

Supporting information for
**Highly Enantioselective Intramolecular Michael Reactions by
D-Camphor-Derived Triazolium Salts**

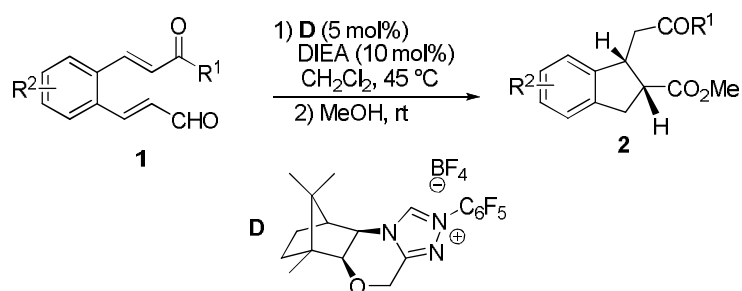
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General Considerations

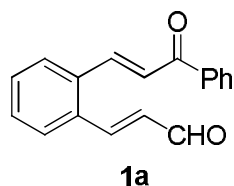
All reactions utilizing air-sensitive reagents were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. ¹H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as [s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant (s) in Hz, integration]. ¹³C NMR spectra were recorded on a VARIAN Mercury 75 MHz spectrometer in chloroform-d. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Catalysts **A-E** were prepared according to the known methods^[1]. All the aldehydes were prepared according to the known methods^[2].

General Procedure for Intramolecular Michael Reaction



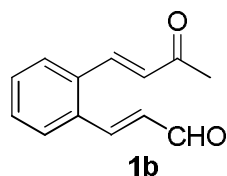
A flame dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added triazolium salt **D** (2.1 mg, 0.005 mmol, 5 mol%), DIEA (2 μ L, 0.010 mmol, 10 mol%), CH₂Cl₂ (2 mL). The mixture was stirred for 0.5h at room temperature, then enal **1** (0.1 mmol) was added and the mixture was refluxed at 45°C. After the reaction was complete (the disappearance of the enal **1**, monitored by TLC), methanol (5 mL) was added and the reaction mixture was stirred at room temperature overnight. The mixture was concentrated under reduced pressure, and then purified by silica-gel column chromatography (hexane/EtOAc) to afford annulation product.

Spectra Data for Compounds 1 and 2



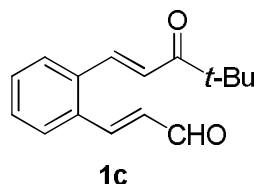
(E)-3-(2-((E)-3-oxo-3-phenylprop-1-enyl)phenyl)acrylaldehyde

1a^[2]: ¹H NMR (300 MHz, CDCl₃) δ 6.69 (dd, *J* = 7.5, 15.9 Hz, 1 H), 7.49 -7.56 (m, 5H), 7.60-7.78 (m, 2 H), 7.96 (d, *J* = 15.9 Hz, 1 H), 8.04-8.07 (m, 2 H), 8.21 (d, *J* = 15.3 Hz, 1 H), 9.78 (d, *J* = 8.1 Hz, 1 H).



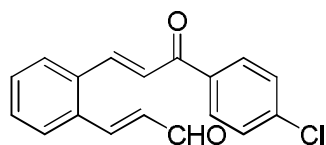
(E)-3-(2-((E)-3-oxobut-1-enyl)phenyl)acrylaldehyde

1b^[2]: ¹H NMR (300 MHz, CDCl₃) δ 2.43 (s, 3 H), 6.67 (d, *J* = 16.2 Hz, 1 H), 6.68 (d, *J* = 16.2 Hz, 1 H), 7.46-7.49 (m, 2 H), 7.62-7.67 (m, 2 H), 7.88 (d, *J* = 15.9 Hz, 1 H), 7.91 (d, *J* = 15.6 Hz, 1 H), 9.78 (d, *J* = 7.8 Hz, 1 H).



(E)-3-(2-((E)-4,4-dimethyl-3-oxopent-1-enyl)phenyl)acrylaldehyde

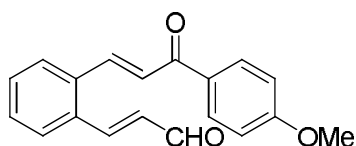
1c: ¹H NMR (300 MHz, CDCl₃) δ 1.13 (s, 9 H), 6.51 (dd, *J* = 7.2, 15.9 Hz, 1 H), 6.97 (d, *J* = 15.3 Hz, 1 H), 7.31-7.35 (m, 2 H), 7.49-7.56 (m, 2 H), 7.76 (d, *J* = 15.6 Hz, 1 H), 7.92 (d, *J* = 15.3 Hz, 1 H), 9.60 (d, *J* = 7.2 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 25.8, 42.9, 124.6, 127.2, 127.5, 129.8, 130.6, 130.7, 133.4, 134.8, 138.4, 148.6, 193.0, 203.2; IR (KBr): ν_{max} (cm⁻¹) = 2968, 1686, 1606, 1477, 1324, 1125, 1075, 974, 761; MS (ESI, *m/z*) 265.3 (M+Na⁺); Anal. calcd for C₁₆H₁₈O₂: C, 79.31; H, 7.49; Found: C, 79.37; H, 7.38.



1d

(E)-3-(2-((E)-3-(4-chlorophenyl)-3-oxoprop-1-enyl)phenyl)acrylaldehyde

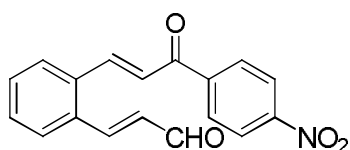
1d: ^1H NMR (300 MHz, CDCl_3) δ 6.69 (dd, $J = 8.1, 15.6$ Hz, 1 H), 7.44-7.52 (m, 5 H), 7.66-7.77 (m, 2 H), 7.92-8.01 (m, 3 H), 8.23 (d, $J = 15.9$ Hz, 1 H), 9.78 (d, $J = 8.1$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 124.7, 127.5, 127.6, 128.8, 129.7, 130.4, 130.8, 131.1, 133.8, 134.5, 135.7, 139.4, 140.7, 148.4, 187.8, 193.2; IR (KBr): ν_{max} (cm^{-1}) = 1671, 1598, 1483, 1286, 1219, 1157, 1122, 1034, 964, 865, 691; MS (ESI, m/z) 319.7 ($\text{M}+\text{Na}^+$); Anal. calcd for $\text{C}_{18}\text{H}_{13}\text{ClO}_2$: C, 72.85; H, 4.42; Found: C, 72.76; H, 4.41.



1e

(E)-3-(2-((E)-3-(4-methoxyphenyl)-3-oxoprop-1-enyl)phenyl)acrylaldehyde

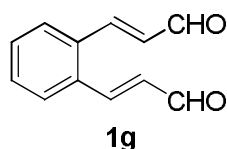
1e^[2]: ^1H NMR (300 MHz, CDCl_3) δ 3.87 (s, 3 H), 6.65 (dd, $J = 8.1, 15.6$ Hz, 1 H), 6.97 (d, $J = 8.4$ Hz, 2 H), 7.44-7.52 (m, 3 H), 7.62-7.65 (m, 1 H), 7.72-7.75 (m, 1 H), 7.93 (d, $J = 15.6$ Hz, 1 H), 8.05 (d, $J = 8.1$ Hz, 2 H), 8.15 (d, $J = 15.3$ Hz, 1H), 9.74 (d, $J = 7.8$ Hz, 1 H).



1f

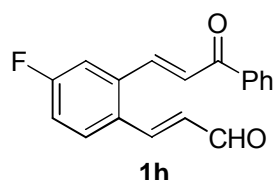
(E)-3-(2-((E)-3-(4-nitrophenyl)-3-oxoprop-1-enyl)phenyl)acrylaldehyde

1f: ^1H NMR (300 MHz, CDCl_3) δ 6.70 (dd, $J = 7.5, 15.6$ Hz, 1 H), 7.46-7.55 (m, 3 H), 7.68-7.80 (m, 2 H), 7.94 (d, $J = 16.2$ Hz, 1 H), 8.18-8.40 (m, 5 H), 9.79 (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 123.8, 124.0, 124.6, 127.9, 128.0, 129.3, 129.5, 131.1, 131.1, 131.9, 134.4, 134.4, 142.4, 142.5, 188.0, 193.2; IR (KBr): ν_{max} (cm^{-1}) = 1674, 1586, 1517, 1345, 1212, 1122, 970, 755; MS (ESI, m/z) 330.9 ($\text{M}+\text{Na}^+$); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{13}\text{NO}_4$ (M^+): 307.0845; Found: 307.0847.



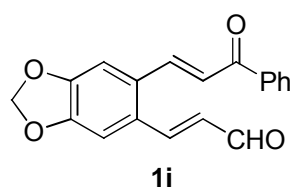
(2E,2'E)-3,3'-(1,2-phenylene)-bis-2-propenal

1g^[2]: ¹H NMR (300 MHz, CDCl₃) δ 6.69 (dd, *J* = 7.5, 15.9 Hz, 2 H), 7.50-7.53 (m, 2 H), 7.66-7.69 (m, 2 H), 7.89 (d, *J* = 15.9 Hz, 2 H), 9.80 (d, *J* = 7.8 Hz, 2 H).



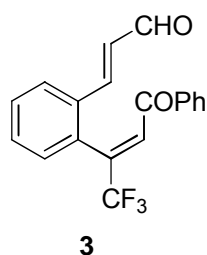
(E)-3-(4-fluoro-2-((E)-3-oxo-3-phenylprop-1-enyl)phenyl)acrylaldehyde

1h^[2]: ¹H NMR (300 MHz, CDCl₃) δ 6.50 (dd, *J* = 7.5, 15.9 Hz, 1 H), 7.11-7.18 (m, 1 H), 7.43-7.64 (m, 6 H), 7.84 (d, *J* = 15.6 Hz, 1 H), 8.04 (d, *J* = 7.8 Hz, 2 H), 8.11 (d, *J* = 15.6 Hz, 1 H), 9.70 (d, *J* = 7.8 Hz, 1 H).



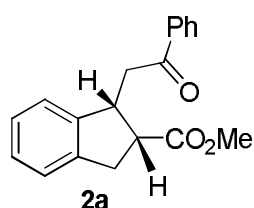
(E)-3-(6-((E)-3-oxo-3-phenylprop-1-enyl)benzo[d][1,3]dioxol-5-yl)acrylaldehyde

1i: ¹H NMR (300 MHz, CDCl₃) δ 6.10 (s, 2 H), 6.57 (dd, *J* = 7.8, 15.6 Hz, 1 H), 7.12 (s, 1 H), 7.23 (s, 1 H), 7.41 (d, *J* = 15.3 Hz, 1 H), 7.51-7.65 (m, 3 H), 7.94 (d, *J* = 15.6 Hz, 1 H), 8.08 (d, *J* = 8.7 Hz, 2 H), 8.20 (d, *J* = 15.3 Hz, 1 H), 9.75 (d, *J* = 7.8 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 77.2, 102.3, 106.4, 106.6, 123.9, 128.5, 128.7, 129.3, 129.7, 130.6, 133.1, 137.8, 139.7, 147.9, 150.1, 150.5, 189.5, 193.4; IR (KBr): ν_{\max} (cm⁻¹) = 3055, 1715, 1599, 1587, 1296, 1269, 1220, 1158, 1123, 1035, 1018, 964, 923, 777, 691; MS (ESI, *m/z*) 329.5 (M+Na⁺); HRMS (EI) calcd for C₁₉H₁₄O₄ (M⁺): 306.0892; Found: 306.0897.



(E)-3-(2-((E)-1,1,1-trifluoro-4-oxo-4-phenylbut-2-en-2-yl)phenyl)acrylaldehyde

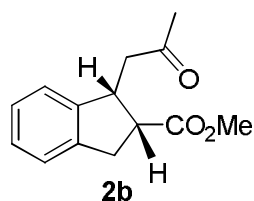
3: ^1H NMR (300 MHz, CDCl_3) δ 6.62 (q, $J = 7.8$ Hz, 1 H), 7.27 (d, $J = 7.2$ Hz, 1 H), 7.40-7.61 (m, 6 H), 7.67-7.68 (m, 2 H), 7.83 (d, $J = 7.2$ Hz, 2 H), 9.59 (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 120.5, 124.2, 126.6, 128.6, 128.9, 129.8, 129.9, 130.2, 130.5, 131.3, 131.9, 132.0, 133.7, 134.3, 135.9, 137.4, 137.9, 149.3, 189.7, 193.4; IR (KBr): ν_{max} (cm^{-1}) = 1680, 1596, 1449, 1279, 1180, 1126, 969, 763, 627; MS (ESI, m/z) 353.2 ($\text{M}+\text{Na}^+$); Anal. calcd for $\text{C}_{19}\text{H}_{13}\text{F}_3\text{O}_2$: C, 69.09; H, 3.97; Found: C, 69.08; H, 4.08.



(1R,2R)-methyl 1-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-indene-2-carboxylate

2a^[3]: Yield 99%, ee 99%. $[\alpha]_{\text{D}}^{20} = +35.4^\circ$ ($c = 1.43$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 3.06-3.17 (m, 2 H), 3.33-3.46 (m, 2 H), 3.55 (s, 3 H), 3.55-3.63 (m, 1 H), 4.26 (q, $J = 8.1$ Hz, 1 H), 7.15-7.26 (m, 4 H), 7.41-7.47 (m, 2 H), 7.52-7.57 (m, 1 H), 7.92 (d, $J = 7.2$ Hz, 2 H).

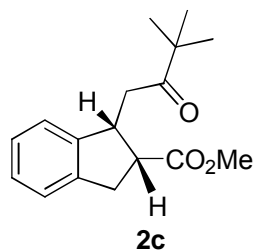
[Daicel Chiralpak AD-H, hexanes/2-propanol = 85/15, $v = 1.0$ mL/min⁻¹, $\lambda = 254$ nm, t_1 (major) = 8.462 min, t_2 (minor) = 10.042 min].



(1R,2R)-methyl 1-(2-oxopropyl)-2,3-dihydro-1H-indene-2-carboxylate

2b^[3]: Yield 93%, ee 95%. $[\alpha]_{\text{D}}^{20} = +13.5^\circ$ ($c = 0.60$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 2.12 (s, 3 H), 2.60 (dd, $J = 6.0, 17.4$ Hz, 1 H), 2.85 (dd, $J = 8.1, 18.0$ Hz, 1 H), 3.05 (dd, $J = 8.1, 15.9$ Hz, 1 H), 3.29 (dd, $J = 8.7, 15.6$ Hz, 1 H), 3.48 (q, $J = 8.4$ Hz, 1 H), 3.67 (s, 3 H), 4.01 (q, $J = 8.1$ Hz, 1 H), 7.14-7.24 (m, 4 H).

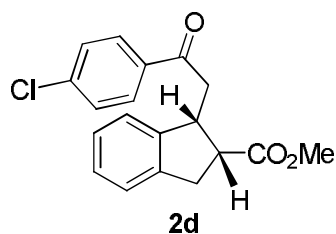
[Daicel Chiralpak AD-H, hexanes/2-propanol = 90/10, $v = 0.7$ mL/min⁻¹, $\lambda = 214$ nm, t_1 (minor) = 8.653 min, t_2 (major) = 9.333 min].



(1R,2R)-methyl-(3,3-dimethyl-2-oxobutyl)-2,3-dihydro-1H-indene-2-carboxylate

2c: Yield 85%, ee 99%. $[\alpha]_D^{20} = +22.5^\circ$ ($c = 1.35$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 1.07 (s, 9 H), 2.72 (dd, $J = 6.0, 18.0$ Hz, 1 H), 2.85 (dd, $J = 7.5, 18.0$ Hz, 1 H), 3.05 (dd, $J = 8.1, 15.9$ Hz, 1 H), 3.29 (dd, $J = 8.4, 15.9$ Hz, 1 H), 3.50 (q, $J = 8.1$ Hz, 1 H), 3.65 (s, 3 H), 4.00 (q, $J = 7.2$ Hz, 1 H), 7.09 -7.26 (m, 4 H); ^{13}C NMR (75 MHz, CDCl_3) δ 26.5, 34.4, 38.6, 41.9, 44.0, 47.3, 51.6, 124.0, 124.4, 126.7, 127.1, 141.1, 144.9, 174.4, 214.4; IR (KBr): ν_{max} (cm^{-1}) = 2959, 2928, 2858, 1727, 1460, 1278, 1190, 1146, 936, 751, 665; MS (ESI, m/z) 297.4 ($\text{M}+\text{Na}^+$); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{O}_3$ (M^+): 274.1596; Found: 274.1565.

[Daicel Chiralpak AD-H, hexanes/2-propanol = 90/10, $v = 0.7$ mL/min $^{-1}$, $\lambda = 214$ nm, t_1 (major) = 6.832 min, t_2 (minor) = 7.583 min].

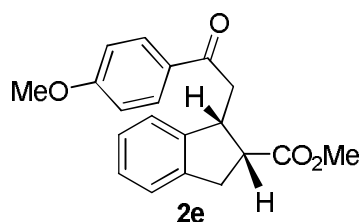


(1R,2R)-methyl-1-(2-(4-chlorophenyl)-2-oxoethyl)-2,3-dihydro-1H-indene-2-carboxylate

2d: Yield 85%, ee 99%. $[\alpha]_D^{20} = +14.0^\circ$ ($c = 1.20$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 3.04-3.14 (m, 2 H), 3.32-3.44 (m, 2 H), 3.54 (s, 3 H), 3.54-3.62 (m, 1 H), 4.23 (q, $J = 7.8$ Hz, 1 H), 7.15-7.26 (m, 4 H), 7.41 (d, $J = 8.4$ Hz, 2 H), 7.86 (d, $J = 8.7$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 34.4, 40.5, 42.4, 47.3, 51.7, 124.0, 124.6, 126.8, 127.3, 128.9, 129.4, 135.2, 139.5, 141.2, 144.4, 174.5, 197.3; IR (KBr): ν_{max} (cm^{-1}) = 2951, 1731, 1687, 1589, 1401, 1214, 1169, 1092, 996, 756; MS (ESI, m/z) 351.3 ($\text{M}+\text{Na}^+$); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{17}\text{O}_3\text{Cl}$ (M^+): 328.0866; Found: 328.0863.

[Daicel Chiralpak AD-H, hexanes/2-propanol = 90/10, $v = 1.0$ mL/min $^{-1}$, $\lambda = 254$ nm,

t_1 (major) = 12.140 min, t_2 (minor) = 14.853 min].

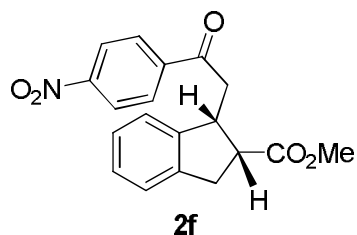


(1R,2R)-methyl-1-(2-(4-methoxyphenyl)-2-oxoethyl)-2,3-dihydro-1H-indene-2-carboxylate

2e^[31]: Yield 96%, ee 99%. $[\alpha]_D^{20} = +29.4^\circ$ (c = 0.70, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 3.04-3.13 (m, 2 H), 3.30-3.41 (m, 2 H), 3.55 (s, 3 H), 3.55-3.62 (m, 1 H), 3.85 (s, 3 H), 4.25 (q, $J = 7.5$ Hz, 1 H), 6.90 (d, $J = 8.7$ Hz, 2 H), 7.14-7.25 (m, 4 H), 7.90 (d, $J = 8.7$ Hz, 2 H).

[Daicel Chiralpak AD-H, hexanes/2-propanol = 85/15, $v = 1.0$ mL/min⁻¹, $\lambda = 254$ nm,

t_1 (major) = 13.875 min, t_2 (minor) = 17.723 min].

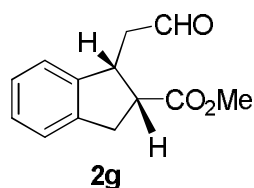


(1R,2R)-methyl-1-(2-(4-nitrophenyl)-2-oxoethyl)-2,3-dihydro-1H-indene-2-carboxylate

2f: Yield 52%, ee 98%. $[\alpha]_D^{20} = +11.4^\circ$ (c = 0.75, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 3.09-3.17 (m, 2 H), 3.32-3.40 (m, 1H), 3.54-3.63 (m, 2 H), 3.58 (s, 3 H), 4.24 (q, $J = 7.8$ Hz, 1 H), 7.19-7.28 (m, 4 H), 8.05-8.13 (m, 2 H), 8.28-8.34 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 34.5, 41.2, 42.3, 47.1, 51.8, 123.8, 123.9, 124.7, 127.0, 127.5, 129.0, 129.3, 141.2, 141.4, 144.1, 174.5, 197.2; IR (KBr): ν_{\max} (cm⁻¹) = 2924, 2853, 1726, 1691, 1527, 1345, 1165, 855, 743, 687; MS (EI, m/z , rel. intensity) 339 (M⁺, 8), 129 (100); HRMS (EI) calcd for C₁₉H₁₇NO₅ (M⁺): 339.1107; Found: 339.1111.

[Daicel Chiralpak AD-H, hexanes/2-propanol = 90/10, $v = 0.8$ mL/min⁻¹, $\lambda = 254$ nm,

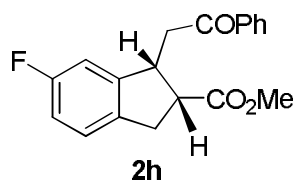
t_1 (major) = 29.535 min, t_2 (minor) = 42.825 min].



(1R,2R)-methyl-1-(2-oxoethyl)-2,3-dihydro-1H-indene-2-carboxylate

2g^[3]: Yield 80%, ee 98%. $[\alpha]_D^{20} = +14.2^\circ$ ($c = 0.70$, CHCl_3). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.64 (dd, $J = 6.0, 18.0$ Hz, 1 H), 2.84 (dd, $J = 7.5, 18.0$ Hz, 1 H), 3.08 (dd, $J = 8.4, 15.9$ Hz, 1 H), 3.33 (dd, $J = 8.4, 15.9$ Hz, 1 H), 3.52 (q, $J = 7.8$ Hz, 1 H), 3.68 (s, 3 H), 4.06 (q, $J = 7.8$ Hz, 1 H), 7.17-7.25 (m, 4 H), 9.79 (s, 1 H).

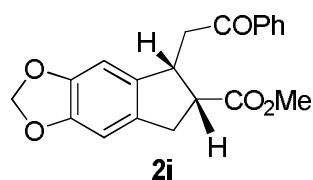
[Daicel Chiralpak AD-H, hexanes/2-propanol = 90/10, $v = 0.7$ mL/min⁻¹, $\lambda = 214$ nm, t_1 (minor) = 9.617 min, t_2 (major) = 10.337 min].



(1R,2R)-methyl-6-fluoro-1-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-indene-2-carboxylate

2h^[3]: Yield 71%, ee 98%. $[\alpha]_D^{20} = +29.1^\circ$ ($c = 0.70$, CHCl_3). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 3.02-3.17 (m, 2 H), 3.26-3.44 (m, 2 H), 3.56 (s, 3 H), 3.57-3.67 (m, 1 H), 4.23 (m, 1 H), 6.85-6.93 (m, 2 H), 7.14-7.19 (m, 1 H), 7.43-7.48 (m, 2 H), 7.53-7.59 (m, 1 H), 7.92-7.94 (m, 2 H).

[Daicel Chiralcel OD-H, hexanes/2-propanol/EtOH = 95/2.5/2.5, $v = 0.8$ mL/min⁻¹, $\lambda = 254$ nm, t_1 (major) = 10.910 min, t_2 (minor) = 11.680 min].

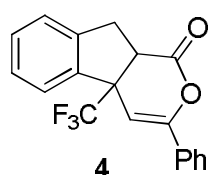


(5R,6R)-methyl-5-(2-oxo-2-phenylethyl)-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxole-6-carboxylate

2i: Yield 80%, ee 99%. $[\alpha]_D^{20} = +11.0^\circ$ ($c = 1.30$, CHCl_3). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.94-3.11 (m, 2 H), 3.22-3.39 (m, 2 H), 3.56 (s, 3 H), 3.56-3.63 (m, 1 H), 4.14 (q, $J = 7.5$ Hz, 1 H), 5.88-5.91 (m, 2 H), 6.68 (d, $J = 6.6$ Hz, 2 H), 7.42-7.47 (m, 2 H),

7.52-7.58 (m, 1 H), 7.91-7.94 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 34.0, 40.5, 42.1, 48.0, 51.6, 101.0, 104.9, 105.0, 128.0, 128.6, 133.1, 133.9, 136.9, 137.2, 146.7, 147.1, 174.2, 198.5; IR (KBr): ν_{max} (cm^{-1}) = 2949, 2891, 1730, 1686, 1475, 1238, 1038, 938, 753, 690; MS (ESI, m/z) 361.2 ($\text{M}+\text{Na}^+$); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{18}\text{O}_5$ (M^+): 338.1154; Found: 338.1156.

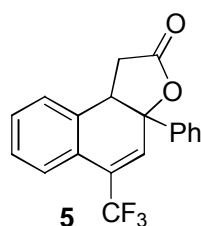
[Daicel Chiralpak AD-H, hexanes/2-propanol = 90/10, $v = 1.0 \text{ mL}/\text{min}^{-1}$, $\lambda = 230 \text{ nm}$, t_1 (minor) = 17.950 min, t_2 (major) = 21.302 min].



3-phenyl-4a-(trifluoromethyl)-9,9a-dihydroindeno[2,1-c]pyran-1(4aH)-one

4 Yield 18%, ee 31%. $[\alpha]_{\text{D}}^{20} = +24.6^\circ$ ($c = 1.67$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 3.32-3.40 (m, 1 H), 3.56-3.63 (m, 1 H), 3.69-3.75 (m, 1 H), 5.67 (s, 1 H), 7.30-7.40 (m, 6 H), 7.48-7.50 (m, 1 H), 7.64-7.67 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 35.6, 42.7, 95.8, 123.7, 124.5, 124.6, 125.1, 125.2, 127.9, 128.3, 128.5, 128.6, 129.3, 130.1, 131.2, 138.6, 140.5, 150.8, 167.6; IR (KBr): ν_{max} (cm^{-1}) = 2964, 2920, 2851, 1770, 1449, 1261, 1147, 1097, 1024, 801, 761, 690; MS (EI, m/z , rel. intensity) 330 (M^+ , 8), 43 (100); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{13}\text{O}_2\text{F}_3$ (M^+): 330.0868; Found: 330.0869.

[Daicel Chiralcel OD-H, hexanes/2-propanol = 99/1, $v = 0.7 \text{ mL}/\text{min}^{-1}$, $\lambda = 230 \text{ nm}$, t_1 (major) = 16.165 min, t_2 (minor) = 19.682 min].



3a-phenyl-5-(trifluoromethyl)-1,9b-dihydronaphtho[2,1-b]furan-2(3aH)-one

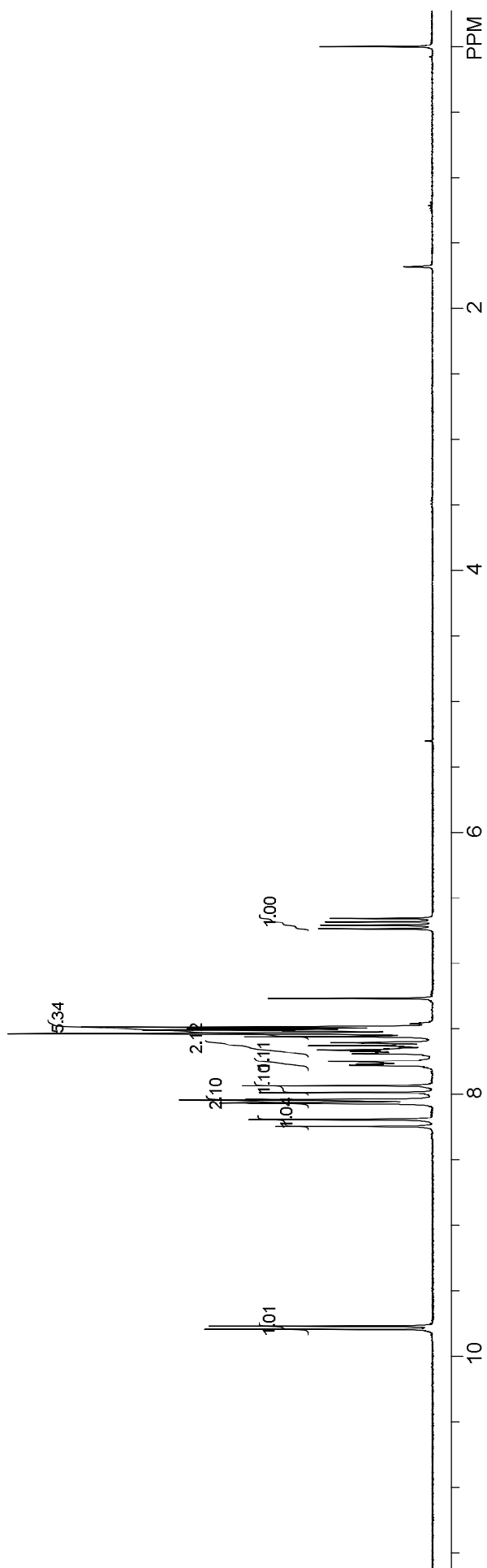
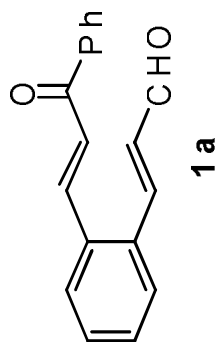
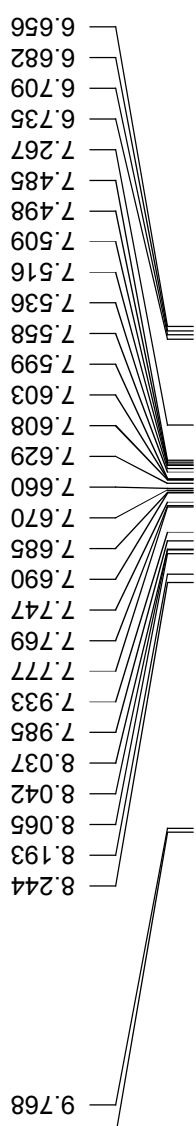
5 Yield 55%, ee 10%. $[\alpha]_{\text{D}}^{20} = +1.50^\circ$ ($c = 0.90$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 2.71-2.81 (m, 1 H), 2.91 (dd, $J = 6.6, 16.2 \text{ Hz}$, 1 H), 4.25 (dd, $J = 6.9, 14.1 \text{ Hz}$, 1 H), 7.05 (d, $J = 7.8 \text{ Hz}$, 2 H), 7.13-7.26 (m, 5 H), 7.39-7.44 (m, 2 H), 7.57-7.59 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 30.5, 48.8, 86.0, 124.8, 125.7, 126.0, 128.1, 128.7,

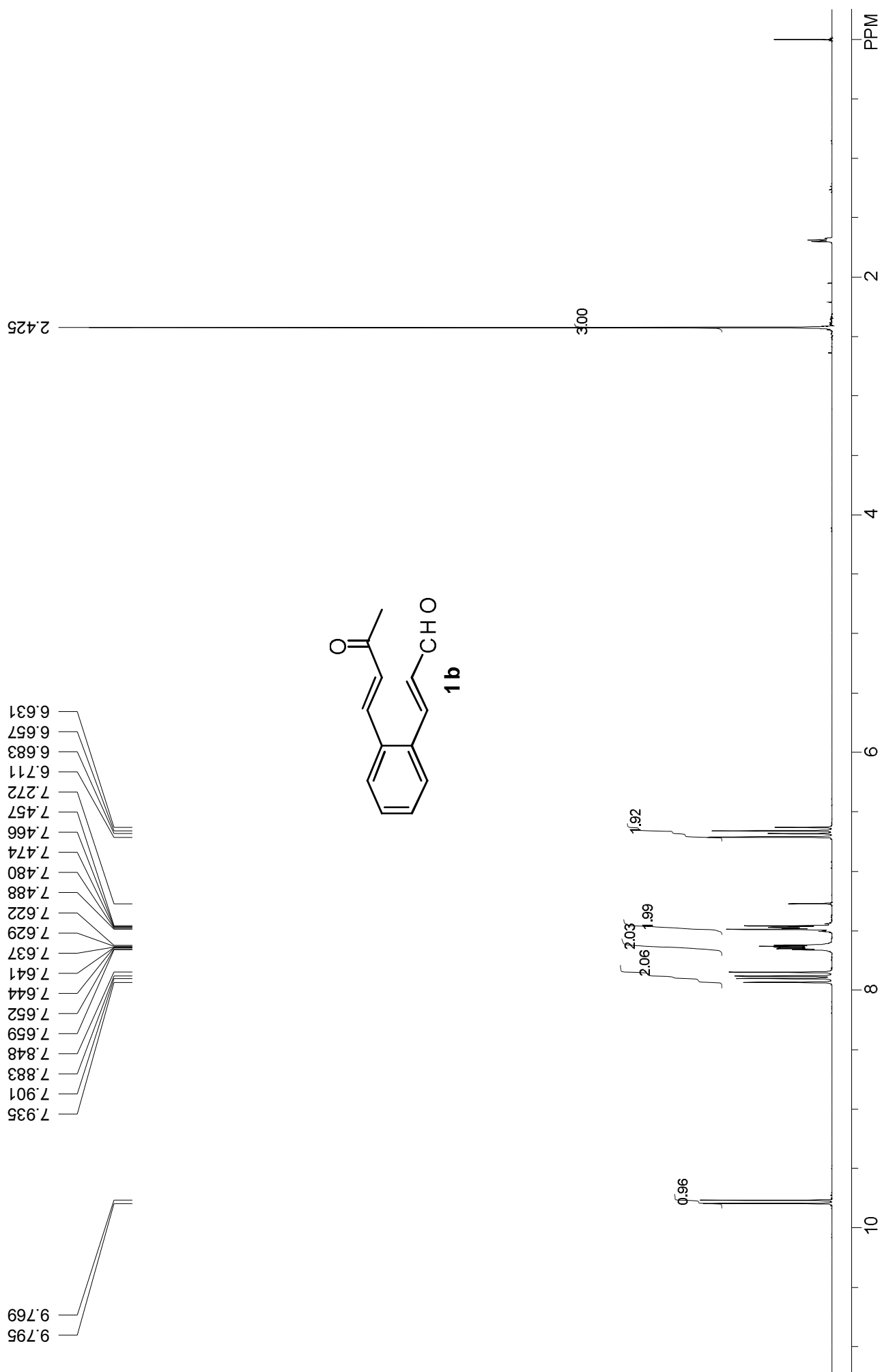
128.8, 128.9, 129.0, 129.3, 129.8, 133.8, 134.9, 135.2, 135.2, 175.1; IR (KBr): ν_{\max} (cm^{-1}) = 2926, 2854, 1801, 1710, 1297, 1173, 1128, 936, 770, 697; MS (EI, m/z , rel. intensity) 330 (M^+ , 36), 57 (100); HRMS (EI) calcd for $C_{19}H_{13}O_2F_3$ (M^+): 330.0868; Found: 330.0872.

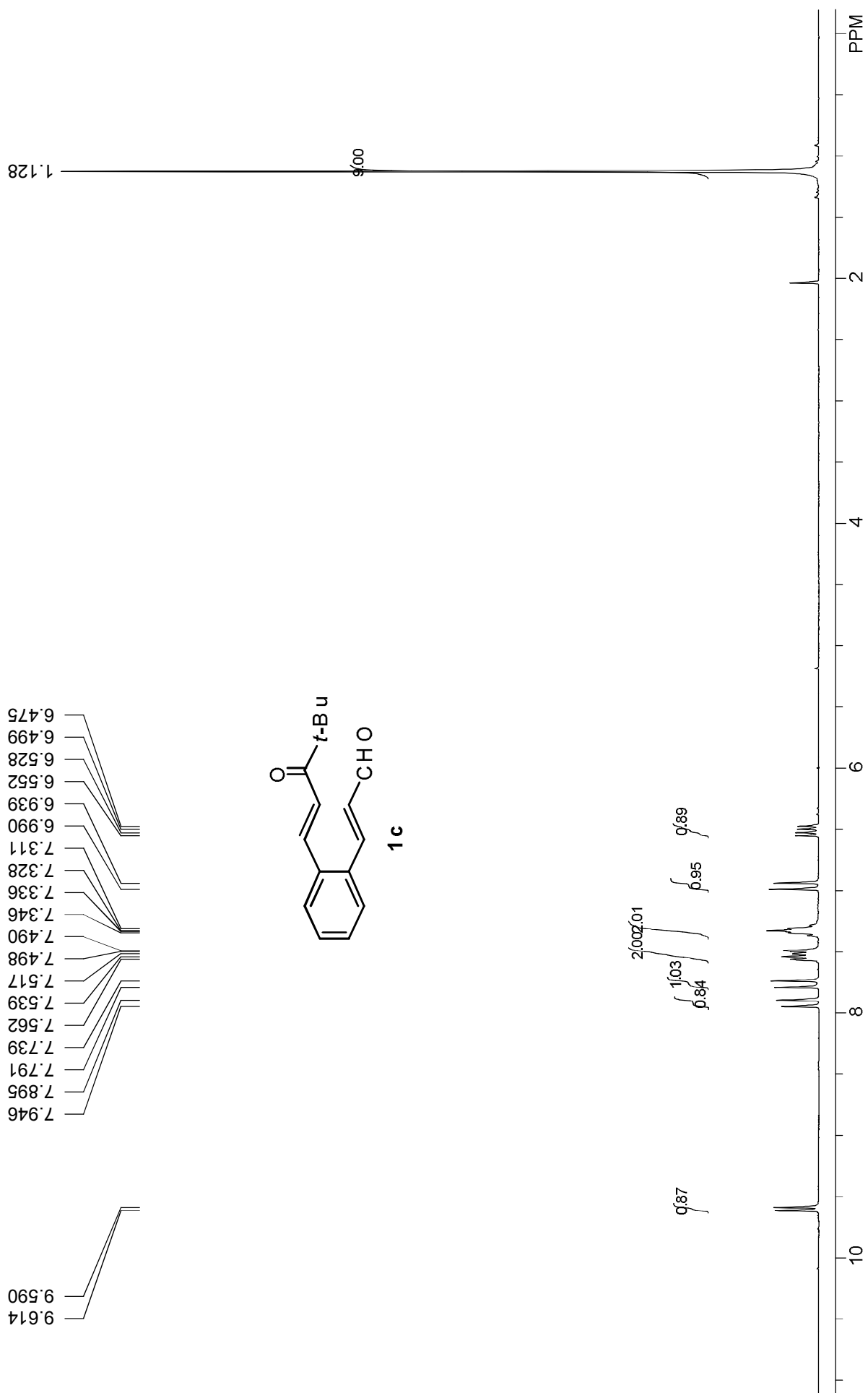
[Daicel Chiralcel OD-H, hexanes/2-propanol = 80/20, $v = 0.7 \text{ mL/min}^{-1}$, $\lambda = 230 \text{ nm}$, t_1 (major) = 10.867 min, t_2 (minor) = 12.718 min].

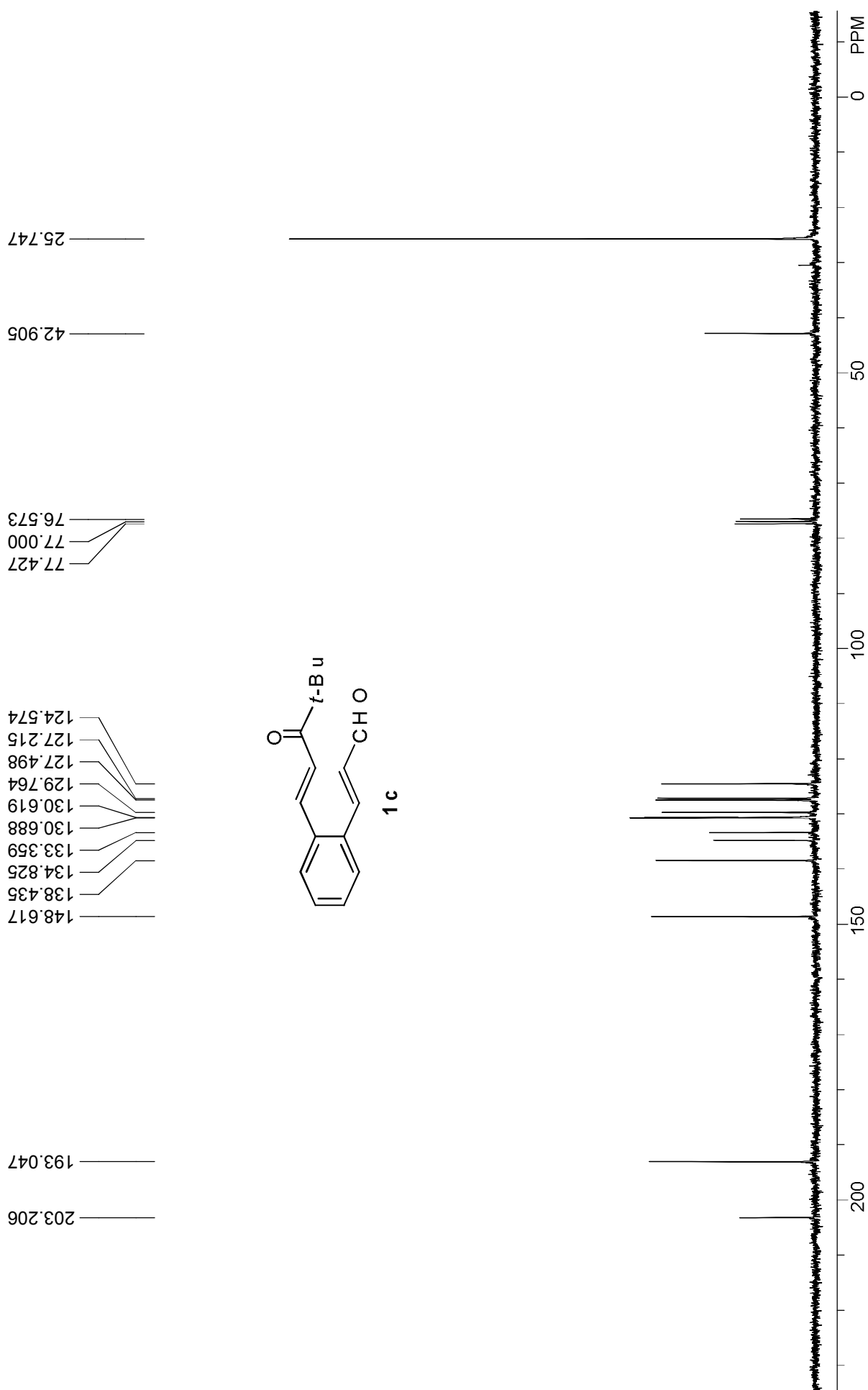
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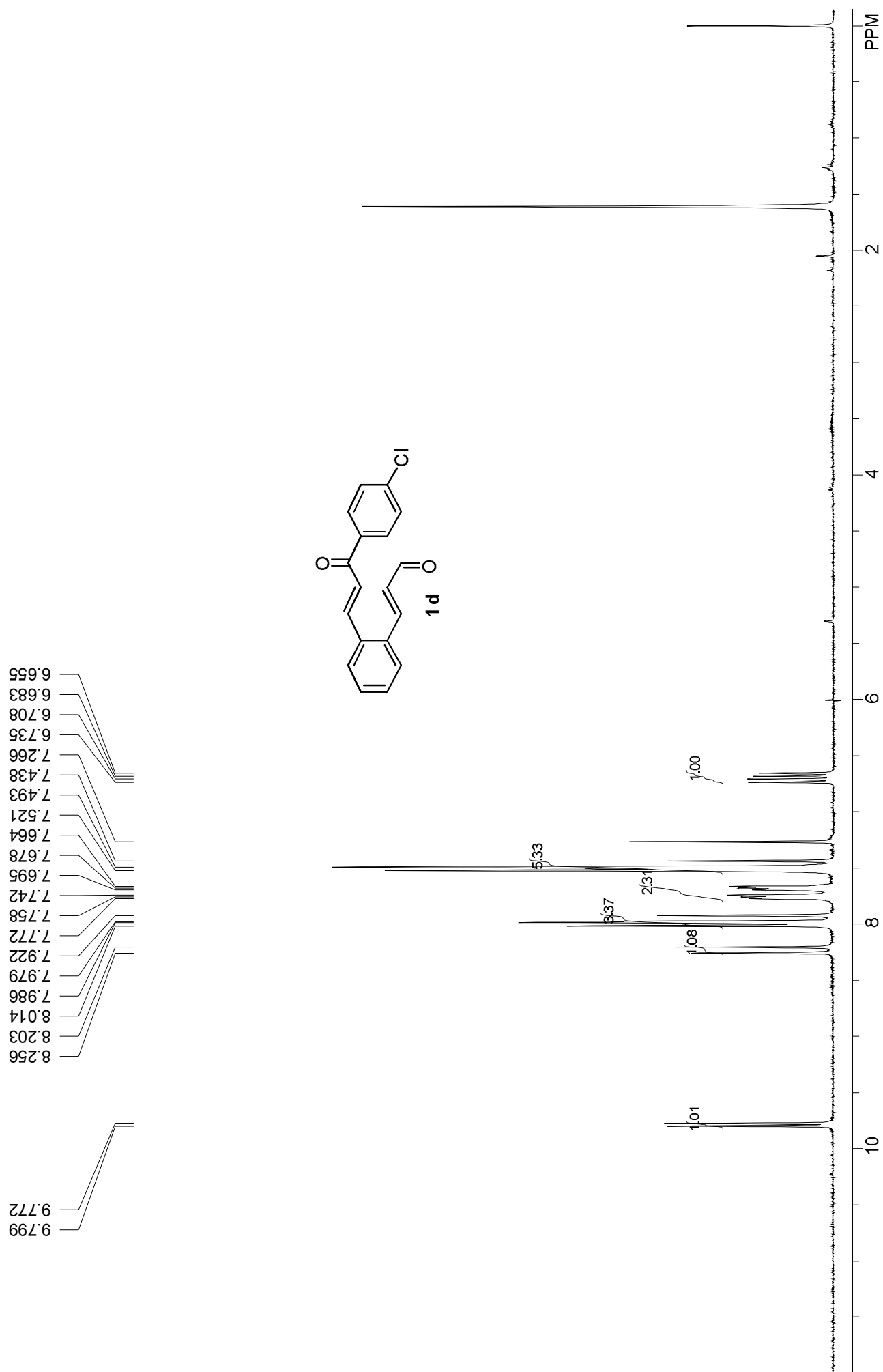
- [1] Y. Li, Z. Feng, S.-L. You, *Chem. Commun.* **2008**, 2263.
- [2] J.-W. Yang, M. Hechavarria, B. List, *J. Am. Chem. Soc.* **2005**, *127*, 15036.
- [3] E. M. Phillips, M. Wadamoto, A. Chan, K. A. Scheidt, *Angew. Chem., Int. Ed.* **2007**, *46*, 3107.

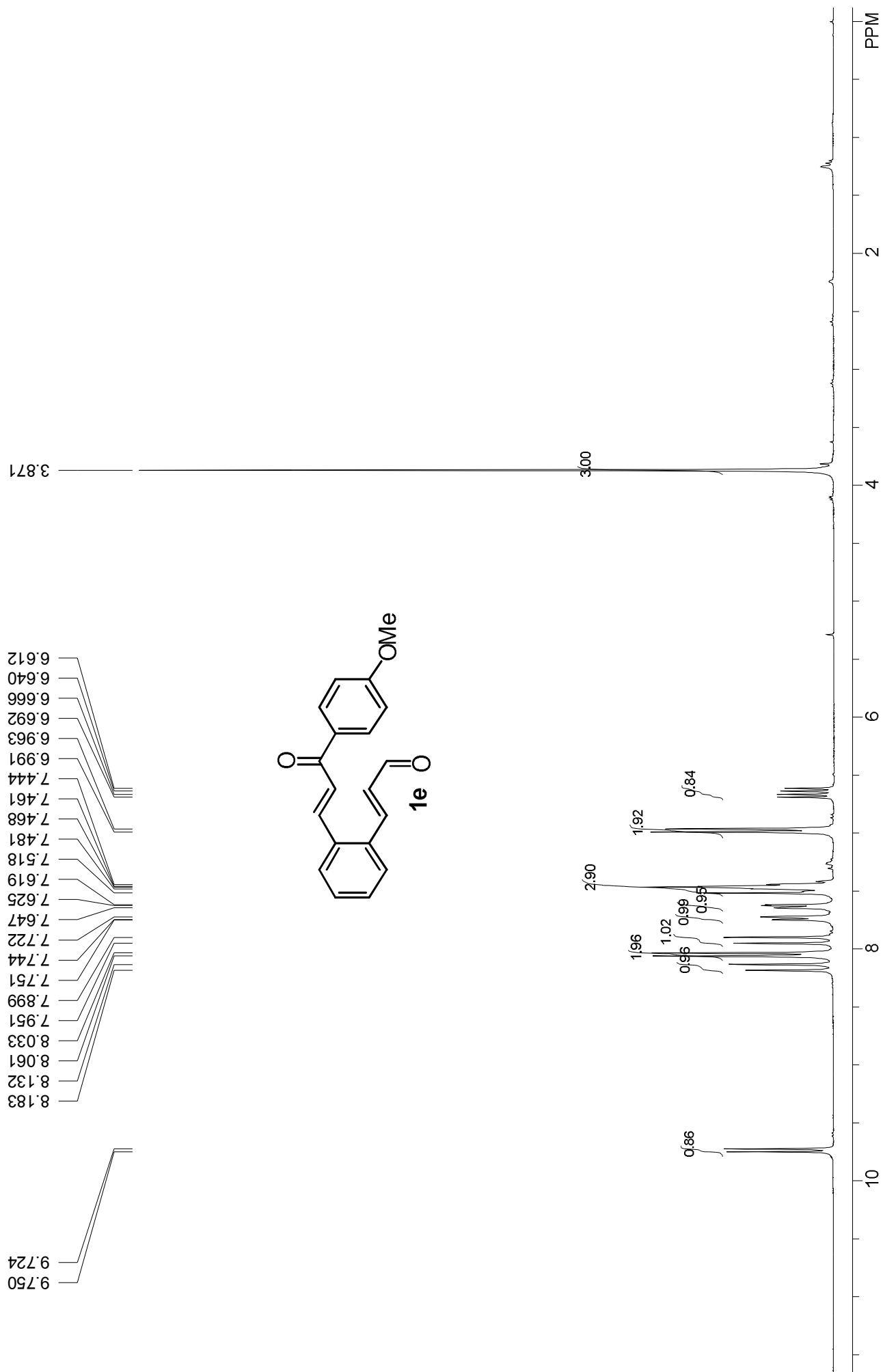


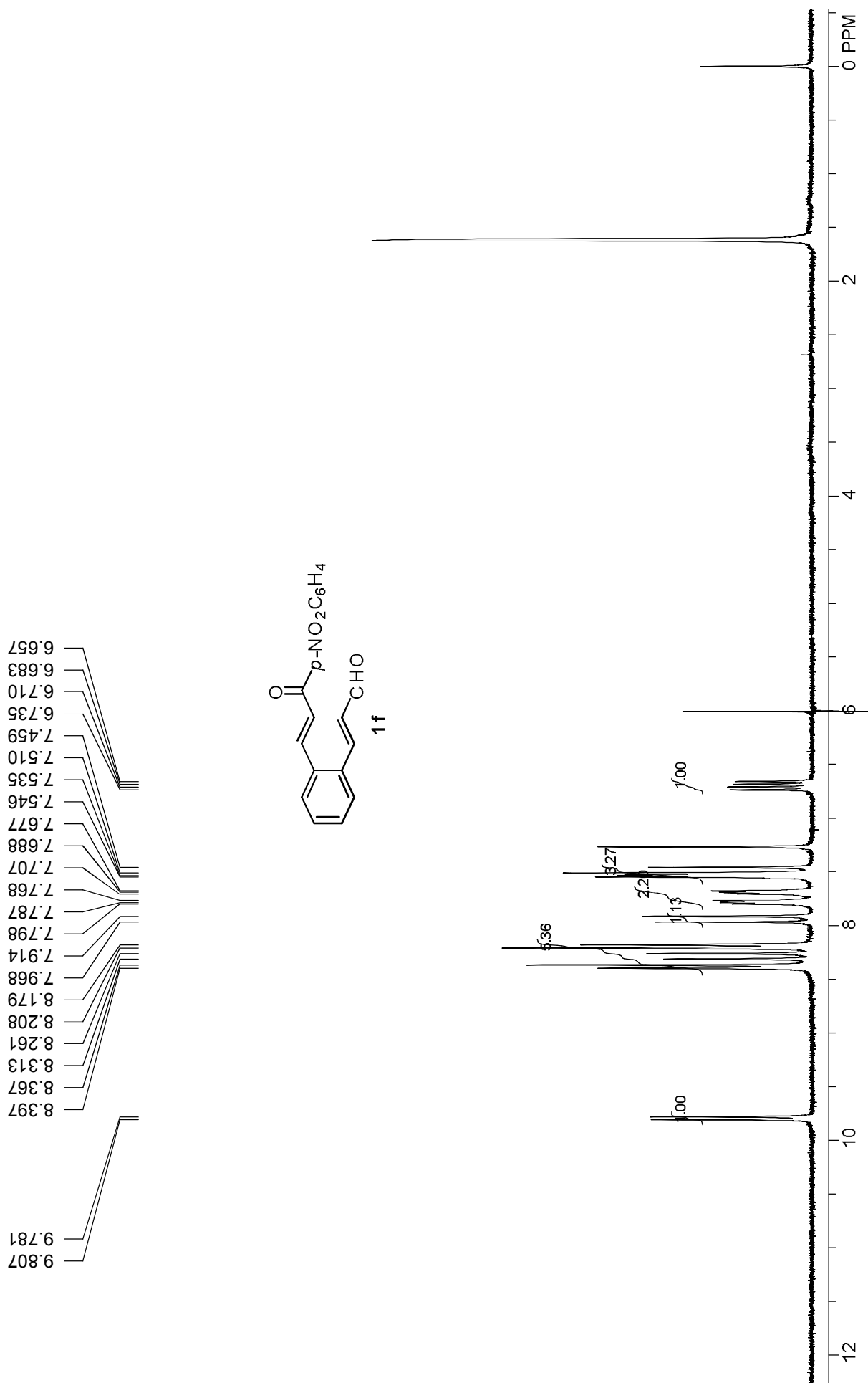


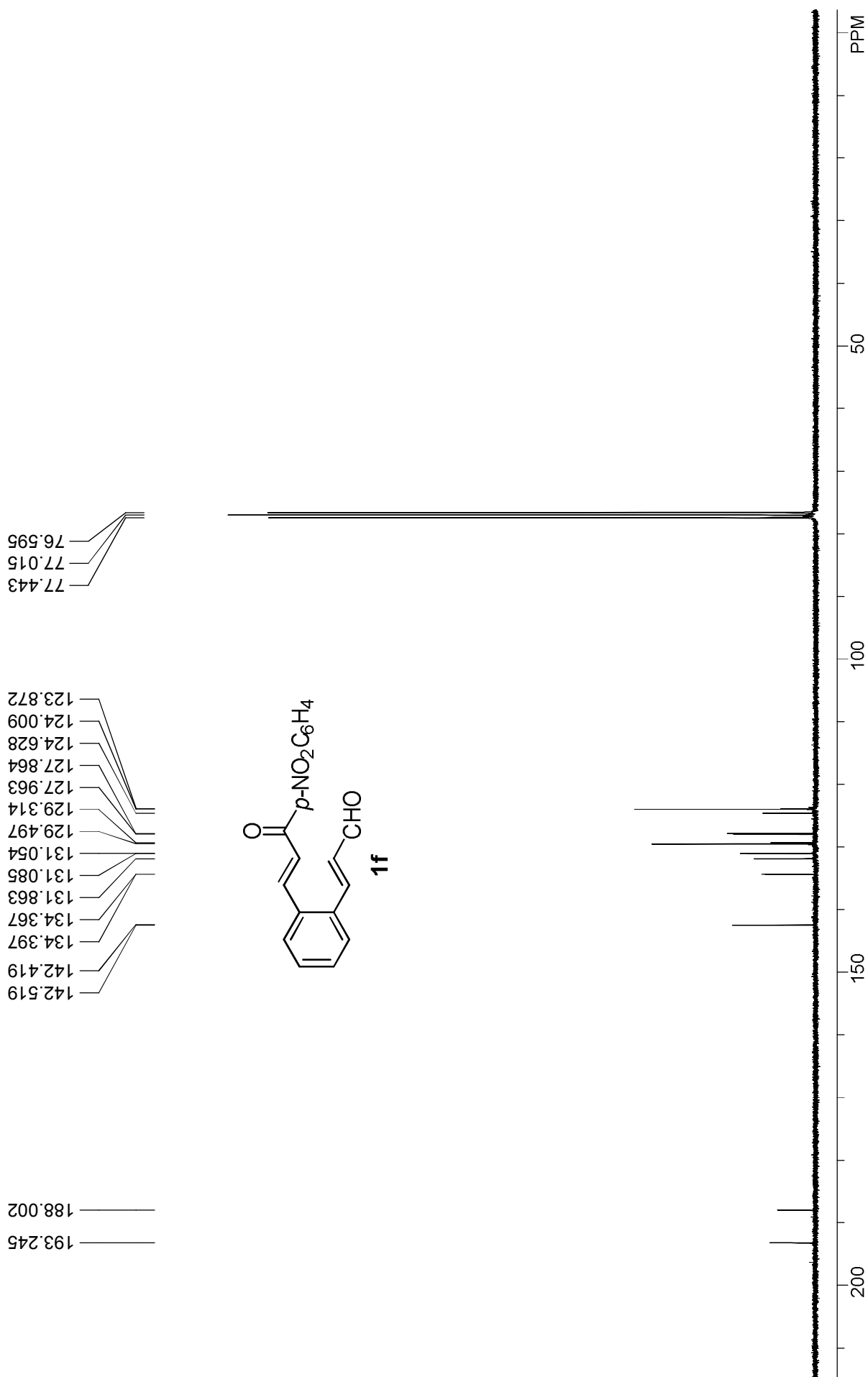


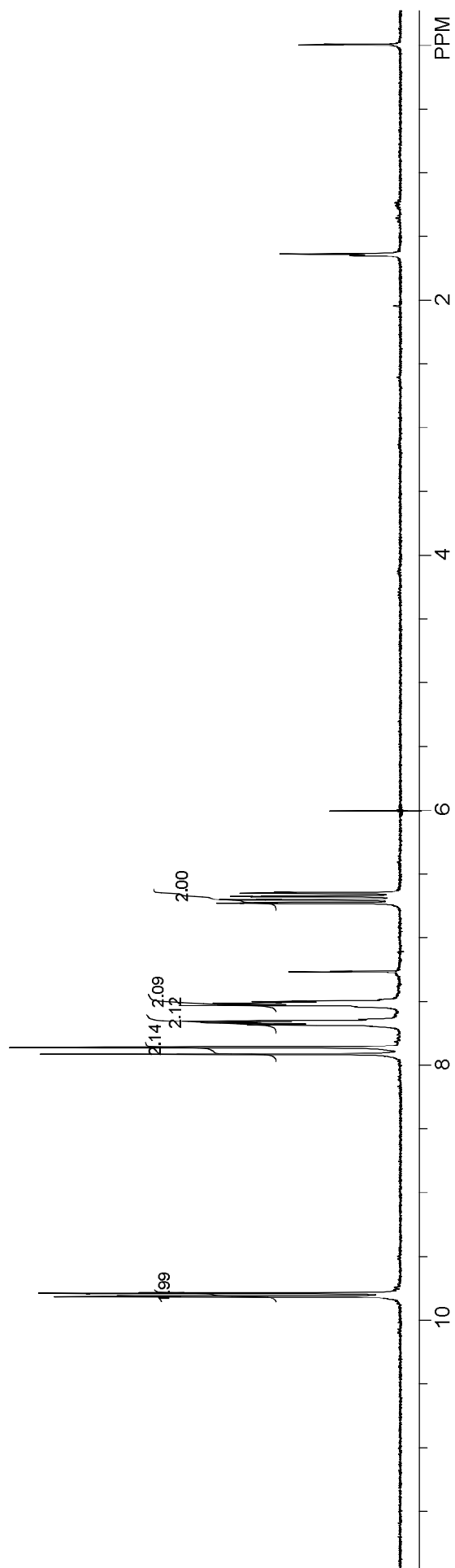
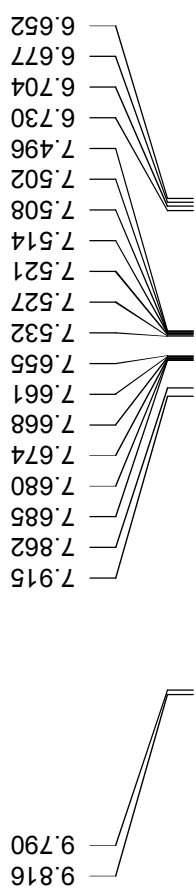


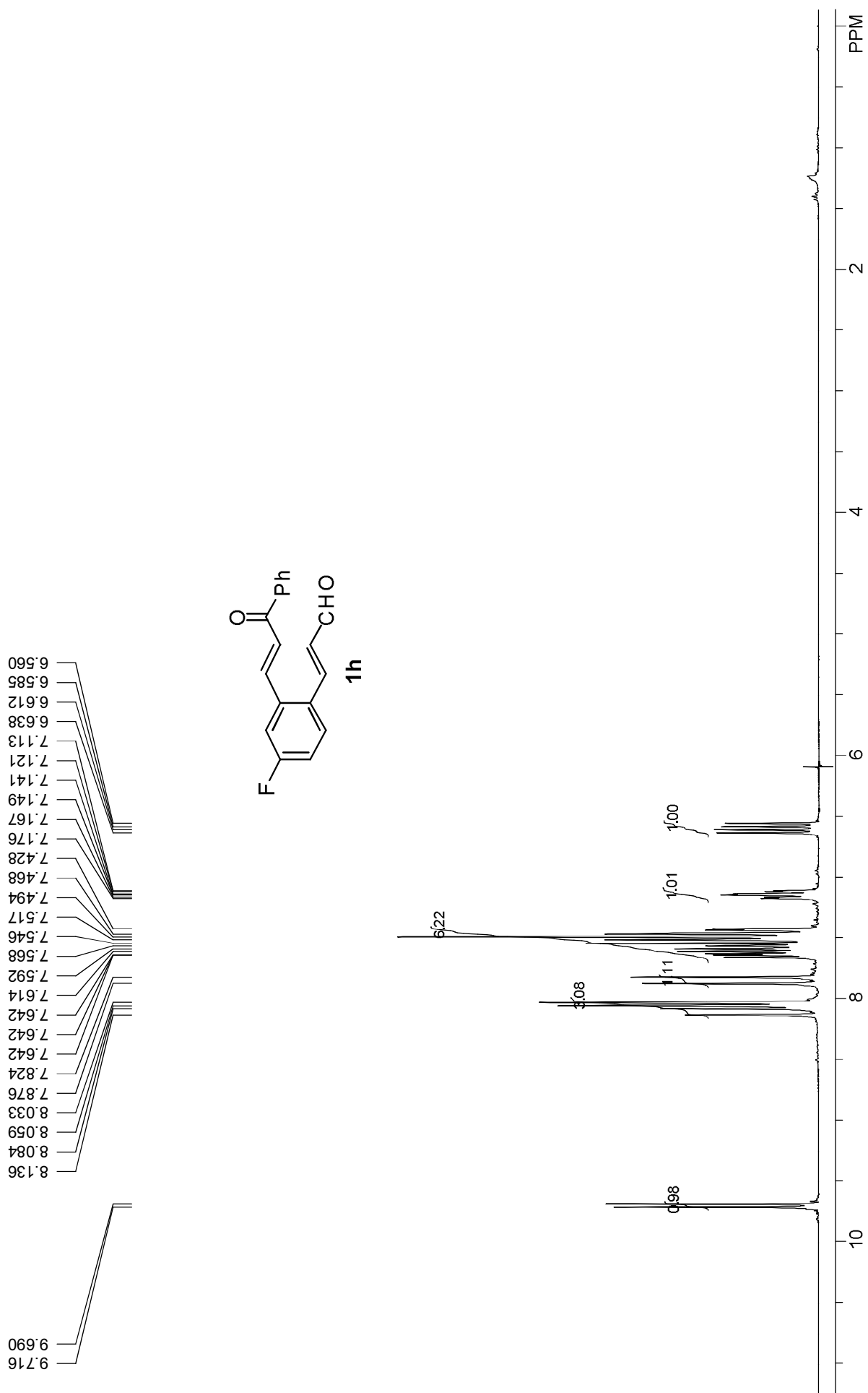


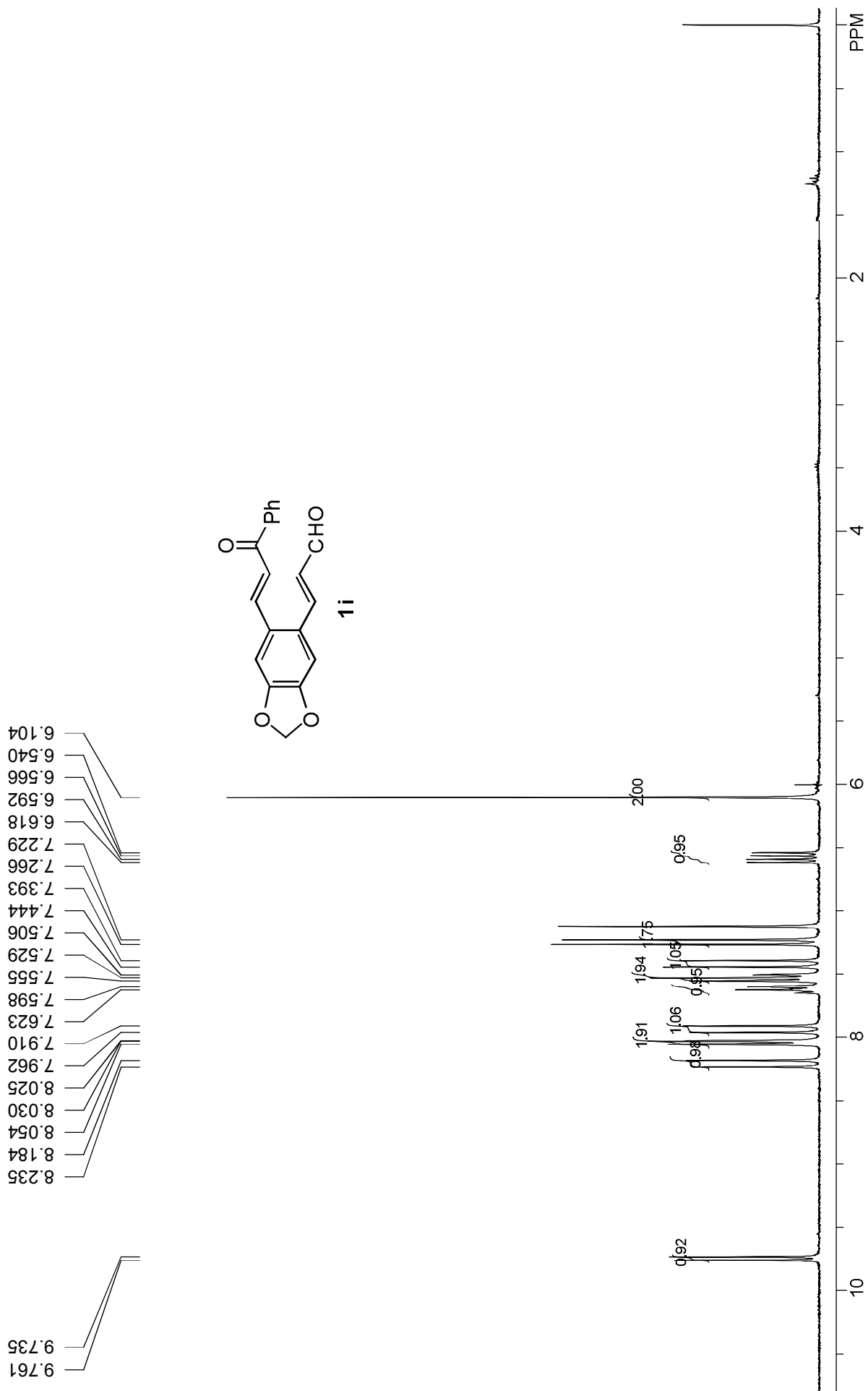


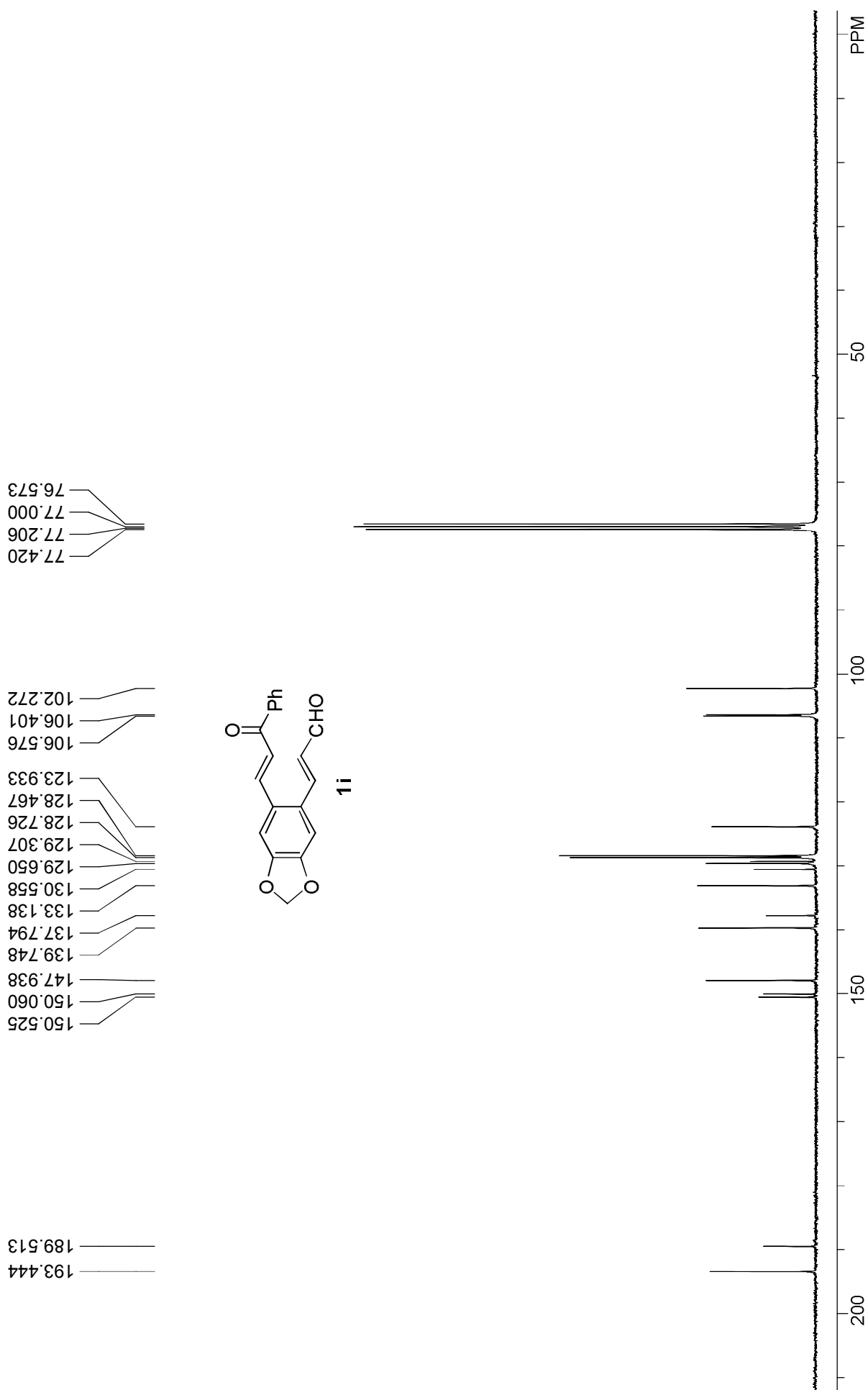


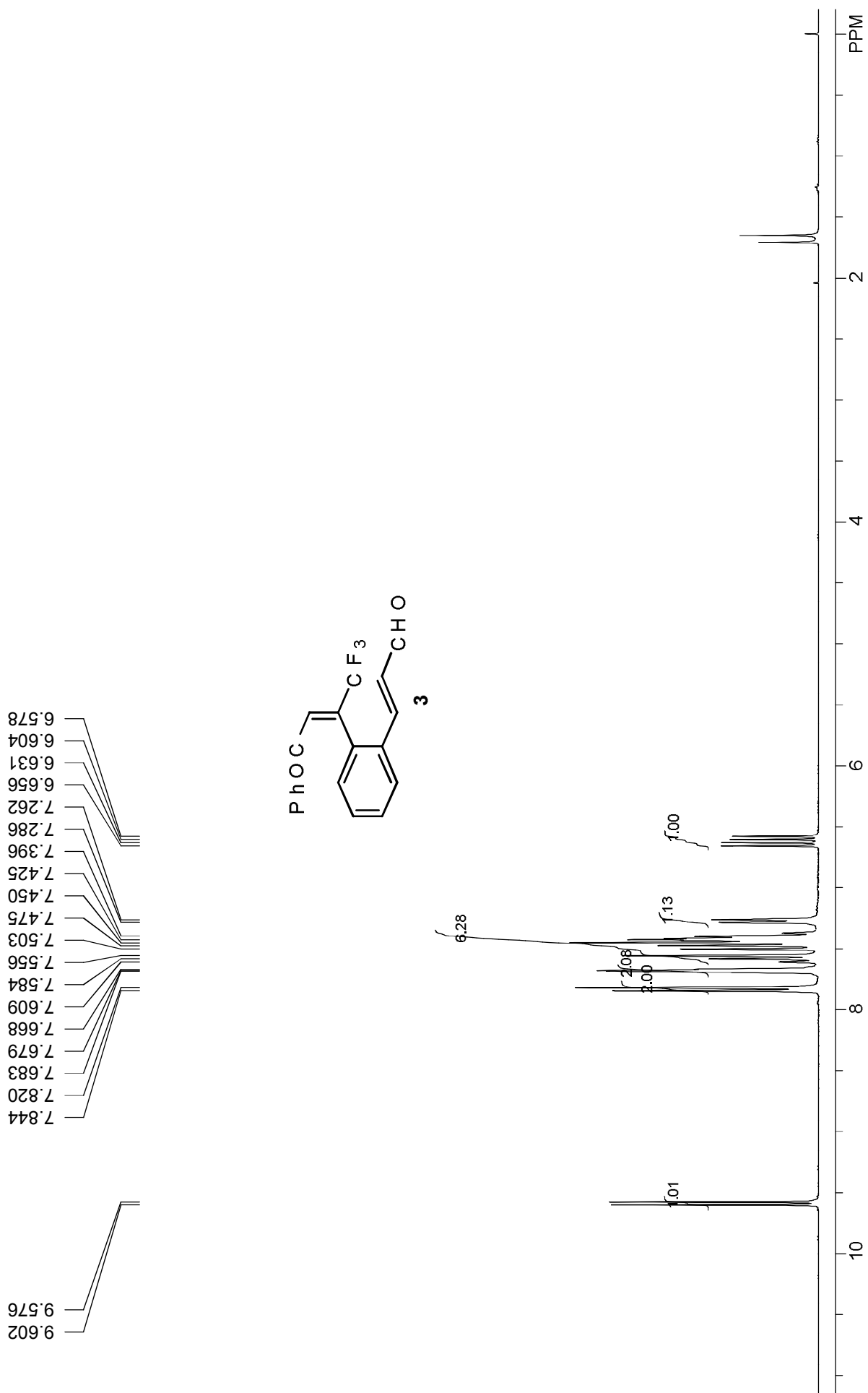


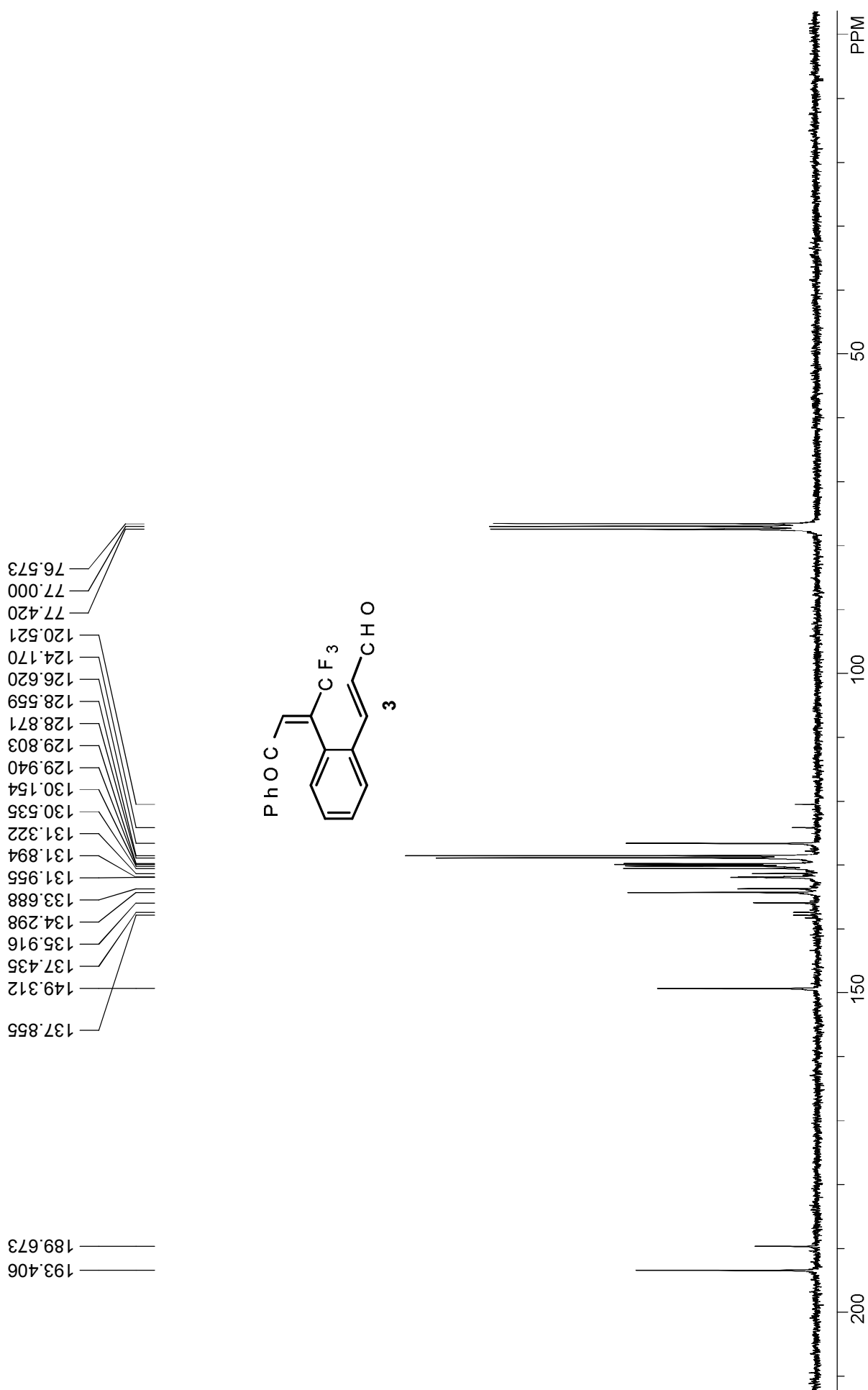


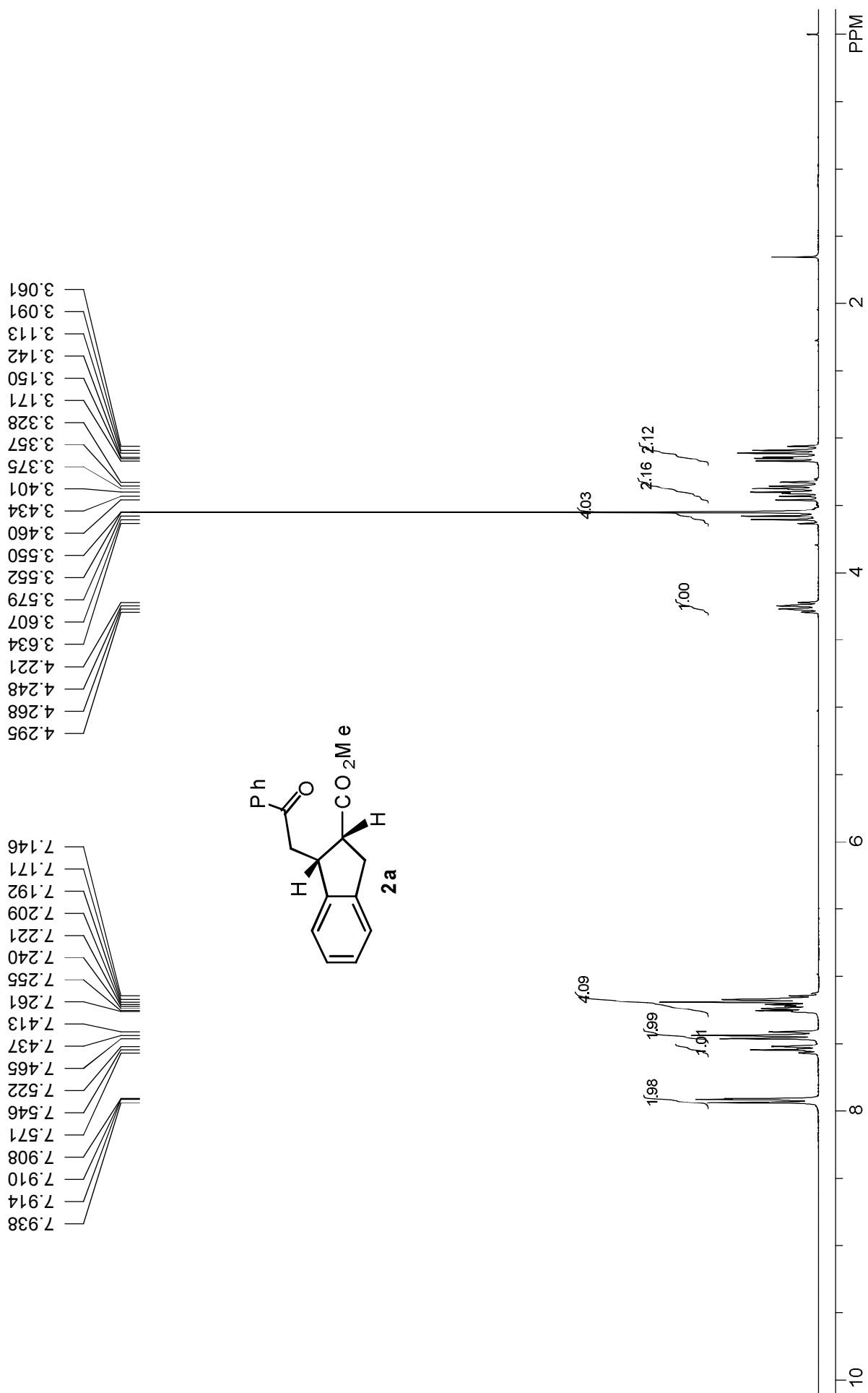


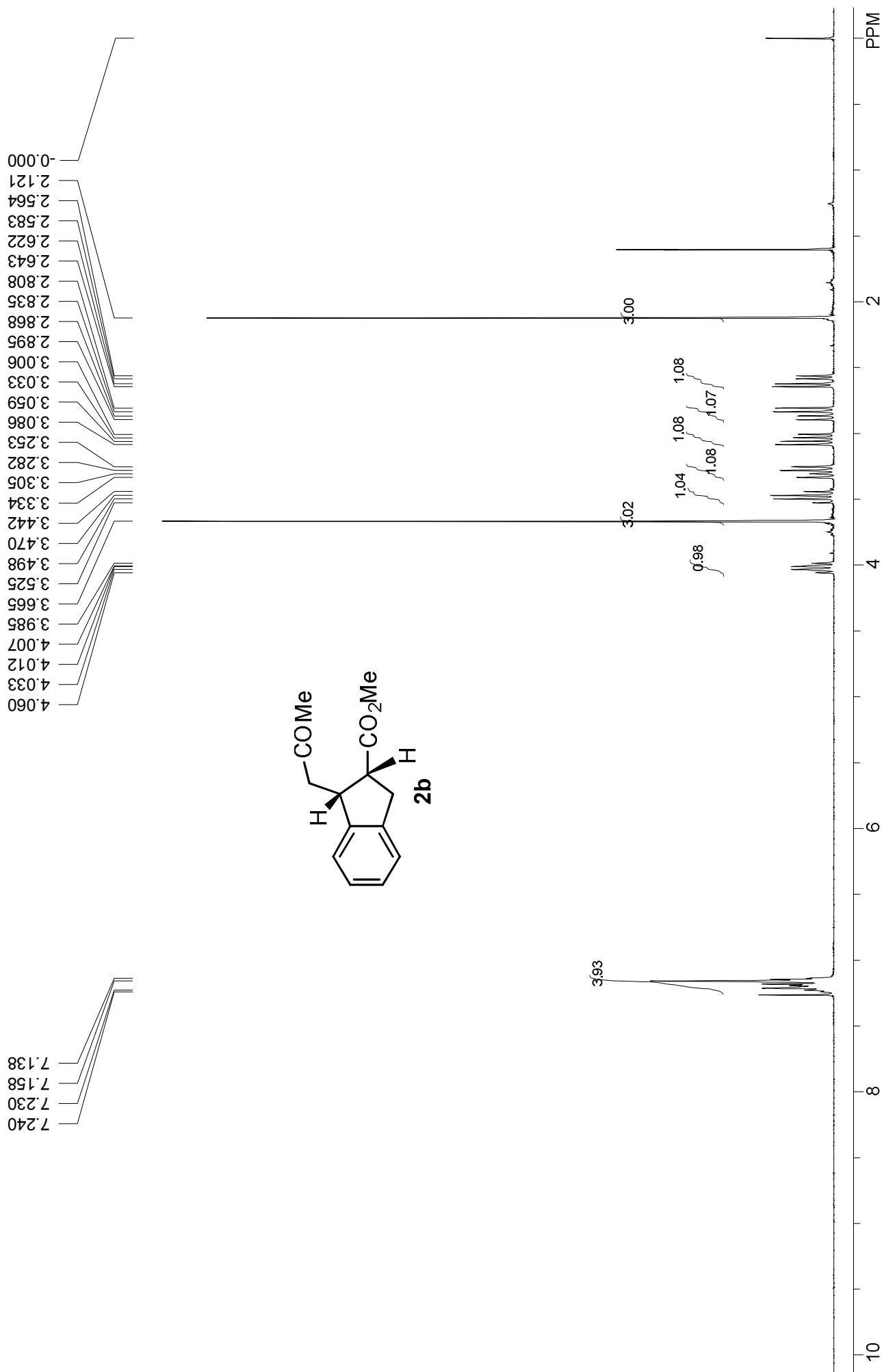


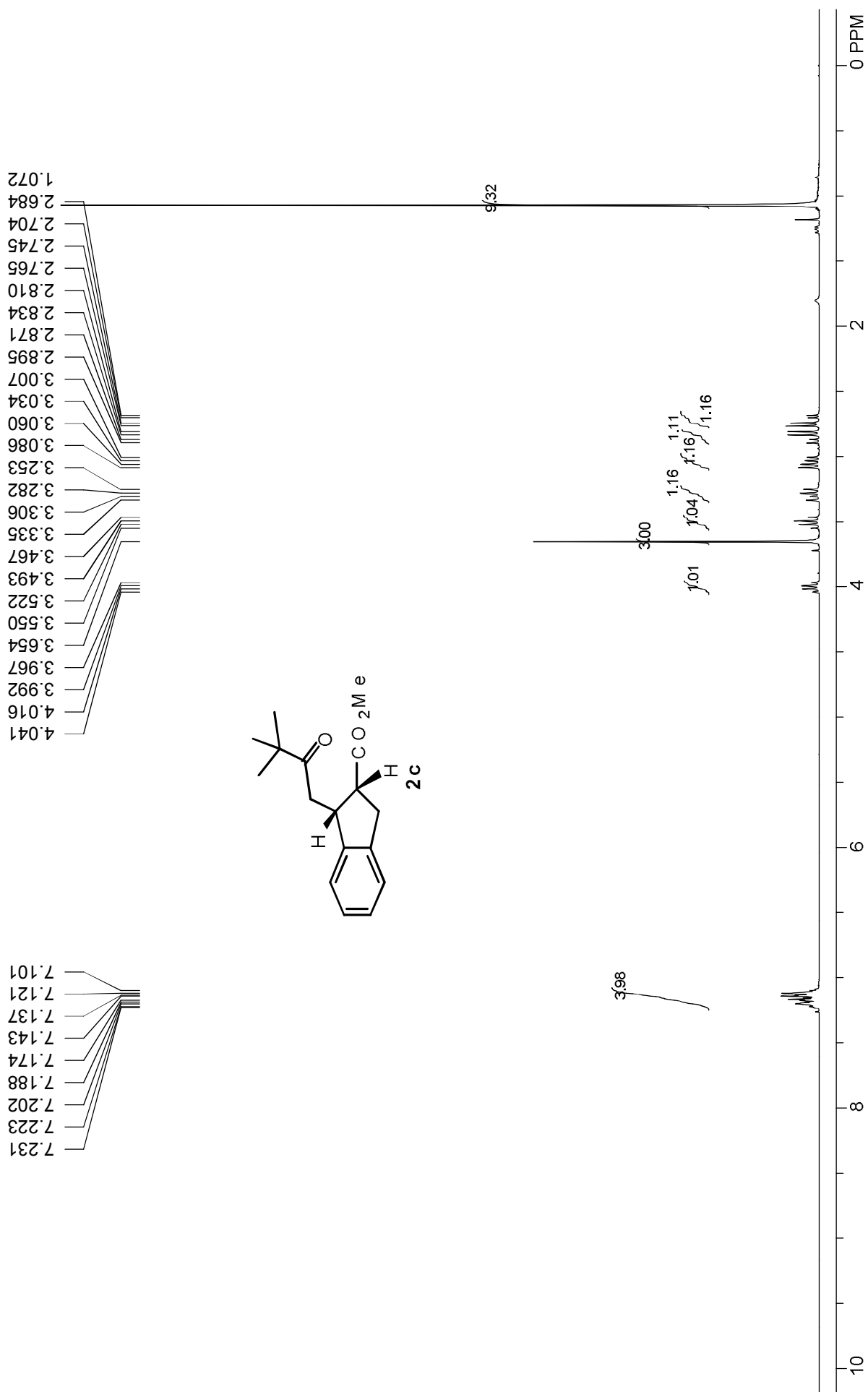


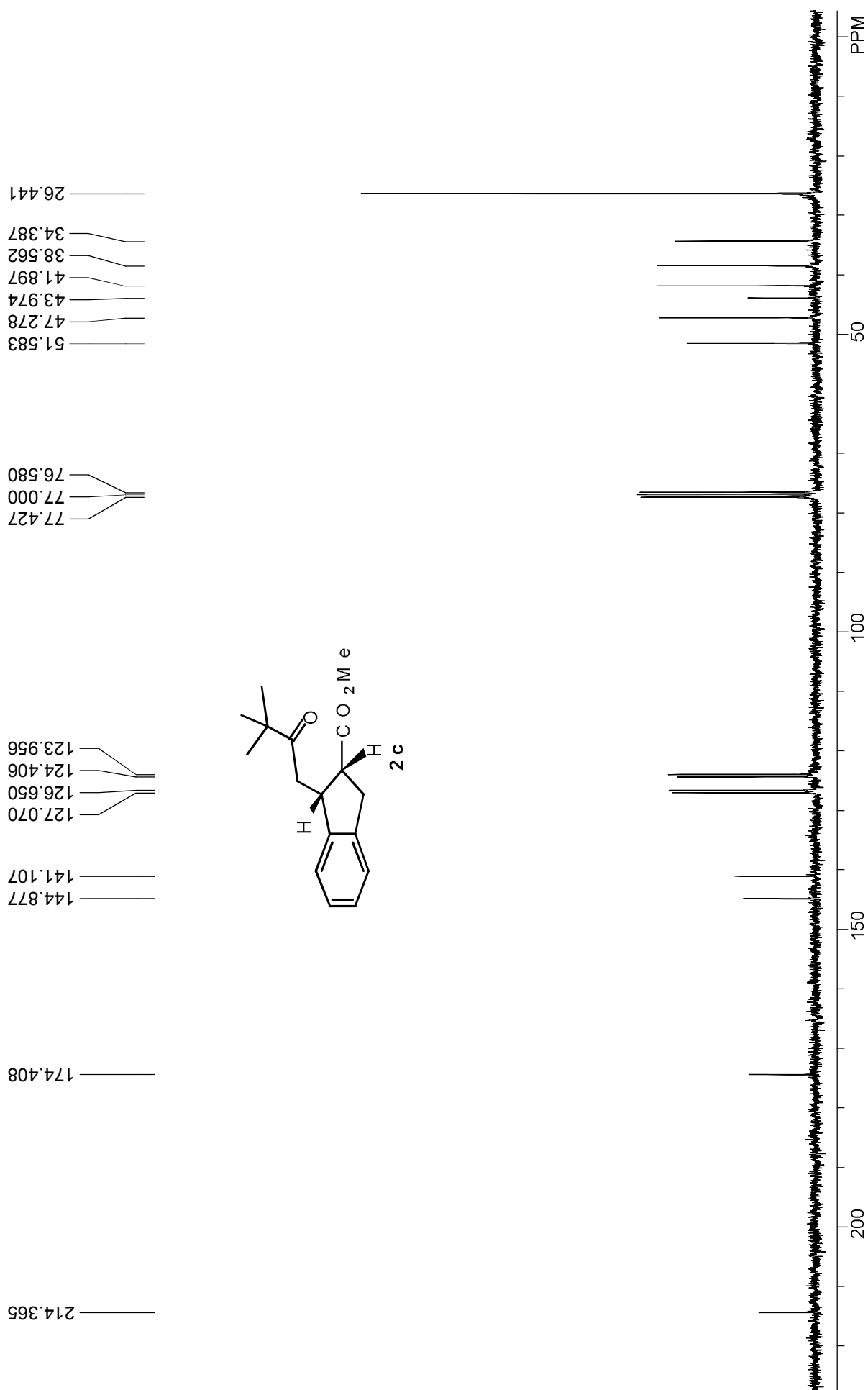


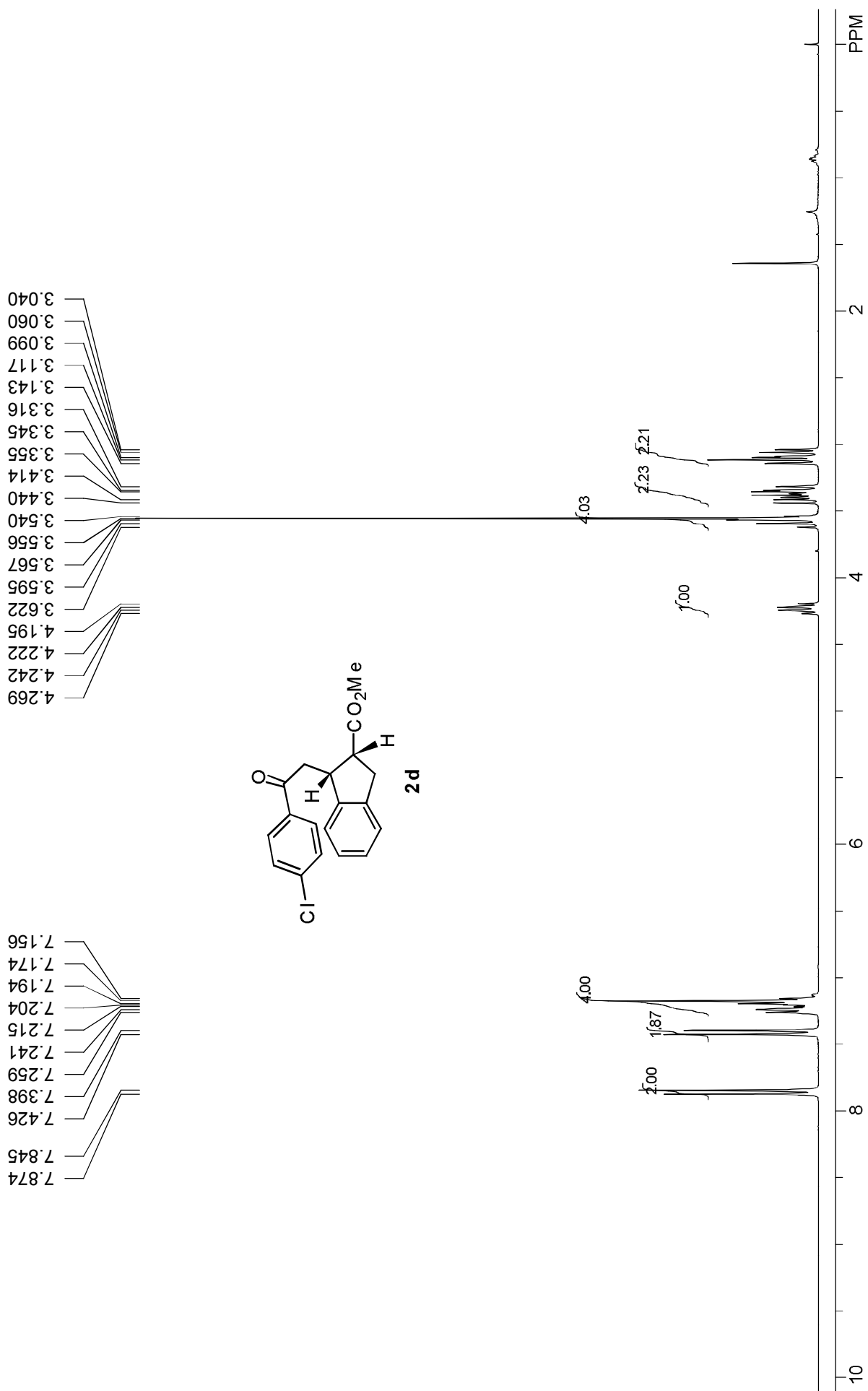


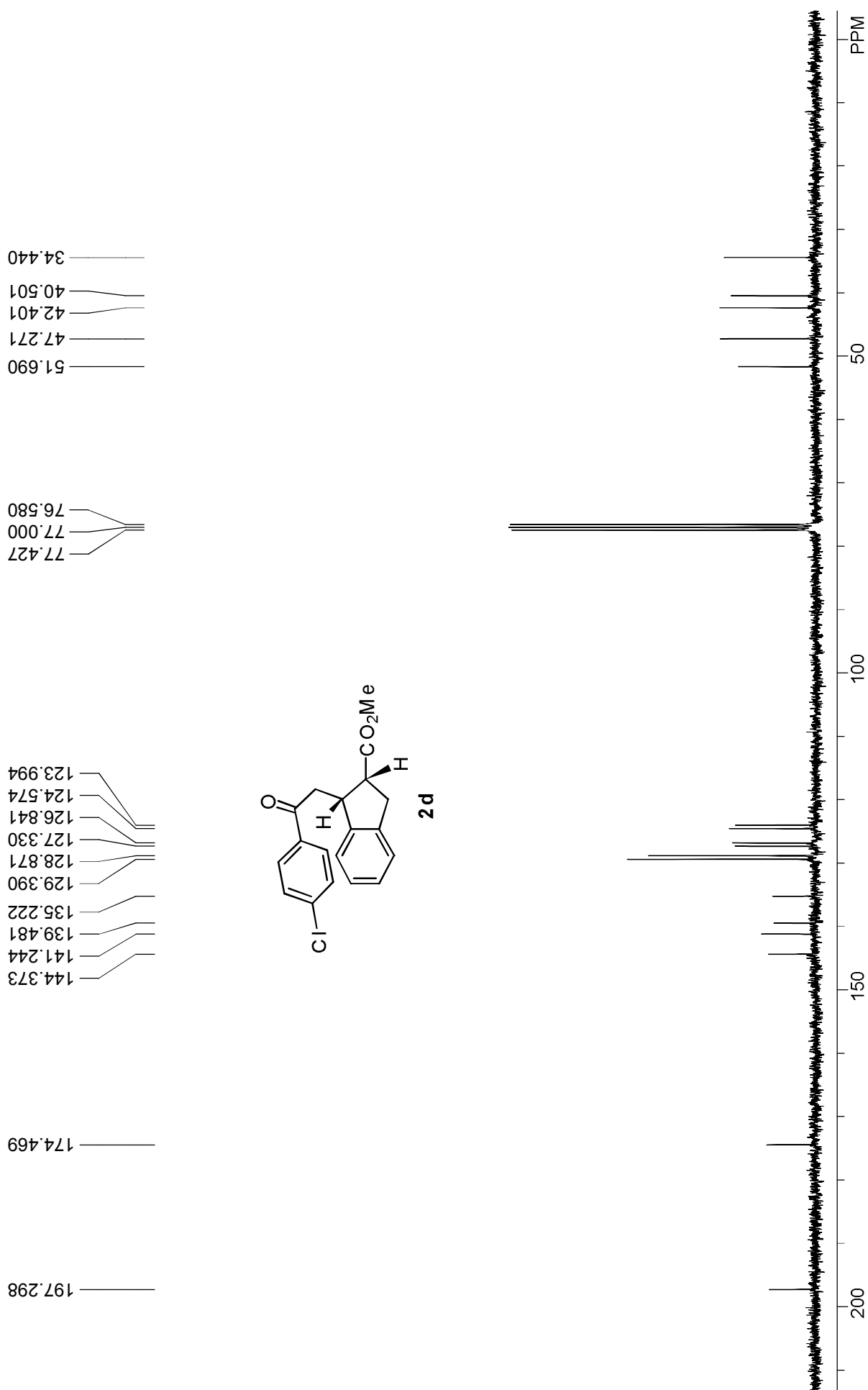


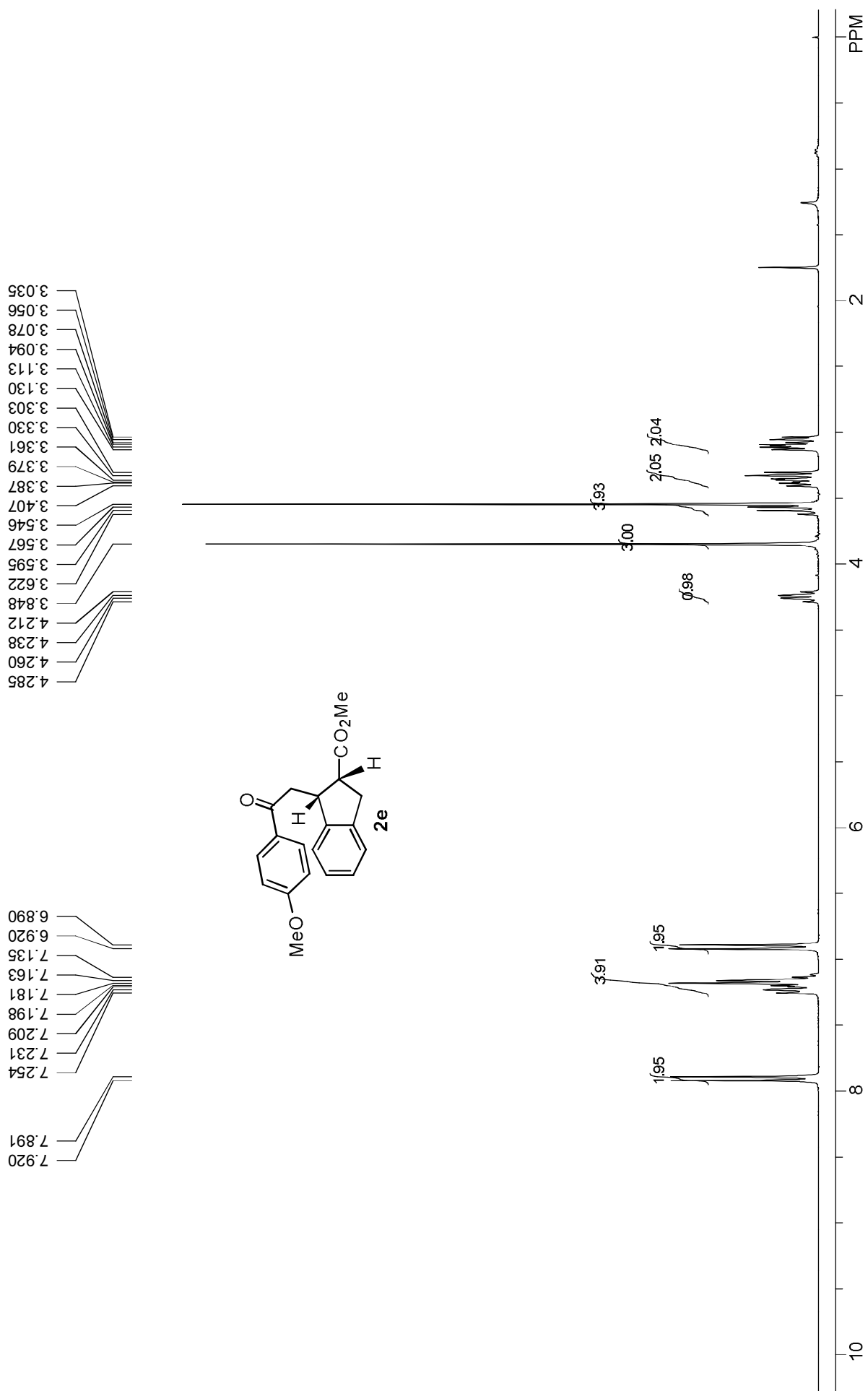


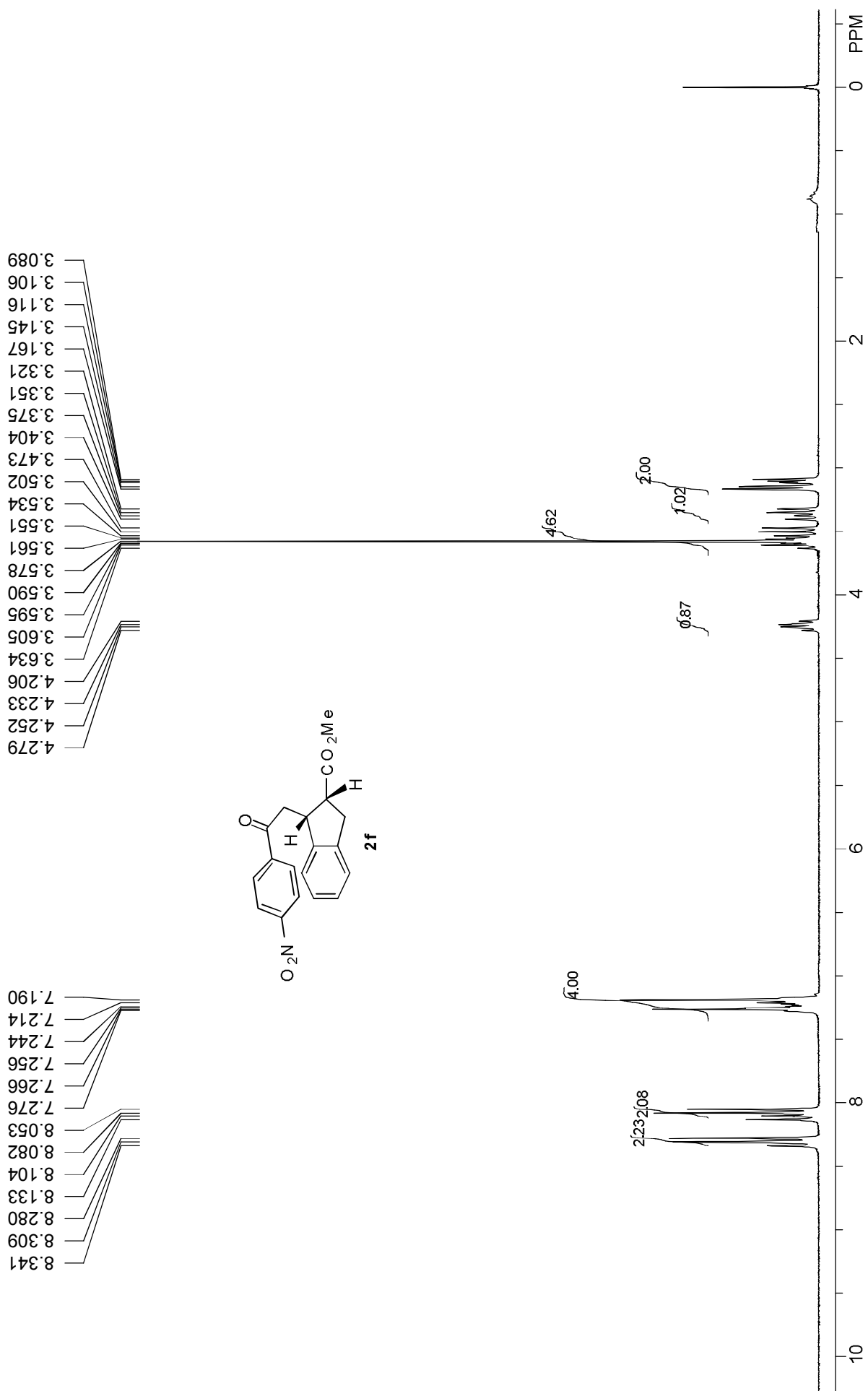


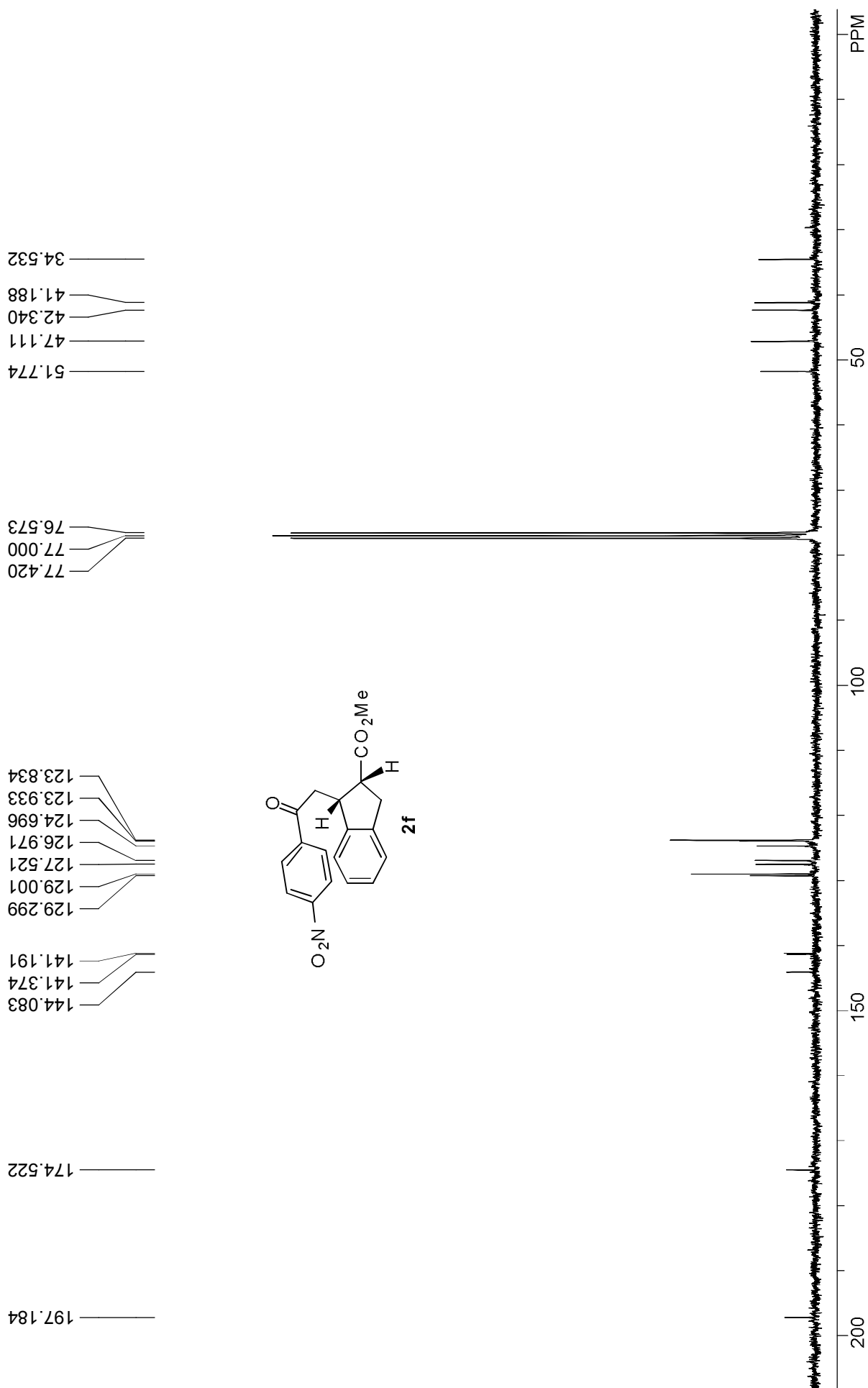


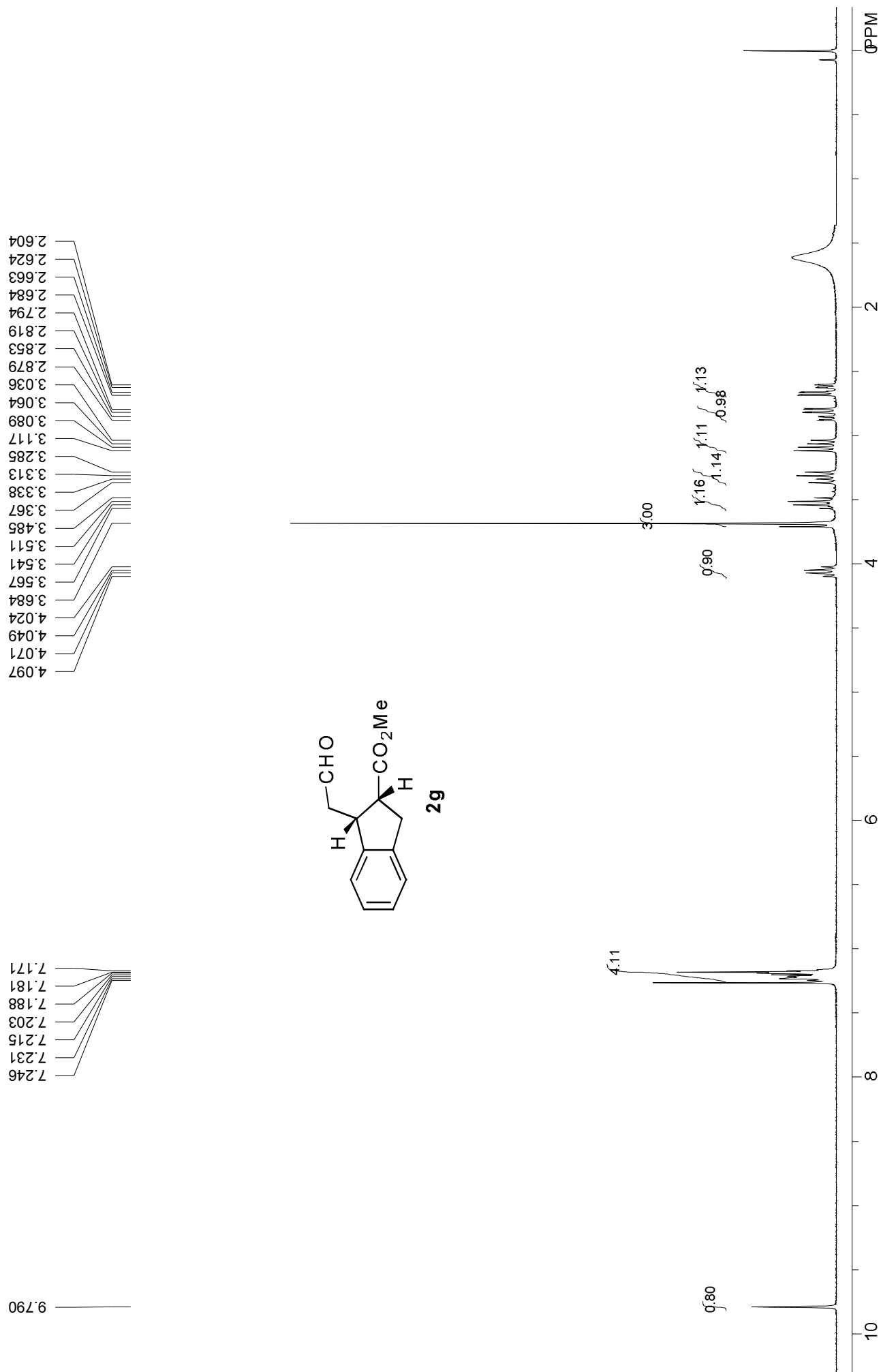


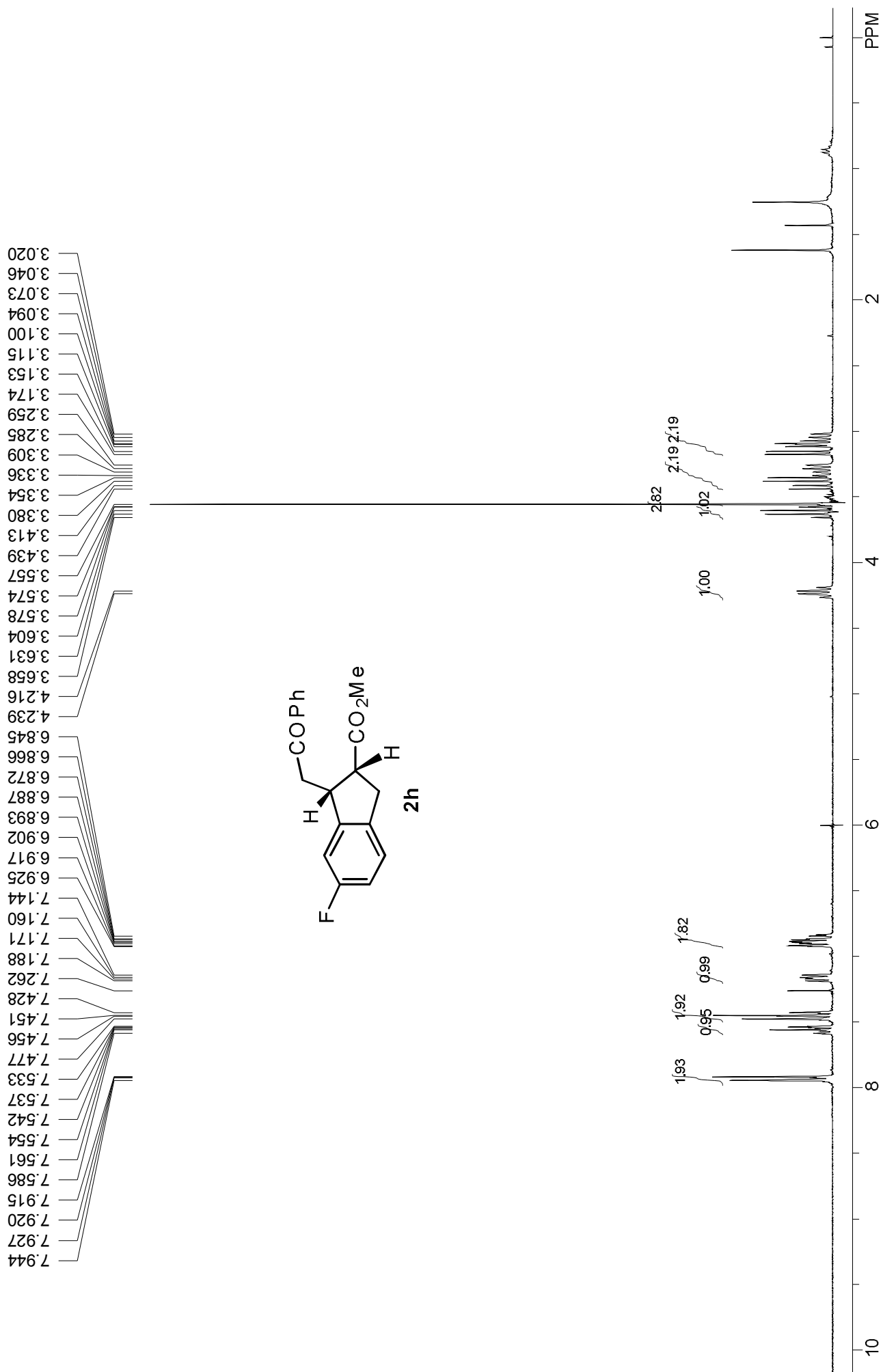


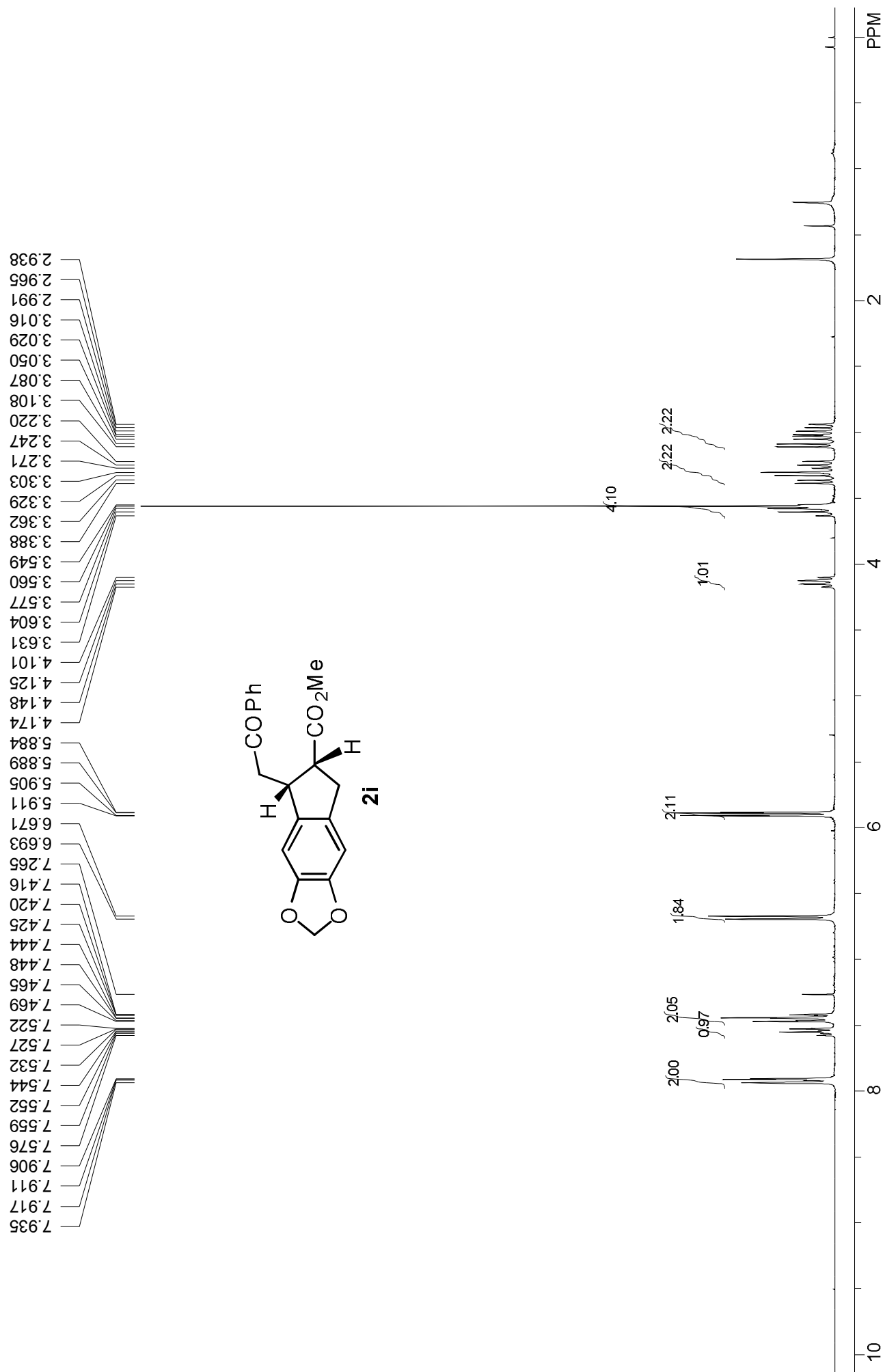


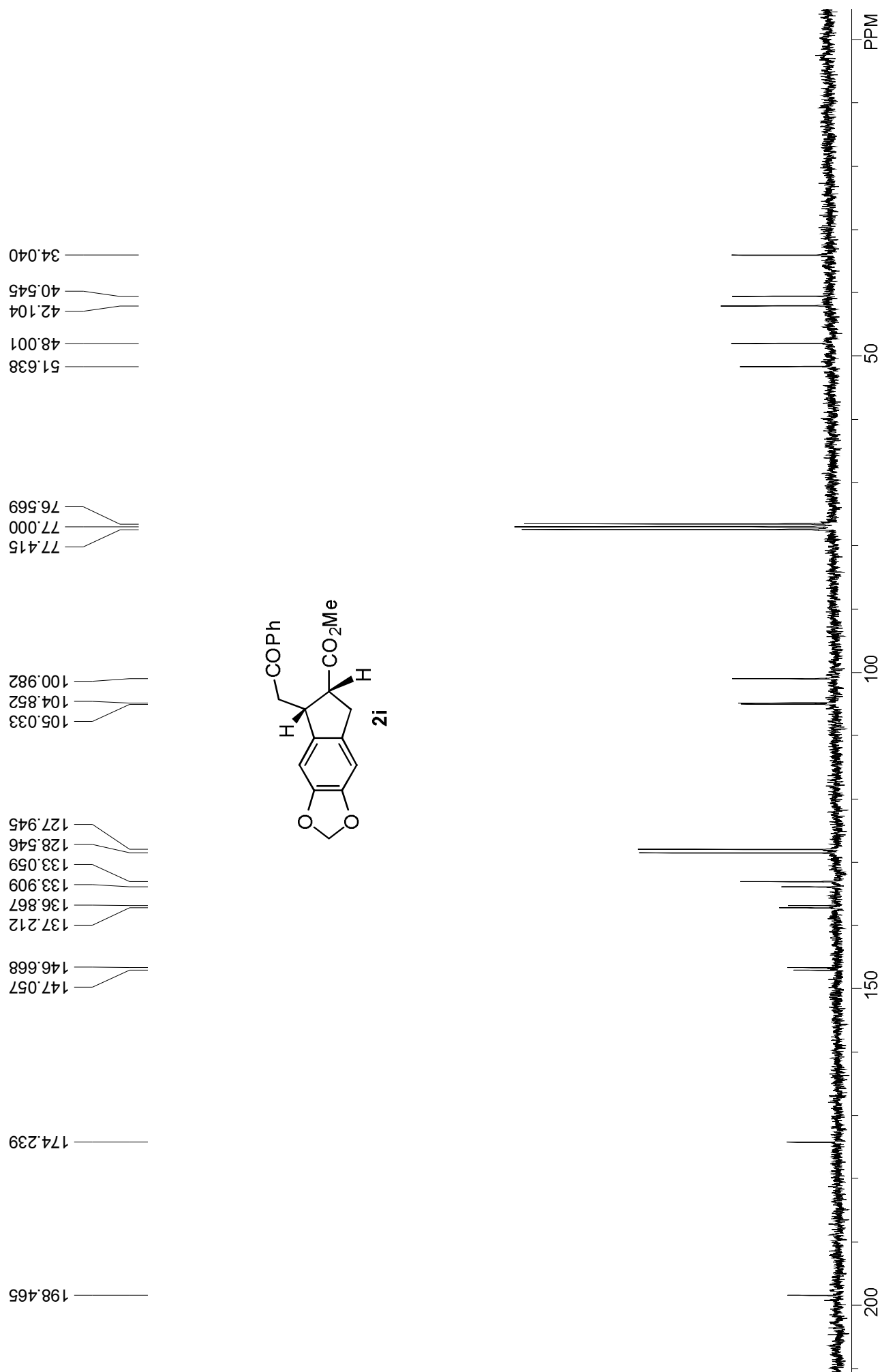


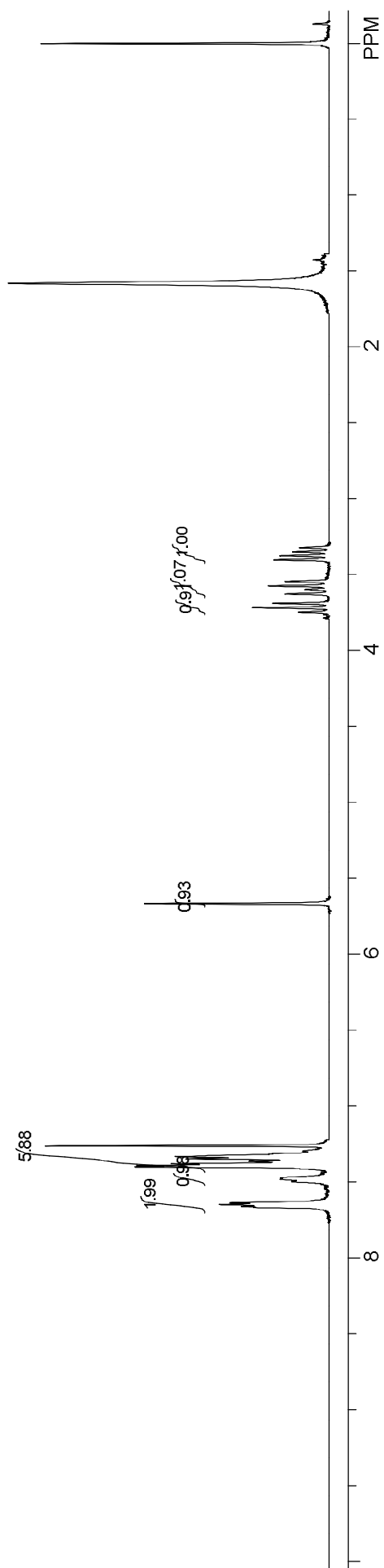
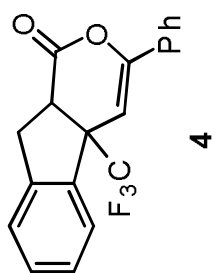
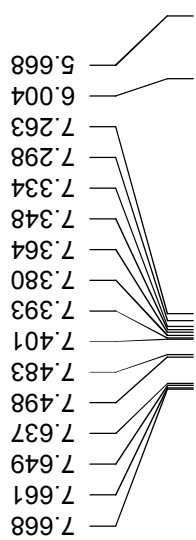
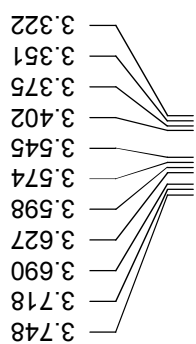


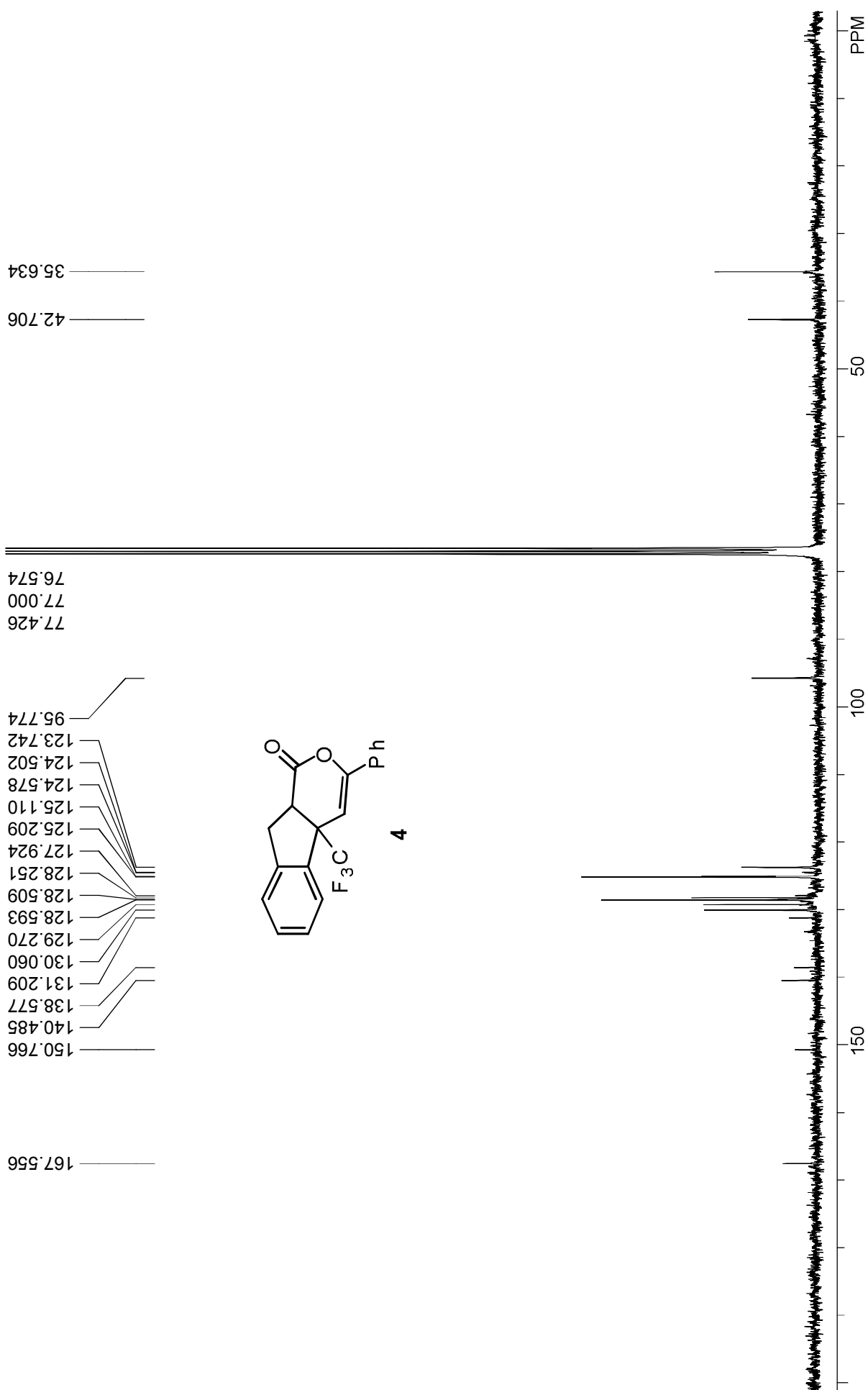


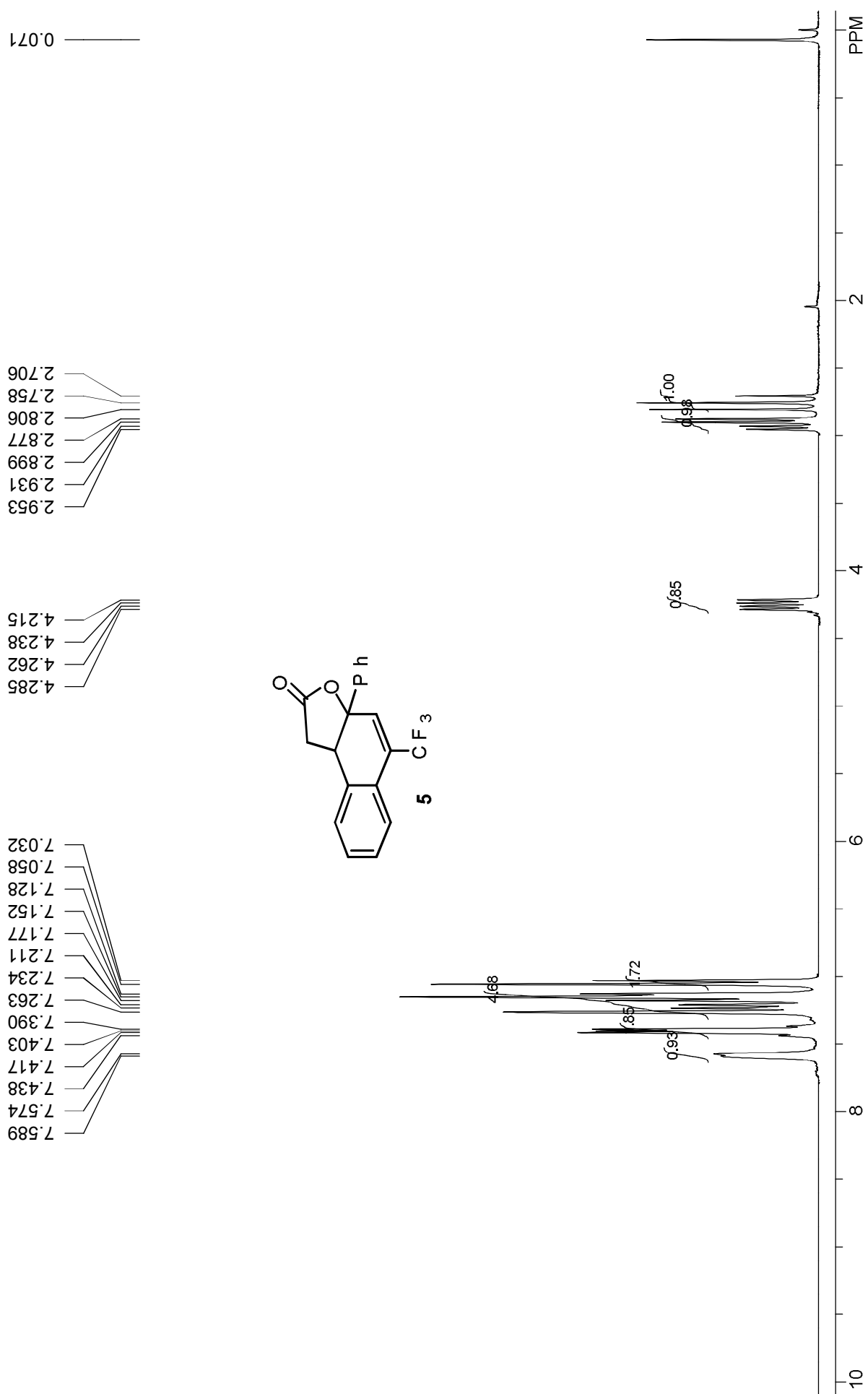


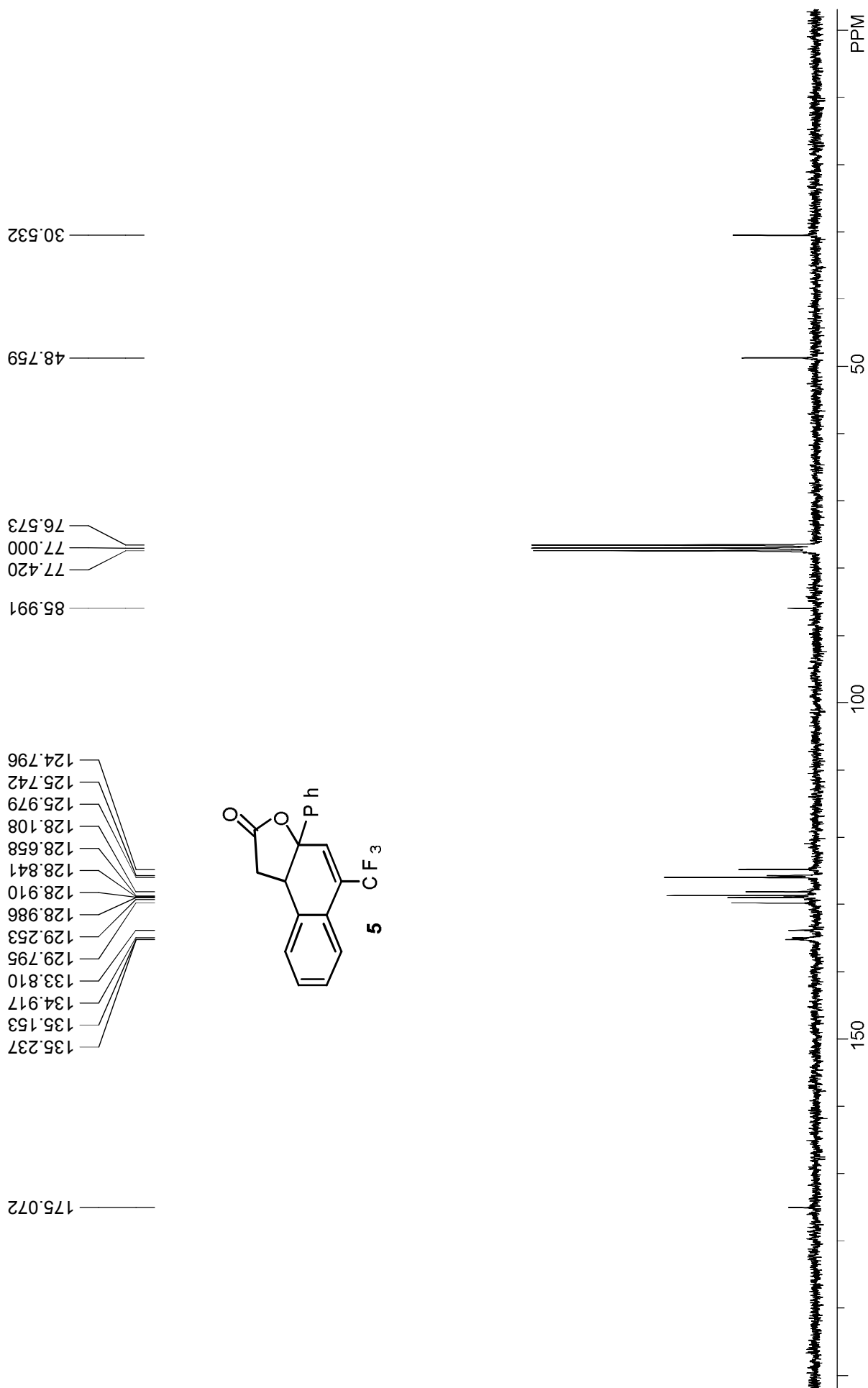


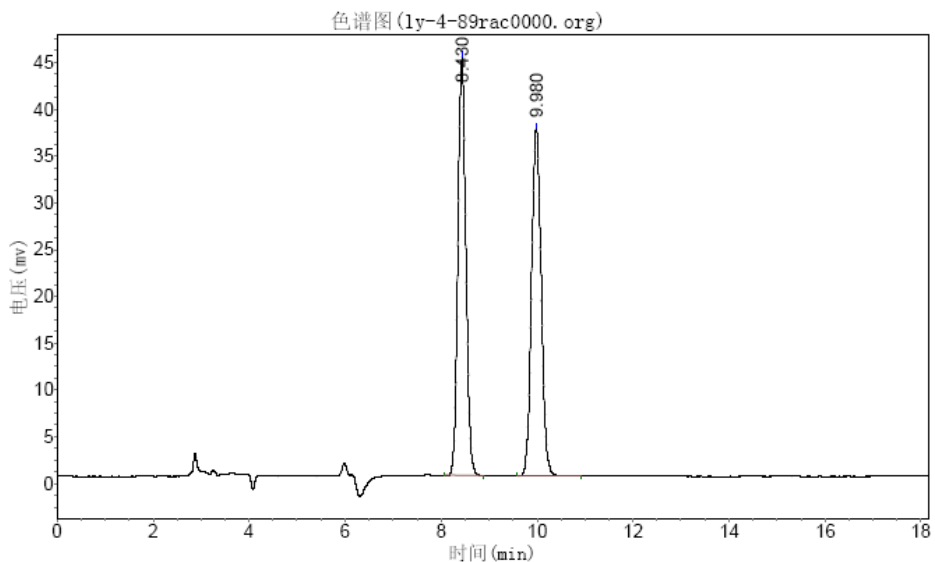
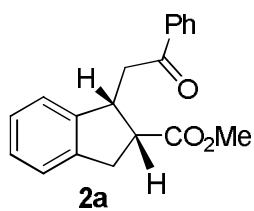






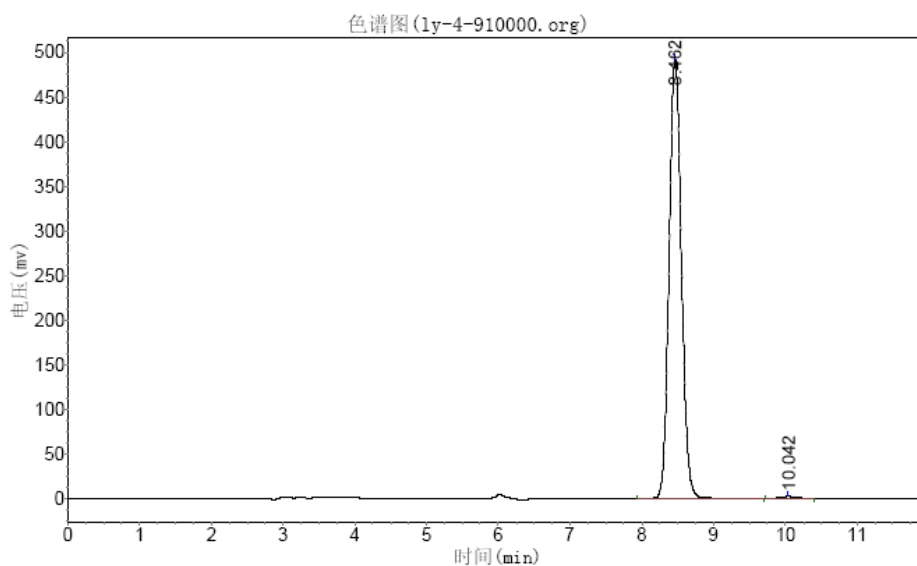






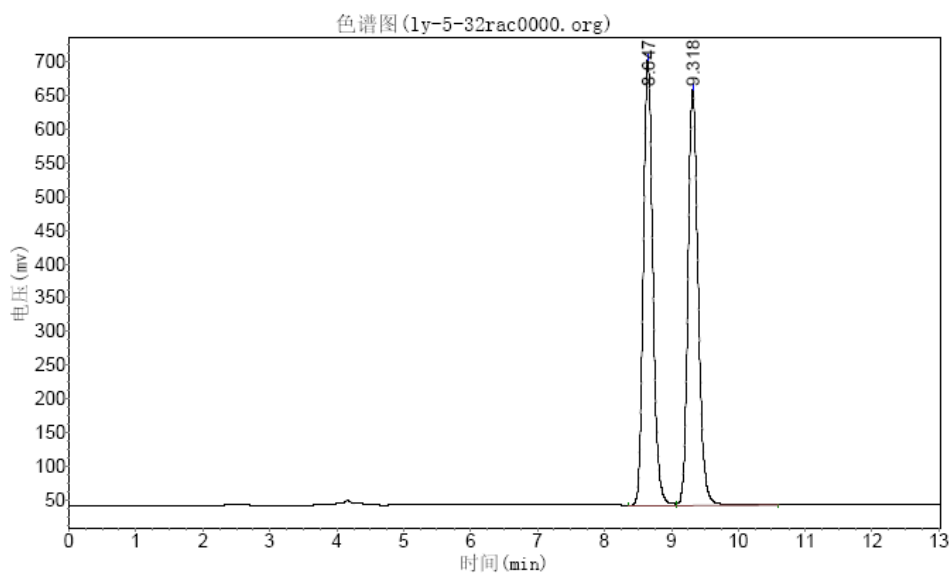
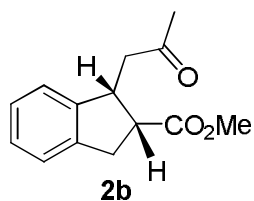
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.430	44818.105	514639.813	49.7477
2		9.980	37208.055	519859.438	50.2523
总计			82026.160	1034499.250	100.0000



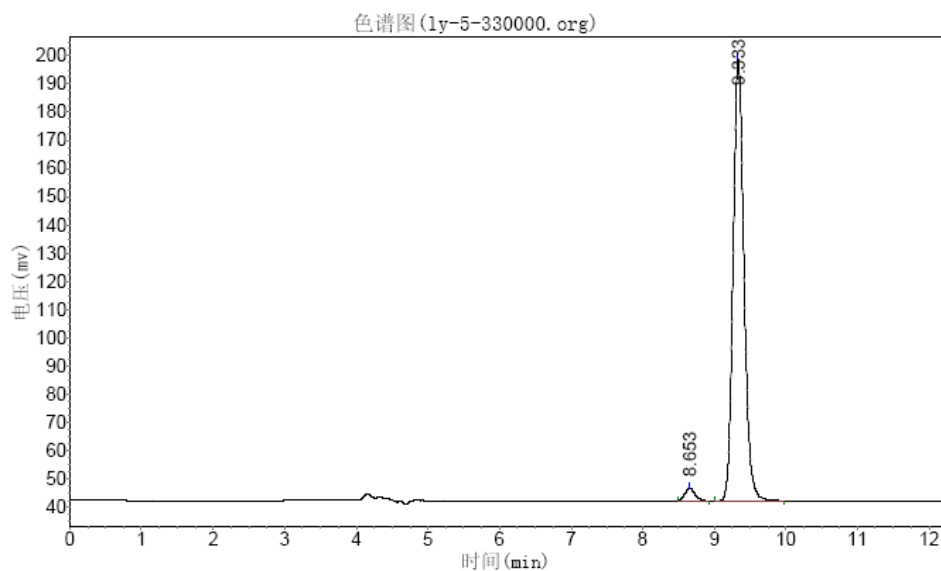
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.462	491685.188	5871702.000	99.4231
2		10.042	2391.502	34068.035	0.5769
总计			494076.690	5905770.035	100.0000



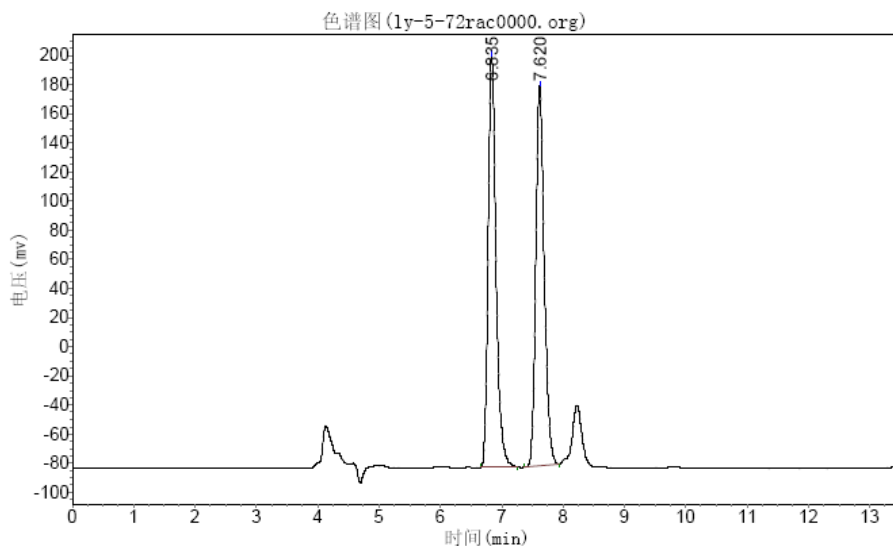
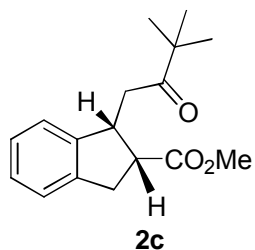
分析结果表

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1		8.647	661712.313	6535179.000	49.8115
2		9.318	617111.563	6584644.000	50.1885
总计			1278823.875	13119823.000	100.0000



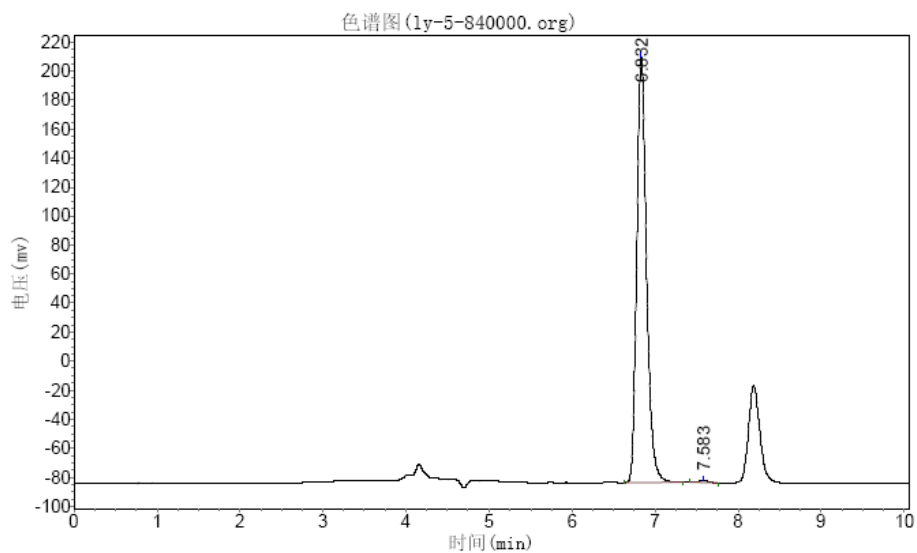
分析结果表

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1		8.653	4522.123	42801.813	2.5430
2		9.333	156544.703	1640341.375	97.4570
总计			161066.826	1683143.188	100.0000



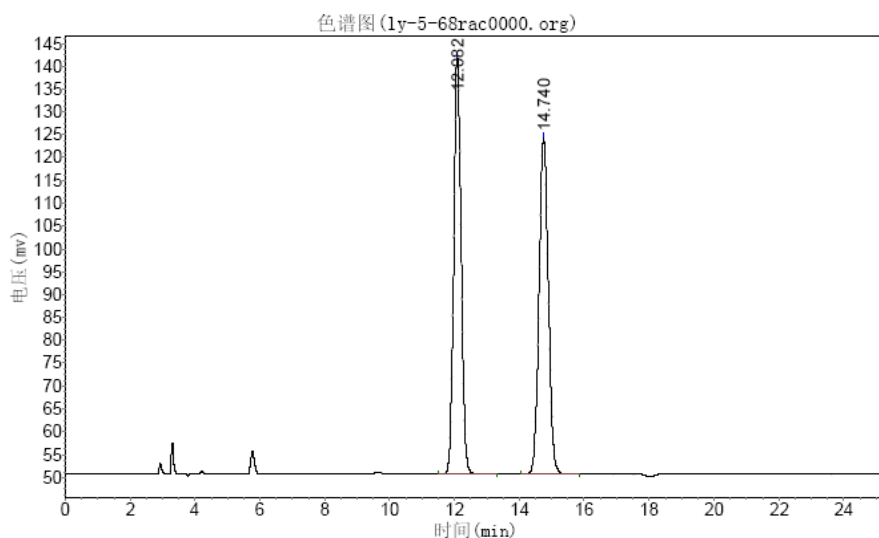
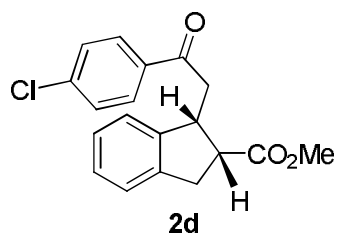
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		6.835	282731.719	2530608.500	50.4016
2		7.620	260645.359	2490283.000	49.5984
总计			543377.078	5020891.500	100.0000



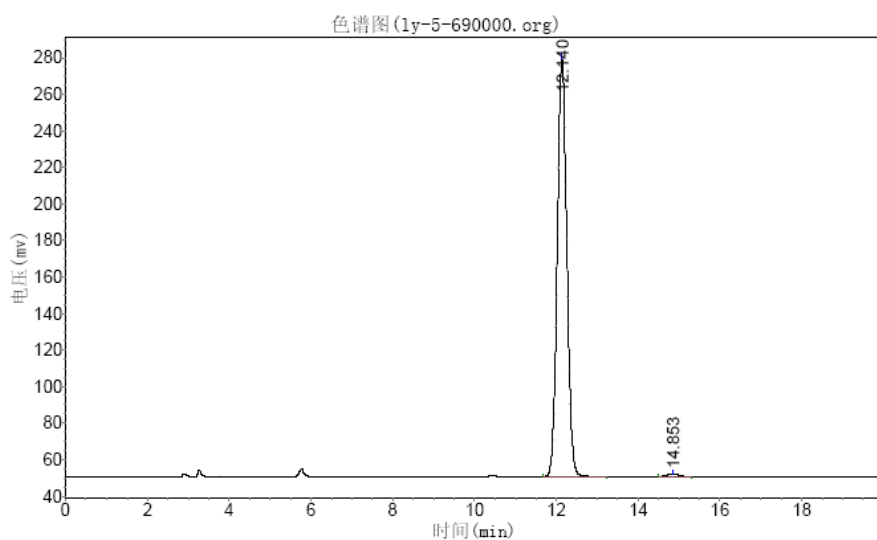
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		6.832	293569.469	2410854.500	99.5605
2		7.583	1281.294	10642.992	0.4395
总计			294850.763	2421497.492	100.0000



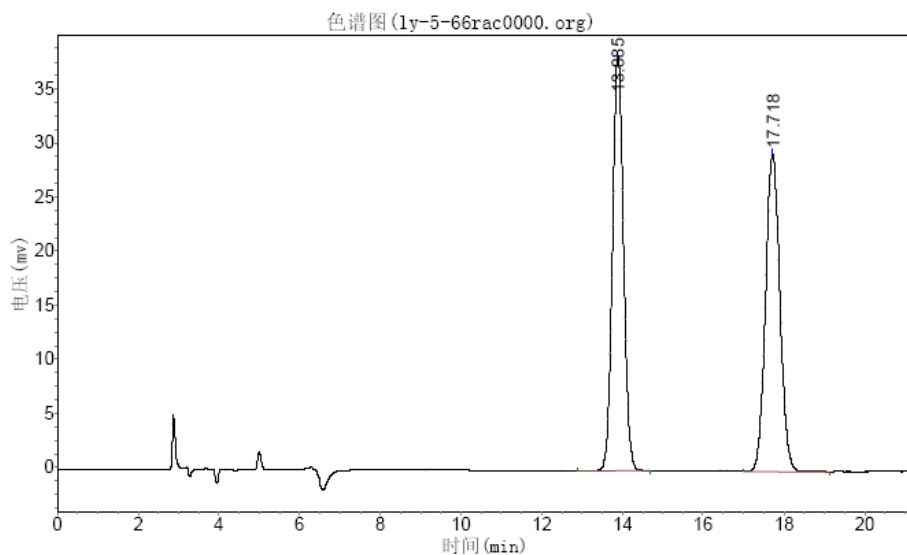
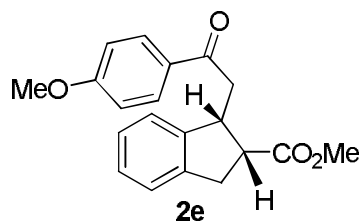
分析结果表

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1		12.082	91373.094	1462822.625	49.9597
2		14.740	73879.477	1465183.125	50.0403
总计			165252.570	2928005.750	100.0000



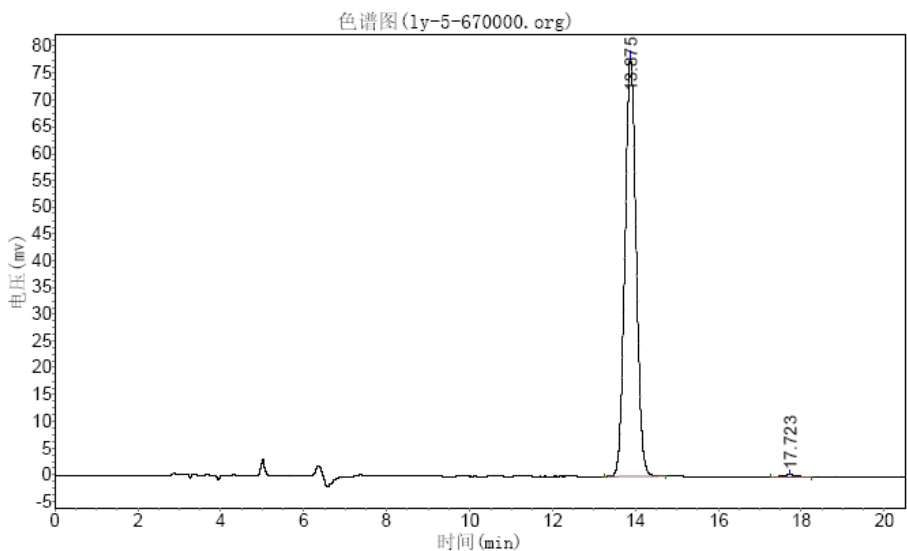
分析结果表

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1		12.140	229353.297	3695632.000	99.3294
2		14.853	1277.580	24950.078	0.6706
总计			230630.876	3720582.078	100.0000



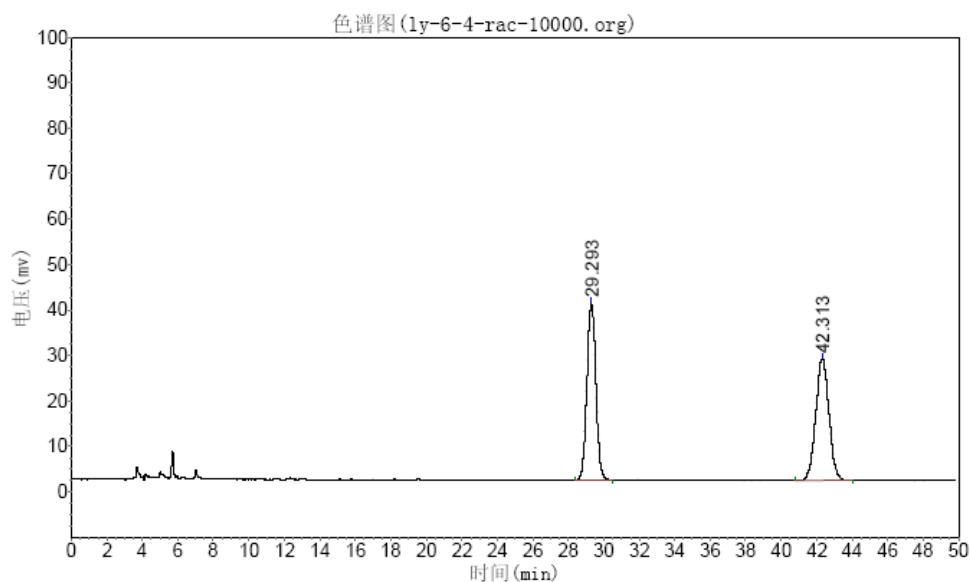
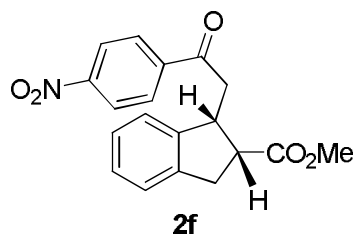
分析结果表

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1		13.885	38297.094	724208.188	49.9499
2		17.718	29400.814	725660.375	50.0501
总计			67697.908	1449868.563	100.0000



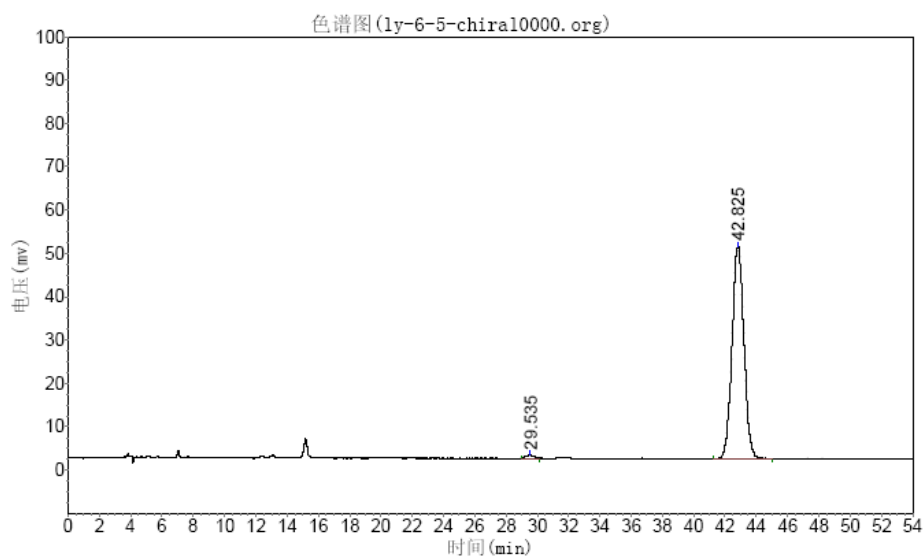
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		13.875	78571.578	1479028.125	99.4464
2		17.723	344.052	8234.000	0.5536
总计			78915.631	1487262.125	100.0000



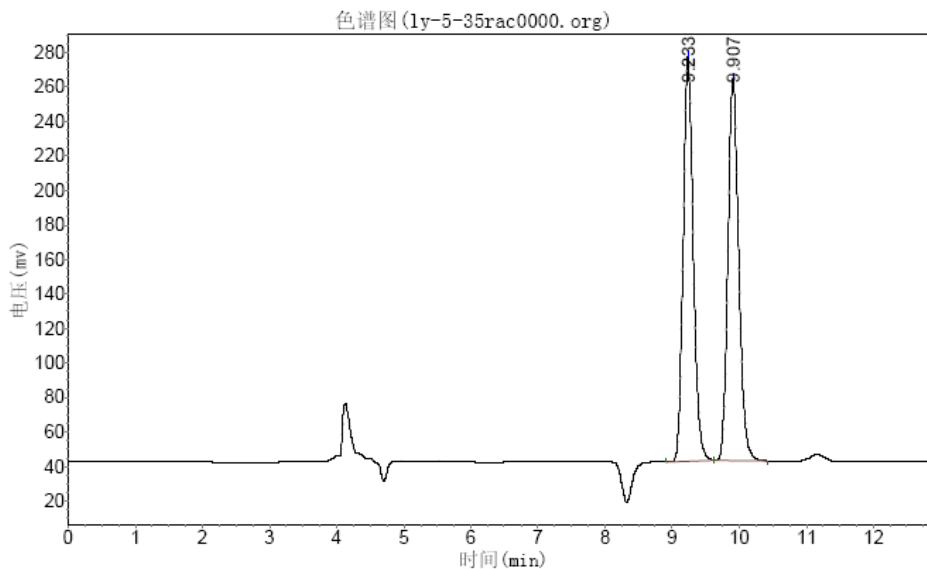
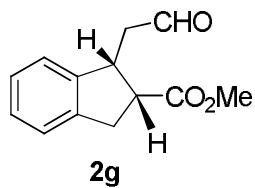
分析结果表

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1		29.293	39012.363	1379360.750	50.0058
2		42.313	26780.814	1379043.250	49.9942
总计			65793.178	2758404.000	100.0000



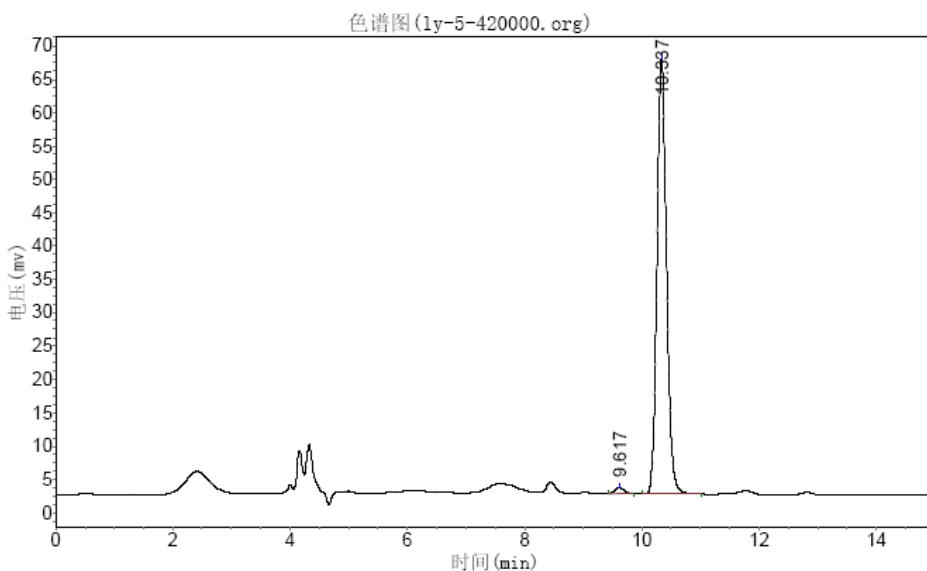
分析结果表

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1		29.535	745.546	24381.398	0.9362
2		42.825	48885.266	2579841.500	99.0638
总计			49630.812	2604222.898	100.0000



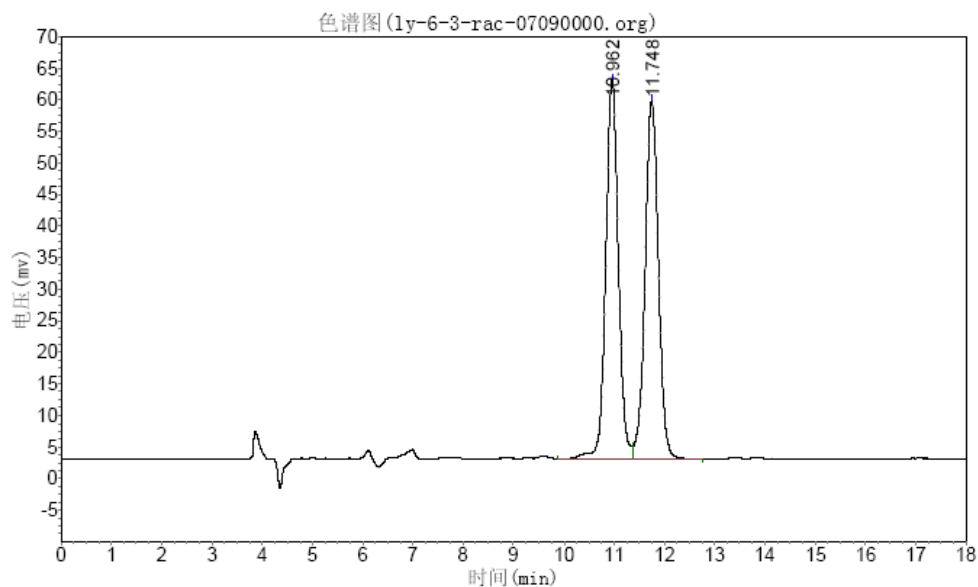
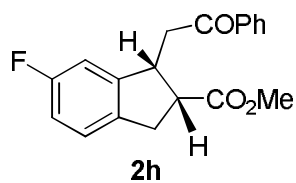
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.233	235027.594	2468364.500	49.9859
2		9.907	221924.031	2469755.250	50.0141
总计			456951.625	4938119.750	100.0000



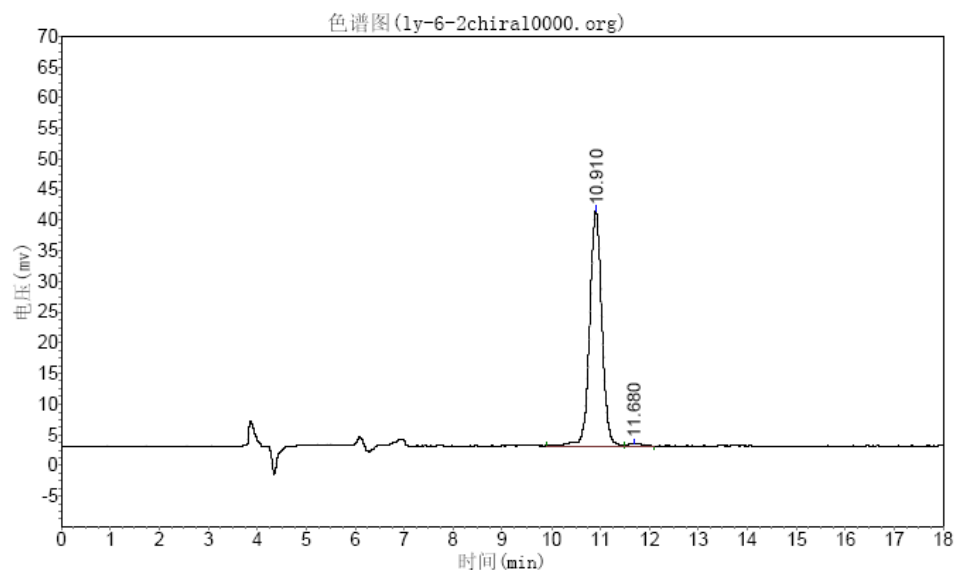
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.617	916.102	9221.451	1.2429
2		10.337	65304.445	732703.625	98.7571
总计			66220.547	741925.076	100.0000



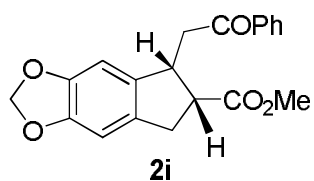
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		10.962	60153.574	1045236.125	50.1799
2		11.748	56884.297	1037743.500	49.8201
总计			117037.871	2082979.625	100.0000

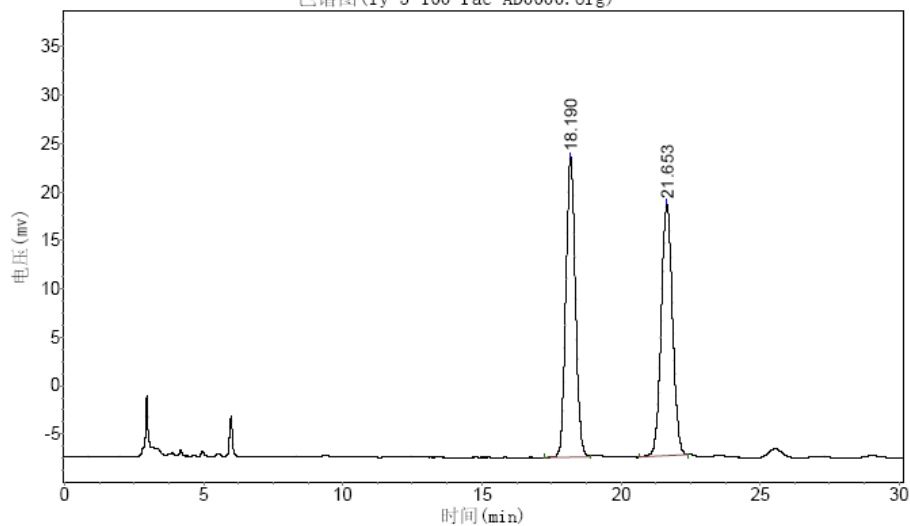


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		10.910	38292.551	655085.625	98.9887
2		11.680	333.082	6692.795	1.0113
总计			38625.632	661778.420	100.0000



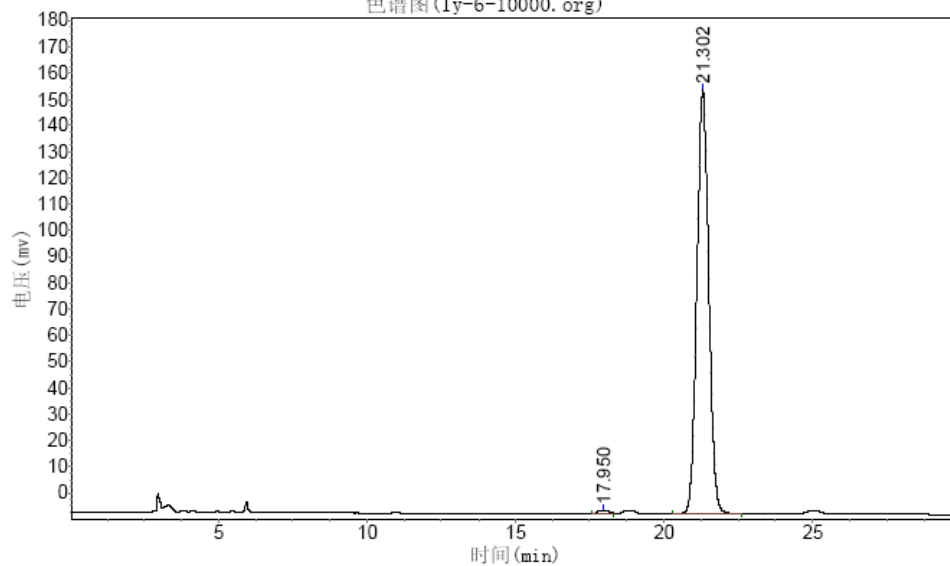
色谱图(ly-5-100-rac-AD0000.org)



分析结果表

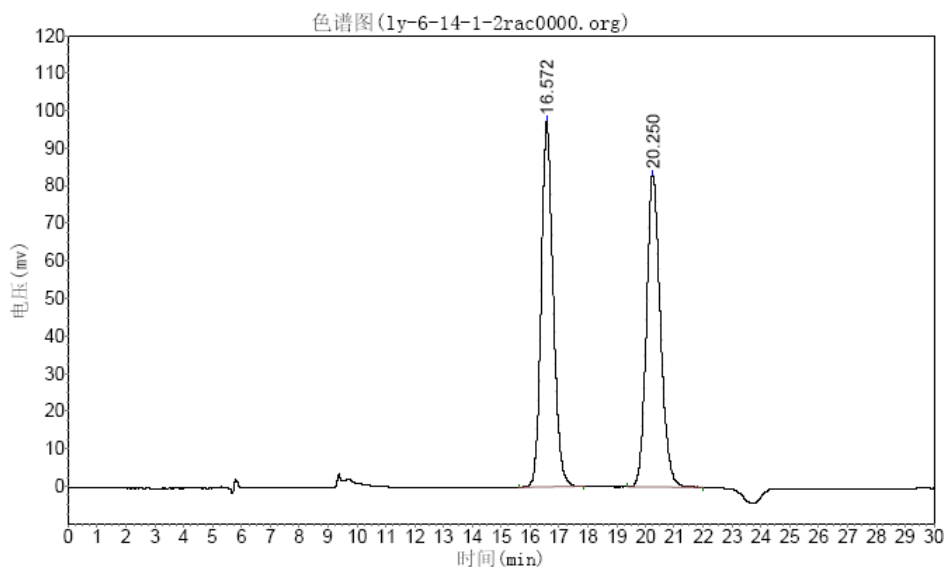
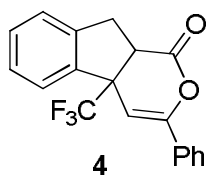
峰号	峰名	保留时间	峰高	峰面积	含量
1		18.190	31043.316	737097.813	49.8967
2		21.653	26021.428	740150.000	50.1033
总计			57064.744	1477247.813	100.0000

色谱图(ly-6-10000.org)



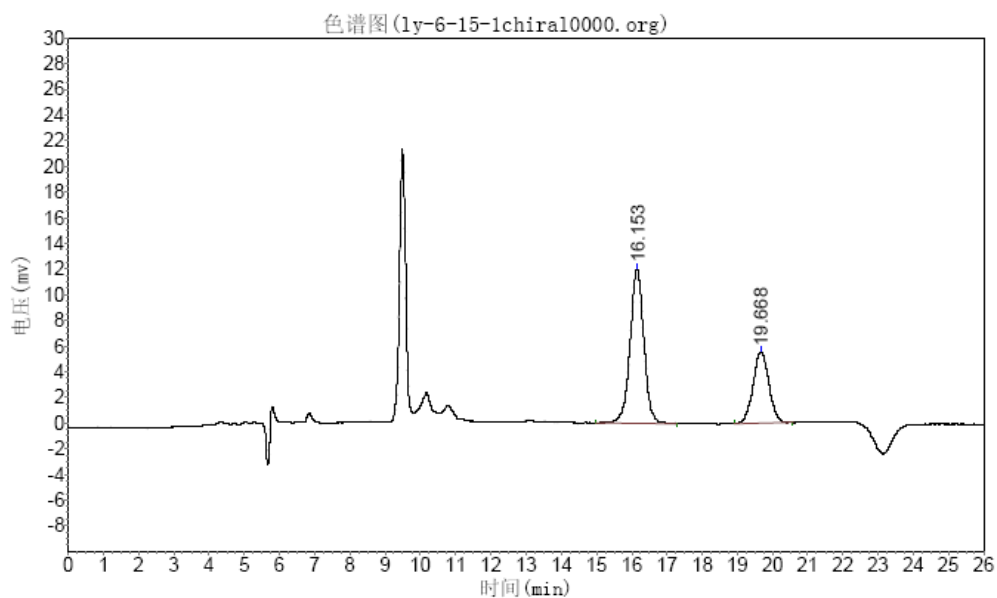
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		17.950	1238.301	26040.285	0.5735
2		21.302	161824.609	4514940.500	99.4266
总计			163062.911	4540980.785	100.0000



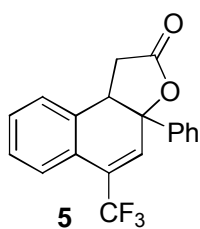
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.572	97502.891	2810401.500	49.9252
2		20.250	83126.211	2818823.750	50.0748
总计			180629.102	5629225.250	100.0000

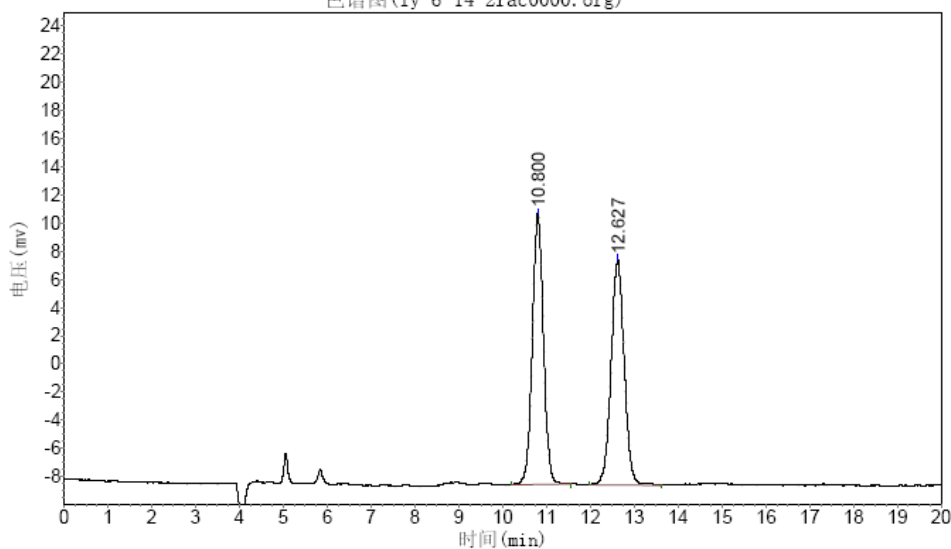


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.153	12064.179	329533.688	65.4523
2		19.668	5566.382	173937.531	34.5477
总计			17630.561	503471.219	100.0000



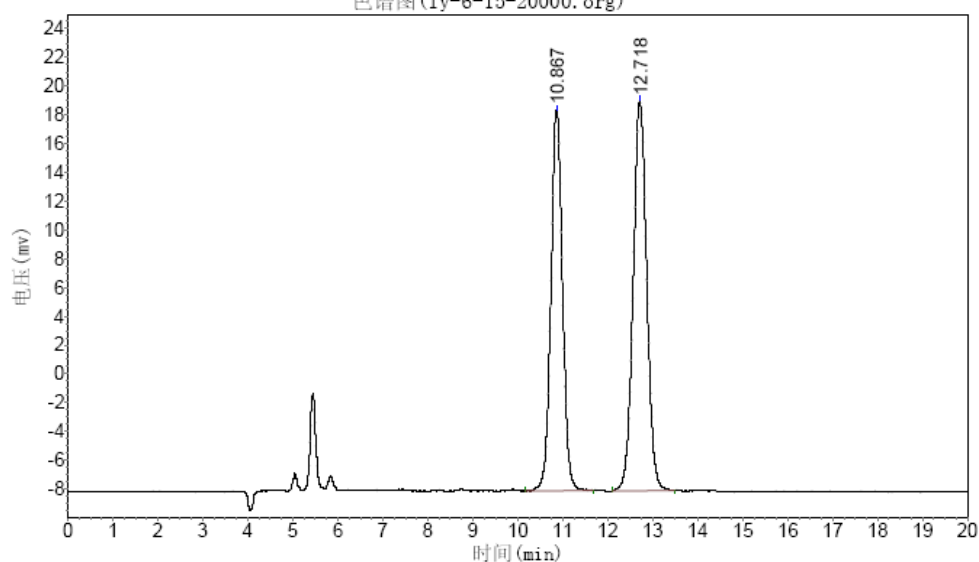
色谱图(1y-6-14-2rac0000.org)



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		10.800	19277.170	339957.063	50.3245
2		12.627	16030.122	335572.344	49.6755
总计			35307.292	675529.406	100.0000

色谱图(1y-6-15-20000.org)



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		10.867	26448.898	471398.406	45.2570
2		12.718	27123.094	570204.188	54.7430
总计			53571.992	1041602.594	100.0000

X-ray structure of **3**

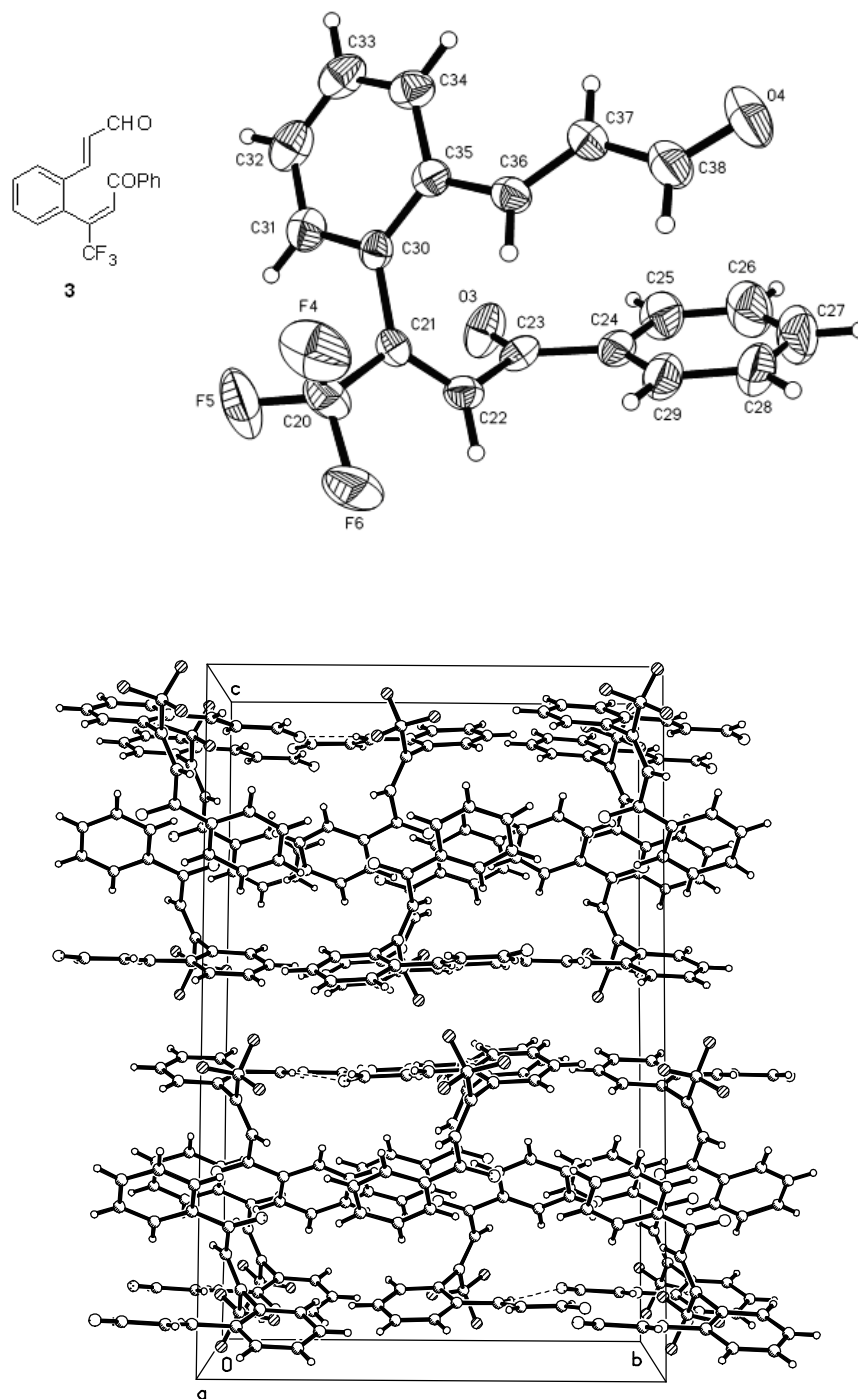


Table 1. Crystal data and structure refinement for **3**.

Identification code	cd28459
Empirical formula	$\text{C}_{19}\text{H}_{13}\text{F}_3\text{O}_2$
Formula weight	330.29
Temperature	293(2) K
Wavelength	0.71073 Å

Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 8.9074(11) Å α = 90 deg. b = 15.5638(19) Å β = 95.334(2) deg. c = 24.123(3) Å γ = 90 deg.
Volume	3329.7(7) Å ³
Z, Calculated density	8, 1.318 Mg/m ³
Absorption coefficient	0.107 mm ⁻¹
F(000)	1360
Crystal size	0.403 x 0.352 x 0.278 mm
Theta range for data collection	1.56 to 25.50 deg.
Limiting indices	-7<=h<=10, -18<=k<=18, -29<=l<=29
Reflections collected / unique	17167 / 6205 [R(int) = 0.0551]
Completeness to theta = 25.50	100.0 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.7964
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6205 / 0 / 433
Goodness-of-fit on F ²	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0815, wR2 = 0.1924
R indices (all data)	R1 = 0.1676, wR2 = 0.2309
Largest diff. peak and hole	0.211 and -0.200 e. Å ⁻³