Supporting Information

A Concise Synthesis of 3-Aroylflavones via Lewis Base 9-Azajulolidine-Catalyzed Tandem Acyl Transfer-Cyclization:

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General Techniques

All commercially available reagents were used as received. Dry THF and DCM (Kanto Chemical Co.) were obtained by passing commercially available pre-dried, oxygen-free formulations. MeOH was distilled from iodide and magnesium turnings. DMF was purchased from Wako (for peptide synthesis, grade: 99.5%).

All reactions in solution-phase were monitored by thin-layer chromatography carried out on Merck silica gel plates (0.2 mm, 60F-254) with UV light, and visualized with anisaldehyde, 10% ethanolic phosphomolybdic acid. Silica gel 60N (Kanto Chemical Co. 100~210 μm) was used for column chromatography, and Merck silica gel plate (2.0 mm, 60F-254) was used for preparative thin layer chromatography.

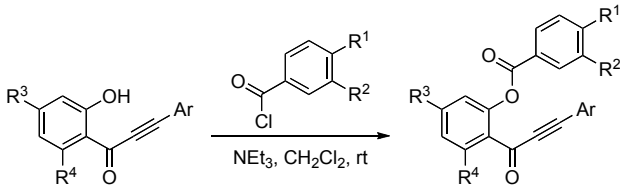
^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on JEOL JNM-AL400 spectrometers in the indicated solvent. Chemical shifts (δ) are reported in units parts per million (ppm) relative to the signal for internal tetramethylsilane (0 ppm for ^{1}H) for solutions in $CDCl_3$. NMR spectral data are reported as follows: chloroform (7.26 ppm for ^{1}H) or chloroform-*d* (77.0 ppm for ^{13}C), methanol-d_4 (3.30 ppm for ^{1}H) when internal standard is not indicated. Multiplicities are reported by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), dt (double triplet), ddd (double double doublet), ddt (double double triplet), dddd (double double double doublet), brs (broad singlet), brd (broad doublet), *J* (coupling constants in Hertz).

Mass spectra and high-resolution mass spectra were measured on JEOL JMS-DX303 and MS-AX500 instruments. IR spectra were recorded on a Shimadzu FTIR-8400. Only the strongest and/or structurally important absorption are reported as the IR data afforded in cm^{-1}.

X-ray crystallographic analysis was performed on a Rigaku Saturn724 diffractometer using multi-layer mirror monochromated Mo-Kα radiation.

Experimental Section

General Procedure: Synthesis of Benzoate Derivatives from *o*-Alkynoylphenols



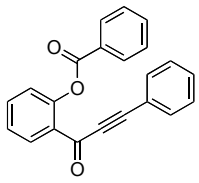
To a solution of *o*-alkynoylphenol (1.0 mmol, 1.00 equiv) and triethylamine (1.50 equiv) in dry CH_2Cl_2 (3 mL/mmol) was added acyl chloride (1.20 equiv) at 0 °C under argon. After being stirred at room temperature for 2 h, the reaction mixture was quenched with saturated aqueous NH_4Cl at 0 °C. The organic layer was separated and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed twice with saturated aqueous $NaHCO_3$, brine, dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo, and then the resulting residue was purified by column chromatography (eluted with Hex/EA=20/1-8/1) on silica gel to afford the benzoate derivatives.

2-(3-Phenylprop-2-ynoyl)phenyl benzoate (2a)

Yield: 98% (320 mg, 0.98 mmol), Reaction time: 0.5 h

Rf 0.56 (Hex/EA=2/1), colorless crystal, mp 78–79 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, 1H, *J* = 7.6, 1.8 Hz), 8.22 (d, 2H, *J* = 7.2 Hz), 7.67 (ddd, 1H, *J* = 8.4, 7.2, 1.8 Hz), 7.58 (t, 1H, *J* = 7.2 Hz), 7.46–7.38 (m, 6H), 7.31–7.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 165.2, 150.3, 134.6, 133.5, 132.8, 132.6, 130.6, 130.4, 129.9, 129.3, 128.5, 128.4, 126.2, 124.1, 119.9, 92.7, 88.0; FT-IR(Neat) 2197, 1740, 1642, 1602 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{14}O_3$ 326.0943, found 326.0925.



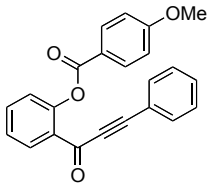
2a

2-(3-Phenylprop-2-ynoyl)phenyl 4-methoxybenzoate (2b)

Yield: 99% (353 mg, 0.99 mmol), Reaction time: 2 h

Rf 0.45 (Hex/EA=2/1), colorless crystal, mp 100–101 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, 1H, *J* = 7.8, 1.9 Hz), 8.16 (d, 2H, *J* = 9.0 Hz), 7.66 (ddd, 1H, *J* = 8.8, 8.4, 1.9 Hz), 7.45–7.38 (m, 4H), 7.29 (m, 3H), 6.90 (d, 2H, *J* = 9.0 Hz), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 164.8, 163.9, 150.4, 134.5, 132.8, 132.6, 132.4, 130.5, 130.1, 128.4, 126.0, 124.2, 121.6, 120.0, 113.7, 92.7, 88.1, 55.5; FT-IR(Neat) 2196, 1734, 1645, 1604, 1255, 1166 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1012.



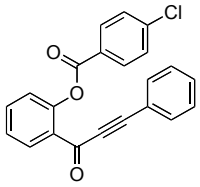
2b

2-(3-Phenylprop-2-ynoyl)phenyl 4-chlorobenzoate (2c)

Yield: 76% (274 mg, 0.76 mmol), Reaction time: 0.5 h

Rf 0.63 (Hex/EA=2/1), colorless needle, mp 109–110 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, 1H, *J* = 7.6, 1.8 Hz), 8.14 (d, 2H, *J* = 8.8 Hz), 7.67 (ddd, 1H, *J* = 7.2, 7.2, 1.8 Hz), 7.48–7.39 (m, 6H), 7.34–7.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 164.4, 150.1, 140.1, 134.7, 132.8, 131.8, 130.7, 129.7, 128.81, 128.79, 128.5, 127.8, 126.4, 124.1, 119.8, 92.9, 87.8; FT-IR(Neat) 2196, 1741, 1642, 1259, 1198, 750 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}ClO_3$ 360.0553, found 360.0573.



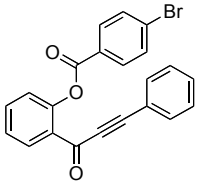
2c

2-(3-Phenylprop-2-ynoyl)phenyl 4-bromobenzoate (2d)

Yield: 88% (357 mg, 0.88 mmol), Reaction time: 3 h

Rf 0.63 (Hex/EA=2/1), white needle, mp 101–102 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, 1H, *J* = 8.0, 2.0 Hz), 8.06 (d, 2H, *J* = 8.8 Hz), 7.68 (ddd, 1H, *J* = 8.0, 8.0, 2.0 Hz), 7.58 (d, 2H, *J* = 8.8 Hz), 7.49–7.41 (m, 4H), 7.35–7.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 175.7, 164.5, 150.1, 134.7, 132.8, 132.7, 131.9, 131.8, 130.7, 129.7, 128.8, 128.5, 128.3, 126.4, 124.1, 119.8, 92.9, 87.9; FT-IR(Neat) 2197, 1741, 1643, 1261, 1070, 1009 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}BrO_3$ 404.0048, found 404.0026.



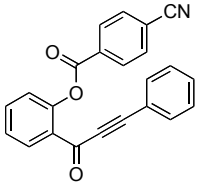
2d

2-(3-Phenylprop-2-ynoyl)phenyl 4-cyanobenzoate (2e)

Yield: 67% (235 mg, 0.67 mmol), Reaction time: 1 h

Rf 0.51 (Hex/EA=2/1), white needle, mp 106–107 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, 1H, *J* = 8.2, 1.8 Hz), 8.30 (d, 2H, *J* = 8.8 Hz), 7.74 (d, 2H, *J* = 8.8 Hz), 7.69 (ddd, 1H, *J* = 8.8, 8.0, 1.8 Hz), 7.51–7.43 (m, 4H), 7.35 (m, 2H), 7.29 (dd, 1H, *J* = 8.0, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 163.7, 149.8, 134.8, 133.3, 133.2, 132.8, 132.2, 130.9, 130.8, 129.3, 128.6, 126.6, 123.9, 119.7, 117.8, 116.8, 93.0, 87.7; FT-IR(Neat) 2197, 1746, 1641, 1262 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{13}NO_3$ 351.0895, found 351.0893.



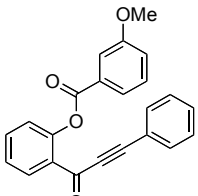
2e

2-(3-Phenylprop-2-ynoyl)phenyl 3-methoxybenzoate (2f)

Yield: 99% (353 mg, 0.99 mmol), Reaction time: 3 h

Rf 0.54 (Hex/EA=2/1), white needle, mp 83–84 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.83 (ddd, 1H, *J* = 8.0, 0.8, 0.8 Hz), 7.71 (dd, 1H, *J* = 2.8, 0.8 Hz), 7.66 (ddd, 1H, *J* = 8.0, 8.0, 1.6 Hz), 7.46–7.37 (m, 4H), 7.34 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.29 (m, 3H), 7.11 (ddd, 1H, *J* = 8.0, 2.8, 0.8 Hz), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 165.0, 159.6, 150.3, 134.6, 132.8, 132.5, 130.5, 129.9, 129.5, 128.4, 126.2, 124.1, 122.9, 120.3, 119.9, 114.6, 92.7, 88.0, 55.4; FT-IR(Neat) 2197, 1740, 1643, 1603, 1489, 1310, 1278, 1205, 1010, 744 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1035.



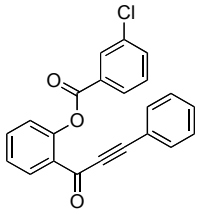
2f

2-(3-Phenylprop-2-ynoyl)phenyl 3-chlorobenzoate (2g)

Yield: 83% (299 mg, 0.83 mmol), Reaction time: 2 h

Rf 0.60 (Hex/EA=2/1), white solid, mp 104–106 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, 1H, *J* = 8.0, 1.6 Hz), 8.19 (dd, 1H, *J* = 2.0, 2.0 Hz), 8.09 (ddd, 1H, *J* = 8.0, 2.0, 1.2 Hz), 7.68 (ddd, 1H, *J* = 8.6, 7.6, 1.6 Hz), 7.54 (ddd, 1H, *J* = 8.4, 2.0, 1.2 Hz), 7.49–7.27 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 164.1, 150.0, 134.7, 134.6, 133.5, 132.9, 132.8, 131.0, 130.7, 130.4, 129.8, 129.6, 128.52, 128.50, 126.4, 124.0, 119.8, 92.9, 87.8; FT-IR(Neat) 2197, 1744, 1642, 1248, 1198 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}ClO_3$ 360.0553, found 360.0547.



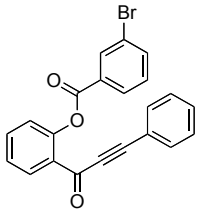
2g

2-(3-Phenylprop-2-ynoyl)phenyl 3-bromobenzoate (2h)

Yield: 96% (389 mg, 0.96 mmol), Reaction time: 1.5 h

Rf 0.60 (Hex/EA=2/1), white needle, mp 94–96 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, 1H, *J* = 1.8, 1.8 Hz), 8.29 (dd, 1H, *J* = 7.8, 1.8 Hz), 8.13 (dd, 1H, *J* = 8.4, 1.8 Hz), 7.68 (m, 2H), 7.49–7.40 (m, 4H), 7.35–7.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 163.9, 150.0, 136.4, 134.7, 133.3, 132.9, 132.8, 131.2, 130.7, 130.0, 129.6, 129.0, 128.5, 126.4, 124.0, 122.5, 119.7, 92.9, 87.8; FT-IR(Neat) 2197, 1744, 1642, 1246, 1197 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}BrO_3$ 404.0048, found 404.0027.



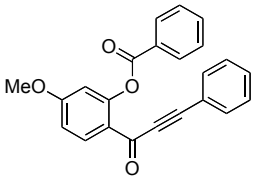
2h

5-Methoxy-2-(3-phenylprop-2-ynoyl)phenyl benzoate (2i)

Yield: 70% (249 mg, 0.70 mmol), Reaction time: 2 h

Rf 0.50 (Hex/EA=2/1), white needle, mp 98–100 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, 1H, *J* = 8.8 Hz), 8.22 (m, 2H), 7.59 (m, 1H), 7.47–7.37 (m, 5H), 7.30 (dd, 2H, *J* = 7.2, 7.2 Hz), 6.94 (dd, 1H, *J* = 8.8, 2.4 Hz), 6.78 (d, 1H, *J* = 2.4 Hz), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 165.1, 164.8, 152.5, 134.9, 133.5, 132.7, 130.4, 130.3, 129.4, 128.5, 128.4, 122.9, 120.2, 112.0, 109.5, 91.9, 87.9, 55.9; FT-IR(Neat) 2196, 1740, 1636, 1607, 1282, 1262, 1240, 1130, 1117 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1022.



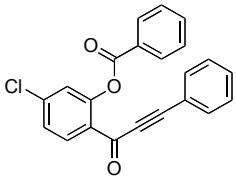
2i

5-Chloro-2-(3-phenylprop-2-ynoyl)phenyl benzoate (2j)

Yield: 72% (260 mg, 0.72 mmol), Reaction time: 15 min

Rf 0.68 (Hex/EA=2/1), colorless needle, mp 110–111 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (m, 3H), 7.58 (dt, 1H, *J* = 7.6, 1.6 Hz), 7.46–7.38 (m, 6H), 7.32–7.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 164.8, 150.8, 140.3, 133.8, 133.5, 132.8, 130.7, 130.5, 128.8, 128.5, 128.44, 128.41, 126.5, 124.7, 119.6, 93.2, 87.1; FT-IR(Neat) 2196, 1745, 1645, 1595, 1261, 1203, 1054, 703 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}ClO_3$ 360.0553, found 360.0538.



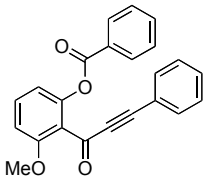
2j

3-Methoxy-2-(3-phenylprop-2-ynoyl)phenyl benzoate (2k)

Yield: 99% (353 mg, 0.99 mmol), Reaction time: 3 h

Rf 0.43 (Hex/EA=2/1), white needle, mp 86–88 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 2H, *J* = 7.6 Hz), 7.54 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.48 (t, 1H, *J* = 8.0 Hz), 7.41–7.36 (m, 5H), 7.27 (m, 2H), 6.93 (m, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 164.6, 158.5, 149.4, 133.6, 132.9, 132.1, 130.5, 130.3, 128.9, 128.4, 128.3, 122.6, 120.0, 115.6, 109.3, 92.0, 89.5, 56.3; FT-IR(Neat) 2195, 1741, 1647, 1604, 1472, 1228, 1092 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1035.



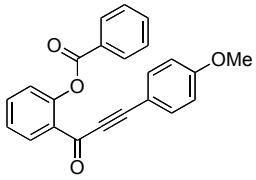
2k

2-[3-(4-Methoxyphenyl)prop-2-ynoyl]phenyl benzoate (2l)

Yield: 99% (353 mg, 0.99 mmol), Reaction time: 1 h

Rf 0.44 (Hex/EA=2/1), colorless crystal, mp 115–116 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (m, 3H), 7.63 (ddd, 1H, *J* = 8.5, 7.8, 1.8 Hz), 7.56 (m, 1H), 7.43 (m, 3H), 7.36 (d, 2H, *J* = 8.8 Hz), 7.27 (d, 1H, *J* = 8.5 Hz), 6.79 (d, 2H, *J* = 8.8 Hz), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 165.1, 161.5, 150.1, 134.9, 134.3, 133.5, 132.4, 130.3, 130.0, 129.3, 128.4, 126.1, 124.0, 114.1, 111.5, 94.0, 88.0, 55.2; FT-IR(Neat) 2190, 1740, 1638, 1602, 1511, 1257 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1012.



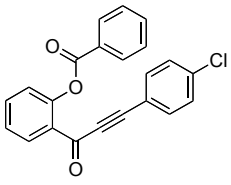
2l

2-[3-(4-Chlorophenyl)prop-2-ynoyl]phenyl benzoate (2m)

Yield: 96% (346 mg, 0.96 mmol), Reaction time: 1 h

Rf 0.65 (Hex/EA=2/1), colorless crystal, mp 86–88 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.20 (m, 3H), 7.68 (m, 1H), 7.60 (m, 1H), 7.45 (m, 3H), 7.32–7.25 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 165.0, 150.2, 136.8, 134.7, 133.8, 133.5, 132.3, 130.3, 129.7, 129.1, 128.8, 128.4, 126.2, 124.1, 118.2, 91.2, 88.6; FT-IR(Neat) 2199, 1741, 1642, 1603, 1262, 1207, 1060, 1006, 704 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}ClO_3$ 360.0553, found 360.0529.



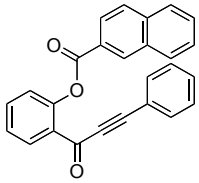
2m

2-(3-Phenylprop-2-ynoyl)phenyl naphthalene-2-carboxylate (2n)

Yield: 86% (323 mg, 0.86 mmol), Reaction time: 2 h

Rf 0.58 (Hex/EA=2/1), colorless needle, mp 103–105 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H) , 8.27 (dd, 1H, *J* = 7.8, 2.0 Hz), 8.19 (dd, 1H, *J* = 8.4, 2.0 Hz), 7.89 (m, 3H), 7.69 (ddd, 1H, *J* = 7.8, 7.8, 2.0 Hz), 7.57 (m, 2H), 7.46 (ddd, 1H, *J* = 7.8, 7.8, 1.6 Hz), 7.35 (m, 3H), 7.29 (m, 1H), 7.17 (dd, 2H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 165.4, 150.4, 135.8, 134.6, 132.7, 132.51, 132.45, 132.4, 130.4, 130.1, 129.5, 128.5, 128.31, 128.28, 127.7, 126.7, 126.5, 126.2, 125.6, 124.2, 119.8, 92.8, 88.1; FT-IR(Neat) 2196, 1737, 1642, 1187 cm^{-1}; HRMS[EI] calcd for $C_{26}H_{16}O_3$ 376.1099, found 376.1084.



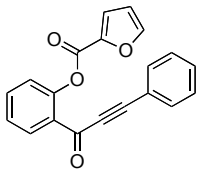
2n

2-(3-Phenylprop-2-ynoyl)phenyl furan-2-carboxylate (2o)

Yield: 99% (313 mg, 0.99 mmol), Reaction time: 1.5 h

Rf 0.46 (Hex/EA=2/1), colorless crystal, mp 97–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, 1H, *J* = 8.0, 2.0 Hz), 7.66 (ddd, 1H, *J* = 8.4, 7.6, 2.0 Hz), 7.59 (d, 1H, *J* = 1.6 Hz), 7.51–7.39 (m, 5H), 7.34 (dd, 2H, *J* = 7.6, 7.6 Hz), 7.29 (dd, 1H, *J* = 8.4, 1.2 Hz), 6.51 (dd, 1H, *J* = 3.6, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 156.7, 149.3, 147.1, 143.8, 134.6, 132.9, 132.6, 130.6, 129.9, 128.5, 126.4, 124.1, 120.0, 119.8, 112.2, 92.9, 87.9; FT-IR(Neat) 2197, 1745, 1642, 1295 cm^{-1}; HRMS[EI] calcd for $C_{20}H_{12}O_4$ 316.0736, found 316.0740.



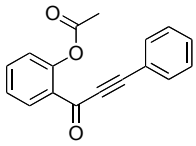
2o

2-(3-Phenylprop-2-ynoyl)phenyl acetate (2p)

Yield: 90% (238 mg, 0.90 mmol), Reaction time: 10 min

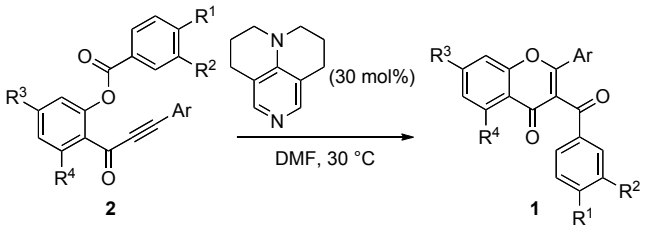
Rf 0.53 (Hex/EA=2/1), white solid, mp 63–64 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, 1H, *J* = 7.8, 1.8 Hz), 7.66–7.61 (m, 3H), 7.48 (m, 1H), 7.42 (m, 3H), 7.15 (d, 1H, *J* = 8.4 Hz), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 169.5, 150.0, 134.6, 133.0, 132.9, 130.8, 129.4, 128.6, 126.1, 124.0, 119.9, 92.6, 87.6; FT-IR(Neat) 2197, 1770, 1641, 1187 cm^{-1}; HRMS[EI] calcd for $C_{17}H_{12}O_3$ 264.0786, found 264.0777.



2p

General Procedure: Synthesis of 3-Aroylflavones by 9-AJ-catalyzed Tandem Acyl Transfer-Cyclization



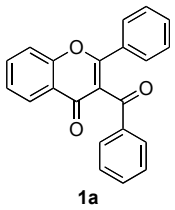
To a solution of phenyl ester (0.1 mmol) in dry DMF (20 mL/mmol) was added 9-azajulolidine (30 mol%) at room temperature under argon. After being stirred at 30 °C, the reaction mixture was diluted with water at room temperature. The organic layer was separated and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with 1 M HCl, saturated aqueous $NaHCO_3$, brine, dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo, and then the resulting residue was purified by preparative thin layer chromatography (eluted with Toluene/EA=6/1) to afford 3-aroylflavone derivatives.

3-Benzoyl-2-phenyl-4H-chromen-4-one (1a)

Yield: 88% (28.8 mg, 0.088 mmol), Reaction time: 6 h

Rf 0.48 (Toluene/EA=6/1), white solid, mp 121–122 °C [lit. 121–122 °C][1)].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.92 (dd, 2H, *J* = 8.0, 1.2 Hz), 7.76 (ddd, 1H, *J* = 8.6, 7.2, 1.6 Hz), 7.65 (m, 2H), 7.59 (d, 1H, *J* = 8.6 Hz), 7.53 (m, 1H), 7.47 (m, 1H), 7.43–7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 176.4, 162.4, 156.2, 137.1, 134.3, 133.7, 131.8, 131.4, 129.4, 128.73, 128.70, 128.5, 126.1, 125.6, 123.4, 122.7, 118.1; FT-IR(Neat) 1673, 1636, 1465, 1375 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{14}O_3$ 326.0943, found 326.0944.

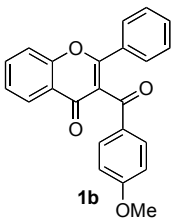


3-[(4-Methoxyphenyl)carbonyl]-2-phenyl-4H-chromen-4-one (1b)

Yield: 63% (22.5 mg, 0.063 mmol), Reaction time: 22 h

Rf 0.35 (Toluene/EA=6/1), colorless crystal, mp 172–174 °C [lit. 169–170 °C][2)].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.90 (d, 2H, *J* = 8.8 Hz), 7.75 (ddd, 1H, *J* = 8.4, 6.8, 1.6 Hz), 7.68 (d, 2H, *J* = 7.6 Hz), 7.58 (d, 1H, *J* = 8.4 Hz), 7.48–7.34 (m, 4H), 6.87 (d, 2H, *J* = 8.8 Hz), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 176.5, 164.0, 162.0, 156.1, 134.2, 131.9, 131.8, 131.3, 130.3, 128.7, 128.5, 126.1, 125.5, 123.3, 122.8, 118.1, 114.0, 55.4; FT-IR(Neat) 1667, 1633, 1598, 1465, 1376, 1256 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1034.

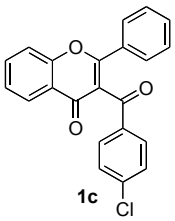


3-[(4-Chlorophenyl)carbonyl]-2-phenyl-4H-chromen-4-one (1c)

Yield: 92% (33.2 mg, 0.092 mmol), Reaction time: 5 h

Rf 0.60 (Toluene/EA=6/1), colorless crystal, mp 157–159 °C [lit. 151–153 °C][3].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, 1H, *J* = 8.0, 1.4 Hz), 7.85 (d, 2H, *J* = 8.8 Hz), 7.76 (ddd, 1H, *J* = 8.4, 7.0, 1.4 Hz), 7.64–7.58 (m, 3H), 7.49–7.42 (m, 2H), 7.39–7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 176.3, 162.8, 156.1, 140.2, 135.5, 134.4, 131.62, 131.59, 130.7, 129.1, 128.8, 128.5, 126.1, 125.8, 123.3, 122.2, 118.2; FT-IR(Neat) 1678, 1636, 1464, 1376 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}ClO_3$ 360.0553, found 360.0552.

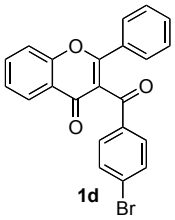


3-[(4-Bromophenyl)carbonyl]-2-phenyl-4H-chromen-4-one (1d)

Yield: 96% (38.9 mg, 0.096 mmol), Reaction time: 3 h

Rf 0.60 (Toluene/EA=6/1), white solid, mp 161–163 °C [lit. 159–160 °C][4].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.76 (m, 3H,), 7.61 (m, 3H), 7.54 (d, 2H, *J* = 8.8 Hz), 7.46 (m, 2H), 7.37 (dd, 1H, *J* = 7.6, 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 176.3, 162.8, 156.1, 135.8, 134.4, 132.1, 131.6, 131.5, 130.8, 129.0, 128.8, 128.4, 126.0, 125.7, 123.2, 122.1, 118.1; FT-IR(Neat) 1677, 1635, 1618, 1464, 1376, 871, 760 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}BrO_3$ 404.0048, found 404.0029.

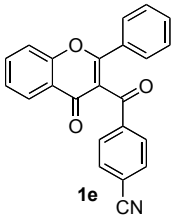


3-[(4-Cyanophenyl)carbonyl]-2-phenyl-4H-chromen-4-one (1e)

Yield: 97% (34.1 mg, 0.097 mmol), Reaction time: 7 h

Rf 0.53 (Toluene/EA=6/1), colorless crystal, mp 180–181 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.99 (d, 2H, *J* = 8.8 Hz), 7.79 (ddd, 1H, *J* = 8.8, 7.2, 1.6 Hz), 7.70 (d, 2H, *J* = 8.8 Hz), 7.62–7.58 (m, 3H), 7.52–7.44 (m, 2H), 7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 176.3, 163.6, 156.1, 140.0, 134.7, 132.6, 131.8, 131.4, 129.5, 128.9, 128.5, 126.02, 125.96, 123.2, 121.7, 118.2, 117.9, 116.7; FT-IR(Neat) 1683, 1634, 1618, 1464, 1377 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{13}NO_3$ 351.0895, found 351.0888.

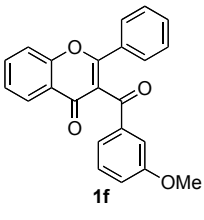


3-[(3-Methoxyphenyl)carbonyl]-2-phenyl-4H-chromen-4-one (1f)

Yield: 90% (32.0 mg, 0.09 mmol), Reaction time: 4 h

Rf 0.51 (Toluene/EA=6/1), white solid, mp 109–111 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.75 (ddd, 1H, *J* = 8.4, 8.0, 1.6 Hz), 7.66 (d, 2H, *J* = 7.4 Hz), 7.59 (d, 1H, *J* = 8.4 Hz), 7.51 (dd, 1H, *J* = 2.4, 2.4 Hz), 7.48–7.41 (m, 3H), 7.37 (dd, 2H, *J* = 7.4, 7.4 Hz), 7.28 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.08 (dd, 1H, *J* = 7.6, 2.4 Hz), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 176.4, 162.3, 159.9, 156.1, 138.3, 134.3, 131.7, 131.4, 129.7, 128.7, 128.5, 126.1, 125.6, 123.3, 122.6, 122.55, 120.48, 118.1, 112.9, 55.4; FT-IR (Neat) 1675, 1636, 1620, 1465, 1376, 1267, 760 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1054.

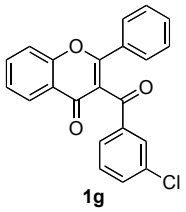


3-[(3-Chlorophenyl)carbonyl]-2-phenyl-4H-chromen-4-one (1g)

Yield: 96% (34.6 mg, 0.096 mmol), Reaction time: 3 h

Rf 0.60 (Toluene/EA=6/1), white needle, mp 157–158 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, 1H, *J* = 8.2, 1.6 Hz), 7.88 (dd, 1H, *J* = 1.6, 1.6 Hz), 7.77 (m, 2H), 7.61 (m, 3H), 7.51–7.43 (m, 3H), 7.40–7.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 176.3, 162.9, 156.1, 138.5, 135.0, 134.5, 133.6, 131.6, 131.5, 130.1, 129.1, 128.8, 128.5, 127.5, 126.0, 125.8, 123.2, 122.0, 118.2; FT-IR(Neat) 1679, 1635, 1618, 1465, 1375, 761 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}ClO_3$ 360.0553, found 360.0553.



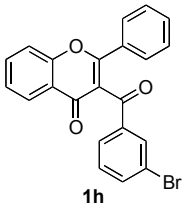
1g

3-[(3-Bromophenyl)carbonyl]-2-phenyl-4H-chromen-4-one (1h)

Yield: 98% (39.7 mg, 0.098 mmol), Reaction time: 3 h

Rf 0.58 (Toluene/EA=6/1), white needle, mp 168–170 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, 1H, *J* = 8.2, 1.6 Hz), 8.04 (dd, 1H, *J* = 1.6, 1.6 Hz), 7.82 (dt, 1H, *J* = 8.0, 1.6 Hz), 7.77 (ddd, 1H, *J* = 8.8, 7.2, 1.6 Hz), 7.66–7.59 (m, 4H), 7.50–7.36 (m, 4H), 7.28 (t, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 176.3, 162.9, 156.1, 138.7, 136.5, 134.5, 132.0, 131.6, 131.5, 130.3, 128.8, 128.5, 128.0, 126.1, 125.8, 123.2, 123.0, 122.0, 118.2; FT-IR(Neat) 1678, 1635, 1618, 1465, 1375, 760 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}BrO_3$ 404.0048, found 404.0045.



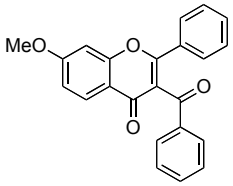
1h

3-Benzoyl-7-methoxy-2-phenyl-4H-chromen-4-one (1i)

Yield: 57% (20.3 mg, 0.057 mmol), Reaction time: 16 h

Rf 0.41 (Toluene/EA=6/1), colorless needle, mp 174–176 °C [lit. 162–163 °C][1)].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 1H, *J* = 8.8 Hz), 7.92 (d, 2H, *J* = 7.4 Hz), 7.63 (d, 2H, *J* = 7.4 Hz), 7.52 (m, 1H), 7.41–7.32 (m, 5H), 7.02 (dd, 1H, *J* = 8.8, 2.4 Hz), 6.97 (d, 1H, *J* = 2.4 Hz), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 175.8, 164.6, 162.0, 157.9, 137.1, 133.6, 131.8, 131.3, 129.4, 128.69, 128.68, 128.4, 127.5, 122.5, 117.1, 114.9, 100.3, 55.9; FT-IR(Neat) 1674, 1625, 1447, 1439, 1378, 1357 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1025.



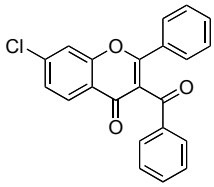
1i

3-Benzoyl-7-chloro-2-phenyl-4H-chromen-4-one (1j)

Yield: 56% (20.2 mg, 0.056 mmol), Reaction time: 4 h

Rf 0.61 (Toluene/EA=6/1), colorless needle, mp 196–198 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, 1H, *J* = 8.4 Hz), 7.91 (d, 2H, *J* = 7.6 Hz), 7.63 (m, 3H), 7.54 (m, 1H), 7.45–7.34 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 175.7, 162.5, 156.2, 140.4, 136.8, 133.9, 131.7, 131.3, 129.4, 128.82 128.78, 128.5, 127.5, 126.5, 122.8, 121.8, 118.2; FT-IR(Neat) 1676, 1641, 1611, 1426, 1369 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}ClO_3$ 360.0553, found 360.0550.



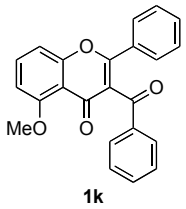
1j

3-Benzoyl-5- methoxy-2-phenyl-4H-chromen-4-one (1k)

Yield: 70% (24.9 mg, 0.07 mmol), Reaction time: 5 h

Rf 0.13 (Toluene/EA=6/1), colorless crystal, mp 235–236 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, 2H, *J* = 7.2 Hz), 7.63 (m, 3H), 7.51 (t, 1H, *J* = 7.2 Hz), 7.42–7.33 (m, 5H), 7.14 (d, 1H, *J* = 8.8 Hz), 6.85 (d, 1H, *J* = 8.0 Hz), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 176.3, 160.2, 160.1, 158.1, 137.3, 134.4, 133.5, 131.4, 131.2, 129.3, 128.7, 128.4, 123.8, 113.9, 110.0, 106.8, 56.4; FT-IR(Neat) 1675, 1637, 1605, 1476, 1378, 1268, 1091 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1031.



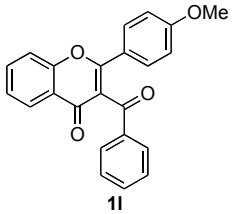
1k

3-Benzoyl-2-(4-methoxyphenyl)-4H-chromen-4-one (1l)

Yield: 71% (25.3 mg, 0.071 mmol), Reaction time: 14 h

Rf 0.33 (Toluene/EA=6/1), colorless needle, mp 146–147 °C [lit. 143 °C][5].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, 1H, *J* = 8.0, 1.2 Hz), 7.94 (d, 2H, *J* = 7.6 Hz), 7.73 (ddd, 1H, *J* = 8.8, 8.0, 1.2 Hz), 7.62 (d, 2H, *J* = 8.8 Hz), 7.57 (d, 1H, *J* = 8.8 Hz), 7.52 (t, 1H, *J* = 7.6 Hz), 7.44–7.38 (m, 3H), 6.84 (d, 2H, *J* = 8.8 Hz), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 176.4, 162.2, 162.0, 156.0, 137.0, 134.1, 133.7, 130.2, 129.3, 128.7, 125.9, 125.4, 123.8, 123.2, 121.5, 118.0, 114.2, 55.3; FT-IR(Neat) 1673, 1633, 1616, 1606, 1374, 760 cm^{-1}; HRMS[EI] calcd for $C_{23}H_{16}O_4$ 356.1049, found 356.1017.



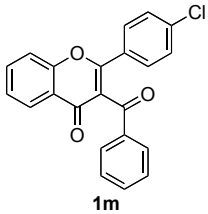
1l

3-Benzoyl-2-(4-chlorophenyl)-4H-chromen-4-one (1m)

Yield: 94% (33.9 mg, 0.094 mmol), Reaction time: 2.5 h

Rf 0.58 (Toluene/EA=6/1), white solid, mp 133–135 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.92 (dd, 2H, *J* = 7.6, 1.6 Hz), 7.76 (ddd, 1H, *J* = 8.4, 8.0, 1.6 Hz), 7.60 (d, 2H, *J* = 8.8 Hz), 7.57 (m, 2H), 7.46 (ddd, 1H, *J* = 8.0, 8.0, 0.8 Hz), 7.41 (dd, 2H, *J* = 7.6, 7.6 Hz), 7.33 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 176.2, 161.0, 155.9, 137.7, 136.7, 134.4, 133.9, 130.0, 129.7, 129.2, 129.0, 128.7, 125.9, 125.6, 123.1, 122.7, 118.0; FT-IR(Neat) 1673, 1635, 1617, 1465, 1374, 760 cm^{-1}; HRMS[EI] calcd for $C_{22}H_{13}ClO_3$ 360.0553, found 360.0538.



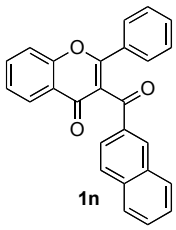
1m

3-[(Naphthalen-2-yl)carbonyl]-2-phenyl-4H-chromen-4-one (1n)

Yield: 91% (34.2 mg, 0.091 mmol), Reaction time: 8 h

Rf 0.53 (Toluene/EA=6/1), colorless crystal, mp 110–112 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, 1H, *J* = 1.6 Hz), 8.27 (dd, 1H, *J* = 7.8, 1.4 Hz), 8.04 (dd, 1H, *J* = 8.2, 1.6 Hz), 7.85 (m, 3H), 7.78 (ddd, 1H, *J* = 8.4, 7.4, 1.4 Hz), 7.69 (d, 2H, *J* = 7.6 Hz), 7.62 (d, 1H, *J* = 8.4 Hz), 7.59–7.46 (m, 2H), 7.48 (m, 1H), 7.40–7.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 176.5, 162.4, 156.2, 136.0, 134.6, 134.3, 132.6, 131.84, 131.78, 131.4, 129.8, 128.73, 128.71, 128.69, 128.5, 127.7, 126.6, 126.1, 125.6, 124.3, 123.4, 122.8, 118.1; FT-IR(Neat) 1670, 1636, 1624, 1376, 758 cm^{-1}; HRMS[EI] calcd for $C_{26}H_{16}O_3$ 376.1099, found 376.1088.



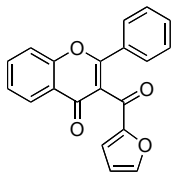
1n

3-[(Furan-2-yl)carbonyl]-2-phenyl-4H-chromen-4-one (1o)

Yield: 60% (19.0 mg, 0.06 mmol), Reaction time: 10 h

Rf 0.35 (Toluene/EA=6/1), white crystal, mp 184–186 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.75 (ddd, 1H, *J* = 8.4, 7.2, 1.6 Hz), 7.69 (d, 2H, *J* = 7.2 Hz), 7.50–7.38 (m, 5H), 7.11 (d, 1H, *J* = 3.6 Hz), 6.44 (dd, 1H, *J* = 3.6, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 176.0, 163.0, 156.0, 153.0, 147.3, 134.3, 131.8, 131.5, 128.8, 128.5, 126.1, 125.7, 123.4, 121.8, 119.8, 118.1, 112.6; FT-IR(Neat) 1660, 1635, 1620, 1464, 1377, 757 cm^{-1}; HRMS[EI] calcd for $C_{20}H_{12}O_4$ 316.0736, found 316.0714.



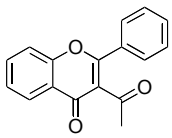
1o

3-Acetyl-2-phenyl-4H-chromen-4-one (1p)

Yield: 38% (10.0 mg, 0.038 mmol), Reaction time: 5 h

Rf 0.48 (Toluene/EA=6/1), white solid, mp 145–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, 1H, *J* = 8.6, 1.6 Hz), 7.73 (ddd, 1H, *J* = 8.6, 7.0, 1.6 Hz), 7.66 (d, 2H, *J* = 7.2 Hz), 7.58–7.44 (m, 5H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 175.9, 162.4, 155.8, 134.3, 131.9, 131.5, 128.8, 128.6, 126.0, 125.6, 124.9, 123.4, 118.1, 32.3; FT-IR(Neat) 1706, 1635, 1617, 1464, 1376, 1073, 760 cm^{-1}; HRMS[EI] calcd for $C_{17}H_{12}O_3$ 264.0786, found 264.0710.



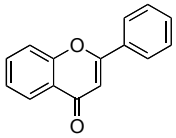
1p

2-Phenyl-4H-chromen-4-one (5a)

Yield: 12% (2.7 mg, 0.012 mmol)

Rf 0.29 (Toluene/EA=6/1), white solid, mp 95–97 °C [lit. 96–97 °C][6].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, 1H, *J* = 7.8, 1.6 Hz), 7.93 (m, 2H), 7.70 (ddd, 1H, *J* = 7.8, 7.8, 1.6 Hz), 7.59–7.50 (m, 4H), 7.43 (dd, 1H, *J* = 7.8, 7.8 Hz), 6.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 163.4, 156.2, 133.7, 131.7, 131.6, 129.0, 126.2, 125.7, 125.2, 123.9, 118.0, 107.5; FT-IR(Neat) 1645, 1465, 1375, 768 cm^{-1}; HRMS[EI] calcd for $C_{15}H_{10}O_2$ 222.0681, found 222.0663.



5a

Procedure for 9-AJ-Catalyzed Tandem Reaction in the presence of D_2O

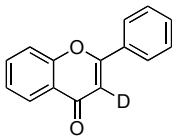
To a solution of phenyl ester **2h** (0.1 mmol) in DMF–D_2O (9:1, 20 mL/mmol) was added 9-azajulolidine (30 mol%) at room temperature under argon. After being stirred at 30 °C for 6 h, the reaction mixture was diluted with water at room temperature. The organic layer was separated and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with 1 M HCl, saturated aqueous $NaHCO_3$, brine, dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo, and then the resulting residue was purified by preparative thin layer chromatography (eluted with Toluene/EA=6/1) to afford 3-aroylflavone **1h** (47%) and deuterated flavone **6**.

2-Phenyl(3-^{2}H)-4H-chromen-4-one (6)

Yield: 37% (8.2 mg, 0.037 mmol),

Rf 0.29 (Toluene/EA=6/1), white solid, mp 91–93 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, 1H, *J* = 7.8, 1.6 Hz), 7.94 (m, 2H), 7.71 (ddd, 1H, *J* = 7.8, 7.8, 1.6 Hz), 7.59–7.51 (m, 4H), 7.43 (dd, 1H, *J* = 7.8, 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 163.3, 156.2, 133.7, 131.7, 131.5, 129.0, 126.2, 125.6, 125.2, 124.0, 118.0, 107.5, 107.3, 107.0; FT-IR(Neat) 1641, 1615, 1561, 1464, 1364, 758 cm^{-1}; HRMS[EI] calcd for $C_{15}H_{10}O_2$ 223.0743, found 223.0728.



6

General Procedure: Synthesis of *o*-Alkynoylphenols S1

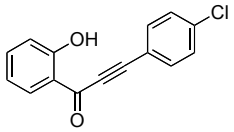
Alkynoylphenols **S1** were prepared by the procedure we previously reported[7].

3-(4-Chlorophenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (S1j)

Yield: 76% (393 mg, 1.53 mmol), use of substrate: 2.0 mmol

Rf 0.71 (Hex/EA=2/1), yellow needle, mp 120–121 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.7 (s, 1H), 8.04 (dd, 1H, *J* = 8.4, 1.4 Hz), 7.57 (d, 2H, *J* = 8.6 Hz), 7.50 (ddd, 1H, *J* = 8.2, 8.0, 1.4 Hz), 7.37 (d, 2H, *J* = 8.6 Hz), 6.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.7, 162.6, 137.4, 137.1, 134.1, 132.7, 129.1, 120.5, 119.3, 118.0, 117.9, 94.3, 86.2; FT-IR(Neat) 2207, 1628, 1592, 1489, 1344, 1257 cm^{-1}; HRMS[EI] calcd for $C_{15}H_9ClO_2$ 256.0291, found 256.0289.



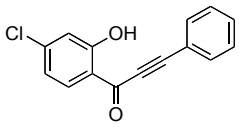
S1j

1-(4-Chloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (S1m)

Yield: 81% (414 mg, 1.61 mmol), use of substrate: 2.0 mmol

Rf 0.70 (Hex/EA=2/1), Yellow needle, mp 115–117 °C.

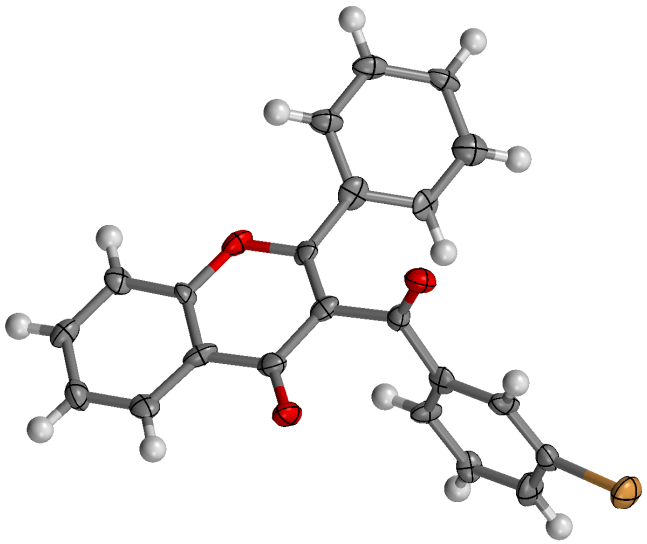
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.8 (s, 1H), 7.90 (d, 1H, *J* = 8.8 Hz), 7.56 (d, 2H, *J* = 7.2 Hz), 7.40 (t, 1H, *J* = 7.2 Hz), 7.32 (dd, 2H, *J* = 7.2, 7.2 Hz), 6.88 (d, 1H, *J* = 2.0 Hz), 6.84 (dd, 1H, *J* = 8.8, 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 163.1, 143.0, 133.8, 133.1, 131.3, 128.7, 120.1, 119.30, 119.29, 118.1, 96.5, 85.4; FT-IR(Neat) 2205, 1624, 1587, 769 cm^{-1}; HRMS[EI] calcd for $C_{15}H_9ClO_2$ 256.0291 found 256.0308.



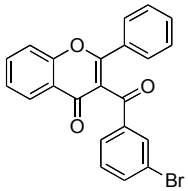
S1m

Structure Determination of 3-Aroylflavones by X-ray Crystallographic Analysis

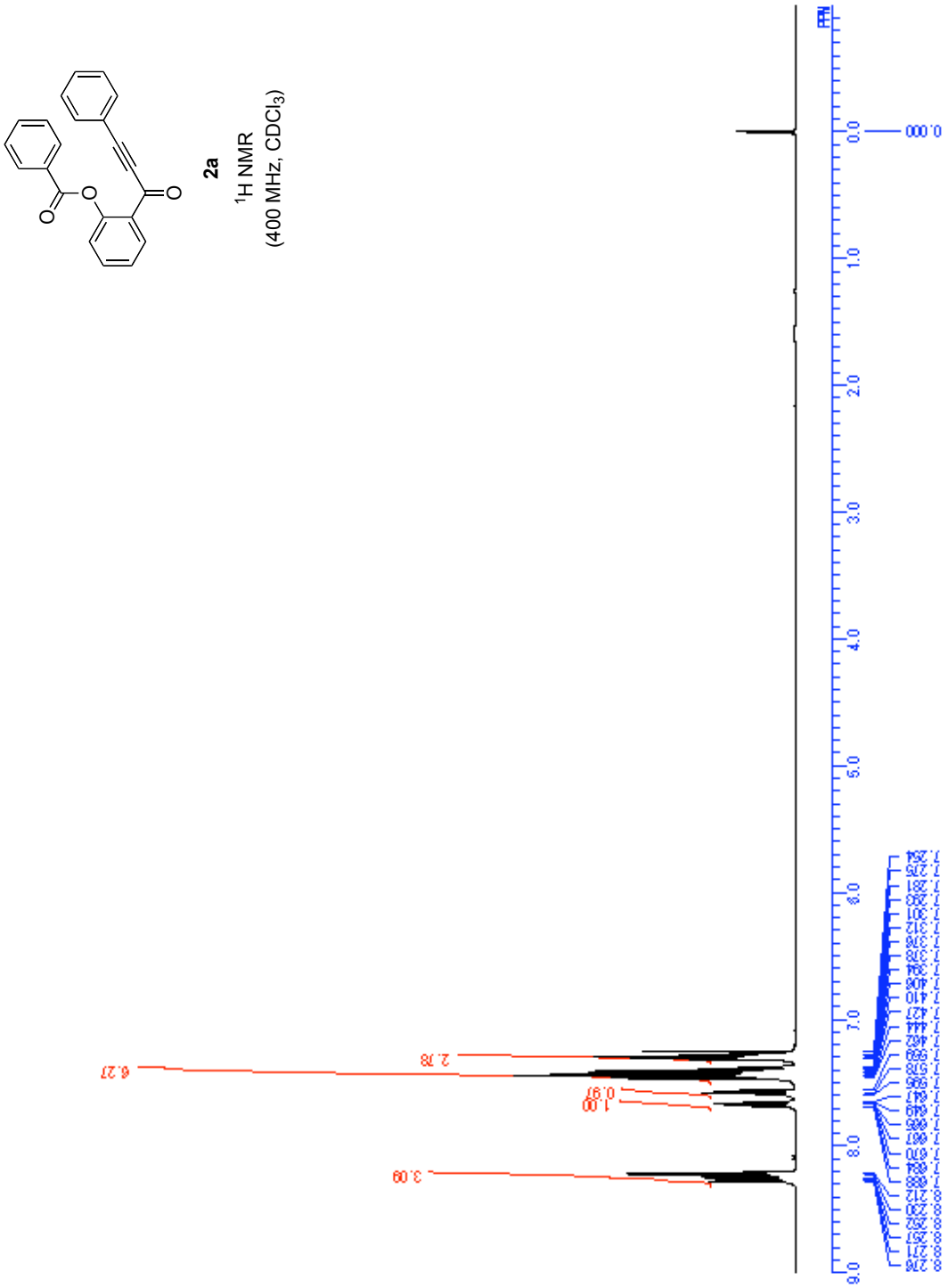
The structure of 3-aroylflavone was confirmed by X-ray crystallographic analysis of **1h**. Single-crystal of **1h** was obtained by recrystallization from diethyl ether. CCDC 897539 (**1h**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

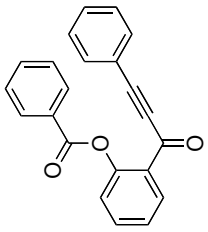


≡



3-Aroylflavone **1h**

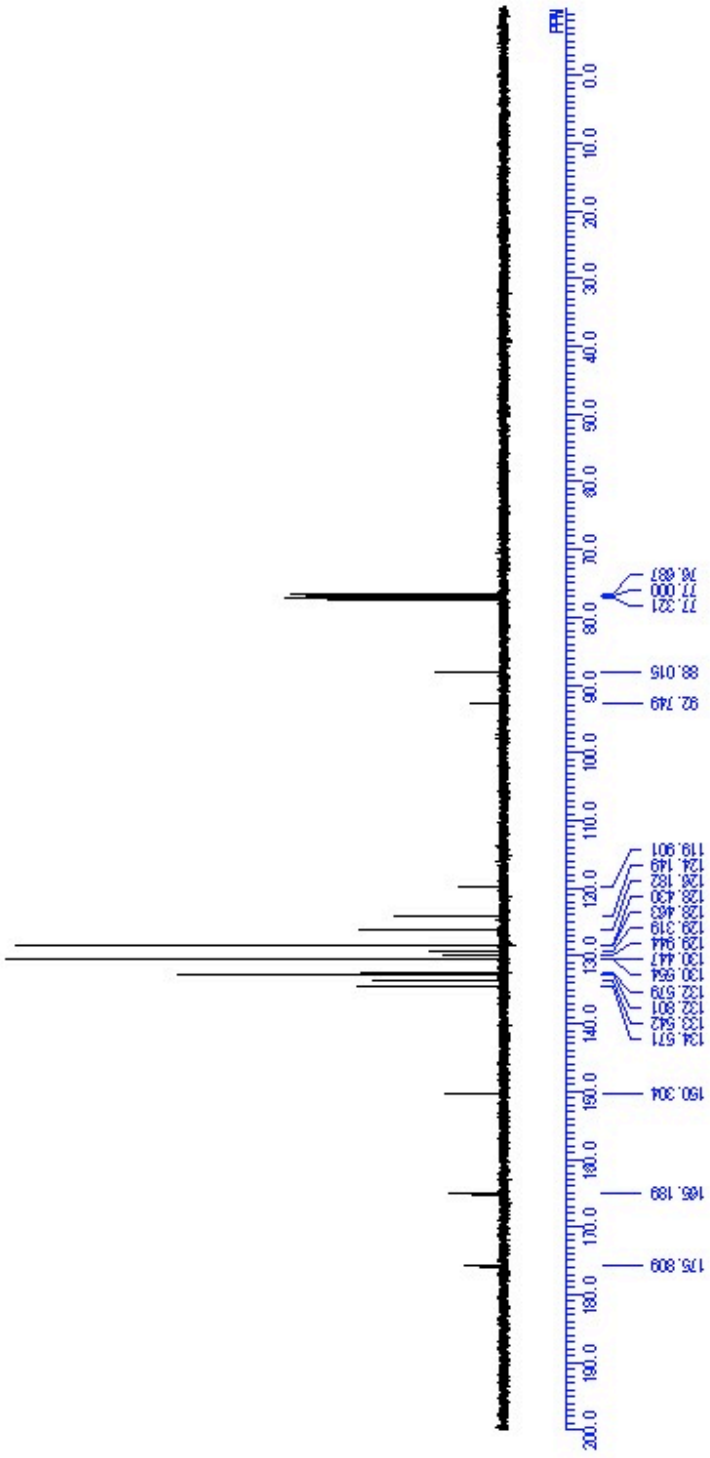

2a
^{1}H NMR
(400 MHz, CDCl$_3$)
6.27
2.78
1.00
0.97
3.09

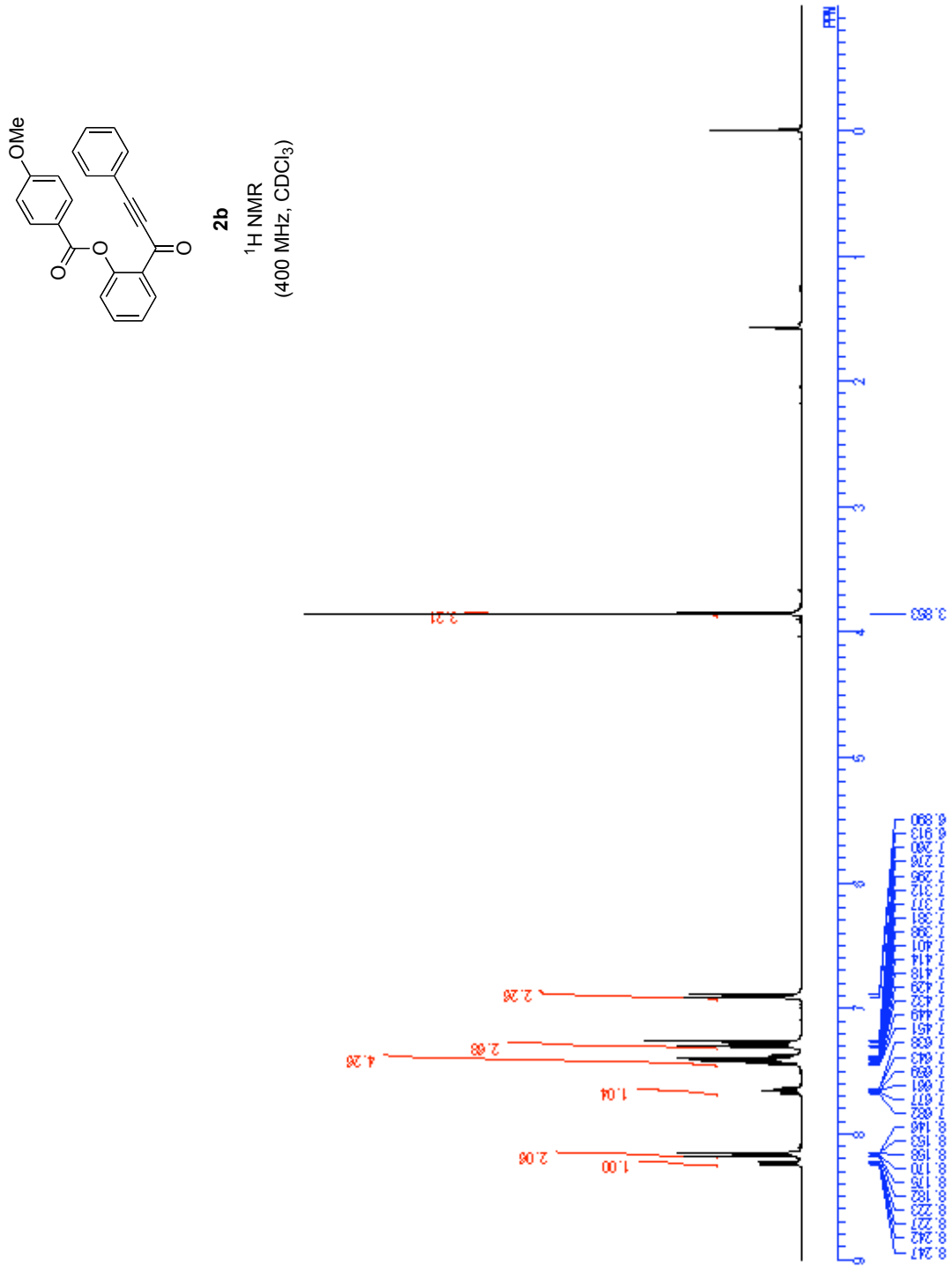


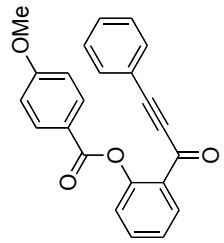
2a

^{13}C NMR

(400 MHz, $CDCl_3$)

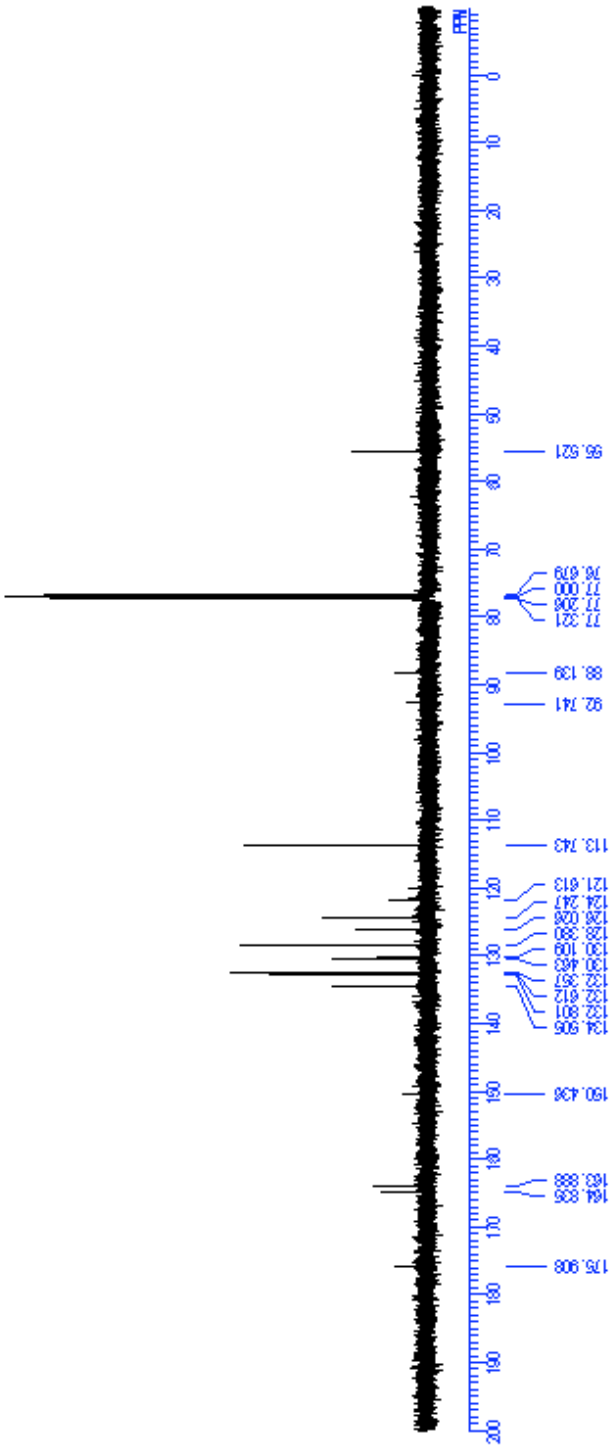


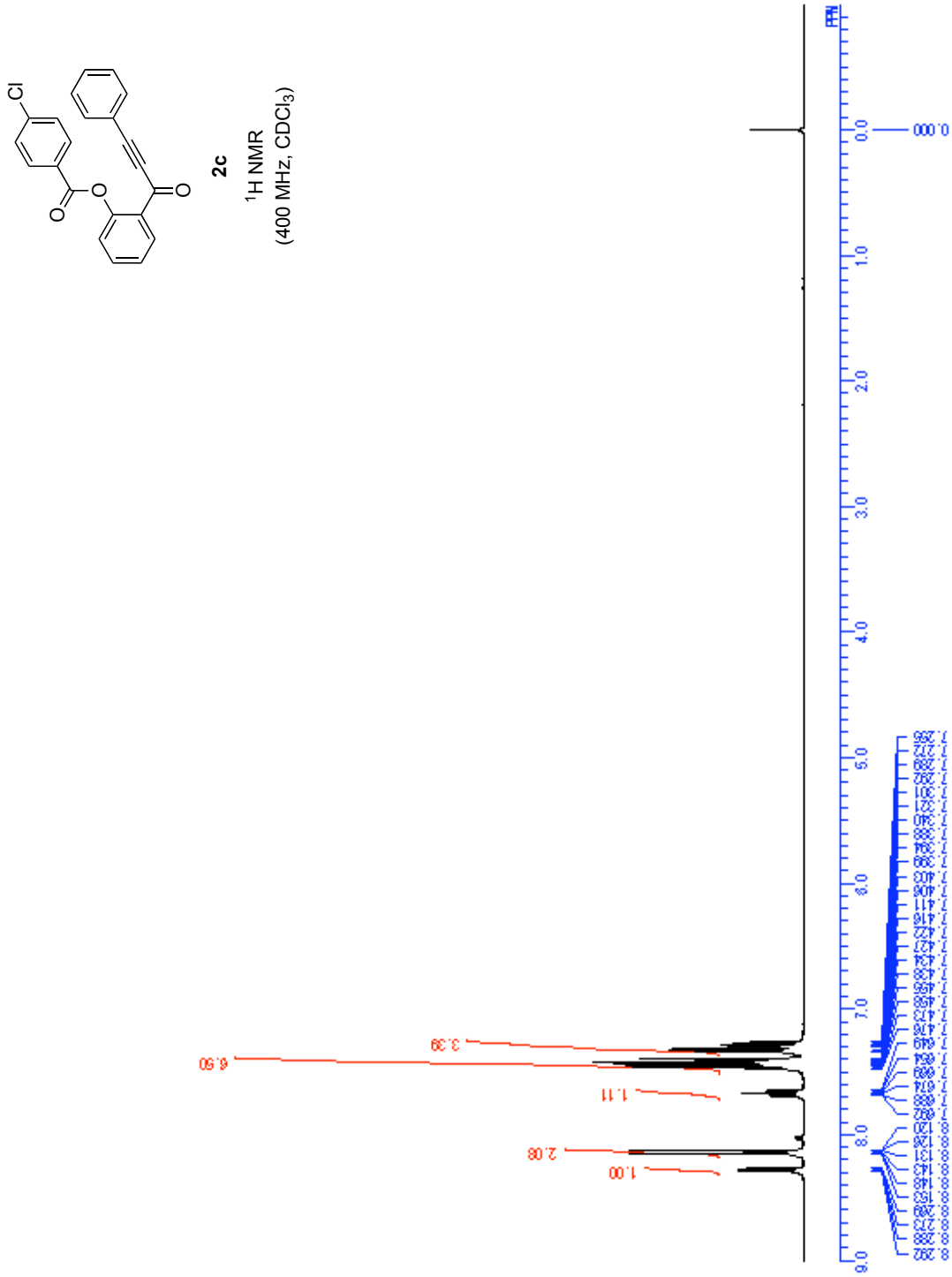

OMe
O
O
O
2b
^{1}H NMR
(400 MHz, CDCl$_3$)
3.21
2.28
2.68
4.28
1.04
2.08
1.00
3.863

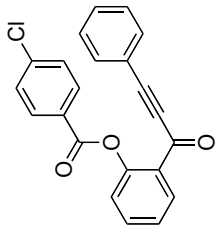


2b

^{13}C NMR
(400 MHz, $CDCl_3$)

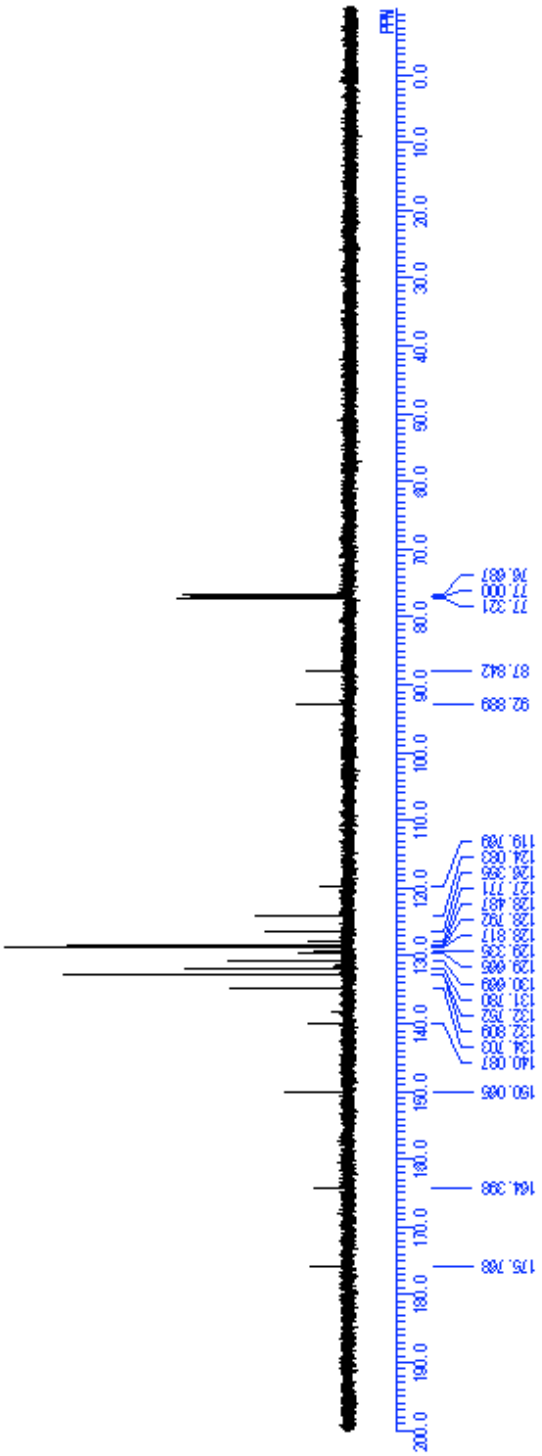


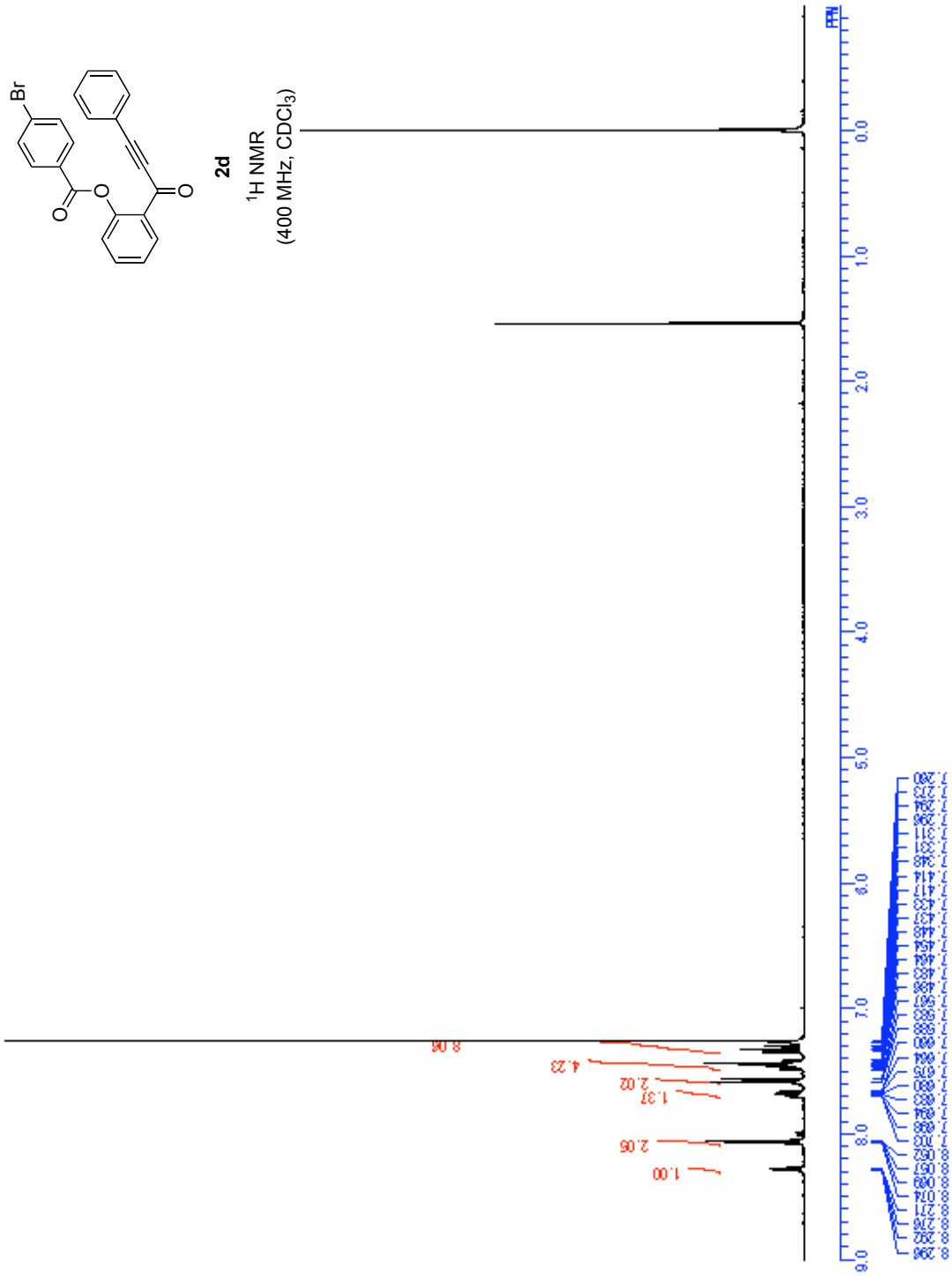

Cl
O
O
O
O
2c
^{1}H NMR
(400 MHz, CDCl$_3$)
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
0.000
3.39
6.50
1.11
2.08
1.00

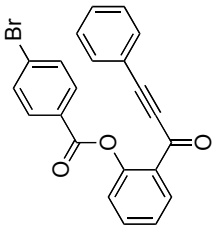


2c

^{13}C NMR
(400 MHz, $CDCl_3$)



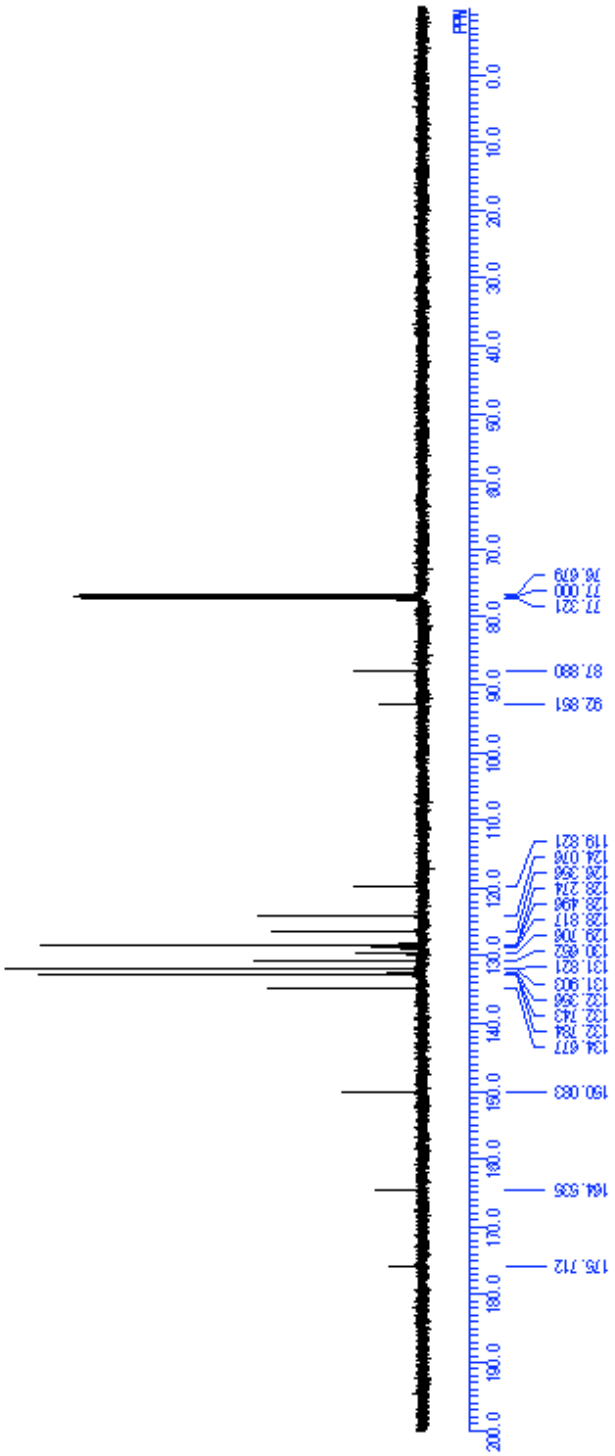

Br
O
O
O
2d
^{1}H NMR
(400 MHz, CDCl$_3$)
8.00
4.23
2.02
1.37
2.06
1.00

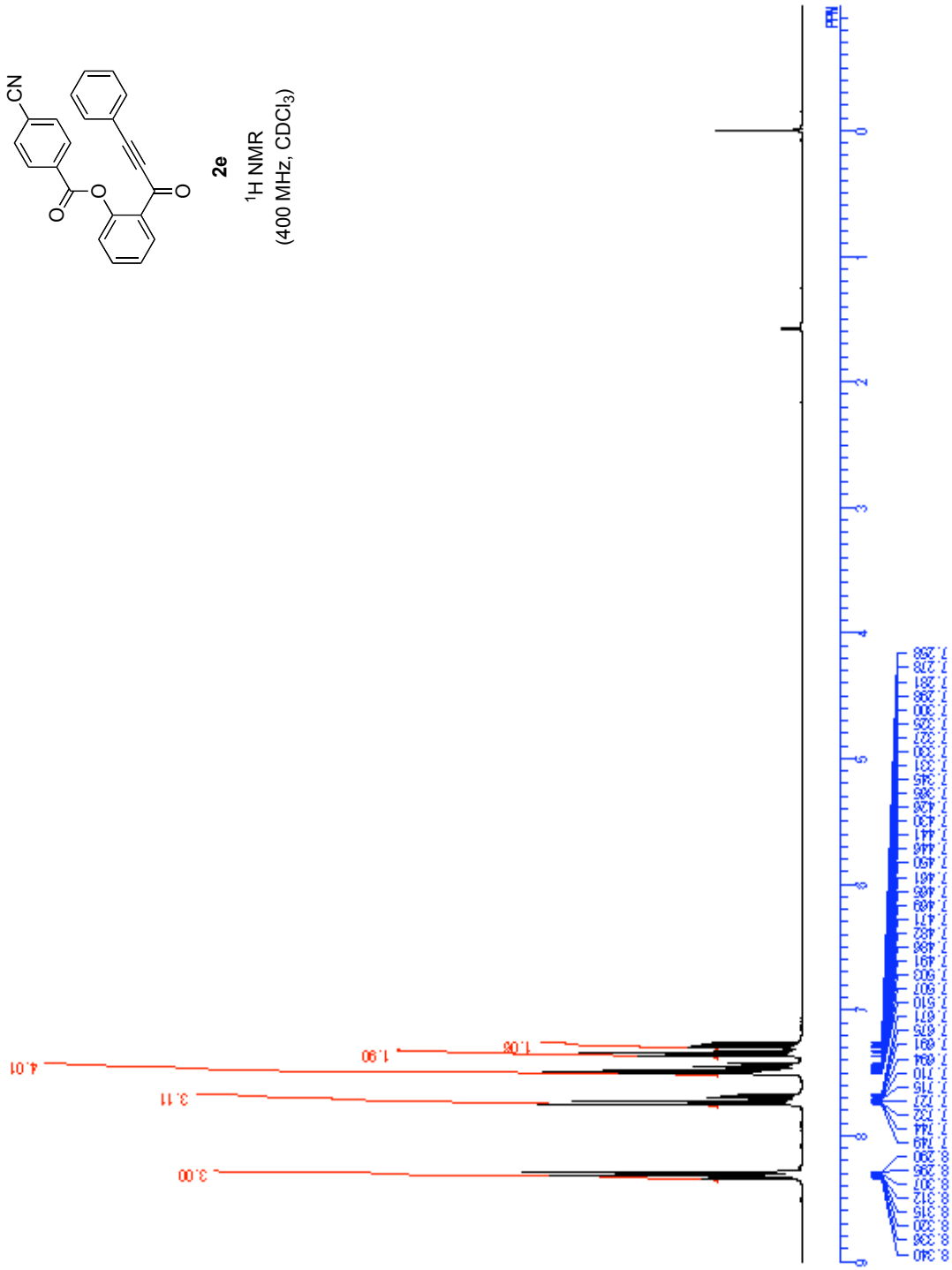


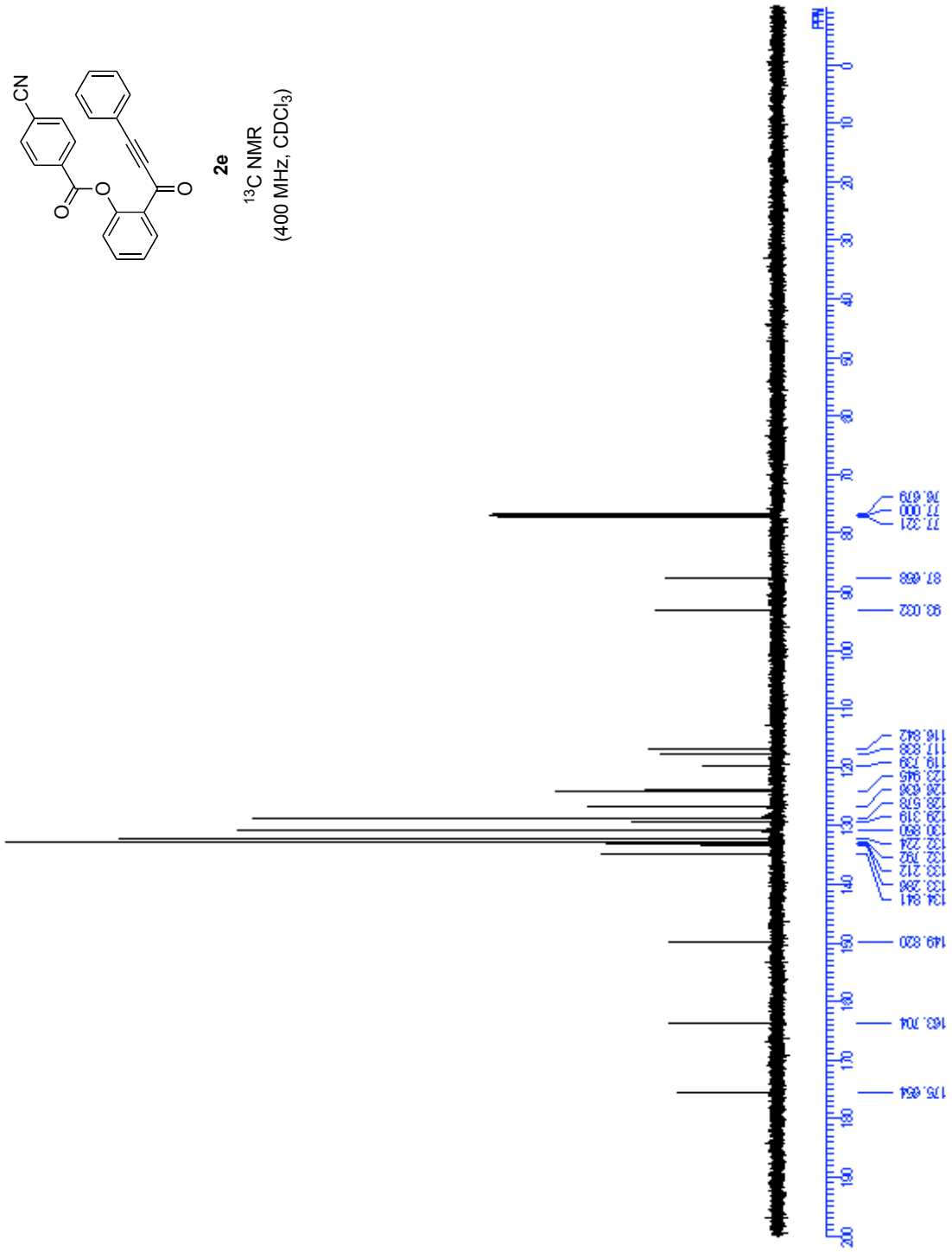
2d

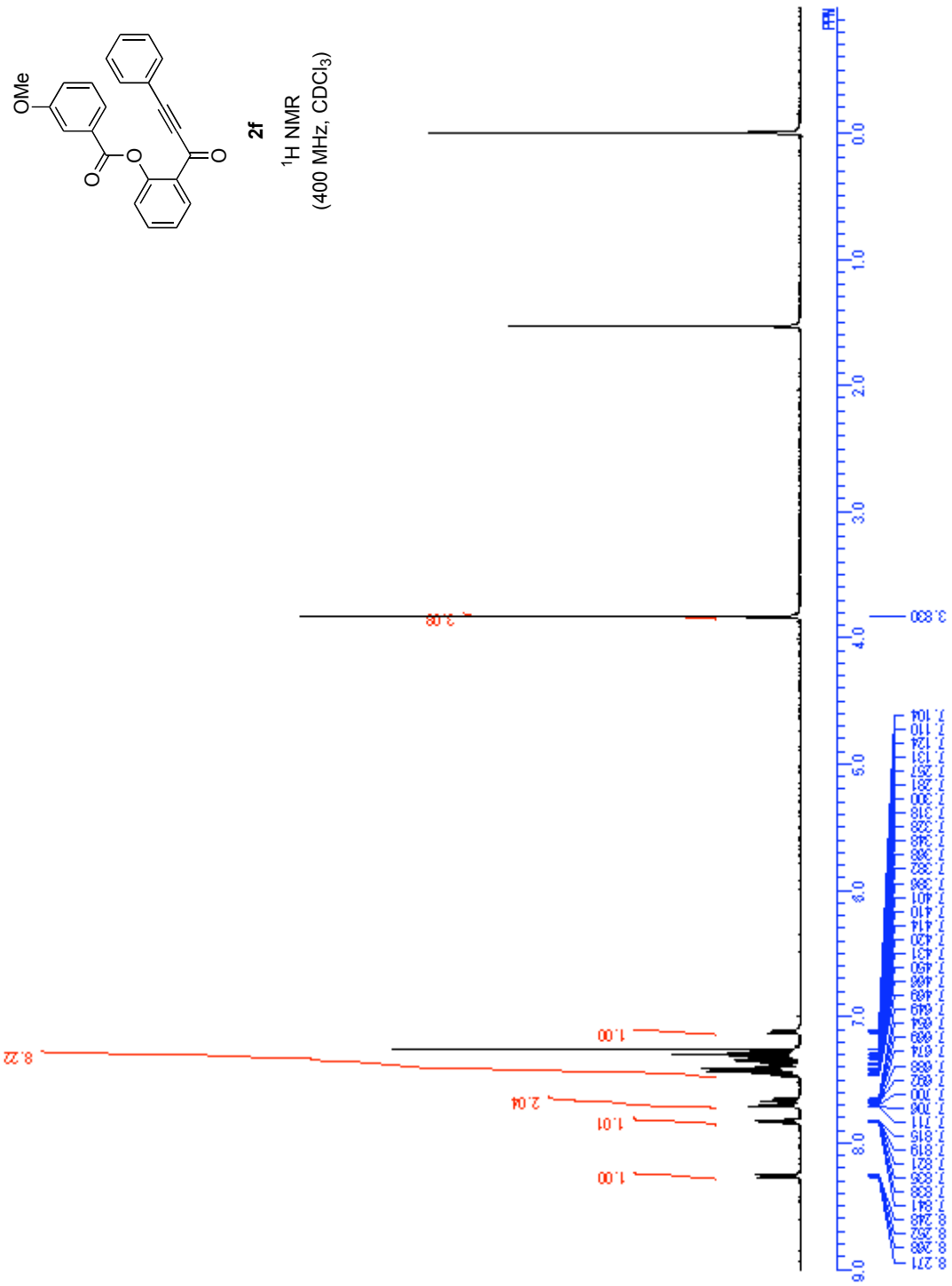
^{13}C NMR

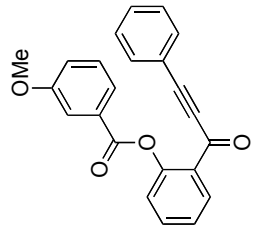
(400 MHz, $CDCl_3$)




CN
O
O
O
2e
^{1}H NMR
(400 MHz, CDCl$_3$)
1.06
1.90
4.01
3.11
3.00

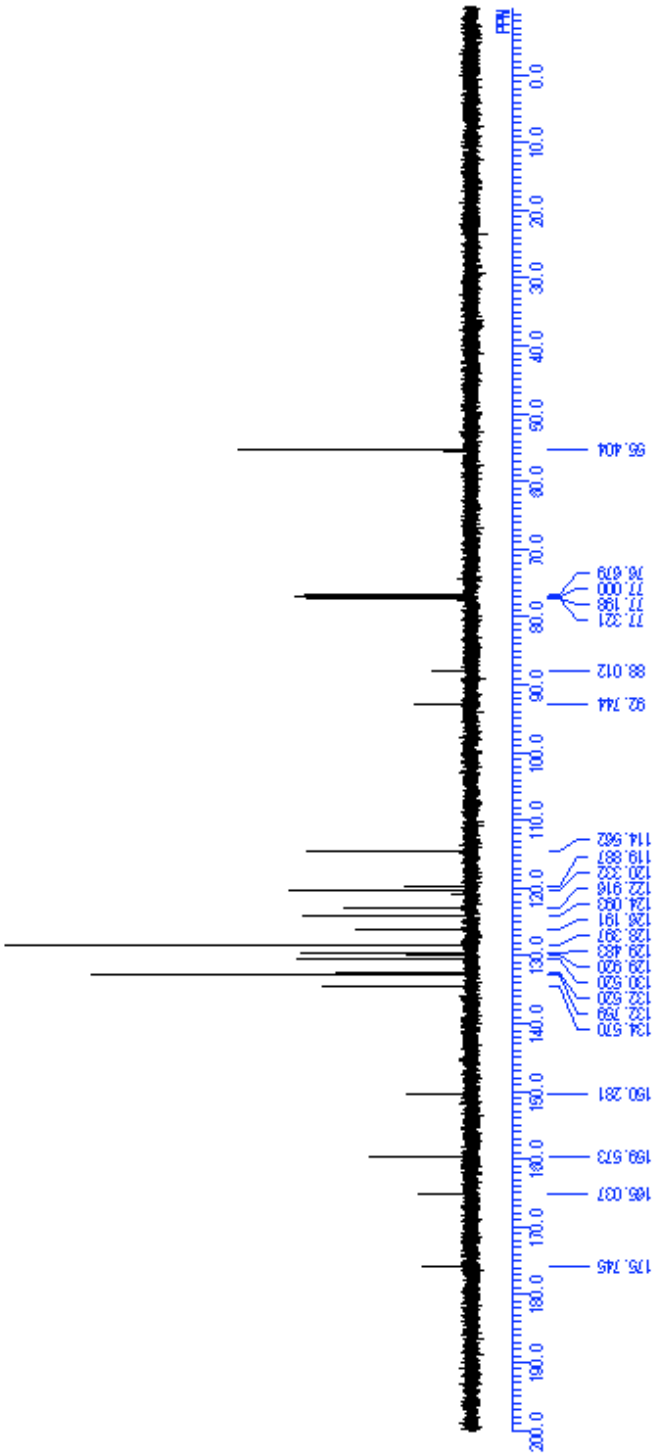

CN
O
O
O
2e
^{13}C NMR
(400 MHz, CDCl$_3$)
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
76.679
77.000
77.321
87.688
92.002
116.842
117.858
119.739
123.945
126.638
128.578
129.319
130.890
132.224
132.742
133.212
133.298
134.841
149.820
163.704
175.654

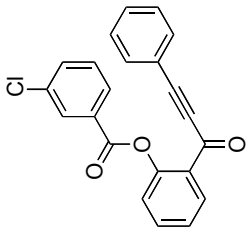

OMe
O
O
O
O
2f
^{1}H NMR
(400 MHz, CDCl$_3$)
8.22
1.00
2.04
1.01
1.00
3.08
3.000
PPM



2f

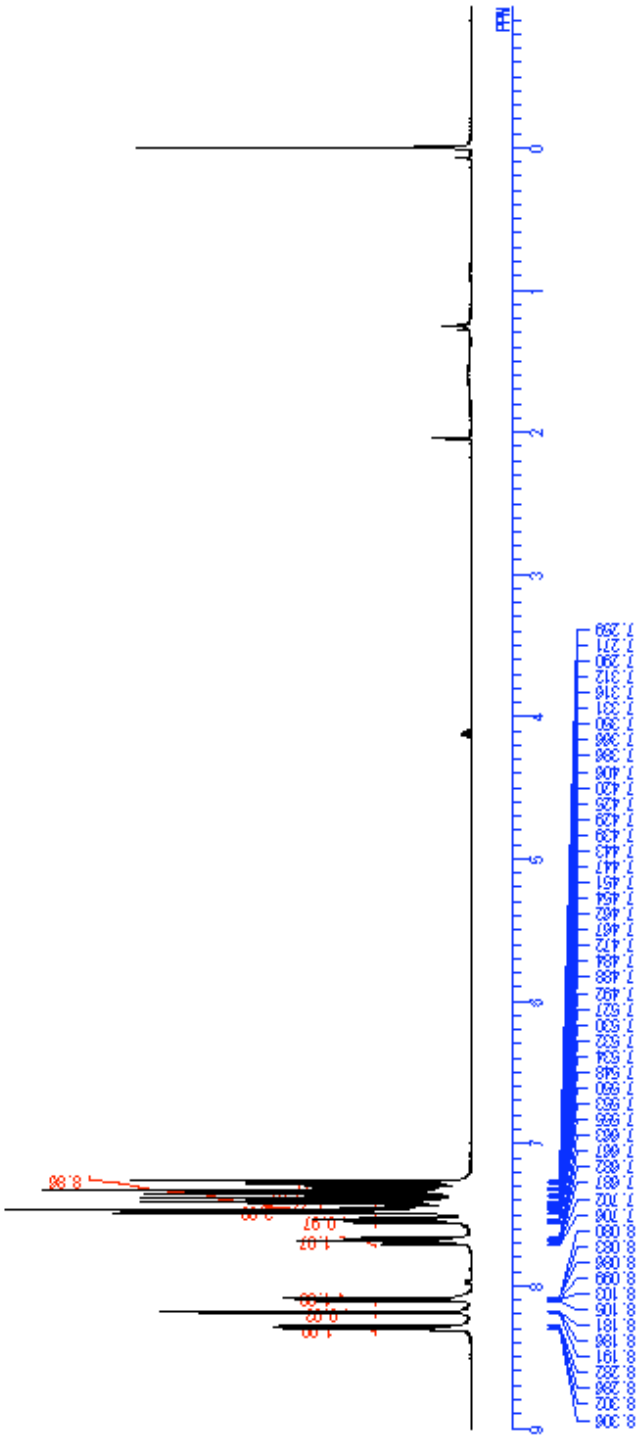
^{13}C NMR
(400 MHz, $CDCl_3$)

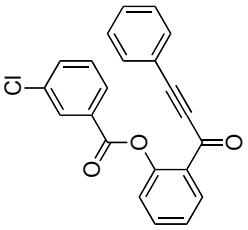




2g

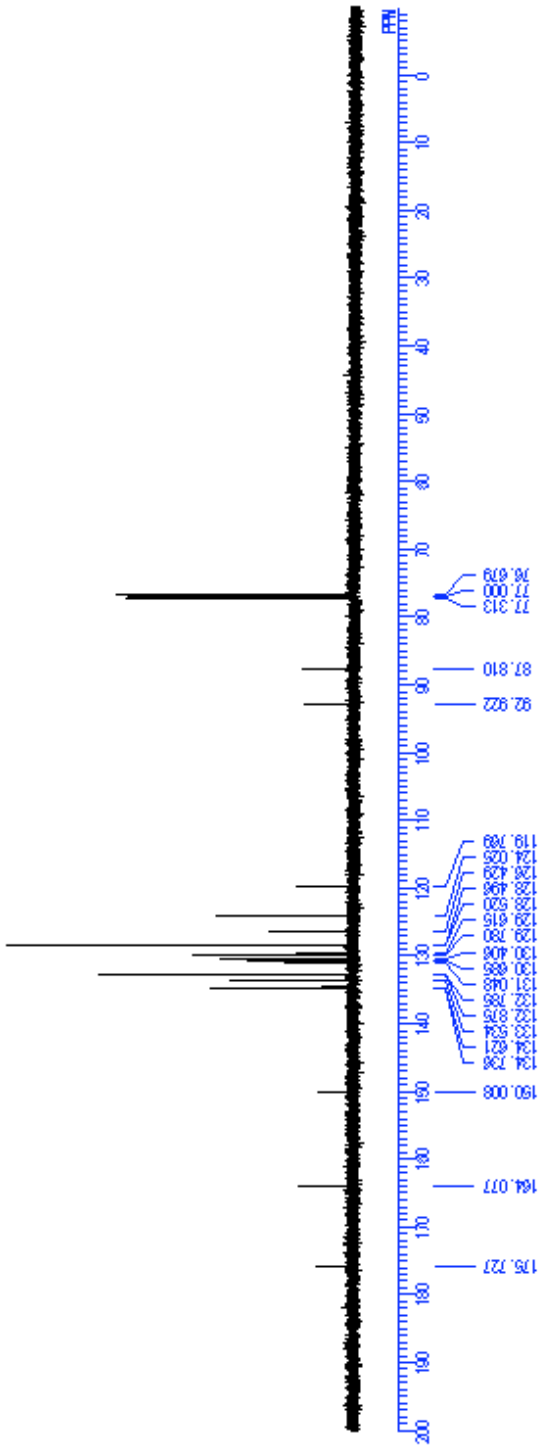
^{1}H NMR
(400 MHz, $CDCl_3$)

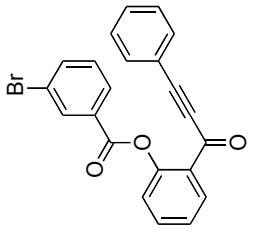




2g

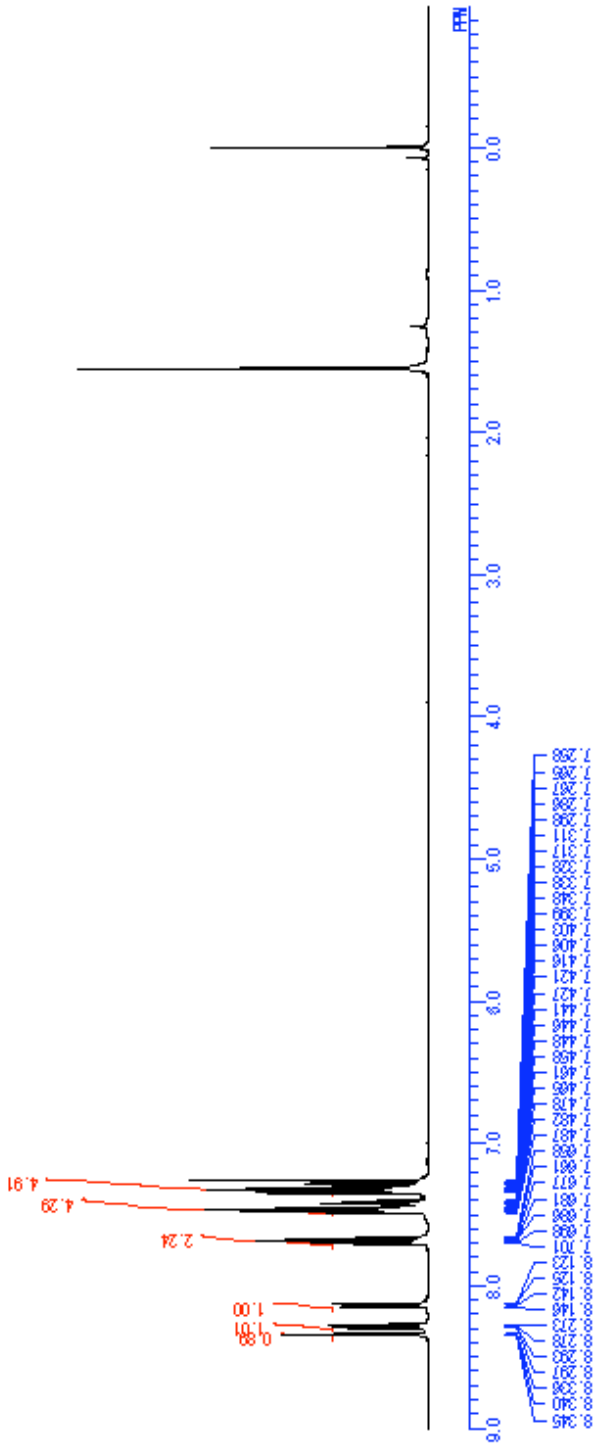
^{13}C NMR
(400 MHz, $CDCl_3$)

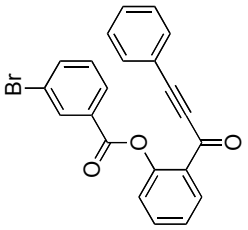




2h

^{1}H NMR
(400 MHz, $CDCl_3$)

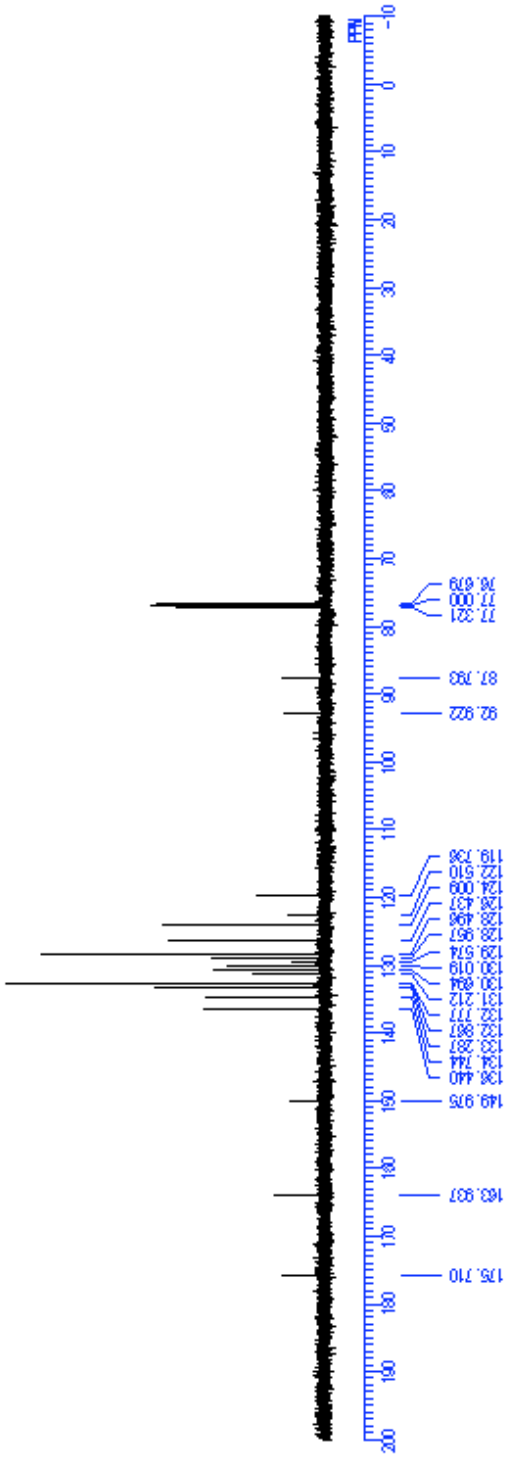


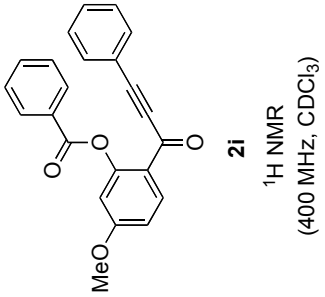


2h

^{13}C NMR

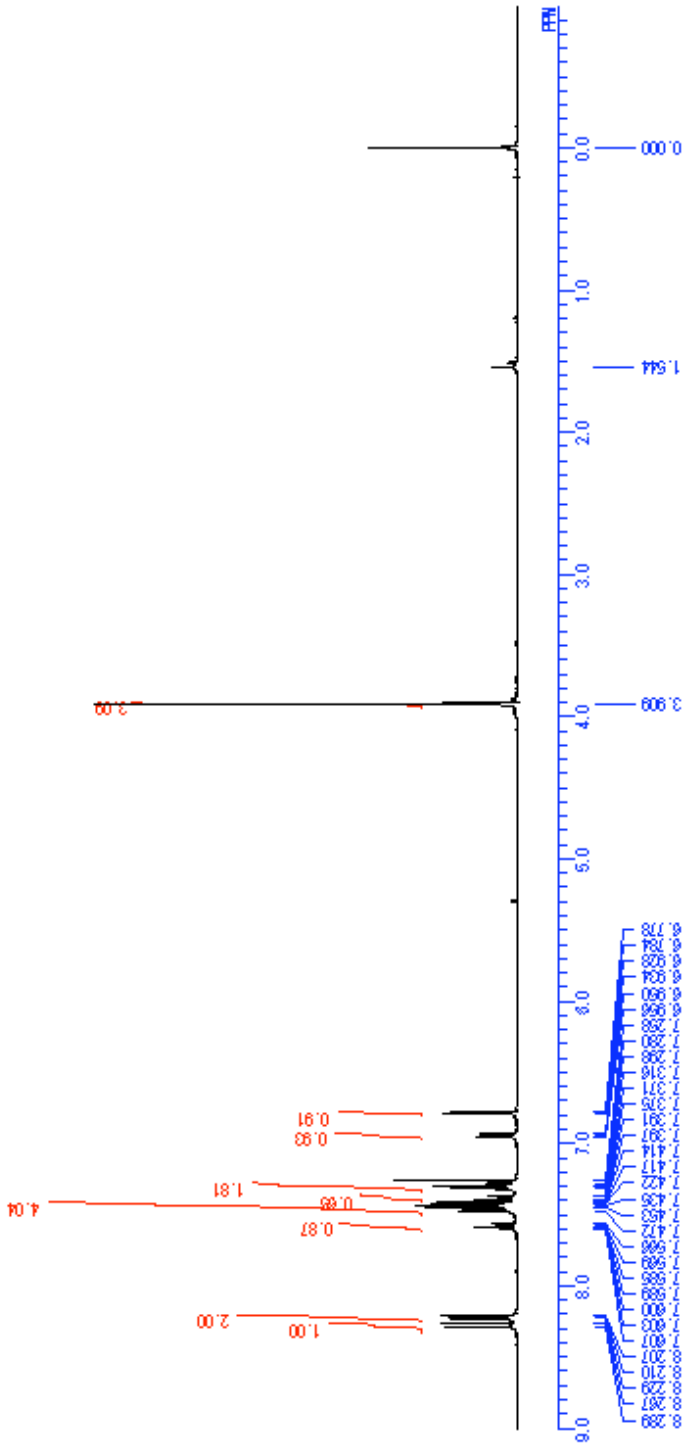
(400 MHz, $CDCl_3$)

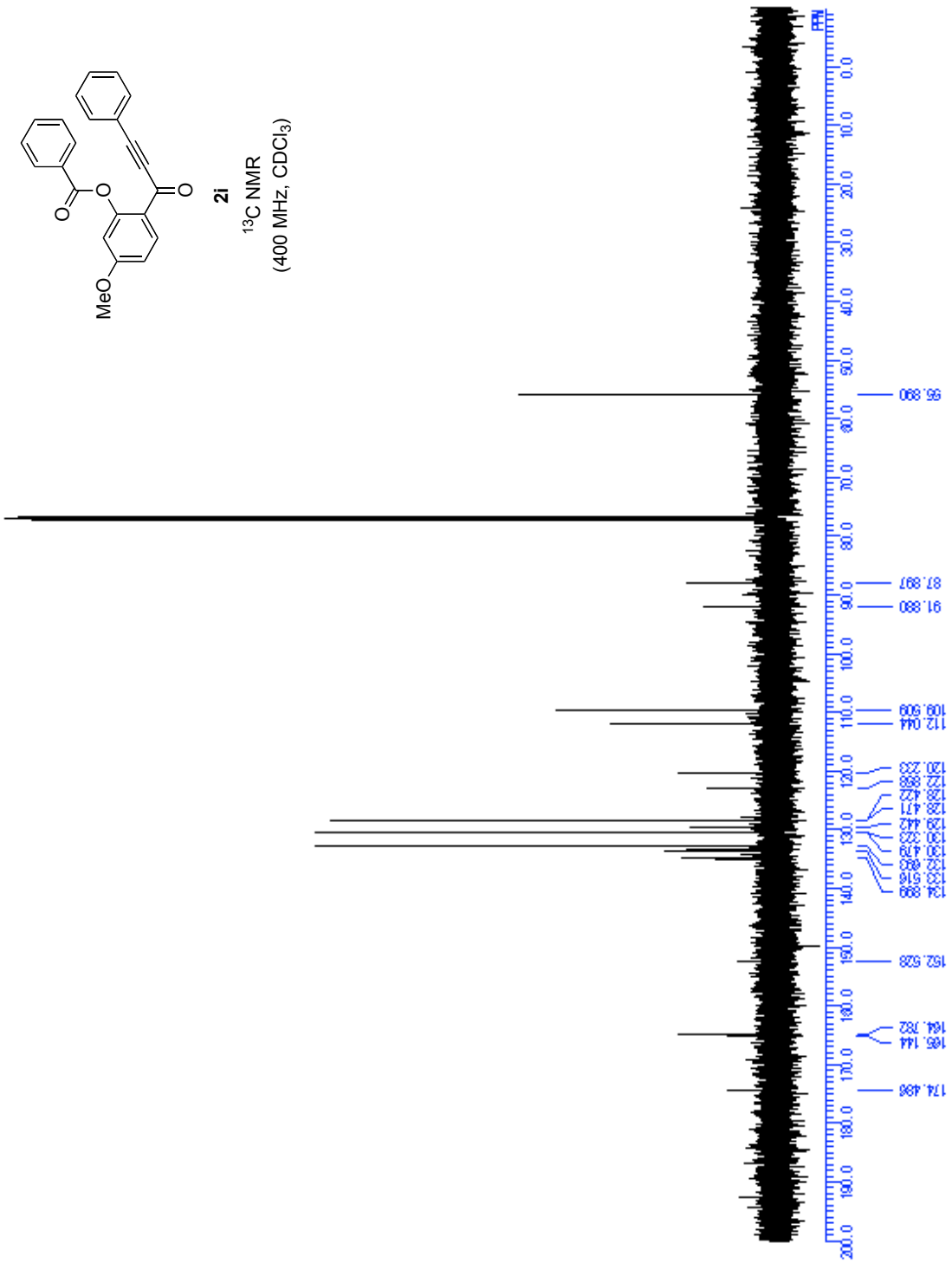


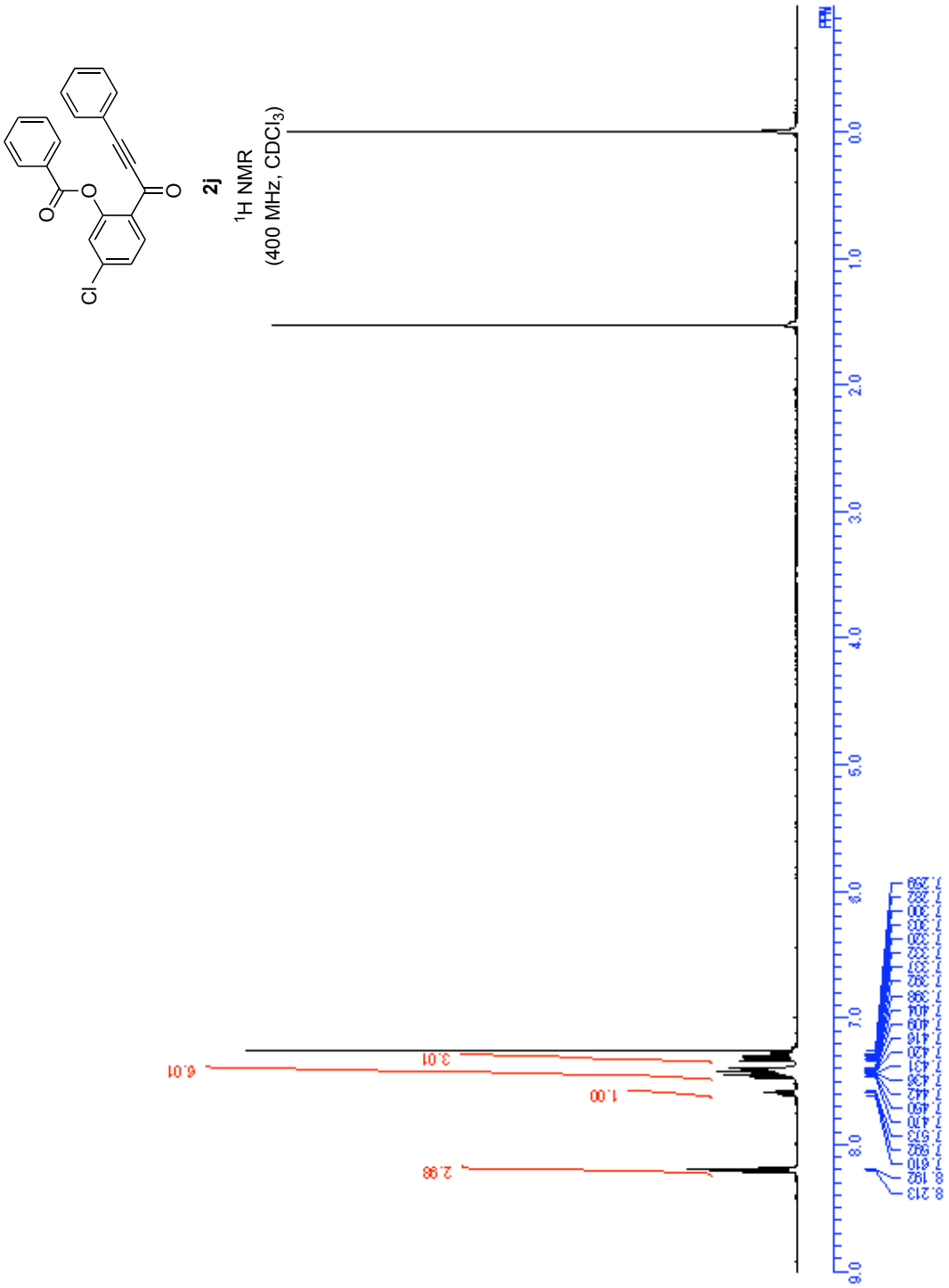


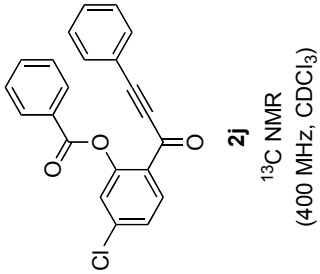
2i

^{1}H NMR
(400 MHz, $CDCl_3$)




MeO
2i
^{13}C NMR
(400 MHz, $CDCl_3$)
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
55.890
87.897
91.880
109.509
112.044
130.233
132.898
133.422
133.471
134.442
135.223
135.479
135.893
136.516
136.899
152.528
164.782
165.144
174.496

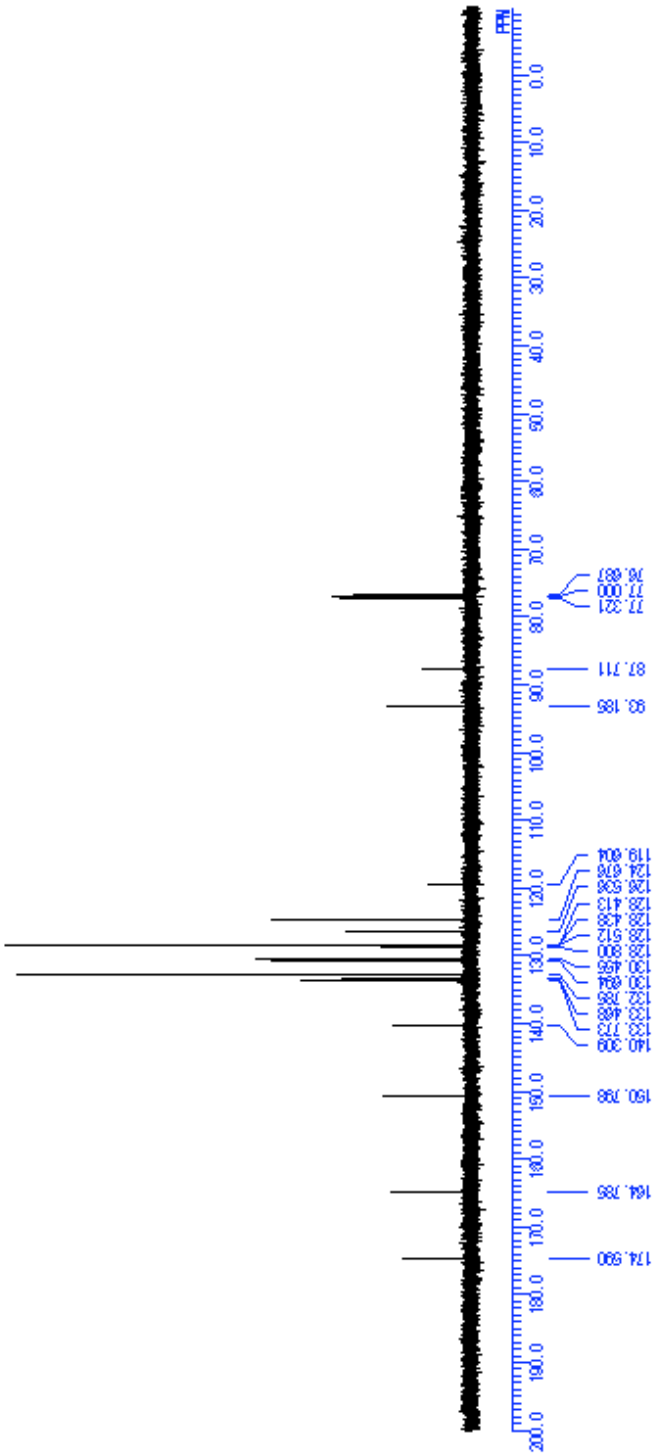

2j
^{1}H NMR
(400 MHz, CDCl$_3$)
Cl
O
O
O
O
6.01
3.01
1.00
2.98

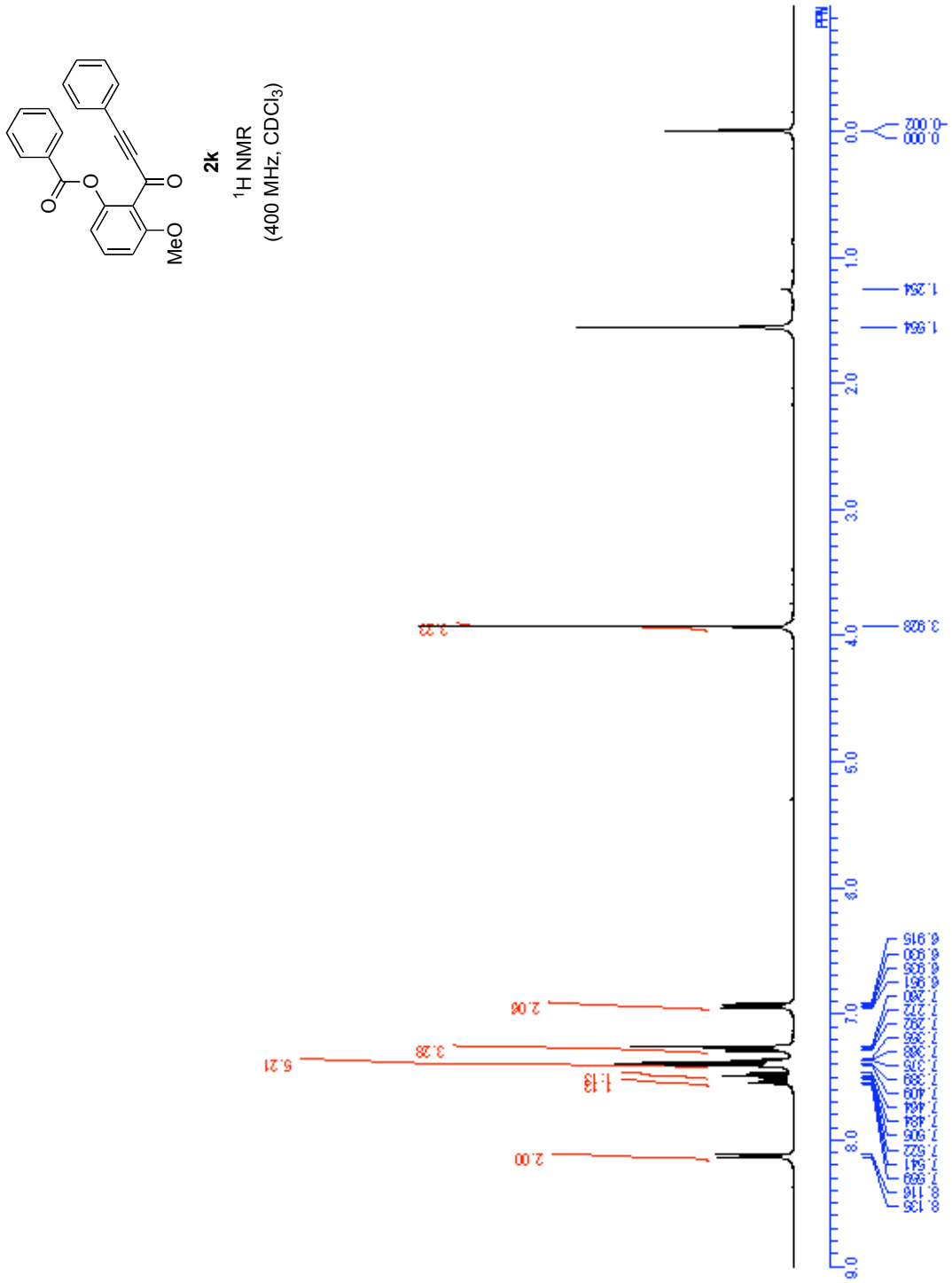


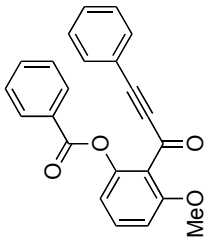
2j

^{13}C NMR

(400 MHz, $CDCl_3$)



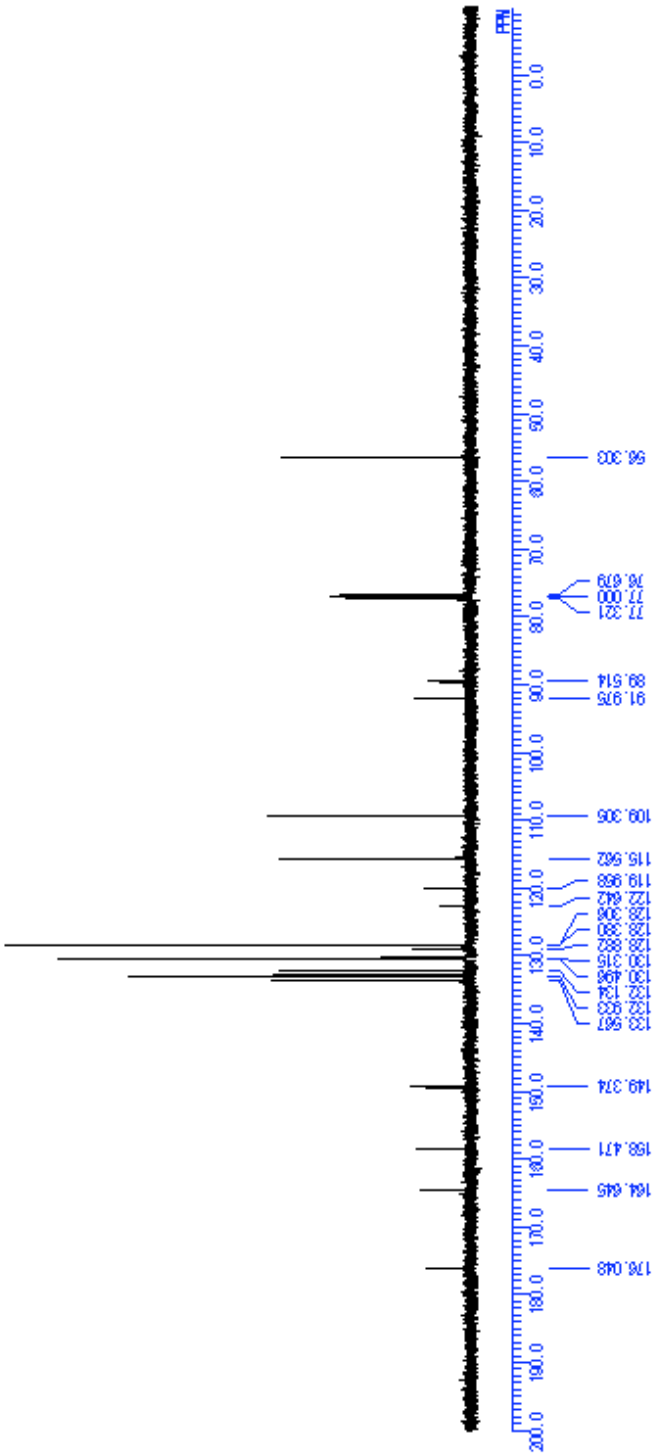

MeO
2k
^{1}H NMR
(400 MHz, CDCl$_3$)
2.00
1.13
3.28
5.21
2.08
3.23
1.954
1.964
3.928
0.000
-0.002

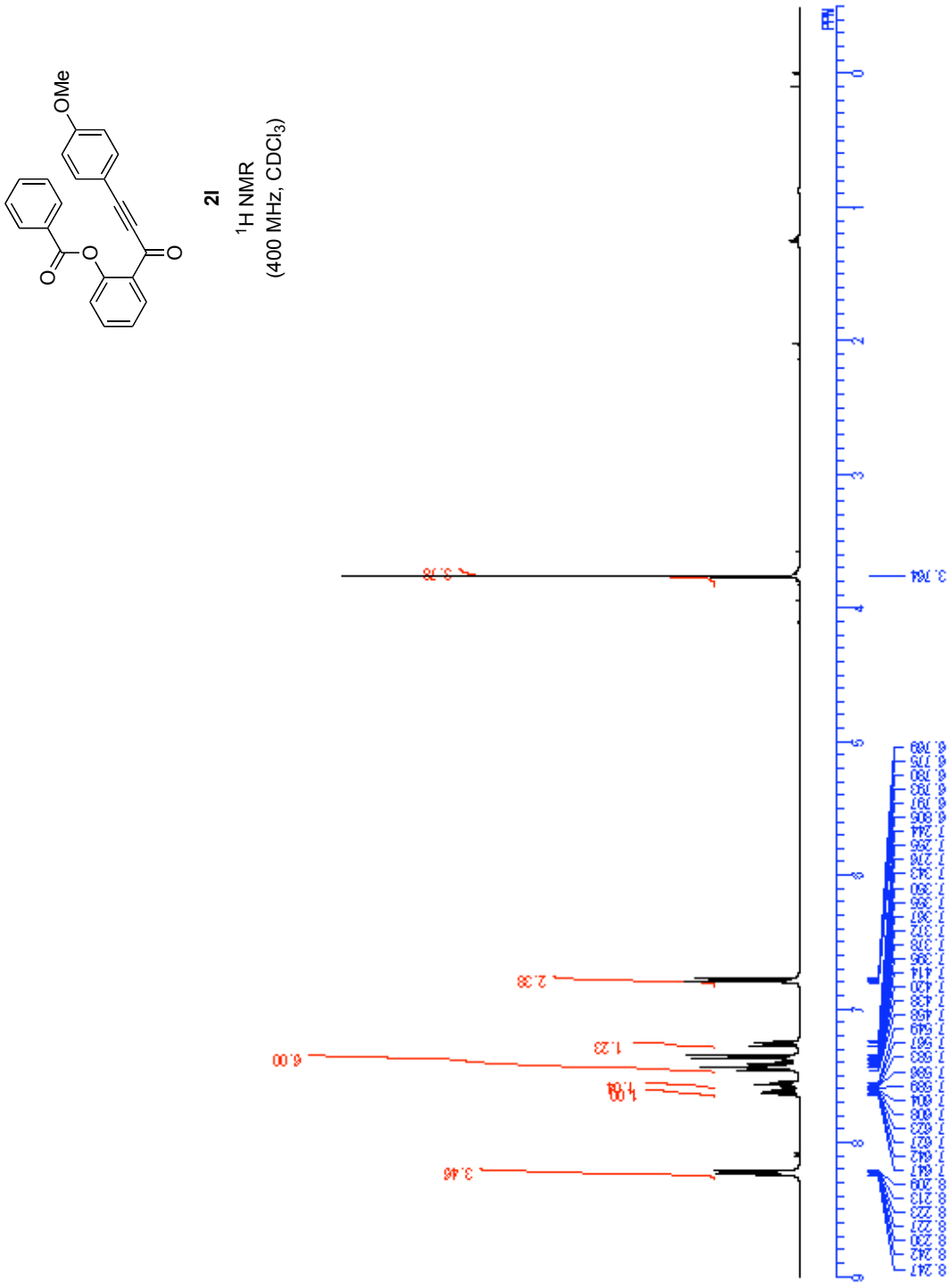


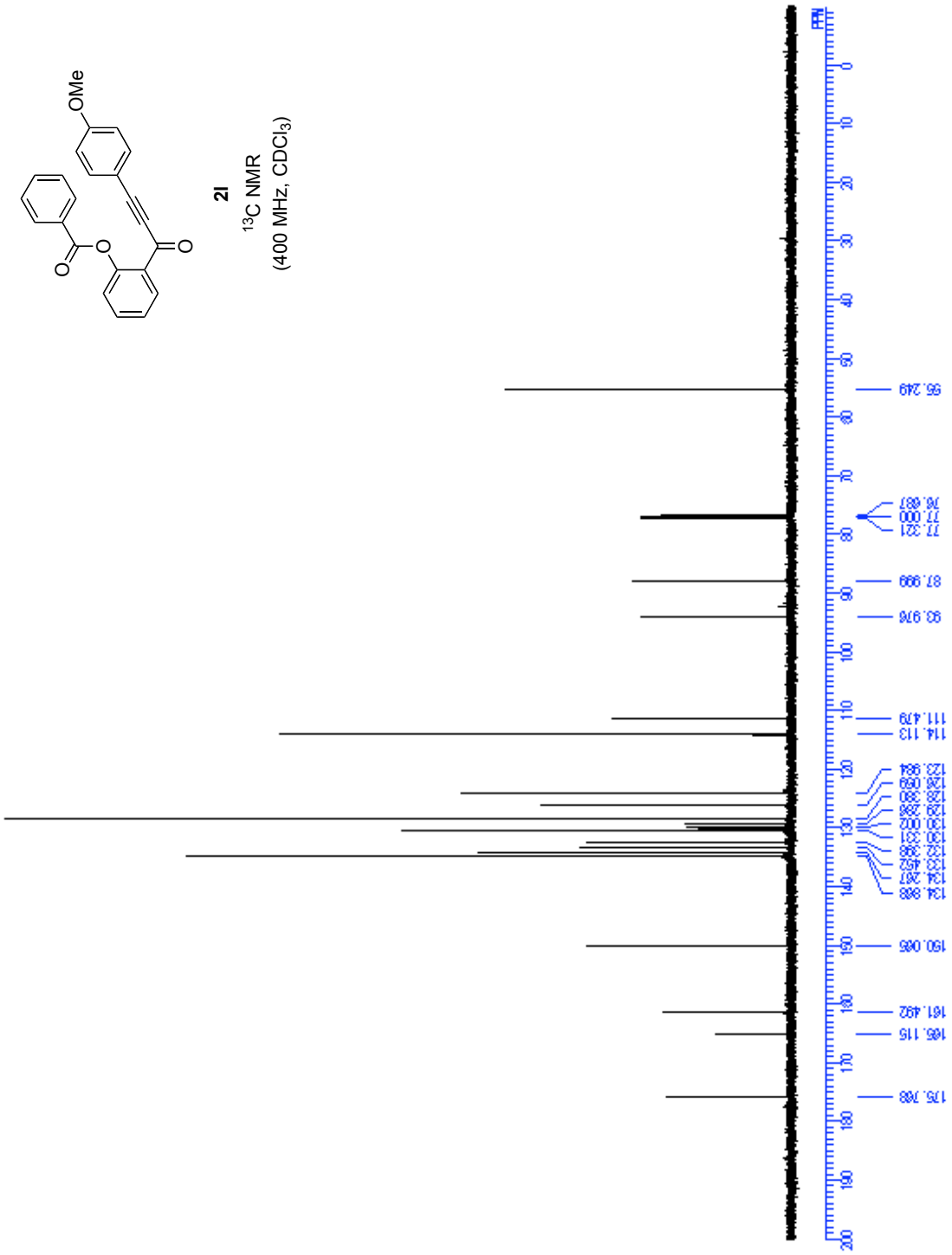
2k

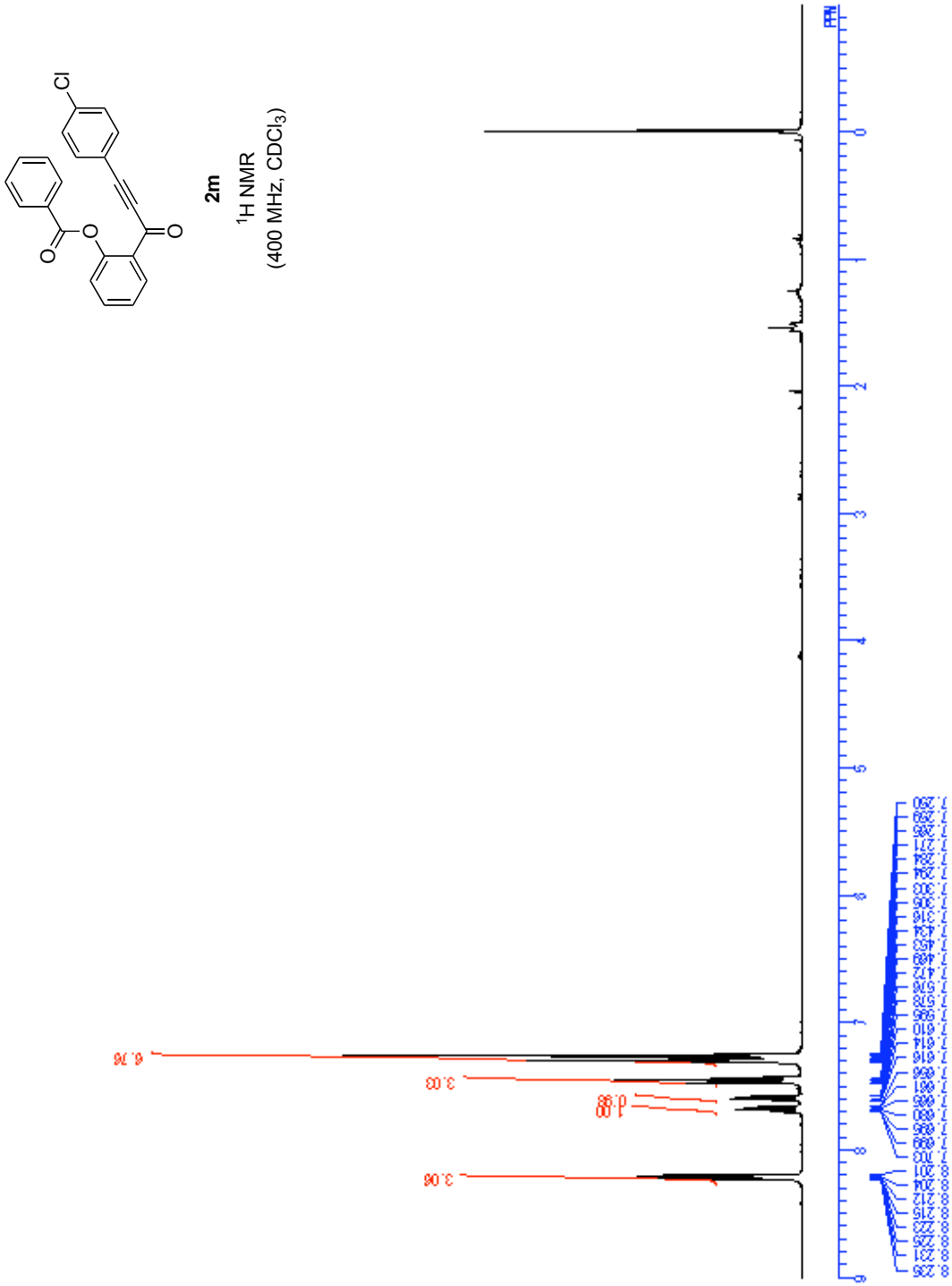
^{13}C NMR

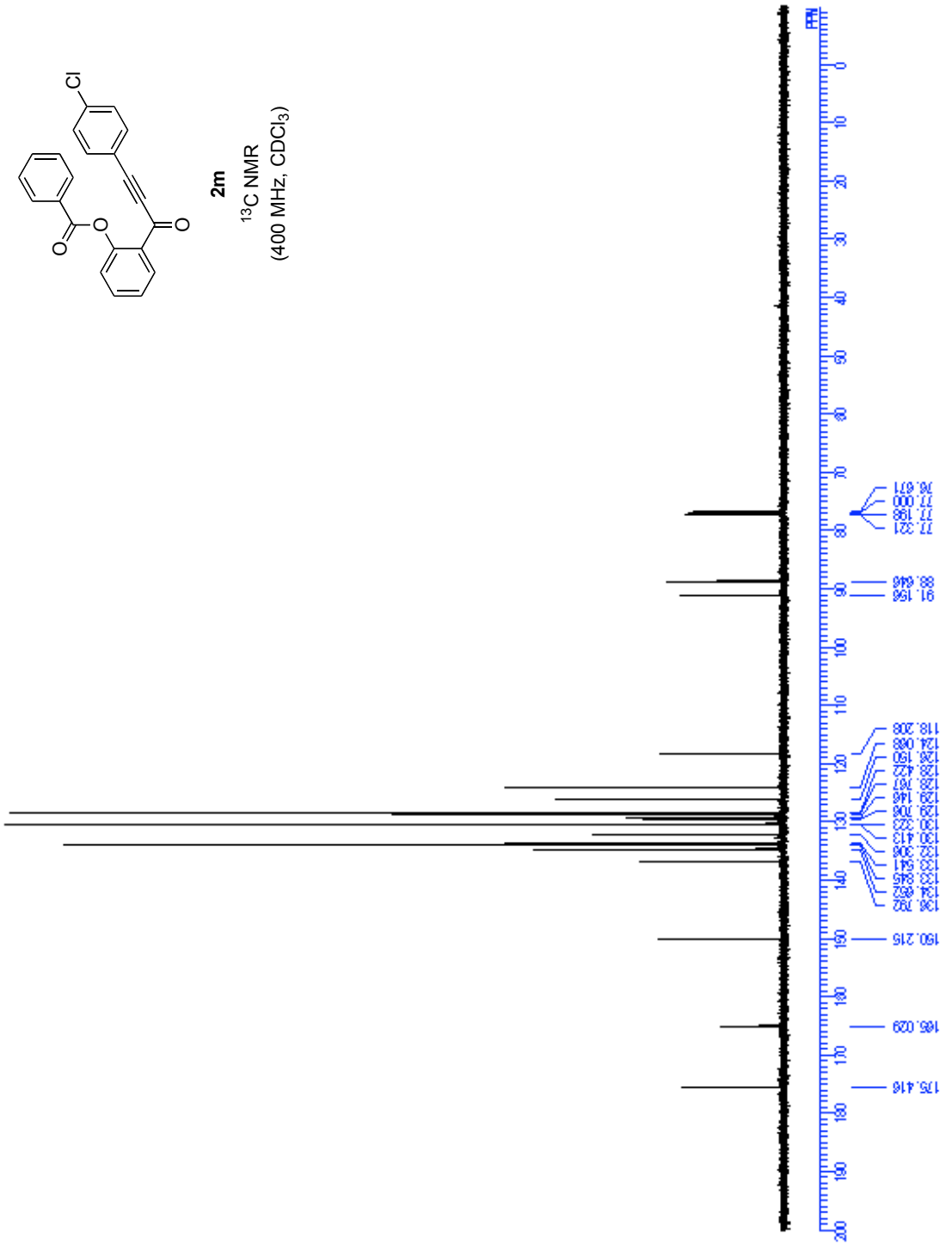
(400 MHz, $CDCl_3$)

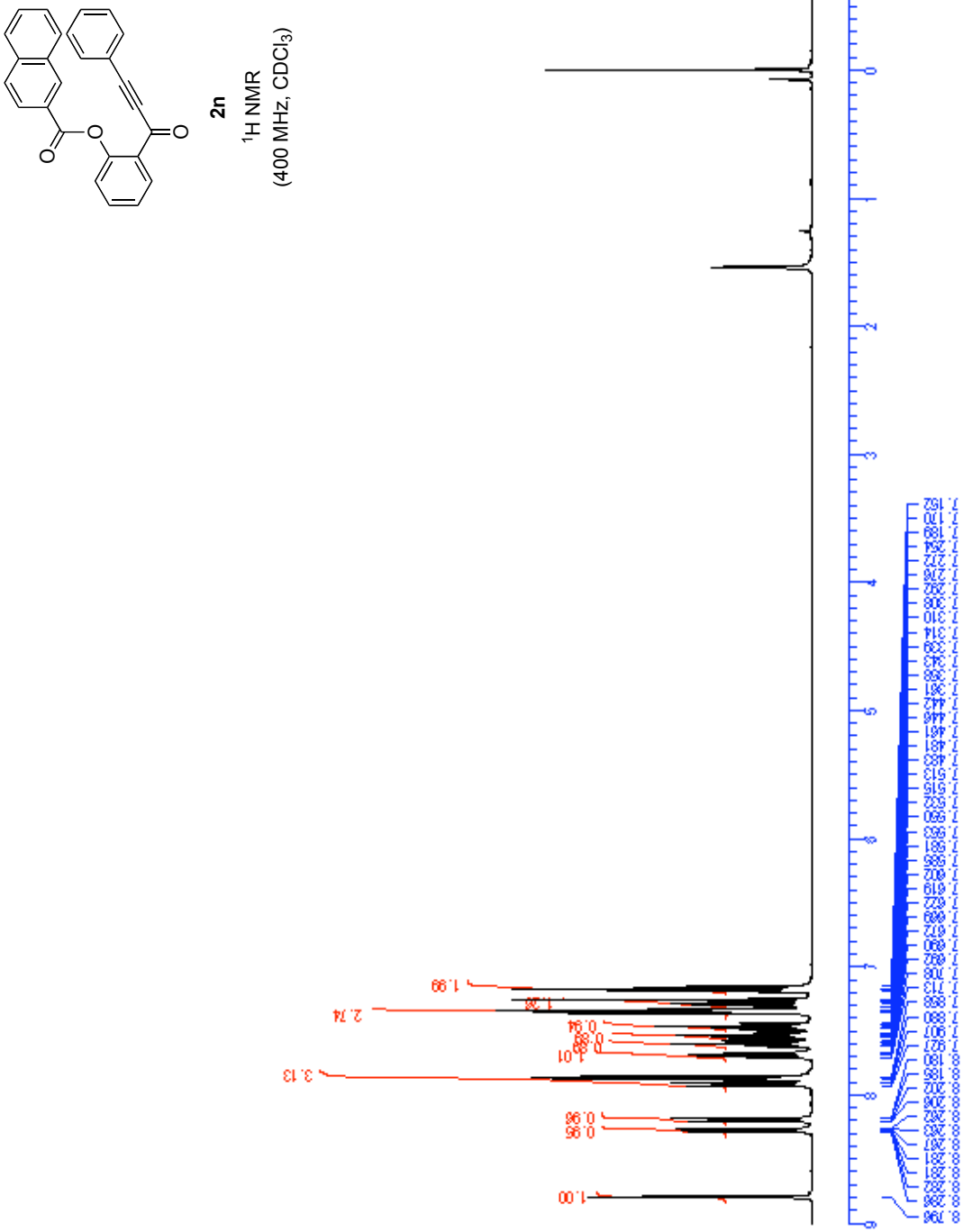


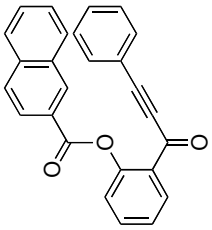

OMe
O
O
O
2l
^{1}H NMR
(400 MHz, CDCl$_3$)
3.78
2.38
1.23
6.00
4.04
3.46
3.784


OMe
O
O
O
2l
^{13}C NMR
(400 MHz, CDCl$_3$)
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
55.249
76.687
77.000
77.321
87.999
93.976
111.479
114.113
123.984
126.099
128.380
129.298
130.002
130.231
132.398
133.492
134.287
134.888
160.065
161.492
165.115
175.788


Cl
O
O
O
2m
^{1}H NMR
(400 MHz, CDCl$_3$)
6.76
3.03
0.98
3.06

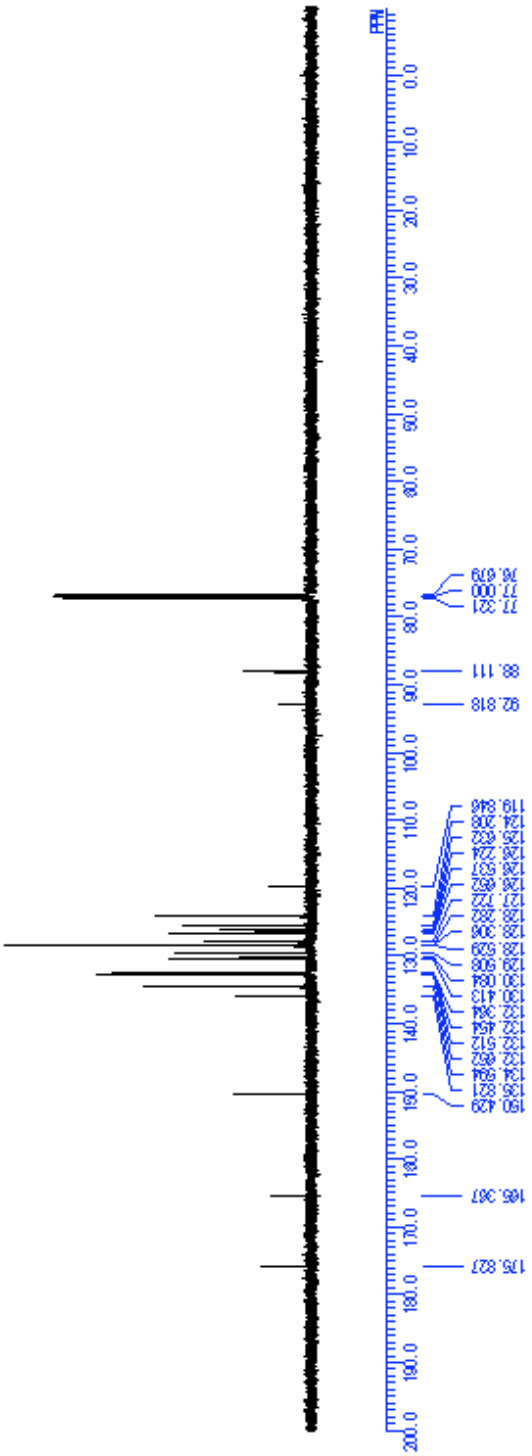

Cl
O
O
O
2m
^{13}C NMR
(400 MHz, CDCl$_3$)
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
77.321
77.000
76.671
91.196
88.646
118.208
124.088
128.190
128.422
128.767
129.146
129.708
130.223
130.413
132.306
133.641
133.845
134.892
136.392
150.215
165.029
175.416

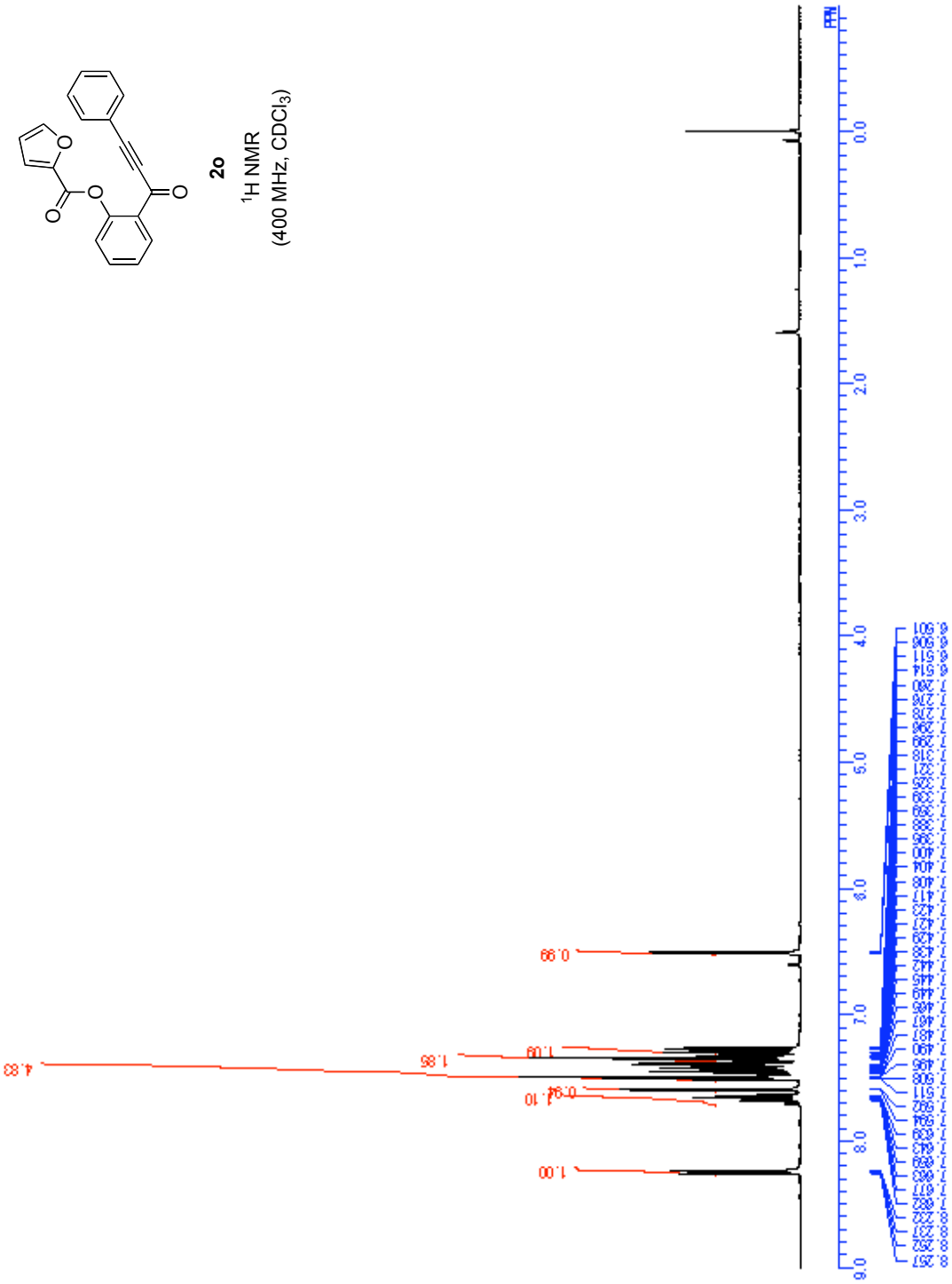

2n
^{1}H NMR
(400 MHz, CDCl$_3$)
1.99
1.99
2.74
0.94
0.89
1.01
3.13
0.95
0.98
1.00

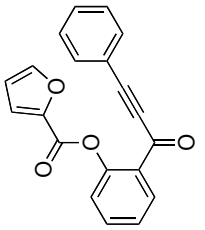


2n

^{13}C NMR
(400 MHz, $CDCl_3$)

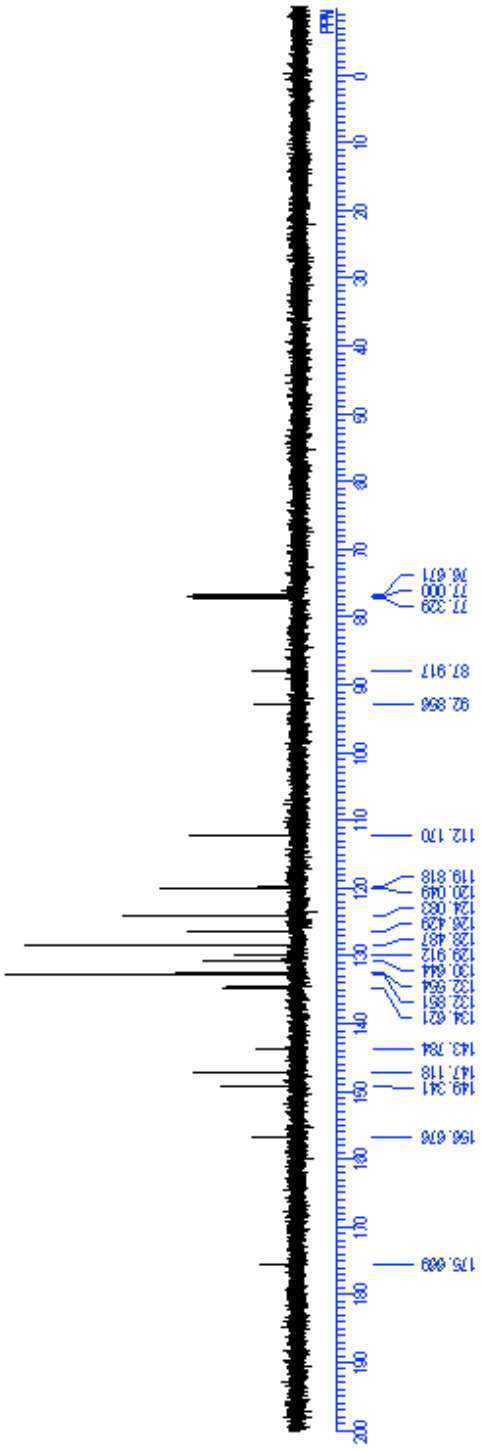


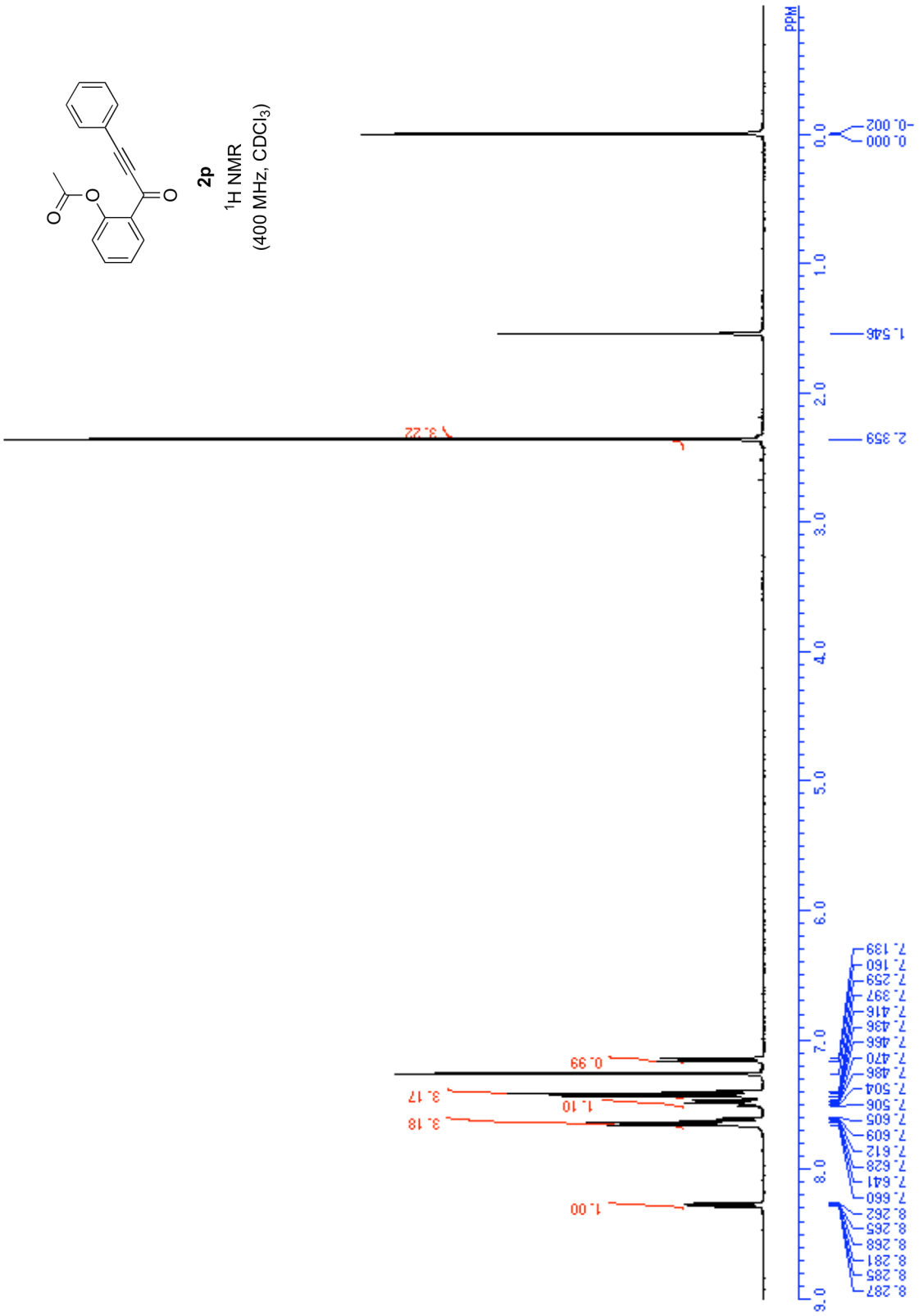

2o
^{1}H NMR
(400 MHz, $CDCl_3$)
4.83
1.86
1.09
0.94
1.00
0.99

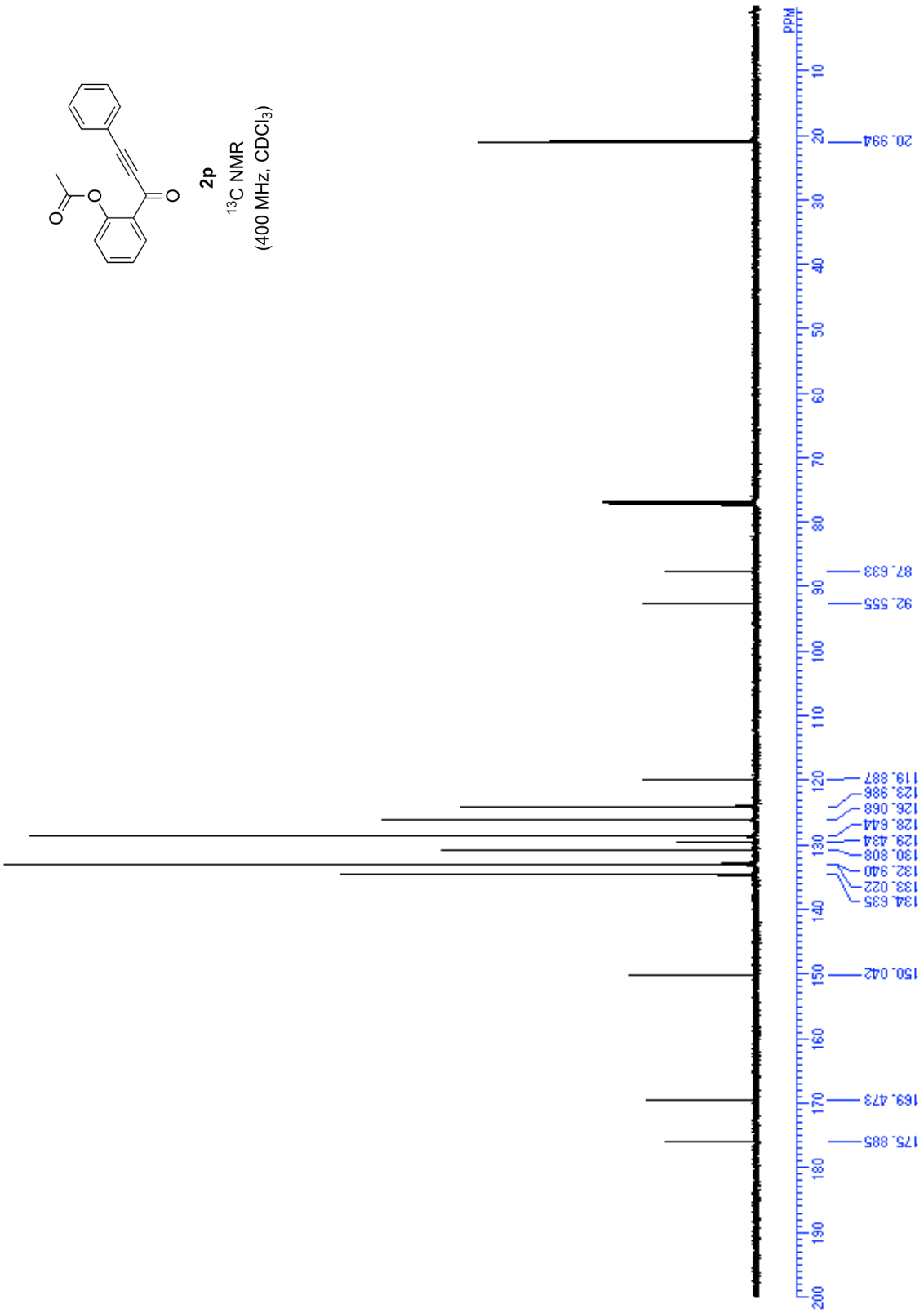


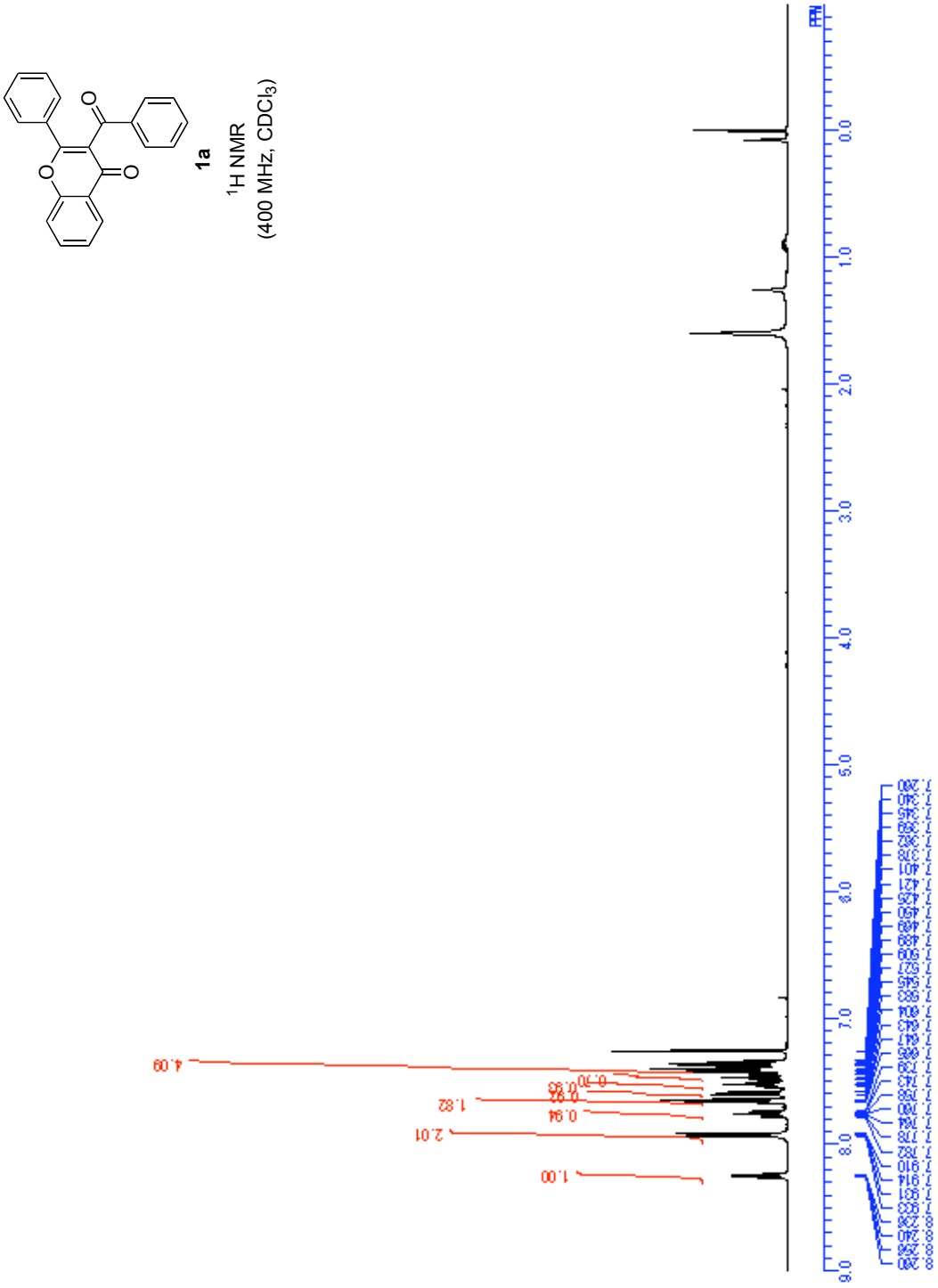
2o

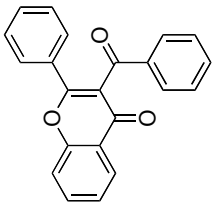
^{13}C NMR
(400 MHz, $CDCl_3$)




2p
^{1}H NMR
(400 MHz, CDCl$_3$)
PPM
0.000
-0.002
1.546
2.359
3.22
0.99
3.17
1.10
3.18
1.00
7.139
7.160
7.259
7.397
7.416
7.436
7.466
7.470
7.486
7.504
7.506
7.605
7.609
7.612
7.628
7.641
7.660
8.262
8.265
8.268
8.281
8.285
8.287

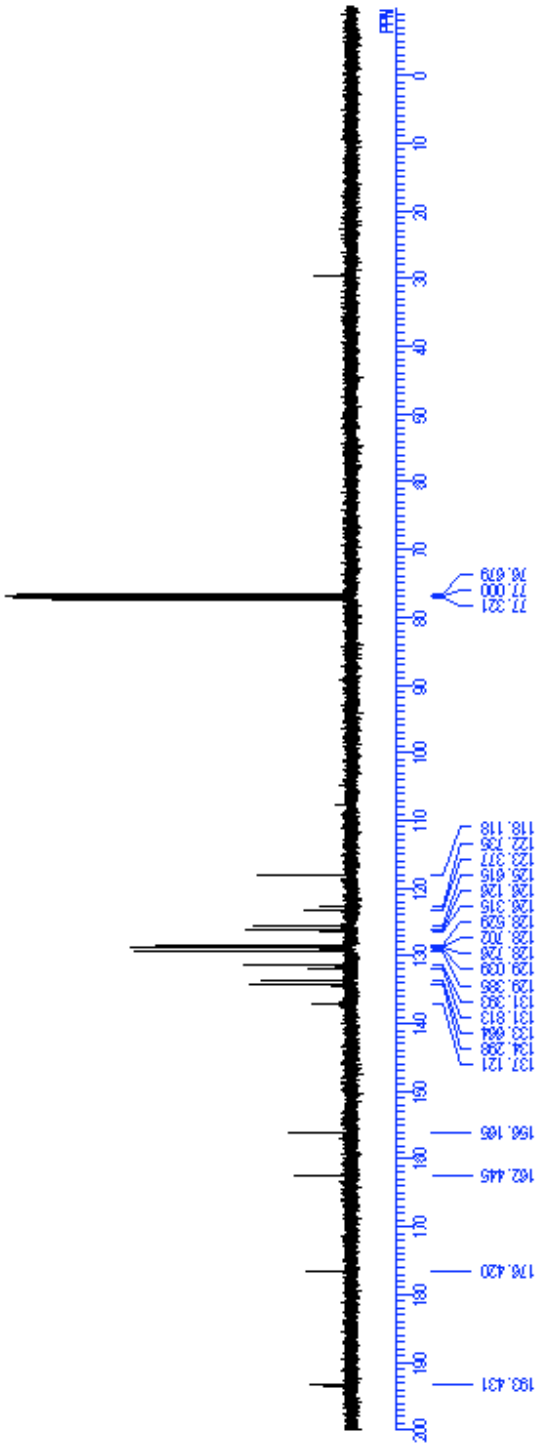

2p
^{13}C NMR
(400 MHz, CDCl$_3$)
PPM
20.994
87.633
92.555
119.887
123.986
126.068
128.644
129.434
130.808
132.940
133.022
134.635
150.042
169.473
175.885

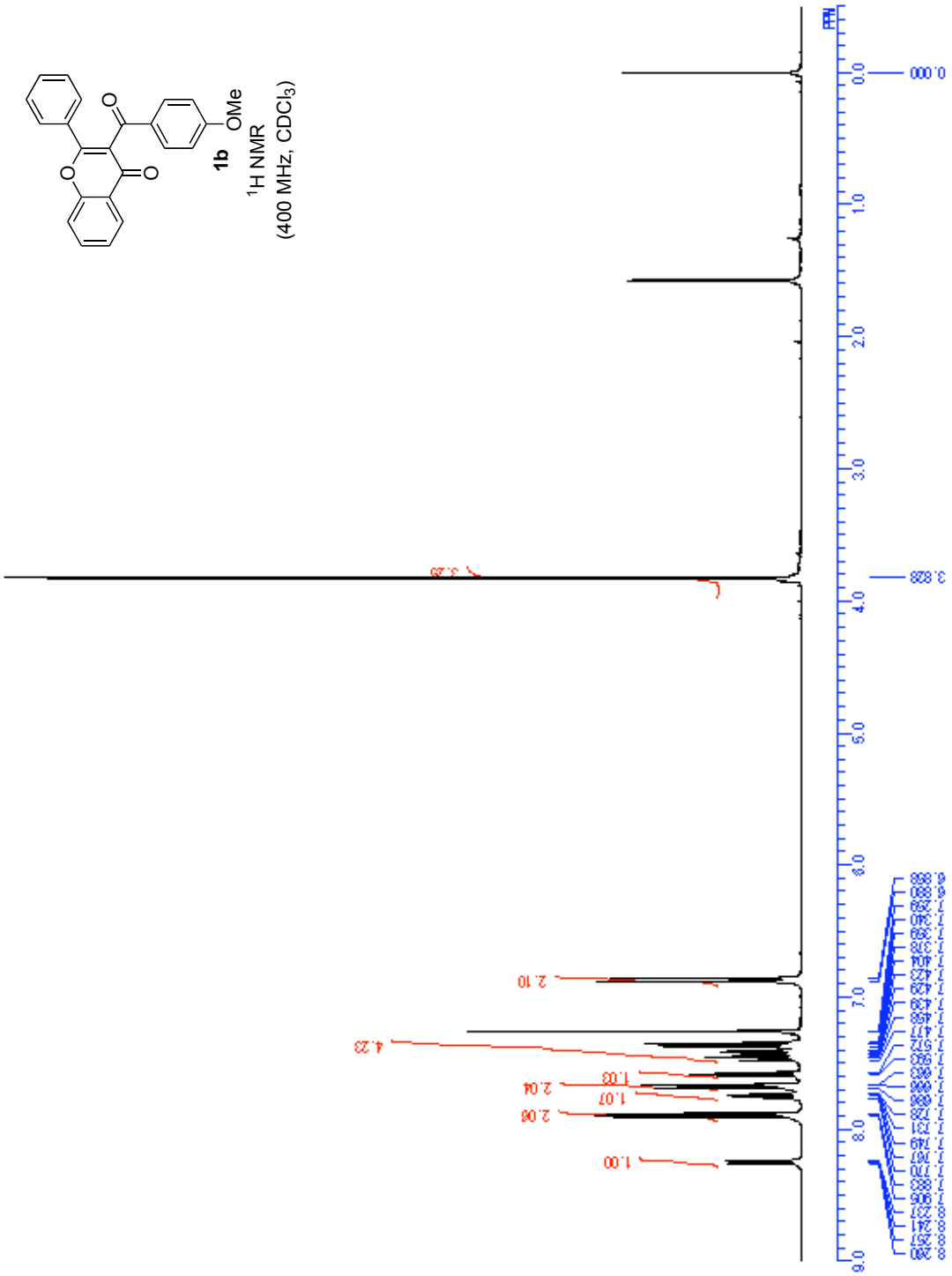

1a
^{1}H NMR
(400 MHz, CDCl$_3$)
4.09
0.30
0.86
0.92
1.82
0.94
2.01
1.00

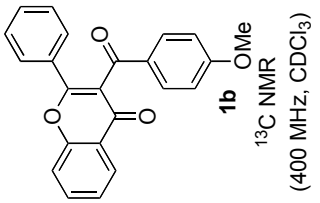


1a

^{13}C NMR
(400 MHz, $CDCl_3$)



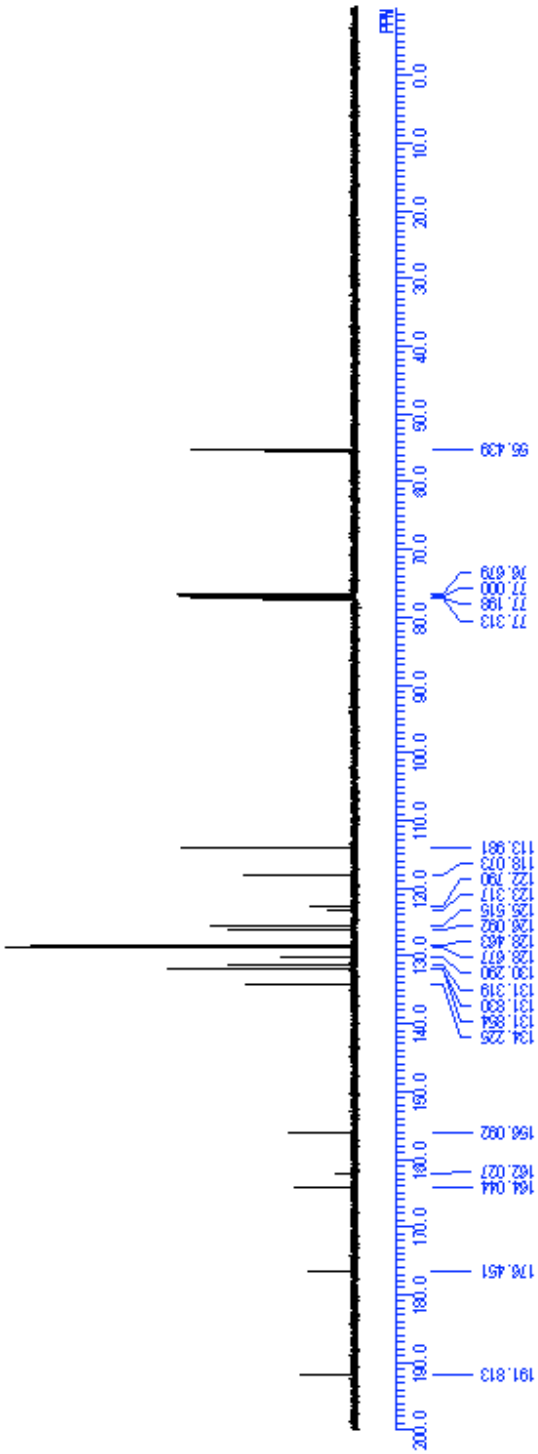

OMe
1b
^{1}H NMR
(400 MHz, CDCl$_3$)
3.89
2.10
4.23
1.00
2.04
1.07
2.08
1.00

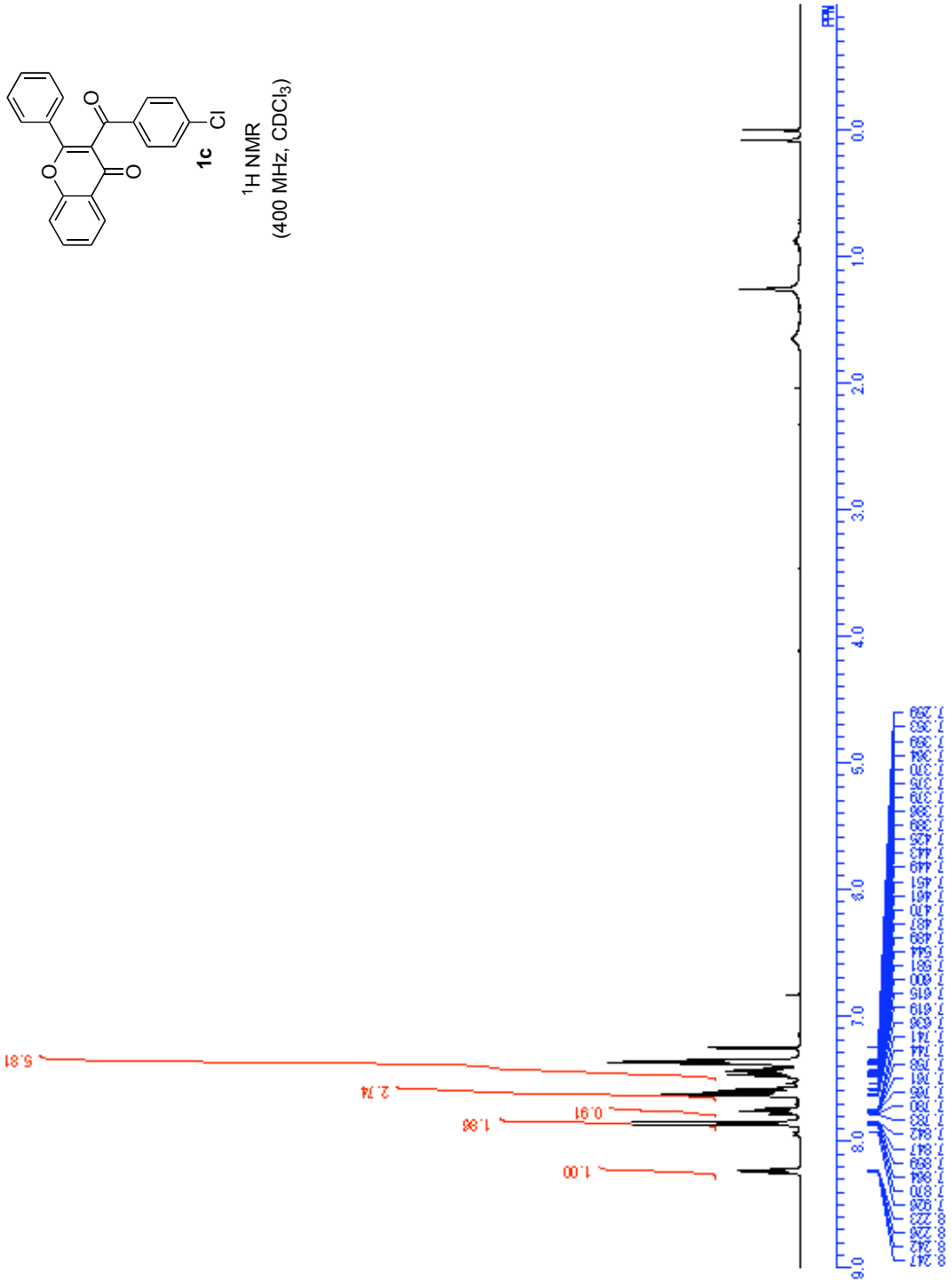


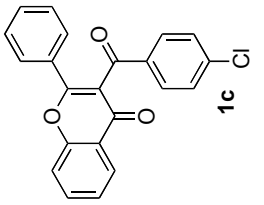
1b

^{13}C NMR

(400 MHz, $CDCl_3$)

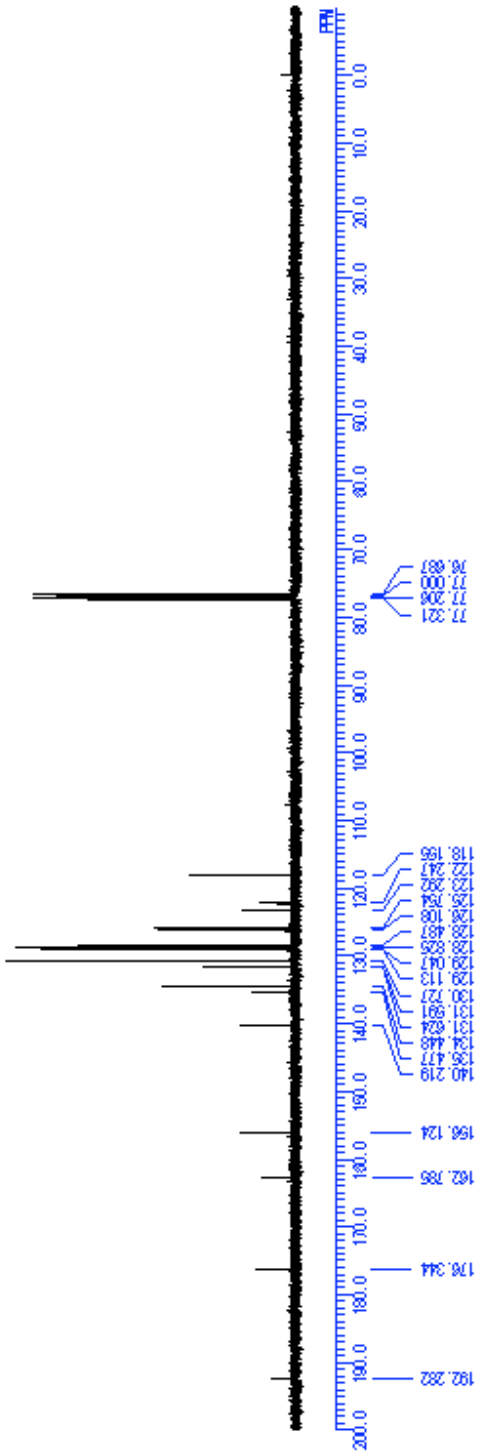


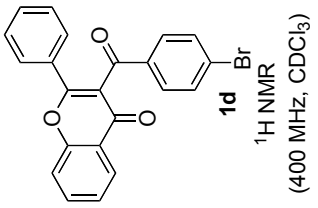

1c
Cl
^{1}H NMR
(400 MHz, $CDCl_3$)
5.81
2.74
0.91
1.88
1.00



1c

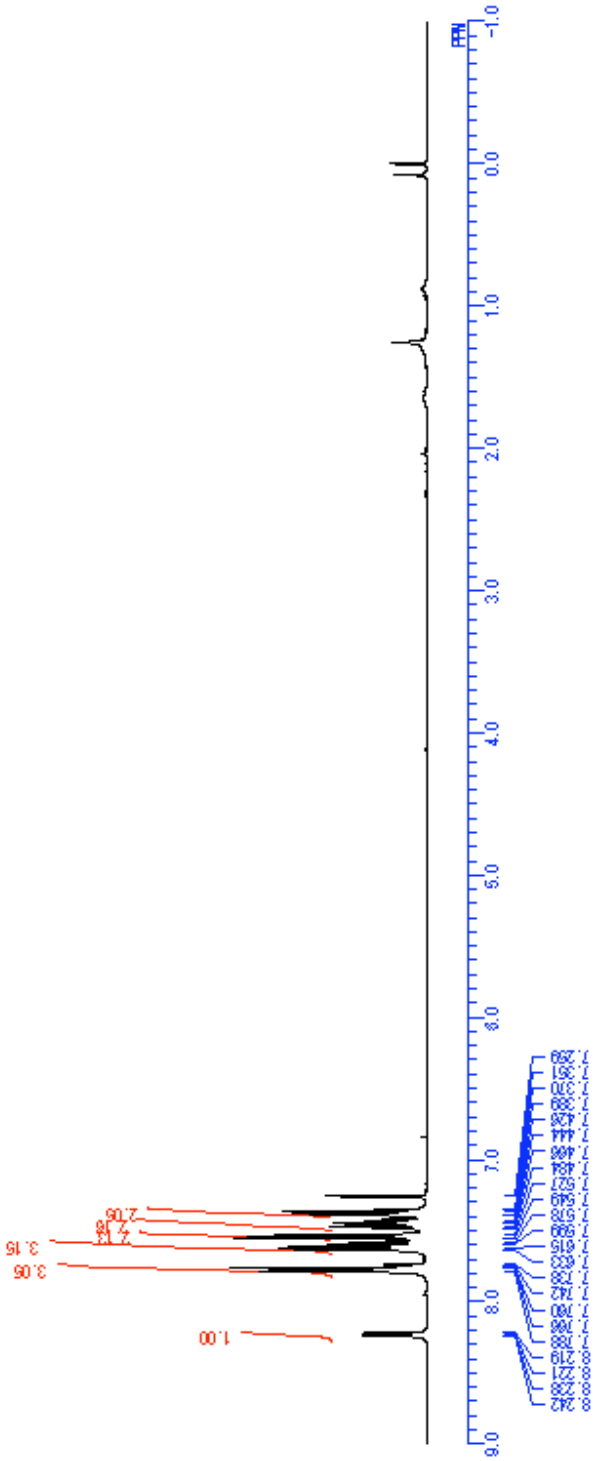
^{13}C NMR
(400 MHz, $CDCl_3$)

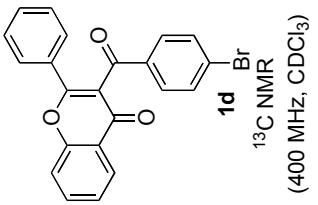




1d

^{1}H NMR
(400 MHz, $CDCl_3$)

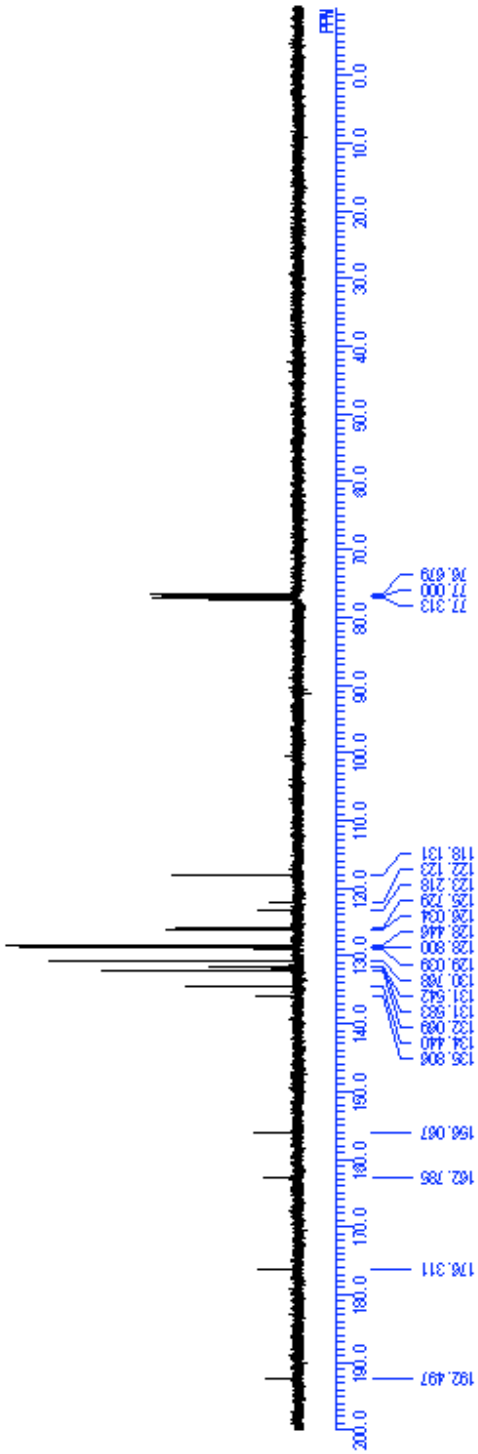


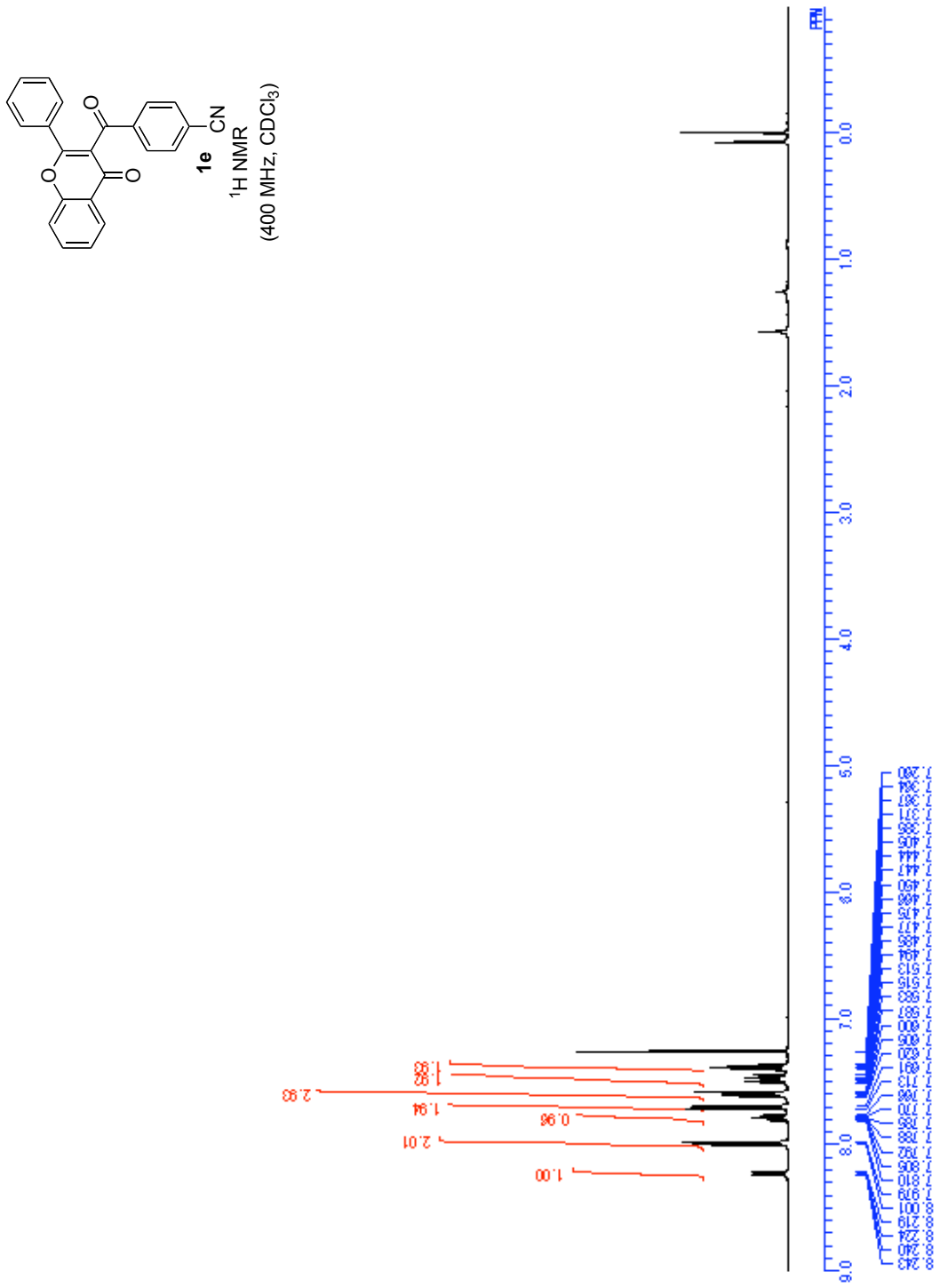


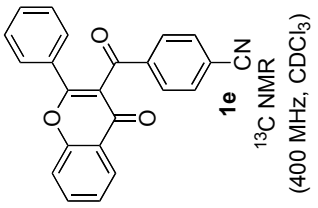
1d

^{13}C NMR

(400 MHz, $CDCl_3$)



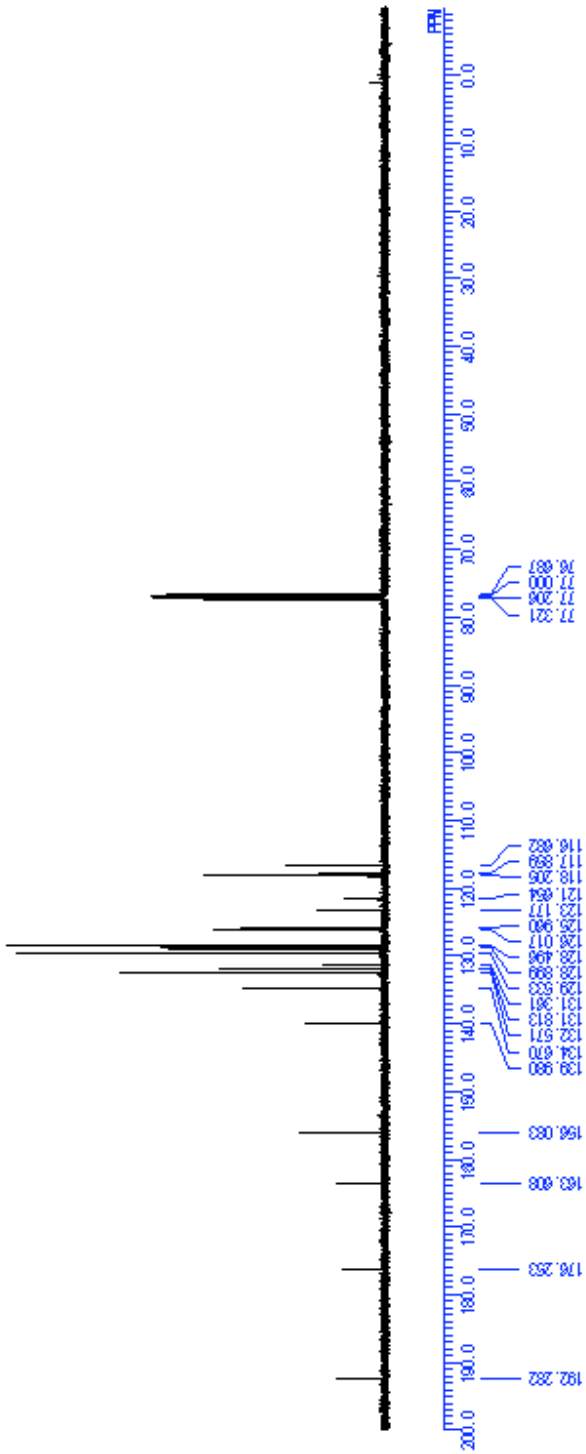

1e
^{1}H NMR
(400 MHz, CDCl$_3$)
CN
O
O
O
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
1.00
2.01
0.96
1.94
2.80
1.88
1.88

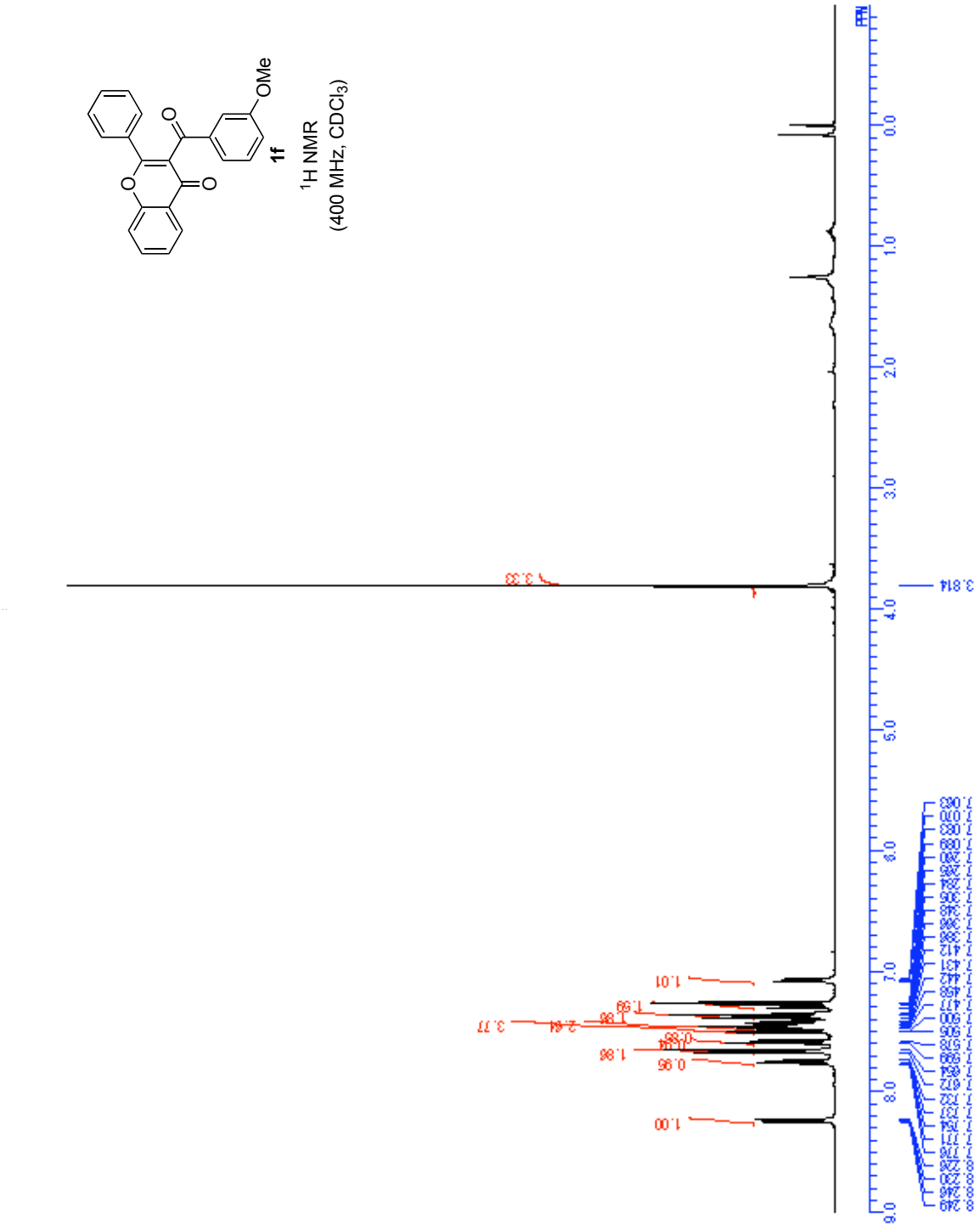


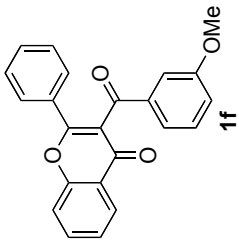
1e

^{13}C NMR

(400 MHz, $CDCl_3$)

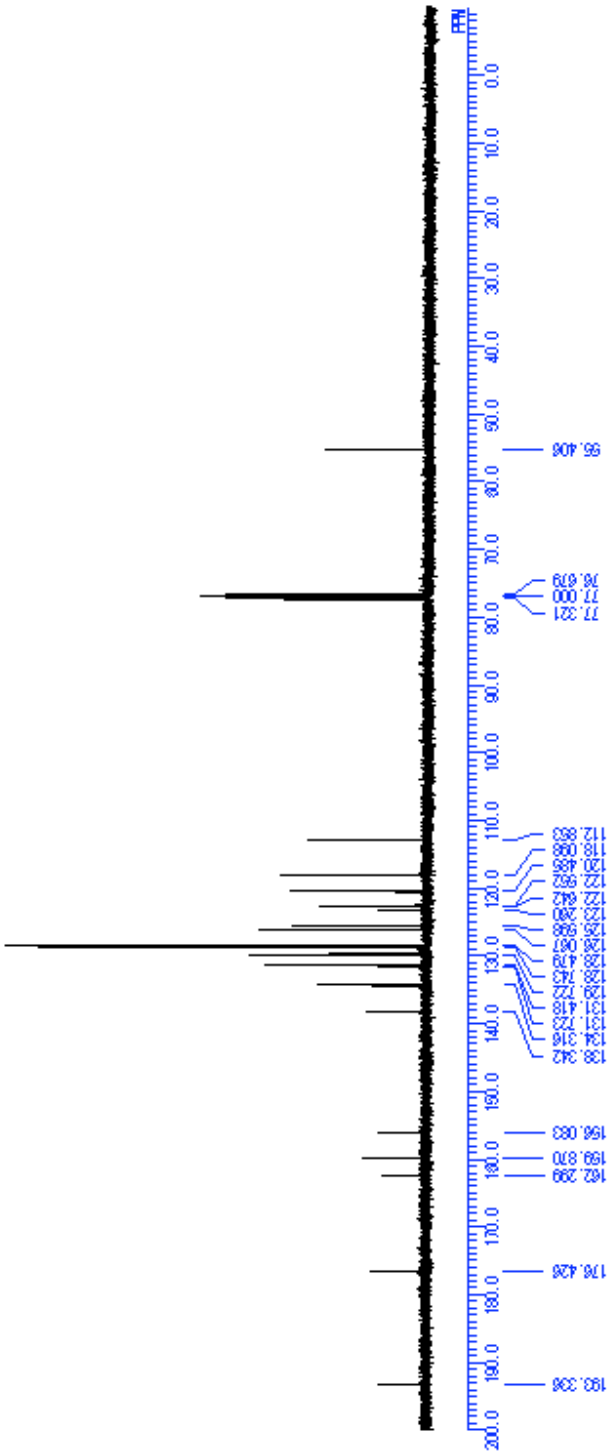


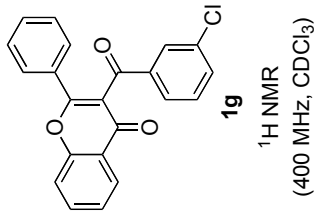

OMe
O
O
O
1f
^{1}H NMR
(400 MHz, CDCl$_3$)
3.30
3.814
1.01
1.99
1.96
3.77
2.64
0.99
1.86
0.96
1.00



1f

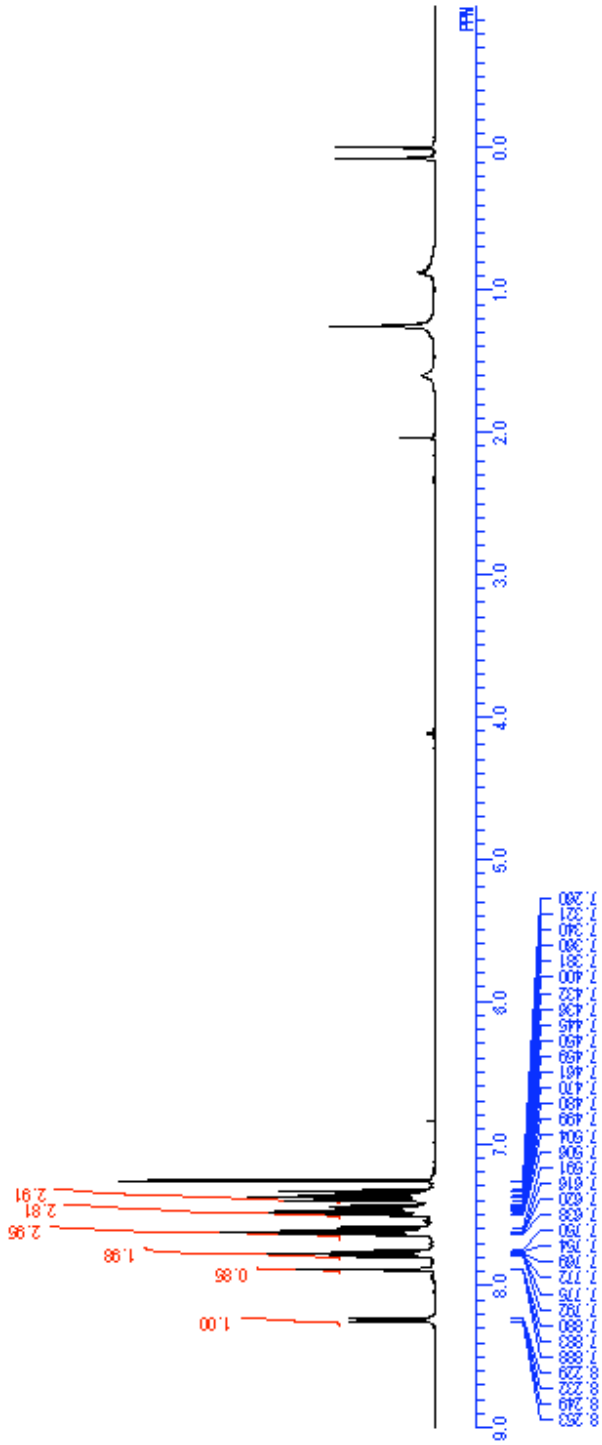
^{13}C NMR
(400 MHz, $CDCl_3$)

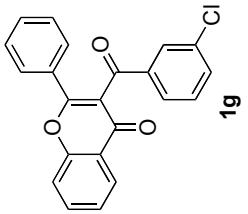




1g

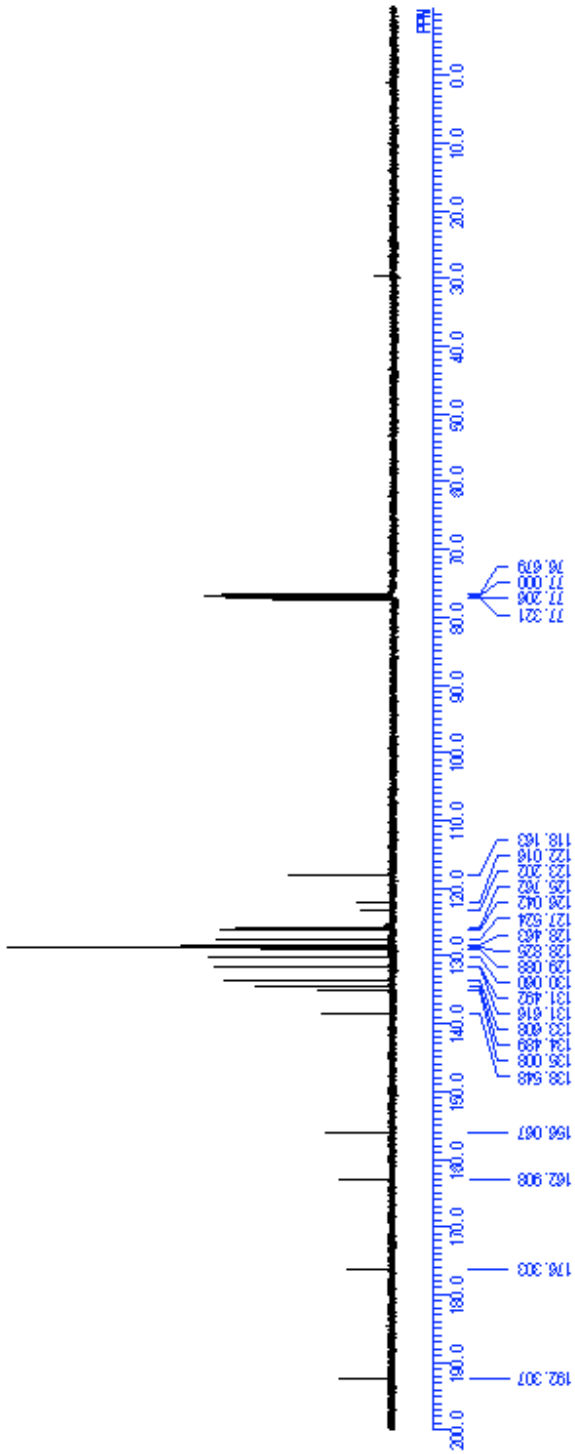
^{1}H NMR
(400 MHz, $CDCl_3$)

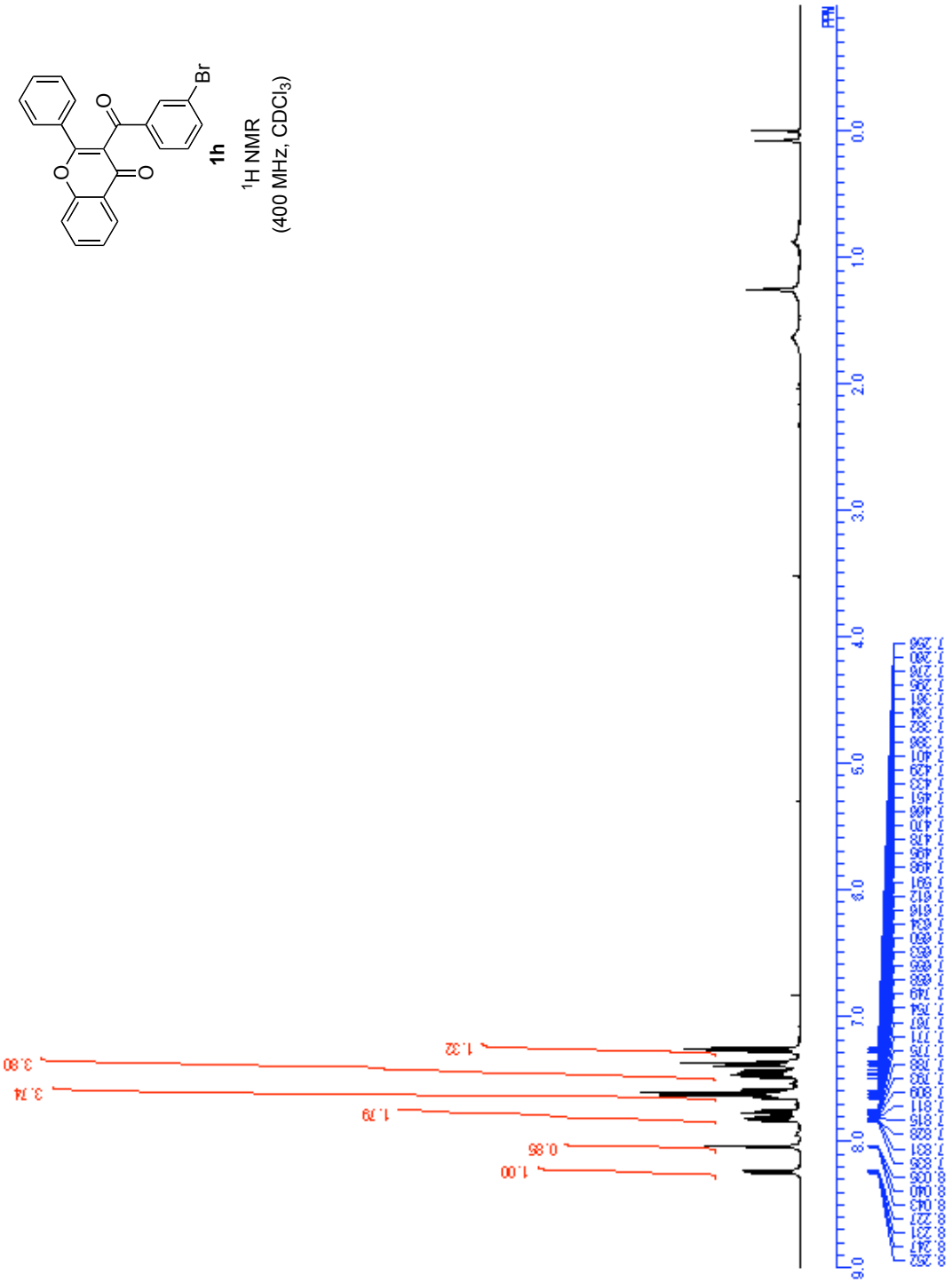


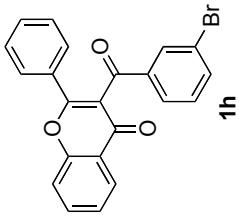


1g

^{13}C NMR
(400 MHz, $CDCl_3$)

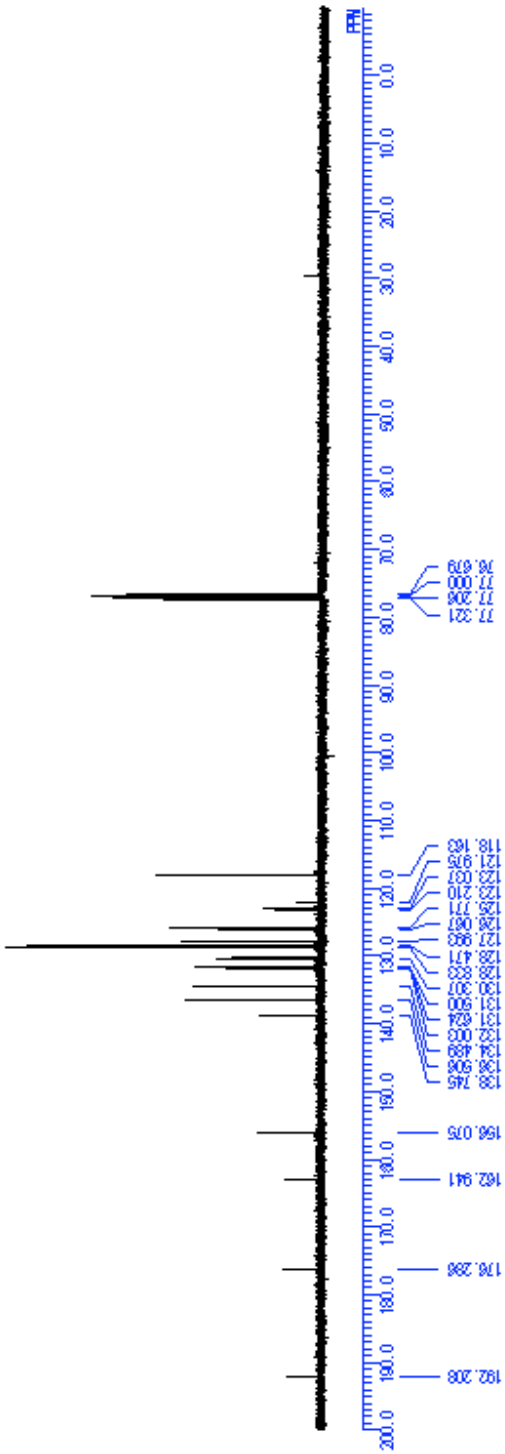


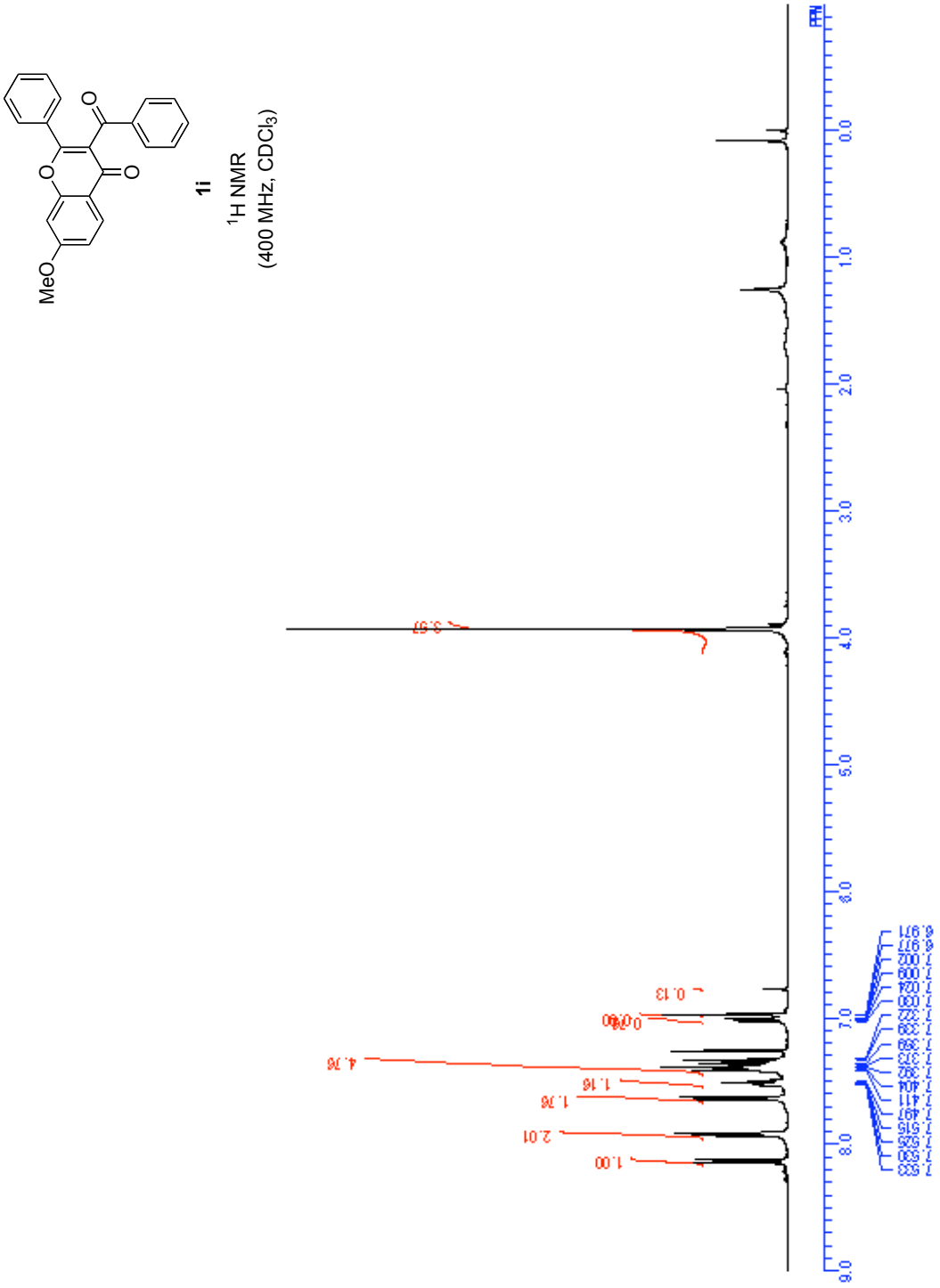

Br
O
O
O
1h
^{1}H NMR
(400 MHz, CDCl$_3$)
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
1.32
3.80
3.74
1.79
0.86
1.00

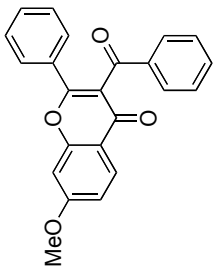


1h

^{13}C NMR
(400 MHz, $CDCl_3$)



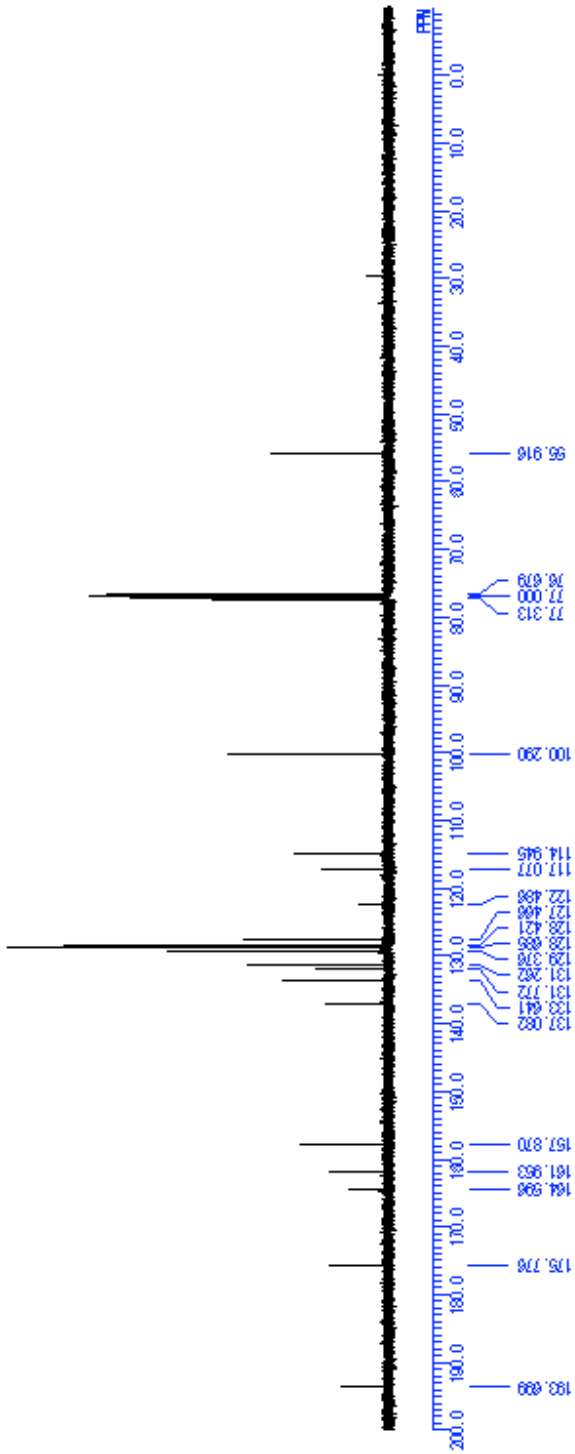

MeO
O
O
O
1i
^{1}H NMR
(400 MHz, CDCl$_3$)
3.97
0.13
4.76
1.18
1.76
2.01
1.00
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0

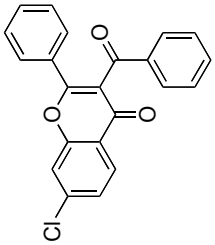


1i

^{13}C NMR

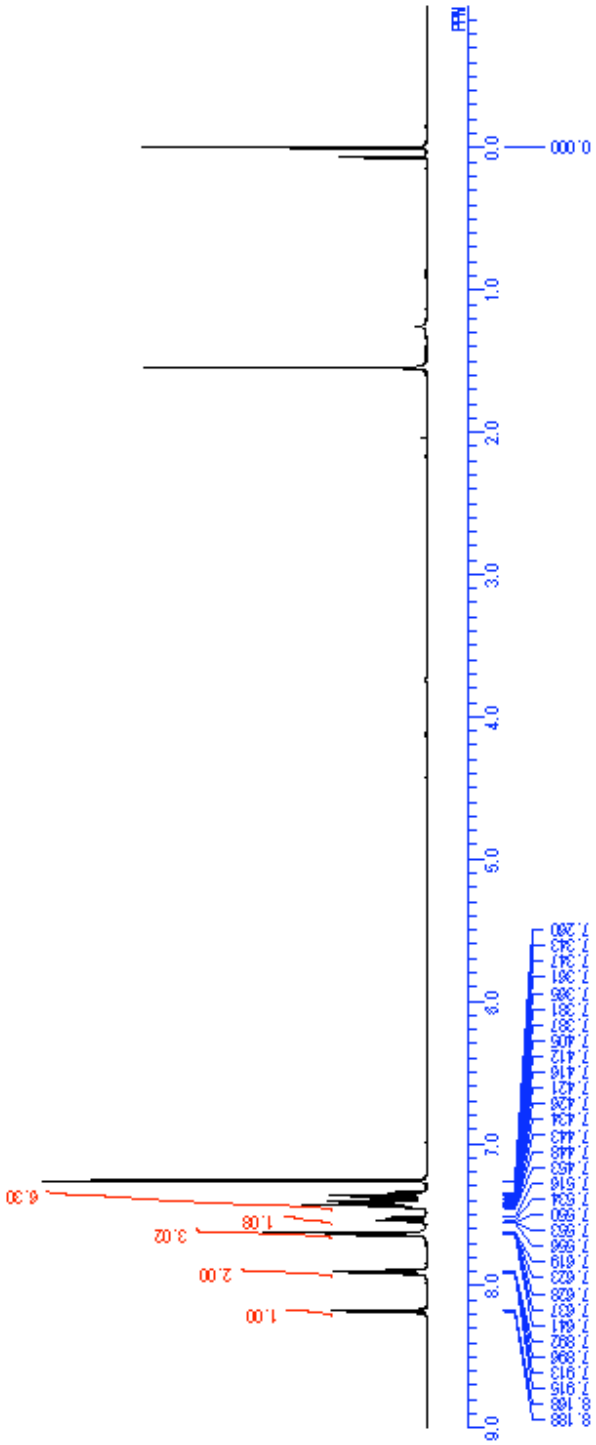
(400 MHz, $CDCl_3$)

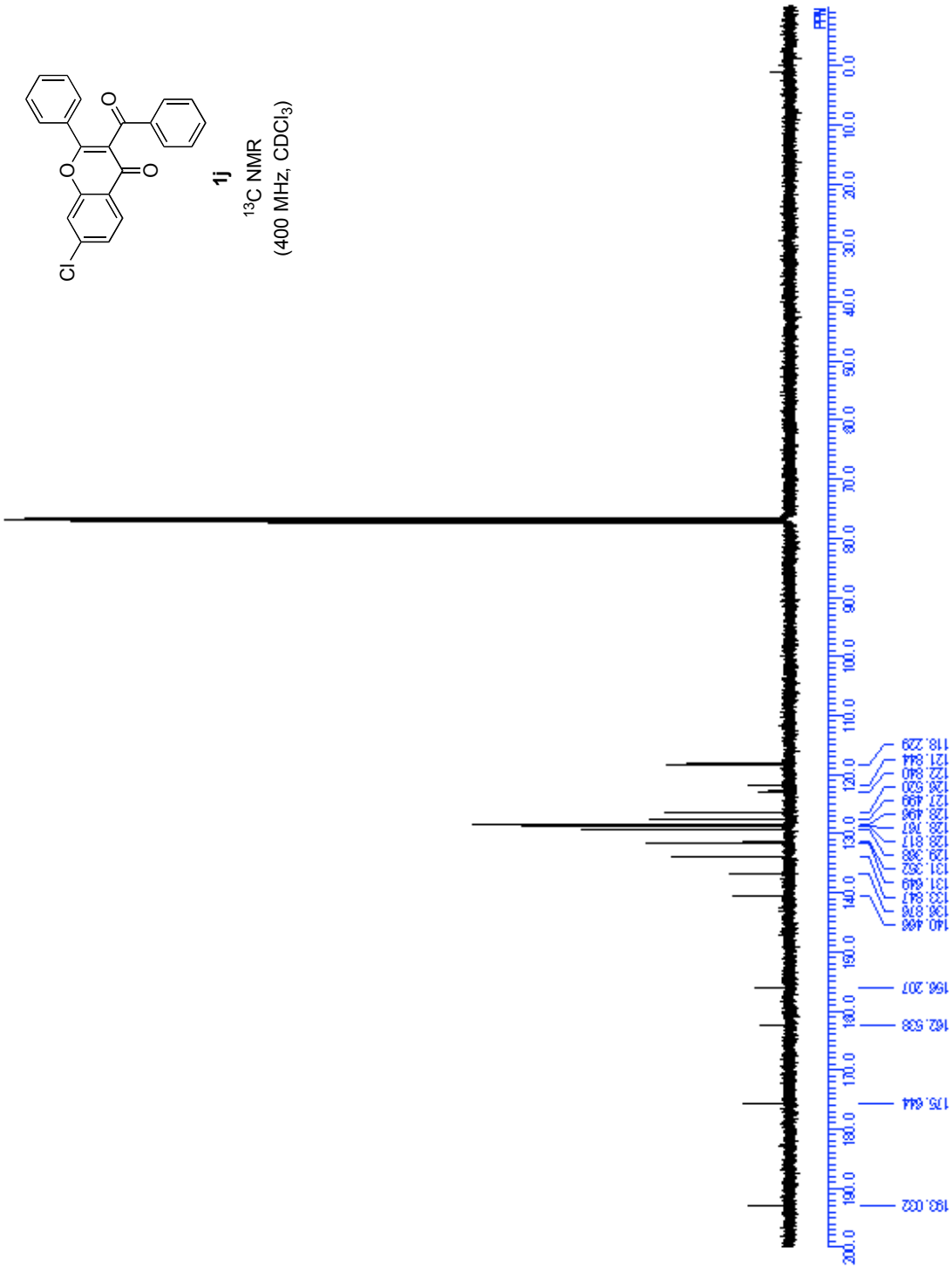


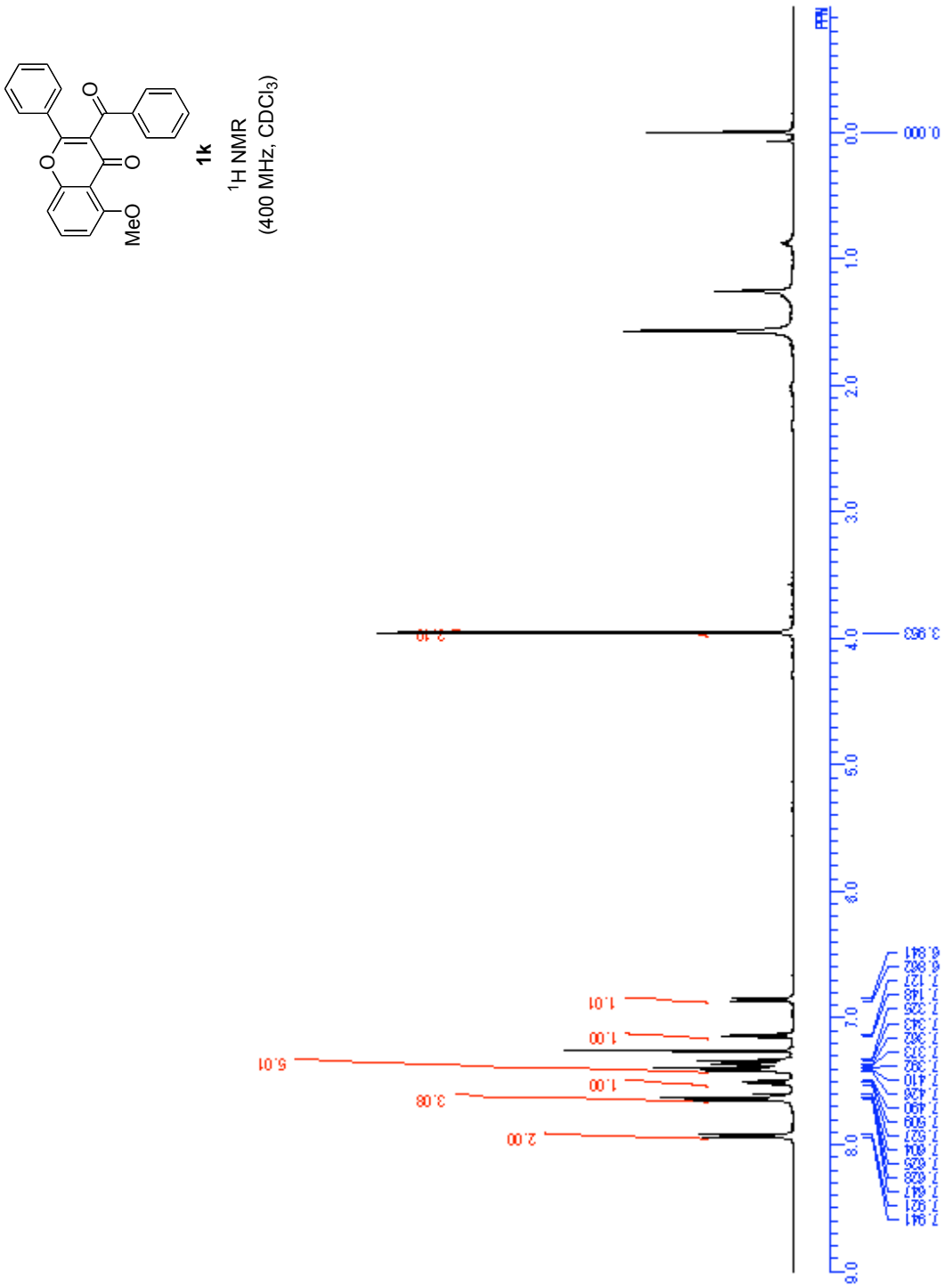


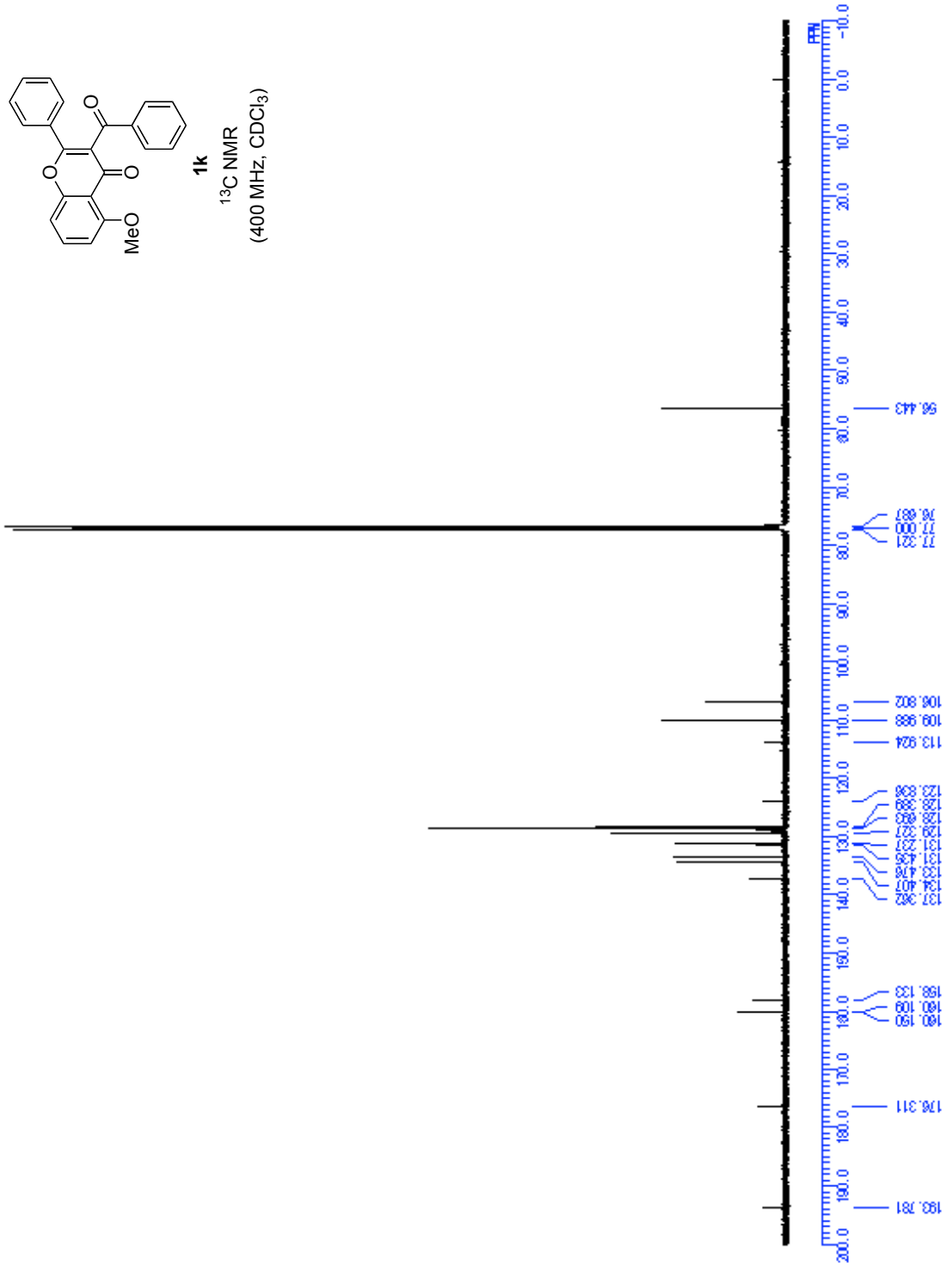
1j

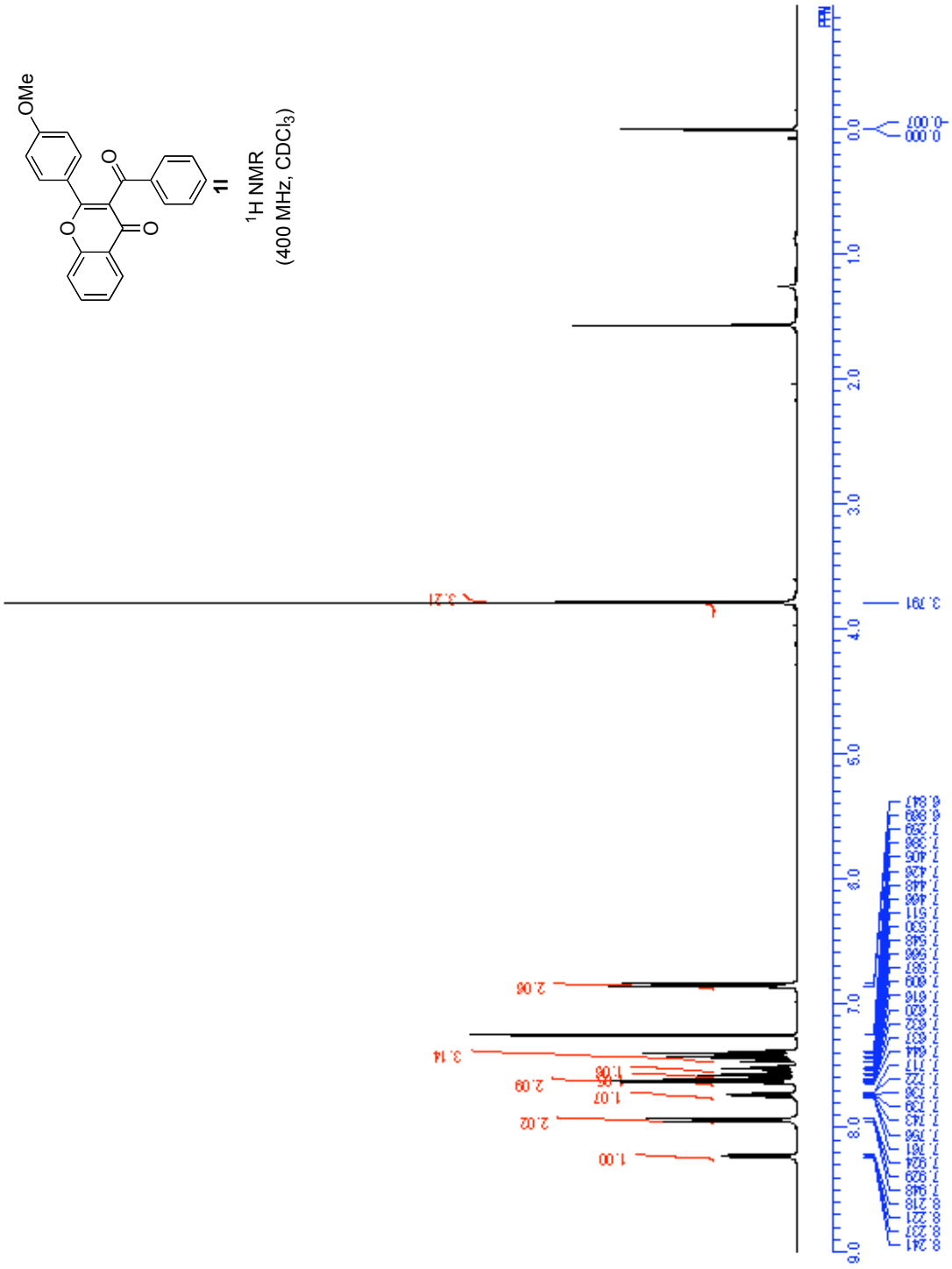
^{1}H NMR
(400 MHz, $CDCl_3$)

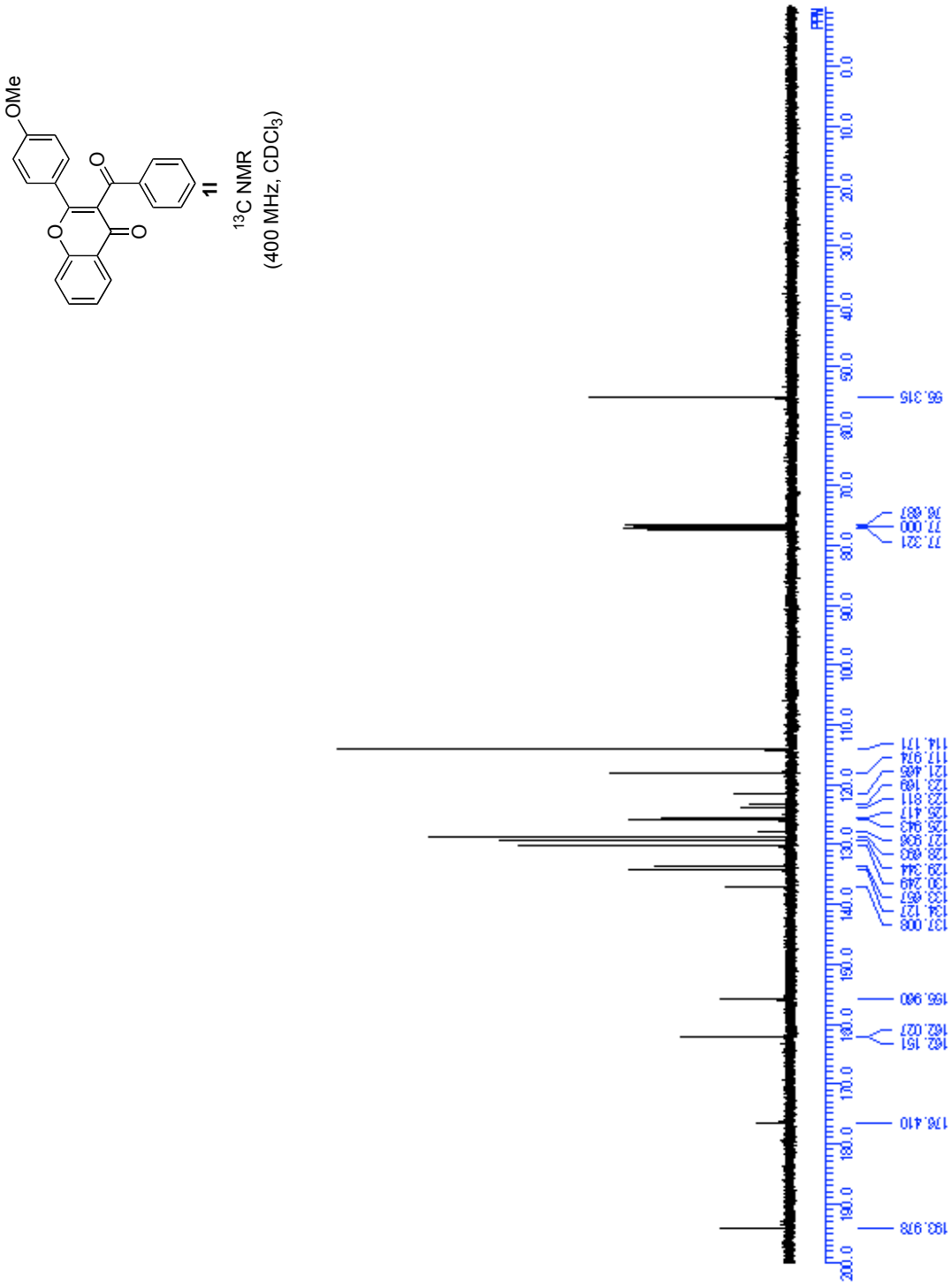


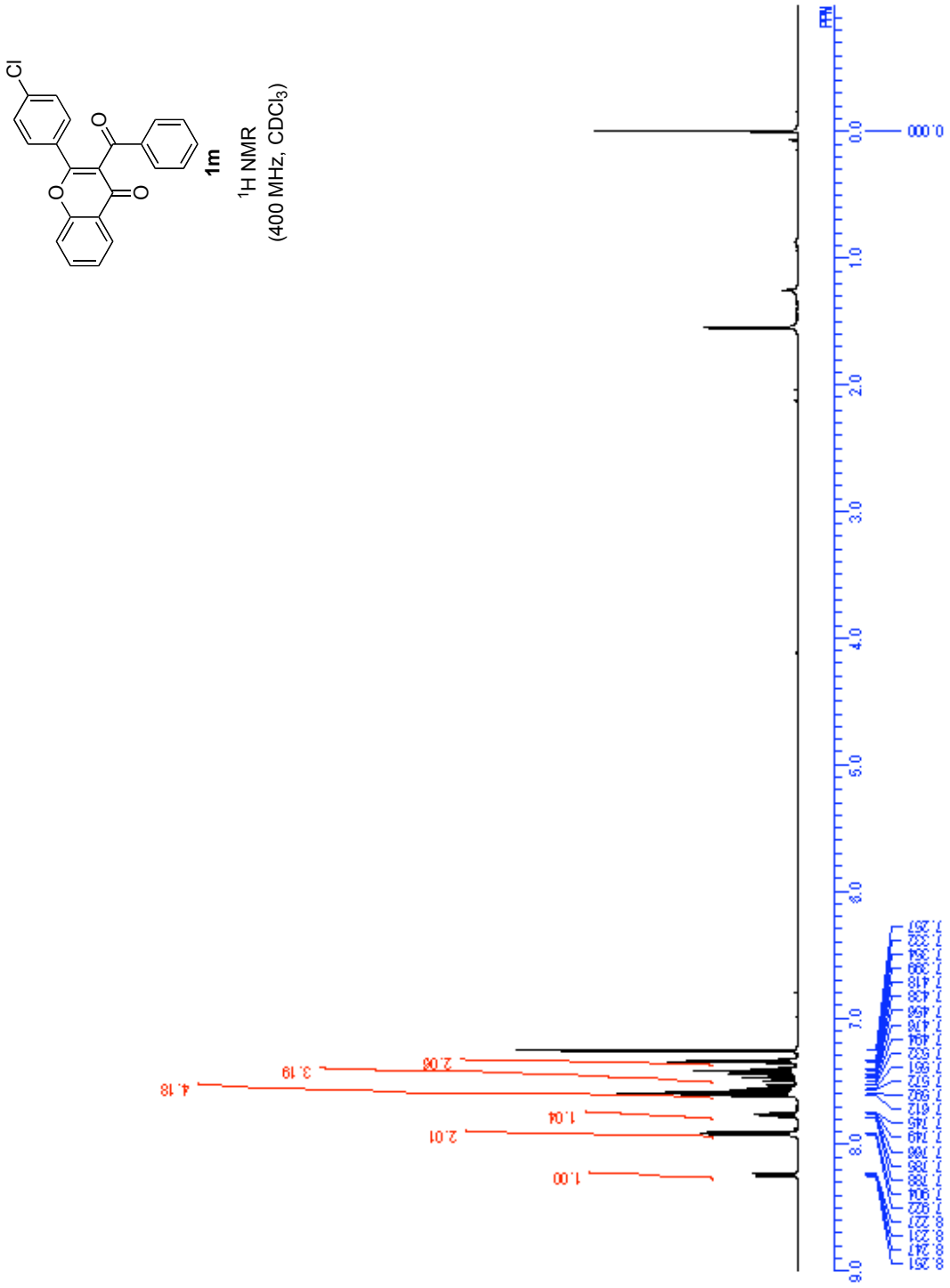

Cl
O
O
O
1j
^{13}C NMR
(400 MHz, CDCl$_3$)
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
118.229
121.844
122.840
126.520
127.499
128.496
128.767
128.817
129.388
131.352
131.649
133.847
136.870
140.496
156.207
162.528
175.644
193.002

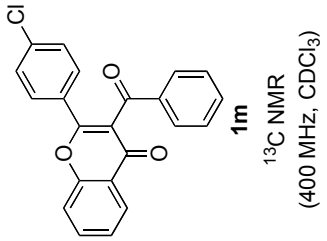

MeO
1k
^{1}H NMR
(400 MHz, CDCl$_3$)
3.10
1.01
1.00
5.01
1.00
3.08
2.00
0.000
3.983


MeO
1k
^{13}C NMR
(400 MHz, CDCl$_3$)
56.443
76.687
77.000
77.321
106.802
109.988
113.924
123.836
128.899
128.980
129.327
131.237
131.436
133.478
134.407
137.362
158.133
160.109
160.190
176.311
182.781


OMe
O
O
O
11
^{1}H NMR
(400 MHz, CDCl$_3$)
3.27
2.08
3.14
2.09
1.08
1.07
2.02
1.00
3.791
PPM

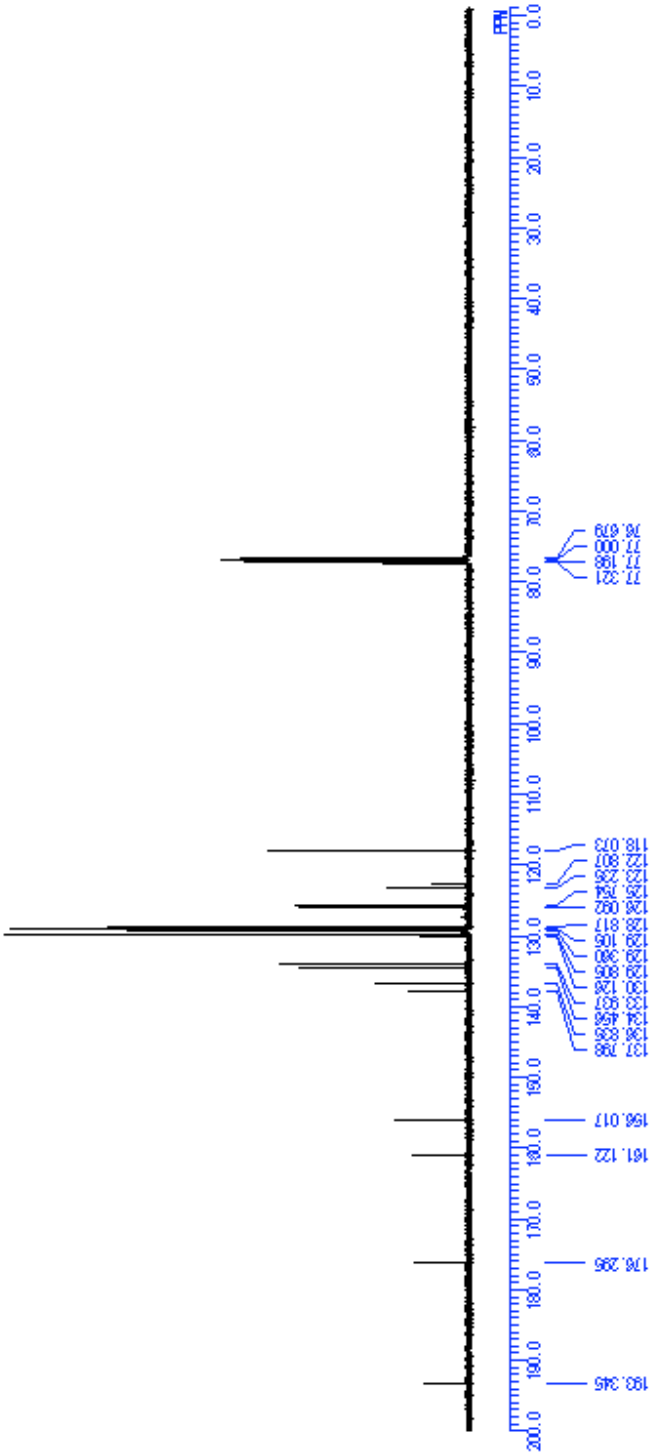

OMe
O
O
O
11
^{13}C NMR
(400 MHz, CDCl$_3$)
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
66.315
77.000
114.171
117.974
121.469
123.169
123.811
125.417
125.943
127.936
128.080
128.344
130.249
133.857
134.127
137.008
156.960
162.151
162.027
176.410
183.978

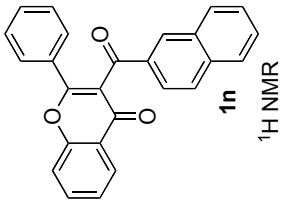

Cl
O
O
O
1m
^{1}H NMR
(400 MHz, CDCl$_3$)
PPM
0.000
1.00
2.01
1.04
4.18
3.19
2.08



1m

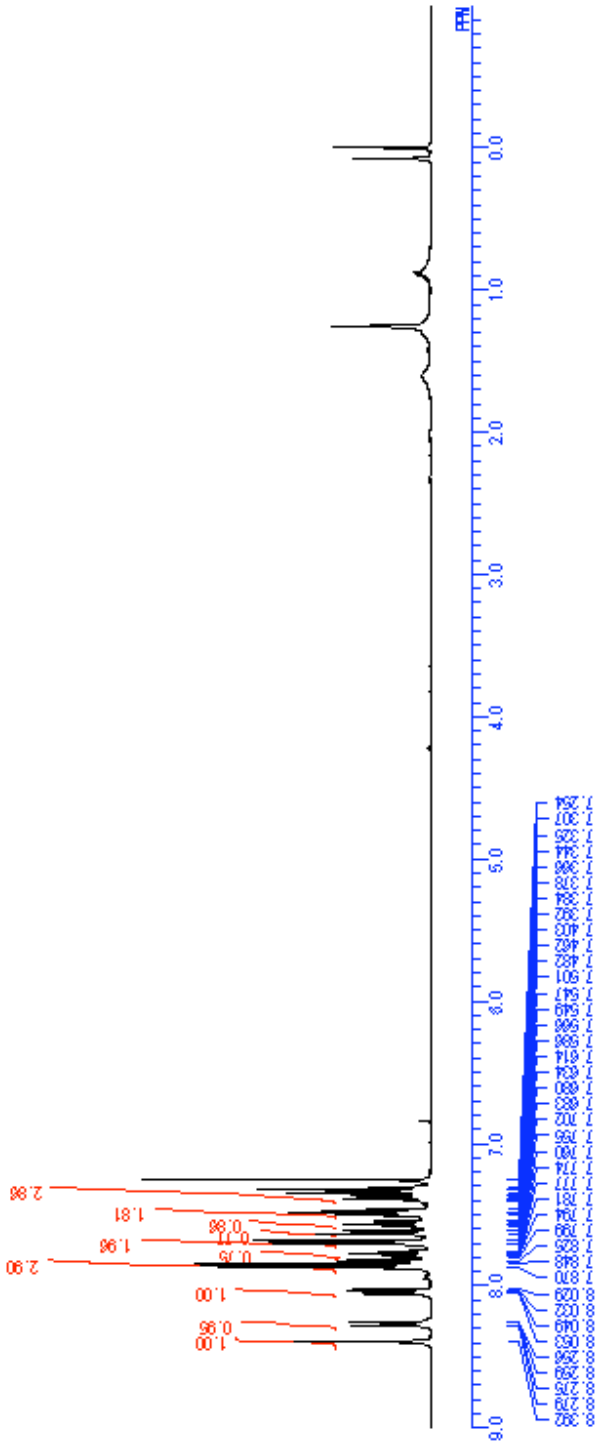
^{13}C NMR
(400 MHz, $CDCl_3$)

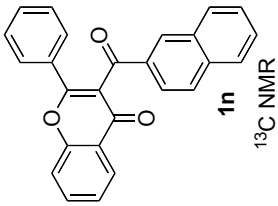




1n

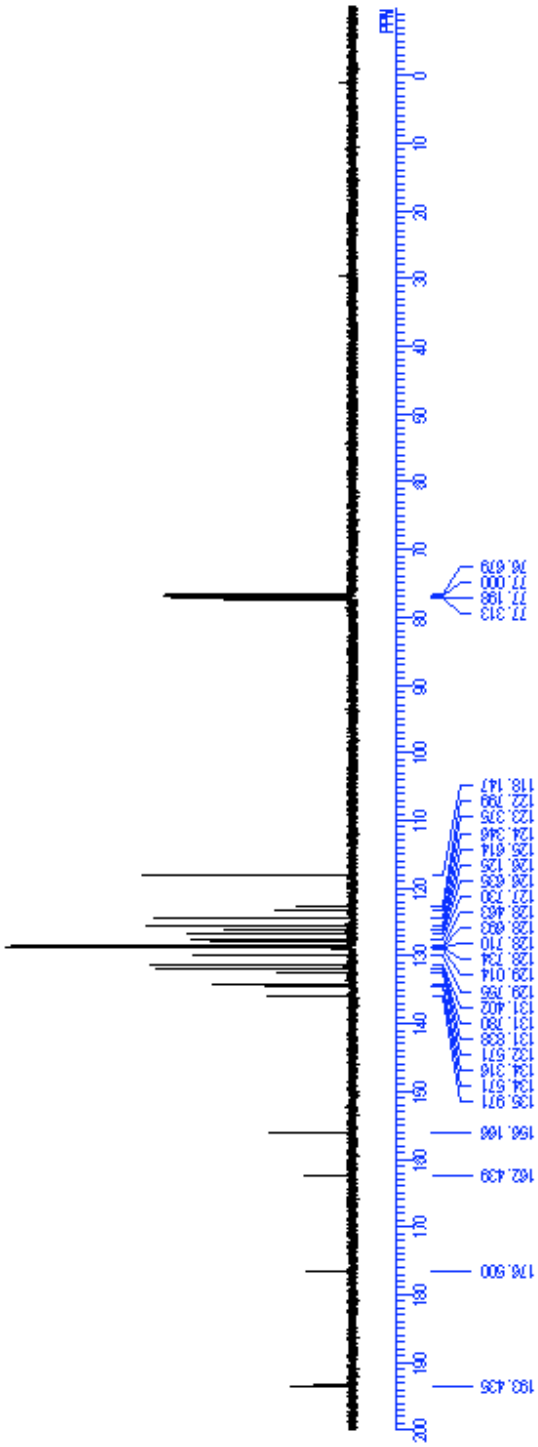
^{1}H NMR
(400 MHz, $CDCl_3$)

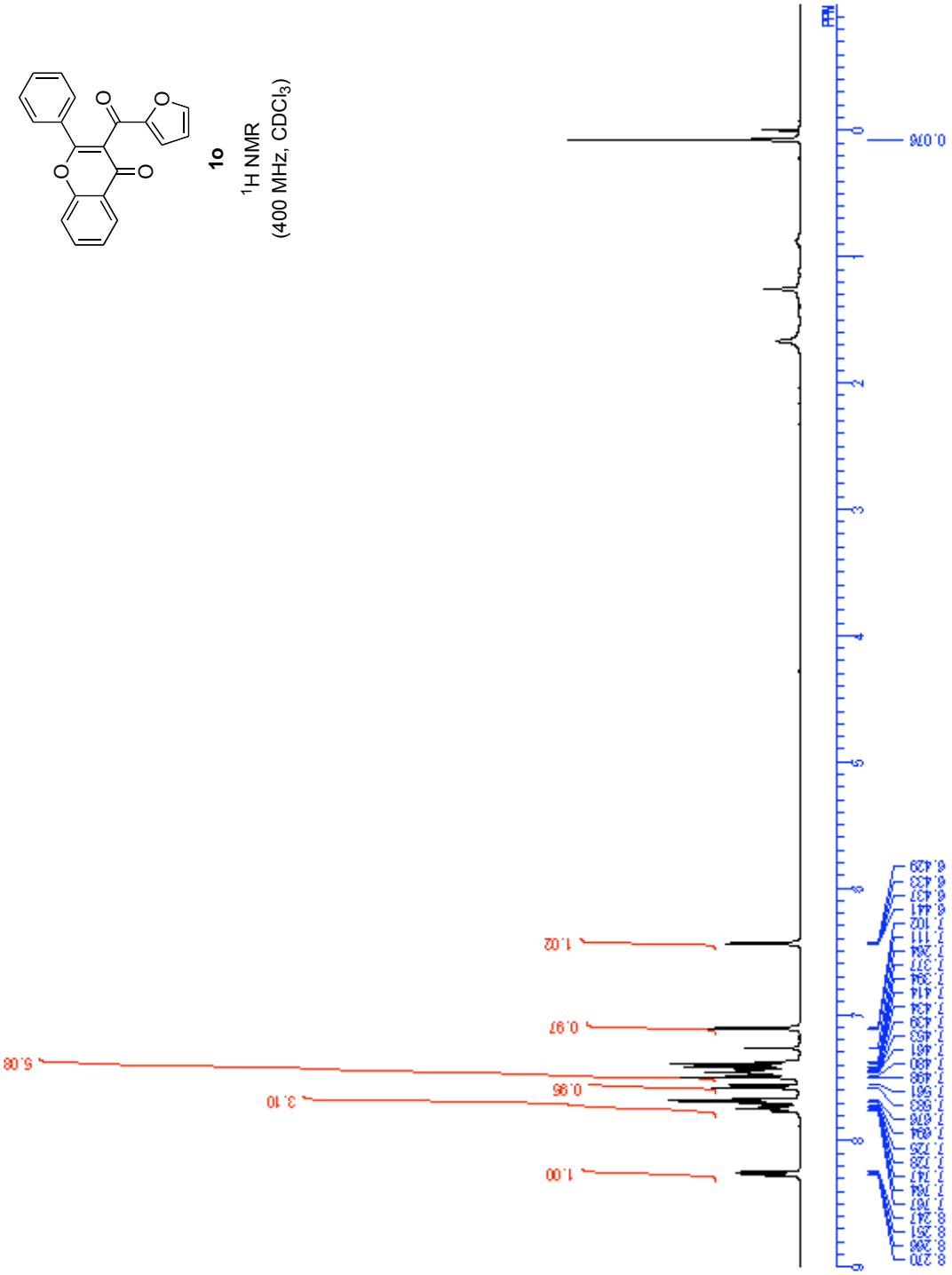


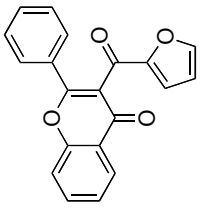


1n

^{13}C NMR
(400 MHz, $CDCl_3$)

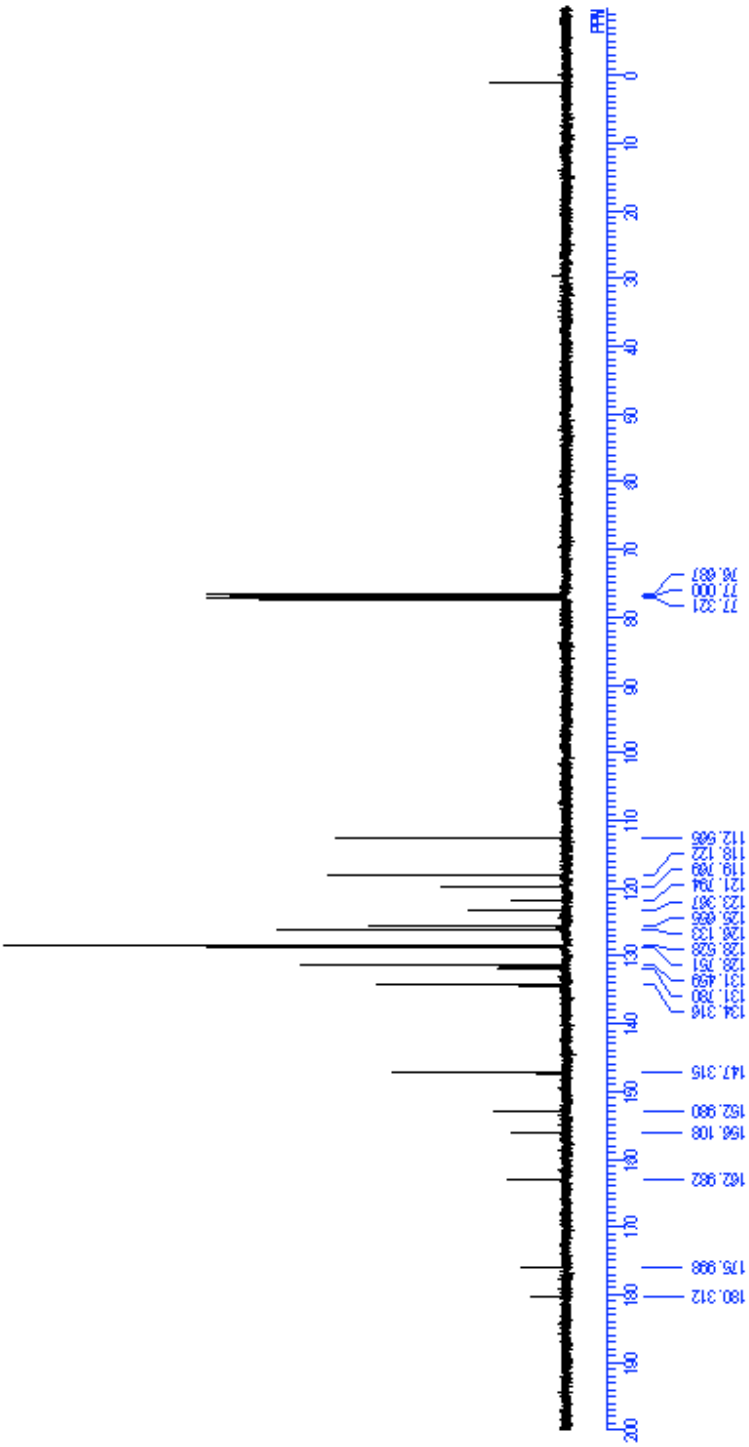


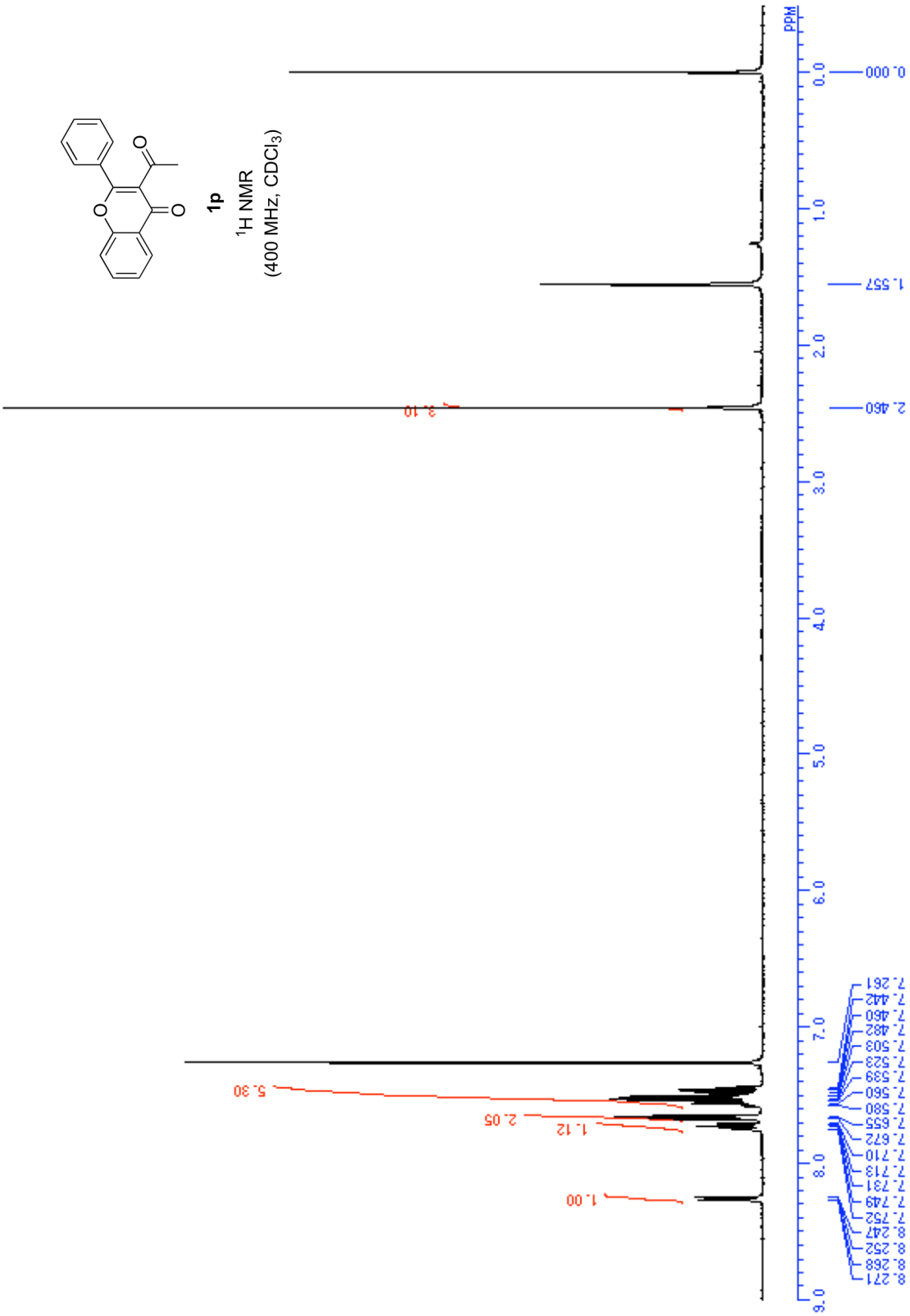

1o
^{1}H NMR
(400 MHz, $CDCl_3$)
0.078
1.02
0.97
5.08
0.96
3.10
1.00

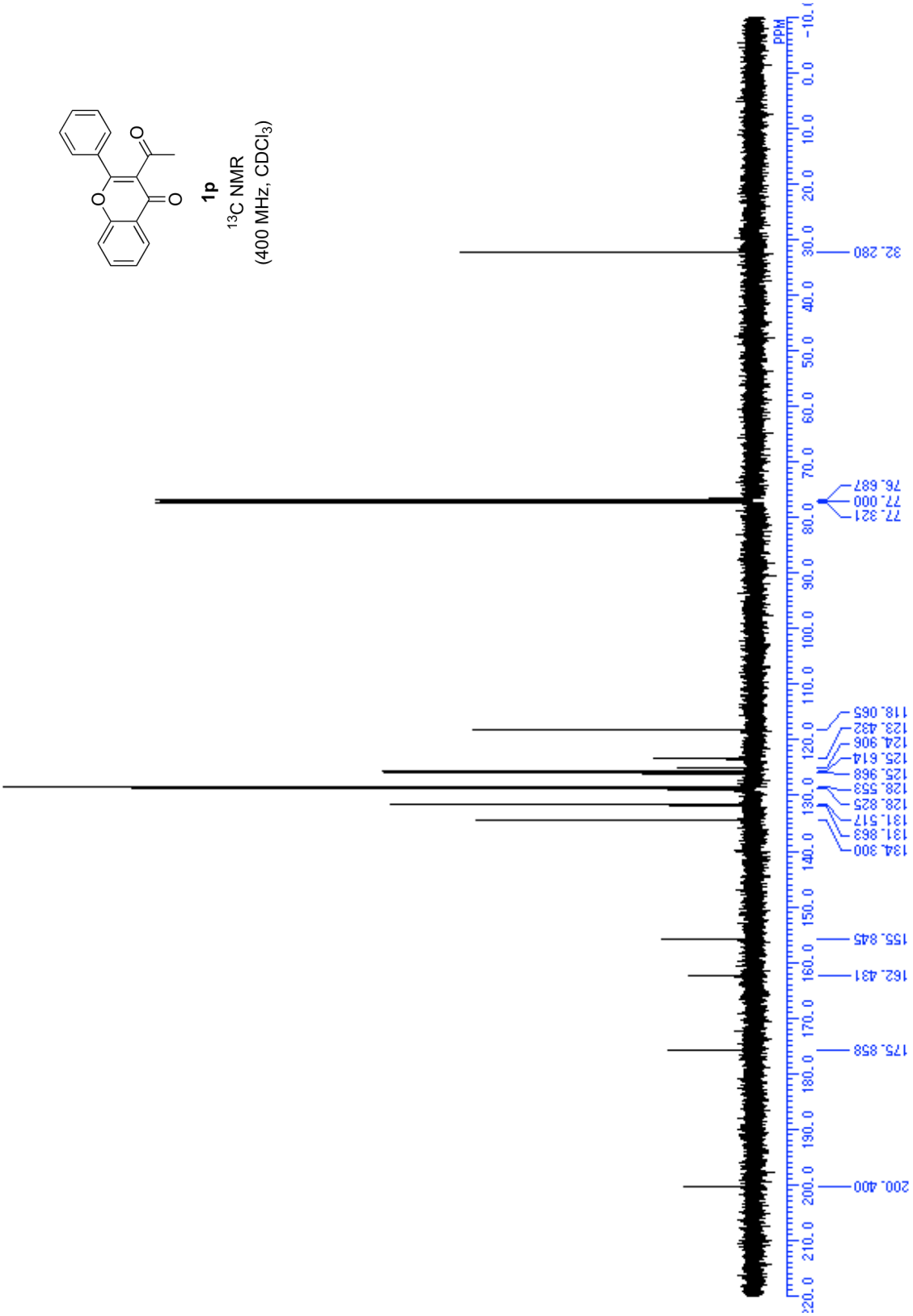


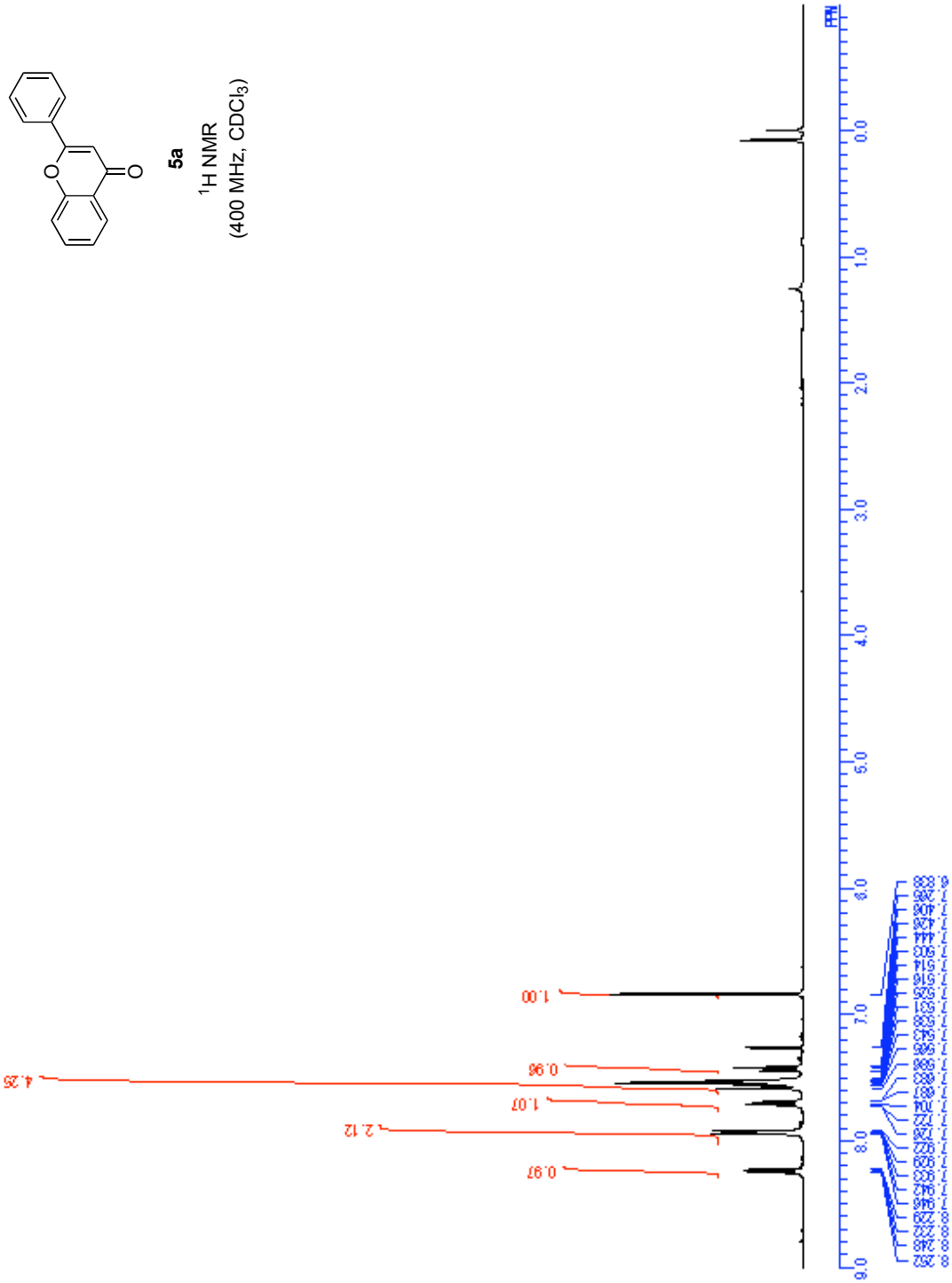
1o

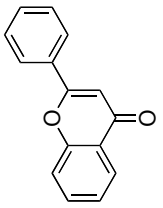
^{13}C NMR
(400 MHz, $CDCl_3$)




1p
^{1}H NMR
(400 MHz, CDCl$_3$)
PPM
0.000
1.557
2.460
3.10
5.30
2.05
1.12
1.00
7.261
7.442
7.460
7.482
7.503
7.529
7.539
7.560
7.580
7.655
7.672
7.710
7.713
7.731
7.749
7.752
8.247
8.252
8.268
8.271


1p
^{13}C NMR
(400 MHz, CDCl$_3$)
PPM
32.280
76.687
77.000
77.321
118.065
123.432
124.906
125.614
125.968
128.559
128.825
131.517
131.863
134.300
155.845
162.431
175.858
200.400

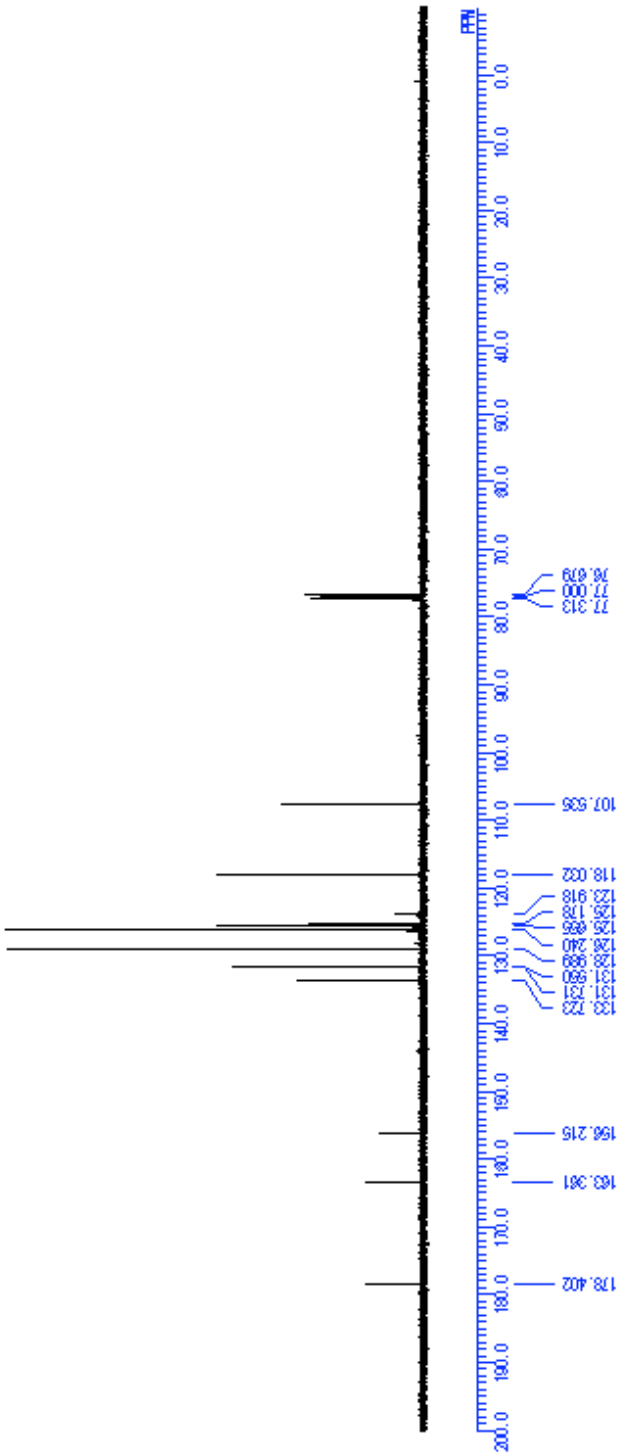

5a
^{1}H NMR
(400 MHz, $CDCl_3$)
1.00
0.98
1.07
2.12
0.97
4.26

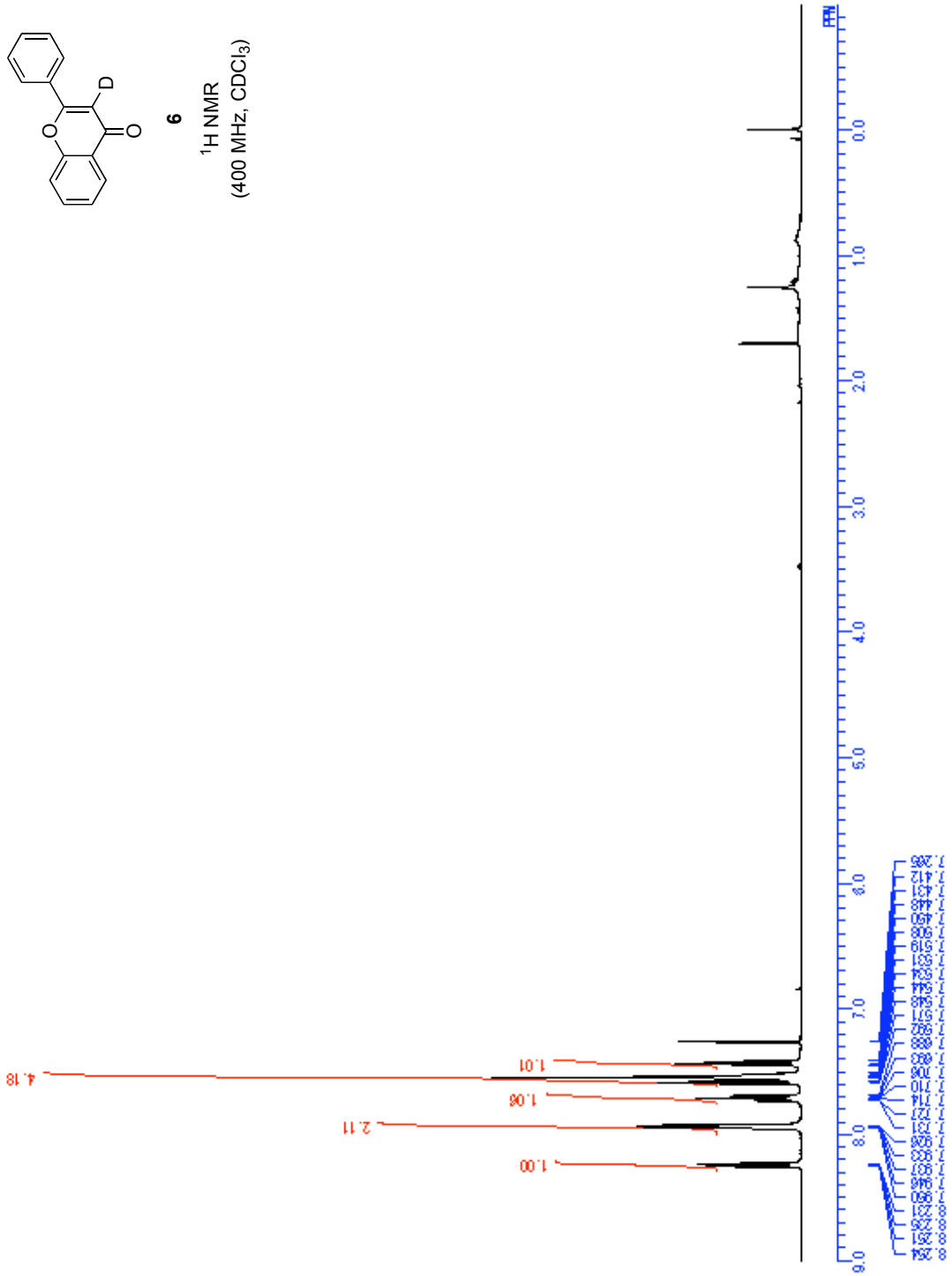


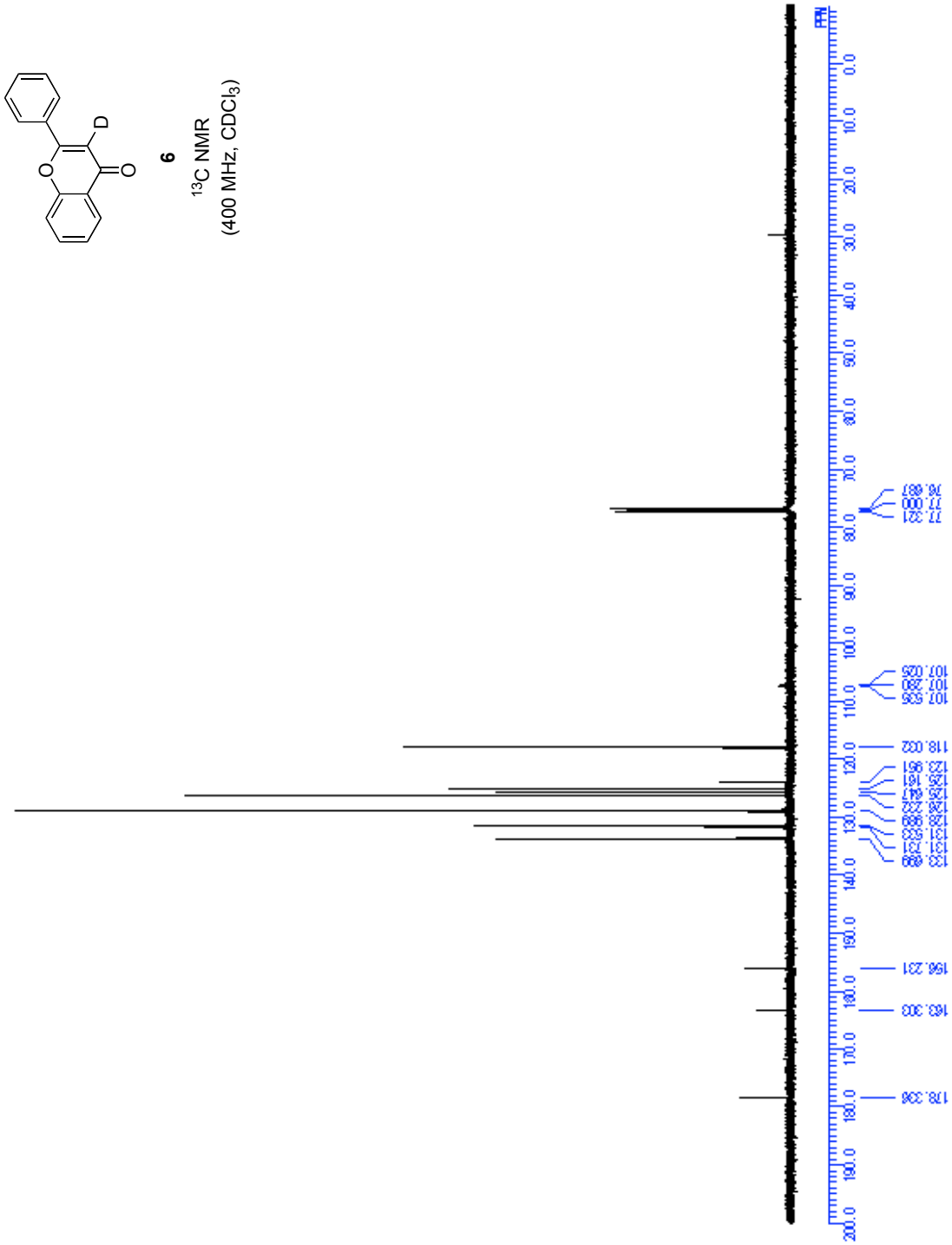
5a

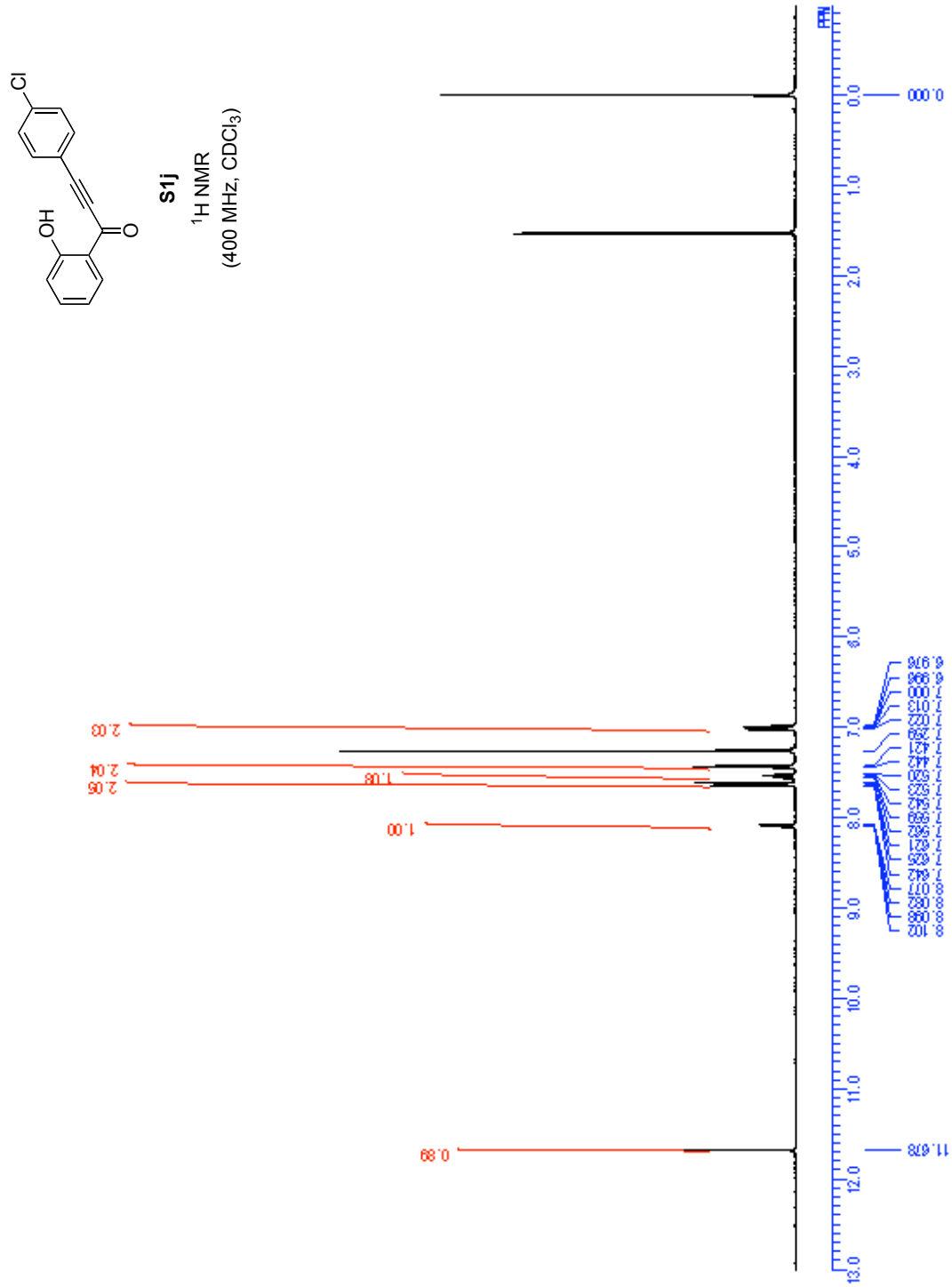
^{13}C NMR

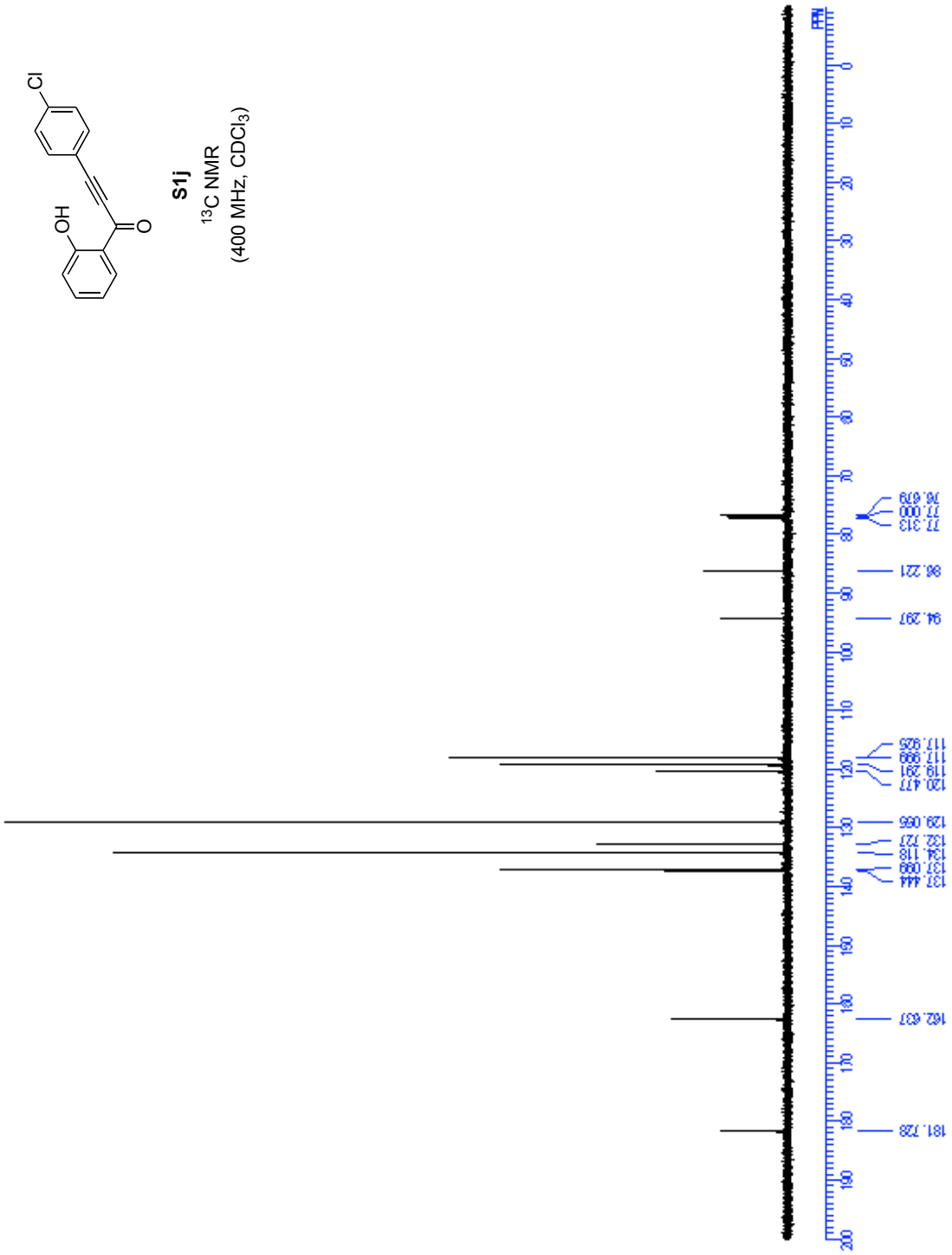
(400 MHz, $CDCl_3$)

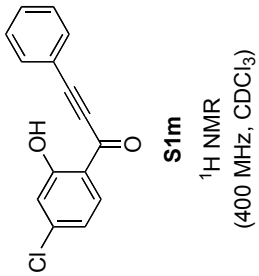



D
O
O
6
^{1}H NMR
(400 MHz, $CDCl_3$)
4.18
1.01
1.08
2.11
1.00
PPM
0.0
1.0
2.0
3.0
4.0
6.0
6.0
7.0
8.0
9.0


D
O
O
6
^{13}C NMR
(400 MHz, CDCl$_3$)
77.231
77.000
76.687
107.026
107.280
107.536
118.022
123.899
131.731
131.923
138.999
139.222
139.447
139.761
139.961
156.231
163.303
178.336


Cl
OH
O
S1j
^{1}H NMR
(400 MHz, CDCl$_3$)
2.00
2.04
2.05
1.08
1.00
0.89
0.000
11.678

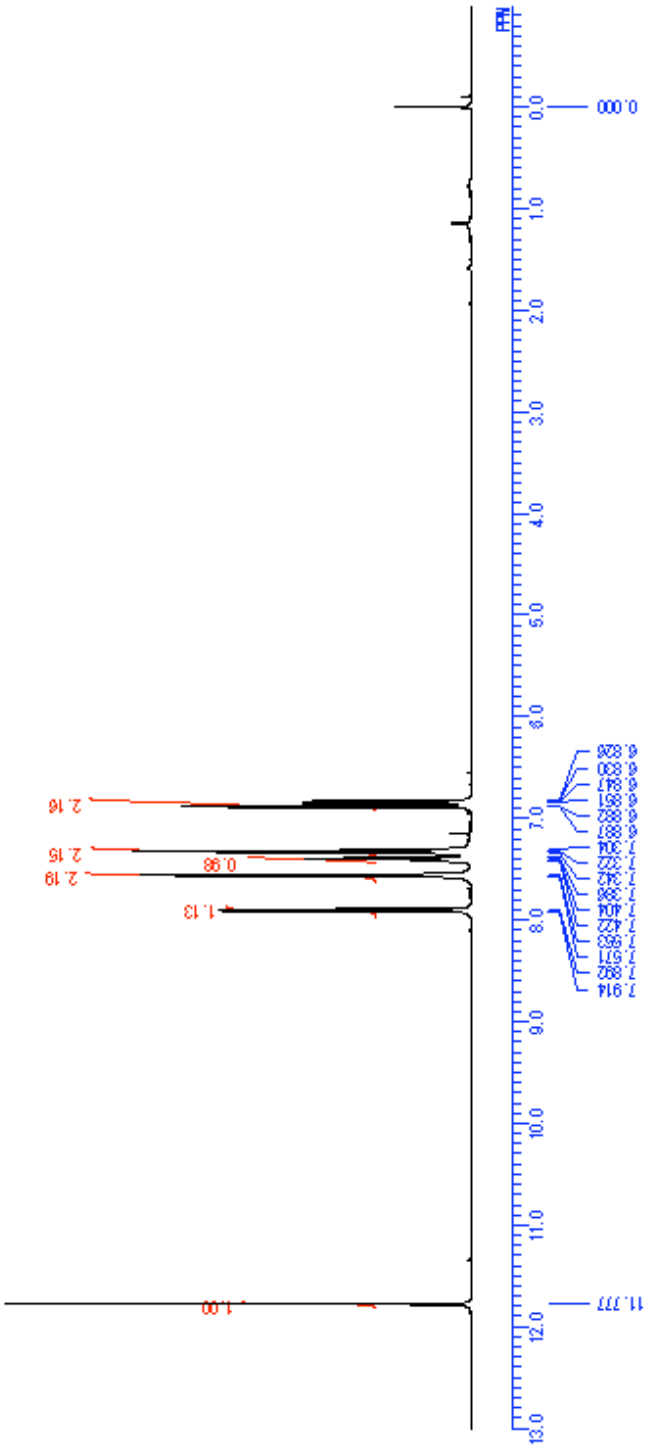

Cl
OH
O
S1j
13C NMR
(400 MHz, CDCl3)
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
76.679
77.000
77.313
86.221
94.297
117.926
117.999
119.291
120.477
129.096
132.727
134.118
137.099
137.444
162.637
181.728

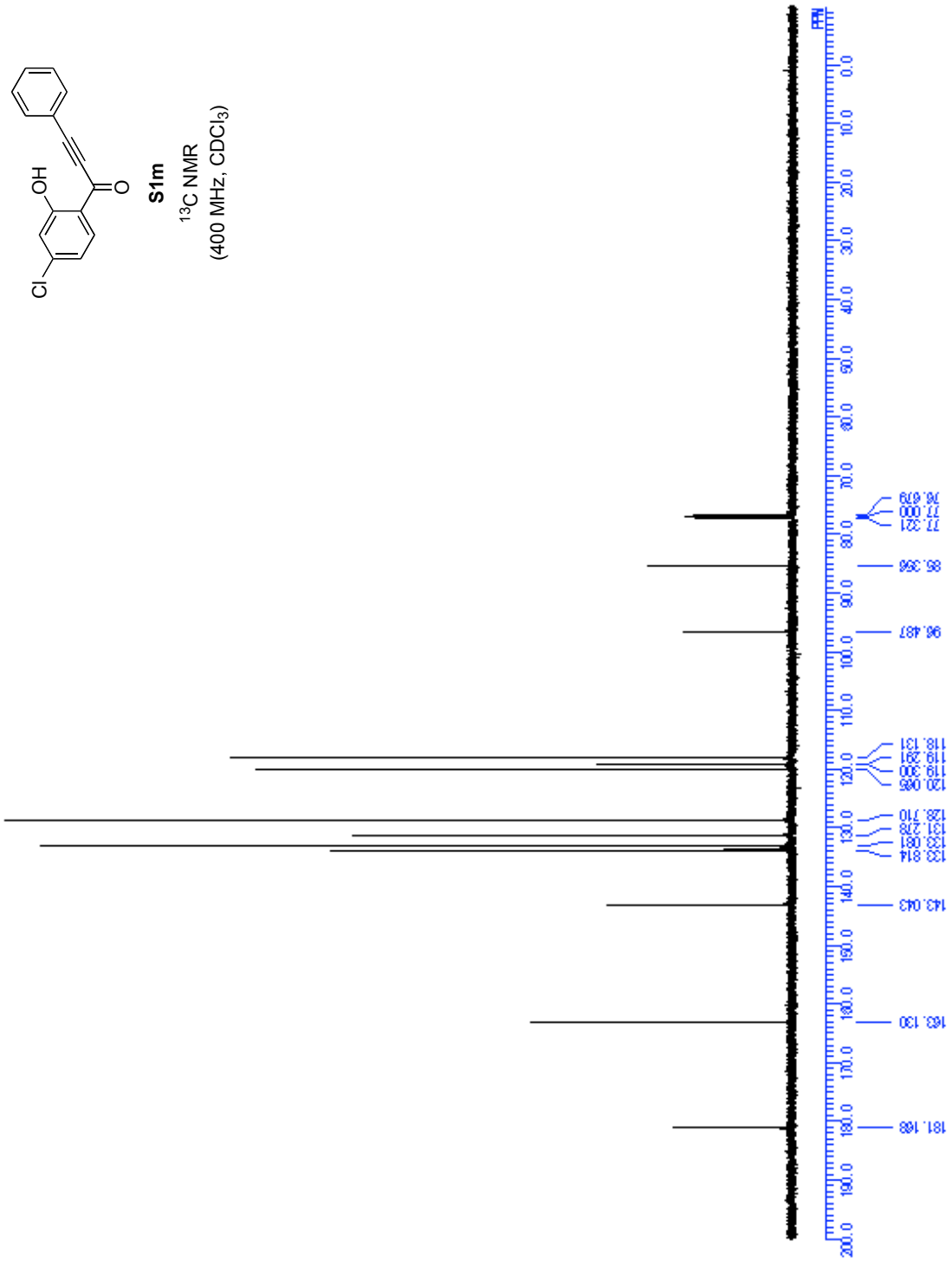


S1m

^{1}H NMR

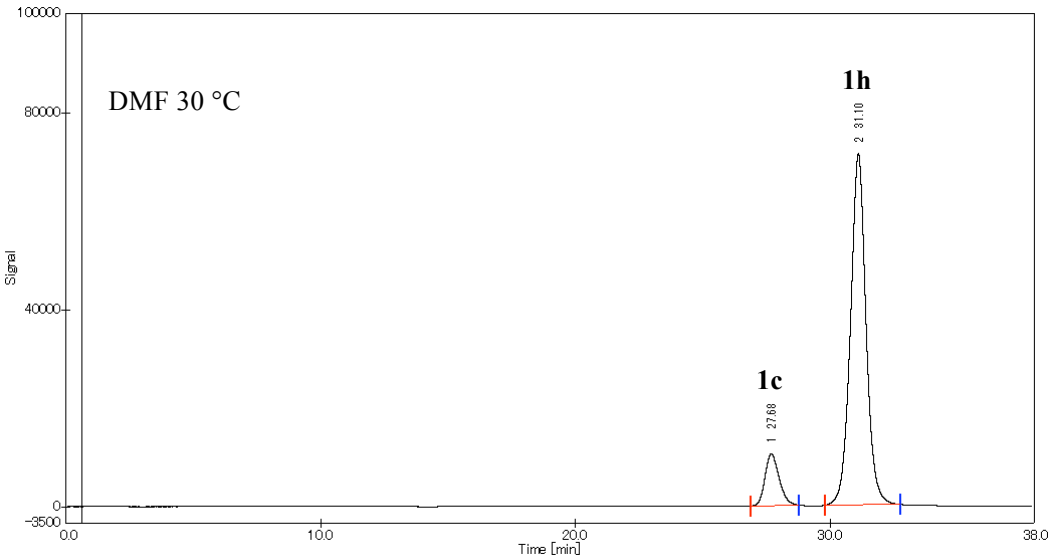
(400 MHz, $CDCl_3$)

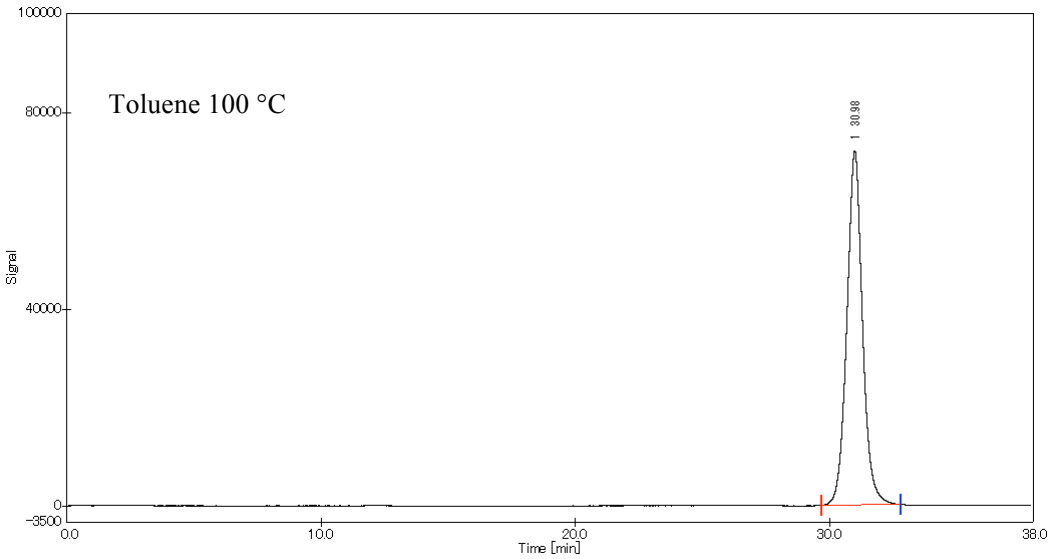


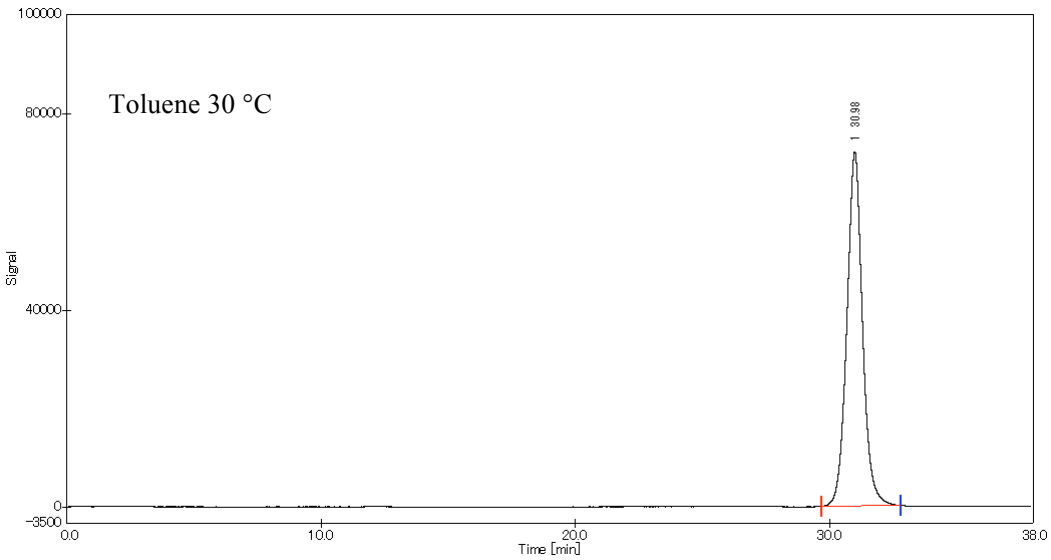

OH
O
Cl
S1m
^{13}C NMR
(400 MHz, CDCl$_3$)
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
76.679
77.000
77.321
86.396
96.487
118.131
119.291
119.300
120.065
128.710
131.278
133.081
133.814
143.043
163.130
181.168

HPLC Trace at UV 310 nm

Solvent: Hex/EA = 3/1, 1.0 mL/min (Column: Senshu-Pak Silica-3301-N)







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3) V. P. Dhande, P. Thakwani, K. G. Marathe, *Tetrahedron* **1988**, *44,* 3015–3023.

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7) M. Yoshida, Y. Fujino, K. Saito, T. Doi, *Tetrahedron* **2011**, *67*, 9993-9997.