Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

A Supramolecular Iridium Bifunctional Photoaminocatalyst for the Enantioselective Alkylation of Aldehydes

Andrea Gualandi,* Francesco Calogero, Ada Martinelli, Arianna Quintavalla, Marianna Marchini, Paola Ceroni*, Marco Lombardo,* Pier Giorgio Cozzi*

Dipartimento di Chimica "G. Ciamician", Alma Mater Studiorum – Università di Bologna Via Selmi 2, 40126, Bologna, Italy

Table of Contents

General Methods and Synthesis

All commercial chemicals and dry solvents were purchased from Sigma Aldrich, Alfa Aesar or TCI Chemicals and used without additional purifications. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 400 NMR instrument with a 5 mm probe. All chemical shifts are referenced using deuterated solvent signals; chemical shifts (δ) are reported in ppm from TMS and coupling constants (J) are reported in Hertz. Multiplicity is reported as: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet). HPLC-MS analyses were performed on an Agilent Technologies HP1100 instrument coupled with an Agilent Technologies MSD1100 single-quadrupole mass spectrometer using a Phenomenex Gemini C18 3 µm (100 x 3 mm) column; mass spectrometric detection was performed in full-scan mode from *m/z* 50 to 2500, scan time 0.1 s in positive ion mode, ESI spray voltage 4500 V, nitrogen gas 35 psi, drying gas flow rate 11.5 mL min^{-1}, fragmentor voltage 30 V. HRMS were performed on Waters Xevo G2-XS QTof, ESI+, cone voltage 40 V, Capillary 3KV, source temperature 120 °C. CSP-HPLC analyses were performed on an Agilent Technologies Series 1200 instrument using chiral columns. The enantiomeric compositions were checked against the corresponding racemic products. Flash chromatography purifications were carried out using VWR or Merck silica gel (40-63 µm particle size). Thin-layer chromatography was performed on Merck 60 F254 plates.

$[Ir(N_3\text{-bpy})(ppy)_2]PF_6$ (1) was prepared following a reported literature procedure.[1]

(*S*)-5-Benzyl-2,2-dimethyl-3-(prop-2-yn-1-yl)imidazolidin-4-one (2a) was prepared following a reported literature procedure.[2]

Photochemical reactions

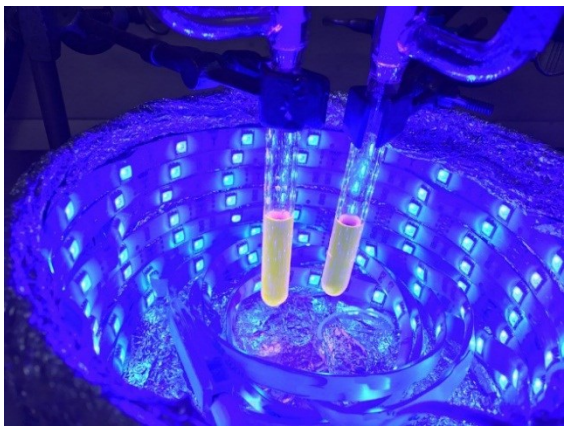


Figure S1. Reaction set-up for the photochemical reaction.

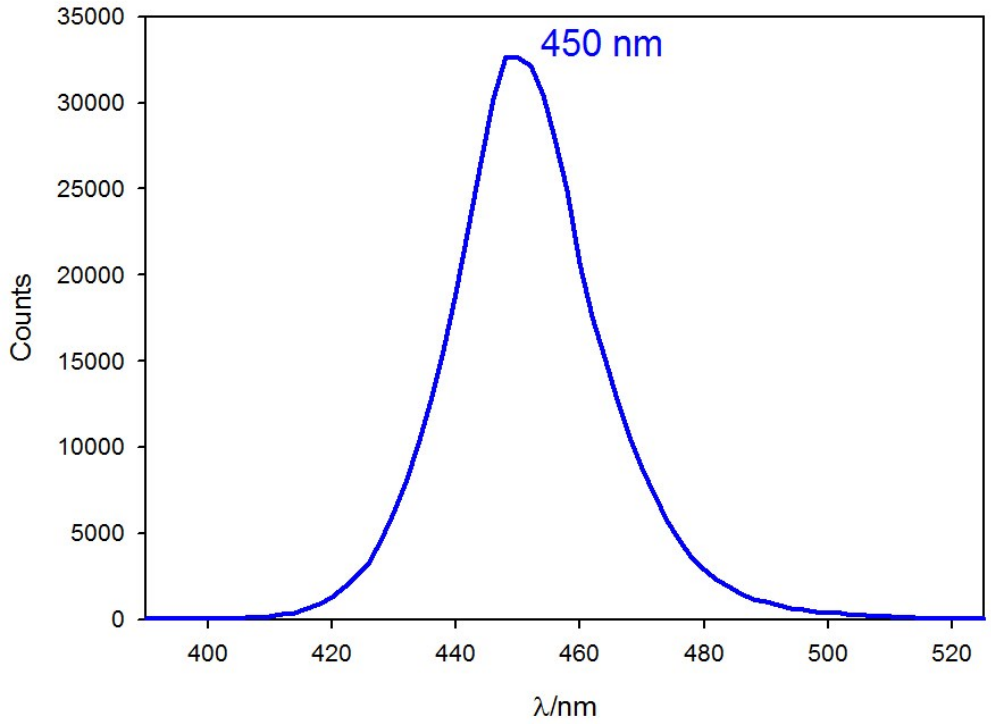


Figure S2. Emission spectrum of 23W blue LEDs used for the irradiation of the reaction mixture.

Preparation of Enamine from catalyst 3b and 4.

The enamine deriving from iridium catalyst **3b** and stoichiometric 2-phenylacetaldehyde **4** was prepared and isolated by column chromatography (0.01 mmol scale), adapting the procedure reported by Mayr and Lakhdar for the simple imidazolidinone **2d**.[3] Due to the presence of both the iridium photocatalytic moiety and the reactive enamine, the product was not stable enough to be fully characterized and was used as soon as possible in photochemical trials.

The formation of the enamine was determined by investigation of the ^{1}H-NMR spectrum of the crude reaction mixture. A new doublet appeared in the expected chemical shift region, relative to the β-proton of the desired (*E*)-configured enamine (5.73 ppm, d, *J* = 14.7 Hz). Moreover, analogously to what observed by Mayr for the corresponding enamine of imidazolidinone **2d**, we also noticed both a significant shielding of one of the diastereotopic methyl groups of the aminal group in the spectrum of the enamine, as well as a shielding of the other (Δδ = 0.56 ppm vs 0.65 ppm reported by Mayr). In the free catalyst **3b**, only a single singlet signal was registered for the methyl groups, thus evidencing the considerably lower conformational mobility of the benzyl group in the corresponding enamine.

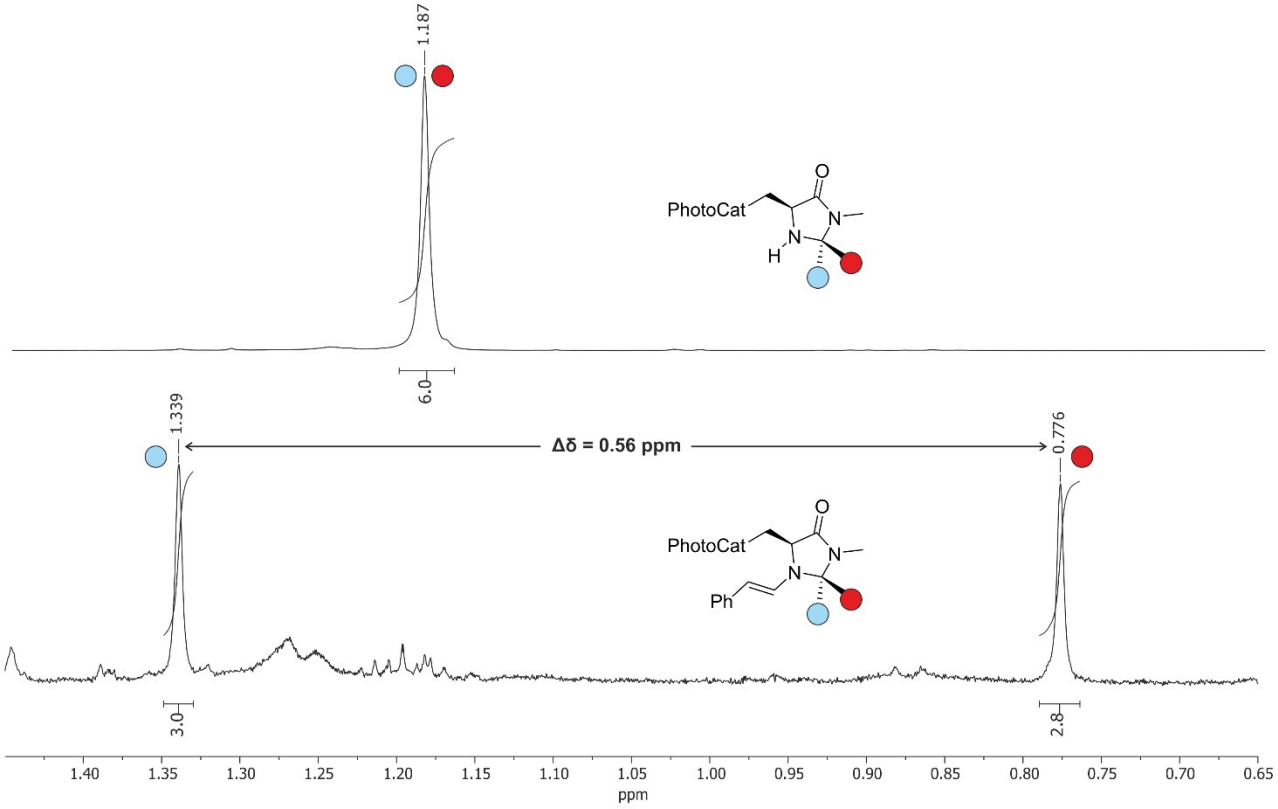


Figure S3. ^{1}H-NMR insets relative to the free catalyst **3b** (up) and to the crude enamine (bottom).

Electrochemical investigations

The electrochemical experiments were carried out in argon-purged CH_3CN (Hi-Dry anhydrous solvent) solution at 298 K. In the cyclic voltammetry (CV) the working electrode was a glassy carbon electrode (0.08 cm^2), the counter electrode was a Pt spiral. The potentials reported are referred to SCE and Ferrocene was used as standard. The concentration of the compounds examined was of the order of $5x10^{-4}$ M; tetraethylammonium hexafluorophosphate ($TEAPF_6$) 0.05M was added as supporting electrolyte. Cyclic voltammograms were obtained with scan rates in the range 0.01–1 V s^{-1}. The estimated experimental error on the $E_{1/2}$ value is ± 10 mV.

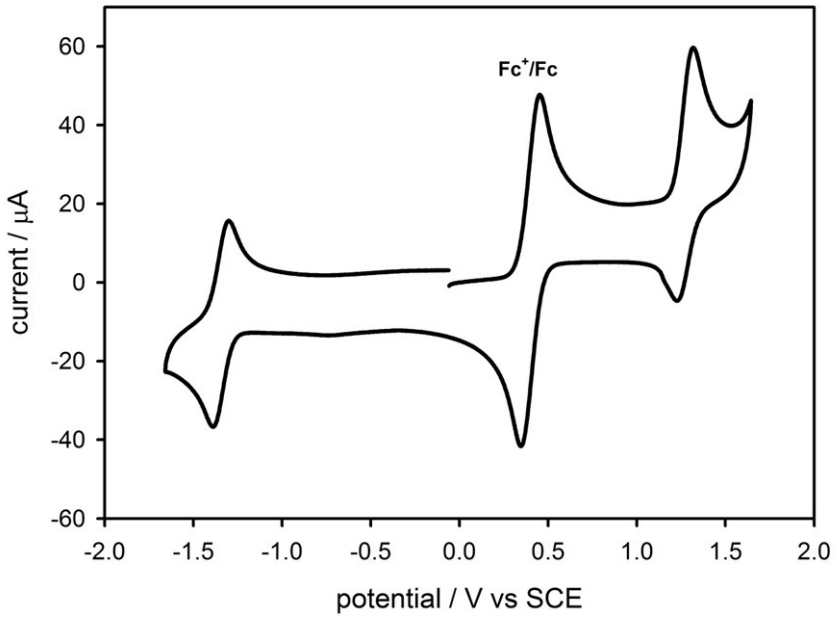


Figure S4. Cyclic voltammetry of an argon-purged solution of **3b** (0.5 mM) in CH_3CN in the presence of 0.05 M tetraethylammonium hexafluorophosphate ($TEAPF_6$). Scan rate=0.5 V s^{-1}; working electrode: glassy carbon. Ferrocene (Fc) was used as internal standard.

	$E_{1/2}^{red}$ (V vs SCE)	$E_{1/2}^{ox}$ (V vs SCE)
Iridium complex **3b**	-1.35	+1.26
Excited state iridium complex **3b**	+0.95	-1.04

Table S1. Redox potentials estimated from cyclic voltammetry performed in argon-purged CH_3CN solution with tetraethylammonium hexafluorophosphate ($TEAPF_6$). Working electrode: glassy carbon. The estimation of the excite state potential is based on the energy of the fluorescent excited state of **3b** (E00 = 2.30 eV).

Photochemical Investigations

Photochemical experiments were carried out at room temperature in air-equilibrated solutions (CH_3CN and DMF Uvasol®), in a quartz cuvette (optical pathlength 1 cm). All absorption spectra were recorded with a spectrophotometer Varian Cary 300 UV-Vis. Phosphorescence spectra were recorded with Perkin Elmer LS 50 spectrofluorometers equipped with Hamamatsu R928 photomultiplier. Lifetime decays measurements were performed using an Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a LDH-P-C-405 pulsed diode laser.

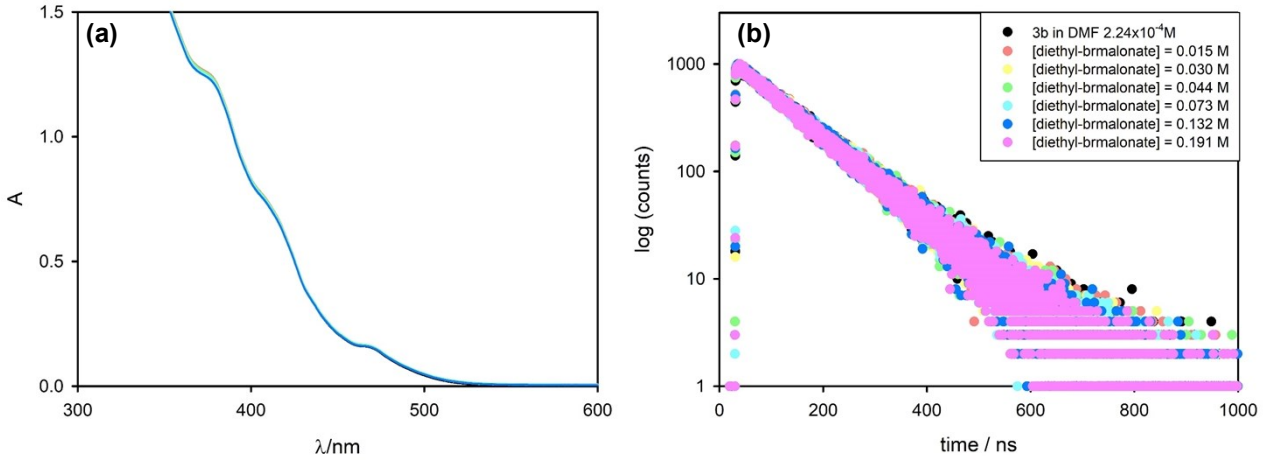


Figure S5. (a) Absorption spectrum of **3b** in air-equilibrated DMF solution (2.24 x 10^{-4} M) with increasing amount of diethyl-bromomalonate up to 0.191 M and (b) the corresponding lifetime decay (excitation 405 nm). Optical path length 1 cm.

Immediately after the addition of phenylacetaldehyde to a **3b** solution in the presence of triflic acid, no quenching was observed (Figure S6).

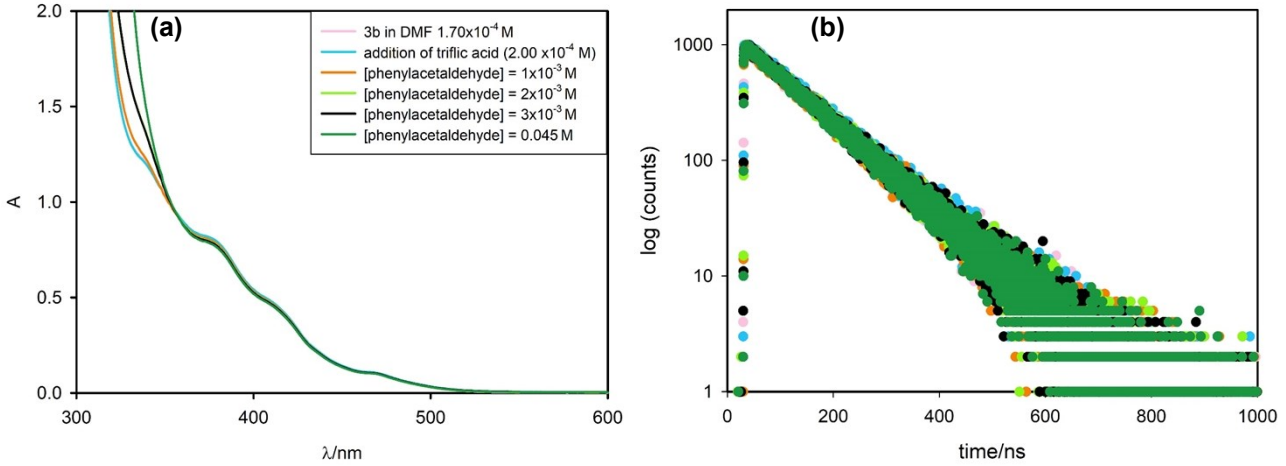


Figure S6. (a) Absorption spectrum of **3b** (1.70 x 10^{-4} M) and equimolar triflic acid in air-equilibrated DMF solution with increasing amount of phenylacetaldehyde up to 0.045 M and (b) the corresponding lifetime decays (excitation 405 nm). Optical path length 1 cm.

The concentration of **3b** along with that of aldehyde and triflic acid were decreased by a factor of 50 with respect to the reaction conditions, in order to have value of absorbance suitable to perform photophysical measurements.

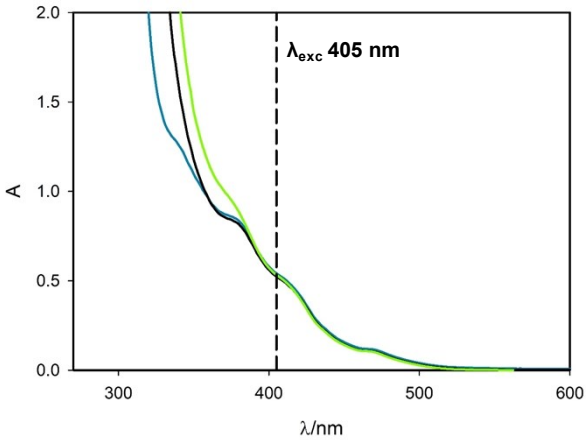


Figure S7. Absorption spectrum of **3b** (1.70 x 10^{-4} M) and equimolar triflic acid in air-equilibrated DMF solution (blue line), upon addition phenylacetaldehyde 0.045 M (black line) and after one day (green line).

The emission decay of the solution containing the isolated enamine derived from **3b** showed two lifetime components: a long one, 99 ns and a short one of 8.4 ns. The values are comparable with those obtained with the generation of the same enamine *in situ* (see main text). Also in that case, the short component is attributed to the intramolecular quenching of the Ir(III) complex by the enamine; the longer lifetime is comparable with the one measured for **3b** in solution (110 ns).

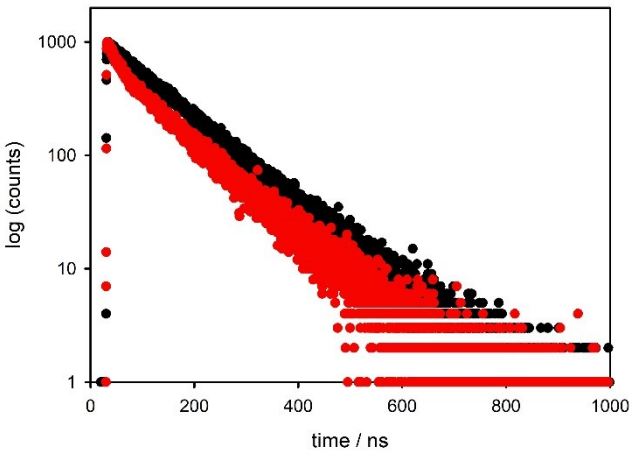


Figure S8. Emission intensity decay of **3b** (1.70 x 10^{-4} M) and equimolar triflic acid (black dots) and isolated enamine (red dots) in air-equilibrated DMF solution. Excitation at 405 nm.

The formation of the enamine was followed with spectrofluorimetric kinetic: an emission spectrum of the solution containing **3b**, triflic acid and an excess of phenylacetaldehyde was collected each hour for 2 days.

The trend of the emission intensity with time shows a decrease of intensity, compatible with the concomitant increasing amount of the enamine formed.

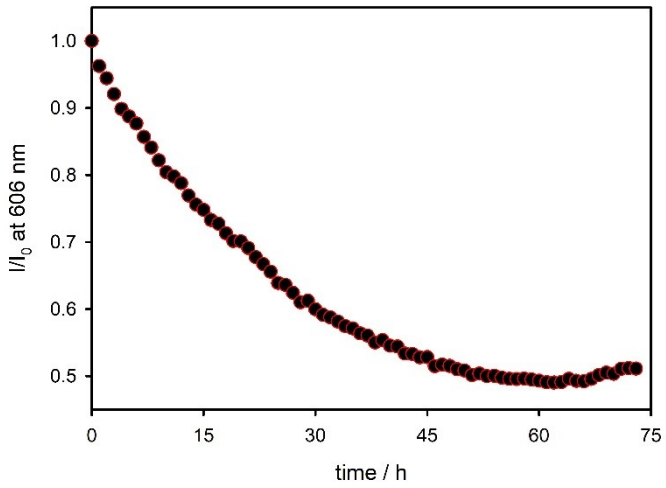


Figure S9. Normalized emission intensity changes at 606 nm as a function of time of a solution containing **3b** (1.70×10^{-4} M), equimolar amount of triflic acid, phenylacetaldehyde 0.045 M in air-equilibrated DMF. λ_{exc} at 405 nm.

The constant k_q of the intramolecular quenching process occurring within the supramolecular photocatalyst **3b'** comprising the Ir(III) photosensitizer and the formed enamine can be evaluated according to the following equation:

$$k_q = \frac{1}{\tau} - \frac{1}{\tau^0}$$

where τ and τ^0 are the lifetime of the Ir(III) complex in **3b'** and **3b**.

The corresponding quenching efficiency is evaluated by the following equation:

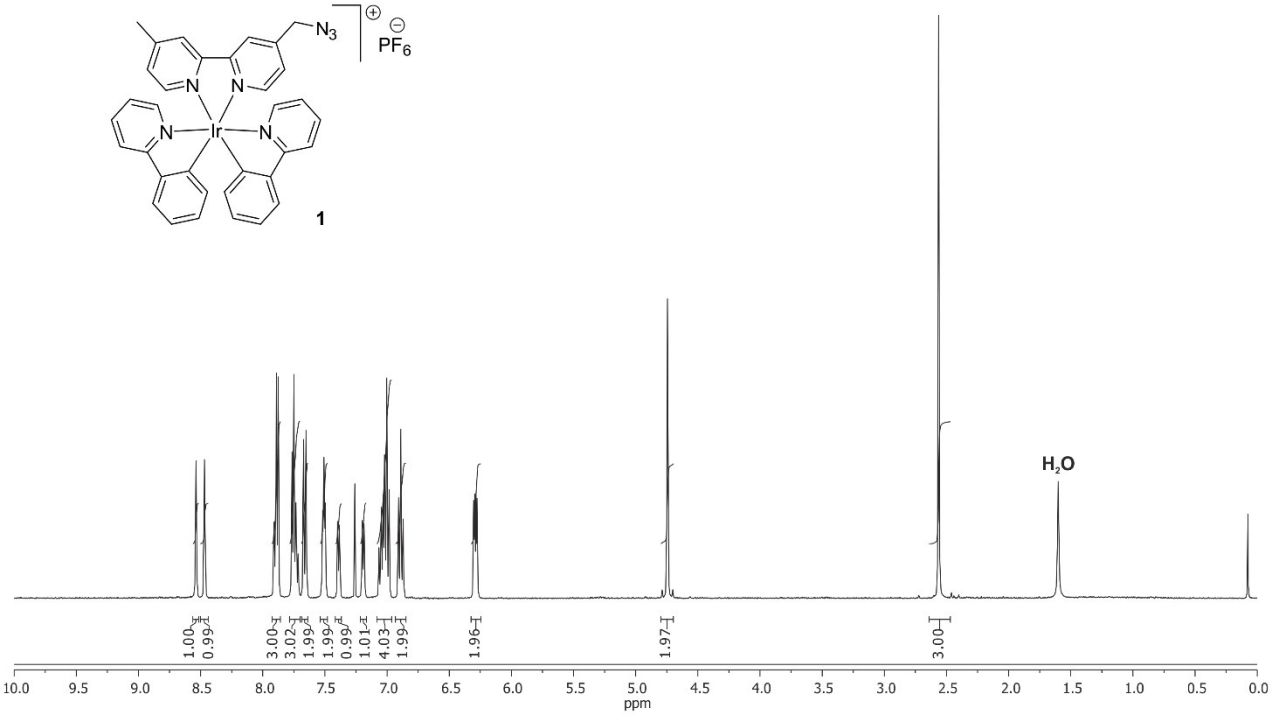
$$\eta_q = \left(1 - \frac{\tau}{\tau^0}\right)$$

Characterization Data

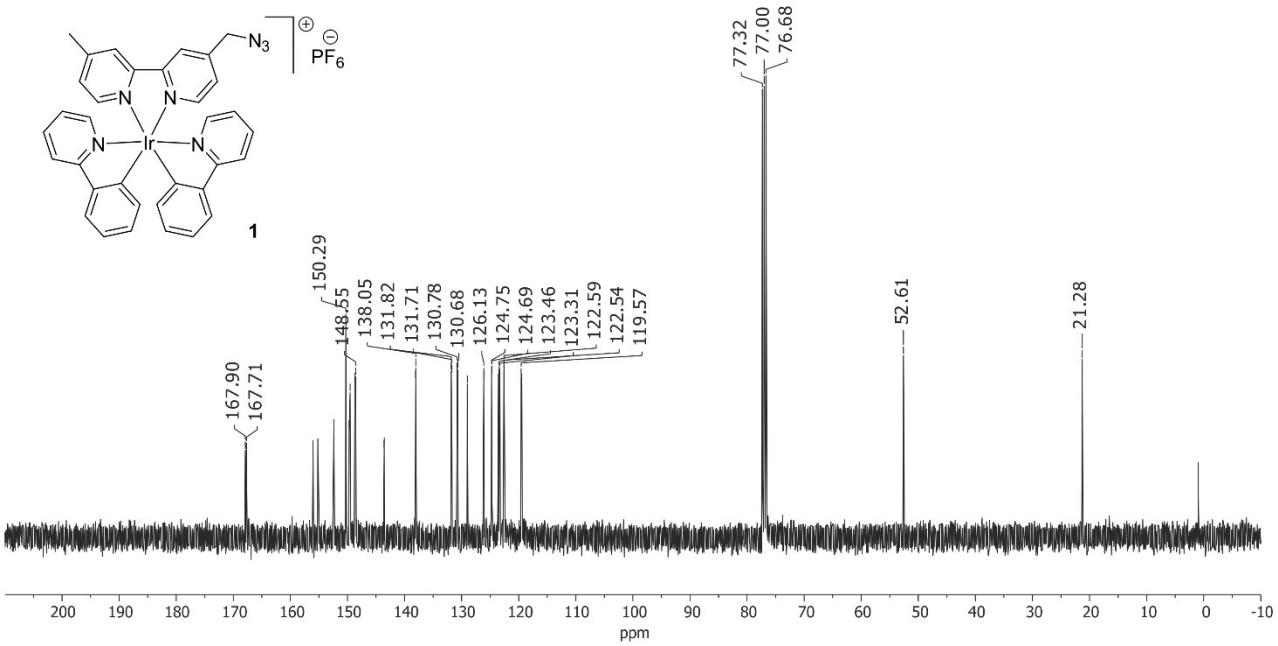
Copies of NMR and of HPLC-MS spectra

$[Ir(N_3\text{-bpy})(ppy)_2]PF_6$ (1).

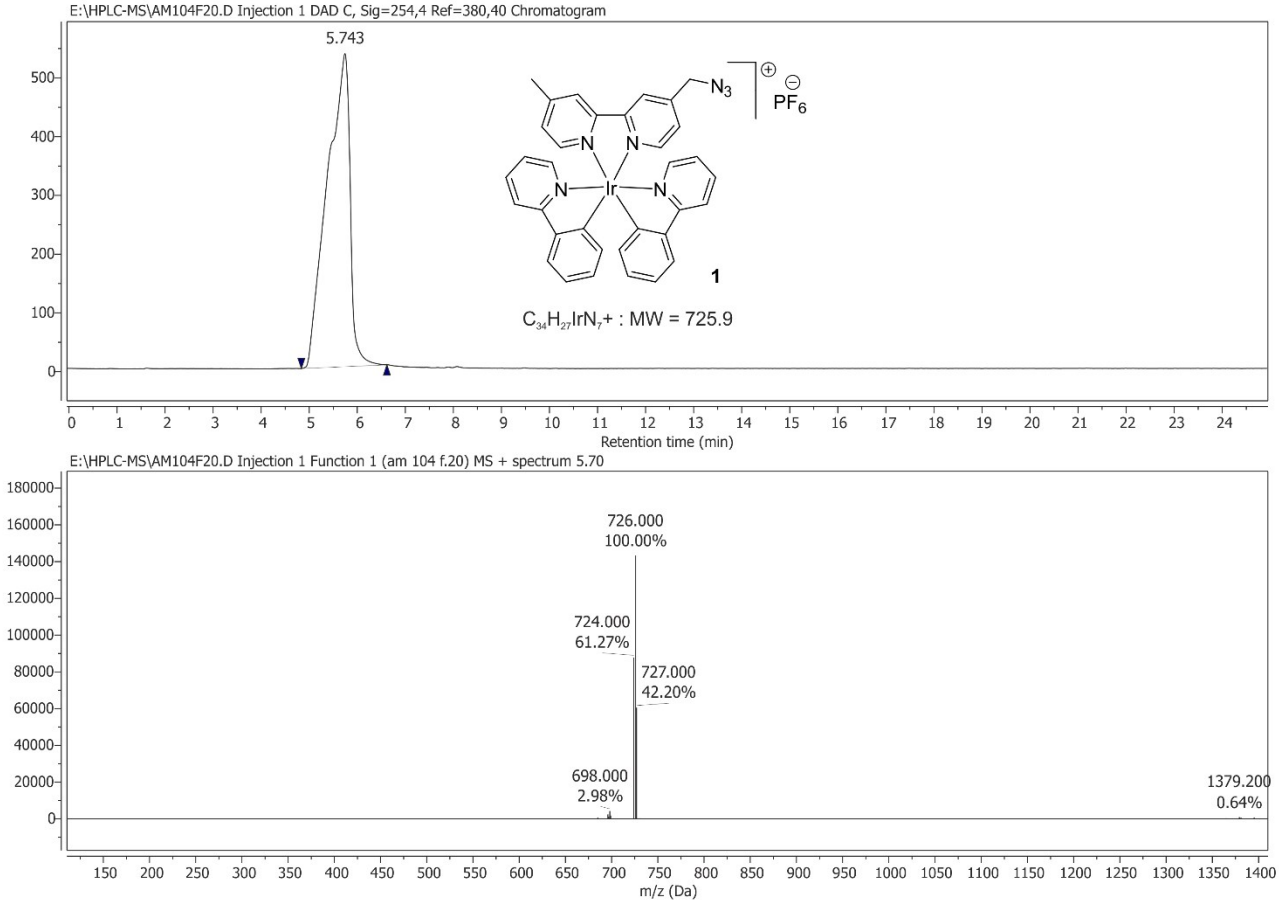
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)

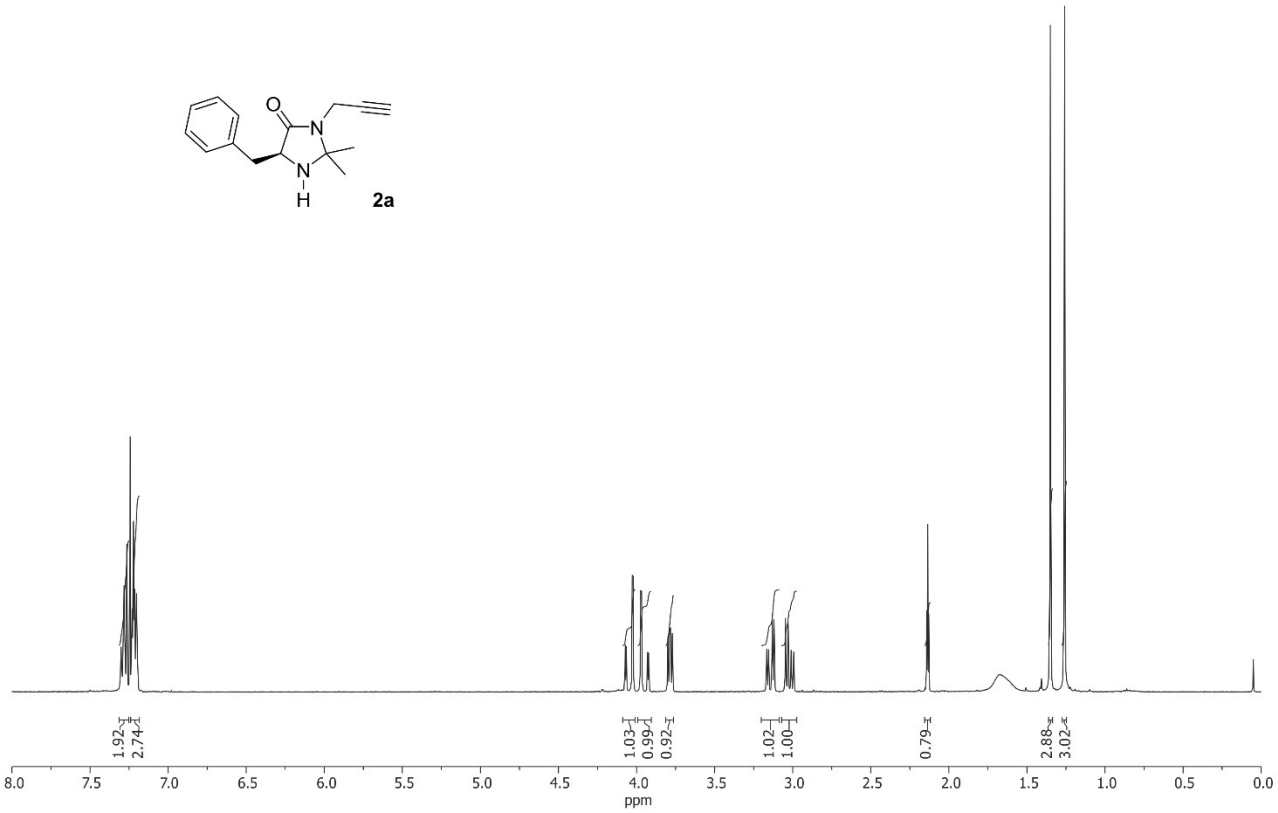


HPLC-MS

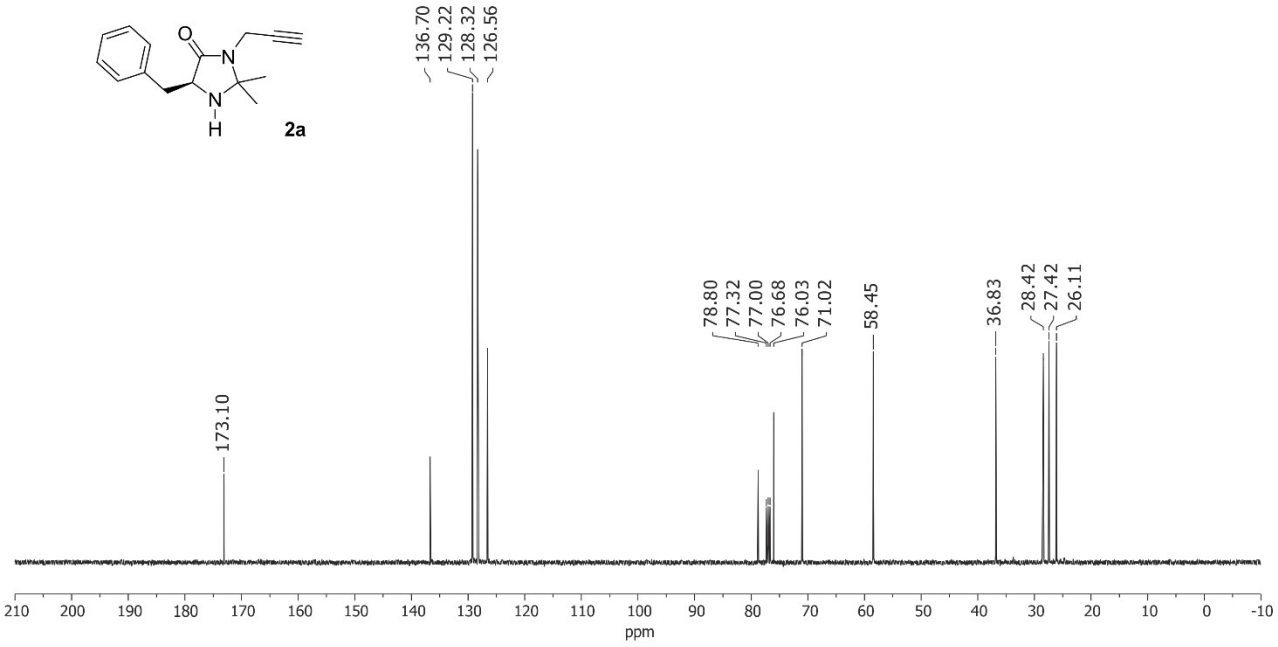

E:\HPLC-MS\AM104F20.D Injection 1 DAD C, Sig=254,4 Ref=380,40 Chromatogram
5.743
Retention time (min)
1
C34H27IrN7+ : MW = 725.9
E:\HPLC-MS\AM104F20.D Injection 1 Function 1 (am 104 f.20) MS + spectrum 5.70
726.000
100.00%
724.000
61.27%
727.000
42.20%
698.000
2.98%
1379.200
0.64%
m/z (Da)

(*S*)-5-Benzyl-2,2-dimethyl-3-(prop-2-yn-1-yl)imidazolidin-4-one (2a).

^{1}H-NMR (400 MHz, $CDCl_3$)

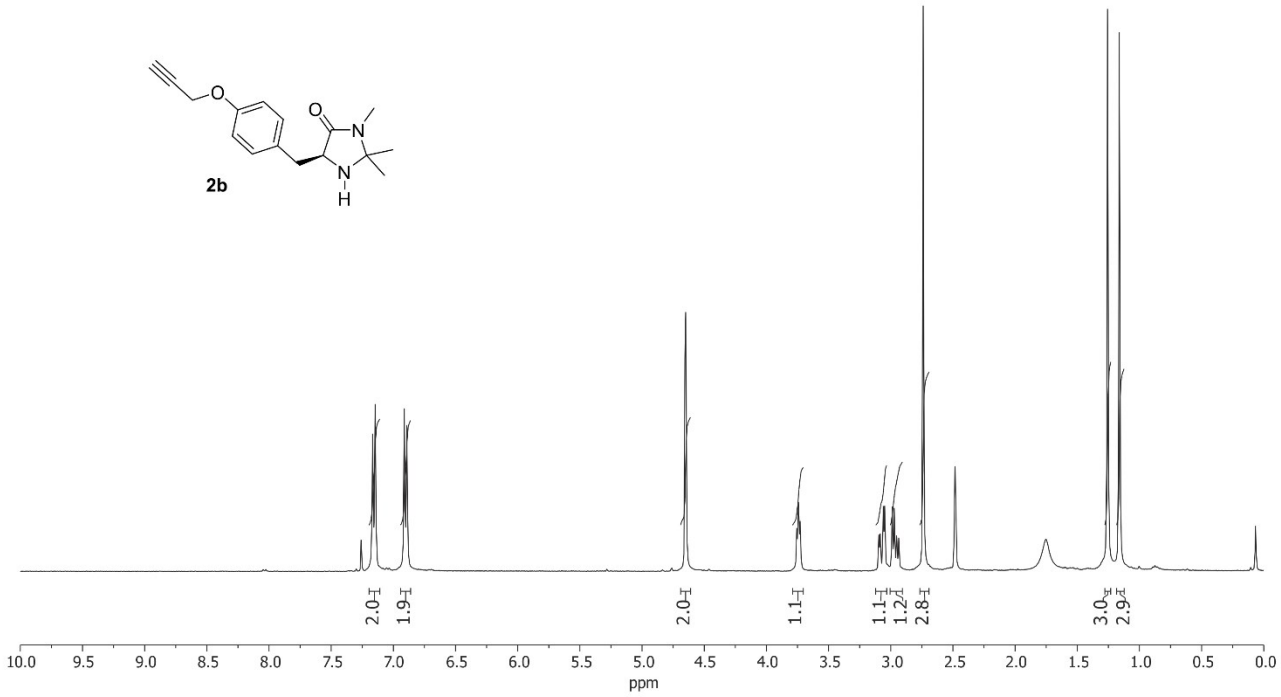


^{13}C-NMR (100 MHz, $CDCl_3$)

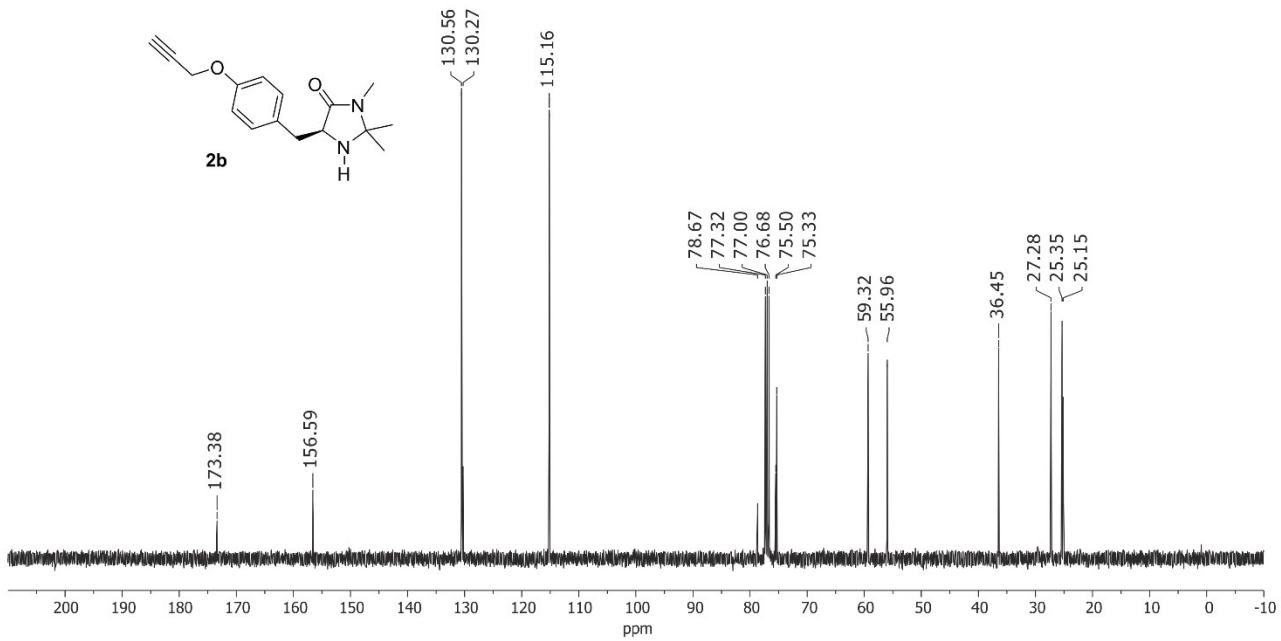


(*S*)-2,2,3-trimethyl-5-(4-(prop-2-yn-1-yloxy)benzyl)imidazolidin-4-one (2b). Prepared following a reported literature procedure.[4]

^{1}H-NMR (400 MHz, $CDCl_3$)

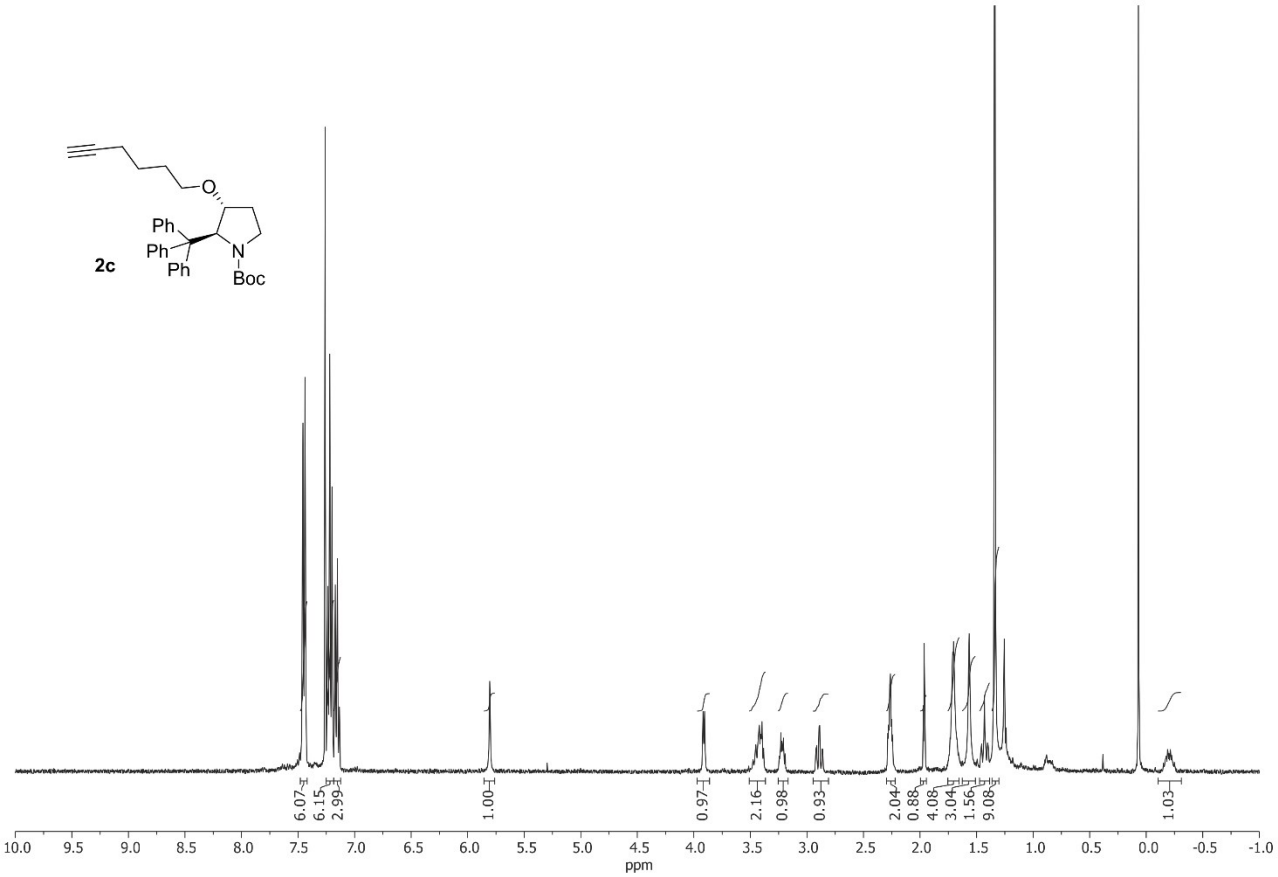


^{13}C-NMR (100 MHz, $CDCl_3$)

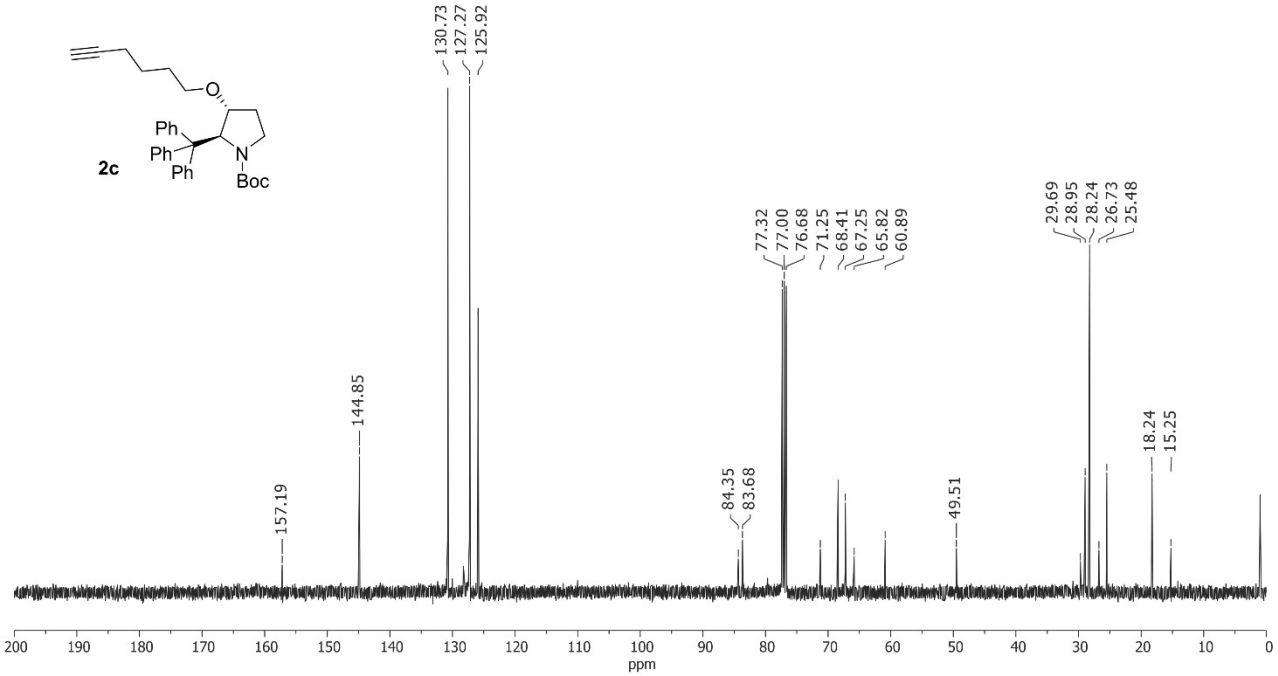


***tert*-butyl-(2*S*,3*R*)-3-(hex-5-yn-1-yloxy)-2-tritylpyrrolidine-1-carboxylate (*N*-Boc-2c).**

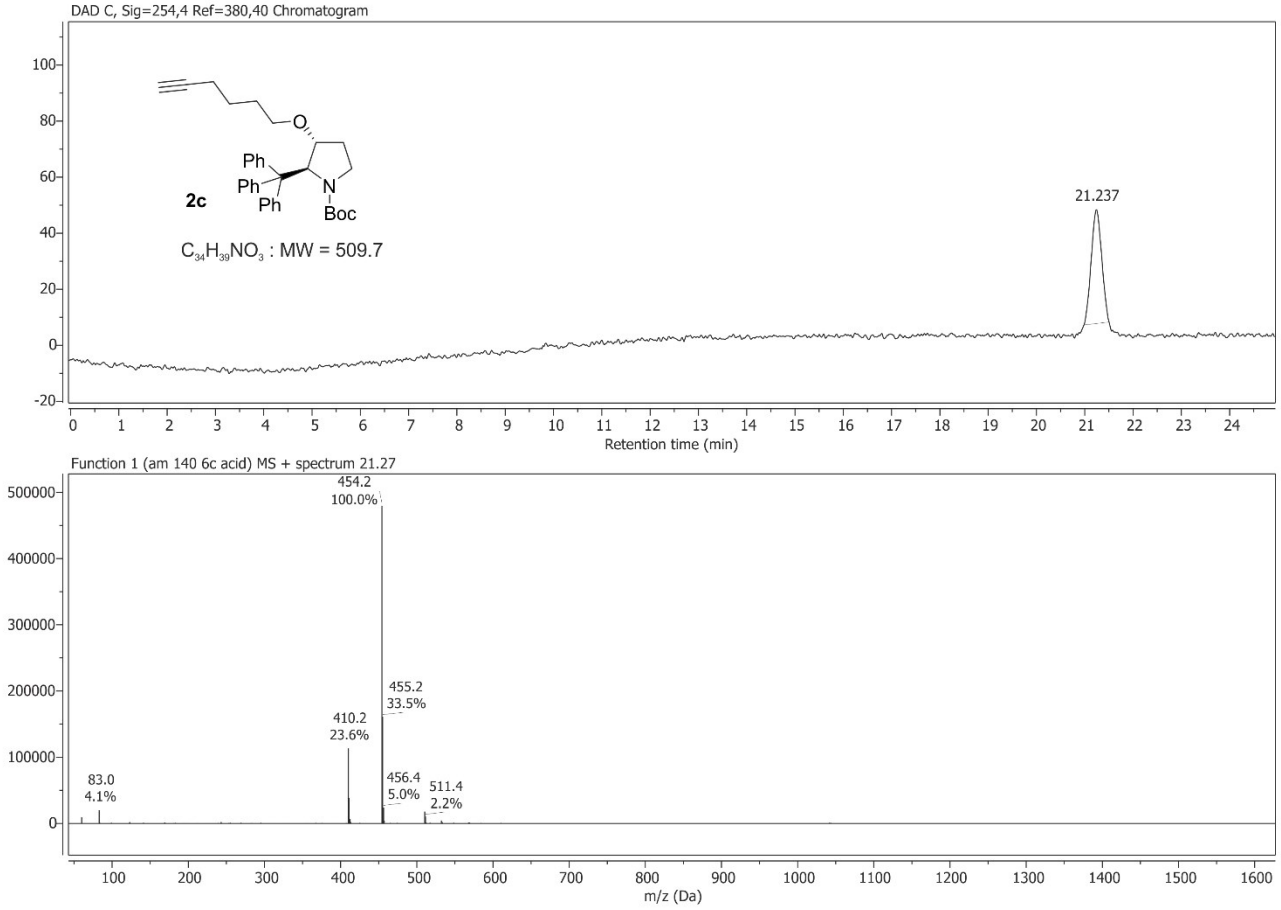
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)

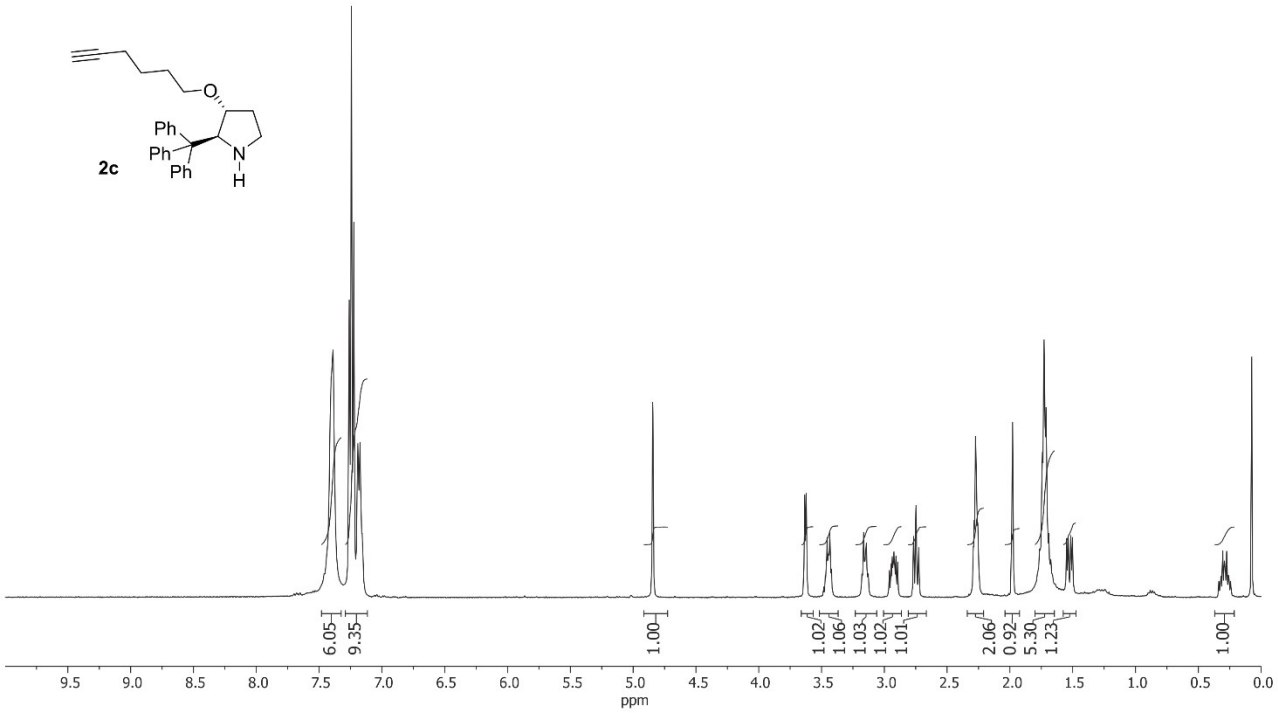


HPLC-MS

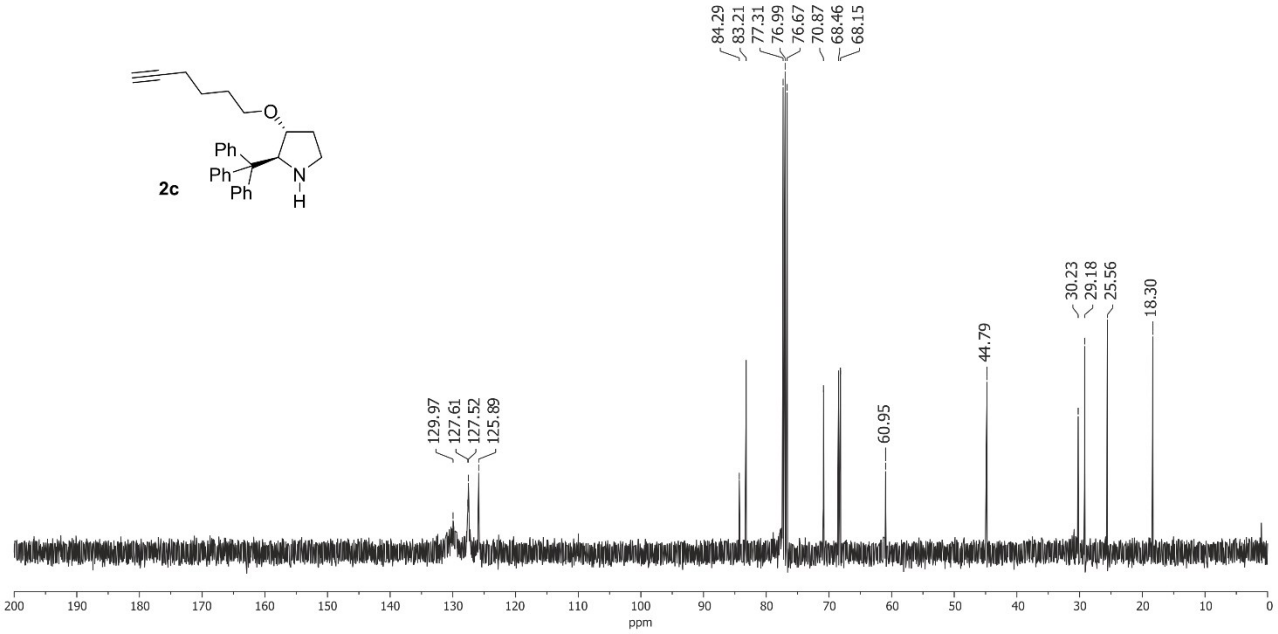

DAD C, Sig=254,4 Ref=380,40 Chromatogram
2c
C34H39NO3 : MW = 509.7
21.237
Retention time (min)
Function 1 (am 140 6c acid) MS + spectrum 21.27
454.2
100.0%
455.2
33.5%
410.2
23.6%
456.4
5.0%
511.4
2.2%
83.0
4.1%
m/z (Da)

(2*S*,3*R*)-3-(hex-5-yn-1-yloxy)-2-tritylpyrrolidine (2c).

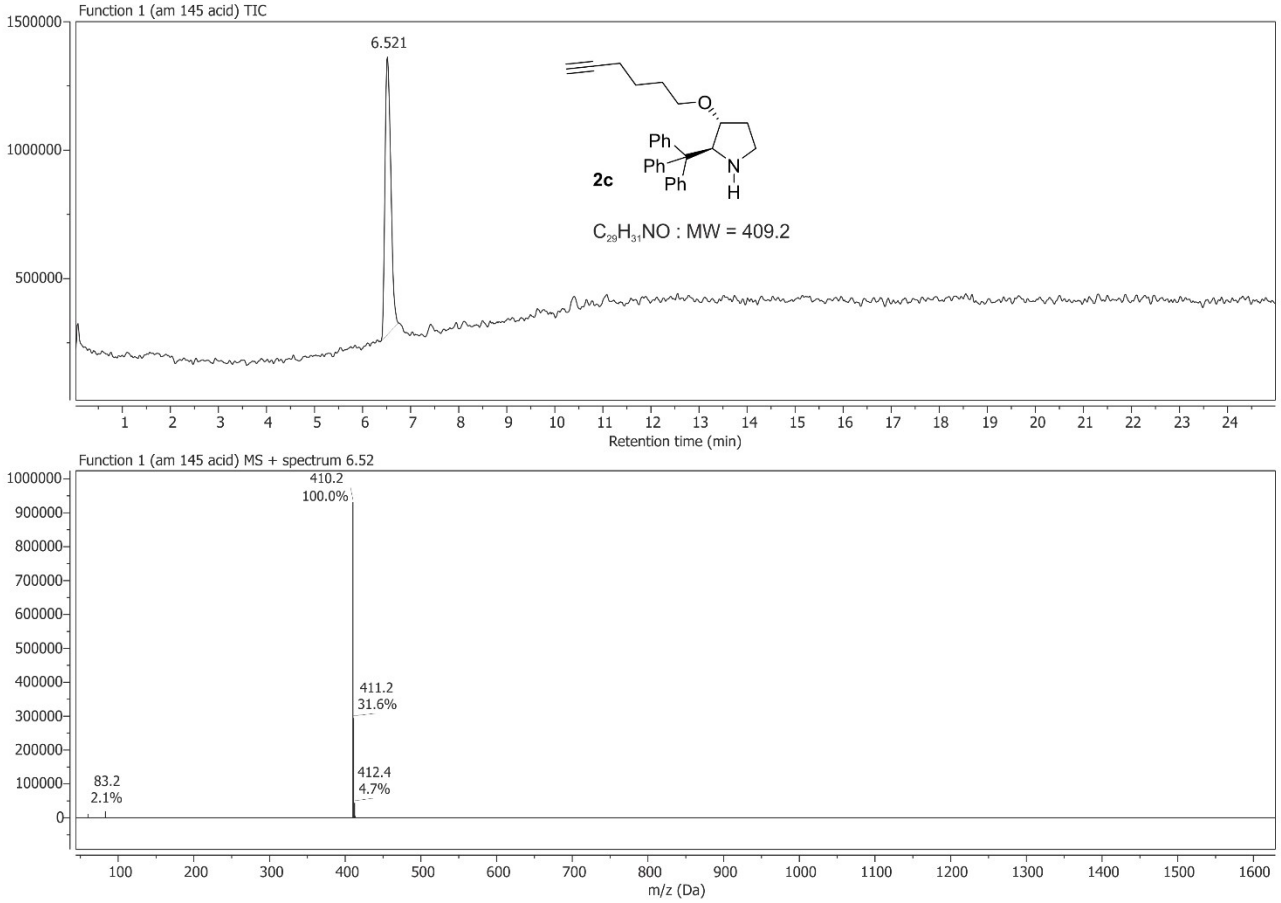
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)

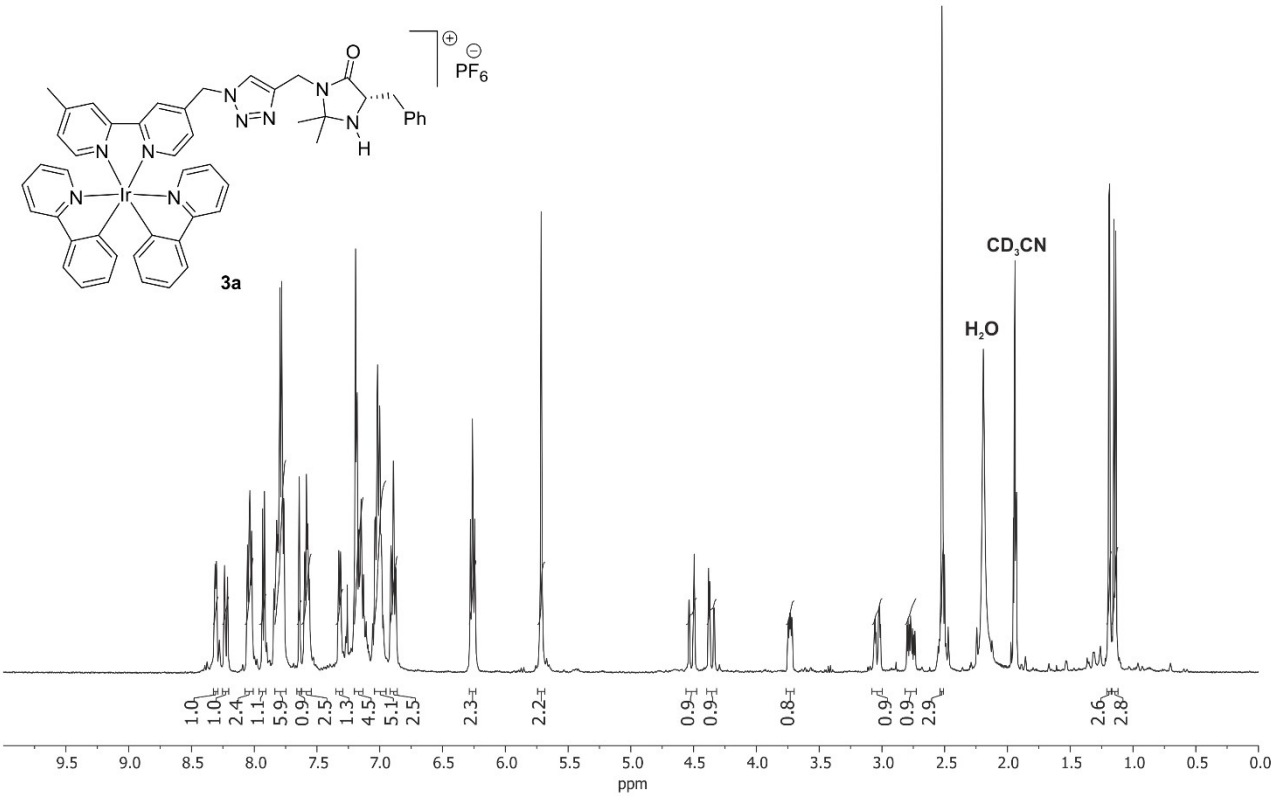


HPLC-MS

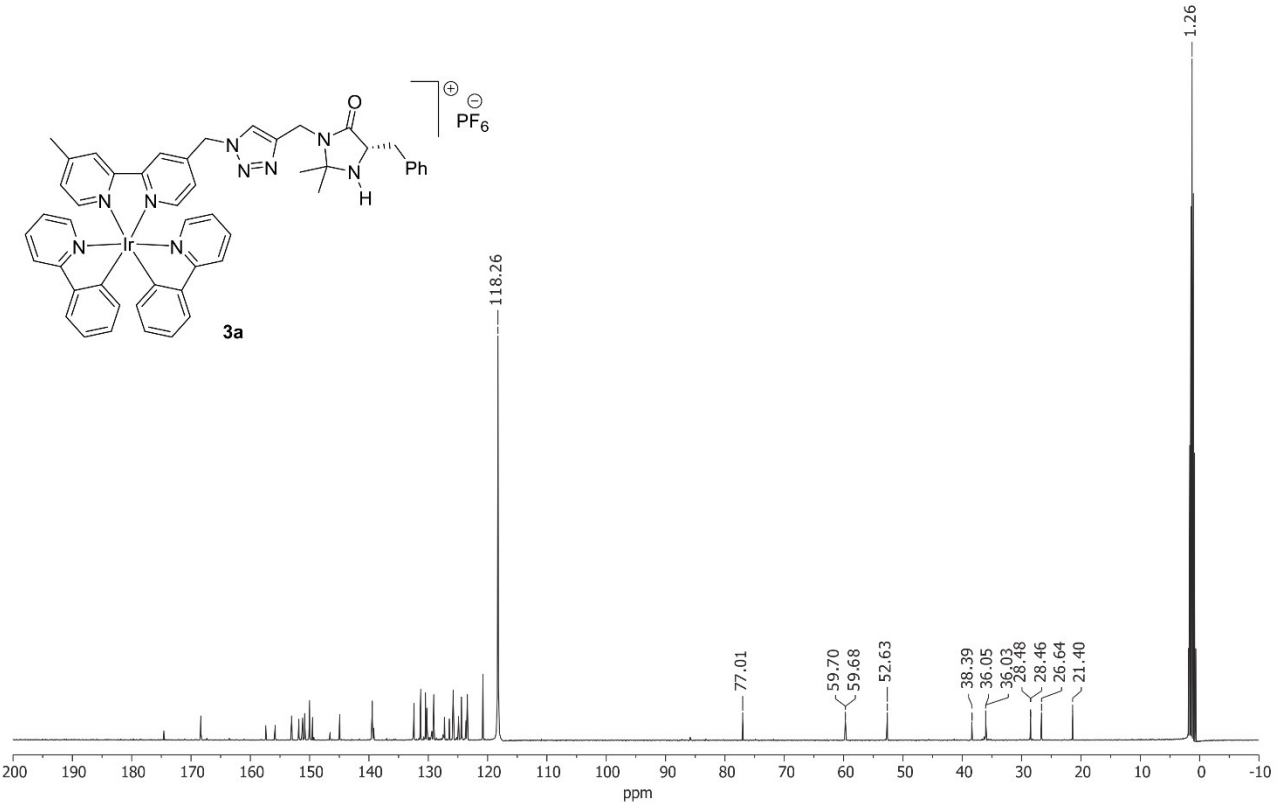

Function 1 (am 145 acid) TIC
6.521
2c
C29H31NO : MW = 409.2
Retention time (min)
Function 1 (am 145 acid) MS + spectrum 6.52
410.2
100.0%
411.2
31.6%
412.4
4.7%
83.2
2.1%
m/z (Da)

Iridium photocatalyst 3a.

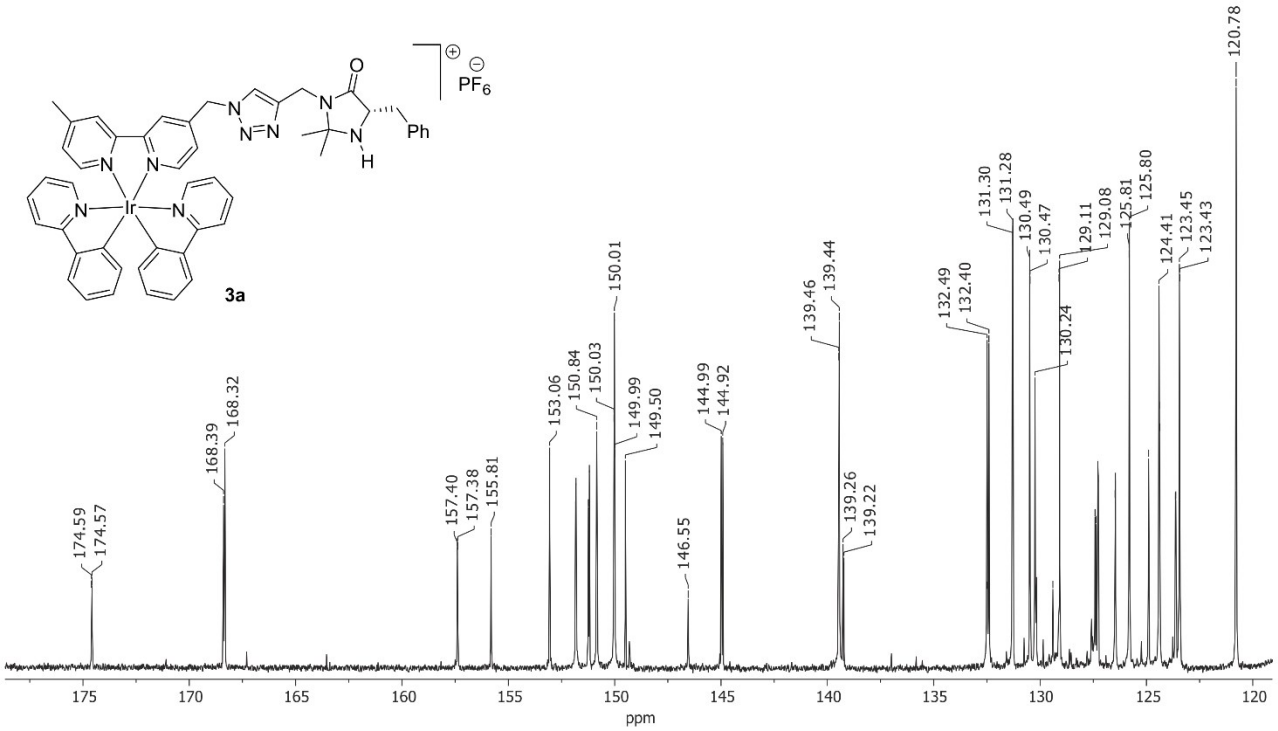
[1]H-NMR (400 MHz, CD_3CN)



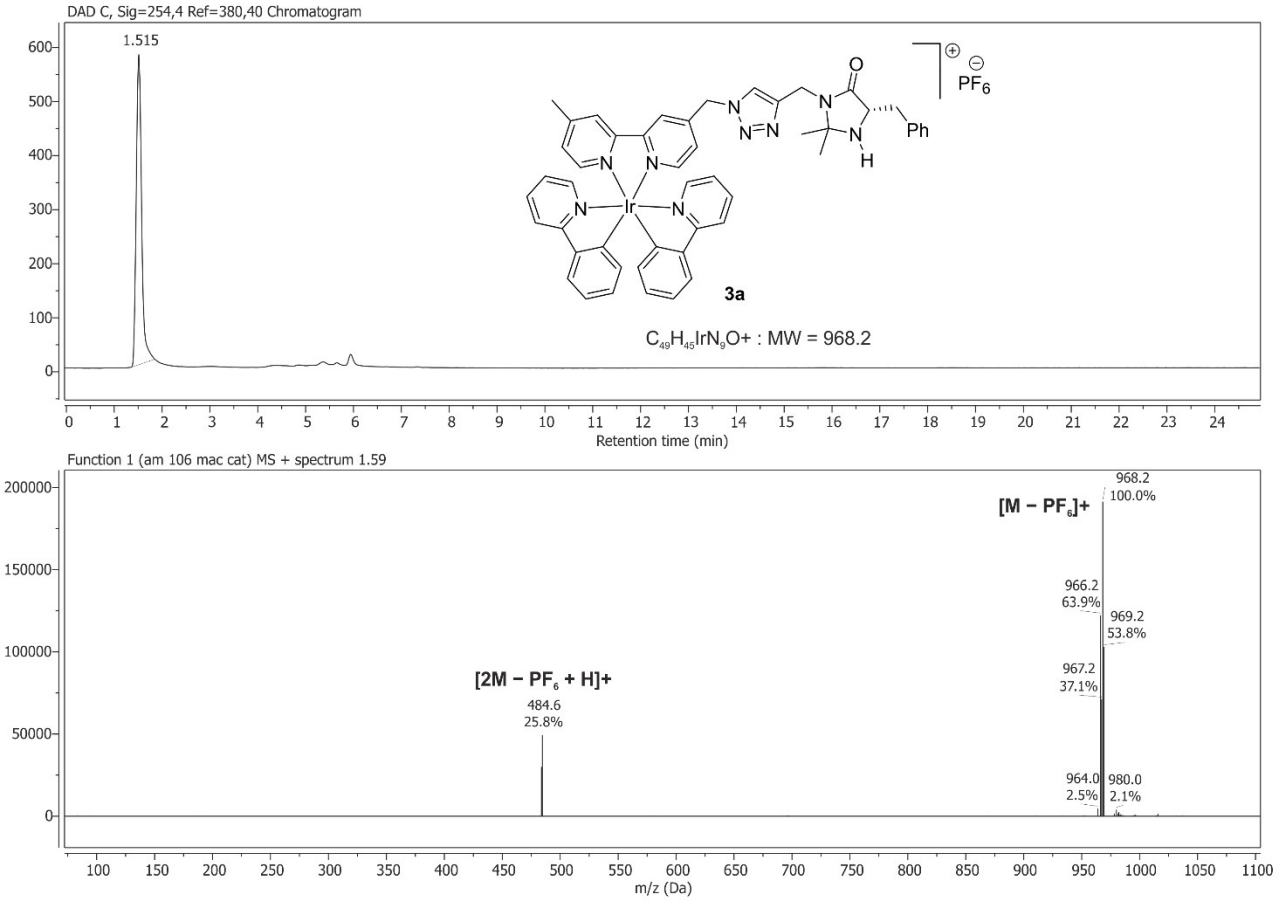
[13]C-NMR (100 MHz, CD_3CN)



^{13}C-NMR (100 MHz, CD_3CN). Aromatic region expansion.



HPLC-MS



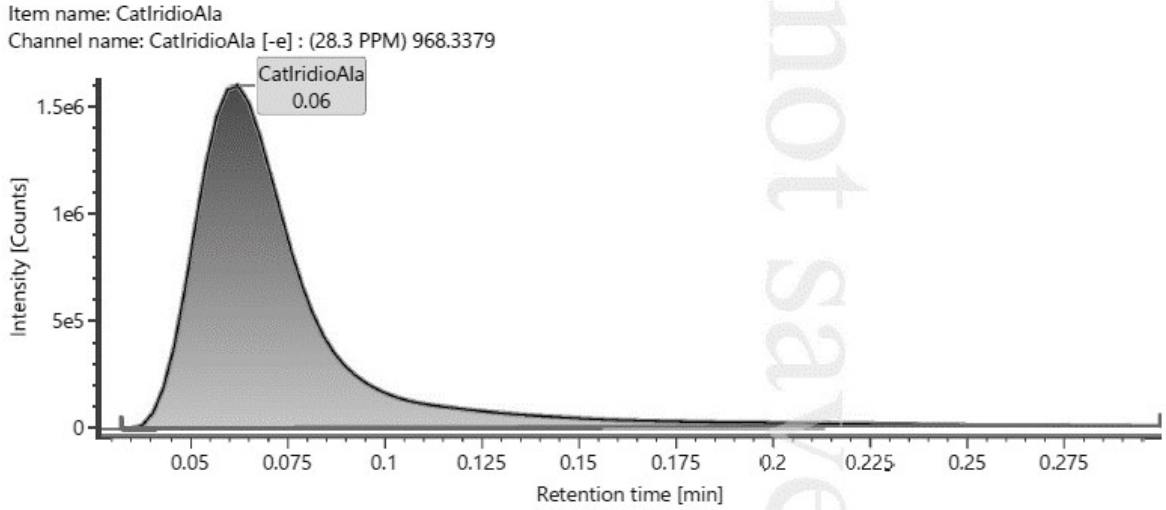
HRMS

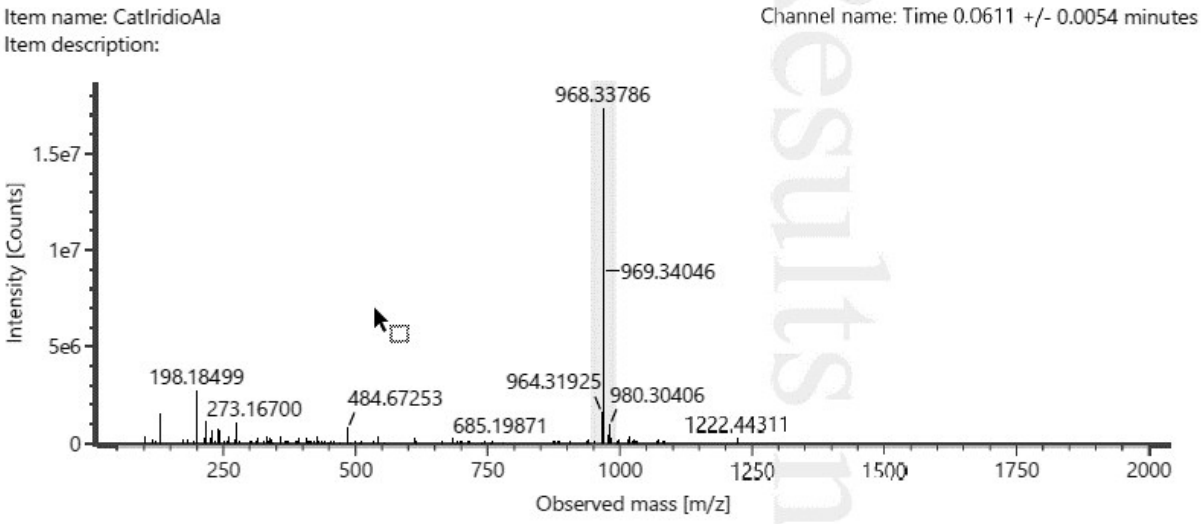
Item name: CatIridioAla, Sample position: 1:A,1, Replicate number: 1

.	Component name	Neutral mass (Da)	Observed m/z	Mass error (mDa)	Mass error (ppm)	Expected RT (min)	Observed RT (min)
1	CatIridioAla	968.33763	968.3379	0.8	0.8		0.06

.	Component name	Neutral mass (Da)	Response	Adducts
1	CatIridioAla	968.33763	609521	-e

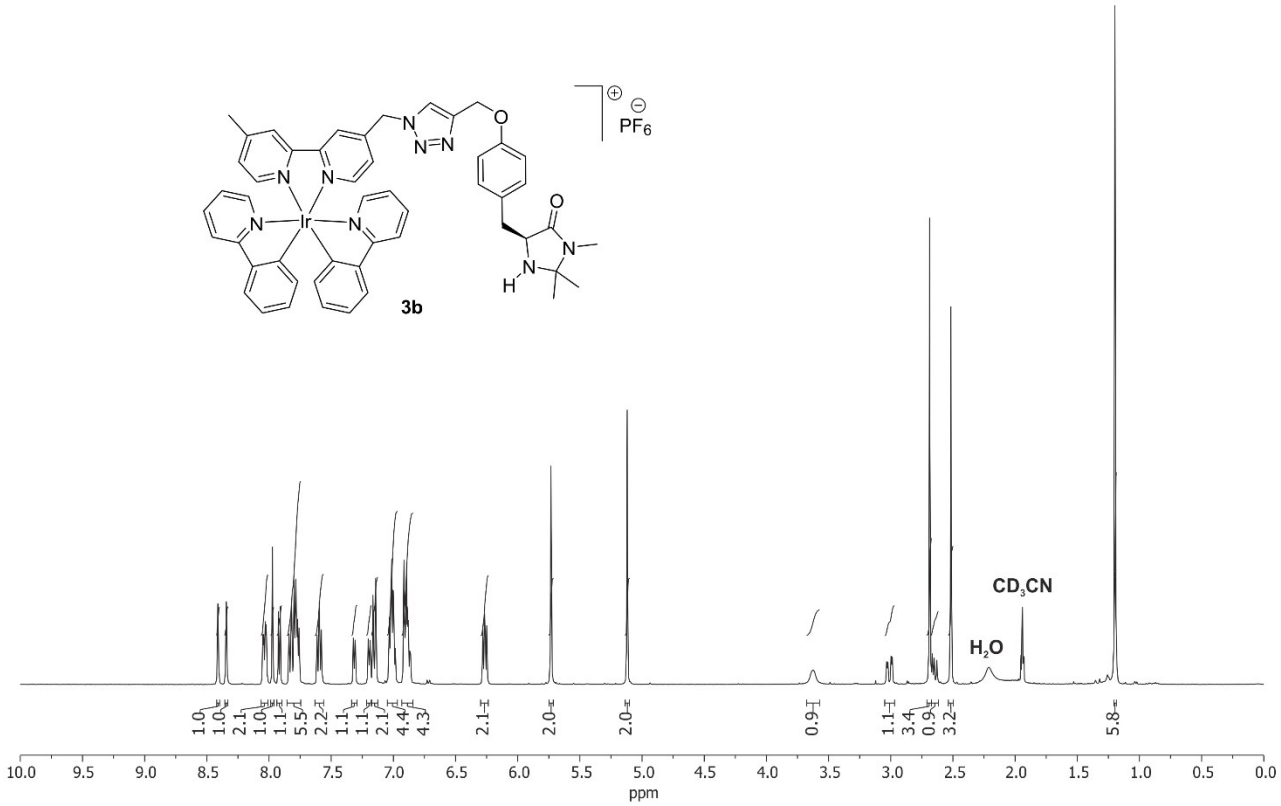
Component name: CatIridioAla



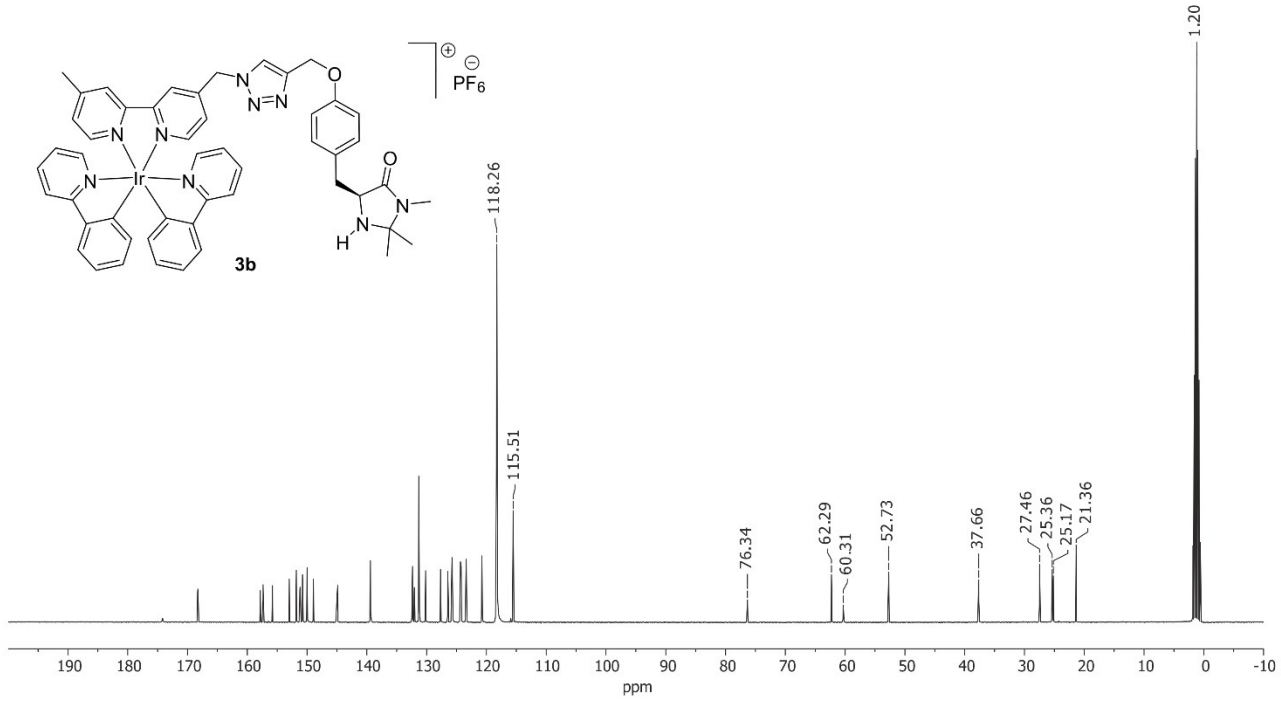


Iridium photocatalyst 3b.

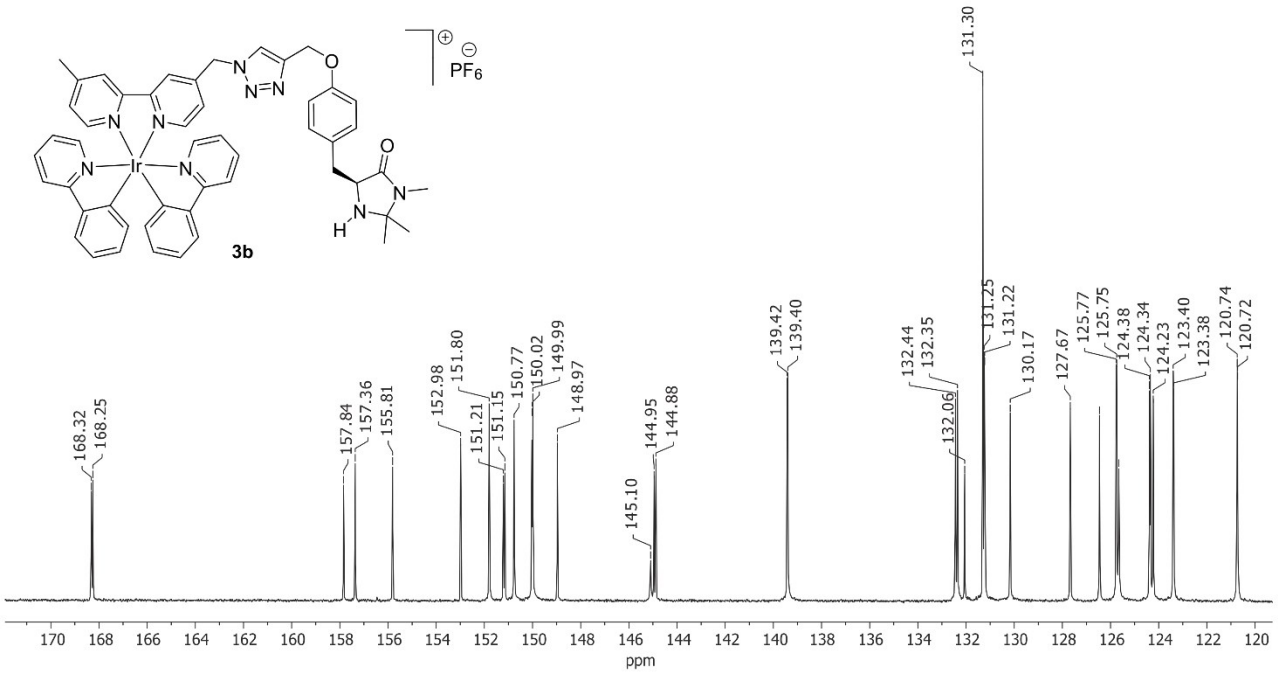
[1]H-NMR (400 MHz, CD_3CN)



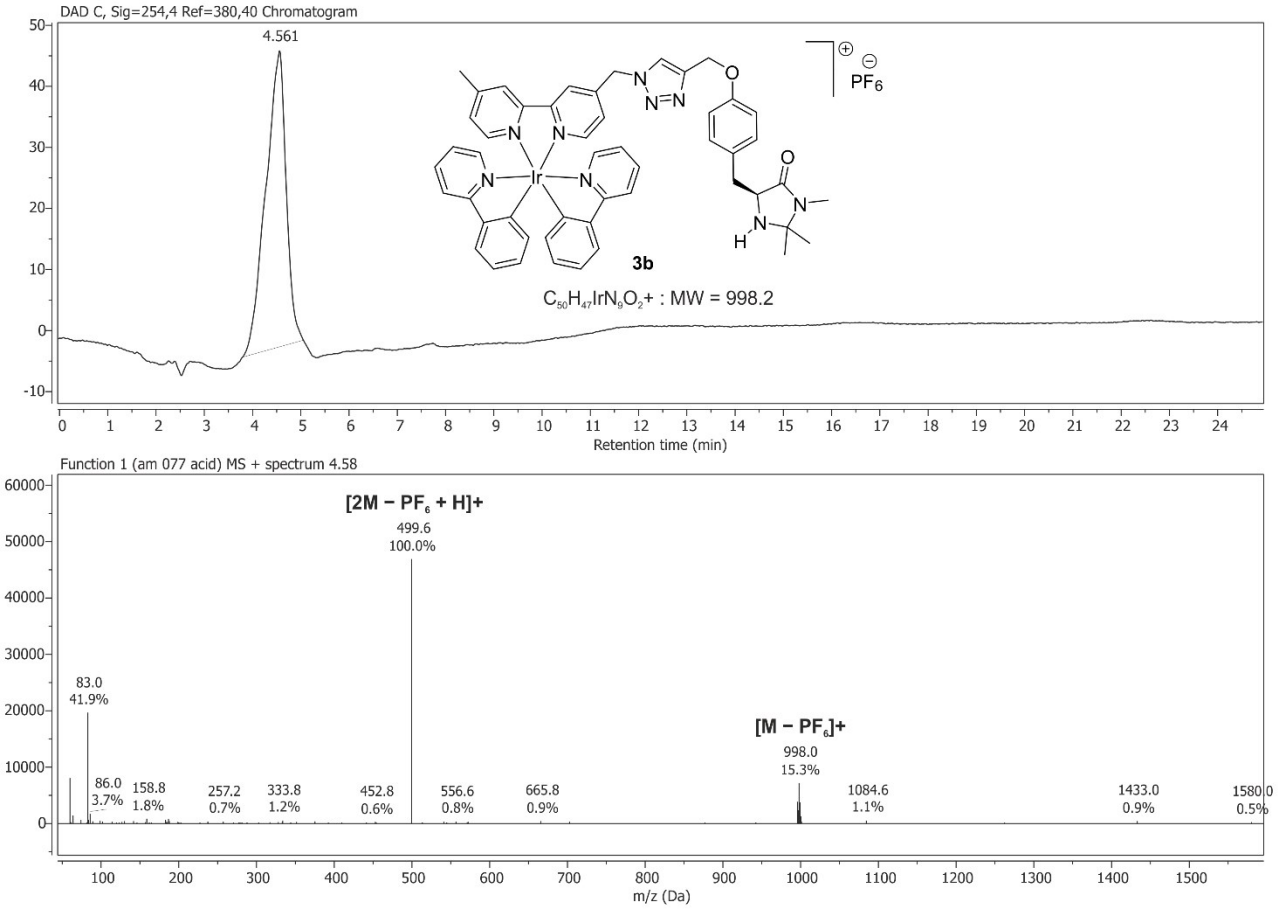
[13]C-NMR (100 MHz, CD_3CN)



^{13}C-NMR (100 MHz, CD_3CN). Aromatic region expansion.



HPLC-MS



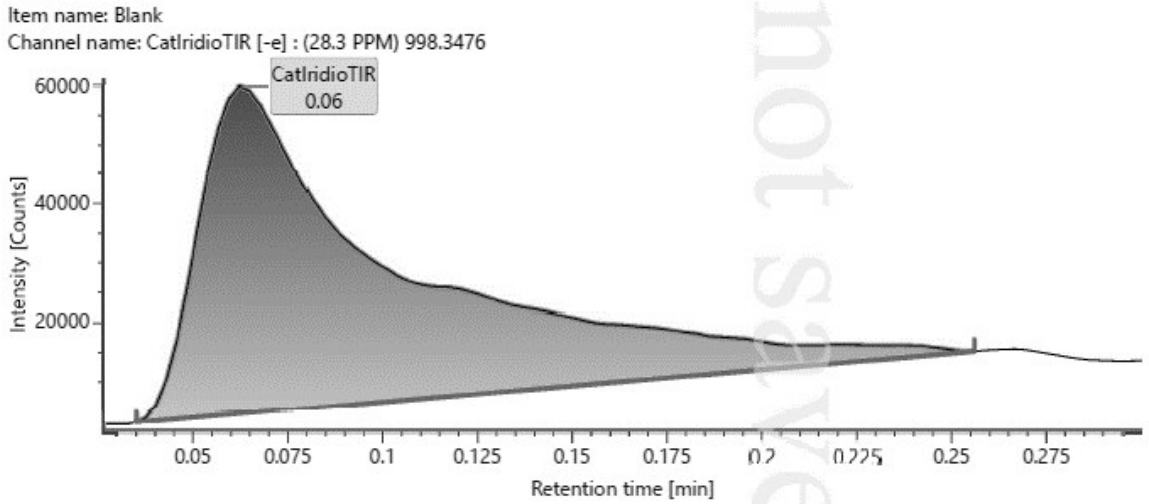
HRMS

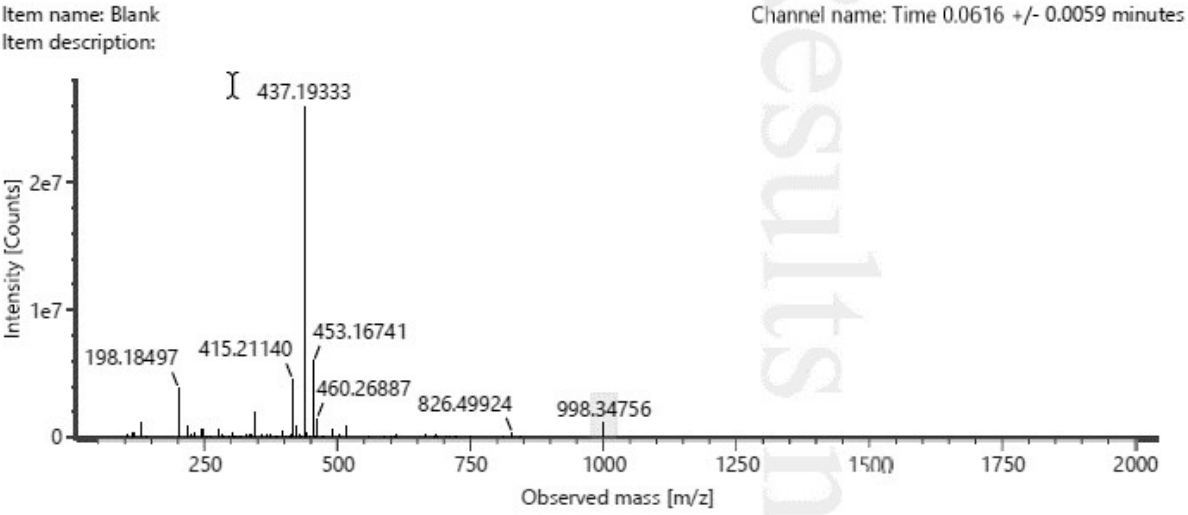
Item name: Blank, Sample position: 1:F,8, Replicate number: 1

.	Component name	Neutral mass (Da)	Observed m/z	Mass error (mDa)	Mass error (ppm)	Expected RT (min)	Observed RT (min)
1	CatIridioTIR	998.34819	998.3476	-0.1	-0.1		0.06

.	Component name	Neutral mass (Da)	Response	Adducts
1	CatIridioTIR	998.34819	39842	-e

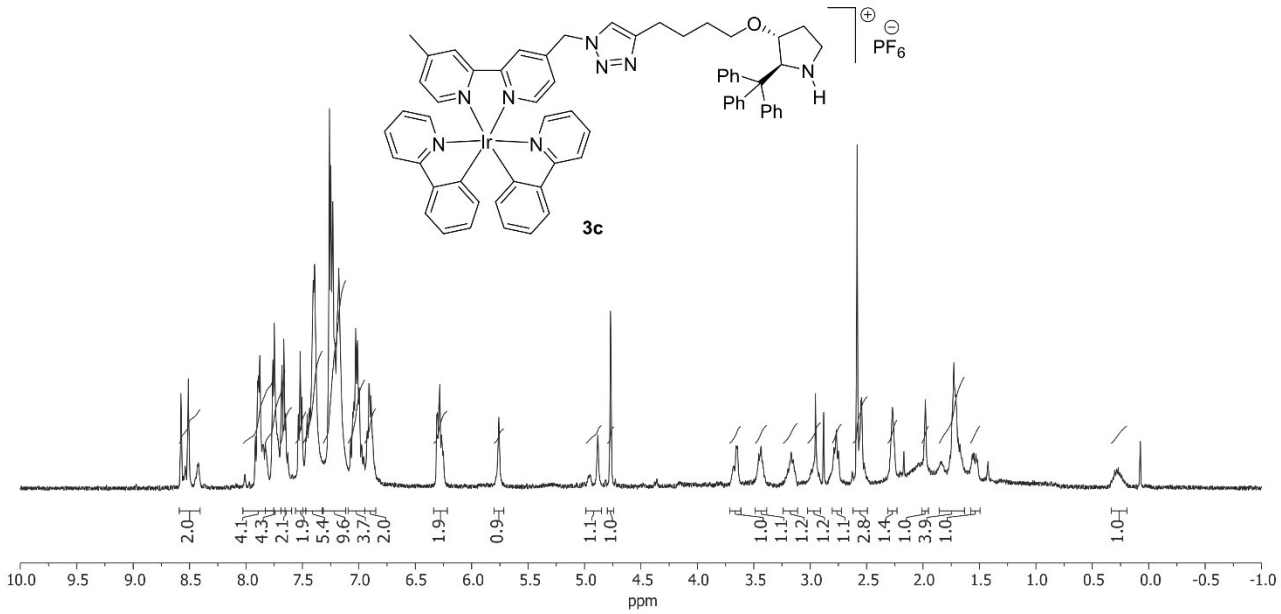
Component name: CatIridioTIR



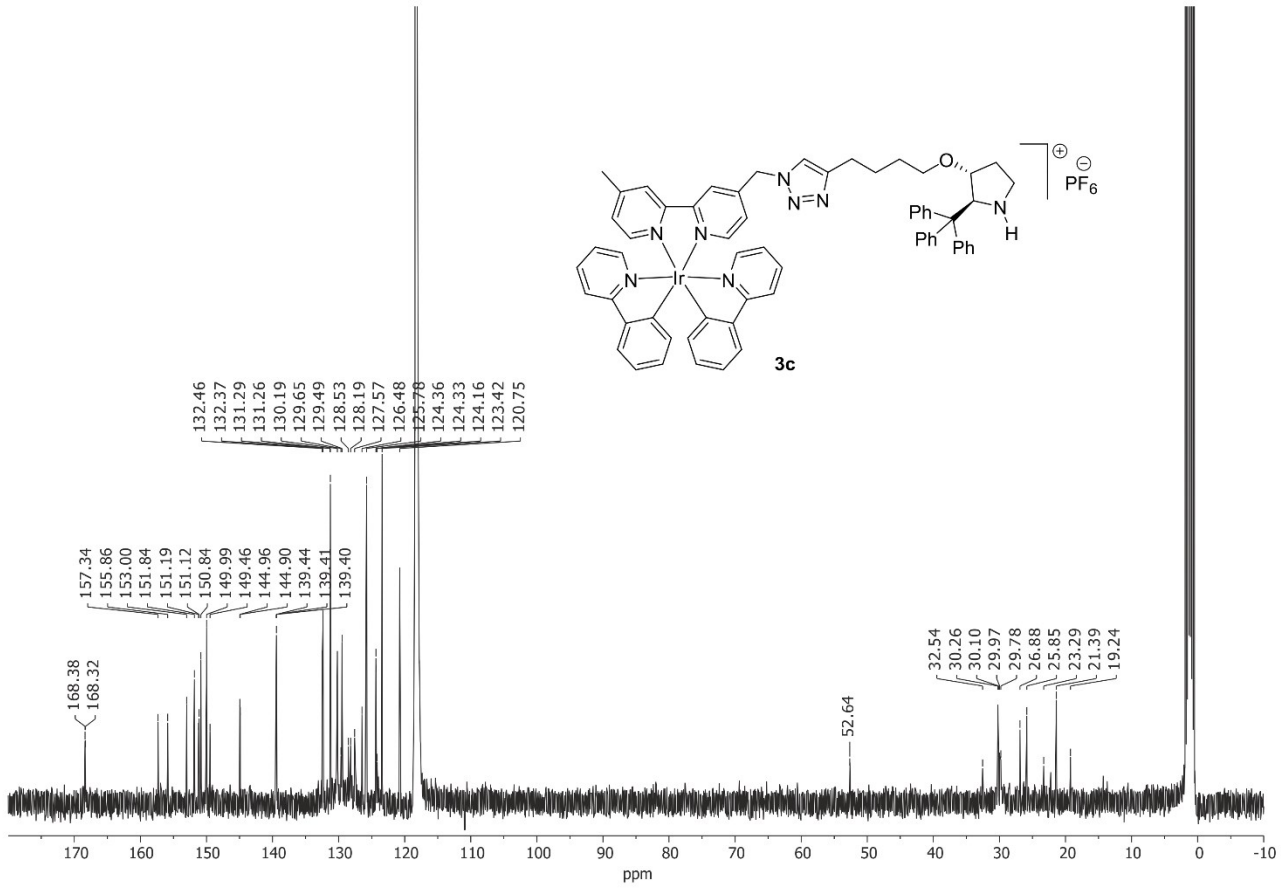


Iridium photocatalyst 3c.

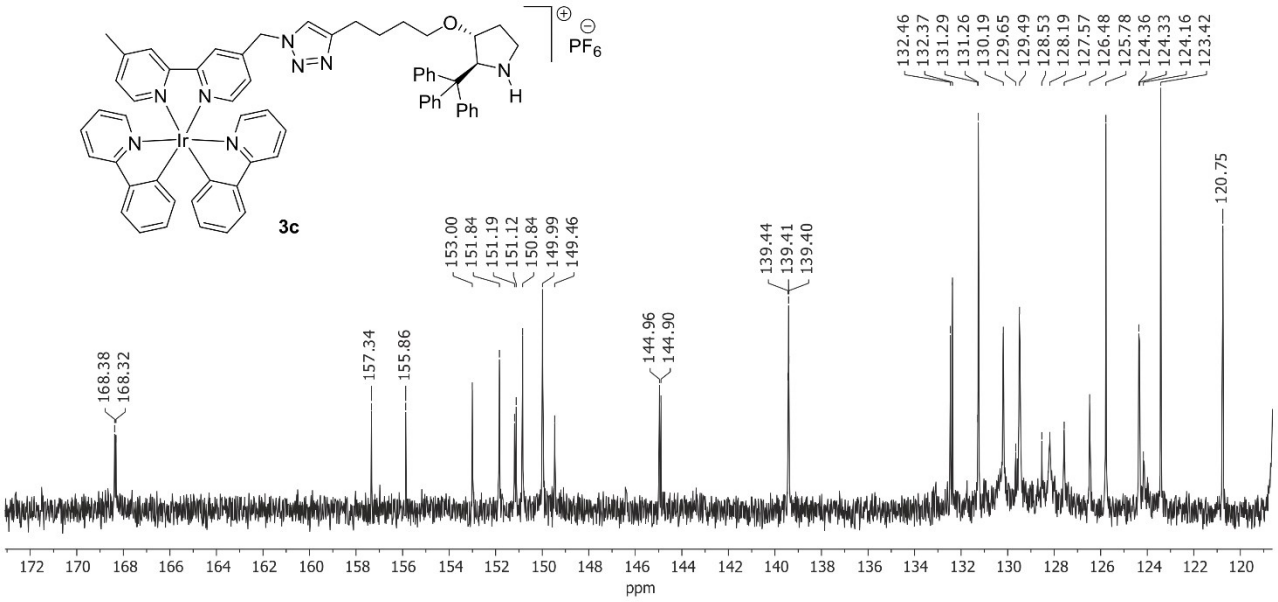
[1]H-NMR (400 MHz, $CDCl_3$)



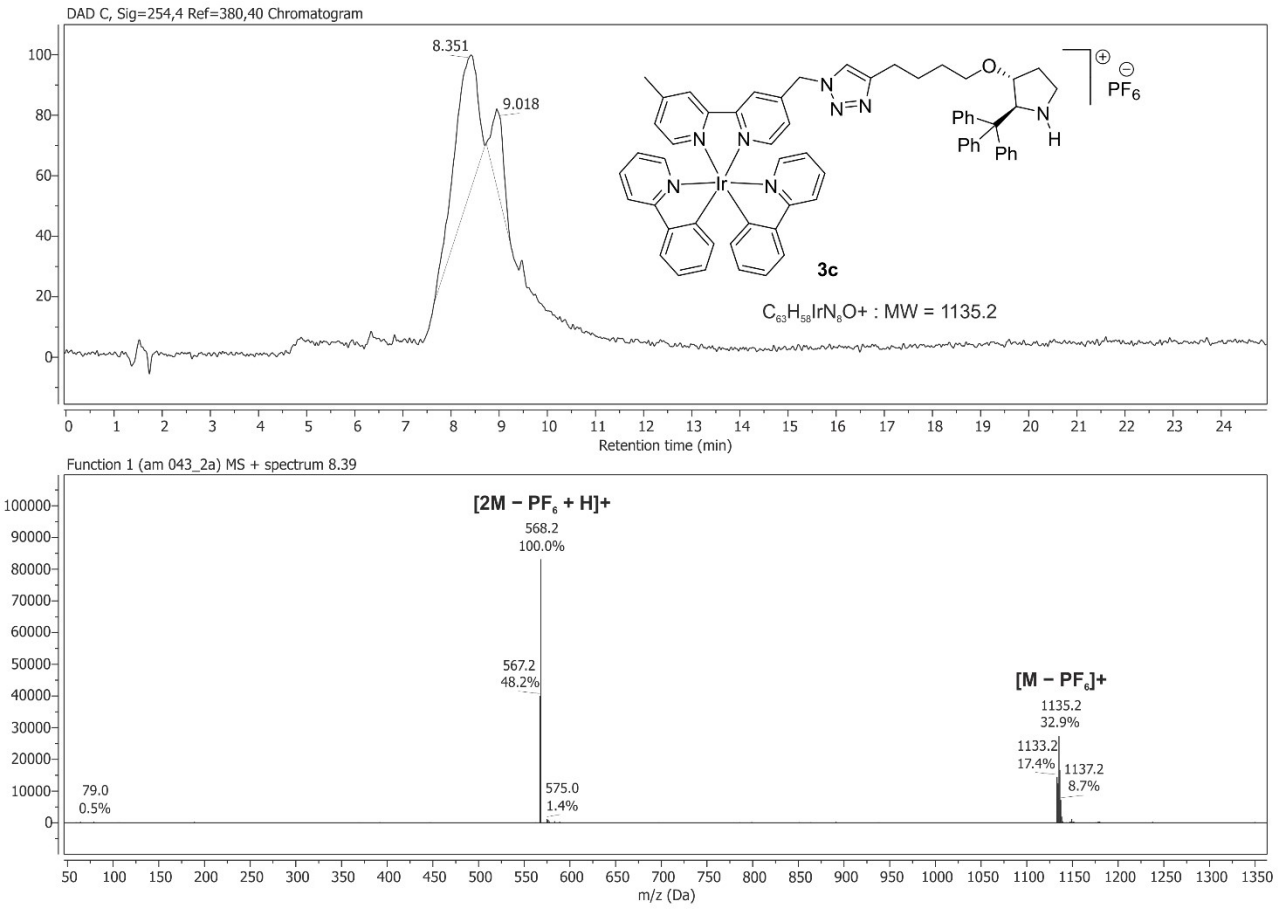
[13]C-NMR (100 MHz, CD_3CN).

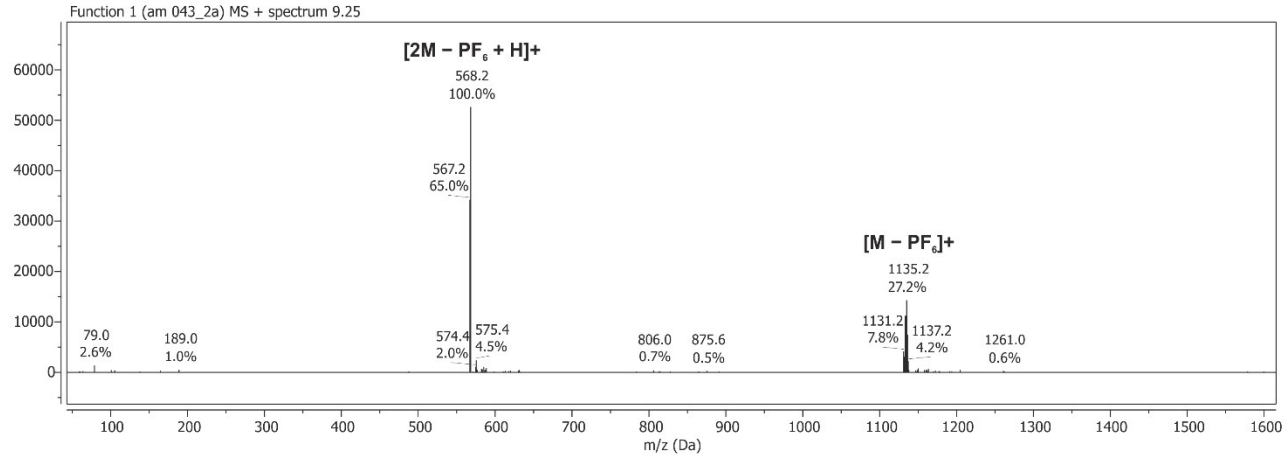


^{13}C-NMR (100 MHz, CD_3CN). Aromatic region expansion.



HPLC-MS





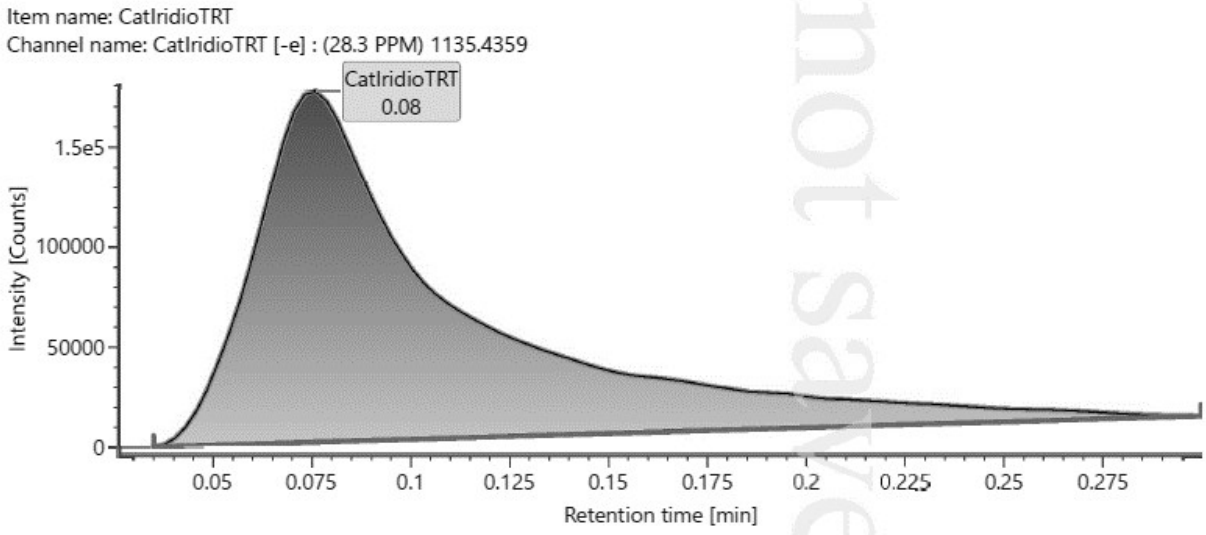
HRMS

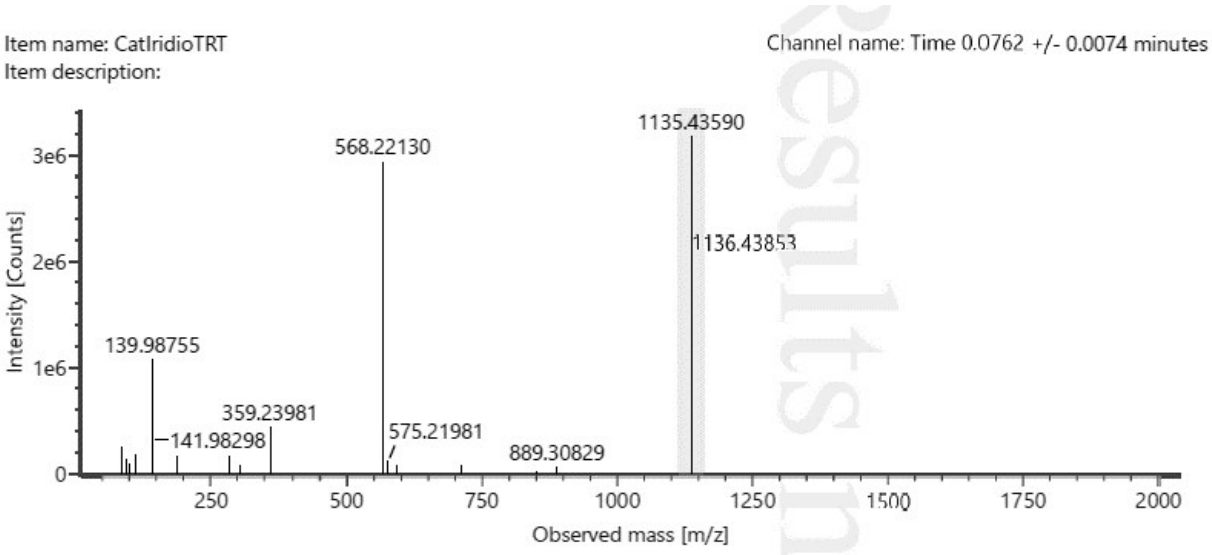
Item name: CatIridioTRT, Sample position: 1:A,1, Replicate number: 1

.	Component name	Neutral mass (Da)	Observed m/z	Mass error (mDa)	Mass error (ppm)	Expected RT (min)	Observed RT (min)
1	CatIridioTRT	1135.43628	1135.4359	0.2	0.1		0.08

.	Component name	Neutral mass (Da)	Response	Adducts
1	CatIridioTRT	1135.43628	121169	-e

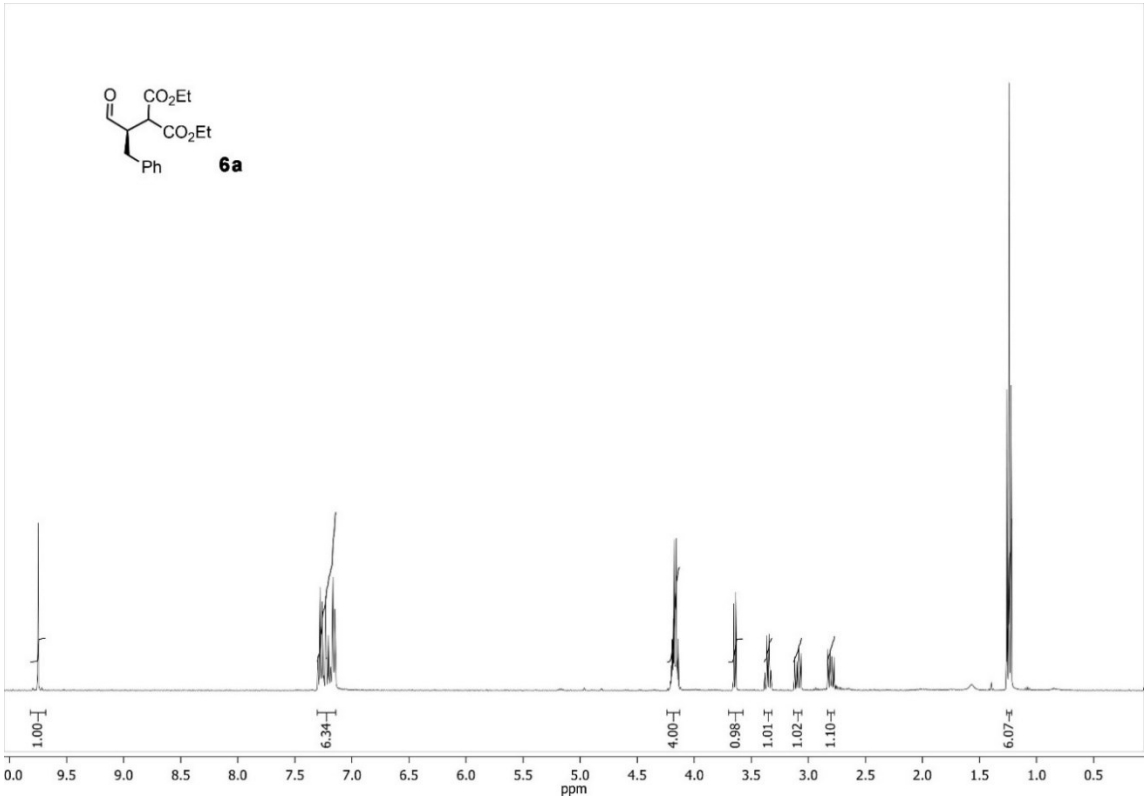
Component name: CatIridioTRT



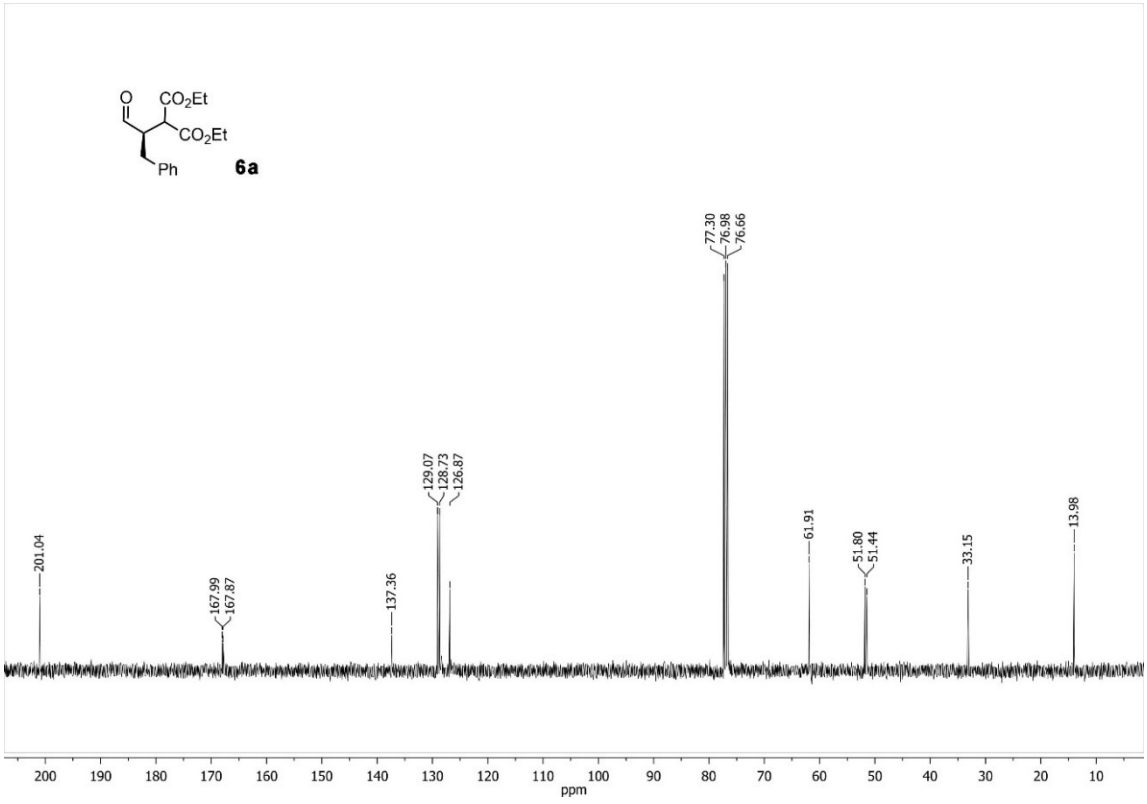

Item name: CatIridioTRT
Item description:
Channel name: Time 0.0762 +/- 0.0074 minutes
1135.43590
568.22130
1136.43853
139.98755
359.23981
141.98298
575.21981
889.30829
Intensity [Counts]
3e6
2e6
1e6
0
250
500
750
1000
1250
1500
1750
2000
Observed mass [m/z]

(*R*)-2-(1-oxo-3-phenylpropan-2-yl)malonate (6a)

^{1}H-NMR (400 MHz, $CDCl_3$).

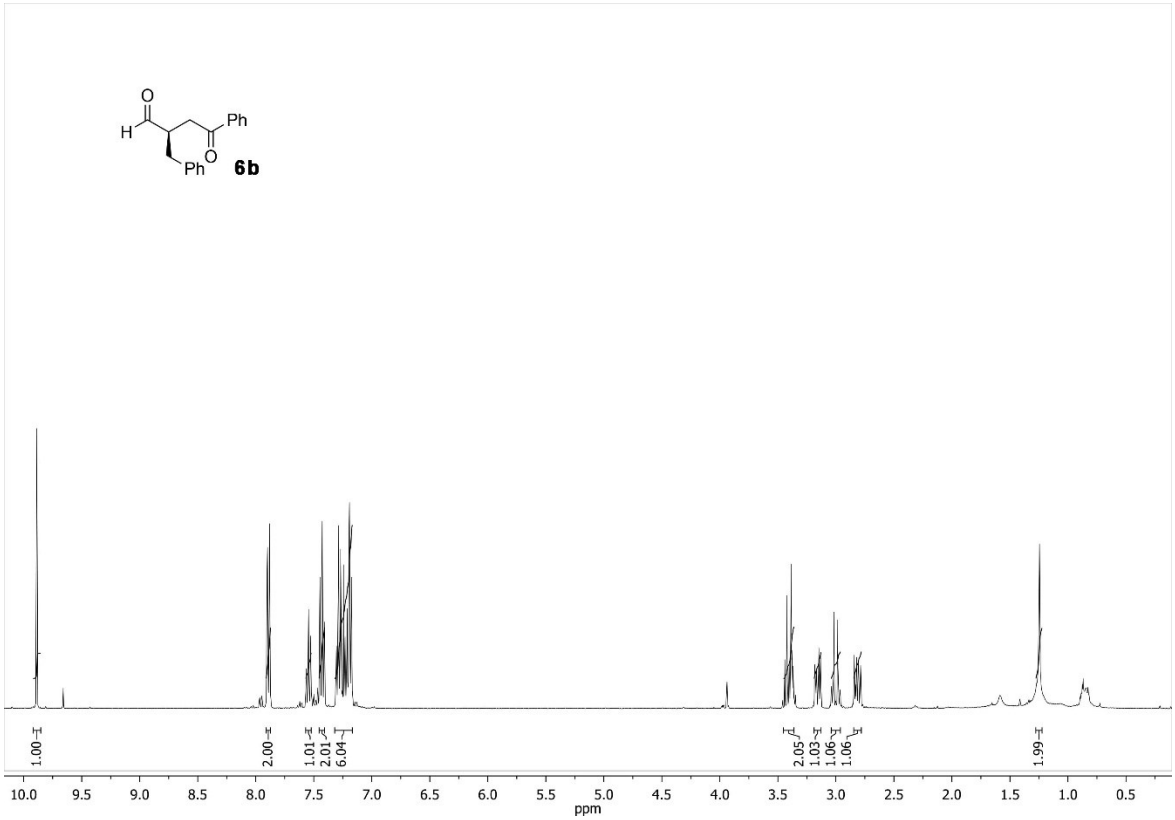


^{13}C-NMR (100 MHz, $CDCl_3$).

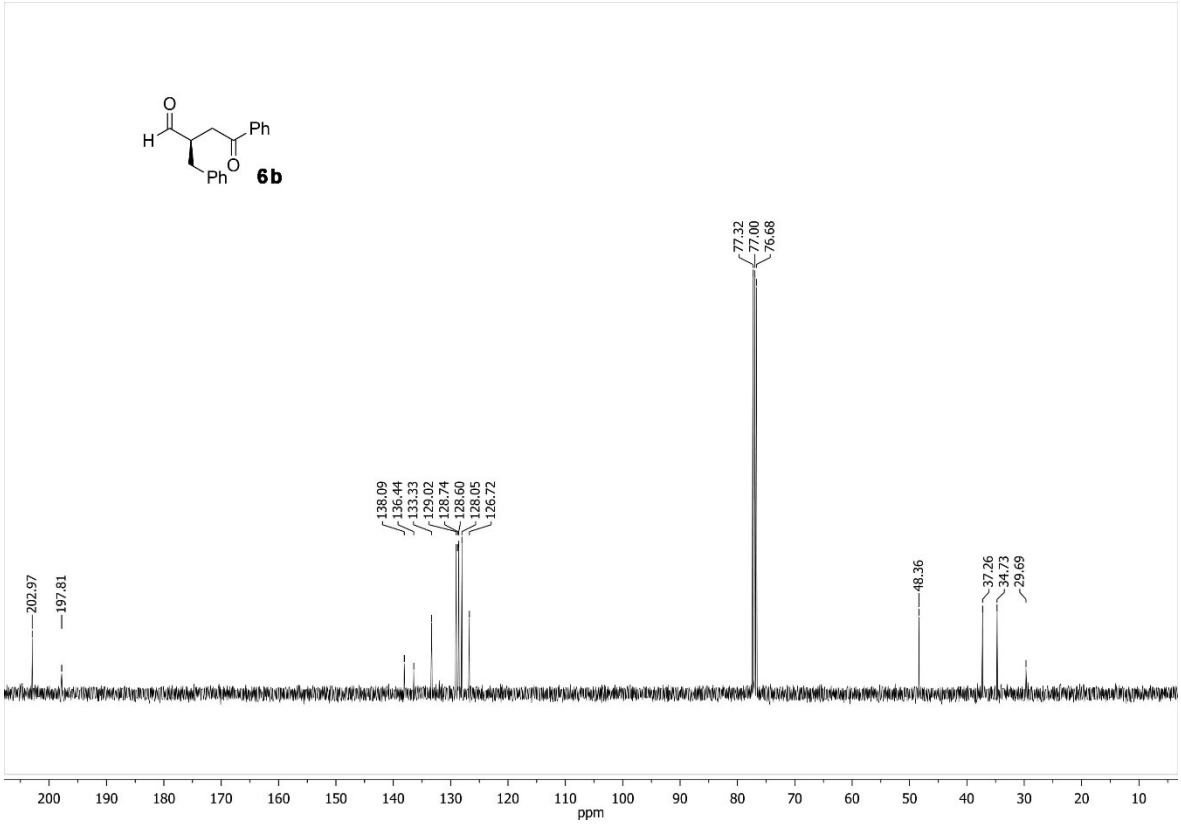


(*R*)-2-benzyl-4-oxo-4-phenylbutanals (6b)

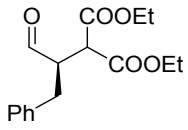
^{1}H-NMR (400 MHz, $CDCl_3$).



^{13}C-NMR (100 MHz, $CDCl_3$).

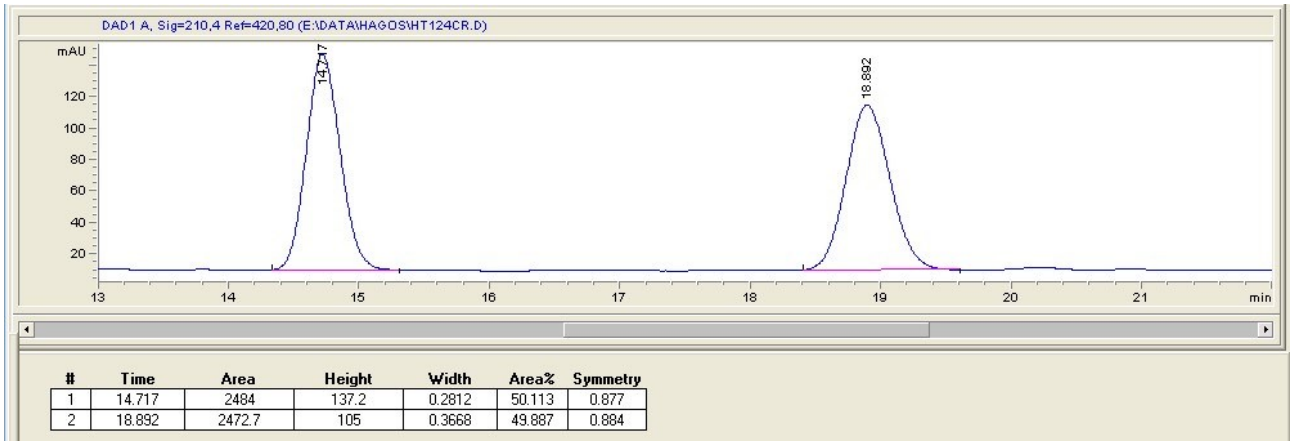


Copies of Chiral Stationary Phase HPLC traces



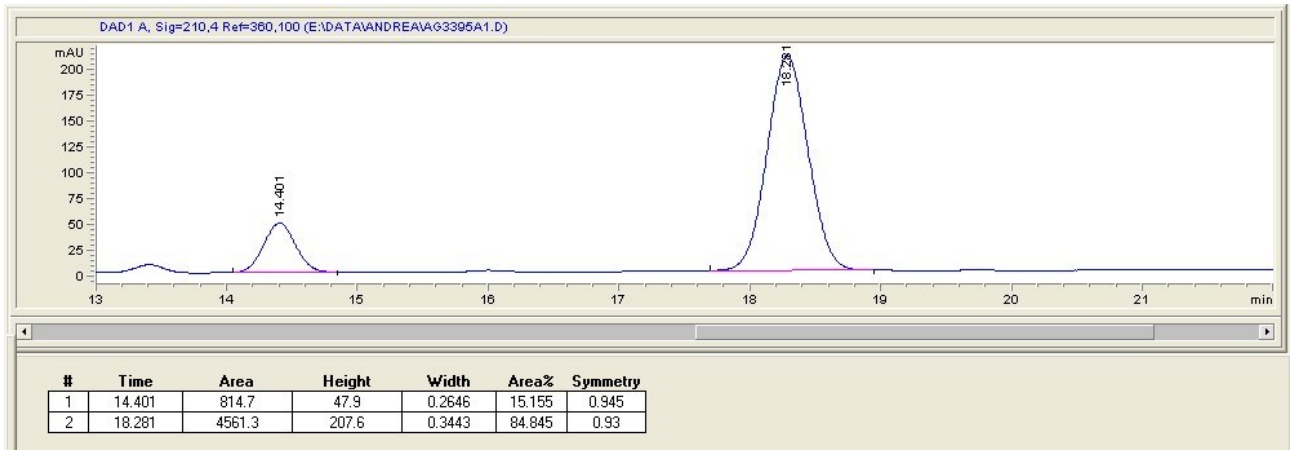
6a

Racemic

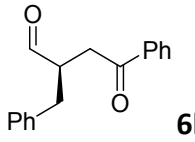


#	Time	Area	Height	Width	Area%	Symmetry
1	14.717	2484	137.2	0.2812	50.113	0.877
2	18.892	2472.7	105	0.3668	49.887	0.884

Active (Table 2, entry 2)

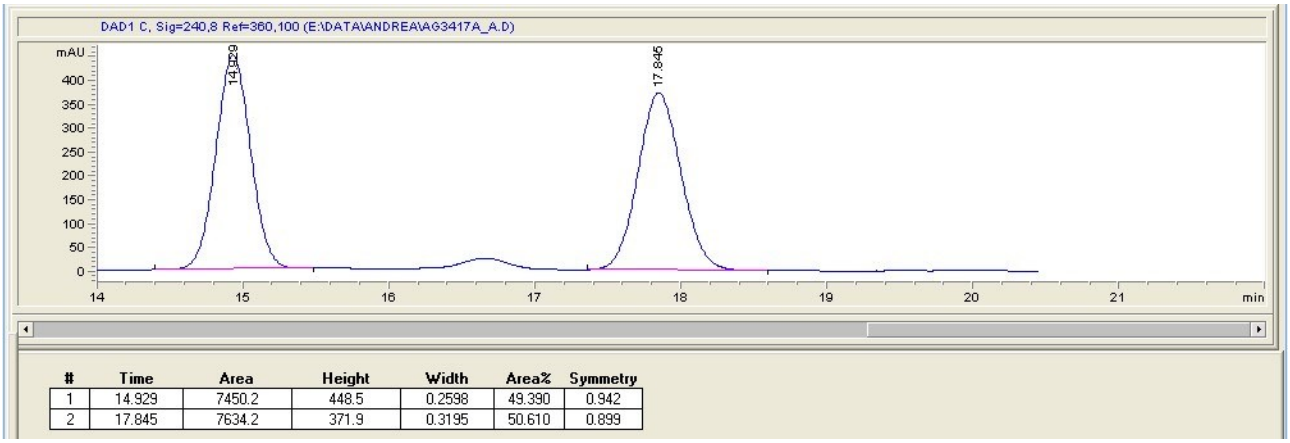


#	Time	Area	Height	Width	Area%	Symmetry
1	14.401	814.7	47.9	0.2646	15.155	0.945
2	18.281	4561.3	207.6	0.3443	84.845	0.93



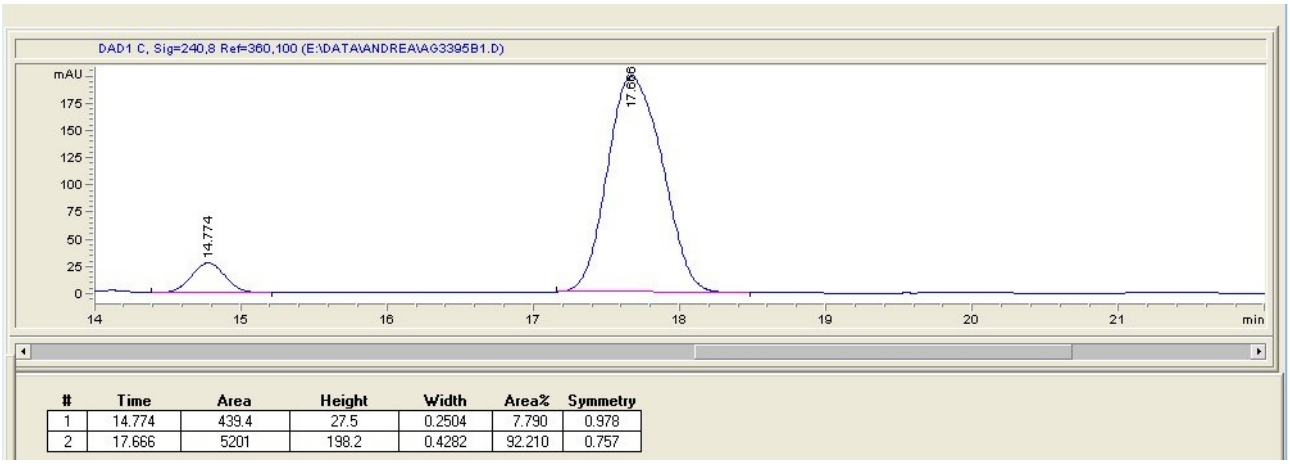
6b

Racemic



#	Time	Area	Height	Width	Area%	Symmetry
1	14.929	7450.2	448.5	0.2598	49.390	0.942
2	17.845	7634.2	371.9	0.3195	50.610	0.899

Active (Table 2, entry 8)

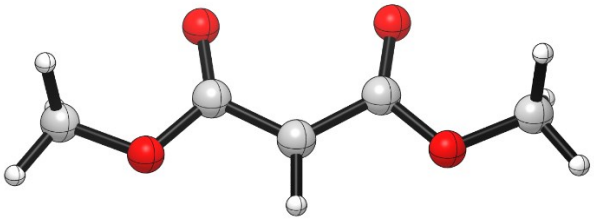


#	Time	Area	Height	Width	Area%	Symmetry
1	14.774	439.4	27.5	0.2504	7.790	0.978
2	17.666	5201	198.2	0.4282	92.210	0.757

Computational Details

Calculations were performed using Gaussian 16.[5] Geometries were optimized using the unrestriceted uBHandHLYP density functional[6] and the 6-31G(d) basis set and further confirmed to be stationary points on the potential energy surface by frequency calculations. Single point energies were calculated using the uBHandHLYP density functional and the triple-ζ cc-pvtz correlation consistent basis set[7] within the IEFPCM model (solvent = *N*,*N*-dimethylformamide).[8] Molecules possessing conformational mobility were first optimized using molecular mechanics (MMFF94 force field); all the conformers within a 10 kcal·mol^{-1} window were then re-optimized using DFT and the lower energy conformer was used in all subsequent calculations. All molecule illustrations were made using with CYLView.[9]

Dimethyl-malonate radical 7



```
   -- Stationary point found.
         Item               Value     Threshold  Converged?
Maximum Force            0.000058     0.000450     YES
RMS     Force            0.000015     0.000300     YES
Maximum Displacement     0.000834     0.001800     YES
RMS     Displacement     0.000250     0.001200     YES
Predicted change in Energy=-2.492081D-08
Optimization completed.

SCF Done:  E(UBHandHLYP) =  -495.329468146     A.U. after   19 cycles

Zero-point correction=                           0.125633 (Hartree/Particle)
Thermal correction to Energy=                    0.135559
Thermal correction to Enthalpy=                  0.136503
Thermal correction to Gibbs Free Energy=         0.088827
Sum of electronic and zero-point Energies=           -495.203835
Sum of electronic and thermal Energies=              -495.193909
Sum of electronic and thermal Enthalpies=            -495.192965
Sum of electronic and thermal Free Energies=         -495.240641
```

Eigenvalues --- 0.00064 0.00304 0.00305 0.00360 0.01362

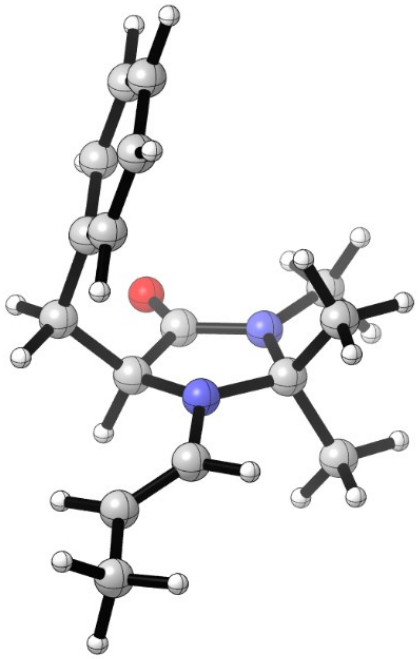
Item	Value	Threshold	Converged?
Maximum Force	0.000058	0.000450	YES
RMS Force	0.000015	0.000300	YES
Maximum Displacement	0.000758	0.001800	YES
RMS Displacement	0.000301	0.001200	YES

Predicted change in Energy=-2.209137D-08
Optimization completed.

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-0.000000	0.000000	0.591480
1	-0.000000	0.000000	1.666304
6	0.000009	1.287306	-0.098041
6	-0.000009	-1.287306	-0.098041
8	0.000021	2.283073	0.797232
8	-0.000021	-2.283073	0.797232
8	-0.000000	1.460074	-1.285815
8	-0.000000	-1.460074	-1.285815
6	0.000010	-3.593510	0.251354
1	0.882273	-3.751587	-0.359096
1	0.000214	-4.265148	1.099075
1	-0.882443	-3.751747	-0.358784
6	-0.000010	3.593510	0.251354
1	-0.882273	3.751587	-0.359096
1	-0.000214	4.265148	1.099075
1	0.882443	3.751747	-0.358784

Single point calculation:
SCF Done: E(UBHandHLYP) = -495.526785593 A.U. after 14 cycles

MacMillan Enamine 8b



```
   -- Stationary point found.
         Item               Value     Threshold  Converged?
Maximum Force            0.000028     0.000450     YES
RMS     Force            0.000004     0.000300     YES
Maximum Displacement     0.000952     0.001800     YES
RMS     Displacement     0.000203     0.001200     YES
Predicted change in Energy=-1.265876D-08
Optimization completed.

SCF Done:  E(RBHandHLYP) =  -807.188189045     A.U. after    7 cycles

Zero-point correction=                           0.368155 (Hartree/Particle)
Thermal correction to Energy=                    0.386844
Thermal correction to Enthalpy=                  0.387788
Thermal correction to Gibbs Free Energy=         0.320724
Sum of electronic and zero-point Energies=           -806.820034
Sum of electronic and thermal Energies=              -806.801345
Sum of electronic and thermal Enthalpies=            -806.800401
Sum of electronic and thermal Free Energies=         -806.867465

    Eigenvalues ---    0.00109   0.00197   0.00237   0.00243   0.00366

         Item               Value     Threshold  Converged?
Maximum Force            0.000028     0.000450     YES
```

RMS Force 0.000004 0.000300 YES
Maximum Displacement 0.001157 0.001800 YES
RMS Displacement 0.000301 0.001200 YES
Predicted change in Energy=-2.100966D-08
Optimization completed.

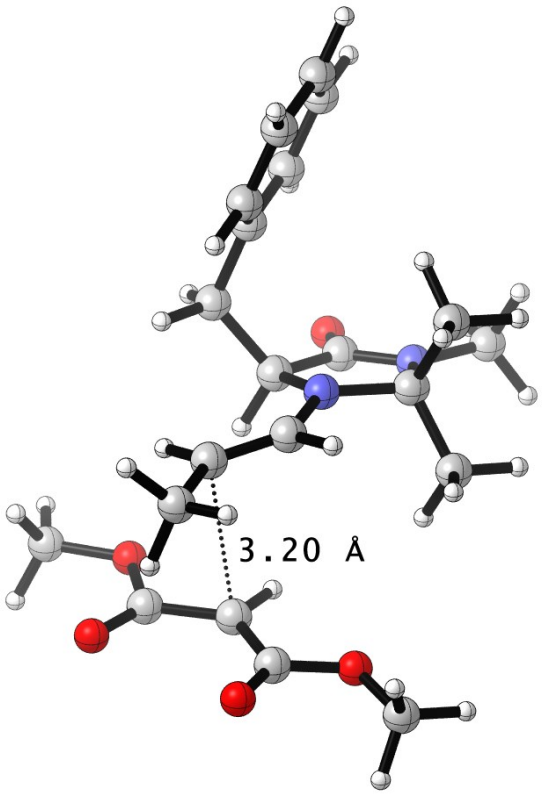
Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-0.642816	0.120336	1.273733
6	-1.214509	1.128309	-0.849773
1	-1.413931	0.099935	2.049997
6	0.465715	-0.865997	1.682534
1	0.023503	-1.847061	1.826139
1	0.830460	-0.529205	2.649325
6	1.601154	-0.961846	0.699769
6	2.699997	-0.112386	0.790458
6	1.567602	-1.898116	-0.329015
6	3.736566	-0.195794	-0.126211
1	2.734793	0.621812	1.579093
6	2.602839	-1.984302	-1.245988
1	0.721989	-2.563270	-0.408387
6	3.691794	-1.131772	-1.147307
1	4.581735	0.468242	-0.038448
1	2.561267	-2.719344	-2.034133
1	4.500571	-1.200127	-1.857181
7	-1.203526	-0.091443	-0.036010
6	-2.625466	1.689358	-1.043977
1	-2.592767	2.641927	-1.566008
1	-3.235907	1.013863	-1.635480
1	-3.107623	1.836763	-0.081880
6	-0.534101	0.883887	-2.193689
1	-1.078641	0.130236	-2.756133
1	-0.513054	1.788656	-2.796179
1	0.479305	0.529952	-2.036972
6	-0.103762	1.530464	1.190557
8	0.521367	2.095550	2.059013
7	-0.430646	2.030643	-0.018344
6	-0.034557	3.352410	-0.426827
1	-0.896856	3.975853	-0.650846

1	0.511036	3.790065	0.399410
1	0.611626	3.318581	-1.300166
6	-2.103220	-1.106291	-0.289490
1	-2.437886	-1.138145	-1.315713
6	-2.548068	-2.033896	0.556596
1	-2.230607	-2.026561	1.587813
6	-3.486589	-3.126432	0.151515
1	-3.769750	-3.036891	-0.895003
1	-3.044902	-4.113636	0.288412
1	-4.401558	-3.108030	0.743401

Single point calculation:

SCF Done: E(RBHandHLYP) = -807.474460061 A.U. after 12 cycles

Dimethyl-malonate radical - MacMillan Enamine Adduct (7-8b)




```
   -- Stationary point found.
         Item               Value     Threshold  Converged?
Maximum Force            0.000000     0.000450     YES
RMS     Force            0.000000     0.000300     YES
Maximum Displacement     0.000720     0.001800     YES
RMS     Displacement     0.000129     0.001200     YES
Predicted change in Energy=-1.030463D-10
Optimization completed.

SCF Done:  E(UBHandHLYP) =  -1302.52359217     A.U. after    7 cycles

Zero-point correction=                           0.494791 (Hartree/Particle)
Thermal correction to Energy=                    0.525505
Thermal correction to Enthalpy=                  0.526449
Thermal correction to Gibbs Free Energy=         0.427247
Sum of electronic and zero-point Energies=          -1302.028801
Sum of electronic and thermal Energies=             -1301.998087
Sum of electronic and thermal Enthalpies=           -1301.997143
Sum of electronic and thermal Free Energies=        -1302.096346
```

Eigenvalues --- 0.00007 0.00039 0.00050 0.00059 0.00090

Item	Value	Threshold	Converged?
Maximum Force	0.000000	0.000450	YES
RMS Force	0.000000	0.000300	YES
Maximum Displacement	0.000897	0.001800	YES
RMS Displacement	0.000162	0.001200	YES

Predicted change in Energy=-9.675465D-11
Optimization completed.

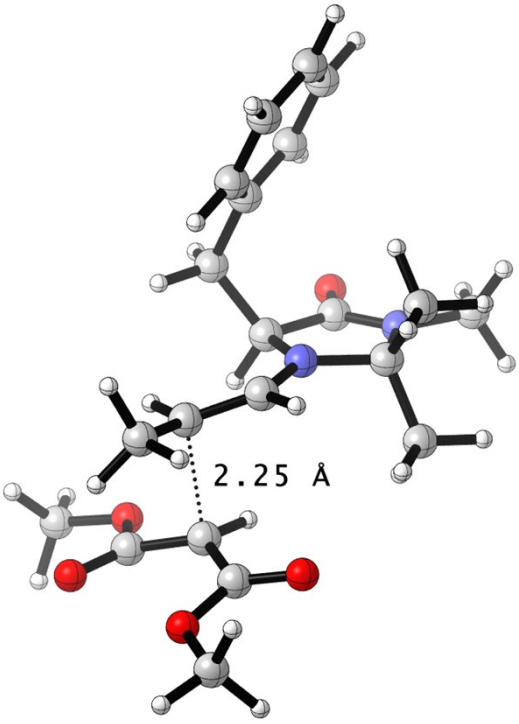
Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-0.809574	-0.477980	-0.750781
6	-1.010252	1.837701	-0.052555
1	0.132477	-0.857307	-1.155532
6	-1.676248	-1.693689	-0.370059
1	-1.111038	-2.328513	0.304957
1	-1.829272	-2.253099	-1.289369
6	-2.998020	-1.342614	0.257094
6	-4.114191	-1.070050	-0.529158
6	-3.124730	-1.268201	1.640535
6	-5.323591	-0.726387	0.054609
1	-4.028657	-1.121844	-1.602723
6	-4.333268	-0.927409	2.226692
1	-2.267170	-1.477669	2.260733
6	-5.437318	-0.653705	1.434252
1	-6.178891	-0.521901	-0.569527
1	-4.413195	-0.878656	3.301032
1	-6.379667	-0.392075	1.888224
7	-0.577738	0.481210	0.299161
6	0.156815	2.823636	-0.127935
1	-0.183006	3.783122	-0.508218
1	0.582735	2.999344	0.855154
1	0.941005	2.446608	-0.776206
6	-2.075832	2.338870	0.920284
1	-1.669752	2.373042	1.927755
1	-2.401873	3.343882	0.663676
1	-2.930615	1.671354	0.917811
6	-1.488062	0.347201	-1.820296

8	-1.899420	-0.076405	-2.876606
7	-1.568535	1.619521	-1.380227
6	-2.227726	2.645118	-2.145557
1	-1.557793	3.473829	-2.359919
1	-2.540019	2.193965	-3.078658
1	-3.103353	3.025437	-1.625528
6	0.315226	0.257987	1.317765
1	0.402918	1.083634	2.007217
6	1.033661	-0.846302	1.551435
1	0.943850	-1.695402	0.892070
6	1.936614	-1.004922	2.734403
1	1.965187	-0.096844	3.332706
1	1.603931	-1.816009	3.382415
1	2.955891	-1.233195	2.429989
6	3.228395	-0.170618	-0.671637
1	2.598025	0.239171	-1.438646
6	3.393690	-1.617266	-0.619643
6	3.903621	0.752091	0.230698
8	2.618744	-2.199847	-1.547579
8	3.625803	2.018912	-0.116081
8	4.106245	-2.232880	0.125851
8	4.610673	0.463892	1.157721
6	4.233574	3.016356	0.688926
1	5.313965	2.931595	0.650330
1	3.913718	3.963776	0.276224
1	3.912242	2.923047	1.720647
6	2.702202	-3.615569	-1.613743
1	2.402312	-4.060199	-0.671114
1	2.027802	-3.912881	-2.405217
1	3.715880	-3.926208	-1.841241

Single point calculation:

SCF Done: E(UBHandHLYP) = -1303.00257398   A.U. after   22 cycles

Dimethyl-malonate radical - MacMillan Enamine Transition State (TSb)




```
   -- Stationary point found.
         Item               Value     Threshold  Converged?
Maximum Force            0.000014     0.000450     YES
RMS     Force            0.000001     0.000300     YES
Maximum Displacement     0.000565     0.001800     YES
RMS     Displacement     0.000122     0.001200     YES
Predicted change in Energy= 3.198873D-09
Optimization completed.

SCF Done:  E(UBHandHLYP) =  -1302.52105618     A.U. after   12 cycles

Zero-point correction=                           0.496595 (Hartree/Particle)
Thermal correction to Energy=                    0.525671
Thermal correction to Enthalpy=                  0.526616
Thermal correction to Gibbs Free Energy=         0.433804
Sum of electronic and zero-point Energies=          -1302.024462
Sum of electronic and thermal Energies=             -1301.995385
Sum of electronic and thermal Enthalpies=           -1301.994441
Sum of electronic and thermal Free Energies=        -1302.087252

    Eigenvalues ---   -0.01156   0.00099   0.00191   0.00252   0.00299
```

Item		Value	Threshold	Converged?
Maximum	Force	0.000014	0.000450	YES
RMS	Force	0.000001	0.000300	YES
Maximum	Displacement	0.000541	0.001800	YES
RMS	Displacement	0.000117	0.001200	YES

Predicted change in Energy= 3.124245D-09

Optimization completed.

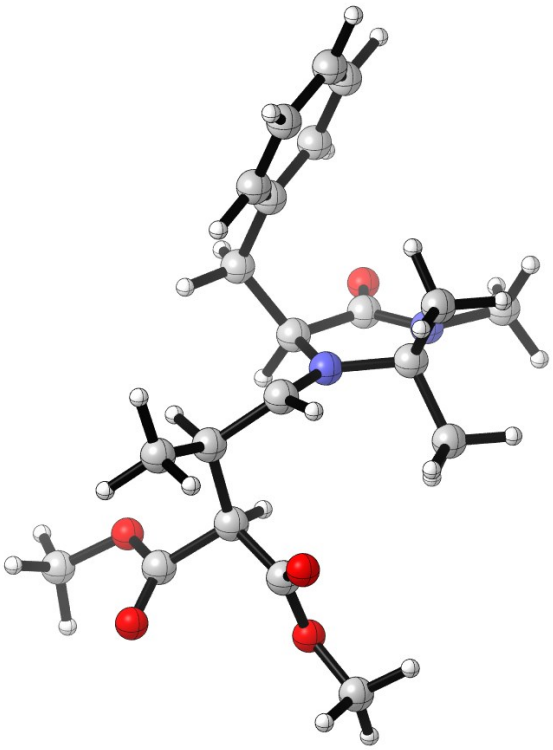
Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-0.977873	-0.683064	-0.881334
6	-1.188796	1.733680	-0.640309
1	-0.122997	-1.124246	-1.395894
6	-1.675869	-1.794897	-0.074124
1	-0.950266	-2.265648	0.581742
1	-1.978155	-2.540448	-0.804852
6	-2.863402	-1.337501	0.730181
6	-4.122307	-1.225201	0.145494
6	-2.723708	-1.009284	2.074709
6	-5.208716	-0.786650	0.885652
1	-4.245989	-1.479019	-0.894986
6	-3.809005	-0.572403	2.817821
1	-1.755835	-1.097779	2.543176
6	-5.055869	-0.457650	2.223730
1	-6.176954	-0.708981	0.417548
1	-3.681260	-0.326527	3.859911
1	-5.902700	-0.121917	2.800330
7	-0.587054	0.490520	-0.129922
6	-0.122917	2.675511	-1.198025
1	-0.576542	3.597788	-1.551247
1	0.619574	2.924176	-0.448018
1	0.393007	2.202382	-2.028557
6	-2.031930	2.420148	0.430625
1	-1.405221	2.741056	1.257787
1	-2.511653	3.307485	0.027097
1	-2.790642	1.743130	0.808075
6	-1.920266	-0.113845	-1.919159
8	-2.495785	-0.762613	-2.762405
7	-2.023405	1.213572	-1.714285

6	-2.861783	2.046855	-2.536992
1	-2.279935	2.806321	-3.052678
1	-3.330541	1.402416	-3.269445
1	-3.633664	2.533126	-1.946440
6	0.358583	0.498947	0.835636
1	0.467892	1.433580	1.359076
6	2.054048	-0.525618	2.366612
1	2.226718	0.482046	2.737046
1	1.516629	-1.073903	3.140144
1	3.016017	-1.008212	2.225427
6	3.446392	-1.338202	-0.551939
6	3.471993	1.130751	0.207254
8	2.802271	-2.046879	-1.506521
8	4.608110	0.871770	0.851240
8	4.325888	-1.820111	0.115373
8	2.974039	2.235994	0.190325
6	5.214659	1.975065	1.499274
1	4.557938	2.385462	2.259215
1	6.117769	1.587346	1.951428
1	5.453356	2.756788	0.786398
6	3.259609	-3.374926	-1.690940
1	3.150256	-3.952226	-0.778953
1	2.645267	-3.792985	-2.477893
1	4.303813	-3.384212	-1.983891
6	1.267231	-0.504289	1.087960
1	1.104336	-1.462927	0.623831
6	2.850707	-0.018675	-0.433434
1	2.162131	0.249482	-1.212197

Single point calculation:

SCF Done: E(UBHandHLYP) = -1302.99828500 A.U. after 17 cycles

Dimethyl-malonate radical - MacMillan Enamine Product (9b)



```
   -- Stationary point found.
         Item               Value     Threshold  Converged?
Maximum Force            0.000000     0.000450     YES
RMS     Force            0.000000     0.000300     YES
Maximum Displacement     0.000086     0.001800     YES
RMS     Displacement     0.000017     0.001200     YES
Predicted change in Energy=-3.741334D-12
Optimization completed.

SCF Done:  E(UBHandHLYP) =  -1302.55016518     A.U. after    6 cycles

Zero-point correction=                           0.498864 (Hartree/Particle)
Thermal correction to Energy=                    0.527925
Thermal correction to Enthalpy=                  0.528869
Thermal correction to Gibbs Free Energy=         0.435796
Sum of electronic and zero-point Energies=          -1302.051302
Sum of electronic and thermal Energies=             -1302.022240
Sum of electronic and thermal Enthalpies=           -1302.021296
Sum of electronic and thermal Free Energies=        -1302.114369

    Eigenvalues ---    0.00050   0.00097   0.00204   0.00224   0.00263
```

Item		Value	Threshold	Converged?
Maximum	Force	0.000000	0.000450	YES
RMS	Force	0.000000	0.000300	YES
Maximum	Displacement	0.000047	0.001800	YES
RMS	Displacement	0.000009	0.001200	YES

Predicted change in Energy=-1.107319D-12

Optimization completed.

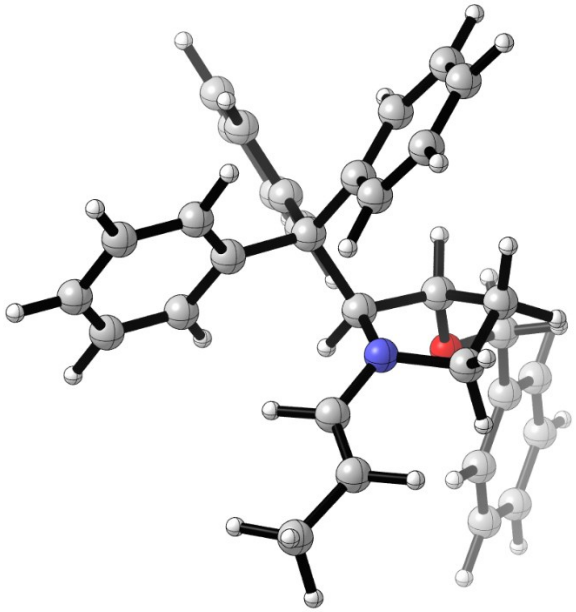
Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.936305	-0.308960	1.127286
6	1.097012	1.738383	-0.164515
1	0.088453	-0.568575	1.764788
6	1.736404	-1.606516	0.900400
1	1.076573	-2.337740	0.441710
1	1.987182	-1.978230	1.891019
6	2.984086	-1.462464	0.070702
6	4.179262	-1.039777	0.647793
6	2.968526	-1.748104	-1.290562
6	5.324254	-0.898404	-0.120005
1	4.206153	-0.815851	1.702089
6	4.113159	-1.610833	-2.059919
1	2.048208	-2.070739	-1.751029
6	5.295397	-1.183366	-1.476550
1	6.241266	-0.572019	0.344123
1	4.081161	-1.839252	-3.113319
1	6.187860	-1.078607	-2.072415
7	0.509095	0.402903	-0.053635
6	0.002231	2.801628	-0.253361
1	0.429223	3.799842	-0.303818
1	-0.597413	2.651080	-1.145804
1	-0.646873	2.742695	0.616019
6	2.060117	1.861474	-1.345165
1	1.533616	1.694331	-2.279979
1	2.489501	2.859240	-1.386765
1	2.858944	1.133366	-1.262358
6	1.763189	0.723937	1.860018
8	2.299085	0.556873	2.932693
7	1.809378	1.838311	1.103197

6	2.569650	2.994200	1.499856
1	1.942563	3.880520	1.550927
1	2.972984	2.788755	2.483182
1	3.391129	3.183259	0.813196
6	-0.243964	-0.162614	-1.061068
1	-0.336618	0.435223	-1.950517
6	-1.885888	-1.801333	-1.969078
1	-2.205466	-1.106194	-2.737147
1	-1.079890	-2.410696	-2.368927
1	-2.722526	-2.456513	-1.741804
6	-3.633312	-1.207542	0.442686
6	-3.131564	0.866500	-0.795774
8	-3.250940	-1.926436	1.496784
8	-3.922554	1.601868	-0.020068
8	-4.694756	-1.334008	-0.098603
8	-2.919469	1.119596	-1.947857
6	-4.603237	2.672351	-0.660073
1	-5.228040	2.295088	-1.461224
1	-5.208884	3.135467	0.106914
1	-3.894244	3.385045	-1.066304
6	-4.186808	-2.891444	1.961084
1	-4.404469	-3.614034	1.182800
1	-3.715975	-3.373979	2.806667
1	-5.108740	-2.408228	2.263231
6	-1.399549	-1.056723	-0.727693
1	-1.079608	-1.799466	0.002184
6	-2.532402	-0.272321	0.001163
1	-2.103515	0.166128	0.898678

Single point calculation:

SCF Done: E(UBHandHLYP) = -1303.02191210   A.U. after   15 cycles

Trityl Enamine 8c



-- Stationary point found.

Item	Value	Threshold	Converged?
Maximum Force	0.000000	0.000450	YES
RMS Force	0.000000	0.000300	YES
Maximum Displacement	0.000168	0.001800	YES
RMS Displacement	0.000028	0.001200	YES

Predicted change in Energy=-1.158491D-11

Optimization completed.

SCF Done: E(RBHandHLYP) = -1406.45088650 A.U. after 6 cycles

Zero-point correction=	0.599735 (Hartree/Particle)
Thermal correction to Energy=	0.629104
Thermal correction to Enthalpy=	0.630048
Thermal correction to Gibbs Free Energy=	0.536546
Sum of electronic and zero-point Energies=	-1405.851152
Sum of electronic and thermal Energies=	-1405.821782
Sum of electronic and thermal Enthalpies=	-1405.820838
Sum of electronic and thermal Free Energies=	-1405.914340

Eigenvalues --- 0.00047 0.00214 0.00253 0.00350 0.00411

Item	Value	Threshold	Converged?
Maximum Force	0.000000	0.000450	YES
RMS Force	0.000000	0.000300	YES

Maximum Displacement 0.000096 0.001800 YES

RMS Displacement 0.000017 0.001200 YES

Predicted change in Energy=-8.032560D-12

Optimization completed.

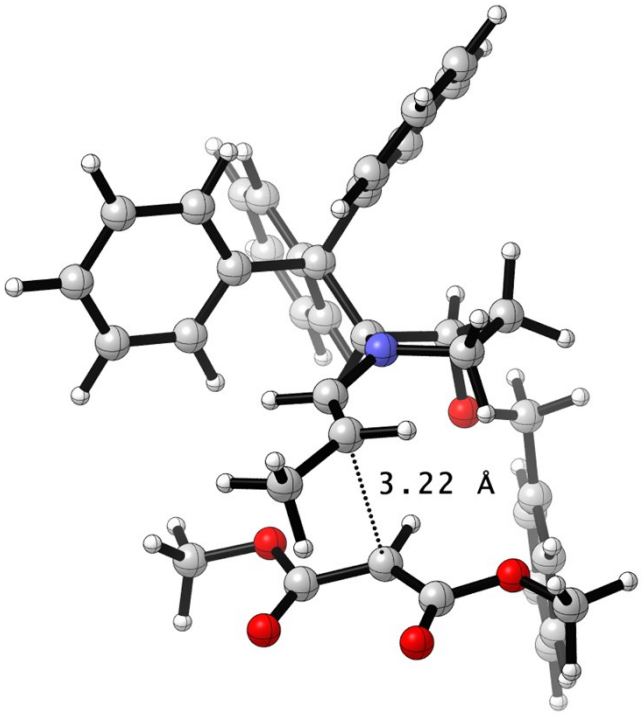
Atomic Number	Coordinates (Angstroms) X	Y	Z
7	0.496673	1.835184	0.554673
6	0.853640	2.842459	-0.323175
6	0.148103	0.502212	0.076724
6	-0.925378	0.023351	1.072903
6	-0.733477	0.889121	2.313017
6	-0.226945	2.205637	1.754238
6	1.366303	-0.493018	-0.060120
6	0.905978	-1.842361	-0.654628
6	1.859139	-2.849033	-0.828477
6	1.534228	-4.062408	-1.402116
6	0.238589	-4.304517	-1.837575
6	-0.713786	-3.316052	-1.688242
6	-0.386054	-2.097690	-1.103020
6	2.372956	0.043179	-1.105218
6	3.741155	0.136818	-0.881530
6	4.608498	0.557433	-1.882064
6	4.129651	0.887395	-3.134913
6	2.770097	0.771577	-3.385538
6	1.912261	0.346258	-2.388946
6	1.972387	-0.665905	1.339978
6	1.756840	-1.812243	2.100836
6	2.213170	-1.911203	3.407937
6	2.900805	-0.862224	3.990111
6	3.123938	0.288684	3.249999
6	2.663183	0.386991	1.948179
8	-2.175734	0.251484	0.452120
6	-3.253768	-0.419251	1.044813
6	-4.526099	-0.106608	0.305728
6	-4.650402	1.042959	-0.462449
6	-5.845530	1.329096	-1.104197
6	-6.928879	0.474322	-0.981743
6	-6.810025	-0.675056	-0.215627

6	-5.614200	-0.963510	0.420069
6	0.847150	4.152179	-0.075132
6	1.282114	5.171752	-1.080321
1	1.187553	2.492340	-1.284643
1	-0.327589	0.578711	-0.895120
1	-0.829845	-1.034147	1.302428
1	-1.052674	2.876735	1.505009
1	0.423271	2.730941	2.451245
1	2.873899	-2.672656	-0.511881
1	2.295180	-4.817655	-1.517157
1	-0.017985	-5.248263	-2.291010
1	-1.724195	-3.480577	-2.027095
1	-1.163383	-1.360206	-1.010371
1	4.151339	-0.125236	0.076533
1	5.664021	0.621703	-1.671011
1	4.802374	1.216715	-3.910072
1	2.376888	1.001753	-4.362806
1	0.867151	0.230428	-2.624163
1	1.224146	-2.644727	1.676838
1	2.027104	-2.814920	3.966006
1	3.259318	-0.938228	5.004029
1	3.656770	1.118356	3.686585
1	2.831910	1.296779	1.402346
1	-3.072026	-1.497139	1.036626
1	-3.357460	-0.125347	2.092275
1	-3.805836	1.702441	-0.561044
1	-5.928647	2.222886	-1.701707
1	-7.857138	0.698789	-1.481951
1	-7.645075	-1.350291	-0.118910
1	-5.525360	-1.865044	1.007796
1	0.533953	4.524802	0.888080
1	2.128335	5.759040	-0.722025
1	1.582807	4.701523	-2.013879
1	0.485209	5.879949	-1.309490
1	0.005064	0.435614	2.965212
1	-1.653777	1.004706	2.876660

Single point calculation:

SCF Done: E(RBHandHLYP) = -1406.92630403   A.U. after   12 cycles

Dimethyl-malonate radical - Trityl Enamine Adduct (7-8c)




```
   -- Stationary point found.
         Item               Value     Threshold  Converged?
Maximum Force            0.000024     0.000450     YES
RMS     Force            0.000002     0.000300     YES
Maximum Displacement     0.001003     0.001800     YES
RMS     Displacement     0.000191     0.001200     YES
Predicted change in Energy=-1.292033D-08
Optimization completed.

SCF Done:  E(UBHandHLYP) =  -1901.79125590     A.U. after   23 cycles

Zero-point correction=                           0.727174 (Hartree/Particle)
Thermal correction to Energy=                    0.768149
Thermal correction to Enthalpy=                  0.769093
Thermal correction to Gibbs Free Energy=         0.647731
Sum of electronic and zero-point Energies=          -1901.064082
Sum of electronic and thermal Energies=             -1901.023107
Sum of electronic and thermal Enthalpies=           -1901.022163
Sum of electronic and thermal Free Energies=        -1901.143524

    Eigenvalues ---    0.00018   0.00051   0.00070   0.00085   0.00108

         Item               Value     Threshold  Converged?
```

```
Maximum Force            0.000024     0.000450     YES
RMS     Force            0.000002     0.000300     YES
Maximum Displacement     0.001718     0.001800     YES
RMS     Displacement     0.000310     0.001200     YES
Predicted change in Energy=-1.947450D-08
Optimization completed.

 Atomic           Coordinates (Angstroms)
 Number         X            Y           Z
---------------------------------------------
   7        -0.431261   -1.086188    1.159379
   6        -0.088999   -2.275992    0.552655
   6        -0.765166    0.088890    0.355971
   6        -0.176689    1.261305    1.162339
   6        -0.048369    0.739356    2.589003
   6         0.235203   -0.739734    2.402218
   6        -2.298874    0.257133    0.028661
   6        -2.523071    1.466742   -0.905824
   6        -3.831440    1.782884   -1.279860
   6        -4.104715    2.815628   -2.155024
   6        -3.068949    3.561835   -2.700018
   6        -1.768061    3.254510   -2.353824
   6        -1.495525    2.219105   -1.466355
   6        -2.802186   -0.946567   -0.802367
   6        -3.973469   -1.638841   -0.518913
   6        -4.426297   -2.659789   -1.345025
   6        -3.722917   -3.008527   -2.481464
   6        -2.566537   -2.309594   -2.795095
   6        -2.122514   -1.290774   -1.973160
   6        -3.037608    0.423391    1.364139
   6        -3.491551    1.662666    1.808177
   6        -4.054727    1.819054    3.067140
   6        -4.180096    0.735400    3.917014
   6        -3.733149   -0.506923    3.493658
   6        -3.167368   -0.659197    2.239422
   8         1.084530    1.551915    0.586473
   6         1.612872    2.806157    0.953449
   6         2.939839    3.009660    0.282258
   6         3.977767    2.107304    0.494682
   6         5.205837    2.297869   -0.113747
```

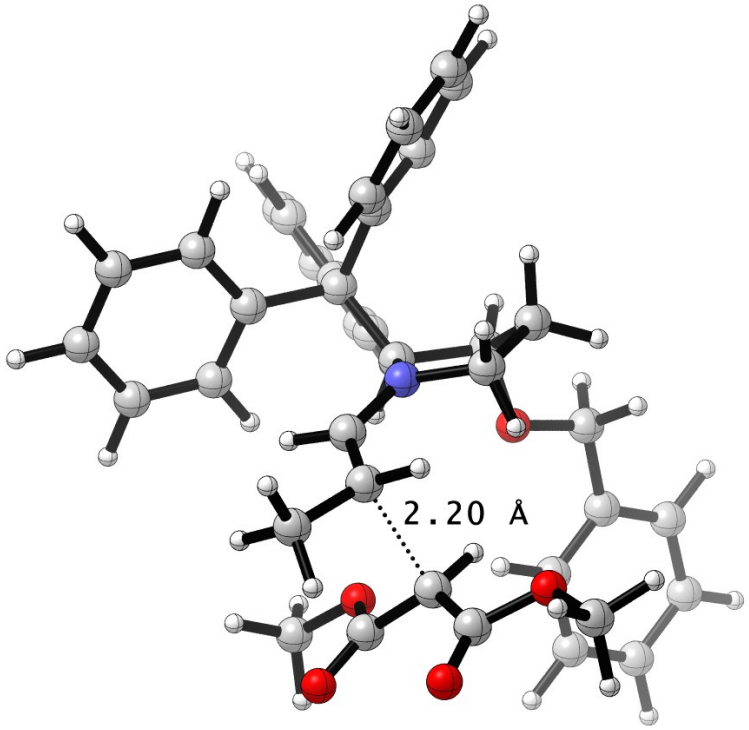
6	5.416393	3.397222	-0.934464
6	4.389694	4.300815	-1.147105
6	3.156198	4.103047	-0.543573
6	0.628365	-3.272056	1.087622
6	0.923893	-4.548608	0.366422
1	-0.476236	-2.390480	-0.444654
1	-0.227438	0.040014	-0.583717
1	-0.801907	2.148051	1.112661
1	1.307613	-0.924551	2.317425
1	-0.141653	-1.346075	3.223494
1	-4.647381	1.203753	-0.880108
1	-5.127286	3.033464	-2.418669
1	-3.277564	4.365231	-3.387832
1	-0.948369	3.816398	-2.772513
1	-0.465511	2.018633	-1.230188
1	-4.554436	-1.385183	0.348935
1	-5.337262	-3.177819	-1.091091
1	-4.072402	-3.802575	-3.121055
1	-2.013934	-2.550851	-3.689133
1	-1.237518	-0.746779	-2.258161
1	-3.406705	2.524705	1.170718
1	-4.395003	2.794232	3.376889
1	-4.620540	0.853989	4.893847
1	-3.821631	-1.364002	4.142047
1	-2.812237	-1.628231	1.940532
1	0.918022	3.596428	0.663253
1	1.729654	2.860339	2.037310
1	3.819036	1.248523	1.126719
1	6.000787	1.588851	0.053170
1	6.374768	3.545383	-1.405473
1	4.543642	5.155828	-1.785565
1	2.356005	4.805599	-0.718785
1	1.003551	-3.188261	2.096243
1	0.543130	-5.411455	0.913425
1	0.471913	-4.558306	-0.622350
1	1.995832	-4.691160	0.238618
1	-0.979632	0.894162	3.122414
1	0.740619	1.243591	3.137883
6	2.825548	-1.454298	-0.402965
1	2.412531	-0.488529	-0.172990

6	2.505274	-2.059172	-1.687713
6	3.717915	-2.082408	0.560294
8	1.652110	-1.275838	-2.373158
8	3.934112	-1.258821	1.605140
8	2.925053	-3.097992	-2.121128
8	4.214574	-3.173532	0.485347
6	4.780480	-1.776710	2.618688
1	5.761720	-2.005693	2.217812
1	4.850206	-1.001147	3.369811
1	4.357636	-2.680020	3.044555
6	1.309653	-1.746786	-3.665840
1	0.789657	-2.696820	-3.602002
1	0.665892	-0.990419	-4.095580
1	2.198309	-1.875350	-4.273788

Single point calculation:

SCF Done: E(UBHandHLYP) = -1902.45661769   A.U. after   22 cycles

Dimethyl-malonate radical - Trityl Enamine Transition State (TSc)




```
   -- Stationary point found.
         Item               Value     Threshold  Converged?
Maximum Force            0.000004     0.000450     YES
RMS     Force            0.000000     0.000300     YES
Maximum Displacement     0.001288     0.001800     YES
RMS     Displacement     0.000206     0.001200     YES
Predicted change in Energy=-4.435063D-10
Optimization completed.

SCF Done:  E(UBHandHLYP) =  -1901.78376637     A.U. after    8 cycles

Zero-point correction=                           0.728262 (Hartree/Particle)
Thermal correction to Energy=                    0.768017
Thermal correction to Enthalpy=                  0.768961
Thermal correction to Gibbs Free Energy=         0.650404
Sum of electronic and zero-point Energies=          -1901.055505
Sum of electronic and thermal Energies=             -1901.015749
Sum of electronic and thermal Enthalpies=           -1901.014805
Sum of electronic and thermal Free Energies=        -1901.133363

    Eigenvalues ---   -0.01391   0.00074   0.00119   0.00199   0.00248
```

Item		Value	Threshold	Converged?
Maximum	Force	0.000004	0.000450	YES
RMS	Force	0.000000	0.000300	YES
Maximum	Displacement	0.001246	0.001800	YES
RMS	Displacement	0.000199	0.001200	YES

Predicted change in Energy=-4.319770D-10

Optimization completed.

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-0.178966	-1.078867	0.831862
6	0.296149	-2.075776	0.043419
6	-0.824893	0.108340	0.266241
6	-0.420778	1.219155	1.250965
6	-0.151973	0.508237	2.572907
6	0.387462	-0.849794	2.155948
6	-2.373654	-0.009271	0.013389
6	-2.901196	1.268898	-0.675732
6	-4.267945	1.355245	-0.950873
6	-4.804557	2.440948	-1.614453
6	-3.982825	3.475474	-2.040071
6	-2.626801	3.400266	-1.790978
6	-2.089586	2.309552	-1.116153
6	-2.658661	-1.127485	-1.017907
6	-3.631831	-2.103873	-0.842352
6	-3.899858	-3.040855	-1.832511
6	-3.206076	-3.019701	-3.026728
6	-2.252295	-2.033402	-3.231616
6	-1.994238	-1.098622	-2.246662
6	-3.047012	-0.245823	1.372692
6	-3.717035	0.769286	2.050514
6	-4.218617	0.575696	3.330077
6	-4.063101	-0.642331	3.966406
6	-3.398103	-1.665422	3.308228
6	-2.895406	-1.468160	2.033555
8	0.749002	1.791045	0.708147
6	1.136837	3.017340	1.261363
6	2.325479	3.566183	0.517579
6	2.949360	2.852542	-0.495724

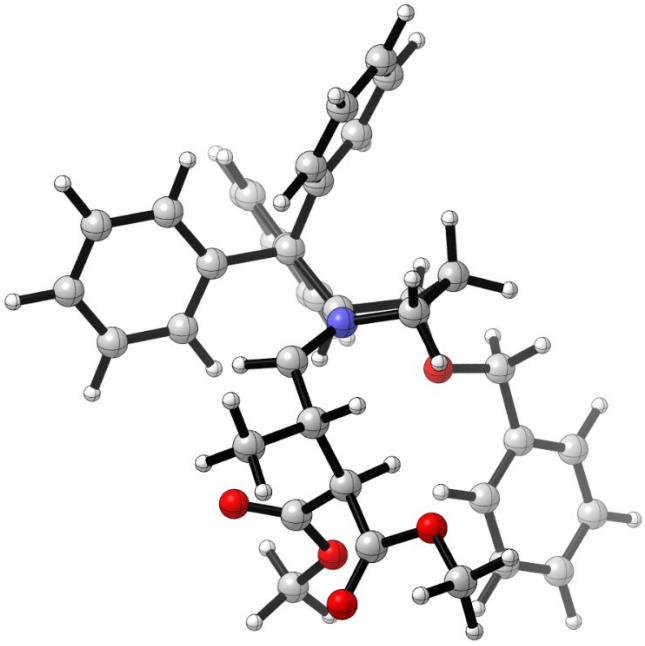
6	4.049323	3.391070	-1.149034
6	4.533065	4.640116	-0.800134
6	3.910493	5.356475	0.211860
6	2.814642	4.821036	0.864612
6	1.599239	-4.147351	-0.460486
1	-0.132985	-2.126472	-0.940033
1	-0.344347	0.327709	-0.678225
1	-1.186921	1.982739	1.353508
1	1.473594	-0.842804	2.108560
1	0.090270	-1.643798	2.837466
1	-4.918885	0.553624	-0.643158
1	-5.864800	2.476116	-1.807049
1	-4.397097	4.322236	-2.562752
1	-1.969971	4.189556	-2.119743
1	-1.027003	2.298178	-0.949084
1	-4.201431	-2.142321	0.068183
1	-4.659315	-3.786530	-1.660032
1	-3.410927	-3.749236	-3.793106
1	-1.715112	-1.984108	-4.165129
1	-1.273852	-0.323620	-2.450069
1	-3.851478	1.728320	1.582927
1	-4.731960	1.384609	3.824681
1	-4.454920	-0.795248	4.958915
1	-3.267382	-2.622553	3.787302
1	-2.372563	-2.273124	1.549510
1	0.304264	3.724905	1.209377
1	1.387620	2.903026	2.318414
1	2.577922	1.881160	-0.772916
1	4.528792	2.826279	-1.932450
1	5.388084	5.053927	-1.309962
1	4.278197	6.330771	0.491441
1	2.334392	5.383839	1.651732
1	1.056706	-4.988303	-0.029108
1	1.262156	-4.022264	-1.485335
1	2.653140	-4.403995	-0.488126
1	-1.075020	0.407639	3.131986
1	0.554456	1.054901	3.188771
6	3.091434	-1.641220	-0.145027
1	2.752730	-0.733766	0.319330
6	3.048091	-1.639076	-1.597747

6	4.120564	-2.367661	0.578040
8	2.294130	-0.599416	-2.037467
8	4.184524	-1.926822	1.856916
8	3.534834	-2.431450	-2.359169
8	4.803770	-3.277064	0.184476
6	5.130821	-2.586896	2.676935
1	6.133753	-2.465333	2.282142
1	5.053531	-2.122988	3.652157
1	4.912396	-3.647456	2.745179
6	2.148403	-0.515277	-3.442821
1	1.645619	-1.394234	-3.833417
1	1.555477	0.371783	-3.627907
1	3.114802	-0.428362	-3.927263
6	1.358904	-2.905749	0.350258
1	1.677787	-2.955774	1.379161

Single point calculation:

SCF Done: E(UBHandHLYP) = -1902.45278850 A.U. after 18 cycles

Dimethyl-malonate radical - Trityl Enamine Product (9c)



```
   -- Stationary point found.
         Item               Value     Threshold  Converged?
Maximum Force            0.000008     0.000450     YES
RMS     Force            0.000001     0.000300     YES
Maximum Displacement     0.000827     0.001800     YES
RMS     Displacement     0.000149     0.001200     YES
Predicted change in Energy=-1.824470D-09
Optimization completed.

SCF Done:  E(UBHandHLYP) =  -1901.81035771     A.U. after    6 cycles

Zero-point correction=                           0.730217 (Hartree/Particle)
Thermal correction to Energy=                    0.770029
Thermal correction to Enthalpy=                  0.770973
Thermal correction to Gibbs Free Energy=         0.651851
Sum of electronic and zero-point Energies=          -1901.080141
Sum of electronic and thermal Energies=             -1901.040329
Sum of electronic and thermal Enthalpies=           -1901.039385
Sum of electronic and thermal Free Energies=        -1901.158507

    Eigenvalues ---    0.00043   0.00069   0.00181   0.00205   0.00260

         Item               Value     Threshold  Converged?
Maximum Force            0.000008     0.000450     YES
```

RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.000801 0.001800 YES
RMS Displacement 0.000174 0.001200 YES
Predicted change in Energy=-2.796207D-09
Optimization completed.

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-0.326800	-1.038223	1.043266
6	0.043813	-2.220014	0.429449
6	-0.849203	0.111206	0.309467
6	-0.441765	1.302142	1.193948
6	-0.295796	0.725920	2.597333
6	0.193877	-0.691676	2.354706
6	-2.386787	0.074985	-0.043400
6	-2.775094	1.310311	-0.887171
6	-4.114645	1.474545	-1.247961
6	-4.526372	2.522129	-2.048259
6	-3.602201	3.438458	-2.530304
6	-2.270954	3.284155	-2.197723
6	-1.860300	2.232996	-1.385561
6	-2.705623	-1.116310	-0.977833
6	-3.812177	-1.939639	-0.800761
6	-4.116384	-2.944074	-1.709700
6	-3.322228	-3.147987	-2.822109
6	-2.227935	-2.321509	-3.026771
6	-1.935980	-1.314950	-2.125140
6	-3.155509	0.018695	1.282489
6	-3.788659	1.134543	1.822625
6	-4.376792	1.094186	3.079478
6	-4.346171	-0.067595	3.828999
6	-3.719769	-1.189552	3.307378
6	-3.131062	-1.145925	2.055402
8	0.796531	1.760966	0.682845
6	1.175621	3.035168	1.122296
6	2.496336	3.430711	0.517565
6	3.262428	2.539488	-0.219109
6	4.486899	2.935554	-0.738530
6	4.955641	4.221417	-0.531388

6	4.190668	5.117147	0.201736
6	2.970557	4.722414	0.721065
6	1.424219	-4.271981	0.145295
1	-0.411309	-2.405022	-0.523409
1	-0.304870	0.201441	-0.623151
1	-1.165033	2.111935	1.162329
1	1.283264	-0.725508	2.376640
1	-0.167899	-1.389435	3.107629
1	-4.844607	0.763404	-0.898703
1	-5.569622	2.618693	-2.303130
1	-3.918609	4.254436	-3.159668
1	-1.535223	3.980378	-2.567623
1	-0.812207	2.157317	-1.156509
1	-4.454618	-1.804594	0.050678
1	-4.980454	-3.566153	-1.538369
1	-3.553224	-3.932639	-3.524191
1	-1.596678	-2.456989	-3.889753
1	-1.089822	-0.680831	-2.327686
1	-3.826087	2.052875	1.263866
1	-4.859009	1.977521	3.466751
1	-4.804975	-0.101845	4.804016
1	-3.686654	-2.104694	3.876886
1	-2.639117	-2.023446	1.676047
1	0.407327	3.763545	0.847975
1	1.255141	3.058814	2.211713
1	2.902671	1.541058	-0.391802
1	5.075381	2.229515	-1.302837
1	5.907389	4.525872	-0.936105
1	4.543959	6.122329	0.367371
1	2.380193	5.425302	1.290424
1	0.671946	-4.865814	0.657063
1	1.219442	-4.301136	-0.918829
1	2.392683	-4.736604	0.314153
1	-1.258116	0.725200	3.096156
1	0.395378	1.303169	3.203389
6	2.522128	-1.941537	0.081008
1	2.463618	-0.971730	0.568187
6	2.420447	-1.681876	-1.406803
6	3.883810	-2.515218	0.390370
8	3.238512	-0.687894	-1.755369

8	4.173584	-2.380357	1.684293
8	1.704360	-2.241210	-2.186576
8	4.605104	-3.060260	-0.396448
6	5.411135	-2.940578	2.102098
1	6.235154	-2.473255	1.575216
1	5.479498	-2.744002	3.163491
1	5.429222	-4.007606	1.910985
6	3.283088	-0.377093	-3.140870
1	2.302216	-0.083580	-3.497006
1	3.979799	0.444578	-3.236077
1	3.626633	-1.235187	-3.706973
6	1.386768	-2.838530	0.669959
1	1.593899	-2.870460	1.738418

Single point calculation:

SCF Done: E(UBHandHLYP) = -1902.47104618 A.U. after 16 cycles

References

[1] Z. Xun, T. Yu, Y. Zeng, J. Chen, X. Zhang, G. Yang and Y. Li, *Journal of Materials Chemistry A*, 2015, **3**, 12965-12971.

[2] S. Pagoti, D. Dutta and J. Dash, *Adv. Synth. Catal.* 2013, **355**, 3532–3538.

[3] S. Lakhdar, B. Maji and H. Mayr, *Angew. Chem. Int. Ed.* 2012, **51**, 1–5.

[4] J. Y. Ying, J. Lim, S. S. Lee and S. N. B. Riduan, **2008**, WO 2008/115154 A1.

[5] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[6] A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648−5652.

[7] H. T. Dunning, *J. Chem. Phys.* 1989, **90**, 1007-1023.

[8] J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.* **2005**, **105**, 2999-3093.

[9] C. Y. Legault, CYLView, Université de Sherbrooke: Sherbrooke, Quebec, Canada, 2009; http://www.cylview.org