Synthesis of α-Alkylidene Cyclic Carbonates via CO_2 Fixation Under Ambient Conditions Promoted by an Easily Available Silver Carbamate

*Giulio Bresciani,[a,b] Marco Bortoluzzi,[b,c] Claudia Ghelarducci,[a] Fabio Marchetti,[a,b] Guido Pampaloni *[,a,b]*

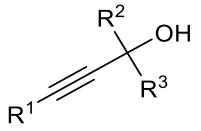
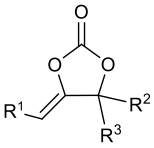
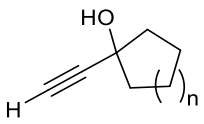
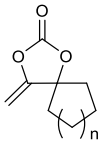
[a] *Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Moruzzi 13, I-56124 Pisa.*

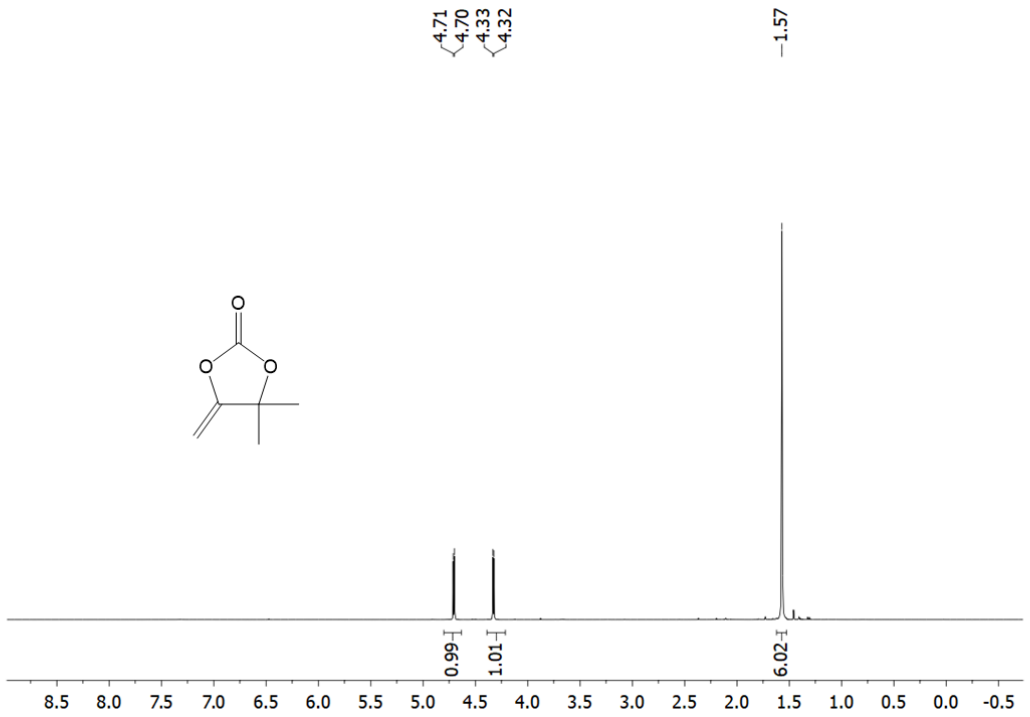
[b] *CIRCC, via Celso Ulpiani 27, I-70126 Bari, Italy.*

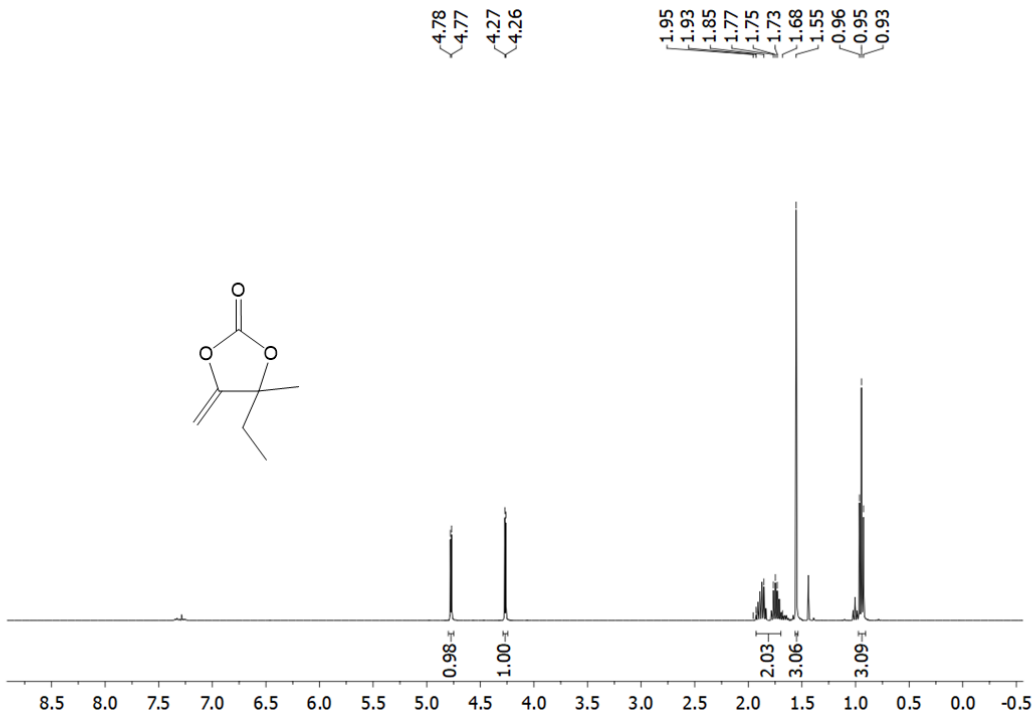
[c] *Ca' Foscari Università di Venezia, Dipartimento di Scienze Molecolari e Nanosistemi, Via Torino 155, I-30170 Mestre (VE), Italy*

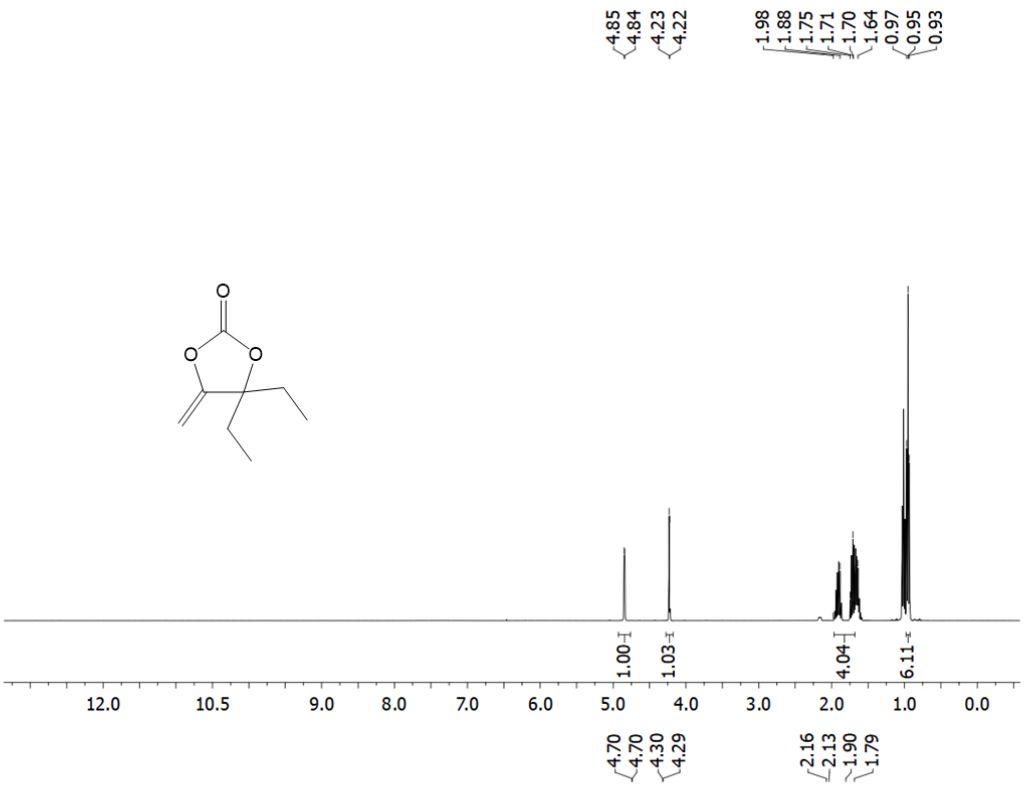
Supporting Information

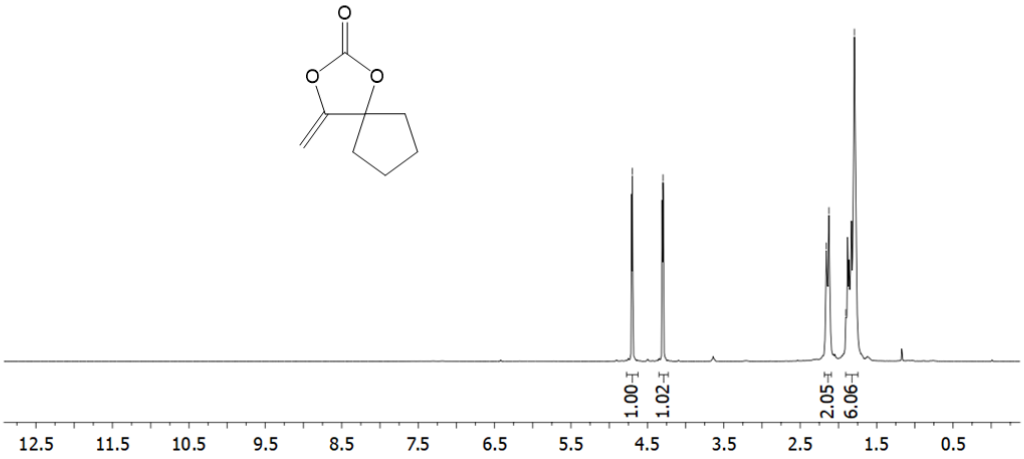
Table S1. *^{1}H NMR data (δ/ppm) of propargyl alcohols and related carboxylation products.*

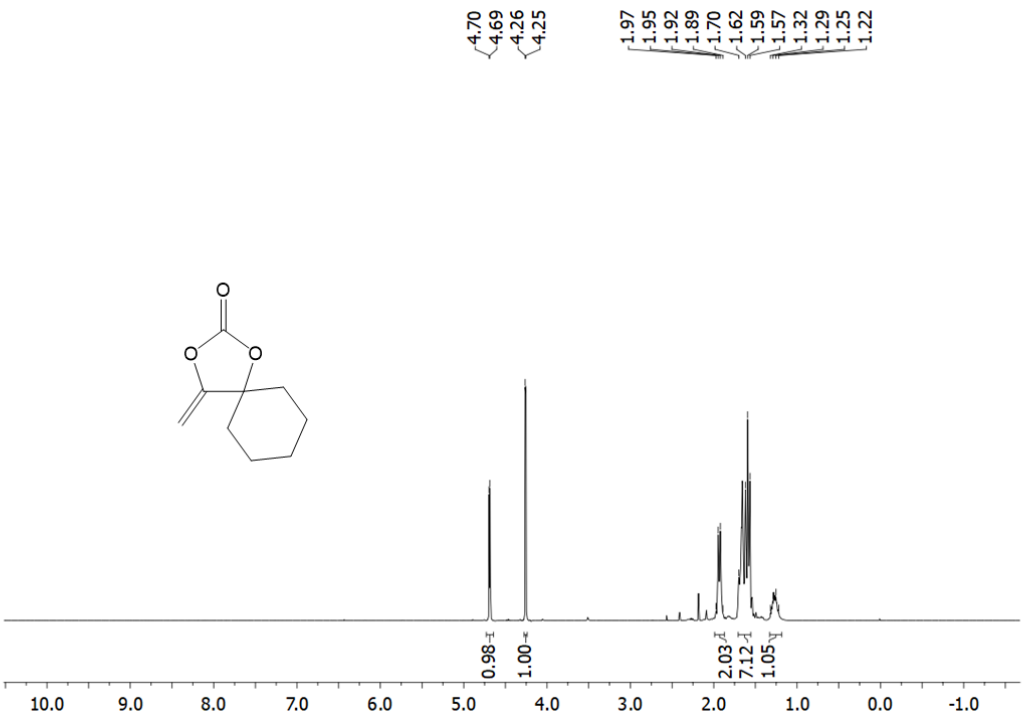
	Solvent		
R^1 = H ***R^2 = R^3 = Me***	$CDCl_3$	3.02 (br, 1H, OH); 2.37 (s, 1H, ≡CH); 1.46 (s, 6H, CH_3)	4.72, 4.30 (d, 2H, =CH_2, J = 4.0 Hz); 1.57 (s, 6H, CH_3)
R^1 = H ***R^2 = Me*** ***R^3 = Et***	$CDCl_3$	2.52 (br, 1H, OH); 2.39 (s, 1H, ≡CH); 2.11 (m, 2H, C*H_2*CH_3); 1.43 (s, 3H, CH_3); 0.99 (t, 3H, CH_2C*H_3*)	4.78, 4.26 (d, 2H, =CH_2, J = 3.9 Hz); 1.95 – 1.67 (m, 2H, C*H_2*CH_3); 1.55 (s, 3H, CH_3); 0.95 (t, 3H, CH_2C*H_3*)
R^1 = H ***R^2 = R^3 = Et***	$CDCl_3$	2.41 (s, 1H, ≡CH); 2.12 (br, 1H, OH); 1.69 – 1.62 (m, 4H, CH_2); 1.02 (t, 6H, CH_3)	4.85, 4.22 (d, 2H, =CH_2, J = 4.2 Hz); 1.98 – 1.64 (m, 4H, C*H_2*CH_3); 0.96 (t, 6H, CH_2C*H_3*)
R^1 = H ***R^2 = Me*** ***R^3 = Ph***	CD_3CN	7.68 – 7.65 (m, 2H, *o*-Ph); 7.40 – 7.35 (m, 2H, *m*-Ph); 7.33 – 7.29 (m, 1H, *p*-Ph); 2.68 (s, 1H, ≡CH); 2.41 (br, 1H, OH); 1.80 (s, 3H, CH_3)	7.49 – 7.46 (m, 2H, *o*-Ph); 7.43 – 7.35 (m, 3H, *m*-Ph + *p*-Ph); 4.92, 4.48 (d, 2H, =CH_2, J = 4.2 Hz); 1.95 (s, 1H, CH_3)
R^1 = H ***R^2 = R^3 = Ph***	CD_3CN	7.63 – 7.60 (m, 4H, *o*-Ph); 7.36 – 7.32 (m, 4H, *m*-Ph); 7.30 – 7.26 (m, 2H, *p*-Ph); 2.88 (br, 1H, OH); 2.80 (s, 1H, ≡CH)	7.60 – 7.40 (m, 10H, Ph); 5.36, 4.71 (d, 2H, =CH_2, J = 4.2 Hz)
R^1 = R^2 = R^3 = Ph	CD_3CN	7.70 – 7.27 (m, 15H, Ph); 2.86 (br, 1H, OH)	8.00 – 7.44 (m, 15H, Ph); 5.03 (s, 1H, =CHPh)
R^1 = Py ***R^2 = R^3 = Me***	CD_3CN	8.52 (d, 1H, Py); 7.71 (m, 1H, Py); 7.41 (d, 1H, Py); 7.29 (m, 1H, Py); 3.58 (br, 1H, OH); 1.53 (s, 6H, CH_3)	8.55 (d, 1H, Py); 7.78 – 7.73 (m, 2H, Py); 7.19 (m, 1H, Py); 5.91 (s, 1H, =CHPy); 1.72 (s, 6H, CH_3)
			
n = 1	$CDCl_3$	2.70 (br, 1H, OH); 2.44 (s, 1H, ≡CH); 1.91 – 1.89 (m, 4H); 1.82 – 1.62 (m, 4H)	4.70, 4.30 (d, 2H, =CH_2, J = 3.8 Hz); 2.17 – 2.13 (m, 2H); 1.91 – 1.79 (m, 6H)
n = 2	$CDCl_3$	2.47 (s, 1H, ≡CH); 1.97 (br, 1H, OH); 1.93 – 1.87 (m, 2H); 1.76 – 1.67 (m, 2H); 1.62 – 1.20 (m, 6H)	4.70, 4.25 (d, 2H, =CH_2, J = 4.0 Hz); 1.97 – 1.89 (m, 2H); 1.70–1.57 (m, 7H); 1.32–1.22 (m, 1H)

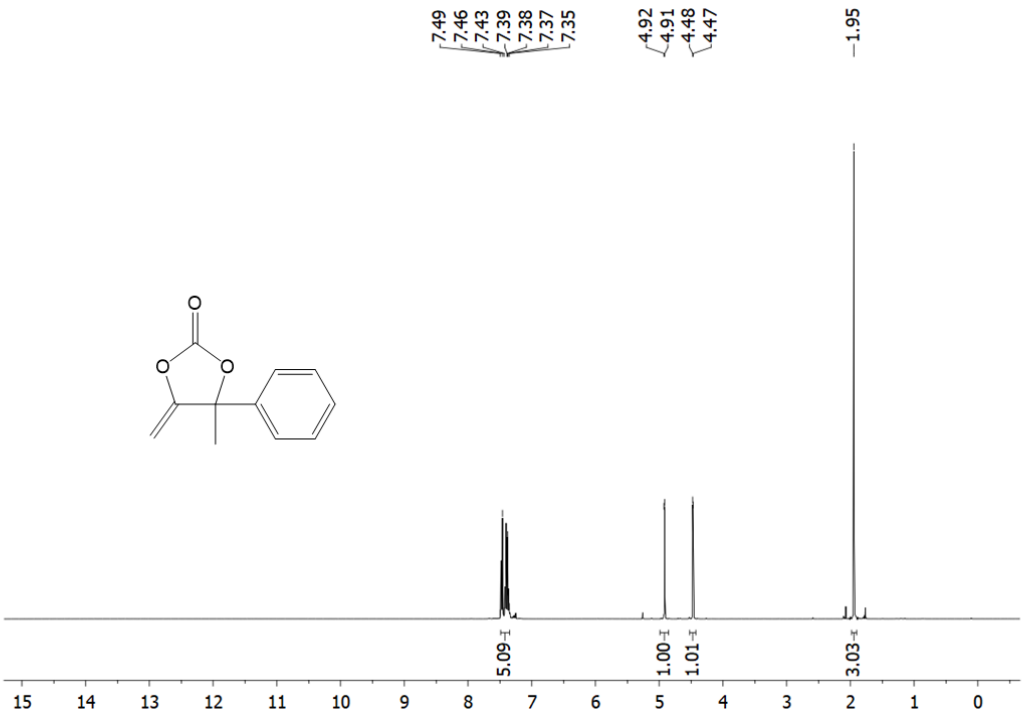

4.71
4.70
4.33
4.32
1.57
0.99
1.01
6.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

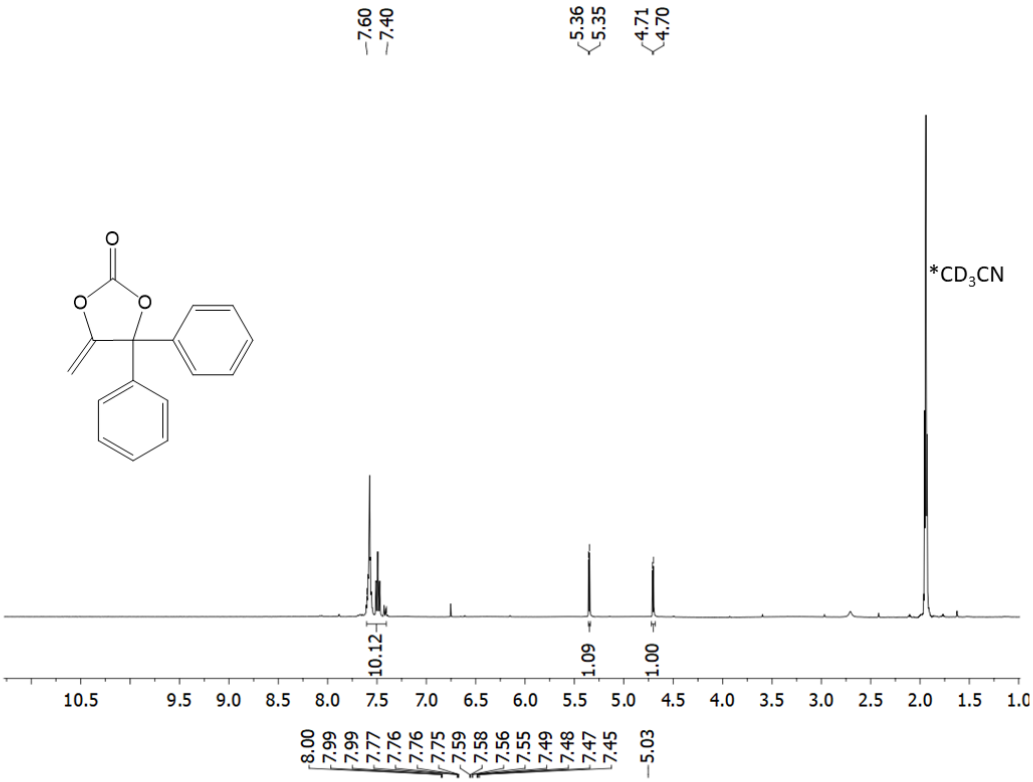

4.78
4.77
4.27
4.26
1.95
1.93
1.85
1.77
1.75
1.73
1.68
1.55
0.96
0.95
0.93
0.98
1.00
2.03
3.06
3.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

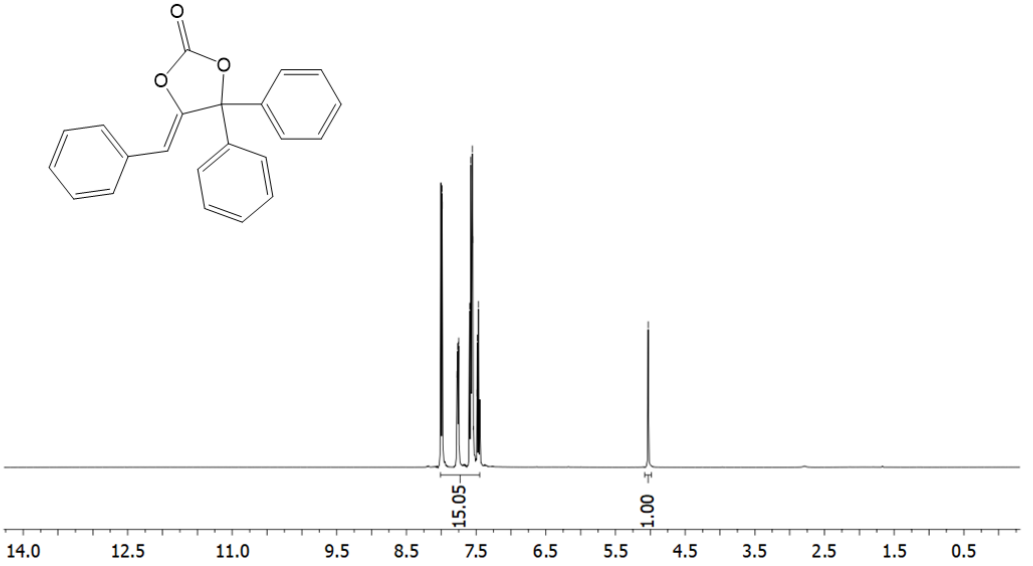

4.85
4.84
4.23
4.22
1.98
1.88
1.75
1.71
1.70
1.64
0.97
0.95
0.93
1.00
1.03
4.04
6.11
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.70
4.70
4.30
4.29
2.16
2.13
1.90
1.79


1.00
1.02
2.05
6.06
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5


4.70
4.69
4.26
4.25
1.97
1.95
1.92
1.89
1.70
1.62
1.59
1.57
1.32
1.29
1.25
1.22
0.98
1.00
2.03
7.12
1.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


7.49
7.46
7.43
7.39
7.38
7.37
7.35
4.92
4.91
4.48
4.47
1.95
5.09
1.00
1.01
3.03
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0


7.60
7.40
5.36
5.35
4.71
4.70
*CD3CN
10.12
1.09
1.00
8.00
7.99
7.99
7.77
7.76
7.76
7.75
7.59
7.58
7.56
7.55
7.49
7.48
7.47
7.45
5.03


15.05
1.00

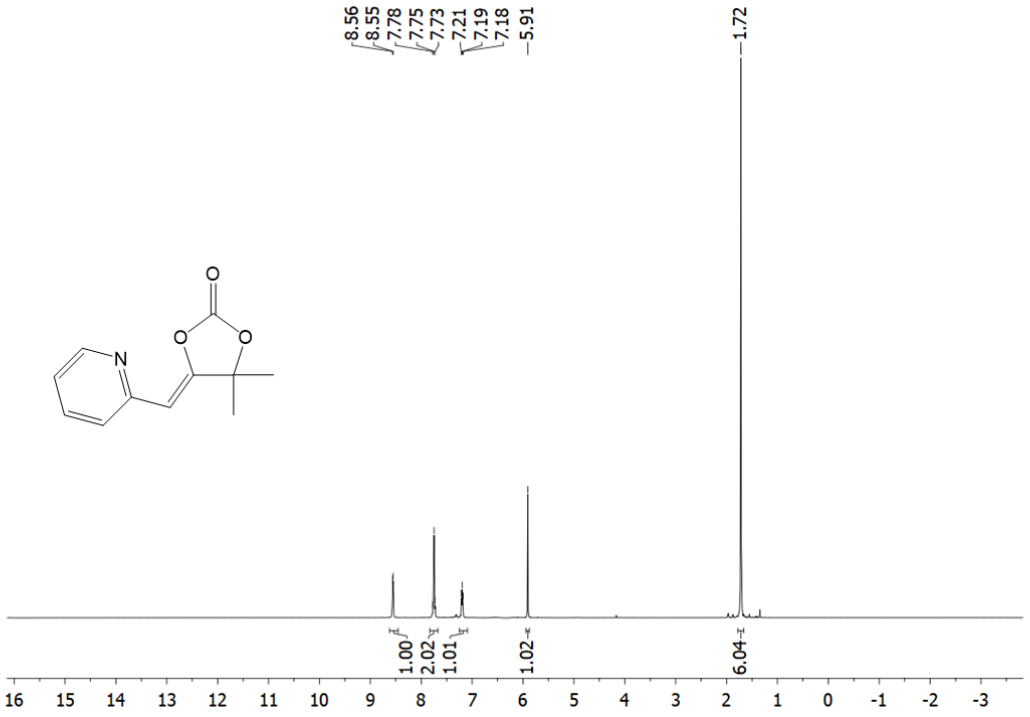

8.56
8.55
7.78
7.75
7.73
7.21
7.19
7.18
5.91
1.72
O
O
O
N
1.00
2.02
1.01
1.02
6.04
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3

Figure S1. DFT-optimized geometries of [Ag(κ^2-O_2CNEt_2)(PPh_3)$_2$] (left) and [Ag(κ^2-O_2CNEt_2)(PPh_3)], right. C-PCM/ωB97X/def2-SVP calculations, acetonitrile as continuous medium. Color map: Ag, cyan; P, orange; o, red; N, blue; C, grey. Hydrogen atoms are omitted for clarity. Selected computed bond lengths (Å) for [Ag(κ^2-O_2CNEt_2)(PPh_3)$_2$] and [Ag(κ^2-O_2CNEt_2)(PPh_3)]: Ag-O 2.403 and 2.467 (left), 2.281 and 2.414 (right); Ag-P 2.451 and 2.561 (left), 2.381 (right).

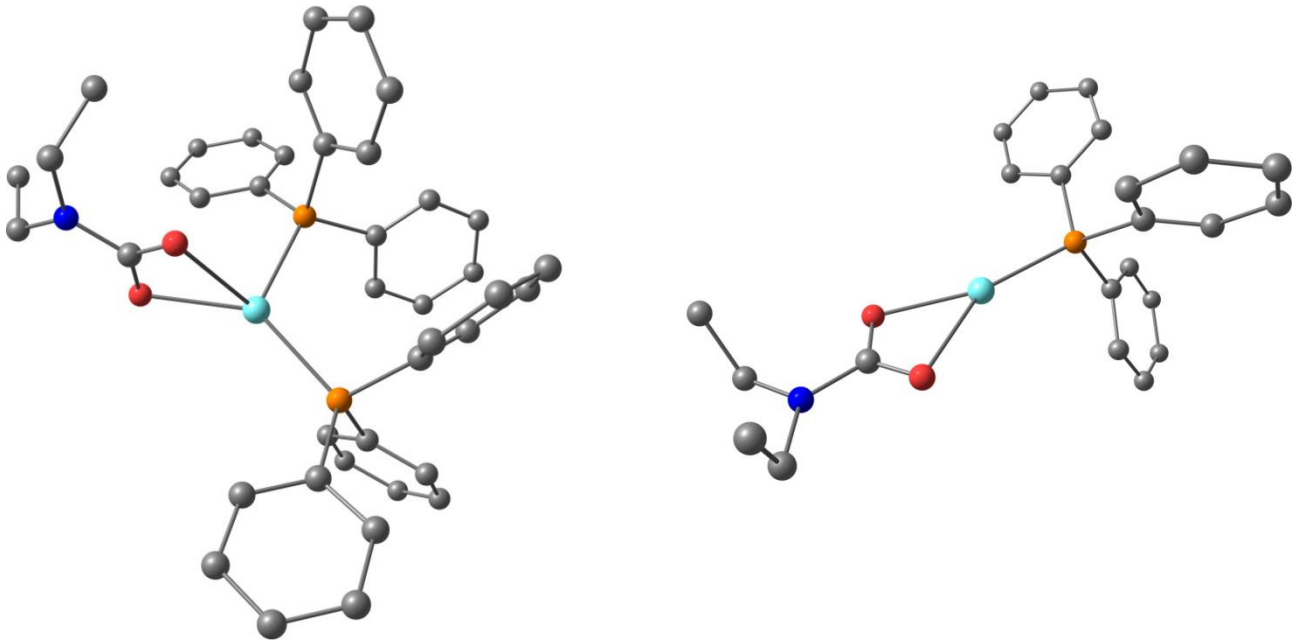


Figure S2. DFT-optimized geometry of **INT1**. C-PCM/ωB97X/def2-SVP calculations, acetonitrile as continuous medium. Color map: Ag, cyan; P, orange; o, red; N, blue; C, grey; H, white. Hydrogen atoms bonded to C are omitted for clarity. Selected computed bond lengths (Å): Ag-O 2.360, 2.372; Ag-P 2.394; O---H 1.701; O-H 0.985.

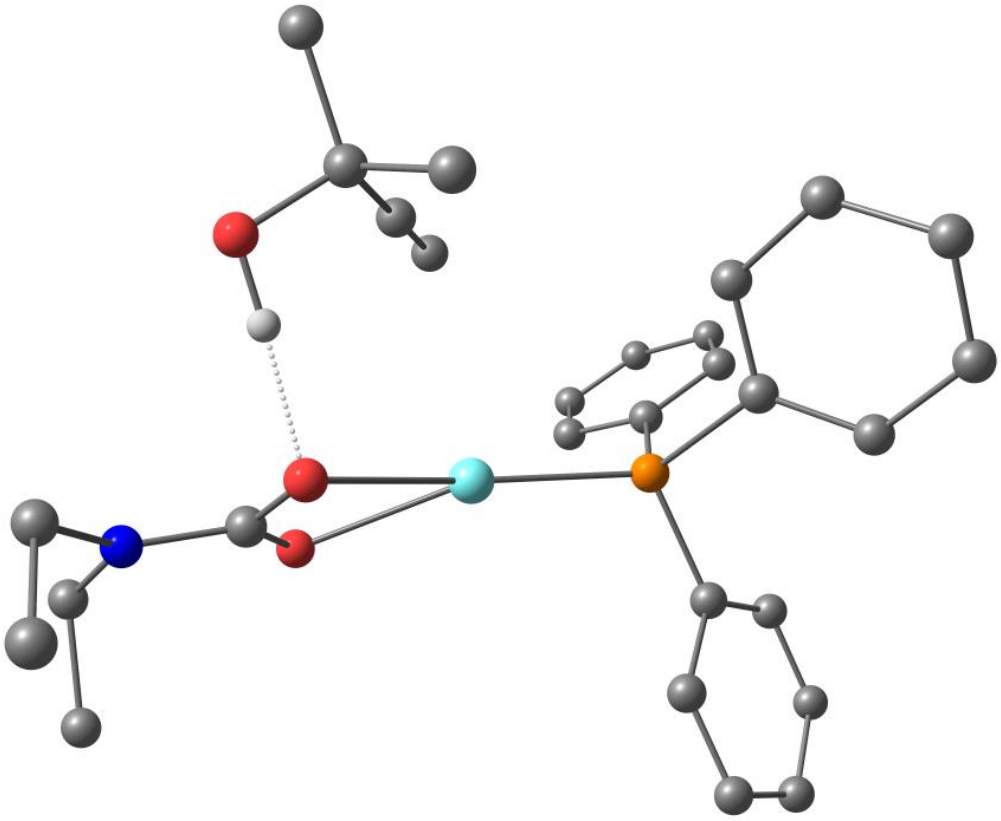


Figure S3. DFT-optimized geometry of **INT2**. C-PCM/ωB97X/def2-SVP calculations, acetonitrile as continuous medium. Color map: Ag, cyan; P, orange; o, red; N, blue; C, grey; H, white. Hydrogen atoms bonded to C are omitted for clarity. Selected computed bond lengths (Å): Ag-O 2.274; Ag-C 2.359, 2.507; Ag-P 2.446.

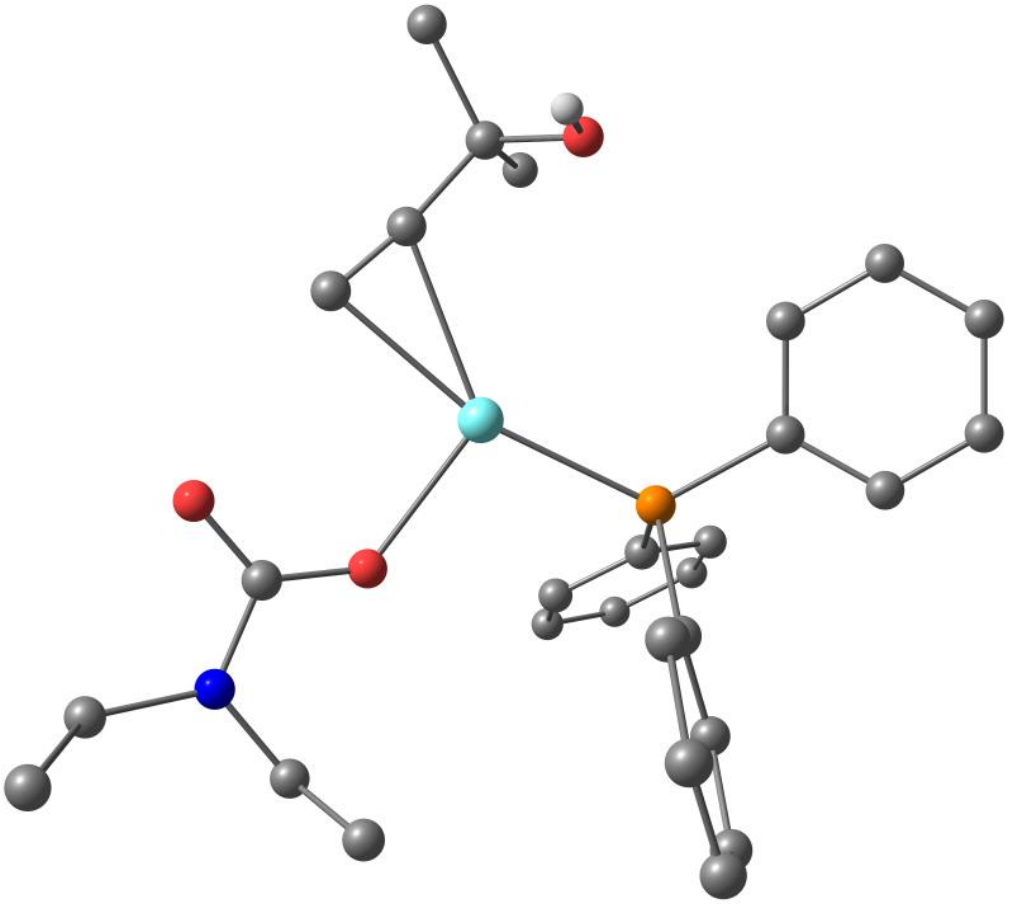


Figure S4. DFT-optimized geometry of **INT3**. C-PCM/ωB97X/def2-SVP calculations, acetonitrile as continuous medium. Color map: Ag, cyan; P, orange; o, red; N, blue; C, grey; H, white. Hydrogen atoms bonded to C are omitted for clarity. Selected computed bond lengths (Å): Ag-C 2.109; Ag-P 2.418.

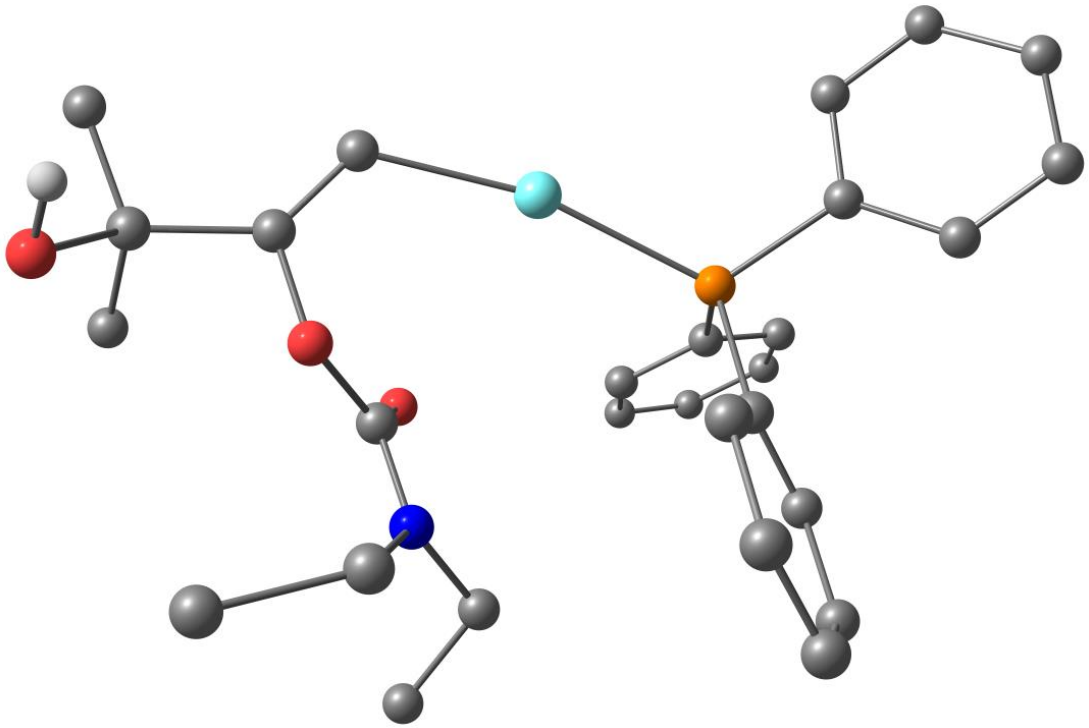


Figure S5. DFT-optimized geometry of **INT4**. C-PCM/ωB97X/def2-SVP calculations, acetonitrile as continuous medium. Color map: Ag, cyan; P, orange; o, red; N, blue; C, grey; H, white. Only the methylene hydrogen atoms are shown for clarity. Selected computed bond lengths (Å): Ag-O 2.059; Ag-P 2.337.

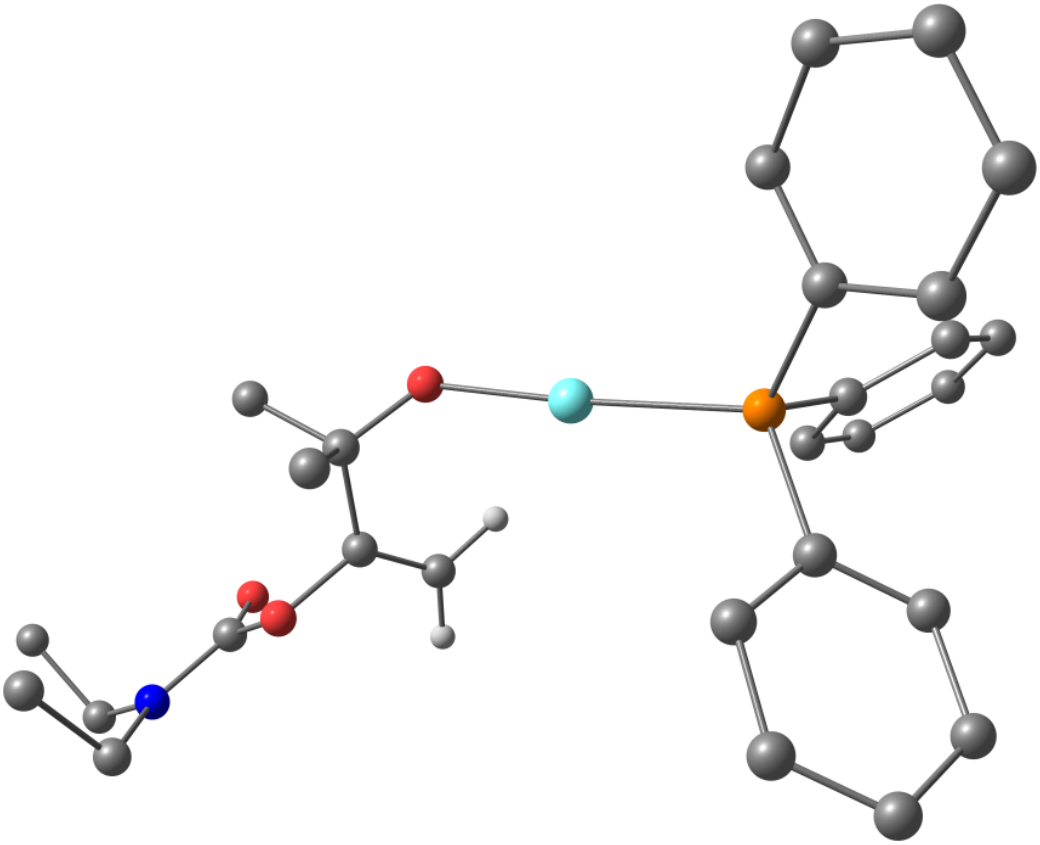


Figure S6. DFT-optimized geometry of **INT5**. C-PCM/ωB97X/def2-SVP calculations, acetonitrile as continuous medium. Color map: Ag, cyan; P, orange; o, red; N, blue; C, grey; H, white. Only the methylene hydrogen atoms are shown for clarity. Selected computed bond lengths (Å): Ag-O 2.183; Ag-P 2.470, 2.545.

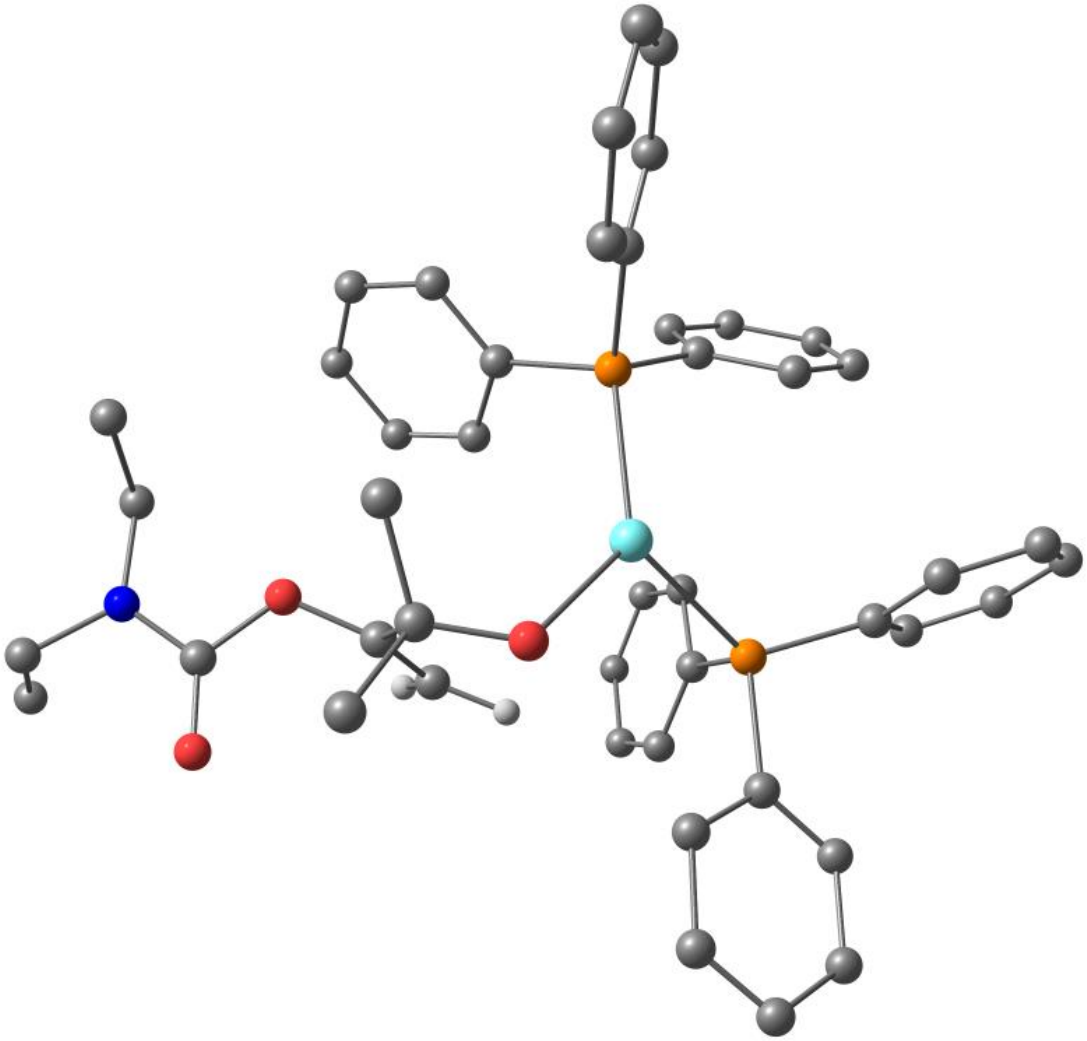


Figure S7. DFT-optimized geometry of **INT6**. C-PCM/ωB97X/def2-SVP calculations, acetonitrile as continuous medium. Color map: Ag, cyan; P, orange; o, red; N, blue; C, grey; H, white. Only the methylene hydrogen atoms are shown for clarity. Selected computed bond lengths (Å): Ag-O 2.236; Ag-P 2.471, 2.508.

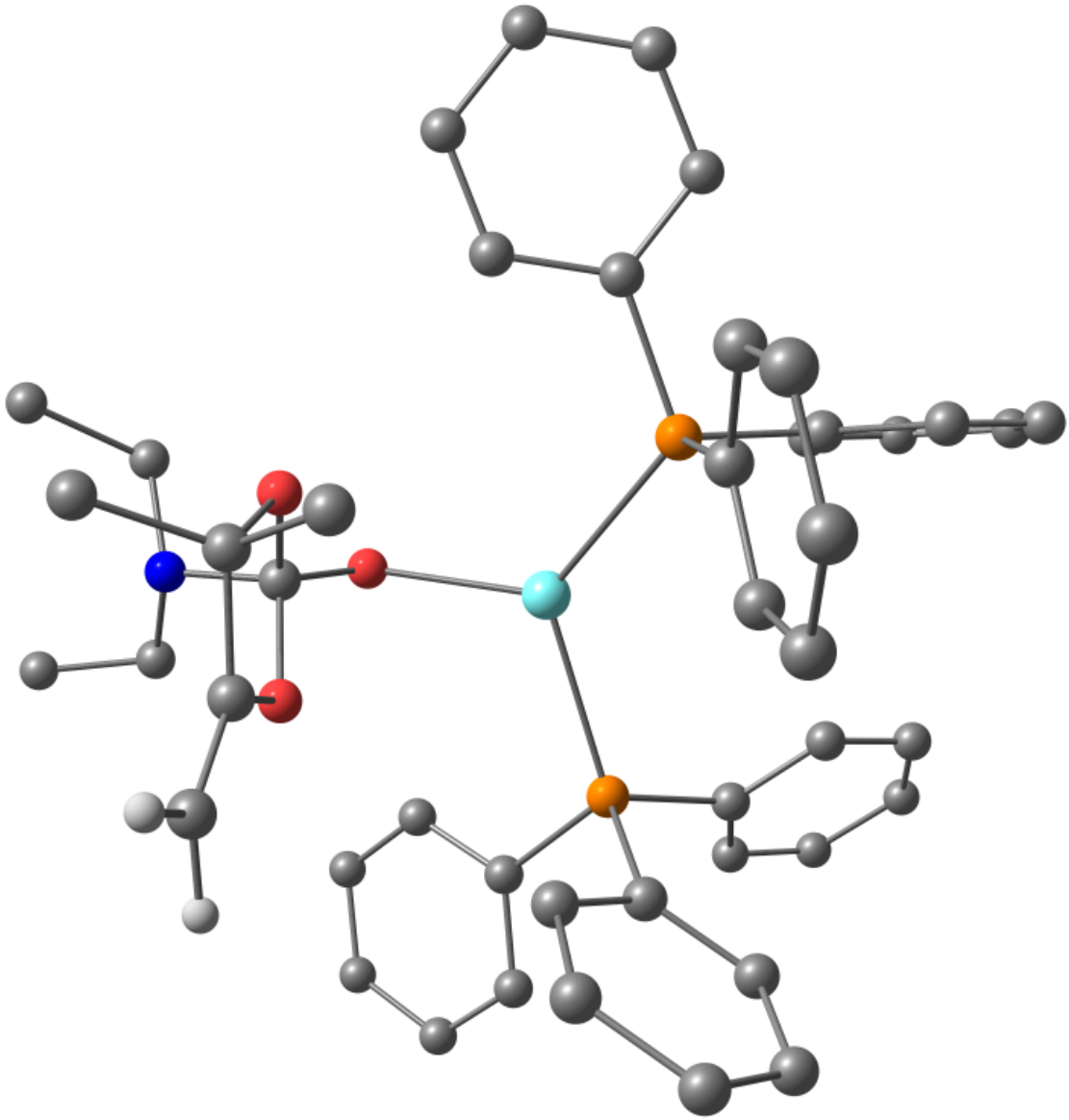


Figure S8. DFT-optimized geometry of **INT7**. C-PCM/ωB97X/def2-SVP calculations, acetonitrile as continuous medium. Color map: Ag, cyan; P, orange; o, red; N, blue; C, grey; H, white. Only the methylene hydrogen atoms are shown for clarity. Selected computed bond lengths (Å): Ag-O 2.333, 2.503; Ag-P 2.480, 2.493.