Supporting Information

Synchronized Biphotonic Process Triggering C-C Coupling Catalytic Reactions

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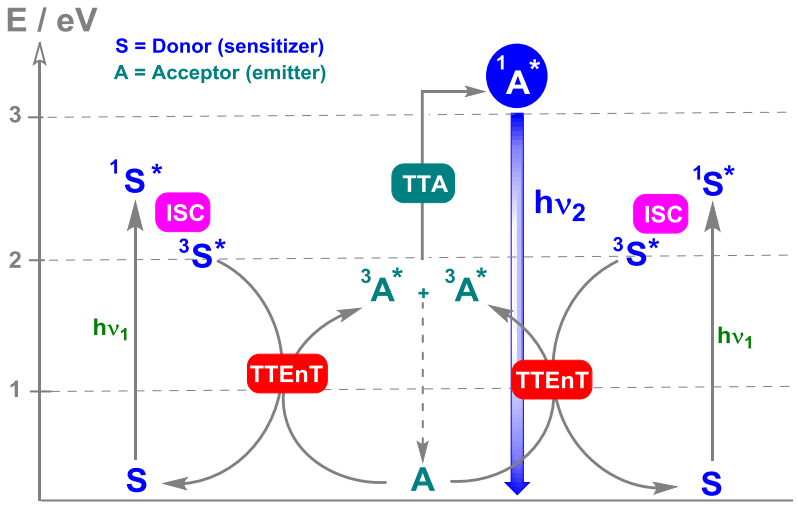
Requirements for the TTA-UC system.

To ensure the suitability of sensitizer/acceptor combinations, several features have to be taken into account. First, sensitizers must possess two main characteristics; i) ability to absorb light in the visible-to-near-IR region of the spectrum allowing for low energy excitation and, ii) a relatively long triplet excited state lifetime, typically on the order of several microseconds and beyond, enabling an efficient quenching at diffusion control rate. Qualitatively, this latter quenching process is allowed when triplet energy of the acceptor is lower than the sensitizer one. The greater the energy difference between the triplet sensitizer and triplet acceptor, the greater the driving force for this reaction and, generally speaking, the more favourable triplet energy transfer process. Besides, values of acceptor fluorescence quantum yield with near unity are advantageous since they ultimately contribute to the overall UC quantum efficiency. Finally, singlet and triplet excited states of the sensitizer should be strategically nested between the singlet and triplet excited states of the acceptor. As long as these specific energy criteria are met and the combined triplet energy from two acceptor molecules is greater than or equal to the acceptor singlet state energy, then conditions are appropriate for the observation of upconverted fluorescence from the sample.

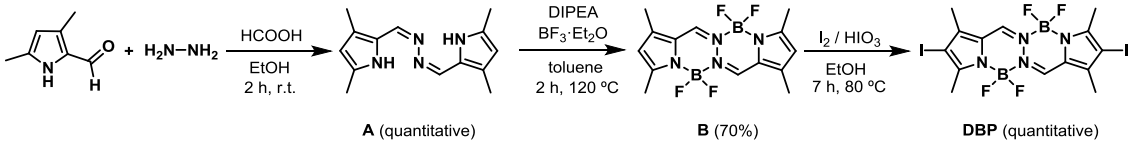


Scheme S1. Schematic illustration of the photochemical events associated to the TTA-UC technology; ISC = intersystem crossing, TTEnT = triplet-triplet energy transfer, TTA = triplet-triplet annihilation. After the absorption of low-energy photons ($h\nu_1$), the triplet excited state (T_1) of the donor (sensitizer) is produced by intersystem crossing (ISC) from the singlet excited state (S_1). Subsequently, triplets of the acceptor (emitter) are populated by triplet-triplet energy transfer (TTET) from the triplets of the sensitizer (Dexter mechanism). When two acceptor molecules in their triplet states are capable to collide during their lifetimes, a higher singlet energy level is formed by TTA and, consequently, generates delayed upconverted fluorescence ($h\nu_2$).

Metal-free TTA-UC system

Synthesis of BOPHY 4,4'-diiodo-bis(difluoroboron)1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine (DBP):

Based on previous reported procedures,[1] the sensitizer **DBP** was synthesized as follows:



Synthesis of A: 3,5-Dimethylpyrrole-2-carboxaldehyde (1.00 g, 8.12 mmol) and hydrazine monohydrate (197 µL, 4.06 mmol) were mixed in ethanol (50 mL) under stirring. Some drops of formic acid were added to the solution, until it took a yellow color. The mixture was stirred during 2 hours at room temperature. The crude was washed with an aqueous saturated solution of KCO_3 and extracted with ethyl acetate. It was dried over magnesium sulfate and the organic solvent was removed, obtaining the yellow product **A** (0.97 g), with quantitative yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 2H), 8.37 (s, 2H), 5.81 (s, 2H), 2.26 (s, 6H), 2.17 (s, 6H). These spectral data were consistent with literature.[1a]

Synthesis of B: To a solution of **A** (1.84 g, 7.61 mmol) in toluene (mL) DIPEA (15.5 mL, 91.32 mmol) was added. The mixture was stirred 30 min at room temperature. Then $BF_3{\cdot}Et_2O$ was incorporated dropwise, and the reaction was refluxed at 120 ºC during 2 hours under stirring. The crude was filtered, washed with water and extracted with dichloromethane. It was dried over magnesium sulfate and the organic solvent was removed. The product was purified by column chromatography using chloroform as eluent giving **B** (1.82 g, 70%) as an orange compound.[1a]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H), 6.18 (s, 2H), 2.49 (s, 6H), 2.33 (s, 6H). These spectral data were consistent with literature.[1a]

Synthesis of DBP following a previous protocol:[1b] BOPHY dye **B** (0.67 g, 1.98 mmol) and I_2 (2.12 g, 8.34 mmol) were mixed in ethanol (100 mL). A solution of HIO_3 (1.22 g, 6.95 mmol) in H_2O was added and the mixture was refluxed at 80 ºC under stirring during 7 hours. The crude was washed with an aqueous saturated solution of $Na_2S_2O_3$ and extracted with DCM. It was dried over magnesium sulfate and the organic solvent was removed, obtaining an orange product **DBP** (1.21 g, 98%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 2.55 (s, 6H), 2.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.8, 15.4, 81.2, 123.5, 135.5, 143.8, 152.4; **MS (EI), m/z (%)** = 590.0 [M^+](93), 522.0 (100), 463.1 (3), 395.1 (26), 275.9 (26), 167.1 (6), 149.1 (6). These spectral data were consistent with literature.[2]

Diphenylanthracene (DPA) is commercially available from Aldrich

[1] a) I.-S. Tamgho, A. Hasheminasab, J. T. Engle, V. N. Nemykin, and C. J. Ziegler. A new highly fluorescent and symmetric pyrrole–BF2 chromophore: BOPHY. *J. Am. Chem. Soc.* **136**, 5623−5626 (2014); b) T. Yogo, Y. Urano, Y. Ishitsuka, F. Maniwa, and T. Nagano. Highly efficient and photostable photosensitizer based on BODIPY chromophore. *J. Am. Chem. Soc.* **127**, 12162−12163 (2005).
[2] X. Li, G. Ji, Y.-A. Son. Tunable emission of hydrazine-containing bipyrrole fluorine–boron complexes by linear extension. *Dyes and Pigments* **124**, 232−240 (2016).

Spectroscopic investigations

Ultraviolet–visible spectra (UV– Vis) of the liquid samples were obtained by a Perkin Elmer Lambda 1050 UV/Vis/NIR spectrometer.

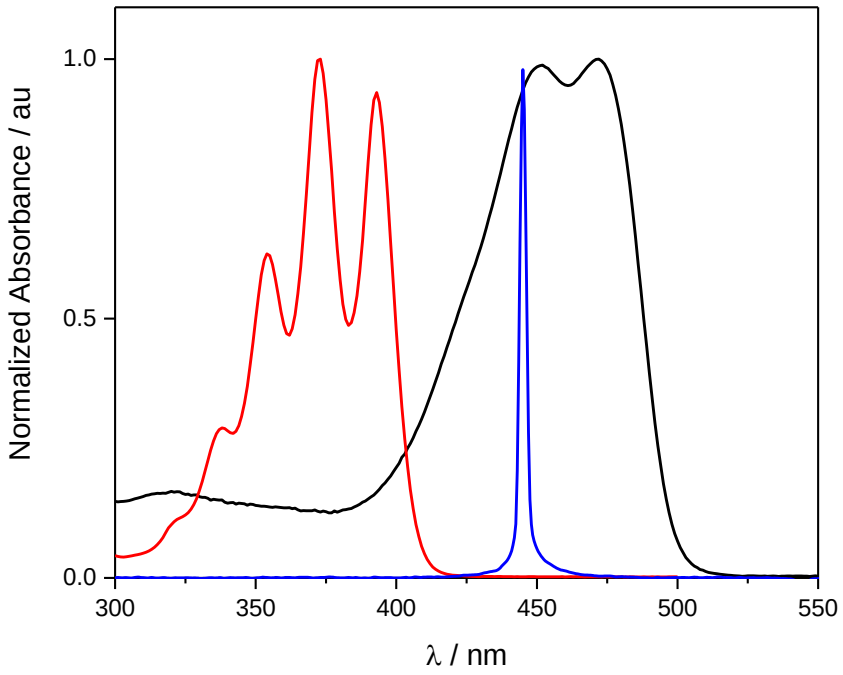


Figure S1. Normalized absorption spectra of **DBP** (—) and **DPA** (—). The blue line corresponds to the emission of the laser pointer recorded with a radiometer.

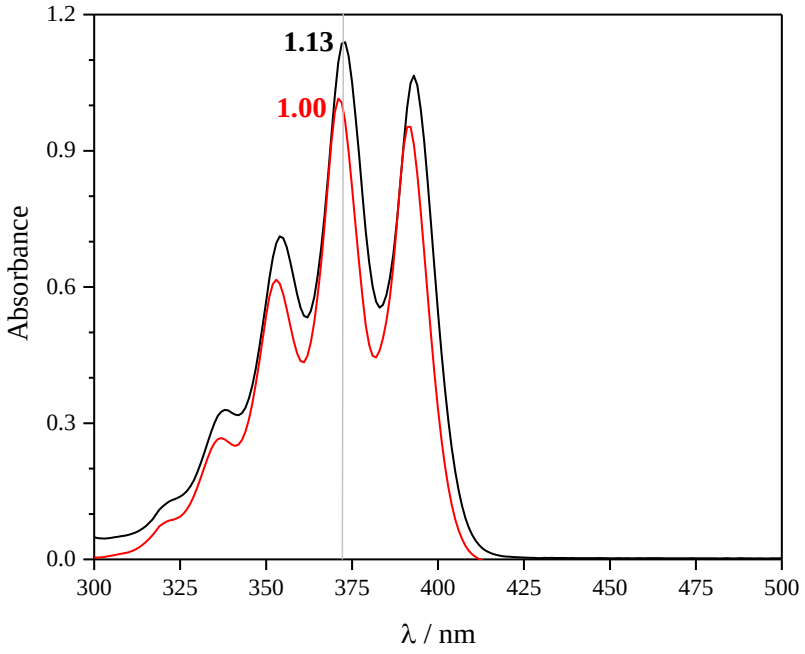


Figure S2. Absorbtion spectra of 0.1 mM **DPA** in ACN/DMF (3/1 v/v, —) and EtOH (—) under aerobic conditions at room temperature.

Transient absorption and emission studies were monitoring using a Edinburgh equipment coupled to a Nd:YAG laser (NT342A-10 model from EKSPLA) with an optical parametric oscillator (OPO).

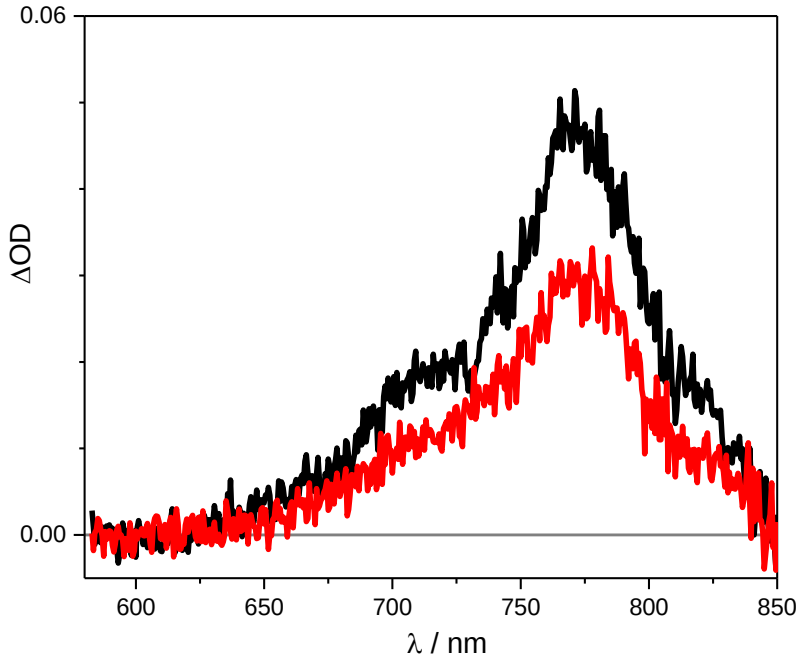


Figure S3. Transient absorption spectra of **DBP** (0.05 mM) in N_2/DMF solution (λ_{exc} = 485 nm) recorded 0.1 μs (black) and 10 μs (red) after the laser pulse.

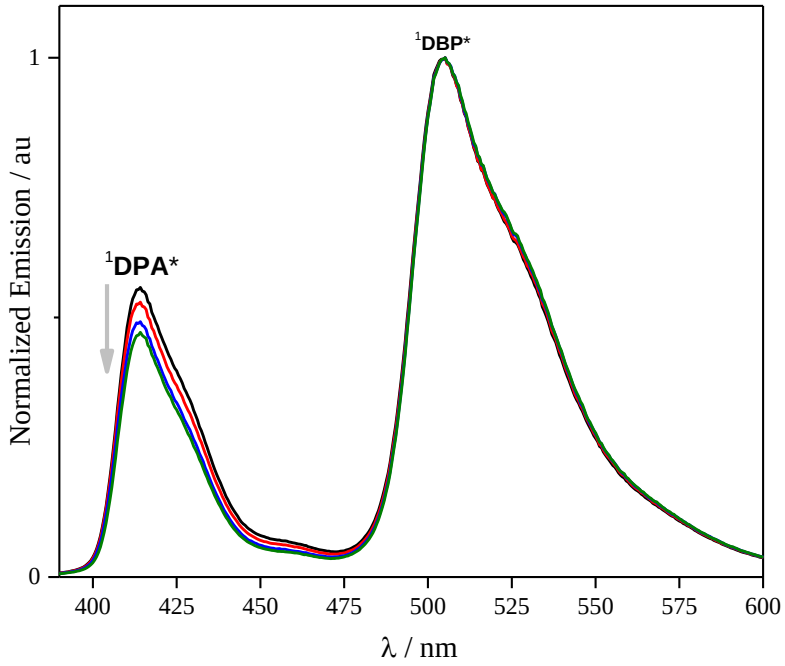


Figure S4. Emission spectra of a mixture of **DBP** (0.1 mM) and **DPA** (1 mM) in bubbled (N_2) ACN/DMF (3/1 v/v) after excitation (485 nm) with a pulsed laser in the presence of increasing amounts of **1** (0mM, 5 mM, 10 mM and 20 mM)

Lifetime measurement of **DPA** (0.1 mM in aerated ACN/DMF 3/1 v/v) was carried out using a Mini-τ equipment from Edinburgh Instruments using as excitation source a laser diode (model EPL375) at 372 nm with a pulse width of 61.2 ps at repetition rate of 1 MHz.

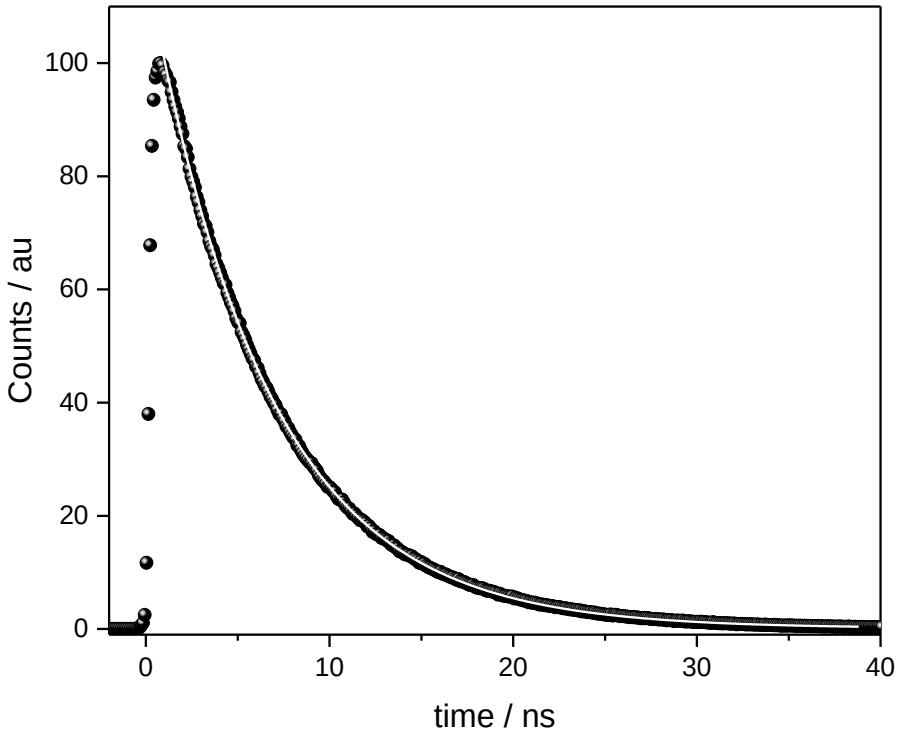


Figure S5. Fluorescence decay trace of 1 mM **DPA** (λ_{exc} = 372 nm) in ACN/DMF 3/1 v/v. The white line indicates the goodness of the lifetime measurement.

Fluorescence spectroscopy. Steady-state emission spectra were carried out using a Perkin-Elmer LS-55 luminescence spectrometer. The samples were placed into quartz cells of 1 cm path length. Compound concentrations were fixed as indicated. The excitation and emission slit widths were 5 nm and 10 nm, respectively. The fluorescence quantum yield was measured by comparing the area of fluorescence and absorbance at the excitation wavelength of 372 nm, using the well-known formula:

$$\phi_{sample} = (a_{sample}/a_{std})\ (A_{std}/A_{sample})\ (\eta_{sample}/\eta_{std})\ \phi_{std}$$

where ϕ_{sample} and ϕ_{std}, a_{sample} and a_{std}, η_{sample} and η_{std} and A_{sample} and A_{std} are the quantum yield, area under emission spectra, refractive index and the absorbance of the sample under study (**DPA**) and the standard (**DPA** in EtOH), respectively.

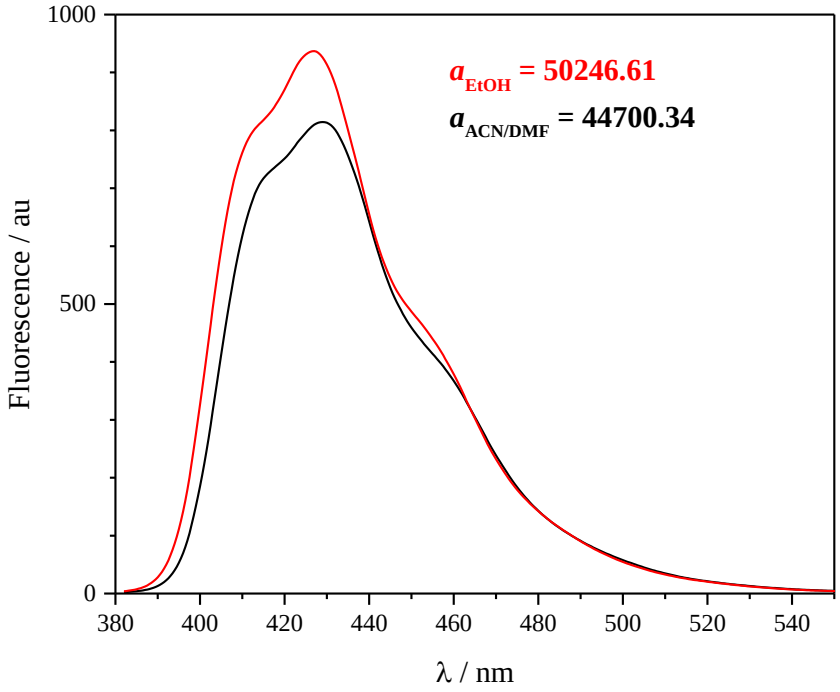


Figure S6. Fluorescence spectra (λ_{exc} = 372 nm) of 0.1 mM **DPA** in ACN/DMF (3/1 v/v, ▬) and EtOH (▬) under aerobic conditions at room temperature.

Theoretical studies

Computational details: Calculations were performed using Gaussian G09 software package.[3] Geometry optimizations of all species were carried out using the B3LYP functional and 6-311++G** basis set, except BOPHY and Iodine atoms on chemical reagents were calculated using LAND2DZ (see optimized geometries Section SI 8). All geometries optimizations were carried out using a polarized continuum model to account for the solvent effects with DMF and acetonitrile. Redox potentials of **DPA** and **Aryl Halides** were obtained from DFT calculations using a modification of a previously reported methodology for the estimation of SET potentials[4] using frequency calculations with above mentioned basis set. This approach has been previously applied.[5]

The vertical transitions (i.e. excitation energies) and geometries optimizations of the **^{1}DPA* (S1) and ^{3}DPA* (T1)** excited states were performed by TD-DFT, employing the unrestricted UB3LYP method and the 6-311++G** basis set using a polarized continuum model to account for the solvent effects[6].

The Marcus theory[7] was used in order to determine the activation barriers ($\Delta G^{\neq}$) for the single ET step from ^{1}**DPA*** to the different substrates. In turn, this was obtained from the ΔG values for each reaction and the parameter λ, the nuclear reorganization energy, by using the following equation:

$$\Delta G^{\neq} = \frac{(\Delta G + \boldsymbol{\lambda})^2}{4\boldsymbol{\lambda}}$$

The value of the nuclear reorganization energy λ was computed following the procedure described previously.[8]

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

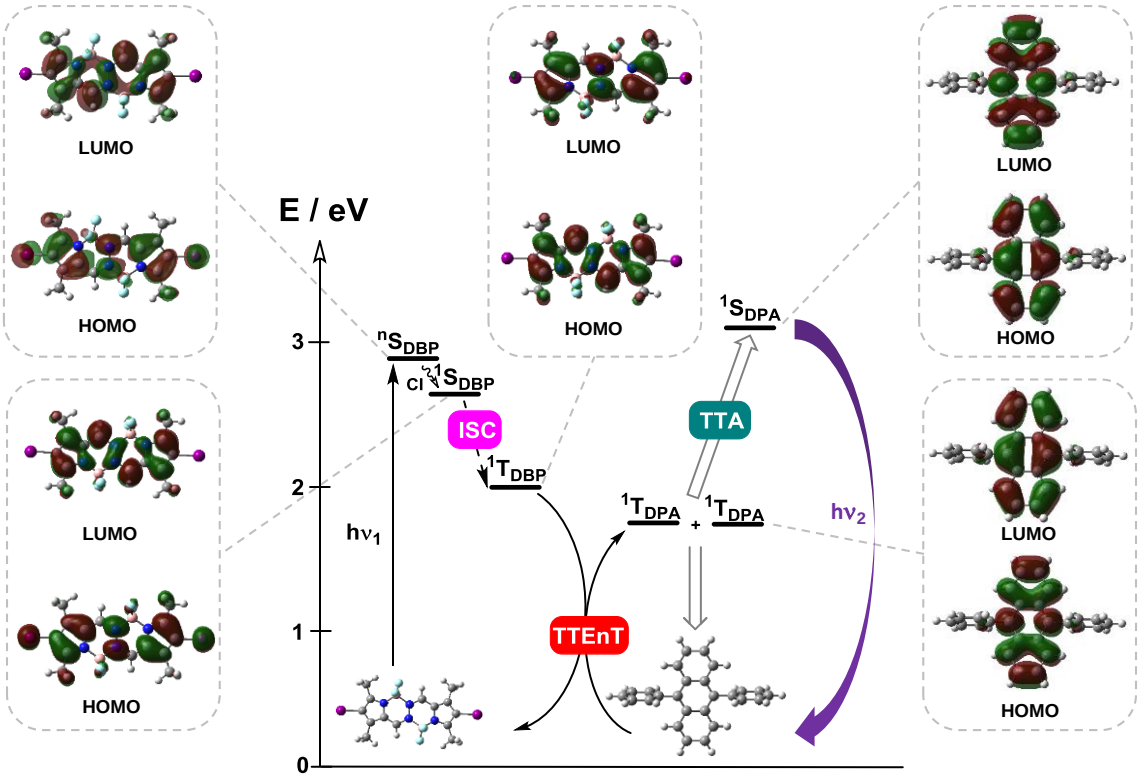
[4] M.-H. Baik, R. A. Friesner, *J. Phys. Chem. A*, **106**, 7407 (2002).

[5] M. Majek, F. Filace, A. Jacobi von Wangelin, *Chem. Eur. J.* **21**, 4518 (2015).

[6] a) Furche, F.; Ahlrichs, R. Adiabatic time-dependent density functional methods for excited state properties. *J. Chem. Phys.* **117**, 7433 (2002); b) Scalmani, G.; Frisch, M.J.; Mennucci, B.; Tomasi, J.; Cammi, R.; Barone, V. Geometries and properties of excited states in the gas phase and in solution: theory and application of a time-dependent density functional theory polarizable continuum model. *J. Chem. Phys.*, **124**, 94107 (2006).

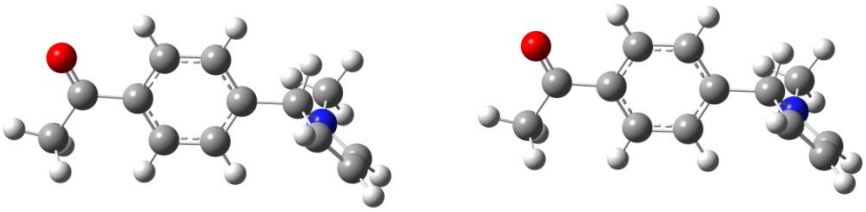
[7] R. A. Marcus. Electron transfer reactions in chemistry. Theory and experiment. *Pure Appl. Chem.* **69**, 13 (1997).

[8] S. F. Nelsen, M. N. Weaver, Y. Luo, J. R. Pladziewicz, L. K. Ausman, T. L. Jentzsch, J. J. O'Konek. Estimation of electronic coupling for intermolecular electron transfer from cross-reaction data. *J. Phys. Chem. A* **110**, 11665 (2006).



Scheme S2. Jablonsky diagram displaying the most significant photophysical reaction pathways of our TTA-UC process. HOMO and LUMO molecular orbitals involved in the excitation and emission steps for DBP and DPA molecules. The calculations are at the B3LYP/6−311++G** level with acetonitrile as solvent using Gaussian 09W

Back electron transfer feasibility:



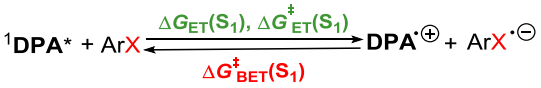
Intermediate a **Intermediate b**

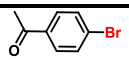
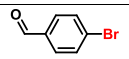
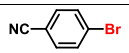
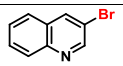
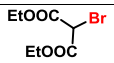
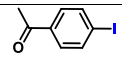
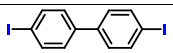
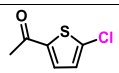
Figure S7. Optimized geometries of intermediates **a** and **b.**

For the back electron transfer process:

DPA$^{+\bullet}$ → **DPA** ΔE = +1.38V
Int **b** → Int **a** ΔE = −0.49 V
DPA$^{+\bullet}$ + Int **a** → ΔE = +0.89V. Therefore: ΔG = –n·F·ΔE ΔG < 0 Exergonic process.

Table S1. Thermodynamic (ΔG) and kinetic ($\Delta G^{\neq}$) data for the ET and BET processes based on DFT calculations.



Substrate	E_{red} (V) SCE[a]	$\Delta G_{ET}(S_1)$ kJ/mol[b]	$\Delta G_{ET}(T_1)$ kJ/mol[b]	λ kJ/mol	$\Delta G^{\neq}_{ET}(S_1)$ kJ/mol[c]	$\Delta G^{\neq}_{BET}(S_1)$ kJ/mol[c]
	1.51	−16.6	102.84	24.27	**0.69**	16.66
	1.57	−10.9	108.57	35.29	**4.36**	14.83
	1.36	−0.25	88.53	22.32	**0.61**	30.31
	1.76	7.33	126.80	17.95	8.69	**1.66**
	1.69	0.76	120.24	21.03	5.63	**4.90**
	1.62	−5.84	113.63	12.47	**0.94**	6.55
	n.d.[e]	n.d.	n.d.	n.d.	n.d.	n.d.
	1.56	−11.27	108.20	23.89	**1.79**	12.61
	2.04	34.25	153.72	26.82	33.22	**0.34**
	1.33	−33.70	85.78	23.80	**0.76**	33.11

[a]reduction potentials of the substrates according to DFT calculations; [b]values of free energy changes (ΔG) obtained by DFT calculations taking into account $E_{red}^{(DPA)}$ = −1.38 V vs SCE; E_S = 3.0564 eV; E_T = 1.8119 eV; [c]from equation page S10; [e]not determined. DFT calculation of the diethyl bromomalonate radical anion is unstable and showing it de-bromation.

Kinetic and thermodynamic analysis.

Stern-Volmer

Equations for the Stern-Volmer analysis:

$\phi_0/\phi = 1 + K_{SV} \cdot [\mathbf{1}]$ eq S1

$K_{SV} = \tau_F \cdot k_q(S_1)$ eq S2

Deactivation pathways of ^{1}DPA*

Equations for calculating the contribution of the different deactivation pathways of the ^{1}**DPA***

$k_D(S_1) = k_q(S_1) \cdot [\mathbf{1}] + k_F + k_{ISC}$ eq S3

$\tau_F \cdot k_F = \phi_F$ eq S4

$\tau_F \cdot k_{ISC} = \phi_{ISC}$ eq S5

Weller equation

$\Delta G_{ET} = 23.06 \cdot [E°_{(\mathbf{DPA}^{\bullet+}/\mathbf{DPA})} - E°_{(\mathbf{1}/\mathbf{1}^{\bullet-})}] - E^*(S_1 \text{ or } T_1)$ eq S6

Photocatalyzed reaction studies

Product distribution was determined from quantitative GC-MS measurements on a Bruker Scion SQ 436-GC. 1-Dodecanenitrile was used as an internal standard in the GC-MS quantitative measurements. Solvents (≥99% purity) were purchased from commercial suppliers and used as received unless otherwise indicated. Reactions were carried out in a quartz cuvette (4 mL, Hellma) sealed with septum. Irradiation was performed using a blue diode laser pointer with a real power of 2000 mW (λ_{exc} = 445 nm ± 10, beam diameter of 10 mm) that was purchased from ®TorLaser. TLC was performed on commercial SiO_2-coated aluminium plates (DC60 F254, Merck). Visualization was done by UV-light (254nm). NMR spectral data were collected on a Varian 400 (400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer at 20 °C. Chemical shifts are reported in δ/ppm, coupling constants J are given in Hertz. High-resolution mass spectrometry (HRMS) was used in case of new products.

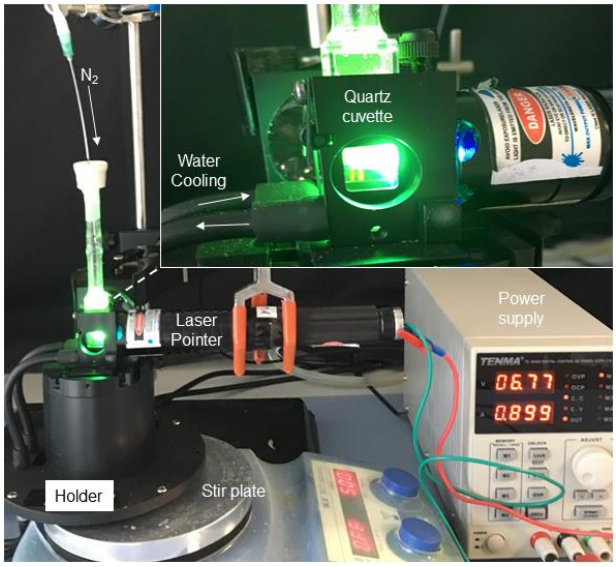
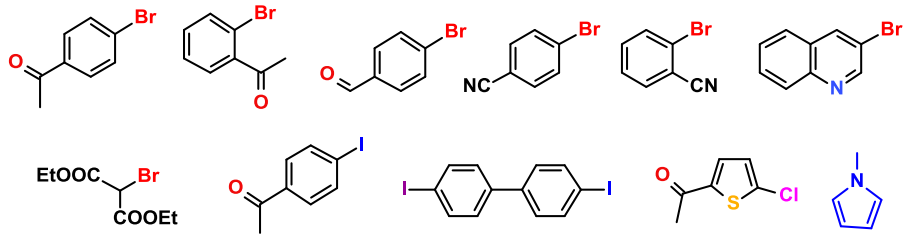


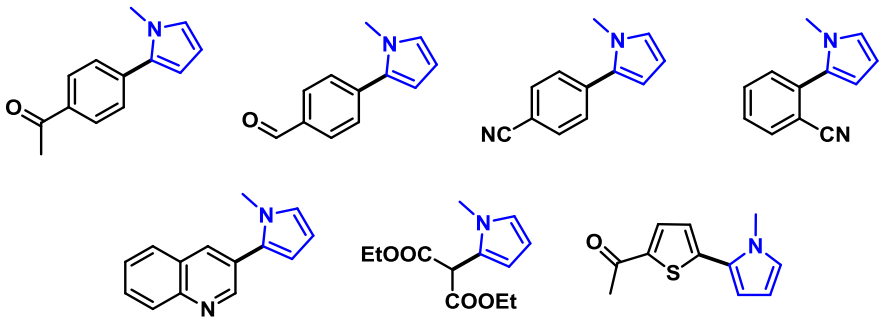
Figure S8. Set-up for the photochemical reaction. Photograph of the photocatalytic C-C coupling reaction by TTA-UC methodology in batch process. Constant reaction temperature was ensured by the use of a water-cooling.

Reagents and products

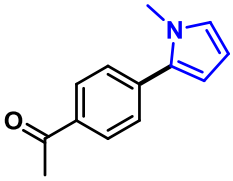
All starting chemicals showed below were commercially available from Aldrich, Alfa Aesar, Merck, Across Organics and Apollo Scientific:



Products showed below were isolated according to the general procedure described in the main text and showed spectroscopic data in agreement with those published.[9]



1-(4-(1-Methyl-1H-pyrrol-2-yl)phenyl)ethan-1-one[9a]



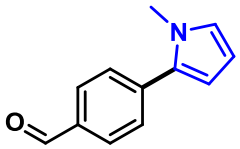
The compound was prepared according to the general procedure described in the main text using 4-bromoacetophenone (5.9 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent. The reaction mixture was irradiated for 2 hours.

The compound was also prepared according to the general procedure described in the main text using 4-iodoacetophenone (7.4 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent. The reaction mixture was irradiated for 2 hours.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03-7.95 (m, 2H), 7.54-7.46 (m, 2H), 6.80-6.75 (m, 1H), 6.35 (dd, J = 3.6 Hz, 1.7 Hz, 1H), 6.23 (dd, J = 3.6 Hz, 2.6 Hz, 1H), 3.73 (s, 3H), 2.63 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 197.7, 138.0, 135.0, 133.5, 128.7, 128.1, 125.5, 110.4, 108.5, 35.6, 26.7. **GC-MS** (EI): m/z (relative intensity) = 199 (94) [$M^{+\bullet}$], 184 (100), 156 (41), 128 (22).

[9] (a) Neumeier, M., Sampedro, D., Majek, M., de la Peña O'Shea, V., Jacobi von Wangelin, A. & Perez-Ruiz, R. Dichromatic Photocatalytic Substitutions of Aryl Halides by a Small organic Dye. *Chem. Eur. J.* **24**, 105-108 (2018); (b) Ghosh, I., Ghosh, T., Bardagi, J. I. & König, B. Reduction of aryl halides by consecutive visible light-induced electron transfer processes. *Science* **346**, 725-728 (2014); (c) Baciocchi, E., Manna, L. & Muraglia, E. Selectivity in the reactions of electron-rich pentatomic heteroaromatic compounds with carbon-centered free radicals. *Gazz. Chim. Ital.* **124**, 249-252 (1994).

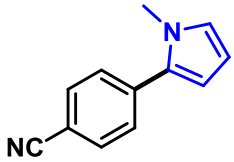
4-(1-Methyl-1H-pyrrol-2-yl)benzaldehyde[9b]



The compound was prepared according to the general procedure described in the main text using 4-bromobenzaldehide (5.5 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent. The reaction mixture was irradiated for 2 hours.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.01 (s, 1H), 7.94 – 7.85 (m, 2H), 7.62 – 7.53 (m, 2H), 6.83 –6.76 (m, 1H), 6.40 (dd, J = 3.7, 1.8 Hz, 1H), 6.25 (dd, J = 3.7, 2.7 Hz, 1H), 3.74 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 191.8, 139.3, 134.3, 133.3, 130.1, 128.3, 125.9, 110.8, 108.6, 35.6. **GC-MS** (EI): m/z (relative intensity) = 185 (100) [$M^{+\bullet}$], 184 (56), 156 (39), 128 (12), 115 (19.

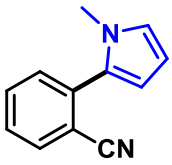
4-(1-Methyl-1H-pyrrol-2-yl)benzonitrile[9a]



The compound was prepared according to the general procedure described in the main text using 4-bromobenzonitrile (5.4 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent. The reaction mixture was irradiated for 2 hours.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.63 (m, 2H), 7.53-7.46 (m, 2H), 6.81-6.77 (m, 1H), 6.35 (dd, J = 3.7 Hz, 1.8 Hz, 1H), 6.23 (dd, J = 3.7 Hz, 2.7 Hz, 1H), 3.72 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8, 132.7, 132.4, 128.4, 126.0, 119.2, 110.9, 109.8, 108.7, 35.6. **GC-MS** (EI): m/z (relative intensity) = 182 (100) [$M^{+\bullet}$], 181 (49), 154 (8.3), 140 (22).

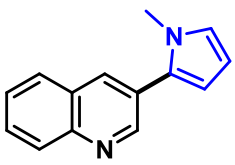
2-(1-Methyl-1H-pyrrol-2-yl)benzonitrile[9a]



The compound was prepared according to the general procedure described in the main text using 2-bromobenzonitrile (5.4 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent. The reaction mixture was irradiated for 2 hours.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78-7.70 (m, 1H), 7.66-7.56 (m, 1H), 7.47-7.35 (m, 2H), 6.80 (dd, J = 2.6 Hz, 1.8 Hz, 1H), 6.41 (dd, J = 3.7 Hz, 1.8 Hz, 1H), 6.25 (dd, J = 3.7, 2.6 Hz, 1H), 3.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 137.0, 133.7, 132.5, 131.0, 130.0, 127.5, 125.0, 118.8, 113.0, 111.6, 108.4, 35.0. **GC-MS** (EI): m/z (relative intensity) = 182 (100) [$M^{+\bullet}$], 181 (86), 154 (21), 140 (14).

3-(1-Methyl-1H-pyrrol-2-yl)quinolone[9a]

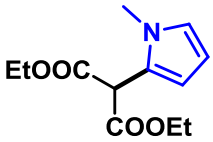


The compound was prepared according to the general procedure described in the main text using 3-bromoquinoline (6.2 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent. The reaction mixture was irradiated for 2 hours.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.03 (d, J = 2.2 Hz, 1H), 8.19-8.11 (m, 2H), 7.88-7.81 (m, 1H), 7.73 (ddd, J = 8.5 Hz, 7.5 Hz, 1.3 Hz, 1H), 7.63-7.54 (m, 1H), 6.86-6.79 (m, 1H), 6.43 (dd, J = 3.6 Hz, 1.8 Hz, 1H), 6.32-6.28 (m, 1H), 3.76 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 146.8, 133.9, 131.1, 129.4, 129.3, 127.9, 127.9, 127.2, 126.6, 125.1, 110.4, 108.6, 35.4. **GC-MS** (EI): m/z (relative intensity) = 208 (100) [$M^{+\bullet}$], 207 (66), 180 (14), 167 (12).

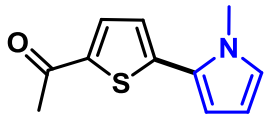
Diethyl 2-(1-methyl-1H-pyrrol-2-yl)malonate[9c]



The compound was prepared according to the general procedure described in the main text using diethyl bromomalonate (7.1 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent. The reaction mixture was irradiated for 2 hours.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.64 – 6.60 (m, 1H), 6.21 (dd, J = 3.5, 1.7 Hz, 1H), 6.12 – 6.07 (m, 1H), 4.71 (s, 1H), 4.24 (dd, J = 7.1, 4.9 Hz, 5H), 3.59 (s, 3H), 1.28 (t, J = 7.1 Hz, 7H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.6, 129.8, 123.7, 109.9, 107.38, 62.1, 50.8, 34.4, 14.2. **GC-MS** (EI): m/z (relative intensity) = 239 (24) [$M^{+\bullet}$], 166 (100), 138 (47), 94 (39).

1-(5-(1-Methyl-1H-pyrrol-2-yl)thiophen-2-yl)ethan-1-one[9a]

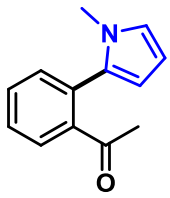


The compound was prepared according to the general procedure described in the main text using 2-acetyl-5-chlorothiophene (7.1 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent. The reaction mixture was irradiated for 2 hours.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 4.0 Hz, 1H), 7.06 (d, J = 4.0 Hz, 1H), 6.77-6.72 (m, 1H), 6.51 (dd, J = 3.8, 1.8 Hz, 1H), 6.18 (dd, J = 3.8 Hz, 2.7 Hz, 1H), 3.81 (s, 3H), 2.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 190.6, 144.0, 141.9, 133.3, 126.9, 126.3, 124.4, 111.7, 108.7, 36.0, 26.7. **GC-MS** (EI): m/z (relative intensity) = 205 (100) [$M^{+\bullet}$], 190 (94), 162 (36), 130 (13), 118 (53).

New products:

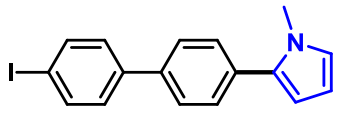
1-(2-(1-Methyl-1H-pyrrol-2-yl)phenyl)ethan-1-one



The compound was prepared according to the general procedure described in the main text using 2-bromoacetophenone (5.9 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent. The reaction mixture was irradiated for 2 hours.

^{1}H NMR (400 MHz, $CDCl_3$):) δ = 7.65 – 7.59 (m, 1H), 7.50 (dd, J = 7.5, 1.5 Hz, 1H), 7.41 (ddd, J = 22.1, 7.5, 1.1 Hz, 2H), 6.79 – 6.72 (m, 1H), 6.22 (dd, J = 3.5, 2.8 Hz, 1H), 6.14 (dd, J = 3.6, 1.7 Hz, 1H), 3.42 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 204.1, 141.6, 131.9, 131.6, 131.4, 130.9, 128.0, 127.9, 123.4, 110.4, 108.4, 34.3, 28.9. **GC-MS** (EI): m/z (relative intensity) = 199 (100) [$M^{+\bullet}$], 198 (32), 184 (32), 168 (15), 156 (43), 129 (33). **HRMS** (EI): m/z = calcd. for $C_{13}H_{13}NO^{+\bullet}$: 199.09971, found: 199.09991

2-(4'-Iodo-[1,1'-biphenyl]-4-yl)-1-methyl-1H-pyrrole



The compound was prepared according to the general procedure described in the main text using 4,4'-diiodobiphenyl (5.9 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent. The reaction mixture was irradiated for 2 hours.

^{1}H NMR (400 MHz, $CDCl_3$): 7.78 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.36 (d, J = 8.3 Hz, 1H), 6.75 (m, 1H), 6.28 (m, 1H), 6.22 (m, 1H), 3.73 (s, 3H). **GC-MS** (EI): m/z (relative intensity) = 359 (100) [$M^{+\bullet}$], 232 (20), 217 (21), 190 (12), 189 (23), 115 (13). **HRMS** (EI): m/z = calcd. for $C_{17}H_{14}IN^{+\bullet}$: 359.01709, found: 359.01637.

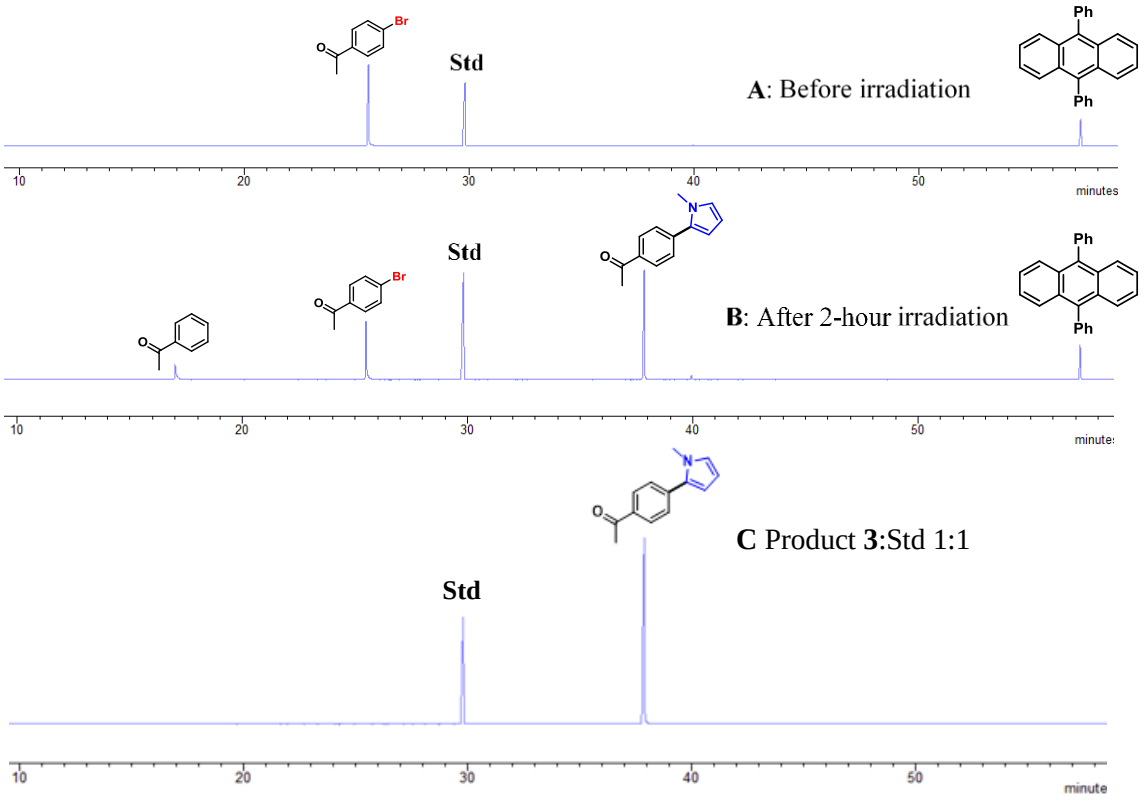
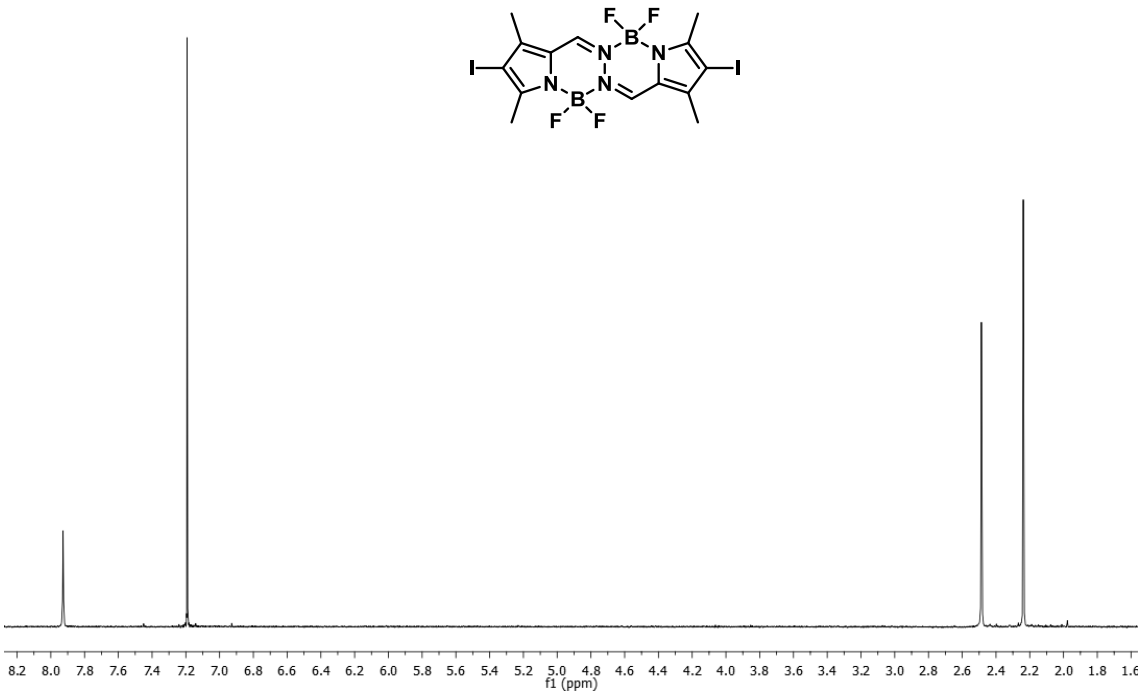
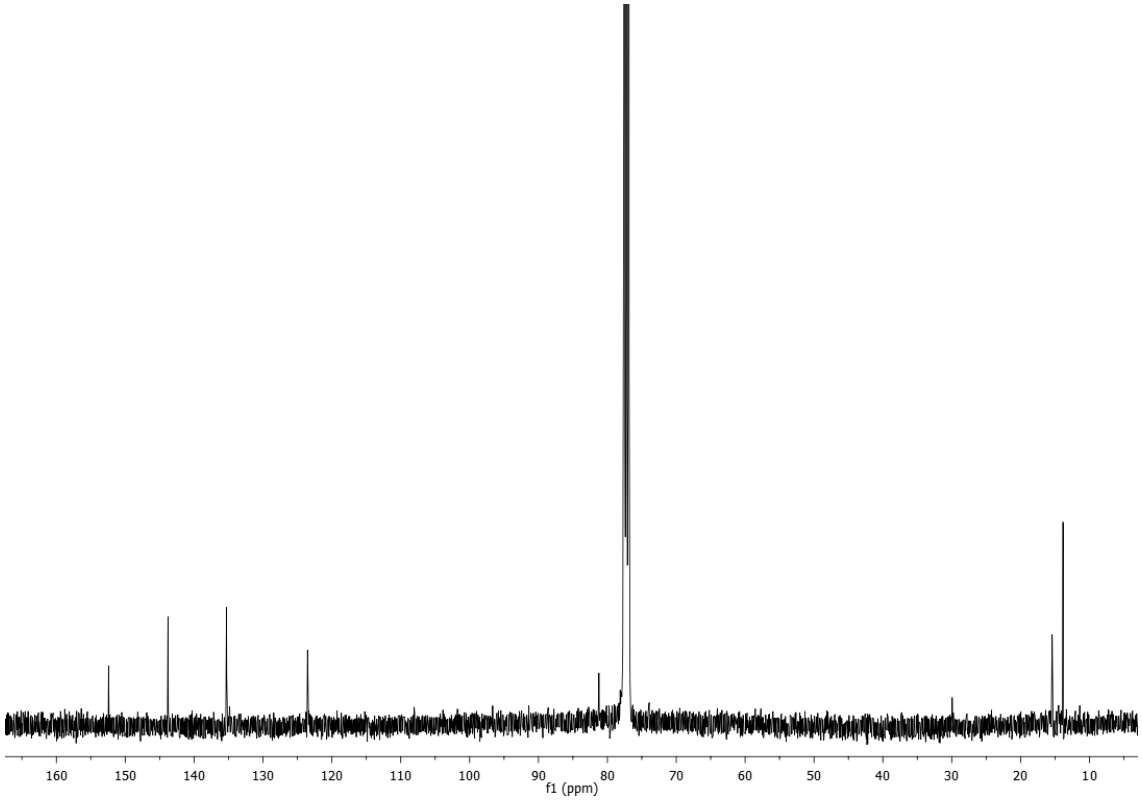


Figure S9. Representative GC chromatograms for the catalytic C-C coupling of 4-bromoacetophenone (1 equiv.) and *N*-methyl pyrrole (80 equiv.) in the presence of the TTA system (**DBP**, 0.01 equiv. + **DPA**, 0.1 equiv.) in deaerated ACN/DMF 3/1 v/v.

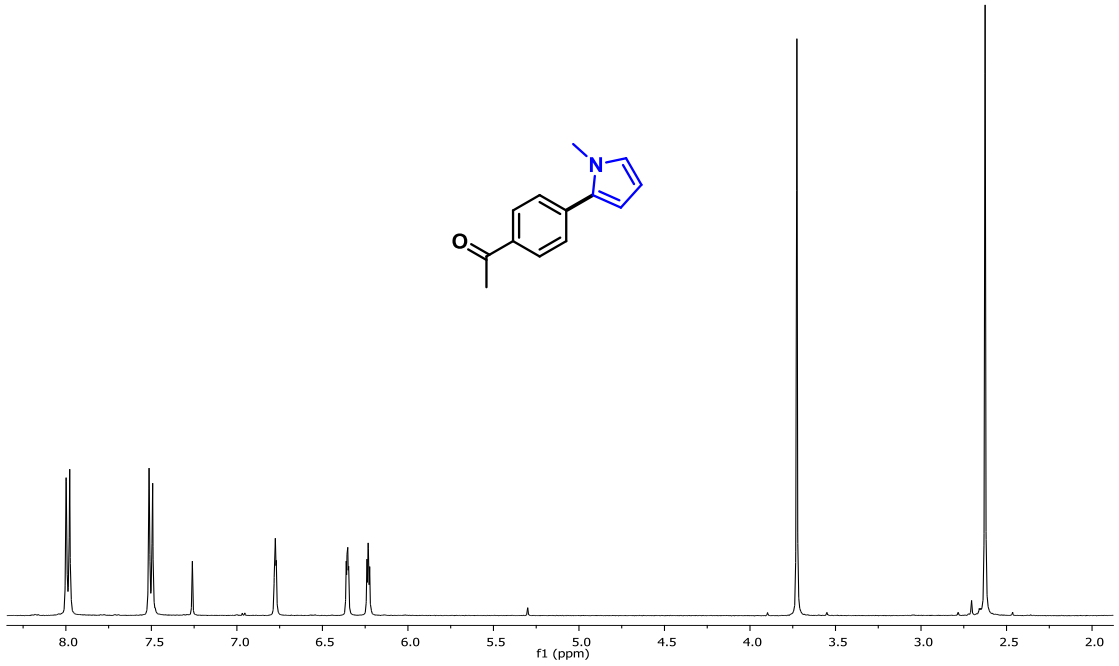
NMR spectra

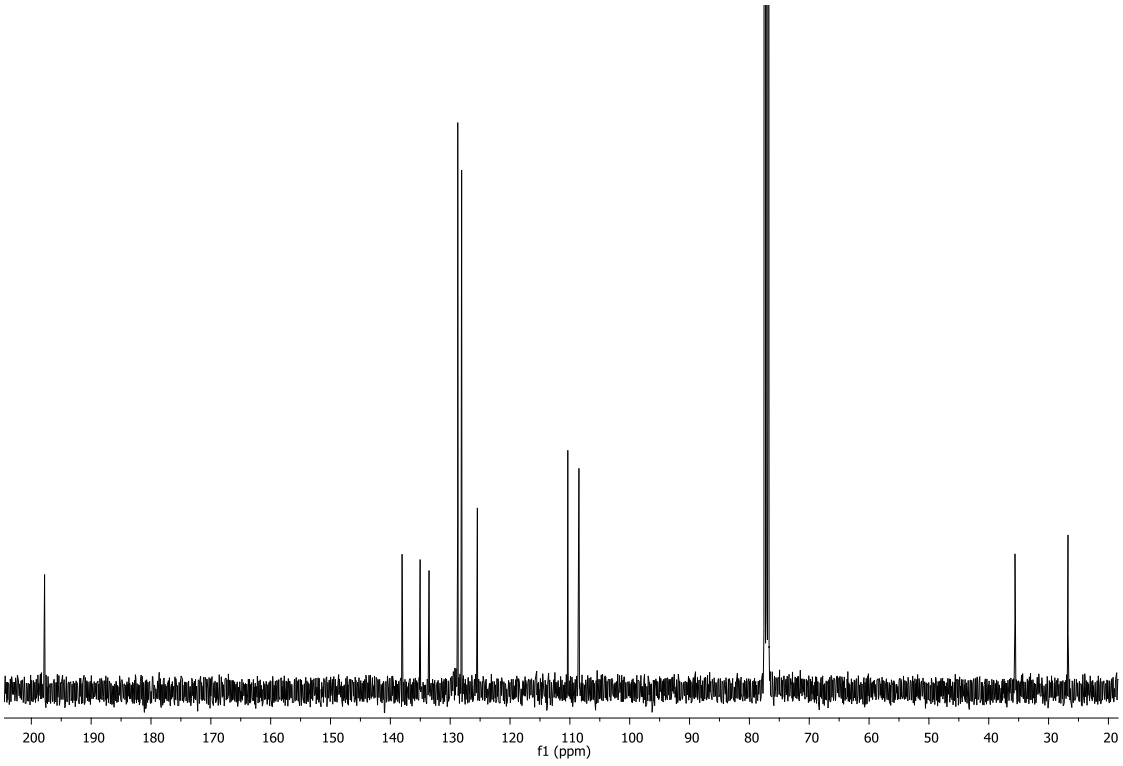
^{1}H and ^{13}C NMR of DBP



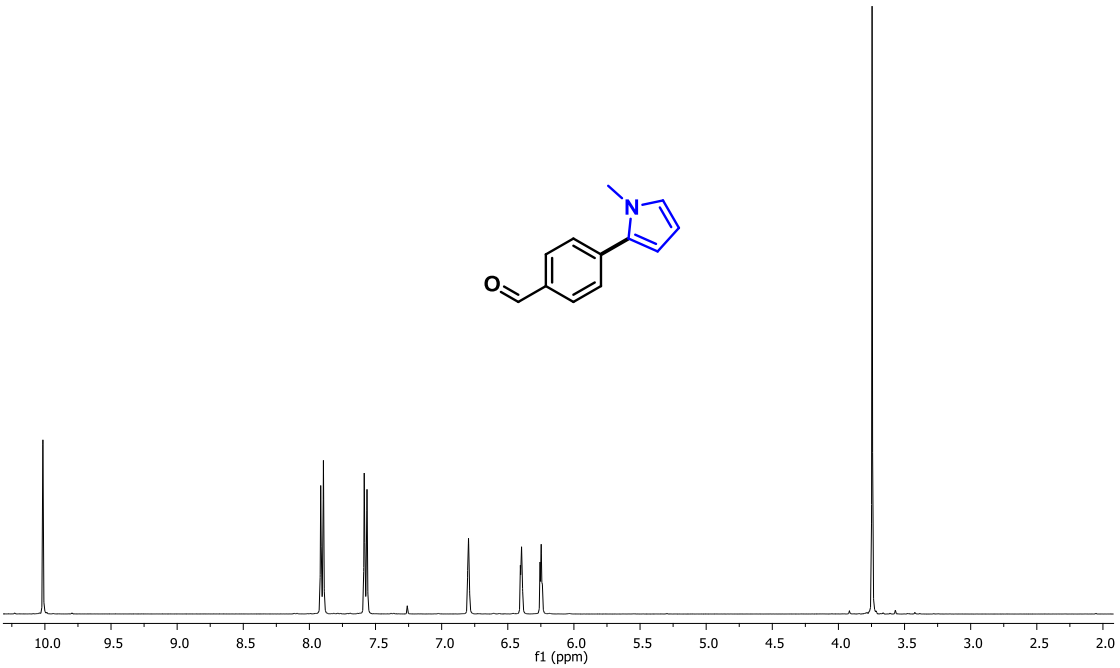


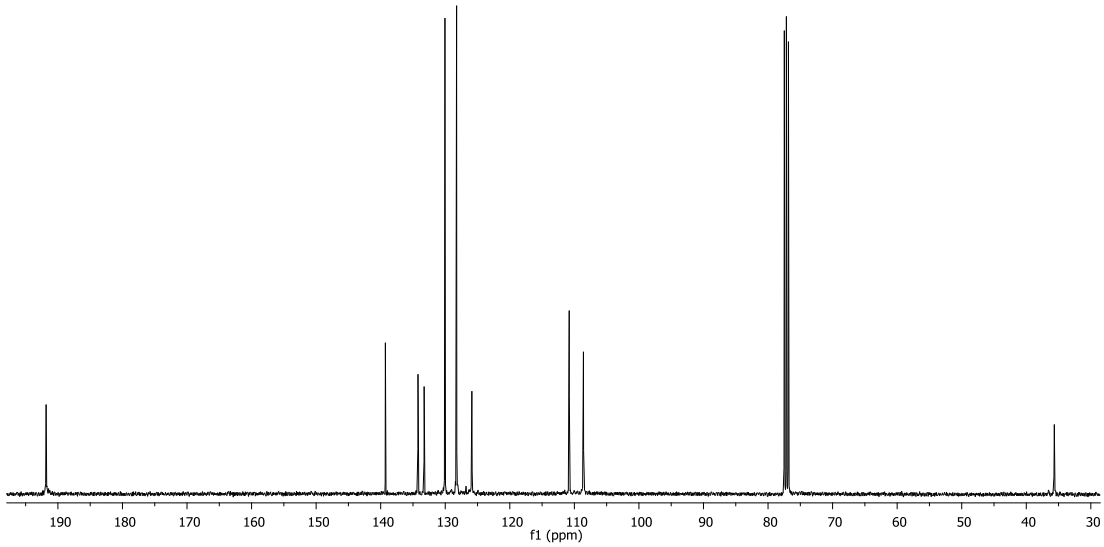
^{1}H and ^{13}C NMR of 1-(4-(1-Methyl-1H-pyrrol-2-yl)phenyl)ethan-1-one



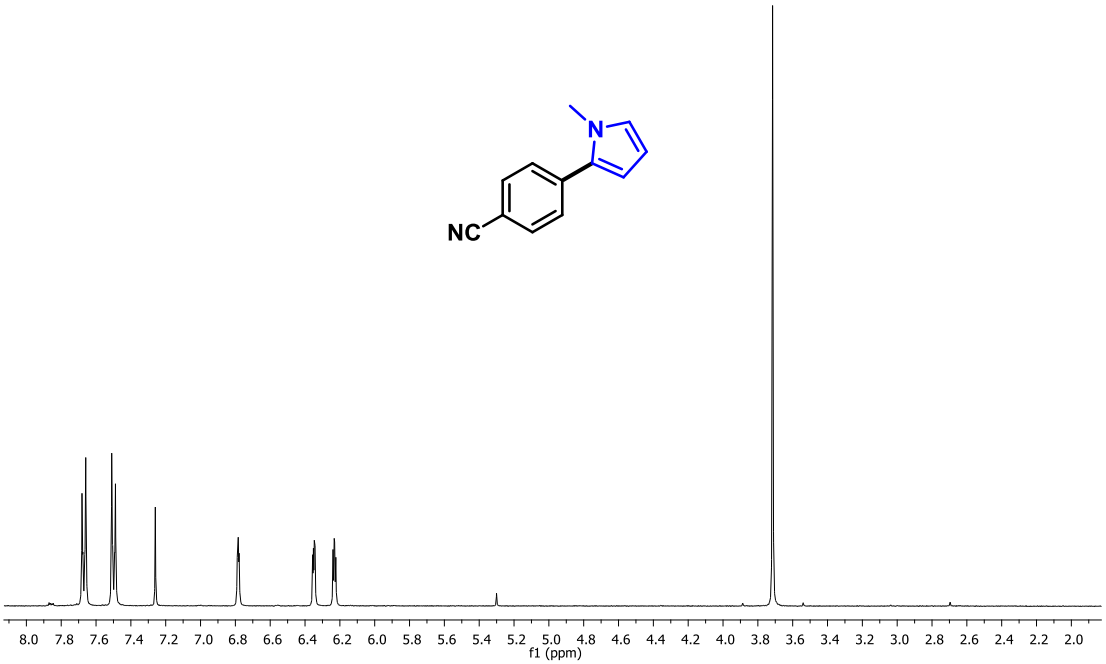


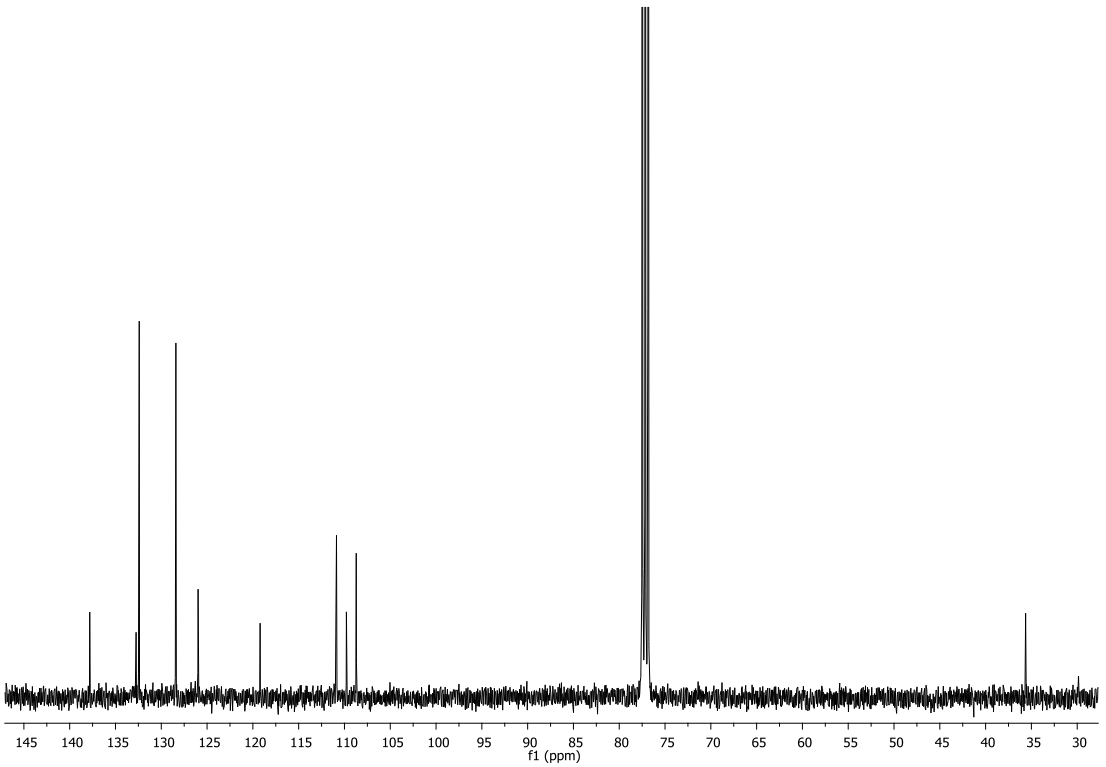
^{1}H and ^{13}C NMR of 4-(1-methyl-1H-pyrrol-2-yl)benzaldehyde



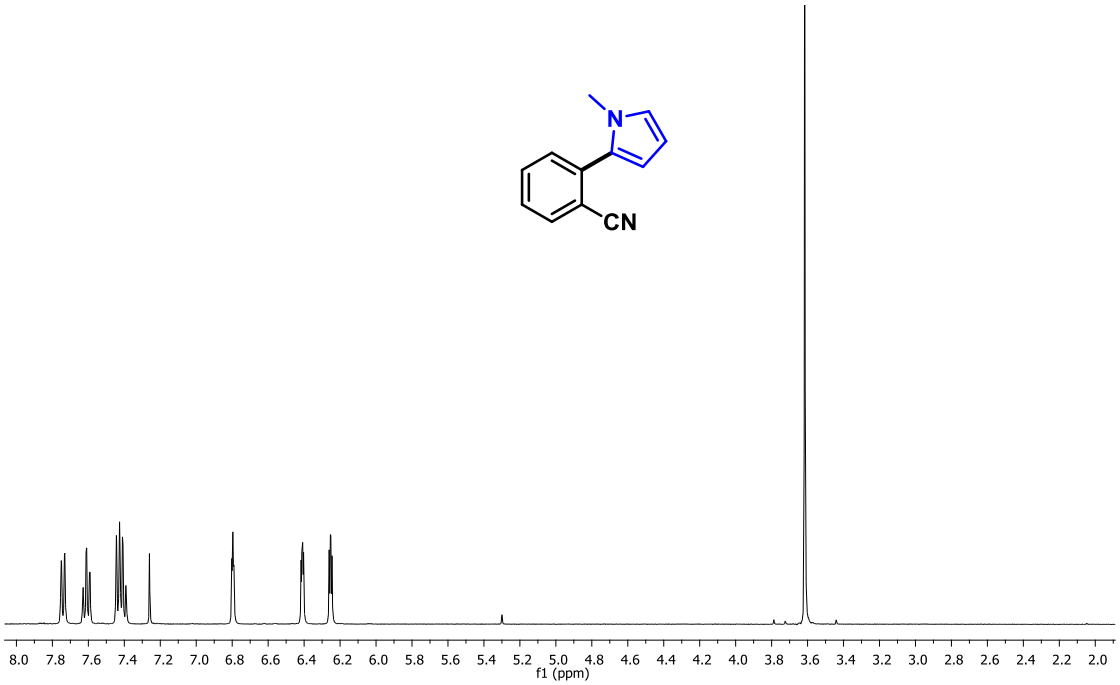


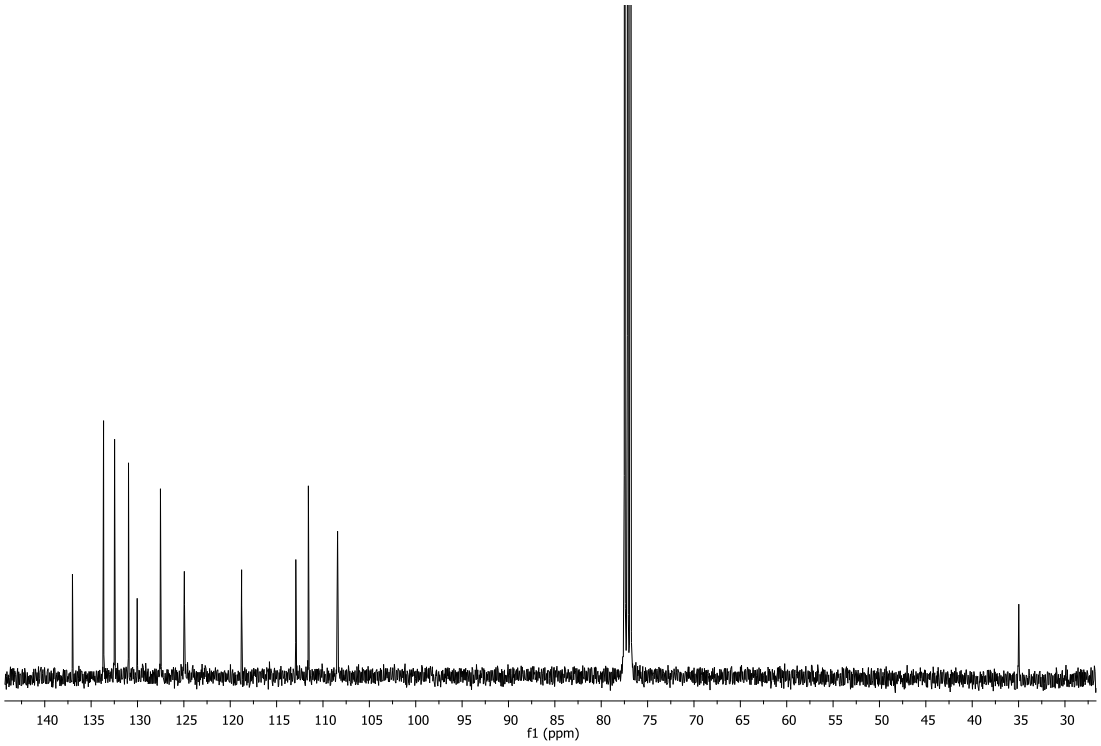
^{1}H and ^{13}C NMR of 4-(1-Methyl-1H-pyrrol-2-yl)benzonitrile



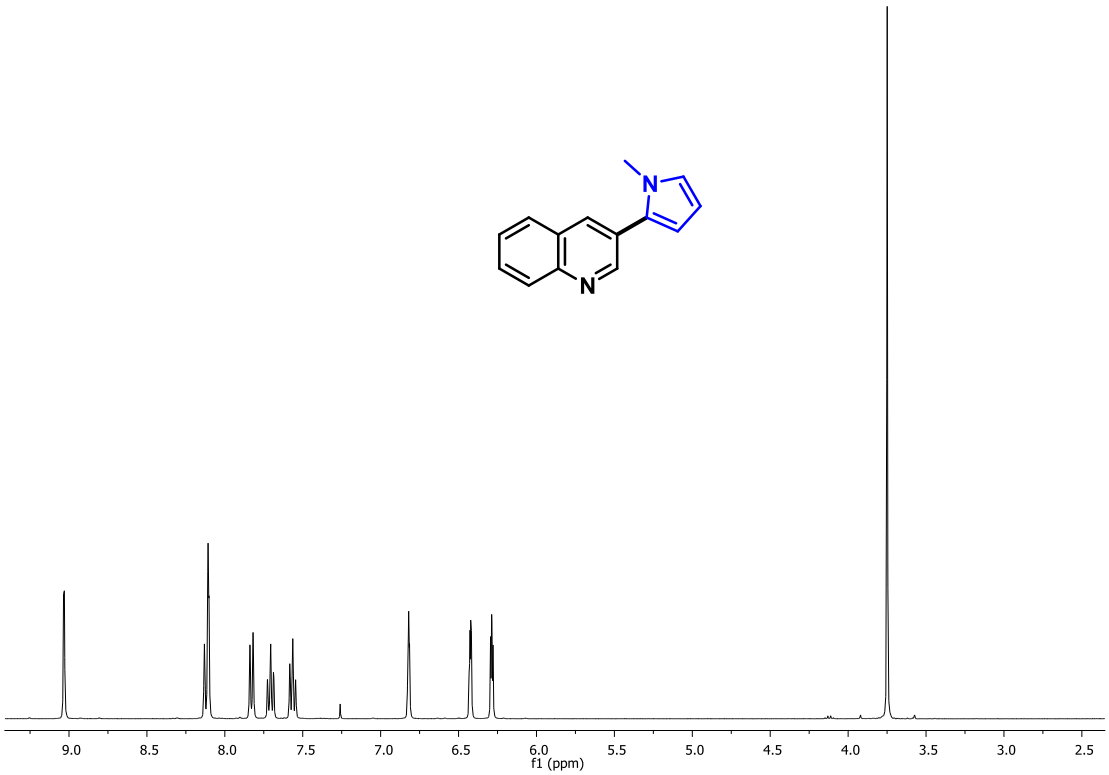


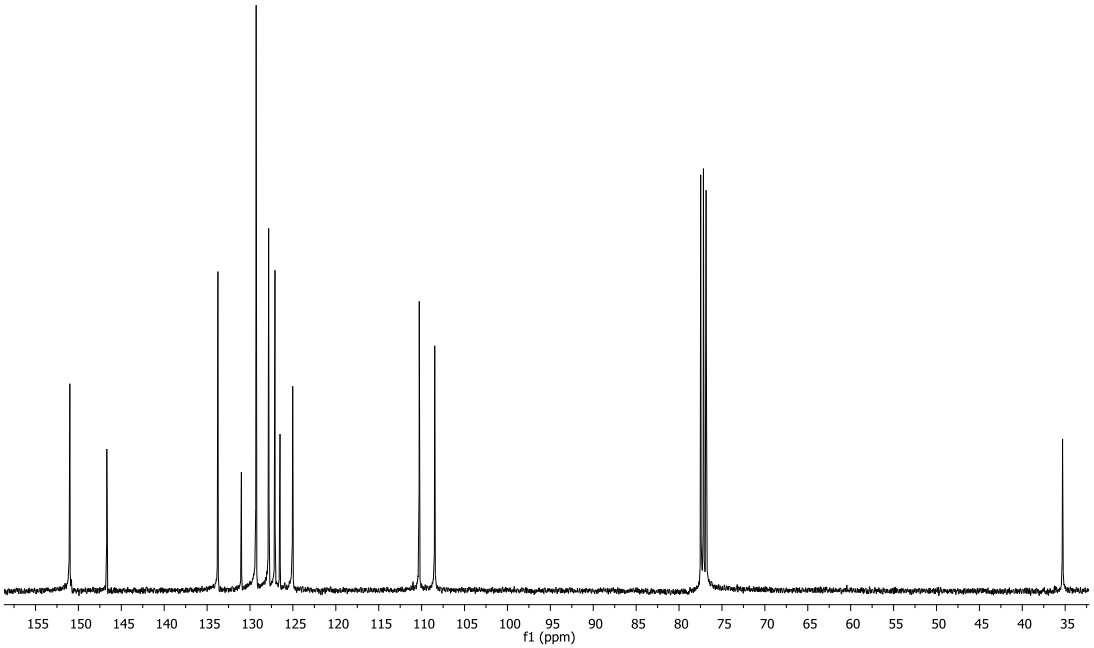
^{1}H and ^{13}C NMR of 2-(1-Methyl-1H-pyrrol-2-yl)benzonitrile



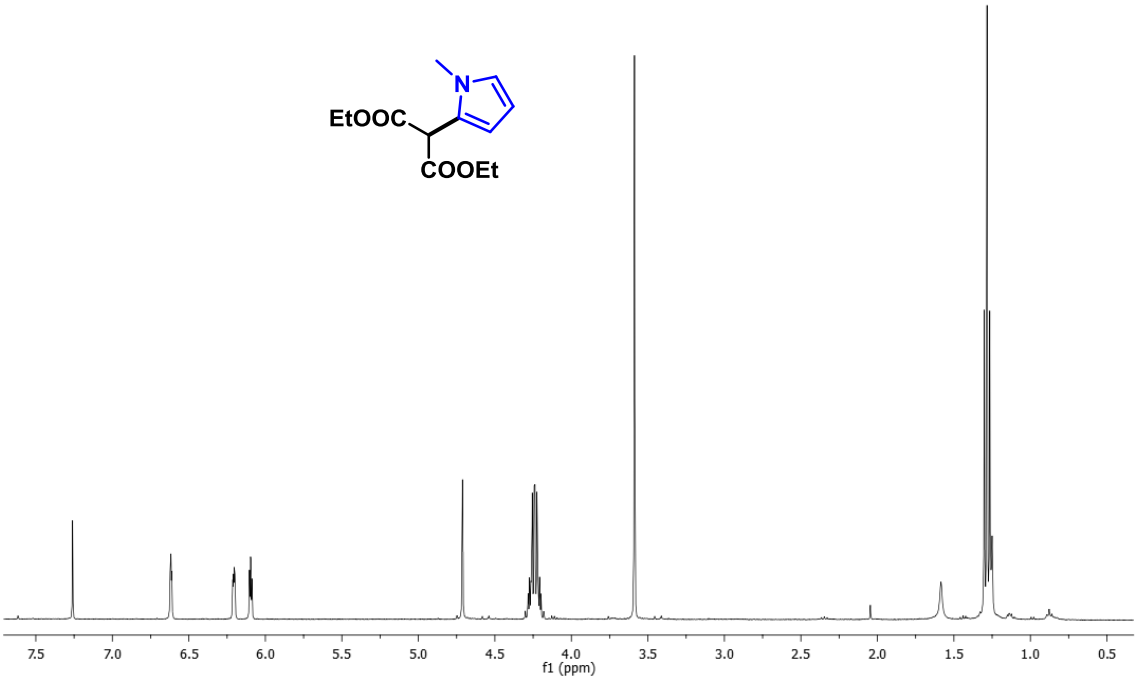


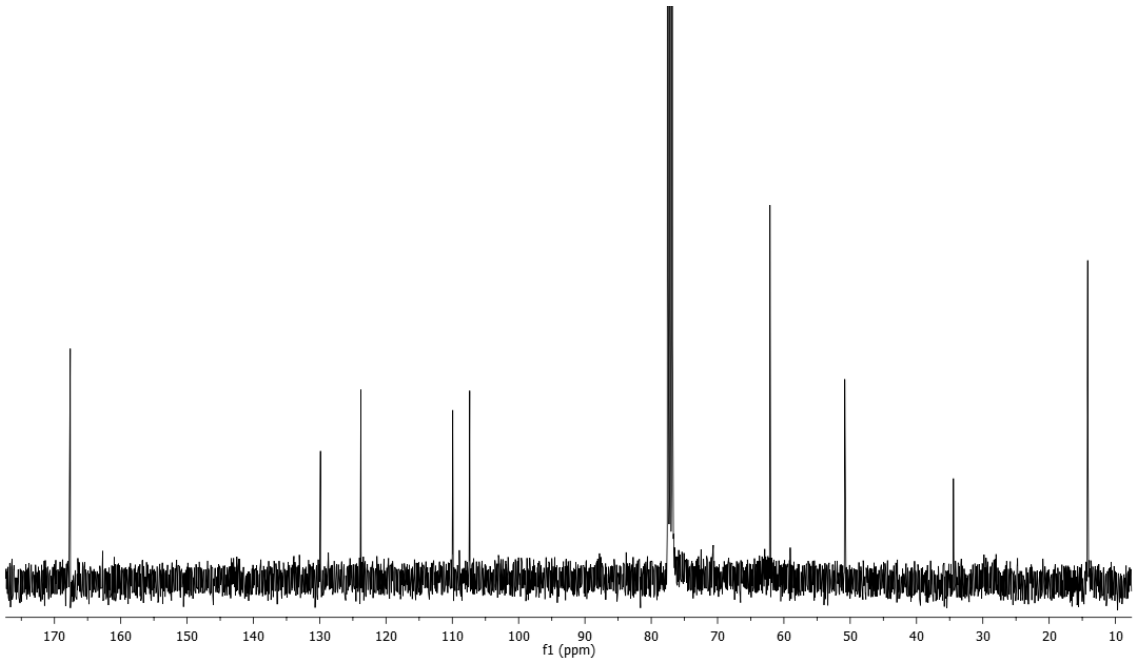
^{1}H and ^{13}C NMR of 3-(1-Methyl-1H-pyrrol-2-yl)quinolone



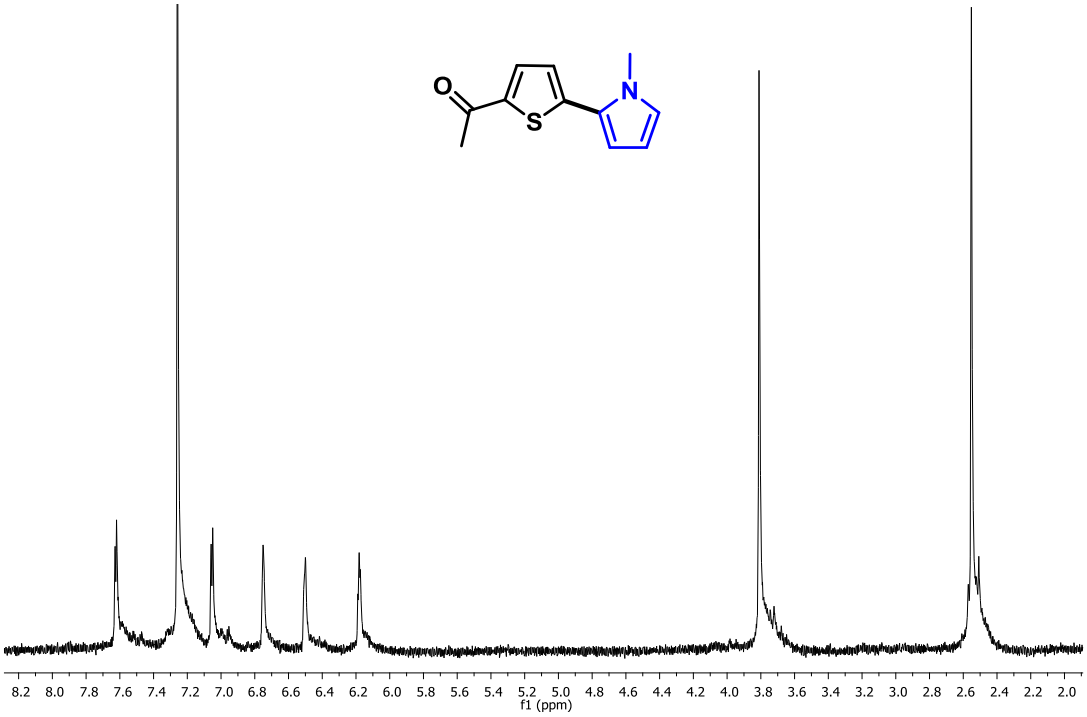


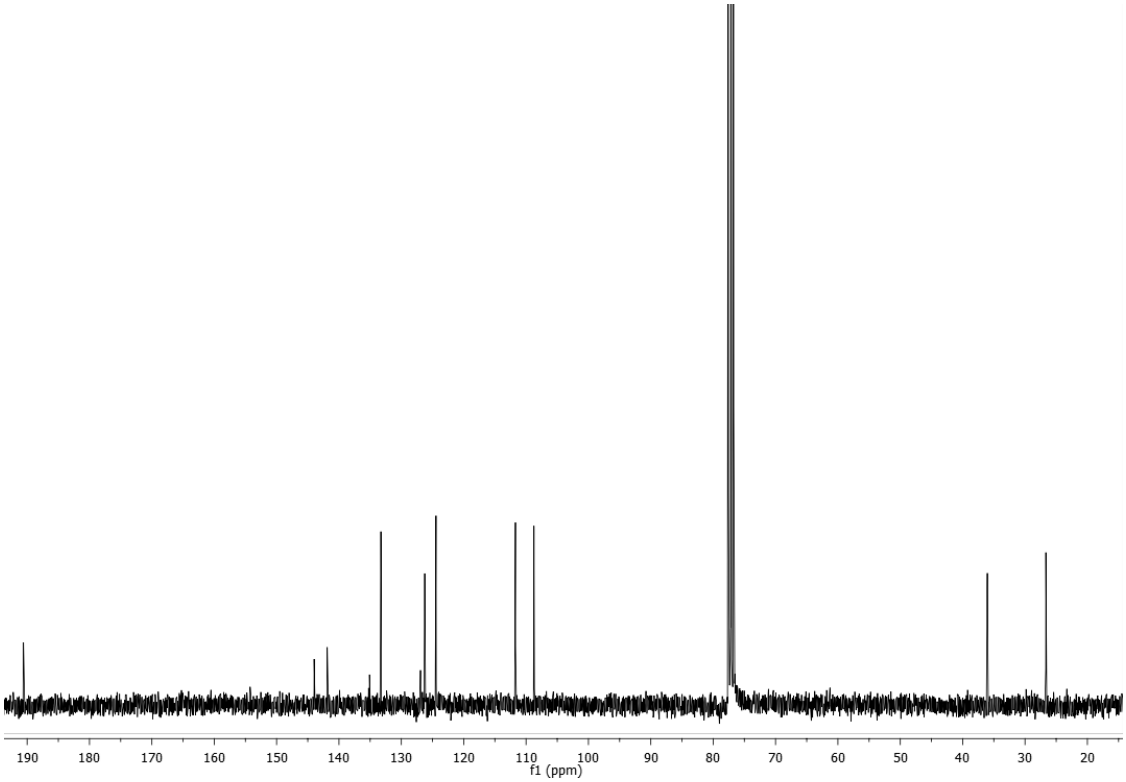
^{1}H and ^{13}C NMR of diethyl 2-(1-methyl-1H-pyrrol-2-yl)malonate



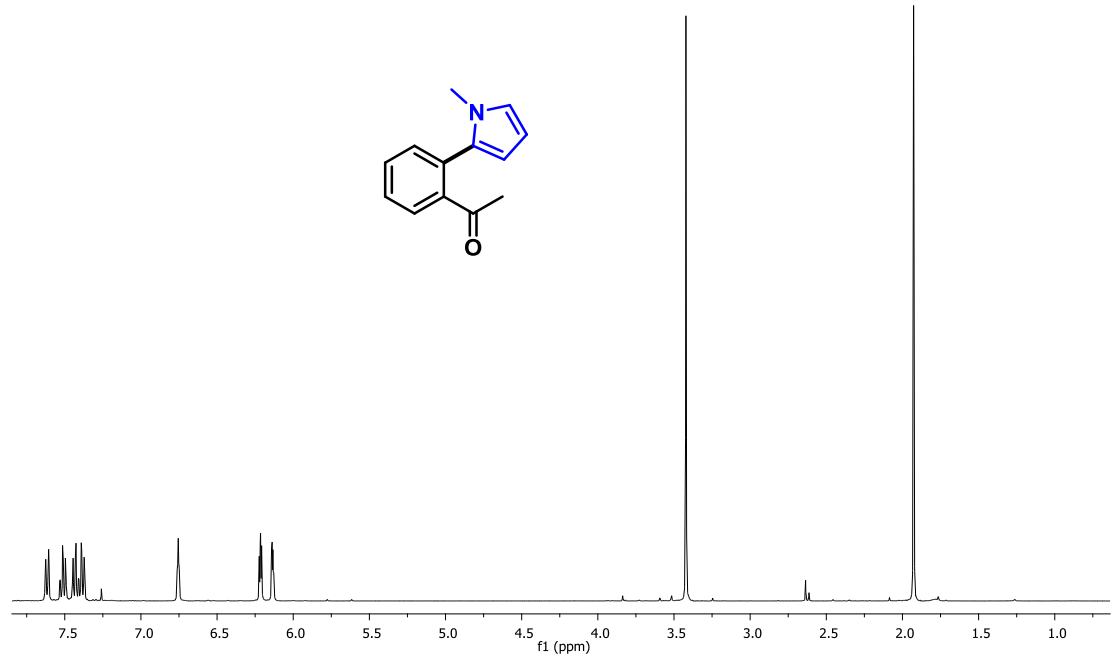


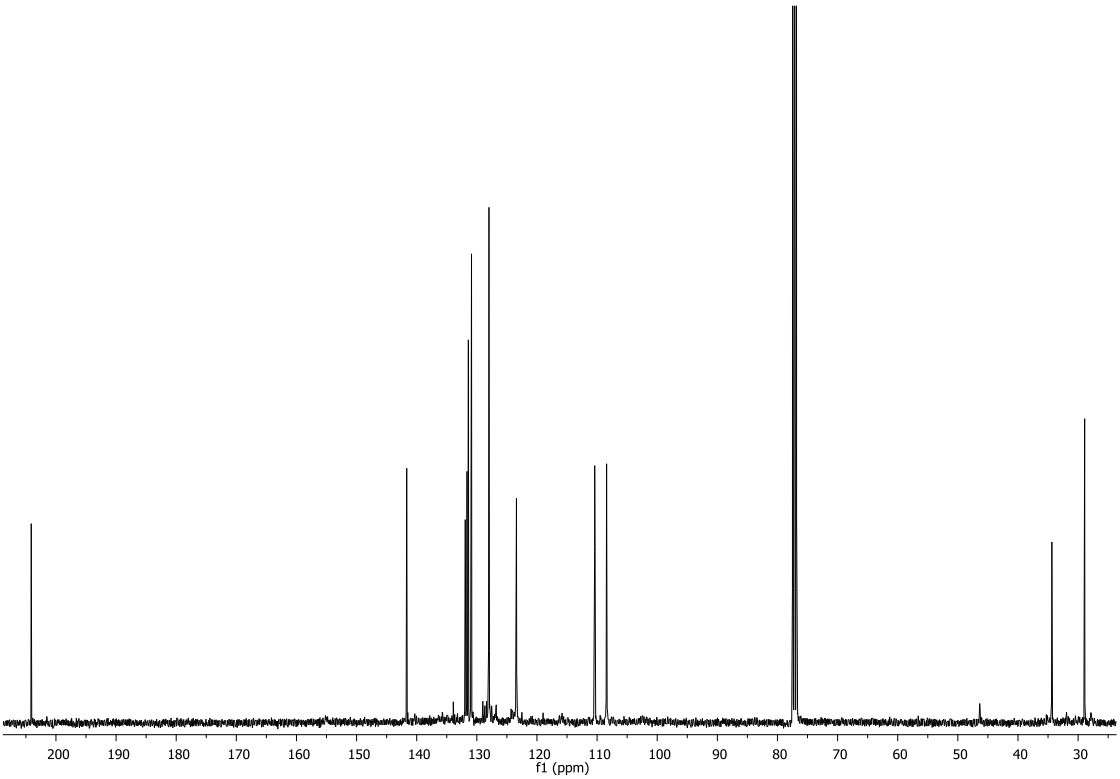
^{1}H and ^{13}C NMR of 1-(5-(1-Methyl-1H-pyrrol-2-yl)thiophen-2-yl)ethan-1-one





^{1}H and ^{13}C NMR of 1-(2-(1-Methyl-1H-pyrrol-2-yl)phenyl)ethan-1-one



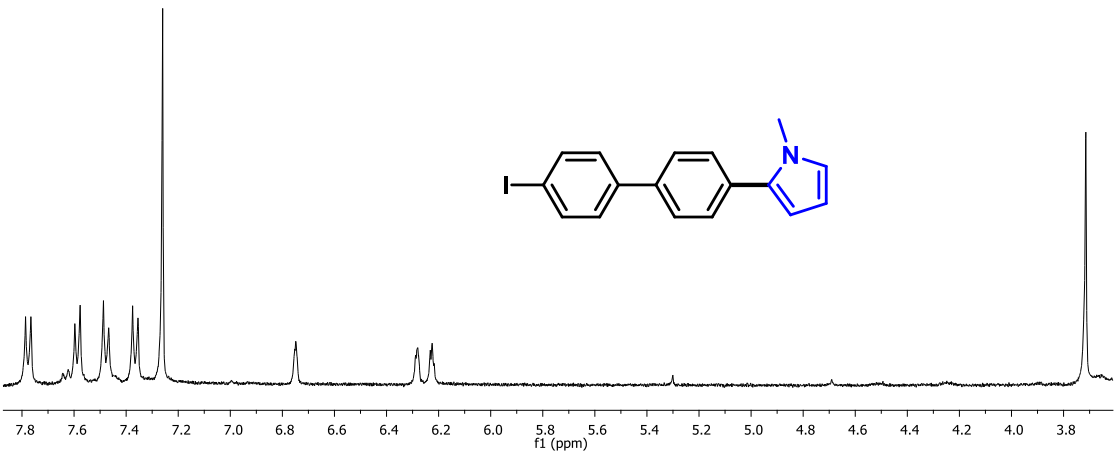


Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C13 H13 N O	0.339	199.09991	110234	C13 H13 N O	199.09971	0.97

Compound Label	RT	Algorithm	Mass
Cpd 1: C13 H13 N O	0.339	Find By Formula	199.09991

^{1}H of 2-(4'-iodo-[1,1'-biphenyl]-4-yl)-1-methyl-1H-pyrrole



Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C17 H14 I N	0.637	359.01637	340	C17 H14 I N	359.01709	-2.01

Compound Label	RT	Algorithm	Mass
Cpd 1: C17 H14 I N	0.637	Find By Formula	359.01637

Optimized geometries of ^{1}DPA(S_0), ^{1}DPA(S_1), ^{3}DPA(T_1) , DPA$^{\bullet+}$, ^{1}BOPHY(S_0), ^{1}BOPHY(S_1), ^{3}BOPHY(T_1), Intermediate a, Intermediate b and aryl halides (neutral and radical anion).

^{1}DPA(S_0)

C	0.71115300	-3.66675500	0.00003600
C	1.40199900	-2.48480900	0.00003000
C	0.72328300	-1.22279300	0.00001800
C	-0.72328700	-1.22278800	0.00001900
C	-1.40201300	-2.48479800	0.00003000
C	-0.71117600	-3.66675000	0.00003700
C	1.42871600	-0.00000300	0.00000800
C	-1.42871400	0.00000300	0.00001100
C	-0.72328000	1.22280400	-0.00000700
C	0.72328600	1.22280100	-0.00000800
C	1.40200900	2.48480400	-0.00003200
H	2.48590400	2.48913600	-0.00003200
C	0.71116700	3.66676100	-0.00005300
C	-0.71115200	3.66676400	-0.00005500
C	-1.40199800	2.48480900	-0.00003300
H	1.24923000	-4.61024400	0.00004300
H	2.48589400	-2.48913700	0.00003600
H	-2.48590800	-2.48911900	0.00003600
H	-1.24925900	-4.61023500	0.00004400
H	1.24925800	4.61024100	-0.00007000
H	-1.24924100	4.61024500	-0.00007500
H	-2.48589200	2.48914000	-0.00003800
C	-2.92710600	0.00000500	0.00001100
C	-3.64370000	0.00010000	1.20615000
C	-3.64368500	-0.00009800	-1.20613900
C	-5.03930700	0.00009500	1.20649900
H	-3.09966000	0.00017800	2.14625500
C	-5.03929100	-0.00010100	-1.20650700
H	-3.09963000	-0.00017500	-2.14623500
C	-5.74100300	-0.00000400	-0.00000800
H	-5.57772000	0.00016900	2.14998800
H	-5.57769400	-0.00018100	-2.15000200
H	-6.82711400	-0.00000800	-0.00001600
C	2.92710800	-0.00000200	0.00000500
C	3.64368900	-0.00007600	-1.20614100
C	3.64369900	0.00007000	1.20615000
C	5.03929700	-0.00008600	-1.20650600
H	3.09963300	-0.00012100	-2.14623700
C	5.03930300	0.00006500	1.20650200
H	3.09965300	0.00013700	2.14625300
C	5.74100300	-0.00001600	-0.00000600
H	5.57769900	-0.00014600	-2.15000100
H	5.57771900	0.00012400	2.14999000
H	6.82711400	-0.00002300	-0.00000600

^{1}DPA(S_1)

C	0.69389600	-3.70727200	-0.00012300
C	1.39395600	-2.48515600	-0.00008300

C	0.72224900	-1.24410100	-0.00005400
C	-0.72224900	-1.24410100	-0.00005400
C	-1.39395600	-2.48515600	-0.00007700
C	-0.69389700	-3.70727200	-0.00011900
C	1.42419900	0.00000000	0.00000000
C	-1.42419900	0.00000000	0.00000000
C	-0.72224900	1.24410100	0.00005300
C	0.72224900	1.24410100	0.00005400
C	1.39395600	2.48515600	0.00008400
H	2.47771500	2.49417000	0.00007200
C	0.69389700	3.70727200	0.00012300
C	-0.69389600	3.70727200	0.00011900
C	-1.39395600	2.48515600	0.00007600
H	1.24771400	-4.64099700	-0.00014800
H	2.47771500	-2.49417000	-0.00007100
H	-2.47771500	-2.49417000	-0.00005700
H	-1.24771500	-4.64099700	-0.00014100
H	1.24771500	4.64099700	0.00014900
H	-1.24771400	4.64099700	0.00014000
H	-2.47771500	2.49417100	0.00005600
C	-2.91724900	0.00000000	-0.00000100
C	-3.63547000	0.00036100	1.20654200
C	-3.63547000	-0.00036100	-1.20654400
C	-5.03105200	0.00035700	1.20638600
H	-3.09143700	0.00064000	2.14659700
C	-5.03105100	-0.00035700	-1.20638800
H	-3.09143600	-0.00064000	-2.14659900
C	-5.73291200	0.00000000	-0.00000100
H	-5.56932200	0.00063300	2.15006500
H	-5.56932100	-0.00063300	-2.15006800
H	-6.81903400	0.00000000	-0.00000100
C	2.91724900	0.00000000	0.00000100
C	3.63547000	-0.00024800	-1.20654200
C	3.63546900	0.00024800	1.20654400
C	5.03105200	-0.00024500	-1.20638500
H	3.09143700	-0.00044000	-2.14659700
C	5.03105100	0.00024500	1.20638900
H	3.09143500	0.00044000	2.14659800
C	5.73291200	0.00000000	0.00000200
H	5.56932200	-0.00043500	-2.15006500
H	5.56932100	0.00043400	2.15006800
H	6.81903400	0.00000000	0.00000200

^{3}DPA(T_1)

C	0.69085500	-3.71077300	0.00000500
C	1.39089600	-2.48635000	0.00000200
C	0.72045000	-1.25561300	-0.00000500
C	-0.72045000	-1.25561300	-0.00000500
C	-1.39089600	-2.48635000	0.00000400
C	-0.69085500	-3.71077300	0.00000600
C	1.43334500	0.00000000	0.00000000
C	-1.43334500	0.00000000	-0.00000100
C	-0.72045000	1.25561300	0.00000300
C	0.72045000	1.25561300	0.00000400
C	1.39089600	2.48635000	-0.00000300

H	2.47491300	2.49492200	-0.00000600
C	0.69085500	3.71077300	-0.00000600
C	-0.69085500	3.71077400	-0.00000800
C	-1.39089600	2.48635000	-0.00000500
H	1.24562000	-4.64417600	0.00000900
H	2.47491300	-2.49492200	0.00000600
H	-2.47491300	-2.49492100	0.00001000
H	-1.24562000	-4.64417600	0.00001100
H	1.24562100	4.64417600	-0.00001000
H	-1.24562000	4.64417700	-0.00001300
H	-2.47491300	2.49492200	-0.00001200
C	-2.92557000	0.00000000	-0.00000100
C	-3.64370100	0.00016200	1.20638900
C	-3.64370200	-0.00016200	-1.20639000
C	-5.03923700	0.00016100	1.20647000
H	-3.10019000	0.00028900	2.14679300
C	-5.03923800	-0.00016100	-1.20647000
H	-3.10019100	-0.00028900	-2.14679400
C	-5.74093800	0.00000000	0.00000000
H	-5.57765300	0.00028600	2.14998800
H	-5.57765300	-0.00028600	-2.14998900
H	-6.82704900	0.00000000	0.00000000
C	2.92557000	0.00000000	0.00000100
C	3.64370200	-0.00011700	-1.20638800
C	3.64370100	0.00011600	1.20639100
C	5.03923800	-0.00011600	-1.20646800
H	3.10019200	-0.00020700	-2.14679300
C	5.03923700	0.00011500	1.20647200
H	3.10018900	0.00020700	2.14679500
C	5.74093800	0.00000000	0.00000300
H	5.57765400	-0.00020600	-2.14998600
H	5.57765100	0.00020500	2.14999100
H	6.82704900	0.00000000	0.00000300

DPA$^{\bullet+}$

C	-0.69863500	3.67853500	-0.06370500
C	-1.39315600	2.47892800	-0.10467400
C	-0.72062100	1.23318600	-0.02206000
C	0.72055500	1.23322900	0.02177300
C	1.39300000	2.47904200	0.10408900
C	0.69839600	3.67859200	0.06290100
C	-1.44310800	-0.00003200	0.00015600
C	1.44310600	0.00005500	-0.00025800
C	0.72060700	-1.23315800	-0.02238300
C	-0.72055300	-1.23320100	0.02209500
C	-1.39296000	-2.47899500	0.10502400
H	-2.47053200	-2.49086400	0.20633100
C	-0.69837800	-3.67855700	0.06339900
C	0.69855400	-3.67850900	-0.06423200
C	1.39307600	-2.47890300	-0.10548600
H	-1.24039800	4.61667800	-0.12349300
H	-2.47081300	2.49063100	-0.20505800
H	2.47067200	2.49084200	0.20424700
H	1.24010400	4.61678200	0.12245100
H	-1.24004500	-4.61674000	0.12341800

H	1.24027100	-4.61664800	-0.12448400
H	2.47066800	-2.49065800	-0.20650600
C	2.92535000	0.00003200	0.00003800
C	3.64055600	-0.59799300	1.05565400
C	3.64106600	0.59809800	-1.05519100
C	5.03337200	-0.58458200	1.05912900
H	3.10095100	-1.04456200	1.88503400
C	5.03388000	0.58456100	-1.05809400
H	3.10179700	1.04502100	-1.88458600
C	5.73268300	-0.00008400	0.00064600
H	5.57258800	-1.03013600	1.88889500
H	5.57348800	1.03014800	-1.88758700
H	6.81794100	-0.00014800	0.00086800
C	-2.92533400	-0.00007000	0.00020800
C	-3.64078500	-0.59819600	-1.05517800
C	-3.64080000	0.59810400	1.05556000
C	-5.03360200	-0.58471100	-1.05838100
H	-3.10133100	-1.04492400	-1.88457000
C	-5.03361100	0.58463300	1.05873700
H	-3.10135500	1.04488600	1.88492700
C	-5.73266300	-0.00003900	0.00017000
H	-5.57300800	-1.03034400	-1.88798100
H	-5.57303300	1.03028800	1.88831500
H	-6.81792000	-0.00002600	0.00016000

^{1}BOPHY(S_0)

C	4.56467600	0.07962100	-0.15324300
C	3.71079800	1.20166000	-0.12875900
C	2.40866800	0.67885700	0.13540000
N	2.49741700	-0.72280600	0.26321100
C	3.80168200	-1.09931200	0.10222400
C	1.18171600	1.32974700	0.26538200
N	0.00539200	0.70645000	0.43536500
N	-0.00539200	-0.70643300	0.43538600
B	1.30236200	-1.56213900	0.69274500
B	-1.30236500	1.56216300	0.69267800
N	-2.49741200	0.72282000	0.26313800
C	-2.40866100	-0.67884600	0.13536400
C	-1.18171300	-1.32973500	0.26539900
C	-3.80167700	1.09932000	0.10213700
C	-4.56467700	-0.07962800	-0.15325000
C	-3.71077100	-1.20164800	-0.12888700
C	4.07381000	2.64249200	-0.34411900
C	4.24564000	-2.52259800	0.22777500
C	-4.24564100	2.52260500	0.22767100
C	-4.07375900	-2.64247500	-0.34433100
F	1.16783700	-2.76608700	-0.07413900
F	1.37618000	-1.90081000	2.08368000
F	-1.16782200	2.76609200	-0.07423200
F	-1.37621200	1.90086600	2.08360300
H	1.11662000	2.40999500	0.22834100

H	-1.11661400	-2.40998200	0.22836600
H	4.84288900	2.96106400	0.37103100
H	4.48827900	2.79686000	-1.34897400
H	3.21060800	3.30602600	-0.23032700
H	4.03810800	-2.90010400	1.23770100
H	3.69590100	-3.16393000	-0.47043600
H	5.31698500	-2.61432200	0.03368500
H	-4.03806200	2.90014100	1.23757600
H	-3.69594300	3.16392200	-0.47058600
H	-5.31699700	2.61431400	0.03363100
H	-4.84297300	-2.96104200	0.37067500
H	-4.48804400	-2.79683300	-1.34926400
H	-3.21058500	-3.30601800	-0.23038100
I	-6.63872200	-0.13949400	-0.50724100
I	6.63871100	0.13946900	-0.50730000

^{1}BOPHY(S_1)

C	4.58895000	-0.07351700	-0.00110400
C	3.75549300	-1.19407000	-0.00141700
C	2.42533000	-0.68041900	-0.00004000
N	2.49015900	0.71121800	0.00078600
C	3.79769900	1.09621000	0.00022500
C	1.20039700	-1.33128500	0.00069400
N	0.02037300	-0.67151400	0.00140300
N	-0.02037400	0.67151400	0.00140800
B	1.27451300	1.58904600	0.00285500
B	-1.27451300	-1.58904600	0.00287200
N	-2.49015900	-0.71121800	0.00084300
C	-2.42533000	0.68041900	0.00002100
C	-1.20039700	1.33128500	0.00073100
C	-3.79769900	-1.09621000	0.00031200
C	-4.58895000	0.07351700	-0.00099300
C	-3.75549300	1.19407100	-0.00131800
C	4.14483700	-2.64170600	-0.00190400
C	4.19996500	2.53353200	0.00095900
C	-4.19996500	-2.53353200	0.00104700
C	-4.14483600	2.64170700	-0.00177900
F	1.20036600	2.42426300	1.15110400
F	1.19957300	2.42874600	-1.14202900
F	-1.20033700	-2.42427700	1.15110900
F	-1.19960200	-2.42873300	-1.14202500
H	1.12604900	-2.39382700	0.00068100
H	-1.12604900	2.39382700	0.00072400
H	4.75454200	-2.87738200	-0.86689500
H	4.72609000	-2.88580800	0.88040600
H	3.27846600	-3.28850600	-0.01915700
H	3.79960200	3.03662800	-0.87149700
H	3.79909200	3.03590700	0.87359200

H	5.27375900	2.63230800	0.00131100
H	-3.79962100	-3.03662300	-0.87142100
H	-3.79907200	-3.03591200	0.87366800
H	-5.27375900	-2.63230800	0.00142200
H	-4.75469700	2.87735600	-0.86666500
H	-4.72592900	2.88583700	0.88063000
H	-3.27846800	3.28850500	-0.01920900
I	-6.68196900	0.12905200	-0.00174000
I	6.68196900	-0.12905200	-0.00190800

^{3}BOPHY(T_1),

C	-4.62466400	0.09555300	-0.05879000
C	-3.78307500	1.22044000	-0.01925000
C	-2.43916300	0.68839200	0.08005800
N	-2.50364100	-0.70677300	0.09678200
C	-3.83739400	-1.09622600	0.01574700
C	-1.21765300	1.35376500	0.13810600
N	-0.01371000	0.67647200	0.18268800
N	0.01371500	-0.67651900	0.18237600
B	-1.29234400	-1.58966400	0.27160400
B	1.29234600	1.58973200	0.27058000
N	2.50365200	0.70671400	0.09649100
C	2.43912400	-0.68843200	0.07896300
C	1.21761200	-1.35381600	0.13676000
C	3.83742800	1.09616700	0.01579100
C	4.62466500	-0.09559700	-0.05932800
C	3.78303200	-1.22047100	-0.02051800
C	-4.12021100	2.68045400	-0.06867900
C	-4.24173000	-2.53247800	0.02332300
C	4.24176800	2.53241100	0.02441300
C	4.12011100	-2.68047100	-0.07075200
F	-1.26923400	-2.24536800	1.54924500
F	-1.18375100	-2.58996300	-0.75010100
F	1.26948100	2.24702300	1.54738300
F	1.18348500	2.58885600	-0.75231300
H	-1.13729100	2.42969600	0.13453900
H	1.13720800	-2.42974100	0.13247500
H	-5.20110600	2.83418900	-0.13603500
H	-3.76092700	3.20257900	0.82920000
H	-3.65569500	3.16827600	-0.93723900
H	-3.82217100	-3.05745200	-0.84507200
H	-3.84917400	-3.03870100	0.91524900
H	-5.32958100	-2.63282800	0.00788300
H	3.81934000	3.05878100	-0.84171900
H	3.85205200	3.03711400	0.91847300
H	5.32955700	2.63283900	0.00573200
H	5.20111700	-2.83424900	-0.13619300
H	3.75902700	-3.20346200	0.82589200
H	3.65724200	-3.16737500	-0.94071500
I	6.72235900	-0.12697000	-0.20946000
I	-6.72233300	0.12692600	-0.20930800

Intermediate a

C	2.26282200	0.05846300	-0.02989100
C	1.38746700	-1.03711500	-0.10870700
C	0.00991300	-0.84261700	-0.13918100
C	-0.52820500	0.44916600	-0.08486300
C	0.34407200	1.54145900	-0.00057900
C	1.72166000	1.35111200	0.02267100
H	1.77863300	-2.04876300	-0.14783800
H	-0.66403500	-1.69138000	-0.19838400
H	-0.06364000	2.54839800	0.04971500
H	2.40593700	2.19025300	0.08920300
C	-2.03651600	0.66683700	-0.15881800
H	-2.23374600	1.70493300	0.18400500
C	-2.64314300	0.43433900	-1.52603900
H	-2.26350300	0.89583800	-2.42663300
C	-3.73054800	-0.41195100	-1.39376700
H	-4.37503500	-0.75603600	-2.19276300
C	-3.85487600	-0.79016300	-0.05665600
H	-4.57731900	-1.44580400	0.40968700
N	-2.79969800	-0.27336100	0.68369400
C	-2.88068300	-0.04081400	2.10985700
H	-3.40266300	-0.87466400	2.58709900
H	-1.87348000	0.01637800	2.53338600
H	-3.41469000	0.89082500	2.36003300
C	3.75323400	-0.08932800	0.00580500
O	4.47655900	0.89324400	0.08052300
C	4.35432200	-1.48415100	-0.05264400
H	5.44052300	-1.39653000	-0.02177400
H	4.01470700	-2.09434500	0.79145700
H	4.05660700	-2.00294900	-0.97035200

Intermediate b

C	2.21272300	0.00085500	-0.07342100
C	1.36053700	-1.01295600	0.38652900
C	-0.01635800	-0.91985100	0.19494200
C	-0.55609400	0.19630600	-0.45749200
C	0.29006900	1.21232300	-0.91937800
C	1.66407400	1.11153300	-0.72757600
H	1.76465900	-1.88394400	0.89079600
H	-0.66264500	-1.71870800	0.54820600
H	-0.12136700	2.07736000	-1.43288000
H	2.33936000	1.88493000	-1.07739500
C	-2.05772600	0.31418400	-0.67622300
H	-2.25984800	1.21345300	-1.27693300
C	-2.73798700	-0.85989100	-1.30980500
H	-2.42901000	-1.25953500	-2.26755900
C	-3.74628000	-1.29612900	-0.52009400
H	-4.42890000	-2.11652000	-0.69288500
C	-3.77177800	-0.44166500	0.64038700
H	-4.45935600	-0.49107100	1.47886200
N	-2.83534000	0.46646900	0.58654300
C	-2.54984300	1.50482000	1.57751200
H	-3.20702200	1.37137300	2.43652200
H	-1.50659300	1.42195400	1.88875600
H	-2.71865200	2.49020100	1.13642000

C	3.71747500	-0.03907800	0.09886200
O	4.38290600	0.89508800	-0.30879000
C	4.34934800	-1.23770400	0.77125400
H	5.42943000	-1.09559800	0.79605700
H	3.97743300	-1.35558300	1.79532200
H	4.11768100	-2.16079500	0.22825400

4-bromoacetophenone

C	-1.44147000	-2.49470300	-0.03321900
C	-2.49958500	-1.59113300	-0.07727800
C	-2.23355600	-0.22725200	-0.07859200
C	-0.92142900	0.27237000	-0.06539800
C	0.12849800	-0.66010500	-0.01779700
C	-0.13042600	-2.02913700	0.00797000
Br	1.96975200	-0.14161200	0.09673900
C	-0.71468000	1.76473300	-0.15287800
O	0.20106000	2.23876800	-0.78804200
C	-1.71140200	2.65769000	0.56670600
H	-1.62932100	-3.56222600	-0.02361200
H	-3.52359600	-1.94399800	-0.10671900
H	-3.06128500	0.47041800	-0.11094000
H	0.69617900	-2.72572700	0.06071200
H	-1.92132600	2.29645400	1.57623400
H	-1.30562600	3.66769100	0.60336200
H	-2.66051300	2.68886700	0.02233600

4-bromoacetophenone radical anion

C	-1.09588800	2.69561000	-0.00009100
C	-2.27121000	1.91570500	-0.00005500
C	-2.20879800	0.54004600	-0.00002100
C	-0.97755400	-0.21766100	-0.00002400
C	0.19622200	0.63287600	-0.00006800
C	0.13199000	2.01280800	-0.00010000
Br	2.01174900	-0.07309900	-0.00007300
C	-0.96429300	-1.65721500	0.00003900
O	0.07776500	-2.36554600	0.00019900
C	-2.27835700	-2.45176100	0.00032400
H	-1.12664300	3.77914300	-0.00011100
H	-3.24527800	2.39896100	-0.00005200
H	-3.14453000	-0.00282500	0.00001200
H	1.05921600	2.57513800	-0.00013100
H	-3.20502100	-1.87640200	-0.00009600
H	-2.28175900	-3.10727400	-0.87890700
H	-2.28199600	-3.10636200	0.88024300

2-bromoacetophenone

C	-1.08853500	-1.15276600	0.00005200
C	0.30348900	-1.19190000	0.00003900
C	1.01198500	0.00570300	0.00001400

C	0.35544100	1.23596700	-0.00000400
C	-1.03283900	1.25805100	-0.00001100
C	-1.77363800	0.06826000	0.00003300
H	-1.63205000	-2.08955100	0.00007400
H	0.82784600	-2.13858200	0.00004700
H	0.92227700	2.15806800	-0.00002400
H	-1.56827000	2.19961300	-0.00003900
Br	2.92513800	-0.03743500	-0.00001200
C	-3.27214800	0.15894400	0.00000800
O	-3.82385500	1.24306100	0.00003300
C	-4.08381100	-1.12244000	-0.00007200
H	-5.14161900	-0.86546200	-0.00035400
H	-3.85819400	-1.72870800	-0.88233400
H	-3.85863900	-1.72853800	0.88242100

2-bromoacetophenone radical anion

C	1.09457500	-1.16180900	0.00009700
C	-0.28936700	-1.19453700	0.00006900
C	-1.01220500	0.00837700	0.00003800
C	-0.34088200	1.24627200	0.00008500
C	1.03800500	1.27391900	0.00006700
C	1.82719700	0.07302100	0.00003900
H	1.62750000	-2.10628500	0.00016800
H	-0.81222100	-2.14473000	0.00010200
H	-0.90733700	2.17141000	0.00011500
H	1.56722600	2.21953700	0.00009000
Br	-2.95113800	-0.03602300	-0.00004100
C	3.25838200	0.15493700	-0.00004000
O	3.89111300	1.25123200	-0.00006600
C	4.06538900	-1.14533600	-0.00007100
H	5.12523800	-0.88504900	-0.00032400
H	3.85717700	-1.76638100	0.88249100
H	3.85679300	-1.76661500	-0.88237000

4-bromobenzaldehyde

C	-1.34316600	1.36699500	0.00000000
C	-2.12015200	0.20423800	0.00000000
C	-1.49125000	-1.04800700	0.00000100
C	-0.10663800	-1.13747600	0.00000000
C	0.64895100	0.03732100	0.00000000
C	0.04647100	1.29298300	0.00000000
Br	2.55737700	-0.08332600	0.00000000
C	-3.59669000	0.30908400	0.00000100
O	-4.35633600	-0.63366100	-0.00000100
H	-1.82850600	2.33800500	0.00000000
H	-2.10465400	-1.94142600	0.00000100
H	0.38608800	-2.10103900	0.00000100
H	0.65080700	2.19060400	0.00000000

H	-3.98639900	1.34871500	0.00000200

4-bromobenzaldehyde radical anion

C	-1.34341700	1.38077000	0.00000000
C	-2.17550600	0.21620600	0.00000000
C	-1.50019600	-1.05266600	0.00000100
C	-0.12114600	-1.13795700	0.00000100
C	0.65187900	0.03462800	0.00000100
C	0.03458000	1.30274100	0.00000100
Br	2.58744700	-0.08677900	0.00000000
C	-3.59885800	0.31253400	-0.00000100
O	-4.41744600	-0.64529300	-0.00000100
H	-1.81687800	2.36010200	0.00000000
H	-2.10629300	-1.95146800	0.00000100
H	0.36636600	-2.10717300	0.00000100
H	0.63834600	2.20350000	0.00000100
H	-3.98664600	1.35709000	-0.00000100

4-bromobenzonitrile

C	1.49148000	-1.21277600	0.00002000
C	2.19512900	0.00001400	0.00002100
C	1.49147100	1.21279800	0.00002000
C	0.10181500	1.21456100	0.00001200
C	-0.58099200	0.00000200	0.00000600
C	0.10182400	-1.21455200	0.00001200
Br	-2.49173600	-0.00000600	-0.00000900
C	3.62578600	0.00002400	0.00001200
N	4.78131100	-0.00003800	-0.00005300
H	2.03451100	-2.14968400	0.00002600
H	2.03449400	2.14971100	0.00002600
H	-0.44325100	2.14932500	0.00000900
H	-0.44323400	-2.14932000	0.00000900

4-bromobenzonitrile radical anion

C	-1.49447300	-1.23155200	0.00002300
C	-2.25122100	0.00007400	0.00001000
C	-1.49442300	1.23166900	0.00002300
C	-0.11841700	1.22819600	0.00003700
C	0.58527100	0.00001100	0.00004500
C	-0.11846800	-1.22814700	0.00003700
Br	2.51968600	-0.00003000	-0.00002000
C	-3.64675800	0.00012000	-0.00003500
N	-4.82225300	-0.00019100	-0.00004600
H	-2.02623100	-2.17720800	0.00003400
H	-2.02613900	2.17734700	0.00003400
H	0.42507800	2.16658900	0.00005300
H	0.42498800	-2.16656300	0.00005300

2-bromobenzonbitrile

C	-2.28553200	-1.50230200	0.00000000
C	-2.92747300	-0.26463800	0.00000000
C	-2.17584200	0.90209900	0.00000000
C	-0.77168400	0.84742200	0.00000000
C	-0.14001500	-0.40789600	0.00000000
C	-0.89469500	-1.57658200	0.00000000
Br	1.76154100	-0.53488600	0.00000000
C	-0.03326700	2.07135000	0.00000000
N	0.52067500	3.08502400	0.00000000
H	-2.86572300	-2.41772800	0.00000000
H	-4.00913600	-0.20875500	0.00000000
H	-2.65779200	1.87187300	0.00000000
H	-0.39494500	-2.53627500	0.00000000

2-bromobenzonbitrile radical anion

C	2.27486000	-1.58084600	0.00000000
C	2.93044000	-0.32024900	0.00000000
C	2.22423300	0.85722000	-0.00000100
C	0.77306900	0.88502800	0.00000000
C	0.14596500	-0.41784800	0.00000000
C	0.85641600	-1.59072700	0.00000000
Br	-1.79168500	-0.51902400	0.00000000
C	0.09157500	2.10013800	0.00000000
N	-0.42645400	3.15509800	0.00000000
H	2.83086200	-2.51047900	0.00000100
H	4.01693500	-0.28045600	-0.00000100
H	2.74614100	1.80848700	-0.00000100
H	0.32086000	-2.53367600	0.00000100

3-bromoquinolin

C	-3.60339300	-1.19874400	0.00000000
C	-3.96405900	0.17043400	-0.00000100
C	-2.99817200	1.14801600	0.00000000
C	-1.62468200	0.79752000	0.00000000
C	-1.26055100	-0.58439200	0.00000000
C	-2.28054200	-1.57051900	0.00000000
N	-0.69359200	1.79424600	0.00000000
C	0.57714200	1.46870400	0.00000000
C	1.02666900	0.12393800	0.00000000
C	0.12047000	-0.90235900	0.00000000
Br	2.90855400	-0.21964800	0.00000000
H	-4.37932300	-1.95575300	0.00000000
H	-5.01288200	0.44479700	-0.00000100
H	-3.25088600	2.20145600	0.00000000
H	-2.00067700	-2.61873800	0.00000200
H	1.30104000	2.27807700	0.00000100
H	0.44118000	-1.93748100	-0.00000200

3-bromoquinolin radical anion

C	-3.60339300	-1.19874400	0.00000000
C	-3.96405900	0.17043400	-0.00000100
C	-2.99817200	1.14801600	0.00000000
C	-1.62468200	0.79752000	0.00000000
C	-1.26055100	-0.58439200	0.00000000
C	-2.28054200	-1.57051900	0.00000000
N	-0.69359200	1.79424600	0.00000000
C	0.57714200	1.46870400	0.00000000
C	1.02666900	0.12393800	0.00000000
C	0.12047000	-0.90235900	0.00000000
Br	2.90855400	-0.21964800	0.00000000
H	-4.37932300	-1.95575300	0.00000000
H	-5.01288200	0.44479700	-0.00000100
H	-3.25088600	2.20145600	0.00000000
H	-2.00067700	-2.61873800	0.00000200
H	1.30104000	2.27807700	0.00000100
H	0.44118000	-1.93748100	-0.00000200

Diethyl-bromomalonate

C	0.21295700	-0.34064500	0.00000000
C	-0.36260500	0.31349000	1.26085600
C	-0.36260500	0.31349000	-1.26085600
Br	2.17136100	-0.20141100	0.00000000
O	-0.10088200	1.41346500	1.66088400
O	-0.10088200	1.41346500	-1.66088400
O	-1.23583900	-0.53662300	1.83031000
O	-1.23583900	-0.53662300	-1.83031000
C	-1.91770800	-0.07681500	-3.03343800
H	-2.85595300	-0.63117500	-3.02933500
H	-2.12211600	0.98909200	-2.92920800
C	-1.09639000	-0.37066800	-4.27622700
H	-1.66352700	-0.07628100	-5.16390700
H	-0.16065600	0.19075100	-4.26977700
H	-0.87173600	-1.43693900	-4.35240100
C	-1.91770800	-0.07681500	3.03343800
H	-2.85595300	-0.63117500	3.02933500
H	-2.12211600	0.98909200	2.92920800
C	-1.09639000	-0.37066800	4.27622700
H	-0.16065600	0.19075100	4.26977700
H	-1.66352700	-0.07628100	5.16390700
H	-0.87173600	-1.43693900	4.35240100
H	-0.01944100	-1.39919000	0.00000000

Diethyl-bromomalonate radical anion

C	-0.20424800	1.10535200	0.00000000
C	0.26769700	0.72285000	1.31569600
C	0.26769700	0.72285000	-1.31569600

Br	-2.60122500	-0.40920300	0.00000000
O	0.03609100	1.37531800	2.32554700
O	0.03609100	1.37531800	-2.32554700
O	1.01342000	-0.42090100	1.36217700
O	1.01342000	-0.42090100	-1.36217700
C	1.43298300	-0.85559200	-2.66010400
H	1.54427000	-1.93835400	-2.56419400
H	0.64848300	-0.63893100	-3.38761500
C	2.74951300	-0.21108500	-3.07950000
H	3.08162500	-0.62269500	-4.03936300
H	2.62681500	0.86775000	-3.19063400
H	3.52754400	-0.40273000	-2.33511600
C	1.43298300	-0.85559200	2.66010400
H	1.54427000	-1.93835400	2.56419400
H	0.64848300	-0.63893100	3.38761500
C	2.74951300	-0.21108500	3.07950000
H	2.62681500	0.86775000	3.19063400
H	3.08162500	-0.62269500	4.03936300
H	3.52754400	-0.40273000	2.33511600
H	-0.78360600	2.01516500	0.00000000

4-iodoacetophenone

C	-1.62845900	-1.16599400	-0.00006400
C	-2.32691700	0.04729100	-0.00010500
C	-1.59170300	1.24219300	-0.00009000
C	-0.20363800	1.23188200	-0.00006200
C	0.46775300	0.00856600	-0.00002900
C	-0.23521900	-1.19202400	-0.00002400
I	2.59613000	-0.02257200	0.00002200
C	-3.82536400	0.14892800	-0.00011700
O	-4.36143700	1.24175600	0.00016000
C	-4.69267700	-1.09867200	0.00003800
H	-2.15585600	-2.11071500	-0.00004200
H	-2.13366000	2.17997300	-0.00010500
H	0.34790700	2.16312000	-0.00006000
H	0.28869000	-2.13879100	0.00001000
H	-4.15143300	-2.04226000	-0.00159600
H	-5.33954900	-1.06184300	0.88002200
H	-5.34216600	-1.06022000	-0.87792600

4-iodoacetophenone radical anion

C	2.85720700	-1.13289900	-0.42156300
C	3.54677500	0.00008400	-0.00000600
C	2.85717800	1.13299800	0.42157600
C	1.46468700	1.12578100	0.41834900
C	0.74201900	-0.00003900	0.00009500
C	1.46472300	-1.12578500	-0.41822600
C	-0.74201900	-0.00002700	0.00014000

C	-1.46475100	-1.12576200	0.41844100
C	-2.85723400	-1.13287000	0.42170600
C	-3.54677500	0.00011100	0.00009800
C	-2.85715100	1.13302700	-0.42143400
C	-1.46466000	1.12580400	-0.41813500
I	5.67908400	-0.00002600	-0.00004700
I	-5.67908400	-0.00003000	-0.00008500
H	3.39215200	-2.01090900	-0.75954500
H	3.39202600	2.01111500	0.75944600
H	0.93577900	2.00358400	0.77187500
H	0.93591000	-2.00366200	-0.77173200
H	-0.93595900	-2.00363600	0.77198800
H	-3.39220100	-2.01087000	0.75967700
H	-3.39197700	2.01115400	-0.75931400
H	-0.93573000	2.00361000	-0.77161900

4,4’-diiodobiphenyl

C	2.85720700	-1.13289900	-0.42156300
C	3.54677500	0.00008400	-0.00000600
C	2.85717800	1.13299800	0.42157600
C	1.46468700	1.12578100	0.41834900
C	0.74201900	-0.00003900	0.00009500
C	1.46472300	-1.12578500	-0.41822600
C	-0.74201900	-0.00002700	0.00014000
C	-1.46475100	-1.12576200	0.41844100
C	-2.85723400	-1.13287000	0.42170600
C	-3.54677500	0.00011100	0.00009800
C	-2.85715100	1.13302700	-0.42143400
C	-1.46466000	1.12580400	-0.41813500
I	5.67908400	-0.00002600	-0.00004700
I	-5.67908400	-0.00003000	-0.00008500
H	3.39215200	-2.01090900	-0.75954500
H	3.39202600	2.01111500	0.75944600
H	0.93577900	2.00358400	0.77187500
H	0.93591000	-2.00366200	-0.77173200
H	-0.93595900	-2.00363600	0.77198800
H	-3.39220100	-2.01087000	0.75967700
H	-3.39197700	2.01115400	-0.75931400
H	-0.93573000	2.00361000	-0.77161900

4,4’-diiodobiphenyl radical anion

C	-2.87772300	-1.21278100	0.00153900
C	-3.58132800	0.00003100	0.00038500
C	-2.87783800	1.21290700	-0.00089200
C	-1.49431900	1.20884300	-0.00087000
C	-0.71883700	0.00016400	0.00027200
C	-1.49420500	-1.20858200	0.00148100
C	0.71883700	0.00016400	0.00020900

C	1.49420400	-1.20858200	-0.00099800
C	2.87772300	-1.21278200	-0.00107500
C	3.58132900	0.00003000	0.00015100
C	2.87783800	1.21290700	0.00135500
C	1.49432000	1.20884300	0.00135400
I	-5.73195600	-0.00007300	-0.00021000
I	5.73195600	-0.00007300	-0.00015800
H	-3.40875400	-2.15799300	0.00261500
H	-3.40896000	2.15806800	-0.00194400
H	-0.99711900	2.17122300	-0.00213900
H	-0.99688900	-2.17091100	0.00288700
H	0.99688800	-2.17091100	-0.00232300
H	3.40875300	-2.15799400	-0.00217100
H	3.40896000	2.15806700	0.00238800
H	0.99712000	2.17122200	0.00270300

2-acetyl-5-chlorothiophene

C	-1.52146300	0.22408600	0.00000200
C	-1.00007900	1.49126000	-0.00000800
C	0.41622900	1.46753600	-0.00003300
C	0.94926700	0.19705600	-0.00004200
S	-0.31427900	-1.01750900	-0.00001600
C	2.34622400	-0.26225900	-0.00004800
O	2.60507500	-1.45459000	0.00001200
C	3.46106100	0.76786700	0.00004300
Cl	-3.20126800	-0.18504100	0.00002300
H	-1.60506300	2.38674100	0.00000000
H	1.01892100	2.36535000	-0.00004000
H	3.11764300	1.80132900	-0.00069500
H	4.08473100	0.59840600	0.88094000
H	4.08575400	0.59744600	-0.87993200

2-acetyl-5-chlorothiophene radical anion

C	-1.52881500	0.22162500	-0.00001100
C	-0.99546700	1.49383200	-0.00001900
C	0.40836800	1.49626200	-0.00012700
C	0.99303100	0.20269000	-0.00023600
S	-0.30197300	-1.04474500	-0.00017300
C	2.33174300	-0.24901400	-0.00035100
O	2.65335100	-1.47205300	0.00026500
C	3.45270000	0.78752100	0.00023600
Cl	-3.23692600	-0.18288700	0.00015600
H	-1.60662300	2.38869500	0.00006000
H	0.99455900	2.40575200	-0.00012600
H	3.10262600	1.82294900	0.00003600
H	4.08587700	0.63330500	0.88252600
H	4.08670500	0.63321800	-0.88143100