Supplementary Information

An Investigation into the Photochemistry of, and the Electrochemically Induced CO-loss from, [(CO)5MC(OMe)Me](M = Cr or W) Using Low-temperature Matrix Isolation, Picosecond Infrared Spectroscopy, Cyclic Voltammetry, and Time-dependent Density Functional Theory

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Table S1. A comparison of Bond Lengths of $Cr(CO)_5$=C(OMe)Me Calculated (B3LYP/Tzvp) and Observed (X-Ray Diffraction) in Related Complexes $Cr(CO)_4(PPh_3)$=C(OMe)Me [a] and $Cr(CO)_5$=C(OMe)Ph[b]

Bond	Bond-Length (Å) Observed r_o[a]	Bond-Length (Å) Calculated r_c	r_o-r_c
Cr-C(carbene)	2.04[a], 2.04[b]	2.027	
Cr-C(cis-carbonyl (average))	1.86[a], 1.88[b]	1.915	
Cr-C(trans-carbonyl)	1.83[a], 1.87[b]	1.916	
C(carbene)-O	1.33[b]	1.321	
C(carbene)-C(methyl)		1.503	

[a]Mills, O.S.; Redhouse, A.D. *J. Chem. Soc., Chem. Commun*. **1966**, 814, [b]Mills, O.S.; Redhouse, A.D., J. Chem. Soc. (A), **1968**, 642.

Table S2. The Correction Factor for Simulated IR Spectra at the B3LYP/TZVP level for *syn* and *anti* (**1**)

						Correction	
Calculated		Calculated		Calculated	Observed	Factor	
anti		syn		Average			
2029.5		2035.7		2032.6			
2034.5		2036.5		2035.5	1945	0.955539	
2047.4		2049.3		2048.35	1952	0.952962	
2058.3		2064.3		2061.3	1961	0.951341	
2136		2138		2137	2067	0.967244	
				Average Factor		**0.956772**	

Anti to syn activation energy variable temperature NMR experiments

The activation energy for the *anti* to *syn* isomerisation for [$(CO)_5$CrC(OMe)Me] was determined by variable temperature ^{1}H NMR experiments over the temperature range 20 to – 25˚C in deuterodichloromethane. The methyl protons resonate ~ 2.8 ppm while the methoxy protons are evident at ~ 4.55 ppm relative to TMS. The Me signal was used in this determination and the peak width at half height was measured at each temperature, and a new peak was evident at 2.91 ppm at temperatures lower than -5˚C.

The rate constant for the isomerisation (*anti-syn*) was estimated using the method described by Gasparro and Kolodny (Gasparro, F.P. and Kolodny, N.H. J. Chem. Ed., 1977,

54, 258-261). The rate data are presented in Table S3. An Arrhenius plot of these data yielded an activation energy of 57 kJ mol^{-1}.

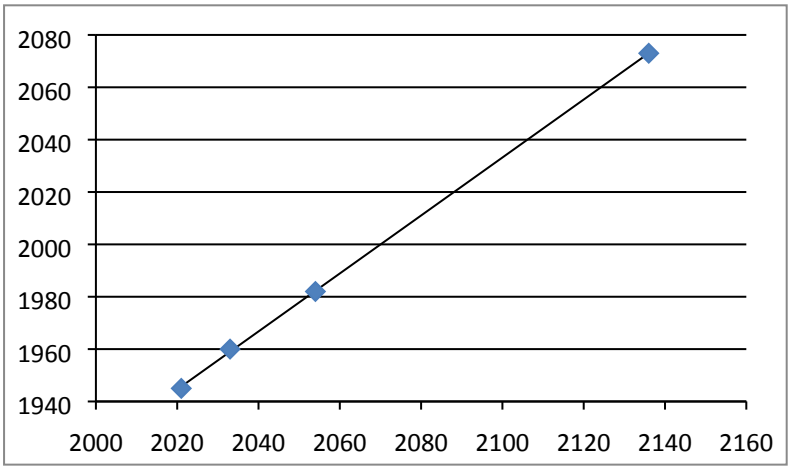
Table S3. The temperature and rate data for the *anti-syn* isomerisation of (**1**).

1/T	lnk
0.003533	1.8628
0.003731	0.4414
0.003952	-0.7981
0.004032	-1.6736

slope= -6796, which yields a value of 57 kJ/mol for the activation energy of the isomerisation process.

Table S4. The calibration of calculated IR bands (B3LYP/TZVP for Cr systems B3LYP/Def2TZVP for W systems) using PCM solvent correction for heptane

Tungsten system

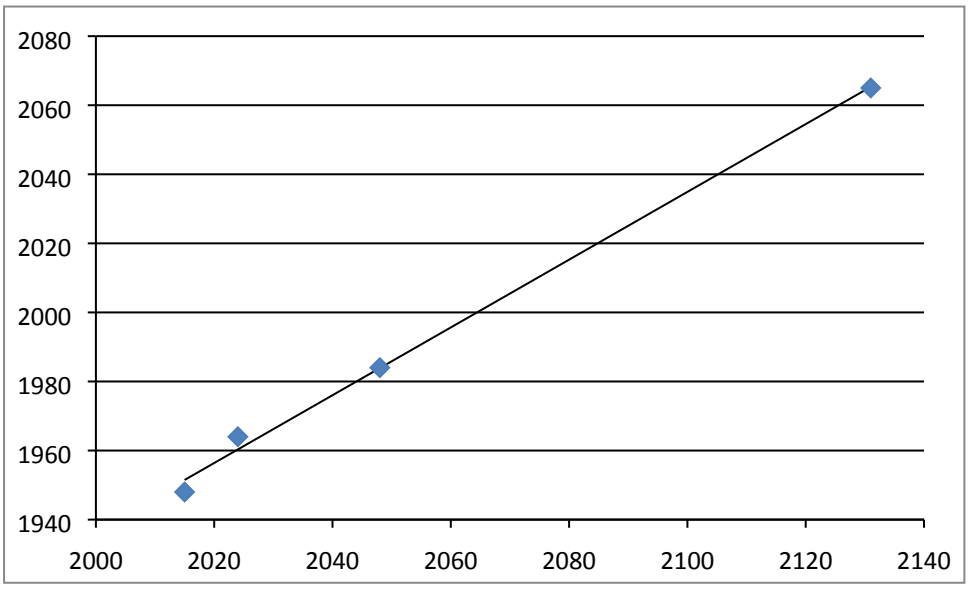


Exp	Calc
2073	2136
1982	2054
1960	2033
1945	2021

Corrected band positions for (**6**) B3LYP/Def2TZVP solvent = heptane

Calc	Corrected		Intensity
1940.5	1856	vw	193
1980.22	1900	m	1144
2020.7	1945	vs	2114
2035	1961	m	963
2116.17	2051	w	377

Chromium System



Exp	Calc	Intensity
1948	2015	4700
1964	2024	1499
1984	2048	165
2065	2131	295

The corrected band positions for (**3**) (B3LYP/TZVP Solvent = heptane)

Calc	corrected	Intensity
1980	1917	975
2000	1937	745
2016	1952	2485
2032	1968	1105
2116	2050	448

Anti-Syn Isomerisation Reaction Coordinate Plot.

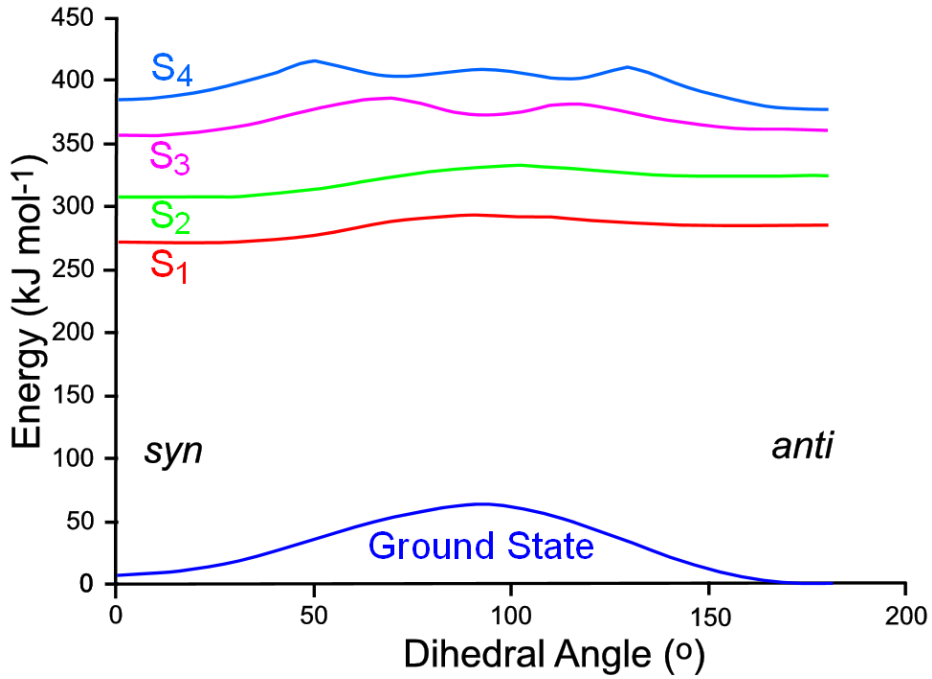


Figure S1. Plot of the variation of ground-state and thefour lowest energy singlet excited states (S1 to S4) with dihedral angle (see text for more details) in (**1**).

Table S5. Table of optimised coordinates for (**1**) at the B3LYP/TZVP level .mol format

```
21 19  0  0  0  0  0  0  0  0  0    0
   -0.5183   -0.0393   -0.0000 Cr  0  0  0  0  0  0  0  0  0  0  0  0
   -0.1713   -1.3644   -1.3430 C   0  0  0  0  0  0  0  0  0  0  0  0
   -0.8117    1.2762   -1.3559 C   0  0  0  0  0  0  0  0  0  0  0  0
   -0.8118    1.2764    1.3558 C   0  0  0  0  0  0  0  0  0  0  0  0
   -0.1713   -1.3643    1.3431 C   0  0  0  0  0  0  0  0  0  0  0  0
   -2.3848   -0.4720   -0.0000 C   0  0  0  0  0  0  0  0  0  0  0  0
    0.0553   -2.1527   -2.1402 O   0  0  0  0  0  0  0  0  0  0  0  0
   -0.9868    2.0654   -2.1687 O   0  0  0  0  0  0  0  0  0  0  0  0
   -0.9870    2.0656    2.1685 O   0  0  0  0  0  0  0  0  0  0  0  0
    0.0553   -2.1525    2.1405 O   0  0  0  0  0  0  0  0  0  0  0  0
   -3.5007   -0.7316   -0.0000 O   0  0  0  0  0  0  0  0  0  0  0  0
    1.4560    0.4195    0.0000 C   0  0  0  0  0  0  0  0  0  0  0  0
    2.3412   -0.5619    0.0000 O   0  0  0  0  0  0  0  0  0  0  0  0
    3.7775   -0.3654    0.0000 C   0  0  0  0  0  0  0  0  0  0  0  0
    4.0951    0.1703    0.8941 H   0  0  0  0  0  0  0  0  0  0  0  0
    4.1973   -1.3668   -0.0001 H   0  0  0  0  0  0  0  0  0  0  0  0
    4.0951    0.1705   -0.8941 H   0  0  0  0  0  0  0  0  0  0  0  0
    2.0492    1.8010    0.0000 C   0  0  0  0  0  0  0  0  0  0  0  0
    2.6839    1.9542    0.8803 H   0  0  0  0  0  0  0  0  0  0  0  0
    2.6838    1.9543   -0.8803 H   0  0  0  0  0  0  0  0  0  0  0  0
    1.2747    2.5603    0.0001 H   0  0  0  0  0  0  0  0  0  0  0  0
1  2  1  0  0  0  0
1  3  1  0  0  0  0
1  4  1  0  0  0  0
1  5  1  0  0  0  0
1  6  1  0  0  0  0
2  7  3  0  0  0  0
3  8  3  0  0  0  0
4  9  3  0  0  0  0
  5 10  3  0  0  0  0
  6 11  3  0  0  0  0
 12 13  4  0  0  0  0
 12 18  1  0  0  0  0
 13 14  1  0  0  0  0
 14 15  1  0  0  0  0
 14 16  1  0  0  0  0
 14 17  1  0  0  0  0
 18 19  1  0  0  0  0
 18 20  1  0  0  0  0
 18 21  1  0  0  0  0
```

The vertical excitation energies and oscillator strengths for the twenty lowest energy singlet excited states of (1) at the TDDFT/B3LYP/TZVP level.

```
Excitation energies and oscillator strengths:

Excited State   1:      Singlet-A      2.7437 eV  451.90 nm  f=0.0000  <S**2>=0.000
      63 -> 64         0.70227

 Excited State   2:      Singlet-A      3.1181 eV  397.63 nm  f=0.0010  <S**2>=0.000
      61 -> 64         0.69870

 Excited State   3:      Singlet-A      3.6189 eV  342.60 nm  f=0.1608  <S**2>=0.000
      62 -> 64         0.67376

 Excited State   4:      Singlet-A      3.9146 eV  316.72 nm  f=0.0067  <S**2>=0.000
      61 -> 66        -0.28233
      63 -> 65         0.64208

 Excited State   5:      Singlet-A      4.0175 eV  308.61 nm  f=0.0162  <S**2>=0.000
      61 -> 65        -0.25865
      62 -> 67         0.10239
      63 -> 66         0.63430

 Excited State   6:      Singlet-A      4.0391 eV  306.96 nm  f=0.0000  <S**2>=0.000
      62 -> 66         0.27183
      63 -> 67         0.62953
      63 -> 71         0.14841

 Excited State   7:      Singlet-A      4.1075 eV  301.85 nm  f=0.0050  <S**2>=0.000
      61 -> 67        -0.29244
      62 -> 65         0.63627

 Excited State   8:      Singlet-A      4.1133 eV  301.42 nm  f=0.0001  <S**2>=0.000
      61 -> 65         0.65028
      63 -> 66         0.27019

 Excited State   9:      Singlet-A      4.2466 eV  291.96 nm  f=0.0001  <S**2>=0.000
      62 -> 66         0.64358
      63 -> 67        -0.27224

 Excited State  10:      Singlet-A      4.3275 eV  286.51 nm  f=0.0001  <S**2>=0.000
      61 -> 70         0.11849
      63 -> 69        -0.12561
      63 -> 72         0.64103
      63 -> 78         0.13524

 Excited State  11:      Singlet-A      4.3670 eV  283.91 nm  f=0.0052  <S**2>=0.000
      61 -> 66         0.10287
      62 -> 67         0.67253

 Excited State  12:      Singlet-A      4.4077 eV  281.29 nm  f=0.0002  <S**2>=0.000
      61 -> 67        -0.35386
      63 -> 68         0.55579
      63 -> 71        -0.14614

 Excited State  13:      Singlet-A      4.4710 eV  277.31 nm  f=0.0002  <S**2>=0.000
      61 -> 67        -0.11584
      62 -> 70        -0.25127
      63 -> 67        -0.14347
      63 -> 68         0.10461
      63 -> 71         0.59893

 Excited State  14:      Singlet-A      4.5372 eV  273.26 nm  f=0.0107  <S**2>=0.000
      61 -> 66        -0.41128
      61 -> 70         0.12623
      62 -> 68         0.51377
      63 -> 65        -0.13991

 Excited State  15:      Singlet-A      4.5867 eV  270.31 nm  f=0.0000  <S**2>=0.000
      60 -> 64        -0.15608
      62 -> 69        -0.14240
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     62 -> 72         0.57982
     63 -> 76         0.11760
     63 -> 77         0.29934

Excited State  16:      Singlet-A      4.6426 eV  267.06 nm  f=0.0021  <S**2>=0.000
     60 -> 64         0.63068
     61 -> 68        -0.23159
     62 -> 72         0.14090

Excited State  17:      Singlet-A      4.6567 eV  266.25 nm  f=0.0064  <S**2>=0.000
     61 -> 75        -0.11185
     61 -> 78         0.17489
     62 -> 71        -0.41387
     63 -> 70         0.47823
     63 -> 73         0.15772

Excited State  18:      Singlet-A      4.6733 eV  265.30 nm  f=0.0003  <S**2>=0.000
     60 -> 64         0.23997
     61 -> 68         0.61181
     61 -> 71        -0.13361
     63 -> 68        -0.13672
     63 -> 77         0.12150

Excited State  19:      Singlet-A      4.7312 eV  262.05 nm  f=0.0007  <S**2>=0.000
     61 -> 68         0.23301
     61 -> 71         0.45888
     61 -> 74        -0.12759
     62 -> 72         0.17840
     63 -> 68         0.12369
     63 -> 76        -0.17370
     63 -> 77        -0.31624

Excited State  20:      Singlet-A      4.7559 eV  260.70 nm  f=0.0007  <S**2>=0.000
     61 -> 70        -0.29383
     61 -> 73        -0.13347
     63 -> 69         0.12738
     63 -> 75        -0.32255
     63 -> 78         0.45264
     63 -> 79         0.12119
     63 -> 81         0.12715
```

Table S6. Compositions of Molecular Orbitals of (**1**) (gross contributions, %) and overlap populations (OP) between fragments

Molecule:[$(CO)_5$Cr=C(OMe)Me]
335 orbitals(335 canonical) 63 alpha + 63 beta electrons
Number of fragments: 3
Fragment 1 (1 atoms, 33 orbitals): Cr atom
Fragment 2 (10 atoms, 190 orbitals): CO Ligands
Fragment 3 (10 atoms, 112 orbitals): Carbene ligand

Alpha MO:	41	42	43	44	45	46	47	48	49	50
	HOMO-22	HOMO-21	HOMO-20	HOMO-19	HOMO-18	HOMO-17	HOMO-16	HOMO-15	HOMO-14	HOMO-13
Energy(eV):	-13.19	-12.84	-12.70	-12.70	-12.61	-12.60	-12.55	-12.38	-12.21	-12.16
Symmetry:	A	AAAAAAAAA								
FRAG# 1:	21.06	2.53	3.00	3.54	2.67	2.44	2.23	0.11	0.57	0.04
s orbitals:	18.82	0.00	0.00	0.00	0.23	0.00	0.20	0.00	0.00	0.00
p orbitals:	0.82	0.00	1.53	2.31	0.99	1.99	1.25	0.00	0.19	0.00
d orbitals:	1.41	2.54	1.47	1.23	1.45	0.45	0.78	0.10	0.38	0.04
FRAG# 2:	67.06	95.47	94.23	96.33	79.06	83.51	93.98	88.19	63.47	99.55
s orbitals:	9.61	0.01	0.61	0.88	1.34	1.89	1.10	0.07	0.42	0.02
p orbitals:	57.18	94.57	92.71	94.53	76.88	80.73	91.82	86.95	62.19	98.05
d orbitals:	0.27	0.89	0.91	0.91	0.84	0.89	1.05	1.18	0.86	1.48
FRAG# 3:	11.88	1.99	2.77	0.13	18.27	14.05	3.79	11.70	35.96	0.41
s orbitals:	4.14	0.90	1.02	0.06	7.09	4.94	1.78	4.43	14.13	0.17
p orbitals:	7.66	1.07	1.73	0.07	11.04	9.06	1.94	7.20	21.67	0.24
d orbitals:	0.08	0.01	0.01	0.00	0.14	0.05	0.07	0.07	0.16	0.00
OP(1 & 2)	0.099	0.025	0.035	0.042	0.029	0.027	0.030	0.001	0.004	0.000
OP(1 & 3)	-0.046	0.000	0.000	0.001	-0.002	0.004	-0.008	0.000	0.002	0.000
OP(2 & 3)	0.009	0.003	0.002	-0.002	-0.006	0.013	-0.020	0.008	-0.003	0.000

Alpha MO:	51	52	53	54	55	56	57	58	59	60
	HOMO-12	HOMO-11	HOMO-10	HOMO-9	HOMO-8	HOMO-7	HOMO-6	HOMO-5	HOMO-4	HOMO-3
Energy(eV):	-12.14	-12.08	-11.79	-11.77	-11.36	-11.05	-10.92	-10.56	-10.43	-8.22
Symmetry:	A	AAAAAAAAA								
FRAG# 1:	0.28	0.38	1.89	31.93	24.15	8.41	9.71	0.51	1.97	14.96
s orbitals:	0.02	0.00	0.21	0.00	0.15	0.00	0.00	-0.10	0.00	0.98
p orbitals:	0.25	0.02	0.08	0.00	3.42	8.19	9.67	0.55	1.54	5.59
d orbitals:	0.01	0.36	1.60	31.93	20.58	0.22	0.04	0.07	0.42	8.39
FRAG# 2:	97.38	64.64	18.33	64.99	71.15	70.00	82.80	10.80	20.58	7.30
s orbitals:	0.40	0.30	1.17	22.21	23.02	23.51	29.76	3.56	8.29	2.37
p orbitals:	95.62	63.41	16.92	42.68	47.78	45.89	52.37	7.12	12.13	4.71
d orbitals:	1.36	0.93	0.24	0.10	0.35	0.60	0.66	0.13	0.16	0.23
FRAG# 3:	2.34	34.97	79.78	3.08	4.70	21.59	7.49	88.69	77.45	77.74
s orbitals:	1.10	14.49	32.33	1.22	1.59	6.86	2.63	23.66	17.09	17.39
p orbitals:	1.22	20.29	46.98	1.84	3.06	14.51	4.73	64.19	59.40	59.74
d orbitals:	0.02	0.18	0.48	0.02	0.05	0.22	0.13	0.83	0.96	0.61
OP(1 & 2)	0.004	0.003	0.019	0.244	0.187	0.080	0.103	0.025	0.021	-0.016
OP(1 & 3)	-0.001	0.001	-0.012	0.000	0.005	0.009	-0.003	-0.045	-0.004	0.113
OP(2 & 3)	-0.002	-0.020	-0.044	0.000	-0.006	0.013	-0.015	-0.061	-0.042	-0.026

Alpha MO:	61	62	63	64	65	66	67	68	69	70
	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6
Energy(eV):	-6.37	-6.24	-6.04	-2.07	-1.03	-0.82	-0.73	-0.43	-0.06	0.02
Symmetry:	A	AAAAAAAAA								
FRAG# 1:	63.98	60.23	68.89	7.39	5.91	4.99	4.51	0.10	65.55	20.93
s orbitals:	0.01	0.00	-0.02	0.00	0.04	0.09	0.00	0.00	64.25	0.78
p orbitals:	0.02	0.03	0.09	1.60	5.78	4.37	3.45	0.02	-0.10	0.85
d orbitals:	63.95	60.21	68.82	5.79	0.09	0.53	1.06	0.08	1.40	19.30
FRAG# 2:	35.78	26.60	29.96	14.07	89.07	95.57	92.39	98.20	-17.38	77.58
s orbitals:	0.01	0.01	0.03	0.93	0.70	2.92	0.49	0.04	-20.74	-1.05
p orbitals:	34.31	25.52	28.75	12.95	87.75	91.97	91.20	97.40	3.26	78.24
d orbitals:	1.46	1.08	1.18	0.20	0.63	0.68	0.69	0.75	0.11	0.39
FRAG# 3:	0.24	13.17	1.15	78.54	5.02	-0.56	3.10	1.70	51.82	1.49
s orbitals:	0.07	1.38	0.73	7.65	1.78	1.24	0.81	0.57	40.23	-0.01
p orbitals:	0.16	11.52	0.22	69.78	3.17	-1.82	2.21	1.08	11.43	1.43
d orbitals:	0.01	0.27	0.20	1.11	0.07	0.02	0.08	0.05	0.16	0.07
OP(1 & 2)	0.146	0.109	0.134	-0.019	0.134	0.005	-0.009	0.000	-3.739	-0.269
OP(1 & 3)	-0.002	0.042	-0.028	-0.020	-0.170	-0.057	-0.038	0.000	-1.130	0.063
OP(2 & 3)	-0.001	0.008	-0.011	-0.167	-0.368	-0.015	0.002	-0.009	0.573	-0.105

Alpha MO:	71	72	73	74	75	76	77	78	79	80
	LUMO+7	LUMO+8	LUMO+9	LUMO+10	LUMO+11	LUMO+12	LUMO+13	LUMO+14	LUMO+15	LUMO+16
Energy(eV):	0.14	0.15	0.52	0.66	0.77	0.95	0.98	1.02	1.53	1.54
Symmetry:	A	AAAAAAAAA								
FRAG# 1:	28.30	36.16	21.43	5.73	72.86	10.98	45.31	35.22	29.50	1.60
s orbitals:	0.00	1.69	9.88	0.00	62.57	0.00	0.00	2.70	24.97	0.00
p orbitals:	0.46	0.00	0.29	0.16	0.03	0.00	0.00	0.23	0.56	0.06
d orbitals:	27.84	34.46	11.26	5.56	10.27	10.98	45.31	32.30	3.97	1.55
FRAG# 2:	69.42	60.95	67.48	91.68	-10.78	88.56	50.85	20.12	1.95	2.99
s orbitals:	0.11	-0.63	-3.83	0.78	-21.12	5.68	23.60	11.58	-21.54	0.24
p orbitals:	69.04	61.47	70.94	90.39	9.74	82.01	25.36	7.69	23.26	2.69
d orbitals:	0.27	0.11	0.37	0.51	0.60	0.88	1.89	0.85	0.22	0.07
FRAG# 3:	2.29	2.89	11.09	2.59	37.92	0.46	3.84	44.65	68.55	95.40
s orbitals:	0.29	2.13	-4.64	0.57	35.62	0.22	2.84	9.22	9.47	124.63
p orbitals:	1.94	0.75	15.55	1.96	2.06	0.24	0.96	34.66	58.01	-29.82
d orbitals:	0.06	0.02	0.17	0.06	0.24	0.00	0.04	0.77	1.07	0.59
OP(1 & 2)	-0.282	-0.501	-0.894	-0.073	-4.654	-0.077	-0.311	-0.713	-4.956	-0.074
OP(1 & 3)	-0.038	-0.027	-0.238	0.012	-2.391	-0.001	-0.008	0.019	-0.013	0.020
OP(2 & 3)	0.035	0.011	0.149	-0.080	0.769	0.004	0.023	-0.700	-0.396	-0.073

Table S7. Optimised coordinates for (**3**) at the B3LYP/TZVP level .mol format

```
21 19  0  0  0  0  0  0  0  0  0    0
   -0.6536   -0.0487   -0.1779 Cr  0  0  0  0  0  0  0  0  0  0  0  0
   -0.1792   -1.9058   -0.3880 C   0  0  0  0  0  0  0  0  0  0  0  0
    0.8243    0.5835   -1.4606 C   0  0  0  0  0  0  0  0  0  0  0  0
   -1.2347    1.7498    0.1355 C   0  0  0  0  0  0  0  0  0  0  0  0
   -0.4262   -0.2198    1.6495 C   0  0  0  0  0  0  0  0  0  0  0  0
   -2.4768   -0.5646   -0.1694 C   0  0  0  0  0  0  0  0  0  0  0  0
    0.0651   -3.0212   -0.4460 O   0  0  0  0  0  0  0  0  0  0  0  0
    0.2080    0.5537   -2.4772 O   0  0  0  0  0  0  0  0  0  0  0  0
   -1.6174    2.7996    0.3894 O   0  0  0  0  0  0  0  0  0  0  0  0
   -0.2642   -0.3037    2.7877 O   0  0  0  0  0  0  0  0  0  0  0  0
   -3.5790   -0.8755   -0.1714 O   0  0  0  0  0  0  0  0  0  0  0  0
    1.7357    0.6306   -0.4575 C   0  0  0  0  0  0  0  0  0  0  0  0
    2.6554   -0.3948   -0.4547 O   0  0  0  0  0  0  0  0  0  0  0  0
    3.0328   -0.9148    0.8263 C   0  0  0  0  0  0  0  0  0  0  0  0
    2.1665   -1.3236    1.3496 H   0  0  0  0  0  0  0  0  0  0  0  0
    3.7464   -1.7088    0.6203 H   0  0  0  0  0  0  0  0  0  0  0  0
    3.5094   -0.1501    1.4435 H   0  0  0  0  0  0  0  0  0  0  0  0
    2.0644    1.9058    0.2760 C   0  0  0  0  0  0  0  0  0  0  0  0
    2.0074    1.7846    1.3581 H   0  0  0  0  0  0  0  0  0  0  0  0
    3.0835    2.2034    0.0115 H   0  0  0  0  0  0  0  0  0  0  0  0
    1.3871    2.7093   -0.0064 H   0  0  0  0  0  0  0  0  0  0  0  0
1  2  1  0  0  0  0
1  4  1  0  0  0  0
1  5  1  0  0  0  0
1  6  1  0  0  0  0
2  7  3  0  0  0  0
3  8  2  0  0  0  0
  3 12  2  0  0  0  0
4  9  3  0  0  0  0
  5 10  3  0  0  0  0
  6 11  3  0  0  0  0
 12 13  1  0  0  0  0
 12 18  1  0  0  0  0
 13 14  1  0  0  0  0
 14 15  1  0  0  0  0
 14 16  1  0  0  0  0
 14 17  1  0  0  0  0
 18 19  1  0  0  0  0
 18 20  1  0  0  0  0
 18 21  1  0  0  0  0
```

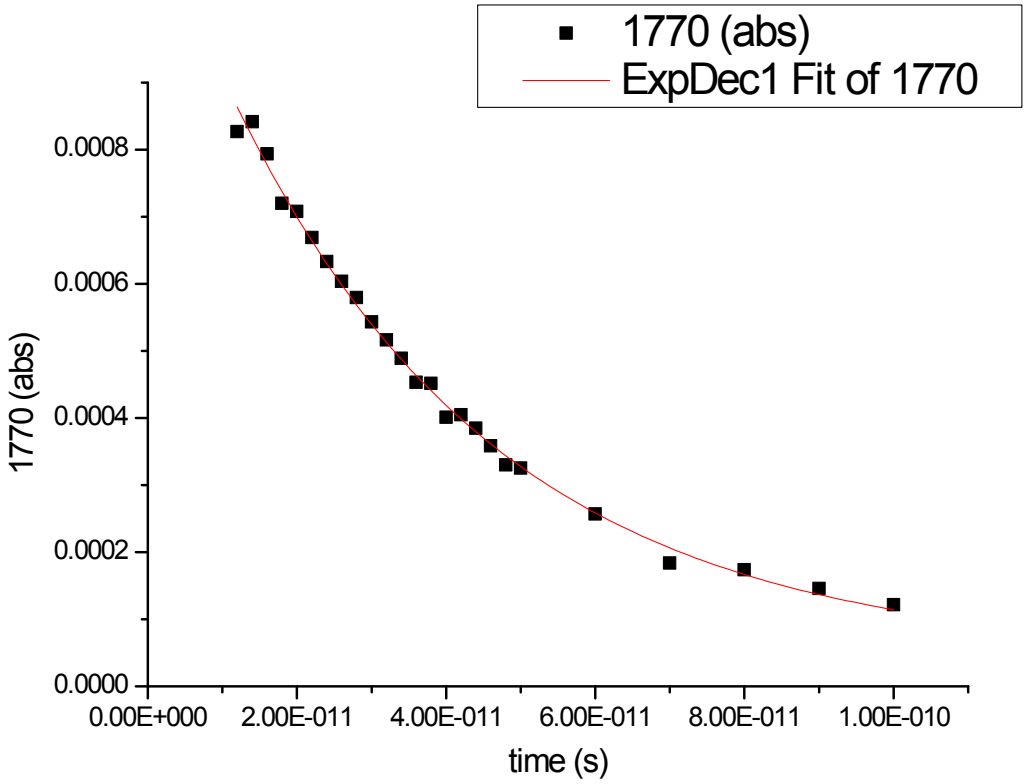
Table S8. Optimised coordinates for (**4**) at the B3LYP/Def2TZVP level .mol format

```
21 20  0  0  0  0  0  0  0  0  0    0
    0.0450   -1.4769    1.4466 C   0  0  0  0  0  0  0  0  0  0  0  0
    0.6881    1.4119    1.4563 C   0  0  0  0  0  0  0  0  0  0  0  0
    0.6880    1.4119   -1.4563 C   0  0  0  0  0  0  0  0  0  0  0  0
    0.0450   -1.4769   -1.4466 C   0  0  0  0  0  0  0  0  0  0  0  0
    2.4068   -0.4543   -0.0000 C   0  0  0  0  0  0  0  0  0  0  0  0
   -0.1480   -2.2807    2.2360 O   0  0  0  0  0  0  0  0  0  0  0  0
    0.8613    2.2105    2.2588 O   0  0  0  0  0  0  0  0  0  0  0  0
    0.8613    2.2105   -2.2588 O   0  0  0  0  0  0  0  0  0  0  0  0
   -0.1480   -2.2807   -2.2360 O   0  0  0  0  0  0  0  0  0  0  0  0
    3.5267   -0.6937   -0.0000 O   0  0  0  0  0  0  0  0  0  0  0  0
   -1.7519    0.4318    0.0000 C   0  0  0  0  0  0  0  0  0  0  0  0
   -2.6224   -0.5620    0.0000 O   0  0  0  0  0  0  0  0  0  0  0  0
   -4.0562   -0.3824    0.0000 C   0  0  0  0  0  0  0  0  0  0  0  0
   -4.3800    0.1505   -0.8933 H   0  0  0  0  0  0  0  0  0  0  0  0
   -4.4672   -1.3874    0.0000 H   0  0  0  0  0  0  0  0  0  0  0  0
   -4.3800    0.1506    0.8934 H   0  0  0  0  0  0  0  0  0  0  0  0
   -2.3601    1.8045    0.0000 C   0  0  0  0  0  0  0  0  0  0  0  0
   -2.9967    1.9503   -0.8798 H   0  0  0  0  0  0  0  0  0  0  0  0
   -2.9967    1.9503    0.8798 H   0  0  0  0  0  0  0  0  0  0  0  0
   -1.5930    2.5714    0.0000 H   0  0  0  0  0  0  0  0  0  0  0  0
    0.3776   -0.0248   -0.0000 W   0  0  0  0  0  0  0  0  0  0  0  0
1  6  3  0  0  0  0
  1 21  1  0  0  0  0
2  7  3  0  0  0  0
  2 21  1  0  0  0  0
3  8  3  0  0  0  0
  3 21  1  0  0  0  0
4  9  3  0  0  0  0
  4 21  1  0  0  0  0
  5 10  3  0  0  0  0
  5 21  1  0  0  0  0
 11 12  4  0  0  0  0
 11 17  1  0  0  0  0
 11 21  1  0  0  0  0
 12 13  1  0  0  0  0
 13 14  1  0  0  0  0
 13 15  1  0  0  0  0
 13 16  1  0  0  0  0
 17 18  1  0  0  0  0
 17 19  1  0  0  0  0
 17 20  1  0  0  0  0
```

Table S9. Optimised coordinates for (**6**) at the B3LYP/Def2TZVP level .mol format

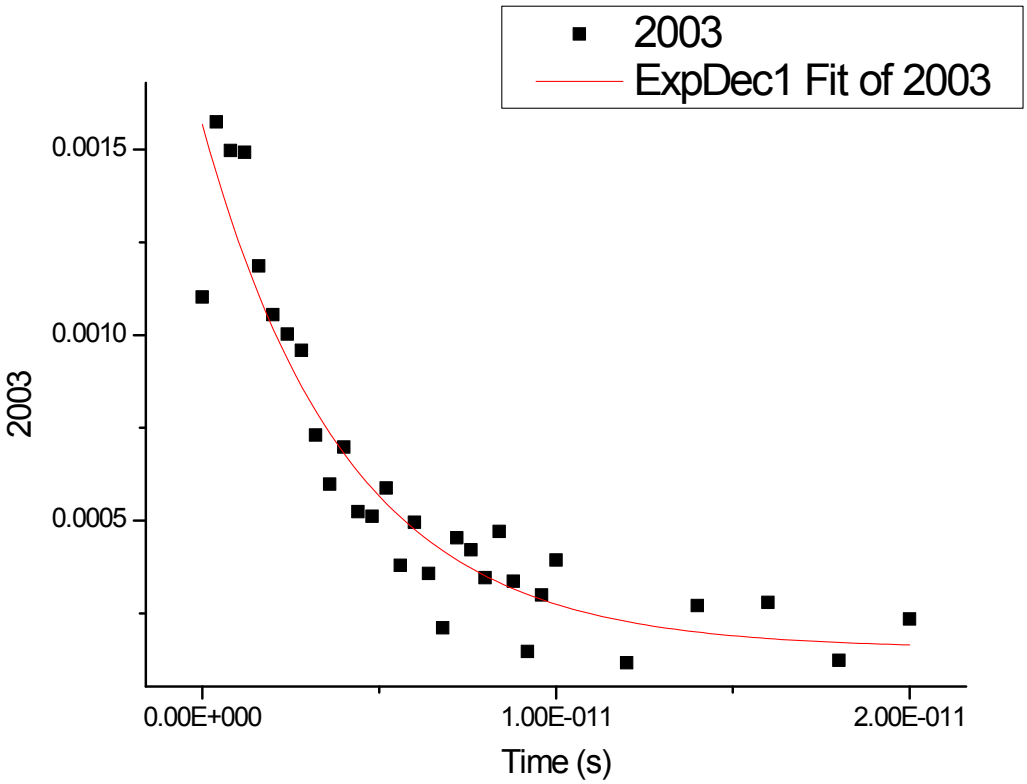
```
21 20  0  0  0  0  0  0  0  0  0    0
    1.1535    0.6037   -1.4193 C   0  0  0  0  0  0  0  0  0  0  0  0
   -1.0546    1.9279    0.1824 C   0  0  0  0  0  0  0  0  0  0  0  0
   -0.3151   -0.2214    1.8056 C   0  0  0  0  0  0  0  0  0  0  0  0
   -0.0231   -2.0371   -0.3633 C   0  0  0  0  0  0  0  0  0  0  0  0
   -2.4751   -0.5229   -0.1300 C   0  0  0  0  0  0  0  0  0  0  0  0
    0.6862    0.6249   -2.5208 O   0  0  0  0  0  0  0  0  0  0  0  0
   -1.3772    3.0027    0.4104 O   0  0  0  0  0  0  0  0  0  0  0  0
   -0.1700   -0.3124    2.9482 O   0  0  0  0  0  0  0  0  0  0  0  0
    0.2217   -3.1510   -0.4382 O   0  0  0  0  0  0  0  0  0  0  0  0
   -3.5881   -0.7934   -0.1631 O   0  0  0  0  0  0  0  0  0  0  0  0
    2.0598    0.6198   -0.3928 C   0  0  0  0  0  0  0  0  0  0  0  0
    2.9378   -0.4300   -0.3699 O   0  0  0  0  0  0  0  0  0  0  0  0
    3.2815   -0.9638    0.9125 C   0  0  0  0  0  0  0  0  0  0  0  0
    2.3891   -1.3220    1.4298 H   0  0  0  0  0  0  0  0  0  0  0  0
    3.9525   -1.7957    0.7140 H   0  0  0  0  0  0  0  0  0  0  0  0
    3.7935   -0.2227    1.5293 H   0  0  0  0  0  0  0  0  0  0  0  0
    2.3876    1.8735    0.3738 C   0  0  0  0  0  0  0  0  0  0  0  0
    2.3267    1.7324    1.4527 H   0  0  0  0  0  0  0  0  0  0  0  0
    3.4105    2.1704    0.1205 H   0  0  0  0  0  0  0  0  0  0  0  0
    1.7165    2.6853    0.1022 H   0  0  0  0  0  0  0  0  0  0  0  0
   -0.5049   -0.0331   -0.1364 W   0  0  0  0  0  0  0  0  0  0  0  0
1  6  2  0  0  0  0
  1 11  2  0  0  0  0
  1 21  1  0  0  0  0
2  7  3  0  0  0  0
  2 21  1  0  0  0  0
3  8  3  0  0  0  0
  3 21  1  0  0  0  0
4  9  3  0  0  0  0
  4 21  1  0  0  0  0
  5 10  3  0  0  0  0
  5 21  1  0  0  0  0
 11 12  1  0  0  0  0
 11 17  1  0  0  0  0
 12 13  1  0  0  0  0
 13 14  1  0  0  0  0
 13 15  1  0  0  0  0
 13 16  1  0  0  0  0
 17 18  1  0  0  0  0
 17 19  1  0  0  0  0
 17 20  1  0  0  0  0
```

Figure S2 Single exponential curve fit for decay of 1970 cm^{-1} feature following 400 nm excitation of (**1**) in *n*-heptane at 298 K.



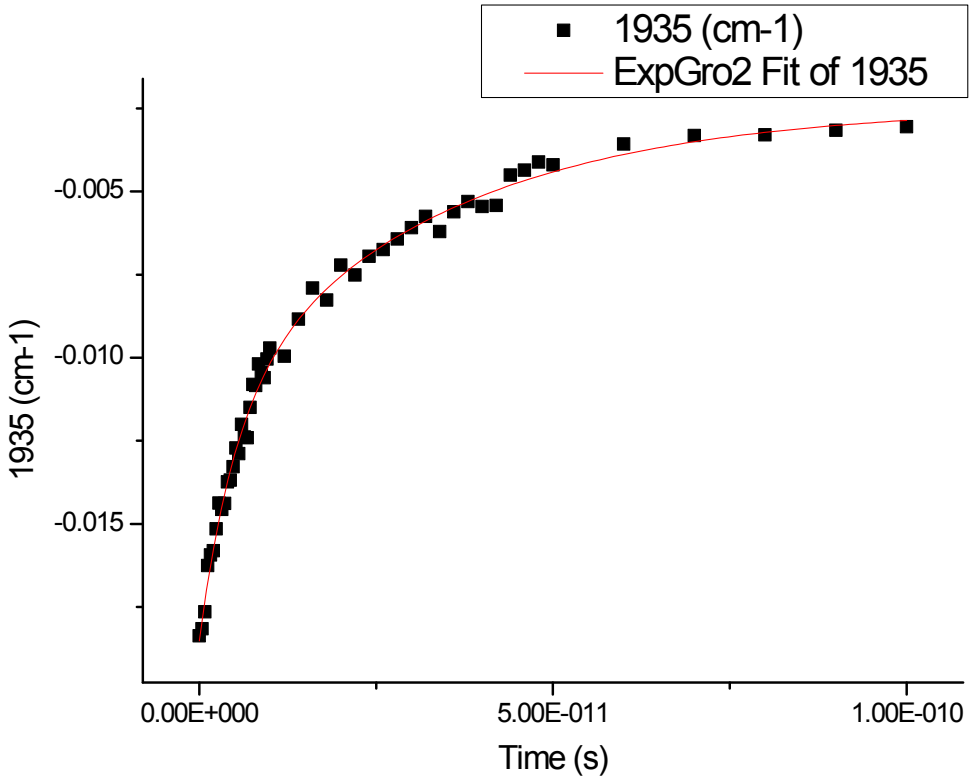
	y0	y0	A1	A1	t1	t1	Statistics	Statistics
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
1970	5.39E-04	3.43E-05	0.00377	4.71E-05	3.86E-12	1.20E-13	5.25E-09	0.99534

Figure S3. Single exponential curve fit for the decay of absorbance at 2003 cm^{-1} following 400 nm excitation of (**1**) in *n*-heptane at 298 K.



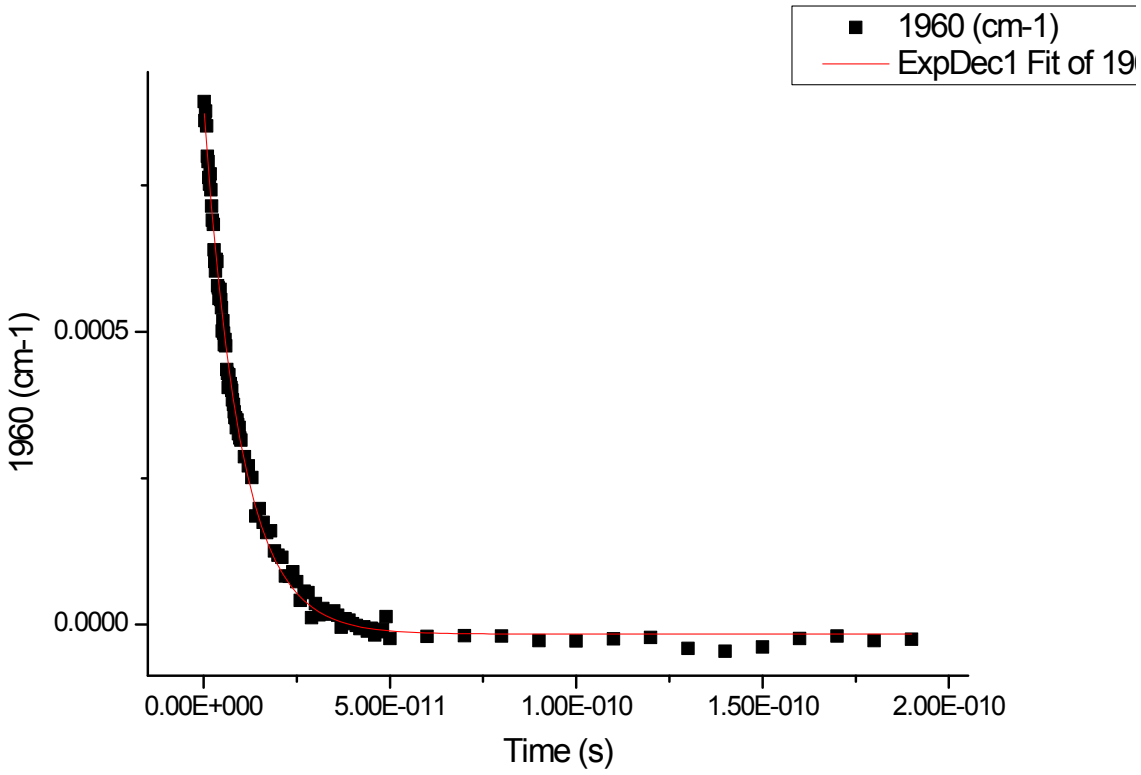
	y0	y0	A1	A1	t1	t1	Statistics	Statistics
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
2003	1.56E-04	7.14E-05	0.00141	9.37E-05	4.05E-12	6.80E-13	2.07E-08	0.88246

Figure S4. Biexponential curve fit for the recovery of parent depletion (measure at 1935 cm^{-1}) following 400 nm excitation of (**1**) in n-heptane at 298 K



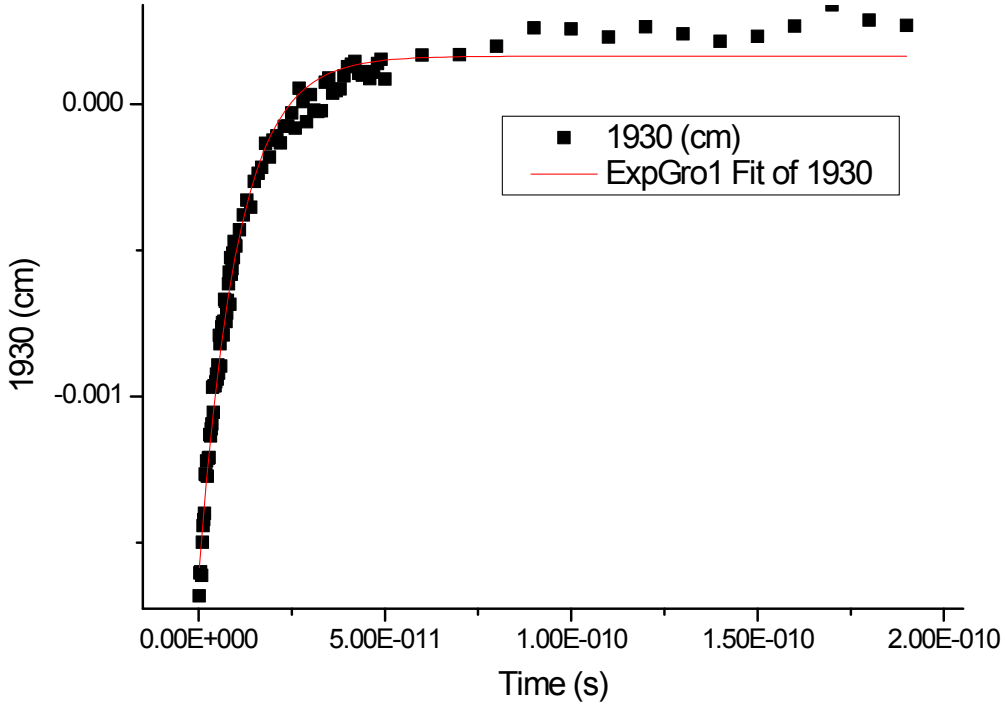
y0	y0	A1	A1	t1	t1	A2	A2	t2	t2	Statistics	Statistics
Value	St Error	Value	St Error	Value	St Error	Value	St Error	Value	St Error	Reduced Chi-Sqr	Adj. R-Square
-2.44E-03	3.89E-04	-0.00685	9.24E-04	-5.06E-12	8.03E-13	-9.23E-03	7.45E-04	-3.23E-11	5.64E-12	1.09E-07	0.99452

Figure S5. Decay curve fit for the excited state decay (measure at 1960 cm^{-1}) following 400 nm excitation of (**4**) in *n*-heptane at 298 K



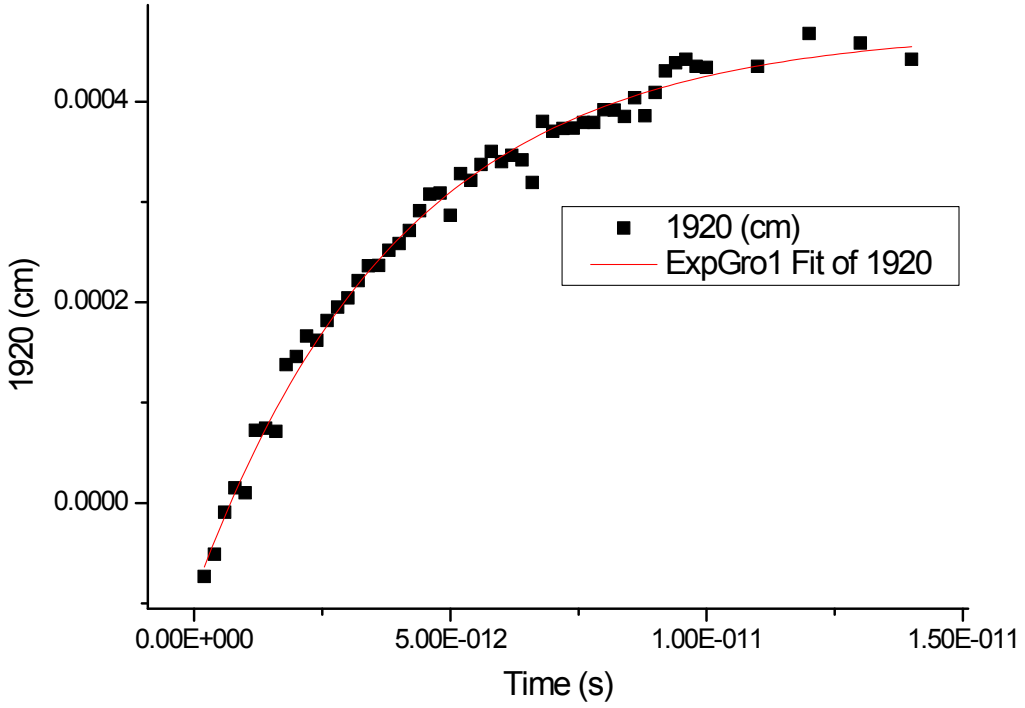
	y0	y0	A1	A1	t1	t1	A2	A2	t2	t2
	Value	StError	Value	StError	Value	StError	Value	StError	Value	StError
1960	-2.77943E-5	3.05202E-6	2.23842E-4	6.37668E-5	3.77858E-12	3.77858E-12	6.99716E-5	1.23109E-11	7.60733E-13	1.44596E-10

Figure S6. Grow-in of metallaketene (measure at 1930 cm^{-1}) following 400 nm excitation of (**4**) in *n*-heptane at 298 K



	y0	y0	A1	A1	t1	t1
1930	Value	StError	Value	StError	Value	StError
	1.63949E-4	1.09714E-5	-0.00178	2.00354E-5	-1.02787E-11	2.78631E-13

Figure S7. Grow-in of second excited state (measure at 1920 cm^{-1}) following 400 nm excitation of (**4**) in *n*-heptane at 298 K



	Y0	Y0	A1	A1	t1	t1
1920	Value	StError	Value	StError	Value	StError
	4.7206E-4	7.66502E-6	-5.63225E-4	7.72674E-6	-4.01934E-12	1.69223E-13

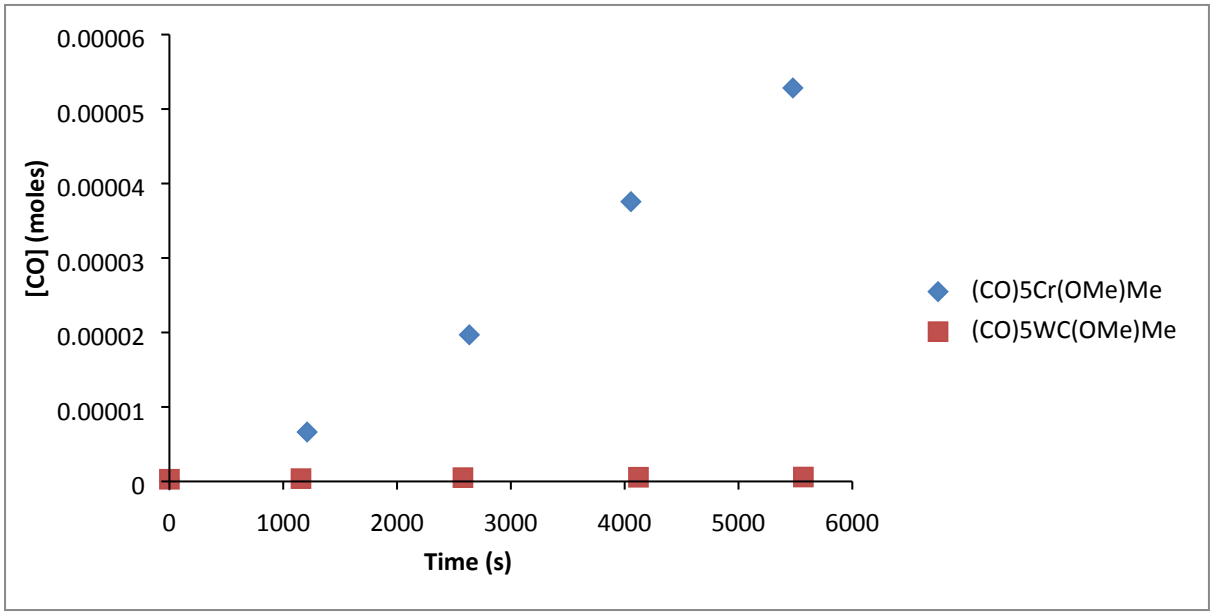
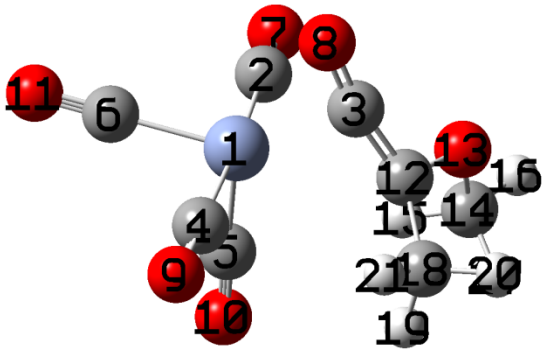


Figure S8. The CO yield profile for the electrochemically induced CO release over time from $[(CO)_5CrC(OMe)Me]$ or $[(CO)_5WC(OMe)Me]$ in acetonitrile under potentiostatic conditions (E = + 0.57 V and + 0.88 V *vs*. Fc/Fc^+, respectively). The concentration of both complexes was 0.1mM and the solution was continuously stirred.

Cyclic Voltammetry and Gas Chromatography

Cyclic Voltammograms (CVs) and bulk electrolysis profiles were recorded in anhydrous acetonitrile (Sigma-Aldrich) with tetrabutylammonium hexafluorophosphate ($TBAPF_6$), (0.1 M) as a supporting electrolyte. The concentration of the sample was 0.001 M throughout. Experiments were carried out using both a CH Instruments 600A and CH Instruments 750C electrochemical potentiostats (Pico-Amp Booster and Faraday Cage). All electrochemical experiments were performed at room temperature (20°C). A three electrode cell was employed which consisted of a glassy carbon working electrode, a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 0.1 V s^{-1} unless otherwise stated. The scan rate dependency of the redox processes was analysed by varying the scan rate from 0.01 V s^{-1} to 0.05, 0.08, 0.1, 0.5, 0.8, 1.0, 10.0 15.0 1nd 20.0 V s^{-1}. Cited potentials are referenced relative to the ferrocene/ferrocenium (Fc/Fc^+) redox couple. The electrochemical cell was deaerated with argon prior to all experiments.

For the bulk electrolysis experiments, deaeration of the solutions with argon prior to the experiment ensured that any CO detected in the headspace resulted from CO-release from the complex. The bulk electrolysis experiments were repeated using a clean glassy carbon electrode in analyte-free electrolyte solution for comparison purposes. A control experiment was also carried out where the complex was dissolved in the electrolyte and kept in the dark with no potential applied. CO-release was detected using a Shimadzu GC-2010 Plus unit (Lab Solutions version 5.57 software) with a dielectric barrier discharge ionization detector (BID) and a ShinCarbon micropacked column with 0.53 mm internal diameter.



The atom numbering used for chromium ketene complex

Distance matrix (angstroms) for chromium ketene complex

		1	2	3	4	5
1	Cr	0.000000				
2	C	1.928247	0.000000			
3	C	2.056538	2.890384	0.000000		
4	C	1.915850	3.840802	2.854339	0.000000	
5	C	1.849365	2.656042	3.446972	2.612526	0.000000
6	C	1.894753	2.669382	3.725900	2.644278	2.762624
7	O	3.069962	1.143361	3.821015	4.979044	3.532763
8	O	2.528266	3.250248	1.189181	3.215294	4.246149
9	O	3.059921	4.981283	3.780880	1.145798	3.481892
10	O	3.001934	3.557938	4.474450	3.491902	1.152816
11	O	3.039979	3.559077	4.814530	3.533054	3.699424
12	C	2.499645	3.178813	1.356141	3.229100	3.136214
13	O	3.338575	3.212868	2.306920	4.481127	3.735549
14	C	3.917706	3.574000	3.514629	5.078296	3.622881
15	H	3.451377	2.976646	3.651900	4.742209	2.833795
16	H	4.770015	4.057759	4.257168	6.083424	4.548235
17	H	4.468726	4.476824	4.022671	5.275085	3.941515
18	C	3.378393	4.472445	2.510429	3.305728	3.550685
19	H	3.577818	4.631235	3.284393	3.465090	3.166161
20	H	4.367366	5.262140	3.145672	4.343735	4.568669
21	H	3.435160	4.888543	2.636386	2.795429	3.822210

		6	7	8	9	10
6	C	0.000000				
7	O	3.545838	0.000000			
8	O	3.712721	4.114184	0.000000		
9	O	3.516846	6.116422	4.073436	0.000000	
10	O	3.702473	4.236823	5.355169	4.148960	0.000000
11	O	1.145240	4.237801	4.658374	4.203416	4.480109
12	C	4.388157	4.015846	2.533577	4.082185	3.924771
13	O	5.142904	3.688912	3.313600	5.401209	4.364179
14	C	5.609794	3.855298	4.587965	5.967571	3.884727
15	H	4.944076	3.243797	4.690948	5.678111	3.002806
16	H	6.376561	4.051099	5.218589	7.010604	4.770418
17	H	6.213447	4.865861	5.173641	6.007932	4.008758
18	C	5.188753	5.366034	3.585342	3.790380	4.075901
19	H	5.287643	5.488435	4.411588	3.886846	3.400728
20	H	6.213788	6.051185	4.145337	4.753612	5.019996
21	H	5.066972	5.897455	3.484520	3.031777	4.428545

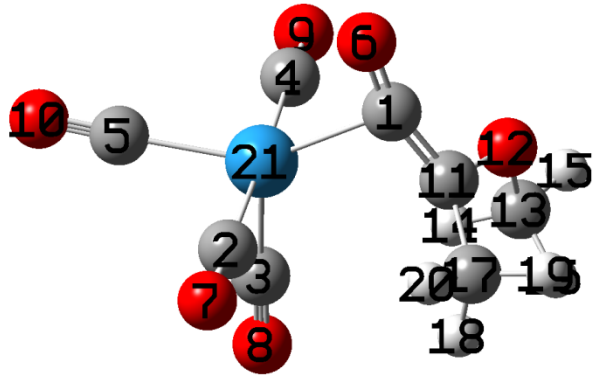
		11	12	13	14	15
11	O	0.000000				
12	C	5.531331	0.000000			
13	O	6.259313	1.377466	0.000000		
14	C	6.686781	2.391454	1.433142	0.000000	
15	H	5.960307	2.696364	2.087460	1.091561	0.000000
16	H	7.414994	3.267633	2.018042	1.087205	1.782199
17	H	7.306069	2.714655	2.095824	1.092147	1.785812
18	C	6.307417	1.507376	2.485162	3.032569	3.404749

```
   19  H    6.373601   2.168310   2.907863   2.936121   3.112270
   20  H    7.341810   2.123735   2.674139   3.223257   3.882166
   21  H    6.127000   2.155412   3.383017   4.066402   4.325574
                 16         17         18         19         20
   16  H    0.000000
   17  H    1.778585   0.000000
   18  C    4.001611   2.770881   0.000000
   19  H    3.971376   2.450740   1.090296   0.000000
   20  H    4.014332   2.787632   1.094170   1.773910   0.000000
   21  H    5.047586   3.844762   1.088121   1.761111   1.770349
                 21
   21  H    0.000000
Stoichiometry    C8H6CrO6
Framework group  C1[X(C8H6CrO6)]
Deg. of freedom    57
```

Atomic Coordinates of [(CO)5CrC(OMe)Me]

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	24	0	-0.653611	-0.048675	-0.177874
2	6	0	-0.179165	-1.905798	-0.387950
3	6	0	0.824288	0.583529	-1.460636
4	6	0	-1.234676	1.749836	0.135498
5	6	0	-0.426152	-0.219813	1.649453
6	6	0	-2.476760	-0.564569	-0.169403
7	8	0	0.065126	-3.021246	-0.446027
8	8	0	0.207968	0.553726	-2.477205
9	8	0	-1.617378	2.799574	0.389354
10	8	0	-0.264174	-0.303719	2.787745
11	8	0	-3.578972	-0.875533	-0.171396
12	6	0	1.735652	0.630635	-0.457482
13	8	0	2.655413	-0.394764	-0.454750
14	6	0	3.032846	-0.914779	0.826275
15	1	0	2.166548	-1.323622	1.349612
16	1	0	3.746405	-1.708760	0.620259
17	1	0	3.509361	-0.150096	1.443509
18	6	0	2.064379	1.905818	0.276022
19	1	0	2.007391	1.784565	1.358055
20	1	0	3.083536	2.203382	0.011481
21	1	0	1.387106	2.709291	-0.006365



The atom numbering used for tungsten ketene complex

Distance matrix (angstroms) for tungsten ketene complex:

		1	2	3	4	5
1	C	0.000000				
2	C	3.032265	0.000000			
3	C	3.638363	2.793071	0.000000		
4	C	3.077870	4.133171	2.843639	0.000000	
5	C	4.012296	2.849896	2.916030	2.891344	0.000000
6	O	1.196763	3.469227	4.520727	3.499167	4.126422
7	O	3.937943	1.145076	3.670072	5.275572	3.731895
8	O	4.654693	3.667621	1.155400	3.736662	3.851467
9	O	3.991084	5.273466	3.729001	1.142943	3.778208
10	O	5.100311	3.734117	3.862036	3.781057	1.145865
11	C	1.369427	3.426613	3.343781	3.376118	4.684065
12	O	2.313741	4.669468	3.918911	3.368919	5.419043
13	C	3.524617	5.262823	3.779524	3.701369	5.866910
14	H	3.654110	4.896605	2.943645	3.089557	5.170325
15	H	4.259360	6.262468	4.677845	4.125972	6.606534
16	H	4.043110	5.472050	4.117891	4.630368	6.491473
17	C	2.519993	3.447923	3.707164	4.652634	5.444469
18	H	3.301327	3.617362	3.304742	4.798825	5.536180
19	H	3.149516	4.472135	4.737156	5.452193	6.477452
20	H	2.639116	2.873879	3.934205	5.054089	5.283589
21	W	2.191249	2.061457	1.960325	2.073498	2.030241

		6	7	8	9	10
6	O	0.000000				
7	O	4.301569	0.000000			
8	O	5.614471	4.346010	0.000000		
9	O	4.337125	6.414397	4.436124	0.000000	
10	O	5.083352	4.430258	4.647067	4.488715	0.000000
11	C	2.532869	4.258714	4.123514	4.195174	5.826577
12	O	3.287710	5.568792	4.547765	3.845246	6.539301
13	C	4.587782	6.139165	4.059745	3.996366	6.955435
14	H	4.722093	5.824674	3.142193	3.395976	6.208340
15	H	5.195378	7.177893	4.917977	4.133157	7.657281
16	H	5.174701	6.196075	4.210749	5.020357	7.594602
17	C	3.582254	3.930672	4.236348	5.531339	6.565768
18	H	4.439251	4.052067	3.556872	5.643987	6.631430
19	H	4.097203	4.868199	5.194244	6.228795	7.605618
20	H	3.491012	3.125218	4.543646	6.048880	6.349090
21	W	2.745380	3.205662	3.115313	3.215584	3.175721

		11	12	13	14	15
11	C	0.000000				
12	O	1.368700	0.000000			
13	C	2.388337	1.430987	0.000000		
14	H	2.683432	2.082290	1.091991	0.000000	
15	H	3.262138	2.017316	1.087000	1.783560	0.000000
16	H	2.722113	2.093382	1.091706	1.786250	1.778882
17	C	1.505612	2.482278	3.023165	3.365411	4.003420
18	H	2.171432	2.893319	2.910873	3.055102	3.954285
19	H	2.119496	2.688080	3.235280	3.867068	4.046688
20	H	2.151578	3.379248	4.052385	4.274695	5.045094

```
   21  W    2.658867   3.473309   4.037720   3.533986   4.867995
                16         17         18         19         20
   16  H    0.000000
   17  C    2.775909   0.000000
   18  H    2.445348   1.089776   0.000000
   19  H    2.803247   1.094878   1.772347   0.000000
   20  H    3.847956   1.087719   1.761850   1.770629   0.000000
   21  W    4.613716   3.501662   3.695995   4.500192   3.518719
                21
   21  W    0.000000
Stoichiometry    C8H6O6W
Framework group  C1[X(C8H6O6W)]
Deg. of freedom    57
Full point group                 C1      NOp   1
Largest Abelian subgroup         C1      NOp   1
Largest concise Abelian subgroup C1      NOp   1
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.153515	0.603738	-1.419288
2	6	0	-1.054601	1.927912	0.182405
3	6	0	-0.315115	-0.221420	1.805604
4	6	0	-0.023065	-2.037083	-0.363349
5	6	0	-2.475131	-0.522881	-0.130031
6	8	0	0.686187	0.624948	-2.520830
7	8	0	-1.377228	3.002678	0.410419
8	8	0	-0.169964	-0.312412	2.948233
9	8	0	0.221696	-3.150996	-0.438247
10	8	0	-3.588112	-0.793413	-0.163059
11	6	0	2.059818	0.619777	-0.392794
12	8	0	2.937803	-0.429964	-0.369919
13	6	0	3.281549	-0.963816	0.912487
14	1	0	2.389075	-1.321968	1.429847
15	1	0	3.952458	-1.795704	0.713960
16	1	0	3.793497	-0.222697	1.529312
17	6	0	2.387574	1.873467	0.373825
18	1	0	2.326728	1.732412	1.452719
19	1	0	3.410527	2.170379	0.120512
20	1	0	1.716522	2.685297	0.102247
21	74	0	-0.504853	-0.033143	-0.136412

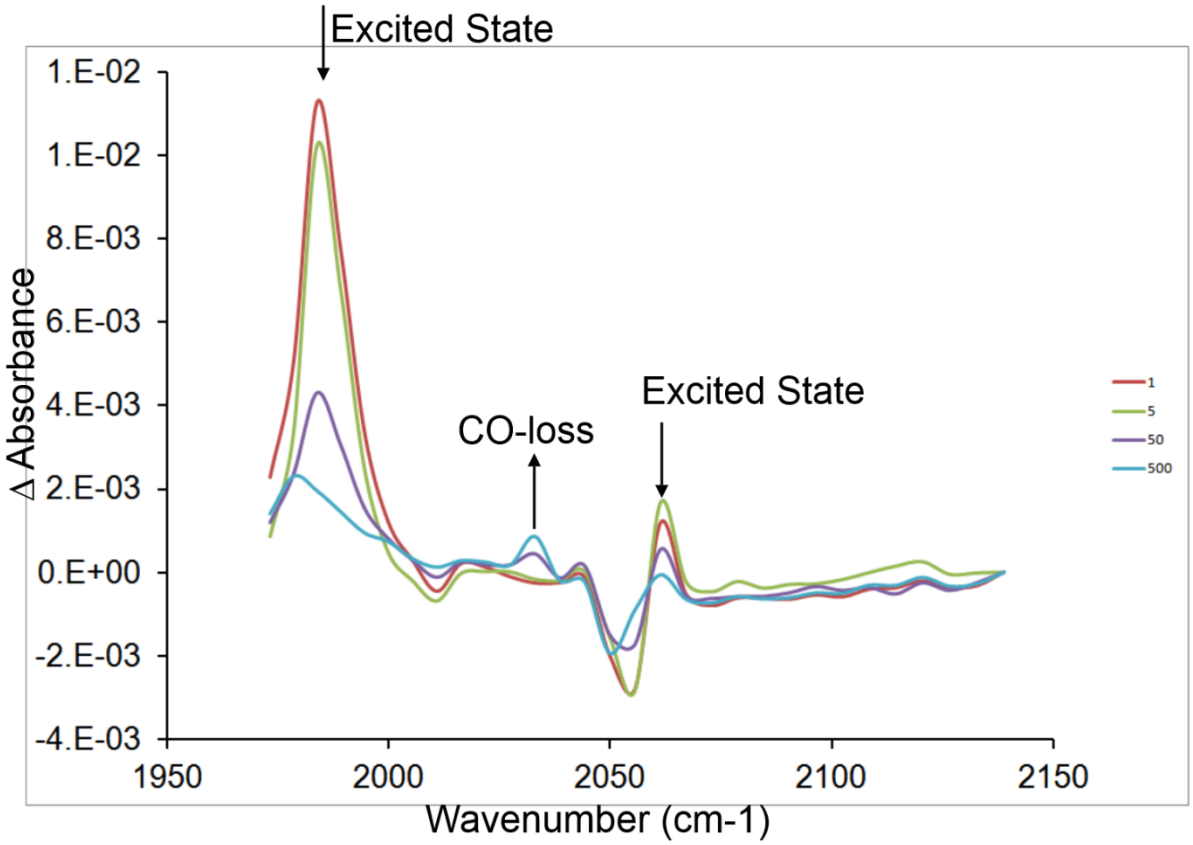


Figure S9. The ps-TRIR spectra obtained following photolysis of (**1**) at 400 nm using a pulse energy of 8 μJ, the spectra were recorded at 1, 5, 50, and 500 ps after the excitation pulse, showing the formation of the CO-loss species. This process was not observed following 0.8 μJ pulse photolysis at the same excitation wavelength.

The contribution of two fragments ($Cr(CO)_4$, Fr 1; $C_4O_2H_6$, Fr2) to the valence orbitals of (**3**)

LUMO+6[#70, -0.147 eV]= Fr 1: 97.6%L+5
LUMO+5[#69, -0.312 eV]= Fr 1: 66.0%L+2 15.1%L+4 3.5%L+6 1.6%L+1 1.2%L+7
Fr 2: 2.5%L+1 S(0.038 -0.044 -0.040 -0.118 -0.028) OP(-0.01 -0.01 0.00 -0.01 0.00)
2.1%H-0 S(-0.052 0.044 -0.024 0.184 -0.009) OP(-0.02 -0.01 0.00 -0.01 0.00)
1.5%L+2 S(-0.002 -0.075 -0.148 -0.063 -0.097) OP(0.00 0.01 -0.01 0.00 0.00)

LUMO+4[#68, -0.407 eV]= Fr 1: 94.2%L+3 1.0%L+4
Fr 2: 2.4%L+0 S(-0.015 -0.002) OP(-0.01 0.00)

LUMO+3[#67, -0.590 eV]= Fr 1: 46.9%L+4 24.8%L+2 3.3%L+0 2.4%L+6 2.0%L+10 1.3%H-0
Fr 2: 13.2%L+1 S(-0.044 0.038 0.136 -0.040 -0.145 -0.103) OP(-0.02 0.01 -0.02 0.00 0.01 -0.01)
1.5%L+3 S(-0.003 0.004 0.148 0.102 0.055 0.035) OP(0.00 0.00 0.01 0.00 0.00 0.00)

LUMO+2[#66, -1.714 eV]= Fr 1: 44.5%L+1 19.2%L+0 4.0%L+4 3.5%L+2
Fr 2: 6.7%L+2 S(-0.063 -0.263 -0.075 -0.002) OP(0.02 0.05 0.00 0.00)
6.4%H-0 S(0.184 0.087 0.044 -0.052) OP(-0.10 -0.03 0.01 0.01)
5.4%L+1 S(-0.118 0.136 -0.044 0.038) OP(-0.04 0.03 0.00 0.00)
2.5%L+0 S(0.003 -0.031 -0.002 -0.004) OP(0.00 -0.01 0.00 0.00)

LUMO+1[#65, -2.303 eV]= Fr 1: 8.2%L+1 3.4%H-2 3.3%H-1 2.0%L+3 1.6%L+0
Fr 2: 77.5%L+0 S(0.003 0.075 -0.085 -0.015 -0.031) OP(0.00 -0.03 -0.04 0.00 -0.01)

LUMO+0[#64, -2.674 eV]= Fr 1: 46.0%L+0 29.1%L+1 1.4%H-0
Fr 2: 9.3%L+1 S(0.136 -0.118 -0.103) OP(0.05 0.03 -0.01)
7.8%L+0 S(-0.031 0.003 0.022) OP(0.01 0.00 0.00)
1.7%L+2 S(-0.263 -0.063 0.000) OP(0.03 -0.01 0.00)

HOMO-0[#63, -6.368 eV]= Fr 1: 85.4%H-0 2.2%H-1
Fr 2: 4.0%H-0 S(0.010 -0.002) OP(0.00 0.00)
3.8%L+1 S(-0.103 0.002) OP(0.03 0.00)

HOMO-1[#62, -6.456 eV]= Fr 1: 58.7%H-1 39.6%H-2 1.2%H-0
HOMO-2[#61, -6.537 eV]= Fr 1: 55.1%H-2 35.1%H-1
Fr 2: 7.7%L+0 S(0.075 -0.085) OP(0.03 0.02)

HOMO-3[#60, -7.351 eV]= Fr 1: 10.3%L+1 4.4%H-0 1.3%L+0
Fr 2: 76.7%H-0 S(0.184 0.010 0.087) OP(0.09 0.00 0.02)

HOMO-4[#59, -9.117 eV]= Fr 2: 98.5%H-1
HOMO-5[#58, -10.467 eV]= Fr 2: 98.2%H-2
HOMO-6[#57, -11.150 eV]= Fr 1: 90.9%H-3
Fr 2: 5.9%H-5 S(0.044) OP(-0.02)

HOMO-7[#56, -11.532 eV]= Fr 1: 89.2%H-4 9.4%H-5
HOMO-8[#55, -11.658 eV]= Fr 1: 84.6%H-5 9.3%H-4
Fr 2: 4.4%H-3 S(0.004 -0.001) OP(0.00 0.00)

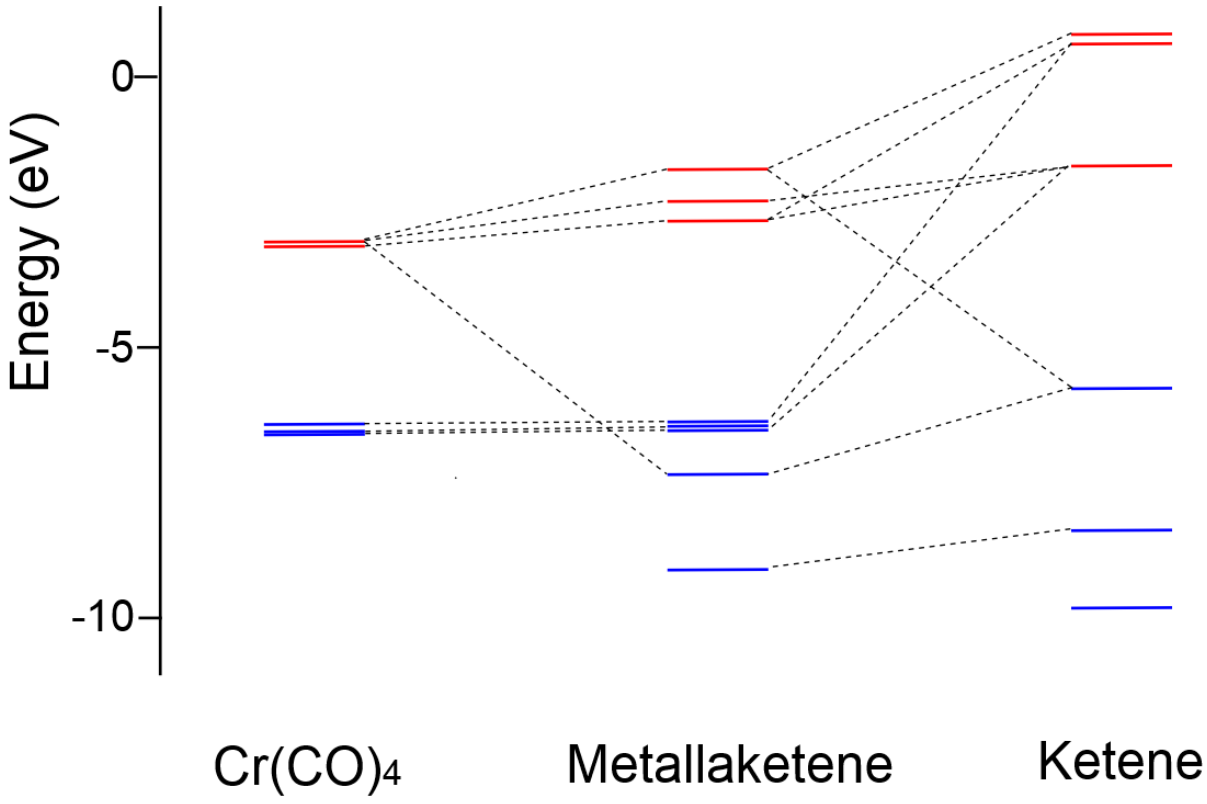


Figure S10. A Molecular orbital interaction diagram showing the molecular orbitals of (**3**) and the corresponding orbitals of the constituent fragments, occupied levels are indicated in blue and virtual orbitals are in red. Energies and percentage compositions are presented above the plot. This plot shows the ketene HOMO acting as a two electron donor by interaction with a virtual $Cr(CO)_4$ fragment orbital.

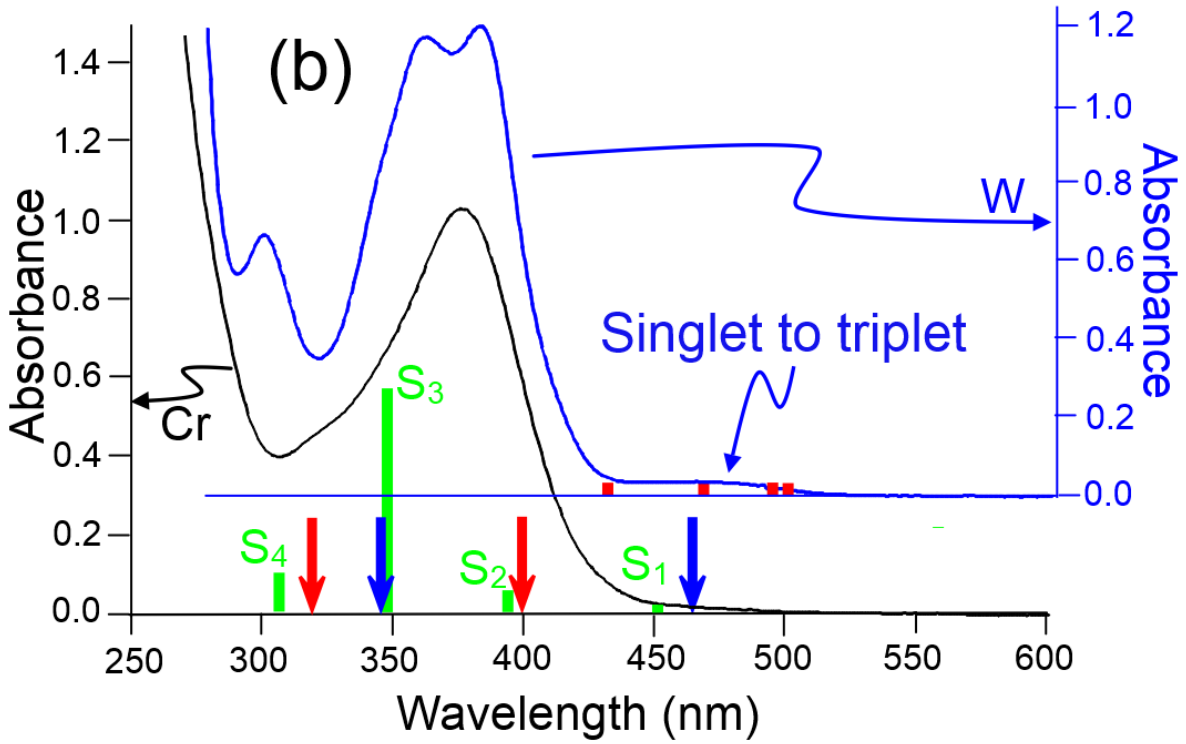


Figure S11. The calculated vertical excitations superimposed on the experimental UV/vis. Spectra for (1) and (4) including the excitation wavelengths used in the psTIR experiments. The blue spectrum is that of (4) with the calculated vertical excitation to the lowest four triplet excited states. The UV/vis spectrum of (1) is represented in black with the vertical excitation energies of the four lowest energy singlet excited states. The downward red arrows indicate the excitation wavelengths used in psTRIR and the blue arrows indicate the excitation wavelengths used in matrix isolation experiments