SUPPORTING INFORMATION

Synthesis of dicobalt hexacarbonyl 5-*p*-tolylethynyl-2'-deoxyuridine

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Experimental Section

General: Commercial chemicals were treated as follows: DMF, distilled from CaH_2 and degassed (freeze and thaw) three times prior to use; Et_3N, distilled from P_2O_5; THF distilled from Na/benzophenone; $(CH_3CO)_2O$ distilled prior to use. 5-Iodo-2'-deoxyuridine (Berry&Associates), HC≡C-*p*-C_6H_4Me (Aldrich, Lancaster), $Pd(PPh_3)_4$ and CuI 99.999% (Aldrich), *n*-Bu_4NI (Avocado), Ph_3P (Fluka), $Co_2(CO)_8$ (Acros), silica gel (J. T. Baker, 60-200 mesh), preparative plates (Analtech, 20 × 20 cm 1000 μ), TLC plates Analtech GF, cat. number 2521 or Merck 60, cat. number 5715 used as received. Other materials not listed were used as received.

IR and UV-visible spectra were recorded on a Bio Rad FTS-175C/ FTS-375C and Cary 50 spectrometers. Fluorescence measurements were carried out on a Amico-Bowman Series 2 Luminescence Spectrometer, cells 1 and 3 mL, bandwidths 4 nm each, PMT 650 V (24 ºC). NMR spectra were obtained on a Bruker BVT-3300 spectrometer (^1H of 200 MHz, and ^{13}C of 50 MHz). Mass spectra were recorded on a Finnigan MAT 95 high resolution instrument. Differential scanning calorimetry (DSC) were obtained on a DuPont Automotive 912 DS Calorimeter. Samples (2-3 mg) were loaded in crimped Al pans and heated to 250 °C at 10 °C/min under N_2. Microanalyses were conducted by Atlantic Microlab. M.p. were recorded on Büchi or Gallen Kamp apparatus. For cyclic voltammetry an EG&G Princeton Applied Research Model 283 potentiostat with the 270/250 Research Electrochemistry Software 4.30 was employed. Cells were fitted with Pt working (2.0-1.6 mm^2) and counter electrodes, and a Ag wire pseudoreference electrode. All CH_2Cl_2 solutions were 7-

9×10^{-3} M in substrate, 0.1 M in *n*-Bu_4N^+ BF_4^- (crystallized from ethanol/hexane and dried by oil pump vacuum), and prepared under nitrogen. Ferrocene was subsequently added,[S1] and calibration voltammograms recorded. The ambient laboratory temperature was 22.5 ± 1 °C.

3',5'-di-*O*-acetyl-5-iodo-2'-deoxyuridine (1b).[S2]

A round bottom flask was charged with 5-iodo-2'-deoxyuridine (1.000 g, 2.824 mmol), pyridine (15 mL), and $(CH_3CO)_2O$ (3.0 mL, 28 mmol). The reaction was stirred for 16 h. The solvent was removed by rotary evaporation. The residue was coevaporated with benzene/CH_2Cl_2 (10/10 mL), and CH_2Cl_2 (2 × 10 mL). The residue was dissolved in CH_2Cl_2 (250 mL), and washed with $NaHCO_3$ (0.5 M, 4 × 50 mL). The organic phase was dried over Na_2SO_4 and filtered. Solvent was removed by rotary evaporator. The residue was precipitated from ethanol (ca. 1.5 mL) and was kept at -20 ºC (freezer) for 24 h. A white powder was collected by filtration and dried on an oil vacuum pump to give **1b** (1.0853 g, 2.4769 mmol, 88%). R_f = 0.30 ($CHCl_3/CH_3OH$)[S3a]

NMR ($CDCl_3$):[S4] ^{1}H (δ, 200 MHz) 8.92 (br s, 1H, N3), 7.98 (s, 1H, H6), 6.30 (dd, *J* = 8.2, 5.7 Hz, 1H, H1'), 5.26 (dt, *J* = 6.5, 2.1 Hz, 1H, H3'), 4.40 and 4.37 (2d, *J* = 3.0 and 2.8 Hz, 2H, H5'), 4.33-4.28 (m, 1H, H4'), 2.59 and 2.52 (2dd, *J* = 5.7, 2.0 and 5.7, 2.0 Hz, 2H, H2'), 2.22 and 2.13 (2s, 2 × 3H, 2 $COCH_3$); ^{13}C (ppm, 50 MHz)[S5] 170.4 and 170.3 (2 *C*OCH_3), 160.0 (d, *J* = 9.6 Hz, C4), 150.1 (d, *J* = 7.7 Hz, C2), 143.9 (dd, *J* = 184.9, 3.0 Hz, C6), 85.7 (dm, *J* = 171.6 Hz, C1'), 82.5 (dm, *J* = 151.7 Hz, C4'), 74.2 (dm, *J* = 158.3 Hz, C3'), 69.2 (d, *J* = 4.9 Hz, C5), 64.0 (t, *J* = 149.1 Hz, C5'), 38.5 (dd, *J* = 138.5, 132.2 Hz, C2'), 21.3 (q, *J* = 129.9 Hz, CO*C*H_3), 21.1 (q, *J* = 130.1 Hz, CO*C*H_3).

5-*p*-tolylethynyl-2'-deoxyuridine (2a).

A Schlenk flask was charged with 5-iodo-2'-deoxyuridine (0.600 g, 1.70 mmol), Ph_3P (0.445 g, 1.70 mmol), *n*-Bu_4NI (0.631 g, 1.71 mmol), $Pd(PPh_3)_4$ (0.216 g, 0.187 mmol), DMF (10 mL), Et_3N (0.47 mL, 3.4 mmol), 4-ethynyltoluene (0.25 mL, 2.0 mmol), and CuI (0.0323 g, 0.170 mmol). The orange-brown mixture was stirred for 2.5 h at room temperature. Solvent was removed by oil pump vacuum and the residue was extracted with CH_3OH (10 mL). The solid was filtered off and washed with CH_3OH (3 × 10 mL). The solvent was removed from combined filtrates by rotary evaporation. The residue was dried by oil pump vacuum for 20 min, dissolved in $CHCl_3$ (15 mL), and kept at -15 ºC

(freezer) for 26 h. The precipitate was filtered off and washed with cold $CHCl_3$ (3 × 10 mL). Silica gel column chromatography (40 × 2 cm; $CHCl_3/CH_3OH$[S3b]) gave a colorless fraction (purple fluorescence on TLC). Solvent was removed by rotary evaporator and the residue dried by oil pump vacuum to give **2a** (0.488 g, 1.43 mmol, 84%) as a white powder. DSC ($T_i/T_e/T_p$)[S6] 181/192/209 °C. Calcd for $C_{18}H_{18}N_2O_5$: C, 63.15; H, 5.30. Found: C, 62.73; H, 5.58. R_f = 0.60 ($CHCl_3/CH_3OH$).[S3b] IR (cm^{-1}, KBr) ν_{NH} 3433 s br, ν_{OH} 3190 m br, $\nu_{C\equiv C}$ 2220 vw, ν_{CO} 1722 vs, 1669 vs, 1652 vs, $\nu_{C=C}$ 1618 m, $\nu_{p\text{-}C6H4}$ 817 m. UV-vis (CH_3OH, 5.5 × 10^{-5} M)[S8] 252 (9500), 266 (11000), 280 (9900), 311 (12000). Fluorescence (CH_3OH, 6.1 × 10^{-6} M) λ_{em} = 401 nm (λ_{ex} = 311 nm). MS[S7] (FAB, gly, positive) 435 ($(M + gly + 1)^+$, 10%), 343 ($(M + 1)^+$, 42%), 227 ($(M – C\equiv CC_6H_4CH_3)^+$, 100%); no other peaks above 200 of >6%; (negative) 433 ($(M + gly – 1)^-$, 13%), 341 ($(M – 1)^-$, 65%), 227 ($(M – C\equiv CC_6H_4CH_3 – 2)^-$, 100%); no other peaks above 200 of >9%.
NMR (DMSO-d_6,): ^{1}H (δ, 200 MHz) 11.68 (s, 1H, N3),[S9] 8.33 (s, 1H, H6), 7.35 (AB, *J* = 8.1 Hz, 2H, *m*-$C_6H_4CH_3$),[S10] 7.21 (AB, *J* = 8.1 Hz, 2H, *o*-$C_6H_4CH_3$), 6.13 (t, *J* = 6.5 Hz, 1H, H1'), 5.27 (d, *J* = 3.8 Hz, 1H, OH3'),[S9] 5.17 (t, *J* = 4.3 Hz, 1H, OH5'),[S9] 4.26 (q, *J* = 4.2 Hz, 1H, H3'), 3.81 (q, *J* = 3.6 Hz, 1H, H4'), 3.71-3.52 (m, 2H, H5'), 2.33 (s, 3H, CH_3), 2.16 (t, *J* = 5.6 Hz, 2H, H2'); ^{13}C (ppm, 50 MHz) 162.1 (d, *J* = 9.3 Hz, C4), 149.9 (d, *J* = 7.5 Hz, C2), 143.6 (dd, *J* = 181.2, 2.2 Hz, C6), 138.3 (m, *i*-$C_6H_4CH_3$), 131.1 (dd, *J* = 162.3, 6.2 Hz, *m*-$C_6H_4CH_3$), 129.4 (dquintet, *J* = 159.6, 5.4 Hz, *o*-$C_6H_4CH_3$), 119.5 (t, *J* = 8.2 Hz, *p*-$C_6H_4CH_3$), 98.3 (s, C5), 91.8 (t, *J* = 5.4 Hz, C≡*C*C_6H_4), 87.6 (d, *J* = 147.9 Hz, C4'), 84.8 (d, *J* = 170.8 Hz, C1'), 82.1 (d, *J* = 5.5 Hz, *C*≡CC_6H_4), 69.9 (d, *J* = 148.0 Hz, C3'), 60.9 (t, *J* = 140.4 Hz, C5'), 40.2 (t, *J* = 133.5 Hz, C2'), 21.1 (qt, *J* = 126.2, 4.3 Hz, CH_3).

3',5'-di-*O*-acetyl-5-*p*-tolylethynyl-2'-deoxyuridine (2b).

A Schlenk flask was charged with 3',5'-di-*O*-acetyl-5-iodo-2'-deoxyuridine (0.176 g, 0.402 mmol), 4-ethynyl toluene (0.060 mL, 0.47 mmol), triethylamine (0.11 mL, 0.83 mmol), DMF (10 mL), $Pd(PPh_3)_4$ (0.0511 g, 0.0442 mmol), and CuI (0.0794 g, 0.417 mmol). The mixture was stirred at room temperature for 5 h. The solvent was removed by oil pump vacuum at 50 °C (water bath) and the residue was coevaporated with MeOH. The residue was dissolved in a minimum amount of $CHCl_3$/MeOH[S3c] and filtered over a silica gel column (15 × 2 cm). The solvent was removed by

rotary evaporator. Silica gel column chromatography (hexane/EtOAc gradient, 80:20->65:35->50:50, 35 × 2 cm) gave **2b** as a white powder (0.0646 g, 0.157 mmol, 77%), m.p. 158-160 °C. R_f = 0.44 ($CHCl_3$/MeOH),[S3a] 0.44 (hexane/EtOAc).[S3d] IR (cm^{-1}, $CHCl_3$) ν_{NH} 3384 w, $\nu_{C\equiv C}$ 2224 vw, ν_{CO} 1744 s, 1719 vs, 1702 vs, $\nu_{C=C}$ 1629 vw, $\nu_{p\text{-}C6H4}$ 819 vw.

NMR ($CDCl_3$):[S4] ^{1}H (δ, 200 MHz) 9.94 (br s, 1H, N3), 7.85 (s, 1H, H6), 7.34 (AB, *J* = 8.1 Hz, 2H, *m*-$C_6H_4CH_3$),[S10] 7.11 (AB, *J* = 8.1 Hz, 2H, *o*-$C_6H_4CH_3$), 6.33 (dd, *J* = 7.8, 5.9 Hz, 1H, H1'), 5.23 (dt, *J* = 6.5, 2.5 Hz, 1H, H3'), 4.34 (d, *J* = 3.0 Hz, 2H, H5'), 4.27 (q, *J* = 2.7 Hz, 1H, H4'), 2.59 and 2.52 (2dd, *J* = 6.0, 2.4 and 5.8, 2.3 Hz, 2H, H2'), 2.32 (s, 3H, CH_3), 2.14 and 2.09 (2s, 2 × 3H, 2 $COCH_3$); $^{13}C\{^1H\}$ (ppm, 50 MHz)[S5] 170.6, 170.3 (2 *C*OCH_3), 161.5 (C4), 149.6 (C2), 141.3 (C6), 139.0 (*i*-$C_6H_4CH_3$), 131.6 (*m*-$C_6H_4CH_3$), 129.2 (*o*-$C_6H_4CH_3$), 119.4 (*p*-$C_6H_4CH_3$), 101.2 (C5), 94.0 (C≡*C*C_6H_4), 85.5 (C1'), 82.6 (C4'), 79.7 (*C*≡CC_6H_4), 74.2 (C3'), 64.0 (C5'), 38.2 (C2'), 21.6 (CH_3), 21.0 (CO*C*H_3), 20.9 (CO*C*H_3).

Dicobalt hexacarbonyl 5-*p*-tolylethynyl-2'-deoxyuridine (3a).

A Schlenk flask was charged with **2a** (0.1016 g, 0.2968 mmol), THF (5 mL), $Co_2(CO)_8$ (0.2030 g, 0.5937 mmol). The mixture was stirred for 1.5 h. Solvent was removed by rotary evaporation and the red residue was dried by oil pump vacuum. The residue was dissolved in a minimum amount of $CHCl_3/CH_3OH$[S3a] (ca. 1 mL). Silica gel column chromatography (30 × 2 cm; $CHCl_3/CH_3OH$[S3a]) gave a red-brown fraction. Solvent was removed by rotary evaporation and the residue was dried by oil pump vacuum to give **3a** (0.1716 g, 0.2731 mmol, 92%) as a dark brown powder which was stored in a freezer at –18 °C. DSC ($T_i/T_e/T_p$)[S6] 114/125/140 °C (endothermic decomposition without melting). Calcd for $C_{24}H_{18}Co_2N_2O_{11}$: C, 45.88; H, 2.89. Found: C, 45.66; H, 3.36. R_f = 0.62.[S3c] IR (cm^{-1}, KBr) ν_{NH} 3428 s br, ν_{OH} 3166 w br, $\nu_{C\equiv C}$ 2220 vw, $\nu_{CoC=O}$ 2092 s, 2055 vs, 2023 vs, $\nu_{NC=O}$ 1690 m br, $\nu_{C=C}$ 1605 sh, $\nu_{p\text{-}C6H4}$ 818 w. UV see Figure. MS[S7] (ES, MeOH + KCl, positive) 1295 ($(2M + K)^+$, 36%), 667 ($(M + K)^+$, 92%), 639 ($(M + K – CO)^+$, 100%), 629 ($(M + H)^+$, 12%), no other peaks above 90 of >9%; (negative) 1291 ($(2M + Cl)^-$, 8%), 663 ($(M + Cl)^-$, 100%), 635 ($(M + Cl – CO)^-$, 18%), 627 ($(M – H)^-$, 5%), 607 ($(M + Cl – 2CO)^-$, 56%), 599 ((M – H

– CO)$^-$, 16%), 579 ((M + Cl – 3CO)$^-$, 63%), 571 ((M – H – 2CO)$^-$, 20%), 551 ((M + Cl – 4CO)$^-$, 61%), 543 ((M – H – 3CO)$^-$, 32%), 515 ((M – H – 4CO)$^-$, 12%); no other peaks above 270 of >5%.

NMR (acetone-d_6): ^{1}H (δ, 200 MHz) 10.32 (s, 1H, N3),[S9] 8.43 (s, 1H, H6), 7.53 (AB, *J* = 8.0 Hz, 2H, *m*-$C_6H_4CH_3$),[S10] 7.19 (AB, *J* = 8.0 Hz, 2H, *o*-$C_6H_4CH_3$), 6.43 (t, *J* = 6.9 Hz, 1H, H1'), 4.52 (br, 1H, OH5'),[S9] 4.43 (d, *J* = 2.7 Hz, 1H, OH3'),[S9] 4.24 (t, *J* = 4.5 Hz, 1H, H3'), 4.06-4.02 (m, 1H, H4'), 3.83-3.68 (m, 2H, H5'), 2.32 (s, 3H, CH_3),[S11] 2.08-2.02 (m, 2H, H2'); ^{13}C{^{1}H} (ppm, 50 MHz)[S5] 200.5 (CoCO), 160.8 (C4), 150.8 (C2), 139.8 (C6), 138.8 (*i* to $C_6H_4CH_3$), 136.3 (*p* to $C_6H_4CH_3$), 130.6 and 130.2 (*m* and *o* to $C_6H_4CH_3$), 113.6 (C5), 89.2 (C4'), 86.4 (C1'), 96.7 and 86.2 (*C*≡*C*C_6H_4), 73.1 (C3'), 63.3 (C5'), 41.9 (C2'), 21.4 (CH_3).

Dicobalt hexacarbonyl 3',5'-di-*O*-acetyl-5-*p*-tolylethynyl-2'-deoxyuridine (3b).

The procedure as for **3a** was carried out using **2b** (0.0523 g, 0.122 mmol), $Co_2(CO)_8$ (0.0823 mg, 0.241 mmol) and THF (10 mL), which gave after column chromatography ($CHCl_3$/MeOH gradient, 100:0->98:2->95:5) **3b** (0.0565 g, 0.0816 mmol, 66%) as a dark brown powder, m.p. 159-162 °C. Calcd for $C_{28}H_{22}Co_2N_2O_{13}$: C, 47.21; H, 3.11. Found: C, 46.81; H, 3.43. R_f = 0.49 ($CHCl_3$/MeOH),[S3a] 0.57 (ethyl acetate/hexane).[S3d] IR (cm^{-1}, $CHCl_3$) ν_{NH} 3435 w, ν_{OH} 3132 w, $\nu_{CoC=O}$ 2094 s, 2058 vs, 2031 vs, ν_{CO} 1745 m, 1714 m, 1698 m, $\nu_{C=C}$ 1698 m, $\nu_{p\text{-}C6H4}$ 819 vw. MS[S7] (FAB, gly, positive) 713 ((M + 1)$^+$, 10%), 629 ((M + 2 – 2CH_3CO)$^+$, 17%), 572 ((M + 3 – $Co(CO)_3$)$^+$, 100%), 545 ((M – 6CO)$^+$, 36%), 427 ((M + 1 – $Co_2(CO)_6$)$^+$, 40%); 344 (41%), no other peaks above 290 of >22%; (negative) 684 ((M – CO)$^-$, 100%), 652 ((M – 2CO)$^-$, 18%), 628 ((M – 3CO)$^-$, 62%), 600 ((M – 4CO)$^-$, 29%), 572 ((M – 5CO)$^-$, 13%), 544 ((M – 6CO)$^-$, 11%), 425 (22%); no other peaks above 260 of >13%.

NMR ($CDCl_3$): ^{1}H (δ, 200 MHz) 9.73 (s, 1H, N3), 7.91 (s, 1H, H6), 7.43 (AB, *J* = 7.8 Hz, 2H, *m*-$C_6H_4CH_3$),[S10] 7.16 (AB, *J* = 7.8 Hz, 2H, *o*-$C_6H_4CH_3$), 6.32 (dd, *J* = 8.6, 5.1 Hz, 1H, H1'), 5.14 (d, *J* = 5.7, 1H, H3'), 4.38-4.22 (m, 2H, H5'), 4.17-4.02 (m, 1H, H4'), 2.56 (dd, *J* = 14.0, 4.9 Hz, 2H, H2'), 2.35 (s, 3H, CH_3), 2.12 and 1.81 (2s, 2 × 3H, 2 $COCH_3$); ^{13}C (ppm, 50 MHz) 199.2 (s, CoCO), 170.5, 170.3 (m, 2 *C*OCH_3), 160.8 (d, *J* = 9.5 Hz, C4), 150.0 (d, *J* = 8.7 Hz, C2), 138.5 (m, *i*-$C_6H_4CH_3$), 135.4 (dd, *J* = 180.4, 2.7 Hz, C6), 135.2 (t, *J* = 8.1 Hz, *p*-$C_6H_4CH_3$), 129.8 (dquintet, *J* =

159.2, 5.7 Hz, *o*-$C_6H_4CH_3$), 129.3 (dd, *J* = 159.4, 6.2 Hz, *m*-$C_6H_4CH_3$), 113.8 (d, *J* = 3.9 Hz, C5), 93.6 (td, *J* = 7.7, 2.8 Hz, C≡CC_6H_4), 85.5 (dm, *J* = 170.8 Hz, C1'), 82.5 (dm, *J* = 149.6 Hz, C4'), 81.1 (C≡CC_6H_4),[S12] 74.4 (dm, *J* = 162.0 Hz, C3'), 63.9 (td, *J* = 148.5, 1.7 Hz, C5'), 38.1 (dd, *J* = 139.4, 131.3 Hz, C2'), 21.5 (qt, *J* = 126.4, 4.2 Hz, CH_3), 21.1 (q, *J* = 130.0 Hz, COCH_3), 20.4 (q, *J* = 129.8 Hz, COCH_3).

References and Notes

(S1) In response to conventions proposed in a review (Connelly, N. G.; Geiger, W. E. *Chem. Rev*. **1996**, *96*, 877), we present our CV data relative to a new E°' value for ferrocene (0.46 V).

(S2) Chang, P. K.; Welch, A. D. *J. Med. Chem*. **1963**, *6*, 428-430.

(S3) Solvents for column chromatography and TLC (v/v): a) 95:5, b) 85:15, c) 80:20, d) 50:50.

(S4) Assignment based in part on the trends for **2a.**

(S5) A ^{13}C NMR spectrum of **2a** and **3b** were recorded without proton decoupling (gated decoupling). From intensity relationships and the magnitude of the coupling to the methyl protons, the signals were assigned as ipso, ortho, meta, and para to the methyl group. These chemical shift trends were used to assign resonances for the other *p*-tolyl containing compounds, **2b** and **3a**, respectively.

(S6) T_i, initial peak temperature; T_e, extrapolated peak-onset temperature; T_p, maximum peak temperature; Cammenga, H. K.; Epple, M. *Angew. Chem*. **1995**, *107*, 1284-1301; *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 1171-1187.

(S7) *m*/*z* for most intense peak of isotope envelope; relative intensities are for the specified mass range; matrix peaks omitted; gly = glycerol.

(S8) UV-visible spectra were recorded in CH_2Cl_2, and absorbances are in nm (ε, $M^{-1}cm^{-1}$).

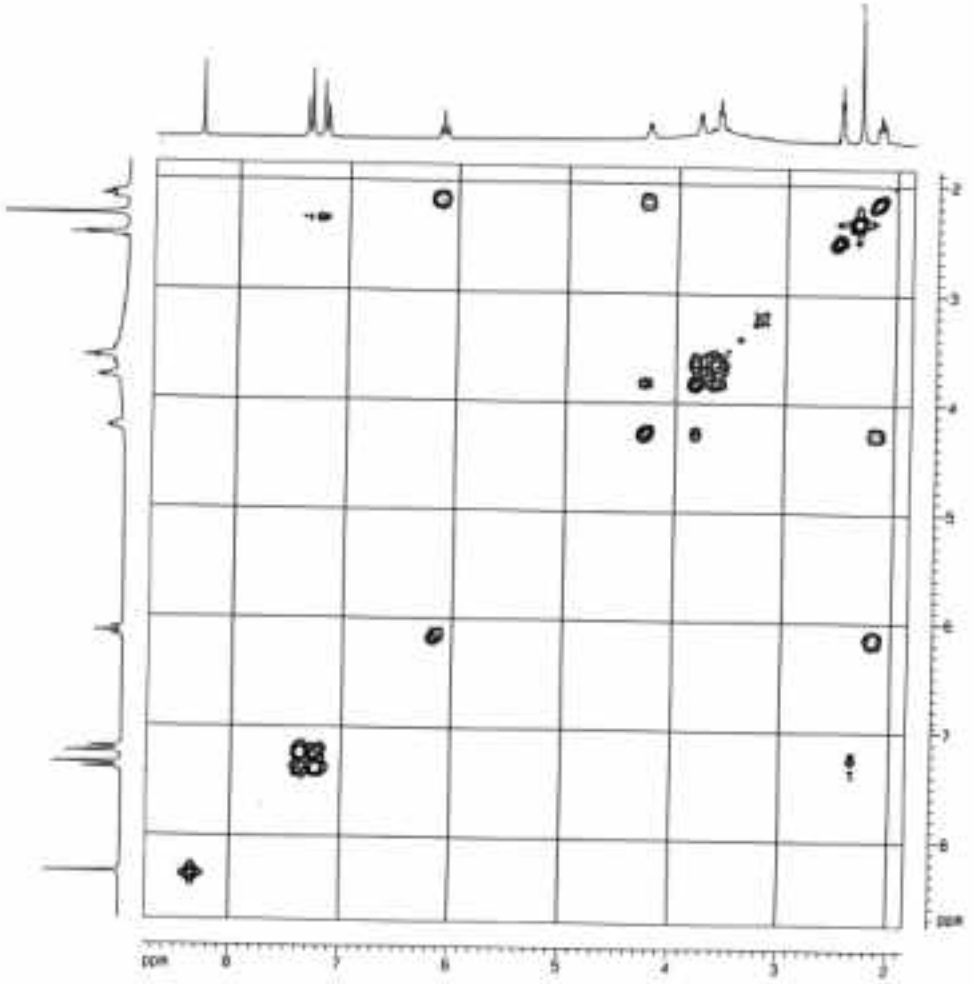
(S9) Coupling pattern or signal observed only when the NMR tube was filled in anhydrous conditions.

(S10) The *p*/*m*/*o*/*i* positions are assigned with respect to the CH_3 group.

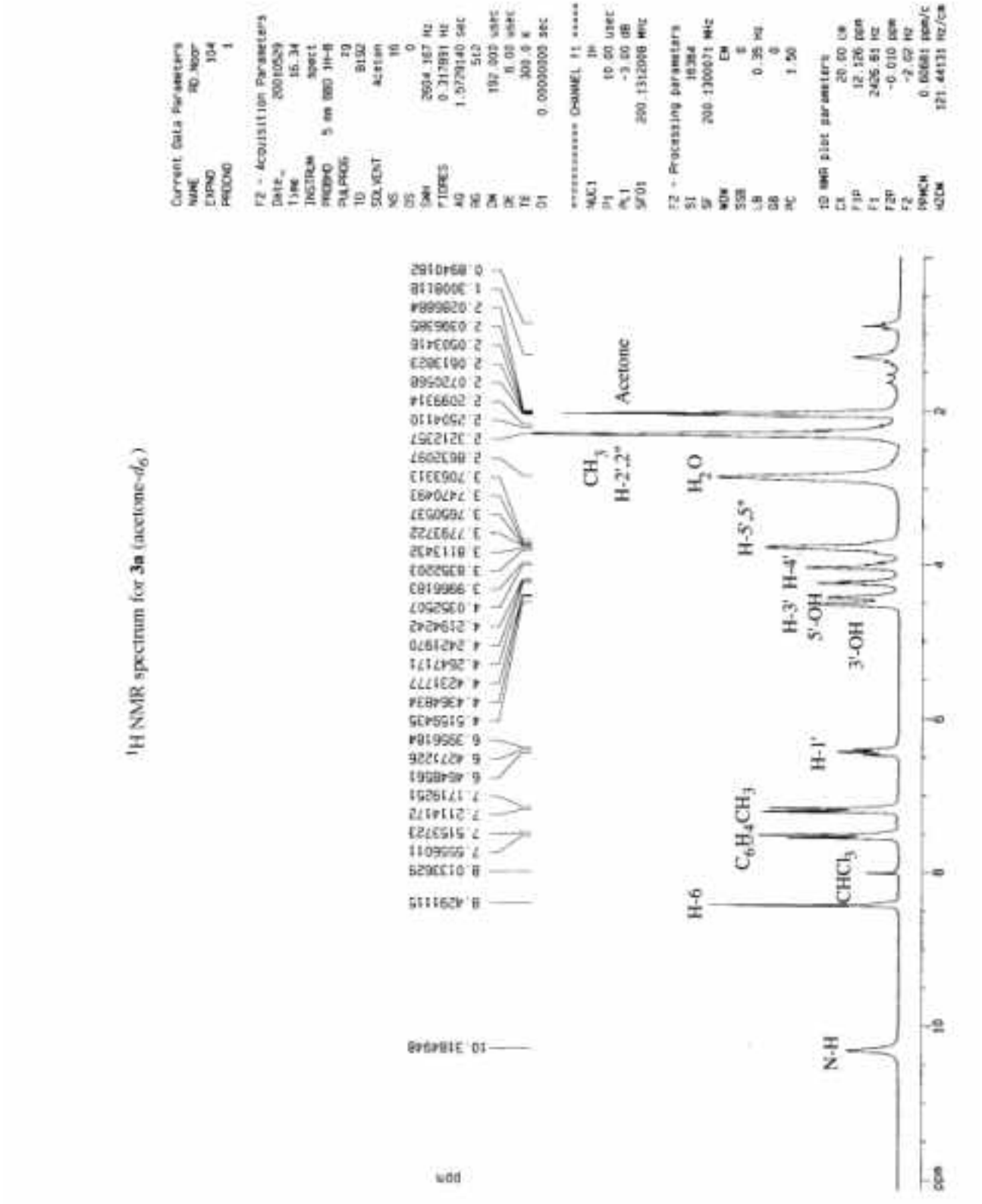
(S11) H2' signal obscured by CH_3.

(S12) *C*≡ signal obscured by C1', chemical shift from $^{13}C\{^1H\}$ spectrum.

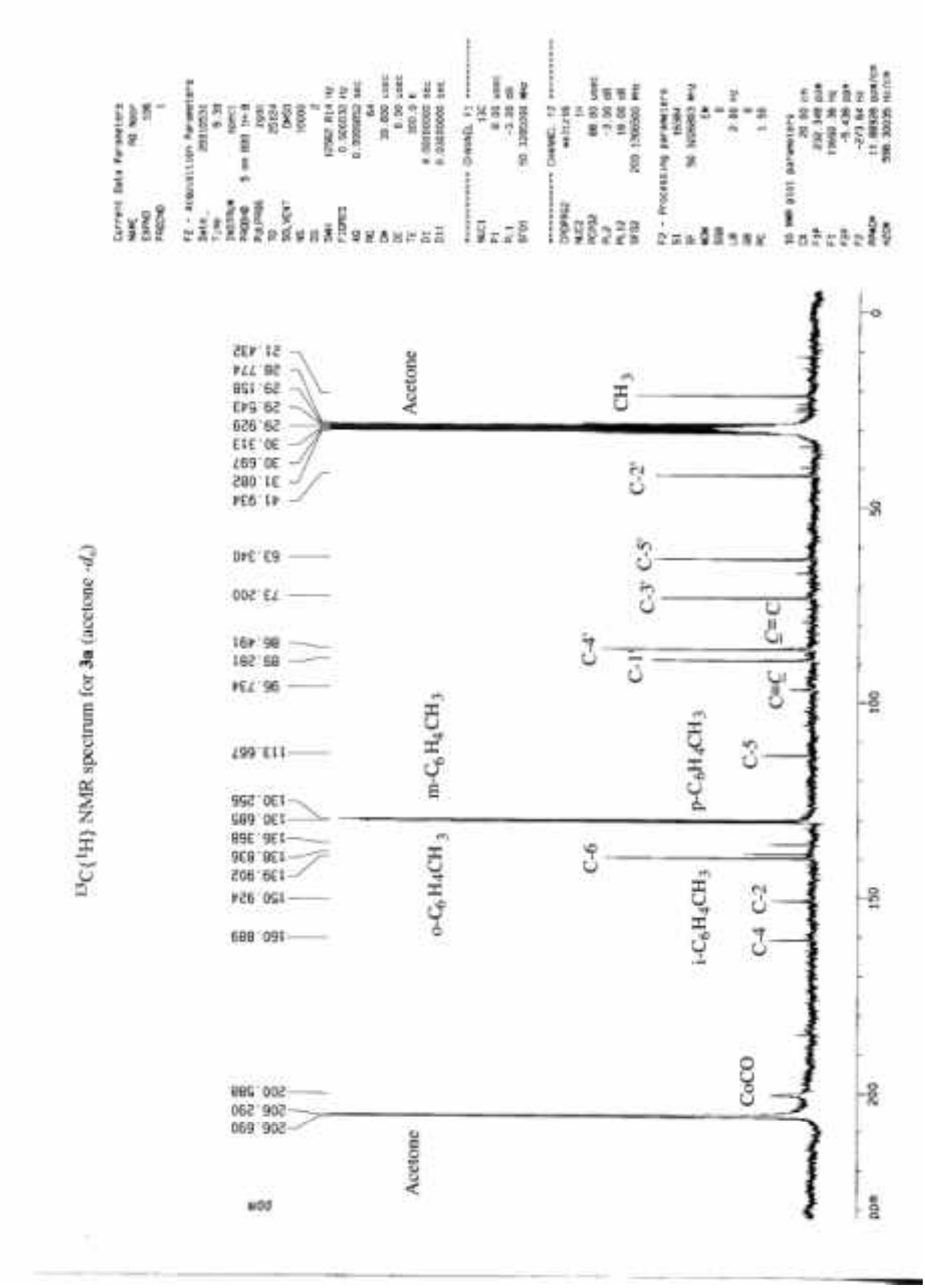
Expanded COSY (^{1}H-2D) Counter Plot for **2a**

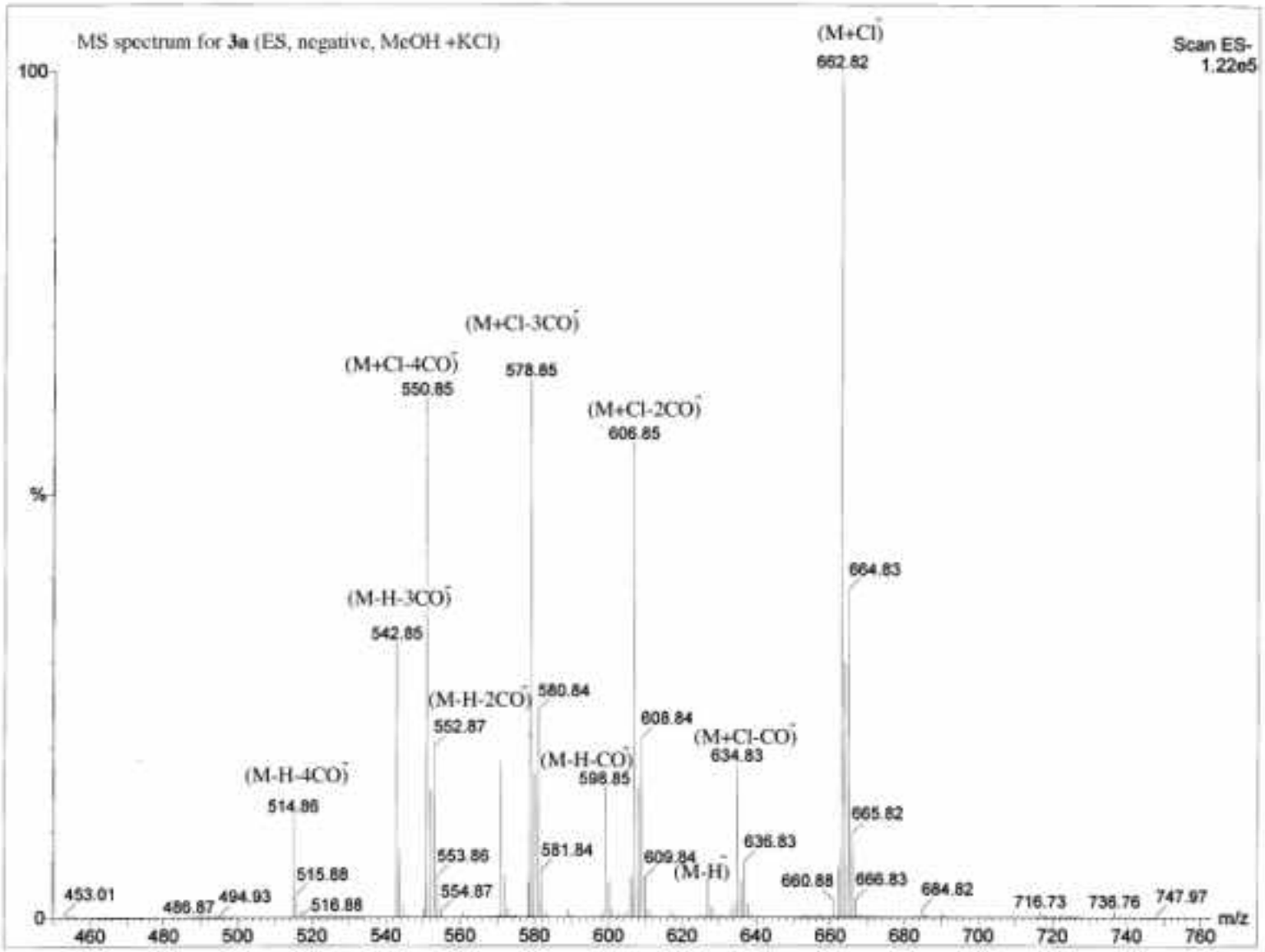


^{1}H NMR spectrum for **3a** (acetone-d_6)



$^{13}C\{^1H\}$ NMR spectrum for **3a** (acetone-d_6)




MS spectrum for 3a (ES, negative, MeOH +KCl)
Scan ES-
1.22e5
100
%
0
(M+Cl)
662.82
(M+Cl-3CO)
578.85
(M+Cl-4CO)
550.85
(M+Cl-2CO)
606.85
(M-H-3CO)
542.85
(M-H-2CO)
580.84
552.87
608.84
(M+Cl-CO)
634.83
(M-H-CO)
598.85
(M-H-4CO)
514.86
664.83
665.82
636.83
553.86
581.84
609.84
(M-H)
515.88
554.87
660.88
666.83
684.82
453.01
486.87
494.93
516.88
716.73
736.76
747.97
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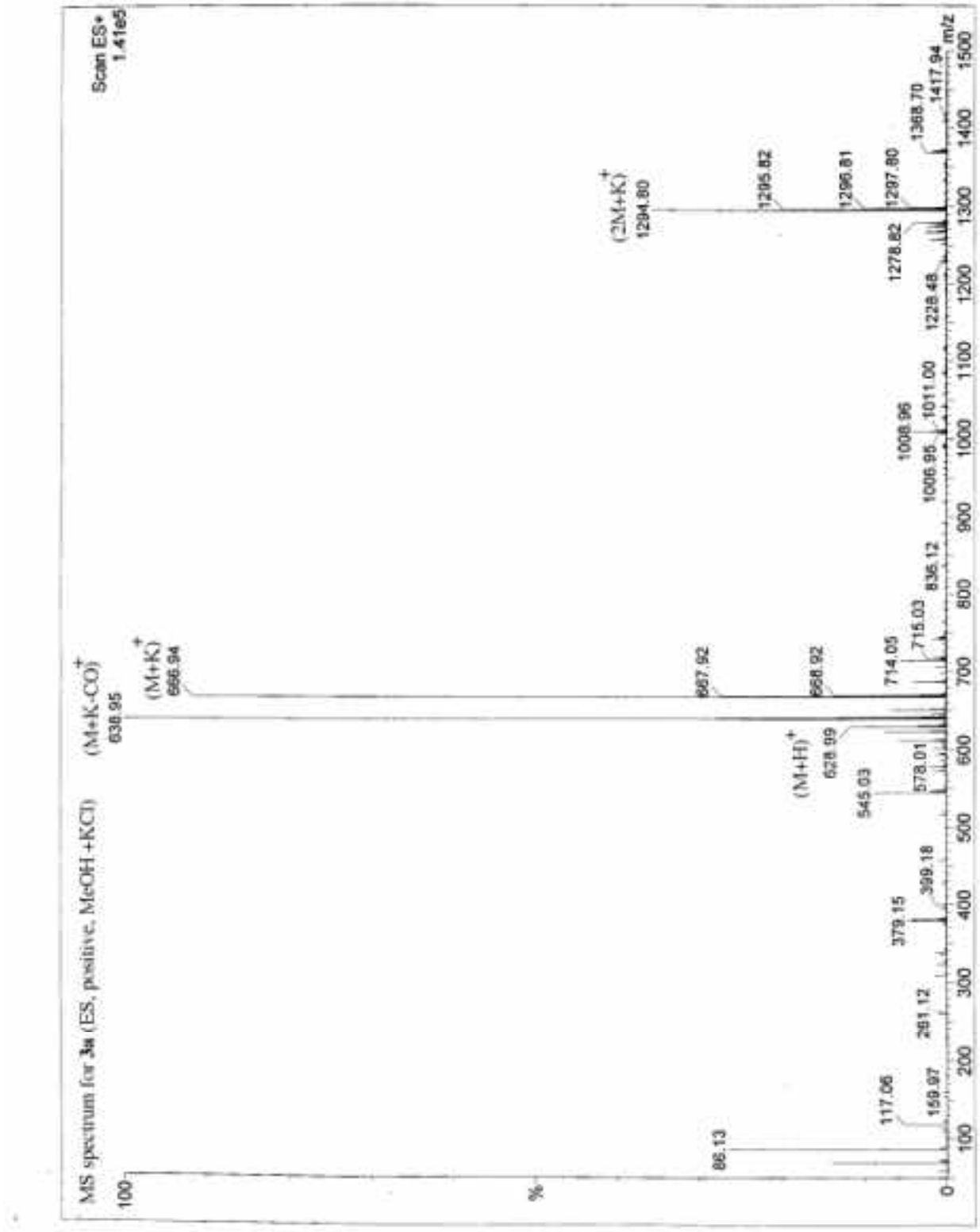
620
640
660
680
700
720
740
760
m/z


MS spectrum for 3a (ES, positive, MeOH+KCl)
Scan ES+
1.41e5
100
%
0
(M+K-CO)+
638.95
(M+K)+
666.94
(M+H)+
628.99
(2M+K)+
1294.80
86.13
117.06
159.97
261.12
379.15
399.18
545.03
578.01
667.92
668.92
714.05
715.03
836.12
1006.95
1008.96
1011.00
1228.48
1278.82
1295.82
1296.81
1297.80
1368.70
1417.94
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
m/z

Cyclic Voltammograms of **3a** and **3b** (0.1 M $Bu_4N^+BF_4^-$/ CH_2Cl_2 at 22.5 ^oC)