Electronic Supplementary Material (ESI) for ChemComm.

How electrophilic are 3-nitroindoles? Mechanistic investigations and application to a reagentless (4+2) cycloaddition

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Supporting information:

1. Materials and method

All manipulations were performed under an inert atmosphere of dry argon by using standard vacuum line and Schlenk tube techniques. Glassware was dried at 75°C in an oven before use. THF was purified using an Innovative Technology PURESOLV® solvent purification system. DMSO was dried (with < 50 ppm H_2O content) and stored over activated 3 Å MS under argon. NMR spectra were recorded on Bruker AV300 or AV400 spectrometers. Chemical shifts are reported in ppm (δ) compared to TMS (^{1}H and ^{13}C) using the residual peak of deuterated solvent as internal standard.[1] High-resolution mass spectra were performed on a Waters Xevo G2-XS QTof or a Shimadzu QP2010 hybrid ionisation apparatus (HP5-MS stationary phase, l = 30 m, d = 0.25 mm, film thickness = 0.25 µm). Infrared spectra were recorded on a Perkin Elmer ATR universal sampler 100 spectrum. Melting points were measured on a Stuart SMP30 Digital Melting Point apparatus.

2. Kinetics

The kinetic investigations were performed at 20°C in DMSO as the solvent using a stopped-flow spectrophotometer system (Applied Photophysics SX.18MV-R). The carbanions **2a–i** (Scheme therafter) were either used as preformed potassium salts or generated in the solutions by treatment of the corresponding CH acids with 1.05 eq. of potassium *tert*-butoxide and used for the kinetic investigations.[2] The kinetic runs were initiated by mixing equal volumes of DMSO solutions of the electrophiles and nucleophiles. From the exponential decays of the absorbances of the electrophiles (**1**) or from the exponential growth of the corresponding adduct, the first-order rate constants k_{obs} (s^{-1}) were obtained. The rate constants k_{obs} (s^{-1}), which were obtained by least-squares fitting to the single exponential curve $A_t = A_0e^{-k(obs)t} + C$, depended linearly on the nucleophile concentrations. The second-order rate constants k_2 (M^{-1} s^{-1}) for the combination reactions with nucleophiles were derived from the slopes of plots of k_{obs} for each nucleophile concentration versus the nucleophile concentrations.

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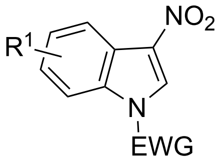
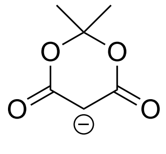
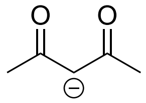
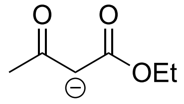
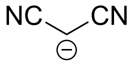
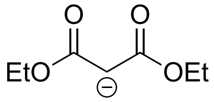
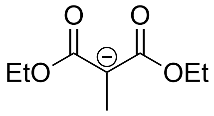
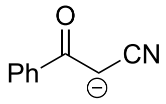
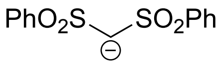
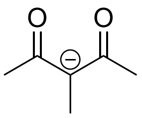
[1] G. R. Fulmer, A. J. M. Miller, N. H. Sherder, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, and K. I. Goldberg, *Organometallics* 2010, **29**, 2176.

[2] O. Kaumanns and H. Mayr, *J. Org. Chem.* 2008, **73**, 2738.



1a: EWG = *p*-Ts, R^1 = H
1b: EWG = CO_2Et, R^1 = H
1c: EWG = *p*-Ts, R^1 = 6-NO_2
1d:EWG = *p*-Ts, R^1 = 4-Br

	N/s_N
 **2a**	13.91 / 0.86
 **2b**	17.64 / 0.73
 **2c**	18.82 / 0.69
 **2d**	19.36 / 0.67
 **2e**	20.22 / 0.65
 **2f**	21.13 / 0.68
 **2g**	16.55 / 0.78
 **2h**	15.68 / 0.74
 **2i**	18.38 / 0.72

For the N/s_N values, see https://www.cup.lmu.de/oc/mayr/reaktionsdatenbank/

Table S1: Rate constants for the reaction of nitroindole (**1a**) with carbanion (**2a**) in DMSO (stopped–flow method, 20 °C, λ = 333 nm).

[**1a**] / M	[**2a**] / M	k_{obs} / s^{-1}
2.02×10^{-4}	1.59×10^{-2}	3.90×10^{-3}
2.02×10^{-4}	3.33×10^{-2}	7.70×10^{-3}
2.02×10^{-4}	4.09×10^{-2}	9.16×10^{-3}
2.02×10^{-4}	4.88×10^{-2}	1.03×10^{-2}
$k_2 = 1.97 \times 10^{-1}$ M^{-1} s^{-1}		

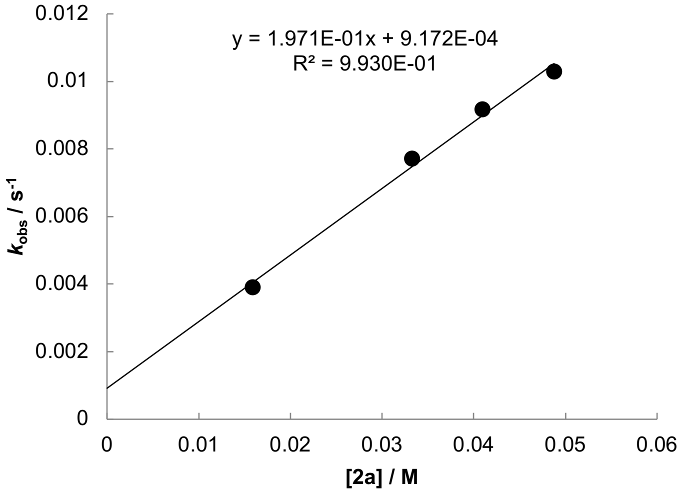


Table S2: Rate constants for the formation of adduct of nitroindole (**1a**) with carbanion (**2b**) in DMSO (stopped–flow method, 20 °C, λ = 473 nm).

[**1a**] / M	[**2b**] / M	k_{obs} / s^{-1}
2.02×10^{-4}	4.14×10^{-3}	0.708
2.02×10^{-4}	5.98×10^{-3}	1.08
2.02×10^{-4}	8.10×10^{-3}	1.46
2.02×10^{-4}	1.01×10^{-2}	1.86
2.02×10^{-4}	1.22×10^{-2}	2.31
$k_2 = 1.96 \times 10^{2}$ M^{-1} s^{-1}		

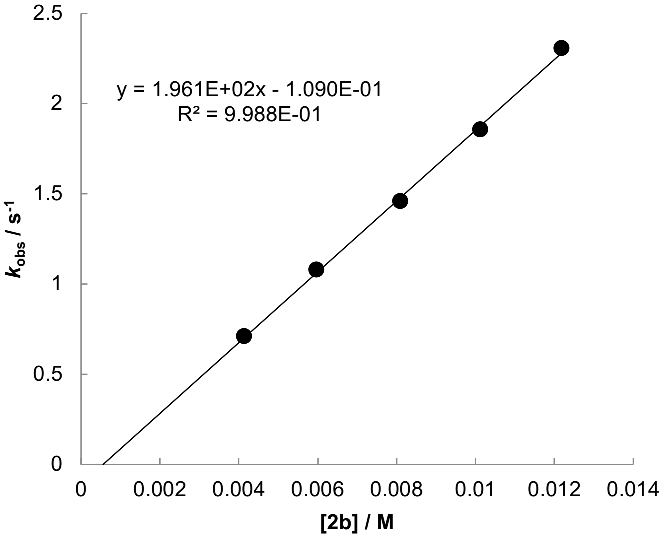


Table S3: Rate constants for the formation of adduct of nitroindole (**1a**) with carbanion (**2c**) in DMSO (stopped–flow method, 20 °C, λ = 462 nm).[3]

[**1a**] / M	[**2c**] / M	k_{obs} / s^{-1}
2.02×10^{-4}	4.14×10^{-3}	3.60
2.02×10^{-4}	6.11×10^{-3}	4.77
2.02×10^{-4}	8.23×10^{-3}	5.94
2.02×10^{-4}	1.03×10^{-2}	7.08
2.02×10^{-4}	1.23×10^{-2}	8.18
$k_2 = 5.58 \times 10^2$ M^{-1} s^{-1}		

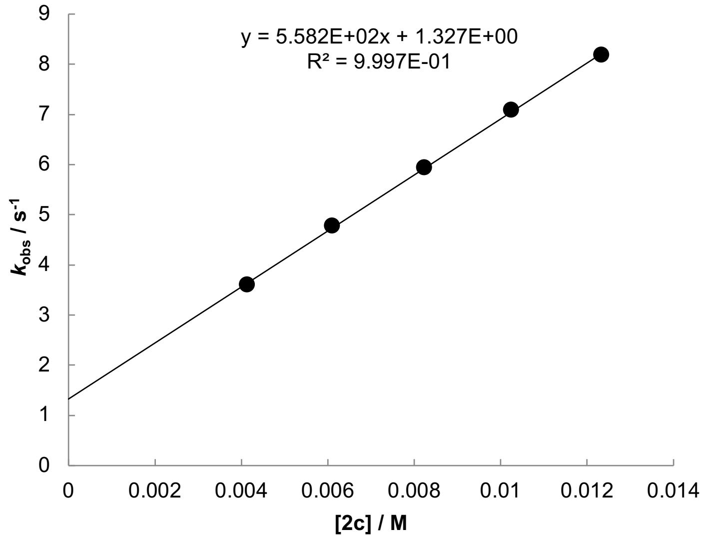
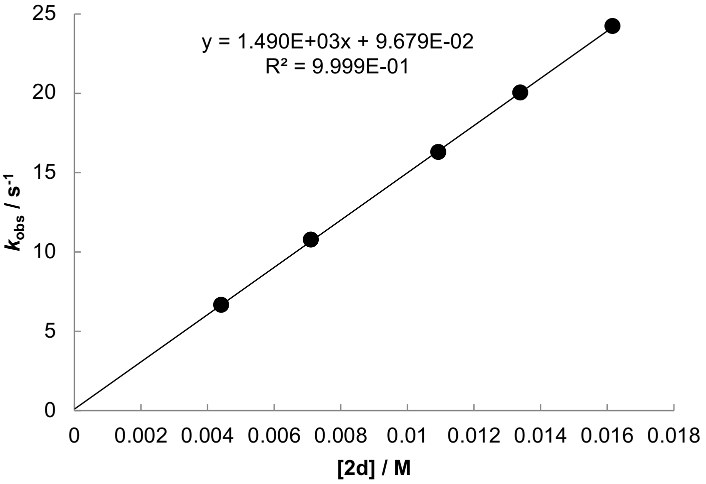


Table S4: Rate constants for the formation of adduct of nitroindole (**1a**) with carbanion (**2d**) in DMSO (stopped–flow method, 20 °C, λ = 437 nm).

[**1a**] / M	[**2d**] / M	k_{obs} / s^{-1}
2.02×10^{-4}	4.42×10^{-3}	6.66
2.02×10^{-4}	7.11×10^{-3}	10.77
2.02×10^{-4}	1.09×10^{-2}	16.31
2.02×10^{-4}	1.34×10^{-2}	20.0
2.02×10^{-4}	1.62×10^{-2}	24.3
$k_2 = 1.49 \times 10^3$ M^{-1} s^{-1}		



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[3] The reactions of proceeded reversibly in certain cases, as the positive intercepts show when plotting k_{obs} *vs* [**2**]

Table S5: Rate constants for the formation of adduct of nitroindole (**1a**) with carbanion (**2e**) in DMSO (stopped–flow method, 20 °C, λ = 380 nm).[3]

[**1a**] / M	[**2e**] / M	k_{obs} / s^{-1}
2.05 x 10^{-4}	3.09 x 10^{-3}	1.72 x 10^{1}
2.05 x 10^{-4}	4.07 x 10^{-3}	2.29 x 10^{1}
2.05 x 10^{-4}	5.12 x 10^{-3}	2.63 x 10^{1}
2.05 x 10^{-4}	7.22 x 10^{-3}	3.48 x 10^{1}
2.05 x 10^{-4}	8.21 x 10^{-3}	3.96 x 10^{1}
k_2 = 4.22 x 10^{3} M^{-1} s^{-1}		

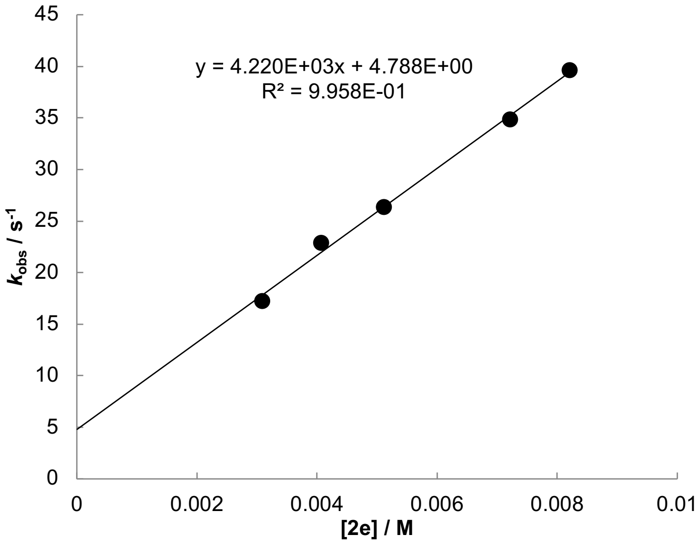


Table S6: Rate constants for the formation of adduct of nitroindole (**1a**) with carbanion (**2f**) in DMSO (stopped–flow method, 20 °C, λ = 380 nm).[3]

[**1a**] / M	[**2f**] / M	k_{obs} / s^{-1}
2.02 x 10^{-4}	4.08 x 10^{-3}	3.72 x 10^{1}
2.02 x 10^{-4}	5.10 x 10^{-3}	4.39 x 10^{1}
2.02 x 10^{-4}	6.01 x 10^{-3}	4.90 x 10^{1}
2.02 x 10^{-4}	7.28 x 10^{-3}	5.89 x 10^{1}
2.02 x 10^{-4}	8.31 x 10^{-2}	6.76 x 10^{1}
k_2 = 7.12 x 10^{3} M^{-1} s^{-1}		

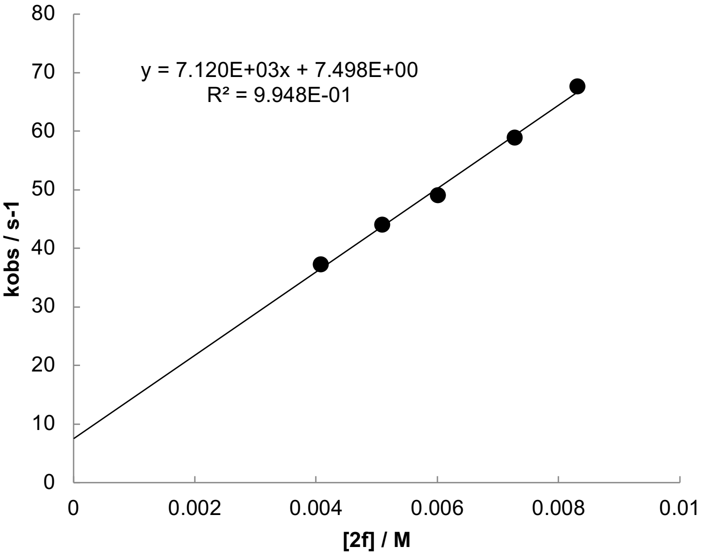


Table S7: Rate constants for the formation of adduct of nitroindole (**1b**) with carbanion (**2b**) in DMSO (stopped–flow method, 20 °C, λ = 350 nm).[3]

[**1b**] / M	[**2b**] / M	k_{obs} / s^{-1}
2.16×10^{-4}	1.98×10^{-2}	1.79×10^{1}
2.16×10^{-4}	1.19×10^{-2}	1.08×10^{1}
2.16×10^{-4}	1.08×10^{-2}	1.04×10^{1}
2.16×10^{-4}	5.41×10^{-3}	6.14
2.16×10^{-4}	2.70×10^{-3}	3.94

$$k_2 = 8.07 \times 10^2\ M^{-1}s^{-1}$$

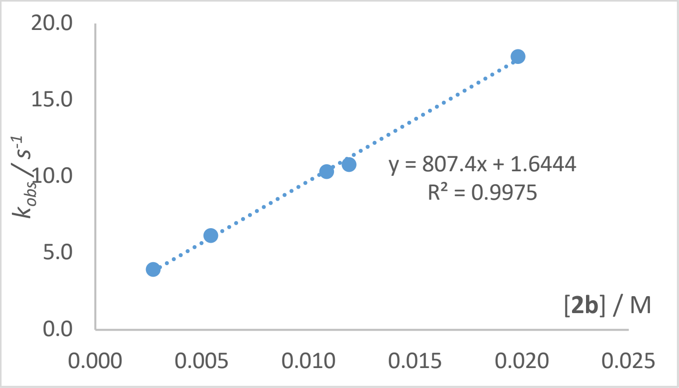


Table S8: Rate constants for the formation of adduct of nitroindole (**1b**) with carbanion (**2c**) in DMSO (stopped–flow method, 20 °C, λ = 360 nm).[3]

[**1b**] / M	[**2c**] / M	k_{obs} / s^{-1}
2.00×10^{-4}	4.00×10^{-4}	$1{,}64 \times 10^{2}$
2.00×10^{-4}	2.40×10^{-4}	$1{,}07 \times 10^{2}$
2.00×10^{-4}	1.44×10^{-4}	7.49×10^{1}
2.00×10^{-4}	8.64×10^{-4}	4.48×10^{1}
2.00×10^{-4}	5.18×10^{-4}	2.92×10^{1}

$$k_2 = 3.84 \times 10^3\ \mathrm{M}^{-1}\mathrm{s}^{-1}$$

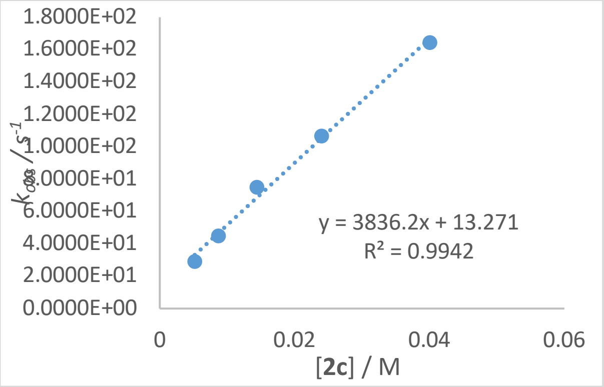


Table S9: Rate constants for the formation of adduct of nitroindole (**1b**) with carbanion (**2h**) in DMSO (stopped–flow method, 20 °C, λ = 400 nm).[3]

[**1b**] / M	[**2h**] / M	k_{obs} / s^{-1}
2.05×10^{-4}	3.98×10^{-2}	1.96×10^{-1}
2.05×10^{-4}	2.39×10^{-2}	1.44×10^{-1}
2.05×10^{-4}	1.43×10^{-2}	1.19×10^{-1}
2.05×10^{-4}	8.61×10^{-3}	8.79×10^{-2}
2.05×10^{-4}	5.16×10^{-3}	7.92×10^{-2}

$$k_2 = 3.37\ M^{-1}s^{-1}$$

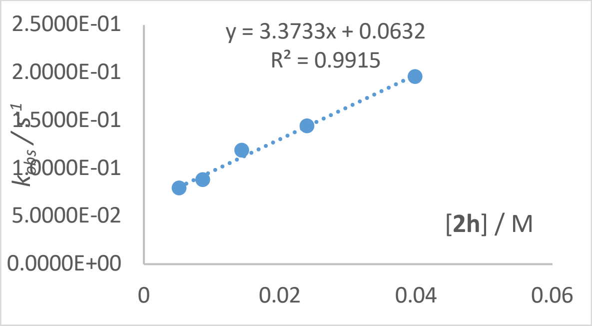


Table S10: Rate constants for the formation of adduct of nitroindole (**1c**) with carbanion (**2a**) in DMSO (stopped–flow method, 20 °C, λ = 425 nm).[3]

[**1c**] / M	[**2a**] / M	k_{obs} / s^{-1}
2.16×10^{-4}	4.02×10^{-2}	2.02
2.16×10^{-4}	2.41×10^{-2}	1.23
2.16×10^{-4}	1.45×10^{-2}	7.40×10^{-1}
2.16×10^{-4}	8.69×10^{-3}	4.43×10^{-1}
2.16×10^{-4}	5.21×10^{-3}	2.60×10^{-1}
$\boldsymbol{k_2 = 5.01 \times 10^1\ M^{-1}s^{-1}}$		

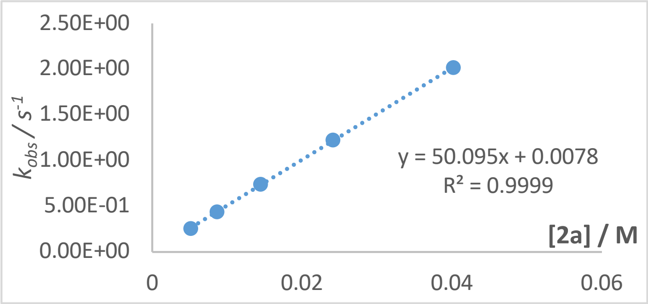


Table S11: Rate constants for the formation of adduct of nitroindole (**1c**) with carbanion (**2b**) in DMSO (stopped–flow method, 20 °C, λ = 450 nm).[3]

[**1c**] / M	[**2b**] / M	k_{obs} / s^{-1}
2.16×10^{-4}	1.58×10^{-2}	7.31×10^{1}
2.16×10^{-4}	1.10×10^{-2}	5.65×10^{1}
2.16×10^{-4}	1.03×10^{-2}	5.44×10^{1}
2.16×10^{-4}	5.16×10^{-3}	3.33×10^{1}
2.16×10^{-4}	1.55×10^{-3}	1.83×10^{1}
$\boldsymbol{k_2 = 3.88 \times 10^3\ M^{-1}s^{-1}}$		

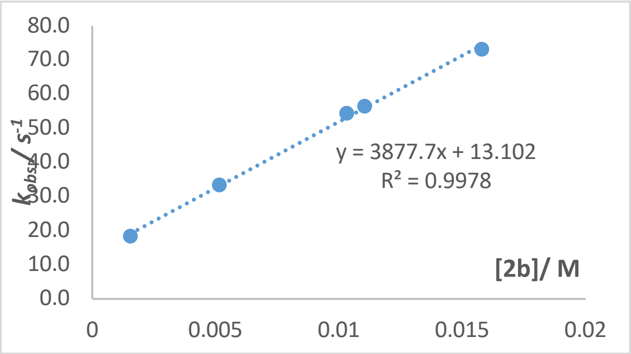


Table S12: Rate constants for the formation of adduct of nitroindole (**1c**) with carbanion (**2d**) in DMSO (stopped–flow method, 20 °C, λ = 425 nm).[3]

[**1c**] / M	[**2d**] / M	k_{obs} / s^{-1}
2.16×10^{-4}	4.00×10^{-2}	9.82×10^{2}
2.16×10^{-4}	2.40×10^{-2}	6.31×10^{2}
2.16×10^{-4}	1.44×10^{-2}	4.38×10^{2}
2.16×10^{-4}	8.64×10^{-3}	3.07×10^{2}
2.16×10^{-4}	5.18×10^{-3}	2.17×10^{2}
$\boldsymbol{k_2 = 2.17 \times 10^4\ M^{-1}s^{-1}}$		

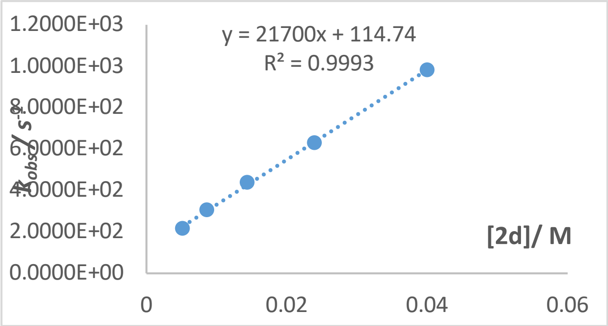


Table S13: Rate constants for the formation of adduct of nitroindole (**1c**) with carbanion (**2e**) in DMSO (stopped–flow method, 20 °C, λ = 450 nm).[3]

[**1c**] / M	[**2e**] / M	k_{obs} / s^{-1}
2.21×10^{-4}	4.00×10^{-2}	6.39×10^{2}
2.21×10^{-4}	2.40×10^{-2}	4.93×10^{2}
2.21×10^{-4}	1.44×10^{-2}	4.06×10^{2}
2.21×10^{-4}	8.64×10^{-3}	4.43×10^{2}
2.21×10^{-4}	5.18×10^{-3}	3.10×10^{2}

$$\boldsymbol{k_2 = 9.44 \times 10^{3}\ M^{-1}s^{-1}}$$

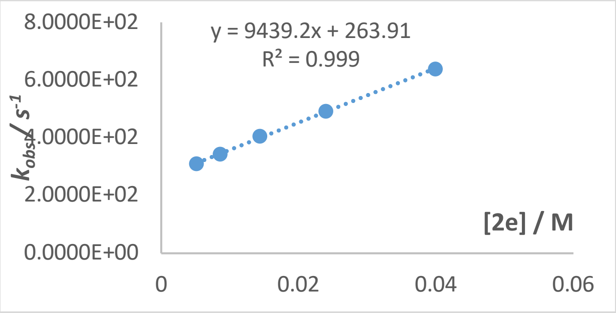


Table S14: Rate constants for the formation of adduct of nitroindole (**1c**) with carbanion (**2g**) in DMSO (stopped–flow method, 20 °C, λ = 455 nm).

[**1c**] / M	[**2g**] / M	k_{obs} / s^{-1}
2.16×10^{-4}	3.97×10^{-2}	7.44×10^{1}
2.16×10^{-4}	2.38×10^{-2}	4.43×10^{1}
2.16×10^{-4}	1.43×10^{-2}	2.57×10^{1}
2.16×10^{-4}	8.58×10^{-3}	1.51×10^{1}
2.16×10^{-4}	5.15×10^{-3}	9.00

$$\boldsymbol{k_2 = 1.90 \times 10^{3}\ M^{-1}s^{-1}}$$

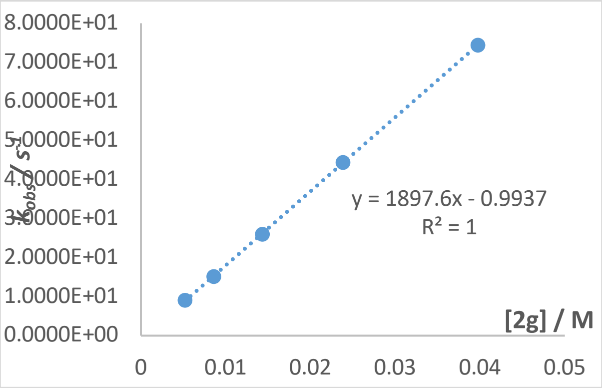


Table S15: Rate constants for the formation of adduct of nitroindole (**1c**) with carbanion (**2h**) in DMSO (stopped–flow method, 20 °C, λ = 415 nm).

[**1c**] / M	[**2h**] / M	k_{obs} / s^{-1}
2.16×10^{-4}	3.98×10^{-2}	1.52
2.16×10^{-4}	2.39×10^{-2}	8.65×10^{-1}
2.16×10^{-4}	1.43×10^{-2}	4.73×10^{-1}
2.16×10^{-4}	8.61×10^{-3}	2.63×10^{-1}
2.16×10^{-4}	5.16×10^{-3}	1.39×10^{-1}

$$\boldsymbol{k_2 = 3.99 \times 10^{1}\ M^{-1}s^{-1}}$$

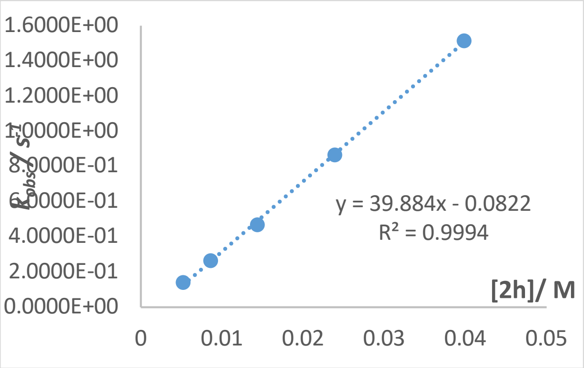


Table S16: Rate constants for the formation of adduct of nitroindole (**1c**) with carbanion (**2i**) in DMSO (stopped–flow method, 20 °C, λ = 525 nm).

[**1c**] / M	[**2i**] / M	k_{obs} / s^{-1}
2.21×10^{-4}	4.00×10^{-2}	1.25×10^{3}
2.21×10^{-4}	2.40×10^{-2}	6.56×10^{2}
2.21×10^{-4}	1.44×10^{-2}	3.82×10^{2}
2.21×10^{-4}	8.63×10^{-3}	1.58×10^{2}
2.21×10^{-4}	5.18×10^{-3}	1.06×10^{2}

$$k_2 = 3.34 \times 10^4\ M^{-1}s^{-1}$$

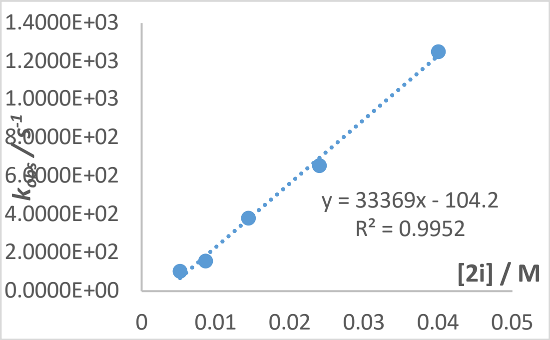


Table S17: Rate constants for the formation of adduct of nitroindole (**1d**) with carbanion (**2a**) in DMSO (stopped–flow method, 20 °C, λ = 425 nm).

[**1d**] / M	[**2a**] / M	k_{obs} / s^{-1}
2.16×10^{-4}	5.55×10^{-2}	7.99×10^{-2}
2.16×10^{-4}	3.33×10^{-2}	4.85×10^{-2}
2.16×10^{-4}	2.00×10^{-2}	2.72×10^{-2}
2.16×10^{-4}	1.20×10^{-2}	1.21×10^{-2}
2.16×10^{-4}	7.20×10^{-3}	6.64×10^{-3}

$$k_2 = 1.54\ \mathrm{M}^{-1}\mathrm{s}^{-1}$$

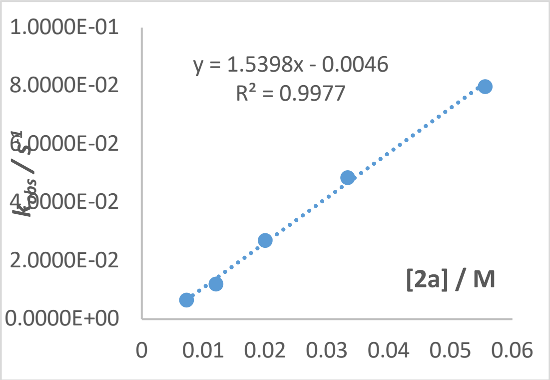


Table S18: Rate constants for the formation of adduct of nitroindole (**1d**) with carbanion (**2b**) in DMSO (stopped–flow method, 20 °C, λ = 450 nm).

[**1d**] / M	[**2b**] / M	k_{obs} / s^{-1}
1.92×10^{-4}	2.08×10^{-2}	7.62
1.92×10^{-4}	1.25×10^{-2}	3.80
1.92×10^{-4}	9.52×10^{-3}	2.91
1.92×10^{-4}	4.76×10^{-3}	1.28
1.92×10^{-4}	3.81×10^{-3}	9.22×10^{-1}

$$k_2 = 3.90\ \times\ 10^2\ M^{-1}s^{-1}$$

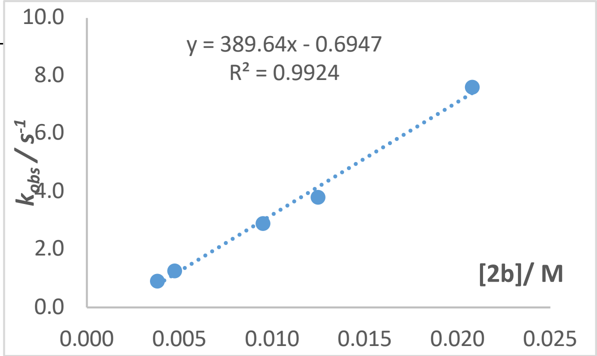


Table S19: Rate constants for the formation of adduct of nitroindole (**1d**) with carbanion (**2d**) in DMSO (stopped–flow method, 20 °C, λ = 425 nm).

[**1d**] / M	[**2d**] / M	k_{obs} / s^{-1}
1.97×10^{-4}	4.00×10^{-2}	3.13×10^{1}
1.97×10^{-4}	2.40×10^{-2}	1.85×10^{1}
1.97×10^{-4}	8.64×10^{-3}	6.50
1.97×10^{-4}	5.18×10^{-3}	3.92

$$\boldsymbol{k_2 = 7.86 \times 10^{2}\ \mathrm{M^{-1}s^{-1}}}$$

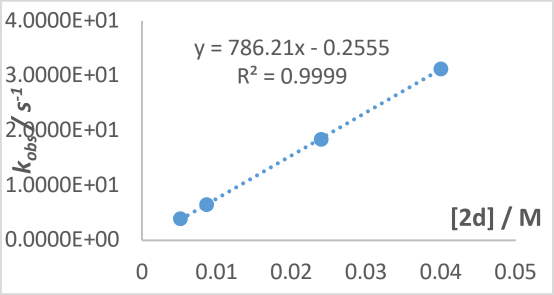


Table S20: Rate constants for the formation of adduct of nitroindole (**1d**) with carbanion (**2e**) in DMSO (stopped–flow method, 20 °C, λ = 450 nm).[3]

[**1d**] / M	[**2e**] / M	k_{obs} / s^{-1}
2.21×10^{-4}	4.00×10^{-2}	5.25×10^{1}
2.21×10^{-4}	2.40×10^{-2}	4.76×10^{1}
2.21×10^{-4}	1.44×10^{-2}	4.48×10^{1}
2.21×10^{-4}	8.64×10^{-3}	4.20×10^{1}
2.21×10^{-4}	5.18×10^{-3}	4.15×10^{1}

$$\boldsymbol{\mathrm{k_2} = 3.23 \times 10^{2}\ \mathrm{M^{-1}s^{-1}}}$$

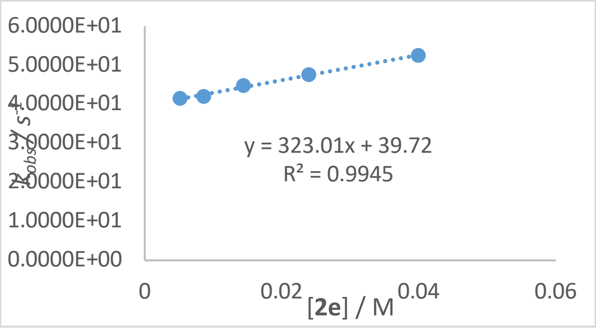


Table S21: Rate constants for the formation of adduct of nitroindole (**1d**) with carbanion (**2g**) in DMSO (stopped–flow method, 20 °C, λ = 455 nm).

[**1d**] / M	[**2g**] / M	k_{obs} / s^{-1}
2.16×10^{-4}	3.97×10^{-2}	7.44×10^{1}
2.16×10^{-4}	2.38×10^{-2}	4.43×10^{1}
2.16×10^{-4}	1.43×10^{-2}	2.57×10^{1}
2.16×10^{-4}	8.58×10^{-3}	1.51×10^{1}
2.16×10^{-4}	5.15×10^{-3}	9.00

$$\boldsymbol{k_2 = 6,04 \times 10^{2}\ M^{-1}s^{-1}}$$

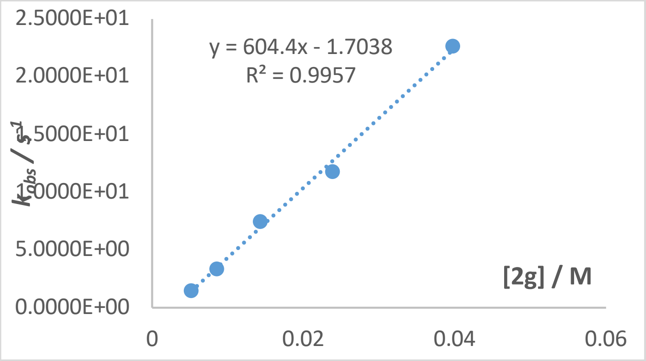


Table S22: Rate constants for the formation of adduct of nitroindole (**1d**) with carbanion (**2h**) in DMSO (stopped–flow method, 20 °C, λ = 415 nm).

[**1d**] / M	[**2h**] / M	k_{obs} / s^{-1}
1.92×10^{-4}	3.98×10^{-2}	2.01×10^{-1}
1.92×10^{-4}	2.39×10^{-2}	1.10×10^{-1}
1.92×10^{-4}	1.43×10^{-2}	5.43×10^{-2}
1.92×10^{-4}	8.61×10^{-3}	2.60×10^{-2}
1.92×10^{-4}	5.16×10^{-3}	5.13×10^{-3}
$\boldsymbol{k_2 = 5.64\ M^{-1}s^{-1}}$		

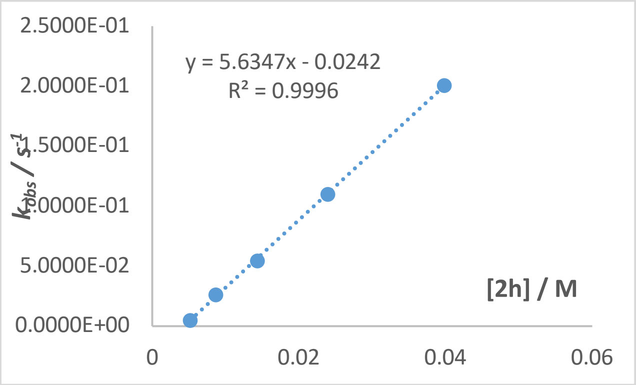
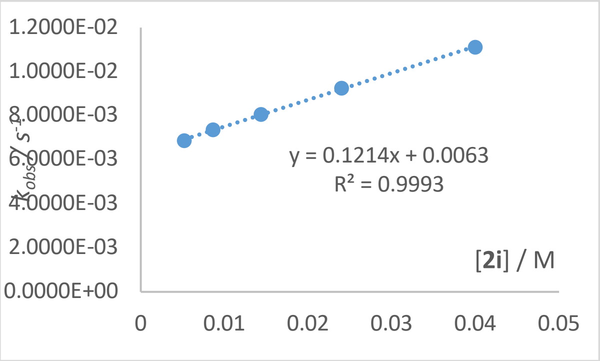


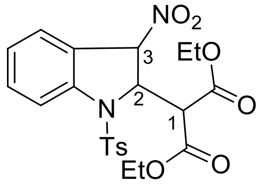
Table S23: Rate constants for the formation of adduct of nitroindole (**1d**) with carbanion (**2i**) in DMSO (stopped–flow method, 20 °C, λ = 450 nm).[3]

[**1d**] / M	[**2i**] / M	k_{obs} / s^{-1}
2.21×10^{-4}	4.00×10^{-2}	1.11×10^{-2}
2.21×10^{-4}	2.40×10^{-2}	9.27×10^{-3}
2.21×10^{-4}	1.44×10^{-2}	8.05×10^{-3}
2.21×10^{-4}	8.63×10^{-3}	7.36×10^{-3}
2.21×10^{-4}	5.18×10^{-3}	6.87×10^{-3}
$\boldsymbol{k_2 = 1.21 \times 10^{-1}\ M^{-1}s^{-1}}$		



3. Procedures and analytical data

Protonated σ-complex: Adduct 3ae



To solution of diethylmalonate potassium enolate (**2e**) (41.6 mg, 0.25 mmol, 2.5 eq.) in THF (2 mL) at 0°C was added dropwise a solution nitroindole (**1a**) (31.4 mg, 0.10 mmol) in THF (2 mL) and stirred at the same temperature for 15 min and then at r.t. for 30 min The reaction mixture was subsequently quenched by acidification (pH<2) with aqueous HCl solution (2M), diluted with distilled water (10 mL) and extracted with Et_2O (3x10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was triturated 3 times with pentane and dried under vacuum to give the corresponding protonated adduct **3ae** as a yellow oil (16,4 mg, 36%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.2 Hz, 1H, $CH_{\text{Ar Indoline}}$), 7.69 (d, *J* = 8.1 Hz, 2H, CH_{Tosyl}), 7.45 (d, *J* = 7.7 Hz, 1H, $CH_{\text{Ar Indoline}}$), 7.40 (t, *J* = 8.0 Hz, 1H, $CH_{\text{Ar Indoline}}$), 7.22 (d, *J* = 8.1 Hz, 2H, CH_{Tosyl}), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H, $CH_{\text{Ar Indoline}}$), 6.21 (d, *J* = 2.8 Hz, 1H, $H_{(3)}$), 5.38 (dd, *J* = 4.8, 2.9 Hz, 1H, $H_{(2)}$), 4.58 (d, *J* = 4.8 Hz, 1H, $H_{(1)}$), 4.30-4.21 (m, 2H, O-CH_2CH_3), 4.08-3.92 (m, 2H, O-CH_2CH_3), 2.36 (s, 3H, $CH_{3\,\text{Tosyl}}$), 1.29 (t, *J* = 7.1 Hz, 3H, O-CH_2CH_3), 1.02 (t, *J* = 7.1 Hz, 3H, O-CH_2CH_3); **^{13}C{^{1}H} NMR** (100.6 MHz, CDCl3): δ = 166.6 (*C*=O), 166.4 (*C*=O), 145.1 (C_{Tosyl}), 142.7 ($C_{\text{Ar Indoline}}$), 132.7 (C_{Tosyl}), 131.8 ($CH_{\text{Ar Indoline}}$), 129.8 (CH_{Tosyl}), 127.7 (CH_{Tosyl}), 125.7 ($CH_{\text{Ar Indoline}}$), 125.6 ($C_{\text{Ar Indoline}}$), 124.7 ($CH_{\text{Ar Indoline}}$), 116.0 ($CH_{\text{Ar Indoline}}$), 87.1 ($C_{(3)}$), 63.3 ($C_{(2)}$), 62.5 (O-CH_2CH_3), 62.1 (O-CH_2CH_3), 55.0 ($C_{(1)}$), 21.6 ($CH_{3\,\text{Tosyl}}$), 13.8 (O-CH_2CH_3), 13.6 (O-CH_2CH_3); **HRMS** (ESI, positive mode) *calcd* (m/z) for $C_{22}H_{24}N_2O_8Na$ $[M + Na]^+$: 499.1151, *found*: 499.1150, ε_r: 0.2 ppm.

General Procedure for the cycloaddition reaction between nitro-indoles or -benzofuran and Danishefsky's diene 4.

To a stirred solution of the heteroaromatic (0.2 mmol, 1 equiv) in dry CH_2Cl_2 (1 mL) was added Danishefsky's diene (0.24 mmol or 0.48 mmol, 1.2 equiv or 2.4 equiv). The solution was stirred under argon atmosphere for the required time at room temperature. The solvent was then evaporated under reduced pressure. The reaction residue was dissolved in 1 mL dry methanol and NH_4F (1.2 mmol, 6 equiv) was added at -25 °C. The reaction mixture was stirred for 30 min after which methanol was evaporated. The reaction residue was dissolved in EtOAc (5 mL), extracted with saturated aqueous $NaHCO_3$ solution (3 x 2 mL) and brine (2 x 2 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel (Cyclohexane/Acetone: 80/20).

4-Methoxy-4a-nitro-9a-tosyl-4,4,9,9-tetrahydro-1H-carbazol-2(3*H*)-one (4*S,4a*R**,9a*S**) and (4*R**,4a*R**,9a*S**) diastereomers (5a)**

5a was prepared according to the general procedure: 1.2 equiv Danishefsky's diene **4** (46 µL, 0.24 mmol) were added to a stirred solution of 3-nitro-1-tosyl-1*H*-indole **1a** (63 mg, 0.2 mmol) in 1 mL dry CH_2Cl_2. The reaction mixture was stirred at room temperature for 24 h. The crude 54 : 46 mixture of diastereomers was purified by flash chromatography to afford **5a** (88 mg, 95%). *(4R*, 4aR*,9aS*) major diastereomer:* **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.20 – 7.13 (m, 3H), 5.08 (dd≈t, *J* = 6.2, 4.9 Hz, 1H), 4.67 (dd, *J* = 10.1, 4.5 Hz, 1H), 3.35 (s, 3H), 3.12 (dd, *J* = 16.2, 6.2 Hz, 1H), 3.05 (dd, *J* = 16.2, 4.9 Hz, 1H), 2.71 (dd, *J* = 18.6, 4.5 Hz, 1H), 2.35 (s, 3H), 2.07 (dd, *J* = 18.6, 10.1 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 203.0, 145.3, 143.4, 132.9, 132.6, 130.0 (2C), 129.7, 127.3 (2C), 125.2, 123.6, 116.8, 95.8, 78.2, 63.6, 58.3, 44.6, 40.3, 21.8. *(4S*, 4aR*,9aS*) minor diastereomer:* **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.2, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.20 – 7.05 (m, 3H), 5.78 (dd, *J* = 4.9, 3.5 Hz, 1H), 4.65– 4.63 (m, 1H), 3.35 (s, 3H), 3.28– 3.22 (m, 2H), 2.67 – 2.60 (m, 1H), 2.35 (s, 3H), 1.91 (dd, *J* = 18.9, 2.5 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 204.3, 145.4, 142.7, 133.2, 133.1, 130.0 (2C), 127.8 (2C), 125.5, 125.3, 125.3, 117.1, 97.0, 80.5, 61.7, 58.4, 44.2, 37.7, 21.8. **HRMS** (ESI, positive mode) calcd m/z for $C_{20}H_{24}N_3O_6S$ $[M+NH_4]^+$: 434.1389; found: 434.1386. **IR** (neat) ν = 1726, 1550, 1477, 1357, 1167, 1087, 1014, 659, 571 cm^{-1}.

Ethyl-4-methoxy-4a-nitro-2-oxo-2,3,4,4-tetrahydro-1*H*-carbazole-9(9*H*)-carboxylate (4*S,4a*R**,9a*S**) and (4*R**,4a*R**,9a*S**) diastereomers (5b)**

5b was prepared according to the general procedure: 2.4 equiv of **4** (93 µL, 0.48 mmol) were added to a stirred solution of ethyl-3-nitro-1*H*-indole-1-carboxylate **1b** (47 mg, 0.2 mmol) in 1 mL dry CH_2Cl_2. The reaction mixture was stirred at room temperature for 48 h. The crude 64:36 mixture of diastereomers was purified by flash chromatography to afford **5b** (46mg, 69%). (4*R**, 4a*R**,9a*S**) major diastereomer: **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.78 – 7.67 (m, 1H), 7.64 – 7.54 (m, 1H), 7.50 – 7.36 (m, 1H), 7.17 – 7.12 (m, 1H), 5.99 (dd, *J* = 7.0, 2.1 Hz, 1H), 4.88 – 4.77 (m, 1H), 4.41 – 4.20 (m, 2H), 3.43 (s, 3H), 3.05 (dd, *J* = 16.2, 7.0 Hz, 1H), 2.80 (dd, *J* = 18.4, 4.4 Hz, 1H), 2.71 (dd, *J* = 18.4, 3.1 Hz, 1H), 2.13 – 1.99 (m, 1H), 1.42 – 1.32 (m, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 205.2, 152.2, 132.4, 129.3, 125.0, 121.8, 116.4, 115.9, 97.0, 80.1, 61.4, 58.3, 58.2, 42.2, 40.6, 14.5. (4*S**,4a*R**,9a*S**) minor diastereomer: **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.78 – 7.67 (m, 1H), 7.64 – 7.54 (m, 1H), 7.50 – 7.36 (m, 1H), 7.17 – 7.12 (m, 1H), 5.37 – 5.25 (m, 1H), 4.92 – 4.80 (m, 1H), 4.41 – 4.20 (m, 2H), 3.43 (s, 3H), 3.24 (dd, *J* = 16.3, 7.0 Hz, 1H), 3.05 (dd, *J* = 16.3, 6.3 Hz, 1H), 2.80 (dd, *J* = 18.4, 4.5 Hz, 1H), 2.71 (dd, *J* = 18.4, 3.1 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H).**^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 203.8, 152.2, 133.0, 129.3, 124.0, 123.6, 116.4, 115.9, 95.6, 78.2, 62.7, 59.8, 58.3, 42.3, 38.1, 14.5. **HRMS**

(ESI, negative mode) calcd m/z for $C_{16}H_{17}N_2O_6$ $[M-H]^-$: 333.1087; found: 333.1080. **IR** (neat) ν = 1709, 1553, 1380, 1257, 1096,758, 665 cm^{-1}.

6-Bromo-4-methoxy-4a-nitro-9-tosyl-1,3,4,4a,9,9a-hexahydro-2*H*-carbazol-2-one (4*S**,4a*R**,9a*S**) and(4*R**,4a*R**,9a*S**) diastereomers (5c)

5c was prepared according to the general procedure: 2.4 equiv of **4** (93 μL, 0.48 mmol) were added to a stirred solution of 5-bromo-3-nitro-1-tosyl-1*H*-indole (79 mg, 0.2 mmol) in 1 mL dry CH_2Cl_2. The reaction was stirred at room temperature for 48 h. The crude 50:50 mixture of diastereomers was purified by flash chromatography to afford **5c** (89 mg, 90%).

(4R,4aR*,9aS*) diastereomer:* **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 1.9, 0.5 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.04 (dd≈t, *J* = 5.3, 5.3 Hz, 1H), 4.64 (dd, *J* = 10.5, 4.6 Hz, 1H), 3.34 (s, 3H), 3.11 – 3.06 (m, 2H), 2.76 (dd, *J* = 18.7, 4.6 Hz, 1H), 2.36 (s, 3H), 2.04 (dd, *J* = 18.7, 10.5 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 202.5, 145.7, 142.5, 135.6, 132.6, 132.5 (2C), 130.2, 127.2 (2C), 125.4, 118.3, 118.0, 96.3, 77.9, 63.9, 58.3, 44.5, 40.1, 21.7. *(4S*,4aR*,9aS*) diastereomer (m.p. = 155°C):* **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.68 (d, *J* = 2.0 Hz, 1H), 7.63 – 7.59 (m, 3H), 7.56 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.75 (dd≈t, *J* = 4.3, 4.3 Hz, 1H), 4.59 (dd, *J* = 3.5, 2.5 Hz, 1H), 3.35 (s, 3H), 3.31 – 3.19 (m, 2H), 2.70 (dd, *J* = 18.9, 3.5 Hz, 1H), 2.37 (s, 3H), 1.94 (dd, *J* = 18.9, 2.5 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 203.7, 145.7, 141.9, 136.3, 132.7, 130.2 (2C), 128.6, 127.8 (2C), 126.9, 118.2, 117.8, 95.1, 80.5, 62.0, 58.4, 43.9, 37.7, 21.8. **HRMS** (ESI, negative mode) calcd m/z for $C_{20}H_{18}N_2O_6SBr$ $[M-H]^-$: 493.0069; found: 493.0061. **IR** (neat) ν = 1733, 1555, 1467, 1362, 1168, 1101, 1086, 666, 576 cm^{-1}.

5-bromo-4-methoxy-4a-nitro-9-tosyl-4,4a,9,9a-tetrahydro-1*H*-carbazol-2(3*H*)-one (4*S**,4a*R**,9a*S**) and (4*R**,4a*R**,9a*S**) diastereomers (5d)

5d was prepared according to the general procedure: 2.4 equiv Danishefsky's diene **4** (93 μL, 0.48 mmol) were added to a stirred solution of 4-bromo-3-nitro-1-tosyl-1*H*-indole **1d** (79 mg, 0.2 mmol) in 1 mL dry CH_2Cl_2. The reaction was stirred at 40 °C for 24 h. The crude 60:40 mixture of diastereomers was purified by flash chromatography to afford **5d** (66 mg, 67%).*(4R*,4aR*,9aS*) major diastereomer:* **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.72 – 7.63 (m, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.18 (m, 3H), 5.59 (dd≈t, *J* = 3.4, 2.9 Hz, 1H), 4.86 (dd≈t, *J* = 3.6, 3.6 Hz, 1H), 3.42 (dd, *J* = 16.4, 3.4 Hz, 1H), 3.24 (s, 3H), 3.19 (dd, *J* = 16.4, 2.9 Hz, 1H), 3.00-2.75 (m, 2H), 2.32 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 203.9, 145.5, 145.1, 134.2, 133.2, 130.1 (2C), 130.0, 127.3 (2C), 125.9, 122.1, 115.7, 97.6, 74.1, 64.8, 57.5, 43.8, 39.2, 21.8. *(4S*,4aR*,9aS*) minor diastereomer:* **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.85-7.75 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.30-7.25 (m, 1H), 7.21 (d, *J* = 2.5 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.59 (dd≈t, *J* = 3.4, 2.9 Hz, 1H), 4.90 (dd≈t, *J* = 3.1, 2.3 Hz, 1H), 3.37 (s, 3H), 3.03 (dd, *J* =

16.8, 3.4 Hz, 1H), 2.92 (d, *J* = 16.8, 2.9 Hz, 1H), 2.71 (dd, *J* = 18.3, 3.1 Hz, 1H), 2.33 (s, 3H), 2.23 (dd, *J* = 18.3, 2.3 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$): δ 203.8, 145.5, 145.3, 134.4, 133.5, 130.0 (2C), 129.4, 127.7 (2C), 122.7, 120.6, 114.9, 97.0, 76.6, 63.5, 58.4, 46.1, 38.1, 21.8. **HRMS** (ESI, negative mode) calcd m/z for $C_{20}H_{18}N_2O_6SBr$ [M-H]$^-$: 493.0069; found: 493.0070. **IR** (neat) ν = 1726, 1554, 1360, 1168, 1089,677, 576 cm^{-1}.

4-Methoxy-4a,6-dinitro-9-tosyl-1,3,4,4a,9,9a-hexahydro-2*H*-carbazol-2-one (4*S**,4a*R**,9a*S**) and (4*R**,4a*R**,9a*S**) diastereomers (5e)

5e was prepared according to the general procedure: 1.2 equiv of Danishefsky’s diene **4** (46 µL, 0.24 mmol) were added to a stirred solution of 3,5-dinitro-1-tosyl-1*H*-indole (72 mg, 0.2 mmol) in 1 mL dry CH_2Cl_2. The reaction was stirred at room temperature for 48 h. The crude 68:32 mixture of diastereomers was purified by flash chromatography to afford **5e** (86 mg, 93%). *(4R*,4aR*,9aS*) major diastereomer* (m.p. = 168 °C): **^{1}H NMR** (300 MHz, CDCl$_3$): δ 8.45 (d, *J* = 2.3 Hz, 1H), 8.36 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.85 (d, *J* = 9.1 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.19 (dd, *J* = 6.1, 5.0 Hz, 1H), 4.72 (dd, *J* = 9.8, 4.4 Hz, 1H), 3.40 (s, 3H), 3.18 (dd, *J* = 15.4, 6.1 Hz, 1H), 3.11 (dd, *J* = 15.4, 5.0 Hz, 1H), 2.80 (dd, *J* = 18.7, 4.4 Hz, 1H), 2.38 (s, 3H), 2.14 (dd, *J* = 18.7, 9.8 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$): δ 201.9, 148.3, 146.3, 144.9, 132.7, 130.5 (2C), 128.5, 127.1 (2C), 126.0, 124.5, 116.2, 95.8, 77.7, 64.6, 58.4, 44.1, 40.1, 21.8. (4*S**,4a*R**,9a*S**) minor *diastereomer* (m.p. = 199 °C): **^{1}H** NMR (300 MHz, CDCl$_3$): δ 8.45 (d, *J* = 2.3 Hz, 1H), 8.35 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.84 (d, *J* = 9.1 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 5.90 (dd, *J* = 5.4, 3.5 Hz, 1H), 4.73 (dd≈t, *J* = 3.4, 2.6 Hz, 1H), 3.40 (s, 3H), 3.33 – 3.28 (m, 2H), 2.79 (dd, *J* = 19.1, 3.4 Hz, 1H), 2.38 (s, 3H), 1.97 (dd, *J* = 19.1, 2.6 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, CDCl$_3$): δ 203.1, 147.7, 146.3, 144.7, 132.7, 130.4 (2C), 129.2, 127.6 (2C), 125.7, 122.1, 116.1, 94.5, 80.2, 62.9, 58.5, 43.7, 37.6, 21.8. **HRMS** (ESI, negative mode) calcd m/z for $C_{20}H_{18}N_3O_8S$ [M-H]$^-$: 460.0815; found: 460.0818. **IR** (neat) ν = 1734, 1557, 1529, 1371, 1345, 1171, 1096, 1087, 725, 665 cm^{-1}.

4-Methoxy-4a,7-dinitro-9-tosyl-1,3,4,4a,9,9a-hexahydro-2*H*-carbazol-2-one (4*S**,4a*R**,9a*S**) and (4*R**,4a*R**,9a*S**) diastereomers (5f)

5f was prepared according to the general procedure: 2.4 equiv Danishefsky’s diene **4** (93 µL, 0.48 mmol) were added to a stirred solution of 3,6-dinitro-1-tosyl-1*H*-indole **1c** (73 mg, 0.2 mmol) in 1 mL dry CH_2Cl_2. The reaction was stirred at room temperature for 48 h. The crude 68:32 mixture of diastereomers was purified by flash chromatography to afford **5f** (87 mg, 95%). *(4R*,4aR*,9aS*) major diastereomer:* **^{1}H NMR** (300 MHz, CDCl$_3$): δ 8.51 (d, *J* = 2.0 Hz, 1H), 8.01 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 5.18 (dd≈t, *J* = 5.5, 5.5 Hz, 1H), 4.72 (dd, *J* = 9.9, 4.4 Hz, 1H), 3.37 (s, 3H), 3.25 – 3.01 (m, 2H), 2.79 (dd, *J* = 18.7, 4.4 Hz, 1H), 2.37 (s, 3H), 2.08 (dd, *J* = 18.7, 9.9 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 202.0, 151.0, 146.2, 144.3, 132.4, 130.7, 130.4 (2C), 129.5, 127.2 (2C), 119.9, 111.6, 95.8, 77.7, 64.3, 58.3, 44.2, 40.0, 21.8. *(4S*,4aR*,9aS*) minor diastereomer:* **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.50 (d, *J* = 2.0 Hz, 1H), 7.96 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.87 (dd≈t, *J* = 4.4, 4.4 Hz, 1H), 4.66 (dd, *J* = 3.6, 2.5 Hz, 1H), 3.39 (s, 3H), 3.17 – 3.00 (m, 2H), 2.74 (dd, *J* = 18.9, 3.6 Hz, 1H), 2.37 (s, 3H), 1.93 (dd, *J* = 18.9, 2.5 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 203.1, 151.1, 146.2, 144.4, 132.5, 130.7, 130.4, 129.5 (2C), 127.8 (2C), 120.0, 111.5, 94.8, 80.3, 62.6, 58.5, 43.8, 37.6, 29.8. **HRMS** (ESI, negative mode) calcd m/z for $C_{20}H_{18}N_3O_8S$ [M-H]$^-$: 460.0815; Found: 460.0817. **IR** (neat) ν = 1728, 1558, 1530, 1347, 1168, 1088, 664 cm^{-1}.

4-Methoxy-4a,8-dinitro-9-tosyl-1,3,4,4a,9,9a-hexahydro-2*H*-carbazol-2-one (4*S**,4a*R**,9a*S**) and (4*R**,4a*R**,9a*S**) diastereomers (5g)

5g was prepared according to the general procedure: 1.2 equiv Danishefsky's diene **4** (46 µL, 0.24 mmol) were added to a stirred solution of 3,7-dinitro-1-tosyl-1*H*-indole (72 mg, 0.2 mmol) in 1 mL dry CH_2Cl_2. The reaction was stirred at room temperature for 24 h. The crude 55:45 mixture of diastereomers was purified by flash chromatography to afford **5g** (74 mg, 80%). *(4R*,4aR*,9aS*) major diastereomer:* **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.01 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.94 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.45 (dd≈t, *J* = 8.1, 7.8 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.27 (dd, *J* = 7.0, 4.6 Hz, 1H), 4.61 (dd, *J* = 9.9, 4.7 Hz, 1H), 3.34 (s, 3H), 2.95 (dd, *J* = 16.1, 7.0 Hz, 1H), 2.82 (dd, *J* = 18.3, 4.7 Hz, 1H), 2.74 (dd, *J* = 16.1, 4.6 Hz, 1H), 2.43 (s, 3H), 2.00 (dd, *J* = 18.3, 9.9 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 201.6, 146.4, 142.2, 135.8, 134.5, 132.7 (2C), 130.4, 129.4, 128.2, 128.1 (2C), 126.9, 96.5, 78.3, 64.4, 58.4, 43.9, 40.3, 21.9. *(4S*,4aR*,9aS*) minor diastereomer:* **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.02 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.94 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.43 (dd≈t, *J* = 8.1, 7.8 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 5.78 (dd, *J* = 6.8, 3.6 Hz, 1H), 4.46 (dd, *J* = 4.3, 3.0 Hz, 1H), 3.35 (s, 3H), 3.14 (dd, *J* = 16.6, 6.8 Hz, 1H), 2.92 (d, *J* = 18.4, 4.3 Hz, 1H), 2.68 (dd, *J* = 16.6, 3.6 Hz, 1H), 2.43 (s, 3H), 1.98 (dd, *J* = 18.4, 3.0 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 202.5, 146.2, 145.2, 141.9, 135.0, 132.8 (2C), 131.1, 130.6, 128.5, 128.1 (2C), 127.0, 94.7, 80.7, 62.8, 58.4, 43.2, 37.9, 21.8. **HRMS** (ESI, positive mode) calcd m/z for $C_{20}H_{23}N_4O_8S$ [M+NH$_4$]$^+$: 479.1237; Found: 479.1236. **IR** (neat) ν = 1728, 1558, 1539, 1356, 1167, 1088, 660 cm^{-1}.

Ethyl-4-methoxy-4a,7-dinitro-2-oxo-1,2,3,4,4a-9a-hexahydro-9H-carbazole-9-carboxylate (4*S**, 4a*R**, 9a*S**) and (4*R**, 4a*R**, 9a*S**) diastereomers (5h)

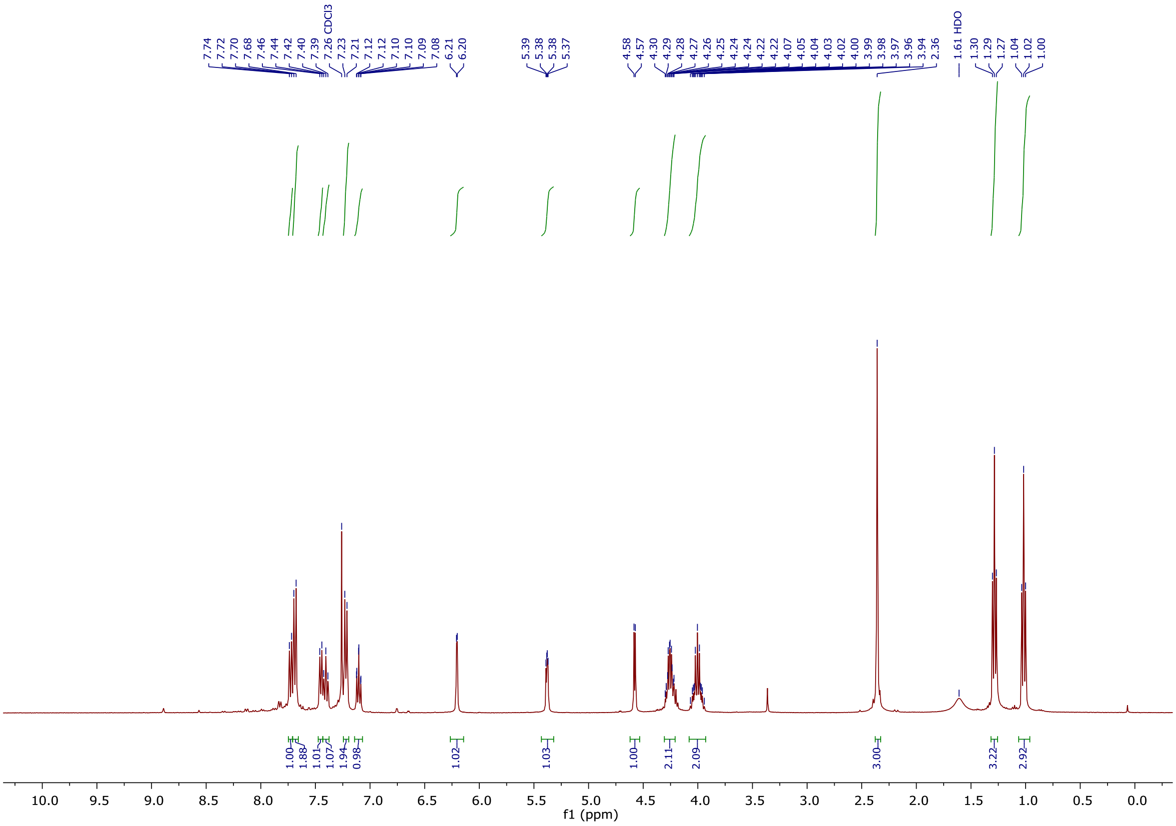
5h was prepared according to the general procedure: 1.2 equiv Danishefsky's diene **4** (46 µL, 0.24 mmol) were added to a stirred solution of ethyl-3,5-dinitro-1*H*-indole-1-carboxylate (56 mg, 0.2 mmol) in 1 mL dry CH_2Cl_2. The reaction was stirred at room temperature for 48 h. The crude 64:36 mixture of diastereomers was purified by flash chromatography to afford **5h** (72 mg, 94%). (4*R**, 4a*R**, 9a*S**) major diastereomer (m.p. = 155 °C): **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.59 (d, *J* = 2.4 Hz, 1H), 8.35 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.95 – 7.93 (m, 1H), 5.39 (dd, *J* = 6.1, 4.7 Hz, 1H), 4.84 (dd, *J* = 10.0, 4.6 Hz, 1H), 4.36 – 4.32 (m, 2H), 3.47 (s, 3H), 3.09 (dd, *J* = 16.3, 6.1 Hz, 1H), 2.96 (dd, *J* = 16.3, 4.7 Hz, 1H), 2.88 (dd, *J* = 18.6, 4.6 Hz, 1H), 2.20 (dd, *J* = 18.6, 10.0 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 202.7, 151.3, 148.3, 143.7, 128.6, 125.9, 122.8, 115.7, 95.6, 78.0, 63.8, 62.5, 58.5, 42.0, 40.5, 14.5. (4*S**, 4a*R**, 9a*S**) minor diastereomer (m.p. = 136 °C): **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.53 (d, *J* = 2.3 Hz, 1H), 8.34 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.95 – 7.93 (m, 1H), 6.08 (dd, *J* = 6.8, 1.8 Hz, 1H), 4.88 (dd≈t, *J* = 2.9, 2.9 Hz, 1H), 4.39 – 4.35 (m, 2H), 3.46 (s, 3H), 3.29 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.98 (d, *J* = 16.8, 1.8 Hz, 1H), 2.78 (dd, *J* = 19.1, 2.9 Hz, 1H), 2.07 (dd, *J* = 19.1, 2.9 Hz, 1H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 204.0, 151.6, 147.9, 143.8, 129.2, 124.6, 121.7, 116.2, 94.3, 80.1, 63.8, 61.0, 58.6, 42.0, 38.1, 14.5. **HRMS** (ESI, negative mode) calcd m/z for $C_{16}H_{16}N_3O_8$ $[M-H]^-$: 378.0937; Found: 378.0931. **IR** (neat) ν = 1716, 1600, 1445, 1400, 1248, 1173, 1093, 734 cm^{-1}.

9-methoxy-9a-nitro-7-oxo-5a,6,7,8,9,9a-hexahyrodibenzo[*b,d*]furan-2-yl acetate (5a*R**, 9*R**, 9a*R**) and (5a*R**, 9*S**, 9a*R**) diastereomers (6)

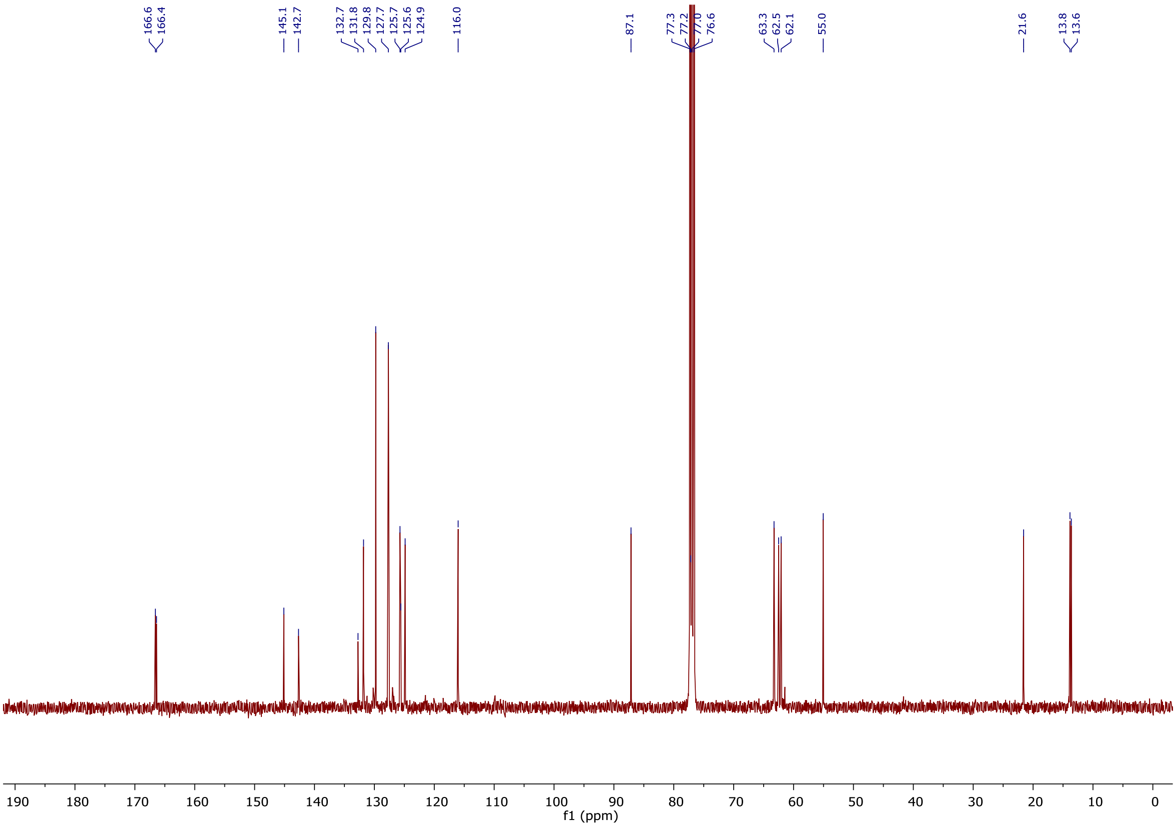
6 was prepared according to the general procedure: 1.2 equiv Danishefsky's diene **4** (46.5 µL, 0.24 mmol) were added to a stirred solution of 3-nitrobenzofuran-5-yl acetate (44 mg, 0.2 mmol) in 1 mL dry CH_2Cl_2. The reaction was stirred at room temperature for 24 h. The crude 50:50 mixture of diastereomers was purified by flash chromatography to afford **6** (55 mg, 85%). (5a*R**, 9*S**, 9a*R**) diastereomer (m.p. = 107°C): **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.43 (d, *J* = 2.6 Hz, 1H), 7.12 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 5.44 – 5.40 (m, 1H), 4.64 (dd, *J* = 12.2, 4.4 Hz, 1H), 3.42 (s, 3H), 3.04 – 2.89 (m, 2H), 2.82 (dd, *J* = 18.4, 4.4 Hz, 1H), 2.30 (s, 3H), 1.97 (dd, *J* = 18.4, 12.2 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 203.0, 169.7, 158.0, 145.0, 126.4, 123.4, 119.2, 110.8, 98.2, 83.1, 78.9, 58.3, 42.6, 40.4, 21.2. (5a*R**, 9*R**, 9a*R**) diastereomer (m.p. = 120°C): **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 2.5 Hz, 1H), 7.09 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.16 (dd, *J* = 4.5, 2.5 Hz, 1H), 4.53 (dd, *J* = 3.7, 2.0 Hz, 1H), 3.37 (s, 3H), 3.13 (dd, *J* = 17.5, 4.5 Hz, 1H), 2.95 (dd, *J* = 17.5, 2.5 Hz, 1H), 2.76 (dd, *J* = 18.4, 3.7 Hz, 1H), 2.29 (s, 3H), 2.05 (dd, *J* = 18.4, 2.0 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 203.7, 169.6, 157.1, 145.2, 126.8, 122.3, 118.7, 111.6, 96.1, 81.6, 80.7, 58.4, 41.6, 38.2, 21.1. **HRMS** (ESI, negative mode) calcd m/z for $C_{13}H_{12}NO_6$ for $[M-C_2H_3O]^-$: 278.0665; Found: 278.0667. **IR** (neat) ν = 1757, 1726, 1618, 1554, 1480, 1178, 499 cm^{-1}.

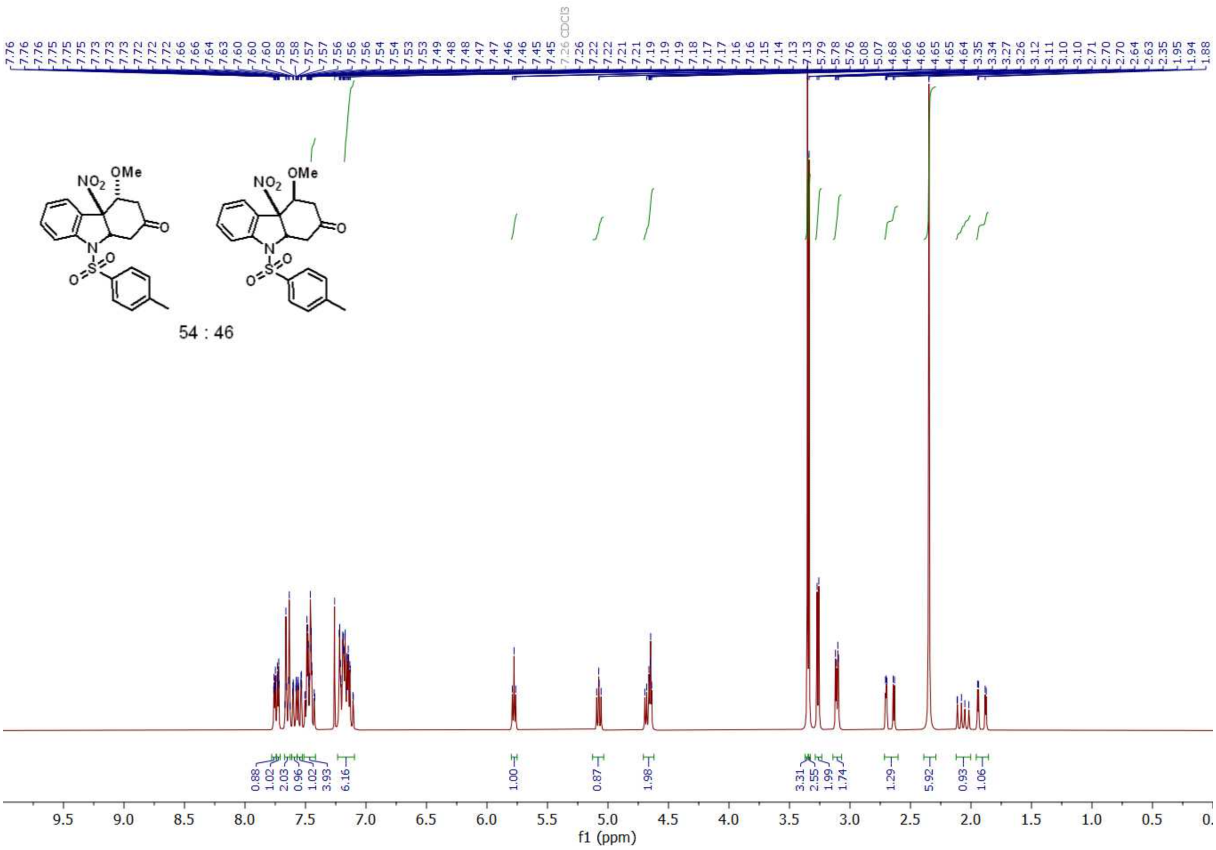
4. NMR spectra

^{1}H NMR spectrum of the addition protonated σ-complex 3ae ($CDCl_3$, 400 MHz)



$^{13}C\{^1H\}$ NMR spectrum of 3ae ($CDCl_3$, 100.6 MHz)

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NO2
OMe
N
S
O
54 : 46
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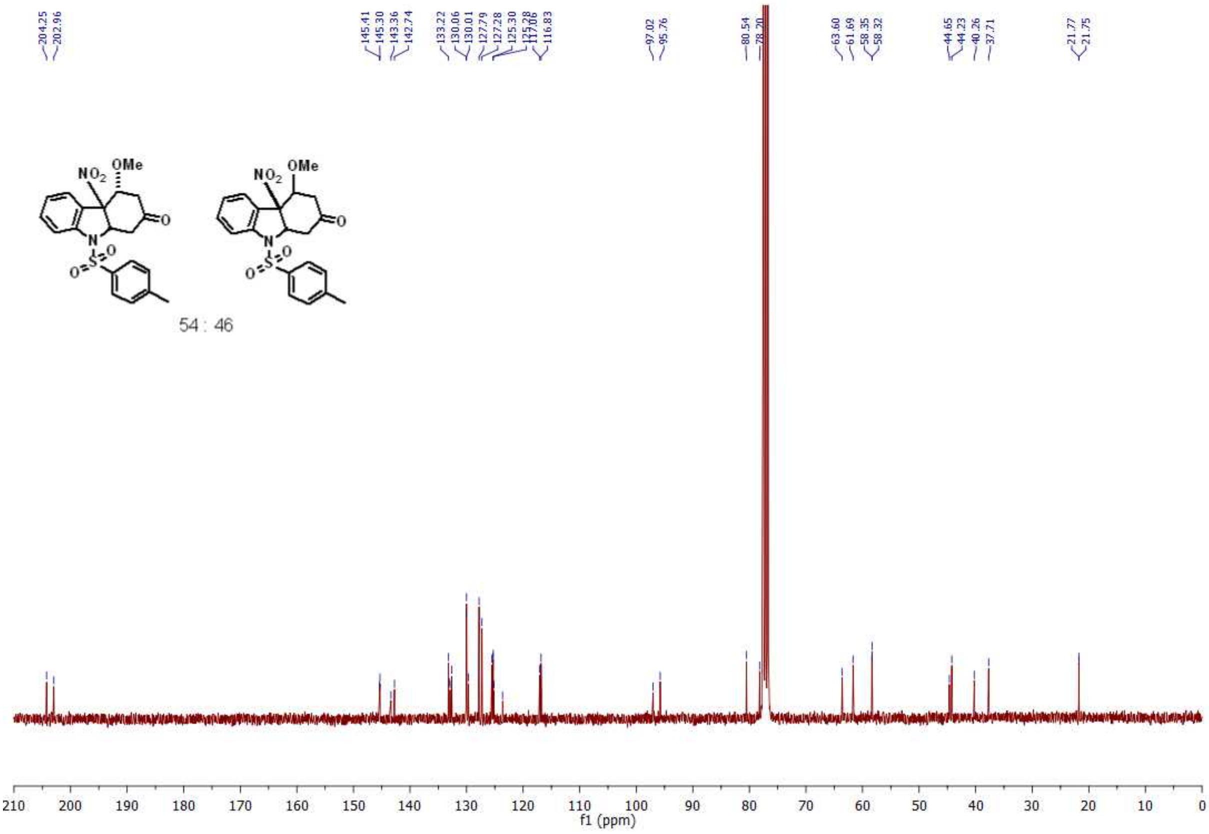
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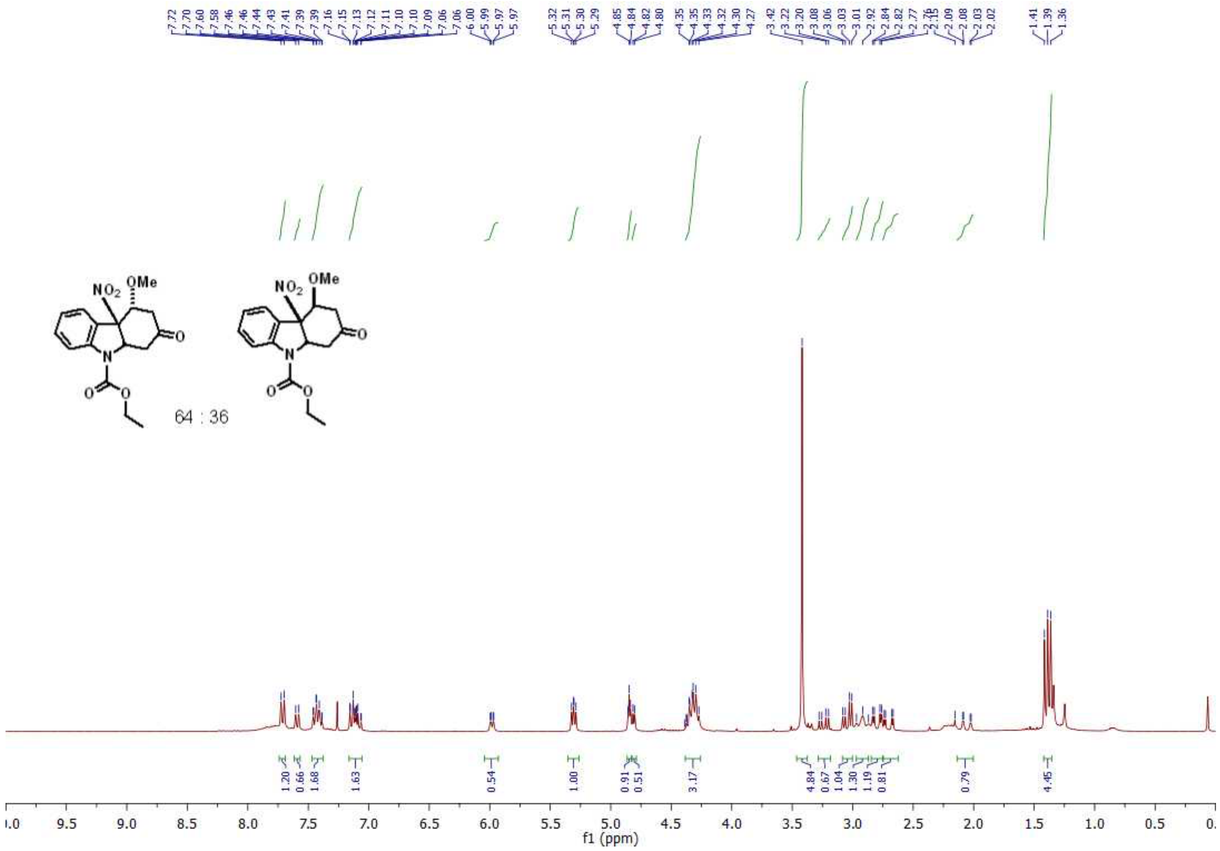
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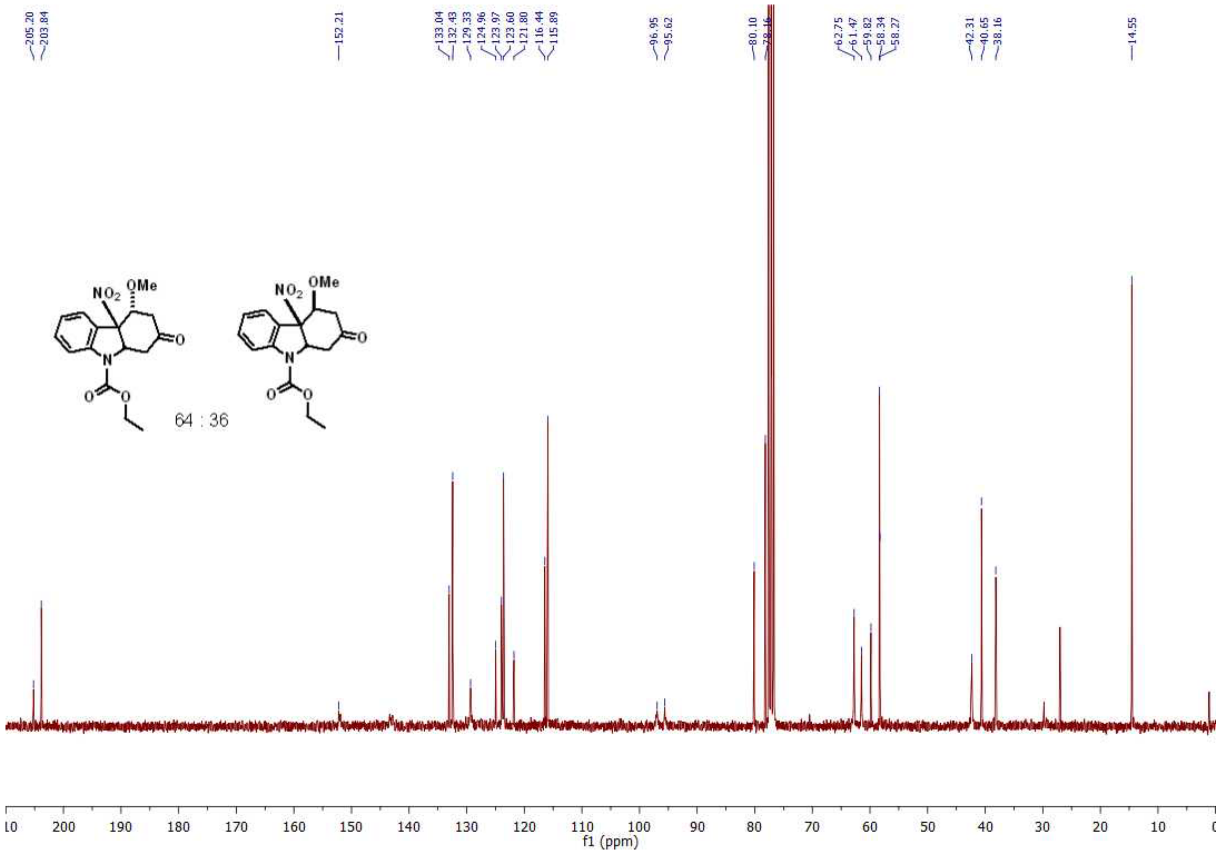
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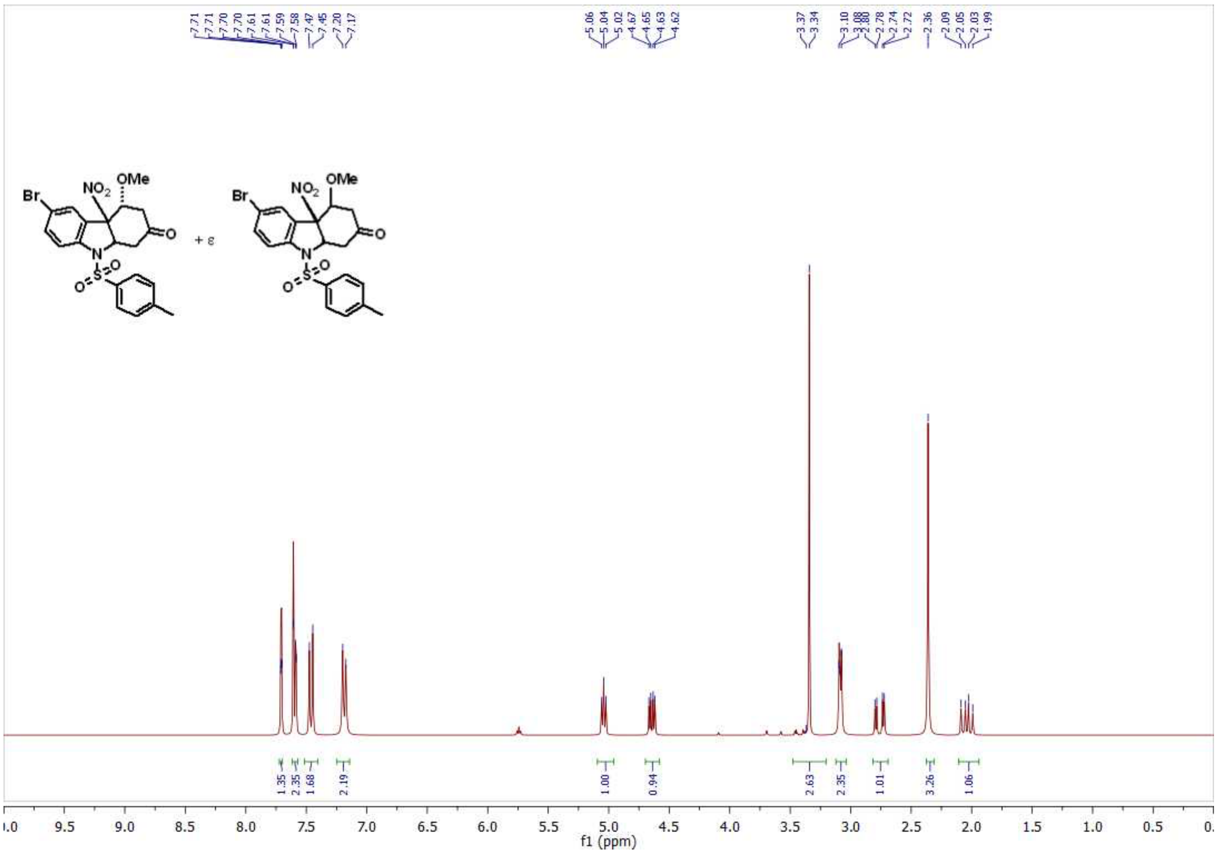
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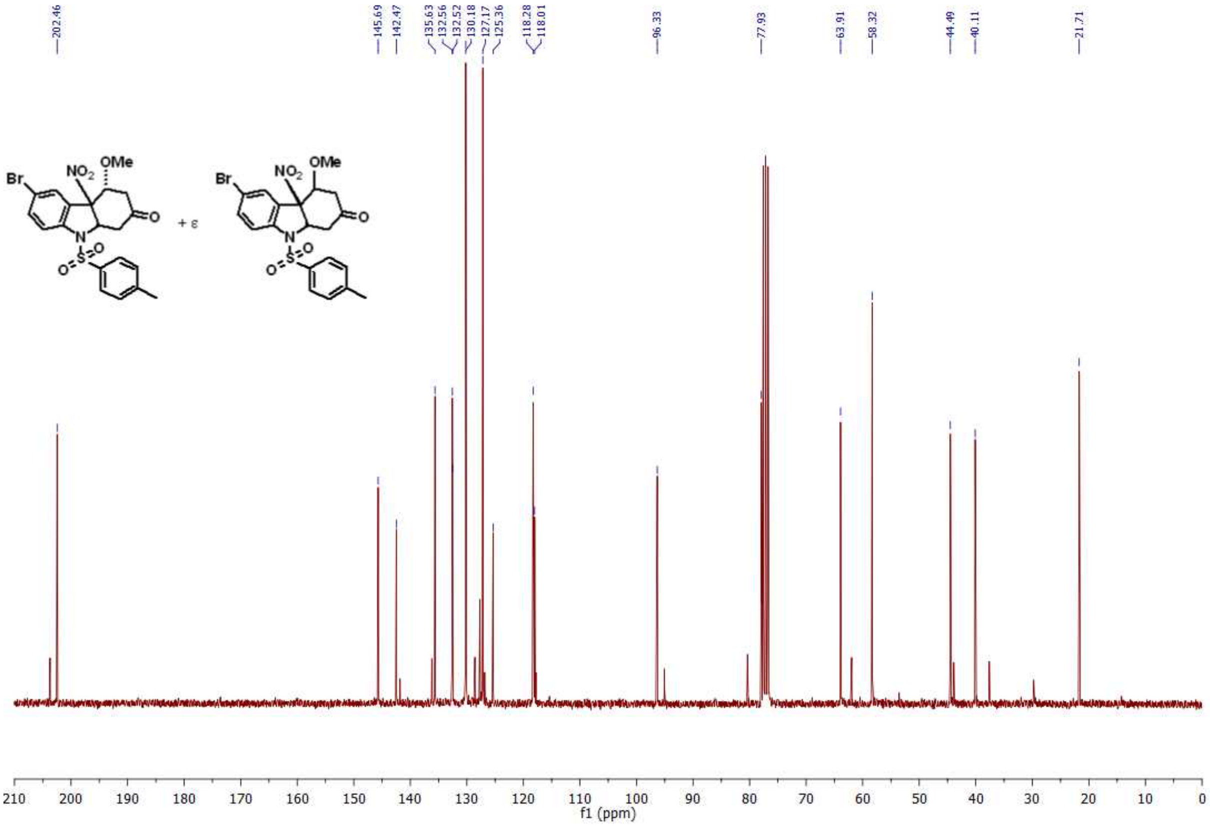
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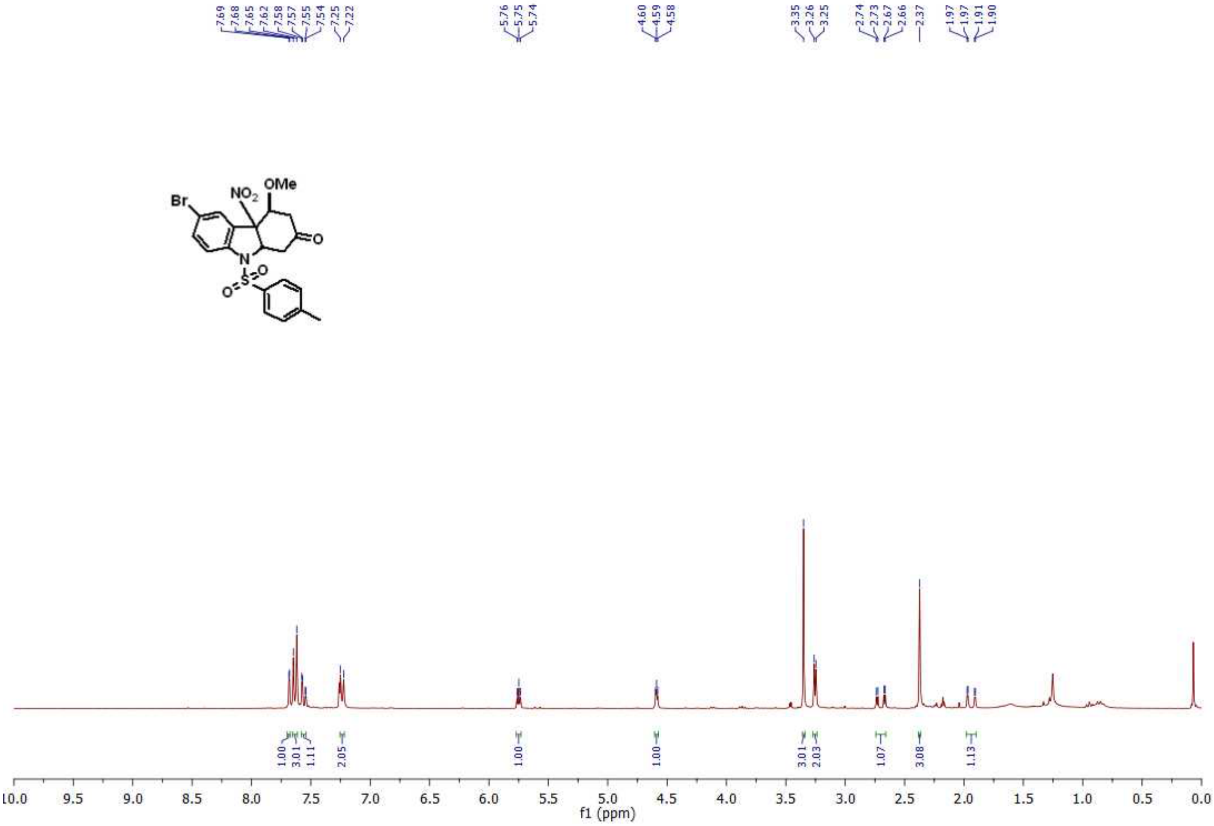
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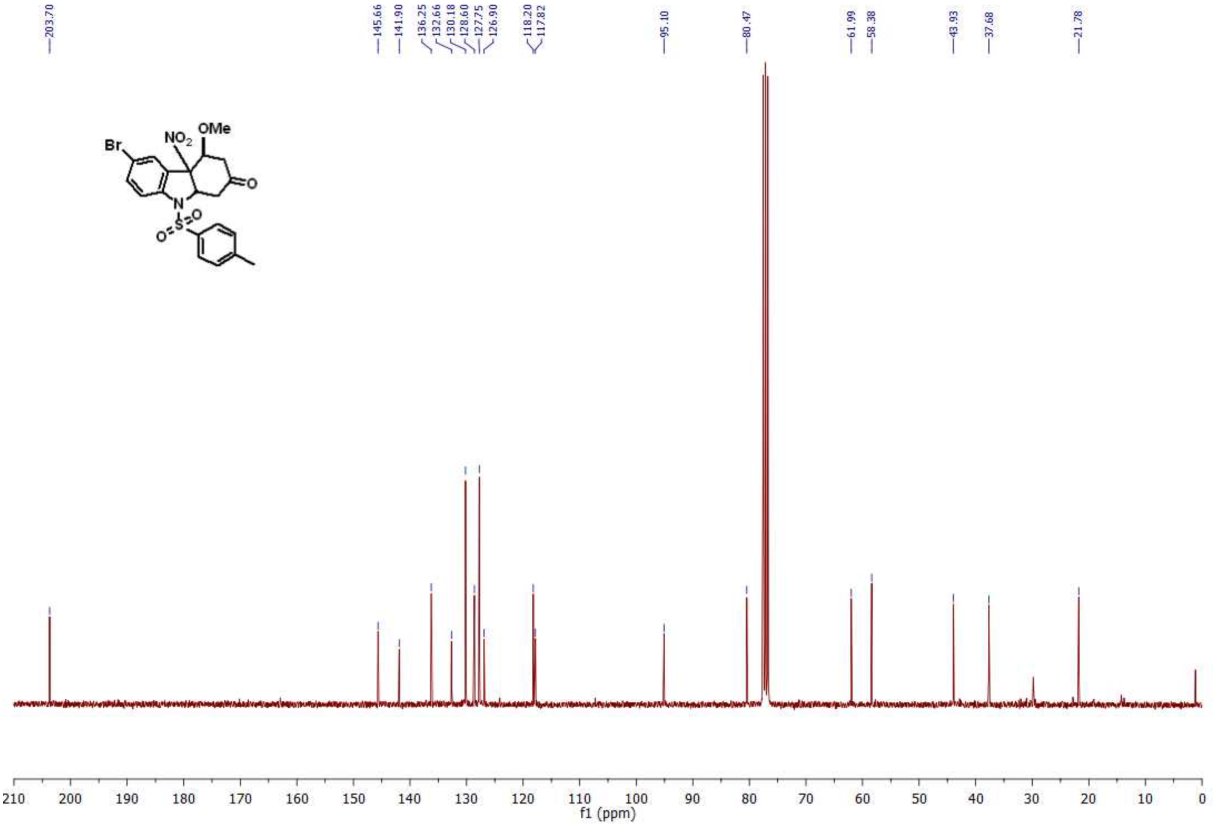
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37.68
21.78
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NO2
OMe
N
S
O
O
O
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200
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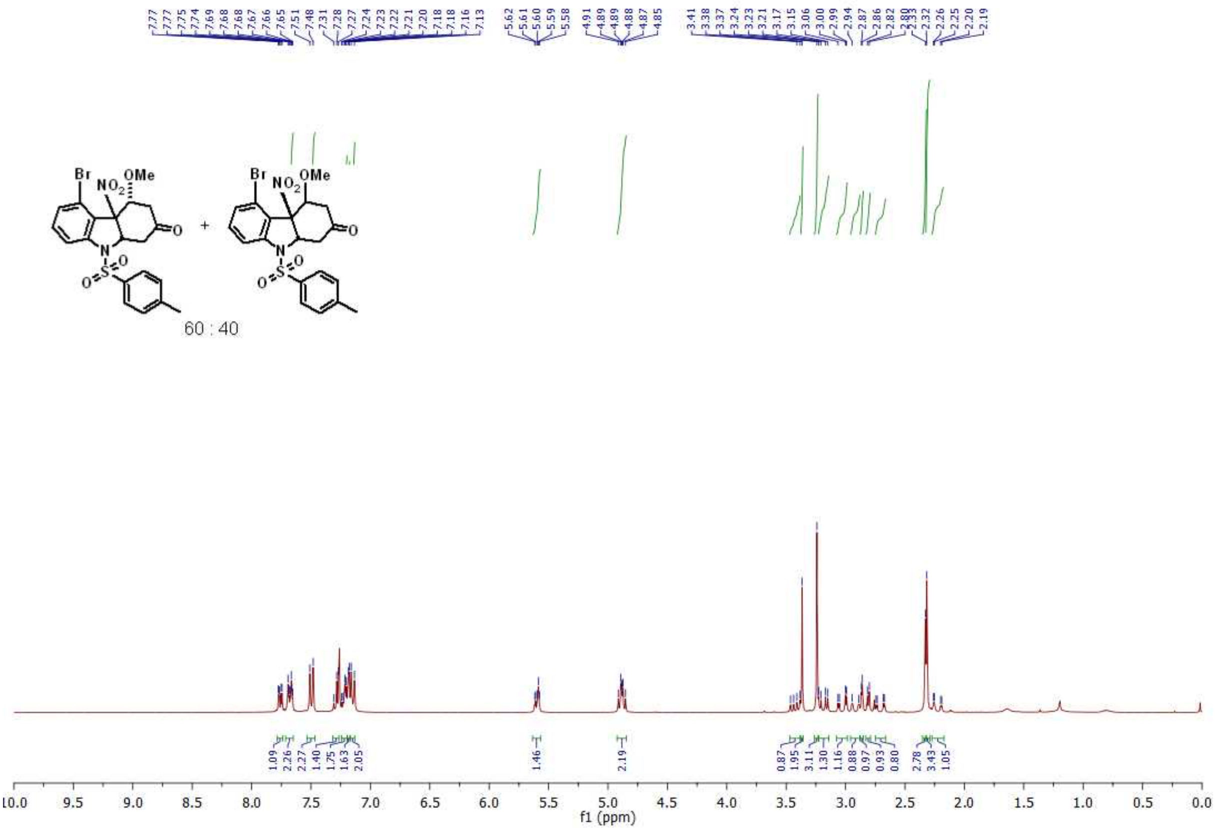
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5.59
5.58
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4.87
4.85
3.41
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3.37
3.24
3.23
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3.17
3.15
3.06
3.00
2.99
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2.86
2.82
2.80
2.33
2.32
2.26
2.25
2.20
2.19
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OMe
O
N
O=S=O
+
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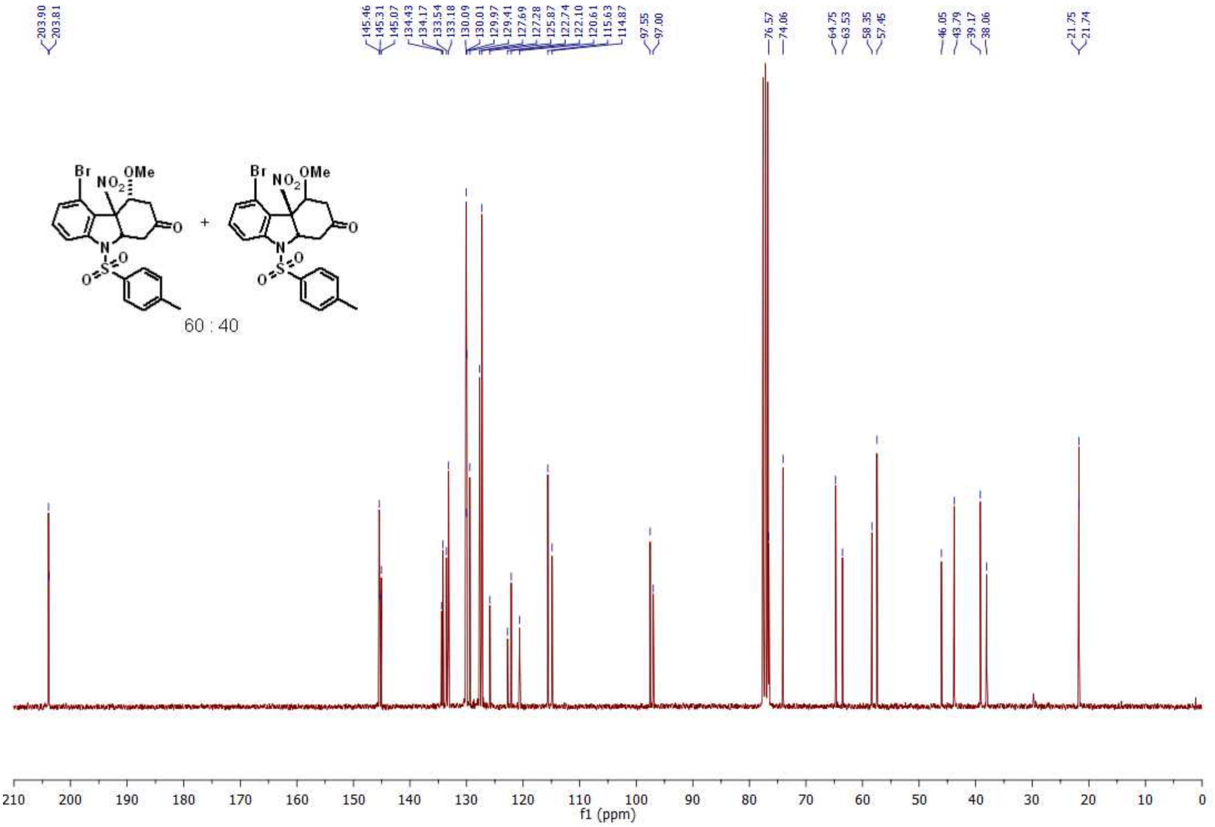
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21.74
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OMe
O
N
O=S=O
+
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200
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180
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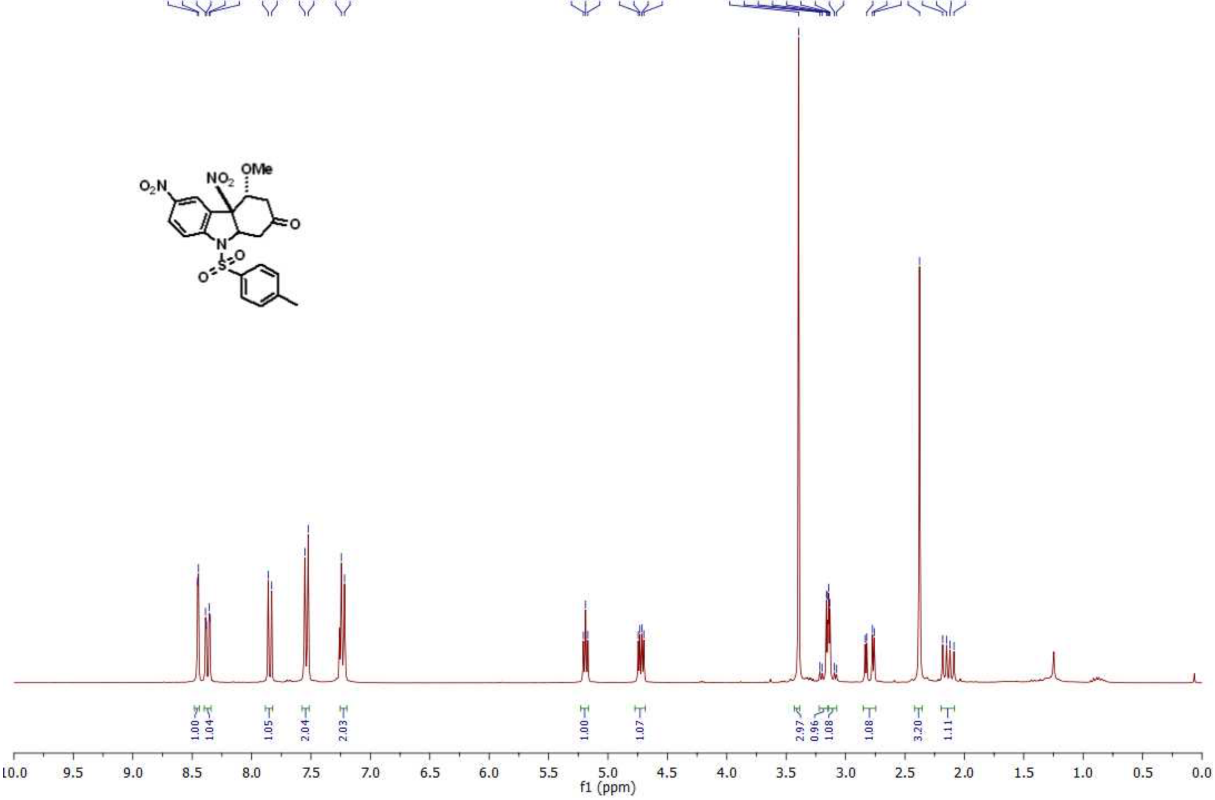
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3.13
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3.08
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2.18
2.15
2.12
2.09
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NO_2
OMe
N
S
O
O
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1.04
1.05
2.04
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1.07
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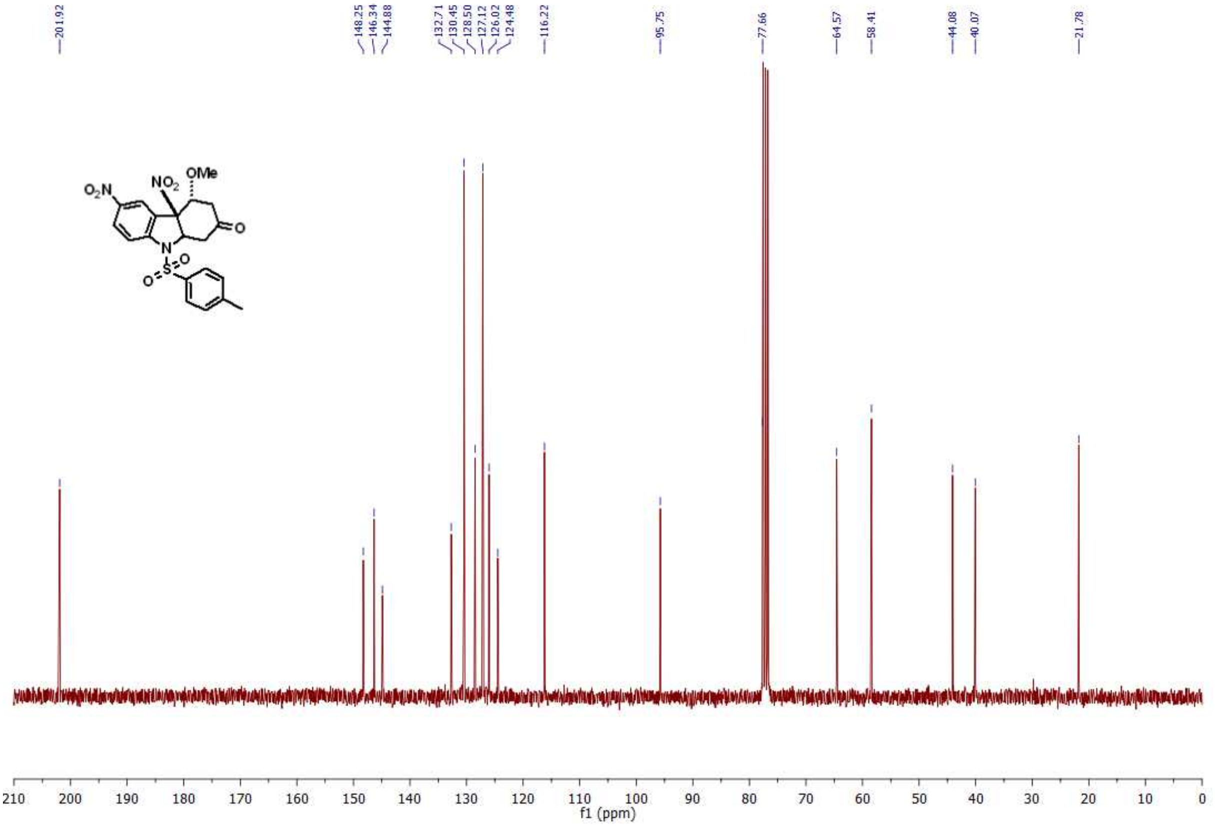
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21.78
O_2N
NO_2
OMe
N
S
O
O
210
200
190
180
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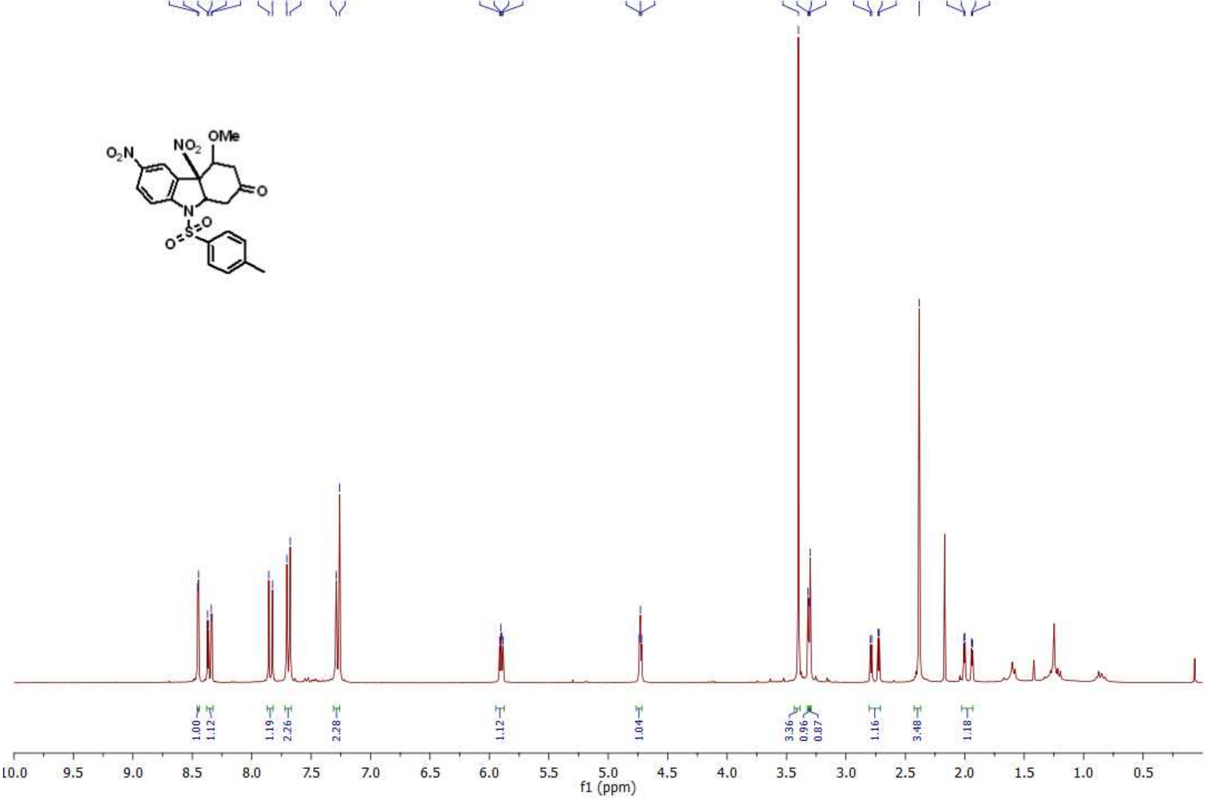
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5.90
5.89
4.74
4.73
4.72
3.40
3.32
3.31
3.30
2.79
2.78
2.73
2.72
2.38
2.01
2.00
1.94
1.93
O_2N
NO_2
OMe
N
S
O
O
1.00
1.12
1.19
2.26
2.28
1.12
1.04
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0.87
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3.48
1.18
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9.0
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8.0
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6.0
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3.0
2.5
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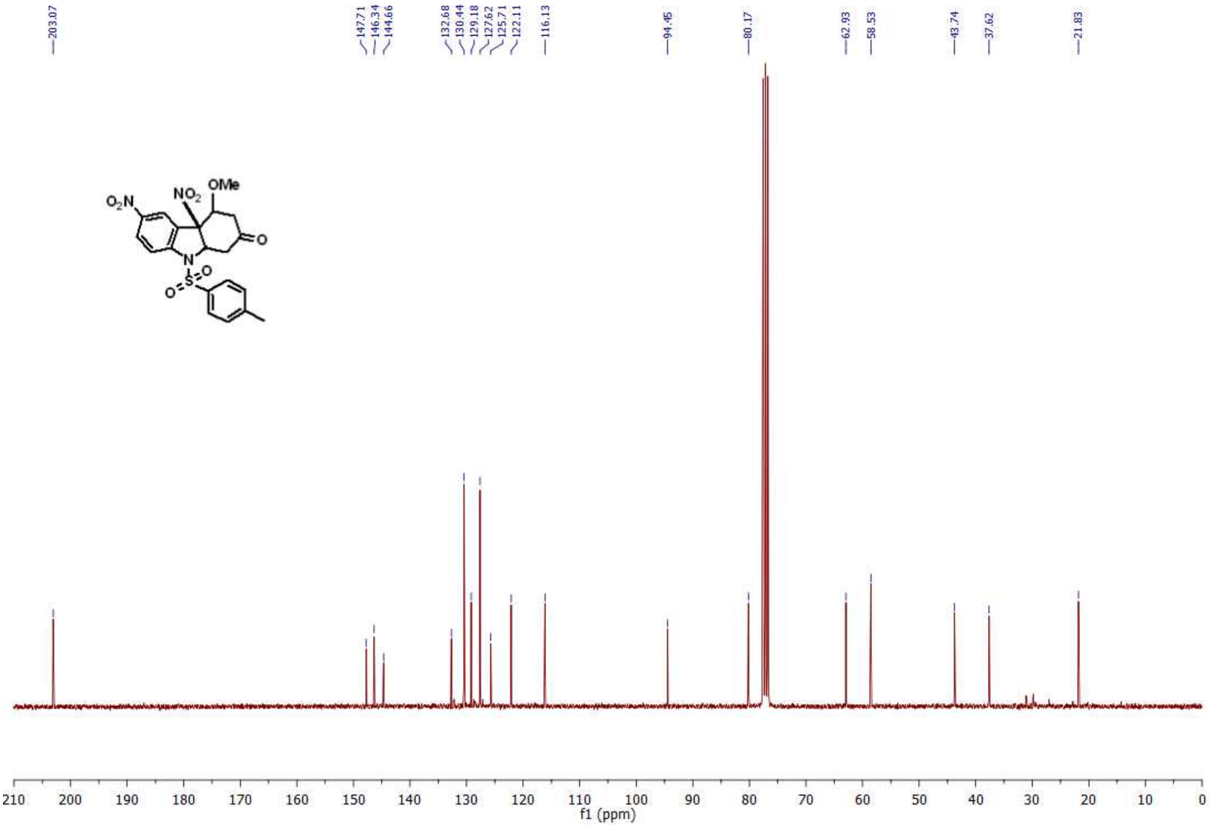
f1 (ppm)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58.53
43.74
37.62
21.83
O_2N
NO_2
OMe
N
S
O
O
210
200
190
180
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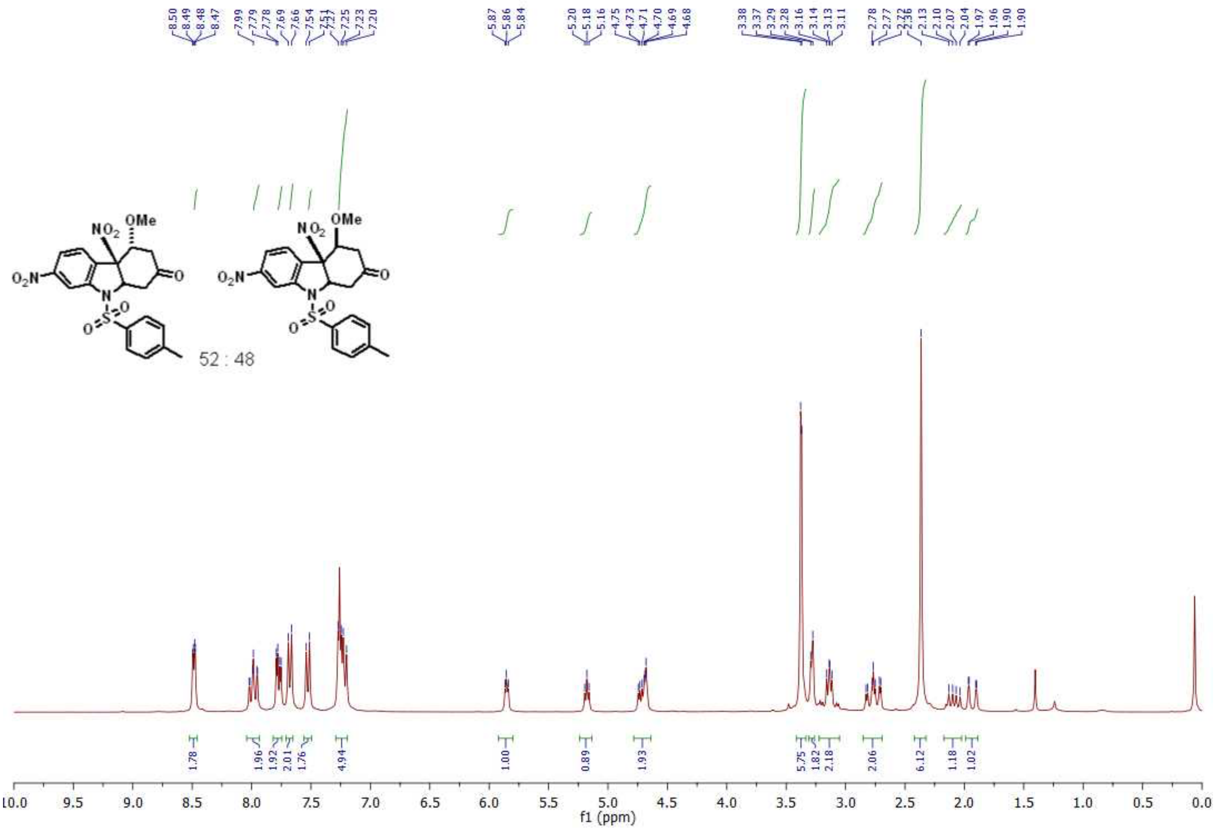
f1 (ppm)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5.18
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4.70
4.69
4.68
3.38
3.37
3.29
3.28
3.16
3.14
3.13
3.11
2.78
2.77
2.72
2.36
2.13
2.10
2.07
2.04
1.97
1.96
1.90
1.90
NO2
OMe
O2N
N
S
O
O
52 : 48
1.78
1.96
1.92
2.01
1.76
4.94
1.00
0.89
1.93
5.75
1.82
2.18
2.06
6.12
1.18
1.02
10.0
9.5
9.0
8.5
8.0
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6.5
6.0
5.5
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3.0
2.5
2.0
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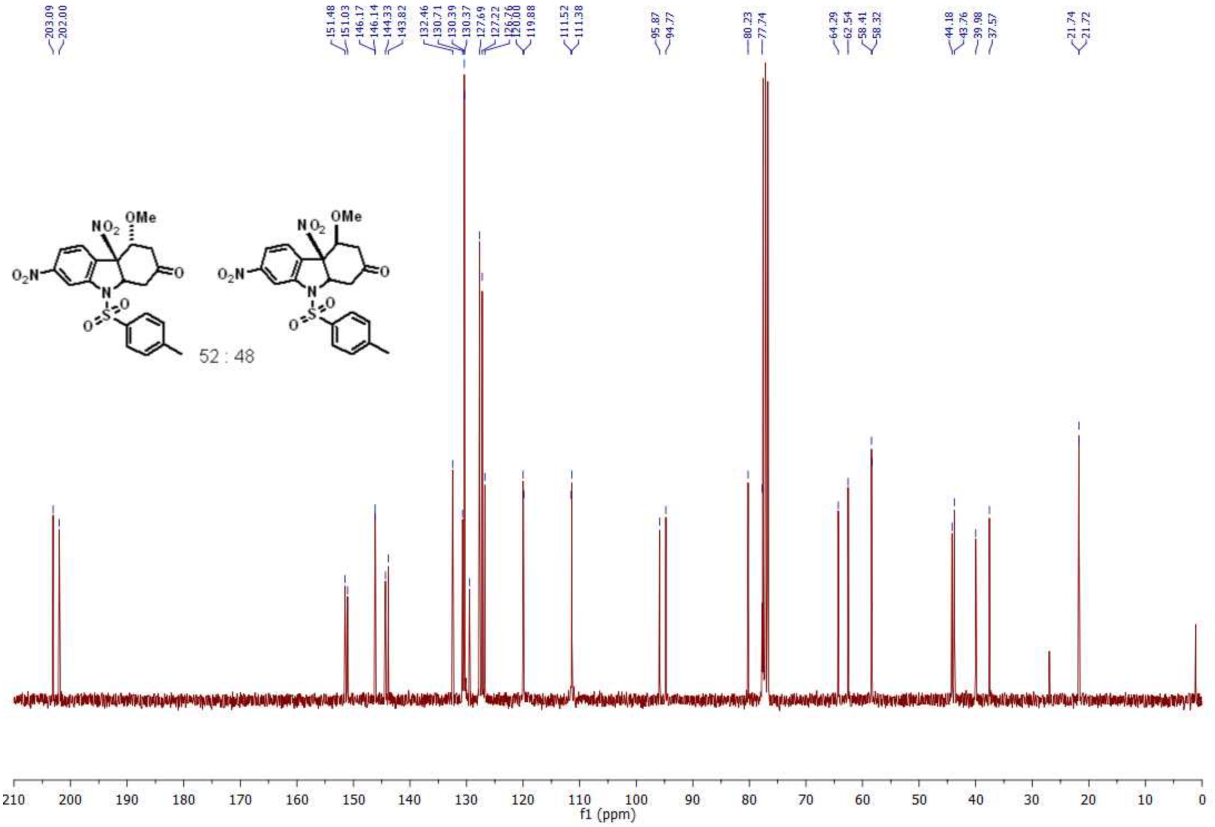
f1 (ppm)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126.76
126.00
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111.38
95.87
94.77
80.23
77.74
64.29
62.54
58.41
58.32
44.18
43.76
39.98
37.57
21.74
21.72
NO2
OMe
O2N
N
S
O
O
52 : 48
210
200
190
180
170
160
150
140
130
120
110
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90
80
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50
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30
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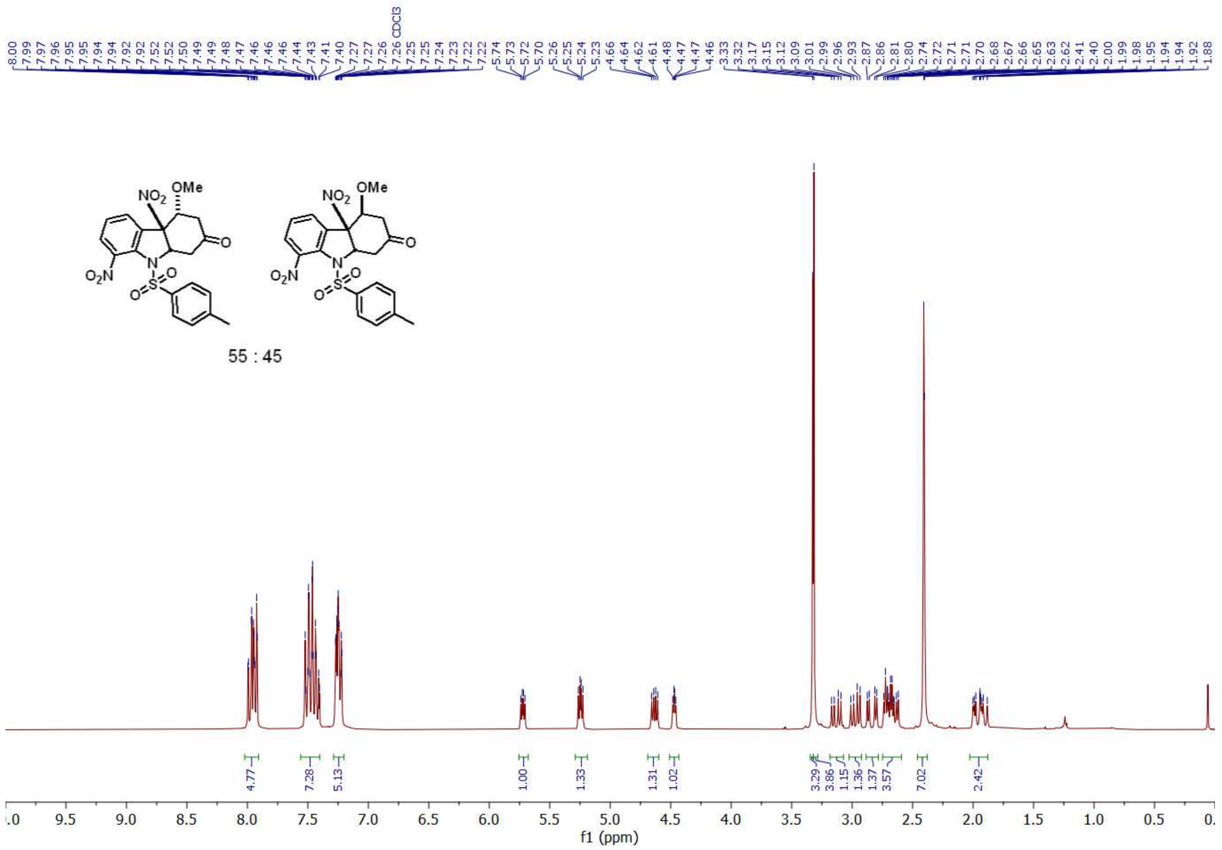
f1 (ppm)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7.49
7.48
7.47
7.46
7.46
7.44
7.43
7.41
7.40
7.27
7.27
7.26 CDCl3
7.25
7.25
7.24
7.23
7.22
7.22
5.74
5.73
5.72
5.70
5.26
5.25
5.24
5.23
4.66
4.64
4.62
4.61
4.48
4.47
4.47
4.46
3.33
3.32
3.17
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2.86
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2.71
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2.40
2.00
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1.94
1.92
1.88
NO2
OMe
O
N
O2N
S
O
O
55 : 45
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1.02
3.29
3.86
1.15
1.36
1.37
3.57
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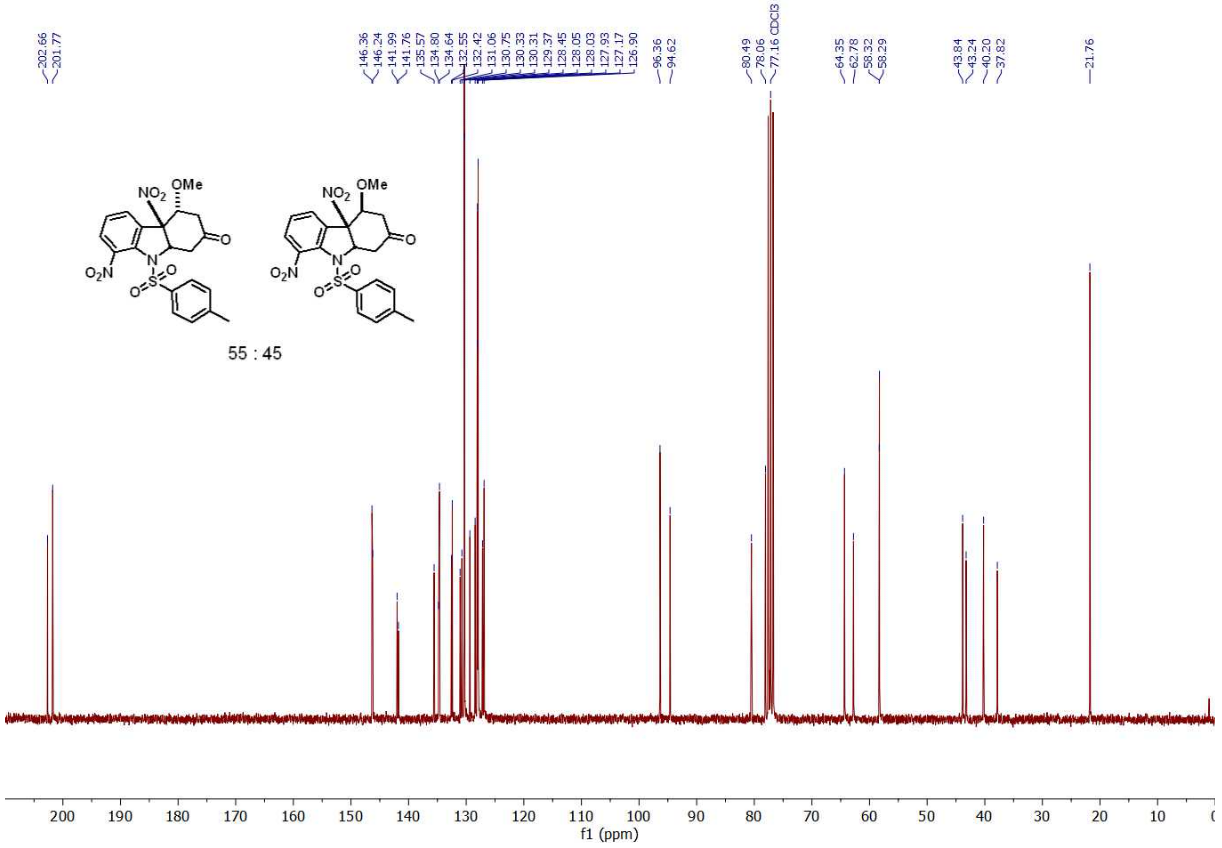
f1 (ppm)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130.33
130.31
129.37
128.45
128.05
128.03
127.93
127.17
126.90
96.36
94.62
80.49
78.06
77.16 CDCl3
64.35
62.78
58.32
58.29
43.84
43.24
40.20
37.82
21.76
NO2
OMe
O
N
O2N
S
O
O
55 : 45
200
190
180
170
160
150
140
130
120
110
100
90
80
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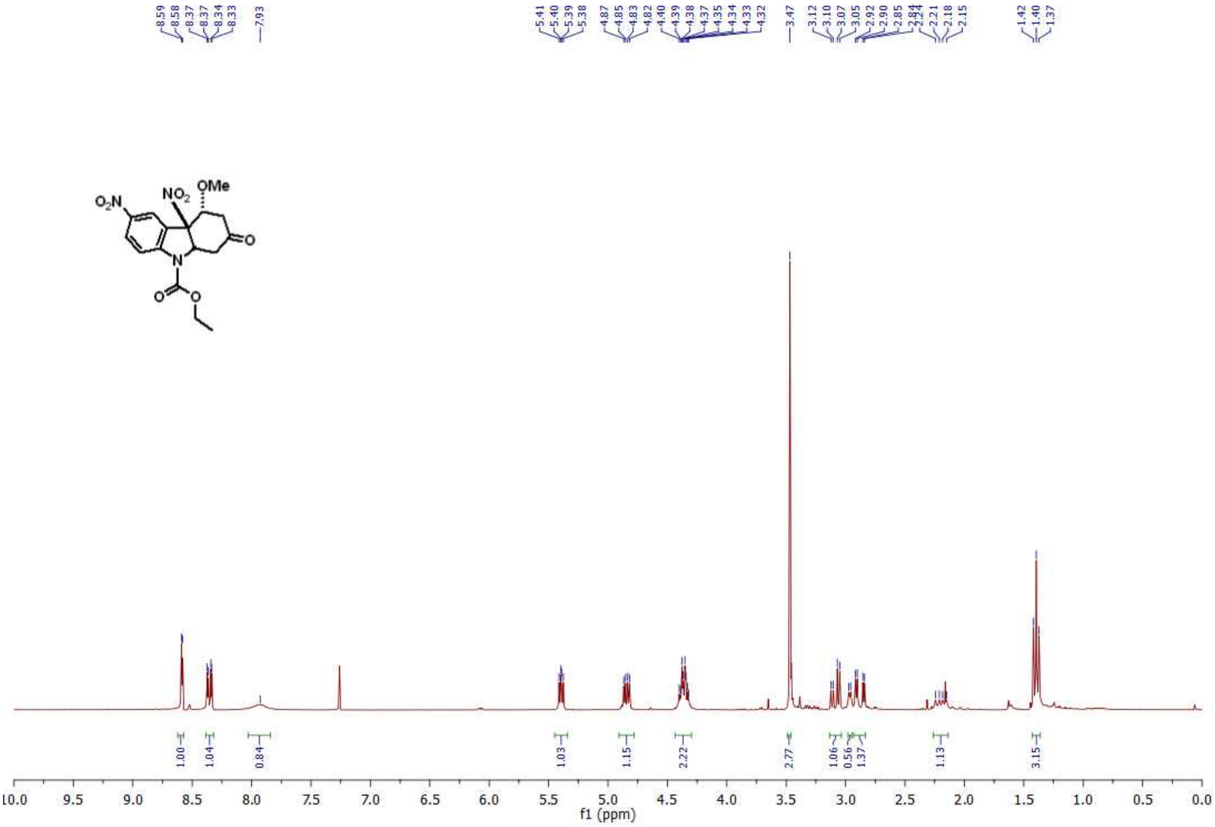
60
50
40
30
20
10
f1 (ppm)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4.85
4.83
4.82
4.40
4.39
4.38
4.37
4.35
4.34
4.33
4.32
3.47
3.12
3.10
3.07
3.05
2.92
2.90
2.85
2.84
2.24
2.21
2.18
2.15
1.42
1.40
1.37
O$_2$N
NO$_2$
OMe
N
O
1.00
1.04
0.84
1.03
1.15
2.22
2.77
1.06
0.56
1.37
1.13
3.15
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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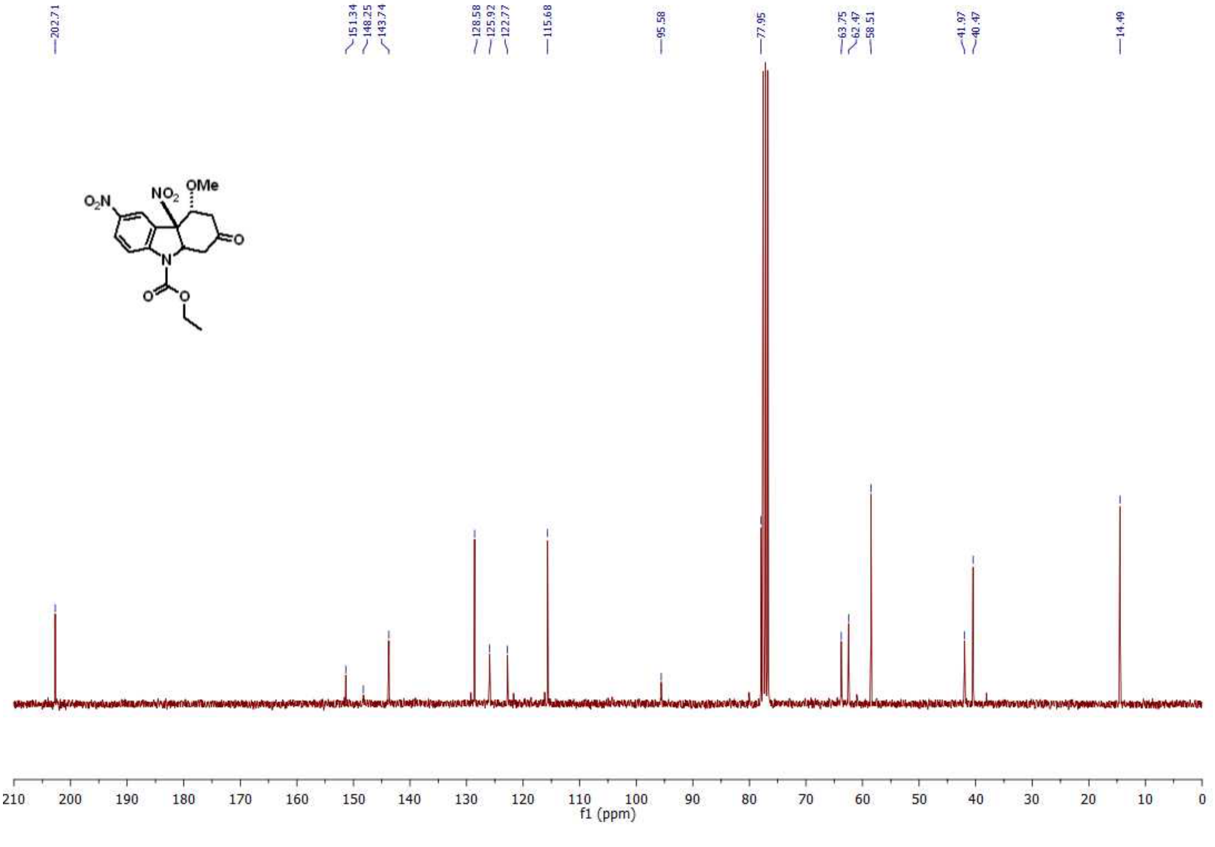
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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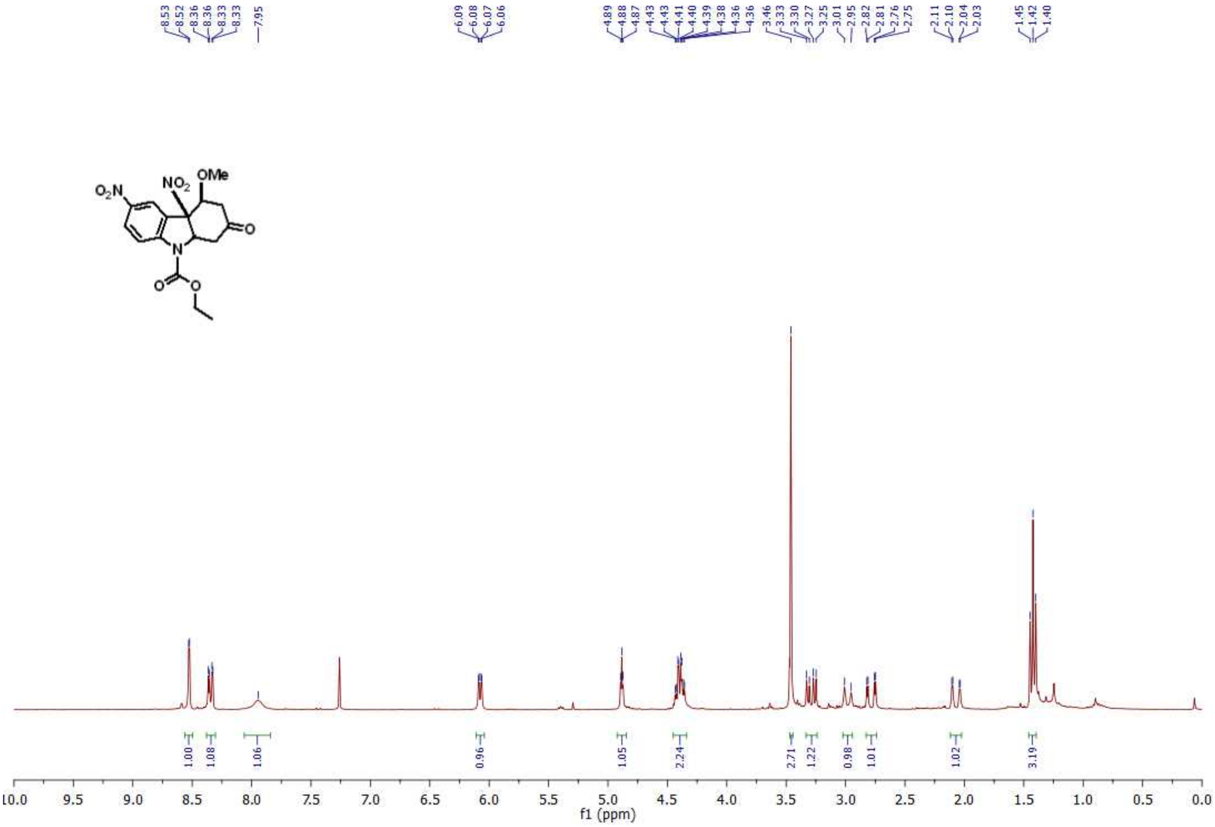
77.95
63.75
62.47
58.51
41.97
40.47
14.49
O$_2$N
NO$_2$
OMe
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.06
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4.88
4.87
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4.43
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4.40
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4.36
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3.30
3.27
3.25
3.01
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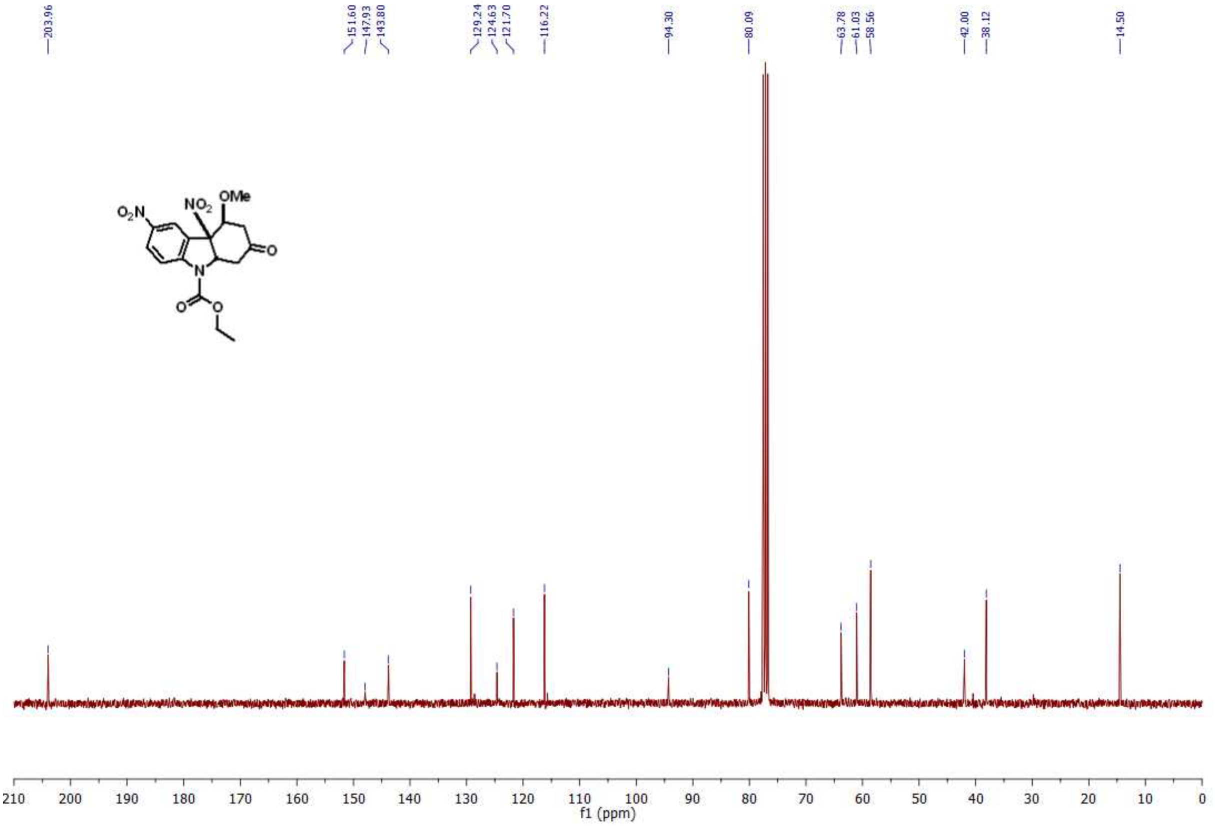
2.82
2.81
2.76
2.75
2.11
2.10
2.04
2.03
1.45
1.42
1.40
O$_2$N
NO$_2$
OMe
N
O
O
O
1.00
1.08
1.06
0.96
1.05
2.24
2.71
1.22
0.98
1.01
1.02
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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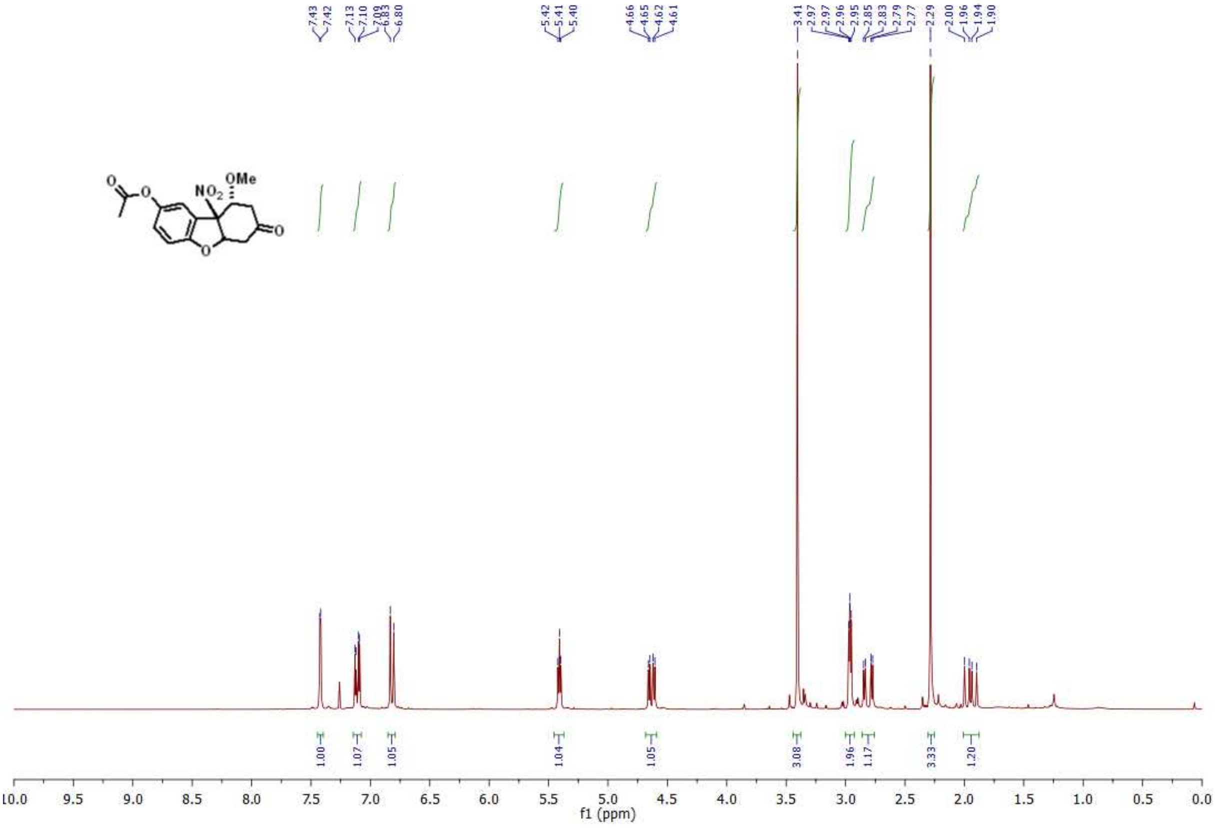
63.78
61.03
58.56
42.00
38.12
14.50
O$_2$N
NO$_2$
OMe
N
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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4.62
4.61
3.41
2.97
2.97
2.96
2.95
2.85
2.83
2.79
2.77
2.29
2.00
1.96
1.94
1.90
OMe
NO2
O
1.00
1.07
1.05
1.04
1.05
3.08
1.96
1.17
3.33
1.20
10.0
9.5
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
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1.0
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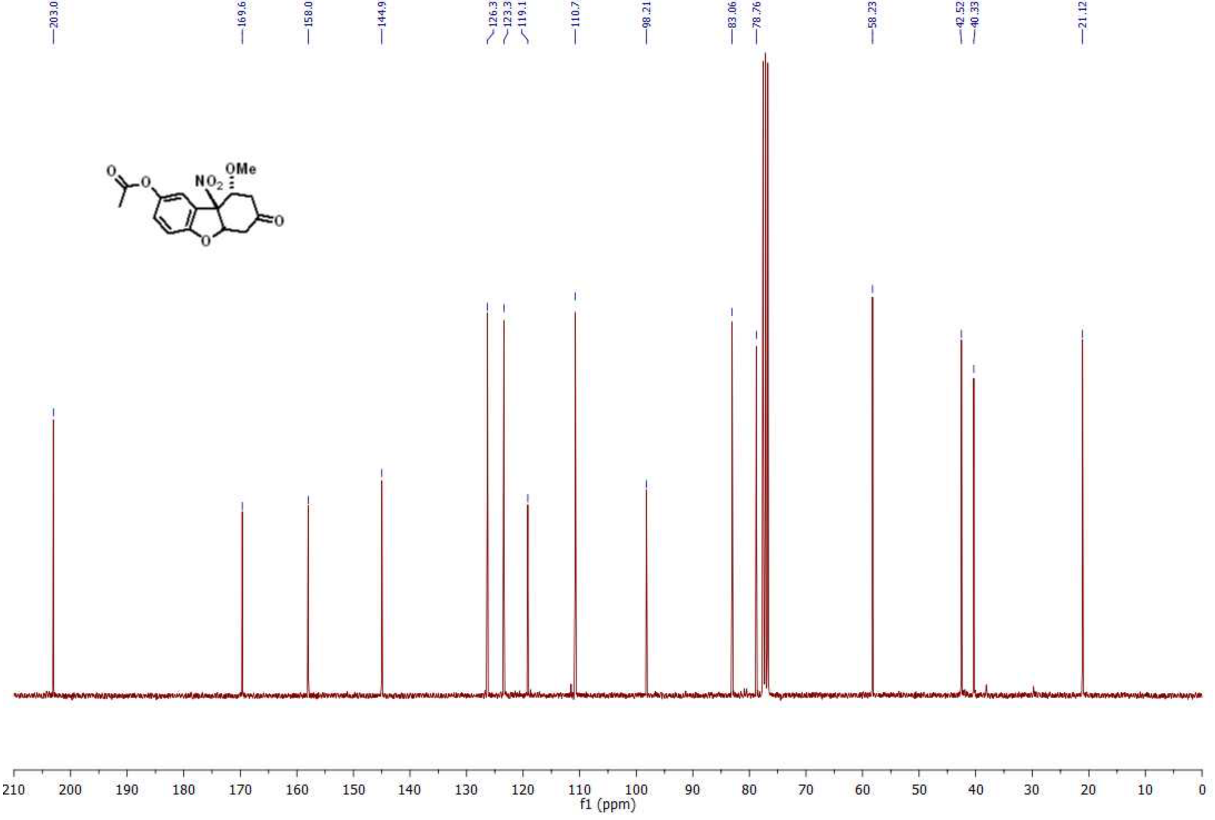
f1 (ppm)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42.52
40.33
21.12
OMe
NO2
O
210
200
190
180
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90
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40
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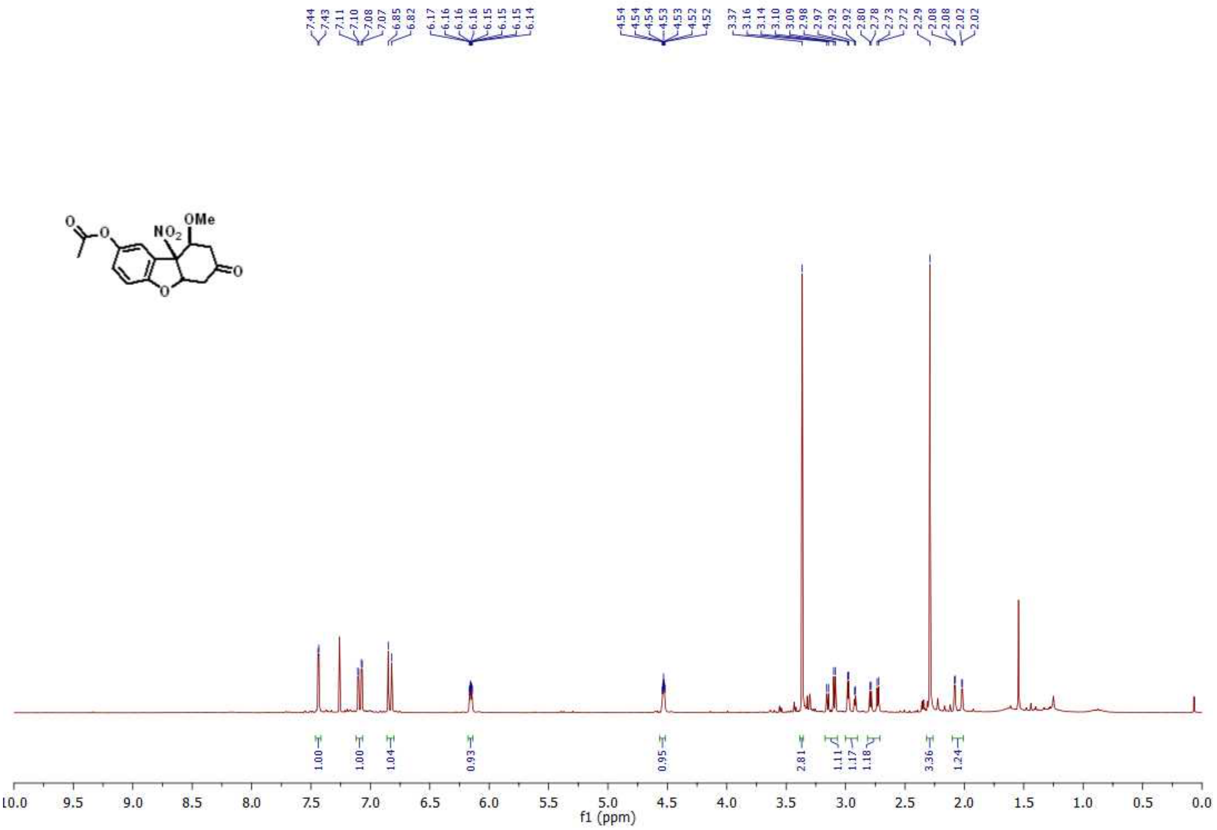
0
f1 (ppm)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6.15
6.14
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4.54
4.54
4.53
4.53
4.52
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3.14
3.10
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2.92
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2.72
2.29
2.08
2.08
2.02
2.02
1.00
1.00
1.04
0.93
0.95
2.81
1.11
1.17
1.18
3.36
1.24
NO2
OMe
O
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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2.0
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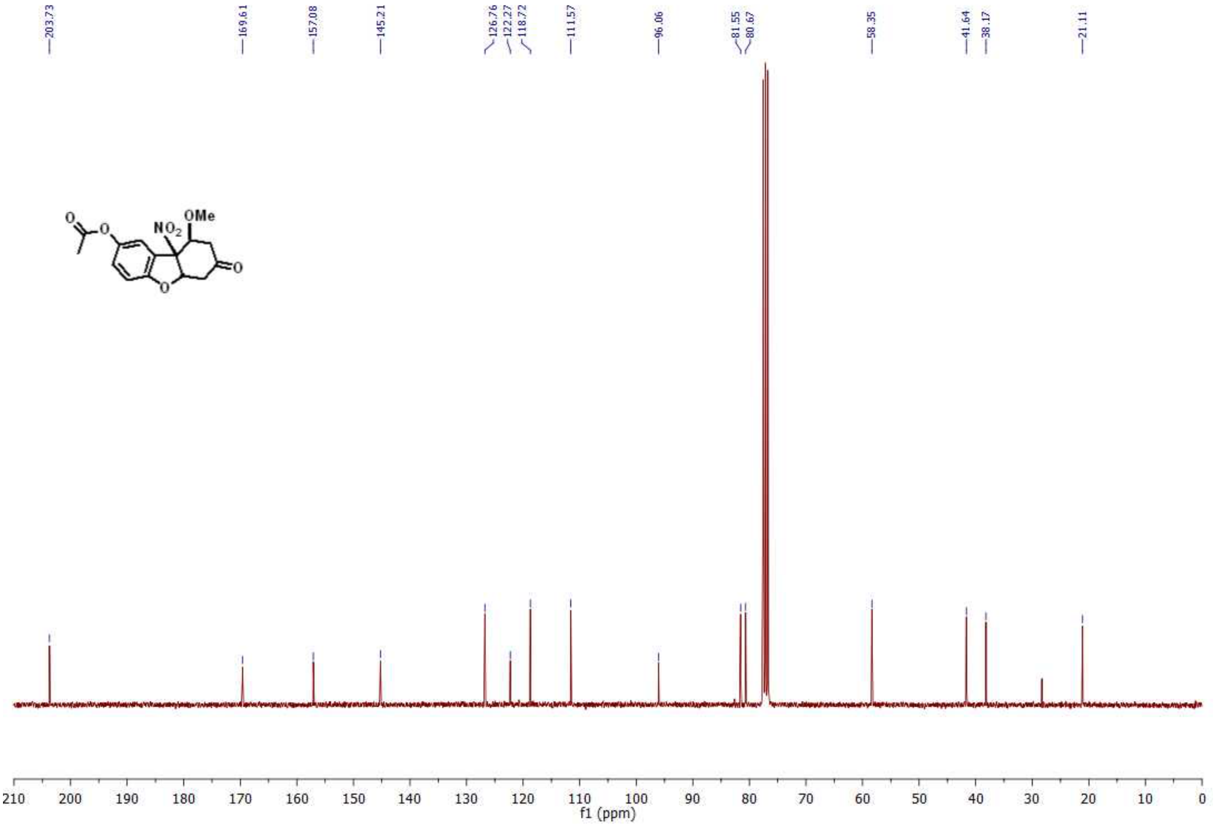
0.0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80.67
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41.64
38.17
21.11
NO2
OMe
O
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

5 Computations

Computational Details

Computations were run by using the Gaussian 09, Revision D.01, set of programs.[4] Full geometry optimizations were carried out in the absence of symmetry constraints at the M062X/6-31+G(d,p) level of theory,[5,6] considering a polarized continuum (SMD:DCM) to mimic the experimental solvent effects,[7] a level which had proven adequate in previous related calculations. Single points calculations were then run on the optimized geometries, using the same functional and def2TZVPP basis set. The nature of the minima (or TS) were checked by harmonic frequency evaluations to show the presence of no (or one and only one) imaginary frequencies. The connectivity between reactants and products was confirmed by IRC calculations and computing force constants at every step. After the IRC calculations, all adducts were optimized. The harmonic frequencies were used unscaled for the evaluation of the thermodynamic data of the reaction. They were computed by using the standard Gaussian values (T = 298.15 K and P = 1 atm). The activation/reaction Gibbs free energies were computed as the difference between the separated reactants and the TS/products.

Energy profiles

Calculations involved a *N*-methylsulfonyl-3-nitroindole derivative as model substrate, very close to the experimentally used *N*-tosyl substrate, and 1-methoxy-3-trimethylsilyloxybutadiene.

Two approaches (*endo* and *exo*) and four conformations for each were considered (rotation around the OMe and O-TMS bonds) for the diene in its s-cis conformation. Considering these 8 approaches with the s-cis diene, single points calculations for the most favoured path for the *endo* and *exo* approaches, leading to the *trans* and *cis* cycloadducts respectively, were then effected at the M062X/def2TZVPP (SMD:DCM). The values are depicted on Figure below. In

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[4] 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. Men- nucci, 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. Ko- bayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyen- gar, 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cio- slowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[5] Y. Zhao and D. G. Truhlar, "The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals," *Theor. Chem. Acc.*, **120** (2008) 215-41.

[6] A. V. Marenich, C. J. Cramer, and D. G. Truhlar, "Universal solvation model based on solute electron density and a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions," *J. Phys. Chem. B*, **113** (2009) 6378-96

[7] J. Ho and M. Z. Ertem, *J. Phys. Chem. B*, 2016, **120**, 1319–1329.

order to confirm the choice of the smaller *N*-methylsulfonyl indole substrate model, the endo/exo most favoured transition states of the process were compared for the *N*-Ms and *N*-Ts substrates, at the SMD-M062X/631G(d) level and confirmed the small influence of the sulfonamide group on both the barriers ($\Delta\Delta G^{\ddagger} \leq 0.6$ kcal.mol^{-1}) and the endo/exo activation energy difference ($\Delta\Delta G^{\ddagger} \leq 0.2$ kcal.mol^{-1}).

A stepwise mechanism was calculated for this cycloaddition process, involving the formation of a zwitterionic primary adduct (**PA**) in the first step and the cyclisation via a Michael addition to generate the cycloadduct (**CA**) in the second. Considering the very low energy barrier for the cyclization step compared to the first step (0.2-3.4 kcal.mol^{-1} compared to 23.4 and 23.2 kcal.mol^{-1}), this can be considered as an inflection point of the potential energy surface and the cycloaddition as *pseudo*-concerted pathway. The differences between the *endo* and *exo* approaches for the rate determining step is very small ($\Delta\Delta G^{\ddagger}$ = 0.2 kcal.mol^{-1}), in line with the experimental data (d.r. between 1:1 and 2:1). This lack of selectivity can be interpreted as a balance of steric effects and stabilising interactions, especially with the aromatic part of the indole ring.

Surprisingly, when considering a *s*-trans conformation for the diene in the first addition step (2 geometries considered for the *pseudo*-“endo” and “exo” approaches), more demanding processes were computed at the M062X/6-31+G(d,p) (SMD : DCM) level ($\Delta\Delta G^{\ddagger} \geq 2.7$ kcal. mol^{-1} for the “endo” approach, and $\Delta\Delta G^{\ddagger} \geq 1.5$ kcal.mol^{-1} for the “exo” approach).

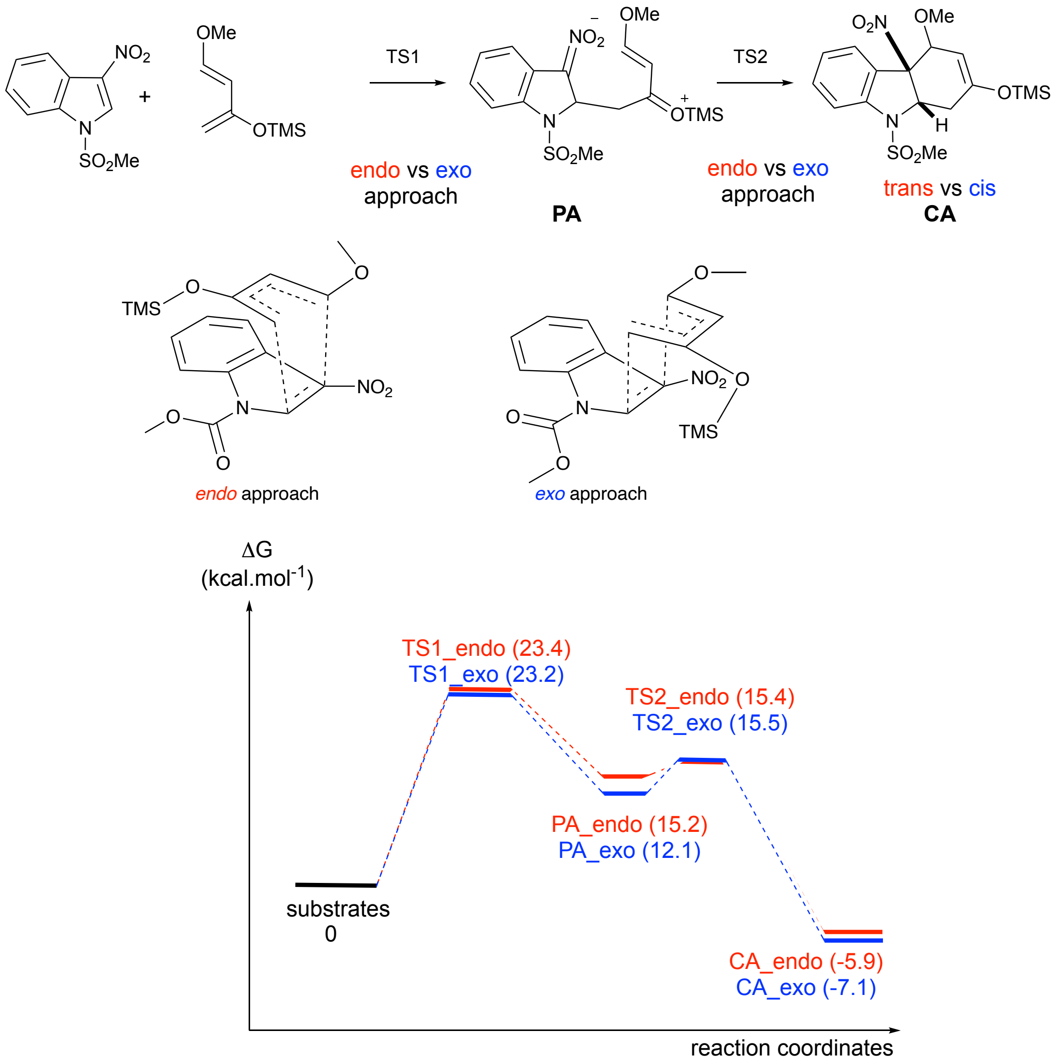
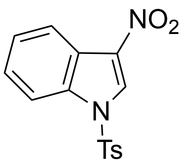


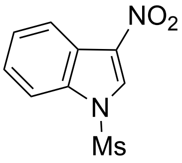
Figure: Energy profiles for the cycloaddition of *N*-methylsulfonyl-3-nitroindole with diene **4**; *endo* approach (red); *exo* approach (blue).

In order to confirm the choice of the smaller *N*-methylsulfonyl indole substrate model, the influence of the *N*-Ts vs *N*-Ms indole substituent was evaluated (Table below, substrates **A** and **B**), at the SMD-M062X/631G(d) level. As the first step of the process proved to be the determining one, we compared the first TSs for both the *endo* and *exo* approaches (considering the most favoured geometries calculated above as starting geometries). This confirmed the small influence of the sulfonamide group on both the barriers ($\Delta\Delta G^{\ddagger} \leq 0.6$ kcal.mol^{-1}) and endo/exo activation energy difference ($\Delta\Delta G^{\ddagger} \leq 0.2$ kcal.mol^{-1}) and validated the choice of the smaller NMs substrates in the calculations.

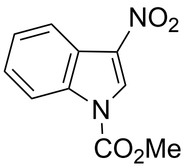
We also checked the influence of the other substituents. Thus, TS1 for the *endo* and *exo* approaches were compared for the sulfonamide and carbamate indoles **B**-**E** depicted below, bearing either no or a 1-methoxycarbonyl, a 4-bromo or a 6-nitro substituent (close models for **1a**-**1d**), at the SMD-M062X/631G(d) level. This confirmed the small influence of the substituents on the *endo*/*exo* activation energy difference ($\Delta\Delta G^{\ddagger} \leq 0.1$ kcal.mol^{-1}), whatever the substituent, in line with the low diastereoselectivities of the (4+2) cycloaddition reactions. The 4-bromo and 6-nitroindoles have similar activation energies, slightly lower than the non-substituted one and the N-carbamate.



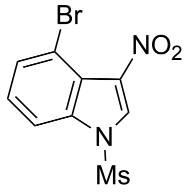
A



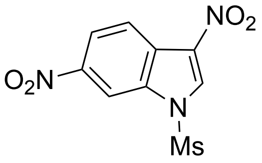
B



C



D



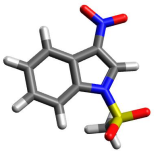
E

Entry	Indoles	TS1-endo	TS1-exo
1	**A**	17.7	17.8
2	**B**	17.2	17.2
3	**C**	18.3	18.3
4	**D**	14.7	14.8
5	**E**	15.0	15.0

Total energy and cartesina coordinates:

- N-Methylsulfonyl-3-nitro-1*H*-indole

Electronic Energy = -1156.269562 a.u.
Sum of electronic and thermal free energies = -1156.137335 a.u.
Number of imaginary frequencies: 0

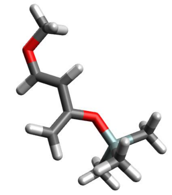


C	-2.82644	-1.00991	2.23161
C	-2.64548	0.33370	2.41048
C	-1.26416	0.60098	2.72161
C	-0.63083	-0.65944	2.71135
N	-1.61138	-1.61909	2.39986
N	-3.69909	1.28441	2.29874
O	-4.82031	0.88419	2.00837
O	-3.42284	2.46009	2.50488
H	-3.71741	-1.57377	1.99144
C	-0.51232	1.75124	3.00076
C	0.84069	1.59904	3.26626
C	1.45278	0.33253	3.25473
C	0.73084	-0.81967	2.97452
H	1.20736	-1.79316	2.94804
H	2.51479	0.25117	3.46326
H	1.44105	2.47592	3.48687
H	-0.98196	2.72755	3.00784
S	-1.40945	-3.31969	2.42663
O	-0.11308	-3.58042	1.82988
O	-2.62525	-3.84797	1.83531
C	-1.36198	-3.67780	4.15922
H	-1.23283	-4.75952	4.25001
H	-0.51333	-3.14894	4.59769
H	-2.30849	-3.35717	4.59763

- (*Z*)-((4-methoxybuta-1,3-dien-2-yl)oxy)trimethylsilane

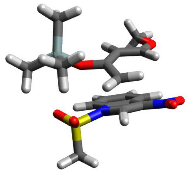
Electronic Energy = -754.433898 a.u.
Sum of electronic and thermal free energies = -754.248600 a.u.
Number of imaginary frequencies: 0

C	-0.30361	-0.23180	0.19132
C	-0.13681	-0.15666	1.52340
O	1.03785	0.17288	2.12891
Si	2.59307	0.27193	1.45275
C	-1.19372	-0.42097	2.51515
C	-2.47579	-0.09906	2.28167
H	0.48303	0.03587	-0.50543
H	-1.24877	-0.56920	-0.21682
H	-0.87235	-0.85323	3.45777
O	-3.52989	-0.31206	3.09181
H	-2.78642	0.39819	1.36602
C	3.68154	0.51004	2.94871
C	3.00255	-1.32324	0.56285
C	2.71604	1.75077	0.31051
C	-3.26975	-0.95839	4.33098
H	-4.23449	-1.06946	4.82548
H	-2.82061	-1.94422	4.16693
H	-2.60390	-0.34894	4.95205
H	4.73352	0.58885	2.65221
H	3.41316	1.42491	3.48775
H	3.58874	-0.33205	3.64287
H	4.07458	-1.34568	0.33327
H	2.77636	-2.19116	1.19204
H	2.45696	-1.43195	-0.37911
H	3.77012	1.95321	0.08567
H	2.19637	1.60097	-0.64085
H	2.30135	2.64540	0.78828



- TS1 *endo* approach

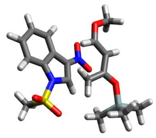
Electronic Energy = -1910.691030 a.u. ($\Delta Ee^{\ddagger}$ = 7.8 kcal.mol^{-1})
Sum of electronic and thermal free energies = -1910.348566 a.u. ($\Delta G^{\ddagger}$ = 23.4 kcal.mol^{-1})
Number of imaginary frequencies: 1 at -472.38



C	0.67200	-0.01622	0.24180
C	1.82049	-0.40182	-0.43775
C	2.98946	-0.82128	0.23267
C	3.01331	-0.85146	1.62914
C	1.86834	-0.45355	2.32026
C	0.71780	-0.04269	1.63864
C	3.92546	-1.19741	-0.79563
C	3.32789	-1.06320	-2.07469
N	2.06731	-0.49733	-1.83258
S	1.14833	0.20392	-3.05428
C	1.67168	1.89814	-3.05557
N	5.20872	-1.65859	-0.62357
O	5.67646	-1.72461	0.52533
O	5.85379	-2.01765	-1.62807
O	1.58651	-0.43769	-4.28622
O	-0.24383	0.13717	-2.64085
C	3.08785	-2.93442	-2.93553
C	1.95629	-3.31330	-2.23699
O	0.74981	-2.99397	-2.72980
Si	-0.01610	-3.56875	-4.15093
C	-0.48357	-5.33656	-3.76011
C	1.93760	-3.79086	-0.88097
C	3.08053	-4.04924	-0.19429
O	3.17710	-4.33908	1.09816
C	1.97992	-4.33574	1.87782
C	-1.50418	-2.47373	-4.35792
C	1.11329	-3.51280	-5.63841
H	3.86696	-0.78789	-2.97304
H	2.95514	-2.62737	-3.96658
H	4.07225	-3.31013	-2.67017
H	0.96524	-3.83751	-0.40299
H	4.05911	-4.06672	-0.66805
H	3.90470	-1.18045	2.15097
H	1.87026	-0.46752	3.40604
H	-0.16254	0.25481	2.19969
H	-0.22486	0.28209	-0.28699
H	2.29165	-4.52280	2.90442
H	1.48059	-3.36401	1.80779
H	1.30543	-5.12997	1.54199
H	-1.12231	-5.38180	-2.87126
H	-1.02683	-5.79571	-4.59377
H	0.41330	-5.93749	-3.56986
H	0.52842	-3.80274	-6.52036
H	1.50130	-2.50352	-5.80584
H	1.95145	-4.21248	-5.55563
H	-2.03330	-2.34199	-3.40951
H	-1.21817	-1.48751	-4.73549
H	-2.19902	-2.92848	-5.07371
H	1.10091	2.40558	-3.83695
H	1.45250	2.32591	-2.07535
H	2.74066	1.92512	-3.27395

- TS1 *exo* approach

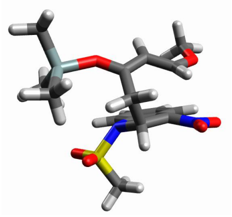
Electronic Energy = -1910.691799 a.u. ($\Delta Ee^{\ddagger}$ = 7.3 kcal.mol^{-1})
Sum of electronic and thermal free energies = -1910.348911 a.u. ($\Delta G^{\ddagger}$ = 23.2 kcal.mol^{-1})
Number of imaginary frequencies: 1 at -517.01



C	0.06691	0.06658	1.40134
C	1.37447	0.08593	1.87131
C	2.47432	0.38878	1.03862
C	2.25656	0.69126	-0.30869
C	0.94824	0.66564	-0.79036
C	-0.12821	0.35502	0.04858
N	1.87593	-0.16592	3.17299
C	3.25699	0.08914	3.22319
C	3.64134	0.32323	1.88092
N	4.96157	0.45402	1.51466
O	5.24264	0.67060	0.32144
S	1.04401	-0.93752	4.41190
O	5.82836	0.35130	2.40260
C	3.29937	1.89481	4.26816
C	4.53346	2.49398	4.03421
C	4.87536	3.16298	2.80592
C	3.98693	3.33073	1.79449
O	4.25311	3.80603	0.58201
C	5.61810	4.08455	0.26122
O	5.54992	2.40535	4.88953
Si	5.64168	1.73445	6.46501
H	3.86281	-0.43201	3.95655
H	3.07011	1.52159	5.26125
H	2.44593	2.26426	3.71048
H	5.91955	3.42932	2.68820
H	2.92878	3.10477	1.89273
H	3.09345	0.93738	-0.95168
H	0.76092	0.89489	-1.83487
H	-1.13700	0.34468	-0.35164
H	-0.76817	-0.15725	2.05545
C	7.42140	2.04070	6.91995
C	4.47110	2.66791	7.58299
C	5.25541	-0.09212	6.39739
H	5.62332	4.37988	-0.78694
H	5.99432	4.90460	0.88135
H	6.22786	3.18728	0.40248
H	7.63458	1.64107	7.91756
H	8.09550	1.55341	6.20763
H	7.64885	3.11193	6.92662
H	5.55936	-0.55559	7.34391
H	4.18936	-0.30639	6.25808
H	5.81900	-0.57934	5.59364
H	4.72084	2.45836	8.62978
H	4.56799	3.74828	7.42882
H	3.42448	2.38941	7.42671
O	1.93317	-0.87247	5.56402
O	-0.28260	-0.34128	4.46925
C	0.89895	-2.61618	3.85686
H	0.36305	-3.15707	4.64082
H	0.32507	-2.61924	2.92764
H	1.90242	-3.02151	3.71612

-PA *endo* approach

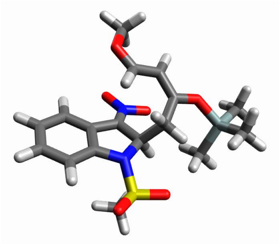
Electronic Energy = -1910.707195 a.u. (ΔEe = -2.3 kcal.mol^{-1})
Sum of electronic and thermal free energies = -1910.361678 a.u. (ΔG = 15.2 kcal.mol^{-1})
Number of imaginary frequencies: 0



N	-0.19458	1.04916	-0.49637
C	-0.34479	1.32917	0.90491
C	0.87186	1.12395	1.58144
C	1.81205	0.58625	0.62185
C	1.17803	0.51150	-0.73830
C	0.95320	1.36260	2.95417
C	-0.19391	1.79510	3.62507
C	-1.39979	1.97260	2.94461
C	-1.49329	1.73831	1.56695
N	3.17134	0.62917	0.73591
O	3.85579	0.27682	-0.25931
C	1.08276	-0.90650	-1.37636
C	0.23195	-1.79300	-0.53278
C	0.59102	-2.08466	0.76406
C	1.85730	-1.68722	1.24160
O	2.19435	-1.71384	2.51063
C	1.18161	-1.96283	3.49993
S	-0.70093	2.22034	-1.59291
O	-2.10799	2.48496	-1.31613
C	0.23576	3.68138	-1.21256
O	-0.29875	1.71971	-2.90488
O	3.69937	0.91764	1.83160
O	-0.93520	-2.21498	-0.96125
Si	-2.02218	-2.07164	-2.29509
C	-1.15801	-1.57683	-3.86967
C	-2.70302	-3.80142	-2.43024
C	-3.31175	-0.83818	-1.75841
H	1.72628	1.13135	-1.45610
H	0.67574	-0.80996	-2.38231
H	2.10579	-1.29029	-1.45049
H	-0.14016	-2.54358	1.41940
H	2.73218	-1.65493	0.59266
H	1.89041	1.20438	3.47499
H	-0.14734	1.98750	4.69278
H	-2.28259	2.29813	3.48623
H	-2.42606	1.88326	1.03435
H	1.63428	-1.70165	4.45491
H	0.30020	-1.34407	3.31818
H	0.91651	-3.02338	3.48815
H	-3.05353	-4.16329	-1.45838
H	-3.54783	-3.82432	-3.12809
H	-1.94171	-4.49524	-2.80309
H	-1.87119	-1.72898	-4.69022
H	-0.86245	-0.52301	-3.88307
H	-0.28304	-2.20149	-4.07798
H	-3.95446	-0.54926	-2.59802
H	-3.94868	-1.26659	-0.97677
H	-2.84708	0.07350	-1.36685
H	-0.03974	4.43399	-1.95474
H	-0.03967	4.01185	-0.20903
H	1.30018	3.44830	-1.28164

-PA *exo* approach

Electronic Energy = --1910.712367 a.u. (ΔEe = -5.6 kcal.mol^{-1})
Sum of electronic and thermal free energies = -1910.366618 a.u. (ΔG = 12.1 kcal.mol^{-1})
Number of imaginary frequencies: 0

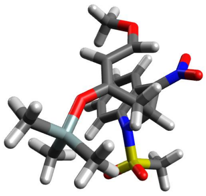


C	-1.32891	1.96546	1.92842
C	-0.25857	1.41648	1.24101
C	0.93296	1.03254	1.89130
C	1.05760	1.21963	3.26942
C	-0.01336	1.78746	3.96982
C	-1.18721	2.15177	3.31242
C	1.80052	0.46111	0.89153
C	1.16572	0.49132	-0.46323
N	-0.15817	1.10227	-0.15165
S	-0.86483	2.07164	-1.31063
C	-0.04325	3.65468	-1.21981
N	3.07220	0.07449	1.05291
O	3.60347	0.07816	2.20063
O	3.68544	-0.41421	0.04788
O	-0.54945	1.43445	-2.59423
O	-2.26891	2.25107	-0.93829
C	0.98334	-0.90124	-1.16803
C	-0.13566	-1.62341	-0.50768
O	-1.31558	-1.61620	-1.06821
Si	-2.00307	-1.90202	-2.63837
C	-2.47528	-3.70740	-2.60135
C	-0.04719	-2.09765	0.79799
C	1.18928	-2.13823	1.43347
O	1.37485	-2.36084	2.70277
C	0.23702	-2.43045	3.58974
C	-3.46962	-0.75644	-2.67292
C	-0.79484	-1.58162	-4.02610
H	1.74457	1.10597	-1.16578
H	0.75652	-0.71916	-2.21620
H	1.93870	-1.42643	-1.08546
H	-0.95957	-2.38179	1.30992
H	2.12939	-2.08402	0.88836
H	1.97191	0.92257	3.76760
H	0.07223	1.93907	5.04154
H	-2.01082	2.58618	3.87014
H	-2.24611	2.23490	1.41817
H	0.65053	-2.47729	4.59484
H	-0.38364	-1.53895	3.47225
H	-0.33819	-3.33430	3.37563
H	-3.16976	-3.92964	-1.78501
H	-2.96296	-3.97653	-3.54534
H	-1.59259	-4.34587	-2.48496
H	-1.31391	-1.81511	-4.96474
H	-0.48010	-0.53530	-4.06827
H	0.08923	-2.22596	-3.97538
H	-4.06924	-0.85923	-1.76239
H	-3.13802	0.28314	-2.74967
H	-4.11235	-0.97747	-3.53254
H	-0.50038	4.30026	-1.97261
H	-0.19766	4.06010	-0.21787
H	1.01763	3.50299	-1.42955

- TS2 *endo* approach

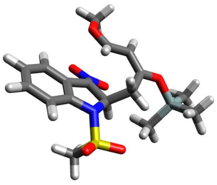
Electronic Energy = -1910.707869 a.u. (ΔEe‡ = -2.8 kcal.mol^{-1})
Sum of electronic and thermal free energies = -1910.361334 a.u. (ΔG‡ = 15.4 kcal.mol^{-1})
Number of imaginary frequencies: 1 at -162.15

N	-0.19458	1.04916	-0.49637
C	-0.34479	1.32917	0.90491
C	0.87186	1.12395	1.58144
C	1.81205	0.58625	0.62185
C	1.17803	0.51150	-0.73830
C	0.95320	1.36260	2.95417
C	-0.19391	1.79510	3.62507
C	-1.39979	1.97260	2.94461
C	-1.49329	1.73831	1.56695
N	3.17134	0.62917	0.73591
O	3.85579	0.27682	-0.25931
C	1.08276	-0.90650	-1.37636
C	0.23195	-1.79300	-0.53278
C	0.59102	-2.08466	0.76406
C	1.85730	-1.68722	1.24160
O	2.19435	-1.71384	2.51063
C	1.18161	-1.96283	3.49993
S	-0.70093	2.22034	-1.59291
O	-2.10799	2.48496	-1.31613
C	0.23576	3.68138	-1.21256
O	-0.29875	1.71971	-2.90488
O	3.69937	0.91764	1.83160
O	-0.93520	-2.21498	-0.96125
Si	-2.02218	-2.07164	-2.29509
C	-1.15801	-1.57683	-3.86967
C	-2.70302	-3.80142	-2.43024
C	-3.31175	-0.83818	-1.75841
H	1.72628	1.13135	-1.45610
H	0.67574	-0.80996	-2.38231
H	2.10579	-1.29029	-1.45049
H	-0.14016	-2.54358	1.41940
H	2.73218	-1.65493	0.59266
H	1.89041	1.20438	3.47499
H	-0.14734	1.98750	4.69278
H	-2.28259	2.29813	3.48623
H	-2.42606	1.88326	1.03435
H	1.63428	-1.70165	4.45491
H	0.30020	-1.34407	3.31818
H	0.91651	-3.02338	3.48815
H	-3.05353	-4.16329	-1.45838
H	-3.54783	-3.82432	-3.12809
H	-1.94171	-4.49524	-2.80309
H	-1.87119	-1.72898	-4.69022
H	-0.86245	-0.52301	-3.88307
H	-0.28304	-2.20149	-4.07798
H	-3.95446	-0.54926	-2.59802
H	-3.94868	-1.26659	-0.97677
H	-2.84708	0.07350	-1.36685
H	-0.03974	4.43399	-1.95474
H	-0.03967	4.01185	-0.20903
H	1.30018	3.44830	-1.28164



- TS2 *exo* approach

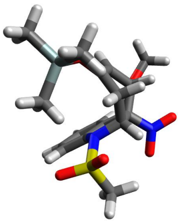
Electronic Energy = -1910.708858 a.u. ($\Delta Ee^{\ddagger}$ = -3.4 kcal.mol^{-1})
Sum of electronic and thermal free energies = -1910.361252 a.u. ($\Delta G^{\ddagger}$ = 15.5 kcal.mol^{-1})
Number of imaginary frequencies: 1 at -158.08



C	-1.33604	-0.19764	0.25718
C	-3.00987	1.44229	0.33048
C	-0.66709	0.12289	-1.04627
C	-1.38452	1.18556	-1.94708
C	-2.86473	1.01377	-2.02181
C	-3.64310	1.14996	-0.89274
N	0.64123	0.68751	-0.61871
C	0.70060	0.72894	0.81103
C	-0.47045	0.17284	1.36019
C	-0.63115	0.11649	2.74434
C	0.39643	0.60690	3.55581
C	1.55105	1.15661	2.99646
C	1.71790	1.23329	1.60799
N	-2.26362	-1.19517	0.29029
O	-2.70183	-1.60613	1.39099
O	-3.58558	1.33823	1.50921
C	-4.85982	0.67729	1.61373
O	-3.44751	0.69079	-3.15819
Si	-2.81125	-0.01476	-4.60535
S	1.98023	0.18213	-1.50100
O	-2.70921	-1.61653	-0.80651
H	-0.52672	-0.78478	-1.64200
H	-0.92004	1.16785	-2.93342
H	-1.16373	2.16280	-1.50536
H	-4.68447	0.85385	-0.93689
H	-2.12645	2.07228	0.38095
H	-1.53512	-0.31007	3.16346
H	0.29154	0.56318	4.63557
H	2.33538	1.53631	3.64392
H	2.61169	1.66053	1.16824
C	-4.33695	-0.74103	-5.38657
C	-2.07745	1.35075	-5.63807
C	-1.56491	-1.32063	-4.12474
H	-4.84506	-0.27733	1.08623
H	-5.01351	0.50968	2.67833
H	-5.64126	1.33286	1.21974
H	-4.09652	-1.18184	-6.36027
H	-4.75878	-1.52622	-4.75012
H	-5.10398	0.02505	-5.54037
H	-1.57861	0.92180	-6.51511
H	-2.85740	2.03322	-5.99273
H	-1.33415	1.93682	-5.08854
H	-1.47381	-2.05492	-4.93352
H	-0.57019	-0.89667	-3.94265
H	-1.89338	-1.84784	-3.22104
O	3.09236	1.04406	-1.11576
C	2.33091	-1.47125	-0.94884
O	1.53704	0.14535	-2.89258
H	3.21372	-1.81007	-1.49552
H	2.53622	-1.42833	0.12275
H	1.46975	-2.10571	-1.16625

-CA *endo* approach

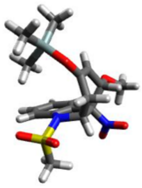
Electronic Energy = -1910.744925 a.u. (ΔEe = -26.0 kcal.mol^{-1})
Sum of electronic and thermal free energies = -1910.395406 a.u. (ΔG = -5.9 kcal.mol^{-1})
Number of imaginary frequencies: 0



C	1.15287	-0.46834	1.31415
C	1.29928	-1.98179	1.52798
C	1.14358	-0.09712	-0.20450
C	1.13586	-1.32110	-1.13179
C	0.20179	-2.39080	-0.61533
C	0.27598	-2.70131	0.68444
N	-0.10299	0.69420	-0.39053
C	-0.80613	0.79170	0.84050
C	-0.11896	0.13093	1.85646
C	-0.63667	0.08114	3.14614
C	-1.85688	0.70882	3.39968
C	-2.54359	1.35858	2.37107
C	-2.03543	1.40516	1.07240
N	2.35760	0.25116	1.94904
O	3.34792	-0.39560	2.22448
O	1.15336	-2.23904	2.90425
C	1.77584	-3.45093	3.29818
O	-0.63052	-3.04431	-1.45409
Si	-1.22594	-2.64649	-2.99641
C	-1.88585	-0.89616	-2.99988
S	-0.01353	2.01770	-1.42138
C	0.84073	3.29668	-0.53004
O	0.81946	1.57615	-2.53609
O	-1.38004	2.45760	-1.67009
O	2.25813	1.45573	2.09892
C	0.13004	-2.87448	-4.26753
C	-2.59063	-3.89328	-3.24996
H	2.01565	0.51726	-0.44797
H	0.86907	-0.97113	-2.13054
H	2.15655	-1.72218	-1.18907
H	-0.35458	-3.45457	1.14630
H	2.31869	-2.25712	1.21484
H	-0.09720	-0.43376	3.93295
H	-2.27679	0.68503	4.40001
H	-3.49787	1.83367	2.57791
H	-2.57445	1.89832	0.27279
H	1.57356	-3.58376	4.36209
H	1.36936	-4.30785	2.74605
H	2.86031	-3.39877	3.13533
H	-2.57259	-0.76665	-3.84535
H	-2.44424	-0.68337	-2.08131
H	-1.09274	-0.15018	-3.10605
H	0.93694	-2.14271	-4.15444
H	0.56421	-3.87791	-4.19902
H	-0.28477	-2.75585	-5.27560
H	-3.04339	-3.77081	-4.24022
H	-2.20602	-4.91629	-3.17830
H	-3.37920	-3.77215	-2.49984
H	0.88729	4.16343	-1.19351
H	0.26967	3.53080	0.37074
H	1.84519	2.94621	-0.28667

-CA *exo* approach

Electronic Energy = -1910.745960 a.u. (ΔEe = -26.7 kcal.mol^{-1})
Sum of electronic and thermal free energies = -1910.397204 a.u. (ΔG = -7.1 kcal.mol^{-1})
Number of imaginary frequencies: 0



C	2.24887	-2.36775	1.33842
C	1.61510	-0.95403	1.09553
C	1.15743	-0.78051	-0.39065
C	1.42649	-2.01730	-1.25439
C	0.94138	-3.23982	-0.52400
C	1.33261	-3.40328	0.74624
C	0.38472	-0.69177	1.91076
C	-0.70168	-0.45848	1.07083
N	-0.30986	-0.53265	-0.29408
C	0.22026	-0.70567	3.29270
C	-1.04821	-0.46478	3.81804
C	-2.13102	-0.23030	2.96549
C	-1.98000	-0.22986	1.57932
S	-0.96301	0.55222	-1.39949
C	-0.59444	2.17327	-0.76567
N	2.69151	0.10994	1.33971
O	3.73749	-0.03406	0.73013
O	0.12591	-4.05972	-1.22270
Si	-1.24473	-4.86423	-0.60016
O	2.41579	-2.66019	2.70026
C	3.55315	-2.07329	3.31589
O	2.45337	1.03886	2.08605
O	-0.21826	0.34486	-2.63663
O	-2.40765	0.36103	-1.38254
H	1.65464	0.08758	-0.83560
H	-0.98708	2.89157	-1.48904
H	-1.08791	2.29192	0.20061
H	0.48920	2.27454	-0.67466
H	0.91297	-1.90176	-2.20996
H	2.50529	-2.07972	-1.44626
H	1.04069	-4.23727	1.37543
H	3.22763	-2.36784	0.83366
H	1.06533	-0.88828	3.94765
H	-1.19608	-0.46282	4.89289
H	-3.11627	-0.05426	3.38661
H	-2.82584	-0.06836	0.92144
C	-2.08767	-5.50281	-2.13497
C	-0.73643	-6.28264	0.51312
C	-2.27402	-3.60687	0.32201
H	3.68175	-2.57469	4.27660
H	4.45195	-2.22288	2.70512
H	3.41511	-1.00101	3.50568
H	-3.00008	-6.05132	-1.87607
H	-2.36272	-4.68021	-2.80346
H	-1.42992	-6.18378	-2.68597
H	-1.56413	-6.99759	0.59276
H	0.12620	-6.81735	0.09966
H	-0.48463	-5.95420	1.52635
H	-3.22592	-4.05263	0.63408
H	-1.76072	-3.25226	1.22272
H	-2.49435	-2.74147	-0.31359