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Supporting Information

Visible Light Driven Hydro-/Deuterodefunctionalization of Anilines

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Supporting Information

General methods

Commercial chemicals were used as obtained from Sigma-Aldrich, TCI Europe or Fisher. Solvents were used without further purification. d_1-DMF, d_6-DMF and d_7-DMF were obtained from Deutero GmbH. TLC was performed on commercial silica gel coated aluminium plates (DC60 F254, Merck). Visualization was done with UV light or by staining with phosphomolybdenic acid for UV-inactive compounds. Column chromatography was performed using silica gel (60 Å pore size, Acros Organics) as the stationary phase. Product yields were determined by GC-FID (7820A Agilent) using *n*-pentadecane as internal standard. The purity and structure of isolated compounds were confirmed by ^{1}H NMR, ^{2}D NMR, ^{13}C NMR, and MS spectra and comparison with authentic samples. NMR spectral data were collected on a Bruker Avance 400 (400 MHz for ^{1}H; 100 MHz for ^{13}C) or on a Bruker Avance 600 (92.1 MHz for ^{2}D) spectrometers at 25 °C. Chemical shifts are reported in δ/ppm, and coupling constants *J* are given in Hertz. Solvent residual peaks were used as internal reference for all NMR measurements. Abbreviations: s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, dd – doublet of doublet.

General procedure for the synthesis of arenediazonium tetrafluoroborates:

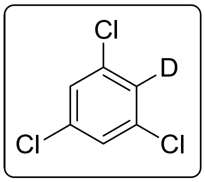
The aniline (4.5 mmol) was dissolved in glacial acetic acid (3 mL) and 48 % aqueous tetrafluoroboric acid (1.3 mL). Then, a solution of iso-amylnitrite (1 mL) in glacial acetic acid (2 mL) was added at room temperature over 5 min. Diethylether (15 mL) was added and the reaction mixture was cooled down to -30 °C in order to induce crystallization of the product. The crystals were filtered off in vacuo, washed with diethylether (2 x 10 mL) and dried on air.

General procedure for the hydrodediazonation:

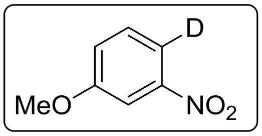
The arenediazonium tetrafluoroborate (0.25 mmol) and eosin B, disodium salt (3.2 mg, 5 μmol, 2 mol%) were dissolved in DMF (2 mL) in the dark. Nitrogen was bubbled through the solution during vigorous stirring, and the reaction vessel was capped. The solution was subjected to irradiation with green light (LEDs, 3.8 W each, λ_{max} 535 nm) for 30 min at ambient temperature (18 °C). The end point of the reaction was indicated by the cessation of gas evolution and/or TLC analysis. The reaction mixture was diluted with diethyl ether (5 mL) and washed with water (5 mL). The aqueous layer was extracted with diethyl ether (2×5 mL), the organic layers were combined, washed with brine (5 mL), and dried (Na_2SO_4). Products with high boiling points can easily be separated from the solvent DMF by distillation; non-polar arenes can be separated by liquid extraction with pentane. The residues were subjected to SiO_2 flash chromatography to isolate the pure benzenes or deuterobenzenes. For screening purposes, the internal GC standard *n*-pentadecane (20 μL) was added and the yield was determined by quantitative GC-FID.

General procedure for the deutero dediazonation:

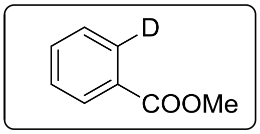
The arenediazonium tetrafluoroborate (0.25 mmol) and eosin B, disodium salt (3.2 mg, 5 µmol, 2 mol%) were dissolved in d_7-DMF (0.8 mL) in the dark. Nitrogen was bubbled through the solution during vigorous stirring, and the reaction vessel was capped. The solution was subjected to irradiation with green light (LEDs, 3.8 W each, λ_{max} 535 nm) for 7 h at ambient temperature (18 °C). The end point of the reaction was indicated by the cessation of gas evolution and/or TLC analysis. The reaction mixture was diluted with diethyl ether (5 mL) and washed with water (5 mL). The aqueous layer was extracted with diethyl ether (2×5 ml), the organic layers were combined, washed with brine (5 mL), and dried (Na_2SO_4). The solvent was evaporated *in vacuo* and the residue purified by column chromatography (silica gel, eluent: pentane) to obtain the pure deuterated arene.



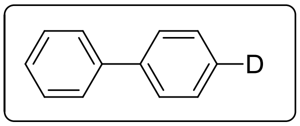
1,3,5-Trichloro[2-^{2}H]benzene: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.6 (C), 135.5 (C), 127.2 (CH), 126.9 (t, $^1J_{CD}$ = 26 Hz, CD); ^{2}H NMR (92.1 MHz, CH_3COCH_3, ppm): δ 7.55 (s, 1D); HRMS: calc'd: 180.9363; found: 180.93625.



1-Methoxy-3-nitro[4-^{2}H]benzene: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.68 (d, $^4J_{HH}$ = 2.5 Hz, 1H), 7.39 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.18 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.2 (C), 149.2 (C), 129.9 (CH), 121.4 (CH), 115.6 (t, $^1J_{CD}$ = 26 Hz, CD) 108.1 (CH); ^{2}H NMR (92.1 MHz, CH_3COCH_3, ppm): δ 7.91 (s, 1D); HRMS: calc'd: 154.0489; found: 154.04864.



Methyl [2-^{2}H]benzoate: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04 (dd, $^3J(H\text{-}H)$ = 8.1 Hz, $^4J(H\text{-}H)$ = 1.2 Hz, 1H), 7.56 (dt, $J^3(H\text{-}H)$ = 7.5 Hz, $^3J_{HH}$ = 1.2 Hz, 1H), 7.45-7.42 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.1 (CO), 132.9 (CH), 130.1 (C), 129.6 (CH), 129.3 (t, $^1J_{CD}$ = 25 Hz, CD), 128.4 (CH) 128.3 (CH), 52.1 (CH_3); ^{2}H NMR (92.1 MHz, CH_3COCH_3, ppm): δ 7.91 (s, 1D).



[4-^{2}H]Biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.62 (d, $^3J_{HH}$ = 8.2 Hz, 4H), 7.49-7.44 (m, 4H), 7.37 (tt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ =

1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 141.3 (2 C), 128.8 (2 CH), 128.7 (2 CH), 127.3 (CH), 127.2 (4 CH), 127.0 (t, $^{1}J_{CD}$ = 25 Hz, CD); ^{2}H NMR (92.1 MHz, CH_3COCH_3, ppm): δ 7.91 (s, 1D).

Calculation of redox potentials:

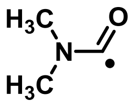
All reported values are referenced against SCE. The redox potential of eosin B in its excited state can be obtained from the literature values of the triplet state energy[1d] and from the ground state reduction potential.[1c]

$E_{red}(EB^{\cdot+}/EB(T_1))$

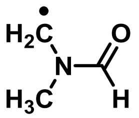
$= [E(EB(T_1)) – E(EB(S_1))] – E_{red}(EB^{\cdot+}/EB(S_1))$

$= -1.97 + 0.60\ V = -1.37\ V.$

Redox potentials of the $\mathrm{dmf}^{+}/\mathrm{dmf}^{\cdot}$ couples (DMF-based cations **1A** or **1B**; radicals **2A** or **2B**) were not available but were obtained from DFT calculations (Gaussian G03)[2] following a well-precedented method[3] for the estimation of SET redox potentials. The geometries were optimized at the 6-31+G(d,p)/UB3LYP level, single point calculations with aug-cc-pVTZ/UB3LYP. The solvation was considered in both optimizations as well as single point calculations using the PCM model with universal force field radii to approximate the molecule surface. The following values were used to implement DMF as solvent into the PCM model: permittivity = 36.7; solvent radius = 5.04 Å; density = 0.00781 molecules per cubic Ångström. Both forms of DMF-based radical and cation (**1A**, **1B** and **2A**, **2B**) were taken into consideration.

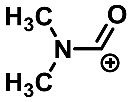


1A

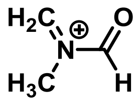


1B

DMF$^{\bullet}$



2A



2B

DMF$^{\oplus}$

DFT: ΔE(**2A**/**1A**) = 4.44 V; ΔE(**2B**/**1B**) = 4.48 V.

These are absolute values referenced to infinity. Reference against SCE requires abstraction of 4.19 V from these values:[3]

E_{red}(**2A**/**1A**) = 0.25 V; E_{red} (**2B**/**1B**) = 0.29 V.

Calculation of transition state energies:

All DFT calculations were performed using the Gaussian G03 package.[2] Instead of the standard UB3LYP, the UMPW1K functional was used, which has been shown to perform better in cases of proton-coupled electron transfer processes.[4]

Estimation of isotope incorporation:

For determination of H/D isotope incorporation, *p*-nitrobenzenediazonium tetrafluoroborate was chosen as model system. The H/D ratio was obtained from integration of ^{1}H NMR spectra by comparing signal intensities of the product mixture (nitrobenzene and 4-deuteronitrobenzene at ^{1}H signals at 8.25 ppm and 7.55 ppm, only H) with the resonance of the *para*-CH at 7.71 ppm (H or D). The selectivity of H/D abstraction from DMF were calculated from this ratio.

References:

1 Redox potentials of arenediazonium salts: a) McCreery, R. L.; Yang, H.-H. *Anal. Chem.* **1999**, *71*, 4081-4087; b) Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Saveant, J.-M. *J. Am. Chem. Soc.* **1997**, *119*, 201-207. Eosin B ground state reduction potential: c) McSkimming, A.; Colbran, S. B. *Chem. Soc. Rev.* **2013**, *42*, 5439-5488. Eosin B tripet energy: d) DeRosa, M. C.; Crutchley, R. J. *Coord. Chem. Rev.* **2002**, *233-234*, 351-371.

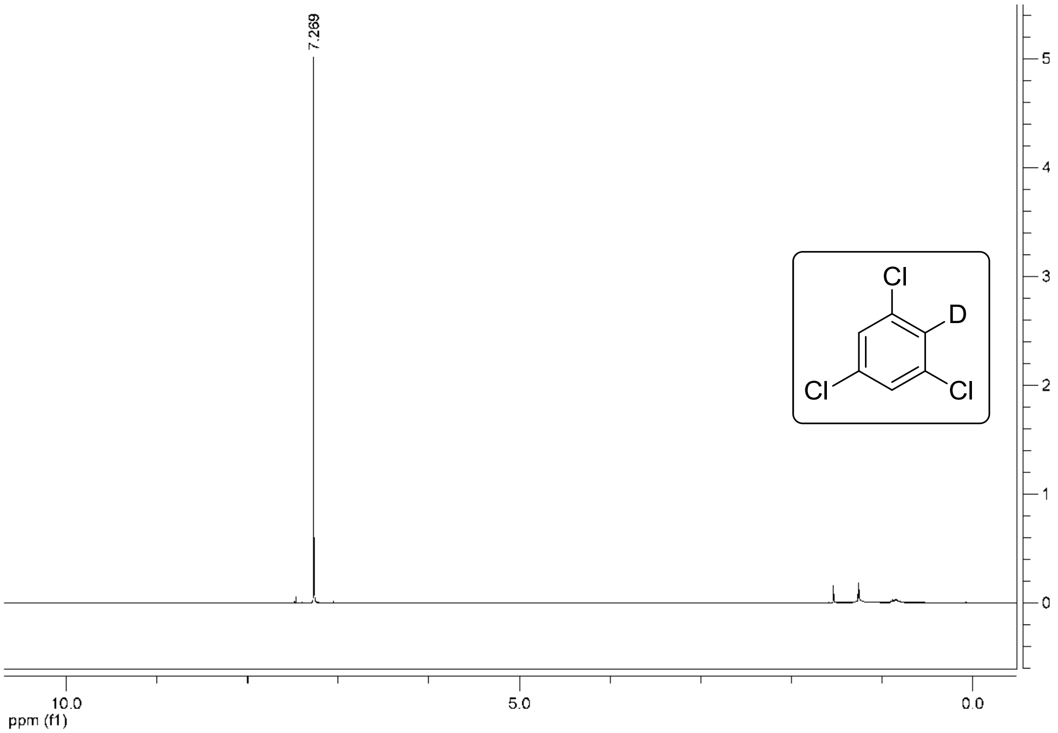
2 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Rev. C.02*, Gaussian Inc., Wallingford, **2004**.

3 Baik, M.-H.; Friesner, R. A. *J. Phys. Chem. A* **2002**, *106*, 7407-7412.

4 a) Lingwood, M.; Hammond, J. R.; Hrovat, D. A.; Mayer, J. M.; Borden, W. T. *J. Chem. Theory Comput.* **2006**, *2*, 740-745; b) Jing, L.; Nash, J. J.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **2008**, *130*, 17697-17709.

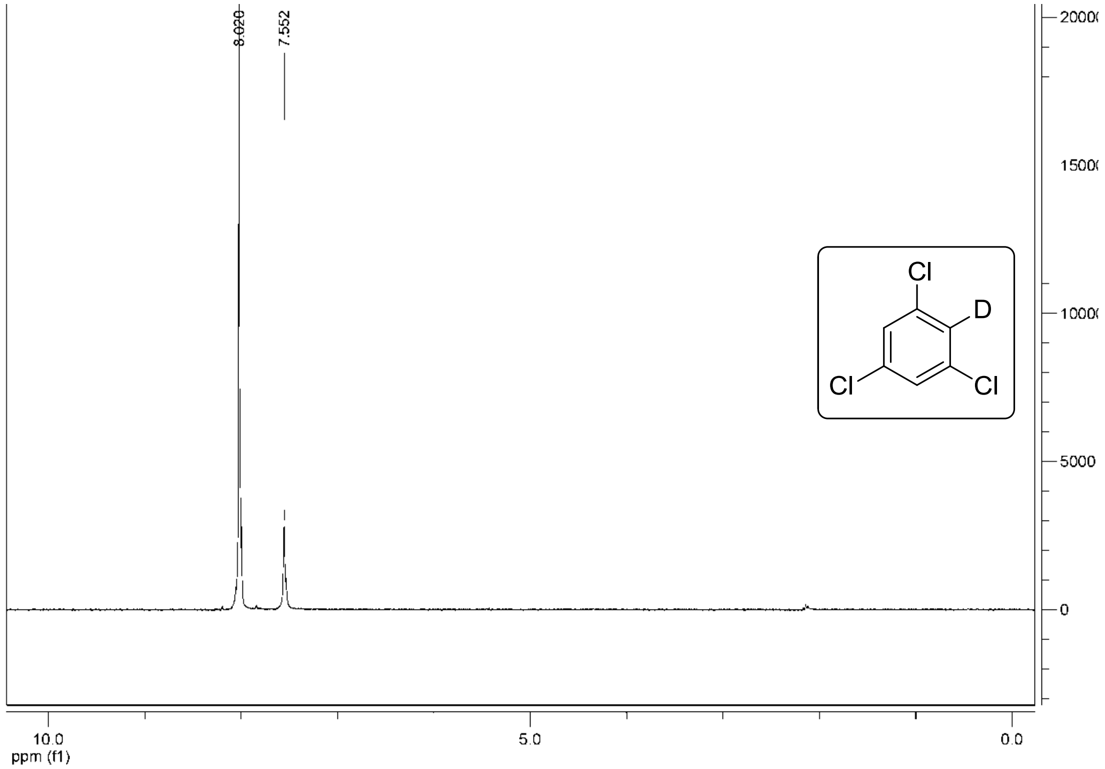
Selected NMR spectra of products:

^{1}H:

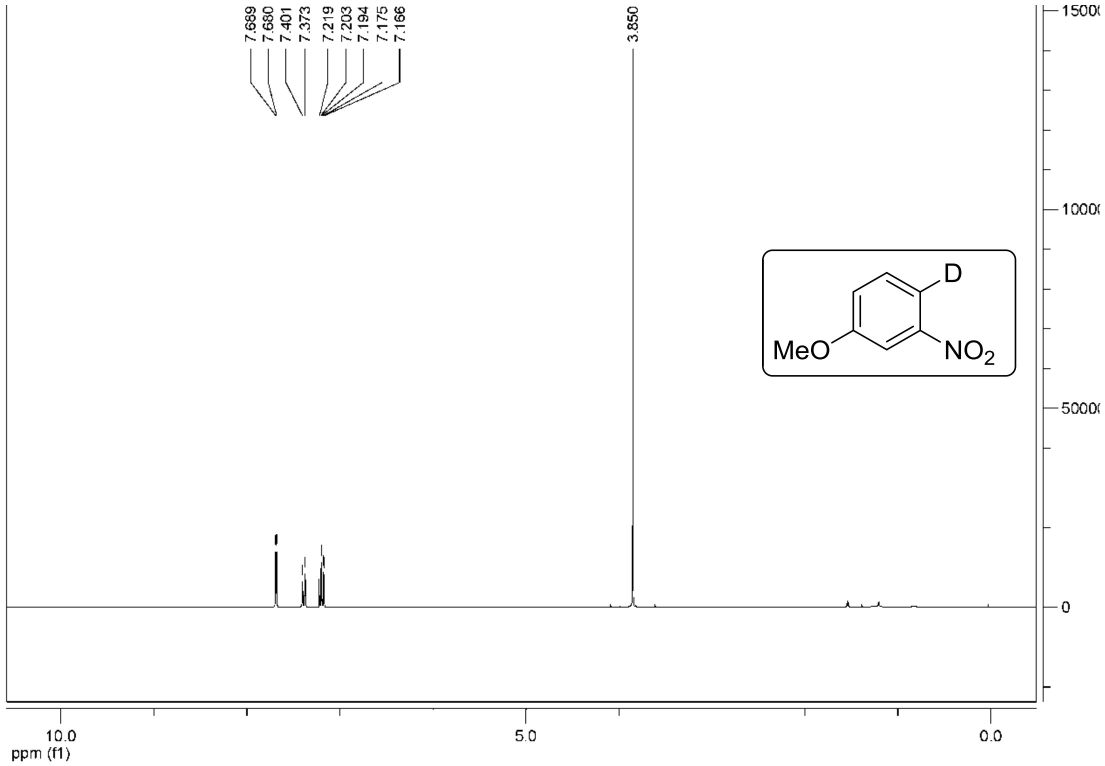


^{13}C:

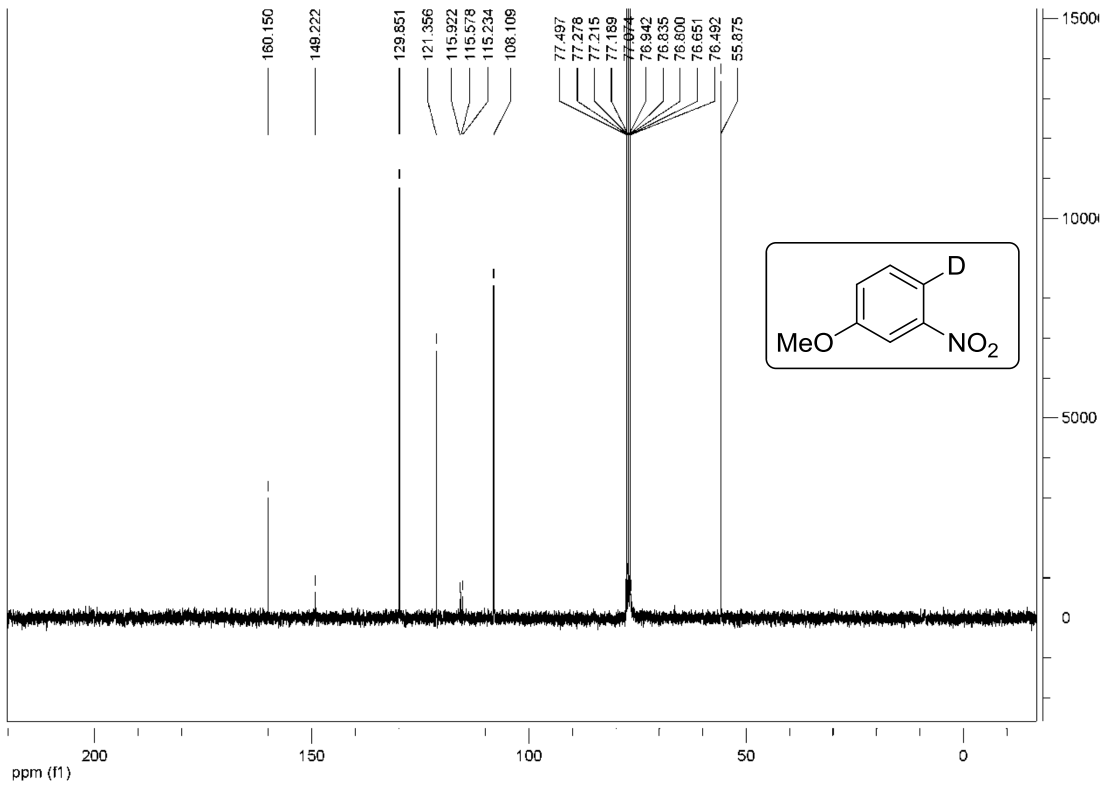
^{2}H:


8.020
7.552
2000
1500
1000
5000
0
Cl
D
Cl
Cl
10.0
ppm (f1)
5.0
0.0

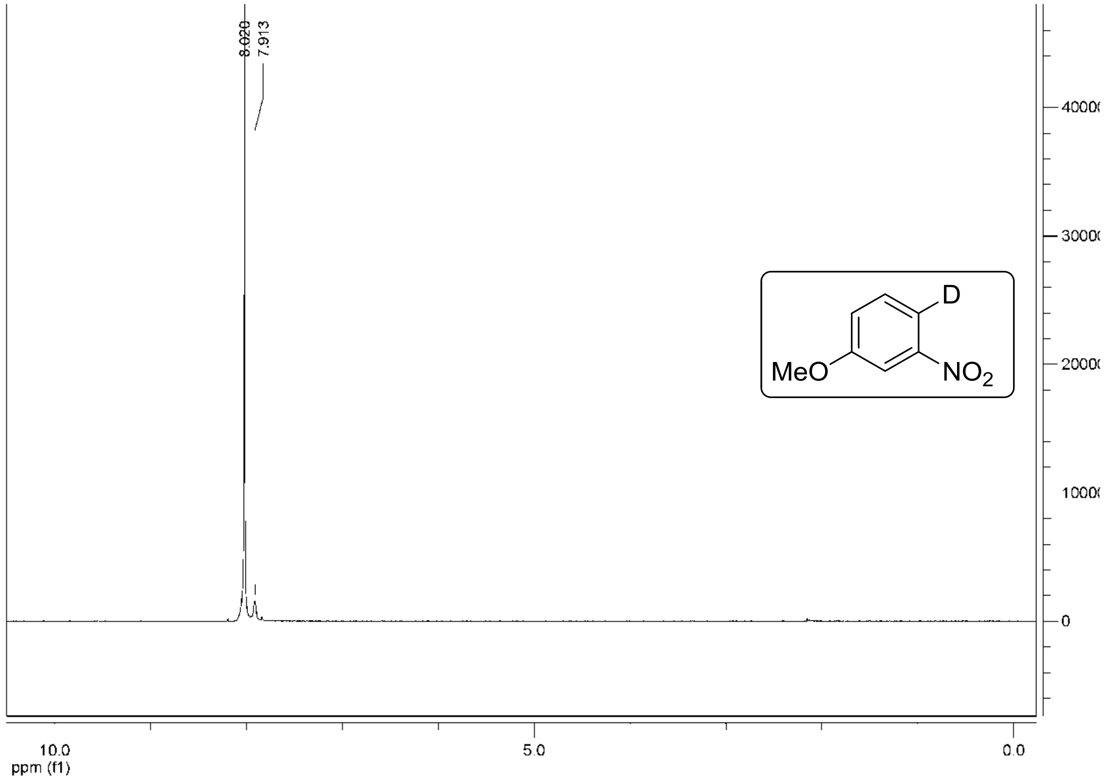
^{1}H:


7.689
7.680
7.401
7.373
7.219
7.203
7.194
7.175
7.166
3.850
1500
1000
5000
0
D
MeO
NO$_2$
10.0
ppm (f1)
5.0
0.0

^{13}C:


160.150
149.222
129.851
121.356
115.922
115.578
115.234
108.109
77.497
77.278
77.215
77.189
77.074
76.942
76.835
76.800
76.651
76.492
55.875
D
MeO
NO$_2$
1500
1000
5000
0
200
150
100
50
0
ppm (f1)

^{2}H:


8.020
7.913
D
MeO
NO$_2$
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3000
2000
1000
0
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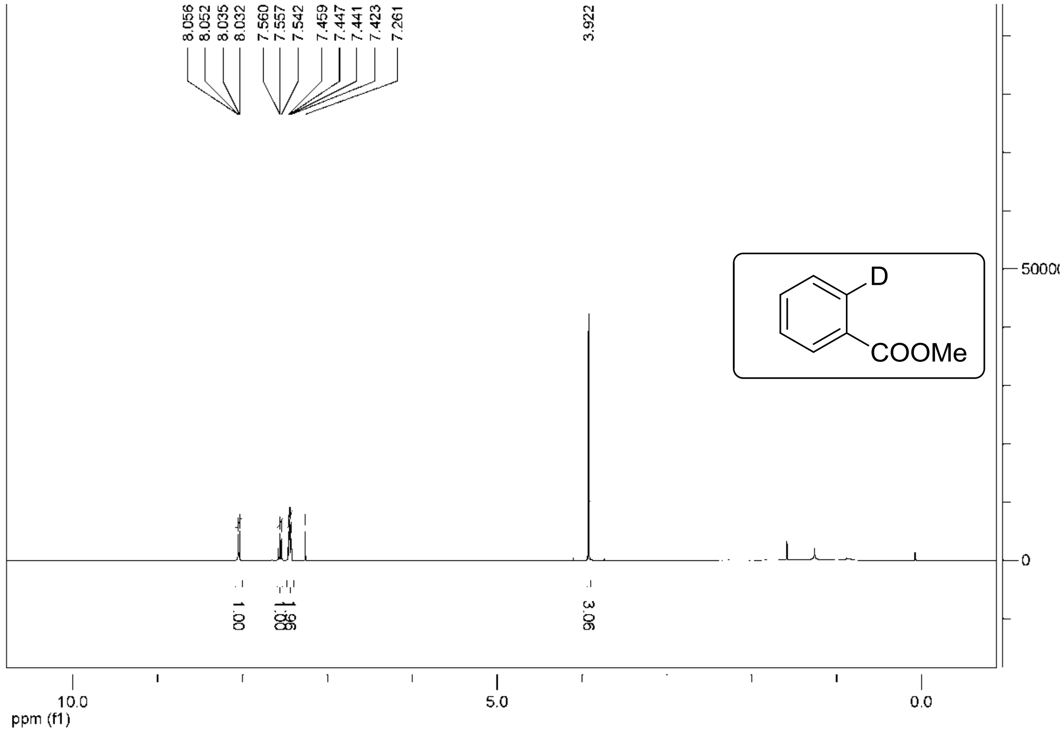
5.0
0.0
ppm (f1)

^{1}H: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8.035
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7.560
7.557
7.542
7.459
7.447
7.441
7.423
7.261
3.922
D
COOMe
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1.00
1.00
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3.06
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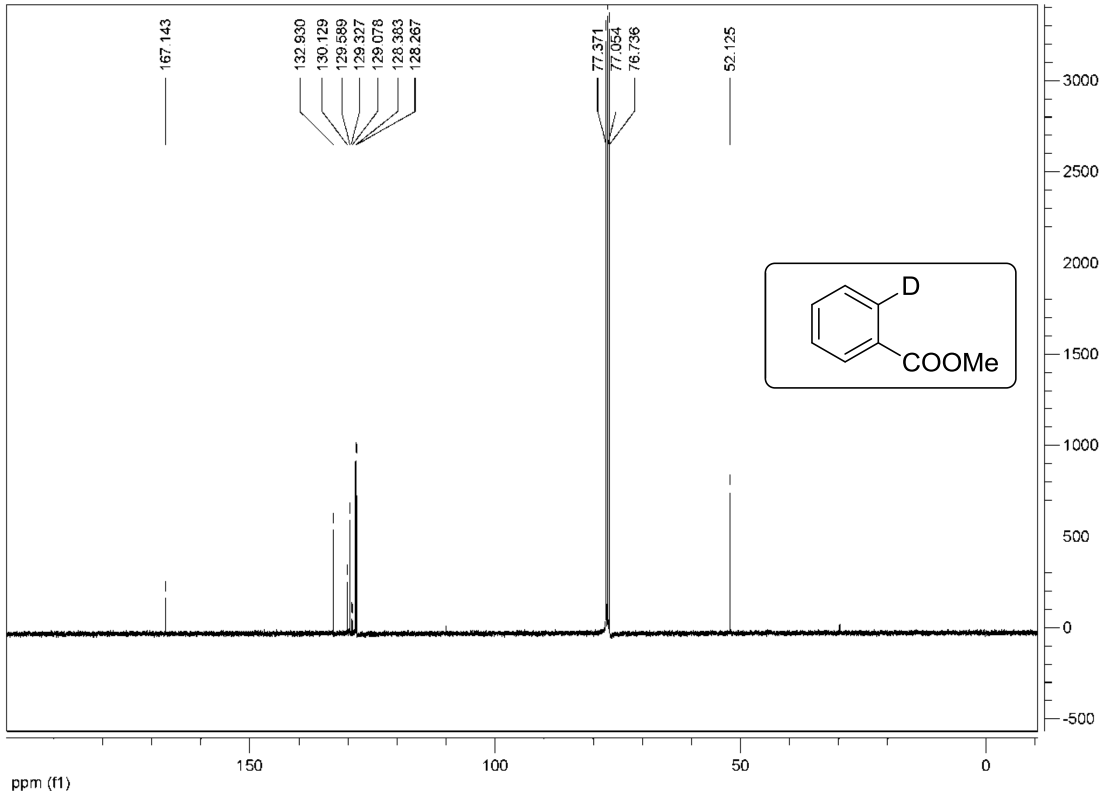
5.0
0.0
ppm (f1)

^{13}C: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132.930
130.129
129.589
129.327
129.078
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128.267
77.371
77.054
76.736
52.125
D
COOMe
3000
2500
2000
1500
1000
500
0
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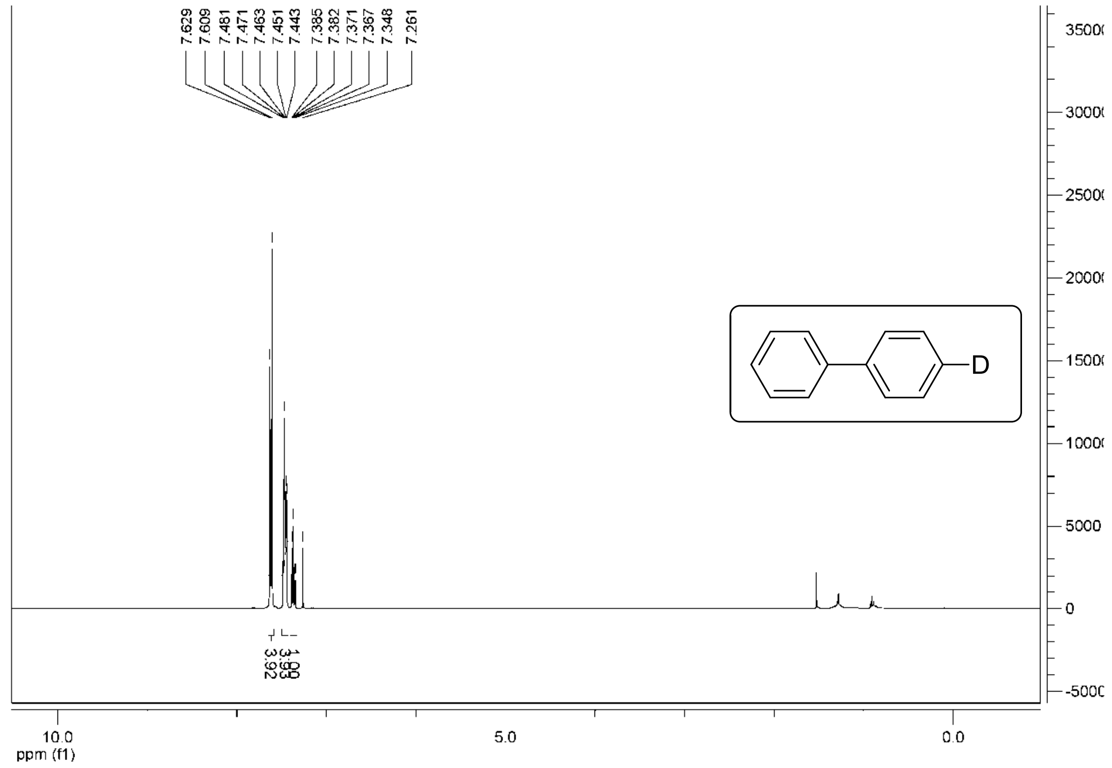
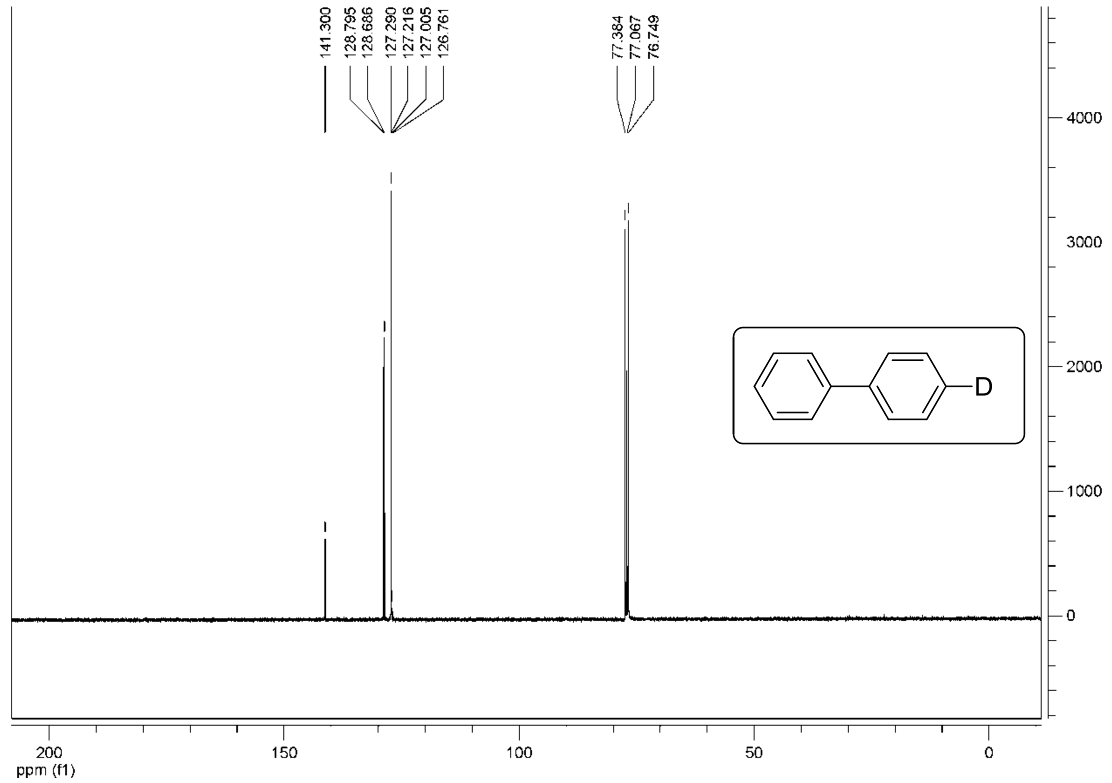
150
100
50
0
ppm (f1)

^{1}H:



7.629
7.609
7.481
7.471
7.463
7.451
7.443
7.385
7.382
7.371
7.367
7.348
7.261
D
3.92
3.93
1.00
35000
30000
25000
20000
15000
10000
5000
0
-5000
10.0
5.0
0.0
ppm (f1)

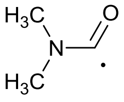
^{13}C:



141.300
128.795
128.686
127.290
127.216
127.005
126.761
77.384
77.067
76.749
D
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)

Optimized geometries:

H-abstraction from DMF:



1A

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C	-0.44432400	1.41960600	0.00012700
H	-0.99481800	1.74153500	-0.88928300
H	-0.98864400	1.74122600	0.89349100
H	0.54829700	1.86860200	-0.00323200
C	-1.55242200	-0.82683300	0.00023700
H	-2.14566400	-0.58886800	-0.88856500
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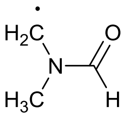

1B

C	-0.82474500	-0.63638800	-0.00005300
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N	0.35629300	0.06331800	-0.00005500
C	0.37775100	1.43419500	0.00008000
H	1.33637900	1.93074200	-0.00051000
H	-0.56419900	1.96048700	0.00010900
C	1.63197300	-0.66715700	0.00005300
H	2.20735600	-0.40990100	0.89270000
H	1.43463800	-1.73921900	-0.00061900
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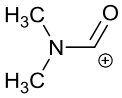

2A

C	-0.94945200	-0.00255000	0.00007500
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N	0.30942100	-0.00038800	-0.00013800
C	1.06672200	1.29317100	0.00007100

H	1.68645400	1.30440300	0.89615600
H	1.67260100	1.31339200	-0.90527100
H	0.36668600	2.12578100	0.00932200
C	1.07347700	-1.28941600	0.00001200
H	1.67723300	-1.30848300	0.90686100
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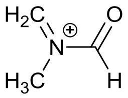

2B

C	0.87485100	-0.65919000	-0.00208900
O	1.93134300	-0.10522800	0.00103800
N	-0.39525500	0.10842800	-0.00103900
C	-0.34352500	1.39218500	-0.00175600
H	-1.26230400	1.96897000	0.00497000
H	0.62893300	1.87576500	0.00540100
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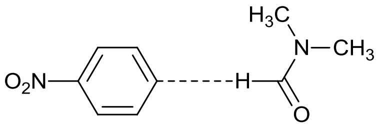
Transition states of H-abstraction:



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C	1.83130700	-1.21525100	-0.09875500
C	0.45075200	-1.21130600	-0.23530600
C	-0.20183500	0.00252800	-0.28719400
H	-0.08862600	2.14911500	-0.27434300
H	2.39755300	2.13241200	-0.02287300
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N	-3.65598700	-0.00322700	0.40264700
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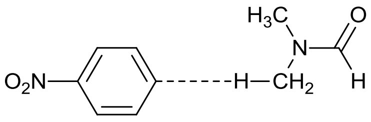
H	-5.50890400	-0.89197600	0.77859400
H	-5.50933800	0.87868200	0.79241300
H	-5.37282300	0.00533600	-0.74523400
C	-3.08430000	-0.01366600	1.72327200

H	-3.39987500	-0.90227700	2.26957700
H	-2.00129300	-0.01279200	1.65938700
H	-3.40045100	0.86584100	2.28379000
N	3.93986100	-0.00115800	0.12472200
O	4.49764600	-1.07321900	0.17450600
O	4.49803200	1.06988100	0.18980900



C	-2.19313700	1.30872900	-0.06553700
C	-0.86337300	1.68937600	-0.17236600
C	0.10028500	0.70487600	-0.23827800
C	-0.19294000	-0.64231400	-0.20294700
C	-1.52148900	-1.02842400	-0.09610100
C	-2.49240300	-0.04309500	-0.02971900
H	-2.99051900	2.03201000	-0.01034000
H	-0.60245000	2.73707300	-0.20254200
H	1.53002500	1.09850200	-0.36650700
H	0.58458600	-1.39043700	-0.25637400
H	-1.81212600	-2.06597900	-0.06382800
C	2.73190600	1.34742400	-0.47850000
H	2.91154000	1.44592400	-1.54459800
H	2.87607200	2.29446900	0.03625400
N	3.49694600	0.30618700	0.09182200
C	3.51835200	0.18005400	1.52814200
H	4.14095600	-0.66841000	1.78729000
H	3.92752700	1.08335000	1.97755600
H	2.51198400	0.02116200	1.91443100
C	4.08806500	-0.63867300	-0.68177300
H	3.98363000	-0.42744900	-1.75430700
O	4.67741300	-1.60786200	-0.26726700
N	-3.88779800	-0.44506900	0.08288100
O	-4.72028100	0.43046200	0.14015300
O	-4.12924100	-1.62957000	0.11242800