

Supporting information

Unexpected Reaction of Dimethyl Acetylenedicarboxylate with in Situ Generated Arylketenes Catalyzed By 1-Methylimidazole

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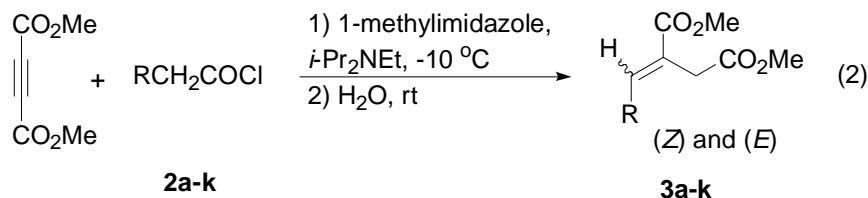
Experimental Procedures

General :

Melting points are uncorrected. NMR experiments were performed at 500 MHz or 400 MHz (Bruker Avance DMX 500 and 400 instruments) with internal standard TMS (¹H NMR) and the solvent signal (¹³C NMR). GC-MS analyses were performed on a HP-5973 spectrometer.

General experimental Procedure for **1** and **3a-k**:

A mixture of DMAD (2 mmol) and phenylacetyl chloride (2 mmol) in DCM (3 ml) was added dropwise to the solution of 1-methylimidazole (2 mmol) and *i*-Pr₂NEt (3 mmol) in dry DCM (5 ml) under a nitrogen atmosphere at -10 °C, and the resulting solution was stirred for 6 h. Afterward, the reaction solution was allowed to warm to r.t, and water (2 mmol) was added. After additional 2 days at this temperature, the solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ethyl acetate mixture (7:1) to afford dimethyl 2-arylidene-succinates (*E*)-**3a**, and (*Z*)-**3a**.

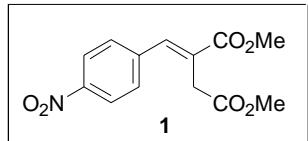


Isotopic Labeling Experiment (Compound **4**)

A mixture of DMAD (2 mmol) and phenylacetyl chloride (2 mmol) in DCM (3 ml) was added dropwise to the solution of 1-methylimidazole (2 mmol) and *i*-Pr₂NEt (3 mmol) in dry DCM (5 ml) under a nitrogen atmosphere at -10 °C, and the resulting solution was stirred for 6 h. Afterward, the reaction solution was allowed to warm to r.t, and D₂O (2 mmol) was added. After additional 2 days at this temperature, the solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a hexane-ethyl acetate mixture (7:1) to afford compound (*Z*)-**4**.

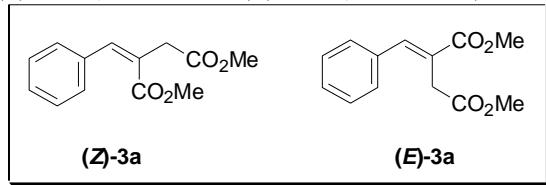
Characterization Data:

Compound **1**



1: Pale yellow crystal, yield: 363 mg, 65%, **m.p.** 111-112 °C. **IR** (KBr): ν_{max} 2954, 1736, 1716, 1637, 1517, 1436, 1348, 1295, 1207, 853 cm⁻¹; **¹H NMR** (500MHz, CDCl₃, TMS) δ 8.26 (d, 2H, *J*=8.5Hz), 7.92 (s, 1H), 7.52 (d, 2H, *J*=8.5Hz), 3.86 (s, 3H), 3.76 (s, 3H), 3.49 (s, 2H); **¹³C NMR** (125MHz, CDCl₃, TMS) δ 171.2, 167.2, 148.0, 141.6, 139.8, 129.9, 129.2, 124.1, 52.8, 52.7, 33.7; **MS** (EI) *m/z*: 279 (M⁺), 247 [(M-32)⁺], 130 [(M-149)⁺], 115 [(M-164)⁺], 59 [(M-220)⁺].

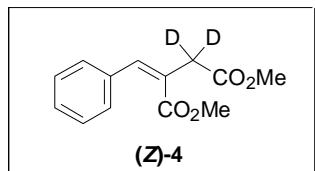
Compound **3a** (GC-MS: (*Z*)-**3a**, $R_t = 6.19$ min; (*E*)-**3a**, $R_t = 6.42$ min)



(Z)-3a: Colorless oil, yield: 214 mg, 46%. **IR** (Neat): ν_{max} 2953, 1743, 1716, 1637, 1494, 1462, 1436, 1377, 1342, 1259, 1125, 693 cm⁻¹; **¹H NMR** (500MHz, CDCl₃, TMS) δ 7.32-7.28 (m, 5H), 6.89 (s, 1H), 3.72 (s, 3H), 3.65 (s, 3H), 3.48 (s, 2H); **¹³C NMR** (125MHz, CDCl₃, TMS) δ 171.4, 168.4, 139.7, 135.7, 128.8, 128.5, 128.2, 126.5, 52.4, 52.0, 40.9; **MS** (EI) m/z: 234 (M⁺), 202 [(M-32)⁺], 174 [(M-60)⁺], 115 [(M-119)⁺].

(E)-3a: Colorless oil, yield: 57 mg, 12%. **IR** (Neat): ν_{max} 2952, 1740, 1713, 1640, 1494, 1436, 1374, 1270, 1203, 703 cm⁻¹; **¹H NMR** (500MHz, CDCl₃, TMS) δ 7.91 (s, 1H), 7.41-7.33 (m, 5H), 3.83 (s, 3H), 3.74 (s, 3H), 3.55 (s, 2H); **¹³C NMR** (125MHz, CDCl₃, TMS) δ 171.9, 168.1, 142.4, 135.1, 129.3, 129.2, 128.9, 126.1, 52.6, 52.4, 33.7; **MS** (EI) m/z: 234 (M⁺), 202 [(M-32)⁺], 174 [(M-60)⁺], 115 [(M-119)⁺].

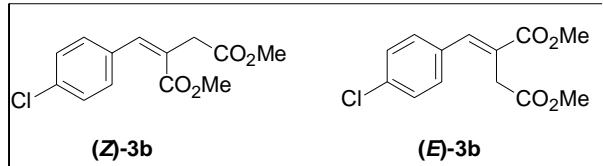
Compound (*Z*)-**4**



(Z)-4: Colorless oil, yield: 208 mg, 44%.

¹H NMR(500MHz, CDCl₃, TMS) δ 7.32-7.28 (m, 5H), 6.89 (s, 1H), 3.72 (s, 3H), 3.65 (s, 3H).

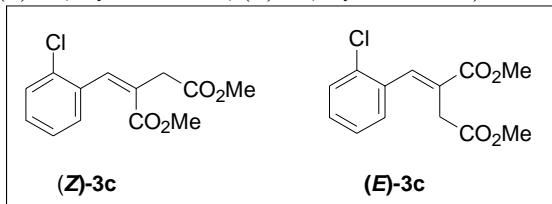
Compound **3b** (GC-MS: (*Z*)-**3b**, $R_t = 5.97$ min; (*E*)-**3b**, $R_t = 6.10$ min)



(Z)-3b: Colorless oil, yield: 242 mg, 45%. **IR** (Neat): ν_{max} 2952, 1738, 1720, 1641, 1490, 1436, 1343, 1208, 806 cm⁻¹; **¹H NMR** (500MHz, CDCl₃, TMS) δ 7.29 (d, $J=8.5$ Hz, 2H), 7.23 (d, $J=8.5$ Hz, 2H), 6.83 (s, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 3.47 (s, 2H); **¹³C NMR** (100MHz, CDCl₃, TMS) δ 171.1, 167.8, 138.6, 134.3, 134.0, 130.0, 128.3, 127.1, 52.2, 51.9, 40.6; **MS** (EI) m/z: 268 (M⁺), 236 [(M-32)⁺], 208 [(M-60)⁺], 149 [(M-119)⁺], 115 [(M-153)⁺].

(E)-3b: Colorless oil, yield: 37 mg, 7%. **IR** (Neat): ν_{max} 2953, 1740, 1716, 1642, 1491, 1436, 1330, 1282, 1202, 843 cm^{-1} ; **$^1\text{H NMR}$** (500MHz, CDCl_3 , TMS) δ 7.85 (s, 1H), 7.37 (d, $J=8.5\text{Hz}$, 2H), 7.28 (d, $J=8.5\text{Hz}$, 2H), 3.83 (s, 3H), 3.74 (s, 3H), 3.51 (s, 2H); **$^{13}\text{C NMR}$** (100MHz, CDCl_3 , TMS) δ 171.8, 168.0, 141.1, 135.3, 133.6, 130.6, 129.2, 126.8, 52.7, 52.5, 33.7; **MS** (EI) m/z: 268 (M^+), 236 [$(\text{M}-32)^+$], 208 [$(\text{M}-60)^+$], 149 [$(\text{M}-119)^+$], 115 [$(\text{M}-153)^+$].

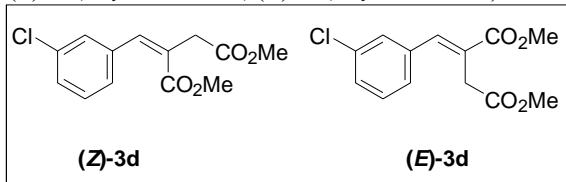
Compound **3c** (GC-MS: **(Z)-3c**, $R_t = 8.79$ min; **(E)-3c**, $R_t = 9.05$ min)



(Z)-3c: Colorless oil, yield: 140 mg, 26%. **IR** (Neat): ν_{max} 2952, 1738, 1716, 1646, 1435, 1212, 1055, 756 cm^{-1} ; **$^1\text{H NMR}$** (400MHz, CDCl_3 , TMS) 87.37 (d, $J=7.2\text{Hz}$, 1H), 7.26-7.21 (m, 3H), 6.99 (s, 1H), 3.74 (s, 3H), 3.59 (s, 3H), 3.52 (s, 2H); **$^{13}\text{C NMR}$** (100MHz, CDCl_3 , TMS) δ 171.1, 167.4, 137.5, 134.7, 133.0, 130.2, 129.5, 129.2, 128.3, 126.2, 52.2, 51.8, 40.1; **MS** (EI) m/z: 233 [$(\text{M}-35)^+$], 149 [$(\text{M}-119)^+$], 115 [$(\text{M}-153)^+$], 59 [$(\text{M}-209)^+$].

(E)-3c: Colorless oil, yield: 64 mg, 12%. **IR** (Neat): ν_{max} 2922, 1740, 1716, 1646, 1469, 1437, 1330, 1290, 1204, 771 cm^{-1} ; **$^1\text{H NMR}$** (500MHz, CDCl_3 , TMS) δ 7.95 (s, 1H), 7.43 (d, $J=7.5\text{Hz}$, 1H), 7.32-7.30 (m, 3H), 3.85 (s, 3H), 3.73 (s, 3H), 3.42 (s, 2H); **$^{13}\text{C NMR}$** (125MHz, CDCl_3 , TMS) δ 171.7, 167.5, 139.6, 134.3, 133.8, 130.4, 130.2, 129.9, 127.9, 127.1, 52.7, 52.5, 33.9; **MS** (EI) m/z: 233 [$(\text{M}-35)^+$], 149 [$(\text{M}-119)^+$], 115 [$(\text{M}-153)^+$], 59 [$(\text{M}-209)^+$].

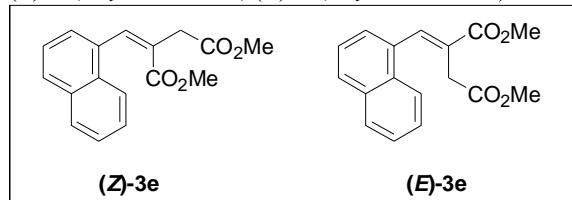
Compound **3d** (GC-MS: **(Z)-3d**, $R_t = 9.04$ min; **(E)-3d**, $R_t = 9.14$ min)



(Z)-3d: Colorless oil, yield: 200 mg, 37%. **IR** (Neat): ν_{max} 2952, 1736, 1718, 1643, 1566, 1437, 1342, 1284, 1208, 785 cm^{-1} ; **$^1\text{H NMR}$** (500MHz, CDCl_3 , TMS) δ 7.25-7.23 (m, 3H), 7.13 (d, $J=6.1\text{Hz}$, 1H), 6.80 (s, 1H), 3.70 (s, 3H), 3.63 (s, 3H), 3.45 (s, 2H); **$^{13}\text{C NMR}$** (100MHz, CDCl_3 , TMS) δ 171.0, 167.7, 138.1, 137.3, 134.0, 129.3, 128.6, 128.3, 127.9, 126.7, 52.2, 51.9, 40.5; **MS** (EI) m/z: 268 (M^+), 236 [$(\text{M}-32)^+$], 208 [$(\text{M}-60)^+$], 149 [$(\text{M}-119)^+$], 129 [$(\text{M}-139)^+$], 115 [$(\text{M}-153)^+$], 59 [$(\text{M}-209)^+$].

(E)-3d: Colorless oil, yield: 47 mg, 9%. IR (Neat): ν_{max} 2953, 1732, 1716, 1644, 1566, 1436, 1330, 1284, 1204, 790 cm⁻¹; **¹H NMR** (500MHz, CDCl₃, TMS) δ 7.83 (s, 1H), 7.33 (d, *J*=4.5Hz, 3H), 7.23-7.22 (m, 1H, Ar), 3.83 (s, 3H), 3.74 (s, 3H), 3.51 (s, 2H); **¹³C NMR** (100MHz, CDCl₃, TMS) δ 171.3, 167.5, 140.6, 136.8, 134.7, 130.0, 129.0, 128.9, 127.3, 127.0, 52.5, 52.3, 33.5; **MS (EI)** m/z: 268 (M⁺), 236 [(M-32)⁺], 208 [(M-60)⁺], 149 [(M-119)⁺], 129 [(M-139)⁺], 115 [(M-153)⁺], 59 [(M-209)⁺].

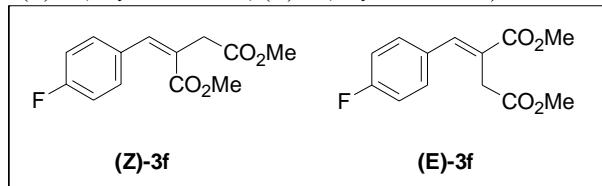
Compound **3e** (GC-MS: (Z)-3e, R_t = 9.58 min; (E)-3e, R_t = 10.31 min)



(Z)-3e: Colorless oil, yield: 187 mg, 33%. **IR** (Neat): ν_{max} 2951, 1737, 1712, 1643, 1507, 1435, 1341, 1212, 779 cm⁻¹; **¹H NMR** (500MHz, CDCl₃, TMS) δ 7.92 (d, *J*=9.0Hz, 1H), 7.85 (d, *J*=9.0Hz, 1H), 7.80 (d, *J*=8.5Hz, 1H), 7.51-7.48 (m, 2H), 7.44-7.34 (m, 3H), 3.77 (s, 3H), 3.61 (s, 2H), 3.41 (s, 3H); **¹³C NMR** (125MHz, CDCl₃, TMS) δ 171.6, 167.8, 139.4, 134.0, 133.5, 131.3, 129.0, 128.7, 128.6, 126.5, 126.2, 126.0, 125.3, 124.8, 52.4, 51.8, 40.3; **MS (EI)** m/z: 284 (M⁺), 224 [(M-60)⁺], 210 [(M-74)⁺], 165 [(M-119)⁺].

(E)-3e: Colorless oil, yield: 125 mg, 22%. **IR** (Neat): ν_{max} 2951, 1740, 1716, 1643, 1508, 1436, 1329, 1282, 1200, 806 cm⁻¹; **¹H NMR** (500MHz, CDCl₃, TMS) δ 8.41 (s, 1H), 7.93-7.87 (m, 3H), 7.55-7.53 (m, 2H), 7.50-7.41 (m, 2H), 3.90 (s, 3H), 3.71 (s, 3H), 3.45 (s, 2H); **¹³C NMR** (125MHz, CDCl₃, TMS) δ 171.9, 167.7, 141.1, 133.6, 132.5, 131.6, 129.5, 128.8, 128.3, 126.8, 126.6, 126.5, 125.5, 124.8, 52.6, 52.3, 34.0; **MS (EI)** m/z: 284 (M⁺), 224 [(M-60)⁺], 210 [(M-74)⁺], 165 [(M-119)⁺].

Compound **3f** (GC-MS: (Z)-3f, R_t = 4.57 min; (E)-3f, R_t = 4.69 min)

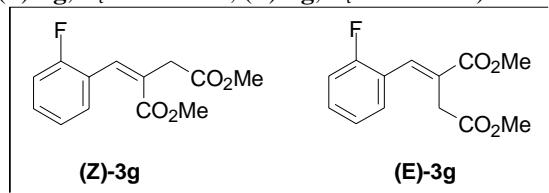


(Z)-3f: Colorless oil, yield: 210 mg, 42%. **IR** (Neat): ν_{max} 2954, 1739, 1716, 1602, 1509, 1437, 1343, 1270, 1223, 845 cm⁻¹; **¹H NMR** (500MHz, CDCl₃, TMS) δ 7.31-7.28 (m, 2H), 7.01 (t, *J*=8.5Hz, 2H), 6.84 (s, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 3.47 (s, 2H); **¹³C NMR** (125MHz, CDCl₃, TMS) δ 171.3,

168.0, 163.8, 161.8, 139.0, 131.7, 130.8, 126.5, 115.3, 115.2, 52.3, 52.0, 40.8; **MS** (EI) m/z: 252 (M^+), 220 [(M-32) $^+$], 192 [(M-60) $^+$], 133 [(M-119) $^+$].

(E)-3f: Colorless oil, yield: 56 mg, 11%. **IR** (Neat): ν_{max} 2954, 1740, 1712, 1601, 1509, 1437, 1331, 1269, 1227, 845 cm $^{-1}$; **¹H NMR** (500MHz, CDCl $_3$, TMS) δ 7.86 (s, 1H), 7.36-7.33 (m, 2H), 7.10 (t, J =8.5Hz, 2H), 3.84 (s, 3H), 3.74 (s, 3H), 3.52 (s, 2H); **¹³C NMR** (125MHz, CDCl $_3$, TMS) δ 171.8, 167.9, 164.2, 162.2, 141.3, 131.3, 131.2, 126.0, 116.1, 116.0, 52.6, 52.5, 33.6; **MS** (EI) m/z: 252 (M^+), 220 [(M-32) $^+$], 192 [(M-60) $^+$], 133 [(M-119) $^+$].

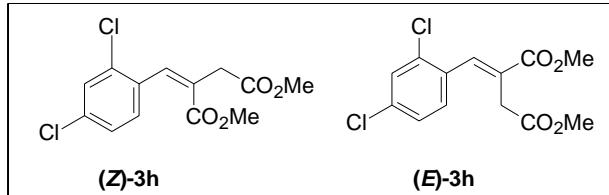
Compound **3g** (GC-MS: (Z)-3g, R $_t$ = 7.90 min; (E)-3g, R $_t$ = 8.03 min)



(Z)-3g: Colorless oil, yield: 149 mg, 30%. **IR** (Neat): ν_{max} 2954, 1740, 1716, 1612, 1489, 1437, 1344, 1272, 1209, 760 cm $^{-1}$; **¹H NMR** (500MHz, CDCl $_3$, TMS) δ 7.30-7.26 (m, 2H), 7.11-7.02 (m, 2H), 6.85 (s, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.51 (s, 2H); **¹³C NMR** (125MHz, CDCl $_3$, TMS) δ 171.2, 167.7, 161.1, 159.1, 132.9, 130.5, 130.3, 129.0, 123.8, 115.5, 52.4, 52.0, 40.6; **MS** (EI) m/z: 252 (M^+), 220 [(M-32) $^+$], 192 [(M-60) $^+$], 133 [(M-119) $^+$].

(E)-3g: Colorless oil, yield: 58 mg, 11%. **IR** (Neat): ν_{max} 2954, 1740, 1716, 1647, 1486, 1436, 1331, 1273, 1201, 760 cm $^{-1}$; **¹H NMR** (500MHz, CDCl $_3$, TMS) δ 7.89 (s, 1H), 7.37-7.31 (m, 2H), 7.18-7.09 (m, 2H), 3.84 (s, 3H), 3.73 (s, 3H), 3.48 (s, 2H); **¹³C NMR** (125MHz, CDCl $_3$, TMS) δ 171.6, 167.5, 161.5, 159.5, 135.3, 131.1, 130.3, 128.3, 124.4, 116.1, 52.6, 52.4, 34.0; **MS** (EI) m/z: 252 (M^+), 220 [(M-32) $^+$], 192 [(M-60) $^+$], 133 [(M-119) $^+$].

Compound **3h** (GC-MS: (Z)-3h, R $_t$ = 6.62 min; (E)-3h, R $_t$ = 6.86 min)

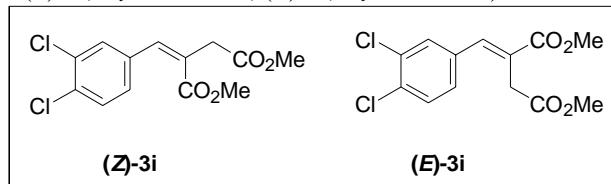


(Z)-3h: Colorless oil, yield: 275 mg, 45%. **IR** (Neat): ν_{max} 2953, 1740, 1716, 1585, 1470, 1436, 1343, 1262, 1221, 766 cm $^{-1}$; **¹H NMR** (500MHz, CDCl $_3$, TMS) δ 7.39 (d, J =2.0Hz, 1H), 7.22-7.18 (m, 2H), 6.90 (s, 1H), 3.73 (s, 3H), 3.60 (s, 3H), 3.50 (s, 2H); **¹³C NMR** (125MHz, CDCl $_3$, TMS) δ 171.1, 167.1, 136.7, 134.8, 133.9, 123.4, 131.2, 129.2, 129.1, 126.8, 52.4, 52.1, 40.2; **MS** (EI) m/z: 267

$[(M-35)^+]$, 183 $[(M-119)^+]$, 149 $[(M-153)^+]$, 59 $[(M-243)^+]$.

(E)-3h: Colorless oil, yield: 106 mg, 18%. **IR** (Neat): ν_{\max} 2954, 1738, 1717, 1585, 1470, 1436, 1330, 1285, 1205, 766 cm^{-1} ; **$^1\text{H NMR}$** (500MHz, CDCl_3 , TMS) δ 7.87 (s, 1H), 7.45 (d, $J=1.5\text{Hz}$, 1H), 7.30-7.26 (m, 2H), 3.85 (s, 3H), 3.73 (s, 3H), 3.39 (s, 2H); **$^{13}\text{C NMR}$** (125MHz, CDCl_3 , TMS) δ 171.5, 167.3, 138.5, 135.7, 135.1, 132.3, 130.9, 129.9, 128.5, 127.5, 52.7, 52.5, 33.9; **MS** (EI) m/z: 267 $[(M-35)^+]$, 183 $[(M-119)^+]$, 149 $[(M-153)^+]$, 59 $[(M-243)^+]$.

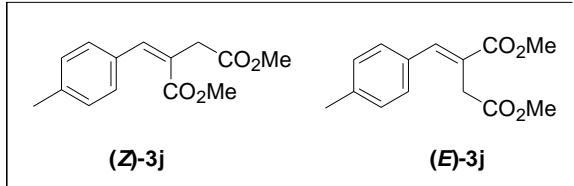
Compound **3i** (GC-MS: *(Z)*-**3i**, $R_t = 7.52 \text{ min}$; *(E)*-**3i**, $R_t = 7.61 \text{ min}$)



(Z)-3i: Waxy solid, yield: 279 mg, 46%. **IR** (Neat): ν_{\max} 2953, 1738, 1716, 1640, 1470, 1436, 1330, 1263, 1205, 818 cm^{-1} ; **$^1\text{H NMR}$** (500MHz, CDCl_3 , TMS) δ 7.38 (d, $J=2.0\text{Hz}$, 1H), 7.37 (s, 1H), 7.13-7.11 (m, 1H), 6.77 (s, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.46 (s, 2H); **$^{13}\text{C NMR}$** (125MHz, CDCl_3 , TMS) δ 171.0, 167.5, 137.4, 135.6, 132.5, 132.4, 130.6, 130.2, 128.4, 128.1, 52.4, 52.2, 40.7; **MS** (EI) m/z: 302 (M^+), 270 $[(M-32)^+]$, 342 $[(M-60)^+]$, 183 $[(M-119)^+]$, 149 $[(M-153)^+]$, 59 $[(M-243)^+]$.

(E)-3i: Colorless oil, yield: 109 mg, 18%. **IR** (Neat): ν_{\max} 2953, 1732, 1716, 1644, 1472, 1436, 1330, 1286, 1204, 824 cm^{-1} ; **$^1\text{H NMR}$** (500MHz, CDCl_3 , TMS) δ 7.79 (s, 1H), 7.49-7.45 (m, 2H), 7.21-7.19 (m, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 3.50 (s, 2H); **$^{13}\text{C NMR}$** (125MHz, CDCl_3 , TMS) δ 171.4, 167.5, 139.8, 135.0, 131.7, 131.0, 130.9, 129.1, 128.3, 127.8, 52.7, 52.6, 33.6; **MS** (EI) m/z: 302 (M^+), 270 $[(M-32)^+]$, 342 $[(M-60)^+]$, 183 $[(M-119)^+]$, 149 $[(M-153)^+]$, 59 $[(M-243)^+]$.

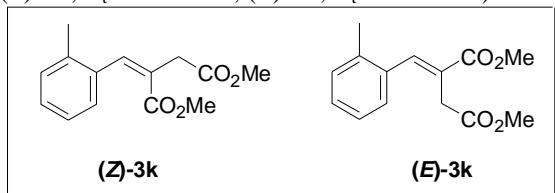
Compound **3j** (GC-MS: *(Z)*-**3j**, $R_t = 5.43 \text{ min}$; *(E)*-**3j**, $R_t = 5.61 \text{ min}$)



(Z)-3j: Colorless oil, yield: 140 mg, 28%. **IR** (Neat): ν_{\max} 2952, 1740, 1713, 1610, 1512, 1436, 1342, 1242, 1206, 810 cm^{-1} ; **$^1\text{H NMR}$** (500MHz, CDCl_3 , TMS) δ 7.19 (d, $J=8.0\text{Hz}$, 2H), 7.12 (d, $J=8.0\text{Hz}$, 2H), 6.84 (s, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.46 (s, 2H), 2.34 (s, 3H); **$^{13}\text{C NMR}$** (125MHz, CDCl_3 , TMS) δ 171.5, 168.5, 139.9, 138.6, 132.7, 129.0, 128.9, 125.6, 52.3, 51.9, 41.0, 21.5; **MS** (EI) m/z: 248 (M^+), 216 $[(M-32)^+]$, 188 $[(M-60)^+]$, 129 $[(M-119)^+]$, 115 $[(M-133)^+]$.

(E)-3j: Colorless oil, yield: 44 mg, 9%. **IR** (Neat): ν_{max} 2952, 1740, 1712, 1640, 1512, 1436, 1330, 1272, 1202, 813 cm^{-1} ; **$^1\text{H NMR}$** (500MHz, CDCl_3 , TMS) δ 7.88 (s, 1H), 7.26-7.21 (m, 4H), 3.83 (s, 3H), 3.74 (s, 3H), 3.56 (s, 2H), 2.37 (s, 3H); **$^{13}\text{C NMR}$** (125MHz, CDCl_3 , TMS) δ 171.9, 168.2, 142.4, 139.4, 132.2, 129.6, 129.3, 125.2, 52.5, 52.4, 33.7, 21.6; **MS (EI)** m/z: 248 (M^+), 216 [$(\text{M}-32)^+$], 188[$(\text{M}-60)^+$], 129 [$(\text{M}-119)^+$], 115 [$(\text{M}-133)^+$].

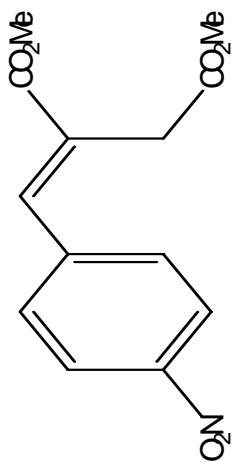
Compound **3k** (GC-MS: **(Z)-3k**, $R_t = 5.02$ min; **(E)-3k**, $R_t = 5.25$ min)



(Z)-3k: Colorless oil, yield: 99 mg, 20%. **IR** (Neat): ν_{max} 2952, 1740, 1713, 1643, 1486, 1342, 1248, 1211, 750 cm^{-1} ; **$^1\text{H NMR}$** (500MHz, CDCl_3 , TMS) δ 7.22-7.20 (m, 2H), 7.19-7.14 (m, 2H), 7.01 (s, 1H), 3.75 (s, 3H), 3.57 (s, 3H), 3.52 (s, 2H), 2.30 (s, 3H); **$^{13}\text{C NMR}$** (125MHz, CDCl_3 , TMS) δ 172.8, 169.1, 141.7, 137.1, 137.0, 131.0, 129.5, 129.4, 128.5, 126.7, 53.5, 53.0, 41.5, 21.3; **MS (EI)** m/z: 248 (M^+), 216 [$(\text{M}-32)^+$], 184[$(\text{M}-64)^+$], 157 [$(\text{M}-91)^+$], 129 [$(\text{M}-119)^+$], 115 [$(\text{M}-133)^+$].

(E)-3k: Colorless oil, yield: 75 mg, 15%. **IR** (Neat): ν_{max} 2952, 1740, 1716, 1643, 1485, 1436, 1329, 1269, 1120, 772 cm^{-1} ; **$^1\text{H NMR}$** (500MHz, CDCl_3 , TMS) δ 7.95 (s, 1H), 7.26-7.19 (m, 4H), 3.84 (s, 3H), 3.71 (s, 3H), 3.40 (s, 2H), 2.29 (s, 3H); **$^{13}\text{C NMR}$** (125MHz, CDCl_3 , TMS) δ 171.9, 167.8, 142.0, 137.1, 134.5, 130.4, 129.0, 128.4, 126.8, 126.1, 52.5, 52.3, 33.6, 20.1; **MS (EI)** m/z: 248 (M^+), 216 [$(\text{M}-32)^+$], 184[$(\text{M}-64)^+$], 157 [$(\text{M}-91)^+$], 129 [$(\text{M}-119)^+$], 115 [$(\text{M}-133)^+$].

0.003



3.489

3.756

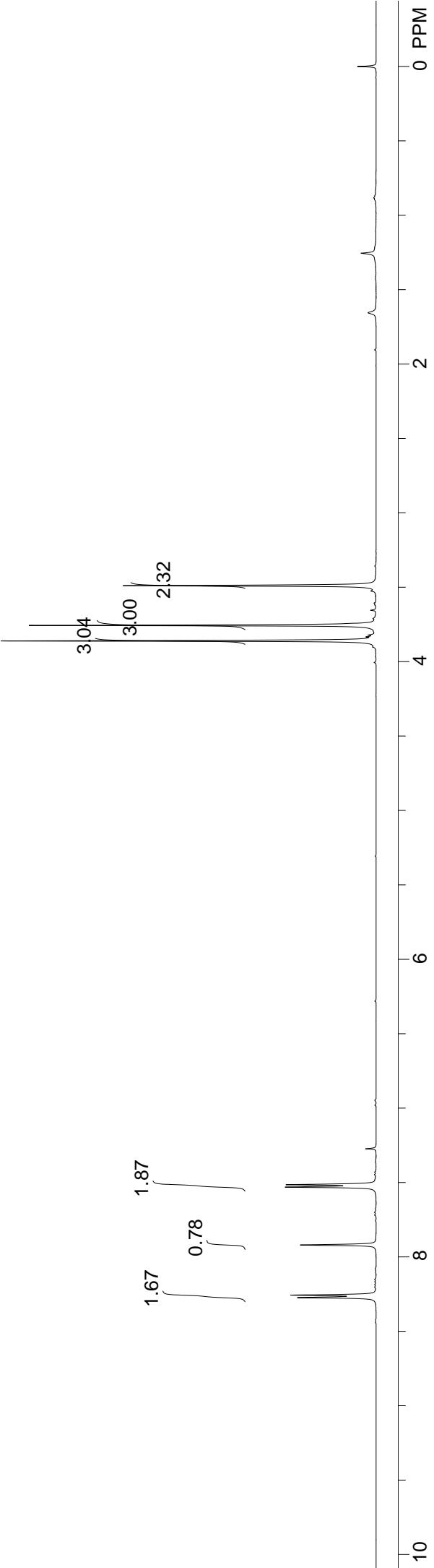
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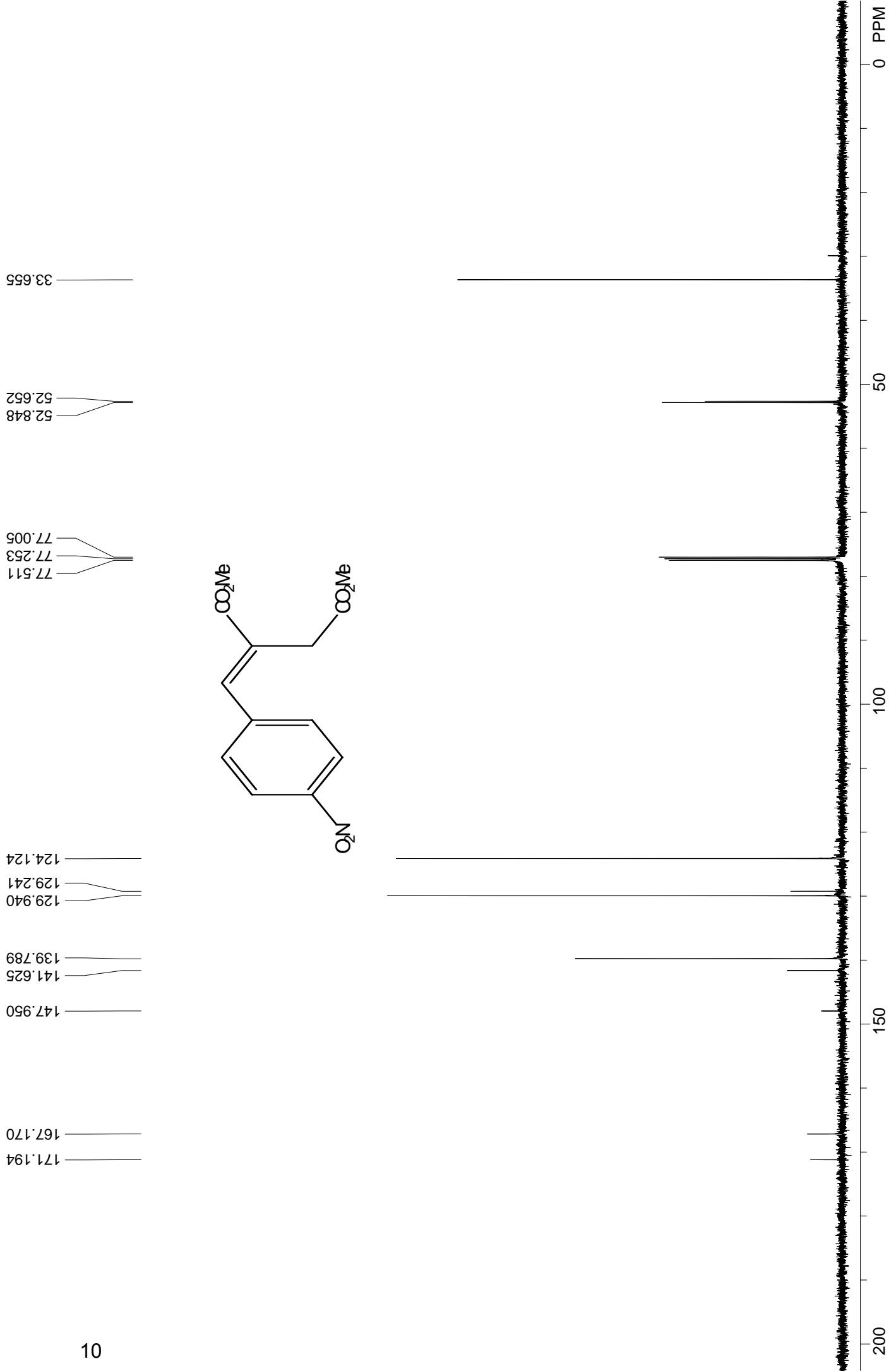
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7.920

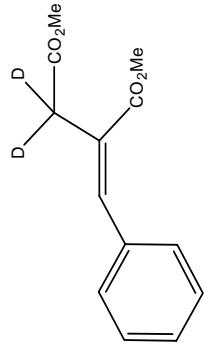
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8.257

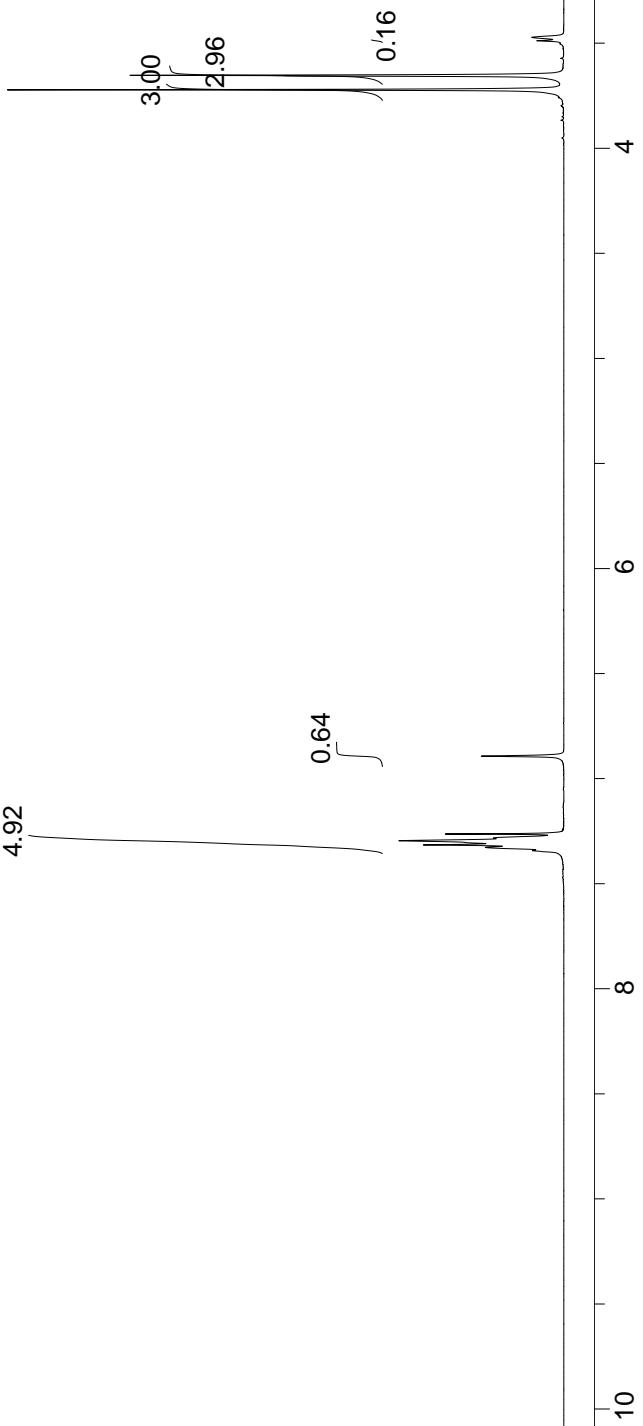




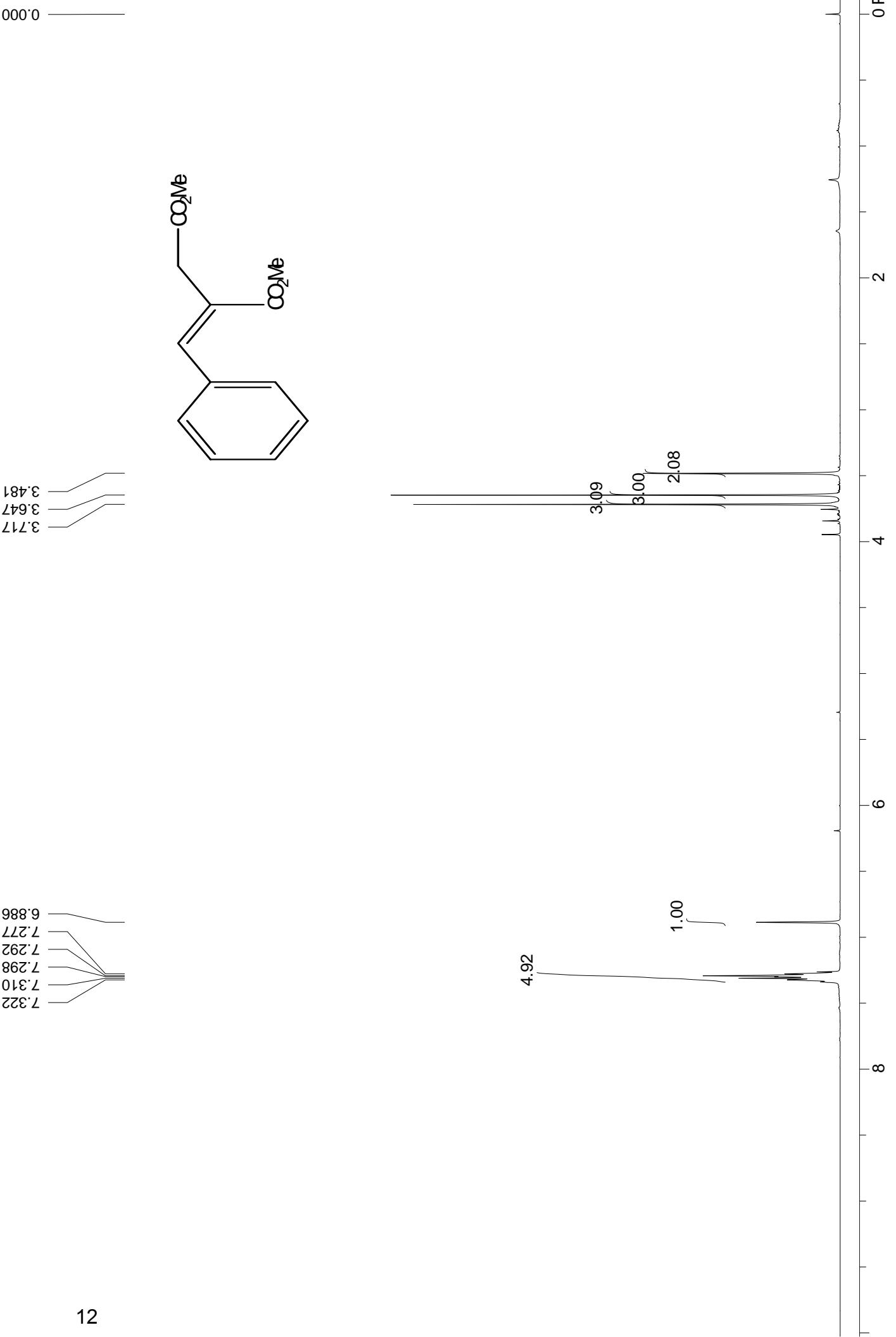
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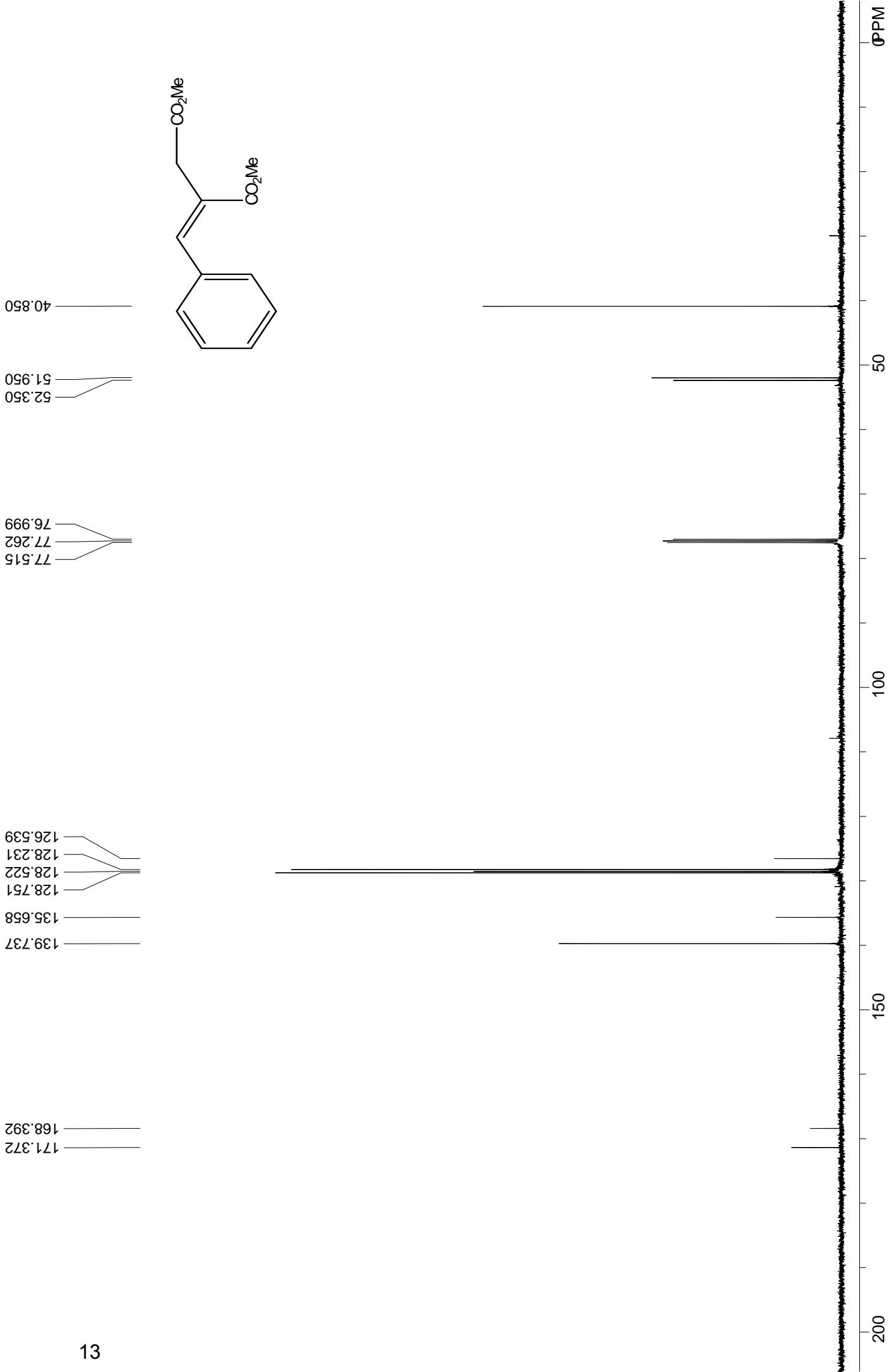


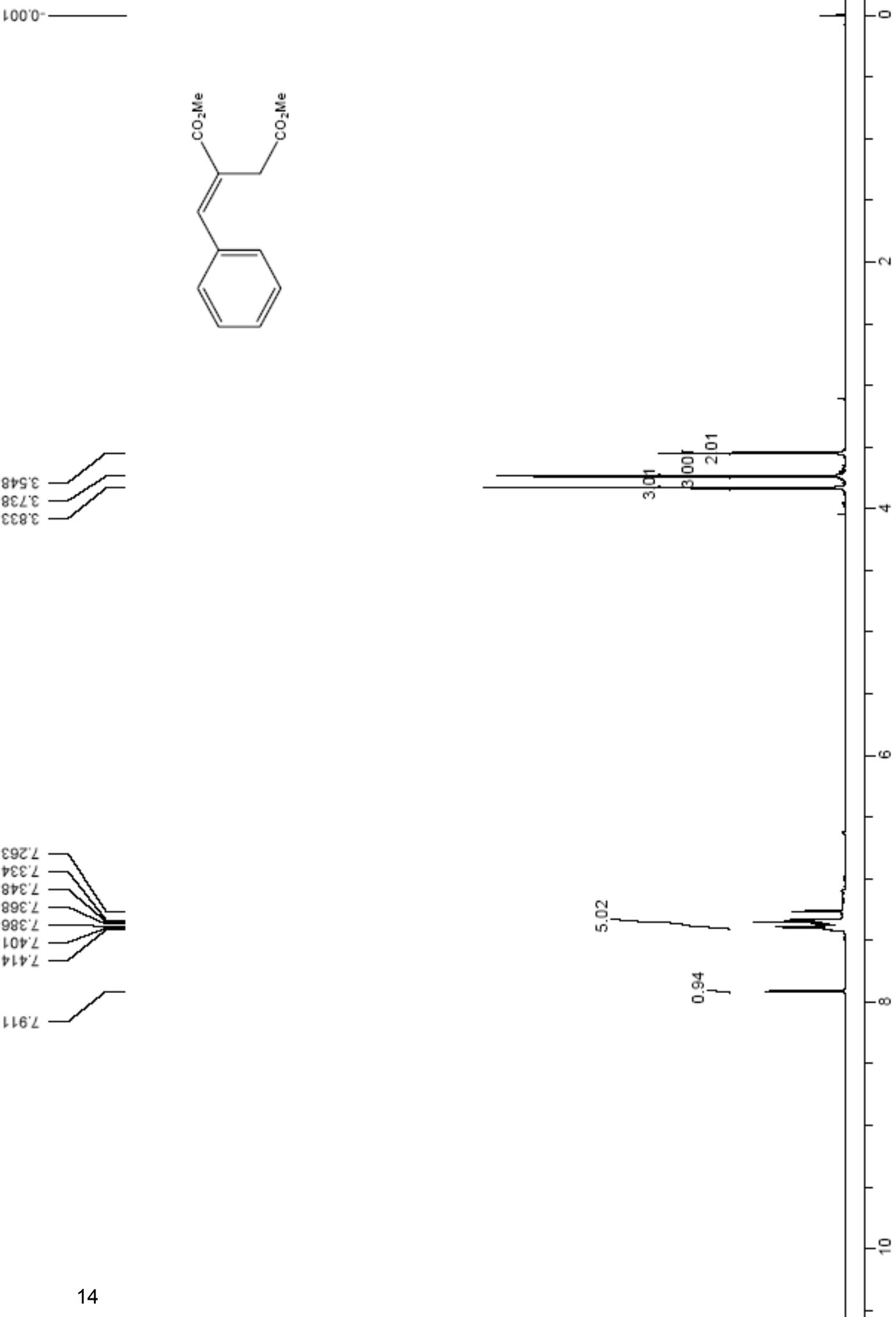
3.721
3.652
3.488

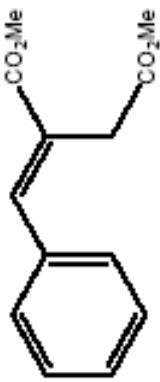


7.327
7.315
7.295
7.282
7.263
6.893









33.697

52.545
52.447

77.511
77.264
77.009

135.130
129.247
129.177
128.878
126.085

142.399

171.868
168.053

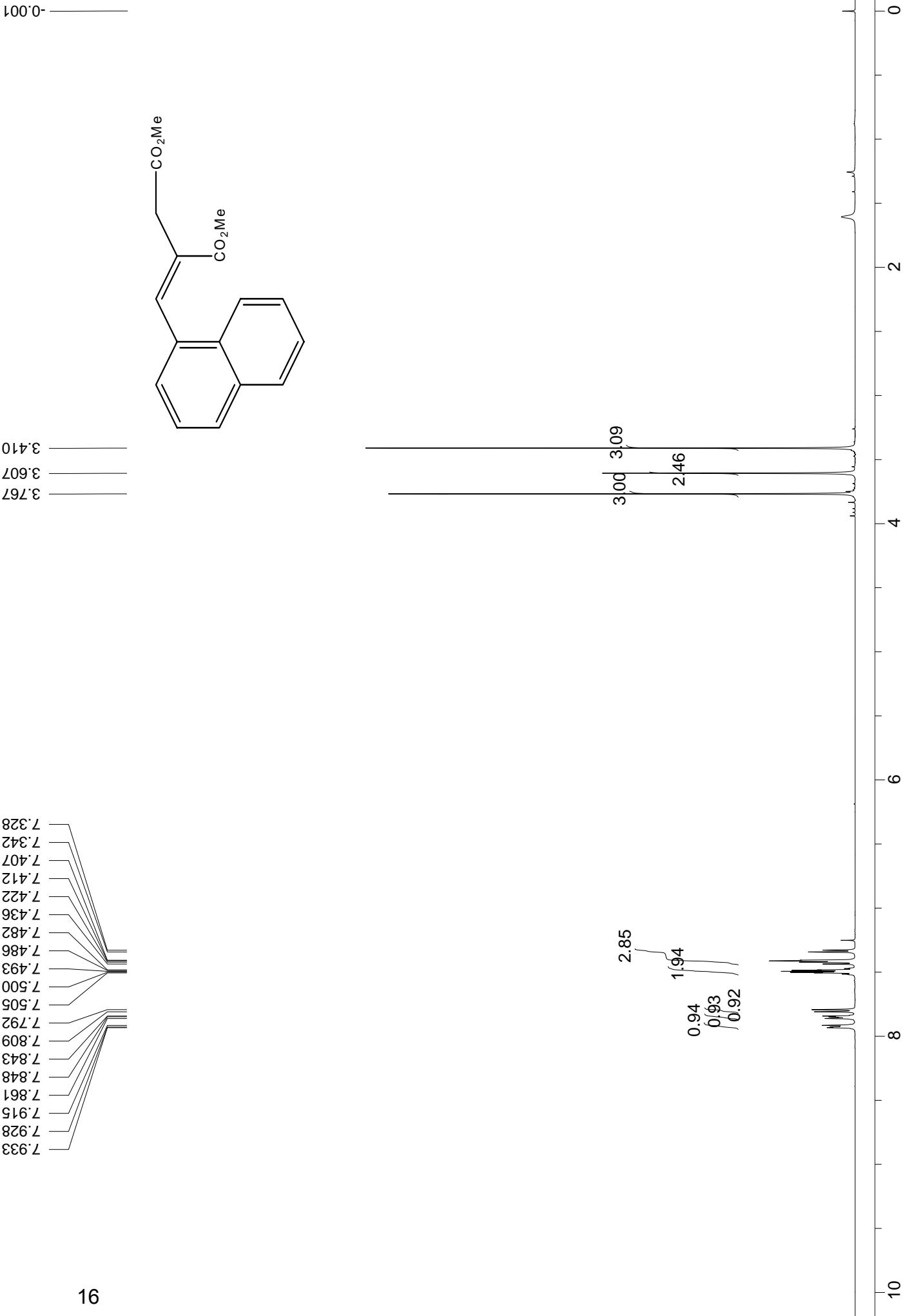
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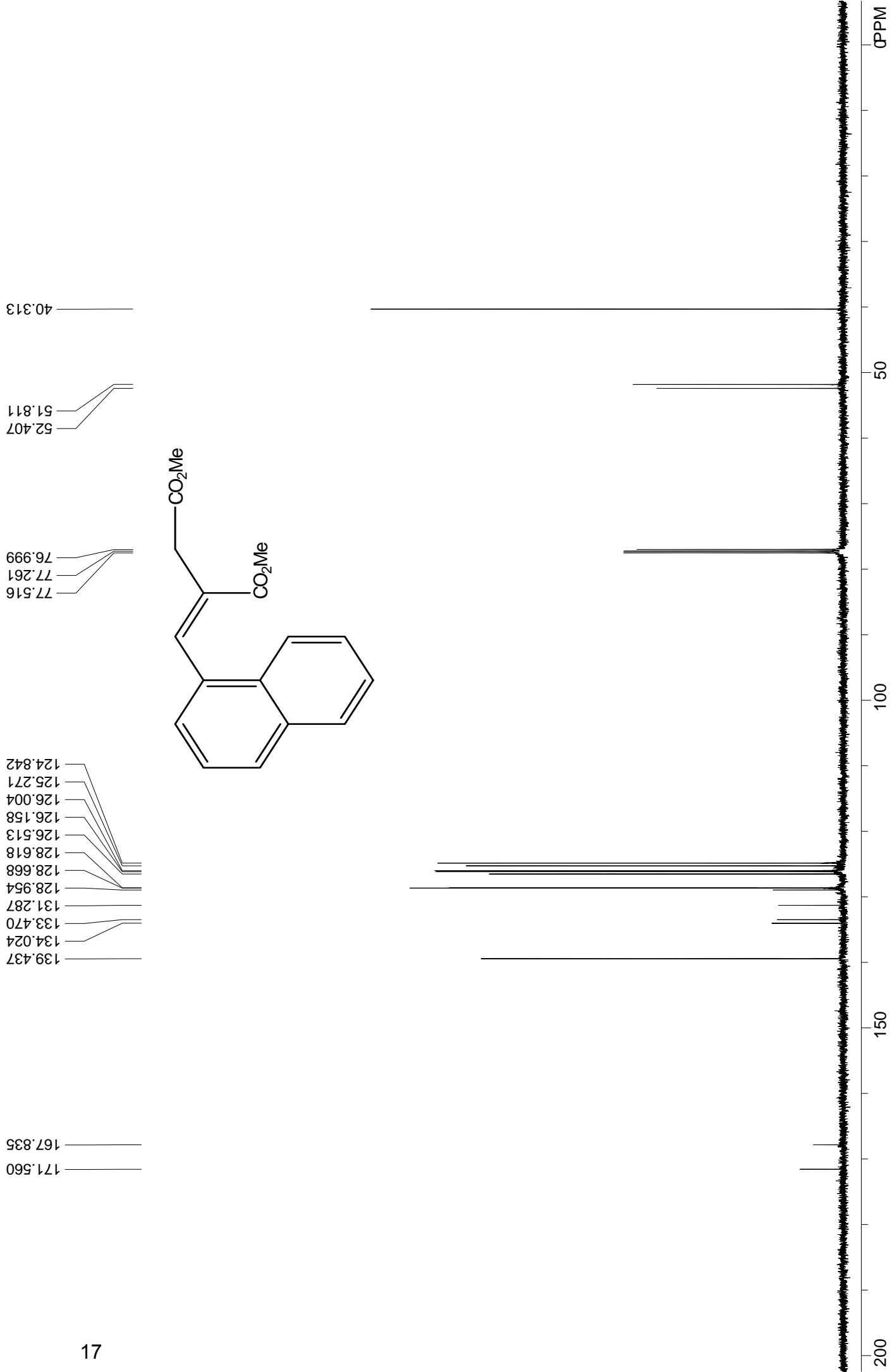
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100

150

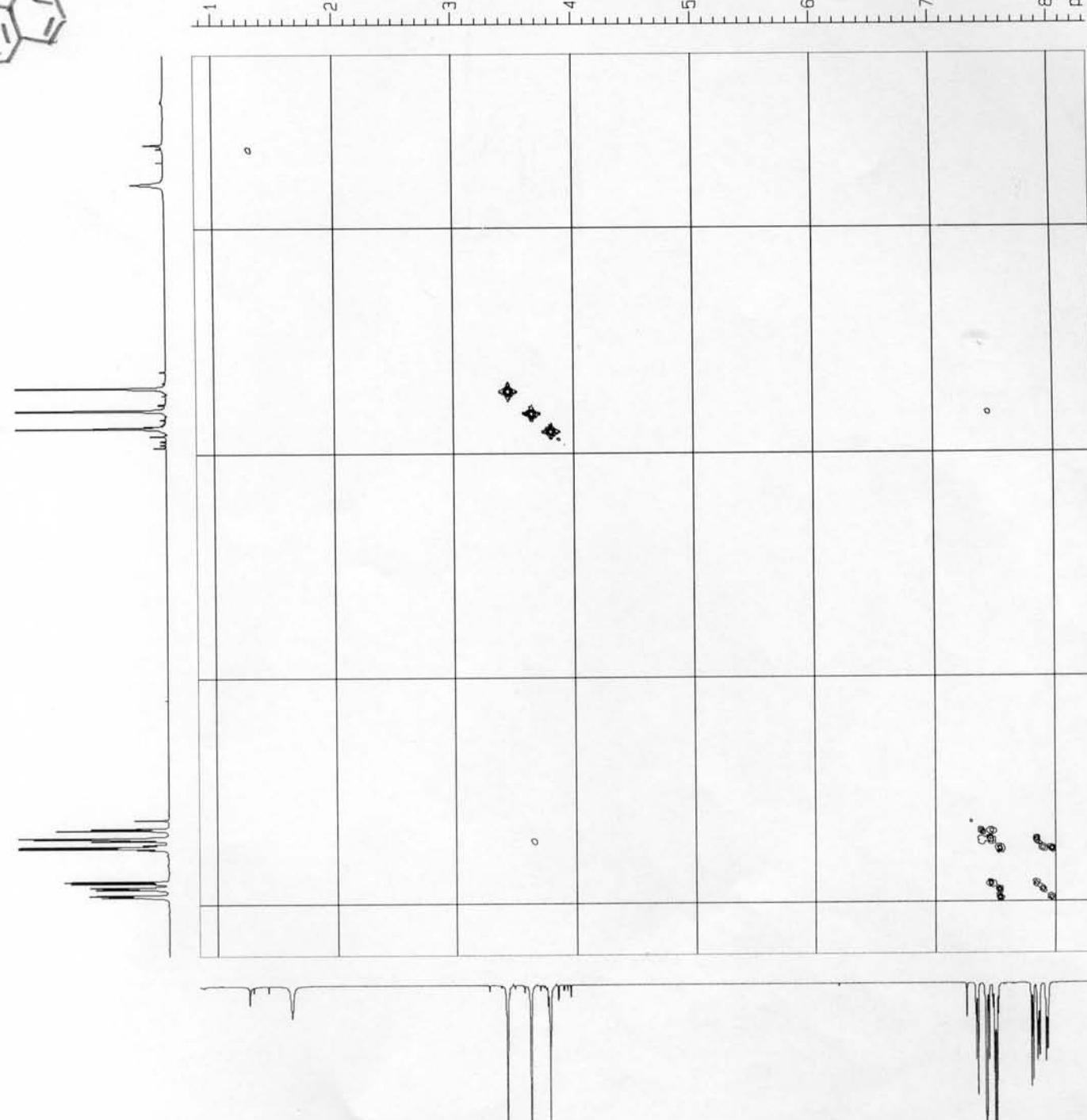
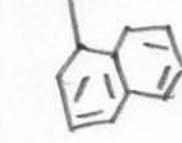
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COSY

CO₂Me
CO₂Me



Current Data Parameters

NAME

nc2004-3

EXPTD

763

FIDNO

1

F2 - Acquisition Parameters

Date -

2004/12/3

Time -

22:05

INSTRUM

dmx500

PROBHD

5 mm QNP 1H/15

PULPROG

cosy1d

TO

1024

SOLVENT

DCCl₃

NS

4

DS

8

SWH

4.464286 Hz

FORES

4.395854 Hz

AQ

0.1148500 sec

RG

256

TD

112,000

usdc

DE

6.00

TE

300.5 K

0.0

0.0000030 sec

0.01

1.46869198 sec

0.13

0.00000400 sec

0.16

0.00002000 sec

1.60

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HCREST

0.00000000 sec

HMGR

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1H

PO

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P1

8.70 usdc

PL1

4.00 dB

SP01

500.1321552 MHz

===== GRADIENT CHANNEL =====

GRADNAME1

SINE,100

GRADNAME2

SINE,100

GP1

0.00 %

GP2

0.00 %

GP1R

0.00 %

GP2R

0.00 %

GP2I

10.00 %

GP2R

10.00 %

PI15

1000.00 usdc

===== Processing parameters =====

ND0

1024

SF

500.130000 MHz

NU1

0

SSB

0

LB

0.00 Hz

GB

0

PC

1.40

===== 2D NMR plot parameters =====

SL

1024

OF

500.130000 MHz

SINE

0

LB

0.00 Hz

GB

0

PC

0

===== 1D NMR plot parameters =====

CH2

15.00 ppm

CH1

8.486 ppm

F2P,0

4230.4 Hz

F2L,0

0.486 ppm

F2H,1

227.87 Hz

F1H,0

8.338 ppm

F1L,0

4169.90 Hz

F1H,1

0.846 ppm

F2P,1

423.26 Hz

F2P,0H

0.53348 ppm/cm

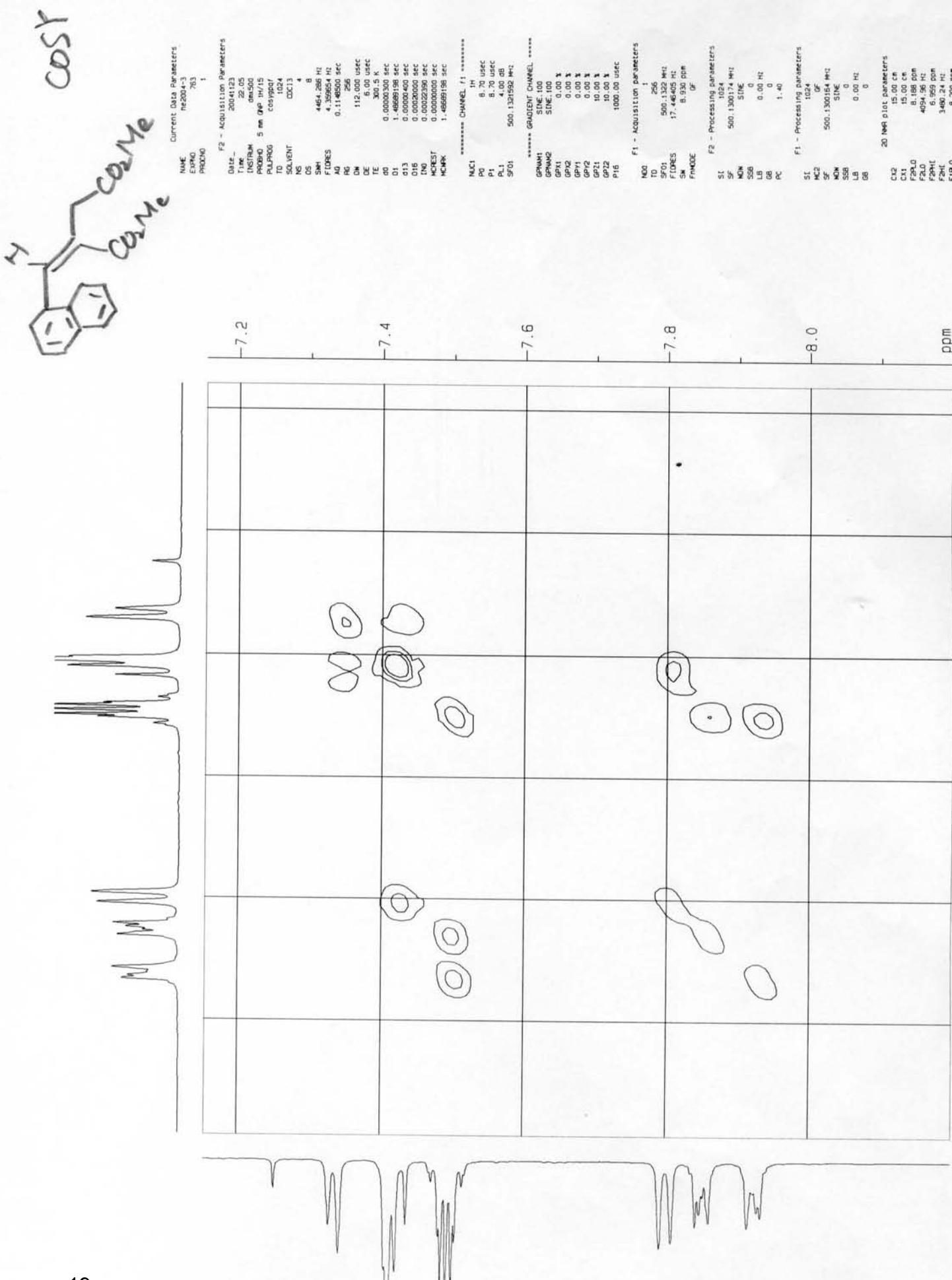
F2L,0H

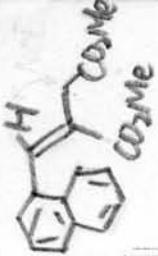
265.81042 Hz/cm

F2H,1H

0.00000 ppm

18





HMBC

20

8

7

6

5

4

3

ppm

40

60

80

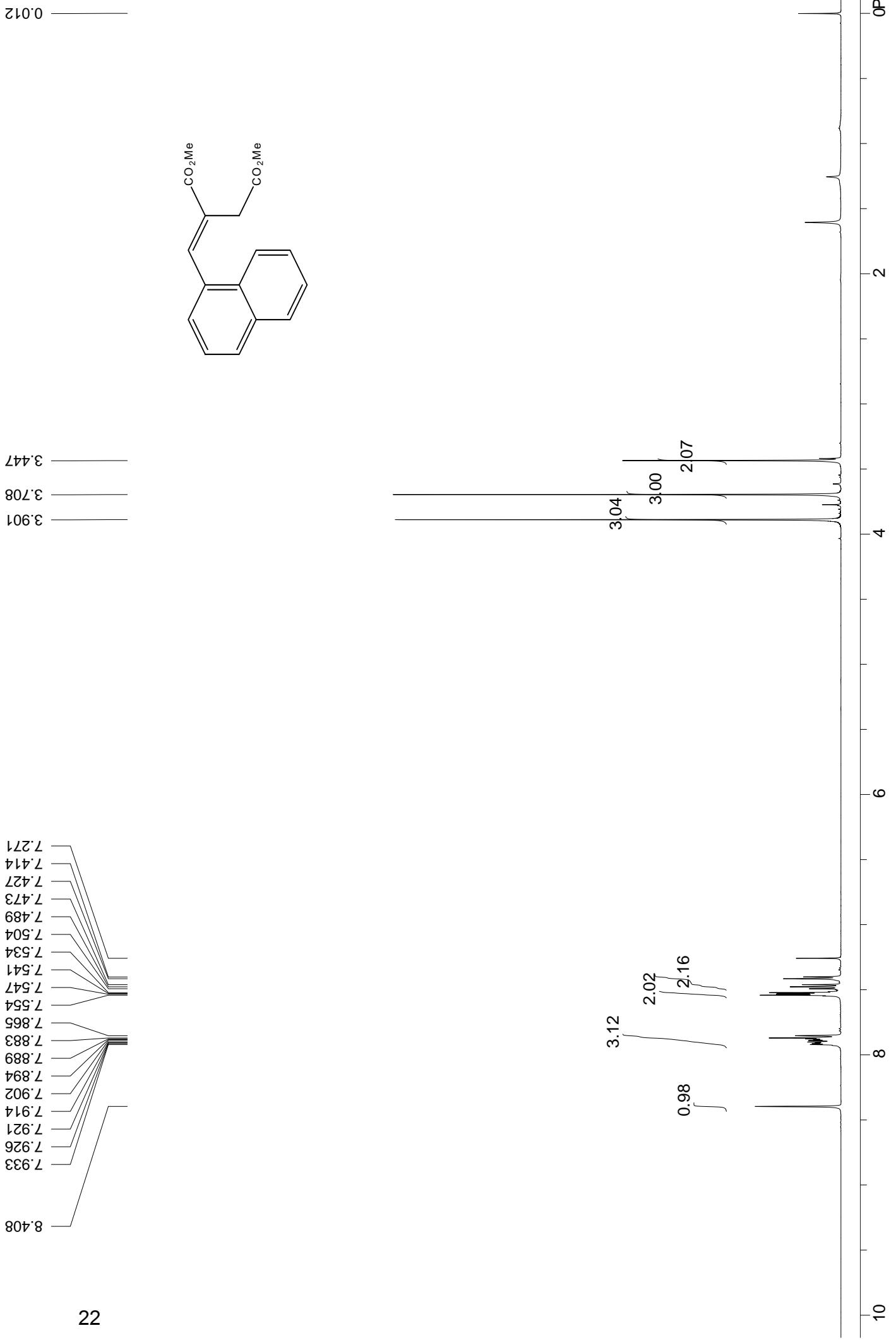
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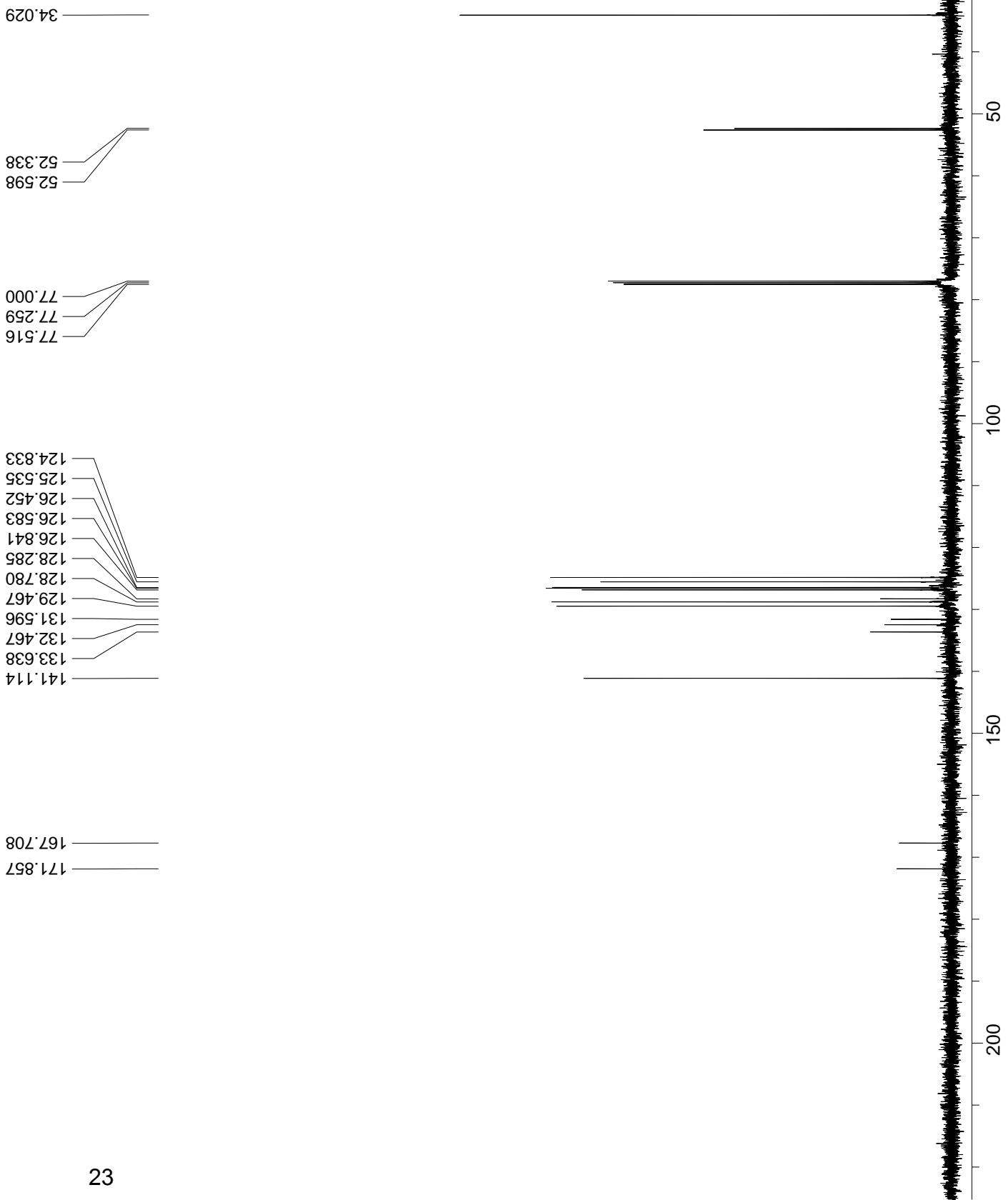
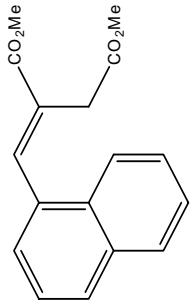
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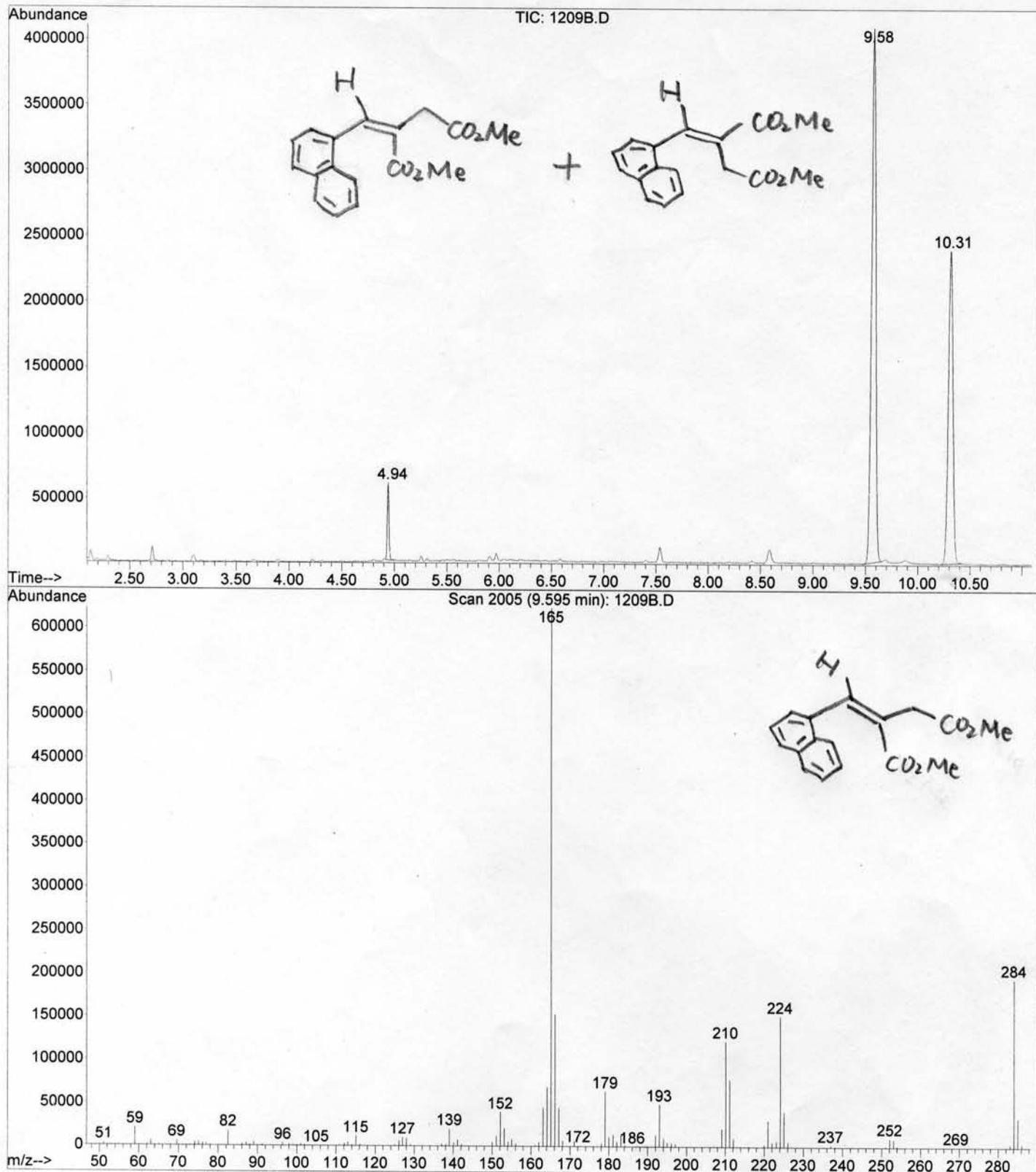
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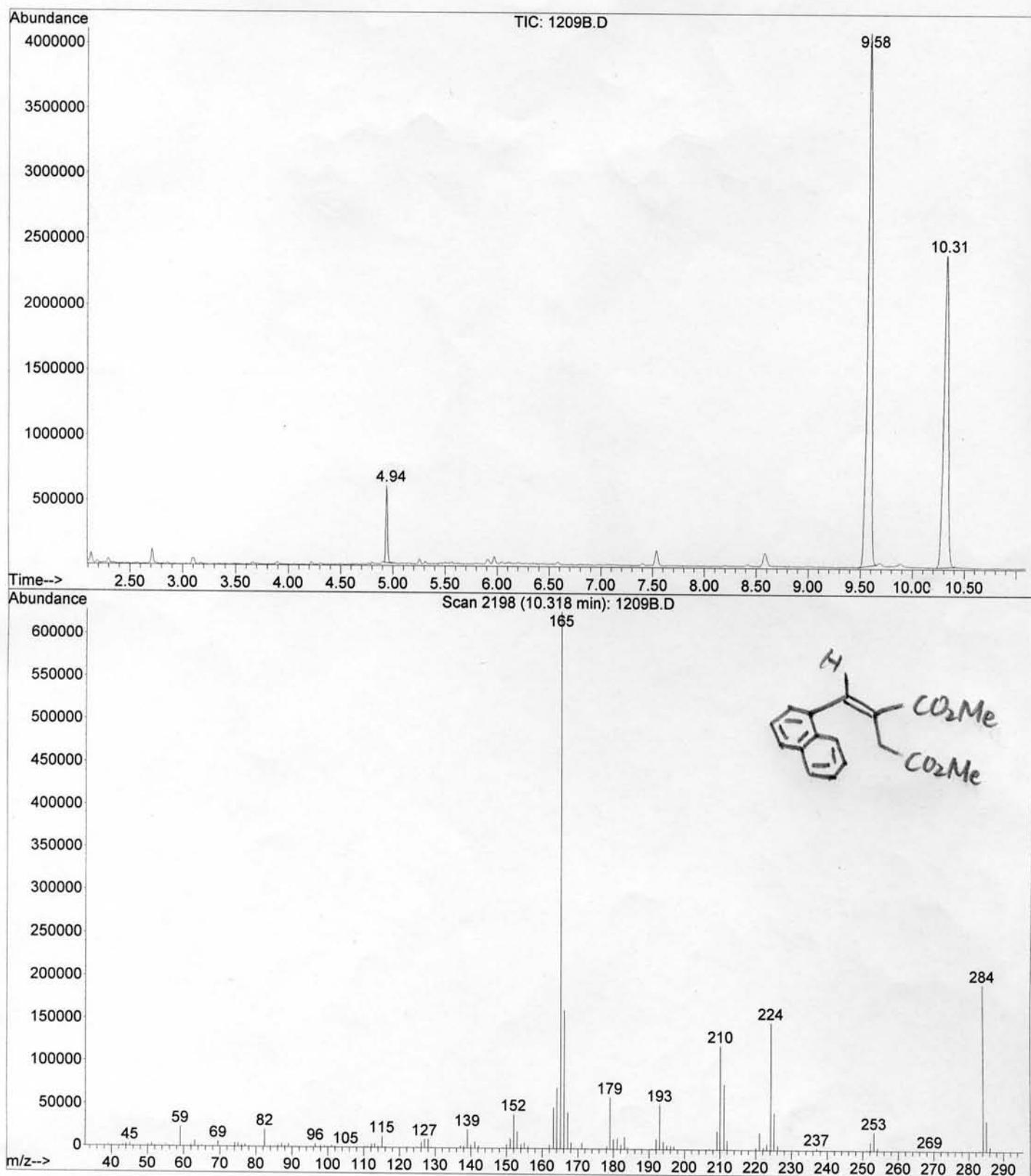




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Instrument : GC/MS Ins
Sample Name:
Misc Info :
Vial Number: 1



File : D:\MC\1209B.D
Operator :
Acquired : 9 Dec 2004 12:51 using AcqMethod ZJU
Instrument : GC/MS Ins
Sample Name:
Misc Info :
Vial Number: 1



Information from Data File:

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 Method File: ZJU
 Sample Name:
 Misc Info:
 Vial Number: 1

Search Libraries: C:\DATABASE\NIST98.L Minimum Quality: 0

Unknown Spectrum: Apex

Integration Events: Chemstation Integrator - autoint1.e

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			1-Naphthaleneacetic acid, methyl e	122944	002876-78-0	91
			Phenylacetic acid, 2-fluoro-4,5-di	64080	141523-25-3	45
2	9.58	58.48	C:\DATABASE\NIST98.L			
			Phenylamine, 2-nitro-N-(ethoxycarb	88541	1000128-22-7	37
			9-Fluorenebenzenesulfonyl	72671	1000222-93-0	32
			9H-Fluorene-9-carboxylic acid, eth	72805	026878-12-6	28
3	10.31	37.99	C:\DATABASE\NIST98.L			
			9-Benzylfluorene	124554	001572-46-9	37
			9-Fluorenebenzenesulfonyl	72671	1000222-93-0	32
			9H-Fluorene, 9-(dichloromethyl)-	72663	031859-82-2	28