*Supporting Information for*

# Pd-Catalyzed Intermolecular Asymmetric Allylic Dearomatization of 1-Nitro-2-naphthols with MBH Adducts

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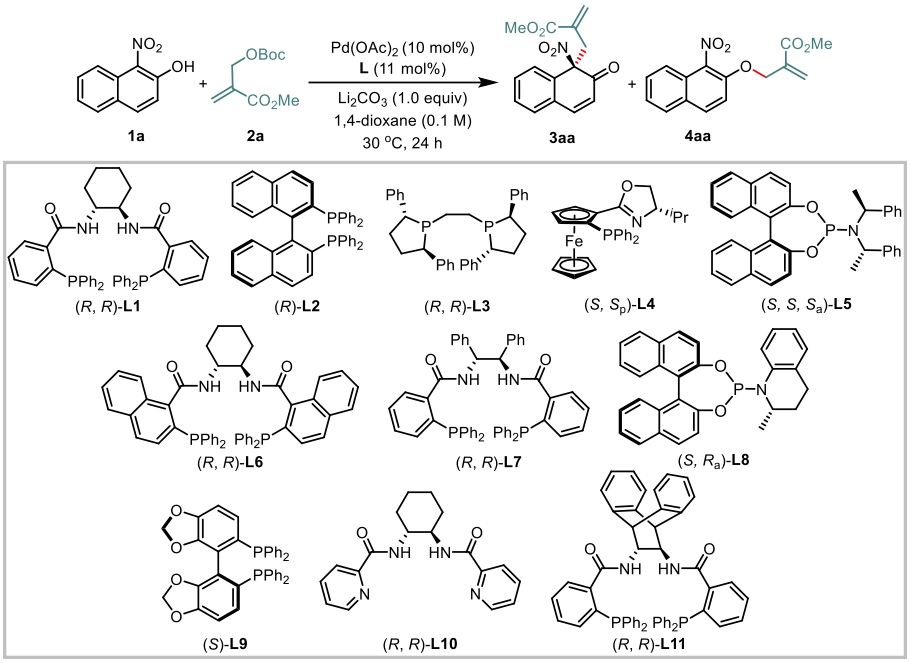
## 1. General Information

Materials were purchased from commercial suppliers and used without further purification unless otherwise stated. All solvents were distilled according to standard methods. Flash column chromatography was performed using 200–300 mesh silica gel. $^{1}H$ and $^{13}C$ NMR spectra were recorded on Bruker, Agilent, and Varian instruments (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protic solvent signals. $^{1}H$ NMR data are recorded as follows: chemical shift ($\delta$, ppm), multiplicity (s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad singlet, *AB* = *AB* system, coupling constant (s) in Hz, integration). Data for $^{13}C$ NMR and $^{19}F$ NMR are reported in terms of chemical shift ($\delta$, ppm). All air- and moisture-sensitive reactions were performed under an atmosphere of argon in flame-dried glassware. IR spectra were obtained on Bruker Tensor 27 instruments with Bruker Platinum ATR accessory. Melting points were measured on Shenguang X-4 melting point apparatus. ESI was recorded on Agilent 6224 TOF LC/MS.

Substrates **1**[1], **2**[2] and Trost ligands[3] were synthesized according to the known procedures.

## 2. Details for Condition Optimization

**Table S1**. Screening of ligands.[a]

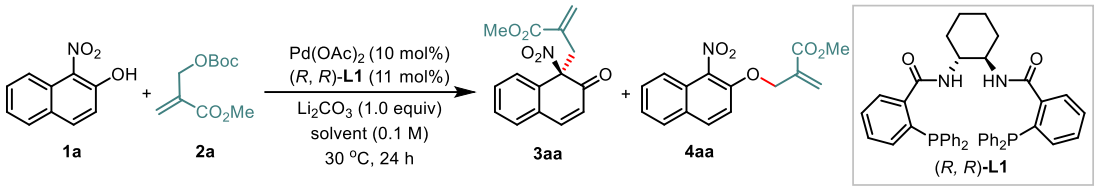



| entry | ligand | yield of **3aa** (%)[b] | C/O[c] | ee (%)[d] |
|---|---|---|---|---|
| 1 | **L1** | 78 | 5/1 | 84 |
| 2 | **L2** | n.d. | -- | -- |
| 3 | **L3** | n.d. | -- | -- |
| 4 | **L4** | n.d. | -- | -- |
| 5[e] | **L5** | 97 | >19/1 | 0 |
| 6 | **L6** | <5% | -- | -- |
| 7 | **L7** | 11 | 2/5 | 80 |
| 8[f] | **L8** | 95 | 19/1 | 9 |
| 9 | **L9** | n.d. | -- | -- |
| 10 | **L10** | n.d. | -- | -- |
| 11 | **L11** | 5% | 1/8 | -- |

[a]General conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(OAc)_2$ (10 mol%), ligand (11 mol%), $Li_2CO_3$ (1.0 equiv) in 1,4-dioxane (0.1 M) at 30 °C. [b]NMR yields using 1,3,5-trimethylbenzene as an internal standard. [c]Determined by $^1H$ NMR analysis of

the crude reaction mixture. [d]Determined by HPLC analysis with a chiral stationary phase. [e]22 mol% of (*S*, *S*, $S_a$)-**L5** was used. [f]22 mol% of (*S*, $R_a$)-**L8** was used. N.D. = not detected.

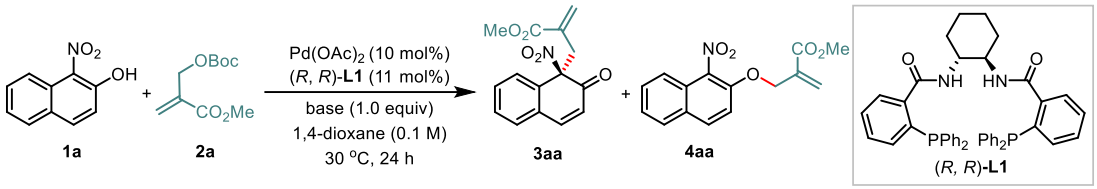
**Table S2**. Screening of solvents.[a]




| entry | solvent | yield of **3aa** (%)[b] | C/O[c] | ee (%)[d] |
|---|---|---|---|---|
| 1 | 1,4-dioxane | 78 | 5/1 | 84 |
| 2 | DCE | 43 | 2/1 | 87 |
| 3 | DCM | 21 | 1/1 | 82 |
| 4 | toluene | 13 | 1/2 | 74 |
| 5 | $CH_3CN$ | n.d. | 32% (**4aa**) | -- |
| 6 | THF | 30 | 5/11 | 87 |
| 7 | $Et_2O$ | n.d. | n.d. | -- |

[a]General conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(OAc)_2$ (10 mol%), (*R*, *R*)-**L1** (11 mol%), $Li_2CO_3$ (1.0 equiv) in solvent (0.1 M) at 30 °C. [b]NMR yields using 1,3,5-trimethylbenzene as an internal standard. [c]Determined by $^1H$ NMR analysis of the crude reaction mixture. [d]Determined by HPLC analysis with a chiral stationary phase. N.D. = not detected.

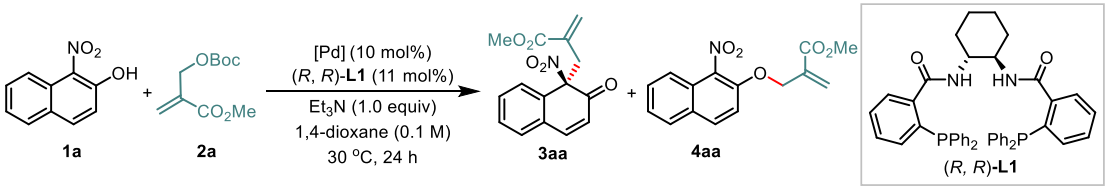
**Table S3**. Screening of bases.[a]




| entry | base | yield of **3aa** (%)[b] | C/O[c] | ee (%)[d] |
|---|---|---|---|---|
| 1 | $Li_2CO_3$ | 78 | 5/1 | 84 |
| 2 | $K_2CO_3$ | 65 | 33/10 | 84 |
| 3 | $Cs_2CO_3$ | 66 | 33/10 | 85 |
| 4 | $Et_3N$ | 92 | >19/1 | 85 |
| 5[e] | $Et_3N$ | 60 | 15/1 | 87 |
| 6 | DBU | 5 | 3/1 | -- |
| 7[f] | -- | 61 | 11/5 | 82 |
| 8[g] | $Et_3N$ | 83 | >19/1 | 85 |
| 9[h] | $Et_3N$ | 91 | >19/1 | 85 |

[a]General conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(OAc)_2$ (10 mol%), (*R*, *R*)-**L1** (11 mol%), base (1.0 equiv) in 1,4-dioxane (0.1 M) at 30 °C. [b]NMR yields using 1,3,5-trimethylbenzene as an internal standard. [c]Determined by $^1$H NMR analysis of the crude reaction mixture. [d]Determined by HPLC analysis with a chiral stationary phase. [e]THF was used instead of 1, 4-dioxane as solvent. [f]Without base. [g]0.5 equiv of $Et_3N$ was used. [h]1.0 equiv of $Et_3N$ was used. N.D. = not detected.

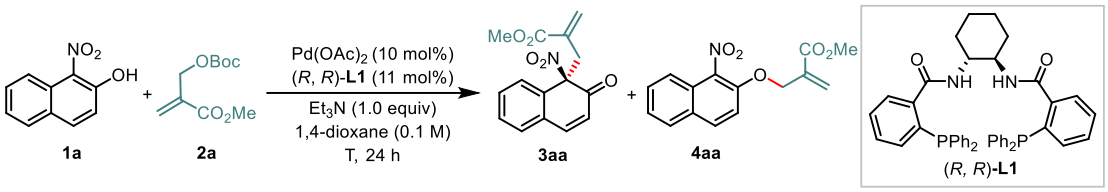
**Table S4**. Screening of [Pd] precursors.[a]




| entry | [Pd] | yield of **3aa** (%)[b] | C/O[c] | ee (%)[d] |
|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | 92 | >19/1 | 85 |
| 2 | $[Pd(C_3H_5)Cl]_2$ | 81 | >19/1 | 80 |
| 3 | $Pd_2dba_3$ | 76 | >19/1 | 82 |

[a]General conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), [Pd] (10 mol%), (*R*, *R*)-**L1** (11 mol%), $Et_3N$ (1.0 equiv) in 1,4-dioxane (0.1 M) at 30 °C. [b]NMR yields using 1,3,5-trimethylbenzene as an internal standard. [c]Determined by $^1H$ NMR analysis of the crude reaction mixture. [d]Determined by HPLC analysis with a chiral stationary phase.

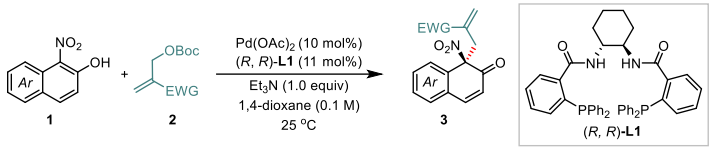
**Table S5**. Screening of temperature.[a]




| entry | T | yield of **3aa** (%)[b] | C/O[c] | ee (%)[d] |
|---|---|---|---|---|
| 1 | 30 °C | 92 | >19/1 | 84 |
| 2 | 25 °C | 90 | >19/1 | 86 |
| 3 | 50 °C | 70 | 38/5 | 85 |
| 4 | 80 °C | trace | 43% **4aa** | -- |
| 5[e] | 25 °C | 92[f] | >19/1 | 86 |

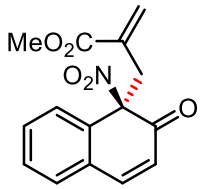
[a]General conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(OAc)_2$ (10 mol%), (*R*, *R*)-**L1** (11 mol%), $Et_3N$ (1.0 equiv) in 1,4-dioxane (0.1 M). [b]NMR yields using 1,3,5-trimethylbenzene as an internal standard. [c]Determined by $^1H$ NMR analysis of the crude reaction mixture. [d]Determined by HPLC analysis with a chiral stationary phase. [e]The reaction was carried out in 0.2 mmol scale. [f]Isolated yields.

## 3. Pd-Catalyzed Intermolecular Asymmetric Allylic Dearomatization of 1-Nitro-2-naphthols with MBH Adducts



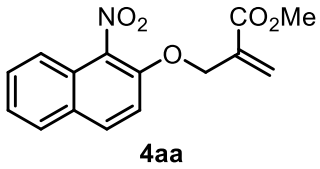

Under Ar atmosphere, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 10 mol%) and (*R*, *R*)-**L1** (15.2 mg, 0.022 mmol, 11 mol%) were added to an oven-dried Schlenk tube. The reaction tube was evacuated and refilled with argon three times. Freshly redistilled 1,4-dioxane (2.0 mL) was added to the flask. After the mixture was stirred for 30 minutes, Boc-protected MBH carbonate (0.24 mmol, 1.2 equiv), α-substituted β-naphthol derivatives (0.20 mmol, 1.0 equiv) and $Et_3N$ (28.0 μL, 0.20 mmol, 1.0 equiv) were successively added to the flask. The reaction was stirred at 25 $^oC$ and monitored by TLC. After the reaction was complete, the mixture was filtered with a celite pad. The filter cake was rinsed with EtOAc (5 mL × 3) and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1, V/V) to afford the target product **3**.

## 4. Characterization Data of Products 3




**3aa**

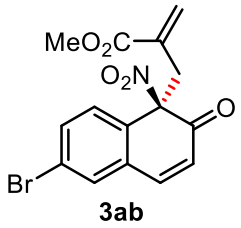
**3aa** was isolated as yellow solid (55.1 mg, 92% yield, 86% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). m.p. = 99.2-101.8 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.51-7.42 (m, 3H), 7.41-7.33 (m, 2H), 6.27 (d, $J$ = 10.0 Hz, 1H), 6.12 (d, $J$ = 0.8 Hz, 1H), 5.48 (d, $J$ = 0.8 Hz, 1H), 3.68 (d, $J$ = 13.6 Hz, 1H), 3.61 (d, $J$ = 13.6 Hz, 1H), 3.46 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.0, 166.5, 146.5, 135.5, 132.2, 131.3, 130.8, 130.4, 130.2, 129.8, 127.4, 124.7, 94.8, 52.0, 40.5. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2953, 2855, 1720, 1676, 1620, 1550, 1438, 1397, 1338, 1300, 1260, 1235, 1198, 1150, 959, 911, 884, 834, 803, 761, 732, 636, 610, 506, 451. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C. $t_R$ (major) = 42.83 min, $t_R$ (minor) = 52.77 min. $[\alpha]_D^{27}$ = +6.1 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{15}H_{12}O_5N$ $[M-H]^-$: 286.0721; Found: 286.0716.




**4aa**

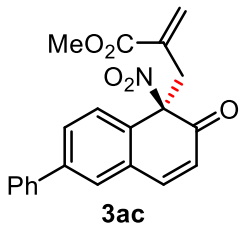
**4aa**, yellow solid, m.p. = 109.3-110.4 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, $J$ = 8.8 Hz, 1H), 7.83 (d, $J$ = 8.0 Hz, 1H), 7.70 (d, $J$ = 8.4 Hz, 1H), 7.60 (t, $J$ = 7.6 Hz, 1H), 7.46 (t, $J$ = 7.6 Hz, 1H), 7.33 (d, $J$ = 9.2 Hz, 1H), 6.43 (s, 1H), 6.04 (s, 1H), 4.98 (s, 2H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.6, 147.4, 136.7, 134.7, 132.4, 129.3, 128.7, 128.2, 127.5, 125.7, 125.6, 120.7, 114.3, 67.9, 52.3. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3085, 3033, 2952, 2882, 2809, 1715, 1694, 1638, 1603, 1518, 1483, 1436, 1357, 1338, 1280, 1240, 1202, 1155, 1065, 1017, 968, 931, 868, 842, 817, 800, 770,

742, 669. HRMS (ESI-TOF) calcd for $C_{15}H_{13}O_5NNa$ $[M+Na]^+$: 310.0686; Found: 310.0689.




**3ab**

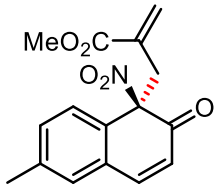
**3ab** was isolated as colorless oil (46.8 mg, 64% yield, 66% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.57 (d, $J$ = 8.4 Hz, 1H), 7.52 (d, $J$ = 2.0 Hz, 1H), 7.41 (d, $J$ = 10.0 Hz, 1H), 7.24 (d, $J$ = 8.4 Hz, 1H), 6.29 (d, $J$ = 10.0 Hz, 1H), 6.16 (s, 1H), 5.52 (s, 1H), 3.66 (d, $J$ = 13.6 Hz, 1H), 3.60 (d, $J$ = 14.0 Hz, 1H), 3.50 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 190.1, 166.3, 144.7, 133.9, 133.4, 132.6, 131.9, 131.52, 131.46, 128.9, 125.7, 124.4, 94.2, 52.1, 40.1. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2952, 2926, 2853, 1719, 1679, 1630, 1552, 1487, 1439, 1337, 1293, 1260, 1233, 1206, 1152, 1084, 969, 887, 802, 708, 651, 612, 553, 469. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda$ = 254 nm, 25 ℃. $t_R$ (major) = 15.36 min, $t_R$ (minor) = 18.11 min. $[\alpha]_D^{25}$ = -21.3 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{15}H_{12}O_5N^{79}BrNa$ $[M+Na]^+$: 387.9791; Found: 387.9792.




**3ac**

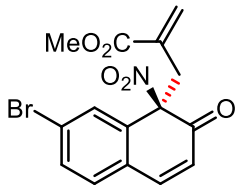
**3ac** was isolated as colorless oil (39.3 mg, 54% yield, 78% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.66 (d, $J$ = 8.0 Hz, 1H), 7.59-7.53 (m, 4H), 7.50-7.40 (m, 4H), 6.30 (d, $J$ = 10.0 Hz, 1H), 6.15 (d, $J$ = 2.0 Hz, 1H), 5.53 (d, $J$ = 2.0 Hz, 1H), 3.73 (d, $J$ = 13.6 Hz, 1H), 3.65 (d, $J$ = 14.4 Hz, 1H), 3.46 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 190.9, 166.5, 146.5, 143.6, 139.0, 134.0, 132.3, 131.3, 130.2, 129.2, 128.7, 128.6, 128.0, 127.1, 125.0, 94.6, 52.1, 40.4. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2963, 2923, 1720, 1677, 1550, 1439, 1411, 1260, 1084, 1017, 865, 797, 698. HPLC conditions: Daicel

Chiralpak IC column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ℃. $t_R$ (major) = 23.81 min, $t_R$ (minor) = 28.20 min. $[\alpha]_D^{25}$ = -28.9 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{21}H_{17}O_5NNa$ $[M+Na]^+$: 386.0999; Found: 386.0995.




**3ad**

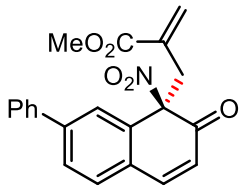
**3ad** was isolated as colorless oil (50.0 mg, 83% yield, 81% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz, $CDCl_3$) *δ* 7.43 (d, *J* = 10.0 Hz, 1H), 7.26 (d, *J* = 2.4 Hz, 2H), 7.16 (s, 1H), 6.22 (d, *J* = 10.0 Hz, 1H), 6.11 (d, *J* = 1.2 Hz, 1H), 5.45 (d, *J* = 1.2 Hz, 1H), 3.67 (d, *J* = 14.0 Hz, 1H), 3.61 (d, *J* = 13.6 Hz, 1H), 3.47 (s, 3H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 191.2, 166.6, 146.7, 140.7, 132.5, 132.4, 131.5, 131.1, 130.8, 129.7, 127.4, 124.7, 94.5, 52.0, 40.3, 21.2. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3852, 3797, 3732, 3666, 3575, 3549, 2956, 2929, 2902, 2863, 2562, 2259, 2213, 2169, 2096, 2014, 1946, 1721, 1677, 1630, 1552, 1440, 1338, 1300, 1261, 1203, 1150, 1024, 799, 712, 602, 562, 505, 476, 439. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ℃. $t_R$ (major) = 17.49 min, $t_R$ (minor) = 19.90 min. $[\alpha]_D^{28}$ = -13.4 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{16}H_{19}O_5N_2$ $[M+NH_4]^+$: 319.1288; Found: 319.1288.




**3ae**

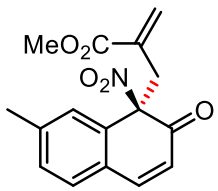
**3ae** was isolated as colorless oil (52.0 mg, 71% yield, 58% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz, $CDCl_3$) *δ* 7.59 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.44 (d, *J* = 10.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.27 (d, *J* = 10.0 Hz, 1H), 6.19 (s, 1H), 5.55 (d, *J* = 1.2 Hz, 1H), 3.66 (d, *J* = 14.0 Hz, 1H), 3.60 (d, *J* = 14.0 Hz, 1H), 3.52 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 189.9, 166.3, 145.3, 136.8, 133.6, 131.8, 131.2, 130.7, 128.6, 125.4,

124.8, 94.0, 52.1, 40.2. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2951, 2927, 2852, 1719, 1677, 1619, 1585, 1550, 1488, 1438, 1386, 1336, 1287, 1258, 1235, 1198, 1150, 1083, 960, 888, 848, 820, 756, 708, 643, 613, 547, 450, 424. HPLC conditions: Daicel Chiralpak AD–H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C. $t_R$ (minor) = 10.88 min, $t_R$ (major) = 13.19 min. $[\alpha]_D^{25}$ = -18.7 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{15}H_{11}O_5N^{79}Br$ $[M-H]^-$: 363.9826; Found: 363.9822.




**3af**

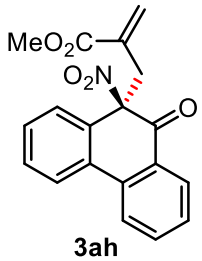
**3af** was isolated as colorless oil (58.8 mg, 81% yield, 80% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1H$ NMR (400 MHz, $CDCl_3$) *δ* 7.66 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.56-7.51 (m, 2H), 7.51-7.38 (m, 4H), 6.27 (d, *J* = 9.6 Hz, 1H), 6.17 (s, 1H), 5.58 (s, 1H), 3.79 (d, *J* = 13.6 Hz, 1H), 3.63 (d, *J* = 13.6 Hz, 1H), 3.38 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) *δ* 191.0, 166.6, 146.4, 143.8, 139.1, 135.8, 132.3, 131.3, 130.7, 129.3, 128.9, 128.7, 128.6, 127.2, 126.4, 124.3, 94.8, 52.1, 40.3. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2951, 2926, 2852, 1720, 1675, 1605, 1550, 1486, 1439, 1393, 1337, 1259, 1231, 1197, 1151, 1077, 962, 910, 853, 812, 762, 732, 697, 647, 606, 531, 420. HPLC conditions: Daicel Chiralcel OD–3 column, $CO_2$/MeOH, 95:05 v/v, flow rate 1 mL/min, λ = 214 nm, 33 ℃. $t_R$ (minor) = 10.65 min, $t_R$ (major) = 11.59 min. $[\alpha]_D^{29}$ = -46.4 (*c* = 0.5, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{21}H_{16}O_5N$ $[M-H]^-$: 362.1034; Found: 362.1031.




**3ag**

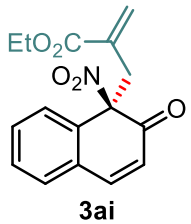
**3ag** was isolated as colorless oil (52.4 mg, 87% yield, 82% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1H$ NMR (400 MHz, $CDCl_3$) *δ* 7.45 (d, *J* = 10.0 Hz, 1H), 7.24 (s, 2H), 7.16 (s, 1H), 6.18 (d, *J* = 10.0 Hz, 1H), 6.12 (s, 1H), 5.47 (d, *J* = 1.2 Hz, 1H), 3.65 (d, *J* = 14.0 Hz, 1H), 3.59 (d, *J* = 14.0

Hz, 1H), 3.46 (s, 3H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.1, 166.5, 146.7, 141.8, 135.5, 132.3, 131.1, 131.0, 130.2, 128.2, 127.2, 123.6, 94.8, 52.0, 40.5, 21.7. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2961, 2923, 2853, 1720, 1674, 1609, 1549, 1438, 1337, 1296, 1259, 1217, 1015, 797, 708, 609, 547, 457. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ℃. $t_R$ (major) = 13.95 min, $t_R$ (minor) = 16.24 min. $[\alpha]_D^{25}$ = -18.4 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{16}H_{14}O_5N$ $[M-H]^-$: 300.0877; Found: 300.0872.



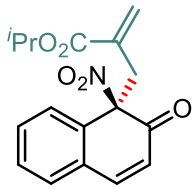

**3ah**

**3ah** was isolated as white solid (59.0 mg, 88% yield, 68% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). m.p. = 95.9-97.6 ºC. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.10 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.4 Hz, 2H), 7.79-7.68 (m, 1H), 7.56-7.44 (m, 2H), 7.44-7.38 (m, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.00 (s, 1H), 5.39 (s, 1H), 3.71 (d, *J* = 14.0 Hz, 1H), 3.62 (d, *J* = 14.0 Hz, 1H), 3.35 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 190.2, 166.2, 136.7, 136.1, 132.6, 132.3, 131.4, 130.31, 130.29, 129.5, 129.1, 128.5, 128.0, 127.4, 123.9, 123.5, 96.6, 51.8, 40.6. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2950, 2920, 2849, 1721, 1691, 1599, 1549, 1482, 1434, 1336, 1279, 1234, 1200, 1152, 1134, 961, 838, 812, 764, 725, 663, 618. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ℃. $t_R$ (major) = 30.89 min, $t_R$ (minor) = 34.87 min. $[\alpha]_D^{28}$ = +53.2 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{19}H_{15}O_5NNa$ $[M+Na]^+$: 360.0842; Found: 360.0845.



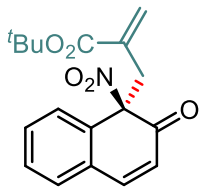

**3ai**

**3ai** was isolated as colorless oil (51.8 mg, 86% yield, 84% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.51-7.41 (m, 3H), 7.40-7.32 (m, 2H), 6.24 (d, $J$ = 10.0 Hz, 1H), 6.12 (s, 1H), 5.46 (s, 1H), 3.98-3.81 (m, 2H), 3.68 (d, $J$ = 13.6 Hz, 1H), 3.61 (d, $J$ = 13.6 Hz, 1H), 1.13 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.0, 166.0, 146.5, 135.5, 132.5, 131.0, 130.8, 130.4, 130.2, 129.8, 127.4, 124.7, 94.9, 61.2, 40.4, 14.1. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2983, 2931, 1712, 1676, 1550, 1396, 1367, 1333, 1299, 1149, 1024, 958, 852, 806, 762, 503. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda$ = 254 nm, 25 °C. $t_R$ (major) = 22.24 min, $t_R$ (minor) = 28.58 min. $[\alpha]_D^{30}$ = +4.2 (*c* = 0.5, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{16}H_{14}O_5N$ $[M-H]^-$: 300.0877; Found: 300.0872.



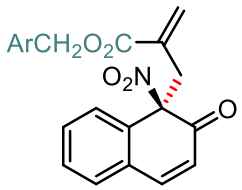

**3aj**

**3aj** was isolated as colorless oil (53.6 mg, 85% yield, 89% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.51-7.40 (m, 3H), 7.43-7.31 (m, 2H), 6.24 (d, $J$ = 10.0 Hz, 1H), 6.09 (s, 1H), 5.43 (s, 1H), 4.84-4.66 (m, 1H), 3.68 (d, $J$ = 13.6 Hz, 1H), 3.61 (d, $J$ = 13.6 Hz, 1H), 1.13 (d, $J$ = 6.4 Hz, 3H), 1.06 (d, $J$ = 6.4 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.0, 165.5, 146.5, 135.5, 132.8, 130.9, 130.6, 130.4, 130.1, 129.8, 127.4, 124.8, 94.9, 68.9, 40.2, 21.7, 21.6. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2982, 2935, 1710, 1676, 1621, 1550, 1453, 1434, 1298, 1260, 1235, 1194, 1104, 956, 915, 802, 757, 708. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, $\lambda$ = 254 nm, 25 °C. $t_R$ (major) = 17.30 min, $t_R$ (minor) = 21.28 min. $[\alpha]_D^{27}$ = +4.3 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{17}H_{17}O_5NNa$ $[M+Na]^+$: 338.0999; Found: 338.0999.



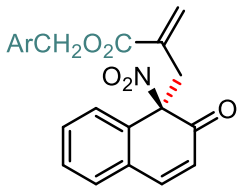
**3ak**

**3ak** was isolated as colorless oil (54.0 mg, 82% yield, 88% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.50-7.41 (m, 3H), 7.40-7.33 (m, 2H), 6.24 (d, $J$ = 10.0 Hz, 1H), 6.04 (s, 1H), 5.38 (s, 1H), 3.64 (d, $J$ = 13.6 Hz, 1H), 3.58 (d, $J$ = 13.6 Hz, 1H), 1.29 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.1, 165.1, 146.4, 135.7, 133.6, 131.0, 130.3, 130.1, 129.9, 127.5, 124.8, 95.1, 81.4, 40.1, 27.9. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2978, 2930, 1708, 1677, 1551, 1455, 1395, 1341, 1147, 957, 847, 808, 761. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 95:05 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ℃. $t_R$ (major) = 9.40 min, $t_R$ (minor) = 10.92 min. $[\alpha]_D^{28}$ = +3.2 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{18}H_{18}O_5N$ $[M-H]^-$: 328.1190; Found: 328.1186.



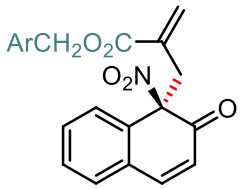
**3al** Ar = $C_6H_5$

**3al** was isolated as colorless oil (58.1 mg, 80% yield, 88% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43-7.31 (m, 7H), 7.28 (d, $J$ = 8.4 Hz, 1H), 7.23 (d, $J$ = 3.2 Hz, 1H), 7.22 (d, $J$ = 2.0 Hz, 1H), 6.33-6.01 (m, 2H), 5.51 (s, 1H), 4.91 (*AB*, $J_{AB}$ = 12.4 Hz, 1H), 4.86 (*BA*, $J_{BA}$ = 12.4 Hz, 1H), 3.70 (d, $J$ = 13.6 Hz, 1H), 3.63 (d, $J$ = 13.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.0, 165.8, 146.5, 135.6, 135.4, 132.3, 131.5, 130.9, 130.4, 130.2, 129.7, 128.7, 128.5, 128.4, 127.4, 124.7, 94.8, 66.9, 40.3. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2925, 2226, 1716, 1677, 1551, 1454, 1398, 1334, 1299, 1187, 1147, 961, 807, 754, 698. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C. $t_R$ (major) = 24.31 min, $t_R$ (minor) = 28.55 min. $[\alpha]_D^{30}$ = +1.5 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{21}H_{16}O_5N$ $[M-H]^-$: 362.1034; Found: 362.1029.



**3am** Ar = 2-$ClC_6H_4$

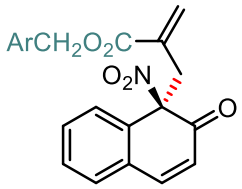
**3am** was isolated as colorless oil (66.8 mg, 84% yield, 88% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.46-7.31 (m, 5H), 7.33-7.25 (m, 2H), 7.27-7.23 (m, 2H), 6.35-5.98 (m, 2H), 5.56 (s, 1H), 4.98 (s, 2H), 3.71 (d, $J$ = 13.6 Hz, 1H), 3.63 (d, $J$ = 14.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.0, 165.7, 146.6, 135.3, 133.8, 133.3, 132.1, 131.8, 130.9, 130.4, 130.2, 130.1, 129.8, 129.72, 129.70, 127.5, 127.0, 124.6, 94.8, 64.2, 40.3. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2963, 2905, 1718, 1676, 1550, 1407, 1258, 1014, 796, 756, 702, 503. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, $\lambda$ = 254 nm, 25 °C. $t_R$ (major) = 18.72 min, $t_R$ (minor) = 21.86 min. $[\alpha]_D^{29}$ = +3.7 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{21}H_{15}O_5NCl$ $[M-H]^-$: 396.0644; Found: 396.0639.



**3an** Ar = 2-$MeC_6H_4$

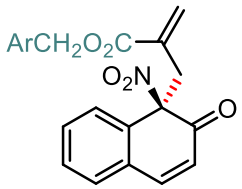
**3an** was isolated as white solid (64.9 mg, 86% yield, 90% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). m.p. = 117.8-119.1 ºC. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.42-7.30 (m, 4H), 7.29-7.21 (m, 2H), 7.17 (d, $J$ = 5.2 Hz, 3H), 6.15 (s, 1H), 6.14 (d, $J$ = 10.0 Hz, 1H), 5.51 (s, 1H), 4.90 (s, 2H), 3.69 (d, $J$ = 13.6 Hz, 1H), 3.62 (d, $J$ = 13.6 Hz, 1H), 2.25 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.0, 165.8, 146.4, 137.1, 135.3, 133.5, 132.3, 131.4, 130.8, 130.5, 130.3, 130.1, 129.7, 129.4, 128.7, 127.4, 126.1, 124.6, 94.8, 65.3, 40.3, 19.0. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2962, 2917, 1710, 1678, 1617, 1552, 1460, 1419, 1392, 1338, 1302, 1258, 1211, 1194, 1142, 1041, 973, 959, 923, 849, 817, 801, 763, 742, 689, 638, 603, 553, 526, 505, 450, 413. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda$ = 254 nm, 25 ℃. $t_R$ (major) = 13.69 min, $t_R$ (minor)

= 15.67 min. $[\alpha]_D^{29}$ = +0.8 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{22}H_{18}O_5N$ $[M-H]^-$: 376.1190; Found: 376.1185.




**3ao** Ar = 2-$CF_3C_6H_4$

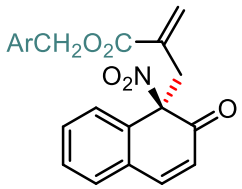
**3ao** was isolated as colorless oil (75.8 mg, 88% yield, 87% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.67 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.41-7.28 (m, 5H), 6.20 (s, 1H), 6.19 (d, *J* = 10.0 Hz, 1H), 5.56 (s, 1H), 5.06 (s, 2H), 3.70 (d, *J* = 13.6 Hz, 1H), 3.63 (d, *J* = 13.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.0, 165.5, 146.6, 135.3, 133.7 (d, *J* = 1.8 Hz), 132.2, 132.0, 131.9, 130.9, 130.4, 130.3, 130.2, 129.7, 128.6, 128.5 (q, *J* = 30.9 Hz), 127.4, 126.3 (q, *J* = 5.7 Hz), 124.6, 124.2 (q, *J* = 272.1 Hz), 94.8, 63.3 (q, *J* = 2.7 Hz), 40.3. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -60.0. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2963, 2923, 1720, 1676, 1619, 1551, 1455, 1398, 1313, 1259, 1112, 1060, 1039, 958, 801, 765, 655, 505, 446. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ℃. $t_R$ (major) = 13.46 min, $t_R$ (minor) = 15.53 min. $[\alpha]_D^{29}$ = -1.5 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{22}H_{15}O_5NF_3$ $[M-H]^-$: 430.0908; Found: 430.0902.




**3ap** Ar = 3-$ClC_6H_4$

**3ap** was isolated as colorless oil (50.9 mg, 64% yield, 88% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.46-7.25 (m, 7H), 7.19 (s, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.23-6.08 (m, 2H), 5.56 (s, 1H), 4.88 (*AB*, $J_{AB}$ = 12.4 Hz, 1H), 4.83 (*BA*, $J_{BA}$ = 12.4 Hz, 1H), 3.69 (d, *J* = 13.6 Hz, 1H), 3.62 (d, *J* = 13.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 190.8, 165.5, 146.4, 137.4, 135.2, 134.4, 132.0, 131.8, 130.7, 130.3, 130.0, 129.8, 129.6, 128.5,

128.2, 127.3, 126.3, 124.5, 94.6, 65.8, 40.2. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3678, 3071, 2966, 2922, 2904, 1718, 1676, 1620, 1550, 1398, 1333, 1299, 1258, 1211, 1185, 1144, 1078, 963, 870, 849, 801, 762, 683, 635, 507, 446. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ℃. $t_R$ (major) = 19.70 min, $t_R$ (minor) = 22.83 min. $[\alpha]_D^{29}$ = -0.9 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{21}H_{15}O_5NCl$ $[M-H]^-$: 396.0644; Found: 396.0639.



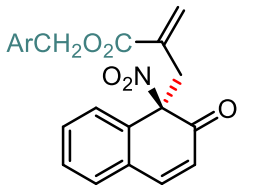

**3aq** Ar = 3-$CF_3C_6H_4$

**3aq** was isolated as colorless oil (62.8 mg, 73% yield, 83% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.60 (d, *J* = 7.6 Hz, 1H), 7.52-7.46 (m, 2H), 7.45-7.39 (m, 2H), 7.38-7.32 (m, 3H), 7.28 (d, *J* = 3.6 Hz, 1H), 6.20 (s, 1H), 6.16 (d, *J* = 10.0 Hz, 1H), 5.56 (s, 1H), 4.96 (*AB*, $J_{AB}$ = 12.4 Hz, 1H), 4.92 (*BA*, $J_{BA}$ = 12.4 Hz, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 3.63 (d, *J* = 14.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 190.9, 165.7, 146.5, 136.6, 135.4, 132.0, 131.9, 131.7 (d, *J* = 1.5 Hz), 131.0 (q, *J* = 32.3 Hz), 130.9, 130.4, 130.2, 129.7, 129.2, 127.4, 125.3 (q, *J* = 3.8 Hz), 125.0 (q, *J* = 3.8 Hz), 124.6, 124.1 (q, *J* = 270.8 Hz), 94.7, 65.9, 40.3. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -62.6. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2989, 2960, 2926, 1720, 1677, 1620, 1551, 1452, 1328, 1259, 1121, 1073, 1010, 965, 884, 801, 762, 701, 661, 635, 505, 456. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ℃. $t_R$ (major) = 10.74 min, $t_R$ (minor) = 12.04 min. $[\alpha]_D^{28}$ = -3.8 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{22}H_{15}O_5NF_3$ $[M-H]^-$: 430.0908; Found: 430.0902.


**3ar** Ar = 4-$BrC_6H_4$

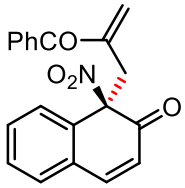
**3ar** was isolated as colorless oil (64.5 mg, 73% yield, 87% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz,

$CDCl_3$) $\delta$ 7.47 (d, $J$ = 8.0 Hz, 2H), 7.43-7.32 (m, 4H), 7.29 (d, $J$ = 8.4 Hz, 1H), 7.10 (d, $J$ = 8.0 Hz, 2H), 6.17 (s, 1H), 6.16 (d, $J$ = 10.0 Hz, 1H), 5.52 (s, 1H), 4.87 (*AB*, $J_{AB}$ = 12.4 Hz, 1H), 4.82 (*BA*, $J_{BA}$ = 12.4 Hz, 1H), 3.67 (d, $J$ = 13.6 Hz, 1H), 3.62 (d, $J$ = 13.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.9, 165.7, 146.5, 135.4, 134.6, 132.1, 131.8, 131.7, 130.9, 130.4, 130.2, 130.1, 129.7, 127.4, 124.6, 122.5, 94.7, 66.0, 40.2. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2959, 2925, 2854, 1717, 1675, 1620, 1550, 1488, 1399, 1332, 1299, 1258, 1211, 1185, 1144, 1070, 1011, 962, 883, 800, 754, 666, 632, 540, 504, 452. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C. $t_R$ (major) = 20.89 min, $t_R$ (minor) = 24.89 min. $[\alpha]_D^{30}$ = -4.9 ($c$ = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{21}H_{15}O_5N^{79}Br$ $[M-H]^-$: 440.0139; Found: 440.0133.



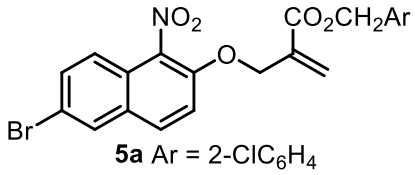

**3as** Ar = 4-$MeC_6H_4$

**3as** was isolated as colorless oil (57.4 mg, 76% yield, 88% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45-7.32 (m, 4H), 7.29 (d, $J$ = 6.8 Hz, 1H), 7.19-7.06 (m, 4H), 6.16 (d, $J$ = 9.2 Hz, 2H), 5.48 (s, 1H), 4.86 (*AB*, $J_{AB}$ = 12.4 Hz, 1H), 4.82 (*BA*, $J_{BA}$ = 12.4 Hz, 1H), 3.69 (d, $J$ = 13.6 Hz, 1H), 3.62 (d, $J$ = 13.6 Hz, 1H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 190.9, 165.8, 146.4, 138.2, 135.3, 132.4, 132.2, 131.3, 130.7, 130.2, 130.0, 129.6, 129.2, 128.4, 127.3, 124.5, 94.7, 66.7, 40.2, 21.2. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2960, 2922, 1716, 1677, 1620, 1551, 1398, 1333, 1299, 1259, 1186, 1147, 1014, 961, 801, 762, 707, 476. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C. $t_R$ (major) = 13.89 min, $t_R$ (minor) = 15.84 min. $[\alpha]_D^{30}$ = +5.2 ($c$ = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{22}H_{18}O_5N$ $[M-H]^-$: 376.1190; Found: 376.1185.



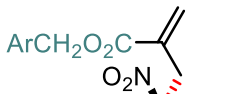

**3at**

**3at** was isolated as white solid (41.2 mg, 62% yield, 60% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). m.p. = 129.7-130.6 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.53-7.44 (m, 2H), 7.43-7.28 (m, 7H), 7.25 (d, *J* = 7.2 Hz, 1H), 6.32 (d, *J* = 10.0 Hz, 1H), 5.90 (s, 1H), 5.67 (s, 1H), 4.00 (d, *J* = 13.6 Hz, 1H), 3.71 (d, *J* = 13.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 195.5, 190.8, 146.4, 139.5, 136.1, 135.3, 132.4, 132.2, 131.1, 130.5, 130.1, 129.43, 129.38, 128.0, 127.5, 124.8, 94.0, 40.4. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3372, 2974, 2898, 1653, 1545, 1444, 1394, 1340, 1264, 1229, 1202, 1085, 1045, 999, 957, 878, 831, 813, 781, 765, 749, 701, 655, 630, 573, 544, 508, 470. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ℃. $t_R$ (major) = 12.88 min, $t_R$ (minor) = 15.56 min. $[\alpha]_D^{29}$ = -15.7 (*c* = 1.0, $CHCl_3$). HRMS (ESI-TOF) calcd for $C_{20}H_{15}O_4NNa$ $[M+Na]^+$: 356.0893; Found: 356.0888.




**5a** Ar = 2-$ClC_6H_4$

**5a**, yellow foam. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.45-7.30 (m, 3H), 7.30-7.21 (m, 2H), 6.51 (s, 1H), 6.07 (s, 1H), 5.35 (s, 2H), 4.99 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.7, 147.7, 136.5, 134.4, 133.9, 133.2, 132.6, 131.4, 130.1, 129.9, 129.8, 129.5, 128.3, 127.1, 124.3, 122.5, 119.4, 115.6, 68.0, 64.4. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2984, 2904, 1722, 1632, 1592, 1529, 1500, 1476, 1446, 1407, 1358, 1305, 1285, 1261, 1200, 1154, 1085, 1052, 1023, 959, 879, 812, 755, 731, 702, 676, 652, 620. HRMS (ESI-TOF) calcd for $C_{21}H_{15}O_5NNaCl^{79}Br$ $[M+Na]^+$: 497.9714; Found: 497.9707.

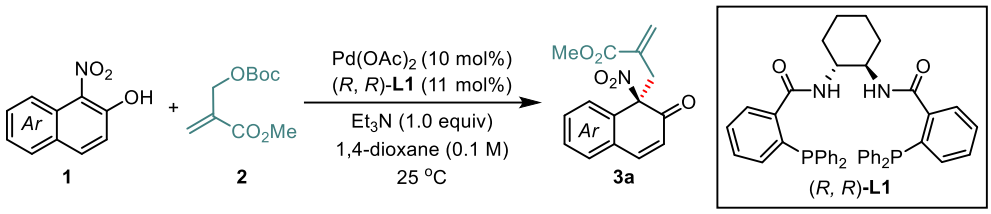



**6a** Ar = 2-$ClC_6H_4$

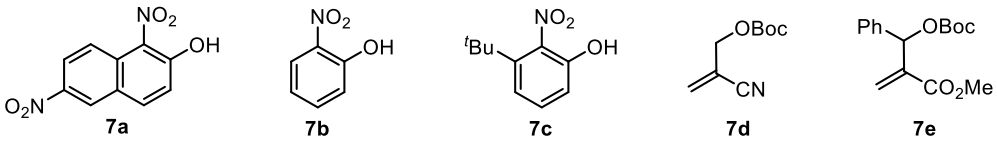
**6a** was isolated as colorless oil (82.6 mg, 87% yield, 0% ee) by flash column chromatography (petroleum ether/ethyl acetate = 5/1, V/V). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.43-7.36 (m, 1H), 7.36-7.25 (m, 3H), 7.26-7.19 (m, 2H), 6.24 (s, 1H), 6.23 (d, *J* = 9.6 Hz, 1H), 5.60 (d, *J* = 1.2 Hz, 1H), 5.02 (*AB*, $J_{AB}$ = 12.8 Hz, 1H), 5.01 (*BA*, $J_{BA}$ = 12.8 Hz, 1H), 3.71 (d, *J* = 14.0 Hz, 1H), 3.61 (d, *J* = 13.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.2, 165.6, 144.8, 134.0, 133.8, 133.5, 133.1, 132.7, 132.1, 131.9, 131.5, 130.2, 129.9, 129.8, 129.1, 127.0, 125.7, 124.5, 94.3, 64.4, 39.8. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2974, 2922, 1720, 1672, 1610, 1552, 1476, 1428, 1400, 1332, 1300, 1256, 1216, 1169, 1144, 1056, 1003, 964, 909, 824, 756, 733, 701, 662. HPLC conditions: Daicel Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C. $t_R$ (major) = 19.32 min, $t_R$ (minor) = 22.06 min. HRMS (ESI-TOF) calcd for $C_{21}H_{15}O_5NNaCl^{79}Br$ $[M+Na]^+$: 497.9714; Found: 497.9715.

## 5. Unsuccessful substrates

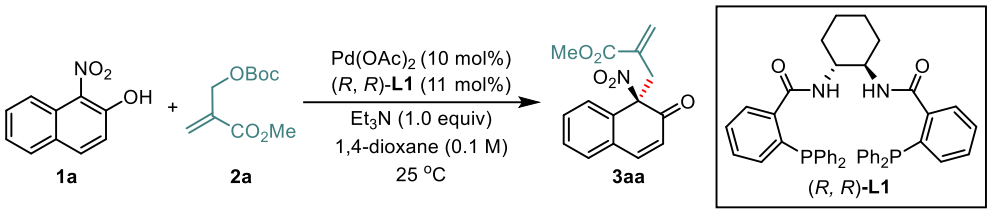
Optimal conditions:




Unsuccessful substrates under optimal conditions:

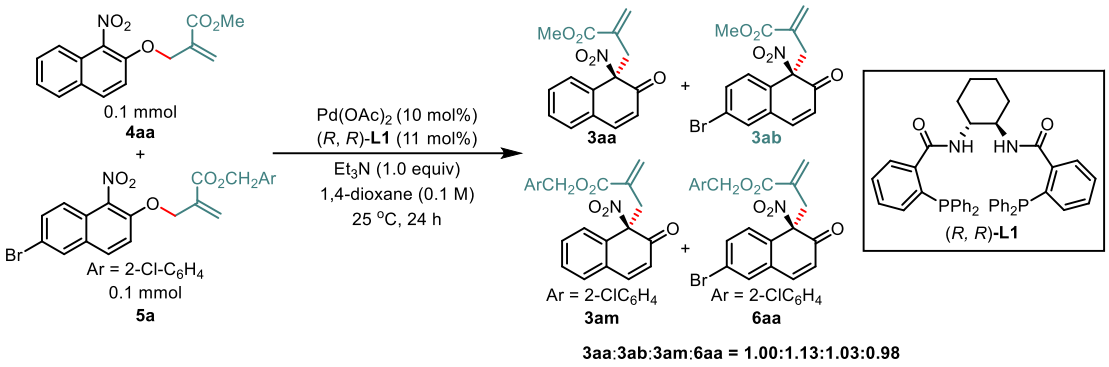


## 6. Mmol-scale Reaction



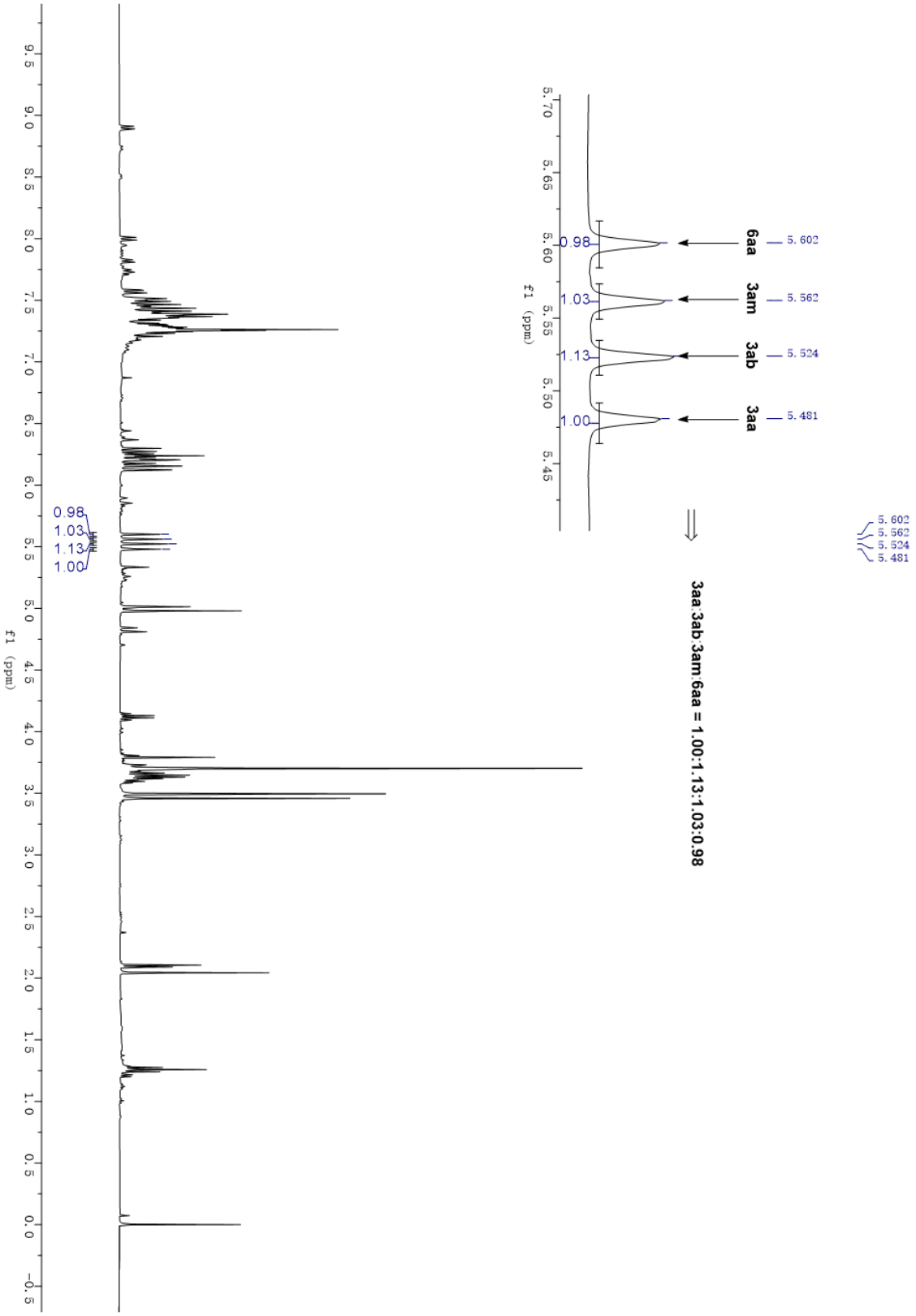

$Pd(OAc)_2$ (99.0 mg, 0.45 mmol, 10 mol%) and (*R*, *R*)-**L1** (342.0 mg, 0.50 mmol, 11 mol%) were added to an oven-dried Schlenk tube under Ar atmosphere. The reaction tube was evacuated and refilled with argon three times. Freshly redistilled 1,4-dioxane (45 mL) was added to the flask. After the mixture was stirred for 30 minutes, Boc-protected MBH carbonate **2a** (1167.6 mg, 5.4 mmol, 1.2 equiv), 1-nitro-2-naphthol (774.0 mg, 4.5 mmol, 1.0 equiv) and $Et_3N$ (630 μL, 4.5 mmol, 1.0 equiv) were successively added. The reaction was stirred at room temperature and monitored by TLC. After the reaction was complete, the mixture was filtered with a celite pad. The filter cake was rinsed with EtOAc (10 mL × 3) and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the target product **3aa** (0.98 g, 76% yield, 84% ee).

## 7. Crossover Experiments

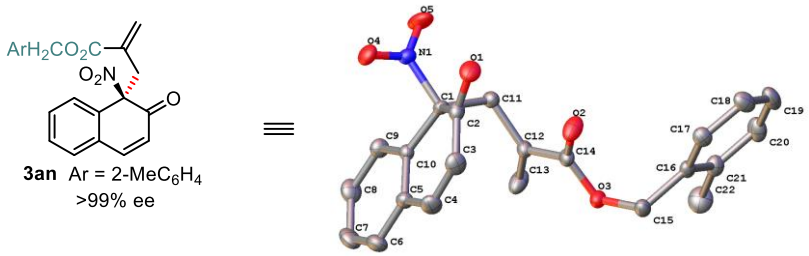



Under Ar atmosphere, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 10 mol%) and (*R*, *R*)-**L1** (15.2 mg, 0.022 mmol, 11 mol%) were added to an oven-dried Schlenk tube. The reaction tube was evacuated and refilled with argon three times. Freshly redistilled 1,4-dioxane (2.0 mL) was added to the flask. After the mixture was stirred for 30 min, **4aa** (28.7 mg, 0.1 mmol), **5a** (47.7 mg, 0.1 mmol) and $Et_3N$ (28.0 μL, 0.20 mmol, 1.0 equiv) were successively added to the flask. The reaction was stirred at 25 °C for 24 h. Subsequently, the mixture was filtered with a celite pad. The filter cake was rinsed with EtOAc (5 mL × 3) and the filtrate was concentrated under reduced pressure. $^1H$ NMR analysis of the crude reaction mixture showed that the reaction produced **3aa**, **3ab**, **3am** and **6aa** in a ratio of 1.00:1.13:1.03:0.98.

$^{1}$H NMR (400 MHz, $CDCl_3$) of the crude reaction mixture:



## 8. X-Ray Crystal Structure of (*R*)-3an




CCDC 2234267 [Thermal ellipsoid plots (30% probability)]

Figure S1. The X-Ray crystal structure of (*R*)-**3an**

The single crystal of **3an** (> 99% ee) is obtained by evaporation of its $Et_2O$/hexane solution at room temperature. The structure of **3an** was then determined by X-ray crystallographic analysis to confirm its absolute configuration as *R* (shown in Figure S1). The X-ray intensity data were measured on a Bruker D8 VENTURE diffractometer.

**Table S6**. Crystal data and structure refinement for mj22278_0m.

| | | |
|---|---|---|
| Identification code | mj22278_0m | |
| Empirical formula | C22 H19 N O5 | |
| Formula weight | 377.38 | |
| Temperature | 213 K | |
| Wavelength | 1.34139 Å | |
| Crystal system | Monoclinic | |
| Space group | P 1 21 1 | |
| Unit cell dimensions | a = 8.01130(10) Å | α= 90 ° |
| | b = 13.9038(2) Å | β=90.3800(10) ° |
| | c = 8.5163(2) Å | γ= 90 ° |
| Volume | 948.59(3) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.321 $Mg/m^3$ | |
| Absorption coefficient | 0.494 $mm^{-1}$ | |

| | |
|---|---|
| F(000) | 396 |
| Crystal size | 0.07 x 0.07 x 0.05 $mm^3$ |
| Theta range for data collection | 4.517 to 54.939 °. |
| Index ranges | -9<=h<=9, -16<=k<=16, -10<=l<=10 |
| Reflections collected | 20296 |
| Independent reflections | 3537 [R(int) = 0.0355] |
| Completeness to theta = 53.594 ° | 98.2 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7508 and 0.5985 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3537 / 1 / 254 |
| Goodness-of-fit on $F^2$ | 1.049 |
| Final R indices [I>2sigma(I)] | R1 = 0.0297, wR2 = 0.0739 |
| R indices (all data) | R1 = 0.0312, wR2 = 0.0753 |
| Absolute structure parameter | 0.03(7) |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.137 and -0.109 e.$Å^{-3}$ |

## 9. References

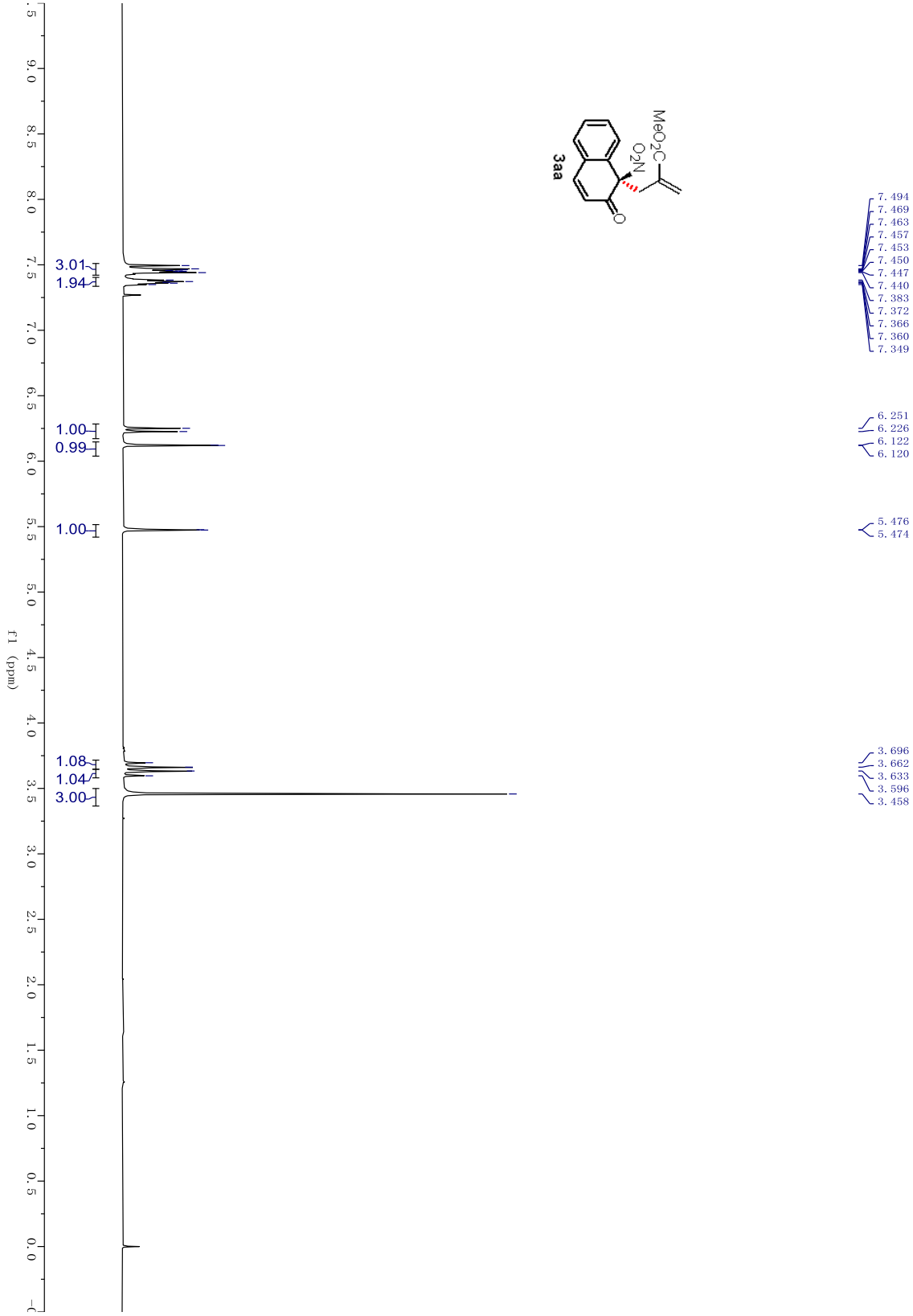
(1) K. A. Juárez-Ornelas, J. O. C. Jiménez-Halla, T. Kato, C. R. Solorio-Alvarado, K. Maruoka, *Org. Lett.*, 2019, **21**, 1315-1319.

(2) (a) G.-H. Yang, H. Zheng, X. Li, J.-P. Cheng, *ACS. Catal.*, **2020**, *10*, 2324-2333. (b) J. B. Kraïem, H. Amri, *Synth. Commun.*, **2012**, *43*, 110-117. (c) X. B. Nguyen, Y. Nakano, N. M. Duggan, L. Scott, M. Breugst, D. W. Lupton, *Angew. Chem., Int. Ed.*, **2019**, *58*, 11483-11490.

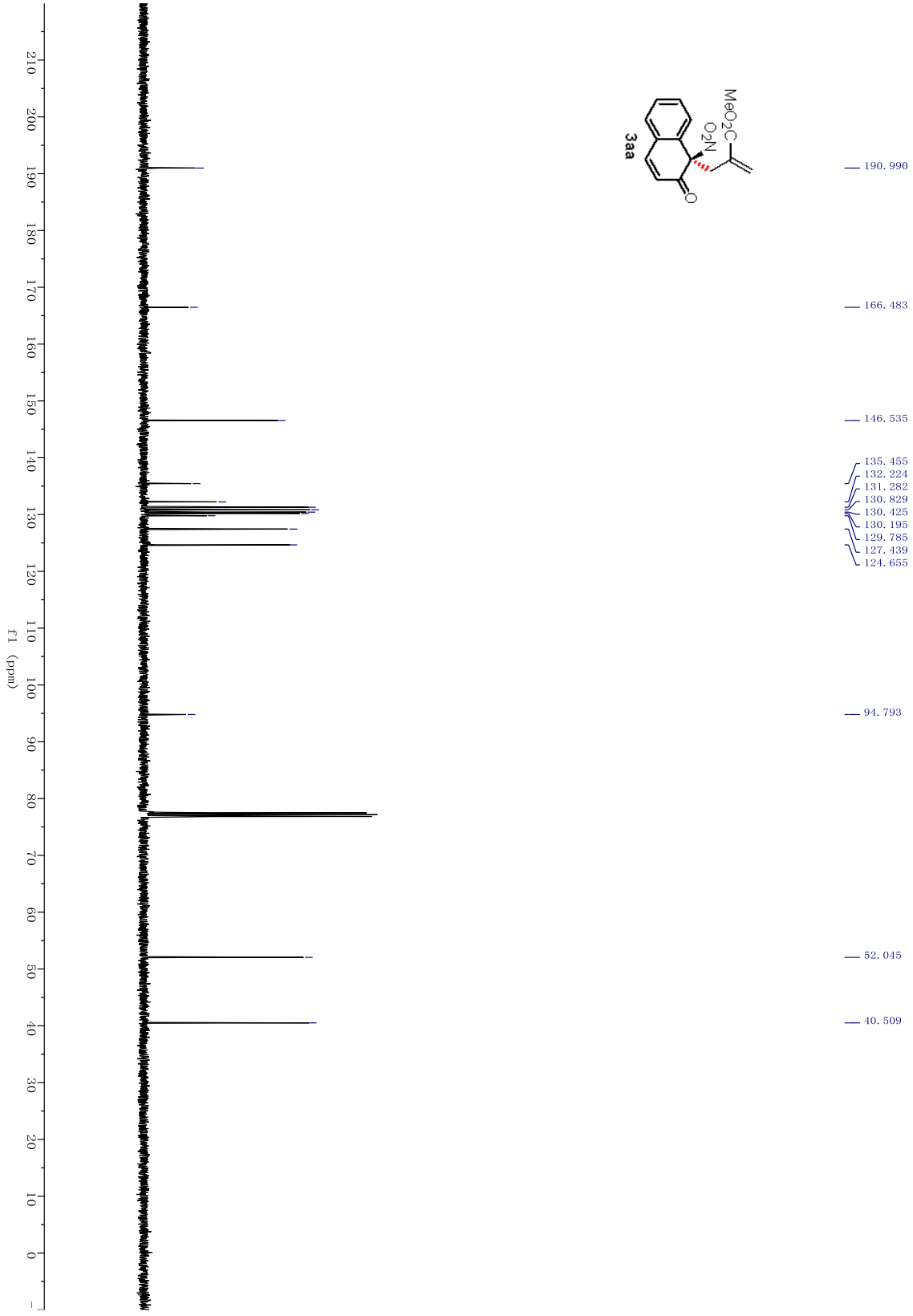
(3) B. M. Trost, D. L. Van Vranken, C. Bingel, *J. Am. Chem. Soc.*, 2002, **114**, 9327-9343.

## 10. Copies of NMR Spectra

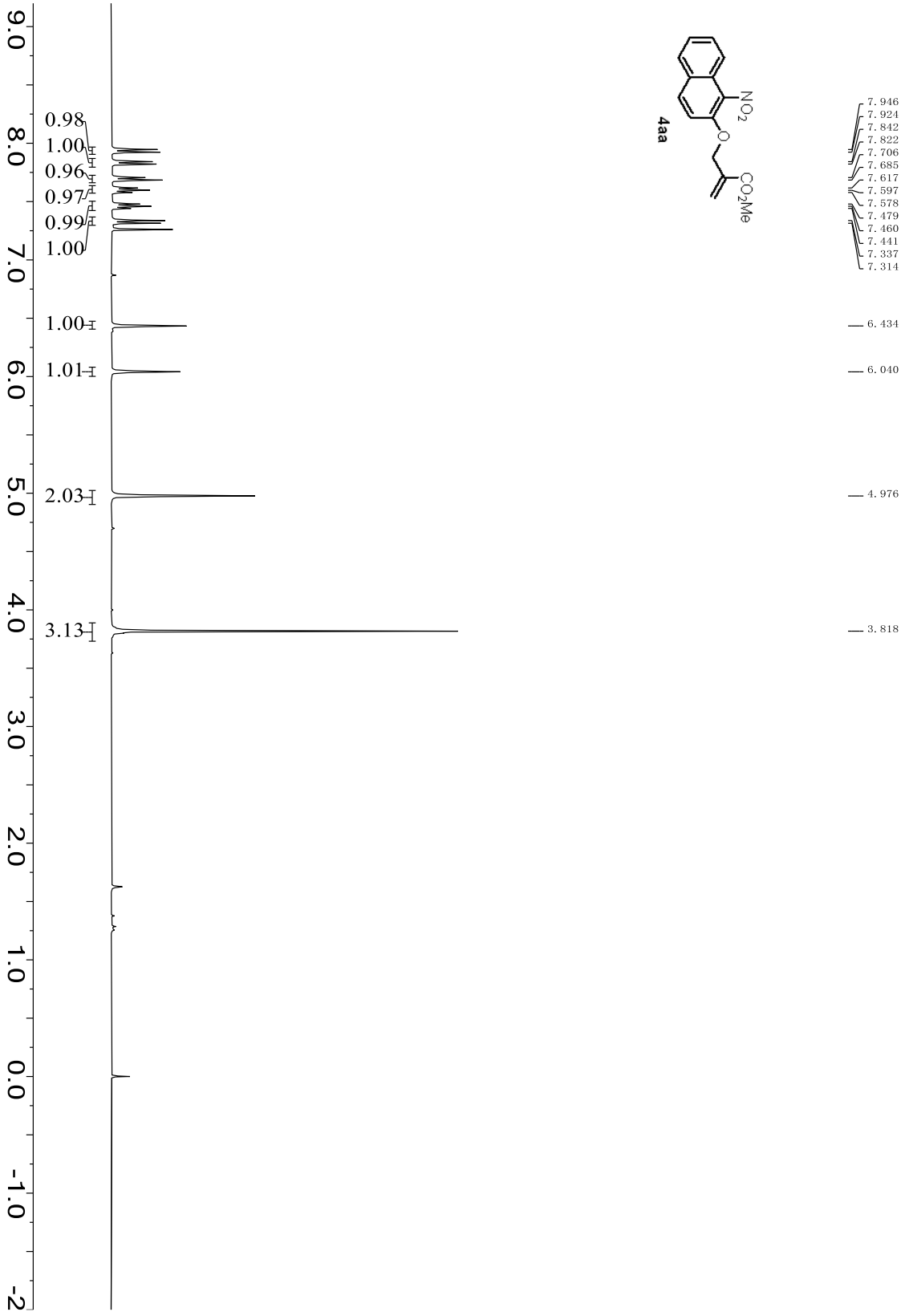
$^1$H NMR (400 MHz, $CDCl_3$) of **3aa**



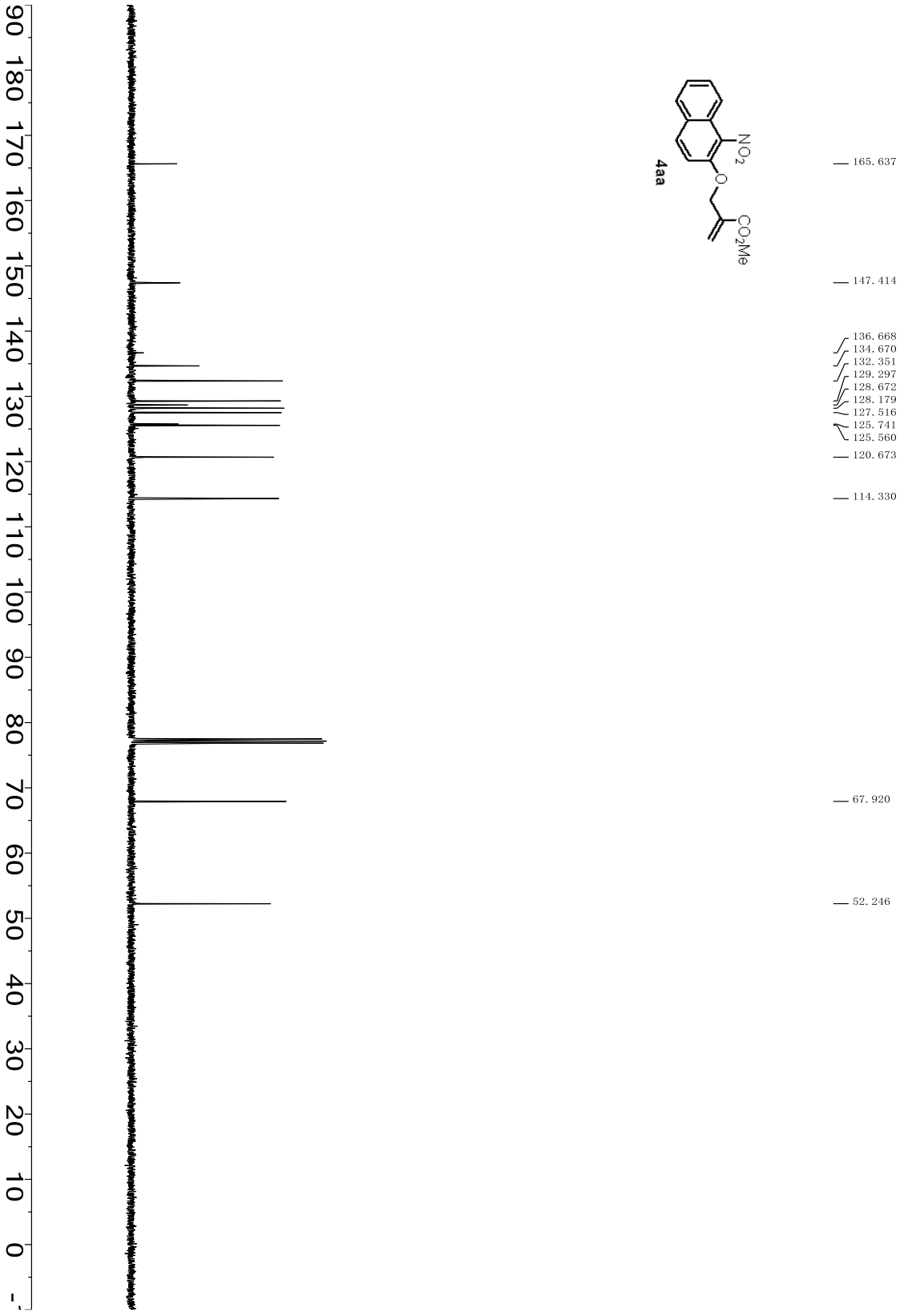
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3aa**



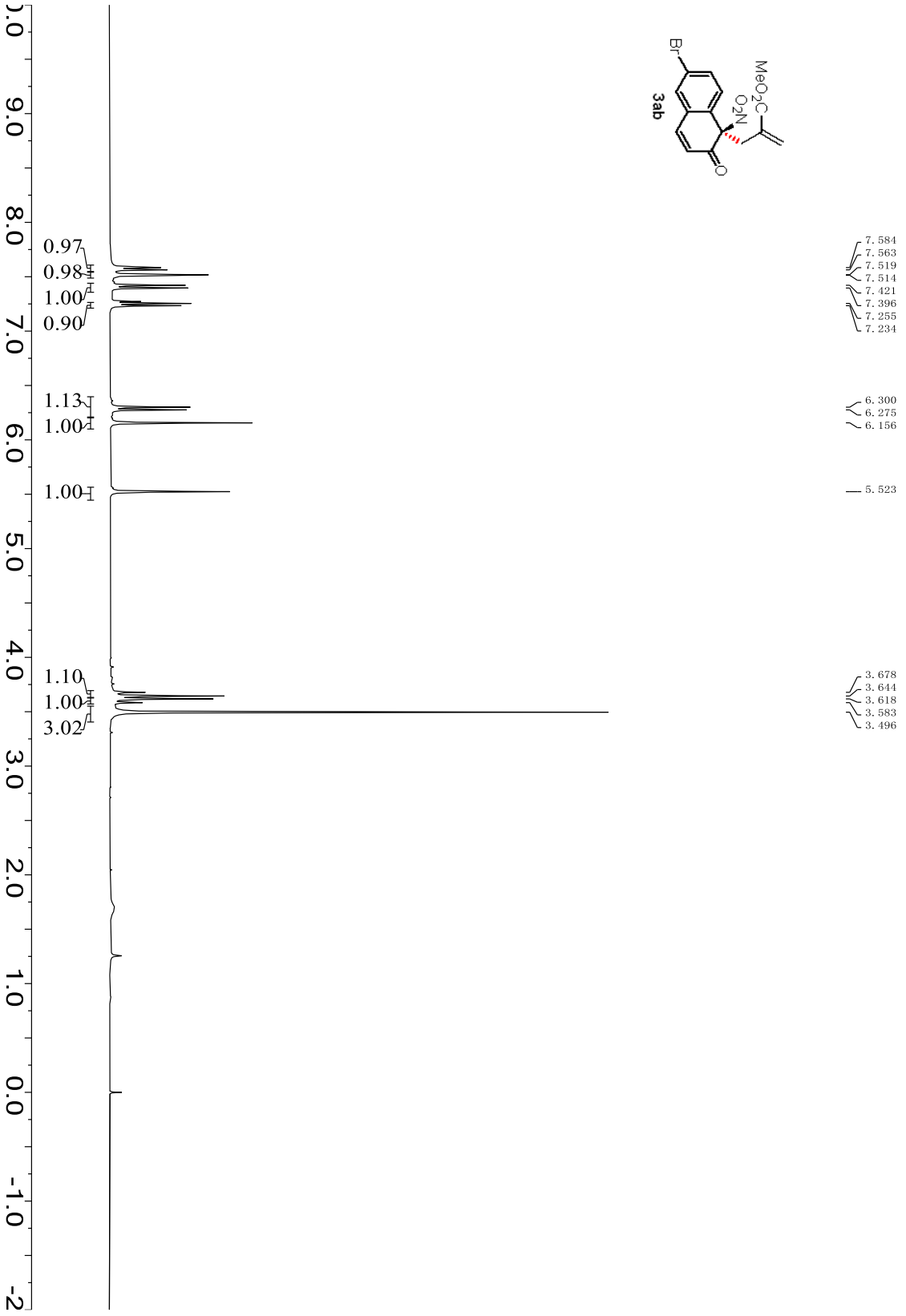
$^{1}$H NMR (400 MHz, $CDCl_3$) of **4aa**



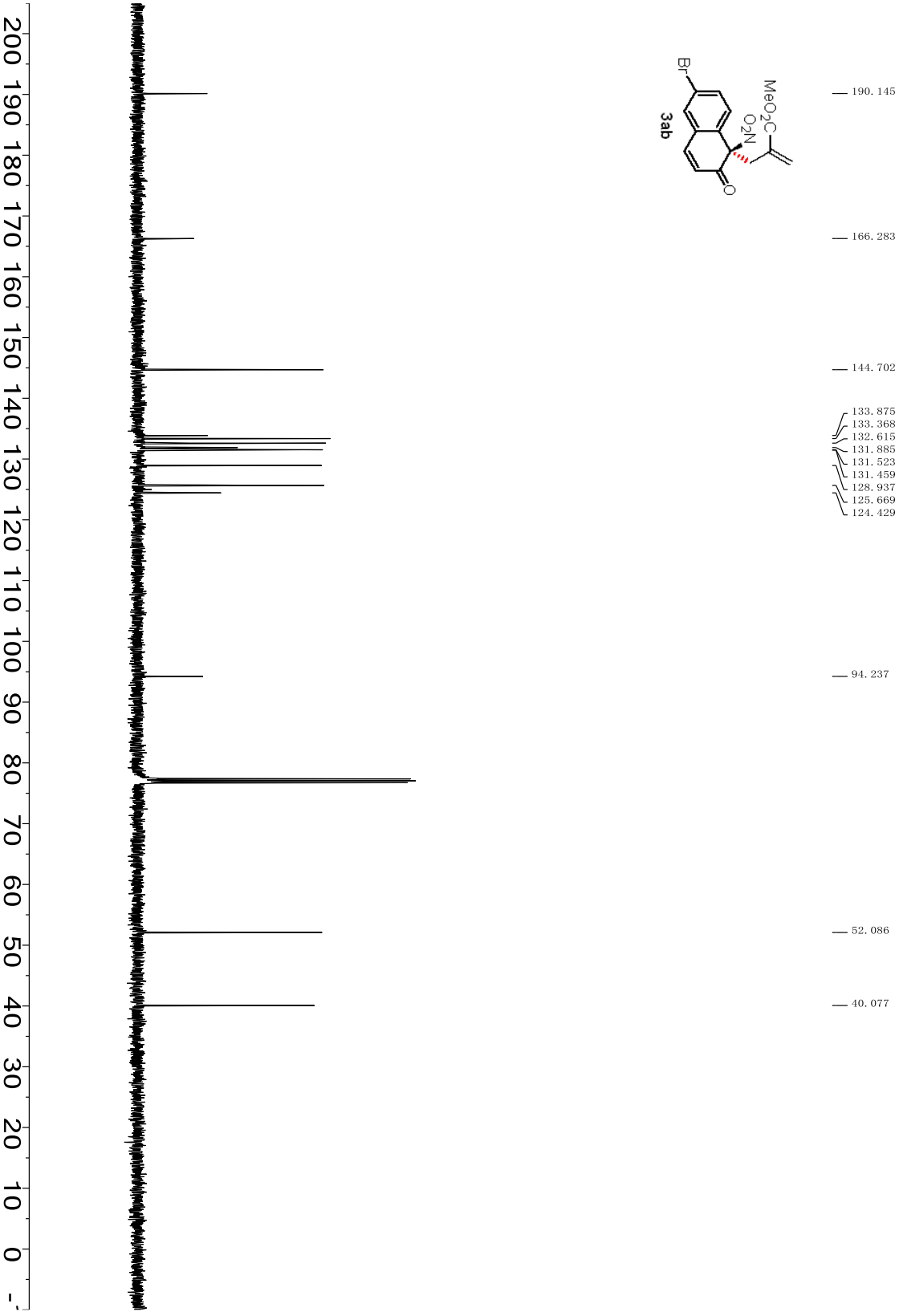
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **4aa**



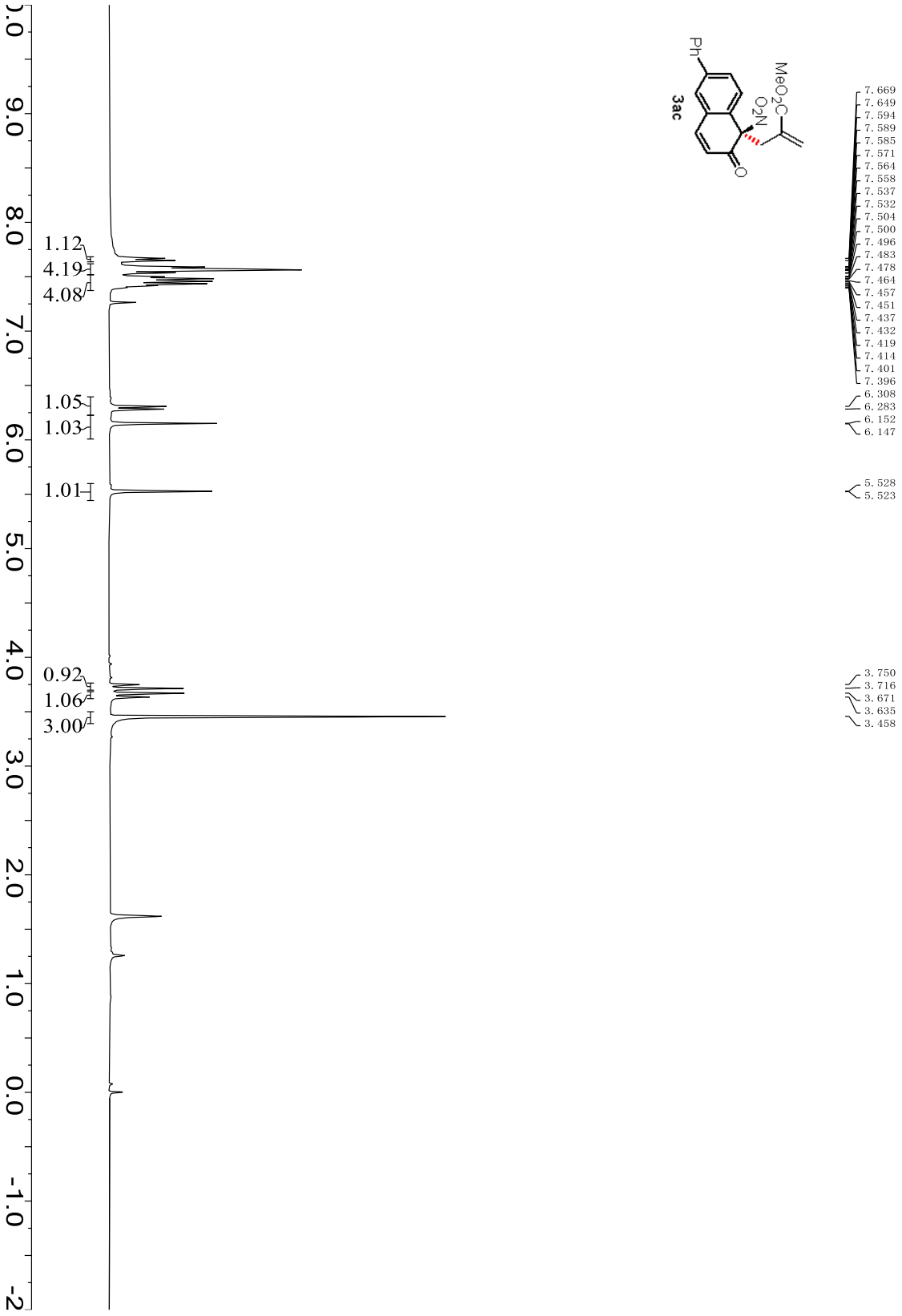
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3ab**



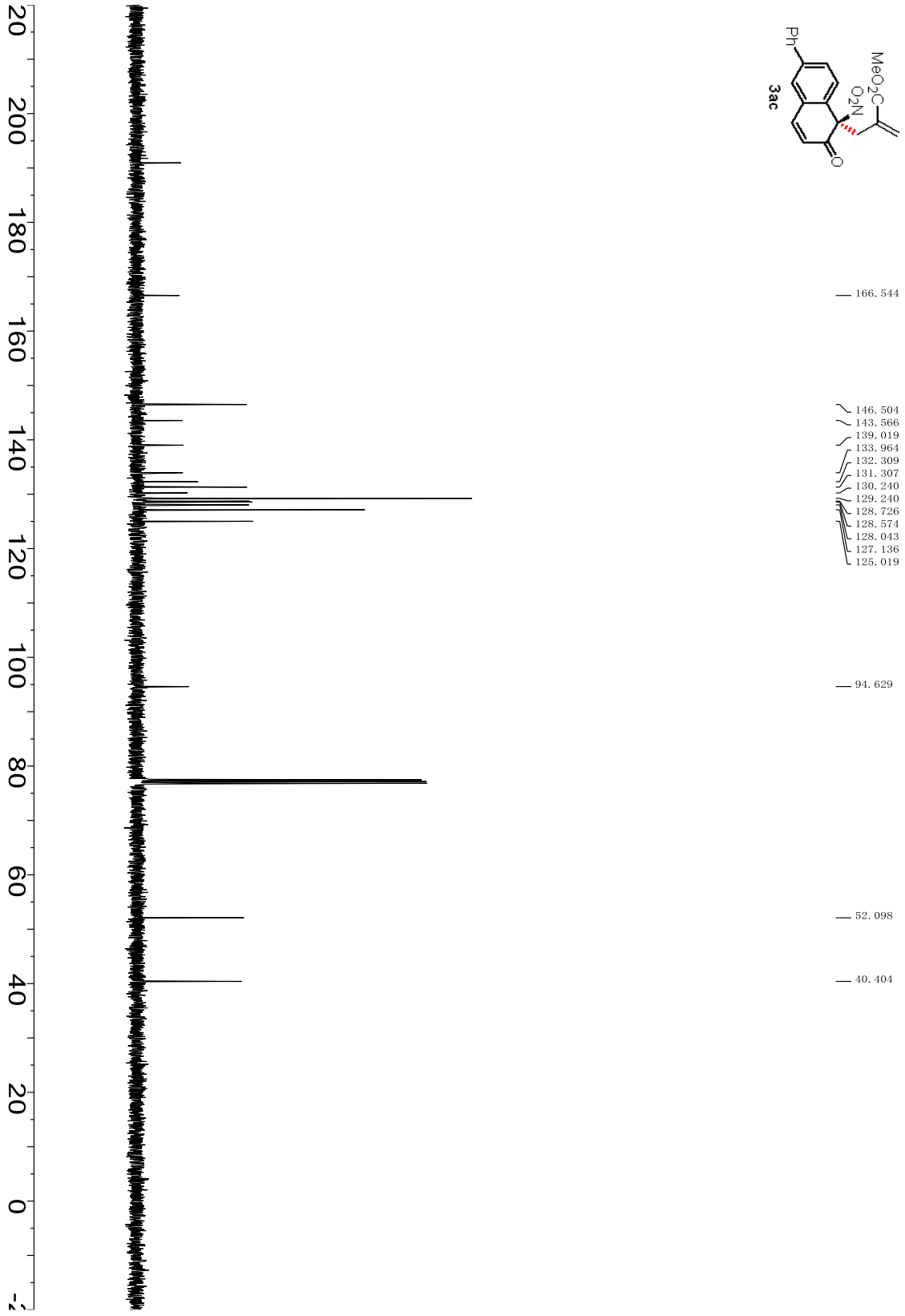
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ab**



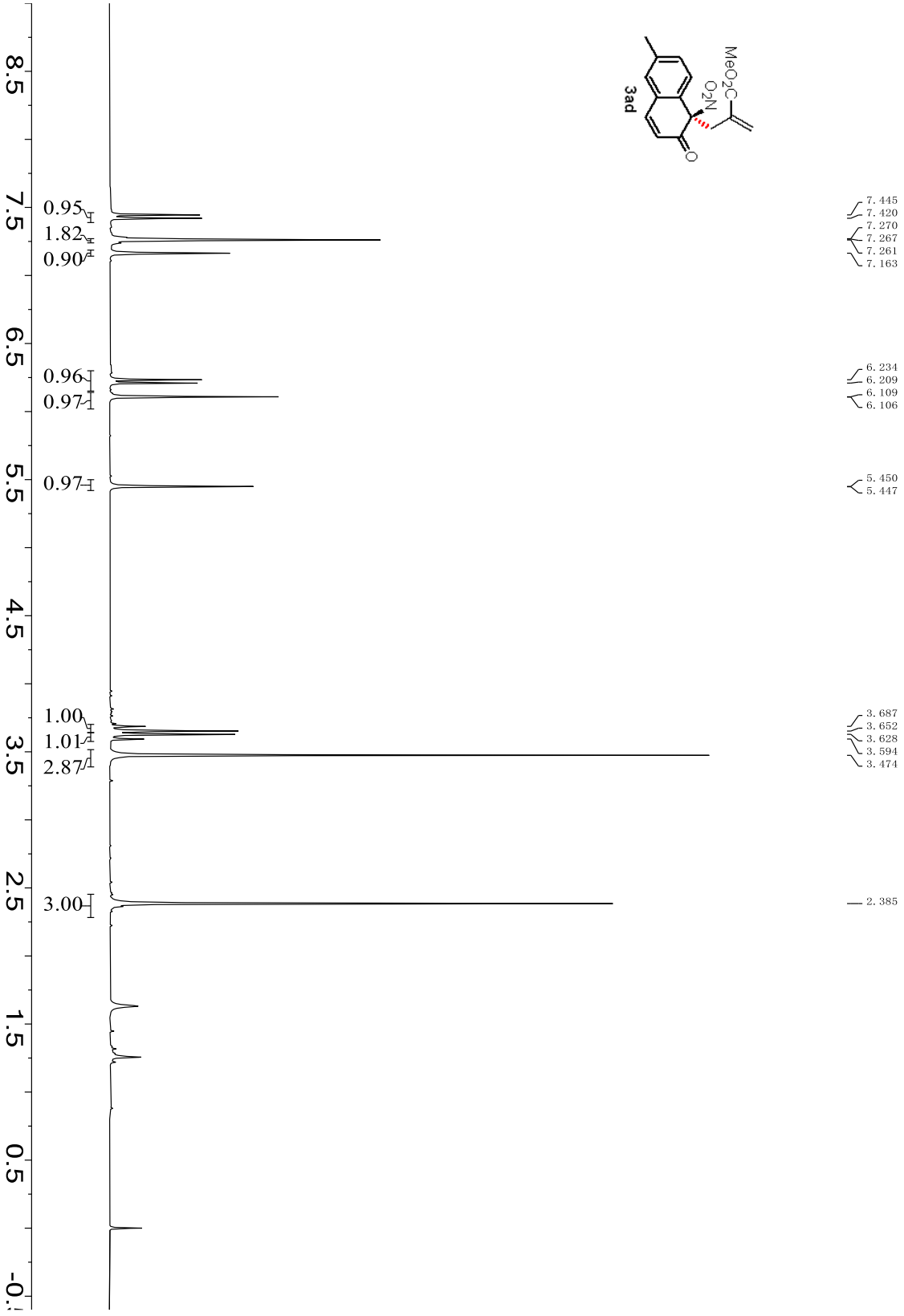
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3ac**



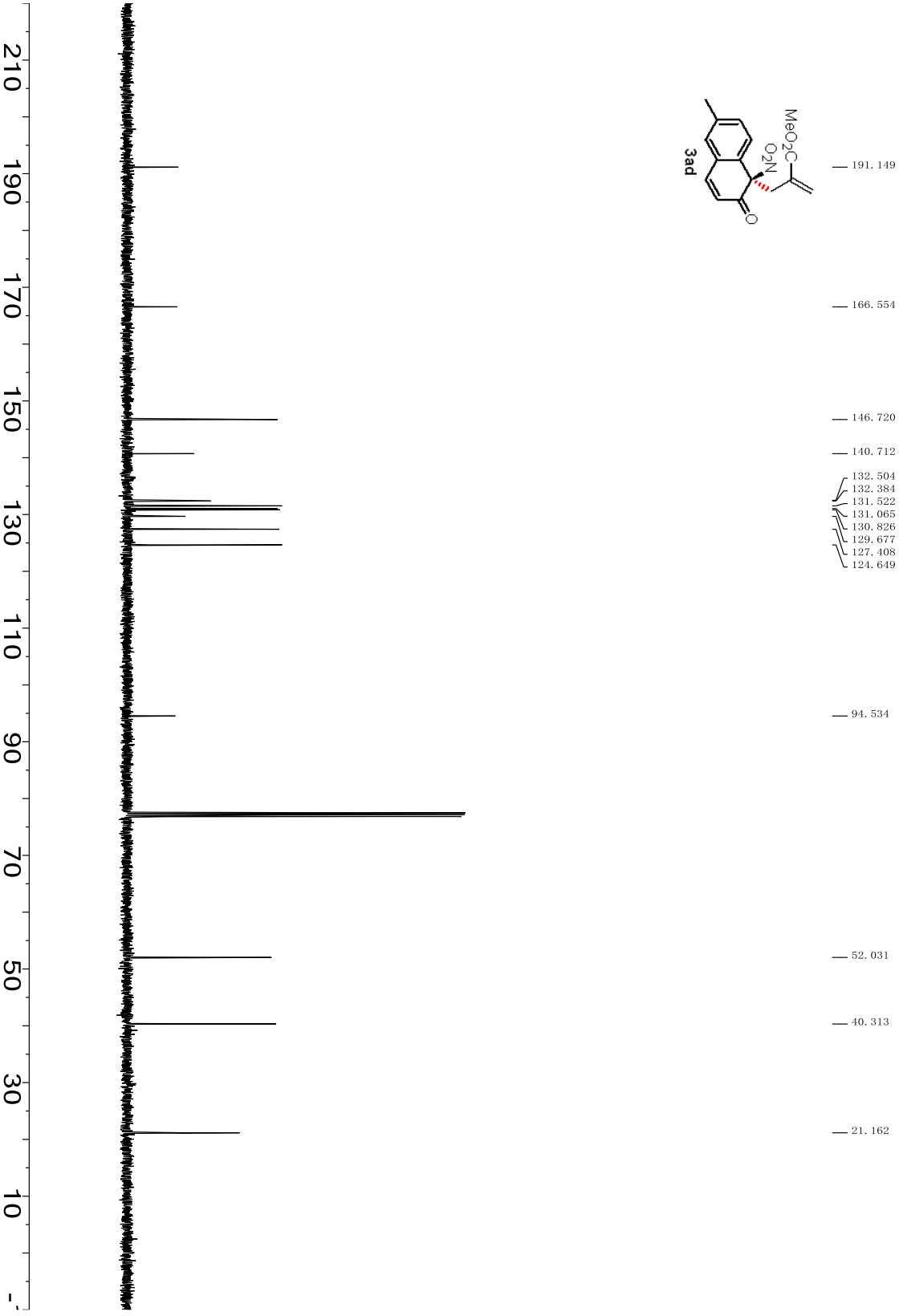
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ac**



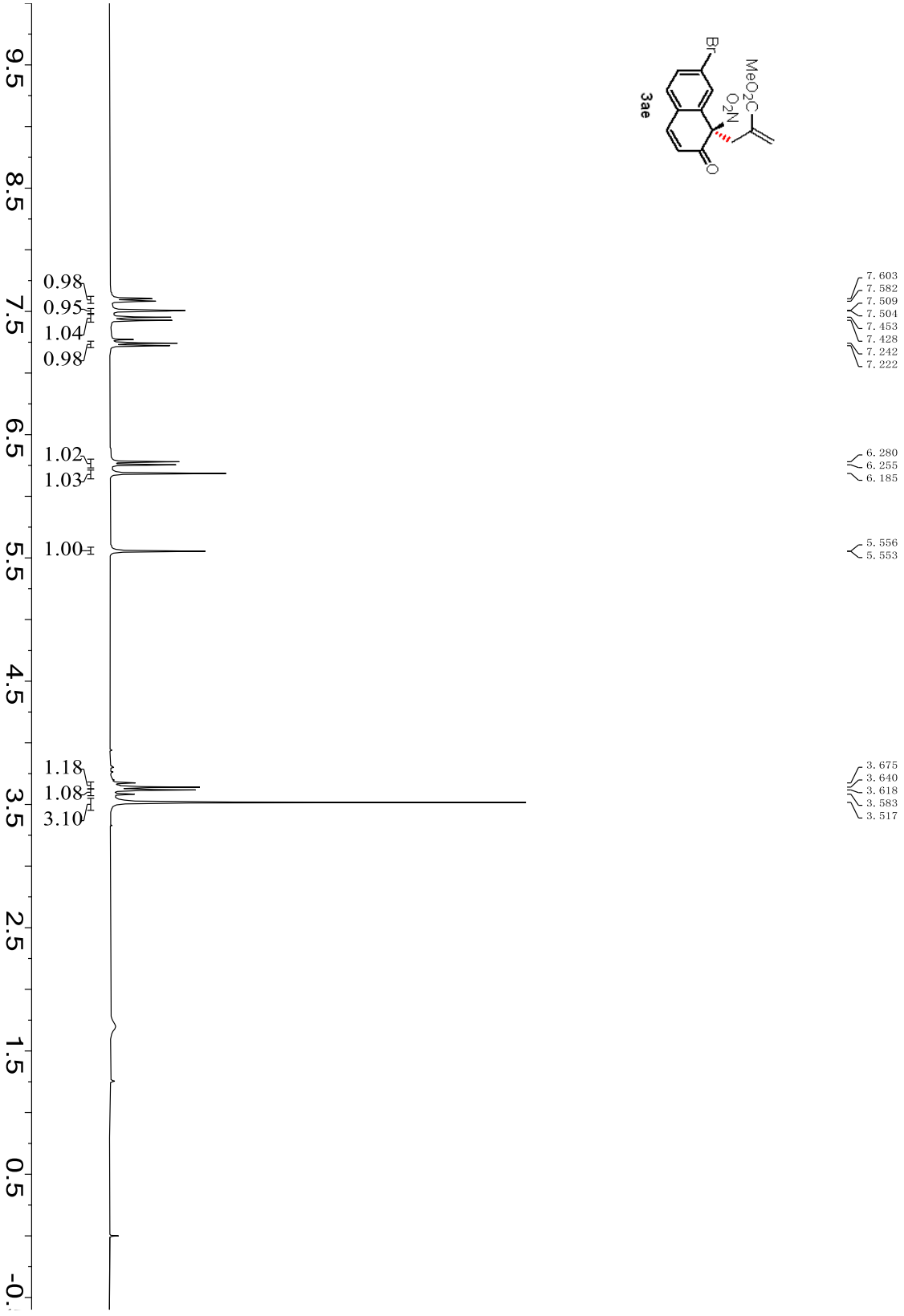
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3ad**



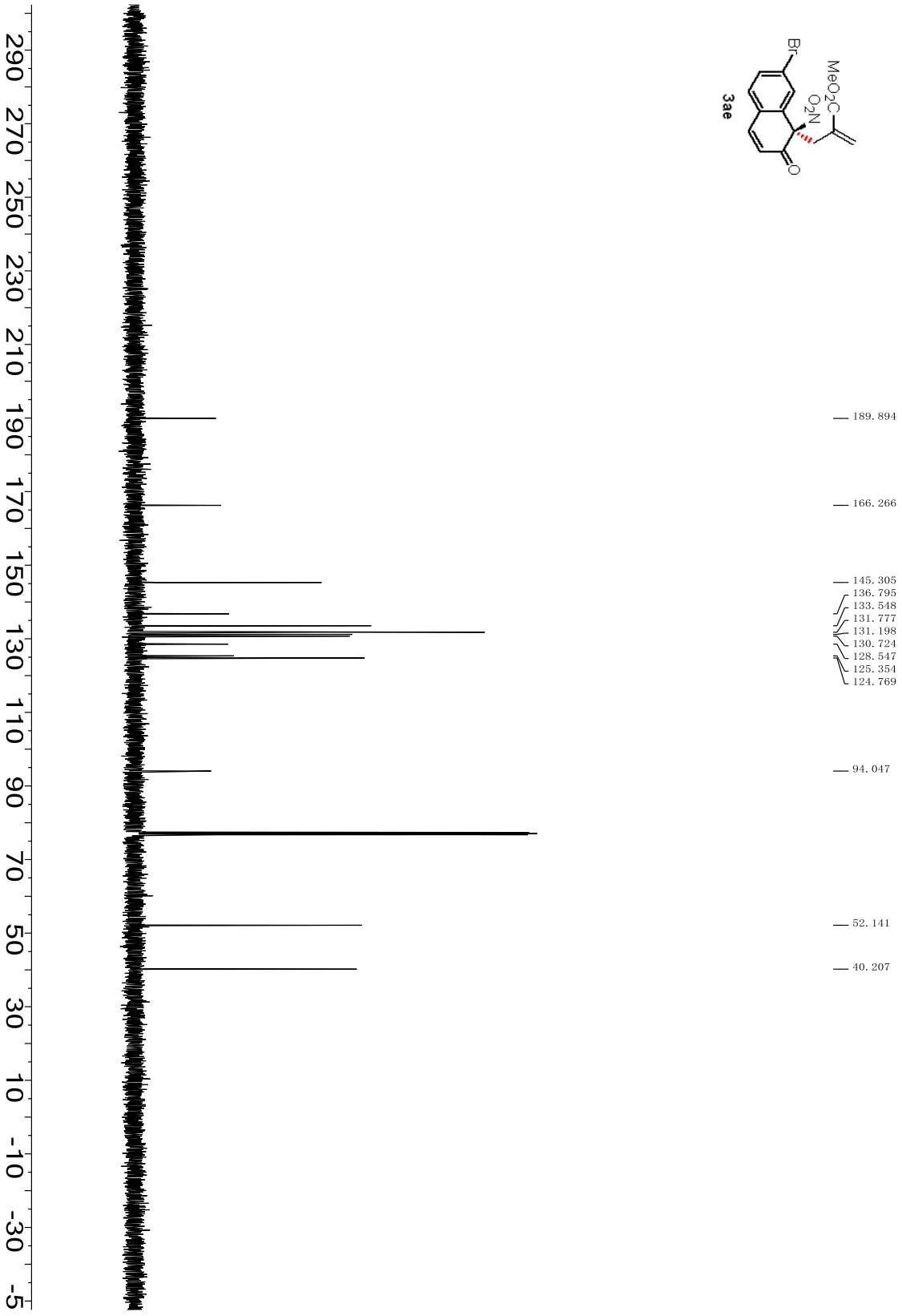
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ad**



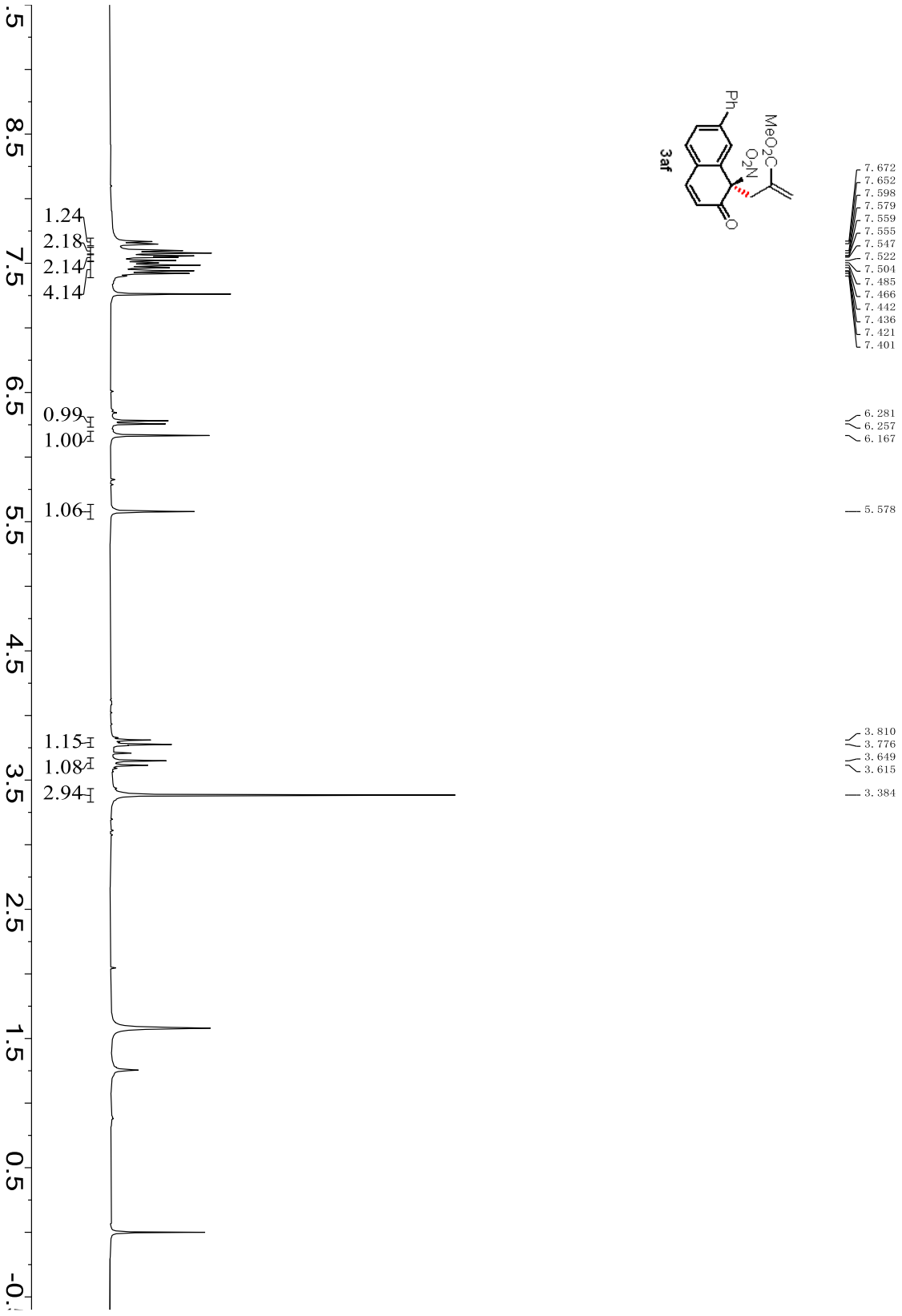
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3ae**



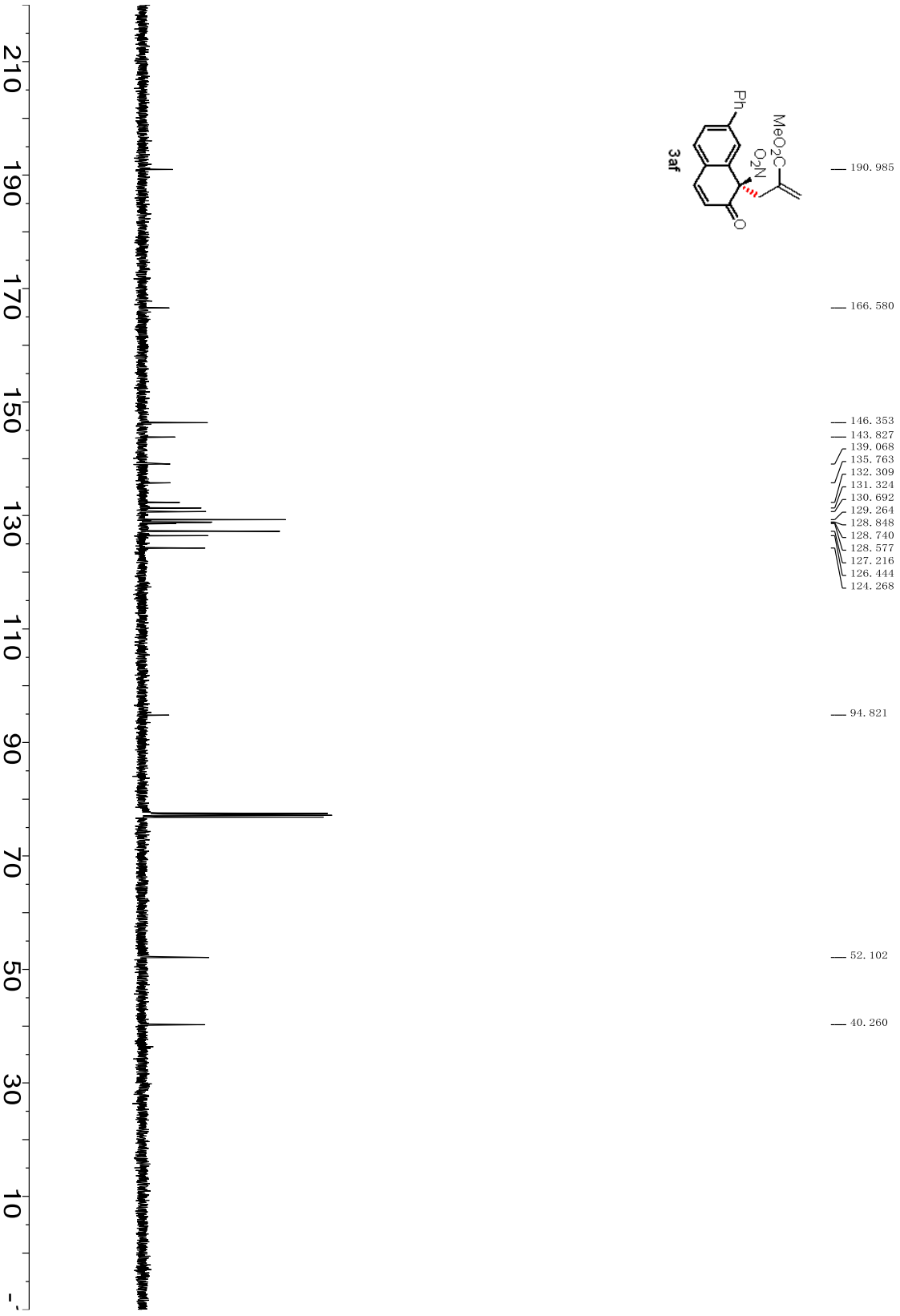
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ae**



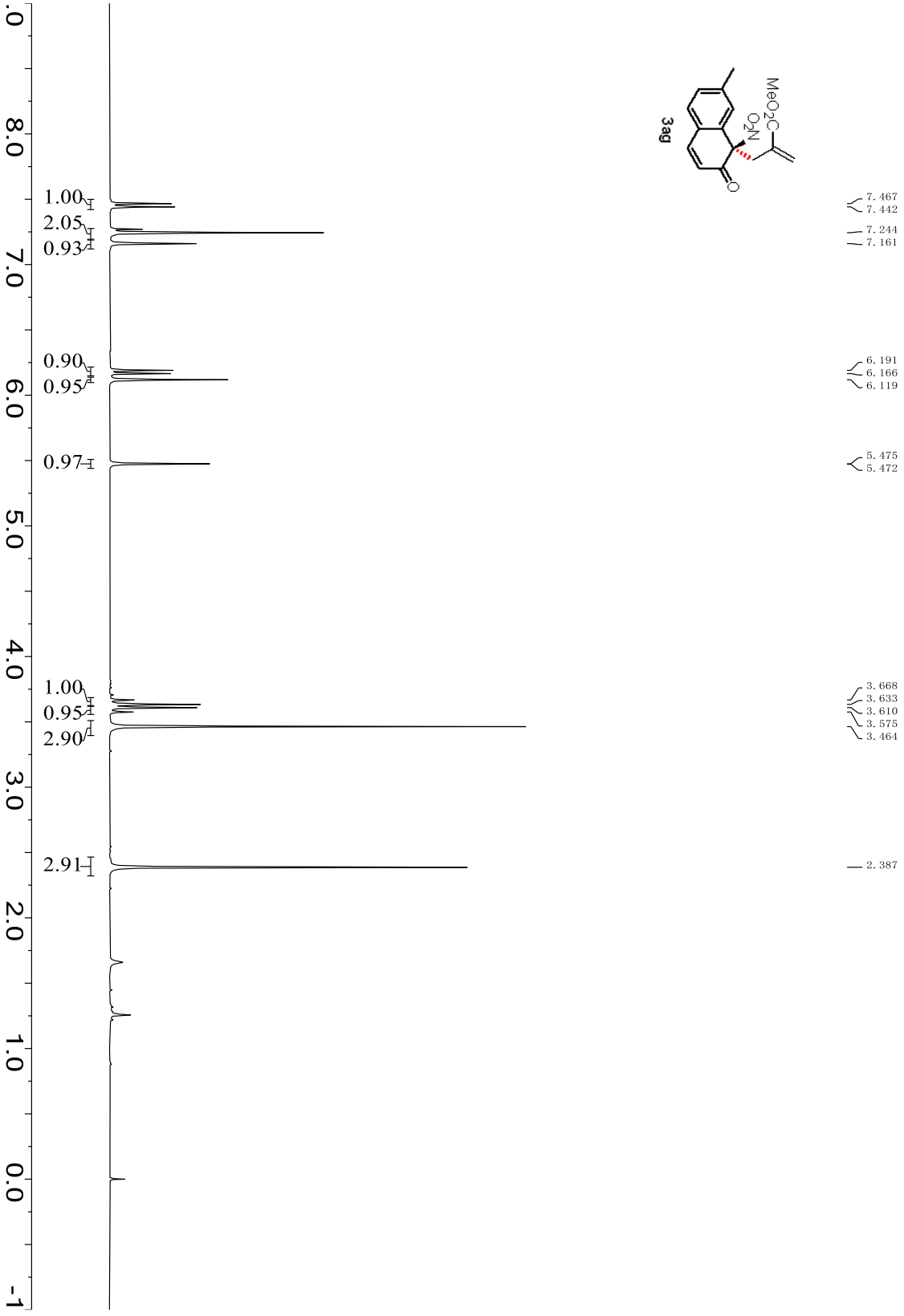
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3af**



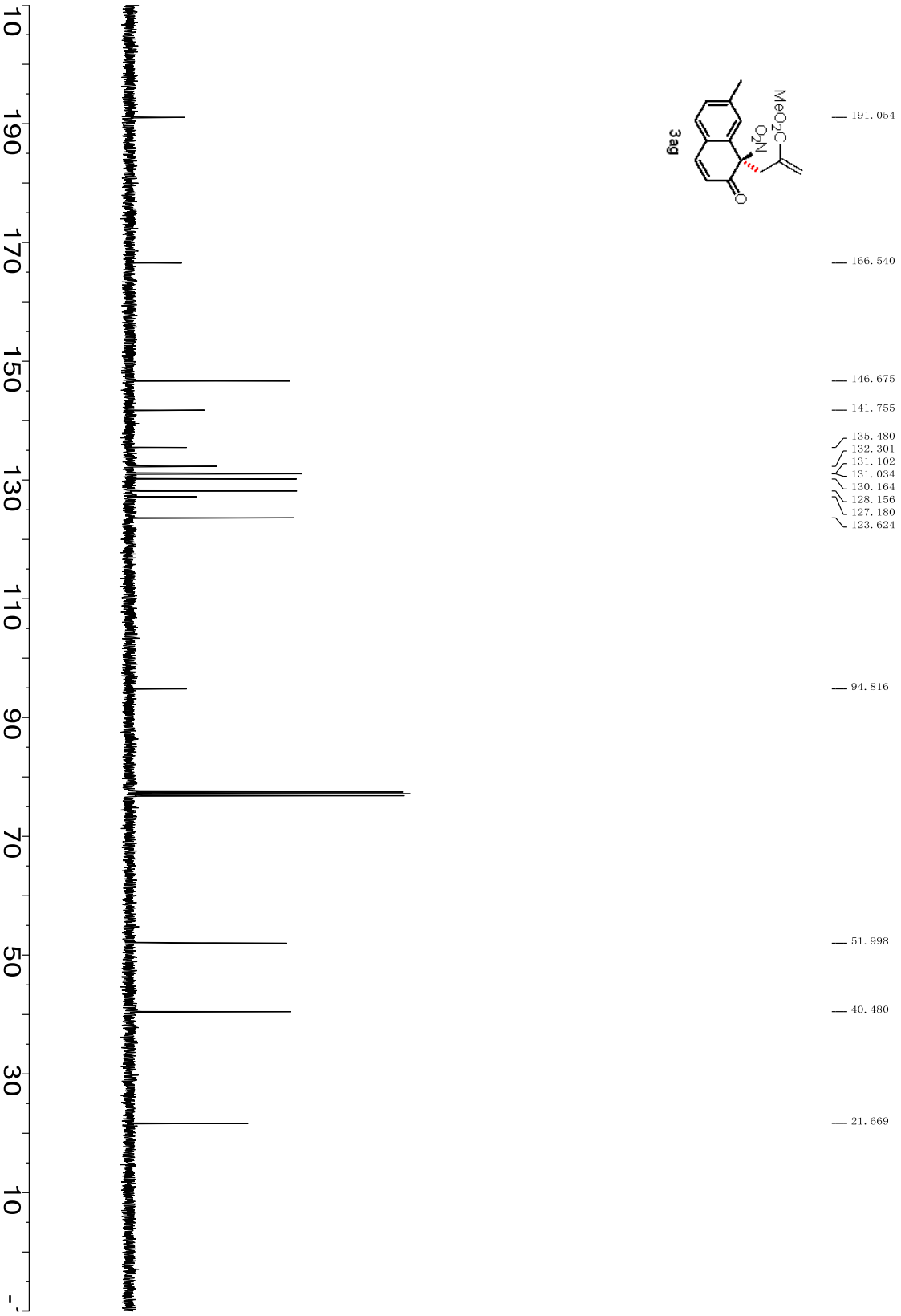
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3af**



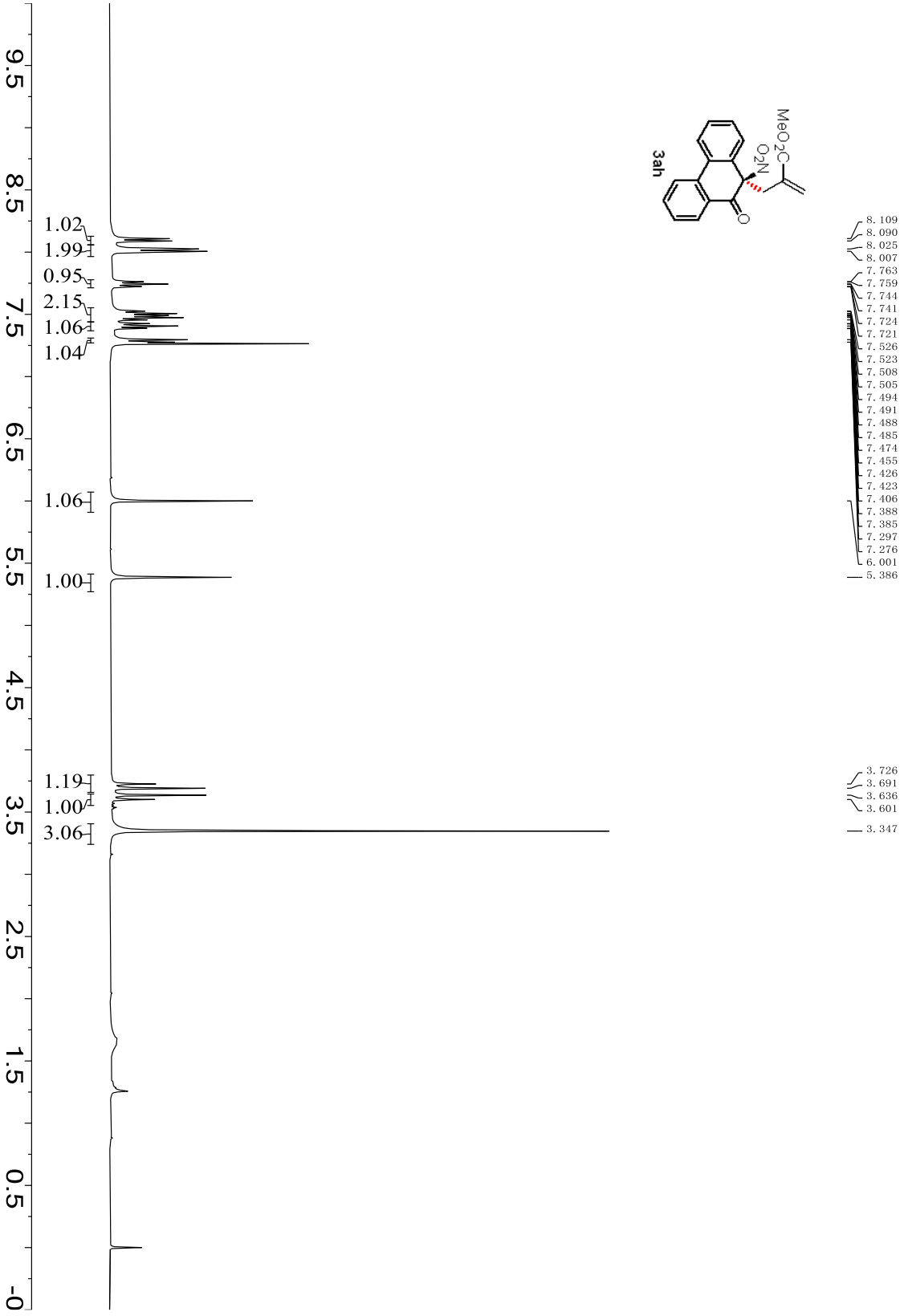
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3ag**



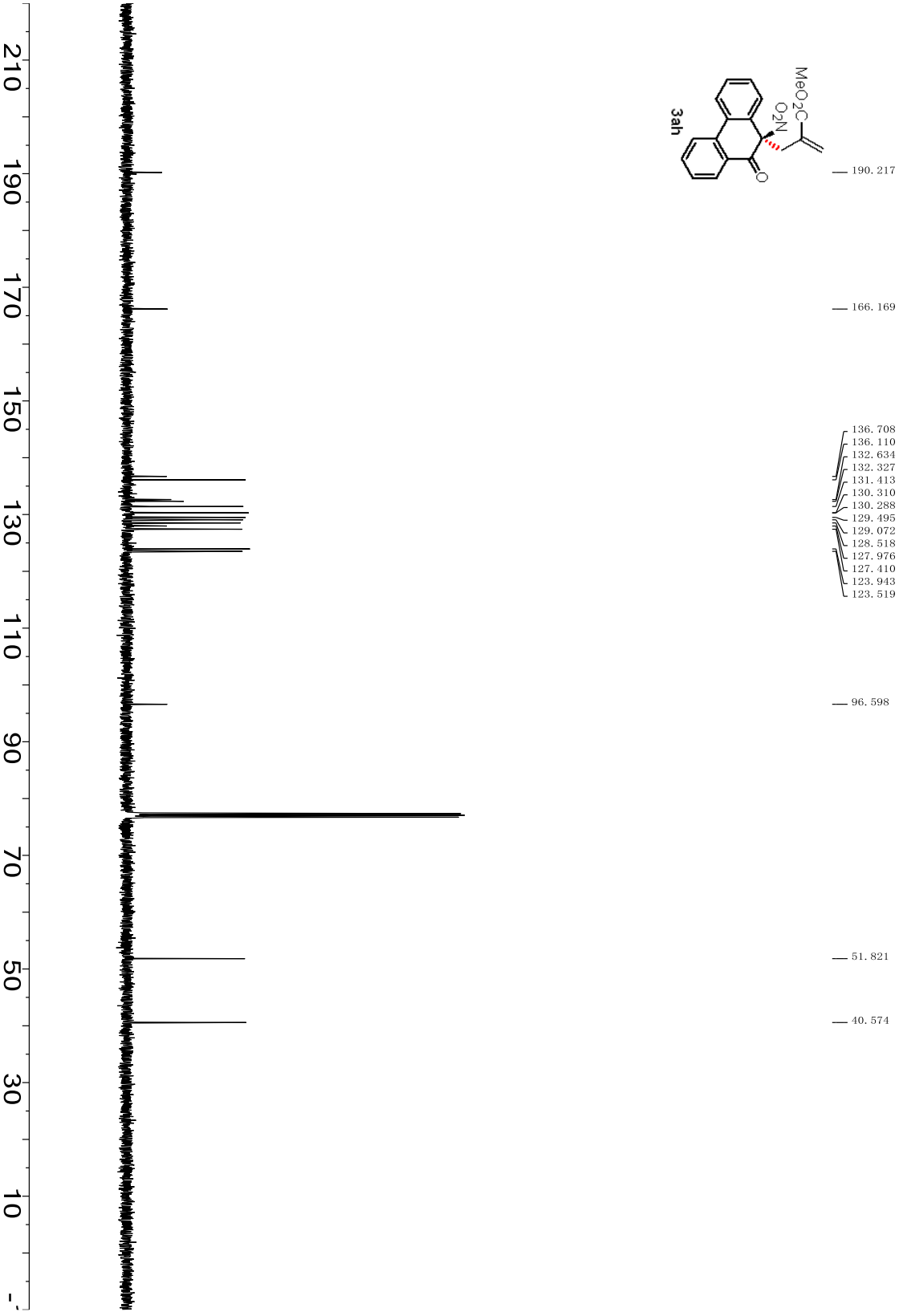
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ag**



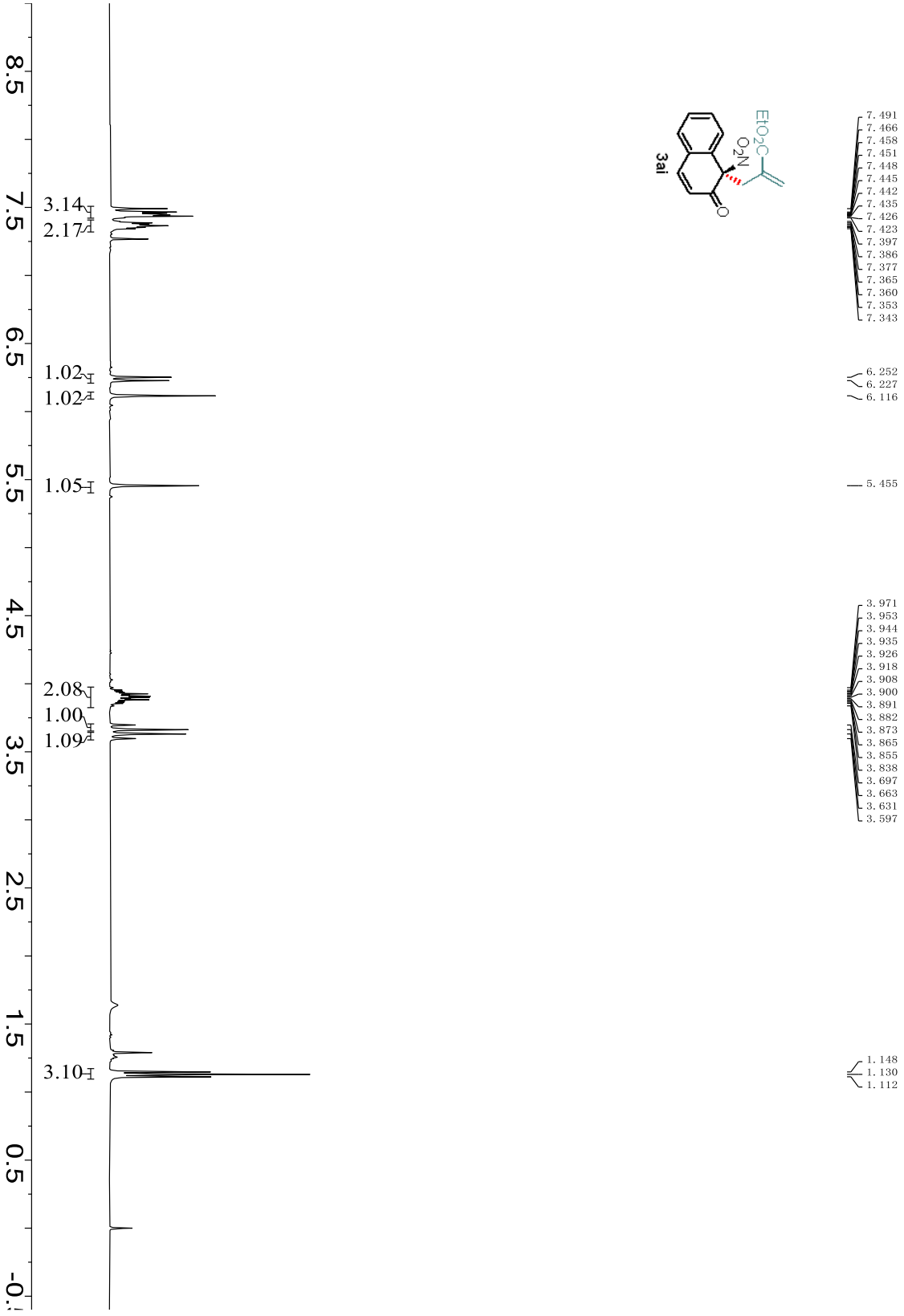
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3ah**



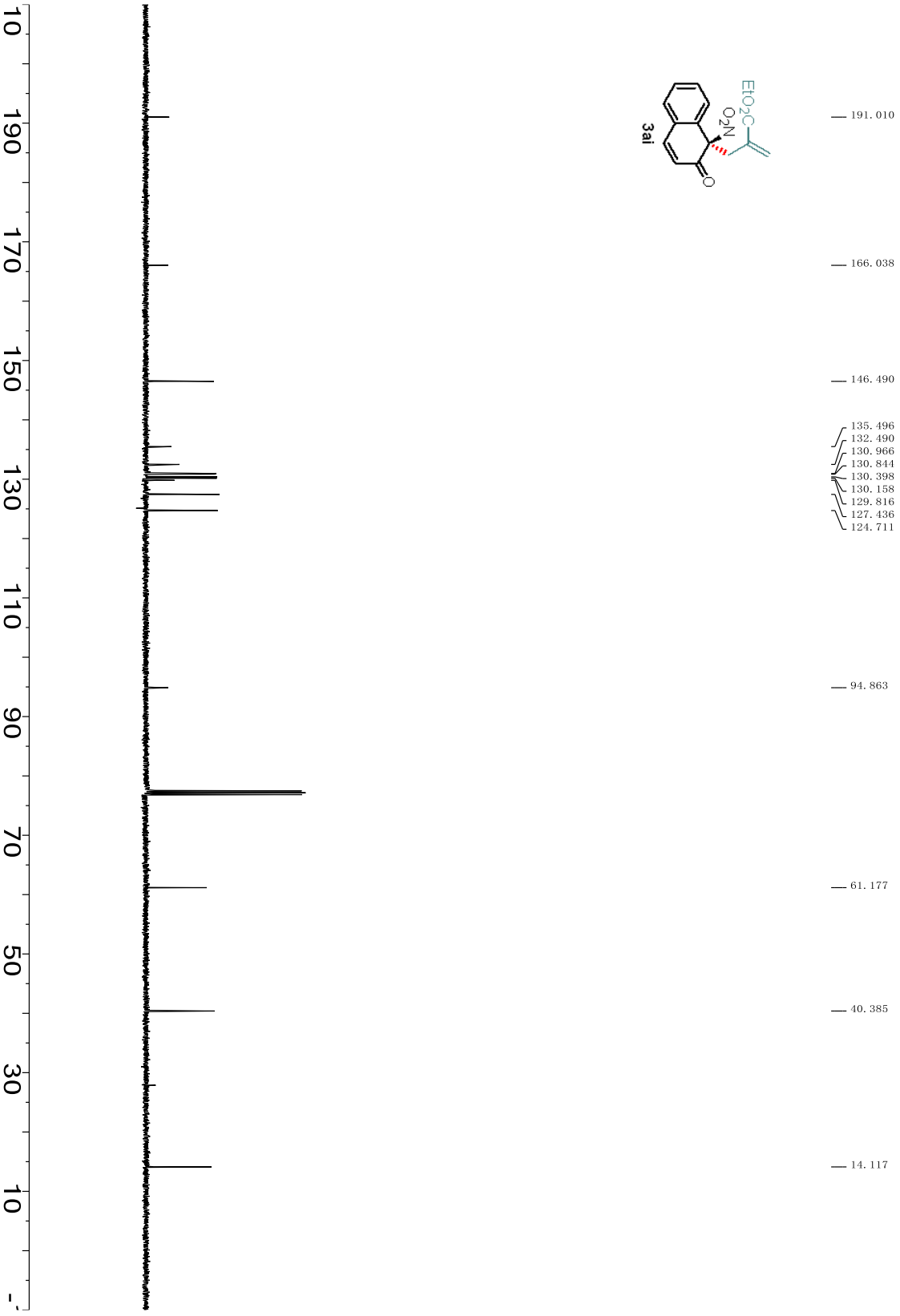
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ah**



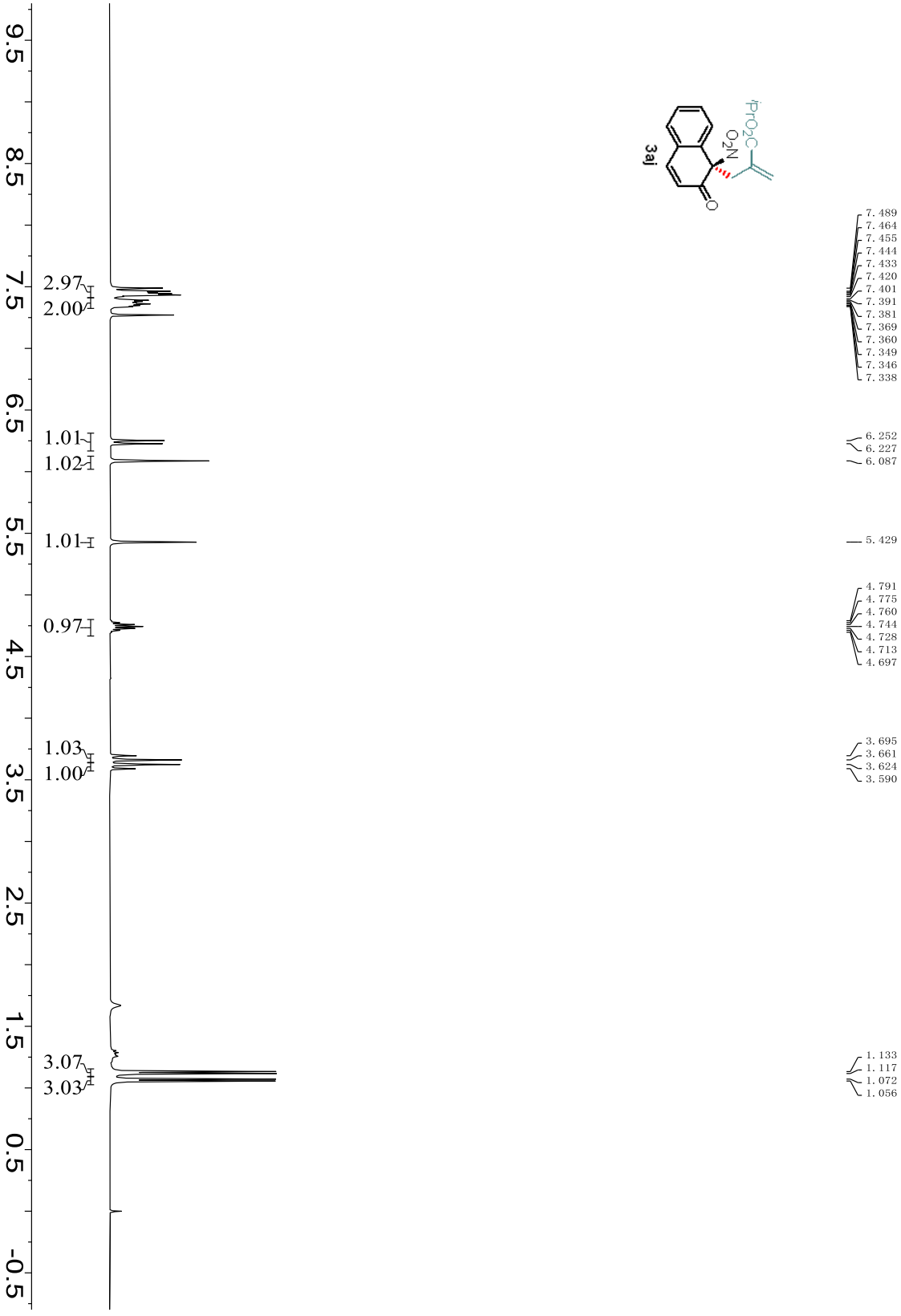
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3ai**



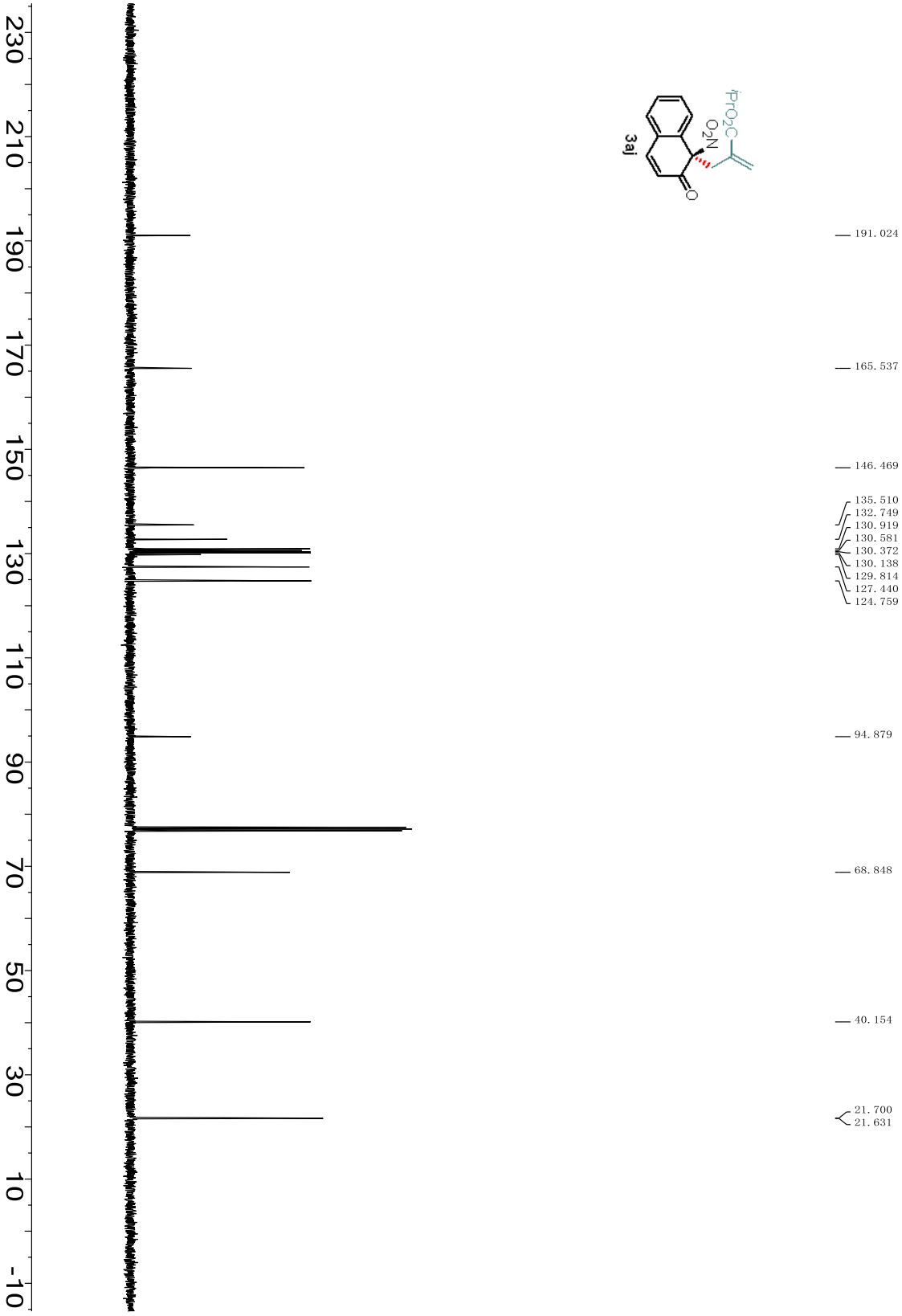
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ai**



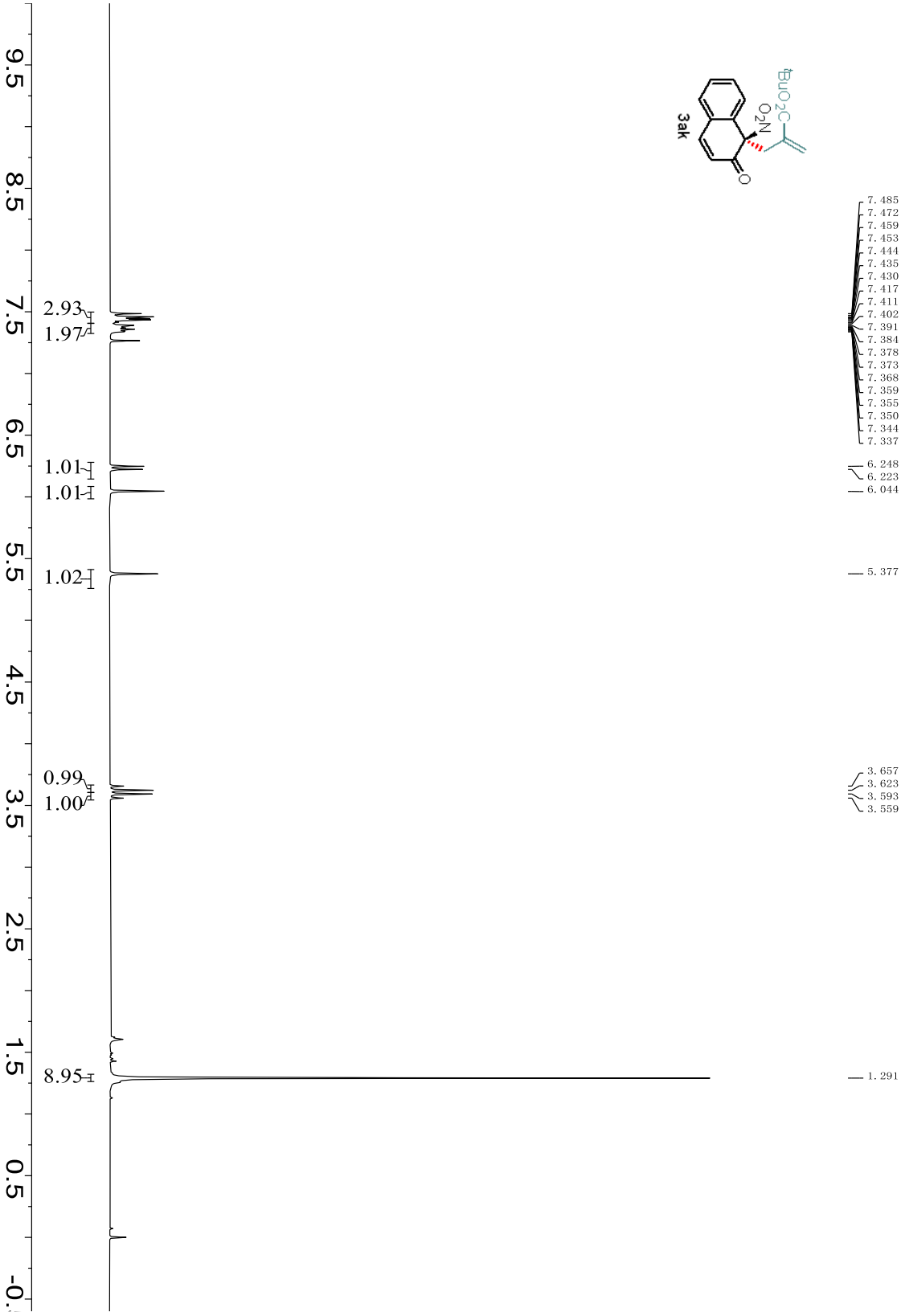
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3aj**



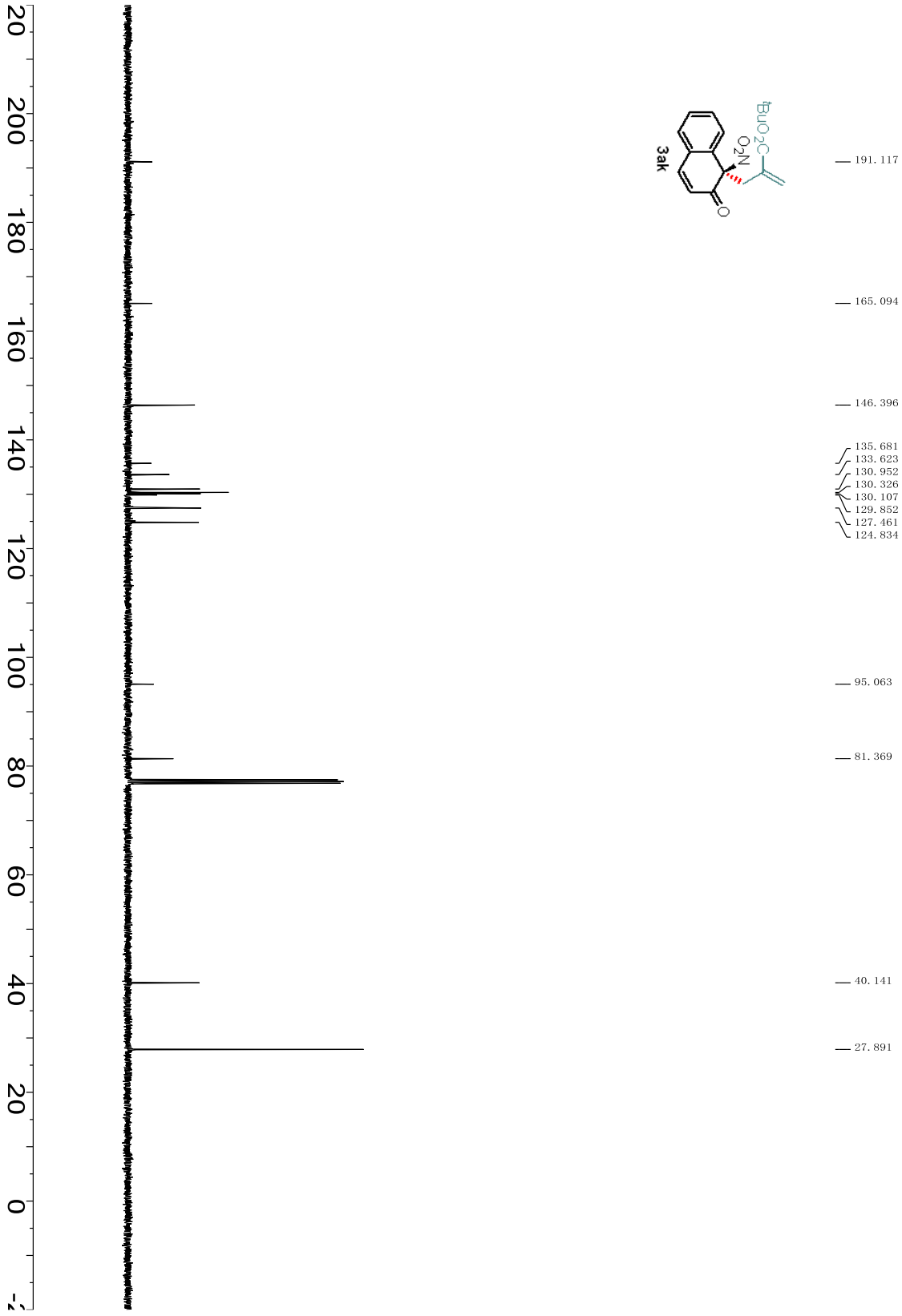
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3aj**



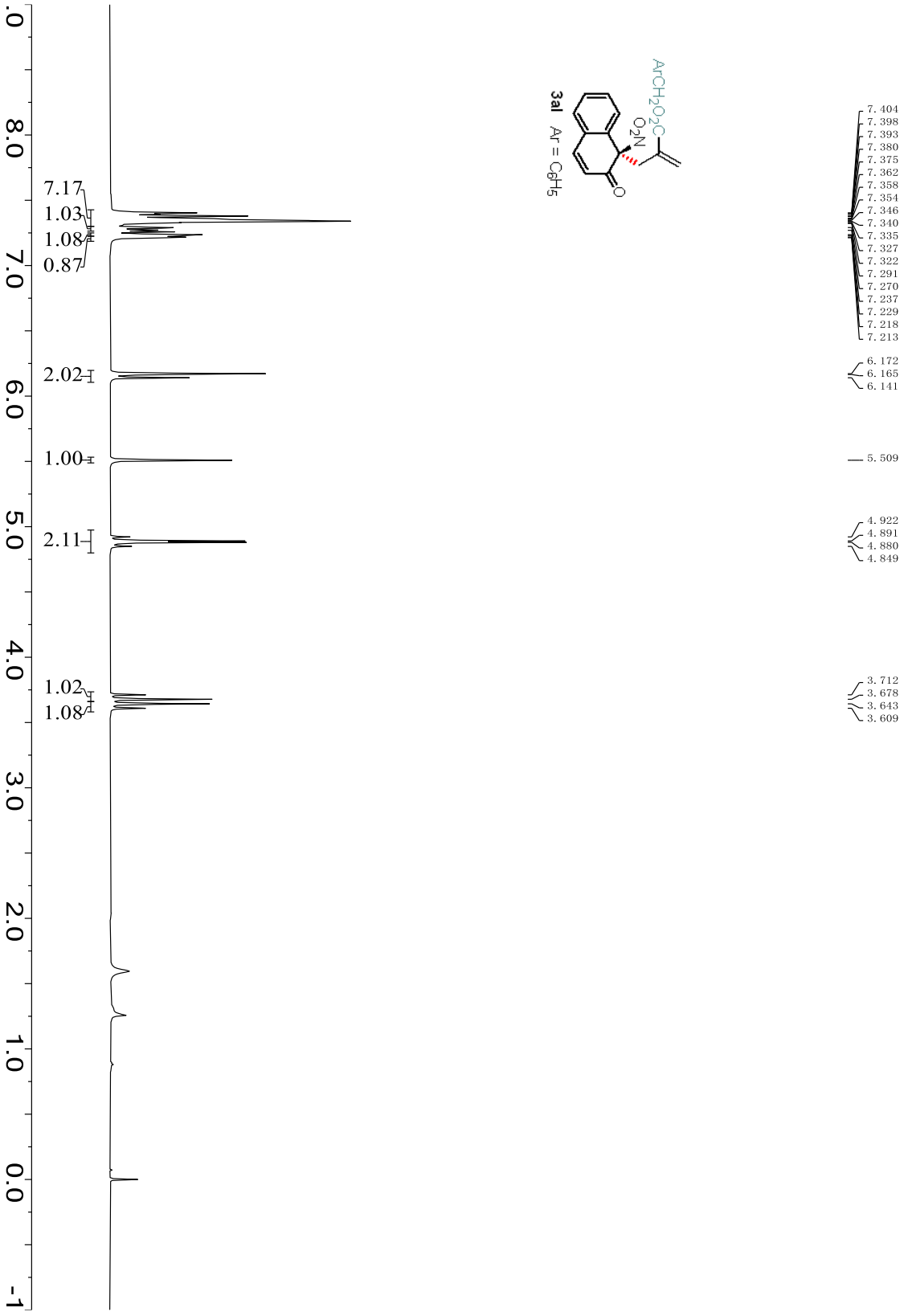
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3ak**



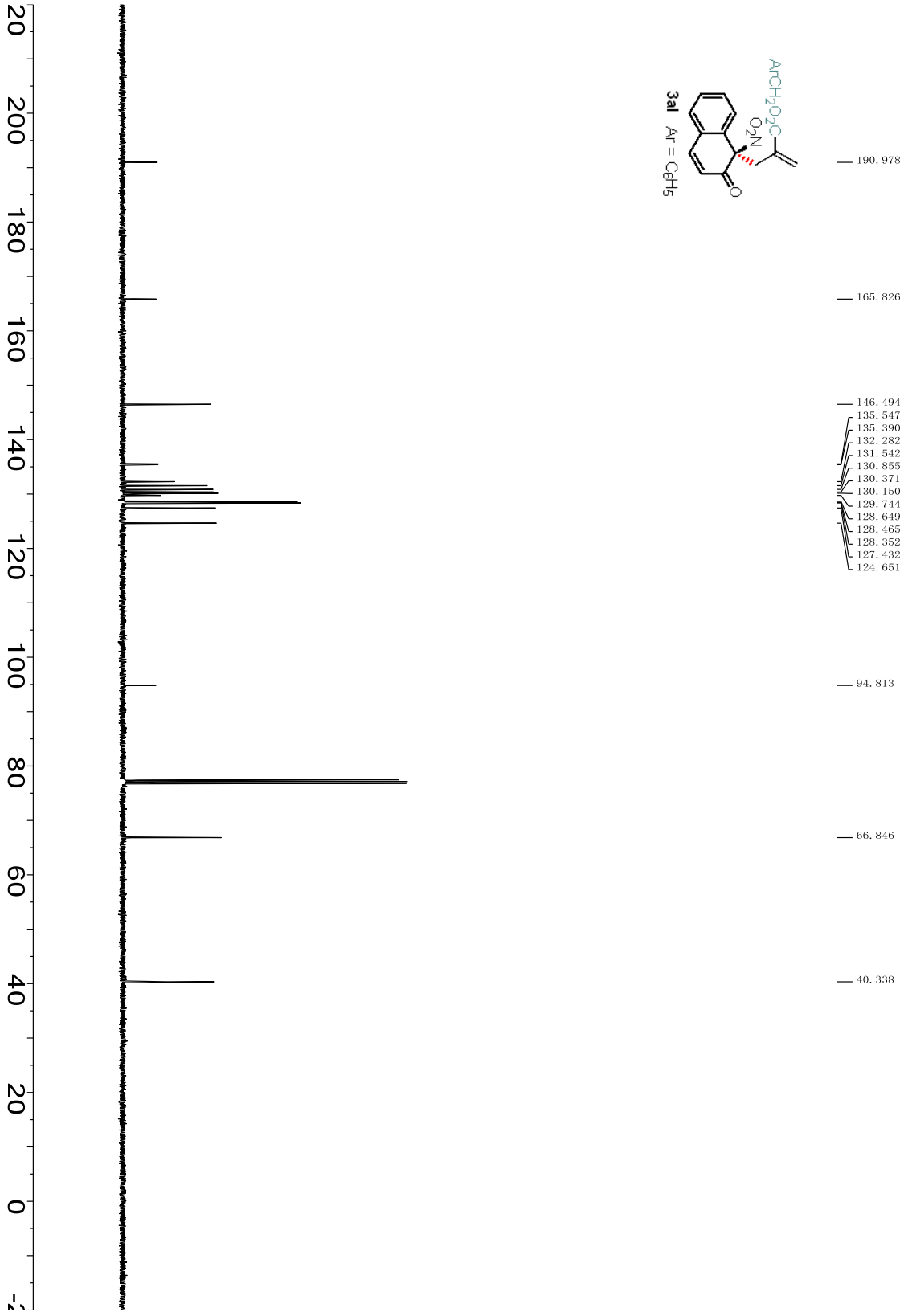
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ak**



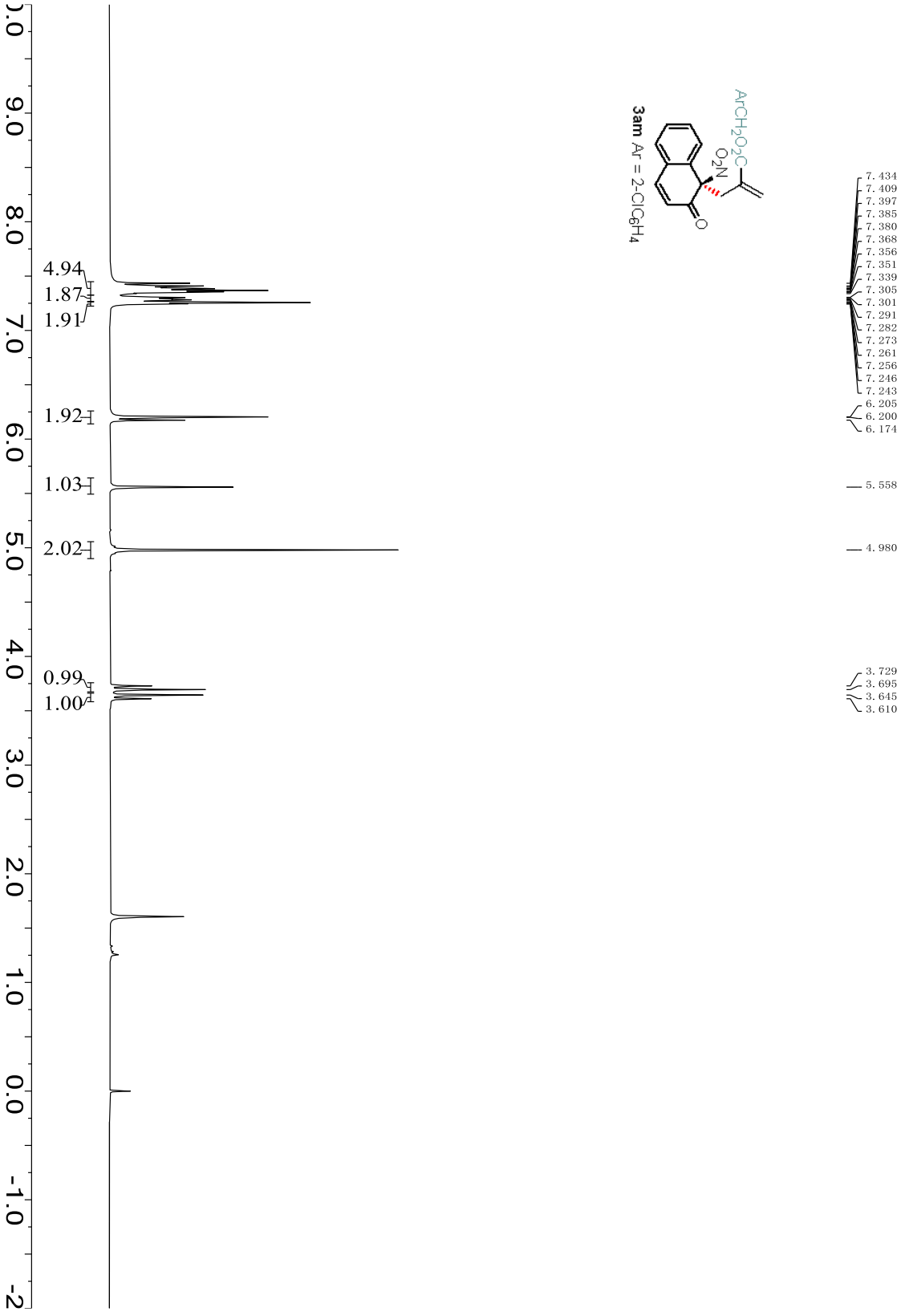
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3al**



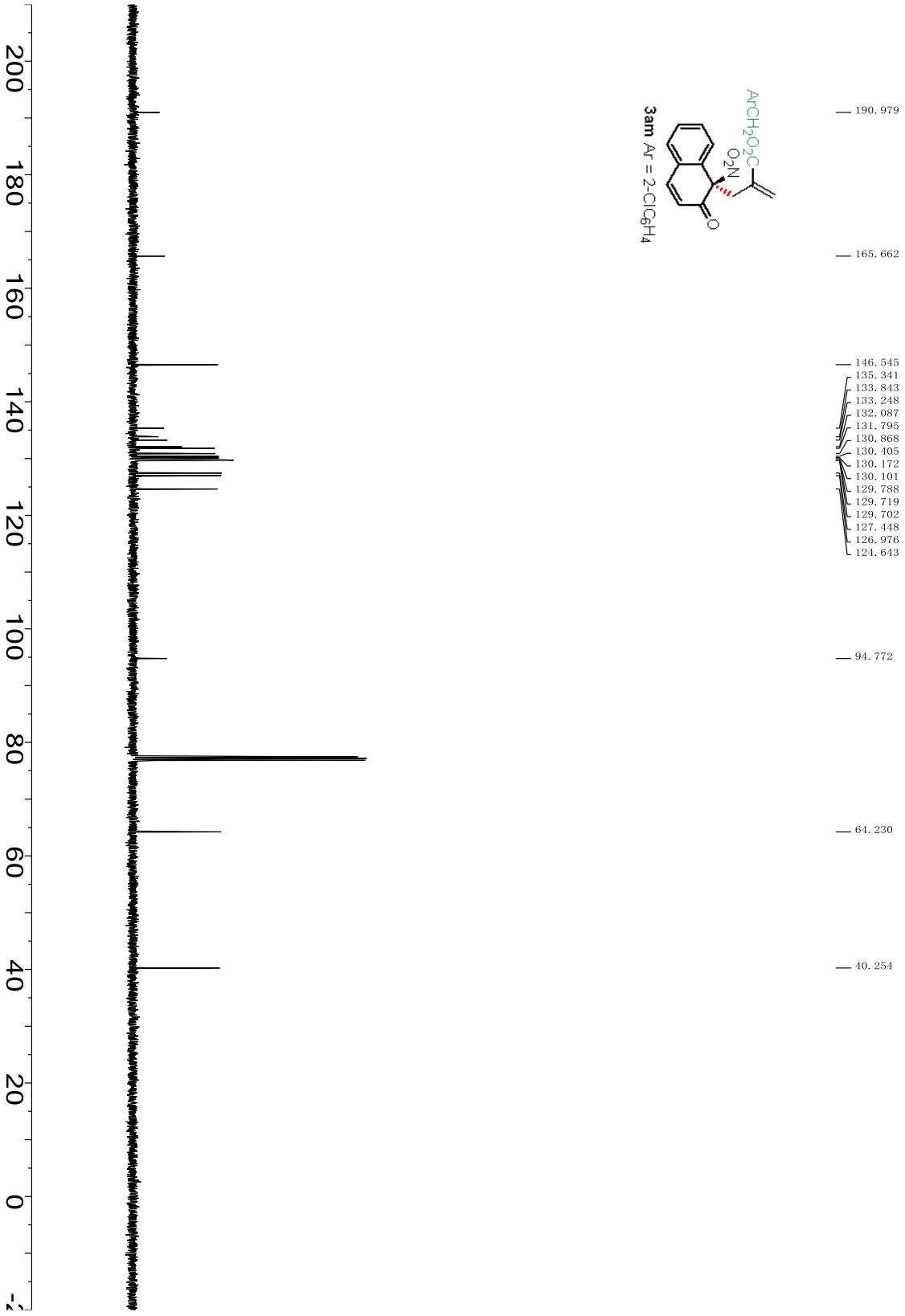
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3al**



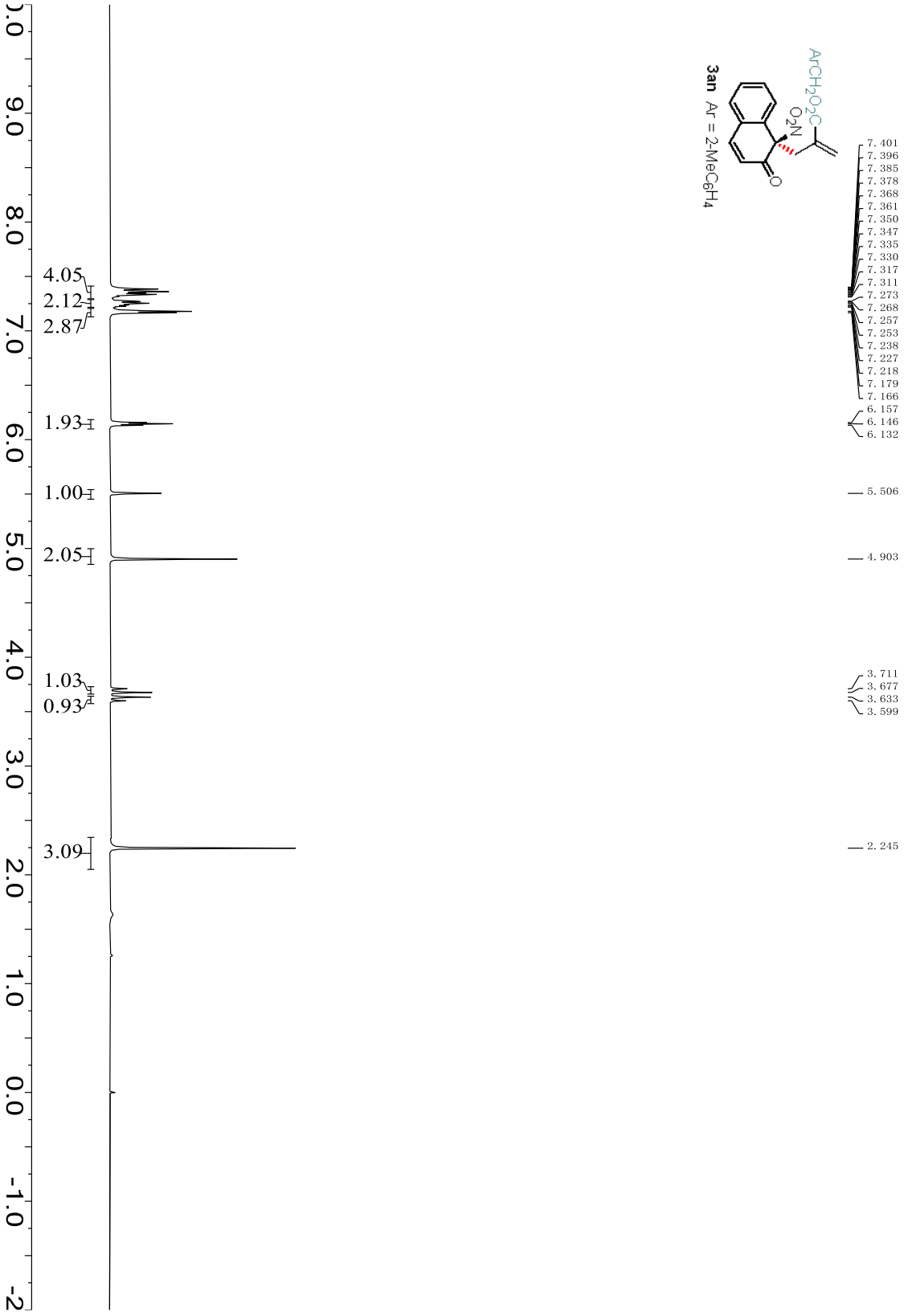
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3am**



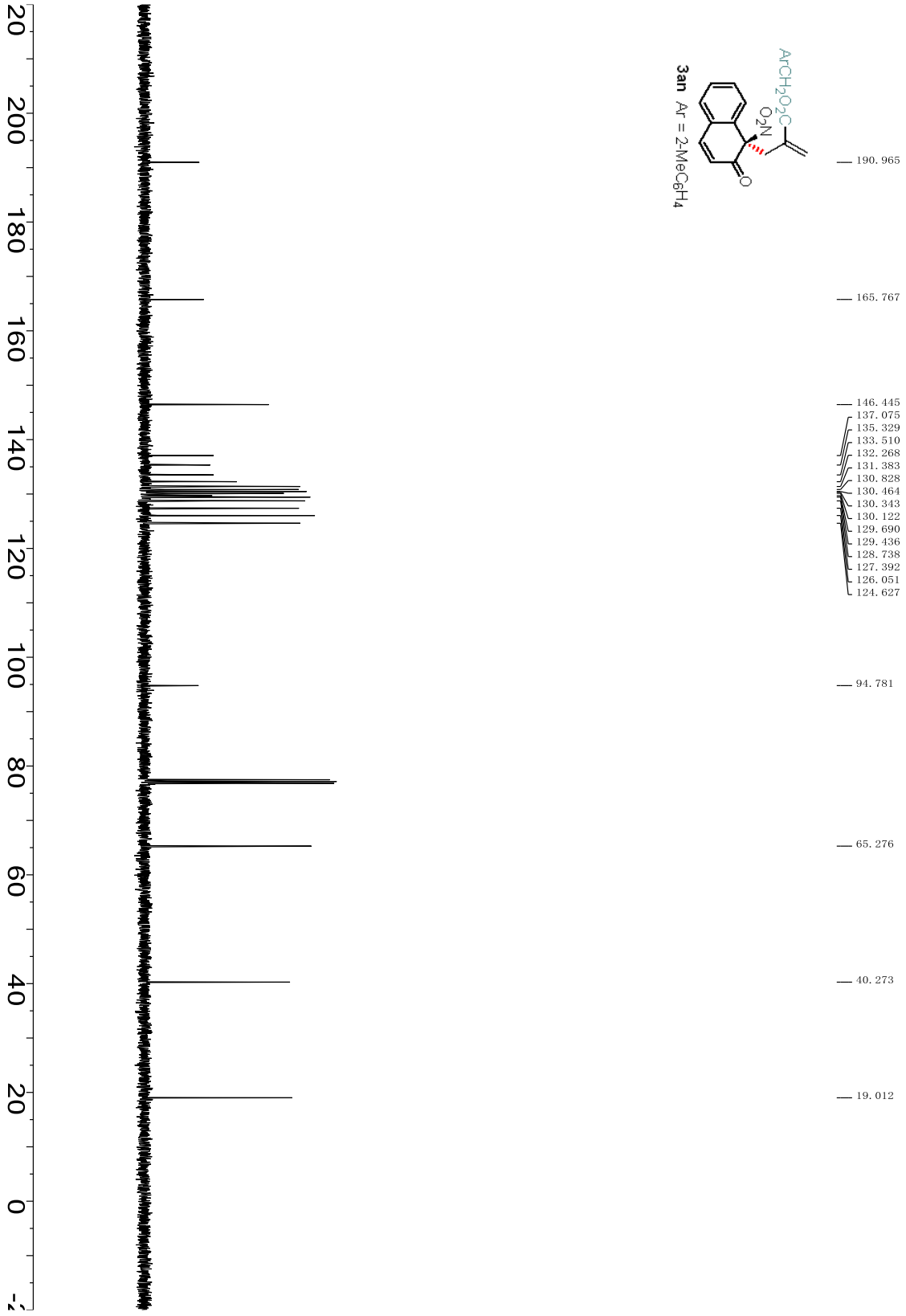
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3am**



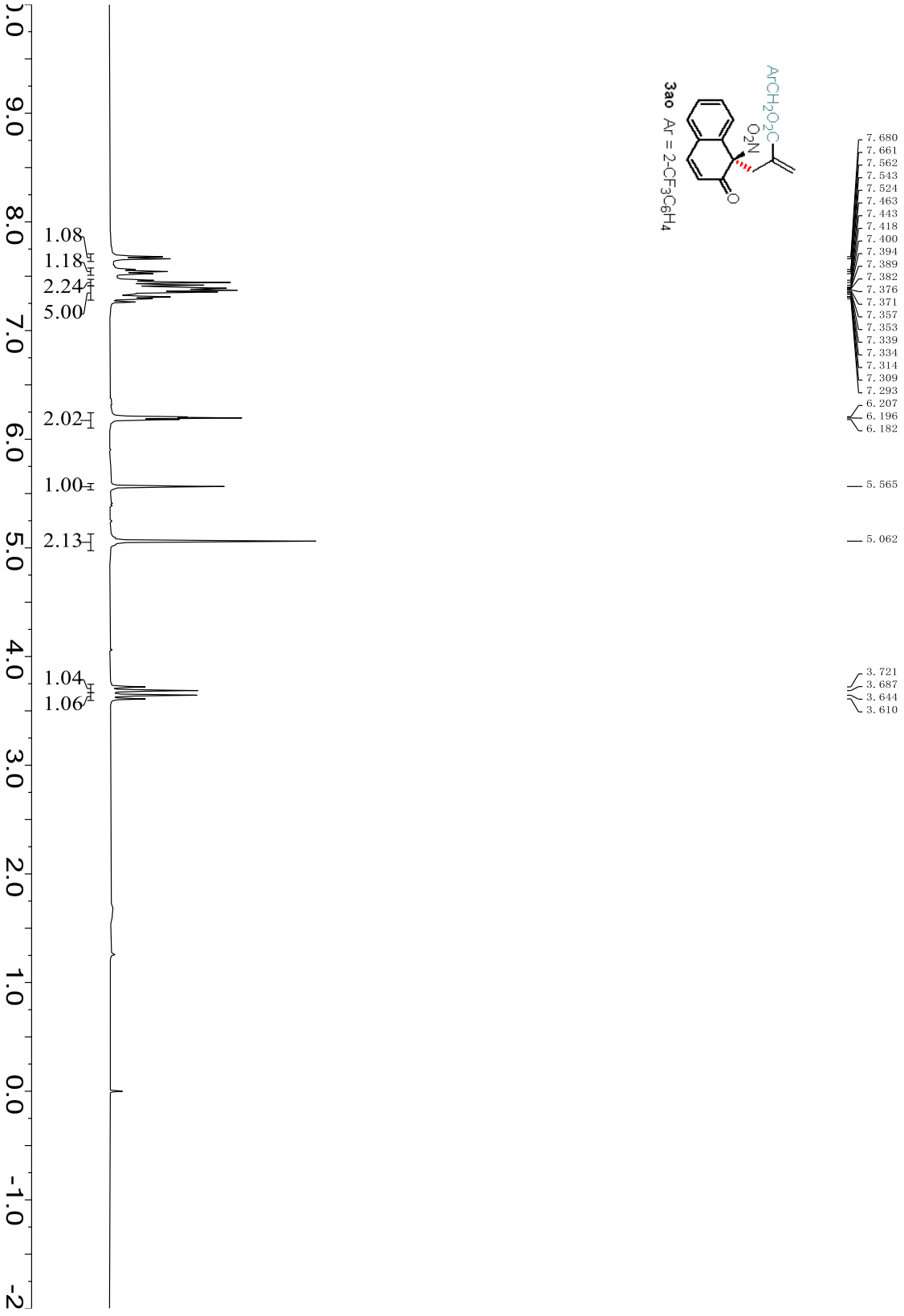
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3an**



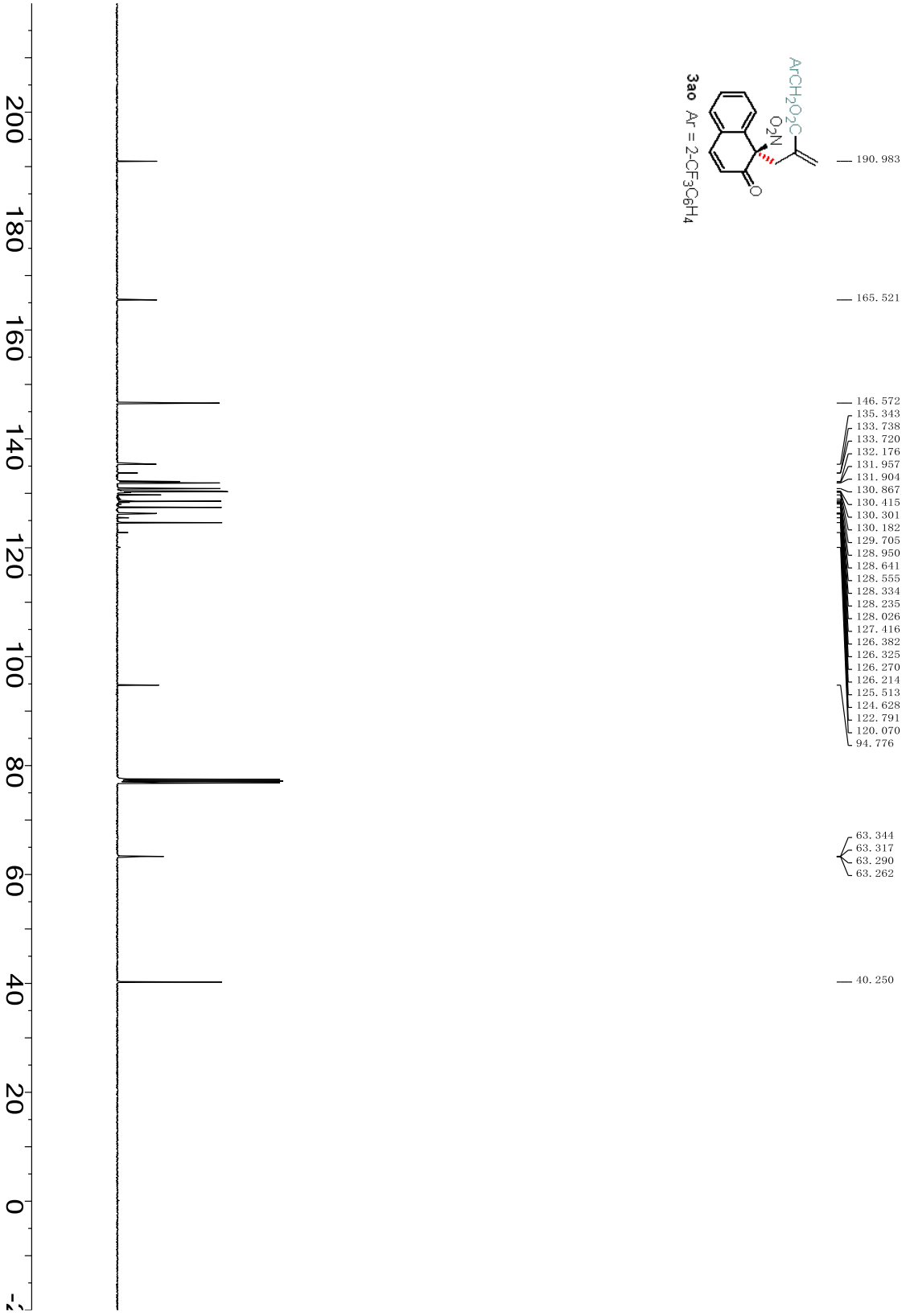
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3an**



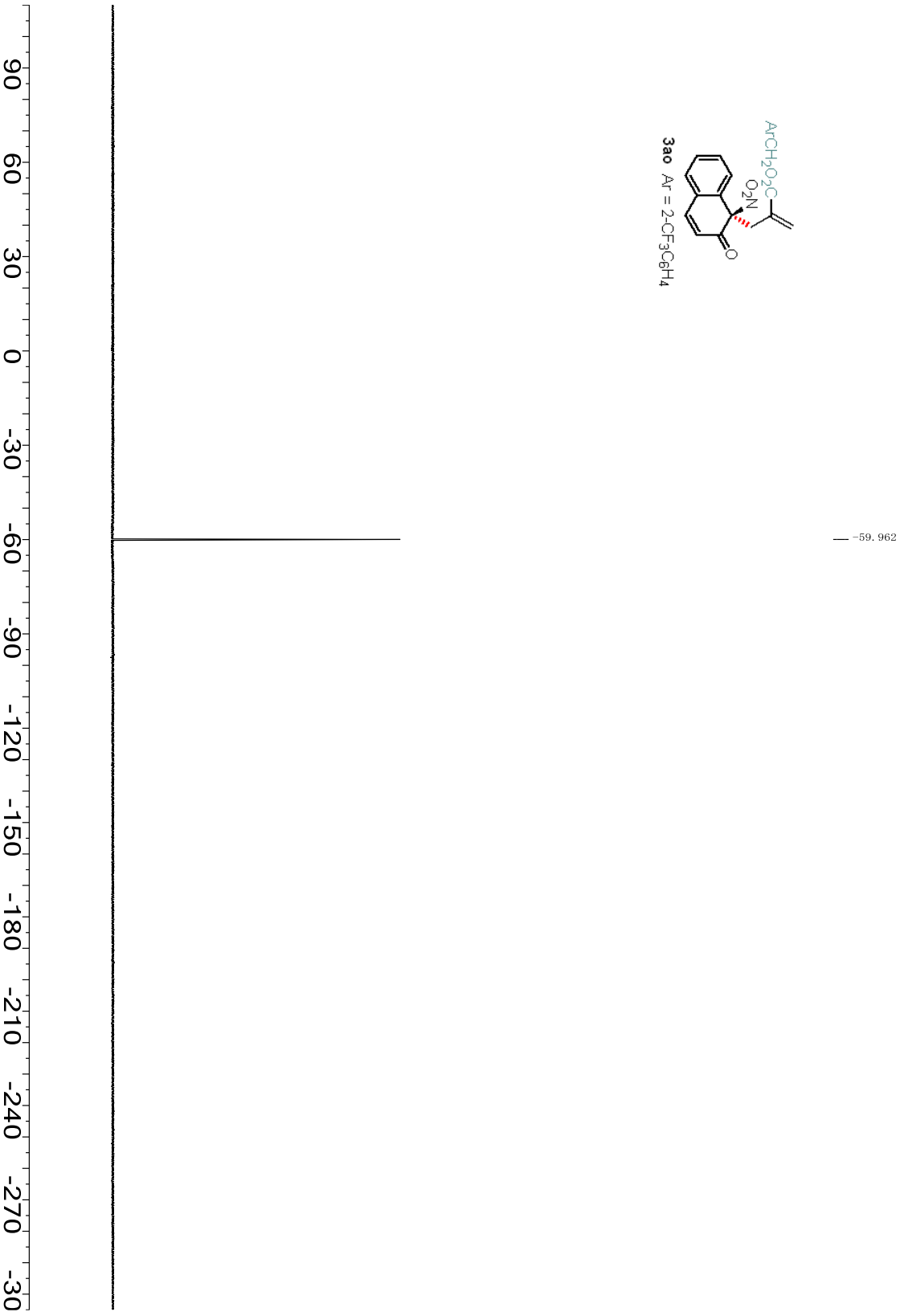
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3ao**



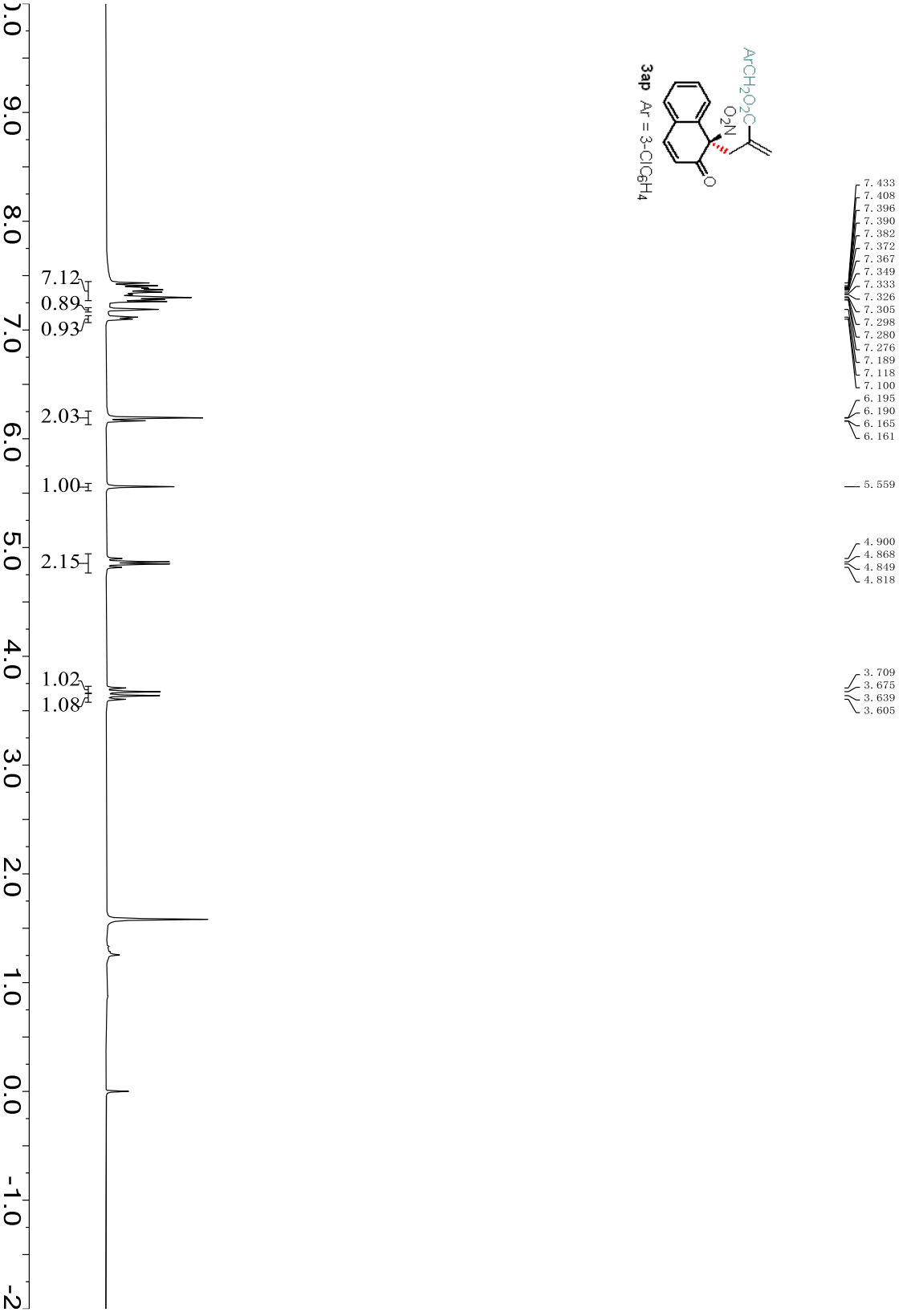
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ao**



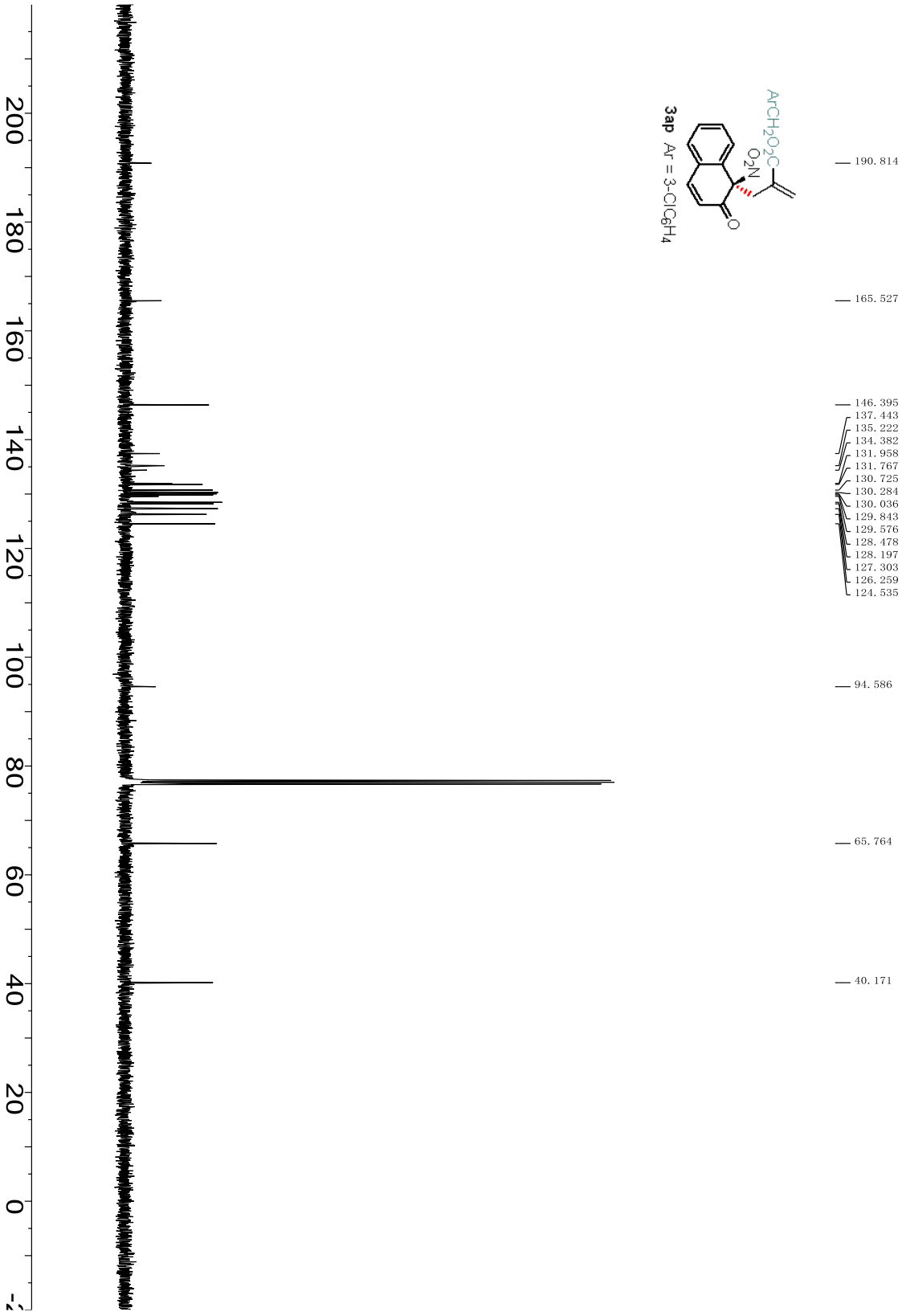
$^{19}$F NMR (376 MHz, $CDCl_3$) of **3ao**



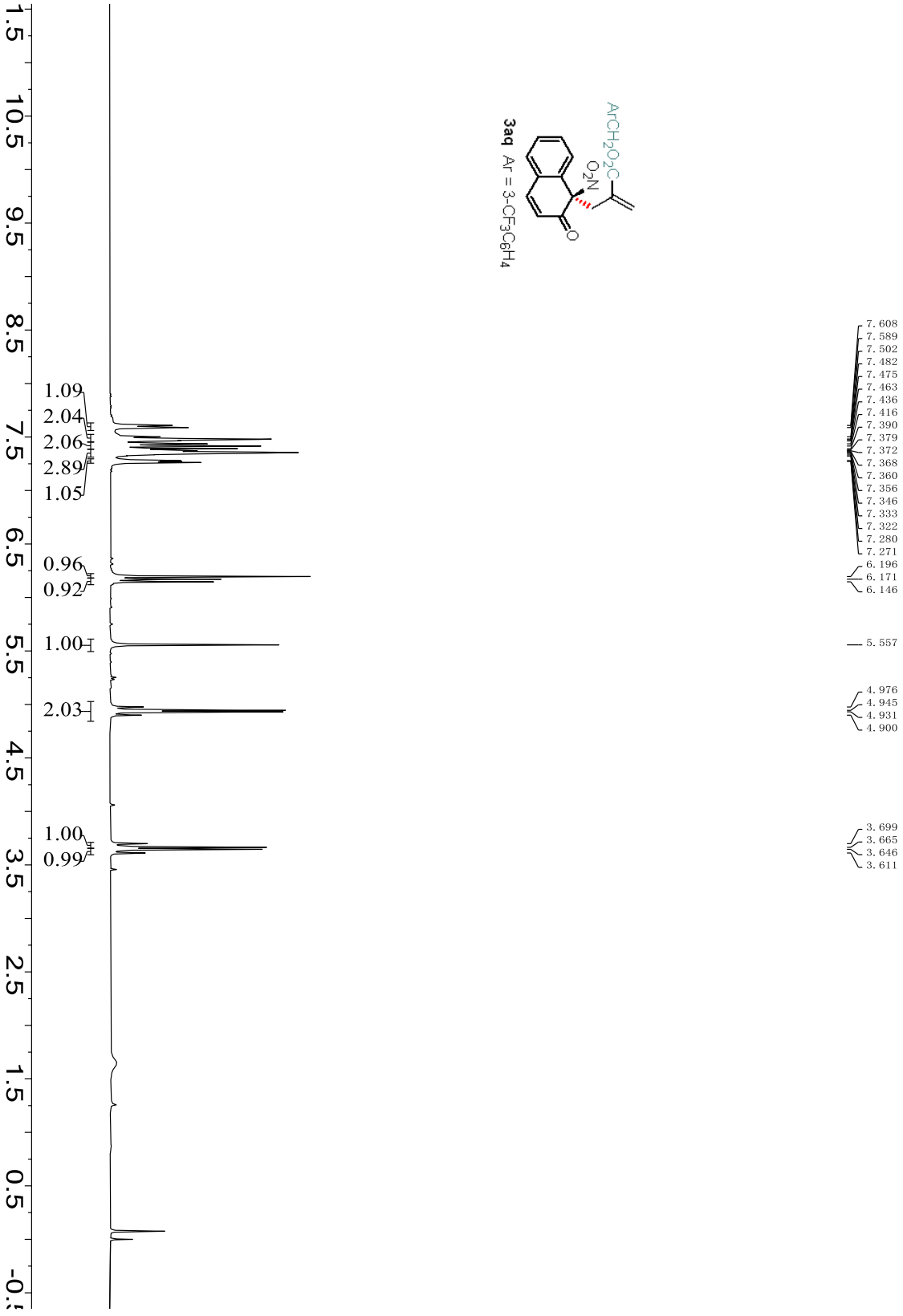
$^1$H NMR (400 MHz, $CDCl_3$) of **3ap**



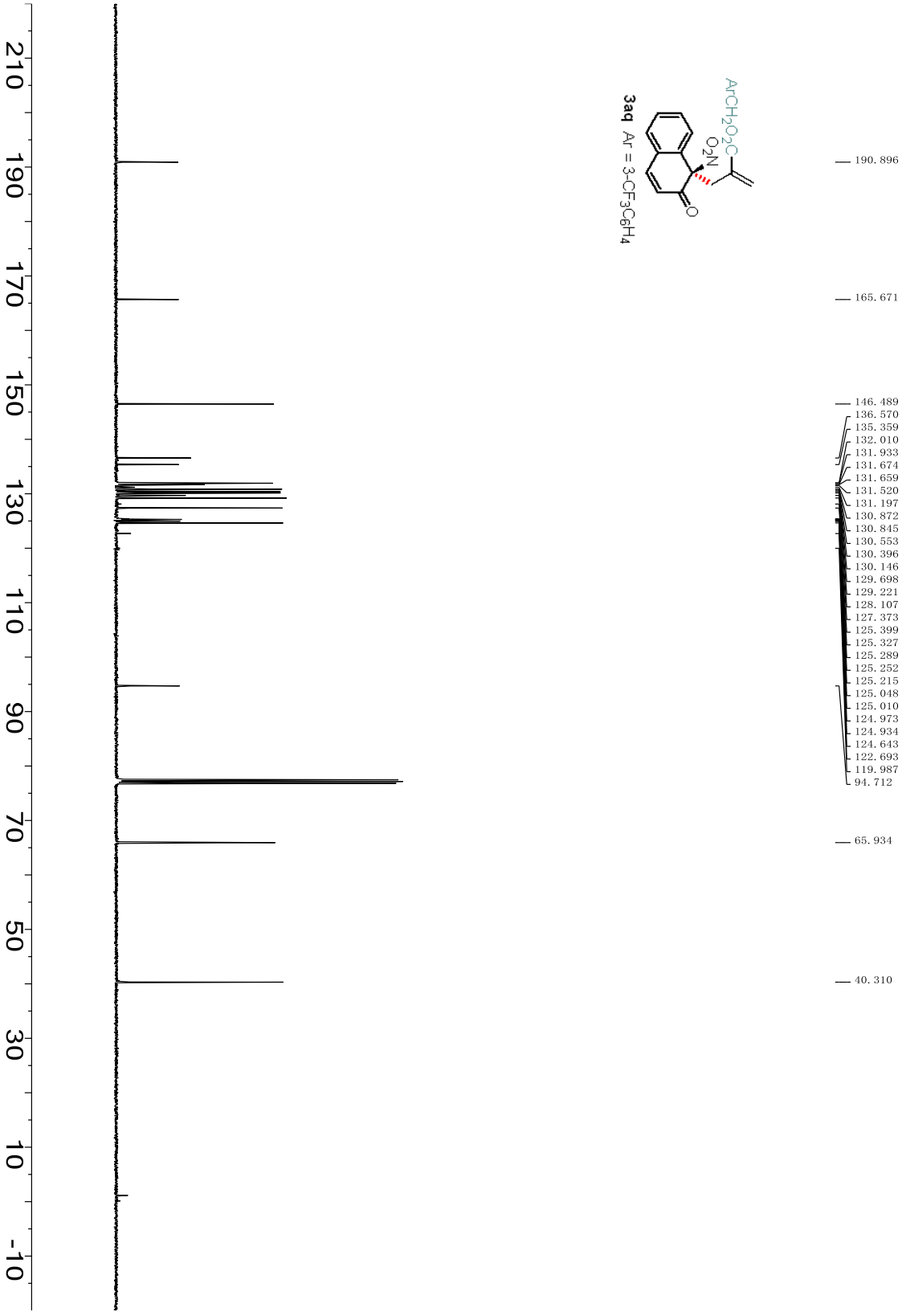
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ap**



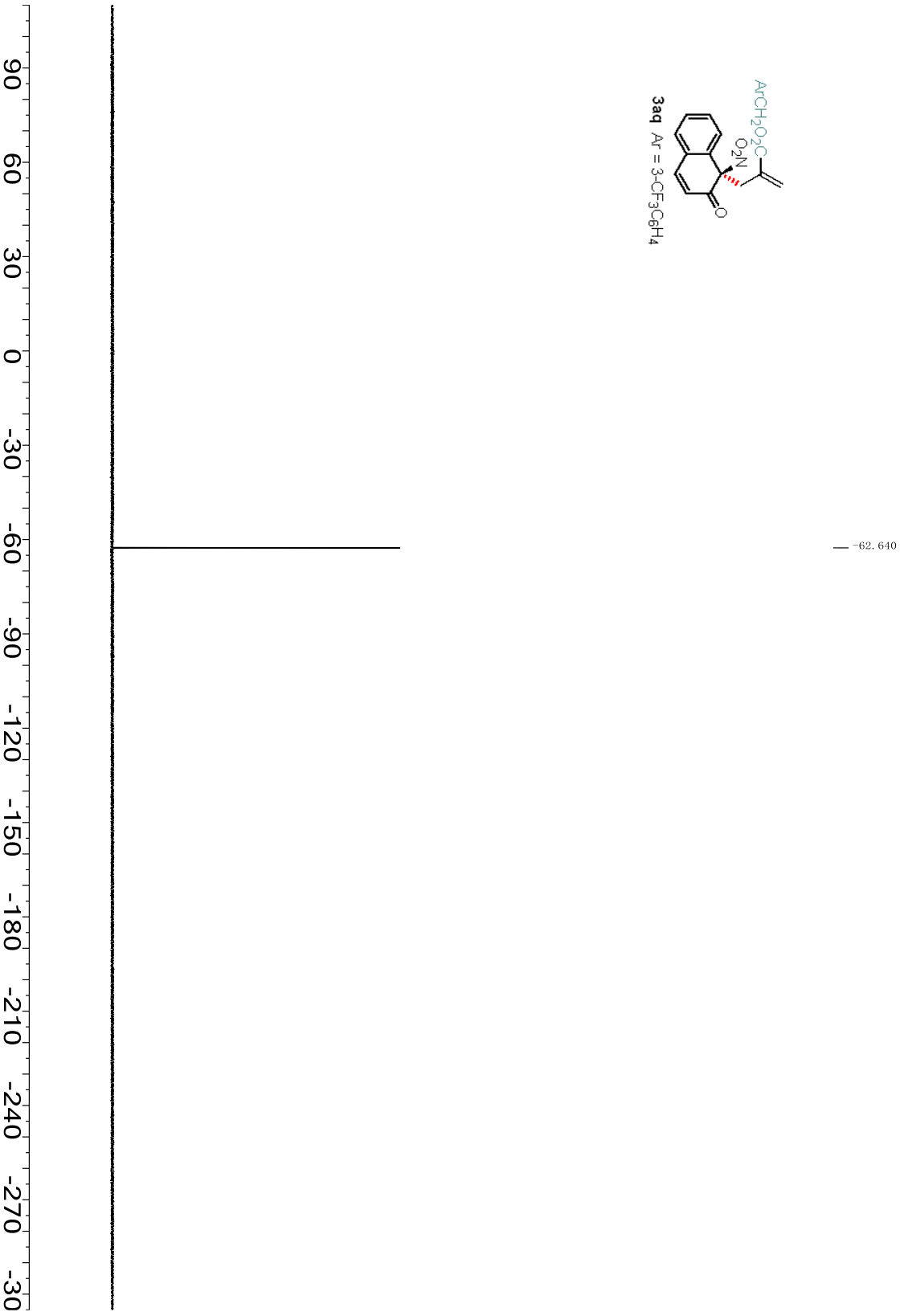
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3aq**



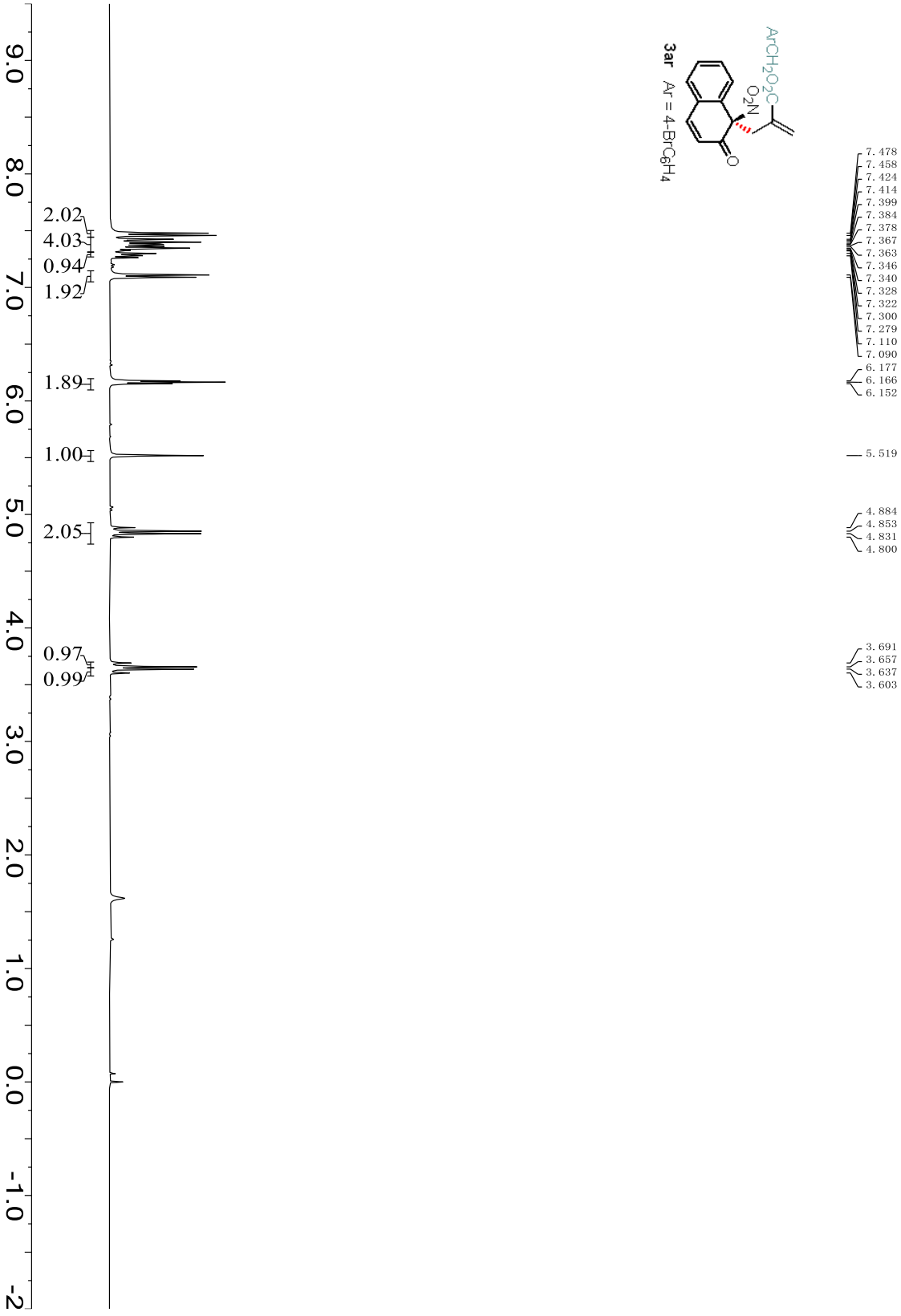
$^{13}$C NMR (100 MHz, $CDCl_3$) of **3aq**



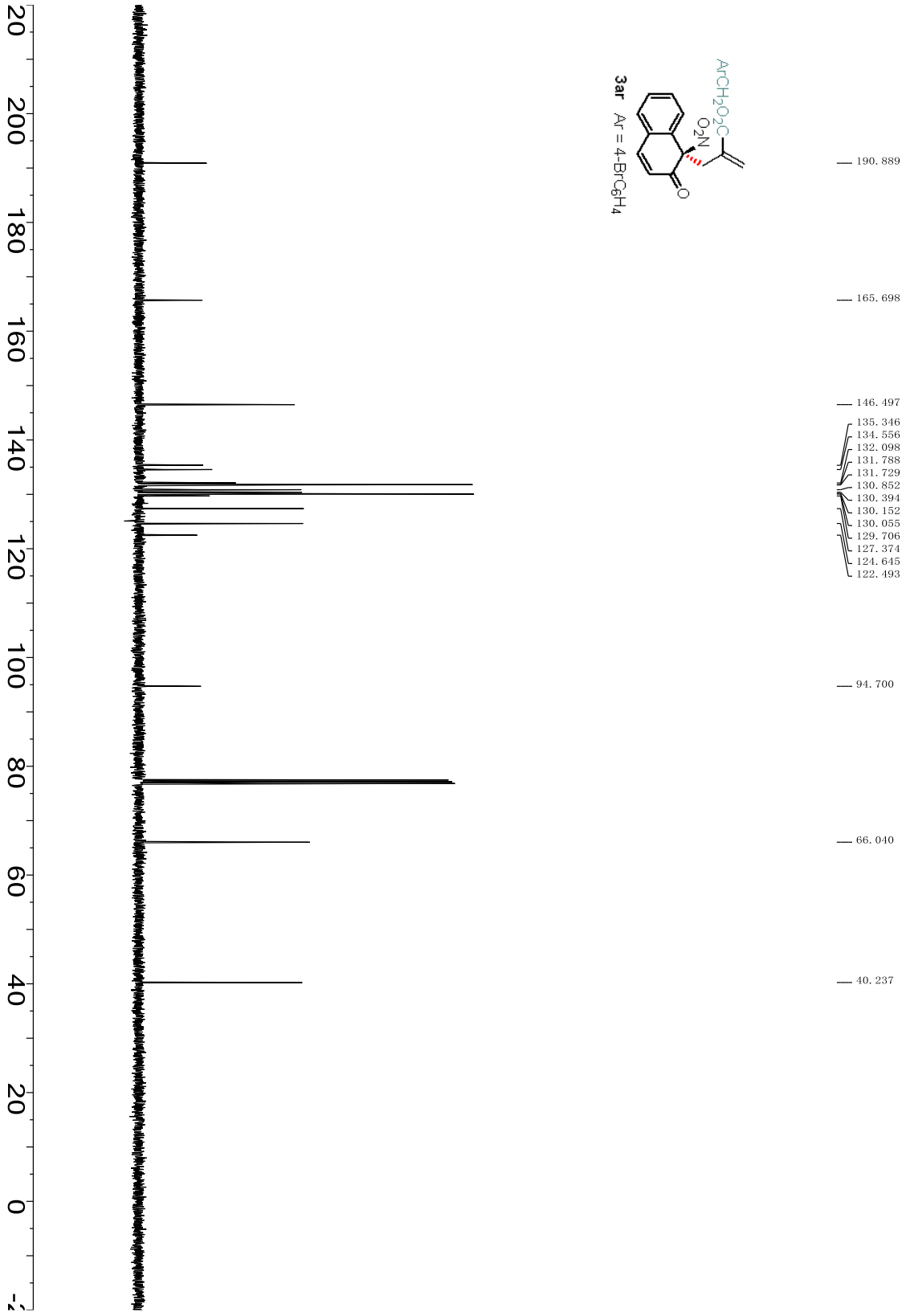
$^{19}$F NMR (376 MHz, $CDCl_3$) of **3aq**



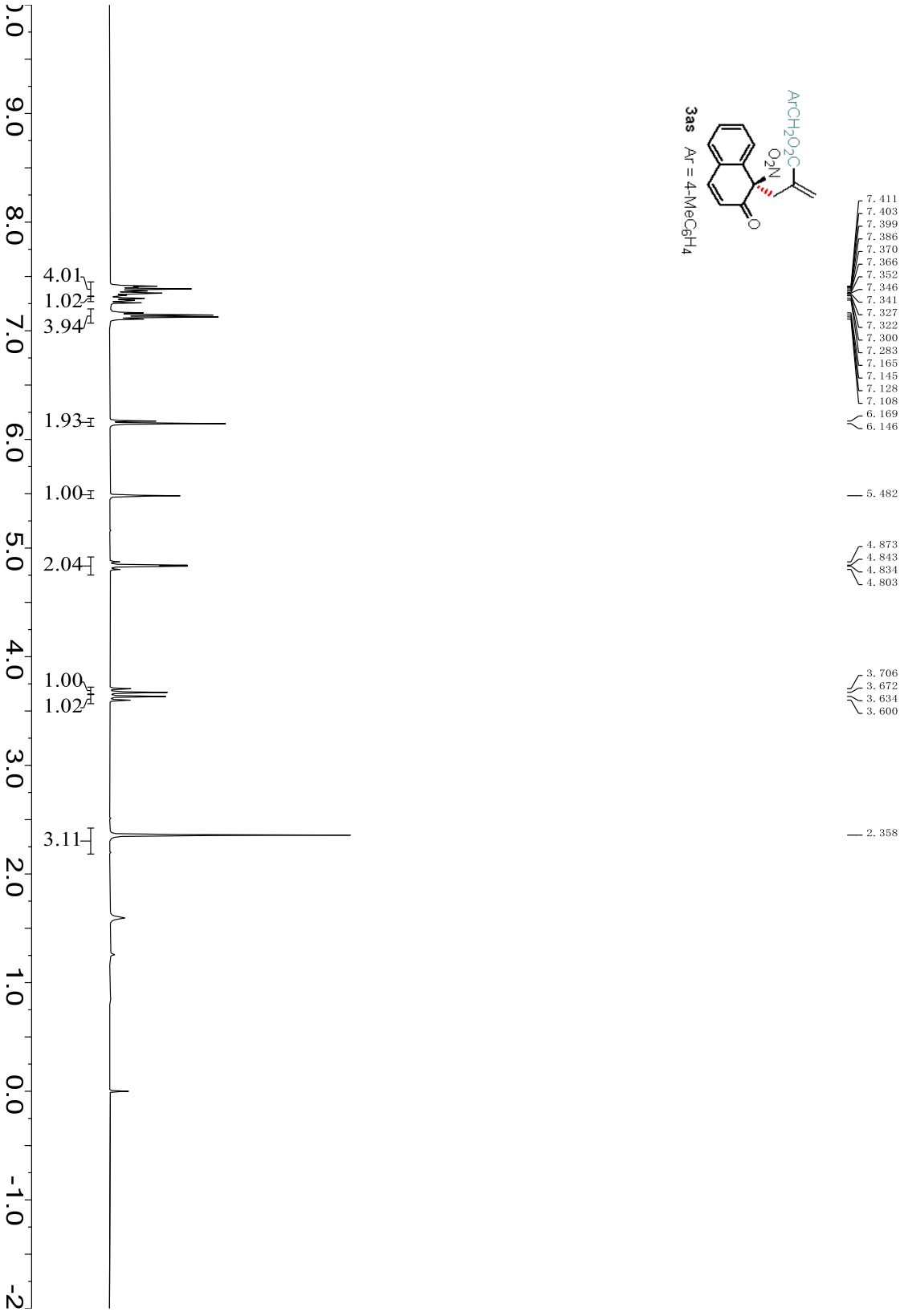
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3ar**



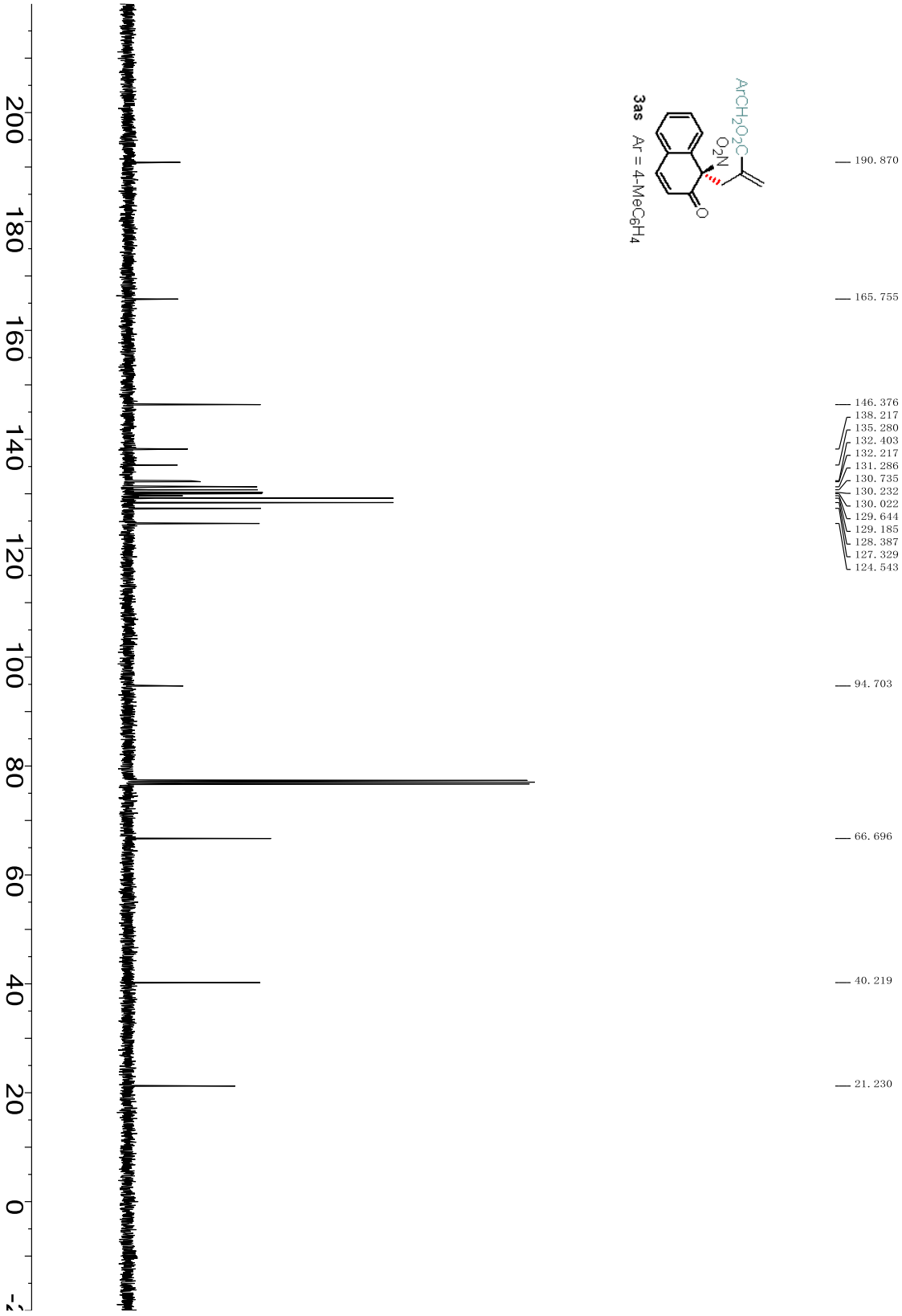
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3ar**



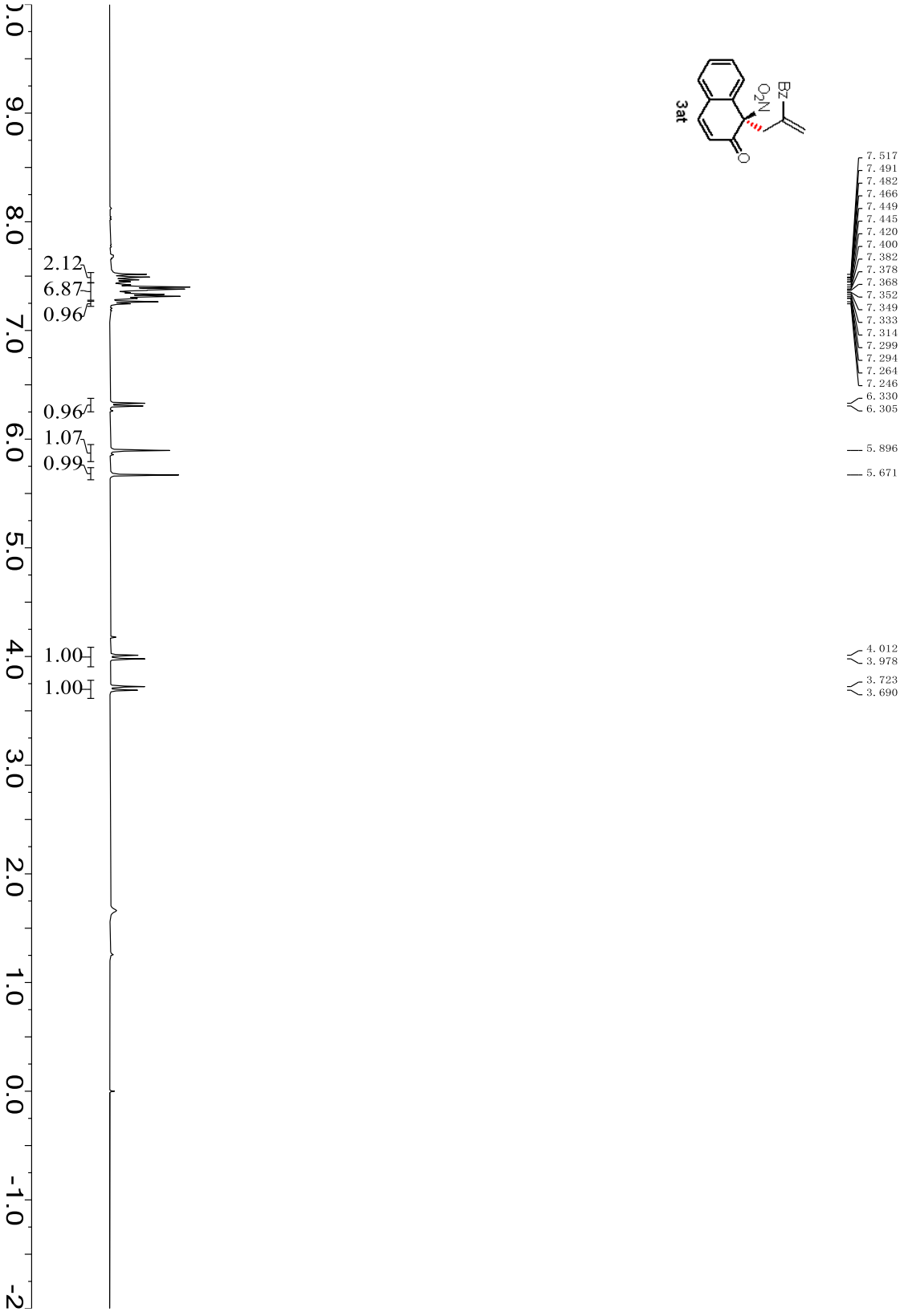
$^1$H NMR (400 MHz, $CDCl_3$) of **3as**



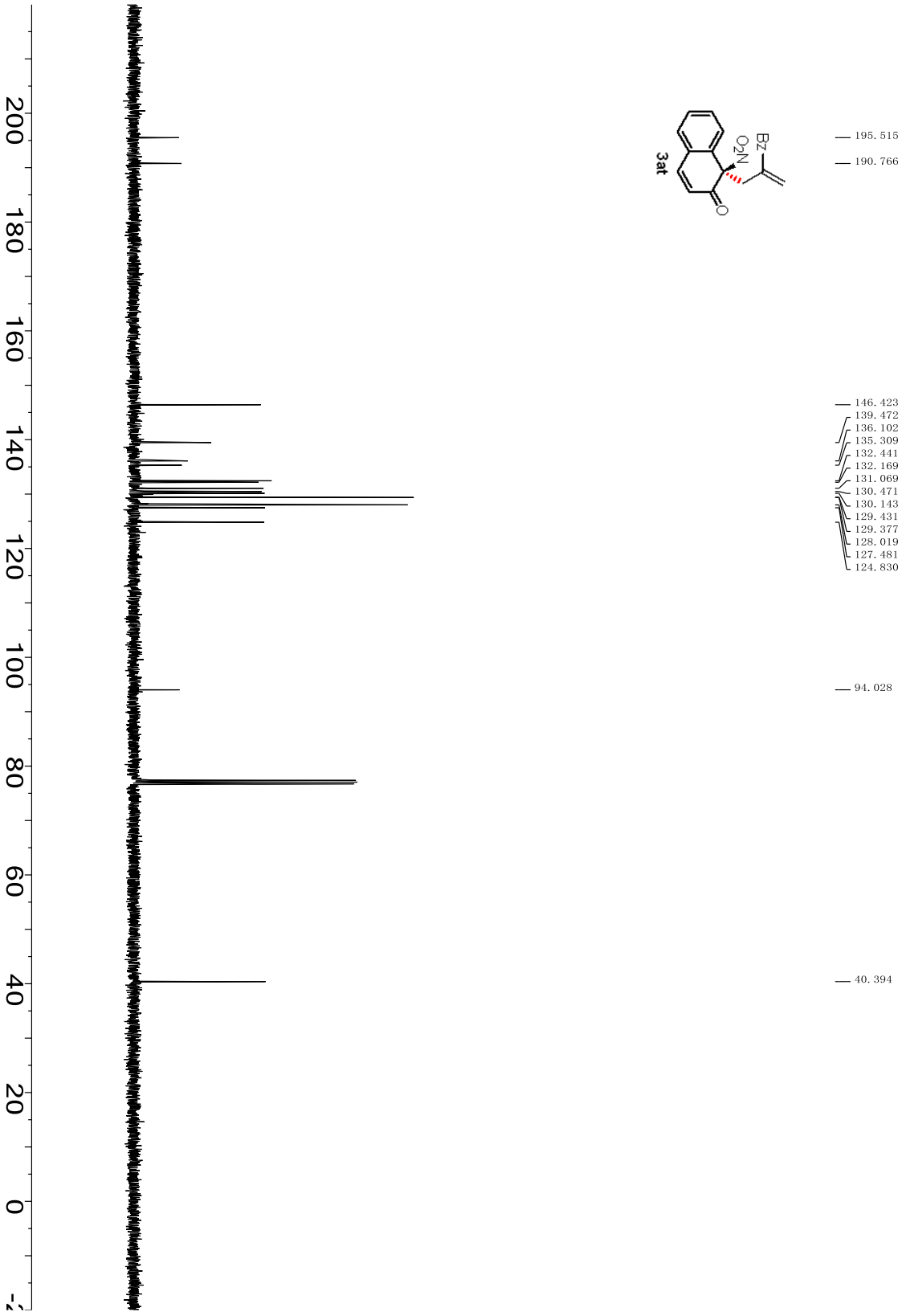
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3as**



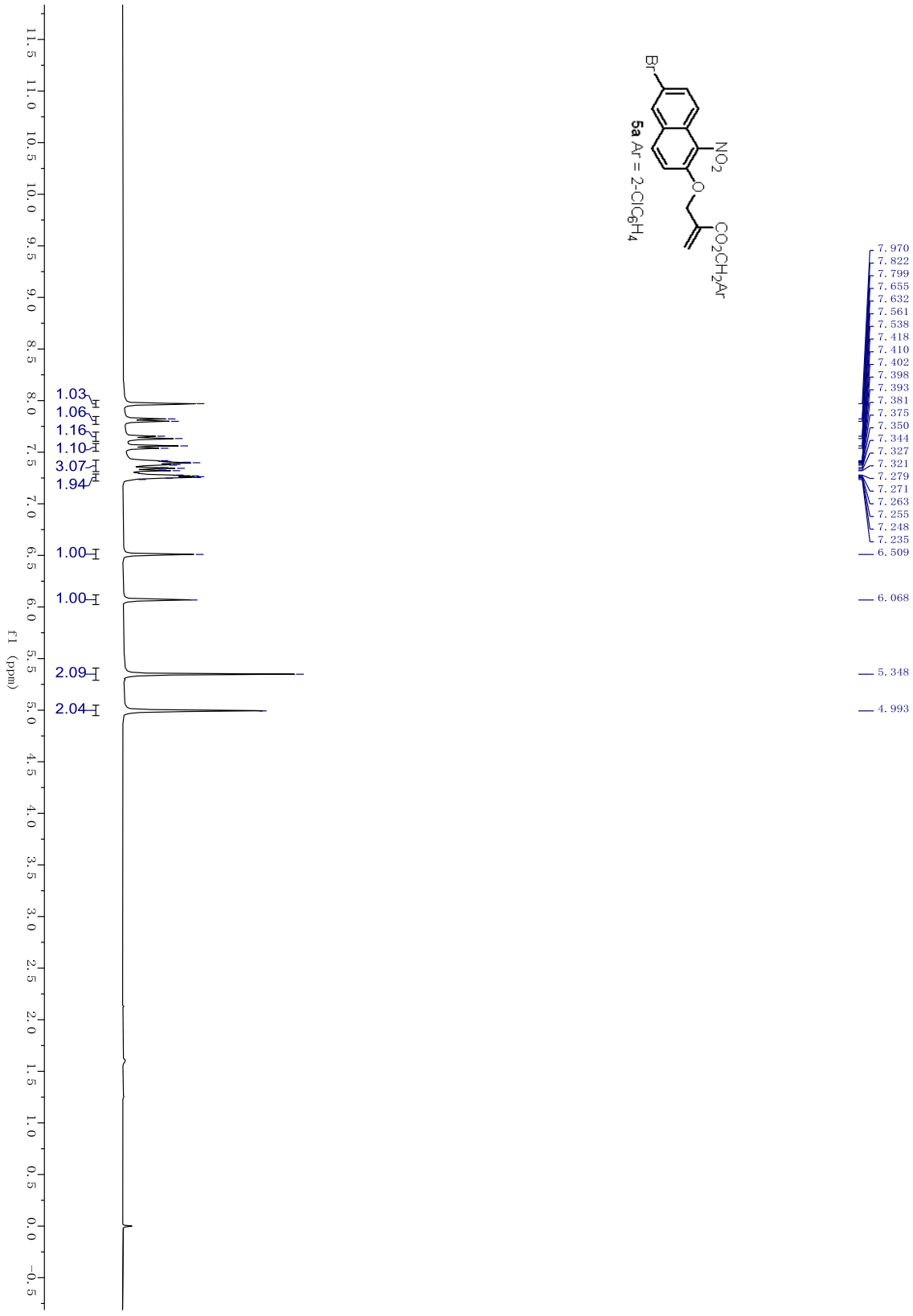
$^{1}$H NMR (400 MHz, $CDCl_3$) of **3at**



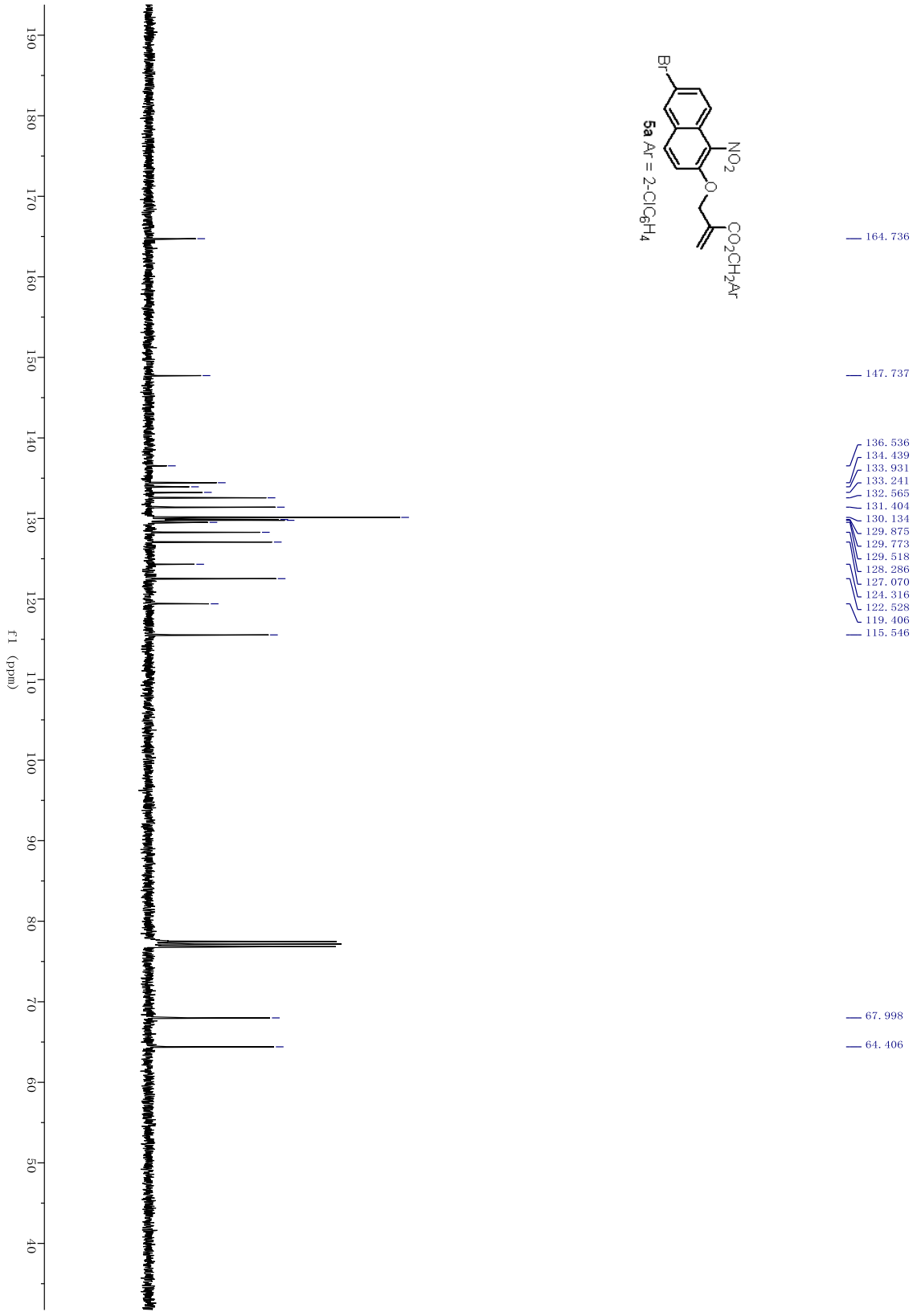
$^{13}C$ NMR (100 MHz, $CDCl_3$) of **3at**



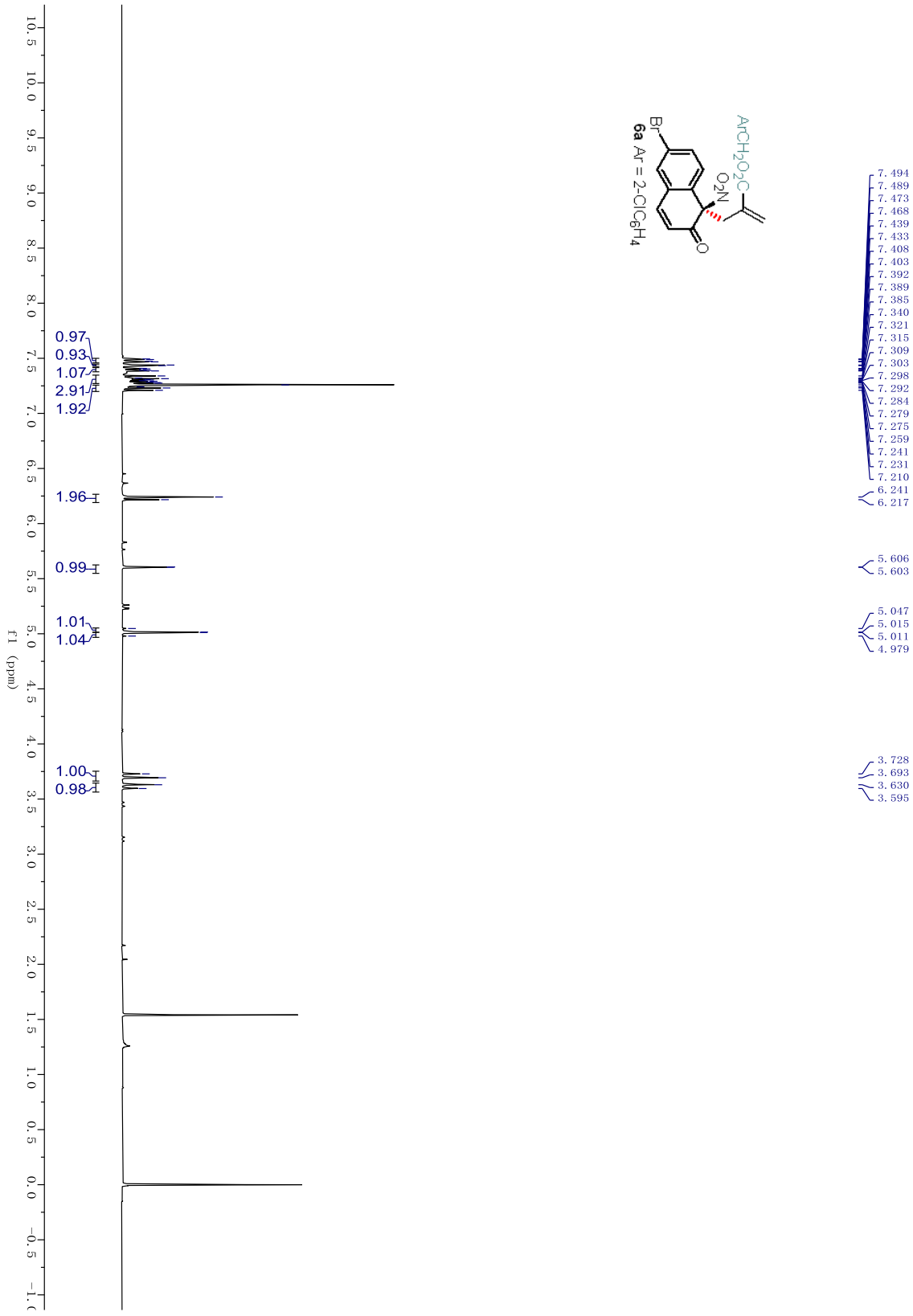
$^1$H NMR (400 MHz, $CDCl_3$) of **5a**



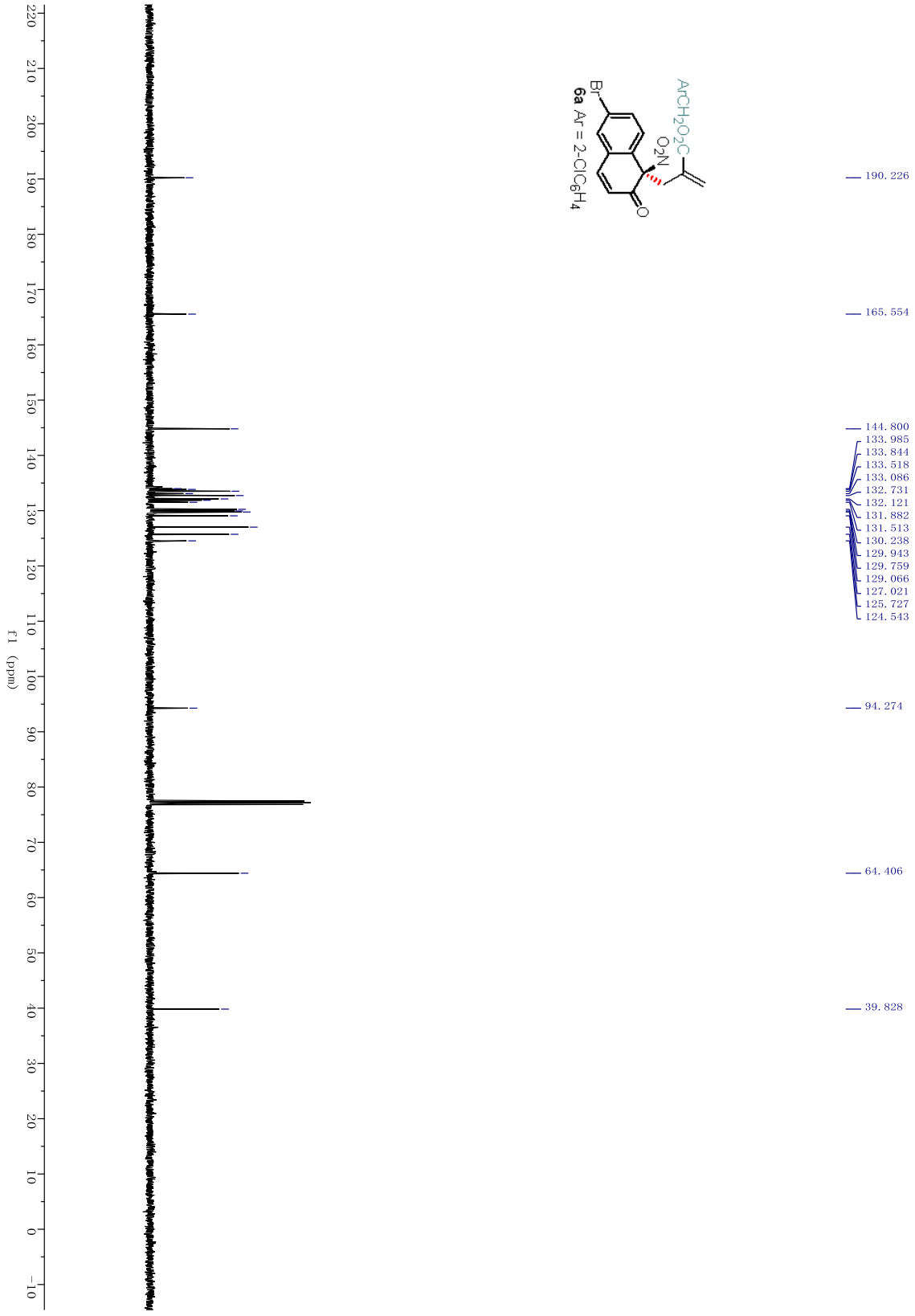
$^{13}$C NMR (100 MHz, $CDCl_3$) of **5a**



$^{1}$H NMR (400 MHz, $CDCl_3$) of **6a**

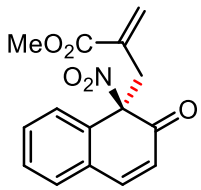


$^{13}$C NMR (100 MHz, $CDCl_3$) of **6a**

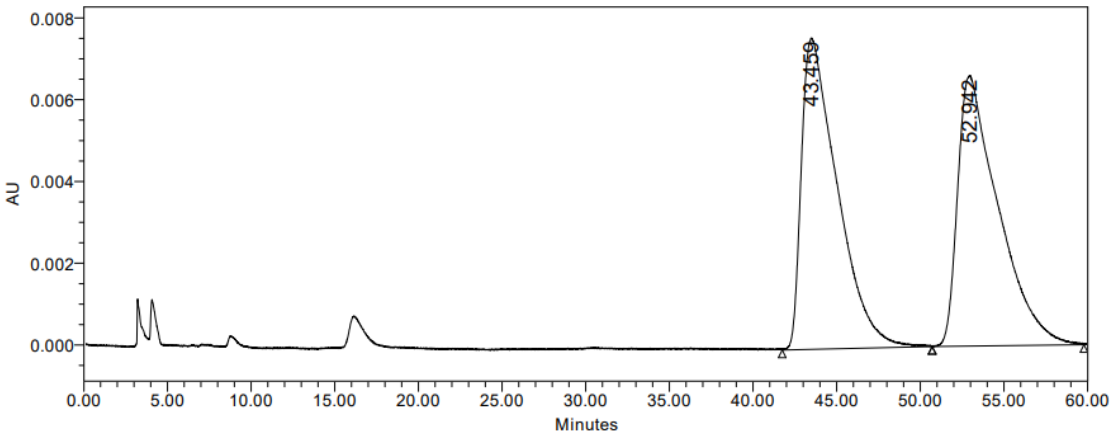


## 11. Copies of HPLC Chromatograms

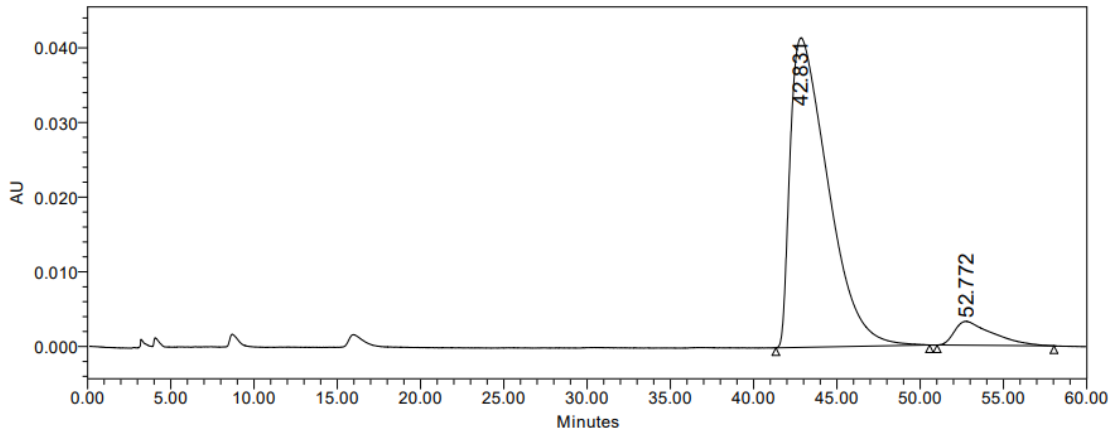
HPLC of **3aa:**




**3aa**

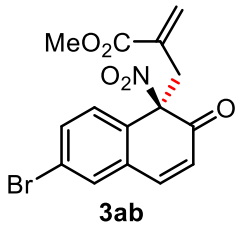



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 43.459 | 1135228 | 50.44 | 7609 |
| 2 | 52.942 | 1115638 | 49.56 | 6619 |

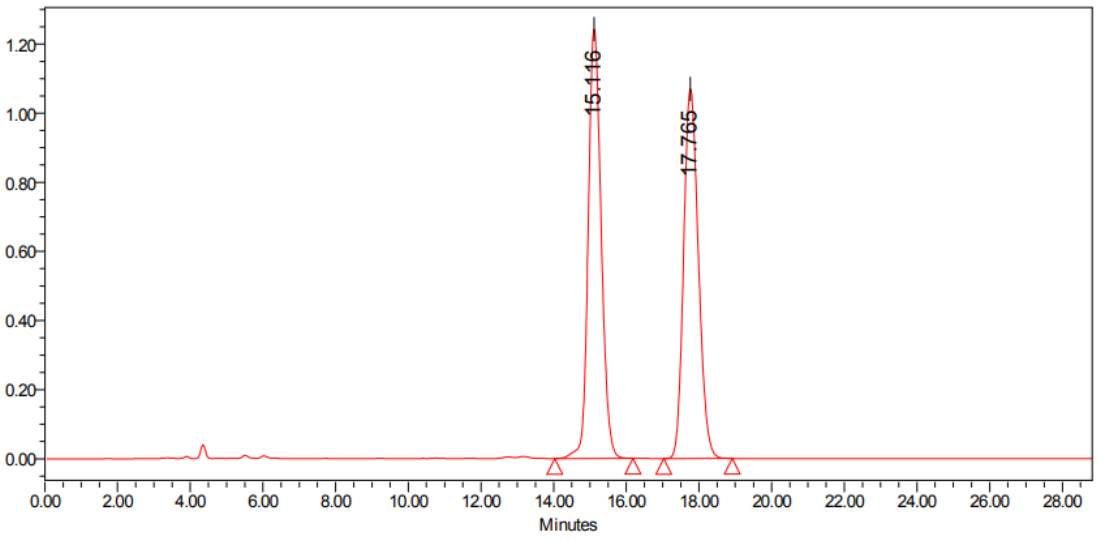



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 42.831 | 6535964 | 92.84 | 41430 |
| 2 | 52.772 | 504170 | 7.16 | 3198 |

HPLC of **3ab:**

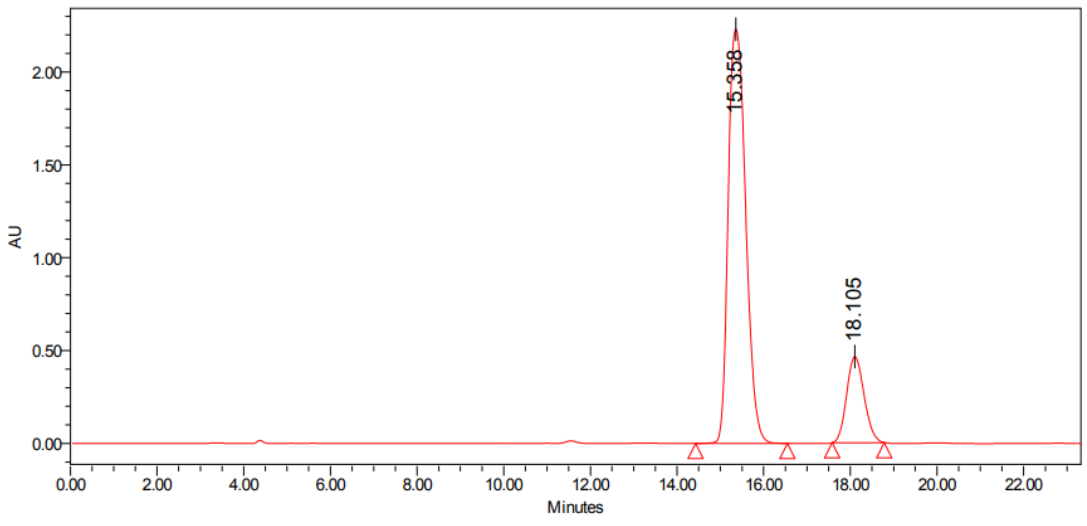



**3ab**




**Peak Results**

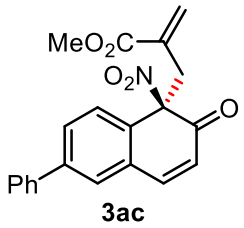
| | Name | RT | Area | Height | Width (sec) | % Area |
|---|---|---|---|---|---|---|
| 1 | | 15.116 | 30700000 | 1242050 | 129.000 | 50.43 |
| 2 | | 17.765 | 30174444 | 1069330 | 113.000 | 49.57 |



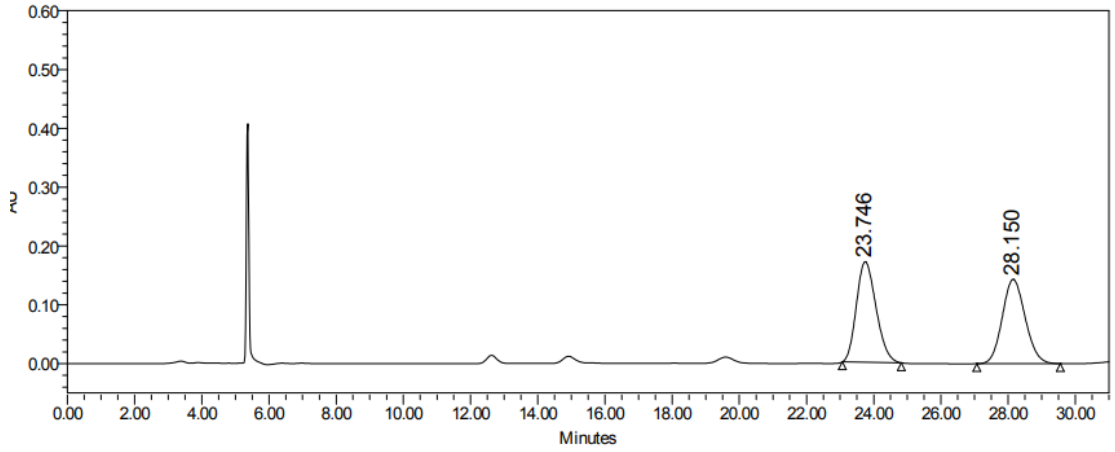

**Peak Results**

| | Name | RT | Area | Height | Width (sec) | % Area |
|---|---|---|---|---|---|---|
| 1 | | 15.358 | 62498816 | 2230935 | 127.000 | 82.80 |
| 2 | | 18.105 | 12985663 | 463993 | 72.000 | 17.20 |

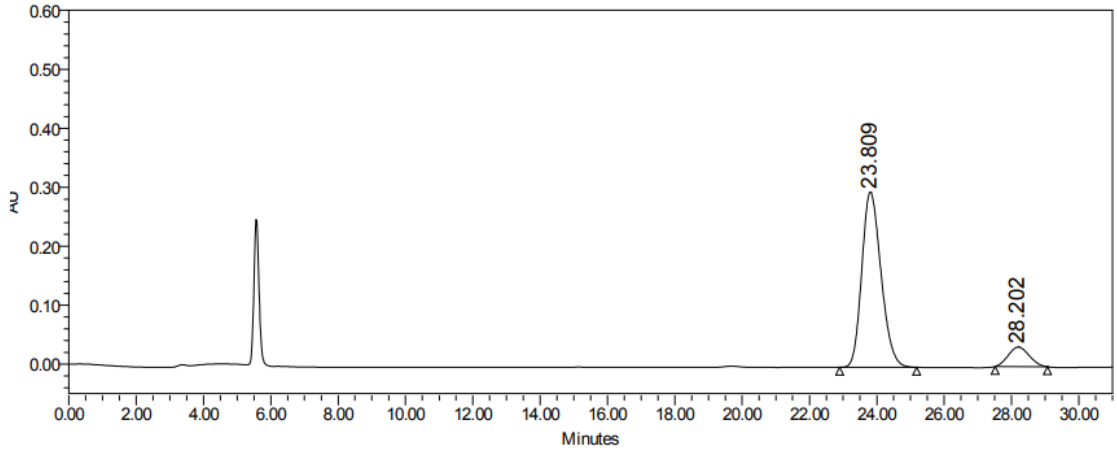
HPLC of **3ac:**




**3ac**

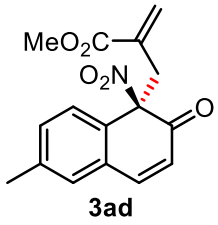



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 23.746 | 6952681 | 50.52 | 170863 |
| 2 | 28.150 | 6808831 | 49.48 | 143418 |

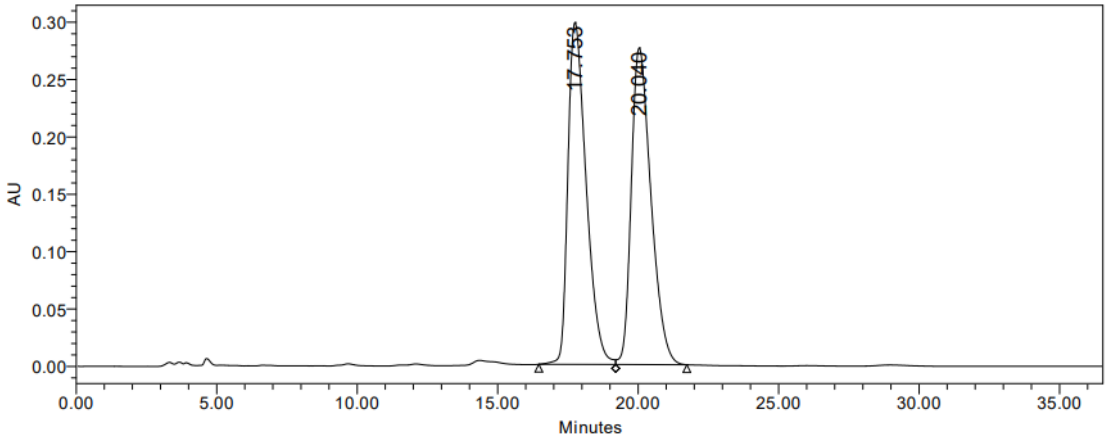



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 23.809 | 11809847 | 89.23 | 297452 |
| 2 | 28.202 | 1425165 | 10.77 | 32961 |

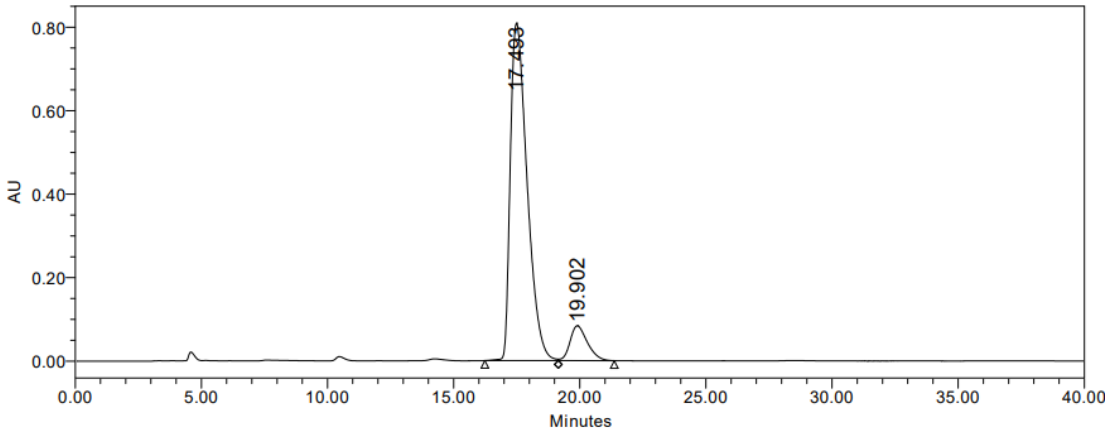
HPLC of **3ad:**




**3ad**

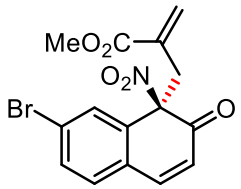



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 17.753 | 13463155 | 50.02 | 298010 |
| 2 | 20.040 | 13454389 | 49.98 | 276020 |

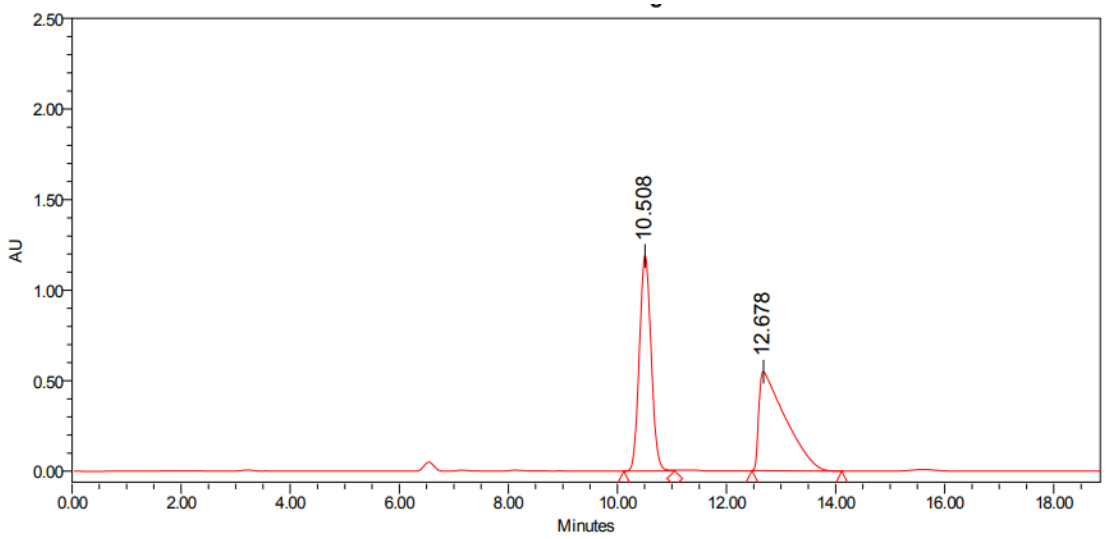



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 17.493 | 37393937 | 90.38 | 808384 |
| 2 | 19.902 | 3981354 | 9.62 | 83567 |

HPLC of **3ae:**

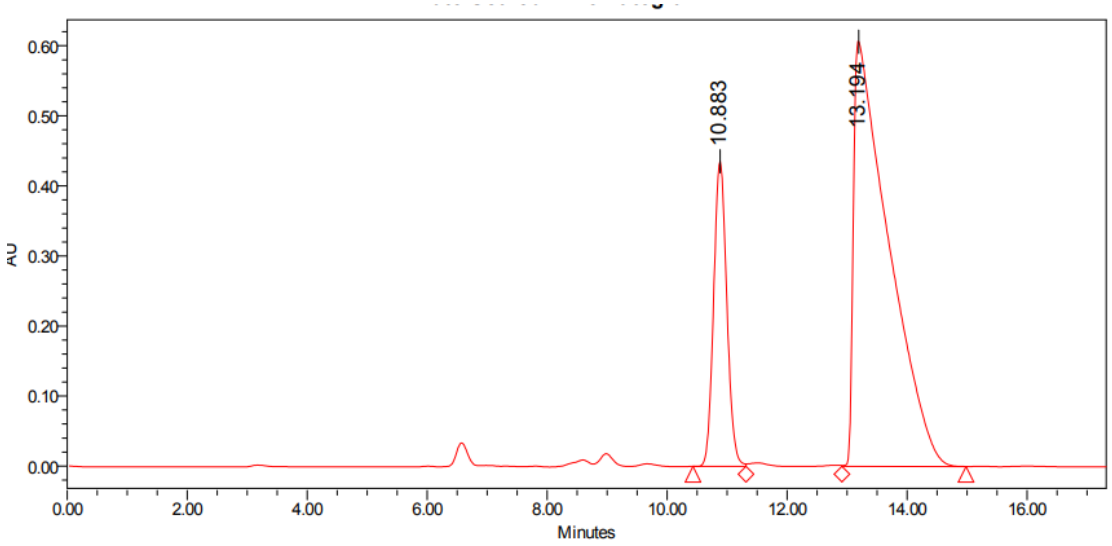



**3ae**




**Peak Results**

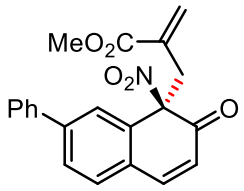
| | Name | RT | Area | Height | Width (sec) | % Area |
|---|---|---|---|---|---|---|
| 1 | | 10.508 | 17841543 | 1190415 | 56.000 | 49.11 |
| 2 | | 12.678 | 18491027 | 548923 | 99.000 | 50.89 |



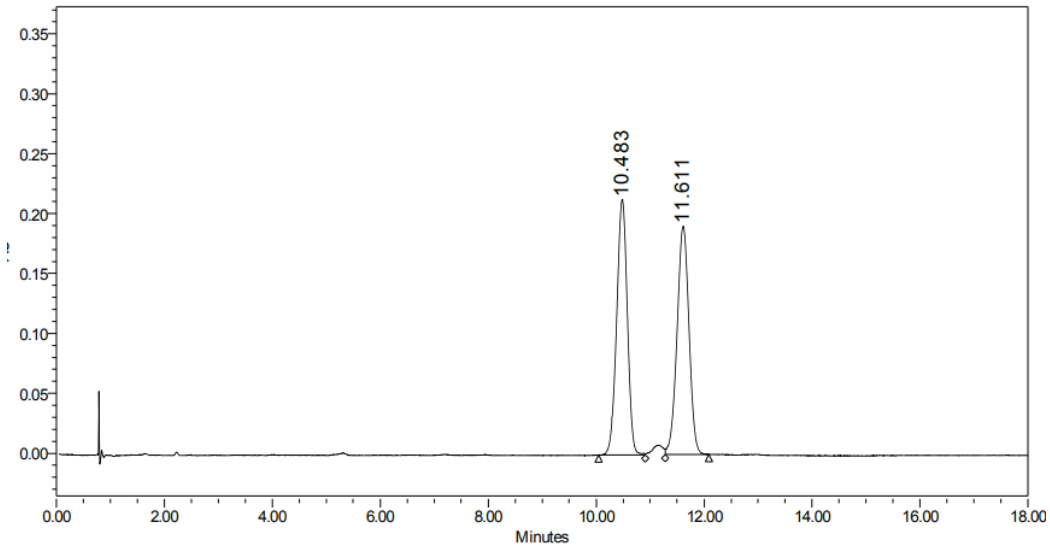

**Peak Results**

| | Name | RT | Area | Height | Width (sec) | % Area |
|---|---|---|---|---|---|---|
| 1 | | 10.883 | 6659920 | 435638 | 53.000 | 21.25 |
| 2 | | 13.194 | 24677276 | 609049 | 124.000 | 78.75 |

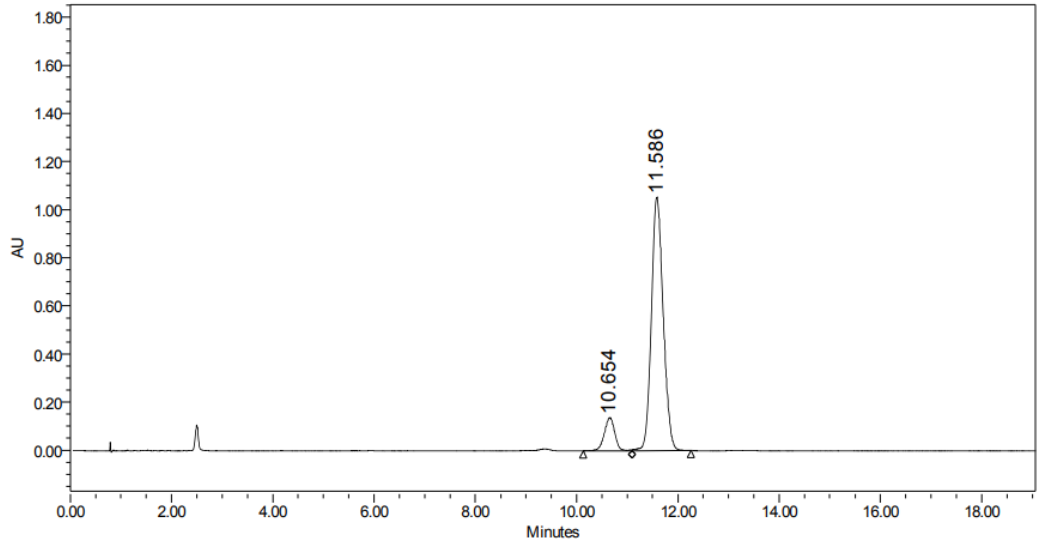
HPLC of **3af:**




**3af**

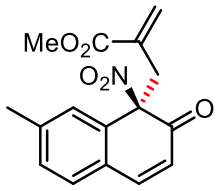



| | RT | Peak Type | Height | Width (sec) | Area | % Area |
|---|---|---|---|---|---|---|
| 1 | 10.483 | Unknown | 212921 | 51.650 | 2937940 | 49.88 |
| 2 | 11.611 | Unknown | 190393 | 48.350 | 2952159 | 50.12 |

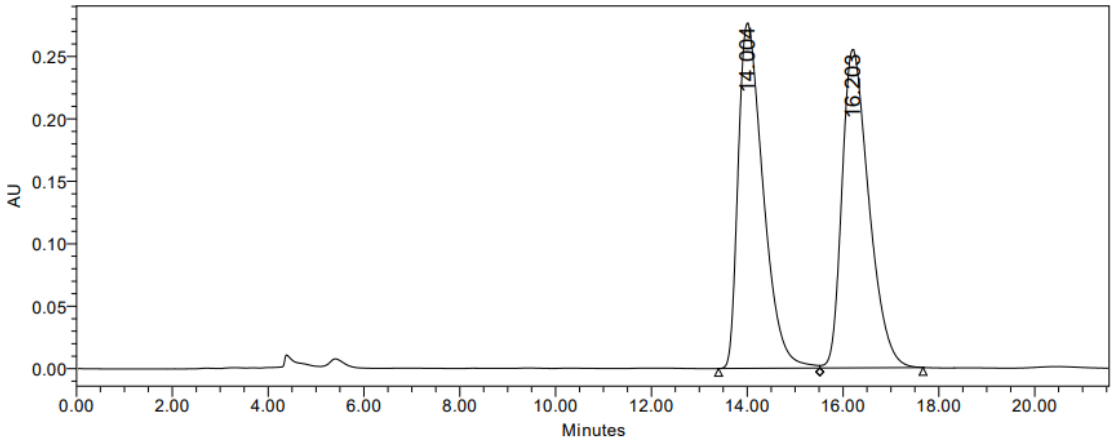



| | RT | Peak Type | Height | Width (sec) | Area | % Area |
|---|---|---|---|---|---|---|
| 1 | 10.654 | Unknown | 137341 | 57.550 | 1928137 | 10.17 |
| 2 | 11.586 | Unknown | 1053406 | 69.800 | 17035956 | 89.83 |

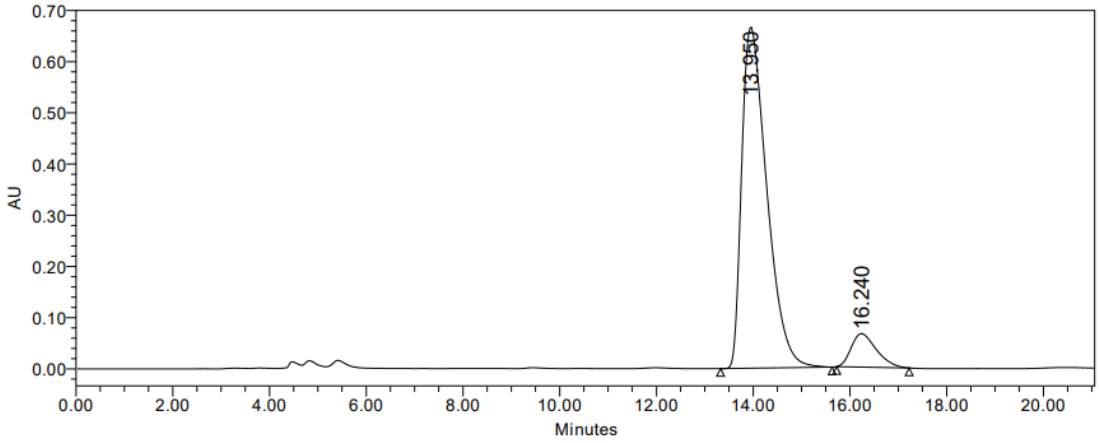
HPLC of **3ag:**




**3ag**

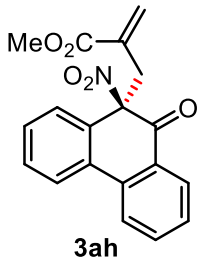



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 14.004 | 10013299 | 50.14 | 276260 |
| 2 | 16.203 | 9956015 | 49.86 | 254881 |

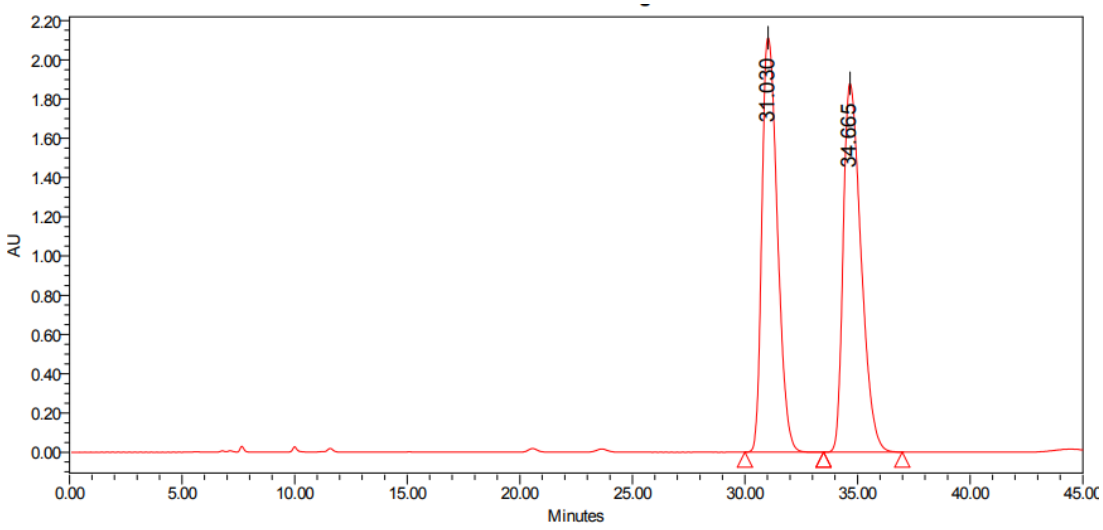



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 13.950 | 23990211 | 91.04 | 665145 |
| 2 | 16.240 | 2361160 | 8.96 | 65248 |

HPLC of **3ah:**

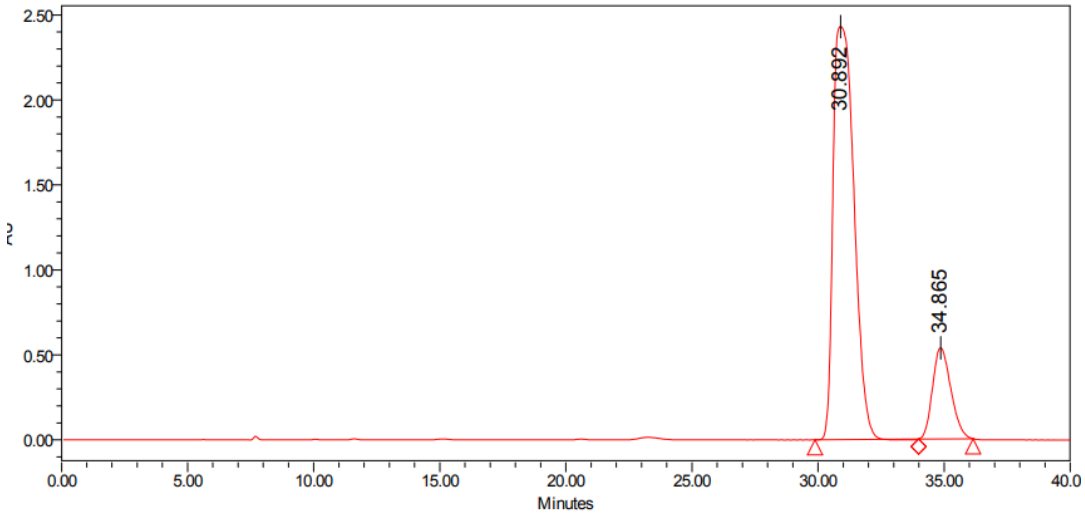



**3ah**




**Peak Results**

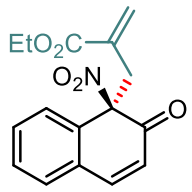
| | Name | RT | Area | Height | Width (sec) | % Area |
|---|---|---|---|---|---|---|
| 1 | | 31.030 | 101185943 | 211178 | 210.000 | 49.35 |
| 2 | | 34.665 | 103850615 | 1879083 | 209.000 | 50.65 |



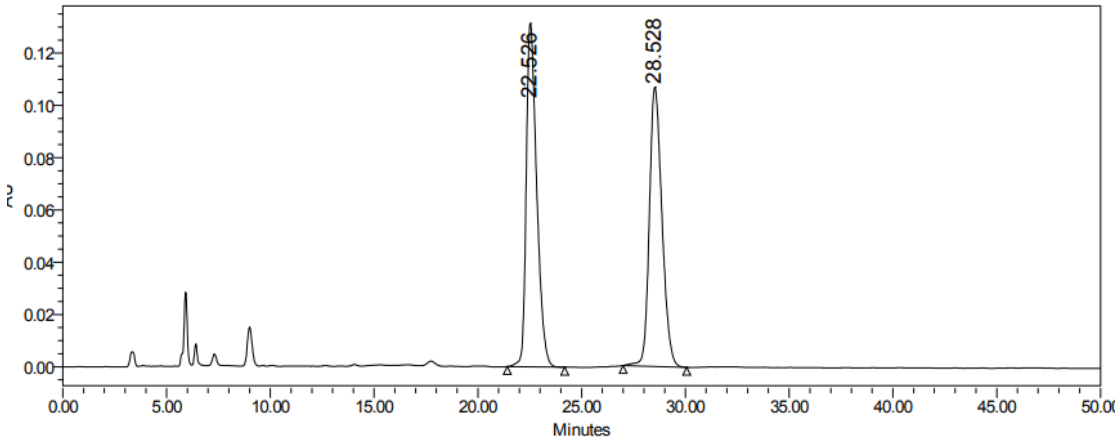

**Peak Results**

| | Name | RT | Area | Height | Width (sec) | % Area |
|---|---|---|---|---|---|---|
| 1 | | 30.892 | 140680743 | 2430431 | 246.000 | 83.82 |
| 2 | | 34.865 | 27146351 | 536098 | 130.000 | 16.18 |

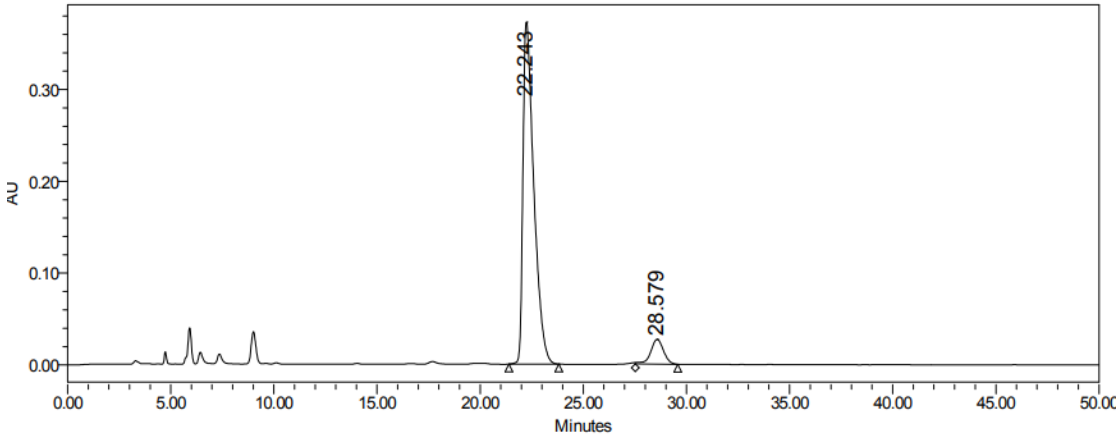
HPLC of **3ai:**




**3ai**

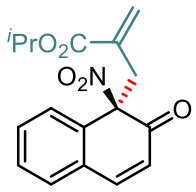



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 22.526 | 4596972 | 50.45 | 131521 |
| 2 | 28.528 | 4514106 | 49.55 | 106924 |

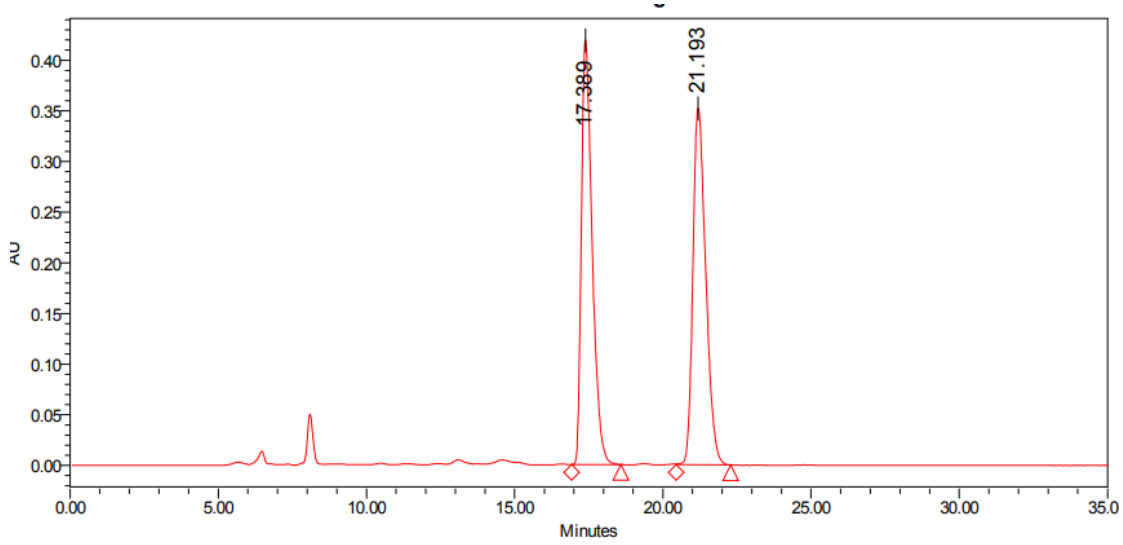



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 22.243 | 13634352 | 92.15 | 372658 |
| 2 | 28.579 | 1161229 | 7.85 | 26981 |

HPLC of **3aj:**

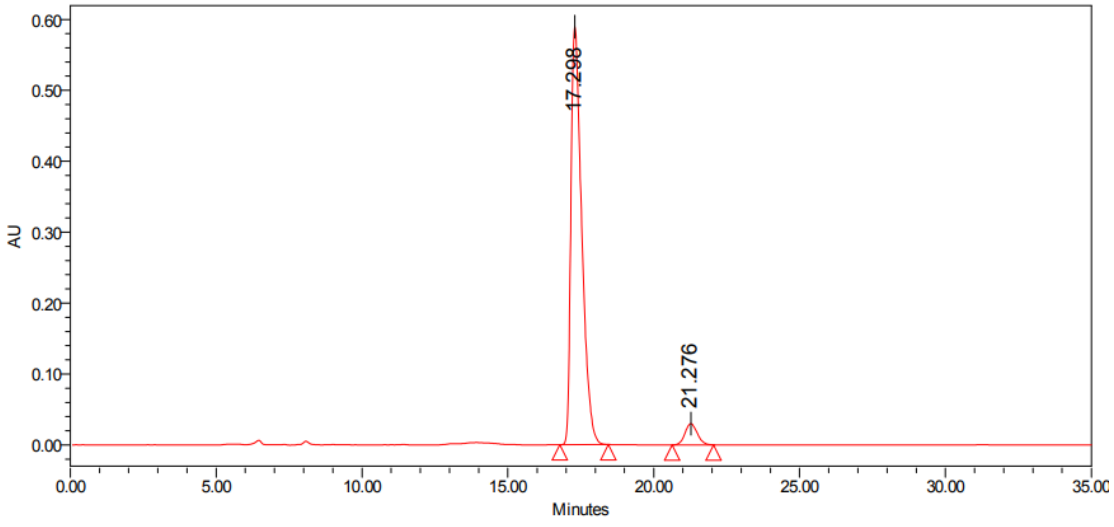



**3aj**




**Peak Results**

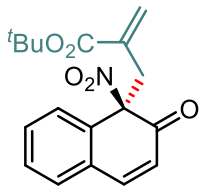
| | Name | RT | Area | Height | Width (sec) | % Area |
|---|---|---|---|---|---|---|
| 1 | | 17.389 | 10591921 | 419615 | 100.000 | 49.95 |
| 2 | | 21.193 | 10614565 | 352062 | 110.000 | 50.05 |



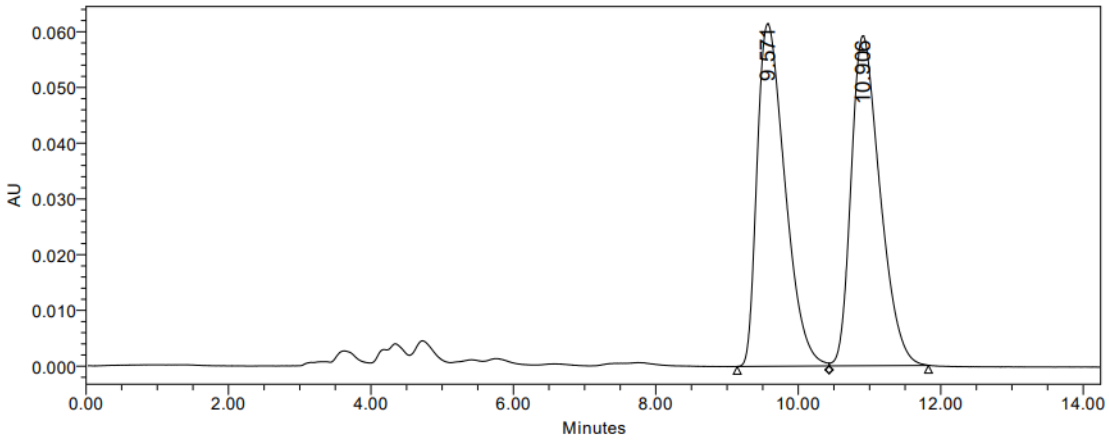

**Peak Results**

| | Name | RT | Area | Height | Width (sec) | % Area |
|---|---|---|---|---|---|---|
| 1 | | 17.298 | 15128076 | 589626 | 100.000 | 94.56 |
| 2 | | 21.276 | 871009 | 29876 | 85.000 | 5.44 |

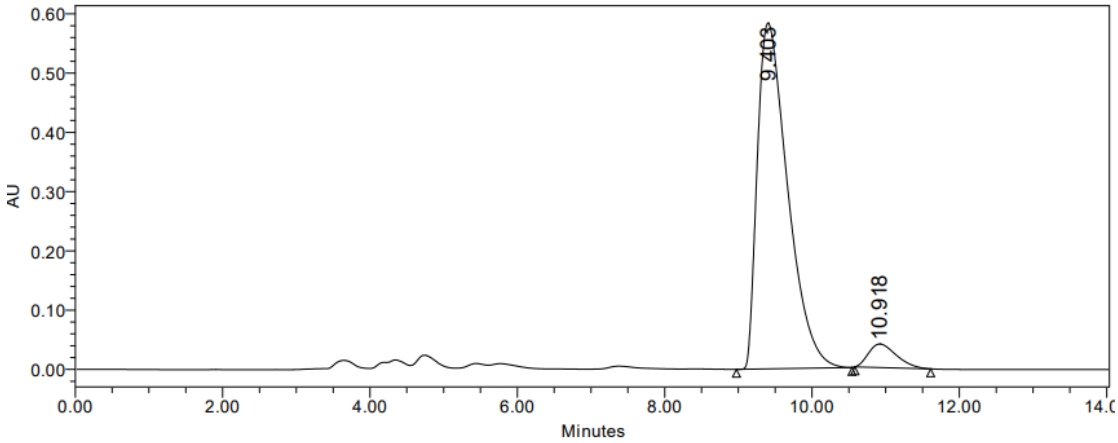
HPLC of **3ak:**




**3ak**

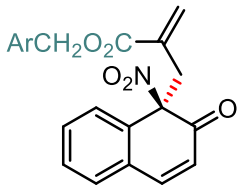



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 9.571 | 1671207 | 50.02 | 61454 |
| 2 | 10.906 | 1670021 | 49.98 | 59205 |

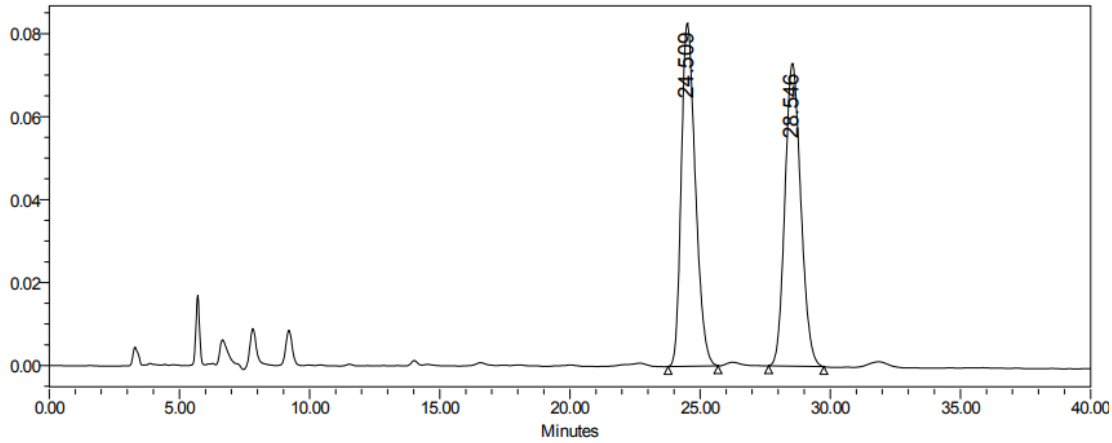



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 9.403 | 16673730 | 94.11 | 583319 |
| 2 | 10.918 | 1043715 | 5.89 | 39693 |

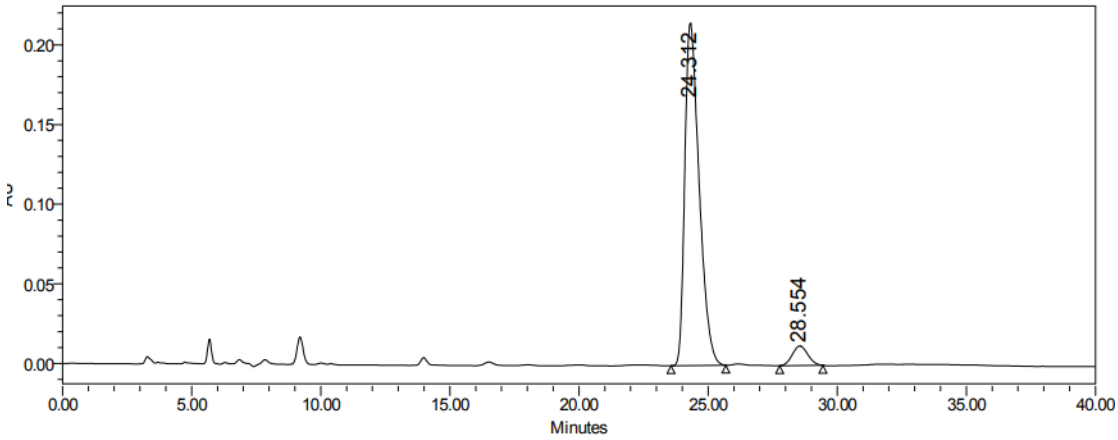
HPLC of **3al:**




**3al** Ar = $C_6H_5$

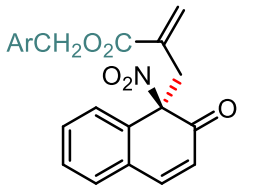



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 24.509 | 3109748 | 50.03 | 82687 |
| 2 | 28.546 | 3105645 | 49.97 | 72946 |

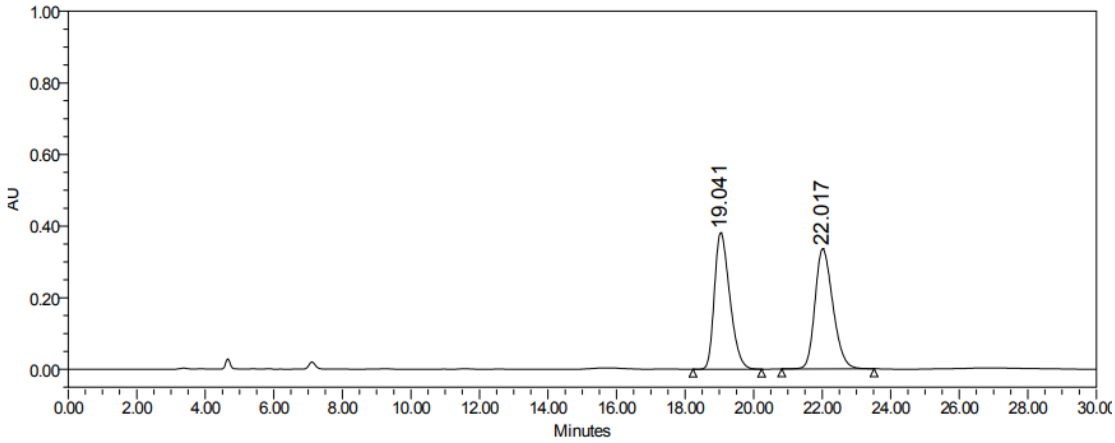



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 24.312 | 8309081 | 94.20 | 214926 |
| 2 | 28.554 | 511201 | 5.80 | 12272 |

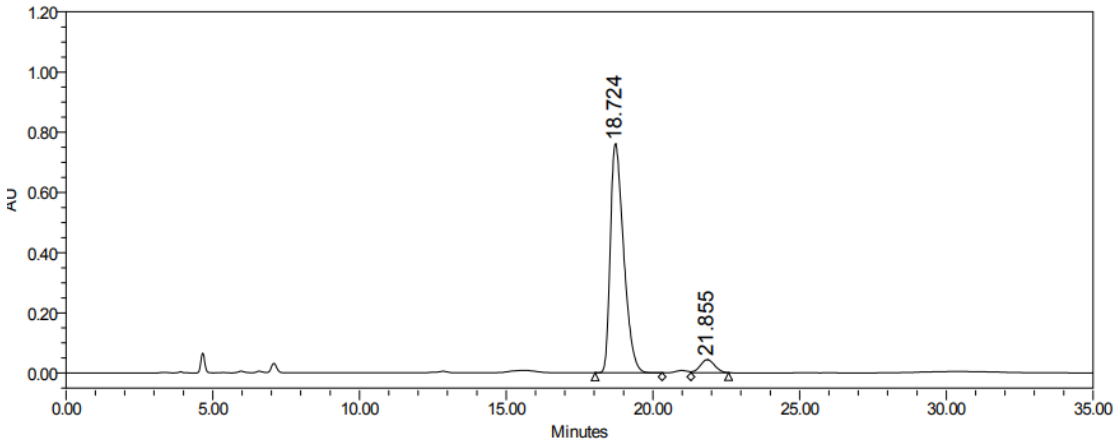
HPLC of **3am:**




**3am** Ar = 2-$ClC_6H_4$

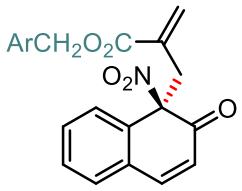



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 19.041 | 11882196 | 49.30 | 381483 |
| 2 | 22.017 | 12217573 | 50.70 | 335838 |

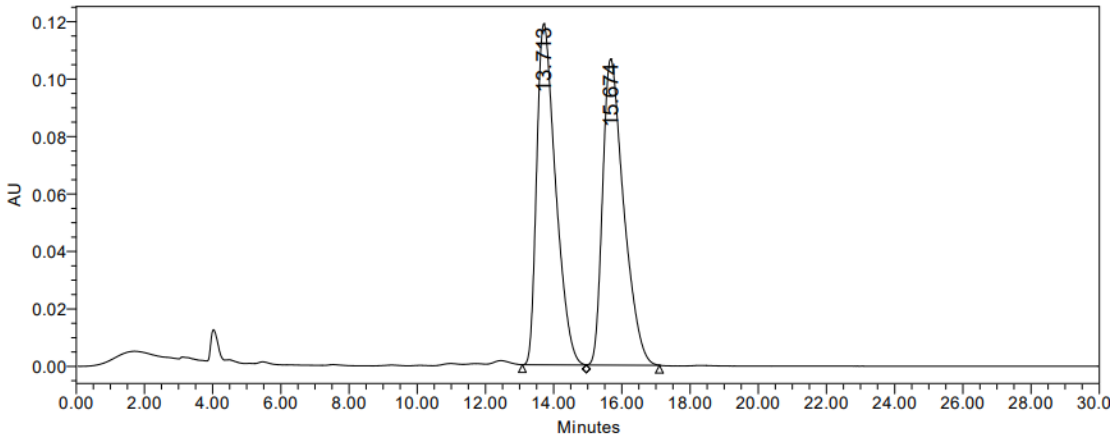



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 18.724 | 24023695 | 94.18 | 760942 |
| 2 | 21.855 | 1484204 | 5.82 | 43558 |

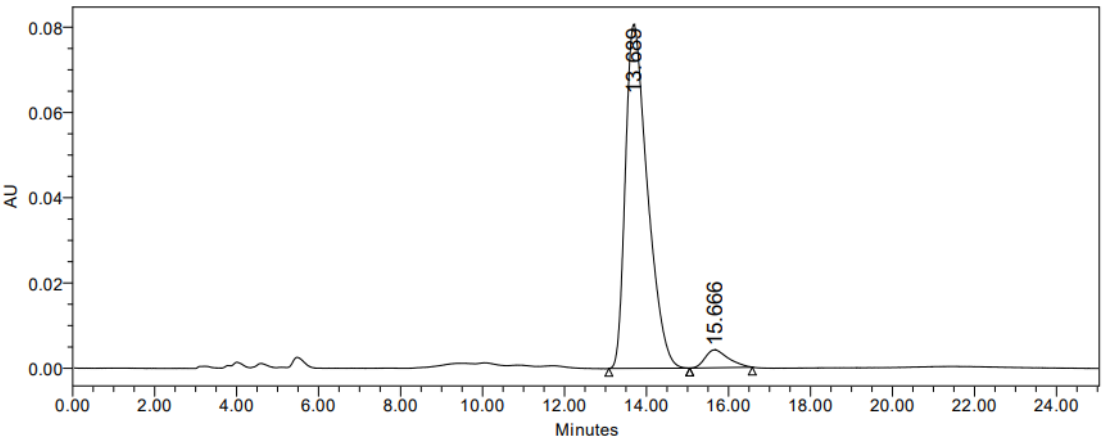
HPLC of **3an:**




**3an** Ar = 2-MeC$_6$H$_4$

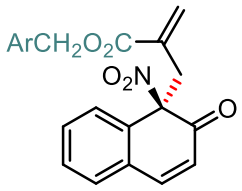



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 13.713 | 4573469 | 49.94 | 118738 |
| 2 | 15.674 | 4583856 | 50.06 | 106564 |

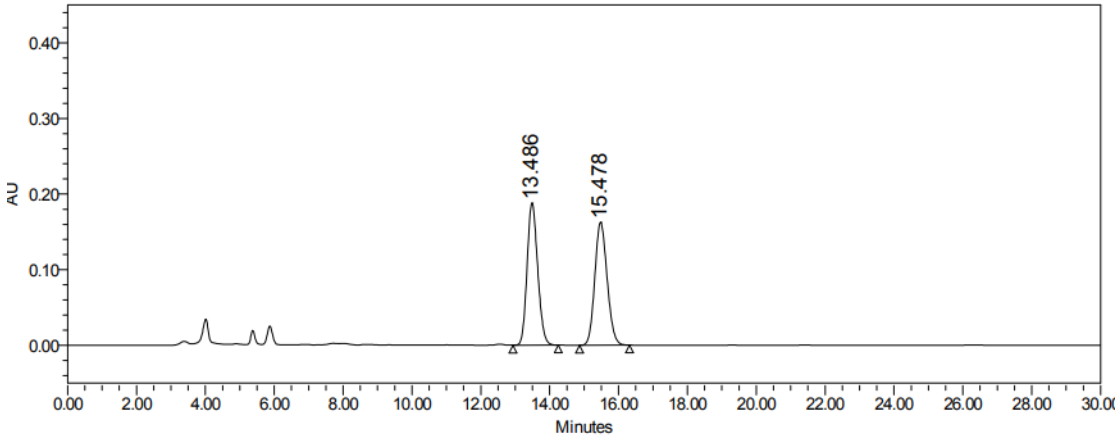



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 13.689 | 3019055 | 94.86 | 80677 |
| 2 | 15.666 | 163589 | 5.14 | 4201 |

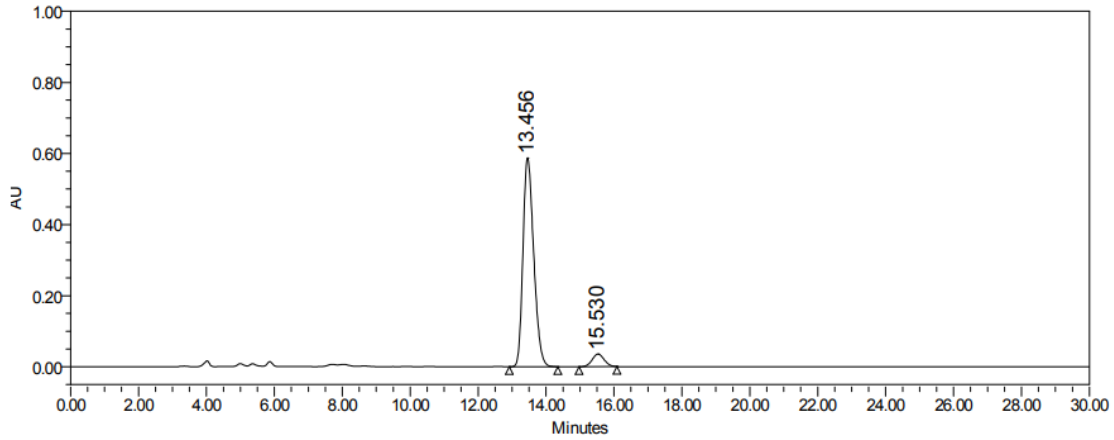
HPLC of **3ao:**




**3ao** Ar = 2-$CF_3C_6H_4$

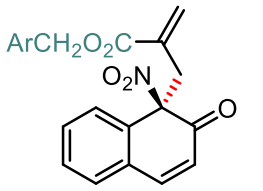



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 13.486 | 4026308 | 49.90 | 188029 |
| 2 | 15.478 | 4042625 | 50.10 | 162648 |

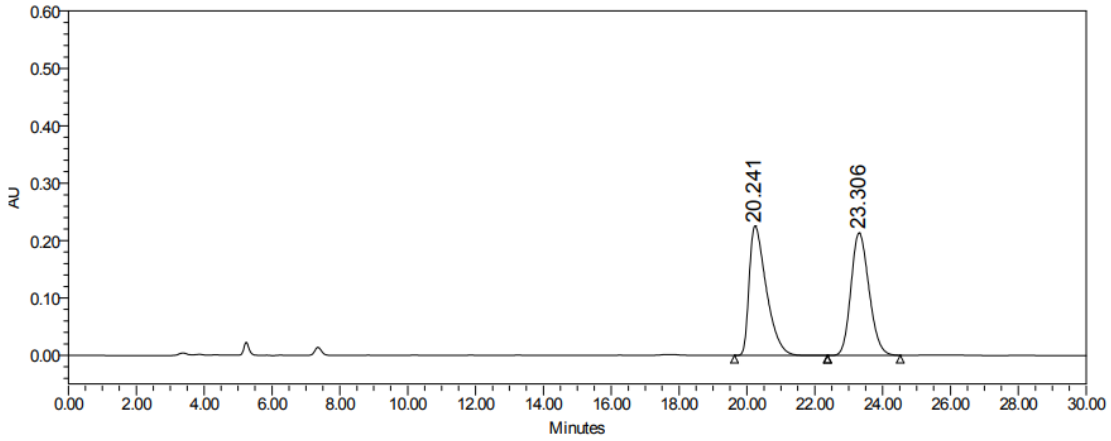



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 13.456 | 12923301 | 93.72 | 588200 |
| 2 | 15.530 | 865725 | 6.28 | 35377 |

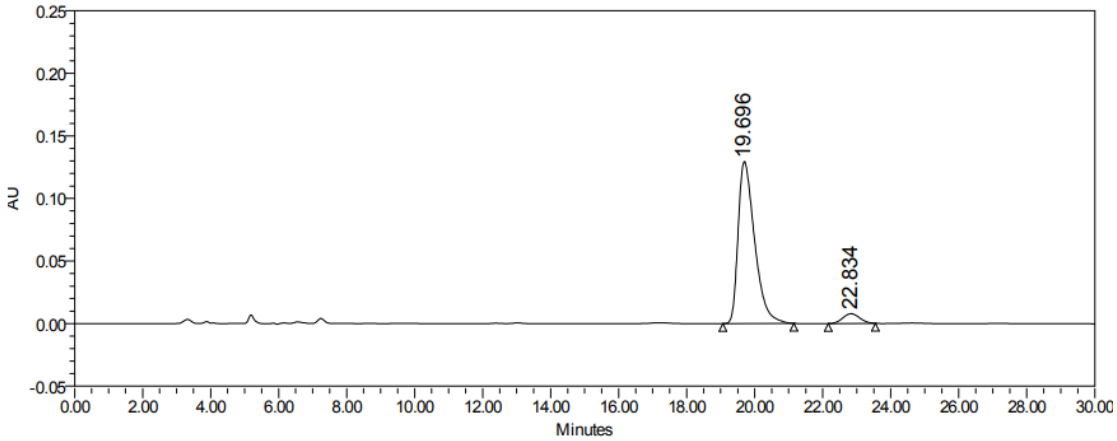
HPLC of **3ap:**




**3ap** Ar = 3-$ClC_6H_4$

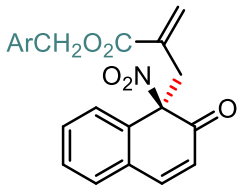



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 20.241 | 7926269 | 50.07 | 225813 |
| 2 | 23.306 | 7903661 | 49.93 | 213454 |

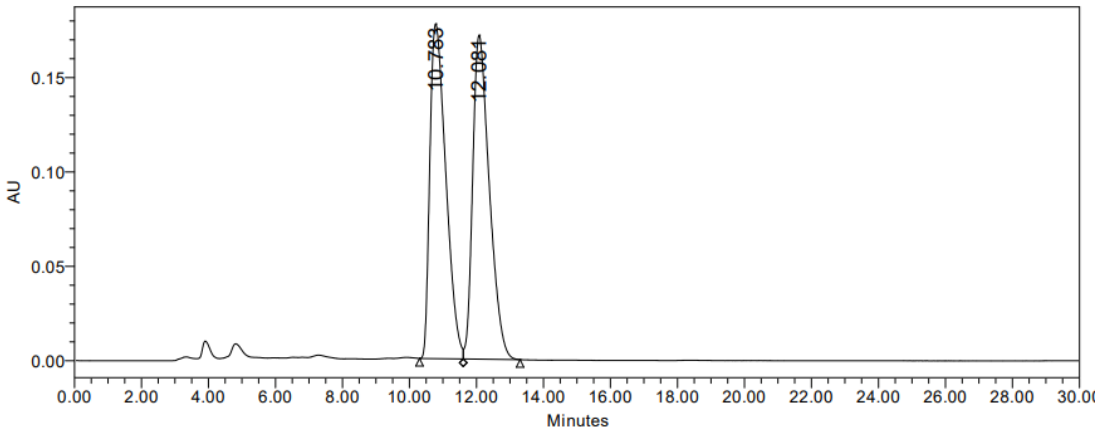



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 19.696 | 4369976 | 94.13 | 129405 |
| 2 | 22.834 | 272430 | 5.87 | 7838 |

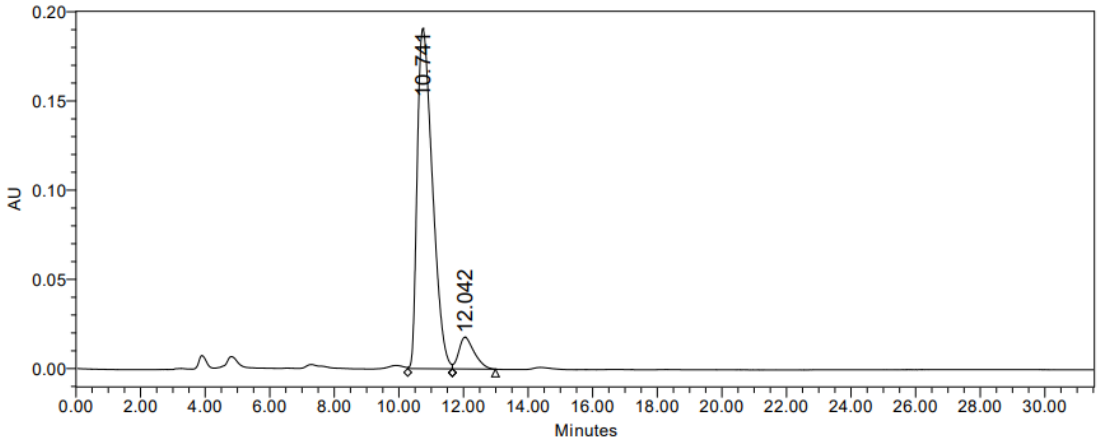
HPLC of **3aq:**




**3aq** Ar = 3-$CF_3C_6H_4$

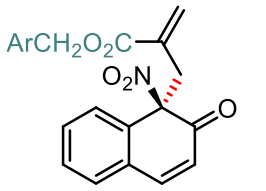



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 10.783 | 5872760 | 49.76 | 177419 |
| 2 | 12.081 | 5929924 | 50.24 | 171680 |

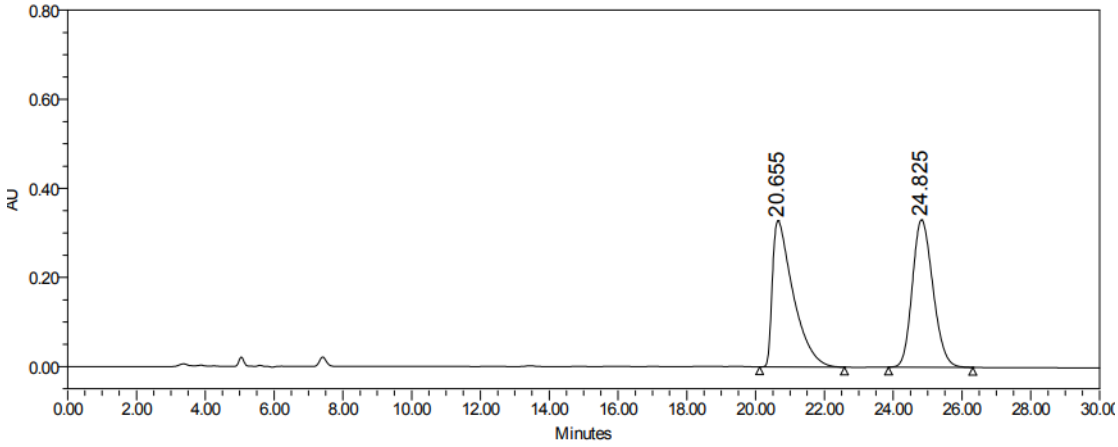



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 10.741 | 6233584 | 91.34 | 190655 |
| 2 | 12.042 | 590867 | 8.66 | 17779 |

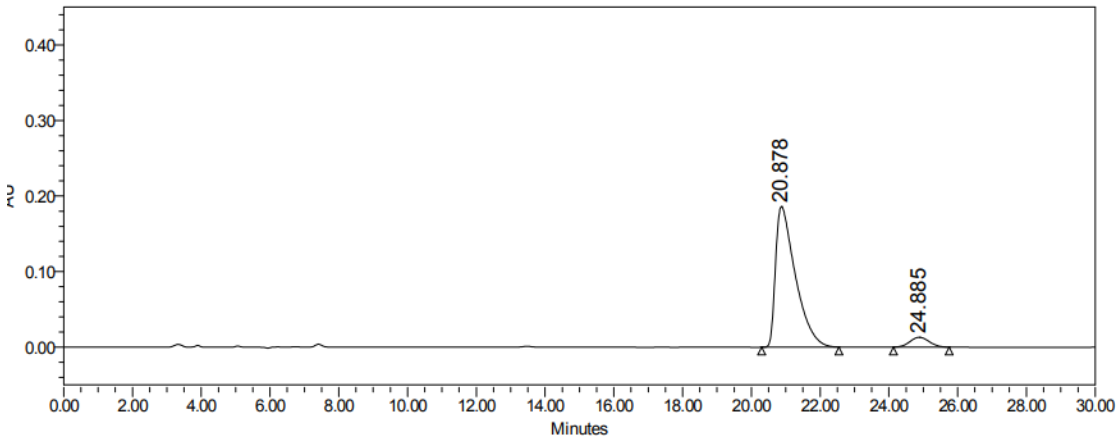
HPLC of **3ar:**




**3ar** Ar = 4-$BrC_6H_4$

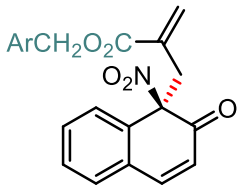



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 20.655 | 13797620 | 50.02 | 328987 |
| 2 | 24.825 | 13786338 | 49.98 | 331066 |

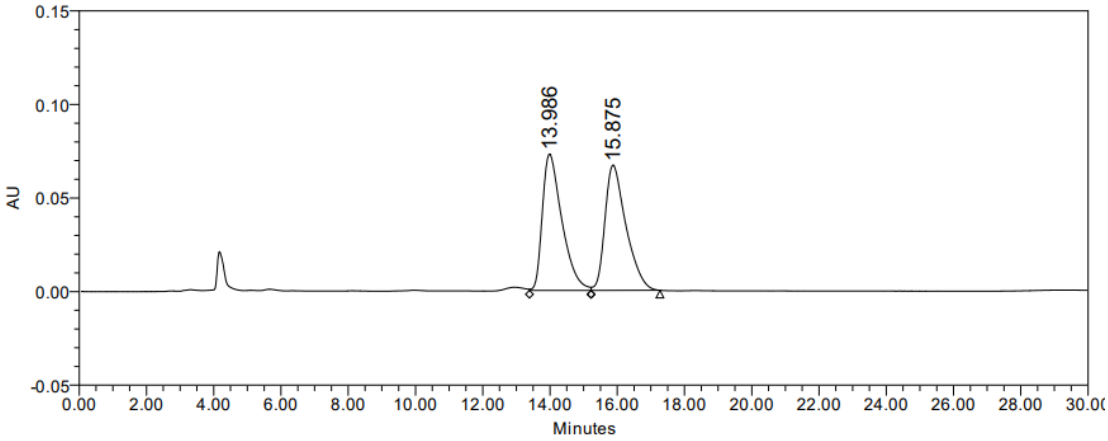



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 20.878 | 7476660 | 93.66 | 186116 |
| 2 | 24.885 | 506065 | 6.34 | 12996 |

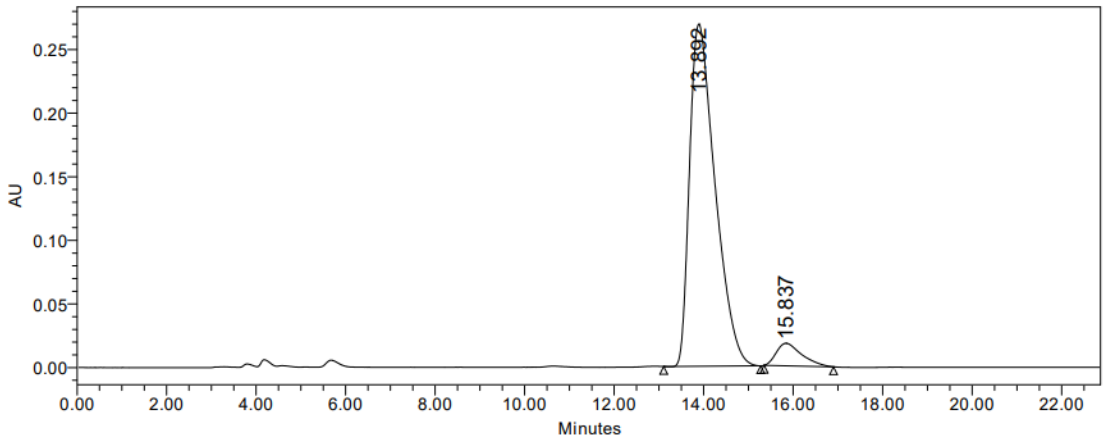
HPLC of **3as:**




**3as** Ar = 4-$MeC_6H_4$

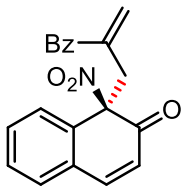



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 13.986 | 2946013 | 50.27 | 72838 |
| 2 | 15.875 | 2914920 | 49.73 | 66860 |

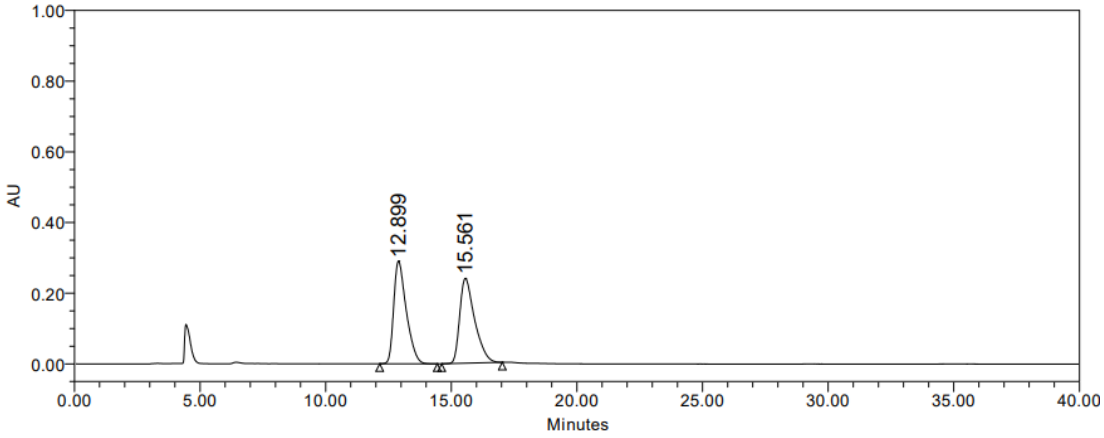



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 13.892 | 10660730 | 93.86 | 268916 |
| 2 | 15.837 | 697011 | 6.14 | 17715 |

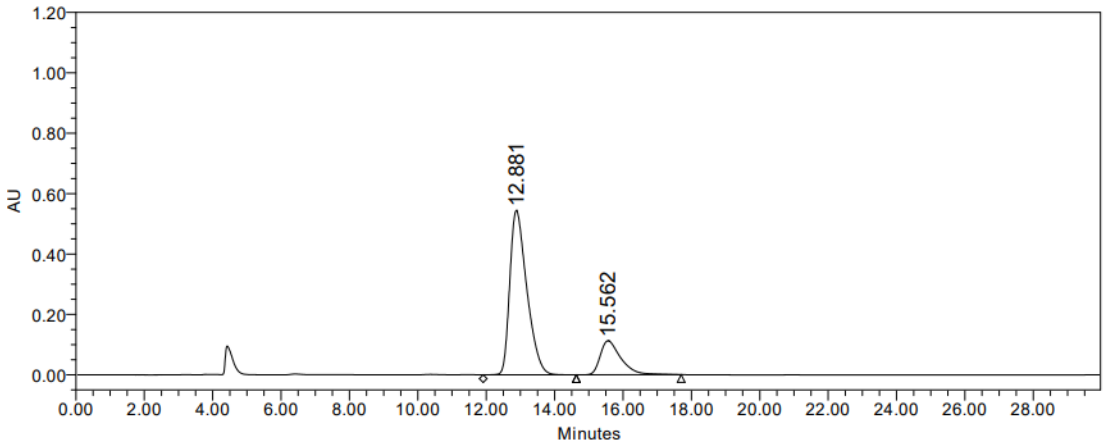
HPLC of **3at:**




**3at**




| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 12.899 | 10115396 | 50.48 | 290823 |
| 2 | 15.561 | 9923870 | 49.52 | 240124 |




| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 12.881 | 18821230 | 79.94 | 544294 |
| 2 | 15.562 | 4724374 | 20.06 | 112681 |