Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Exploring the Intermediates of Photochemical CO_2 Reduction: Reaction of Re(dmb)$(CO)_3$COOH with CO_2

Jay Agarwal,[†,‡] Brian C. Sanders,[¶] Etsuko Fujita,[‡] Henry F. Schaefer III,[*,†] Todd C. Harrop,[¶] and James T. Muckerman[*,‡]

Center for Computational Quantum Chemistry

University of Georgia, Athens, GA 30602, Chemistry Department

Brookhaven National Laboratory, Upton, NY, 11973, and Chemistry Department

University of Georgia, Athens, GA 30602

E-mail: fri@uga.edu; muckerma@bnl.gov

Contents

[†]Center for Computational Quantum Chemistry, University of Georgia
[‡]Chemistry Department, Brookhaven National Laboratory
[¶]Chemistry Department, University of Georgia

A. Complete Citation for Reference 20

(20) Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ĕ.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

B. Data for Computed Stationary Points

1

Charge = 0 Multiplicity = 1
Re -0.870789 -0.000049 -0.168570
N 0.885861 1.321933 -0.216571
N 0.885951 -1.321894 -0.216544
C 2.103548 0.732916 -0.096104
C 2.103602 -0.732794 -0.096116
C 0.815454 -2.664728 -0.261977
C 3.268667 -1.497867 -0.015595
C 3.186132 -2.881597 -0.057186
C 1.934580 -3.478142 -0.187454
C 0.815275 2.664763 -0.261990
C 1.934344 3.478251 -0.187405
C 3.185930 2.881787 -0.057079
C 3.268555 1.498063 -0.015507
C -2.212603 1.341350 0.060429
C -2.212497 -1.341556 0.060466
O -3.011111 2.183232 0.226030
O -3.010941 -2.183515 0.225985
C -1.108530 0.000064 -2.111054
O -1.294616 0.000198 -3.264314
H -0.179685 -3.085271 -0.362014
H 4.233641 -1.014067 0.077972
H 4.085370 -3.485002 0.006111
H 1.819265 -4.554813 -0.229407
H -0.179889 3.085242 -0.362056
H 1.818958 4.554915 -0.229348
H 4.085123 3.485253 0.006273
H 4.233550 1.014322 0.078113
C -0.450029 0.000028 1.997186
O -1.546081 0.000166 2.830941
O 0.663049 -0.000151 2.521452
H -1.206822 0.000188 3.744467

Zero-point correction = 0.210078 (Hartree/Particle)
Thermal correction to Energy = 0.230377
Thermal correction to Enthalpy = 0.231321
Thermal correction to Gibbs Free Energy = 0.159254
Sum of electronic and zero-point Energies = -1103.570744
Sum of electronic and thermal Energies = -1103.550445
Sum of electronic and thermal Enthalpies = -1103.549501
Sum of electronic and thermal Free Energies = -1103.621569

2

Charge = 0 Multiplicity = 1
C 0.000000 0.000000 0.000000
O 0.000000 0.000000 1.168469
O 0.000000 0.000000 -1.168469

Zero-point correction = 0.011748 (Hartree/Particle)
Thermal correction to Energy = 0.014375
Thermal correction to Enthalpy = 0.015319
Thermal correction to Gibbs Free Energy = -0.008961
Sum of electronic and zero-point Energies = -188.571170
Sum of electronic and thermal Energies = -188.568543
Sum of electronic and thermal Enthalpies = -188.567598
Sum of electronic and thermal Free Energies = -188.591878

TS 3

Charge = 0 Multiplicity = 1
Re -0.209337 -0.626366 0.486335
N 1.737200 -0.699012 -0.556850
N 0.630534 1.412895 0.582929
C 2.454897 0.453363 -0.630643
C 1.843536 1.623937 0.008013
C -0.004861 2.444267 1.165988
C 2.439747 2.884682 0.032331
C 1.784114 3.941449 0.648835
C 0.536787 3.718934 1.223538
C 2.231554 -1.812477 -1.126974
C 3.449520 -1.837362 -1.787988
C 4.190719 -0.662530 -1.867347
C 3.686903 0.491410 -1.283602
C -0.771202 -2.432314 0.176380
C -1.869537 -0.251189 1.376589
O -1.090438 -3.535385 -0.039529
O -2.852178 0.023048 1.941464
C 0.595580 -1.159862 2.186851
O 1.068267 -1.501048 3.193582
H -0.978398 2.225254 1.590369
H 3.408821 3.039500 -0.426204
H 2.240927 4.925031 0.676216
H -0.014745 4.513998 1.710971
H 1.619115 -2.703828 -1.042386
H 3.801231 -2.762901 -2.228220
H 5.147673 -0.642365 -2.377841
H 4.248103 1.416660 -1.336283
C -0.953546 -0.022759 -1.432917
O -2.148449 1.363203 -1.062790
O -0.887645 -0.171637 -2.593375
H -1.959052 2.056198 -1.713724
O -3.910455 -0.320733 -1.144577
C -3.811040 0.809930 -1.536950
O -4.329919 1.739530 -2.097674

Imaginary Frequency = 482.94i
Zero-point correction = 0.220213 (Hartree/Particle)
Thermal correction to Energy = 0.244371
Thermal correction to Enthalpy = 0.245315
Thermal correction to Gibbs Free Energy = 0.163018
Sum of electronic and zero-point Energies = -1292.104132
Sum of electronic and thermal Energies = -1292.079974

Sum of electronic and thermal Enthalpies = -1292.079029
Sum of electronic and thermal Free Energies = -1292.161327

4

Charge = 1 Multiplicity = 1
Re -0.883109 -0.000001 0.000173
N 0.878637 1.325293 -0.000214
N 0.878636 -1.325295 -0.000022
C 2.102574 0.732852 -0.000337
C 2.102574 -0.732855 -0.000313
C 0.801766 -2.668504 0.000040
C 3.268029 -1.498174 -0.000591
C 3.181215 -2.883023 -0.000524
C 1.925153 -3.480378 -0.000192
C 0.801770 2.668503 -0.000254
C 1.925158 3.480375 -0.000411
C 3.181219 2.883019 -0.000507
C 3.268031 1.498169 -0.000468
C -2.253429 1.364853 0.000282
C -2.253450 -1.364835 0.000622
O -3.053034 2.207074 -0.000168
O -3.053086 -2.207025 0.000525
C -0.886117 -0.000117 -2.012822
O -0.922620 -0.000918 -3.162901
H -0.196405 -3.091966 0.000277
H 4.237251 -1.014171 -0.000879
H 4.082542 -3.485888 -0.000733
H 1.806338 -4.557136 -0.000125
H -0.196401 3.091967 -0.000155
H 1.806344 4.557133 -0.000441
H 4.082547 3.485882 -0.000610
H 4.237252 1.014164 -0.000520
C -0.885384 0.000130 2.013166
O -0.921490 0.000870 3.163257

Zero-point correction = 0.195284 (Hartree/Particle)
Thermal correction to Energy = 0.214361
Thermal correction to Enthalpy = 0.215305
Thermal correction to Gibbs Free Energy = 0.145781
Sum of electronic and zero-point Energies = -1027.603539
Sum of electronic and thermal Energies = -1027.584461
Sum of electronic and thermal Enthalpies = -1027.583517
Sum of electronic and thermal Free Energies = -1027.653042

5

Charge = -1 Multiplicity = 1
O -1.188587 -0.615036 -0.000094
C -0.139464 0.059107 0.000003
O 0.032379 1.300804 -0.000009
O 1.039754 -0.719341 0.000084
H 1.768411 -0.086054 0.000129

Zero-point correction = 0.026349 (Hartree/Particle)
Thermal correction to Energy = 0.029866
Thermal correction to Enthalpy = 0.030810
Thermal correction to Gibbs Free Energy = 0.000590
Sum of electronic and zero-point Energies = -264.517108
Sum of electronic and thermal Energies = -264.513591
Sum of electronic and thermal Enthalpies = -264.512647
Sum of electronic and thermal Free Energies = -264.542867

TS 6

Charge = 0 Multiplicity = 1
C -0.853149 -1.804361 1.853021
O -0.722896 -0.549059 1.885655
O -0.091844 -2.649244 1.337479
O 2.406773 -2.573057 -0.970575
O 3.584998 1.551720 0.136377
C 1.872403 -1.566229 -0.730031
C 2.586555 0.965720 -0.018206
O 1.184462 0.922747 -3.252085
C 1.079906 0.589214 -2.133218
Re 0.926796 0.065768 -0.349246
H -0.502546 -2.530093 -1.508712
H 1.023025 3.003658 0.806828
C -1.362721 -1.892078 -1.338031
N -1.105826 -0.685429 -0.809199
C -0.047798 2.866617 0.700828
N -0.444667 1.690282 0.183426
C -2.648979 -2.318679 -1.638198
H -2.801992 -3.304686 -2.060886
C -2.137857 0.160753 -0.559099
C -0.938405 3.857855 1.083280
C -1.774201 1.458704 0.018545
H -0.562109 4.786088 1.496432
C -3.712166 -1.459798 -1.383774
C -3.452285 -0.207108 -0.842404
C -2.300424 3.627231 0.921868
C -2.717932 2.418079 0.382744
H -4.731897 -1.757062 -1.604552
H -4.268145 0.476954 -0.641662
H -3.029744 4.376621 1.210705
H -3.774637 2.219210 0.251101
O -2.010128 -2.259491 2.464696
C 1.717739 -0.645602 2.208750
O 1.914279 -0.983208 3.284203
H -1.997456 -3.222456 2.382128

Imaginary Frequency = 175.64i
Zero-point correction = 0.221923 (Hartree/Particle)
Thermal correction to Energy = 0.245663
Thermal correction to Enthalpy = 0.246607
Thermal correction to Gibbs Free Energy = 0.166904
Sum of electronic and zero-point Energies = -1292.100347
Sum of electronic and thermal Energies = -1292.076607

Sum of electronic and thermal Enthalpies = -1292.075663
Sum of electronic and thermal Free Energies = -1292.155366

7

Charge = 0 Multiplicity = 1
C 0.000000 0.000000 -0.651588
O 0.000000 0.000000 0.488691

Zero-point correction = 0.005011 (Hartree/Particle)
Thermal correction to Energy = 0.007372
Thermal correction to Enthalpy = 0.008316
Thermal correction to Gibbs Free Energy = -0.014131
Sum of electronic and zero-point Energies = -113.296325
Sum of electronic and thermal Energies = -113.293964
Sum of electronic and thermal Enthalpies = -113.293020
Sum of electronic and thermal Free Energies = -113.315467

8

Charge = 0 Multiplicity = 1
C -1.528793 0.000470 2.510149
O -0.511613 0.000214 1.727248
O -2.728023 0.000617 2.221558
O -2.893698 2.164239 -0.512977
O -2.893420 -2.164851 -0.512299
C -2.073712 1.331202 -0.482995
C -2.073559 -1.331682 -0.482552
O -0.592748 -0.000699 -3.506408
C -0.630157 -0.000473 -2.334644
Re -0.701634 -0.000148 -0.432718
H 0.001570 3.082866 -0.461685
H 0.002014 -3.083076 -0.460722
C 0.972488 2.664310 -0.217918
N 1.042285 1.322793 -0.175087
C 0.972874 -2.664303 -0.217095
N 1.042473 -1.322762 -0.174666
C 2.065291 3.480251 0.032866
H 1.953790 4.556983 -0.014532
C 2.230120 0.734092 0.120061
C 2.065806 -3.480005 0.033901
C 2.230229 -0.733796 0.120269
H 1.954462 -4.556768 -0.013166
C 3.283828 2.885273 0.343101
C 3.365680 1.500181 0.384369
C 3.284270 -2.884753 0.343899
C 3.365918 -1.499636 0.384743
H 4.160835 3.489392 0.549308
H 4.307647 1.018985 0.619254
H 4.161378 -3.488678 0.550241
H 4.307829 -1.018226 0.619410
O -1.137047 0.000692 3.825018
H -1.949610 0.000921 4.347968

Zero-point correction = 0.215658 (Hartree/Particle)
Thermal correction to Energy = 0.236990
Thermal correction to Enthalpy = 0.237935
Thermal correction to Gibbs Free Energy = 0.161476
Sum of electronic and zero-point Energies = -1178.836413
Sum of electronic and thermal Energies = -1178.815080
Sum of electronic and thermal Enthalpies = -1178.814136
Sum of electronic and thermal Free Energies = -1178.890595

Transition state for equitorial CO ligand loss.

Charge = 0 Multiplicity = 1
C -3.767412 0.211289 0.204109
O -2.772012 0.706368 0.818145
O -3.802634 -0.377857 -0.887703
O -2.335341 2.198414 -1.767464
O -1.951600 -2.746083 0.503334
C -1.596070 1.748489 -1.014311
C -1.357614 -1.750931 0.301185
O -0.626422 -0.919312 -3.000132
C -0.472377 -0.600066 -1.895805
Re -0.319390 -0.202075 0.045771
H -0.041153 3.076996 0.184579
H 0.742446 -3.082749 0.038897
C 0.999528 2.777621 0.130906
N 1.227651 1.458379 0.020241
C 1.669794 -2.525824 -0.012738
N 1.551223 -1.178764 0.013722
C 2.014968 3.719572 0.183501
H 1.767047 4.770636 0.274709
C 2.513625 1.023060 -0.005469
C 2.889505 -3.172358 -0.097317
C 2.691220 -0.427567 -0.043704
H 2.911862 -4.255663 -0.113803
C 3.333849 3.282126 0.117440
C 3.583504 1.920728 0.030791
C 4.055047 -2.413855 -0.155853
C 3.945970 -1.033383 -0.127786
H 4.157689 3.987309 0.146952
H 4.604031 1.559220 0.002227
H 5.028484 -2.886989 -0.223178
H 4.836099 -0.418559 -0.175827
O -4.961266 0.397415 0.889584
C -0.339461 -0.021878 2.033724
O -0.405880 -0.005333 3.189673
H -5.647612 -0.002911 0.339355

Imaginary Frequency = 213.75i
Zero-point correction = 0.220473 (Hartree/Particle)
Thermal correction to Energy = 0.244858
Thermal correction to Enthalpy = 0.245802
Thermal correction to Gibbs Free Energy = 0.162563
Sum of electronic and zero-point Energies = -1292.060251
Sum of electronic and thermal Energies = -1292.035866

Sum of electronic and thermal Enthalpies = -1292.034922
Sum of electronic and thermal Free Energies = -1292.118161

C. Experimental Methods

General Information. All reagents were procured from commercial suppliers and used as received unless otherwise noted. $^{13}CO_{2(g)}$ (^{13}C, 99%) and DMSO-d_6 were purchased from Cambridge Isotope Laboratories and used without further purification. Dichloromethane (CH_2Cl_2) was purified using activated alumina columns in an MBraun MB-SPS solvent purification system and stored over 4 Å molecular sieves under a nitrogen (N_2) atmosphere. All reactions were performed using standard Schlenk-line and glovebox techniques under an atmosphere of purified N_2 with minimal exposure to light.

Physical Methods. FTIR spectra were collected with a ThermoNicolet 6700 spectrophotometer running OMNIC software. Samples were run in a KBr matrix under a stream of dry N_2. All FTIR samples were prepared under N_2 with minimal light exposure. ^1H NMR and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Bruker BZH 400/52 400 MHz NMR spectrometer or a Varian Unity Inova 500 MHz NMR spectrometer at 298 K. Chemical shifts were referenced to TMS or residual protio signal of the deuterated solvent.

***fac*-Re(4,4'-dimethyl-2,2'-bipyridine)(CO)$_3$COOH (1)**. Silver triflate (0.229 g, 1.16 mmol) was dissolved in 20 mL of degassed CH_2Cl_2 and added to a flask containing $Re(CO)_5Cl$ (0.401 g, 1.11 mmol) dissolved in 80 mL of CH_2Cl_2. This clear solution was allowed to stir at room temperature for 18 hrs. The white AgCl precipitate was removed by filtration and washed with CH_2Cl_2. An aliquot of 4,4'-dimethyl-2,2'-bipyridine (0.221 g, 1.20 mmol) was added to the filtrate, and the solution was stirred for 8 hrs. The resulting yellow-green solution was reduced to 20 mL under vacuum. The addition of hexanes afforded a yellow precipitate, which was collected by filtration and dried under vacuum to yield 0.456 g (0.72 mmol, 65 %) of a light yellow solid. This intermediate, *fac*-Re(4,4'-dimethyl-2,2'-bipyridine)$(CO)_4(CF_3SO_3)$, was confirmed by IR spectroscopy and used without further purification. The intermediate (0.456 g, 0.72 mmol) was dissolved in 60 mL of deionized water. Potassium hydroxide (0.040 g, 0.71 mmol) was added to the rhenium solution, which was allowed to stir for 1 hr. A yellow precipitate formed almost immediately after the addition of KOH. The precipitate was collected by filtration and dried under vacuum, yielding 0.266 g (0.56 mmol, 78 %) of product. IR ν_{CO} (KBr, cm^{-1}): 2008 (s), 1916 (sh), 1880 (s). ^1H NMR (DMSO-d_6, 25 °C): δ 9.02 (1H, s), 8.79 (2H, d, J=4Hz), 8.58 (2H, s), 7.50 (2H, d, J=4Hz), 2.53 (6H, s).

Reaction of *fac*-Re(dmb)(CO)$_3$COOH (1) with CO$_2$. Complex **1** (0.035g, 0.07 mmol) was dissolved in approximately 2.25 mL of DMSO-d_6, yielding a dark yellow mixture. The solution was purged with either unlabeled or ^{13}C labeled CO_2 then allowed to stand for 2 hrs in the dark. Reaction of Re(dmb)CO_3COOH and CO_2 in dark after 2 h. ^1H NMR (DMSO-d_6, 25 °C): δ 9.11 (1H, br), 8.86 (2H, d, J=5Hz), 8.59 (2H, s), 7.58 (2H, d, J=5Hz), 2.53 (6H, s). ^{13}C NMR (DMSO-d_6, 25 °C): δ 198.33, 194.61, 158.61 (OCO_2H), 154.95, 152.68, 152.46, 128.09, 124.56, 20.97. IR ν_{CO} (KBr, cm^{-1}): 2028 (s), 1905 (s), 1857 (s), 1621 (m), 1416 (m), 1346 (m) Reaction of Re(dmb)CO_3COOH and $^{13}CO_2$ in dark after 2 h. ^1H NMR (DMSO-d_6, 25 °C): δ 9.10 (1H, br), 8.86 (2H, d, J=8Hz), 8.61 (2H, s), 7.58 (2H, d, J=8Hz), 2.54 (6H, s). ^{13}C NMR (DMSO-d_6, 25 °C): δ 198.33, 194.62, 158.62 ($O^{13}COOH$), 154.94, 152.66, 152.46, 128.08, 124.57, 20.96. IR ν_{CO} (KBr, cm^{-1}): 2027 (s), 1904 (s), 1858 (s), 1574 (m), 1393 (w), 1330 (m)

D. Data from Experiment

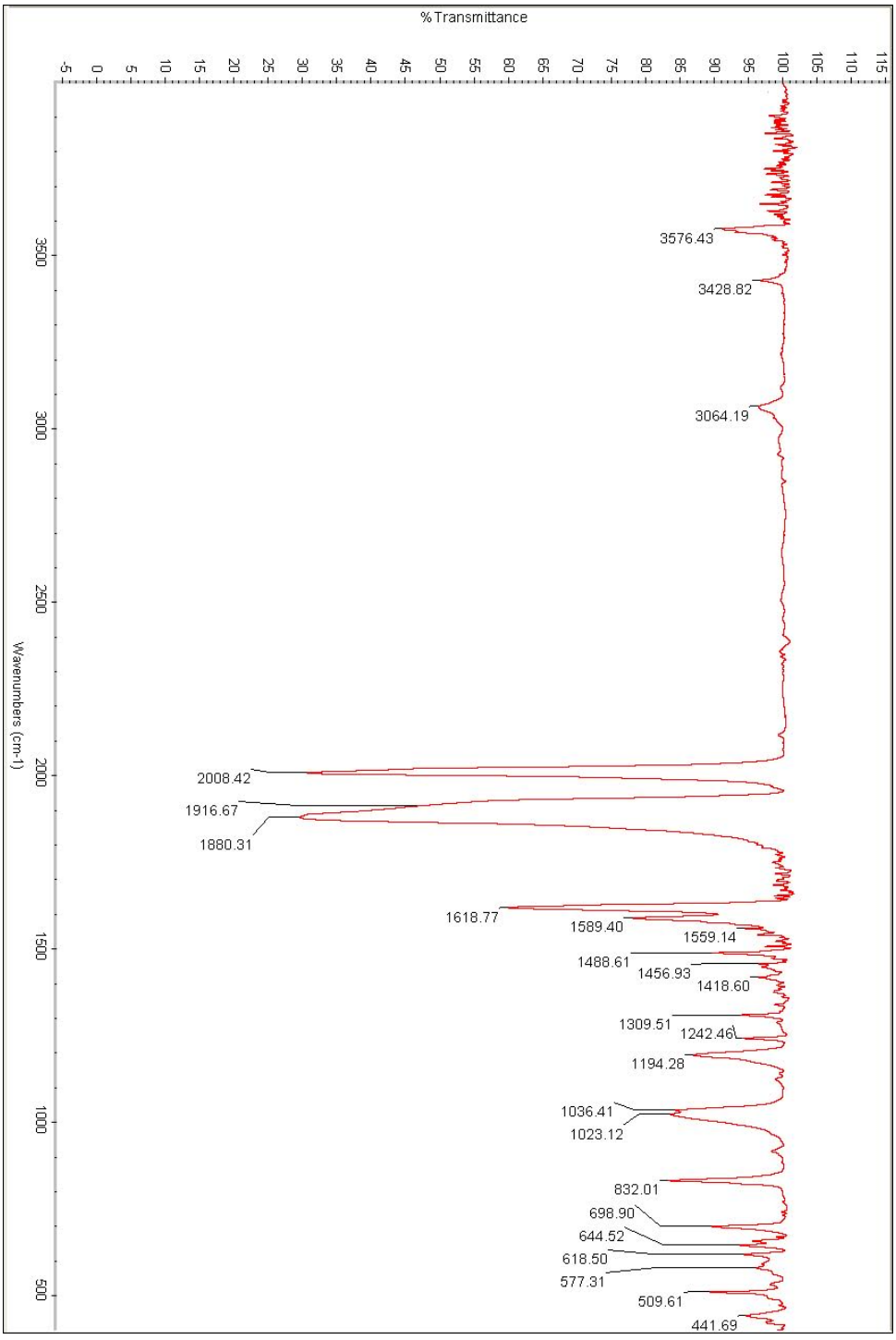

Figure SI-3: FTIR Spectrum of Re(dmb)$(CO)_3$COOH (**1**) (KBr matrix).

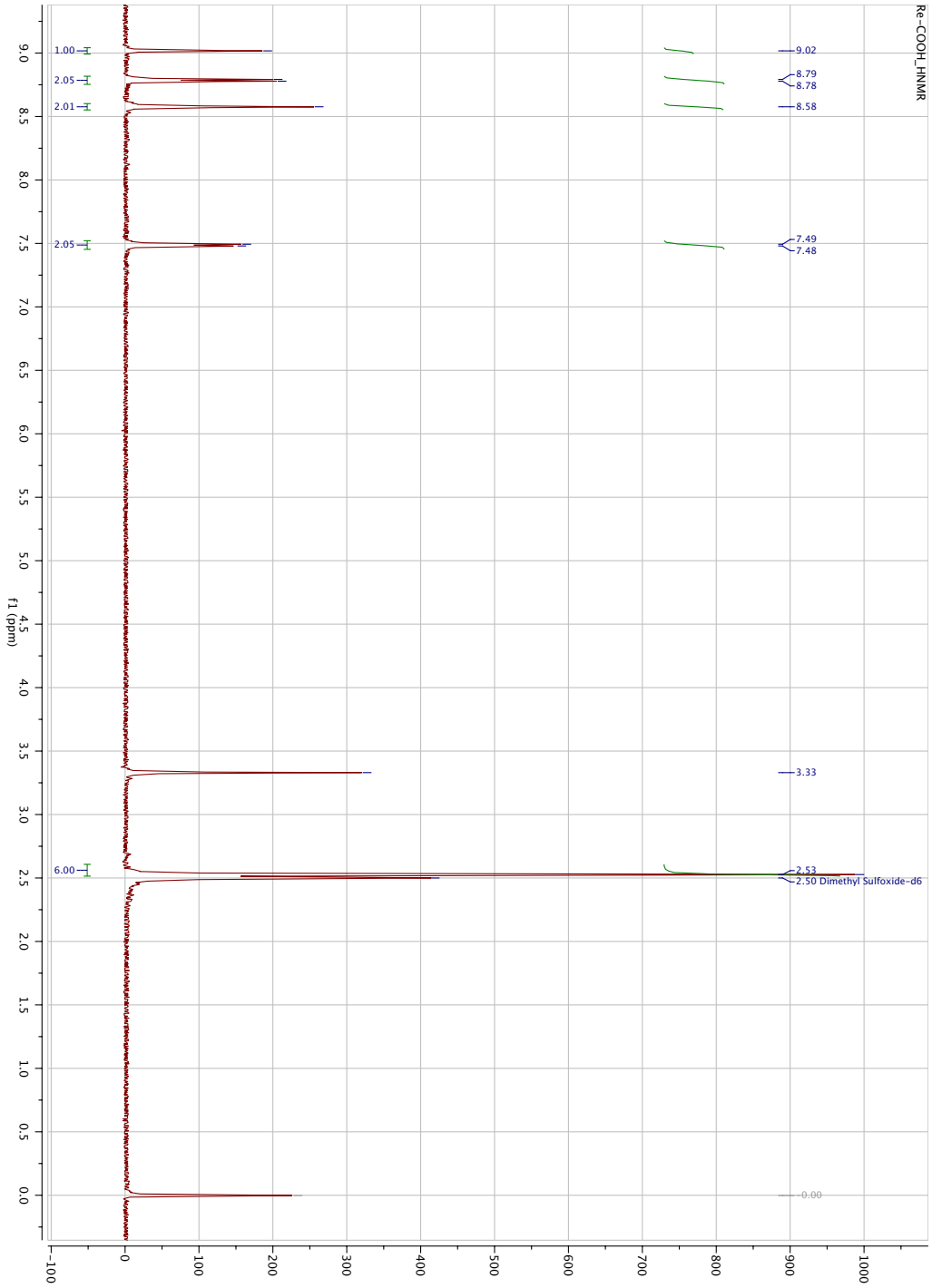

Figure SI-4: ^{1}H NMR Spectrum of Re(dmb)(CO)$_3$COOH (**1**) in DMSO-d_6.

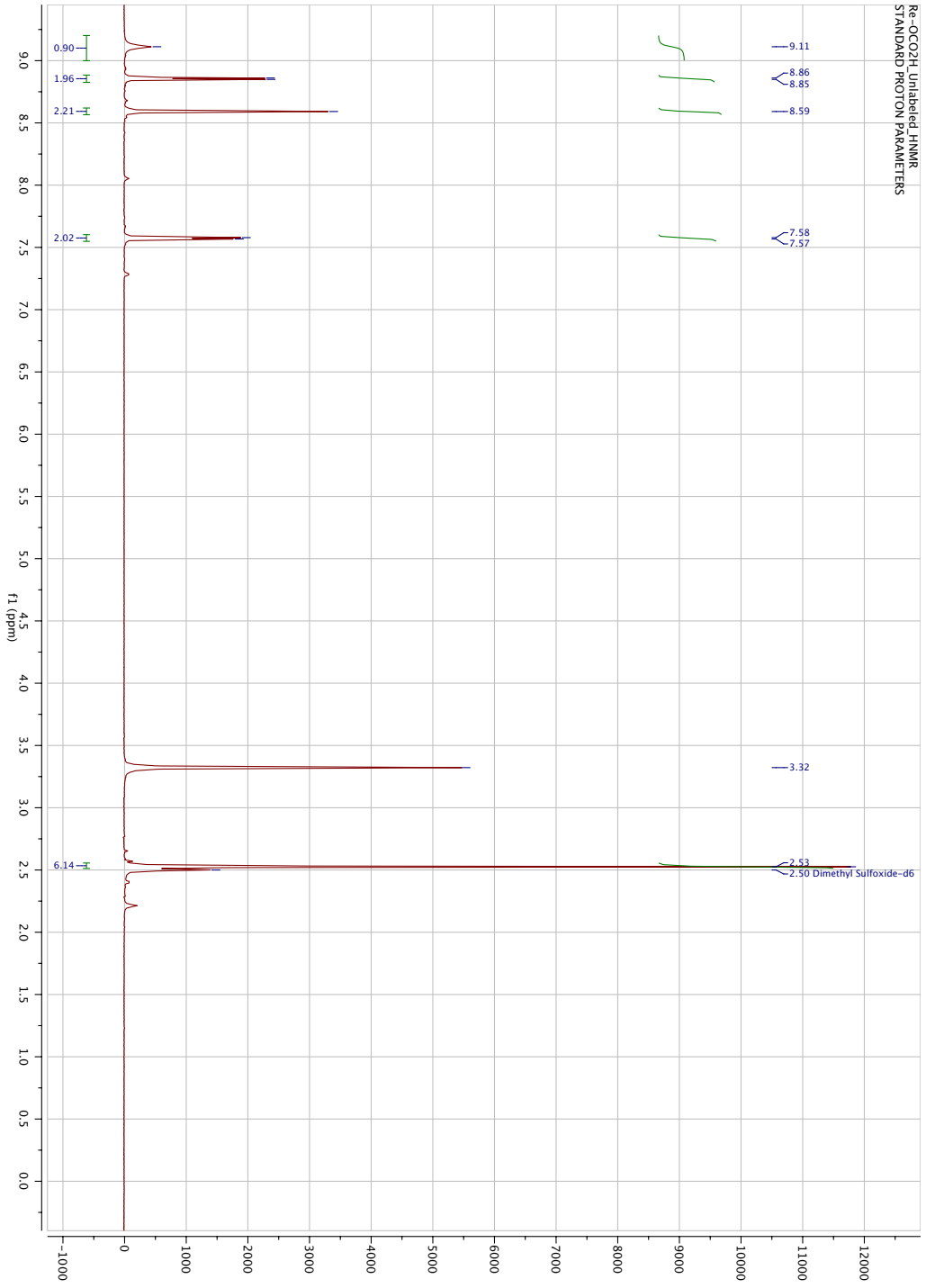

Figure SI-5: ^{1}H NMR Spectrum of Re(dmb)$(CO)_3OCO_2H$ (**8**), from the reaction of Re(dmb)$(CO)_3COOH$ (**1**) with CO_2, in DMSO-d_6.

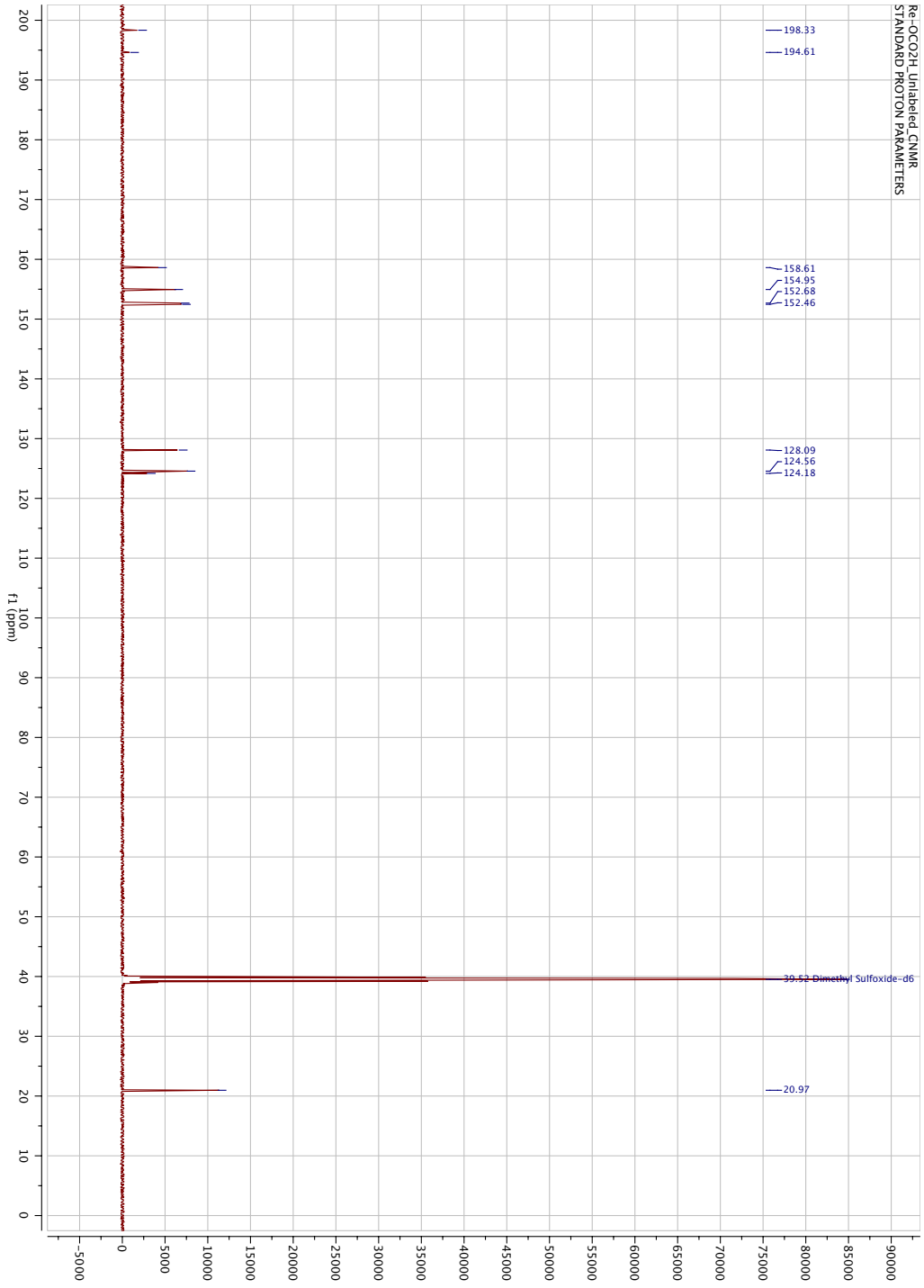

Figure SI-6: ^{13}C NMR Spectrum of Re(dmb)$(CO)_3OCO_2H$ (**8**), from the reaction of Re(dmb)$(CO)_3COOH$ (**1**) with CO_2, in DMSO-d_6. The peak at 124.18 ppm is assigned to the carbon atom of CO_2.

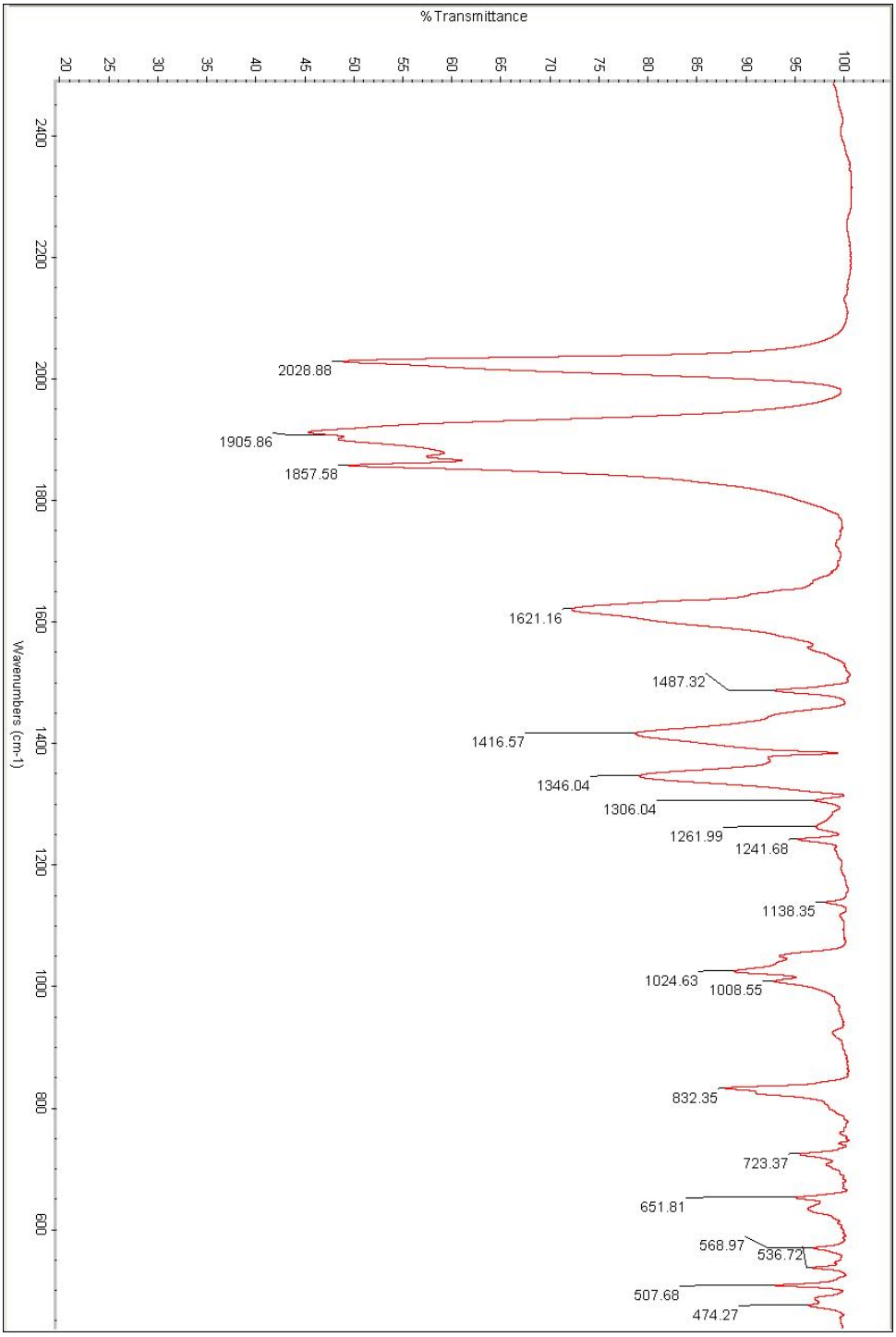

Figure SI-7: FTIR Spectrum of Re(dmb)$(CO)_3OCO_2H$ (**8**), from the reaction of Re(dmb)$(CO)_3COOH$ (**1**) with CO_2 (KBr Matrix).

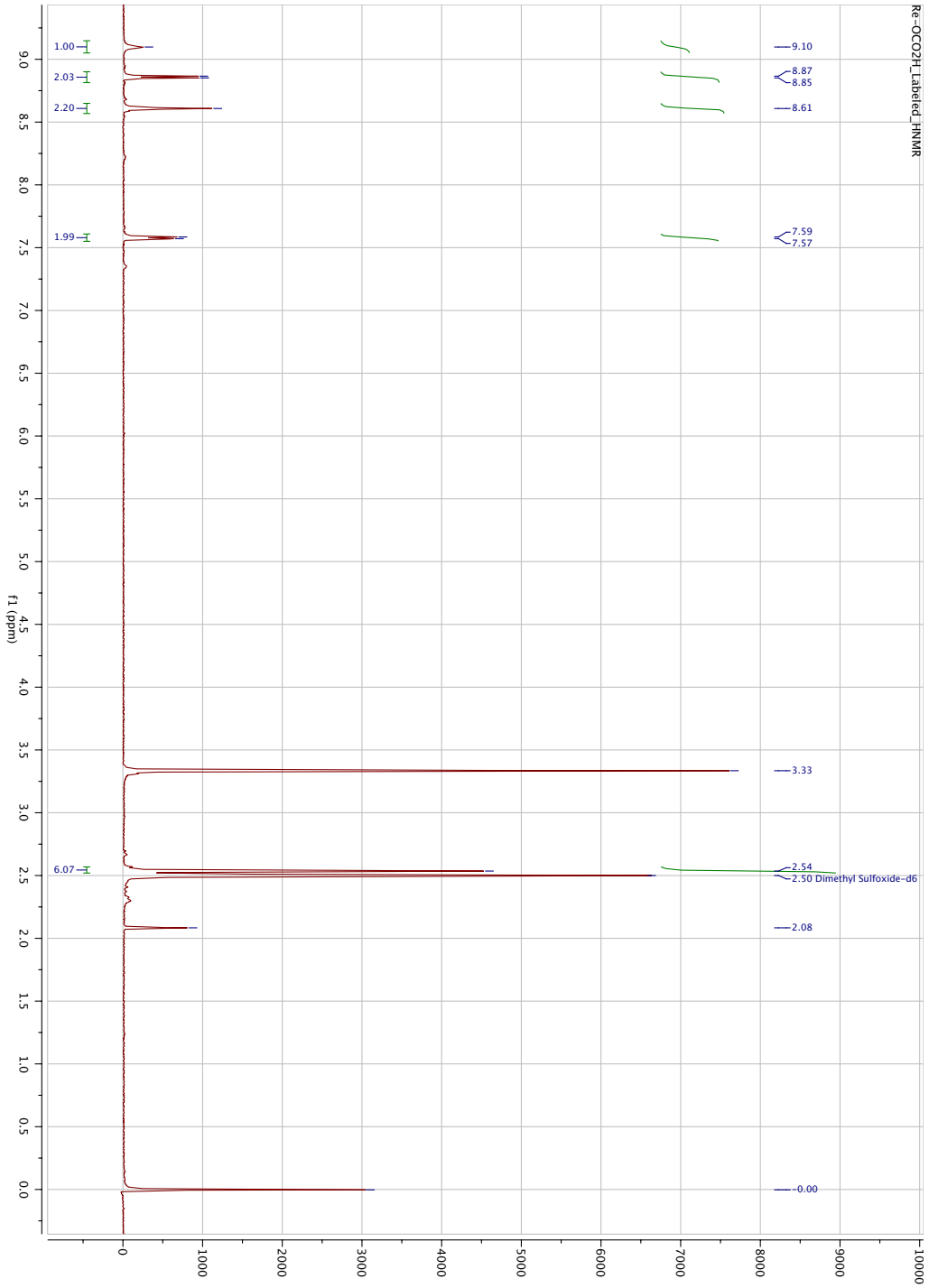

Figure SI-8: ^{1}H NMR Spectrum of Re(dmb)$(CO)_3OCO_2H$ (**8**), from the reaction of Re(dmb)$(CO)_3COOH$ (**1**) with $^{13}CO_2$, in DMSO-d_6. The peak at 2.08 ppm is assigned to acetone.

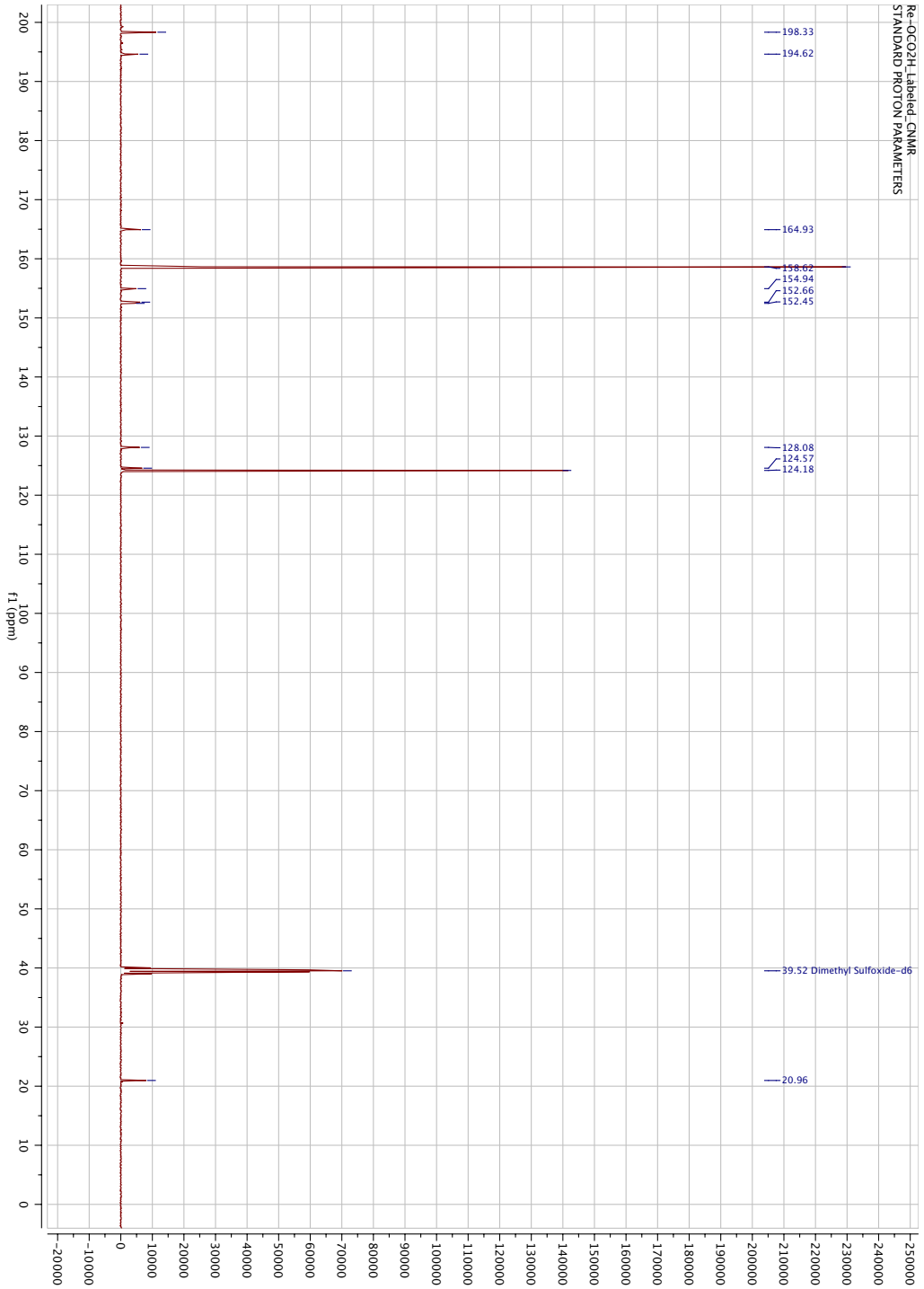

Figure SI-9: ^{13}C NMR Spectrum of Re(dmb)$(CO)_3OCO_2H$ (**8**), from the reaction of Re(dmb)$(CO)_3COOH$ (**1**) with $^{13}CO_2$, in DMSO-d_6. The peak at 124.18 ppm is assigned to the carbon atom of CO_2. The peak at 164.93 ppm is assigned to the carbon atom of $HOCO_2^-$.

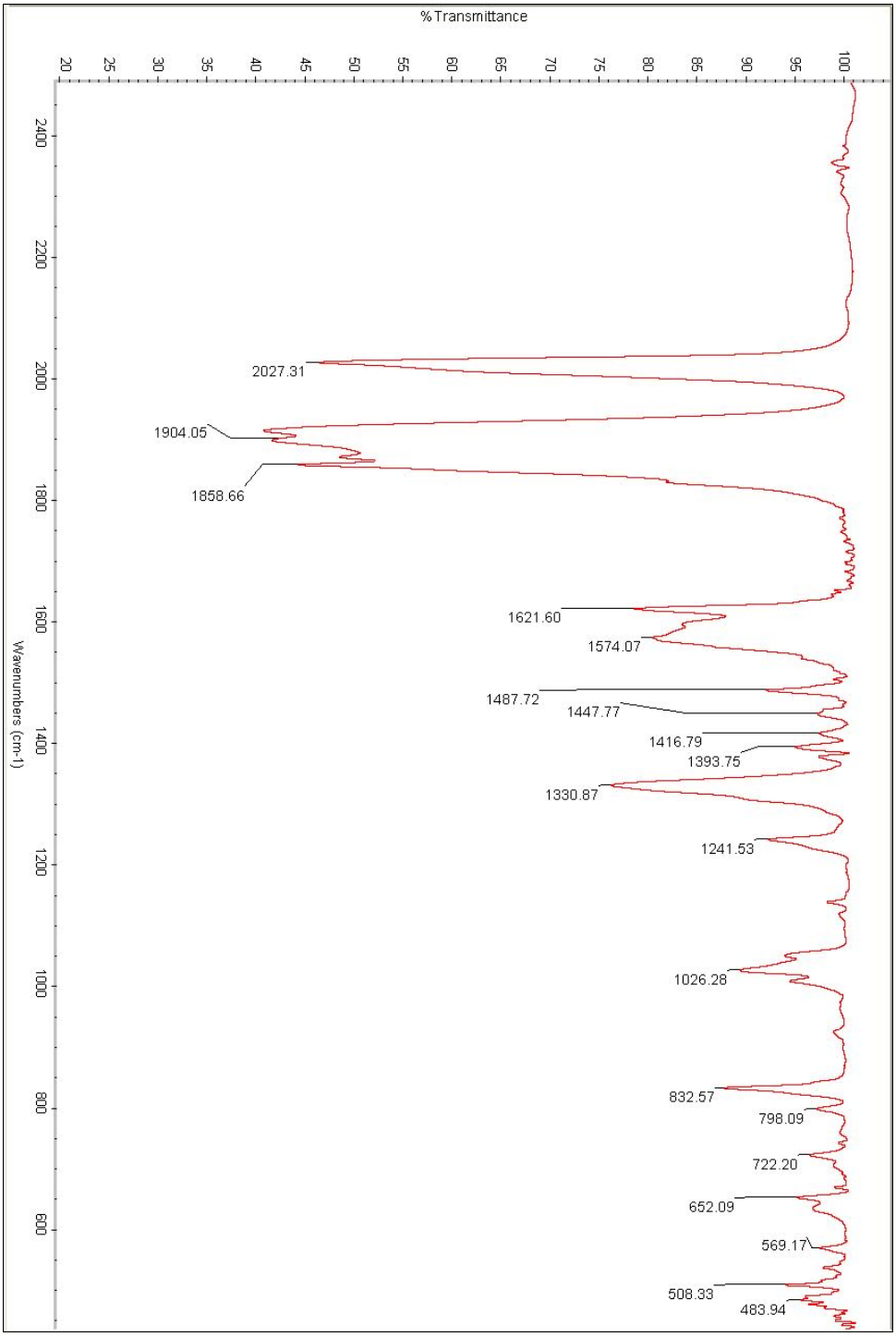

Figure SI-10: FTIR Spectrum of Re(dmb)$(CO)_3OCO_2H$ (**8**), from the reaction of Re(dmb)$(CO)_3COOH$ (**1**) with $^{13}CO_2$ (KBr Matrix).