Supporting Information

Squaraines as Near-Infrared Photocatalysts for Organic Reactions

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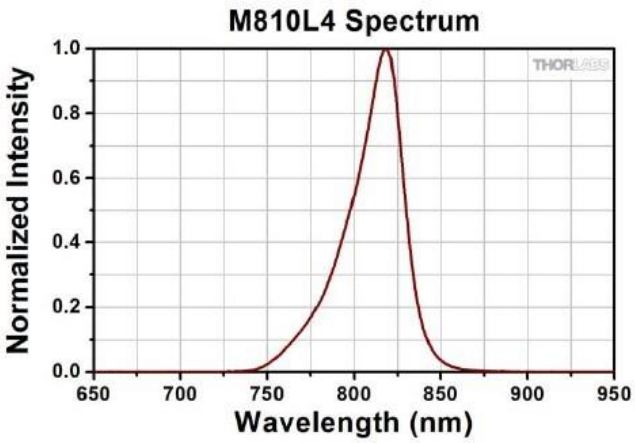
Contents

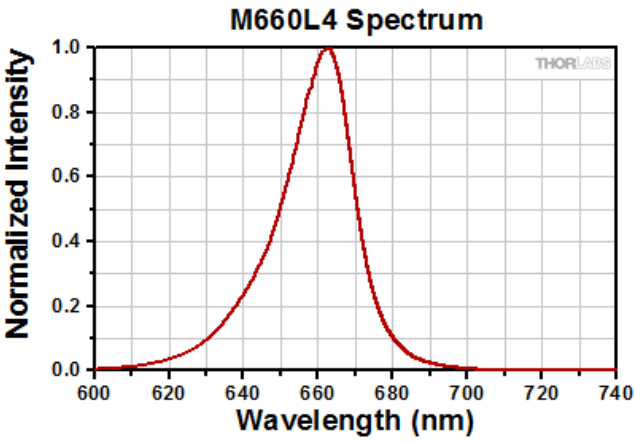
1. General methods

Unless otherwise stated, all the reagents are commercially available and were used without further purification. A newly opened commercial grade dry DMSO was used directly. Other solvents (CH_3CN, DCE, CH_3NO_2) were distillated and stored under N_2 in absence of light. Thin Layer Chromatography (TLC) was performed using Merck© silica gel 60 F254 Aluminum sheets. Column chromatography was performed using Merk© Geduran© Si 60 A° silica gel (0.040-0.063mm) or Fluka© neutral Aluminum oxide (CAS = 1344-28-1). Squaraines photocatalysts (Sq652, Sq660, Sq670, Sq687) were purchased from TCI or Merk.
The absorption and emission spectra were recorded using a Molecular Devices SpectraMax ID3 UV-Visible multimode microplate reader.
IR spectra were recorded on a Perkin Elmer Spectrum Two spectrometer equipped with a detector type (DTGS t) with a resolution of 0.5 cm^{-1}.
Liquid state ^{1}H and ^{13}C NMR spectra were recorded at 400.16 and 100.62 MHz respectively on a Bruker 400 spectrometer or at 500 MHz and 126 MHz on a Bruker 500 spectrometer. All spectra are reported in δ (ppm) relative to TMS, with $CDCl_3$ as solvent. ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quadruplet (q), doublet of doublets (dd), doublets of triplet (dt) or m (multiplets). All the photocatalytic reactions were conducted using the following NIR-LED from Thorlabs:

- M660L4, light-emitting diode (LED, nominal wavelength: 660 nm, output power: 1050 mW, irradiance: 20.9 µW/mm^2).
- M810L4 light-emitting diode (LED, nominal wavelength: 810 nm, output power: 542 mW, irradiance: 23.7 µW/mm^2).

Emission spectra of NIR-LED and red-LED[1]





[1] Spectra and data sheets are available on the Thorlab's website : https://www.thorlabs.com

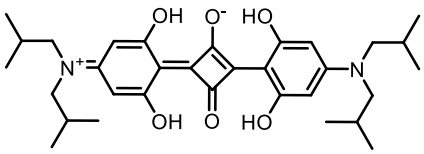
2. Properties of NIR-Photocatalysts

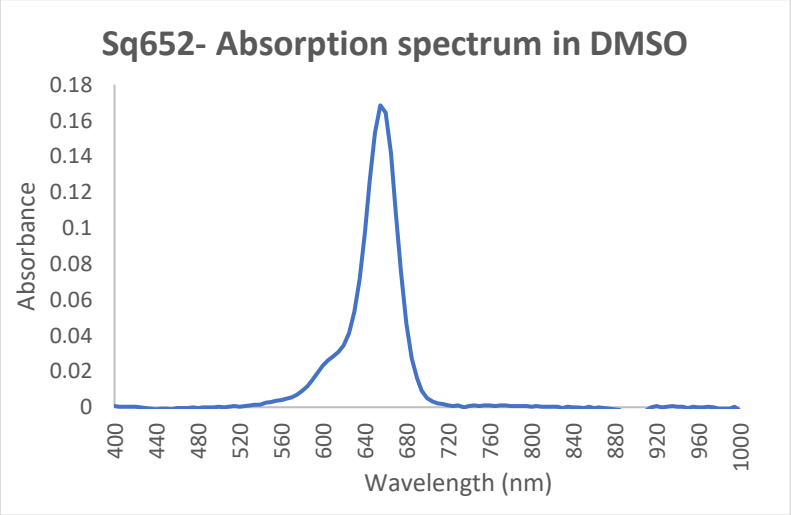
2.1 Procedure for recording Absorption and Fluorescence spectra

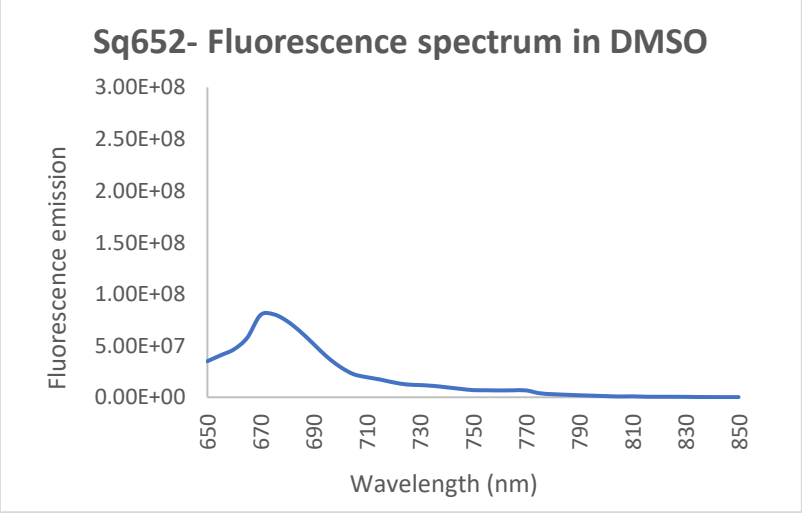
Absorbance and fluorescence spectra of NIR-photocatalysts (Sq687, Sq670, Sq660 and Sq652) were recorded in DMSO (at 20 µM) using a SpectraMax ID3 spectrometer at ambient temperature (20°C). For fluorescence spectra acquisition, λ_{exc} was set 20 nm less than the λ_{max} absorption of the corresponding photocatalyst.

2,4-Bis[4-(N,N-diisobutylamino)-2,6-dihydroxyphenyl] squaraine **(Sq652)**

Chemical Formula : $C_{32}H_{44}N_2O_6$ **Molecular Weight**: 552.70 g/mol **CAS**: / **Merk ID:** 758337

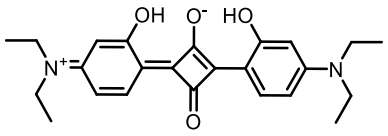


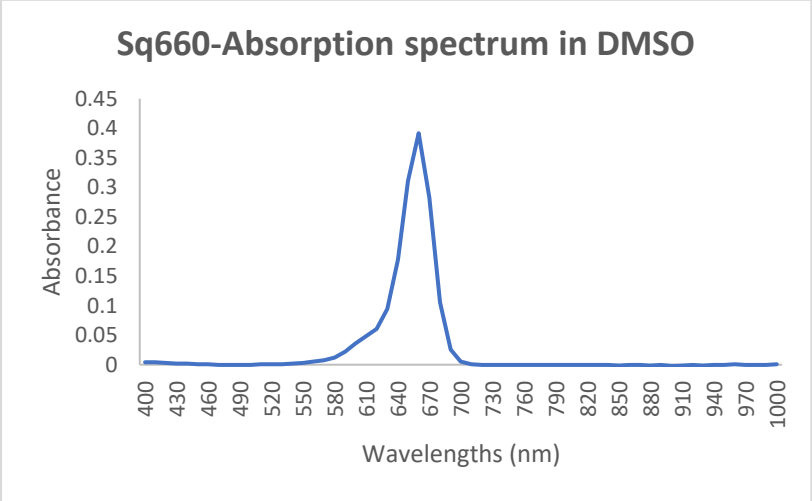


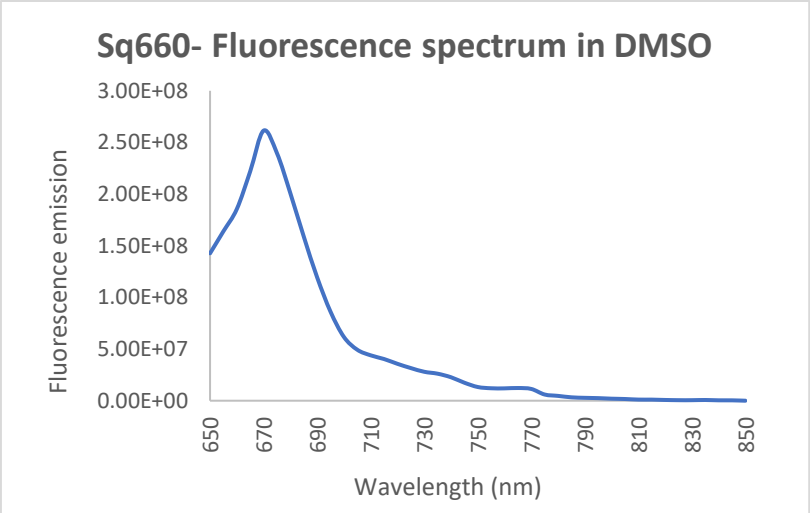


***2,4-Bis[4-(diethylamino)-2-hydroxyphenyl] squaraine* (Sq660)**

Chemical Formula : $C_{24}H_{28}N_2O_4$ **Molecular Weight**: 408.50 g/mol **CAS**: 68842-66-0 **TCI ID:** B4342

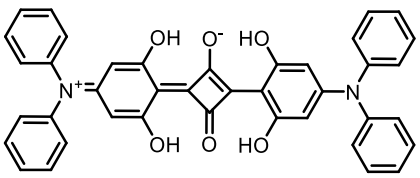


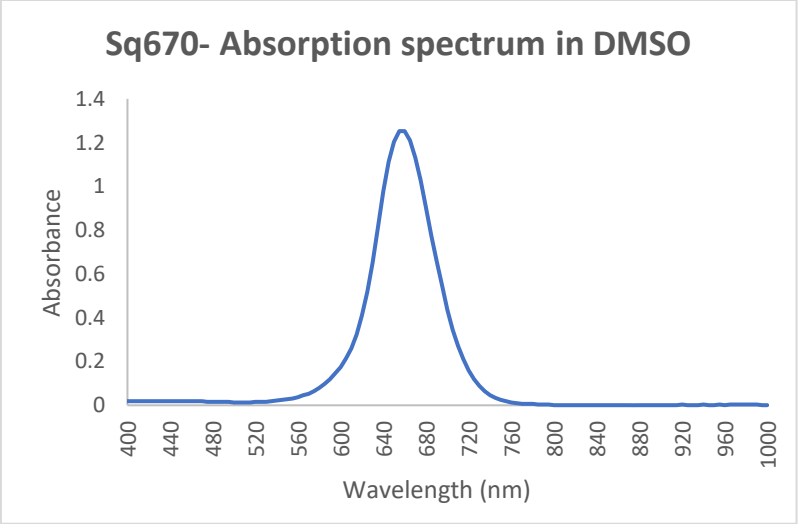


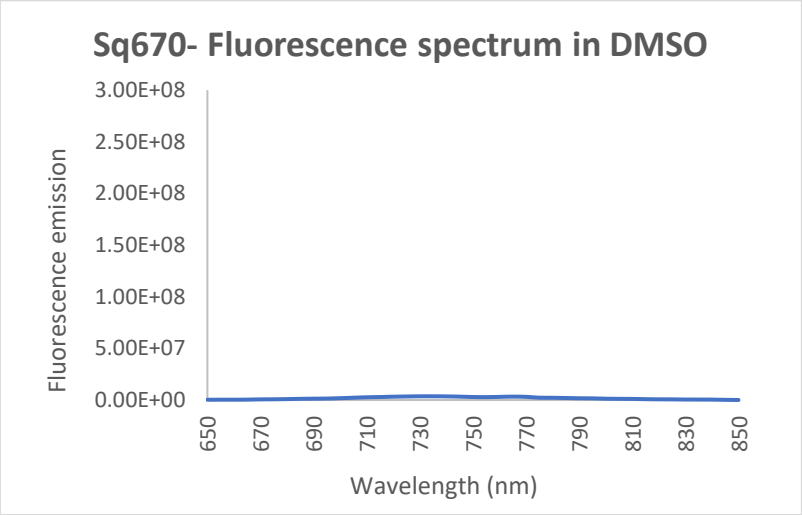


***2,4-Bis[4-(N,N-diphenylamino)-2,6-dihydroxyphenyl] squaraine* (Sq670)**

Chemical Formula : $C_{40}H_{28}N_2O_6$ **Molecular Weight**: 632.66 g/mol **CAS**: 1345272-10-7 **Merk ID:** 757233

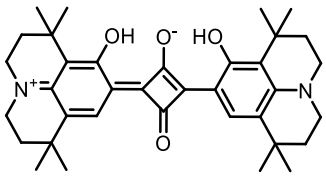


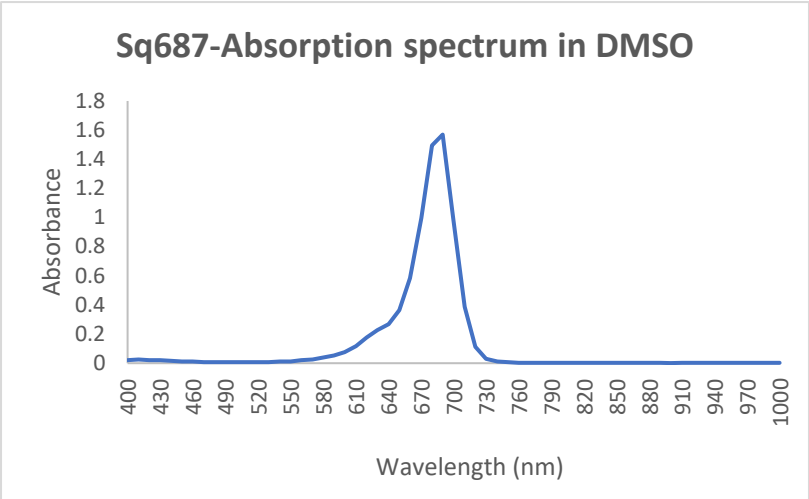


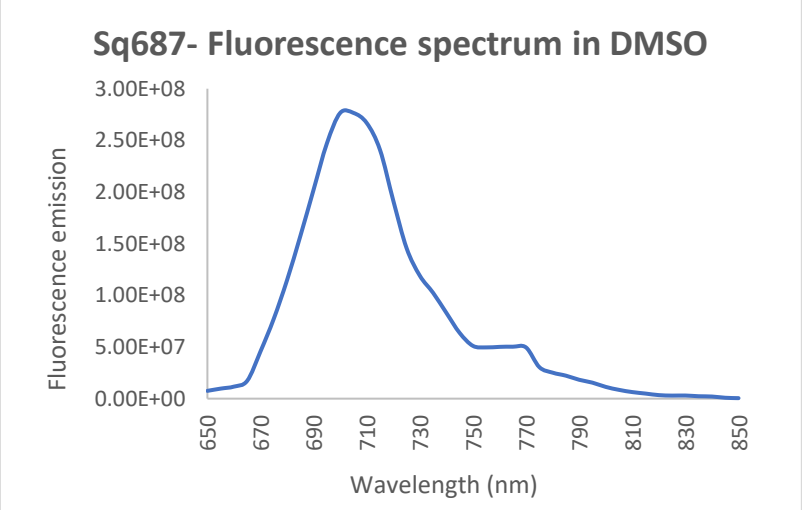


2,4-Bis[8-hydroxy-1,1,7,7-tetramethyljulolidin-9-yl] squaraine **(Sq687)**

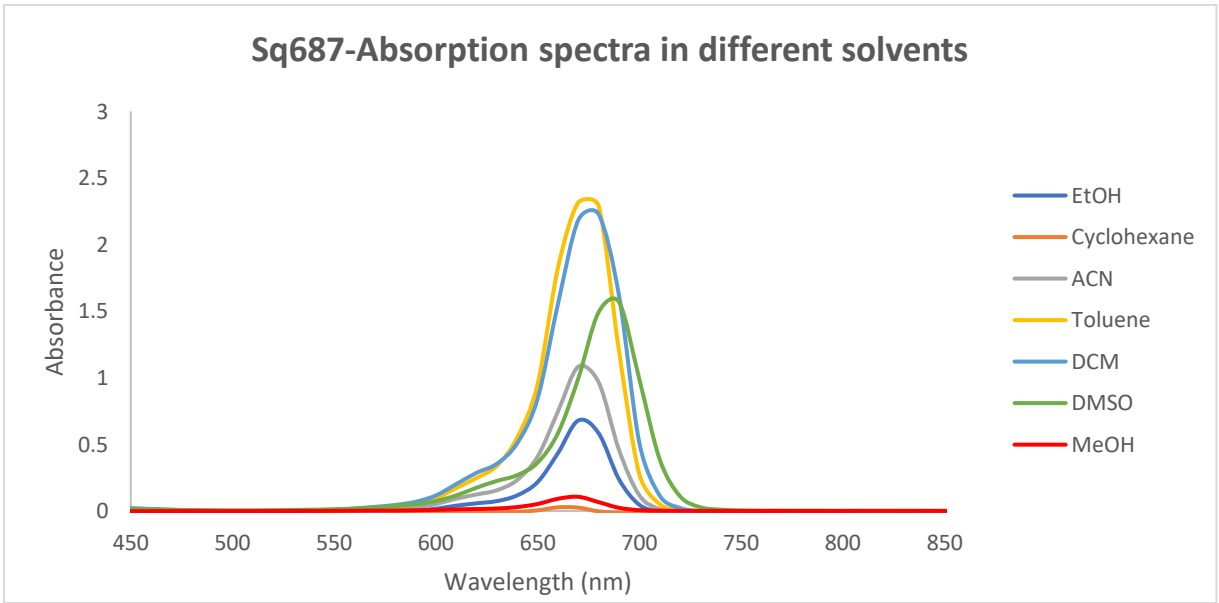
Chemical Formula : $C_{36}H_{44}N_2O_4$ **Molecular Weight**: 568.76 g/mol **CAS**: 358727-55-6 **TCI ID:** B4649





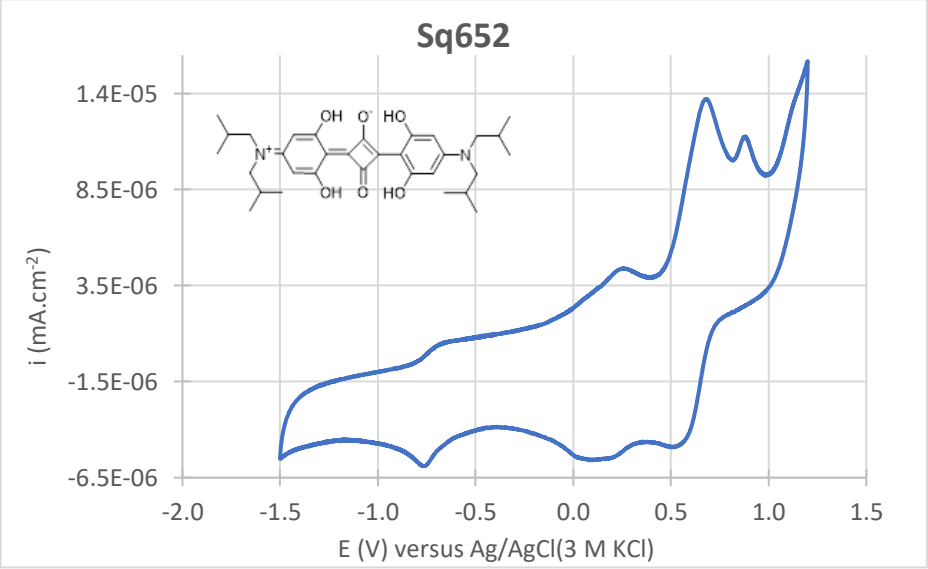


Absorbance of *2,4-Bis[8-hydroxy-1,1,7,7-tetramethyljulolidin-9-yl]squaraine (Sq687)* in different solvents



2.2 Electrochemical measurements

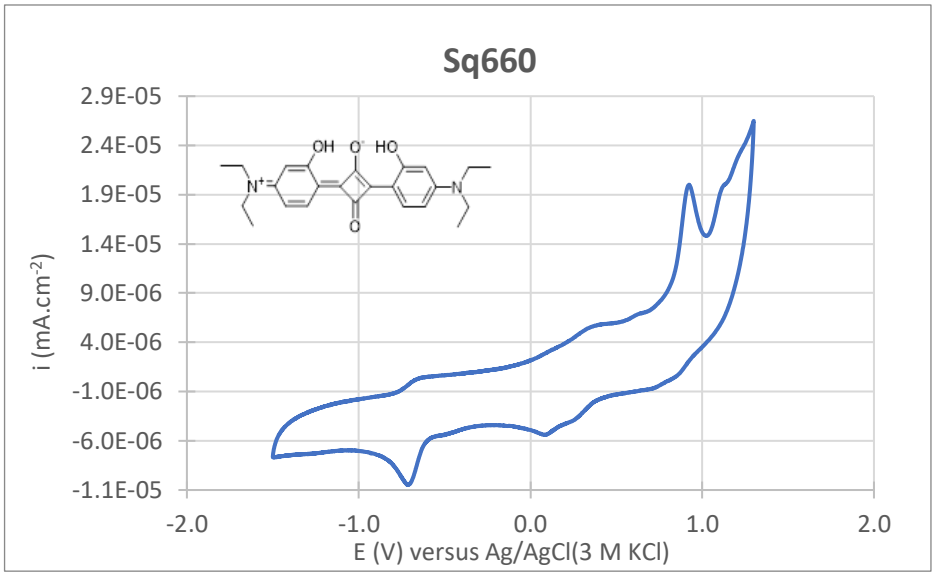
The electrochemical studies were carried out using a Voltalab 50 potentiostat/galvanostat (Radiometer Analytical MDE15 polarographic stand, PST050 analytical voltammetry and CTV101 speed control unit) controlled by the Voltamaster 4 electrochemical software. The cyclic voltammetry experiments were recorded using a conventional three-electrode cell (10 mL) with a glassy carbon disk (GC, s = 0.07 cm^2) set into a Teflon rotating tube as a working electrode, a Pt wire as a counter electrode and KCl(3 M)/Ag/AgCl reference electrode (+210 mV *vs* NHE and -34 mV *vs* SCE).[2] Prior to each measurement, the surface of the GC electrode was carefully polished with 0.3 µm aluminium oxide suspension (ESCIL) on a silicon carbide abrasive sheet of grit 800/2400. The GC electrode was then copiously washed with water and dried with paper towel. All experiments were performed under ambient conditions at 20°C ± 2°C. The PCat solutions (concentration of ~ 1 mM) were prepared in DMSO with 100 mM of tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu_4PF_6) as supporting and inert electrolyte. The solutions containing the PCat were stirred and purged (bubbling) with O_2-free (Sigma Oxiclear cartridge) argon for 10 minutes before the voltammetry experiment was initiated, and maintained under an argon atmosphere during the measurement procedure. The voltage sweep rate was varied from 50 to 300 mV s^{-1} and several cyclic voltammograms were recorded. Peak potentials were measured at a scan rate of 100 mV s^{-1} unless otherwise indicated. According to the Rehm-Weller theory[3], the singlet excited-state redox potentials of each squaraines dyes were estimated from the long wavelength tail (λ_{tail}) of the absorption band lying at lower energies and from the ground-state redox potentials determined by CV.



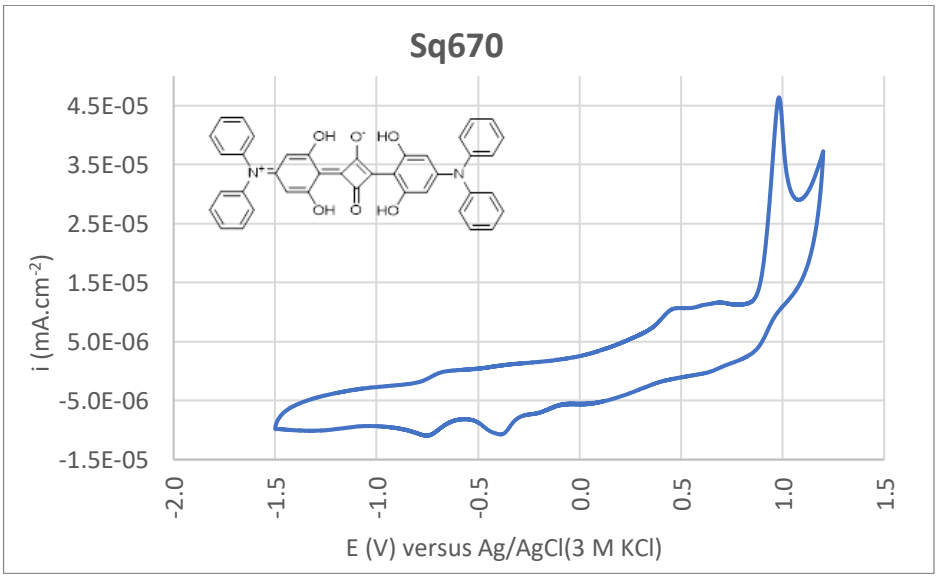
CV profile of **SQ652** (1 mM) measured in DMSO with 0.1 M *n*-Bu_4PF_6 electrolyte support at room temperature (20°C). v = 100 mV s^{-1}; reference electrode = KCl(3 M)/Ag/AgCl; working electrode = glassy carbon disk of 0.07 cm^2 area; counter electrode = Pt wire.

[2] a) D. T. Sawyer, A. Sobkowiak, J. L. Roberts, *Electrochemistry for Chemists*, Wiley, **1995**. B) M. Song, K. E. Daniels, A. Kiani, S. Rashid-Nadimi, M. D. Dickey *Adv. Intell. Syst.* **2021**, 2100024.

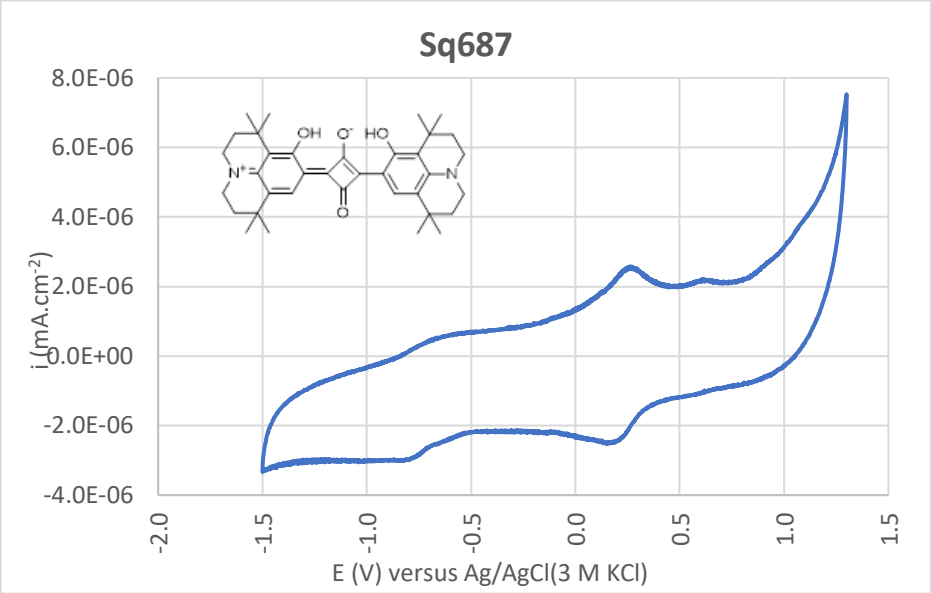
[3] L. Buzzetti, G. E. M. Crisenza, P. Melchiorre *Angew.Chem.Int.Ed.* **2019**, *58*, 3730–3747.



CV profile of **SQ660** (1 mM) measured in DMSO with 0.1 M *n*-Bu_4PF_6 electrolyte support at room temperature (20°C). *v* = 100 mV s^{-1}; reference electrode = KCl(3 M)/Ag/AgCl; working electrode = glassy carbon disk of 0.07 cm^2 area; counter electrode = Pt wire.



CV profile of **SQ670** (1 mM) measured in DMSO with 0.1 M *n*-Bu_4PF_6 electrolyte support at room temperature (20°C). *v* = 100 mV s^{-1}; reference electrode = KCl(3 M)/Ag/AgCl; working electrode = glassy carbon disk of 0.07 cm^2 area; counter electrode = Pt wire.



CV profile of **SQ687** (1 mM) measured in DMSO with 0.1 M *n*-Bu_4PF_6 electrolyte support at room temperature (20°C). *v* = 100 mV s^{-1}; reference electrode = KCl(3 M)/Ag/AgCl; working electrode = glassy carbon disk of 0.07 cm^2 area; counter electrode = Pt wire.

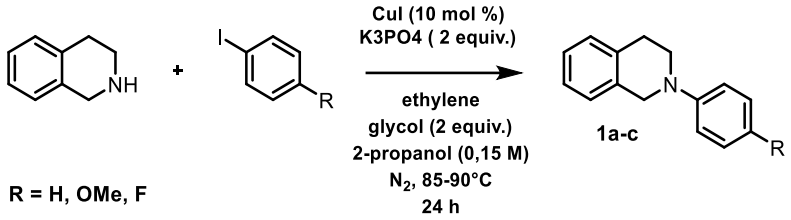
Table : $E_{red/ox}$ of different squaraines measured by cyclic voltammetry (CV) with Ag/AgCl(3M KCl) reference electrode and then corrected[2,4] for referencing against SCE.

	Measured vs Ag/AgCl		Referenced to SCE		$E^*_{red/ox}$ calculated	
Pcat	E_{ox} (V)	E_{red} (V)	E_{ox} (V)	E_{red} (V)	E^*_{ox} (V)	E^*_{red} (V)
Sq652	0.26	-0.76	0.23	-0.80	-1.58	1.01
Sq660	0.39	-0.71	0.36	-0.75	-1.44	1.05
Sq670	0.46	-0.39	0.43	-0.43	-1.22	1.22
Sq687	0.26	-0.80	0.23	-0.83	-1.45	0.84

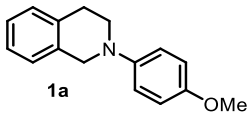
[4] E. P. Friis, J. E. T. Anderson, L. L. Madsen, N. Bonander, P. Moller, J. Ulstrup *Electrochimica Acta* **1998**, *43*, 1114-1122.

3. Synthesis of starting materials

3.1 Synthesis of *N-aryl-tetrahydroisoquinoline* derivatives

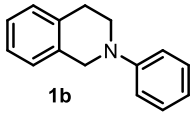


General procedure : The substrates **1a-c** were synthetized according to established procedure[5]: Copper(I) iodide (200 mg, 1.05 mmol, 10 mol%) and potassium phosphate (4.25 g, 20.0 mmol, 2 equiv.) were put into a Schlenk tube. The tube was evacuated and back filled with nitrogen. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL, 20.0 mmol, 2 equiv.), 1,2,3,4-tetrahydroisoquinoline (2.0 mL, 15 mmol, 1.5 equiv.) and iodoarene (10.0 mmol, 1 equiv.) were added successively at room temperature. The reaction mixture was heated at 85-90 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted by diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel (petroleum ether to petroleum ether : EtOAc= 95 :5) to give the pure products **1a-c**.



1a

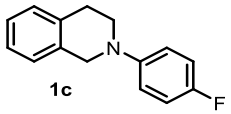
***2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline* 1a :** Following the general procedure, **1a** is obtained as a white solid (m= 2 g, yield= 56%). Data are conformed to the literature.[4] $\mathbf{R_f}$= 0.35 (petroleum ether : EtOAc= 95 :5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 4H), 7.01-6.98 (dt, *J*= 9.1, 3.6 Hz, 2H), 6.90-6.86 (dt, *J* = 9.1, 3.7 Hz, 2H), 4.31 (s, 2H), 3.79 (s, 3H), 3.46 (t, *J* = 5.8 Hz, 2H), 3.00 (t, *J*= 5.8 Hz,2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.6, 145.5, 134.7, 134.6, 128.8, 126.7, 126.4, 126.0, 118.2 (2C),114.7 (2C), 55.8, 52.8, 48.6, 29.2. **FT-IR (ν/cm^{-1}, neat) :** 3037, 2996, 2959, 2918, 2897, 2751, 1630, 1583, 1272, 822, 754.



1b

***2-phenyl-1,2,3,4-tetrahydroisoquinoline* 1b :** Following the general procedure, **1b** is obtained as a light yellow oil (m= 2.1 g, yield= 63 %). Data are conformed to the literature.[4] $\mathbf{R_f}$= 0.45 (petroleum ether : EtOAc= 95 :5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.24 – 7.16 (m, 4H), 7.02-7.00 (m, 2H), 6.87-6.84 (tt, *J* = 7.3, 1.0 Hz, 1H), 4.44 (s, 2H), 3.59 (t, *J* = 5.9 Hz, 2H), 3.01 (t, *J* = 5.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.7, 135.0, 134.6, 129.3 (2C), 128.7, 126.7, 126.5, 126.2, 118.8, 115.3 (2C), 50.9, 46.7, 29.3. **FT-IR (ν/cm^{-1}, neat) :** 3041, 2986, 2969, 2930, 2895, 2752, 1630, 1583, 810, 748.

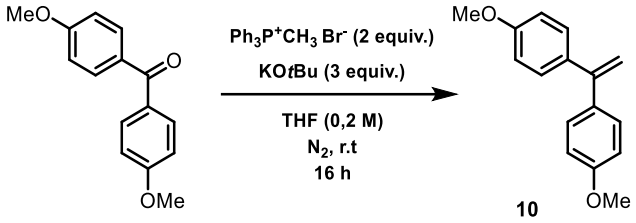
[5] Z. Li, C.-J. Li, *J. Am. Chem. Soc.* **2005**, *127*, 6968-6969



1c

***2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline* 1c :** Following the general procedure, **1c** is obtained as a white solid (m= 1.27g, yield= 37%). Data are conformed to the literature.[6] $\mathbf{R_f}$= 0.50 (petroleum ether : EtOAc= 95 :5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 4H), 7.03 – 6.98 (m, 2H), 6.97-6.93 (m, 2H), 4.35 (s, 2H), 3.50 (t, *J*= 5.9 Hz, 2H), 3.00 (t, *J*= 5.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.8 (d, *J* = 238 Hz), 147.5 (d, *J* = 2 Hz), 134.7, 134.4, 128.8, 126.6, 126.5, 126.2, 117.3, 117.2, 115.8, 115.6, 52.0,47.9, 29.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -125.6. **FT-IR (ν/cm^{-1}, neat) :** 2994, 2926, 2825, 1606, 1591, 1205, 808, 742.

3.2 Synthesis of *1,1-bis(4-methoxyphenyl)ethene* 10



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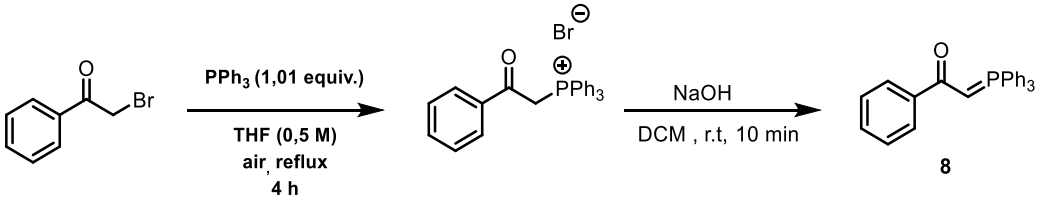
Methyltriphenylphosphonium bromide (2.1 g, 6 mmol, 3 equiv.) was suspended in dry THF (10 mL, 0.2 M) at 0 °C. KO*t*Bu (672 mg, 6 mmol, 3 equiv.) was added to the suspension and a bright yellow color was observed. The mixture was stirred at 0 °C for 30 min. Then 4, 4'-Dimethoxybenzophenone (484 mg, 2 mmol, 1 equiv.) was added and the reaction mixture was stirred at 0 °C to rt for 16 h. The reaction was quenched with H_2O (10 mL) and extracted with diethyl ether (4 x 6 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give crude alkene **19**. The crude was purified by column chromatography on silica gel (cyclohexane : EtOAc = 8 :2) to afford 1,1-bis(4-methoxyphenyl)ethene **19** (m = 475 mg, yield = 99%) as a white solid. Data are conformed to the literature[7]. $\mathbf{R_f}$ = 0.83 (cyclohexane : EtOAc = 8 :2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.26 (dt, *J*= 8.8, 2.9 Hz, 4H), 6.89-6.85 (dt, *J*= 8.8, 2.9 Hz, 4H), 5.30 (s, 2H), 3.83 (s, 6H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.5 (2C), 149.1, 134.5 (2C), 129.6 (4C), 113.6 (4C), 111.8, 55.4 (2C). **FT-IR (ν/cm^{-1}, neat) :** 2930, 2894, 2761, 1653, 1603, 838, 827.

3.3 Synthesis of *(Benzoylmethylene)triphenylphosphorane* 8



8

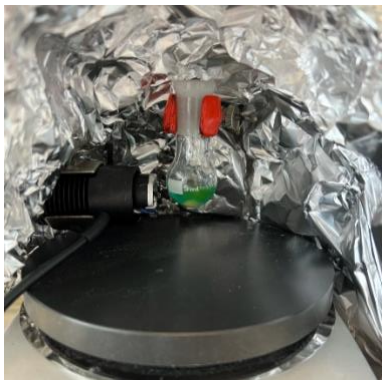
[6] S.M. Soria-Castro, B. Lebeau, M. Cormier, S. Neunlist, T. J. Daou, J.-P. Goddard *Eur. J. Org. Chem.* **2020**, 1572–1578
[7] T. W. Liwosz, S.R. Chemler, *Chem. Eur.J.* **2013**, *19*, 12771–12777

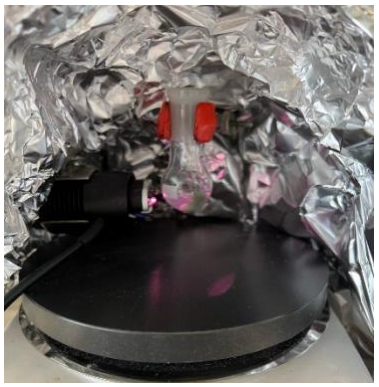
A solution of PPh_3 (1.7 g, 6.4 mmol, 1.01 equiv) and α-bromoacetophenone (1.27 g, 6.3 mmol, 1 equiv) in 13 mL THF was heated under reflux and stirred for 4 hours. Then, the reaction mixture was cooled to room temperature and the crude phosphonium bromide was filtered and washed with THF (3 × 20 mL). Then, the phosphonium was dissolved in 25 mL of CH_2Cl_2 and aqueous NaOH (20 wt %, 25 mL) were added, and the mixture was stirred for 10 minutes. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give the corresponding phosphonium ylide **8** (1.62g, 66% yield). Data are conformed to the literature[8]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99-7.97 (m, 2H), 7.75-7.66 (m, 6H), 7.58-7.54 (m, 3H), 7.49-7.45 (m, 6H), 7.37-7.33 (m, 3H), 4.43 (d, *J*= 24.5 Hz, 1H) .**^{13}C NMR** (126 MHz, $CDCl_3$) (*J* P-C) δ 185.0 (d, *J*= 3.6 Hz, C=O), 141.4 (d, *J*= 14.7 Hz), 133.3 (d, *J*= 10.2 Hz, C2 of P-Ph) ,132.2 (d, *J*= 2.8 Hz, C4 of P-Ph) 129.5 (2C), 129.0 (d, J=12.7 Hz, C3 of P-Ph), 127.9, 127.6 (d, *J*= 91.3 Hz, C1 of P-Ph) 127.0, 51.2 (d, *J*= 112.1 Hz, P=C). **^{31}P NMR** (203 MHz, $CDCl_3$) δ 16.6. **FT-IR (ν/cm^{-1}, neat) :** 3048, 1896, 1587, 708, 688, 506.

4. Near-Infrared Photoredox catalysis

4.1 Set-up

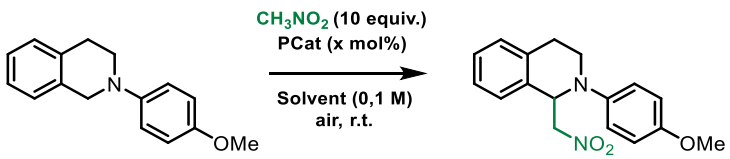
The reactions were run in a 5 mL glass tube or in a 5 mL round bottom single neck flask equipped with magnetic stir bar (closed with a septum for reduction). One NIR LED (810 nm) is placed at 2-3 cm away from the light source. The system is fully covered by aluminum foil to remove the external visible light. Reaction was performed at room temperature.





4.2 Optimization Table of Aza-Henry reaction

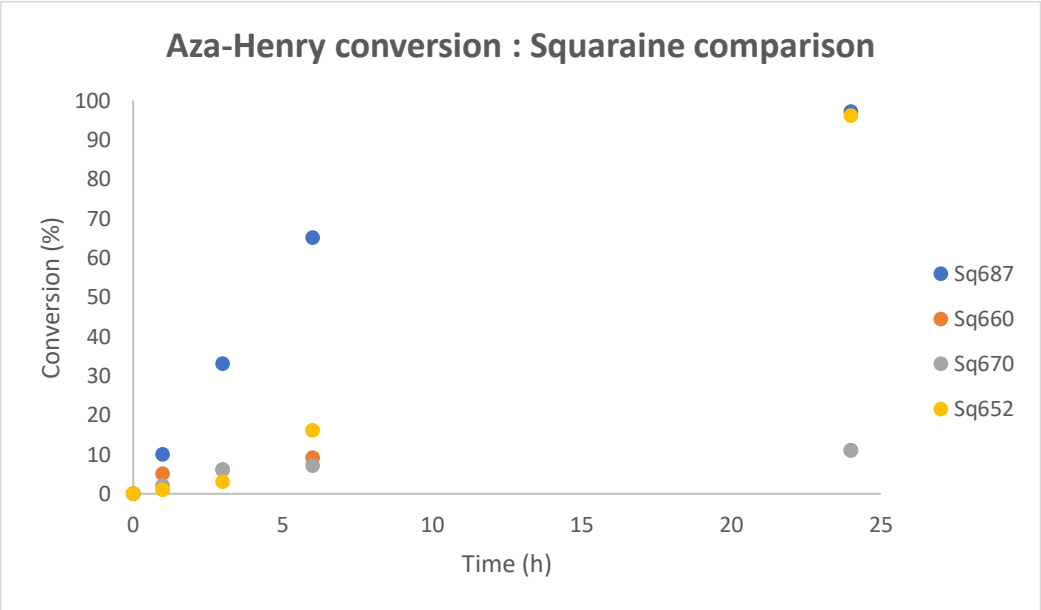
Reactions were run in 0.13 mmol scale, C = 0.1 M and x mol% of Photocatalyst (PC). ^{1}H-NMR conversions determined on the crude reaction mixture.



[8] D. El-Marrouki, S. Touchet, A. Abdelli, H. M'Rabet, M. Lotfi Efrit, P. C. Gros *Beilstein J. Org. Chem.* **2020**, *16*, 1722-1731

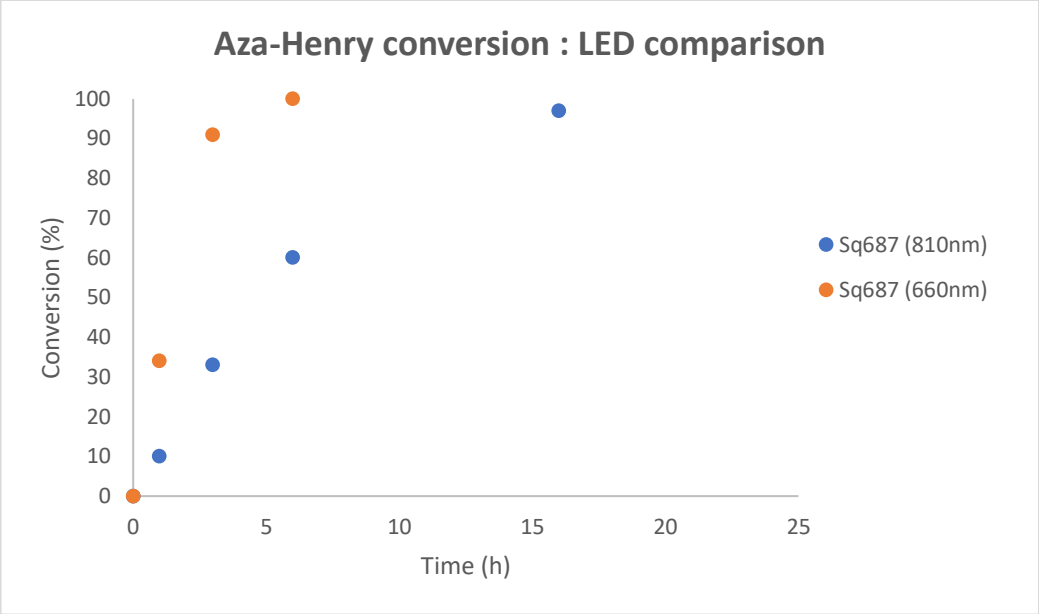
Param.	Entry	PC	x(mol%)	Time (h)	solvent	λ (nm)	Conv.% (yield %)
PCat	1	Sq652	5	24	DMSO	810	100
	2	Sq660	5	24	DMSO	810	11
	3	Sq670	5	24	DMSO	810	10
	4	Sq687	5	24	DMSO	810	100 (48)
Solvent	5	Sq687	5	24	CH_3CN	810	38
	6	Sq687	5	24	iPrOH	810	35
	7	Sq687	5	24	HFIP	810	29
	8	Sq687	5	24	CH_3NO_2	810	8
	9	Sq687	5	24	DMF	810	5
	10	Sq687	5	24	DCM	810	5
Time	**11**	**Sq687**	**5**	**6**	**DMSO**	**810**	**70 (70)**
LED	12	Sq687	5	6	DMSO	660	100 (56)
Control. Exp.	13	/	/	6	DMSO	810	7
	14	Sq687	5	6	DMSO	/	0

Aza-Henry kinetic profil : conversion comparison of different squaraines



(Reaction conditions : 10 equiv. CH_3NO_2, 5 mol% PCat, DMSO, LED-810 nm, kinetic conversion was determined by ^1H NMR after 1, 3, 6 and then 24 h of reaction)

Aza-Henry profil : conversion comparison with different source of illumination (with Sq687)

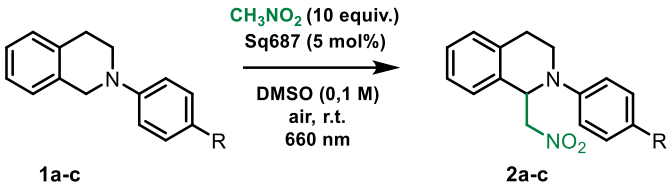


(Reaction conditions : 10 equiv. CH_3NO_2, 5 mol% Sq687, DMSO)

Screening conditions for the substrat scope (LED 810 nm)

Entry	R	Time (h)	Yield (%)
1	H	6	68
2	**H**	**8**	**81**
3	H	16	62
4	**OMe**	**6**	**70**
5	OMe	8	61
6	OMe	16	48
7	F	8	45
8	**F**	**16**	**71**

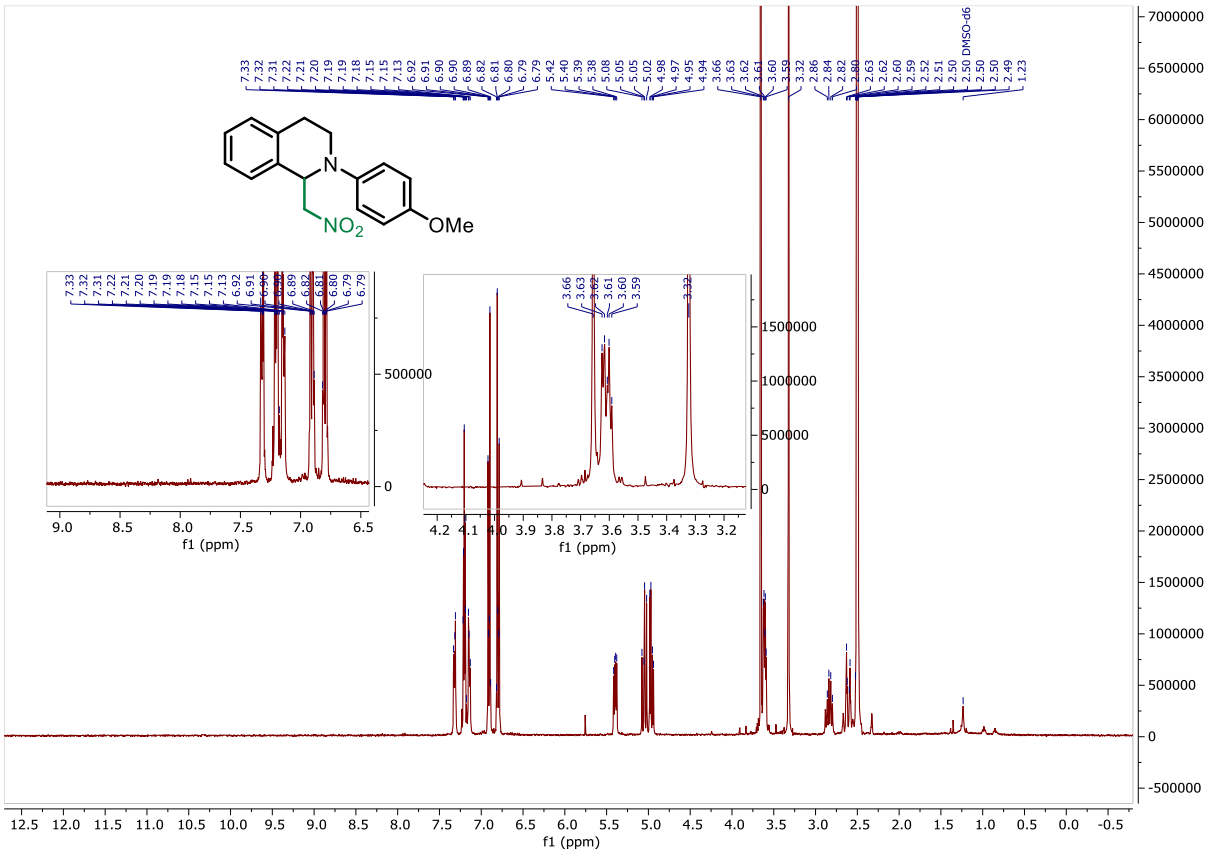
Screening conditions for the substrat scope (LED 660 nm)



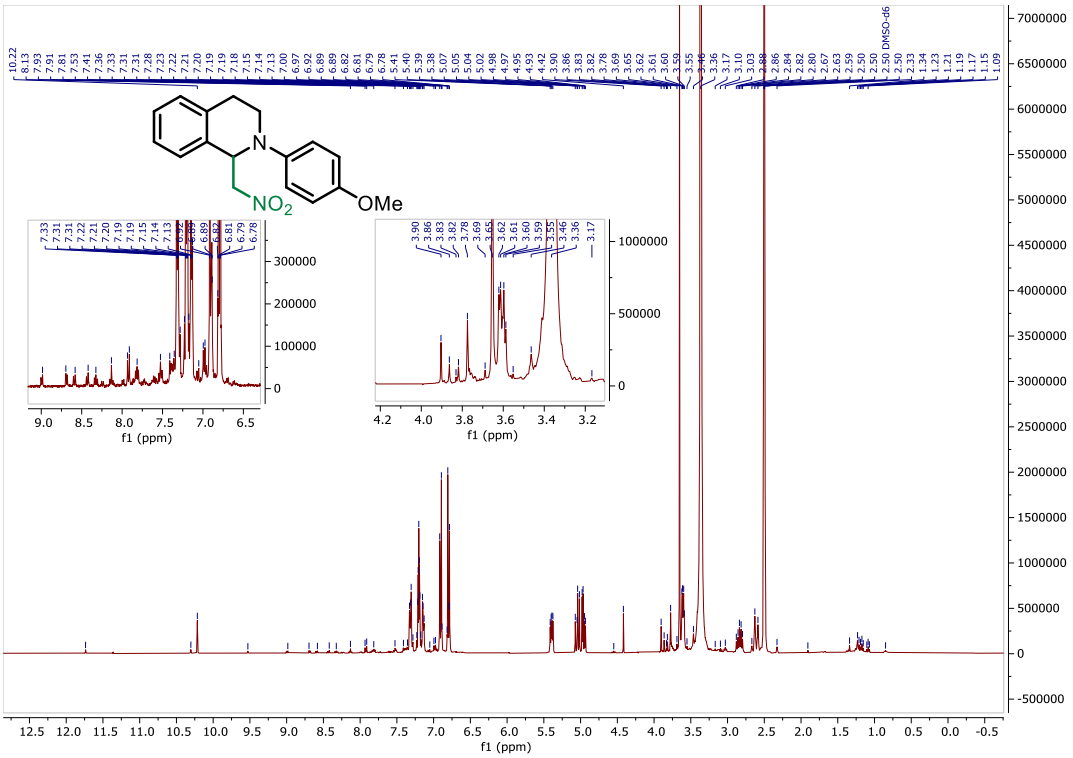
Entry	R	Time (h)	Yield (%)
1	H	6	57
2	OMe	3	48
3	OMe	6	56
5	F	6	25
6	F	48	61

Degradation of Aza-Henry product (^{1}H NMR spectra)

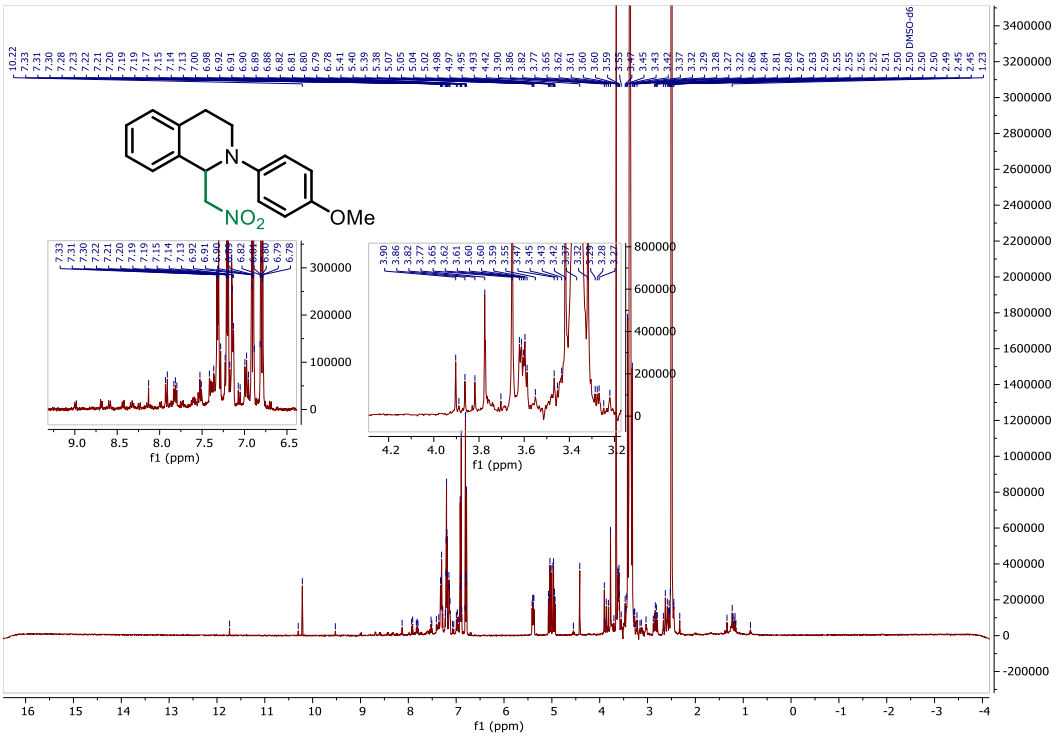
Aza-Henry product was placed in photoredox catalysis conditions (Sq687 5 mol% in DMSO-d6) for 24 or 48 h :



^{1}H NMR spectra in DMSO-d6 before irradiation



^{1}H NMR spectra in DMSO-d6 after 24 h of irradiation

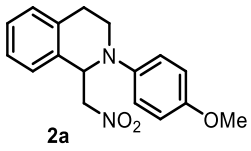


^{1}H NMR spectra in DMSO-d6 after 48 h of irradiation

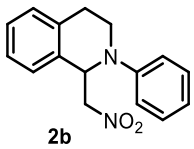
4.3 Aza-Henry: scope of substrat

Entry	R	Time (h)	yield
1	H	8	81 %
2	OMe	6	70 %
3	F	16	71 %

General Procedure: 2-Aryl-1,2,3,4-tetrahydroisoquinoline (0.13 mmol, 1 equiv.), nitromethane (1.3 mmol, 10 equiv.), Sq687 (3.8 mg, 0.0066 mmol, 5 mol%) and DMSO (1.3 mL) were charged in a reaction glass tube with magnetic stirring bar. The reaction mixture was stirred under air atmosphere and near infrared LED (810 nm) irradiation (2-3 cm away from the light source) at room temperature for 6 to 16h. The crude mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum pressure. The crude was purified by column chromatography on silica gel (pentane: Et_2O = 9: 1) to give **2a-c**.

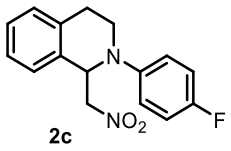


2-(4-methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline **2a:** According to the general procedure, **2a** is obtained after 6 h of reaction as yellow oil (m= 26 mg, yield= 70 %). Data are conformed to the literature[5]. $\mathbf{R_f}$= 0.28 (pentane: Et_2O = 9: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29– 7.16 (m, 4H), 6.95 (dt, *J* = 9.1, 3.5 Hz, 2H), 6.85 (dt, *J* = 9.1, 3.5 Hz, 2H), 5.43 (dd, *J* = 8.4, 5.9 Hz, 1H),4.83 (dd, *J* = 11.9, 8.7 Hz, 1H), 4.58 (dd, *J* = 11.9, 5.9 Hz, 1H), 3.77 (s, 3H), 3.64 - 3.54 (m, 2H), 3.04 (m, 1H), 2.72 (dt, *J* = 16.6, 3.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.0, 143.1, 135.5, 132.9, 129.5, 127.9, 127.0, 126.6, 118.8 (2C), 114.7 (2C), 78.9, 58.9, 55.6, 43.1, 25.8. **FT-IR (ν/cm^{-1}, neat) :** 3675, 2970, 2901, 1550, 1509, 1379, 1244, 1037.



1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline **2b :** According to the general procedure, **2b** is obtained after 8 h of reaction as yellow oil (m= 31 mg, yield= 81%). Data are conformed to the literature.[5] $\mathbf{R_f}$= 0.46 (pentane : Et_2O = 9 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) 7.33 – 7.16 (m, 6H), 7.00 (m, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 5.59 (t, *J* = 7.2 Hz, 1H), 4.90 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.60 (dd, *J* = 11.8, 6.6 Hz, 1H), 3.73 – 3.62 (m, 2H), 3.15 – 3.09 (m, 1H), 2.85-2.80 (dt, *J* = 16.3, 4.9 Hz, 1H). **^{13}C NMR**

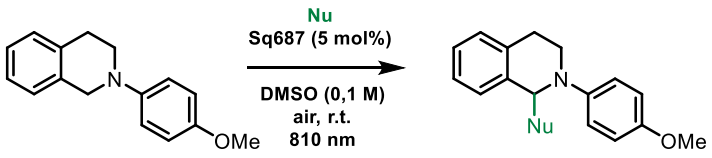
(100 MHz, $CDCl_3$) δ 148.5, 135.4, 133.0, 129.6 (2C), 129.3, 128.2, 127.1, 126.8, 119.5, 115.2 (2C),78.9, 58.3, 42.1, 26.5. **FT-IR (ν/cm^{-1}, neat) :** 3670, 2986, 2923, 1552, 1264, 1086, 737.



2c

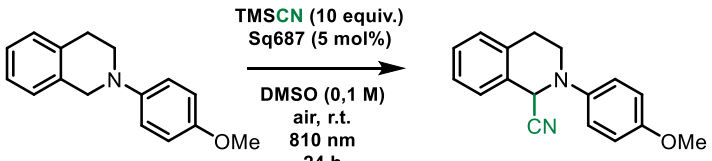
***2-(4-fluorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline* 2c :** According to the general procedure, **2c** is obtained after 16 h of reaction as yellow oil (m = 27 mg, yield = 71%). Data are conformed to the literature[5]. **R_f** = 0.38 (pentane : Et_2O = 9 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28–7.14 (m, 4H), 6.97 – 6.89 (m, 4H), 5.43 (dd, *J* = 8.6, 6.0 Hz, 1H), 4.84 (dd, *J*= 12.0, 8.6 Hz, 1H), 4.58(dd, *J* = 12.0, 5.9 Hz, 1H), 3.60 (m, 2H), 3.07 – 2.99 (m, 1H), 2.73 (dt, *J* = 16.5, 4.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2 (d, *J* = 239.2 Hz), 145.4 (d, *J* = 2.0 Hz), 135.3, 132.6, 129.5, 128.2, 127.0, 126.8, 118.0 (d, *J* = 7.6 Hz, 2C), 115.9 (d, *J* = 22.3 Hz, 2C), 78.9, 58.8, 42.9, 25.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -124.3. **FT-IR (ν/cm^{-1}, neat) :** 3005, 2928, 1555, 1508, 1264, 737.

4.4 Aza-Henry: scope of nucleophiles



2d-f

Synthesis of 2-(*4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile* 2d

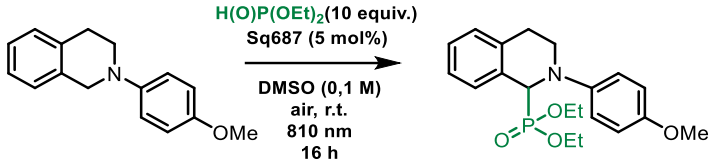


2d

2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (30 mg, 0.13 mmol, 1 equiv.), trimethylsilyl cyanide (TMSCN) (124 mg, 1.3 mmol, 10 equiv.), Sq687 (3.6 mg, 0.0063 mmol, 5 mol%) and DMSO (1.3 mL) were charged in a reaction glass tube with magnetic stirring bar. The reaction mixture was stirred under air atmosphere and near infrared LED (810 nm) irradiation (2-3 cm away from the light source) at room temperature for 24 h. The crude mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum pressure. The crude was purified by column chromatography on aluminum oxide (ether petroleum: EtOAc = 8:2) to give **2d** (m = 24 mg, yield = 72%) as a yellow oil. Data are conformed to the

literature[9]. **R_f** = 0.46 (ether petroleum: EtOAc = 8:2) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 1H), 7.28-7.26 (m, 2H), 7.24-7.23 (m, 1H), 7.09 (dt, *J* = 9.1, 3.6 Hz, 2H), 6.92 (d, *J* = 9.1, 3.6 Hz, 2H), 5.37 (s, 1H), 3.81 (s, 3H), 3.61-3.57 (m, 1H), 3.44 (td, *J* = 12.0, 4.0 Hz, 1H), 3.21-3.14 (m, 1H), 2.96-2.92 (m, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.8, 142.7,134.5, 129.8, 129.6, 128.8, 127.2, 126.8, 121.2 (2C), 117.7, 114.9 (2C), 55.8, 55.7, 45.0, 28.8. **FT-IR (ν/cm^{-1}, neat) :** 2937, 2838, 1612, 1511, 1462, 1245, 1030, 830, 733.

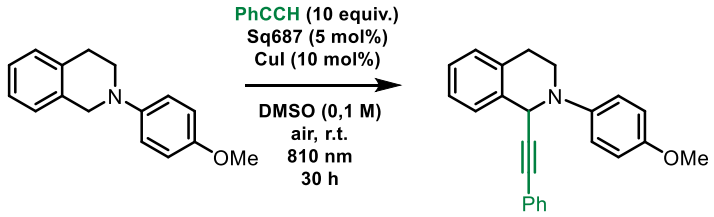
Synthesis of *diethyl (2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate* 2h



2e

2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (30 mg, 0.13 mmol, 1 equiv.), diethyl phosphite (173 mg, 1.3 mmol, 10 equiv.), Sq687 (3.6 mg, 0.0065 mmol, 5 mol%) and DMSO (1.3 mL) were charged in a reaction glass tube with magnetic stirring bar. The reaction mixture was stirred under air atmosphere and near infrared LED (810 nm) irradiation (2-3 cm away from the light source) at room temperature for 24 h. The crude mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum pressure. The crude was purified by column chromatography on silica gel (DCM to ether petroleum: EtOAc = 8:2) to give **2e** (m = 37 mg, yield = 79%). Data are conformed to the literature[10]. **R_f** = 0.36 (ether petroleum: EtOAc = 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.38 (m, 1H), 7.19-7.12 (m, 3H), 6.92 (dt, *J*= 9.1, 3.7 Hz, 2H), 6.81 (d, *J*= 9.1, 3.7 Hz, 2H), 5.02 (d, *J*= 21.5 Hz, 1H), 4.13-3.92 (m, 5H), 3.75 (s, 3H), 3.56-3.53 (dt, *J*=12.7, 5 Hz, 1H), 2.94-2.91 (m, 2H), 1.25 (t, *J*= 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.2, 144.3 (d, *J*= 8.3 Hz), 136.5 (d, *J*= 6.1 Hz), 130.6, 129.0 (d, *J* = 2.8 Hz), 128.3 (d, *J* = 3.7 Hz), 127.4 (d, *J*= 3.7 Hz), 125.9 (d, *J*= 3.7 Hz), 117.7 (2C),114.6 (2C), 63.5 (d, *J*= 7.5 Hz), 62.3 (d, *J*= 7.4 Hz), 60.2, 58.9, 55.8, 44.8, 26.2, 16.6 (dd, *J*= 13.0, 5.6 Hz). **^{31}P NMR** (203 MHz, $CDCl_3$) δ 22.2. **FT-IR (ν/cm^{-1}, neat) :** 3412, 2979, 2905, 2833, 1660, 1628, 1508, 1241, 1019, 960, 742, 562.

Synthesis of *2-(4-methoxyphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline* 2f



2f

2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline **1a** (30 mg, 0.13 mmol, 1 equiv.), phenylethyne (128 mg, 1.3mmol, 10 equiv.), Sq687 (3.6 mg, 0.0063mmol, 5 mol%), CuI (2.4 mg, 0.013 mmol, 10 mol%) and DMSO (1.3 mL) were charged in a reaction glass tube with magnetic stirring bar. The

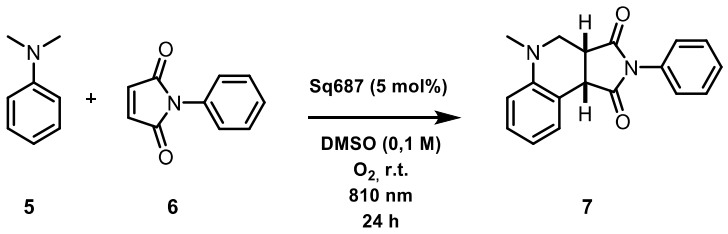
[9] M. Rueping, S. Zhu, R. M. Koenigs *Chem. Commun.* **2011**, *47*, 12709-12711

[10] H. Durga, B. Koenig *Org. Lett.* **2011**, *13*, 3852-3855

reaction mixture was stirred under air atmosphere and near infrared LED (810nm) irradiation (2-3 cm away from the light source) at room temperature for 30 h. The crude mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum pressure. The crude was purified by column chromatography on silica gel (Ether petroleum to ether petroleum: EtOAc = 9:1) to give **2f** (m = 32 mg, yield = 75%) as a yellow oil. Data are conformed to the literature[11]. $\mathbf{R_f}$ = 0.53 (ether petroleum: EtOAc = 9:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.37 (m, 1H), 7.33-7.30 (m, 2H), 7.28-7.20 (m, 6H), 7.12 (dt, *J* = 10.5, 3.7 Hz, 2H), 6.89 (dt, *J* = 10.5, 3.7 Hz, 2H), 5.55 (s, 1H), 3.82 (s, 3H), 3.70-3.50 (m, 1H), 3.61-3.57 (m, 1H), 3.22-3.15 (m, 1H) 2.97 (dt, *J* = 16.3, 3,7 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.4, 144.3, 135.6, 134.2, 131.8 (2C), 129.2, 128.2 (2C), 128.1, 127.6, 127.3, 126.3k, 123.2, 120.3 (2C), 114.5 (2C), 88.6, 85.6, 55.7, 54.5, 44.4, 29.2. **FT-IR (ν/cm^{-1}, neat):** 3283, 2907, 2831, 1657, 1597, 1508, 1241, 1035, 823, 753.

4.5 Other Near-Infrared Photoredox Catalysis

Synthesis of *5-Methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline1,3(2H)-dione* 7

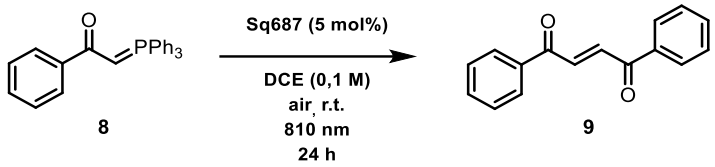


The *N,N*-dimethylaniline **5** (147 mg, 1.21 mmol, 7 equiv), *N*-phenyl maleimide **6** (30 mg, 0.17 mmol, 1 equiv), Sq687 (5 mg, 0.0087 mmol, 5 mol%) and DMSO (1.7 mL) were placed in a standard glass reaction tube with magnetic stir bar. The reaction mixture was stirred under oxygen atmosphere (1 atm, balloon) and near infrared LED (810 nm), irradiation (2-3 cm away from the light source) at room temperature for 24 h. The crude mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum pressure. The crude was purified by column chromatography on silica gel (DCM: cyclohexane = 1:1 to DCM) to give **7** (m= 32 mg, yield = 63 %) as a yellow oil and single diastereoisomer. Data are conformed to the literature[12]. $\mathbf{R_f}$= 0.46 (DCM). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (m, 1H), 7.45--7.41 (m, 2H), 7.38-7.34 (m, 1H), 7.28-7.22 (m, 3H), 6.91 (td, *J* = 7.5, 1.1 Hz, 1H), 6.76 (m, 1H), 4.16 (d, *J*= 9.6 Hz, 1H), 3.62 (dd, *J* = 11.5, 2.7 Hz, 1H), 3.56-3.52 (ddd, *J* = 9.5, 4.4, 2.7 Hz, 1H), 3.13 (dd, *J* = 11.5, 4.4 Hz, 1H), 2.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.8, 175.9, 148.6, 132.1, 130.5, 129.1 (2C), 128.8, 128.6, 126.5 (2C), 119.8, 118.7, 112.7, 50.8, 43.7, 42.3, 39.6. **FT-IR (ν/cm^{-1}, neat) :** 2967, 2861, 2811, 2785, 1706, 1597, 1496, 1391, 1196, 751, 692.

[11] W. Fu, W. Guo, G. Zou, C. Xu *Journal of Fluorine Chemistry* **2012**, *140*, 88-94

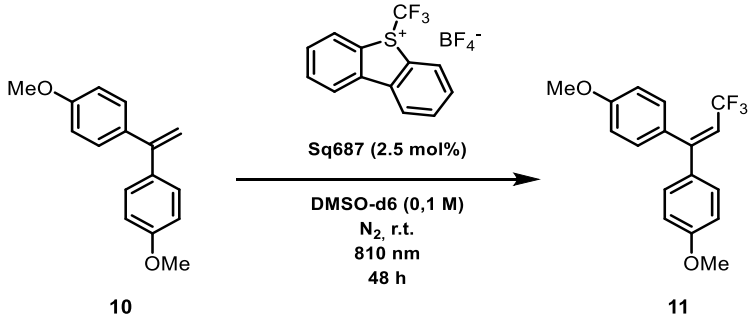
[12] Z. Liang, S. Xu, W. Tian, R. Zhang *Beilstein J. Org. Chem.* **2015**, *11*, 425-430

Synthesis of *(E)-1,4-diphenylbut-2-ene-1,4-dione 9*



(Benzoylmethylene)triphenylphosphorane **8** (30 mg, 0.08 mmol, 1 equiv.), Sq687 (2.3 mg, 0.004 mmol, 5 mol %) were charged in a 5 mL round bottom flask equipped with a magnetic stirring bar. Then DCE (1.6 mL) was added at the round bottom flask and the reaction mixture was stirred and irradiated with a near infrared light source (810 nm, 2-3 cm away from the LED lamp) at room temperature under air conditions for 24 h. Finally, the solvent was removed in vaccum and the crude residue was purified by column chromatography on silica gel (ether petroleum: EtOAc = 9:1) to afford **9** (m= 6 mg, yield = 65%) as a slightly yellow solid. Data are conformed to the literature[13]. **R_f** = 0.44 (ether petroleum: EtOAc = 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 4H), 8.02 (s, 2H), 7.64 (tt, *J*= 14.8, 6.9, 1.3 Hz, 2H), 7.56-7.52 (m, 4H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 190.0 (2C), 137.0 (2C), 135.3 (2C), 134.0 (2C), 129.1 (2C), 129.0 (2C). **FT-IR (ν/cm^{-1}, neat) :** 3063, 2962, 2928, 1708, 1644, 1593, 1290, 1017, 701, 632.

Synthesis of *4,4'-(3,3,3-trifluoroprop-1-ene-1,1-diyl)bis(methoxybenzene)* 11



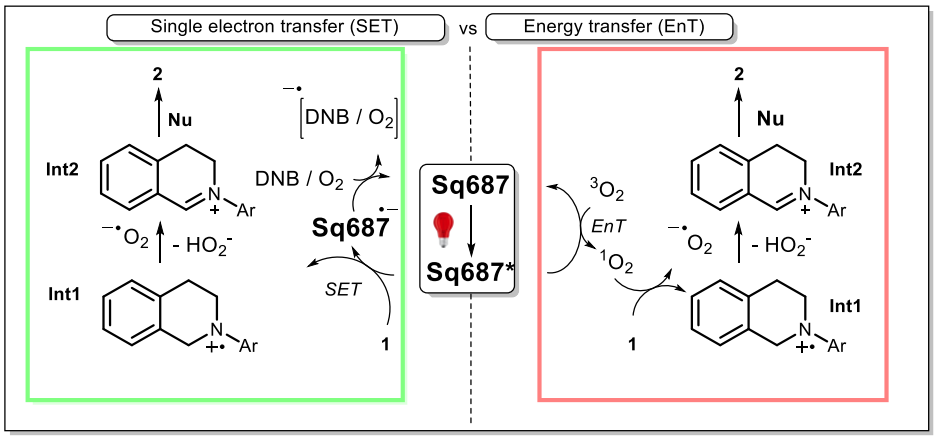
1,1-bis(4-methoxyphenyl)ethene **10** (25 mg, 0.1 mmol, 1 equiv.), Umemoto's reagent [CAS:131880-16-5] (34 mg, 0.1 mmol, 1 equiv.), Sq687 (1.5 mg, 0.003 mmol, 2.5 mol %) were charged in a reaction glass tube with a magnetic stirring bar. The glass tube was placed under N_2. Then DMSO-*d6* (1 mL) was degassed by three cycles of freeze-pump-thaw before being added at the glass tube. The mixture was stirred and irradiated with a near infrared light source (810 nm, 2-3 cm away from the LED lamp) at room temperature. After 48 h of reaction, durene (14 mg, 0.1 mmol, 1 equiv.) was added as an internal standard to the glass tube NMR yield = 75 %. Data are conformed to literature[14].

(The pure product was not isolated, a mixture between the 4,4'-(3,3,3-trifluoroprop-1-ene-1,1-diyl)bis(methoxybenzene) and the 4,4'-(3,3,3-trifluoro-2-(trifluoromethyl)prop-1-ene-1,1-diyl)bis(methoxybenzene) was always obtained)

[13] M. Wang, Y.-Q. He, Y. Zhu, Z.-B. Song, X.-Y. Wang, H.-Y. Huang, B.-P. Cao, W.-F. Tian, Q. Xiao *Org. Chem. Front.* **2021**, *8*, 5934-5940

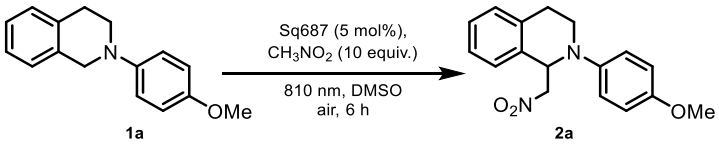
[14] R. Tomita, Y. Yasu, T. Koike, M. Akita *Beilstein J. Org. Chem.* **2014**, *10*, 1099-1106

4.6 Mechanistic study



With the controlled experiments (see below) we can supposed that single electron transfer is the privileged mechanism for the aza-Henry transformation with the use of Sq687 as photocatalyst.

Single electron transfer vs Energy transfer investigation



	conversion of **1a**	
	6 h	24 h
optimized conditions	70%	100%
N_2 instead of air	0%	0%
$^1O_2$ quencher : NaN_3	26 %	30 %
N_2, 1,3-dinitrobenzene	13 %	62 %
N_2, 1,3-dinitrobenzene (dark)	0 %	0 %
N_2, 1,3-dinitrobenzene (without PCat)	0 %	0 %

General procedure under N_2

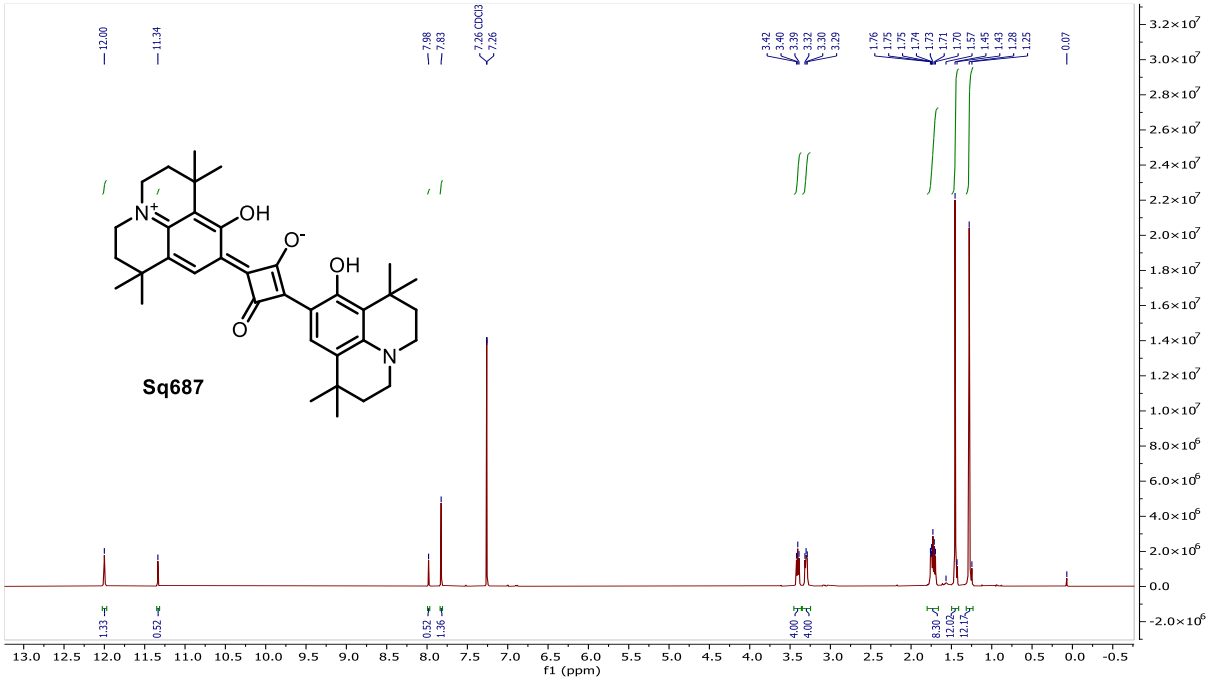
2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (0.13 mmol, 1 equiv.), Sq687 (3.8 mg, 0.0066 mmol, 5 mol%) and 1,3-dinitrobenzene (0.13 mmol, 1 equiv.) were charged in a reaction glass tube with magnetic stirring bar. The reaction media was purged 3 times with N_2. Then DMSO-d_6 was degassed by 3 freeze-pump-thaw cycles and refill with N_2 before being added to the reaction media. Finally, nitromethane (1.3 mmol, 10 equiv.) was added to the mixture. Then the mixture was stirred under N_2 atmosphere and near infrared LED (810 nm) irradiation (2-3 cm away from the light source) at room temperature for 24 h. Conversions were measured after 6 and 24 h of irradiation.

General procedure under air

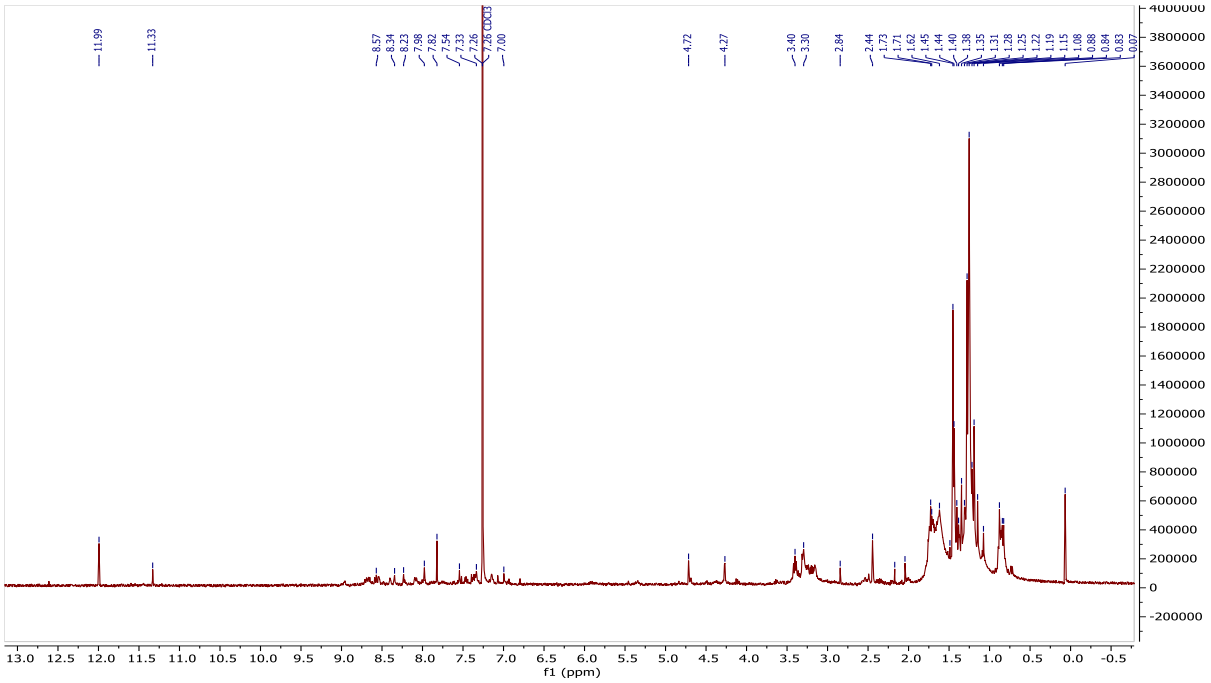
2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (0.13 mmol, 1 equiv.), nitromethane (1.3 mmol, 10 equiv.), Sq687 (3.8 mg, 0.0066 mmol, 5 mol%), NaN_3 (0.39 mmol, 3 equiv.) and DMSO-d_6 (1.3 mL) were charged in a reaction glass tube with magnetic stirring bar. The reaction mixture was stirred under air atmosphere and near infrared LED (810 nm) irradiation (2-3 cm away from the light source) at room temperature for 24 h (vial capped). Conversions were measured after 6 and 24 h of irradiation.

Degradation of Sq687 with NaN3:

Sq687 (0.007 mmol, 1 equiv.) and NaN_3 (0.387 mmol, 3 equiv.) and DMSO (1.3 mL) was placed in a microwave tube and placed under near infrared LED (810 nm) irradiation (2-3 cm away from the light source) at room temperature for 24 h. The crude mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum pressure. The crude was analyzed by NMR to give the corresponding ^{1}H NMR spectra below.



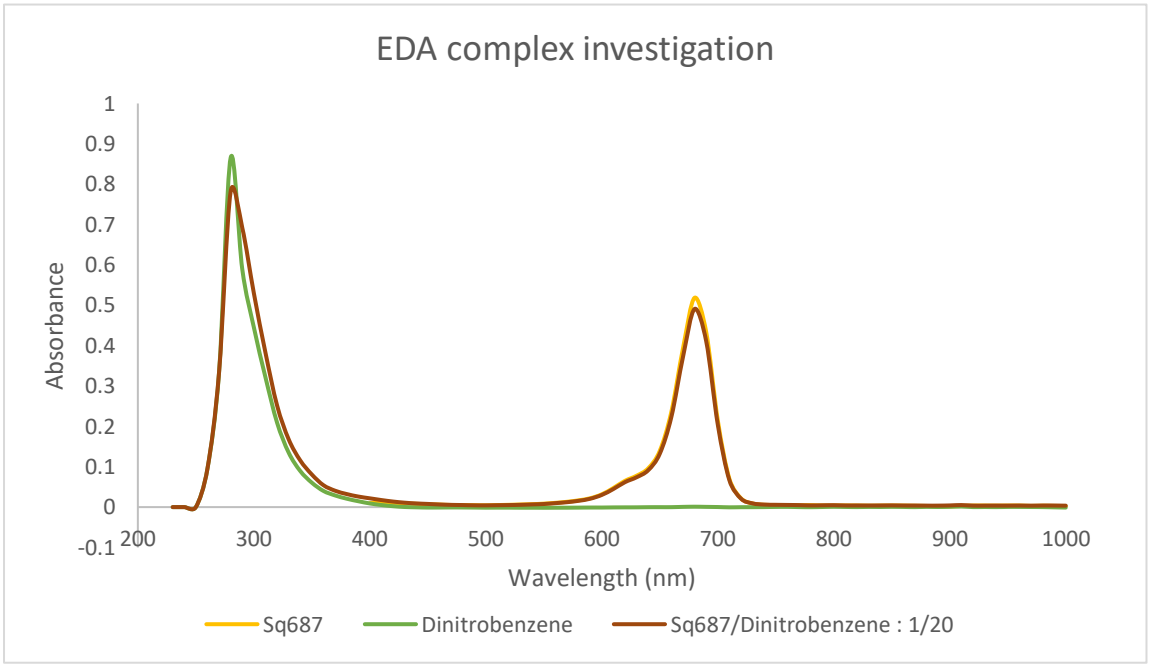
^{1}H NMR spectra of Sq687 in $CDCl_3$ before irradiation



^{1}H NMR spectra of the crude product in $CDCl_3$ after 24h of irradiation

EDA complex investigation:

To control if any electron donor-acceptor complex took place in the mechanism of the photocatalysis in the case who 1,3-dinitrobenzene was used as co-oxidant, we measured the absorbance of the mixture Sq687/1,3-dinitrobenzene. (With the same proportion as in the reaction media) For the spectrum of Sq687 and 1,3-dinitrobenzene, concentrations were plot at 20 µmol and 20 mM respectively in DMSO.



$^{1}O_2$ generation: control experiment

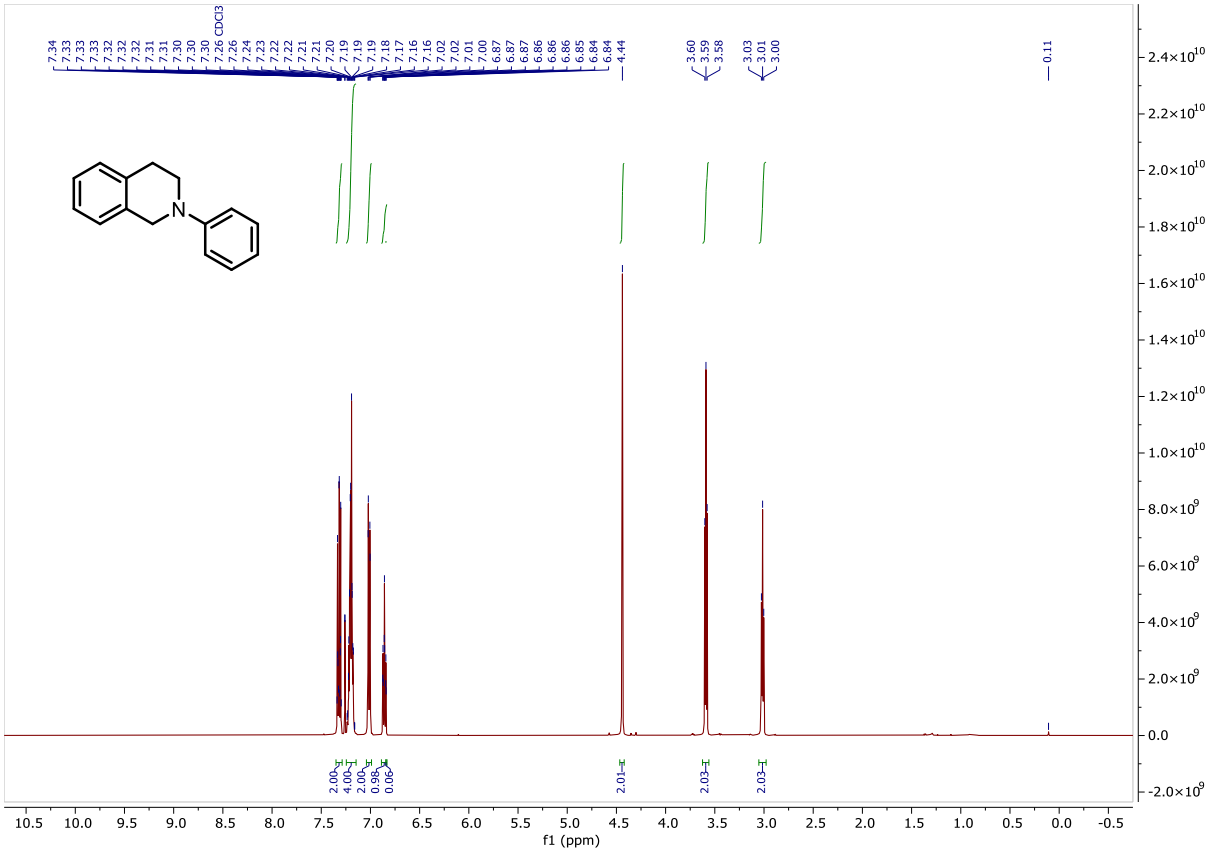
3 **4**

1,2,3,4-tetraphenylcyclopentadienone **3** (70 mg, 0.13 mmol, 1 equiv.), Sq687 (5.3 mg, 0.009 mmol, 5 mol%) and DMSO-d6 (2 mL) were charged in a reaction glass tube with magnetic stirring bar. Then O_2 was bubbled for 15 min, after, the reaction mixture was stirred under O2 atmosphere (1 atm., balloon) and near infrared LED (810 nm) irradiation (2-3 cm away from the light source) at room temperature for 24 h. No conversion of start was observed after 24 h, only few traces of the corresponding product **4**.

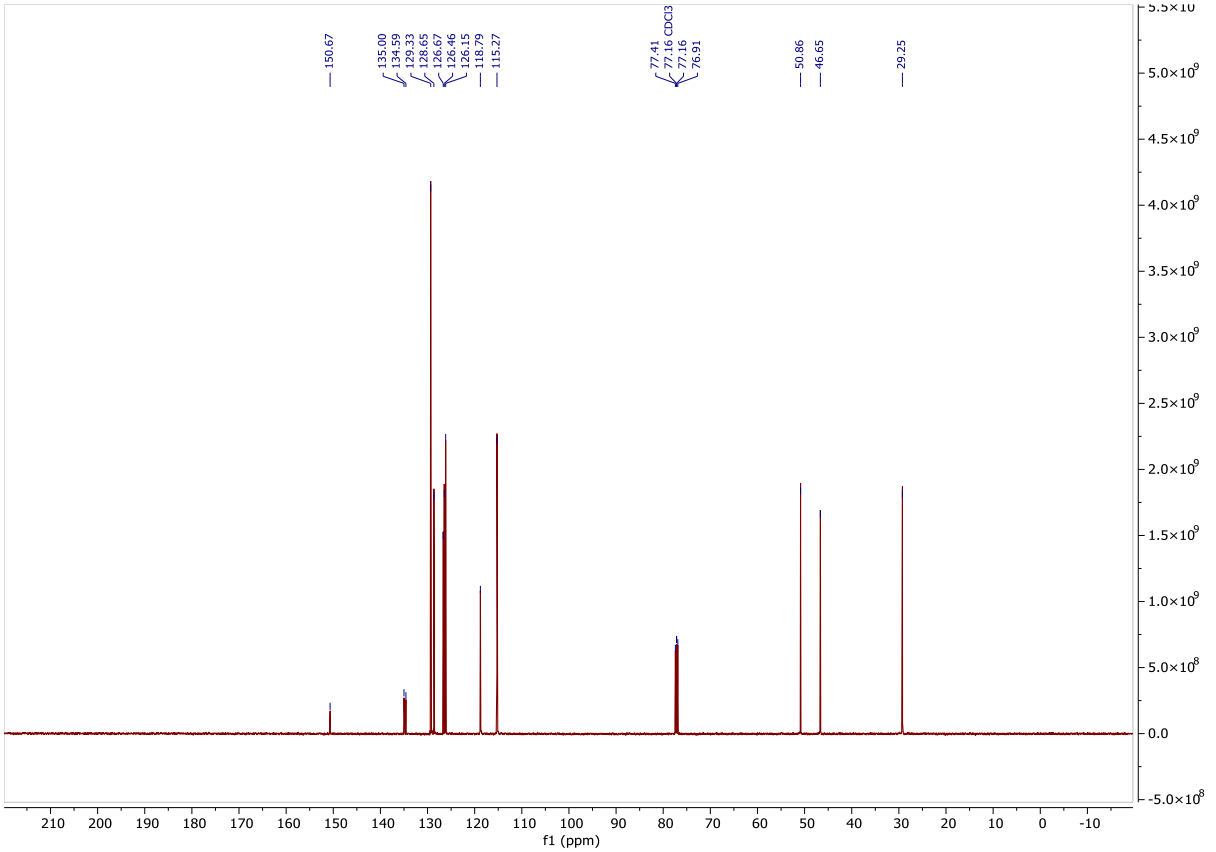
5. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra of products:

2-phenyl-1,2,3,4-Tetrahydroisoquinoline (1a)

^{1}H $CDCl_3$

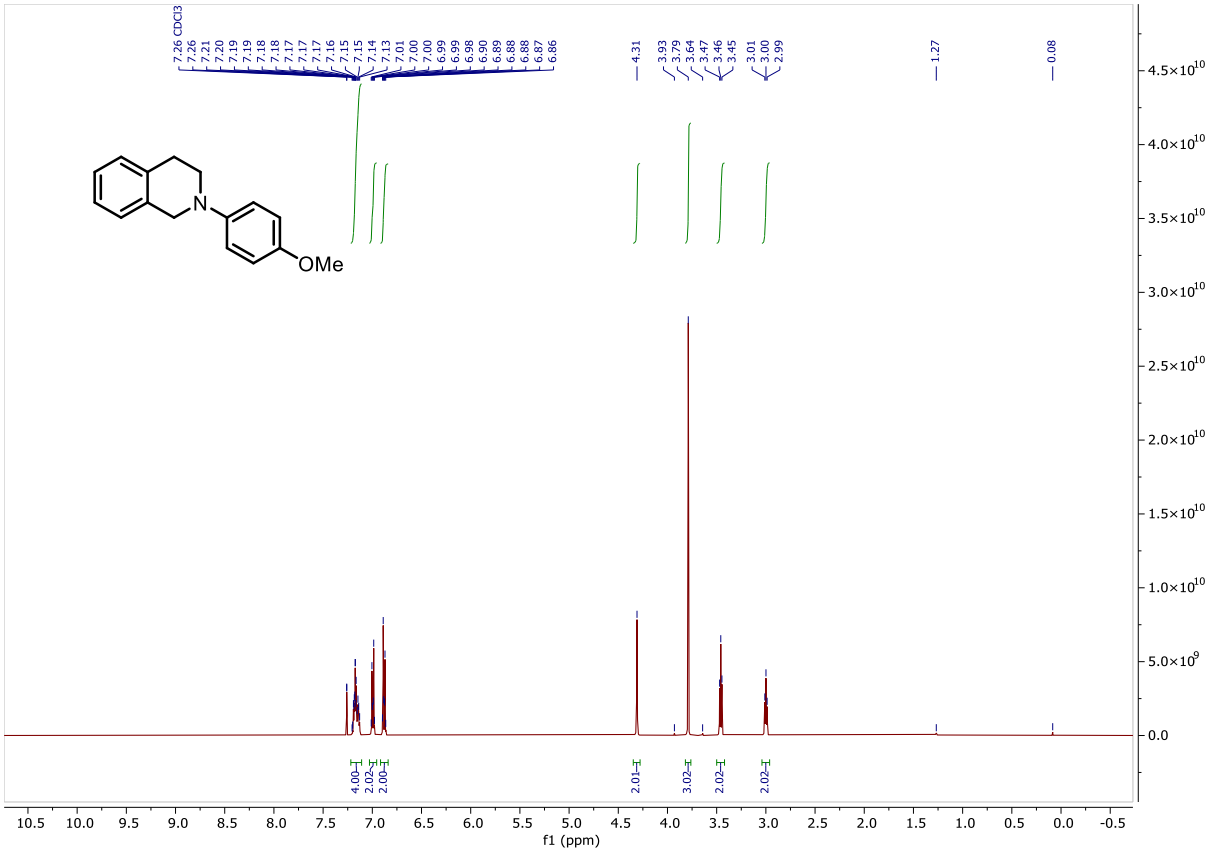


^{13}C $CDCl_3$

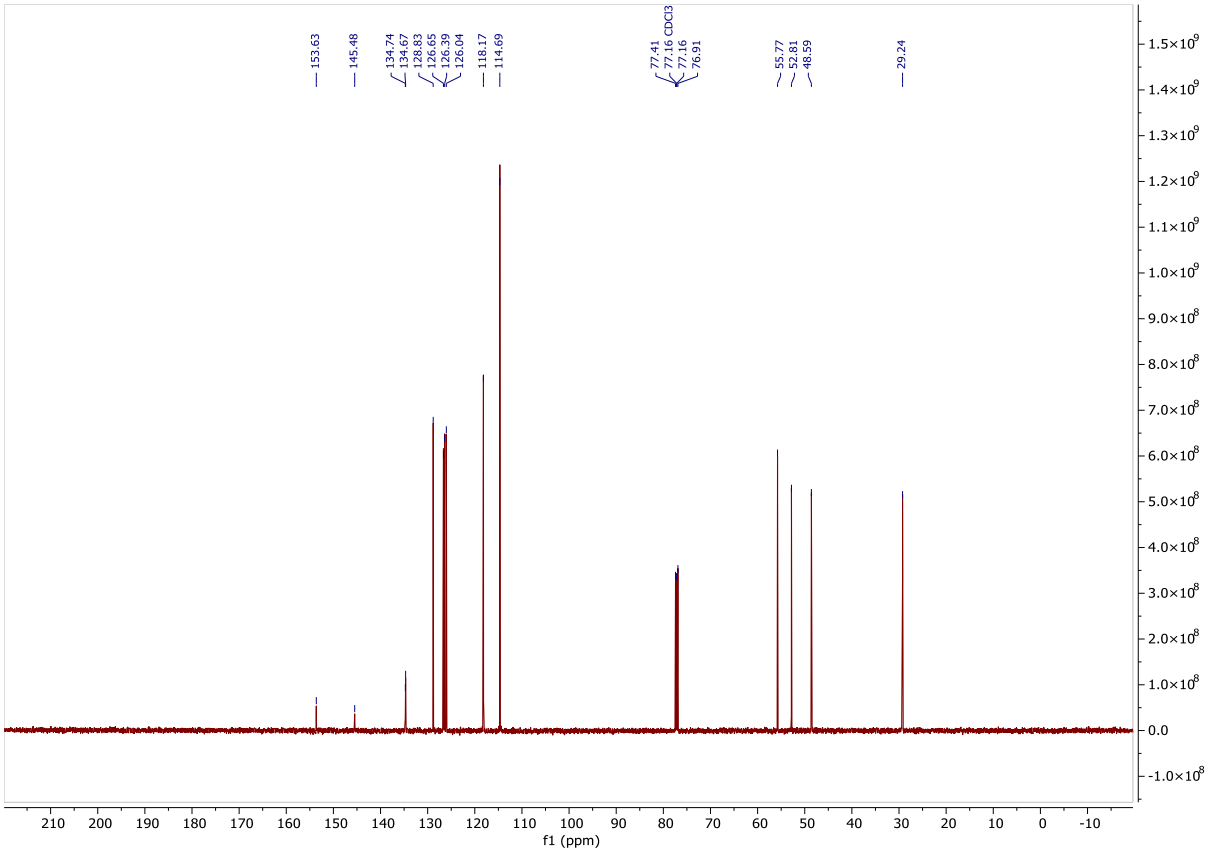


2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (1b)

^{1}H $CDCl_3$

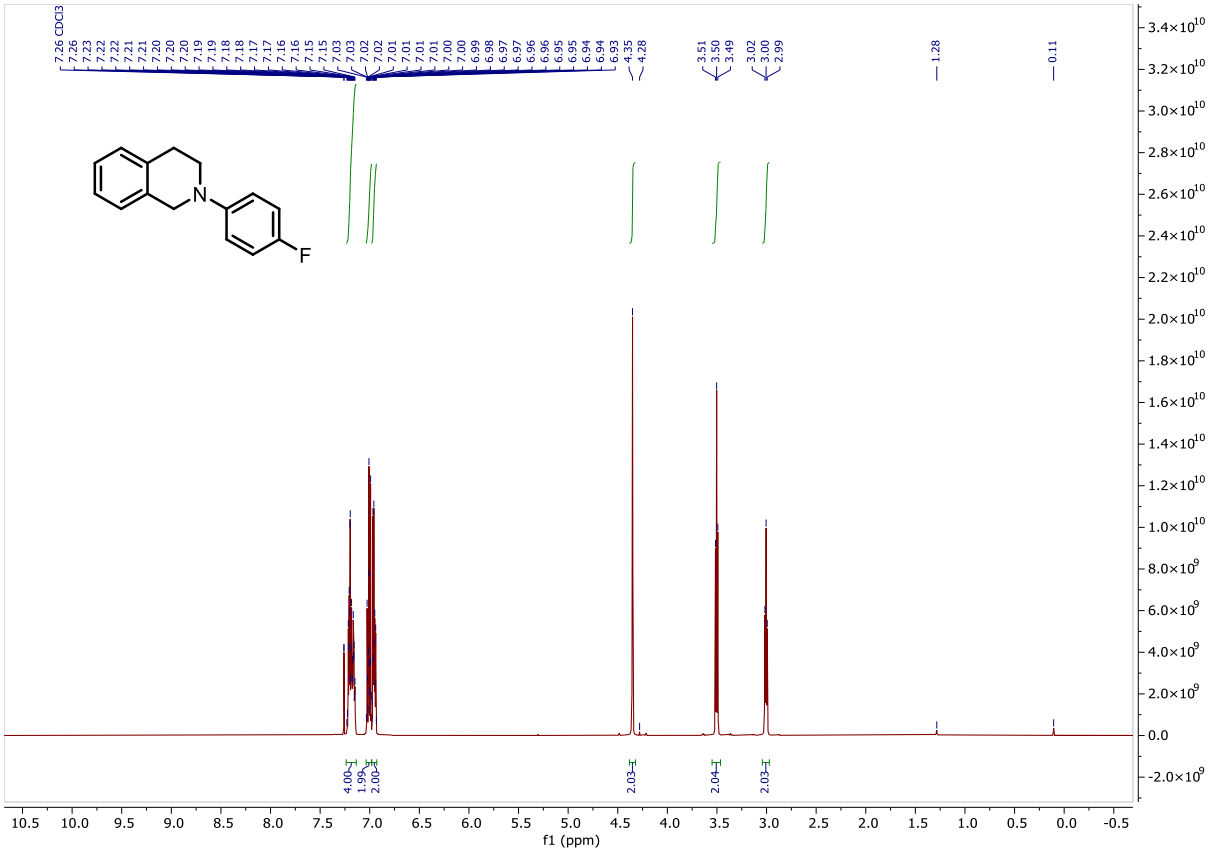


^{13}C $CDCl_3$

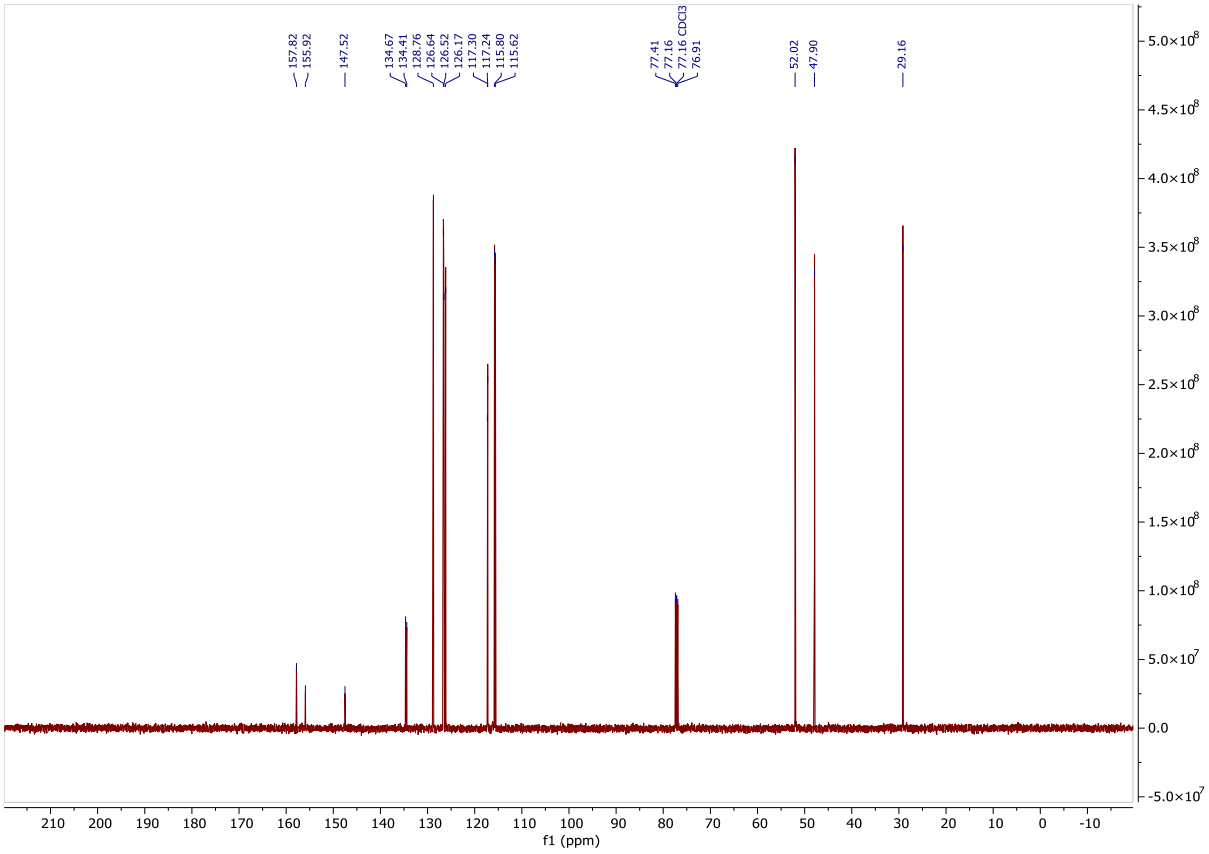


2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (1c)

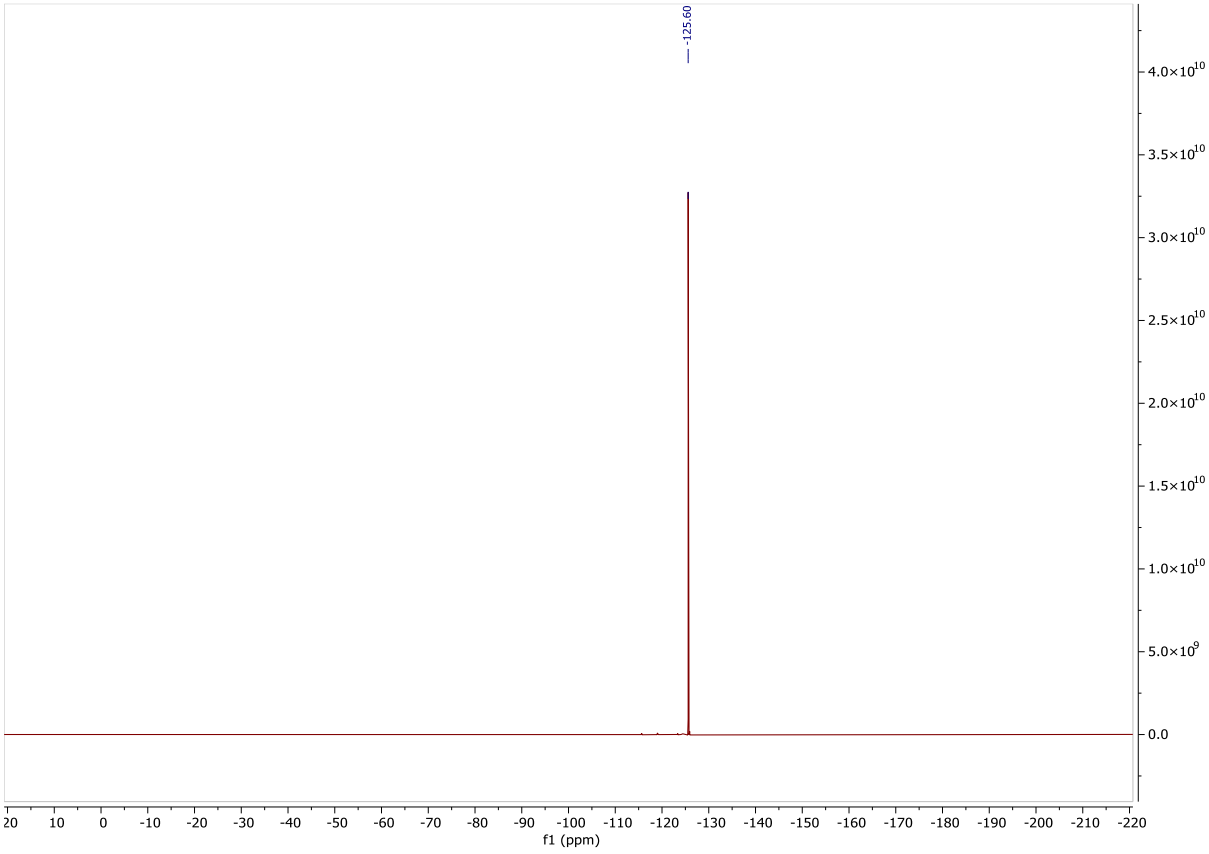
^{1}H $CDCl_3$



^{13}C $CDCl_3$

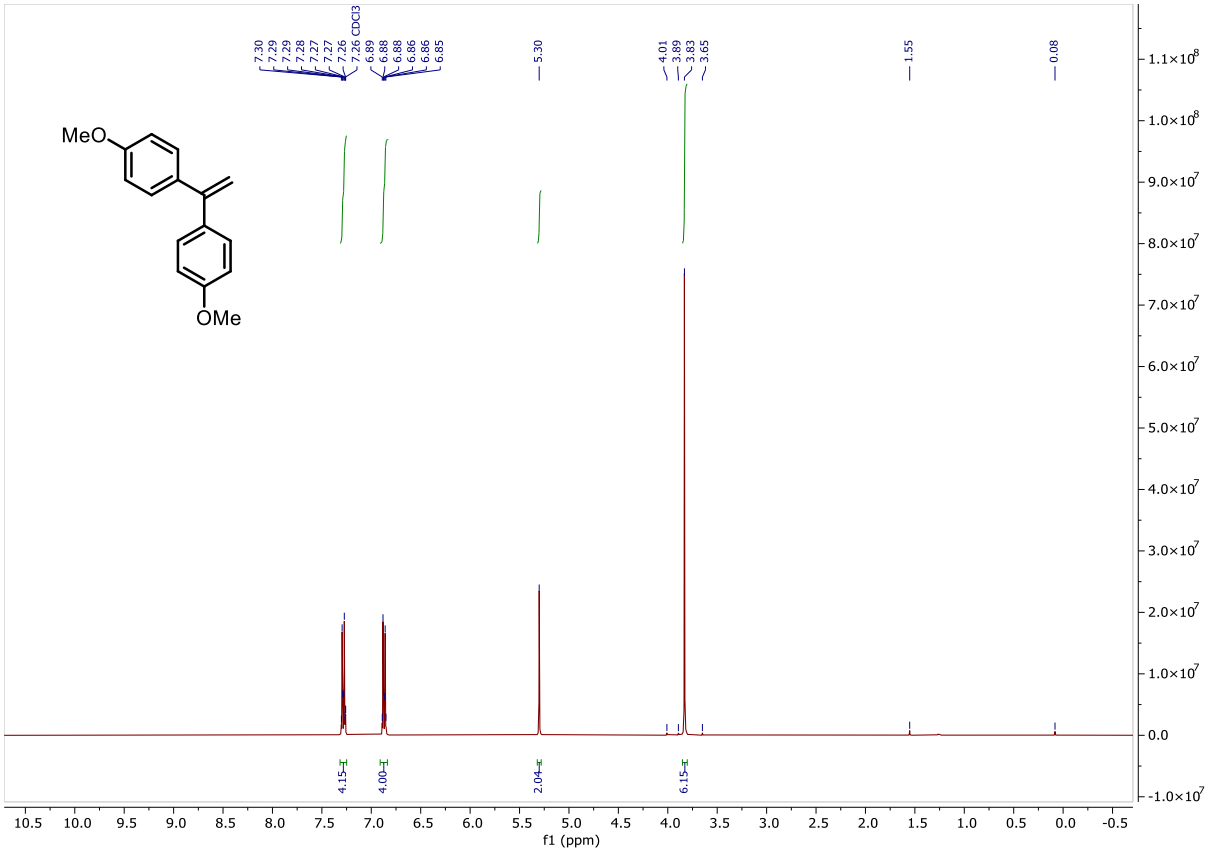


^{19}F $CDCl_3$

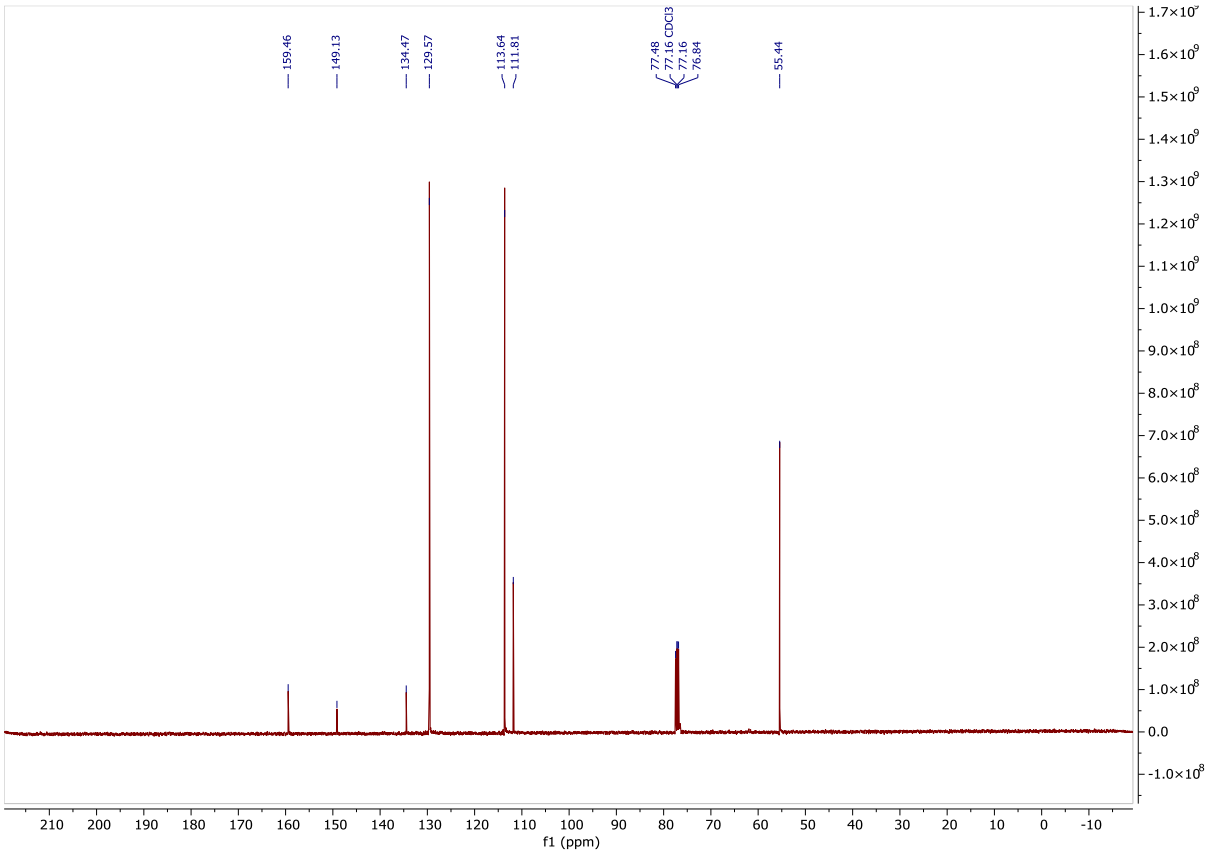


***1,1-bis(4-methoxyphenyl)ethene* (3)**

^{1}H $CDCl_3$

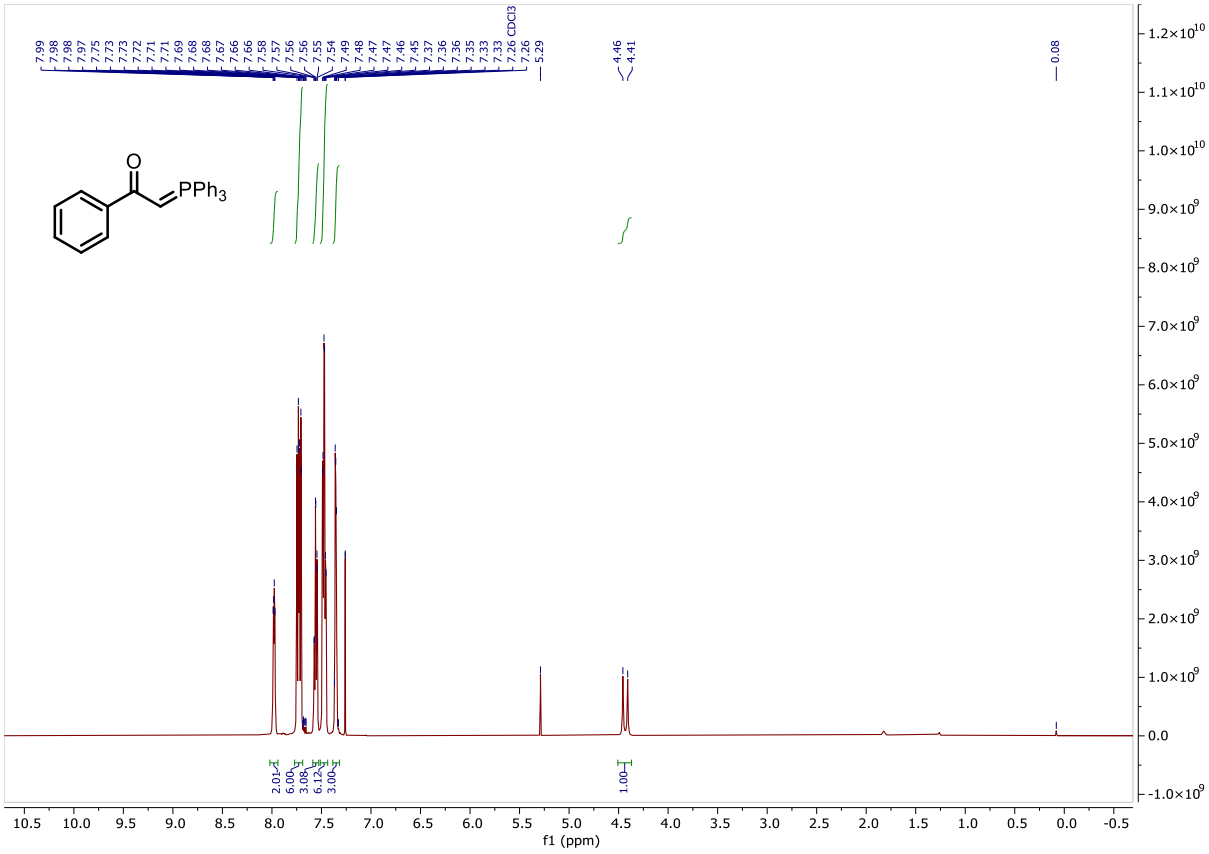


^{13}C $CDCl_3$

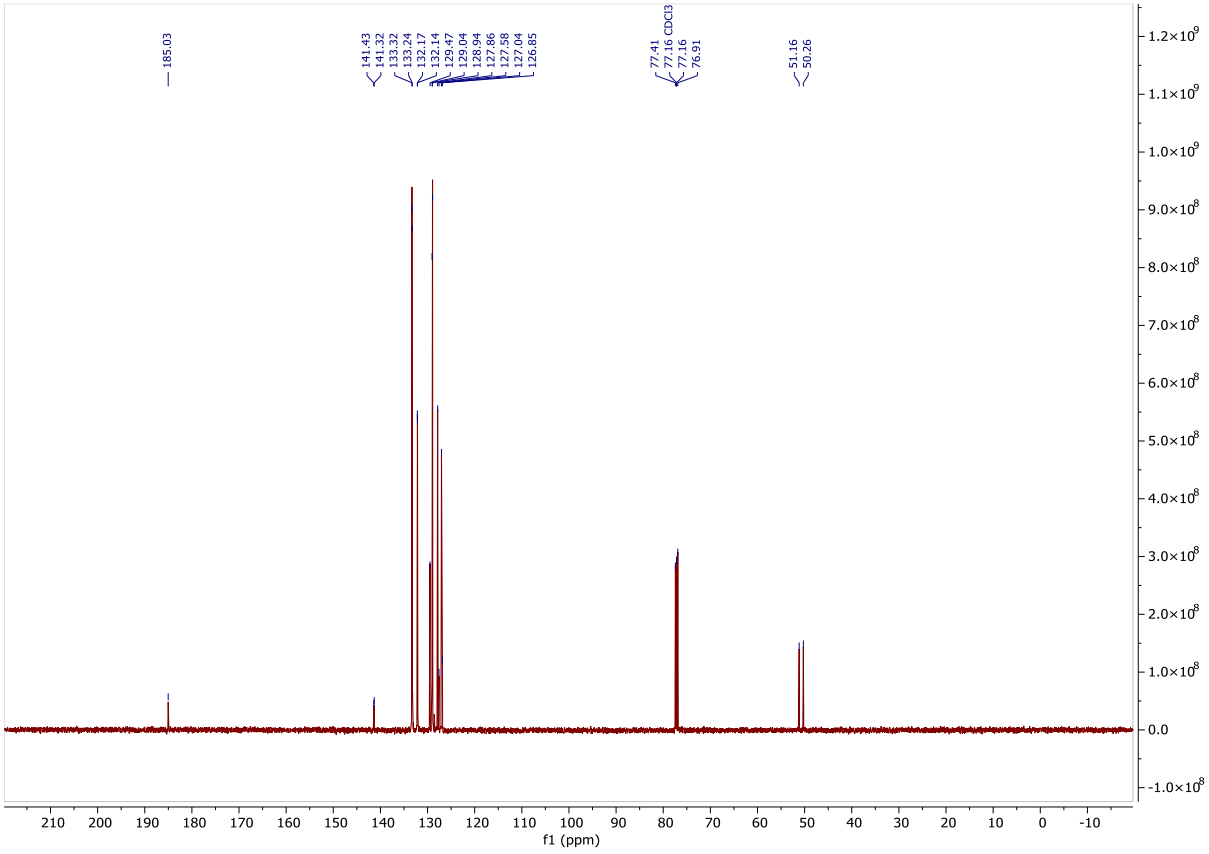


(Benzoylmethylene)triphenylphosphorane (7)

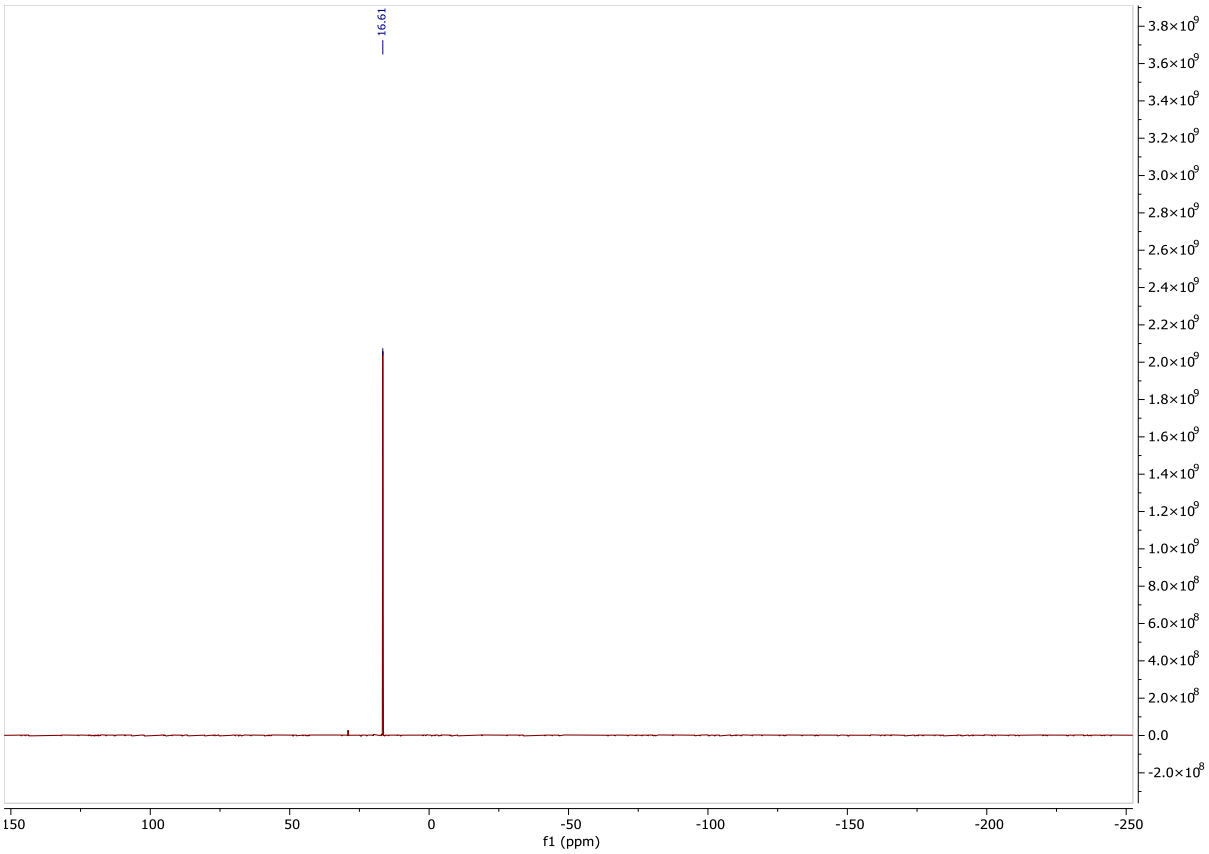
^{1}H $CDCl_3$



^{13}C $CDCl_3$

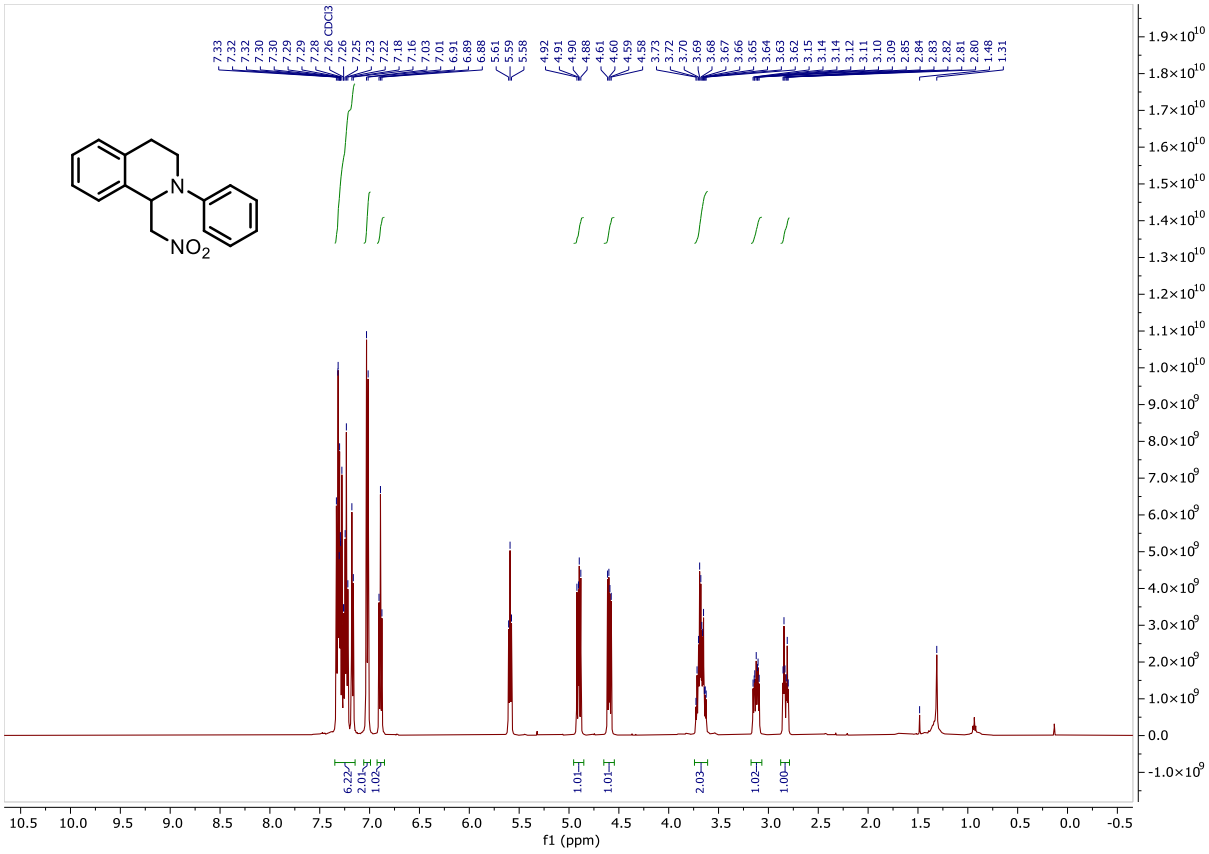

185.03
141.43
141.32
133.32
133.24
132.17
132.14
129.47
129.04
128.94
127.86
127.58
127.04
126.85
77.41
77.16 CDCl3
77.16
76.91
51.16
50.26
f1 (ppm)

^{31}P $CDCl_3$

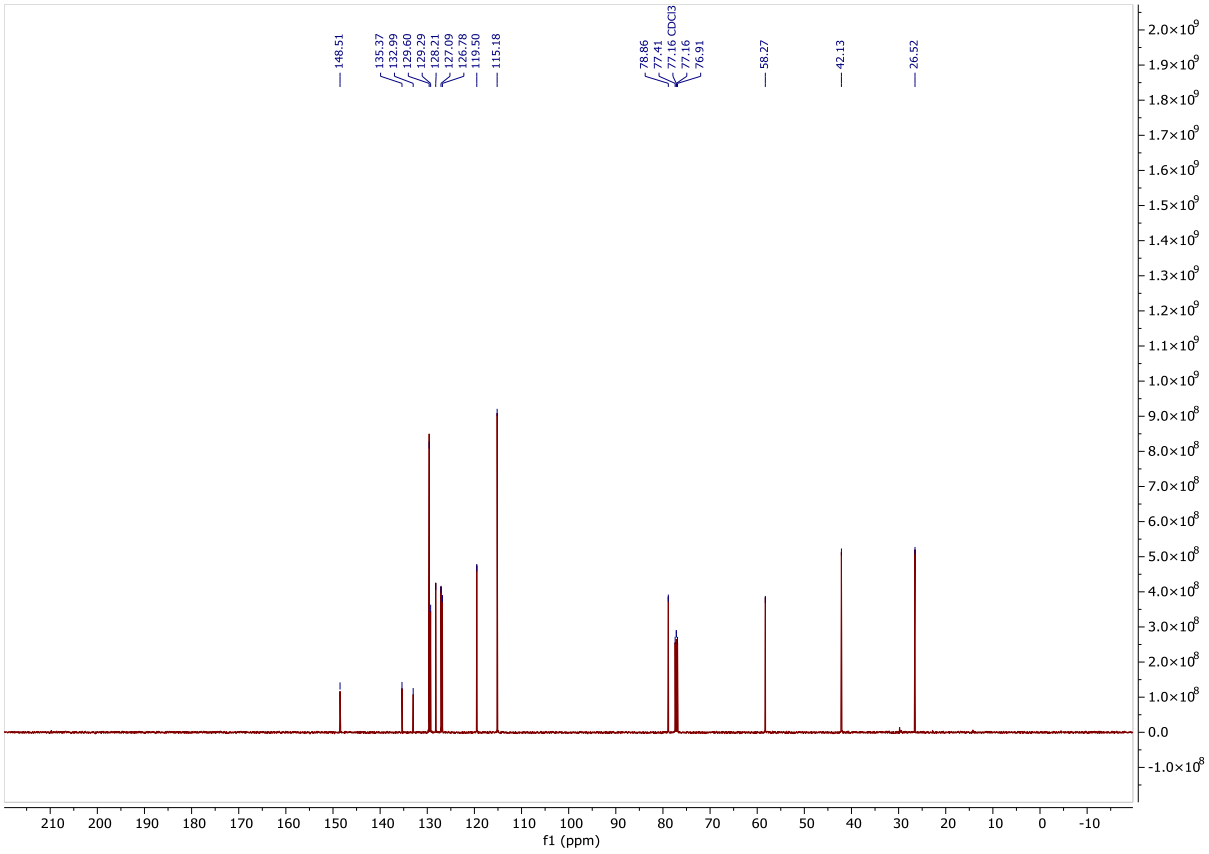

16.61
f1 (ppm)

***1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline* (2a)**

^{1}H $CDCl_3$

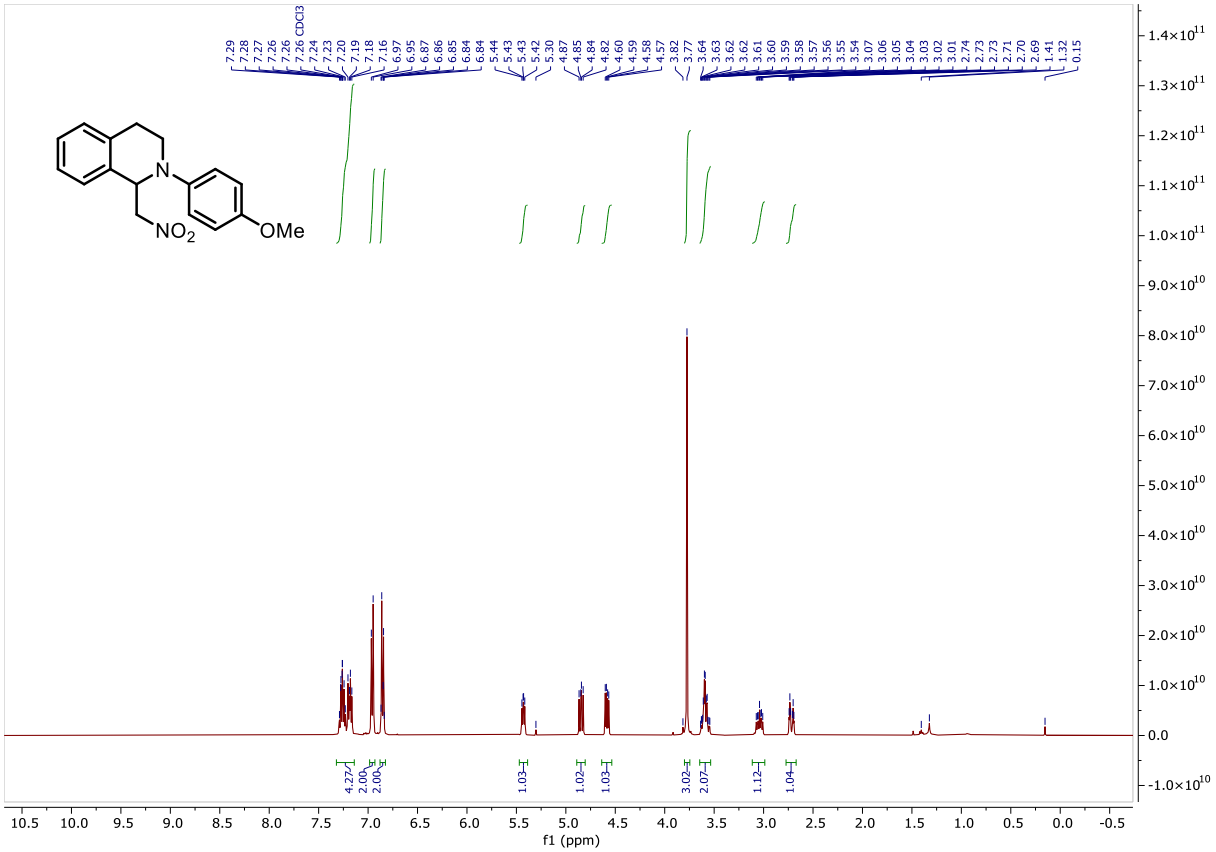


^{13}C $CDCl_3$

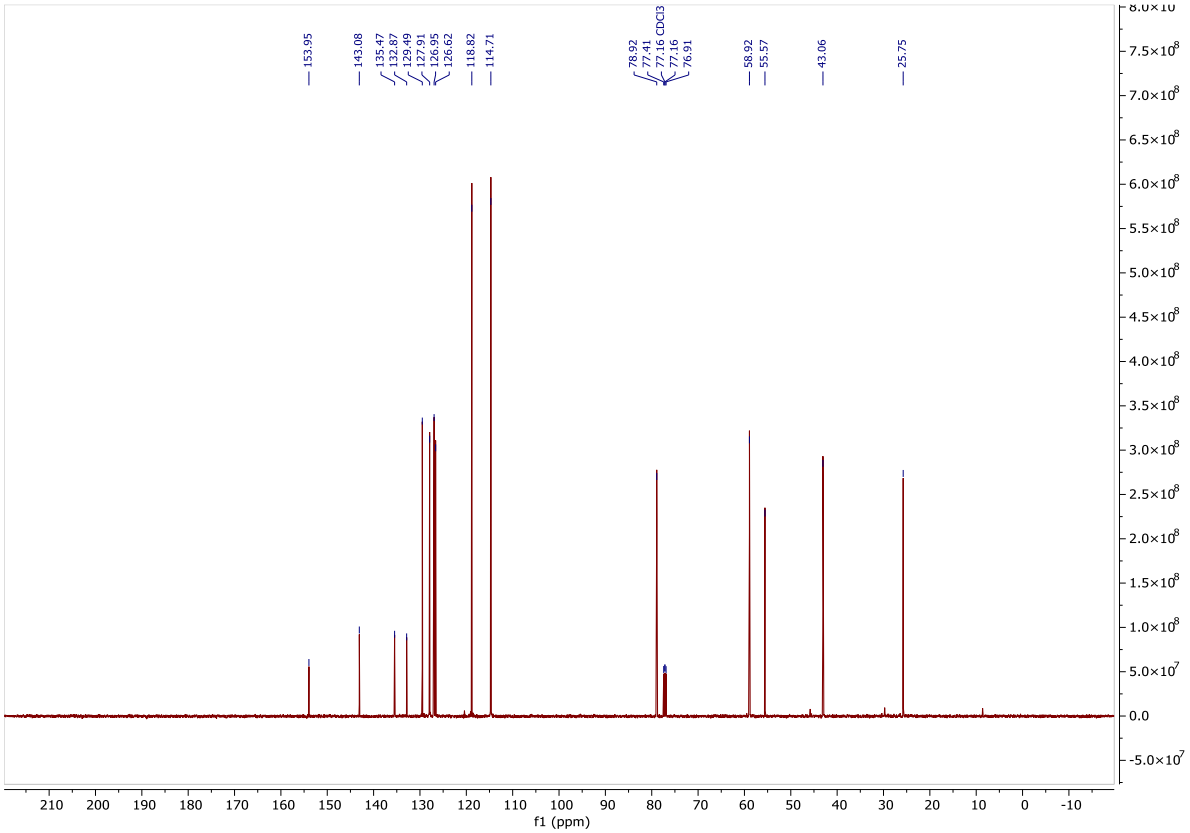


***2-(4-methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline* (2b)**

^{1}H $CDCl_3$

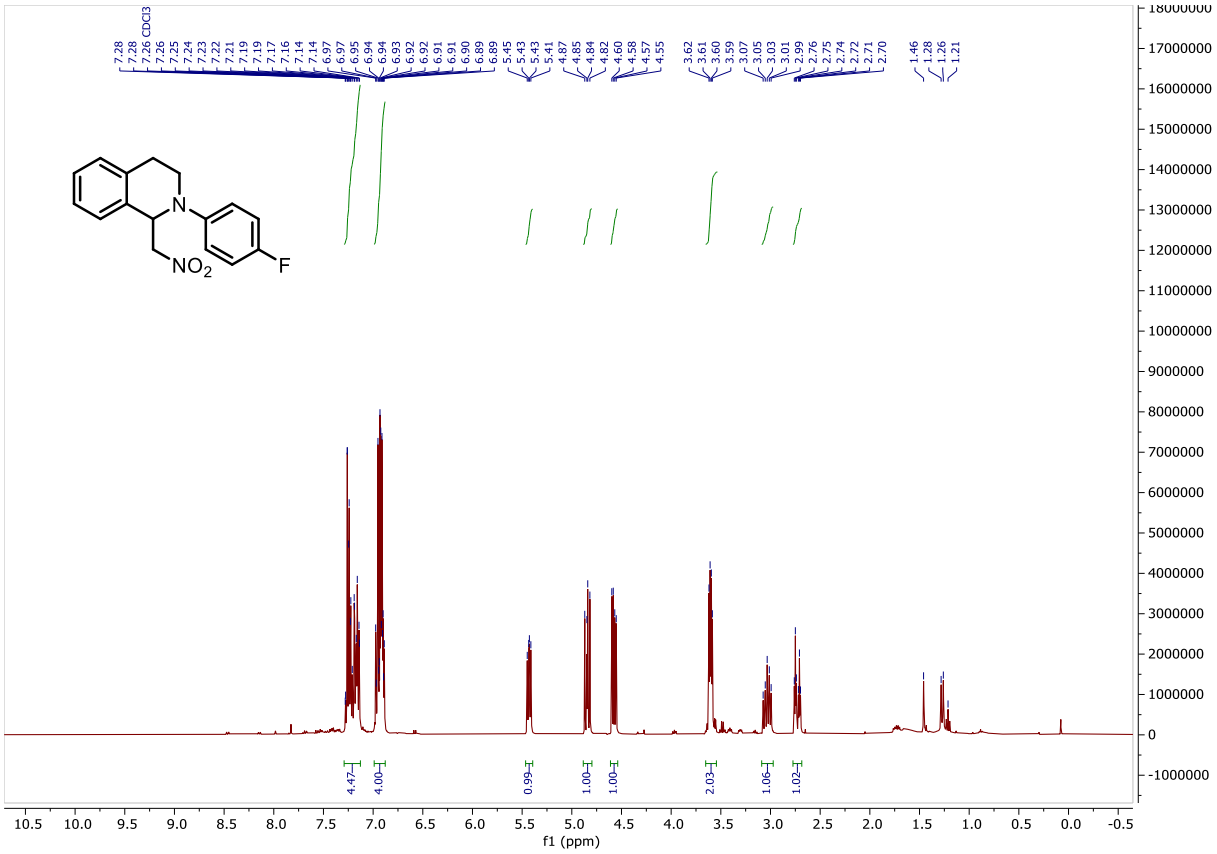


^{13}C $CDCl_3$

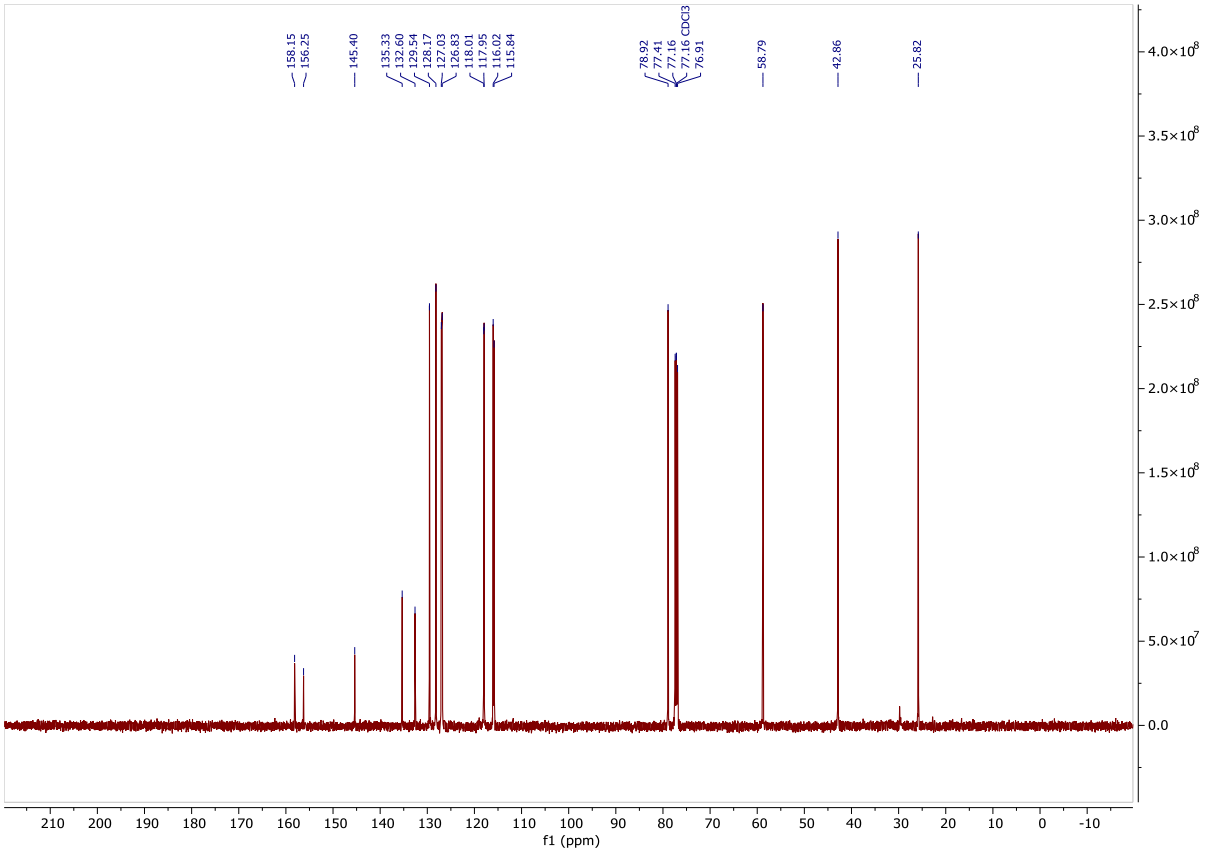


***2-(4-fluorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline* (2c)**

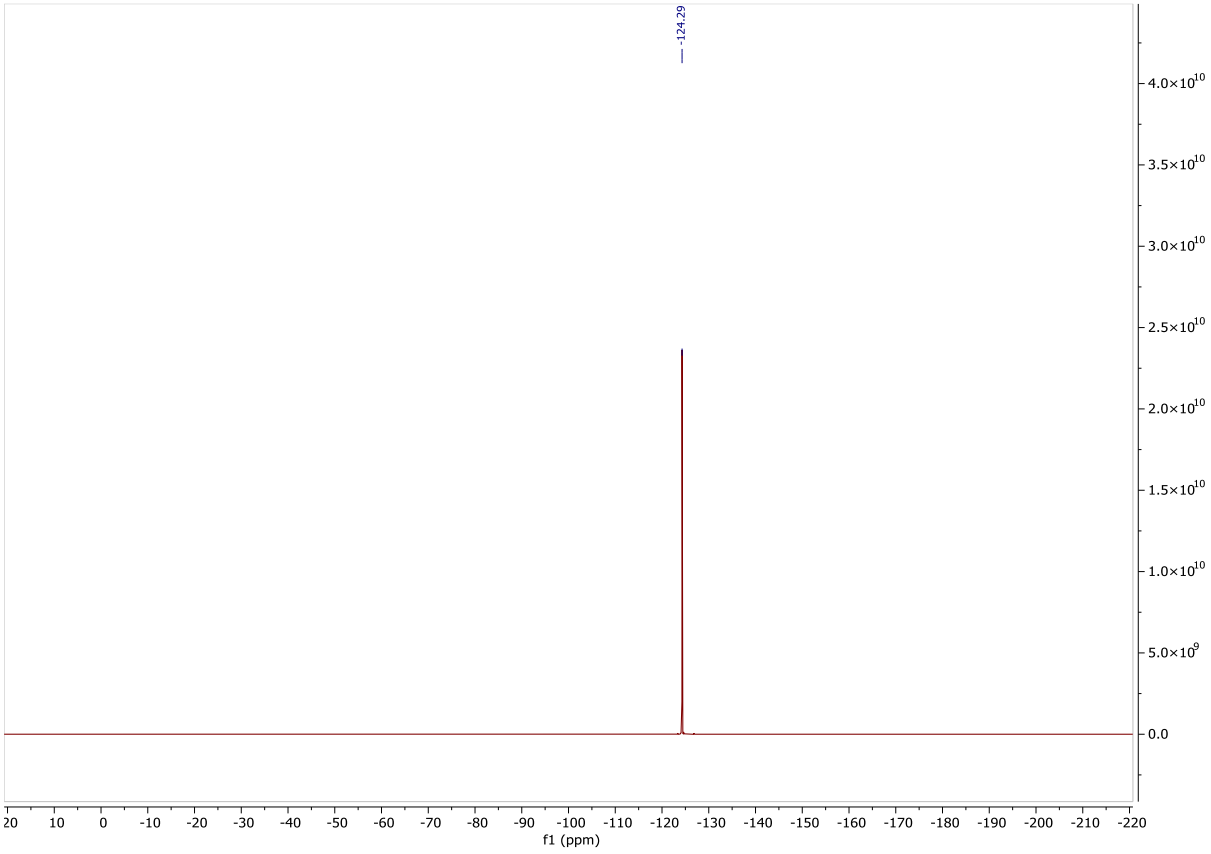
^{1}H $CDCl_3$



^{13}C $CDCl_3$

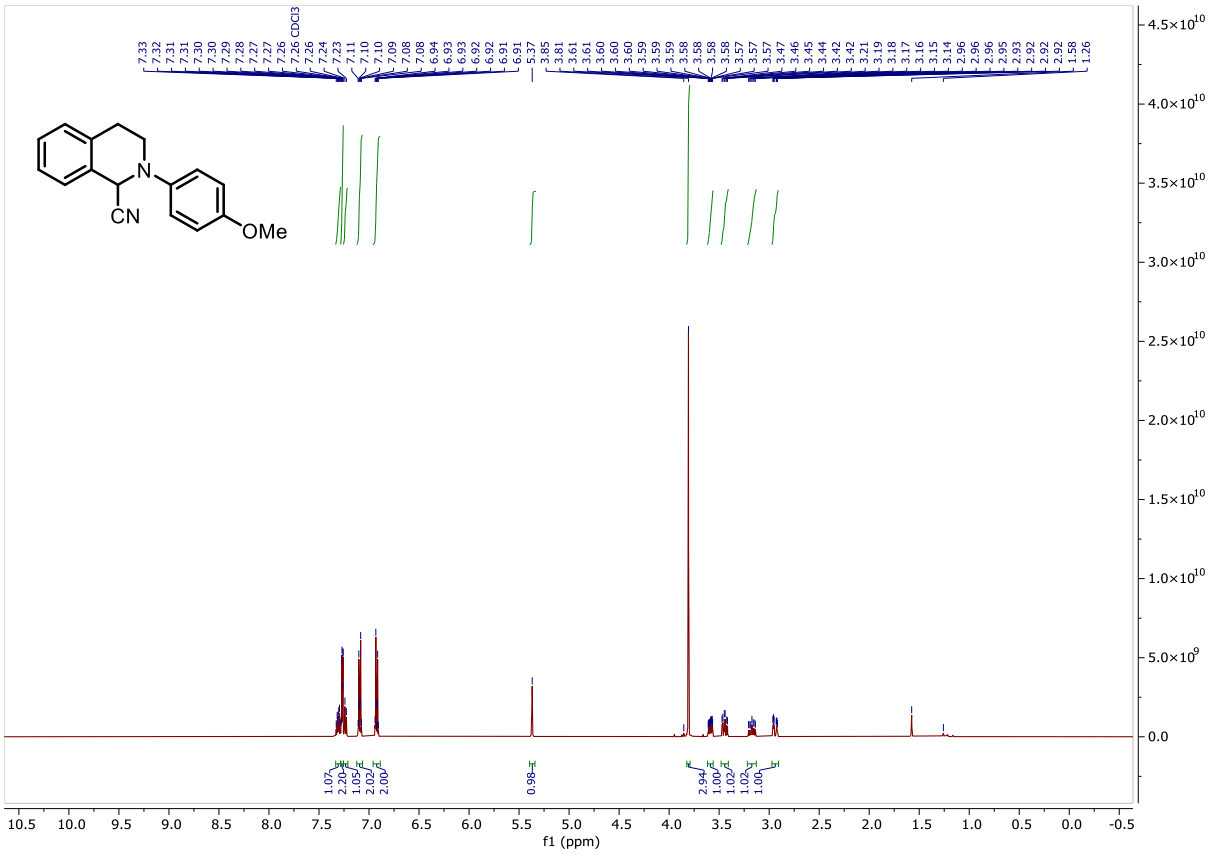


^{19}F $CDCl_3$

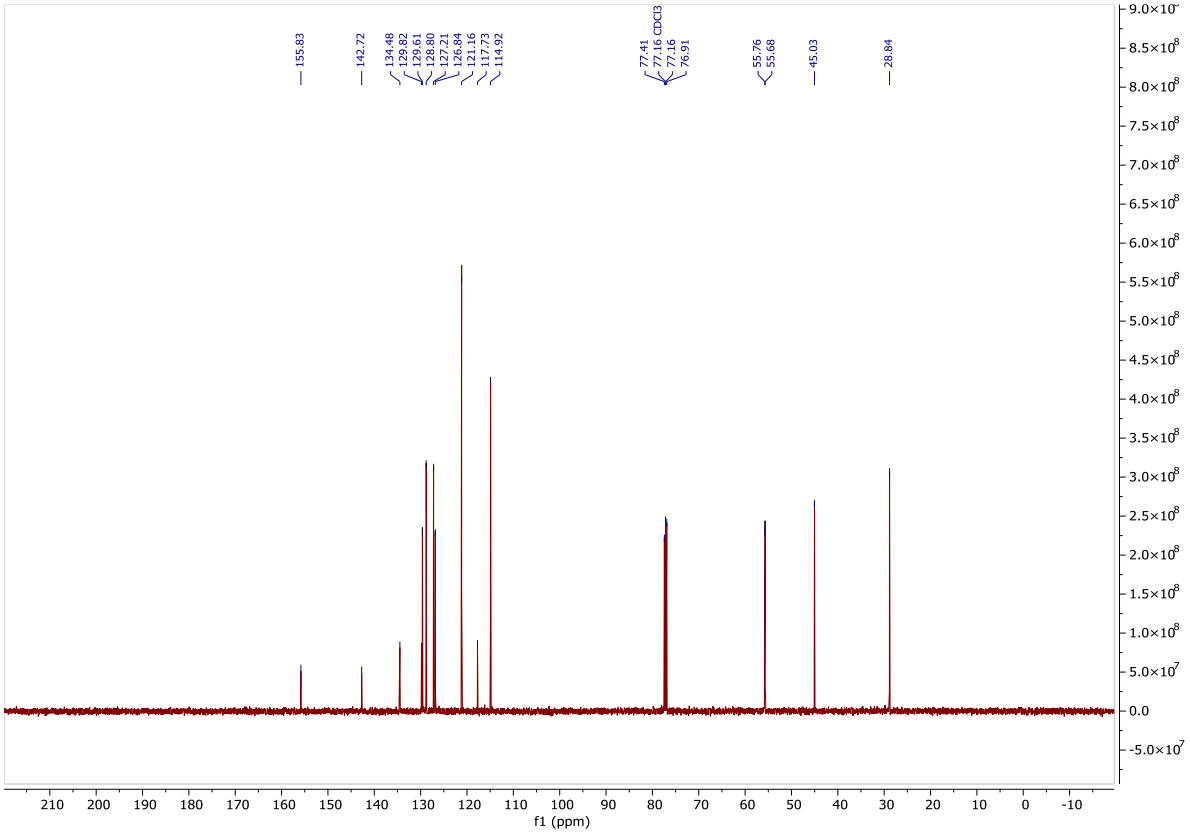


2-(*4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile* (2d)

^{1}H $CDCl_3$

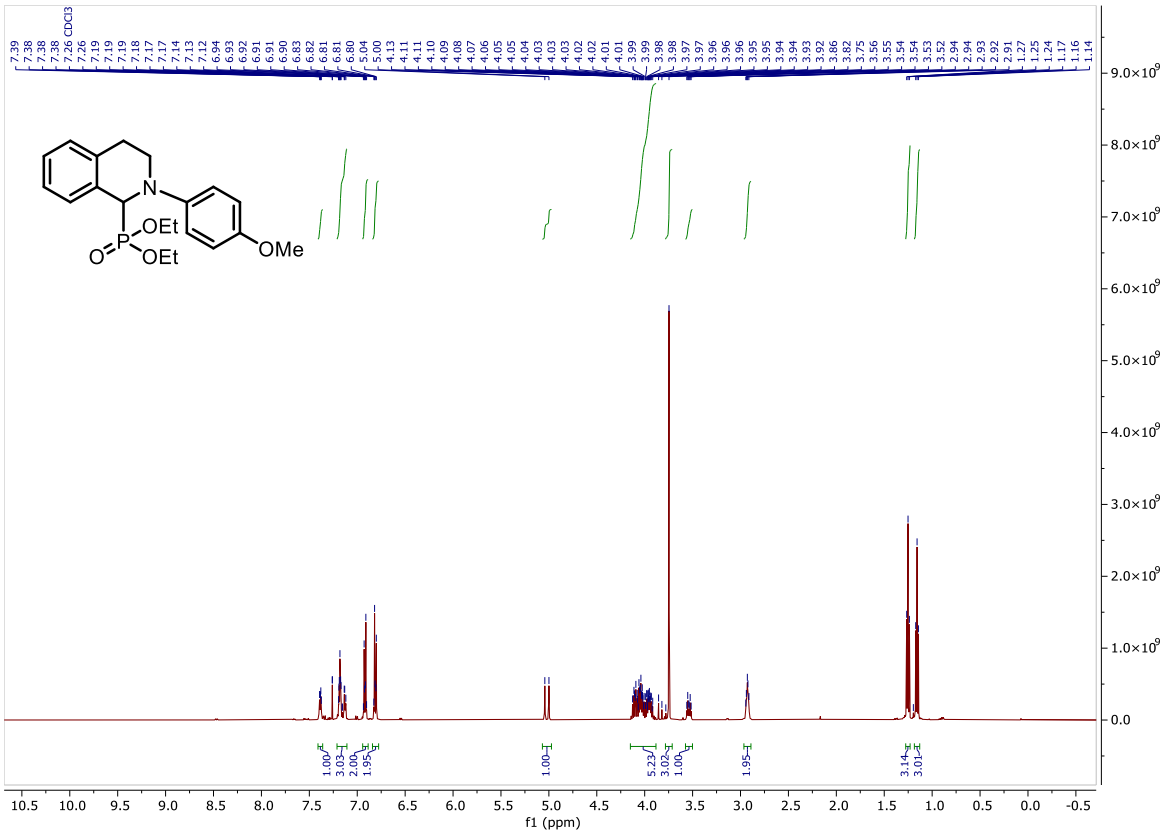


^{13}C $CDCl_3$

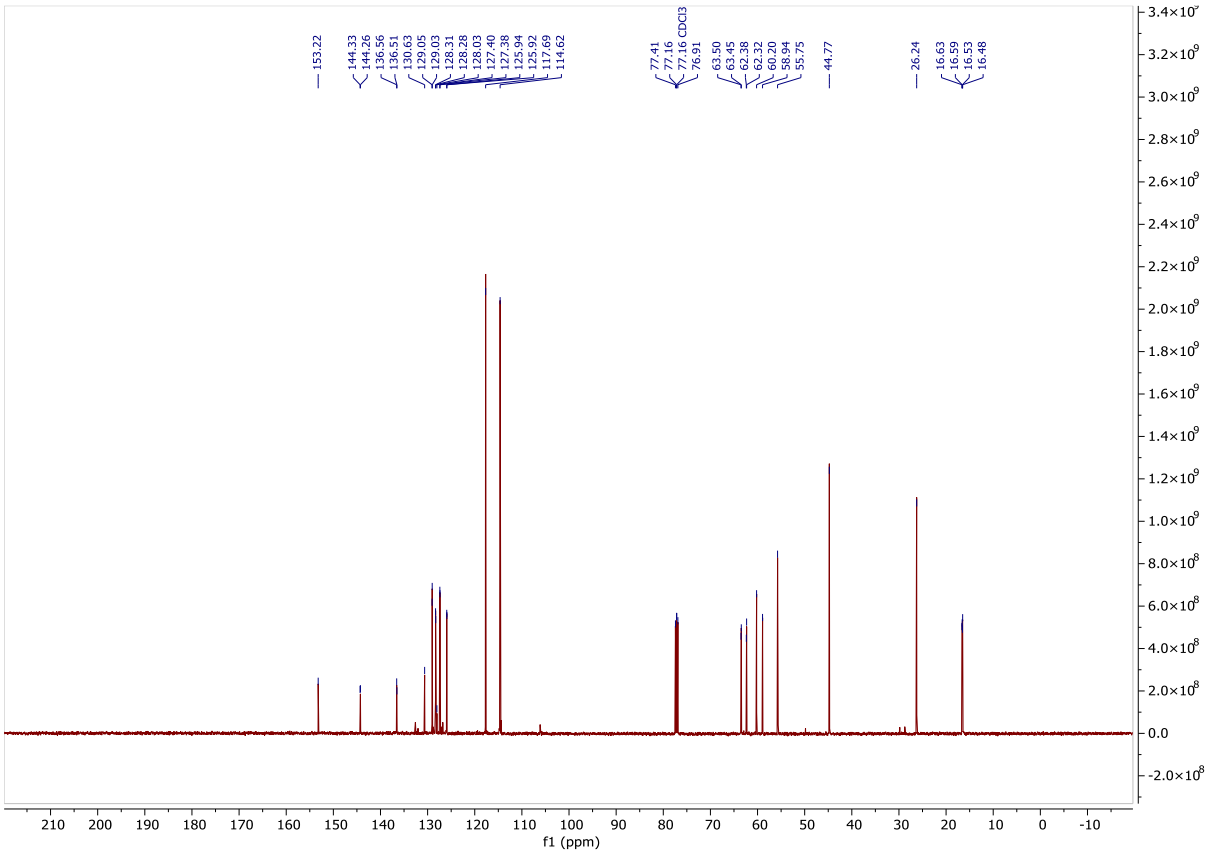


diethyl (2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate **(2 h)**

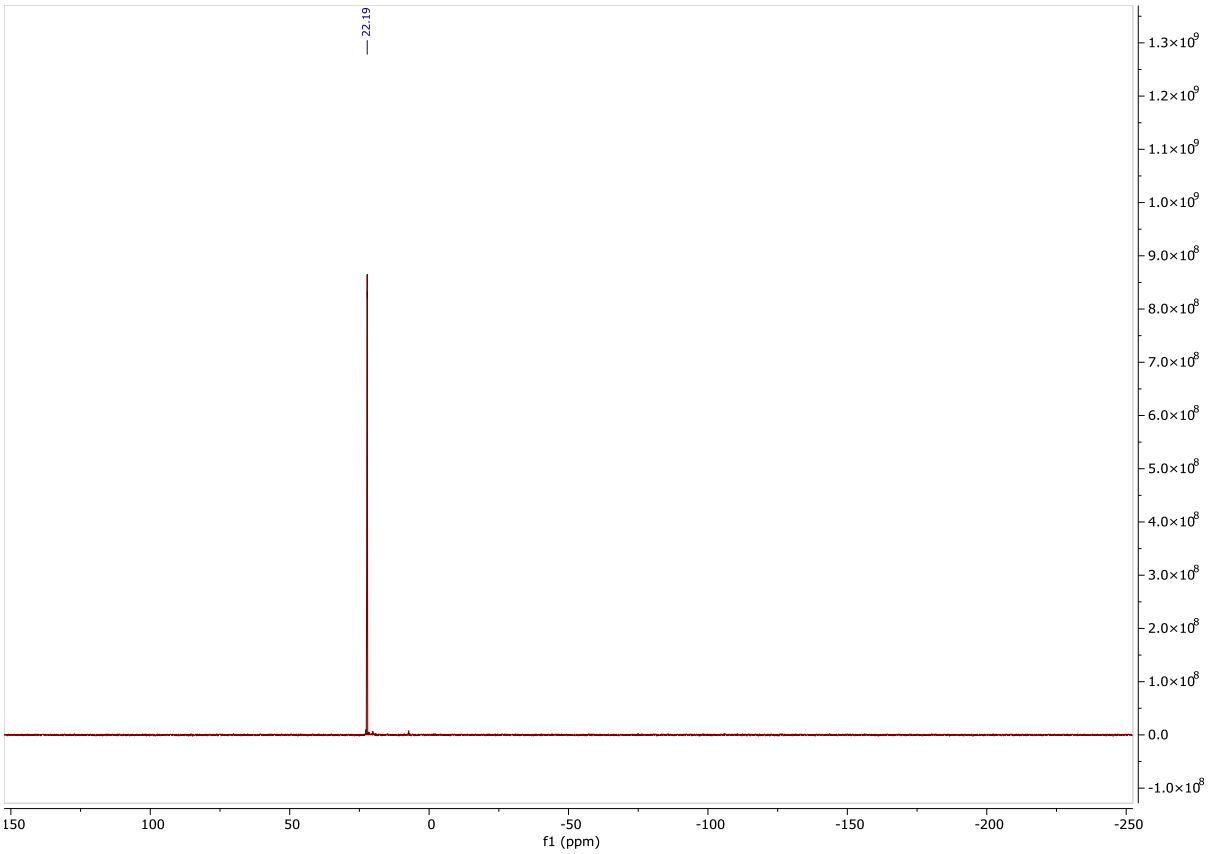
^{1}H $CDCl_3$



^{13}C $CDCl_3$

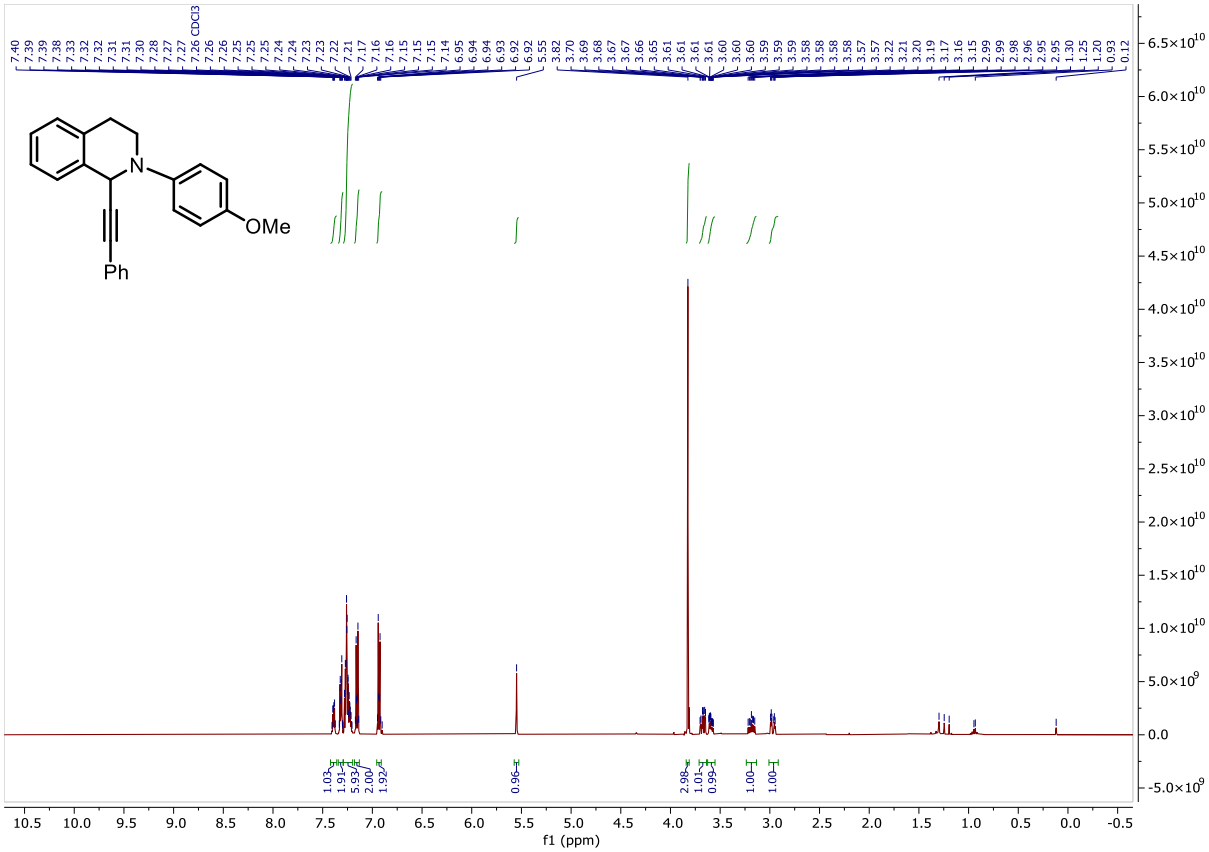

153.22
144.33
144.26
136.56
136.51
130.63
129.05
129.03
128.31
128.28
128.03
127.40
127.38
125.94
125.92
117.69
114.62
77.41
77.16
77.16 CDCl3
76.91
63.50
63.45
62.38
62.32
60.20
58.94
55.75
44.77
26.24
16.63
16.59
16.53
16.48
f1 (ppm)

^{31}P $CDCl_3$

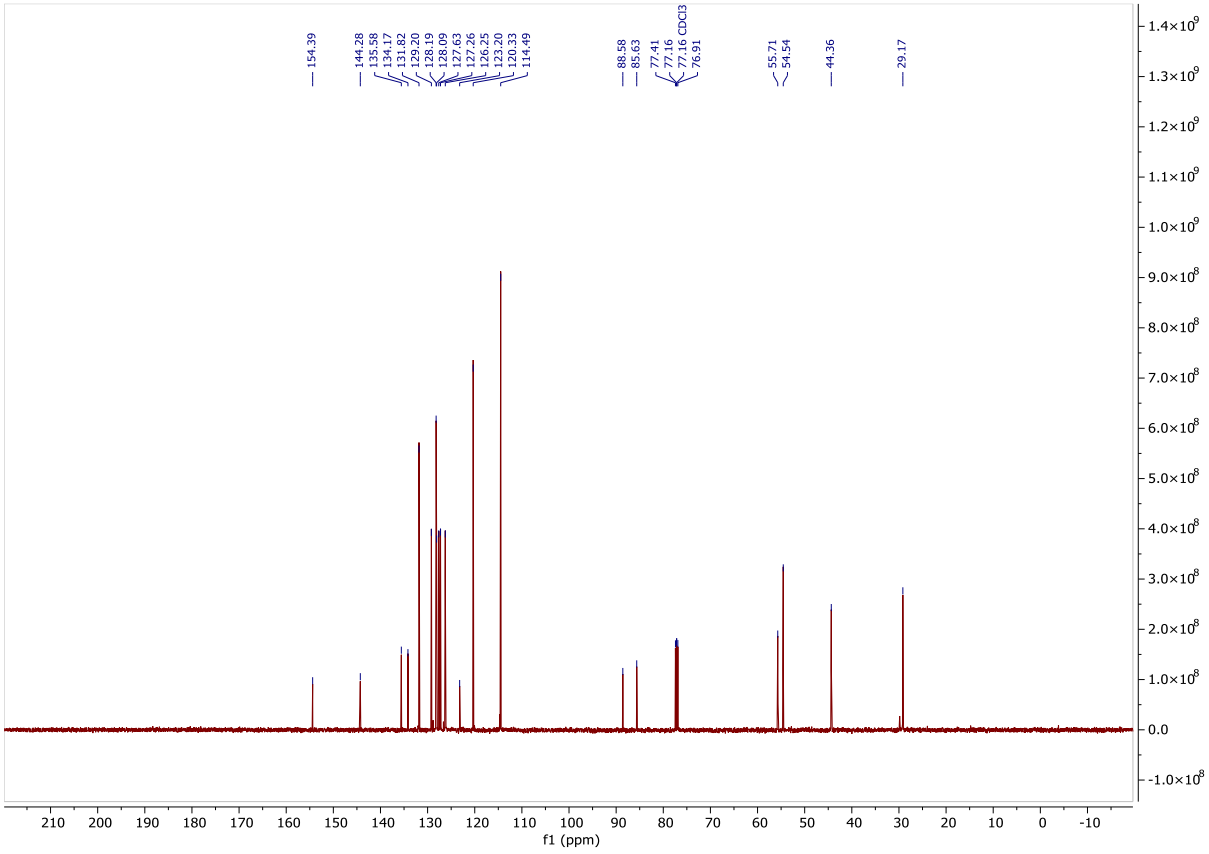

22.19
f1 (ppm)

2-(4-methoxyphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (2f)

^{1}H $CDCl_3$

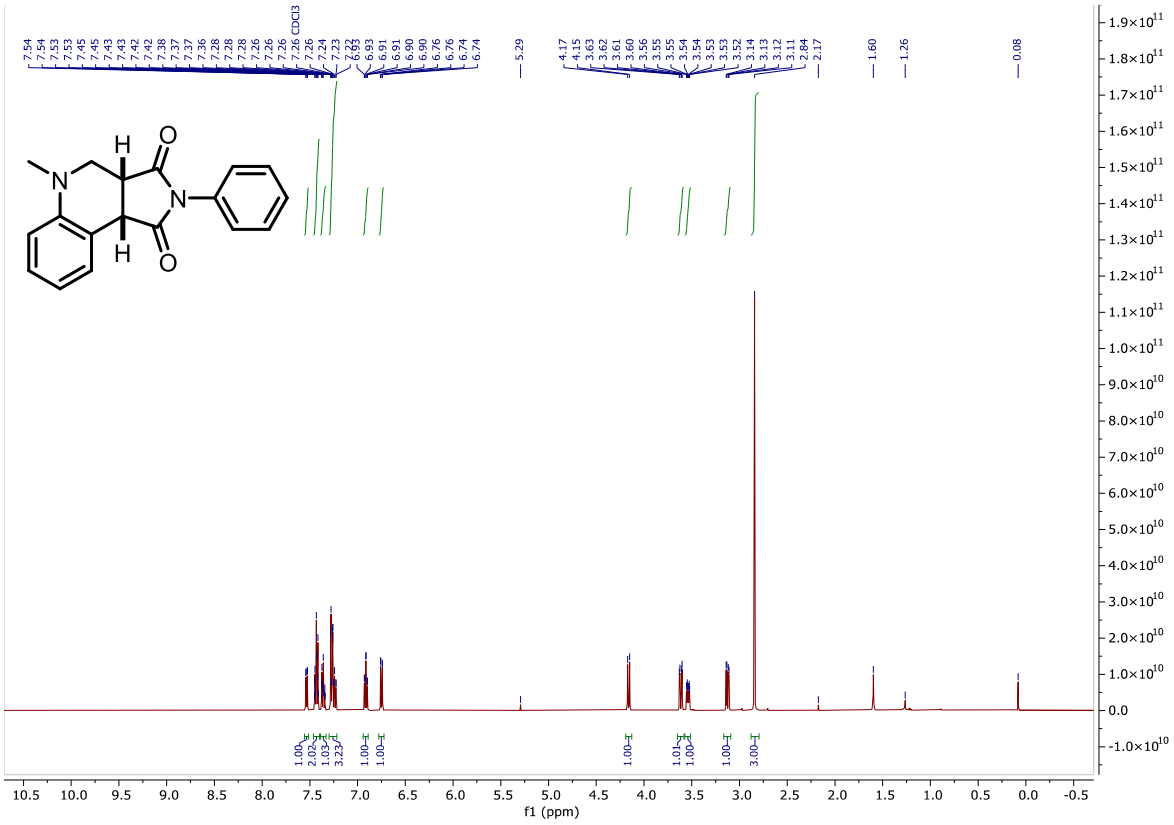


^{13}C $CDCl_3$

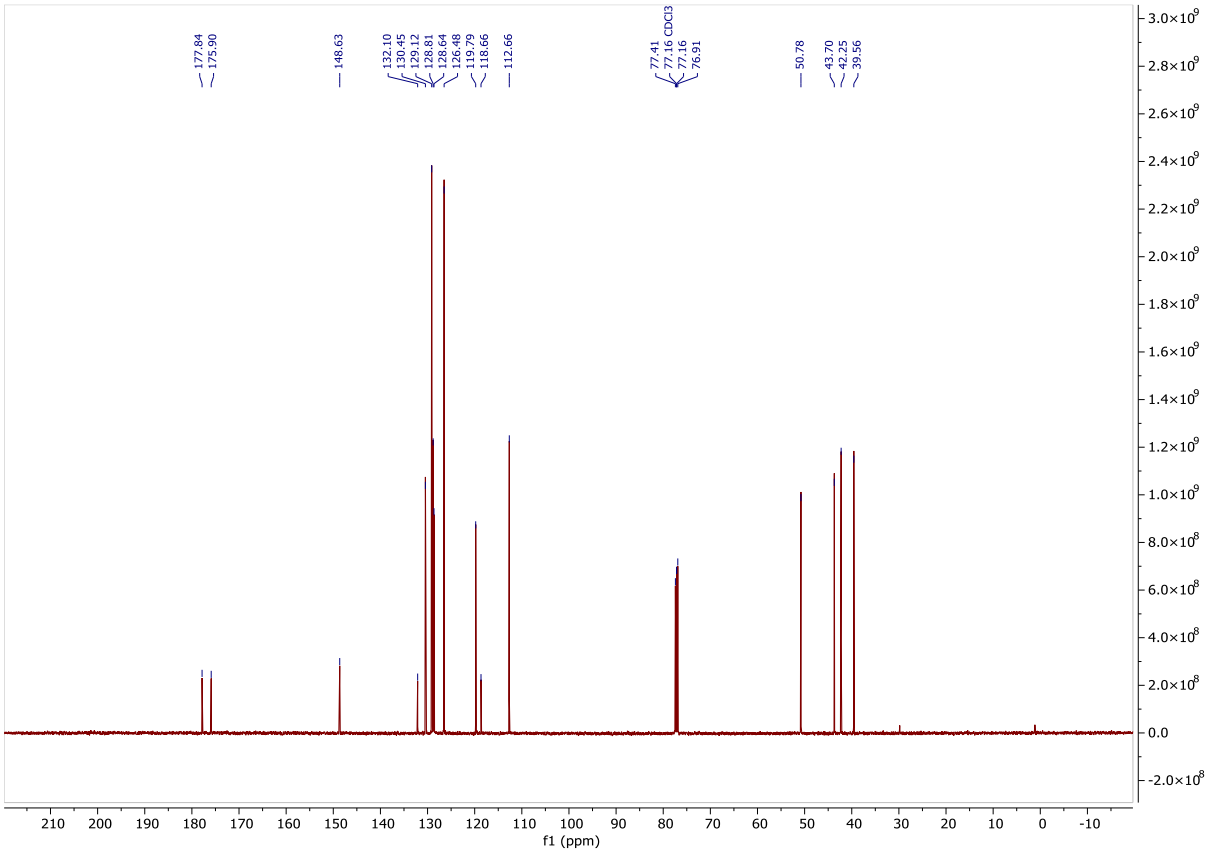


***5-Methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline1,3(2H)-dione* (5)**

^{1}H $CDCl_3$

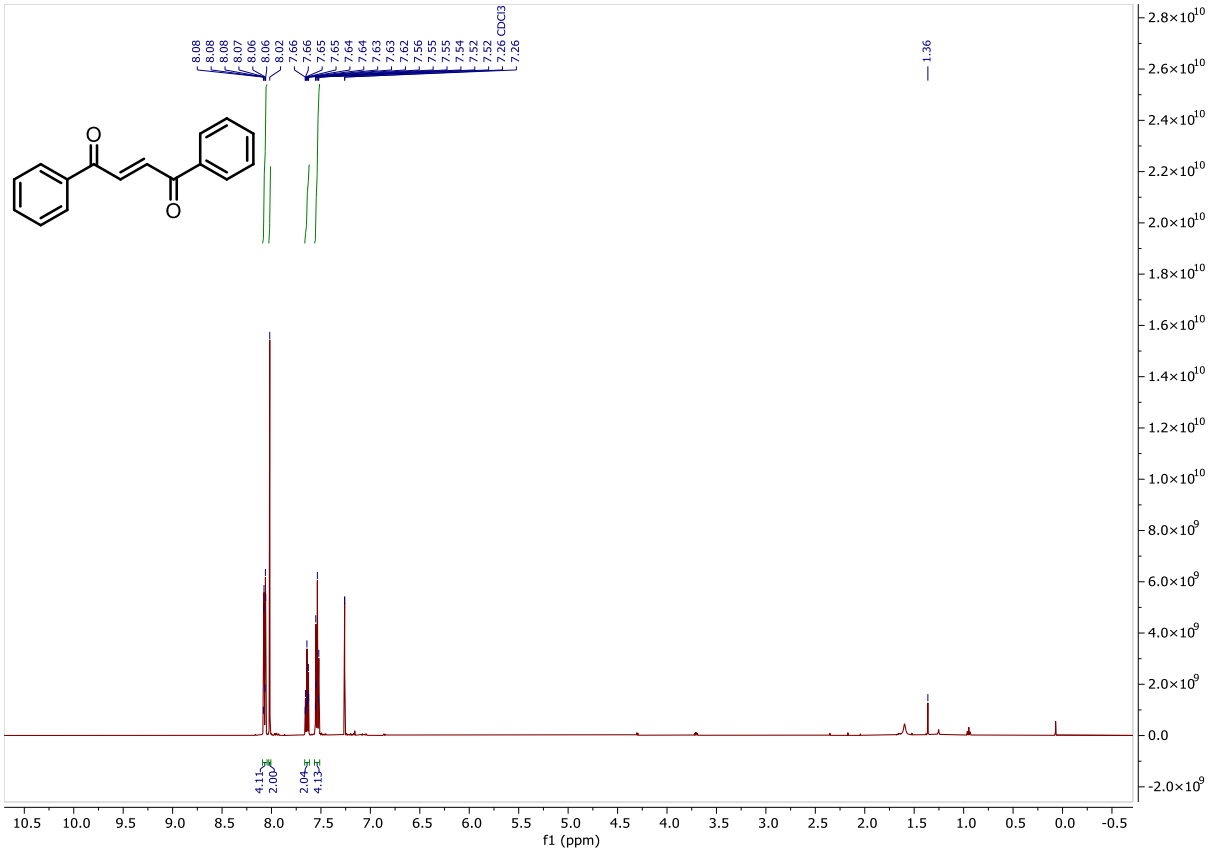


^{13}C $CDCl_3$

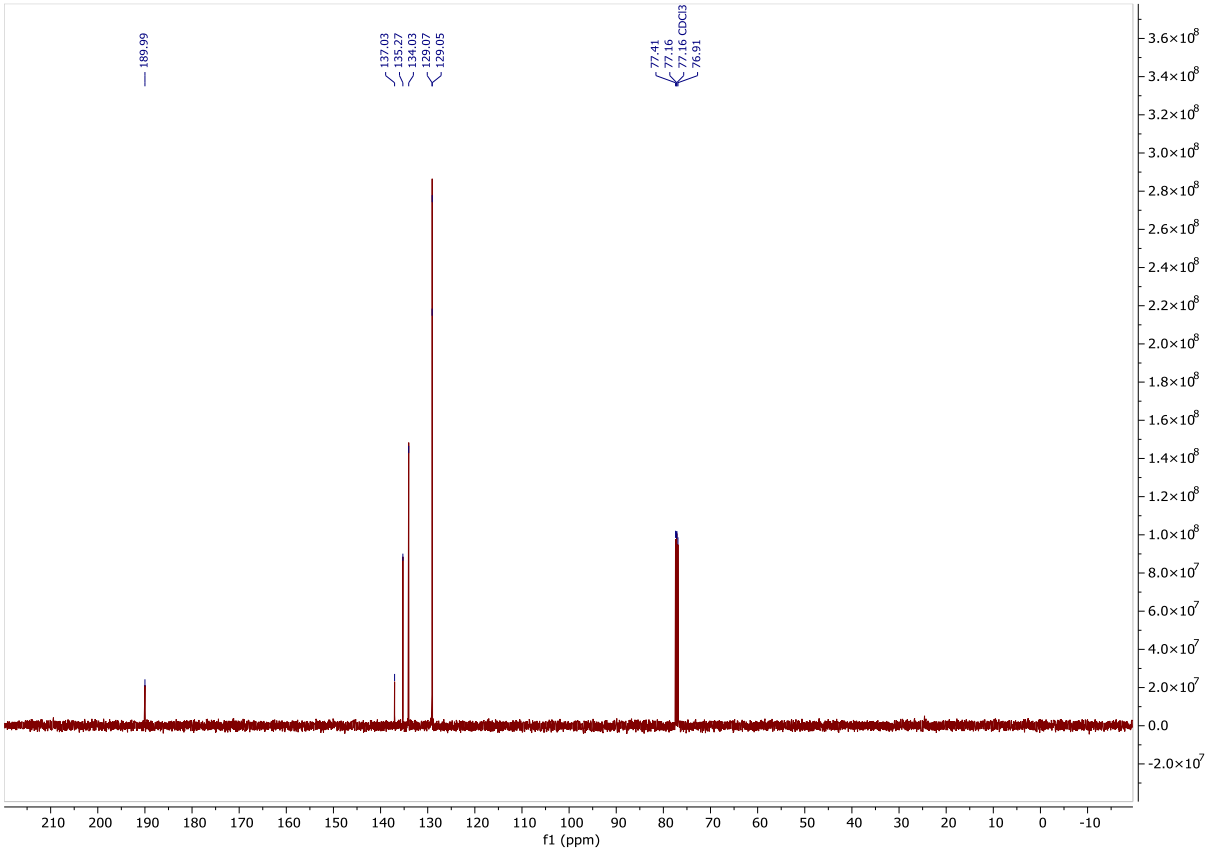


(E)-1,4-diphenylbut-2-ene-1,4-dione (10)

^{1}H $CDCl_3$

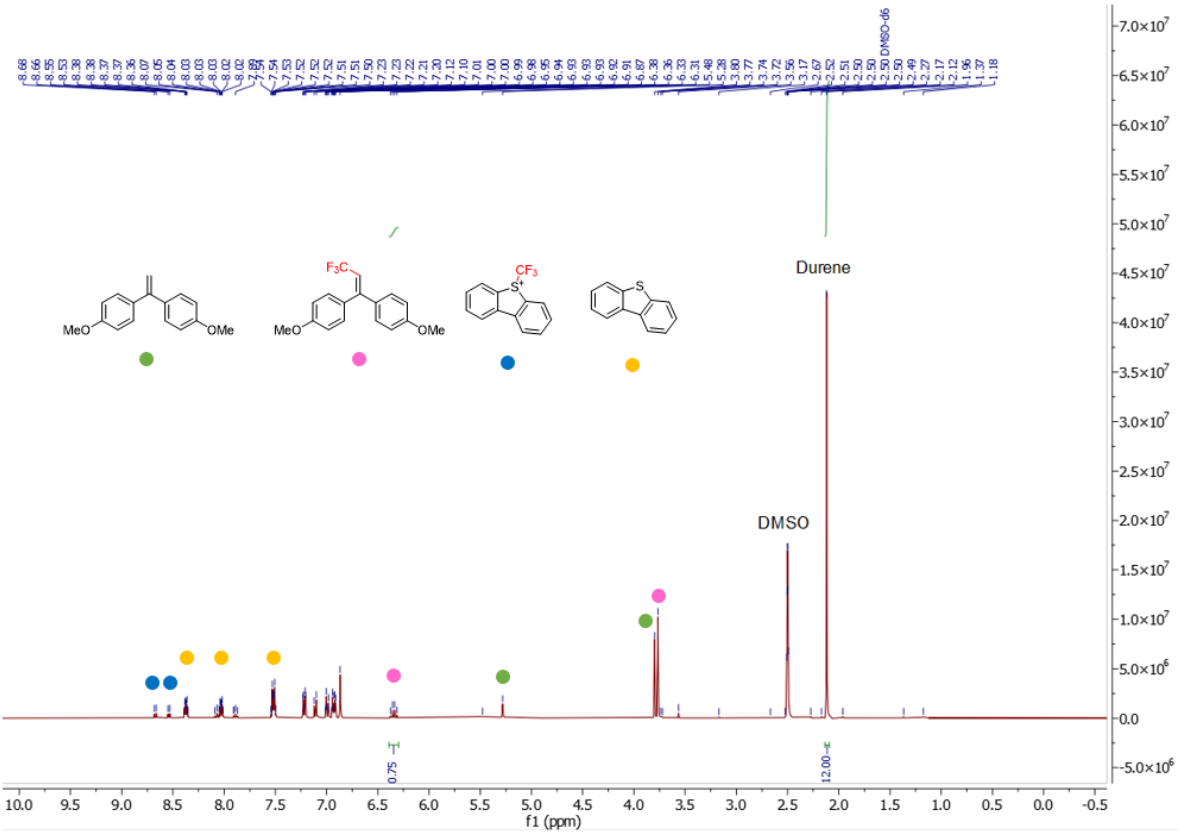


^{13}C $CDCl_3$



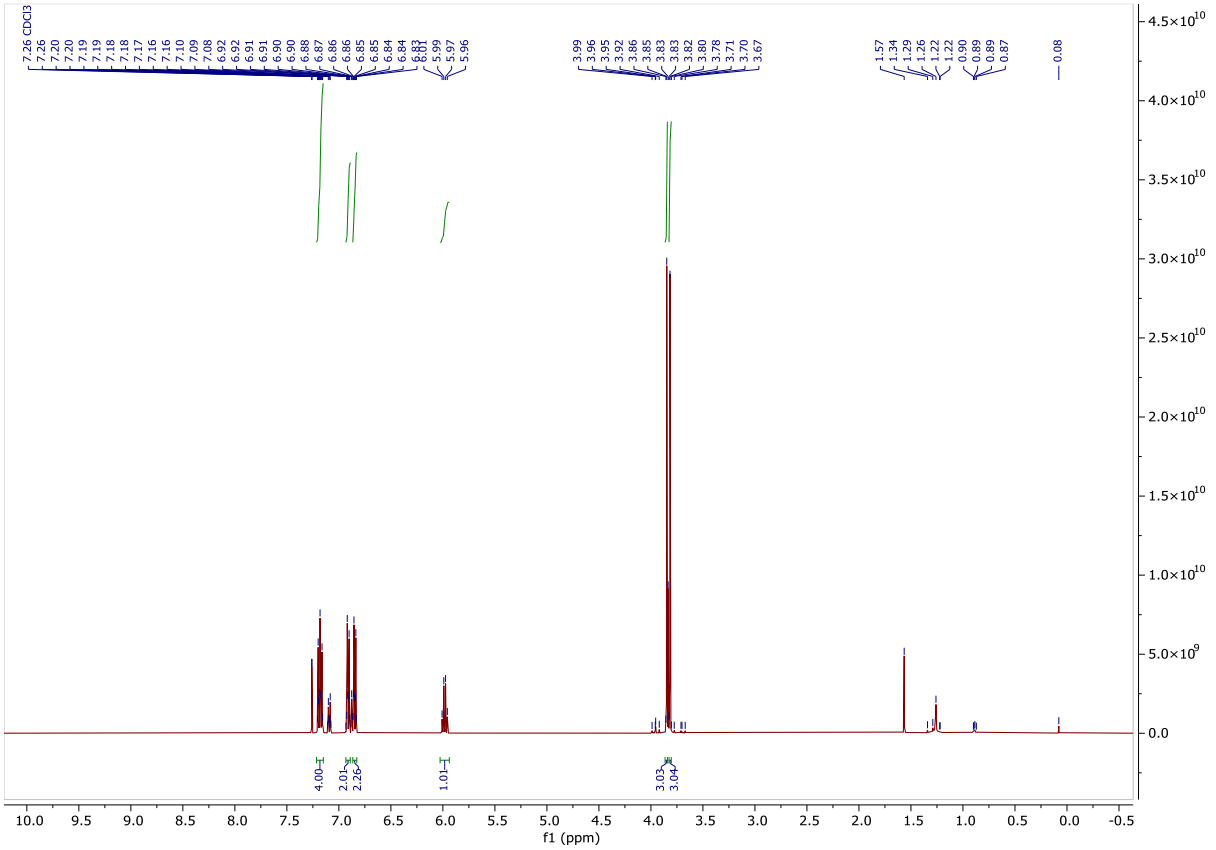
4,4'-(3,3,3-trifluoroprop-1-ene-1,1-diyl)bis(methoxybenzene)

^{1}H DMSO-d_6 (durene as standard)

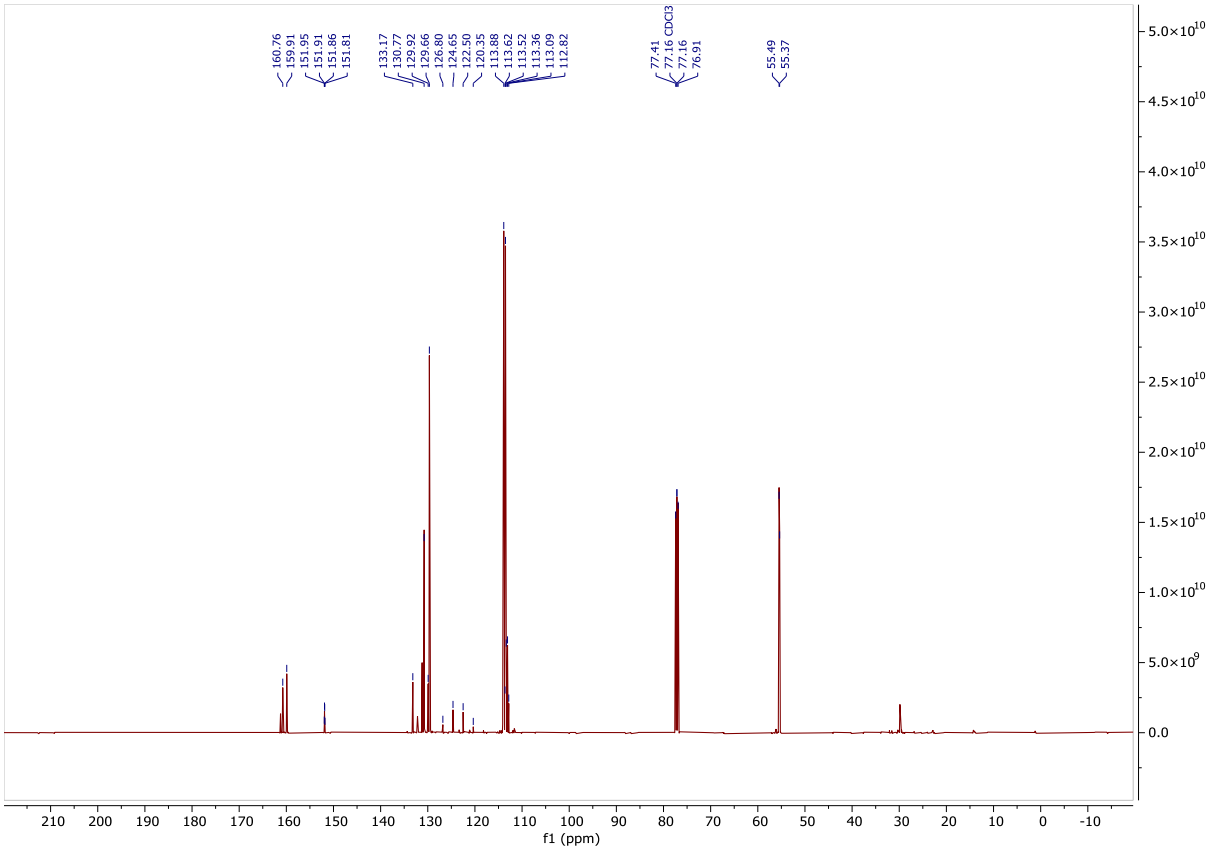


4,4'-(3,3,3-trifluoroprop-1-ene-1,1-diyl)bis(methoxybenzene)

^{1}H $CDCl_3$



^{13}C $CDCl_3$



^{19}F $CDCl_3$