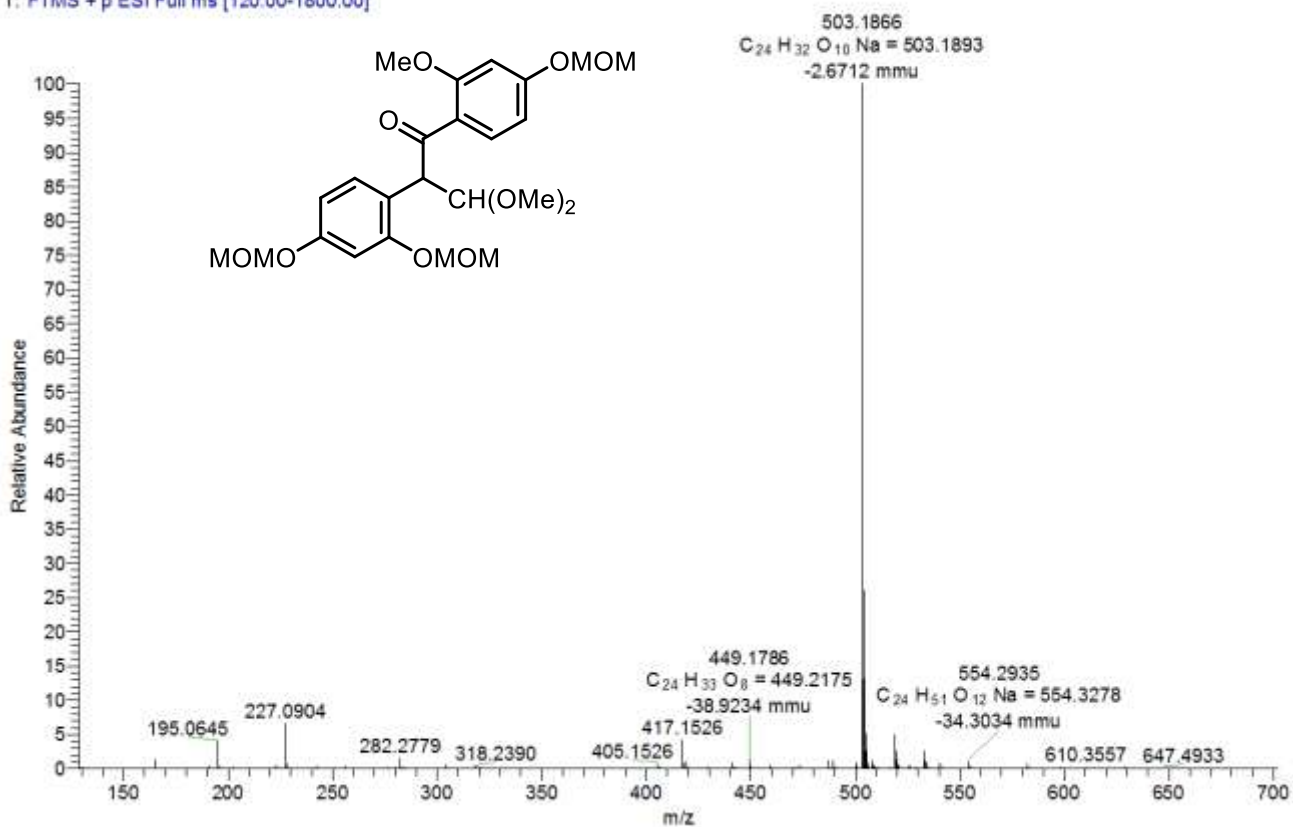
HRMS (ESI) 8

IKGM-135 #23 RT: 0.12 AV: 1 NL: 9.30E8
T: FTMS + p ESI Full ms [120.00-1800.00]



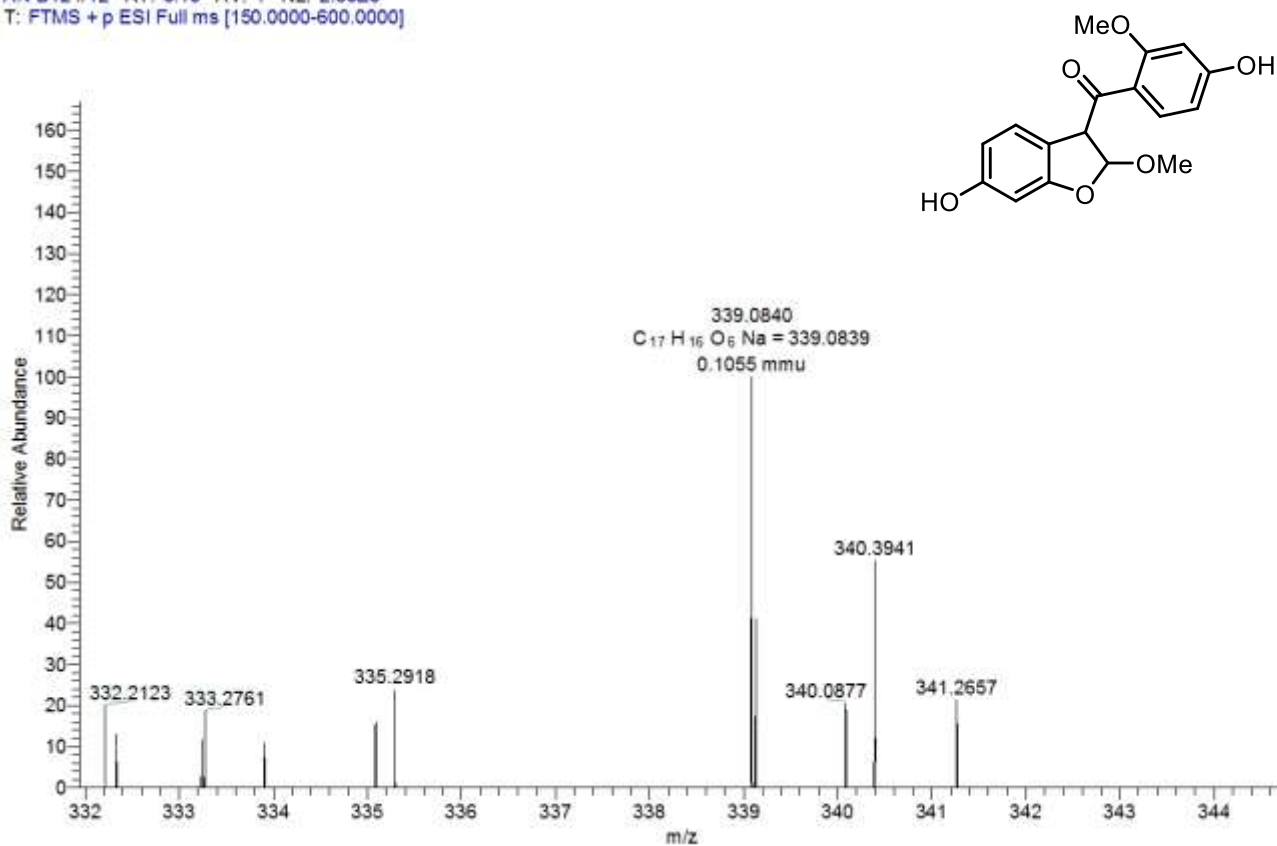
HRMS (ESI) 9

IKGM148 #23 RT: 0.12 AV: 1 NL: 9.62E8
T: FTMS + p ESI Full ms [120.00-1800.00]



HRMS (ESI) 10

AN-B12 #12 RT: 0.10 AV: 1 NL: 2.35E3
T: FTMS + p ESI Full ms [150.0000-600.0000]



HRMS (ESI) Puerariafuran

IKGM-Puerariafuran #14-16 RT: 0.08-0.09 AV: 3 NL: 1.91E8
T: FTMS + p ESI Full ms [120.0000-1800.0000]

