Supplementary Material

A Facile Access to [60]Fullerene-Fused *δ*-Lactones: Unexpected Reaction Pathway of Benzenediazonium-2-carboxylates Controlled by Organic Bases

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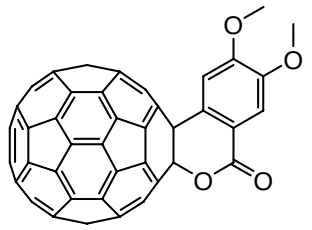
General procedure for the effect of bases on the reaction of C_{60} with 1a and isoamyl nitrite.

To a solution of C_{60} (36.0 mg, 0.05 mmol) in chlorobenzene (8 mL) was sequentially added 2-amino-4,5-dimethoxybenzoic acid **1a** (49.3 mg, 0.25 mmol), the employed base (0.1 mmol) and isoamyl nitrite (40 uL, 0.3 mmol). After being stirred at 60 ^{o}C for the designated time, the reaction mixture was filtered through a silica gel plug in order to remove any insoluble material and evaporated *in vacuo*. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} and then product **3**, subsequent elution with carbon disulfide/dichloromethane afforded C_{60}-fused lactone **2a**.

Synthesis of C_{60}-fused lactone 2a.

To a solution of C_{60} (36.0 mg, 0.05 mmol) in chlorobenzene (8 mL) was sequentially added 2-amino-4,5-dimethoxybenzoic acid **1a** (49.3 mg, 0.25 mmol), Et_3N (14 uL, 0.1 mmol) and isoamyl nitrite (40 uL, 0.3 mmol). After being stirred at 60 ^{o}C for 1.5 h, the reaction mixture was filtered through a silica gel plug in order to remove any insoluble material and evaporated *in vacuo*. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} (21.8 mg, 61%), then with carbon disulfide/dichloromethane as the eluent to afford C_{60}-fused lactone **2a** (16.8 mg, 37%).



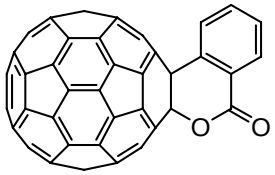
2a

Spectral data of **2a**: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.01 (s, 1H), 7.99 (s, 1H), 4.12 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 160.49 (1C, *C*O), 154.46 (1C, aryl *C*), 152.82, 149.13 (1C, aryl *C*), 148.18 (1C), 148.01, 147.69 (1C), 146.22, 146.16, 145.90, 145.85, 145.83, 145.28, 144.95, 144.92, 144.85, 144.42 (4C), 144.02 (4C), 142.58, 142.35, 142.30, 142.13, 142.04, 141.71, 141.55, 140.74, 140.66, 139.55, 139.40, 135.05, 134.11, 130.05 (1C, aryl *C*), 114.71 (1C, aryl *C*), 111.87 (1C, aryl *C*), 110.83 (1C, aryl *C*), 95.06 (1C, sp^3-*C* of C_{60}), 57.86 (1C, sp^3-*C* of C_{60}), 55.94 (1C, O*C*H_3), 55.78 (1C, O*C*H_3); FT-IR ν/cm^{-1} (KBr) 2924, 1728, 1632, 1603, 1515, 1446, 1403, 1280, 1168, 1067, 877, 774, 528; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 268 (4.95), 317 (4.70), 416 (3.57), 688 (2.49); MS (ESI) m/z 900. MALDI FT-ICR MS m/z calcd for $C_{69}H_8O_4$ [M$^-$] 900.0423, found 900.0411.

Synthesis of C_{60}-fused lactone 2b.

To a solution of C_{60} (36.0 mg, 0.05 mmol) in chlorobenzene (8 mL) was sequentially

added 2-amino-benzoic acid **1b** (34.3 mg, 0.25 mmol), Et_3N (14 uL, 0.1 mmol) and isoamyl nitrite (40 uL, 0.3 mmol). After being stirred at 60 ^oC for 1 h, the reaction mixture was filtered through a silica gel plug in order to remove any insoluble material and evaporated *in vacuo*. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} (25.3 mg, 70%), then with carbon disulfide/dichloromethane as the eluent to afford C_{60}-fused lactone **2b** (11.4 mg, 27%).

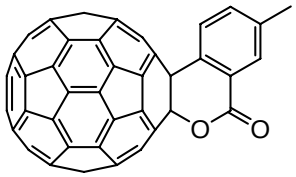


2b

Spectral data of **2b**: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.62 (d, J = 7.8 Hz, 1H), 8.57 (d, J = 7.8 Hz, 1H), 7.87 (t, J = 7.7 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 160.75 (1C, *C*O), 153.48, 148.55 (1C), 148.24, 148.03 (1C), 146.62, 146.56, 146.28, 146.26, 146.21, 145.66, 145.35, 145.32, 145.22, 145.15, 144.76, 144.43, 144.35, 142.94, 142.72, 142.69, 142.49, 142.32, 142.15, 141.91, 141.12, 141.06, 139.93, 139.70, 136.95 (1C, aryl *C*), 135.45, 134.86 (1C, aryl *C*), 134.47, 131.62 (1C, aryl *C*), 129.41 (1C, aryl *C*), 128.59 (1C, aryl *C*), 122.40 (1C, aryl *C*), 95.44 (1C, sp^3-*C* of C_{60}), 58.29 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2921, 1732, 1640, 1509, 1449, 1295, 1126, 1037, 996, 799, 738, 528; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 265 (4.96), 318 (4.73), 416 (3.61), 688 (2.55); MS (ESI) m/z 840. MALDI FT-ICR MS m/z calcd for $C_{67}H_4O_2$ [M^-] 840.0211, found 840.0206.

Synthesis of C_{60}-fused lactone 2c.

To a solution of C_{60} (36.0 mg, 0.05 mmol) in chlorobenzene (8 mL) was sequentially added 2-amino-5-methylbenzoic acid **1c** (37.8 mg, 0.25 mmol), Et_3N (14 uL, 0.1 mmol) and isoamyl nitrite (40 uL, 0.3 mmol). After being stirred at room temperature for 4 h, the reaction mixture was filtered through a silica gel plug in order to remove any insoluble material and evaporated *in vacuo*. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} (20.2 mg, 56%), then with carbon disulfide/dichloromethane as the eluent to afford C_{60}-fused lactone **2c** (12.8 mg, 30%).



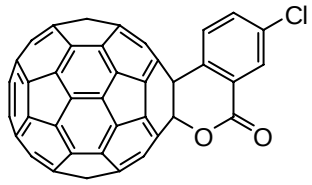
2c

Spectral data of **2c**: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.50 (d, J = 8.4 Hz, 1H), 8.42 (s, 1H), 7.69 (d, J = 8.1 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with

$Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 160.87 (1C, *C*O), 153.45, 148.38 (1C), 148.11, 147.85 (1C), 146.44, 146.36, 146.10, 146.08, 146.03, 145.50, 145.14 (4C), 145.03, 145.00, 144.58, 144.28, 144.22, 142.76, 142.53, 142.51, 142.31, 142.20, 141.97, 141.73, 140.95, 140.89, 139.73, 139.54, 138.61 (1C, aryl *C*), 135.77 (1C, aryl *C*), 135.33, 134.16, 133.85 (1C, aryl *C*), 131.60 (1C, aryl *C*), 129.32 (1C, aryl *C*), 121.87 (1C, aryl *C*), 95.30 (1C, sp^3-*C* of C_{60}), 57.99 (1C, sp^3-*C* of C_{60}), 20.85 (1C, *C*H_3); FT-IR ν/cm^{-1} (KBr) 2915, 1729, 1615, 1507, 1418, 1311, 1253, 1192, 1150, 1080, 1049, 1000, 821, 757, 704, 585, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.03), 318 (4.68), 416 (3.57), 690 (2.48); MS (ESI) m/z 854. MALDI FT-ICR MS m/z calcd for $C_{68}H_6O_2$ [M^-] 854.0368, found 854.0379.

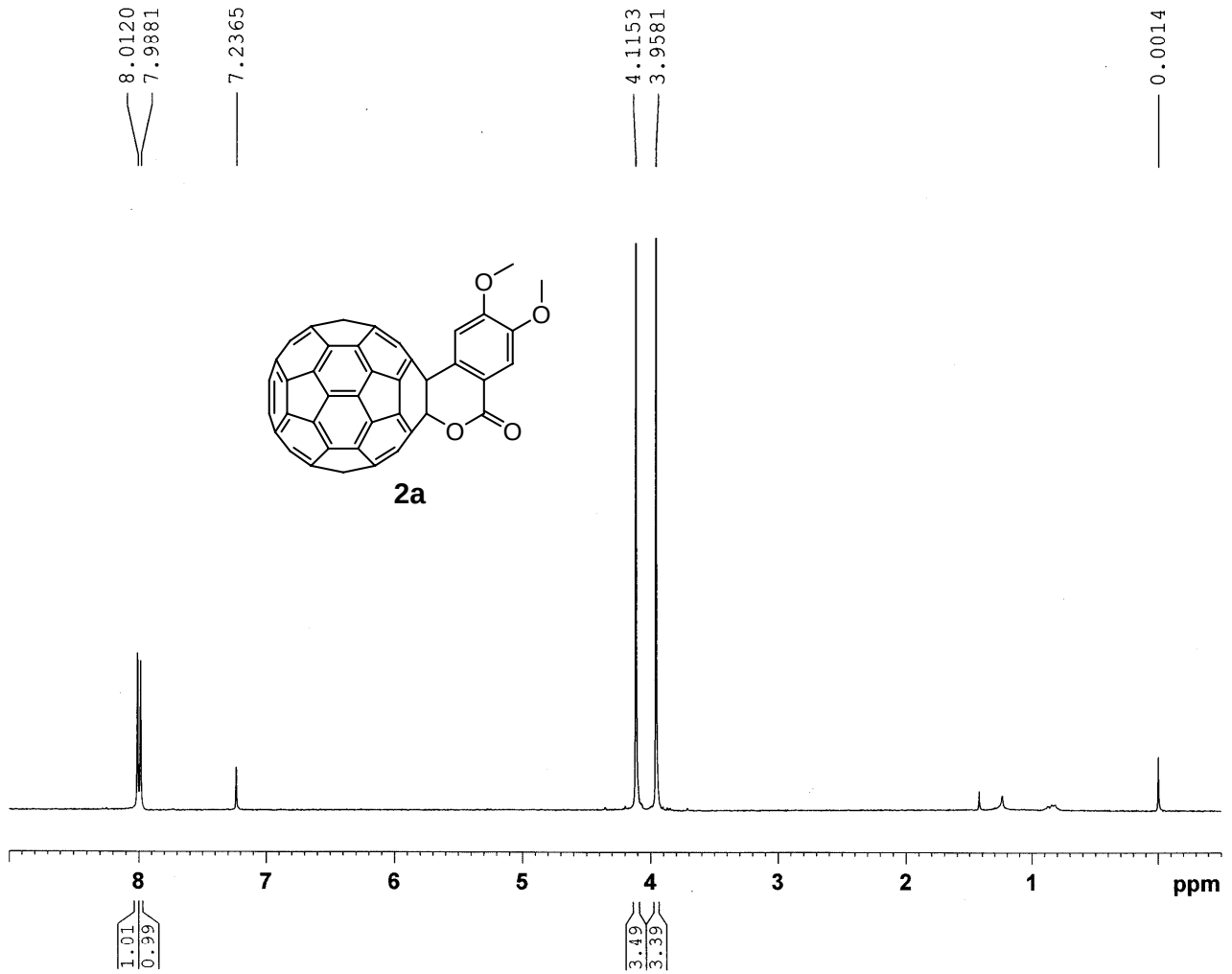
Synthesis of C_{60}-fused lactone 2d.

To a solution of C_{60} (36.0 mg, 0.05 mmol) in chlorobenzene (8 mL) was sequentially added 2-amino-5-chlorobenzoic acid **1d** (42.9 mg, 0.25 mmol), Et_3N (14 uL, 0.1 mmol) and isoamyl nitrite (40 uL, 0.3 mmol). After being stirred at 60 ^oC for 4 h, the reaction mixture was filtered through a silica gel plug in order to remove any insoluble material and evaporated *in vacuo*. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} (26.9 mg, 75%), then with carbon disulfide/dichloromethane as the eluent to afford C_{60}-fused lactone **2d** (8.4 mg, 19%).



2d

Spectral data of **2d**: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 8.59 (d, J = 8.7 Hz, 1H), 8.55 (d, J = 2.4 Hz, 1H), 7.81 (dd, J = 8.7, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$ with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 159.08 (1C, *C*O), 152.83, 148.37 (1C), 147.87 (1C), 147.74, 146.44, 146.41, 146.11 (4C), 146.05, 145.42, 145.23, 145.15, 145.07, 144.67, 144.59, 144.21, 144.03, 142.78, 142.57, 142.53, 142.33, 142.09, 141.94, 141.75, 140.93, 140.91, 139.81, 139.59, 135.36 (1C, aryl *C*), 135.17, 135.11 (1C, aryl *C*), 134.70 (1C, aryl *C*), 134.38, 130.88 (1C, aryl *C*), 130.83 (1C, aryl *C*), 123.73 (1C, aryl *C*), 95.35 (1C, sp^3-*C* of C_{60}), 57.69 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2934, 2858, 1736, 1678, 1638, 1511, 1446, 1406, 1308, 1263, 1248, 1206, 1145, 995, 966, 934, 904, 881, 860, 734, 577, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 288 (4.57), 318 (4.67), 418 (3.54), 688 (2.50); MS (ESI) m/z 874. MALDI FT-ICR MS m/z calcd for $C_{67}H_3ClO_2$ [M^-] 873.9822, found 873.9828.

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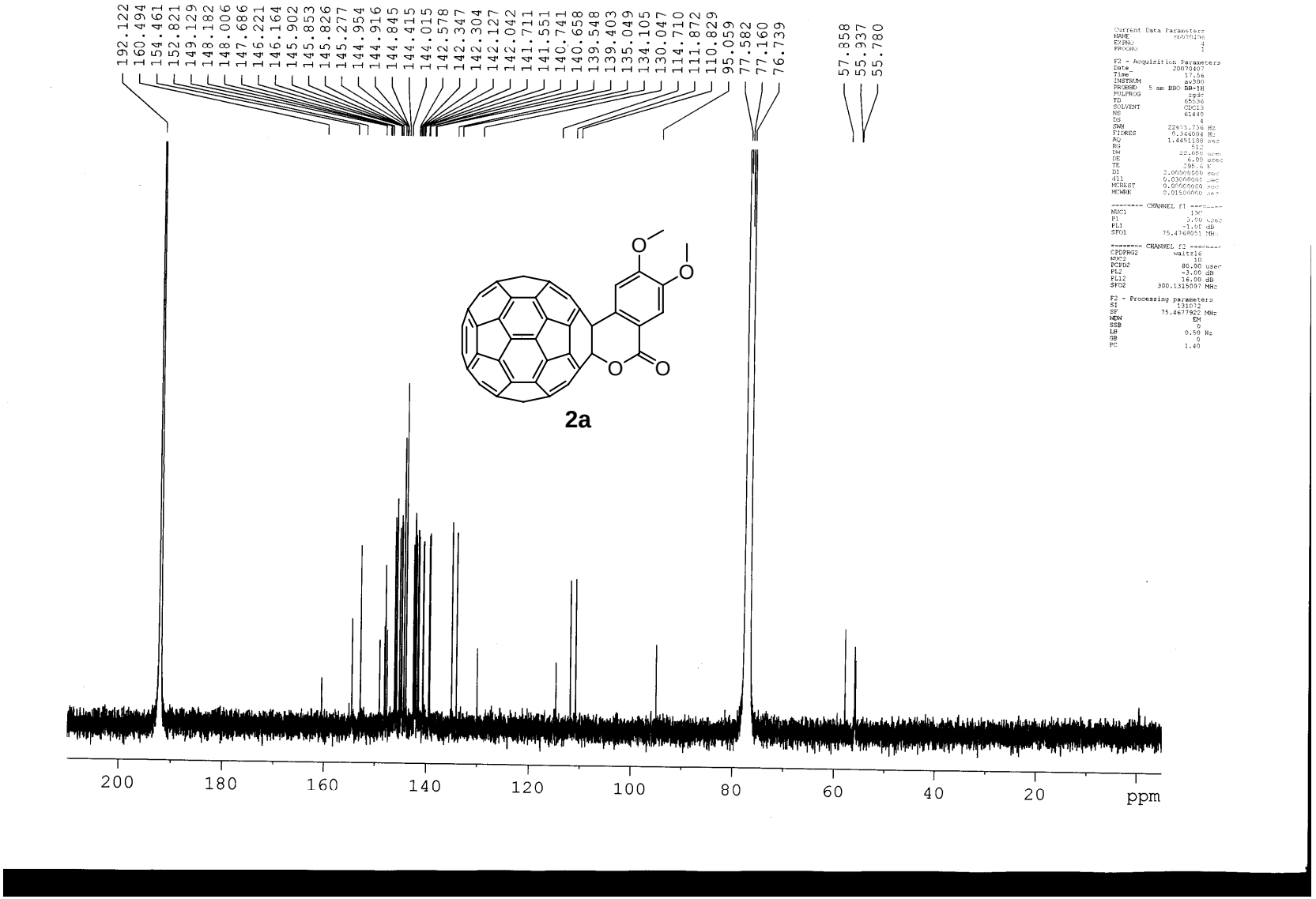
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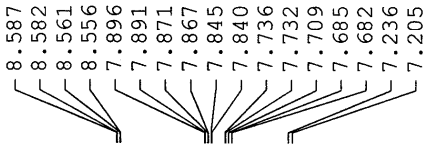
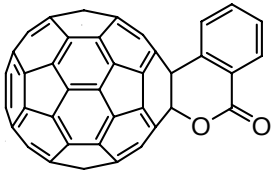
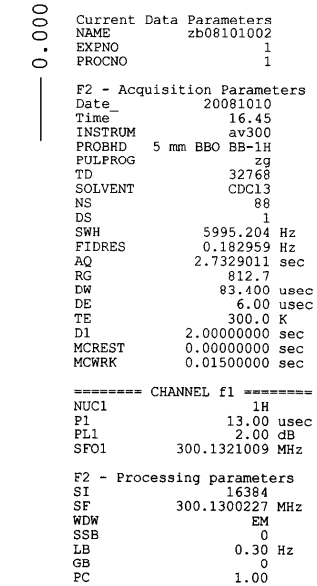




2b



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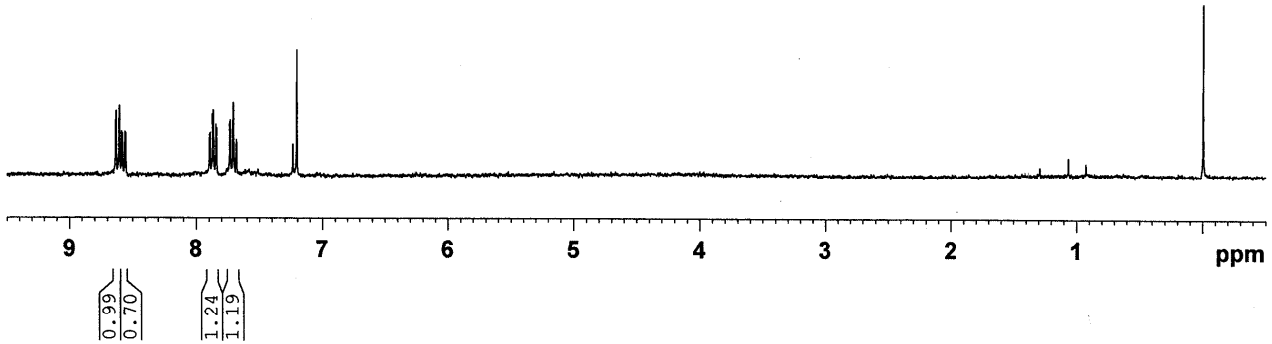

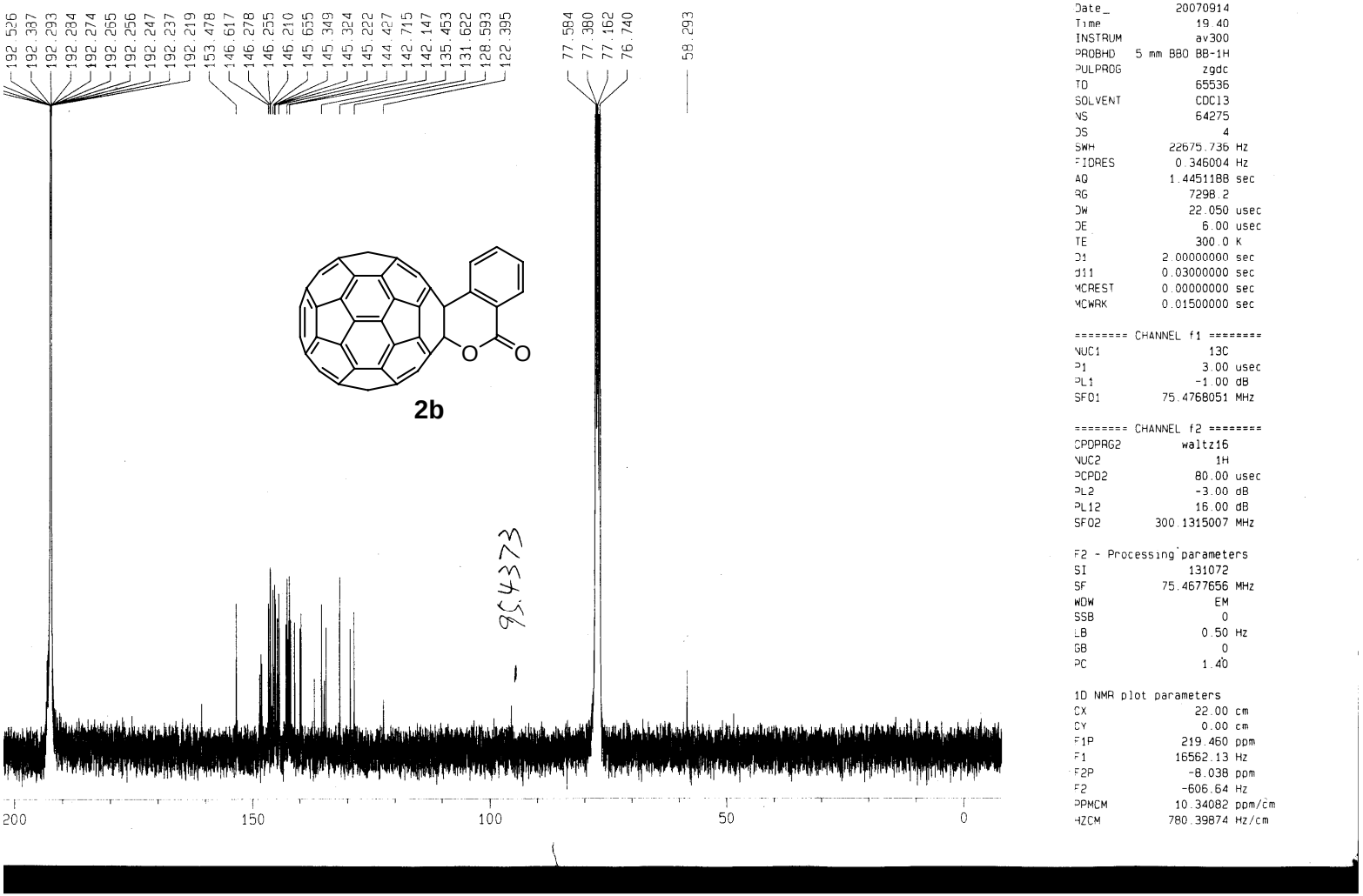


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MCWRK             0.01500000 sec

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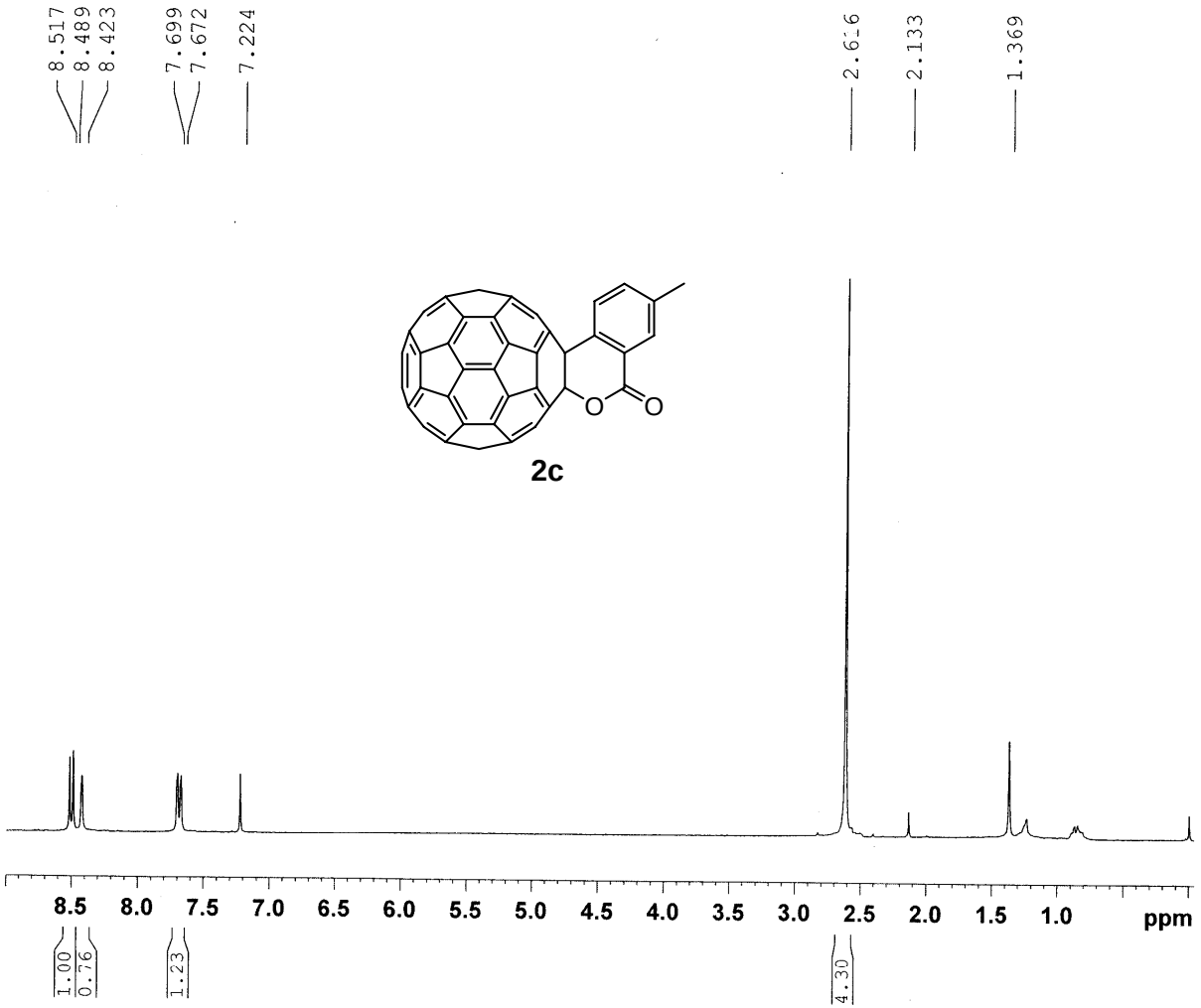


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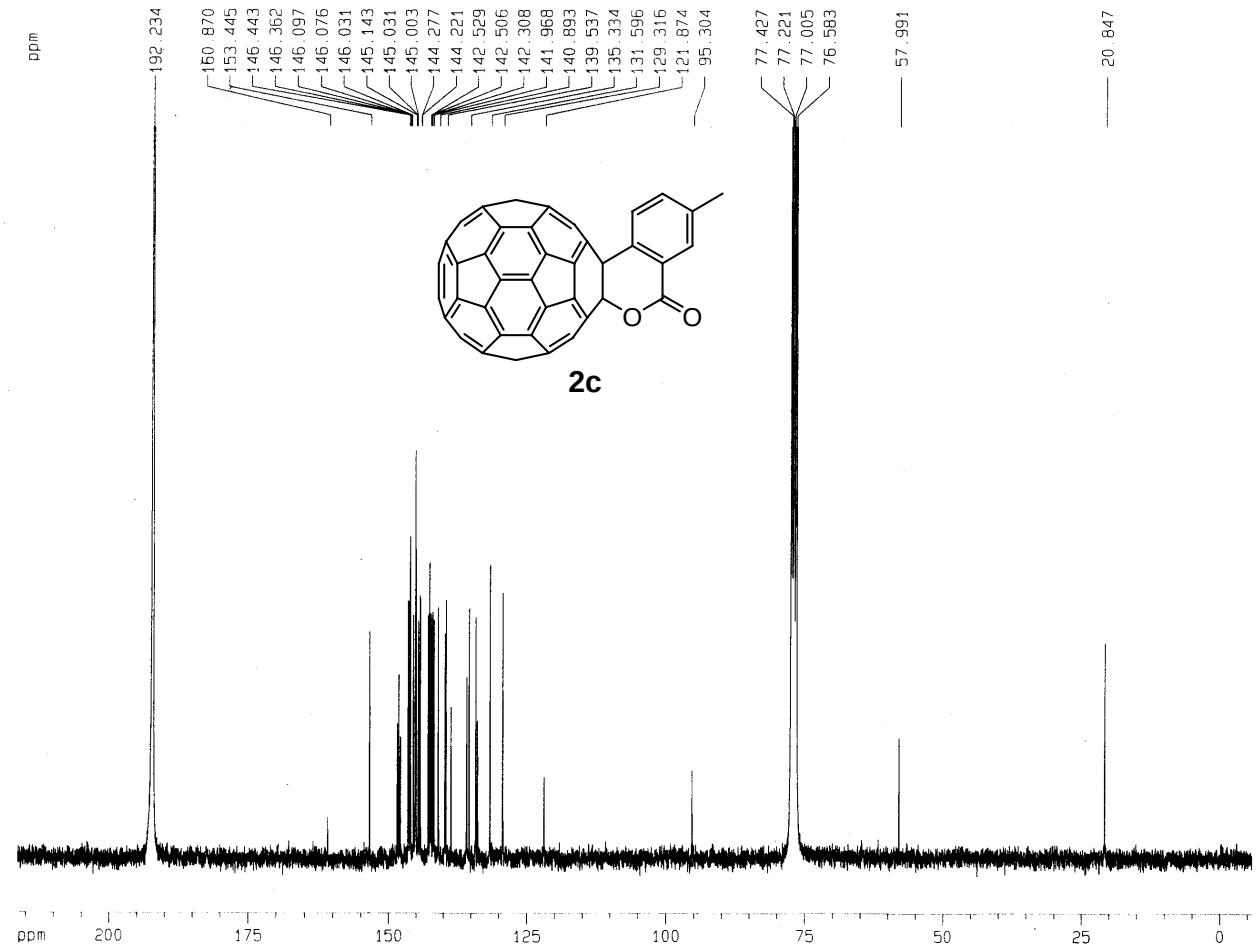


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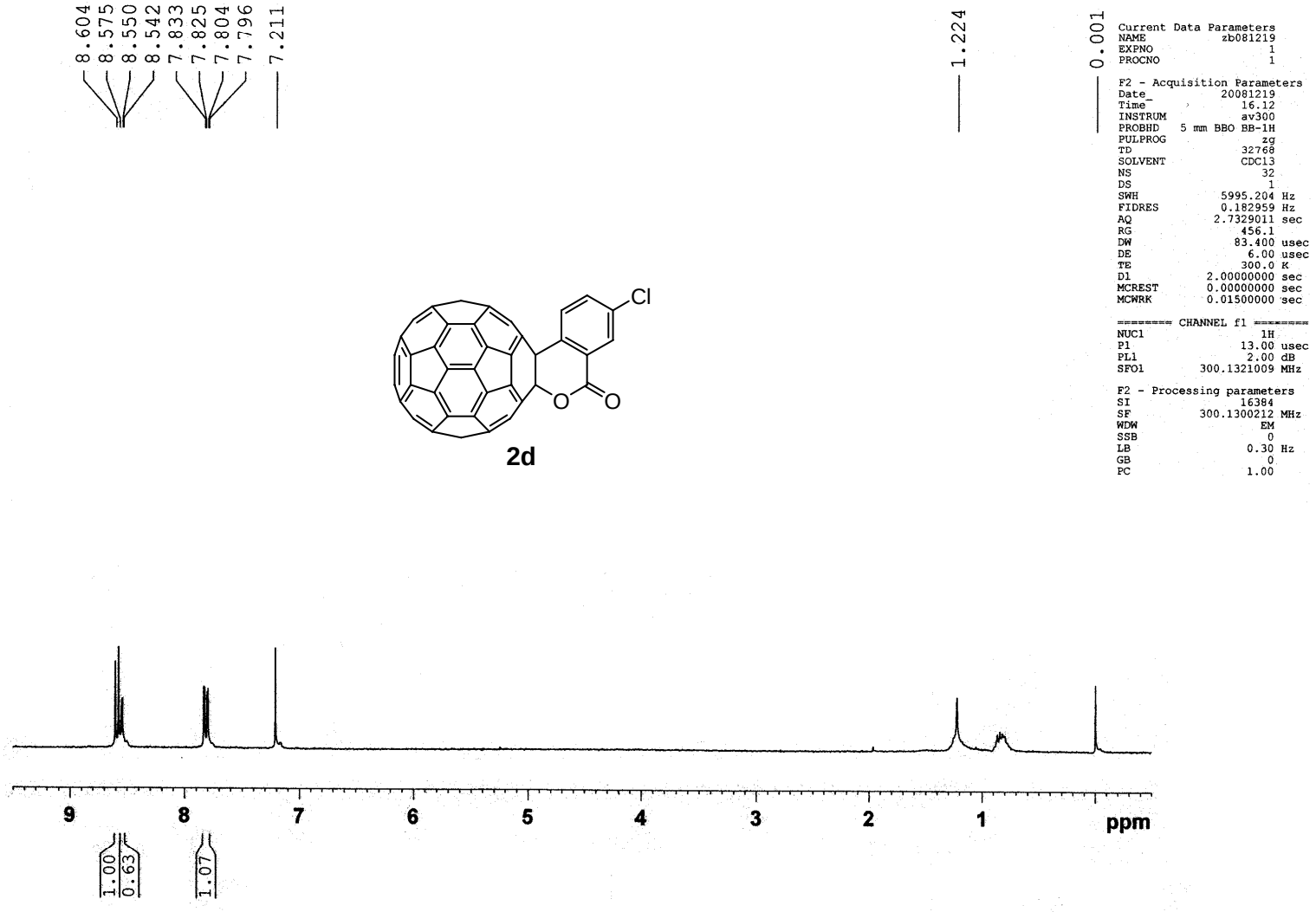

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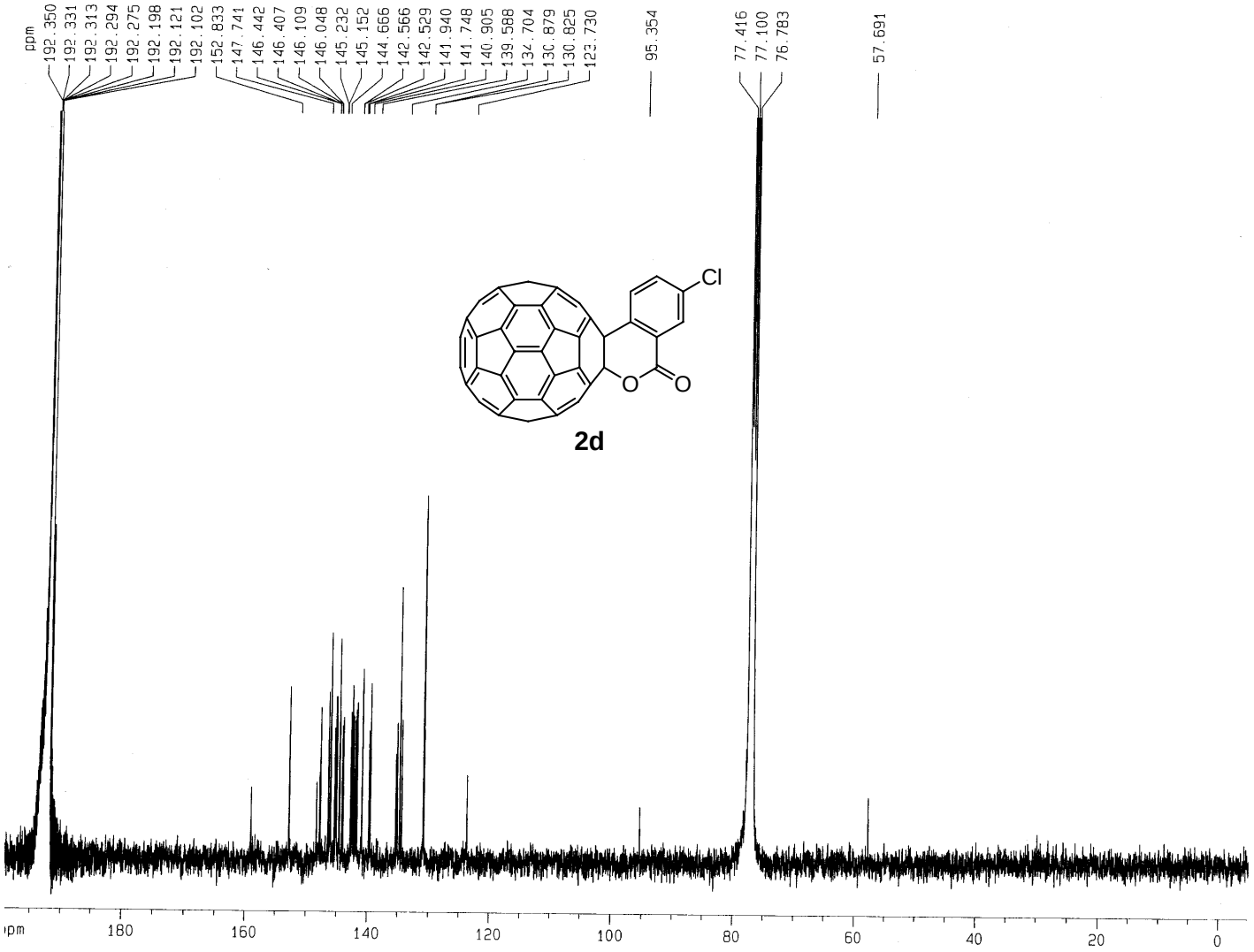


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d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                12.40 usec
PL1                2.00 dB
SFO1         100.6226678 MHz

======== CHANNEL f2 ========
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PL2                0.00 dB
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F2 - Processing parameters
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F2              -503.06 Hz
PPMCM          8.54167 ppm/cm
HZCM          859.40106 Hz/cm
```